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General approach to benzo[*b*]thiophenes, benzo[*b*]furans, and dibenzofurans via gold-catalyzed cyclization of 1-heteroarylalka-2,3-dienyl acetates

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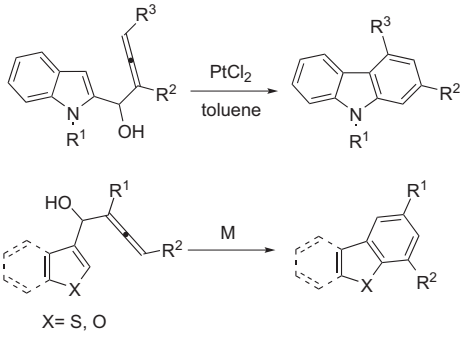
ABSTRACT

An efficient and mild route to a series of benzo[*b*]thiophenes, benzo[*b*]furans, and dibenzofurans through gold-catalyzed benzannulation of 1-heteroarylalka-2,3-dienyl acetates was developed. Two possible pathways of this reaction involving gold carbene and aryl gold intermediates have been proposed on the basis of mechanistic studies.

1. Introduction

Benzo[*b*]thiophenes,[1] benzo[*b*]furans,[2] and dibenzofurans[3] are important heterocyclic scaffolds because of their widespread occurrence among natural products and material chemistry. Thus, the synthesis of functionalized heterocycles is an important topic in synthetic organic chemistry,[4] and many methodologies for the construction of benzo[*b*]thiophenes, benzo[*b*]furans, and other fused-ring compounds by metal-catalyzed cyclization reactions have been developed.[5] However, there still remain some limitations such as low yields, harsh reaction conditions, and not readily available starting materials in these methods. Thus, a mild, efficient, regiocontrolled, and diversified preparation of these compounds is still desirable.

We recently reported a route to construct carbazole alkaloids via the $PtCl_2$-catalyzed cyclization of 1-(indol-2-yl)-2,3-allenols.[6] Then, we described a Au-catalyzed approach to a series of naturally carbazoles.[7] Considering the interests in synthesis of heterocyclic compounds, we reasoned that benzo[*b*]thiophenes, benzo[*b*]furans, and dibenzofurans could be afforded by using thiophenes, furans, and benzo[*b*]furans instead of the indole unit in the starting material (Scheme 1). In this paper, we wish to report our recent observation on efficient synthesis of benzo[*b*]thiophenes, benzo[*b*]furans, and dibenzofurans through gold-catalyzed cyclization of 1-heteroarylalka-2,3-dienyl acetates.



Scheme 1. Cyclization of 2,3-allenols for the formation of the benzene ring.

2. Results and discussion

Initially, we tried the reaction of 2-phenyl-1-(3-thienyl)buta-2,3-dienol (**1a**) in toluene under the catalysis of $PtCl_2$ (5 mol %),[6] however, **1a** was recovered in 92% (Scheme 2). With AuCl as the catalyst,[8] the cycloisomerization product **4** was afforded in 71% yield, instead of the expected benzo[*b*]thiophene derivative (**3a**).

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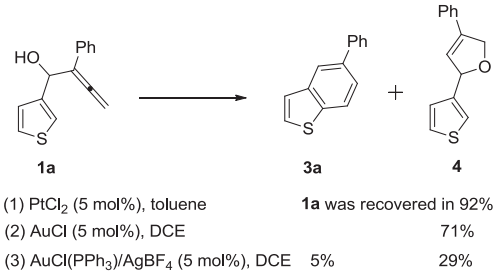
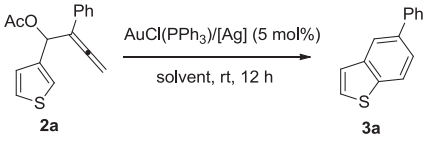


Scheme 2. Metal-catalyzed cyclization of allenol **1a**.

Interestingly, 5-phenylbenzo[*b*]thiophene **3a** was formed in 5% NMR yield together with cycloisomerization product **4** in 29% NMR yield when $AuCl(PPh_3)/AgBF_4$ was used.

Thus, the hydroxy group was protected in order to prevent the cycloisomerization reaction forming the dihydrofuran product. The reaction of 2-phenyl-1-(3-thienyl)buta-2,3-dienyl acetate **2a** in DCE with $AuCl(PPh_3)/AgBF_4$ gave the desired product **3a** in only 8% yield (entry 1, Table 1). Fortunately, the yield was improved to 84% when THF was used instead of DCE (entry 2, Table 1). Notably, the solvent effect was obvious, further study showed that dioxane was the best solvent for this transformation, affording **3a** in 95% yield (entry 5, Table 1)! Then, several combinations of $AuCl(PPh_3)$ with different silver salts were tested, among which $AgBF_4$ was still the best (entries 5–10, Table 1). Thus, we defined the standard conditions as follows: 5 mol % of $AuCl(PPh_3)/AgBF_4$ in dioxane at room temperature.

Table 1
Optimization of reaction conditions for the cyclization reaction of 2-phenyl-1-(3-thienyl)buta-2,3-dienyl acetate (**2a**)[a]

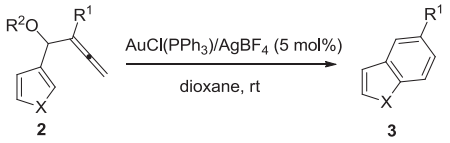


Entry	[Ag]	Solvent	Yield of **3a**[b] (%)
1	$AgBF_4$	DCE	8
2	$AgBF_4$	THF	84
3	$AgBF_4$	Et_2O	52
4	$AgBF_4$	Toluene	18
5	$AgBF_4$	Dioxane	95
6	$AgSbF_6$	Dioxane	85
7	AgOTf	Dioxane	77
8	$AgPF_6$	Dioxane	90
9[c]	AgOAc	Dioxane	—
10[d]	$AgOOCCF_3$	Dioxane	—

[a] The reaction was conducted with **2a** (0.2 mmol) and catalyst (0.01 mmol) in 2 mL of solvent at room temperature.
[b] Determined by ^1H NMR of crude product using dibromomethane as internal standard.
[c] The recovery of **2a** was 97%.
[d] The recovery of **2a** was 87%.

Then, other substrates were screened under the optimal reaction condition. The R^1 group could be aryl (entries 1 and 5–8, Table 2) or alkyl group (entries 2–4, Table 2). In addition to acetate, the protecting group could also be methyl ether (entry 5, Table 2). It is noteworthy that this reaction shows an interesting exclusive elimination of the OAc group to form the benzothiophene ring even when R^1 is CH_2OEt (entry 4, Table 2). Moreover, the reaction can be easily conducted in a scale of 4 mmol (1.0811 g) in a slightly higher yield (entry 6, Table 2). Interestingly, benzo[*b*]furan was also formed in a good yield, when furan was used instead of thiophene (entry 8, Table 2).

