

Three Component Reaction of Arynes with Cyclic Ethers and Active Methines: Synthesis of ω-Trichloroalkyl Phenyl Ethers

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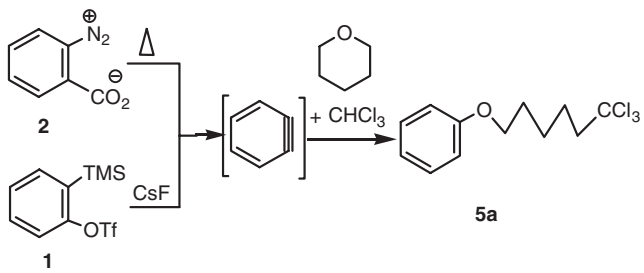
Synthesis of ω-chlorinated alkyl phenyl ethers by tandem reaction of arynes with cyclic ethers and active methines was achieved. Reaction of benzenediazonium 2-carboxylate with tetrahydropyran or tetrahydrofuran in refluxing chloroform afforded 6,6,6-trichlorohexyl phenyl ether or 5,5,5-trichloropentyl phenyl ether in 40% and 61% yields, respectively. When dichloroacetonitrile was used as a reactant, 5,5-dichloro-5-cyanopentyl phenyl ether was obtained in 61% yield. While benzenediazonium carboxylate did not react with epoxides, reaction of benzyne derived from 2-(trimethylsilyl)phenyl triflate with epoxides afforded 3,3,3-trichloropropyl phenyl ethers in good yields as isomeric mixtures. The reaction of oxetanes with benzyne was also reported.

Arynes are widely used as reactive intermediates, which are clearly evident from an elegant array of work that has appeared in the recent literature covering a number of different synthetic transformation.[1] We have reported the synthesis of benzothietes, benzothianes, and 1,3-benzodithioles by using 2-(trimethylsilyl)phenyl triflate (**1**), benzenediazonium carboxylate (**2**), or phenyl[2-(trimethylsilyl)-phenyl]iodonium triflate as benzyne precursors.[2] Recently, many insertion reactions of benzyne with single bonds containing Sn–Sn, Sn–C, N–C, and C–C using triflate **1** as a benzyne precursor have been reported.[3] Although C–O bond insertion of arynes with ethers was reported more than 4 decades ago,[4] there are very few reports on the reaction of benzyne with cyclic ethers. Cyclic ethers such as tetrahydrofuran (THF) reacted with benzyne prepared from **2** to afford *N*-4-phenoxybutyl-*N*-phenylanthranilic acid (17%) and 1,4-diphenoxybutane (4%).[5] The reaction of 1,2-epoxypropane (**3a**) with benzyne prepared from **2** afforded *N*-(9-carbazolyl)-2-chloroaniline (1.3%).[6] Nakayama et al. also reported that the reaction of benzyne with 1,3-benzodithiole-2-thione in the presence of **3a** gave tetracyclic sulfonium chloride.[7] While **3a** was only used as a proton trapping reagent in these reactions, benzyne inserts into one of the C–O bonds of (1,2-epoxylethyl)benzene to form 2,3-dihydrobenzofuran (32%) as the major product together with five other reaction products.[8] 1,2-Epoxycyclohexane was allowed to react with benzyne to afford 3-phenoxycyclohexene in 23% yield.[9] Palladium-catalyzed three component coupling reaction of allylic epoxides with benzyne was also reported.[10] Recently, we have communicated the three component reaction of cyclic ethers with arynes.[11] In this paper, we would like to describe the full details of novel tandem reaction of benzyne with active methines and ethers such as tetrahydropyran (THP), THF, oxetanes **4**, and epoxides **3**.

Results and Discussion

Reaction of Tetrahydropyran with Benzyne. We first chose THP as a cyclic ether. Treatment of **2**, prepared from anthranilic acid and isoamyl nitrite, with THP (10 equiv) in refluxing chloroform resulted in the formation of 6,6,6-trichlorohexyl phenyl ether (**5a**) in 40% yield along with a small amount of benzoic acid (7%) (Scheme 1). The structure of **5a** was confirmed by ^{1}H- and ^{13}C NMR, and finally X-ray crystallographic analysis.[11] In the absence of chloroform, the reaction provided a complex mixture of unidentified products. Since triflate **1** is a commercially available and stable reagent to generate benzyne under very mild reaction conditions,[3,12] we then tried the reaction of triflate **1** with THP and chloroform at rt. Treatment of **1** with THP (10 equiv) and chloroform (10 equiv) in the presence of CsF (4 equiv) resulted in the formation of ether **5a** in 52% yield (Scheme 1).

To investigate the scope and limitation of this novel tandem reaction, we then tried the reaction of benzyne with other active methylenes and methines. The reaction of triflate **1** with acetylacetone or methyl acetoacetate was already reported by Yoshida et al., which led to C–C bond insertion products.[13] The reaction of triflate **1** with methyl acetoacetate was also reported



Scheme 1.

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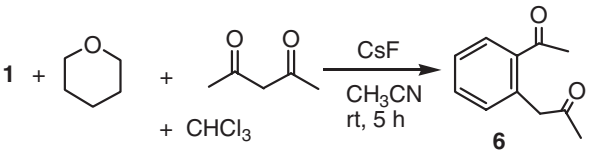
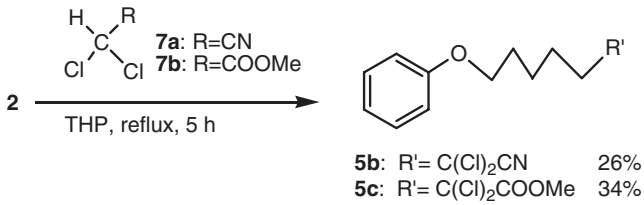


Scheme 2.



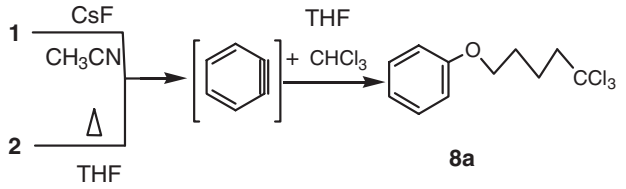
Scheme 3.

by Tambar and Stoltz.[3c] Thus, we have tried these reactions in the presence of THP. When triflate **1** was added to a suspension of THP (20 equiv), chloroform (20 equiv), CsF (3 equiv), and acetylacetone (2 equiv) at rt, 1-(2-acetylphenyl)-2-propanone (**6**) was obtained in 52% yield. No product relating to THP was obtained, suggesting that acetylacetone is more reactive than THP toward benzyne (Scheme 2).

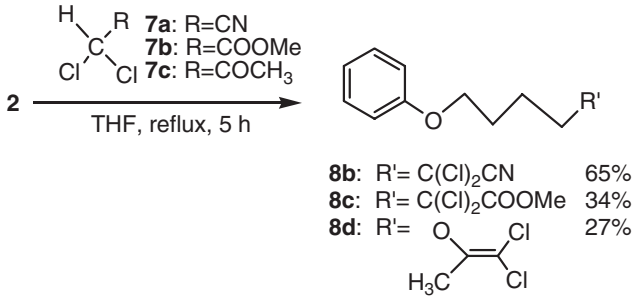
The reaction of **2** with THP and dichloroacetonitrile (**7a**) or methyl dichloroacetate (**7b**) gave 6,6-dichloro-6-cyanohexyl phenyl ether (**5b**) or methyl 2,2-dichloro-7-phenoxyheptanoate (**5c**) in 26% and 34% yields, respectively (Scheme 3). Unfortunately, when triflate **1** was treated with **7a** and chloroform in the presence of CsF, starting triflate **1** was recovered unchanged due to the lability of active methines toward CsF. When **7a** was mixed with CsF in acetonitrile, the color of the solution immediately turned black, which led to a polymeric tar.

Reaction of THF with Benzyne. Recently, Feltenberger et al. have reported the reaction of benzyne with THF at 110 °C, which led to the formation of C–O insertion product (2,3,4,5-tetrahydrobenzo[*b*]oxepine).[14] We have tried the reaction of benzyne with THF in refluxing chloroform to investigate whether the ring expansion product would be formed as Feltenberger stated. Treatment of carboxylate **2** with 20 equiv of chloroform in refluxing THF resulted in the formation of 5,5,5-trichloropentyl phenyl ether (**8a**) and benzoic acid in 61% and 8% yields, respectively. When **2** was treated with THF (10 equiv) in refluxing chloroform, **8a** was afforded in 48% yield. When a mixture of **2** and chloroform (3 equiv) was refluxed in THF, **8a** was obtained in 32% yield along with benzoic acid (10%). In all cases, no ring expansion product was obtained. When triflate **1** was treated with CsF, THF, and chloroform in acetonitrile, ether **8a** was obtained in 61% yield (Scheme 4). When tetrabutylammonium fluoride (TBAF) was used as a fluoride source, the yield of **8a** was decreased to 17%.

