Oxidative Biaryl Coupling Reaction of Phenol Ether Derivatives Using a Hypervalent Iodine(III) Reagent

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The hypervalent iodine(III)-induced intramolecular biaryl coupling reaction of phenol ether derivatives (nonphenolic derivatives) was investigated with the aim of preparing various dibenzo heterocyclic compounds. 1,3-Diarylpropanes (**1a**−**e**), *N*-benzyl-*N*-phenethylamines (**2a**−**c**) and *N*,*N*-dibenzylamines (**3a**−**e**) react with a hypervalent iodine reagent, phenyliodine(III) bis(trifluoroacetate) (PIFA), containing BF_3·Et_2O in CH_2Cl_2 to give the biaryl coupling products (**4**−**6**) in good yield. As an application of the reaction, we examined the synthesis of oxygen- and sulfur-containing dibenzoheterocyclic compounds (**12**−**15**), whose side chain moiety could be easily cleaved by the known method to give 2,2′-substituted biphenyl compounds (**16**−**18**).

Introduction

The biaryl substructure is a central building block in a very large number of natural products, such as polyketides, terpenes, lignanes, coumarins, flavonoids, tannins, and many alkaloids.[1] Because of their interesting properties not only as bioactive natural products but also as chiral ligands in asymmetric reactions,[2] natural and unnatural biaryls are considered attractive synthetic targets. The reported methods for construction of these biaryl skeletons can be classified into two types: (1) the classical Ullmann reaction and other reductive processes and (2) the oxidative (biomimetic) phenolic coupling reaction using a heavy metal oxidant.

The reductive processes include (1) the Ullmann coupling reaction of aryl halides using copper bronze as a reducing reagent,[3] (2) Semmelhack's method using Ni(0) complexes such as $[Ni(cod)_2]$ used in stoichiometric amounts to replace copper,[4] (3) a coupling reaction of aryl halides using a catalytic amount of low-valent nickel species which can be regenerated either electrochemically or by coreductants such as zinc or sodium hydride,[5] (4) a reaction of aryl-Grignard or organozinc compounds with aryl halides (the "Kharash reaction") catalyzed by nickel or palladium derivatives,[6] (5) a palladium-catalyzed coupling reaction of arylboronic acids (or aryl tin compounds) with aryl halides (or triflates),[7] (6) the Meyers oxazoline method,[8] (7) a cyanocuprate-mediated biaryl coupling reaction,[9] etc. Cross-coupled products can be obtained in moderate yields by methods 4−7.

On the other hand, intramolecular oxidative biaryl coupling reactions of phenol ether derivatives are also convenient for the synthesis of cross-coupled products. The biomimetic syntheses of aporphine alkaloids, lignans, and tannins were achieved using heavy metal oxidants, such as thallium(III), vanadium(V), ruthenium(IV), and iron(III) salts.[10]

However, the unsatisfactory results obtained in the synthesis of highly functionalized symmetrical or unsymmetrical biaryl compounds using these reductive and oxidative methods have remained a problem. Moreover, heavy metal oxidants are highly toxic and must be handled very carefully. To solve these problems, we examined the oxidative biaryl coupling reaction using hypervalent iodine(III) reagents, which are safe and useful synthetic reagents.

Recently, we reported the novel and direct nucleophilic substitution of phenol ethers by nitrogen, carbon, oxygen and sulfur nucleophiles using a hypervalent iodine(III) reagent, phenyliodine bis(trifluoroacetate) (PIFA), in 1,1,1,3,3,3-hexafluoropropane-2-ol ($(CF_3)_2CHOH$) or 2,2,2-

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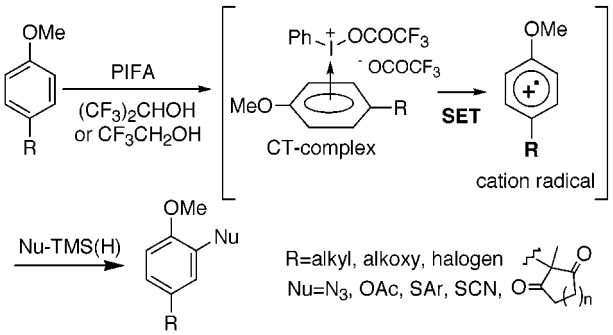
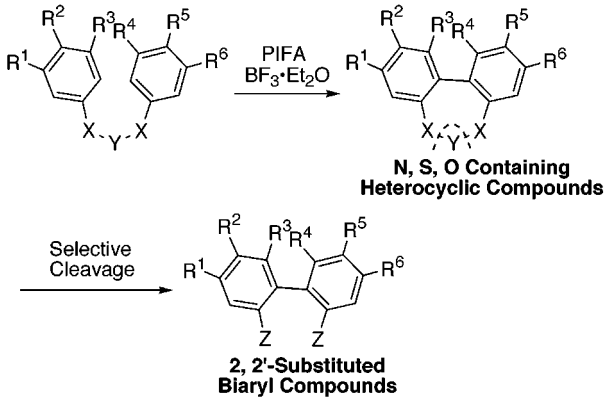
Scheme 1. Nucleophilic Substitution of Phenol Ethers Using PIFA



Scheme 2

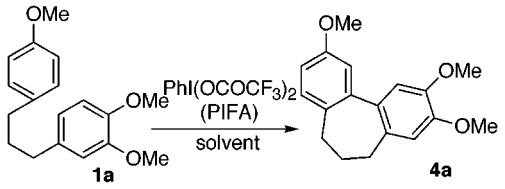


trifluoroethanol (CF_3CH_2OH) (Scheme 1).[11] As part of our continued studies concerning PIFA-induced nucleophilic substitution of phenol ethers, we have briefly communicated the intramolecular oxidative biaryl coupling reactions of phenol ether derivatives using PIFA activated by BF_3•Et_2O.[12] In this paper, we describe a full account of our studies on the intramolecular nonphenolic oxidative coupling reactions leading to the dibenzoheterocyclic compounds, which could be easily converted into the 2,2′-substituted biaryl compounds possessing formyl, methyl, and hydroxy groups (Scheme 2).

Results and Discussion

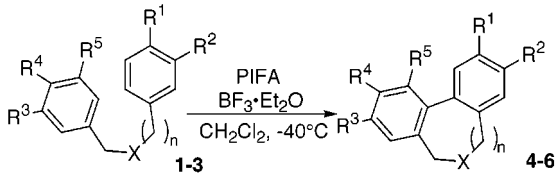
At first, we examined the biaryl coupling reaction of 1,3-diarylpropanes (**1a**−**e**), *N*-benzyl-*N*-phenethylamine derivatives (**2a**−**c**), and *N*,*N*-dibenzylamine derivatives (**3a**−**e**) under the same conditions as an intermolecular nucleophilic substitution of phenol ethers using PIFA. The starting compounds (**1a**−**e**, **2a**−**c**, **3a**−**e**) were prepared by the reaction of a corresponding benzaldehyde with an acetophenone, a tyramine, or a benzylamine derivative according to the reported method.[13] Treatment of 1-(3,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-propane (**1a**) with PIFA in $(CF_3)_2CHOH$ gave a biaryl coupling compound (**4a**) in 63% yield. The reaction in other solvents, such as CF_3CH_2OH, acetonitrile, and dichloromethane, also gave **4a** in 65, 46, and 25% yields, respectively.[12] When the reaction was carried out in the presence of BF_3•Et_2O, which could coordinate with the trifluoroacetoxy ligands to activate it, the yield of **4a** was dramatically improved. Thus, the biaryl coupling reaction proceeded smoothly at low temperature (−40 °C) to give **4a** in good yield. In dichloromethane, the yield of **4a** from **1a** increased to 91% (Table 1).

Table 1. Intramolecular Cyclization of 1a in Various Solvents



		yield of **4a** (%)	
solvent	temp (°C)	none	containing BF_3•Et_2O
$(CF_3)_2CHOH$	0	63	63
CF_3CH_2OH	−40	65	84
CH_3CN	−40	46	73
CH_2Cl_2	−40	25	91

Table 2. Biaryl Coupling Reaction of 1−3 with PIFA



1−3	R^1	R^2	R^3	R^4	R^5	*n*	X	**4−6**	yield (%)
1a	OMe	H	OMe	OMe	H	1	CH_2	**4a**	91
1b	−OCH_2O−		−OCH_2O−		H	1	CH_2	**4b**	91
1c	OMe	OMe	OMe	OMe	H	1	CH_2	**4c**	99
1d	OMe	OMe	OMe	OMe	OMe	1	CH_2	**4d**	92
1e	OMe	OMe	OMe	OTBS	H	1	CH_2	**4e**	75
2a	OMe	H	OMe	OMe	H	2	$NCOCF_3$	**5a**	89
2b	OMe	OMe	OMe	OMe	H	2	$NCOCF_3$	**5b**	68
2c	OMe	OMe	OMe	OMe	OMe	2	$NCOCF_3$	**5c**	52
3a	−OCH_2O−		−OCH_2O−		H	1	$NCOCF_3$	**6a**	94
3b	OMe	OMe	OMe	OMe	H	1	$NCOCF_3$	**6b**	85
3c	OMe	OMe	OMe	OMe	OMe	1	$NCOCF_3$	**6c**	85
3d	OMe	OMe	OMe	OTBS	H	1	$NCOCF_3$	**6d**	64
3e	OMe	OMe	OMe	OAc	H	1	$NCOCF_3$	**6e**	60

Other 1,3-diarylpropanes (**1b**−**e**), *N*-benzyl-*N*-phenethylamine derivatives (**2a**−**c**), and *N*,*N*-dibenzylamine derivatives (**3a**−**e**) were similarly converted into the biaryl compounds (**4b**−**e**, **5a**−**c**, **6a**−**e**) in good yields under the same condition. These results are summarized in Table 2.

As an application of the PIFA-induced biaryl coupling reaction, we next examined the synthesis of various dibenzo heterocyclic compounds, whose side chain moiety could be easily cleaved by the known methods to give various 2,2′-substituted biaryl compounds. We investigated the intramolecular coupling reaction of five types of compounds, silaketal derivatives (**7a**−**f**), dibenzyl sulfide (**8**), dibenzyl sulfoxides (**9a**−**d**), dibenzyl sulfones (**10a**,**b**), and dibenzyl ethers (**11a**−**f**) using the combined reagent PIFA−BF_3•Et_2O. These phenol ether derivatives (**7**−**11**) were prepared from the corresponding benzyl alcohols, benzyl bromides, or alkoxyphenols (Scheme 3).

