JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

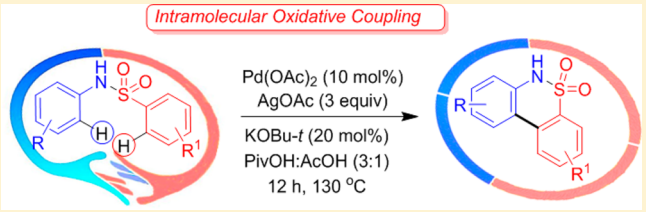
Palladium-Catalyzed Intramolecular Oxidative Coupling Involving Double C(sp^2)−H Bonds for the Synthesis of Annulated Biaryl Sultams

Joydev K. Laha,* Krupal P. Jethava, and Neetu Dayal

Department of Pharmaceutical Technology (Process Chemistry), National Institute of Pharmaceutical Education and Research, S. A. S. Nagar, Punjab 160062 India

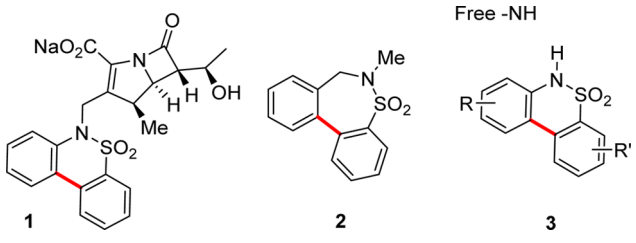
Supporting Information

ABSTRACT: The palladium-catalyzed intramolecular oxidative coupling described herein involves a double C(sp^2)−H bond functionalization in sulfonanilides, providing a workable access to biaryl sultams annulated into a six-membered ring that are otherwise difficult to obtain by literature methods. The other synthetic applications of this protocol including the synthesis of biaryl sultams containing a seven-membered ring and analogous sultones are also presented.



INTRODUCTION

Biaryl embedded in a ring is a key structural motif in many biologically active compounds, natural products, and compounds used in materials science.[1] Transition-metal-catalyzed oxidative C−H coupling[2] is a powerful variant of traditional cross-couplings[3] or direct arylations[4] providing expedient access to biaryls embedded in a ring. The synthesis of these biaryls through intramolecular oxidative coupling (IOC) of two C(sp^2)−H bonds is a method of choice that obviates the need for the use of prefunctionalized substrates and alleviates the generation of salt waste, thereby rendering superior sustainability and environmental compatibility. Seminal work since the year 2006 has established the wide applications of IOC in the synthesis of biaryls embedded in a ring, including, but not limited to, the synthesis of N-fused heterocycles,[5] carbazoles,[6] phenanthridin-6-ones,[7] and other related biaryls,[8] which indicates the importance and growing interest of this constantly evolving synthetic technology. Of particular importance, biaryls embedded in cyclic sulfonamide (biaryl sultams) such as **1** and **2** have emerged as privileged structures in drug discovery due to their inhibitory activities against a diverse array of enzymes, such as COX-2, HIV integrase, lipoxygenase, Calpain 1, and MMP-2, and also play an active role in selective serotonin reuptake inhibition as well as in nuclear factor-κB (NFκB) down regulation.[9−11]



1 2 3

To the best of our knowledge, the approach to the synthesis of biaryl sultam **3** via IOC is unprecedented, despite the potential of biaryl sultams as active pharmaceutical components. Among the repertoire of synthetic methods known for the synthesis of fused sultams,[12] the significant approaches to biaryl sultams include intramolecular radical cyclization of *N*-alkyl-2′-bromoarylsulfonamides,[13] palladium-catalyzed intramolecular direct arylation of *N*-alkyl-2-bromoarylsulfonamides,[11,14] or intramolecular oxidative C−H amination of an elaborated precursor 2-phenylarylsulfonamide under metal-free conditions,[15] thereby requiring several reaction steps (Scheme 1). We reasoned that IOC of double C(sp^2)−H bonds in sulfonanilides would represent an atom-economical green approach to the synthesis of biaryl sultams considering that the starting materials could be easily prepared with synthetic convergency.

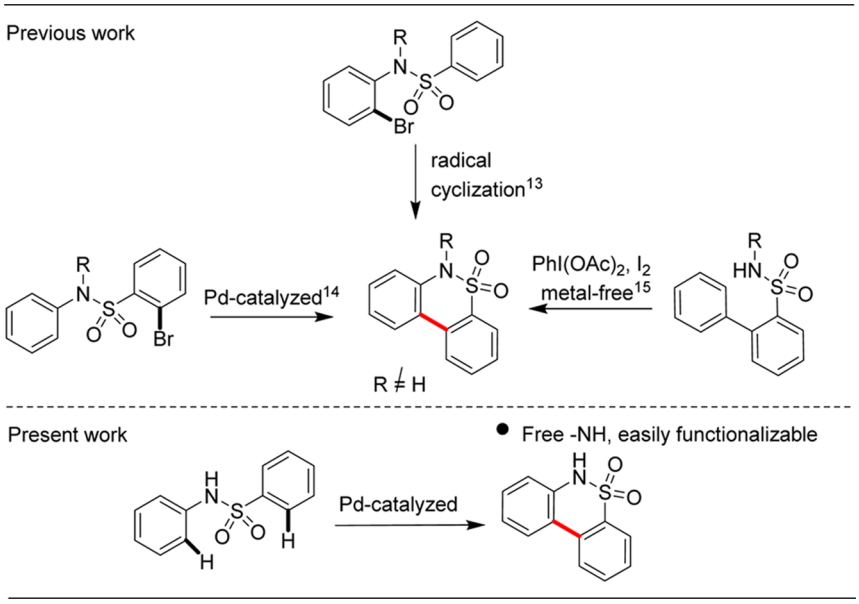
Notably, only a few examples of *ortho* C−H functionalization in sulfonanilides under metal-catalyzed conditions are known (Scheme 2). While palladium-[16] or copper-catalyzed[17] *ortho*-halogenation has been achieved in an aniline ring, the only example of *ortho*-arylation of N-Ms aniline[18] has been supplemented in a recent report. The pioneering study carried out by Yu and co-workers described the use of perfluoroaryl substitution in sulfonamides as a competent directing group in the palladium-catalyzed arylation of sulfonanilide with pinacol phenylboronate.[19] A rhodium-catalyzed *ortho* C−H activation of *N*-acyl sulphonamides, and subsequent addition of internal alkynes to give benzosultams, has also been reported.[20]

Our renewed interest in the concise synthesis of fused nitrogen-containing heterocycles[21] prompted us to develop a workable access to biaryl sultams with a free NH group that are otherwise difficult to obtain by literature methods. Herein, we

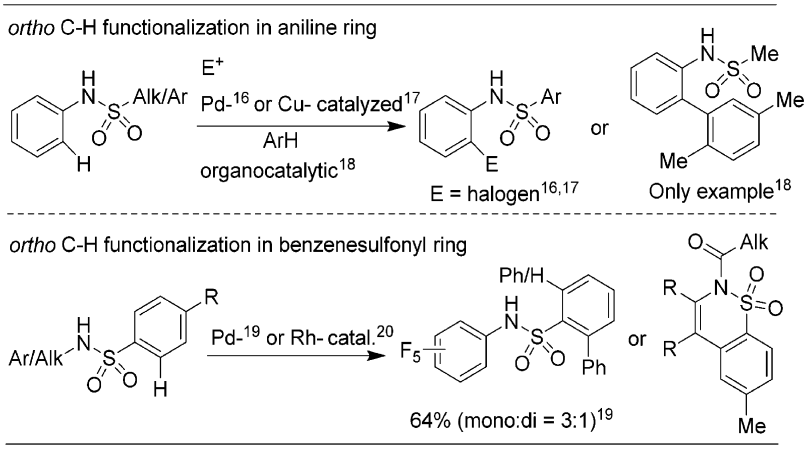
Received: May 22, 2014
Published: August 14, 2014

dx.doi.org/10.1021/jo5011334 | J. Org. Chem. 2014, 79, 8010−8019

Scheme 1. Concise Approaches to Biaryl Sultams



Scheme 2. *Ortho* C−H Functionalizations in Sulfonanilides



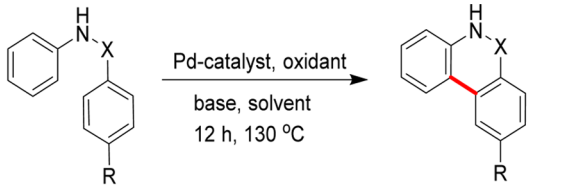
describe the first example of palladium-catalyzed IOC involving double C(sp^2)−H bonds in sulfonanilides providing access to annulated biaryl sultams with a free NH group that are amenable to functionalization at nitrogen. The other synthetic applications of this protocol including the synthesis of biaryl sultams containing a seven-membered ring and analogous sultones have also been demonstrated.

RESULTS AND DISCUSSION

Our initial investigation on the IOC of **4** using conditions [5 mol % $Pd(TFA)_2$, 10 g of benzoic acid/mmol of **4**, 120 °C, 24 h, 1 atm O_2] reported for related intramolecular oxidative C−H coupling of benzanilide **5** to the synthesis of (NH)-phenanthridinone **7** was futile.[7b] We began our optimization study using $Pd(OAc)_2$ as the catalyst and a mild or strong oxidant (Table 1). Among the mild oxidants [$Cu(OAc)_2$ and/or air, DDQ, silver compounds] examined, the silver oxidant proved effective (entries 1−4). While the IOC of **4** in the presence of $Pd(OAc)_2$ and Ag_2O in acetic acid gave **6**, *albeit* in low yield, substantial improvement in the yield was observed using AgOAc (entries 3 and 4). A strong oxidant such as oxone or $K_2S_2O_8$ did not give the desired product in an isolable quantity (entries 5 and 6). Whereas TFA did not produce the cyclized compound, pivalic acid proved more effective (entries 7 and 8). A substoichiometric amount of a base such as Cs_2CO_3 or KOBu-*t* further improved the yield (entries 9 and 10). However, the effect of the use of a stoichiometric quantity of KOBu-*t* was detrimental (entry 11). A mixture of acids can also be used in place of one acid (entries 12−14). However, not only the ratio but also the concentration of the acids is critical for better yield (compare 13 vs 15). The effect of other silver compounds was also examined (entries 16−20).[22] Whereas Ag_2O, Ag_2CO_3, or AgF afforded compound **6** in reduced yields, $AgNO_3$ and AgOTf did not produce the compound **6** in an isolable quantity. Similarly, a catalytic amount of AgOAc in combination with a co-oxidant was ineffective (entry 21). Other palladium(II) sources exhibited a deleterious effect (entries 22 and 23). While lowering the catalyst loading demonstrated a negative effect, the desired product was not obtained without a Pd catalyst (entries 24 and 25). A reduced molar quantity of AgOAc produced an inferior result (entry 26).[22] For comparison, benzanilide **5** under the optimized condition gave (NH)-phenanthridinone **7** in 71% yield (entry 27), while **5** was reported to give **7** in 91% yield using the conditions

dx.doi.org/10.1021/jo5011334 | J. Org. Chem. 2014, 79, 8010−8019

Table 1. Optimization Study of the IOC of 4 to 6[a]



