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Catalytic Sulfur-Enabled Dehydrobicyclization of 1,6-Enynes toward Arylated Indeno[1,2-*c*]thiophenes

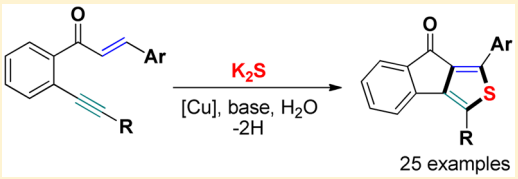
Ya-Nan Wu,[†] Rong Fu,[†] Nan-Nan Wang,[†] Wen-Juan Hao,*[,†] Guigen Li,[‡] Shu-Jiang Tu,*[,†] and Bo Jiang*[,†]

[†]School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, PR China

[‡]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, United States

Supporting Information

ABSTRACT: A new copper-catalyzed sulfur-enabled dehydrobicyclization of 1,6-enynes using potassium sulfide as a sulfurating reagent has been established, providing a straightforward access toward arylated indeno[1,2-*c*]thiophenes with moderate to good yields. This sulfur incorporation pathway involves Michael addition, 5-*exo*-*dig*/5-*endo*-*trig* bicyclization and dehydrogenation sequence, resulting in continuous multiple bond-forming events including C−S and C−C bonds to rapidly construct functional organic molecules.

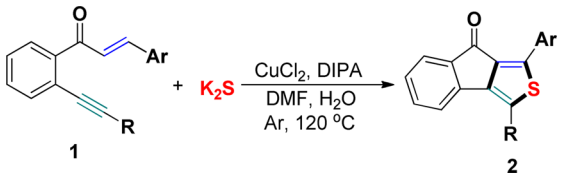


INTRODUCTION

Sulfur-containing compounds have been extensively applied in pharmaceuticals, agrochemicals, and functional materials, and served as synthetic intermediates.[1] Organosulfur compounds are widespread in natural products and synthetically bioactive molecules.[2] Considerable efforts have been devoted to powerful and reliable methods for the incorporation of sulfur into organic frameworks.[3] Since Migita and co-workers reported Pd-catalyzed coupling of thiols and aryl halides,[4] a variety of transition-metal species, such as Pd,[5] Cu,[6] Fe,[7] and Rh,[8] have been utilized in C−S bond formation. However, in most cases, the use of foul-smelling and volatile sulfur sources such as thiols and disulfides is indispensable. To address these issues, some alternative sulfur transfer reagents like thiourea,[9] potassium ethyl xanthogenate,[10] and thiocyanate[11] have been developed to construct C−S bonds. Recently, metal sulfides as promising sulfurating reagents were employed to synthesize *S*-heterocycle through metal-catalyzed double C−S bonds formation.[12] For example, Xi et al. developed Cu-catalyzed double *S*-alkenylation of potassium sulfide with dienyl diiodides toward the formation of highly substituted thiophenes.[12d] Afterward, Liang and co-workers reported a copper-catalyzed synthesis of benzothiazoles using potassium sulfide as a sulfurating reagent.[12e] Li and co-workers presented a copper-catalyzed cascade cyclization of 1,7-enynes with potassium sulfide leading to 3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-ones.[12f] However, in sharp contrast, a practical metal-catalyzed dehydrobicyclization of 1,6-eyens with potassium sulfide allowing direct formation of richly decorated indeno-fused thiophenes has met with little success but represents a highly desirable methodology considering its bond-forming efficiency and highly functional group tolerance.

The increasingly popular bicyclization strategy represents a uniquely powerful tool to access highly functionalized polycyclic structures of chemical and biomedical importance.[13] With both unsaturated moieties, 1,6-enynes are significant building blocks for metal-catalyzed tandem additions and result in functionalized cyclic structures via synergistic domino bicyclizations across C=C and C≡C bonds of various substrates in an atom- and step-economical manner.[14] In recent years, we have developed domino bicyclization reactions for polycyclic framework formations.[15] As a continuation of our project on these bicyclizations, we became interested in metal-catalyzed cycloadditions between 1,6-enynes and nucleophiles. Considering the significant applications of Cu-catalyzed C−S bond forming reactions,[6] we envisioned that in the presence of suitable copper catalyst, potassium sulfide could be engaged in additional bond-forming events with C=C and C≡C bonds of 1,6-enyne conjugate system,[12f] thereby facilitating the construction of densely functionalized indeno[1,2-*c*]thiophenes with concomitant multiple C−S and C−C bond formation (Scheme 1). Herein, we would like to report the realization of this concept via $CuCl_2$-catalyzed cyclization cascades which enabled the one-pot synthesis of important indeno[1,2-*c*]thiophenes. To the best of our knowledge, the present work represents the first example of 1,6-enyne-dehydrobicyclization for forming important types of tricyclic products containing indene and thiophene motifs using potassium sulfide

Scheme 1. Domino Synthesis of Indeno[1,2-*c*]thiophenes



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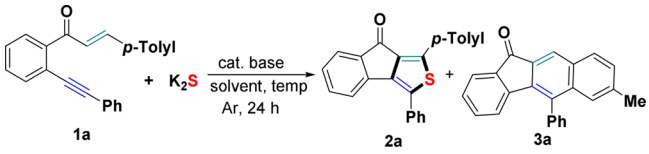
as a sulfurating reagent through incorporation of a sulfur atom into the desired structure system.

RESULTS AND DISCUSSION

Our initial investigations focused on the cascade cyclization of 1,6-enynes **1a** with K_2S for reaction condition optimization using different catalysts, bases and solvents (Table 1). First, the

Table 1. Optimization of Reaction Conditions[a]



entry	cat. (mol %)	base	solvent	t/°C	yield (%)[b] 2a/3a
1	$CuCl_2$ (20)	Cs_2CO_3	DMF	120	35/50
2	$CuCl_2$ (20)	K_2CO_3	DMF	120	34/53
3	$CuCl_2$ (20)	Et_3N	DMF	120	46/44
4	$CuCl_2$ (20)	Bu_3N	DMF	120	trace/80
5	$CuCl_2$ (20)	^{t}BuOLi	DMF	120	44/41
6	$CuCl_2$ (20)	DIPA	DMF	120	67/16
7	CuCl (20)	DIPA	DMF	120	32/56
8	CuBr (20)	DIPA	DMF	120	32/50
9	CuI (20)	DIPA	DMF	120	33/51
10	$Cu(OTf)_2$ (20)	DIPA	DMF	120	40/43
11	$Cu(OAc)_2$ (20)	DIPA	DMF	120	23/37
12	$FeCl_3$ (20)	DIPA	DMF	120	15/47
13	$PdCl_2$ (20)	DIPA	DMF	120	34/61
14	$Pd(OAc)_2$ (20)	DIPA	DMF	120	37/50
15	$CuCl_2$ (20)	DIPA	1,4-dioxane	120	15/57
16	$CuCl_2$ (20)	DIPA	DMSO	120	10/62
17	$CuCl_2$ (20)	DIPA	CH_3CN	120	24/47
18	$CuCl_2$ (20)	DIPA	toluene	120	trace/84
19	$CuCl_2$ (20)	DIPA	DMF	110	38/36
20	$CuCl_2$ (20)	DIPA	DMF	130	57/32
21	$CuCl_2$ (25)	DIPA	DMF	120	66/20
22	$CuCl_2$ (15)	DIPA	DMF	120	42/44
23	$CuCl_2$ (20)	DIPA	DMF	120	34/53[c]
24	$CuCl_2$ (20)	DIPA	DMF	120	54/32[d]
25	$CuCl_2$ (20)	DIPA	DMF	120	43/50[e]
26	$CuCl_2$ (20)	DIPA	DMF	120	27/56[f]
27	$CuCl_2$ (20)	DIPA	DMF	120	75/8[g]
28	–	DIPA	DMF	120	0/52[g]
29	$CuCl_2$ (20)	–	DMF	120	trace/41[g]

