A Novel and Useful Oxidative Intramolecular Coupling Reaction of Phenol Ether Derivatives on Treatment with a Combination of Hypervalent Iodine(III) Reagent and Heteropoly Acid

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Abstract: The oxidative intramolecular coupling reaction of phenol ether derivatives (nonphenolic derivatives) on treatment with a novel combination of a hypervalent iodine(III) reagent, phenyliodine bis(trifluoroacetate) (PIFA), and heteropoly acid (HPA) was studied. Biaryl compounds were obtained in excellent yields on treatment of highly substituted phenol ethers. On the other hand, spirodienones were specifically formed when one of the preferred arylic coupling sites was substituted with a methoxy group in the *para* position.

Keywords: biaryls · C–C coupling · heteropoly acids · hypervalent iodine reagents · spirodienones

Introduction

The oxidative aryl–aryl coupling reaction is an important strategy for the construction of the biaryl or spirodienone skeleton, which is a key intermediate in the biosynthesis of many classes of natural products.[1, 2] A number of biogenetic-type aryl–aryl coupling reactions on treatment with heavy metal oxidizing reagents such as mercury(II), thallium(III), vanadium(V), iron(III), manganese(IV), or ruthenium(IV) salts have been investigated.[3, 4] However, the yields are not always satisfactory. Moreover, heavy metal reagents are highly toxic and must be handled very carefully.

On the other hand, oxidative aryl–aryl coupling reactions with hypervalent iodine(III) reagents, which are less toxic and easier to handle, have received much attention because their reactivities are similar to those of heavy metals.[5] Although the reactions between phenols themselves and hypervalent iodine(III) reagent lead to resinous products,[5a,b, 6] many *para*-substituted phenols have been observed to react with various types of nucleophiles, giving the cross-conjugated cyclohexadienones.[7–14] In contrast to the oxidation of phenol derivatives, reactions of phenol ethers with hypervalent iodine reagents have been limited and have yielded mostly iodonium salts.[15] However, in the case of *para*-substituted phenol ethers with PIFA, we found that treatment with various types of nucleophiles in the presence of PIFA in polar but poorly nucleophilic solvents such as 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) resulted in substitution reactions.[16–18]

Afterwards, useful oxidative aryl–aryl coupling reactions with PIFA were developed[19, 20] and then applied to the synthesis of biologically active alkaloids and some heterocycles.[21–23] Regarding the oxidation of phenol derivatives, *para*-substituted phenols react intramolecularly with an electron-rich aromatic ring in the presence of PIFA in standard polar solvent to give the cross-conjugated spirodienones (Scheme 1, type I). In the type I reaction, the oxygen atom of the phenol reacts with the iodine center of the hypervalent iodine reagent. On the other hand, *para*-substituted phenol ethers react smoothly with another site on the biaryl compounds in the presence of PIFA in a fluorinated solvent such as TFE or HFIP or of two equivalents of $BF_3 \cdot Et_2O$ in CH_2Cl_2 (Scheme 1, type II). The type II reaction involves phenol ethers, in which the aromatic ring reacts with PIFA and generates a radical-cation intermediate by the single-electron transfer (SET) process.[16]

Currently, due to the worldwide concern over environmental safety, organic reactions that make use of the expensive fluorinated alcohols as solvents or of two equivalents of $BF_3 \cdot Et_2O$ in CH_2Cl_2 are not recommended. Very recently we found that heteropoly acids (HPAs)—which are readily available, inexpensive, easy to handle, noncorrosive, nonvolatile, and odorless solid acids[24]—effectively activate PIFA, and that the PIFA/HPA reagent system smoothly facilitates oxidative biaryl coupling of phenol ethers.[25] As an extension of this methodology, we have now found that the spirodienones, an unexpected product from the biaryl coupling reaction, can be selectively formed by the intramolecular coupling of *para*-methoxy-substituted phenol ether derivatives. The direct formation of spirodienones from

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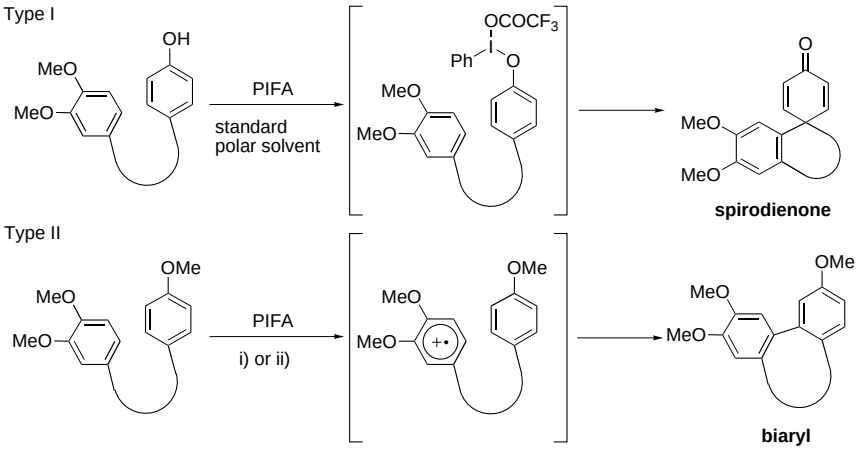
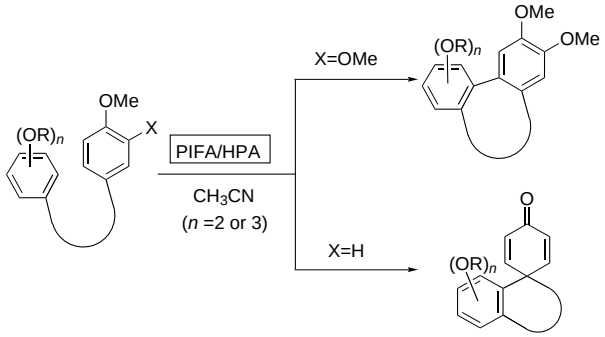


Scheme 1. Formation of spirodienones and biaryls by treatment with PIFA. i) $(CF_3)_2CHOH$ or CF_3CH_2OH, ii) $BF_3 \cdot Et_2O$ in CH_2Cl_2.

phenol ethers is interesting in terms of its mechanistic aspects and would be an attractive method, since phenol ethers are more stable and easier to handle than the phenols themselves under various reaction conditions. In this paper, we provide a full account of our studies on the oxidative intramolecular coupling of phenol ether derivatives (nonphenolic derivatives) to provide biaryls and spirodienones on treatment with the reagent system comprised of PIFA and HPAs (Scheme 2).



