Palladium-Catalyzed Coupling of Aryl Triflates with Organostannanes

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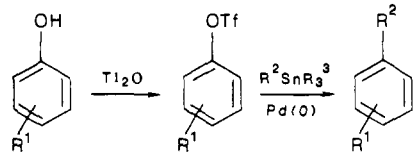
Abstract: The palladium-catalyzed coupling reaction of aryl triflates with alkyl, vinyl, acetylenic, and aryl tin reagents in the presence of lithium chloride takes place in high yields under mild conditions. However, allyltrialkyltin reagents coupled in lower yields, and unselective transfer of the allyl group was observed. The aryl coupling reaction was applied to a synthesis of the quinoline alkaloid dubamine. The palladium-catalyzed coupling of aryl triflates with hexamethylditin gave aryltrimethylstannanes or homocoupled products depending on the amount of tin reagent. *p*-Bromophenyl triflate could be coupled selectively with vinyltributyltin through either the carbon–halogen or the carbon–oxygen bond by using different palladium catalysts.

The palladium-catalyzed coupling of organic electrophiles with functionalized organostannanes has emerged as a versatile method for carbon–carbon bond formation.[1,2] This reaction has many of the attractive features of a general carbon–carbon bond construction method: yields are high under mild conditions; virtually all functional groups, including aldehydes, are tolerated; the reaction is relatively insensitive to steric hindrance; and high turnovers of the palladium catalyst are observed. Furthermore, a diverse array of functionalized organostannanes are readily available by a number of different reaction types.[1,3]

A variety of organic electrophiles undergo the cross-coupling reaction, the aryl halides being one of the most thoroughly studied.[4] Usually aryl iodides and bromides lead to coupled products under mild conditions, while aryl chlorides require activation with electron-withdrawing substituents.

The recent discovery that vinyl trifluoromethanesulfonates (triflates) undergo the coupling reaction with organostannanes[5,6] prompted us to study the related reaction of aryl triflates. These compounds are valuable starting materials for carbon–carbon bond formation because of their stability and great availability from phenols.[7] Moreover, the phenolic group can be used as a means to introduce the desired functionality in the aromatic ring and then be converted into a carbon–carbon bond via the corresponding triflate (eq 1).



(1)

Herein we now report on the scope of the palladium-catalyzed cross-coupling reaction of aryl triflates with organostannanes.[8-10]

Results and Discussion

Reaction Conditions. A first series of experiments was effected with *p*-acetylphenyl triflate (**1**) and vinyltri-*n*-butylstannane as partners to establish the best reaction conditions (Table I). The coupling reaction works well in dioxane at reflux with tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, as catalyst, in the presence of 3 equiv of lithium chloride—which is moderately soluble in dioxane—to give *p*-vinylacetophenone (**2**) (entry 2). DMF, a solvent that can both solubilize lithium chloride and act as a ligand for palladium, accelerates the reaction, although a 10% yield of the product of cleavage of the triflate was obtained (entry 3). Coupling in the presence of a palladium catalyst[2b] containing weakly coordinating ligands resulted in lower yields of **2** with the accompanying formation of substantial amounts of cleavage product **3**[11] (entries 4–7). In addition, under these conditions, the catalyst decomposed during the reaction, resulting in lower conversions. However, with the bis(triphenylphosphine)palladium(II) catalysts in DMF, fast reactions were obtained (entries 8 and 9).[12] THF and dioxane were less effective with these catalysts (entries 12 vs. 11 and 13 vs. 9).

Lithium chloride is essential for the success of the reaction.[5] In the absence of LiCl decomposition of the catalyst takes place (entry 10). Presumably, as in the case of vinyl triflates, chloride is necessary in order to produce the aryl palladium chloride and allow transmetalation to take place. Noteworthy is the fact that under all the reaction conditions examined none of the tertiary alcohol resulting from addition of the tin reagent to the carbonyl group was detected in the crude reaction mixtures.

Reaction Scope. The palladium-catalyzed reaction of aryl and heteroaryl triflates is a very general reaction (Table II). Vinyl, alkyl, allyl, aryl, and acetylenic groups on tin all transfer in good yields. Additionally, hexamethyldistannane can be used to provide aryltrimethylstannanes.[13,14] Both $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$

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(2) (a) Mitchell, T. N. *J. Organomet. Chem.* **1986**, *304*, 1–16. (b) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551–564. (c) Kosugi, M.; Migita, T. *Yuki Gosei Kagaku Kyokaishi* **1980**, *38*, 1142–1150; *Chem. Abstr.* **1981**, *95*, 81044d.

(3) Gielen, M. *Rev. Silicon Germanium Tin Lead Compd.* **1981**, *5*, 6–152.

(4) For recent reports, see: (a) Yokoyama, Y.; Ito, S.; Murakami, Y. *Tetrahedron Lett.* **1985**, *26*, 6457–6460. (b) Bumagin, N. A.; Gulevich, Y. V.; Beletskaya, I. P. *Dokl. Akad. Nauk. SSSR* **1985**, *280*, 630–636; (*Engl. Transl.*) **1985**, *280*, 17–20. (c) Yamamoto, Y.; Azuma, Y. *Synthesis* **1986**, 564–565. (d) Biley, T. R. *Tetrahedron Lett.* **1986**, *27*, 4407–4410. (e) McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422–424.

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(6) For the reaction of vinyl triflates with $Pt(PPh_3)_4$, see: Kowalski, M. H.; Stang, P. J. *Organometallics* **1986**, *5*, 2392–2395.

(7) For a review of the chemistry of triflates, see: Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85–126.

(8) For the carbon–carbon bond formation by the reactions of aryl fluoroalkanesulfonates, see: (a) Reaction with organocopper reagents: McMurry, J. E.; Mohanraj, S. *Tetrahedron Lett.* **1983**, *24*, 2723–2726. (b) Heck reaction: Chen, Q.-Y.; Yang, Z.-Y. *Tetrahedron Lett.* **1986**, *27*, 1171–1174. (c) Palladium-catalyzed carbonylation: Cacchi, S.; Ciattini, P. G.; Morera, E.; Otar, G. *Tetrahedron Lett.* **1986**, *27*, 3921–3934.

(9) For the palladium-catalyzed reduction of aryl fluoroalkanesulfonates, see: (a) Subramanian, L. R.; Martinez, A. G.; Fernandez, A. H.; Alvarez, R. M. *Synthesis* **1984**, 481–485. (b) Chen, Q.-Y.; He, Y.-B.; Yang, Z.-Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1452–1453. (c) Cacchi, S.; Ciattini, P. G.; Morera, E.; Otar, G. *Tetrahedron Lett.* **1986**, *27*, 5541–5544.

(10) For the nickel-catalyzed reaction of aryl phosphates with Grignard and organoaluminum reagents, see: Hayashi, T.; Katsuro, Y.; Okamoto, Y.; Kumada, M. *Tetrahedron Lett.* **1981**, *22*, 4449–4452.

(11) For a report on the sulfur–oxygen bond cleavage of aryl fluoroalkanesulfonates with nucleophiles, see: Subramanian, L. R.; Hanack, M.; Chang, L. W. K.; Imhoff, M. A.; Schleyer, P. v. R.; Effenberger, F.; Kurtz, W.; Stang, P. J.; Dueber, T. E. *J. Org. Chem.* **1976**, *41*, 4099–4103.

(12) The active catalyst is a bis(triphenylphosphine)palladium(0) species, see: Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338–1339.

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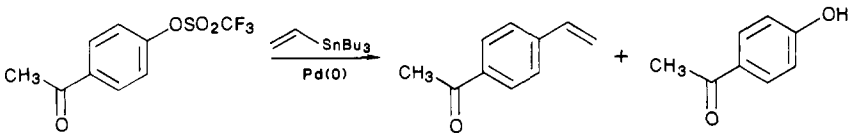
Table I. Effect of Varying Catalyst and Reaction Conditions on the Coupling Reaction[a]



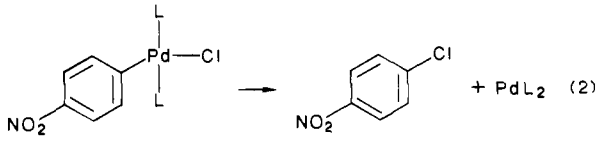
1 2 3

entry	catalyst	(mol %)	solvent	T (°C)	reaction time (h)	yield (%)[b] 2	3	1
1	$Pd(PPh_3)_4$	(5)	dioxane	23	24	30	0	70
2		(2)		98	4	>98 (95)	0	0
3			DMF	23	24	90(81)	10	0
4	$PdCl_2(CH_3CN)_2$	(5)				55	15	30
5		(3)		70	26	50	15	35
6	$[(\eta^3\text{-}C_4H_7)PdCl]_2$	(5)		23	24	45	25	30
7	$Pd(dba)_2$	(5)				50	20	30
8	$PhCH_2PdCl(PPh_3)_2$	(5)				80	10	10
9	$PdCl_2(PPh_3)_2$	(5)			9	95 (90)	5	0
10[c]					24	20	0	80
11		(2)		60	0.5	95 (91)	5	0
12			THF	62	5	94	4	2
13		(5)	dioxane	23	24	35	0	65
14		(2)		98	4	96	0	4

[a] Unless otherwise stated LiCl (3 equiv) was used in the reaction (see Experimental Section). [b] ^1H NMR yields determined by integration on the crude reaction mixture. Numbers in parentheses are for pure, isolated **2**. [c] Reaction run in the absence of LiCl.

usually gave good results, although with the latter catalyst much shorter reaction times were required. The yields of a given coupled product are usually essentially the same with both catalysts, although some important differences were noted (see below).