[a]Reaction conditions: **1a** (0.5 mmol), K_2S (3.0 mmol), catalyst (x mol %), base (3.0 equiv) and solvent (4.0 mL) under argon atmosphere for 24 h. [b]Isolated yields based on **1a**. [c]Isolated yield using 4.0 equiv of DIPA. [d]Isolated yield using 2.0 equiv of DIPA. [e]Isolated yield in 1:4 ratio of **1a** with K_2S. [f]Isolated yield under air conditions. [g]Isolated yield using 6.0 equiv of H_2O as additive.

reaction between 1,6-enynes **1a** and K_2S was conducted with 20 mol % $CuCl_2$ and 3.0 equiv of Cs_2CO_3 at 120 °C under an argon atmosphere in *N*,*N*-dimethylformamide (DMF) for 24 h. This set of conditions gave the desired product **2a** in a 35% yield, but with an intramolecular cycloaddition product **3a** in a 50% yield[16] (entry 1). To improve the yield of **2a**, a series of different bases, including K_2CO_3, Et_3N, Bu_3N, *t*-BuOLi, and diisopropylamine (DIPA), were then evaluated (entries 2–6), and the results showed that DIPA was proven to be most effective for this transformation, affording a 67% chemical yield of **2a** (entry 6). Several other copper salts used in this reaction like CuCl, CuBr, CuI, $Cu(OTf)_2$ and $Cu(OAc)_2$, all showed poor catalytic activities toward the formation of **2a** (entries 7–11). Similarly, the inferior outcomes were also observed when the reactions were carried out using $FeCl_3$, $PdCl_2$ and $Pd(OAc)_2$ as catalysts (entries 12–14). Afterward, taking the combination of $CuCl_2$ with DIPA, we varied other parameters. The effect of the solvent was subsequently investigated. Unluckily, the use of other aprotic solvents, such as 1,4-dioxane, dimethyl sulfoxide (DMSO), acetonitrile (CH_3CN), and toluene, failed to improve the yield of **2a**, but favorably gave access to product **3a** (entries 15–18). It was also found that the reaction temperatures affected the reaction efficiency. The relatively lower conversion into **2a** was detected with reaction temperature being at either 110 or 130 °C (entries 19 and 20). An increased or decreased loading of $CuCl_2$ or DIPA did not significantly improve the yield (compare entry 6 vs entries 21–24). Adjusting the ratio of **1a** with K_2S to 1:4 decreased the yield of **2a** (entry 25). The identical reaction performed under air conditions dramatically lowered the yield to 27% (entry 26). After careful optimizations, some water can promote this transformation, leading to the higher yield of **2a** (75%) and suppressing the formation of **3a** (entry 27). Without $CuCl_2$ or DIPA, the reaction is beneficial to form product **3a** without observation of product **2a** (entries 28–29).

After determining the optimal reaction conditions (Table 1, entry 27), we then set out to investigate the scope of sulfur-enabled dehydrobicyclization toward the formation of indeno[1,2-*c*]thiophenes **2** by examining 1,6-enyne component with potassium sulfide (Scheme 2). A wide range of 1,6-enynes **1** smoothly reacted with potassium sulfide to deliver the corresponding densely functionalized indeno[1,2-*c*]thiophenes **2a**–**2y** with yields ranging from 45–79%. 1,6-Enynes **1** possessing both arylvinyl and arylalkynyl moieties attached by electron-donating or electron-withdrawing groups did not hamper the reaction process. A large variety of diverse functional groups directly bounded phenyl ring, including methyl, methoxy, ethyl, *t*-butyl, fluoro, and chloro, can tolerate the catalytic conditions well. Electronic properties of substituents on both arylvinyl and the arylalkynyl moieties imposed an obvious impact on the reaction efficiency and the obtained yields. For instance, with the methyl group on the arylvinyl moiety (Ar), upon treatment of substrates **1** with electron-donating groups like methoxy (**1c**) and ethyl (**1d**), and the desired products **2c** and **2d** were provided in 68% and 76% yields, respectively. In contrast, the presence of a fluoro group of substrate **1g** resulted in a 45% chemical yield. These observations indicated that substrates **1** bearing electron-donating groups showed the higher reactivity than those with electron-withdrawing counterparts. Alternatively, 1,6-enynes **1h** carrying a *n*-butyl group on the alkynyl moiety still showed high reactivity in current dehydrobicyclization, delivering the corresponding product **2h** in a 59% yield. Unluckily, 1,5-enyne **4a** was not an adaptable substrate for this dehydrobicyclization reaction without observation of the expected product **5a**, as the reaction did not proceed at all under the standard conditions (Scheme 2, **5a**). Highly substituted indeno[1,2-*c*]thiophenes **2** were fully characterized by their NMR spectroscopy and HRMS. Furthermore, the structure of product **2a** was determined by single crystal X-ray diffraction (see Supporting Information). In general, the current protocol represents a new and practical pathway for directly constructing richly decorated indeno[1,2-*c*]thiophenes.[17]

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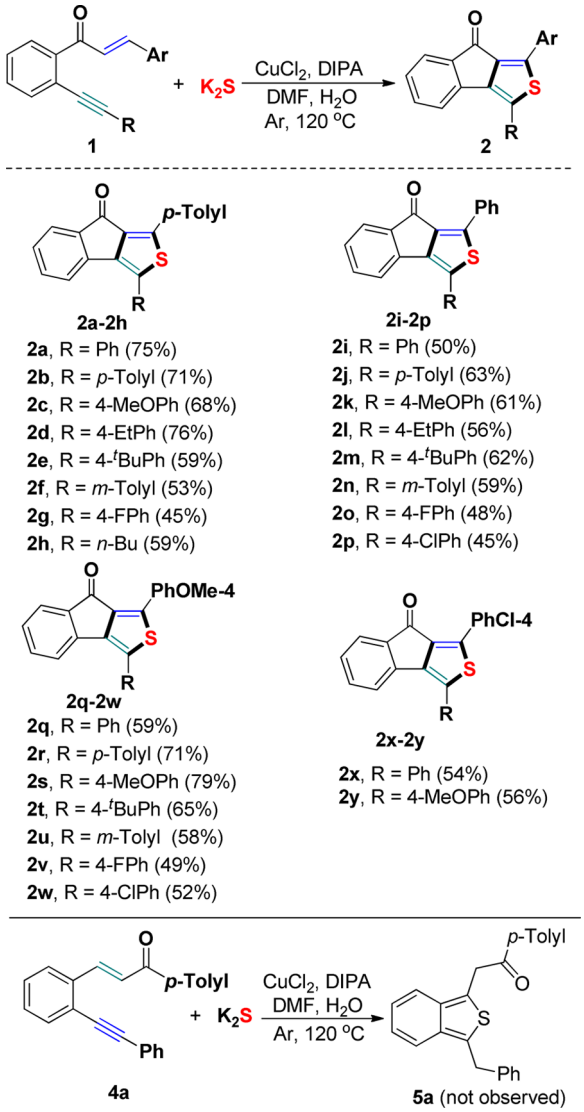
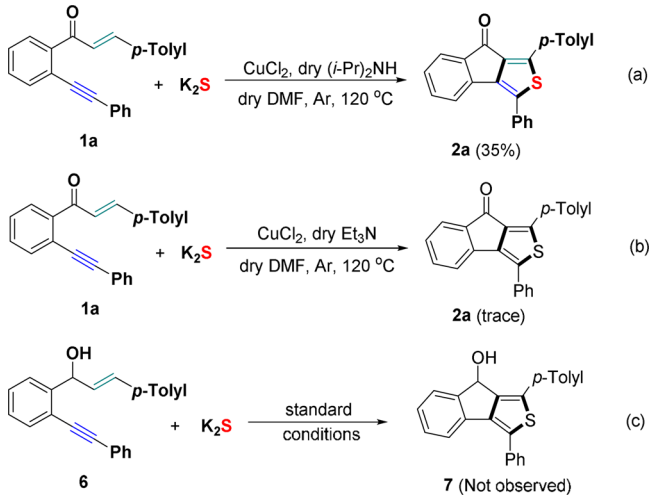
Scheme 2. Dehydrocyclization of 1,6-Enynes with K_2S[a,b]



[a]Reaction conditions: **1** (0.5 mmol), K_2S (3 mmol), $CuCl_2$ (20 mol %), DIPA (1.5 mmol), DMF (4 mL), and H_2O (3.0 mmol) under argon atmosphere and 120 °C for 24 h. [b]Isolated yields based on **1**.