Scheme 2. Formation of spirodienones and biaryls by treatment with PIFA/HPA.

Results and Discussion

Generation of radical cations: Previously, we reported that PIFA reacted with *para*-substituted anisole in polar and poorly nucleophilic solvents such as TFE or HFIP to give a radical-cation intermediate, and that an activated hypervalent iodine reagent such as PIFA/$BF_3 \cdot Et_2O$ or PIFA/Me_3SiOTf in CH_2Cl_2 was similarly effective for the generation of radical-cation intermediates. As an extension of these studies, we have now found that treatment of *para-tert*-butylanisole with PIFA/HPA also readily generates stable radical-cation species, which were detected by ESR spectroscopy (Figure 1). The spectrum obtained was almost identical to that reported previously by us.[16] Additionally, UV spectroscopic examination of the reaction of dimethoxybenzene in the same reagent system also showed radical-cation species, represented by absorption bands between 400 and 600 nm (Figure 2).[16] When HPA was used in the absence of PIFA in these reactions, no radical-cation species could be observed in either the UV or the ESR spectra.

The methodology for generating a radical species by treatment with PIFA/HPA in CH_3CN is practical, safe, and economical. We were thus prompted to apply this efficient process to oxidative coupling reactions of various types of phenol ether derivatives **1**–**3**.

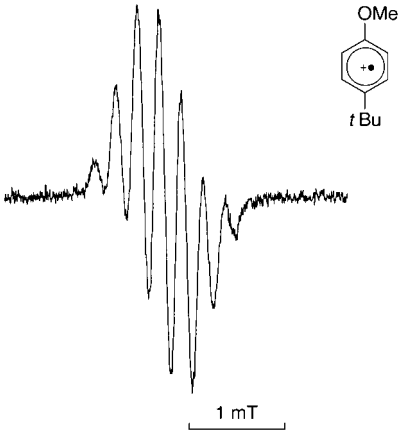


Figure 1. ESR spectrum of *para-tert*-butylanisole radical cation produced by oxidation with PIFA/HPA in CH_3CN.

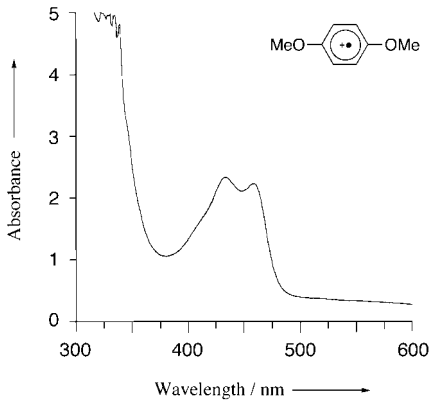


Figure 2. UV/visible absorption spectrum of *para*-dimethoxybenzene radical cation produced by oxidation with PIFA/HPA in CH_3CN.

Oxidative nonphenolic coupling reaction leading to biaryls: As a representative reaction, the conversion of the *N*-benzyl-*N*-phenethylamine derivative **1a** into the dibenzazocine derivative **4a** was initially studied, and the results are shown in Table 1. Four heteropoly acids (HPAs)—$H_3[PW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, and $H_4[SiMo_{12}O_{40}]$—were examined for their activation of PIFA in the biaryl coupling reaction, and all were found to give **4a** in excellent yields

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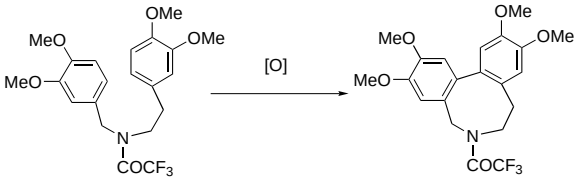
Table 1. Intramolecular oxidative coupling reaction of **1a**.



	Reagents and solvents	T [°C]	t [h]	Yield [%][a]
1	PIFA, $H_3[PW_{12}O_{40}]$,[b] CH_3CN	–20 to 0	0.66	97
2	PIFA, $H_3[PMo_{12}O_{40}]$,[b] CH_3CN	–20 to 0	0.66	94
3	PIFA, $H_4[SiW_{12}O_{40}]$,[b] CH_3CN	–20 to 0	0.66	94
4	PIFA, $H_4[SiMo_{12}O_{40}]$,[b] CH_3CN	–20 to 0	0.66	97
5	PIFA, CH_3CN	–20 to RT	24	4[d]
6	$H_3[PMo_{12}O_{40}]$,[c] CH_3CN	–20 to RT	24	nr[d]
7	PIFA, $BF_3 \cdot Et_2O$, CH_2Cl_2	–40	0.16	68
8	PIFA, HFIP	0	6	77
9	Tl_2O_3, $BF_3 \cdot Et_2O$, TFA, TFAA, CH_2Cl_2	0	2	56
10	RuO_2, $BF_3 \cdot Et_2O$, TFA, TFAA, CH_2Cl_2	0	8	45
11	VOF_3, TFA, TFAA, CH_2Cl_2	–20	4	89

[a] Yield of isolated **4a**. [b] 0.2 g mmol^{-1}. [c] 2 g mmol^{-1}. [d] nr = not recorded; starting material was also recovered.

under homogeneous conditions (entries 1–4). In the absence of HPA, on the other hand, **4a** was obtained only in 4% yield and the starting material was recovered even after a long reaction time (entry 5). The reaction did not proceed when $H_3[PMo_{12}O_{40}]$, which has the highest oxidation potential of the four heteropoly acids, was used in the absence of PIFA (entry 6).