When carboxylate **2** was used as a benzyne precursor, active methylenes such as dichloromethane, malononitrile, and methyl acetoacetate did not afford the corresponding tandem reaction products.[15] When **2** was added to a refluxing solution of **7a** (5 equiv) in THF, the corresponding ether **8b** was obtained in 61% yield along with benzoic acid (8%). Similarly, **7b** gave **8c** in 34% yield. Interestingly, when **2** was added to a



Scheme 4.



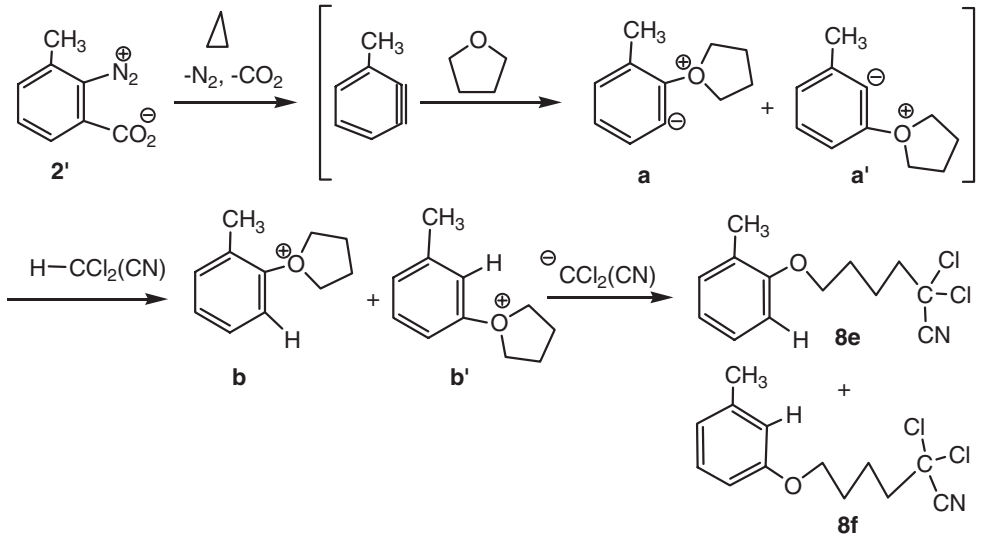
Scheme 5.

refluxing solution of dichloroacetone (**7c**) (3 equiv) in THF, the corresponding O-attacked ether **8d** was obtained in 27% yield (Scheme 5).

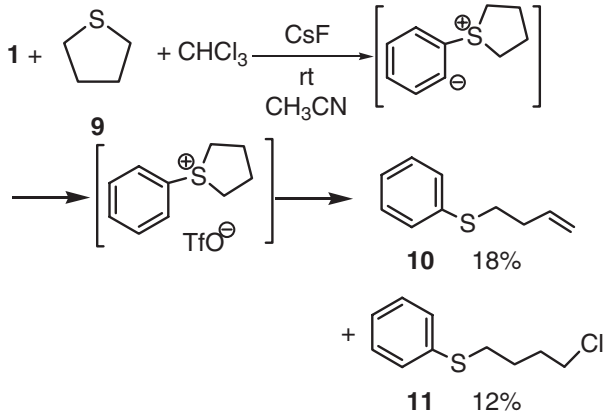
When 2-diazonio-3-methylbenzoate (**2′**) was treated with **7a** in refluxing THF, 5,5-dichloro-5-cyanopentyl 2-methylphenyl ether (**8e**) and 5,5-dichloro-5-cyanopentyl 3-methylphenyl ether (**8f**) were obtained in 25% and 17% yields, respectively. Thus, the reaction might proceed as follows. Carboxylate **2′** initially extruded molecular nitrogen and carbon dioxide to afford benzyne, which reacted with THF to give THF-stabilized dipole intermediates (**a** and **a′**). These dipoles abstracted protons of dichloroacetonitrile to afford oxonium ions (**b** and **b′**) and dichlorocyanomethyl anion. When cations **b** and **b′** were finally attacked by the methyl anion, the corresponding ethers **8e** and **8f** were formed (Scheme 6).

Since Nakayama et al. have reported that the reaction of cyclic thioethers with benzyne prepared from 2-carboxybenzenediazonium chloride gave the corresponding ω-chloroalkyl phenyl thioethers in moderate yields,[16] we have tried the reaction of tetrahydrothiophene (**9**) with triflate **1** in the presence of chloroform to determine whether trichloroalkyl phenyl thioether would be obtained. Treatment of thiophene **9** with triflate **1** in the presence of chloroform and CsF resulted in the formation of 4-phenylsulfanylbut-1-ene (**10**) and 4-chlorobutyl phenyl thioether (**11**) in 18% and 12% yields, respectively. Sulfonium ion intermediate was isolated as an tetraphenylborate in a separate experiment (Scheme 7).

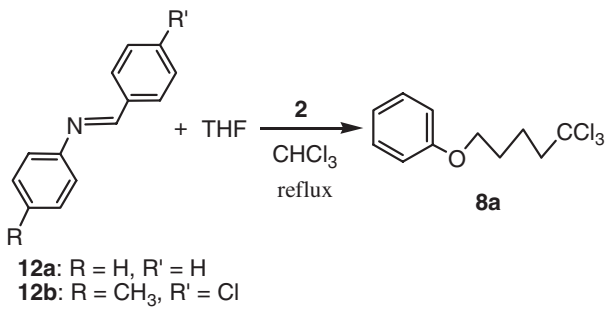
Singal et al. reported the formation of 1,2-diarylbenzazetidines by the reaction of azomethines with benzyne derived from **2**,[17] whereas Shou et al. have recently reported the formation of 6-arylphenanthridines by the reaction of aromatic aldehydes with anilines and carboxylate **2**,[18] suggesting that in situ formed benzylideneanilines **12** further reacted with benzyne to give cycloadducts. Aly et al. also reported that the reaction of diarylazines with benzyne gave acridines.[19] These different results prompted us to compare the reactivity between imines and cyclic ethers. Thus, we have tried the competitive reaction of carboxylate **2** with THF and benzylideneanilines **12**.



Scheme 6.



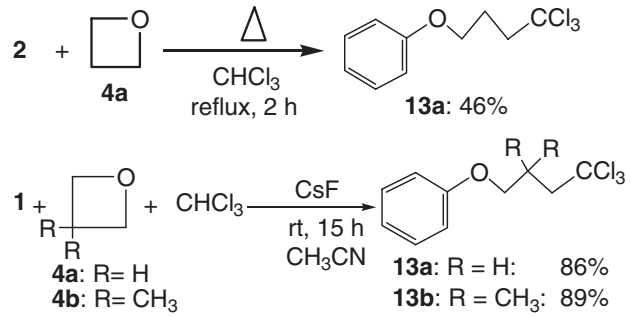
Scheme 7.



Scheme 8.

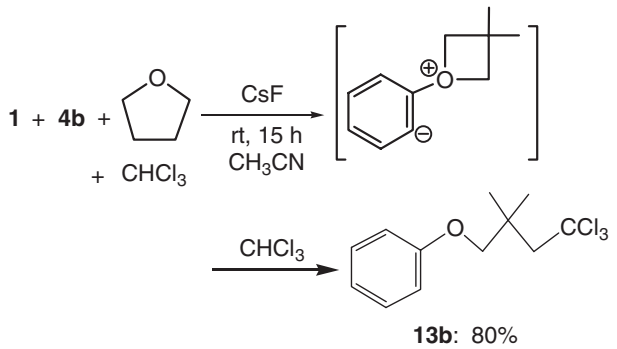
When a solution of benzylideneaniline (**12a**) and THF (20 equiv) in refluxing chloroform was added to carboxylate **2**, phenyl ether **8a** was obtained in 28% yield. Starting **12a** was recovered unchanged. When *p*-chlorobenzylidene-*p*-toluidine (**12b**) was used as an imine, **8a** was obtained in 21% yield (Scheme 8). These results clearly showed that cyclic ether is more reactive than azomethines.

