# Oxidative Cross-Coupling of *N*-(2′-Phenylphenyl)benzenesulfonamides or Benzoic and Naphthoic Acids with Alkenes Using a Palladium−Copper Catalyst System under Air

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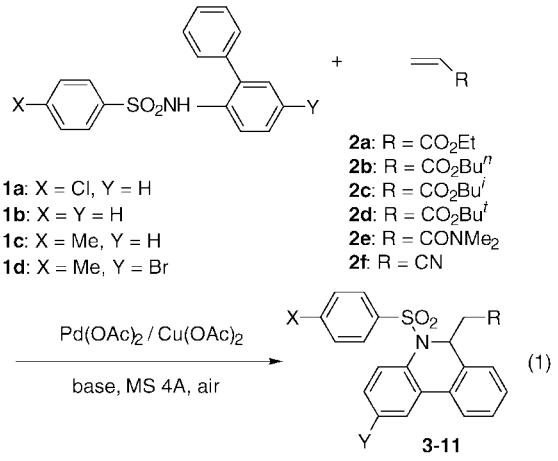
*N*-(2′-Phenylphenyl)benzenesulfonamides react with acrylate esters accompanied via cleavage of the C−H bond at their 2′-position in the presence of a catalyst system of $Pd(OAc)_2$ and $Cu(OAc)_2$ and a base under air to produce 5,6-dihydro-5-(benzenesulfonyl)phenanthridine-6-acetate derivatives in high yields. The reactions of benzoic acid with butyl acrylate and styrene can also give 3-[(butoxycarbonyl)methyl]phthalide and 3-phenylisocoumarin, respectively.

## Introduction

The activation of C−H bonds in organic compounds by transition-metal complexes is currently one of the most significant subjects in both organic and organometallic chemistry. An effective strategy to regioselectively activate the aromatic C−H bond by transition-metal complexes has been known to introduce a functional group having ligating ability at an appropriate position of a given aromatic substrate.[1] Recently, a number of catalytic coupling reactions of aromatic compounds bearing carbonyl or nitrogen-containing groups with alkenes and/or alkynes involving such a C−H bond activation mode as the key step have also been successfully developed, especially by using ruthenium and rhodium complexes.[2,3] Meanwhile, in our study of palladium-catalyzed reactions using phenolic compounds as substrates,[4] we observed that 2-phenylphenols could catalytically react with aryl iodides and alkenes such as acrylate esters under the conditions similar to those for the Heck- and Wacker-type reactions to give 2-(2′-arylphenyl)phenols[4h] and 6-substituted 6*H*-dibenzo[*b*,*d*]pyran derivatives,[4i] respectively. Both the reactions apparently involve the regioselective cleavage of the C−H bond at the 2′-position of the substrates, and the phenolic function appears to act as an effective ligating group for its promotion. For the development of these new palladium-catalyzed reactions, it seems to be very crucial to find effective functional groups other than phenolic function. Therefore, we examined the oxidative coupling with alkenes employing a number of N-containing substrates, including *N*-benzylideneaniline,[3d] 2-phenylpyridine,[3c,f] and 2-phenylaniline, which are known to readily undergo stoichiometric orthopalladation by treatment with palladium(II) species,[5] in the presence of $Pd(OAc)_2$ and $Cu(OAc)_2$ under air.[4i] While none of them could be used, it was found that the *N*-(arylsulfonyl) derivatives of the third compound, which are rather acidic, very efficiently react with acrylate esters by adding an appropriate base to give 5,6-dihydro-5-(benzenesulfonyl)phenanthridine-6-acetate derivatives (eq 1). Furthermore, structurally related acidic compounds, benzoic and naphthoic acids, were observed to be capable of reacting with acrylate esters and styrene.[6,7] These findings are reported herein.




(1) For reviews, see: (a) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(2) Carbonyl-directed catalytic reactions: (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature (London)* **1993**, *366*, 529. (b) Murai, S. *J. Synth. Org. Chem. Jpn.* **1994**, *54*, 992. (c) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62. (d) Kakiuchi, F.; Tanaka, Y.; Sato, T.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 679. (e) Kakiuchi, F.; Yamamoto, Y.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 681. (f) Sonoda, M.; Kakiuchi, F.; Kamatani, A.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 109. (g) Trost, B. M.; Imi, K. Davies, I. W. *J. Am. Chem. Soc.* **1995**, *117*, 5371.

(3) Nitrogen-directed catalytic reactions: (a) Moore, E. J.; Pretzer, W. R.; O'Connell, T. J.; Harris, J.; LaBounty, L.; Chou, L.; Grimmer, S. S. *J. Am. Chem. Soc.* **1992**, *114*, 5888. (b) Aulwurm, U. R.; Melchinger, J. U.; Kisch, H. *Organometallics* **1995**, *14*, 3385. (c) Lim, Y.-G.; Kang, J.-B.; Kim, Y. H. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2201. (d) Kakiuchi, F.; Yamauchi, M.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 111. (e) Chatani, N.; Fukuyama, T.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1996**, *118*, 493. (f) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Org. Chem.* **1997**, *62*, 2604.

(4) (a) Itoh, K.; Miura, M.; Nomura, M. *Tetrahedron Lett.* **1992**, *33*, 5369. (b) Satoh, T.; Kokubo, K.; Miura, M.; Nomura, M. *Organometallics* **1994**, *13*, 4431. (c) Satoh, T.; Ikeda, M.; Miura, M.; Nomura, M. *J. Mol. Catal. A: Chem.* **1996**, *111*, 25. (d) Satoh, T.; Tsuda, T.; Kushino, Y.; Miura, M.; Nomura, M. *J. Org. Chem.* **1996**, *61*, 6476. (e) Satoh, T.; Itaya, T.; Miura, M.; Nomura, M. *Chem. Lett.* **1996**, 823. (f) Satoh, T.; Ikeda, M.; Kushino, Y.; Miura, M.; Nomura, M. *J. Org. Chem.* **1997**, *62*, 2662. (g) Satoh, T.; Ikeda, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1997**, *62*, 4877. (h) Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1740. (i) Miura, M.; Tsuda, Satoh, T.; T.; Nomura, M. *Chem. Lett.* **1997**, 1103.

