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Mechanistic Study of a Pd/C-Catalyzed Reduction of Aryl Sulfonates Using the Mg–MeOH–NH_4OAc System

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Abstract: A method for the deoxygenation of phenolic hydroxy groups via aryl triflates or mesylates has been established by using a combination of Pd/C–Mg–MeOH. The addition of NH_4OAc to the system markedly accelerated the reaction rate and expanded the scope of the reaction. Mechanistic studies suggested that a single-electron transfer process from the Pd^0 center to the benzene ring is involved in the reduction of aryl sulfonates and that NH_4OAc works as a solubilization reagent of the Mg salt and as an accelerator of the electron transfer, thus enhancing the reaction process. Our method was also applicable to the regioselective deuteration of benzene derivatives with CH_3OD as the solvent and deuterium source: the original hydroxy group could be efficiently replaced with a deuterium atom.

Keywords: aryl sulfonates · deoxygenation · heterogeneous catalysis · palladium · single-electron transfer

Introduction

The development of a deoxygenation method for phenol derivatives is one of the most important subjects in synthetic organic and medicinal chemistry. Many organic compounds containing a phenolic moiety are well known as biologically and functionally important compounds, and phenolic hydroxy groups frequently play a crucial role in expressing those activities.[1] In many cases, the preparation of the corresponding non-phenolic derivatives as reference compounds is necessary for structure–activity relationship studies. Direct deoxygenation methods require both excess amounts of the reagents and drastic reaction conditions[2] and have a narrow substrate scope,[2b,c] because it is difficult to directly cleave phenolic hydroxy groups from the aromatic rings as a result of their stability.

To improve the leaving ability of the phenolic hydroxy group, it was converted into the corresponding sulfonate,[1a,3–5] isourea,[1a,6] dimethyl thiocarbamate,[1a] aryl ether,[7] 5-phenyltetrazolyl ether,[8] and phosphate ether group.[9] However, these methods include disadvantages such as poor stability of the activated phenols, severe reaction conditions, the use of environmentally harmful phosphine ligands, and the use more than stoichiometric quantities of metal-reducing reagents. Therefore, establishment of a generally applicable method for the deoxygenation of phenol derivatives is still a broad developing area.

Recently, we reported a method for a Pd/C–Mg-mediated cleavage of a phenolic hydroxy group after conversion into the corresponding aryl triflate or mesylate.[10] This reaction was remarkably accelerated by the addition of NH_4OAc to the reaction mixture. Herein, we discuss the mechanism of the reductive cleavage of aryl sulfonates by using the Pd/C–Mg–MeOH system, including the effect of NH_4OAc, and report on further applications and detailed experimental procedures.

Results and Discussion

In the course of our investigation of novel Pd/C-catalyzed reactions, we found that the Pd/C-catalyzed reductive cleavage of 3,4,5-trimethoxyphenyl triflate (**1a**) in MeOH took place in the presence of 0.5 equivalents of Mg metal to give 1,2,3-trimethoxybenzene (**2a**) in 45% yield (Scheme 1).

This result encouraged us to tune the reaction conditions (Table 1). No reaction was observed in the absence of the metal or Pd/C (Table 1, entries 1 and 4, respectively). Moreover, the reduction did not proceed in an oxygen atmos-

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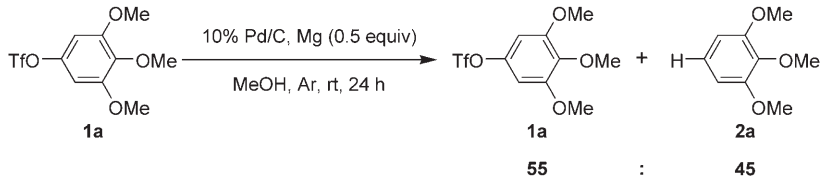
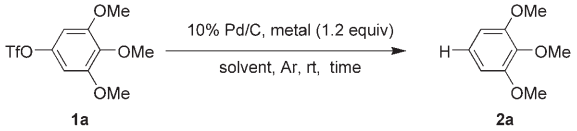


Scheme 1. Our initial study of a Pd/C-catalyzed reductive cleavage of an aryl triflate.

Table 1. Pd/C-Catalyzed reductive cleavage of 3,4,5-trimethoxyphenyl triflate (**1a**) using various metals and solvents.[a]



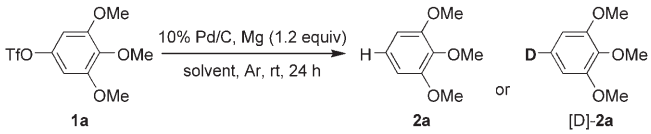
Entry	Metal	Solvent	T [h]	**1a**/**2a**[b]
1	none	MeOH	24	100:0
2	Mg[c]	MeOH	24	55:45
3	Mg	MeOH	12	0:100
4[d]	Mg	MeOH	24	100:0
5[e]	Mg	MeOH	24	100:0
6	$Mg(OMe)_2$	MeOH	24	100:0
7	Zn	MeOH	24	100:0
8	Al	MeOH	24	100:0
9	Fe	MeOH	24	100:0
10	Ni	MeOH	24	100:0
11	Mg	dry MeOH	24	0:100
12	Mg	$MeOH/H_2O$[f]	24	100:0
13	Mg	H_2O	24	100:0
14	Mg	EtOH	24	100:0
15	Mg	dry EtOH	24	100:0
16	Mg	EtOH/MeOH[g]	24	100:0
17	Mg	EtOH/MeOH[h]	24	41:59
18	Mg	*i*PrOH	24	100:0
19	Mg	CF_3CH_2OH	24	100:0
20	Mg	THF	24	100:0
21[i]	Mg	MeOH	24	100:0

[a] Reaction conditions: **1a** (158 mg, 500 μmol), 10% Pd/C (15.9 mg, 10 wt% of **1a**), metal (600 μmol), and solvent (2.0 mL) in an Ar atmosphere at room temperature. [b] The ratio was determined by using ^{1}H NMR spectroscopic analysis. [c] 0.5 equivalents. [d] Without 10% Pd/C. [e] In an O_2 atmosphere. [f] 4:1 ratio. [g] Addition of 20 equivalents of MeOH. [h] 1:1 ratio. [i] With TCNQ (0.01 equiv).

