Generation of Aryl Radicals by the Oxidation of α-(Arylazo)triphenylmethanes by Cerium(IV) Ammonium Nitrate

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The one-electron oxidation of α-(arylazo)triphenylmethanes by cerium(IV) ammonium nitrate (CAN) generated aryl radicals along with the triphenylmethyl cation. When the reaction was carried out in the presence of appropriate radical-trapping agents, such as arenes and olefins, the corresponding addition products were obtained in moderate yield. The oxidation of the arylazo compounds with CAN was accelerated by the addition of acids.

Although radical addition reactions have attracted attention as a useful synthetic tool in recent years, the use of aryl radicals for constructing carbon skeletons is rather restricted compared with those of alkyl radicals,[1,2] because hydrogen (or certain atoms) abstraction by aryl radicals is much faster than that by alkyl radicals.[3] This makes it difficult to perform the desired intermolecular addition reaction of aryl radicals to olefins. For instance, when aryl radicals are generated from the corresponding aryl halides by using tributylstannane in the presence of acrylonitrile, hydrogen abstraction by the aryl radicals from the stannane is faster than the intermolecular addition reaction to acrylonitrile, yielding the addition product in poor yield.[1] Arene diazonium salts, well known aryl radical sources, have been used in carbon–carbon bond formation (the Gomberg–Bachmann reaction[4—6] and the Meerwein reaction[7]). Though intermolecular addition reactions of aryl radicals to olefinic compounds are achieved in moderate to good yield in these reactions, they must be carried out under strongly acidic conditions at low temperature to keep the diazonium salts stable, or the unstable diazonium salts have to be isolated.[8]

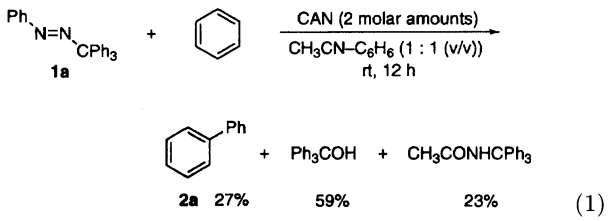
The thermal decomposition of α-(arylazo)triphenylmethane is one of the representative methods for the generation of aryl radicals, and many kinetic studies of radical generation or hydrogen-abstraction reactions of aryl radicals have been performed using this method.[9—12] In these reactions, however, both aryl and triphenylmethyl radicals are simultaneously generated, and side reactions by the triphenylmethyl radical take place.[13] Aryl radicals are also formed by the decomposition of aryltriazenes in acidic media[14] or the reaction of arylhydrazines with potassium superoxide;[15] the addition reaction of the aryl radicals to arenes gives biaryls in moderate yield.

We previously developed carbon–carbon bond-forming reactions between organostannyl compounds and olefins by using metallic oxidants. In the case of α-stannyl sulfides[16] and *N*-(α-stannylalkyl)amides,[17] the one-electron oxidation of these stannyl compounds gives their cation radicals, from which the stannyl radical is eliminated to leave carbocations. When α-stannyl esters and amides are employed, the elimination of stannyl cation occurs and carbon radicals are generated.[18] We attempted to generate aryl radicals by designing a similar bond cleavage of cation radicals which possess a suitable leaving group. It was expected that the one-electron oxidation of α-(arylazo)triphenylmethanes with a metallic oxidizing agent would form their cation radicals, from which nitrogen and the triphenylmethyl cation would be eliminated to afford aryl radicals. Accordingly, the oxidation of some α-(arylazo)triphenylmethanes was examined with cerium(IV) ammonium nitrate (CAN) in the presence of radical acceptors, such as benzene derivatives and olefins.

Results and Discussion

Generation of Aryl Radicals in the Presence of Aromatic Compounds. The reaction of α-(phenylazo)triphenylmethane (**1a**) with CAN was examined in the presence of large excess amounts of aromatic compounds. When the azo compound **1a** was treated with 3 molar amounts of CAN in acetonitrile–benzene (1 : 1, v/v), biphenyl was obtained in 27% yield, accompanied by triphenylmethanol (59%) and *N*-triphenylmethylacetamide (23%), which were derived from the triphenylmethyl cation (Eq. 1).[19] The molar amounts and yields shown in the equations or tables hereafter

are all based on the azo compounds, unless otherwise noted.

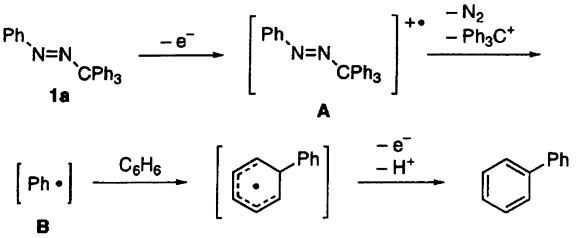


(1)

There are two possible ways for the formation of biphenyl: One is the addition of the phenyl radical to benzene; the other is a route via the phenyl cation. The former is considered to be more reasonable based on the following experimental facts. As described in Eq. 1, products derived from the triphenylmethyl cation were obtained, while those from the phenyl cation (such as phenol) were not. Furthermore, when the reaction was carried out in the presence of 10 molar amounts of carbon tetrabromide, bromobenzene was formed. Thus, the phenyl radical was generated from the azo compound **1a**, which abstracted a bromine atom from carbon tetrabromide. Accordingly, this reaction is supposed to proceed as follows (Scheme 1). The one-electron oxidation of the azo compound **1a** generates a cation radical **A**, from which nitrogen and the triphenylmethyl cation are eliminated to afford the phenyl radical **B**. This radical attacks benzene to give biphenyl by successive oxidation. Although the reaction of the phenylazo compound **1a** with some aromatic compounds was examined, the yield of biphenyl derivatives was not good (Table 1). The ortho selectivity of the products was in accord with the reported results in the addition reaction of the phenyl radical to arenes.[20,21]

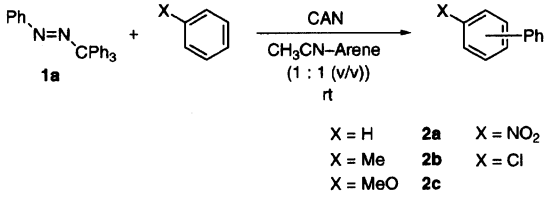
Effect of a Substituent on Aryl Radicals. α-(Phenylazo)triphenylmethane **1a** and the azo compounds **1b**—**e**, which possess a substituent on the para position, were treated with 2—5 molar amounts of CAN in acetonitrile–benzene (1 : 1, v/v) at room temperature; the results are shown in Table 2.

