Synthesis of 4*H*-Indeno[1,2-*b*]thiophenes, 8*H*-Indeno[2,1-*b*]-thiophenes and 8*H*-Indeno[2,1-*b*]furans Having Acrylic Acid Unit

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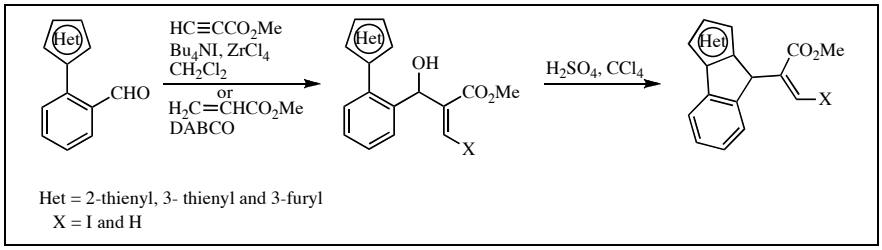

Treatment of methyl propiolate and 2-(thiophen-2-yl)benzaldehyde, 2-(thiophen-3-yl)benzaldehyde or 2-(furan-3-yl)benzaldehyde with tetrabutylammonium iodide/zirconium (IV) chloride or treatment of methyl acrylate and the same aldehydes with 1,4-diazabicyclo[2,2,2]octane and triethanolamine induce an aldol-type reaction to furnish Baylis-Hillman adducts β-iodo-α-(hydroxymethyl)acrylates or α-(hydroxy-methyl)acrylates, respectively. These can be used for the preparation of indenothiophenes and indenofurans having acrylic acid unit by intramolecular Friedel-Crafts reaction with sulfuric acid in tetrachloromethane.

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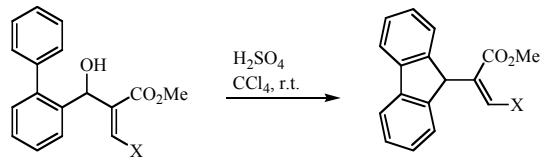
The Baylis-Hillman (BH) reaction has become a powerful tool for construction of carbon-carbon bonds in organic chemistry because it is completely atom economical and provides densely functionalized structural units, which have been successfully employed in a variety of interesting organic transformations [1]. The Friedel-Crafts reaction is one of the most fundamental carbon-carbon bond forming reaction in organic synthesis [2]. Recently, we reported the synthesis of 2-(9-fluorenyl)-acrylic acid derivatives from BH adducts of 2-biphenylcarboxaldehydes by an intramolecular Friedel-Crafts reaction as shown in Scheme 1 [3]. During continued efforts to develop BH chemistry [4], we subsequently envisioned that application of this protocol to BH adducts of several thiophene- or furan-substituted benzaldehydes might lead to indenothiophenes or indenofurans having acrylic acid unit.