Treatment of silaketal derivatives (**7a**−**f**) with PIFA activated by BF_3•Et_2O afforded the corresponding cou-

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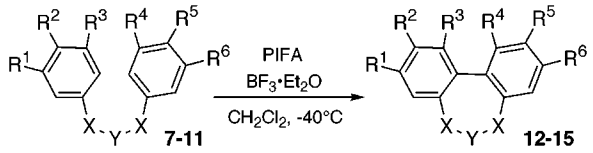
Table 3. Biaryl Coupling Reaction of Compounds 7−11 with PIFA



7−11	R^1	R^2	R^3	R^4	R^5	R^6	X	Y	12−15	yield (%)
7a	OMe	OMe	H	H	OMe	OMe	O	Si^iPr_2	**12a**	56
7b	$-OCH_2O-$		H	H	$-OCH_2O-$		O	Si^iPr_2	**12b**	69
7c	OMe	OMe	H	H	$-OCH_2O-$		O	Si^iPr_2	**12c**	46
7d	OMe	OMe	H	H	OMe	OMe	O	Si^tBu_2	**12d**	81
7e	$-OCH_2O-$		H	H	$-OCH_2O-$		O	Si^tBu_2	**12e**	89
7f	OMe	OMe	H	H	$-OCH_2O-$		O	Si^tBu_2	**12f**	83
8	OMe	OMe	H	H	OMe	OMe	CH_2	S		
9a	OMe	OMe	H	H	OMe	OMe	CH_2	SO	**13a**	73
9b	$-OCH_2O-$		H	H	$-OCH_2O-$		CH_2	SO	**13b**	71
9c	OMe	OMe	H	H	$-OCH_2O-$		CH_2	SO	**13c**	59 (73)[a]
9d	OMe	OMe	OMe	H	OMe	OMe	CH_2	SO	**13d**	42 (73)[a]
10a	OMe	OMe	H	H	OMe	OMe	CH_2	SO_2	**14a**	78
10b	$-OCH_2O-$		H	H	$-OCH_2O-$		CH_2	SO_2	**14b**	72
11a	OMe	OMe	H	H	OMe	OMe	CH_2	O	**15a**	85
11b	$-OCH_2O-$		H	H	$-OCH_2O-$		CH_2	O	**15b**	80
11c	OMe	OMe	H	H	$-OCH_2O-$		CH_2	O	**15c**	51
11d	OMe	OMe	OMe	H	OMe	OMe	CH_2	O	**15d**	50
11e	OMe	OMe	OMe	OMe	OMe	OMe	CH_2	O	**15e**	38

[a] Yields based on the reacted substrates are given in parentheses.

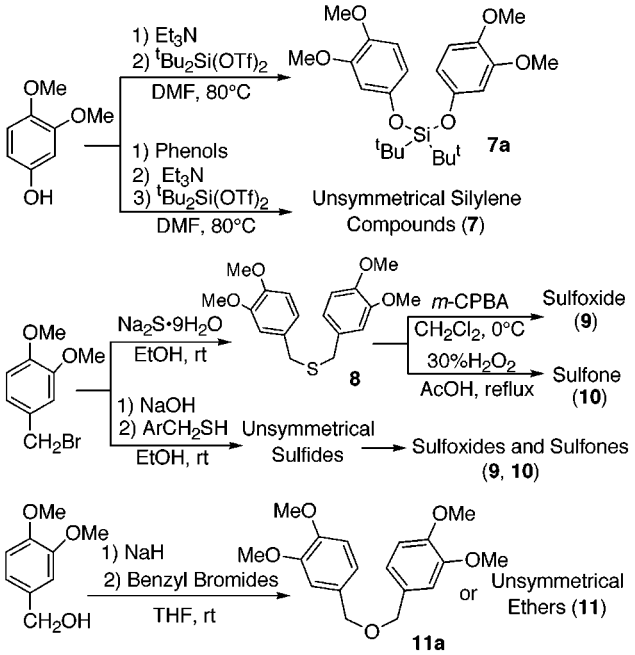
pling products (**12a**−**f**). Di-*tert*-butyl silaketals (**7d**−**f**) caused a favorable biaryl coupling reaction to give **12d**−**f** in good yields. The silaketal moiety of **12a**−**f** was not cleaved during the reaction. Silaketals are used for a silicon tether to link two alcohol compounds. For example, silicon-tethered Diels−Alder reactions have been reported.[14] We found that the silaketals could also be applicable as a tether to link two phenol derivatives, and the silaketal moiety was stable under the PIFA oxidation conditions.

Next, we investigated the biaryl coupling reaction of sulfur-containing phenol ether derivatives (**8**−**10**). Although the sulfoxide (**9a**−**d**) and sulfone (**10a**,**b**) derivatives caused a favorable biaryl coupling reaction upon treatment with PIFA, no coupling products were obtained from the sulfide (**8**) derivative. Due to the high reactivity of the sulfide moiety of **8** toward PIFA, many oxidized products were generated.

The dibenzyl ethers (**11a**−**e**) were also converted into the coupled biaryl compounds (**15a**−**e**) under the same conditions. The oxidation of the benzyl position of **11** did not appreciably take place. Highly functionalized biaryl compounds (**15d**−**e**) were also obtained (Table 3).

The methods of the selective cleavage of the tether moiety of the coupling product are as follows. Treatment of the silylene derivatives (**12d**−**f**) with tetrabutylammonium fluoride afforded the corresponding 2,2′-dihydroxybiphenyl compounds (**16d**−**f**) in good yields. Hydrogenolysis of the sulfoxide (**13b**) in EtOH containing Raney Ni as a catalyst gave a 2,2′-dimethylbiphenyl compound (**17b**) in good yield. Because of poor solubility, hydrogenolysis of other sulfoxides (**13**) did not proceed well. Oxidative cleavage of the dibenzyl ether derivatives (**15a**,**b**,**d**) took place with DDQ[15] to give the 2,2′-diformylbiphenyl compounds (**18a**,**b**,**d**) in moderate yields. These results are summarized in Table 4.

Scheme 3. Preparation of Phenol Ethers 7−11



The reaction mechanism for the biaryl coupling reaction of phenol ether derivatives with PIFA possibly involves a one-electron oxidation step.[12] It is assumed that the reaction of an electron-rich aromatic ring with the reagent PIFA−BF_3•Et_2O results in the formation of a cation radical intermediate. The nucleophilic attack by the other aromatic ring on the cation radical then occurs to give the corresponding biaryl product.

In our continuing effort to develop hypervalent iodine chemistry, a novel biaryl coupling reaction of phenol ether derivatives has been developed using a hypervalent iodine reagent. By using these reactions, we can obtain the dibenzo heterocyclic compounds, which can be easily converted into the 2,2′-substituted biaryl compounds possessing hydroxy, methyl, and formyl groups. The

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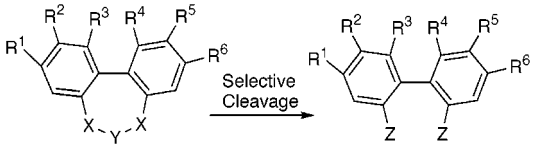
Table 4. Cleavage of the Side Chain[a]



sub.	R^1	R^2	R^3	R^4	R^5	R^6	X	Y	method	prod	Z	yield (%)
12d	OMe	OMe	H	H	OMe	OMe	O	Si^tBu_2	A	**16d**	OH	98
12e	$-OCH_2O-$		H	H	$-OCH_2O-$		O	Si^tBu_2	A	**16e**	OH	96
13b	$-OCH_2O-$		H	H	$-OCH_2O-$		CH_2	SO	B	**17b**	CH_3	97
15a	OMe	OMe	H	H	OMe	OMe	CH_2	O	C	**18a**	CHO	66
15b	$-OCH_2O-$		H	H	$-OCH_2O-$		CH_2	O	C	**18b**	CHO	56
15d	OMe	OMe	OMe	H	OMe	OMe	CH_2	O	C	**18d**	CHO	46

[a] Method: (A) TBAF/THF, rt, 2 h; (B) Raney Ni (w-1)/EtOH, reflux, 6 h; (C) DDQ/S $CH_2Cl_2-H_2O$ (18:1), reflux, 24 h.

chemistry of 2,2′-disubstituted symmetrical or unsymmetrical biphenyls has attracted considerable interest because of the presence of these moieties in a number of natural products, such as vancomycin, elladitannins, and dibenzocyclooctalignans.

Further application of this reaction to the synthesis of natural products and development of the atropisomer-selective biaryl coupling reaction are currently in progress.

Experimental Section

All melting points are uncorrected. Infrared (IR) absorption spectra (cm^{-1}) were recorded as KBr pellets. ^1H NMR (and ^{13}C NMR) spectra were recorded, with TMS or $CHCl_3$ as an internal standard. Most of the ^1H (and ^{13}C) NMR spectra of amido compounds exhibited the presence of two rotamers. E. Merck silica gel 60 for column chromatography and E. Merck precoated TLC plates, silica gel F_{254} for preparative thin-layer chromatography were used. Organic layers were dried with anhydrous $MgSO_4$ or Na_2SO_4. PIFA is commercially available. $BF_3{\cdot}Et_2O$ was obtained from commercial suppliers and was used without further purification. Compounds **1a**,**c**, **2a**, **10b**, and **11a** were prepared by known methods.[13b,16]

General Procedure for Preparing 1,3-Diarylpropanes (1). 1,3-Diarylpropanes (**1**) were prepared by the reaction of a corresponding benzaldehyde with an acetophenone derivative according to the reported method.[13a]

1,3-Bis(3,4-(methylenedioxy)phenyl)propane (1b): colorless solid; mp 70−72 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.85 (qui, 2H, J = 7.6 Hz), 2.55 (t, 4H, J = 7.6 Hz), 5.92 (s, 4H), 6.61 (dd, 2H, J = 7.8, 1.6 Hz), 6.67 (d, 2H, J = 1.6 Hz), 6.72 (d, 2H, J = 7.8 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 33.4, 35.0, 100.7, 108.1, 108.8, 121.1, 136.1, 145.5, 147.5; HRMS calcd for $C_{17}H_{16}O_4$ (M^+) *m/e* 284.1048, *m/e* found 284.1049.

1-(3,4-Dimethoxyphenyl)-3-(3,4,5-trimethoxyphenyl)-propane (1d): colorless amorphous; ^1H NMR (270 MHz, $CDCl_3$) δ 1.94 (qui, 2H, J = 7.6 Hz), 2.59 (t, 2H, J = 7.6 Hz), 2.62 (t, 2H, J = 7.6 Hz), 3.82 (s, 3H), 3.85 (s, 6H), 3.87 (s, 3H), 3.88 (s, 3H), 6.40 (s, 2H), 6.71−6.75 (m, 2H), 6.81 (d, 1H, J = 7.9 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 33.0, 35.0, 35.7, 55.7, 55.8, 55.9, 60.7, 105.2, 111.1, 111.7, 120.1, 134.7, 138.0, 147.1, 148.7, 153.0; HRMS calcd for $C_{20}H_{26}O_5$ (M^+) *m/e* 346.1780, found *m/e* 346.1784.

