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SYNTHESIS OF ARENO[*e*]INDENES BY THE FLASH VACUUM PYROLYSIS OF 4-METHOXYSTYRYLARENES

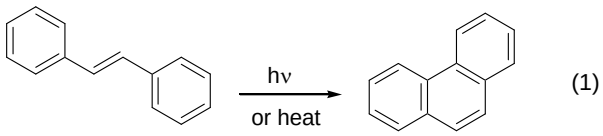
Li-Tse Chu, Pin-Chih Yu, Bo-Jian Wu, Ying-Chi Liao, and Chin-Hsing Chou*

Department of Chemistry and Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan, 804, R.O.C
ch-chou@mail.nsysu.edu.tw

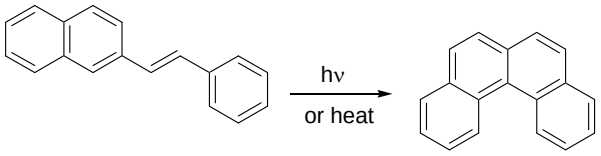
Abstract –Flash vacuum pyrolysis of 4-methoxystyrylarenes (**1b-e**) at 800 °C and ca. $1x10^{-2}$ Torr gave the corresponding areno[e]indenes (**3b-e**) as the major products and 4-hydroxystyrylarenes (**4b-e**) as the miner ones.

INTRODUCTION

Cyclization of stilbene-type compounds to form phenanthrenes is an important methodology used to prepare polycyclic aromatic hydrocarbons (PAH).[1,2] The cyclization reactions have been performed both under thermal and photochemical conditions (eqs. 1 and 2).[1-8]

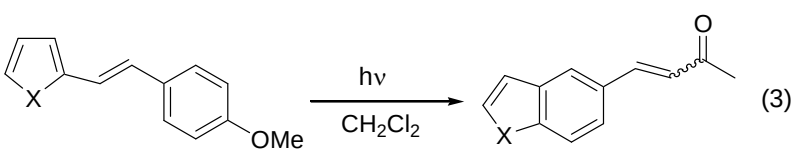


(1)



(2)

Recently, a novel photochemical rearrangement reaction of stilbene-type compounds has been reported by Ho and co-workers.[9-13] Direct photolysis of 2-(4-methoxystyryl)furan (**1a**) and 2-(4-methoxystyryl)thiophene (**1b**) in hydrated CH_2Cl_2 gave 5-(3-oxo-1-butenyl)benzo[*b*]furan (**2a**) and 5-(3-oxo-1-butenyl)benzo[*b*]thiophene (**2b**), respectively, as the major products (eq. 3).