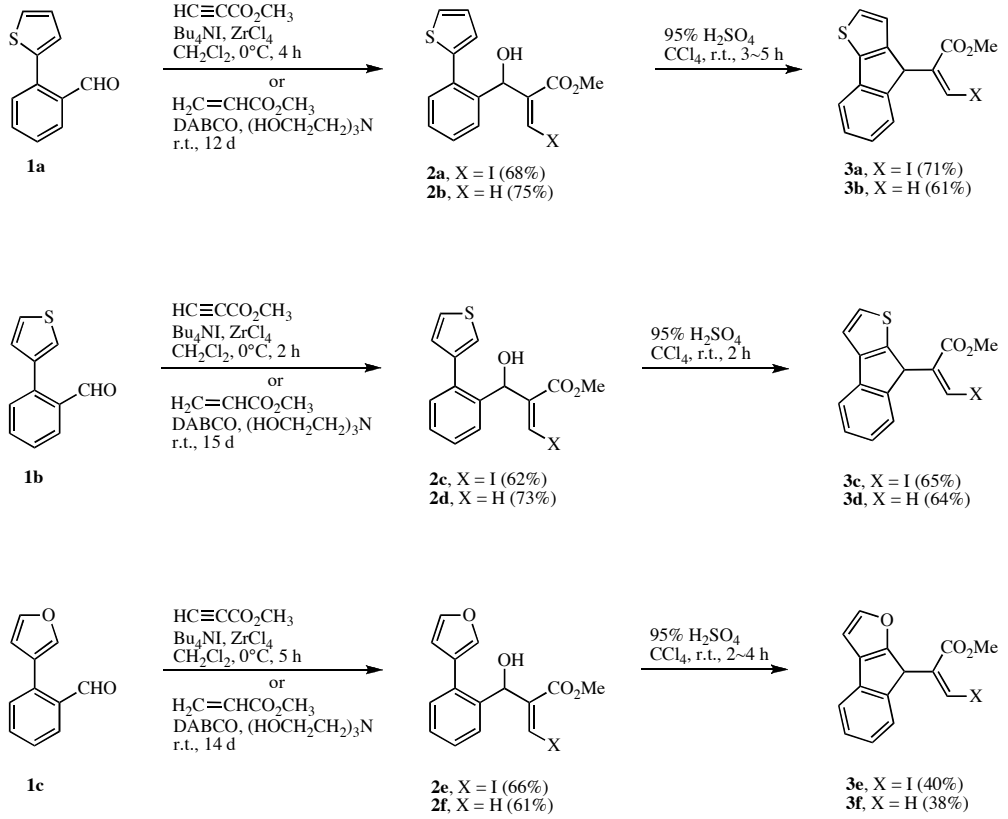
Scheme 1



Indenothiophene derivatives have received considerable attention in the field of organometallic chemistry because their transition metal complexes have been found to be promising catalysts for olefin polymerization [5-7]. Indenothiophene is the core structure of potent molecules such as inhibitors of 1kk-β phosphorylation of 1kB [8] and neurotransmitter release enhancers useful in the treatment of cognitive disorders [9]. A general method for the synthesis of indenothiophenes is reduction of corresponding indenothiophenones. The most useful syntheses of indenothiophenones include Friedel-Crafts ring closures of 2-thienylbenzoic acids and derivatives [10], cycloaromatization of non-conjugated thienyl tetraynes [11], palladium-catalyzed cyclocarbonylation of *o*-haloheteroaryls [12], and direct double metalation of the appropriate 3-phenylhetarene with butyllithium followed by treatment of the resulting dilithium compound with ethyl *N,N*-dimethylcarbamate [13]. However, far less attention has been devoted to indenofurans synthesis in the literature to date [12-14].

The required *β*-iodo-BH adducts **2a**, **2c**, **2e** were prepared by the reaction of methyl propiolate with tetrabutylammonium iodide, followed by an aldol process with aldehydes **1a**-**c** in the presence of zirconium (IV) chloride in 62-68% yields, originally reported by Taniguchi [15] and Lu [16]. The typical BH reaction of **1a**-**c** with methyl acrylate, 1,4-diazabicyclo[2,2,2]octane (DABCO), and triethanolamine without solvent gave BH adducts **2b**, **2d**, **2f** in 61-75% yields. On Friedel-Crafts cyclization of **2a**-**2f** with 95% sulfuric acid in tetrachloro-methane at room temperature for 2-5 hours, 4*H*-indeno-[1,2-*b*]thiophenes **3a**, **3b**, 8*H*-Indeno[2,1-*b*]thiophenes **3c**, **3d** or 8*H*-Indeno[2,1-*b*]furans **3e**, **3f** were produced in 38-71% yields, respectively, presumably through the

Scheme 2

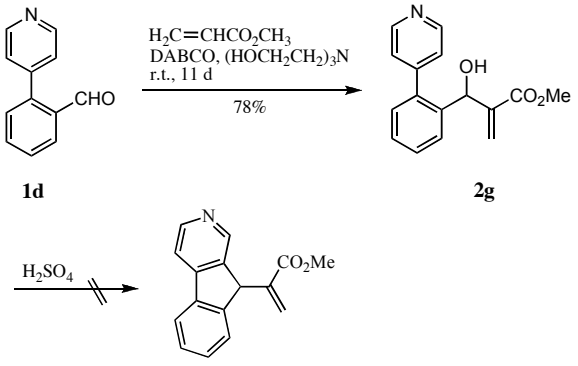


resonance-stabilized, more stable benzylic carbocation (Scheme 2).

