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Modular synthesis of 3-substituted isocoumarins *via* silver-catalyzed aerobic oxidation/*6-endo* heterocyclization of *ortho*-alkynylbenzaldehydes†

Hao Wu,‡[a] Yi-Chun Wang,‡[a] Andrey Shatskiy,[b] Qiu-Yan Li,[a] Jian-Quan Liu,*[a,b] Markus D. Kärkäs*[b] and Xiang-Shan Wang*[a]

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A method involving silver-catalyzed aerobic oxidation/*6-endo* heterocyclization of *ortho*-alkynylbenzaldehydes to yield 3-substituted isocoumarins is described. The developed protocol allows convenient access to a range of synthetically useful 3-substituted isocoumarins and related fused heterocyclolactones in good to high yields, using silver tetrafluoroborate as the catalyst, and atmospheric oxygen as the terminal oxidant and the source of endocyclic oxygen. Mechanistic studies suggest the involvement of a free-radical pathway.

Introduction

Derivatives of isocoumarin are valuable synthetic intermediates in organic synthesis and are present in numerous natural products and pharmaceuticals (Fig. 1).[1,2] Over the years, various synthetic methods for accessing such heterocyclic compounds have been established primarily with the aid of transition metal catalysis.[3]

Intramolecular cyclization of alkynyl-substituted carboxylic acids or esters mediated by π-electrophilic transition metal catalysts[4,5] or metal-free catalysts,[6] such as I_2 and $BF_3{\cdot}Et_2O$, is a common strategy for the construction of isocoumarin derivatives. Typically, such protocols rely on the activation of the carbon–carbon triple bond, triggering *6-endo-dig* heterocyclization to yield structurally diverse six-membered heterocyclic compounds. Another approach for accessing isocoumarin scaffolds is through transition metal catalyzed cross-coupling reactions, in which the key C–C and C–O bond-forming steps typically proceed *via* reductive elimination or migratory insertion.[7,8] These strategies enable direct access to various five- and six-membered heterocycles from relatively simple organic building blocks. However, the development of synthetic methodologies for acquiring isocoumarins from readily available starting materials in a cost-efficient manner under benign reaction conditions is still an important objective in heterocyclic chemistry.

ortho-Alkynylbenzaldehydes constitute multifaceted and readily available building blocks suitable for the construction of various heterocyclic compounds.[9] Heterocyclization of *ortho*-alkynylbenzaldehydes could offer a convenient route towards substituted isocoumarins; however, only a handful of related synthetic protocols have been disclosed to date. Notably, Youn and co-workers reported a pioneering study on the NHC-catalyzed oxidative intramolecular heterocyclization of *ortho*-alkynylbenzaldehydes to furnish five- and six-membered heterocyclic scaffolds (Fig. 1).[10] Unfortunately, this protocol provided the respective products with low regioselectivity and was highly dependent on the nature of the substituents on the starting *ortho*-alkynylbenzaldehydes. Subsequently, the Singh and Ghorai groups expanded the substrate scope for the heterocyclization of *ortho*-alkynylpyridinealdehydes, achieving selective formation of pyrano[4,3-*b*]quinolinones (Fig. 1).[11] Concerning the structurally related *ortho*-alkynylbenzaldehydes, only two reports of their heterocyclization have been disclosed to date.[11] As a continuation of our efforts in the development of transition metal catalyzed heterocyclization of functionalized alkynylated aromatic compounds,[12] herein we report an unprecedented regioselective silver-catalyzed aerobic oxidation/heterocyclization reaction of *ortho*-alkynylbenzaldehydes *via* a free-radical process, providing a convenient and modular approach to isocoumarins and related heterocyclolactones.

[a]*School of Chemistry and Materials Science, Jiangsu Key Laboratory of Green Synthesis for Functional Materials, Jiangsu Normal University, Xuzhou, Jiangsu 221116, China. E-mail: liujq316@jsnu.edu.cn, xswang1974@yahoo.com*
[b]*Department of Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden. E-mail: karkas@kth.se*

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‡These authors contributed equally to this work.

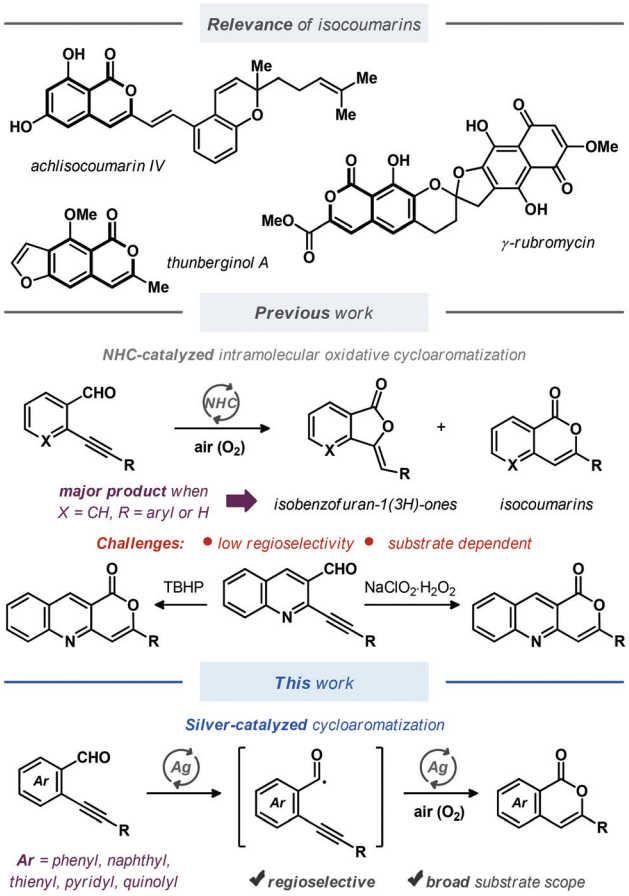
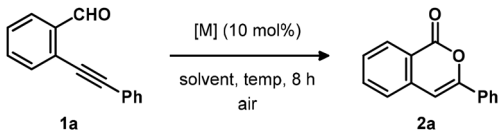


Fig. 1 Relevance of isocoumarins and strategies for their synthesis using *ortho*-alkynylaromatics.

