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A Stereoselective Synthesis of 1,2-Diarylethenyl Ethyl Ethers *via* the Carbocupration-Cross Coupling Sequence

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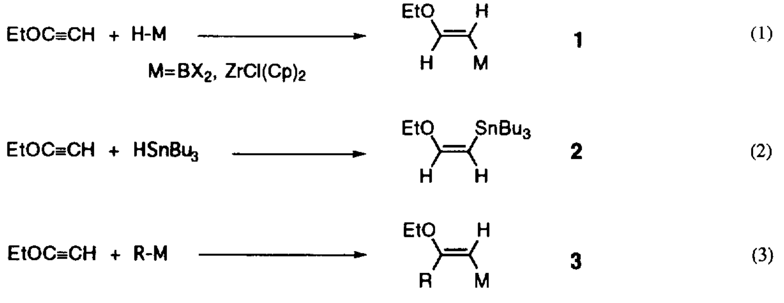
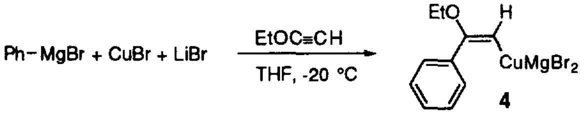
Abstract: *The synthesis of vinyl ethers [Ph(EtO)C=CHAr] was carried out by a sequence of carbocupration of ethoxyethyne with phenylcopper(I) followed by the palladium-catalyzed cross-coupling reaction of the resulting 2-ethoxyvinylcopper(I) complex with iodoarenes. The 2-ethoxyvinylcopper(I) species thus obtained were sufficiently stable to undergo the cross-coupling reaction at 0-20 °C in the presence of a catalytic amount of* $PdCl_2(dppf)$ *or* $Pd(PPh_3)_4$ *and 1 equivalent of* $ZnBr_2$*. The syntheses of 2-phenylbenzo[b]furan and 2-phenylindole demonstrated the utility of the present one-pot, two-step procedure for the synthesis of vinyl ethers.*

2-Alkoxy-1-alkenylmetal reagents are valuable precursors for the synthesis of 1-alkenyl ethers *via* the cross-coupling reaction with organic halides.[1-6] A various methods have been developed for the synthesis of 2-alkoxy-1-alkenylmetal reagents; however, the addition of metal hydrides to alkoxyalkynes can be the most convenient to stereo- and regioselectively obtain these reagents. The hydrometalation of ethoxyethyne with boranes or $ZrCl(Cp)_2H$ quantitatively provides (*E*)-2-ethoxyethenylborane[2,3] or -zirconium reagents[1] (Eq. 1). The hydrostannylation of ethoxyethyne, in contrast, predominantly produces the (*Z*)-derivative (**2**)[6] (Eq. 2). The hydroboration of thioalkynes or the thioboration of alkynes has been also studied for the synthesis of their thio analogs.[7] However, 2-alkoxy-1-alkenylmetal reagents such as **3** are not available by hydrometalation, and can be best obtained by the carbometalation reaction (Eq. 3).



We wish to report a one-pot, two-step procedure that allows the synthesis of stereo-defined arylated vinyl ethers. The method demonstrates the synthetic utility of two reactions: the addition of organocopper reagents to ethoxyalkyne to provide 2-ethoxy-1-alkenylcopper reagents[8,9] and their palladium-catalyzed cross-coupling reaction with iodoarenes,[10, 11] both of which were originally reported by Normant (Eqs. 4 and 5).

The addition of alkyl- or arylcopper reagents to alkynes is a general reaction to synthesize variously substituted vinylcopper(I) reagents.[8] The addition of the copper atom to 1-alkoxy-1-alkynes occurs preferentially at the carbon β to oxygen to give (*E*)-2-alkoxy-1-alkenylcopper(I) compounds (**4**, Eq. 4).



