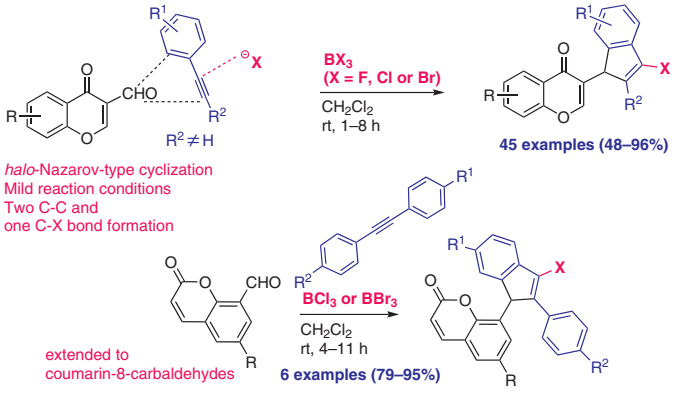
Synthesis A. Kumari, R. A. Fernandes Paper

BX_3-Mediated Intermolecular Formation of Functionalized 3-Halo-1*H*-indenes via Cascade *Halo*-Nazarov-Type Cyclization

Anupama Kumari
Rodney A. Fernandes*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, Maharashtra, India
rfernand@chem.iitb.ac.in



Received: 31.01.2020
Accepted after revision: 10.03.2020
Published online: 06.04.2020
DOI: 10.1055/s-0039-1690881; Art ID: ss-2019-n0717-op

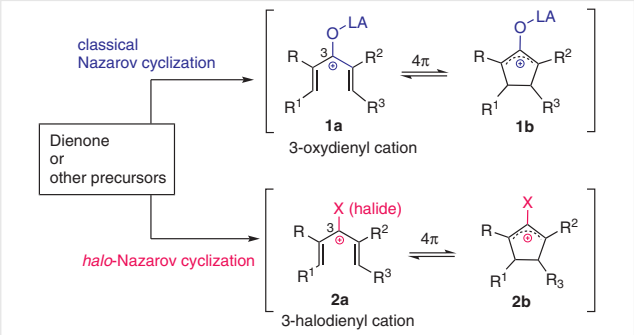
Abstract A BX_3-promoted, intermolecular regioselective synthesis of 3-halo-functionalized 1*H*-indenes from 4-oxo-4*H*-chromene-3-carbaldehydes and alkynes has been developed. BX_3 displays a dual role of Lewis acid catalyst and halide source for haloallyl cation formation for the intended *halo*-Nazarov-type cyclization. The overall transformation represents an efficient cascade annulation that employs readily available starting materials, inexpensive reagents and a convenient and mild reaction procedure to generate halo-functionalized indenes (45 examples). The reaction was also extended to 8-formylcoumarins to deliver coumarin-based 3-halo-1*H*-indenes in 79–95% yield (6 examples). The reaction involves conversion of the aldehyde into an sp^3 carbon with two new C–C bonds and additionally a C–X bond is formed (X = halide).

Key words Lewis acids, Nazarov cyclization, hybrid structures, C–C bond formation, electrocyclic reactions

Indenes[1] and chromones[2] are very promising targets and central structural units ubiquitous in many biologically active molecules. A hybrid displaying both these units might hold promise for resourceful biological activities. Combination of two different bioactive pharmacophores in a single molecule has been shown to possess better activity.[3] The Nazarov cyclization has been well explored since its discovery in the middle of the last century.[4] Traditionally, the reaction is based on cross-conjugated divinyl ketones undergoing ring closure to give the cyclopentenone or indanone products. Several natural products and valuable compounds have been synthesized employing this reaction.[4,5] However, it is also associated with some limitations, like the difficulty to synthesize and handle dienone precursors, especially when terminal disubstituted vinyl groups are needed. Recently, there have been interesting reports on *halo*-Nazarov-type cyclizations to provide the haloindene and halocyclopentene products.[6] However, most of these reactions involved the generation of vinylhalo compounds that were then subjected to *halo*-Nazarov cyclization, thus involving two steps in the protocol.

The traditional 4π-electrocyclization of an oxy- or aza-arylallyl cation or -dienyl cation **1a** (OH or NR_2) would be slower, affecting the equilibrium between **1a** and **1b** (Scheme 1). This can be attributed to the electron-releasing ability of oxygen or nitrogen to stabilize the cation, thereby decreasing its reactivity. Frontier and co-workers[6] have recently demonstrated that generation of a halo cation **2a** (X = halide) would speed up the reaction delivering the useful vinylhalo compounds. By computational studies, it has been observed that the arylallyl cation cyclizations are thermodynamically disfavoured and endothermic by >15 kcal/mol, due to aromaticity loss.[6c,7] However, the corresponding halo cation cyclizations were thermoneutral, despite aromaticity loss, and were predicted to be exothermic. Experimentally, the reactions occurred efficiently at 0 °C validating the computational data. Over the past decade, isolated examples of similar reactions have emerged, although these were considered as intramolecular Friedel–Crafts arylations.[8] The reaction now termed as '*halo*-Nazarov cyclization' is underdeveloped,[6,8] probably due to a lack of direct methods to prepare the intermediates of type **2a** from suitable precursors. While the work of Frontier and co-workers[6] marks an excellent beginning, there exists immense potential for further development in this area, as the vinylhalo compounds are useful intermediates in various transition-metal-catalyzed coupling reactions.[6a,b,8b,d,9]

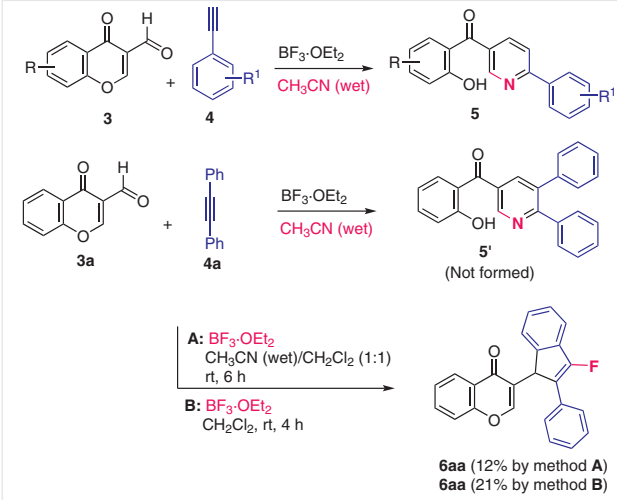
Our venture into the *halo*-Nazarov cyclization came serendipitously. Lee and co-workers[10] recently reported the $BF_3{\cdot}OEt_2$-promoted cyclization of chromenone-3-carbaldehydes **3** with terminal arylacetylenes **4** in CH_3CN for the construction of 2,5-disubstituted 2-arylpyridines **5**



Scheme 1 *Oxy*- and *halo*-Nazarov cyclization processes (LA = Lewis acid)

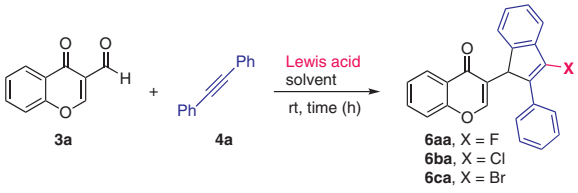
(Scheme 2). The nitrogen source for the pyridine moiety is derived from the solvent, CH_3CN. We visualized to explore the outcome with internal alkynes, to result in the expected 2,3,5-trisubstituted pyridine **5′** that can be further subjected to an intramolecular oxa-Michael addition resulting in the fused chromenone–pyridine hybrid. The reaction of **3a** with diphenylacetylene (**4a**) in CH_3CN failed to deliver 2,3,5-trisubstituted pyridine **5′**, even with excess $BF_3{\cdot}OEt_2$ or under heating conditions. A change to the solvent mixture CH_3CN/CH_2Cl_2 (1:1) furnished a new product, characterized to be a chromenone–3-indene incorporating the aryl ring, the alkyne and the aldehyde group of the chromenone with a further interesting incorporation of fluoride from $BF_3{\cdot}OEt_2$ leading to the functionalized five-membered-ring compound **6aa** (12%, Scheme 2). The reaction in only CH_2Cl_2 provided **6aa** in an improved yield of 21% and can be visualized as an intermolecular cascade *halo*-Nazarov-type cyclization with the incorporation of the vinyl halide group and differs in the substrates used by Frontier and co-workers[6] for similar cyclizations. Often the aryl vinyl ketone substrates for such reactions need to be synthesized with a heavy bias toward reactivity and the intended Nazarov cyclization becomes an intramolecular process. The present reaction being intermolecular and interesting in having the indene cyclopentene ring functionalized, the added vinyl-fluoro group, and the 4-chromenone moiety, we considered studying the scope and limitations of this cyclization reaction. It also holds the promise that a change of Lewis acid $BF_3{\cdot}OEt_2$ could incorporate other halide groups in the products.

