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Synthesis of substituted phenanthrofurans

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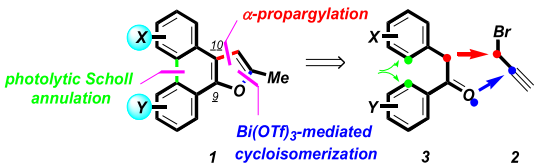
ABSTRACT

A three-step protocol toward phenanthrofurans **1** starting with deoxybenzoins **3** is developed with moderate to good yield. A facile process is carried out for the (1) α-propargylation of **3** with NaH and propargyl bromide **2** in refluxing THF, (2) $Bi(OTf)_3$-mediated cycloisomerization of γ-ynones **4** with 4 Å molecular sieves in $MeNO_2$ at rt, and (3) photolytic Scholl annulation of 2,3-diarylfurans **5** with I_2 in EtOAc at rt. The key structures of **1** are confirmed by X-ray crystallographic analysis.

1. Introduction

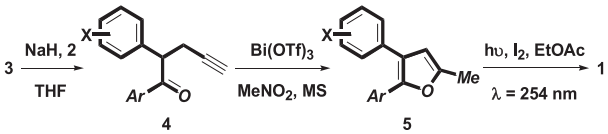
Applications for a phenanthro-based furan core system have been developed in electronic devices from BASF SE, especially in electroluminescent devices.[1] This core skeleton may function with phosphorescent materials to provide improved efficiency, stability, manufacturability, or spectral characteristics of electroluminescent devices. To the best of our knowledge, few synthetic routes for preparing the skeleton of phenanthrofuran have been early reported.[2] For its analogues, phenanthro-fused benzofurans are also large planar building blocks in the supramolecular field of molecular materials.[3,4] Depending on literature reports, **1** can be obtained in great quantities via photolytic irradiation of 2,3-diarylfurans.[2a,b] Although prepared protocols of **1**, with a specific substitution pattern, have been investigated, newly prepared methodologies are needed. Based on the above encouraged interests in the structural framework of phenanthro-conjugated oxygen-containing heterocycles, we envisage a three-step synthetic route to functionalized phenanthro[9,10-*b*]furan **1** starting from deoxybenzoin **3** using an easy-operational, high-yielding and efficient sequence of α-propargylation, $Bi(OTf)_3$-mediated cycloisomerization, and photolytic Scholl annulation, as shown in Scheme 1.



Scheme 1. Synthetic analysis of **1**.

2. Results and discussion

In continuation of our investigation on the skeleton of metal triflate-mediated reactions,[5] a facile three-step route toward **1** is explored, including (1) α-propargylation of **3** with NaH and **2** in refluxing THF, (2) $Bi(OTf)_3$-mediated (3+2) cycloisomerization of γ-ynone **4** with 4 Å molecular sieves (MS) in $MeNO_2$ at rt, and (3) photolytic Scholl annulation of 2,3-diarylfuran **5** with I_2 in EtOAc at rt, as shown in Scheme 2.



Scheme 2. Three-step synthesis of **1**.

Initially, treatment of the mode substrate deoxybenzoin **3a** (X=H, Ar=Ph, prepared from PPA/TFAA-mediated Friedel–Crafts acylation of benzene with phenylacetic acid in MeCN) with NaH and propargyl bromide (**2**, 1.2 equiv) in boiling THF produces **4a** with an 85% yield, as shown in Table 1. Next, the reaction of **4a** with catalytic amounts of $Bi(OTf)_3$ (2 mol %) in the presence of molecular sieves (4 Å, MS) in $MeNO_2$ affords furan **5a** with the 2,3-diphenyl group in an 88% yield. The 5-*exo*-dig cycloisomerization provides facile, mild, less-toxic, and atom-economic conditions. Among

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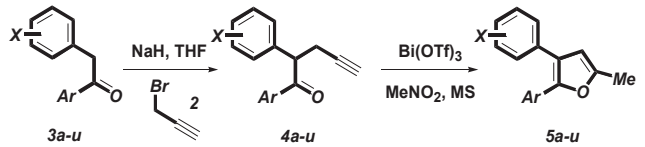
0040-4020/

Table 1
Synthesis of **5**[a,b]



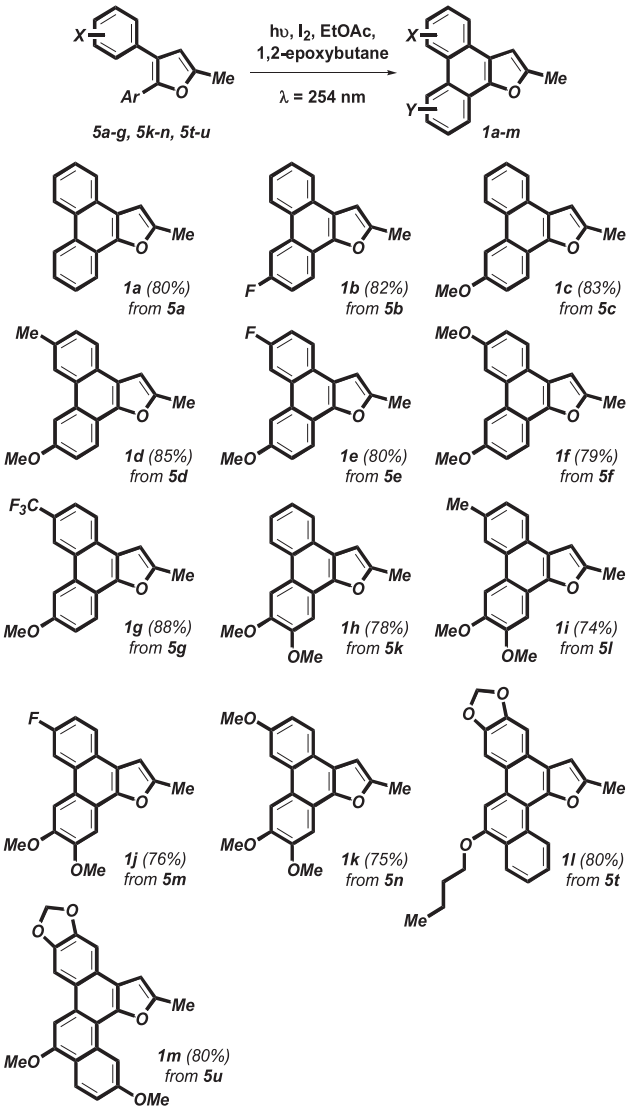
Entry	**3**, X=, Ar=	**4** (%)[c]	**5** (%)[c]
1	**3a**, H, Ph	**4a**, 85	**5a**, 88
2	**3b**, H, 4-FC_6H_4	**4b**, 80	**5b**, 86
3	**3c**, H, 4-$MeOC_6H_4$	**4c**, 76	**5c**, 82
4	**3d**, 4-Me, 4-$MeOC_6H_4$	**4d**, 75	**5d**, 84
5	**3e**, 4-F, 4-$MeOC_6H_4$	**4e**, 72	**5e**, 79
6	**3f**, 4-OMe, 4-$MeOC_6H_4$	**4f**, 77	**5f**, 80
7	**3g**, 4-CF_3, 4-$MeOC_6H_4$	**4g**, 80	**5g**, 80
8	**3h**, 3,5-F_2, 4-$MeOC_6H_4$	**4h**, 74	**5h**, 83
9	**3i**, 4-Ph, 4-$MeOC_6H_4$	**4i**, 70	**5i**, 75
10	**3j**, 2-naphthalene, 4-$MeOC_6H_4$	**4j**, 80	**5j**, 77
11	**3k**, H, 3,4-$(MeO)_2C_6H_3$	**4k**, 82	**5k**, 80
12	**3l**, 4-Me, 3,4-$(MeO)_2C_6H_3$	**4l**, 80	**5l**, 81
13	**3m**, 4-F, 3,4-$(MeO)_2C_6H_3$	**4m**, 76	**5m**, 76
14	**3n**, 4-OMe, 3,4-$(MeO)_2C_6H_3$	**4n**, 78	**5n**, 78
15	**3o**, 4-Ph, 3,4-$(MeO)_2C_6H_3$	**4o**, 82	**5o**, 76
16	**3p**, 3,5-F_2, 3,4-$(MeO)_2C_6H_3$	**4p**, 78	**5p**, 80
17	**3q**, 4-F, 2,3,4-$(MeO)_3C_6H_2$	**4q**, 80	**5q**, 76
18	**3r**, 3,4-$(OMe)_2$, 4-MeO-naphthalene	**4r**, 82	**5r**, 73
19	**3s**, 3,4-CH_2O_2, 4-MeO-naphthalene	**4s**, 80	**5s**, 74
20	**3t**, 3,4-CH_2O_2, 4-*n*BuO-naphthalene	**4t**, 73	**5t**, 75
21	**3u**, 3,4-CH_2O_2, 4,7-$(MeO)_2$-naphthalene	**4u**, 74	**5u**, 74

[a] The reaction was run on **3** (1.0 mmol), **2** (1.2 mmol), NaH (60% in oil, 120 mg, 3.0 mmol), THF (10 mL), reflux, 8 h.
[b] The reaction was run on **4** (1.0 mmol), $Bi(OTf)_3$ (13 mg, 2 mol %), $MeNO_2$ (5 mL), MS (4 Å, 100 mg), rt, 3 h.
[c] Isolated yields.

these routes, transition metals (Pd^{2+}, Ag^+/Au^{3+}, In^{3+} or Zn^{2+}) promoting cycloisomerization of diversified γ-alkynones represent a major pathway.[6,7] With the results in hand, different aryl substituents (X=H, 4-Me, 4-F, 4-MeO, 4-CF_3, 3,5-F_2, 4-Ph, 2-naphthalene, 3,4-$(OMe)_2$, 3,4-CH_2O_2; Ar=Ph, 4-FC_6H_4, 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 2,3,4-$(MeO)_3C_6H_2$, 4-MeO-naphthalene, 4-*n*BuO-naphthalene, 4,7-$(MeO)_2$-naphthalene) are examined to investigate the synthetic pathway of **5**. In Table 1, entries 1–21 show that **4a**-**u** and **5a**-**u** are isolated in a range of 70%–85% and 73%–88% yields, respectively. From the above results, we observe that no obvious yield changes were exhibited for the generation of **4** and **5** among the electron-donating, electron-neutral, and electron-withdrawing groups.

