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Formation of epoxides from pentacoordinated organoarsenic compounds with a β-hydroxyethyl group†‡§

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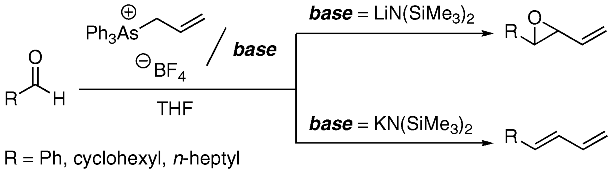
A series of pentacoordinated organoarsenic compounds (arsoranes) bearing a β-hydroxyethyl group (**4a**, **6a** and **6b**) was synthesized. The crystal structures were determined by single crystal X-ray analysis. Treatment of these arsoranes with KH almost quantitatively gave the corresponding epoxide. The reaction of **4a** having an unsubstituted β-hydroxyethyl group with KH was monitored by ^{1}H and ^{19}F NMR in CD_3CN, suggesting that a hexacoordinate arsenic anion was formed as the intermediate. However, a further stereochemical study of the epoxide formation suggested that the reaction proceeded in the S_N2 manner and not in the ligand coupling reaction (LCR) of the intermediate hexacoordinate arsenic anion.

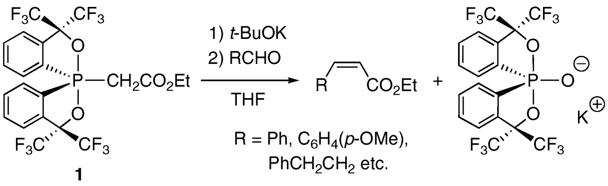
Introduction

The reaction of a phosphonium ylide with a ketone or an aldehyde producing an olefin, called the Wittig reaction, is one of the most useful methods for carbon–carbon double bond formation, and thus extensively used in organic synthesis.[1] The stereoselectivity of the produced olefin generally depends on the substituents of the ylide; phosphonium ylides bearing electron-donating groups on the ylidic carbon (unstabilized ylides) produce *Z*-olefins, whereas those having electron-withdrawing groups (stabilized ylides) produce the thermodynamically favorable *E*-olefins.

Unlike the phosphonium ylides, arsenic analogues (arsonium ylides) are much less common.[2] However, arsonium ylides are essentially more reactive than phosphonium ylides due to the higher nucleophilicity of the ylidic carbon of the former. In addition, it is attractive that the product type varies depending on the nature of the substituent. For example, the reactions of arsonium ylides with carbonyl compounds form olefins or epoxides. Stabilized ylides, *e.g.*, $Ph_3As{=}CHCOPh$, produce olefins with a high *E*-selectivity under mild reaction conditions, whereas the unstabilized ylides, *e.g.*, $Ph_3As{=}CHMe$, form epoxides with a moderate to high *E*-selectivity.[3] Semistabilized (benzylic and allylic) ylides generally give a mixture of olefins and epoxides. Hsi and Koreeda have shown that the product distribution from the reaction of an allylic ylide with several aldehydes can be controlled by the cation of the base (Scheme 1).[4]



Scheme 1



Scheme 2

During the course of our study on hypervalent compounds involving the group 15 elements,[5] we have found that the α-anion of the 10-P-5 spirophosphorane having an ethoxycarbonylmethyl group (**1**) works as a Wittig-type reagent.[6] The reactions of the α-anion with aromatic and aliphatic aldehydes produce olefins with an excellent *Z*-selectivity (up to Z/E = >98 : 2) (Scheme 2). Furthermore, the phosphoranes with a cyano or an amide functionality also form olefins.[7] The cyano derivative showed a high *Z*-selectivity only when reacted with aliphatic aldehydes, whereas the amide derivatives reacted with both aliphatic and aromatic aldehydes to exclusively give the *Z*-olefins. The detailed stereochemical study of the decomposition reactions of the diastereomeric phosphoranes having an α,β-diphenyl-β-hydroxyethyl group (**2**) clarified that the rate of formation of the *Z*-olefin was faster than that of the *E*-olefin (Scheme 3).[8]

In this context, we focused on the decomposition reaction of the 10-As-5 spiroarsorane with a β-hydroxyethyl group. We now report the synthesis and structure of 10-As-5 β-hydroxyethylspiroarsoranes, and the exclusive epoxide formation from these arsoranes under basic conditions.

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† Dedicated to the memory of Pascal Le Floch.

