syn-**5a**: ^{1}H NMR (200 MHz, DMSO-d_6, 393 K, vs DMSO) δ 3.30 (1 H, dd, J_{vic} = 3 Hz, J_{gem} = 17 Hz), 3.61 (1 H, dd, J_{vic} = 7.7 Hz, J_{gem} = 17 Hz), 3.86 (3 H, s), 5.12 (2 H, s), 5.65 (1 H, dd, J_{vic} = 7.7, 3 Hz), 5.68 (1 H, d, J = 3 Hz), 6.36 (1 H, d, J = 3 Hz), 6.9-7.9 (19 H, m); IR (NaCl, CH_2Cl_2) 1750, 1700, 1675, 1595 cm^{-1}; mass spectrum (NH_3, Cl) m/e 534.8 (M^+, 0.2), 387.3 (0.8); $[\alpha]^{25}_D$ +27.9° (c 1.02, CH_2Cl_2).

An improved ratio of anti/syn could be realized by running the reaction in THF with 1 equiv of AgOTf (25 °C) (Table II, entry 8).

(*S*)-4-Methoxyhomophenylalanine (25). To a stirred solution of **5a** (BOC = CBz, R = *p*-methoxyacetophenone; 100 mg, 0.18 mmol, 1 equiv) in THF (3 mL) and EtOH (3 mL) was added $PdCl_2$ (19 mg, 0.05 mmol, 0.3 equiv). The mixture was hydrogenated for 24 h at 40 psi H_2. The reaction mixture was then purged with N_2, filtered through Celite, concentrated, and triturated several times with Et_2O, leaving 48 mg (122%) of **25** (adjusted chemical yield 94%) as a pure white solid: % ee ≥98; ^{1}H NMR (200 MHz, D_2O + DCl, vs HOD) δ 1.9-2.1 (2 H, m), 2.4-2.6 (2 H, m), 3.61 (3 H, s), 3.87 (1 H, t, J = 6 Hz), 6.71 (2 H, d, J = 8.6 Hz), 7.06 (2 H, d, J = 8.6 Hz); $[\alpha]^{25}_D$ +34.6° (c 0.5, 1 N HCl).

(3*S*,5*S*,6*R*)-3-Chloro-4-(benzyloxycarbonyl)-5,6-diphenyl-2,3,5,6-tetrahydro-4*H*-1,4-oxazin-2-one (4a, X = Cl). To a stirred solution of (+)-(5*R*,6*S*)-**3** (105 mg, 0.271 mmol, 1.0 equiv) in CCl_4 (40 mL) at reflux temperature was added *tert*-butyl hypochlorite (294 mg, 2.71 mmol, 10 equiv). The reaction mixture was stirred for 2 h at reflux, cooled to room temperature, and evaporated under reduced pressure, leaving a solid white residue (120 mg; mp 182.5-185 °C dec) that was directly used without further purification: ^{1}H NMR (270 MHz, $CDCl_3$, vs $(CH_3)_4Si$) δ 4.7-5.4 (5 H, m), 6.2-7.7 (15 H, m); IR (NaCl, neat) 1770, 1730 cm^{-1}; mass spectrum (NH_3, Cl) m/e 388 (M^+ + 1 - Cl, 28), 387 (M^+ - Cl, 100).

Determination of Optical Purity of Amino Alcohols 2a and 2b. To a stirred solution of *dl-erythro*-α,β-diphenyl-β-hydroxyethylamine (**2**, racemic) (100 mg, 0.47 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added saturated $NaHCO_3$ (5 mL) and (-)-camphanic acid chloride (102 mg, 0.5 mmol, 1.1 equiv) in CH_2Cl_2 (5 mL). The mixture was allowed to stir at room temperature for 5 h and was thoroughly extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, concentrated, and separated by PTLC silica gel chromatography (eluted with 3:1 hexanes/EtOAc) to afford 118 mg (86%) of the corresponding camphanic acid amides as a 1:1 diastereomeric mixture that was used for ^{1}H NMR and HPLC comparison with those obtained individually from **2a** and **2b**.

From **2a**: yield 83%; mp 190-190.5 °C; $[\alpha]^{25}_D$ -5.88° (c 0.51, DMF); ^{1}H NMR (270 MHz, $CDCl_3$, vs $(CH_3)_4Si$) δ 0.75 (3 H, s), 1.00 (3 H, s), 1.08 (3 H, s), 1.63-1.96 (4 H, m), 2.39-2.48 (1 H, m), 2.60 (1 H, d), 5.04 (1 H, t), 5.26-5.31 (1 H, q), 7.07-7.26 (10 H, m); IR (KBr) 3500, 3320, 1770, 1665 cm^{-1}.

From **2b**: yield 83%; mp 246-247.5 °C; $[\alpha]^{25}_D$ +5.45° (c 0.44, DMF); ^{1}H NMR (270 MHz, $CDCl_3$, vs $(CH_3)_4Si$) δ 0.69 (3 H, s), 1.04 (3 H, s), 1.08 (3 H, s), 1.60-1.94 (4 H, m), 2.36-2.45 (1 H, m), 2.60 (1 H, t), 4.98 (1 H, d), 5.31-5.36 (1 H, m), 7.05-7.44 (10 H, m); IR (KBr) 3500, 3320, 1770, 1665 cm^{-1}.

Analyses of the crude samples obtained separately (above) were compared with the authentic diastereomeric mixture obtained from the racemate by ^{1}H NMR and by HPLC (silica gel, waters; eluted with 3:1 hexanes/EtOAc at 4.5 mL/min). The integration of the ^{1}H NMR absorptions of the CH_3 resonances and the HPLC peaks were taken and averaged. The amino alcohols melting at 143 °C were consistently determined to be >98% ee by this method.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Grant CHE 8412055) for financial support of this work. We also thank Dr. Manfred Weigele of Hoffman-LaRoche for providing an authentic sample of lactone **17**.

Note Added in Proof: Lactones **3a** and **3b** (both the CBz and *t*-BOC derivatives) as well as the racemic compounds are now commercially available (Aldrich). Amino alcohols **2a** and **2b** are also commercially available (Aldrich and Yamakawa Chemical Industry, Japan).

Palladium-Catalyzed Carbonylative Coupling of Aryl Triflates with Organostannanes

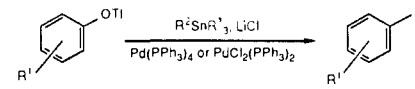
Antonio M. Echavarren† and J. K. Stille*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received August 28, 1987*

Abstract: The palladium-catalyzed coupling reaction of aryl triflates with organostannanes in the presence of carbon monoxide and lithium chloride takes place under relatively mild conditions to give good yields of aryl ketones. Dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) is unique in that it is the only one of several catalysts tried that gives consistently high yields of product. The coupling takes place even in the presence of reactive functional groups such as alcohol, aldehyde, and ester on the coupling partners. In the presence of strong electron-withdrawing groups on the tin partner, however, the coupling reaction is slow, leading primarily to decomposition of both the tin reagent and the triflate. Vinyl, acetylenic, alkyl, and aryl groups transfer to yield the corresponding ketones. Allylstannanes do not, however, give good yields of ketones; instead, direct coupling occurs without the intervention of carbon monoxide.

The palladium-catalyzed coupling reaction of aryl halides with organostannanes in the presence of carbon monoxide is a valuable synthetic procedure for the preparation of a variety of aryl ketones.[1-3] While the same ketones can be prepared by the palladium-catalyzed reaction of acid chlorides,[1] the utility of this route is limited by the availability of the corresponding carboxylic acids. Furthermore, since an acid chloride is not involved in the carbonylative cross coupling, functional groups capable of reaction with the acid chloride can be present in the aryl substrate.

We have recently reported that the palladium-catalyzed coupling of aryl triflates with organostannanes provides an efficient method for carbon–carbon bond formation on aromatic substrates[4,5] (eq 1). The cross coupling reaction proceeds under



(1)

neutral conditions with triphenylphosphine-coordinated palladium catalysts in either 1,4-dioxane or *N*,*N*-dimethylformamide. The

† Present address: Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006-Madrid, Spain.

(1) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(2) (a) Tanaka, M. *Tetrahedron Lett.* **1979**, 2601. (b) Bumagin, N. A.; Bumagina, I. G.; Nashin, A. N.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1981**, *261*, 1141; (*Engl. Transl.*) **1981**, *261*, 532.

(3) For the palladium-catalyzed carbonylative cross coupling of aryl halides with other carbon nucleophiles, see: (a) (organozincs): Tamaru, Y.; Ochiari, H.; Yamada, Y.; Yoshida, Z. *Tetrahedron Lett.* **1983**, *24*, 3869. (b) (alkylaluminums): Wakita, Y.; Yasunaga, T.; Kojima, M. *J. Organomet. Chem.* **1985**, *288*, 261. (c) (arylaluminums): Bumagin, N. A.; Ponomaryov, A. B.; Beletskaya, I. P. *Tetrahedron Lett.* **1985**, *26*, 4819. (d) (organoboranes): Wakita, Y.; Yasunaga, T.; Akita, M.; Kojima, M. *J. Organomet. Chem.* **1986**, *301*, C17.

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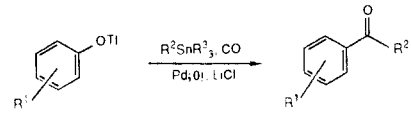
presence of LiCl is essential in order to assure the formation of the reactive arylchloropalladium(II) species,[6,7] which undergoes transmetalation with the organotin nucleophile.

Recently, the alkoxy- and aminocarbonylation of aryl triflates in the presence of palladium to yield esters and amides also has been reported.[8] These results suggest that aryl triflates, readily available from phenols,[9] could serve as substrates for the carbonylative cross coupling reaction with organotin reagents.

We report herein the scope and limitations of the palladium-catalyzed carbonylative coupling of aryl triflates with organostannanes (eq 2).