Results and discussion

Initially, 2-(phenylethynyl)benzaldehyde (**1a**) was selected as the model substrate for the optimization of the reaction conditions. To our delight, heating of **1a** in toluene (80 °C) in the presence of $AgBF_4$ (10 mol%) under aerobic conditions exclusively afforded the isocoumarin product **2a** (3-phenyl-1*H*-isochromen-1-one) in 75% isolated yield (Table 1, entry 1). Employing other silver-based catalysts, including Ag_2CO_3, $AgNTf_2$, $AgNO_3$, and AgOTf, did not improve the yield of the desired product (Table 1, entries 2–5), and other metal-based catalysts, such as $FeCl_3$, $InCl_3$, $AuCl_3$, and $Cu(OTf)_2$, provided a complex mixture of products, containing no or only trace amounts of product **2a** (Table 1, entries 6–9). Switching the solvent from toluene (Table 1, entry 1) to *N,N*-dimethylformamide (DMF) greatly increased the yield of product **2a** up to 91% (Table 1, entry 10), while other polar and aprotic solvents, such as DCE, CH_3CN and *N,N*-dimethylacetamide (DMA), had a negative effect on the reaction and delivered **2a** in diminished yields (Table 1, entries 11–13). Conducting the reaction in diethylene glycol (DEG) resulted in the formation of only trace amounts of product **2a** (Table 1, entry 14). Decreasing the temperature from 80 °C to 40 °C resulted in diminished yield of the desired product (Table 1, entry 15). Conducting the reaction under conditions utilized for a related transformation by the Singh and Ghorai groups failed to produce product **2a** even upon extending the reaction time (up to 24 h, Table 1, entries 16 and 17).[11] Finally, several control experiments were performed under different reaction conditions including low catalytic loading, high temperature and O_2 atmosphere, respectively, with none of them matching the ideal conditions (Table 1, entries 18–20). Owing to the large steric hindrance of tetrafluoroborate, *6-endo-dig* heterocyclization was easily carried out in this reaction. The conditions from entry 10 (Table 1) were therefore selected as optimal and were employed for the investigation of the substrate scope of the reaction (Scheme 1).

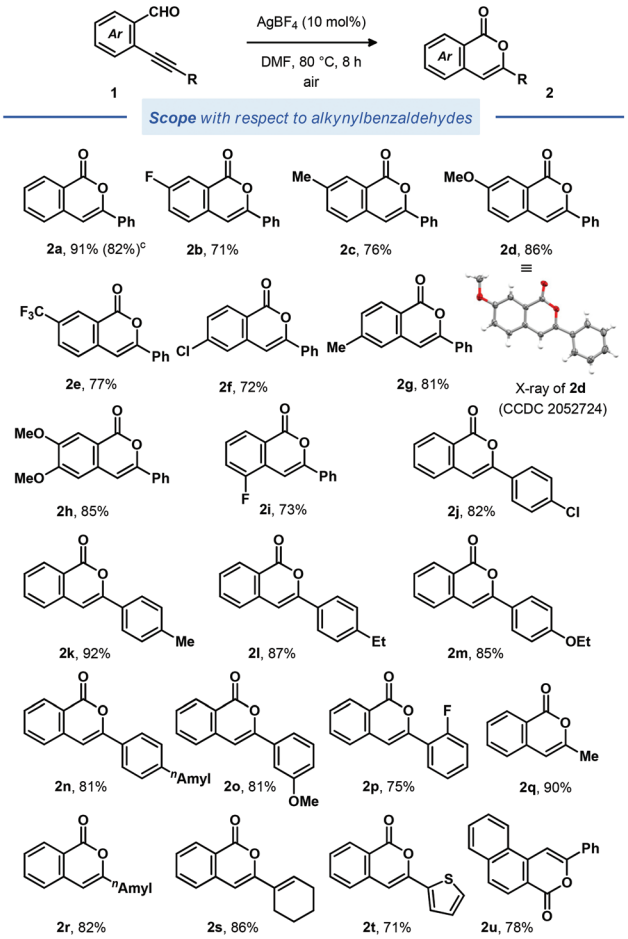
Table 1 Optimization of the reaction conditions[a,b]



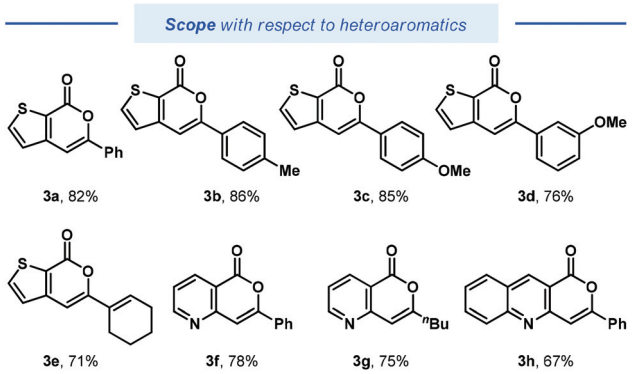
Entry	[M]	Solvent	Temp (°C)	Conversion	Yield[b] (%)
1	$AgBF_4$	Toluene	80	100%	75
2	Ag_2CO_3	Toluene	80	100%	26
3	$AgNTf_2$	Toluene	80	100%	37
4	$AgNO_3$	Toluene	80	100%	51
5	AgOTf	Toluene	80	100%	0
6[c]	$FeCl_3$	Toluene	80	100%	0
7[c]	$InCl_3$	Toluene	80	100%	15
8[c]	$AuCl_3$	Toluene	80	0	0
9[c]	$Cu(OTf)_2$	Toluene	80	100%	17
10	$AgBF_4$	DMF	80	100%	91
11	$AgBF_4$	DCE	80	100%	79
12	$AgBF_4$	CH_3CN	80	100%	69
13	$AgBF_4$	DMA	80	100%	83
14	$AgBF_4$	DEG	80	100%	Trace
15	$AgBF_4$	DMF	40	100%	43
16[d,e]	TBHP	DCE	80	0	0
17[e,f]	$NaClO_2$-H_2O_2	*t*-BuOH-H_2O	RT	0	0
18[g]	$AgBF_4$	DMF	80	100%	52
19	$AgBF_4$	DMF	120	100%	79
20[h]	$AgBF_4$	DMF	80	100%	93

[a] Reaction conditions: **1a** (0.5 mmol) and 0.05 mmol catalyst in solvent (1.0 mL) under air for 8 h. [b] Isolated yields. [c] Detected by ^1H NMR analysis of the mixture. [d] Reaction conditions as in ref. 11*b*. [e] 24 h reaction time. [f] Reaction conditions as in ref. 11*a*. [g] 5 mol% $AgBF_4$. [h] Oxygen atmosphere.