Reaction of Benzyne with Oxetanes. Since 5- and 6-membered cyclic ethers provided moderate yields of ring-opened products, we then tried the reaction of benzyne with oxetanes **4**. Treatment of carboxylate **2** with oxetane (**4a**) in refluxing chloroform resulted in the formation of 4,4,4-trichlorobutyl phenyl ether (**13a**) in 46% yield, whereas when a solution of **4a** (10 equiv) and chloroform (10 equiv) in acetonitrile was added to a mixture of triflate **1** and CsF, ether **13a** was obtained in 86% yield. Similarly, by using 3,3-dimethyloxetane (**4b**) as a substrate, phenyl ether **13b** was obtained in 89% yield (Scheme 9).

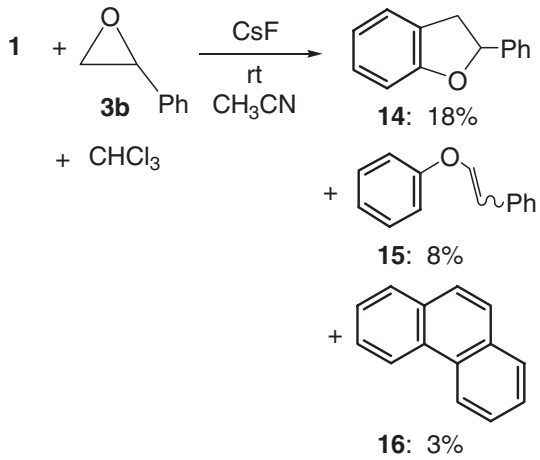


Scheme 9.

A notable difference in the reactivity toward **4a** between **1** and **2** might be the difference in the formation rate of benzyne. When carboxylate **2** was treated with refluxing chloroform, benzyne immediately formed within a few seconds, which reacted with oxetane to afford phenyl ether **13a** in 46% yield. Similarly, Friedman et al. reported that careful thermolysis of **2** in hot dichloroethane resulted in the formation of biphenylene in 30% yield, due to the relatively high rate of benzyne formation under similar conditions.[20] On the other hand, when triflate **1** was used as a benzyne precursor, the solubility of CsF toward acetonitrile was low, indicating that small amount of fluoride reacted with **1** to afford benzyne gradually. In this case, oxetane can react with benzyne more efficiently to afford betaine intermediate, which resulted in the formation of phenyl ether **13a** in good yield. Partial complexation of Cs^+ with oxetane might also play an important role for improvement of the yield of **13a**.[21] When a suspension of **4b** (10 equiv), THF (10 equiv), $CHCl_3$ (10 equiv), and CsF (3 equiv) in acetonitrile was treated with **1** at rt for 15 h, only



Scheme 10.

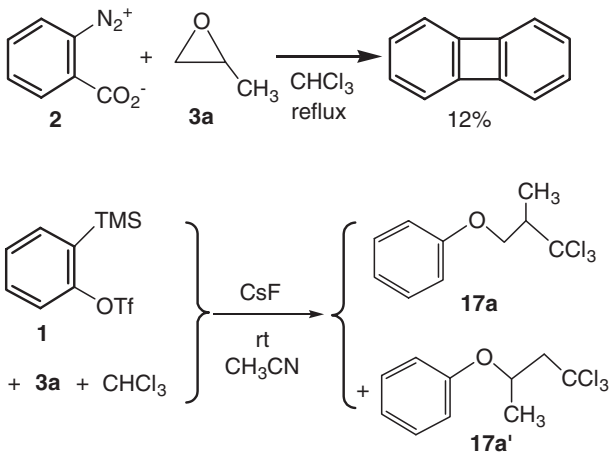


Scheme 11.

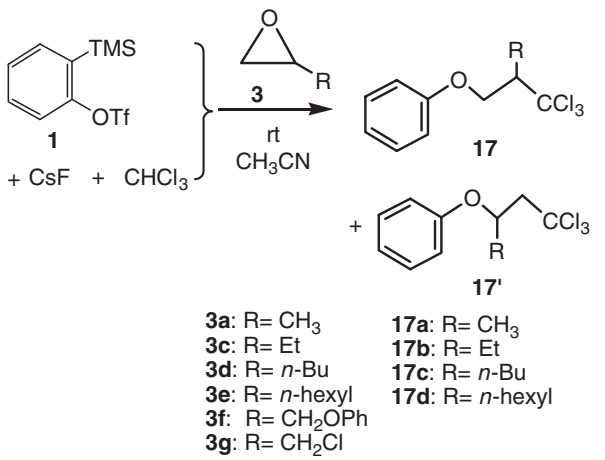
13b was obtained in 80% yield, indicating that oxetane **4b** is more reactive than THF (Scheme 10).

Reaction of Benzyne with Epoxides. Peña et al. have reported that the reaction of benzyne with (1,2-epoxyethyl)-benzene (**3b**) gave ring expansion product, 2-phenyl-2,3-dihydrobenzofuran (**14**) (32%), and other products.[8] Thus, we have tried the reaction of benzyne with epoxides to determine whether the corresponding ring expansion products would be formed. Treatment of **3b** with carboxylate **2** in refluxing chloroform gave a complex mixture of unidentified products. When the reaction was carried out by using triflate **1** as a benzyne precursor, benzofuran **14** (18%), phenyl styryl ether (**15**) (8%), and phenanthrene (**16**) (3%) were obtained, the result of which was quite similar to that of Peña et al. These results suggested that intramolecular cyclization (ring expansion) occurred more easily than intermolecular reaction with chloroform by the use of **3b** (Scheme 11).

We then investigated the reaction of **3a** with benzyne. Reaction of **3a** with carboxylate **2** in refluxing chloroform afforded biphenylene in 12% yield. No ring expansion product was obtained. However, when triflate **1** was used as a benzyne precursor, an isomeric mixture of 3,3,3-trichloro-2-methylpropyl phenyl ether (**17a**) and 3,3,3-trichloro-1-methylpropyl phenyl ether (**17a′**) was obtained (Scheme 12). When TBAF was used as a fluoride source, phenyl ethers **17a** and **17a′** were obtained in 26% and 10% yields, respectively. By using CsF as a fluoride source, the yields were increased to 48 and 24%



Scheme 12.



Scheme 13.

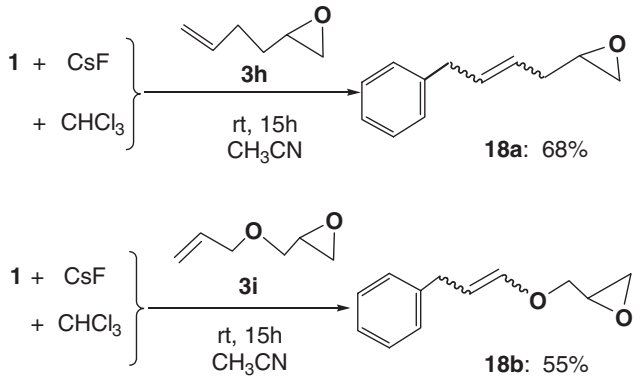
yields, respectively. In the absence of chloroform, products relating to **3a** were not obtained.

Since CsF found to be a good fluoride source, we then investigated the other epoxides under these conditions (Scheme 13). Treatment of 1,2-epoxylbutane (**3c**) (10 equiv) with triflate **1**, CsF, and chloroform at rt resulted in the formation of 2-trichloromethylbutyl phenyl ether (**17b**) and 3,3,3-trichloro-1-ethylpropyl phenyl ether (**17b′**) in 39 and 26% yields, respectively (Entry 3, Table 1). Similarly, 1,2-epoxyhexane (**3d**) afforded **17c** and **17c′** in 37 and 25% yields, respectively (Entry 4). However, when 2,3-epoxypropyl phenyl ether (**3f**) and 3-chloro-1,2-epoxypropane (**3g**) were used as substrates, starting epoxides were recovered unchanged (Entries 6 and 7). Thus, tandem reaction of benzyne, epoxides **3**, and chloroform to give phenyl ethers **17** was achieved.

