Study on Radical Amidation onto Aromatic Rings with (Diacyloxyiodo)arenes

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Sulfonamides of primary amines bearing an aromatic ring at the γ-position were treated with (diacyloxyiodo)arenes and iodine under irradiation conditions with a tungsten lamp to give the corresponding 1,2,3,4-tetrahydroquinoline derivatives in moderate to good yields. Here, the reactivity depends on the Z-group (protecting group) of the starting amides. Under the same reaction conditions, some sulfonamides were treated with (diacetoxyiodo)benzene and iodine in the presence of aromatics to give the corresponding N-arylated amides. These reactions proceed through the intramolecular and intermolecular amidations onto aromatic rings via the sulfonamidyl radicals formed.

Introduction

Trivalent iodine compounds have been used for various organic syntheses. For example, oxidation, halogenation, alkylation, and arylation have been studied, and most of these reactions proceed through ionic reaction pathways.[1] On the other hand, the reactions through radical pathways have also been studied extensively as follows. For instance, (diacyloxyiodo)arenes can generate alkyl,[2] alkoxy[3] and aminyl radicals[4] by the reactions of carboxylic acids, alcohols, and amines. Here, the alkyl radicals formed were used for C−C bond formation such as the alkylation of π-deficient heteroaromatic compounds, the addition to the activated olefins having electron-withdrawing groups, and functionalization. Oxygen-centered radicals, such as carbonyloxy radicals and alkoxy radicals, were used for intramolecular cyclization[5] and fragmentation. In the case of nitrogen-centered radicals, the Hofmann−Löffler−Freytag-type reaction of nitroamines and cyanoamides derived from steroidal compounds, with (diacetoxyiodo)benzene or iodosobenzene, has been studied by Suárez et al.[4] However, the cyclic amination onto aromatics has been not studied.[6]

Many natural products contain six- or five-membered heterocyclic rings bearing nitrogen atoms. 1,2,3,4-Tetrahydroquinoline skeletons are of particular interest because of their importance in the total synthesis of natural products as well as in medicinal chemistry;[7] virantmycin[8] and 2,3-dihydro-4-quinolone derivatives[9] may serve as examples. Extensive studies on the prepa-

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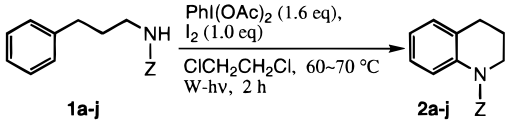
ration of these skeletons have been carried out, mainly with condensation and cycloaddition methods.[10] Among these preparations, the method with radical reaction is very useful.[11] However, study on the radical cyclization onto the aromatic ring via an aminyl radical is extremely limited, i.e., the formation of an aminium radical generated by the photolytic or ferrous ion-catalyzed decomposition of *N*-chloroamines in strong acidic media,[12] and the yields in these reactions are less than satisfactory.

Here, we would like to report a good preparative method of six-membered cyclic aromatic amines from primary amines bearing an aromatic ring at the γ-position, which is easily operable under neutral conditions, through the radical amination onto the aromatic ring. The intermolecular reactions between sulfonamides and aromatics under the same conditions were also carried out in further extension of the methodology.

Results and Discussion

Conversion to 1,2,3,4-Tetrahydroquinoline Derivatives. To carry out the cyclization to 1,2,3,4-tetrahydroquinoline derivatives via an aminyl radical, 3-phenyl-1-propylamine was protected by several kinds of protecting groups to prevent the oxidation of the amino group by (diacyloxyiodo)arenes. At first, the amide **1e** protected by a tosyl group was treated with (diacetoxyiodo)benzene and iodine in 1,2-dichloroethane under irradiation with a tungsten lamp, and the desired cyclization product, *N*-tosyl-1,2,3,4-tetrahydroquinoline **2e**, could be obtained in moderate yield under the best conditions. The addition of trifluoroacetic acid or potassium carbonate to the solution retarded the formation of compound **2e**. Then, other sulfonamides protected with various kinds of sulfonyl groups were treated with (diacetoxyiodo)benzene and iodine under the same conditions, and the corresponding cyclization products were obtained in moderate to good yields as shown in Table 1. However, when the amine was protected by *p*-methylbenzoyl **1h**, trifluoroacetyl **1i**, ethoxycarbonyl, and ethyl oxalyl groups, the cyclization onto the aromatic ring did not occur at all, and the starting amides were recovered. The amide protected by diethyl phosphate did not give the cyclized product (Table 1, entry 7) and the starting amide was recovered again. Here, the electron-withdrawing substituents on the aromatic ring in para-substituted benzenesulfonamides accelerated the reactivity and gave the cyclized products in good yields. Thus, the trifluoromethanesulfonyl group, the most powerful electron-withdrawing group, showed the best reactivity. A good relationship between the ^{13}C NMR chemical shift of the $NHCH_2$ group in the starting compound **1** and the yield of the cyclized product **2** was observed, though the difference is small. Thus, the reaction requires a chemical shift value lower field than 42 ppm in compound **1**. Namely, this reactivity probably depends on the acidity of sulfonamides and the stability of sulfonamidyl radicals. Practically, there is ~10 order difference in pK_a values of the NH proton between sulfonamides and amides.[13] Sulfonamide protected by 2-nitrobenzenesulfonyl group **1j** was also treated, and the desired compound **2j** was obtained in 34% yield together with an iodinated compound at the 6-position (**2j-I**) of compound **2j** in 17% yield. It might be caused by the reduction of electron-withdrawing ability by steric hindrance at the ortho position. These cyclization reactions do not proceed with iodine alone or with (diacyloxyiodo)-arene and bromine instead of iodine. Moreover, galvinoxyl radical (1.0 equiv based on compound **1a**) completely retarded these reactions. The present reactions proceed under fluorescent lighting, instead of under irradiation with a tungsten lamp. However, the irradiation with ultrasonic wave was ineffective.

Table 1. Relationship between Chemical Shift of Starting Sulfonamides 1 and Yields of Compound 2



1a-j **2a-j**

Entry	Z	1	^{13}C-NMR[a] δ(NH-**C**H$_2$) ppm	2, Yield / %
1	SO_2CF_3	**1a**	43.93	71
2	SO_2-C$_6$H$_4$-NO_2	**1b**	42.69	67
3	SO_2-C$_6$H$_4$-Br	**1c**	42.56	57
4	SO_2-C$_6$H$_5$	**1d**	42.58	59
5	SO_2-C$_6$H$_4$-CH_3	**1e**	42.56	48
6	SO_2-C$_6$H$_4$-OCH_3	**1f**	42.51	6 (6[b])
7	$PO(OC_2H_5)_2$	**1g**	40.85	0
8	CO-C$_6$H$_4$-CH_3	**1h**	39.70	0[c]
9	$COCF_3$	**1i**	39.58	0[c]
10	SO_2-C$_6$H$_4$-NO_2	**1j**	43.10	34 (17[b])

[a] $CDCl_3$−TMS. [b] Yield in 6-iodo compound of **2**. [c] Starting amide was recovered in >80% yield.