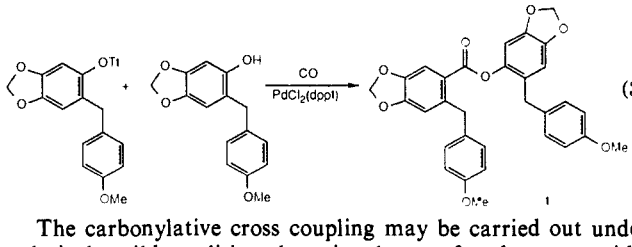


(2)

Results and Discussion

The palladium-catalyzed reaction of aryl triflates with organostannanes in the presence of an atmosphere of carbon monoxide gives good yields of aryl ketones (Table I). Our initial work on the cross-coupling of aryl triflates with organotin reagents[4] suggested that both tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, and dichlorobis(triphenylphosphine)palladium(II), $PdCl_2(PPh_3)_2$, could be catalysts for the carbonylative coupling reaction. However, as shown in entries 4b, 7b, 7c, 24b, and 24c, when triphenylphosphine-based catalysts were used, the coupling proceeded only sluggishly affording the corresponding ketones in modest to poor yields. The best results were obtained by using dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II), $PdCl_2(dppf)$,[10] as the catalyst. The unique efficacy of dppf as a ligand in this reaction is most intriguing, since other seemingly similar chelating phosphines failed to furnish the desired coupled products under the same reaction conditions (see entries 6b, 10c, and 25b). Particularly, the results with dichlorobis(diphenylphosphino)propanepalladium(II), $PdCl_2(dppp)$, are surprising, since this catalyst has been reported to be the catalyst of choice for the alkoxycarbonylation of aryl triflates.[8b,c]

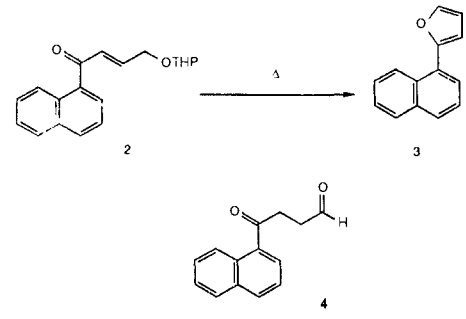
The carbonylative coupling of aryl triflates with organotin reagents is a quite general reaction. Vinyl, alkyl, aryl, and acetylenic groups on the tin partner all transfer in good yields. However, the presence of strong electron-withdrawing substituents on the stannane led to no coupling; instead, slow decomposition of the organostannane and the aryl triflate was observed (entries 8, 19, and 22). The result in entry 22 is in keeping with the previously observed cleavage of the oxygen–sulfur bond of the triflate under vigorous reaction conditions.[4] The ester **1** arises by palladium-catalyzed alkoxycarbonylation of the resulting free phenol with the aryl triflate (eq 3).



(3)

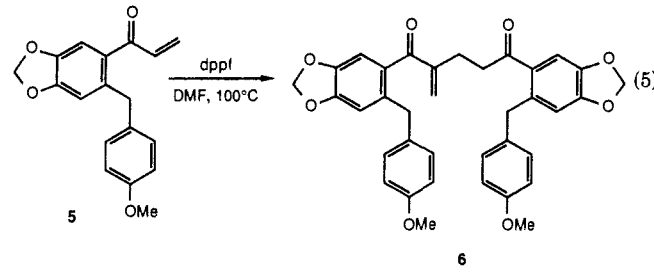
The carbonylative cross coupling may be carried out under relatively mild conditions by using 1 atm of carbon monoxide, although higher temperatures or carbon monoxide pressures were required to obtain satisfactory yields with the less reactive aryl and alkyl tin reagents.

In none of the carbonylative cross coupling reactions were products from further addition of the stannane to the aryl ketone product detected. The moderate yield in entry 24a can be attributed to the decomposition of the ketone **2** under the reaction conditions. In fact, prolonged heating of a concentrated solution of **2** in toluene afforded 1-α-naphthylfuran (**3**), presumably through the involvement of **4** as an intermediate. Aldehyde **4** was also observed in the crude reaction mixtures. A similar result was obtained on attempted bulb-to-bulb distillation of **2** (eq 4).



(4)

The high Michael acceptor ability of the vinyl ketone **5** is responsible for the formation of the dimeric byproduct **6** (entries 21a and 21b). Heating **5** with dppf in DMF at 100 °C led to an almost quantitative conversion into **6** (eq 5). No reaction was



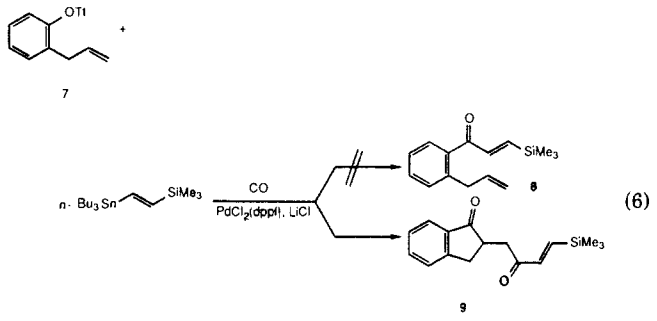
(5)

observed in the absence of phosphine. This result can be rationalized by a reaction pathway initiated by the conjugate addition of the phosphine to **5**, followed by a Michael reaction of the generated zwitterion with a second molecule of **5**.

A variety of functional groups in both the aryl triflate and the organotin are tolerated in the coupling reaction. Noteworthy is the fact that a free hydroxyl group on the organostannane does not interfere with the cross coupling reaction (entry 2). However, *o*-hydroxymethylphenyl triflate was converted to phthalide under the reaction conditions[11] (entry 17). Although both aldehyde and ester groups on the aryl triflate can be present, a nitro group is not tolerated (entry 9), a result that is not unexpected in light of the complications encountered in other palladium-catalyzed reactions of nitroaryl substrates.[8a,12]

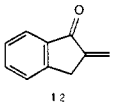
A particularly interesting transformation occurred with the *o*-allyltriflate **7** (entries 15a and 15b). Reaction of **7** under the standard carbonylative coupling conditions did not furnish any of the expected vinyl ketone **8**; instead, diketone **9** was obtained in 50–60% yield (eq 6). The structure of **9** follows unambiguously from its ^1H and ^{13}C NMR spectra. Particularly, this substance exhibits 68-MHz ^{13}C NMR signals for the carbonyl groups at 206.97 and 197.97, assigned to the five-membered ring ketone[13] and the vinyl ketone, respectively. This remarkable transformation, in which four carbon–carbon bonds are generated, may be envisioned to involve the migratory insertion of the alkene into the acylpalladium (acylmetalation)[14,15] to give the indanone inter-

(4) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.
(5) Recently the palladium-catalyzed reaction of several aryl fluoroalkenesulfonates with alkyl and acetylenic zinc reagents has been reported: Chen, G. Y.; He, Y. B. *Tetrahedron Lett.* **1987**, *28*, 2387.
(6) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.
(7) For the reaction of vinyl triflates with $Pt(PPh_3)_4$ and the role of added salts, see: Kowalski, M. H.; Stang, P. J. *Organometallics* **1986**, *5*, 2392.
(8) (a) Cacchi, S.; Ciattini, P. G.; Morera, E.; Otar, G. *Tetrahedron Lett.* **1986**, *27*, 3921. (b) Dolle, R. E.; Schmidt, S. J.; Kruse, L. I. *J. Chem. Soc., Chem. Commun.* **1987**, 904.
(9) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.
(10) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.
(11) Cowell, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4193.
(12) (a) Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 7175. (b) Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 452. (c) See, however: ref 2b and 3c.
(13) The ^{13}C resonance of the carbonyl group of indenone appears at δ 206.5 ($CDCl_3$): Hughes, D. W.; Nalliah, B. C.; Holland, H. L.; MacLean, D. B. *Can. J. Chem.* **1977**, *55*, 3304.

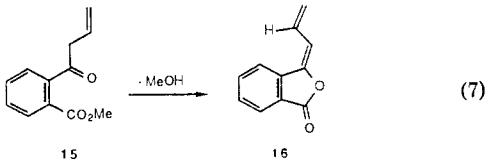


(6)

mediate **11** (Scheme I). The facility with which **11** undergoes carbon monoxide insertion is also remarkable, since none of the product of β-hydride elimination (e.g., **12**) was observed in the crude reaction mixtures. 2-Methylideneindanone (**12**)[15] was, however, one of the products of the carbonylative coupling of **7** with the less reactive allyltri-*n*-butyltin (vide infra).



Although the directly coupled products (without CO intervention) were not obtained with vinyl-, alkyl-, acetylenic-, or aryltin reagents, this was not the case in the cross coupling reaction with an allyl group. The coupling of *o*-methoxycarbonylphenyl triflate (**13**) with allyltri-*n*-butylstannane gave predominantly the directly coupled product **14** (entry 12). The primary product of carbonylative coupling, **15**, suffers lactonization to yield the rather unstable phthalide **16** (eq 7). The tentative assignment of the



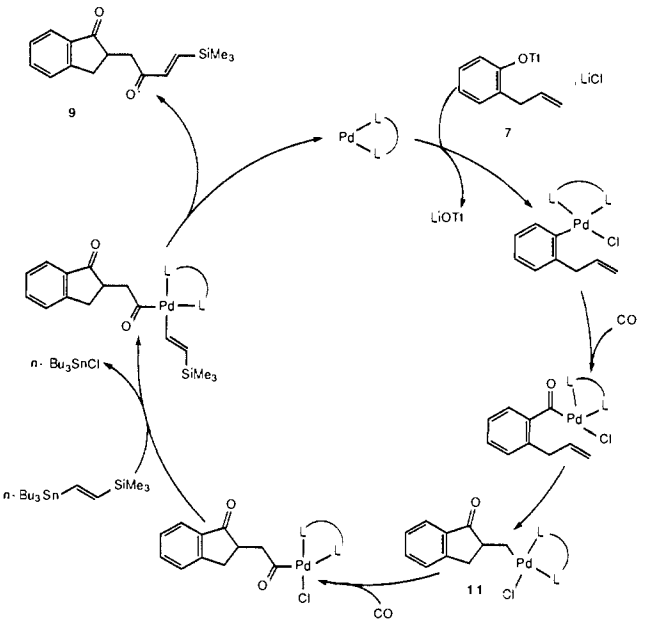
(7)

stereochemistry of **16** as *E* followed from the downfield shift of the 2′ olefinic proton at δ 6.96 (ddd, J = 17.1, 11.2, 10.3 Hz; $CDCl_3$ solution), as a result of its positioning within the deshielding region of the aromatic ring.[16,17]

Similarly, treatment of triflate **7** with the allyltin nucleophile gave *o*-diallylbenzene[18] as the major product (entry 16). In this example the carbonylated product suffers double-bond migration into conjugation with the ketone. Small amounts of 2-methylideneindanone (**12**) were also produced in the reaction, as a result of β-hydride elimination on intermediate **11** (see Scheme I). When the cross coupling reaction was conducted in the absence of carbon monoxide, diallylbenzene was obtained in 78% yield (see Experimental Section).

An additional feature of the reaction is worthy of further comment. The carbonylative cross coupling reaction of *p*-bromophenyl triflate (**17**) takes place selectively at the triflate site even in the absence of LiCl (entries 13 and 14). This is in contrast to the direct coupling reaction of aryl triflates with organostannanes, in which exclusive coupling through the carbon–halogen bond of the triflate could be accomplished by running the reaction in the absence of LiCl.[4] The reaction of **17** with *p*-methoxyphenyltri-*n*-butylstannane proceeds sluggishly to furnish, along with benzophenone **18**, the byproducts **19** and **20**, resulting

Scheme I



from the transfer of the alkyl groups of the stannane (entry 14a).