In order to synthesize the phenanthro-based furan core structure **1**,[8] the Scholl ring-closure of **5** is studied according to previous experiences.[9] By the addition of molecular iodine and 1,2-epoxybutane, **1a** is isolated in an 80% yield in ethyl acetate at rt for 80 h under a 254 nm wavelength irradiation. A number of processes are available for the Scholl reaction. The following combination of Lewis acid (or oxidant) and a reaction solvent has been reported in literature: $FeCl_3$ in CH_2Cl_2,[10a] $MoCl_5$ in CH_2Cl_2,[10b] $CuCl_2/AlCl_3$ in CS_2,[10c] $Tl(OTf)_3$ in CF_3CO_2H,[10d] $PhI(OTf)_2/BF_3{-}OEt_2$ in CH_2Cl_2,[10e] MsOH/DDQ in CH_2Cl_2,[10f] and I_2/photolysis in benzene.[10g] Attempts to apply Lewis acid-mediated Scholl annulation of **5a** failed to afford **1** due to the low stability of the furan ring. Of these methods in previous literature, the photolytic Scholl oxidative annulation provides the most convenient operation and higher yields. As shown in Table 2, functionalized phenanthrofurans **1a**–**k** with a tetracyclic skeleton and **1l**–**m** with a polycyclic skeleton are isolated in 74%–85% yields by photolytic annulation of **5a**–**g**, **5k**–**n** and **5t**–**u**. The structural skeletons of **1d**, **1e** and **1k** (see Fig. 1) were determined by single-crystal X-ray crystallography.[11]

Table 2
Synthesis of **1**[a]



[a]The reaction was run on **5** (0.2 mmol), I_2 (100 mg, 0.4 equiv), EtOAc (15 mL), 1,2-epoxybutane (440 mg, 6.0 mmol), rt, 80 h.
[b]Isolated yields.

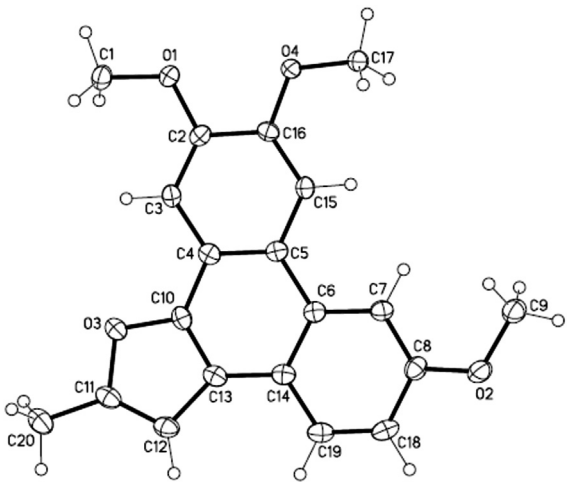


Fig. 1. X-ray structure of **1k**.

3. Conclusion

We have developed a three-step protocol toward phenanthrofurans **1** starting with deoxybenzoins **3**. The facile process was carried out for the (1) α-propargylation of **3** with NaH and propargylic bromide **2** in refluxing THF, (2) $Bi(OTf)_3$-mediated cycloisomerization of γ-ynones **4** with 4 Å MS in $MeNO_2$ at rt, and (3) photolytic Scholl annulation of 2,3-diarylfurans **5** with I_2 in EtOAc at rt in acceptable yields. The key structures were confirmed by X-ray crystallographic analysis. This synthesis begins with simple starting materials and reagents, and provides a potential methodology for electroluminescent research.

4. Experimental section

4.1. General

All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 200/400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

4.2. A representative synthetic procedure of skeleton 3 is as follows

PPA ($H_6P_4O_{13}$, polyphosphoric acid, 1.7 g, 5.0 mmol) was added to a solution of substituted arenes (3.3 mmol) and phenylacetic acids (3.0 mmol) in MeCN (10 mL) at rt. The reaction mixture was stirred at rt for 10 min. TFAA (trifluoroacetic anhydride, 850 mg, 4.0 mmol) was added to the reaction mixture at rt. The reaction mixture was stirred at rt for 8 h. The solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=8/1–4/1) afforded **3**.

*4.2.1. 1,2-Diphenyl-ethanone (**3a**).*[12a] Yield=58% (341 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 8.04–7.99 (m, 2H), 7.56–7.45 (m, 3H), 7.33–7.24 (m, 5H), 4.29 (s, 2H).

*4.2.2. 1-(4-Fluorophenyl)-2-phenyl-ethanone (**3b**).*[12a] Yield=32% (205 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 7.98–7.94 (m, 2H), 7.29–7.19 (m, 5H), 7.02–6.99 (m, 2H), 4.17 (s, 2H).

*4.2.3. 1-(4-Methoxyphenyl)-2-phenyl-ethanone (**3c**).*[12a] Yield=75% (509 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 7.95–7.92 (m, 2H), 7.29–7.15 (m, 5H), 6.85–6.83 (m, 2H), 4.16 (s, 2H), 3.70 (s, 3H).

*4.2.4. 1-(4-Methoxyphenyl)-2-p-tolyl-ethanone (**3d**).*[12a] Yield=80% (576 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 7.93 (d, J=8.0 Hz, 2H), 7.12–7.05 (m, 4H), 6.81 (d, J=8.0 Hz, 2H), 4.09 (s, 2H), 3.68 (s, 3H), 2.24 (s, 3H).

*4.2.5. 2-(4-Fluorophenyl)-1-(4-methoxyphenyl)-ethanone (**3e**).*[12b] Yield=76% (556 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 8.00 (d, J=8.8 Hz, 2H), 7.29–7.19 (m, 2H), 7.05–6.92 (m, 4H), 4.21 (s, 2H), 3.87 (s, 3H).

*4.2.6. 1,2-Bis-(4-methoxyphenyl)-ethanone (**3f**).*[12b] Yield=70% (538 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 8.01 (d, J=8.8 Hz, 2H), 7.17 (d, J=8.4 Hz, 2H), 7.04 (d, J=8.8 Hz, 2H), 6.86 (d, J=8.4 Hz, 2H), 4.22 (s, 2H), 3.83 (s, 3H), 3.71 (s, 3H).

*4.2.7. 1-(4-Methoxyphenyl)-2-(4-trifluoromethylphenyl)-ethanone (**3g**).*[12c] Yield=75% (662 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 8.00 (d, J=8.8 Hz, 2H), 7.58 (d, J=8.0 Hz, 2H), 7.38 (d, J=8.0 Hz, 2H), 6.94 (d, J=8.8 Hz, 2H), 4.30 (s, 2H), 3.87 (s, 3H).

*4.2.8. 2-(3,5-Difluorophenyl)-1-(4-methoxyphenyl)-ethanone (**3h**).* HRMS (ESI, M^++1) calcd for $C_{15}H_{13}F_2O_2$ 263.0884, found 263.0885; Yield=76% (597 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 8.00 (d, J=8.8 Hz, 2H), 6.91–6.85 (m, 4H), 6.67 (tt, J=2.4, 8.8 Hz, 1H), 4.23 (s, 2H), 3.89 (s, 3H).

*4.2.9. 2-Biphenyl-4-yl-1-(4-methoxyphenyl)-ethanone (**3i**).*[12d] Yield=80% (725 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 8.02 (d, J=8.8 Hz, 2H), 7.58–7.54 (m, 4H), 7.41–7.38 (m, 2H), 7.31–7.36 (m, 3H), 6.95 (d, J=8.8 Hz, 2H), 4.28 (s, 2H), 3.87 (s, 3H).

*4.2.10. 1-(4-Methoxyphenyl)-2-naphthalen-2-yl-ethanone (**3j**).*[12e] Yield=76% (629 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 8.08 (d, J=8.8 Hz, 2H), 7.85–7.75 (m, 3H), 7.71 (br s, 1H), 7.54–7.43 (m, 2H), 7.42–7.36 (m, 1H), 6.98 (d, J=8.8 Hz, 2H), 4.38 (s, 2H), 3.81 (s, 3H).

*4.2.11. 1-(3,4-Dimethoxyphenyl)-2-phenyl-ethanone (**3k**).*[12f] Yield=78% (599 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 7.58 (dd, J=2.0, 8.4 Hz, 1H), 7.45 (d, J=2.0 Hz, 1H), 7.24–7.20 (m, 5H), 6.82 (d, J=8.4 Hz, 1H), 4.15 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H).

*4.2.12. 1-(3,4-Dimethoxyphenyl)-2-p-tolyl-ethanone (**3l**).* Yield=74% (599 mg); HRMS (ESI, M^++1) calcd for $C_{17}H_{19}O_3$ 271.1334, found 271.1335; ^1H NMR (200 MHz, $CDCl_3$): δ 7.56 (dd, J=2.0, 8.0 Hz, 1H), 7.48 (d, J=2.0 Hz, 1H), 7.16 (d, J=8.4 Hz, 2H), 7.06 (d, J=8.0 Hz, 2H), 6.69 (d, J=8.4 Hz, 1H), 4.18 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 2.20 (s, 3H).

*4.2.13. 1-(3,4-Dimethoxyphenyl)-2-(4-fluorophenyl)-ethanone (**3m**).*[12f] Yield=70% (575 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 7.55 (dd, J=2.0, 8.4 Hz, 1H), 7.48 (d, J=2.0 Hz, 1H), 7.27–7.23 (m, 2H), 6.98–6.91 (m, 2H), 6.76 (d, J=8.4 Hz, 1H), 4.17 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H).

*4.2.14. 1-(3,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)-ethanone (**3n**).*[12g] Yield=72% (618 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 7.58 (dd, J=2.0, 8.4 Hz, 1H), 7.55 (d, J=2.0 Hz, 1H), 7.23 (d, J=8.4 Hz, 2H), 6.81 (d, J=8.4 Hz, 2H), 6.78 (d, J=8.4 Hz, 1H), 4.18 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H).