Table 2
Gold-catalyzed cyclization of 1-heteroarylalka-2,3-dienyl acetates[a]

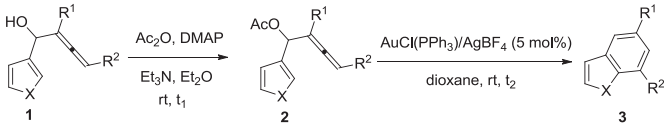


Entry	X	R^1	R^2	Time (h)	Yield of **3**[b] (%)
1	S	Ph	Ac (**2a**)	12	84 (**3a**)
2	S	Bu	Ac (**2b**)	10	85 (**3b**)
3	S	C_7H_{15}	Ac (**2c**)	24	89 (**3c**)
4	S	CH_2OEt	Ac (**2d**)	12	89 (**3d**)
5	S	Ph	Me (**2e**)	12	87 (**3e**)
6[c]	S	Ph	Ac (**2a**)	24	88 (**3a**)
7	S	*p*-MeC_6H_4	Ac (**2f**)	12	93 (**3f**)
8	O	Ph	Ac (**2g**)	24	85 (**3g**)

[a] Reaction conditions: 1.0 mmol **2** and 0.05 mmol $AuCl(PPh_3)/AgBF_4$ in 10 mL of dioxane.
[b] Isolated yield.
[c] The reaction was conducted with 4 mmol (1.0811 g) scale of **2a**.

We found that even the crude residue **2** without any purification can be used directly for the gold-catalyzed cyclization reactions. Thus, as shown in Table 3, R^1 could be H (entries 3 and 4, Table 3), aryl (entry 1, Table 3), or alkyl group (entries 2 and 5–7, Table 3). R^2 could be H (entries 1–2 and 5–7, Table 3), phenyl (entry 4, Table 3), or alkyl group (entry 3, Table 3). Benzo[*b*]furans were also afforded under standard reaction conditions (entries 5–7,Table 3).

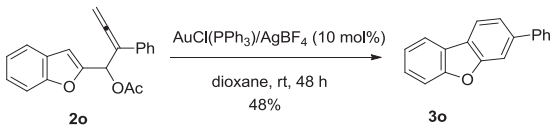
Table 3
Synthesis of benzothiophenes and benzofurans from 1-arylalka-2,3-dienols



Entry	X	R^1	R^2	t_1/t_2 (h)	Yield of **3** (%)[a]
1	S	*p*-$MeOC_6H_4$	H (**2h**)	24/12	73 (**3h**)
2	S	Allyl	H (**2i**)	24/48	38 (**3i**)
3	S	H	Pr (**2j**)	12/24	44 (**3j**)
4	S	H	Ph (**2k**)	18/12	62 (**3k**)
5	O	Bu	H (**2l**)	12/36	52 (**3l**)
6	O	C_7H_{15}	H (**2m**)	12/30	60 (**3m**)
7	O	CH_2OEt	H (**2n**)	12/18	53 (**3n**)

[a] Isolated yield (from **1** to **3**).

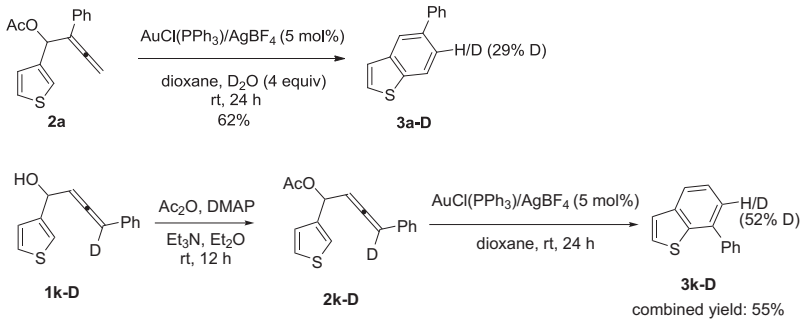
In addition, we have tested the reaction of the benzofuran-derived substrate 1-(benzofuran-2-yl)-2-phenylbuta-2,3-dienyl acetate **2o** in dioxane under the catalysis of $AuCl(PPh_3)/AgBF_4$ (10 mol %) to give dibenzofuran **3o** in 48% yield (Scheme 3).



Scheme 3. Synthesis of dibenzofuran through the gold-catalyzed cyclization.

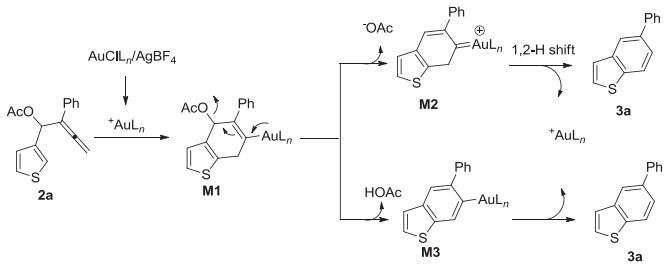
In order to unveil the mechanism, we added D_2O to the reaction mixture of **2a**, the reaction proceeded smoothly to afford **3a**-D in 62% yield with 29% D-incorporation at the 6-position of benzothiophene **3a**-D. The result shows that the reaction may proceed through a carbocation gold intermediate, final protonolysis would release the gold catalyst into the catalytic cycle to afford benzothiophene **3a**-D. Then, we prepared the deuterium-labeled **2k**-D. To our surprise, the **3k**-D was afforded in 55% yield with 52% D-incorporation at the *ortho*-position of phenyl

group (Scheme 4). This means that the reaction may also involve a gold carbene intermediate, subsequent 1,2-D shift would afford **3k**-D.



Scheme 4. The deuterium-labeling reactions.

On the basis of these results, we proposed two possible mechanistic pathways for this reaction.[6,9] The reaction of cationic gold with **2a** would form the intermediate **M1** via the coordination of the allene moiety with gold atom followed by nucleophilic attack of the C2 in the thiophene ring. Subsequent elimination of $^{-}$OAc would afford gold carbene intermediate **M2** followed by 1,2-H shift to afford the final product **3a** with regeneration of the catalytically cationic gold species. Alternatively, elimination of acetic acid would form aromatic gold intermediate **M3**, which would be followed by protonolysis to release the catalytically active species by protonation to afford the target product **3a** (Scheme 5).



Scheme 5. Two proposed pathways.

3. Conclusions

In conclusion, we have developed a general Au-catalyzed reaction of 1-heteroarylalka-2,3-dienyl acetates, providing a series of benzo[*b*]thiophenes, benzo[*b*]furans, and dibenzofurans. Two possible pathways of this reaction are involved in the reaction as indicated by the mechanistic studies. Due to the easy availability of the starting materials, mild conditions, and the potential of the products, this method may be useful in organic synthesis, material science, and medicinal chemistry. Further studies on synthesis applications of this reaction are being carried out in our laboratory.

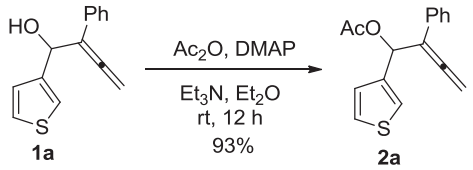
4. Experimental section

4.1. General information

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded with an instrument operated at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. $CDCl_3$ was used as solvent in all NMR experiments. Chemical shifts (δ) are given in parts per million (ppm). Infrared spectra were recorded on an FT-IR spectrometer. Mass spectra were carried out in EI mode. HRMS spectra were carried out in EI mode. Flash column chromatography was performed on silica gel. Et_2O and dioxane were refluxed in the presence of sodium using diphenyl ketone as indicator and distilled right before use. $AuCl(PPh_3)$ was purchased from Alfa.