Although this result seems to indicate that the presence of LiCl was not required for the reaction to proceed at a normal rate, lower yields of cross coupled carbonylated products were obtained in the absence of LiCl (compare entries 10a and 10b).

The palladium-catalyzed reaction of the triflates of 2-tropolone with organostannanes in the presence of carbon monoxide was also briefly studied[19] (Table II). The cross coupling affords troponyl ketones—which are not readily available[20]—under neutral conditions at relatively low temperatures, in the presence of the $PdCl_2$(dppf) catalyst. When the less reactive aryltin reagent was used, the reaction required higher temperatures and led to direct coupling of both partners as a major side reaction (Table II, entry 3). Addition of LiCl was again required for the reaction to proceed smoothly (Table II, entry 2b).

Conclusions

Aryl triflates couple with organostannanes in the presence of carbon monoxide, lithium chlroide, and the dichloro[1,1′-bis-(diphenylphosphino)ferrocene]palladium(II) catalyst to afford a variety of aryl ketones. Many functional groups are tolerated in both coupling partners. However, the presence of strong electron-withdrawing groups on the organotin reagent led to slow decomposition of both the aryl triflate and the stannane, and no coupling was observed. Although transfer of vinyl, acetylenic, alkyl, and aryl groups on the organostannane affords the corresponding ketones, the coupling with an allylstannane leads to the selective formation of products of direct cross coupling reaction. The carbonylative cross coupling of troponyl triflate with organotin reagents provides a ready access to 2-tropone ketones.

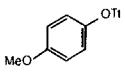
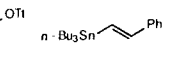
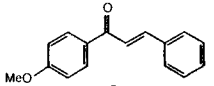
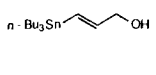
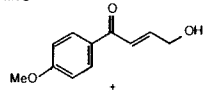
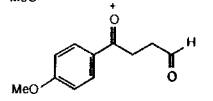
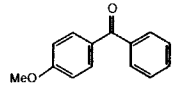
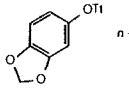
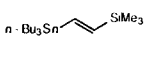
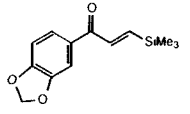
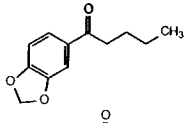
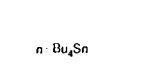
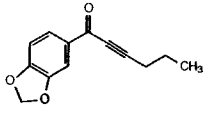
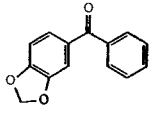
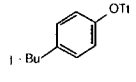
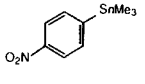
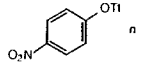
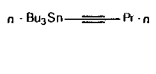
One of the remarkable features of this reaction is that phenols can be converted to aryl ketones by replacement of the phenolic OH. Thus the phenolic group can be utilized to direct substitution on the aromatic ring or even effect reactions characteristic of phenols (Kolbe, Claissen, Fries, Reimer-Tiemann, Gattermann, etc.) and then be utilized in a carbon–carbon bond-forming reaction which generates a deactivating, meta-directing substituent.

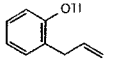
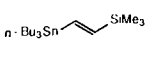
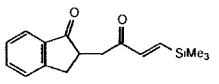
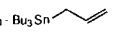
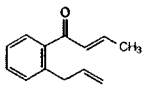
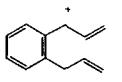
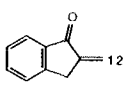
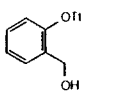
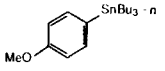
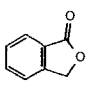
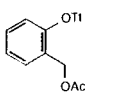
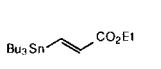
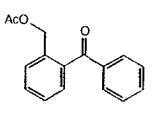
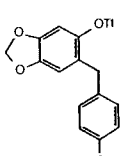
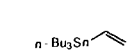
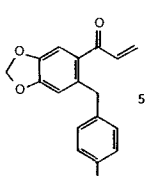
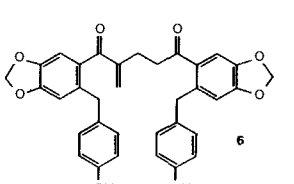
Experimental Section

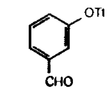
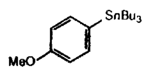
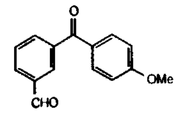
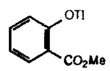
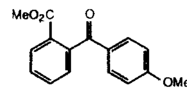
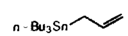
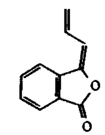
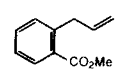
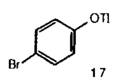
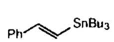
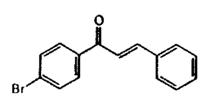
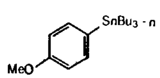
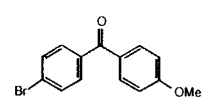
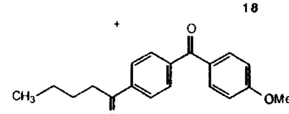
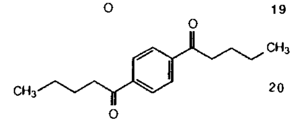
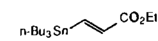
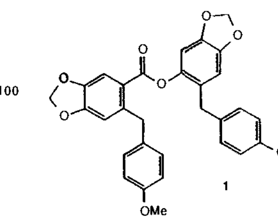
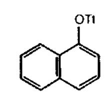
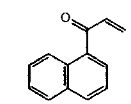
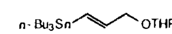
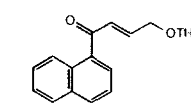
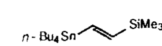
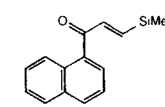
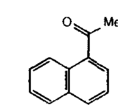
^1H NMR spectra were recorded on an IBM WP 200 (200 MHz) or an IBM 270 (270 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR were recorded on an IBM WP 270 (68 MHz) spectrometer with $CDCl_3$ as solvent and internal standard.

(14) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 391–392.
(15) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289.
(16) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1969; pp 94–98.
(17) For the stereochemistry of alkylidenephthalides, see: Gijbels, M. J. M.; Scheffer, J. J. C.; Svendsen, A. B. *Planta Med.* **1980** (supplement), 41; **1982**, *44*, 207.
(18) (a) Losev, I. P.; Smirnova, O. V.; Pfeifer, T. A. *Zh. Obshch. Khim.* **1951**, *21*, 668; (*Engl. Transl.*) **1951**, *21*, 737. (b) Tiecco, M.; Testaferri, L.; Tingoli, M.; Wenkert, E. *Tetrahedron* **1983**, *39*, 2289.
(19) For the Heck reaction of halotropones, see: Horino, H.; Inoue, N.; Asao, T. *Tetrahedron Lett.* **1981**, *22*, 741.
(20) For a synthesis of 2-troponyl ketones, see: Frank-Neumann, M.; Brion, F.; Martina, D. *Tetrahedron Lett.* **1978**, 5033.

Table I. Palladium-Catalyzed Carbonylative Coupling of Aryltriflates with Organostannanes[a]

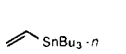
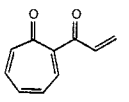
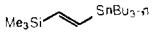
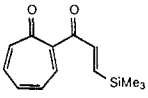
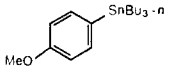
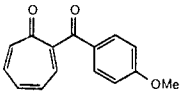
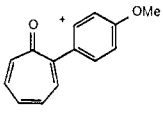
Entry	Triflate	Organostannane	Catalyst	T(°C)	CO Pressure (atm)	Reaction time (h)	Product(s)	Yield (%)
1			$PdCl_2(dppt)$	70	1	23		68
2				100		2		37
								20
3	$PhSnMe_3$					21		69
4a				75		5		96
4b			$Pd(PPh_3)_4$[b]	80	3.5	34		22
5		$n\text{-}Bu_4Sn$	$PdCl_2(dppt)$	110	1	44		65
6a				70		6		68
6b			$PdCl_2(dppp)$			6.5		<5[c]
7a		$PhSnMe_3$	$PdCl_2(dppf)$	90		7		88
7b			$Pd(Ph_3)_4$[b]	80	3.5	40		39
7c			$PdCl_2(PPh_3)_2$			9		27
8			$PdCl_2(dppf)$	95	1	11	no reaction[d]	
9				100		6	no reaction[e]	

Entry	Triflate	Organostannane	Catalyst	T(°C)	CO Pressure (atm)	Reaction time (h)	Product(s)	Yield (%)
15a	 7			50		72	 9	52
15b				70	3.5	15		60
16								16
								44
							 12	19
17				90	1	13		62
18				90		18	no reaction[d]	
19		$PhSnMe_3$		100		15		78
20a	 5			75		21	 5	67
							 6	5

10a				90		8		98
10b[i]								33
10c			$PdCl_2(dppp)$					<5[c]
11a	 13		$PdCl_2(dppf)$	95		14		35
11b				90	3 5	21		64
12				80		21	 16 +  14	ca 15; 45[h]
13a	 17			70	1	7		80
13b[j]								84
14a				95		27	 18 +  19  20	45; 17; 6
14b[l]				100	1	30	18	39[f]
20b				100	1	23	5 + 6	21; 44
21				95	1	100	 1	35[m]
22			$PdCl_2(dppf)$	90	1	2		84
23a				70	3.5	3		54
23b			$PdCl_2(PPh_2)_2$	60	1	5		36
23c			$PdCl_2PdCl(PPh_2)_2$		2	11		<5[c]
24a			$PdCl_2(dppf)$	70		4		72
24b			$PdCl_2(dppe)$	75		10		<5[c]
25		Me_4Sn	$PdCl_2(dppf)$	90	3 5	1 5		83

[a] Unless otherwise stated the carbonylations were carried out in DMF (ca. 0.2 M substrate) in the presence of 3.0 equiv of LiCl with 4% of the corresponding palladium catalyst. [b] PPh_3 (12%) was also added. [c] Product not observed in the ^1H NMR of the crude reaction mixture. [d] The triflate was recovered. [e] The triflate decomposed to unidentified products. [f] Reaction run in the absence of LiCl. [g] The phthalide was contaminated with starting material. [h] Product contained 10% of a 1:1 E/Z mixture of the conjugated isomers. [i] Several other minor products formed were not isolated. [j] 6% of catalyst was used. [k] Conversion: 58%. [l] Conversion: 71%. [m] Conversion: 64%.

