

Synthesis, Solubility, and Reaction of Long Alkyl-Chained Hypervalent Iodine Benzyne Precursors

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Long-chained hypervalent iodine benzyne precursors bearing ethyl, butyl, hexyl, octyl, decyl, dodecyl, and tetradecyl groups were synthesized, respectively. As the alkyl chain of the benzyne precursors is lengthened, the solubility in nonpolar organic solvents and the yield of the benzyne adduct with furan gradually increases.

Benzyne is one of the important reactive intermediates in organic chemistry, and has been extensively applied to mechanistic studies and syntheses of functionalized materials.¹ Recently, we reported that (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**1a**) is an excellent benzyne precursor.² The reaction of [2-(trimethylsilyl)phenyl]iodonium triflate **1a** with tetrabutylammonium fluoride generates benzyne quantitatively under mild conditions (room temperature and neutral conditions) and affords a benzyne adduct in the presence of a trapping agent in high yield, as shown in Scheme 1. This methodology can be applied to the generation of various types of strained species, such as a cyclic alkyne,³ didehydroheterocycles,⁴ didehydronaphthalene,⁵ and didehydrocarboranes.⁶ Also, this benzyne precursor **1a** has been used satisfactorily in the reaction of benzyne with thioketones that are very unstable, and are not tolerable under alkaline conditions.⁷

In spite of such advantages, this benzyne precursor **1a** has a low solubility in most organic solvents (hexane, diethyl ether, benzene, toluene, THF, and so on). Accordingly, the choice of solvents is limited to polar solvents, such as dichloromethane and MeCN.

In order to improve the solubility of the benzyne precursor **1a**, we prepared (4-dodecylphenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**1b**) and the tetradecyl derivative (**1c**), as described in Fig. 1. These benzyne precursors, **1b** and **1c**, dissolved even in organic solvents of low polarity, such as diethyl ether, THF, benzene, and toluene. The reaction of ben-

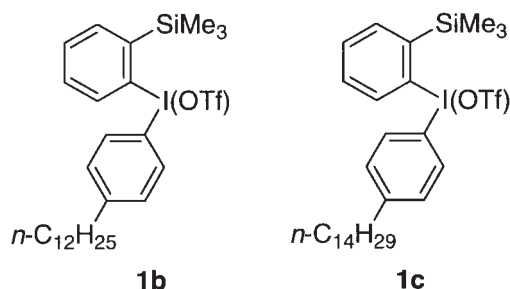


Fig. 1.

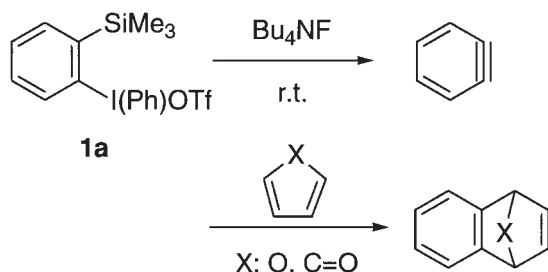
zyne with an appropriate trapping agent in the above solvent gave a benzyne adduct in high yield. Surprisingly, even in the lowest polar solvent, hexane, the trapping of benzyne proceeded efficiently. Therefore, the introduction of a long alkyl chain on the benzyne precursor **1a** improves the solubility and enable to the use of solvents of low polarity.

In this study, we synthesized various hypervalent iodine benzyne precursors bearing alkyl chains of different lengths. We examined the relation between the solubility and the trapping efficiency of benzyne in the reaction in low polar solvents, toluene or hexane.

