有机化学 DOI: 10.6023/cjoc201712002 研究论文
Chinese Journal of Organic Chemistry ARTICLE

1,5-溴三氯甲基化产物及三取代苯乙烯的 *E-Z* 异构化

李 进 陈靖之 黄文浩 程 旭*
(南京大学化学化工学院 南京 210023)

摘要 在可见光照射下, 以 Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ 为光催化剂, *α*-环丙烷苯乙烯通过自由基链式反应机理进行 1,5-溴三氯甲基化反应, 生成三取代的苯乙烯类化合物, 起始的 *Z*/*E* 比例为 30∶70. 当反应化合物进一步进行光照的时候, 产物的 *Z*/*E* 比例最高可达 99∶1. 利用这一方法, 成功合成了一系列的含溴三氯甲基的三取代苯乙烯化合物, 产率从良好到优秀, 都以 *Z* 构型为主. 通过量子产率实验和荧光淬灭实验, 提出了一个串联的反应历程, 包含可见光引发的自由基链式反应及光催化剂催化的 *E-Z* 异构化反应. 在此基础上, 直接对容易制备的 *E* 构型的三取代苯乙烯类化合物进行可见光条件下的构型翻转, 获得 *Z* 构型产物.

关键词 光化学; 自由基; 烯烃; 异构

E-Z Isomerization of 1,5-Bromotrichloromethylation Reaction Products and Trisubstituted Styrenes

Li, Jin Chen, Jingzhi Huang, Wenhao Cheng, Xu*
([a] *School of Chemistry and Chemical Engineering*, *Nanjing University*, *Nanjing 210023*)

Abstract 1,5-Bromotrichloromethylation of *α*-cyclopropylstyrenes via a radical chain pathway was achieved with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ as a photoinitiator under visible-light irradiation to give trisubstituted styrenes with *Z*/*E* ratio of 30∶70. When the reaction mixture was further irradiated, the *Z*/*E* ratio could be reversed and increased to 99∶1, probably via an energy-transfer pathway involving the Ir photocatalyst. This visible-light-induced catalytic isomerization protocol could also be applied to trisubstituted styrenes to obtain products with *Z*/*E* ratios up to 99∶1.

Keywords photochemistry; radical; alkene; isomerization

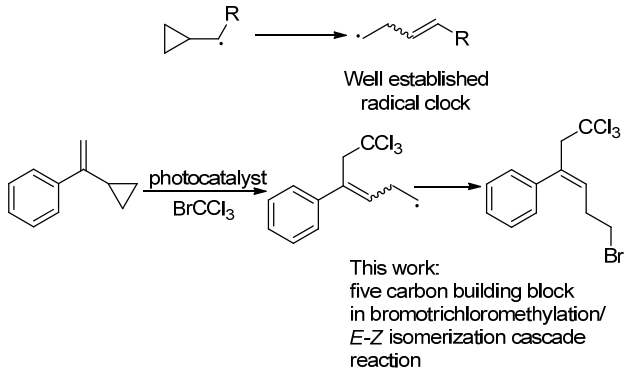
1 Introduction

Introduction of a trifluoromethyl group to a molecule can modify its biological properties. This strategy has been used extensively in pharmaceutical research,[1] and synthetic protocols have been established for construction of C—CF$_3$ bonds.[2] The analogous trichloromethyl group is present in various natural products[3] and has also been applied in medicinal chemistry.[4] However, methods for introduction of a trichloromethyl group have not been systematically explored. Photoredox catalysis is one powerful method for this transformation. For example, 1,2-Kharasch addition of trichloromethyl radical to alkene under visible-light irradiation occurs in the presence or absence of a photoredox catalyst.[5] In 2015, Meggers and co-workers[6] reported catalytic enantioselective trichloromethylation of 2-acyl imidazoles with a chiral Ir catalyst via visible-light photoredox catalysis. In 2016, Li and co-workers[7] reported a work on *α*-trichloromethylation of 2-acylpyridines with Ir-Co capsule as photocatalyst.

The utilization of cyclopropyl group as radical clock was well-known for decades in mechanistic study to elucidate a radical pathway. Despite extensive examples of cyclopropyl group as radical probe, its corresponding synthetic application was well explored. We recently reported that *α*-cyclopropyl styrenes underwent an photoredox Ir-catalyzed difluoroalkylation/C—H cascade to give partially hydrogenated naphthalene and quinoline derivatives (Scheme 1).[8] In this reaction, *α*-cyclopropyl styrenes was a building block of five carbons with high reactivity in radical annulation reaction.[9] We postulated that this annulation could be interrupted if the radical intermediate could be trapped and a chain product would be the desired product. Herein, we report a method for ring-opening

* Corresponding author. E-mail: chengxu@nju.edu.cn
Received December 2, 2017; revised January 30, 2018; published online February 6, 2018.
Project supported by the National Natural Science Foundation of China (Nos. 21572099, 21332005).
国家自然科学基金(No. 21572099, 21332005)资助项目.

1,5-bromotrichloromethylation of α-cyclopropyl styrene followed by *E*-*Z* isomerization via visible-light photocatalysis with Ir catalyst, as well as extension of the method to trisubstituted styrenes.



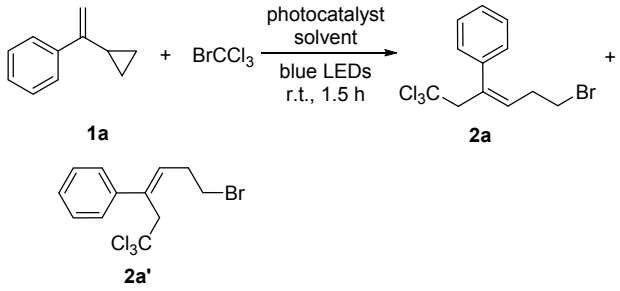
Scheme 1 Application of α-cyclopropyl radical 1,5-difunctionalizaton

2 Results and discussion

We began by carrying out reactions of α-cyclopropyl styrene (**1a**) with $BrCCl_3$ in the presence of various photocatalysts under irradiation with blue LEDs at room temperature under argon (Table 1). With Ru or Ir complexes as catalysts, the desired ring-opening products were obtained in good to excellent yields (Entries 1～3), although the *Z*/*E* ratios of the products varied considerably. With $Ru(bpy)_3Cl_2$ as the catalyst, the major product was a mixture of **2a** (*Z*) and **2a'** (*E*) (*Z* : *E*＝30 : 70, Entry 1). A similar *Z*/*E* ratio was achieved with 1 mol% *fac*-$Ir(ppy)_3$ as the catalyst (Entry 2). The *Z*/*E* selectivity changed to 60 : 40 in the presence of $Ir(ppy)_2(dtbbpy)PF_6$ (Entry 3). However, when $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ was the catalyst, **2a** became the predominant product, with a *Z*/*E* ratio of 96 : 4 (Entry 4). Experiments with various solvents, such as *N*,*N*-dimethylformamide (DMF), CH_2Cl_2, and EtOH, revealed that acetonitrile was optimal (Entries 5～8). The photocatalyst was essential (Entry 9). When white LEDs were used instead of blue LEDs, the *Z*/*E* ratio dropped to 75 : 25 (Entry 10). The reaction did not proceed in the absence of light (Entry 11). When the reaction was carried out under air, the yield and *Z*/*E* ratio dropped (Entry 12).