1-(4-((*tert*-Butyldimethylsilyl)oxy)-3-methoxyphenyl)-3-(3,4-dimethoxyphenyl)propane (1e): colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.99 (s, 9H), 1.91 (qui, 2H, J = 7.8 Hz), 2.59 (t, 4H, J = 7.8 Hz), 3.79 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 6.62−6.81 (m, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −4.7, 18.4, 25.7, 33.3, 35.0, 35.1, 55.5, 55.8, 55.9, 111.2, 111.8, 112.5, 120.2, 120.5, 120.6, 135.0, 135.8, 142.9, 147.1, 148.7, 150.6; HRMS calcd for $C_{24}H_{36}O_4Si$ (M^+) *m/e* 416.2383, found *m/e* 416.2387.

General Procedure of Preparing *N*-Benzyl-*N*-phenethylamine Derivatives (2) and *N*,*N*-Dibenzylamine Derivatives (3). *N*-Benzyl-*N*-phenethylamine derivatives (**2**) and *N*,*N*-dibenzylamine derivatives (**3**) were prepared from corresponding to the benzaldehyde and the tyramine or the benzylamine derivative according to the reported method.[13b]

***N*-(3,4-Dimethoxybenzyl)-*N*-(3,4-dimethoxyphenethyl)-2,2,2-trifluoroacetamide (2b):** colorless solid; mp 68−69 °C; IR 1690; ^1H NMR (270 MHz, $CDCl_3$) δ 2.75−2.86 (m, 2H), 3.46−3.54 (m, 2H), 3.85, 3.86, 3.87, 3.88 (s, 12H), 4.31, 4.59 (s, 2H), 6.61−6.68 (m, 3H), 6.76−6.85 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 32.5, 34.9, 48.3, 48.5, 49.8, 51.7, 55.8, 56.1, 60.8, 104.2, 105.0, 111.3, 111.5, 111.7, 111.9, 116.5 (J = 287 Hz), 116.7 (J = 287 Hz), 120.6, 120.7, 129.8, 130.3, 130.7, 130.9, 147.8, 148.1, 149.0, 149.2, 153.6, 156.9 (J = 36 Hz); HRMS calcd for $C_{21}H_{24}F_3NO_5$ (M^+) *m/e* 427.1606, found *m/e* 427.1608. Anal. Calcd for $C_{21}H_{24}F_3NO_5$: C, 59.01; H, 5.66; N, 3.28. Found: C, 59.08; H, 5.69; N, 3.30.

***N*-(3,4-Dimethoxyphenethyl)-*N*-(3,4,5-trimethoxybenzyl)-2,2,2-trifluoroacetamide (2c):** colorless solid; mp 100−101 °C; IR 1690; ^1H NMR (270 MHz, $CDCl_3$) δ 2.78−2.88 (m, 2H), 3.49−3.57 (m, 2H), 3.83, 3.84, 3.86 (s, 15H), 4.30, 4.58 (s, 2H), 6.30, 6.42 (s, 2H), 6.62−6.83 (m, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 32.1, 34.5, 48.1, 49.4, 51.3, 55.5, 55.7, 60.4, 104.0, 104.6, 111.0, 111.2, 111.4, 111.6, 116.2 (J = 288 Hz), 116.4 (J = 288 Hz), 120.3, 129.6, 130.0, 130.4, 130.7, 137.4, 137.5, 147.5, 147.7, 148.7, 148.8, 153.3, 156.4 (J = 35 Hz), 156.9 (J = 36 Hz). Anal. Calcd for $C_{22}H_{26}F_3NO_6$: C, 57.76; H, 5.73; N, 3.06. Found: C, 57.88; H, 5.73; N, 3.10.

***N*,*N*-Bis(3,4-(methylenedioxy)benzyl)-2,2,2-trifluoroacetamide (3a):** white solid; mp 109−110 °C; IR 1692; ^1H NMR (270 MHz, CD_3OD) δ 4.43, 4.50 (s, 4H), 5.93, 5.96 (s, 4H), 6.62−6.84 (m, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 47.4, 48.9, 101.1, 101.3, 107.6, 108.2, 108.4, 108.7, 116.7 (J = 288 Hz), 121.1, 122.0, 127.9, 128.7, 147.4, 147.6, 148.0, 148.3, 157.1 (J = 36 Hz). Anal. Calcd for $C_{18}H_{14}F_3NO_5$: C, 56.70; H, 3.70; N, 3.67. Found: C, 56.62; H, 3.83; N, 3.69.

***N*,*N*-Bis(3,4-dimethoxybenzyl)-2,2,2-trifluoroacetamide (3b):** colorless solid; mp 91−92 °C; IR 1690; ^1H NMR (270 MHz, $CDCl_3$) δ 3.84, 3.86 (s, 6H), 3.88, 3.90 (s, 6H), 4.46, 4.47 (s, 4H), 6.66−6.76 (m, 4H), 6.82, 6.87 (d, 2H, J = 8.3, 7.9 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 47.7, 49.0, 55.9, 110.3, 111.0, 111.2, 111.5, 116.8 (J = 288 Hz), 120.0, 121.0, 126.7, 127.5, 148.8, 149.0, 149.2, 149.4, 157.3 (J = 35 Hz). Anal. Calcd for $C_{20}H_{22}F_3NO_5$: C, 58.11; H, 5.36; N, 3.39. Found: C, 58.17; H, 5.29; N, 3.45.

***N*-(3,4-Dimethoxybenzyl)-*N*-(3,4,5-trimethoxybenzyl)-2,2,2-trifluoroacetamide (3c):** colorless solid; mp 126−128 °C; IR 1692; ^1H NMR (270 MHz, $CDCl_3$) δ 3.82, 3.84, 3.85, 3.87, 3.89, 3.91 (s, 15H), 4.45−4.50 (m, 4H), 6.37 (s, 2H), 6.68, 6.75 (dd, 1H, J = 7.6, 2.0 Hz), 6.73 (s, 1H), 6.82, 6.87 (d, 1H, J = 8.3, 7.9 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 47.7, 47.9, 49.0, 55.1, 55.3, 60.0, 103.8, 104.8, 109.9, 110.5, 110.7, 111.0,

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116.2 (J = 288 Hz), 119.5, 120.4, 126.1, 127.1, 127.6, 129.5, 130.3, 137.0, 137.1, 148.3, 148.4, 148.6, 148.8, 152.8, 153.1, 156.6 (J = 36 Hz). Anal. Calcd for $C_{21}H_{24}F_3NO_6$: C, 56.88; H, 5.46; N, 3.16. Found: C, 56.98; H, 5.45; N, 3.20.

***N*-(4-((*tert*-Butyldimethylsilyl)oxy)-3-methoxybenzyl)-*N*-(3,4-dimethoxybenzyl)-2,2,2-trifluoroacetamide (3d):** colorless oil; IR 1692; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16, 0.17 (s, 6H), 0.99, 1.00 (s, 9H), 3.76, 3.78 (s, 3H), 3.83, 3.85 (s, 3H), 3.88, 3.90 (s, 3H), 4.43−4.45 (m, 4H), 6.59−6.73 (m, 4H), 6.78−6.87 (m, 2H); HRMS calcd for $C_{25}H_{34}F_3NO_5Si$ (M^+) *m/e* 513.2158, found *m/e* 513.2158.

***N*-(4-Acetoxy-3-methoxybenzyl)-*N*-(3,4-dimethoxybenzyl)-2,2,2-trifluoroacetamide (3e):** colorless solid; mp 86−87 °C; IR 1692; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16, 0.17 (s, 6H), 0.99, 1.00 (s, 9H), 3.76, 3.78 (s, 3H), 3.83, 3.85 (s, 3H), 3.88, 3.90 (s, 3H), 4.43−4.45 (m, 4H), 6.59−6.73 (m, 4H), 6.78−6.87 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.6, 47.6, 48.1, 49.0, 49.1, 49.3, 49.4, 55.8, 55.9, 110.3, 111.0, 111.3, 111.5, 112.4, 116.7 (J = 288 Hz), 119.5, 120.0, 120.6, 121.0, 122.9, 123.1, 126.5, 127.3, 133.4, 134.0, 139.5, 139.6, 148.9, 149.0, 149.3, 149.5, 151.4, 151.6, 157.4 (J = 35 Hz). Anal. Calcd for $C_{21}H_{22}F_3NO_6$: C, 57.14; H, 5.02; N, 3.17. Found: C, 57.05; H, 5.05; N, 3.22.

General Procedure for the Preparation of Silaketals (7a,b,d,e). Dialkyldichlorosilane or dialkylsilyl bis(trifluoromethanesulfonate) (0.1 mmol) was added to the solution of the alkoxyphenol (0.05 mmol) and Et_3N (0.15 mmol) in DMF at room temperature. The mixture was stirred for 3 h at 60 °C and then cooled. The solution was extracted with Et_2O. The extracts were washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (AcOEt−*n*-hexane) to give the corresponding to the silaketal (**7**).

Bis(3,4-dimethoxyphenoxy)diisopropylsilane (7a). Reactants: diisopropyldichlorosilane (0.050 mL, 0.28 mmol); 3,4-dimethoxyphenol (167 mg, 1.08 mmol); Et_3N (0.150 mL, 1.08 mmol); DMF (2.5 mL). **7a** (66 mg, 58%): colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10 (d, 12H, J = 5.8 Hz), 1.19 (m, 2H), 3.77 (s, 6H), 3.82 (s, 6H), 6.48−6.53 (m, 4H), 6.71 (d, 2H, J = 8.4 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.5, 17.1, 55.7, 56.2, 104.4, 110.3, 111.6, 143.9, 148.8, 149.5. Anal. Calcd for $C_{22}H_{32}O_6Si$: C, 62.83; H, 7.67. Found: C, 62.83; H, 7.63.

Bis(3,4-(dimethylenedioxy)phenoxy)diisopropylsilane (7b). Reactants: diisopropyldichlorosilane (0.050 mL, 0.27 mmol); sesamol (149 mg, 1.08 mmol); Et_3N (0.15 mL, 1.08 mmol); DMF (2.5 mL). **7b** (62 mg, 59%): colorless solid; mp 90−91 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.07 (d, 12H, J = 6.2 Hz), 1.20 (m, 2H), 5.91 (s, 4H), 6.42 (d, 2H, J = 8.2, 2.4 Hz), 6.52 (d, 2H, J = 2.4 Hz), 6.65 (d, 2H, J = 8.2 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.4, 17.0, 101.2, 102.0, 108.0, 111.2, 142.2, 148.0, 149.5. Anal. Calcd for $C_{20}H_{24}O_6Si$: C, 61.83; H, 6.23. Found: C, 61.96; H, 6.18.

Di-*tert*-butylbis(3,4-dimethoxyphenoxy)silane (7d). Reactants: di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (0.066 mL, 0.18 mmol); 3,4-dimethoxyphenol (111 mg, 0.72 mmol); Et_3N (0.10 mL, 0.72 mmol); DMF (3.0 mL). **7d** (66 mg, 81%): colorless solid; mp 76−77 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.10 (s, 18H), 3.73 (s, 6H), 3.83 (s, 6H), 6.52−6.54 (m, 4H), 6.71 (d, 2H, J = 9.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 27.8, 55.7, 56.2, 104.7, 110.7, 111.6, 143.7, 149.3. Anal. Calcd for $C_{24}H_{36}O_6Si$: C, 64.25; H, 8.09. Found: C, 64.30; H, 8.02.