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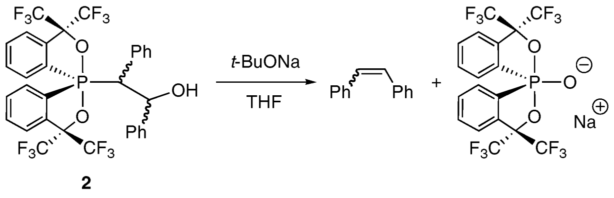
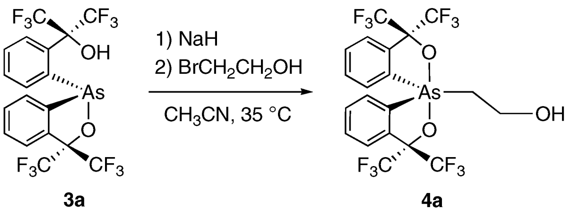


Scheme 3

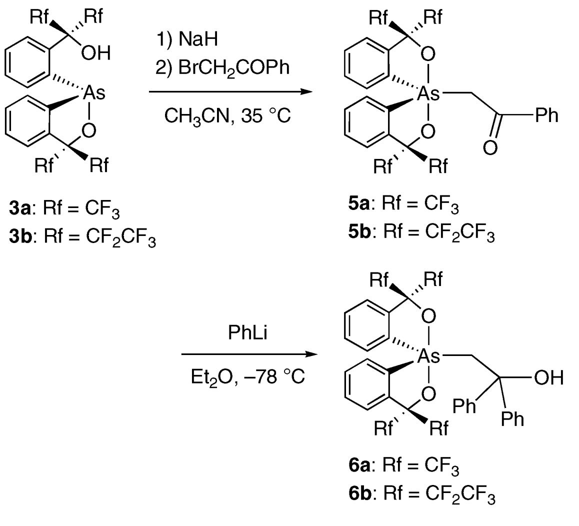
Results and discussion

At first, the syntheses of β-hydroxyethylarsoranes using two kinds of bidentate ligands were examined. The Martin ligand derived from the hexafluorocumyl alcohol[9] and our ligand derived from 1,1,1,2,2,4,4,5,5,5-decafluoro-3-phenyl-3-pentanol[10] were used as the bidentate ligand. The reaction of the arsine **3a**[11] with 2-bromoethanol in the presence of NaH gave the α,β-unsubstituted derivative **4a** in 35% yield (Scheme 4). The synthesis of the β,β-diphenyl derivative was next examined. The treatment of **3a** with NaH, followed by 2-chloro-1,1-diphenylethanol ($ClCH_2CPh_2OH$), resulted in recovery of the reagents. Thus, arsines **3a** and **3b** were treated with phenacyl bromide ($BrCH_2COPh$) to form the corresponding β-keto derivatives **5a** (20%) and **5b** (20%), respectively. The β-keto derivatives were then treated with PhLi to afford the desired β,β-diphenyl derivatives **6a** (74%) and **6b** (67%) (Scheme 5).

Single crystals of **4a**, **5a**, **5b**, **6a** and **6b** grown from hexane/dichloromethane mixed solutions were subjected to single crystal X-ray analysis. For **6a**, two independent molecules were found in the unit cell. The crystal of **6b** contained solvated dichloromethane. The ORTEP diagrams are shown in Fig. 1, and the selected bond parameters are summarized in Table 1. For all the structures, the arsenic atoms are pentacoordinated, the geometries around the arsenic atoms are a slightly distorted trigonal bipyramid (TBP), and the oxygen atoms occupy the apical sites. As a whole, As–O and As–C lengths for **6a** and **6b** are longer than those for the other compounds due to steric repulsions originating from the bulky monodentate ligand. The As–O1 lengths for **6a** (1.937(3) and 1.938(3) Å) and **6b** (1.940(3) Å) are longer than the As–O2 lengths by 0.02–0.04 Å. The O1···O3 lengths for **6a** are 2.80 Å (1st molecule) and 2.73 Å (2nd), and that of **6b** is 2.78 Å. This suggests that, for **6a** and **6b**, the hydroxy proton forms a hydrogen bond with the apical oxygen atom (O1), giving rise to the elongation of the As–O1 lengths. On the other hand, the hydroxy group of **4a** forms intermolecular O–H···F hydrogen bonds, where the interatomic distance between O3 and F5 ($3/2 - x$, $-1/2 + y$, z) is 3.463(4) Å, and that between O3 and F12 ($-1/2 + x$, y, $1/2 - z$) is 2.974(3) Å. As for the bond angles, the O1–As–O2 angles for the C_2F_5 derivatives **5b** and **6b** (167.7–170.2°) are farther from the ideal 180° than those for the CF_3 derivatives (173.1–177.5°), and the C1–As–C2 angles for the former (134.6–134.8°) are farther from the ideal 120° than those for the latter (120.6–127.7°). These results indicate that the geometries for the C_2F_5 derivatives are more distorted from an ideal TBP than that for the CF_3 derivatives.