Substrates **1d** and **1e**, which possess an electron-withdrawing group at the para-position, gave addition products in better yield than those (**1b** and **1c**) possessing an electron-donating group. This tendency is consistent with the reported results concerning the arylation of benzene by aryl radicals generated by other methods, such as the decomposition of aryltriazenes[14]



Scheme 1.

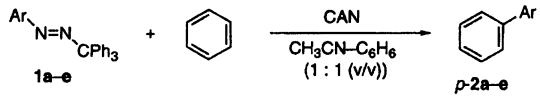
Table 1. Reaction of α-(Phenylazo)triphenylmethane (**1a**) with Arenes by Oxidation with CAN[a]



Arene	Product	Reaction time/h	Yield/%	*o*:*m*:*p*
Benzene	**2a**	12	27	—
Toluene	**2b**	6	11	49:32:19[b]
Anisole	**2c**	6	14	71:24:5[b]
Nitrobenzene	**2d**	12	37	57:11:32[b]
Chlorobenzene	**2f**	6	26	74:14:12[c]

a) 2 molar amounts of CAN were used. 2) Determined by ^{1}H NMR. 3) Determined by GC.

Table 2. Effect of Substituent on the Aryl Radical[a]

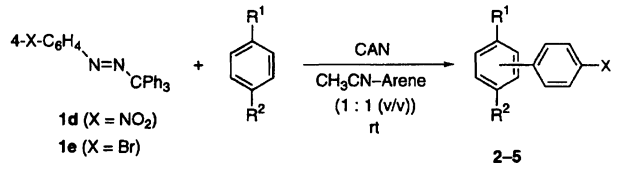


Ar	Conditions	Product	Yield/%
Ph (**1a**)	r.t., 12 h	**2a**	27
4-MeC$_6$H$_4$ (**1b**)	r.t., 3 h	*p*-**2b**	20
4-MeOC$_6$H$_4$ (**1c**)	0 °C, 1 h	*p*-**2c**	<10
4-O$_2$NC$_6$H$_4$ (**1d**)	r.t., 26 h	*p*-**2d**	73[b]
4-BrC$_6$H$_4$ (**1e**)	r.t., 18 h	*p*-**2e**	78[c]

a) 2 molar amounts of CAN were used unless otherwise noted. b) 5 molar amounts of CAN were used. c) 3 molar amounts of CAN were used.

or *N*-nitroso-*N*-acetylarylamines.[20] The low yield of products when Ar is Ph, 4-MeC$_6$H$_4$, and 4-MeOC$_6$H$_4$, is mainly due to hydrogen abstraction from acetonitrile by the aryl radicals. In fact, when α-(4-methoxyphenylazo)triphenylmethane (**1c**) was oxidized with CAN in C$_6$H$_6$–CD$_3$CN, 4-DC$_6$H$_4$OMe was detected in the reaction mixture (43% D).[22] In contrast, the oxidation of α-(4-nitrophenylazo)triphenylmethane (**1d**) with CAN in C$_6$H$_6$–CD$_3$CN, gave 4-nitrobiphenyl and nitrobenzene, in both of which no deuterium was incorporated. The oxidation of **1d** in C$_6$D$_6$–CH$_3$CN afforded 4-C$_6$D$_5$C$_6$H$_4$NO$_2$ (68% yield) and C$_6$D$_5$NO$_2$ (ca. 30% yield).[23] Accordingly, in the reaction in C$_6$H$_6$–CD$_3$CN, nitrobenzene is not derived by hydrogen abstraction with 4-nitrophenyl radical from acetonitrile, but by the nitration of benzene.[24] These results could be explained by an orbital interaction between an aryl radical and a solvent molecule.[21] Since aryl radicals which have a more electron-withdrawing group at the para position, have a lower SOMO level, the interaction with the σ^*_{C-H} orbital of acetonitrile becomes smaller than the phenyl radical, while the interaction with HOMO of benzene becomes more effective.

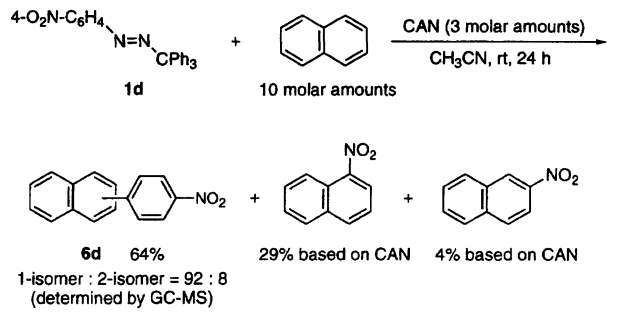
Table 3. Reaction of α-(4-Nitro and 4-Bromophenylazo)triphenylmethanes with Arenes



Substrate	R^1	R^2	Reaction time/h	Product	Yield/%	*o*:*m*:*p*[a]
1d[b]	H	H	49	**2d**	73	—
	Me	H	24	**3d**	46	60:24:16
	Me	Me	24	**4d**	60	—
	MeO	H	2	**5d**	65	68:16:16
1e[c]	H	H	18	**2e**	78	—
	Me	H	20	**3e**	42	62:23:15
	Me	Me	16	**4e**	38	—
	MeO	H	16	**5e**	43	78:22:<1

a) Determined by ^{1}H NMR. 2) 5 molar amounts of CAN were used. c) 3 molar amounts of CAN were used.

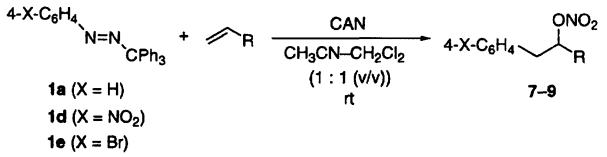
The generality of the addition reactions of α-(4-nitrophenylazo)triphenylmethane (**1d**) and α-(4-bromophenylazo)triphenylmethane (**1e**) was then examined by reactions with various aromatic compounds. As shown in Table 3 and Eq. 2, the desired addition products were obtained in moderate to good yield. The reaction of **1d** required 1—2 d for the complete consumption of **1d**, and that of **1e** did 16—20 h. In the reaction with anisole, the azo compound **1d** disappeared after 2 h, exceptionally.