We screened various halide sources and available Lewis acids containing halides for the reaction of **3a** and diphenylacetylene (**4a**) as model substrates with variation of solvent and temperature, as shown in Table 1. Various solvents were initially screened with $BF_3{\cdot}OEt_2$ (1.0 equiv) at room temperature (for full details, see the Supporting Information). Except CH_2Cl_2 (entry 1), other solvents were not compatible for this reaction (entries 2–6). In benzene, the reaction occurred with addition of a phenyl group (**6**, X = Ph, entry 7), in 8% yield. We considered raising the amount of



Scheme 2 Strategies for 2-arylpyridines and haloindenes

Table 1 Optimization of the *Halo*-Nazarov Reaction Conditions[a]



Entry	Acid (equiv)	Solvent	Temp	Time (h)	X	Yield (%)[b]
1	$BF_3{\cdot}OEt_2$ (1.0)	CH_2Cl_2	rt	4	F	21
2	$BF_3{\cdot}OEt_2$ (1.0)	THF	rt	36	F	NR
3	$BF_3{\cdot}OEt_2$ (1.0)	DMF	rt	36	F	NR
4	$BF_3{\cdot}OEt_2$ (1.0)	DMSO	rt	22	F	NR
5	$BF_3{\cdot}OEt_2$ (1.0)	CH_3CN	rt	1	F	CM
6	$BF_3{\cdot}OEt_2$ (1.0)	DCE	rt	24	F	NR
7	$BF_3{\cdot}OEt_2$ (1.0)	benzene	rt	16	F	8[c]
8	**$BF_3{\cdot}OEt_2$ (2.5)**	**CH_2Cl_2**	**rt**	**3.5**	**F**	**58**
9	$BF_3{\cdot}OEt_2$ (3.0)	CH_2Cl_2	rt	3.5	F	60
10	$BF_3{\cdot}OEt_2$ (3.0)	CH_2Cl_2	reflux	3.0	F	57
11	$BF_3{\cdot}THF$ (2.5)	CH_2Cl_2	rt	8	F	CM
12	HF–pyridine (2.5)	CH_2Cl_2	rt	6	F	CM
13	**BCl_3 (2.5)**	**CH_2Cl_2**	**rt**	**5**	**Cl**	**87**
14	**BBr_3 (2.5)**	**CH_2Cl_2**	**rt**	**5.5**	**Br**	**85**
15	$BF_3{\cdot}OEt_2$ (2.5)/PhI$(OAc)_2$ (1.0)	CH_2Cl_2	rt	8	I	CM
16	BCl_3 (2.5)/I_2 (1.0)	CH_2Cl_2	rt	24	I	NR
17	BCl_3 (2.5)/KI (1.0)	CH_2Cl_2	rt	24	I	NR

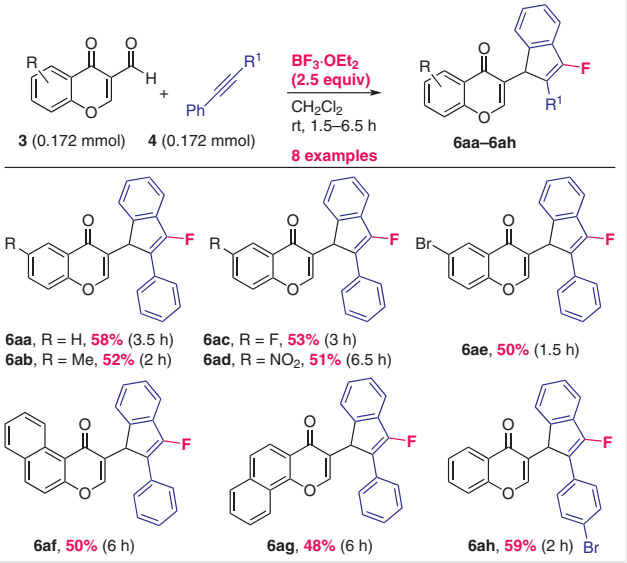
[a] Reaction conditions: **3a** (0.172 mmol), **4a** (0.172 mmol), acid (1.0–3.0 equiv), solvent (2 mL), rt or reflux, 1–36 h.
[b] Isolated yield. NR = no reaction, CM = complex mixture.
[c] In place of halogen, solvent addition observed (X = Ph).

$BF_3{\cdot}OEt_2$ used (1.5–3.0 equiv), the yield of **6aa** being increased with 2.5–3.0 equivalents (entries 8 and 9). There was no change in yield in carrying out the reaction at reflux in CH_2Cl_2 (entry 10). Other sources of fluoride like $BF_3{\cdot}THF$ or HF–pyridine did not yield product **6aa** (entries 11 and 12). We considered 2.5 equivalents of $BF_3{\cdot}OEt_2$ to be optimal. Further, the reaction was mimicked for chlorine incorporation using various chloride sources ($AlCl_3$, $FeCl_3$, $TiCl_4$ and BCl_3). Except BCl_3 (entry 13), other chloride sources were not successful (see the Supporting Information). The optimum requirement was 2.5 equivalents. Similarly, the use of BBr_3 in 2.5 equivalents was optimum for bromide incorporation (entry 14). The reactions for iodine incorporation using various iodide sources in combination with $BF_3{\cdot}OEt_2$ or BCl_3 (entries 15–17) failed to deliver the iodine-incorporated products. This study revealed that $BF_3{\cdot}OEt_2$, BCl_3 or BBr_3 (each 2.5 equiv) among the various halide sources in CH_2Cl_2 at room temperature are the optimum requirements. Among the three, the fluoride incorporation occurred in moderate yield in comparison to bromide and chloride.

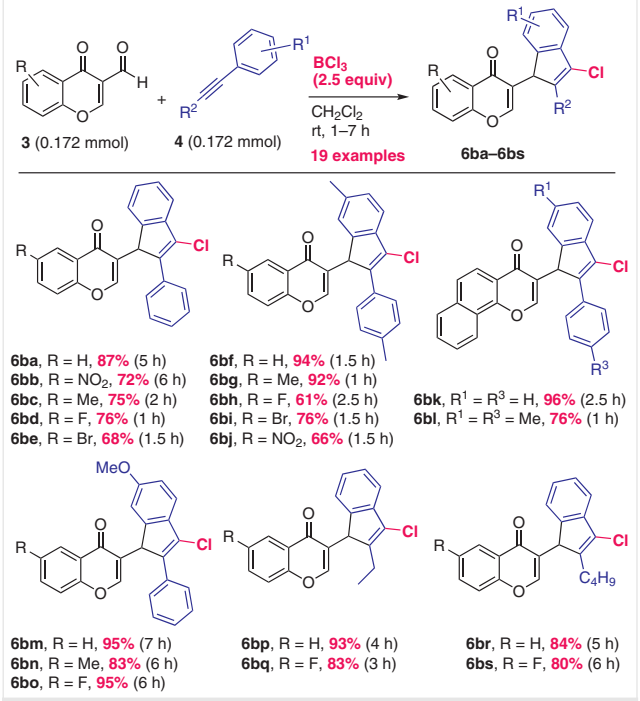
The scope and limitations of this method were next investigated on a series of substituted 4-oxo-4*H*-chromene-3-carbaldehydes **3** with diarylacetylenes **4** (Scheme 3) using $BF_3{\cdot}OEt_2$ for fluoride incorporation. Substrates **3** with a Me, F, NO_2 or Br group reacted well with **4a** giving the 3-fluoroindenes **6ab–6ae** in moderate yields. Compound **6ae** gave suitable crystals for X-ray analysis,[11] unambiguously confirming the structure. The naphthalene-based substrates also reacted well to provide **6af** and **6ag** in 50% and 48% yield, respectively. The use of the unsymmetrical alkyne 1-(4-bromophenyl)-2-phenylacetylene gave 3-fluoroindene **6ah** in 59% yield, with the unsubstituted benzene chemoselectively involved in indene formation.

