# Hypervalent Iodine-Induced Nucleophilic Substitution of *para*-Substituted Phenol Ethers. Generation of Cation Radicals as Reactive Intermediates†

**Yasuyuki Kita,*,‡ Hirofumi Tohma,‡ Kenji Hatanaka,‡ Takeshi Takada,‡ Shigekazu Fujita,‡ Shizue Mitoh,‡ Hiromu Sakurai,§ and Shigenori Oka§**

*Contribution from the Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamada-oka, Suita, Osaka 565, Japan, and Kyoto Pharmaceutical University, 5 Nakauchicho Misasagi, Yamashina-ku, Kyoto 607, Japan*

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**Abstract:** A novel hypervalent iodine induced nucleophilic substitution of *para*-substituted phenol ethers in the presence of a variety of nucleophiles is described. UV and ESR spectroscopic studies indicate that this reaction proceeds via cation radicals, [ArH$^{\bullet+}$], as reactive intermediates generated by single-electron transfer (SET) from a charge-transfer (CT) complex of phenol ethers with phenyliodine(III) bis(trifluoroacetate) (PIFA). This is the first case that involves a radical intermediate on hypervalent iodine oxidations of aromatic compounds.

## Introduction

There is an increasing interest in the hypervalent iodine oxidation of phenols and related compounds.[1] Although the reaction of phenols themselves with phenyliodine(III) diacetate (PIDA) or phenyliodine(III) bis(trifluoroacetate) (PIFA) frequently leads to resinous products,[2] phenols bearing electron-withdrawing *o*-nitro and *o,p*-dinitro groups react with PIDA to give the corresponding iodonium salts.[3] Hypervalent iodine reagents have also been used for the oxidative cyclization of binaphthols to spiro compounds,[4] for intramolecular oxidative aryl-aryl coupling,[5] and for carbon-carbon bond cleavage of $NH_2$-tyrosine dipeptides.[6] As part of our continuing studies concerning hypervalent iodine chemistry,[7] we have reported the oxidation of *para*-substituted phenol derivatives leading to *p*-benzoquinone monoacetals,[8] spiro compounds,[9] *p*-benzoquinones,[10] and azacarbocyclic spirodienones.[11,12] Since our reports about the hypervalent iodine oxidation of phenol derivatives to *p*-quinone derivatives, similar types of reactions[13] and their applications to the synthesis of biologically active compounds have been extensively reported.[14] In most of the cases, the reactions of phenol derivatives with PIFA first proceed via the reaction of the phenolic OH group with an iodine center. On the other hand, it is well-known that diaryliodonium salts[15] are obtained by the reaction of unsubstituted or *meta*-substituted phenol ethers with hypervalent iodine species; we have also reported a novel intramolecular cyclization reaction via diaryliodonium salts.[16]

In the case of *para*-substituted phenol ethers with PIFA, however, diaryliodonium salts were not obtained, but nucleophilic substitution reaction occurred. As an extension of this novel oxidative azidation[17] of aromatic compounds with hypervalent iodine reagent, PIFA, and trimethylsilyl azide (TMSA), we now report the generality of the hypervalent iodine-induced nucleophilic substitution of *para*-substituted phenol ethers with various

* Author to whom correspondence should be directed.

†Dedicated to Professor Yasumitsu Tamura on the occasion of his 70th birthday.

‡ Osaka University.

§ Kyoto Pharmaceutical University.

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**Scheme 1**

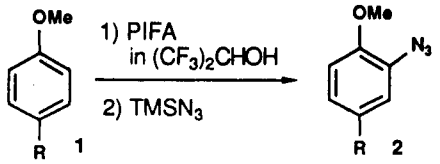
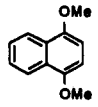
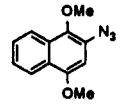
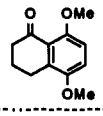
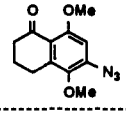
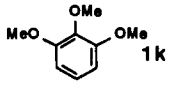
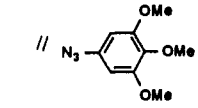



**Table 1**

| runs | substrates | Nu | products | yields (%)[a] |
|---|---|---|---|---|
| 1 | R=$OCH_3$(**1a**) | TMSA | **2a** | 68 |
| 2 | R=$CH_3$ (**1b**) | // | **2b** | 45 |
| 3 | R=$CH(CH_3)_2$(**1c**) | // | **2c** | 49(53) |
| 4 | R=Br (**1d**) | // | **2d** | 39(58) |
| 5 | R=Cl (**1e**) | // | **2e** | 45(54) |
| 6 | R=$C(CH_3)_3$(**1f**) | // | **2f** | 31(53) |
| 7 | R=$CH_2CO_2CH_3$(**1g**) | // | **2g** | 41(50) |
| 8 | R=$CH_2CN$(**1h**) | // | **2h** | 47(57) |
| 9 |  **1i** | // |  **2i** | 85 |
| 10 |  **1j** | // |  **2j** | 48(70) |
| 11 |  **1k** | // |  **2k** | 82 |

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

nucleophiles ($N_3^-$, $OAc^-$, and β-dicarbonyl compounds) and discuss the mechanisms.

## Results and Discussion

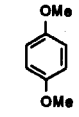
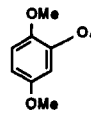
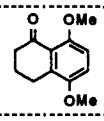
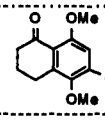
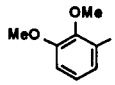
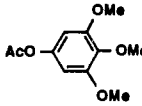
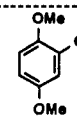
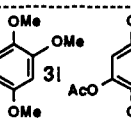
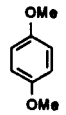
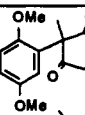
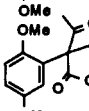
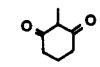
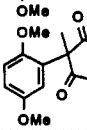
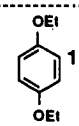
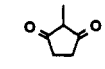
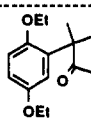
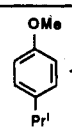
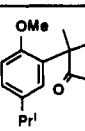
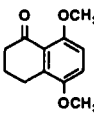
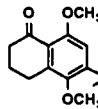
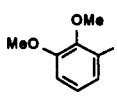
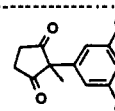
**1. Oxidative Nucleophilic Substitution.** The oxidative nucleophilic substitution reaction of *para*-substituted phenol ethers (**1**) with PIFA proceeded clearly in poorly nucleophilic polar solvents such as 2,2,2-trifluoroethanol ($CF_3CH_2OH$) and 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2CHOH$), as we have previously described in the azidation of **1** with PIFA[17] (Scheme 1).

The typical experimental procedure for the reaction of 1,4-dimethoxybenzene (**1a**) is as follows. To a solution of **1a** in anhydrous $(CF_3)_2CHOH$ was added 1.2 equiv of PIFA at room temperature under nitrogen. After a few minutes, 5.0 equiv of TMSA was added to the mixture. The mixture was stirred for 15 min under the same conditions to give 2-azido-1,4-dimethoxybenzene (**2a**) in 68% yield. Similarly, the naphthalene **1i**, the tetralone **1j**, and 1,2,3-trimethoxybenzene (**1k**) as well as the aromatic compounds **1b–h** bearing electron-donating groups or halogens at the *para*-positions reacted smoothly with PIFA to give the corresponding azide compounds **2b–k** in significant yields. The results are listed in Table 1.

Other nucleophiles ($OAc^-$, and β-dicarbonyl compounds) could be introduced in moderate yields under the same conditions of azidation (Table 2). Thus, this reaction is useful for the introduction of various types of oxygen, nitrogen, and carbon nucleophiles to *para*-substituted phenol ethers.

**2. Effect of Solvents.** The effect of solvents was examined by the reaction of **1a**, PIFA, and TMSA. The yields of **2a** strongly depend upon the solvents used. Polar and low-nucleophilic protic solvent such as $(CF_3)_2CHOH$ are the best. Other polar solvents such as $CF_3CH_2OH$ and $CH_3CN$ gave **2a**, but in unsatisfactory yields. In trifluoroacetic acid, a small amount of aromatic hydroxy compound was obtained instead of **2a**. Furthermore, **2a** could not be obtained at all in $CH_2Cl_2$, 1,4-dioxane, dimethylformamide, tetrahydrofuran, or methanol (Table 3).