To understand dehydrogenation process and the roles of water and base promoter, the reaction of 1,6-enyne **1a** was carried out in dry DMF solvent using dry DIPA as a base promoter, and a significantly dropped yield (35%) of **2a** was obtained (Scheme 3a), whereas using dry Et_3N as a base promoter under the same conditions, only trace amount of **2a** was observed (Scheme 3b). These experimental outcomes indicated that free proton from DIPA may be served a hydrogen acceptor to generate hydrogen gas during dehydrogenation process. Compared with DIPA base, water is more suitable as a hydrogen acceptor to facilitate dehydrogenation transformation under DIPA-mediated conditions. Upon exchanging the carbonyl group for hydroxy functionality on the 1,6-enyne unit, unactivated 1,6-enyne **6** failed to give product **7** under the standard conditions (Scheme 3c), showing that the carbonyl group located in the 1,6-enyne unit plays a key role in the success of this reaction, which may activate alkenyl and alkynyl groups of 1,6-conjugated enynes **1**.

Scheme 3. Control Experiments



On the basis of literature reports[12f,18] and from the observations of the experiment results, a possible mechanism for the present dehydrobicyclization is proposed in Scheme 4. In the presence of Cu(II) catalyst, Michael addition and subsequent 5-*exo-dig* cyclization of 1,6-enynes **1** and potassium sulfide occur to give indenone intermediate **B**, followed by Cu(II)-catalyzed intramolecular 5-*endo-trig* cyclization to deliver intermediate **C**. Intermediate **C** undergoes an enol-ketone tautomerization and successive dehydrogenation[18] mediated by DIPA to convert into the final indeno[1,2-*c*]thiophenes **2**. Although a detailed mechanism for forming products **2** is not yet clear to us, it seems that free protons from DIPA and water play an important role in the dehydrogenation process.

In summary, we have developed an unprecedented cascade dehydrobicyclization reaction of 1,6-enynes using potassium sulfide as a sulfurating reagent, enabling a new Cu(II)-catalyzed protocol toward arylated indeno[1,2-*c*]thiophenes with substituted diversity in an atom-economic fashion. The reaction pathway involves a twice *S*-addition and leads to the formation of two new ring and three new chemical bonds. The annulation efficiency, high atom-economy, and flexible skeletal modification as well as workable reaction conditions provide a facile and practical entry to potentially bioactive indeno[1,2-*c*]thiophenes in acceptable yields. A further investigation on evaluating biological activity of these resultant compounds is currently underway.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of Compounds 1. *Example for the Synthesis of 1a.* Under argon conditions, 2-iodophenylethanone (1.23 g, 5.0 mmol), ethynylbenzene (0.612 g. 6.0 mmol), and Et_3N (dry, 20 mL), $Pd(PPh_3)_2Cl_2$ (0.1 mmol) and CuI (0.05 mmol) were successively introduced into dry 100 mL Schlenk tube. Then the mixture was stirred at 50 °C for 12 h. The reaction mixture was diluted with EtOAc (60 mL) and washed with water (3 × 20 mL). The organic layer was dried over Na_2SO_4, concentrated under the reduced pressure to give dark brown oil, which was further purified via column chromatography on silica gel (petroleum ether and EtOAc) to give pure 1-(2-(phenylethynyl)phenyl)ethanone in a 89% yield (0.979 g). Next, the resulting 1-(2-(phenylethynyl) phenyl)ethanone (220 mg, 1.0 mmol) and 4-methylbenzaldehyde (144 mg, 1.2 mmol) were added into 4.0 mL of 95% EtOH at 0 °C. Then, 10% NaOH solution (1.0 mL) was slowly added into the reaction system and stirred for 2.0 h at 0 °C. After the completion of reaction, 5% HCl

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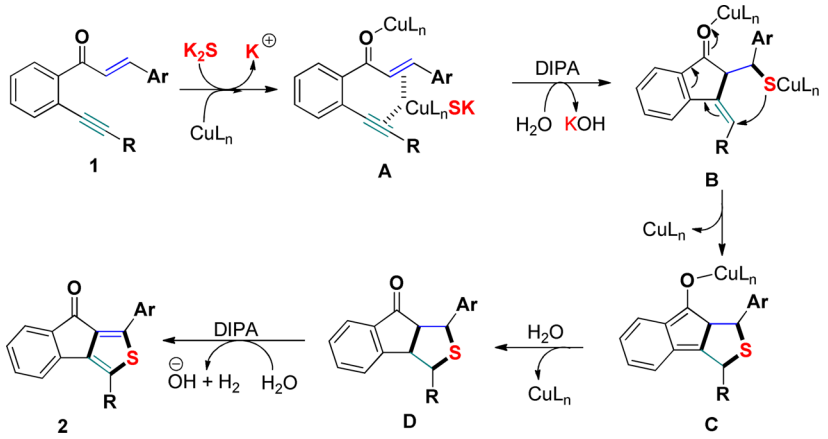
Scheme 4. Proposed Mechanism



solution was added until the mixture was neutralized (pH = 7.0). The reaction mixture was extracted with diethyl ether (3 × 10 mL). The organic phase was separated and washed with saturated aqueous NH_4Cl and dried over Na_2SO_4. The solvent was evaporated and the crude material was purified by flash gel column chromatography (petroleum ether and EtOAc) to afford pure 1,6-enynes **1a** in a 97% yield (322 mg).

*1-(2-(Phenylethynyl)phenyl)-3-(p-tolyl)prop-2-en-1-one (**1a**).* Pale yellow solid, 277 mg, total 86%; mp 61−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.75−7.65 (m, 3H), 7.57−7.39 (m, 7H), 7.32−7.17 (m, 5H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.9, 144.7, 142.1, 141.1, 133.2, 132.3, 132.1, 130.7, 129.7, 128.6, 128.3, 124.9, 122.8, 121.5, 95.4, 88.0, 21.5; IR (KBr, ν) 3045, 1654, 1598, 1583, 1509, 1490, 1437, 1326, 1249, 1200, 1019, 976, 813 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{24}H_{19}O$, 323.1436 $[M + H]^+$, found 323.1432.

*3-(p-Tolyl)-1-(2-(p-tolylethynyl)phenyl)prop-2-en-1-one (**1b**).* Pale yellow solid, 297 mg, total 88%; mp 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.75−7.63 (m, 3H), 7.57−7.41 (m, 5H), 7.31−7.27 (m, 2H,), 7.19 (d, J = 8.0 Hz, 2H, Ar), 7.05 (d, J = 8.8 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.0, 144.6, 142.0, 141.0, 138.8, 133.1, 132.2, 131.5, 130.7, 129.6, 129.0, 128.6, 128.2, 124.9, 121.8, 119.7, 95.7, 87.4, 21.5; IR (KBr, ν) 3057, 3020, 1667, 1601, 1566, 1510, 1441, 1326, 1202, 1050, 1020, 976, 809 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{25}H_{21}O$, 337.1592 $[M + H]^+$, found 337.1588.

*1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-3-(p-tolyl)prop-2-en-1-one (**1c**).* Pale yellow solid, 299 mg, total 85%; mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.73−7.63 (m, 3H), 7.57−7.48 (m, 4H), 7.45−7.41 (m, 1H), 7.34−7.30 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.78−6.74 (m, 2H), 3.80 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.0, 159.8, 144.4, 141.9, 141.0, 133.1, 132.9, 132.2, 130.7, 129.7, 128.6, 128.0, 125.0, 121.9, 114.9, 113.9, 95.6, 86.9, 55.3, 21.6; IR (KBr, ν) 3052, 3012, 1664, 1600, 1568, 1513, 1439, 1334, 1290, 1203, 1189, 1052, 1030, 978, 825 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{25}H_{21}O_2$, 353.1542 $[M + H]^+$, found 353.1510.