phere, as the Mg metal surface was readily coated by a layer of MgO (Table 1, entry 5). Whereas the use of 0.5 equivalents of Mg metal did not lead to complete cleavage of the triflate group (Scheme 1 and Table 1, entry 2), an increase in the amount of Mg metal up to 1.2 equivalents led to completion of the deoxygenation reaction (Table 1, entry 3). Neither $Mg(OMe)_2$ nor other metals, such as Zn, Al, Fe, and Ni, in the place of the Mg metal affected the reaction progress (Table 1, entries 6–10). The reaction was entirely solvent specific: 1) progress of the reaction was only observed in MeOH as the solvent (Table 1, entries 3 and 11); 2) the reduction did not proceed at all in H_2O, THF, and other alcoholic solvents, such as EtOH, *i*PrOH, and CF_3CH_2OH (Table 1, entries 14, 15, and 18–20, respectively); 3) H_2O and EtOH suppressed the reaction (Table 1, entries 12, 13, 16, and 17). The Mg metal dissolved only in MeOH, thus suggesting the solubility of the Mg metal in the solvent is an important factor in the progress of the reaction. From these experimental results, the use of a catalytic amount of Pd/C, a stoichiometric amount of Mg metal, and MeOH as the solvent was found to be indispensable for the completion of the reduction of the aryl triflates. Addition of a catalytic amount of 7,7,8,8-tetracyanoquinodimethane (TCNQ), a single-electron capture, to the reaction mixture thoroughly suppressed the reaction, thus suggesting the participation of a single-electron-transfer (SET) mechanism in the catalytic process.

To clarify the hydrogen source in this reaction, an investigation was carried out with four types of deuterated methanol as the solvent. It is apparent that the hydrogen (deuterium) source in these reactions is the acidic hydrogen (deuterium) atom of the methanol used as the solvent (Table 2); thus, MeOH works as a proton donor in this reaction.

Table 2. Determination of the hydrogen source.[a]

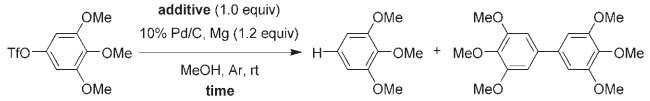


Entry	Solvent	**2a** or [D]-**2a**	Yield [%][b]
1	CH_3OH	**2a**	89
2	CD_3OH	**2a**	80
3	CH_3OD	[D]-**2a**	86
4	CD_3OD	[D]-**2a**	76

[a] Reaction conditions: **1a** (79.1 mg, 250 μmol), 10% Pd/C (8.0 mg, 10 wt% of **1a**), Mg (7.3 mg, 300 μmol), and solvent (1.0 mL) in an Ar atmosphere at room temperature for 24 h. [b] Yield of the isolated product.

Recently, we reported an acceleration effect caused by the addition of NH_4OAc to the Pd/C-catalyzed monoalkylation of primary amines using nitrile compounds as the alkylating reagents.[11] We expected that such an enhancement of the reactivity could be applicable to the present deoxygenation of the phenolic alcohol moiety, thus leading to the rapid formation of the deoxygenated product. Therefore, we investigated the acceleration effect of additives by using **1a** as a substrate (Table 3). The addition of NH_4OAc was very effective for the reaction: the reaction was completed within 1 h (Table 3, entries 2 and 3); furthermore, even only a catalytic amount of NH_4OAc produced the acceleration effect (Table 3, entry 4). As shown in Table 3, entries 5–8, other acetate salts were not effective as additives, as they rather suppressed the reduction. Moreover, other ammonium salts, such as NH_4HCO_3 and $(NH_4)_2CO_3$, exerted a suppressive effect on the reaction and caused the hydrolysis of the triflate, thus affording a mixture of the starting material **1a**, product **2a**, and hydrolyzed phenol (Table 3, entries 9 and 10).

Table 3. Effect of an additive on the Pd/C-catalyzed reductive cleavage of **1a**.[a]

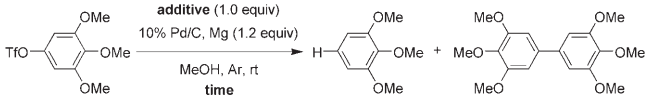


Entry	Additive	T [h]	**1a**/**2a**/**4a**[b]
1	none	12	0:100:0
2	NH_4OAc	0.5	2:98:0
3	NH_4OAc	1	0:100:0
4	NH_4OAc (0.01 equiv)	6	0:100:0
5	NaOAc	24	73:22:6
6	KOAc	24	79:15:6
7	LiOAc	24	80:16:4
8	$Cu(OAc)_2$	24	100:0:0
9	NH_4HCO_3	24	9:89:0[c]
10	$(NH_4)_2CO_3$	24	17:81:0[c]

[a] Reaction conditions: **1a** (79.1 mg, 250 μmol), 10% Pd/C (8.0 mg, 10 wt% of **1a**), Mg (7.3 mg, 300 μmol), additive (250 μmol), and MeOH (1.00 mL) in an Ar atmosphere at room temperature. [b] The ratio was determined by using ^{1}H NMR spectroscopic analysis. [c] Formation of 3,4,5-trimethoxyphenol was observed (2%).

To explain the acceleration effect of NH_4OAc rationally, we investigated the difference in the reactivity on the basis of the acidity of the acid counterpart and steric hindrance of the additives (Table 4). The use of ammonium salts consisting of more acidic counterparts, such as NH_4Cl, NH_4OCOCF_3, and HCO_2NH_4, accelerated the reaction to an extent similar to that with NH_4OAc, whereas NH_4OBz was not so effective (Table 4, entries 2–5). NH_4OAc, NH_4Cl, NH_4OCOCF_3, and HCO_2NH_4 probably facilitate the dissolution of the Mg metal in MeOH. The addition of AcOH afforded a similar result to that of NH_4OAc, thus suggesting that AcOH would work as a solubulizing agent for Mg metal (Table 4, entry 11).

