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Synthetic use of 1,1,2,2-tetraphenyldisilane for the preparation of biaryls through the intramolecular free radical *ipso*-substitution of *N*-(2-bromoaryl)arenesulfonamides

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Abstract—Treatment of various *N*-methyl-*N*-(2-bromoaryl)arenesulfonamides (**1a**–**g**, **1i**, and **1m**) with 1,1,2,2-tetraphenyldisilane and AIBN under heating conditions gave the corresponding biaryl products (**2a**–**g**, **2i**, and **2m**) in moderate yields through the intramolecular radical *ipso*-substitution. However, *N*–H free *N*-(2-bromoaryl)arenesulfonamides **1h** and 2-bromoaryl arenesulfonate **1j** did not give the corresponding biarys. 1,1,2,2-Tetraphenyldisilane is the most effective reagent for 1,5-*ipso*-substitution on the sulfonamides among typical radical reagents such as diphenylsilane, tributyltin hydride, tris(trimethylsilyl)silane, and 1,1,2,2-tetraphenyldisilane. Furthermore, 1,1,2,2-tetraphenyldisilane has the advantages of low toxicity, stability, and ease of preparation.

1. Introduction

The biaryl skeleton is pharmacologically interesting and important as a building block for a large number of natural products,[1] biologically active compounds,[1] chiral ligands in asymmetric synthesis,[2] polymers, and advanced materials. Various methods for the construction of biaryls from monoaryl precursors such as the Ullmann coupling reaction of aryl halides using Cu(0),[3] and the Stille coupling reaction of aryl tin compounds with aryl halides[4] have been reported.[5] Radical methods of mostly two types are also used for the construction of biaryls. One is an oxidative radical arylation of arenes using Tl(III), V(V), Ru(IV), and Fe(III) salts under photochemical conditions.[6] The other is a reductive intramolecular radical arylation through the *ipso*-substitution using tributyltin hydride/AIBN under heating conditions.[7] For example, *ipso*-substitution of 2-(2-bromophenyl)-3-(arylmethyl)-4-oxazolidinones,[8] 2-bromobenzyl aryl ethers,[9] 2-iodoazobenzenes,[10] 1-(2-bromophenyl)-ethyl diaryl phosphinates,[11] [1-(2-bromophenyl)-ethoxy]triphenylsilane,[12] *N*-(2-haloaryl)arenesulfonamides[13] have been studied with a tributyltin hydride/AIBN system. A intramolecular radical arylation method through the *ipso*-substitution using tributyltin hydride is popular and versatile.[14] However, it is well known that the use of tributyltin hydride brings about several problems such as high toxicity and disposal, work-up and complete removal of the tin species from the products, though radical *ipso*-substitution of 3-iodoalkyldimethylphenylstannanes with Et_3B,[15] 2-[methyl(arenesulfonyl)amino]benzene-diazonium salts and $TiCl_3$,[16] and 2-[(arenesulfonyl)oxy]benzaldehydes with di-*tert*-butyl peroxide[17] were recently reported as a non-tin method.[18] We have reported the synthetic utilization of 1,1,2,2-tetraphenyldisilane, which is air-stable crystals, and an easily handled reagent for four types of radical reactions with alkyl bromides or xanthates, such as reduction, reductive addition to olefins, alkylation of heteroaromatic bases, and cyclization of *O*-glycosides.[19] Here, as a part of our study on the synthetic utility of 1,1,2,2-tetraphenyldisilane for organic synthesis, we report the intramolecular free radical *ipso*-substitution of *N*-(2-bromoaryl)arenesulfonamides using 1,1,2,2-tetraphenyldisilane and AIBN under heating conditions, to form the corresponding biaryl products, and the reactivities are compared with those of *n*-Bu_3SnH. The key points in these reactions are the formation of σ aryl radical, the cyclization at the *ipso* position to form a spiro cyclic intermediate, the ring-opening and rearomatization of the spiro cyclic intermediate, and the loss of SO_2 (Scheme 1).

2. Results and discussion

Optimum conditions for radical *ipso*-substitution with $Ph_4Si_2H_2$ and AIBN were studied and the results are shown in Table 1. When the reaction was carried out in ethyl acetate (bp 78°C, entry 1), the yield of biaryl **2a** was below 10%, the starting sulfonamide **1a** and the cyclized product **3a** were obtained in 63 and 9% yields, respectively. To improve the yield of the *ipso*-substitution product,