*1-(2-((4-Ethylphenyl)ethynyl)phenyl)-3-(p-tolyl)prop-2-en-1-one (**1d**).* Pale yellow solid, 280 mg, total 80%; mp 50−51 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.72−7.64 (m, 3H), 7.57−7.42 (m, 5H), 7.31 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.67−2.60 (m, 2H), 2.40 (s, 3H), 1.26−1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.0, 145.1, 144.6, 142.0, 141.0, 133.1, 132.2, 131.6, 130.7, 129.6, 128.7, 128.6, 128.2, 127.8, 124.9, 121.8, 119.9, 95.7, 87.4, 28.8, 21.6, 15.3; IR (KBr, ν) 3050, 1698, 1597, 1558, 1507, 1456, 1385, 1327, 1180, 1021, 983, 872, 816 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{26}H_{23}O$, 351.1749 $[M + H]^+$, found 351.1753.

*1-(2-((4-(tert-Butyl)phenyl)ethynyl)phenyl)-3-(p-tolyl)prop-2-en-1-one (**1e**).* Pale yellow solid, 310 mg, total 82%; mp 75−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.73−7.64 (m, 3H), 7.57−7.42 (m, 5H), 7.34−7.28 (m, 3H), 7.24 (s, 1H), 7.18 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.0, 151.9, 144.5, 142.0, 141.0, 132.2, 131.3, 130.7, 129.6, 128.7, 128.6, 128.4, 128.2, 125.2, 125.0, 121.8, 119.7, 95.7, 87.4, 34.8, 31.1, 21.5; IR (KBr, ν) 3055, 1660, 1596, 1586, 1568, 1508, 1332, 1199, 1178,1091, 1053, 1023, 979, 836 cm^{-1}; HRMS (APCI-TOF) m/z calcd for$C_{28}H_{27}O$, 379.2062 $[M + H]^+$, found 379.2057.

*3-(p-Tolyl)-1-(2-(m-tolylethynyl)phenyl)prop-2-en-1-one (**1f**).* Pale yellow solid, 286 mg, total 85%; mp 84−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.75−7.64 (m, 3H), 7.60−7.43 (m, 5H), 7.23−7.08 (m, 6H), 2.39 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.9, 144.4, 141.1, 137.9, 133.1, 132.2, 132.1, 130.8, 128.7, 128.6, 128.3, 128.1, 124.9, 122.5, 121.6, 95.7, 87.7, 21.5, 20.9, 1.04; IR (KBr, ν) 3055, 1683, 1596, 1509, 1488,1456, 1325, 1257,1199, 1177, 1052, 1020, 967, 813 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{25}H_{21}O$, 337.1592 $[M + H]^+$, found 337.1598.

*1-(2-((4-Fluorophenyl)ethynyl)phenyl)-3-(p-tolyl)prop-2-en-1-one (**1g**).* Pale yellow solid, 286 mg, total 84%; mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.79−7.58 (m, 3H), 7.56−7.42 (m, 5H), 7.40−7.33 (m, 2H), 7.19 (d, J = 7.8 Hz, 2H), 6.98−6.85 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.8, 162.1 (J_{CF} = 248.5 Hz), 143.4, 141.2, 133.5 (J_{CF} = 8.4 Hz), 133.1, 132.1, 130.7, 129.7, 128.7, 128.5, 128.4, 124.9, 120.1, 118.8 (J_{CF} = 3.4 Hz), 115.6 (J_{CF} = 22.0 Hz), 94.2, 87.7, 21.6; IR (KBr, ν) 3074, 3024, 1655, 1587, 1508, 1335,1227, 1181, 1157,1093, 1054, 1022, 982, 884 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{24}H_{18}FO$, 341.1342 $[M + H]^+$, found 341.1340.

*1-(2-(Hex-1-yn-1-yl)phenyl)-3-(p-tolyl)prop-2-en-1-one (**1h**).* Yellow oil, 272 mg, total 90%; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.63−7.57 (m, 2H), 7.54−7.49 (m, 3H), 7.45−7.32 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 2.38−2.33 (m, 2H), 1.49−1.41 (m, 2H), 1.40−1.28 (m, 2H), 0.84−0.77 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 194.6, 191.9, 144.3, 142.3, 141.0, 133.2, 132.2, 130.4, 129.7, 128.5, 128.3, 127.6, 125.1, 122.3, 97.0, 30.6, 21.9, 21.5, 19.3, 13.5; IR (KBr, ν) 3058, 1655, 1600, 1559, 1485,1399, 1206, 1094, 974, 866 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{22}H_{23}O$, 303.1743 $[M + H]^+$, found 303.1718.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one (**1i**).* Pale yellow solid, 277 mg, total 90%; mp 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.78−7.71 (m, 2H), 7.68 (d, J = 7.6 Hz, 1H), 7.64−7.58 (m, 3H), 7.55−7.44 (m, 2H), 7.42−7.36 (m, 5H), 7.32−7.20 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.7, 144.4, 141.9, 134.9, 133.2, 131.6, 130.9, 130.6, 128.9, 129.8, 128.6, 128.4, 128.2, 125.8, 122.7, 121.6, 95.5, 88.0; IR (KBr, ν) 3074, 3022, 1712, 1600, 1491, 1442, 1331, 1178, 1056, 956, 881 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{23}H_{17}O$, 309.1279 $[M + H]^+$, found 309.1280.

*3-Phenyl-1-(2-(p-tolylethynyl)phenyl)prop-2-en-1-one (**1j**).* Pale yellow solid, 283 mg, total 88%; mp 78−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.81−7.69 (m, 2H), 7.69−7.58 (m, 4H), 7.58−7.31 (m, 6H), 7.28 (s, 1H), 7.04 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.8, 144.3, 141.8, 138.8, 134.9, 133.1, 131.5, 130.8, 130.5, 129.5, 129.0, 128.9, 128.8, 128.6, 128.2,

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125.9, 121.8, 119.6, 95.8, 87.4, 21.5; IR (KBr, ν) 3079, 3061, 3029, 1655, 1597, 1584, 1510, 1447, 1335, 1225, 1207, 1106, 1005, 1018, 978, 818 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{24}H_{19}O$, 323.1486 $[M + H]^+$, found 323.1438.

1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-3-phenylprop-2-en-1-one (**1k**). Pale yellow solid, 304 mg, total 90%; mp 57−58 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.77−7.69 (m, 2H), 7.69−7.59 (m, 4H), 7.54−7.48 (m, 1H), 7.46−7.35 (m, 4H), 7.34−7.28 (m, 2H), 6.75 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.8, 159.89 (s, 6H), 144.2, 141.7, 134.9, 133.1, 133.0, 130.9, 130.5, 128.9, 128.8, 128.5, 128.0, 125.9, 122.0, 114.8, 113.9, 95.8, 86.9, 55.3; IR (KBr, ν) 3056, 3024, 1665, 1606, 1574, 1512, 1494, 1447, 1332, 1289, 1251, 1205, 1174, 1051, 975, 827 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{24}H_{19}O_2$, 339.1385 $[M + H]^+$, found 339.1386.

1-(2-((4-Ethylphenyl)ethynyl)phenyl)-3-phenylprop-2-en-1-one (**1l**). Pale yellow solid, 289 mg, total 86%; mp 55−56 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.77−7.71 (m, 2H), 7.69−7.60 (m, 4H), 7.54−7.49 (m, 1H), 7.47−7.35 (m, 4H), 7.31 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 2.63 (d, J = 7.6 Hz, 2H), 1.27−1.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.8, 145.1, 144.3, 141.9, 134.9, 133.2, 131.6, 130.9, 130.5, 128.9, 128.8), 128.6, 128.2, 127.9, 125.9, 121.9, 119.9, 95.9, 87.4, 28.8, 15.3; IR (KBr, ν) 3062, 3027, 2342, 1662, 1607, 1509, 1448, 1330, 1205, 1157, 1092, 1054, 1018, 971, 832 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{25}H_{21}O$, 337.1592 $[M + H]^+$, found 337.1591.

1-(2-((4-(tert-Butyl)phenyl)ethynyl)phenyl)-3-phenylprop-2-en-1-one (**1m**). Pale yellow solid, 306 mg, total 84%; mp 85−86 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.77−7.70 (m, 2H), 7.68−7.59 (m, 4H), 7.54−7.35 (m, 5H), 7.32 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.8, 152.0, 144.3, 141.9, 134.9, 133.1, 131.3, 130.8, 130.4, 128.9, 128.8, 128.6, 128.2, 125.9, 125.3, 121.8, 119.6, 95.8, 87.4, 34.8, 31.1, 31.0; IR (KBr, ν) 3084, 3053, 1662, 1599, 1505, 1447, 1334, 1203, 1115, 1053, 1021, 977, 832 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{27}H_{25}O$, 365.1905 $[M + H]^+$, found 365.1884.