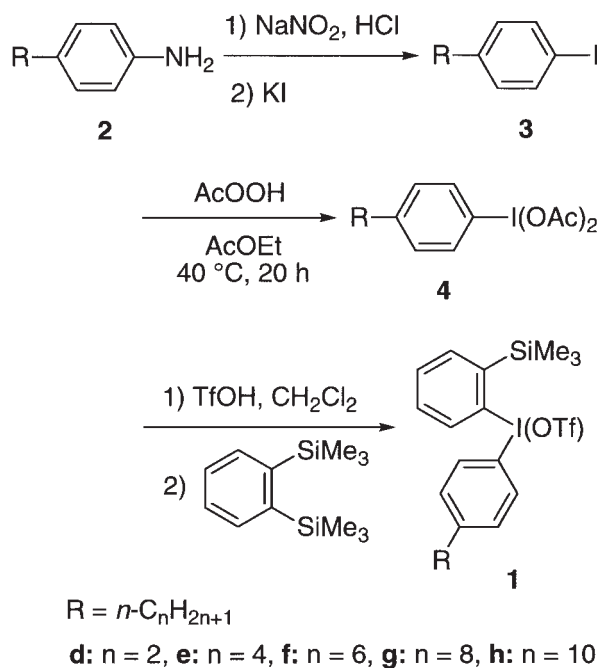
Results and Discussion

Synthesis of Hypervalent Iodine Benzyne Precursors 1 Bearing Various Lengths of Alkyl Chain. The synthetic procedure for benzyne precursors **1d–1h** is outlined in Scheme 2. Diazotization of alkyl-substituted anilines **2** was conducted with sodium nitrite and hydrochloric acid, followed by a treatment with potassium iodide to give 1-alkyl-4-iodobenzenes **3**. The crude 1-alkyl-4-iodobenzenes **3** were purified by column chromatography on silica gel.

The subsequent oxidation of 1-alkyl-4-iodobenzenes **3** was conducted with peracetic acid (30% in acetic acid) in ethyl acetate at 40 °C. Extraction with CH₂Cl₂ gave crude 1-alkyl-4-(diacetoxyiodo)benzenes **4**. The crude 1-alkyl-4-(diacetoxyiodo)benzenes **4** were used for an aryliodination reaction without



Scheme 1.



Scheme 2.

Table 1. Isolated Yield of Hypervalent Iodine Benzyne Precursors **1**

Entry	Benzyne precursor 1	Isolated yield/% ^{a)}
1	1d : $n = 2$	50
2	1e : $n = 4$	40
3	1f : $n = 6$	46
4	1g : $n = 8$	30
5	1h : $n = 10$	35

a) Based on **3**.

further purification.

1-Alkyl-4-(diacetoxyiodo)benzenes **4** were treated with trifluoromethanesulfonic acid (TfOH) in CH_2Cl_2 at -20°C , and then reacted with 1,2-bis(trimethylsilyl)benzene to give the corresponding (4-alkylphenyl)[2-(trimethylsilyl)phenyl]iodonium triflates **1** as crystals. The isolated yields of benzyne precursors **1** are given in Table 1.

We then examined the solubility of the prepared benzyne precursors **1** in toluene or hexane. In the case of hexane as a solvent, a mixture (v/v 82:18) of hexane and THF was employed, since the addition of a THF solution of Bu_4NF to a hexane solution led to an 82:18 ratio in the reaction. The solubility of each hypervalent iodine benzyne precursors **1** is expressed in wt % against the employed solvent at 20°C . The results are given in Table 2. Particularly, dodecylphenyl- and tetradecylphenyl-substituted benzyne precursors, **1b** and **1c**, dissolved freely in toluene, while phenyl- and ethylphenyl-substituted ones, **1a** and **1d**, did not dissolve. Benzyne precursors **1** did not dissolve in hexane, but become soluble in a mixed solvent of hexane and THF (v/v 82:18) in the cases of longer alkyl chains ($n > 10$).

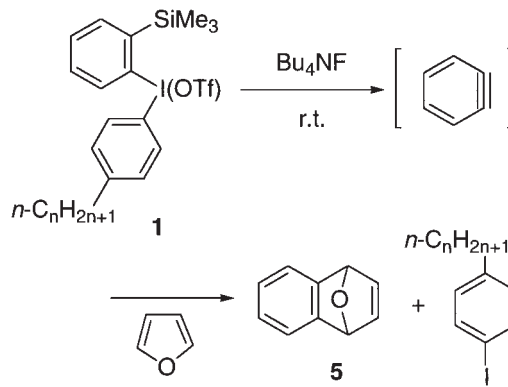
Trapping Reaction of Benzyne in Low Polar Solvents. A trapping reaction of benzyne was conducted by adding a solution of Bu_4NF in THF to a solution or suspension of a benzyne

Table 2. Solubility of Hypervalent Iodine Benzyne Precursors **1**

Benzyne precursor 1	Solubility/wt % ^{a)}	
	Toluene	Hexane/THF (82:18)
1a : $n = 0$	— ^{b)}	— ^{b)}
1d : $n = 2$	— ^{b)}	— ^{b)}
1e : $n = 4$	2.4	— ^{b)}
1f : $n = 6$	45.6	0.42
1g : $n = 8$	61.4	0.83
1h : $n = 10$	187.6	7.52
1b : $n = 12$	— ^{c)}	37.09
1c : $n = 14$	— ^{c)}	46.45

a) Solubility (wt %) of **1** (g) against a solvent (g). b) Difficult to measure because of the insolubility. c) Freely soluble.