*4.2.15. 2-Biphenyl-4-yl-1-(3,4-dimethoxyphenyl)-ethanone (**3o**).* Yield=76% (757 mg); HRMS (ESI, M^++1) calcd for $C_{22}H_{21}O_3$ 333.1491, found 333.1492; ^1H NMR (200 MHz, $CDCl_3$): δ 7.65–7.52 (m, 6H), 7.47–7.29 (m, 5H), 6.82 (d, J=8.4 Hz, 1H), 4.22 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H).

*4.2.16. 2-(3,5-Difluorophenyl)-1-(3,4-dimethoxyphenyl)-ethanone (**3p**).* Yield=70% (613 mg); HRMS (ESI, M^++1) calcd for $C_{16}H_{15}F_2O_3$ 293.0989, found 293.0985; ^1H NMR (200 MHz, $CDCl_3$): δ 7.54 (dd, J=2.0, 8.4 Hz, 1H), 7.52 (d, J=2.0 Hz, 1H), 6.89–6.83 (m, 2H), 6.81 (br s, 1H), 6.66 (tt, J=2.4, 8.8 Hz, 1H), 4.21 (s, 2H), 3.87 (s, 3H), 3.84 (s, 3H).

*4.2.17. 2-(4-Fluorophenyl)-1-(2,3,4-trimethoxyphenyl)-ethanone (**3q**).*[12h] Yield=68% (620 mg); ^1H NMR (200 MHz, $CDCl_3$): δ 7.33 (d,

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J=8.8 Hz, 1H), 7.26–7.20 (m, 2H), 6.95–6.90 (m, 2H), 6.60 (d, *J*=8.8 Hz, 1H), 4.25 (s, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H).

*4.2.18. 2-(3,4-Dimethoxyphenyl)-1-(4-methoxynaphthalen-1-yl)-ethanone (**3r**).* Yield=60% (605 mg); HRMS (ESI, M^++1) calcd for $C_{21}H_{21}O_4$ 337.1440, found 337.1447; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.76–8.73 (m, 1H), 8.27 (dd, *J*=1.6, 8.4 Hz, 1H), 7.99 (d, *J*=8.0 Hz, 1H), 7.57 (dt, *J*=1.6, 8.4 Hz, 1H), 7.48 (dt, *J*=1.6, 8.4 Hz, 1H), 6.89 (dd, *J*=2.0, 8.4 Hz, 1H), 6.85 (d, *J*=2.0 Hz, 1H), 6.74 (d, *J*=8.4 Hz, 1H), 6.70 (d, *J*=8.4 Hz, 1H), 4.28 (s, 2H), 4.00 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H).

*4.2.19. 2-Benzo[1,3]dioxol-5-yl-1-(4-methoxynaphthalen-1-yl)-ethanone (**3s**).* Yield=60% (576 mg); HRMS (ESI, M^++1) calcd for $C_{20}H_{17}O_4$ 321.1127, found 321.1131; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.78 (d, *J*=8.4 Hz, 1H), 8.25 (d, *J*=8.4 Hz, 1H), 7.97 (d, *J*=8.4 Hz, 1H), 7.63–7.55 (m, 1H), 7.50–7.47 (m, 1H), 6.85 (d, *J*=2.0 Hz, 1H), 6.80 (dd, *J*=2.0, 8.0 Hz, 1H), 6.75 (d, *J*=2.8 Hz, 1H), 6.70 (d, *J*=2.8 Hz, 1H), 5.87 (s, 2H), 4.22 (s, 2H), 3.99 (s, 3H).

*4.2.20. 2-Benzo[1,3]dioxol-5-yl-1-(4-butoxynaphthalen-1-yl)-ethanone (**3t**).* Yield=55% (597 mg); HRMS (ESI, M^++1) calcd for $C_{23}H_{23}O_4$ 363.1596, found 363.1598; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.81 (d, *J*=8.8 Hz, 1H), 8.32 (d, *J*=8.4 Hz, 1H), 7.96 (d, *J*=8.4 Hz, 1H), 7.60–7.57 (m, 1H), 7.50–7.46 (m, 1H), 6.85 (d, *J*=1.6 Hz, 1H), 6.81 (dd, *J*=1.6, 8.0 Hz, 1H), 6.71 (d, *J*=8.0 Hz, 1H), 6.69 (d, *J*=8.0 Hz, 1H), 5.88 (s, 2H), 4.18 (s, 2H), 4.20–4.14 (m, 2H), 1.93–1.87 (m, 2H), 1.63–1.52 (m, 2H), 1.00 (t, *J*=7.2 Hz, 3H).

*4.2.21. 2-Benzo[1,3]dioxol-5-yl-1-(4,7-dimethoxynaphthalen-1-yl)-ethanone (**3u**).* Yield=50% (525 mg); HRMS (ESI, M^++1) calcd for $C_{21}H_{19}O_5$ 351.1233, found 351.1239; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.46 (d, *J*=2.0 Hz, 1H), 8.18 (d, *J*=8.8 Hz, 1H), 8.02 (d, *J*=8.8 Hz, 1H), 7.15 (dd, *J*=2.8, 8.8 Hz, 1H), 6.84 (d, *J*=2.0 Hz, 1H), 6.81 (dd, *J*=2.0, 8.0 Hz, 1H), 6.73 (d, *J*=8.0 Hz, 1H), 6.62 (d, *J*=8.4 Hz, 1H), 5.88 (s, 2H), 4.22 (s, 2H), 3.98 (s, 3H), 3.95 (s, 3H).

4.3. A representative synthetic procedure of skeleton 4 is as follows

NaH (120 mg, 60% in oil, 3.0 mmol) was added to a solution of **3** (1.0 mmol) in THF (10 mL) at rt. The reaction mixture was stirred at rt for 10 min. Propargyl bromide (140 mg, 1.2 mmol) was added to the reaction mixture at rt. The reaction mixture was stirred at reflux for 8 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=8/1–4/1) afforded **4**.

*4.3.1. 1,2-Diphenylpent-4-yn-1-one (**4a**).* Yield=78% (183 mg); Colorless solid; mp=59–61 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{15}O$ 235.1123, found 235.1122; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.98 (m, 2H), 7.50–7.22 (m, 8H), 4.83 (t, *J*=7.2 Hz, 1H), 3.08 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 2.74 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 1.97 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.76, 137.92, 135.98, 132.97, 128.91 (2×), 128.69 (2×), 128.41 (2×), 127.98 (2×), 127.46, 82.11, 69.77, 52.76, 23.23.

*4.3.2. 1-(4-Fluorophenyl)-2-phenylpent-4-yn-1-one (**4b**).* Yield=80% (202 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{17}H_{14}FO$ 253.1029, found 253.1032; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–7.97 (m, 2H), 7.32–7.30 (m, 4H), 7.27–7.22 (m, 1H), 7.06–7.01 (m, 2H), 4.75 (t, *J*=7.2 Hz, 1H), 3.05 (ddd, *J*=2.8, 7.6, 16.8 Hz, 1H), 2.71 (ddd, *J*=2.8, 7.6, 16.8 Hz, 1H), 1.96 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.22, 165.48 (d, *J*=254.0 Hz), 137.83, 132.41 (d, *J*=3.0 Hz), 131.39 (d, *J*=9.1 Hz, 2×), 129.02 (2×), 127.94 (2×), 127.61, 115.57 (d, *J*=21.2 Hz, 2×), 82.03, 69.84, 52.86, 23.25.

*4.3.3. 1-(4-Methoxyphenyl)-2-phenylpent-4-yn-1-one (**4c**).*[5b] Yield=76% (201 mg); Colorless solid; mp=77–78 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_2$ 265.1229, found 265.1232; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J*=8.8 Hz, 2H), 7.39–7.27 (m, 4H), 7.24–7.20 (m, 1H), 6.85 (d, *J*=8.8 Hz, 2H), 4.75 (t, *J*=7.2 Hz, 1H), 3.77 (s, 3H), 3.04 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 2.71 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 1.95 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.26, 163.31, 138.41, 131.01 (2×), 128.98, 128.85 (2×), 127.93 (2×), 127.34, 113.62 (2×), 82.31, 69.66, 55.24, 52.42, 23.23.

*4.3.4. 1-(4-Methoxyphenyl)-2-p-tolylpent-4-yn-1-one (**4d**).* Yield=75% (209 mg); Colorless solid; mp=86–88 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{19}O_2$ 279.1385, found 279.1385; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J*=9.2 Hz, 2H), 7.24 (d, *J*=8.4 Hz, 2H), 7.12 (d, *J*=8.0 Hz, 2H), 6.85 (d, *J*=8.8 Hz, 2H), 4.74 (t, *J*=7.2 Hz, 1H), 3.76 (s, 3H), 3.04 (ddd, *J*=2.8, 7.6, 16.8 Hz, 1H), 2.71 (ddd, *J*=2.8, 7.6, 16.8 Hz, 1H), 1.97 (t, *J*=2.8 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.32, 163.19, 136.91, 135.35, 130.94 (2×), 129.51 (2×), 128.90, 127.71 (2×), 113.52 (2×), 82.41, 69.56, 55.14, 51.97, 23.17, 20.84.

*4.3.5. 2-(4-Fluorophenyl)-1-(4-methoxyphenyl)pent-4-yn-1-one (**4e**).*[5b] Yield=72% (203 mg); Colorless solid; mp=83–84 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{16}FO_2$ 283.1134, found 283.1139; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J*=8.8 Hz, 2H), 7.30–7.26 (m, 2H), 7.01–6.96 (m, 2H), 6.86 (d, *J*=8.8 Hz, 2H), 4.72 (t, *J*=7.6 Hz, 1H), 3.80 (s, 3H), 2.97 (ddd, *J*=2.4, 7.6, 16.8 Hz, 1H), 2.68 (ddd, *J*=2.4, 7.6, 16.8 Hz, 1H), 1.94 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.25, 163.49, 162.00 (d, *J*=244.8 Hz), 134.16 (d, *J*=3.0 Hz), 131.03 (2×), 129.59 (d, *J*=7.6 Hz, 2×), 128.80, 115.79 (d, *J*=21.2 Hz, 2×), 113.73 (2×), 82.06, 69.95, 55.31, 51.47, 23.32.