3-Phenyl-1-(2-(m-tolylethynyl)phenyl)prop-2-en-1-one (**1n**). Pale yellow solid, 283 mg, total 88%; mp 65−66 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.80−7.72 (m, 2H), 7.69−7.62 (m, 4H), 7.55−7.35 (m, 5H), 7.22 (d, J = 8.4 Hz, 1H), 7.18−7.07 (m, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.7, 144.1, 142.0, 138.0, 134.9, 133.2, 132.2, 131.0, 130.5, 129.6, 128.9, 128.8, 128.6, 128.4, 128.2, 125.8, 122.4, 121.7, 95.9, 87.7, 21.0; IR (KBr, ν) 3053, 1661, 1601, 1446, 1331, 1209, 1094, 1052, 1020, 974, 864 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $[M + H]^+$ $C_{24}H_{19}O$ 323.1436, found 323.1438.

1-(2-((4-Fluorophenyl)ethynyl)phenyl)-3-phenylprop-2-en-1-one (**1o**). Pale yellow solid, 290 mg, total 89%; mp 83−84 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.76−7.69 (m, 2H), 7.67−7.43 (m, 6H), 7.43−7.31 (m, 5H), 6.96−6.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.6, 162.2 (J_{CF} = 248.7 Hz), 144.4, 141.9, 134.8, 133.5 (J_{CF} = 8.4 Hz), 133.1, 130.9, 130.6, 129.0, 128.8, 128.5, 128.4, 125.8, 121.4, 118.8 (J_{CF} = 3.5 Hz), 115.6 (J_{CF} = 22.0 Hz), 94.3, 87.7; IR (KBr, ν) 3078, 3062, 3026, 1660, 1599, 1508, 1448, 1334, 1226, 1153, 1092, 1019, 981, 828 cm^{-1} ; HRMS (APCI-TOF) m/z calcd for $C_{23}H_{16}FO$, 327.1185 $[M + H]^+$, found 327.1183.

1-(2-((4-Chlorophenyl)ethynyl)phenyl)-3-phenylprop-2-en-1-one (**1p**). Pale yellow solid, 296 mg, total 87%; mp 86−87 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.74−7.60 (m, 5H), 7.57−7.36 (m, 7H), 7.30 (s, 1H), 7.20 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.7, 144.6, 142.0, 134.8, 132.7, 130.7, 128.8, 128.5, 125.8, 121.3, 121.2, 94.2, 88.9; IR (KBr, ν) 3078, 3062, 1669, 1590, 1558, 1507, 1457, 1384, 1259, 1173, 1090, 975, 834 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{23}H_{16}ClO$, 343.0890 $[M + H]^+$, found 343.0872.

3-(4-Methoxyphenyl)-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one (**1q**). Pale yellow solid, 297 mg, total 88%; mp 70−71 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.71−7.65 (m, 3H), 7.58 (d, J = 8.8 Hz, 2H), 7.47−7.38 (m, 7H), 7.27−7.22 (m, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.7, 161.7, 144.4, 142.3, 133.2, 131.6, 130.7, 130.4, 130.0, 128.7, 128.6, 128.4, 128.3, 127.6, 123.6, 122.8, 121.5, 114.4, 95.3, 88.2, 55.4; IR (KBr, ν) 3074, 1683, 1596, 1507, 1456,1255, 1172, 1105, 975, 868 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{24}H_{19}O_2$, 339.1380 $[M + H]^+$, found 339.1353.

3-(4-Methoxyphenyl)-1-(2-(p-tolylethynyl)phenyl)prop-2-en-1-one (**1r**). Pale yellow solid, 296 mg, total 84%; mp 77−78 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.73−7.63 (m, 3H), 7.58 (d, J = 8.4 Hz, 2H), 7.53−7.42 (m, 3H), 7.31−7.27 (m, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.9, 161.7, 144.3, 142.2, 138.8, 133.0, 131.5, 130.6, 130.3, 129.0, 128.7, 128.2, 127.7, 123.7, 121.7, 119.7, 114.4, 95.6, 87.5, 55.4, 21.5; IR (KBr, ν) 3057, 3009, 1655, 1596, 1512, 1441, 1306, 1293, 1180, 1024, 986, 816 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{25}H_{21}O_2$, 353.1542 $[M + H]^+$, found 353.1546.

3-(4-Methoxyphenyl)-1-(2-((4-methoxyphenyl)ethynyl)phenyl)-prop-2-en-1-one (**1s**). Pale yellow solid, 313 mg, total 85%; mp 58−59 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.78−7.24 (m, 10H), 6.90 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.9, 161.6, 159.8, 144.2, 142.0, 133.1, 133.0, 130.6, 130.3, 128.7, 128.0, 127.7, 123.8, 121.9, 114.9, 114.4, 114.1, 114.0, 95.5, 86.9, 55.3; IR (KBr, ν) 3050, 3009, 1654, 1597, 1511, 1461, 1335, 1252, 1171, 1054, 1022, 985, 825 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{25}H_{21}O_3$, 369.1491 $[M + H]^+$, found 369.1494.

1-(2-((4-(tert-Butyl)phenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)-prop-2-en-1-one (**1t**). Pale yellow solid, 315 mg, total 80%; mp 96−97 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.71−7.64 (m, 3H), 7.57 (d, J = 8.8 Hz, 2H), 7.52−7.42 (m, 3H), 7.33 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.9, 161.6, 151.9, 144.3, 142.2, 133.1, 131.3, 130.6, 130.3, 128.7, 128.2, 127.7, 125.2, 123.8, 121.7, 119.7, 114.3, 95.6, 87.5, 55.4, 34.8, 31.1; IR (KBr, ν) 3061, 1654, 1596, 1570, 1508, 1422, 1305, 1252, 1176, 1026, 984, 824 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{28}H_{27}O$, 395.2011$[M + H]^+$, found 395.2006.

3-(4-Methoxyphenyl)-1-(2-(m-tolylethynyl)phenyl)prop-2-en-1-one (**1u**). Pale yellow solid, 285 mg, total 81%; mp 54−55 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.77−7.63 (m, 3H), 7.59 (d, J = 8.4 Hz, 2H), 7.54−7.42 (m, 3H), 7.28−7.04 (m, 4H), 6.90 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.7, 161.7, 144.1, 142.3, 138.0, 133.1, 132.2, 130.7, 130.4, 129.5, 128.6, 128.3, 128.2, 127.6, 123.7, 122.5, 121.6, 114.4, 95.7, 87.8, 55.4, 21.0; IR (KBr, ν) 3058, 3034, 3005, 1655, 1596, 1572, 1513, 1424, 1306, 1293, 1255, 1182, 1024, 949, 824 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{25}H_{21}O_2$, 353.1542 $[M + H]^+$, found 353.1540.

1-(2-((4-Fluorophenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)-prop-2-en-1-one (**1v**). Pale yellow solid, 296 mg, total 83%; mp 83−84 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.71−7.63 (m, 3H), 7.60−7.42 (m, 5H), 7.39−7.35 (m, 2H), 6.97−6.88 (m, 4H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.8, 162.8 (J_{CF} = 213.1 Hz), 143.4, 133.5 (J_{CF} = 8.4 Hz), 131.8, 130.3, 128.5 (J_{CF} = 3.5 Hz), 127.5, 123.7, 121.3, 118.9, 115.6 (J_{CF} = 22.0 Hz), 114.4, 94.1, 87.8, 55.4; IR (KBr, ν) 3098, 3060, 3043, 1663, 1589, 1513, 1462, 1439, 1421, 1337, 1303, 1258, 1221, 1173, 1094, 1054, 1024, 980, 836, cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{24}H_{18}FO_2$, 357.1291 $[M + H]^+$, found 357.1284.