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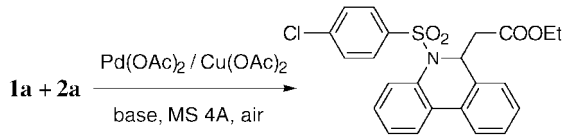
**Table 1. Reaction of *N*-(2′-Phenylphenyl)-4-chlorobenzenesulfonamide (1a) with Ethyl Acrylate (2a)[a]**




**3**

| entry | base | time/h | yield of **3**[b]/% |
|---|---|---|---|
| 1 | none | 27 | 33 |
| 2 | NaOAc | 9 | 92 (91) |
| 3 | KOAc | 14 | 92 |
| 4 | $Na_2CO_3$ | 9 | 91 |
| 5[c] | NaOAc | 48 | 57 |

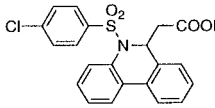
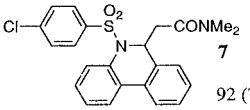
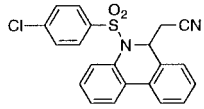
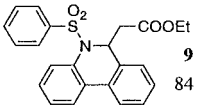
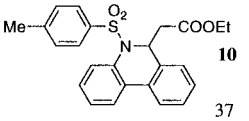
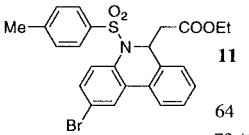
[a] Reaction conditions: **1a** (1 mmol), **2a** (3 mmol), $Pd(OAc)_2$ (0.05 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.05 mmol), base (0.5 mmol), MS 4A (400 mg), in DMF (5 mL) under air (1 atm). [b] GLC yield based on amount of **1a** used. Value in parentheses indicates isolated yield. [c] Without $Cu(OAc)_2 \cdot H_2O$.

## Results and Discussion

When a mixture of *N*-(2′-phenylphenyl)-4-chlorobenzenesulfonamide (**1a**, X = Cl, Y = H) (1 mmol) and ethyl acrylate (**2a**) (3 mmol) was stirred in the presence of $Pd(OAc)_2$ (0.05 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.05 mmol), and molecular sieves (MS 4A) (400 mg) in DMF (5 mL) under air (1 atm) at 100 °C for 27 h, ethyl 5,6-dihydro-5-[(4′-chlorophenyl)sulfonyl]phenanthridine-6-acetate (**3**) was formed in a yield of 33% (entry 1 in Table 1). The structure of **3** was unambiguously determined by its 2D-NMR spectra (H,H- and C,H-COSY) and NOE experiments (see the Experimental Section). Addition of an inorganic base was found to significantly enhance the reaction. Thus, product **3a** was obtained in 92% yield in the presence of NaOAc within 9 h (Table 1, entry 2).[8] Other bases, KOAc and $Na_2CO_3$, could also be used as well as NaOAc (Table 1, entries 3 and 4). While the reaction took place in the absence of $Cu(OAc)_2$, it was rather sluggish (Table 1, entry 5).[9]

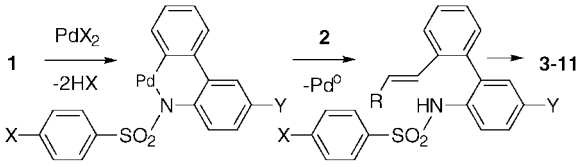
Table 2 summarizes the results for the reaction of **1a** with alkenes **2b**−**f** and *N*-(2′-phenylphenyl)benzenesulfonamide (**1b**), *N*-(2′-phenylphenyl)-4-methylbenzenesulfonamide (**1c**), or *N*-(2′-phenyl-4′-bromophenyl)-4-methylbenzenesulfonamide (**1d**) with **2a**. When acrylate esters **2b**−**d** and amide **2e** were used in place of **2a**, the corresponding 5,6-dihydrophenanthridine-6-acetic acid derivatives **4**−**7** were produced in excellent yields, as was **3**. The reaction with acrylonitrile (**2f**) also gave the corresponding product **8**. However, styrene (**2g**) did not react with **1a**. Substituents on the benzenesulfonyl moiety were found to considerably affect the reactivity of **1**. The reactivity order of **1a**−**c** judged from the reaction progress under the same conditions using NaOAc as base followed the sequence **1a** (X = Cl) > **1b** (X = H) > **1c** (X = Me), suggesting that an electron-withdrawing group in X may enhance the reaction. Consistent with this, **1d** appeared to be more reactive than **1c**. It should be noted that in the case of **1c** the use of KOAc in place of NaOAc significantly improved the reaction efficiency, giving product **10** in a yield of 90%.