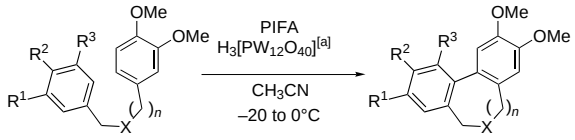
To determine the best coupling method, cyclization was also carried out under various conditions: a) PIFA in the presence of $BF_3 \cdot Et_2O$ in CH_2Cl_2,[20b] b) PIFA in HFIP,[20b] c) thallium(III) tris(trifluoroacetate) (TTFA) [prepared in situ by combination of thallium(III) oxide with trifluoroacetic acid and its anhydride],[4e] d) ruthenium(IV) tetrakis(trifluoroacetate) (RUTFA) [prepared in situ by combination of ruthenium(IV) oxide with trifluoroacetic acid and its anhydride],[4f] and e) vanadium(V) oxytrifluoride (entries 7–11).[4b] Although a considerable amount of the biaryl coupling product **4a** was obtained in some cases, no other conditions gave a yield higher than that provided by PIFA in the presence of HPA. These results clearly indicate that the combination of PIFA and HPA is the best condition for the oxidative biaryl coupling reaction.

One possible explanation for the remarkable control exerted by HPA is that HPA plays important roles not only in the activation of PIFA, but also in stabilizing the radical-cation intermediate, due to the greater softness of the heteropoly anion.[26] The better yield obtained with the one-electron oxidant VOF_3, which would smoothly give the radical-cation intermediate, than the two-electron oxidants such as thallium(III), ruthenium(IV), and hypervalent iodine(III), supports this explanation.

Similarly, treatment of other substrates such as the *N*-benzyl-*N*-phenethylamine derivative **1b**, the *N*,*N*-dibenzylamine derivatives **2a–c**, and the 1,3-diarylpropanes **3a–c** with PIFA and tungsto(VI) phosphoric acid ($H_3[PW_{12}O_{40}]$), which has the highest thermal and hydrolytic stability and the lowest oxidation potential among the four HPAs, gave the corresponding biaryl compounds **4b**, **5a–c**, and **6a–c**, respectively, in excellent yields (Table 2).

The best result obtained on treatment of the diaryl substrates **1–3** prompted us to extend our procedure to the silaketal derivatives **7a–c**. The resulting products could easily be converted into the 2,2′-substituted biaryl compounds that have hydroxy groups after hydrolysis by a known method.[20b] Treatment of the silaketal derivatives **7a–c** with PIFA activated by $H_3[PW_{12}O_{40}]$ afforded the corresponding coupling products **8a–c** in high yields (Table 3). It is noteworthy that the silaketal moiety in **8a–c** was not cleaved during the reaction.

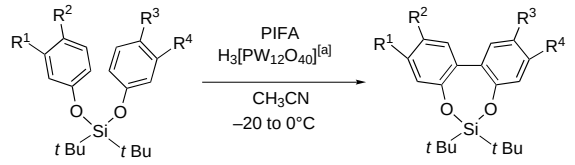
Table 2. Intramolecular oxidative coupling reaction of **1–3**.



	Substrate	R^1	R^2	R^3	X	n	Product	Yield [%][b]
1	**1a**	OMe	OMe	H	$NCOCF_3$	2	**4a**	97
2	**1b**	OMe	OMe	OMe	$NCOCF_3$	2	**4b**	93
3	**2a**	OMe	OMe	H	$NCOCF_3$	1	**5a**	95
4	**2b**	OMe	OMe	OMe	$NCOCF_3$	1	**5b**	92
5	**2c**	$-OCH_2O-$		H	$NCOCF_3$	1	**5c**	94
6	**3a**	OMe	OMe	H	CH_2	1	**6a**	99
7	**3b**	OMe	OMe	OMe	CH_2	1	**6b**	95
8	**3c**	$-OCH_2O-$		H	CH_2	1	**6c**	99

[a] 0.2 g mmol^{-1}. [b] Yield of isolated product.

Table 3. Intramolecular oxidative coupling reaction of **7**.

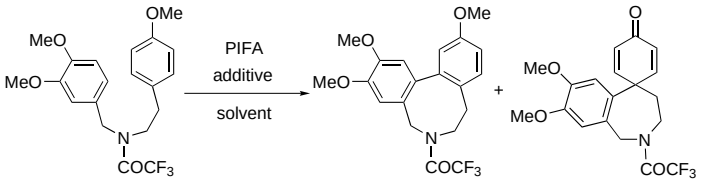


	Substrate	R^1	R^2	R^3	R^4	Product	Yield [%][b]
1	**7a**	OMe	OMe	OMe	OMe	**8a**	94
2	**7b**	OMe	OMe	$-OCH_2O-$		**8b**	86
3	**7c**	$-OCH_2O-$		$-OCH_2O-$		**8c**	93

[a] 0.2 g mmol^{-1}. [b] Yield of isolated product.

Oxidative nonphenolic coupling reaction leading to spirodienones: Treatment of phenol ethers with hypervalent iodine reagents is known to give the biaryl compounds, but no method has so far been reported to give spirodienones.[27] Thus, treatment of norbelladine derivative **1c** with the previously described PIFA/$BF_3 \cdot Et_2O$ reagent system in CH_2Cl_2 gave the biaryl **4c** (Table 4, entry 1).[20b] On the other hand, treatment of **1c** with the PIFA/HPA reagent system in CH_3CN afforded spirodienone **9** in 46% yield (entry 2). Exclusive formation of **9** in good yield occurred when the amount of HPA was increased (entries 3–6). The HPA used in these experiments is a hydrate; it therefore seemed likely that selective formation of spirodienone was due to the presence

Table 4. Intramolecular oxidative coupling reaction of **1c**.