Table II. Palladium-Catalyzed Carbonylative Coupling of Troponyltriflate[a]

Entry	Organostannane	T(°C)	Reaction time (h)	Product(s)	Yield %
1		23	19		50
2a			18		84
2b[b]					9
3		70	1		29
					23

[a] The reactions were carried out with CO (1 atm) in DMF in the presence of $PdCl_2$(dppf) (4%) and LiCl (3.0 equiv). [b] Reaction run in the absence of LiCl.

Infrared spectra were obtained on a Beckman 4250 spectrometer. Low-resolution mass spectra (LRMS) were obtained on a V.G. Micromass 16F spectrometer. High-resolution mass spectra (HRMS) were obtained from the Midwest Center for Mass Spectroscopy at the University of Nebraska. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Dimethylformamide (DMF), dichloromethane, and pyridine were distilled from calcium hydride and stored over activated 4Å 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 60F-254 (0.2 mm) (Merck). Column chromatographic purifications were performed with Woelm 230–400 mesh silica gel.

Palladium Catalyst. Tetrakis(triphenylphosphine)palladium(0) [Pd-$(PPh_3)_4$],[21] dichlorobis(triphenylphosphine)palladium(II) [$PdCl_2$-$(PPh_3)_2$],[22] dichloro[1,2-bis(diphenylphosphino)ethane]palladium(II) [$PdCl_2$(dppe)],[23] dichloro[1,3-bis(diphenylphosphino)propane]palladium(II) [$PdCl_2$(dppp)],[23] and dichloro[1,1′-bis(diphenylphosphino)ferocene]palladium(II) [$PdCl_2$(dppf)],[10] were prepared according to published procedures.

Organostannanes. The following organostannanes were prepared according to literature methods: (*E*)-β-tri-*n*-butylstyrylstannane,[24] (*E*)-1-(tri-*n*-butylstannyl)-1-propen-3-ol,[25] (*E*)-1-(trimethylsilyl)-2-(tri-*n*-butylstannyl)ethylene,[25] tri-*n*-butylethenylstannane,[27] (*E*)-1-(tri-*n*-butylstannyl)-1-propenyl 3-tetrahydropyranyl ether (7:1 mixture of *E* and *Z* isomers),[28] ethyl (*E*)-3-(tri-*n*-butylstannyl)propenoate,[24,25b] allyltri-*n*-butylstannane,[29] 1-(tri-*n*-butylstannyl)pentyne,[30] phenyltrimethylstannane,[31] tri-*n*-butyl(4-methoxyphenyl)stannane,[32] and trimethyl(4-nitrophenyl)stannane.[33] Tetramethyltin (Columbia) and tetrabutyltin (Alfa Products) were used as received.

Aryl Triflates. 4-Methoxyphenyl trifluoromethanesulfonate, 5-[(trifluoromethylsulfonyl)oxy]-1,3-benzodioxole, 4-nitrophenyl trifluoromethanesulfonate, 4-bromophenyl trifluoromethanesulfonate (**17**), 2-(2-propenyl)phenyl trifluoromethanesulfonate (**7**), and 1-naphthalenyl trifluoromethanesulfonate were prepared according to published procedures. The following triflates were prepared in an analogous manner. The phenols were either commercial products or were prepared according to literature methods.[34]

3-Formylphenyl trifluoromethanesulfonate (88%): colorless oil; bp (bulb-to-bulb) 50–51 °C (0.01 mmHg); IR (neat) 3080, 2840, 2730, 1705, 1585, 1480, 1450, 1420, 1245, 1230–1190, 1135, 1100, 950, 925, 830, 785 cm^{-1}; ^1H NMR (270 MHz) δ 10.05 (s, 1 H), 7.94 (dt, *J* = 7.5, 1.3 Hz, 1 H), 7.80 (dd, *J* = 2.4, 1.6 Hz, 1 H), 7.68 (t, *J* = 7.9 Hz, 1 H), 7.56 (ddd, *J* = 8.2, 2.6, 1.2 Hz, 1 H). Anal. Calcd for $C_8H_5F_3O_4S$: C, 37.80; H, 1.98. Found: C, 37.90; H, 2.03.

2-(Methoxycarbonyl)phenyl trifluoromethanesulfonate (13) (94%): colorless oil; bp (bulb-to-bulb) 70–72 °C (0.03 mmHg), lit.[35] 92 °C (0.2 mmHg); IR (neat) 2960, 1735, 1610, 1480, 1445, 1420, 1300, 1270, 1245, 1225–1190, 1135, 1070, 1035, 955, 885, 815, 770, 730, 685 cm^{-1}; ^1H NMR (270 MHz) δ 8.09 (dd, *J* = 7.8, 1.9 Hz, 1 H), 7.63 (td, *J* = 7.9, 1.9 Hz, 1 H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.31 (br d, *J* = 8.2 Hz, 1 H), 3.94 (s, 3 H).

5-[((Trifluoromethyl)sulfonyl)oxy]-6-(4-methoxyphenyl)methyl-1,3-benzodioxole (95%): colorless oil; bp (bulb-to-bulb) 113–114 °C (0.05 mmHg); IR (neat) 3000, 2950, 2900, 2830, 1610, 1505, 1480, 1415, 1300, 1260–1200, 1140, 1040, 930, 910, 880, 825 cm^{-1}; ^1H NMR (270 MHz) δ 7.08 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 6.75 (s, 1 H), 6.55 (s, 1 H), 5.96 (s, 2 H), 3.89 (s, 2 H), 3.77 (s, 3 H). Anal. Calcd for $C_{16}H_{13}F_3O_6S$: C, 49.23; H, 3.36. Found: C, 49.32; H, 3.36.

2-[((Trifluoromethyl)sulfonyl)oxy]-2,4,6-cycloheptatrienone (62%): white solid; mp 57–58 °C (hexanes–cyclohexane 1:1); IR (KBr) 1640, 1605, 1585, 1520, 1470, 1415, 1390, 1240, 1220, 1145, 1085, 1025, 940, 865, 830, 765, 730, 700, 590 cm^{-1}; ^1H NMR (270 MHz) δ 7.47–7.23 (m, 4 H), 7.09 (t, *J* = 10.2 Hz, 1 H); ^{13}C NMR (68 MHz) δ 177.55, 156.02, 140.58, 137.12, 136.00, 130.17, 128.12, 118.69 (q, $^1J(^{13}C-^{19}F)$ = 320.8 Hz). Anal. Calcd for $C_8H_5F_3O_4S$: C, 37.80; H, 1.98. Found: C, 37.94; H, 1.95.

2-(Hydroxymethyl)phenyl Trifluoromethanesulfonate. To a solution of 2-(methoxycarbonyl)phenyl trifluoromethanesulfonate (1.50 g, 5.28 mmol) in 7.5 mL of dichloromethane at −78 °C under Ar was slowly added diisobutylaluminum hydride (DIBAH) (12.7 mL of 1 M solution in hexanes, 12.7 mmol, 2.4 equiv). The mixture was stirred at −78 °C for 30 min, warmed up to 23 °C, and stirred at this temperature for 30 min. Excess MeOH was added to the reaction mixture to decompose the aluminum reagent. The mixture was filtered, and the filtrate was extracted with dichloromethane. The organic layer was washed with water (2×), dried (Na_2SO_4), and evaporated to give an oil. Chromatography (flash column, 5:1 hexanes–EtOAc) afforded the alcohol as an oil (1.24 g, 92%): bp (bulb-to-bulb) 70–72 °C (0.04 mmHg); IR (neat) 3580, 3420–3320, 1610, 1580, 1495, 1485, 1450, 1415, 1205, 1135, 1080, 1035, 880 cm^{-1}; ^1H NMR (200 MHz) δ 7.60–7.55 (m, 1 H), 7.42–7.32 (m, 2 H), 7.28–7.23 (m, 1 H), 4.75 (s, 2 H), 2.65 (br s, 1 H). Anal. Calcd for $C_8H_7F_3O_4S$: C, 37.50; H, 2.75. Found: C, 37.64; H, 2.81.

2-(Acetyloxymethyl)phenyl Trifluoromethanesulfonate. To a solution of 2-(hydroxymethyl)phenyl trifluoromethanesulfonate (814 mg, 3.18 mmol) in 2 mL of pyridine at 23 °C was added acetic anhydride (1.50 mL, 1.62 g, 15.90 mmol). The resulting solution was stirred at 23 °C for 20 h. The mixture was then treated with 2 mL of methanol and stirred at 25 °C for 2 h. The resulting mixture was partitioned between diethyl ether and water. The organic layer was washed with 10% HCl (2×), water, and a saturated sodium chloride solution. The solution was dried ($MgSO_4$) and concentrated to give pure acetate as an oil (900 mg, 95%): bp (bulb-to-bulb) 77–78 °C (0.06 mmHg); IR (neat) 1750, 1490, 1450, 1420, 1380, 1360, 1245–1200, 1140–1130, 1085, 1020, 880, 810, 745 cm^{-1}; ^1H NMR (200 MHz) δ 7.55–7.30 (m, 4 H), 5.19 (s, 2 H), 2.11 (s, 3 H). Anal. Calcd for $C_{10}H_9F_3O_5S$: C, 40.27; H, 3.04. Found: C, 40.38; H, 3.09.