**Table 2. Reaction of *N*-(2′-Phenylphenyl)benzenesulfonamides 1 with Alkenes 2[a]**

| 1 | 2 | temp / °C | time / h | product | yield / %[b] |
|---|---|---|---|---|---|
| | | | |  | |
| 1a | 2b | 120 | 5 | R = $Bu^n$ **4** | ~100 (97) |
| 1a | 2c | 120 | 5 | R = $Bu^i$ **5** | 95 (92) |
| 1a | 2d | 120 | 5 | R = $Bu^t$ **6** | (95) |
| | | | |  **7** | |
| 1a | 2e | 100 | 5 | | 92 (76) |
| | | | |  **8** | |
| 1a | 2f | 100 | 36 | | 43 (38) |
| | | | |  **9** | |
| 1b | 2a | 100 | 15 | | 84 (84) |
| | | | |  **10** | |
| 1c | 2a | 100 | 39 | | 37 |
| 1c | 2a | 100 | 15[c] | | 90 (88) |
| | | | |  **11** | |
| 1d | 2a | 100 | 25 | | 64 |
| 1d | 2a | 100 | 9[c] | | 73 (68) |

[a] Reaction conditions: **1** (1 mmol), **2** (3 mmol), $Pd(OAc)_2$ (0.05 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.05 mmol), NaOAc (0.5 mmol), MS 4A (400 mg) in DMF (5 mL) under air (1 atm). [b] GLC yield based on amount of **1** used. Value in parentheses indicates isolated yield. [c] KOAc (0.5 mmol) was used in place of NaOAc.

**Scheme 1**




It may be reasonable to consider that the present coupling involves initial orthopalladation by the reaction of **1** with Pd(II) species and the subsequent reaction with **2** followed by intramolecular nucleophilic cyclization produces the dihydrophenanthridines (Scheme 1). Pd(0) species formed may be reoxidized by the added copper species and air.[10] The initial step may take place after the coordination of **1** to Pd(II) species accompanied by

(5) (a) Canty, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 9, Chapter 5, p 225. (b) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, 1995; pp 87−94.

(6) Preliminary attempts of coupling of the sulfonamides or acids with aryl iodides have not yet succeeded.

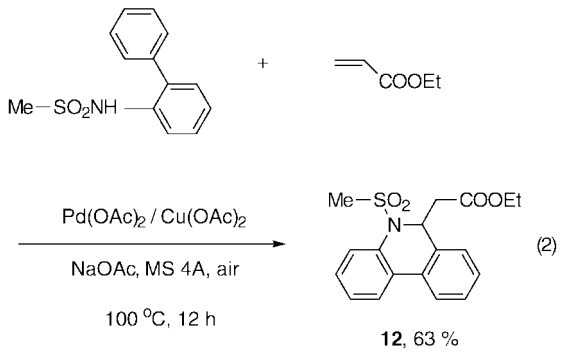
(7) Palladium-catalyzed reaction of aromatic compounds with alkenes, which does not involve orthopalladation: Fujiwara, Y.; Jintoku, T.; Takaki, K. *CHEMTECH* **1990**, 636. Reference 5b, pp 55−59.

(8) Predrying of the base was found to be important (see the Experimental Section); without this process and/or in the absence of MS 4A, the yield of **3a** was reduced to 77−84%. In the reaction of acid **13** with **2b** without using MS 4A, the product yield was less than 10%. Thus, MS 4A as desiccant was always used.

(9) In this case, air itself may directly act as an oxidant: Satoh, T.; Miura, M.; Nomura, M. *J. Mol. Catal. A: Chem.* **1996**, *112*, 211.

deprotonation, which seems to be enhanced by base. The observed substituent electronic effect is attributable to the perturbation of acidity of **1**; a small change in the acidity appears to significantly affect the reaction efficiency, an electron-withdrawing group in X or Y enhancing the deprotonation step. The result that KOAc was significantly more effective than NaOAc in the reaction of **1c** may be attributed to the fact that potassium carboxylate is relatively more effective as base as well as nucleophile than the corresponding sodium salt in DMF.[11]

In contrast to the good efficiency of sulfonamides **1** for the oxidative coupling with alkenes, the reaction of 2-phenylaniline itself as well as *N*-benzylideneaniline and 2-phenylpyridine with **2a** did not proceed, although the aniline is known to react with $Pd(OAc)_2$ stoichiometrically to produce the corresponding orthopalladated complex as mentioned above.[12] These facts suggest that the relatively acidic nature of N−H proton in **1** as well as O−H proton in 2-phenylphenols seems to be one of crucial factors making the catalytic coupling effective.[13] It was confirmed that treatment of less acidic substrates, *N*-acetyl- and *N*-(trifluoroacetyl)-2-phenylanilines, with **2a** gave no expected products, whereas that of *N*-(methylsulfonyl)-2-phenylaniline did afford compound **12** (eq 2). The reaction of *N*-(1-naphthyl)-4-chlorobenzenesulfonamide with **2a**, however, did not occur.[4h]

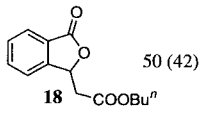
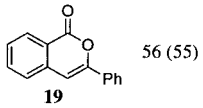
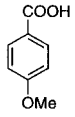
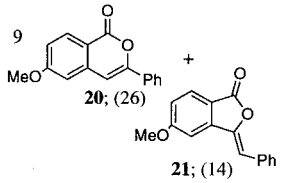
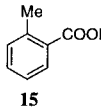
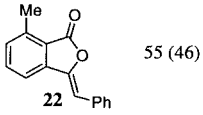
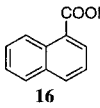
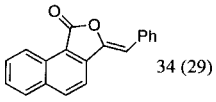
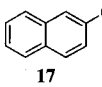
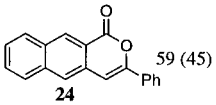



The above information obtained in the reaction of sulfonamides prompted us to investigate applicability of aromatic carboxylic acids for the coupling; the functional group may be regarded as a structural relative of sulfonamide, while it is considerably more acidic than the amide. It was found that benzoic acid (**13**) can react with **2b** to give 3-(butoxycarbonyl)methylphthalide (**18**) in 50% yield as the single major product (Table 3). In this case, no positive result was obtained by addition of NaOAc. From the reaction of **13** with styrene (**2g**) was obtained 3-phenylisocoumarin (**19**).