A plausible reaction mechanism for the present reaction is shown in Scheme 1. Here, the formation of monosubstituted trivalent iodine compound **A** from sulfonamide **1a** and (diacetoxyiodo)benzene was not observed by NMR. Addition of iodine gave the N-iodinated

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Scheme 1

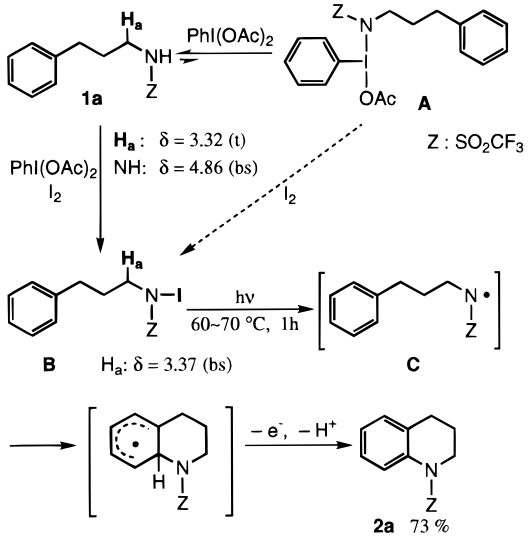
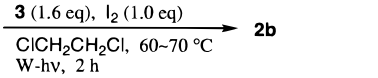
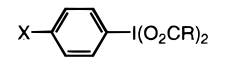
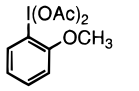
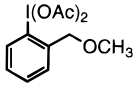
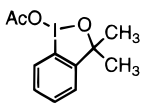


Table 2. Substituent Effect of (Diacyloxyiodo)arenes 3 in the Cyclization of Compound 1b





3	X	R	Yield / %
3ii	NO_2	CH_3	71
3iii	Cl	CH_3	66
3i	H	CH_3	67
3iv	CH_3	CH_3	65
3v	OCH_3	CH_3	61
3vi	H	C_2H_5	64
3vii	H	CF_3	0

3		Yield / %
3viii		67
3ix		62
3x		63
3xi	$C_6F_5I(O_2CCF_3)$	0

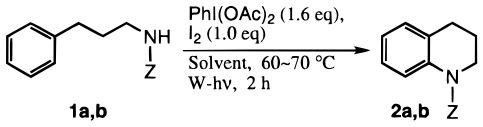
compound **B** in the NMR sample tube. Thus, compound **B** is one of the reactive intermediates, and the homolytic cleavage of N−I bond occurs to give the sulfonamidyl radical **C** under the irradiation conditions. Finally, the radical added to the aromatic ring to give the compound **2a** via oxidative aromatization. The present reaction does not proceed at all in the dark or without (diacetoxyiodo)benzene.

The substituent effect of (diacyloxyiodo)arenes was studied under the same conditions as shown in Table 2; however, no big difference was observed. [Bis(trifluoroacetoxy)iodo]benzene **3vii** and [bis(trifluoroacetoxy)iodo]-pentafluorobenzene **3xi** did not give the compound **2b**.

The solvent effect was studied continuously as shown in Table 3. Ethyl acetate gave the compound **2** as well as 1,2-dichloroethane (Table 3, entry 1). Though chloroform also gave the compound **2**, the yield was decreased slightly (Table 3, entry 4). In ethanol and 1,2-dimethoxyethane, the reactions were inhibited and the starting amides were recovered in nearly 90% yield (Table 3, entries 2 and 5).

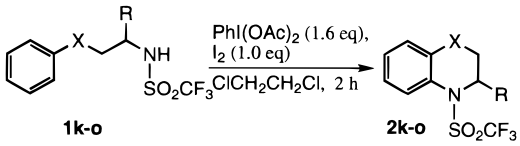
Other amides protected by a trifluoromethanesulfonyl group were treated with (diacetoxyiodo)benzene and iodine under the best conditions. The results are shown in Table 4. The sulfonamides derived from primary

Table 3. Solvent Effect in the Reaction with Compounds 1a and 1b



entry	1	solvent	**2** yield/%	recovery of **1a** or **1b**/%
1	**1a**	AcOEt	73	0
2	**1a**	EtOH	0	88
3	**1b**	AcOEt	60	22
4	**1b**	$CHCl_3$	53	37
5	**1b**	$CH_3OCH_2CH_2OCH_3$	5	86

Table 4. Conversion of Various Amides to 6-Membered Cyclic Amides (I)



				yields/%	
entry	**1**	X	R	$W-h\nu$ 60−70 °C	fluorescent lamp rt
1	**1k**	$CHCH_3$	H	80	
2	**1l**	O	H	72[a]	
3	**1m**	CH_2	CH_3	43	28
4	**1n**	CH_2	Ph	43	26
5	**1o**	CH_2	n-C_4H_9	13[b]	6

[a] 6-Iodo compound (**2l-I**) was also formed in ~9% yield. [b] PhI(OAc)$_2$ (2.4 equiv) and I_2 (1.5 equiv).

alkyl-branched amines were converted to the corresponding cyclic aromatic sulfonamides in good yields. Since the yields in alkyl-branched sulfonamides were low due to the occurrence of side reactions (β-fragmentation of the formed sulfonamidyl radical), they were treated under milder conditions, at room temperature under irradiation with fluorescent lighting, instead of a tungsten lamp. However, each yield went down (Table 3, entries 3−5). The sulfonamides having a naphthyl (**1p**) group and a biphenyl (**1q**) group were also converted to the corresponding cyclized products **2p** and **2q**, respectively, in moderate to good yields as shown in Scheme 2. Here, it is noteworthy that the ratio of **2r** and **2r-I** was largely inverted by changing the solvents. Therefore, deliberate control of the products is possible.

The following sulfonamide **1s** was used to study the electrophilicity of sulfonamidyl radical intermediate **D** (Scheme 3). As a consequence, the sulfonamidyl radical **D** seems to be less selective than the corresponding alkoxy radical intermediate **E**, which is formed from the corresponding alcohol **4**, because of the formation of **2s-II**. Probably, this is due to the more reactive character of sulfonamidyl radical **D** than the corresponding alkoxy radical **E**.

The cyclic products obtained here could be easily deprotected by using lithium aluminum hydride or thiophenol[14] in good yields (>90%) (Scheme 4). Thus, the present reaction is a good method for preparation of 1,2,3,4-tetrahydroquinoline derivatives, which can be converted to a quinoline skeleton in good yields by

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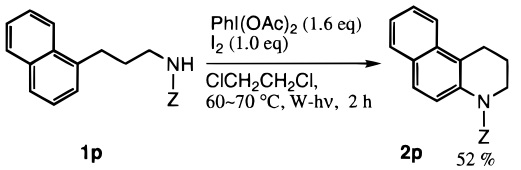
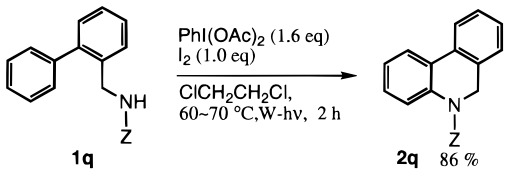
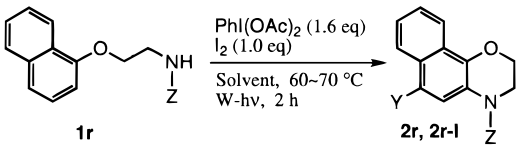
Scheme 2







Solvent	Yields / %	
	2r (Y = H)	**2r-I** (Y = I)
$ClCH_2CH_2Cl$	20	47
AcOEt	75	5

(Z = SO_2CF_3)

treatment with DDQ under refluxing conditions in toluene. Therefore, the present reaction is finally a good method for the preparation of quinoline derivatives from primary amines containing an aromatic ring at the γ-position.