**Table 2**

| runs | substrates | Nu | products | yields (%)[a] |
|---|---|---|---|---|
| 1<br>2 |  **1a** | TMSOAc |  **3a** | 43(55) |
| 3 |  **1j** | // |  **3j** | 49(54) |
| 4 |  **1k** | // |  **3k** | 43 |
| 5 |  **1l** | // |  **3l** **3m** | 67 (3l:3m=34:33) |
| 6 |  **1a** |  |  **4a** | 66 |
| 7 | |  |  **4b** | 39 |
| 8 | |  |  **4c** | 45 |
| 9 |  **1m** |  |  **4d** | 56 (76) |
| 10 |  **1c** | // |  **4e** | 39 (52) |
| 11 |  **1j** | // |  **4f** | 62 (80) |
| 12 |  **1k** | // |  **4g** | 67 (83) |

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

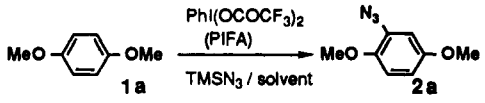
**3. Reaction Mechanism.** The combination of hypervalent iodine reagent and TMSA has been known to generate hypervalent azidoiodine(III) species (**5**)[18] and has been used for the oxidative azidation of olefins into α-azido ketones[19] and vicinal diazides, of β-dicarbonyl compounds into α-azido β-dicarbonyl compounds,[20]

(18) (a) Zbiral, E.; Nestler, G. *Tetrahedron* **1970**, *26*, 2945. (b) Arimoto, M.; Yamaguchi, H.; Fujita, E.; Ochiai, M.; Nagao, Y. *Tetrahedron Lett.* **1987**, *28*, 6289. (c) Fontana, F.; Minisci, F.; Yan, Y. M.; Zhao, L. *Tetrahedron Lett.* **1993**, *34*, 2517.

(19) Moriarty, R. M.; Khosrowshahi, J. S. *Tetrahedron Lett.* **1986**, *27*, 2809; *Synth. Commun.* **1987**, *17*, 89.

(20) Moriarty, R. M.; Vaid, R. K.; Ravikumar, V. T.; Vaid, B. K.; Hopkins, T. E. *Tetrahedron* **1988**, *44*, 1603.

Table 3




| runs | solvents | yield (%) |
|---|---|---|
| 1 | $(CF_3)_2CHOH$ | 68 |
| 2 | $CF_3CH_2OH$ | 60 |
| 3 | $CH_3CN$ | 7 |
| 4 | $CF_3CO_2H$ | *a* |
| 5 | $CH_2Cl_2$, THF, DMF, 1,4-dioxane, etc. | no reaction |

[a] 2,5-Dimethoxyphenol was obtained as a main product.

of 2-((trimethylsilyl)oxy)furan into 5-azido-2(5*H*)-furanone,[21] and of triisopropylsilyl enol ether into β-azido triisopropylsilyl enol ether.[22] These hypervalent azidoiodine(III) species, however, may not be active enough for the oxidative azidation of aromatic carbons, and this is the first case of a radical intermediate for hypervalent iodine oxidations of aromatic compounds. In fact, treatment of **1a** with **5** generated from PIFA and TMSA did not give any aromatic azido compounds. Therefore, we first considered one possible mechanism involving the diaryliodonium salt **A**. It is well-known that diaryliodonium salts are obtained by the reaction of unsubstituted or *meta*-substituted phenol ethers with hypervalent iodine species, but they are stable and unreactive with azido anions. The route involving the diaryliodonium salt **A** is excluded for the following reason. Even if nucleophilic substitution occurs due to the azide anion, the more electron-deficient aromatic carbon of the iodonium salt is thought to selectively react with nucleophiles and this reaction should give azido benzene instead of **2a**. Next, we assumed that the π-complex **B** of **1** with PIFA was formed at the first step, as proposed during the reaction of **1** with the active hypervalent iodine reagent perfluoroalkylated iodonium trifluoromethanesulfonate,[23] and then transformed to a σ-complex **C** with reductive elimination of iodobenzene. According to the extensive UV and ESR spectroscopic studies of this reaction, however, we now propose the plausible reaction mechanism shown in Scheme 2.

That is, the reaction proceeds via cation radicals [ArH$^{\bullet+}$] (**E**), as reactive intermediates generated by single-electron transfer (SET) from the charge-transfer (CT) complex of phenol ethers with PIFA. This is the first case in which a radical intermediate was detected during hypervalent iodine oxidations.

**4. UV–Vis Spectra of Reaction Intermediates.** In order to identify the reactive intermediates in the nucleophilic substitutions of *para*-substituted phenol ethers using PIFA, we examined the UV–vis spectra at room temperature using $(CF_3)_2CHOH$ as the solvent. An intense absorption band was observed in the visible region between 400 and 500 nm during the course of the reaction of *p*-dimethoxybenzene (**1a**) with PIFA (Figure 1).

The absorption band appeared (a fluorescent yellow-green color) immediately upon mixing **1a** and PIFA and disappeared upon completion of dropwise addition of TMSA. The intensity of the absorption band increased as the reaction proceeded and finally diminished after completion of the reaction. The reactive intermediates are very stable in the absence of nucleophiles for a few hours in $(CF_3)_2CHOH$ ($9.7 \times 10^{-3}$ M). In $CF_3CH_2OH$, the absorption band in about the same region as that in $(CF_3)_2CHOH$ was observed during the reaction process, but the life span of the reactive intermediates was about three times as short as that in $(CF_3)_2CHOH$ using the same concentrations. UV–vis spectra of the reaction of **1a** and PIFA were measured in other solvents ($CH_3CN$ and $CH_2Cl_2$). Figure 1 shows that the yields and intensity of absorption are directly related. Furthermore, characteristic absorption bands were observed in the course of the reactions of **1b,d,f,j** with PIFA in $(CF_3)_2CHOH$ (Figure 2). In these cases, the characteristic absorption bands were only slightly observed or not at all in $CF_3CH_2OH$. These electronic absorptions can be assigned to arene cation radicals.

Of course, there is no absorption band between 400 and 600 nm in the cases of PIFA, the hypervalent azide iodine(III) reagent, and the diaryliodonium salt alone. Therefore, the observed nucleophilic substitution with PIFA can be rationalized by assuming that the novel cation radicals [ArH$^{\bullet+}$] corresponding to the above-mentioned absorption bands are energized to make SET feasible, as reported by Kochi *et al.*[24] Their structural identity has already been confirmed by UV spectra[25] as well as by electron spin resonance (ESR) spectroscopy.[26]

**5. ESR Spectra of Reaction Intermediates.** During the course of the reaction of **1a** and PIFA in $(CF_3)_2CHOH$ ($9.7 \times 10^{-3}$ M **1a** and PIFA) at room temperature, fairly stable radical species[27] were detected in the ESR spectrum (Figure 3a).

The intensity of the spectrum ($g = 2.0036$; reference: Mn(II) doped in MgO) increased with time and then disappeared upon completion of the reaction through a steady state. Of course, radical species were not detected in the cases of $(CF_3)_2CHOH$, PIFA, and **1a** alone. The radical cation generated from **1a** by chemical or electrolytic oxidation was identical to that observed during the PIFA reaction of **1a**.

Hyperfine coupling constants (*A*, 0.346 mT; *B*, 0.333 mT) for the spectrum of Figure 3c were almost identical to those (*A*, 0.345 mT; *B*, 0.337 mT) reported previously.[27] Thus, Figure 3 supported the structure of radical intermediates of **1a** using the hyperfine coupling constant. Next, we examined ESR studies of the presumably more stable cation radical of **1f** and PIFA to explain the regioselectivity (*ortho* orientation of the methoxy group) of this reaction (Figure 4).

