Organic & Biomolecular Chemistry

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ROYAL SOCIETY OF CHEMISTRY

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View Article Online
DOI: 10.1039/C8OB01684D

Journal Name

ARTICLE

Syntheses of 12*H*-Benzo[*a*]xanthen-12-ones and Benzo[*a*]acridin-12(7*H*)-ones through Au(I)-Catalyzed Michael Addition/6-*Endo*-Trig Cyclization/Aromatization Cascade Annulation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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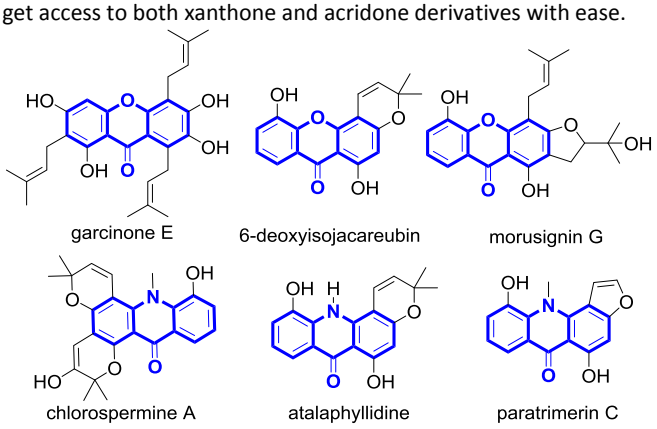
A multifaced gold(I)-catalyzed aromaticity-drived double 6-*endo* cascade cyclization strategy to synthesize both 12*H*-benzo[*a*]xanthen-12-ones and benzo[*a*]acridin-12(7*H*)-ones, whose core motifs xanthone and acridone both exist as important scaffolds in immense number of bioactive compounds, was developed. The scopes of this strategy were examined by using a batch of synthetic 1,3-diphenylprop-2-yn-1-one substrates. To probe the mechanism of this cyclization a control experiment in capturing of intermediate was proceeded. Thus, a putative mechanism was given according to this experiment and previous studies.

Introduction

Xanthone and acridone derivatives, both natural and synthetic,[1] have shown multiple kinds of biological activities,[2] including antitumor,[2g,h,l,m] anti-inflammatory,[2b,f,r,s] antimalarial,[2i,j,n] antimicrobial,[2o,p] antioxidant[2c,e,k,s] and hepatoprotective,[2a,d,q] and have attracted considerable attention in the community of synthesis for their therapeutic usages and intriguing structures (Scheme 1).

A number of classic synthetic strategies,[3] e.g. Friedel-Crafts acylation,[3b,d,e] dehydration[3a,c] and dehydrohalogenation,[3f] were developed and widely demonstrated. In recent years novel synthetic strategies were booming.[3f,4] Larock group, using cascade intermolecular nucleophilic coupling of the substituted benzoates and fluoride ion-induced arynes, generated xanthones and acridones.[3f] Deng and co-workers synthesized acridones via copper-catalyzed intramolecular amination.[4b] Studer group developed oxidative coupling to synthesize xanthones.[4e] Gerbino and colleagues applied copper-based strategy by using 2-substituted benzaldehydes and phenols as starting materials in synthesizing xanthones.[4f] Lei group developed a palladium/copper co-catalyzed carbonylation strategy to acridones (Scheme 2).[4i] To date, most strategies are confined into Friedel-Crafts acylation, oxidation and transition metal-meditated coupling, and cannot be applied in the synthesis of both xanthones and acridones. Inspired by the precedent literatures, especially the versatile work of Larock,[3f] where xanthones and acridones were generated in only one methodology, and our proceeding work on gold(I)-catalyzed cycloisomerization of 1,5-enynes with electron-rich alkenes to synthesize benzene ring,[5] a gold(I)-catalyzed Michael addition[6]/6-*endo*-trig cyclization/aromatization cascade strategy based on 1,3-diphenylprop-2-yn-1-one substrates was proposed to synthesize benzoxanthones and benzoacridones (Scheme 2). This strategy can get access to both xanthone and acridone derivatives with ease.



Scheme 1. Bioactive compounds containing xanthone and acridone scaffolds.

Results and discussion

To test our idea, the 1,3-diphenylprop-2-yn-1-one substrate **5**[7] was prepared through the Sonogashira coupling of 2-bromoaldehyde **1** and trimethylsilylacetylene followed by a Wittig reaction, removal of the protective group, nucleophilic addition and oxidation (Scheme 3). To our delight, when the substrate **5** was subjected to 5 mol % [bis(trifluoromethanesulfonyl)imidate] (triphenylphosphine) gold(I) ($Ph_3PAuNTf_2$)[8] at 100 °C in toluene under the microwave irradiation, 12*H*-benzo[*a*]xanthen-12-one **6** could

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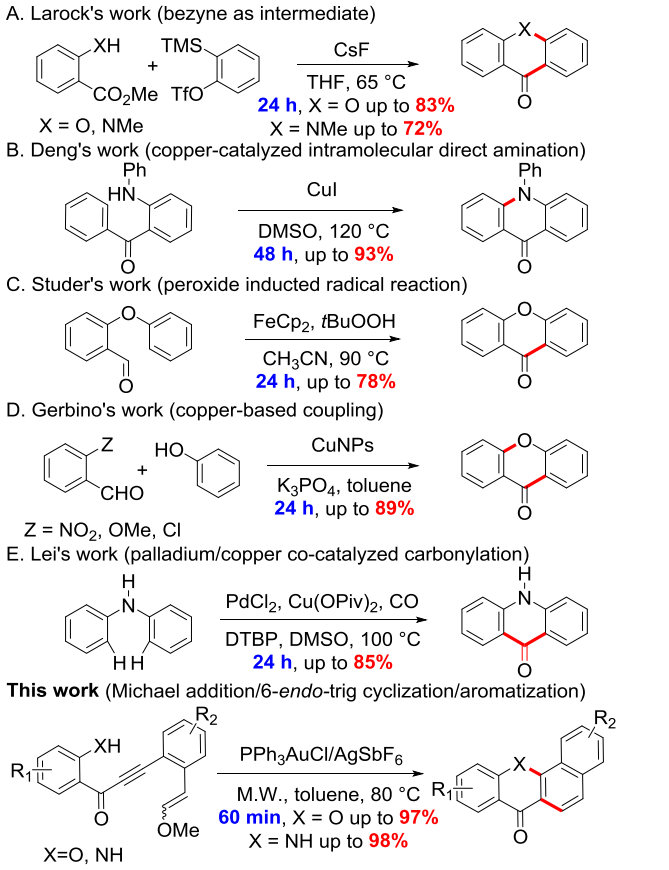
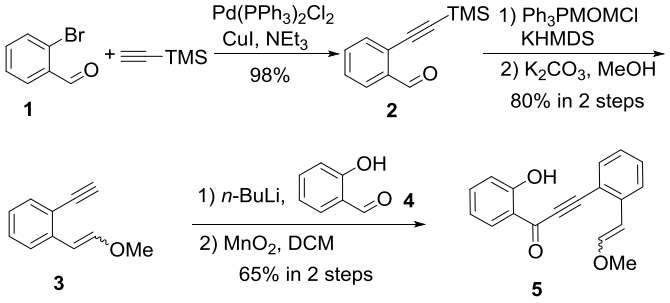
Electronic Supplementary Information (ESI) available: NMR spectra of all the new compounds. See DOI: 10.1039/x0xx00000x

be generated in 72% yield. With our design certified, our study was commenced with



Scheme 2. Reported and our strategies to the xanthone and acridone scaffolds.

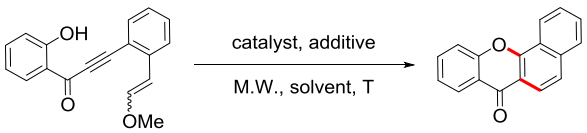
optimization of the conditions in catalysts, temperatures and catalyst loadings. The combination of chloro(triphenyl phosphine)gold(I) (Ph_3PAuCl) and silver hexafluoroantimonate ($AgSbF_6$)[9] was found to be the optimal conditions among the catalytic conditions screened (Table 1, entries 1-4). During the study on temperatures, it is found that lowering the temperature to 80 °C gave no compromise in yield; the yield plunged when the temperature was switched to 50 °C (Table 1, entries 4-6). Decreasing catalyst loading to 3 mol % or below



Scheme 3. The synthetic route to substrate **5**.

gave poor yield, however increasing the loading to 10 mol % gave no significant increasing in yield, therefore the optimal catalyst loading was determined as 5 mol % (Table 1, entries 6, 9-11). As for the screening of solvents, toluene and tetrahydrofuran (THF) were found to be better than both acetonitrile and 1,2-dicloroethane (DCE) in yield, however, the toluene was chosen, due to THF causing high pressure at the reaction temperature for its low boiling point (Table 1, entries 6, 12-14). Thus, the optimal conditions were determined as to

Table 1. Condition screening of the synthesis of 12*H*-benzo[*a*]xanthen-12-one **6**.[a]

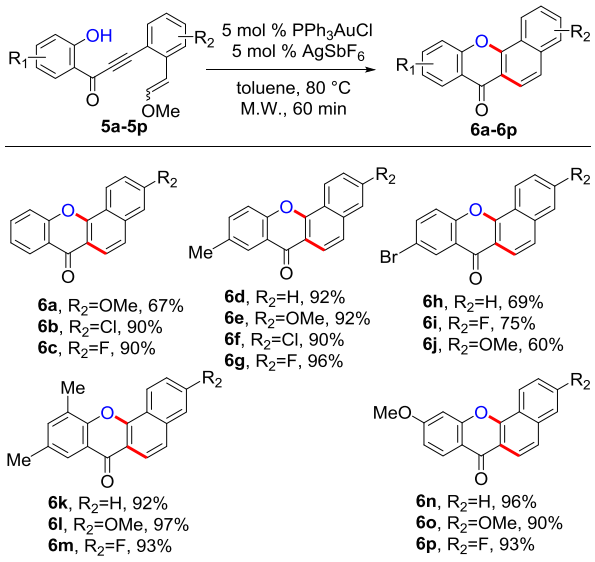


entry	catalyst	additive	catalyst loading (mol %)	additive loading (mol %)	T (°C)	solvent	yield[b] (%)
1	$Ph_3PAuNTf_2$		5		100	toluene	72
2	Ph_3PAuCl		5		100	toluene	0
3	Ph_3PAuCl	AgOTf	5	5	100	toluene	81
4	Ph_3PAuCl	$AgSbF_6$	5	5	100	toluene	94
5	Ph_3PAuCl	$AgSbF_6$	5	5	50	toluene	38
6	**Ph_3PAuCl**	**$AgSbF_6$**	**5**	**5**	**80**	**toluene**	**95**
7	$AgSbF_6$		5		100	toluene	0
8	$HNTf_2$		5		80	toluene	14
9	Ph_3PAuCl	$AgSbF_6$	1	1	80	toluene	36
10	Ph_3PAuCl	$AgSbF_6$	3	3	80	toluene	85
11	Ph_3PAuCl	$AgSbF_6$	10	10	80	toluene	96
12	Ph_3PAuCl	$AgSbF_6$	5	5	80	acetonitrile	0
13	Ph_3PAuCl	$AgSbF_6$	5	5	80	THF	95
14	Ph_3PAuCl	$AgSbF_6$	5	5	80	DCE	52
15	Ph_3PAuCl	$AgSbF_6$	5	5	110	toluene	51[c]

Note: [a] All these screening experiments were performed on a 0.1 mmol scale under microwave irradiation. [b] Isolated yields and the reactions were due in 60 min. [c] Refluxed for 3 hours without microwave irradiation.

stir the reaction at the catalysis of 5 mol % Ph_3PAuCl/5 mol % $AgSbF_6$ in toluene at 80 °C for 1 h under the irradiation of microwave. Microwave irradiation was proved only to boost the reaction and increase the yield by a control experiment (Table 1, entry 15).

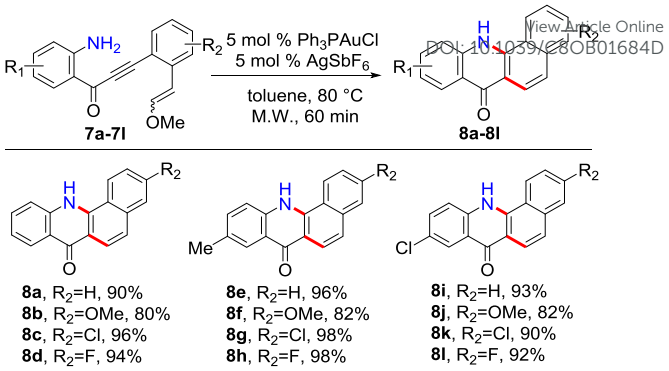
With the optimal conditions in hand, the substituent tolerance was examined by a series of synthetic 1-(2-hydroxyphenyl)-3-(2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one substrates **5a-5p**. The substrates with electron-withdrawing groups (EWG) on the methoxyvinyl phenyl ring gave higher yields than these with electron-donating groups (EDG) (Scheme 4, **6a-6c**). To test the influence of substituents on the phenol ring, substrates **5d-5p** were synthesized in the same way.When it was EDG, e.g. methyl and methoxyl, on the phenol ring, substituents on the methoxyvinyl phenyl ring gave minor influence on the yields, which were all above 90% (Scheme 4, **6d-6g, 6k-6p**). However, the substrates with EWG on the phenol ring gave poor yields, regardless of the substitutions on the methoxyvinyl phenyl ring (Scheme 4, **6h-6j**).



Scheme 4. Substrate scopes for the syntheses of 12*H*-benzo[*a*]xanthen-12-ones.

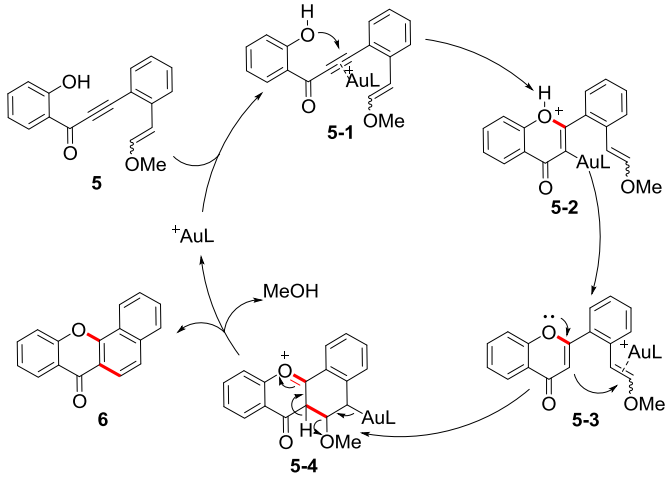
The optimized conditions were then applied to the synthesis of benzo[*a*]acridin-12(7*H*)-one, only by replacing the oxygen with the nitrogen in the substrates. Therefore, the substrates **7a-7l** were synthesized and subjected to the optimal conditions. These tested substrates all gave acceptable to excellent yields, higher than 80%. But, it is worth mention that the substrates with EDG on the methoxyvinyl benzene ring gave a little worse yield in comparison with the EWG substituent globally, which was similar to the screened results in the synthesis of 12*H*-benzo[*a*]xanthen-12-ones.