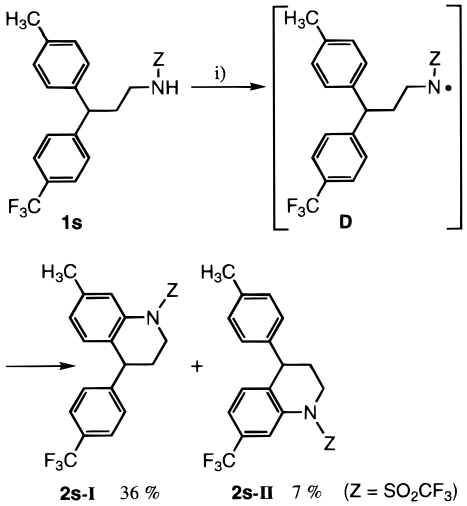
In addition, as one of the synthetic uses of the present reaction, a model study for virantmycin was carried out to give the compound **7** in good yield as shown in Scheme 5.

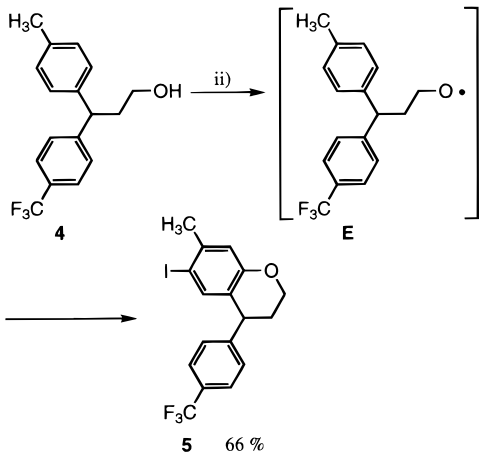
Conversion to Other Cyclic Amines. Next, we worked on changing the number of methylene units. The sulfonamide bearing an aromatic ring at the β-position was treated under the same conditions. However, the dihydroindole skeleton was not formed, but benzyl iodide was obtained mainly. It was caused by the β-fragmentation of the corresponding sulfonamidyl radical formed. This β-fragmentation reaction occurred even at 0 °C. On the other hand, the sulfonamides bearing an aromatic ring at the δ-position **8t**−**v** gave the pyrrolidine derivatives **9t**−**v** via the Hofmann−Löffler−Freytag-type reaction[15] in good yields without formation of seven-membered cyclic amides (Table 5). Here, the *p*-nitrobenzenesulfonyl group gave the products in better yield than the trifluoromethanesulfonyl group.

Intermolecular Reactions. At first, saccharin **10** that has lower pK_a value than the general sulfonamides was warmed to 60−70 °C in the presence of (diacetoxyiodo)benzene and iodine in benzene under irradiation with a tungsten lamp to give *N*-phenylsaccharin **11c′** (Table 6). The reaction requires 3 equiv of (diacetoxyiodo)benzene to increase the yield of *N*-phenylsaccharin, and here, the compound was obtained in 83% yield. Anisole, toluene, chlorobenzene, and nitrobenzene were treated as a solvent under the same conditions, and the corresponding *N*-arylsaccharins **11** could be obtained in good yields in toluene and chlorobenzene, respectively.

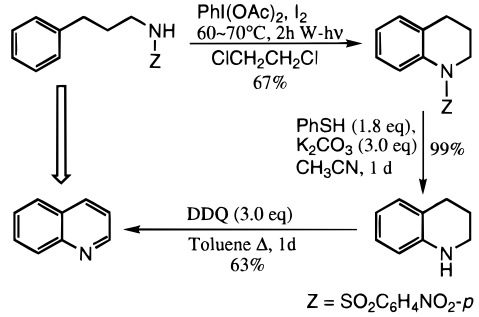
(15) (a) Neale, R. S. *Synthesis* **1971**, 1. (b) Wolff, M. E. *Chem. Rev.* **1963**, *63*, 55.

Scheme 3





Scheme 4



However, anisole, a π-electron-rich aromatic, gave little product due to the formation of iodoanisole. In the case of nitrobenzene, the reactivity seems to be poor because of the strong electron-withdrawing group. Then, naphthalene (5 equiv) and benzothiophene (5 equiv) were treated in 1,2-dichloroethane as a solvent under the same conditions. Though the yields were not so good (56% and 42% yields, respectively), the substitution products could be obtained with high regioselectivity.

Next, *N*-alkylsulfonamides were treated under the same conditions. Methylamine protected by the *p*-nitrobenzenesulfonyl group was phenylated in good yield.

Scheme 5

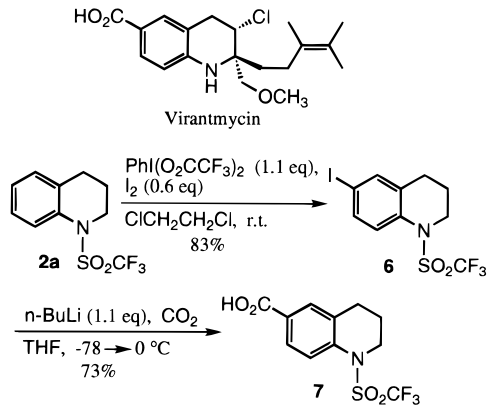
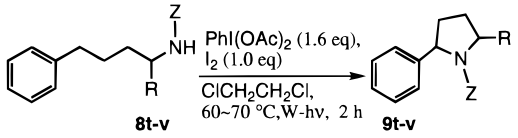


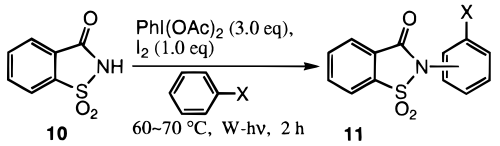
Table 5. Cyclization with *N*-(4-Phenylbutyl)-4-nitrobenzenesulfonamides: Conversion to Pyrrolidine Derivative



entry	**8**	Z	R	yield/%
1	**8t**	SO_2CF_3	H	54
2	**8u**	$SO_2C_6H_4NO_2$-*p*	H	84
3	**8v**	$SO_2C_6H_4NO_2$-*p*	CH_3	71[a]

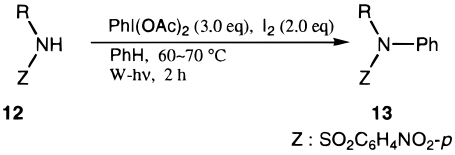
[a] cis:trans = 35:65.