Using the optimized conditions, we explored the scope of the reaction with a series of α-cyclopropyl styrenes as substrates (Table 2). Our initial experiments revealed that *para* substitution on the phenyl ring did not affect the outcome of the reaction: products with either electron-withdrawing or electron-donating group could be prepared with high *Z*/*E* ratios and in excellent yields (**2b**～**2h**, the yields in Table 2 are for isolated *Z* isomers). Substrates with a *meta* substituent on the phenyl ring were tested as well, and desired *Z* products **2i** and **2j** could be achieved in good to excellent yields. Subsequently, we evaluated *ortho*-substituted substrates **1k** and **1l** and found that *ortho* substitution disturbed the conjugation between the

Table 1 Optimization of 1,5-bromotrichloromethylation/isomerization cascade reaction of α-cyclopropylstyrene[a]



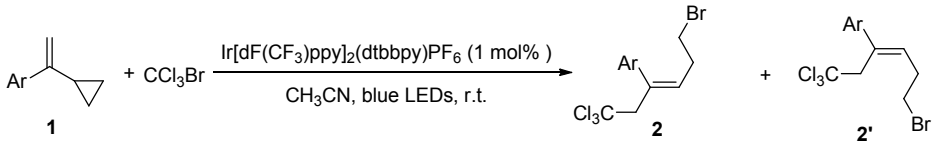
Entry	Photocatalyst	Solvent	Yield[b]/%	*Z* : *E*[c]
1	$Ru(bpy)_3Cl_2$	CH_3CN	92	30 : 70
2	*fac*-$Ir(ppy)_3$	CH_3CN	90	31 : 69
3	$Ir(ppy)_2(dtbbpy)PF_6$	CH_3CN	95	60 : 40
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CH_3CN	95	96 : 4
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMF	91	74 : 26
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMSO	90	91 : 9
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CH_2Cl_2	89	73 : 27
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	EtOH	94	94 : 6
9	None	CH_3CN	N.R.	—
10[d]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CH_3CN	93	75 : 25
11[e]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CH_3CN	N.R.	—
12[f]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	CH_3CN	81	76 : 24

[a] Reaction conditions: **1a** (0.1 mmol), $BrCCl_3$ (0.1 mmol), photocatalyst (0.001 mmol, 1.0 mol%), anhydrous solvent (1.0 mL), 24 W blue LEDs, 1.5 h, r.t., argon atmosphere. [b] Isolated yield of *Z*/*E* mixture. N.R.＝no reaction. [c] Determined by GC-MS. [d] White LEDs. [e] No light. [f] Under air.

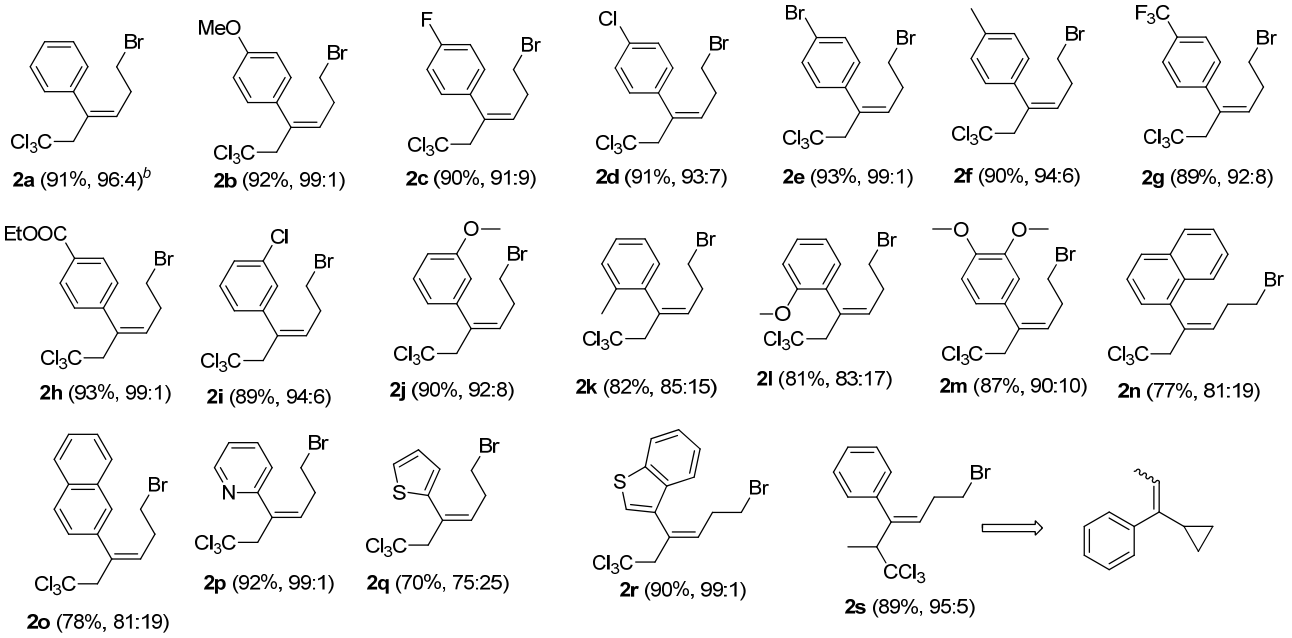
phenyl ring and the double bond. Product **2k**, which has an *ortho* methyl group, was obtained with a moderate *Z*/*E* ratio of 85 : 15 (as indicated by GC-MS), and was isolated in a good yield (82%). Substrates **1n** and **1o**, which have a naphthalene moiety, were synthesized and subjected to the standard reaction conditions to obtain α- and β-naphthalenyl products **2n** and **2o** in good yields. To our delight, the reaction of substrate **1p**, which bears a pyridine ring, with $BrCCl_3$ in the presence of 1 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ proceeded with excellent *Z*/*E* selectivity to afford **2p** in 92% yield. α-Cyclopropyl vinyl thiophene **1q** underwent the ring-opening reaction as well, offering **2q** with moderate *Z* selectivity in 70% yield. We were interested to find that benzothiophene **2r** could also be prepared with excellent *Z* selectivity and yield. A α-cyclpropyl-β-methyl styrene was also compatible with this conditions, and corresponding **2s** was obtained in 89% yield with *Z* isomer as major product.

Subsequently, we carried out several control reactions to track the steps of this process (Scheme 2). Ring-opening 1,5-bromotrichloromethylation of **1a** for 10 min using 1 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ under irradiation with light gave **2a** and **2a'** with a conversion of 30% and a *Z*/*E* ratio of 30 : 70. This reaction reached full conversion after additional 1.5 h with *Z*/*E* ratio of 95 : 5 (Scheme 2a). On the other hand, under irradiation of LEDs, the isolated mixture of **2a** and **2a'**, with a ratio of 30 : 70 reamained

Table 2 Substrate scope of 1,5-bromotrichloromethylation/isomerization cascade reaction[a]



1 2 2'