To probe the mechanism, a set of control experiments were proceeded. When the substrate **5** was subjected to Ph_3PAuCl (5 mol %)/$AgSbF_6$ (5 mol %), the intermediate **5-3** was isolated by lowering reaction temperature (50 °C) and shortening the reaction



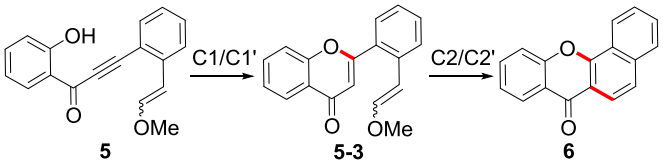
Scheme 5. Substrate scopes for the syntheses of benzo[*a*]acridin-12(7*H*)-ones.

time (10 minutes), then the intermediate **5-3** was subjected to standard conditions for another 10 minutes (Table 2, C1 and C2), the desired product **6** was obtained. The control experiments without the gold catalyst, gave neither **5-3** nor **6**, suggesting that the gold catalyst was indispensable in both cyclization steps (Table 2, C1' and C2'). To figure out the true catalytic species in the second cyclization, 2,6-di*tert*-butylpyridine (5 mol %) was introduced as a scavenger of the trace amount of acid, resulting the formation of the product **6** in 85% yield, which implied that the second cyclization was catalyzed by gold(I) catalyst.



Scheme 6. The proposed mechanism.

Table 2. Control experiments in probing the mechanism.[a]



condition	catalyst	additive	T (°C)	yield (%)
C1	Ph_3PAuCl	$AgSbF_6$	50	98
C1'			50	0
C2	Ph_3PAuCl	$AgSbF_6$	80	93 (85)[b]
C2'			80	0

[a] All these control reactions were performed in toluene as solvent and under microwave irradiation for 10 min. [b] 5 mol % 2,6-di*tert*-Butylpyridine was added.

A putative mechanism of cyclization to 12*H*-benzo[*a*]xanthen-12-ones, according to our previous studies[5b] and the isolation of intermediate **5-3** in the control experiments, was finally shown in Scheme 6. The reactant **5** was activated by the gold(I)-catalyst in forming **5-1** complex, which is then attacked by the hydroxyl group in a 6-*endo*-dig manner to give the intermediate **5-2**. Protodeauration of the intermediate **5-2** afforded **5-3**, in which the new formed enolether would attack the electron-rich methoxyl vinyl ether under the activation of gold(I) species to give the final product **6** after isomerization and aromatization by the release of a methanol from **5-4**.[10] This mechanism can be applied to the cycloisomerization of benzo[*a*]acridin-12(7*H*)-one by simply altering the nucleophile group of 6-*endo*-dig from the hydroxyl group into amine group.

Conclusion

In summary, a unique Michael addition/6-*endo* cascade cyclization/aromatization strategy to yielding both benzoxanthone and benzoacridone derivatives was designed and applied in a series of substrates with acceptable to excellent yields. A predicted mechanism based on the isolated intermediate and precedent study was given. Further applications of this strategy to synthesizing compounds with more complexity and bioactivities are underway in our laboratory.

Experimental section

General experiment methods

Unless otherwise noted, reagents were obtained commercially and used without further purification. Tetrahydrofuran (THF) was distilled from sodium under a nitrogen atmosphere. Dichloromethane (DCM) was distilled from calcium hydride under a nitrogen atmosphere. Toluene was distilled from sodium under a nitrogen atmosphere. TLC analysis of reaction mixtures was performed on Dynamic Adsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 (200-300 mesh) silica gel. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to $CDCl_3$ and DMSO-d_6. HR-ESI-MS was recorded on a Bruker micro-TOFQ-Q instrument. IR spectra were recorded on a Bruker IFS 55 spectrometer. Melting points (mp) were tested on Thomas Hoover capillary melting point apparatus. Microwave reactions were performed using microwave oven CEM Discover in sealed reaction vessels. The temperature was monitored using an internal vertically focused IR temperature sensor.

General procedures for the preparation of 2-alknyl benzaldehydes 2, 2a-2c.

To a mixture of 2-bromobenzaldehyde **1, 1a-1c** (10 mmol), $(Ph_3P)_2PdCl_2$ (0.2 mmol, 140 mg) and CuI (0.1 mmol, 19 mg) was added degassed THF (50 mL) under a nitrogen atmosphere. Then ethynyl trimethylsilane (20 mmol, 2.8 mL) and Et_3N (30 mmol, 4.2 mL) were added by syringe under a nitrogen atmosphere. The solution was stirred at 25 °C for 5 h till the consumption of the starting material. The reaction mixture was filtrated through Celite. The crude materials were purified by a flash column chromatography (EtOAc/petroleum ether) on silica gel to afford the products **2, 2a-2c**.

Spectral data of **2, 2a-2c** were consistent with those reported in the literatures.[5a,10]

General procedures for the preparation of 3, 3a-3c and characterization data.

A magnetically stirred emulsion of (methoxymethyl)triphenylphosphonium chloride (6 mmol, 2 g) in dry THF (30 mL) maintained at –78 °C under a nitrogen atmosphere was treated with potassium bis(trimethylsilyl)amide (1 M in THF, 6 mmol). The reaction was stirred for 0.5 h followed by the addition of **2, 2a-2c** (3 mmol) in dry THF (10 mL) dropwise. The resulting mixture was stirred at –78 °C for 0.5 h and filtered through Celite. The filtrate was concentrated *in vacuo*.

To a solution of the residue obtained above in MeOH (40 mL) was added anhydrous K_2CO_3 (6 mmol, 829 mg). The resulting mixture was stirred at room temperature for 20 min till TLC showed the starting materials were completely consumed, which was then concentrated under the reduced pressure. The reaction mixture was filtrated through Celite. The filtrate was concentrated and purified by a flash column chromatography (EtOAc/petroleum ether) on alkaline aluminum oxide to afford the products **3, 3a-3c**.

Spectral data of **3, 3a-3b** were consistent with those reported in the literatures.[12]

1-Ethynyl-4-fluoro-2-(2-methoxyvinyl)benzene (3c).

Colorless oil (422 mg, 1:0.4 *E*/*Z*) in 80% yield (EtOAc/petroleum ether = 1:200): ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.74 (dd, *J* = 11.3, 2.7 Hz, 1H, *Z*), 7.52 (d, *J* = 12.9 Hz, 1H, *E*), 7.50 – 7.41 (m, 2H, *E* + 1H, *Z*), 6.98 (td, *J* = 8.5, 2.7 Hz, 1H, *Z*), 6.95 (td, *J* = 8.5, 2.7 Hz, 1H, *E*), 6.56 (d, *J* = 7.1 Hz, 1H, *Z*), 6.12 (dd, *J* = 12.9, 1.4 Hz, 1H, *E*), 5.66 (dd, *J* = 7.1, 1.6 Hz, 1H, *Z*), 4.40 (s, 1H, *Z*), 4.39 (s, 1H, *E*), 3.83 (s, 3H, *Z*), 3.68 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 162.2 (d, *J* = 245.9 Hz, *E*), 161.7 (d, *J* = 245.3 Hz, *Z*), 152.8 (*E*), 152.0 (*Z*), 141.0 (d, *J* = 9.1 Hz, *E*), 139.8 (d, *J* = 9.6 Hz, *Z*), 134.8 (d, *J* = 9.3 Hz, *E*), 134.4 (d, *J* = 9.3 Hz, *Z*), 115.5 (d, *J* = 2.8 Hz, *Z*), 115.1 (d, *J* = 2.7 Hz, *E*), 114.2 (d, *J* = 24.0 Hz, *Z*), 112.8 (d, *J* = 22.6 Hz, *Z*), 112.7 (d, *J* = 22.7 Hz, *E*), 109.7 (d, *J* = 23.3 Hz, *E*), 101.8 (d, *J* = 2.5 Hz, *E*), 100.6 (d, *J* = 2.5 Hz, *Z*), 84.6 (*E* + *Z*), 81.3 (*Z*), 81.2 (*E*), 61.2 (*Z*), 56.9 (*E*); IR (thin film, cm^{-1}) 3864, 3672, 1734, 1705, 1685, 1549; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{11}H_{10}FO$ 177.0710, found 177.0715.

General procedures for the preparation of 5, 5a-5p, 7a-7l and characterization data.

To a stirring solution of **3, 3a-3c** (2.1 mmol) in THF (11 mL) was added a solution of *n*-BuLi (1 M in THF, 2.1 mL) dropwise at –78 °C under a nitrogen atmosphere. The reaction was stirred at –78 °C for 1 h followed by the addition of **4, 4a-4g** (1 mmol) dropwise. After stirring at –78 °C for 1 h, the solution was warmed to 0 °C and stir for another 1 h. The reaction mixture was quenched by the addition of a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with ethyl acetate. The combined organic portions were washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*.

To a solution of the residue obtained above in DCM (11 mL) was added activated MnO_2 (5 mmol, 434 mg). The mixture was stirred at room temperature for 3 h till TLC showed the consumption of the starting material. The reaction mixture was filtrated through Celite. The filtrate was concentrated and purified by a flash column chromatography (EtOAc/petroleum ether) on silica gel to afford the products **5**, **5a-5p**, **7a-7l**.

1-(2-Hydroxyphenyl)-3-(2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (5).

Yellow solid (181 mg, 1:0.2 *E*/*Z*) in 65% yield (EtOAc/petroleum ether = 1:70): mp 81.9 – 82.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.83 (s, 1H, *Z*), 11.82 (s, 1H, *E*), 8.16 (dd, *J* = 7.9, 1.6 Hz, 1H, *E*), 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H, *Z*), 7.63 (dd, *J* = 7.7, 0.8 Hz, 1H, *E* + 1H, *Z*), 7.55 – 7.48 (m, 1H, *E* + 1H, *Z*), 7.43 – 7.31 (m, 2H, *E* + 2H, *Z*), 7.22 (d, *J* = 12.9 Hz, 1H, *E*), 7.20 – 7.12 (m, 1H, *E* + 1H, *Z*), 7.04 – 6.88 (m, 2H, *E* + 2H, *Z*), 6.34 (d, *J* = 7.1 Hz, 1H, *Z*), 6.30 (d, *J* = 12.9 Hz, 1H, *E*), 5.82 (d, *J* = 7.1 Hz, 1H, *Z*), 3.83 (s, 3H, *Z*), 3.77 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.3 (*Z*), 182.2 (*E*), 162.9 (*E*), 162.8 (*Z*), 151.6 (*E*), 150.5 (*Z*), 140.9 (*E*), 139.6 (*Z*), 137.1 (*E*), 137.0 (*Z*), 134.3 (*E*), 133.8 (*Z*), 133.01 (*Z*), 132.9 (*E*), 131.5 (*E*), 131.2 (*Z*), 129.0 (*Z*), 125.71 (*E*), 125.66 (*Z*), 124.0 (*E*), 121.0 (*Z*), 120.9 (*E*), 119.4 (*Z*), 119.3 (*E*), 118.25 (*E*), 118.17 (*Z*), 117.1 (*Z*), 116.9 (*E*), 102.6 (*E*), 102.4 (*Z*), 95.8 (*Z*), 95.6 (*E*), 90.2 (*E*), 90.0 (*Z*), 61.2 (*Z*), 56.6 (*E*); IR (thin film, cm^{-1}) 3424, 2924, 2191, 1633, 1591, 1338, 1305, 1201, 1012; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{14}NaO_3$ 301.0835, found 301.0845.

1-(2-Hydroxyphenyl)-3-(4-methoxy-2-(2-methoxyvinyl)phenyl)-prop-2-yn-1-one (5a).

Yellow solid (179 mg, 1:0.3 *E*/*Z*) in 58% yield (EtOAc/petroleum ether = 1:70): mp 91.2 – 93.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.91 (s, 1H, *Z*), 11.89 (s, 1H, *E*), 8.15 (dd, *J* = 7.9, 1.7 Hz, 1H, *E*), 8.12 (dd, *J* = 7.9, 1.6 Hz, 1H, *Z*), 7.72 (d, *J* = 2.6 Hz, 1H, *Z*), 7.59 (d, *J* = 8.6 Hz, 1H, *E* + 1H, *Z*), 7.53 – 7.46 (m, 1H, *E* + 1H, *Z*), 7.23 (d, *J* = 12.9 Hz, 1H, *E*), 7.01 – 6.93 (m, 2H, *E* + 2H, *Z*), 6.90 (d, *J* = 2.5 Hz, 1H, *E*), 6.75 (dd, *J* = 8.6, 2.5 Hz, 1H, *E* + 1H, *Z*), 6.36 (d, *J* = 7.1 Hz, 1H, *Z*), 6.28 (d, *J* = 12.9 Hz, 1H, *E*), 5.82 (d, *J* = 7.1 Hz, 1H, *Z*), 3.86 (s, 3H, *Z*), 3.86 (s, 3H, *E*), 3.85 (s, 3H, *Z*), 3.78 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.4 (*Z*), 182.2 (*E*), 162.9 (*E*), 162.8 (*Z*), 162.3 (*E*), 162.1 (*Z*), 151.9 (*E*), 150.9 (*Z*), 143.1 (*E*), 141.7 (*Z*), 136.84 (*E*), 136.79 (*Z*), 136.4 (*E*), 135.8 (*Z*), 133.0 (*Z*), 132.9 (*E*), 121.1 (*Z*), 121.0 (*E*), 119.3 (*Z*), 119.2 (*E*), 118.3 (*E*), 118.2 (*Z*), 114.1 (*Z*), 112.4 (*Z*), 112.3 (*E*), 109.6 (*Z*), 109.4 (*E*), 109.2 (*E*), 102.7 (*E*), 102.5 (*Z*), 97.3 (*Z*), 97.1 (*E*), 90.3 (*E*), 90.1 (*Z*), 61.4 (*Z*), 56.7 (*E*), 55.5 (*E*), 55.4 (*Z*); IR (thin film, cm^{-1}) 3423, 2937, 2835, 2181, 1629, 1595, 1243, 1012; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}NaO_4$ 331.0941, found 331.0949.

3-(4-Chloro-2-(2-methoxyvinyl)phenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (5b).