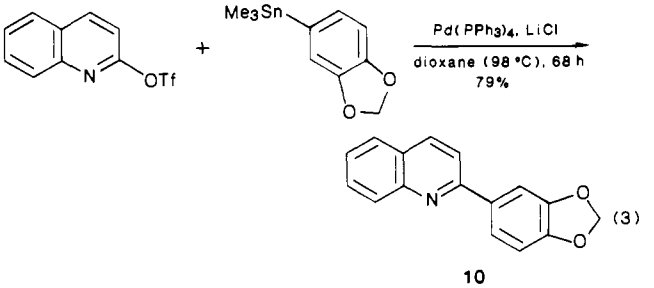
$PdCl_2(PPh_3)_2$ is a particularly effective catalyst for the alkyl transfer reaction; both methyl and *n*-butyl groups coupled in good yield with aryl triflates (entries 4, 13, and 28). Selective transfer of the less hindered alkyl takes place with ((trimethylsilyl)-methyl)trimethyltin[15] (entry 3). The more hindered tetrakis-((trimethylsilyl)methyl)stannane[15a] failed to react with *p*-nitrophenyl triflate, affording *p*-chloronitrobenzene under forcing conditions (entry 21). Thus, in the absence of an effective transmetalation step the product of initial oxidative addition undergoes reductive elimination to form the coupled product (eq 2).



(2)

The reaction between aryl triflate **1** and allyltri-*n*-butyltin, in the presence of $Pd(PPh_3)_4$, gave a 1:3 mixture of **4** and its conjugated isomer **5** (entry 5a). Although a synthesis of **4** by the palladium-catalyzed coupling reaction of *p*-bromoacetophenone and allyltri-*n*-butyltin has been reported,[16] in our hands, under identical conditions, **5** was obtained (ratio of **4** to **5** = 1:16) in 67% yield. When the coupling was carried out in toluene at reflux with the $Pd(PPh_3)_4$ catalyst, the reaction afforded pure **5**. Isomerization of some of the allyl aromatic compounds prepared by palladium-catalyzed reaction of arylmercuric salts with allylic halides has been reported to proceed at room temperature.[17] However, the isomerization of the initially formed allyl aromatic compounds into the 1-propenyl derivative with $Pd(PPh_3)_4$ as catalyst is not a general phenomenon, since under the reported conditions[16] *p*-bromomethoxybenzene yielded *p*-allylmethoxybenzene. Surprisingly, when $PdCl_2(PPh_3)_2$ was the catalyst, selective formation of **6** was obtained, although in poor yield (entry 5b). Again, selective transfer of the alkyl vs. the allyl group took place with crotyltri-*n*-butylstannane (entry 6). The coupling reaction of substituted allyltin reagents has been reported to proceed with extensive allylic rearrangement.[18] In this example, in addition to the normal coupled products **7**, some of the ketone **8** arising from allylic rearrangement was formed, as well as homocoupled biaryl **9**.

Aryltrialkylstannanes gave the expected coupled products with selective transfer to the aryl group (entries 7, 22, 26, and 29). However, the products of alkyl transfer were obtained as by-products in the presence of $PdCl_2(PPh_3)_2$ (entries 7b and 29b). This reaction was applied to a short synthesis of the quinoline alkaloid dubamine (**10**)[19] (eq 3). Dubamine has been synthesized in 20% yield by a remarkable one-pot process before its occurrence in nature was known.[19a] A synthesis that proceeds in only 1% yield has been recently reported.[19c] The palladium-catalyzed coupling of 2-quinolyltriflate with 5-(trimethylstannyl)-1,3-benzodioxole afforded dubamine in 79% yield.



(3)

10

Acetylenic tin reagents coupled in good yields (entries 14 and 23). Noteworthy in the latter example is that no isomerization of the allyl group already substituted was observed. The cross-

(13) For an isolated example of this reaction, see: Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277–279.

(14) For the synthesis of arylstannanes by palladium-catalyzed reaction of aryl halides with distannanes, see: (a) Azarian, D.; Dua, S. S.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1976**, *117*, C55–C57. (b) Kashin, A. N.; Bumagina, I. G.; Bumagin, N. A.; Bakunin, V. N.; Beletskaya, I. P. *Zh. Org. Khim.* **1981**, *17*, 905–911; (*Engl. Transl.*) **1981**, *17*, 789–794. (c) Kosugi, M.; Shimizu, K.; Ohtani, A.; Migita, T. *Chem. Lett.* **1981**, 829–830. (d) Bumagin, N. A.; Gulevich, Y. V.; Beletskaya, I. P. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1984**, *33*, 1137–1142; (*Engl. Transl.*) **1984**, *33*, 1044–1049. (e) Bumagin, N. A.; Bumagina, I. G.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1984**, *274*, 1103–1106; (*Engl. Transl.*) **1984**, *274*, 653–655. (f) Reference 4b.

(15) (a) Seyferth, D. *J. Am. Chem. Soc.* **1957**, *79*, 5881–5884. (b) Papeti, S.; Post, H. W. *J. Org. Chem.* **1957**, *22*, 526–528.

(16) Kosugi, M.; Sasazawa, K.; Shimizu, Y.; Migita, T. *Chem. Lett.* **1977**, 301–302.

(17) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5531–5534.

(18) (a) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595–2598. (b) Godschalx, J.; Stille, J. K. *Tetrahedron Lett.* **1980**, *21*, 2599–2602.

(19) (a) Kozlov, N. S.; Kostromina, O. E. *Sbornik Statei Obshchei Khim.* **1953**, *2*, 937–938; *Chem. Abstr.* **1955**, *49*, 6955e. (b) Structure determination: Sidyakin, G. P.; Pastukhova, V. I.; Yunusov, S. Y. *Uzbeksk. Khim. Zh.* **1962**, *6*, 56–59; *Chem. Abstr.* **1963**, *58*, 14010g. (c) Kametani, T.; Takeda, H.; Suzuki, Y.; Kasai, H.; Honda, T. *Heterocycles* **1986**, *24*, 3385–3395.

Table II. Palladium-Catalyzed Coupling of Aryl Triflates with Organostannanes

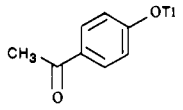
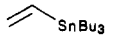
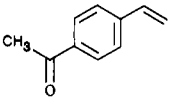
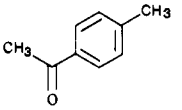
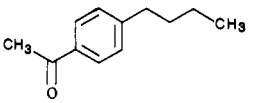
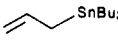
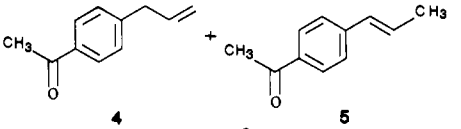
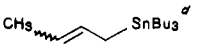
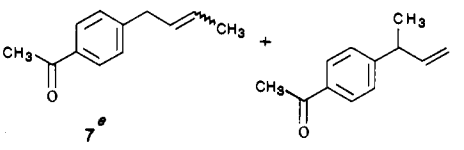
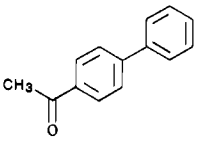
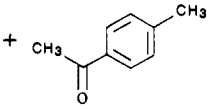
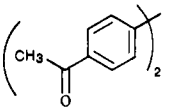
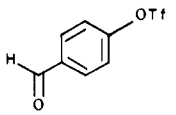
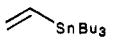
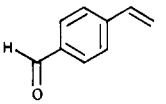
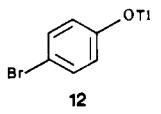
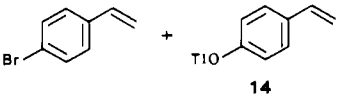
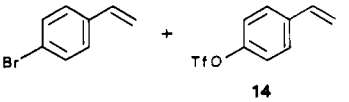
entry	triflate	organostannane	reaction conditions[a]	T (°C)	reaction time (h)	product(s)	isolated yield (%)
1a	 **1**		A	98	4	 **2**	95
1b			B	60	0.5	**2**	91
2		Me_4Sn	A	100[b]	16		75
3a		$Me_3SiCH_2SnMe_3$	A	98	65		83
3b			B	100	2		80
4a		Bu_4Sn	A	98	48	 **6**	82
4b			B	100	2		81
5a			A	98	43	 **4** 1:3 **5**	72
5b			B	100[c]	2	**6**, **4**, **5** (ratio 92:3:5)	46
6			A	98	31	**6** (+)  **7**[e] **8** (ratio **6**:**7**:**8** = 65:20:15) + **9**	11 29
7a		**Ph**$SnMe_3$	A	98	23		85
7b			B	90	1		54 16
8		$(Me_3Sn)_2$[f]	A	98	24	 **9**	94
9a			A	98	3		90
9b			B	60	0.5		86
10a	 **12**		A	98	7	 **14** (ratio 1:6)	75[g]
10b			A[h]		2.5	**14**	77[i]
10c			B	70	3	 **14** (ratio 5:1)	45[g]

Table II (Continued)