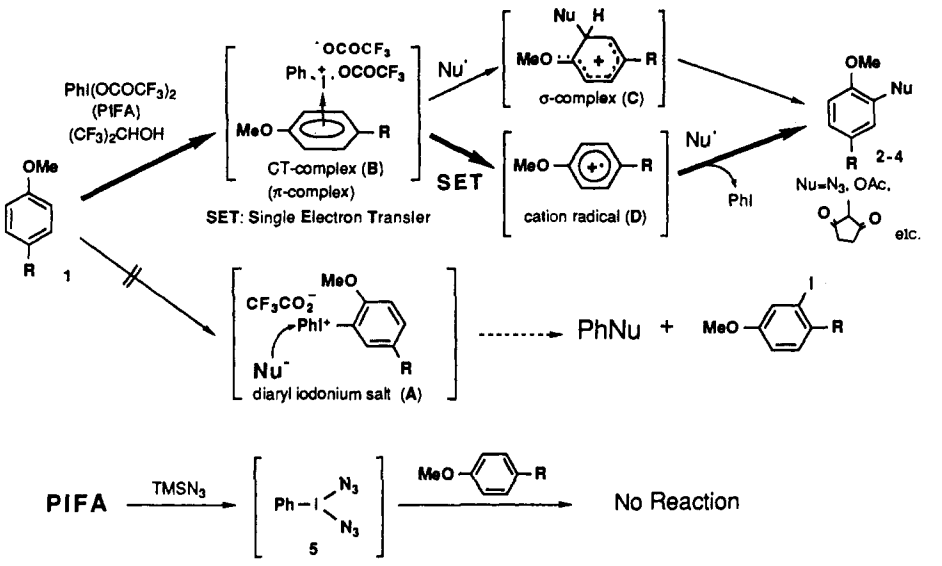
In fact, in $(CF_3)_2CHOH$ ($1.34 \times 10^{-2}$ M), the cation radical [ArH$^{\bullet+}$] (Ar = *p*-*tert*-butylanisole) is very stable at room temperature probably because of its bulky *tert*-butyl substitution. The hyperfine coupling constants for the cation radical [ArH$^{\bullet+}$] were found to be $a$(H2,6) = 0.209 mT and $a$(H3,5) = 0.089 mT.[28] Time-dependent UV and ESR spectra are shown in Figure 5. The intensity of both spectra increased with time and then disappeared upon completion of the reaction, just as in the case of **1a**.

The electron spin density for the cation radicals of **1f** was calculated according to the Hückel molecular orbital calculation method[24,29] and from the ESR spectrum for **1f**.[27] The results are summarized in Figure 6, in which the values from both methods were found to be almost identical. The result of the calculation rationalized the regiospecificity during the nucleophilic substitution of **1f**; the cation radical of **1f** is concentrated at the *ortho* position relative to the methoxy group.[30]

**6. Effect of Metal Salts.** As this reaction proceeds via cation radicals, the addition of metal salts is expected to promote the reaction involving radical species. That is, as the metal salts coordinate to the radical pair, the efficiency of the degradation to the free radical species is enhanced and the yields of the reaction increase (Scheme 3).

(21) Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Tuncay, A. *Tetrahedron Lett.* **1989**, *30*, 3019.
(22) (a) Magnus, P.; Lacour, J. *J. Am. Chem. Soc.* **1992**, *114*, 767; (b) **1992**, *114*, 3993.
(23) Umemoto, T.; Kuriu, Y.; Shuyama, H. *Chem. Lett.* **1981**, 1663. Umemoto, T.; Nakamura, T. *Chem. Lett.* **1984**, 983.
(24) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824; **1987**, *109*, 5235.
(25) Bhatt, M. V.; Hosur, B. M. *Indian J. Chem., Sect. B* **1986**, 1004.
(26) Fritz, H. P.; Gebauer, H. *Z. Naturforsch B* **1978**, *33B*, 702.
(27) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124.
(28) Experimental ring proton spin densities were calculated from $a = \rho Q$, in which $Q = 0.264$ mT, which is derived from benzene. McConnell, H. M.; Chesnut, D. B. *J. Chem. Phys.* **1958**, *28*, 107.
(29) Forbes, W. F.; Sullivan, P. D.; Wang, H. M. *J. Am. Chem. Soc.* **1967**, *89*, 2705.
(30) Calculations were carried out using the McLachlan perturbation corrections to the Hückel LCAO-MO method where $\lambda = 1.20$ was used: McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 323.

**Scheme 2**



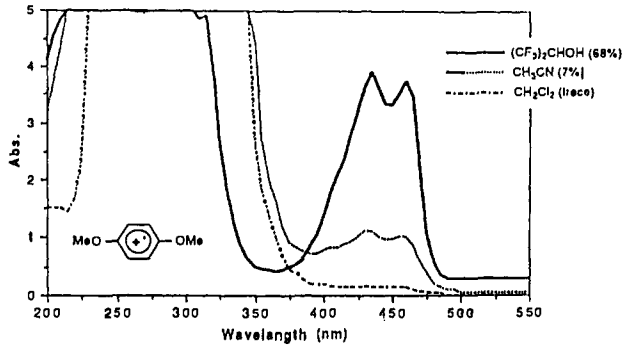




**Figure 1.** Effect of solvents.

As expected, the addition of a catalytic amount of $Mg(ClO_4)_2$ in $CH_3CN$ considerably enhanced the yield of **2a** (Table 4).

Upon examination of the UV spectral data, the intensity of the absorption band was enhanced more in the presence of $Mg(ClO_4)_2$ than in its absence. It was found that yields of the reaction and intensity of the absorption bands were directly related (Figure 7).

## Conclusions

The nucleophilic substitution of *para*-substituted phenol ethers has been found to proceed via cation radicals as reactive intermediates by SET from the CT complex of **1** and PIFA. The mechanism was confirmed by UV and ESR spectroscopic studies and through the effects of metal salts. This is the first case that does not involve diaryliodonium salts but cation radicals in the reaction of aromatic compounds with hypervalent iodine reagents. Furthermore, we have found that the reaction type depends upon the substitution pattern of phenol ethers (*i.e.*, this type of substitution reaction occurred only in the case of *para*- or *ortho*-substituted phenol ethers, whereas, in the case of *meta*-substituted phenol ethers, diaryliodonium salts were obtained).

## Experimental Section

All melting points are uncorrected. Infrared (IR) absorption spectra were recorded on a JASCO HPIR-102 spectrophotometer with $CHCl_3$ as a solvent. Proton nuclear magnetic resonance ($^1$H-NMR) spectra were measured on Varian-VXR200 (200 MHz), JEOL JNM-EX270 (270 MHz), and JEOL JNM-GX500 (500 MHz) spectrometers with $CDCl_3$ as a solvent unless otherwise noted with tetramethylsilane as an internal standard. Mass spectra (MS) and high-resolution MS were obtained by ESCO EMD-05A and JEOL JMS-D300 mass spectrometers. UV spectra were taken on a SHIMADZU 2200 UV–vis spectrometer, and ESR spectra were taken on a JEOL JES-RE 1X spectrometer. E. Merck silica gel 60 (70–230 mesh ASTM) for column chromatography and E. Merck precoated TLC plates, silica gel $F_{254}$, for preparative thin-layer chromatography (preparative TLC) were used. Organic layers were dried with anhydrous $MgSO_4$. PIFA is commercially available. Starting materials (**1a,b,d,e,g,h,k,l**) were purchased, and other known starting materials were prepared by the reported method.[31]

**General Experimental Procedures. 1. Oxidative Azidation Reaction of *para*-Substituted Phenol Ethers (Method i).** To a stirred solution of **1** (0.1 mmol) and TMSA (0.5 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2CHOH$) (0.5 mL) was added PIFA (0.1 mmol) at room temperature under nitrogen. (Or to a solution of **1a** in $(CF_3)_2CHOH$ was added 1.0 equiv of PIFA at room temperature under nitrogen. After a few minutes, 5.0 equiv of TMSA was added to the mixture.) The reaction mixture was stirred for 15 min and then was evaporated in vacuo. The residue was purified by column chromatography (*n*-hexane/ethyl acetate) on silica gel to give the corresponding aromatic azido compound **2**.

**2. Oxidative Acetoxylation Reaction of *para*-Substituted Phenol Ethers (Method ii).** To a stirred solution of **1** (0.1 mmol) and TMSOAc (0.5 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2CHOH$) (0.5 mL) was added PIFA (0.1 mmol) at room temperature under nitrogen. The reaction mixture was stirred for 15 min and then was evaporated in vacuo. The residue was purified by column chromatography (*n*-hexane/ethyl acetate) on silica gel to give the corresponding aromatic acetoxy compound **3**.