The structures of **3a**, **3c**, **3e** were elucidated by ^{1}H and ^{13}C NMR and elemental analyses. In the ^{1}H NMR spectra, the characteristic chemical shift of the methine protons of indene were found at δ = 4.85-5.04 as a singlet and the alkenic protons were observed at δ = 6.91-7.06 as a doublet (J = 0.9 Hz) for indenothiophenes **3a**, **3c**, and at δ = 6.98 as a singlet for indenofuran **3e**. The two vinyl protons of **3b**, **3d**, **3f** were found at δ = 5.44-5.53 and 6.16-6.21, and the indene methine protons were observed at δ =4.87-5.03 as singlets. The two thiophene protons of indenothiophenes **3a**-**3d** resonated at δ =7.02-7.25 and δ = 7.30-7.38 as two doublet (J = 4.9 Hz) and one of the two furan protons of indenofurans **3e**, **3f** was found at δ = 6.63-6.65 as a doublet (J = 1.8 Hz) and another one was observed at aromatic region. The Z-stereoselectivity of **3a**-**f** was determined from ^{1}H NMR analysis by comparison with the chemical shift of the olefinic protons of the known methyl (*Z*)-2-(9*H*-fluoren-9-yl)-3-iodopropenoate [3]. In the ^{13}C NMR spectra, the characteristic sp^{3} carbon atom of hetarenoindenes were observed at δ = 44.3-51.1.

In order to extend the scope of this methodology we have also examined 2-(pyridin-4-yl)benzaldehyde (**1d**) as an aldehyde in this study. The corresponding β-iodo-BH adduct was not produced by the reaction of methyl propiolate with tetrabutylammonium iodide and zirconium (IV) chloride, presumably due to basic nature of the pyridine. When using excess zirconium (IV) chloride and tetrabutylammonium iodide the reaction was unsuccessful. On the other hand, the typical BH reaction of **1d** with methyl acrylate, DABCO, and triethanolamine without solvent gave BH adduct **2g** in 78% yield. However, on Friedel-Crafts cyclization of **2g** with sulfuric

Scheme 3



acid or *p*-toluenesulfonic acid in tetrachloromethane or tetrahydrofuran at room or reflux temperature the desired methyl 2-(9*H*-indeno[2,1-*c*]pyridin-9-yl)propenoate (**3g**) was not produced, instead only decomposition was observed (Scheme 3).

In conclusion, we have demonstrated a new synthetic method for the preparation of indenothiophenes and indenofurans having acrylic acid unit by Friedel-Crafts cyclization of Baylis-Hillman adducts of hetarenobenzaldehydes. There is some limitation as regards the reactivity of Baylis-Hillman adduct having pyridine ring with sulfuric acid.

EXPERIMENTAL

Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} TLC plates. Melting points were measured by an Electrothermal melting point apparatus and were uncorrected. Microanalysis was obtained using a Thermo Electron Corporation Flash EA 1112 element analyzer. Infrared spectra were recorded with a Nicolet Magna 550 FTIR spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Gemini 300 spectrometer using deuteriochloroform. All chemical shifts are reported in parts per million relative to tetramethylsilane. The coupling constants (*J*) are expressed in Hertz.

The known 2-(thiophen-2-yl)benzaldehyde (**1a**) [17], 2-(thiophen-3-yl)benzaldehyde (**1b**) [18], 2-(furan-3-yl)benz-aldehyde (**1c**) [19] and 2-(pyridin-4-yl)benzaldehyde (**1d**) [20] were prepared from commercially available 2-formylphenyl-boronic acid with 2-bromo-, 3-bromothiophene, 3-bromofuran and 4-bromopyridine by Suzuki reaction according to the literature procedure.