4 X = SO_2, R = Me
5 X = CO, R = H

6 X = SO_2, R = Me
7 X = CO, R = H

entry	oxidant	base	solvent	yield of **6** (%)[b]
1	$Cu(OAc)_2$		AcOH:xylene (1:3)	0
2	DDQ		PivOH	0
3	Ag_2O		AcOH	12
4	AgOAc		AcOH	53
5	Oxone		AcOH	0
6	$K_2S_2O_8$		AcOH	0
7	AgOAc		TFA	0
8	AgOAc		PivOH	60
9	AgOAc	Cs_2CO_3	PivOH	67
10	AgOAc	KOBu-*t*	PivOH	81
11[c]	AgOAc	KOBu-*t*	PivOH	77
12	AgOAc	KOBu-*t*	PivOH:AcOH (1:1)	73
13[d]	AgOAc	KOBu-*t*	PivOH:AcOH (3:1)	**85 (81)**
14	AgOAc	KOBu-*t*	PivOH:AcOH (1:3)	45
15[e]	AgOAc	KOBu-*t*	DMF + (PivOH:AcOH)	trace
16	Ag_2O	KOBu-*t*	PivOH:AcOH (3:1)	66
17	Ag_2CO_3	KOBu-*t*	PivOH:AcOH (3:1)	78
18	AgF	KOBu-*t*	PivOH:AcOH (3:1)	55
19	$AgNO_3$	KOBu-*t*	PivOH:AcOH (3:1)	0
20	AgOTf	KOBu-*t*	PivOH:AcOH (3:1)	0
21[f]	AgOAc	KOBu-*t*	PivOH:AcOH (3:1)	0
22[g]	AgOAc	KOBu-*t*	PivOH:AcOH (3:1)	70
23[h]	AgOAc	KOBu-*t*	PivOH:AcOH (3:1)	58
24[i]	AgOAc	KOBu-*t*	PivOH:AcOH (3:1)	53
25[j]	AgOAc	KOBu-*t*	PivOH:AcOH (3:1)	0
26[k]	AgOAc	KOBu-*t*	PivOH:AcOH (3:1)	65
27[l]	AgOAc	KOBu-*t*	PivOH:AcOH (3:1)	71 (of **7**)

[a]Conditions: substrate (0.5 mmol), $Pd(OAc)_2$ (10 mol %), oxidant (1.5 mmol), base (20 mol %, if any), solvent (2 mL), 130 °C, 12 h. [b]GC-MS yield. [c]KOBu-*t* (100 mol %). [d]81% isolated yield. [e]PivOH:AcOH (3:1, 0.3 mL), DMF (1.7 mL). [f]Used AgOAc (20 mol %) and a co-oxidant such as oxone, $K_2S_2O_8$, $Cu(OAc)_2$, or $Cu(OTf)_2$ (1.5 mmol). [g]$Pd(TFA)_2$ (10 mol %). [h]$PdCl_2$ (10 mol %). [i]$Pd(OAc)_2$ (5 mol %). [j]Without any Pd catalyst. [k]AgOAc (1.0 mmol). [l]Benzanilide (0.5 mmol).

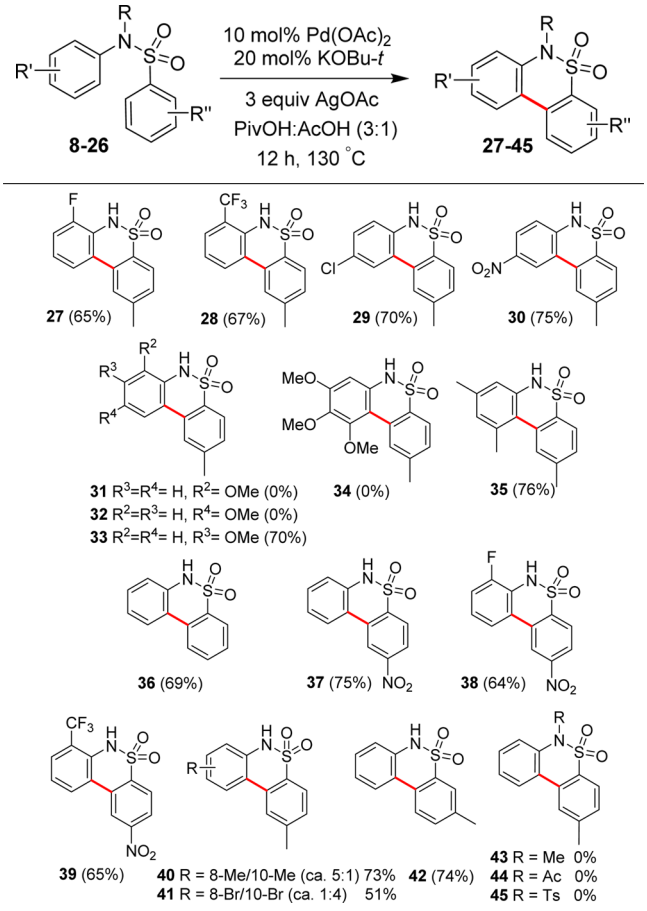
described by Murakami et al.[7b] However, our optimized conditions work for both the benzanilide and the sulfonanilides, whereas those reported for the benzanilide[7b] apparently fail to work with the sulfonanilides. This indicates that the new conditions described herein have a broader scope of substrates.

With the optimized conditions in hand [substrate (0.5 mmol), $Pd(OAc)_2$ (10 mol %), AgOAc (1.5 mmol), KOBu-*t* (20 mol %), PivOH:AcOH (3:1, 2 mL), 130 °C, 12 h], we investigated the scope of substrates. The substrates **8**−**26** were prepared by reacting commercially available anilines and sulfonyl chlorides. It has been documented that a subtle change in the acidity of the NH moiety, as a result of a substituent effect on the aniline ring in sulfonanilide, can have a drastic effect on the chemical reactivity.[23] Under the optimized conditions, the presence of electron-withdrawing substituents such as F or CF_3 group at C2-position of the aniline ring resulted in a notable reduction in chemical yield, affording sultams **27** and **28** in 65% and 67% yields, respectively (Table 2). Similarly, Cl or a NO_2 group at the 4-position delivered biaryl sultams **29** and **30** also in reduced yields compared to the parent system (70% and 75%, respectively). In contrast, a strong electron-donating OMe group at the C-2 or C-4 position did not give the desired biaryl sultams **31** and **32**, respectively. However, sulfonanilide **14** containing a OMe group at the C-3 position afforded the biaryl sultam **33** in 70% yield. The complete regiocontrol in the IOC of **14** is particularly noteworthy. Interestingly, the presence of three OMe groups at 2,3- and 4-positions, however, resulted in an adverse effect on the chemical reactivity of **15**; thus, the synthesis of **34** was unsuccessful.

To further confirm the electronic effect of a OMe group at the 2- or 4-position causing an adverse effect on chemical reactivity, we carried out the biaryl sultam formation using 3,5-dimethyl aniline sulfonamide **16**. To our delight, biaryl sultam **35** was obtained in 76% isolated yield, suggesting that this IOC is independent of a steric effect. A completely unsubstituted biaryl sultam **36** was obtained in 69% yield. A *p*-nitrobenzenesulfonyl ring exhibited relatively less reactivity to that of a *p*-toluenesulfonyl ring, resulting in a somewhat reduced yield of biaryl sultam **37**. The presence of an additional electron-

dx.doi.org/10.1021/jo5011334 | J. Org. Chem. 2014, 79, 8010−8019

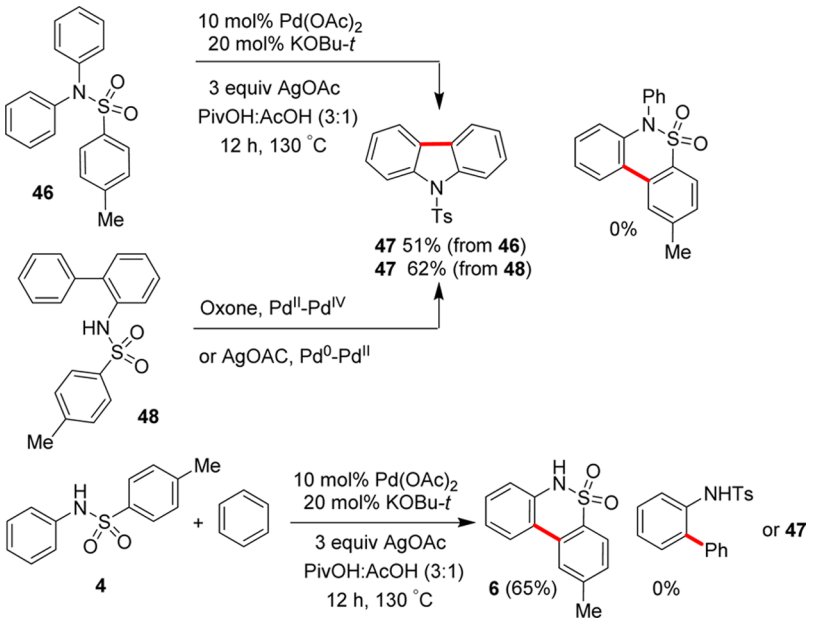
Table 2. Synthesis of Various Substituted Biaryl Sultams



withdrawing group on the aniline ring further reduces the yield of sultams **38** and **39**. Sulfonanilide **21** with a methyl group at the 3-position underwent cyclization both at 2- and 6-positions, giving rise to an inseparable mixture of biaryl sultam **40**. However, a small quantity of a pure sample of an isomer corresponding to cyclization at the 6-position was obtained by chromatography. By comparing the ^{1}H NMR spectrum of the isolated sample with the ^{1}H NMR of their mixture, we were able to interpret each peak in the ^{1}H NMR spectrum of **40** without any ambiguity and confirm the formation of two cyclized compounds (see the Supporting Information). The ratio of the two regioisomers (C-2/C-6 = ca. 1:2) was determined from the ^{1}H NMR of the crude product. Sulfonanilide **22** with a bromo group at the 3-position, however, resulted in a different regioisomeric ratio (C-2/C-6 = ca. 3:1) of the biaryl sultam **41**. In this case, a pure sample of an isomer corresponding to cyclization at the 2-position was obtained. By comparing the ^{1}H NMR spectrum of the isolated sample with the ^{1}H NMR of their mixture, we were able to interpret each peak in the ^{1}H NMR spectrum of **41** and confirm the formation of two cyclized compounds (see the Supporting Information). Interestingly, the bromo group remains unaffected under our optimized conditions. While the regioselectivity issue was observed with a 3-substitution on the aniline ring, sulfonanilide with a substitution at the 3-position on the benzenesulfonyl ring gave the sultam **42** exclusively. In our study, sulfonanilide with a free −NH moiety is essential to effect the cyclization. Thus, attempted syntheses of N-substituted biaryl sultams (*N*-methyl **43**, *N*-acetyl **44**, or *N*-tosyl **45**) were unsuccessful.