Table 4. Additive effect on the reductive cleavage of **1a** using the derivatives of NH_4OAc.[a]



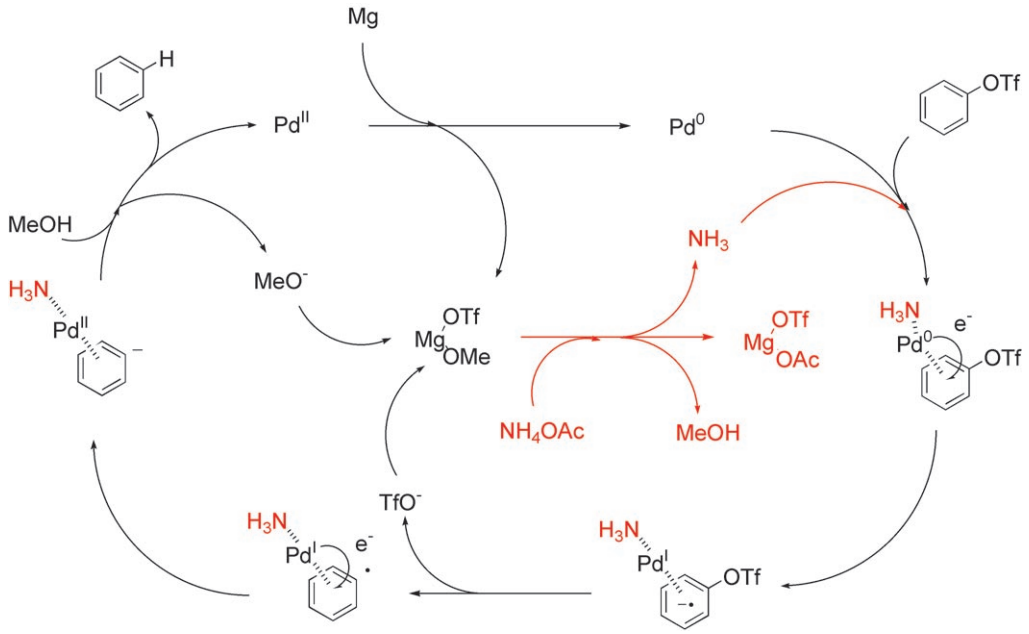
Entry	Additive	T [h]	**1a**/**2a**/**4a**[b]
1	none	12	0:100:0
2	NH_4Cl	1	0:100:0
3	NH_4OCOCF_3	0.5	0:100:0
4	HCO_2NH_4	1	0:100:0
5	NH_4OBz	48	18:82:0
6	NH_4OAc	1	0:100:0
7	$EtNH_3OAc$[c]	2	0:96:4
8	Et_2NH_2OAc	1	0:99:1
9	Et_3NHOAc[c]	24	71:24:5
10	Et_4NOAc	24	87:10:3
11	AcOH	1.5	0:95:5
12	NH_3[d]	1.5	0:97:2[e]
13	Et_3N[d]	24	34:65:trace[e]

[a] Reaction conditions: **1a** (79.1 mg, 250 μmol), 10% Pd/C (8.0 mg, 10 wt% of **1a**), Mg (7.3 mg, 300 μmol), additive (250 μmol), and MeOH (1.00 mL) in an Ar atmosphere at room temperature. [b] The ratio was determined by using ^{1}H NMR spectroscopic analysis. [c] The additive was prepared in situ. [d] Reaction conditions: **1a** (79.1 mg, 250 μmol), 10% Pd/C (8.0 mg, 3.00 mol% of **1a**), Mg (7.3 mg, 300 μmol), additive (6.00 mol%), and MeOH (1.00 mL) in an Ar atmosphere at room temperature. [e] Formation of 3,4,5-trimethoxyphenol was observed (1%).

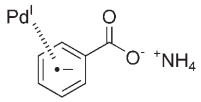
Next, we found that the number of substituents on the nitrogen atom of NH_4OAc was very important in producing the acceleration effect. Whereas Et_3NHOAc or Et_4NOAc depressed the reaction progress (Table 4, entries 9 and 10), $EtNH_3OAc$ or Et_2NH_2OAc afforded a comparable result to NH_4OAc (Table 4, entries 7 and 8). Furthermore, the addition of a catalytic amount of NH_3 (2 equivalents of Pd/C) could also accelerate the reaction as well as NH_4OAc, but the same amount of Et_3N suppressed the reaction (Table 4, entries 12 and 13). During the reaction, NH_4OAc or Et_3NHOAc would dissociate to NH_3 and AcOH or Et_3N and AcOH, respectively. We anticipated that such a difference between NH_4OAc and Et_3NHOAc in the additive effect depends on the coordination ability of the amine moiety to Pd metal, that is, bulky Et_3N should be harder to coordinate to the Pd center (see also Scheme 2).

Based on the above experimental results, we speculated that the present reductive deoxygenation process proceeds through the pathway outlined in Scheme 2. An initial SET[12] from the Pd^0 center to the aromatic ring of the aryl triflate should afford an anion radical, which could be converted into an aryl radical by the elimination of the trifluoromethanesulfonyloxy (OTf) anion. Then, the second SET process from the Pd^I center would take place to give an aryl anion, and protonation of the anion by MeOH would give the corresponding deoxygenated arene product together with Pd^{II}, which should be reduced to Pd^0 by the Mg metal. The resulting magnesium salt Mg(OTf)(OMe) would be converted into Mg(OTf)(OAc) in the presence of AcOH, based on the stabilization of the salt, thus generating MeOH and NH_3. Subsequently, the generated NH_3 could coordinate to the Pd^0 center to enhance the electron density of Pd; as a result, Pd-mediated electron transfer to the benzene ring could be accelerated. NH_4OAc works as a dual activator: NH_4OAc should contribute to both the enhanced solubility of the Mg metal by the formation of AcOH, which causes the quick reduction of Pd^{II} to Pd^0, and the acceleration of the SET process by the coordination of NH_3 to the Pd^0 center. On the other hand, in the case of the addition of NH_4OBz rather than NH_4OAc, the acceleration effect did not take place because a Pd-mediated electron transfer might have taken place competitively at the benzene ring of NH_4OBz or the substrate (Table 4, entry 5 and Scheme 3).

To explore the scope of the method, the deoxygenation of a variety of phenol derivatives was investigated (Table 5). AcOH, some ammonium salts (e.g, NH_4Cl), and ammonia exhibited an acceleration effect as well as NH_4OAc, but NH_4OAc was chosen as the additive because of its cost efficiency and near neutrality. The addition of one equivalent of NH_4OAc (Method B) dramatically improved the reactivity of electron-sufficient aryl triflates to afford the corresponding reduced products within 1 h (Table 5, entries 1–



Scheme 2. Plausible reaction mechanism.



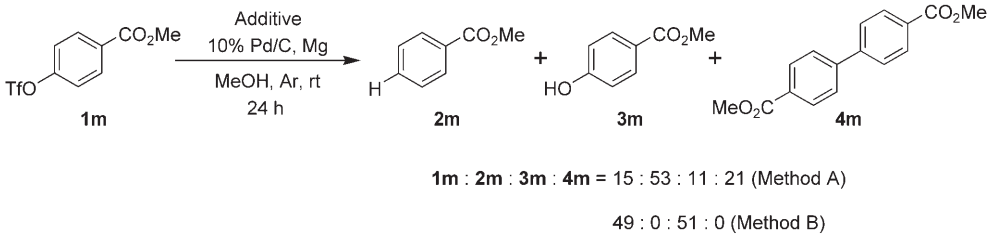
Scheme 3. The direction of the SET in NH_4OBz.