Methyl (Z)-2-[1-Hydroxy-1-{2-(thiophen-2-yl)phenyl}-methyl]-3-iodopropenoate (2a). To a mixture of **1a** (1.88 g, 10 mmoles), methyl propiolate (0.98 mL, 11 mmoles) and tetrabutylammonium iodide (Bu_4NI) (4.43 g, 12 mmoles) in anhydrous dichloromethane (40 mL) was added zirconium chloride ($ZrCl_4$) (2.80 g, 12 mmoles) at 0 °C. The mixture was stirred at 0 °C under nitrogen atmosphere for 4 hours. Then, water (20 mL) was added and the mixture was extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 2.72 g (68%) of **2a** as a solid; mp 62-63 °C; ir (potassium bromide): 3485, 1724, 1597, 1482, 1447, 1432 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.65 (d, *J* = 4.9 Hz, 1 H), 3.70 (s, 3 H), 5.84 (d, *J* = 4.0 Hz, 1 H), 7.03-7.11 (m, 3 H), 7.33-7.44 (m, 4 H), 7.50-7.53 (m, 1 H); ^{13}C nmr (deuteriochloroform): δ 52.0, 72.2, 87.7, 126.1, 127.0, 127.1, 127.3, 128.3, 128.7, 131.4, 133.7, 138.0, 140.9, 145.0, 166.2. *Anal.* Calcd. for $C_{15}H_{13}IO_3S$: C, 45.01; H, 3.27; S, 8.01. Found: C, 44.87; H, 3.15; S, 7.79.

Methyl 2-[1-Hydroxy-1-{2-(thiophen-2-yl)phenyl}methyl] propenoate (2b). A mixture of **1a** (1.88 g, 10 mmoles), methyl acrylate (2.70 mL, 30 mmoles), DABCO (1.12 g, 10 mmoles) and triethanolamine (0.93 mL, 8 mmoles) without solvent was stirred at room temperature for 12 days. The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 2.06 g (75%) of **2b** as an oil; ir (potassium bromide): 3469, 1727, 1630, 1600, 1531, 1483, 1440 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.84 (br s, 1 H), 3.71 (s, 3 H), 5.67 (s, 1 H), 5.89 (s, 1 H), 6.37 (s, 1 H), 7.05-7.08 (m, 2 H), 7.31-7.43 (m, 4 H), 7.53-7.56 (m, 1 H); ^{13}C nmr (deuteriochloroform): δ 52.0, 69.2, 125.8, 126.7, 127.0, 127.1 (two), 127.9, 128.4, 131.2, 133.8, 138.9, 141.3, 142.2, 166.8. *Anal.* Calcd. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14; S, 11.69. Found: C, 65.49; H, 5.03; S, 11.51.

Methyl (*Z*)-2-[1-Hydroxy-1-{2-(thiophen-3-yl)phenyl} methyl]-3-iodopropenoate (2c). To a mixture **1b** (1.88 g, 10 mmoles), methyl propiolate (0.98 mL, 11 mmoles) and Bu_4NI (4.43 g, 12 mmoles) in anhydrous dichloromethane (40 mL) was added $ZrCl_4$ (2.80 g, 12 mmoles) at 0 °C. The mixture was stirred at 0 °C under nitrogen atmosphere for 2 hours. Then, water (20 mL) was added and the mixture was extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 2.48 g (62%) of **2c** as an oil; ir (potassium bromide): 3500, 1731, 1598, 1484, 1434 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.64 (d, *J* = 5.2 Hz, 1 H), 3.68 (s, 3 H), 5.71 (d, *J* = 3.6 Hz, 1 H), 7.05 (d, *J* = 1.6 Hz, 1 H), 7.10-7.12 (m, 1 H), 7.22-7.24 (m, 1 H), 7.31-7.41 (m, 4 H), 7.46-7.50 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 51.9, 72.5, 87.1, 123.2, 125.6, 126.8, 128.1, 128.3, 128.8, 130.4, 136.2, 137.4, 140.3, 145.3, 166.3. *Anal.* Calcd. for $C_{15}H_{13}IO_3S$: C, 45.01; H, 3.27; S, 8.01. Found: C, 45.25; H, 3.03; S, 7.75.