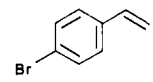
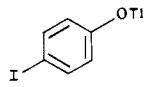
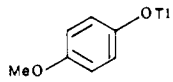
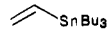
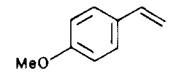
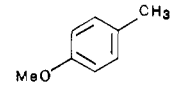
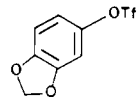
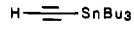
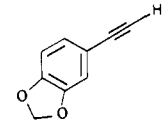
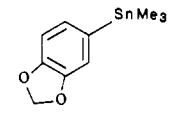
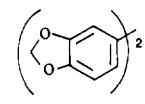
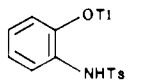
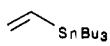
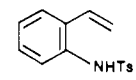
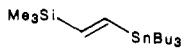
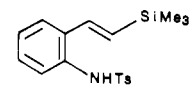
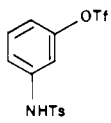
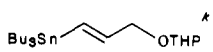
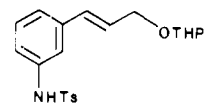
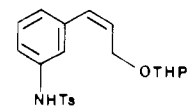
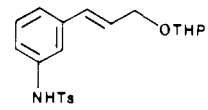
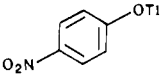
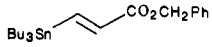
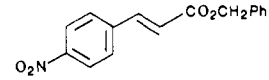
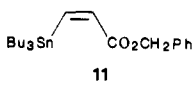
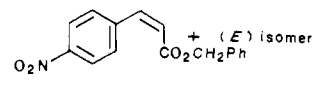
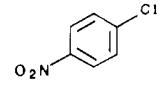
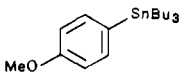
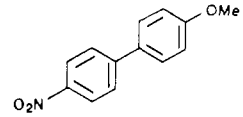
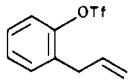
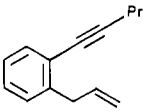
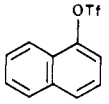
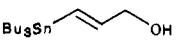
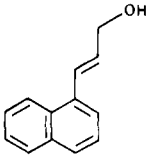
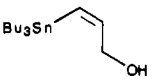
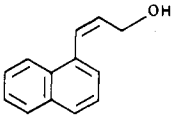
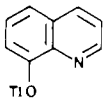
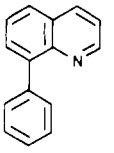
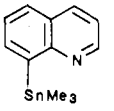
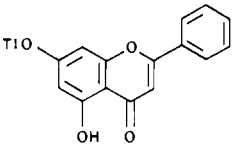
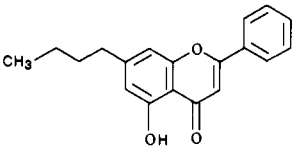
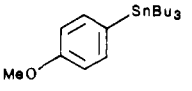
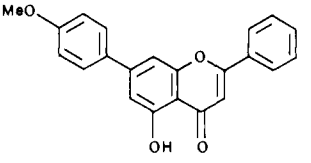
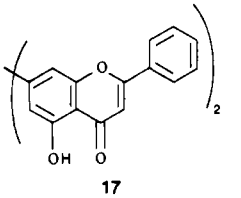
entry	triflate	organostannane	reaction conditions[a]	T (°C)	reaction time (h)	product(s)	isolated yield (%)
10d			B	24	18	 **14**	77
11a	 **13**		A[h]	98	16	**14**	73
11b			B	24	7	**14**	82
12			A	98	6.5		74
13a		Me_4Sn	A	100[b]	9	no reaction[j]	
13b			B	85	13		84
14			A	98	4		73
15		$(Me_3Sn)_2$	A		22		61
							23
16a			A		5		80
16b			B	60	4		78
17			A	98	11		81
18a			A	98	12		54
							18
18b			B	24	53		51[j]
19			A	98	9		82
20a		 **11**	A	98	66		5
20b			B	100	5	 (ratio 2:1)	47
21a		$(Me_3SiCH_2)_4Sn$	A	98	10	no reaction[j]	
21b			B	110	50		25
22a			A	98	36		74

Table II (Continued)

entry	triflate	organostannane	reaction conditions[a]	T (°C)	reaction time (h)	product(s)	isolated yield (%)
22b			B	100	2		80
23a		Bu_3Sn—≡—Pr	A	98	48		31
23b			B	60	7		65
24			B	60	3		82
25			B	60	6		62[m]
26		$PhSnMe_3$	A	98	82		61
27		$(Me_3Sn)_2$	A		75		67
28		Bu_4Sn	B	100	12	 **15**	92
29a			A	98	92	 **16**	28
29b			B	100	27	**16** + **15**	53 **29**
30		$(Me_3Sn)_2$[f]	A	98	60	 **17**	(92)[n]

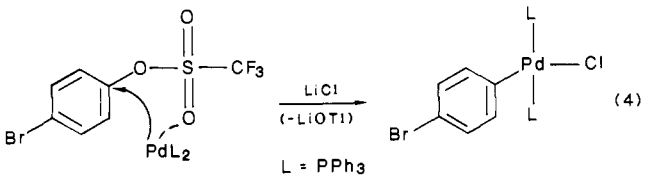
[a] A = $Pd(PPh_3)_4$ in dioxane; B = $PdCl_2(PPh_3)_2$ in DMF. 2 mol % palladium catalyst, 3 equiv of LiCl. [b] Reaction run in a sealed tube. [c] At 60 °C a mixture of **6**, **4**, and **5** (ratio = 50:30:20) was obtained in 33% yield. [d] As a 2:1 *E*/*Z* mixture. [e] As a 4:1 *E*/*Z* mixture. [f] 0.5 equiv of distannane was used. [g] Ca. 10% of 1,4-divinylbenzene was also formed. [h] Reaction run in the absence of LiCl. [i] A 33:1 ratio of *p*-bromostyrene/**14** was determined by ^1H NMR of the crude reaction mixture. [j] Starting materials were recovered. [k] As a 7:1 mixture of *E* and *Z* isomers. Additionally 5% of the 2-stannyl regioisomer was also present. [l] The catalyst decomposed under these conditions (conversion: 62%). [m] A 33% yield of 1-naphthol was obtained. [n] Characterized as the diacetate.

coupling reaction of aryl triflates with vinylstannanes gave good yields of styrene derivatives (entries 1, 9, 10, 12, 16, 17, 18, 19, 24, and 25). The reaction proceeded with retention of the double bond geometry (see particularly entries 24 and 25). Comparison of coupling experiments with benzyl (*E*)- and (*Z*)-3-(tri-*n*-butylstannyl)propenoate (entries 19 and 20) and (*E*)- and (*Z*)-1-(tri-*n*-butylstannyl)-1-propen-3-ol (entries 24 and 25) showed that the *E* isomers coupled more rapidly than the *Z* isomers. However, because of the tendency for cinnamate derivatives to undergo facile double bond isomerization, the geometry of the double bond was not maintained in the coupled product in this case (entries 19 and 20). The reaction of (*E*)-1-(tri-*n*-butylstannyl)-1-propenyl 3-tetrahydropyranyl ether (*E*/*Z* ratio of 7) in the presence of $Pd(PPh_3)_4$ resulted in a 3:1 mixture of *E* and *Z* coupled products (entry 18a). Similarly a mixture of *E* and *Z* isomers was obtained in the coupling of *Z* tin reagent **11** (entry 20a). Since no isomerization of the stannane **11** was observed under the same conditions,[20] the loss of stereochemisty seems to take place at the product stage.[21]

(20) Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6417–6422.

In the palladium-catalyzed coupling of aryl halides, the order of reactivity I > Br >> Cl is usually observed.[1] In an effort to establish the relative reactivity of the triflate group *p*-bromophenyl- (**12**) and *p*-iodophenyl triflates (**13**) were allowed to react with vinyltri-*n*-butylstannane under different reaction conditions (entries 10 and 11). A highly selective coupling of the tin reagent through the carbon–halogen bond can be accomplished by simply running the reaction with the $Pd(PPh_3)_4$ catalyst in the absence of lithium chloride (entries 10b and 11a). Remarkably, introduction of the catalyst as $PdCl_2(PPh_3)_2$ produced a reversal of the selectivity with *p*-bromophenyl triflate (**12**) giving *p*-bromostyrene in good yield (entry 10d). However, iodide **13** gave exclusively **14** with this catalyst in the presence of LiCl (entry 11b).

The change in selectivity on going from $Pd(PPh_3)_4$, I > Br > OTf, to $PdCl_2(PPh_3)_2$, I > OTf > Br, can be explained as a consequence of the highly coordinatively unsaturated nature of the catalyst formed with the latter system.[12] Coordination of the catalyst with the basic triflate group could direct the oxidative addition of the carbon–oxygen bond of the aryl triflate (eq 4).



(4)

The palladium-catalyzed coupling of aryl triflates with hexamethyldistannane[13,14] gave the aryltrimethyltin derivatives in good yields (entries 15 and 27). Small amounts of homocoupled products were obtained as a result of the competition of the formed arylstannane. The use of only 0.5 equiv of distannane gave the symmetrical biaryls in excellent yields (entries 8 and 30).

Conclusion

Aryl triflates couple with a variety of organostannanes under neutral conditions in the presence of lithium chloride and a palladium(0) catalyst to form a new carbon–carbon bond. Many functional groups are tolerated, both on the aryl triflate and on the organotin reagent, including alcohol, ester, nitro, acetal, ketone, and aldehyde groups. The new synthetic method can be applied to the selective cross-coupling of aryl, acetylenic, alkyl, and vinyl groups with an aromatic or heteroaromatic ring. Lower yields and unselective transfer of allyl groups were observed. Use of hexamethylditin leads to aryltrimethylstannanes or to symmetrical biaryls, depending on the amount of tin reagent.