Table 3. Trapping Reaction of Benzyne with Furan



Entry	Benzyne precursor 1	Solvent	Isolated yield/%	
			5	3
1	1a : $n = 0$	Toluene	64	—
2	1d : $n = 2$		71	75
3	1e : $n = 4$		73	98
4	1f : $n = 6$		73	99
5	1g : $n = 8$		80	96
6	1h : $n = 10$	Hexane	82	91
7	1b : $n = 12$		86 ^{a)}	92 ^{a)}
8	1c : $n = 14$		82 ^{a)}	100 ^{a)}
9	1a : $n = 0$		61	—
10	1d : $n = 2$		66	78
11	1e : $n = 4$		63	96
12	1f : $n = 6$		70	91
13	1g : $n = 8$		72	96
14	1h : $n = 10$		72	94
15	1b : $n = 12$		87 ^{a)}	93 ^{a)}
16	1c : $n = 14$		89 ^{a)}	90 ^{a)}

a) Ref. 8.

precursor **1** and furan in toluene or in hexane. None of the benzyne precursors **1** dissolved in hexane, but the benzyne precursors having alkyl groups longer than the butyl group dissolved in toluene completely. The benzyne adduct, 1,4-dihydro-1,4-epoxynaphthalene (**5**), was isolated by column chromatography together with 1-alkyl-4-iodobenzene **3**. The results are given in Table 3.

The yield of benzyne adduct **5** increased with increasing the length of the alkyl chain. This result is consistent with an im-

provement in the solubility of benzyne precursors **1**. Even in hexane, the benzyne adduct was obtained in good yields. When a THF solution of Bu₄NF is used as a desilylating agent, the solvent composition leads to a mixture (v/v 82:18) of hexane and THF under the reaction conditions. As a result, the solubility of benzyne precursors **1** is improved. Even in the cases of unsubstituted and short alkyl group-substituted phenyl groups, benzyne adduct **5** was obtained in good yields. Such benzyne precursors **1** did not dissolve, even in a mixed solvent of hexane and THF. Therefore, in these cases the reaction may proceed even in the interface between solid and liquid. Although, in a previous study,⁸ we did not conduct a reaction of the unsubstituted benzyne precursor **1a** in nonpolar solvents, we realized that the generation and reaction of benzyne effectively proceeded even in nonpolar solvents, such as hexane and toluene. This fact, therefore, indicates that hypervalent iodine benzyne precursors **1** have a high reactivity toward a fluoride source.

Conclusion

We have demonstrated the synthesis, solubility, and reaction of hypervalent iodine benzyne precursors having various alkyl chains. As the alkyl chain of benzyne precursor **1** is lengthened, the solubility in a solvent of low polarity increases. The improvement in the solubility gives a better yield of benzyne adduct **5**. Therefore, the long-chained benzyne precursors **1** are widely available in synthetic and mechanistic studies using a less-polar organic solvent.

Experimental

General. Melting points were measured with a Yanaco melting apparatus, and are uncorrected. NMR spectra were taken with a JEOL JNM AL 300 spectrometer. Elemental analyses were conducted by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. Phenyl[2-(trimethylsilyl)phenyl]iodonium triflate (**1a**),² (4-dodecylphenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**1b**),⁸ and (4-tetradecylphenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**1c**)⁸ were prepared according to the literature.

General Procedure for Preparation of 1-Alkyl-4-iodobenzenes 3. To a suspension of a 4-alkylaniline **2** (10 mmol) in H₂O (20 cm³) was added aqueous HCl (10 mol dm⁻³, 1.0 cm³) at room temperature. After the mixture was cooled to 0 °C, an HCl solution (10 mol dm⁻³, 1.1 cm³) was added, and then a solution of NaNO₂ (0.69 g, 10 mmol) in H₂O (5 cm³) was slowly added dropwise. To the resulting arenediazonium chloride solution was added a solution of KI (1.66 g, 10 mmol) in H₂O (5 cm³) dropwise. The reaction mixture was heated with stirring at 40 °C until an oil was completely separated from the solution. After the addition of aqueous sodium thiosulfate to decolorize, the product was extracted with ether. The ethereal extract was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residual oil was purified by column chromatography on silica gel. Elution with hexane gave a 1-alkyl-4-iodobenzene **3** as a colorless oil.