1a, X = O
1b, X = S

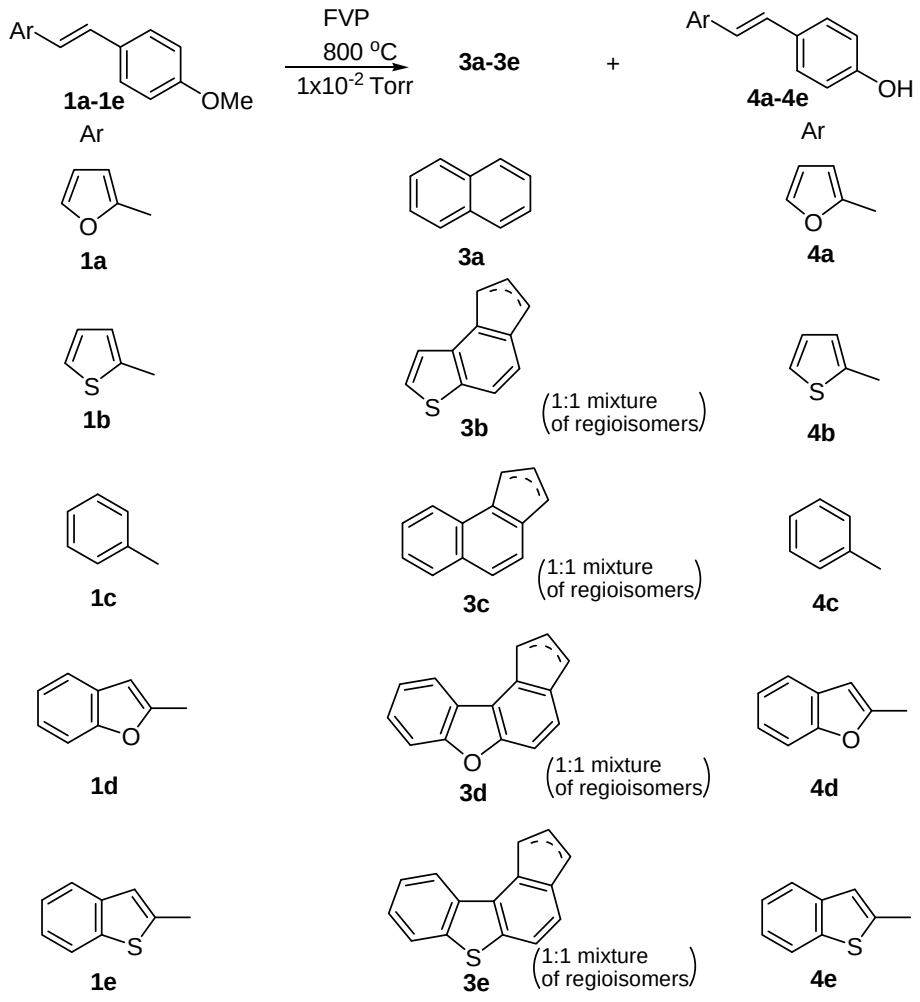
2a, X = O
2b, X = S

(3)

Such an unusual rearrangement reaction has stimulated our interest and prompted us to carried out pyrolytic study on 4-methoxystilbene-type compounds. We wish to present our results herein.

RESULTS AND DISCUSSION

Compounds (**1a**), (**1b**), 4-methoxystilbene (**1c**), 2-(4-methoxystyryl)benzo[*b*]furan (**1d**) and 2-(4-methoxystyryl)benzo[*b*]thiophene (**1e**) were prepared from 4-methoxybenzyl chloride and the corresponding aldehydes through a Wittig reaction[14] and existed mainly as *E*-form isomers. Flash vacuum pyrolysis (FVP) of **1a-1e** were performed using the pyrolysis set-up that has been previously described.[15] The pyrolysis temperature at 800 ^{o}C and ca. 1x10^{-2} Torr appeared to be the optimum reaction conditions for our study. FVP of **1a-1e** at temperatures lower than 800 ^{o}C would leave unreacted starting materials. With the exception of **1a**, which gave naphthalene (**3a**) as the major product, FVP of **1b-1e** gave areno[*e*]indenes (**3b-3e**) as the major products, all consist of 1:1 mixture of regioisomers, and 4-hydroxystyrylarenes (**4b-4e**) as the minor ones (Scheme 1). The yields for the pyrolysis products from FVP of **1a-1e** are listed in Table 1.

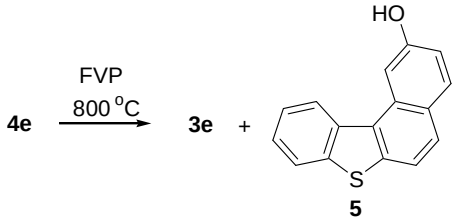


Scheme 1

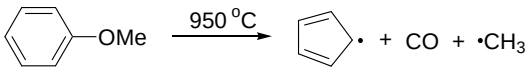
Table 1. Products from FVP of **1a-1e** at 800 °C and ca. 1x10 $^{-2}$ Torr

Precursors	Products (yields, %)	
1a	**3a** (68%)	**4a** (12%)
1b	**3b** (65%)	**4b** (15%)
1c	**3c** (70%)	**4c** (18%)
1d	**3d** (43%)	**4d** (17%)
1e	**3e** (45%)	**4e** (20%)

The structure of **3b-3e** were confirmed by comparing ^{1}H NMR spectrum of **3c** with that of the reported data.[16] Generation of **4b-4e** suggests that, under the pyrolysis conditions, cleavage of Me-O bond should be the initial step of a series of elimination and rearrangement reactions that led to the final products (**3b-3e**). In fact, FVP of isolated 2-(4-hydroxystyryl)benzo[*b*]thiophene (**4e**) gave not only **3e** but also a trace of benzo[*b*]naphta[1,2-*d*] thiophene-2-ol (**5**) (eq.4). Furthermore, pyrolysis of methoxybenzene has been reported to give a cyclopentadienyl radical which has been detected by mass spectroscopic method (eq.5).[17]