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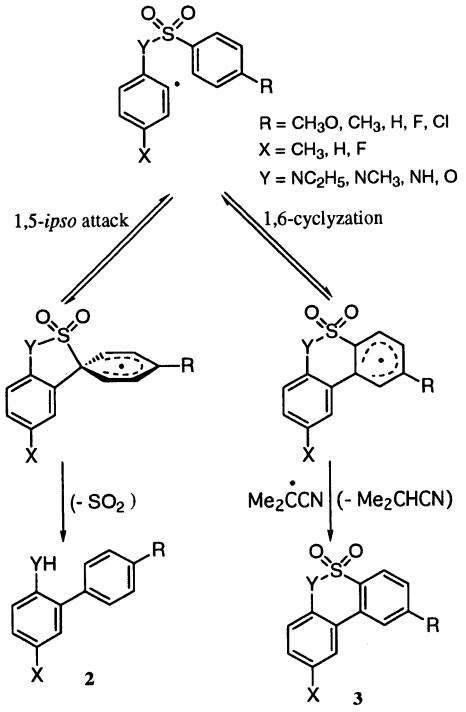
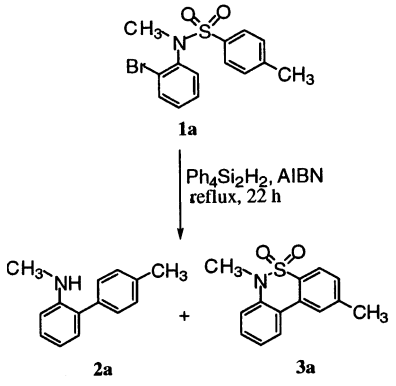


Scheme 1. Reaction mechanism.

Table 1. Study on optimum reaction conditions

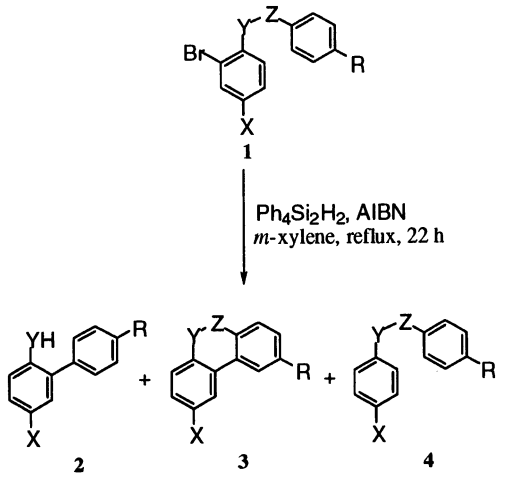


Entry	$Ph_4Si_2H_2$ (equiv.)	AIBN (equiv.)	Solvent	Yields (%)		
				1	**2**	**3**
1	1.3	1.5	Ethyl acetate	63	10	9
2	1.3	1.5[a]	Toluene	58	19	10
3	1.3	1.5[a]	*m*-Xylene	27	30	20
4	2.0+1.0[b]	1.5[a]	*m*-Xylene	11	55	28
5	2.0+2.0[b]	2.0[a]	*m*-Xylene	0	56	31

[a] Slow addition of AIBN with a dropping funnel.
[b] $Ph_4Si_2H_2$ was added again after 7 h.

toluene and *m*-xylene were also used as a solvent. The reaction proceeded efficiently in refluxing *m*-xylene (bp 140°C, entry 3). When the amounts of $Ph_4Si_2H_2$ and AIBN were increased, the starting sulfonamide **1a** disappeared after 22 h to give the *ipso*-substitution product **2a** in the better yield (entry 5). The present reaction requires a large amount of AIBN to improve the yield. Since the half-life period of AIBN in refluxing *m*-xylene is a few minutes, slow addition of AIBN is important through a dropping funnel.

Table 2. Radical *ipso*-substitution of compounds **1a**–**1** using $Ph_4Si_2H_2$/AIBN



Entry	**R-**	**X-**	**Y-**	**Z**	**1**	Yields (%)		
						2	**3**	**4**
1	CH_3–	H–	CH_3N–	SO_2	**1a**	56	31	–
2	CH_3O–	H–	CH_3N–	SO_2	**1b**	61	32	–
3	H–	H–	CH_3N–	SO_2	**1c**	60	31	–
4	F–	H–	CH_3N–	SO_2	**1d**	44	35	–
5	Cl–	H–	CH_3N–	SO_2	**1e**	46	14	–
6	CH_3–	CH_3–	CH_3N–	SO_2	**1f**	50	34	–
7	CH_3–	F–	CH_3N–	SO_2	**1g**	42	31	–
8	CH_3–	H–	HN–	SO_2	**1h**	0	38	38
9	CH_3–	H–	C_2H_5N–	SO_2	**1i**	59	28	–
10	H–	CH_3–	O–	SO_2	**1j**	0	47	23
11	H–	CH_3–	CH_3N–	CH_2	**1k**	6	–	–
12	H–	CH_3–	O–	CH_2	**1l**	0	56	13

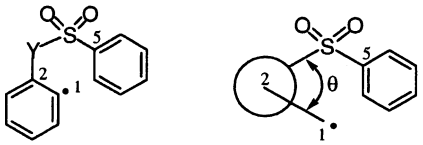
The substituent effect at the *para*-position of *N*-methyl-*N*-(2-bromophenyl)arenesulfonamides was shown in Table 2 (entries 1–5). When the electron-withdrawing substituents were introduced into the *para*-position of the sulfonyl group in sulfonamides (**1d** and **1e**), the yields of *ipso*-substitution products (**2d** and **2e**) were slightly decreased. The substituent effect of X at the aniline moiety of sulfonamides (**1a** and **1g**) was also studied (entries 1 and 7). Here, the amount of the *ipso*-substitution product was decreased again by the introduction of an electron-withdrawing substituent, rather than an electron-donating substituent. From these results, the introduction of electron-donating groups on the two aromatic rings in *N*-methyl-*N*-(2-bromoaryl)arenesulfonamides was more effective than that of electron-withdrawing groups for the rearrangement to give biaryls. The same tendency was observed in the reactions of *N*-(2-haloaryl)arenesulfonamides with a tributyltin hydride/AIBN system.[13]

The substitutent effect of the *N*-alkyl group (-Y) was studied (entries 1, 8, and 9). Here, *N*-methyl and *N*-ethyl sulfonamides (**1a** and **1i**) gave the corresponding rearranged biaryls (**2a** and **2i**) in reasonable yields.