It is noted that benzoic acid is known to undergo orthothallation on treatment with a stoichiometric amount of $Tl(OCOCF_3)_3$, and the thallated species reacts with alkenes in the presence of a catalytic amount of $PdCl_2$ to give either phthalide and/or isocoumarin derivatives.[14] Thus, this reaction sequence appears to be mechanistically relevant to the present oxidative coupling, while its initial stage seems to involve direct orthopalladation, $Tl(OCOCF_3)_3$ being replaced by a catalytic amount of $Cu(OAc)_2$ and air. The formation of isocoumarin **19** in the present system is of particular interest, since two different oxidative catalytic cycles are considered to participate, four hydrogens being eliminated during the coupling. Consequently, a number of aromatic acids **14**−**17** were also subjected to the reaction with **2g** (Table 3). It was of considerable interest that the reaction of 2-methylbenzoic acid (**15**) and 1-naphthoic acid (**16**) selectively produced benzylidenephthalides **22** and **23**, whereas that of 2-naphthoic acid (**17**) afforded isocoumarin **24**. The reaction of 4-methoxybenzoic acid (**14**) gave a mixture of isocoumarin **20** and benzylidenephthalide **21**.

Scheme 2 illustrates possible paths leading to phthalides and isocoumarins, which involve ortho-vinylation and nucleophilic cyclization or Wacker-type oxidative cyclization.[14] The observed structures of products from the reactions using styrene may imply that both the regiochemistry of initial orthopalladation and the mode of oxidative cyclization are sterically controlled. The fact

**Table 3. Reaction of Aromatic Carboxylic Acids with Butyl Acrylate (2b) or Styrene (2g)**[a]

| ArCOOH | 2 | temp / °C | time / h | product(s) | yield / %[b] |
|---|---|---|---|---|---|
|  **13** | **2b**[c,d] | 120 | 7 |  **18** | 50 (42) |
| **13** | **2g** | 100 | 10 |  **19** | 56 (55) |
|  **14** | **2g** | 100 | 9 |  **20**; (26) + **21**; (14) | |
|  **15** | **2g**[e] | 100 | 18 |  **22** | 55 (46) |
|  **16** | **2g** | 100 | 6 |  **23** | 34 (29) |
|  **17** | **2g** | 100 | 9 |  **24** | 59 (45) |

[a] Reaction conditions: ArCOOH (1 mmol), **2** (3 mmol), $Pd(OAc)_2$ (0.1 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.1 mmol), MS 4A (400 mg) in DMF (5 mL) under $N_2$−air (5:1, 900 mL). [b] GLC yield based on amount of ArCOOH used. Value in parentheses indicates isolated yield. [c] Pd(OAc)2 (0.05 mmol) was used. [d] $Cu(OAc)_2 \cdot H_2O$ (0.05 mmol) was used.

(10) There would be also a possibility that a Pd−Cu complex participates in the reaction: Hosokawa, T.; Murahashi, S.-I. *Acc. Chem. Res.* **1990**, *23*, 49.

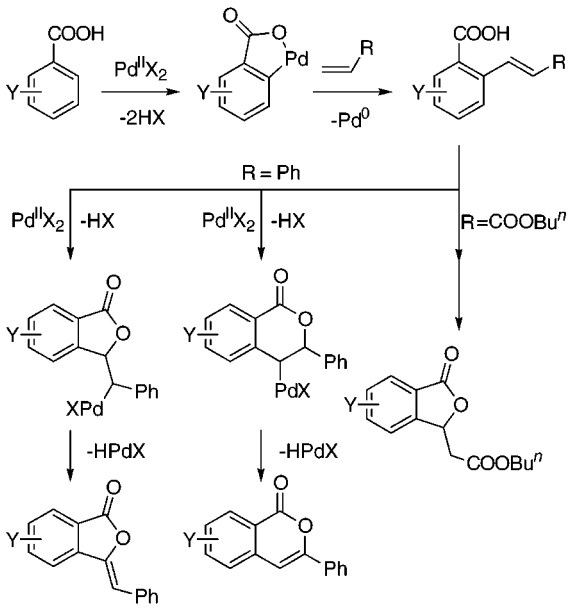
(11) Dijkstra, G.; Kruizinga, W. H.; Kellogg, R. M. *J. Org. Chem.* **1987**, *52*, 4230.

(12) See, for example: Albert, J.; Granell, J.; Luque, A.; Mínguez, J.; Moragas, R.; Font-Bardía, M.; Solans, X. *J. Organomet. Chem.* **1996**, *522*, 87.

(13) Wolfe, J. P.; Rennels, R. A.; Buchwald, S. L. *Tetrahedron* **1996**, *52*, 7525 and references therein.

(14) Larock, R. C.; Varaprath, S.; Lau, H. H.; Fellows, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 5274.

**Scheme 2**




that the initial vinylation of **17** exclusively takes place at the 3-position may be due to the presence of the hydrogen at the 8-position. The selective formation of benzylidenephthalides **22** and **23** from **15** and **16** may also be attributed to the presence of the *o*-methyl group and *peri*-hydrogen, respectively; steric repulsion between them and the carbonyl oxygen seems to be smaller in phthalide-type intermediates. In the case of **13** and **17**, such a repulsion is not involved, and hence, six-membered-cyclization, which may be energetically favorable, predominantly occurs, giving **19** and **24**. The formation of isocoumarin **20** and phthalide **21** in comparable yields from **14** suggests that another factor also intervenes. The detail is, however, unclear at the present stage.

In summary, we have described herein that *N*-(2′-phenylphenyl)benzenesulfonamides or benzoic and naphthoic acids efficiently react with alkenes such as acrylate esters via cleavage of an aromatic C−H bond under palladium catalysis, which may provide convenient routes to prepare some nitrogen- and oxygen-containing heterocyclic compounds.