Under the optimized conditions, *N*-tosyl diphenylamine **46** underwent cyclization uneventfully with the delivery of *N*-tosyl carbazole **47** in 51% yield (Scheme 3).[6] Notably, in this case, IOC occurs involving double C−H bonds present in phenyl rings directly attached to nitrogen. Interestingly, 2-phenyl-*N*-tosylamide **48** under the same condition also gave **47** in 62% yield, suggesting that an IOC of N−H/C−H bonds is involved. However, a different palladium catalytic cycle is likely to be operative in this case, as opposed to the reported conversion of **48** to **47**, in which a strong oxidant oxone has been used and a Pd^{II}/Pd^{IV} catalytic cycle is proposed to be involved.[24] Subsequent efforts to effect an intermolecular reaction of **4** and excess benzene under the optimized conditions resulted in

Scheme 3. Cyclization of *N*-Phenyl or *ortho*-Phenyl Sulfonanilides under the Optimized Conditions

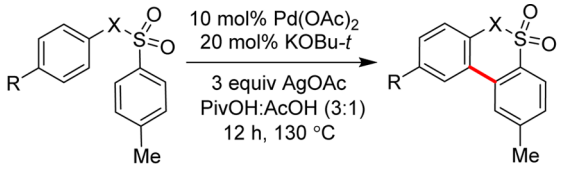


dx.doi.org/10.1021/jo5011334 | J. Org. Chem. 2014, 79, 8010−8019

the formation of **6** in 65% yield, which indicated that the intramolecular palladium-catalyzed oxidative coupling is more competent than intermolecular coupling.[3]

The application of the present protocol was explored to the synthesis of biaryl sultones (Scheme 4).[14a] Under the optimized

Scheme 4. Synthesis of Biaryl Sultones, but Not Cyclic Sulfones



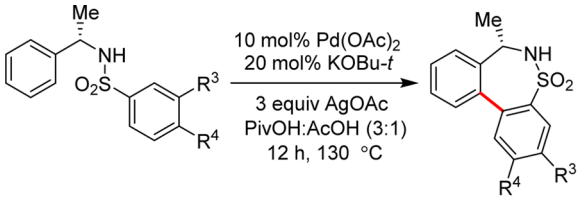
49 R = H, X = O
51 R = Cl, X = O
53 R = H, X = CH_2

50 R = H, X = O, 47%
52 R = Cl, X = O, 52%
54 R = H, X = CH_2, 0%

conditions, phenyl benzenesulfonates **49** and **51** demonstrated sluggish reactivity, yielding the corresponding sultones **50**[25] and **52** in 47% and 52% yields, respectively. However, tolyl benzyl sulfone **53** did not undergo IOC to produce the cyclic sulfone **54**, revealing that *ortho* C−H bond functionalization in the benzyl ring was difficult.

During the course of our current investigations, we also uncovered that this protocol could be extended to the synthesis of seven-membered biaryl sultams.[11] Under the optimized conditions, the sulfonamides **55** and **57** exhibited different reactivity toward IOC, resulting in optically pure biaryl sultams **56** and **58** in 63% and 83% yields, respectively (Scheme 5).

Scheme 5. Synthesis of Biaryl Sultams with a Seven-Membered Ring



55 R^3= H, R^4= Me
57 R^3= Me, R^4= H

56 R^3= H, R^4= Me (63%)
58 R^3= Me, R^4= H (83%)

Similar to our previous observation in the synthesis of **42**, sulfonamide **57** with a methyl group at the 3-position of the benzenesulfonyl ring gave **58** exclusively, which resulted from the cyclization at the 6-position.

On the basis of the above studies, the following mechanism is proposed (Scheme 6). The electrophilic palladation of the *ortho* C−H bond is likely to be facilitated in the aniline ring compared to the benzenesulfonyl ring,[16−19] which could result in the formation of **59**. Alternatively, the acidity of the NH moiety in sulfonanilide **4** could be a controlling factor to the formation of **60**. Subsequent cyclopalladation of **59** or **60** could lead to the formation of **61**. The transmetalation in **61** by the CMD pathway could form **62**, which, upon reductive elimination, could give **6** with concomitant formation of palladium(0). Alternatively, **62** could be generated directly from **59** without involvement of **61**. The palladium(II) may be regenerated by oxidation with AgOAc. A detailed mechanistic study to support the proposed mechanism is currently underway.

CONCLUSION

Incongruent to literature methods dealing with the preparation of N-alkylated biaryl sultams, our optimized conditions open a direct access to biaryl sultams with a free NH group required for late stage diversification in drug discovery. As demonstrated, the optimized conditions were quite resourceful, warranting a broad application to the synthesis of annulated biaryl sultams embedded into a seven-membered ring, analogous biaryl sultones, and phenanthridinones. While our protocol augurs interesting synthetic applications, understanding the detailed mechanism would be a successive development to the current intramolecular oxidative coupling reactions.

EXPERIMENTAL SECTION

General. Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All palladium-catalyzed reactions were performed in a screw-capped vial. The proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained in $CDCl_3$ using a 400 MHz spectrometer referenced to TMS and are reported in δ units. Coupling constants (J values) are reported in Hz. Column chromatography was performed on silica gel (60−120 or 230−400 mesh). High-resolution mass spectra (HRMS) was obtained using the electron spray ionization (ESI) technique and a TOF mass analyzer. All melting points were taken using a melting point apparatus equipped with a calibrated thermometer and are uncorrected. New compounds were characterized by melting point, ^{1}H NMR, ^{13}C NMR, IR, and HRMS data. *p*-Toluenesulfonanilide (**4**) and *N*-phenylbenzamide (**5**) were purchased from commercial vendors.

General Procedure for the Synthesis of Sulfonanilides Using Procedure A [8−10, 12−17, 19−24, 46]. A suspension of substituted benzenesulfonyl chloride (1 mmol), substituted aniline (1.2 mmol), and silica gel (1.0 g, 60−120 mesh) was stirred overnight at room temperature. Ethyl acetate or CH_2Cl_2 (20 mL) was added, and the resulting reaction mixture was filtered. The filtrate was concentrated under reduced pressure, which, upon purification by column chromatography [silica, ethyl acetate/hexane = 1:9−2:8], afforded the desired product.

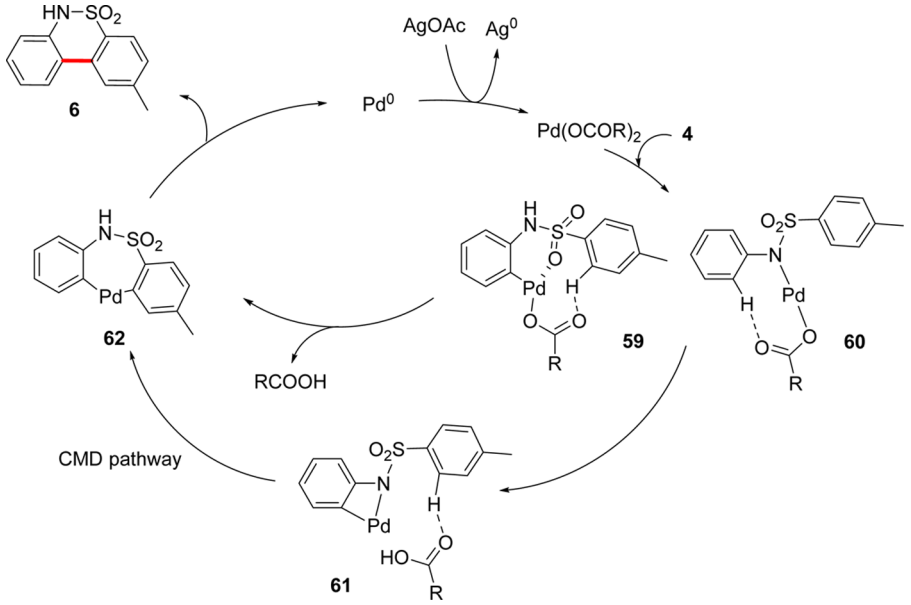
General Procedure for the Synthesis of Sulfonanilides Using Procedure B [11, 18]. A solution of substituted benzenesulfonyl chloride (1 mmol), substituted aniline (1.2 mmol), and pyridine (2 mmol) in CH_2Cl_2 (2.5 mL) was stirred at room temperature for 12 h. Water (20 mL) was added, and the reaction mixture was extracted with CH_2Cl_2 (2 × 10 mL). The organic layers were combined, dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography (silica, ethyl acetate/hexane = 3:7) to give the desired product.

General Procedure for the Synthesis of Benzenesulfonates [49, 51] and Sulfonamides [55, 57] Using Procedure C. A solution of substituted benzenesulfonyl chloride (1 mmol), substituted alcohol (1.1 mmol) or (*S*)-1-phenylethan-1-amine (1.1 mmol), and triethylamine (1 mmol) in CH_2Cl_2 (5 mL) was stirred at 45 °C for 6 h. Water (20 mL) was added, and the reaction mixture was extracted with CH_2Cl_2 (2 × 10 mL). The organic layers were combined, dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography [silica ethyl acetate/hexane = 1:9−2:8) to give the desired product.