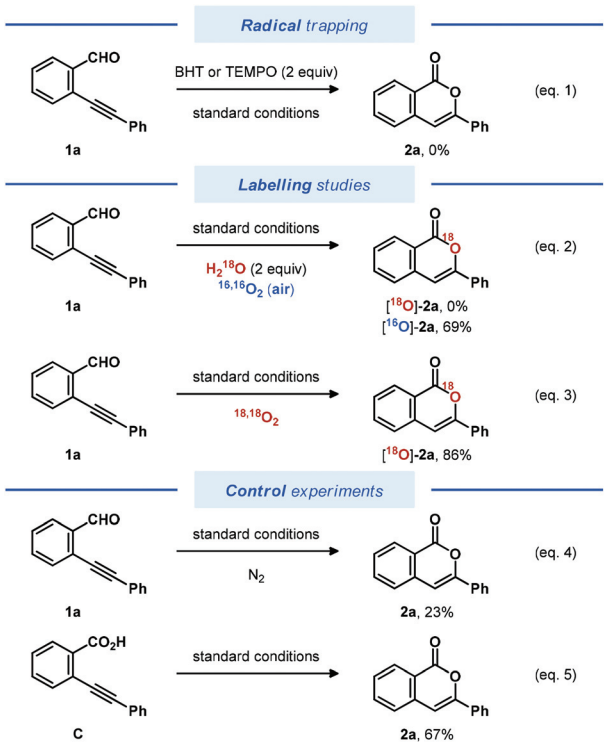
With the optimized reaction conditions in hand, we proceeded with exploring the generality of the developed protocol (Scheme 1). A diverse range of *ortho*-alkynylbenzaldehydes **1** smoothly afforded the corresponding products **2** in high yields. Several common functional groups on the aromatic ring, including F, Cl, Me, OMe and CF_3, were compatible with the developed protocol, providing the expected products **2b–2i** in 71–85% yields. Importantly, *ortho*-alkynylbenzaldehydes with various substituents on the alkynyl moiety, including aryl-, heteroaryl- and alkyl groups, were also efficiently con-



Scheme 1 Scope investigations. Reaction conditions: **1** (0.5 mmol), $AgBF_4$ (9.7 mg, 0.05 mmol), DMF (2.0 mL), 80 °C, air. Yields are of isolated products after purification by column chromatography. [a]2 mmol scale synthesis of **2a**.



Scheme 2 Application to heterocyclic substrates.

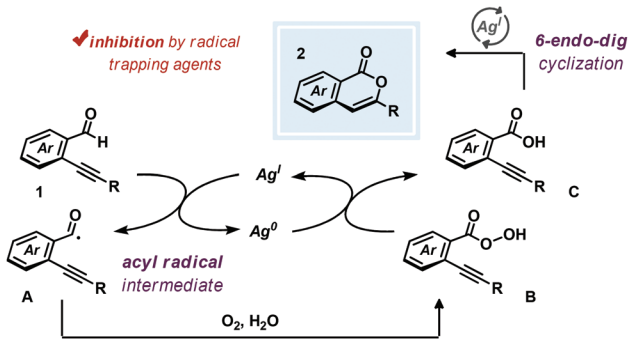


Scheme 3 Mechanistic investigations.

verted to the desired products **2j–2t** in up to 92% yield.[7,8] Conducting the reaction with the fused aromatic *ortho*-alkynylbenzaldehyde **1u** generated the expected product **2u** in 78% yield. When the scale of **2a** was increased to 2 mmol, the target compound could also be obtained in 82% yield. The structure of product **2d** was further confirmed by single crystal X-ray analysis (CCDC 2052724,† see Scheme 1).

Subsequently, a diverse range of *ortho*-alkynylheteroarylaldehydes **3** was investigated under the optimal reaction conditions to evaluate the broader applicability of the established protocol (Scheme 2). Delightfully, all of the heteroaryl-containing substrates were smoothly converted to the target products (**3a–3h**) in high yields. Notably, the previously reported synthetic methods are mostly limited to benzo-,[8] pyridyl-[10] and quinuclidinyl-[11]containing substrates, while the current synthetic protocol is also applicable to thiophene-derived *ortho*-alkynylheteroarylaldehydes.[13]

A series of mechanistic experiments was conducted in order to gain insight into the mechanism of the disclosed transformation (Scheme 3). First, we observed that subjecting substrate **1a** to the standard reaction conditions in the presence of radical scavengers, such as 3,5-di-*tert*-4-butylhydroxytoluene (BHT) or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), completely suppresses the reaction, suggesting that the reaction proceeds *via* a free-radical pathway (Scheme 3, eqn (1)).[14] Unfortunately, we failed to isolate the adducts of the reaction intermediates with the radical scavengers, likely due to the low stability of such adducts. In order to determine the source of the endocyclic oxygen in product **2a**, experiments with **1a** were conducted in the presence of two equivalents of $H_2{}^{18}O$ (Scheme 3, eqn (2)) and under $^{18}O_2$ (Scheme 3, eqn (3)). In the presence of $H_2{}^{18}O$, the reaction with **1a** provided exclusively the [^{16}O]-**2a** product. In contrast, under an $^{18,18}O_2$ atmosphere,



Scheme 4 Plausible mechanism.