Palladium-Catalyzed Carbonylative Coupling Reaction: General Procedure (Tables I and II). (*E*)-1-(4-Methoxyphenyl)-3-phenyl-2-propen-1-one (*p*-Methoxychalcone) (Table I, Entry 1). To a solution of 4-methoxyphenyl triflate (390 mg, 1.52 mmol) in 7 mL of *N*,*N*-dimethylformamide were added (*E*)-β-tri-*n*-butylstyrylstannane (645 mg, 1.64 mmol), LiCl (200 mg, 4.72 mmol), $PdCl_2$ (dppf) (45 mg, 0.06

(21) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(22) (a) Itatani, H.; Bailar, J. C., Jr. *J. Am. Oil Chemists' Soc.* **1967**, *44*, 147. (b) Tayim, H. A.; Bouldoukian, A.; Award, F. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3799.
(23) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.
(24) Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285.
(25) (a) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851. (b) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813.
(26) Cunico, R. F.; Clayton, F. J. *J. Org. Chem.* **1976**, *41*, 1480.
(27) Seyferth, D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1957**, *79*, 515.
(28) Corey, E. J.; Wollenberg, R. H. *J. Org. Chem.* **1975**, *40*, 2265.
(29) Jones, W. J.; Davies, W. C.; Bowden, S. T.; Edwards, C.; Davis, V. E.; Thomas, L. H. *J. Chem. Soc.* **1974**, 1446.
(30) Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6417.
(31) Eaborn, C.; Waters, J. A. *J. Chem. Soc.* **1962**, 1131.
(32) Wardell, J. L.; Ahmed, S. *J. Organomet. Chem.* **1974**, *78*, 395.
(33) (a) Bumagin, N. A.; Bumagina, I. G.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1984**, *274*, 1103; (*Engl. Transl.*) **1984**, *274*, 653. (b) Kashin, A. N.; Bumagina, I. G.; Bumagin, N. A.; Bakunin, V. N.; Beletskaya, I. P. *Zh. Org. Khim.* **1981**, *17*, 905; (*Engl. Transl.*) **1981**, *17*, 789.
(34) 5-Hydroxy-6-(4-methoxyphenyl)methyl-1,3-benzodioxole: Jurd, L.; Fye, R. L.; Morgan, J., Jr. *J. Agric. Food Chem.* **1979**, *27*, 1007.
(35) Beyl, V.; Niederprüm, H.; Voss, P. *Liebigs Ann. Chem.* **1970**, *731*, 58.

mmol), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol, and 4Å molecular sieves (100 mg). The resulting mixture was heated at 70 °C under CO (1 atm). After 23 h the reaction was cooled to room temperature, diluted with diethyl ether, and filtered. The filtrate was washed with water (3×) and a saturated sodium chloride solution. The solution was dried ($MgSO_4$) and concentrated. Chromatography (flash column, 10:1 hexanes–EtOAc) afforded *p*-methoxychalcone as a white solid (246 mg, 68%): mp 105–106 °C (20:1 hexanes–EtOAc), lit.[36] 106–107 °C; IR (KBr) 1650, 1600, 1560, 1430, 1325, 1250, 1175, 1020, 960, 815, 745, 680 cm^{-1}; ^1H NMR (270 MHz) δ 8.03 (d, J = 8.9 Hz, 2 H), 7.79 (d, J = 15.7 Hz, 1 H), 7.63–7.59 (m, 2 H), 7.53 (d, J = 15.7 Hz, 1 H), 7.39–7.36 (m, 3 H), 6.94 (d, J = 8.8 Hz, 2 H), 3.82 (s, 3 H).

When higher carbon monoxide pressures were used, the reaction was carried out in a Fisher-Porter tube.

Mixtures of hexanes–EtOAc were used as eluents in the following ratios: 35:1 (entry 12, Table I), 30:1 (entries 3, 4, 5, and 24, Table I), 20:1 (entries 6, 7, 13, 14, 15, 16, and 22, Table I), 10:1 (entries 10, 11, 19, 21, 23, and 25, Table I), 4:1 (entry 20, Table I), 3:1 (entries 1–3, Table II).

The following compounds were prepared according to the general procedure:

4-(4-Methoxyphenyl)-4-oxobutanal (Table I, entry 2): viscous oil; crystallizes at 0 °C; IR (neat) 2900, 2840, 2720, 1720, 1675, 1600, 1585, 1510, 1415, 1360, 1305, 1260, 1240, 1165, 1020, 975, 825 cm^{-1}; ^1H NMR (270 MHz) δ 9.90 (s, 1 H), 7.97 (d, J = 8.9 Hz, 2 H), 6.94 (d, J = 8.9 Hz, 2 H), 3.87 (s, 3 H), 3.28 (t, J = 6.3 Hz, 2 H), 2.91 (t, J = 6.3 Hz, 2 H); ^{13}C NMR (68 MHz) δ 200.35, 196.21, 163.81, 130.31, 129.88, 113.90, 55.42, 37.79, 30.76. HRMS calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0783. Eluting with EtOAc afforded a second fraction, **(*E*)-4-Hydroxy-1-(4-methoxyphenyl)-2-buten-1-one**: viscous oil; decomposes on attempted distillation; IR (neat) 3440–3420, 2930, 2840, 1665, 1620, 1595, 1570, 1510, 1420, 1260, 1170, 1120, 800 cm^{-1}; ^1H NMR (270 MHz) δ 7.97 (d, J = 8.8 Hz, 2 H), 7.23 (dt, J = 15.4, 1.6 Hz, 1 H), 7.10 (dt, J = 15.3, 3.4 Hz, 1 H), 6.92 (d, J = 8.8 Hz, 2 H), 4.45 (dd, J = 3.3, 1.7 Hz, 2 H), 3.86 (d, 3 H), 2.86 (br s, 1 H); ^{13}C NMR (68 MHz) δ 188.97, 163.51, 146.27, 130.89, 130.59, 130.26, 113.80, 62.01, 55.36. HRMS calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0785.

4-Methoxybenzophenone (entry 3): white solid; mp 59–60 °C (hexanes); lit.[37] 61–62 °C; bp (bulb-to-bulb) 97–98 °C (0.15 mmHg); IR (KBr) 1640, 1590, 1435, 1310, 1270, 1250, 1010, 830, 780, 725, 680 cm^{-1}; ^1H NMR (270 MHz) δ 7.81 (d, J = 8.8 Hz, 2 H), 7.75–7.72 (m, 2 H), 7.56–7.41 (m, 3 H), 6.94 (d, J = 8.8 Hz, 2 H), 3.84 (s, 3 H).

(*E*)-1-(1,3-Benzodioxol-5-yl)-3-trimethylsilyl-2-propen-1-one (entry 4): colorless oil; bp (bulb-to-bulb) 90–91 °C (0.03 mmHg); IR (neat) 2960, 1660, 1605, 1505, 1490, 1445, 1250, 1035, 860, 840 cm^{-1}; ^1H NMR (270 MHz) δ 7.58 (dd, J = 8.1, 1.7 Hz, 1 H), 7.46 (d, J = 1.7 Hz, 1 H), AB system (δ_A = 7.28, δ_B = 7.23, J_{AB} = 18.6 Hz), 6.87 (d, J = 8.2 Hz, 1 H), 6.05 (s, 2 H), 0.19 (s, 9 H); ^{13}C NMR (68 MHz) δ 188.22, 151.68, 148.47, 148.25, 147.90, 132.40, 124.94, 108.67, 107.82, 101.74, 1.77. Anal. Calcd for $C_{13}H_{16}O_3Si$: C, 62.87; H, 6.49. Found: C, 62.84; H, 6.52.

1-(1,3-Benzodioxol-5-yl)-1-pentanone (entry 5): colorless oil, solidifies on standing at 0 °C as white crystals; mp 42–44 °C, lit.[38] 47 °C; bp (bulb-to-bulb) 83–84 °C (0.2 mmHg); IR (melt) 2960, 2930, 2870, 1680, 1615, 1605, 1505, 1485, 1440, 1255–1235, 1030, 930, 800 cm^{-1}; ^1H NMR (270 MHz) δ 7.55 (dd, J = 8.2, 1.7 Hz, 1 H), 7.43 (d, J = 1.7 Hz, 1 H), 6.83 (d, J = 8.2 Hz, 1 H), 6.03 (s, 2 H), 2.83 (t, J = 7.5 Hz, 2 H), 1.70 (quintet, J = 7.5 Hz, 2 H), 1.38 (sextet, J = 7.4 Hz, 2 H), 0.94 (t, J = 7.3 Hz, 3 H).

1-(1,3-Benzodioxol-5-yl)-2-hexyn-1-one (entry 6): colorless oil, solidifies on standing at −25 °C as white crystals; mp 34–35 °C (hexanes); IR (melt) 2960, 2200, 1640, 1600, 1500, 1485, 1445, 1360, 1280, 1260, 1035, 930, 740 cm^{-1}; ^1H NMR (270 MHz) δ 7.78 (dd, J = 8.1, 1.7 Hz, 1 H), 7.51 (d, J = 1.7 Hz, 1 H), 6.85 (d, J = 8.2 Hz, 1 H), 6.05 (s, 2 H), 2.46 (t, J = 7.0 Hz, 2 H), 1.69 (sextet, J = 7.2 Hz, 2 H), 1.07 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (68 MHz) δ 175.87, 152.45, 147.99, 132.27, 126.51, 108.18, 107.64, 101.84, 95.27, 79.65, 21.23, 20.88, 17.43. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.05; H, 5.61.

5-Benzoyl-1,3-benzodioxole (entry 7): colorless oil; bp (bulb-to-bulb) 116–117 °C (0.2 mmHg); IR (neat) 1655, 1600, 1500, 1485, 1445, 1280, 1260, 1035 cm^{-1}; ^1H NMR (270 MHz) δ 7.75–7.71 (m, 2 H), 7.57–7.51 (m, 1 H), 7.48–7.41 (m, 2 H), 7.37–7.34 (m, 2 H), 6.83 (d, J = 8.7 Hz, 1 H), 6.04 (s, 2 H); ^{13}C NMR (68 MHz) δ 194.71, 151.43, 147.93, 138.27, 132.05, 131.76, 129.50, 128.07, 126.58, 109.80, 107.60, 101.74. Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.36; H, 4.50.

2-(4-Methoxybenzoyl)benzaldehyde (entry 10): white solid; mp 63–64 °C (10:1 hexanes–EtOAc); IR (KBr) 1700, 1690, 1645, 1595, 1505, 1320, 1260, 1170, 1155, 835, 745, 695, 590 cm^{-1}; ^1H NMR (270 MHz) δ 10.07 (s, 1 H), 8.22 (t, J = 1.6 Hz, 1 H), 8.08 (dt, J = 7.6, 1.4 Hz, 1 H), 8.01 (dt, J = 7.7, 1.5 Hz, 1 H), 7.81 (d, J = 8.8 Hz, 2 H), 7.66 (t, J = 7.6 Hz, 1 H), 6.98 (d, J = 8.8 Hz, 2 H), 3.88 (s, 3 H); ^{13}C NMR (68 MHz) δ 193.54, 190.89, 163.52, 139.20, 136.34, 134.64, 132.17, 131.82, 130.40, 129.44, 128.84, 113.73, 55.27. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.80; H, 5.10.

Methyl 2-(4-methoxybenzoyl)benzoate (entry 11): colorless semisolid, solidifies on standing as white crystals; mp 77–78 °C (cyclohexane), lit.[39] 82–83 °C; bp (bulb-to-bulb) 124–125 °C (0.05 mmHg); IR (melt) 2950, 2835, 1725, 1660, 1595, 1570, 1505, 1430, 1310, 1280, 1250, 1170, 1145, 1130, 1075, 1020, 925, 835, 745, 705 cm^{-1}; ^1H NMR (270 MHz) δ 8.04 (dd, J = 7.7, 1.5 Hz, 1 H), 7.73 (d, J = 9.0 Hz, 2 H), 7.63 (td, J = 7.5, 1.5 Hz, 1 H), 7.55 (td, J = 7.5, 1.6 Hz, 1 H), 7.36 (dd, J = 7.6, 1.5 Hz, 1 H), 6.91 (d, J = 8.9 Hz, 2 H), 3.86 (s, 3 H), 3.65 (s, 3 H); ^{13}C NMR (68 MHz) δ 195.29, 166.32, 163.48, 142.00, 132.02, 131.46, 130.37, 129.93, 129.18, 127.62, 113.68, 55.29, 51.85 (one carbon signal overlaps). Saponification (LiOH, aqueous THF, 50 °C, 2.5 h) yielded the corresponding carboxylic acid (100%) as white crystals; mp 143–144 °C, lit.[39] 146–147 °C.