1c **4c** **9**

	Additive	Solvent	t [h]	T [°C]	Yield [%][c] **4c**	**9**
1	$BF_3 \cdot Et_2O$	CH_2Cl_2	0.16	– 40	89	0
2	$H_3[PW_{12}O_{40}]$[a]	CH_3CN	0.66	– 20 to 0	36	46
3	$H_3[PMo_{12}O_{40}]$[b]	CH_3CN	0.66	– 40 to 0	0	68
4	$H_3[PMo_{12}O_{40}]$[b]	CH_3CN	0.66	– 40 to 0	0	72
5	$H_4[SiW_{12}O_{40}]$[b]	CH_3CN	0.66	– 40 to 0	0	74
6	$H_4[SiMo_{12}O_{40}]$[b]	CH_3CN	0.66	– 40 to 0	0	66
7	$BF_3 \cdot Et_2O$	CH_3CN[d]	0.5	– 40	7	44
8	(none)	CH_3CN[d]	12	– 40 to RT	9	7[f]
9	TfOH	CH_3CN[d]	0.5	– 40	25	42
10	TFA	CH_3CN[d]	12	– 40 to RT	14	19[f]
11	MK 10[c]	CH_3CN[d]	12	– 40 to RT	18	27[f]
12	Nafion-H	CH_3CN[d]	12	– 40 to RT	16	23[f]

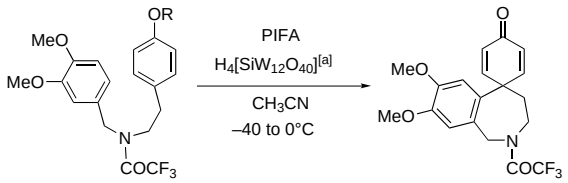
[a] 0.2 g mmol^{-1}. [b] 0.8 g mmol^{-1}. [c] MK 10: montmorillonite K10. [d] In wet (0.3%) CH_3CN. [e] Yield of isolated products. [f] Starting material was also isolated.

of water in the reaction medium. Indeed, selective formation of spirodienone **9** was observed when treatment of **1c** with PIFA/$BF_3 \cdot Et_2O$ was carried out in wet CH_3CN (entry 7). We also investigated several other acid additives such as TfOH, TFA, montmorillonite K10, and Nafion-H, but low yields and low selectivities were observed in most cases, and none of the conditions gave better results in terms both of the yield and of the selectivity than that given by PIFA/HPA (entries 9 – 12).

A plausible reaction mechanism leading to the biaryl **4c** or spirodienone **9** is envisaged as follows (Scheme 3). First, SET oxidation of the more electron-rich aromatic ring leads to intermediate [A]. Nucleophilic capture of [A] by the second aromatic ring gives intermediate [B]. The transformation of [B] into **4c** occurs by a dienone/phenol-type rearrangement (migration of the aryl group, path a), while **9** is formed through nucleophilic addition of H_2O, which is present in the vicinity of the electrophilic site as water of hydration of HPA (path b).

Next, the oxidative cyclization of substrates with a protected hydroxy group at the C-4 position was investigated (Table 5). Treatment of the substrates protected as ethers selectively gave the spirodienones **9** in moderate yields, while no biaryl product could be detected and the methoxy derivative showed the highest yield (entries 1 – 5). On the other hand, substrate **1h**, which contains an electron-withdrawing acetoxy group, did not produce the desired product (entry 6).

Table 5. Reactions of substrates with a protected hydroxy group at the C-4 position



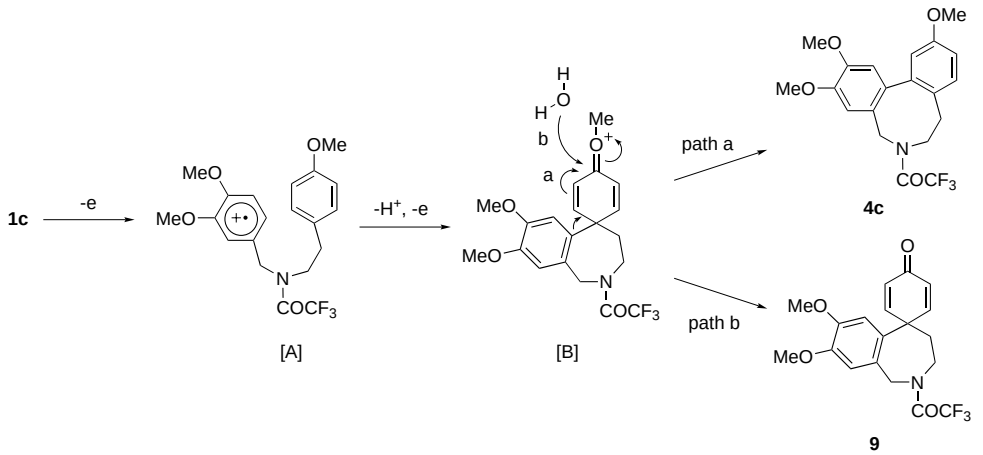
1 **9**

	Substrate	R	Yield [%][b]
1	**1c**	Me	74
2	**1d**	TBDMS	50
3	**1e**	TBDPS	32
4	**1f**	$PhCH_2$	53
5	**1g**	H	66
6	**1h**	Ac	complex mixture

[a] 0.8 g mmol^{-1}. [b] Yield of isolated **9**.

The generality of the direct formation of spirodienones from phenol ethers by treatment with PIFA/$H_4[SiW_{12}O_{40}]$ in CH_3CN was examined with the *N*,*N*-dibenzylamine derivatives **2d** and **2e** and the diarylpropanes **3d**–**f**, as shown in Table 6. In all cases, the desired spirodienones were selectively obtained in good yields.

Treatment of the highly substituted phenol ether **2a** under conditions leading to spirodienones provided biaryl **5a** as the major product, along with 11% of **10a** (Scheme 4). This implies that the intramolecular coupling reaction of the



Scheme 3. Possible reaction formation mechanisms for the biaryls and spirodienones.