Scheme 4



Scheme 5

The decomposition reactions were then examined (Scheme 6). We found that the treatment of compound **4a** with KH in CD_3CN quantitatively gave the arsoranide **7a-K**. The reaction was thus monitored by ^1H and ^{19}F NMR at 25 °C (Fig. 2). After 10 min, four signals at $\delta = -73.3$ (br s), −73.5 (br s), −73.9 (br m) and −74.2 (br s) ppm (A) were mainly observed in the ^{19}F NMR along with a pair of low-intensity quartets corresponding to the arsoranide **7a-K** ($\delta = -73.3$ and −76.0 ppm). Additional signals (B) appeared at $\delta = -74.3$ (q), −74.4 (m), −74.6 (m) and −74.9 (q) ppm during the reaction. The A and B signals gradually decreased and the signals for **7a-K** increased as the reaction proceeded, and finally only the latter ones could be observed. After monitoring for 6.5 h at 25 °C and then heating for 4 h at 45 °C, the crude mixture was separated to give the arsoranide **7a-K** in 96% as an isolated product. Although ethylene oxide (**8**) was detected at $\delta = 2.54$ ppm in the ^1H NMR (CD_3CN), the highly volatile **8** (bp 10 °C) could not be isolated. Thus, similar reactions using the β,β-diphenyl derivatives **6a** and **6b** were carried out to almost quantitatively form the 1,1-diphenylethylene oxide (**9**) (isolated yield 93% from **6a**, 94% from **6b**) together with the corresponding arsoranide **7a-K** and **7b-K**, respectively. The reactions of **6a** and **6b** were completed within 20 min at 30 °C. Although the reaction rates have not yet been measured, the decomposition reactions of the β,β-diphenyl derivatives **6** are obviously faster than that of the unsubstituted **4a**. This should be due to the steric crowding of **6** compared to **4a**, *i.e.*, the greater steric repulsion of **6** should be a driving force for the decomposition.

Two mechanisms for the epoxide formation can be considered (Scheme 7). One is the S_N2 reaction, in which the alkoxide anion attacks the α-carbon, and the other is the ligand coupling reaction (LCR),[12] in which hexacoordinate intermediates once

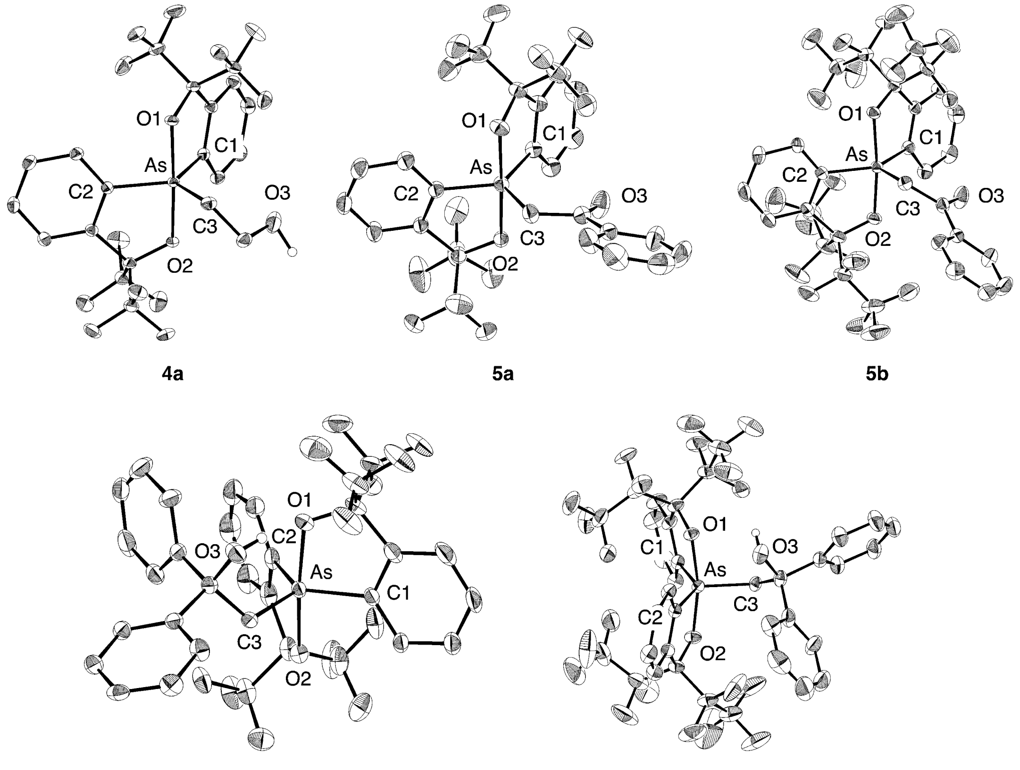
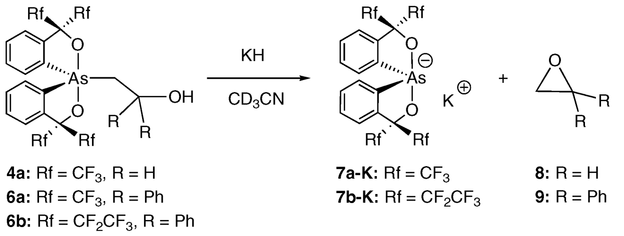


Fig. 1 The ORTEP diagrams of **4a**, **5a**, **5b**, **6a** and **6b** showing the thermal ellipsoids at the 30% probability level. For **6a**, one of the two independent molecules is shown. The hydrogen atoms other than those of the hydroxy group and the solvated molecules are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for **4a**, **5a**, **5b**, **6a** and **6b**