Yellow solid (218 mg, 1:0.9 *E*/*Z*) in 70% yield (EtOAc/petroleum ether = 1:70): mp 83.8 – 85.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.76 (s, 1H, *Z*), 11.74 (s, 1H, *E*), 8.17 (d, *J* = 2.1 Hz, 1H, *Z*), 8.12 (dd, *J* = 7.9, 1.6 Hz, 1H, *E*), 8.09 (dd, *J* = 7.9, 1.6 Hz, 1H, *Z*), 7.59 – 7.51 (m, 2H, *E* + 2H, *Z*), 7.41 (d, *J* = 2.0 Hz, 1H, *E*), 7.23 (d, *J* = 12.9 Hz, 1H, *E*), 7.18 – 7.13 (m, 1H, *E* + 1H, *Z*), 7.03 – 6.94 (m, 2H, *E* + 2H, *Z*), 6.39 (d, *J* = 7.1 Hz, 1H, *Z*), 6.24 (d, *J* = 12.9 Hz, 1H, *E*), 5.77 (d, *J* = 7.1 Hz, 1H, *Z*), 3.88 (s, 3H, *Z*), 3.78 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.2 (*Z*), 182.1 (*E*), 163.01 (*E*), 162.98 (*Z*), 152.6 (*E*), 151.7 (*Z*), 142.6 (*E*), 141.1 (*Z*), 137.8 (*E*), 137.6 (*Z*), 137.3 (*E*), 137.2 (*Z*), 135.4 (*E*), 134.8 (*Z*), 133.0 (*Z*), 132.9 (*E*), 129.0 (*Z*), 126.1 (*E*), 126.0 (*Z*), 124.1 (*E*), 121.0 (*Z*), 120.9 (*E*), 119.5 (*Z*), 119.4 (*E*), 118.4 (*E*), 118.3 (*Z*), 115.5 (*Z*), 115.4 (*E*), 101.9 (*E*), 101.5 (*Z*), 94.5 (*Z*), 94.3 (*E*), 90.8 (*E*), 90.6 (*Z*), 61.6 (*Z*), 57.0 (*E*); IR (thin film, cm^{-1}) 3424, 2928, 2194, 1645, 1625, 1341, 1226, 1155, 1014; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{13}ClNaO_3$ 335.0445, found 335.0433.

3-(4-Fluoro-2-(2-methoxyvinyl)phenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (5c).

Yellow solid (186 mg, 1:0.4 *E*/*Z*) in 63% yield (EtOAc/petroleum ether = 1:70): mp 82.3 – 84.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.79 (s, 1H, *Z*), 11.77 (s, 1H, *E*), 8.11 (dd, *J* = 7.9, 1.6 Hz, 1H, *E*), 8.08 (dd, *J* = 7.9, 1.5 Hz, 1H, *Z*), 7.89 (dd, *J* = 11.1, 2.6 Hz, 1H, *Z*), 7.60 (dd, *J* = 8.6, 5.9 Hz, 1H, *E* + 1H, *Z*), 7.54 – 7.48 (m, 1H, *E* + 1H, *Z*), 7.21 (d, *J* = 12.9 Hz, 1H, *E*), 7.08 (dd, *J* = 10.2, 2.5 Hz, 1H, *E*), 7.02 – 6.91 (m, 2H, *E* + 2H, *Z*), 6.89 – 6.84 (m, 1H, *E* + 1H, *Z*), 6.38 (d, *J* = 7.1 Hz, 1H, *Z*), 6.25 (d, *J* = 12.9 Hz, 1H, *E*), 5.80 (dd, *J* = 7.1, 1.4 Hz, 1H, *Z*), 3.86 (s, 3H, *Z*), 3.77 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.2 (*Z*), 182.1 (*E*), 164.5 (d, *J* = 253.1 Hz, *E*), 164.3 (d, *J* = 251.8 Hz, *Z*), 163.0 (*E*), 162.9 (*Z*), 152.7 (*E*), 151.7 (*Z*), 143.8 (d, *J* = 9.4 Hz, *E*), 142.3 (d, *J* = 10.4 Hz, *Z*), 137.2 (*E*), 137.1 (*Z*), 136.5 (d, *J* = 9.7 Hz, *E*), 135.8 (d, *J* = 9.6 Hz, *Z*), 133.0 (*Z*), 132.9 (*E*), 121.0 (*Z*), 120.9 (*E*), 119.5 (*Z*), 119.4 (*E*), 118.4 (*E*), 118.3 (*Z*), 115.9 (d, *J* = 24.3 Hz, *Z*), 113.5 (d, *J* = 22.9 Hz, *E*), 113.4 (d, *J* = 23.2 Hz, *Z*), 113.2 (d, *J* = 2.8 Hz, *Z*), 113.1 (d, *J* = 2.8 Hz, *E*), 110.7 (d, *J* = 23.2 Hz, *E*), 102.1 (d, *J* = 2.4 Hz, *E*), 101.9 (d, *J* = 2.4 Hz, *Z*), 94.9 (*Z*), 94.7 (*E*), 90.2 (*E*), 89.9 (*Z*), 61.5 (*Z*), 56.9 (*E*); IR (thin film, cm^{-1}) 3440, 2925, 2193, 1630, 1596, 1245, 1207, 1013; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{13}FNaO_3$ 319.0741, found 319.0746.

1-(2-Hydroxy-5-methylphenyl)-3-(2-(2-methoxyvinyl)-phenyl)prop-2-yn-1-one (5d).

Yellow solid (196 mg, 1:0.1 *E*/*Z*) in 67% yield (EtOAc/petroleum ether = 1:70): mp 91.7 – 93.2°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.27 (s, 1H, *E*), 11.24 (s, 1H, *Z*), 8.08 (d, *J* = 8.1 Hz, 1H, *Z*), 7.88 (s, 1H, *E* + 1H, *Z*), 7.72 (d, *J* = 7.7 Hz, 1H, *E* + 1H, *Z*), 7.66 (d, *J* = 8.0 Hz, 1H, *E* + 1H, *Z*), 7.55 – 7.41 (m, 3H, *E* + 2H, *Z*), 7.28 – 7.25 (m, 1H, *E* + 1H, *Z*), 6.95 (d, *J* = 8.4 Hz, 1H, *E*), 6.62 (d, *J* = 7.1 Hz, 1H, *Z*), 6.27 (d, *J* = 12.8 Hz, 1H, *E*), 5.73 (d, *J* = 7.1 Hz, 1H, *Z*), 3.84 (s, 3H, *Z*), 3.72 (s, 3H, *E*), 2.33 (s, 3H, *Z*), 2.31 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 180.5 (*E*), 180.3 (*Z*), 159.4 (*E*), 159.3 (*Z*), 152.8 (*E*), 151.8 (*Z*), 140.6 (*E*), 139.4 (*Z*), 138.4 (*E*), 138.4 (*Z*), 134.2 (*E*), 134.0 (*Z*), 132.0 (*Z*), 131.91 (*E*), 131.88 (*E*), 131.6 (*Z*), 129.6 (*Z*), 128.71 (*Z*), 128.68 (*E*), 128.4 (*Z*), 125.9 (*E*), 124.1 (*E*), 120.60 (*Z*), 120.56 (*E*), 117.82 (*E*), 117.79 (*Z*), 116.0 (*Z*), 115.6 (*E*), 102.2 (*E*), 100.8 (*Z*), 94.4 (*E*), 94.2 (*Z*), 90.5 (*E*), 90.4 (*Z*), 61.2 (*Z*), 57.0 (*E*), 20.00 (*Z*), 19.9 (*E*); IR (thin film, cm^{-1}) 3425, 2933, 2187, 1633, 1594, 1343, 1209, 1168, 1086; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{16}NaO_3$ 315.0992, found 315.0992.

1-(2-Hydroxy-5-methylphenyl)-3-(4-methoxy-2-(2-methoxyvinyl)-phenyl)prop-2-yn-1-one (5e).

Yellow solid (200 mg, 1:0.3 *E*/*Z*) in 62% yield (EtOAc/petroleum ether = 1:70): mp 72.5 – 74.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.44 (s, 1H, *E*), 11.40 (s, 1H, *Z*), 7.81 (s, 1H, *E* + 1H, *Z*), 7.67 (d, *J* = 8.6 Hz, 1H, *Z*), 7.62 (d, *J* = 8.6 Hz, 1H, *E* + 1H, *Z*), 7.54 (d, *J* = 12.8 Hz,

1H, *E*), 7.39 (dd, *J* = 8.4, 1.8 Hz, 1H, *E* + 1H, *Z*), 7.14 (d, *J* = 2.4 Hz, 1H, *E*), 6.89 (d, *J* = 8.4 Hz, 1H, *E* + 1H, *Z*), 6.84 (dd, *J* = 8.6, 2.6 Hz, 1H, *Z*), 6.80 (dd, *J* = 8.6, 2.5 Hz, 1H, *E*), 6.60 (d, *J* = 7.1 Hz, 1H, *Z*), 6.21 (d, *J* = 12.8 Hz, 1H, *E*), 5.68 (d, *J* = 7.1 Hz, 1H, *Z*), 3.84 (s, 3H, *Z*), 3.83 (s, 3H, *E*), 3.80 (s, 3H, *Z*), 3.72 (s, 3H, *E*), 2.30 (s, 3H, *Z*), 2.28 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 180.7 (*E*), 180.6 (*Z*), 162.1 (*E*), 161.8 (*Z*), 159.5 (*E*), 159.4 (*Z*), 153.1 (*E*), 152.0 (*Z*), 142.9 (*E*), 141.4 (*Z*), 138.1 (*E*), 138.0 (*Z*), 136.2 (*E*), 136.0 (*Z*), 131.9 (*Z*), 131.8 (*E*), 128.49 (*Z*), 128.46 (*E*), 120.33 (*Z*), 120.28 (*E*), 117.7 (*E*), 117.6 (*Z*), 113.9 (*Z*), 112.91 (*E*), 112.0 (*Z*), 108.6 (*E*), 108.2 (*Z*), 107.8 (*E*), 102.2 (*E*), 100.9 (*Z*), 96.4 (*E*), 96.1 (*Z*), 90.5 (*E*), 90.2 (*Z*), 61.2 (*Z*), 57.0 (*E*), 55.5 (*E*), 55.3 (*Z*), 20.0 (*Z*), 19.8 (*E*); IR (thin film, cm^{-1}) 3423, 2932, 2833, 1634, 1597, 1483, 1297, 1225, 1040; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{20}H_{18}NaO_4$ 345.1097, found 345.1095.

(E)-3-(4-Chloro-2-(2-methoxyvinyl)phenyl)-1-(2-hydroxy-5-methylphenyl)prop-2-yn-1-one (5f).

Yellow solid (209 mg) in 64% yield (EtOAc/petroleum ether = 1:70): mp 76.5 – 78.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.59 (s, 1H), 7.87 (s, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.40 (s, 1H), 7.34 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.21 (d, *J* = 12.9 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.25 (d, *J* = 12.9 Hz, 1H), 3.77 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.0, 161.0, 152.7, 142.5, 138.5, 137.7, 135.3, 132.5, 128.7, 126.1, 124.2, 120.6, 118.2, 115.5, 102.2, 94.1, 90.9, 57.2, 20.6; IR (thin film, cm^{-1}) 3424, 2924, 2189, 1632, 1588, 1478, 1348, 1170, 1081; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{19}H_{15}ClNaO_3$ 349.0602, found 349.0618.

3-(4-Fluoro-2-(2-methoxyvinyl)phenyl)-1-(2-hydroxy-5-methylphenyl)prop-2-yn-1-one (5g).

Yellow solid (183 mg, 1:0.7 *E*/*Z*) in 59% yield (EtOAc/petroleum ether = 1:70): mp 84.5 – 86.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.26 (s, 1H, *E*), 11.22 (s, 1H, *Z*), 7.89 – 7.75 (m, 2H, *E* + 3H, *Z*), 7.63 (d, *J* = 12.7 Hz, 1H, *E*), 7.55 (dd, *J* = 10.9, 2.1 Hz, 1H, *E*), 7.44 (d, *J* = 7.4 Hz, 1H, *E* + 1H, *Z*), 7.13 (td, *J* = 8.5, 2.5 Hz, 1H, *Z*), 7.09 (td, *J* = 8.5, 2.3 Hz, 1H, *E*), 6.93 (d, *J* = 8.4 Hz, 1H, *E* + 1H, *Z*), 6.71 (d, *J* = 7.0 Hz, 1H, *Z*), 6.23 (d, *J* = 12.7 Hz, 1H, *E*), 5.74 (d, *J* = 6.9 Hz, 1H, *Z*), 3.88 (s, 3H, *Z*), 3.73 (s, 3H, *E*), 2.32 (s, 3H, *Z*), 2.30 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 180.4 (*E*), 180.2 (*Z*), 164.0 (d, *J* = 250.3 Hz, *E*), 163.6 (d, *J* = 249.8 Hz, *Z*), 159.4 (*E*), 159.3 (*Z*), 154.2 (*E*), 153.3 (*Z*), 143.8 (d, *J* = 9.9 Hz, *E*), 142.1 (d, *J* = 10.6 Hz, *Z*), 138.4 (*E*), 138.3 (*Z*), 136.9 (d, *J* = 10.0 Hz, *E*), 136.5 (d, *J* = 9.7 Hz, *Z*), 131.9 (*Z*), 131.8 (*E*), 128.7 (*Z*), 128.6 (*E*), 120.5 (*Z*), 120.4 (*E*), 117.8 (*E*), 117.7 (*Z*), 114.7 (d, *J* = 24.1 Hz, *Z*), 113.44 (d, *J* = 22.9 Hz, *Z*), 113.41 (d, *J* = 23.2 Hz, *E*), 112.5 (d, *J* = 2.2 Hz, *Z*), 112.1 (d, *J* = 2.0 Hz, *E*), 110.4 (d, *J* = 23.4 Hz, *E*), 101.6 (d, *J* = 1.6 Hz, *E*), 100.2 (d, *J* = 1.6 Hz, *Z*), 93.5 (*E*), 93.3 (*Z*), 90.5 (*E*), 90.3 (*Z*), 61.5 (*Z*), 57.2 (*E*), 20.0 (*Z*), 19.9 (*E*); IR (thin film, cm^{-1}) 3425, 2924, 2187, 1632, 1597, 1345, 1244, 1209, 1018; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{19}H_{15}FNaO_3$ 333.0897, found 333.0896.

1-(5-Bromo-2-hydroxyphenyl)-3-(2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (5h).

Yellow solid (189 mg, 1:0.3 *E*/*Z*) in 53% yield (EtOAc/petroleum ether = 1:70): mp 72.7 – 74.6 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.33 (s, 1H, *E*), 11.29 (s, 1H, *Z*), 8.14 – 8.01 (m, 1H, *E* + 1H, *Z*), 7.79 – 7.61 (m, 3H, *E* + 3H, *Z*), 7.58 – 7.43 (m, 2H, *E* + 1H, *Z*), 7.32 – 7.21 (m, 1H, *E* + 1H, *Z*), 7.02 (d, *J* = 8.7 Hz, 1H, *E* + 1H, *Z*), 6.59 (d, *J* = 6.9 Hz, 1H, *Z*), 6.24 (d, *J* = 12.8 Hz, 1H, *E*), 5.74 (d, *J* = 7.0 Hz, 1H, *Z*), 3.83 (s, 3H, *Z*), 3.72 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 178.3 (*E*), 178.0 (*Z*), 159.8 (*E*), 159.7 (*Z*), 152.7 (*E*), 151.7 (*Z*), 140.6 (*E*), 139.6 (*Z*), 139.2 (*E*), 139.1 (*Z*), 134.3 (*E*), 134.0 (*Z*), 133.8 (*Z*), 133.7 (*E*), 131.9 (*E*), 131.7 (*Z*), 128.5 (*Z*), 125.92 (*Z*), 125.86 (*E*), 123.9 (*E*), 123.2 (*Z*), 123.1 (*E*), 120.5 (*E* + *Z*), 116.0 (*Z*), 115.5 (*E*), 110.40 (*E* + *Z*), 101.8 (*E*), 100.9 (*Z*), 94.6 (*E*), 94.4 (*Z*), 90.8 (*E*), 90.7 (*Z*), 61.2 (*Z*), 56.8 (*E*); IR (thin film, cm^{-1}) 3425, 2924, 2853, 2183, 1631, 1548, 1160, 1012; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{18}H_{13}BrNaO_3$ 378.9940, found 378.9940.