However, *N*–H free sulfonamide **1h** did not give the rearranged biaryl **2h**, the cyclization and the reduction products (**3h** and **4h**) were obtained in moderate yields.

A sulfonate compound showed the same tendency as the

Table 3. Calculation of bond angles, torsion angles and atomic distances in optimum radical transition states with molecular orbital method



Y–	CH_3N–	HN–	O–
Bond angles (°)			
C_1–C_2–Y	122.1	122.9	124.4
C_2–Y–S	124.2	125.2	123.7
Torsion angle θ (°)			
C_1–C_2–Y–S	12.9	37.9	68.4
Atomic distance (Å)			
C_1–C_5	3.005	3.435	3.478

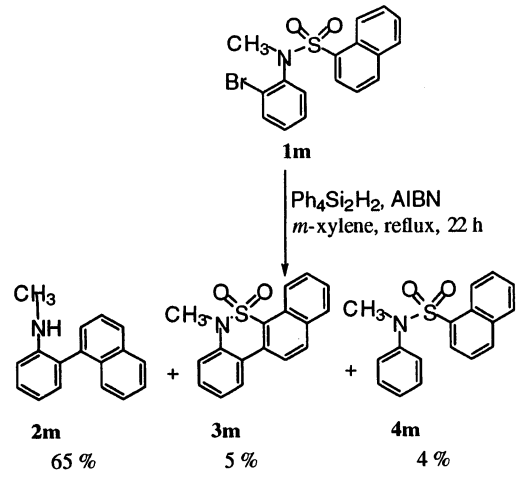
N–H free sulfonamide. Thus, the *ipso*-substitution product **2j** was not formed from the 2-bromo-4-methylphenyl benzenesulfonate **1j**, the cyclization product **3j** and the direct reduction product **4j** were obtained (entry 10). These results can be explained by the calculations of the molecular orbital method as shown in Table 3.[20]

When the torsion angles of C_1–C_2–Y–S and atomic distances between the aryl radical (C_1) and the *ipso* position (C_5) in optimum radical transition states were compared, torsion angle θ in *N*-methyl-*N*-phenyl-benzenesulfonamide radical is smaller than those of *N*–H free *N*-phenylbenzenesulfonamide and phenyl benzenesulfonate radicals. Moreover, the location of the aryl radical (C_1) generated from *N*-methyl-*N*-(2-bromophenyl)benzenesulfonamide is closer to the *ipso* position (C_5) than those derived from *N*–H free *N*-(2-bromophenyl)benzenesulfonamide and 2-bromophenyl benzenesulfonate.

Additionally, it is well known that *N*-alkylbenzanilide exists in *cis* conformation in the crystal and in solution.[21] On the other hand, benzanilide has *trans* conformation due to the σ–π interaction between *N*–H and the aromatic ring in the crystal,[22] and phenyl benzoate also prefers *trans* conformation.[23] These results support that the introduction of the *N*-alkyl group to *N*-(2-bromoaryl)arenesulfonamides is the key point for the formation of biaryls through the radical *ipso*-substitution.

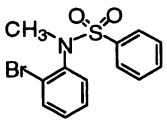
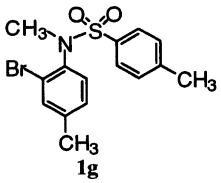
Next, *N*-methyl-*N*-(2-bromo-4-methylphenyl)benzyl amine **1k** and (2-bromo-4-methyl)phenyl benzyl ether **1l**, which have a methylene group instead of a sulfonyl group, were studied (entries 11 and 12). However, the formation of the corresponding biaryls did not occur. Thus, the sulfonyl group in *N*-alkyl-*N*-(2-bromoaryl)arenesulfonamides is the second key point for the formation of biaryls through the radical *ipso*-substitution. Moreover, naphthalenesulfonamide was studied, and the result is shown in Scheme 2. *N*-Methyl-*N*-(2-bromophenyl)-1-naphthalenesulfonamide **1m** showed high *ipso* selectivity to form the corresponding biaryl **2m**, and the formation of small amounts of the cyclization and the direct reduction products (**3m** and **4m**) was identified by ^{1}H NMR and mass spectra.

The reactivities of radical mediators such as diphenylsilane



Scheme 2. Reaction of *N*-methyl-*N*-(2-bromophenyl)-1-naphthalenesulfonamide **1m**.