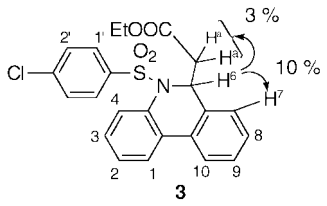
## Experimental Section

$^1$H NMR spectra were recorded at 400 or 600 MHz in $CDCl_3$ as solvent. MS data were obtained by EI, unless otherwise noted. GLC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m) or with a CBP-1 capillary column (i.d. 0.5 mm × 25 m).

*N*-Aryl and -(methylsulfonyl)-2-phenylanilines and *N*-(1-naphthyl)-4-chlorobenzenesulfonamide were prepared by treatment of 2-phenylaniline or 1-aminonaphthalene with the corresponding sulfonyl chlorides or acetyl chloride in pyridine. Sulfonamide **1d** was prepared from **1c** according to the published procedure.[15] Other starting materials were commercially available. Solvents were purified by standard methods before use.

**Reaction of Benzenesulfonamides with Alkenes.** In a 100-mL two-necked flask was placed NaOAc (41 mg, 0.5 mmol), which was then dried at 150 °C in vacuo for 2 h. Then, $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $Cu(OAc)_2 \cdot H_2O$ (10.0 mg, 0.05 mmol), **1** (1 mmol), **2** (3 mmol), MS 4A (400 mg), and DMF (5 mL) were added, and the resulting mixture was stirred under air (1 atm) at 100−120 °C for 5−39 h. After cooling, the reaction mixture was extracted with diethyl ether and dried over sodium sulfate. Product was isolated by column chromatography on silica gel using hexanes−ethyl acetate as eluent.

**Ethyl 5,6-dihydro-5-[(4′-chlorophenyl)sulfonyl]phenanthridine-6-acetate (3):** mp 106.5−107 °C; $^1$H NMR $\delta$ 1.28 (t, 3H, $J$ = 6.8 Hz, $CH_3$), 2.42 (dd, 1H, $J$ = 7.3, 15.1 Hz, H$^a$), 2.55 (dd, 1H, $J$ = 8.3, 15.1 Hz, H$^a$), 4.18 (dq, 2H, $J$ = 1.5, 6.8 Hz, $CH_2O$), 5.79 (dd, 1H, $J$ = 7.3, 8.3 Hz, H$^6$), 6.86 (d, 2H, $J$ = 8.8 Hz, H$^{2'}$), 6.93 (d, 2H, = 8.8 Hz, H$^{1'}$), 7.16−7.19 (m, 3H, H,$^7$ H,$^8$ H$^9$), 7.25−7.28 (m, 1H, H$^{10}$), 7.38 (dt, 1H, $J$ = 1.5, 7.3 Hz, H$^3$), 7.43 (dt, 1H, $J$ = 1.5, 7.3 Hz, H$^2$), 7.60 (dd, 1H, $J$ = 2.0, 7.8 Hz, H$^1$), 7.77 (dd, 1H, $J$ = 1.5, 7.8 Hz, H$^4$); $^{13}$C NMR $\delta$ 14.22, 40.19, 55.86, 60.94, 123.47, 123.67, 126.72, 127.88, 128.02, 128.08, 128.21, 128.37, 128.86, 129.45, 129.58, 129.81, 132.50, 133.55, 135.17, 138.76, 169.50; HRMS *m*/*z* (M$^+$) calcd for $C_{23}H_{20}ClNO_4S$ 441.0818, found 441.0819. Anal. Calcd for $C_{23}H_{20}ClNO_4S$: C, 62.51; H, 4.56; N, 3.17. Found: C, 62.39; H, 4.66; N, 3.17. The observed NOE peak enhancements were as follows:




**3**

***n*-Butyl 5,6-dihydro-5-[(4′-chlorophenyl)sulfonyl]-phenanthridine-6-acetate (4):** mp 54.5−55.5 °C; $^1$H NMR $\delta$ 0.93 (t, 3H, $J$ = 7.3 Hz), 1.36 (tq, 2H, $J$ = 7.3, 7.3 Hz), 1.56−1.65 (m, 2H), 242 (dd, 1H, $J$ = 6.8, 15.1 Hz), 2.56 (dd, 1H, $J$ = 7.8, 15.1 Hz), 4.07−4.14 (m, 2H), 5.79 (dd, 1H, $J$ = 7.3, 8.3 Hz), 6.84 (d, 2H, $J$ = 8.8 Hz), 6.92 (d, 2H, $J$ = 8.8 Hz), 7.16−7.18 (m, 3H), 7.25−7.27 (m, 1H), 7.37 (dd, 1H, $J$ = 1.5, 7.3 Hz), 7.42 (dt, 1H, $J$ = 1.5, 7.3 Hz), 7.60 (dd, 1H, $J$ = 2.0, 7.8 Hz), 7.76 (dd, 1H, $J$ = 1.5, 7.8 Hz); HRMS *m*/*z* (M$^+$) calcd for $C_{25}H_{24}NClO_4S$ 470.1131, found 470.1198. Anal. Calcd for $C_{25}H_{24}NClO_4S$: C, 63.89; H, 5.15; N, 2.98. Found: C, 63.96; H, 5.20; N, 2.97.