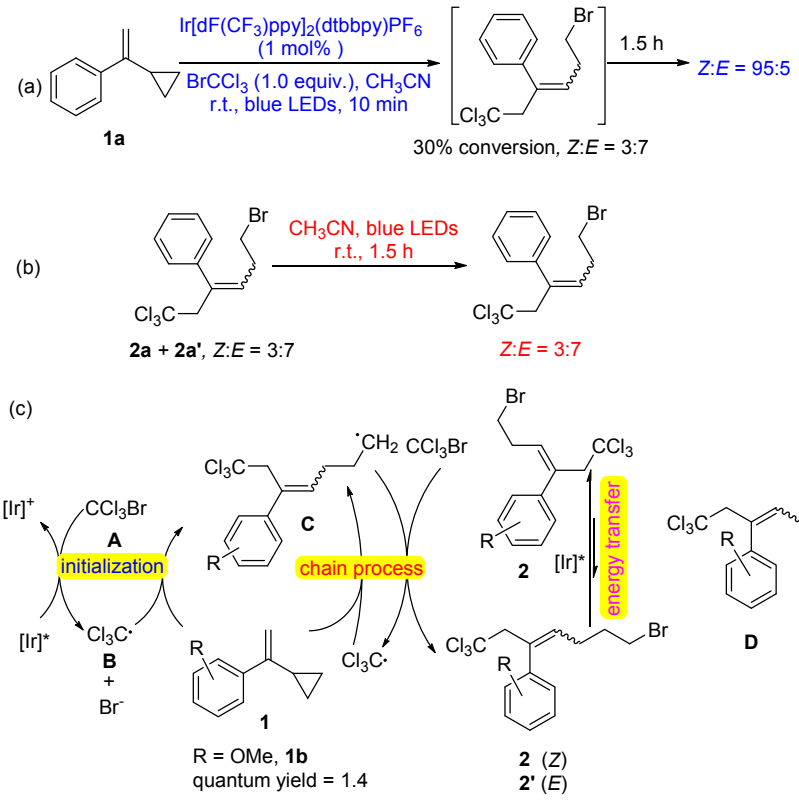
[a] Reaction conditions: **1** (0.1 mmol), $BrCCl_3$ (0.1 mmol, 1 equiv.), and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.001 mmol, 1 mol%) in anhydrous CH_3CN (1.0 mL) with irradiation by blue LEDs for 1.5 h at room temperature under argon. [b] Isolated yield of *Z* product; ratio of **2** to **2'** determined by GC-MS.

intact if catalyst was absent (Scheme 2b).

With the other catalysts listed in Table 1, the ring-opening 1,5-bromotrichloromethylation reaction occurred at a similar rate to that using $Ir[dF(CF_3)$- $ppy]_2(dtbbpy)PF_6$ within 10 min. In comparison, the redox radical annulation reaction of the radical intermediate with *Z* configuration deriving from *α*-cyclopropyl styrene takes more than 10 h.[10] This difference suggested that the first step of the reaction might proceed via a chain pathway, a process much faster than the radical annulation pathway.[11] Next, control experiment showed the subsequent *Z*-*E* isomerization took place only when the catalyst was $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (Scheme 2b). From these results, we postulated the mechanism shown in Scheme 2c. First, the excited photocatalyst donates an electron to $BrCCl_3$ (**A**), which then undergoes mesolysis to yield bromide anion and trichloromethyl radical **B**. Addition of this radical to the vinyl group of **1** leads to opening of the cyclopropyl ring. The resulting highly reactive intermediate **C**, which bears a terminal carbon radical, can react directly with $BrCCl_3$ to initiate another chain cycle and to afford a product with the *E* configuration (**2'**) as the major product at this stage. In this innate chain reaction of **1b**, a quantum yield of 1.4 was measured with a procedure reported by Yoon *et al*.[12] Alternatively, the photocatalyst in the M^+ state can oxidize intermediate **C** to produce carbocation **D**, which can combine with bromide anion to terminate the chain process. Subsequent *E*-*Z* isomerization can take place via energy transfer from excited-state $Ir[dF(CF_3)$-$ppy]_2(dtbbpy)PF_6$ to afford the *Z* product (**2**). *E*-*Z* isomerization of double bond was achieved with UV light.[13] Recently, *E* to *Z* isomerization of substituted styrenes,[14] stilbene[15] and *α*,*β*-unsaturated compounds[16] were realized with visible-light-induced catalysis. However, to our knowledge, a cascade reaction involving bromotrichloromethylation and *E*-*Z* isomerization to give trisubstituted styrenes has not previously been demonstrated.

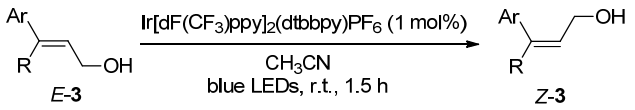
We further explored the *E*-*Z* isomerization of trisubstituted styrenes **3** of *E* configuration that were readily available from Horner-Wadsworth-Emmons reaction and following reduction reaction (Table 3).[17] With 1 mol% $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as catalyst under irradiation of blule LEDs for 1.5 h, *Z*-**3a** could be achieved in excellent yield with *Z*/*E* ratio of 99∶1 observed on GC. Electron-affacting groups in *Z*-**3b** and *Z*-**3c** did not impact this conversion of *E*-*Z* configuration, and corresponding *Z*-**3b** and *Z*-**3c** could be isolated in 95% and 96% yields, respectively. The size of substitution of alkene was changed in substrate *E*-**3d** and *E*-**3e**, and to our delight, *Z*-products could be generated with excellent yields as well.

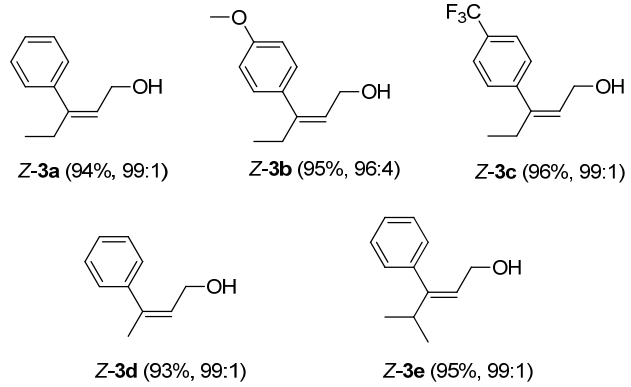
Next, we demonstrated transformation of bromo atom in product **2b** with nucleophilic substitution reaction (Scheme



Scheme 2 Control experiments and proposed mechanism

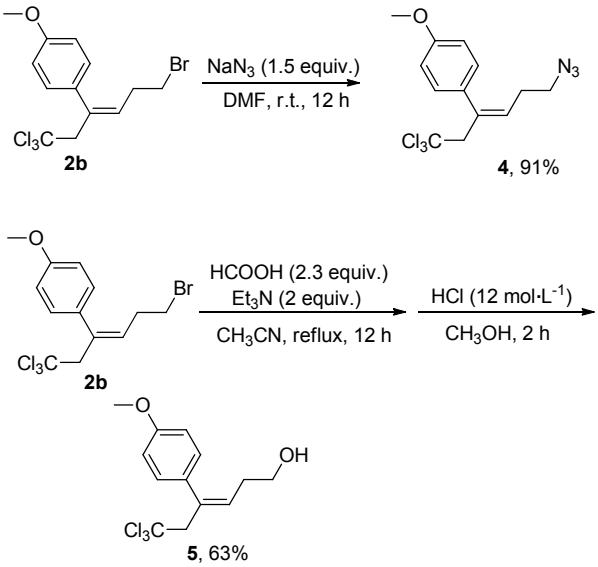
Table 3 *E*-*Z* isomerization of trisubstituted styrenes





[a] Reaction conditions: *E*-**3** (0.2 mmol) and Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol, 1 mol%) in anhydrous CH$_3$CN (2.0 mL) with irradiation by blue LEDs for 1.5 h at room temperature under argon. [b] Trace of *E*-**3** was detected with GC-MS upon completion but could not be observed during the isolation of *Z*-**3**. Ratio of *Z* to *E* determined by GC-MS.