	4a	5a	5b	6a[a]	6b
Bond length/Å					
As–O1	1.912(2)	1.915(2)	1.9138(16)	1.937(3), 1.938(3)	1.940(3)
As–O2	1.9119(19)	1.914(2)	1.9009(16)	1.914(3), 1.915(3)	1.904(3)
As–C1	1.917(3)	1.917(3)	1.929(2)	1.931(4), 1.938(4)	1.933(4)
As–C2	1.925(2)	1.916(3)	1.917(3)	1.938(4), 1.933(4)	1.924(4)
As–C3	1.935(3)	1.931(3)	1.938(3)	1.951(4), 1.963(4)	1.946(4)
Bond angle/°					
O1–As–O2	176.09(8)	177.51(9)	170.17(8)	174.23(15), 173.07(13)	167.67(14)
C1–As–C2	120.64(11)	121.73(13)	134.60(11)	125.7(2), 127.66(18)	134.84(17)
C1–As–C3	120.73(12)	123.70(13)	116.49(11)	115.01(19), 108.96(18)	106.39(17)
C2–As–C3	118.62(12)	114.53(14)	108.89(11)	119.22(19), 123.36(18)	118.76(17)

[a] Bond lengths and angles for the two independent molecules are shown.



Scheme 6

formed after deprotonation decompose to give the epoxide.[13] The four broad signals A observed in the above-described reaction (Fig. 2) could be those corresponding to a hexacoordinate arsenic anion bearing an oxaarsetane ring, *e.g.* **Int-2**, because the four CF_3 groups of such an anion are magnetically unequivalent. However, there is no proof on the direct formation of the epoxide from the hexacoordinate anions derived from **4** or **6**. Although it is not yet clear, the B signals might correspond to the isomeric hexacoordinate anions **Int-2′** or **Int-2″** because we observed the two types of isomerizations in the hexacoordinate phosphate anions of this type (**10A** to **10B**,[13b,c] **11A** to **11B**[10c]) (Scheme 8).

The two mechanisms should differ in the stereochemistry of the product, *i.e.*, S_N2 mechanism results in inversion of the stereochemistry of the carbon α to the arsenic atom, whereas the LCR mechanism retains it. To stereochemically clarify the mechanism, some preliminary investigations were carried out.[14] We synthesized the diastereomeric α,β-dimethyl-β-phenyl derivatives **12a**, and one diastereomer **12a-S_{As}*RR***

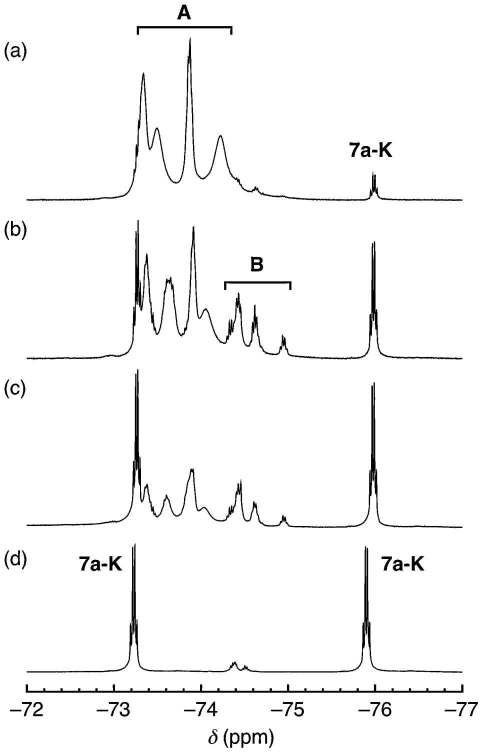
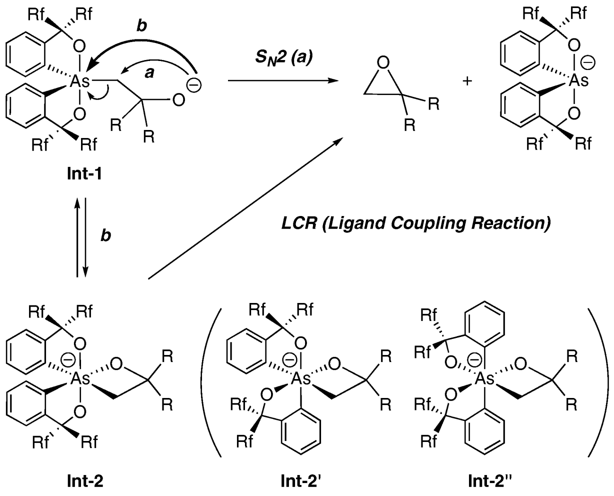
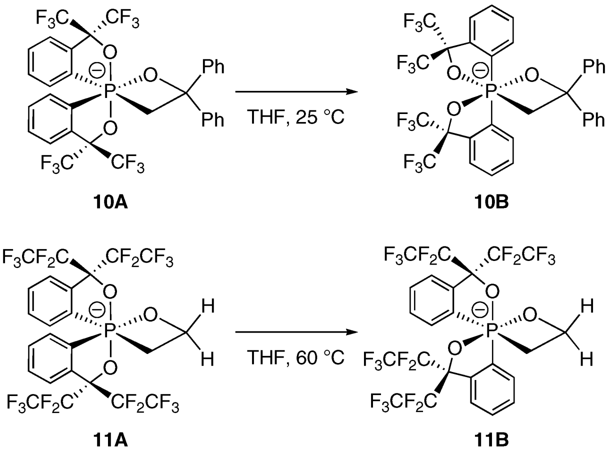


Fig. 2 Time course of the reaction of **4a** with KH in CD_3CN at 25 °C. (a) 10 min, (b) 3 h, (c) 6.5 h, and (d) after heating at 45 °C for 4 h from (c).