We continued the scope of substrates for chloride incorporation using BCl_3 (2.5 equiv), as shown in Scheme 4. Substrates **3** with a NO_2, Me, F or Br group reacted well with **4a** giving the 3-chloroindenes **6bb–6be** in good yields (68–76%). Similarly, di-*p*-tolylacetylene reacted with various 4-oxo-4*H*-chromene-3-carbaldehydes **3** to deliver the 3-chloroindene compounds **6bf–6bj** in good to excellent yields (61–94%). The naphthalene-based substrates also reacted well to provide **6bk** and **6bl** in 96% and 76% yield, respectively. The unsymmetrical diarylalkyne 1-(4-methoxyphenyl)-2-phenylacetylene also worked well to regio- and chemoselectively provide the 3-chloroindenes **6bm–6bo** in up to 95% yield, in which the electron-rich methoxybenzene ring is chemoselectively involved in indene formation. Arylalkylalkynes (1-butyn-1-ylbenzene and 1-hexyn-1-ylbenzene) also reacted to give the 3-chloroindenes **6bp–6bs** in 80–93% yield. In these cases also, the benzene ring is involved in the annulation reaction. Compounds **6bb**, **6bi** and **6bm** provided suitable crystals for X-ray analysis.[11]

We next examined BBr_3, for bromine incorporation in the intermolecular cascade *bromo*-Nazarov indene formation (Scheme 5). With **4a** and with di-*p*-tolylacetylene, the reaction with various 4-oxo-4*H*-chromene-3-carbaldehydes **3** in the presence of BBr_3 furnished the 3-bromo-



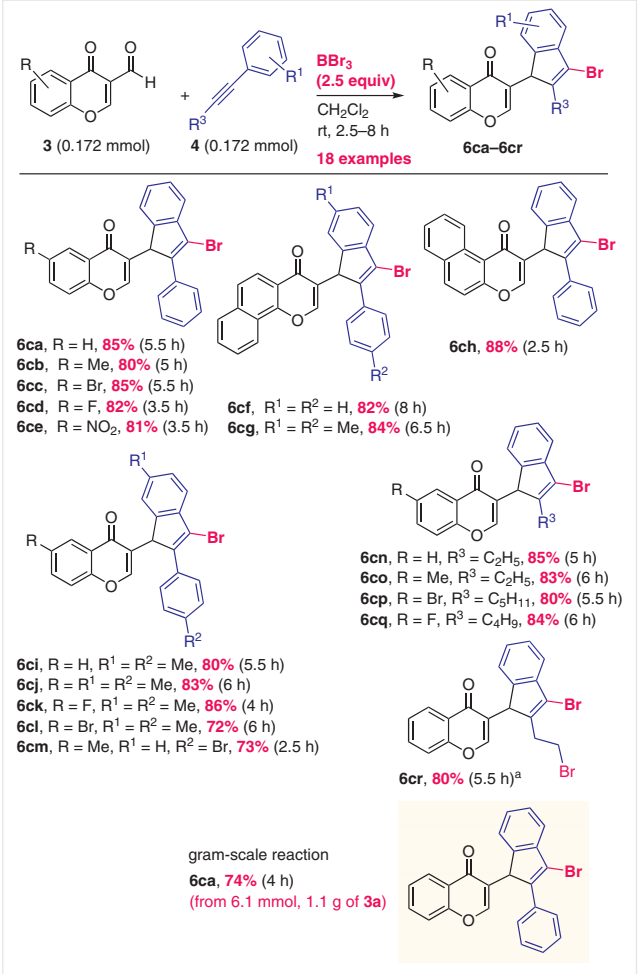
Scheme 3 Substrate scope for 3-fluoro-functionalized 1*H*-indene synthesis. *Reagents and conditions*: **3** (0.172 mmol), **4** (0.172 mmol), $BF_3{\cdot}OEt_2$ (2.5 equiv), CH_2Cl_2 (2 mL), rt, 1.5–6.5 h. Isolated yields were recorded.



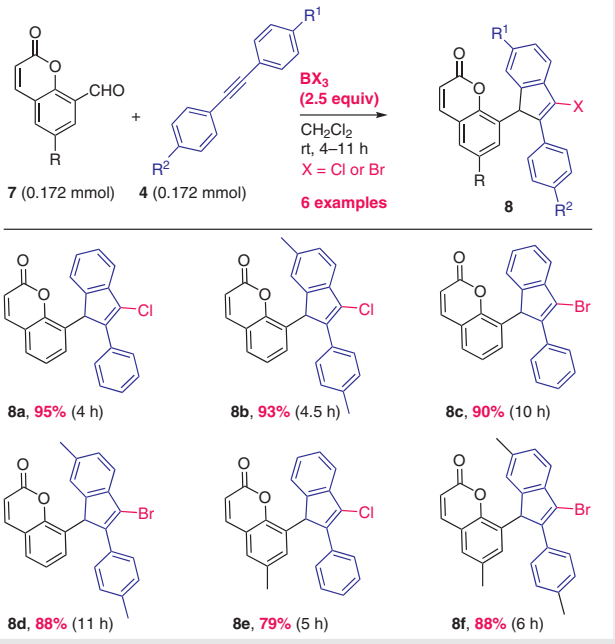
Scheme 4 Substrate scope for 3-chloro-functionalized 1*H*-indene synthesis. *Reagents and conditions*: **3** (0.172 mmol), **4** (0.172 mmol), BCl_3 (2.5 equiv), CH_2Cl_2 (2 mL), rt, 1–7 h. Isolated yields were recorded.

indenes **6ca–6cl** in good yields (72–88%). The unsymmetrical alkyne 1-(4-bromophenyl)-2-phenylacetylene provided 3-bromoindene **6cm** selectively, with the unsubstituted benzene ring undergoing the indene ring formation. This was further confirmed by X-ray analysis of **6cm**.[11] Arylalkylalkynes (1-butyn-1-ylbenzene, 1-heptyn-1-ylbenzene and 1-hexyn-1-ylbenzene) also reacted to give 3-bromoindenes **6cn–6cq** in 80–85% yield. In the case of 4-phenylbut-3-yn-1-ol, reaction with **3a** gave product **6cr** (80% yield), with the hydroxyl group converted into a bromide with the additional 1.0 equivalent of BBr_3. A reaction with 6.1 mmol of **3a** (R = H, 1.1 g) delivered **6ca** in 74% yield, indicating possible scale-up of the reaction (Scheme 5).

The present method was extended to 8-formylcoumarins **7**, as shown in Scheme 6. These, on reaction with diphenylacetylene (**4a**) or di-*p*-tolylacetylene, delivered the 3-chloro- or 3-bromo-functionalized 1*H*-indenes **8a–8f** in good to excellent yields (79–95%). Compound **8e** gave suitable crystals for X-ray analysis, confirming the structure.[11]



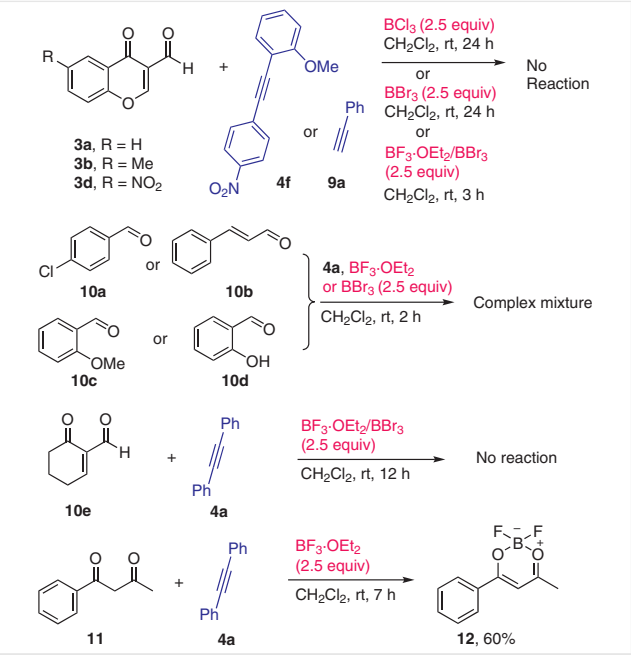
Scheme 5 Substrate scope for 3-bromo-functionalized 1*H*-indene synthesis and a gram-scale reaction. *Reagents and conditions*: **3** (0.172 mmol), **4** (0.172 mmol), BBr_3 (2.5 equiv), CH_2Cl_2 (2 mL), rt, 2.5–8 h. Isolated yields were recorded. [a] BBr_3 (3.5 equiv) used.