1-(2-((4-Chlorophenyl)ethynyl)phenyl)-3-(4-methoxyphenyl)-prop-2-en-1-one (**1w**). Pale yellow solid, 316 mg, total 85%; mp 96−97 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.71−7.64 (m, 3H), 7.58−7.41 (m, 5H), 7.33−7.28 (m, 2H), 7.21 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.7, 161.8, 144.6, 142.3, 134.6, 133.1, 132.7, 130.6, 130.3, 128.6, 128.5, 127.5, 123.6, 121.3, 121.1, 114.4, 93.9, 89.0, 55.4; IR (KBr, ν) 3064, 1655, 1597, 1514, 1492, 1441, 1425, 1306, 1255, 1183, 1089, 1052, 1025, 986, 823 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{24}H_{18}ClO_2$, 373.0995 $[M + H]^+$, found 373.0984.

3-(4-Chlorophenyl)-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one (**1x**). Pale yellow solid, 304 mg, total 89%; mp 89−90 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.75−7.65 (m, 3H), 7.61−7.44 (m, 5H), 7.39−7.23 (m, 7H); 2961, 2862, 6.76 (d, J = 8.8 Hz, 2H), 3.83 (d, J = 22.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.4, 142.7,

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141.7, 136.4, 133.4, 133.3, 131.5, 131.1, 129.7, 129.2, 128.9, 128.8, 128.5, 128.4, 128.3, 126.3, 122.6, 121.6, 95.7, 88.0; IR (KBr, ν) 3061, 1659, 1601, 1561, 1489, 1440, 1403, 1328, 1205, 1091, 975, 821 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{23}H_{16}ClO$, 343.0890 $[M + H]^+$, found 343.0881.

*3-(4-Chlorophenyl)-1-(2-((4-methoxyphenyl)ethynyl)phenyl)-prop-2-en-1-one (**1y**).* Pale yellow solid, 312 mg, 84%; mp 83−84 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.88−7.15 (m, 13H), 6.83−6.69 (m, 2H), 3.79 (d, J = 18.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 193.4, 160.0, 142.3, 141.5, 136.3, 133.5, 133.0, 131.0, 129.6, 129.2, 128.8, 128.1, 126.3, 122.0, 114.7, 114.0, 96.0, 86.9, 55.3; IR (KBr, ν) 3015, 1655, 1605, 1514, 1489, 1324, 1292, 1259, 1204,1139, 1092, 1053, 1021, 982, 822 cm^{-1}; HRMS (APCI-TOF) m/z calcd for $C_{24}H_{18}ClO_2$ 373.0995 $[M + H]^+$, found 373.0984.

General Procedure for the Synthesis of Products 2. *Example for the Synthesis of **2a**.* A suspension of $CuCl_2$ (0.10 mmol), diisopropanolamine (1.5 mmol, 3.0 equiv), K_2S (3.0 mmol, 6.0 equiv), H_2O (3.0 mmol, 6.0 equiv) in 3.0 mL of dimethylformamide (DMF) was stirred at room temperature under an argon atmosphere for 30 min. 1,6-Enyne **1a** (1-(2-(Phenylethynyl)phenyl)-3-(*p*-tolyl)prop-2-en-1-one, 0.5 mmol, 1.0 equiv) in 1.0 mL of DMF was added into the suspension. With completion of the addition, the reaction system was stirred at 120 °C for an additional 24 h. After completion of the reaction (monitored by TLC), the reaction system was cooled to room temperature and was diluted with cold water (30 mL), followed by neutralization with a suitable amount of 10% HCl. Then, the crude solid was collected by Büchner filtration and purified by flash column chromatography (silica gel, mixtures of petroleum ether/ethyl acetate) to afford the pure product **2a**.

*3-Phenyl-1-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2a**).* Yellow solid, 132 mg, 75% yield; mp 171−173 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.74−7.69 (m, 3H), 7.55−7.46 (m, 4H), 7.37 (t, J = 7.6 Hz, 1H), 7.30−7.25 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm) 180.4, 143.9, 136.4, 136.1, 135.3, 135.2, 130.5, 128.7, 128.6, 127.3, 124.2, 123.7, 123.7, 123.4, 122.9, 122.6, 119.7, 115.7, 16.3; IR (KBr, ν) 2915, 1697, 1604, 1532, 1489, 1312, 1263, 1186, 963, 770, 755, 728, 696 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}OS$, 353.0995 $[M + H]^+$, found 353.1019.

*1,3-Di-p-tolyl-8H-indeno[1,2-c]thiophen-8-one (**2b**).* Yellow solid, 130 mg, 71% yield; mp 186−188 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.40−7.30 (m, 5H), 7.27−7.26 (m, 1H), 2.47 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 148.9, 141.6, 141.0, 140.7, 140.3, 139.0, 135.7, 134.1, 133.9, 129.7, 129.6, 129.4, 129.1, 128.5, 128.0, 127.83, 124.9, 121.0, 21.5, 21.4; IR (KBr, ν) 2963, 1696, 1637, 1617, 1492, 1261, 1183, 1031, 962, 804, 762, 728 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}OS$, 367.1151 $[M + H]^+$, found 367.1164.

*3-(4-Methoxyphenyl)-1-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2c**).* Yellow solid; 130 mg, 68% yield; mp 225−227 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 7.6 Hz, 1H), 9.39−7.35 (m, 1H), 7.30−7.25(m, 3H), 7.05 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 160.1, 148.65, 141.6, 140.7, 140.3, 135.7, 133.9, 133.9, 130.0, 129.4, 129.1, 128.0, 127.8, 124.9, 124.8, 120.8, 114.4, 55.4, 21.5; IR (KBr, ν) 2967, 1694, 1602, 1591, 1526, 1496, 1456, 1292, 1242, 1182, 1171, 1024, 960, 862, 819, 799, 766 cm^{-1}; HRMS (ESI-TOF) m/z calcd for$C_{25}H_{19}O_2S$, 383.1101 $[M + H]^+$, found 383.1117.

*3-(4-Ethylphenyl)-1-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2d**).* Yellow solid; 144 mg, 76% yield; mp 170−171 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.39−7.35 (m, 3H), 7.30−7.25 (m, 3H), 2.77 (q, J = 7.6 Hz, 2H), 2.43 (s, 3H), 1.35 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 148.9, 145.3, 141.6, 141.0, 140.7, 140.3, 135.8, 134.2, 133.9, 129.8, 129.4, 129.1, 128.6, 128.5, 128.0, 127.8, 124.9, 121.0, 113.2, 28.8, 21.6, 15.5; IR (KBr, ν) 3022, 2967, 1694, 1601, 1525, 1495 1311, 1006, 963, 818, 763, 726 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{21}OS$, 381.1307 $[M + H]^+$, found 381.1315.

*3-(4-(tert-Butyl)phenyl)-1-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2e**).* Yellow solid, 120 mg, 59% yield; mp 208−210 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.58−7.53(m, 3H), 7.41−7.37 (s, 1H), 7.30−7.26 (m, 3H), 2.43 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm) 180.5, 146.9, 143.6, 136.3, 135.7, 135.5, 135.1, 130.5, 128.9, 128.7, 124.3, 124.2, 123.8, 123.0, 122.8, 122.6, 120.7, 119.6, 115.9, 29.6, 26.1, 16.3; IR (KBr, ν) 2961, 1691, 1637, 1617, 1496, 1265, 1181, 1005, 963, 816, 794, 761, 725 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{25}OS$, 409.1621 $[M + H]^+$, found 409.1599.

*3-(m-Tolyl)-1-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2f**).* Yellow solid, 97 mg, 53% yield; mp 149−151 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.53−7.51 (m, 3H), 7.43−7.36 (m, 2H), 7.30−7.26 (m, 4H), 2.48 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 149.0, 141.6, 141.2, 140.7, 140.4, 138.79, 135.7, 134.1, 133.9, 132.4, 129.7, 129.4, 129.3, 129.0, 128.9, 128.1, 127.9, 125.7, 124.9, 121.0, 21.6, 21.5; IR (KBr, ν) 3021, 2915, 1698, 1603, 1538, 1499, 1465, 1311, 1270, 1182, 1126, 1094, 814, 778, 759, 723 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}OS$, 367.1151 $[M + H]^+$, found 367.1168.