Interestingly, when 5,6-epoxy-1-hexene (**3h**) was used as a substrate, a mixture of (*E*)- and (*Z*)-5,6-epoxy-1-phenyl-2-hexene (**18a**) was obtained in 68% yield (*E*:*Z* = 2:1). Similarly, allyl 2,3-epoxypropyl ether (**3i**) reacted with triflate **1** to give 3-phenylprop-1-enyl 2,3-epoxylpropyl ether (**18b**) in 55% yield (*E*:*Z* = 1:1), suggesting that ene reaction proceeded predominantly (Scheme 14). Although a variety of ene-type reactions of benzyne with alkenes and thiones appeared, many of them gave [2 + 2] or [4 + 2] cycloadducts as side products.[2b,22]

Table 1. Reaction of Epoxide **3** with Benzyne and Chloroform

Entry	3	equiv	Time/h	Products (Yield/%)	
				17	**17′**
1	**3a**	10	16	**17a** 48	**17a′** 24
2	**3a**	5	24	**17a** 43	**17a′** 21
3	**3c**	10	24	**17b** 39	**17b′** 26
4	**3d**	10	16	**17c** 37	**17c′** 25
5	**3e**	10	24	**17d** 19	**17d′** 6
6	**3f**	5	24	—	—
7	**3g**	5	24	—	—

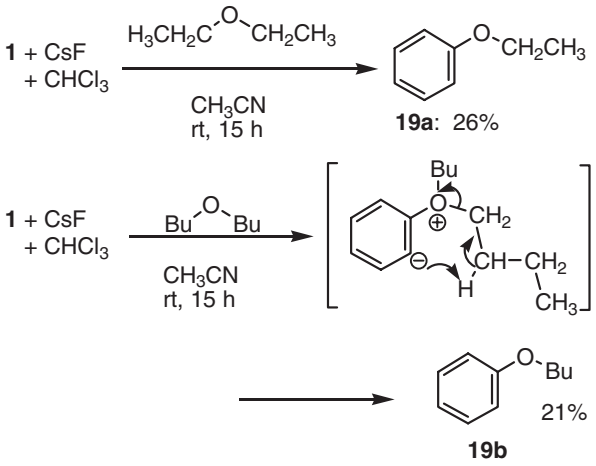


Scheme 14.

Reaction of Benzyne with Acyclic Ethers. Finally, we have investigated the reaction of benzyne prepared from **1** and CsF with acyclic ethers. The reaction of **2** with diethyl ether in refluxing chloroform was already reported by Richmond and Spendel more than 4 decades ago,[9] which resulted in the formation of ethyl phenyl ether (**19a**) in 40% yield, indicating that intramolecular proton abstraction of betaine intermediate is faster. This result prompted us to investigate the reaction of **1** with ether and chloroform to see whether intermolecular proton abstraction of chloroform would proceed. Treatment of **1** with diethyl ether, chloroform, and CsF in acetonitrile at rt for 15 h resulted in the formation of **19a** in 26% yield. Similarly, the reaction of **1** with dibutyl ether, chloroform, and CsF gave butyl phenyl ether (**19b**) in 21% yield. No products relating to chloroform were obtained. These results clearly showed that intramolecular hydrogen abstraction is faster than proton abstraction of chloroform (Scheme 15).

Conclusion

Reaction of THP, THF, and oxetanes with benzyne in the presence of chloroform gave the corresponding ω-trichlorinated alkyl phenyl ethers in moderate yields. Reaction of benzyne prepared from **1** and CsF with epoxides and chloroform gave phenyl ethers or ene reaction products. Thus, a cascade approach to trichloroalkyl phenyl ethers was achieved by using triflate **1**, diazonium carboxylate **2**, and cyclic ethers in the presence of chloroform. On the other hand, reaction of diethyl ether or dibutyl ether gave intramolecular reaction products. This method provides a new route to ω-chlorinated alkyl phenyl ethers.



Scheme 15.

Experimental

General. All chemicals were obtained from commercial suppliers and were used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and flash column chromatography was performed with silica (Merck, 70–230 mesh). NMR spectra (^{1}H at 400 MHz; ^{13}C at 100 MHz) were recorded in $CDCl_3$, and chemical shifts are expressed in ppm relative to internal TMS (δ 0.00) and $CDCl_3$ (δ 77.00) for ^{1}H- and ^{13}C NMR. Melting points are uncorrected.

Materials. Benzenediazonium 2-carboxylate was synthesized by the reaction of anthranilic acid with isoamylnitrite in THF.[20,23] 2-(Trimethylsilyl)phenyl triflate (**1**) was synthesized by a method described by Sonoda et al.[24]

Reaction of Triflate 1 with THP, Chloroform, and CsF in Acetonitrile. A solution of triflate **1** (0.30 g, 1.0 mmol) in acetonitrile (3.0 mL) was added to a suspension of CsF (0.61 g, 4.0 mmol), THP (0.86 g, 10 mmol), and chloroform (1.19 g, 10 mmol) in acetonitrile (5.0 mL). After stirring for 15 h at rt, the reaction mixture was evaporated and water (15 mL) was added. The reaction mixture was extracted with ether (5 mL × 3). The combined extract was dried over sodium sulfate, filtered, and evaporated to give pale brown oil, which was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to give phenyl ether **5a** (0.145 g, 0.52 mmol). 6,6,6-Trichlorohexyl phenyl ether (**5a**): colorless crystals, mp 50–51 °C. ^{1}H NMR ($CDCl_3$): δ 1.58–1.62 (m, 2H, CH_2), 1.83–1.91 (m, 4H, CH_2), 2.72 (dd, 2H, J = 7.0 Hz and 7.2 Hz, CH_2), 3.99 (t, 2H, J = 5.6 Hz, OCH_2), 6.90 (d, 2H, J = 8.0 Hz, *o*-Ph), 6.95 (t, 1H, J = 7.2 Hz, *p*-Ph), 7.28 (dd, 2H, J = 7.2 Hz and 8.0 Hz, *m*-Ph). ^{13}C NMR ($CDCl_3$): δ 25.27 (CH_2), 26.50 (CH_2), 29.29 (CH_2), 55.33 (CH_2), 67.62 (OCH_2), 100.30 (q-C), 114.72 (Ph), 120.91 (Ph), 129.74 (Ph), 159.22 (Ph). Anal. Found: C, 50.82; H, 4.97%. Calcd for $C_{12}H_{15}Cl_3O$: C, 51.18; H, 5.37%.

Reaction of Benzenediazonium 2-Carboxylate (2) with THP and Chloroform. To a solution of THP (0.860 g, 10.0 mmol) in chloroform (10 mL) was added carboxylate **2** (0.148 g, 1.0 mmol) in one portion. After refluxing for 2 h, the reaction mixture was evaporated and chromatographed over silica gel by elution with hexane–EtOAc (5:1) to afford **5a**

(0.112 g, 0.40 mmol). Further elution with hexane–EtOAc (1:1) gave benzoic acid (0.009 g, 0.07 mmol), which was shown to be identical to an authentic sample (mp 110–112 °C).

Reaction of Benzenediazonium 2-Carboxylate (2) with THP and Methyl Dichloroacetate (7b). To a solution of THP (0.860 g, 10.0 mmol) and methyl dichloroacetate (**7b**) (1.42 g, 10.0 mmol) in dichloromethane (10 mL) was added carboxylate **2** (0.148 g, 1.0 mmol) in one portion. After refluxing for 3 h, the reaction mixture was evaporated and chromatographed over silica gel by elution with hexane–EtOAc (5:1) to afford methyl 2,2-dichloro-7-phenoxyheptanoate (**5c**) (0.071 g, 0.34 mmol).

Compound **5c**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.54–1.60 (m, 2H, CH_2), 1.63–1.69 (m, 2H, CH_2), 1.79–1.86 (m, 2H, CH_2), 2.46 (dd, 2H, $J = 7.0$ Hz and 7.2 Hz, CH_2), 3.89 (s, 3H, CH_3), 3.97 (t, 2H, $J = 5.6$ Hz, OCH_2), 6.90 (d, 2H, $J = 8.0$ Hz, *o*-Ph), 6.94 (t, 1H, $J = 7.2$ Hz, *p*-Ph), 7.28 (dd, 2H, $J = 7.2$ Hz and 8.0 Hz, *m*-Ph). ^{13}C NMR ($CDCl_3$): δ 25.12 (CH_2), 25.70 (CH_2), 29.22 (CH_2), 45.29 (CH_2), 54.62 (OCH_3), 67.64 (OCH_2), 84.69 (q-C), 114.69 (Ph), 120.83 (Ph), 129.67 (Ph), 159.20 (Ph), 166.86 (C=O). Anal. Found: C, 55.14; H, 5.96%. Calcd for $C_{14}H_{18}Cl_2O_3$: C, 55.10; H, 5.94%.

Phenyl ethers **5a** and **5b** were synthesized in a similar manner: Compound **5a** (0.113 g, 0.40 mmol).