Table 4. Radical reactivity of organosilanes and tinhydride

Substrate	Reagent	Yields (%)			
		1	**2**	**3**	**4**
 **1c**	Ph_2SiH_2	32	20	23	–
	n-Bu_3SnH	0	41	37	18
	$(TMS)_3SiH$	0	56	22	–
	$Ph_4Si_2H_2$	0	60	31	–
 **1g**	Ph_2SiH_2	60	10	13	–
	n-Bu_3SnH	0	42	37	17
	$(TMS)_3SiH$	0	47	37	–
	$Ph_4Si_2H_2$	0	50	34	–

(Ph_2SiH_2), tributyltin hydride (*n*-Bu_3SnH), tris(trimethylsilyl)silane [$(TMS)_3SiH$], and tetraphenyldisilane ($Ph_4Si_2H_2$) with sulfonamides **1c** and **1g** were compared under the same reaction conditions, as shown in Table 4. Ph_2SiH_2 was not so reactive, and the starting sulfonamides were recovered mainly after 22 h.

Tributyltin hydride-mediated reactions gave the *ipso*-substitution products in 41 and 42% yields, together with the cyclization products in 37 and 37% yields, and the reduction products in 18 and 17% yields, respectively. Tris(trimethylsilyl)silane-mediated reactions gave the *ipso*-substitution products in 56 and 47% yields, together with the cyclization products, 22 and 37% yields, respectively. Tetraphenyldisilane-mediated reactions gave the *ipso*-substitution products in 60 and 50% yields, together with the cyclization products, 31 and 34% yields, respectively. Probably, these results arise from the difference in bond strength between the 14-metal atom and the hydrogen atom. Thus, $Ph_4Si_2H_2$ showed high selectivity for 1,5-*ipso*-substitution on sulfonamides.

3. Conclusions

$Ph_4Si_2H_2$ is a useful reagent for the synthesis of biaryls

through the radical *ipso*-substitution of *N*-alkyl-*N*-(2-bromoaryl)arenesulfonamides, since this organodisilane is a less toxic, air-stable, easily handled. It is a mild and more effective reagent for the formation of biaryls as compared with the known radical reagents such as tributyltin hydride,[24] tris(trimethylsilyl)silane,[25] and organomonosilane compounds.[26] The use of organodisilane as a radical reagent is preferable methodology from the practical and environmental points of view.

4. Experimental

4.1. General

^{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. *J*-Values are given in Hz. 3-Nitrobenzyl alcohol was used as the matrix of mass spectra (FAB). Melting points were determined on electrothermal apparatus in open capillary tubes and are uncorrected. Kieselgel 60 F254 was used for TLC, Silica Gel 60 (Kanto Kagaku) was used for column chromatography, and Wakogel B-5F was used for preparative TLC. Solvents were purified and dried by standard techniques.

4.2. Material

1,1,2,2-Tetraphenyldisilane was prepared by the previously reported method.[19,27] *N*-Alkyl-*N*-(2-bromoaryl)arenesulfonamides (**1a–i** and **1m**) were obtained by *N*-alkylation of *N*-(2-bromoaryl)-arenesulfonamides which were prepared from commercially available arenesulfonyl chlorides, triethylamine, and 2-bromoarylamines.

4.3. General procedure

AIBN (1.0 mmol) in *m*-xylene (10 ml) was added dropwise over 22 h by slow addition using a dropping funnel to a refluxing solution of *N*-(2-bromoaryl)arenesulfonamide (0.5 mmol), 1,1,2,2-tetraphenyldisilane (1.0 mmol) in *m*-xylene (2 ml). Seven hours after the start of the reaction, 1,1,2,2-tetraphenyldisilane (1.0 mmol) was added again. After the reaction, the solvent was removed and the residue was purified by preparative TLC using a mixture of hexane and ethyl acetate (4:1–10:1) as an eluent, or recycling preparative HPLC (eluent: $CHCl_3$).

4.3.1. 2-Methylamino-4′-methylbiphenyl 2a. Oil; IR (neat) 3430, 3030, 2920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.39 (3H, s), 2.78 (3H, s), 3.59 (1H, bs), 6.68 (1H, d, *J*=8.0 Hz), 6.76 (1H, td, *J*=1.1, 7.4 Hz), 7.08 (1H, dd, *J*=1.6, 7.4 Hz), 7.24 (2H, d, *J*=7.7 Hz), 7.28 (1H, td, *J*= 1.6, 7.4 Hz), 7.30 (2H, d, *J*=7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.4 (p), 31.1 (p), 110.2 (t), 117.2 (t), 128.0 (q), 128.8 (t), 129.5 (t), 129.8 (t), 130.3 (t), 136.6 (q), 137.1 (q), 146.3 (q); MS (EI): *m*/*z* 197; Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10%. Found: C, 85.12; H, 7.79; N, 7.12%.

4.3.2. 2,6-Dimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3a. Mp 142–144°C; IR (KBr) 3080, 2920, 1320, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.51 (3H, s), 3.42 (3H, s), 7.29 (1H, d, *J*=8.0 Hz), 7.32 (1H, t, *J*=8.3 Hz), 7.36 (1H, d, *J*=7.7 Hz), 7.48 (1H, t, *J*=7.8 Hz), 7.75 (1H, s), 7.89 (1H, d, *J*=8.0 Hz), 7.99 (1H, d, *J*=7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.9 (p), 32.6 (p), 119.4 (t), 122.5 (t), 124.0 (q), 124.5 (t), 125.4 (t), 125.7 (t), 129.0 (t), 130.2 (t), 131.6 (q), 132.3 (q), 139.6 (q), 143.0 (q); MS (EI): *m*/*z* 259; HRMS (FAB) Found: M+H 260.0749, Calcd for $C_{14}H_{14}NO_2S$: M+H=260.0745.