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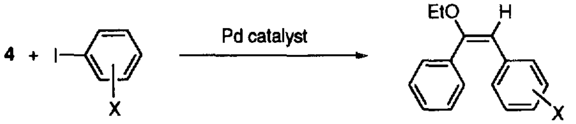


(5)

5a: X = 4-CO_2Me
5b: X = 2-CO_2Me
5c: X = 4-C≡N
5d: X= 2,3-CH=CHCH=CH-
5e: X = 4-NH_2
5f: X = 2-NH_2
5g: X = 4-OMOM (OCH_2OCH_3)
5h: X = 2-OMOM
5i: X = 2-OTBDMS ($OSiMe_2{}^tBu$)
5j: X = 2-$COCH_3$

1-Alkenylcopper species are stable at low temperature, but they have been reported to decompose to their dimer and metallic copper at room temperature.[12] Meanwhile, 2-alkoxy-1-alkenylcopper(I) compounds such as **4** undergo *trans* β-elimination of copper alkoxide at over - 40 °C.[8] It was also reported that the presence of zinc bromide accelerates the palladium-catalyzed cross-coupling reaction of vinylcopper(I) compounds.[10, 11] Indeed, the addition of metal halides greatly affected the thermal stability of **4** and its cross-coupling rate with aryl halides, as shown in Tables 1 and 2.

The vinylcopper(I) complex (**4**),[9] *in situ* prepared from ethoxyethyne and the phenylcopper (I) complex at - 20 °C, was stirred for 1 h at the temperatures shown in Table 1. The formation of **4** was estimated from the yields of acetophenone by quenching the mixture with aqueous hydrochloric acid. The copper(I) species thus obtained was rather stable even at 50 °C (Entry 1), but the complex was converted into a more unstable species, partially decomposing at higher than room temperature in the presence of $ZnBr_2$ (Entry 2). However, the addition of LiBr (1 equiv) did not affect the thermal stability of **4**.

The reaction conditions for the cross-coupling reaction of **4** with iodobenzene were examined using various palladium catalysts and in the absence or in the presence of the metal halides (Eq. 5 and Table 2). $Pd(PPh_3)_4$ resulted in a low yield in the absence of the additive (Entry 1), but the addition of $ZnBr_2$ greatly improved the rate of the cross-coupling (Entry 2). The action of $ZnBr_2$ has been ascribed to the equilibrium formation of 1-alkenylzinc bromide which participates in the catalytic cycle more efficiently than the corresponding copper species (Eq. 6).[10]

$$(RCH{=}CH)_2CuLi + ZnX_2 \rightleftharpoons RCH{=}CHZnX + RCH{=}CHCu{\bullet}LiX \quad (6)$$

However, such equilibrium may not be involved in the catalytic cycle because various other metal halides such as LiBr and LiCl were similarly effective in accelerating the cross-coupling reaction of **4** (Entries 3, and 4). Although the effects of added metal halides have not yet been fully elucidated at present, it may be reasonably speculated that ligation of the halo anion to either or both the copper(I)[13,14] and the palladium(II) metal occurs,[15] which may affect the rate of the oxidative addition, the transmetalation or the thermal stability of the alkenylcopper(I) species. However, large excess of metal halides should be avoided because the presence of two equivalents of metal halides reversely reduced the yields of the product. The use of a palladium complex having less than four triphenylphosphines gave relatively higher yields of the product with similar effects of the metal halides to that of $Pd(PPh_3)_4$ (entries 5 and 6). Finally, $PdCl_2(dppf)$ was recognized to be the most effective catalyst to achieve an 80% yield even in the absence of additional metal halides and a 95% yield in the presence of $ZnBr_2$ (Entry 8). Nickel catalysts such as $NiCl_2(PPh_3)_2$ and $NiCl_2(dppf)$ were less effective.