2a was obtained in 86% yield with a high degree of ^{18}O incorporation, as determined by the ESI-HRMS measurements. These results suggest that molecular oxygen from air is the sole source of oxygen in the heterocyclization product. Furthermore, control experiments revealed that the yield of **2a** sharply diminished to 23% when the reaction was conducted under a N_2 atmosphere (Scheme 3, eqn (4)). Additionally, *ortho*-alkynylbenzoic acid **C** could be readily converted to the expected product **2a** under the optimized reaction conditions, identifying carboxylic acid **C** as a plausible reaction intermediate (Scheme 3, eqn (5)).

Based on the results from the described experiments and related literature precedents,[15,16] a plausible mechanism for the disclosed transformation was proposed and is outlined in Scheme 4. Initially, $AgBF_4$ mediates the oxidation of **1a**, resulting in the formation of the acyl radical intermediate **A**.[17] The concomitant reduction of Ag^I and the formation of free Ag^0 species were consistent with the deposition of small amounts of silver on the walls of the reaction vessel and formation of a silver mirror.[18] Subsequently, oxygenation of **A** with molecular O_2 leads to the formation of peracid **B**.[19] The following one-electron reduction of **B** by Ag^0 results in the formation of the carboxylic acid intermediate **C** and regeneration of the Ag^I catalyst.[20] Finally, intermediate **C** undergoes silver-promoted *6-endo-dig* heterocyclization to provide the desired product **2a**.

Conclusions

In summary, we have developed a novel silver-catalyzed aerobic oxidation/*6-endo* heterocyclization of *ortho*-alkynylbenzaldehydes, providing an atom-economical and step-efficient approach for the construction of synthetically valuable 3-substituted isocoumarins and related heterocyclolactones in good to high yields. The reaction is proposed to proceed through a radical mechanism based on preliminary mechanistic investigations. This report presents a straightforward strategy for the synthesis of *ortho*-alkynylbenzaldehydes, and considering the importance of isocoumarin scaffolds in medicinal chemistry, this protocol will undoubtedly find wide applications in future synthetic endeavors.

Experimental

General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C using a Varian spectrometer at 400 MHz and 101 MHz, respectively, using TMS as the internal standard. Mass spectra were recorded using a Bruker AutoflexIII Smartbeam MS spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruck microTof by using ESI-TOF and EI methods.

Typical synthetic procedure for the synthesis of 1 (with 1a as an example)

A mixture of 2-bromobenzaldehyde (233 μL, 2.0 mmol), CuI (19 mg, 0.10 mmol) and $Pd(PPh_3)Cl_2$ (70 mg, 0.10 mmol) in Et_3N (10.0 mL) was stirred at 50 °C in an oil bath. To the mixture was added phenylacetylene (320 μL, 2.5 mmol). The reaction mixture was stirred under a nitrogen atmosphere until 2-bromobenzaldehyde was consumed as indicated by TLC (about 12 h). The resulting mixture was concentrated and the residue was taken up in Et_2O. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 20 : 1) afforded 2-(phenylethynyl)benzaldehyde in 90% yield as a white solid.

Typical synthetic procedure for the synthesis of 2 and 3 (with 2a as an example)

To a 10 mL Schlenk tube, a mixture of **1a** (103 mg, 0.50 mmol) and $AgBF_4$ (9.7 mg, 0.05 mmol) in DMF (2.0 mL) was added. The mixture was stirred at 80 °C in an oil bath under an air atmosphere until substrate **1a** was consumed as indicated by TLC (about 10 h). The resulting mixture was concentrated under reduced pressure. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 15 : 1) afforded **2a** in 91% yield (101 mg) as a light yellow oil. **2** mmol-scale synthesis of **2a**: to a 10 mL Schlenk tube, a mixture of **1a** (412 mg, 2 mmol) and $AgBF_4$ (39 mg, 0.2 mmol) in DMF (8.0 mL) was added. The mixture was stirred at 80 °C in an oil bath under an air atmosphere until substrate **1a** was consumed as indicated by TLC (about 10 h). The resulting mixture was concentrated under reduced pressure. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 15 : 1) afforded **2a** in 82% yield (364 mg) as a light yellow oil.

3-Phenyl-1*H*-isochromen-1-one (2a).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 15) as the eluent. Yield: 91% (101 mg), 73% (811 mg, 5 mmol scale). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, J = 8.0 Hz, 1H), 7.91–7.88 (m, 2H), 7.75–7.71 (m, 1H), 7.53–7.43 (m, 5H), 6.97 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.4, 153.7, 137.5, 134.9, 132.0, 130.0, 129.7, 128.9, 128.2, 126.0, 125.3, 120.6, 101.8, 76.7; IR (KBr): ν 3057, 3028, 1708, 1640, 1610, 1566, 1495, 1353, 1338,

1319, 1305, 1262, 1240, 1014, 913, 802, 760, 641, 627 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{11}O_2$ $[M + H]^+$: 223.0754, found 223.0772.

7-Fluoro-3-phenyl-1*H*-isochromen-1-one (2b).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 71% (85 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 8.4, 1H), 7.88–7.86 (m, 2H), 7.54–7.42 (m, 5H), 6.95 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.9 (d, J_{C-F} = 248.5 Hz), 161.5, 153.2 (d, J_{C-F} = 2.8 Hz), 134.1 (d, J_{C-F} = 2.8 Hz), 131.7, 130.1, 128.9, 128.2 (d, J_{C-F} = 7.7 Hz), 125.2, 123.4 (d, J_{C-F} = 23.1 Hz), 122.2 (d, J_{C-F} = 8.0 Hz), 115.3 (d, J_{C-F} = 23.2 Hz), 101.0; IR (KBr): ν 3043, 3005, 1750, 1632, 1600, 1542, 1483, 1362, 1320, 1300, 1279, 1262, 1101, 1083, 925, 843, 750, 668, 627 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{10}FO_2$ $[M + H]^+$: 241.0659, found 241.0679.