4.3.3. 2-Methylamino-4′-methoxybiphenyl 2b. Oil; IR (neat) 3430, 3030, 2920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.79 (3H, s), 3.17 (1H, bs), 3.84 (3H, s), 6.68 (1H, d, *J*=8.2 Hz), 6.76 (1H, t, *J*=7.5 Hz), 6.97 (2H, d, *J*=8.6 Hz), 7.06 (1H, dd, *J*=1.7, 7.2 Hz), 7.23–7.27 (1H, m), 7.33 (2H, d, *J*=8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=30.9 (p), 55.3 (p), 109.9 (t), 114.3 (t), 116.9 (t), 127.4 (q), 128.5 (t), 130.1 (t), 130.5 (t), 131.6 (q), 146.3 (q), 158.8 (q); MS (EI): *m*/*z* 213; HRMS (FAB) Found: *m*/*z* 213.1163, Calcd for $C_{14}H_{15}NO$: M^+=213.1154.

4.3.4. 2-Methoxy-6-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3b. Mp 143°C; IR (KBr) 3080, 2920, 1310, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.42 (3H, s), 3.95 (3H, s), 7.07 (1H, dd, *J*=1.9, 8.7 Hz), 7.30 (1H, d, *J*=8.2 Hz), 7.33 (1H, t, *J*=7.5 Hz), 7.39 (1H, d, *J*= 1.9 Hz), 7.50 (1H, t, *J*=7.7 Hz), 7.94 (1H, d, *J*=8.7 Hz), 7.96 (1H, d, *J*=7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=32.6 (p), 55.8 (p), 110.3 (t), 114.0 (t), 119.5 (t), 123.9 (q), 124.6 (t), 124.7 (t), 125.6 (t), 127.1 (q), 130.5 (t), 134.4 (q), 139.9 (q), 162.7 (q); MS (EI): *m*/*z* 275; HRMS (FAB) Found: M+H 276.0701, Calcd for $C_{14}H_{14}NO_3S$: M+H=276.0694.

4.3.5. 2-Methylaminobiphenyl 2c. Oil; IR (neat) 3430, 3080, 2920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.78 (3H, s), 3.14 (1H, bs), 6.69 (1H, d, *J*=8.2 Hz), 6.77 (1H, td, *J*=1.1, 7.4 Hz), 7.09 (1H, d, *J*=7.4 Hz), 7.27 (2H, d, *J*=7.7 Hz), 7.31–7.36 (1H, m), 7.39–7.45 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ=30.8 (p), 109.9 (t), 110.9 (t), 127.2 (t), 127.7 (q), 128.7 (t), 128.8 (t), 129.4 (t), 130.0 (t), 139.5 (q), 146.0 (q); MS (EI): *m*/*z* 183; Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64%. Found: C, 84.86; H, 7.00; N, 7.55%.

4.3.6. 6-Methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3c. Mp 102–103°C; IR (KBr) 3080, 2920, 1320, 1180 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.45 (3H, s), 7.31 (1H, dd, *J*=1.0, 7.7 Hz), 7.34 (1H, dt, *J*=1.0, 7.7 Hz), 7.51 (1H, dt, *J*=1.5, 7.8 Hz), 7.56 (1H, t, *J*=7.7 Hz), 7.71 (1H, dt, *J*=1.5, 7.8 Hz), 7.96 (1H, t, *J*=7.8 Hz), 8.01 (1H, d, *J*=7.5 Hz), 8.01 (1H, d, *J*=7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=32.7 (p), 119.4 (t), 122.5 (t), 124.0 (q), 124.7 (t), 125.4 (t), 125.5 (q), 125.5 (t), 128.2 (t), 130.4 (t), 132.4 (t), 134.2 (q), 139.5 (q); MS (EI): *m*/*z* 245; HRMS (FAB) Found: *m*/*z* 245.0498, Calcd for $C_{13}H_{11}NO_2S$: M^+= 245.0511.

4.3.7. *N*-Methyl-*N*-phenylbenzenesulfonamide 4c. Mp 77.5–78.5°C (lit. 28) Mp 79–79.5°C); IR (KBr) 3070, 2980, 1350, 1180, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.18 (3H, s), 7.08~7.10 (2H, m), 7.28–7.33 (3H, m), 7.43–7.47 (2H, m), 7.56–7.60 (3H, m).

4.3.8. 2-Methylamino-4′-fluorobiphenyl 2d. Oil; IR (neat) 3430, 3020, 2920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.80 (3H, s), 3.83 (1H, bs), 6.69 (1H, d, J=7.9 Hz), 6.77 (1H, t, J=7.5 Hz), 7.05 (1H, dd, J=1.6, 7.4 Hz), 7.12 (2H, t, J=8.8 Hz), 7.27 (1H, dt, J=1.6, 7.9 Hz), 7.37 (2H, dd, J=5.5, 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=30.7 (p), 109.9 (t), 115.7 (t, J_{C-F}=21.7 Hz), 116.9 (t), 126.5 (q), 128.9 (t), 130.1 (t), 131.1 (t, J_{C-F}=8.3 Hz), 135.3 (q, J_{C-F}=3.1 Hz), 146.2 (q), 162.1 (q, J_{C-F}=246.2 Hz); MS (FAB): m/z 201; HRMS (FAB) Found: m/z 201.0949, Calcd for $C_{13}H_{12}FN$: M^+=201.0954.