**3. Oxidative C–C Bond Formation Reaction of *para*-Substituted Phenol Ethers (Method iii).** To a stirred solution of **1** (0.1 mmol) and β-dicarbonyl compound (0.5 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2CHOH$) (0.5 mL) was added PIFA (0.1 mmol) at room temperature under nitrogen. The reaction mixture was stirred for 15 min and then was evaporated in vacuo. The residue was purified by column chromatography (*n*-hexane/ethyl acetate) on silica gel to give α-aryl β-dicarbonyl compound **4**.

**2-Azido-4-methoxyanisole (2a) (Method i).** **1a** (13.0 mg, 0.094 mmol); TMSA (0.062 mL, 0.47 mmol); PIFA (48.0 mg, 0.113 mmol); $(CF_3)_2CHOH$ (0.5 mL). **2a** (11.5 mg, 68%); colorless oil; IR ($CHCl_3$) 2950, 2120, 1615, 1585, 1500 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 3.77 (s, 3H, $OCH_3$), 3.83 (s, 3H, $OCH_3$), 6.61 (dd, 1H, $J$ = 8.8, 2.2 Hz, ArH), 6.82 (d, 1H, $J$ = 8.8 Hz, ArH), 6.84 (s, 1H, ArH); HRMS calcd for $C_8H_9N_3O_2$ ($M^+$) 179.0695, found 179.0698. Compound **2a** was reduced by lithium aluminum hydride (LAH)/$Et_2O$ to 2,5-dimethoxyaniline which is identical with the sample from Aldrich, colorless crystals, mp 80–81 °C (from $CCl_4$) (lit. mp 80–82 °C).

(31) (a) Klages, A. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 3987 (**1c**). (b) Olson, W. T.; Hipsher, H. F.; Buess, C. M.; Goodman, I. A.; Hart, I.; Lamneok, J. H., Jr.; Gibbons, L. C. *J. Am. Chem. Soc.* **1947**, *69*, 2451 (**1f**). (c) Inoue, A.; Nakano, K.; Kuroki, N.; Konishi, K. *Yuki Gosei Kagaku Kyokaishi* **1956**, *14*, 513 (**1i**). (d) Momose, T.; Oya, H.; Ohkura, Y.; Iwasaki, M. *Chem. Pharm. Bull.* **1954**, *2*, 119 (**1j**).

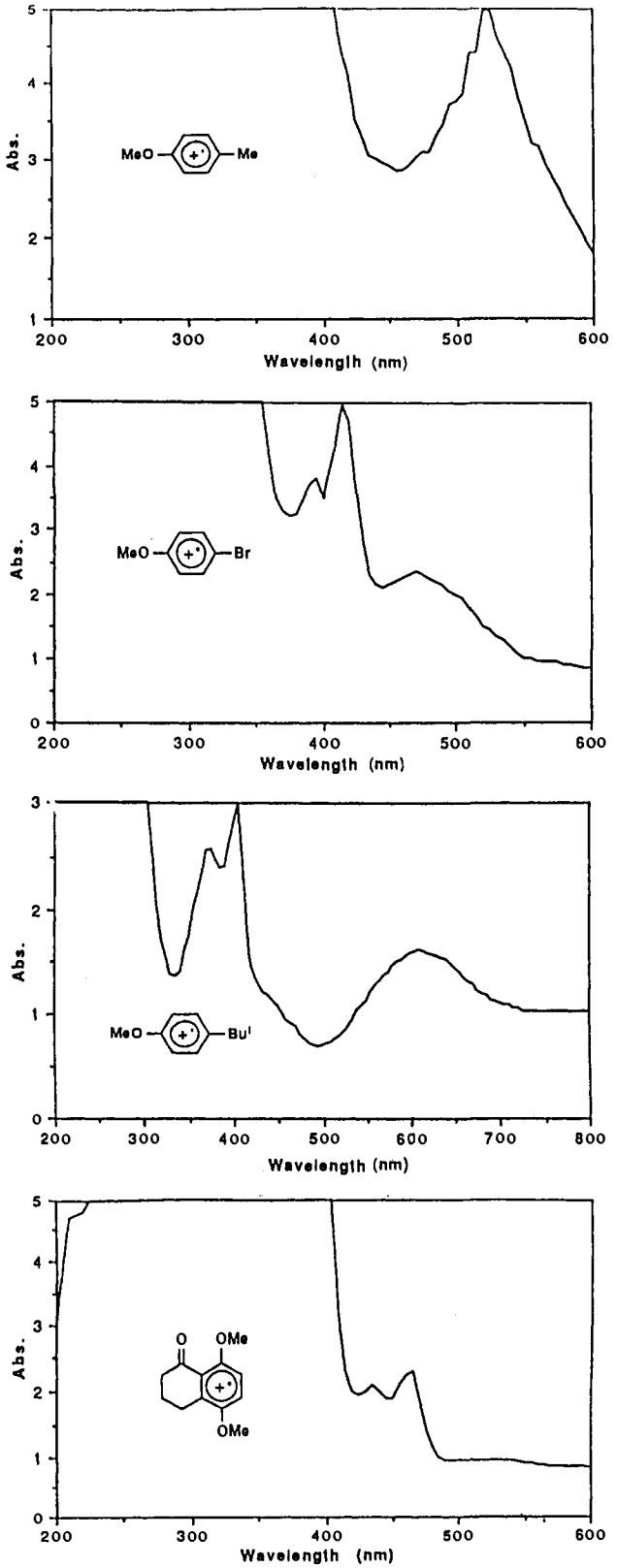



Figure 2.

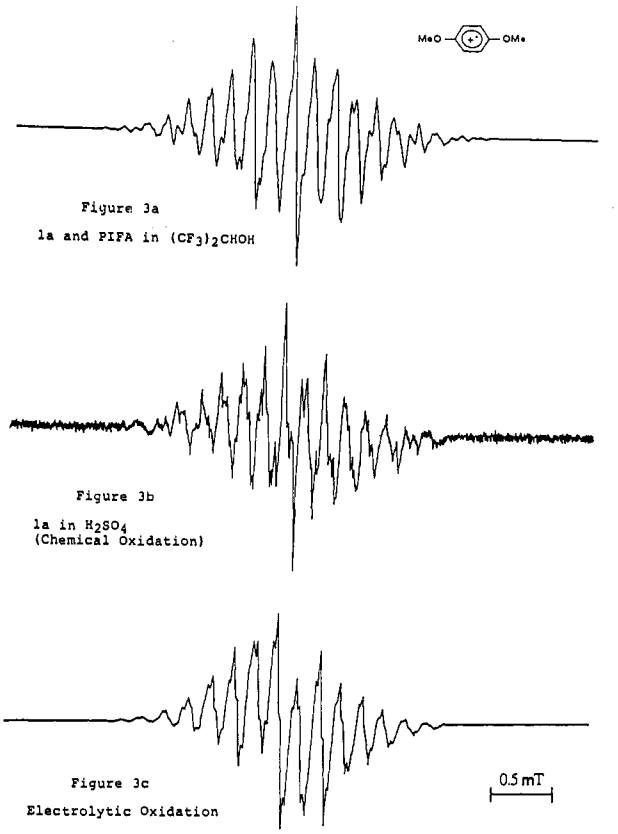



Figure 3. ESR spectra of reaction intermediates.

**2-Azido-4-methylanisole (2b) (Method i).** **1b** (10.6 mg, 0.087 mmol); TMSA (0.057 mL, 0.44 mmol); PIFA (44.0 mg, 0.104 mmol); $(CF_3)_2$-CHOH (0.5 mL). **2b** (6.4 mg, 45%); colorless oil; IR ($CHCl_3$) 3000, 2935, 2840, 2120, 1665, 1610, 1510 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.28 (s, 3H, $CH_3$), 3.85 (s, 3H, $OCH_3$), 6.78 (d, 1H, $J$ = 8.0 Hz, ArH), 6.83 (d, 1H, $J$ = 2.2 Hz, ArH), 6.89 (dd, 1H, J = 2.2, 8.0 Hz, ArH); HRMS calcd for $C_8H_9N_3O$ ($M^+$) 163.0746, found 163.0749. Compound **2b** was reduced by LAH/$Et_2O$ to 2-methoxy-5-methylaniline which is identical with the sample from Aldrich, colorless crystals, mp 51–52 °C (from $CCl_4$) (lit. mp 52–54 °C).