7-Methyl-3-phenyl-1*H*-isochromen-1-one (2c).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 23) as the eluent. Yield: 76% (90 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.06 (s, 1H), 7.83–7.80 (m, 2H), 7.48 (dd, J = 8.0, 2.0 Hz, 1H), 7.44–7.38 (m, 3H), 7.35 (d, J = 8.0 Hz, 1H), 6.87 (s, 1H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.5, 152.8, 138.5, 136.2, 135.1, 132.1, 129.8, 129.4, 128.8, 125.9, 125.1, 120.4, 101.8, 21.4; IR (KBr): ν 3052, 3011, 2920, 1732, 1685, 1610, 1535, 1442, 1355, 1300, 1292, 1250, 1203, 1165, 1077, 973, 831, 783, 685, 633 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{13}O_2$ $[M + H]^+$: 237.0910, found 237.0947.

7-Methoxy-3-phenyl-1*H*-isochromen-1-one (2d).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 12) as the eluent. Yield: 86% (108 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.82 (m, 2H), 7.69 (d, J = 2.0 Hz, 1H), 7.45–7.38 (m, 4H), 7.28 (dd, J = 8.4, 2.8 Hz, 1H), 6.91 (s, 1H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.4, 159.5, 151.6, 132.0, 131.1, 129.5, 128.7, 127.5, 124.9, 124.7, 121.6, 109.9, 101.5, 55.7; IR (KBr): ν 3081, 3033, 2980, 1723, 1633, 1605, 1538, 1466, 1387, 1365, 1321, 1293, 1267, 1135, 1070, 945, 873, 735, 638, 601 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{13}O_3$ $[M + H]^+$: 253.0859, found 253.0874.

3-Phenyl-6-(trifluoromethyl)-1*H*-isochromen-1-one (2e).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 10) as the eluent. Yield: 77% (112 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.57 (s, 1H), 7.93–7.87 (m, 3H), 7.62 (d, J = 8.0 Hz, 1H), 7.51–7.46 (m, 3H), 7.00 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.2, 155.8, 140.3, 131.3, 131.1 (d, J = 3.0 Hz), 130.8, 130.1 (d, J = 33.1 Hz), 129.0, 127.3 (d, J = 3.9 Hz), 126.8, 125.5, 123.5 (d, J = 271.1 Hz), 120.5, 100.9; IR (KBr): ν 3053, 3010, 1769, 1686, 1643, 1511, 1489, 1373, 1311, 1303, 1243, 1201, 1183, 1069, 934, 878, 724, 649 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{16}H_9F_3O_2$ $[M]^+$: 290.05546, found 290.05499.

6-Chloro-3-phenyl-1*H*-isochromen-1-one (2f).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 72% (92 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz,): δ 8.25 (d, J = 8.4 Hz, 1H), 7.90–7.87 (m, 2H), 7.51–7.44 (m, 5H), 6.89 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.2, 154.0, 135.9, 135.3, 133.9, 131.6, 130.3, 129.2, 128.9, 127.5, 125.3, 121.7, 101.0; IR (KBr): ν 3043, 3005, 1750, 1632, 1600, 1542, 1483, 1362, 1320, 1300, 1279, 1262, 1101, 1083, 925, 843, 750, 668, 627 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_9ClNaO_2$ $[M + H]^+$: 279.0183, found 279.0207.

6-Methyl-3-phenyl-1*H*-isochromen-1-one (2g).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 18) as the eluent. Yield: 81% (96 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.15 (d, J = 8.0 Hz, 1H), 7.85–7.82 (m, 2H), 7.46–7.39 (m, 2H), 7.28–7.24 (m, 2H), 6.85 (s, 1H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.3, 153.5, 145.9, 137.5, 132.0, 129.8, 129.53, 129.51, 128.8, 125.9, 125.1, 118.1, 101.7, 21.9; IR (KBr): ν 3057, 3025, 2987, 1743, 1635, 1610, 1538, 1439, 1348, 1310, 1301, 1289, 1278, 1154, 1042, 985, 842, 764, 688, 672 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{13}O_2$ $[M + H]^+$: 237.0910, found 237.0958.

6,7-Dimethoxy-3-phenyl-1*H*-isochromen-1-one (2h).[8a] Purified using ethyl acetate and petroleum ether (v/v = 1 : 10) as the eluent. Yield: 85% (120 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89–7.86 (m, 2H), 7.70–7.69 (m, 1H), 7.49–7.40 (m, 3H), 6.92 (s, 1H), 6.89 (s, 1H), 4.03 (s, 3H), 4.01 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.3, 155.2, 152.7, 149.8, 135.2, 132.2, 129.7, 128.8, 125.0, 113.8, 109.5, 106.5, 101.6, 56.4, 56.3; IR (KBr): ν 3043, 3021, 2963, 1772, 1663, 1642, 1531, 1430, 1357, 1363, 1321, 1249, 1201, 1132, 1011, 943, 884, 738, 693, 613 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}O_4$ $[M + H]^+$: 283.0965, found 283.0998.

5-Fluoro-3-phenyl-1*H*-isochromen-1-one (2i). Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 73% (88 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.14–8.09 (m, 1H), 7.93–7.89 (m, 2H), 7.51–7.42 (m, 5H), 7.18 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.7 (d, J_{C-F} = 255.2 Hz), 161.4, 154.9, 140.2 (d, J_{C-F} = 10.9 Hz), 133.0 (d, J_{C-F} = 10.4 Hz), 131.5, 130.4, 128.9, 125.4, 117.0 (d, J_{C-F} = 1.4 Hz), 116.5 (d, J_{C-F} = 23.2 Hz), 111.5 (d, J_{C-F} = 22.5 Hz), 101.2 (d, J_{C-F} = 2.7 Hz); IR (KBr): ν 3045, 3025, 1753, 1671, 1620, 1551, 1462, 1371, 1321, 1311, 1287, 1261, 1131, 1098, 901, 849, 787, 689, 632 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{10}FO_2$ $[M + H]^+$: 241.0659, found 241.0684.