Methyl 2-[1-Hydroxy-1-{2-(thiophen-3-yl)phenyl}methyl] propenoate (2d). A mixture of **1b** (1.88 g, 10 mmoles), methyl acrylate (2.70 mL, 30 mmoles), DABCO (1.12 g, 10 mmoles) and triethanolamine (0.93 mL, 8 mmoles) without solvent was stirred at room temperature for 15 days. The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 2.00 g (73%) of **2d** as an oil; ir (potassium bromide): 3444, 1724, 1630, 1601, 1484, 1440 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.76 (br s, 1 H), 3.70 (s, 3 H), 5.69 (s, 1 H), 5.77 (s, 1 H), 6.36 (s, 1 H), 7.16-7.18 (m, 1 H), 7.27-7.28 (m, 1 H), 7.32-7.40 (m, 4 H), 7.49-7.52 (m, 1 H); ^{13}C nmr (deuteriochloroform): δ 52.0, 69.3, 123.1, 125.3, 126.5, 126.8, 127.8, 127.9, 129.0, 130.2, 136.3, 138.4, 140.7, 142.2, 166.7. *Anal.* Calcd. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14; S, 11.69. Found: C, 65.83; H, 4.89; S, 11.47.

Methyl (Z)-2-[1-{2-(Furan-3-yl)phenyl}-1-hydroxymethyl]-3-iodopropenoate (2e). To a mixture of **1c** (1.72 g, 10 mmoles), methyl propiolate (0.98 mL, 11 mmoles) and Bu_4NI (4.43 g, 12 mmoles) in anhydrous dichloromethane (40 mL) was added $ZrCl_4$ (2.80 g, 12 mmoles) at 0 °C. The mixture was stirred at 0 °C under nitrogen atmosphere for 5 hours. Then, water (20 mL) was added and the mixture was extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in*

vacuo. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 2.53 g (66%) of **2e** as an oil; ir (potassium bromide): 3500, 1731, 1601, 1505, 1434 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.55 (d, J = 5.2 Hz, 1 H), 3.72 (s, 3 H), 5.79 (d, J = 3.7 Hz, 1 H), 6.52-6.53 (m, 1 H), 7.07 (d, J = 1.8 Hz, 1 H), 7.31-7.40 (m, 3 H), 7.46-7.51 (m, 3 H); ^{13}C nmr (deuteriochloroform): δ 52.0, 72.4, 87.1, 111.7, 124.0, 127.0, 128.0, 128.5, 130.3, 132.1, 137.4, 140.1, 143.0, 145.5, 166.4. *Anal*. Calcd. for $C_{15}H_{13}IO_4$: C, 46.90; H, 3.41. Found: C, 46.67; H, 3.37.

Methyl 2-[1-{2-(Furan-3-yl)phenyl}-1-hydroxymethyl] propenoate (2f). A mixture of **1c** (1.72 g, 10 mmoles), methyl acrylate (2.70 mL, 30 mmoles), DABCO (1.12 g, 10 mmoles) and triethanolamine (0.93 mL, 8 mmoles) without solvent was stirred at room temperature for 14 days. The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 1.57 g (61%) of **2f** as an oil; ir (potassium bromide): 3437, 1722, 1631, 1506, 1439 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.77 (d, J = 4.3 Hz, 1 H), 3.72 (s, 3 H), 5.70 (s, 1 H), 5.83 (s, 1 H), 6.38 (s, 1 H), 6.56-6.57 (m, 1 H), 7.33-7.38 (m, 3 H), 7.47-7.52 (m, 3 H); ^{13}C nmr (deuteriochloroform): δ 52.0, 69.3, 111.8, 124.3, 126.5, 126.9, 127.8, 128.0, 130.1, 132.2, 138.4, 140.1, 142.3, 142.8, 166.8. *Anal*. Calcd. for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.55; H, 5.24.

Methyl 2-[1-Hydroxy-1-{2-(pyridin-4-yl)phenyl}methyl] propenoate (2g). A mixture of **1d** (1.85 g, 10 mmoles), methyl acrylate (2.70 mL, 30 mmoles), DABCO (1.12 g, 10 mmoles) and triethanolamine (0.93 mL, 8 mmoles) without solvent was stirred at room temperature for 11 days. The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 2.10 g (78%) of **2g** as a white solid; mp 116-117 ℃; ir (potassium bromide): 3190, 1712, 1628, 1598, 1541, 1478, 1437, 1152, 1045 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.65 (s, 3 H), 3.68 (br s, 1 H), 5.61 (s, 1 H), 5.89 (s, 1 H), 6.40 (s, 1 H), 7.21-7.24 (m, 1 H), 7.35-7.52 (m, 5 H), 8.52-8.54 (m, 2 H); ^{13}C nmr (deuteriochloroform): δ 51.9, 68.7, 124.4, 126.1, 127.1, 128.1, 128.9, 129.6, 138.1, 138.9, 142.3, 149.0, 149.3, 166.4. *Anal*. Calcd. for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.12; H, 5.39; N, 5.07.