1-Ethyl-4-iodobenzene (3d):⁹ Yield 65%. ¹H NMR (300 MHz, CDCl₃) δ 1.21 (t, *J* = 7.7 Hz, 3H, Me), 2.59 (q, *J* = 7.7 Hz, 2H, CH₂), 6.95 (d, *J* = 8.4 Hz, 2H, ArH), 7.59 (d, *J* = 8.4 Hz, 2H, ArH). ¹³C NMR (75 Hz, CDCl₃) δ 15.4, 28.4, 90.5, 130.0, 137.3, 143.8.

1-Butyl-4-iodobenzene (3e):¹⁰ Yield 56%. ¹H NMR (300

MHz, CDCl₃) δ 0.91 (t, *J* = 7.2 Hz, 3H, Me), 1.27–1.39 (m, 2H, CH₂), 1.51–1.61 (m, 2H, CH₂), 2.55 (t, *J* = 7.7 Hz, 2H, CH₂), 6.93 (d, *J* = 8.4 Hz, 2H, ArH), 7.58 (d, *J* = 8.4 Hz, 2H, ArH). ¹³C NMR (75 Hz, CDCl₃) δ 13.9, 22.2, 33.4, 35.1, 90.5, 137.2, 142.5.

1-Hexyl-4-iodobenzene (3f):¹¹ Yield 56%. ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, *J* = 6.6 Hz, 3H, Me), 1.28 (br s, 6H, CH₂), 1.52–1.59 (m, 2H, CH₂), 2.54 (t, *J* = 7.6 Hz, 2H, CH₂), 6.93 (d, *J* = 8.4 Hz, 2H, ArH), 7.58 (d, *J* = 8.4 Hz, 2H, ArH). ¹³C NMR (75 Hz, CDCl₃) δ 14.1, 22.6, 28.8, 31.3, 31.6, 35.4, 90.5, 130.5, 137.2, 142.5.

1-Iodo-4-octylbenzene (3g): Yield 54%. ¹H NMR (300 MHz, CDCl₃) δ 0.87 (t, *J* = 6.8 Hz, 3H, Me), 1.26 (br s, 10H, CH₂), 1.52–1.61 (m, 2H, CH₂), 2.53 (t, *J* = 7.7 Hz, 2H, CH₂), 6.91 (d, *J* = 8.4 Hz, 2H, ArH), 7.57 (d, *J* = 8.4 Hz, 2H, ArH). ¹³C NMR (75 Hz, CDCl₃) δ 14.1, 22.6, 29.2 (two carbons), 29.4, 31.3, 31.8, 35.4, 90.5, 130.5, 137.2, 142.5. Anal. Calcd for C₁₄H₂₁I: C, 53.17; H, 6.69%. Found: C, 53.30; H, 6.71%.

1-Decyl-4-iodobenzene (3h):¹² Yield 58%. ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, *J* = 6.8 Hz, 3H, Me), 1.25 (br s, 14H, CH₂), 1.52–1.59 (m, 2H, CH₂), 2.53 (t, *J* = 7.8 Hz, 2H, CH₂), 6.93 (d, *J* = 8.4 Hz, 2H, ArH), 7.58 (d, *J* = 8.4 Hz, 2H, ArH). ¹³C NMR (75 Hz, CDCl₃) δ 14.1, 22.7, 29.2, 29.3, 29.4, 29.6 (two carbons), 31.3, 31.9, 35.4, 90.5, 130.6, 137.2, 142.5.

General Procedure for Preparation of 1-Alkyl-4-(diacetoxyiodo)benzenes (4). To a solution of a 1-alkyl-4-iodobenzene **3** (2.0 mmol) in ethyl acetate (10 cm³) was added dropwise a solution of peracetic acid in acetic acid (30%, 8 cm³) at 0 °C. The mixture was stirred at 40 °C for 20 h. The product was extracted with CH₂Cl₂, washed with water, and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to give a crude (diacetoxyiodo)benzene derivative **4** in 79–86% yield. Although the crude (diacetoxyiodo)benzenes **4** contained a small amount of inseparable impurities, the ¹H NMR spectra showed that they were pure enough to be used for the subsequent reaction. Accordingly, the crude products were used to prepare benzyne precursors **1**.