4.3.9. 2-Fluoro-6-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3d. Mp 145–146°C; IR (KBr) 3080, 2950, 1340, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=3.45 (3H, s), 7.26 (1H, dt, J=2.5, 7.9 Hz), 7.31 (1H, d, J=7.7 Hz), 7.35 (1H, d, J=8.1 Hz), 7.54 (1H, dt, J=1.5, 7.8 Hz), 7.62 (1H, dd, J=2.5, 10.2 Hz), 7.93 (1H, dd, J=1.5, 8.1 Hz), 8.01 (1H, dd, J=2.5, 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=32.7 (p), 112.2 (t, J_{C-F}=23.8 Hz), 115.7 (t, J_{C-F}=23.8 Hz), 119.5 (t), 123.1 (q, J_{C-F}= 2.1 Hz), 124.8 (t), 125.4 (t, J_{C-F}=9.3 Hz), 125.6 (t), 130.4 (q, J_{C-F}=3.1 Hz), 131.1 (t), 135.3 (q, J_{C-F}=9.3 Hz), 139.7 (q), 164.9 (q, J_{C-F}=252.4 Hz); MS (EI): m/z 263; HRMS (FAB) Found: M+H 264.0484, Calcd for $C_{13}H_{11}FNO_2S$: M+H=264.0495.

4.3.10. 2-Methylamino-4′-chlorobiphenyl 2e. Oil; IR (neat) 3430, 3040, 2920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.79 (3H, s), 3.85 (1H, bs), 6.69 (1H, d, J=8.1 Hz), 6.77 (1H, td, J=1.1, 7.5 Hz), 7.05 (1H, dd, J=1.7, 7.3 Hz), 7.27 (1H, td, J=1.7, 7.7 Hz), 7.35 (2H, d, J=7.6 Hz), 7.41 (2H, d, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=30.8 (p), 110.1 (t), 117.1 (t), 126.4 (q), 129.0 (t), 129.1 (t), 130.0 (t), 130.8 (t), 133.1 (q), 137.9 (q), 145.9 (q); MS (FAB): m/z 217; HRMS (FAB) Found: m/z 217.0656 (^{35}Cl), 219.0648 (^{37}Cl), Calcd for $C_{13}H_{12}{}^{35}ClN$: M^+= 217.0658, $C_{13}H_{12}{}^{37}ClN$: M^+=219.0632.

4.3.11. 2-Chloro-6-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3e. Mp 123°C; IR (KBr) 2920, 1320, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=3.45 (3H, s), 7.32 (1H, d, J=8.3 Hz), 7.35 (1H, t, J=7.9 Hz), 7.54 (1H, dd, J=2.0, 8.4 Hz), 7.54 (1H, td, J=1.4, 7.8 Hz), 7.94 (1H, d, J=2.0 Hz), 7.94 (1H, d, J=8.5 Hz), 7.96 (1H, dd, J=7.7, 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=32.8 (p), 119.5 (t), 122.9 (q), 124.1 (t), 124.8 (t), 125.5 (t), 125.6 (t), 128.3 (t), 131.1 (t), 132.5 (q), 134.1 (q), 138.8 (q), 140.0 (q); MS (EI): m/z 279; HRMS (FAB) Found: M+H 280.0192 (^{35}Cl), 282.0164 (^{37}Cl), Calcd for $C_{13}H_{11}{}^{35}ClNO_2S$: M+H= 280.0199, $C_{13}H_{11}{}^{37}ClNO_2S$: M+H=282.0172.

4.3.12. 2-Methylamino-4′,5-dimethylbiphenyl 2f. Oil; IR (neat) 3430, 3030, 2920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.27 (3H, s), 2.50 (3H, s), 2.77 (3H, s), 3.11 (1H, bs), 6.63 (1H, d, J=8.2 Hz), 6.91 (1H, d, J=2.2 Hz), 7.07 (1H, dd, J=2.2, 8.2 Hz), 7.23 (2H, d, J=7.7 Hz), 7.30 (2H, d, J=8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ= 20.3 (p), 21.1 (p), 31.3 (p), 110.4 (t), 126.3 (q), 127.9 (q), 128.9 (t), 129.2 (t), 129.5 (t), 130.8 (t), 136.5 (q), 136.8 (q), 143.8 (q); MS (EI): m/z 211; HRMS (FAB) Found: m/z 211.1355, Calcd for $C_{15}H_{17}N$: M^+= 211.1361.