Table 1. Thermal Stability of **4** (Eq. 1)[a]

Entry	Additive	Yield of acetophenone (%)		
		0 °C	20 °C	50 °C
1	none	83	81	72
2	$ZnBr_2$	81	70	50

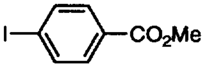
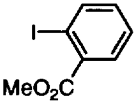
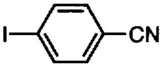
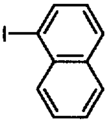
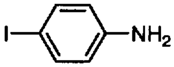
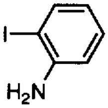
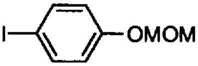
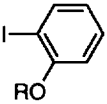
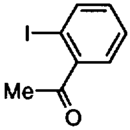
[a] The THF solution of **4** *in situ* prepared from PhCu•LiBr and EtOC≡CH was stirred for 1 h at the temperature indicated in the Table. The reaction mixture was quenched with aqueous HCl to give acetophenone.

Table 2. Reaction Conditions (Eq. 5)[a]

Entry	Catalyst	Additive (equivalents)	Yield / %[b]
1	$Pd(PPh_3)_4$	none	27
2	$Pd(PPh_3)_4$	$ZnBr_2$ (1)	69
3	$Pd(PPh_3)_4$	LiBr (1)	89
4	$Pd(PPh_3)_4$	LiCl (1)	86
5	$Pd(OAc)_2$/3 PPh_3	none	68
6	$Pd(OAc)_2$/3 PPh_3	$ZnBr_2$ (1)	78
7	$PdCl_2(dppf)$[c]	none	80
8	$PdCl_2(dppf)$[c]	$ZnBr_2$ (1)	95
9	$PdCl_2(dppf)$[c]	LiBr (1)	54
10	$PdCl_2(dppf)$[c]	LiCl (1)	78

[a] For the experimental procedure, see the text. [b] Isolated yields of 1-ethoxy-1,2-diphenyl-ethene based on iodobenzene. [c] 1,1'-Bis(diphenylphosphino)ferrocene.

Table 3. Synthesis of **5** *via* the Cross-Coupling Reaction with Iodoarenes (Eq. 5)

Entry	Iodoarene		Conditions	Product	Yield / %[a]
1			PdCl$_2$(dppf)/ZnBr$_2$ /-20→8 °C over 2 h	**5a**	73
2			PdCl$_2$(dppf)/ZnBr$_2$ /-20→10 °C over 2 h	**5b**	73
3			PdCl$_2$(dppf)/ZnBr$_2$ /-20→7 °C over 2 h	**5c**	69
4			PdCl$_2$(dppf)/ZnBr$_2$ /-20→10 °C over 2 h	**5d**	83
5			PdCl$_2$(dppf)/ZnBr$_2$ /room temp. for 16 h	**5e**	69
6			Pd(PPh$_3$)$_4$/ZnBr$_2$ /-20→5 °C over 2 h	**5f**	81
7			PdCl$_2$(dppf)/ZnBr$_2$ /room temp for 16 h	**5g**	58
8		R=MOM	PdCl$_2$(dppf) + Ph$_3$As /ZnBr$_2$/-20→5 °C over 2 h	**5h**	84
9		R=TBDMS	PdCl$_2$(dppf)/ZnBr$_2$ /room temp. for 16 h	**5i**	66
10			PdCl$_2$(dppf)/ZnBr$_2$ /-20→9 °C over 2 h	**5j**	63

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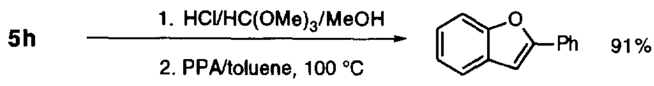
[a] Isolated yields were based on iodoarenes employed.

The results of the cross-coupling reaction of **4** with representative iodoarenes are summarized in Table 3. The cross-coupling reaction with *para*-substituted iodoarenes readily proceeded under mild conditions catalyzed by $PdCl_2$(dppf) and $ZnBr_2$ (Entries 1-5, 7, 9, and 10). When using iodoarenes having an electron-withdrawing group, the coupling was very fast and the reaction completed at lower than 10 °C (Entry 1). The electron-donating group decreased the rate of coupling due to its slow rate of oxidative addition to the palladium(0) complex (Entries 5 and 7). Due to the thermal instability of **4**, the reaction at room temperature overnight gave better results than the reaction at the higher temperatures.