1-Ethyl-4-(diacetoxyiodo)benzene (4d): ¹H NMR (300 MHz, CDCl₃) δ 1.27 (t, *J* = 6.9 Hz, 3H, Me), 2.01 (s, 6H, Me), 2.74 (q, *J* = 6.9 Hz, 2H, CH₂), 7.32 (d, *J* = 8.7 Hz, 2H, ArH), 8.00 (d, *J* = 8.7 Hz, 2H, ArH).

1-Butyl-4-(diacetoxyiodo)benzene (4e): ¹H NMR (300 MHz, CDCl₃) δ 0.94 (t, *J* = 7.2 Hz, 3H, Me), 1.34–1.42 (m, 2H, CH₂), 1.57–1.67 (m, 2H, CH₂), 2.01 (s, 6H, Me), 2.68 (t, *J* = 7.8 Hz, 2H, CH₂), 7.30 (d, *J* = 8.4 Hz, 2H, ArH), 7.98 (d, *J* = 8.4 Hz, 2H, ArH).

1-(Diacetoxyiodo)-4-hexylbenzene (4f): ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, *J* = 6.8 Hz, 3H, Me), 1.32 (br s, 6H, CH₂), 1.56–1.65 (m, 2H, CH₂), 2.01 (s, 6H, Me), 2.67 (t, *J* = 7.8 Hz, 2H, CH₂), 7.29 (d, *J* = 8.4 Hz, 2H, ArH), 7.98 (d, *J* = 8.4 Hz, 2H, ArH).

1-(Diacetoxyiodo)-4-octylbenzene (4g): ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, *J* = 6.8 Hz, 3H, Me), 1.27 (br s, 10H, CH₂), 1.58–1.65 (m, 2H, CH₂), 2.01 (s, 6H, Me), 2.67 (t, *J* = 7.8 Hz, 2H, CH₂), 7.29 (d, *J* = 8.4 Hz, 2H, ArH), 7.98 (d, *J* = 8.4 Hz, 2H, ArH).

1-Decyl-4-(diacetoxyiodo)benzene (4h): ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, *J* = 6.8 Hz, 3H, Me), 1.26 (br s, 14H, CH₂), 1.58–1.65 (m, 2H, CH₂), 2.02 (s, 6H, Me), 2.67 (t, *J* = 7.8 Hz, 2H, CH₂), 7.30 (d, *J* = 8.4 Hz, 2H, ArH), 7.98 (d, *J* = 8.4 Hz, 2H, ArH).

General Procedure for Preparation of Hypervalent Iodine Benzyne Precursors 1. To a solution of the crude 1-alkyl-4-(di-

acetoxyiodo)benzene **4** (1.65 mmol) prepared as mentioned above in CH_2Cl_2 (10 cm^3) was added dropwise TFOH (0.29 cm^3 , 0.32 mmol) at -20°C . The solution was stirred at -20°C for 30 min. At that temperature, 1,2-bis(trimethylsilyl)benzene (0.366 g, 1.65 mmol) was added and the reaction mixture was stirred at -20°C and at room temperature for 15 min. The reaction mixture was washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to give light-brown crystals or oil. Crystallization from ether or hexane afforded benzyne precursor **1**. The isolated yield of **1** in Table 1 was calculated based on 1-alkyl-4-iodobenzene **3**. The contamination of **4** with impurities may cause a decrease in the yield of benzyne precursors **1**. An analytically pure sample was obtained by recrystallization from a mixed solvent of CH_2Cl_2 and hexane or CH_2Cl_2 and ether.

(4-Ethylphenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate (1d): Isolated yield 50%. Mp $134\text{--}135^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 0.43 (s, 9H, Me), 1.21 (t, $J = 7.6$ Hz, 3H, Me), 2.67 (q, $J = 7.6$ Hz, 2H, CH_2), 7.26–8.12 (m, 8H, ArH). ^{13}C NMR (75 Hz, CDCl_3) δ 0.06, 14.9, 28.4, 110.2, 121.9, 132.0, 132.1, 133.3, 133.5, 138.3, 138.6, 146.9, 149.3. Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{F}_3\text{IO}_3\text{SSi}$: C, 40.76; H, 4.18%. Found: C, 40.61; H, 4.16%.