4.2. Synthesis of 1-heteroarylalka-2,3-dienyl acetates 2a–2d, 2f–2g, and 2o

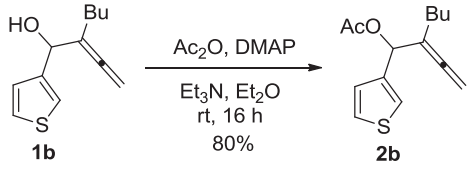
*4.2.1. 2-Phenyl-1-(3-thienyl)buta-2,3-dienyl acetate (**2a**).*



Typical procedure: To a solution of **1a**[6,9b,10] (1.5626 g, 6.86 mmol) and Et_2O (40 mL) were added DMAP (0.1676 g, 1.37 mmol), Et_3N (4.0 mL, d=0.73 g/mL, 2.92 g, 28.9 mmol), and Ac_2O (2.6 mL, d=1.08 g/mL, 2.79 g, 27.4 mmol). The resulting mixture was stirred at room temperature until the reaction was complete as monitored by TLC. After being stirred for 12 h, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL), and extracted with diethyl ether (20 mL×3), then washed by water (10 mL). The ether layer was dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel afforded **2a** (1.7207 g, 93%) (petroleum ether/ethyl acetate=20:1, it should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether and triethylamine (100:1) before loading the sample) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.31 (m, 2H, ArH), 7.30–7.11 (m, 5H, ArH), 7.16 (dd, J_1=5.1 Hz and J_2=0.9 Hz, 1H, thienyl–H), 6.95 (s, 1H, OCH), 5.26 (d, J=1.8 Hz, 2H, =CH_2), 2.13 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 169.8, 139.3, 133.5, 128.3, 127.0, 126.7, 126.5, 125.7, 123.4, 106.5, 80.4, 69.5, 20.9; IR (KBr) ν (cm^{-1}) 3105, 3057, 3033, 2979, 2937, 1941, 1747, 1597, 1578, 1495, 1450, 1423, 1368, 1228, 1152, 1077, 1024; MS (70 eV, EI) m/z (%) 227 (M^{+}-CH_3CO, 33.11), 43 (100). Elemental analysis calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 71.06; H, 5.27.

The following compounds **2b**–**2d**, **2f**–**2g**, and **2o** were prepared according to this procedure.

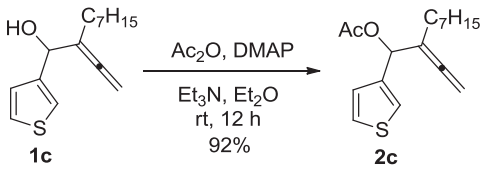
*4.2.2. 2-Butyl-1-(3-thienyl)buta-2,3-dienyl acetate (**2b**).*



The reaction of **1b** (0.6869 g, 3.3 mmol), Et_2O (20 mL), DMAP (0.0812 g, 0.66 mmol), Et_3N (2.0 mL, d=0.73 g/mL, 1.46 g, 14.5 mmol), and Ac_2O (1.25 mL, d=1.08 g/mL, 1.35 g, 13.2 mmol) at

room temperature for 16 h afforded **2b** (0.6568 g, 80%) (petroleum ether/ethyl acetate=40:1, it should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether and triethylamine (100:1) before loading the sample) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.21 (m, 2H, thienyl–H), 7.06 (d, J=4.8 Hz, 1H, thienyl–H), 6.27 (s, 1H, OCH), 4.82–4.61 (m, 2H, =CH_2), 2.10 (s, 3H, CH_3), 1.94–1.83 (m, 2H, CH_2), 1.46–1.21 (m, 4H, 2×CH_2), 0.86 (t, J=7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 169.9, 139.7, 126.6, 125.8, 122.9, 104.1, 78.5, 71.8, 29.5, 27.7, 22.2, 21.1, 13.9; IR (neat) ν (cm^{-1}) 3106, 2957, 2930, 2860, 1958, 1746, 1369, 1231, 1024; MS (70 eV, EI) m/z (%) 251 (M^++1, 2.03), 250 (M^+, 16.31), 249 (100); HRMS calcd for $C_{14}H_{18}O_2S$ (M^+): 250.1028, found: 250.1028.

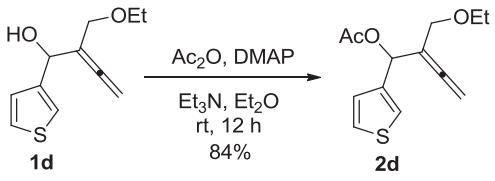
*4.2.3. 2-Heptyl-1-(3-thienyl)buta-2,3-dienyl acetate (**2c**).*



1c **2c**

The reaction of **1c** (0.6256 g, 2.5 mmol), Et_2O (20 mL), DMAP (0.0613 g, 0.5 mmol), Et_3N (2.0 mL, d=0.73 g/mL, 1.46 g, 14.5 mmol), and Ac_2O (0.94 mL, d=1.08 g/mL, 1.02 g, 10.0 mmol) at room temperature for 12 h afforded **2c** (0.6710 g, 92%) (petroleum ether/ethyl acetate=50:1, it should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether and triethylamine (100:1) before loading the sample) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.18 (m, 2H, thienyl–H), 7.05 (dd, J_1=4.7 Hz and J_2=1.5 Hz, 1H, thienyl–H), 6.27 (s, 1H, OCH), 4.90–4.75 (m, 2H, =CH_2), 2.10 (s, 3H, CH_3), 1.94–1.81 (m, 2H, CH_2), 1.47–1.33 (m, 2H, CH_2), 1.33–1.16 (m, 8H, 4×CH_2), 0.87 (t, J=6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 169.9, 139.7, 126.6, 125.8, 122.8, 104.2, 78.4, 71.9, 31.8, 29.1, 29.0, 28.1, 27.3, 22.6, 21.1, 14.0; IR (neat) ν (cm^{-1}) 3107, 2955, 2927, 2856, 1958, 1746, 1465, 1368, 1230, 1150, 1079, 1021; MS (70 eV, EI) m/z (%) 292 (M^+, 1.35), 147 (100); HRMS calcd for $C_{17}H_{24}O_2S$ (M^+): 292.1497, found: 292.1502.

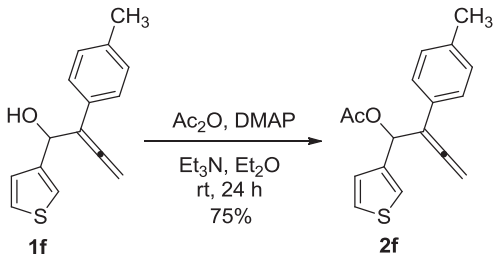
*4.2.4. 2-(Ethoxymethyl)-1-(3-thienyl)buta-2,3-dienyl acetate (**2d**).*



1d **2d**

The reaction of **1d** (0.5698 g, 2.7 mmol), Et_2O (20 mL), DMAP (0.0677 g, 0.54 mmol), Et_3N (2.0 mL, d=0.73 g/mL, 1.46 g, 14.5 mmol), and Ac_2O (1.0 mL, d=1.08 g/mL, 1.10 g, 10.8 mmol) at room temperature for 12 h afforded **2d** (0.5756 g, 84%) (petroleum ether/ethyl acetate=10:1, it should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether and triethylamine (100:1) before loading the sample) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.18 (m, 2H, thienyl–H), 7.09 (dd, J_1=4.8 Hz and J_2=0.9 Hz, 1H, thienyl–H), 6.41 (s, 1H, OCH), 5.03–4.77 (m, 2H, =CH_2), 4.12–3.82 (m, 2H, OCH_2), 3.58–3.30 (m, 2H, OCH_2), 2.08 (s, 3H, CH_3), 1.16 (t, J=7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.4, 169.6, 139.1, 126.5, 125.7, 123.0, 101.7, 78.3, 69.4, 68.7, 65.2, 20.9, 14.9; IR (neat) ν (cm^{-1}) 3105, 2975, 2930, 2865, 1958, 1744, 1369, 1231, 1094, 1024; MS (70 eV, EI) m/z (%) 252 (M^+, 0.02), 209 (M^+–43, 0.48), 43 (100). Elemental analysis calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 61.66; H, 6.34.