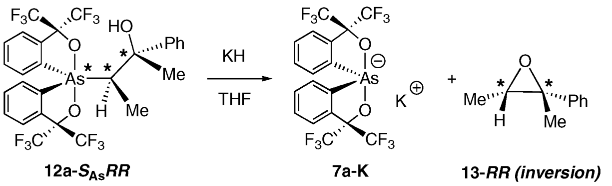


Scheme 7

(S configuration at As,[15] R at the α and β carbon) was isolated. The stereochemistry of **12a-$S_{As}RR$** was determined by single crystal X-ray analysis. The treatment of **12a-$S_{As}RR$** with KH in THF for 20 min exclusively gave (2R,3R)-2,3-dimethyl-2-phenyloxirane (**13-*RR***), indicating that the stereochemistry at the α-carbon was inverted (Scheme 9). This result suggests that the reaction proceeds in the S_N2 manner, hence this should be true for the reaction of **4a** and **6**. Thus, for the reaction of **4a**, the hexacoordinate anion **Int-2** should exist as a stable intermediate which does not form the epoxide (Fig. 2).



Scheme 8



Scheme 9

In conclusion, we synthesized a series of pentacoordinated organoarsenic compounds bearing a β-hydroxyethyl group, and the structures were determined by single crystal X-ray analysis. We found that these compounds decomposed upon treatment with KH in CD_3CN to almost quantitatively give the corresponding epoxide. Further investigations on the mechanism of the epoxide formation are in progress.

Experimental

General

The melting points were measured using a Yanaco micro-melting point apparatus. The ^1H NMR (400 MHz) and ^{19}F NMR (376 MHz) were recorded using JEOL EX-400 or JEOL AL-400 spectrometers. The ^1H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by residual chloroform (δ = 7.26 ppm) or acetonitrile (δ = 1.90 ppm). The ^{19}F NMR chemical shifts (δ) are given in ppm downfield from the external $CFCl_3$. The elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. All reactions were carried out under N_2. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from Na-benzophenone, *n*-hexane was distilled from Na, and the other solvents were distilled from CaH_2. Merck silica gel 60 was used for the column chromatography.

Syntheses

4a. Under N_2, a solution of **3a** (151.2 mg, 0.269 mmol) in CH_3CN (3 mL) was added to a solution of NaH (70.0 mg, 1.75 mmol) in CH_3CN (3 mL) at 0 °C, and the mixture was stirred for 10 min at room temperature. The mixture was then cooled to 0 °C, $BrCH_2CH_2OH$ (0.08 mL, 1.13 mmol) was added, and the mixture was stirred for 18 h at 35 °C. The mixture was extracted with Et_2O (2 × 30 mL), the organic layer was washed with brine (2 × 20 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude mixture was separated by preparative TLC (*n*-hexane : CH_2Cl_2 = 2 : 1) to afford **4a** (57.8 mg, 0.0956 mmol, 35%) as a white solid. Colorless crystals of **4a** suitable for the X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. Mp: 149.3–150 °C; ^{1}H NMR ($CDCl_3$): δ = 7.31–8.35 (m, 2H), 7.80 (br s, 2H), 7.71–7.75 (m, 4H), 3.96–4.06 (m, 1H), 3.90–3.98 (m, 1H), 3.00–3.09 (m, 1H), 2.85–2.93 (m, 1H), 2.61 ppm (s, 1H); ^{19}F NMR ($CDCl_3$): δ = −75.4 (q, $^{4}J_{FF}$ = 8.6 Hz, 6F), −75.5 ppm (q, $^{4}J_{FF}$ = 8.6 Hz, 6F); elemental analysis: calcd (%) for $C_{20}H_{13}F_{12}O_3As$: C 39.76, H 2.17; found: C 39.56, H 2.06.

5a. Under N_2, a solution of **3a** (160.9 mg, 0.287 mmol) in CH_3CN (5 mL) was added to a solution of NaH (18.9 mg, 0.472 mmol) in CH_3CN (5 mL) at 0 °C, and the mixture was stirred for 10 min at room temperature. The mixture was then cooled to 0 °C, $BrCH_2COPh$ (74.4 mg, 0.373 mmol) in CH_3CN (5 mL) was added, and the mixture was stirred for 19 h at 35 °C. The mixture was extracted with Et_2O (2 × 40 mL), and the organic layer was washed with brine (2 × 30 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude mixture was separated by preparative TLC (*n*-hexane : CH_2Cl_2 = 3 : 1) to afford **5a** (39.0 mg, 0.0574 mmol, 20%) as a white solid. Colorless crystals of **5a** suitable for the X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. Mp: 98.1–99.0 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ = 8.34–8.36 (m, 2H), 7.81 (br s, 2H), 7.78 (d, $^{3}J_{HH}$ = 8 Hz, 2H), 7.71–7.74 (m, 4H), 7.55 (t, $^{3}J_{HH}$ = 8 Hz, 1H), 7.39 (t, $^{3}J_{HH}$ = 8 Hz, 2H), 4.40 (d, $^{2}J_{HH}$ = 14.6 Hz, 1H), 4.25 ppm (d, $^{2}J_{HH}$ = 14.6 Hz, 1H); ^{19}F NMR ($CDCl_3$): δ = −75.2 (q, $^{4}J_{FF}$ = 8.6 Hz, 6F), −75.6 ppm (q, $^{4}J_{FF}$ = 8.6 Hz, 6F); elemental analysis: calcd (%) for $C_{26}H_{15}F_{12}O_3As$: C 46.04, H 2.23; found: C 46.18, H 2.07.