6,6-Dichloro-6-cyanohexyl phenyl ether (**5b**) (0.070 g, 0.26 mmol): colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.60–1.66 (m, 2H, CH_2), 1.78–1.89 (m, 4H, CH_2), 2.52 (dd, 2H, $J = 7.0$ Hz and 7.2 Hz, CH_2), 3.99 (t, 2H, $J = 5.6$ Hz, OCH_2), 6.88 (d, 2H, $J = 8.0$ Hz, *o*-Ph), 6.96 (t, 1H, $J = 7.2$ Hz, *p*-Ph), 7.28 (t, 2H, $J = 7.6$ Hz, *m*-Ph). ^{13}C NMR ($CDCl_3$): δ 25.33 (CH_2), 25.64 (CH_2), 29.13 (CH_2), 48.22 (CH_2), 67.45 (OCH_2), 69.09 (q-C), 114.67 (Ph), 115.77 (CN), 120.95 (Ph), 129.72 (Ph), 159.11 (Ph). Anal. Found: C, 57.30; H, 5.54; N, 5.12%. Calcd for $C_{13}H_{15}Cl_2NO$: C, 57.37; H, 5.56; N, 5.15%. MS (EI): m/z 271.2. Calcd for $C_{13}H_{15}Cl_2NO$, 271.0 (M^+).

Reaction of Triflate 1 with THP, Chloroform, Acetylacetone, and CsF. To a suspension of acetylacetone (0.100 g, 1.0 mmol), THP (0.860 g, 10.0 mmol), chloroform (1.19 g, 10.0 mmol), and CsF (0.226 g, 1.5 mmol) in acetonitrile (3.0 mL) was added triflate **1** (0.149 g, 0.50 mmol) in acetonitrile (2.0 mL) in one portion. After stirring for 5 h at rt, the reaction mixture was evaporated and extracted with hexane (7 mL × 3) and CH_2Cl_2 (6 mL × 3). The combined extract was chromatographed over silica gel by elution with hexane–CH_2Cl_2 (1:1) to afford 1-(2-acetylphenyl)propan-2-one (**6**) (0.046 g, 0.026 mmol). Compound **6**: colorless oil.[13] ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 4.02 (s, 2H, CH_2), 7.17 (dd, 1H, $J = 8.0$ Hz and 1.2 Hz, Ar), 7.38 (ddd, 1H, $J = 8.0$ Hz, 8.0 Hz, and 1.2 Hz, Ar), 7.47 (ddd, 1H, $J = 8.0$ Hz, 8.0 Hz, and 1.2 Hz, Ar), 7.84 (dd, 1H, $J = 8.0$ Hz and 1.2 Hz, Ar).

Reaction of Carboxylate 2 with THF and Chloroform. A mixture of carboxylate **2** (0.148 g, 1.0 mmol), chloroform (2.38 g, 20 mmol), and molecular sieves 3A (0.2 g) in THF (6.0 mL) was stirred for 1 h then refluxed for 2 h. The reaction mixture was evaporated and the residue was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to give 5,5,5-trichloropentyl phenyl ether (**8a**) (0.163 g, 0.61 mmol). Further elution with hexane–EtOAc (3:1) gave benzoic acid (0.010 g, 0.080 mmol).

5,5,5-Trichloropentyl phenyl ether (**8a**): colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.84–2.10 (m, 4H, CH_2), 2.77 (dd, 2H, $J = 7.0$ Hz and 7.2 Hz, CH_2), 4.01 (t, 2H, $J = 5.6$ Hz, OCH_2), 6.90 (d, 2H, $J = 7.6$ Hz, *o*-Ph), 6.95 (t, 1H, $J = 7.2$ Hz, *p*-Ph), 7.24–7.32 (m, 2H, *m*-Ph). ^{13}C NMR ($CDCl_3$): δ 24.05 (CH_2), 28.65 (CH_2), 55.37 (CH_2), 67.64 (OCH_2), 100.28 (q-C), 114.84 (Ph), 121.11 (Ph), 129.76 (Ph), 159.02 (Ph). Anal. Found: C, 49.71; H, 4.76%. Calcd for $C_{11}H_{13}Cl_3O$: C, 49.38; H, 4.90%. HRMS (EI): m/z 265.9928. Calcd for $C_{11}H_{13}{}^{35}Cl_3O$, 266.0032 (M^+).

When a mixture of **2** (0.148 g, 1.0 mmol) and THF (0.72 g, 10.0 mmol) was refluxed in chloroform (6.0 mL), ether **8a** (0.155 g, 0.58 mmol) was isolated along with benzoic acid (0.010 g, 0.080 mmol).

Reaction of Triflate 1 with THF, Chloroform, and CsF in Acetonitrile. A solution of triflate **1** (0.298 g, 1.0 mmol) in acetonitrile (3.0 mL) was added to a suspension of CsF (0.304 g, 2.0 mmol), THF (0.72 g, 10 mmol), and chloroform (1.19 g, 10 mmol) in acetonitrile (6.0 mL). After stirring for 15 h at rt, the reaction mixture was evaporated and water (15 mL) was added. The reaction mixture was extracted with ether (5 mL × 3). The combined extract was dried over sodium sulfate, filtered, and evaporated to give pale brown oil, which was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to give phenyl ether **8a** (0.163 g, 0.61 mmol).

Reaction of Triflate 1 with THF, Chloroform, and Bu_4NF in Acetonitrile. To a solution of triflate **1** (0.149 g, 0.50 mmol), THF (2.0 mL, 24 mmol), and chloroform (1.19 g, 10 mmol) in acetonitrile (5.0 mL) was added a solution of Bu_4NF (1.0 M in THF, 1.0 mL, 1.0 mmol). After stirring for 15 h at rt, the reaction mixture was evaporated and water (15 mL) was added. The reaction mixture was extracted with ether (5 mL × 3). The combined extract was dried over sodium sulfate, filtered, and evaporated to give pale brown oil, which was chromatographed over silica gel by elution with hexane–dichloromethane (5:1) to afford ether **8a** (0.023 g, 0.086 mmol).

Reaction of Carboxylate 2 with THF and Dichloroacetonitrile (7a). A suspension of carboxylate **2** (0.148 g, 1.0 mmol) in THF (3.0 mL) was added to a refluxing suspension of dichloroacetonitrile (**7a**) (0.55 g, 5.0 mmol), molecular sieves 3A (0.2 g) in THF (8 mL). After refluxing for 5 h, the reaction mixture was evaporated and the residue was chromatographed over silica gel by elution with hexane–EtOAc (10:1 to 2:1) to give 5,5-dichloro-5-cyanopentyl phenyl ether (**8b**) (0.158 g, 0.61 mmol) and benzoic acid (0.08 mmol).

5,5-Dichloro-5-cyanopentyl phenyl ether (**8b**) (0.167 g, 0.67 mmol): colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.90–1.94 (m, 4H, CH_2), 2.59 (dd, 2H, $J = 7.0$ Hz and 7.2 Hz, CH_2), 4.02 (t, 2H, $J = 5.6$ Hz, OCH_2), 6.89 (d, 2H, $J = 7.6$ Hz, *o*-Ph), 6.96 (t, 1H, $J = 7.2$ Hz, *p*-Ph), 7.30 (t, 2H, $J = 7.6$ Hz, *m*-Ph). ^{13}C NMR ($CDCl_3$): δ 22.66 (CH_2), 28.02 (CH_2), 47.80 (CH_2), 66.89 (OCH_2), 68.79 (q-C), 114.46 (Ph), 115.50 (CN), 120.91 (Ph), 129.52 (Ph), 158.68 (Ph). Anal. Found: C, 56.05; H, 5.07; N, 5.43%. Calcd for $C_{12}H_{13}Cl_2NO$: C, 55.83; H, 5.08; N, 5.43%. MS (EI): m/z 257.0. Calcd for $C_{12}H_{13}{}^{35}Cl_2NO$, 257.0 ($M^+$).

Methyl 2,2-dichloro-6-phenoxyhexanoate (**8c**) (0.099 g, 0.34 mmol): colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.77–1.89 (m, 4H, CH_2), 2.51 (dd, 2H, $J = 7.0$ Hz and 7.2 Hz, CH_2), 3.89 (s,

3H, CH_3), 3.99 (t, 2H, $J = 5.6$ Hz, OCH_2), 6.90 (d, 2H, $J =$ 7.6 Hz, *o*-Ph), 6.94 (t, 1H, $J = 7.2$ Hz, *p*-Ph), 7.28 (t, 2H, $J = 7.2$ Hz, *m*-Ph). ^{13}C NMR ($CDCl_3$): δ 22.22 (CH_2), 28.77 (CH_2), 45.07 (CH_2), 57.64 (OCH_3), 67.38 (OCH_2), 84.56 (q-C), 114.72 (Ph), 120.96 (Ph), 129.69 (Ph), 159.09 (Ph), 166.81 (C=O). Anal. Found: C, 53.65; H, 5.54%. Calcd for $C_{13}H_{16}Cl_2O_3$: C, 53.62; H, 5.54%. MS (EI): *m/z* 290.0. Calcd for $C_{13}H_{16}{}^{35}Cl_2O_3$, 290.0 ($M^+$).