*4.2.5. 2-(p-Methylphenyl)-1-(3-thienyl)buta-2,3-dienyl acetate (**2f**)*



1f **2f**

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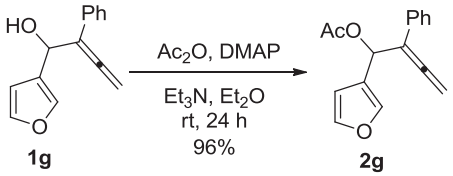
The reaction of **1f** (0.7268 g, 3.0 mmol), Et_2O (20 mL), DMAP (0.0738 g, 0.6 mmol), Et_3N (2.0 mL, d=0.73 g/mL, 1.46 g, 14.5 mmol), and Ac_2O (1.1 mL, d=1.08 g/mL, 1.22 g, 12.0 mmol) at room temperature for 24 h afforded **2f** (0.6424 g, 75%) (petroleum ether/ethyl acetate=20:1, it should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether and triethylamine (100:1) before loading the sample) as a solid: mp 72.9–74.5 °C (n-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.17 (m, 4H, ArH), 7.07–6.90 (m, 3H, ArH), 6.76 (s, 1H, OCH), 5.10 (s, 2H, =CH_2), 2.20 (s, 3H, CH_3), 2.00 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.5, 169.9, 139.5, 136.8, 130.5, 129.1, 126.8, 126.5, 125.8, 123.5, 106.4, 80.4, 69.7, 21.1, 21.0; IR (KBr) ν (cm^{-1}) 1941, 1745, 1606, 1512, 1432, 1369, 1229, 1151, 1079, 1030; MS (70 eV, EI) m/z (%) 284 (M^+, 0.30), 243 (M^+-CH_3CO, 28.28), 242 (100). Elemental analysis calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.62; H, 5.72.

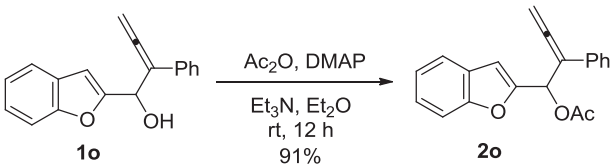
*4.2.6. 1-(3-Furyl)-2-phenylbuta-2,3-dienyl acetate (**2g**).*



1g **2g**

The reaction of **1g** (0.6786 g, 3.2 mmol), Et_2O (20 mL), DMAP (0.0786 g, 0.64 mmol), Et_3N (2.0 mL, d=0.73 g/mL, 1.46 g, 14.5 mmol), and Ac_2O (1.2 mL, d=1.08 g/mL, 1.31 g, 12.8 mmol) at room temperature for 24 h afforded **2g** (0.7779 g, 96%) (petroleum ether/ethyl acetate=30:1, it should be noted that the column packed with silica gel was eluted with a mixture of petroleum ether and triethylamine (100:1) before loading the sample) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.34 (m, 3H, ArH), 7.34–7.23 (m, 3H, ArH), 7.18 (t, J=7.2 Hz, 1H, ArH), 6.76 (s, 1H, furyl-H), 6.40 (s, 1H, OCH), 5.24–5.18 (m, 2H, =CH_2), 2.06 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 170.0, 143.0, 141.1, 133.5, 128.4, 127.1, 126.5, 123.6, 109.7, 106.1, 80.6, 66.7, 21.0; IR (neat) ν (cm^{-1}) 1942, 1746, 1598, 1496, 1450, 1429, 1370, 1232, 1159, 1023; MS (70 eV, EI) m/z (%) 254 (M^+, 1.14), 212 (100); HRMS calcd for $C_{16}H_{14}O_3$ (M^+): 254.0943, found: 254.0943.

*4.2.7. 1-(Benzofuran-2-yl)-2-phenylbuta-2,3-dienyl acetate (**2o**).*

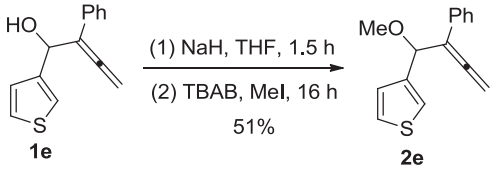


1o **2o**

The reaction of **1o** (1.2839 g, 4.9 mmol), Et_2O (30 mL), DMAP (0.1216 g, 0.98 mmol), Et_3N (3.0 mL, d=0.73 g/mL, 2.19 g,

21.7 mmol), and Ac_2O (1.85 mL, d=1.08 g/mL, 2.00 g, 19.6 mmol) at room temperature for 12 h afforded **2o** (1.3620 g, 91%) (petroleum ether/ethyl acetate=50:1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (t, J=8.9 Hz, 2H, ArH), 7.41 (d, J=7.2 Hz, 2H, ArH), 7.32–7.13 (m, 5H, ArH), 6.95 (s, 1H, ArH), 6.74 (s, 1H, OCH), 5.34–5.23 (m, 2H, =CH_2), 2.14 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 169.5, 154.9, 153.4, 133.1, 128.4, 127.2, 126.3, 124.5, 122.7, 121.1, 111.3, 106.3, 104.4, 81.0, 67.3, 20.8; IR (KBr) ν (cm^{-1}) 1942, 1747, 1598, 1496, 1453, 1370, 1254, 1225, 1027; MS (70 eV, EI) m/z (%) 304 (M^+, 1.36), 262 (100); HRMS calcd for $C_{20}H_{16}O_3$ (M^+): 304.1099, found: 304.1098.

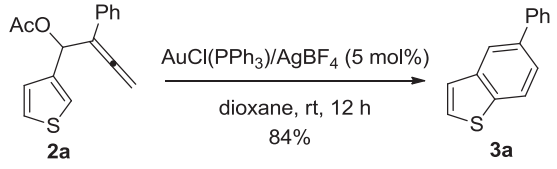
4.3. Synthesis of methyl 2-phenyl-1-(3-thienyl)buta-2,3-dienyl ether (2e)



To a solution of NaH (0.2228 g, 5.55 mmol) and THF (10 mL) was added dropwise **1e** (0.8449, 3.7 mmol)/THF (10 mL) at 0 °C with stirring under a nitrogen atmosphere within 15 min. Then the mixture was allowed to warm up to room temperature. After being stirred for 1.5 h, TBAB (0.1236 g, 0.37 mmol) and MeI (0.35 mL, d=2.28 g/mL, 7.88 g, 5.55 mmol) were added. The resulting mixture was stirred at room temperature until the reaction was complete as monitored by TLC. After being stirred for 16 h, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL), and extracted with diethyl ether (20 mL×3), then washed by water (10 mL) and brine (10 mL). The ether layer was dried over anhydrous Na_2SO_4, filtration, evaporation, and column chromatography on silica gel afforded **2a** (0.4554 g, 51%) (petroleum ether/ethyl acetate=50:1) as a liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J=7.5 Hz, 2H, ArH), 7.29–7.20 (m, 4H, ArH), 7.19–7.14 (m, 1H, ArH), 7.07 (dd, J_1=4.8 Hz and J_2=1.3 Hz, 1H, thienyl–H), 5.27 (s, 1H, OCH), 5.18 (dd, J_1=12.5 Hz and J_2=1.5 Hz, 1H, one proton of =CH_2), 5.14 (dd, J_1=12.3 Hz and J_2=0.8 Hz, 1H, one proton of =CH_2), 3.44 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 141.8, 134.1, 128.3, 127.0, 126.9, 126.7, 125.4, 122.2, 106.1, 79.7, 79.0, 56.7; IR (neat) ν (cm^{-1}) 3055, 2981, 2819, 1938, 1597, 1495, 1450, 1415, 1317, 1217, 1187, 1150, 1091; MS (70 eV, EI) m/z (%) 243 (M^++1, 2.26), 242 (M^+, 9.93), 127 (100); HRMS calcd for $C_{15}H_{14}OS$ (M^+): 242.0765, found: 242.0769.