The ligation of *ortho*-functionality to the palladium(II) metal center often greatly slows down the cross-coupling rate. Although, quite unexpectedly, 2-iodoaniline smoothly coupled with **4** (Entry 6), the reactions with 2-(methoxymethyl)iodobenzene apparently gave a higher yield in the presence of an additional triphenylarsine ligand (Entry 8). However, the effects of triphenylarsine[16] have not yet been studied for 2-(t-butyldimethylsilyloxy)iodobenzene or 2-iodoacetophenone (Entries 9 and 10), but it was not effective for the coupling with 2-iodoacetanilide (38%).

1,2-Diarylethenyl ethers (**5**) are a valuable precursor for aryl benzyl ketones by hydrolysis with acids or benzo-fused heteroaromatic compounds by condensation with *ortho*-amino or -hydroxy functionalities.[3,6] For example, the syntheses of 2-phenylindole and 2-phenylbenzo[b]furan were readily achieved by using the reactions shown in Entries 6 and 8 (Table 3). Thus, 2-phenylbenzo[b]furan was obtained in a 91% yield by the sequential treatment of **5h** with HCl in methanol in the presence of trimethyl orthoformate to give a cyclic acetal and demethoxylation with polyphosphoric acid (PPA) at 100 °C (Eq. 7).[3] Alternatively, the conversion of **5i** to the corresponding phenol with NH_4F in THF, followed by cyclization with the sequence of HCl/MeOH and PPA, provided an 80% of 2-phenylbenzo[b]furan. The treatment of **5f** with p-TsOH in refluxing benzene gave a quantitative yield of 2-phenylindole (Eq. 8).[6]



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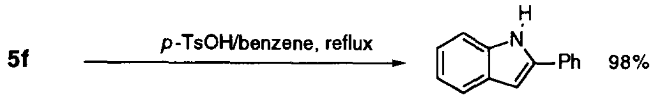

(8)

EXPERIMENTAL SECTION

All experiments were carried out under nitrogen atmosphere. THF was purified by distillation from diphenylketyl under nitrogen. Tetrakis(triphenylphosphine)palladium(0), palladium(II) acetate, and ethoxyethyne were commercially available. Dichloro[1,1'-(diphenylphosphino)ferrocene]palladium(II) ($PdCl_2$(dppf)) was prepared by the reported procedure.[17] LiBr, LiCl, and $ZnBr_2$ were dried in vacuo (10^{-2} mmHg) for 3 h at 150 °C and used as a THF solution. Commercially available CuBr was purified by the procedure reported in Inorganic Synthesis and dried in vacuo (10^{-2} mmHg) for 2 h at 100 °C.[18] ^{1}H-NMR spectra were measured on a JEOL EX-270 (270 MHz) using $CDCl_3$ and TMS as internal standards.

The Effects of $ZnBr_2$ on the Thermal Stability of 4 (Table 1): The flask was charged with CuBr (148 mg, 1.03 mmol) and flushed with nitrogen. THF (3 ml) and a THF solution of LiBr (3.0 M, 0.34 ml, 1.02 mmol) were added and stirred for 30 min at room temperature to give a clear solution of $LiCuBr_2$. A solution of PhMgBr (0.64 M in THF, 1.56 ml, 1.0 mmol) was then added at - 50 °C. After being stirred for 1 h, ethoxyethyne (72 mg, 1.03 mmol) was added at - 50 °C. The reaction mixture was stirred for 1 h at -20 °C to add the phenylcopper(I) complex to ethoxyethyne. A THF solution of LiBr (3.0 M, 0.33 ml, 1.0 mmol) or $ZnBr_2$ (1.0 M, 1.0 ml, 1.0 mmol) was added before slowly warming to the temperature indicated in Table 1. The stirring was continued for 1 h at that temperature. The reaction was quenched with aqueous HCl (1.0 M, 3.0 ml) at room temperature overnight to hydrolyze the vinyl ether to acetophenone. The yield of acetophenone was analyzed by GC (10% OV-17 on Uniport B, 2 m) using heptadecane as an internal standard.