1-(5-Bromo-2-hydroxyphenyl)-3-(4-fluoro-2-(2-methoxyvinyl)-phenyl)prop-2-yn-1-one (5i).

Yellow solid (206 mg, 1:1.5 *E*/*Z*) in 55% yield (EtOAc/petroleum ether = 1:70): mp 92.5 – 94.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.32 (s, 1H, *E*), 11.29 (s, 1H, *Z*), 8.05 (s, 1H, *Z*), 8.05 (s, 1H, *E*), 7.85 – 7.70 (m, 3H, *E* + 2H, *Z*), 7.65 (d, *J* = 12.7 Hz, 1H, *Z*), 7.56 (d, *J* = 10.5 Hz, 1H, *E*), 7.15 – 7.05 (m, 1H, *E* + 1H, *Z*), 7.01 (d, *J* = 8.7 Hz, 1H, *E* + 1H, *Z*), 6.68 (d, *J* = 6.8 Hz, 1H, *Z*), 6.20 (d, *J* = 12.7 Hz, 1H, *E*), 5.74 (d, *J* = 6.7 Hz, 1H, *Z*), 3.87 (s, 3H, *Z*), 3.73 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 178.0 (*E*), 177.6 (*Z*), 164.1 (d, *J* = 250.3 Hz, *E*), 163.6 (d, *J* = 250.0 Hz, *Z*), 159.7 (*E*), 159.5 (*Z*), 154.2 (*E*), 153.2 (*Z*), 143.8 (d, *J* = 10.0 Hz, *E*), 142.2 (d, *J* = 10.4 Hz, *Z*), 139.1 (*E*), 139.0 (*Z*), 136.9 (d, *J* = 9.9 Hz, *E*), 136.6 (d, *J* = 9.9 Hz, *Z*), 133.7 (*Z*), 133.6 (*E*), 123.3 (*Z*), 123.2 (*E*), 120.45 (*E*), 120.4 (*Z*), 114.7 (d, *J* = 24.2 Hz, *E*), 113.5 (d, *J* = 23.0 Hz, *Z*), 113.5 (d, *J* = 23.2 Hz, *Z*), 112.4 (d, *J* = 2.1 Hz, *Z*), 112.0 (d, *J* = 1.5 Hz, *E*), 110.39 (*E*), 110.35 (*Z*), 110.3 (d, *J* = 20.5 Hz, *E*), 101.2 (*E*), 100.2 (*Z*), 93.5 (*E*), 93.1 (*Z*), 90.90 (*E*), 90.87 (*Z*), 61.5 (*Z*), 57.0 (*E*); IR (thin film, cm^{-1}) 3426, 2927, 2184, 1627, 1587, 1462, 1180, 1097, 1013; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{18}H_{12}BrFNaO_3$ 396.9846, found 396.9840.

1-(5-Bromo-2-hydroxyphenyl)-3-(4-methoxy-2-(2-methoxyvinyl)-phenyl)prop-2-yn-1-one (5j).

Yellow solid (197 mg, 1:0.3 *E*/*Z*) in 51% yield (EtOAc/petroleum ether = 1:70): mp 86.5 – 88.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.87 (s, 1H, *E*), 11.83 (s, 1H, *Z*), 8.26 (d, *J* = 2.3 Hz, 1H, *Z*), 8.20 (d, *J* = 2.3 Hz, 1H, *E*), 7.68 (d, *J* = 2.3 Hz, 1H, *Z*), 7.60 (d, *J* = 8.6 Hz, 1H, *E* + 1H, *Z*), 7.56 (dd, *J* = 8.8, 2.4 Hz, 1H, *E* + 1H, *Z*), 7.24 (d, *J* = 12.9 Hz, 1H, *E*), 6.93 – 6.87 (m, 2H, *E* + 1H, *Z*), 6.75 (dd, *J* = 8.6, 2.0 Hz, 1H, *E* + 1H, *Z*), 6.42 (d, *J* = 7.1 Hz, 1H, *Z*), 6.24 (d, *J* = 12.9 Hz, 1H, *E*), 5.80 (d, *J* = 7.1 Hz, 1H, *Z*), 3.86 (s, 3H, *E* + 6H, *Z*), 3.81 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.1 (*Z*), 181.0 (*E*), 162.5 (*E*), 162.4 (*Z*), 161.8 (*E*), 161.7 (*Z*), 152.1 (*E*), 151.1 (*Z*), 143.4 (*E*), 142.2 (*Z*), 139.4 (*E*), 139.2 (*Z*), 136.7 (*E*), 136.1 (*Z*), 135.1 (*Z*), 134.7 (*E*), 122.3 (*Z*), 122.2 (*E*), 120.4 (*E*), 120.3 (*Z*), 114.3 (*Z*), 113.2 (*Z*), 112.5 (*Z*), 112.4 (*E*), 110.8 (*E*), 109.23 (*Z*), 109.19 (*E*), 109.0 (*E*), 102.5 (*Z*), 102.4 (*E*), 98.7 (*Z*), 98.4 (*E*), 90.2 (*E*), 90.1 (*Z*), 61.4 (*Z*), 56.9 (*E*), 55.6 (*E*), 55.5 (*Z*); IR (thin film, cm^{-1}) 3431, 2933, 2178, 1637, 1585, 1466, 1231, 1013; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{19}H_{15}BrNaO_4$ 409.0046, found 409.0059.

1-(2-Hydroxy-3,5-dimethylphenyl)-3-(2-(2-methoxyvinyl)-phenyl)prop-2-yn-1-one (5k).

Yellow solid (187 mg, 1:0.1 *E*/*Z*) in 61% yield (EtOAc/petroleum ether = 1:70): mp 68.5 – 70.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.74 (s, 1H, *E*), 11.71 (s, 1H, *Z*), 8.08 (d, *J* = 8.1 Hz, 1H, *Z*), 7.75 (s, 1H, *E* + 1H, *Z*), 7.72 (d, *J* = 7.5 Hz, 1H, *E*), 7.65 (d, *J* = 8.0 Hz, 1H, *E*),

DOI: 10.1039/C8OB01684D

7.56 – 7.45 (m, 2H, *E* + 2H, *Z*), 7.37 (s, 1H, *E* + 1H, *Z*), 7.28 – 7.24 (m, 1H, *E* + 1H, *Z*), 6.62 (d, *J* = 7.1 Hz, 1H, *Z*), 6.25 (d, *J* = 12.8 Hz, 1H, *E*), 5.70 (d, *J* = 7.1 Hz, 1H, *Z*), 3.83 (s, 3H, *Z*), 3.72 (s, 3H, *E*), 2.30 (s, 3H, *Z*), 2.27 (s, 3H, *E*), 2.17 (s, 3H, *E* + 3H, *Z*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.3 (*E* + *Z*), 158.31 (*E*), 158.26 (*Z*), 152.8 (*E*), 151.8 (*Z*), 140.6 (*E*), 140.6 (*Z*), 139.5 (*E*), 139.4 (*Z*), 134.2 (*E*), 134.0 (*Z*), 131.9 (*E*), 131.6 (*Z*), 129.7 (*Z*), 129.6 (*E*), 128.4 (*Z*), 128.1 (*Z*), 128.0 (*E*), 126.4 (*E*), 126.3 (*Z*), 125.88 (*Z*), 125.86 (*E*), 124.1 (*E*), 119.4 (*E* + *Z*), 115.9 (*Z*), 115.5 (*E*), 102.1 (*E*), 100.8 (*Z*), 94.9 (*E*), 94.8 (*Z*), 90.2 (*E*), 89.9 (*Z*), 61.2 (*Z*), 57.0 (*E*), 20.0 (*Z*), 19.9 (*E*), 14.9 (*E* + *Z*); IR (thin film, cm^{-1}) 3422, 2920, 2837, 2182, 1649, 1580, 1352, 1252, 1096; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{20}H_{18}NaO_3$ 329.1148, found 329.1149.

1-(2-Hydroxy-3,5-dimethylphenyl)-3-(4-methoxy-2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (5l).

Yellow solid (202 mg, 1:0.1 *E*/*Z*) in 60% yield (EtOAc/petroleum ether = 1:70): mp 77.3 – 79.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.02 (s, 1H, *E*), 12.02 (s, 1H, *Z*), 7.76 (s, 1H, *E*), 7.71 (d, *J* = 2.5 Hz, 1H, *Z*), 7.59 (d, *J* = 8.6 Hz, 1H, *E* + 1H, *Z*), 7.22 – 7.20 (m, 2H, *E* + 1H, *Z*), 6.90 (d, *J* = 2.5 Hz, 1H, *E* + 1H, *Z*), 6.75 (dd, *J* = 8.6, 2.5 Hz, 1H, *E* + 1H, *Z*), 6.35 (d, *J* = 7.1 Hz, 1H, *Z*), 6.30 (d, *J* = 12.9 Hz, 1H, *E*), 5.86 (d, *J* = 7.1 Hz, 1H, *Z*), 3.86 (s, 3H, *E* + 3H, *Z*), 3.85 (s, 3H, *Z*), 3.76 (s, 3H, *E*), 2.32 (s, 3H, *Z*), 2.30 (s, 3H, *E*), 2.25 (s, 3H, *E* + 3H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.43 (*Z*), 182.42 (*E*), 162.1 (*E*), 162.0 (*Z*), 159.43 (*E*), 159.35 (*Z*), 151.8 (*E*), 150.7 (*Z*), 142.9 (*E*), 141.6 (*Z*), 139.0 (*E*), 138.9 (*Z*), 136.3 (*E*), 135.7 (*Z*), 130.2 (*Z*), 130.1 (*E*), 127.8 (*E*), 127.7 (*Z*), 127.1 (*E*), 127.0 (*Z*), 120.11 (*Z*), 120.06 (*E*), 114.2 (*Z*), 112.4 (*Z*), 112.3 (*E*), 109.9 (*Z*), 109.7 (*E*), 109.3 (*E*), 103.1 (*E*), 102.8 (*Z*), 96.4 (*E* + *Z*), 90.6 (*E*), 90.4 (*Z*), 61.4 (*Z*), 57.0 (*E*), 55.6 (*E*), 55.5 (*Z*), 20.7 (*Z*), 20.6 (*E*), 15.4 (*E* + *Z*); IR (thin film, cm^{-1}) 3423, 2921, 2852, 2172, 1635, 1598, 1347, 1217, 1076; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{21}H_{20}NaO_4$ 359.1254, found 359.1247.

3-(4-Fluoro-2-(2-methoxyvinyl)phenyl)-1-(2-hydroxy-3,5-dimethylphenyl)prop-2-yn-1-one (5m).

Yellow solid (188 mg, 1:0.8 *E*/*Z*) in 58% yield (EtOAc/petroleum ether = 1:70): mp 75.9 – 77.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.72 (s, 1H, *E*), 11.69 (s, 1H, *Z*), 7.85 – 7.74 (m, 1H, *E* + 2H, *Z*), 7.70 (s, 1H, *E* + 1H, *Z*), 7.62 (d, *J* = 12.7 Hz, 1H, *E*), 7.54 (dd, *J* = 10.9, 2.5 Hz, 1H, *E*), 7.34 (s, 1H, *E* + 1H, *Z*), 7.12 (td, *J* = 8.4, 2.7 Hz, 1H, *Z*), 7.08 (td, *J* = 8.5, 2.5 Hz, 1H, *E*), 6.71 (d, *J* = 7.1 Hz, 1H, *Z*), 6.20 (d, *J* = 12.7 Hz, 1H, *E*), 5.69 (dd, *J* = 7.0, 0.9 Hz, 1H, *Z*), 3.87 (s, 3H, *Z*), 3.73 (s, 3H, *E*), 2.29 (s, 3H, *Z*), 2.26 (s, 3H, *E*), 2.16 (s, 3H, *E* + 3H, *Z*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 181.2 (*E* + *Z*), 164.1 (d, *J* = 250.4 Hz, *E*), 163.6 (d, *J* = 250.0 Hz, *Z*), 158.31 (*E*), 158.26 (*Z*), 154.3 (*E*), 153.4 (*Z*), 143.8 (d, *J* = 10.0 Hz, *E*), 142.2 (d, *J* = 10.4 Hz, *Z*), 139.4 (*E* + *Z*), 136.9 (d, *J* = 10.0 Hz, *E*), 136.6 (d, *J* = 9.9 Hz, *Z*), 129.7 (*Z*), 129.6 (*E*), 128.1 (*Z*), 128.0 (*E*), 126.4 (*E*), 126.3 (*Z*), 119.3 (*E* + *Z*), 114.7 (d, *J* = 24.2 Hz, *Z*), 113.5 (d, *J* = 23.0 Hz, *Z*), 113.4 (d, *J* = 23.1 Hz, *E*), 112.3 (d, *J* = 2.5 Hz, *Z*), 112.0 (d, *J* = 2.3 Hz, *E*), 110.4 (d, *J* = 23.6 Hz, *E*), 101.5 (d, *J* = 2.2 Hz, *E*), 100.1 (d, *J* = 2.1 Hz, *Z*), 94.0 (*E*), 93.8 (*Z*), 90.2 (*E*), 89.9 (*Z*), 61.5 (*Z*), 57.2 (*E*), 20.0 (*Z*), 19.9 (*E*), 14.9 (*E* + *Z*); IR (thin film, cm^{-1}) 3423, 2960, 2921, 2192, 1633, 1604, 1358, 1230, 1076; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{20}H_{17}FNaO_3$ 347.1054, found 347.1063.

1-(2-Hydroxy-4-methoxyphenyl)-3-(2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (5n).