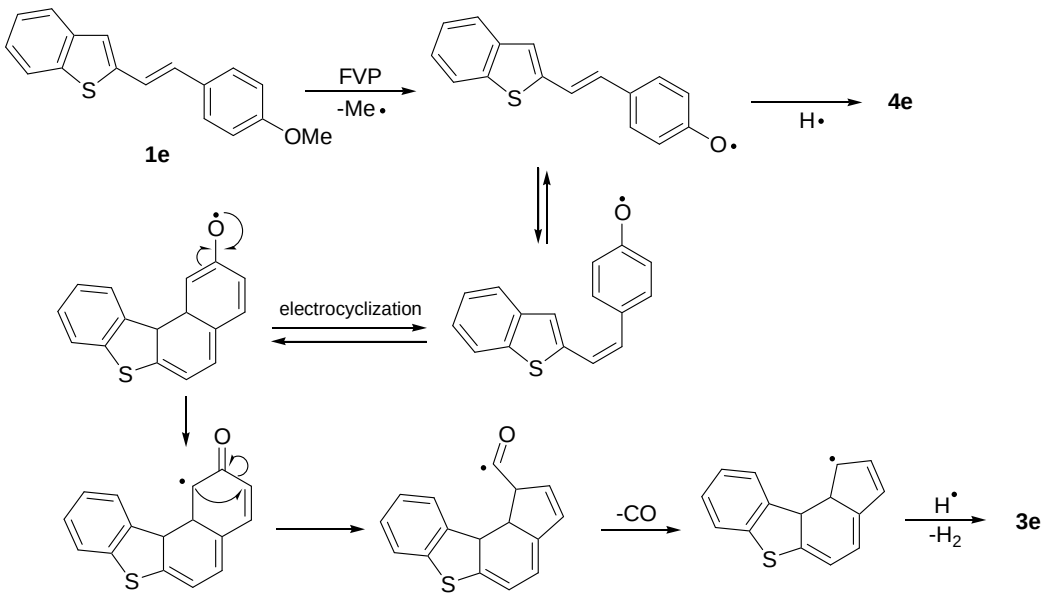
(4)



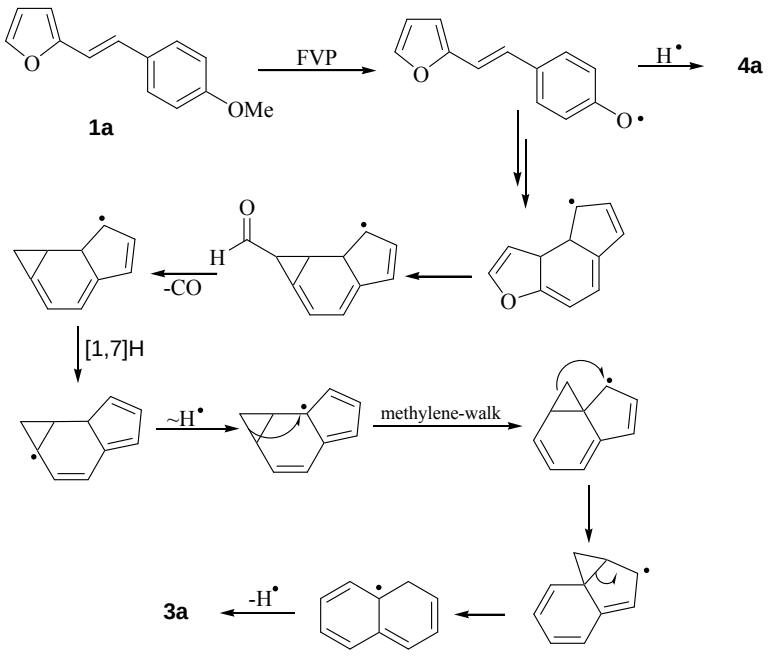
(5)

Based on the above information, a mechanism to account for the formation of areno[*e*]indenes (**3b-3e**) from **1b-1e** is proposed, using **1e** as an example, and shown as Scheme 2. It is noteworthy that although **3c** has been prepared previously,[16,18] the heteroatom analogues (**3b**, **3d** and **3e**) still remain unknown. Since **3b-3e** will be hydrolyzed and used as new building blocks for the synthesis of dendrimers[19-21] in our future study, attempt was made only to separate the regioisomers in **3e**. It appeared that **3e** can be separated into individual isomers by simple column chromatography.