Di-*tert*-butylbis(3,4-(dimethylenedioxy)phenoxy)silane (7e). Reactants: di-*tert*-butylsilyl bis(trifluoromethnesulfonate) (0.083 mL, 0.23 mmol); sesamol (127 mg, 0.92 mmol); Et_3N (0.13 mL, 0.92 mmol); DMF (4.0 mL). **7e** (74 mg, 78%): colorless solid; mp 75−77 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.07 (s, 18H), 5.91 (s, 4H), 6.42 (dd, 2H, J = 8.5, 2.5 Hz), 6.53 (d, 2H, J = 2.5 Hz), 6.65 (d, 2H, J = 8.5 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 21.7, 27.8, 101.2, 102.4, 107.9, 111.6, 141.9, 147.9, 150.0. Anal. Calcd for $C_{22}H_{26}O_6Si$: C, 63.44; H, 6.78. Found: C, 63.59; H, 6.82.

Procedure for the Preparation of Silaketals (7c,f). Diisopropyldichlorosilane or di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (0.2 mmol) was added to the solution of 3,4-dimethoxyphenol (0.2 mmol) and Et_3N (0.2 mmol) in DMF (1.0 mL) at room temperature. The mixture was stirred for 0.5 h at 60 °C and then added the solution of sesamol (0.2 mmol) and Et_3N (0.2 mmol) in DMF (1.5 mL). The mixture was stirred for 4 h at 60 °C and then cooled. The solution was extracted by Et_2O. The extracts were washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (AcOEt−*n*-hexane) to give the corresponding to the silaketal (**7c** or **7f**).

(3,4-Dimethoxyphenoxy)(3,4-(methylenedioxy)phenoxy)diisopropylsilane (7c). Reactants: diisopropyldichlorosilane (0.050 mL, 0.28 mmol); 3,4-dimethoxyphenol (42.0 mg, 0.28 mmol); Et_3N (0.038 mL, 0.28 mmol); DMF (1.0 mL); sesamol (37.0 mg, 0.28 mmol); Et_3N (0.038 mL, 0.28 mmol); DMF (1.5 mL). **7c** (52 mg, 48%): colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (d, 12H, J = 5.2 Hz), 1.20 (m, 2H), 3.78 (s, 3H), 3.83 (s, 3H), 5.91 (s, 2H), 6.38−6.50 (m, 2H), 6.53 (d, 1H, J = 2.2 Hz), 6.54 (d, 1H, J = 2.2 Hz), 6.65 (d, 1H, J = 8.4 Hz), 6.71 (d, 1H, J = 8.4 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.4, 17.1, 55.7, 56.2, 101.2, 102.1, 104.4, 108.0, 110.2, 111.3, 111.7, 142.0, 143.9, 148.0, 148.8, 149.5, 149.6. Anal. Calcd for $C_{21}H_{28}O_6Si$: C, 62.35; H, 6.98. Found: C, 62.34; H, 6.89.

Di-*tert*-butyl(3,4-dimethoxyphenoxy)(3,4-(methylenedioxy)phenoxy)silane (7f). Reactants: di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (0.21 mL, 0.57 mmol); 3,4-dimethoxyphenol (88.0 mg, 0.57 mmol); Et_3N (0.080 mL, 0.57 mmol); DMF (3.0 mL); sesamol (79.0 mg, 0.57 mmol); Et_3N (0.080 mL, 0.57 mmol); DMF (3.0 mL). **7f** (117 mg, 48%): colorless solid; mp 72−73 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.08 (s, 18H), 3.75 (s, 3H), 3.83 (s, 3H), 5.91 (s, 2H), 6.45 (dd, 1H, J = 8.5, 2.5 Hz), 6.50−6.56 (m, 3H), 6.65 (d, 1H, J = 8.5 Hz), 6.72 (d, 1H, J = 8.5 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 21.7, 27.8, 55.7, 56.3, 101.2, 102.4, 104.7, 107.9, 110.6, 111.6, 141.9, 143.7, 148.0, 149.3, 150.1. Anal. Calcd for $C_{23}H_{32}O_6Si$: C, 63.86; H, 7.46. Found: C, 63.95; H, 7.45.

Bis(3,4-dimethoxybenzyl) Sulfide (8). A solution of $Na_2S{\cdot}9H_2O$ (659 mg, 2.74 mmol) in EtOH (10 mL) was added to 3,4-dimethoxybenzyl bromide (792 mg, 3.43 mmol) at room temperature. The suspension was refluxed for 1.5 h and then cooled. The mixture was concentrated, and then the residue was dissolved in AcOEt. The solution was washed with water and brine and then evaporated. The residue was purified by chromatography on silica gel (AcOEt−*n*-hexane) to give **8** (518 mg, 90%) as a colorless solid; mp 94−96 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.58 (s, 4H), 3.88 (s, 12H), 6.80 (s, 4H), 6.85 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 35.2, 55.6, 55.7, 110.6, 111.8, 120.9, 130.4, 147.8, 148.8; HRMS calcd for $C_{18}H_{22}O_4S$ (M^+) *m/e* 334.1238, found *m/e* 334.1243.

Bis(3,4-dimethoxybenzyl) Sulfoxide (9a). *m*-Chloroperbenzoic acid (80 mg, 0.37 mmol) was added to the solution of **8** (62 mg, 0.37 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The mixture was stirred for 24 h at room temperature and then quenched with aqueous potassium carbonate. The organic layer was washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (CH_2Cl_2−MeOH) to give **9a** (52 mg, 80%) as a colorless solid: mp 146−148 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.86 (m, 4H), 3.89 (s, 12H), 6.82−6.87 (m, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 55.9, 55.9, 57.1, 111.3, 112.9, 122.5, 149.1; HRMS calcd for $C_{18}H_{22}O_5S$ (M^+) *m/e* 350.1188, found *m/e* 350.1188. Anal. Calcd for $C_{18}H_{22}O_5S$: C, 61.70; H, 6.33; S, 9.15. Found: C, 61.57; H, 6.30; S, 8.97.

Bis(3,4-(methylenedioxy)benzyl) Sulfoxide (9b). *m*-Chloroperbenzoic acid (124 mg, 0.58 mmol) was added to the solution of bis(3,4-methylenedioxybenzyl) sulfide[16c] (183 mg, 0.58 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The mixture was stirred for 48 h at room temperature and then quenched with aqueous potassium carbonate. The organic layer was washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (CH_2Cl_2−MeOH) to give **9b** (93 mg, 48%) as a colorless solid: mp 128−130 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.77 (d, 2H, J = 12.9 Hz), 3.84 (d, 2H, J = 12.9 Hz), 5.97 (s, 4H), 6.72−6.82 (m, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 57.0, 101.3, 108.6, 110.2, 123.5, 123.6, 147.8, 148.1; HRMS calcd for $C_{16}H_{14}O_5S$ (M^+) *m/e* 318.0570,

found *m/e* 318.0562. Anal. Calcd for $C_{16}H_{14}O_5S$: C, 60.37; H, 4.43; S, 10.07. Found: C, 60.38; H, 4.51; S, 10.05.

3,4-Dimethoxybenzyl 3,4-(Methylenedioxy)benzyl Sulfoxide (9c). Sodium hydroxide (44 mg, 1.1 mmol) was added to the solution of 3,4-dimethoxybenzyl mercaptan (203 mg, 1.1 mmol) in EtOH (5 mL). The mixture was stirred for a few minutes at room temperature, and then 3,4-(methylenedioxy)-benzyl bromide (237 mg, 1.0 mmol) was added to the solution. After the solution was stirred for 1.5 h at room temperature, the solvent was evaporated and then the residue was dissolved in AcOEt. The solution was washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (AcOEt−*n*-hexane) to give 3,4-dimethoxybenzyl 3,4-(methylenedioxy)benzyl sulfide (183 mg, 52%).

m-Chloroperbenzoic acid (124 mg, 0.58 mmol) was added to a solution of 3,4-dimethoxybenzyl 3,4-(methylenedioxy)-benzyl sulfide (183 mg, 0.58 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The mixture was stirred for 48 h at room temperature and then quenched with aqueous potassium carbonate. The organic layer was washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (CH_2Cl_2−MeOH) to give **9c** (93 mg, 48%) as a colorless solid: mp 148−150 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.80−3.86 (m, 4H), 3.89 (s, 6H), 5.98 (s, 2H), 6.78−6.86 (m, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 55.9, 56.0, 57.0, 101.3, 108.6, 110.3, 111.4, 112.9, 122.4, 122.5, 123.6, 123.6, 147.8, 148.1, 149.2; HRMS calcd for $C_{17}H_{18}O_5S$ (M^+) *m/e* 334.0875, found *m/e* 334.0880. Anal. Calcd for $C_{17}H_{18}O_5S$: C, 61.06; H, 5.43. Found: C, 60.62; H, 5.34.

3,4-Dimethoxybenzyl-3,4,5-trimethoxybenzyl Sulfoxide (9d). Sodium hydroxide (28 mg, 0.71 mmol) was added to a solution of 3,4,5-trimethoxybenzyl mercaptan (152 mg, 0.71 mmol) in EtOH (10 mL). The mixture was stirred for a few minutes at room temperature, and then 3,4-(methylenedioxy)benzyl bromide (164 mg, 0.71 mmol) was added to the solution. After the solution was stirred for 3 h at room temperature, the mixture was evaporated and then the residue was dissolved in AcOEt. The solution was washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (AcOEt−*n*-hexane) to give 3,4-dimethoxybenzyl-3,4,5-tetramethoxybenzyl sulfide (181 mg, 70%).

m-Chloroperbenzoic acid (107 mg, 0.50 mmol) was added to a solution of 3,4-dimethoxybenzyl-3,4,5-tetramethoxybenzyl sulfide (181 mg, 0.50 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The mixture was stirred for 30 h at room temperature and then quenched with aqueous potassium carbonate. The organic layer was washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (CH_2Cl_2−MeOH) to give **9d** (98 mg, 52%) as a colorless solid: mp 127−128 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.82−3.91 (m, 4H), 3.85 (s, 3H), 3.86 (s, 6H), 3.89 (s, 6H), 6.50 (s, 2H), 6.83 (s, 1H), 6.84 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 55.8, 55.9, 56.0, 57.5, 57.8, 60.7, 106.9, 111.3, 112.8, 122.3, 122.4, 125.8, 137.9, 149.1, 153.3; HRMS calcd for $C_{19}H_{24}O_6S$ (M^+) *m/e* 380.1293, found *m/e* 380.1285. Anal. Calcd for $C_{19}H_{24}O_6S$: C, 59.98; H, 6.36; S, 8.43. Found: C, 59.83; H, 6.28; S, 8.48.