Methyl (Z)-2-(4*H*-Indeno[1,2-*b*]thiophen-4-yl)-3-iodopropenoate (3a). To a stirred solution of **2a** (0.80 g, 2 mmoles) in carbon tetrachloride (5 mL) was added 95% sulfuric acid (0.11 mL, 2 mmoles) at room temperature. After 3 hour, the mixture was neutralized with saturated sodium bicarbonate solution and extracted with dichloromethane (5 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 0.54 g (71%) of **3a** as a solid; mp: 83-84 °C; ir (potassium bromide): 1731, 1605, 1581, 1455, 1433 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.85 (s, 3 H), 4.91 (s, 1 H), 6.91 (d, J = 0.9 Hz, 1 H), 7.02 (d, J = 4.9 Hz, 1 H), 7.18-7.24 (m, 1 H), 7.32 (d, J = 4.9 Hz, 1 H), 7.34-7.39 (m, 2 H), 7.45-7.48 (m, 1 H); ^{13}C nmr (deuteriochloroform): δ 50.7, 52.1, 85.4, 119.2, 122.4, 125.0, 125.6, 127.9 (two), 137.9, 141.5, 143.1, 146.8, 148.0, 166.8. *Anal*. Calcd. for $C_{15}H_{11}IO_2S$: C, 47.14; H, 2.90; S, 8.39. Found: C, 47.30; H, 2.78; S, 8.12.

Methyl 2-(4*H*-Indeno[1,2-*b*]thiophen-4-yl)propenoate (3b). To a stirred solution of **2b** (0.55 g, 2 mmoles) in carbon tetrachloride (5 mL) was added 95% sulfuric acid (0.11 mL, 2 mmoles) at room temperature. After 5 hours, the mixture was neutralized with saturated sodium bicarbonate solution and extracted with dichloromethane (5 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 0.31 g (61%) of **3b** as a solid; mp 42-43 ℃; ir (potassium bromide): 1723, 1626, 1605, 1455, 1438 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.86 (s, 3 H), 4.93 (s, 1 H), 5.44 (s, 1 H), 6.16 (s, 1 H), 7.02 (d, J = 4.9 Hz, 1 H), 7.16-7.21 (m, 1 H), 7.30 (d, J = 4.9 Hz, 1 H), 7.32-7.48 (m, 3 H); ^{13}C nmr (deuteriochloroform): δ 47.1, 52.2, 119.0, 122.7, 125.0, 125.2, 125.3, 127.5 (two), 138.1, 139.0, 142.7, 148.3, 149.7, 167.4. *Anal*. Calcd. for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72; S, 12.51. Found: C, 69.98; H, 4.50; S, 12.29.

Methyl (Z)-2-(8*H*-Indeno[2,1-*b*]thiophen-8-yl)-3-iodopropenoate (3c). To a stirred solution of **2c** (0.80 g, 2 mmoles) in carbon tetrachloride (5 mL) was added 95% sulfuric acid (0.11 mL, 2 mmoles) at room temperature. After 2 hours, the mixture was neutralized with saturated sodium bicarbonate solution and extracted with dichloromethane (5 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 0.49 g (65%) of **3c** as an oil; ir (potassium bromide): 1728, 1606, 1588, 1487, 1453, 1436 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.90 (s, 3 H), 5.04 (s, 1 H), 7.06 (d, J = 0.9 Hz, 1 H), 7.18-7.23 (m, 1 H), 7.24 (d, J = 4.9 Hz, 1 H), 7.32-7.36 (m, 2 H), 7.38 (d, J = 4.9 Hz, 1 H), 7.50-7.53 (m, 1 H); ^{13}C nmr (deuteriochloroform): δ 51.1, 52.2, 87.1, 118.6, 119.7, 125.1, 125.2, 127.9, 129.8, 138.7, 140.9, 145.6, 146.4, 147.1, 166.3. *Anal*. Calcd. for $C_{15}H_{11}IO_2S$: C, 47.14; H, 2.90; S, 8.39. Found: C, 47.05; H, 2.78; S, 8.17.