Table 6. Conversion to *N*-Arylsaccharins (I)



entry	X	**11**	yield/%	orientation
1	OCH_3	**11a′**	5	o:p = 42:58
2	CH_3	**11b′**	75	o:p = 50:50
3	H	**11c′**	83	
4	Cl	**11d′**	80	o:p = 60:40
5	NO_2	**11e′**	18	m alone

Table 7. *N*-Phenylation of *N*-Alkylsulfonamides

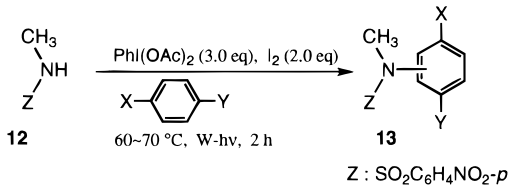


entry	R	**13**	yield/%	recovery of **12**/%
1[a]	CH_3	**13h′**	90	0
2[b]	C_2H_5	**13i′**	52	9
3[b]	*n*-C_4H_9	**13j′**	7	9
4	$CH(CH_3)_2$	**13k′**	trace	80
5	$C(CH_3)_3$	**13l′**	0	96
6	OCH_3	**13m′**	0	7

[a] I_2 (1.0 equiv). [b] $PhI(OAc)_2$ (4.0 equiv).

Again, *N*-phenyl compound **13** was not obtained in the dark. The *p*-nitrobenzenesulfonyl group gave the reaction product **13** in better yield than the tosyl group. Other *N*-alkylsulfonamides were treated in benzene to give the corresponding *N*-alkyl-*N*-phenylsulfonamide; however, the yields were decreased as the alkyl group tended to be bulky. *N*-Methylamides protected by the *p*-nitrobenzenesulfonyl group were also arylated with toluene, chlorobenzene, and *p*-xylene in good yields, respectively.

Table 8. *N*-Arylation of *N*-Methylsulfonamides



entry	X	X	**13**	yield/%	o:m:p/%
1	CH_3	H	**13n′**	90	66:17:17
2	Cl	H	**13o′**	71	66:17:17
3[a]	CH_3	CH_3	**13p′**	60	

[a] $PhI(OAc)_2$ (4.0 equiv) and I_2 (3 equiv).

Finally, phthalimide was treated in benzene under the same conditions, and *N*-phenylphthalimide was obtained in 56% yield and phthalimide was recovered in 32% yield under the same conditions as above. This is due to the poor solubility of phthalimide in benzene. Finally, 3.0 equiv of (diacetoxyiodo)benzene and 2.0 equiv of iodine were added twice at 2-h intervals, to increase the yield of *N*-phenylphthalimide to 79%.

In conclusion, the present reactions are very useful for the preparation of 1,2,3,4-tetrahydroquinoline derivatives and pyrrolidine derivatives from primary amines bearing an aromatic ring at the γ- and δ-positions, respectively, because the reaction proceeds by a simple operation and under mild and neutral conditions.

Experimental Section

General Methods. Melting points were determined on an electrothermal apparatus in open capillary tubes and are uncorrected. ^{1}H NMR spectra were recorded on 400 and 500 MHz spectrometers and ^{13}C NMR spectra were recorded on 100 and 125 MHz spectrometers. Chemical shifts are reported as ppm downfield from tetramethylsilane (TMS) in δ units. Mass spectra were measured with JEOL-JMS-AMII15 (EI), and high-resolution mass spectra (HRMS) were measured with a JEOL-HX 110A mass spectrometer. Wakogel C-200 and C-300 were used for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

Materials. (Diacetoxyiodo)benzene and [bis(trifluoroacetoxy)iodo]benzene are commercially available. The other (diacetoxyiodo)arenes were prepared by the oxidation of the corresponding iodoarenes.[2f,16] Most sulfonamides are prepared by reaction with sulfonyl chlorides, triethylamine, and amines, which are commercially available or prepared by the Mitsunobu reaction from the corresponding alcohols.[17]

Typical Procedures. Conversion of Amides to the Corresponding Cyclic Amides. (Diacyloxyiodo)arene and iodine were added to a solution of sulfonamide (0.5 mmol) in 1,2-dichloroethane (7 mL). The mixture was irradiated with a tungsten lamp (500 W) at 60−70 °C (or irradiated with fluorescent lighting at room temperature) for 2 h under an argon atmosphere. After the reaction, the mixture was poured into saturated aqueous sodium sulfite solution and extracted with ethyl acetate three times. The organic layer was dried over sodium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed by pre-

(16) (a)Mckillop, A.; Kemp, D. *Tetrahedron* **1989**, *45*, 3299. (b) Schmeisser, M.; Dahmen, K.; Sartori, P. *Chem. Ber.* **1967**, 100, 1633.
(17) (a) Mitsunobu, O.; Wada, M.; Sano, T. *J. Am. Chem. Soc.* **1972**, *94*, 679. (b) Mitsunobu, O. *Synthesis* **1981**, 1.

parative TLC (pTLC) on silica gel using hexane and ethyl acetate (2:1−8:1) as an eluent.

Conversion of Sulfonamides to *N*-Arylsulfonamides with Aromatics as a Solvent. (Diacetoxyiodo)benzene and iodine were added to a solution of sulfonamide (0.5 mmol) in an aromatic (10 mL). The mixture was irradiated with a tungsten lamp (500 W) at 60−70 °C for 2 h under an argon atmosphere. After the reaction, the mixture was poured into saturated aqueous sodium sulfite solution and extracted with ethyl acetate three times. The organic layer was dried over sodium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed by pTLC on silica gel using hexane and ethyl acetate as an eluent.

Conversion of Sulfonamides to *N*-Arylsulfonamides with Aromatics in 1,2-Dichloroethane. (Diacetoxyiodo)-benzene and iodine were added to a solution of the appropriate sulfonamide (0.5 mmol) and aromatic (2.5 mmol) in 1,2-dichloroethane (10 mL). The mixture was irradiated with a tungsten lamp (500 W) at 60−70 °C for 2 h under an argon atmosphere. After the reaction, the mixture was poured into saturated aqueous sodium sulfite solution and extracted with ethyl acetate three times. The organic layer was dried over sodium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel by pTLC using hexane and ethyl acetate as eluent.

***N*-(Trifluoromethanesulfonyl)-1,2,3,4-tetrahydroquinoline (2a)**: oil; IR (neat) 2900, 1580, 1480, 1220, 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (quint, J = 6.4 Hz, 2H), 2.88 (t, J = 6.8 Hz, 2H), 3.87 (t, J = 6.0 Hz, 2H), 7.15−7.22 (m, 3H), 7.52 (d, J = 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.39 (s), 26.13 (s), 47.94 (s), 120.11 (q, J_{C-F} = 328 Hz, q, CF_3), 123.34 (t), 126.15 (t), 126.79 (t), 129.46 (t), 130.91 (q), 135.31 (q); HRMS (EI) found M^+ 265.0390, calcd for $C_{10}H_{10}F_3NO_2S$ M 265.0384.