As for the furan analogue (**1a**), possibly dued to low aromaticity of furan ring, FVP of **1a** would result in further cleavage of furan ring and led to the formation of naphthalene. A mechanism involving methylene-walk process[22] is proposed to account for the observed results and shown as Scheme 3.



Scheme 2



Scheme 3

In summary, we have provided a new method for the synthesis of areno[*e*]indenes (**3b-3e**). We are currently extending our study to other heterocyclic systems.

EXPERIMENTAL

Infrared spectra were recorded with a Bio-Rad FTS-155 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured with Varian VXR-500 NMR spectrometer, with tetramethylsilane as an internal standard.

GC was performed on a HP 5890 instrument equipped with a 60m × 0.25nm i.d. column (DB-5). Mass spectra were recorded with a VG QUATTRO 5022 spectrometer. High resolution mass spectra (HRMS) were recorded with a VG70-250S spectrometer.

General procedure for the synthesis of *p*-methoxystyrylarenes (**1a-1e**).

p-Methoxystyrylarenes (**1a-1e**) were prepared from 4-methoxybenzyl chloride and the corresponding aldehydes through a Wittig reaction.[14] The mixture of *p*-methoxybenzyl choride (24 mmol) and triphenyl phosphite (30 mmol) in *p*-xylene was refluxed under nitrogen atmosphere for 10 h. After refluxing, the reaction was cooled down to rt and the product was filtered and washed with ether to yield [4-(methoxy)benzyl]triphenylphosphonium chloride (85%). To a solution of the phosphonium choride (20 mmol) in dry MeOH (20 mL) was added sodium methoxide (22 mmol). After stirring the solution at 0 °C for 10 min, an appropriate aldehyde (20 mmol) was added slowly. After the addition was completed, the reaction mixture was kept stirring for 6 h at rt. The solvent was removed in *vacuo* and the residue was dissolved in AcOEt (40 mL). The solution was then washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. The crude products were purified by column chromatography on silica gel (*n*-hexane : AcOEt = 10 : 1) to give *p*-methoxystyrylarenes (**1a-1e**).

(E)-p-Methoxystyrylfuran (**1a**) was generously donated by professor Ho Tong-Ing. Spectral data for compound (**1a**)[10]: mp 73-74 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36-7.41 (m, 3H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 16.3 Hz, 1H), 6.39 (dd, *J* = 1.9, 3.3 Hz, 1H), 6.28 (d, *J* = 3.3 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.3, 153.5, 141.7, 129.8, 127.5, 126.8, 114.6, 114.1, 111.5, 107.6, 55.3; MS *m/z* (%) 186 (M^+, 69), 185 (42), 171 (100), 143 (43), 115 (45).

(E)-p-Methoxystyrylthiophene (**1b**): mp 135-136 °C; IR ($CHCl_3$, cm^{-1}) 1712, 1609, 1505, 1362, 1250, 1169, 1030; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 5.0 Hz, 1H), 7.11 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 3.5 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.26, 143.24, 129.74, 127.95, 127.51, 127.50, 125.37, 123.71, 119.78, 114.15, 55.31; MS *m/z* (%) 216 (M^+, 79.3), 201 (26.0), 171 (48.5).
[lit.[10] **1b**: mp 134-135 °C; ^{1}H NMR (200 MHz, CDCl3) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 5.4 Hz, 1H), 7.10 (d, *J* = 16.1 Hz, 1H), 6.96-7.06 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 16.1 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (50 MHz, CDCl3) δ 159.2, 143.2, 129.7, 128.0, 127.5, 127.4,125.3, 123.7, 119.7, 114.1, 55.2; MS *m/z* (%) 216 (M^+, 100), 201 (36),171 (22), 129 (32), 115 (42)]