The Reaction Conditions (Table 2): The flask was charged with CuBr (110 mg, 0.77 mmol) and flushed with nitrogen. To the flask were added THF (1.5 ml) and a solution of LiBr (3.0 M in THF, 0.77 mmol) and the mixture was stirred for 30 min to give a solution of $LiCuBr_2$. A solution of PhMgBr (0.63 M in THF, 1.23 ml, 0.77 mmol) was added at - 50 °C. After being stirred for 1 h at - 50 °C, ethoxyethyne (0.048 ml, 0.70 mmol) was then injected using a syringe. The mixture was stirred for 1 h to prepare a vinylcopper(I) complex (**4**). An additive ($ZnBr_2$, LiBr, or LiCl solution in THF, 0.77 mmol), iodobenzene (0.056 ml, 0.50 mmol), and a palladium catalyst ($Pd(PPh_3)_4$ (17 mg), $Pd(OAc)_2$ (4.0 mg) + PPh_3 (16 mg), or $PdCl_2(dppf)$ (11 mg)) were successively added to the flask at -20 °C. The bath temperature was then allowed to warm to 5-8 °C over 2 h. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl. Isolation of 1-ethoxy-1,2-diphenylethene was carried out by chromatography over silica gel with hexane/benzene=3/1. Isolated yields based on iodobenzene are summarized in Table 2.

Synthesis of 5 via the Cross-Coupling Reaction with Iodoarenes (Table 3): The general procedure for the preparation of vinyl ethers is illustrated by the preparation of 2-(2-aminophenyl)-1-ethoxy-1-phenylethene (**5f**). A dry 50 ml-flask equipped with a septum inlet, a magnetic stirring bar, and an oil bubbler connected to the nitrogen inlet was charged with CuBr (400 mg, 2.8 mmol) and flushed with nitrogen. THF (6 ml) and a solution of LiBr (3.0 M in THF, 0.90 ml, 2.7 mmol) were injected using syringes. The mixture was stirred for 1 h to give a clear solution of $LiCuBr_2$. At - 50 °C, a solution of PhMgBr in THF (0.66 M, 4.3 ml, 2.8 mmol) was added and the mixture was stirred for 1 h to give a solution of the phenylcopper(I) complex. Ethoxyethyne (195 mg, 2.8 mmol) was added at - 50 °C. The mixture was then slowly warmed to - 20 °C and stirred for 1 h at - 20 °C to give a solution of vinylcopper(I) complex (**4**). The solution of $ZnBr_2$ (2.8 mmol), $Pd(PPh_3)_4$ (88 mg, 0.080 mmol), and 2-iodoaniline (566 mg, 2.58 mmol) in 5 ml of THF was prepared in another flask and this mixture was added to the vinylcopper solution via a cannula using nitrogen pressure. The bath cooling was stopped and the temperature was then allowed to rise to 5-10 °C over 2 h. The reaction mixture was diluted with benzene/ether=1/1 (8 ml) and then treated with a saturated NH_4Cl (8 ml) for 30 min. The product was extracted with water, washed with brine, and finally dried over $MgSO_4$. Isolation by chromatography over silica gel with hexane/ethyl acetate=4/1 gave 516 mg (84%) of the ether (**5f**): ^1H NMR δ=1.44 (t, 3H, *J*=6.92 Hz), 3.71 (broad s, 2H), 4.04 (q, 2H, *J*=6.92 Hz), 5.63 (s, 1H), 6.52 (t, 1H, *J*=7.26 Hz), 6.64 (d, 1H, *J*=7.58 Hz), 6.75 (d, 1H, *J*=7.26 Hz), 6.96 (dd, 1H, *J*=7.58 and 7.29 Hz), 7.1-7.5 (m, 5H). IR (neat) 3450, 3360, 1740, 1635, 1615, 1230, 1115, 775, 750, 695 cm^{-1}. EIMS: 132 (67), 152 (4), 165

(17), 182 (17), 194 (100), 210 (10), 239 (43). HRMS (EI) Calcd for $C_{16}H_{17}ON$: 239.1310. Found: *m/z* 239.1325.