*3-(4-Fluorophenyl)-1-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2g**).* Yellow solid, 83 mg, 45% yield; mp 205−206 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.67 (dd, J = 8.4 Hz, 5.2 Hz, 2H), 7.44−7.36 (m, 2H), 7.30−7.25 (m, 2H), 7.24−7.20 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.5, 163.0 (J_{CF} = 247.9 Hz), 149.1, 141.6, 141.5, 140.5, 140.4, 135.7, 133.9, 132.4, 130.6 (J_{CF} = 8.2 Hz), 129.5, 128.9, 128.5 (J_{CF} = 3.4 Hz), 128.2, 127.8, 125.0, 120.7, 116.1 (J_{CF} = 21.6 Hz), 21.5; IR (KBr, ν) 2963, 1695,1603, 1528, 1497, 1261, 1157, 1095, 1030, 963, 807, 722 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{16}FOS$, 371.0901 $[M + H]^+$, found 371.0895.

*1,3-Diphenyl-8H-indeno[1,2-c]thiophen-8-one (**2h**).* Yellow solid, 84 mg, 50% yield; mp 171−173 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.20 (d, J = 7.2 Hz, 2H), 7.76−7.70 (m, 3H), 7.56−7.43 (m, 8H), 7.38 (t, J = 7.6 Hz, 1H);7.30−7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.6, 148.7, 141.5, 141.5, 140.6, 136.2, 134.3, 134.0, 132.4, 131.7, 121.0, 129.0, 128.8, 128.7, 128.2, 127.9, 125.0, 121.0; IR (KBr, ν) 3050, 2963, 1696, 1599, 1528, 1485, 1442, 1309, 1261, 1192, 1072, 962, 801, 730 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{15}OS$, 339.0838 $[M + H]^+$, found 339.0847.

*3-Butyl-1-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2i**).* Yellow solid, 100 mg, 59% yield; mp 125−126 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.17−8.01 (m, 2H), 7.77−7.69 (m, 1H), 7.54−7.44 (m, 2H), 7.31−7.24 (m, 3H), 3.09−2.91 (m, 2H), 2.49 (s, 3H), 1.85−1.72 (m, 2H), 1.60−1.49 (m, 2H), 1.12−0.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 147.3, 141.7, 141.4, 141.1, 139.9, 135.9, 135.0, 133.9, 129.3, 127.6, 127.4, 124.9, 121.1, 33.0, 28.1, 22.4, 21.5, 13.9; IR (KBr, ν) 3050, 3023, 2957, 1686, 1600, 1527, 1496, 1465, 1273, 1178, 1156, 998, 947, 813 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{21}OS$, 333.1308 $[M + H]^+$, found 333.1309.

*1-Phenyl-3-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2j**).* Yellow solid, 111 mg, 63% yield; mp 194−196 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.21−8.19 (m, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.54−7.44 (m, 4H), 7.40−7.33 (m, 3H), 7.30−7.26 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 148.46, 141.5, 141.1, 140.7, 139.10, 136.17, 134.62, 133.99, 131.73, 129.90, 129.68, 129.46, 128.74, 128.5, 128.1, 127.9, 124.9, 121.0, 21.4; IR (KBr, ν) 2963, 1694, 1617, 1540, 1506, 1486, 1261, 1183, 1100,1040, 965, 802, 762, 726 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}OS$, 353.0994$[M + H]^+$, found 353.1006.

*3-(4-Methoxyphenyl)-1-phenyl-8H-indeno[1,2-c]thiophen-8-one (**2k**).* Yellow solid, 112 mg, 61% yield; mp 171−173 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) δ 8.20−8.18 (m, 2H), 7.74 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.51−7.42 (m, 4H),7.40−7.36 (m, 1H), 7.28−7.25 (m, 1H), 7.06 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 160.2, 148.2, 141.5, 140.8, 140.8, 136.1, 134.4, 134.0, 131.8, 130.0, 129.9, 128.7, 128.0, 127.9, 125.0,

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124.6, 120.9, 114.4, 55.5; IR (KBr, ν) 2955, 1699, 1605, 1522, 1506, 1478, 1296, 1253, 1173, 1106, 1029, 962, 832, 800, 762, 726 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}O_2S$, 369.0943 $[M + H]^+$, found 369.0962.

3-(4-Ethylphenyl)-1-phenyl-8H-indeno[1,2-c]thiophen-8-one (**2l**). Yellow solid, 102 mg, 56% yield; mp 139−140 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.21−8.18 (m, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.511−7.44 (m, 3H), 7.40−7.35 (m, 3H), 7.29−7.25 (m, 1H), 2.77 (q, J = 7.6 Hz, 2H), 1.35 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 148.4, 145.4, 141.5, 141.1, 140.7, 136.2, 134.7, 134.0, 131.7, 129.9, 129.7, 128.7, 128.6, 128.5, 128.1, 127.9, 124.9, 121.0, 28.8, 15.4; IR (KBr, ν) 2962, 1696, 1600, 1539, 1505, 1486, 1311, 1278, 1262, 1187, 1081 1041, 967, 857, 833, 779, 763, 724 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}OS$, 367.1151 $[M + H]^+$, found 367.1159.

3-(4-(tert-Butyl)phenyl)-1-phenyl-8H-indeno[1,2-c]thiophen-8-one (**2m**). Yellow solid, 122 mg, 62% yield; mp 161−162 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.21−8.19 (m, 2H), 7.74 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.59−7.38 (m, 7H), 7.30−7.26 (m, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 152.3, 148.5, 141.5, 141.1, 140.8, 136.2, 134.7, 134.0, 131.4, 129.9, 129.5, 128.9, 128.3, 128.5, 128.3, 128.1, 127.9, 126.1, 125.9, 125.7, 124.9, 121.1, 34.9, 31.4, 31.3; IR (KBr, ν) 2961, 1697, 1601, 1519, 1488, 1310, 1262, 1186, 1040, 963, 865, 795, 765 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{27}H_{23}OS$, 395.1464 $[M + H]^+$, found 395.1473.

1-Phenyl-3-(m-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2n**). Yellow solid, 104 mg, 59% yield; mp 123−125 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.20 (m, 2H), 7.75 (d, J = 7.2 Hz, 1H), 7.54−7.37 (m, 8H), 7.31−7.26 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 148.6, 141.5, 141.3, 140.7, 138.8, 136.2, 134.6, 134.0, 132.3, 131.1, 129.9, 129.8, 129.3, 128.9, 128.8, 128.2, 127.9, 125.7, 125.0, 121.0, 21.5; IR (KBr, ν) 3065, 2963, 1702, 1637, 1617, 1603, 1520, 1487, 1312, 1262, 1185, 1088, 1041, 971, 801, 778, 758 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}OS$, 353.0994 $[M + H]^+$, found 353.1008.

3-(4-Fluorophenyl)-1-phenyl-8H-indeno[1,2-c]thiophen-8-one (**2o**). Yellow solid, 85 mg, 48% yield; mp 191−193 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.19−8.17 (m, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.69−7.66 (m, 2H), 7.51−7.39 (m, 5H), 7.31−7.27 (m, 1H), 7.25−7.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.5, 163.1 (J_{CF} = 248.1 Hz), 148.7, 141.7, 141.5, 140.4, 136.1, 134.1, 132.9, 131.6, 130.6 (J_{CF} = 8.2 Hz), 130.1, 128.8, 128.5 (J_{CF} = 3.4 Hz), 128.3, 127.9, 125.1, 120.8, 116.1 (J_{CF} = 21.7 Hz); IR (KBr, ν) 2963, 1696, 1600, 1522, 1502, 1488, 1261, 1221, 1187, 1158, 1097, 966, 835, 760 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{14}FOS$, 357.0743 $[M + H]^+$, found 357.0757.

3-(4-Chlorophenyl)-1-phenyl-8H-indeno[1,2-c]thiophen-8-one (**2p**). Yellow solid, 84 mg, 45% yield; mp 222−224 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.18 (dd, J = 8.0 Hz, 2.0 Hz, 2H), 7.75 (d, J = 7.2 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.52−7.38 (m, 7H), 7.31 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.5, 148.9, 141.9, 141.5, 140.4, 136.2, 135.0, 134.1, 132.7, 131.5, 130.9, 130.1, 123.0, 129.3, 128.8, 128.4, 127.9, 125.1, 120.9; IR (KBr, ν) 2963, 1697, 1602, 1520, 1488, 1397, 1261, 1091, 966, 862, 798, 760, 726 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{14}ClOS$, 373.0448 $[M + H]^+$, found 373.0450.