(2)

Besides aromatic compounds, the aryl radicals generated by the present method react with some olefinic compounds (Table 4). For instance, when α-(phenylazo)triphenylmethane (**1a**) was treated with CAN in the presence of styrene (5 molar amounts in CH_3CN–CH_2Cl_2 (r.t., 5 h), 1,2-diphenylethyl nitrate (**7a**) was obtained in 60% yield (Table 4, Entry 1), accompanied by the 1-phenyl-1,2-ethanediol dinitrate (**10**) (5% based on CAN), which was formed by oxidation of styrene.[25] When the nitrophenylazo compound **1d** was employed in place of **1a**, the yield of product **7d** was somewhat low (48%) and a considerable amount of **1d** was recovered, even after 2 d (Table 4, Entry 4), and the dinitrate **10** was produced in 23% yield based on

Table 4. Reaction of α-(Arylazo)triphenylmethanes with Olefinic Compounds[a]

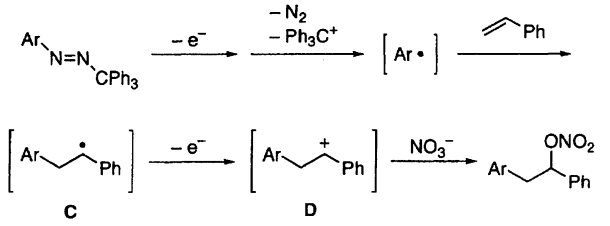


Entry	Substrate	R	Reaction time/h	Product	Yield/%[b]
1	**1a**	Ph	5	**7a**	60
2		OAc	5	**8a**	—[c]
3		2-$MeO_2CC_6H_4$	5	**9a**	43
4	**1d**	Ph	30	**7d**	48 (69)
5		OAc	30	**8d**	46 (53)
6[d]		2-$MeO_2CC_6H_4$	36	**9d**	58
7[d]	**1e**	Ph	26	**7e**	61[e]
8		OAc	22	**8e**	22
9		2-$MeO_2CC_6H_4$	29	**9e**	52

a) 5 molar amounts of CAN and olefin were used unless otherwise noted. b) Figures in parentheses represent the yields based on the recovery. c) Decomposed during isolation. d) 3 molar amounts of olefin were used. e) 3 molar amounts of CAN were used.

CAN. Comparing the reaction of **1a** with **1d**, the oxidation of **1d** with CAN is more difficult than that of **1a**. However, the yield of the addition product based on the recovery (Table 4, Entry 4, in parentheses) is better than that of the non-substituted **1a**. This indicates that addition of the 4-nitrophenyl radical to the olefins proceeds more efficiently than that of the phenyl radical. The bromophenylazo compound **1e** exhibited a character between **1a** and **1d** both in easiness of oxidation and in efficiency of the addition reaction. The reaction of **1e** with styrene proceed to afford product **7e** in 61% yield after 1 d (Table 4, Entry 7).

It is supposed that an aryl radical attacks the terminal of the olefin to give an intermediate radical **C**, which is oxidized to a cation **D** and is trapped by a nitrate ion (Scheme 2). In reactions between **1** and olefins, though the amounts of olefins are not in large excess (5 molar amounts), the addition reaction of aryl radicals is rather predominant over hydrogen abstraction from the solvents.[26] When the reaction of α-(phenylazo)triphenylmethane (**1a**) with styrene was carried out by means of a thermal radical generation method in place of the oxidative method with CAN, a 1:1 addition product



Scheme 2.

corresponding to **7a** was not obtained at all, giving a complex mixture, probably by forming teromers of styrene. Thus, CAN acts not only as a radical-generating agent, but also as an effective radical-terminating agent.

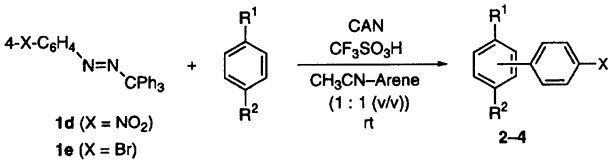
Acceleration of the Oxidation Reaction with Acids. In previous reactions, the one-electron oxidation of arylazo compounds generated aryl radicals, which reacted with aromatic or olefinic compounds to afford addition products in moderate to good yield. However, in these reactions the oxidation of the azo compounds generally required a rather long reaction time, especially when the arylazo compound had an electron-withdrawing group. For example, the reaction of α-(4-nitrophenylazo)triphenylmethane (**1d**) with benzene required about two days for complete consumption of the substrate (Table 3, Entry 1). In order to shorten the reaction time, we tried the reaction of α-(4-nitrophenylazo)triphenylmethane (**1d**) with benzene in the presence of various additives, and the addition of acids was found to accelerate the reaction considerably (Table 5). Trifluoromethanesulfonic acid (TfOH) showed the most significant effect to accelerate the reaction (Entries 2, 3, and 4), and the reaction became faster as the amount of trifluoromethanesulfonic acid was increased (Entries 4, 5, 6, and 7). Although BF_3·OEt_2 was effective as well as Brønsteds acids in terms of the acceleration of the oxidation, the yield of the product was somewhat low (Entry 8). In the reactions described above, the azo compound **1d** was added into the solution of CAN and TfOH (Method A). The yield of the product was found to be improved by adding TfOH into the mixture of **1d** and CAN (Method B) (Entry 4, in parentheses). This acceleration effect is thought to be due to a ligand exchange of hexanitratocerate ($[Ce(NO_3)_6]^{2-}$), though details are not clear.[27,28] When potassium carbonate was added in place of an acid, the acceleration was not observed

Table 5. Effect of Additives in the Reaction of **1d** with Benzene[a]

Entry	Additive (Molar amounts)	Reaction time/h	Yield of *p*-**2d**/%
1	None	49	73
2	4-Me–$C_6H_4SO_3H$·H_2O (3)	24	68
3	(+)-10-Camphorsulfonic acid (3)	16	70
4	CF_3SO_3H (3)	2	57 (77)[b]
5	CF_3SO_3H (2)	3.5	60
6	CF_3SO_3H (1)	23	69
7	CF_3SO_3H (0.5)	48	65
8	BF_3·OEt_2 (3)	0.5	50
9	K_2CO_3 (5)	67	77

a) The reactions were carried out by Method A unless otherwise noted. All reactions were quenched when the azo compound **1d** was completely consumed. b) Trifluoromethanesulfonic acid was added into the solution of the azo compound and cerium(IV) ammonium nitrate (Method B).