***N*-(4′-Nitrobenzenesulfonyl)-1,2,3,4-tetrahydroquinoline (2b)**: mp 116.5−117.5 °C; IR (KBr) 3080, 2930, 1600, 1520, 1340, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.66 (quint, J = 6.4 Hz, 2H), 2.43 (t, J = 6.6 Hz, 2H), 3.86 (t, J = 6.0 Hz, 2H), 7.03 (d, J = 7.7 Hz, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 8.6 Hz, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 9.2 Hz, 1H), 8.24 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.73 (s), 26.40 (s), 46.88 (s), 124.13 (t), 124.89 (t), 125.79 (t), 126.83 (q), 128.22 (t), 129.34 (t), 130.89 (q), 135.91 (t), 145.22 (q), 149.99 (q); HRMS (EI) found M^+ 318.0684, calcd for $C_{15}H_{14}N_2O_4S$ M 318.0674. Anal. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.43; N, 8.80; S, 10.07. Found: C, 56.37; H, 4.41; N, 8.77; S, 9.99.

***N*-(4′-Bromobenzenesulfonyl)-1,2,3,4-tetrahydroquinoline (2c)**: mp 128.0−129.0 °C; IR (KBr) 3050, 2900, 1560, 1480, 1340, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.65 (quint, J = 6.3 Hz, 2H), 2.45 (t, J = 6.6 Hz, 2H), 3.81 (t, J = 6.0 Hz, 2H), 7.02 (d, J = 7.7 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.60 (s), 26.49 (s), 46.64 (s), 124.93 (t), 125.31 (t), 126.61 (t), 127.68 (q), 128.51 (t), 129.18 (t), 130.77 (q), 132.17 (t), 136.40 (q), 138.65 (q); HRMS (EI) found M^+ 350.9941, calcd for $C_{15}H_{14}{}^{79}BrNO_2S$ M 350.9929; Anal. Calcd for $C_{15}H_{14}BrNO_2S$: C, 51.15; H, 4.01; N, 3.98; S, 9.12. Found: C, 51.03; H, 3.85; N, 4.05; S, 8.97.

***N*-(Benzenesulfonyl)-1,2,3,4-tetrahydroquinoline (2d)**: oil; IR (neat) 3030, 2900, 1600, 1580, 1480, 1440, 1340, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.62 (quint, J = 6.3 Hz, 2H), 2.41 (t, 6.8 Hz, 2H), 3.80 (t, J = 6.0 Hz, 2H), 7.00 (d, J = 7.3 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.59 (d, J = 7.7 Hz, 2H), 7.78 (d, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.54 (s), 26.43 (s), 46.48 (s), 124.90 (t), 125.00 (t), 126.45 (t), 126.96 (t), 128.89 (t), 129.02 (t), 130.70 (q), 132.64 (t), 136.69 (q), 139.58 (q); HRMS (EI) found M^+ 273.0820, calcd for $C_{15}H_{15}NO_2S$ M 273.0824.

***N*-(4′-Methylbenzenesulfonyl)-1,2,3,4-tetrahydroquinoline (2e)**: mp 83.0−85.0 °C; IR (KBr) 3000, 2900, 2850, 1580, 1480, 1330 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.63 (quint, J = 6.3 Hz, 2H), 2.38 (s, 3H), 2.44 (t, J = 6.6 Hz, 2H), 3.80 (t, J = 6.0 Hz, 2H), 7.00 (d, J = 7.3 Hz, 1H), 7.07 (t, J = 7.3 Hz, 1H), 7.17−7.19 (m, 3H), 7.47 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.51 (p), 26.54 (s), 46.47 (s), 124.92 (t), 126.45 (t), 127.03 (t), 129.03 (t), 129.51 (t), 130.62 (q), 136.72 (q), 136.83 (q), 143.45 (q); HRMS (EI) found M^+ 287.0965, calcd for $C_{16}H_{17}NO_2S$ M 287.0980. Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.74; H, 6.07; N, 4.72.

***N*-(4′-Methoxybenzenesulfonyl)-1,2,3,4-tetrahydroquinoline (2f), *N*-(4′-methoxybenzenesulfonyl)-6-iodo-1,2,3,4-tetrahydroquinoline (2f−I) 1:1 mixture**: IR (KBr) 2930, 2830, 1600, 1500, 1340, 1260, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58−1.65 (m), 2.40−2.47 (m), 3.74−3.80 (m), 3.82 (s), 3.84 (s), 6.84−6.89 (m), 7.00 (d, J = 7.3 Hz), 7.06 (t, J = 7.5 Hz), 7.18 (t, J = 8.1 Hz), 7.34 (s), 7.46−7.57 (m), 7.79 (d, J = 8.4 Hz); HRMS (EI) found M^+ 303.0919 and 428.9907, calcd for $C_{16}H_{17}NO_3S$ M 287.0980 and $C_{16}H_{16}NO_3SI$ M 428.9896.

***N*-(2′-Nitrobenzenesulfonyl)-1,2,3,4-tetrahydroquinoline (2j)**: mp 130.5−132.0 °C; IR (KBr) 2940, 1530, 1490, 1340, 1160, 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.89 (quint, J = 6.4 Hz, 2H), 2.63 (t, J = 6.8 Hz, 2H), 3.87 (t, J = 6.0 Hz, 2H), 7.07−7.19 (m, 3H), 7.51−7.62 (m, 3H), 7.65−7.72 (m, 2H). Anal. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.43; N, 8.80. Found: C, 56.44; H, 4.24; N, 8.66.

***N*-(2′-Nitrobenzenesulfonyl)-6-iodo-1,2,3,4-tetrahydroquinoline (2j−I)**: mp 122.0−123.5 °C; IR (KBr) 2950, 1540, 1480, 1360, 1250, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (quint, J = 6.4 Hz, 2H), 2.61 (t, J = 6.8 Hz, 2H), 3.84 (t, J = 6.0 Hz, 2H), 7.29 (d, J = 8.5 Hz, 1H), 7.43−7.48 (m, 2H), 7.58−7.64 (m, 2H), 7.71 (t, J = 8.3 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H); HRMS (EI) found M^+ 443.9638, calcd for $C_{15}H_{13}N_2O_4SI$ M 443.9639.

***N*-(Trifluoromethanesulfonyl)-4-methyl-1,2,3,4-tetrahydroquinoline (2k)**: oil; IR (neat) 2900, 1480, 1400, 1230, 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (d, J = 7.0 Hz, 3H), 1.70−1.79 (m, 1H), 2.11−2.29 (m, 1H), 2.97−3.02 (m, 1H), 3.83−3.90 (m, 2H), 7.18−7.22 (m, 2H), 7.25−7.28 (m, 1H), 7.51 (d, J = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.49 (p), 30.12 (t), 31.70 (s), 46.37 (s), 118.35 (q), 121.56 (q), 123.19 (t), 126.23 (t), 126.74 (t), 127.97 (t), 134.61 (q), 135.80 (q); HRMS (EI) found M^+ 279.0540, calcd for $C_{11}H_{12}F_3NO_2S$ M 279.0540.

***N*-(Trifluoromethanesulfonyl)-5,6-didehydro-5,6-benzomorpholine (2l)**: oil; IR (neat) 1580, 1500, 1400, 1320,-1260, 1230, 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.97 (t, J = 4.6 Hz, 2H), 4.37 (t, J = 4.6 Hz, 2H), 6.91−6.96 (m, 2H), 7.13 (t, J = 7.7 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.53 (s), 65.11 (s), 118.04 (t), 118.09 (q), 121.14 (t), 121.31 (q), 122.13 (q), 122.51 (t), 127.18 (t), 146.43 (q); HRMS (EI) found M^+ 267.0169, calcd for $C_9H_8F_3NO_3S$ M 267.0177.