The following compounds were prepared by the above general procedure with a slight modification of the reaction conditions (The exact catalyst, the reaction temperature, or the reaction period are shown in Table 3).

5a: ^{1}H NMR δ=1.43 (t, 3H, *J*=6.93 Hz), 3.84 (s, 3H), 4.02 (q, 2H, *J*=6.93 Hz), 5.82 (s, 1H), 6.97 (d, 2H, *J*=8.40 Hz), 7.2-7.4 (m, 5H), 7.74 (d, 2H, *J*=8.40 Hz). IR (neat) 1720, 1280, 1120, 780, 700 cm^{-1}. HRMS (EI) Calcd for $C_{18}H_{18}O_3$: 282.1256. Found: *m/z* 282.1247.

5b: ^{1}H NMR δ=1.44 (t, 3H, *J*=6.93 Hz), 3.89 (s, 3H), 4.08 (q, 2H, *J*=6.93 Hz), 6.44 (s, 1H), 6.8-7.3 (m, 9H). IR (neat) 1730, 1640, 1610 cm^{-1}. EIMS: 105 (100), 163 (40), 165 (30), 194 (40), 222 (19), 237 (9), 253 (4), 282 (51). HRMS (EI) Calcd for $C_{18}H_{18}O_3$: 282.1255. Found: *m/z* 282.1237.

5c: ^{1}H NMR δ=1.44 (t, 3H, *J*=6.93 Hz), 4.03 (q, 2H, *J*=6.93 Hz), 5.77 (s, 1H), 6.97 (d, 2H, *J*=8.58 Hz), 7.3-7.4 (m, 7H). IR (neat) 2240, 1635, 1605, 775, 700 cm^{-1}. HRMS (EI) Calcd for $C_{17}H_{15}ON$: 249.1154. Found: *m/z* 249.1135.

5d: ^{1}H NMR δ=1.50 (t, 3H, *J*=6.93 Hz), 4.15 (q, 2H, *J*=6.93 Hz), 6.23 (s, 1H), 6.9-8.4 (m, 12H). IR (neat) 1640, 1605, 1580 cm^{-1}. HRMS (EI) Calcd for $C_{20}H_{18}O$: 274.1358. Found: *m/z* 274.1367.

5e: ^{1}H NMR δ=1.39 (t, 3H, *J*=6.93 Hz), 3.49 (broad s, 2H), 3.95 (q, 2H, *J*=6.93 Hz), 5.77 (s, 1H), 6.45 (d, 2H, *J*=8.41 Hz), 6.76 (d, 2H, *J*=8.41 Hz), 7.2-7.4 (m, 5H). IR (nujol) 3440, 3350, 1630, 1580, 775, 700 cm^{-1}. HRMS (EI) Calcd for $C_{16}H_{17}ON$: 239.1310. Found: *m/z* 239.1325.

5g: ^{1}H NMR δ=1.40 (t, 3H, *J*=6.93 Hz), 3.45 (s, 3H), 3.97 (q, 2H, *J*=6.93 Hz), 5.10 (s, 2H), 5.79 (s, 1H), 6.78 (d, 2H, *J*=8.90 Hz), 6.87 (d, 2 H, *J*=8.90 Hz), 7.2-7.4 (m, 5H). HRMS (EI) Calcd for $C_{18}H_{20}O_3$: 284.1412. Found: *m/z* 284.1409.