10). In the case of the electron-deficient substrates **1k** and **1l** (Table 5, entries 11 and 12), the addition of NH_4OAc was not necessary, and the formation of deoxygenated products was determined by analysis with GC/MS (100% conversion, respectively, because of the volatile nature of the products). When the benzoic ester derivatives **1m** and **1n** were employed as substrates, we encountered difficulty in selective deoxygenation under the optimized conditions (see Table 5, entries 13 and 14; Methods A and B; and Scheme 4). After minor tuning of the reaction conditions, an excess amount of NH_4OAc (1.2–5.0 equiv) or/and Mg metal (1.2–2.4 equiv) achieved the selective reduction of **1m** and **1n** (Table 5, entries 13 and 14).

We attempted to apply the present method to aryl tosylates and mesylates. When aryl tosylate **5h** was used as the substrate, partial hydrolysis was only observed in the absence of NH_4OAc, whereas no reaction took place in the presence of NH_4OAc (Scheme 5). Deoxygenation did not proceed presumably because electron transfer from the Pd^0 center toward the benzene ring of the toluenesulfonyl group occurred in preference to that of the phenolic moiety.

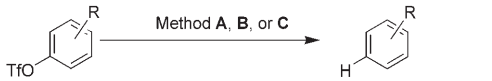
The reduction of methyl 4-methanesulfonyloxyphenylacetate (**6h**) did not proceed well in the absence of NH_4OAc (Table 6, entry 1), even after 24 h; however, the addition of NH_4OAc enhanced the reactivity remarkably, thus giving the desirable methyl phenylacetate in excellent yield (Table 6, entries 2 and 3). Other aryl mesylates are also applicable to this reductive deoxygenation process, with excess amounts of Mg metal and NH_4OAc affording the corresponding reduced products in good-to-excellent yields (Table 6, entries 3–9).

As deuterium-labeled compounds have been useful in the analysis of drug metabolism, investigation of reaction mechanisms, and so forth,[13] the development of facile and regioselective deuteration methods is the subject of great interest. The presented deoxygenation method with CH_3OD instead MeOH as the solvent was examined (Table 7), as the hydrogen source in the present method is the acidic hydrogen atom in MeOH (Table 2). The regioselective deuteration of the aromatic rings was achieved with a quantitative deuterium efficiency (Table 7). The deuteration method with

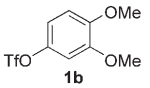
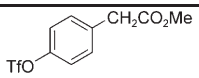
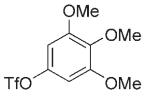
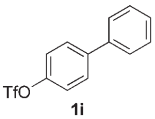
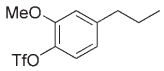
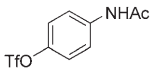
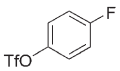
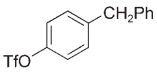
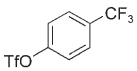
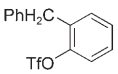
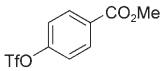
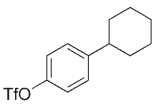
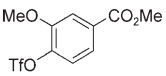


Scheme 4. Reductive cleavage of the triflate group of **1m**.

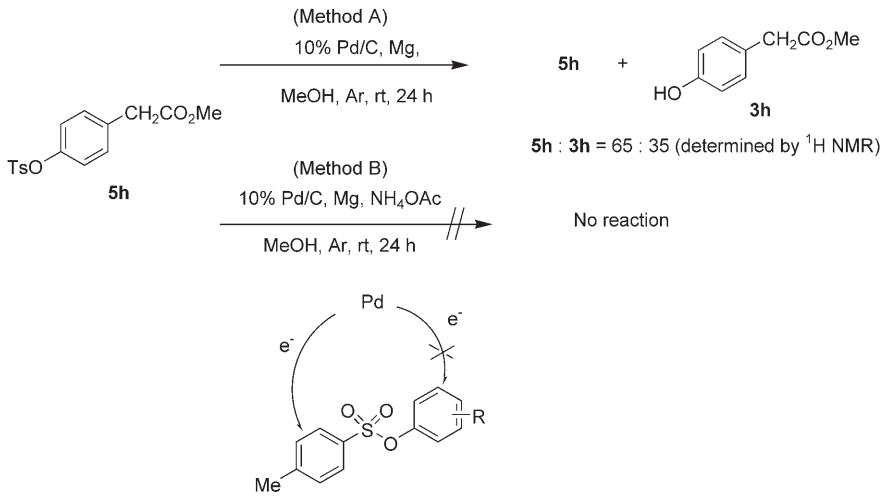
Table 5. Pd/C-catalyzed reductive cleavage of various aryl triflates.[a]



Method **A** : Without NH_4OAc
Method **B** and **C** : With NH_4OAc

Entry	Substrate	Method	*T* [h]	Yield [%][b]	Entry	Substrate	Method	*T* [h]	Yield [%][b]
1	 **1b**	A	24	95	8	 **1h**	A	24	80
		B	1	99			B	1	83
2	 **1a**	A	12	95	9	 **1i**	A	24	90
		B	1	89			B	1	92
3	 **1c**	B	0.5	95	10	 **1j**	A	24	90
							B	0.5	84
4	 **1d**	A	24	58	11	 **1k**	A	24	100[c]
		B	1	97					
5	 **1e**	A	24	98	12	 **1l**	A	24	100[c]
		B	0.5	95					
6	 **1f**	A	24	93	13	 **1m**	A	24	53[d]
		B	0.5	98			B	24	0[d]
							C	24	87
7	 **1g**	A	24	99	14	 **1n**	B	2.5	92[e]
		B	1	94					

[a] Method A: substrate (250 μmol), 10% Pd/C (10 wt% of the substrate), Mg (7.3 mg, 300 μmol), and MeOH (1.00 mL) in an Ar atmosphere at room temperature. Method B: substrate (250 μmol), 10% Pd/C (10 wt% of the substrate), Mg (7.3 mg, 300 μmol), NH_4OAc (19.3 mg, 250 μmol), and MeOH (1.00 mL) in an Ar atmosphere at room temperature. Method C: substrate (250 μmol), 10% Pd/C (10 wt% of the substrate), Mg (14.6 mg, 600 μmol), NH_4OAc (96.4 mg, 1.25 mmol), and MeOH (1.00 mL) in an Ar atmosphere at room temperature. [b] Yield of the isolated product. [c] The yield was determined by using GC/mass-spectrometric analysis because of the low boiling point of the product. [d] See Scheme 4. [e] $NH_4OAc = 3.0$ equivalents.