Table 6. Reaction of α-(4-Nitro and 4-Bromophenylazo)triphenylmethanes with Arenes in the Presence of Trifluoromethanesulfonic Acid[a]

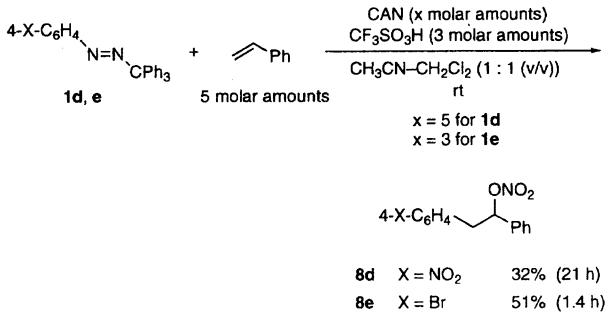


Substrate	R^1	R^2	Reaction time/h	Product	Yield/%	*o*:*m*:*p*[b]
1d[c]	H	H	2	**2d**	77	—
	Me	H	2	**3d**	58	63:22:15
	Me	Me	2	**4d**	56	—
1e[d]	H	H	2	**2e**	53	—
	Me	H	2.5	**3e**	39	66:21:13
	Me	Me	0.7	**4e**	34	—

a) Trifluoromethanesulfonic acid (3 molar amounts) was added into the mixture of the azo compound and cerium(IV) ammonium nitrate (Method B). b) Determined by ^{1}H NMR. c) 5 molar amounts of CAN were used. d) 3 molar amounts of CAN were used.

but the yield of the product **2d** was slightly improved (Entry 9).

The addition of acid was effective not only in the reaction of the nitrophenylazo compound **1d** with benzene, but in the reaction of the phenylazo compound **1a** and the bromophenylazo compound **1e** with arenes and olefins (Table 6 and Eq. 3) when reactions were carried out by Method B. The reaction time was shortened in every case (2 d to 2 h for **1d**, 1 d to 1.5 h for **1e**), except for the reaction of **1d** with styrene in which the oxidation of styrene was prior to that of **1d**. The reaction of **1a** with CAN was sufficiently fast and the addition of acid is considered not to be necessary.



(3)

In conclusion, the one-electron oxidation of α-(arylazo)triphenylmethanes with CAN generated aryl radicals without the formation of triphenylmethyl radical, and the aryl radicals reacted with various aromatic compounds and olefins to afford the corresponding addition products in moderate to good yields. The oxidation of the arylazo compounds with CAN was significantly accelerated by the addition of TfOH.

Experimental

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker AM 500 spectrometer in $CDCl_3$ solutions using $CHCl_3$ (δ=7.24) as an internal standard. IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-SX102A mass spectrometer at an ionization energy of 70 eV. A GC-MS analysis was performed on Shimadzu GC-14A (column, Shimadzu CBP1-M25-0.25, carrier gas, He (0.5—0.75 kg cm^{-2}); injection, 270 °C; temperature programming, held at 180 °C for 4 min, then elevated at a rate of 20 °C min^{-1} to 250 °C) and QP-2000 GC-MS instruments. Analytical high-performance liquid chromatography (HPLC) was carried out with Shimadzu LC-6A and C-R6A instruments using 6 mm × 25 cm Chromato Packings Center ULTRON SIL column (mobile phase: hexane–ethyl acetate, 500:1). Preparative HPLC was carried out with Japan Analytical Industry Co., Ltd, LC-908 liquid chromatograph using JAIGEL-1H and -2H GPC column (mobile phase: chloroform). The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Acetonitrile and dichloromethane were distilled from P_2O_5, then from CaH_2, and dried over Molecular Sieves 4A. Benzene and toluene were distilled after the azeotropic removal of water. Other aromatic solvents were distilled from CaH_2. CAN (Kanto Chemical Co., Inc., guaranteed grade) was dried under vacuum at 80 °C before use. α-(Arylazo)triphenylmethanes (**1a—d**) were synthesized according to the literature procedures.[29] Preparative TLC was performed on a silica gel (Wakogel B-5F). All reactions were carried out under an argon atmosphere.

Typical Procedure for the Reaction of α-(Arylazo)triphenylmethanes with Aromatic Compounds. To a solution of CAN (452.0 mg, 0.824 mmol) in acetonitrile (2 ml) was added a solution of α-(4-nitrophenylazo)triphenylmethane (**1d**) (65.6 mg, 0.167 mmol) in benzene (2 ml) at room temperature. After the resulting solution was stirred for 49 h, water was added. The mixture was extracted with dichloromethane (15 ml×4) and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by TLC (hexane–benzene, 1:1) to afford the product 4-nitrobiphenyl (***p*-2d**) (24.4 mg, 0.122 mmol, 73%). When the electron-rich substrates were employed, the quantity of CAN was reduced (2—3 molar amounts).

A larger scale run (**1d**, 395.4 mg, 1.00 mmol; CAN, 2.71 g, 4.95 mmol) afforded the same result (***p*-2d**, 149.7 mg, 0.751 mmol, 75% yield).

The spectral data are as follows, which show good agreement with those of the literature or authentic samples:

Biphenyl (2a): 9.1 mg (0.059 mmol, 27%) from 74.8 mg (0.215 mmol) of **1a**. Colorless crystals; mp 67.5—68.5 °C (MeOH) (lit,[4] 70.5 °C); IR (KBr) 3030, 1477, 1429, 731, 696 cm^{-1}; ^{1}H NMR δ=7.32—7.36 (1H, m (t-like)), 7.42—7.45 (2H, m (t-like)), 7.58—7.60 (2H, m (d-like)).