Yellow solid (98 mg, 1:0.4 *E*/*Z*) in 32% yield (EtOAc/petroleum ether = 1:70): mp 87.5 – 89.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.30 (s, 1H, *Z*), 12.29 (s, 1H, *E*), 8.14 (d, *J* = 8.0 Hz, 1H, *Z*), 8.04 (d, *J* = 8.9 Hz, 1H, *E*), 8.01 (d, *J* = 8.9 Hz, 1H, *Z*), 7.62 (d, *J* = 7.5 Hz, 1H, *E* + 1H, *Z*), 7.44 – 7.34 (m, 2H, *E* + 1H, *Z*), 7.22 (d, *J* = 12.9 Hz, 1H, *E*), 7.20 – 7.15 (m, 1H, *E* + 1H, *Z*), 6.52 (dd, *J* = 9.0, 2.4 Hz, 1H, *Z*), 6.50 (dd, *J* = 8.9, 2.4 Hz, 1H, *E*), 6.45 – 6.44 (m, 1H, *E* + 1H, *Z*), 6.33 (d, *J* = 7.1 Hz, 1H, *Z*), 6.29 (d, *J* = 12.9 Hz, 1H, *E*), 5.82 (d, *J* = 7.1 Hz, 1H, *Z*), 3.87 (s, 3H, *E* + 3H, *Z*), 3.84 (s, 3H, *Z*), 3.76 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.4 (*Z*), 180.3 (*E*), 167.0 (*E*), 166.9 (*Z*), 165.83 (*E*), 165.77 (*Z*), 151.5 (*E*), 150.4 (*Z*), 140.6 (*E*), 139.4 (*Z*), 134.7 (*Z*), 134.6 (*E*), 134.1 (*E*), 133.7 (*Z*), 131.2 (*E*), 130.9 (*Z*), 129.0 (*Z*), 125.71 (*E*), 125.66 (*Z*), 124.0 (*E*), 117.4 (*Z*), 117.2 (*E*), 115.5 (*Z*), 115.4 (*E*), 108.5 (*E* + *Z*), 102.7 (*E*), 102.5 (*Z*), 100.70 (*Z*), 100.68 (*E*), 94.9 (*Z*), 94.7 (*E*), 90.1 (*E*), 89.9 (*Z*), 61.2 (*Z*), 56.7 (*E*), 55.80 (*E*), 55.79 (*Z*); IR (thin film, cm^{-1}) 3421, 2932, 2192, 1633, 1587, 1350, 1265, 1162, 1008; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{19}H_{16}NaO_4$ 331.0941, found 331.0950.

1-(2-Hydroxy-4-methoxyphenyl)-3-(4-methoxy-2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (5o).

Yellow solid (118 mg, 1:0.5 *E*/*Z*) in 35% yield (EtOAc/petroleum ether = 1:70): mp 76.5 – 78.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.38 (s, 1H, *Z*), 12.36 (s, 1H, *E*), 8.03 (d, *J* = 8.9 Hz, 1H, *E*), 8.00 (d, *J* = 8.9 Hz, 1H, *Z*), 7.71 (d, *J* = 2.6 Hz, 1H, *Z*), 7.57 (d, *J* = 8.6 Hz, 1H, *E* + 1H, *Z*), 7.22 (d, *J* = 12.9 Hz, 1H, *E*), 6.90 (d, *J* = 2.4 Hz, 1H, *E*), 6.74 (dd, *J* = 8.6, 2.3 Hz, 1H, *E* + 1H, *Z*), 6.52 (dd, *J* = 8.9, 2.4 Hz, 1H, *Z*), 6.49 (dd, *J* = 8.9, 2.4 Hz, 1H, *E*), 6.44 – 6.43 (m, 1H, *E* + 1H, *Z*), 6.35 (d, *J* = 7.1 Hz, 1H, *Z*), 6.27 (d, *J* = 12.9 Hz, 1H, *E*), 5.82 (d, *J* = 7.1 Hz, 1H, *Z*), 3.86 (s, 3H, *E* + 3H, *Z*), 3.86 (s, 3H, *E* + 3H, *Z*), 3.85 (s, 3H, *Z*), 3.77 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 179.20 (*Z*), 179.18 (*E*), 166.6 (*E* + *Z*), 164.6 (*Z*), 164.5 (*E*), 162.0 (*Z*), 161.6 (*E*), 153.0 (*Z*), 152.2 (*E*), 142.7 (*Z*), 141.1 (*E*), 136.0 (*Z*), 135.9 (*E*), 134.4 (*E*), 134.3 (*Z*), 114.8 (*E*), 114.7 (*Z*), 113.9 (*E*), 112.9 (*Z*), 112.0 (*E*), 108.51 (*Z*), 108.48 (*Z*), 108.4 (*E*), 108.3 (*E*), 108.0 (*Z*), 101.9 (*Z*), 100.9 (*E*), 100.84 (*E*), 100.76 (*Z*), 95.7 (*Z*), 95.5 (*E*), 89.9 (*Z*), 89.7 (*E*), 61.3 (*Z*), 56.7 (*E*), 56.0 (*E* + *Z*), 55.6 (*Z*), 55.3 (*E*); IR (thin film, cm^{-1}) 3422, 2924, 2169, 1631, 1384, 1271, 1115, 1009; HRMS (ESI) *m/z* [M+H]$^+$ calcd for $C_{20}H_{19}O_5$ 339.1227, found 339.1231.

(E)-3-(4-Fluoro-2-(2-methoxyvinyl)phenyl)-1-(2-hydroxy-4-methoxyphenyl)prop-2-yn-1-one (5p).

Yellow solid (107 mg) in 33% yield (EtOAc/petroleum ether = 1:70): mp 92.5 – 94.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.99 (s, 1H), 8.04 (d, *J* = 8.9 Hz, 1H), 7.79 (dd, *J* = 8.2, 6.3 Hz 1H), 7.66 (d, *J* = 12.8 Hz, 1H), 7.57 (dd, *J* = 10.8, 1.6 Hz 1H), 7.11 (dt, *J* = 8.3, 1.8 Hz, 1H), 6.63 (dd, *J* = 8.8, 1.7 Hz, 1H), 6.56 (d, *J* = 1.5 Hz, 1H), 6.20 (d, *J* = 12.8 Hz, 1H), 3.86 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 178.9, 164.0 (d, *J* = 250.0 Hz), 154.2, 143.6 (d, *J* = 9.9 Hz), 136.7 (d, *J* = 9.9 Hz), 134.5, 131.5, 128.7, 114.8, 113.4 (d, *J* = 23.1 Hz), 112.1 (d, *J* = 2.3 Hz), 110.3 (d, *J* = 23.6 Hz), 108.6, 101.3 (d, *J* = 2.2 Hz), 100.9, 93.1, 89.9, 56.9, 56.1; IR (thin film, cm^{-1}) 3424, 2925, 2191, 2169, 1631, 1384, 1261, 1121, 1009; HRMS (ESI) *m/z* [M-H]$^-$ calcd for $C_{19}H_{14}FO_4$ 325.0882, found 325.0879.

(E)-1-(2-Aminophenyl)-3-(2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (7a).

Yellow solid (158 mg) in 57% yield (EtOAc/petroleum ether = 1:50): mp 72.3 – 74.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.22 (d, *J* = 13.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.71 – 6.67 (m, 2H), 6.33 (d, *J* = 13.0 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 177.9, 152.25, 152.18, 139.9, 135.5, 133.7, 133.6, 131.1, 125.8, 123.9, 117.3, 117.0, 116.5, 114.9, 102.1, 91.4, 90.5, 56.6; IR (thin film, cm^{-1}) 3449, 3335, 3065, 2926, 2184, 1632, 1618, 1232, 1159, 1003; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{15}NNaO_2$ 300.0995, found 300.1010.

1-(2-Aminophenyl)-3-(4-methoxy-2-(2-methoxyvinyl)phen-yl)prop-2-yn-1-one (7b).

Yellow solid (187 mg, 1:0.2 *E*/*Z*) in 61% yield (EtOAc/petroleum ether = 1:50): mp 63.5 – 65.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.07 (dd, *J* = 8.1, 1.2 Hz, 1H, *E*), 8.04 (dd, *J* = 8.1, 1.2 Hz, 1H, *Z*), 7.63 (d, *J* = 8.6 Hz, 1H, *Z*), 7.62 (d, *J* = 2.6 Hz, 1H, *Z*), 7.59 (d, *J* = 8.8 Hz, 1H, *E*), 7.57 (d, *J* = 13.1 Hz, 1H, *E*), 7.41 (s, 2H, *E* + 2H, *Z*), 7.34 – 7.29 (m, 1H, *E* + 1H, *Z*), 7.16 (d, *J* = 2.4 Hz, 1H, *E*), 6.85 (dd, *J* = 8.6, 2.6 Hz, 1H, *Z*), 6.82 – 6.81 (m, 2H, *E* + 1H, *Z*), 6.67 – 6.64 (m, 1H, *Z*), 6.63 – 6.59 (m, 1H, *E* + 1H, *Z*), 6.21 (d, *J* = 12.8 Hz, 1H, *E*), 5.66 (d, *J* = 7.1 Hz, 1H, *Z*), 3.83 (s, 3H, *Z*), 3.83 (s, 3H, *E*), 3.80 (s, 3H, *Z*), 3.73 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 178.09 (*Z*), 178.07 (*E*), 161.4 (*E*), 161.0 (*Z*), 152.6 (*E* + *Z*), 152.0 (*E*), 151.8 (*Z*), 142.1 (*E*), 140.6 (*Z*), 135.5 (*E* + *Z*), 135.2 (*Z*), 135.1 (*E*), 133.5 (*Z*), 133.4 (*E*), 117.4 (*Z*), 117.3 (*E*), 116.91 (*E*), 116.86 (*Z*), 115.0 (*Z*), 114.8 (*E*), 113.9 (*Z*), 112.7 (*E*), 111.8 (*Z*), 109.1 (*Z*), 108.8 (*E*), 108.5 (*E*), 102.1 (*E*), 101.0 (*Z*), 91.7 (*E*), 91.5 (*Z*), 91.2 (*E*), 90.9 (*Z*), 61.2 (*Z*), 56.5 (*E*), 55.4 (*E*), 55.2 (*Z*); IR (thin film, cm^{-1}) 3434, 3315, 2925, 2853, 2178, 1619, 1539, 1233, 1159, 1001; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{17}NNaO_3$ 330.1101, found 330.1101.

(E)-1-(2-Aminophenyl)-3-(4-chloro-2-(2-methoxyvinyl)phen-yl)prop-2-yn-1-one (7c).

Yellow solid (187 mg) in 60% yield (EtOAc/petroleum ether = 1:50): mp 83.5 – 85.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.38 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 12.9 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.70 – 6.68 (m, 2H), 6.37 (s, 2H), 6.26 (d, *J* = 12.9 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 177.6, 153.8, 152.2, 141.9, 136.1, 135.5, 135.3, 133.5, 125.7, 123.4, 117.1, 117.0, 115.2, 114.9, 101.1, 92.0, 89.2, 56.9; IR (thin film, cm^{-1}) 3415, 2924, 2853, 2192, 1632, 1583, 1384, 1229, 1160; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}ClNO_2$ 312.0786, found 312.0791.

1-(2-Aminophenyl)-3-(4-fluoro-2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (7d).

Yellow solid (183 mg, 1:0.3 *E*/*Z*) in 62% yield (EtOAc/petroleum ether = 1:50): mp 77.5 – 79.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.06 (dd, *J* = 8.1, 1.4 Hz, 1H, *E*), 8.03 (dd, *J* = 8.1, 1.4 Hz, 1H, *Z*), 7.81 (dd, *J* = 11.3, 2.6 Hz, 1H, *Z*), 7.75 (dd, *J* = 8.5, 6.2 Hz, 1H, *Z*), 7.71 (dd, *J* = 8.5, 6.2 Hz, 1H, *E*), 7.63 (d, *J* = 12.8 Hz, 1H, *E*), 7.53 (dd, *J* = 10.9, 2.1 Hz, 1H, *E*), 7.46 (s, 2H, *E* + 2H, *Z*), 7.33 (m, 1H, *E* + 1H, *Z*), 7.11 – 7.04 (m, 1H, *E* + 1H, *Z*), 6.82 (d, *J* = 8.4 Hz, 1H, *E* + 1H, *Z*), 6.69 (d, *J* = 7.1 Hz, 1H, *Z*), 6.67 – 6.63 (m, 1H, *Z*), 6.61 (t, *J* = 7.5 Hz, 1H, *E*), 6.21 (d, *J* = 12.8 Hz, 1H, *E*), 5.69 (dd, *J* = 7.0, 1.4 Hz, 1H, *Z*), 3.86 (s, 3H, *Z*), 3.73 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 177.78 (*E*), 177.75 (*Z*), 163.6 (d, *J* = 249.1 Hz, *E*), 163.1 (d, *J* = 248.5 Hz, *Z*), 153.7 (*E*), 153.0 (*Z*), 152.14 (*E*), 152.10 (*Z*), 143.0 (d, *J* = 9.7 Hz, *E*), 141.4 (d, *J* = 10.2 Hz, *Z*), 136.2 (d, *J* = 9.5 Hz, *E*), 135.8 (d, *J* = 9.5 Hz, *Z*), 135.4 (*E*), 135.3 (*Z*), 133.6 (*Z*), 133.5 (*E*), 117.21 (*Z*), 117.18 (*E*), 117.0 (*E*), 116.9 (*Z*), 115.1 (*Z*), 114.9 (*E*), 114.6 (d, *J* = 24.2 Hz, *Z*), 113.3 (d, *J* = 22.6 Hz, *E*), 113.2 (d, *J* = 3.0 Hz, *Z*), 112.9 (d, *J* = 2.3 Hz, *E*), 110.22 (d, *J* = 23.5 Hz, *E*), 110.18 (d, *J* = 21.1 Hz, *Z*), 101.4 (d, *J* = 2.2 Hz, *E*), 100.3 (d, *J* = 1.8 Hz, *Z*), 91.3 (*E*), 91.1 (*Z*), 89.6 (*E*), 89.4 (*Z*), 61.4 (*Z*), 56.8 (*E*); IR (thin film, cm^{-1}) 3401, 3303, 2928, 2192, 1638, 1618, 1243, 1159; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{14}FNNaO_2$ 318.0901, found 318.0902.

1-(2-Amino-5-methylphenyl)-3-(2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (7e).