Scheme 6 Substrate scope for coumarin-based 3-halo-functionalized 1*H*-indene synthesis. *Reagents and conditions*: **7** (0.172 mmol), **4** (0.172 mmol), BX_3 (2.5 equiv), CH_2Cl_2 (2 mL), rt, 4–11 h. Isolated yields were recorded.

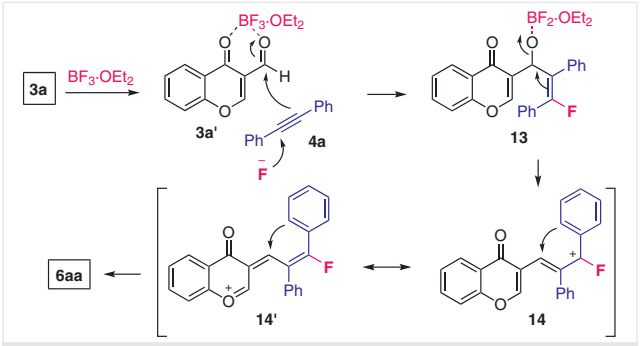
We also considered exploring alkynes with an electron-withdrawing group and various other aldehydes to gain insight into the mechanism of the reaction (Scheme 7). The reaction of 4-oxo-4*H*-chromene-3-carbaldehydes **3a**, **3b** or **3d** with 1-(2-methoxyphenyl)-2-(4-nitrophenyl)acetylene (**4f**) in the presence of BCl_3 or BBr_3 failed to deliver the chloro- or bromoindene compounds. Similarly, the reaction of aldehyde **3a** with phenylacetylene (**9a**) (terminal alkyne) in the presence of $BF_3{\cdot}OEt_2$ did not yield the corresponding indene product. Most of the starting materials were recovered in all these cases. This indicated that the alkyne should be nucleophilic enough for reaction with the aldehyde. The reaction of various other aldehydes, like *p*-chlorobenzaldehyde (**10a**), cinnamaldehyde (**10b**), *o*-anisaldehyde (**10c**), salicylaldehyde (**10d**) and 3-oxocyclohex-1-ene-2-carbaldehyde (**10e**), with diphenylacetylene (**4a**) in the presence of $BF_3{\cdot}OEt_2$ or BBr_3 gave either a complex mixture or no reaction, with the substrates being recovered unreacted. Comparison of ^{13}C NMR and IR spectral values for the aldehyde carbonyl of **10e** with that of chromonecarbaldehyde **3a** was not conclusive for the reactivity difference. The reaction studied is substrate specific and at this stage only the chromone- and coumarincarbaldehydes react. It appears clear that simple aryl aldehydes do not react probably due to lack of a β-keto group that is required for complexation with the Lewis acid. Also, the chromone oxygen stabilizes

the benzylic carbocation, as shown by intermediate **14′** in Scheme 8. This oxygen is absent in **10e**. The reaction of benzoylacetone (**11**) and **4a** with $BF_3{\cdot}OEt_2$ delivered the BF_2 complex **12** in 60% yield, the structure of which was established by X-ray analysis.[11] Thus, the β-keto group in 4-oxo-4*H*-chromene-3-carbaldehydes **3** is necessary for the reaction apart from the chromone oxygen. It has also been observed in this work that chloride and bromide incorporation gave superior yields in comparison to fluoride (Schemes 4 and 5 vs Scheme 3).



Scheme 7 Reactivity of alkyne with an electron-withdrawing group on the aryl ring and scope of other aldehydes

Considering the selective reactivity of 4-oxo-4*H*-chromene-3-carbaldehydes and not other aldehydes in this reaction, we considered the plausible mechanism as shown in Scheme 8, with probable involvement of the chromone oxygen. Suitably placed neighbouring groups accelerating the reaction has been developed earlier.[12] Thus, coordination of Lewis acid $BF_3{\cdot}OEt_2$ (or BCl_3 or BBr_3) with the aldehyde carbonyl initiates alkyne attack on the boron-complexed aldehyde **3a′**, with fluoride attack on the alkyne, giving intermediate **13**. Further generation of the fluoroallylic cation **14** triggers the *halo*-Nazarov-type cyclization. The chromone oxygen probably stabilizes the carbocation, generating the extended oxocarbenium ion **14′**. Intramolecular aryl ring closure produces the vinylfluoroindene product **6aa**. Terminal arylacetylenes may not be reactive as the intermediate cation before halide attack may not be stable or formed. This substrate bias is evident in the Nazarov cyclization being mostly explored with substituted vinyl bonds.



Scheme 8 Plausible mechanism (F incorporation in **6aa** is representative)

In summary, we have developed an efficient intermolecular *halo*-Nazarov-type cyclization of 4-oxo-4*H*-chromene-3-carbaldehydes and 1,2-disubstituted acetylenes in the presence of a halide source, $BF_3{\cdot}OEt_2$, BCl_3 or BBr_3, which also acts as a Lewis acid to mediate the reaction, giving vinylhaloindenes (45 examples).[13] The aldehyde carbon of 4-oxo-4*H*-chromene-3-carbaldehydes is converted from sp^2 into the sp^3 carbon in the product by formation of two new C–C bonds. An additional C–X bond formed by incorporation of a halide into the cyclopentene ring is remarkable, generating the functionalized indene moiety. The reaction was also extended to 8-formylcoumarins to deliver coumarin-based 3-halo-1*H*-indenes in good to excellent yields (6 examples). The overall transformation represents an efficient intermolecular cascade *halo*-Nazarov-type cyclization strategy that employs readily available starting materials, inexpensive reagents and a convenient and mild reaction procedure to generate halo-functionalized indenes.

TLC was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or by using a UV lamp. ^1H and ^{13}C NMR spectra were recorded with spectrometers operating at 400 or 500 and at 100 or 125 MHz for proton and carbon nuclei, respectively. The chemical shifts are based on the TMS peak at δ = 0.00 pm for proton NMR and the $CDCl_3$ peak at δ = 77.00 ppm (t) for carbon NMR. IR spectra were obtained on a FT-IR spectrophotometer. HRMS (ESI-TOF) spectra were recorded using positive electrospray ionization by the TOF method. CH_2Cl_2 was dried by refluxing over P_2O_5 and distillation on calcium hydride. THF and benzene were dried over sodium. All chromenone-3-carbaldehydes (except 3-formylbenzo[*h*]chromone that was prepared[14]) were obtained from Aldrich Chemical Co. All Lewis acids, phenylacetylene and 1-butyn-1-ylbenzene are commercial reagents and were used as such without further purification. Other alkynes were prepared using established literature protocols.[15] Room temperature = 32–35 °C.

3-(2-Aryl-3-fluoro-1*H*-inden-1-yl)-4*H*-chromen-4-ones 6aa–6ah; General Procedure

To a mixture of carbaldehyde **3** (0.172 mmol, 1.0 equiv) and alkyne **4** (0.172 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added $BF_3{\cdot}OEt_2$ (0.43 mmol, 2.5 equiv) at room temperature. The mixture was stirred for

the required time (monitored by TLC). After completion of the reaction, it was quenched with a few drops of sat. $Na_2S_2O_3$ solution. The solvent was removed through vacuum and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to afford **6aa–6ah**.

3-(3-Fluoro-2-phenyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6aa)

Yield: 35.4 mg (58%, reaction time = 3.5 h); white solid; mp 182–184 °C.