4.3.13. 2,6,9-Trimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3f. Mp 145–146°C; IR (KBr) 3030, 2920, 1330, 1190, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.44 (3H, s), 2.50 (3H, s), 3.36 (3H, s), 7.22 (1H, d, J=8.3 Hz), 7.28 (1H, dd, J=1.6, 8.6 Hz), 7.34 (1H, d, J=7.6 Hz), 7.74 (1H, s), 7.77 (1H, s), 7.87 (1H, d, J=8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.0 (p), 21.9 (p), 33.2 (p), 120.0 (t), 122.6 (t), 124.0 (q), 125.7 (t), 125.8 (t), 128.9 (t), 131.0 (t), 131.6 (q), 132.4 (q), 134.4 (q), 137.4 (q), 142.9 (q); MS (EI): m/z 273; HRMS (FAB) Found: m/z 273.0789, Calcd for $C_{15}H_{15}NO_2S$: M^+=273.0824.

4.3.14. *N*-Methyl-*N*-(4-methylphenyl)-*p*-toluenesulfonamide 4f. Mp 59–59.5°C (lit. 29 Mp 60°C); IR (KBr) 2980, 2920, 1340, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)=2.33 (3H, s), 2.42 (3H, s), 3.14 (3H, s), 6.96 (2H, d, J=8.5 Hz), 7.09 (2H, d, J=8.5 Hz), 7.24 (2H, d, J=8.2 Hz), 7.44 (2H, d, J=8.5 Hz).

4.3.15. 2-Methylamino-5-fluoro-4′-methylbiphenyl 2g. Oil; IR (neat) 3430, 3030, 2920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.40 (3H, s), 2.76 (3H, s), 2.93 (1H, bs), 6.58 (1H, dd, J=4.7, 8.8 Hz), 6.83 (1H, dd, J=3.1, 9.1 Hz), 6.95 (1H, dt, J=3.1, 9.1 Hz), 7.25 (2H, d, J=8.0 Hz), 7.28 (2H, d, J=8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.2 (p), 31.4 (p), 110.7 (t, J_{C-F}=7.2 Hz), 114.4 (t, J_{C-F}=21.7 Hz), 116.8 (t, J_{C-F}=21.7 Hz), 128.8 (q, J_{C-F}=10.3 Hz), 129.0 (t), 129.7 (t), 135.4 (q), 137.4 (q), 142.5 (q), 155.5 (q, J_{C-F}=235.7 Hz); MS (EI): m/z 215; HRMS (FAB) Found: m/z 215.1096, Calcd for $C_{14}H_{14}N$: M^+=215.1110.

4.3.16. 9-Fluoro-2,6-dimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3g. Mp 184–186°C; IR (KBr) 3090, 2920, 1320, 1170, 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.52 (3H, s), 3.35 (3H, s), 7.17 (1H, dt, J=2.9, 8.4 Hz), 7.28 (1H, dd, J=5.0, 9.1 Hz), 7.40 (1H, d, J=8.1 Hz), 7.64 (1H, d, J=2.9 Hz), 7.67 (1H, s), 7.88 (1H, d, J=8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.9 (p), 34.0 (p), 112.0 (t, J_{C-F}=23.8 Hz), 117.2 (t, J_{C-F}=23.0 Hz), 122.1 (t, J_{C-F}=9.0 Hz), 122.9 (t), 125.9 (t), 126.0 (q), 129.8 (t), 131.3 (q, J_{C-F}=2.5 Hz), 131.6 (q), 136.0 (q, J_{C-F}=2.5 Hz), 143.3 (q), 159.8 (q, J_{C-F}= 244.5 Hz); MS (EI): m/z 277; HRMS (FAB) Found: M+H 278.0629, Calcd for $C_{14}H_{13}FNO_2S$: M+H=278.0651.

4.3.17. 2-Methyldibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3h. Mp 199–201°C; IR (KBr) 3240, 2920, 1320, 1170, 1140 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.53 (3H, s), 7.12 (1H, dd, J=1.5, 8.0 Hz), 7.26 (1H, bs), 7.31(1H, dd, J=1.3, 7.5 Hz), 7.38 (1H, d, J=7.9 Hz), 7.48 (1H, dt, J=1.5, 7.5 Hz), 7.79 (1H, s), 7.90 (1H, d, J=8.0 Hz), 8.00 (1H, dd, J=1.3, 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=22.1 (p), 120.8 (t), 122.3 (t), 123.2 (q), 125.2 (t), 125.5 (t), 125.9 (t), 129.2 (t), 130.4 (t), 132.5 (q), 132.6 (q), 135.7 (q), 143.3 (q); MS (FAB): (m+H)/z 246; HRMS (FAB) Found: M+H 246.0566, Calcd for $C_{13}H_{12}NO_2S$: M+H=246.0589.

4.3.18. 2-Ethylamino-4′-methylbiphenyl 2i. Oil; IR (neat) 3420, 3020, 2920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=1.16 (3H, t, J=7.1 Hz), 2.39 (3H, s), 3.13 (2H, q, J=7.1 Hz), 3.69 (1H, bs), 6.69 (1H, d, J=8.2 Hz), 6.74

(1H, t, J=7.3 Hz), 7.07 (1H, d, J=7.3 Hz), 7.21 (1H, t, J=7.3 Hz), 7.24 (2H, d, J=8.2 Hz), 7.31 (2H, d, J=7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.7 (p), 21.1 (p), 38.5 (s), 110.4 (t), 116.7 (t), 127.5 (q), 128.5 (t), 129.2 (t), 129.5 (t), 130.2 (t), 136.5 (q), 136.8 (q), 145.3 (q); MS (EI): m/z 211; Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63%. Found: C, 85.24; H, 8.22; N, 6.53%.