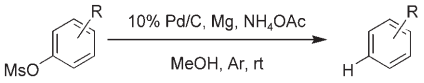
Scheme 5. Application of the methodology to an aryl tosylate.

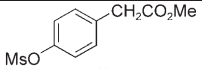
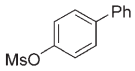
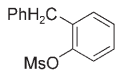
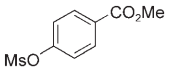
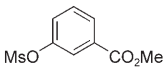
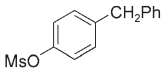
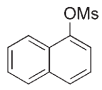
phenol derivatives as the starting material and CH_3OD (inexpensive relative to CD_3OD) as the deuterium source is very useful for acquiring the deuterated compounds with generality and in a cost-efficient method (Table 7, entries 1–5).

Conclusion

We have developed a facile and mild method for the deoxygenation of a wide variety of

Table 6. Pd/C-catalyzed reductive cleavage of aryl mesylates.[a]



Entry	Substrate	Mg [equiv]	NH_4OAc [equiv]	*T* [h]	Yield [%][b]
1	 **6h**	1.2	none	24	14[c]
2		1.2	1.0	12	98[d]
3		2.4	3.0	3	92
4	 **6i**	2.4	30	5	89
5	 **6f**	1.2	5.0	24	78
6	 **6m**	2.4	30	2	80
7	 **6o**	2.4	30	6	57
8	 **6e**	2.4	3.0	24	85
9	 **6j**	2.4	30	24	32[e]

[a] Reaction conditions: substrate (250 μmol), 10% Pd/C (10 wt% of the substrate), Mg (7.3 mg, 300 μmol or 14.6 mg, 600 μmol), NH_4OAc, and MeOH (1.00 mL) in an Ar atmosphere at room temperature. [b] Yield of the isolated product. [c] Based on ^1H NMR spectroscopic analysis, 86% of the starting material was recovered. [d] Based on ^1H NMR spectroscopic analysis, 2% of the starting material was recovered. [e] The low yield of the isolated product is due to its volatile nature.

phenol derivatives via aryl triflates or mesylates by using the combination of Pd/C, Mg metal, and MeOH. In addition, we also found an acceleration effect through the addition of NH_4OAc. From mechanistic studies, we speculate that NH_4OAc enhanced the reaction rate as a result of a dual activating effect caused by AcOH and NH_3: the increase in the solubility of the Mg species by AcOH and the activation of Pd/C by the coordination of NH_3. The deoxygenation method has the following advantages: it is hydrogen gas- and phosphine-free, requires mild reaction conditions, is simple, and provides ready access to the reagents. Furthermore, the present method can be applied to the regioselective deuteration of benzene rings by using CH_3OD as a cost-effective deuterium source and will be practically useful with generality in the areas of synthetic organic, medicinal, and process chemistry.

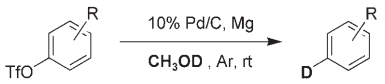
Experimental Section

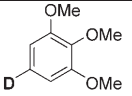
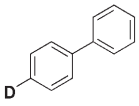
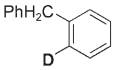
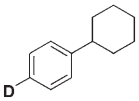
General experimental: 10% Pd/C was purchased from Aldrich (catalogue No. 205699). MeOH, *i*PrOH, and distilled water for HPLC and dehydrated EtOAc were purchased from Wako Pure Chemical Industries, Ltd. and used without purification. THF and CH_2Cl_2 were distilled from sodium benzophenone ketyl and calcium hydride, respectively. CH_3OD was obtained from Wako Pure Chemical Inc. (catalogue No. 537-7439; 99% D). All other reagents were purchased from commercial sources and used without further purification. Flash column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM) or Kanto Chemical Co., Inc. 60N (63–210 μm spherical, neutral). ^1H and ^{13}C NMR spectra were recorded on JEOL AL 400 or JEOL EX 400 spectrometers (400 and 100 MHz for the ^1H and ^{13}C NMR spectra, respectively). Chemical shifts (δ) are expressed in ppm and are internally referenced (0.00 and 77.0 ppm for TMS in $CDCl_3$ for the ^1H and ^{13}C NMR spectra, respectively). Elemental analyses were performed by a YANAKO CHN CORDER MT-5 instrument. EI and FAB mass spectra were taken on a JEOL JMS-SX102 A instrument.

General procedure for the preparation of aryl triflates:[14] Phenol (5.00 mmol) was dissolved in toluene (10 mL), and 30% K_3PO_4 solution (10 mL) was added. The reaction mixture was cooled to 0°C and triflic anhydride (1.0 mL, 6.00 mmol) was added dropwise with stirring to maintain a reaction temperature of <10°C. The reaction mixture was allowed to warm to room temperature, stirred for a further 30 minutes, and then extracted with ethyl acetate (2×10 mL). The combined organic layers were washed with water (30 mL), dried over $MgSO_4$, and evaporated to give **1a–n**.

3,4,5-Trimethoxyphenyl trifluoromethanesulfonate (1a): Following the general procedure for the preparation of aryl mesylates, **1a** was obtained from 3,4,5-trimethoxyphenol (921 mg, 5.00 mmol) after a reaction time of

Table 7. Regioselective deuteration of various aryl triflates with CH_3OD as the solvent.[a]



Entry	Product	T [h]	Yield [%]
1		4.5	86[b]
2		24	81
3		18	95
4		24	84
5		12	83[c]

[a] Reaction conditions: substrate (250 μmol), 10% Pd/C (10 wt% of the substrate), Mg (7.3 mg, 300 μmol), and CH_3OD (1.00 mL) in an Ar atmosphere at room temperature. [b] 0.01 equivalents of NH_4OAc were used. [c] 2.4 equivalents of Mg were used.

0.5 h, without subsequent purification, in 97% yield (1.54 g) as a colorless solid. The ^{1}H NMR spectrum of **1a** was identical with that given in the literature.[15]

3,4-Dimethoxyphenyl trifluoromethanesulfonate (1b): Following the general procedure for the preparation of aryl triflates, reaction of 3,4-dimethoxyphenol (771 mg, 5.00 mmol) for 1 h, followed by flash column chromatography on silica gel (*n*-hexane/Et_2O 10:1), gave **1b** in 94% yield (1.34 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.85$ (d, $J=2.4$ Hz, 2H), 6.78 (d, $J=2.2$ Hz, 1H), 3.90 (s, 3H), 3.89 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.5$, 148.6, 142.7, 118.5 (q, $J=321$ Hz), 112.7, 111.0, 105.1, 55.9, 49.7 ppm; MS (EI): m/z (%): 286 (28) [M^+], 153 (100), 125 (30); HRMS (EI): m/z: calcd for $C_9H_9O_5F_3S$ [M^+]: 286.0123; found: 286.0116.