Bis(3,4-dimethoxybenzyl) Sulfone (10a). A 30% solution of H_2O_2 (237 mg, 1.12 mmol) was added to a solution of **8** (208 mg, 0.62 mmol) in AcOH (10 mL) at room temperature. After the solution was stirred for 0.5 h at room temperature, additional 30% H_2O_2 (392 mg, 1.87 mmol) was added to the reaction mixture. The mixture was stirred for 0.5 h at 100 °C and then cooled. The mixture was quenched with aqueous NaOH. The solution was extracted with AcOEt, and then the organic layer was washed with water and brine and concentrated in vacuo. The residue was purified by chromatography on silica gel (*n*-hexane−AcOEt) to give **10a** (71 mg, 31%) as a colorless solid: mp 164−166 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.90 (s, 12H), 4.08 (s, 4H), 6.88−6.93 (m, 6H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 53.4, 55.9, 56.0, 57.6, 111.1, 113.5, 119.7, 123.4, 149.2, 149.5; HRMS calcd for $C_{18}H_{22}O_6S$ (M^+) *m/e* 366.1138, found *m/e* 366.1139.

General Procedure for Preparing Dibenzyl Ethers (11). Dibenzyl ethers (**11**) were prepared by the reaction of the corresponding alkoxybenzyl alcohol with an alkoxybenzyl bromide according to the reported method.[17]

1,3-Bis(3,4-(methylenedioxy)benzyl) Ether (11b): colorless solid; mp 41−43 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.42 (s, 4H), 5.95 (s, 4H), 6.78 (s, 4H), 6.86 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 71.6, 100.9, 108.0, 108.5, 121.3, 132.0, 147.1, 147.7; HRMS calcd for $C_{16}H_{14}O_5$ (M^+) *m/e* 286.0841, found *m/e* 286.0826. Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.06; H, 5.00.

3,4-Dimethoxybenzyl 3,4-(Methylenedioxy)benzyl Ether (11c): colorless oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.88 (s, 3H), 3.89 (s, 3H), 4.43 (s, 2H), 4.46 (s, 2H), 5.95 (s, 2H), 6.78−6.91 (m, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 55.7, 55.8, 71.7, 100.9, 108.0, 108.5, 110.8, 111.0, 120.3, 121.3, 130.7, 132.1, 147.0, 147.7, 148.5, 148.9; HRMS calcd for $C_{17}H_{18}O_5$ (M^+) *m/e* 302.1154, found *m/e* 302.1147. Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.64; H, 6.04.

3,4-Dimethoxybenzyl 3,4,5-Trimethoxybenzyl Ether (11d): colorless solid; mp 58−59 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.87 (s, 6H), 3.89 (s, 6H), 4.47 (s, 2H), 4.51 (s, 2H), 6.59 (s, 2H), 6.87−6.93 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.6, 55.7, 55.9, 60.6, 71.8, 71.9, 104.5, 110.7, 111.0, 120.3, 130.5, 133.8, 137.2, 148.5, 148.9, 153.1; HRMS calcd for $C_{19}H_{24}O_6$ (M^+) *m/e* 348.1573, found *m/e* 348.1581. Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.36; H, 6.85.

1,3-Bis(3,4,5-trimethoxybenzyl) Ether (11e): colorless solid; mp 86−87 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.83 (s, 6H), 3.85 (s, 12H), 4.48 (s, 4H), 6.59 (s, 4H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 55.7, 60.4, 72.0, 104.3, 133.5, 137.0, 152.9. Anal. Calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 6.92. Found: C, 63.42; H, 6.88.

General Procedure for the Biaryl Coupling Reaction of Phenol Ether Derivatives Using PIFA−BF_3·Et_2O.[22] To a stirred −40 °C solution of the phenol ether derivatives (0.05 mmol) in CH_2Cl_2 (1.0 mL) was added a solution of PIFA (0.05 mmol) and BF_3·Et_2O (0.10 mmol) in CH_2Cl_2 (1.0 mL) dropwise under a nitrogen atmosphere. The reaction mixture was then stirred at −40 °C for 1.5 h and then evaporated in vacuo. Purification of the residue on silica gel gave the biaryl coupling products.

2,3,10-Trimethoxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*]-cycloheptene[16a] (4a). Reactants: **1a** (14.2 mg, 0.0498 mmol); PIFA (21.4 mg, 0.0498 mmol); BF_3·Et_2O (6.0 mg, 0.0423 mmol); CH_2Cl_2 (1 + 1 mL). **4a** (12.8 mg, 91%): colorless solid; mp 70−71 °C (lit.[16a] mp 79−80 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.13 (qui, 2H, J = 6.8 Hz), 2.44 (t, 4H, J = 6.8 Hz), 3.85 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 6.77 (s, 1H), 6.94 (d, 1H, J = 2.6 Hz), 7.15 (d, 1H, J = 8.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 30.5, 31.0, 33.6, 55.4, 56.0, 56.1, 111.8, 111.9, 114.0, 129.3, 132.0, 132.1, 132.9, 142.2, 147.4, 148.1, 158.3; HRMS calcd for $C_{18}H_{20}O_3$ (M^+) *m/e* 284.1409, found *m/e* 284.1403.

2,3,9,10-Bis(methylenedioxy)-6,7-dihydro-5*H*-dibenzo-[*a*,*c*]cycloheptene (4b). Reactants: **1b** (21.6 mg, 0.0760 mmol); PIFA (32.7 mg, 0.0760 mmol); BF_3·Et_2O (11.6 mg, 0.0817 mmol); CH_2Cl_2 (1.5 + 1.5 mL). **4b** (19.6 mg, 91%): colorless solid; mp 149−151 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.10 (qui, 2H, J = 6.5 Hz), 2.38 (t, 4H, J = 6.5 Hz), 5.96 (s, 4H), 6.72 (s, 2H), 6.81 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ

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(22) We adopted the ratio, substrate−PIFA−BF_3·Et_2O of 1:1:2, from experimental optimization, though for some substrates without heteroatoms only 1 equiv of BF_3·Et_2O was enough and for some substrates having some functional groups that could react with BF_3·Et_2O a little excess of BF_3·Et_2O was required.

31.2, 33.9, 100.8, 108.6, 108.8, 133.2, 134.1, 146.2, 146.3; HRMS calcd for $C_{17}H_{14}O_4$ (M^+) *m/e* 282.0893, found *m/e* 282.0900.

2,3,9,10-Tetramethoxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*]-cycloheptene[10a] (4c). Reactants: **1c** (22.1 mg, 0.0698 mmol); PIFA (30.0 mg, 0.0698 mmol); $BF_3{\cdot}Et_2O$ (5.8 mg, 0.0409 mmol); CH_2Cl_2 (1.5 + 1.5 mL). **4c** (21.7 mg, 99%): colorless solid; mp 159−160 °C (lit[10a] mp 153−155 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.20 (qui, 2H, J = 7.0 Hz), 2.44 (t, 4H, J = 7.0 Hz), 3.93 (s, 12H), 6.78 (s, 2H), 6.90 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 31.1, 33.9, 56.0, 56.2, 111.7, 112.0, 132.2, 133.0, 147.5, 147.9; HRMS calcd for $C_{19}H_{22}O_4$ (M^+) *m/e* 314.1519, found *m/e* 314.1519.

1,2,3,9,10-Pentamethoxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*]-cycloheptene (4d). Reactants: **1d** (24.7 mg, 0.0713 mmol); PIFA (30.7 mg, 0.0713 mmol); $BF_3{\cdot}Et_2O$ (20.2 mg, 0.143 mmol); CH_2Cl_2 (1.5 + 1.5 mL). **4d** (22.5 mg, 92%): colorless solid; mp 110−111 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.04−2.14 (m, 2H), 2.29−2.48 (m, 4H), 3.57 (s, 3H), 3.89 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 6.59 (s, 1H), 6.76 (s, 1H), 7.08 (s, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 30.9, 31.7, 33.3, 55.8, 56.0, 60.6, 61.2, 107.7, 111.3, 113.5, 126.0, 128.2, 132.3, 136.0, 140.8, 146.7, 147.7, 150.7, 152.1; HRMS calcd for $C_{20}H_{24}O_5$ (M^+) *m/e* 344.1624, found *m/e* 344.1626.

2-((*tert*-Butyldimethylsilyl)oxy)-3,9,10-trimethoxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (4e). Reactants: **1e** (27.6 mg, 0.0662 mmol); PIFA (28.5 mg, 0.0662 mmol); $BF_3{\cdot}Et_2O$ (18.8 mg, 0.132 mmol); CH_2Cl_2 (1.5 + 1.5 mL). **4e** (20.7 mg, 75%): colorless solid; mp 113−115 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.18 (s, 6H), 1.01 (s, 9H), 2.17 (m, 2H), 2.42 (m, 4H), 3.85 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 6.73 (s, 1H), 6.76 (s, 1H), 6.85 (s, 1H), 6.86 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −4.5, 18.5, 25.8, 31.1, 31.2, 33.8, 55.7, 56.0, 56.1, 111.8, 111.9, 112.7, 120.7, 132.0, 133.0, 133.3, 143.4, 147.4, 147.7, 149.7; HRMS calcd for $C_{24}H_{34}O_4Si$ (M^+) *m/e* 414.2227, found *m/e* 414.2232.

6-(Trifluoroacetyl)-2,3,11-trimethoxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine[13b] (5a). Reactants: **2a** (31.1 mg, 0.0783 mmol); PIFA (37.0 mg, 0.0861 mmol); $BF_3{\cdot}Et_2O$ (12.2 mg, 0.0861 mmol); CH_2Cl_2 (0.5 + 2 mL). **5a** (27.7 mg, 89%): colorless solid; mp 134−136 °C; IR 1686; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.41 (dd, 1H, J = 14.7, 9.7 Hz), 2.99 (dd, 1H, J = 14.7, 7.1 Hz), 3.19 (dd, 1H, J = 14.2, 10.6 Hz), 3.31 (d, 1H, J = 13.9 Hz), 3.85 (s, 3H), 3.90 (s, 3H), 3.94 (s, 3H), 4.26 (dd, 1H, J = 12.7, 6.4 Hz), 5.19 (d, 1H, J = 13.9 Hz), 6.82 (s, 1H), 6.86 (d, 1H, J = 2.6 Hz), 6.93 (dd, 1H, J = 8.6, 2.6 Hz), 7.18 (d, 1H, J = 8.6 Hz), 7.40 (s, 1H); HRMS calcd for $C_{20}H_{20}F_3NO_4$ (M^+) *m/e* 395.1341, found *m/e* 395.1338. Anal. Calcd for $C_{20}H_{20}F_3NO_4$: C, 60.76; H, 5.10; N, 3.54. Found C, 60.56; H, 5.07; N, 3.55.