5b. Under N_2, a solution of **3b** (367.6 mg, 0.469 mmol) in CH_3CN (5 mL) was added to a solution of NaH (17.8 mg, 0.445 mmol) in CH_3CN (5 mL) at 0 °C, and the mixture was stirred for 10 min at room temperature. The mixture was then cooled to 0 °C, $BrCH_2COPh$ (70.0 mg, 0.351 mmol) in CH_3CN (5 mL) was added, and the mixture was stirred for 21 h at 35 °C. The mixture was extracted with Et_2O (2 × 40 mL), and the organic layer was washed with brine (2 × 40 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude mixture was separated by preparative TLC (*n*-hexane : CH_2Cl_2 = 3 : 1) to afford **5b** (83.6 mg, 0.0951 mmol, 20%) as a white solid. Colorless crystals of **5b** suitable for the X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. Mp: 148.7–149.5 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ = 8.57 (d, $^{3}J_{HH}$ = 8 Hz, 2H), 7.75–7.82 (m, 6H), 7.71 (d, $^{3}J_{HH}$ = 8 Hz, 2H), 7.54 (t, $^{3}J_{HH}$ = 8 Hz, 1H), 7.39 (t, $^{3}J_{HH}$ = 8 Hz, 2H), 4.30 (d, $^{2}J_{HH}$ = 16.1 Hz, 1H), 4.08 ppm (d, $^{2}J_{HH}$ = 16.1 Hz, 1H); ^{19}F NMR ($CDCl_3$): δ = −78.1 (s, 6F), −79.2(dd, $^{3}J_{FF}$ = 17.2 Hz, $^{5}J_{FF}$ = 4.9 Hz, 6F), −115.6 (dq, $^{2}J_{FF}$ = 283.4 Hz, $^{3}J_{FF}$ = 17.2 Hz, 2F), −116.1 (d, $^{2}J_{FF}$ = 283.4 Hz, 1F), −116.2 (d, $^{2}J_{FF}$ = 283.4 Hz, 1F), −117.2 (d, $^{2}J_{FF}$ = 283.4 Hz, 2F), −119.8 (dm, $^{2}J_{FF}$ = 283.4 Hz, 1F), −120.1 ppm (dm, $^{2}J_{FF}$ = 283.4 Hz, 1F); elemental analysis: calcd (%) for $C_{30}H_{15}F_{20}O_3As$: C 41.02, H 1.72; found: C 40.98, H 1.51.

6a. Under N_2, PhLi (1.14 M cyclohexane/Et_2O solution, 0.14 mL, 0.159 mmol) was added to a solution of **5a** (55.7 mg, 0.0821 mmol) in Et_2O (3.0 mL) at −78 °C. The mixture was then stirred for 2 h at −78 °C. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) at −78 °C. The mixture was extracted with Et_2O (2 × 40 mL), and the organic layer was washed with brine (2 × 30 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude mixture was separated by preparative TLC (*n*-hexane : CH_2Cl_2 = 4 : 1), followed by HPLC (ODS, MeCN) to afford **6a** (RT = 25.6 min: 46.2 mg, 0.0610 mmol, 74%) as a white solid. Colorless crystals of **6a** suitable for the X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. Mp: 57.0–58.0 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ = 7.93 (d, $^{3}J_{HH}$ = 8 Hz, 2H), 7.70 (br d, $^{3}J_{HH}$ = 8 Hz, 2H), 7.60 (t, $^{3}J_{HH}$ = 8 Hz, 2H), 7.49 (t, $^{3}J_{HH}$ = 8 Hz, 2H), 7.33–7.35 (m, 3H), 7.22 (t, $^{3}J_{HH}$ = 8 Hz, 2H), 7.18 (t, $^{3}J_{HH}$ = 8 Hz, 2H), 6.94–6.97 (m, 3H), 5.35 (s, 1H), 3.87 (d, $^{2}J_{HH}$ = 13.9 Hz, 1H), 3.80 ppm (d, $^{2}J_{HH}$ = 13.9 Hz, 1H); ^{19}F NMR ($CDCl_3$): δ = −74.3 (q, $^{4}J_{FF}$ = 8.6 Hz, 6F), −75.1 ppm (q, $^{4}J_{FF}$ = 8.6 Hz, 6F); elemental analysis: calcd (%) for $C_{32}H_{21}F_{12}O_3As{\cdot}H_2O$: C 49.63, H 2.99; found: C 49.94, H 2.64; MS(EI(+)): *m*/*z* = 756 $[M]^+$, 757 $[M + 1]^+$, 758 $[M + 2]^+$, 559 $[M - CH_2CPh_2OH]^+$.