*4.3.6. 1,2-Bis-(4-methoxyphenyl)pent-4-yn-1-one (**4f**).*[5b] Yield=77% (226 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1336; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J*=8.8 Hz, 2H), 7.22 (d, *J*=8.8 Hz, 2H), 6.85–6.80 (m, 4H), 4.68 (t, *J*=7.2 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 2.97 (ddd, *J*=2.4, 7.6, 16.8 Hz, 1H), 2.66 (ddd, *J*=2.4, 7.6, 16.8 Hz, 1H), 1.94 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.47, 163.24, 158.73, 130.97 (2×), 130.39, 128.96 (2×), 114.23 (2×), 114.14, 113.57 (2×), 82.45, 69.59, 55.23, 54.97, 51.52, 23.25.

*4.3.7. 1-(4-Methoxyphenyl)-2-(4-trifluoromethylphenyl)pent-4-yn-1-one (**4g**).* Yield=80% (266 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{16}F_3O_2$ 333.1102, found 333.1105; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J*=8.8 Hz, 2H), 7.57 (d, *J*=8.4 Hz, 2H), 7.45 (d, *J*=8.4 Hz, 2H), 6.88 (d, *J*=8.8 Hz, 2H), 4.80 (dd, *J*=6.8, 8.0 Hz, 1H), 3.82 (s, 3H), 3.01 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 2.73 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 1.95 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.74, 163.74, 142.35, 131.12 (2×), 130.81, 129.87, 128.66, 128.47 (2×), 125.94 (d, *J*=3.8 Hz, 2×), 125.84 (d, *J*=2.8 Hz, 2×), 81.66, 70.30, 55.41, 52.04, 23.22.

*4.3.8. 2-(3,5-Difluorophenyl)-1-(4-methoxyphenyl)pent-4-yn-1-one (**4h**).* Yield=74% (222 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{18}H_{15}F_2O_2$ 301.1040, found 301.1045; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J*=8.8 Hz, 2H), 6.91–6.85 (m, 4H), 6.67 (tt, *J*=2.4, 8.8 Hz, 1H), 4.69 (dd, *J*=6.8, 7.6 Hz, 1H), 3.82 (s, 3H), 2.95 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 2.70 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 1.97 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.32, 163.79, 163.14 (d,

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J=247.9 Hz), 163.01 (d, *J*=247.9 Hz), 142.00 (t, *J*=9.1 Hz), 131.07 (2×), 128.55, 113.90 (2×), 111.12 (d, *J*=25.0 Hz), 111.12 (d, *J*=11.4 Hz), 103.08 (t, *J*=25.0 Hz), 81.42, 70.42, 55.40, 51.69, 23.10.

*4.3.9. 2-Biphenyl-4-yl-1-(4-methoxyphenyl)pent-4-yn-1-one (**4i**).* Yield=70% (238 mg); Colorless solid; mp=104–106 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{21}O_2$ 341.1542, found 341.1547; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J*=8.8 Hz, 2H), 7.56–7.52 (m, 4H), 7.45–7.30 (m, 5H), 6.88 (d, *J*=8.8 Hz, 2H), 4.79 (t, *J*=7.2 Hz, 1H), 3.81 (s, 3H), 3.07 (ddd, *J*=2.4, 7.6, 16.8 Hz, 1H), 2.74 (ddd, *J*=2.4, 7.6, 16.8 Hz, 1H), 1.97 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.34, 163.47, 140.41, 140.28, 137.44, 131.16 (2×), 129.05, 128.70 (2×), 128.41 (2×), 127.65 (2×), 127.30, 126.94 (2×), 113.74 (2×), 82.38, 69.77, 55.38, 52.14, 23.32.

*4.3.10. 1-(4-Methoxyphenyl)-2-naphthalen-2-yl-pent-4-yn-1-one (**4j**).*[5b] Yield=80% (251 mg); Colorless solid; mp=93–94 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{22}H_{19}O_2$ 315.1385, found 315.1388; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J*=8.4 Hz, 1H), 7.90 (dd, *J*=0.8, 8.0 Hz, 1H), 7.87 (d, *J*=9.2 Hz, 2H), 7.75 (d, *J*=8.0 Hz, 1H), 7.67 (dt, *J*=1.2, 8.4 Hz, 1H), 7.56 (dt, *J*=1.2, 8.0 Hz, 1H), 7.34 (t, *J*=8.4 Hz, 1H), 7.27 (dd, *J*=1.2, 8.4 Hz, 1H), 6.74 (d, *J*=8.8 Hz, 2H), 5.53 (dd, *J*=5.6, 8.4 Hz, 1H), 3.72 (s, 3H), 3.19 (ddd, *J*=2.8, 8.4, 16.8 Hz, 1H), 2.75 (ddd, *J*=2.8, 8.4, 16.8 Hz, 1H), 1.93 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.47, 163.27, 134.92, 134.27, 130.84 (2×), 130.71, 129.28, 129.02, 128.13, 126.83, 125.86, 125.62, 125.37, 122.54, 113.64 (2×), 82.67, 69.53, 55.25, 48.06, 22.78.

*4.3.11. 1-(3,4-Dimethoxyphenyl)-2-phenylpent-4-yn-1-one (**4k**).* Yield=82% (241 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1336; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J*=2.0, 8.4 Hz, 1H), 7.51 (d, *J*=2.0 Hz, 1H), 7.31–7.25 (m, 2H), 7.27 (d, *J*=8.4 Hz, 2H), 7.21–7.16 (m, 1H), 6.75 (d, *J*=8.4 Hz, 1H), 4.73 (t, *J*=7.6 Hz, 1H), 3.82 (s, 6H), 3.00 (ddd, *J*=2.4, 7.2, 16.8 Hz, 1H), 2.67 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 1.92 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.23, 153.06, 148.74, 138.99, 128.99, 128.83 (2×), 127.79 (2×), 127.33, 123.43, 110.72, 109.79, 82.22, 69.61, 55.78, 55.64, 52.31, 23.20.

*4.3.12. 1-(3,4-Dimethoxyphenyl)-2-p-tolylpent-4-yn-1-one (**4l**).* Yield=80% (246 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{21}O_3$ 309.1491, found 309.1493; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, *J*=2.0, 8.4 Hz, 1H), 7.49 (d, *J*=2.0 Hz, 1H), 7.17 (d, *J*=8.0 Hz, 2H), 7.04 (d, *J*=8.0 Hz, 2H), 6.69 (d, *J*=8.4 Hz, 1H), 4.69 (t, *J*=7.6 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.97 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 2.64 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 2.19 (s, 3H), 1.93 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.07, 152.79, 148.50, 136.68, 135.29, 129.30 (2×), 128.77, 127.44 (2×), 123.17, 110.50, 109.60, 82.18, 69.44, 55.46, 55.32, 51.67, 22.97, 20.58.

*4.3.13. 1-(3,4-Dimethoxyphenyl)-2-(4-fluorophenyl)pent-4-yn-1-one (**4m**).* Yield=76% (237 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{18}FO_3$ 313.1240, found 313.1241; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, *J*=2.0, 8.4 Hz, 1H), 7.49 (d, *J*=2.0 Hz, 1H), 7.28–7.24 (m, 2H), 6.97–6.92 (m, 2H), 6.76 (d, *J*=8.4 Hz, 1H), 4.72 (t, *J*=7.6 Hz, 1H), 3.82 (s, 6H), 2.94 (ddd, *J*=2, 7.2, 16.8 Hz, 1H), 2.65 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 1.94 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.09, 161.78 (d, *J*=244.8 Hz), 153.13, 148.76, 134.13 (d, *J*=3.2 Hz), 129.35 (d, *J*=8.3 Hz, 2×), 128.68, 123.32, 115.62 (d, *J*=21.2 Hz, 2×), 110.57, 109.73, 81.88, 69.87, 55.68, 55.53, 51.15, 23.15.

*4.3.14. 1-(3,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)pent-4-yn-1-one (**4n**).* Yield=78% (253 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{21}O_4$ 325.1440, found 325.1442; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, *J*=2.0, 8.4 Hz, 1H), 7.53 (d, *J*=2.0 Hz, 1H), 7.22 (d, *J*=8.4 Hz, 2H), 6.82 (d, *J*=8.8 Hz, 2H), 6.79 (d, *J*=8.4 Hz, 1H), 4.69 (t, *J*=7.6 Hz, 1H), 3.86 (s, 6H), 3.72 (s, 3H), 2.97 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 2.66 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 1.93 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.57, 158.80, 153.09, 148.83, 130.56, 129.11, 128.93 (2×), 123.46, 114.30 (2×), 110.83, 109.86, 82.45, 69.58, 55.89, 55.75, 55.06, 51.55, 23.33.

*4.3.15. 2-Biphenyl-4-yl-1-(3,4-dimethoxyphenyl)pent-4-yn-1-one (**4o**).* Yield=82% (303 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{25}H_{23}O_3$ 371.1647, found 371.1652; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.52 (m, 6H), 7.48–7.30 (m, 5H), 6.83 (d, *J*=8.4 Hz, 1H), 4.80 (t, *J*=7.2 Hz, 1H), 3.90 (s, 6H), 3.07 (ddd, *J*=2.4, 7.2, 16.8 Hz, 1H), 2.74 (ddd, *J*=2.4, 7.2, 16.8 Hz, 1H), 1.96 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.42, 153.33, 148.99, 140.37, 137.58, 129.21, 128.73 (2×), 128.36 (2×), 127.70 (2×), 127.43, 127.35, 127.30, 126.96 (2×), 123.64, 110.93, 109.98, 69.78, 56.00, 55.87, 52.13, 23.38.