3-(4-Chlorophenyl)-1*H*-isochromen-1-one (2j).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 82% (104 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.55–7.47 (m, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.92 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.0, 152.5, 137.2, 136.0, 135.0, 130.4, 129.7, 129.1, 128.4, 126.4, 126.0, 120.5, 102.1; IR (KBr): ν 3038, 3003, 1786, 1631, 1620, 1541, 1435, 1363, 1340, 1311, 1273, 1263, 1191, 1087, 996, 823, 741, 642, 637 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{20}ClO_2$ $[M + H]^+$: 257.0364, found 257.0384.

3-(p-Tolyl)-1*H*-isochromen-1-one (2k).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 92% (109 mg). Light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, J = 8.0 Hz, 1H), 7.77–7.75 (m, 2H), 7.71–7.67 (m, 1H), 7.48–7.44 (m, 2H), 7.26–7.24 (m, 2H), 6.89 (s, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.4, 153.8, 140.3, 137.7, 134.8, 129.6, 129.5, 129.2, 127.9, 125.8, 125.2, 120.4, 101.1, 17.1; IR (KBr): ν 3041, 3029, 2928, 1734, 1628, 1637, 1519, 1437, 1342, 1321, 1301, 1293, 1212, 1135, 1037, 989, 813, 724,

682, 632 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{13}O_2$ [M + H]$^+$: 237.0910, found 237.0951.

3-(4-Ethylphenyl)-1*H*-isochromen-1-one (2l).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 87% (109 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, J = 7.6 Hz, 1H), 7.81–7.79 (m, 2H), 7.72–7.68 (m, 1H), 7.49–7.45 (m, 2H), 7.29–7.27 (m, 2H), 6.90 (s, 1H), 2.70 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.5, 153.9, 146.6, 137.7, 134.8, 129.6, 129.4, 128.4, 127.9, 125.9, 125.3, 120.4, 101.1, 28.7, 15.3; IR (KBr): ν 3073, 3025, 2945, 1713, 1637, 1614, 1598, 1434, 1325, 1312, 1307, 1298, 1245, 1132, 1045, 925, 878, 762, 645, 612 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}O_3$ [M + H]$^+$: 251.1067, found 251.1067.

3-(4-Ethoxyphenyl)-1*H*-isochromen-1-one (2m).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 16) as the eluent. Yield: 85% (113 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, J = 8.0 Hz, 1H), 7.83–7.81 (m, 2H), 7.72–7.68 (m, 1H), 7.48–7.44 (m, 2H), 6.97–6.95 (m, 2H), 6.83 (s, 1H), 4.10 (q, J = 6.8 Hz, 2H), 1.45 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.5, 160.5, 153.8, 137.9, 134.8, 129.6, 127.6, 126.8, 125.7, 124.3, 120.1, 114.7, 100.1, 63.6, 14.8; IR (KBr): ν 3072, 3045, 2912, 1756, 1612, 1601, 1558, 1434, 1347, 1328, 1312, 1281, 1224, 1145, 1025, 927, 812, 758, 635, 623 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}O_3$ [M + H]$^+$: 267.1016, found 267.1041.

3-(4-Pentylphenyl)-1*H*-isochromen-1-one (2n).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 81% (118 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, J = 7.2 Hz, 1H), 7.81–7.79 (m, 2H), 7.72–7.68 (m, 1H), 7.50–7.46 (m, 2H), 7.28 (s, 1H), 6.91 (s, 1H), 2.65 (t, J = 7.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.41–1.31 (m, 4H), 0.90 (t, J = 6.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.5, 153.9, 145.4, 137.8, 134.8, 129.7, 129.4, 128.9, 127.9, 125.9, 125.2, 120.4, 101.1, 35.8, 31.5, 30.9, 22.5, 14.0; IR (KBr): ν 3042, 3012, 2927, 1712, 1672, 1642, 1512, 1424, 1385, 1323, 1312, 1286, 1227, 1158, 1012, 932, 842, 725, 627, 610 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{21}O_2$ [M + H]$^+$: 293.1536, found 293.1561.

3-(3-Methoxyphenyl)-1*H*-isochromen-1-one (2o).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 15) as the eluent. Yield: 81% (102 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, J = 8.0 Hz, 1H), 7.74–7.71 (m, 1H), 7.52–7.46 (m, 3H), 7.42 (s, 1H), 7.39–7.35 (m, 1H), 6.98 (dd, J = 8.0, 2.4 Hz, 1H), 6.95 (s, 1H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.3, 160.1, 153.5, 137.5, 134.9, 133.4, 129.9, 129.7, 128.2, 126.0, 120.7, 117.7, 116.0, 110.5, 102.1, 55.5; IR (KBr): ν 3027, 3001, 2942, 1782, 1627, 1601, 1528, 1404, 1371, 1340, 1307, 1287, 1225, 1110, 1058, 901, 885, 712, 658, 623 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{13}O_3$ [M + H]$^+$: 253.0859, found 253.0888.

3-(2-Fluorophenyl)-1*H*-isochromen-1-one (2p).[21] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 75% (90 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33–8.32 (m, 1H), 8.04–8.00 (m, 1H), 7.76–7.73 (m, 1H), 7.55–7.52 (m, 2H), 7.43–7.37 (m, 1H), 7.29–7.26 (m, 1H), 7.22 (s, 1H), 7.21–7.16 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.1, 160.1 (d, J_{C-F} = 251.3 Hz), 148.1 (d, J_{C-F} = 5.0 Hz), 137.5, 134.9, 131.2 (d, J_{C-F} = 8.9 Hz), 129.6, 128.6, 128.5 (d, J_{C-F} = 1.8 Hz), 126.4, 124.6 (d, J_{C-F} = 3.6 Hz), 120.8, 120.2 (d, J_{C-F} = 9.8 Hz), 116.5 (d, J_{C-F} = 22.8 Hz), 107.3 (d, J_{C-F} = 15.4 Hz); IR (KBr): ν 3028, 3001, 1758, 1645, 1623, 1558, 1423, 1312, 1301, 1299, 1285, 1245, 1124, 1012, 942, 882, 737, 656, 642 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{10}FO_2$ [M + H]$^+$: 241.0659, found 241.0684.