Yellow solid (189 mg, 1:0.2 *E*/*Z*) in 65% yield (EtOAc/petroleum ether = 1:50): mp 81.5 – 83.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.07 (d, *J* = 8.0 Hz, 1H, *Z*), 7.85 (s, 1H, *E* + 1H, *Z*), 7.68 – 7.62 (m, 1H, *E* + 1H, *Z*), 7.61 (d, *J* = 8.0 Hz, 1H, *E*), 7.49 – 7.45 (m, 1H, *E* + 1H, *Z*), 7.42 (t, *J* = 7.7 Hz, 1H, *E*), 7.33 (s, 2H, *E* + 2H, *Z*), 7.25 – 7.21 (m, 1H, *E* + 1H, *Z*), 7.18 (dd, *J* = 8.5, 1.9 Hz, 1H, *E* + 1H, *Z*), 6.77 (d, *J* = 8.5 Hz, 1H, *E* + 1H, *Z*), 6.57 (d, *J* = 7.1 Hz, 1H, *Z*), 6.27 (d, *J* = 12.8 Hz, 1H, *E*), 5.73 (d, *J* = 7.1 Hz, 1H, *Z*), 3.82 (s, 3H, *Z*), 3.71 (s, 3H, *E*), 2.23 (s, 3H, *Z*), 2.21 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 177.7 (*E*), 177.6 (*Z*), 152.2 (*E*), 151.3 (*Z*), 150.32 (*E*), 150.27 (*Z*), 139.8 (*E*), 138.8 (*Z*), 136.83 (*E*), 136.80 (*Z*), 133.6 (*E*), 133.3 (*Z*), 132.6 (*Z*), 132.5 (*E*), 130.9 (*E*), 130.7 (*Z*), 128.4 (*Z*), 125.8 (*Z*), 125.7 (*E*), 124.0 (*E*), 123.34 (*Z*), 123.31 (*E*), 117.12 (*Z*), 117.10 (*E*), 117.08 (*E*), 117.06 (*Z*), 116.9 (*Z*), 116.6 (*E*), 102.4 (*E*), 101.1 (*Z*), 91.5 (*E*), 91.3 (*Z*), 90.4 (*E*), 90.3 (*Z*), 61.0 (*Z*), 56.9 (*E*), 20.0 (*Z*), 19.9 (*E*); IR (thin film, cm^{-1}) 3417, 3316, 2956, 2925, 2187, 1633, 1587, 1303, 1162, 1085; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{18}NO_2$ 292.1332, found 292.1344.

(E)-1-(2-Amino-5-methylphenyl)-3-(4-methoxy-2-(2-methoxy-vinyl)phenyl)prop-2-yn-1-one (7f).

Yellow solid (189 mg) in 59% yield (EtOAc/petroleum ether = 1:50): mp 75.5 – 77.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.83 (d, *J* = 0.7 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 12.8 Hz, 1H), 7.27 (s, 2H), 7.18 – 7.16 (m, 2H), 6.82 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.24 (d, *J* = 12.8 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 177.9, 161.4, 152.8, 150.1, 142.0, 136.6, 135.5, 132.5, 123.2, 117.12, 117.07, 112.8, 108.8, 108.6, 102.4, 91.6, 91.3, 57.0, 55.5, 19.9; IR (thin film, cm^{-1}) 3425, 2921, 2839, 2186, 1689, 1594, 1298, 1108, 1020; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{20}H_{19}NNaO_3$ 344.1257, found 344.1260.

(E)-1-(2-Amino-5-methylphenyl)-3-(4-chloro-2-(2-methoxy-vinyl)phenyl)prop-2-yn-1-one (7g).

Yellow solid (188 mg) in 58% yield (EtOAc/petroleum ether = 1:50): mp 72.5 – 74.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.81 (s, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 12.8 Hz, 1H), 7.33 (s, 2H), 7.26 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.18 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.20 (d, *J* = 12.8 Hz, 1H), 3.72 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 177.4, 153.9, 150.4, 141.9, 137.0, 136.0, 135.2, 132.4, 125.7, 123.5, 123.4, 117.1, 116.9, 115.3, 101.4, 92.1, 89.2, 57.2, 19.9; IR (thin film, cm^{-1}) 3412, 2924, 2182, 1630, 1585, 1384, 1234, 1112, 1015; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{17}ClNO_2$ 326.0942, found 326.0943.

DOI: 10.1039/C8OB01784D

1-(2-Amino-5-methylphenyl)-3-(4-fluoro-2-(2-methoxyvinyl)-phenyl)prop-2-yn-1-one (7h).

Yellow solid (204 mg, 1:0.4 *E*/*Z*) in 66% yield (EtOAc/petroleum ether = 1:50): mp 91.5 – 93.5°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.84 – 7.79 (m, 1H, *E* + 2H, *Z*), 7.75 (dd, *J* = 8.6, 6.1 Hz, 1H, *Z*), 7.71 (dd, *J* = 8.6, 6.1 Hz, 1H, *E*), 7.61 (d, *J* = 12.8 Hz, 1H, *E*), 7.53 (dd, *J* = 10.9, 2.6 Hz, 1H, *E*), 7.31 (s, 2H, *E* + 2H, *Z*), 7.19 – 7.17 (m, 1H, *E* + 1H, *Z*), 7.10 (td, *J* = 8.5, 2.7 Hz, 1H, *Z*), 7.07 (td, *J* = 8.5, 2.6 Hz, 1H, *E*), 6.76 (d, *J* = 8.5 Hz, 1H, *E* + 1H, *Z*), 6.69 (d, *J* = 7.1 Hz, 1H, *Z*), 6.23 (dd, *J* = 12.8, 1.1 Hz, 1H, *E*), 5.72 (dd, *J* = 7.1, 1.4 Hz, 1H, *Z*), 3.87 (s, 3H, *Z*), 3.72 (s, 3H, *E*), 2.23 (s, 3H, *Z*), 2.20 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 177.59 (*E*), 177.57 (*Z*), 163.5 (d, *J* = 249.0 Hz, *E*), 163.1 (d, *J* = 248.6 Hz, *Z*), 153.9 (*E*), 152.9 (*Z*), 150.32 (*E*), 150.28 (*Z*), 143.0 (d, *J* = 9.7 Hz, *E*), 141.4 (d, *J* = 10.1 Hz, *Z*), 136.9 (*E*), 136.8 (*Z*), 136.2 (d, *J* = 9.7 Hz, *E*), 135.8 (d, *J* = 9.9 Hz, *Z*), 132.6 (*Z*), 132.5 (*E*), 123.4 (*Z*), 123.3 (*E*), 117.11 (*E*), 117.08 (*Z*), 117.01 (*Z*), 116.99 (*E*), 114.6 (d, *J* = 24.1 Hz, *Z*), 113.33 (d, *J* = 22.8 Hz, *Z*), 113.31 (d, *J* = 2.7 Hz, *Z*), 113.27 (d, *J* = 22.9 Hz, *E*), 112.96 (d, *J* = 2.3 Hz, *E*), 110.4 (d, *J* = 23.5 Hz, *E*), 101.7 (d, *J* = 2.2 Hz, *E*), 100.3 (d, *J* = 1.4 Hz, *Z*), 91.4 (*E*), 91.2 (*Z*), 89.5 (*E*), 89.4 (*Z*), 61.4 (*Z*), 57.1 (*E*), 20.0 (*Z*), 19.9 (*E*); IR (thin film, cm^{-1}) 3481, 3353, 2923, 2188, 1649, 1630, 1546, 1300, 1243, 1126, 1079; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{19}H_{16}FNNaO_2$ 332.1057, found 332.1063.

1-(2-Amino-5-chlorophenyl)-3-(2-(2-methoxyvinyl)phenyl)prop-2-yn-1-one (7i).

Yellow solid (174 mg, 1:0.2 *E*/*Z*) in 56% yield (EtOAc/petroleum ether = 1:50): mp 85.5 – 87.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.5 Hz, 1H, *Z*), 8.16 (d, *J* = 2.5 Hz, 1H, *E*), 8.11 (d, *J* = 8.0 Hz, 1H, *Z*), 7.63 (d, *J* = 7.7 Hz, 1H, *E* + 1H, *Z*), 7.42 (d, *J* = 7.9 Hz, 1H, *E* + 1H, *Z*), 7.36 (t, *J* = 7.6 Hz, 1H, *E*), 7.27 – 7.22 (m, 2H, *E* + 1H, *Z*), 7.17 (t, *J* = 7.5 Hz, 1H, *E* + 1H, *Z*), 6.64 (d, *J* = 8.8 Hz, 1H, *E*), 6.63 (d, *J* = 8.8 Hz, 1H, *Z*), 6.40 (s, 2H, *E* + 2H, *Z*), 6.36 (d, *J* = 7.1 Hz, 1H, *Z*), 6.30 (d, *J* = 13.0 Hz, 1H, *E*), 5.84 (d, *J* = 7.1 Hz, 1H, *Z*), 3.83 (s, 3H, *Z*), 3.78 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.6 (*Z*), 178.5 (*E*), 151.5 (*E*), 150.4 (*Z*), 149.7 (*E*), 149.6 (*Z*), 140.5 (*E*), 139.5 (*Z*), 135.3 (*E*), 135.2 (*Z*), 134.3 (*E*), 133.7 (*Z*), 133.3 (*Z*), 133.0 (*E*), 131.0 (*E*), 130.8 (*Z*), 129.0 (*Z*), 125.73 (*Z*), 125.71 (*E*), 123.9 (*E*), 120.5 (*Z*), 120.4 (*E*), 119.7 (*Z*), 119.5 (*E*), 118.6 (*E*), 118.5 (*Z*), 117.7 (*Z*), 117.5 (*E*), 102.7 (*Z*), 102.5 (*E*), 92.9 (*Z*), 92.7 (*E*), 91.2 (*E*), 91.0 (*Z*), 61.2 (*Z*), 56.7 (*E*); IR (thin film, cm^{-1}) 3416, 3302, 2925, 2184, 1631, 1539, 1231, 1189, 1006; HRMS (ESI) *m/z* [M+H]$^+$ calcd for $C_{18}H_{15}ClNO_2$ 312.0786, found 312.0788.

1-(2-Amino-5-chlorophenyl)-3-(4-methoxy-2-(2-methoxyvinyl)-phenyl)prop-2-yn-1-one (7j).

Yellow solid (198 mg, 1:0.2 *E*/*Z*) in 58% yield (EtOAc/petroleum ether = 1:50): mp 86.5 – 88.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.99 (d, *J* = 2.5 Hz, 1H, *Z*), 7.97 (d, *J* = 2.5 Hz, 1H, *E*), 7.63 – 7.61 (m, 2H, *Z*), 7.60 (d, *J* = 6.5 Hz, 1H, *E*), 7.58 (d, *J* = 2.2 Hz, 1H, *E*), 7.56 (s, 2H, *E* + 2H, *Z*), 7.35 (dd, *J* = 9.0, 2.6 Hz, 1H, *E* + 1H, *Z*), 7.17 (d, *J* = 2.4 Hz, 1H, *E*), 6.88 – 6.86 (m, 1H, *E* + 2H, *Z*), 6.83 (dd, *J* = 8.6, 2.5 Hz, 1H, *E*), 6.59 (d, *J* = 7.1 Hz, 1H, *Z*), 6.19 (d, *J* = 12.8 Hz, 1H, *E*), 5.66 (d, *J* = 7.1 Hz, 1H, *Z*), 3.84 (s, 3H, *Z*), 3.84 (s, 3H, *E*), 3.81 (s, 3H, *Z*), 3.74 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 176.9 (*E*), 176.6 (*Z*), 161.6 (*E*), 161.3 (*Z*), 152.9 (*E*), 151.8 (*Z*), 150.7 (*E*), 150.6 (*Z*), 142.2 (*E*), 140.8 (*Z*), 135.7 (*E*), 135.4 (*Z*), 135.02 (*E*), 134.97 (*Z*), 131.8 (*Z*), 131.5 (*E*), 119.2 (*E*), 119.1 (*Z*), 117.75 (*Z*), 117.72 (*E*), 117.69 (*E*), 117.67 (*Z*), 114.0 (*Z*), 112.9 (*E*), 112.0 (*Z*), 109.5 (*Z*), 108.5 (*E*), 108.4 (*E*), 101.8 (*E*), 100.9 (*Z*), 92.5 (*E*), 91.7 (*Z*), 90.7 (*E*), 90.4 (*Z*), 61.2 (*Z*), 56.7 (*E*), 55.5 (*E*), 55.3 (*Z*); IR (thin film, cm^{-1}) 3483, 3351, 2923, 2182, 1653, 1575, 1295, 1216, 1095, 1005; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{19}H_{16}ClNNaO_3$ 364.0711, found 364.0715.

1-(2-Amino-5-chlorophenyl)-3-(4-chloro-2-(2-methoxyvinyl)-phenyl)prop-2-yn-1-one (7k).

Yellow solid (214 mg, 1:0.4 *E*/*Z*) in 62% yield (EtOAc/petroleum ether = 1:50): mp 75.3 – 77.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.05 (s, 1H, *Z*), 7.96 – 7.94 (m, 1H, *E* + 1H, *Z*), 7.76 (s, 1H, *E*), 7.69 (d, *J* = 8.3 Hz, 1H, *Z*), 7.66 (s, 1H, *E*), 7.64 (d, *J* = 5.2 Hz, 1H, *E*), 7.60 (s, 2H, *E* + 2H, *Z*), 7.36 (d, *J* = 9.0 Hz, 1H, *E* + 1H, *Z*), 7.31 (d, *J* = 8.3 Hz, 1H, *Z*), 7.27 (d, *J* = 8.3 Hz, 1H, *E*), 6.88 (d, *J* = 9.0 Hz, 1H, *E* + 1H, *Z*), 6.66 (d, *J* = 7.1 Hz, 1H, *Z*), 6.15 (d, *J* = 12.8 Hz, 1H, *E*), 5.64 (d, *J* = 7.1 Hz, 1H, *Z*), 3.87 (s, 3H, *Z*), 3.73 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 176.58 (*E*), 176.57 (*Z*), 153.9 (*E*), 152.9 (*Z*), 151.0 (*E*), 150.9 (*Z*), 142.0 (*E*), 140.6 (*Z*), 136.4 (*E*), 135.9 (*Z*), 135.41 (*E*), 135.37 (*E*), 135.35 (*Z*), 135.0 (*Z*), 131.8 (*Z*), 131.6 (*E*), 127.7 (*Z*), 125.9 (*Z*), 125.8 (*E*), 123.5 (*E*), 119.3 (*E*), 119.2 (*Z*), 118.0 (*Z*), 117.9 (*E*), 117.62 (*Z*), 117.56 (*E*), 115.3 (*Z*), 114.9 (*E*), 101.0 (*E*), 99.9 (*Z*), 91.6 (*E*), 91.4 (*Z*), 90.1 (*E*), 89.9 (*Z*), 61.6 (*Z*), 56.9 (*E*); IR (thin film, cm^{-1}) 3443, 3330, 2186, 1632, 1582, 1384, 1228, 1160, 1006; HRMS (ESI) *m/z* [M+H]$^+$ calcd for $C_{18}H_{14}Cl_2NO_2$ 346.0396, found 346.0395.

1-(2-Amino-5-chlorophenyl)-3-(4-fluoro-2-(2-methoxyvinyl)phen-yl)prop-2-yn-1-one (7l).