The cross-coupling proceeds rapidly with both $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ catalyst, although faster rates were obtained with the latter catalyst. However, coupling with aryl and allyl trialkyltin reagents in the presence of the $PdCl_2(PPh_3)_2$ catalyst was not selective, giving rise to some coupling of the alkyl groups on tin. Both catalysts showed remarkably different selectivity in the coupling of vinyltri-*n*-butylstannane with 4-bromophenyl triflate.

Experimental Section

^1H NMR spectra were recorded on an IBM WP 270 (270 MHz) or a Nicolet NT 360 (360 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR were recorded on an IBM WP 270 (68 MHz) spectrometer with $CDCl_3$ as solvent and internal standard. Infrared spectra were obtained on a Beckman 4250 or a Beckman Acculab spectrometer. Low-resolution mass spectra (LRMS) were obtained on a V.G. Micromass 16F spectrometer. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

1,4-Dioxane and toluene were distilled from sodium and stored over activated 4A sieves. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Dimethylformamide (DMF), dichloromethane, and pyridine were distilled from calcium hydride and stored over activated 4A sieves.

Melting points were determined with a Melt-Temp capillary melting point apparatus and are uncorrected. Bulb-to-bulb distillations were conducted with a Büchi Kugelrohr apparatus. Thin-layer chromatographic analyses (TLC) were performed on aluminum sheets precoated with silica gel 60 F-254 (0.2 mm) (Merck). Column chromatographic purifications were performed with Woelm 230–400 mesh silica gel.

Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$),[22] dichlorobis(triphenylphosphine)palladium(II) ($PdCl_2(PPh_3)_2$),[23] bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$),[24] dichlorobis(acetonitrile)palladium(II),[25] chlorobenzylbis(triphenylphosphine)palladium(II) ($PhCH_2PdCl(PPh_3)_2$),[26] and chloro-2-methylpropenylpalladium(II) dimer ($[(\eta^3\text{-}C_4H_7)PdCl]_2$)[27] were prepared according to published procedures.

Organostannanes. The following organostannanes were prepared according to literature methods: ((trimethylsilyl)methyl)trimethylstannane,[15] tetrakis((trimethyl)methyl)stannane,[15a] tri-*n*-butylethenylstannane,[28] (*E*)-1-(trimethylsilyl)-2-(tri-*n*-butylstannyl)ethylene,[29] benzyl (*E*)- and (*Z*)-3-(tri-*n*-butylstannyl)propenoate,[30] (*E*)-1-(tri-*n*-butylstannyl)-1-propenyl 3-tetrahydropyranyl ether,[31] (*E*)-1-(tri-*n*-butylstannyl)-1-propen-3-ol,[32] (*Z*)-1-(tri-*n*-butylstannyl)-1-propen-3-ol,[33] allyltri-*n*-butylstannane,[34] tri-*n*-butylcrotylstannane (2:1 mixture of *E* and *Z* isomers),[35] tri-*n*-butylethynylstannane,[36] 1-(tri-*n*-butylstannyl)pentyne,[20] phenyltrimethylstannane,[37] and tri-*n*-butyl-(4-methoxyphenyl)-stannane.[38] 5-(Trimethylstannyl)-1,3-benzodioxole was prepared by palladium-catalyzed reaction of hexamethyldistannane with 5-[((trifluoromethyl)sulfonyl)oxy]-1,3-benzodioxole (Table II, entry 15). Tetramethyltin (Columbia), tetra-*n*-butyltin, and hexamethylditin (Alfa Products) were used as received.

Aryl Triflates. General Procedure: 4-Acetylphenyl Trifluoromethanesulfonate (1). To a solution of 4-hydroxyacetophenone (4.00 g, 29.4 mmol) in 15 mL of pyridine at 0 °C was slowly added trifluoromethanesulfonic anhydride (5.50 mL, 9.22 g, 32.7 mmol). The resulting mixture was stirred at 0 °C for 5 min and then allowed to warm to 23 °C and stirred at this temperature for 25 h. The resulting mixture was poured into water and extracted with ethyl ether. The ether extract was washed sequentially with water, 10% aqueous hydrochloric acid solution (2×), water, and a concentrated sodium chloride solution, dried ($MgSO_4$), and concentrated to yield an oil. Chromatography (flash column, hexanes–EtOAc 20:1) afforded **1** as a colorless oil (6.81 g, 86%): bp (bulb-to-bulb) 75–76 °C (0.35 mmHg); IR (neat) 1700, 1600, 1500, 1430, 1270–1210, 1140 cm^{-1}; ^1H NMR (270 MHz) δ 8.07 (d, J = 8.8 Hz, 2 H), 7.39 (d, J = 8.8 Hz, 2 H), 2.64 (s, 3 H). Anal. Calcd for $C_9H_7F_3O_4S$: C, 40.30; H, 2.63. Found: C, 40.36; H, 2.66.

The following compounds were prepared in an analogous manner. The phenols either were commerical products or were prepared according to literature methods.[39]

4-Formylphenyl trifluoromethanesulfonate (85%): colorless oil; bp (bulb-to-bulb) 68–69 °C (0.1 mmHg) [lit.[40] bp 77–79 °C (0.6 mmHg)];

(21) For the facile isomerization of (*Z*)-cinnamic acid derivatives, see for example: *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam; Vol. III-E, p 196.

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IR (neat) 2840, 2820, 1715, 1695, 1500, 1430, 1250, 1230–1200, 1135, 880 cm^{-1}; ^1H NMR (270 MHz) δ 10.05 (s, 1 H), 8.01 (d, J = 8.7 Hz, 2 H), 7.47 (d, J = 8.7 Hz, 2 H).

4-Bromophenyl trifluoromethanesulfonate (12) (92%): colorless oil; bp (bulb-to-bulb) 100–102 °C (3.2 mmHg); IR (neat) 1480, 1430, 1250, 1220, 1145, 1070, 1010, 885, 830, 740 cm^{-1}; ^1H NMR (270 MHz) δ 7.59 (d, J = 8.9 Hz, 2 H), 7.17 (d, J = 9.0 Hz, 2 H). Anal. Calcd for $C_7H_4BrF_3O_3S$: C, 27.56; H, 1.32. Found: C, 27.57; H, 1.34.

4-Iodophenyl trifluoromethanesulfonate (13) (87%): colorless oil; bp (bulb-to-bulb) 74–75 °C (0.4 mmHg); IR (neat) 1480, 1420, 1240, 1210, 1130, 1000, 870 cm^{-1}; ^1H NMR (270 MHz) δ 7.77 (d, J = 8.9 Hz, 2 H), 7.03 (d, J = 8.9 Hz, 2 H). Anal. Calcd for $C_7H_4F_3IO_3S$: C, 23.88; H, 1.15. Found: C, 23.93; H, 1.20.

4-Methoxyphenyl trifluoromethanesulfonate (93%): colorless oil; bp (bulb-to-bulb) 90–92 °C (3.5 mmHg); IR (neat) 2840, 1600, 1500, 1430–1410, 1245, 1200, 1135, 1030, 875, 825 cm^{-1}; ^1H NMR (270 MHz) δ 7.19 (d, J = 9.3 Hz, 2 H) 6.92 (d, J = 9.1 Hz, 2 H), 3.81 (s, 3 H). Anal. Calcd for $C_8H_7F_3O_4S$: C, 37.50; H, 2.75. Found: C, 37.66; H, 2.80.

5-[((Trifluoromethyl)sulfonyl)oxy]-1,3-benzodioxole (87%): colorless oil; bp (bulb-to-bulb) 66–67 °C (0.2 mmHg); IR (neat) 2900, 1640, 1610, 1505, 1425, 1250, 1210, 1140, 1110, 1035, 940, 860 cm^{-1}; ^1H NMR (270 MHz) δ 6.81–6.72 (m, 3 H), 6.04 (s, 2 H). Anal. Calcd for $C_8H_5F_3O_5S$: C, 35.56; H, 1.87. Found: C, 35.67; H, 1.90.

2-((4-Methylbenzenesulfonyl)amino)phenyl trifluoromethanesulfonate (75%): white solid; mp 86–87 °C (hexanes); IR (KBr) 3210, 1590, 1490, 1415, 1330, 1215–1195, 1160 cm^{-1}; ^1H NMR (270 MHz) δ 7.71–7.66 (m, 3 H), 7.34–7.18 (m, 5 H), 6.80 (br s, 1 H), 2.39 (s, 3 H). Anal. Calcd for $C_{14}H_{12}F_3NO_5S_2$: C, 42.53; H, 3.06. Found: C, 42.60; H, 3.11.

3-((4-Methylbenzenesulfonyl)amino)phenyl trifluoromethanesulfonate (87%): white solid; mp 108–109 °C (cyclohexane–benzene 3:1); IR (KBr) 3260, 1580, 1450, 1380, 1300, 1210, 1190, 1180, 1170, 1125, 1105, 930, 925, 560 cm^{-1}; ^1H NMR (270 MHz) δ 7.72 (d, J = 8.2 Hz, 2 H), 7.52 (br s, 1 H), 7.29 (t, J = 8.3 Hz, 1 H), 7.26 (d, J = 8.2 Hz, 2 H), 7.15 (t, J = 2.1 Hz, 1 H), 7.06 (dd, J = 8.1, 2.1, Hz, 1 H), 6.99 (dd, J = 8.3, 2.2 Hz, 1 H), 2.38 (s, 3 H). Anal. Calcd for $C_{14}H_{12}F_3NO_5S_2$: C, 42.53; H, 3.06. Found: C, 42.39; H, 3.09.