3). Sodium azide reacted with **2b** and gave rise to **4** in 91% yield. The basic hydrolysis of **2b** in the presence of trichloromethyl group resulted in decomposition. A two-step procedure[19] of esterification and acidic hydrolysis could prepare alcohol **5** in 63% yield.



Scheme 3 Transformation of bromo atom in product **2b**

3 Conclusions

In summary, we developed a catalytic method for a 1,5-bromotrichloromethylation/*E*-*Z* isomerization cascade reaction. *Z* products were generated in nearly quantitative yields via a radical chain/energy-transfer pathway. This method could also be used for *E*-*Z* isomerization of trisubstituted styrenes with *Z*/*E* ratio up to 99∶1 in excellent yields.

4 Experimental section

4.1 General information

All reactions that required anhydrous conditions were carried out with standard procedures under argon atmosphere. Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. The solvents were dried by distillation over the appropriate drying reagents. Column chromatography was generally performed on silica gel (300～400 mesh) and reactions were monitored by thin-layer chromatography (TLC) using 254 nm of UV light to visualize the progress. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) were measured on 400M spectrometer. IR spectra were recorded as a thin film on a KBr disk (2 cm diameter) using an FT-IR spectrometer and reported in wavenumbers (cm^{-1}). A Hitachi F-4500 fluorescence spectrophotometer with a 150 W Xe lamp was used as the light source for the quantum yield measurements. High-resolution mass spectra (HRMS) were equipped with an EI source and a TOF detector mass spectrometer. The melting points were measured with digital melting point detector.

4.2 Synthesis of substrates

Substrates **1**[18] and *E*-**3**[19] were synthesized according to the reported literature.

Ethyl 4-(1-cyclopropylvinyl)benzoate (**1h**): 81% yield, chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=98∶2), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J*=7.6 Hz, 2H), 7.64 (d, *J*=7.7 Hz, 2H), 5.37 (s, 1H), 5.03 (s, 1H), 4.38 (q, *J*=7.1 Hz, 2H), 1.68～1.68 (m, 1H), 1.40 (t, *J*=7.1 Hz, 3H), 0.91～0.82 (m, 3H), 0.60～0.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 148.6, 146.0, 129.4, 129.4 126.0, 111.0, 60.9, 15.5, 14.3, 6.7; IR (film) *v*: 2983, 1770, 1759, 1716, 1368, 1276, 1247, 1108, 1020, 863, 781, 718 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1153.

1-Chloro-3-(1-cyclopropylvinyl)benzene (**1i**): 91% yield, chromatography on silica gel (petroleum ether), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 1H), 7.50 (s, 1H), 7.29 (s, 2H), 5.32 (s, 1H), 5.01 (s, 1H), 1.70～1.59 (m, 1H), 0.89 (d, *J*=7.2 Hz, 2H), 0.62 (d, *J*=4.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.2, 143.5, 134.1, 129.3, 127.4, 126.3, 124.3, 110.2, 15.5, 6.7; IR (film) *v*: 3085, 1594, 1563, 1475, 885, 787, 757 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}Cl$ 178.0549, found 178.0556.

1-(1-Cyclopropylvinyl)-2-methylbenzene (**1k**): 92% yield, chromatography on silica gel (petroleum ether), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23～7.10 (m, 3H), 7.06 (d, *J*=7.0 Hz, 1H), 5.16～5.12 (m, 1H), 4.79 (d, *J*=1.7 Hz, 1H), 2.32 (s, 3H), 1.59～1.66 (m, 1H), 0.76～0.68 (m, 2H), 0.45～0.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2, 141.3, 135.4, 129.7, 128.9, 126.9, 125.1, 110.8, 19.9, 17.2, 6.4; IR (film) *v*: 3083, 3015, 1627, 1488, 882, 761, 731 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}$ 158.1096, found 158.1095.

3-(1-Cyclopropylvinyl)benzo[*b*]thiophene (**1r**): 85% yield, chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=98∶2), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (dt, *J*=8.0, 1.1 Hz, 1H), 7.89～7.83 (m, 1H), 7.43～7.32 (m, 3H), 5.20 (dd, *J*=3.4, 1.3 Hz, 2H), 1.79～1.69 (m, 1H), 0.85～0.79 (m, 2H), 0.66～0.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.1, 140.3, 138.3, 138.2, 124.2, 124.1, 123.4, 122.8, 122.7, 111.1, 17.1, 7.2; IR (film) *v*: 3082, 3009, 1622, 1426, 1020, 762, 737 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}S$ 200.0660, found 200.0657.

(1-Cyclopropylprop-1-en-1-yl)benzene (**1s**): 88% yield, chromatography on silica gel (petroleum ether), colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.43～7.16 (m, 11H), 5.88～5.82 (m, 1H), 5.63～5.52 (m, 1H), 1.96 (dd, *J*=6.9, 1.1 Hz, 3H), 1.80～1.72 (m, 1H), 1.67～1.59 (m, 1H), 1.59～1.54 (m, 4H), 0.88～0.82 (m, 2H), 0.69～0.63 (m, 2H), 0.50～0.44 (m, 2H), 0.39～0.31 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ: 142.7, 142.3, 141.2, 140.3, 128.8, 127.9, 127.7, 127.1, 126.4, 126.1, 125.7, 119.5, 18.4, 14.6, 14.2, 11.2, 6.5, 5.1; HRMS (EI) calcd for $C_{12}H_{14}$ 158.1096, found 158.1092.

(*E*)-3-(4-Methoxyphenyl)pent-2-en-1-ol (*E*-**3b**): 85% yield, chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=5∶1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, *J*=8.1 Hz, 2H), 6.86 (d, *J*=8.1 Hz, 2H), 5.78 (t, *J*=6.8 Hz, 1H), 4.33 (d, *J*=6.7 Hz, 2H), 3.81 (s, 3H), 2.51 (q, *J*=7.4 Hz, 2H), 1.84 (s, 1H), 0.98 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 144.1, 134.2, 127.4, 124.7, 113.6, 59.5, 55.2, 23.1, 13.9; IR (film) *v*: 3354, 2966, 2874, 2836, 1607, 1510, 1464, 1287, 1247, 1035, 828, 799 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1154.

(*E*)-3-(4-(Trifluoromethyl)phenyl)pent-2-en-1-ol (*E*-**3c**): 82% yield, chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=5∶1), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J*=8.1 Hz, 2H), 7.45 (d, *J*=8.1 Hz, 2H), 5.87 (t, *J*=6.6 Hz, 1H), 4.37 (d, *J*=6.6 Hz, 2H), 2.53 (q, *J*=7.5 Hz, 2H), 1.99 (s, 1H), 0.97 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.5, 143.4, 129.1 (q, *J*=32.5 Hz), 128.1, 126.6, 125.2 (q, *J*=3.8 Hz), 124.2 (q, *J*=270 Hz), 59.4, 23.1, 13.6; IR (film) *v*: 3332, 2972, 2937, 2878, 16151327, 1166, 1121, 1068, 1016, 835, 749 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{13}OF_3$ 230.0918, found 230.0927.

4.3 Synthesis of compound 2

An oven-dried reaction vial was equipped with a magnetic stir bar, compound **1** (0.1 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.001 mmol), and bromotrichloromethane (0.1 mmol). The flask was evacuated and backfilled with argon for 3 times. Anhydrous CH_3CN (1 mL) was added with syringe. The vial was placed at a distance (app. 5 cm) from 24 W blue LED strip, and the resulting solution was stirred at ambient temperature for 1.5 h. The mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product.