Yellow solid (201 mg, 1:0.1 *E*/*Z*) in 61% yield (EtOAc/petroleum ether = 1:50): mp 83.4 – 85.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.97 (d, *J* = 2.7 Hz, 1H, *Z*), 7.96 (d, *J* = 2.4 Hz, 1H, *E*), 7.80 (dd, *J* = 11.2, 2.6 Hz, 1H, *Z*), 7.75 (dd, *J* = 8.6, 6.2 Hz, 1H, *Z*), 7.71 (dd, *J* = 8.6, 6.1 Hz, 1H, *E*), 7.64 (d, *J* = 12.8 Hz, 1H, *E*), 7.59 (s, 2H, *E* + 2H, *Z*), 7.54 (dd, *J* = 10.9, 2.3 Hz, 1H, *E*), 7.36 (dd, *J* = 9.0, 2.5 Hz, 1H, *E* + 1H, *Z*), 7.12 (td, *J* = 8.5, 2.6 Hz, 1H, *Z*), 7.08 (td, *J* = 8.5, 2.4 Hz, 1H, *E*), 6.88 (d, *J* = 9.0 Hz, 1H, *E* + 1H, *Z*), 6.67 (d, *J* = 7.1 Hz, 1H, *Z*), 6.19 (d, *J* = 12.8 Hz, 1H, *E*), 5.68 (d, *J* = 7.0 Hz, 1H, *Z*), 3.87 (s, 3H, *Z*), 3.74 (s, 3H, *E*); ^{13}C NMR (150 MHz, DMSO-d_6) δ 176.62 (*E*), 176.59 (*Z*), 163.70 (d, *J* = 250.8 Hz, *Z*), 163.67 (d, *J* = 249.5 Hz, *E*), 153.9 (*E*), 153.0 (*Z*), 150.9 (*E*), 150.8 (*Z*), 143.1 (d, *J* = 9.8 Hz, *E*), 141.5 (d, *J* = 9.9 Hz, *Z*), 136.4 (d, *J* = 9.9 Hz, *E*), 135.9 (d, *J* = 9.2 Hz, *Z*), 135.24 (*E*), 135.21 (*Z*), 131.8 (*Z*), 131.6 (*E*), 119.20 (*E*), 119.16 (*Z*), 117.82 (*Z*), 117.78 (*E*), 117.6 (*Z*), 117.5 (*E*), 114.7 (d, *J* = 22.8 Hz, *Z*), 113.4 (d, *J* = 23.3 Hz, *Z*), 113.3 (d, *J* = 22.9 Hz, *E*), 112.6 (d, *J* = 1.8 Hz, *Z*), 112.5 (d, *J* = 2.4 Hz, *E*), 110.3 (d, *J* = 23.6 Hz, *E*), 101.2 (d, *J* = 2.3 Hz, *E*), 100.2 (d, *J* = 4.0 Hz, *Z*), 90.8 (*E*), 90.5 (*Z*), 90.3 (*E*), 90.2 (*Z*), 61.5 (*Z*), 56.8 (*E*); IR (thin film, cm^{-1}) 3431, 3316, 2925, 2185, 1637, 1618, 1467, 1241, 1201, 1007; HRMS (ESI) *m/z* [M+Na]$^+$ calcd for $C_{18}H_{13}ClFNNaO_2$ 352.0511, found 352.0509.

The procedure for the preparation of 5-3 and characterization data.

To a solution of the substrate **5** (0.5 mmol, 139 mg) in dry toluene (2 mL) was added the gold catalyst, which was generated by being stirred for 30 min at room temperature after the mixture of PPh_3AuCl (0.025 mmol, 12 mg) and $AgSbF_6$ (0.025 mmol, 9 mg) in dry toluene (2 mL) under a nitrogen atmosphere. The reaction mixture was reacted under the irradiation of microwave at 50 °C for

DOI: 10.1039/C8OB01684D

10 min. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography (EtOAc/petroleum ether = 1:20) to afford the product **5-3** (137 mg, 1:0.2 *E*/*Z*) as a yellow solid with a yield of 98%: mp 45.2 – 47.2 °C.

2-(2-(2-Methoxyvinyl)phenyl)-4H-chromen-4-one (5-3).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 – 8.22 (m, 1H, *E* + 1H, *Z*), 8.07 (d, *J* = 8.0 Hz, 1H, *Z*), 7.72 – 7.63 (m, 1H, *E* + 1H, *Z*), 7.56 – 7.53 (m, 1H, *E* + 1H, *Z*), 7.49 (d, *J* = 8.4 Hz, 1H, *E* + 1H, *Z*), 7.47 – 7.38 (m, 3H, *E* + 2H, *Z*), 7.32 – 7.27 (m, 1H, *E* + 1H, *Z*), 6.99 (d, *J* = 12.8 Hz, 1H, *E*), 6.56 (s, 1H, *E*), 6.54 (s, 1H, *Z*), 6.18 (d, *J* = 7.2 Hz, 1H, *Z*), 5.99 (d, *J* = 12.8 Hz, 1H, *E*), 5.38 (d, *J* = 7.2 Hz, 1H, *Z*), 3.73 (s, 3H, *Z*), 3.61 (s, 3H, *E*); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.3 (*Z*), 178.2 (*E*), 165.6 (*Z*), 165.4 (*E*), 156.74 (*Z*), 156.67 (*E*), 150.7 (*E*),149.4 (*Z*), 135.6 (*E*), 134.4 (*Z*), 133.9 (*E*), 133.8 (*Z*), 131.0 (*E*), 130.8 (*Z*), 130.6 (*E*), 130.5 (*Z*), 130.2 (*Z*), 129.5 (*E*), 129.1 (*Z*), 126.21 (*E*), 126.16 (*E*), 126.1 (*Z*), 125.84 (*E*), 125.77 (*Z*), 125.3 (*E*), 125.2 (*Z*), 124.0 (*E*), 123.9 (*Z*), 118.2 (*Z*), 118.1 (*E*), 112.8 (*Z*), 112.7 (*E*), 103.0 (*E*), 102.4 (*Z*), 60.9 (*Z*), 56.8 (*E*); IR (thin film, cm^{-1}) 3424, 2930, 1631, 1463, 1383, 1222, 1127, 1010; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{15}O_3$ 279.1016, found 279.1018.

The procedure for the preparation of 6 from the substrate 5-3 and characterization data.

To a solution of the substrate **5-3** (0.4 mmol, 111 mg) in dry toluene (2 mL) was added the gold catalyst, which was generated by being stirred for 30 min at room temperature after the mixture of PPh_3AuCl (0.020 mmol, 10 mg) and $AgSbF_6$ (0.020 mmol, 7 mg) in dry toluene (2 mL) under a nitrogen atmosphere. The reaction mixture was reacted under the irradiation of microwave at 80 °C for 10 min. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography (EtOAc/petroleum ether = 1:50) to afford the product **6** (92 mg) with a yield of 93%.

General procedures for the preparation of 6, 6a-6p, 8a-8l and characterization data.

To a solution of the substrates **5**, **5a-5p**, **7a-7l** (0.5 mmol) in dry toluene (2 mL) was added the gold catalyst, which was generated by being stirred for 30 min at room temperature after the mixture of PPh_3AuCl (0.025 mmol, 12 mg) and $AgSbF_6$ (0.025 mmol, 9 mg) in dry toluene (2 mL) under a nitrogen atmosphere. The reaction mixture was reacted under the irradiation of microwave at 80 °C for 60 min. The solvent was removed *in vacuo* and the residue was purified by a flash column chromatography to afford the products **6**, **6a-6p**, **8a-8l**.

Spectral data of **6**, **6a**, **8a** were consistent with those reported in the literatures. [13]

3-Chloro-7H-benzo[c]xanthen-7-one (6b).

White solid (126 mg) in 90% yield (EtOAc/petroleum ether = 1:50): mp 132.5–134.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.9 Hz, 1H), 8.37 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.26 (d, *J* = 8.7 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.76 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.47 – 7.40 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.6, 155.7, 153.5, 137.4, 136.0, 134.6, 127.8, 127.1, 126.7, 124.74, 124.66, 123.1 (2C), 122.5, 122.4, 118.1, 117.8; IR (thin film, cm^{-1}) 3423, 2924, 1631, 1468, 1384, 1271, 1185, 1096; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{10}ClO_2$ 281.0364, found 281.0378.

3-Fluoro-7H-benzo[c]xanthen-7-one (6c).

White solid (119 mg) in 90% yield (EtOAc/petroleum ether = 1:50): mp 122.5–124.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 9.1, 5.5 Hz, 1H), 8.39 (d, *J* = 7.9 Hz, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.65 – 7.64 (m, 2H), 7.52 (dd, *J* = 9.4, 2.3 Hz, 1H), 7.46 – 7.41 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.7, 163.2 (d, *J* = 251.5 Hz), 155.8, 153.7, 138.3 (d, *J* = 9.8 Hz), 134.6, 126.8, 125.9 (d, *J* = 9.6 Hz), 124.7, 123.4 (d, *J* = 4.4 Hz), 123.2, 122.5, 121.0 (d, *J* = 0.9 Hz), 118.1, 117.3, 117.0 (d, *J* = 24.9 Hz), 112.1 (d, *J* = 21.0 Hz); IR (thin film, cm^{-1}) 3423, 2925, 1631, 1474, 1412, 1384, 1240, 1142, 1008; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{10}FO_2$ 265.0659, found 265.0668.

9-Methyl-7H-benzo[c]xanthen-7-one (6d).

White solid (120 mg) in 92% yield (EtOAc/petroleum ether = 1:50): mp 162.5–164.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.7 Hz, 1H), 8.17 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.559 (s, 1H), 7.557 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 154.1, 153.8, 136.6, 135.7, 134.4, 129.6, 128.2, 126.9, 126.0, 124.3, 123.9, 123.0, 122.2, 121.7, 117.9, 117.7, 21.1; IR (thin film, cm^{-1}) 3423, 2923, 1648, 1631, 1486, 1383, 1128, 1085; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}O_2$ 261.0910, found 261.0915.

3-Methoxy-9-methyl-7H-benzo[c]xanthen-7-one (6e).

Yellow solid (133 mg) in 92% yield (EtOAc/petroleum ether = 1:50): mp 157.5–159.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 9.1 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 1H), 8.16 (s, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.28 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 3.97 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.9, 160.7, 154.1, 154.0, 138.7, 135.5, 134.2, 126.0, 124.8, 123.0, 122.6, 122.2, 118.9, 118.8, 117.8, 116.3, 107.0, 55.6, 21.1; IR (thin film, cm^{-1}) 3423, 2924, 1653, 1630, 1462, 1384, 1259, 1117, 1031; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{15}O_3$ 291.1016, found 291.1019.

3-Chloro-9-methyl-7H-benzo[c]xanthen-7-one (6f).

Yellow solid (132 mg) in 90% yield (EtOAc/petroleum ether = 1:50): mp 168.5–170.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.9 Hz, 1H), 8.24 (d, *J* = 8.7 Hz, 1H), 8.12 (s, 1H), 7.84 (d, *J* = 1.8 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.50 (d, *J* = 8.5 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.7, 154.0, 153.5, 137.3, 135.9, 135.8, 134.6, 127.7, 127.1, 126.0, 124.7, 123.2, 122.9, 122.5, 122.1, 117.9, 117.7, 21.1; IR (thin film, cm^{-1}) 3423, 2922, 1652, 1630, 1485, 1407, 1141, 1094; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{12}ClO_2$ 295.0520, found 295.0529.

3-Fluoro-9-methyl-7H-benzo[c]xanthen-7-one (6g).

Yellow solid (133 mg) in 96% yield (EtOAc/petroleum ether = 1:50): mp 137.5–139.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 9.0, 5.6 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 8.13 (s, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.42 – 7.35 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.7, 163.1 (d, *J* = 251.3 Hz), 154.0, 153.6, 138.1 (d, *J* = 9.7 Hz), 135.8, 134.6, 126.0, 125.9 (d, *J* = 9.5 Hz), 123.20, 123.15 (d, *J* = 4.3 Hz), 122.1, 121.0, 117.8, 117.2 (d, *J* = 1.8 Hz), 116.8 (d, *J* = 24.8 Hz), 112.0 (d, *J* = 21.1 Hz), 21.0; IR (thin film, cm^{-1}) 3423, 2923,

1648, 1631, 1486, 1383, 1230, 1128, 1085; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{12}FO_2$ 279.0816, found 279.0809.

9-Bromo-7H-benzo[c]xanthen-7-one (6h).

White solid (112 mg) in 69% yield (EtOAc/petroleum ether = 1:50): mp 152.5–154.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.2 Hz, 1H), 8.50 (d, *J* = 2.4 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.84 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.76 – 7.67 (m, 3H), 7.57 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8, 154.7, 153.8, 137.4, 136.8, 130.0, 129.3, 128.3, 127.3, 124.6, 124.1, 123.9, 123.0, 121.5, 120.2, 117.8, 117.6; IR (thin film, cm^{-1}) 3423, 2962, 2169, 1654, 1631, 1382, 1263, 1087, 1029; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{10}BrO_2$ 324.9859, found 324.9869.

9-Bromo-3-fluoro-7H-benzo[c]xanthen-7-one (6i).

White solid (128 mg) in 75% yield (EtOAc/petroleum ether = 1:50): mp 181.5–183.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.76 (dd, *J* = 9.2, 5.6 Hz, 1H), 8.28 (d, *J* = 2.5 Hz, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 8.09 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.96 (dd, *J* = 10.0, 2.6 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.73 (td, *J* = 8.9, 2.6 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.5, 162.6 (d, *J* = 249.3 Hz), 154.2, 153.0, 137.9 (d, *J* = 10.4 Hz), 137.7, 127.7, 126.2 (d, *J* = 9.9 Hz), 124.0 (d, *J* = 4.3 Hz), 123.2, 122.2, 121.3, 120.4, 117.4 (d, *J* = 25.1 Hz), 117.2, 116.4 (d, *J* = 1.6 Hz), 112.2 (d, *J* = 21.4 Hz); IR (thin film, cm^{-1}) 3422, 2924, 2196, 1631, 1469, 1385, 1086, 1008; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_9BrFO_2$ 342.9764, found 342.9771.

9-Bromo-3-methoxy-7H-benzo[c]xanthen-7-one (6j).

White solid (106 mg) in 60% yield (EtOAc/petroleum ether = 1:50): mp 176.2–178.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.63 (d, *J* = 9.1 Hz, 1H), 8.30 (d, *J* = 2.5 Hz, 1H), 8.11 – 8.07 (m, 2H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 2.5 Hz, 1H), 7.46 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.4, 160.7, 154.3, 153.4, 138.6, 137.5, 127.7, 124.6, 123.8, 123.3, 121.5, 121.2, 119.4, 117.8, 117.0, 115.3, 107.6, 55.7; IR (thin film, cm^{-1}) 3423, 2925, 2169, 1631, 1384, 1271, 1126, 1038, 1008; HRMS (ESI) *m/z* $[M+H]^+$calcd for $C_{18}H_{12}BrO_3$ 354.9964, found 354.9960.

9,11-Dimethyl-7H-benzo[c]xanthen-7-one (6k).

White solid (126 mg) in 92% yield (EtOAc/petroleum ether = 1:50): mp 142.8–144.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.7 Hz, 1H), 8.00 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.61 (m, 3H), 7.40 (s, 1H), 2.67 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.3, 153.4, 152.5, 136.7, 136.5, 133.8, 129.5, 128.2, 127.2, 126.9, 124.5, 123.8, 123.6, 122.9, 122.0, 121.7, 117.4, 21.0, 15.9; IR (thin film, cm^{-1}) 3423, 2919, 1642, 1614, 1475, 1384, 1264, 1211, 1024; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{15}O_2$ 275.1067, found 275.1070.