*4.3.16. 2-(3,5-Difluorophenyl)-1-(3,4-dimethoxyphenyl)pent-4-yn-1-one (**4p**).* Yield=78% (257 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{17}F_2O_3$ 331.1146, found 331.1152; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, *J*=2.0, 8.4 Hz, 1H), 7.52 (d, *J*=2.0 Hz, 1H), 6.89–6.83 (m, 2H), 6.82 (s, 1H), 6.68 (tt, *J*=2.4, 8.8 Hz, 1H), 4.70 (dd, *J*=6.8, 7.6 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.95 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 2.70 (ddd, *J*=2.8, 7.2, 16.8 Hz, 1H), 1.96 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.41, 163.19 (d, *J*=247.9 Hz), 163.06 (d, *J*=248.7 Hz), 153.68, 142.09 (t, *J*=9.1 Hz), 128.71, 123.54 (2×), 111.06 (d, *J*=25.8 Hz), 111.06 (d, *J*=11.3 Hz), 109.98 (2×), 103.15 (t, *J*=24.2 Hz), 81.39, 70.41, 56.04, 55.89, 51.62, 23.16.

*4.3.17. 2-(4-Fluorophenyl)-1-(2,3,4-trimethoxyphenyl)pent-4-yn-1-one (**4q**).* Yield=80% (274 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{20}FO_4$ 343.1346, found 343.1348; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J*=8.8 Hz, 1H), 7.27–7.22 (m, 2H), 6.98–6.92 (m, 2H), 6.63 (d, *J*=8.8 Hz, 1H), 4.86 (t, *J*=7.6 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 2.99 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 2.62 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 1.92 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.32, 162.00 (d, *J*=244.9 Hz), 157.26, 153.38, 141.88, 133.94 (d, *J*=3.1 Hz), 129.96 (d, *J*=8.3 Hz, 2×), 125.87, 125.56, 115.40 (d, *J*=21.2 Hz, 2×), 107.07, 82.38, 69.59, 61.76, 60.85, 55.99, 54.99, 23.19.

*4.3.18. 2-(3,4-Dimethoxyphenyl)-1-(4-methoxynaphthalen-1-yl) pent-4-yn-1-one (**4r**).* Yield=82% (307 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{24}H_{23}O_4$ 375.1596, found 375.1601; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76–8.73 (m, 1H), 8.26 (ddd, *J*=0.8, 1.6, 8.4 Hz, 1H), 7.96 (d, *J*=8.0 Hz, 1H), 7.58 (dt, *J*=1.6, 8.4 Hz, 1H), 7.48 (dt, *J*=1.6, 8.4 Hz, 1H), 6.88 (dd, *J*=2.0, 8.4 Hz, 1H), 6.86 (d, *J*=2.0 Hz, 1H), 6.76 (d, *J*=8.4 Hz, 1H), 6.72 (d, *J*=8.4 Hz, 1H), 4.78 (d, *J*=7.6 Hz, 1H), 4.00 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 3.12 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 2.73 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 1.97 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.24, 158.86, 149.09, 148.24, 132.22, 130.99, 130.51, 128.50, 127.55, 125.91, 125.77, 125.73, 122.05, 120.41, 111.28, 110.52, 101.97, 82.60, 71.76, 69.72, 55.81, 55.68, 54.64, 23.57.

*4.3.19. 2-Benzo[1,3]dioxol-5-yl-1-(4-methoxynaphthalen-1-yl)pent-4-yn-1-one (**4s**).* Yield=80% (286 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{23}H_{19}O_4$ 359.1283, found 359.1285; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J*=8.8 Hz, 1H), 8.27 (dd, *J*=1.2, 8.4 Hz, 1H), 7.98 (d, *J*=8.4 Hz, 1H), 7.62–7.57 (m, 1H), 7.51–7.47 (m, 1H), 6.86 (d, *J*=1.6 Hz, 1H), 6.81 (dd, *J*=1.6, 8.0 Hz, 1H), 6.72 (d, *J*=2.8 Hz, 1H), 6.70 (d, *J*=2.8 Hz, 1H), 5.88 (d, *J*=1.2 Hz, 1H), 5.87 (d, *J*=1.2 Hz, 1H), 4.77 (t, *J*=7.6 Hz, 1H), 3.99 (s, 3H), 3.11 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 2.73 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 1.99 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.74, 158.96, 147.94, 146.85, 132.29,

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132.22, 130.72, 129.56, 127.18, 125.84, 125.77, 125.74, 122.01, 121.39, 108.54, 108.12, 101.98, 101.02, 82.47, 69.81, 55.68, 54.46, 23.51.

*4.3.20. 2-Benzo[1,3]dioxol-5-yl-1-(4-butoxynaphthalen-1-yl)pent-4-yn-1-one (**4t**).* Yield=73% (292 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1755; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J*=8.8 Hz, 1H), 8.30 (dd, *J*=0.8, 8.4 Hz, 1H), 7.97 (d, *J*=8.4 Hz, 1H), 7.61–7.58 (m, 1H), 7.51–7.47 (m, 1H), 6.84 (d, *J*=1.6 Hz, 1H), 6.80 (dd, *J*=1.6, 8.0 Hz, 1H), 6.72 (d, *J*=8.0 Hz, 1H), 6.70 (d, *J*=8.0 Hz, 1H), 5.89 (d, *J*=1.6 Hz, 1H), 5.88 (d, *J*=1.6 Hz, 1H), 4.76 (t, *J*=7.6 Hz, 1H), 4.21–4.14 (m, 2H), 3.09 (ddd, *J*=2.4, 7.2, 16.8 Hz, 1H), 2.72 (ddd, *J*=2.4, 7.2, 16.8 Hz, 1H), 1.97 (t, *J*=2.4 Hz, 1H), 1.93–1.88 (m, 2H), 1.63–1.54 (m, 2H), 1.02 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.72, 158.57, 147.96, 146.87, 132.42, 132.35, 130.94, 128.57, 126.86, 125.91, 125.89, 125.70, 122.15, 121.42, 108.57, 108.16, 102.63, 101.05, 82.53, 69.78, 68.15, 54.44, 31.09, 23.57, 19.40, 13.83.

*4.3.21. 2-Benzo[1,3]dioxol-5-yl-1-(4,7-dimethoxynaphthalen-1-yl) pent-4-yn-1-one (**4u**).* Yield=74% (287 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{24}H_{21}O_5$ 389.1389, found 389.1390; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J*=2.4 Hz, 1H), 8.17 (d, *J*=9.2 Hz, 1H), 8.04 (d, *J*=8.4 Hz, 1H), 7.13 (dd, *J*=2.8, 9.2 Hz, 1H), 6.85 (d, *J*=1.6 Hz, 1H), 6.82 (dd, *J*=2.0, 8.0 Hz, 1H), 6.71 (d, *J*=8.0 Hz, 1H), 6.61 (d, *J*=8.4 Hz, 1H), 5.89 (d, *J*=1.6 Hz, 1H), 5.88 (d, *J*=1.6 Hz, 1H), 4.79 (t, *J*=7.6 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 3.08 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 2.71 (ddd, *J*=2.8, 6.8, 16.8 Hz, 1H), 1.97 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.62, 160.22, 159.48, 147.95, 146.83, 134.41, 132.66, 132.57, 125.11, 123.73, 121.32, 120.75, 118.03, 108.57, 108.05, 104.73, 101.04, 100.52, 82.57, 69.76, 55.65, 55.31, 54.15, 23.68.

4.4. A representative synthetic procedure of skeleton 5 is as follows

$Bi(OTf)_3$ (13 mg, 0.02 mmol) and molecular sieves (4 Å MS, 100 mg) was added to a solution of **4** (1.0 mmol) in dry $MeNO_2$ (5 mL) at rt. The reaction mixture was stirred at rt for 3 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=10/1–4/1) afforded **5**.

*4.4.1. 5-Methyl-2,3-diphenyl-furan (**5a**).* Yield=88% (206 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{17}H_{15}O$ 235.1123, found 235.1126; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 2H), 7.43–7.19 (m, 8H), 6.18 (d, *J*=0.8 Hz, 1H), 2.41 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.27, 146.76, 134.69, 131.46, 128.56 (2×), 128.53 (2×), 128.29 (2×), 127.01, 126.92, 125.90 (2×), 123.13, 110.12, 13.56; Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.38; H, 6.18.

*4.4.2. 2-(4-Fluorophenyl)-5-methyl-3-phenyl-furan (**5b**).* Yield=86% (217 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{17}H_{14}FO$ 253.1029, found 253.1031; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.28 (m, 7H), 7.00–6.94 (m, 2H), 6.17 (d, *J*=0.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.83 (d, *J*=245.6 Hz), 151.24, 145.90, 134.45, 131.26, 129.20, 128.60 (2×), 128.47 (2×), 127.70 (d, *J*=7.6 Hz, 2×), 127.11, 115.29 (d, *J*=21.9 Hz, 2×), 110.01, 13.51.

*4.4.3. 2-(4-Methoxyphenyl)-5-methyl-3-phenyl-furan (**5c**).*[5b] Yield=82% (216 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_2$ 265.1229, found 265.1230; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J*=9.2 Hz, 2H), 7.42–7.24 (m, 5H), 6.82 (d, *J*=9.2 Hz, 2H), 6.15 (d, *J*=0.8 Hz, 1H), 3.80 (s, 3H), 2.38 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.76, 150.69, 146.89, 134.82, 128.49 (2×), 128.46 (2×), 127.51 (2×), 126.70, 124.35, 121.67, 113.78 (2×), 109.73, 55.21, 13.54.

*4.4.4. 2-(4-Methoxyphenyl)-5-methyl-3-p-tolyl-furan (**5d**).* Yield=84% (234 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{19}O_2$ 279.1385, found 279.1391; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J*=8.8 Hz, 2H), 7.30 (d, *J*=8.0 Hz, 2H), 7.16 (d, *J*=8.0 Hz, 2H), 6.84 (d, *J*=8.8 Hz, 2H), 6.15 (d, *J*=0.8 Hz, 1H), 3.81 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.63, 150.56, 146.63, 136.35, 131.78, 129.21 (2×), 128.29 (2×), 127.40 (2×), 124.45, 121.57, 113.72 (2×), 109.80, 55.18, 21.17, 13.53.