2-Methoxy-4-propylphenyl trifluoromethanesulfonate (1c): Following the general procedure for the preparation of aryl triflates, reaction of 2-methoxy-4-propylphenol (832 mg, 5.00 mmol) for 0.5 h, followed by flash column chromatography on silica gel (*n*-hexane), gave **1c** in 75% yield (1.11 g) as a colorless oil. The ^{1}H NMR spectrum of **1c** was identical with that given in the literature.[16]

4-Acetamidophenyl trifluoromethanesulfonate (1d): Following the general procedure for the preparation of aryl triflates, reaction of 4-acetamidophenol (756 mg, 5.00 mmol) for 0.5 h, followed by flash column chromatography on silica gel ($CHCl_3$/MeOH 100:1), gave **1d** in 53% yield (747 mg) as a colorless solid. The ^{1}H NMR spectrum of **1d** was identical with that given in the literature.[17]

4-Benzylphenyl trifluoromethanesulfonate (1e): Following the general procedure for the preparation for aryl triflates, reaction of 4-benzylphenol (921 mg, 5.00 mmol) for 1 h, followed by flash column chromatography on silica gel (*n*-hexane), gave **1e** in 92% yield (1.45 g) as a colorless oil. The ^{1}H NMR spectrum of **1e** was identical with that given in the literature.[18]

2-Benzylphenyl trifluoromethanesulfonate (1f): Following the general procedure for the preparation for aryl triflates, reaction of 2-benzylphenol (921 mg, 5.00 mmol) for 1 h, followed by flash column chromatography on silica gel (*n*-hexane), gave **1f** in 54% yield (846 mg) as a colorless oil. The ^{1}H NMR spectrum of **1f** was identical with that given in the literature.[19]

4-Cyclohexylphenyl trifluoromethanesulfonate (1g): Following the general procedure for the preparation of aryl triflates, reaction of 4-cyclohexylphenol (881 mg, 5.00 mmol) for 0.5 h, followed by flash column chromatography on silica gel (*n*-hexane), gave **1g** in 94% yield (1.44 g) as a colorless solid. The ^{1}H NMR spectrum of **1g** was identical with that given in the literature.[20]

Methyl 4-[(trifluoromethylsulfonyl)oxy]phenylacetate (1h): Following the general procedure for the preparation of aryl triflates, reaction of methyl 2-(4-hydroxyphenyl)acetate (831 mg, 5.00 mmol) for 0.5 h, without subsequent purification, gave **1h** in 72% yield (1.07 g) as a colorless oil. The ^{1}H NMR spectrum of **1h** was identical with that given in the literature.[21]

4-Phenylphenyl trifluoromethanesulfonate (1i): Following the general procedure for the preparation for aryl triflates, reaction of 4-phenylphenol (1.70 g, 10.0 mmol) for 1 h, followed by flash column chromatography on silica gel (*n*-hexane), gave **1i** in 93% yield (2.81 g) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.64$ (d, $J=8.7$ Hz, 2H), 7.55 (d, $J=7.2$ Hz, 2H), 7.46 (t, $J=7.2$ Hz, 2H), 7.39 (t, $J=7.2$ Hz, 1H), 7.34 ppm (d, $J=8.7$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=148.9$, 141.7, 139.3, 129.0, 128.9, 128.0, 127.2, 121.6, 118.8 ppm (q, $J=321$ Hz); MS (EI): m/z (%): 302 (40) [M^+], 169 (100), 141 (46), 115 (28); HRMS (EI): m/z: calcd for $C_{13}H_9O_3F_3S$ [M^+]: 302.0225; found: 302.0213; elemental analysis calcd (%) for $C_{13}H_9O_3F_3S$: C 51.66, H 3.00; found: C 51.44, H 3.15.

1-Naphthalenyl trifluoromethanesulfonate (1j): Following the general procedure for the preparation for aryl triflates, reaction of 1-naphthol (721 mg, 5.00 mmol) for 0.5 h, followed by flash column chromatography on silica gel (*n*-hexane), gave **1j** in 84% yield (1.16 g) as a colorless oil. The ^{1}H NMR spectrum of **1j** was identical with that given in the literature.[4g]

4-Fluorophenyl trifluoromethanesulfonate (1k): Following the general procedure for the preparation for aryl triflates, reaction of 4-fluorophenol (1.12 g, 10.0 mmol) for 0.5 h, without subsequent purification, gave **1k** in 93% yield (2.26 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.24$ (td, $J=5.0$, 2.6 Hz, 2H), 7.12 ppm (td, $J=7.2$, 2.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=161.7$ (d, $J=249$ Hz), 145.3 (d, $J=3.3$ Hz), 123.1 (d, $J=9.0$ Hz), 118.7 (q, $J=321$ Hz), 117.1 ppm (d, $J=24.6$ Hz); MS (EI): m/z (%): 244 (45) [M^+], 111 (100), 83 (78); HRMS (EI): m/z: calcd for $C_7H_4O_3F_4S$: 243.9817; found: 243.9812.

4-(Trifluoromethyl)phenyl trifluoromethanesulfonate (1l): Following the general procedure for the preparation for aryl triflates, reaction of α,α,α-trifluoromethylphenol (1.62 g, 10.0 mmol) for 0.5 h, without subsequent purification, gave **1l** in 71% yield (630 mg) as a colorless oil. The ^{1}H NMR spectrum of **1l** was identical with that given in the literature.[22]

Methyl 4-[(trifluoromethylsulfonyl)oxy]benzoate (1m): Following the general procedure for the preparation of aryl triflates, reaction of methyl 4-hydroxybenzoate (761 mg, 5.00 mmol) for 1 h, without subsequent purification, gave **1m** in 98% yield (1.40 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.15$ (d, $J=9.0$ Hz, 2H), 7.36 (d, $J=9.0$ Hz, 2H), 3.95 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.4$, 152.5, 131.9, 130.4, 121.4, 118.7 ppm (q, $J=321$ Hz); MS (EI): m/z (%): 284 (77) [M^+], 253 (90), 189 (100), 161 (22), 123 (45), 95 (38), 69 (20); HRMS (EI): m/z: calcd for $C_9H_7O_5F_3S$ [M^+]: 283.9966; found: 283.9971.