3-Methyl-1*H*-isochromen-1-one (2q).[7f] Ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 90% (72 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, J = 8.0 Hz, 1H), 7.69–7.65 (m, 1H), 7.47–7.43 (m, 1H), 7.34 (d, J = 7.6 Hz, 1H), 6.26 (s, 1H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.0, 154.6, 137.6, 134.7, 129.5, 127.6, 124.9, 119.9, 103.5, 19.7; IR (KBr): ν 3028, 3001, 2945, 1725, 1612, 1601, 1542, 1453, 1345, 1317, 1301, 1256, 1212, 1123, 1078, 953, 837, 713, 676, 643 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{10}H_9O_2$ [M + H]$^+$: 161.0597, found 161.0605.

3-Pentyl-1*H*-isochromen-1-one (2r).[7f] Purified using ethyl acetate and petroleum ether (v/v = 1 : 17) as the eluent. Yield: 82% (89 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, J = 8.0 Hz, 1H), 7.69–7.65 (m, 1H), 7.47–7.43 (m, 1H), 7.35 (d, J = 8.0 Hz, 1H), 6.25 (s, 1H), 2.52 (t, J = 7.6 Hz, 2H), 1.75–1.68 (m, 2H), 1.37–1.34 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.1, 158.4, 137.7, 134.7, 129.5, 127.5, 125.0, 120.2, 102.9, 33.5, 31.2, 26.6, 22.4, 14.0; IR (KBr): ν 3079, 3042, 2943, 1725, 1642, 1615, 1525, 1442, 1382, 1347, 1301, 1213, 1145, 1132, 1086, 943, 837, 728, 614, 601 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{17}O_2$ [M + H]$^+$: 217.1223, found 217.1241.

3-(Cyclohex-1-en-1-yl)-1*H*-isochromen-1-one (2s).[4c] Purified using ethyl acetate and petroleum ether (v/v = 1 : 15) as the eluent. Yield: 86% (97 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, J = 8.0 Hz, 1H), 1.68–1.62 (m, 2H), 7.66–7.62 (m, 1H), 7.43–7.37 (m, 2H), 6.80 (t, J = 4.4 Hz, 1H), 6.35 (s, 1H), 2.30–2.23 (m, 4H), 1.80–1.74 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.3, 153.3, 136.8, 133.6, 129.0, 128.5, 127.3, 126.5, 124.8, 119.6, 99.1, 24.6, 23.1, 21.3, 20.8; IR (KBr): ν 3078, 3042, 2928, 1740, 1627, 1608, 1540, 1445, 1328, 1319, 1308, 1278, 1256, 1143, 1014, 958, 872, 747, 675, 628 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{15}O_2$ [M + H]$^+$: 227.1067, found 227.1083.

3-(Thiophen-2-yl)-1*H*-isochromen-1-one (2t).[4d] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 71% (81 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, J = 8.0 Hz, 1H), 7.73–7.69 (m, 1H), 7.62 (d, J = 3.6 Hz, 1H), 7.50–7.45 (m, 2H), 7.41 (d, J = 5.2 Hz, 1H), 7.13–7.11 (m, 1H), 6.80 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.7, 149.8, 137.1, 135.7, 134.4, 129.9, 128.2, 128.0, 127.4, 126.2, 125.7, 119.9, 99.3; IR (KBr): ν 3075, 3042, 1758, 1643, 1612, 1573, 1428, 1345, 1327, 1310, 1275, 1228, 1123, 1079, 972, 823, 775, 685, 640 cm^{-1}. HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_9O_2S$ [M + H]$^+$: 229.0318, found 229.0341.

2-Phenyl-4*H*-benzo[*f*]isochromen-4-one (2u).[22] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the

eluent. Yield: 78% (106 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.47–8.44 (m, 1H), 8.27 (d, J = 8.8 Hz, 1H), 8.04–8.00 (m, 2H), 7.97–7.95 (m, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.76–7.70 (m, 3H), 7.55–7.46 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.7, 135.0, 136.8, 136.1, 132.2, 130.3, 129.4, 129.04, 128.95, 128.5, 127.9, 127.3, 125.5, 124.3, 124.0, 117.6, 97.6; IR (KBr): ν 3057, 3028, 1778, 1625, 1612, 1575, 1443, 1358, 1324, 1310, 1275, 1212, 1184, 1027, 943, 882, 775, 627, 604 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{19}H_{13}O_2$ $[M + H]^+$: 273.0910, found 273.0946.

5-Phenyl-7*H*-thieno[2,3-*c*]pyran-7-one (3a).[7b] Purified using ethyl acetate and petroleum ether (v/v = 1 : 15) as the eluent. Yield: 82% (94 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88–7.83 (m, 3H), 7.46–7.44 (m, 3H), 7.24 (d, J = 5.2 Hz, 1H), 7.12 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.3, 155.4, 146.5, 135.8, 130.8, 129.1, 127.9, 124.4, 123.7, 121.9, 98.1; IR (KBr): ν 3067, 3001, 1750, 1627, 1601, 1550, 1478, 1356, 1342, 1312, 1224, 1201, 1172, 1049, 972, 872, 789, 637, 612 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{13}H_9O_2S$ $[M + H]^+$: 229.0318, found 229.0353.

5-(*p*-Tolyl)-7*H*-thieno[2,3-*c*]pyran-7-one (3b). Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 86% (104 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (d, J = 5.2 Hz, 1H), 7.78–7.76 (m, 2H), 7.28–7.26 (m, 2H), 7.23 (d, J = 5.2 Hz, 1H), 7.08 (s, 1H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.4, 156.7, 147.7, 140.5, 136.7, 129.6, 129.1, 125.3, 124.6, 122.6, 98.4, 21.4; IR (KBr): ν 3037, 3013, 2957, 1737, 1645, 1629, 1539, 1428, 1356, 1325, 1307, 1272, 1258, 1142, 1035, 958, 853, 775, 653, 621 cm^{-1}. HRMS (EI) m/z calcd for $C_{14}H_{11}O_2S$ $[M]^+$: 242.04015, found 242.03974.