IR ($CHCl_3$): 3058, 2850, 1648, 1617, 1465, 1350, 1220, 1176, 696, 594 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.38 (t, *J* = 6.1 Hz, 1 H), 7.66–7.61 (m, 3 H), 7.53 (t, *J* = 5.7 Hz, 1 H), 7.47–7.43 (m, 2 H), 7.39–7.32 (m, 5 H), 7.27–7.21 (m, 2 H), 5.63 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 177.8, 157.3 (d, $^1J_{C-F}$ = 248.4 Hz), 156.0, 153.0, 144.5, 135.5, 135.3, 133.7, 131.3 (d, $^4J_{C-F}$ = 4.1 Hz), 128.8, 128.6, 127.7 (d, $^3J_{C-F}$ = 6.2 Hz), 127.4, 127.2, 125.9, 125.2, 124.0, 123.8, 122.7, 119.8, 118.1 (d, $^2J_{C-F}$ = 18.9 Hz), 40.7.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –128.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{16}FO_2$: 355.1129; found: 355.1130.

3-(3-Fluoro-2-phenyl-1*H*-inden-1-yl)-6-methyl-4*H*-chromen-4-one (6ab)

Yield: 33 mg (52%, reaction time = 2 h); white solid; mp 162–164 °C.

IR ($CHCl_3$): 3056, 2924, 1642, 1618, 1484, 1376, 1319, 1161, 911, 812, 693, 544 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.60 (d, *J* = 8.1 Hz, 2 H), 7.51 (d, *J* = 7.3 Hz, 1 H), 7.45 (d, *J* = 7.5 Hz, 2 H), 7.36–7.32 (m, 4 H), 7.24–7.19 (m, 3 H), 5.63 (d, *J* = 5.4 Hz, 1 H), 2.49 (s, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 177.8, 157.1 (d, $^1J_{C-F}$ = 280.2 Hz), 154.6, 152.9, 144.6 (d, $^3J_{C-F}$ = 6.9 Hz), 135.5, 135.3, 134.9, 131.4, 131.38, 128.8, 127.5 (d, $^3J_{C-F}$ = 6.5 Hz), 127.4, 127.2, 125.2, 124.1, 123.6, 122.4, 119.9, 117.98 (d, $^4J_{C-F}$ = 2.5 Hz), 117.9, 40.7, 21.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –128.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{17}FNaO_2$: 391.1105; found: 391.1106.

6-Fluoro-3-(3-fluoro-2-phenyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6ac)

Yield: 34 mg (53%, reaction time = 3 h); white solid; mp 220–222 °C.

IR ($CHCl_3$): 2932, 2857, 1637, 1625, 1476, 1457, 1049, 910, 610 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 7.9, 2.6 Hz, 1 H), 7.60–7.58 (m, 2 H), 7.51–7.45 (m, 2 H), 7.39 (s, 1 H), 7.38–7.33 (m, 5 H), 7.23 (t, *J* = 7.3 Hz, 2 H), 5.58 (d, *J* = 5.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 177.1, 159.7 (d, $^1J_{C-F}$ = 248.6 Hz), 155.8, 153.2, 152.6, 144.4 (d, $^3J_{C-F}$ = 7.3 Hz), 135.5, 135.3, 131.3 (d, $^4J_{C-F}$ = 4.9 Hz), 128.8, 127.7 (d, $^3J_{C-F}$ = 6.4 Hz), 127.6, 127.3, 124.9 (d, $^3J_{C-F}$ = 7.5 Hz), 124.0 (d, $^4J_{C-F}$ = 2.5 Hz), 122.2 (d, $^4J_{C-F}$ = 4.6 Hz), 121.9, 120.3 (d, $^3J_{C-F}$ = 8.1 Hz), 119.7, 118.1 (d, $^4J_{C-F}$ = 2.3 Hz), 110.8 (d, $^2J_{C-F}$ = 23.9 Hz), 40.7.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.8, –128.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{15}F_2O_2$: 373.1035; found: 373.1042.

3-(3-Fluoro-2-phenyl-1*H*-inden-1-yl)-6-nitro-4*H*-chromen-4-one (6ad)

Yield: 35 mg (51%, reaction time = 6.5 h); white solid; mp 189–191 °C.

IR ($CHCl_3$): 1652, 1632, 1531, 1467, 1345, 826, 695 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 9.23 (d, *J* = 2.4 Hz, 1 H), 8.46 (dd, *J* = 9.2, 2.3 Hz, 1 H), 7.58 (d, *J* = 8.3 Hz, 2 H), 7.50–7.45 (m, 4 H), 7.39–7.34 (m, 3 H), 7.26–7.23 (m, 2 H), 5.58 (d, *J* = 5.3 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.5, 159.0, 157.3 (d, $^1J_{C-F}$ = 280.4 Hz), 153.3, 144.8, 143.7, 135.4 (d, $^2J_{C-F}$ = 24.8 Hz), 131.1, 128.9, 128.0, 127.8, 127.7, 127.6, 127.5, 124.0, 123.9, 123.8, 122.8, 120.0, 119.3, 118.2, 40.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –127.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{14}FNNaO_4$: 422.0799; found: 422.0788.

6-Bromo-3-(3-fluoro-2-phenyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6ae)

Yield: 37.2 mg (50%, reaction time = 1.5 h); white solid; mp 156–158 °C.

IR ($CHCl_3$): 2923, 2857, 1676, 1641, 1605, 1461, 1376, 910, 815, 734, 693 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 2.3 Hz, 1 H), 7.71 (dd, *J* = 8.8, 2.5 Hz, 1 H), 7.58 (d, *J* = 7.3 Hz, 2 H), 7.49–7.45 (m, 2 H), 7.38–7.33 (m, 4 H), 7.24–7.21 (m, 3 H), 5.58 (d, *J* = 5.7 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.5, 157.2 (d, $^1J_{C-F}$ = 279.2 Hz), 155.1, 153.1, 144.3 (d, $^3J_{C-F}$ = 7.2 Hz), 136.7, 135.5, 135.3, 131.3 (d, $^4J_{C-F}$ = 4.9 Hz), 128.8, 128.6, 127.7 (d, $^3J_{C-F}$ = 6.4 Hz), 127.6, 127.4, 125.2, 124.0, 123.1, 120.1, 119.7, 118.7, 118.1, 40.7.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –128.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{14}BrFNaO_2$: 457.0036; found: 457.0035.

2-(3-Fluoro-2-phenyl-1*H*-inden-1-yl)-1*H*-benzo[*f*]chromen-1-one (6af)

Yield: 34.8 mg (50%, reaction time = 6 h); white solid; mp 185–187 °C.

IR ($CHCl_3$): 2926, 2855, 1642, 1609, 1516, 1441, 1375, 910, 820, 732, 693, 607 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.26 (d, *J* = 8.4 Hz, 1 H), 8.04 (d, *J* = 8.9 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.85 (t, *J* = 7.8 Hz, 1 H), 7.69–7.60 (m, 4 H), 7.48–7.44 (m, 2 H), 7.38–7.33 (m, 4 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 5.78 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 179.2, 157.5, 157.2 (d, $^1J_{C-F}$ = 279.3 Hz), 150.4, 144.6, 135.5, 135.3, 131.4, 130.6, 130.5, 129.3, 128.8, 128.3, 127.7 (d, $^3J_{C-F}$ = 6.3 Hz), 127.4, 127.2, 127.1, 126.7, 125.3, 124.1, 119.9, 118.0, 117.5, 117.1, 40.8.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –128.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{17}FNaO_2$: 427.1105; found: 427.1098.

3-(3-Fluoro-2-phenyl-1*H*-inden-1-yl)-4*H*-benzo[*h*]chromen-4-one (6ag)

Yield: 33.4 mg (48%, reaction time = 6 h); white solid; mp 138–140 °C.

IR ($CHCl_3$): 1683, 1642, 1601, 1445, 1380, 910, 694, 668 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30–8.26 (m, 2 H), 7.90 (d, *J* = 8.1 Hz, 1 H), 7.80 (d, *J* = 8.7 Hz, 1 H), 7.68–7.64 (m, 3 H), 7.60–7.57 (m, 3 H), 7.47 (d, *J* = 7.4 Hz, 1 H), 7.37–7.34 (m, 3 H), 7.24–7.20 (m, 2 H), 5.70 (d, *J* = 5.3 Hz, 1 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.5, 157.3 (d, $^1J_{C-F}$ = 279.9 Hz), 153.9, 152.1, 144.5, 135.7, 135.4 (d, $^2J_{C-F}$ = 25.7 Hz), 131.4, 129.4, 128.8, 128.7, 128.0, 127.7 (d, $^3J_{C-F}$ = 6.2 Hz), 127.5, 127.3, 127.2, 126.7, 125.5, 124.2 (d, $^2J_{C-F}$ = 13.5 Hz), 123.9, 122.1, 120.8, 120.2, 119.8, 118.0, 40.8.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –128.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{17}FNaO_2$: 427.1105; found: 427.1100.