4.4. Synthesis of 3a–3g and 3o

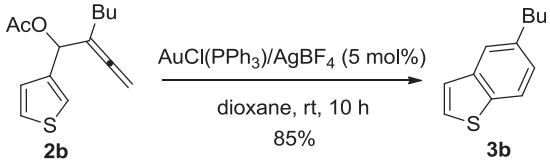
4.4.1. 5-Phenylbenzo[b]thiophene (*3a*).



Typical procedure: A dry Schlenk tube was charged with $AgBF_4$ (10.2 mg, 0.052 mmol, weighed in a glove box), $AuCl(PPh_3)$ (25.1 mg, 0.05 mmol), **2a** (271.8 mg, 1.0 mmol), and dioxane (10 mL) under N_2. The resulting mixture was stirred at room temperature until the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: Et_2O), evaporation, and column chromatography on silica gel afforded **3a** (177.8 mg, 84%) (petroleum ether) as a solid: mp 98.5–99.2 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 1H, ArH), 8.00 (d, J=8.7 Hz, 1H, ArH), 7.74 (d, J=7.5 Hz, 2H, ArH), 7.67 (dd, J_1=8.4 Hz and J_2=1.2 Hz, 1H, ArH), 7.60–7.49 (m, 3H, ArH), 7.49–7.39 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 140.1, 138.7, 137.6, 128.8, 127.4, 127.1, 127.0, 124.0, 123.8, 122.6, 121.9; IR (KBr) ν (cm^{-1}) 1537, 1487, 1447, 1436, 1410, 1180, 1153, 1054, 1031; MS (70 eV, EI) m/z (%) 211 (M^++1, 16.79), 210 (M^+, 100). Elemental analysis calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79. Found: C, 79.80; H, 4.72.

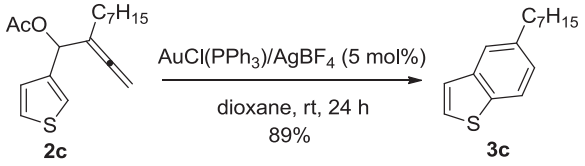
The following compounds **3b**–**3g**, and **3o** were prepared according to this procedure.

4.4.2. 5-Butylbenzo[b]thiophene (*3b*).



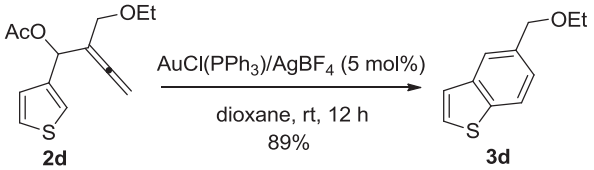
The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (24.8 mg, 0.05 mmol), and **2b** (250.7 mg, 1.0 mmol) in dioxane (10 mL) at room temperature for 10 h afforded **3b** (162.2 mg, 85%) (eluent: petroleum ether) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J=8.1 Hz, 1H, ArH), 7.78 (s, 1H, ArH), 7.52 (d, J=5.4 Hz, 1H, ArH), 7.40 (d, J=5.4 Hz, 1H, ArH), 7.34 (d, J=8.1 Hz, 1H, ArH), 2.89 (t, J=7.8 Hz, 2H, CH_2), 1.91–1.76 (m, 2H, CH_2), 1.63–1.48 (m, 2H, CH_2), 1.13 (t, J=7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 138.9, 137.1, 126.2, 125.4, 123.5, 122.9, 122.0, 35.5, 33.9, 22.3, 14.0; IR (neat) ν (cm^{-1}) 2955, 2927, 2856, 1605, 1502, 1437, 1421, 1089, 1050; MS (70 eV, EI) m/z (%) 191 (M^++1, 3.51), 190 (M^+, 20.32), 147 (100); HRMS calcd for $C_{12}H_{14}S$ (M^+): 190.0816, found: 190.0821.

4.4.3. 5-Heptylbenzo[b]thiophene (*3c*).



The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.05 mmol), and **2c** (292.1 mg, 1.0 mmol) in dioxane (10 mL) at room temperature for 24 h afforded **3c** (206.8 mg, 89%) (eluent: petroleum ether) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J=8.1 Hz, 1H, ArH), 7.66 (s, 1H, ArH), 7.43 (d, J=5.4 Hz, 1H, ArH), 7.31 (d, J=5.4 Hz, 1H, ArH), 7.22 (d, J=8.1 Hz, 1H, ArH), 2.76 (t, J=7.7 Hz, 2H, CH_2), 1.80–1.64 (m, 2H, CH_2), 1.47–1.23 (m, 8H, 4×CH_2), 0.93 (t, J=6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 139.0, 137.1, 126.3, 125.4, 123.6, 122.9, 122.1, 35.9, 31.9, 31.8, 29.3, 29.2, 22.7, 14.1; IR (neat) ν (cm^{-1}) 2954, 2926, 2853, 1459, 1437, 1420, 1089, 1050; MS (70 eV, EI) m/z (%) 233 (M^++1, 2.25), 232 (M^+, 13.35), 147 (100); HRMS calcd for $C_{15}H_{20}S$ (M^+): 232.1286, found: 232.1287.

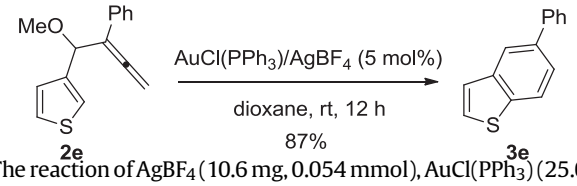
4.4.4. 5-(Ethoxymethyl)benzo[b]thiophene (*3d*).



The reaction of $AgBF_4$ (10.3 mg, 0.053 mmol), $AuCl(PPh_3)$ (24.6 mg, 0.05 mmol), and **2d** (252.6 mg, 1.0 mmol) in dioxane

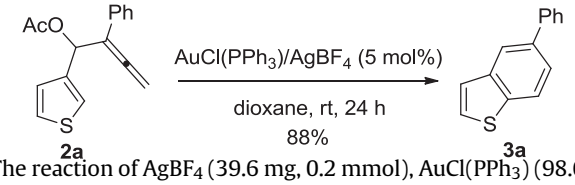
(10 mL) at room temperature for 12 h afforded **3d** (170.8 mg, 89%) (eluent: petroleum ether→petroleum ether/ethyl acetate=100:1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J=8.4 Hz, 1H, ArH), 7.77 (s, 1H, ArH), 7.39 (d, J=5.4 Hz, 1H, ArH), 7.35–7.24 (m, 2H, ArH), 4.59 (s, 2H, CH_2), 3.54 (q, J=7.0 Hz, 2H, CH_2), 1.24 (t, J=7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 138.9, 134.7, 126.6, 124.2, 123.7, 122.6, 122.3, 72.7, 65.6, 15.2; IR (neat) ν (cm^{-1}) 2973, 2928, 2862, 1436, 1373, 1354, 1325, 1148, 1097, 1050, 1015; MS (70 eV, EI) m/z (%) 193 (M^++1, 3.71), 192 (M^+, 27.41), 147 (100); HRMS calcd for $C_{11}H_{12}OS$ (M^+): 192.0609, found: 192.0611.