3-Methoxy-9,11-dimethyl-7H-benzo[c]xanthen-7-one (6l).

White solid (147 mg) in 97% yield (EtOAc/petroleum ether = 1:50): mp 132.5–134.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, *J* = 9.1 Hz, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 7.98 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.38 (s, 1H), 7.26 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 3.96 (s, 3H), 2.64 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 175.6, 160.4, 152.9, 151.8, 138.2, 136.7, 133.5, 129.6, 127.2, 124.3, 123.3, 122.6, 121.6, 119.3, 118.0, 115.1, 107.4, 55.6, 20.4, 15.3; IR (thin film, cm^{-1}) 3423, 2922, 1655, 1630, 1483, 1426, 1366, 1255, 1024; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{17}O_3$ 305.1172, found 305.1167.

3-Fluoro-9,11-dimethyl-7H-benzo[c]xanthen-7-one (6m).

White solid (136 mg) in 93% yield (EtOAc/petroleum ether = 1:50): mp 166.5–168.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 9.0, 5.5 Hz, 1H), 8.21 (d, *J* = 8.7 Hz, 1H), 7.93 (s, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.45 (dd, *J* = 9.4, 2.3 Hz, 1H), 7.39 – 7.31 (m, 2H), 2.60 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 175.7, 162.5 (d, *J* = 248.7 Hz), 152.7, 151.8, 137.7 (d, *J* = 10.4 Hz), 137.0, 133.9, 127.3, 125.9 (d, *J* = 9.9 Hz), 123.5 (d, *J* = 4.2 Hz), 122.7, 122.4, 121.2, 120.7, 117.3 (d, *J* = 25.2 Hz), 116.3 (d, *J* = 1.2 Hz), 112.2 (d, *J* = 21.3 Hz), 20.5, 15.3; IR (thin film, cm^{-1}) 3423, 2920, 1651, 1631, 1480, 1418, 1209, 1151; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{14}FO_2$ 293.0972, found 293.0977.

10-Methoxy-7H-benzo[c]xanthen-7-one (6n).

Yellow solid (132 mg) in 96% yield (EtOAc/petroleum ether = 1:50): mp 153.5–155.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 8.7 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.74 – 7.63 (m, 3H), 7.05 (d, *J* = 2.3 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.3 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 164.9, 157.7, 153.7, 136.5, 129.4, 128.20, 128.17, 126.9, 124.1, 124.0, 122.8, 121.7, 117.8, 116.5, 113.9, 100.5, 56.0; IR (thin film, cm^{-1}) 3423, 2936, 1631, 1500, 1440, 1384, 1281, 1119, 1027; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}O_3$ 277.0859, found 277.0866.

3,10-Dimethoxy-7H-benzo[c]xanthen-7-one (6o).

Yellow solid (138 mg) in 90% yield (EtOAc/petroleum ether = 1:50): mp 173.5–175.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.1 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.29 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.1, 164.7, 160.6, 157.6, 153.9, 138.5, 128.1, 124.6, 123.1, 122.6, 119.0, 118.7, 116.5, 116.3, 113.6, 106.9, 100.4, 56.0, 55.6; IR (thin film, cm^{-1}) 3422, 2924, 2169, 1630, 1476, 1422, 1234, 1184, 1019; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{15}O_4$ 307.0965, found 307.0957.

3-Fluoro-10-methoxy-7H-benzo[c]xanthen-7-one (6p).

White solid (137 mg) in 93% yield (EtOAc/petroleum ether = 1:50): mp 148.5–150.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 9.1, 5.5 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.29 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.54 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 7.01 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.0, 165.0, 163.0 (d, *J* = 251.2 Hz), 157.7, 153.7, 138.1 (d, *J* = 9.7 Hz), 128.3, 125.7 (d, *J* = 9.4 Hz), 123.31 (d, *J* = 4.5 Hz), 123.26, 121.0, 117.4 (d, *J* = 2.0 Hz), 116.9 (d, *J* = 25.0 Hz), 116.4, 114.0, 112.0 (d, *J* = 21.0 Hz), 100.5, 56.1; IR (thin film, cm^{-1}) 3423, 2925, 1631, 1412, 1384, 1270, 1120, 1026; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{12}FO_3$ 295.0765, found 295.0767.

3-Methoxybenzo[c]acridin-7(12H)-one (8b).

Yellow solid (110 mg) in 80% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 183.5–185.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.10 (d, *J* = 7.3 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.13 (s, 1H), 7.07 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.86 (d, *J* = 2.5 Hz, 1H), 6.73 (d, *J* = 7.7

Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.3, 162.1, 144.9, 137.8, 132.7, 131.9, 127.3, 127.03, 127.01, 125.7, 124.1, 118.9, 117.7, 115.1, 111.9, 108.3, 102.3, 55.7; IR (thin film, cm^{-1}) 3423, 2925, 1631, 1594, 1414, 1352, 1239, 1124, 1009; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{14}NO_2$ 276.1019, found 276.1025.

3-Chlorobenzo[c]acridin-7(12H)-one (8c).

Yellow solid (134 mg) in 96% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 194.5–196.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.78 (d, *J* = 7.8 Hz, 1H), 8.51 (d, *J* = 8.9 Hz, 1H), 8.46 (d, *J* = 8.8 Hz, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 7.92 – 7.82 (m, 2H), 7.65 – 7.56 (m, 2H), 7.25 (s, 1H), 7.04 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 174.0, 143.6, 137.9, 136.5, 132.4, 132.3, 128.5, 127.6, 126.8, 126.6, 125.9, 125.8, 125.6, 123.7, 117.0, 110.1, 102.7; IR (thin film, cm^{-1}) 3423, 2962, 1631, 1542, 1384, 1261, 1097, 1030; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{11}ClNO$ 280.0524, found 280.0535.

3-Fluorobenzo[c]acridin-7(12H)-one (8d).

Yellow solid (124 mg) in 94% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 195.7–197.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.70 (d, *J* = 7.8 Hz, 1H), 8.50 (dd, *J* = 9.0, 5.2 Hz, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 8.33 – 8.26 (m, 1H), 7.81 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 9.1, 2.4 Hz, 1H), 7.36 (td, *J* = 8.8, 2.5 Hz, 1H), 7.17 (s, 1H), 6.97 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.8, 163.6 (d, *J* = 250.3 Hz), 143.6, 137.7, 133.1 (d, *J* = 10.3 Hz), 132.1, 128.6 (d, *J* = 9.4 Hz), 126.7, 126.3, 125.7, 125.6, 121.5 (d, *J* = 1.9 Hz), 116.8, 116.5 (d, *J* = 23.2 Hz), 111.7 (d, *J* = 22.0 Hz), 110.4 (d, *J* = 2.7 Hz), 102.3; IR (thin film, cm^{-1}) 3404, 2923, 1631, 1602, 1383, 1269, 1121, 1051; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{11}FNO$ 264.0819, found 264.0814.

9-Methylbenzo[c]acridin-7(12H)-one (8e).

Yellow solid (124 mg) in 96% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 187.5–189.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.69 (d, *J* = 7.6 Hz, 1H), 8.47 (d, *J* = 8.2 Hz, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 8.12 (s, 1H), 7.74 – 7.68 (m, 2H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.21 (s, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.7, 143.9, 136.0, 135.4, 133.4, 131.6, 130.7, 128.6, 126.8, 125.3, 125.2, 125.0, 124.9, 118.8, 116.9, 111.2, 102.1, 20.5; IR (thin film, cm^{-1}) 3408, 2962, 1631, 1596, 1384, 1261, 1097, 1028; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{14}NO$ 260.1070, found 260.1075.

3-Methoxy-9-methylbenzo[c]acridin-7(12H)-one (8f).

Yellow solid (118 mg) in 82% yield (EtOAc/petroleum ether = 1:50): mp 177.5–179.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.67 (d, *J* = 7.7 Hz, 1H), 8.36 (d, *J* = 9.1 Hz, 1H), 8.30 (d, *J* = 8.9 Hz, 1H), 8.09 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 2.3 Hz, 1H), 7.14 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.07 (s, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 3.89 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.4, 161.7, 144.1, 135.9, 135.2, 133.1, 132.8, 127.3, 126.7, 125.7, 125.1, 118.1, 117.4, 116.7, 111.2, 108.5, 100.9, 55.7, 20.5; IR (thin film, cm^{-1}) 3408, 2924, 2169, 1596, 1384, 1261, 1127, 1076; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{16}NO_2$ 290.1176, found 290.1187.

3-Chloro-9-methylbenzo[c]acridin-7(12H)-one (8g).

Yellow solid (144 mg) in 98% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 185.5–187.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.77 (d, *J* = 7.9 Hz, 1H), 8.51 (d, *J* = 8.9 Hz, 1H), 8.37 (d, *J* = 9.0 Hz, 1H), 8.12 (d, *J* = 1.1 Hz, 1H), 7.88 (d, *J* = 2.2 Hz, 1H), 7.69 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.59 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.22 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.9, 143.3, 136.3, 136.0, 135.6, 133.5, 132.4, 128.4, 127.6, 126.7, 126.6, 125.8, 125.0, 123.7, 116.9, 110.0, 102.5, 20.5; IR (thin film, cm^{-1}) 3422, 2923, 2169, 1631, 1591, 1384, 1269, 1127, 1076; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}ClNO$ 294.0680, found 294.0682.

3-Fluoro-9-methylbenzo[c]acridin-7(12H)-one (8h).

Yellow solid (136 mg) in 98% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 186.7–188.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.71 (d, *J* = 7.8 Hz, 1H), 8.51 (dd, *J* = 9.1, 5.3 Hz, 1H), 8.31 (d, *J* = 8.9 Hz, 1H), 8.08 (d, *J* = 0.7 Hz, 1H), 7.64 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.55 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.40 (td, *J* = 8.8, 2.6 Hz, 1H), 7.15 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 164.4 (d, *J* = 252.8 Hz), 144.0, 136.3, 135.9, 133.6, 133.1 (d, *J* = 9.9 Hz), 127.9 (d, *J* = 9.2 Hz), 127.1, 126.5, 125.0, 122.2, 117.2 (d, *J* = 23.2 Hz), 115.2, 112.0 (d, *J* = 21.8 Hz), 111.1 (d, *J* = 2.7 Hz), 103.1, 21.0; IR (thin film, cm^{-1}) 3404, 2924, 2169, 1631, 1597, 1384, 1271, 1119; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}FNO$ 278.0976, found 278.0981.

9-Chlorobenzo[c]acridin-7(12H)-one (8i).

Yellow solid (130 mg) in 93% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 193.5–195.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.77 (d, *J* = 7.8 Hz, 1H), 8.59 (d, *J* = 9.4 Hz, 1H), 8.56 (d, *J* = 8.3 Hz, 1H), 8.28 (d, *J* = 2.7 Hz, 1H), 7.93 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.82 – 7.73 (m, 2H), 7.67 – 7.60 (m, 1H), 7.35 (s, 1H), 7.15 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.6, 144.6, 136.7, 132.0, 131.9, 130.8, 130.7, 128.8, 128.1, 126.9, 125.5, 125.2, 124.7, 124.5, 119.9, 111.8, 102.7; IR (thin film, cm^{-1}) 3440, 2923, 1631, 1403, 1384, 1271, 1126, 1032, 1010; HRMS (ESI) *m/z* $[M+H]^+$ calcd. for $C_{17}H_{11}ClNO$ 280.0524, found 280.0528.

9-Chloro-3-methoxybenzo[c]acridin-7(12H)-one (8j).

Yellow solid (127 mg) in 82% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 191.5–193.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.75 (d, *J* = 7.9 Hz, 1H), 8.54 (d, *J* = 9.4 Hz, 1H), 8.47 (d, *J* = 9.2 Hz, 1H), 8.26 (d, *J* = 2.7 Hz, 1H), 7.89 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.32 (d, *J* = 2.7 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.2, 162.0, 144.8, 136.5, 132.9, 131.7, 130.7, 128.1, 127.6, 125.7, 124.5, 119.6, 117.9, 117.6, 111.8, 108.6, 101.4, 55.7; IR (thin film, cm^{-1}) 3422, 2923, 1631, 1402, 1387, 1287, 1265, 1010; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{13}ClNO_2$ 310.0629, found 310.0632.

3,9-Dichlorobenzo[c]acridin-7(12H)-one (8k).

Yellow solid (141 mg) in 90% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 185.5–187.4 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.79 (d, *J* = 7.9 Hz, 1H), 8.56 – 8.54 (m, 2H), 8.25 (d, *J* = 2.4 Hz, 1H), 7.96 – 7.84 (m, 2H), 7.62 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.32 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.7, 144.0, 136.7, 136.6, 132.4, 132.1, 130.9, 128.6, 128.1, 127.8, 126.7, 125.9, 124.5, 123.6, 119.9, 110.5, 103.0; IR (thin film, cm^{-1}) 3423, 2924, 1631, 1592, 1402, 1384, 1269, 1008; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{10}Cl_2NO$ 314.0134, found 314.0141.

9-Chloro-3-fluorobenzo[c]acridin-7(12H)-one (8l).

DOI: 10.1039/C8OB01884D

Yellow solid (137 mg) in 92% yield ($MeOH/CH_2Cl_2$ = 1:50): mp 191.5–193.3 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.78 (d, *J* = 7.9 Hz, 1H), 8.62 (dd, *J* = 9.2, 5.2 Hz, 1H), 8.54 (d, *J* = 9.4 Hz, 1H), 8.25 (d, *J* = 2.7 Hz, 1H), 7.91 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.63 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.46 (td, *J* = 8.8, 2.7 Hz, 1H), 7.30 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.6, 163.9 (d, *J* = 250.7 Hz), 144.1, 136.6, 133.3 (d, *J* = 10.4 Hz), 132.0, 130.9, 129.0 (d, *J* = 9.5 Hz), 128.0, 126.5, 124.5, 121.5 (d, *J* = 2.1 Hz), 119.8, 116.8 (d, *J* = 23.2 Hz), 111.9 (d, *J* = 22.1 Hz), 111.0 (d, *J* = 2.8 Hz), 102.7; IR (thin film, cm^{-1}) 3422, 2924, 1649, 1631, 1537, 1406, 1387, 1286, 1226; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{10}ClFNO$ 298.0429, found 298.0434.

Acknowledgements

We were grateful to the National Natural Science Foundation of China (Grants 21372157) and the Foundation of Liaoning Province Education Administration of China (Grants 2017LQN08). We acknowledged the program for innovative research team of the Ministry of Education and the program for Liaoning innovative research team in university and Career Development Support Plan for Young and Middle-aged Teachers in Shenyang Pharmaceutical University. The project is sponsored by "Liaoning BaiQianWan Talents Program".

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