***N*-(Trifluoromethanesulfonyl)-2-methyl-1,2,3,4-tetrahydroquinoline (2m)**: oil; IR (neat) 2900, 1480, 1450, 1380, 1220, 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, J = 6.6 Hz, 3H), 1.57−1.70 (m, 1H), 2.37−2.46 (m, 1H), 2.76 (t, J = 6.7 Hz, 2H), 4.55−4.65 (m, 1H), 7.15−7.25 (m, 3H), 7.50 (d, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9 (p), 24.44 (s), 31.08 (s), 54.57 (s), 118.55 (q), 121.78 (q), 125.54 (t), 126.70 (t), 126.99 (t), 128.41 (t), 133.22 (q); HRMS (EI) found M^+ 279.0550, calcd for $C_{11}H_{12}F_3NO_2S$ M 279.0540.

***N*-(Trifluoromethanesulfonyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (2n)**: mp 62.0−64.0 °C; IR (KBr) 2960, 1500, 1390, 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (bs, 1H), 2.64−2.72 (m, 2H), 2.75−2.82 (m, 1H), 5.52 (dd, J = 6.8, 6.8 Hz, 1H), 7.15−7.30 (m, 8H), 7.67 (d, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.45 (s), 33.16 (s), 61.88 (t), 125.24 (t), 125.84 (t), 126.83 (t), 127.44 (t), 127.57 (t), 128.26 (t), 128.71 (t), 134.52 (q); HRMS (EI) found M^+ 341.0673, calcd for $C_{16}H_{14}F_3NO_2S$ M 341.0697. Anal. Calcd for $C_{16}H_{14}F_3NO_2S$: C, 56.30; H, 4.13, N, 4.10. Found: C, 56.15; H, 4.16; N, 3.92.

***N*-(Trifluoromethanesulfonyl)-2-butyl-1,2,3,4-tetrahydroquinoline (2o)**: oil; IR (neat) 2900, 2850, 1480, 1450, 1390, 1220, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 7.1 Hz, 3H), 1.25−1.74 (m, 7H), 2.37−2.42 (m, 1H), 2.77 (t, J = 7.0 Hz, 2H), 4.41 (m, 1H), 7.15−7.26 (m, 3H), 7.52 (d,

J = 6.6 Hz, 1H); HRMS (EI) found M^+ 321.1018, calcd for $C_{14}H_{18}F_3NO_2S$ M 321.1010.

***N*-(Trifluoromethyl)benzo[*f*]-1,2,3,4-tetrahydroquinoline (2p)**: mp 82.0−84.0 °C; IR (KBr) 2950, 2360, 1600, 1520, 1400, 1200 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.29 (quint, J = 6.4 Hz, 2H), 3.24 (t, J = 7.1 Hz, 2H), 3.90 (t, J = 5.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 9.2 Hz, 1H), 7.68 (d, J = 9.2 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.73 (s), 23.29 (s), 44.88 (s), 119.86 (q, J = 324 Hz, q, CF_3), 122.22 (t), 124.83 (q), 125.93 (t), 126.91 (t,), 127.12 (t), 128.53 (t), 133.40 (q), 132.02 (q), 132.86 (q); MS (EI) M^+ 315. Anal. Calcd for $C_{14}H_{12}F_3NO_2S$: C, 53.33; H, 3.84; N, 4.44. Found: C, 53.40; H, 3.72; N, 4.42.

***N*-(Trifluoromethyl)-5,6-dihydrophenanthridine (2q)**: mp 61.0−62.0 °C; IR (KBr) 3020, 1480, 1440, 1390, 1220, 1200, 1140 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.87 (s, 2H), 7.27 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.59 (s), 119.82 (q, J = 325 Hz, q, CF_3), 123.74 (t), 124.52 (t), 125.28 (t), 125.71 (t,), 127.97 (t), 128.58 (t), 128.98 (t), 130.10 (q), 130.89 (q), 131.91 (q), 134.05 (q); MS (EI) M^+ 313. Anal. Calcd for $C_{14}H_{10}F_3NO_2S$: C, 53.67; H, 3.22; N, 4.47. Found: C, 53.56; H, 2.97; N, 4.19.

***N*-(Trifluoromethanesulfonyl)-2,3-dihydronaphtho-[2,1-e]morpholine (2r)**: mp 104.0−106.0 °C; IR (KBr) 1580, 1480, 1380, 1220, 1180, 1120 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.04 (t, J = 4.5 Hz, 2H), 4.58 (t, J = 4.6 Hz, 2H), 7.40 (d, J = 9.3 Hz, 1H), 7.47−7.53 (m, 2H), 7.64 (d, J = 9.0 Hz, 1H), 7.74−7.78 (m, 1H), 8.14−8.17 (m, 1H); MS (EI) M^+ 317. Anal. Calcd for $C_{13}H_{10}F_3NO_3S$: C, 49.21; H, 3.18; N, 4.41. Found: C, 49.17; H, 3.19; N, 4.36.

***N*-(Trifluoromethanesulfonyl)-2,3-dihydro-4′-iodonaphtho[2,1-*e*]morpholine (2r-I)**: mp 72.5−73.5 °C; IR (KBr) 1600, 1400, 1230, 1200, 1180, 1140, 1120, 1090, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.02 (t, J = 4.5 Hz, 2H), 4.59 (t, J = 4.6 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.99 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 8.22 (s, 1H); HRMS (EI) found M^+ 442.9296, calcd for $C_{13}H_9F_3NO_3SI$ M 442.9300.

***N*-(Trifluoromethanesulfonyl)-4-[4′-(trifluoromethyl)-phenyl]-7-methyl-1,2,3,4-tetrahydroquinoline (2s-I)**: oil; IR (neat) 2940, 1620, 1500, 1400, 1330, 1200, 1130, 1070 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09−2.19 (m, 1H), 2.34 (s, 3H), 2.40−2.49 (m, 1H), 3.79−3.86 (m, 1H), 3.98−4.04 (m, 1H), 4.27 (dd, J = 7.7, 7.7 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.43 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H); HRMS (EI) found M^+ 423.0716, calcd for $C_{18}H_{15}F_6NO_2S$ M 423.0728.

4-[4′-(Trifluoromethyl)phenyl]-6-iodo-7-methylchromane (5): mp 94.5−95.5 °C; IR (KBr) 2950, 1620, 1550, 1320, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.98−2.07 (1H, m, 3-H), 2.25−2.32 (1H, m, 3-H), 2.35 (3H, s, CH_3), 4.08−4.22 (3H, m, 2, 4-H), 6.81 (1H, s, 8-H) 7.19 (1H, s, 5-H), 7.24 (2H, d, J = 8.1 Hz, 2′, 6′-H), 7.57 (2H, d, J = 8.1 Hz, 3′, 5′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.70 (p, CH_3), 31.35 (s, 3-C), 40.21 (t, 4-C), 63.53 (s, 2-C), 89.63 (q, 6-C), 118.36 (t, 8-C), 123.39 (q, 10-C), 125.59 (t, 3′, 5′-C), 128.87 (t, 2′, 6′-C), 139.90 (t, 5-C), 141.33 (q, 1′-C), 149.10 (q, 7-C), 155.37 (q, 9-C); HRMS (FAB) found M^+ 418.0025, calcd for $C_{17}H_{14}OF_3I$ M 418.0042. Anal. Calcd for $C_{17}H_{14}OF_3I$: C, 48.82; H, 3.37. Found: C, 48.86; H, 3.28.