**Isobutyl 5,6-dihydro-5-[(4′-chlorophenyl)sulfonyl]-phenanthridine-6-acetate (5):** mp 78.0−79.0 °C; $^1$H NMR $\delta$ 0.91 (dd, 6H, $J$ = 1.5, 6.8 Hz), 1.92 (qq, 1H, $J$ = 6.8, 6.8 Hz), 2.43 (dd, 1H, $J$ = 6.8, 15.1 Hz), 2.59 (dd, 1H, $J$ = 7.8, 15.1 Hz), 3.89 (dd, 2H, $J$ = 6.8, 8.8 Hz), 5.79 (t, 1H, $J$ = 7.8 Hz), 6.83 (d, 2H, $J$ = 8.8 Hz), 6.93 (d, 2H, $J$ = 8.8 Hz), 7.16−7.19 (m, 3H), 7.25−7.27 (m, 1H), 7.38 (dt, 1H, $J$ = 1.5, 7.8 Hz), 7.42 (dt, 1H, $J$ = 2.0, 7.3 Hz), 7.60 (dd, 1H, $J$ = 2.0, 7.3 Hz), 7.77 (dd, 1H, $J$ = 1.5, 7.8 Hz); HRMS *m*/*z* (M$^+$) calcd for $C_{25}H_{24}NClO_4S$ 470.1131, found 470.1199. Anal. Calcd for $C_{25}H_{24}NClO_4S$: C, 63.89; H, 5.15; N, 2.98. Found: C, 63.65; H, 5.05; N, 2.93.

***tert*-Butyl 5,6-dihydro-5-[(4′-chlorophenyl)sulfonyl]-phenanthridine-6-acetate (6):** mp 125.5−126.5 °C; $^1$H NMR $\delta$ 1.51 (s, 9H), 2.37 (d, 2H, $J$ = 7.8 Hz), 5.74 (dd, 1H, $J$ = 7.3, 8.3 Hz), 6.83 (d, 2H, $J$ = 8.8 Hz), 6.91 (d, 2H, $J$ = 8.8 Hz), 7.15−7.18 (m, 3H), 7.24−7.25 (m, 1H), 7.37 (dt, 1H, $J$ = 1.5, 7.3 Hz), 7.42 (dt, 1H, $J$ = 1.5, 7.3 Hz), 7.59 (dd, 1H, $J$ = 1.5, 7.3 Hz), 7.76 (d, 1H, $J$ = 7.3 Hz); HRMS *m*/*z* (M$^+$) calcd for $C_{25}H_{24}ClNO_4S$ 469.9819, found 470.1213. Anal. Calcd for $C_{25}H_{24}ClNO_4S$: C, 63.89; H, 5.15; N, 2.98. Found: C, 63.51; H, 5.08; N, 2.96.

***N*,*N*-Dimethyl-5,6-dihydro-5-[(4′-chlorophenyl)sulfonyl]-phenanthridine-6-acetamide (7):** mp 194−195 °C; $^1$H NMR $\delta$ 2.42 (dd, 1H, $J$ = 8.3, 15.1 Hz), 2.62 (s, 3H), 2.68 (1H, dd, $J$ = 5.9, 15.1 Hz), 2.88 (s, 3H), 5.91 (dd, 1H, $J$ = 5.9, 8.3 Hz), 7.15−7.18 (m, 2H), 7.25−7.31 (m, 2H), 7.38 (dt, 2H, $J$ = 1.5, 7.3 Hz), 7.42 (dt, 1H, $J$ = 1.5, 7.3 Hz), 7.62 (dd, 1H, $J$ = 2.0, 7.3 Hz), 7.80 (dd, 1H, $J$ = 1.0, 7.3 Hz); HRMS CI *m*/*z* ([M + H]$^+$) calcd for $C_{23}H_{22}ClN_2O_3S$ 441.1056, found 441.1021. Anal. Calcd for $C_{23}H_{21}ClN_2O_3S$: C, 62.65; H, 4.80; N, 6.35. Found: C, 62.60; H, 4.76; N, 6.05.

(15) Bell, F. *J. Chem. Soc.* **1928**, 2770.

**5,6-Dihydro-5-[(4′-chlorophenyl)sulfonyl]phenanthridine-6-acetonitrile (8):** mp 171.5−172.5 °C; $^1$H NMR $\delta$ 2.49 (dd, 1H, $J$ = 7.8, 16.6 Hz), 2.64 (dd, 1H, $J$ = 7.3, 16.6 Hz), 5.61 (t, 1H, $J$ = 7.8 Hz), 6.88 (d, 2H, $J$ = 8.8 Hz), 6.94 (d, 2H, $J$ = 8.8 Hz), 7.20−7.34 (m, 4H), 7.42 (dt, 1H, $J$ = 1.5, 7.3 Hz), 7.47 (dt, 1H, $J$ = 1.5, 7.3 Hz), 7.64 (dd, 1H, $J$ = 2.0, 7.8 Hz), 7.84 (dd, 1H, $J$ = 1.5, 7.8 Hz); $^{13}$C NMR $\delta$ 23.85, 55.27, 115.94, 123.62, 123.90, 127.02, 128.08, 128.33, 128.47, 128.52, 129.12, 129.15, 129.18, 129.27, 129.47, 131.19, 131.42, 134.64, 139.22; MS CI *m*/*z* 395, 397 ([M + H]$^+$). Anal. Calcd for $C_{21}H_{15}ClN_2O_2S$: C, 63.88; H, 3.83; N, 7.09. Found: C, 63.63; H, 3.81; N, 7.02.

**Ethyl 5,6-dihydro-5-(phenylsulfonyl)phenanthridine-6-acetate (9):** mp 117.5−118.0 °C; $^1$H NMR $\delta$ 1.29 (t, 3H, $J$ = 6.8 Hz), 2.42 (dd, 1H, $J$ = 6.8, 15.1 Hz), 2.55 (dd, 1H, $J$ = 8.3, 15.1 Hz), 4.18 (dq, 2H, $J$ = 2.4, 6.8 Hz), 5.82 (t, 1H, $J$ = 7.8 Hz), 6.90 (t, 2H, $J$ = 7.8 Hz), 7.04−7.18 (m, 6H), 7.24 (d, 1H, $J$ = 7.3 Hz), 7.35 (dt, 1H, $J$ = 1.0, 7.3 Hz), 7.42 (dt, 1H, $J$ = 1.5, 7.3 Hz), 7.58 (dd, 1H, $J$ = 1.5, 7.8 Hz), 7.79 (dd, 1H, $J$ = 1.0, 7.8 Hz); HRMS *m*/*z* (M$^+$) calcd for $C_{23}H_{21}NO_4S$ 407.1208, found 407.1204. Anal. Calcd for $C_{23}H_{21}NO_4S$: C, 67.80; H, 5.19; N, 3.44. Found: C, 67.75; H, 5.21; N, 3.41.