**2-Azido-4-isopropylanisole (2c) (Method i).** **1c** (15.3 mg, 0.102 mmol); TMSA (0.067 mL, 0.51 mmol); PIFA (44.0 mg, 0.102 mmol); $(CF_3)_2$-CHOH (0.5 mL). **2c** (9.6 mg, 49%); colorless oil; IR ($CHCl_3$) 2965, 2950, 2120, 1605, 1585, 1515, 1500 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.22 (d, 6H, $J$ = 7.0 Hz, 2 × $CH_3$), 2.84 (m, 1H, C*H*($CH_3$)$_2$), 3.85 (s, 1H, $OCH_3$), 6.82 (d, 1H, $J$ = 8.4 Hz, ArH), 6.86 (d, 1H, $J$ = 2.0 Hz, ArH), 6.95 (dd, 1H, $J$ = 8.4, 2.0 Hz, ArH); HRMS calcd for $C_{10}H_{13}N_3O$ ($M^+$) 191.1057, found 191.1057.

**2-Azido-4-bromoanisole (2d) (Method i).** **1d** (26.9 mg, 0.144 mmol); TMSA (0.095 mL, 0.72 mmol); PIFA (62.0 mg, 0.144 mmol); $(CF_3)_2$-CHOH (1.0 mL). **2d** (12.8 mg, 39%); colorless oil; IR ($CHCl_3$) 3010, 2965, 2840, 2120, 1590, 1490 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.86 (s, 3H, $OCH_3$), 6.76 (d, 1H, $J$ = 8.6 Hz, ArH), 7.12 (d, 1H, $J$ = 2.2 Hz, ArH), 7.20 (dd, 1H, $J$ = 2.2, 8.6 Hz, ArH); HRMS calcd for $C_{11}H_6N_3BrO$ ($M^+$) 226.9695, found 226.9702. Compound **2d** was reduced by LAH/$Et_2O$ to 3-bromo-6-methoxyaniline which is identical with the sample from Aldrich, colorless crystals, mp 93–95 °C (from $CCl_4$) (lit. mp 94–96 °C).

**2-Azido-4-chloroanisole (2e) (Method i).** **1e** (12.2 mg, 0.086 mmol); TMSA (0.057 mL, 0.43 mmol); PIFA (73.0 mg, 0.172 mmol); $(CF_3)_2$-CHOH (0.5 mL). **2e** (7.0 mg, 45%); colorless oil; IR ($CHCl_3$) 2950, 2120, 1590, 1500 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.87 (s, 3H, $OCH_3$), 6.80 (d, 1H, $J$ = 8.6 Hz, ArH), 6.98 (d, 1H, $J$ = 2.2 Hz, ArH), 7.06 (dd, 1H, $J$ = 2.2, 8.6 Hz, ArH); HRMS calcd for $C_7H_6N_3ClO$ ($M^+$) 183.0198, found 183.0188. Compound **2e** was reduced by LAH/$Et_2O$ to 2-methoxy-5-chloroaniline which is identical with the sample from Aldrich, colorless crystals, mp 82–83 °C (from *n*-hexane) (lit. mp 83–85 °C).

**2-Azido-4-*tert*-butylanisole (2f) (Method i).** **1f** (17.8 mg, 0.108 mmol); TMSA (0.070 mL, 0.530 mmol); PIFA (55.0 mg, 0.130 mmol); $(CF_3)_2$-CHOH (1.0 mL). **2f** (6.9 mg, 31%); colorless oil; IR ($CHCl_3$) 2950, 2120, 1590, 1500 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.29 (s, 9H, $C(CH_3)_3$), 3.86 (s, 3H, $OCH_3$), 6.82 (d, 1H, $J$ = 8.6 Hz, ArH), 7.01 (d, 1H, $J$ = 2.2 Hz, ArH), 7.10 (dd, 1H, $J$ = 2.2, 8.6 Hz, ArH); HRMS calcd for $C_{11}H_{15}N_3O$ ($M^+$) 205.1214, found 205.1204.

**Methyl (3-Azido-4-methoxyphenyl)acetate (2g) (Method i).** **1g** (21.8 mg, 0.121 mmol); TMSA (0.080 mL, 0.605 mmol); PIFA (52.0 mg, 0.121 mmol); $(CF_3)_2CHOH$ (1.5 mL). **2g** (10.9 mg, 41%); colorless oil; IR ($CHCl_3$) 3025, 2125, 1730, 1610, 1515 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$

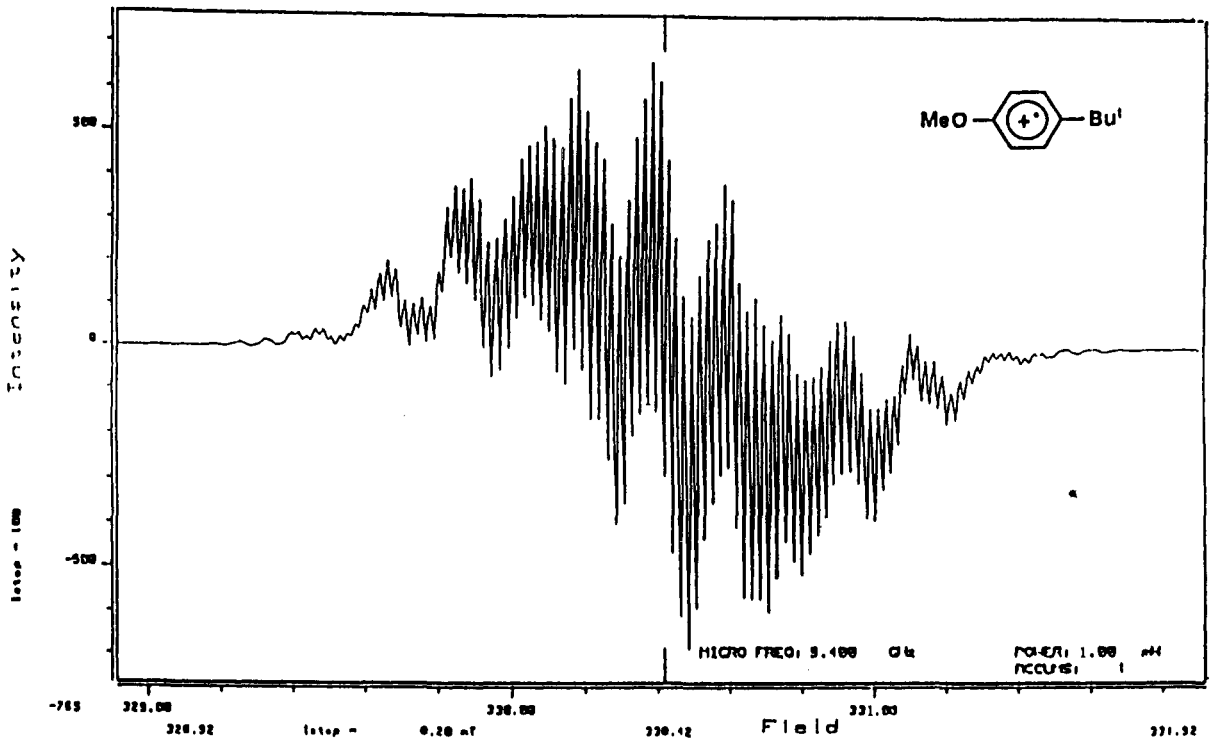



**Figure 4.** ESR spectrum of **1f**.

3.56 (s, 2H, 2-$CH_2$), 3.68 (s, 3H, $CO_2CH_3$), 3.80 (s, 3H, $OCH_3$), 6.85 (dd, 1H, $J$ = 9, 2 Hz, 6′-CH), 6.90 (d, 1H, $J$ = 2 Hz, 2′-CH), 7.18 (d, 1H, $J$ = 9 Hz, 5′-CH); HRMS calcd for $C_{10}H_{11}N_3O_3$ ($M^+$) 221.0800, found 221.0776.

**(3-Azido-4-methoxyphenyl)acetonitrile (2h) (Method i).** **1h** (15.5 mg, 0.105 mmol); TMSA (0.069 mL, 0.525 mmol); PIFA (54.0 mg, 0.126 mmol); $(CF_3)_2CHOH$ (0.5 mL). **2h** (9.3 mg, 47%); colorless crystals; mp 72–74 °C from $CCl_4$; IR ($CHCl_3$) 2970, 2250, 2120, 1610, 1510 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.67 (s, 2H, 2-$CH_2$), 3.89 (s, 3H, $OCH_3$), 6.88 (d, 1H, $J$ = 8.4 Hz, ArH), 6.93 (d, 1H, $J$ = 2.4 Hz, ArH), 7.07 (dd, 1H, $J$ = 2.4, 8.4 Hz, ArH); HRMS calcd for $C_9H_8N_4O$ ($M^+$) 188.0698, found 188.0704.