6b. Under N_2, PhLi (1.14 M cyclohexane/Et_2O solution, 0.08 mL, 0.0912 mmol) was added to a solution of **5b** (50.7 mg, 0.0577 mmol) in Et_2O (3.0 mL) at −78 °C. The mixture was then stirred for 2 h at −78 °C. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) at −78 °C. The mixture was extracted with Et_2O (2 × 40 mL), and the organic layer was washed with brine (2 × 30 mL) and dried over anhydrous $MgSO_4$. After filtering the organic layer through SiO_2 and removing the solvents by evaporation, the resulting crude mixture was separated by HPLC (ODS, MeCN) to afford **6b** (RT = 32.0 min: 37.0 mg, 0.0386 mmol, 67%) as a white solid. Colorless crystals of **6b** suitable for the X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. Mp: 139.0–140.0 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ = 8.21 (d, $^{3}J_{HH}$ = 8 Hz, 2H), 7.71 (br d, $^{3}J_{HH}$ = 8 Hz, 2H), 7.75–7.62 (m, 4H), 7.32 (d, $^{3}J_{HH}$ = 8 Hz, 2H), 7.12–7.23 (m, 6H), 6.91–6.98 (m, 2H), 4.85 (s, 1H), 3.76 ppm (s, 2H); ^{19}F NMR ($CDCl_3$): δ = −78.2 (t, $^{3}J_{FF}$ = 8.6 Hz, $^{5}J_{FF}$ = 8.6 Hz, 6F), −78.4 (d, $^{3}J_{FF}$ = 8.6 Hz, 6F), −114.6 (dm, $^{2}J_{FF}$ = 287.1 Hz, 2F), −115.2 (dm, $^{2}J_{FF}$ = 287.1 Hz, 2F), −116.3 (d, $^{2}J_{FF}$ = 287.1 Hz, 2F), −118.1 ppm (dm, $^{2}J_{FF}$ = 287.1 Hz, 2F); elemental analysis: calcd (%) for $C_{36}H_{21}F_{20}O_3As$: C 45.21, H 2.21; found: C 45.42, H 2.00; MS(EI(+)): *m*/*z* = 956 $[M]^+$, 957 $[M + 1]^+$, 958 $[M + 2]^+$, 759 $[M - CH_2CPh_2OH]^+$.

Reactions with KH

4a. A CD_3CN (0.5 mL) solution of **4a** (26.2 mg, 0.0433 mmol) was added to a CD_3CN (0.3 mL) suspension of KH (excess), then the mixture was stirred for 10 min at 0 °C.

The supernatant was transferred to an NMR tube under N_2, and the reaction was monitored by ^{1}H and ^{19}F NMR at 25 °C. During the reaction, the ^{1}H NMR (CD_3CN) showed a signal for **8** (δ = 2.54 ppm), however, the signal disappeared probably due to the low boiling point of **8** (10 °C). After monitoring for 6.5 h at 25 °C, the mixture was heated at 45 °C for 4 h to complete the reaction. The mixture was quenched with aqueous NH_4Cl (10 mL). The mixture was extracted with Et_2O (2 × 20 mL), the organic layer was washed with water (2 × 20 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude mixture was separated by preparative TLC (*n*-hexane : CH_2Cl_2 = 3 : 1), followed by HPLC (ODS, MeCN) to afford **7a-K** (RT = 15.6 min: 25.1 mg, 0.0419 mmol, 96%) as a white solid. **7a-K**: ^{1}H NMR ($CDCl_3$): δ = 8.05 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 7.55 (br d, $^3J_{HH}$ = 7.6 Hz, 2H), 7.37 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 7.30 ppm (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ = −74.0 (q, $^4J_{FF}$ = 8.6 Hz, 6F), −76.6 ppm (q, $^4J_{FF}$ = 8.6 Hz, 6F).

6a. A CD_3CN (0.5 mL) solution of **6a** (24.7 mg, 0.0326 mmol) was added to a CD_3CN (0.3 mL) suspension of KH (excess), then the mixture was stirred for 10 min at 0 °C. The supernatant was transferred to an NMR tube under N_2, and the reaction was monitored by ^{1}H and ^{19}F NMR at 30 °C. The ^{1}H NMR (CD_3CN) showed a characteristic signal for **9** (δ = 3.29 ppm). The reaction was completed within 20 min. The mixture was quenched with aqueous NH_4Cl (10 mL). The mixture was then extracted with Et_2O (2 × 20 mL), the organic layer was washed with water (2 × 20 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude mixture was separated by preparative TLC (*n*-hexane : CH_2Cl_2 = 3 : 1), followed by HPLC (ODS, MeCN) to afford **9** (RT = 16.8 min: 6.0 mg, 0.031 mmol, 93%) as a colorless liquid and **7a-K** (RT = 14 min: 18.6 mg, 0.031 mmol, 95%) as a white solid. **9**: ^{1}H NMR ($CDCl_3$): δ = 7.30–7.37 (m, 10H), 3.29 ppm (s, 2H); MS(EI(+)): m/z = 196 $[M]^+$, 197 $[M + 1]^+$, 198$[M + 2]^+$, 166 $[M - CH_2O]^+$. The spectral data of **7a-K** were consistent with those of the same product described above.