4-Nitrophenyl trifluoromethanesulfonate (85%): white solid; mp 52–53 °C (hexanes) [lit.[41] mp 53 °C]; IR (KBr) 3120, 3090, 1625, 1590, 1535, 1485, 1420, 1350, 1250, 1210, 1130, 1010, 890, 855, 755, 735, 680, 600 cm^{-1}; ^1H NMR (270 MHz) δ 8.38 (d, J = 9.2 Hz, 2 H), 7.50 (d, J = 9.2 Hz, 2 H).

2-(2-Propenyl)phenyl trifluoromethanesulfonate (91%): colorless oil; bp (bulb-to-bulb) 62–63 °C (0.15 mmHg); IR (neat) 1645, 1485, 1455, 1425–1410, 1250, 1230–1200, 1145–1130, 880 cm^{-1}; ^1H NMR (270 MHz) δ 7.34–7.25 (m, 4 H), 5.92 (ddt, J = 16.9, 10.2, 6.6 Hz, 1 H), 5.15 (dd, J = 10.0, 1.4 Hz, 1 H), 5.12 (dd, J = 16.7, 1.5 Hz, 1 H), 3.48 (d, J = 6.6 Hz, 2 H). Anal. Calcd for $C_{10}H_{19}F_3O_2S$: C, 45.11; H, 3.41. Found: C, 45.37; H, 3.44.

1-Naphthyl trifluoromethanesulfonate (90%): colorless oil; bp (bulb-to-bulb) 97–98 °C (0.3 mmHg); IR (neat) 1600, 1425, 1245, 1220–1200, 1140, 1130, 1000, 890, 805, 760 cm^{-1}; ^1H NMR (270 MHz) δ 8.08 (br d, J = 8.2 Hz, 1 H), 7.92–7.84 (m, 2 H), 7.67–7.56 (m, 2 H), 7.51–7.46 (m, 2 H). Anal. Calcd for $C_{11}H_7F_3O_3S$: C, 47.83; H, 2.55. Found: C, 47.72; H, 2.57.

8-Quinolyl trifluoromethanesulfonate (80%): white solid; mp 61–62 °C (hexanes); IR (KBr) 1600, 1595, 1430, 1420, 1220, 1200, 1130, 820 cm^{-1}; ^1H NMR (270 MHz) δ 9.05 (dd, J = 4.2, 1.4 Hz, 1 H), 8.22 (dd, J = 8.3, 1.4 Hz, 1 H), 7.86 (dd, J = 7.9, 1.3 Hz, 1 H), 7.64–7.50 (m, 3 H). Anal. Calcd for $C_{10}H_6F_3NO_3S$: C, 43.32; H, 2.18. Found: C, 43.45; H, 2.22.

2-Quinolyl trifluoromethanesulfonate (84%): colorless oil; bp (bulb-to-bulb) 124–125 °C (2 mmHg); IR (neat) 1620, 1600, 1580, 1505, 1430–1415, 1230–1210, 1160, 1145, 1100, 955, 910, 840 cm^{-1}; ^1H NMR (270 MHz) δ 8.31 (d, J = 8.7 Hz, 1 H), 8.03 (d, J = 8.5 Hz, 1 H), 7.87 (d, J = 8.2 Hz, 1 H), 7.78 (t, J = 7.8 Hz, 1 H), 7.61 (dd, J = 7.9, 7.2 Hz, 1 H), 7.22 (d, J = 8.8 Hz, 1 H). Anal. Calcd for $C_{10}H_6F_3NO_3S$: C, 43.32; H, 2.18. Found: C, 43.27; H, 2.20.

5-Hydroxy-2-phenyl-7-(trifluoromethanesulfonyl)oxy-4*H*-1-benzopyran-4-one. To a solution of 5,7-dihydroxyflavone (Chrysin, Aldrich) (540 mg, 2.12 mmol) in 20 mL of dichloromethane and 5 mL of pyridine at 0 °C was slowly added trifluoromethanesulfonic anhydride (0.37 mL, 620 mg, 2.20 mmol). The mixture was allowed to warm to 23 °C and stirred at this temperature for 20 h. The mixture was concentrated and the residue chromatographed (flash column, hexanes–EtOAc 8:1) to give pale yellow needles (651 mg, 79%): mp 129–130 °C (hexanes); TLC (hexanes–EtOAc 5:1) R_f 0.34; IR (KBr) 1650, 1635, 1420, 1250, 1215, 1190 cm^{-1}; ^1H NMR (270 MHz) 12.92 (s, 1 H), 7.90–7.86 (m, 2 H), 7.59–7.50 (m, 3 H), 6.97 (d, J = 2.2 Hz, 1 H), 6.67 (s, 1 H), 6.72 (d, J = 2.2 Hz, 1 H). Anal. Calcd for $C_{16}H_9F_3O_6S$: C, 49.75; H, 2.35. Found: C, 49.76; H, 2.38. A second fraction, 2-phenyl-5,7-bis((trifluoromethanesulfonyl)oxy)-4*H*-1-benzopyran-4-one, was isolated as small white crystals (75 mg, 7%): mp 206–207 °C (cyclohexane–benzene 5:1); TLC (hexanes–EtOAc 5:1) R_f 0.19; IR (KBr) 1660, 1625, 1440, 1370, 1250, 1225, 1135, 1010 cm^{-1}; ^1H NMR (270 MHz) δ 7.92–7.88 (m, 2 H), 7.64 (d, J = 2.4 Hz, 1 H), 7.62–7.56 (m, 3 H), 7.16 (d, J = 2.4 Hz, 1 H), 6.84 (s, 1 H). Anal. Calcd for $C_{17}H_8F_6O_8S_2$: C, 39.39; H, 1.56. Found: C, 39.49; H, 1.61.

Reaction Condition Studies (Table I). Coupling reactions listed in Table I were run according to the general procedure as follows: A 0.2 M solution of **1** in the corresponding solvent was allowed to react with 1.04 equiv of tri-*n*-butylethenylstannane. A polymerization inhibitor (2,6-di-*tert*-butyl-4-methylphenol or 4-*tert*-butylcatechol) was added when the reaction mixture was heated. The reaction mixtures were treated with pyridine and a 1.4 M pyridinium fluoride solution[42] to remove the organotin chloride byproduct,[43] followed by filtration (Celite) and extractive workup. The ratios of **1**, **2**, and **3** in the crude reaction mixtures were determined from the ^1H NMR by integration of the methyl (δ 2.64, 2.58, and 2.52, respectively) and the aromatic resonances [δ (8.07, 7.39), (7.91, 7.47), and (7.92, 6.97), respectively].

Palladium-Catalyzed Coupling Reaction: General Procedure (Table II). 4-Vinylacetophenone (2) (Table II, Entry 1) To a solution of **1** (530 mg, 1.98 mmol) in 9 mL of 1,4-dioxane were added tri-*n*-butylethenylstannane (650 mg, 2.05 mmol), LiCl (252 mg, 5.94 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), and a few crystals of 2,6-di-*tert*-butyl-4-methylphenol. The resulting suspension was heated to reflux (98 °C) for 4 h, cooled to room temperature, and treated with 1 mL of pyridine and 2 mL of pyridinium fluoride (1.4 M solution in THF, 2.8 mmol). The resulting mixture was stirred at 23 °C for 16 h. The mixture was diluted with diethyl ether, filtered through a small pad of Celite, and washed with water, 10% HCl, water, and a concentrated sodium chloride solution. The solution was dried ($MgSO_4$) and concentrated to yield an oil. Chromatography (flash column, hexanes–EtOAc 50:1) afforded **2** as a colorless oil, which solidified on standing (273 mg, 95%): mp 29–30 °C [lit.[44] mp 33 °C]; bp (bulb-to-bulb) 85–87 °C (2.5 mmHg) [lit.[44] bp 110 °C (12 mmHg)]; IR (neat) 1680, 1600, 1395, 1350, 1260, 1170, 975, 940, 905, 840 cm^{-1}; ^1H NMR (270 MHz) δ 7.91 (d, J = 8.3 Hz, 2 H), 7.47 (d, J = 8.3 Hz, 2 H), 6.74 (dd, J = 17.6, 10.9 Hz, 1 H), 5.86 (d, J = 17.6 Hz, 1 H), 5.39 (d, J = 10.8 Hz, 1 H), 2.58 (s, 3 H).

When trimethyltin chloride was the byproduct (entries 2, 7, 13, 15, 26, and 27 and eq 3) a simple 10% aqueous NH_4OH washing replaced the treatment with pyridinium hydrofluoride. Compounds in entries 8 and 30 crystallized directly from the reaction mixture and were isolated by filtration.

Mixtures of hexanes–EtOAc were used as eluents in the following ratios: 1:0 (entries 10, 11, 12, and 23), 50:1 (entries 1, 4, 5, 9, 14, 15, 26, and 27), 40:1 (entries 3, 6, and 7), 30:1 (entry 21), 20:1 (entry 22 and eq 3), 10:1 (entry 28), 8:1 (entries 20, 25, and 29), 6:1 (entry 19), 5:1 (entries 17 and 18), 4:1 (entries 16 and 24). Compounds in entries 2 and 13 were isolated by bulb-to-bulb distillation.