4.4.5. 5-Phenylbenzo[b]thiophene (**2e**).



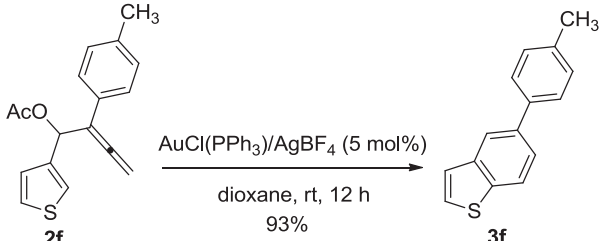
The reaction of $AgBF_4$ (10.6 mg, 0.054 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.05 mmol), and **2e** (243.1 mg, 1.0 mmol) in dioxane (10 mL) at room temperature for 12 h afforded **3e** (184.0 mg, 87%) (eluent: petroleum ether→petroleum ether/ethyl acetate=100:1) as a solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J=1.2 Hz, 1H, ArH), 8.03 (d, J=8.4 Hz, 1H, ArH), 7.78 (d, J=7.2 Hz, 2H, ArH), 7.70 (dd, J_1=8.3 Hz and J_2=1.4 Hz, 1H, ArH), 7.63–7.42 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 140.1, 138.7, 137.6, 128.8, 127.3, 127.1, 126.9, 124.0, 123.8, 122.6, 121.9.

4.4.6. 5-Phenylbenzo[b]thiophene (**3a**).



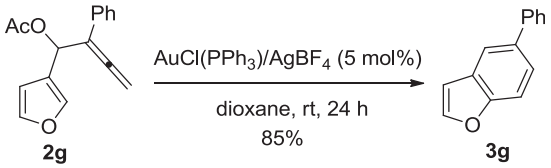
The reaction of $AgBF_4$ (39.6 mg, 0.2 mmol), $AuCl(PPh_3)$ (98.6 mg, 0.2 mmol), and **2a** (1081.1 mg, 4.0 mmol) in dioxane (40 mL) at room temperature for 24 h afforded **3a** (739.2 mg, 88%) (eluent: petroleum ether→petroleum ether/ethyl acetate=100:1) as a solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J=1.2 Hz, 1H, ArH), 8.03 (d, J=8.1 Hz, 1H, ArH), 7.83–7.73 (m, 2H, ArH), 7.70 (dd, J_1=8.6 Hz and J_2=1.4 Hz, 1H, ArH), 7.63–7.42 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 140.1, 138.7, 137.6, 128.7, 127.3, 127.0, 126.9, 124.0, 123.8, 122.6, 121.9.

4.4.7. 5-(p-Methylphenyl)benzo[b]thiophene (**3f**).



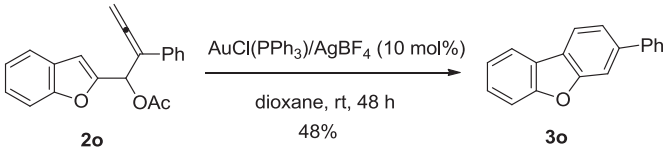
The reaction of $AgBF_4$ (10.3 mg, 0.053 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.05 mmol), and **2f** (285.6 mg, 1.0 mmol) in dioxane (10 mL) at room temperature for 12 h afforded **3f** (208.7 mg, 93%) (eluent: petroleum ether) as a solid: mp 121.8–123.9 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (s, 1H, ArH), 7.91 (d, J=8.7 Hz, 1H, ArH), 7.62–7.50 (m, 3H, ArH), 7.45 (d, J=5.4 Hz, 1H, ArH), 7.36 (d, J=5.1 Hz, 1H, ArH), 7.26 (d, J=8.1 Hz, 2H, ArH), 2.40 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 138.5, 138.4, 137.6, 136.9, 129.5, 127.2, 126.9, 124.0, 123.8, 122.6, 121.7, 21.1; IR (KBr) ν (cm^{-1}) 1542, 1519, 1497, 1437, 1421, 1401, 1177, 1158, 1115, 1089, 1057, 1025; MS (70 eV, EI) m/z (%) 225 (M^++1, 20.00), 224 (M^+, 100). Elemental analysis calcd for $C_{15}H_{12}S$: C, 80.31; H, 5.39. Found: C, 80.38; H, 5.39.

4.4.8. 5-Phenylbenzo[b]furan (**3g**).



The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.05 mmol), and **2g** (254.1 mg, 1.0 mmol) in dioxane (10 mL) at room temperature for 24 h afforded **3g**[11] (164.6 mg, 85%) (eluent: petroleum ether→petroleum ether/ethyl acetate=100:1) as a solid: mp 58.6–59.9 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (s, 1H, ArH), 7.79–7.62 (m, 5H, ArH), 7.57 (t, J=7.7 Hz, 2H, ArH), 7.47 (t, J=7.2 Hz, 1H, ArH), 6.90 (d, J=1.5 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 145.4, 141.6, 136.4, 128.7, 127.9, 127.4, 126.8, 123.9, 119.6, 111.4, 106.7; IR (KBr) ν (cm^{-1}) 1601, 1536, 1463, 1428, 1330, 1296, 1261, 1229, 1160, 1132, 1111, 1031, 1015; MS (70 eV, EI) m/z (%) 195 (M^++1, 15.43), 194 (M^+, 100).

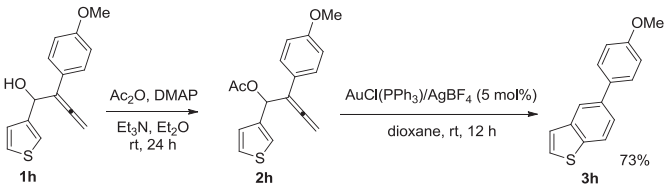
4.4.9. 3-Phenyldibenzofuran (**3o**).



The reaction of $AgBF_4$ (20.1 mg, 0.1 mmol), $AuCl(PPh_3)$ (49.8 mg, 0.1 mmol), and **2o** (304.6 mg, 1.0 mmol) in dioxane (10 mL) at room temperature for 48 h afforded **3o** (118.0 mg, 48%) (eluent: petroleum ether→petroleum ether/dichloromethane=10:1) as a solid: mp 131.9–132.9 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06–7.96 (m, 2H, ArH), 7.85 (s, 1H, ArH), 7.78–7.71 (m, 2H, ArH), 7.68–7.61 (m, 2H, ArH), 7.58–7.37 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 156.5, 140.9, 140.6, 128.8, 127.4, 127.3, 127.0, 124.0, 123.2, 122.7, 122.1, 120.7, 120.6, 111.6, 110.0; IR (KBr) ν (cm^{-1}) 1597, 1571, 1514, 1484, 1456, 1416, 1356, 1299, 1228, 1175, 1103; MS (70 eV, EI) m/z (%) 245 (M^++1, 18.42), 244 (M^+, 100). Elemental analysis calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.40; H, 4.98.