4-Phenoxybutyl 2,2-dichloro-1-methylethenyl ether (**8d**) (0.074 g, 0.27 mmol): colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.83–1.96 (m, 4H, CH_2), 2.03 (s, 3H, CH_3), 3.88 (dd, 2H, $J = 7.0$ Hz and 7.2 Hz, OCH_2), 4.01 (t, 2H, $J = 5.6$ Hz, OCH_2), 6.88 (d, 2H, $J = 7.6$ Hz, *o*-Ph), 6.94 (t, 1H, $J = 7.2$ Hz, *p*-Ph), 7.28 (t, 2H, $J = 7.6$ Hz, *m*-Ph). ^{13}C NMR ($CDCl_3$): δ 15.45 (CH_3), 26.09 (CH_2), 26.72 (CH_2), 67.47 (OCH_2), 69.38 (OCH_2), 106.68 (CCl_2), 114.70 (Ph), 120.87 (Ph), 129.68 (Ph), 149.27 (=C), 159.16 (Ph). Anal. Found: C, 56.77; H, 5.76%. Calcd for $C_{13}H_{16}Cl_2O_2$: C, 56.74; H, 5.86%.

Reaction of 2-Diazonio-3-methylbenzoate (2′) with THF and Dichloroacetonitrile (7a). A mixture of 2-diazonio-3-methylbenzoate (**2′**) (0.162 g, 1.0 mmol), dichloroacetonitrile (**7a**) (1.10 g, 10 mmol), molecular sieves 3A (0.2 g) in THF (8 mL) was stirred for 1 h then refluxed for 2 h. The reaction mixture was evaporated and the residue was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to give 5,5-dichloro-5-cyanopentyl 2-methylphenyl ether (**8e**) (0.068 g, 0.25 mmol) and 5,5-dichloro-5-cyanopentyl 3-methylphenyl ether (**8f**) (0.046 g, 0.17 mmol).

Compound **8e**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.94–2.00 (m, 4H, CH_2), 2.23 (s, 3H, CH_3), 2.62 (dd, 2H, $J = 7.0$ Hz and 7.2 Hz, CH_2), 4.03 (t, 2H, $J = 5.6$ Hz, OCH_2), 6.80 (d, 1H, $J =$ 7.6 Hz, Ar), 6.87 (t, 1H, $J = 7.2$ Hz, Ar), 7.14 (t, 1H, $J =$ 7.6 Hz, Ar), 7.16 (t, 1H, $J = 7.2$ Hz, Ar). ^{13}C NMR ($CDCl_3$): δ 16.53 (CH_3), 22.98 (CH_2), 28.28 (CH_2), 48.04 (CH_2), 67.05 (OCH_2), 69.10 (q-C), 110.97 (Ph), 115.74 (CN), 120.75 (Ph), 127.00 (q-C), 127.04 (Ph), 157.02 (Ph). Anal. Found: C, 57.62; H, 5.48; N, 5.11%. Calcd for $C_{13}H_{15}Cl_2NO$: C, 57.37; H, 5.56; N, 5.15%. MS (EI): *m/z* 271.1. Calcd for $C_{13}H_{15}{}^{35}Cl_2NO$, 271.0 ($M^+$).

Compound **8f**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.89–1.96 (m, 4H, CH_2), 2.33 (s, 3H, CH_3), 2.58 (dd, 2H, $J = 7.0$ Hz and 7.2 Hz, CH_2), 4.00 (t, 2H, $J = 5.6$ Hz, OCH_2), 6.69–6.79 (m, 3H, Ar), 7.17 (t, 1H, $J = 7.2$ Hz, Ar). ^{13}C NMR ($CDCl_3$): δ 21.75 (CH_3), 22.90 (CH_2), 28.26 (CH_2), 48.02 (CH_2), 67.07 (OCH_2), 69.03 (q-C), 111.51 (Ph), 115.59 (Ph), 115.73 (CN), 121.97 (Ph), 129.47 (Ph), 139.81 (Ph), 158.94 (Ph). HRMS (EI): *m/z* 271.0516. Calcd for $C_{13}H_{15}{}^{35}Cl_2NO$, 271.0531 ($M^+$).

Reaction of Triflate 1 with Tetrahydrothiophene (9), Chloroform, and CsF. To a mixture of CsF (460 mg, 3.0 mmol), chloroform (241 mg, 2.0 mmol), and tetrahydrothiophene (**9**) (176 mg, 2.0 mmol) in acetonitrile (10 mL) was added triflate **1** (303 mg, 1.0 mmol). After stirring for 6 h, the mixture was evaporated to give colorless oily crystals, which were chromatographed over silica gel by elution with hexane–EtOAc (10:1) to afford 4-phenylsulfanylbut-1-ene (**10**) (30 mg, 0.18 mmol) and 4-chlorobutyl phenyl thioether (**11**) (24 mg, 0.12 mmol). Compound **10**: colorless oil.[25] ^{1}H NMR ($CDCl_3$): δ 2.38 (m, 2H, CH_2), 3.00 (t, 2H, $J = 7.6$ Hz, SCH_2), 5.01 (d, 1H, $J = 6.8$ Hz, =CH), 5.06 (d, 1H, $J = 14.0$ Hz, =CH), 5.78 (m, 1H, =CH), 7.05–7.40 (m, 5H, Ph). MS: Calcd for $C_{10}H_{12}S$; 164.0660. Found (M^+): 164.0648. Compound **11**: colorless oil.[26] ^{1}H NMR ($CDCl_3$): δ 1.78 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), 2.92 (t, 2H, $J = 7.2$ Hz, CH_2), 3.54 (t, 2H, $J = 7.2$ Hz, CH_2), 7.10–7.40 (m, 5H, Ph). MS: Calcd for $C_{10}H_{13}ClS$; 200.0426. Found: (M^+) 200.0435.

Reaction of Triflate 1 with Tetrahydrothiophene (9) and CsF: Isolation of *S*-Phenylthiolanium Tetraphenylborate. To a mixture of CsF (270 mg, 1.8 mmol) and tetrahydrothiophene (**9**) (83 mg, 0.6 mmol) in acetonitrile (4 mL) was added triflate **1** (91 mg, 0.3 mmol). After stirring for 5 h, the mixture was evaporated to give pale yellow oil, which was filtered through short silica gel column by elution with ethyl acetate to give colorless oil of *S*-phenylthiolanium triflate (0.068 g, 0.21 mmol). ^{1}H NMR ($CDCl_3$): δ 2.35 (m, 4H, CH_2), 3.70 (m, 2H, CH_2), 4.18 (m, 2H, CH_2), 7.58–7.70 (m, 3H, Ph), 7.81 (d, 2H, $J = 7.2$ Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 29.36 (CH_2), 48.83 (CH_2), 120.92 (q, $J_{CF} = 318$ Hz, CF_3), 126.25, 129.99, 131.57, 134.31 (Ph). The resulting oil was dissolved in acetonitrile (5 mL) and added to a solution of sodium tetraphenylborate (342 mg, 1.0 mmol) in acetonitrile (6 mL). Immediately, colorless crystals were precipitated, which were filtered and washed with water. The residue was recrystallized from methanol–ether to afford colorless crystals (51 mg, 0.16 mmol). Mp 199–201 °C. Anal. Found: C, 84.07; H, 6.78%. Calcd for $C_{34}H_{33}BS$: C, 84.29; H, 6.87%.[27]

Reaction of Benzylideneaniline (12a) with Carboxylate 2 and THF in Refluxing Chloroform. A mixture of carboxylate **2** (1.48 g, 1.0 mmol, molecular sieves 3A (0.2 g), benzylideneaniline (**12a**) (181 mg, 1.0 mmol), and THF (720 mg, 10 mmol) in chloroform (6 mL) was stirred for 1 h then refluxed for 2 h. The reaction mixture was evaporated and the residue was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to give phenyl ether **8a** (74 mg, 0.28 mmol).