6-(Trifluoroacetyl)-2,3,10,11-tetramethoxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (5b). Reactants: **2b** (19.7 mg, 0.0461 mmol); PIFA (21.8 mg, 0.0507 mmol); $BF_3{\cdot}Et_2O$ (13.1 mg, 0.0922 mmol); CH_2Cl_2 (1 + 2 mL). **5b** (13.3 mg, 68%): colorless solid; mp 157−158 °C; IR 1686; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.42 (dd, 1H, J = 15.0, 10.0 Hz), 2.96 (dd, 1H, J = 14.5, 6.8 Hz), 3.22 (dd, 1H, J = 14.0, 10.3 Hz), 3.31 (d, 1H, J = 13.5 Hz), 3.92 (s, 6H), 3.95 (s, 6H), 4.26 (dd, 1H, J = 13.5, 6.8 Hz), 5.20 (d, 1H, J = 13.5 Hz), 6.75 (s, 1H), 6.82 (s, 2H), 7.40 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 34.5, 48.3, 48.5, 56.0, 56.1, 111.9, 112.1, 112.9, 114.0, 116.7 (J = 287 Hz), 127.2, 131.0, 132.0, 132.9, 147.7, 148.5, 148.6, 148.9, 156.3 (J = 35 Hz); HRMS calcd for $C_{21}H_{22}F_3NO_5$ (M^+) *m/e* 425.1443, found *m/e* 425.1445. Anal. Calcd for $C_{21}H_{22}F_3NO_5$: C, 59.21; H, 5.21; N, 3.29. Found: C, 59.33; H, 5.26; N, 3.30.

6-(Trifluoroacetyl)-1,2,3,10,11-pentamethoxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (5c). Reactants: **2c** (30.6 mg, 0.0669 mmol); PIFA (31.6 mg, 0.0736 mmol); $BF_3{\cdot}Et_2O$ (19.0 mg, 0.134 mmol); CH_2Cl_2 (1.5 + 2 mL). **5c** (15.9 mg, 52%): colorless solid; mp 135−136 °C; IR 1685; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.43 (dd, 1H, J = 14.5, 10.5 Hz), 2.94 (dd, 1H, J = 14.5, 6.8 Hz), 3.18 (dd, 1H, J = 14.3, 10.5 Hz), 3.26 (d, 1H, J = 14.0 Hz), 3.55 (s, 3H), 3.87 (s, 3H), 3.90 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 4.23 (dd, 1H, J = 14.3, 6.3 Hz), 5.13 (d, 1H, J = 13.5 Hz), 6.74 (s, 1H), 6.84 (s, 1H), 6.93 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 34.3, 48.5, 48.6, 55.9, 56.0, 60.9, 61.1, 110.2, 111.6, 114.1, 116.7 (J = 287 Hz), 126.7, 127.3, 131.0, 131.4, 142.1, 147.1, 149.0, 151.0, 153.0, 156.3 (J = 38 Hz); HRMS calcd for $C_{22}H_{24}F_3NO_6$ (M^+) *m/e* 455.1555, found *m/e* 455.1558. Anal. Calcd for $C_{22}H_{24}F_3NO_6$: C, 57.76; H, 5.73; N, 3.06. Found: C, 57.86; H, 5.38; N, 3.05.

6-(Trifluoroacetyl)-2,3,9,10-bis(methylenedioxy)-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine (6a). Reactants: **3a** (24.7 mg, 0.0648 mmol); PIFA (30.6 mg, 0.0713 mmol); $BF_3{\cdot}Et_2O$ (18.5 mg, 0.130 mmol); CH_2Cl_2 (1 + 2 mL). **6a** (23.2 mg, 94%): colorless solid; mp 282−285 °C; IR 1686; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.23 (br, 4H), 6.04 (s, 4H), 6.83, 6.89 (s, 2H), 6.92, 6.94 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 47.6, 47.9, 48.0, 101.6, 108.2, 108.3, 109.2, 110.5, 116.7 (J = 288 Hz), 125.5, 125.7, 134.4, 134.6, 147.5, 148.5, 154.7 (J = 37 Hz); HRMS calcd for $C_{18}H_{12}F_3NO_5$ (M^+) *m/e* 379.0665, found *m/e* 379.0659. Anal. Calcd for $C_{18}H_{12}F_3NO_5{\cdot}{}^1/_2H_2O$: C, 55.68; H, 3.37; N, 3.60. Found: C, 56.02; H, 3.30; N, 3.64.

6-(Trifluoroacetyl)-2,3,9,10-tetramethoxy-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine (6b). Reactants: **3b** (23.3 mg, 0.0564 mmol); PIFA (26.7 mg, 0.0620 mmol); $BF_3{\cdot}Et_2O$ (16.0 mg, 0.113 mmol); CH_2Cl_2 (1 + 2 mL). **6b** (19.6 mg, 85%): colorless solid; mp 166−167 °C; IR 1686; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (s, 6H), 3.98 (s, 6H), 4.30, 4.41 (br., 4H), 6.86, 6.94 (s, 2H), 7.00, 7.02 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 47.7, 48.2, 56.1, 56.2, 110.8, 110.9, 112.1, 113.3, 116.7 (J = 288 Hz), 124.5, 124.6, 133.1, 148.7, 149.5, 149.7, 154.6 (J = 35 Hz); HRMS calcd for $C_{20}H_{20}F_3NO_5$ (M^+) *m/e* 411.1293, found *m/e* 411.1303. Anal. Calcd for $C_{20}H_{20}F_3NO_5$: C, 58.39; H, 4.90; N, 3.40. Found: C, 58.31; H, 4.96; N, 3.39.

6-(Trifluoroacetyl)-1,2,3,9,10-pentamethoxy-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine (6c). Reactants: **3c** (23.1 mg, 0.0521 mmol); PIFA (24.6 mg, 0.0573 mmol); $BF_3{\cdot}Et_2O$ (14.8 mg, 0.104 mmol); CH_2Cl_2 (1 + 2 mL). **6c** (19.6 mg, 85%): colorless solid; mp 142−144 °C; IR 1686; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.67, 3.92, 3.93, 3.94, 3.95, 3.96 (s, 15H), 3.51−3.98 (m, 2H), 4.61 (dd, 1H, J = 11.9, 9.9 Hz), 5.06 (dd, 1H, J = 13.9, 11.6 Hz), 6.68, 6.77, 6.84, 6.93 (s, 2H), 7.24−7.27 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 47.8, 48.2, 48.3, 48.4, 48.5, 56.0, 56.1, 60.9, 61.0, 61.2, 108.2, 109.4, 111.5, 112.7, 113.0, 116.7 (J = 288 Hz), 124.5, 124.7, 126.0, 128.2, 128.3, 142.8, 143.0, 148.5, 148.6, 148.8, 150.8, 150.9, 153.1, 154.6 (J = 36 Hz); HRMS calcd for $C_{21}H_{22}F_3NO_6$ (M^+) *m/e* 441.1397, found *m/e* 441.1397. Anal. Calcd for $C_{21}H_{22}F_3NO_6$: C, 57.14; H, 5.02; N, 3.17. Found: C, 57.18; H, 5.14; N, 3.14.

6-(Trifluoroacetyl)-2-((*tert*-butyldimethylsilyl)oxy)-3,9,10-trimethoxy-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine (6d). Reactants: **3d** (28.4 mg, 0.0553 mmol); PIFA (26.2 mg, 0.0608 mmol); $BF_3{\cdot}Et_2O$ (15.7 mg, 0.111 mmol); CH_2Cl_2 (1 + 2 mL). **6d** (18.0 mg, 64%): colorless solid; mp 172−173 °C; IR 1688; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.19, 0.20 (s, 6H), 0.97, 0.98 (s, 9H), 3.86 (s, 3H), 3.93 (s, 3H), 3.96 (s, 3H), 4.28, 4.36 (br, 4H), 6.81, 6.83, 6.90, 6.92, 6.94, 6.95, 6.98, 7.00 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −3.9, 19.1, 26.3, 48.4, 48.5, 48.8, 48.9, 56.2, 56.7, 111.5, 111.6, 112.6, 113.4, 113.9, 114.6, 117.4 (J = 287 Hz), 120.8, 120.9, 124.8, 125.0, 125.9, 126.1, 133.6, 133.8, 146.2, 146.4, 149.2, 150.1, 150.2, 151.2, 155.3 (J = 36 Hz); HRMS calcd for $C_{25}H_{32}F_3NO_5Si$ (M^+) *m/e* 511.2002, found *m/e* 551.1972. Anal. Calcd for $C_{25}H_{32}F_3NO_5Si$: C, 58.69; H, 6.30; N, 2.74. Found: C, 58.39; H, 6.24; N, 2.80.

6-(Trifluoroacetyl)-2-acetoxy-3,9,10-trimethoxy-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine (6e). Reactants: **3e** (28.0 mg, 0.0634 mmol); PIFA (30.0 mg, 0.0698 mmol); $BF_3{\cdot}Et_2O$ (18.0 mg, 0.127 mmol); CH_2Cl_2 (1 + 2 mL). **6e** (16.7 mg, 60%): colorless solid; mp 174−176 °C; IR 1767, 1684; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.90 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 4.33 (s, 2H), 4.40 (brs, 2H), 6.84, 6.93, 6.95, 6.97, 7.05 (s, 3H), 7.21, 7.23 (s, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 20.7, 47.9, 48.3, 110.9, 111.0, 112.1, 113.3, 114.5, 116.7 (J = 287 Hz), 122.3, 124.2, 124.3, 130.6, 132.2, 133.2, 140.2, 140.4, 148.9, 149.6, 149.8, 154.8 (J = 36 Hz), 168.9; HRMS calcd for $C_{21}H_{20}NO_6F_3$ (M^+) *m/e* 439.1283, found *m/e* 439.1264.

6,6-Diisopropyl-2,3,9,10-tetramethoxy-6,7-dihydro-5*H*-6-siladibenzo[*a*,*c*]cycloheptene (12a). Reactants: **7a** (19.1 mg, 0.0454 mmol); PIFA (19.5 mg, 0.0454 mmol); $BF_3{\cdot}Et_2O$

(12.9 mg, 0.0908 mmol); CH_2Cl_2 (1 + 1 mL). **12a** (13.3 mg, 56%): colorless solid; mp 132−133 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (d, 12H, J = 5.4 Hz), 1.18 (m, 2H), 3.90 (s, 12H), 6.62 (s, 2H), 6.81 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.4, 17.0, 56.0, 56.5, 105.0, 113.3, 120.3, 144.7, 146.4, 149.3; HRMS calcd for $C_{22}H_{30}O_6Si$ (M^+) *m/e* 418.1811, found *m/e* 418.1813.