*4.4.5. 3-(4-Fluorophenyl)-2-(4-methoxyphenyl)-5-methyl-furan (**5e**).*[5b] Yield=79% (223 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{18}H_{16}FO_2$ 283.1134, found 283.1133; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J*=8.8 Hz, 2H), 7.35–7.32 (m, 2H), 7.04–7.00 (m, 2H), 6.83 (d, *J*=8.8 Hz, 2H), 6.11 (d, *J*=0.8 Hz, 1H), 3.81 (s, 3H), 2.37 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.80 (d, *J*=244.1 Hz), 158.82, 150.78, 146.90, 130.79 (d, *J*=3.0 Hz), 130.03 (d, *J*=7.6 Hz, 2×), 127.47 (2×), 124.13, 120.65, 115.44 (d, *J*=21.2 Hz, 2×), 113.84 (2×), 109.63, 55.22, 13.52 (d, *J*=2.3 Hz); Anal. Calcd for $C_{18}H_{15}FO_2$: C, 76.58; H, 5.36. Found: C, 76.82; H, 5.55.

*4.4.6. 2,3-Bis-(4-methoxyphenyl)-5-methyl-furan (**5f**).*[5b] Yield=80% (235 mg); Colorless solid; mp=95–97 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1339; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J*=8.8 Hz, 2H), 7.31 (d, *J*=8.8 Hz, 2H), 6.88 (d, *J*=8.8 Hz, 2H), 6.82 (d, *J*=8.8 Hz, 2H), 6.11 (d, *J*=1.2 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 2.37 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.60, 158.47, 150.52, 146.44, 129.56 (2×), 127.33 (2×), 127.15, 124.49, 121.28, 113.95 (2×), 113.75 (2×), 109.82, 55.22, 55.20, 13.54; Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.82; H, 6.01. Single-crystal X-ray diagram: crystal of compound **5f** was grown by slow diffusion of EtOAc into a solution of compound **5f** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P b c n, *a*=7.867 (2) Å, *b*=9.448 (3) Å, *c*=21.293 (6) Å, *V*=1582.5 (7) $Å^3$, *Z*=4, d_{calcd}=1.235 g/cm_3, *F*(000)=624, 2θ range 1.913–26.588°, *R* indices (all data) *R*1=0.0931, wR2=0.1279.

*4.4.7. 2-(4-Methoxyphenyl)-5-methyl-3-(4-trifluoromethylphenyl)-furan (**5g**).* Yield=80% (266 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{16}F_3O_2$ 333.1102, found 333.1103; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J*=8.0 Hz, 2H), 7.49 (d, *J*=8.0 Hz, 2H), 7.42 (d, *J*=8.8 Hz, 2H), 6.86 (d, *J*=8.8 Hz, 2H), 6.17 (d, *J*=0.8 Hz, 1H), 3.82 (s, 3H), 2.39 (d, *J*=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.16, 151.26, 147.81, 138.56, 128.49 (2×), 127.84 (2×), 125.47 (d, *J*=3.8 Hz, 2×), 125.40 (d, *J*=3.8 Hz, 2×), 123.73, 120.32, 113.96 (2×), 109.17, 55.22, 13.49.

*4.4.8. 3-(3,5-Difluorophenyl)-2-(4-methoxyphenyl)-5-methyl-furan (**5h**).* Yield=83% (249 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{18}H_{15}F_2O_2$ 301.1040, found 301.1042; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J*=8.8 Hz, 2H), 6.92–6.84 (m, 4H), 6.72–6.66 (m, 1H), 6.12 (d, *J*=1.2 Hz, 1H), 3.82 (s, 3H), 2.37 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.15 (d, *J*=245.7 Hz), 163.02 (d, *J*=245.6 Hz), 151.22, 147.87, 138.08, 127.96 (2×), 123.47, 119.65, 114.29, 114.00 (2×), 111.02 (d, *J*=25.0 Hz), 111.02 (d, *J*=11.4 Hz), 108.97, 102.00 (t, *J*=25.0 Hz), 55.25, 13.47.

*4.4.9. 3-Biphenyl-4-yl-2-(4-methoxyphenyl)-5-methyl-furan (**5i**).* Yield=75% (255 mg); Colorless solid; mp=126–128 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{21}O_2$ 341.1542, found 341.1545; ^{1}H NMR (400 MHz, $CDCl_3$):

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δ 7.65–7.62 (m, 2H), 7.60–7.56 (m, 2H), 7.51–7.43 (m, 6H), 7.37–7.33 (m, 1H), 6.85 (d, *J*=8.8 Hz, 2H), 6.20 (d, *J*=1.2 Hz, 1H), 3.82 (s, 3H), 2.40 (d, *J*=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.82, 150.83, 147.04, 140.73, 139.37, 133.78, 128.77 (2×), 128.74 (2×), 127.64 (2×), 127.21, 127.15 (2×), 126.90 (2×), 124.32, 121.22, 113.81 (2×), 109.59, 55.22, 13.57.

*4.4.10. 2-(4-Methoxyphenyl)-5-methyl-3-naphthalen-2-yl-furan (**5j**).*[5b] Yield=77% (242 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{22}H_{19}O_2$ 315.1385, found 315.1389; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J*=8.4 Hz, 1H), 7.91 (d, *J*=8.4 Hz, 1H), 7.87 (dd, *J*=1.6, 8.0 Hz, 1H), 7.52–7.39 (m, 4H), 7.25 (d, *J*=8.8 Hz, 2H), 6.67 (d, *J*=8.8 Hz, 2H), 6.16 (d, *J*=0.8 Hz, 1H), 3.71 (s, 3H), 2.46 (d, *J*=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.29, 150.23, 147.68, 133.85, 132.97, 132.13, 128.21, 127.68, 127.63, 126.23 (2×), 126.21, 126.05, 125.88, 125.66, 124.16, 119.41, 113.67 (2×), 111.76, 55.09, 13.63.

*4.4.11. 2-(3,4-Dimethoxyphenyl)-5-methyl-3-phenyl-furan (**5k**).* Yield=80% (235 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{19}O_3$ 295.1334, found 295.1336; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.40 (m, 2H), 7.37–7.32 (m, 2H), 7.29–7.25 (m, 1H), 7.10 (dd, *J*=2.0, 8.4 Hz, 1H), 7.01 (d, *J*=2.0 Hz, 1H), 6.79 (d, *J*=8.4 Hz, 1H), 6.16 (d, *J*=0.8 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 2.39 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.66, 148.49, 148.13, 146.71, 134.79, 128.62 (2×), 128.40 (2×), 126.78, 124.38, 121.92, 118.50, 110.96, 109.82, 109.26, 55.75, 55.50, 13.51.

*4.4.12. 2-(3,4-Dimethoxyphenyl)-5-methyl-3-p-tolyl-furan (**5l**).* Yield=81% (249 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{21}O_3$ 309.1491, found 309.1486; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.29 (m, 2H), 7.16–7.14 (m, 2H), 7.09 (dd, *J*=2.0, 8.4 Hz, 1H), 7.04 (d, *J*=2.0 Hz, 1H), 6.79 (d, *J*=8.4 Hz, 1H), 6.14 (d, *J*=0.8 Hz, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.57, 148.54, 148.08, 146.51, 136.44, 131.78, 129.12 (2×), 128.48 (2×), 124.58, 121.88, 118.51, 110.98, 109.93, 109.29, 55.78, 55.58, 21.14, 13.54; Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 78.02; H, 6.80.

*4.4.13. 2-(3,4-Dimethoxyphenyl)-3-(4-fluorophenyl)-5-methyl-furan (**5m**).* Yield=76% (237 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{18}FO_3$ 313.1240, found 313.1245; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.33 (m, 2H), 7.06–7.01 (m, 3H), 6.98 (d, *J*=2.0 Hz, 1H), 6.79 (d, *J*=8.4 Hz, 1H), 6.11 (d, *J*=0.8 Hz, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 2.38 (d, *J*=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.79 (d, *J*=244.0 Hz), 150.78, 148.60, 148.25, 146.75, 130.77 (d, *J*=3.0 Hz), 130.21 (d, *J*=7.6 Hz, 2×), 124.19, 120.88, 118.58, 115.35 (d, *J*=21.2 Hz, 2×), 111.01, 109.76, 109.22, 55.78, 55.58, 13.51.

*4.4.14. 2-(3,4-Dimethoxyphenyl)-3-(4-methoxyphenyl)-5-methyl-furan (**5n**).* Yield=78% (253 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{21}O_4$ 325.1440, found 325.1442; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J*=8.8 Hz, 2H), 7.08 (dd, *J*=2.0, 8.4 Hz, 1H), 7.03 (d, *J*=2.0 Hz, 1H), 6.89 (d, *J*=8.8 Hz, 2H), 6.79 (d, *J*=8.4 Hz, 1H), 6.11 (d, *J*=0.8 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H), 2.38 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.53, 150.52, 148.55, 148.05, 146.32, 129.72 (2×), 127.11, 124.60, 121.56, 118.43, 113.86 (2×), 111.02, 109.94, 109.22, 55.78, 55.59, 55.21, 13.51.

*4.4.15. 3-Biphenyl-4-yl-2-(3,4-dimethoxyphenyl)-5-methyl-furan (**5o**).* Yield=76% (281 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{25}H_{23}O_3$ 371.1647, found 371.1649; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.58 (m, 4H), 7.51–7.44 (m, 4H), 7.38–7.34 (m, 1H), 7.15 (dd, *J*=2.0, 8.4 Hz, 1H), 7.08 (d, *J*=2.0 Hz, 1H), 6.82 (d, *J*=8.4 Hz, 1H), 6.21 (d, *J*=0.8 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 2.41 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.83, 148.57, 148.25, 146.92, 140.66, 139.48, 133.79, 128.95 (2×), 128.77 (2×), 127.24, 127.06 (2×), 126.85 (2×), 124.40, 121.51, 118.74, 111.01, 109.71, 109.41, 55.79, 55.60, 13.56.