Reaction of Carboxylate 2 with Oxetane (4a) in Refluxing Chloroform. A mixture of carboxylate **2** (1.48 g, 1.0 mmol), molecular sieves 3A (0.2 g), and oxetane (**4a**) (0.58 g, 10 mmol) in chloroform (6 mL) was stirred for 1 h then refluxed for 2 h. The reaction mixture was evaporated and the residue was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to give 4,4,4-trichlorobutyl phenyl ether (**13a**) (0.116 g, 0.46 mmol). **13a**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.24–2.31 (m, 2H, CH_2), 2.89–2.95 (m, 2H, CH_2), 4.07 (t, 2H, $J = 6.4$ Hz, OCH_2), 6.89 (d, 2H, $J = 7.6$ Hz, *o*-Ph), 6.94 (t, 1H, $J = 7.6$ Hz, *p*-Ph), 7.29 (t, 2H, $J = 7.6$ Hz, *m*-Ph). ^{13}C NMR ($CDCl_3$): δ 26.92 (CH_2), 52.45 (CH_2), 66.24 (OCH_2), 99.97 (q-C), 114.69 (Ph), 121.24 (Ph), 129.77 (Ph), 158.85 (Ph). HRMS (EI): *m/z* 251.9859. Calcd for $C_{10}H_{11}{}^{35}Cl_3O$, 251.9875 (M^+).

Reaction of Triflate 1 with Oxetane (4a), Chloroform, and CsF. To a dried mixture of triflate **1** (0.149 g, 0.50 mmol) and CsF (0.46 g, 3.0 mmol) in acetonitrile (2.0 mL) was added a solution of oxetane (**4a**) (0.580 g, 10 mmol) and chloroform (1.19 g, 10 mmol) in acetonitrile (3.0 mL). After stirring for 15 h at rt, the reaction mixture was evaporated to give pale brown oil, which was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to give phenyl ether **13a** (0.109 g, 0.43 mmol).

The reaction of 3,3-dimethyloxetane (**4b**) with triflate **1** was carried out in a similar manner.

Compound **13b** (0.125 g, 0.45 mmol): pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 6H, CH_3), 3.06 (s, 2H, CH_2), 3.82 (s, 2H, OCH_2), 6.90 (d, 2H, $J = 7.6$ Hz, Ph), 6.95 (t, 1H, $J = 7.2$ Hz, Ph), 7.29 (dd, 2H, $J = 7.2$ Hz and 7.6 Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 25.55 (CH_3), 37.30 (CH_2), 60.55 (CH_2), 75.53 (OCH_2), 98.38 (CCl_3), 114.53, 120.82, 129.42, 158.82 (Ph). HRMS (EI): m/z 280.0183. Calcd for $C_{12}H_{15}{}^{35}Cl_3O$, 280.0183 (M^+).

Reaction of Triflate 1 with 3,3-Dimethyloxetane (4b), THF, Chloroform, and CsF. To a dried mixture of triflate **1** (0.059 g, 0.20 mmol), 3,3-dimethyloxetane (**4b**) (0.172 g, 2.0 mmol), THF (0.144 g, 2.0 mmol), and CsF (0.092 g, 0.60 mmol) in acetonitrile (3.0 mL) was added a solution of chloroform (0.60 g, 5.0 mmol) in acetonitrile (2.0 mL). After stirring for 15 h at rt, the reaction mixture was evaporated to give pale brown oil, which was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to give phenyl ether **13b** (0.045 g, 0.16 mmol).

Reaction of Triflate 1 with (1,2-Epoxyethyl)benzene (3b). To a dried mixture of triflate **1** (0.298 g, 1.0 mmol) and CsF (0.46 g, 3.0 mmol) was added a solution of epoxide **3b** (1.20 g, 10 mmol) and chloroform (1.19 g, 10 mmol) in acetonitrile (5.0 mL). After stirring for 16 h at rt, the reaction mixture was evaporated and to it was added water (15 mL). The reaction mixture was extracted with ether (5 mL × 3). The combined extract was dried over sodium sulfate, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane–EtOAc (5:1) to give 2-phenyl-2,3-dihydrobenzofuran (**14**) (0.035 g, 0.18 mmol), phenyl styryl ether (**15**) (0.016 g, 0.080 mmol), and phenanthrene (**16**) (0.005 g, 0.03 mmol). Benzofuran **14**: colorless oil. ^{1}H NMR spectral data of **14** and **15** were identical with that reported.[8] (*E*) and (*Z*) mixture of styryl ether **15**: colorless oil.[28] Phenanthrene (**16**): colorless crystals, mp 98–100 °C. ^{1}H NMR spectral data of **16** were identical with an authentic sample.

Reaction of Triflate 1 with 1,2-Epoxypropane (3a), Chloroform, and CsF. To a dried mixture of triflate **1** (0.149 g, 0.50 mmol) and CsF (0.46 g, 3.0 mmol) was added a solution of epoxide **3a** (0.58 g, 10 mmol) and chloroform (1.19 g, 10 mmol) in acetonitrile (3.0 mL). After stirring for 16 h at rt, the reaction mixture was evaporated to give pale brown oily solid, which was chromatographed over silica gel by elution with hexane–EtOAc (5:1) to give phenyl ether **17a** (0.061 g, 0.24 mmol) and **17a′** (0.030 g, 0.12 mmol). Compound **17a**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.66 (d, 3H, $J = 7.6$ Hz, CH_3), 3.00 (m, 1H, CH), 3.89 (dd, 1H, $J = 7.2$ Hz and 7.6 Hz, OC*H*H), 4.40 (dd, 1H, $J = 7.2$ Hz and 6.0 Hz, OC*H*H), 6.75–6.90 (m, 3H, Ph), 7.30 (dd, 2H, $J = 7.2$ Hz and 7.6 Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 18.00 (CH_3), 52.00 (CH), 69.00 (OCH_2), 103.00 (CCl_3), 113.00, 121.00, 129.00, 158.50 (Ph). HRMS (EI): m/z 251.9867. Calcd for $C_{10}H_{11}{}^{35}Cl_3O$, 251.9875 (M^+). Compound **17a′**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.49 (d, 3H, $J = 7.2$ Hz, CH_3), 2.95 (dd, 1H, $J = 10.5$ Hz and 3.2 Hz, C*H*H), 3.28 (dd, 1H, $J = 10.5$ Hz and 3.6 Hz, C*H*H), 4.80 (m, 1H, OCH), 6.88–7.02 (m, 3H, Ph), 7.32 (dd, 2H, $J = 7.2$ Hz and 7.6 Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 20.05 (CH_3), 61.00 (CH_2), 71.00 (OCH), 96.00 (CCl_3), 116.00, 121.00, 127.50, 157.00 (Ph). HRMS (EI): m/z 251.9840. Calcd for $C_{10}H_{11}{}^{35}Cl_3O$, 251.9875 (M^+).

Other reactions were carried out in a similar manner (0.5 mmol of **1** was used).

Compound **17b** (39%): pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.17 (t, 3H, $J = 7.6$ Hz, CH_3), 1.80–1.95 (m, 1H, C*H*H), 2.10–2.20 (m, 1H, C*H*H), 2.75–2.81 (m, 1H, CH), 4.15 (dd, 1H, $J = 6.4$ Hz and 10.0 Hz, C*H*H), 4.47 (dd, 1H, $J = 4.0$ Hz and 10.0 Hz, OC*H*H), 6.91–7.01 (m, 3H, Ph), 7.29 (t, 2H, $J = 7.6$ Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 12.49 (CH_3), 23.94 (CH_2), 60.65 (CH_2), 68.25 (OCH_2), 97.88 (CCl_3), 114.63, 121.17, 129.53, 158.34 (Ph). HRMS (EI): m/z 266.0036. Calcd for $C_{11}H_{13}{}^{35}Cl_3O$, 266.0032 (M^+).

Compound **17b′** (26%): pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.03 (t, 3H, $J = 7.2$ Hz, CH_3), 1.80–1.95 (m, 2H, CH_2), 3.00 (dd, 1H, $J = 15.2$ Hz and 2.4 Hz, C*H*H), 3.22 (dd, 1H, $J = 15.2$ Hz and 4.8 Hz, C*H*H), 4.68 (dd, 1H, $J = 4.8$ Hz and 2.4 Hz, OCH), 6.91–6.99 (m, 3H, Ph), 7.27 (t, 2H, $J = 7.2$ Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 9.00 (CH_3), 27.24 (CH_2), 58.64 (CH_2), 76.31 (OCH), 97.88 (CCl_3), 116.32, 121.41, 129.79, 157.73 (Ph). HRMS (EI): m/z 266.0079. Calcd for $C_{11}H_{13}{}^{35}Cl_3O$, 266.0032 (M^+).