(E)-p-Methoxystilbene (**1c**): mp 132-134 °C; IR ($CHCl_3$, cm^{-1}) 3033, 2841, 1605, 1512, 1252, 1176, 1036; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 16.0 Hz, 1H), 7.00 (d, *J* = 16.0 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H),

3.84 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.28, 137.62, 130.12, 128.62, 128.18, 127.69, 127.19, 126.59, 126.23, 114.11, 55.30; MS *m/z* (%) 210 (M^+, 59.8), 165 (100), 152 (59.8).
[lit.,[23] **1c**: mp 135 °C; ^{1}H NMR ($CDCl_3$) δ 7.5-6.7 (m, 11H), 3.75 (s, 3H)]

(E)-2-[2-(4-Methoxyphenyl)vinyl]benzo[*b*]furan (**1d**): mp 146-148 °C; IR ($CHCl_3$, cm^{-1}) 3056, 2983, 1265; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54-7.39 (m, 8H), 7.32-7.20 (m, 6H), 6.94-6.87 (m, 4H), 6.66-6.63 (m, 2H), 6.43-6.41 (m, 2H), 3.86-3.85 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 159.69, 159.23, 155.40, 154.74, 154.16, 154.15, 131.38, 130.35, 129.86, 129.32, 129.24, 129.22, 128.66, 127.97, 124.33, 124.27, 122.77, 122.76, 120.68, 120.60, 116.49, 114.34, 114.20, 113.52, 110.99, 110.74, 105.74, 104.25, 55.29, 55.23; MS *m/z* (%) 250 (M^+, 100), 235 (7); HRMS: Calcd for $C_{17}H_{14}O_2$: 250.0994, found: 250.0997.

(E)-2-[2-(4-Methoxyphenyl)vinyl]benzo[*b*]thiophene (**1e**): mp 226-227 °C; IR ($CHCl_3$, cm^{-1}) 3053, 1603, 1419, 1265, 1031; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86-7.74 (m, 4H), 7.55-7.30 (m, 11H), 7.06-6.97 (m, 5H), 6.82-6.75 (m, 2H), 3.94 (s, 3H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.61, 159.31, 143.30, 140.31, 140.26, 139.98, 139.13, 138.68, 131.07, 130.49, 130.35, 129.39, 128.99, 127.85, 124.68, 124.47, 124.42, 124.40, 124.15, 123.20, 123.18, 122.83, 122.44, 122.15, 121.99, 120.23, 114.22, 113.81, 55.33, 55.23; MS *m/z* (%) 266 (M^+, 27), 251 (2), 134 (14); HRMS: Calcd for $C_{17}H_{14}OS$: 266.0765, found: 266.0766.

Pyrolysis of *p*-methoxystyrylarenes (**1a-1e**).
The pyrolysis set-up has been described previously.[15] The furnace was maintained at 800 ℃. A compound of *p*-methoxystyrylarenes (**1a-1e**) (0.40-0.52 g) was placed into the sample chamber and the system was evacuated to 1×10^{-2} Torr. During the pyrolysis, $CDCl_3$ was deposited into the trap through a side arm. After pyrolysis was completed, nitrogen was introduced into the system and the trap cooled with liquid nitrogen was warmed to rt, the pyrolysis products were collected and separated by column chromatography on silica gel and examined by spectrometers.

A 1:1 mixture of 1*H*-thieno[2,3-*e*]indene and 3*H*-thieno[2,3-*e*]indene (**3b**): yellow oil; IR ($CHCl_3$, cm^{-1}) 3157, 1802, 1474, 1382, 1092; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, *J* = 8.5 Hz, 0.5H), 7.74 (d, *J* = 7.5 Hz, 0.5H), 7.54 (d, *J* = 5.5 Hz, 0.5H), 7.52 (d, *J* = 8.5 Hz, 0.5H), 7.50 (d, *J* = 6.0 Hz, 0.5H), 7.49 (d, *J* = 5.5 Hz, 0.5H), 7.46 (d, *J* = 7.5 Hz, 0.5H), 7.42 (d, *J* = 5.5 Hz, 0.5H), 7.28-7.26 (m, 0.5H), 7.00 (dt, *J* = 5.5, 2.0 Hz, 0.5H), 6.72 (dt, *J* = 5.5, 2.0 Hz, 0.5H), 6.58 (dt, *J* = 5.5, 2.0 Hz, 0.5H), 3.64 (d, *J* = 1.5 Hz, 1H), 3.54 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.32, 139.82, 139.36, 138.43, 138.22, 136.94, 135.93, 134.81, 133.39, 132.37, 132.29, 130.23, 127.17, 126.12, 121.41, 121.26, 120.50, 120.28, 118.41, 118.12, 39.52, 38.39; HRMS: Calcd for $C_{11}H_8S$: 172.0347, found: 172.0345.