(*Z*)-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)benzene (**2a**): chromatography on silica gel (petroleum ether), 91% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.32 (m, 2H), 7.32～.27 (m, 1H), 7.20～7.22 (m, 2H), 5.88 (t, J=7.1 Hz, 1H), 3.78 (s, 2H), 3.38 (t, J=6.8 Hz, 2H), 2.64 (q, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.6, 133.8, 128.8, 128.2, 127.4, 98.4, 62.6, 32.2, 32.1. IR (film) ν: 3022, 2962, 2924, 1442, 1268, 964, 812, 701, 643 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{12}Cl_3Br$ 339.9188, found 339.9193.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-4-methoxybenzene (**2b**): chromatography on silica gel (petroleum ether/EtOAc, V∶V=99∶1), 92% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17～7.07 (m, 2H), 6.93～6.84 (m, 2H), 5.83 (t, J=7.1 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 2H), 3.37 (t, J=6.8 Hz, 2H), 2.65 (q, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 136.3, 133.4, 131.1, 129.9, 113.6, 98.5, 62.6, 55.2, 32.3, 32.1; IR (film) ν: 2958, 2930, 2836, 1608, 1511, 1248, 1177, 1033, 839, 711 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}OCl_3Br$ 369.9294, found 369.9290.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-4-fluorobenzene (**2c**): chromatography on silica gel (petroleum ether), 90% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21～7.14 (m, 2H), 7.08～7.01 (m, 2H), 5.87 (t, J=7.1 Hz, 1H), 3.74 (s, 2H), 3.38 (t, J=6.7 Hz, 2H), 2.62 (q, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.1 (d, J=246.8 Hz), 135.7, 134.8 (d, J=3.5 Hz), 134.3, 130.5 (d, J=8.0 Hz), 115.4, 115.2, 98.2, 62.7, 32.1, 31.9. IR (film) ν: 2961, 2925, 2853, 1603, 1509, 1223, 844, 728, 712, 623 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{11}FCl_3Br$ 357.9094, found 357.9088.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-4-chlorobenzene (**2d**): chromatography on silica gel (petroleum ether), 91% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.30 (m, 2H), 7.18～7.12 (m, 2H), 5.89 (t, J=7.2 Hz, 1H), 3.75 (s, 2H), 3.38 (t, J=6.7 Hz, 2H), 2.62 (q, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3, 135.6, 134.6, 133.30, 130.2, 128.5, 98.2, 62.5, 32.1, 31.8; IR (film) ν: 2962, 2965, 1491, 1269, 1091, 1014, 841, 725, 710, 650 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{11}Cl_4Br$ 373.8798, found 373.8799.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-4-bromobenzene (**2e**): chromatography on silica gel (petroleum ether), 93% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54～7.45 (m, 2H), 7.14～7.04 (m, 2H), 5.89 (t, J=7.2 Hz, 1H), 3.74 (s, 2H), 3.37 (t, J=6.7 Hz, 2H), 2.62 (q, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.8, 135.6, 134.6, 131.4, 130.5, 121.5, 98.2, 62.4, 32.1, 31.8; IR (film) ν: 2920, 2850, 1655, 1631, 1484, 1073, 1008, 837, 706 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{11}Cl_3Br_2$ 417.8293, found 417.8289.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-4-methylbenzene (**2f**): chromatography on silica gel (petroleum ether), 90% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (d, J=7.9 Hz, 2H), 7.11～7.05 (m, 2H), 5.85 (t, J=7.1 Hz, 1H), 3.75 (s, 2H), 3.37 (t, J=6.8 Hz, 2H), 2.64 (q, J=6.9 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1, 136.6, 135.9, 133.5, 128.9, 128.7, 98.5, 62.6, 32.2, 32.1, 21.2; IR (film) ν: 2962, 2922, 1513, 1421, 1268, 832, 788, 711, 628 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}Cl_3Br$ 353.9344, found 353.9343.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-4-(trifluoromethyl)benzene (**2g**): chromatography on silica gel (petroleum ether), 89% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, J=8.1 Hz, 2H), 7.34 (d, J=8.0 Hz, 2H), 5.95 (t, J=7.2 Hz, 1H), 3.79 (s, 2H), 3.39 (t, J=6.6 Hz, 2H), 2.62 (q, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.8, 135.5, 135.4, 129.6 (q, J=32 Hz), 129.3, 125.3 (q, J=3.7 Hz), 124.1 (q, J=70 Hz), 98.0, 62.4, 32.1, 31.7; IR (film) ν: 2965, 2928, 1616, 1406, 1325, 1166, 1128, 1067, 1017, 852, 709 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{11}F_3Cl_3Br$ 407.9062, found 407.9057.

(*Z*)-Ethyl 4-(6-bromo-1,1,1-trichlorohex-3-en-3-yl)-benzoate (**2h**): chromatography on silica gel (petroleum ether/EtOAc, V∶V=95∶5), 93% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J=8.3 Hz, 2H), 7.29 (d, J=8.3 Hz, 2H), 5.93 (t, J=7.2 Hz, 1H), 4.38 (q, J=7.1 Hz, 2H), 3.79 (s, 2H), 3.38 (t, J=6.7 Hz, 2H), 2.62 (q, J=6.8 Hz, 2H), 1.40 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 143.7, 135.9, 135.0, 129.6, 129.5, 128.9, 98.1 (s), 62.4, 61.0, 32.1, 31.7, 14.3; IR (film) ν: 2980, 29287, 1716, 1609, 1271, 1103, 1020, 865, 807, 710 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}O_2Cl_3Br$ 411.9399, found 411.9390.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-3-chlorobenzene (**2i**): chromatography on silica gel (petroleum ether), 89% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (t, J=5.9 Hz, 2H), 7.21 (s, 1H), 7.10 (d, J=6.6 Hz, 1H), 5.91 (t, J=7.1 Hz, 1H), 3.75 (s, 2H), 3.39 (t, J=6.7 Hz, 2H), 2.63 (q, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.8, 135.4, 135.0, 134.1, 129.5, 128.8, 127.6, 127.2, 98.1, 62.4, 32.1, 31.8; IR (film) ν: 2962, 2925, 2853, 1593, 1563, 1475, 1420, 1269, 965, 796, 703, 678, 648 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{11}Cl_4Br$ 373.8798, found 373.8802.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-3-methoxybenzene (**2j**): chromatography on silica gel (petroleum ether), 90% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (t, J=7.9 Hz, 1H), 6.85～6.73 (m, 3H), 5.87 (t, J=7.1 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 2H), 3.38 (t, J=6.8 Hz, 2H), 2.66 (q, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 140.4, 136.5, 133.9, 129.2, 121.3, 114.8, 112.5, 98.3, 77.3, 77.0, 76.7, 62.5, 55.3, 32.2, 32.1; IR (film) ν: 2957, 2928, 1599, 1577, 1488, 1286, 1257, 1045, 804, 705 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}OCl_3Br$ 369.9294, found 369.9293.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-2-methylbenzene (**2k**): chromatography on silica gel (petroleum ether), 82% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22～7.08 (m, 4H), 5.94 (t, J=7.0 Hz, 1H), 3.72 (s, 2H), 3.34 (t, J=6.7 Hz, 2H), 2.45 (q, J=8 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.1, 136.2, 135.6, 134.3, 130.2, 129.7, 127.5, 125.5, 98.2, 62.4,

32.3, 31.8, 19.7; IR (film) *v*: 2961, 2924, 1489, 1419, 1268, 964, 800, 730, 713, 646, 601 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}Cl_3Br$ 353.9344, found 353.9341.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-2-methoxybenzene (**2l**): chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=95∶5), 81% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.30～7.26 (m, 1H), 7.12 (dd, *J*=7.4, 1.5 Hz, 1H), 6.97～6.86 (m, 2H), 5.89 (t, *J*=7.1 Hz, 1H), 3.82 (s, 5H), 3.37 (t, *J*=7.0 Hz, 2H), 2.56 (q, *J*=7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 156.6, 134.5, 134.3, 131.5, 129.0, 127.1, 120.3, 110.7, 98.8, 61.3, 55.4, 32.5, 32.0; IR (film) *v*: 2959, 2931, 1599, 1489, 1461, 1435, 1244, 1027, 754, 714, 647 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}OCl_3Br$ 369.9294, found 369.9287.