4.5. Synthesis of 3h–3n

4.5.1. 5-(p-Methoxyphenyl)benzo[b]thiophene (**3h**).



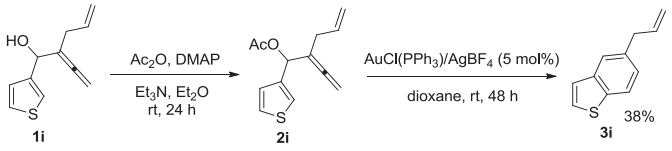
Typical procedure: To a solution of **1h** (0.2418 g, 0.94 mmol) and Et_2O (10 mL) were added DMAP (0.0246 g, 0.2 mmol), Et_3N (1.0 mL, d=0.73 g/mL, 0.73 g, 7.2 mmol), and Ac_2O (0.38 mL, d=1.08 g/mL, 0.41 g, 4.0 mmol). The resulting mixture was stirred at room temperature until the reaction was complete as monitored by TLC. After being stirred for 12 h, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL), and extracted with diethyl ether (20 mL×3), then washed by water and brine. The ether layer was dried over anhydrous Na_2SO_4. Filtration through a short column of silica gel (eluent: Et_2O), evaporation, and filtration through a short column of silica gel (eluent: Et_2O) and evaporation afforded **2h**. The product **2h** was then used without further purification.

A dry Schlenk tube was charged with $AgBF_4$ (10.3 mg, 0.053 mmol, weighed in a glove box), $AuCl(PPh_3)$ (24.6 mg,

0.05 mmol), **2h** (prepared in the previous step), and dioxane (10 mL) under N_2. The resulting mixture was stirred at room temperature until the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: Et_2O), evaporation, and column chromatography on silica gel afforded **3h** (163.8 mg, 73%, from **1h** to **3h**) (eluent: petroleum ether→petroleum ether/ethyl acetate=50:1) as a solid: mp 140.6–141.8 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J=0.9 Hz, 1H, ArH), 7.94 (d, J=8.4 Hz, 1H, ArH), 7.67–7.55 (m, 3H, ArH), 7.49 (d, J=5.1 Hz, 1H, ArH), 7.39 (d, J=5.7 Hz, 1H, ArH), 7.03 (d, J=9.0 Hz, 2H, ArH), 3.88 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 140.2, 138.1, 137.3, 133.8, 128.3, 126.9, 124.0, 123.6, 122.6, 121.4, 114.2, 55.3; IR (KBr) ν (cm^{-1}) 1607, 1575, 1523, 1496, 1303, 1283, 1264, 1249, 1092, 1034, 1016; MS (70 eV, EI) m/z (%) 241 (M^++1, 14.98), 240 (M^+, 100). Elemental analysis calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03. Found: C, 74.97, H, 5.33.

The following compounds **3i**–**3n** were prepared according to this procedure.

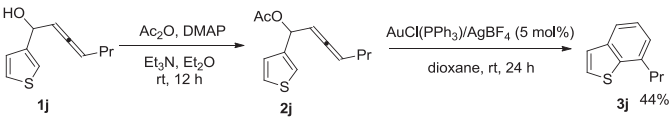
*4.5.2. 5-Allylbenzo[b]thiophene (**3i**).*



The reaction of **1i** (0.1930 g, 1.0 mmol), Et_2O (10 mL), DMAP (0.0246 g, 0.2 mmol), Et_3N (1.0 mL, d=0.73 g/mL, 0.73 g, 7.2 mmol), and Ac_2O (0.38 mL, d=1.08 g/mL, 0.41 g, 4.0 mmol) at room temperature for 24 h afforded **2i**. The product **2i** was then used without further purification.

The reaction of $AgBF_4$ (10.7 mg, 0.055 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.05 mmol), and **2i** (prepared in the previous step) in dioxane (10 mL) at room temperature for 48 h afforded **3i** (65.6 mg, 38%, from **1i** to **3i**) (eluent: petroleum ether) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J=8.1 Hz, 1H, ArH), 7.61 (s, 1H, ArH), 7.37 (d, J=5.1 Hz, 1H, ArH), 7.24 (d, J=5.4 Hz, 1H, ArH), 7.16 (dd, J_1=8.1 Hz and J_2=0.6 Hz, 1H, ArH), 6.09–5.89 (m, 1H, =CH), 5.18–4.97 (m, 2H, =CH_2), 3.48 (d, J=6.6 Hz, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 137.6, 137.5, 136.1, 126.5, 125.4, 123.6, 123.2, 122.3, 115.8, 40.1; IR (neat) ν (cm^{-1}) 3075, 3003, 2976, 2901, 1638, 1606, 1503, 1435, 1421, 1327, 1259, 1222, 1158, 1143, 1089, 1050; MS (70 eV, EI) m/z (%) 175 (M^++1, 17.35), 174 (M^+, 100); HRMS calcd for $C_{11}H_{10}S$ (M^+): 174.0503, found: 174.0502.

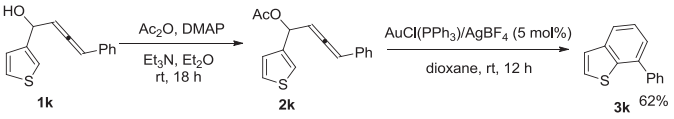
*4.5.3. 7-Propylbenzo[b]thiophene (**3j**).*



The reaction of **1j** (0.1932 g, 1.0 mmol), Et_2O (10 mL), DMAP (0.0250 g, 0.2 mmol), Et_3N (1.0 mL, d=0.73 g/mL, 0.73 g, 7.2 mmol), and Ac_2O (0.38 mL, d=1.08 g/mL, 0.41 g, 4.0 mmol) at room temperature for 12 h afforded **2j**. The product **2j** was then used without further purification.

The reaction of $AgBF_4$ (10.3 mg, 0.052 mmol), $AuCl(PPh_3)$ (25.0 mg, 0.05 mmol), and **2j** (prepared in the previous step) in dioxane (10 mL) at room temperature for 24 h afforded **3j** (76.3 mg, 44%, from **1j** to **3j**) (eluent: petroleum ether) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J=7.8 Hz, 1H, ArH), 7.46 (d, J=5.1 Hz, 1H, ArH), 7.42–7.32 (m, 2H, ArH), 7.21 (d, J=6.9 Hz, 1H, ArH), 2.93 (t, J=7.5 Hz, 2H, CH_2), 2.00–1.80 (m, 2H, CH_2), 1.07 (t, J=7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 139.6, 136.6, 125.5, 124.5, 123.4, 121.3, 37.1, 22.4, 14.1; IR (neat) ν (cm^{-1}) 2958, 2930, 2870, 1571, 1461, 1394, 1378, 1250, 1109, 1087, 1036; MS (70 eV, EI) m/z (%) 177 (M^++1, 4.69), 176 (M^+, 35.42), 84 (100); HRMS calcd for $C_{11}H_{12}S$ (M^+): 176.0660, found: 176.0662.