**2-Azido-1,4-dimethoxynaphthalene (2i) (Method i).** **1i** (18.1 mg, 0.0962 mmol); TMSA (0.064 mL, 0.48 mmol); PIFA (41.4 mg, 0.0962 mmol); $(CF_3)_2CHOH$ (0.5 mL). **2i** (18.7 mg, 85%); colorless plates; mp 42–43 °C (*n*-hexane); IR ($CHCl_3$) 2950, 2120, 1620, 1600 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.94 (s, 3H, $OCH_3$), 3.97 (s, 3H, $OCH_3$), 6.43 (s, 1H, ArH), 7.42 (dd, 1H, $J$ = 8.0, 6.9 Hz, ArH), 7.54 (dd, 1H, $J$ = 8.2, 6.9 Hz, ArH), 8.00 (d, 1H, $J$ = 8.0 Hz, ArH), 8.18 (d, 1H, $J$ = 8.2 Hz, ArH); HRMS calcd for $C_{12}H_{11}N_3O_2$ ($M^+$) 229.0851, found 229.0877. Compound **2i** was reduced by LAH/$Et_2O$ to 2-amino-1,4-dimethoxynaphthalene as a colorless plate which is identical with the authentical sample, mp 101–103 °C (from $CCl_4$) (lit.[28] mp 100–101 °C).

**6-Azido-5,8-dimethoxy-α-tetralone (2j) (Method i).** **1j** (32.7 mg, 0.159 mmol); TMSA (0.105 mL, 0.795 mmol); PIFA (82.0 mg, 0.191 mmol); $(CF_3)_2CHOH$ (1.0 mL). **2j** (19.0 mg, 48%); brownish plates; mp 84–87 °C (MeOH); IR ($CHCl_3$) 2950, 2110, 1685, 1590, 1470 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.98–2.19 (m, 2H, 3-$CH_2$), 2.62 (t, 2H, $J$ = 6.4 Hz, 2-$CH_2$), 2.83 (t, 2H, $J$ = 6.4 Hz, 4-$CH_2$), 3.81 (s, 3H, $OCH_3$), 3.83 (s, 3H, $OCH_3$), 6.62 (s, 1H, ArH); HRMS calcd for $C_{12}H_{13}N_3O_3$ ($M^+$) 247.0957, found 247.0965. Anal. Calcd for $C_{12}H_{13}N_3O_3$: C, 58.29; H, 5.30; N, 17.00. Found: C, 58.43; H, 5.47; N, 17.03.

**3,4,5-Trimethoxyazidobenzene (2k) (Method i).** **1k** (32.5 mg, 0.193 mmol); TMSA (0.127 mL, 0.965 mmol); PIFA (83.0 mg, 0.193 mmol); $(CF_3)_2CHOH$ (1.0 mL). **2k** (33.0 mg, 83%); colorless crystals; mp 40–42 °C (*n*-hexane); IR ($CHCl_3$) 2940, 2110, 1590, 1500 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.81 (s, 3H, $OCH_3$), 3.86 (s, 6H, 2 × $OCH_3$), 6.25 (s, 2H, ArH); HRMS calcd for $C_9H_{11}N_3O_3$ ($M^+$) 209.0800, found 209.0787.

**2-Acetoxy-4-methoxyanisole (3a) (Method ii).** **1a** (10.0 mg, 0.072 mmol); TMSOAc (0.106 mL, 0.720 mmol); PIFA (37.0 mg, 0.086 mmol); $(CF_3)_2CHOH$ (0.5 mL). **3a** (6.1 mg, 43%); colorless needles; mp 63–64 °C ($CCl_4$); IR ($CHCl_3$) 3000, 2940, 2840, 1760, 1590, 1510 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.31 (s, 3H, $COCH_3$), 3.75 (s, 3H, $OCH_3$), 3.78 (s, 3H, $OCH_3$), 6.64 (d, 1H, $J$ = 2.7 Hz, ArH), 6.73 (dd, 1H, $J$ = 2.7, 9.0 Hz, ArH), 6.90 (d, 1H, $J$ = 9.0 Hz, ArH); HRMS calcd for $C_{10}H_{12}O_4$ ($M^+$) 196.0736, found 196.0737.

**6-Acetoxy-5,8-dimethoxy-α-tetralone (3j) (Method ii).** **1j** (34.5 mg, 0.167 mmol); TMSOAc (0.122 mL, 0.835 mmol); PIFA (72.0 mg, 0.167 mmol); $(CF_3)_2CHOH$ (1.0 mL). **3j** (21.5 mg, 49%); colorless oil; IR ($CHCl_3$) 2990, 2920, 2820, 1720, 1670, 1580, 1480 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.98–2.11 (m, 2H, 3-$CH_2$), 2.36 (s, 3H, $COCH_3$), 2.61 (t, 2H, $J$ = 6.4 Hz, 2-$CH_2$), 2.94 (t, 2H, $J$ = 6.1 Hz, 4-$CH_2$), 3.73 (s, 3H, $OCH_3$), 3.86 (s, 3H, $OCH_3$), 6.61 (s, 1H, ArH); HRMS calcd for $C_{14}H_{16}O_5$ ($M^+$) 264.0998, found 264.0999.

**3,4,5-Trimethoxyacetoxybenzene (3k) (Method ii).** **1k** (30.0 mg, 0.178 mmol); TMSOAc (0.13 mL, 0.890 mmol); PIFA (92.0 mg, 0.214 mmol); $(CF_3)_2CHOH$ (0.5 mL). **3k** (17.3 mg, 43%); colorless plates; mp 72–74 °C ($CCl_4$) (lit.[26] mp 73–75 °C); IR ($CHCl_3$) 2945, 2850, 1750, 1660, 1630, 1610, 1550, 1500 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.14 (s, 3H, $COCH_3$), 3.41 (s, 3H, $OCH_3$), 3.77 (s, 6H, 2 × $OCH_3$), 5.56 (s, 2H, ArH).

**2,3,5-Trimethoxyacetoxybenzene (3l) and 2,4,5-Trimethoxyacetoxybenzene (3m) (Method ii).** **1l** (27.8 mg, 0.165 mmol); TMSOAc (0.121 mL, 0.825 mmol); PIFA (71.0 mg, 0.165 mmol); $(CF_3)_2CHOH$ (1.0 mL). **3l** (12.8 mg, 34%); colorless oil; IR ($CHCl_3$) 3000, 2950, 2850, 1760, 1615, 1590, 1505 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.27 (s, 3H, $COCH_3$), 3.75 (s, 3H, $OCH_3$), 3.76 (s, 3H, $OCH_3$), 3.85 (s, 3H, $OCH_3$), 6.20 (d, 1H, $J$ = 3 Hz, ArH), 6.39 (d, 1H, $J$ = 3 Hz, ArH); HRMS calcd for $C_{11}H_{14}O_5$ ($M^+$) 226.0838, found 226.0836. **3m** (12.5 mg, 33%); colorless oil; IR ($CHCl_3$) 3000, 2950, 1760, 1600, 1515 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.31 (s, 3H, $COCH_3$), 3.81 (s, 6H, 2 × $OCH_3$), 3.88 (s, 3H, $OCH_3$), 6.61 (s, 1H, ArH), 6.63 (s, 1H, ArH); HRMS calcd for $C_{11}H_{14}O_5$ ($M^+$) 226.0838, found 226.0839.