(*Z*)-4-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)-1,2-dimethoxybenzene (**2m**): chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=95∶5), 87% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 6.83 (d, *J*=8.0 Hz, 1H), 6.74 (dd, *J*=11.3, 1.8 Hz, 2H), 5.82 (t, *J*=7.1 Hz, 1H), 3.87 (d, *J*=1.6 Hz, 6H), 3.73 (s, 2H), 3.38 (t, *J*=6.8 Hz, 2H), 2.65 (q, *J*=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 148.6, 148.3, 136.4, 133.5, 131.4, 121.2, 112.2, 110.8, 98.4, 62.6, 56.0, 55.8, 32.2, 32.1; IR (film) *v*: 2958, 2934, 2835, 1515, 1258, 1139, 1028, 817, 711 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{16}O_2Cl_3Br$ 399.9399, found 399.9398.

(*Z*)-1-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)naphthalene (**2n**): chromatography on silica gel (petroleum ether), 77% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.90～7.83 (m, 2H), 7.81 (d, *J*=8.2 Hz, 1H), 7.51～7.46 (m, 2H), 7.36 (dd, *J*=7.0, 1.1 Hz, 1H), 6.20 (t, *J*=7.0 Hz, 1H), 3.90 (s, 2H), 3.31 (t, *J*=6.7 Hz, 2H), 2.51～2.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 136.4, 135.8, 134.9, 133.7, 131.1, 128.6, 128.0, 127.1, 126.3, 125.8, 125.4, 125.2, 98.2, 62.9, 32.5, 31.9; IR (film) *v*: 2923, 2852, 1419, 1268, 965, 810, 775, 712 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}Cl_3Br$ 389.9344, found 389.9338.

(*Z*)-2-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)naphthalene (**2o**): chromatography on silica gel (petroleum ether), 78% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.86 (d, *J*=8.0 Hz, 3H), 7.69 (s, 1H), 7.57～7.47 (m, 2H), 7.37 (d, *J*=8.4 Hz, 1H), 6.00 (t, *J*=7.1 Hz, 1H), 3.90 (s, 2H), 3.42 (t, *J*=6.7 Hz, 2H), 2.72 (q, *J*=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 136.6, 136.5, 134.4, 133.1, 132.5, 128.0, 127.9, 127.7, 127.7, 126.9, 126.6, 126.1, 98.4, 62.6, 32.2, 32.0; IR (film) *v*: 3055, 2925, 2853, 1597, 1504, 1421, 860, 823, 711, 683 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}Cl_3Br$ 389.9344, found 389.9346.

(*Z*)-2-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)pyridine (**2p**): chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=7∶3), 92% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 8.55 (d, *J*=4.7 Hz, 1H), 7.67 (t, *J*=7.7 Hz, 1H), 7.44 (d, *J*=7.9 Hz, 1H), 7.17 (dd, *J*=7.2, 5.1 Hz, 1H), 6.26 (t, *J*=7.3 Hz, 1H), 4.29 (s, 2H), 3.51 (t, *J*=6.8 Hz, 2H), 3.02 (q, *J*=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.7, 148.5, 136.8, 136.7, 135.9, 122.2, 121.6, 98.8, 51.9, 33.2, 31.3; IR (film) *v*: 2925, 2852, 1585, 1565, 1466, 1433, 1265, 1150, 1034, 828, 777, 744, 705, 640 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}NCl_3Br$ 340.9140, found 340.9135.

(*Z*)-2-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)thiophene (**2q**): chromatography on silica gel (petroleum ether), 70% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.31 (dd, *J*=5.1, 1.1 Hz, 1H), 7.02 (dd, *J*=5.0, 3.6 Hz, 1H), 6.98 (dd, *J*=3.5, 1.0 Hz, 1H), 5.97 (t, *J*=7.1 Hz, 1H), 3.78 (s, 2H), 3.45 (t, *J*=6.8 Hz, 2H), 2.87 (q, *J*=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 140.5, 135.6, 129.2, 127.1, 127.0, 125.5), 98.2, 62.8, 32.6, 31.8; IR (film) *v*: 2961, 2925, 2853, 1423, 1268, 1231, 963, 798, 703 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{10}SCl_3Br$ 345.8752, found 345.8745.

(*Z*)-3-(6-Bromo-1,1,1-trichlorohex-3-en-3-yl)benzo[*b*]thiophene (**2r**): chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=95∶5), 90% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.92～7.85 (m, 1H), 7.66～7.59 (m, 1H), 7.41～7.34 (m, 2H), 7.28 (s, 1H), 6.14 (t, *J*=7.0 Hz, 1H), 3.83 (s, 2H), 3.35 (t, *J*=6.6 Hz, 2H), 2.54 (q, *J*=6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 139.9, 138.1, 136.8, 134.3, 130.6, 124.7, 124.4, 124.3, 122.9, 122.8, 98.2, 62.1, 32.5, 31.93; HRMS (EI) calcd for $C_{14}H_{12}SCl_3Br$ 395.8909, found 395.8899.

(*Z*)-(6-Bromo-1,1,1-trichloro-2-methylhex-3-en-3-yl)benzene (**2s**): chromatography on silica gel (petroleum ether), 89% yield, colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) *δ*: 7.37～7.32 (m, 2H), 7.31～7.28 (m, 1H), 7.23～7.17 (m, 2H), 5.96 (t, *J*=7.1 Hz, 1H), 3.62 (q, *J*=6.9 Hz, 1H), 3.35 (t, *J*=6.8 Hz, 2H), 2.50 (q, *J*=7.0 Hz, 2H), 1.65 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 142.0, 139.2, 130.8, 129.3, 128.0, 127.2, 103.9, 62.0, 321, 18.4; HRMS (EI) calcd for $C_{13}H_{14}BrCl$: 353.9344, found 353.9346.

4.4 Synthesis of compound 3

An oven-dried reaction vial was equipped with a magnetic stir bar, compound *E*-**3** (0.2 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol). The flask was evacuated and backfilled with argon for 3 times. Anhydrous CH_3CN (2 mL) was added with syringe. The vial was placed at a distance (app. 5 cm) from 24 W blue LEDs strip, and the resulting solution was stirred at ambient temperature for 1.5 h. The mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product.