3-(2-(4-Bromophenyl)-3-fluoro-1*H*-inden-1-yl)-4*H*-chromen-4-one (6ah)

Yield: 44 mg (59%, reaction time = 2 h); white solid; mp 103–105 °C.

IR ($CHCl_3$): 2945, 2833, 1686, 1640, 1608, 1465, 1395, 1028, 824, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 7.1 Hz, 1 H), 7.45 (dt, *J* = 7.7, 1.7 Hz, 1 H), 7.29–7.24 (m, 6 H), 7.16–7.13 (m, 3 H), 7.06 (s, 1 H), 7.03 (dt, *J* = 7.5, 1.0 Hz, 1 H), 5.38 (s, 1 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.7, 157.6 (d, $^1J_{C-F}$ = 262.5 Hz), 156.2, 153.0, 144.5, 135.3, 135.0, 133.8, 132.0, 131.6, 130.3, 129.2 (d, $^3J_{C-F}$ = 6.3 Hz), 127.6, 126.0, 125.4, 124.1, 123.8, 122.4, 121.2, 119.0, 118.2, 40.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –127.5.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{14}BrFNaO_2$: 455.0053; found: 455.0056.

3-(2-Aryl-3-chloro-1*H*-inden-1-yl)-4*H*-chromen-4-ones 6ba–6bs; General Procedure

Compounds **6ba–6bs** were prepared by following a similar procedure as described for compounds **6aa–6ah**, using BCl_3 (2.5 equiv) instead of BF_3·OEt_2 and 0.172 mmol each of **3** and **4**.

3-(3-Chloro-2-phenyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6ba)

Yield: 55.5 mg (87%, reaction time = 5 h); white semisolid.

IR ($CHCl_3$): 3057, 2923, 2850, 1650, 1617, 1465, 1349, 1220, 912, 736, 701, 592 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 7.7 Hz, 1 H), 7.78 (d, *J* = 7.5 Hz, 2 H), 7.60 (dt, *J* = 6.9, 1.6 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.50 (d, *J* = 7.4 Hz, 1 H), 7.40–7.34 (m, 4 H), 7.32 (s, 1 H), 7.30–7.27 (m, 2 H), 7.24–7.22 (m, 1 H), 5.80 (s, 1 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.4, 156.2, 153.2, 144.9, 141.4, 139.9, 133.6, 132.7, 128.9, 128.6, 128.0, 127.6, 127.0, 125.9, 125.2, 123.8, 123.5, 122.6, 119.6, 118.1, 45.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{15}ClNaO_2$: 393.0653; found: 393.0650.

3-(3-Chloro-2-phenyl-1*H*-inden-1-yl)-6-nitro-4*H*-chromen-4-one (6bb)

Yield: 51.5 mg (72%, reaction time = 6 h); white solid; mp 73–74 °C.

IR ($CHCl_3$): 2923, 2853, 1651, 1629, 1465, 1345, 911, 746, 593 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.18 (d, *J* = 2.5 Hz, 1 H), 8.44 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.74 (d, *J* = 7.6 Hz, 2 H), 7.56 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 8.9 Hz, 2 H), 7.42–7.37 (m, 4 H), 7.30–7.22 (m, 2 H), 5.74 (s, 1 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 176.1, 158.9, 153.5, 144.8, 144.1, 141.5, 139.3, 132.5, 129.5, 128.7, 128.5, 128.2, 127.93, 127.9, 127.2, 123.8, 123.7, 123.4, 122.8, 120.0, 119.9, 45.1.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{14}ClNNaO_4$: 438.0504; found: 438.0501.

3-(3-Chloro-2-phenyl-1*H*-inden-1-yl)-6-methyl-4*H*-chromen-4-one (6bc)

Yield: 49.6 mg (75%, reaction time = 2 h); white solid; mp 140–142 °C.

IR ($CHCl_3$): 3057, 2924, 2853, 1641, 1622, 1483, 1319, 1160, 910, 748, 695 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.76 (d, *J* = 6.9 Hz, 2 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.49–7.48 (m, 1 H), 7.42–7.35 (m, 4 H), 7.29 (s, 1 H), 7.27–7.23 (m, 2 H), 7.22–7.19 (m, 1 H), 5.81 (s, 1 H), 2.46 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.5, 154.5, 153.1, 145.1, 141.4, 140.0, 135.2, 134.9, 132.8, 128.9, 128.61, 128.6, 128.0, 127.5, 127.0, 125.2, 123.52, 123.5, 122.4, 119.6, 117.9, 45.3, 20.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{17}ClNaO_2$: 407.0809; found: 407.0811.

3-(3-Chloro-2-phenyl-1*H*-inden-1-yl)-6-fluoro-4*H*-chromen-4-one (6bd)

Yield: 50.7 mg (76%, reaction time = 1 h); white solid; mp 183–186 °C.

IR ($CHCl_3$): 3057, 2922, 2850, 1635, 1617, 1476, 1265, 1129, 817, 725, 509 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (dd, *J* = 7.9, 2.4 Hz, 1 H), 7.74 (d, *J* = 7.4 Hz, 2 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 7.4 Hz, 1 H), 7.41–7.35 (m, 3 H), 7.34–7.31 (m, 3 H), 7.28–7.22 (m, 2 H), 5.76 (s, 1 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 176.8, 159.6 (d, $^1J_{C-F}$ = 247.3 Hz), 153.4, 152.5, 144.8, 141.4, 139.7, 132.7, 129.1, 128.6 (d, $^3J_{C-F}$ = 6.3 Hz), 128.1, 127.7, 127.1, 124.91, 124.9, 123.5, 122.1 (d, $^3J_{C-F}$ = 5.5 Hz), 121.9, 120.3 (d, $^3J_{C-F}$ = 8.1 Hz), 119.7, 110.7 (d, $^2J_{C-F}$ = 23.6 Hz), 45.2.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.8.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{14}ClFNaO_2$: 411.0559; found: 411.0551.

6-Bromo-3-(3-chloro-2-phenyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6be)

Yield: 52.6 mg (68%, reaction time = 1.5 h); white solid; mp 88–90 °C.

IR ($CHCl_3$): 3066, 2925, 1641, 1604, 1461, 1312, 1266, 1146, 908, 732, 697, 595 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.43 (s, 1 H), 7.75 (d, *J* = 7.7 Hz, 2 H), 7.67 (dd, *J* = 8.7, 1.7 Hz, 1 H), 7.55 (d, *J* = 7.5 Hz, 1 H), 7.47 (d, *J* = 7.4 Hz, 1 H), 7.41–7.36 (m, 3 H), 7.31–7.28 (m, 2 H), 7.24–7.23 (m, 1 H), 7.18 (d, *J* = 8.8 Hz, 1 H), 5.76 (s, 1 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 176.1, 154.9, 153.3, 144.6, 141.4, 139.6, 136.6, 132.6, 129.1, 128.6, 128.5, 128.1, 127.7, 127.1, 125.0, 123.4, 122.9, 120.0, 119.7, 118.6, 45.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{15}BrClO_2$: 448.9938; found: 448.9936.

3-(3-Chloro-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-4*H*-chromen-4-one (6bf)

Yield: 64.5 mg (94%, reaction time = 1.5 h); white solid; mp 221–224 °C.

IR ($CHCl_3$): 2921, 2856, 1633, 1610, 1466, 1354, 1164, 817, 601 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 7.8 Hz, 1 H), 7.66–7.60 (m, 3 H), 7.44–7.39 (m, 2 H), 7.32–7.29 (m, 3 H), 7.19–7.16 (m, 3 H), 5.74 (s, 1 H), 2.34 (s, 3 H), 2.32 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.6, 156.2, 153.3, 145.1, 139.0, 138.8, 137.8, 137.0, 133.6, 130.0, 129.3, 128.4, 128.3, 126.0, 125.2, 124.3, 123.8, 123.0, 119.2, 118.1, 44.9, 21.5, 21.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{20}ClO_2$: 399.1146; found: 399.1145.