General Procedure for the Palladium-Catalyzed Intramolecular Oxidative Coupling. A mixture of substrate (0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), AgOAc (174 mg, 1.5 mmol), and KOBu-*t* (11.2 mg, 0.1 mmol) in acid [PivOH:AcOH (3:1), 2 mL] was heated at 130 °C for 12 h. The reaction mixture was passed through a Celite bed, and the bed was washed with ethyl acetate (20 mL). The filtrate was neutralized by the addition of a saturated solution of $NaHCO_3$ (10 mL) and ammonium chloride (20 mL) with constant stirring. Extraction with ethyl acetate (3 × 20 mL), followed by concentration of the organic layer, gave a crude product, which, upon purification by column chromatography [silica (230−400

dx.doi.org/10.1021/jo5011334 | J. Org. Chem. 2014, 79, 8010−8019

Scheme 6. Proposed Mechanism for the IOC



mesh), ethyl acetate/hexane = 1:9−2:8], afforded the desired cyclized product.

2-Methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (6). Yield 85% (104 mg); off-white solid; mp. 161−163 °C; ^{1}H NMR: δ 7.99 (d, J = 7.32 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.36−7.42 (m, 2H), 7.28−7.32 (m, 1H), 7.11 (d, J = 7.8 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR: δ 145.0, 143.1, 136.9, 136.1, 135.6, 132.4, 130.0, 129.1, 125.3, 123.0, 122.1, 120.6, 21.7; HRMS: calcd for $C_{13}H_{12}NO_2S$ [M + H]$^+$ 246.0589, found 246.0588; IR (KBr): 3428, 3232, 2917, 1604, 1440 cm^{-1}.

Phenanthridin-6(5*H*)-one (7):[7b] Yield 71% (69 mg); off-white solid; ^{1}H NMR (DMSO-d_6): δ 11.70 (br. s, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 7.84−7.90 (m, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.47−7.53 (m, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.25−7.30 (m, 1H); ^{13}C NMR (DMSO-d_6): δ 161.3, 137.0, 134.7, 133.3, 130.1, 128.4, 127.9, 126.1, 123.7, 123.1, 122.8, 118.0, 116.6; HRMS: calcd for $C_{13}H_{10}NO$ [M + H]$^+$ 196.0762, found 196.0771; IR (KBr): 3412, 2879, 1657, 1609 cm^{-1}.

***N*-(2-Fluorophenyl)-4-methylbenzenesulfonamide (8):**[27] Yield 95% (251 mg); off-white solid; mp. 110−112 °C; ^{1}H NMR: δ 7.68 (d, J = 8.0 Hz, 2H), 7.60 (td, J = 8.0, 2.7 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.06−7.11 (m, 2H), 6.95−6.99 (m, 1H), 6.84 (br. s, 1H), 2.39 (s, 3H); ^{13}C NMR: δ 155.1 (d. J = 243 Hz), 152.7, 144.2, 135.8, 129.7, 127.2, 126.0 (d, J = 7 Hz), 124.7 (d, J = 4 Hz), 123.2, 115.5, 115.3, 21.5; HRMS: calcd for $C_{13}H_{13}FNO_2S$ [M + H]$^+$ 266.0651, found 266.0646; IR (KBr): 3254, 1338, 1167 cm^{-1}.

4-Methyl-*N*-[2-(trifluoromethyl)phenyl]benzenesulfonamide (9):[28] Yield 95% (299 mg); off-white solid; mp. 115−117 °C; ^{1}H NMR: δ 7.84 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.50−7.53 (m, 2H), 7.19−7.28 (m, 3H), 6.88 (br. s, 1H), 2.39 (s, 3H); ^{13}C NMR: δ 144.3, 135.7, 134.5, 138.1, 129.6, 127.7, 126.6 (q, J = 5 Hz), 124.9 (q, J = 271 Hz), 124.8, 122.9, 120.6 (q, J = 30 Hz), 21.5; HRMS: calcd for $C_{14}H_{13}F_3NO_2S$ [M + H]$^+$ 316.0619, found 316.0610; IR (KBr): 3313, 1321, 1120 cm^{-1}.

***N*-(4-Chlorophenyl)-4-methylbenzenesulfonamide (10):**[27] Yield 92% (258 mg); off-white solid; mp. 118−119 °C; ^{1}H NMR: δ 7.65−7.69 (m, 2H), 7.22−7.26 (m, 2H), 7.21 (s, 1H), 7.19−7.20 (m, 1H), 7.17−7.19 (m, 1H), 7.01−7.05 (m, 2H), 2.38 (s, 3H); ^{13}C NMR: δ 144.3, 135.6, 135.1, 130.9, 129.8, 129.4, 127.3, 122.9, 21.6; HRMS: calcd for $C_{13}H_{13}ClNO_2S$ [M + H]$^+$ 282.0356, found 282.0360; IR (KBr): 3235, 2905, 1599, 1489, 1329, 678 cm^{-1}.

4-Methyl-*N*-(4-nitrophenyl)benzenesulfonamide (11):[28] Yield 94% (274 mg); yellow solid; mp. 250−252 °C; ^{1}H NMR: δ 8.11 (td, J = 8.0, 3.0 Hz, 2H), 7.77 (dd, J = 8.0, 1.7 Hz, 2H), 7.49 (br. s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.20 (td, J = 8.0, 3.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR: δ 145.02, 143.9, 142.6, 135.4, 130.1, 127.2, 125.4, 118.6, 21.6; HRMS: calcd for $C_{13}H_{13}N_2O_4S$ [M + H]$^+$ 293.0596, found 293.0591; IR (KBr): 3334, 1522, 1339, 1160 cm^{-1}.

***N*-(2-Methoxyphenyl)-4-methylbenzenesulfonamide (12):**[30] Yield 88% (242 mg); off-white solid; ^{1}H NMR: δ 7.66 (d, J = 8.3 Hz, 2H), 7.53 (dd, J = 7.9, 1.6 Hz, 1H), 7.20 (d, J = 8.2 Hz, 1H), 7.04 (td, J = 7.9, 1.5 Hz, 1H), 7.04 (br. s, 1H), 6.90 (t, J = 7.8 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 3.65 (s, 3H), 2.37 (s, 3H); ^{13}C NMR: δ 149.5, 143.6, 136.2, 129.3, 127.2, 126.0, 125.3, 121.0, 110.6, 55.6, 21.4; HRMS: calcd for $C_{14}H_{16}NO_3S$ [M + H]$^+$ 278.0851, found 278.0860; IR (KBr): 3401, 2917, 1591, 1432, 1371 cm^{-1}.

***N*-(4-Methoxyphenyl)-4-methylbenzenesulfonamide (13):**[30] Yield 89% (246 mg); off-white solid; ^{1}H NMR: δ 7.60 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.98 (d, J = 8.9 Hz, 2H), 6.77 (d, J = 8.9 Hz, 2H), 6.52 (br. s, 1H), 3.77 (s, 3H), 2.40 (s, 3H); ^{13}C NMR: δ 157.9, 143.6, 136.0, 129.5, 128.9, 127.3, 125.4, 114.4, 55.4, 21.5; HRMS: calcd for $C_{14}H_{16}NO_3S$ [M + H]$^+$ 278.0851, found 278.0856; IR (KBr): 3401, 2917, 1591, 1432, 1371 cm^{-1}.

***N*-(3-Methoxyphenyl)-4-methylbenzenesulfonamide (14):**[30] Yield 86% (238 mg); off-white solid; ^{1}H NMR: δ 7.79 (br. s, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 7.09 (t, J = 8.1 Hz, 1H), 6.77 (s, 1H), 6.72 (d, J = 7.9 Hz, 1H), 6.61 (d, J = 8.3 Hz, 1H), 3.7 (s, 3H), 2.33 (s, 3H); ^{13}C NMR: δ 160.2, 143.9, 137.9, 135.9, 130.9, 129.6, 127.3, 113.1, 110.7, 106.6, 55.3, 21.5; HRMS: calcd for $C_{14}H_{16}NO_3S$ [M + H]$^+$ 278.0851, found 278.0861; IR (KBr): 3401, 2917, 1591, 1432, 1371 cm^{-1}.

4-Methyl-*N*-(3,4,5-trimethoxyphenyl)benzenesulfonamide (15):[29] Yield 90% (303 mg); off-white solid; mp. 117−119 °C; ^{1}H NMR: δ 7.69 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.86 (br. s, 1H), 6.32−6.33 (m, 2H), 3.78 (s, 3H), 3.75. (s, 6H), 2.40 (s, 3H); ^{13}C NMR: δ 153.4, 143.9, 135.9, 135.7, 132.3, 129.6, 127.4, 99.7, 60.9, 56.1, 21.5; HRMS: calcd for $C_{16}H_{20}NO_5S$ [M + H]$^+$ 338.1062, found 338.1053; IR (KBr): 3237, 2961, 1598, 1504, 1391, 1150, 814 cm^{-1}.

***N*-(3,4-Dimethylphenyl)-4-methylbenzenesulfonamide (16):**[30] Yield 95% (260 mg); off-white solid; ^{1}H NMR: δ 7.69 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.74 (s, 1H), 6.71 (s, 2H), 2.40 (s, 3H), 2.23 (s, 6H).

***N*-Phenyl Benzenesulfonamide (17):**[14] Yield 97% (226 mg); off-white solid; mp. 100−101 °C; ^{1}H NMR: δ 7.78−7.84 (m, 2H), 7.49−7.55 (m, 1H), 7.39−7.46 (m, 2H), 7.30 (s, 1H), 7.19−7.25 (m, 2H), 7.06−7.13 (m, 3H); ^{13}C NMR: δ 138.9, 136.4, 133.1, 129.4, 127.3, 125.4, 121.6; HRMS: calcd for $C_{12}H_{12}NO_2S$ [M + H]$^+$ 234.0589, found 234.0590; IR (KBr): 3213, 3065, 1597, 1475 cm^{-1}.

dx.doi.org/10.1021/jo5011334 | J. Org. Chem. 2014, 79, 8010−8019

4-Nitro-*N*-phenylbenzenesulfonamide (18):[30] Yield 75% (208 mg); light yellow solid; mp. 86−88 °C; ^{1}H NMR: δ 8.28 (d, J = 8.8 Hz, 2H), 7.93 (m, J = 8.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2H), 6.73 (br. s, 1H); ^{13}C NMR: δ 144.6, 135.3, 129.7, 128.5, 126.6, 124.3, 122.5; HRMS: calcd for $C_{12}H_{10}N_2O_4S$ $[M]^+$ 278.0361, found 278.0363; IR (KBr): 3280, 3054, 1594, 1378, 778 cm^{-1}.