(*Z*)-3-Phenylpent-2-en-1-ol (*Z*-**3a**): chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=5∶1), 94% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.35～7.32 (m, 2H), 7.29～7.25 (m, 1H), 7.18～7.10 (m, 2H), 5.67 (t, *J*=6.9 Hz, 1H), 4.04 (d, *J*=6.9 Hz, 2H), 2.40 (q, *J*=7.4 Hz, 2H), 1.55 (s, 1H), 1.00 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 146.2, 140.2, 128.1, 127.0, 124.3, 60.2, 31.7, 12.7. These data were identical to reported values.[20]

(*Z*)-3-(4-Methoxyphenyl)pent-2-en-1-ol (*Z*-**3b**): chromatography on silica gel (petroleum ether/EtOAc, *V*∶*V*=5∶1), 95% yield, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.07 (d, *J*=8.3 Hz, 2H), 6.87 (d, *J*=8.3 Hz,

2H), 5.64 (t, J=6.9 Hz, 1H), 4.06 (d, J=6.7 Hz, 2H), 3.81 (s, 3H), 2.37 (q, J=7.3 Hz, 2H), 1.27 (s, 1H), 0.99 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 58.6, 145.9, 132.4, 129.2, 124.0, 113.4, 60.4, 55.2, 31.8, 12.8; IR (film) v: 3348, 2964, 2933, 1609, 1511, 1246, 1178, 1034, 834, 750 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1143.

(*Z*)-3-(4-(Trifluoromethyl)phenyl)pent-2-en-1-ol (*Z*-**3c**): chromatography on silica gel (petroleum ether/EtOAc, V∶V=5∶1), 96% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J=7.9 Hz, 2H), 7.27 (d, J=8.0 Hz, 2H), 5.74 (t, J=6.9 Hz, 1H), 4.01 (d, J=6.9 Hz, 2H), 2.41 (q, J=7.3 Hz, 2H), 1.90 (s, 1H), 1.01 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.9, 144.0, 129.2 (q, J=32.4 Hz), 128.4, 125.4, 125.1 (q, J=3.7 Hz), 124.1 (q, J=271 Hz), 59.9, 31.5, 12.5; IR (film) v: 3332, 2970, 2936, 2879, 1616, 1325, 1166, 1127, 1066, 1018, 848 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{13}OF_3$ 230.0918, found 230.0923.

(*Z*)-3-phenylbut-2-en-1-ol (*Z*-**3d**): chromatography on silica gel (petroleum ether/EtOAc, V∶V=5∶1), 93% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.35 (m, 2H), 7.31～7.24 (m, 1H), 7.18 (d, J=7.1 Hz, 2H), 5.71 (t, J=6.9 Hz, 1H), 4.07 (d, J=7.0 Hz, 2H), 2.09 (s, 3H), 1.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 140.0, 128.1, 127.7, 127.1, 126.1, 60.1, 25.3. The data were identical to reported values.[21]

(*Z*)-4-Methyl-3-phenylpent-2-en-1-ol (*Z*-**3e**): chromatography on silica gel (petroleum ether/EtOAc, V∶V=5∶1), 95% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.21 (m, 3H), 7.10 (d, J=7.0 Hz, 2H), 5.66 (t, J=6.7 Hz, 1H), 3.97 (d, J=6.8 Hz, 2H), 2.56～2.66 (m, 1H), 1.68 (s, 1H), 1.07 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.8, 140.1, 128.4, 127.9, 126.8, 123.1, 60.4, 35.6, 21.5. These data were identical to reported values.[22]

4.5 Synthesis of (*Z*)-1-(6-azido-1,1,1-trichlorohex-3-en-3-yl)-4-methoxybenzene (4)

To a solution of **2b** (74 mg, 0.2 mmol) in anhydrous DMF (2 mL) was added sodium azide (65 mg, 0.3 mmol) at room temperature. The reaction was covered with Al foil and stirred for 12 h. The mixture then was diluted with EtOAc, cautiously washed with water and brine, dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (petroleumether/EtOAc, V∶V=95∶5) to provide the desired product **4**[23] as colorless oil, 60 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (d, J=8.5 Hz, 2H), 6.88 (d, J=8.5 Hz, 2H), 5.81 (t, J=7.1 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 2H), 3.30 (t, J=6.6 Hz, 2H), 2.38 (q, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 136.5, 132.4, 131.1, 129.9, 113.6, 98.5, 62.6, 55.2, 50.9, 28.94; IR (film) v: 2956, 2933, 2837, 2097, 1609, 1511, 1290, 1248, 1177, 1033, 840, 712 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}N_3OCl_3$ 333.0202, found 333.0199.

4.6 Synthesis of (*Z*)-6,6,6-Trichloro-4-(4-methoxyphenyl)hex-3-en-1-ol (5)

To a solution of (*Z*)-**2b** (74 mg, 0.2 mmol) and HCOOH (0.46 mmol) in anhydrous CH_3CN (2 mL) was added trimethylamine (0.4 mmol) dropwise at 0 ℃, then the reaction mixture was reflux for 12 h. After addition of brine (5 mL), the reaction mixture was extracted with EtOA. The organic layer was washed with H_2O, 1 mol•L^{-1} HCl and $NaHCO_3$ solution in turn. The organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. Then to the residue dissolved in 2 mL of MeOH was added 2 drop of 12 mol•L^{-1} HCl at room temperature. The solution was stirred for 2 h and then diluted with EtOAc, The mixture was cautiously washed with $NaHCO_3$ solution, H_2O and brine, dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (petroleumether/EtOAc, V∶V=4∶1) to provide the desired product **5**[17] as colorless oil, 39 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 (d, J=8.3 Hz, 2H), 6.87 (d, J=8.3 Hz, 2H), 5.85 (t, J=7.3 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 2H), 3.68 (t, J=5.7 Hz, 2H), 2.37 (q, J=6.6 Hz, 2H), 1.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 136.1, 133.0, 131.3, 130.1, 113.5, 98.7, 62.7, 62.2, 55.2, 32.6; IR (film) v: 3362, 2955, 2933, 2837, 1609, 1512, 1247, 1177, 1034, 840, 711 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{15}O_2Cl_3$ 308.0138, found 308.0131.

Supporting Information Control experiments, ^{1}H NMR and ^{13}C NMR spectra for all new compounds. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

References

[1] (a) Yale, H. L. *J. Med. Chem.* **1959**, *1*, 121.
(b) Hagmann, W. K. *J. Med. Chem.* **2008**, *51*, 4359.
(c) Tomashenko, O. A.; Grushin, V. V. *Chem. Rev.* **2011**, *111*, 4475.
(d) Mullard, A. *Nat. Rev. Drug. Discovery* **2013**, *12*, 87.

[2] (a) Ma, J.-A.; Cahard, D. *Chem. Rev.* **2008**, *108*, PR1.
(b) Chen, P.; Liu, G. *Synthesis* **2013**, *45*, 2919.
(c) Liu, H.; Gu, Z.; Jiang, X. *Adv. Synth. Catal.* **2013**, *355*, 617.
(d) Chu, L.; Qing, F.-L. *Acc. Chem. Res.* **2014**, *47*, 15132.
(e) Zhang, C. *Org. Biomol. Chem.* **2014**, *12*, 6580.
(f) Alonso, C.; Martínez de Marigorta, E.; Rubiales, G.; Palacios, F. *Chem. Rev.* **2015**, *115*, 1847.
(g) Liu, X.; Xu, C.; Wang, M.; Liu, Q. *Chem. Rev.* **2015**, *115*, 683.