*4.4.16. 3-(3,5-Difluorophenyl)-2-(3,4-dimethoxyphenyl)-5-methyl-furan (**5p**).* Yield=80% (264 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{17}F_2O_3$ 331.1146, found 331.1147; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (dd, *J*=2.0, 8.4 Hz, 1H), 7.01 (d, *J*=2.0 Hz, 1H), 6.94–6.89 (m, 2H), 6.82 (d, *J*=8.4 Hz, 1H), 6.72–6.66 (m, 1H), 6.12 (d, *J*=0.8 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 2.37 (d, *J*=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.09 (d, *J*=246.3 Hz), 162.96 (d, *J*=245.6 Hz), 151.24, 148.77, 147.70, 138.07 (t, *J*=9.8 Hz), 123.56, 119.87, 119.22, 111.17 (d, *J*=25.8 Hz), 111.18 (d, *J*=9.1 Hz, 2×), 109.64, 109.09, 102.02 (t, *J*=25.0 Hz, 2×), 55.83, 55.70, 13.46.

*4.4.17. 3-(4-Fluorophenyl)-5-methyl-2-(2,3,4-trimethoxyphenyl)-furan (**5q**).* Yield=76% (260 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{20}FO_4$ 343.1346, found 343.1348; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.21 (m, 2H), 7.02 (d, *J*=8.8 Hz, 1H), 6.96–6.91 (m, 2H), 6.65 (d, *J*=8.4 Hz, 1H), 6.25 (d, *J*=0.8 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.64 (s, 3H), 2.37 (d, *J*=0.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.44 (d, *J*=243.4 Hz), 154.09, 152.24, 151.48, 144.27, 142.38, 130.37 (d, *J*=3.0 Hz), 128.72 (d, *J*=7.6 Hz, 2×), 125.74, 122.44, 118.41, 115.06 (d, *J*=21.2 Hz, 2×), 107.60, 107.06, 60.88, 60.84, 55.89, 13.57.

*4.4.18. 3-(3,4-Dimethoxyphenyl)-2-(4-methoxynaphthalen-1-yl)-5-methyl-furan (**5r**).* Yield=73% (273 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{24}H_{23}O_4$ 375.1596, found 375.1596; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (dd, *J*=1.2, 8.4 Hz, 1H), 7.79 (dd, *J*=1.2, 8.4 Hz, 1H), 7.47 (d, *J*=7.6 Hz, 2H), 7.44–7.39 (m, 1H), 6.85–6.81 (m, 2H), 6.69 (d, *J*=8.4 Hz, 1H), 6.63 (d, *J*=1.6 Hz, 1H), 6.40 (d, *J*=0.8 Hz, 1H), 4.03 (s, 3H), 3.80 (s, 3H), 3.34 (s, 3H), 2.42 (d, *J*=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.01, 151.55, 148.42, 147.42, 146.10, 132.99, 129.27, 126.95, 126.53, 125.93, 125.67, 125.32, 123.50, 122.04, 122.01, 119.31, 110.98, 110.58, 107.11, 103.39, 55.71, 55.58, 55.24, 13.72.

*4.4.19. 5-[2-(4-Methoxynaphthalen-1-yl)-5-methyl-furan-3-yl]-benzo[1,3]dioxole (**5s**).* Yield=74% (265 mg); Colorless solid; mp=140–142 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{23}H_{19}O_4$ 359.1283, found 359.1286; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (dd, *J*=1.2, 8.4 Hz, 1H), 7.78 (dd, *J*=1.2, 8.4 Hz, 1H), 7.49–7.40 (m, 3H), 6.81 (d, *J*=8.4 Hz, 1H), 6.71 (dd, *J*=1.6, 8.0 Hz, 1H), 6.66 (d, *J*=1.6 Hz, 1H), 6.61 (d, *J*=8.0 Hz, 1H), 6.33 (d, *J*=1.2 Hz, 1H), 5.85 (s, 2H), 4.03 (s, 3H), 2.41 (d, *J*=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.07, 151.51, 147.44, 146.32, 145.91, 133.04, 129.23, 127.96, 126.89, 125.81, 125.77, 125.30, 123.60, 122.10, 121.70, 120.77, 108.23, 107.85, 107.49, 103.46, 100.73, 55.55, 13.69.

*4.4.20. 5-[2-(4-Butoxynaphthalen-1-yl)-5-methyl-furan-3-yl]-benzo[1,3]dioxole (**5t**).* Yield=75% (300 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1752; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (dd, *J*=1.6, 7.6 Hz, 1H), 7.78 (dd, *J*=1.2, 7.6 Hz, 1H), 7.49–7.40 (m, 3H), 6.80 (d, *J*=8.0 Hz, 1H), 6.72 (dd, *J*=1.2, 8.0 Hz, 1H), 6.68 (d, *J*=1.2 Hz, 1H), 6.62 (d, *J*=8.0 Hz, 1H), 6.34 (d, *J*=0.8 Hz, 1H), 5.85 (s, 2H), 4.18 (t, *J*=6.4 Hz, 2H), 2.41 (d, *J*=1.2 Hz, 3H), 1.98–1.91 (m, 2H), 1.68–1.89 (m, 2H), 1.05 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.54, 151.46, 147.41, 146.39, 145.87, 133.02, 129.29, 127.96, 126.82, 125.92, 125.72, 125.16, 123.49, 122.22, 121.34, 120.74, 108.22, 107.83, 107.45, 104.12, 100.71, 67.84, 31.32, 19.49, 13.94, 13.70.

*4.4.21. 5-[2-(4,7-Dimethoxynaphthalen-1-yl)-5-methyl-furan-3-yl]-benzo[1,3]dioxole (**5u**).* Yield=74% (287 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{24}H_{21}O_5$ 389.1389, found 389.1390; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J*=9.2 Hz, 1H), 7.49 (d, *J*=8.0 Hz, 1H),

7.08 (dd, J=2.4, 9.2 Hz, 1H), 7.02 (d, J=2.4 Hz, 1H), 6.73 (d, J=8.0 Hz, 1H), 6.72 (d, J=8.0 Hz, 1H), 6.67 (d, J=1.2 Hz, 1H), 6.62 (d, J=8.0 Hz, 1H), 6.33 (s, 1H), 5.85 (s, 2H), 4.01 (s, 3H), 3.61 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.33, 156.19, 151.49, 147.48, 146.30, 145.94, 133.77, 129.75, 128.12, 123.78, 123.16, 120.82, 120.73, 120.66, 117.50, 108.24, 107.84, 107.66, 104.49, 101.83, 100.74, 55.48, 54.94, 13.67.

4.5. A representative synthetic procedure of skeleton 1 is as follows

5 (0.2 mmol) and I_2 (100 mg, 0.4 mmol) was dissolved in EtOAc (15 mL) at rt. Then, 1,2-epoxybutane (440 mg, 6.0 mmol) was added to the reaction mixture and irradiated under a nitrogen atmosphere with a lamp (λ=2540 Å), using a Pyrex glass filter at rt for 80 h. The solvent was evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc=8/1–2/1) afforded **1**.

*4.5.1. 2-Methyl-1-oxa-cyclopenta[l]phenanthrene (**1a**).* Yield=80% (37 mg); Colorless solid; mp=122–124 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{13}O$ 233.0966, found 233.0968; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72–8.69 (m, 2H), 8.30 (dd, J=1.6, 7.6 Hz, 1H), 8.08 (dd, J=1.6, 7.6 Hz, 1H), 7.68–7.58 (m, 4H), 6.87 (q, J=1.2 Hz, 1H), 2.62 (d, J=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.28, 148.16, 127.96, 127.42, 126.89, 126.76, 125.89, 125.19, 124.86, 123.90, 123.54, 123.41, 122.40, 121.40, 120.16, 102.42, 14.23.

*4.5.2. 9-Fluoro-2-methyl-1-oxa-cyclopenta[l]phenanthrene (**1b**).* Yield=82% (41 mg); Colorless solid; mp=82–84 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{12}FO$ 251.0872, found 251.0875; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J=8.4 Hz, 1H), 8.28 (dd, J=2.4, 11.6 Hz, 1H), 8.24 (dd, J=6.0, 8.8 Hz, 1H), 8.04 (d, J=7.6 Hz, 1H), 7.65 (dt, J=0.8, 8.0 Hz, 1H), 7.58 (dt, J=0.8, 8.0 Hz, 1H), 7.39 (dt, J=2.0, 8.4 Hz, 1H), 6.82 (s, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.79 (d, J=241.8 Hz), 154.13, 147.80, 129.96 (d, J=7.5 Hz), 128.55 (d, J=12.2 Hz), 127.86, 127.32, 124.85, 123.97, 123.69, 122.16 (d, J=8.3 Hz), 120.68, 119.12, 115.65 (d, J=23.5 Hz), 108.79 (d, J=22.7 Hz), 102.30, 14.14.

*4.5.3. 9-Methoxy-2-methyl-1-oxa-cyclopenta[l]phenanthrene (**1c**).* Yield=83% (43 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{18}H_{15}O_2$ 263.1072, found 263.1077; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (dd, J=0.8, 8.4 Hz, 1H), 8.22 (d, J=8.8 Hz, 1H), 8.09 (d, J=2.4 Hz, 1H), 8.06 (ddd, J=0.8, 1.2, 8.0 Hz, 1H), 7.63 (dt, J=1.2, 8.4 Hz, 1H), 7.57 (dt, J=1.2, 8.4 Hz, 1H), 7.31 (dd, J=2.4, 8.8 Hz, 1H), 6.84 (d, J=1.2 Hz, 1H), 4.03 (s, 3H), 2.60 (d, J=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.53, 153.46, 148.42, 129.87, 127.90, 127.43, 126.86, 124.47, 123.98, 123.56, 121.69, 119.46, 117.15, 116.56, 105.47, 102.23, 55.51, 14.19.