***N*-(2-Fluorophenyl)-4-nitrobenzenesulfonamide (19):**[31] Yield 88% (260 mg); yellow solid; mp. 120−122 °C; ^{1}H NMR: δ 8.30 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.61−7.65 (m, 1H), 7.16−7.19 (m, 2H), 6.98−7.03 (m, 1H), 6.91 (br. s, 1H); ^{13}C NMR: δ 155.7 (d, J = 244 Hz), 153.2, 150.4, 144.4, 128.5, 127.6 (d, J = 8 Hz), 125.1 (d, J = 4 Hz), 124.6, 124.3, 123.4, 123.2, 115.8, 115.6; HRMS: calcd for $C_{12}H_{10}FN_2O_4S$ $[M + H]^+$ 297.0345, found 297.0341; IR (KBr): 3262, 1521, 1340 cm^{-1}.

4-Nitro-*N*-[2-(trifluoromethyl)phenyl]benzenesulfonamide (20). Yield 89% (308 mg); yellow solid; mp. 128−130 °C; ^{1}H NMR: δ 8.29 (td, J = 8.0, 2.3 Hz, 2H), 7.89−7.95 (m, 3H), 7.62 (t, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H), 6.91 (br. s, 1H); ^{13}C NMR (DMSO-d_6): δ 150.2, 147.0, 133.9, 133.7, 129.6, 128.7, 128.5, 127.6 (q, J = 5 Hz), 127.3, 127.3(q, J = 30 Hz), 125.1, 124.9 (q, J = 272 Hz), 123.8; HRMS: calcd for $C_{13}H_{10}F_3N_2O_4S$ $[M + H]^+$ 347.0313, found 347.0311; IR (KBr): 3290, 1526, 1321 cm^{-1}.

4-Methyl-*N*-(*m*-tolyl)benzenesulfonamide (21):[32] Yield 92% (240 mg); off-white solid; mp. 107−108 °C; ^{1}H NMR: δ 7.68 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.09 (t, J = 8.0 Hz, 1H), 6.85−6.93 (m, 4H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C NMR: δ 143.8, 139.3, 136.5, 129.6, 129.1, 127.3, 126.1, 122.1, 118.3, 21.6, 21.4; HRMS: calcd for $C_{14}H_{16}NO_2S$ $[M + H]^+$ 262.0902, found 262.0900; IR (KBr): 3257, 1592, 1400, 1153, 783 cm^{-1}.

***N*-(3-Bromophenyl)-4-methylbenzenesulfonamide (22):**[33] Yield 87% (283 mg); off-white solid; mp. 118−119 °C; ^{1}H NMR: δ 7.66−7.70 (m, 2H), 7.27 (d, J = 0.8 Hz, 1H), 7.21−7.26 (m, 3H), 7.10 (t, J = 7.9 Hz, 1H), 7.01 (qd, J = 8.1, 1.1 Hz, 1H), 6.74 (br. s, 1H), 2.40 (s, 3H); ^{13}C NMR: δ 144.3, 137.9, 135.7, 130.6, 129.8, 128.3, 127.3, 123.9, 122.8, 119.5, 21.6; HRMS: calcd for $C_{13}H_{13}BrNO_2S$ $[M + H]^+$ 325.9850, found 325.9850; IR (KBr): 3248, 2932, 1595, 1479, 1160, 563 cm^{-1}.

3-Methyl-*N*-phenylbenzenesulfonamide (23). Yield 74% (183 mg); off-white solid; mp. 88−90 °C; ^{1}H NMR: δ 7.61−7.63 (m, 1H), 7.57−7.61 (m, 1H), 7.27−7.35 (m, 2H), 7.20−7.25 (m, 2H), 7.06−7.13 (m, 4H), 2.34 (s, 3H); ^{13}C NMR: δ 139.3, 138.9, 136.5, 133.8, 129.3, 128.9, 127.6, 125.3, 124.4, 121.6, 21.3; HRMS: calcd for $C_{13}H_{14}NO_2S$ $[M + H]^+$ 248.0745, found 248.0755; IR (KBr): 3265, 1482, 1151, 703 cm^{-1}.

***N*,4-Dimethyl-*N*-phenylbenzenesulfonamide (24):.**[27,34] Yield 94% (246 mg); off-white solid; mp. 90−92 °C; ^{1}H NMR: δ 7.44 (d, J = 8.2 Hz, 2H), 7.24−7.34 (m, 5H), 7.10- 7.13 (m, 2H), 3.18 (s, 3H), 2.43 (s, 3H); ^{13}C NMR: δ 143.5, 141.6, 133.5, 129.3, 128.8, 127.9, 127.2, 126.6, 38.0, 21.5; HRMS: calcd for $C_{14}H_{16}NO_2S$ $[M + H]^+$ 262.0902, found 262.0902; IR (KBr): 3412, 2917, 1595, 1492, 1345 cm^{-1}.

***N*-Phenyl-*N*-tosylacetamide (25):**[35] A stirred solution of *p*-toluenesulfonanilide (0.494 g, 2 mmol) and triethylamine (0.242 g, 2.4 mmol) in dry CH_2Cl_2 (15 mL) was treated dropwise with acetic anhydride (0.245 g, 2.4 mmol) over 15 min at room temperature. The progress of the reaction was monitored by TLC. The reaction mixture was stirred at room temperature for 48 h. Concentration of the reaction gave an off-white solid (274 mg, 95% yield); mp. 139−140 °C; ^{1}H NMR: δ 7.91−7.95 (m, 2H), 7.48−7.51 (m, 3H), 7.32−7.37 (m, 2H), 7.25−7.29 (m, 2H), 2.46 (s, 3H), 1.87 (s, 3H); ^{13}C NMR: δ 170.1, 145.0, 136.9, 136.1, 130.0, 129.9, 129.4, 129.2, 25.1, 21.7; HRMS: calcd for $C_{15}H_{15}NO_3S$ $[M]^+$ 289.0773, found 289.0777; IR (KBr): 3390, 2923, 1705, 1596, 1489, 1356 cm^{-1}.

4-Methyl-*N*-phenyl-*N*-tosylbenzenesulfonamide (26). A solution of aniline (1 mmol), *p*-toluenesulfonyl chloride (2 mmol) in pyridine (2.5 mL) was heated at 45 °C stirred for 5 h. The reaction mixture was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers was dried (Na_2SO_4) and then concentrated under reduced pressure. Purification of the crude by column chromatography [silica, ethyl acetate/hexane = 1:4] gave an off-white solid (284 mg, 88% yield); mp. 167−169 °C; ^{1}H NMR: δ 7.84 (d, J = 8.0 Hz, 4H), 7.45 (t, J = 7.4 Hz, 1H), 7.34−7.43 (m, 6H), 7.05 (d, J = 8.0 Hz, 2H), 2.49 (s, 6H); ^{13}C NMR: δ 145.0, 136.6, 134.4, 131.6, 130.1, 129.5, 129.1, 128.6, 21.7; HRMS: calcd for $C_{20}H_{20}NO_4S_2$ $[M + H]^+$ 402.0834, found 402.0830; IR (KBr): 3395, 3065, 1490, 1378 cm^{-1}.

7-Fluoro-2-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (27). Yield 65% (85 mg); off-white solid; mp. 175−176 °C; ^{1}H NMR: δ 7.95 (d, J = 8.0 Hz, 1H), 7.80 (m, 2H), 7.50−7.53 (d, J = 8.0 Hz, 1H), 7.21−7.26 (m, 2H), 2.56 (s, 3H); ^{13}C NMR: δ 153.5 (d, J = 243 Hz), 151.1, 143.4, 132.1, 131.7, 129.6, 125.9, 124.1 (d, J = 8 Hz), 122.2, 120.4 (d, J = 4 Hz), 115.9, 115.7, 21.9; HRMS: calcd for $C_{13}H_{11}FNO_2S$ $[M + H]^+$ 264.0495, found 264.0492; IR (KBr): 3227, 1373, 1246 cm^{-1}.

2-Methyl-7-(trifluoromethyl)-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (28). Yield 67% (104 mg); off-white solid; mp. 210−211 °C; ^{1}H NMR: δ 8.23 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.42−7.48 (m, 2H), 7.24 (br. s, 1H), 2.57 (s, 3H); ^{13}C NMR: δ 143.4, 133.3, 132.8, 131.4, 129.8, 129.3, 127.3 (q, J = 5 Hz), 126.4, 125.2, 124.8 (q, J = 272 Hz), 124.4, 122.1, 121.1 (q, J = 30 Hz), 21.9; HRMS: calcd for $C_{14}H_{11}F_3NO_2S$ $[M + H]^+$ 314.0463, found 314.0469; IR (KBr): 3432, 1324, 1131 cm^{-1}.

9-Chloro-2-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (29). Yield 70% (97 mg); off-white solid; mp. 155−158 °C; ^{1}H NMR (DMSO-d_6): δ 8.32 (d, J = 2.3 Hz, 1H), 8.18 (s, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.53 (dd, J = 8.7, 2.1 Hz, 2H), 7.22 (d, J = 8.6 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (DMSO-d_6): δ 143.9, 143.4, 136.7, 132.3, 130.9, 129.6, 128.5, 127.2, 126.7, 125.3, 121.8, 121.6, 121.6, HRMS: calcd for $C_{13}H_{11}ClNO_2S$ $[M + H]^+$ 280.0199, found 280.0194; IR (KBr): 3246, 1602, 1419, 1308, 577 cm^{-1}.

2-Methyl-9-nitro-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (30). Yield 75% (108 mg); orange solid; mp. 256−257 °C; ^{1}H NMR (DMSO-d_6): δ 9.10 (d, J = 8.0 Hz, 1H), 8.08 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.46 (dd, J = 8.0, 2.6 Hz, 1H), 7.40 (s, 1H), 7.22 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (DMSO-d_6): δ 152.9, 140.3, 139.5, 138.7, 131.9, 129.9, 128.1, 127.9, 123.5, 122.1, 121.1, 117.4, 21.9; HRMS: calcd for $C_{13}H_{11}N_2O_4S$ $[M + H]^+$ 291.0440, found 291.0448; IR (KBr). 3335, 1467, 1343 cm^{-1}.