A 1:1 mixture of 1*H*-benzo[*e*]indene and 3*H*-benzo[*e*]indene (**3c**): yellow oil; IR ($CHCl_3$, cm^{-1}) 3161,

1795, 1472, 1384, 1097; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.16 (d, *J* = 8.0 Hz, 0.5H), 7.98 (d, *J* = 8.0 Hz, 0.5H), 7.92 (d, *J* = 8.5 Hz, 0.5H), 7.88 (d, *J* = 8.5 Hz, 0.5H), 7.82-7.39 (m, 4.5H), 7.02 (dt, *J* = 5.5, 2.0 Hz, 0.5H), 6.77 (dt, *J* = 5.5, 2.0 Hz, 0.5H), 6.68 (dt, *J* = 5.5, 2.0 Hz, 0.5H), 3.74 (s, 1H), 3.59 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.22, 141.23, 140.95, 140.18, 134.29, 133.64, 132.62, 132.54, 131.46, 130.07, 129.54, 128.80, 128.34, 127.80, 127.15, 126.12, 125.54, 124.87, 124.72, 124.45, 123.79, 123.49, 122.42, 120.49, 40.36, 38.02; MS *m/z* (%) 166 (M^+, 100).
[lit.,[16] **3c**: ^{1}H NMR ($CDCl_3$) δ 8.21-7.34 (m, 6.5H), 6.99 (td, *J* = 5.4, 1.8Hz, 0.5H), 6.73 (td, *J* = 5.4, 1.8Hz, 0.5H), 6.65 (dt, *J* = 5.4, 1.8Hz, 0.5H), 3.71 (dd, *J* = 0.1, 1.8Hz, 1H), 3.56 (dd, *J* = 0.1, 1.8Hz, 1H)]

A 1:1 mixture of 1*H*-6-oxacyclopenta[*c*]fluorine and 3*H*-6-oxacyclopenta[*c*]fluorine (**3d**): yellow oil; IR ($CHCl_3$, cm^{-1}) 1466; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.07 (d, *J* = 8.0 Hz, 0.5H), 7.96 (d, *J* = 8.0 Hz, 0.5H), 7.62-7.39 (m, 6.5H), 7.04-7.03 (m, 0.5H), 6.85 (d, *J* = 5.5 Hz, 0.5H), 6.66 (d, *J* = 5.5 Hz, 0.5H), 3.74 (s, 1H), 3.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.49, 156.22, 155.79, 154.85, 140.17, 138.46, 138.30, 136.92, 137.04, 132.32, 131.98, 129.59, 126.84, 126.45, 126.45, 122.62, 122.57, 122.00, 121.65, 121.44, 119.71, 111.56, 111.51, 109.26, 107.22, 38.66, 37.97; MS *m/z* (%) 206 (M^+, 92), 205 (100), 176 (20); HRMS: Calcd for $C_{15}H_{10}O$: 206.0732, found: 206.0734.