4.3.19. 6-Ethyl-2-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide 3i. Mp 104–105°C; IR (KBr) 3020, 2920, 1320, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.15 (3H, t, J=7.1 Hz), 2.52 (3H, s), 3.95 (3H, t, J=7.1 Hz), 7.33 (1H, dd, J=1.2, 7.7 Hz), 7.36 (1H, t, J=7.7 Hz), 7.37 (1H, d, J=8.2 Hz), 7.48 (1H, td, J=1.2, 7.7 Hz), 7.73 (1H, s), 7.87 (1H, d, J=8.0 Hz), 7.99 (1H, dd, J=1.2, 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=13.8 (p), 21.8 (p), 44.1 (s), 121.7 (t), 122.2 (t), 125.1 (t), 125.5 (t), 125.6 (q), 125.9 (t), 129.0 (t), 130.0 (q), 132.3 (q), 133.0 (q), 138.5 (q), 142.8 (q); MS (EI): m/z 273; HRMS (FAB) Found: M+H 274.0886, Calcd for $C_{15}H_{15}NO_2S$: M+H=274.0902.

4.3.20. 2-Methyldibenz[*c*,*e*][1,2]oxathin-6,6-dioxide 3j. Mp 146–148°C; IR (KBr) 2920, 1360, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.44 (3H, s), 7.21 (1H, d, J=8.5 Hz), 7.27 (1H, dd, J=1.2, 8.5 Hz), 7.56 (1H, t, J=7.5 Hz), 7.71 (1H, d, J=1.2 Hz), 7.74 (1H, td, J=1.2, 7.5 Hz), 7.92 (1H, d, J=7.7 Hz), 7.98 (1H, dd, J=1.2, 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.1 (p), 119.7 (t), 121.1 (q), 124.2 (t), 124.8 (t), 125.5 (t), 128.9 (t), 131.8 (t), 131.9 (q), 132.3 (q), 133.6 (t), 136.5 (q), 147.7 (q); MS (FAB): (m+H)/z 247; HRMS (FAB) Found: M+H 247.0413, Calcd for $C_{13}H_{11}O_3S$: M+H=247.0429.

4.3.21. 2-Methyl-6*H*-dibenzo[*b*,*d*]pyran 3l. Oil; IR (neat) 2920, 2840, 1500, 1450, 1240, 1200, 1020 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.34 (3H, s), 5.08 (2H, s), 6.92 (1H, d, J=8.2 Hz), 7.04 (1H, dd, J=1.9, 8.1 Hz), 7.14 (1H, d, J=7.5 Hz), 7.26 (1H, d, J=7.5 Hz), 7.36 (1H, t, J=7.6 Hz), 7.53 (1H, d, J=1.9 Hz), 7.68 (1H, d, J=7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=20.9 (p), 68.5 (s), 117.0 (t), 121.9 (t), 122.6 (q), 123.6 (t), 124.6 (t), 127.5 (t), 128.3 (t), 130.1 (t), 130.2 (q), 131.3 (q), 131.6 (q), 152.6 (q); MS (EI): m/z 196; HRMS (FAB) Found: m/z 196.0886, Calcd for $C_{14}H_{12}O$: M^+=196.0888.

4.3.22. Benzyl 4-methylphenyl ether 4l. Mp 33°C (lit. 30 Bp 126°C/ 4mmHg); IR (KBr) 3020, 1520, 1240, 1010 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.28 (3H, s), 5.02 (2H, s), 6.87 (2H, d, J=8.7 Hz), 7.07 (2H, d, J=8.7 Hz), 7.31 (1H, t, J=7.1 Hz), 7.37 (2H, t, J=7.1 Hz), 7.42 (2H, d, J=7.8 Hz); MS (EI): m/z 198.

4.3.23. *N*-Methyl-2-(1-naphthyl)aniline 2m. Mp 121–122°C; IR (KBr) 3420, 3020, 2920, 2820, 1510 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.72 (3H, s), 3.54 (1H, bs), 6.78 (1H, d, J=8.2 Hz), 6.84 (1H, t, J=7.4 Hz), 7.13 (1H, dd, J=1.6, 7.4 Hz), 7.37 (1H, dt, J=1.6, 7.8 Hz), 7.40 (1H, t, J=7.5 Hz), 7.44 (1H, dd, J=1.2, 7.1 Hz), 7.49 (1H, dd, J=1.2, 7.5 Hz), 7.56 (1H, t, J=7.6 Hz), 7.60 (1H, d, J=8.4 Hz), 7.89 (1H, d, J=8.5 Hz), 7.91 (1H, d, J=8.9 Hz),; ^{13}C NMR (100 MHz, $CDCl_3$) δ=30.6 (p), 109.6 (t), 116.6 (t), 125.6 (q), 125.9 (t), 126.0 (t), 126.1 (t), 126.2 (t), 127.8 (t), 128.0 (t), 128.2 (t), 129.0 (t), 130.7 (t), 131.9 (q), 133.8 (q), 136.9 (q), 147.0 (q); MS (FAB): m/z 233; HRMS (FAB) Found: m/z 233.1213, Calcd for $C_{17}H_{15}N$: M^+=233.1204.

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