The following compounds were prepared according to the general procedure:

4-Methylacetophenone (entries 2 and 3): colorless oil; bp (bulb-to-bulb) 79–80 °C (3.5 mmHg) [lit.[45] bp 75.5–76 °C (2.5 mmHg)]; IR (neat) 2920, 1680, 1405, 1355, 1265, 1180, 1010, 950, 810 cm^{-1}; ^1H NMR (270 MHz) δ 7.86 (d, J = 8.2 Hz, 2 H), 7.26 (d, J = 8.2 Hz, 2 H), 2.58 (s, 3 H), 2.41 (s, 3 H).

4-Butylacetophenone (entries 4 and 5b): colorless oil; bp (bulb-to-bulb) 89–90 °C (3.2 mmHg) [lit.[46] bp 140–141 °C (14 mmHg)]; IR (neat) 2940, 2860, 1680, 1600, 1350, 1260, 1170, 950, 825 cm^{-1}; ^1H NMR (270 MHz) δ 7.87 (d, J = 8.3 Hz, 2 H), 7.26 (d, J = 8.3 Hz, 2 H), 2.66 (t, J = 7.7 Hz, 2 H), 2.57 (s, 3 H), 1.61 (m, 2 H), 1.34 (m, 2 H), 0.93 (t, J = 7.3 Hz, 3 H).

4-(2-Propenyl)acetophenone (4) and (*E*)-4-(1-propenyl)acetophenone (5) (entry 5a): colorless oil; bp (bulb-to-bulb) 86–87 °C (1.5 mmHg); IR (neat) 1680, 1605, 1355, 1265, 1180, 960 cm^{-1}; ^1H NMR (270 MHz) δ 7.89 (d, J = 8.3 Hz, 2 H, **4**), 7.88 (d, J = 8.3 Hz, 2 H, **5**), 7.38 (d, J = 8.4 Hz, 2 H, **5**), 7.27 (d, J = 8.2 Hz, **4**), 6.41 (m, 2 H, **5**), 5.94 (m,

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1 H, **4**), 5.13–5.06 (m, 2 H, **4**), 3.43 (d, J = 6.7 Hz, 2 H, **4**), 2.57 (s, 3 H, **4**), 2.53 (s, 3 H, **5**), 1.91 (d, J = 5.0 Hz, 3 H, **5**). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.31; H, 7.60.

Compound **5** was synthesized by a coupling reaction of 4-bromoacetophenone and allyltributylstannane (2% $Pd(PPh_3)_4$, an additional 2% catalyst was added after 19 h, toluene at reflux, 22 h; 83%): colorless oil; bp (bulb-to-bulb) 75–76 °C (0.3 mmHg) [lit.[47] bp 90–92 °C (0.35 mmHg)]; IR (neat) 2960, 2910, 1680, 1605, 1355, 1265, 1180, 960, 780 cm^{-1}; ^1H NMR (270 MHz) δ 7.85 (d, J = 8.2 Hz, 2 H), 7.34 (d, J = 8.3 Hz, 2 H), 6.42–6.30 (m, 2 H), 2.53 (s, 3 H), 1.88 (d, J = 5 Hz, 3 H); ^{13}C NMR (68 MHz) δ 196.67, 142.39, 135.51, 130.28, 128.44, 128.01, 125.63, 25.96, 18.16.

4-(1-Methyl-2-propenyl)acetophenone (8) and (*E* and *Z*)-4-(1-methyl-1-propenyl)acetophenone (7) (entry 6): An inseparable mixture of **6**, **8**, ***E*-7**, and ***Z*-7** (ratio = 65:15:16:4) was obtained as a colorless oil; bp (bulb-to-bulb) 83–85 °C (0.25 mmHg); IR (neat) 2980, 2940, 2880, 1690, 1610, 1360, 1270 cm^{-1}; ^1H NMR (270 MHz) δ 7.90–7.85 (overlapping doublets, 2 H), 7.27–7.23 (overlapping d, 2 H), 5.97 (ddd, J = 17.5, 10.0, 6.5 Hz, 1 H, **8**), 5.64–5.54 (m, 2 H, **7**), 5.11–5.02 (m, 2 H, **8**), 3.51 (br quintet, J = 6.8 Hz, 1 H, **8**), 3.44 (br d, J = 6.6 Hz, 2 H, ***Z*-7**), 3.35 (br d, J = 4.6 Hz, 2 H, ***E*-7**), 2.65 (t, J = 7.7 Hz, 2 H, **6**), 2.56 (s, 3 H, **6**, **7**, **8**), 1.70–1.67 (m, 3 H, ***E*-7** and ***Z*-7**), 1.60 (m, 3 H, **6**), 1.36 (d, J = 7.1 Hz, 3 H, **8**), 1.35 (m, 2 H, **6**), 0.92 (t, J = 7.3 Hz, **6**). The assignment of the structures of **8**, ***E*-7**, and ***Z*-7** was based on homodecoupling experiments and comparison with the published spectral data for the conjugated isomers.[48]

4-Acetylbiphenyl (entry 7): white needles; mp 119–120 °C (EtOH) [lit.[49] mp 121 °C]; IR (KBr) 1675, 1595, 1395, 1355, 1260, 755 cm^{-1}; ^1H NMR (270 MHz) δ 8.03 (d, J = 8.5 Hz, 2 H), 7.69 (partially overlapping d, J = 8.3 Hz, 2 H), 7.65–7.62 (m, 2 H), 7.51–7.40 (m, 3 H), 2.64 (s, 3 H).

4,4′-Diacetylbiphenyl (9) (entry 8): pale yellow solid; mp 189–190 °C (EtOH) [lit.[49] mp 191 °C]; IR (Nujol) 1680, 1605, 810 cm^{-1}; ^1H NMR (270 MHz) δ 8.06 (d, J = 7.6 Hz, 4 H), 7.72 (d, J = 7.9 Hz, 4 H), 2.65 (s, 6 H).

4-Vinylbenzaldehyde (entry 9): colorless oil; bp (bulb-to-bulb) 69–70 °C (0.45 mmHg) [lit.[50] bp 92–93 °C (14 mmHg)]; IR (neat) 2820, 2730, 1705–1690, 1570, 1210, 1160, 835, 735 cm^{-1}; ^1H NMR (270 MHz) δ 9.99 (s, 1 H), 7.85 (d, J = 8.3 Hz, 2 H), 7.56 (d, J = 8.3 Hz, 2 H), 6.78 (dd, J = 17.6, 10.9 Hz, 1 H), 5.92 (d, J = 17.6 Hz, 1 H), 5.45 (d, J = 10.7 Hz, 1 H).

4-Vinylphenyl Trifluoromethanesulfonate (14) (entries 10a, 10b, and 11): colorless oil; bp (bulb-to-bulb) 59–60 °C (0.15 mmHg); IR (neat) 1500, 1425, 1300, 1210, 1135, 885, 840 cm^{-1}; ^1H NMR (270 MHz) δ 7.45 (d, J = 8.7 Hz, 2 H), 7.22 (d, J = 8.7 Hz, 2 H), 6.69 (dd, J = 17.6, 10.9 Hz, 1 H), 5.76 (d, J = 17.6 Hz, 1 H), 5.33 (d, J = 10.9 Hz, 1 H); ^{13}C NMR (68 MHz) δ 148 .98, 138.14, 135.05, 127.80, 121.30, 118.93 (q, $^1J(^{13}C-^{19}F)$ = 321 Hz), 115.66. Anal. Calcd for $C_9H_7F_3O_3S$: C, 42.86; H, 2.80. Found: C, 42.99; H, 2.84.

4-Bromostyrene (entries 10c and 10d): colorless oil; bp (bulb-to-bulb) 50–52 °C (0.25 mmHg) [lit.[51] bp 83.5–84.5 °C (11 mmHg)]; IR (neat) 3070, 2920, 1630, 1590, 1485, 1390, 1100, 1060, 1000, 980, 900, 820, 770, 715 cm^{-1}; ^1H NMR (270 MHz) δ 7.42 (d, J = 8.4 Hz, 2 H), 7.24 (d, J = 8.4 Hz, 2 H), 6.63 (dd, J = 17.6, 10.9 Hz, 1 H), 5.72 (d, J = 7.6 Hz, 1 H), 5.22 (d, J = 10.8 Hz, 1 H).

4-Methoxystyrene (entry 12): colorless oil; bp (bulb-to-bulb) 74–75 °C (3.5 mmHg) [lit.[52] bp 85 °C (14 mmHg)]; IR (neat) 3000, 2955, 2825, 1630, 1610, 1515, 1300, 1250, 1175, 1035, 895, 830 cm^{-1}; ^1H NMR (270 MHz) δ 7.35 (d, J = 8.7 Hz, 2 H), 6.86 (d, J = 8.7 Hz, 2 H), 6.66 (dd, J = 17.6, 10.9 Hz, 1 H), 5.61 (d, J = 17.6 Hz, 1 H), 5.12 (d, J = 10.8 Hz, 1 H), 3.80 (s, 3 H).

4-Methoxytoluene (entry 13b): colorless oil; bp (bulb-to-bulb) 60–61 °C (0.3 mmHg) [lit.[53] bp 176.5 °C]; IR (neat) 3000, 2940, 2820, 1610, 1505, 1455, 1290, 1170, 1030, 805 cm^{-1}; ^1H NMR (270 MHz) δ 7.06 (d, J = 8.5 Hz, 2 H), 6.78 (d, J = 8.5 Hz, 2 H), 3.74 (s, 3 H), 2.27 (s, 3 H).