**Ethyl 5,6-dihydro-5-[(4′-methylphenyl)sulfonyl]phenanthridine-6-acetate (10):** mp 103.0−104.0 °C; $^1$H NMR $\delta$ 1.28 (t, 3H, $J$ = 6.8 Hz), 2.14 (s, 3H), 2.42 (dd, 1H, $J$ = 7.3, 15.1 Hz), 2.55 (dd, 1H, $J$ = 8.3, 15.1 Hz), 4.17 (dq, 2H, $J$ = 2.4, 6.8 Hz), 5.80 (dd, 1H, $J$ = 7.3, 8.3 Hz), 6.67 (d, 2H, $J$ = 8.3 Hz), 6.91(d, 2H, $J$ = 8.3 Hz), 7.08−7.17 (m, 3H), 7.23−7.25 (m, 1H), 7.34 (dt, 1H, $J$ = 1.5, 7.8 Hz), 7.40 (dt, 1H, $J$ = 2.0, 7.8 Hz), 7.58 (dd, 1H, $J$ = 2.0, 7.8 Hz), 7.78 (dd, 1H, $J$ = 1.5, 7.8 Hz); MS *m*/*z* 421 (M$^+$). Anal. Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32; S, 7.61. Found: C, 68.18; H, 5.56; N, 3.28; S, 7.53.

**Ethyl 2-bromo-5,6-dihydro-5-[(4′-methylphenyl)sulfonyl]phenanthridine-6-acetate (11):** mp 154.5−155.5 °C; $^1$H NMR $\delta$ 1.28 (t, 3H, $J$ = 7.3 Hz), 2.15 (s, 3H), 2.41 (dt, 1H, $J$ = 6.8, 14.6 Hz), 2.52 (dt, 1H, $J$ = 8.3, 14.6 Hz), 4.17 (dq, 2H, $J$ = 2.0, 7.3 Hz), 5.79 (dd, 1H, $J$ = 6.8, 7.3 Hz), 6.71 (d, 2H, $J$ = 7.8 Hz), 6.94 (d, 2H, $J$ = 6.8 Hz), 7.11−7.21 (m, 4H), 7.52 (dd, 1H, $J$ = 2.0, 8.3 Hz), 7.66 (d, 1H, $J$ = 8.3 Hz), 7.72 (s, 1H); $^{13}$C NMR $\delta$ 14.21, 21.25, 40.37, 55.63, 60.94, 121.33, 123.35, 126.55, 126.7, 126.99, 127.97, 128.33, 128.50, 128.56, 131.08, 131.52, 131.55, 131.99, 133.90, 133.93, 143.20, 169.41; HRMS *m*/*z* (M$^+$) calcd for $C_{24}H_{22}BrNO_4S$ 499.0470, found 499.0468. Anal. Calcd for $C_{24}H_{22}BrNO_4S$: C, 57.61; H, 4.43; N, 2.80. Found: C, 57.69; H, 4.41; N, 2.80.

**Ethyl 5,6-dihydro-5-(methylsulfonyl)phenanthridine-6-acetate (12):** mp 108.0−109.0 °C; $^1$H NMR $\delta$ 1.26 (t, 3H, $J$ = 6.8 Hz), 2.26 (s, 3H), 2.47 (dd, 1H, $J$ = 7.3, 15.1 Hz), 2.59 (dd, 1H, $J$ = 7.8, 15.1 Hz), 4.15 (dq, 2H, $J$ = 3.9, 6.8 Hz), 5.76 (dd, 1H, $J$ = 7.3, 7.8 Hz), 7.34−7.46 (m, 5H), 7.66−7.69 (m, 1H), 7.82−7.87 (m, 2H); GC/MS *m*/*z* 345 (M$^+$). Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06; S, 9.28. Found: C, 62.72; H, 5.57; N, 3.97; S, 9.13.

**Reaction of Aromatic Carboxylic Acids with Alkenes.** In a 100-mL two-necked flask was placed MS 4A (400 mg), which was then dried at 150 °C in vacuo overnight. Then, $Pd(OAc)_2$ (0.05−0.1 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.05−0.1 mmol) were added. After the apparatus was evacuated by pumping, nitrogen (750 mL) was introduced. Then, an acid (1 mmol), **2** (3 mmol), DMF (5 mL), and air (150 mL) were injected into the flask, and the resulting mixture was stirred at 100−120 °C for 6−18 h. After cooling, the reaction mixture was extracted with diethyl ether and dried over sodium sulfate. Product was isolated by column chromatography on silica gel using hexanes−ethyl acetate as eluent.

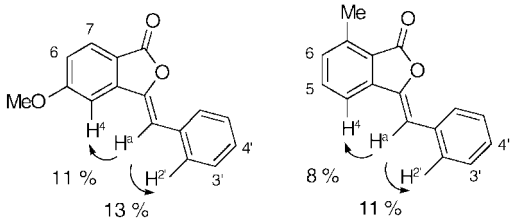
**3-(Butoxycarbonyl)methylphthalide (18):** oil; $^1$H NMR $\delta$ 0.94 (t, 3H, $J$ = 7.3 Hz), 1.37 (tq, 2H, $J$ = 7.3, 7.3 Hz), 1.62 (m, 2H), 2.88 (dd, 1H, $J$ = 6.6, 16.6 Hz), 2.95 (dd, 1H, $J$ = 6.8, 16.6 Hz), 4.17 (t, 2H, $J$ = 6.8 Hz), 5.89 (t, 1H, $J$ = 6.8 Hz), 7.51 (d, 1H, $J$ = 7.8 Hz), 7.56 (t, 1H, $J$ = 7.3 Hz), 7.69 (dt, 1H, $J$ = 1.0, 7.8 Hz), 7.92 (d, 1H, $J$ = 7.3 Hz); HRMS *m*/*z* (M$^+$) calcd for $C_{14}H_{16}O_4$ 248.1048, found 248.1046. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.67; H, 6.57.