Methylbiphenyls (2b): 3.8 mg (0.023 mmol, 11%) from 74.9 mg (0.215 mmol) of **1a**. Isomer mixture (*o*, *m*, *p*). Colorless oil: ^{1}H NMR δ=2.25 (3H×0.19, s, *para*-isomer), 2.38 (3H×0.32, s, *meta*-isomer), 2.40 (3H×0.49, s, *ortho*-isomer), 7.14—7.15 (2H×0.32, m, *meta*), 7.22—7.24 (1.06H, m), 7.30—7.33 (2.17H, m), 7.37—7.43 (2.98H, m), 7.47—7.48 (2H×0.32, m (d-like), *meta*), 7.55—7.57 (1.51H, m), GC-MS analysis, t_R=4.0 min (*o*-isomer), *m*/*z* (rel intensity) 168 (M$^+$; 100), 167 (99), 153 (44), 152 (36); t_R=4.7 min (*m*-isomer), *m*/*z* (rel intensity) 168 (M$^+$; 100), 167 (61), 153 (18), 152 (26); t_R=4.8 min (*p*-isomer), *m*/*z* (rel intensity) 168 (M$^+$; 100), 167 (84), 153 (23), 152 (25).

The isomer ratio was determined by the integral value of methyl protons.

Methoxybiphenyls (2c): 8.3 mg (0.045 mmol, 14%) from 111.4 mg (0.320 mmol) of **1a**. Isomer mixture (*o*, *m*, *p*). Colorless oil; ^{1}H NMR δ=3.80 (3H×0.71, s, *ortho*-isomer), 3.84 (3H×0.05, s, *para*-isomer), 3.85 (3H×0.24, s, *meta*-isomer), 6.88—6.90 (1H×0.24, m, *meta*), 6.97—6.98 (0.81H, m, *ortho* and *para*), 7.00—7.03 (1H×0.71, m (t-like), *ortho*), 7.11—7.12 (1H×0.24, m (s-like), *meta*), 7.17—7.19 (1H×0.24, m (d-like), *meta*), 7.29—7.36 (2.76H, m), 7.38—7.44 (2.00H, m), 7.50—7.52 (1.52H, m, *ortho* and *para*), 7.57—7.58 (2H×0.24, m (d-like), *meta*). GC-MS analysis, t_R=5.2 min (*o*-isomer), *m*/*z* (rel intensity) 184 (M$^+$; 100), 169 (57), 141 (36), 115 (37); t_R=5.8 min (*m*- and *p*-isomer), *m*/*z* (rel intensity) 184 (M$^+$; 100), 154 (23), 153 (20), 141 (26), 115 (29).

The isomer ratio was determined by the integral value of methoxy protons.

Nitrobiphenyls (2d): Only ortho isomer could be separated. 11.9 mg (0.0597 mmol, 21%) from 99.1 mg (0.284 mmol) of **1a**. Pale yellow oil; IR (CCl_4) 3066, 1531, 1355 cm^{-1}; ^{1}H NMR δ=7.29—7.32 (2H, m), 7.39—7.41 (4H, m), 7.43 (1H, dd, *J*=1.4 and 7.5 Hz), 7.45—7.48 (1H, m (dt-like)), 7.58—7.62 (1H, m (dt-like)), 7.84 (1H, dd, *J*=1.1 and 8.1 Hz). Meta and para isomers were obtained as a mixture. 9.0 mg (0.045 mmol, 16%) from 99.1 mg (0.284 mmol) of **1a**. Faintly yellow oil; ^{1}H NMR δ=7.41—7.45 (1H (*para*), m (t-like)), 7.47—7.50 (3H (*meta*) and 2H (*para*) m), 7.60—7.62 (3H (*meta*) and 2H (*para*), m), 7.72 (2H (*para*), d, *J*=8.9 Hz), 7.89—7.91 (1H (*meta*), m), 8.18—8.20 (1H (*meta*), m), 8.28 (2H (*para*), d, *J*=8.9 Hz), 8.45 (1H (*meta*), t, *J*=2.0 Hz). GC-MS analysis, t_R=6.2 min (*o*-isomer), *m*/*z* (rel intensity) 199 (M$^+$; 20), 152 (100), 76 (65); t_R=7.1 min (*m*-isomer), *m*/*z* (rel intensity) 199 (M$^+$; 89), 152 (100), 76 (34); t_R=7.3 min (*p*-isomer), *m*/*z* (rel intensity) 199 (M$^+$; 99), 152 (100), 76 (25).

The isomer ratio was determined by the integral value of protons on aromatic ring.

4-Nitrobiphenyl (*p*-2d): 24.4 mg (0.122 mmol, 73%) from 65.6 mg (0.167 mmol) of **1d**. Faintly yellow crystals; mp 111.5—112.0 °C (hexane–ethyl acetate) (lit, 114 °C,[4] also reported as 113 °C[30]); IR (KBr) 1597, 1514, 1346, 852, 742, 696 cm^{-1}; ^{1}H NMR δ=7.41—7.45 (1H, m (t-like)), 7.47—7.50 (2H, m (t-like)), 7.60—7.62 (2H, m (t-like)), 7.72 (2H, d, *J*=8.9 Hz), 8.28 (2H, d, *J*=8.9 Hz).

4-Bromobiphenyl (*p*-2e): 24.8 mg (0.105 mmol, 78%) from 58.0 mg (0.136 mmol) of **1e**. Off-white crystals; mp 89.0—90.0 °C (hexane) (lit,[4] 91.2 °C); IR (KBr) 3060, 3032, 1475, 1390, 1078, 1003, 829, 756, 688 cm^{-1}; ^{1}H NMR δ=7.34—7.37 (1H, m), 7.41—7.46 (2H, m), 7.45 (2H, d, *J*=8.5 Hz), 7.53—7.56 (2H, m), 7.55 (2H, d, *J*=8.5 Hz).

Chlorobiphenyls (2f): 16.9 mg (0.0895 mmol, 26%) from 111.3 mg (0.319 mmol) of **1a**. Isomer mixture (*o*, *m*, *p*). ^{1}H NMR measurement afforded complex signals in a

range from δ=7.18 to 7.56. GC-MS analysis, t_R=4.8 min (*o*-isomer), *m/z* (rel intensity) 190 ($(M+2)^+$; 32), 188 (M^+; 100), 153 (23), 152 (48), 151 (15), 76 (35); t_R=5.35 min (*m*-isomer), *m/z* (rel intensity) 190 ($(M+2)^+$; 37), 188 (M^+, 100), 153 (23), 152 (52), 151 (13), 76 (37); t_R=5.40 min (*p*-isomer), *m/z* (rel intensity) 190 ($(M+2)^+$; 32), 188 (M^+; 100), 153 (20), 152 (44), 151 (14), 76 (31).