5-Ethynyl-1,3-benzodioxole (entry 14): colorless oil; bp (bulb-to-bulb) 80–82 °C (2.0 mmHg) [lit.[54] bp 103 °C (11 mmHg)]; IR (neat) 3300, 2900, 2100, 1505, 1490–1480, 1245, 1140 cm^{-1}; ^1H NMR (270 MHz) δ 7.01 (dd, J = 8.0, 1.6 Hz, 1 H), 6.92 (d, J = 1.5 Hz, 1 H), 6.73 (d, J = 8.0 Hz, 1 H), 5.97 (s, 2 H); ^{13}C NMR (68 MHz) δ 148.30, 147.46, 126.85, 115.49, 112.05, 108.35, 101.27, 83.61, 75.42.

5-(Trimethylstannyl)-1,3-benzodioxole (entry 15): colorless oil; bp 83–84 °C (0.9 mmHg); TLC (hexanes–EtOAc 30:1) R_f 0.57; IR (neat) 2990, 2910, 2880, 1500, 1485, 1480, 1410, 1315, 1230, 1140, 930, 795, 760 cm^{-1}; ^1H NMR (270 MHz) δ 6.95 (br s, 1 H), 6.92 (dd, J = 7.3, 0.9 Hz, 1 H), 6.84 (d, J = 7.3 Hz, 1 H), 5.90 (s, 2 H), 0.26 [s, 9 H, $^2J(^{119}SnCH_3)$ = 55.2 Hz, $^2J(^{117}SnCH_3)$ = 52.8 Hz]; ^{13}C NMR (68 MHz) δ 147.99, 147.75, 134.45, 129.07, 115.06, 108.93, 100.27, −9.42. Anal. Calcd for $C_{10}H_{14}O_2Sn$: C, 42.16; H, 4.95. Found: C, 42.23; H, 4.96. A second fraction, 5,5′-bi-1,3-benzodioxole, was isolated as white solid: mp 143–144 °C (cyclohexane) [lit.[55] mp 145–146 °C]; TLC (hexanes–EtOAc 30:1) R_f 0.37; ^1H NMR (270 MHz) δ 6.98 (s, 2 H), 6.96 (partially overlapping d, J = 8.0 Hz, 2 H), 6.84 (d, J = 8.1 Hz, 2 H), 5.97 (s, 4 H).

***N*-*p*-Toluenesulfonyl-2-vinylaniline** (entry 16): white crystals; mp 120–121 °C (cyclohexane) [lit.[56] mp 123.5–124.5 °C]; IR (KBr) 3230, 1590, 1485, 1390, 1320, 1155 cm^{-1}; ^1H NMR (270 MHz) δ 7.61 (d, J = 8.2 Hz, 2 H), 7.37–7.30 (m, 2 H), 7.26–7.15 (m, 4 H), 6.62 (br s, 1 H), 6.56 (dd, J = 17.5, 11.1 Hz, 1 H), 5.50 (d, J = 17.5 Hz, 1 H), 5.25 (d, J = 11.1 Hz, 1 H), 2.38 (s, 3 H); ^{13}C NMR (68 MHz) δ 143.76, 137.03, 133.50, 132.76, 131.86, 129.58, 128.54, 127.33, 127.06, 126.30, 124.68, 118.13, 21.39. Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53. Found: C, 65.84; H, 5.56.

***N*-*p*-Toluenesulfonyl-2-[(*E*)-2-(trimethylsilyl)ethenyl]aniline** (entry 17): white crystals; mp 87–88 °C (hexanes); IR (KBr) 3280, 2850, 1600, 1485, 1400, 1330, 1170, 1155 cm^{-1}; ^1H NMR (270 MHz) δ 7.57 (d, J = 8.2 Hz, 2 H), 7.44–7.37 (m, 2 H), 7.26–7.14 (m, 1 H), 6.79 (br s, 1 H), AB system (δ_A = 6.56, δ_B = 6.24, J_{AB} = 18.0 Hz), 2.37 (s, 3 H), 0.07 (s, 9 H); ^{13}C NMR (68 MHz) δ 143.55, 137.77, 136.89, 134.71, 133.99, 133.03, 129.54, 128.43, 127.11, 126.63, 126.54, 126.10, 21.39, −1.44. Anal. Calcd for $C_{18}H_{23}NO_2SSi$: C, 62.47; H, 6.71. Found: C, 62.58; H, 6.72.

***N*-*p*-Toluenesulfonyl-3-[(*E*)-3-tetrahydropyranoxyl-1-propenyl]aniline** (entry 18): white crystals; mp 101–102 °C (cyclohexane); TLC (hexanes–EtOAc 3:1) R_f 0.15; IR (KBr) 3140, 2950, 1600, 1580, 1470, 1330, 1150, 1105, 1005 cm^{-1}; ^1H NMR (270 MHz) δ 7.69 (d, J = 8.2 Hz, 2 H), 7.29 (br s, 1 H), 7.21 (d, J = 8.1 Hz, 2 H), 7.16–7.11 (m, 3 H), 6.97 (br d, J = 7.3 Hz, 1 H), 6.51 (d, J = 15.9 Hz, 1 H), 6.24 (dt, J = 15.9, 5.9 Hz, 1 H), 4.69 (br t, J = 2.9 Hz, 1 H), 4.37 (dd, J = 13.1, 5.4 Hz, 1 H), 4.11 (dd, J = 13.1, 6.3 Hz, 1 H), 3.95–3.86 (m, 1 H), 3.56–3.52 (m, 1 H), 2.36 (s, 3 H), 1.89–1.53 (m, 6 H); ^{13}C NMR (68 MHz) δ 143.70, 138.33, 137.16, 136.67, 131.10, 129.88, 129.55, 127.43, 127.28, 123.29, 120.51, 119.55, 98.19, 67.42, 62.25, 30.66, 25.47, 21.30, 19.48. Anal. Calcd for $C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50. Found: C, 65.20; H, 6.51. In entry 18a the (*Z*) isomer was also obtained as an oil (partially isomerizes to the (*E*) isomer on attempted crystallization from boiling hexanes); TLC (hexanes–EtOAc 3:1) R_f 0.21; IR (neat) 3260, 2940, 1605, 1465, 1335, 1165, 1090, 1030 cm^{-1}; ^1H NMR (270 MHz) δ 7.69 (d, J = 8.3 Hz, 2 H), 7.26–7.15 (m, 2 H), 7.22 (partially overlapping d, J = 8.2 Hz, 2 H), 7.00–6.93 (m, 3 H), 6.46 (d, J = 11.9 Hz, 1 H), 4.19 (ddd, J = 13.0, 6.7, 1.4, Hz, 1 H), 3.89–3.83 (m, 1 H), 3.54–3.48 (m, 1 H), 2.36 (s, 3 H), 1.86–1.52 (m, 6 H); ^{13}C NMR (68 MHz) δ 143.78, 138.05, 136.82, 130.45, 130.11, 129.65, 129.12, 127.34, 125.73, 121.87, 120.20, 98.67, 64.11, 62.44, 30.81, 25.52, 21.40, 19.60 (one carbon signal overlaps).

Benzyl (*E*)-4-nitrocinnamate (entries 19 and 20): white needles; mp 112–113 °C (hexanes); TLC (hexanes–EtOAc 5:1) R_f 0.40; IR (KBr) 1715, 1520, 1340, 1310, 1170, 840, 750, 690 cm^{-1}; ^1H NMR (270 MHz) δ 8.23 (d, J = 8.8 Hz, 2 H), 7.74 (d, J = 16.1 Hz, 1 H), 7.65 (d, J = 8.8 Hz, 2 H), 7.41–7.37 (m, 5 H), 6.60 (d, J = 16.1 Hz, 1 H), 5.27 (s, 2 H); ^{13}C NMR (68 MHz) δ 165.64, 148.73, 141.99, 140.58, 135.90, 128.61, 128.58, 128.35, 128.26, 124.08, 122.45, 66.73. Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63. Found: C, 67.78; H, 4.67.

Benzyl (*Z*)-4-nitrocinnamate (entry 20b): white solid; mp 86–88 °C (hexanes–cyclohexane 5:1); TLC (hexanes–EtOAc 5:1) R_f 0.35; IR (KBr) 1720, 1510, 1345, 1190, 860, 725 cm^{-1}; ^1H NMR (270 MHz) δ 8.11 (d, J = 8.8 Hz, 2 H), 7.58 (d, J = 8.7 Hz, 2 H), 7.41–7.27 (m, 5 H), 7.03 (d, J = 12.5 Hz, 1 H), 6.17 (d, J = 12.5 Hz, 1 H), 5.14 (s, 2 H); ^{13}C NMR (68 MHz) δ 165.05, 147.88, 141.44, 140.48, 135.46, 130.03, 128.55, 128.47, 124.14, 123.24, 123.15, 66.59. Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63. Found: C, 67.65; H, 4.64.

4-Methoxy-4′-nitrobiphenyl (entry 22): yellow needles; mp 106–107 °C (hexanes) [lit.[57] mp 111 °C]; IR (Nujol) 1600, 1590, 1505, 1465,

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1430, 1250, 1180 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.25 (d, J = 8.7 Hz, 2 H), 7.68 (d, J = 8.7 Hz, 2 H), 7.57 (d, J = 8.8 Hz, 2 H), 7.01 (d, J = 8.8 Hz, 2 H), 3.87 (s, 3 H).