5h: ^{1}H NMR δ=1.43 (t, 3H, *J*=6.93 Hz), 3.49 (s, 3H), 4.04 (q, 2H, *J*=6.93 Hz), 5.16 (s, 2H), 5.93 (s, 1H), 7.0-7.4 (m, 9H). IR (neat) 1690, 1600, 1580, 775, 755, 700 cm^{-1}. HRMS (EI) Calcd for $C_{18}H_{20}O_3$: 284.1413. Found: *m/z* 284.1392.

5i: ^{1}H NMR δ=0.0 (s, 6H), 0.80 (s, 9H), 1.16 (t, 3H, *J*=6.93 Hz), 3.75 (q, 2H, *J*=6.93 Hz), 5.69 (s, 1H), 6.2-6.8 (m, 4H), 6.9-7.2 (m, 5H). IR (neat) 1640, 1605, 1580, 1260, 1210, 1125, 925 cm^{-1}. EIMS: 75 (36), 103 (100), 135 (4), 163 (3), 251 (3), 269 (12), 297 (2), 354 (16). HRMS (EI) Calcd for $C_{22}H_{30}O_2Si$: 354.2015. Found: *m/z* 354.2016.

5j: ^{1}H NMR δ=1.44 (t, 3H, *J*=6.92 Hz), 2.51 (s, 3H), 4.05 (q, 2H, 6.92 Hz), 6.22 (s, 1H), 6.8-7.8 (m, 9H). EIMS: 77 (39), 105 (100), 221 (39), 237 (6), 266 (13). IR (neat) 1685, 1630, 1600, 760, 695 cm^{-1}. HRMS (EI) Calcd for $C_{18}H_{18}O_2$: 266.1307. Found: *m/z* 266.1311.

The Synthesis 2-Phenylbenzo[b]furan. A mixture of (*E*)-1-ethoxy-2-(2-methoxymethoxyphenyl)-1-phenylethene (**5h**) (200 mg, 0.70 mmol), 6 M HCl in ether (1.5 ml), and trimethyl orthoformate (0.17 ml) in methanol (6 ml) was stirred for 1 h at room temperature and then for 3 h at refluxing temperature. The solvent and other volatiles were completely evaporated in vacuo (10^{-1} mmHg) to give an oily residue. The residue was dissolved in toluene (6 ml) and treated with polyphosphoric acid (10 ml) for 12 h at 100 °C. The product was extracted with benzene (ca. 30 ml), washed with brine and 10% Na_2CO_3, dried over $MgSO_4$, and finally isolated by chromatography over silica gel with hexane

/benzene=10/1 to give 124 mg (91%) of 2-phenylbenzo[b]furan: ^{1}H NMR δ=7.02 (d, 1H, J=0.99 Hz), 7.2-7.6 (m, 7H), 7.8-7.9 (m, 2H). IR (nujol) 1575, 1220, 1050, 1030, 930, 820, 775, 760, 700 cm^{-1}. EIMS: 97 (8), 115 (3), 139 (7), 165 (44), 194 (100). HRMS (EI) Calcd for $C_{14}H_{10}O$: 194.0731. Found: *m/z* 194.0709.

The Synthesis of 2-Phenylindole. A solution of (*E*)-2-(2-aminophenyl)-1-ethoxy-1-phenylethene (**5f**) (215 mg. 0.90 mmol) in benzene (5 ml) was treated with *p*-TsOH•H_2O (100 mg) overnight at the refluxing temperature. Chromatography over silica gel with benzene gave 170 mg (98%) of 2-phenylindole: ^{1}H NMR δ=6.82 (m, 1H), 7.1-7.4 (m, 6H), 7.6-7.7 (m, 3H), 8.26 (broad s, 1H). IR (nujor) 3440, 1350, 1300, 800, 765, 740, 690 cm^{-1}. EIMS: 96 (11), 139 (2), 165 (19), 193 (100). HRMS (EI) Calcd for $C_{14}H_{11}N$: 193.0892. Found: *m/z* 193.0918.

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