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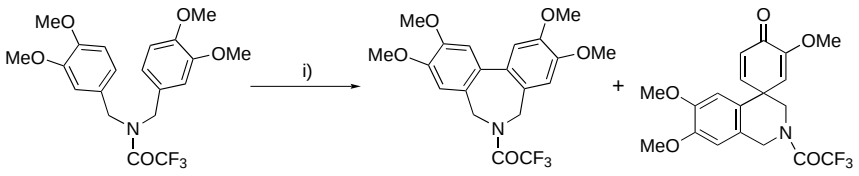
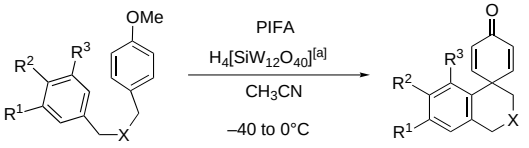


2a **5a** **10a**

84% 11%

Scheme 4. Intramolecular oxidative coupling reaction of **2a**. i) PIFA/$H_4[SiW_{12}O_{40}]$ (0.8g $mmol^{-1}$), CH_3CN, -40 to 0 °C, 40 min.

Table 6. Intramolecular oxidative coupling reaction of **2**–**3**.



2-3 **9-11**

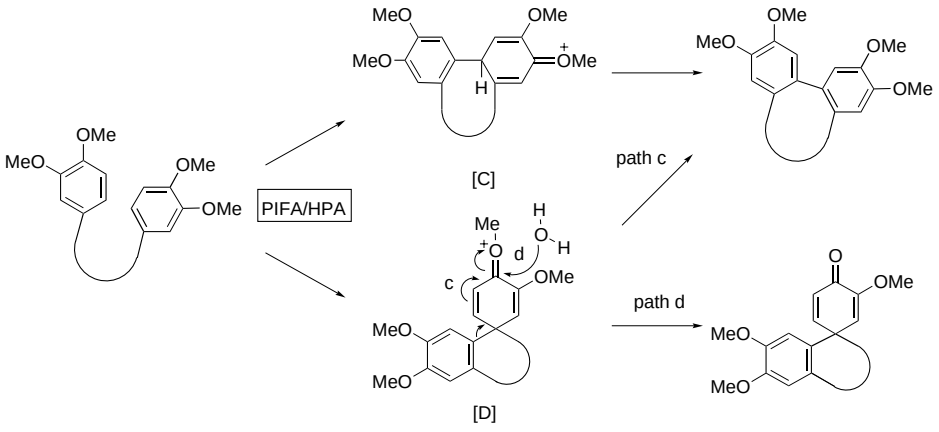
	Substrate	R^1	R^2	R^3	X	Product	Yield [%][b]
1	**2d**	OMe	OMe	H	$NCOCF_3$	**10d**	81
2	**2e**	$-OCH_2O-$		H	$NCOCF_3$	**10e**	72
3	**3d**	OMe	OMe	H	CH_2	**11d**	80
4	**3e**	OMe	OMe	OMe	CH_2	**11e**	75
5	**3f**	$-OCH_2O-$		H	CH_2	**11f**	71

[a] 0.8 g $mmol^{-1}$. [b] Yield of isolated product.

dimethoxyphenyl derivatives, such as the substrates shown in Table 2, proceeds via both intermediates [C] and [D] (Scheme 5).

Conclusion

A study of the oxidative intramolecular coupling reaction of phenol ether derivatives on treatment with a novel combination of PIFA and HPA gave the following results: 1) on treatment of highly substituted phenol ethers, the biaryl compounds were obtained in excellent yields; and 2) when one of the preferred coupling sites was substituted with a *para*-methoxy group, spirodienones were selectively formed in good yields. The simplicity of the reaction protocol may find wide application in the synthesis of many types of biaryls or spirodienones. Further studies along these lines and detailed investigations on the reaction mechanism are now in progress.



Scheme 5. A possible mechanism for the reaction of the highly substituted substrates.

Experimental Section

All melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively. All NMR spectra were recorded in $CDCl_3$ with either TMS or residual $CHCl_3$ as the internal standard. Most ^1H NMR and ^{13}C NMR spectra of the amido compounds exhibited the presence of two rotamers.[20b] Infrared (IR) absorption spectra (cm^{-1}) were recorded as KBr pellets. UV spectra were taken on a SHIMADZU 2200 UV-Vis spectrometer, and ESR spectra were taken on a JEOL JES-TE 200 spectrometer. Aluminium oxide 60 (basic, Merck) and silica gel 60 N (Kanto Chemical Company) were used for column chromatography. The organic layer was dried with anhydrous $MgSO_4$ or Na_2SO_4. PIFA is commercially available. $H_3[PW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ were a Kanto Chemical Company product. $H_4[SiW_{12}O_{40}]$, Montmorillonite K 10, and Nafion NR50 (beads) were purchased from Aldrich. $H_4[SiMo_{12}O_{40}]$ was purchased from Wako Pure Chemical Industries. Compounds **1a**–**g**, **2a**, **2b**, **3a**, **3b**, **3d**–**f**, and **7a**–**c** were prepared by known methods.[19, 20b, 28] Compounds **4a**–**c**, **5a**, **5b**, **6a**, **6b**, **8a**–**c**, and **9** have been previously reported by us and the spectral data were in full agreement with those reported.[19, 20b]

Measurement of electron spin resonance spectra: $H_3[PW_{12}O_{40}]$ (0.8 g $mmol^{-1}$) and PIFA (1.0 equiv) was added at -20 °C to a 0.01M solution of *para-tert*-butylanisole in CH_3CN. An aliquot from this mixture was then placed on a flat cell and inserted into the ESR cavity. The spectra were recorded at room temperature on a JEOL JES-TE 200 spectrometer. Instrument conditions were as follows: magnetic field, 336.2 ± 5.0 mT; modulation frequency, 100 kHz; modulation amplitude, 100; output power, 2.0 mW; time constant, 0.10 sec; sweep time, 2.0 min; amplitude, 400.

Measurement of UV/visible absorption spectra: $H_3[PW_{12}O_{40}]$ (5.0 mg) and PIFA (8.60 mg, 2.0×10^{-2} mmol) were added at -20 °C, under a nitrogen atmosphere, to a stirred solution of dimethoxybenzene (2.76 mg, 2.0×10^{-2} mmol) in CH_3CN (3.0 mL). UV-Vis absorption spectra of the reaction mixture were measured on a SHIMADZU 2200 UV-Vis spectrometer.