***N*-(Trifluoromethanesulfonyl)-1,2,3,4-tetrahydroquinoline-6-carboxylic acid (7)**: mp 153.0−155.0 °C; IR (KBr) 3000, 1700, 1610, 1380, 1200 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.15 (quint, J = 6.3 Hz, 2H, 3-H), 2.96 (t, J = 6.8 Hz, 2H, 4-H), 3.93 (t, J = 5.9 Hz, 2H, 2-H), 7.67 (d, J = 9.3 Hz, 1H, 5-H), 7.93−7.95 (m, 2H, 7,8-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.95 (s, 3-C), 26.42 (s, 4-C), 48.27 (s, 2-C), 120.10 (q, J_{C-F} = 328 Hz, q, CF_3), 122.89 (t), 126.50 (q), 128.77 (t), 130.42 (q), 131.74 (t), 140.12 (q), 171.39 (q, CO_2H). Anal. Calcd for $C_{11}H_{10}NO_4S$: C, 40.41; H, 3.39; N, 4.71; S, 10.79. Found: C, 41.85; H, 3.23; N, 4.74; S, 10.36.

***N*-(Trifluoromethanesulfonyl)-2-phenylpyrrolidine (9t)**: mp 56.0−57.5 °C; IR (KBr) 3000, 1600, 1500, 1450, 1380, 1230, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.01−2.12 (m, 3H), 2.40−2.49 (m, 1H), 3.76−3.80 (m, 2H), 5.12 (dd, J = 7.0, 2.9 Hz, 1H), 7.25−7.30 (m, 3H), 7.36 (t, J = 7.2 Hz, 2H); HRMS (EI) found M^+ 279.0553, calcd for $C_{11}H_{12}F_3NO_2S$ M 279.0540.

***N*-(4′-Nitrobenzenesulfonyl)-2-phenylpyrrolidine (9u)**: mp 131.5−132.0 °C; IR (KBr) 3080, 2950, 2850, 1600, 1520, 1340, 1160 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.80−1.92 (m, 2H, 3,4-H), 1.94−2.01 (m, 1H, 4-H), 2.14−2.21 (m, 1H, 3-H), 3.59−3.66 (m, 2H, 5-H), 4.87 (dd, J = 7.8, 4.4 Hz, 1H, 2-H), 7.17 (d, J = 6.8 Hz, 2H, Ph(o)-H), 7.22−7.25 (m, 3H, Ph(m,p)-H), 7.80 (d, J = 8.9 Hz, 2H, 2′,6′-H), 8.22 (d, J = 8.9 Hz, 2H, 3′,5′-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.20 (s, 4-C), 35.93 (s, 3-C), 49.40 (s, 5-C), 63.67 (t, 2-C), 123.95 (t, 3′,5′-C), 126.37 (t, Ph-2″,6″-C), 127.44 (t, Ph-4″-C), 128.27 (t, 2′,6′-C), 128.38 (t, Ph-3″,5″-C), 141.79 (q, Ph-1″-C), 144.66 (q, 1′-C), 149.74 (q, 4′-C); MS (EI) M^+ 322. Anal. Calcd for $C_{16}H_{16}N_2O_4S$: C, 57.82; H, 4.85; N, 8.43; S, 9.65. Found: C, 57.59; H, 4.82; N, 8.41; S, 9.65.

***N*-(4′-Nitrobenzenesulfonyl)-2-methyl-5-phenylpyrrolidine (9v) (*cis*)**: mp 174.0−175.5 °C; IR (KBr) 2970, 1600, 1520, 1350, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.49 (d, J = 6.3 Hz, 3H), 1.59−1.66 (m, 1H), 1.82−1.99 (m, 2H), 2.01−2.10 (m, 1H), 4.08−4.16 (m, 1H), 4.78 (dd, J = 6.8, 6.8 Hz, 1H), 7.20−7.30 (m, 5H), 7.83 (d, J = 8.9 Hz, 2H), 8.24 (d, J = 9.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.46 (p), 32.19 (s), 34.71 (s), 58.08 (t), 65.39 (t), 123.94 (t), 126.55 (t), 127.45 (t), 128.43 (t), 128.57 (t), 141.41 (q), 144.87 (q), 149.81 (q). Anal. Calcd for $C_{17}H_{18}N_2O_4S$: C, 58.95; H, 5.24; N, 8.09. Found: C, 58.96; H, 4.95; N, 7.85. **(*trans*)**: mp 113.0−114.0 °C; IR (KBr) 1600, 1520, 1350, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.49 (d, J = 6.3 Hz, 3H), 1.69−1.74 (m, 1H), 1.79−1.85 (m, 1H), 2.29−2.40 (m, 1H), 2.50−2.62 (m, 1H), 4.30−4.37 (m, 1H), 5.01 (dd, J = 8.9, 1.2 Hz, 1H), 6.94 (d, J = 7.7 Hz, 2H), 7.06 (t, J = 7.4 Hz, 2H), 7.14 (t, J = 6.6 Hz, 1H), 7.52 (d, J = 9.2 Hz, 2H), 8.02 (d, J = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.31 (p), 31.89 (s), 32.92 (s), 58.20 (t), 63.70 (t), 123.41 (t), 126.95 (t), 127.37 (t), 128.86 (t), 128.17 (t), 141.19 (q), 147.20 (q), 149.10 (q).

***N*-(4-Methoxyphenyl)saccharin (11a′) (ortho, para mixture)**: IR (KBr) 3080, 2840, 1740, 1520, 1340, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (s), 3.87 (s), 7.06 (d, J = 9.0 Hz), 7.08−7.12 (m), 7.43 (d, J = 9.0 Hz), 7.48−7.55 (m), 7.85−7.96 (m), 8.00 (d, J = 8.1 Hz), 8.15 (d, J = 7.8 Hz); HRMS (EI) found M^+ 289.0419, calcd for $C_{14}H_{11}NO_4S$ M 289.0419.

***N*-(4-Methylphenyl)saccharin (11b′) (ortho, para mixture)**: IR (KBr) 3100, 1740, 1460, 1340, 1320, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.32 (s), 2.43 (s), 7.34−7.46 (m), 7.87−7.94 (m), 7.98−8.02 (m); HRMS (EI) found M^+ 273.0461, calcd for $C_{14}H_{11}NO_3S$ M 273.0460.

***N*-Phenylsaccharin (11c′)**: mp 189.0−191.0 °C; IR (KBr) 1740, 1720, 1590, 1340, 1300, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.58 (m, 5H), 7.88 (t, J = 7.1 Hz, 1H), 7.93 (t, J = 7.5 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.20 (t), 125.61 (t), 127.17 (q), 128.74 (t), 129.90 (t), 130.08 (t), 134.43 (t), 135.06 (t), 137.60 (q), 158.37 (q); MS (EI) M^+ 259. Anal. Calcd for $C_{13}H_9NO_3S$: C, 60.22; H, 3.50; N, 5.40; S, 12.37. Found: C, 59.89; H, 3.48; N, 5.37; S, 12.29.