Methyl 3-methoxy-4-[(trifluoromethylsulfonyl)oxy]benzoate (1n): Following the general procedure for the preparation of aryl triflates, reaction of methyl vanillate (547 mg, 3.00 mmol) for 0.5 h, followed by flash column chromatography on silica gel (*n*-hexane/Et_2O 10:1), gave **1n** in 93% yield (872 mg) as a colorless oil. The ^{1}H NMR spectrum of **1n** was identical with that given in the literature.[23]

General procedure for reductive cleavage of 3,4,5-trimethoxyphenyl trifluoromethanesulfonate (1a) using various metals and solvents (Table 1): After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of **1a** (158 mg, 500 μmol), 10% Pd/C (15.9 mg, 10 wt% of **1a**), and the metal (600 μmol) in the solvent (2.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for the appropriate time. The reaction mixture was filtered by using a membrane filter (Millipore,

Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The ratio of the substrate **1a** to the product **2a** was confirmed by ^{1}H NMR spectroscopic analysis of the crude mixture in $CDCl_3$.

General procedure for Table 2: After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of **1a** (79.1 mg, 250 μmol), 10% Pd/C (8.0 mg, 10 wt% of **1a**), and Mg metal (7.3 mg, 300 μmol) in deuterated methanol (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for 24 h. The reaction mixture was filtered using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The hydrogen source in the reaction was confirmed by ^{1}H NMR spectroscopic analysis of the crude mixture in $CDCl_3$.

General procedure for Tables 3 and 4: After two vacuum/Ar cycles to remove air from the reaction tube, the mixture of **1a** (79.1 mg, 250 μmol), 10% Pd/C (8.0 mg, 10 wt% of **1a**), Mg metal (7.3 mg, 300 μmol), and an additive (250 μmol) in MeOH (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for the appropriate time. The reaction mixture was filtered by using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The ratio of the substrate **1a**, the product **2a**, and the homo-coupling product **4a** was confirmed by ^{1}H NMR spectroscopic analysis of the crude mixture in $CDCl_3$.

General procedure for reductive cleavage of various aryl triflates (Table 5): *Method A:* After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of the aryl triflate (250 μmol), 10% Pd/C (10 wt% of the aryl triflate), and Mg metal (7.3 mg, 300 μmol) in MeOH (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for the appropriate time. The reaction mixture was filtered by using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure.

Method B: After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of the aryl triflate (250 μmol), 10% Pd/C (10 wt% of the aryl triflate), Mg metal (7.3 mg, 300 μmol), and ammonium acetate (19.3 mg, 250 μmol) in MeOH (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for the appropriate time. The reaction mixture was filtered by using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure.

Method C: After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of the aryl triflate (250 μmol), 10% Pd/C (10 wt% of the aryl triflate), Mg metal (14.6 mg, 600 μmol), and ammonium acetate (96.4 mg, 1.25 mmol) in MeOH (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for the appropriate time. The reaction mixture was filtered by using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure.

Reductive cleavage of 5h (Scheme 5): *Method A*: After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of **5h** (80.1 mg, 250 μmol), 10% Pd/C (8.1 mg, 10 wt% of **5h**), and Mg metal (7.3 mg, 300 μmol) in MeOH (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for the appropriate time. The reaction mixture was filtered using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure.

Method B: After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of **5h** (80.1 mg, 250 μmol), 10% Pd/C (8.1 mg, 10 wt% of **5h**), Mg metal (7.3 mg, 300 μmol), and ammonium acetate (19.3 mg, 250 μmol) in MeOH (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for the appropriate time. The reaction mixture was filtered using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure.

Preparation of methyl 4-[(4-methylphenylsulfonyl)oxy]phenylacetate (6h): 4-Toluenesulfonyl chloride (4.19 g, 22.0 mmol) was added to a solution of methyl 4-hydroxyphenylacetate (3.32 g, 20.0 mmol) and triethylamine (3.07 mL, 22.0 mmol) in dichloromethane (10 mL), and the reaction mixture was stirred at ambient temperature (ca. 20°C). After 10 h, the solvent was concentrated under reduced pressure. The residue was extracted with ethyl acetate (20 mL) and water (20 mL). The organic layer was washed successively with saturated aqueous sodium hydrogen carbonate solution (20 mL), 10% aqueous sodium hydrogen sulfonate solution (20 mL), and brine (20 mL); dried over $MgSO_4$; and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate 10:1→5:1) to afford **6h** in 90% yield (5.77 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.3 Hz, 2H), 3.61 (s, 3H), 3.58 (s, 2H), 2.45 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5, 148.7, 145.3, 132.5, 130.5, 129.7, 128.5, 122.4, 52.1, 40.4, 21.7 ppm; MS (EI): *m*/*z* (%): 320 (75) [M^+], 261 (14), 155 (100), 91 (84); HRMS (EI): *m*/*z*: calcd for $C_{16}H_{16}O_5S$ [M^+]: 320.0718; found: 320.0721.

General procedure for reductive cleavage of aryl mesylates (Table 6): After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of the aryl mesylate (250 μmol), 10% Pd/C (10 wt% of the aryl mesylate), Mg metal (7.3 mg, 300 μmol), and ammonium acetate (19.3 mg–5.78 g, 0.250–7.50 mmol) in MeOH (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20°C) for the appropriate time. The reaction mixture was filtered using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3×10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure.

General procedure for the preparation of aryl mesylates: Methanesulfonyl chloride (0.929 mL, 12.0 mmol) was added dropwise to a solution of a phenol (10.0 mmol) and triethylamine (1.67 mL, 12.0 mmol) in dichloromethane, THF, or *N*,*N*-dimethylformamide (DMF; 20 mL), and the reaction mixture was stirred at ambient temperature. After the appropriate reaction time, the reaction mixture was concentrated under reduced pressure. The residue was extracted with ethyl acetate (20 mL) and water (20 mL). The organic layer was washed successively with saturated aqueous sodium hydrogen carbonate solution (20 mL), 10% aqueous sodium hydrogen sulfonate solution (20 mL), and brine (20 mL); dried over $MgSO_4$; and concentrated under reduced pressure. If necessary, the residue was purified by flash column chromatography on silica gel or recrystallization.