General procedure for the preparation of *N*,*N*-dibenzylamine derivatives (2): *N*,*N*-Dibenzylamine derivatives **2** were prepared from the corresponding benzaldehyde and benzylamine derivatives by the reported method.[19]

***N*-(3,4-Dimethoxybenzyl)-*N*-(3,4-methylenedioxybenzyl)-2,2,2-trifluoroacetamide (2c)**: Colorless solid; m.p. 89–90 °C; ^1H NMR: $\delta = 3.84$, 3.86, 3.88, 3.90 (s, 6H; OCH_3), 4.42, 4.45 (s, 4H; CH_2), 5.97, 6.00 (s, 2H; OCH_2O), 6.64–6.88 ppm (m, 6H; ArH); ^{13}C NMR: $\delta = 47.6$, 49.0, 55.8, 55.9, 101.2, 101.3, 107.7, 108.3, 108.5, 108.8, 110.3, 111.0, 111.2, 111.5, 116.7 ($J = 287$ Hz), 120.1, 121.1, 122.1, 122.4, 126.6, 127.5, 128.1, 128.8, 147.4, 147.6, 148.1, 148.4, 148.9, 149.0, 149.3, 149.5, 157.2 ppm ($J = 35$ Hz); IR (KBr): $\tilde{\nu} = 1686$ cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{18}F_3NO_5$ (397.4): C 57.43, H 4.57, N 3.53; found C 57.62, H 4.63, N 3.36.

***N*-(3,4-Dimethoxybenzyl)-*N*-(4-methoxybenzyl)-2,2,2-trifluoroacetamide (2d)**: Colorless oil; ^1H NMR: $\delta = 3.81$, 3.83, 3.84, 3.86, 3.88, 3.91 (s, 9H; OCH_3), 4.45, 4.46 (s, 4H; CH_2), 6.66–6.93 (m, 5H; ArH), 7.11, 7.12 ppm (d, $J = 8.7$ Hz, 2H; ArH); ^{13}C NMR: $\delta = 47.3$, 47.6, 48.7, 49.0, 55.2, 55.3, 55.8, 110.3, 111.0, 111.2, 111.5, 114.1, 114.3, 116.7 ($J = 287$ Hz), 120.1, 121.1, 126.3, 126.7, 127.1, 127.5, 128.8, 129.9, 148.8, 149.0, 149.2, 149.4, 157.2 ($J = 35$ Hz), 159.4, 159.5 ppm; IR (KBr): $\tilde{\nu} = 1690$ cm^{-1}; elemental anal-

ysis calcd (%) for $C_{19}H_{20}F_3NO_4$ (383.4): C 59.53, H 5.26, N 3.65; found C 59.42, H 5.23, N 3.51.

***N*-(4-Methoxybenzyl)-*N*-(3,4-methylenedioxybenzyl)-2,2,2-trifluoroacetamide (2e)**: Colorless solid; m.p. 74 °C; ^{1}H NMR: $\delta = 3.80$, 3.82 (s, 3H; OCH_3), 4.40, 4.45 (s, 4H; CH_2), 5.95, 5.98 (s, 2H; OCH_2O), 6.60 – 6.93 (m, 5H; ArH), 7.11 ppm (d, $J = 8.4$ Hz, 2H; ArH); ^{13}C NMR: $\delta = 47.3$, 47.6, 48.7, 49.0, 55.2, 55.3, 101.2, 101.4, 107.8, 108.4, 108.5, 108.9, 114.3, 114.4, 116.8 ($J = 287$ Hz), 121.2, 122.1, 126.3, 127.2, 128.2, 128.9, 129.9, 147.5, 147.7, 148.2, 148.5, 157.2 ($J = 35$ Hz), 157.3 ($J = 35$ Hz), 159.5, 159.6 ppm; IR (KBr): $\tilde{\nu} = 1692$ cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{16}F_3NO_4$ (367.3): C 58.86, H 4.39, N 3.81; found C 58.92, H 4.41, N 3.83.

1-(3,4-Dimethoxyphenyl)-3-(3,4-methylenedioxyphenyl)propane (3c): 1,3-Diarylpropane **3c** was obtained as a colorless solid by the reported method,[28] from piperonal and 3′,4′-dimethoxyacetophenone. M.p. 34 °C; ^{1}H NMR: $\delta = 1.89$ (qui, $J = 7.5$ Hz, 2H; CH_2), 2.57 (t, $J = 7.5$ Hz, 2H; CH_2), 2.58 (t, $J = 7.5$ Hz, 2H; CH_2), 3.85 (s, 3H; OCH_3), 3.87 (s, 3H; OCH_3), 5.91 (s, 2H; OCH_2O), 6.61 – 6.80 ppm (m, 6H; ArH); ^{13}C NMR: $\delta = 33.4$, 34.9, 35.1, 55.8, 55.9, 100.7, 108.1, 108.9, 111.2, 111.8, 120.2, 121.1, 134.9, 136.2, 145.5, 147.1, 147.5, 148.8 ppm; elemental analysis calcd (%) for $C_{18}H_{20}O_4$ (300.4): C 71.98, H 6.71; found C 71.91, H 6.74.

General coupling procedure leading to biaryls by treatment with PIFA/HPA: HPA (20 mg) and PIFA (43.0 mg, 0.10 mmol) were added at − 20 °C to a stirred solution of open-chain precursor **1** – **3** or **7** (0.10 mmol) in MeCN (4.0 mL). Stirring was continued for 40 min (or as required according to GC-MS) at − 20 to 0 °C. The solution was then filtered through a short column of basic alumina and concentrated in vacuo. Purification of the residue by flash column chromatography on silica gel gave the corresponding biaryl coupling product **4** – **6** or **8**.

Coupling procedures with PIFA/$BF_3 \cdot Et_2O$,[20b] PIFA/HFIP,[20b] thallium(III),[4e] ruthenium(IV),[4f] and vanadium(V)[4b] were performed according to the literature procedures.