**2-(2,5-Dimethoxyphenyl)-2-methyl-1,3-cyclopentanedione (4a) (Method iii).** **1a** (20.0 mg, 0.145 mmol); 2-methyl-1,3-cyclopentanedione (16.2 mg, 0.145 mmol); PIFA (62.4 mg, 0.145 mmol); $(CF_3)_2CHOH$ (1.5 mL). **4a** (23.8 mg, 66%); colorless needles; mp 165–166 °C (MeOH); IR ($CHCl_3$) 2950, 1725, 1590, 1495, 1460 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.46 (s, 3H, $CH_3$), 2.93 (dd, 4H, $J$ = 3.5, 1.3 Hz, 4,5-$CH_2$), 3.64 (s, 3H, $OCH_3$), 3.78 (s, 3H, $OCH_3$), 6.72 (d, 1H, $J$ = 8.8 Hz, ArH), 6.79 (dd, 1H, $J$ = 8.8, 2.5 Hz, ArH), 6.91 (d, 1H, $J$ = 2.5 Hz, ArH); HRMS calcd for $C_{14}H_{16}O_4$ ($M^+$) 248.1049, found 248.1062. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.56; H, 6.47.

**2-Acetyl-2-(2,5-dimethoxyphenyl) γ-Lactone 4b (Method iii).** **1a** (25.0 mg, 0.180 mmol); 2-acetyl γ-lactone (25.0 mg, 0.180 mmol); PIFA (78.0 mg, 0.181 mmol); $(CF_3)_2CHOH$ (0.5 mL). **4b** (18.4 mg, 39%); brownish plates; mp 68–70 °C ($Et_2O$); IR ($CHCl_3$) 3000, 2950, 2840, 1760, 1720, 1605, 1590, 1500 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.11–2.20 (m, 1H, $^1/_2$ × 3-$CH_2$), 2.16 (s, 3H, $COCH_3$), 3.47 (dt, 1H, $J$ = 13.2, 7.2 Hz, $^1/_2$ ×

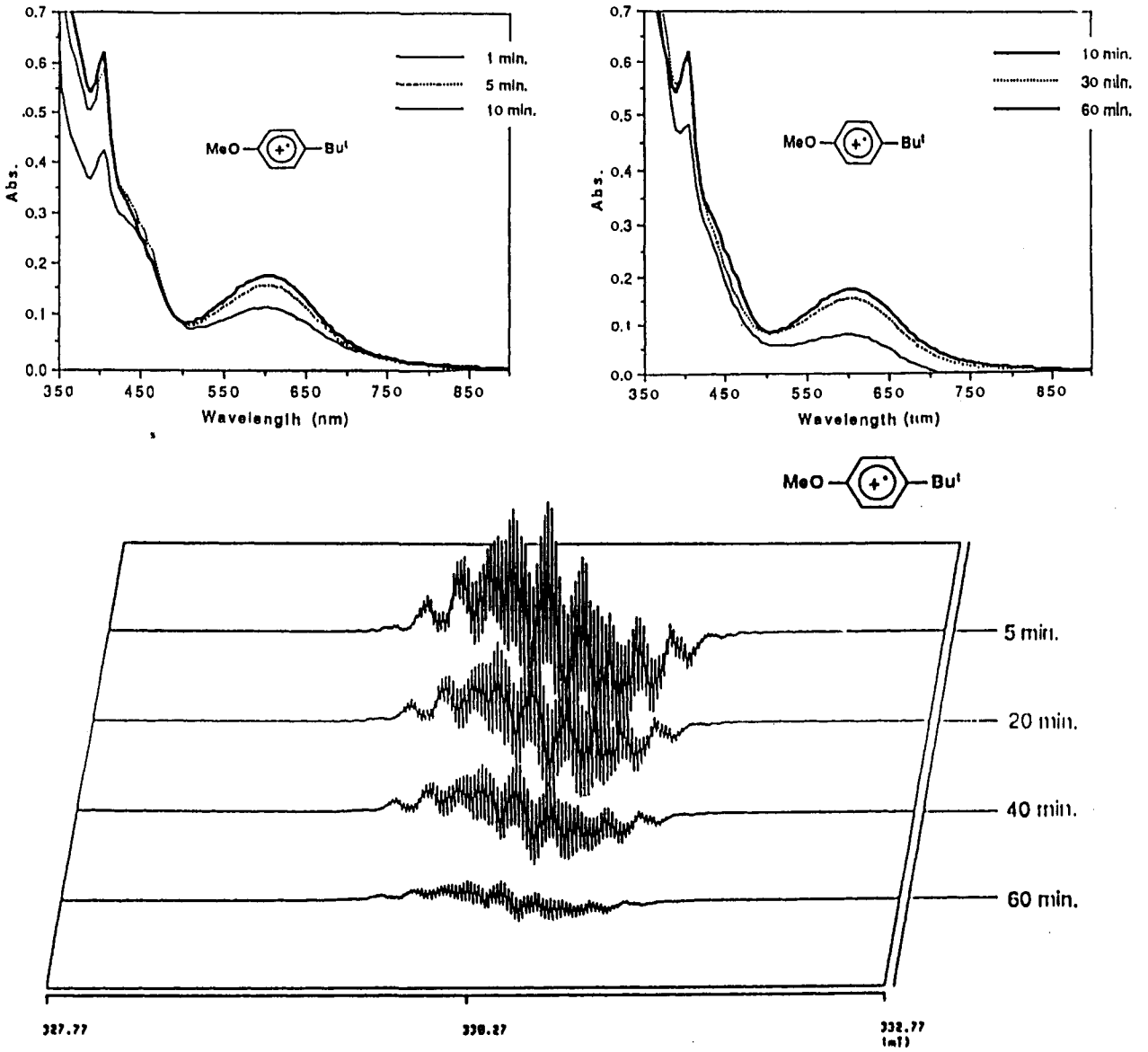



Figure 5. Time-dependent ESR spectra.

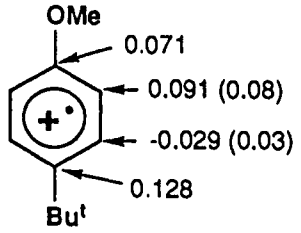
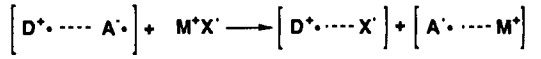


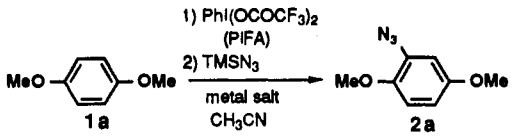

Figure 6. Electron spin density of cation radical **1f**. The values in parentheses were obtained from the ESR spectrum (Figure 4). The $\pi$-electron densities were calculated by the Huckel molecular orbital theory (without overlap). Parameters used were *hoo* = 2.2, *kco* = 0.8; for the methyl groups the inductive model was used C–C–X; *hcc* = –0.10, *hc'c* = –0.18, *kc'x* = 0.7.[24]

**Scheme 3**




3-$CH_2$), 3.74 (s, 3H, $OCH_3$), 3.79 (s, 3H, $OCH_3$), 4.20 (dt, 1H, $J$ = 8, 8.3 Hz, $^1/_2$ × 4-$CH_2$), 4.40 (dt, 1H, $J$ = 5.6, 8.3 Hz, $^1/_2$ × 4-$CH_2$), 6.83–6.92 (m, 3H, ArH); HRMS calcd for $C_{14}H_{16}O_5$ ($M^+$) 264.0995, found 264.0993. Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.35; H, 6.08

**Table 4**




| runs | metal salts | concentration | yield (%) |
|---|---|---|---|
| 1 | none | | 7 |
| 2 | $LiClO_4$ | 1 mol % | 11 |
| 3 | $LiBF_4$ | 1 mol % | 14 |
| 4 | $Mg(ClO_4)_2$ | 1 mol % | 40 |
| 5 | $Mg(ClO_4)_2$ | 100 mol % | complex mixture |

**2-(2,5-Dimethoxyphenyl)-2-methyl-1,3-cyclohexanedione (4c) (Method iii).** **1a** (15.0 mg, 0.109 mmol); 2-methyl-1,3-cyclohexanedione (14.0 mg, 0.109 mmol); PIFA (56.0 mg, 0.131 mmol); $(CF_3)_2CHOH$ (1.0 mL). **4c** (12.4 mg, 43%); colorless plates; mp 126–128 °C (MeOH); IR ($CHCl_3$) 3030, 3010, 1730, 1700, 1590, 1500, 1460 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.57 (s, 3H, $CH_3$), 1.95–2.11 (m, 2H, $CH_2$), 2.76 (td, 4H, $J$ = 2.2, 6.7 Hz, 2 × $CH_2$), 3.66 (s, 3H, $OCH_3$), 3.77 (s, 3H, $OCH_3$), 6.78 (s, 3H, ArH); HRMS calcd for $C_{15}H_{18}O_4$ ($M^+$) 262.1205, found 262.1211. Anal. Calcd for $C_{16}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.35; H, 7.00.