Methyl 2-(8*H*-Indeno[2,1-*b*]thiophen-8-yl)propenoate (3d). To a stirred solution of **2d** (0.55 g, 2 mmoles) in carbon tetrachloride (5 mL) was added 95% sulfuric acid (0.11 mL, 2 mmoles) at room temperature. After 2 hours, the mixture was neutralized with saturated sodium bicarbonate solution and extracted with dichloromethane (5 × 10 mL). The combined organic layers were dried anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 0.32 g (64%) of **3d** as an oil; ir (potassium bromide): 1716, 1629, 1607, 1488, 1454, 1437 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.90 (s, 3 H), 5.03 (s, 1 H), 5.53 (s, 1 H), 6.19 (s, 1 H), 7.16-7.22 (m, 1 H), 7.25 (d, J = 4.9 Hz, 1 H), 7.30-7.33 (m, 1 H), 7.35 (d, J = 4.9 Hz, 1 H), 7.38-7.41 (m, 1 H), 7.51-7.54 (m, 1 H); ^{13}C nmr (deuteriochloroform): δ 47.8, 52.3, 118.5, 119.5, 124.8, 125.2, 125.3, 127.4, 129.3, 138.9, 139.2, 146.0, 147.0, 148.3, 167.2. *Anal*. Calcd. for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72; S, 12.51. Found: C, 70.11; H, 4.50; S, 12.39.

Methyl (Z)-2-(8*H*-Indeno[1,2-*c*]furan-8-yl)-3-iodopropenoate (3e). To a stirred solution of **2e** (0.77 g, 2 mmoles) in carbon tetrachloride (5 mL) was added 95% sulfuric acid (0.11 mL, 2 mmoles) at room temperature. After 4 hours, the mixture was neutralized with saturated sodium bicarbonate solution and

extracted with dichloromethane (5 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 0.29 g (40%) of **3e** as an oil; ir (potassium bromide): 1728, 1613, 1548, 1482, 1451, 1433 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.84 (s, 3 H), 4.85 (s, 1 H), 6.63 (d, J = 1.8 Hz, 1 H), 6.98 (s, 1 H), 7.12-7.17 (m, 1 H), 7.28-7.40 (m, 3 H), 7.49-7.50 (m, 1 H); ^{13}C nmr (deuteriochloroform): δ 47.7, 52.2, 86.3, 105.2, 119.7, 124.8, 124.9, 127.9, 128.6, 136.4, 139.6, 144.3, 147.6, 161.5, 166.2. *Anal*. Calcd. for $C_{15}H_{11}IO_3$: C, 49.20; H, 3.03. Found: C, 48.87; H, 2.80.

Methyl 2-(8*H*-Indeno[1,2-*c*]furan-8-yl)propenoate (3f). To a stirred solution of **2f** (0.52 g, mmoles) in carbon tetrachloride (5 mL) was added 95% sulfuric acid (0.11 mL, 2 mmoles) at room temperature. After 2 hours, the mixture was neutralized with saturated sodium bicarbonate solution and extracted with dichloromethane (5 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (6:1) to produce 0.18 g (38%) of **3f** as an oil; ir (potassium bromide): 1723, 1626, 1614, 1483, 1453, 1438 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.85 (s, 3 H), 4.87 (s, 1 H), 5.45 (s, 1 H), 6.21 (s, 1 H), 6.65 (d, J = 1.8 Hz, 1 H), 7.10-7.15 (m, 1 H), 7.28-7.40 (m, 3 H), 7.49-7.50 (m, 1 H); ^{13}C nmr (deuteriochloroform): δ 44.3, 52.2, 105.1, 119.4, 124.6, 124.9, 125.9, 127.4, 128.2, 136.5, 137.4, 146.0, 147.1, 163.0, 166.9. *Anal*. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.82; H, 4.78.

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