6-(Trifluoroacetyl)-2,3-dimethoxy-9.10-methylenedioxy-6,7-dihydro-5*H*-dibenz[*c*,*e*]azepine (5c): Colorless solid; m.p. 162 – 163 °C; ^{1}H NMR: $\delta =$ 3.89, 3.91, 3.94, 3.96 (s, 6H; OCH_3), 4.24, 4.29 (br, 4H; CH_2), 6.00, 6.05 (s, 2H; OCH_2O), 6.83, 6.84, 6.91, 6.92, 6.95, 6.97, 6.99, 7.00 ppm (s, 4H; ArH); ^{13}C NMR: $\delta = 47.7$, 47.8, 48.0, 48.1, 56.1, 101.6, 108.1, 109.3, 110.6, 110.9, 111.0, 112.0, 113.3, 116.7 ($J = 288$ Hz), 124.3, 124.5, 125.6, 125.8, 133.0, 133.1, 134.6, 134.7, 147.4, 148.5, 148.8, 149.5, 149.7, 154.7 ppm ($J = 35$ Hz); IR (KBr): $\tilde{\nu} = 1686$ cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{16}F_3NO_5$ (395.3): C 57.72, H 4.08, N 3.54; found C 57.38, H 4.23, N 3.37.

2,3-Dimethoxy-9.10-methylenedioxy-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene (6c): Colorless solid; m.p. 116 – 117 °C; ^{1}H NMR: $\delta = 2.10 - 1.15$ (m, 2H; CH_2), 2.34 – 2.45 (m, 4H; CH_2), 3.90 (s, 3H; OCH_3), 3.92 (s, 3H; OCH_3), 5.96 (s, 2H; OCH_2O), 6.73 (s, 1H; ArH), 6.76 (s, 1H; ArH), 6.85 (s, 1H; ArH), 6.87 ppm (s, 1H; ArH); ^{13}C NMR: $\delta = 31.0$, 31.4, 33.9, 56.0, 56.1, 100.8, 108.5, 108.9, 111.7, 111.9, 132.0, 132.9, 133.2, 134.2, 146.2, 146.3, 147.5, 147.9 ppm; elemental analysis calcd (%) for $C_{18}H_{18}O_4$ (298.3): C 72.47, H 6.08; found C 72.52, H 6.11.

***N*-(4-Acetoxyphenethyl)-*N*-(3,4-dimethoxybenzyl)trifluoroacetamide (1h)**: Acetic anhydride (1.5 mL) was added dropwise at 0 °C to a solution of **1g** (381 mg, 1.0 mmol) in pyridine (3.0 mL). The solution was stirred at RT for 6 h, quenched by the addition of ice chips followed by cold water, and extracted three times with AcOEt. The organic layer was washed successively with 10% HCl, water, and brine, and concentrated in vacuo. The residue was purified by chromatography on silica gel to give **1h** (388 mg, 91%) as a colorless oil. ^{1}H NMR: $\delta = 2.29$ (s, 3H; CH_3), 279 (t, $J = 7.5$ Hz, 1H; CH_2), 2.87 (t, $J = 7.5$ Hz, 1H; CH_2), 3.46 – 3.54 (m, 2H; CH_2), 3.85, 3.86, 3.88 (s, 6H; OCH_3), 4.37 (s, 1H; CH_2), 4.61 (s, 1H; CH_2), 6.63 – 6.86 (m, 3H; ArH), 7.00, 7.02 (d, $J = 8.1$ Hz, 2H; ArH), 7.13 ppm (d, $J = 8.1$ Hz, 2H; ArH); ^{13}C NMR: $\delta = 21.1$, 32.3, 34.6, 47.9, 48.0, 49.5, 51.3, 55.9, 110.4, 111.1, 111.2, 116.6 ($J = 287$ Hz), 120.1, 120.8, 121.8, 122.0, 126.9, 127.8, 129.6 129.7, 134.9, 145.8, 149.1, 149.2, 149.5, 149.6, 156.8 ($J = 35$ Hz), 169.5 ppm; IR (KBr): $\tilde{\nu} = 1762$, 1689 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{22}F_3NO_5$ (425.4): C 59.29, H 5.21, N 3.29; found C 58.97, H 5.22, N 3.35.

General coupling procedure leading to spirodienones by treatment with PIFA/HPA: HPA (80 mg) and PIFA (43.0 mg, 0.10 mmol) were added at − 20 °C to a stirred solution of open-chain precursor **1** – **3** (0.10 mmol) in MeCN (4.0 mL). Stirring was continued for 40 min (or as required according to GC-MS) at − 40 to 0 °C. The solution was then filtered through a short column of basic alumina and concentrated in vacuo. Purification of the residue by flash column chromatography on silica gel gave the corresponding biaryl coupling products **9** – **11**.

2-(Trifluoroacetyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline-4-spiro-1′-(3′-methoxy)cyclohexa-2′,5′-dien-4′-one (10a): Colorless solid; m.p. 214 – 215 °C; ^{1}H NMR: $\delta = 3.66$ (s, 3H: OCH_3), 3.75 (s, 3H: OCH_3), 3.79 – 3.98 (m, 2H; CH_2), 3.88, 3.89 (s, 3H; OCH_3), 4.80 – 4.97 (m, 2H; CH_2), 5.73, 5.74 (d, $J = 20.7$ Hz, 1H; CH), 6.44, 6.45 (s, 1H; ArH), 6.45 (d, $J = 18.6$ Hz, 1H; CH), 6.61, 6.67 (s, 1H; ArH), 6.73, 6.79, 6.84, 6.86 ppm (d, $J = 20.7$, 18.6 Hz, 1H; CH); ^{13}C NMR: $\delta = 45.1$, 45.2, 45.5, 49.9, 55.0, 56.1, 65.8, 108.8, 109.2, 109.3, 109.8, 116.7 ($J = 288$ Hz), 117.1, 117.6, 122.2, 122.4, 124.4, 125.0, 128.6, 128.9, 148.8, 149.0, 149.5, 149.9, 150.3, 151.1, 151.4, 156.7 (m), 180.5 ppm; IR (KBr): $\tilde{\nu} = 1697$, 1672 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{18}F_3NO_5$ (397.4): C 57.43, H 4.57, N 3.53; found C 57.39, H 4.80, N 3.43.