The isomer ratio was determined by the integral value of GC, comparing the retention times to those of authentic samples prepared by the literature method.[31]

n-Methyl-4′-nitrobiphenyls (3d):[15,32] 15.5 mg (0.0727 mmol, 46%) from 62.7 mg (0.159 mmol) of **1d**. Isomer mixture (n=2, 3, 4). ^{1}H NMR δ=2.25 (3H×0.60, s, *ortho*-isomer), 2.41 (3H×0.16, s, *para*-isomer), 2.43 (3H×0.24, s, *meta*-isomer), 7.20 (1H×0.60, d, J=7.5 Hz, *ortho*), 7.25—7.32 (2.60H, m), 7.36—7.38 (1H×0.24, m (t-like), *meta*), 7.40—7.42 (2H×0.24, m (d-like), *meta*), 7.47 (2H×0.60, d, J=8.7 Hz, *ortho*), 7.50—7.52 (2H×0.16, m (d-like), *para*), 7.69—7.72 (0.80H, m, *meta* and *para*), 8.25—8.28 (0.80H, m, *meta* and *para*), 8.26 (2H×0.60, d, J=8.7 Hz, *ortho*).

The isomer ratio was determined by the integral value of methyl protons.

4-Bromo-n′-methylbiphenyls (3e):[33] 17.2 mg (0.0696 mmol, 42%) from 71.0 mg (0.166 mmol) of **1e**. Isomer mixture (n=2, 3, 4). ^{1}H NMR δ=2.24 (3H×0.62, s, *ortho*-isomer), 2.38 (3H×0.15, s, *para*-isomer), 2.41 (3H×0.23, s, *meta*-isomer), 7.17—7.19 (2.19H, m) 7.32—7.35 (0.78H, m), 7.42—7.44 (1.16H, m), 7.52—7.57 (1.98H, m).

The isomer ratio was determined by the integral value of methyl protons.

2,5-Dimethyl-4′-nitrobiphenyl (4d):[5] 21.9 mg (0.0964 mmol, 60%) from 62.4 mg (0.159 mmol) of **1d**. Light yellow crystals; mp 97.5—98.5 °C (hexane) (lit,[5] 87—88 °C);[34] IR (KBr) 2945, 1599, 1523, 1350, 1105, 854, 818 cm^{-1}; ^{1}H NMR δ=2.21 (3H, s), 2.35 (3H, s), 7.02 (1H, s), 7.13 (1H, d, J=7.8 Hz), 7.18 (1H, d, J=7.8 Hz), 7.47 (2H, d, J=8.8 Hz), 8.25 (2H, d, J=8.8 Hz).

4-Bromo-2′,5′-dimethylbiphenyl (4e):[5] 17.1 mg (0.0655 mmol, 38%) from 73.1 mg (0.171 mmol) of **1e**. Colorless oil; IR (neat) 3008, 2922, 1483, 1072, 1011, 827, 812 cm^{-1}; ^{1}H NMR δ=2.19 (3H, s), 2.33 (3H, s), 7.00 (1H, s), 7.07 (1H, br d), 7.14 (1H, d, J=7.7 Hz), 7.17 (2H, d, J=8.4 Hz), 7.51 (2H, d, J=8.4 Hz).

n-Methoxy-4′-nitrobiphenyls (5d):[35] Only *ortho* isomer (n=2) could be separated. 16.5 mg (0.0720 mmol, 44%) from 64.9 mg (0.165 mmol) of **1d**. Yellow oil; IR (neat) 3073, 2941, 1599, 1514, 1346, 1263, 1242, 858, 758, 735 cm^{-1}; ^{1}H NMR δ=3.82 (3H, s), 7.00—7.02 (1H, m (d-like)), 7.04—7.07 (1H, m (t-like)), 7.31—7.32 (1H, m (d-like)), 7.37—7.40 (1H, m (t-like)), 7.67 (2H, d, J=8.8 Hz), 8.24 (2H, d, J=8.8 Hz). *Meta* and *para* isomers (n=3, 4) were obtained as a mixture with 4-nitroanisole and further purification with GPC was required. 8.0 mg (0.035 mmol, 21%) from 64.9 mg (0.165 mmol) of **1d**. Yellow crystals; ^{1}H NMR δ=3.86 (3H (*para*), s), 3.87 (3H (*meta*), s), 6.96—6.98 (1H (*meta*), br dd), 7.00 (2H (*para*), d, J=8.8 Hz), 7.12 (1H (*meta*), t, J=2.1 Hz), 7.18—7.19 (1H (*meta*), br d), 7.39 (1H (*meta*), t, J=8.0 Hz), 7.56 (2H (*para*), d, J=8.8 Hz), 7.67 (2H (*para*), d, J=8.8 Hz), 7.71 (2H (*meta*), d, J=8.8 Hz), 8.25 (2H (*para*), d, J=8.8 Hz), 8.27 (2H (*meta*), d, J=8.8 Hz).

The isomer ratio was determined by the integral value of methoxy protons.

4-Bromo-2′-methoxybiphenyl (*o*-5e): 14.7 mg (0.0559 mmol, 33%) from 72.0 mg (0.168 mmol) of **1e**. Colorless oil; IR (neat) 3062, 2941, 1587, 1498, 1477, 1390, 1259, 1238, 825, 754 cm^{-1}; ^{1}H NMR δ=3.80 (3H, s), 6.97 (1H, d, J=8.2 Hz), 7.02 (1H, br dd), 7.28 (1H, dd, J=1.7 and 7.5 Hz), 7.33 (1H, dt, J_d=1.7, J_t=8.2 Hz), 7.40 (2H, d, J=8.5 Hz), 7.52 (2H, d, J=8.5 Hz). HRMS: *m/z* 261.9966. Calcd for $C_{13}H_{11}{}^{79}BrO$: M, 261.9993.

4-Bromo-3′-methoxybiphenyl (*m*-5e): 4.2 mg (0.016 mmol, 9.5%) from 72.0 mg (0.168 mmol) of **1e**. Colorless oil; IR (neat) 2999, 2939, 1604, 1477, 1296, 1217, 823, 781 cm^{-1}; ^{1}H NMR δ=3.84 (3H, s), 6.89 (1H, dd, J=2.5 and 8.3 Hz), 7.06 (1H, br t), 7.12 (1H, br ddd (t-like)), 7.34 (1H, br dd), 7.43 (2H, d, J=8.5 Hz), 7.53 (2H, d, J=8.5 Hz). HRMS: Found: *m/z* 262.0019. Calcd for $C_{13}H_{11}{}^{79}BrO$: M, 261.9993.