3-(3-Chloro-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-6-methyl-4*H*-chromen-4-one (6bg)

Yield: 65.3 mg (92%, reaction time = 1 h); white solid; mp 233–236 °C.

IR ($CHCl_3$): 2920, 2881, 1642, 1624, 1509, 1483, 1320, 1167, 818, 726, 508 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 7.43–7.39 (m, 2 H), 7.31–7.29 (m, 2 H), 7.18 (dd, *J* = 14.9, 8.4 Hz, 4 H), 5.75 (s, 1 H), 2.47 (s, 3 H), 2.34 (s, 3 H), 2.32 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.6, 154.5, 153.1, 145.2, 138.9, 138.8, 137.7, 136.9, 135.1, 134.8, 130.0, 129.2, 128.4, 128.2, 128.1, 125.2, 124.2, 123.5, 122.7, 119.1, 117.8, 44.9, 21.5, 21.2, 20.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}ClO_2$: 413.1303; found: 413.1308.

3-(3-Chloro-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-6-fluoro-4*H*-chromen-4-one (6bh)

Yield: 43.7 mg (61%, reaction time = 2.5 h); white solid; mp 155–158 °C.

IR ($CHCl_3$): 2912, 1636, 1626, 1613, 1478, 1326, 964, 816, 725, 603, 508 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, *J* = 8.1, 2.6 Hz, 1 H), 7.63 (d, *J* = 7.1 Hz, 2 H), 7.40 (d, *J* = 7.3 Hz, 1 H), 7.37–7.29 (m, 3 H), 7.28 (s, 1 H), 7.19–7.16 (m, 3 H), 5.70 (s, 1 H), 2.34 (s, 3 H), 2.32 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.9, 159.5 (d, $^1J_{C\text{-}F}$ = 247.5 Hz), 153.5, 152.5, 144.9, 139.0, 138.6, 137.9, 137.1, 129.9, 129.3, 128.4, 128.36, 124.9 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 124.2, 122.5, 122.0, 121.8, 120.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 119.3, 110.8 (d, $^2J_{C\text{-}F}$ = 23.8 Hz), 44.9, 21.5, 21.2.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}ClFO_2$: 417.1052; found: 417.1054.

6-Bromo-3-(3-chloro-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-4*H*-chromen-4-one (6bi)

Yield: 62.5 mg (76%, reaction time = 1.5 h); white solid; mp 218–220 °C.

IR ($CHCl_3$): 2920, 1642, 1604, 1462, 1437, 1335, 1313, 1267, 819, 733, 598 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 2.5 Hz, 1 H), 7.69 (dd, *J* = 8.9, 2.4 Hz, 1 H), 7.62 (d, *J* = 8.2 Hz, 2 H), 7.40 (d, *J* = 7.7 Hz, 1 H), 7.31 (s, 1 H), 7.26 (s, 1 H), 7.22–7.16 (m, 4 H), 5.69 (s, 1 H), 2.34 (s, 3 H), 2.32 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.3, 155.0, 153.4, 144.8, 139.0, 138.5, 137.9, 137.1, 136.6, 129.9, 129.4, 128.6, 128.43, 128.4, 125.1, 124.2, 123.3, 120.1, 119.3, 118.6, 44.9, 21.5, 21.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}BrClO_2$: 477.0251; found: 477.0251.

3-(3-Chloro-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-6-nitro-4*H*-chromen-4-one (6bj)

Yield: 50.4 mg (66%, reaction time = 1.5 h); white solid; mp 230–232 °C.

IR ($CHCl_3$): 2925, 2857, 1641, 1629, 1529, 1464, 1341, 1263, 814, 690, 593 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (d, *J* = 2.6 Hz, 1 H), 8.43 (dd, *J* = 6.5, 2.9 Hz, 1 H), 7.62 (d, *J* = 8.1 Hz, 2 H), 7.46 (d, *J* = 9.2 Hz, 1 H), 7.40 (d, *J* = 7.7 Hz, 1 H), 7.37 (s, 1 H), 7.27 (s, 1 H), 7.21–7.17 (m, 3 H), 5.68 (s, 1 H), 2.35 (s, 3 H), 2.33 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.3, 159.0, 153.5, 144.7, 144.3, 140.0, 138.12, 138.1, 137.3, 129.7, 129.4, 128.8, 128.6, 128.3, 127.9, 124.2, 123.8, 122.9, 119.9, 119.4, 44.8, 21.5, 21.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}ClNO_4$: 444.0997; found: 444.0995.

3-(3-Chloro-2-phenyl-1*H*-inden-1-yl)-4*H*-benzo[*h*]chromen-4-one (6bk)

Yield: 69.5 mg (96%, reaction time = 2.5 h); white solid; mp 80–84 °C.

IR ($CHCl_3$): 3061, 2925, 2850, 1642, 1462, 1400, 1265, 1156, 698, 583 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (dd, *J* = 8.5, 4.5 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 1 H), 7.81 (d, *J* = 7.6 Hz, 2 H), 7.77 (d, *J* = 8.7 Hz, 1 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.58–7.52 (m, 4 H), 7.41–7.36 (m, 3 H), 7.27–7.26 (m, 1 H), 7.24–7.22 (m, 1 H), 5.87 (s, 1 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.2, 153.8, 152.3, 144.9, 141.5, 139.9, 135.7, 134.9, 132.8, 129.4, 129.0, 128.6, 128.03, 128.0, 127.6, 127.13, 127.1, 125.4, 124.2, 123.9, 123.6, 122.1, 120.8, 120.1, 119.7, 45.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{18}ClO_2$: 421.0990; found: 421.0985.

3-(3-Chloro-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-4*H*-benzo[*h*]-chromen-4-one (6bl)

Yield: 58.7 mg (76%, reaction time = 1 h); white solid; mp 223–226 °C.

IR ($CHCl_3$): 2983, 2928, 2850, 1637, 1625, 1444, 1415, 1374, 1241, 1047, 814, 639 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (t, *J* = 8.5 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 1 H), 7.77 (d, *J* = 78.8 Hz, 1 H), 7.69 (d, *J* = 8.2 Hz, 2 H), 7.67–7.62 (m, 1 H), 7.56 (dt, *J* = 7.1, 0.9 Hz, 1 H), 7.50 (s, 1 H), 7.42 (d, *J* = 7.7 Hz, 1 H), 7.35 (s, 1 H), 7.20–7.17 (m, 3 H), 5.81 (s, 1 H), 2.34 (s, 3 H), 2.30 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.3, 153.8, 152.4, 145.1, 139.0, 138.7, 137.8, 137.0, 135.7, 130.0, 129.33, 129.3, 128.4, 128.3, 128.0, 127.1, 125.4, 124.5, 124.3, 123.9, 122.1, 120.9, 120.1, 119.2, 45.0, 21.5, 21.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{22}ClO_2$: 449.1303; found: 449.1297.

3-(3-Chloro-6-methoxy-2-phenyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6bm)

Yield: 65.5 mg (95%, reaction time = 7 h); white solid; mp 83–86 °C.

IR ($CHCl_3$): 3003, 2955, 2833, 1638, 1622, 1484, 1320, 1285, 1031, 817, 695, 609 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 6.7 Hz, 1 H), 7.74 (d, *J* = 7.3 Hz, 2 H), 7.61 (dt, *J* = 7.7, 1.6 Hz, 1 H), 7.44–7.41 (m, 2 H), 7.39–7.34 (m, 3 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 7.25–7.22 (m, 1 H), 7.08 (d, *J* = 1.6 Hz, 1 H), 6.93 (dd, *J* = 8.4, 2.2 Hz, 1 H), 5.76 (s, 1 H), 3.78 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.7, 159.8, 156.4, 153.6, 147.0, 137.8, 134.6, 133.8, 133.2, 128.8, 127.8, 126.1, 125.4, 124.0, 123.0, 120.5, 118.3, 113.7, 109.8, 55.8, 45.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{17}ClNaO_3$: 423.0758; found: 423.0754.