6b. A CD_3CN (0.5 mL) solution of **6b** (28.4 mg, 0.0296 mmol) was added to a CD_3CN (0.3 mL) suspension of KH (excess), then the mixture was stirred for 10 min at 0 °C. The supernatant was transferred to an NMR tube under N_2, and the reaction was monitored by ^{1}H and ^{19}F NMR at 30 °C. The ^{1}H NMR (CD_3CN) showed a characteristic signal for **9** (δ = 3.29 ppm). The reaction was completed within 20 min. The mixture was quenched with aqueous NH_4Cl (10 mL). The mixture was then extracted with Et_2O (2 × 30 mL), the organic layer was washed with water (2 × 20 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude mixture was separated by preparative TLC (*n*-hexane : CH_2Cl_2 = 4 : 1), followed by HPLC (ODS, MeCN) to afford **9** (RT = 16.8 min: 5.5 mg, 0.031 mmol, 94%) as a colorless liquid and **7b-K** (RT = 14 min: 22.4 mg, 0.0281 mmol, 95%) as a white solid. **7b-K**: ^{1}H NMR ($CDCl_3$): δ = 7.99 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.63 (br d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.45 (t, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 7.37 ppm (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 2H); ^{19}F NMR ($CDCl_3$): δ = −78.0 (dd, $^3J_{FF}$ = 16.0 Hz, $^5J_{FF}$ = 3.8 Hz, 6F), −78.6 (s, 6F), −115.2 (s, 4F), −117.3 (dm, $^2J_{FF}$ = 284.6 Hz, 2F), −119.5 ppm (dm, $^2J_{FF}$ = 284.6 Hz, 2F). The spectral data of **9** were consistent with those of the same product described above.

Table 2 Crystallographic data for **4a**, **5a**, **5b**, **6a** and **6b**

	Compound				
	4a	**5a**	**5b**	**6a**	**6b**·CH_2Cl_2
Formula	$C_{20}H_{13}AsF_{12}O_3$	$C_{26}H_{15}AsF_{12}O_3$	$C_{30}H_{15}AsF_{20}O_3$	$C_{32}H_{21}AsF_{12}O_3$	$C_{37}H_{23}AsCl_2F_{20}O_3$
Molecular weight	604.22	678.30	878.34	756.41	1041.37
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	$C2/c$	$C2/c$
Color	Colorless	Colorless	Colorless	Colorless	Colorless
Habit	Plate	Plate	Plate	Plate	Plate
Crystal dimensions/mm	0.60 × 0.40 × 0.40	0.60 × 0.40 × 0.30	0.60 × 0.40 × 0.40	0.30 × 0.20 × 0.20	0.60 × 0.40 × 0.30
a/Å	9.8110(1)	9.2340(1)	9.9960(1)	40.3950(8)	39.9674(1)
b/Å	17.1930(3)	10.9850(2)	12.3680(2)	12.0720(2)	9.5830(5)
c/Å	24.8070(5)	14.1180(4)	14.9450(3)	26.7000(6)	26.4609(6)
α/°	90	85.094(1)	105.926(1)	90	90
β/°	90	80.621(1)	105.845(1)	93.526(1)	127.3997(10)
γ/°	90	66.995(1)	103.150(1)	90	90
V/Å^3	4184.46(12)	1300.18(5)	1615.31(4)	12995.6(4)	8051.2(5)
Z	8	2	2	16	8
D_{calcd}/g cm^{-3}	1.918	1.733	1.806	1.546	1.718
Abs. coeff./mm^{-1}	1.754	1.422	1.201	1.147	1.107
F(000)	2384	672	864	6048	4128
Radiation, λ/Å	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
T/K	173	293	293	173	293
Data, collected	$+h, +k, +l$	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$	$+h, +k, \pm l$	$\pm h, +k, \pm l$
Data/restrains/parameters	4676/1/329	5599/0/379	7112/0/487	14609/0/912	15491/0/568
$R_1[I > 2\sigma(I)]$	0.0398	0.0505	0.0381	0.0640	0.0658
wR_2 (all data)	0.1305	0.1446	0.1215	0.2135	0.2053
GOF	1.123	1.178	1.145	1.112	1.162
Solvent for crystallization	*n*-Hexane/CH_2Cl_2	*n*-Hexane/CH_2Cl_2	*n*-Hexane/CH_2Cl_2	*n*-Hexane/CH_2Cl_2	*n*-Hexane/CH_2Cl_2

Single crystal X-ray analyses

Crystals of **4a**, **5a**, **5b**, **6a** and **6b** suitable for the X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (MAC Science).[16] For each data set, the rotation images were collected in 3 degree increments with a total rotation of 180° about the ϕ axis. The data were processed using SCALEPACK. The structure was solved by a direct method using the SHELX-97 program.[17] Refinement on F^2 was carried out using the full-matrix least-squares by the SHELX-97 program.[17] All non-hydrogen atoms were refined using the anisotropic thermal parameters except for the disordered fluorine atoms. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters. The crystallographic data are summarized in Table 2.§

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