4-Bromo-4′-methoxybiphenyl was not detected.

4′-Nitro-1-phenylnaphthalene (6d):[36] Purification by TLC (hexane–benzene, 1:1) afforded a mixture with 1- and 2-nitronaphthalenes and further purification by GPC was required. 35.6 mg (0.143 mmol, 64%) from 87.9 mg (0.223 mmol) of **1d**. This sample contained small amount (8%) of 4′-nitro-2-phenylnaphthalene (analyzed by GC-MS).[37] Yellow crystals; IR (KBr) 1595, 1514, 1348, 860, 802, 779 cm^{-1}; ^{1}H NMR δ=7.41 (1H, d, J=7.0 Hz), 7.45—7.48 (1H, m (t-like)), 7.51—7.54 (1H, m (t-like)), 7.52—7.56 (1H, m (t-like)), 7.66 (2H, d, J=8.6 Hz), 7.92 (1H, d, J=8.2 Hz), 7.93 (1H, d, J=8.1 Hz), 8.34 (2H, d, J=8.6 Hz).

Typical Procedure for the Reaction of α-(Arylazo)triphenylmethanes with Olefinic Compounds. To a solution of CAN (455.4 mg, 0.831 mmol) in acetonitrile (2 ml) was added a solution of α-(phenylazo)triphenylmethan (**1a**) (59.9 mg, 0.172 mmol) and styrene (87.9 mg, 0.844 mmol) in dichloromethane (2 ml) at room temperature. After the resulting solution was stirred for 5 h, water was added. The mixture was extracted with dichloromethane (15 ml×4), and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by TLC (hexane–benzene, 3:1) to afford the product 1,2-diphenylethyl nitrate (**7a**) (25.1 mg, 0.103 mmol, 60%).

A larger scale run (**1a**, 349.5 mg, 1.00 mmol; styrene, 525.9 mg, 5.05 mmol; CAN, 2.72 mg, 4.95 mmol) afforded a somewhat poor result (**7a**, 101.3 mg, 0.416 mmol, 41% yield).

Spectral data are as follows.

1,2-Diphenylethyl Nitrate (7a): 25.1 mg (0.103 mmol, 60%) from 59.9 mg (0.172 mmol) of **1a**. Pale yellow oil; IR (neat) 3031, 1631, 1277, 862, 756, 700 cm^{-1}; ^{1}H NMR δ=3.09 (1H, dd, J=6.2 and 14.1 Hz), 3.27 (1H, dd, J=8.0 and 14.1 Hz), 5.93 (1H, dd, J=6.2 and 8.0 Hz), 7.12—7.13 (2H, m), 7.19—7.37 (8H, m); ^{13}C NMR δ=41.06, 86.11, 126.60, 127.08, 128.54, 128.71, 128.99, 129.43, 135.61, 137.37. Found: C, 69.10; H, 5.64; N, 5.96%. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76%.

2-(4-Nitrophenyl)-1-phenylethyl Nitrate (7d): 24.6 mg (0.0853 mmol, 48%) from 70.2 mg (0.178 mmol) of **1d**. Pale yellow crystals; mp 85.5—86.5 °C (petroleum ether–diethyl ether); IR (KBr) 1633, 1604, 1518, 1346, 1274, 887, 858, 698 cm^{-1}; ^{1}H NMR δ=3.21 (1H, dd, J=6.2 and 14.1 Hz), 3.36 (1H, dd, J=7.8 and 14.1 Hz), 5.94

(1H, dd, J=6.2 and 7.8 Hz), 7.25—7.29 (4H, m), 7.34—7.36 (3H, m), 8.11 (2H, d, J=9.2 Hz); ^{13}C NMR δ=40.76, 84.87, 123.75, 126.48, 128.95, 129.41, 130.41, 136.47, 142.99, 147.21. Found: C, 58.46; H, 4.20; N, 9.77%. Calcd for $C_{14}H_{12}N_2O_5$: C, 58.33; H, 4.20; N, 9.72%.

2-(4-Bromophenyl)-1-phenylethyl Nitrate (7e): 33.0 mg (0.102 mmol, 61%) from 71.5 mg (0.167 mmol) of **1e**. Colorless crystals; mp 65.0—66.0 °C (petroleum ether–diethyl ether); IR (KBr) 1622, 1489, 1277, 852, 701, 536 cm^{-1}; ^{1}H NMR δ=3.04 (1H, dd, J=6.3 and 14.2 Hz), 3.21 (1H, dd, J=7.8 and 14.2 Hz), 5.87 (1H, dd, J=6.3 and 7.8 Hz), 6.97 (2H, d, J=8.3 Hz), 7.26—7.29 (2H, m), 7.32—7.36 (3H, m), 7.37 (2H, d, J=8.3 Hz), ^{13}C NMR J=40.44, 85.60, 121.14, 126.57, 128.80, 129.13, 131.17, 131.66, 134.49, 136.96. Found: C, 52.21; H, 3.92; N, 4.43%. Calcd for $C_{14}H_{12}BrNO_3$: C, 52.20; H, 3.75; N, 4.35%.

1-Acetoxy-2-(4-nitrophenyl)ethyl Nitrate (8d): 16.9 mg (0.0754 mmol, 46%) from 64.7 mg (0.164 mmol) of **1d**. Light yellow crystals; mp 51.5—52.5 °C (petroleum ether–diethyl ether); IR (KBr) 1761, 1682, 1523, 1348, 1288, 1225, 1201, 1009, 818 cm^{-1}; ^{1}H NMR δ=2.08 (3H, s), 3.22 (2H, d, J=5.8 Hz), 7.07 (1H, t, J=5.8 Hz), 7.43 (2H, J=8.7 Hz), 8.19 (2H, d, J=8.7 Hz); ^{13}C NMR δ=20.54, 37.57, 94.56, 123.93, 130.75, 140.18, 147.59, 168.49. Found: C, 44.50; H, 3.61; N, 10.25%. Calcd for $C_{10}H_{10}N_2O_7$: C, 44.45; H, 3.73; N, 10.37%.