1-(1-Pentynyl)-2-(2-propenyl)benzene (entry 23): colorless oil; bp (bulb-to-bulb) 56–57 °C (0.2 mmHg); IR (neat) 2960, 2930, 2200 (weak), 1640, 1480, 905, 750 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.38 (br d, J = 7.3 Hz, 1 H), 7.23–7.09 (m, 3 H), 5.99 (ddt, J = 16.8, 10.2, 6.6 Hz, 1 H), 5.12–5.04 (m, 2 H), 3.55 (dt, J = 6.7, 1.3 Hz, 2 H), 2.42 (t, J = 6.9 Hz, 2 H), 1.64 (sextet, J = 7.2 Hz, 2 H), 1.05 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (68 MHz) δ 141.79, 136.82, 132.19, 128.59, 127.58, 125.84, 123.77, 115.53, 94.11, 79.47, 38.70, 22.31, 21.56, 13.41. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.16; H, 8.76.

(*E*)-3-α-Naphthyl-2-propen-1-ol (entry 24): white plates; mp 36–37 °C (hexanes); bp (bulb-to-bulb) 103–104 °C (0.03 mmHg); TLC (hexanes–EtOAc 2:1) R_f 0.25; IR (melt) 3360–3280, 1585, 1505, 1340, 1080, 1000, 955, 770 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.04–8.01 (m, 1 H), 7.76–7.73 (m, 1 H), 7.67 (d, J = 8.1 Hz, 1 H), 7.46–7.24 (m, 5 H), 6.26 (dt, J = 15.6, 5.4 Hz, 1 H), 4.30 (dd, J = 5.5, 1.4 Hz, 2 H), 3.20 (br s, 1 H); ^{13}C NMR (68 MHz) δ 134.42, 133.60, 131.79, 131.15, 128.36, 127.86, 127.79, 125.86, 125.78, 125.42, 123.75, 123.65, 63.49. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.51; H, 6.60.

(*Z*)-3-α-Naphthyl-2-propen-1-ol (entry 25): colorless oil; bp (bulb-to-bulb) 82–83 °C (0.02 mmHg); TLC (hexanes–EtOAc 2:1) R_f 0.15; IR (neat) 3380–3320, 1595, 1510, 1340, 1050, 1035, 1020, 805, 780 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.98 (m, 1 H), 7.88–7.78 (m, 2 H), 7.52–7.41 (m, 3 H), 7.27–7.24 (m, 1 H), 7.09 (br d, J = 11.5 Hz, 1 H), 6.14 (dt, J = 11.5, 6.6 Hz, 1 H), 4.29 (ddd, J = 6.7, 5.7, 1.5 Hz, 2 H; after exchange with D_2O: dd, J = 6.6, 1.5 Hz), 1.41 (br t, J = 5.6 Hz, 1 H; exchanges with D_2O); ^{13}C NMR (68 MHz) δ 133.54, 133.47, 132.62, 131.63, 128.85, 128.26, 127.70, 126.37, 125.92, 125.71, 124.99, 124.64, 59.47. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.84; H, 6.59.

8-Phenylquinoline (entry 26): white solid; mp 46–47 °C (hexanes) [lit.[58a] mp 48 °C]; bp (bulb-to-bulb) 148–150 °C (3 mmHg) [lit.[58b] bp 198–200 °C (15 mmHg)]; IR (melt) 3050, 1595, 1490, 955, 820, 780 740 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.94 (dd, J = 4.1, 1.4 Hz, 1 H), 8.17 (dd, J = 8.3, 1.8 Hz, 1 H), 7.80 (dd, J = 8.0, 1.4 Hz, 1 H), 7.74–7.68 (m, 3 H), 7.60–7.36 (m, 5 H).

8-(Trimethylstannyl)quinoline (entry 27): colorless oil; bp (bulb-to-bulb) 103–104 °C (0.4 mmHg); IR (neat) 3050, 2970, 2905, 1485, 810, 785 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.86 (dd, J = 4.2, 1.7 Hz, 1 H), 8.07 (dd, J = 8.2, 1.8 Hz, 1 H), 7.88 (dd, J = 6.5, 1.3 Hz, 1 H), 7.75 (dd, J = 8.1, 1.3 Hz, 1 H), 7.49 (dd, J = 8.1, 6.6 Hz, 1 H), 7.31 (dd, J = 8.2, 4.2 Hz, 1 H), 0.30 [s, 9 H, $^2J(^{119}SnCH_3)$ = 56.3 Hz, $^2J(^{117}SnCH_3)$ = 54.0 Hz]; ^{13}C NMR (68 MHz) δ 153.17, 153.06, 149.35, 147.56, 136.94, 127.97, 126.21, 125.83, −8.32. Anal. Calcd for $C_{12}H_{15}NSn$: C, 49.37; H, 5.18. Found: C, 49.50; H, 5.25.

7-*n*-Butyl-5-hydroxy-2-phenyl-4*H*-1-benzopyran-4-one (**15**) (entry 28): yellow crystals; mp 88–89 °C (hexanes); TLC (hexanes–EtOAc 4:1) R_f 0.43; IR (KBr) 1650, 1610, 1445, 1260, 760 cm^{-1}; ^{1}H NMR (270 MHz) δ 12.46 (s, 1 H), 7.91–7.88 (m, 1 H), 7.56–7.48 (m, 3 H), 6.84 (s, 1 H), 6.69 (s, 1 H), 6.53 (s, 1 H), 2.66 (t, J = 7.7 Hz, 2 H), 1.65 (q, J = 7.3 Hz, 2 H), 1.38 (sextet, J = 7.6 Hz, 2 H), 0.94 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (68 MHz) δ 183.18, 164.29, 160.60, 156.54, 152.21, 131.81, 131.57, 129.06, 126.37, 111.66, 109.11, 106.76, 36.29, 32.76, 22.24, 13.78. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.39; H, 6.17.

5-Hydroxy-7-(4-methoxyphenyl)-2-phenyl-4*H*-1-benzopyran-4-one (**16**) (entry 29): yellow crystals; mp 183–185 °C (EtOAc–hexanes 2:1); TLC (hexanes–EtOAc 4:1) R_f 0.27; IR (KBr) 1660, 1620, 1605, 1450, 1290, 1255, 1175 cm^{-1}; ^{1}H NMR (270 MHz) δ 12.55 (s, 1 H), 7.94–7.91 (m, 2 H), 7.61–7.53 (m, 5 H), 7.19 (d, J = 1.4 Hz, 1 H), 7.02 (partially overlapping d, J = 1.5 Hz, 1 H), 7.0 (d, J = 9.1 Hz, 2 H), 6.73 (s, 1 H), 3.87 (s, 3 H); ^{13}C NMR (68 MHz) δ 183.16, 164.65, 161.05, 160.62, 156.94, 148.41, 131.90, 131.65, 129.14, 128.52, 126.48, 114.63, 109.73, 109.51, 106.36, 104.97, 55.44 (one carbon signal overlaps). Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.58; H, 4.70.

5,5′-Dihydroxy-2,2′-diphenyl-[7,7′-bi-4*H*-1-benzopyran]-4,4′-dione (**17**) (entry 30): yellow solid; mp >335 °C; IR (KBr) 1660, 1620, 1455, 1415, 1255, 755, 670 cm^{-1}. Because of its isolubility **17** was characterized as the diacetate: To a suspension of **17** (129 mg, 0.27 mmol) in 2 mL of pyridine was added acetic anhydride (1 mL) and 4-(dimethylamino)-pyridine (50 mg, 0.41 mmol). The resulting yellow suspension was stirred at 23 °C for 48 h. The mixture was poured into 50 mL of 10% HCl and the insoluble yellow solid was filtered, washed with water, and dried to afford 5,5′-di(acetyloxy)-2,2′-diphenyl[7,7′-bi-4*H*-1-benzopyran]-4,4′-dione as a tan solid (151 mg, 99%): mp 314–316 °C ($CHCl_3$–EtOAc 2:1); IR (KBr) 1745, 1630, 1610, 1595, 1345, 1190 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.93–7.89 (m, 4 H), 7.78 (d, J = 1.7 Hz, 2 H), 7.58–7.54 (m, 6 H), 7.34 (d, J = 1.7 Hz, 2 H), 6.72 (s, 2 H), 2.49 (s, 6 H); LRMS m/z 516 (M^+ − 42 1.1%), 474 (10%). Anal. Calcd for $C_{34}H_{22}O_8$: C, 73.11, H, 3.97. Found: C, 72.99; H, 4.06.

2-(1,3-Benzodioxol-5-yl)quinoline (**dubamine**, **10**): white solid; mp 93–94 °C (hexanes) [lit.[20b] mp 94–95 °C]; IR (KBr) 1660, 1500, 1490, 1255, 810, 795 cm^{-1}; ^{1}H NMR (360 MHz) δ 8.17 (d, J = 8.6 Hz, 1 H), 8.13 (d, J = 8.4 Hz, 1 H), 7.80 (br d, J = 8.1 Hz, 1 H), 7.79 (d, J = 8.6 Hz, 1 H), 7.74 (d, J = 1.7 Hz, 1 H), 7.71 (ddd, J = 8.4, 7.0, 1.5 Hz, 1 H), 7.66 (dd, J = 8.1, 1.7 Hz, 1 H), 7.50 (ddd, J = 8.1, 6.9, 1.2 Hz, 1 H), 6.96 (d, J = 8.1 Hz, 1 H), 6.05 (s, 2 H); ^{13}C NMR (68 MHz) δ 156.60, 148.90, 148.46, 148.36, 136.47, 134.29, 129.70, 129.49, 127.32, 127.06, 125.95, 121.72, 118.44, 108.40, 107.98, 101.27; LRMS m/z 249 (M^+ 100%).

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