6,6-Diisopropyl-2,3,9,10-bis(methylenedioxy)-6,7-dihydro-5*H*-6-siladibenzo[*a*,*c*]cycloheptene (12b). Reactants: **7b** (12.5 mg, 0.0322 mmol); PIFA (13.8 mg, 0.0454 mmol); $BF_3{\cdot}Et_2O$ (9.1 mg, 0.0644 mmol); CH_2Cl_2 (1 + 1 mL). **12b** (13.3 mg, 56%): colorless solid; mp 148−149 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (d, 12H, J = 5.4 Hz), 1.18 (m, 2H), 3.90 (s, 12H), 6.62 (s, 2H), 6.81 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 12.2, 17.0, 101.4, 102.5, 109.4, 121.6, 143.3, 147.0, 147.5. Anal. Calcd for $C_{20}H_{22}O_6Si$: C, 62.16; H, 5.74. Found: C, 62.13; H, 5.73.

6,6-Diisopropyl-2,3-dimethoxy-9,10-(methylenedioxy)-6,7-dihydro-5*H*-6-siladibenzo[*a*,*c*]cycloheptene (12c). Reactants: **7c** (15.4 mg, 0.0381 mmol); PIFA (16.3 mg, 0.0381 mmol); $BF_3{\cdot}Et_2O$ (16.2 mg, 0.144 mmol); CH_2Cl_2 (1 + 1 mL). **12c** (7.0 mg, 46%): colorless solid; mp 129−130 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.08 (d, 12H, J = 6.8 Hz), 1.16 (m, 2H), 3.88 (s, 6H), 5.97 (s, 2H), 6.58 (s, 1H), 6.60 (s, 1H), 6.76 (s, 1H), 6.78 (s, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 12.3, 17.0, 56.0, 56.3, 101.4, 102.5, 104.9, 109.3, 113.2, 120.3, 121.5, 143.2, 144.7, 146.2, 147.1, 147.5, 149.1. Anal. Calcd for $C_{21}H_{26}O_6Si$: C, 62.66; H, 6.51. Found: C, 62.52; H, 6.53.

6,6-Di-*tert*-butyl-2,3,9,10-tetramethoxy-6,7-dihydro-5*H*-6-siladibenzo[*a*,*c*]cycloheptene (12d). Reactants: **7d** (30.7 mg, 0.0684 mmol); PIFA (29.4 mg, 0.0684 mmol); $BF_3{\cdot}Et_2O$ (29.1 mg, 0.205 mmol); CH_2Cl_2 (1 + 1 mL). **12d** (23.9 mg, 78%): colorless solid; mp 193−194 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.06 (s, 18H), 3.89 (s, 6H), 3.90 (s, 6H), 6.61 (s, 2H), 6.80 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 21.4, 27.7, 56.1, 56.6, 105.2, 113.7, 119.9, 144.5, 147.3, 149.3; HRMS calcd for $C_{24}H_{34}O_6Si$ (M^+) *m/e* 446.2124, found *m/e* 446.2124. Anal. Calcd for $C_{24}H_{34}O_6Si$: C, 64.54; H, 7.67. Found: C, 64.70; H, 7.69.

6,6-Di-*tert*-butyl-2,3,9,10-bis(methylenedioxy)-6,7-dihydro-5*H*-6-siladibenzo[*a*,*c*]cycloheptene (12e). Reactants: **7e** (20.8 mg, 0.0499 mmol); PIFA (21.5 mg, 0.0499 mmol); $BF_3{\cdot}Et_2O$ (14.2 mg, 0.0998 mmol); CH_2Cl_2 (1 + 1 mL). **12e** (16.6 mg, 80%): colorless solid; mp 253−254 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.04 (s, 18H), 5.96 (s, 4H), 6.57 (s, 2H), 6.71 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.3, 27.7, 101.4, 102.6, 109.7, 121.1, 143.0, 147.5, 147.9. Anal. Calcd for $C_{22}H_{26}O_6Si$: C, 63.74; H, 6.32. Found: C, 63.79; H, 6.33.

6,6-Di-*tert*-butyl-2,3-dimethoxy-9,10-methylenedioxy-6,7-dihydro-5*H*-6-siladibenzo[*a*,*c*]cycloheptene (12f). Reactants: **7f** (14.3 mg, 0.0331 mmol); PIFA (14.2 mg, 0.0331 mmol); $BF_3{\cdot}Et_2O$ (14.0 mg, 0.0993 mmol); CH_2Cl_2 (1 + 1 mL). **12f** (11.9 mg, 83%): colorless solid; mp 140−142 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.05 (s, 18H), 3.88 (s, 6H), 3.89 (s, 6H), 5.97 (s, 2H), 6.59 (s, 1H), 6.60 (s, 1H), 6.74 (s, 1H), 6.77 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.3, 27.7, 56.0, 56.3, 101.4, 102.6, 104.2, 109.5, 113.5, 119.9, 121.1, 143.0, 144.5, 147.0, 147.4, 148.0, 149.1; HRMS calcd for $C_{23}H_{30}O_6Si$ (M^+) *m/e* 430.1811, found *m/e* 430.1811.

2,3,9,10-Tetramethoxy-5,7-dihydrodibenzo[*c*,*e*]thiepine 6-Oxide (13a). Reactants: **9a** (13.8 mg, 0.0394 mmol); PIFA (16.9 mg, 0.0394 mmol); $BF_3{\cdot}Et_2O$ (11.2 mg, 0.0788 mmol); CH_2Cl_2 (1 + 1 mL). **13a** (10.0 mg, 73%): colorless solid; mp >300 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.25 (d, 1H, J = 12.3 Hz), 3.45 (d, 1H, J = 14.0 Hz), 3.71 (d, 1H, J = 14.8 Hz), 4.12 (d, 1H, J = 12.3 Hz), 3.94 (s, 3H), 3.96 (s, 6H), 6.86 (s, 1H), 6.91 (s, 1H), 6.93 (s, 1H), 6.96 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 53.3, 55.6, 56.1, 56.2, 56.3, 111.9, 112.1, 112.6, 114.2, 121.2, 122.1, 132.9, 133.0, 148.2, 148.5, 149.3, 149.7; HRMS calcd for $C_{18}H_{20}O_5S$ (M^+) *m/e* 348.1030, found *m/e* 348.1028.

2,3,9,10-Bis(methylenedioxy)-5,7-dihydrodibenzo[*c*,*e*]thiepine 6-Oxide (13b). Reactants: **9b** (14.3 mg, 0.0449 mmol); PIFA (19.3 mg, 0.0449 mmol); $BF_3{\cdot}Et_2O$ (19.1 mg, 0.135 mmol); CH_2Cl_2 (1 + 1 mL). **13b** (10.1 mg, 71%): colorless solid; mp 269−270 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.17 (d, 1H, J = 14.8 Hz), 3.37 (d, 1H, J = 17.8 Hz), 3.66 (d, 1H, J = 17.8 Hz), 4.07 (d, 1H, J = 14.8 Hz), 6.03 (dd, 4H, J = 6.0, 2.4 Hz), 6.82 (s, 1H), 6.83 (s, 1H), 6.88 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 53.2, 55.6, 101.5, 101.6, 109.0, 109.5, 109.7, 111.6, 122.1, 123.3, 134.2, 134.3, 147.0, 147.3, 148.3, 148.5; HRMS calcd for $C_{16}H_{12}O_5S$ (M^+) *m/e* 316.0405, found *m/e* 316.0441. Anal. Calcd for $C_{16}H_{12}O_5S$: C, 60.75; H, 3.82. Found: C, 60.33; H, 3.91.

2,3-Dimethoxy-9,10-(methylenedioxy)-5,7-dihydrodibenzo[*c*,*e*]thiepine 6-Oxide (13c). Reactants: **9c** (12.0 mg, 0.0359 mmol); PIFA (19.3 mg, 0.108 mmol); $BF_3{\cdot}Et_2O$ (15.3 mg, 0.108 mmol); CH_2Cl_2 (1 + 1 mL). **13c** (7.1 mg, 59%): colorless solid; mp 247−248 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.19, 3.23 (d, 1H, J = 12.5 Hz), 3.37, 3.45 (d, 1H, J = 14.5 Hz), 3.65, 3.71 (d, 1H, J = 8.3 Hz), 3.92, 3.93 (s, 3H), 3.94, 3.95 (s, 3H), 4,03−4.14 (m, 1H), 6.02−6.06 (m, 2H), 6.83−6.93 (m, 4H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 53.2, 53.3, 55.6, 56.1, 56.2, 101.5, 101.6, 109.0, 109.4, 109.8, 111.6, 111.8, 112.1, 112.5, 114.1, 121.1, 122.2, 123.1, 132.8, 132.8, 134.3, 134.4, 146.9, 147.2, 148.2, 148.5, 149.3, 149.6; HRMS calcd for $C_{17}H_{16}O_5S$ (M^+) *m/e* 332.0718, found *m/e* 333.0711.

1,2,3,9,10-Pentamethoxy-5,7-dihydrodibenzo[*c*,*e*]thiepine 6-Oxide (13d). Reactants: **9d** (13.2 mg, 0.0347 mmol); PIFA (14.9 mg, 0.0347 mmol); $BF_3{\cdot}Et_2O$ (9.8 mg, 0.0694 mmol); CH_2Cl_2 (1 + 1 mL). **13d** (5.6 mg, 42%): colorless solid; mp 193−194 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.15, 3.25 (d, 1H, J = 11.7 Hz), 3.36, 3.47 (d, 1H, J = 13.8 Hz), 3.63, 3.75 (s, 3H), 3.68 (m, 1H), 3.91, 3.92 (s, 3H), 3.94 (s, 6H), 3.95, 3.96 (s, 3H), 4.05−4.17 (m, 1H), 6.69, 6.75 (s, 1H), 6.85, 6.92 (s, 1H), 7.03, 7.09 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 53.4, 53.6, 55.6, 55.8, 56.0, 56.1, 56.2, 60.9, 61.0, 61.1, 109.0, 110.6, 112.1, 113.6, 113.8, 114.1, 121.2, 122.3, 124.4, 125.7, 125.8, 125.9, 128.2, 128.5, 142.6, 143.1, 148.1, 148.4, 148.7, 149.0, 151.0, 151.4, 152.7, 152.9; HRMS calcd for $C_{19}H_{22}O_6S$ (M^+) *m/e* 378.1137, found *m/e* 378.1145.

2,3,9,10-Tetramethoxy-5,7-dihydrodibenzo[*c*,*e*]thiepine 6,6-Dioxide (14a). Reactants: **10a** (39.4 mg, 0.107 mmol); PIFA (48.1 mg, 0.112 mmol); $BF_3{\cdot}Et_2O$ (31.8 mg, 0.223 mmol); CH_2Cl_2 (1 + 1 mL). **14a** (32.3 mg, 83%): colorless solid; mp >300 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.90−4.05 (m, 4H), 3.96 (s, 6H), 3.97 (s, 6H), 6.94 (s, 2H), 6.96 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 56.2, 56.2, 57.3, 111.9, 113.2, 120.6, 132.6, 149.3, 149.6; HRMS calcd for $C_{18}H_{20}O_6S$ (M^+) *m/e* 364.0980, found *m/e* 364.0979.