8-Methoxy-2-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (33). Yield 70% (96 mg); mp. 156−158 °C; off-white solid; ^{1}H NMR (DMSO-d_6): δ 11.2 (br. s, 1H), 8.11 (d, J = 8.9 Hz, 1H), 7.96 (s, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 6.87 (dd, J = 8.8, 2.5 Hz, 1H), 6.70 (s, 1H), 3.82 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (DMSO-d_6): δ 161.1, 143.1, 138.6, 132.3, 131.2, 128.4, 127.2, 125.4, 121.5, 114.7, 111.0, 104.1, 55.9, 21.7; HRMS: calcd for $C_{14}H_{14}NO_3S$ $[M + H]^+$ 276.0694, found 276.0696; IR (KBr): 3417, 3170, 1736, 1614, 1304, 1163 cm^{-1}.

2,8,10-Trimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (35). Yield 76% (103 mg); mp. 115−117 °C; off-white solid; ^{1}H NMR: δ 7.90 (d, J = 7.9 Hz, 1H), 7.66 (s, 1H), 7.33 (d, J = 8.7 Hz, 1H), 7.01 (s, 1H), 6.80 (s, 1H), 2.70 (s, 3H), 2.51 (s, 3H), 2.35 (s, 3H); ^{13}C NMR: δ 141.6,139.5, 136.4, 135.9, 133.8, 132.8, 130.0, 129.6, 127.8, 122.0, 121.1, 118.8, 23.0, 22.0, 21.1. HRMS: calcd for $C_{15}H_{16}NO_2S$ $[M + H]^+$ 274.0902, found 274.0903; IR (KBr): 3277, 2924, 1616, 1599, 1453, 1358, 1313, 1164 cm^{-1}.

6*H*-Dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (36). Yield 69% (67 mg); off-white solid; mp. 194−195 °C; ^{1}H NMR: δ 7.98−8.03 (m, 3H), 7.72 (td, J = 7.5, 1.3, 1H), 7.57 (td, J = 7.6, 1.1, 1H), 7.42 (td, J = 7.7, 1.5 Hz, 1H), 7.32 (td, J = 7.7, 1.3 Hz, 1H), 7.17 (br. s, 1H), 7.14 (dd, J = 7.9, 1.1 Hz, 1H); ^{13}C NMR: δ 135.4, 134.9, 132.5, 130.4, 128.3, 125.4, 125.2, 123.1, 122.1, 120.7; HRMS: calcd for $C_{12}H_{10}NO_2S$ $[M + H]^+$ 232.0432, found 232.0440; IR (KBr): 3219, 2924, 1746, 1314 cm^{-1}.

2-Nitro-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (37). Yield 75% (103 mg), light yellow solid; mp. 182−184 °C; ^{1}H NMR (DMSO-d_6): δ 8.97 (d, J = 2.0 Hz, 1H), 8.44 (dd, J = 8.5, 2.3 Hz, 1H), 8.39−8.42 (m, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.56−7.61 (m, 1H), 7.36−7.42 (m, 1H), 7.28 (dd, J = 8.0, 2.1 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ 150.4, 138.8, 137.1, 133.9, 132.2, 126.6, 124.9, 123.9,

dx.doi.org/10.1021/jo5011334 | J. Org. Chem. 2014, 79, 8010−8019

123.7, 121.4, 121.0, 120.4; HRMS: calcd for $C_{12}H_9N_2O_4S$ $[M + H]^+$ 277.0283, found 277.0280; IR (KBr): 3397, 1651, 764 cm^{-1}.

7-Fluoro-2-nitro-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (38). Yield 64% (94 mg); yellow solid; mp. 244−245 °C; ^1H NMR (DMSO-d_6): δ 8.98 (s, 1H), 8.48 (dd, J = 8.0, 2.1 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.40−7.45 (m, 1H); ^{13}C NMR (DMSO-d_6): δ 155.0 (d, J = 244 Hz), 152.3, 150.4, 139.3, 133.3, 125.6 (d, J = 8 Hz), 124.4, 124.2, 122.3 (d, J = 3 Hz), 122.0, 118.0, 117.9; HRMS: calcd for $C_{12}H_8FN_2O_4S$ $[M + H]^+$ 295.0189, found 295.0197; IR (KBr): 3174, 1534, 1317 cm^{-1}.

2-Nitro-7-(trifluoromethyl)-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (39). Yield 65% (111 mg); off-white solid; mp. 183−185 °C; ^1H NMR (DMSO-d_6): δ 9.0 (s, 1H), 8.68 (d, J = 8.0 Hz, 1H), 8.50 (dd, J = 8.0, 2.0 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 8.3 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ 150.4, 140.1, 135.0, 133.3, 131.3, 129.1 (q, J = 5 Hz), 126.9, 126.6, 125.0 (q, J = 30 Hz), 124.9 (q, J = 272 Hz), 124.8, 124.5, 122.5; HRMS: calcd for $C_{13}H_8F_3N_2O_4S$ $[M + H]^+$ 345.0157, found 345.0152; IR (KBr): 3294, 1530, 1323 cm^{-1}.

2,8-Dimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide and 2,10-Dimethyl-6*H* dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (Inseparable Regioisomers) (40). Yield 73% (94 mg); off-white solid; ^1H NMR: δ 7.97 (d, J = 8.0 Hz, 1H), 7.91 (s, 1H), 7.85 (d, J = 8.4 Hz,1H), 7.82 (d, J = 8.0 Hz, 2H), 7.40−7.45 (m, 2H), 7.29−7.33 (m, 1H), 7.18−7.20 (m, 1H), 7.10 (dd, J = 8.0, 1.0 Hz, 1H), 6.96 (br. s, 1H), 2.74 (s, 1H), 2.53 (s, 3H), 2.39 (s, 3H); ^{13}C NMR: δ 143.0, 141.7, 140.9, 136.7, 136.0, 135.5, 134.1, 132.7, 131.9, 129.6, 129.0, 128.8, 128.6, 128.2, 127.9, 126.9, 125.0, 124.8, 124.7, 121.1, 119.5, 119.4, 23.21, 21.9, 21.5; HRMS: calcd for $C_{14}H_{14}NO_2S$ $[M + H]^+$ 260.0745, found 260.0750; IR (KBr): 3291, 2922, 2852, 1456 cm^{-1}.

2,8-Dimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (40). ^1H NMR: δ 7.87 (d, J = 7.96 Hz, 2H), 7.7 (s, 1H), 7.34 (d, J = 8.6 Hz,1H), 7.12 (d, J = 7.16 Hz, 1H), 6.91 (s, 1H), 6.96 (br. s, 1H), 2.51 (s, 3H), 2.40 (s, 3H); ^{13}C NMR: δ 143.1, 140.9, 135.4, 132.5, 128.7, 126.2, 125.5, 125.3, 122.3, 121.0, 120.5, 22.0, 21.4.

8-Bromo-2-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide and 10-Bromo-2-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (Inseparable Regioisomers) (41). Yield 51%; off-white solid; ^1H NMR: δ 8.45 (s, 1H), 8.02 (dd, J = 7.9, 1.3 Hz, 1H), 7.88−7.94 (m, 2H), 7.81 (s, 1H), 7.62 (dd, J = 8.0, 1.3 Hz, 1H), 7.39−7.44 (m, 2H), 7.30−7.36 (m, 1H), 7.23 (t, J = 7.9 Hz, 1H), 7.14 (dd, J = 8.0, 1.1 Hz, 1H), 7.11 (dd, J = 8.0, 1.3 Hz, 1H), 2.53−2.56 (m, 4H); ^{13}C NMR: δ 141.6, 137.4, 133.9, 131.9, 131.4, 130.3, 130.1, 129.3, 125.7, 121.8, 121.3, 120.0, 21.9; HRMS: calcd for $C_{13}H_{11}BrNO_2S$ $[M + H]^+$ 323.9694, found 323.9699; IR (KBr): 3384, 2923, 2853, 1742, 1436, 1384 cm^{-1}.

10-Bromo-2-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (41). ^1H NMR: δ 8.45 (s, 1H), 7.89 (dd, J = 7.9, 1.3 Hz, 1H), 7.62 (dd, J = 7.9, 1.2 Hz, 1H), 7.41 (td, J = 8.0, 1.36 Hz, 1H), 7.22 (t, J = 8 Hz, 1H), 7.11 (dd, J = 7.9, 1.3 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR: δ 141.6, 137.3, 133.8, 131.8, 131.4, 130.3, 130.0, 129.3, 123.9, 121.7, 121.2, 120.0, 21.9.

3-Methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine-5,5-dioxide (42). Yield 74% (90 mg); off-white solid; mp. 158−159 °C; ^1H NMR (MeOD): δ 8.08 (dd, J = 8.0, 1.3 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.77 (s, 1H), 7.59 (dd, J = 8.0, 1.3 Hz, 1H), 7.42 (td, J = 8.0, 1.3 Hz, 1H), 7.26−7.31 (m, 1H), 7.17 (dd, J = 8.0, 1.0 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (MeOD): 138.7, 136.3, 134.7, 133.0, 129.7, 129.5, 125.0, 124.5, 123.8, 122.2, 121.0, 119.4, 19.7; HRMS: calcd for $C_{13}H_{12}NO_2S$ $[M + H]^+$ 246.0589, found 246.0595; IR (KBr): 3201, 2923, 2851, 1728, 1454 cm^{-1}.

4-Methyl-*N*,*N*-diphenylbenzenesulfonamide (46). Yield 88%; off-white solid; mp. 115−116 °C; ^1H NMR: δ 7.62 (d, J = 8.0 Hz, 2H), 7.26−7.36 (m, 12H), 2.46 (s, 3H); ^{13}C NMR: δ 143.6, 141.6, 137.6, 129.5, 129.2, 128.6, 128.3, 127.8, 127.6, 127.4, 21.5; HRMS: calcd for $C_{19}H_{18}NO_2S$ $[M + H]^+$ 324.1058, found 324.1056; IR (KBr): 3060, 1593, 1487, 1351, 1157 cm^{-1}.

9-Tosyl-9*H*-carbazole (47):.[6,36] Yield 51%; off-white solid; ^1H NMR: δ 8.35 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR: δ 21.5, 115.1, 119.9, 123.8, 126.3, 126.4, 127.3, 129.6, 135.0, 138.4, 144.8; HRMS: calcd for $C_{19}H_{16}NO_2S$ $[M + H]^+$ 322.0902, found 322.0901; IR (KBr): 3401, 2917, 1591, 1432, 1371, cm^{-1}.