1-Acetoxy-2-(4-bromophenyl)ethyl Nitrate (8e): 11.4 mg (0.0375 mmol, 22%) from 73.4 mg (0.172 mmol) of **1e**. Colorless oil; IR (neat) 3002, 2935, 1765, 1658, 1489, 1375, 1286, 1215, 1203, 1011, 822 cm^{-1}; ^{1}H NMR δ=2.07 (3H, s), 3.06 (2H, d, J=5.9 Hz), 7.03 (1H, t, J=5.9 Hz), 7.12 (2H, d, J=8.4 Hz), 7.44 (2H, d, J=8.4 Hz); ^{13}C NMR δ=20.57, 37.25, 95.15, 121.78, 131.42, 131.77, 131.90, 168.53. Found: C, 39.76; H, 3.60; N, 4.43%. Calcd for $C_{10}H_{10}BrNO_5$: C, 39.50; H, 3.31; N, 4.61%.

1-(2-Methoxycarbonylphenyl)-2-phenylethyl Nitrate (9a): 21.9 mg (0.0727 mmol, 43%) from 58.9 mg (0.169 mmol) of **1a**. Colorless crystals; mp 65.5—66.0 °C (hexane); IR (KBr) 3030, 1716, 1627, 1435, 1300, 1273, 1252, 870, 758, 704 cm^{-1}; ^{1}H NMR δ=3.02 (1H, dd, J=9.7 and 14.6 Hz), 3.27 (1H, dd, J=3.3 and 14.6 Hz), 3.94 (3H, s), 7.00 (1H, dd, J=3.3 and 9.7 Hz), 7.23—7.26 (1H, br ddd), 7.29—7.35 (4H, m), 7.38—7.41 (1H, br ddd), 7.54—7.58 (2H, m), 8.01 (1H, d, J=7.3 Hz); ^{13}C NMR δ=41.06, 52.39, 82.59, 125.42, 126.98, 127.91, 128.21, 128.46, 129.52, 130.92, 133.03, 136.43, 140.97, 166.87. Found: C, 63.49; H, 5.08; N, 4.73%. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65%.

1-(2-Methoxycarbonylphenyl)-2-(4-nitrophenyl)ethyl Nitrate (9d): 33.5 mg (0.0967 mmol, 58%) from 65.5 mg (0.166 mmol) of **1d**. Colorless crystals; mp 141.5 °C (hexane–diethyl ether); IR (KBr) 2947, 1714, 1641, 1601, 1522, 1350, 1300, 1273, 1250, 854, 710 cm^{-1}; ^{1}H NMR δ=3.10 (1H, dd, J=9.8 and 14.5 Hz), 3.40 (1H, dd, J=3.0 and 14.5 Hz), 3.95 (3H, s), 6.98 (1H, dd, J=3.0 and 9.8 Hz), 7.41—7.44 (1H, m (t-like)), 7.53—7.60 (2H, m), 7.54 (2H, d, J=8.7 Hz), 8.05 (1H, dd, J=1.0 and 7.8 Hz), 8.17 (2H, d, J=8.7 Hz); ^{13}C NMR δ=40.67, 52.52, 81.85, 123.72, 125.14, 127.60, 128.57, 130.47, 131.18, 133.31, 140.53, 144.14, 147.19, 166.83. Found: C, 55.35; H, 4.15; N, 8.21%. Calcd for $C_{16}H_{14}N_2O_7$: C, 55.49; H, 4.07; N, 8.09%.

2-(4-Bromophenyl)-1-(2-methoxycarbonylphenyl)ethyl Nitrate (9e): 33.1 mg (0.0871 mmol, 52%) from 71.7 mg (0.168 mmol) of **1e**. Colorless crystals; mp 108.0 °C (hexane); IR (KBr) 2947, 1711, 1626, 1484, 1439, 1302, 1273, 1252, 881, 800 cm^{-1}; ^{1}H NMR δ=2.96 (1H, dd, J=9.6 and 14.6 Hz), 3.23 (1H, dd, J=3.2 and 14.6 Hz), 3.93 (3H, s), 6.94 (1H, dd, J=3.2 and 9.6 Hz), 7.22 (2H, d, J=8.3 Hz), 7.38—7.44 (1H, m), 7.43 (2H, d, J=8.3 Hz), 7.53—7.56 (2H, m), 8.02 (1H, d, J=7.7 Hz); ^{13}C NMR δ=40.42, 52.42, 82.25, 121.03, 125.31, 127.78, 128.32, 131.00, 131.30, 131.57, 133.12, 135.45, 140.76, 166.83. Found: C, 50.38; H, 3.85; N, 3.97%. Calcd for $C_{16}H_{14}BrNO_5$: C, 50.55; H, 3.71; N, 3.68%.

Typical Procedure for the Reaction of α-(Arylazo)triphenylmethanes with Aromatic Compounds in the Presence of an Acid. Method A: To a solution of CAN (271.2 mg, 0.495 mmol) in acetonitrile (0.5 ml) was added a solution of TfOH (76.2 mg, 0.508 mmol) in acetonitrile (1.5 ml) and a solution of α-(4-nitrophenylazo)-triphenylmethane (**1d**) (65.4 mg, 0.166 mmol) in benzene (2 ml) successively at room temperature. The color of the solution immediately turned to brown from orange-yellow. After the resulting solution was stirred for 2 h (during which the brown color turned back to orange-yellow), water was added. The mixture was extracted with dichloromethane (15 ml×4), and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by TLC (hexane–benzene, 1 : 1) to afford the product 4-nitrobiphenyl (***p*-2d**, 18.7 mg, 0.0939 mmol, 57%).

Method B: To a solution of CAN (270.4 mg, 0.493 mmol) in acetonitrile (2 ml) was added a solution of α-(4-nitrophenylazo)triphenylmethane (**1d**) (64.6 mg, 0.164 mmol) in benzene (1.5 ml) and a solution of TfOH (76.6 mg, 0.510 mmol) in benzene (0.5 ml) successively at room temperature. The color of the solution immediately turned to brown from orange-yellow. After the resulting solution was stirred for 2 h (during which the brown color turned back to orange-yellow), water was added. The mixture was extracted with dichloromethane (15 ml×4), and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by TLC (hexane–benzene, 1 : 1) to afford the product 4-nitrobiphenyl (***p*-2d**, 25.1 mg, 0.126 mmol, 77%).

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