*4.5.4. 9-Methoxy-2,6-dimethyl-1-oxa-cyclopenta[l]phenanthrene (**1d**).* Yield=85% (47 mg); Colorless solid; mp=123–125 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{17}O_2$ 277.1229, found 277.1230; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (br s, 1H), 8.20 (d, J=8.8 Hz, 1H), 8.07 (d, J=2.4 Hz, 1H), 7.95 (d, J=8.0 Hz, 1H), 7.46 (dd, J=1.2, 8.0 Hz, 1H), 7.29 (dd, J=2.4, 8.8 Hz, 1H), 6.80 (d, J=0.8 Hz, 1H), 4.04 (s, 3H), 2.63 (s, 3H), 2.58 (d, J=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.40, 153.31, 148.01, 133.93, 129.58, 128.48, 127.49, 125.64, 123.84, 123.38, 121.63, 119.41, 117.25, 116.45, 105.42, 102.18, 55.55, 22.01, 14.18. Single-crystal X-ray diagram: crystal of compound **1d** was grown by slow diffusion of EtOAc into a solution of compound **1d** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a=19.7036 (8) Å, b=13.6382 (6) Å, c=10.8241 (4) Å, V=2827.6 (2) Å^3, Z=8, d_{calcd}=1.298 mg/cm^3, F(000)=1168, 2θ range 1.063–26.407°, R indices (all data) R1=0.0622, wR2=0.1816.

*4.5.5. 6-Fluoro-9-methoxy-2-methyl-1-oxa-cyclopenta[l]phenanthrene (**1e**).* Yield=80% (45 mg); Colorless solid; mp=120–122 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{14}FO_2$ 281.0978, found 281.0982; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (dd, J=2.4, 11.6 Hz, 1H), 8.19 (d, J=8.8 Hz, 1H), 7.99 (dd, J=6.0, 8.8 Hz, 1H), 7.90 (d, J=2.4 Hz, 1H), 7.37 (dt, J=2.4, 8.4 Hz, 1H), 7.32 (dd, J=2.4, 8.8 Hz, 1H), 6.77 (d, J=0.8 Hz, 1H), 4.02 (s, 3H), 2.58 (d, J=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.30 (d, J=240.3 Hz), 157.48, 153.66, 129.07, 128.84 (d, J=7.6 Hz), 127.46, 125.70 (d, J=8.3 Hz), 124.38 (d, J=1.5 Hz), 121.81, 119.16, 117.34, 115.49 (d, J=23.5 Hz), 113.82, 108.82 (d, J=22.0 Hz), 105.37, 102.08, 55.51, 14.16. Single-crystal X-ray diagram: crystal of compound **1b** was grown by slow diffusion of EtOAc into a solution of compound **1a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a=31.469 (3) Å, b=5.0480 (4) Å, c=17.5880 (15) Å, V=2704.4 (4) Å^3, Z=4, d_{calcd}=1.377 mg/cm^3, F(000)=1168, 2θ range 0.668–26.686°, R indices (all data) R1=0.0549, wR2=0.1368.

*4.5.6. 6,9-Dimethoxy-2-methyl-1-oxa-cyclopenta[l]phenanthrene (**1f**).* Yield=79% (46 mg); Colorless solid; mp=128–130 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{17}O_3$ 293.1178, found 293.1182; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J=8.8 Hz, 1H), 7.99–7.94 (m, 3H), 7.29 (dt, J=2.4, 8.8 Hz, 2H), 6.76 (t, J=1.2 Hz, 1H), 4.02 (s, 3H), 4.01 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.25, 156.91, 153.36, 147.28, 129.21, 128.66, 125.23, 122.26, 121.70, 119.44, 117.47, 116.34, 116.07, 106.11, 105.90, 102.08, 55.57, 55.56, 14.15.

*4.5.7. 9-Methoxy-2-methyl-6-trifluoromethyl-1-oxa-cyclopenta[l]phenanthrene (**1g**).* Yield=88% (58 mg); Colorless solid; mp=84–86 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{14}F_3O_2$ 331.0946, found 331.0950; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 8.26 (d, J=8.8 Hz, 1H), 8.14 (d, J=8.4 Hz, 1H), 8.07 (d, J=2.0 Hz, 1H), 8.20 (dd, J=2.0, 8.4 Hz, 1H), 7.36 (dd, J=2.0, 8.8 Hz, 1H), 6.86 (d, J=0.8 Hz, 1H), 4.06 (s, 3H), 2.61 (d, J=0.8 Hz, 3H).

*4.5.8. 9,10-Dimethoxy-2-methyl-1-oxa-cyclopenta[l]phenanthrene (**1h**).* Yield=78% (46 mg); Colorless solid; mp=95–97 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{17}O_3$ 293.1178, found 293.1186; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56–8.54 (m, 1H), 8.07–8.05 (m, 1H), 8.04 (s, 1H), 7.65 (s, 1H), 7.61–7.54 (m, 2H), 6.86 (d, J=0.8 Hz, 1H), 4.13 (s, 3H), 4.12 (s, 3H), 2.61 (d, J=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.52, 149.73, 148.23, 129.25, 127.40, 126.64, 125.77, 124.50, 124.02, 122.99, 122.75, 120.11, 117.21, 104.62, 102.40, 100.67, 56.06, 56.03, 14.21.

*4.5.9. 9,10-Dimethoxy-2,6-dimethyl-1-oxa-cyclopenta[l]phenanthrene (**1i**).* Yield=74% (45 mg); Colorless solid; mp=104–106 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{19}O_3$ 307.1334, found 307.1336; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.03 (s, 1H), 7.95 (d, J=8.4 Hz, 1H), 7.63 (s, 1H), 7.41 (dd, J=1.2, 8.0 Hz, 1H), 6.83 (d, J=0.8 Hz, 1H), 4.14 (s, 3H), 4.11 (s, 3H), 2.63 (s, 3H), 2.60 (d, J=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.39, 149.67, 148.11, 147.67, 133.98, 130.88, 127.46, 124.45, 123.91, 122.76, 120.08, 117.34, 104.76, 104.68, 102.37, 100.68, 56.09, 56.05, 22.05, 14.21.

*4.5.10. 6-Fluoro-9,10-dimethoxy-2-methyl-1-oxa-cyclopenta[l]phenanthrene (**1j**).* Yield=76% (47 mg); Colorless solid; mp=135–137 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{16}FO_3$ 311.1084, found 311.1088; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, J=2.4, 11.2 Hz, 1H), 7.76 (dd, J=2.0, 8.8 Hz, 1H), 7.75 (s,

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1H), 7.53 (d, J=1.2 Hz, 1H), 7.29 (dt, J=2.4, 8.0 Hz, 1H), 6.75 (t, J=1.2 Hz, 1H), 4.09 (s, 3H), 4.08 (s, 3H), 2.58 (d, J=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.31 (d, J=239.6 Hz), 153.61, 150.05, 148.11, 147.43 (d, J=2.3 Hz), 128.67 (d, J=7.6 Hz), 125.67 (d, J=7.6 Hz), 123.05, 121.88, 119.73, 117.43, 114.35 (d, J=23.5 Hz), 108.03 (d, J=22.7 Hz), 104.44, 102.20, 100.52, 56.01, 55.93, 14.14.

*4.5.11. 6,9,10-Trimethoxy-2-methyl-1-oxa-cyclopenta[l]phenanthrene (**1k**).* Yield=75% (48 mg); Colorless solid; mp=210–212 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{19}O_4$ 323.1283, found 323.1288; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J=8.8 Hz, 1H), 7.93 (s, 1H), 7.92 (d, J=2.4 Hz, 1H), 7.62 (s, 1H), 7.25 (d, J=2.4, 8.8 Hz, 1H), 6.80 (q, J=0.8 Hz, 1H), 4.11 (s, 6H), 4.02 (s, 3H), 2.59 (d, J=0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.97, 153.46, 149.90, 148.01, 146.97, 128.68, 125.33, 122.04, 121.11, 120.10, 117.62, 114.82, 105.80, 104.86, 102.27, 100.72, 56.12, 56.06, 55.65, 14.21; Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.69; H, 5.58. Single-crystal X-ray diagram: crystal of compound **1k** was grown by slow diffusion of EtOAc into a solution of compound **1k** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a=7.7621 (4) Å, b=8.1857 (5) Å, c=24.7632 (13) Å, V=1563.14 (15) Å^3, Z=4, d_{calcd}=1.370 mg/cm^3, F(000)=680, 2θ range 1.655–26.435°, R indices (all data) R1=0.0596, wR2=0.0962.

*4.5.12. Compound (**1l**).* Yield=80% (64 mg); Colorless solid; mp=170–172 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{26}H_{23}O_4$ 399.1596, found 399.1601; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (d, J=8.4 Hz, 1H), 8.48 (dd, J=0.8, 8.4 Hz, 1H), 7.99 (s, 1H), 7.78 (dt, J=1.6, 8.4 Hz, 1H), 7.12 (s, 1H), 7.66 (dt, J=1.2, 8.4 Hz, 1H), 7.44 (s, 1H), 6.82 (s, 1H), 6.12 (s, 2H), 4.35 (t, J=6.0 Hz, 2H), 2.70 (s, 3H), 2.06–1.99 (m, 2H), 1.74–1.65 (m, 2H), 1.09 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.25, 152.61, 149.02, 147.59, 146.68, 129.65, 127.36, 127.26, 126.85, 125.90, 125.74, 123.52, 123.06, 121.96, 121.79, 112.63, 101.95, 101.60, 101.33, 101.24, 99.31, 67.84, 31.50, 19.60, 14.43, 14.01.

*4.5.13. Compound (**1m**).* Yield=80% (62 mg); Colorless solid; mp>230 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{19}O_5$ 387.1233, found 387.1236; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.35 (d, J=8.8 Hz, 1H), 7.99 (s, 1H), 7.58 (s, 1H), 7.44 (s, 1H), 7.29 (dd, J=2.4, 8.8 Hz, 1H), 6.82 (s, 1H), 6.12 (s, 2H), 4.18 (s, 3H), 4.09 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.98, 157.74, 153.35, 152.87, 149.02, 146.68, 132.67, 131.07, 127.53, 123.42, 123.15, 117.38, 116.21, 112.33, 111.01, 108.16, 102.07, 101.60, 101.36, 101.27, 96.68, 55.43, 55.28, 14.33.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.10.060.

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11. CCDC 1063475 (**1d**), 1063476 (**1e**) and 1406420 (**1k**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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