***N*-([1,1′-Biphenyl]-2-yl)-4-methylbenzenesulfonamide (48):**[37] A solution of phenylboronic acid (0.390 g, 3.20 mmol), K_2CO_3 (1.49 g, 10.8 mmol), $PdCl_2$ (0.048 g, 0.32 mmol), and PPh_3 (0.122 g, 0.64 mmol) in DMF and H_2O (DMF:H_2O = 5:1, 16 mL) was treated dropwise with 2-bromoaniline (0.464 g, 2.7 mmol), and the resulting mixture was heated at 80 °C for 48 h. Water (25 mL) was added to the reaction mixture, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried (Na_2SO_4), followed by concentrated, to obtain a residue, which, upon purification by column chromatography [silica EtOAc:hexane = 1:5], gave 2-aminobiphenyl (280 mg, 61% yield). To a solution of 2-aminobiphenyl (0.215 g) in pyridine (3 mL) was added *p*-toluenesulfonyl chloride (0.347 g) at 0 °C. After stirring at 25 °C for 1 h, the reaction mixture was poured into water and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). Drying (Na_2SO_4), followed by concentration of the organic layer, gave a residue, which, upon chromatography [silica, EtOAc:hexane = 1:9], gave an off-white solid (376 mg, 92% yield). ^1H NMR: δ 7.71 (dd, J = 8.2, 0.9 Hz, 1H), 7.45−7.49 (m, 2H), 7.30−7.37 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H), 7.14 (td, J = 7.6, 1.1 Hz, 1H), 7.09 (dd, J = 7.6, 1,7 Hz, 1H), 6.85−6.87 (m, 2H), 6.57 (br. s, 1H), 2.40 (s, 3H); ^{13}C NMR: δ 143.9, 137.2, 136.2, 133.9, 133.8, 130.3, 129.6, 129.1, 128.9, 128.7, 128.1, 127.2, 124.9, 121.3, 21.6; HRMS: calcd for $C_{19}H_{18}NO_2S$ $[M + H]^+$ 324.1058, found 326.1060; IR (KBr): 3335, 2916, 2848, 1595, 1477, 1333, 1163, 902, 664 cm^{-1}.

Phenyl 4-Methylbenzenesulfonate (49):[38] Yield 97%; off-white solid; mp. 89−90 °C; ^1H NMR: δ 7.73 (d, J = 8.5 Hz, 2H), 7.25−7.35 (m, 5H), 6.99−7.03 (m, 2H), 2.47 (s, 3H); ^{13}C NMR: δ 149.7, 145.3, 132.5, 129.7, 129.6, 128.5, 127.1, 122.4, 21.7; HRMS: calcd for $C_{13}H_{13}O_3S$ $[M + H]^+$ 249.0585, found 249.0588; IR (KBr): 3059, 1594, 1378, 777 cm^{-1}.

9-Methyldibenzo[*c*,*e*][1,2]oxathiine-6,6-dioxide (50):[25] Yield 47% (57 mg); off-white solid; mp. 172−174 °C; ^1H NMR: δ 7.94 (dd, J = 7.8, 1.5 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.48 (dd, J = 7.7, 1.6 Hz, 1H), 7.38−7.43 (m, 2H), 7.34 (dd, J = 8.2, 1.4 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR: δ 149.9, 144.6, 131.6, 129.8, 128.5, 127.1, 126.5, 125.3, 124.2, 122.4, 121.7, 120.1, 22.1; HRMS: calcd for $C_{13}H_{11}O_3S$ $[M + H]^+$ 247.0429, found 247.0433; IR (KBr): 3419, 2922, 1732, 1484, 1369, 1180, 793 cm^{-1}.

4-Chlorophenyl 4-Methylbenzenesulfonate (51):[39] Yield 96%; yellow solid; mp. 75−78 °C; ^1H NMR: δ 7.72 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.26 (td, J = 8.0, 3.1 Hz, 2H), 6.93 (td, J = 8.0, 3.2 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR: δ 148.0, 145.6, 132.7, 132.0, 129.8, 129.7, 128.5, 123.7, 21.7; HRMS: calcd for $C_{13}H_{12}ClO_3S$ $[M + H]^+$ 283.0196, found 283.0190; IR (KBr): 3095, 1173, 1376, 753 cm^{-1}.

2-Chloro-9-methyldibenzo[*c*,*e*][1,2]oxathiine-6,6-dioxide (52). Yield 52% (72 mg); yellow solid; mp. 170−172 °C; ^1H NMR: δ 7.92 (d, J = 8.0 Hz, 2H), 7.73 (s, 1H), 7.44−7.47 (m, 2H), 7.31 (d, J = 8.0 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR: δ 148.2, 144.9, 132.1, 130.8, 130.5, 130.3, 129.6, 125.3, 125.0, 124.3, 123.1, 121.4, 22.0; HRMS: calcd for $C_{13}H_{10}ClO_3S$ $[M + H]^+$ 281.0039, found 281.0033; IR (KBr): 2921, 1363, 734 cm^{-1}.

1-(Benzylsulfonyl)-4-methylbenzene (53):[40] A stirred suspension of *p*-toluenesulfonyl chloride (0.588 g, 3.00 mmol), sodium sulfite (0.752 g, 6.00 mmol), and $NaHCO_3$ (0.504 g, 6.00 mmol) in water (30 mL) was heated at reflux for 3 h. Benzyl bromide (0.641 g, 3.50 mmol), followed by $(n\text{-}Bu)_4NBr$ (0.165 g, 0.045 mmol), were added, and the reaction mixture was stirred overnight at 70 °C. Addition of water (10 mL) to the reaction mixture, extraction with CH_2Cl_2 (20 mL x 2), and then drying (Na_2SO_4), followed by concentration of the combined organic layer, gave a residue, which, upon purification [silica, EtOAc:hexane = 1:9], gave an off-white solid: (530 mg, 72%; yield); ^1H NMR: δ 7.49−7.54 (m, 2 H), 7.31−7.36 (m, 1 H), 7.27−7.31 (m, 2 H), 7.23−7.27 (m, 2 H), 7.08−7.13 (m, 2 H), 4.29−4.32 (m, 2 H), 2.43 (s, 3 H); ^{13}C NMR: δ 144.7, 135.0, 130.8, 129.5, 128.7, 127.8,

dx.doi.org/10.1021/jo5011334 | J. Org. Chem. 2014, 79, 8010−8019

127.0, 126.3, 62.9, 21.6; HRMS: calcd for $C_{14}H_{14}O_2S$ $[M]^+$ 246.0715, found 246.0718; IR (KBr): 3445, 3251, 2972, 1452, 1325 cm^{-1}.

(*S*)-3-Methyl-*N*-(1-phenylethyl)benzenesulfonamide (55):[41] Yield 93% (255 mg); off-white solid; mp. 116−117 °C; ^1H NMR: δ 7.57 (ddd, J = 5.1, 3.5, 1.8 Hz, 1H), 7.50 (s, 1H), 7.27−7.31 (m, 2H), 7.17−7.21 (m, 3H), 7.09−7.14 (m, 2H), 4.51 (q, J = 6.8 Hz, 1H), 2.32 (s, 3H), 1.46 (d, J = 7.0 Hz, 3H); ^{13}C NMR: δ 142.0, 140.4, 138.9, 133.1, 128.7, 128.5, 127.5, 127.5, 126.1, 124.1, 53.8, 23.7, 21.2; HRMS: calcd for $C_{15}H_{18}NO_2S$ $[M + H]^+$ 276.1058, found 276.1054; IR (KBr): 3449, 3262, 2975, 1448, 1336 cm^{-1}.

(*S*)-2,7-Dimethyl-6,7-dihydrodibenzo[*d*,*f*][1,2]thiazepine-5,5-dioxide (56). Yield 63% (86 mg); colorless crystal; mp. 129−130 °C; ^1H NMR: δ 8.07 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 7.2 Hz, 1H), 7.65−7.69 (m, 1H), 7.45−7.51 (m, 2H), 7.36 (d, J = 7.9 Hz, 2H), 5.32−5.37 (m, 1H), 2.45 (s, 3H), 1.82 (d, J = 6.3 Hz, 3H); ^{13}C NMR: δ 147.4, 145.0, 134.0, 129.5, 128.9, 128.8, 128.2, 124.9, 122.4, 58.6, 21.6, 21.4; HRMS: calcd for $C_{15}H_{16}NO_2S$ $[M + H]^+$ 274.0902, found 274.0911; IR (KBr): 3446, 1596, 1358, 1169 cm^{-1}.

(*S*)-4-Methyl-*N*-(1-phenylethyl)benzenesulfonamide (57). Yield 90% (247 mg); off-white solid; mp. 108−110 °C; ^1H NMR: δ 7.63 (d, J = 8.0 Hz, 2H), 7.19−7.25 (m, 5H), 7.11−7.13 (m, 2H), 4.85 (br. s, 1H), 4.45−4.52 (m, 1H), 2.41 (s, 3H), 1.45 (d, J = 6.8 Hz, 3H); ^{13}C NMR: δ 143.1, 142.0, 137.6, 129.4, 128.5, 127.4, 127.1, 126.1, 53.6, 23.5, 21.4; HRMS: calcd for $C_{15}H_{18}NO_2S$ $[M + H]^+$ 276.1058, found 276.1053; IR (KBr): 3251, 1596, 1437, 1319 cm^{-1}.

(*S*)-3,7-Dimethyl-6,7-dihydrodibenzo[*d*,*f*][1,2]thiazepine-5,5-dioxide (58). Yield 83% (113 mg); off-white solid; mp. 136−137 °C; ^1H NMR: δ 8.00 (td, J = 1.5, 0.8 Hz, 1H), 7.95−7.99 (m, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.67 (td, J = 6.5, 1.1 Hz, 1H), 7.46−7.52 (m, 2H), 7.43−7.46 (m, 2H), 5.34 (q, J = 6.5 Hz, 1H), 2.47 (s, 3H), 1.82 (d, J = 6.5 Hz, 3H); ^{13}C NMR: δ 147.4, 139.3, 134.7, 134.1, 128.8, 128.5, 125.3, 125.0, 122.5, 58.7, 21.5, 21.4; HRMS: calcd for $C_{15}H_{16}NO_2S$ $[M + H]^+$ 274.0902, found 274.0905; IR (KBr): 3456, 1591, 1349, 1179 cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jlaha@niper.ac.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Ankur Gupta for helping with the initial optimization study. We greatly appreciate the CSIR, New Delhi, for financial support.