2,3,9,10-Bis(methylenedioxy)-5,7-dihydrodibenzo[*c*,*e*]thiepine 6,6-Dioxide (14b). Reactants: **10b** (22.8 mg, 0.0682 mmol); PIFA (29.3 mg, 0.0682 mmol); $BF_3{\cdot}Et_2O$ (19.4 mg, 0.136 mmol); CH_2Cl_2 (3 + 1 mL). **14b** (16.3 mg, 72%): colorless solid; mp >300 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.90 (m, 4H), 6.06 (dd, 4H, J = 8.0, 1.3 Hz), 6.89 (s, 2H), 6.91 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 57.0, 57.7, 101.5, 101.9, 108.6, 109.3, 110.5, 110.9, 121.7, 124.6, 133.9, 148.1, 148.2, 148.4, 148.6; HRMS calcd for $C_{16}H_{12}O_6S$ (M^+) *m/e* 332.0354, found *m/e* 332.0353.

2,3,9,10-Tetramethoxy-5,7-dihydrodibenz[*c*,*e*]oxepine[10a] (15a). Reactants: **11a** (14.3 mg, 0.0449 mmol); PIFA (19.3 mg, 0.0449 mmol); $BF_3{\cdot}Et_2O$ (12.7 mg, 0.0898 mmol); CH_2Cl_2 (1 + 1 mL). **15a** (12.0 mg, 85%): colorless solid; mp 243−244 °C (lit.[10a] mp 247.1 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.96 (s, 6H), 3.99 (s, 6H), 4.28 (s, 4H) 6.96 (s, 2H), 7.03 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 56.0, 56.2, 67.3, 110.2, 112.7, 127.9, 133.8, 148.5, 149.3.

2,3,9,10-Bis(methylenedioxy)-5,7-dihydrodibenz[*c*,*e*]oxepine (15b). Reactants: **11b** (59.3 mg, 0.207 mmol); PIFA (89.0 mg, 0.207 mmol); $BF_3{\cdot}Et_2O$ (58.8 mg, 0.414 mmol); CH_2Cl_2 (1 + 1 mL). **15b** (47.6 mg, 81%): colorless solid; mp 226−228 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.21 (s, 4H), 6.03 (s, 4H), 6.89 (s, 2H), 6.94 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 67.0, 101.3, 107.5, 109.8, 128.9, 135.2, 147.1, 148.1; HRMS calcd for $C_{16}H_{12}O_5$ (M^+) *m/e* 284.0685, found *m/e* 284.0678.

2,3-Dimethoxy-9,10-(methylenedioxy)-5,7-dihydrodibenz[*c*,*e*]oxepine (15c). Reactants: **11c** (20.6 mg, 0.0681 mmol); PIFA (29.3 mg, 0.0681 mmol); $BF_3{\cdot}Et_2O$ (19.3 mg, 0.136 mmol); CH_2Cl_2 (1 + 1 mL). **15c** (11.0 mg, 54%): colorless solid; mp 221−222 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.95 (s, 3H),

3.96 (s, 3H), 4.21 (s, 2H), 4.28 (s, 2H), 6.03 (s, 2H), 6.91 (s, 1H), 6.94 (s, 1H), 6.98 (s, 1H), 7.01 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 56.1, 67.2, 101.3, 107.4, 109.9, 110.2, 112.6, 127.7, 129.1, 133.7, 135.4, 147.0, 148.1, 148.5, 149.3. Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.02; H, 5.34.

1,2,3,9,10-Pentamethoxy-5,7-dihydrodibenz[*c*,*e*]oxepine (15d). Reactants: **11e** (45.2 mg, 0.130 mmol); PIFA (55.9 mg, 0.130 mmol); BF_3·Et_2O (36.9 mg, 0.260 mmol); CH_2Cl_2 (1 + 1 mL). **15d** (31.4 mg, 70%): colorless solid; mp 124−125 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.93 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 3.96 (s, 3H), 4.10−4.50 (m, 4H), 6.77 (s, 1H), 6.94 (s, 1H), 7.30 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 55.9, 56.1, 60.8, 61.2, 67.3, 67.6, 108.9, 112.1, 112.5, 126.5, 127.9, 129.7, 131.4, 142.6, 148.3, 148.5, 150.4, 152.8. Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.81; H, 6.36.

1,2,3,9,10,11-Hexamethoxy-5,7-dihydrodibenz[*c*,*e*]oxepine (15e). Reactants: **11d** (20.6 mg, 0.0544 mmol); PIFA (23.4 mg, 0.0544 mmol); BF_3·Et_2O (15.5 mg, 0.109 mmol); CH_2Cl_2 (1 + 1 mL). **15d** (7.8 mg, 38%): colorless solid; mp 111−113 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.75 (d, 1H, J = 11.4 Hz), 3.91 (s, 3H), 3.93 (s, 3H), 3.95 (s, 6H), 3.96 (s, 3H), 3.99 (d, 1H), 4.39 (d, 1H, J = 11.2 Hz), 4.98 (d, 1H, J = 11.2 Hz), 6.77 (s, 1H), 7.07 (s, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 56.0, 59.7, 60.9, 61.0, 61.1, 62.1, 67.5, 108.7, 121.6, 126.3, 128.2, 131.4, 133.1, 141.3, 142.5, 150.4, 151.6, 152.7, 153.0; HRMS calcd for $C_{20}H_{24}O_7$ (M^+) *m/e* 376.1522, found *m/e* 376.1521. Anal. Calcd for $C_{20}H_{24}O_7$: C, 63.82; H, 6.43. Found: C, 63.73; H, 6.37.

Preparation of 2,2′-Substituted Biphenyl Derivatives. General Procedure for the Preparation of 2,2′-Dihydroxy Derivatives (16). To a stirred solution of **12** (0.05 mmol) in THF (1.0 mL) was added 1.0 M solution of TBAF in THF (0.05 mL) at room temperature. The reaction mixture was then stirred at room temperature for 2 h and then evaporated in vacuo. Purification of the residue on preparative TLC gave the 2,2′-dihydroxybiphenyl derivatives (**16**).

4,4′,5,5′-Tetramethoxybiphenyl-2,2′-diol[18] (16a). Reactants: **12a** (23.9 mg, 0.054 mmol); 1.0 M TBAF solution in THF (0.054 mL, 0.054 mmol); THF (1.0 mL). **16a** (15.8 mg, 96%): colorless solid; mp 182−184 °C (lit.[18] mp 181.5−182.5 °C); IR 3319; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.84 (s, 6H), 3.87 (s, 6H), 6.62 (s, 2H), 6.72 (s, 2H); HRMS calcd for $C_{16}H_{18}O_6$ (M^+) *m/e* 306.1103, found *m/e* 306.1101.

4,5,4′,5′-Bis(methylenedioxy)biphenyl-2,2′-diol[19] (16b). Reactants: **12b** (16.6 mg, 0.040 mmol); 1.0 M TBAF solution in THF (0.040 mL, 0.040 mmol); THF (2.0 mL). **16b** (10.6 mg, 97%): colorless solid; mp 201−202 °C (lit.[19] mp 207−207.5 °C); IR 3264; ^{1}H NMR (250 MHz, CD_3OD) δ 5.88 (s, 4H), 6.46 (s, 2H), 6.65 (s, 2H); HRMS calcd for $C_{14}H_{10}O_6$ (M^+) *m/e* 274.0477, found *m/e* 274.0469.

2,2′-Dimethyl-4,5,4′,5′-bis(methylenedioxy)biphenyl[20] (17b). To a solution of **13b** (8.9 mg, 0.028 mmol) in EtOH (5.0 mL) was added excess Raney Ni (w-1) as a catalyst. The suspension was refluxed for 7 h and then cooled. The catalyst was filtered, and then the filtrate was evaporated in vacuo. Purification of the residue on a preparative TLC gave **17b** (7.3 mg, 97%): colorless solid; mp 120−121 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.96 (s, 6H), 5.95 (s, 4H), 6.56 (s, 2H), 6.73 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 19.6, 100.8, 109.8, 109.8, 129.3, 134.2, 145.3, 146.5; HRMS calcd for $C_{16}H_{14}O_4$ (M^+) *m/e* 270.0892, found *m/e* 270.0890.

General Procedure for the Preparation of 2,2′-Diformyl Derivatives (18). To a stirred solution of **15** (0.05 mmol) in CH_2Cl_2 (2.0 mL) containing H_2O (0.11−0.15 mL) was added DDQ (0.14−0.15 mmol) at room temperature. The reaction mixture was refluxed for 24 h and then cooled. The mixture was quenched with saturated sodium bicarbonate solution and then washed with water and brine. The organic layer was evaporated in vacuo and then purified by column chromatography on silica gel to give the 2,2′-diformylbiphenyl derivatives (**18**).

2,2′-Diformyl-4,4′,5,5′-tetramethoxybiphenyl[21] (18a). Reactants: **15a** (14.6 mg, 0.046 mmol); DDQ (29.4 mg, 0.123 mmol); CH_2Cl_2 (2.0 mL); H_2O (0.15 mL). **18a** (10.0 mg, 66%): colorless solid; mp 213-215 °C (lit.[21] mp 213−215 °C); IR 1682; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.96 (s, 3H), 4.01 (s, 3H), 6.80 (s, 2H), 7.56 (s, 2H), 9.67 (s, 2H); HRMS calcd for $C_{18}H_{18}O_6$ (M^+) *m/e* 330.1103, found *m/e* 330.1105.

2,2′-Diformyl-4,4′,5,5′-bis(methylenedioxy)biphenyl[21] (18b). Reactants: **15b** (12.6 mg, 0.044 mmol); DDQ (27.1 mg, 0.119 mmol); CH_2Cl_2 (2.0 mL); H_2O (0.11 mL). **18b** (7.3 mg, 56%): colorless solid; mp 245−248 °C (lit.[21] mp 213−215 °C); IR 1682; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.15 (s, 4H), 6.77 (s, 2H), 7.48 (s, 2H), 9.61 (s, 2H); HRMS calcd for $C_{16}H_{10}O_6$ (M^+) *m/e* 298.0477, found *m/e* 298.0479.

2,2′-Diformyl-3,4,4′,5,5′-pentamethoxybiphenyl (18d). Reactants: **15d** (13.2 mg, 0.038 mmol); DDQ (25.9 mg, 0.114 mmol); CH_2Cl_2 (2.0 mL); H_2O (0.11 mL). **18d** (6.0 mg, 46%): colorless solid; mp 152−153 °C; IR 1688, 1682; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.94 (s, 3H), 3.99 (s, 3H), 4.01 (s, 3H), 4.02 (s, 3H), 6.73 (s, 1H), 7.40 (s, 1H), 7.57 (s, 1H), 9.62 (s, 1H), 9.65 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 56.1, 56.2, 56.3, 61.0, 61.2, 105.6, 108.8, 114.3, 128.7, 130.4, 131.2, 149.3, 151.3, 153.2, 153.9, 190.0, 190.1; HRMS calcd for $C_{19}H_{20}O_7$ (M^+) *m/e* 360.1209, found *m/e* 360.1211.

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