**3-Phenylisocoumarin (19):** mp 84−85 °C (lit.[14] mp 87−88 °C); $^1$H NMR $\delta$ 6.95 (s, 1H), 7.40−7.51 (m, 5H), 7.72 (t, 1H, $J$ = 7.3 Hz), 7.88 (dt, 2H, $J$ = 1.5, 8.1 Hz), 8.31 (d, 1H, $J$ = 8.0 Hz); $^{13}$C NMR $\delta$ 101.78, 120.55, 125.24, 125.95, 128.13, 128.81, 129.65, 129.95, 131.96, 134.83, 137.50, 153.63, 162.28; HRMS *m*/*z* (M$^+$) calcd for $C_{15}H_{10}O_2$ 222.0681, found 222.0662.

**6-Methoxy-3-phenylisocoumarin (20):**[16] mp 136.5−137 °C; $^1$H NMR $\delta$ 3.93 (s, 3H), 6.88 (d, 1H, $J$ = 2.4 Hz), 6.89 (s, 1H), 7.03 (dd, 1H, $J$ = 2.4, 8.8 Hz), 7.42−7.48 (m, 3H), 7.83 (dd, 2H, $J$ = 1.5, 8.5 Hz), 8.23 (d, 1H, $J$ = 8.8 Hz); HRMS *m*/*z* (M$^+$) calcd for $C_{16}H_{12}O_3$ 252.0786, found 252.0786.

**(*Z*)-3-Benzylidene-5-methoxyphthalide (21):** mp 137.5−138 °C; $^1$H NMR $\delta$ 3.95 (s, 3H, $CH_3O$), 6.36 (s, 1H, H$^a$), 7.05 (dd, 1H, $J$ = 7.3 Hz, H$^6$), 7.14 (d, 1H, $J$ = 2.4 Hz, H$^4$), 7.31 (t, 1H, $J$ = 7.3 Hz, H$^{4'}$), 7.40 (t, 2H, $J$ = 7.3 Hz, H$^{3'}$), 7.80−7.84 (m, 3H, H,$^7$ H$^{2'}$); $^{13}$C NMR $\delta$ 55.91, 102.68, 106.74, 116.06, 118.18, 127.01, 128.33, 128.72, 130.07, 133.10, 143.17, 144.50, 165.08, 166.70; HRMS *m*/*z* (M$^+$) calcd for $C_{16}H_{12}O_3$ 252.0786, found 252.0780. Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.28; H, 5.07.

**(*Z*)-3-Benzylidene-7-methylphthalide (22):**[17] mp 158−158.5 °C; $^1$H NMR $\delta$ 2.72 (s, 3H, $CH_3$), 6.38 (s, 1H, H$^a$), 7.28−7.33 (m, 2H, H,$^6$ H$^{4'}$), 7.41 (dt, 2H, $J$ = 1.5, 7.3 Hz, H$^{3'}$), 7.55−7.58 (m, 2H, H,$^4$ H$^5$), 7.84−7.86 (m, 2H, H$^{2'}$); HRMS *m*/*z* (M$^+$) calcd for $C_{16}H_{12}O_2$ 236.0837, found 236.0845. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.05; H, 5.14. The observed NOE peak enhancements in **21** and **22** were as follows:




**21** **22**

**(*Z*)-3-Benzylidenenaphtho[1,2-*c*]furan-1(3*H*)-one (23):** mp 213.5−214.5 °C; $^1$H NMR $\delta$ 6.51 (s, 1H), 7.35 (t, 1H, $J$ = 7.3 Hz), 7.44 (t, 2H, $J$ = 7.3 Hz), 7.63 (dt, 1H, $J$ = 1.0, 6.8 Hz), 7.73 (dt, 1H, $J$ = 1.0, 6.8 Hz), 7.76 (d, 1H, $J$ = 8.8 Hz), 7.91 (d, 2H, $J$ = 7.3 Hz), 7.95 (d, 1H, $J$ = 8.3 Hz), 8.13 (d, 1H, $J$ = 8.8 Hz), 8.90 (d, 1H, $J$ = 8.3 Hz); HRMS *m*/*z* (M$^+$) calcd for $C_{19}H_{12}O_2$ 272.0837, found 272.0838. Anal. Calcd for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.63; H, 4.46.

**1*H*-3-Phenylnaphtho[2,3-*c*]pyran-1-one (24):** mp 180.5−181 °C; $^1$H NMR $\delta$ 7.07 (s, 1H), 7.41−7.50 (m, 3H), 7.55 (t, 1H, $J$ = 7.6 Hz), 7.64 (t, 1H, $J$ = 7.6 Hz), 7.91−7.92 (m, 4H), 8.02 (d, 1H, $J$ = 8.3 Hz), 8.93 (s, 1H); $^{13}$C NMR $\delta$ 101.92, 118.97, 124.30, 125.13, 126.67, 127.69, 128.81, 129.43, 129.76, 129.77, 132.00, 132.13, 132.21, 132.39, 136.61, 152.00, 162.62; HRMS *m*/*z* (M$^+$) calcd for $C_{19}H_{12}O_2$: 222.0681, found 222.0662. Anal. Calcd for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.45; H, 4.57.

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