Methyl 2-(2-propenyl)benzoate (entry 12): colorless oil; bp (bulb-to-bulb) 55–57 °C (0.02 mmHg), lit.[40] 130–133 °C (18 mmHg); IR (neat) 3070, 2950, 1720, 1440, 1430, 1285, 1260, 1145, 1125, 1190, 1070, 905, 735, 700 cm^{-1}; ^1H NMR (270 MHz) δ 7.87 (dd, J = 8.1, 1.6 Hz, 1 H), 7.43 (td, J = 7.5, 1.6 Hz, 1 H), 7.29–7.23 (m, 2 H), 6.01 (ddt, J = 16.7, 10.3, 6.4 Hz, 1 H), 5.05–4.97 (m, 2 H), 3.88 (s, 3 H), 3.75 (dt, J = 6.4, 1.5 Hz, 2 H), the resonances corresponding to the methyl groups of the *E* and *Z* conjugated isomers (ca. 10%) were observed at δ 1.91 (dd, J = 6.6, 1.7 Hz, 3 H), and δ 1.72 (dd, J = 7.0, 1.8 Hz, 3 H); ^{13}C NMR (68 MHz) δ 167.94, 141.51, 137.34, 131.85, 130.82, 130.50, 129.86, 126.06, 115.43, 51.66, 38.27. A second fraction, **(*E*)-(2-propenylidene)phthalide (16)** (contaminated with the triflate starting material), was isolated as a colorless oil that readily polymerized on standing or on attempted distillation: ^1H NMR (270 MHz) δ 7.92–7.89 (m, 1 H), 7.70–7.64 (m, 2 H), 7.57–7.52 (m, 1 H), 6.96 (ddd, J = 17.1, 11.2, 10.3 Hz, 1 H), 6.20 (dt, J = 11.2, 1.0 Hz, 1 H), 5.51 (dt, J = 17.1, 1.2 Hz, 1 H), 5.36 (dt, J = 10.2, 1.0 Hz, 1 H).

(*E*)-1-(4-Bromophenyl)-3-phenyl-2-propen-1-one (entry 13): white solid; mp 101–102 °C (20:1 hexanes–EtOAc) lit.[41] 102–103 °C; IR (KBr) 1645, 1565, 1435, 1320, 1205, 1050, 1020, 990, 960, 845, 740, 670 cm^{-1}; ^1H NMR (270 MHz) δ 7.89 (d, J = 8.6 Hz, 2 H), 7.82 (d, J = 15.7, 1 H), 7.64 (overlapping d, J = 8.7 Hz, 2 H), 7.65–7.63 (m, 2 H), 7.47 (d, J = 15.9 Hz, 1 H), 7.43–7.41 (m, 3 H); ^{13}C NMR (68 MHz) δ 189.32, 145.29, 137.15, 134.91, 131.93, 130.65, 129.99, 129.00, 128.46, 127.79, 121.84; LRMS *m/z* 288 (46.7), 287 (99.6), 286 (M^+, 51.5), 285 (91.7), 207 (67.1).

4-Bromo-4′-methoxybenzophenone (18) (entry 14): white solid; mp 153–154 °C (EtOH), lit.[42] 154 °C; TLC (10:1 hexanes–EtOAc) R_f 0.24; IR (KBr) 1625, 1590, 1560, 1400, 1375, 1290, 1275, 1240, 1160, 1130, 1050, 1010, 910, 830, 810, 740 cm^{-1}; ^1H NMR (270 MHz) δ 7.79 (d, J = 8.8 Hz, 2 H), 7.61 (s, 4 H), 6.96 (d, J = 8.8 Hz, 2 H), 3.88 (s, 3 H). **1,1′-(1,4-Phenylene)bis-1-pentanone (20)**: white solid; mp 92–93 °C (1:1 EtOH–H_2O), lit.[43] 96–97 °C; TLC (hexanes–EtOAc, 10:1) R_f 0.38; IR (KBr) 2850, 1670, 1395, 1205 cm^{-1}; ^1H NMR (270 MHz) δ 8.02 (s, 4 H), 3.00 (t, J = 7.4 Hz, 4 H), 1.73 (quintet, J = 7.6 Hz, 4 H), 1.42 (sextet, J = 7.5 Hz, 4 H), 0.96 (t, J = 7.3 Hz, 6 H). **1-[4-(4-Methoxybenzoyl)]-1-pentanone (19)**: white solid; mp 155–157 °C (cyclohexane); TLC (10:1 hexanes–EtOAc) R_f 0.15; IR (KBr) 1675, 1635, 1600, 1300, 1285, 1250, 1170, 1020, 750 cm^{-1}; ^1H NMR (200 MHz) δ 8.05 (d, J = 8.2 Hz, 2 H), 7.82 (d, J = 8.8 Hz, 2 H), 7.80 (d, J = 8.2 Hz, 2 H), 6.97 (d, J = 8.7 Hz, 2 H), 3.89 (s, 3 H), 3.02 (t, J = 7.4 Hz, 2 H), 1.75 (quintet, J = 7.4 Hz, 2 H), 1.39 (sextet, J = 7.3 Hz, 2 H), 0.97 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (68 MHz) δ 199.67, 194.24, 163.73, 142.13, 139.58, 132.39, 129.93, 129.49, 127.75, 113.84, 55.43, 38.56, 26.47, 22.37, 13.64; LRMS *m/z* 296 (M^+, 20.6), 254 (33.4), 239 (78.1), 211 (18.0), 135 (100); HRMS calcd for $C_{19}H_{20}O_3$ 296.1412, found 296.1414.

(*E*)-2-(2-Oxo-4-trimethylsilyl-3-butenyl)-2,3-dihydro-1*H*-inden-1-one (9) (entry 15): colorless oil; bp (bulb-to-bulb) 110–112 °C (0.05 mmHg); IR (neat) 2960, 2920, 1710, 1675, 1610, 1465, 1250, 990, 855,

(36) Stockhausen, F.; Gattermann, L. *Chem. Ber.* **1882**, *25*, 3535.
(37) Rennie, E. H. *J. Chem. Soc.* **1882**, 220.
(38) Mameli, E.; Alagna, E. *Gazz. Chim. Ital.* **1906**, *36 I*, 126.
(39) Blicke, F. F.; Weinkauff, O. *J. Am. Chem. Soc.* **1932**, *54*, 330.
(40) Camaggi, C. M.; Leardini, R.; Zanirato, P. *J. Org. Chem.* **1977**, *42*, 1570.
(41) Ralls, J. O. *J. Am. Chem. Soc.* **1940**, *62*, 3485.
(42) Jones, B. *J. Chem. Soc.* **1936**, 1854.
(43) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329.

835, 740 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.76 (d, J = 7.7 Hz, 1 H), 7.58 (td, J = 7.4, 1.2 Hz, 1 H), 7.44 (d, J = 7.7 Hz, 1 H), 7.37 (t, J = 7.4 Hz, 1 H), 7.13 (d, J = 19.3 Hz, 1 H), 6.51 (d, J = 19.2 Hz, 1 H), 3.48 (dd, J = 17.2, 7.9 Hz, 1 H), 3.37 (dd, J = 17.7, 3.1 Hz, 1 H), 3.08 (dddd, J = 9.3, 7.7, 4.4, 3.0 Hz, 1 H), 2.88 (dd, J = 17.7, 9.2 Hz, 1 H), 2.76 (dd, J = 17.2, 4.4 Hz, 1 H), 0.15 (s, 9 H); ^{13}C NMR (68 MHz) δ 206.97, 197.61, 153.31, 147.06, 141.87, 136.52, 134.51, 127.22, 126.37, 123.73, 43.14, 40.61, 33.33, -2.00; LRMS m/z 272 (M$^+$, 11.2), 145 (100), 127 (36.3), 75 (62.7), 73 (87). Anal. Calcd for $C_{16}H_{20}O_2Si$: C, 70.54; H, 7.40. Found: C, 70.39; H, 7.40.

(*E*)-1-[2-(2-Propenyl)phenyl]-2-buten-1-one (entry 16): colorless oil; bp (bulb-to-bulb) 50–51 °C (0.02 mmHg); TLC (10:1 hexanes–EtOAc) R_f 0.31; IR (neat) 3070, 3020, 2970, 2910, 1660, 1650, 1620, 1440, 1290, 1215, 960, 910, 750 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.40–7.31 (m, 2 H), 7.28–7.23 (m, 2 H), 6.71 (dq, J = 15.7, 6.8 Hz, 1 H), 6.48 (dq, J = 15.7, 1.5 Hz, 1 H), 5.92 (ddt, J = 16.7, 10.3, 6.6 Hz, 1 H), 5.04–4.96 (m, 2 H), 3.48 (dt, J = 6.5, 1.5 Hz, 2 H), 1.93 (dd, J = 6.7, 1.5 Hz, 3 H); ^{13}C NMR (68 MHz) δ 196.28, 145.98, 139.24, 138.64, 137.12, 132.68, 130.32, 130.10, 127.93, 125.64, 115.76, 37.26, 18.03. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.93; H, 7.58. **2-Methylidene-2,3-dihydro-1*H*-inden-1-one (12)**: colorless oil; bp (bulb-to-bulb) 75–77 °C (0.1 mmHg); TLC (10:1 hexanes–EtOAc) R_f 0.20; IR (neat) 1710, 1645, 1610, 1470, 1400, 1325, 1295, 1265, 980, 735 cm^{-1}; ^{1}H NMR[44b] (270 MHz) δ 7.84 (d, J = 7.8 Hz, 1 H), 7.58 (td, J = 7.5, 1.1 Hz, 1 H), 7.47 (dd, J = 7.8, 0.9 Hz, 1 H), 7.38 (t, J = 7.5 Hz, 1 H), 6.35 (td, J = 3.1, 1.1 Hz, 1 H), 5.62 (td, J = 1.9, 1.0 Hz, 1 H), 3.75 (br s, 2 H). ***o*-Diallylbenzene** was synthesized by the following procedure: To a solution of *o*-(2-propenyl)phenyl triflate (1.080 g, 4.06 mmol) in 20 mL of DMF were added allyltri-*n*-butylstannane (1.40 g, 4.23 mmol), $PdCl_2$(dppf) (120 mg, 0.164 mmol), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol, and LiCl (516 mg, 12.17 mmol). The resulting mixture was heated at 90 °C under Ar. After 18 h the mixture was cooled to room temperature, diluted with water, filtered, and extracted with hexanes (3×). The organic extract was washed with water, a saturated potassium fluoride solution[45] (2×), water, and a saturated sodium chloride solution and dried ($MgSO_4$). Careful evaporation of the solvent (bath temperature < 23 °C) gave an oil. Chromatography (flash column, hexanes) afforded pure diallylbenzene as a colorless oil (498 mg, 78%): bp (bulb-to-bulb) 65–67 °C (14 mmHg); lit.[18a] 94 °C (12 mmHg); IR (neat) 3080, 3030, 2980, 2920, 2850, 1830 (weak), 1635, 1485, 1445, 1425, 1210, 985, 905, 740 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.15 (s, 4 H), 5.94 (ddt, J = 16.9, 10.3, 6.3 Hz, 2 H), 5.04 (partially overlapping dq, J = 10.2, 1.2 Hz, 2 H), 4.98 (partially overlapping dq, J = 17.0, 1.3 Hz, 2 H), 3.38 (dt, J = 6.3, 1.3 Hz, 4 H); ^{13}C NMR (68 MHz) δ 137.90, 137.05, 129.55, 126.44, 115.60, 37.03.