1-(4-Methoxyphenyl)-3-phenyl-8H-indeno[1,2-c]thiophen-8-one (**2q**). Yellow solid, 109 mg, 59% yield; mp 182−184 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.21−8.19 (m, 2H), 7.75−7.69 (m, 3H), 7.55−7.48 (m, 4H), 7.38−7.36 (m, 1H), 7.30−7.26 (m, 1H), 7.01 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.6, 161.1, 149.1, 141.7, 141.2, 140.5, 135.0, 133.8, 133.3, 132.6, 129.6, 129.0, 128.9, 128.7, 128.1, 124.9, 124.7, 121.0, 114.1, 55.4; IR (KBr, ν) 2968, 1694, 1609, 1540, 1505, 1308, 1260, 1181, 1026, 967, 820, 798, 747 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{17}O_2S$, 369.0943 $[M + H]^+$, found 369.0949.

1-(4-Methoxyphenyl)-3-(p-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2r**). Yellow solid, 136 mg, 71% yield; mp 189−191 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.19 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.38−7.24 (m, 4H), 6.99 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm) 180.4, 155.7, 143.6, 136.4, 135.6, 135.4, 133.7, 129.8, 128.6, 128.3, 124.4, 124.3, 123.3, 122.7, 119.6, 119.5, 115.7, 108.8, 50.2, 16.2; IR (KBr, ν) 3026, 2971, 1690, 1603, 1537, 1501, 1301, 1283, 1221, 1158, 1114, 1025, 966, 833, 797, 760 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}O_2S$, 383.1101 $[M + H]^+$, found 383.1111.

1,3-Bis(4-Methoxyphenyl)-8H-indeno[1,2-c]thiophen-8-one (**2s**). Yellow solid, 157 mg, 79% yield; mp 196−197 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.20−8.18 (m, 2H), 7.73 (d, J = 7.2 Hz, 1H), 7.62−7.60 (m, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.39−7.35 (m, 1H), 7.28−7.24 (m, 1H), 7.04 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm) 180.4, 155.7, 154.9, 143.4, 136.4, 135.4, 135.4, 129.7, 128.6, 128.1, 124.7, 124.3, 122.7, 119.6, 119.5, 119.5, 115.6, 109.1, 108.8, 50.2, 50.2; IR (KBr, ν) 2926, 2835, 1690, 1609, 1507, 1497, 1304, 1258, 1179, 1041, 1024, 966, 835, 759 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}O_3S$, 399.1049 $[M + H]^+$, found 399.1059.

3-(4-(tert-Butyl)phenyl)-1-(4-methoxyphenyl)-8H-indeno[1,2-c]-thiophen-8-one (**2t**). Yellow solid, 138 mg, 65% yield; mp 162−164 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.20 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.57−7.53 (m, 3H), 7.39−7.37 (m, 1H), 9.29−7.25 (m, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 161.0, 152.1, 148.9, 141.7, 140.8, 140.6, 135.1, 133.8, 133.6, 129.6, 129.3, 128.3, 128.0, 125.9, 124.8, 124.7, 121.1, 114.0, 55.4, 34.9, 31.5, 31.3; IR (KBr, ν) 2961, 1689, 1603, 1495, 1260, 1179, 1104, 1036, 964, 828, 797, 764 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{25}O_2S$, 425.1569 $[M + H]^+$, found 425.1556.

1-(4-Methoxyphenyl)-3-(m-tolyl)-8H-indeno[1,2-c]thiophen-8-one (**2u**). Yellow solid, 111 mg, 58% yield; mp 127−129 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.22−8.18 (m, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.53−7.50 (m, 3H), 7.43−7.37 (m, 2H), 7.29−7.26 (m, 2H), 7.02−7.00 (m, 2H), 3.90 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.6, 161.0, 149.0, 141.7, 141.1, 140.6, 138.8, 135.0, 133.8, 1336, 132.4, 129.6, 129.6, 129.3, 128.8, 128.0, 125.7, 124.8, 124.7, 121.0, 114.0, 55.4, 21.5; IR (KBr, ν) 2965, 1695, 1606, 1534,1505, 1307, 1260, 1180, 1029, 819, 757 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}O_2S$, 383.1101 $[M + H]^+$, found 383.1107.

3-(4-Fuorophenyl)-1-(4-methoxyphenyl)-8H-indeno[1,2-c]-thiophen-8-one (**2v**). Yellow solid, 95 mg, 49% yield; mp 208−210 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.19 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 7.2 Hz, 1H), 7.69−7.65 (m, 2H), 7.45−7.38 (m, 3H), 7.25−7.20 (m, 2H), 7.01 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.5, 163.0 (J_{CF} = 247.9 Hz), 161.1, 149.1, 141.7, 141.4, 140.3, 134.9, 133.9, 131.9, 130.6 (J_{CF} = 8.1 Hz), 129.6, 128.6 (J_{CF} = 3.4 Hz), 128.2, 125.0, 124.5, 120.7, 116.1 (J_{CF} = 21.7 Hz), 114.1, 55.4; IR (KBr, ν) 1695, 1607, 1500, 1308, 1259, 1226, 1181, 1026, 820, 730 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{16}FO_2S$, 387.0849 $[M + H]^+$, found 387.0859.

3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-8H-indeno[1,2-c]-thiophen-8-one (**2w**). Yellow solid, 105 mg, 52% yield; mp 240−242 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.19 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.5, 161.2, 149.3, 141.7, 141.7, 140.2, 135.0, 134.9, 133.9, 131.7, 131.1, 130.0, 130.0, 129.2, 128.3, 125.0, 124.5, 120.8, 114.1, 55.5; IR (KBr, ν) 2924, 1713, 1642, 1490, 1247, 1004, 969, 830, 781, 765, 727 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $[M + H]^+$ $C_{24}H_{16}ClO_2S$ 403.0560, found 403.0568.

1-(4-Chlorophenyl)-3-phenyl-8H-indeno[1,2-c]thiophen-8-one (**2x**). Yellow solid, 100 mg, 54% yield; mp 206−208 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.17−8.15 (m, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.71−7.69 (m, 2H), 7.56−7.44 (m, 6H), 7.41−7.37 (m, 1H), 7.31−7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.6, 147.1, 141.5, 141.4, 140.6, 136.5, 135.8, 134.5, 134.2, 132.2, 130.2, 129.2, 129.1, 129.0, 129.0, 128.7, 128.3, 125.1, 121.1; IR (KBr, ν) 2963, 1697, 1602, 1536, 1484, 1263, 1185, 1095, 967, 855, 750 cm^{-1};

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HRMS (ESI-TOF) m/z calcd for $C_{23}H_{14}ClOS$, 373.0448 $[M + H]^+$, found 373.0442.

*1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-8H-indeno[1,2-c]-thiophen-8-one (**2y**).* Yellow solid, 113 mg, 56% yield; mp 202−204 °C; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.20−8.14 (m, 2H), 7.75−7.72 (m, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.51−7.37 (m, 4H),7.31−7.16 (m, 1H) 7.07−6.99 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 185.7, 160.3, 146.6, 141.3, 140.9, 140.7, 135.7, 134.6, 134.1, 130.3, 13.0, 129.6, 129.2, 129.1, 128.9, 128.1, 125.0, 124.4, 120.9, 114.4, 114.1, 55.5; IR (KBr, ν) 2962, 1699, 1603, 1504, 1490, 1246, 1173, 1090, 1031, 963, 825, 728 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{16}ClO_2S$, 403.0556 $[M + H]^+$, found 403.0573.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00692.

^1H and ^{13}C NMR spectra for all pure products **1a−1y**, **2a−2y**. (PDF)

X-ray crystal data for **2a**. (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail wjhao@jsnu.edu.cn.

*E-mail laotu@jsnu.edu.cn.

*E-mail jiangchem@jsnu.edu.cn.

Notes

The authors declare no competing financial interest.

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