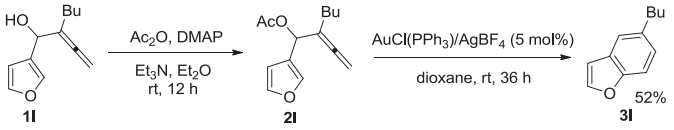
*4.5.4. 7-Phenylbenzo[b]thiophene (**3k**).*



The reaction of **1k** (0.2290 g, 1.0 mmol), Et_2O (10 mL), DMAP (0.0240 g, 0.2 mmol), Et_3N (1.0 mL, d=0.73 g/mL, 0.73 g, 7.2 mmol), and Ac_2O (0.38 mL, d=1.08 g/mL, 0.41 g, 4.0 mmol) at room temperature for 18 h afforded **2k**. The product **2k** was then used without further purification.

The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (25.1 mg, 0.05 mmol), and **2k** (prepared in the previous step) in dioxane (10 mL) at room temperature for 12 h afforded **3k** (130.0 mg, 62%, from **1k** to **3k**) (eluent: petroleum ether) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01–7.82 (m, 3H, ArH), 7.70–7.44 (m, 7H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 140.3, 138.8, 136.7, 128.7, 128.1, 127.8, 126.6, 124.8, 124.23, 124.20, 122.6; IR (neat) ν (cm^{-1}) 3100, 3056, 3027, 1602, 1574, 1510, 1490, 1457, 1444, 1378, 1347, 1217, 1181, 1099, 1076, 1042, 1028; MS (70 eV, EI) m/z (%) 211 (M^++1, 16.23), 210 (M^+, 100); HRMS calcd for $C_{14}H_{10}S$ (M^+): 210.0503, found: 210.0500.

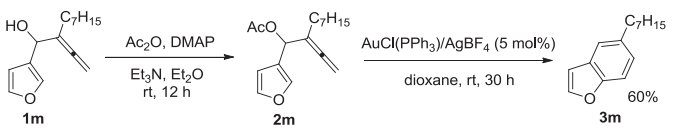
*4.5.5. 5-Butylbenzo[b]furan (**3l**).*



The reaction of **1l** (0.1906 g, 1.0 mmol), Et_2O (10 mL), DMAP (0.0246 g, 0.2 mmol), Et_3N (1.0 mL, d=0.73 g/mL, 0.73 g, 7.2 mmol), and Ac_2O (0.38 mL, d=1.08 g/mL, 0.41 g, 4.0 mmol) at room temperature for 12 h afforded **2l**. The product **2l** was then used without further purification.

The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (25.1 mg, 0.05 mmol), and **2l** (prepared in the previous step) in dioxane (10 mL) at room temperature for 36 h afforded **3l** (90.5 mg, 52%, from **1l** to **3l**) (eluent: petroleum ether) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J=1.8 Hz, 1H, ArH), 7.51–7.40 (m, 2H, ArH), 7.17 (dd, J_1=8.3 Hz and J_2=1.7 Hz, 1H, ArH), 6.75 (d, J=1.5 Hz, 1H, ArH), 2.76 (t, J=7.7 Hz, 2H, CH_2), 1.77–1.62 (m, 2H, CH_2), 1.52–1.36 (m, 2H, CH_2), 1.00 (t, J=7.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 144.9, 137.3, 127.4, 124.9, 120.3, 110.8, 106.3, 35.5, 34.3, 22.3, 13.9; IR (neat) ν (cm^{-1}) 3022, 2956, 2929, 2857, 1614, 1590, 1538, 1469, 1444, 1378, 1329, 1262, 1196, 1127, 1110, 1032; MS (70 eV, EI) m/z (%) 175 (M^++1, 2.93), 174 (M^+, 18.85), 131 (100); HRMS calcd for $C_{12}H_{14}O$ (M^+): 174.1045, found: 174.1044.

*4.5.6. 5-Heptylbenzo[b]furan (**3m**).*

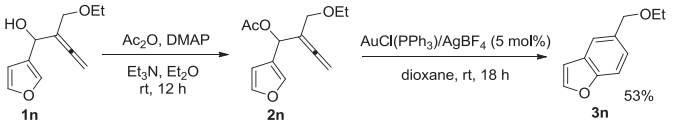


The reaction of **1m** (0.2343 g, 1.0 mmol), Et_2O (10 mL), DMAP (0.0250 g, 0.2 mmol), Et_3N (1.0 mL, d=0.73 g/mL, 0.73 g, 7.2 mmol), and Ac_2O (0.38 mL, d=1.08 g/mL, 0.41 g, 4.0 mmol) at room

temperature for 12 h afforded **2m**. The product **2m** was then used without further purification.

The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (25.1 mg, 0.05 mmol), and **2m** (prepared in the previous step) in dioxane (10 mL) at room temperature for 30 h afforded **3m** (130.0 mg, 60%, from **1m** to **3m**) (eluent: petroleum ether) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J=2.1 Hz, 1H, ArH), 7.52–7.39 (m, 2H, ArH), 7.18 (d, J=8.4 Hz, 1H, ArH), 6.84–6.66 (m, 1H, ArH), 2.76 (t, J=7.5 Hz, 2H, CH_2), 1.80–1.63 (m, 2H, CH_2), 1.48–1.26 (m, 8H, 4×CH_2), 0.96 (t, J=6.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 144.9, 137.4, 127.4, 124.9, 120.3, 110.9, 106.4, 35.9, 32.2, 31.9, 29.3, 29.2, 22.7, 14.1; IR (neat) ν (cm^{-1}) 2955, 2927, 2855, 1538, 1468, 1444, 1262, 1197, 1128, 1110, 1033; MS (70 eV, EI) m/z (%) 217 (M^++1, 3.97), 216 (M^+, 19.82), 131 (100); HRMS calcd for $C_{15}H_{20}O$ (M^+): 216.1514, found: 216.1515.

*4.5.7. 5-(Ethoxymethyl)benzo[b]furan (**3n**).*



The reaction of **1n** (0.1943 g, 1.0 mmol), Et_2O (10 mL), DMAP (0.0250 g, 0.2 mmol), Et_3N (1.0 mL, d=0.73 g/mL, 0.73 g, 7.2 mmol), and Ac_2O (0.38 mL, d=1.08 g/mL, 0.41 g, 4.0 mmol) at room temperature for 12 h afforded **2n**. The product **2n** was then used without further purification.

The reaction of $AgBF_4$ (10.8 mg, 0.055 mmol), $AuCl(PPh_3)$ (24.6 mg, 0.05 mmol), and **2n** (prepared in the previous step) in dioxane (10 mL) at room temperature for 18 h afforded **3n** (92.6 mg, 53%, from **1n** to **3n**) (eluent: petroleum ether/ethyl acetate=100:1 to 50:1) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J=2.1 Hz, 1H, ArH), 7.60 (s, 1H, ArH), 7.49 (d, J=8.4 Hz, 1H, ArH), 7.31 (dd, J_1=8.4 Hz and J_2=1.2 Hz, 1H, ArH), 6.76 (d, J=1.5 Hz, 1H, ArH), 4.61 (s, 2H, CH_2), 3.58 (q, J=6.9 Hz, 2H, CH_2), 1.28 (t, J=7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 145.2, 133.1, 127.4, 124.3, 120.5, 111.1, 106.5, 72.8, 65.5, 15.2; IR (neat) ν (cm^{-1}) 2975, 2930, 2864, 1538, 1470, 1444, 1375, 1355, 1329, 1264, 1197, 1128, 1108, 1032; MS (70 eV, EI) m/z (%) 177 (M^++1, 2.02), 176 (M^+, 17.47), 131 (100); HRMS calcd for $C_{11}H_{12}O_2$ (M^+): 176.0837, found: 176.0835.

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Supplementary data

Supplementary data related to this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.099.

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