Methyl 4-methanesulfonyloxyphenylacetate (6h): Following the general procedure for the preparation of aryl mesylates, reaction of methyl 4-hydroxyphenylacetate (1.66 g, 10.0 mmol), triethylamine (1.67 mL, 12.0 mmol), and methanesulfonyl chloride (0.929 mL, 12.0 mmol) for 1 h, without subsequent purification, gave **6h** in 94% yield (2.29 g) as a color-

less solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.32$ (d, $J = 8.6$ Hz, 2H), 7.23 (d, $J = 8.6$ Hz, 2H), 3.69 (s, 3H), 3.62 (s, 2H), 3.12 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 171.4$, 148.3, 133.4, 131.0, 122.1, 52.2, 40.4, 37.3 ppm; MS (EI): *m/z* (%): 244 (85) [M^+], 185 (75), 166 (42), 107 (100), 78 (34), 44 (30); HRMS (EI): *m/z*: calcd for $C_{10}H_{12}O_5S$: 244.0405; found: 244.0396; elemental analysis (%) calcd for $C_{10}H_{12}O_5S$: C 49.17, H 4.95; found: C 49.08, H 4.99.

4-Phenylphenyl methanesulfonate (6i): Following the general procedure for the preparation of aryl mesylates, reaction of 4-hydroxybiphenyl (1.70 g, 10.0 mmol), triethylamine (1.67 mL, 12.0 mmol), and methanesulfonyl chloride (0.929 mL, 12.0 mmol) for 19 h, followed by recrystallization (ethyl acetate/*n*-hexane), gave **6i** in 63% yield (1.57 g) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.62$ (d, $J = 8.8$ Hz, 2H), 7.55 (d, $J = 7.3$ Hz, 2H), 7.45 (d, $J = 7.3$ Hz, 2H), 7.39–7.35 (m, 3H), 2.97 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.5$, 140.6, 139.7, 128.9, 128.7, 127.7, 127.1, 122.3, 37.3 ppm; MS (EI): *m/z* (%): 248 (43) [M^+], 169 (100), 141 (45), 115 (28); HRMS (EI): *m/z*: calcd for $C_{13}H_{12}O_3S$ [M^+]: 248.0507; found: 248.0500; elemental analysis (%) calcd for $C_{13}H_{12}O_3S$: C 62.88, H 4.87; found: C 62.79, H 4.93.

2-Benzylphenyl methanesulfonate (6f): Following the general procedure for the preparation of aryl mesylates, reaction of 2-benzylphenol (1.84 g, 10.0 mmol), triethylamine (1.67 mL, 12.0 mmol), and methanesulfonyl chloride (0.929 mL, 12.0 mmol) for 2 h, followed by flash column chromatography on silica gel (*n*-hexane/Et_2O 10:1), gave **6f** in 96% yield (2.51 g) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39$ (d, $J =$ 7.8 Hz, 1H), 7.31–7.18 (m, 8H), 4.08 (s, 2H), 2.97 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.6$, 139.5, 133.8, 131.6, 128.9, 128.5, 127.8, 127.2, 126.3, 121.7, 37.7, 36.2 ppm; MS (EI): *m/z* (%): 262 (52) [M^+], 183 (100), 181 (85), 165 (50); HRMS (EI): *m/z*: calcd for $C_{14}H_{14}O_3S$ [M^+]: 262.0664; found: 262.0670; elemental analysis (%) calcd for $C_{14}H_{14}O_3S$: C 64.10, H 5.38; found: C 64.00, H 5.49.

Methyl 4-methylsulfonyloxybenzoate (6m): Following the general procedure for the preparation of aryl mesylates, reaction of methyl 4-hydroxybenzoate (1.52 g, 10.0 mmol), triethylamine (1.67 mL, 12.0 mmol), and methanesulfonyl chloride (0.929 mL, 12.0 mmol) for 20 h, followed by flash column chromatography on silica gel (*n*-hexane), gave **6m** in 94% yield (2.17 g) as a colorless solid. The ^{1}H NMR spectrum of **6m** was identical with that given in the literature.[24]

Methyl 3-methylsulfonyloxybenzoate (6o): Following the general procedure for the preparation of aryl mesylates, reaction of methyl 3-hydroxybenzoate (1.52 g, 10.0 mmol), triethylamine (1.67 mL, 12.0 mmol), and methanesulfonyl chloride (0.929 mL, 12.0 mmol) for 20 h, followed by flash column chromatography on silica gel (*n*-hexane), gave **6o** in 94% yield (2.17 g) as a colorless solid. The ^{1}H NMR spectrum of **6o** was identical with that given in the literature.[24]

4-Benzylphenyl methanesulfonate (6e): Following the general procedure for the preparation of aryl mesylates, reaction of methyl 4-benzylphenol (1.84 g, 10.0 mmol), triethylamine (1.67 mL, 12.0 mmol), and methanesulfonyl chloride (0.929 mL, 12.0 mmol) for 5 h, without subsequent purification, gave **6e** in 99% yield (2.59 g) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.32$–7.16 (m, 9H), 3.98 (s, 2H), 3.11 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.6$, 140.6, 140.2, 130.3, 128.9, 128.6, 126.4, 121.9, 41.3, 37.3 ppm; MS (EI): *m/z* (%): 262 (100) [M^+], 183 (80), 155 (67); HRMS (EI): *m/z*: calcd for $C_{14}H_{14}O_3S$ [M^+]: 262.0664; found: 262.0660; elemental analysis (%) calcd for $C_{14}H_{14}O_3S$: C 64.10, H 5.38; found: C 64.10, H 5.40.

1-Naphthalenyl methanesulfonate (6j): Following the general procedure for the preparation of aryl mesylates, reaction of methyl 1-naphthol (1.44 g, 10.0 mmol), triethylamine (1.67 mL, 12.0 mmol), and methanesulfonyl chloride (0.929 mL, 12.0 mmol) for 2 h, without subsequent purification, gave **6j** in 97% yield (2.16 g) as a brown oil. The ^{1}H NMR spectrum of **6j** was identical with that given in the literature.[4g]

General procedure for Table 7: After two vacuum/Ar cycles to remove air from the reaction tube, a mixture of aryl triflate (250 μmol), 10% Pd/C (10 wt% of the substrate), and Mg metal (7.3 mg, 300 μmol) in CH_3OD (1.0 mL) was stirred at ordinary pressure (balloon) and temperature (ca. 20 °C) for the appropriate time. The reaction mixture was filtered by using a membrane filter (Millipore, Millex-LH, 0.45 μm), and the filtrate was partitioned between diethyl ether (10 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined organic layers were washed with brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure.

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