5-(4-Methoxyphenyl)-7*H*-thieno[2,3-*c*]pyran-7-one (3c).[4d] Purified using ethyl acetate and petroleum ether (v/v = 1 : 10) as the eluent. Yield: 85% (110 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83–7.81 (m, 3H), 7.22 (d, J = 5.2 Hz, 1H), 7.01 (s, 1H), 6.99–6.95 (m, 2H), 3.87 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.2, 159.4, 157.1, 149.1, 135.2, 131.8, 127.8, 124.5, 123.2, 114.3, 97.7, 55.4; IR (KBr): ν 3057, 3018, 2928, 1704, 1650, 1638, 1568, 1458, 1387, 1342, 1313, 1238, 1212, 1198, 1085, 973, 819, 725, 634, 610 cm^{-1}. HRMS (EI) m/z calcd for $C_{14}H_{10}O_3S$ $[M]^+$: 258.03506, found 258.03458.

5-(3-Methoxyphenyl)-7*H*-thieno[2,3-*c*]pyran-7-one (3d). Purified using ethyl acetate and petroleum ether (v/v = 1 : 10) as the eluent. Yield: 76% (98 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (d, J = 5.2 Hz, 1H), 7.46–7.35 (m, 3H), 7.25 (d, J = 5.2 Hz, 1H), 7.12 (s, 1H), 6.99 (dd, J = 4.0, 3.2 Hz, 1H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.1, 158.3, 156.3, 147.5, 136.9, 133.3, 129.9, 124.7, 123.1, 117.8, 116.2, 110.6, 99.4, 55.5; IR (KBr): ν 3087, 3037, 2924, 1728, 1686, 1624, 1567, 1437, 1378, 1312, 1307, 1238, 1212, 1186, 1043, 950, 843, 750, 678, 643 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{14}H_{10}NaO_3S$ $[M + Na]^+$: 281.0243, found 281.0269.

5-(Cyclohex-1-en-1-yl)-7*H*-thieno[2,3-*c*]pyran-7-one (3e). Purified using ethyl acetate and petroleum ether (v/v = 1 : 15) as the eluent. Yield: 71% (82 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 5.2 Hz, 1H), 7.15 (d, J = 5.2 Hz, 1H), 6.85–6.84 (m, 1H), 6.54 (s, 1H), 2.30–2.23 (m, 4H), 1.80–1.74 (m, 2H), 1.68–1.63 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.4, 157.2, 147.8, 136.4, 130.6, 128.3, 124.6, 122.5, 97.4, 25.7, 24.2, 22.3, 21.8; IR (KBr): ν 3072, 3047, 2986, 1742, 1637, 1619, 1576, 1458, 1376, 1358, 1331, 1259, 1278, 1166, 1093, 941, 863, 745, 668, 629 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{13}H_{13}O_2S$ $[M + H]^+$: 233.0631, found 233.0639.

7-Phenyl-5*H*-pyrano[4,3-*b*]pyridin-5-one (3f).[23] Purified using ethyl acetate and petroleum ether (v/v = 1 : 20) as the eluent. Yield: 78% (87 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.95–8.94 (m, 1H), 8.56 (d, J = 8.0 Hz, 1H), 7.94–7.92 (m, 2H), 7.52–7.49 (m, 3H), 7.44 (dd, J = 8.0, 4.4 Hz, 1H), 7.24 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.1, 157.3, 156.4, 155.1, 137.6, 131.3, 130.8, 129.0, 125.7, 122.9, 116.9, 103.7; IR (KBr): ν 3098, 3078, 1787, 1612, 1601, 1528, 1458, 1375, 1319, 1302, 1286, 1234, 1175, 1067, 934, 828, 743, 643, 612 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{14}H_{10}NO_2$ $[M + H]^+$: 224.0706, found 224.0741.

7-Butyl-5*H*-pyrano[4,3-*b*]pyridin-5-one (3g).[9] Purified using ethyl acetate and petroleum ether (v/v = 1 : 15) as the eluent. Yield: 75% (74 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (dd, J = 4.8, 1.6 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.39 (dd, J = 8.0, 4.8 Hz, 1H), 6.54 (s, 1H), 2.60 (t, J = 7.6 Hz, 2H), 1.76–1.68 (m, 2H), 1.43 (q, J = 7.6 Hz, 2H), 0.96 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.8, 162.6, 156.2, 155.0, 137.6, 122.6, 116.4, 105.2, 33.4, 28.8, 22.1, 13.8, 1.0; IR (KBr): ν 3086, 3023, 2958, 1778, 1643, 1628, 1534, 1443, 1383, 1317, 1301, 1252, 1243, 1125, 1045, 983, 845, 758, 619, 604 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{14}NO_2$ $[M + H]^+$: 204.1019, found 204.1030.

3-Phenyl-1*H*-pyrano[4,3-*b*]quinolin-1-one (3h).[11b] Purified using ethyl acetate and petroleum ether (v/v = 1 : 10) as the eluent. Yield: 67% (91 mg). Light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.19 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.99–7.97 (m, 2H), 7.94–7.90 (m, 1H), 7.65–7.61 (m, 1H), 7.65–7.50 (m, 3H), 7.35 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.1, 157.0, 152.7, 151.8, 140.6, 133.6, 131.5, 130.8, 129.0, 127.10, 127.05, 125.7, 115.7, 103.8; IR (KBr): ν 3088, 3024, 1738, 1645, 1635, 1538, 1427, 1381, 1367, 1358, 1298, 1256, 1112, 1012, 925, 837, 724, 628, 601 cm^{-1}. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{12}NO_2$ $[M + H]^+$: 274.0863, found 274.0894.

Conflicts of interest

There are no conflicts to declare.

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