Compound **17c** (37%): pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 0.93 (t, 3H, $J = 7.6$ Hz, CH_3), 1.24–1.61 (m, 4H, CH_2), 1.65–1.82 (m, 1H, C*H*H), 2.05–2.13 (m, 1H, C*H*H), 2.80–2.84 (m, 1H, CH), 4.13 (dd, 1H, $J = 10.0$ Hz and 5.6 Hz, OC*H*H), 4.46 (dd, 1H, $J = 10.0$ Hz and 3.6 Hz, OC*H*H), 6.90–7.00 (m, 3H, Ph), 7.29 (t, 2H, $J = 7.6$ Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 14.13 (CH_3), 22.89 (CH_2), 30.25 (CH_2), 30.76 (CH_2), 59.39 (CH), 68.92 (OCH_2), 103.32 (CCl_3), 114.87, 121.39, 129.77, 158.59 (Ph). HRMS (EI): m/z 294.0358. Calcd for $C_{13}H_{17}{}^{35}Cl_3O$, 294.0345 (M^+).

Compound **17c′** (25%): pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, $J = 6.8$ Hz, CH_3), 1.80–1.95 (m, 4H, CH_2), 1.73–1.79 (m, 2H, CH_2), 2.97 (dd, 1H, $J = 15.2$ Hz and 2.8 Hz, C*H*H), 3.22 (dd, 1H, $J = 15.2$ Hz and 6.4 Hz, C*H*H), 4.66–4.70 (m, 1H, OCH), 6.91–6.99 (m, 3H, Ph), 7.27 (t, 2H, $J = 7.6$ Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 14.83 (CH_3), 23.47 (CH_2), 27.55 (CH_2), 34.83 (CH_2), 59.68 (CH_2), 75.98 (OCH), 98.47 (CCl_3), 116.84, 121.97, 130.40, 158.34 (Ph). HRMS (EI): m/z 294.0348. Calcd for $C_{13}H_{17}{}^{35}Cl_3O$, 294.0345 (M^+).

Compound **17d** (19%): pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 0.93 (t, 3H, $J = 7.2$ Hz, CH_3), 1.30–1.62 (m, 8H, CH_2), 1.75–1.83 (m, 1H, C*H*H), 2.04–2.11 (m, 1H, CH*H*), 2.80–2.88 (m, 1H, CH), 4.13 (dd, 1H, $J = 4.2$ Hz and 10.0 Hz, OC*H*H), 4.46 (dd, 1H, $J = 4.4$ Hz and 10.0 Hz, OCH*H*), 6.92 (d, 2H, $J = 7.6$ Hz, Ph), 6.98 (t, 1H, $J = 7.6$ Hz, Ph), 7.30 (t, 2H, $J = 7.6$ Hz, Ph). HRMS (EI): m/z 322.0662. Calcd for $C_{15}H_{21}{}^{35}Cl_3O$, 322.0658 (M^+).

Compound **17d′** (6%): pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, $J = 7.2$ Hz, CH_3), 1.20–1.80 (m, 10H, CH_2), 2.98 (dd, 1H, $J = 3.2$ Hz and 15.2 Hz, OC*H*H), 3.21 (dd, 1H, $J = 6.4$ Hz and 15.2 Hz, OC*H*H), 4.72 (m, 1H, OCH), 6.89–7.00 (m, 3H, Ph), 7.28 (t, 2H, $J = 7.6$ Hz, Ph). HRMS (EI): m/z 322.0668. Calcd for $C_{12}H_{21}{}^{35}Cl_3O$, 322.0658 (M^+).

Reaction of Carboxylate 2 with 1,2-Epoxypropane (3a), and Chloroform. To a solution of epoxide **3a** (0.58 g, 10.0 mmol) in chloroform (1.19 g, 10 mmol) was added carboxylate **2** (0.148 g, 1.0 mmol). After refluxing for 3 h, the reaction mixture was evaporated and chromatographed over silica gel by elution with hexane to afford biphenylene (0.018 g,

0.12 mmol), which was identical with an authentic sample. Mp 112–113 °C.

Reaction of 1 with 5,6-Epoxy-1-hexene, Chloroform, and CsF. To a dried mixture of triflate **1** (0.149 g, 0.50 mmol) and CsF (3.0 mmol) was added a solution of 5,6-epoxy-1-hexene (**3h**) (0.49 g, 5.0 mmol) and chloroform (1.19 g, 10 mmol) in acetonitrile (3.0 mL). After stirring for 15 h at rt, the reaction mixture was evaporated and to it was added water (15 mL). The reaction mixture was extracted with ether (5 mL × 3). The combined extract was dried over sodium sulfate, filtered, and evaporated to give pale brown oil, which was chromatographed over silica gel by elution with hexane–EtOAc (5:1) to give epoxide **18a** (0.059 g, 0.34 mmol).

Mixture of (*E*)- and (*Z*)-**18a** (2:1): pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.20–2.45 (m, 2H, CH_2), 2.45–2.55 (m, 1H, OC*H*H), 2.72–2.76 (m, 1H, OC*H*H), 2.96–2.99 (m, 1H, OCH), 3.35–3.49 (m, 2H, $PhCH_2$), 5.40–5.62 (m, 1H, =CH), 5.68–5.81 (m, 1H, =CH), 7.15–7.23 (m, 2H, Ph), 7.25–7.32 (m, 3H, Ph). ^{13}C NMR ($CDCl_3$): δ 30.35 (CH_2), 33.77 ($PhCH_2$), 35.50 (CH_2), 39.26 ($PhCH_2$), 46.79 (OCH_2), 46.81 (OCH_2), 51.74 (OCH), 51.80 (OCH), 124.45 (=CH), 125.92 (=CH), 126.21, 126.22, 128.50, 128.61, 128.68, 128.69, 131.41, 132.47 (Ph), 140.60 (=CH), 140.70 (=CH). HRMS (EI): *m*/*z* 174.1049. Calcd for $C_{12}H_{14}O$, 174.1045 (M^+).

Mixture of (*E*)- and (*Z*)-**18b** (1:1): colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.60–2.68 (m, 2H, *E*- and *Z*-OC*H*H), 2.81–2.84 (m, 2H, *E*- and *Z*-OCH*H*), 3.20 (br, 2H, *E*- and *Z*-OCH), 3.24 (d, 1H, $J = 6.0$ Hz, *E*-$PhCH_2$), 3.45 (d, 1H, $J = 6.0$ Hz, *Z*-$PhCH_2$), 3.65 (dd, 1H, $J = 5.6$ Hz and 12.0 Hz, *E*-C*H*H), 3.75 (dd, $J = 5.6$ Hz and 12.0 Hz, *Z*-OC*H*H), 3.95 (dd, 1H, $J = 2.8$ Hz and 12.0 Hz, *E*-OCH*H*), 4.04 (dd, 1H, $J = 12.0$ Hz and 2.8 Hz, *Z*-OC*H*H), 4.61 (dt, 1H, $J = 6.0$ Hz and 7.2 Hz, *Z*-=CH), 4.98 (dt, $J = 7.6$ Hz and 12.8 Hz, *E*-=CH), 6.10 (d, 1H, $J = 6.0$ Hz, *Z*-=CH), 6.37 (d, 1H, $J = 12.8$ Hz, *E*-=CH), 7.00–7.33 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$): δ 31.05 (*Z*-$PhCH_2$), 34.78 (*E*-$PhCH_2$), 44.99 (*E*-CH_2), 45.19 (*Z*-CH_2), 51.01 (*E*-CH), 51.53 (*Z*-CH), 70.49 (*E*-OCH_2), 71.67 (*Z*-OCH_2), 104.74 (*E*-=CH), 107.17 (*Z*-=CH), 126.63, 126.91, 129.16, 129.18, 129.22, 129.27, 142.22, 142.42 (Ph), 146.24 (*Z*-=CH), 147.74 (*E*-=CH). HRMS (EI): *m*/*z* 190.0989 and 190.0988. Calcd for $C_{12}H_{14}O$, 190.0994 (M^+).

Reaction of Triflate 1 with Dibutyl Ether and Chloroform. To a mixture of CsF (465 mg, 3.0 mmol), chloroform (598 mg, 5.0 mmol), and dibutyl ether (642 mg, 5.0 mmol) in acetonitrile (10 mL) was added triflate **1** (150 mg, 0.5 mmol) in one portion. After stirring for 15 h, the reaction mixture was concentrated, taken up in brine (10 mL), and extracted with ethyl acetate (7 mL × 3). The combined extract was dried over sodium sulfate, filtered, and evaporated to give pale yellow oil, which was chromatographed over silica gel by elution with hexane–EtOAc (10:1) to afford butyl phenyl ether (**19b**) (16 mg, 0.10 mmol), the spectral data of which was identical with an authentic sample.

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