[3] (a) Hofheinz, W.; Oberhänsli, W. E. *Helv. Chim. Acta* **1977**, *60*, 660.
(b) Unson, M. D.; Rose, C. B.; Faulkner, D. J.; Brinen, L. S.; Steiner, J. R.; Clardy, J. *J. Org. Chem.* **1993**, *58*, 6336.
(c) Orjala, J.; Gerwick, W. H. *J. Nat. Prod.* **1996**, *59*, 427.
(d) Fu, X.; Zeng, L.-M.; Su, J.-Y.; Pais, M. *J. Nat. Prod.* **1997**, *60*, 695.
(e) MacMillan, J. B.; Trousdale, E. K.; Molinski, T. F. *Org. Lett.* **2000**, *2*, 2721.
(f) Orsini, M. A.; Pannell, L. K.; Erickson, K. L. *J. Nat. Prod.* **2001**, *64*, 572.

[4] (a) Hutt, M. P.; Elslager, E. F.; Werbel, L. M. *J. Heterocycl. Chem.* **1970**, *7*, 511.
(b) Werbel, L. M.; Elslager, E. F.; Hess, C.; Hutt, M. P. *J. Med. Chem.* **1987**, *30*, 1943.
(c) Fujisawa, T.; Ito, T.; Fujimoto, K.; Shimizu, M.; Wynberg, H.;

Staring, E. G. J. *Tetrahedron Lett*. **1997**, *38*, 1593.
(d) Huffman, M. A.; Reider, P. J. *Tetrahedron Lett*. **1999**, *40*, 831.
(e) Bringmann, G.; Feineis, D.; God, R.; Peters, K.; Peters, E.-M.; Scholz, J.; Riederer, F.; Moser, A. *Biorg. Med. Chem*. **2002**, *10*, 2207.

[5] Wallentin, C.-J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc*. **2012**, *134*, 8875.
(b) Arceo, E.; Montroni, E.; Melchiorre, P. *Angew. Chem., Int. Ed*. **2014**, *53*, 12064.
(c) Liu, Y.; Zhang, J.-L.; Song, R.-J.; Li, J.-H. *Eur. J. Org. Chem*. **2014**, *6*, 1177.
(d) Franz, J. F.; Kraus, W. B.; Zeitler, K. *Chem. Commun*. **2015**, *51*, 8280.

[6] Huo, H.; Wang, C.; Harms, K.; Meggers, E. *J. Am. Chem. Soc*. **2015**, *137*, 9551.

[7] Li, X.; Wu, J.; Chen, L.; Zhong, X.; He, C.; Zhang, R.; Duan, C. *Chem. Commun*. **2016**, *52*, 9628.

[8] Li, J.; Chen, J.; Jiao, W.; Wang, G.; Li, Y.; Cheng, X.; Li, G. *J. Org. Chem*. **2016**, *81*, 9992.

[9] For some examples of radical annulation of α-cyclopropylstyrene:
(a) Zhang, F.; Min, Q.-Q.; Zhang, X. *Synthesis* **2015**, *47*, 2912.
(b) Prieto, A.; Melot, R.; Bouyssi, D.; Monteiro, N. *ACS Catal*. **2016**, *6*, 1093.
(c) Prieto, A.; Melot, R.; Bouyssi, D.; Monteiro, N. *Angew. Chem., Int. Ed*. **2016**, *55*, 1885.

[10] (a) Feng, Z.; Xiao, Y.-L.; Zhang, X. *Org. Chem. Front*. **2016**, *3*, 466.
(b) Ke, M.; Song, Q. *Adv. Synth. Catal*. **2017**, *359*, 384.
(c) Nie, X.; Cheng, C.; Zhu, G. *Angew. Chem., Int. Ed*. **2017**, *56*, 1898.

[11] (a) Kimura, T.; Fujita, M.; Sohmiya, H.; Ando, T. *J. Org. Chem*. **1998**, *63*, 6719.
(b) Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett*. **2012**, *14*, 94.

[12] Cismesia, M. A.; Yoon, T. P. *Chem. Sci*. **2015**, *6*, 5426.

[13] (a) Hammond, G. S.; Saltiel, J. *J. Am. Chem. Soc*. **1962**, *84*, 4983.
(b) Saltiel, J.; Hammond, G. S. *J. Am. Chem. Soc*. **1963**, *85*, 2515.
(c) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc*. **1964**, *86*, 3197.
(d) Tatsuo, A.; Hirochika, S.; Katsumi, T. *Chem. Lett*. **1980**, *9*, 261.
(e) Arai, T.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn*. **1982**, *55*, 2204.
(f) Sakaki, S.; Okitaka, I.; Ohkubo, K. *Inorg. Chem*. **1984**, *23*, 198.
(g) Osawa, M.; Hoshino, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed*. **2001**, *40*, 3472.

[14] (a) Singh, K.; Staig, S. J.; Weaver, J. D. *J. Am. Chem. Soc*. **2014**, *136*, 5275.
(b) Singh, A.; Fennell, C. J.; Weaver, J. D. *Chem. Sci*. **2016**, *7*, 6796.

[15] (a) Fabry, D. C.; Ronge, M. A.; Rueping, M. *Chem.-Eur. J*. **2015**, *21*, 5350.
For selected examples involving energy transfer, see: (b) Chen, Y.; Kamlet, A. S.; Steinman, J. B.; Liu, D. R. *Nat. Chem*. **2011**, *3*, 146.
(c) Lu, Z.; Yoon, T. P. *Angew. Chem., Int. Ed*. **2012**, *51*, 10329.
(d) Zou, Y.-Q.; Duan, S.-W.; Meng, X.-G.; Hu, X.-Q.; Gao, S.; Chen, J.-R.; Xiao, W.-J. *Tetrahedron* **2012**, *68*, 6914.
(e) Alonso, R.; Bach, T. *Angew. Chem., Int. Ed*. **2014**, *53*, 4368.
(f) Farney, E. P.; Yoon, T. P. *Angew. Chem., Int. Ed*. **2014**, *53*, 793.
(g) Kumarasamy, E.; Raghunathan, R.; Jockusch, S.; Ugrinov, A.; Sivaguru, J. *J. Am. Chem. Soc*. **2014**, *136*, 8729.

[16] Metternich, J. B.; Gilmour, R. *J. Am. Chem. Soc*. **2015**, *137*, 11254.

[17] Alexander, J.; Renyer, M. L.; Veerapanane, H. *Synth. Commun*. **1995**, *25*, 3875.

[18] Jiang, G.-J.; Fu, X-F.; Li, Q.; Yu, Z.-X. *Org. Lett*. **2012**, *14*, 692.

[19] Li, J.-Q.; Liu, J.-G.; Krajangsri, S.; Chumnanvej, N.; Singh, T.; Andersson, P. G. *ACS Catal*. **2016**, *6*, 8342.

[20] Abascal, N. C.; Lichtor, P. A.; Giuliano, M. W.; Miller, S. J. *Chem. Sci*. **2014**, *5*, 45041.

[21] Miller, D. J.; Yu, F.; Young, N. J.; Allemann, R. K. *Org. Biomol. Chem*. **2007**, *5*, 3287.

[22] Ren, K.; Hu, B.; Zhao, M.-M.; Tu, Y.-H.; Xie, X.-M.; Zhang, Z.-G. *J. Org. Chem*. **2014**, *79*, 2170.

[23] Skapos, H.; Osipov, S. N.; Vorob'eva, D. V.; Odinets, I. L.; Lork, E.; Roeschenthaler, G. *Org. Biomol. Chem*. **2007**, *5*, 2361.

(Zhao, C.)