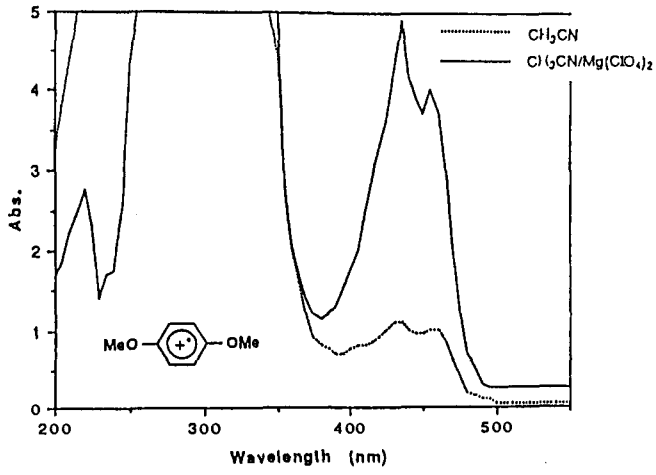



**Figure 7.** Effect of metal salts.

**2-(2,5-Diethoxyphenyl)-2-methyl-1,3-cyclopentanedione (4d) (Method iii).** **1m** (16.6 mg, 0.100 mmol); 2-methyl-1,3-cyclopentanedione (13.5 mg, 0.120 mmol); PIFA (51.6 mg, 0.120 mmol); $(CF_3)_2CHOH$ (1.0 mL). **4d** (15.4 mg, 56%); colorless plates; mp 92–94 °C ($CCl_4$); IR ($CHCl_3$) 3000, 2980, 1730 1590, 1500, 1480 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.32 (t, 3H, $J$ = 7 Hz, $OCH_2CH_3$), 1.39 (t, 3H, $J$ = 7 Hz, $OCH_2CH_3$), 1.46 (s, 3H, $CH_3$), 2.97 (s, 4H, 4,5-$CH_2$), 3.91 (q, 2H, $J$ = 7 Hz, $OCH_2$-$CH_3$), 3.99 (q, 2H, $J$ = 7 Hz, $OCH_2CH_3$), 6.69 (d, 1H, $J$ = 9 Hz, ArH), 6.77 (dd, 1H, $J$ = 9, 2.8 Hz, ArH), 6.91 (d, 1H, $J$ = 2.8 Hz, ArH); HRMS calcd for $C_{16}H_{20}O_4$ ($M^+$) 276.1359, found 276.1359. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.39; H, 7.18.

**2-Methyl-2-(2-methoxy-5-isopropylphenyl)-1,3-cyclopentanedione (4e) (Method iii).** **1c** (22.4 mg, 0.149 mmol); 2-methyl-1,3-cyclopentadione (16.7 mg, 0.149 mmol); PIFA (64.0 mg, 0.181 mmol); $(CF_3)_2CHOH$ (0.5 mL). **4e** (15.0 mg, 39%); colorless plates; mp 113–115 °C (MeOH); IR ($CHCl_3$) 2950, 1760, 1720, 1600, 1500, 1460 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.24 (d, 6H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.49 (s, 3H, $CH_3$), 2.88 (m, 1H, $CH(CH_3)_2$), 2.94 (d, 4H, $J$ = 1.6 Hz, 4,5-$CH_2$), 3.67 (s, 3H, $OCH_3$), 6.73 (d, 1H, $J$ = 9 Hz, ArH), 7.13 (dd, 1H, $J$ = 9, 2 Hz, ArH), 7.15 (d, 1H, $J$ = 2 Hz, ArH); HRMS calcd for $C_{16}H_{20}O_3$ ($M^+$) 260.1412, found 260.1398. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.72; H, 7.65.

**2-Methyl-2-(4-oxo-3,8-dimethoxy-1,2,3,4-tetrahydronaphthyl)-1,3-cyclopentanedione (4f) (Method iii).** **1j** (20.8 mg, 0.101 mmol); 2-methyl-1,3-cyclopentadione (13.6 mg, 0.120 mmol); PIFA (52.1 mg, 0.120 mmol); $(CF_3)_2CHOH$ (0.75 mL). **4f** (19.9 mg, 62%); colorless crystals; mp 219–222 °C (MeOH); IR ($CHCl_3$) 3020, 1730, 1680, 1590, 1460 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.50 (s, 3H, $CH_3$), 1.97–2.12 (m, 2H, $CH_2$), 2.59 (t, 2H, $J$ = 6.6 Hz, $CH_2$), 2.85 (t, 2H, $J$ = 6.6 Hz, $CH_2$), 2.99 (s, 4H, 2 × $CH_2$), 3.55 (s, 3H, OCH3), 3.88 (s, 3H, $OCH_3$), 7.00 (s, 1H, ArH); HRMS calcd for $C_{18}H_{20}O_5$ ($M^+$) 316.1310, found 316.1315. Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.11; H, 6.37.

**2-Methyl-2-(3,4,5-trimethoxyphenyl)-1,3-cyclopentanedione (4g) (Method iii).** **1k** (27.5 mg, 0.163 mmol); 2-methyl-1,3-cyclopentanedione (18.3 mg, 0.163 mmol); PIFA (70.1 mg, 0.163 mmol); $(CF_3)_2CHOH$ (0.5 mL). **4g** (30.3 mg, 67%); colorless crystals; mp 112–114 °C (MeOH); IR ($CHCl_3$) 2950, 1760, 1720, 1580, 1500, 1450 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.41 (s, 3H, $CH_3$), 2.82 (dd, 4H, $J$ = 7.5, 3.1 Hz, 4,5-$CH_2$), 3.79 (s, 3H, $OCH_3$), 3.83 (s, 6H, 2 × $OCH_3$), 6.41 (s, 2H, ArH); HRMS calcd for $C_{15}H_{18}O_5$ ($M^+$) 278.1154, found 278.1129. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.47; H, 6.50.

**Typical Measurement of UV–Vis Absorption Spectra.** Under a nitrogen atmosphere to a stirred solution of **1f** (1.1 mg, 6.70 × $10^{-3}$ mmol) in $(CF_3)_2CHOH$ (1.50 mL) was added a solution of PIFA (3.50 mg, 8.04 × $10^{-3}$ mmol) in $(CF_3)_2CHOH$ (1.50 mL) at −5 °C. The UV–vis absorption spectra of the reaction mixture were measured on SHIMADZU 2200 UV–vis spectrometer.

**Typical Measurement of Electron Spin Resonance Spectra.** Each sample consisting of a solution of **1f** (1.1 mg, 6.70 × $10^{-3}$ mmol) and solid PIFA (3.50 mg, 8.04 × $10^{-3}$ mmol) in $(CF_3)_2CHOH$ (0.50 mL) which was degassed was prepared in 2-mm Pyrex tubes sealed in vacuo. The components were mixed at ca. 0 °C (The mixture was immediately a fluoresced yellow-green color and gradually turned blue.) and inserted into the ESR cavity. The spectra were recorded at room temperature on a JEOL JES-RE 1X spectrometer. Instrument conditions were as follows: magnetic field, 330.3 ± 2.5 mT; modulation frequency, 0.05 mT; modulation amplitude, 100 kHz; output power, 1 mW; time constant, 0.03 s; sweep time, 8 min/5 mT; amplitude, 32.

**Preparation and Detection of Cation Radical of 1,4-Dimethoxybenzene. (a) Chemical Oxidation of 1,4-Dimethoxybenzene.** An aliquot (20 $\mu$L) from the 0.2 M solution of 1,4-dimethoxybenzene in 98% $H_2SO_4$ was placed in a glass capillary tube (Drummond microdispenser, Drummond Scientific Company, Broomall, PA) and inserted into a 5 mm i.d. ESR quartz tube. ESR spectra were recorded at room temperature (22 °C).

**(b) Electrolytic Oxidation of 1,4-Dimethoxybenzene.** Oxidations were carried out using a rotating gold electrode in a dry acetonitrile solution which contained 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrode. A silver electrode (Ag) was used as reference electrode. The compound was electrolytically oxidized at 1.0 V vs Ag. The ESR spectra were obtained at 253 K.

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