A 1:1 mixture of regioisomers in **3e** was separated by column chromatography on silica gel (*n*-hexane) to give individual isomers: 1*H*-6-thiacyclopenta[*c*]fluorine (**3e$_{-1H}$**) and 3*H*-6-thiacyclopenta[*c*]fluorene (**3e$_{-3H}$**). **3e$_{-1H}$**: IR ($CHCl_3$, cm^{-1}) 3066, 2934, 1632, 1454, 1410, 1265; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.21 (d, *J* = 7.0 Hz, 1H), 7.89 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52-7.45 (m, 2H), 7.28 (dt, *J* = 5.5, 2.0 Hz, 1H), 6.67 (dt, *J* = 5.5, 2.0 Hz, 1H), 3.86 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.25, 140.00, 138.38, 136.35, 135.54, 132.46, 131.97, 131.65, 126.19, 124.36, 123.79, 122.83, 120.72, 120.02, 39.16; MS *m/z* (%): 222 (M^+, 90), 221 (100); HRMS Calcd for $C_{15}H_{10}S$: 222.0503, found: 222.0502. **3e$_{-3H}$**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.93-7.49 (m, 5H), 6.86-6.85 (m, 1H), 6.68-6.67(m, 1H), 3.52 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.94, 139.68, 139.53, 137.79, 136.17, 135.83, 129.75, 128.74, 125.76, 124.22, 123.54, 122.73, 122.06, 118.60, 38.58.

4-Hydroxystyrylfuran (**4a**): yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.32 (m, 3H), 6.96 (d, *J* = 16.5 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 16.5 Hz, 1H), 6.39 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.28 (d, *J* = 3.3 Hz, 1H), 4.87 (bs, 1H).
[lit.,[24] **4a**: IR (KBr, cm^{-1}) 1252, 1514; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36 (dm, *J* = 8.4 Hz, 3H), 6.98 (d, *J* = 16.2 Hz, 1H), 6.81 (dm, *J* = 8.7 Hz, 1H), 6.85-6.78 (m, 1H), 6.75 (d, *J* = 16.2 Hz, 1H), 6.41 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.30 (d, *J* = 3.3 Hz, 1H), 5.07 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.2, 153.4, 141.8, 129.9, 127.7, 126.6, 115.6, 114.6, 111.5, 107.7; HRMS: Calcd for $C_{12}H_{10}O_2$: 186.0681, found: 186.0676.]

4-Hydroxystyrylthiophene (**4b**): mp 147-148 °C; IR ($CHCl_3$, cm^{-1}) 2983, 1732, 1376, 1250, 1047; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.36 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 5.0 Hz, 1H), 7.10 (d, *J* = 16.0 Hz, 1H), 7.03 (d, *J* = 3.5 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.95 (bs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.20, 143.16, 129.95, 127.85, 127.70, 127.52, 125.43, 123.76, 119.85, 115.63; MS *m/z* (%): 202 (M^+, 100), 149 (30.8), 115 (45.4); HRMS: Calcd for $C_{12}H_{10}OS$: 202.0452, found: 202.0454; Anal. Calcd: C, 71.25; H, 4.98; S, 15.85. Found: C, 71.24; H, 5.05; S, 15.79.

4-Hydroxystilbene (**4c**): yellow oil; IR ($CHCl_3$, cm^{-1}) 3157, 1791, 1602, 1472, 1383, 1169, 1096; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.49 (d, *J* = 7.0 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 16.5 Hz, 1H), 6.97 (d, *J* = 16.5 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 4.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.24, 137.57, 130.33, 128.64, 128.11, 127.91, 127.24, 126.67, 126.24, 115.59; MS *m/z* (%) 196 (M^+, 100), 165 (40.4).
[lit.,[25] **4c**: ^1H NMR (Acetone-d_6, 250 MHz) δ 7.59-7.51 (m, 2H), 7.50-7.42 (m, 2H), 7.39-7.29 (m, 2H), 7.26-7.17 (m, 1H), 6.91-6.82 (m, 2H), 3.02 (bs, 1H); ^{13}C NMR (Acetone-d_6, 62.5 MHz) δ 158.16, 138.83, 129.94, 129.43, 129.33, 128.73, 127.80, 126.95, 126.44, 116.37.]

4-(2-Benzofuran-2-ylvinyl)phenol (**4d**): mp 192-194 °C; IR ($CHCl_3$, cm^{-1}) 3154, 899, 736, 640; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.52-7.42 (m, 4H), 7.28-7.25 (m, 2H), 7.21-7.18 (m, 1H), 6.88-6.84 (m, 3H), 6.63 (s, 1H), 5.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.75, 155.35, 154.76, 129.79, 129.55, 129.22, 128.20, 124.32, 122.80, 120.63, 115.72, 114.43, 110.77, 104.33; MS *m/z* (%): 236 (M^+, 19), 77 (38), 63 (100); HRMS: Calcd for $C_{16}H_{12}O_2$: 236.0837, found: 236.0839.