***N*-(4-Chlorophenyl)saccharin (11d′) (ortho, para mixture)**: IR (KBr) 3100, 1740, 1490, 1340, 1320, 1190 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.56 (m), 7.57−7.65 (m), 7.85−8.04 (m), 8.13−0.20 (m); HRMS (EI) found M^+ 294.9898, calcd for $C_{13}H_8NO_3S^{37}Cl$ M 294.9886.

***N*-(4-Nitrophenyl)saccharin (11e′) (meta, major)**: mp 153.0−156.0 °C; IR (KBr) 3100, 2920, 1740, 1520, 1350, 1300, 1190 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.78 (m), 7.82−7.87 (m), 7.90−8.05 (m), 8.17−8.28 (m), 8.37−8.44 (m), 8.48 (s); HRMS (EI) found M^+ 304.0129, calcd for $C_{12}H_8N_2O_5S$ M 304.0154.

***N*-(1-Naphthyl)saccharin (11f′)**: mp 219.0−221.0 °C; IR (KBr) 3080, 1740, 1600, 1500, 1480, 1400, 1340, 1300, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53−7.58 (m, 2H), 7.62 (t, J = 7.8 Hz, 1H), 7.70 (d, J = 7.3 Hz, 1H), 7.83−7.86 (m,

1H), 7.90−7.99 (m, 3H), 8.05−8.08 (m, 2H), 8.21 (d, J = 7.6 Hz, 1H); MS (EI) M^+ 309. Anal. Calcd for $C_{17}H_{11}NO_3S$: C, 66.01; H, 3.58; N, 4.53. Found: C, 66.02; H, 3.43; N, 4.46.

***N*-(3-Benzothienyl)saccharin (11g′)**: mp 209−210 °C; IR (KBr) 3100, 1740, 1440, 1340, 1290, 1260, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.45 (m, 2H), 7.61 (s, 1H), 7.83−7.87 (m, 2H), 7.93 (t, J = 7.1 Hz, 1H), 7.97 (t, J = 7.9 Hz, 1H), 8.04 (d, J = 6.8 Hz, 1H), 8.21 (d, J = 7.7 Hz, 1H); HRMS (EI) found M^+ 315.0039, calcd for $C_{15}H_9NO_3S_2$ M 315.0024.

***N*-Methyl-*N*-phenyl-4-nitrobenzenesulfonamide (12h′)**: mp 117.0−118.5 °C; IR (KBr) 1610, 1520, 1350, 1300, 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.24 (s, 3H), 7.07−7.10 (m, 2H), 7.31−7.36 (m, 3H), 7.73 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.32 (p), 123.94 (t), 126.53 (t), 127.92 (t), 128.91 (t), 129.19 (t), 140.54 (q), 142.27 (q), 150.90 (q); MS (EI) M^+ 292. Anal. Calcd for $C_{13}H_{12}N_2O_4S$: C, 53.41; H, 4.14; N, 9.58. Found: C, 53.25; H, 3.96; N, 9.54.

***N*-Ethyl-*N*-phenyl-4-nitrobenzenesulfonamide (12i′)**: mp 120.0−122.0 °C; IR (KBr) 3100, 3000, 1600, 1520, 1350, 1310, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, J = 7.2 Hz, 3H), 3.66 (q, J = 7.2 Hz, 2H), 7.02−7.06 (m, 2H), 7.33−7.36 (m, 3H), 7.78 (d, J = 8.8 Hz, 2H), 8.31 (d, J = 9.0 Hz, 2H); MS (EI) M^+ 306. Calcd for $C_{14}H_{14}N_2O_4S$: C, 54.89; H, 4.61; N, 9.11. Found: C, 54.79; H, 4.46; N, 9.08.

***N*-Butyl-*N*-phenyl-4-nitrobenzenesulfonamide (12j′)**: mp 93.0−95.0 °C; IR (KBr) 3100, 2960, 1590, 1530, 1350, 1160, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3H), 1.24−1.47 (m, 4H), 3.58 (t, J = 7.0 Hz, 2H), 7.00−7.05 (m, 2H), 7.33−7.36 (m, 3H), 7.76 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 8.8 Hz, 2H); HRMS (EI) found M^+ 334.0970, calcd for $C_{16}H_{18}N_2O_4S$ M 334.0987.

***N*-Methyl-*N*-(4-methylphenyl)-4-nitrobenzenesulfonamide (13n′) (ortho, meta, para mixture)**: IR (KBr) 3010, 1600, 1520, 1350, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) **(ortho)** δ 2.39 (s, 3H), 3.20 (s, 3H), 6.54 (d, J = 7.8 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 6.8 Hz, 1H), 7.31 (d, J = 6.6 Hz, 1H), 7.90 (d, J = 8.8 Hz, 2H), 8.37 (d, J = 8.8 Hz, 2H): **(meta and para 1:1 mixture)** δ 2.33 (s), 2.35 (s), 3.21 (s), 3.27 (s), 6.80 (d, J = 8.3 Hz), 6.93−6.96 (m), 7.12 (d, J = 7.8 Hz), 7.20 (t, J = 7.7 Hz), 7.72−7.76 (m), 8.29−8.32 (m); HRMS (EI) found M^+ 303.0663, calcd for $C_{14}H_{14}N_2O_4S$ M 306.0673.

***N*-(Chlorophenyl)-*N*-methyl-4-nitrobenzenesulfonamide (13o′) (ortho, meta, para mixture)**: IR (KBr) 3100, 1600, 1520, 1480, 1350, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) **(ortho)** δ 3.30 (s, 3H), 7.29−7.35 (m, 3H), 7.38−7.42 (m, 1H), 7.94 (d, J = 9.0 Hz, 2H), 8.35 (d, J = 8.8 Hz, 2H): **(ortho, meta, para mixture)** δ 3.21 (s), 3.22 (s), 3.30 (s), 6.98−7.05 (m), 7.12−7.14 (m), 7.26−7.35 (m), 7.37−7.42 (m), 7.72−7.77 (m), 7.72−7.76 (m), 7.90−7.96 (m), 8.29−8.37 (m); HRMS (EI) found M^+ 328.0091, calcd for $C_{13}H_{11}N_2O_4S^{37}Cl$ M 328.0101.

***N*-(2′,5′-Dimethylphenyl)-*N*-methyl-4-nitrobenzenesulfonamide (13p′)**: mp 116.0−168.0 °C; IR (KBr) 3100, 2920, 1600, 1530, 1350, 1320, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.30 (s, 3H), 3.18 (s, 3H), 6.38 (s, 1H), 7.06 (d, J = 6.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 9.0 Hz, 2H), 8.37 (d, J = 9.0 Hz, 2H); MS (EI) M^+ 320. Anal. Calcd for $C_{15}H_{16}N_2O_4S$: C, 56.24; H, 5.03; N, 8.74. Found: C, 55.86; H, 4.79; N, 8.64.

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Supporting Information Available: Copies of ^1H NMR spectra for all compounds described (48 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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