2-(Acetyloxy)methylbenzophenone (entry 19): colorless oil; bp (bulb-to-bulb) 104–105 °C (0.03 mmHg); lit.[46] 160 °C (0.1 mmHg); IR (neat) 1745, 1665, 1600, 1580, 1450, 1380, 1360, 1315, 1265, 1240–1215, 1025, 920, 755, 700, 690, 630 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.83–7.79 (m, 2 H), 7.62–7.38 (m, 7 H), 5.22 (s, 2 H), 1.88 (s, 3 H); ^{13}C NMR (68 MHz) δ 197.15, 169.99, 138.17, 137.48, 135.35, 133.01, 130.30, 129.93, 129.00, 128.68, 128.25, 127.32, 63.78, 20.25.

6-(Methoxyphenyl)methyl-1,3-benzodioxol-5-yl 6-(Methoxyphenyl)-methyl-1,3-benzodioxole-5-carboxylate (1) (entry 20): white crystals; mp 110–111 °C (EtOH); IR (KBr) 2900, 2820, 1725, 1605, 1500, 1475, 1370, 1200, 1135, 1090, 1025 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.50 (s, 1 H), 7.05 (d, J = 8.6 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 6.77 (d, J = 8.5 Hz, 2 H), 6.76 (d, J = 8.8 Hz, 2 H), 6.68 (s, 1 H), 6.56 (s, 1 H), 6.50 (s, 1 H), 5.97 (s, 2 H), 5.89 (s, 2 H), 4.26 (s, 2 H), 3.73 (s, 3 H), 3.71 (s, 3 H), 3.63 (s, 2 H); ^{13}C NMR (68 MHz) δ 164.81, 158.28, 158.19, 151.29, 146.35, 146.00, 145.52, 142.85, 140.85, 132.93, 132.00, 129.76, 129.68, 126.39, 121.60, 114.02, 111.44, 110.68, 109.51, 103.99, 101.71, 101.46, 55.12, 38.62, 35.05 (two carbon signals overlap). Anal. Calcd for $C_{31}H_{26}O_8$: C, 70.71; H, 4.98. Found: C, 70.60; H, 5.04.

6-(Methoxyphenyl)methyl-1,3-benzodioxol-5-yl-2-propen-1-one (5) (entry 21): colorless oil; bp (bulb-to-bulb) 152–154 °C (0.05 mmHg) (partially decomposes); IR (neat) 2910, 2840, 1660, 1610, 1500, 1480, 1400, 1365, 1300, 1250, 1170, 1070, 1030 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.04 (d, J = 8.6 Hz, 2 H), 6.94 (d, 1 H), 6.78 (d, J = 8.6 Hz, 2 H), 6.72 (dd, J = 17.4, 10.5 Hz, 1 H), 6.65 (s, 1 H), 6.11 (dd, J = 17.5, 1.3 Hz, 1 H), 5.93 (s, 2 H), 5.88 (dd, J = 10.6, 1.2 Hz, 1 H), 4.01 (s, 2 H), 3.73 (s, 3 H); ^{13}C NMR (68 MHz) δ 194.48, 158.20, 149.64, 145.55, 136.80, 136.63, 133.00, 131.63, 129.88, 129.15, 113.99, 111.09, 108.66, 101.42, 55.15, 37.78; LRMS m/z 296 (M$^+$, 21.4), 281 (5.7), 188 (18.7), 175 (15.7), 121 (100); HRMS calcd for $C_{18}H_{16}O_4$ 296.1048, found 296.1055. A second fraction was obtained eluting with 2.5:1 hexanes–EtOAc, **1,5-bis[(6-methoxyphenyl)methyl-1,3-benzodioxol-5-yl]-2-methylidene-1,5-pentadione (6)**, as a colorless semisolid: IR (KBr) 2900, 2830, 1675, 1650, 1605, 1505, 1480, 1360, 1240, 1030 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.11 (s, 1 H), 7.05 (d, J = 8.7 Hz, 2 H), 7.00 (d, J = 8.7 Hz, 2 H), 6.79 (d, J = 8.7 Hz, 2 H), 6.76 (d, J = 8.7 Hz, 2 H), 6.71 (s, 1 H), 6.64 (s, 1 H), 6.63 (s, 1 H), 5.96 (s, 2 H), 5.94 (s, 2 H), 5.81 (s, 1 H), 5.54 (s, 1 H), 4.11 (s, 2 H), 3.86 (s, 1 H), 3.75 (s, 3 H), 3.74 (s, 3 H), 2.96 (t, J = 7.3 Hz, 2 H), 2.67 (t, J = 7.3 Hz, 2 H); ^{13}C NMR (68 MHz) δ 201.31, 198.59, 158.15, 158.09, 149.79, 149.01, 148.47, 145.77, 145.22, 137.24, 135.47, 133.14, 132.80, 132.09, 131.75, 129.89, 128.60, 113.91, 111.49, 110.65, 108.76, 108.43, 101.51, 101.29, 55.12, 40.27, 38.18, 37.65, 26.38 (three carbon signals overlap); LRMS m/z 592 (M$^+$, 2.3), 574 (3.0); HRMS calcd for $C_{18}H_{16}O_4$ 592.2097, found 592.2085.

1-(1-Naphthalenyl)propen-1-one (entry 22): colorless oil; bp (bulb-to-bulb) 73–74 °C (0.02 mmHg), lit.[47] 128–130 °C (2 mmHg); IR (neat) 3050, 2960, 1670, 1610, 1510, 1405, 1230, 1100, 900, 790, 780 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.34 (dd, J = 7.8, 1.8 Hz, 1 H), 7.92 (d, J = 8.3 Hz, 1 H), 7.84 (dd, J = 7.1, 2.4 Hz, 1 H), 7.68 (dd, J = 7.1, 1.1 Hz, 1 H), 7.56–7.41 (m, 3 H), 6.91 (dd, J = 17.4, 10.6 Hz, 1 H), 6.22 (dd, J = 17.4, 1.2 Hz, 1 H), 5.98 (dd, J = 10.5, 1.2 Hz, 1 H); ^{13}C NMR (68 MHz) δ 195.48, 136.80, 135.74, 133.80, 131.82, 130.84, 130.50, 128.31, 127.59, 127.38, 126.34, 125.55, 124.22.

(*E*)-1-Naphthalenyl-4-tetrahydropyranyloxy-2-buten-1-one (entry 23): colorless oil; bp (bulb-to-bulb) 120–122 °C (0.02 mmHg) (decomposes to yield 2-(1-naphthalenyl)furan, see below); TLC (10:1 hexanes–EtOAc) R_f 0.12; IR (neat) 2940, 1675, 1650, 1625, 1510, 1285, 1130, 1035, 800, 785, 775 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.31 (br dd, J = 8.4, 1.9 Hz, 1 H), 7.93 (d, J = 8.2 Hz, 1 H), 7.85 (dd, J = 6.9, 2.6 Hz, 1 H), 7.70 (dd, J = 7.1, 1.1 Hz, 1 H), 7.56–7.43 (m, 3 H), 6.96 (dt, J = 15.8, 1.3 Hz, 1 H), 6.86 (dt, J = 15.7, 3.4 Hz, 1 H), 4.67 (t, J = 3.4 Hz, 1 H), 4.48 (ddd, J = 16.9, 3.2, 1.2 Hz, 1 H), 4.19 (ddd, J = 16.9, 3.6, 1.0 Hz, 1 H), 3.88–3.79 (m, 1 H), 3.54–3.49 (m, 1 H), 1.87–1.50 (m, 6 H); ^{13}C NMR (68 MHz) δ 194.99, 145.75, 136.49, 133.73, 131.40, 130.42, 129.67, 128.20, 127.15, 127.08, 126.20, 125.55, 124.21, 98.30, 65.76, 61.99, 30.30, 25.21, 19.11; LRMS m/z 296 (M$^+$, 1.3), 212 (13.6), 195 (7.7), 194 (14.8), 155 (30.2), 127 (44.6); HRMS calcd for $C_{19}H_{20}O_3$ 296.1412, found 296.1416. **2-(1-Naphthyl)furan**: colorless oil; lit. bp[48] 90–91 °C (0.02 mmHg); TLC (10:1 hexanes–EtOAc) R_f 0.60; IR (neat) 3050, 2920, 1510, 1495, 1390, 1150, 1010, 900, 790, 765, 735, 650 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.40 (dd, J = 6.6, 2.9 Hz, 1 H), 7.88–7.80 (m, 2 H), 7.71 (dd, J = 7.2, 1.2 Hz, 1 H), 7.60 (d, J = 1.9 Hz, 1 H), 7.54–7.46 (m, 3 H), 6.71 (d, J = 3.2 Hz, 1 H), 6.56 (d, J = 3.3, 1.9 Hz, 1 H); ^{13}C NMR (68 MHz) δ 153.67, 142.38, 134.10, 130.64, 128.77, 128.49, 128.57, 126.51, 126.21, 125.89, 125.64, 125.27, 111.32, 109.18.