(4-Butylphenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate (1e): Isolated yield 40%. Mp $110\text{--}111^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 0.43 (s, 9H, Me), 0.90 (t, $J = 7.4$ Hz, 3H, Me), 1.28–1.38 (m, 2H, CH_2), 1.51–1.61 (m, 2H, CH_2), 2.62 (q, $J = 7.7$ Hz, 2H, CH_2), 7.24–8.12 (m, 8H, ArH). ^{13}C NMR (75 Hz, CDCl_3) δ 0.05, 13.8, 22.1, 33.0, 35.1, 110.1, 121.8, 132.1, 132.5, 133.3, 133.4, 138.3, 138.6, 146.9, 148.1. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{F}_3\text{IO}_3\text{SSi}$: C, 43.01; H, 4.69%. Found: C, 42.98; H, 4.70%.

(4-Hexylphenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate (1f): Isolated yield 46%. Mp $99\text{--}100^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 0.43 (s, 9H, Me), 0.87 (t, $J = 6.6$ Hz, 3H, Me), 1.27 (br s, 6H, CH_2), 1.52–1.59 (m, 2H, CH_2), 2.62 (q, $J = 7.8$ Hz, 2H, CH_2), 7.24–8.09 (m, 8H, ArH). ^{13}C NMR (75 Hz, CDCl_3) δ 0.09, 14.0, 22.5, 28.8, 30.9, 31.5, 35.5, 110.2, 121.9, 132.1, 132.6, 133.3, 133.4, 138.3, 138.6, 147.1, 148.2. Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{F}_3\text{IO}_3\text{SSi}$: C, 45.05; H, 5.16%. Found: C, 45.15; H, 5.17%.

(4-Octylphenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate (1g): Isolated yield 30%. Mp $90\text{--}91^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 0.43 (s, 9H, Me), 0.87 (t, $J = 6.8$ Hz, 3H, Me), 1.25 (br s, 10H, CH_2), 1.54–1.60 (m, 2H, CH_2), 2.62 (q, $J = 7.8$ Hz, 2H, CH_2), 7.24–8.08 (m, 8H, ArH). ^{13}C NMR (75 Hz, CDCl_3) δ 0.09, 14.0, 22.6, 29.1, 29.3, 30.9, 31.8, 35.5, 110.2, 121.9, 132.1, 132.6, 133.3, 133.4, 138.3, 138.6, 147.1, 148.2. Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{F}_3\text{IO}_3\text{SSi}$: C, 46.90; H, 5.58%. Found: C, 46.75; H, 5.55%.

(4-Decylphenyl)[2-(trimethylsilyl)phenyl]iodonium Triflate (1h): Isolated yield 35%. Mp $88\text{--}89^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 0.43 (s, 9H, Me), 0.87 (t, $J = 6.6$ Hz, 3H, Me), 1.24 (br s, 14H, CH_2), 1.54–1.59 (m, 2H, CH_2), 2.61 (q, $J = 7.6$ Hz, 2H, CH_2), 7.23–8.10 (m, 8H, ArH). ^{13}C NMR (75 Hz, CDCl_3) δ 0.06, 14.1, 22.6, 29.1, 29.3 (two carbons), 29.5 (two carbons), 30.9, 31.8, 35.5, 110.2, 121.8, 132.1, 132.5, 133.3, 133.4, 138.3, 138.6, 147.0, 148.1. Anal. Calcd for $\text{C}_{26}\text{H}_{38}\text{F}_3\text{IO}_3\text{SSi}$: C, 48.59; H, 5.96%. Found: C, 48.10; H, 5.87%.

General Procedure for Trapping Reaction of Benzyne with Furan. To a solution of benzyne precursor **1** (0.5 mmol) and furan (0.170 g, 2.5 mmol) in toluene or hexane (2 cm^3) was added dropwise a THF solution of Bu_4NF (1.0 mol dm^{-3} , 0.6 cm^3) at 0°C . The reaction mixture was stirred at room temperature for 30 min. The solvent was evaporated and water was added to the residue. The product was extracted with CH_2Cl_2 . The organic extract was dried over anhydrous sodium sulfate and concentrated. The residue was submitted to column chromatography on silica gel. Elution with CH_2Cl_2 and hexane gave 1,4-dihydro-1,4-epoxynaphthalene (**5**).

1,4-Dihydro-1,4-epoxynaphthalene (5). Mp $51\text{--}55^\circ\text{C}$ (lit.¹³ mp $55\text{--}56^\circ\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ 5.72 (s, 2H, CH), 6.95–7.00 (m, 2H, ArH), 7.03 (s, 2H, =CH), 7.23–7.27 (m, 2H, ArH). ^{13}C NMR (75 Hz, CDCl_3) δ 82.3, 120.2, 125.0, 143.0, 149.0.

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