■ REFERENCES

(1) (a) Berger, O.; Petit, C.; Deal, E. L.; Montchamp, J.-L. *Adv. Synth. Catal.* **2013**, *355*, 1361. (b) Wang, Z.; Gao, Z.; Feng, Y.; Liu, Y.; Yang, B.; Liu, D.; Lv, Y.; Lu, P.; Ma, Y. *Polymer* **2013**, *54*, 6191. Also, see the reviews: (c) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (d) Schmidt, A. W.; Reddy, K. R.; Knölker, H. J. *Chem. Rev.* **2012**, *112*, 3193. (e) Fan, H.; Peng, J.; Hamann, M. T.; Hu, J. F. *Chem. Rev.* **2008**, *108*, 264. (f) Hassan, J.; Vignon, M. S.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359.

(2) Wu, Y.; Wang, J.; Mao, F.; Kwong, F. Y. *Chem.—Asian. J.* **2014**, *9*, 26 and references cited therein.

(3) See reviews for cross-coupling reactions: (a) Han, F.-S. *Chem. Soc. Rev.* **2013**, *42*, 5270. (b) Modha, S. G.; Mehtaz, V. P.; Van der Eycken, E. V. *Chem. Soc. Rev.* **2013**, *42*, 5042. (c) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780. (d) Kambe, N.; Iwasaki, T.; Terao, J. *Chem. Soc. Rev.* **2011**, *40*, 4937.

(4) (a) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879. (b) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (c) Baudoin, O. *Chem. Soc. Rev.* **2011**, *40*, 4902. (d) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315. (e) Bellina, F.; Rossi, R. *Chem. Rev.* **2010**, *110*, 1082. (f) René, O.; Fagnou, K. *Org. Lett.* **2010**, *12*, 2116.

(5) (a) Kandukuri, S. R.; Oestreich, M. *J. Org. Chem.* **2012**, *77*, 8750. (b) Pintori, D. G.; Greaney, M. F. *J. Am. Chem. Soc.* **2011**, *133*, 1209. (c) Ackermann, L.; Jeyachandran, R.; Potukuchi, H. K.; Novák, P.; Büttner, L. *Org. Lett.* **2010**, *12*, 2056. (d) Liégault, B.; Fagnou, K. *Organometalllics* **2008**, *27*, 4841. (e) Ackermann, L.; Vicente, R.; Althammer, A. *Org. Lett.* **2008**, *10*, 2299. (f) Dwight, T. A.; Rue, N. R.; Charyk, D.; Josselyn, R.; Boef, B. D. *Org. Lett.* **2007**, *9*, 3137.

(6) Yoshikai, N.; Wei, Y. *Asian J. Org. Chem.* **2013**, *2*, 466.

(7) (a) Wang, G. W.; Yuan, T. T.; Li, D. D. *Angew. Chem., Int. Ed.* **2011**, *50*, 1380. (b) Ishida, N.; Nakanishi, Y.; Moriya, T.; Murakami, M. *Chem. Lett.* **2011**, *40*, 1047. (c) Borduas, N.; Lough, A. J.; Dong, V. M. *Inorg. Chim. Acta* **2011**, *369*, 247. (d) Yeung, C. S.; Zhao, X.; Borduas, N.; Dong, V. M. *Chem. Sci.* **2010**, *1*, 331.

(8) Ji, D.-R.; Yang, H.; Zhao, X.-J.; Yang, H.; Liu, Y.-Z.; Liao, D.-H.; Feng, C.; Zhang, C.-G. *Chin. Chem. Lett.* **2014**, *25*, 348.

(9) Xie, Y.; Deng, S.; Thomas, C. J.; Liu, Y.; Zhang, Y.-Q.; Rinderspacher, A.; Huang, W.; Gong, G.; Wyler, M.; Cayanis, E.; Aulner, N.; Többen, U.; Chung, C.; Pampou, S.; Southall, N.; Vidović, D.; Schürer, S.; Branden, L.; Davis, R. E.; Staudt, L. M.; Inglese, J.; Austin, C. P.; Landry, D. W.; Smith, D. H.; Auld, D. S. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 329.

(10) (a) Xie, Y.; Gong, G.; Liu, Y.; Deng, S.; Rinderspacher, A.; Branden, L.; Landry, D. W. *Tetrahedron Lett.* **2008**, *49*, 2320. (b) Wilkening, R. R.; Ratcliffe, R. W.; Wildonger, K. J.; Cama, L. D.; Dykstra, K. D.; DiNinno, F. P.; Blizzard, T. A.; Hammond, M. L.; Heck, J. V.; Dorso, K. L.; Rose, E. S.; Kohler, J.; Hammond, G. G. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 673.

(11) Rayabarapu, D. K.; Zhou, A.; Jeon, K. O.; Samarrakoon, T.; Rolfe, A.; Siddiqui, H.; Hanson, P. R. *Tetrahedron* **2009**, *65*, 3180.

(12) Majumdar, K. C.; Mondal, S. *Chem. Rev.* **2011**, *111*, 7749.

(13) Biswas, D.; Samp, L.; Ganguly, A. K. *Tetrahedron Lett.* **2010**, *51*, 2681.

(14) (a) Bheeter, C. B.; Bera, J. K.; Doucet, H. *Adv. Synth. Catal.* **2012**, *354*, 3533. (b) Rousseaux, S.; Gorelsky, S. I.; Chung, B. K. W.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 10692.

(15) Li, Y.; Ding, Q.; Qiu, G.; Wu, J. *Org. Biomol. Chem.* **2014**, *12*, 149.

(16) Sun, X.; Shan, G.; Sun, Y.; Rao, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 4440.

(17) Urones, B.; Martinez, A. M.; Rodriguez, N.; Arrayas, R. G.; Carretero, J. C. *Chem. Commun.* **2013**, *49*, 11044.

(18) Ito, M.; Kubo, H.; Itani, I.; Morimoto, K.; Dohi, T.; Kita, Y. *J. Am. Chem. Soc.* **2013**, *135*, 14078.

(19) Dai, H.-X.; Stepan, A. F.; Plummer, M. S.; Zhang, Y.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 7222.

(20) Pham, M. V.; Cramer, B.; Ye, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 10610.

(21) (a) Laha, J. K.; Dayal, N.; Singh, S.; Bhimpuria, R. *Eur. J. Org. Chem.* **2014**, DOI: 10.1002/ejoc.201402395. (b) Laha, J. K.; Tummalapalli, K. S. S.; Gupta, A. *Eur. J. Org. Chem.* **2014**, 4773. (c) Laha, J. K.; Tummalapalli, K. S. S.; Gupta, A. *Eur. J. Org. Chem.* **2013**, 8330. (d) Laha, J. K.; Shah, P. U.; Jethava, K. P. *Chem. Commun.* **2013**, *49*, 7623. (e) Laha, J. K.; Cuny, G. D. *J. Org. Chem.* **2011**, *76*, 8477. (f) Laha, J. K.; Barolo, S. M.; Rossi, R. A.; Cuny, G. D. *J. Org. Chem.* **2011**, *76*, 6421. (g) Laha, J. K.; Petrou, P.; Cuny, G. D. *J. Org. Chem.* **2009**, *74*, 3152.

(22) Koutentis, P. A.; Loizou, G.; Re, D. L. *J. Org. Chem.* **2011**, *76*, 5793.

(23) (a) Kim, B. S.; Lee, S. Y.; Youn, S. W. *Chem.—Asian. J.* **2011**, *6*, 1952. (b) Reference 14b. (c) Miura, M.; Tsuda, T.; Satoh, T.; Pivsa-Art, S.; Nomura, M. *J. Org. Chem.* **1998**, *63*, 5211.

(24) Youn, S. W.; Bihn, J. H.; Kim, B. S. *Org. Lett.* **2011**, *13*, 3.

(25) Li, F.; Jiang, T.; Cai, H.; Wang, G. *Chin. J. Chem.* **2012**, *30*, 2041.

(26) (a) Gorelsky, S. I. *Coord. Chem. Rev.* **2013**, *257*, 153. (b) García-Melchor, M.; Braga, A. A. C.; Lledós, A.; Ujaque, G.; Maseras, F. *Acc. Chem. Res.* **2013**, *46*, 2626. (c) Stuart, D. R.; Villemure, E.; Fagnou, K. *J. Am. Chem. Soc.* **2007**, *129*, 12072. (d) Lafrance, M.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 16496.
(27) Park, K. K.; Lee, J. J.; Ryu, J. *Tetrahedron* **2003**, *59*, 7651.
(28) Kilpatrick, B.; Heller, M.; Arns, S. *Chem. Commun.* **2013**, *49*, 514.
(29) Kamal, A.; Reddy, J. S.; Bharathi, E. V.; Dastagiri, D. *Tetrahedron Lett.* **2008**, *49*, 348.
(30) Moon, S.-Y.; Nam, J.; Rathwell, K.; Kim, W.-S. *Org. Lett.* **2014**, *16*, 338.
(31) Fedric, J. L.; Shepher, R. G. *J. Org. Chem.* **1961**, *26*, 4715.
(32) Teo, Y.-C.; Yong, F.-F.; Ithnin, I. K.; Yio, S.-H. T.; Lin, Z. *Eur. J. Org. Chem.* **2013**, *3*, 515.
(33) Sharma, A. K.; Das, S. K. *Synth. Commun.* **2004**, *34*, 3807.
(34) Tang, X.; Huang, L.; Qi, C.; Wu, X.; Wu, W.; Jiang, H. *Chem. Commun.* **2013**, *49*, 6102.
(35) Massaha, A. R.; Asadi, B.; Hoseinpour, M.; Molseghi, A.; Kalbasi, R. J.; Naghash, H. J. *Tetrahedron* **2009**, *65*, 7696.
(36) (a) Liu, Z.; Larock, R. C. *Org. Lett.* **2004**, *6*, 3739. (b) Witulski, B.; Alayrac, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3281.
(37) (a) Reference 22. (b) Nandi, P.; Redko, M. Y.; Petersen, K.; Dye, J. L.; Lefenfeld, M.; Vogt, P. F.; Jackson, J. E. *Org. Lett.* **2008**, *10*, 5441.
(38) Wilson, D. A.; Wilson, C. J.; Moldoveanu, C.; Resmerita, A.-M.; Corcoran, P.; Hoang, L. M.; Rosen, B. M.; Percec, V. *J. Am. Chem. Soc.* **2010**, *132*, 1800.
(39) Reddy, M. B. M.; Pasha, M. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2011**, *186*, 1867.
(40) (a) Niwa, T.; Yorimitsu, H.; Oshim, K. *Tetrahedron* **2009**, *65*, 1971. (b) Procedure followed from ref 12.
(41) Ankner, T.; Hilmersson, G. *Org. Lett.* **2009**, *11*, 503.