(*E*)-1-Naphthelenyl-3-(trimethylsilyl)propen-1-one (entry 24): colorless oil; bp (bulb-to-bulb) 104–105 °C (0.05 mmHg); IR (neat) 2960, 1655, 1590, 1580, 1510, 1280, 1270, 1245, 1230, 1210, 1090, 990, 870–825, 795, 770 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.31 (br dd, J = 8.4, 2.0 Hz, 1 H), 7.94 (br d, J = 8.2 Hz, 1 H), 7.87–7.84 (m, 1 H), 7.69 (dd, J = 7.1, 1.2 Hz, 1 H), 7.54–7.44 (m, 3 H), 7.17 (d, J = 19.0 Hz, 1 H), 7.06 (d, J = 19.0 Hz, 1 H), 0.17 (s, 9 H); ^{13}C NMR (68 MHz) δ 195.04, 150.35, 140.53, 136.25, 133.84, 131.59, 130.67, 128.33, 127.41, 127.26, 126.32, 125.66, 124.28, 1.87. Anal. Calcd for $C_{16}H_{18}OSi$: C, 75.57; H, 7.13. Found: C, 75.47; H, 7.18.

1-Acetylnaphthalene (entry 25): colorless oil; bp 83–84 °C (0.05 mmHg); lit.[49] 145–146 °C (6 mmHg); IR (neat) 3050, 1680, 1600, 1580, 1510, 1360, 1285, 1245, 1200, 1130, 940, 800, 775 cm^{-1}; ^{1}H NMR (270 MHz) δ 8.76 (d, J = 8.6 Hz, 1 H), 7.86 (d, J = 8.2 Hz, 1 H), 7.80–7.74 (m, 2 H), 7.56–7.32 (m, 3 H), 2.62 (s, 3 H).

2-(1-Oxo-2-propenyl)-2,4,6-cycloheptatrienone (Table II, entry 1): white solid; mp 40–41 °C (1:1 hexanes–cyclohexane); IR (KBr) 1680, 1630, 1575, 1520, 1465, 1400, 1255, 980, 955, 780 cm^{-1}; ^{1}H NMR (270 MHz) δ 7.50 (dd, J = 7.2, 2.3 Hz, 1 H), 7.22–7.19 (m, 2 H), 7.15–7.11 (m, 2 H), 6.99 (dd, J = 17.2, 10.4 Hz, 1 H), 6.32 (dd, J = 17.3, 1.2 Hz, 1 H), 5.85 (dd, J = 10.3, 1.3 Hz, 1 H); ^{13}C NMR (68 MHz) 193.68, 185.81, 149.59, 143.32, 136.55, 135.83, 135.57, 134.71, 133.47, 128.02; HRMS calcd for $C_{10}H_8O_2$ 160.0524, found 160.0527.

2-[(*E*)-1-Oxo-3-trimethylsilyl-2-propenyl]-2,4,6-cycloheptatrienone (Table II, entry 2): pale yellow oil; bp (bulb-to-bulb) 104–105 °C (0.06 mmHg); IR (neat) 2960, 1770, 1630, 1590, 1520, 1460, 1245, 1210, 1170, 1135, 985, 860, 830, 775, 690 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.44–7.40 (m, 1 H), 7.22–7.10 (m, 4 H), 7.16 (partially overlapping d, J = 18.8 Hz, 1 H), 6.77 (d, J = 18.9 Hz, 1 H), 0.14 (s, 9 H); ^{13}C NMR (68 MHz) δ 190.09, 185.66, 150.19, 147.71, 143.10, 140.15, 136.20,

(44) (a) Mühlstädt, M.; Gensirch, H. *J. Prakt. Chem.* **1966**, *34*, 139. (b) Neusoroff, G. P.; Sternhell, S. *Aust. J. Chem.* **1972**, *25*, 1669.
(45) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *4*, 449.
(46) Pifferi, G.; Consonni, P., *Il. Farmaco-Ed. Sc.* **1968**, *23*, 949.
(47) Dannenberg, H.; Rahman, A. *Chem. Ber.* **1955**, *88*, 1405.
(48) Johnson, A. W. *J. Chem. Soc.* **1946**, 895.
(49) Blicke, F. F.; Maxwell, C. E. *J. Am. Chem. Soc.* **1939**, *61*, 1780.

135.72, 135.41, 133.44, -2.02; LRMS m/z 232 (M^+, 19.9), 217 (3.7), 189 (9.8), 159 (4.4), 105 (9.6); HRMS calcd for $C_{13}H_{16}O_2Si$ 232.0919, found 232.0917.

2-(4-Methoxybenzoyl)-2,4,6-cycloheptatrienone (Table II, entry 3): tan solid; mp 132-133 (EtOAc); TLC (2:1 hexanes-EtOAc) R_f 0.07; IR (KBr) 1665, 1600, 1570, 1420, 1255, 1240, 1170, 1020, 845 cm^{-1}; ^1H NMR (270 MHz) δ 7.84 (d, J = 8.8 Hz, 2 H), 7.27-7.17 (m, 3 H), 7.13-7.07 (m, 2 H), 6.91 (d, J = 9.0 Hz, 2 H), 3.86 (s, 3 H); ^{13}C NMR (68 MHz) δ 194.11, 185.69, 163.97, 151.83, 142.98, 135.80, 135.49, 134.30, 133.74, 131.63, 128.86, 113.90, 55.38. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.98; H, 5.03. Found: C, 74.78; H, 5.13. A second fraction, **2-(4-Methoxyphenyl)-2,4,6-cycloheptatrienone**, was isolated as small yellow crystals; mp 51-52 °C (1:1 hexanes-cyclohexane); TLC (2:1 hexanes-EtOAc) R_f 0.20; IR (KBr) 1620, 1600, 1565, 1495, 1455, 1250, 1170, 1025, 830, 780, 680 cm^{-1}; ^1H NMR (270 MHz) δ 7.48 (d, J = 8.9 Hz, 2 H)8 7.34 (d, J = 8.2 Hz, 1 H), 7.20-6.95 (m, 4 H), 6.92 (d, J = 8.7 Hz, 2 H), 3.82 (s, 3 H); ^{13}C NMR (68 MHz) δ 186.44, 160.09, 151.80, 141.69, 135.23, 134.65, 133.39, 132.38, 132.26, 130.62, 113.62, 55.24. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.03; H, 5.78.

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Chiral Discrimination in the Structures and Energetics of Association of Stereoisomeric Salts of Mandelic Acid with α-Phenethylamine, Ephedrine, and Pseudoephedrine

S. P. Zingg,[†] Edward M. Arnett,*[‡] Andrew T. McPhail,[‡] Aksel A. Bothner-By,[§] and W. R. Gilkerson[⊥]

Contribution from the Departments of Chemistry, Duke University, Durham, North Carolina 27706, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and University of South Carolina, Columbia, South Carolina 29208. *Received May 13, 1987. Revised Manuscript Received October 14, 1987*

Abstract: A carefully coordinated study of the relations between structure and energetics of association in the crystalline state and solution is reported here. Hydrogen-bonded ion pairs formed from reaction between the enantiomers of mandelic acid, α-phenethylamine, ephedrine, and pseudoephedrine have been studied in dimethyl sulfoxide, dioxane, and water and as solid salts. Single-crystal X-ray analysis, performed on four unique diastereomeric pairs of (±)-ephedrinium and (±)-pseudoephedrinium (±)-mandelates yielded details of the solid-state hydrogen-bonding schemes for all eight diastereomeric salts. ^1H NMR spectra (at 300 and 600 MHz) over a wide concentration range were determined and indicated a simple two-state equilibrium between ion pairs and free ions in dimethyl sulfoxide. The dissociation equilibria in dimethyl sulfoxide were examined more quantitatively by conductance and the results treated by the Fuoss-Justice, Fuoss-1977, and Onsager methods to yield calculated dissociation constants, equivalent conductances, and mean activity coefficients over a wide concentration range. Thermochemical properties determined by various techniques were (1) the heat of fusion by differential scanning calorimetry, (2) heats of solution of the crystalline salts to high dilution by isoperibolic batch calorimetry, and (3) heats of protonation and heats of dissociation from thermometric titration of solutions of mandelic acid with the bases. Extensive use was made of cross-chiral checks (e.g., R,R' vs S,S') to prove that observed chiral discrimination factors were real and accurate. Significant chiral discrimination factors were found for all properties of diastereomeric combinations. In several cases the largest differences in thermochemical properties and ^1H NMR spectra of diastereomeric pairs could be related reasonably to differences in hydrogen-bonding schemes in their crystals.

One of the most important unresolved problems in chemistry is the quantitative understanding and control of stereospecific reactions. This must ultimately come down to a detailed analysis of the strengths and geometrical requirements of the forces that attract and hold molecules together in complexes, aggregates, or transition states. Intermolecular forces range from weak non-directional dispersion forces to hydrogen bonds that have enough strength and direction to provide a good starting point for the understanding and prediction of stereochemistry.

The goal of this research was to explore the relationship between the geometry and strength of intermolecular interactions for a series of closely related chiral ion pairs in solution. Because the energetic differences are small and the geometry of molecular interactions is not easily defined, it is difficult to relate observed energy variations to changes in the shapes of the aggregates. One partial resolution of this problem lies in the use of chiral molecules and stereochemical methodology to study intermolecular interactions.[1-4]

The interactions of chiral molecules produce complexes that are related as enantiomers or as diastereomers. Comparison of

[†] The experimental work reported here was all done by S.P.Z. at the University of Pittsburgh and Duke and appears in her doctoral dissertation, University of Pittsburgh, 1982. Present address: Oak Ridge National Laboratories, Oak Ridge, TN.

[‡] Duke University.

[§] Carnegie-Mellon University.

[⊥] University of South Carolina.

(1) Pasteur, P. L. in lectures delivered before the Societe Chimique de Paris, Jan 20 and Feb 3, 1860. Cf.: Richardson, G. M. *The Foundations of Stereochemistry*; American Book: New York, NY, 1901.

(2) Fisher, E. *Chem. Ber.* **1899**, *32*, 3617.

(3) Craig, D. P.; Mellor, D. P. *Top. Curr. Chem.* **1976**, *63*, 1. Horeau, A. *Tetrahedron Lett.* **1969**, 3121. Wynberg, H.; Feringar, B. *Tetrahedron Lett.* **1976**, *32*, 2831. Fogassy, E.; Faigl, F.; Acs, M. *Tetrahedron Lett.* **1985**, *41*, 2841. Prelog, V.; Dumic, M. *Helv. Chim. Acta* **1986**, *69*, 5. Davidson, R. B.; Bradshaw, J. S.; Jones, B. A.; Dalley, N. K.; Christensen, J. J.; Izatt, R. M. *J. Org. Chem.* **1984**, *49*, 353.

(4) Craig, D. P.; Elsum, I. R. *Chem. Phys.* **1982**, *73*, 349. Schipper, P. E.; Harrowell, P. R. *J. Am. Chem. Soc.* **1983**, *105*, 723.

0002-7863/88/1510-1565$01.50/0