4-(2-Benzo[*b*]thiophen-2-ylvinyl)phenol (**4e**): mp 242-244 °C; IR ($CHCl_3$, cm^{-1}) 3442, 1643, 1423, 1271; ^1H NMR (DMSO-d_6, 500 MHz) δ 9.73 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.37 (s, 1H), 7.34 (d, *J* = 16.0 Hz, 1H), 7.33-7.28 (m, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 157.83, 143.16, 140.13, 137.85, 130.76, 128.23, 127.32, 124.69, 124.63, 123.32, 122.48, 122.32, 119.20, 115.72; MS *m/z* (%): 252 (M^+, 59), 134 (74); HRMS: Calcd for $C_{16}H_{12}OS$: 252.0609, found: 252.0607.

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REFERENCES

1. F. B. Mallory and C. W. Mallory, *Org. React.*, 1980, **30**, 1.
2. L. Liu, B. Yang, T. J. Katz, and M. K. Poindexter, *J. Org. Chem.*, 1991, **56**, 3769.
3. H. Meier, Angew. *Chem., Int. Ed. Engl.*, 1992, **31**, 1402.

4. M. P. Cava, P. Stern, and K. Wakisaka, *Tetrahedron*, 1973, **29**, 2245.
5. M. J. Plater, *Tetrahedron Lett.*, 1994, **35**, 801.
6. G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 243.
7. D. H. Waldeck, *Chem. Rev.*, 1991, **91**, 415.
8. F. D. Lewis, A. M. Bedell, R. E. Dykstra, J. E. Elbert, I. R. Gould, and S. Farid, *J. Am. Chem. Soc.* 1990, **112**, 8055.
9. T. -I. Ho, J. Y. Wu, and S. L. Wang, *Angew. Chem. Int. Ed*., 1999, **38**, 2558.
10. J. Y. Wu, J. H, Ho, S, M, Chih, T. L. Hsieh, and T. -I. Ho, *Org. Lett.*, 1999, **1**, 1039.
11. T. -I. Ho, J. H. Ho, and J. Y. Wu, *J. Am. Chem. Soc.*, 2000, **122**, 8575.
12. J. H. Ho, T. -I. Ho, and R. S. H. Liu, *Org. Lett.*, 2001, **3**, 409.
13. J. H. Ho and T. I. Ho, *Tetrahedron Lett.*, 2003, **44**, 4669.
14. G. Wittig and W. Haag, *Chem. Ber.*, 1955, 1654.
15. W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, *J. Org. Chem.*, 1971, **36**, 3575.
16. J. W. Grissom and D. Klingberg, *J. Org. Chem.*, 1993, **58**, 6559.
17. A. G. Harrison, L. R. Honnen, H. J. Dauben, and F. P. Lossing, *J. Am. Soc. Chem.*, 1960, **82**, 5593.
18. R. F. C. Brown, F. W. Eastwood, and C. J. Smith, *Aust. J. Chem.*, 1992**, 45**, 1315.
19. O. de Frutos, B. Gomez-Lor, T. Granier, M. A. Monge, E. Gutierrez-Puebla, and A. M. Echavarren, *Angew. Chem. Int. Ed*., 1999, **38**, 204.
20. B. Gomez-Lor, O. de Frutos, P. A. Ceballos, T. Granier, and A. M. Echavarren, *Eur. J. Org. Chem.*, 2001, 2107.
21. O. de Frutos, T. Granier, B. Gomez-Lor, J. Jimenez-Barbero, A. Monge, E. Gutierez-Puebla, and A. M. Echavarren, *Chem. Eur. J.*, 2002, **8**, 2879.
22. L. T. Scott and M. A. Kirms, *J. Am. Soc. Chem.*, 1981, **103**, 5875.
23. W. J. Ward, Jr., and W. E. McEwen, *J. Org. Chem*., 1990, **55**, 493.
24. K. Itami, T. Nokami, and J. Yoshida, *J. Am. Chem. Soc.*, 2001, **123**, 5600.
25. R. B. Chhor, K. A. Singh, B. Nosse, and V. K. Tandon, *Synth. Commun*., 2003, **33**, 2519.