2-(Trifluoroacetyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline-4-spiro-1′-cyclohexa-2′,5′-dien-4′-one (10d): Colorless solid; m.p. 204 – 205 °C; ^{1}H NMR: $\delta = 3.76$ (s, 3H; OCH_3), 3.86 (s, 1H; CH_2), 3.88, 3.89 (s, 3H; OCH_3), 3.97 (s, 1H; CH_2), 4.85 (s, 1H; CH_2), 4.88 (s, 1H; CH_2), 6.40 – 6.44 (m, 3H; ArH, CH), 6.64, 6.68 (s, 1H; ArH), 6.76, 6.83 ppm (d, $J = 9.9$ Hz, 2H; CH); ^{13}C NMR: $\delta = 44.5$, 44.6, 45.4, 47.2, 48.7, 51.4, 56.1, 109.0, 109.4, 109.5, 110.0, 116.7 (m), 122.5, 122.6, 123.2, 123.7, 129.4, 148.8, 149.1, 149.5, 149.6, 149.7, 150.0, 156.3 (m), 185.2, 185.3 ppm; IR (KBr): $\tilde{\nu} = 1697$, 1670 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{16}F_3NO_4$ (367.3): C 58.86, H 4.39, N 3.81; found C 58.68, H 4.47, N 3.52.

2-(Trifluoroacetyl)-6,7-(methylenedioxy)-1,2,3,4-tetrahydroisoquinoline-4-spiro-1′-cyclohexa-2′,5′-dien-4′-one (10e): Colorless solid; m.p. 200 – 201 °C; ^{1}H NMR: $\delta = 3.85$ (s, 1H; CH_2), 3.95 (s, 1H; CH_2), 4.81 (s, 1H; CH_2), 4.84 (s, 1H; CH_2), 5.96 (s, 2H; OCH_2O), 6.38, 6.41 (d, $J = 9.9$ Hz, 2H; CH), 6.47 (s, 1H; ArH), 6.63, 6.67 (s, 1H; ArH), 6.75, 6.83 ppm (d, $J =$ 9.9 Hz, 2H; CH); ^{13}C NMR: $\delta = 44.6$, 44.7, 45.7, 47.5, 48.5, 50.4, 101.7, 101.8, 106.3, 106.8, 107.1, 107.6, 116.2 ($J = 288$ Hz), 123.7, 123.8, 124.5, 125.1, 129.4, 147.6, 147.9, 148.3, 148.4, 149.2, 149.7, 156.2 (m), 185.0 ppm; IR (KBr): $\tilde{\nu} =$ 1697, 1670 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{12}F_3NO_4$ (351.3): C 58.13, H 3.44, N 3.99; found C 58.39, H 3.72, N 3.91.

6,7-Dimethoxy-1,2,3,4-tetrahydronaphthalene-4-spiro-1′-cyclohexa-2′,5′-dien-4′-one (11d):[28] Colorless solid; m.p. 89 – 90 °C (lit. 95 – 96 °C[28]); ^{1}H NMR: $\delta = 1.94 - 1.96$ (m, 4H; CH_2), 2.82 – 2.85 (m, 2H; CH_2), 3.72 (s, 3H; OCH_3), 3.86 (s, 3H; OCH_3), 6.28 (d, $J = 9.9$ Hz, 2H; CH), 6.37 (s, 1H; ArH), 6.62 (s, 1H; ArH), 7.01 ppm (d, $J = 9.9$ Hz, 2H; CH); ^{13}C NMR: $\delta =$ 19.4, 29.3, 34.2, 44.5, 55.8, 55.9, 110.9, 112.4, 124.9, 126.8, 128.9, 147.6, 148.5, 155.8, 186.3 ppm; IR (KBr): $\tilde{\nu} = 1662$ cm^{-1}.

5,6,7-Trimethoxy-1,2,3,4-tetrahydronaphthalene-4-spiro-1′-cyclohexa-2′,5′-dien-4′-one (11e):[28] Colorless solid; m.p. 155 – 156 °C (lit.[28] 155 – 157 °C); ^{1}H NMR: $\delta = 1.84 - 1.88$ (m, 4H; CH_2), 2.82 – 2.85 (m, 2H; CH_2), 3.66 (s, 3H; CH_3) 3.80 (s, 3H; CH_3), 3.87 (s, 3H; CH_3), 6.29 (d, $J = 9.6$ Hz, 2H; CH), 6.47 (s, 1H; ArH), 7.00 ppm (d, $J = 9.6$ Hz, 2H; CH); ^{13}C NMR: $\delta =$ 19.9, 30.4, 37.3, 43.1, 55.8, 60.6, 60.9, 107.9, 121.0, 126.5, 132.8, 140.3, 152.9, 153.3, 156.3, 186.4 ppm; IR (KBr): $\tilde{\nu} = 1663$ cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}O_4$ (300.4): C 71.98, H 6.71; found C 71.71, H 6.88.

6,7-Methylenedioxy-1,2,3,4-tetrahydronaphthalene-4-spiro-1′-cyclohexa-2′,5′-dien-4′-one (11f):[28] Colorless solid; m.p. 166 – 168 °C (lit. 169 – 171 °C[28]); ^{1}H NMR: $\delta = 1.91 - 1.94$ (m, 4H; CH_2), 2.79 – 2.82 (m, 2H; CH_2), 5.88 (s, 2H; OCH_2O), 6.25 (d, $J = 9.9$ Hz, 2H; CH), 6.40 (s, 1H; ArH), 6.60 (s, 1H; ArH), 6.97 ppm (d, $J = 9.9$ Hz, 2H; CH); ^{13}C NMR: $\delta =$ 19.4, 29.7, 34.0, 44.7, 101.0, 108.1, 109.5, 126.0, 126.9, 130.1, 146.3, 147.1, 155.5, 186.1 ppm; IR (KBr): $\tilde{\nu} = 1662$ cm^{-1}.

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