3-(3-Chloro-6-methoxy-2-phenyl-1*H*-inden-1-yl)-6-methyl-4*H*-chromen-4-one (6bn)

Yield: 59.2 mg (83%, reaction time = 6 h); white solid; mp 93–95 °C.

IR ($CHCl_3$): 3006, 2925, 2833, 1639, 1618, 1444, 1285, 1032, 817, 695, 543 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1 H), 7.73 (d, *J* = 7.5 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.35 (t, *J* = 7.9 Hz, 2 H), 7.32 (s, 1 H), 7.24 (d, *J* = 7.4 Hz, 1 H), 7.21 (d, *J* = 8.5 Hz, 1 H), 7.07 (d, *J* = 1.6 Hz, 1 H), 6.92 (dd, *J* = 8.4, 2.3 Hz, 1 H), 5.76 (s, 1 H), 3.78 (s, 3 H), 2.46 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.5, 159.6, 154.5, 153.3, 147.0, 137.7, 135.2, 134.9, 134.4, 133.0, 128.5, 128.3, 127.6, 125.2, 123.5, 122.6, 120.3, 117.9, 113.6, 109.5, 55.6, 45.1, 20.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{19}ClNaO_3$: 437.0915; found: 437.0902.

3-(3-Chloro-6-methoxy-2-phenyl-1*H*-inden-1-yl)-6-fluoro-4*H*-chromen-4-one (6bo)

Yield: 68.4 mg (95%, reaction time = 6 h); white solid; mp 165–168 °C.

IR ($CHCl_3$): 3067, 2925, 2844, 1634, 1612, 1479, 1454, 1286, 1029, 829, 688, 558 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (dd, *J* = 8.4, 2.2 Hz, 1 H), 7.72 (d, *J* = 7.5 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 1 H), 7.38–7.32 (m, 5 H), 7.24–7.22 (m, 1 H), 7.06 (s, 1 H), 6.93 (dd, *J* = 8.4, 2.0 Hz, 1 H), 5.72 (s, 1 H), 3.78 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.8, 159.6, 159.5 (d, $^1J_{C-F}$ = 247.3 Hz), 153.6, 152.5, 146.6, 137.4, 134.4, 132.9, 128.8, 128.5 (d, $^2J_{C-F}$ = 27.8 Hz), 127.7, 124.9, 122.3, 122.1, 121.8, 120.4, 120.3 (d, $^3J_{C-F}$ = 8.3 Hz), 113.6, 110.7 (d, $^2J_{C-F}$ = 23.9 Hz), 109.6, 55.6, 45.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.8.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{16}ClFNaO_3$: 441.0664; found: 441.0657.

3-(3-Chloro-2-ethyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6bp)

Yield: 51.6 mg (93%, reaction time = 4 h); white semisolid.

IR ($CHCl_3$): 2964, 2927, 2856, 1643, 1611, 1466, 1349, 1143, 724, 670 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 7.8 Hz, 1 H), 7.67 (dt, *J* = 7.7, 1.7 Hz, 1 H), 7.47–7.39 (m, 3 H), 7.36–7.31 (m, 3 H), 7.18 (dt, *J* = 6.9, 1.2 Hz, 1 H), 5.18 (s, 1 H), 2.74 (sextet, *J* = 7.5 Hz, 1 H), 2.20 (sextet, *J* = 7.4 Hz, 1 H), 1.14 (t, *J* = 7.5 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.3, 156.4, 152.9, 145.8, 144.8, 141.7, 133.7, 127.8, 127.3, 126.0, 126.0, 125.3, 123.8, 123.3, 122.3, 118.8, 118.1, 44.5, 20.0, 13.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{15}ClNaO_2$: 345.0653; found: 345.0655.

3-(3-Chloro-2-ethyl-1*H*-inden-1-yl)-6-fluoro-4*H*-chromen-4-one (6bq)

Yield: 48.7 mg (83%, reaction time = 3 h); white solid; mp 121–123 °C.

IR ($CHCl_3$): 3071, 2970, 2934, 1646, 1479, 1319, 1264, 1175, 960, 824, 722, 600, 555 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 6.0 Hz, 1 H), 7.45–7.37 (m, 3 H), 7.36–7.31 (m, 3 H), 7.18 (dt, *J* = 7.5, 1.0 Hz, 1 H), 5.15 (s, 1 H), 2.74 (sextet, *J* = 7.1 Hz, 1 H), 2.19 (sextet, *J* = 7.4 Hz, 1 H), 1.14 (t, *J* = 7.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.6, 159.7 (d, $^1J_{C-F}$ = 247.2 Hz), 153.1, 152.6, 145.5, 144.5, 141.6, 128.0, 127.4, 126.0, 124.9 (d, $^3J_{C-F}$ = 7.3 Hz), 123.2, 122.1, 121.8 (d, $^3J_{C-F}$ = 6.9 Hz), 120.3 (d, $^3J_{C-F}$ = 8.1 Hz), 118.8, 110.8 (d, $^2J_{C-F}$ = 23.7 Hz), 44.6, 20.0, 13.2.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{14}ClFNaO_2$: 363.0559; found: 363.0556.

3-(2-Butyl-3-chloro-1*H*-inden-1-yl)-4*H*-chromen-4-one (6br)

Yield: 50.7 mg (84%, reaction time = 5 h); pale yellow oil.

IR ($CHCl_3$): 3068, 2929, 2858, 1647, 1480, 1318, 1157, 822, 723, 600 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 7.5 Hz, 1 H), 7.69–7.66 (m, 1 H), 7.46–7.39 (m, 4 H), 7.35–7.33 (m, 2 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 5.16 (s, 1 H), 2.71 (sextet, *J* = 7.9 Hz, 1 H), 2.17 (septet, *J* = 5.5 Hz, 1 H), 1.56–1.46 (m, 2 H), 1.37–1.28 (m, 2 H), 0.89 (t, *J* = 7.3 Hz, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.3, 156.4, 152.9, 145.0, 144.5, 141.6, 133.7, 128.5, 127.3, 126.1, 126.0, 125.3, 123.9, 123.3, 122.4, 118.8, 118.2, 44.9, 30.8, 26.4, 22.5, 13.8.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{19}ClNaO_2$: 373.0966; found: 373.0970.

3-(2-Butyl-3-chloro-1*H*-inden-1-yl)-6-fluoro-4*H*-chromen-4-one (6bs)

Yield: 50.8 mg (80%, reaction time = 6 h); pale yellow oil.

IR ($CHCl_3$): 3067, 2932, 2857, 1645, 1481, 1459, 1315, 1159, 817, 722, 600 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.2 Hz, 1 H), 7.44–7.38 (m, 3 H), 7.36–7.31 (m, 3 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 5.12 (s, 1 H), 2.71 (quint, *J* = 7.9 Hz, 1 H), 2.15 (septet, *J* = 5.6 Hz, 1 H), 1.58–1.45 (m, 2 H), 1.39–1.29 (m, 2 H), 0.89 (t, *J* = 7.3 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.6, 159.7 (d, $^1J_{C-F}$ = 247.0 Hz), 153.1, 152.6, 144.7, 144.3, 141.6, 128.7, 127.4, 126.1, 124.9 (d, $^3J_{C-F}$ = 7.6 Hz), 123.3, 122.1, 121.8 (d, $^4J_{C-F}$ = 4.6 Hz), 120.3 (d, $^3J_{C-F}$ = 8.1 Hz), 118.8, 110.8 (d, $^2J_{C-F}$ = 23.7 Hz), 44.9, 30.8, 26.4, 22.5, 13.8.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{18}ClFNaO_2$: 391.0872; found: 391.0868.

3-(2-Aryl-3-bromo-1*H*-inden-1-yl)-4*H*-chromen-4-ones 6ca–6cr; General Procedure

Compounds **6ca–6cr** were prepared by following a similar procedure as described for compounds **6aa–6ah**, using BBr_3 (2.5 equiv) instead of $BF_3{\cdot}OEt_2$ and 0.172 mmol each of **3** and **4**. In the case of **6cr**, 3.5 equivalents of BBr_3 were used.

3-(3-Bromo-2-phenyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6ca)

Yield: 60.7 mg (85%, reaction time = 5.5 h); white solid; mp 150–153 °C.

IR ($CHCl_3$): 2915, 2857, 1631, 1613, 1465, 1395, 1351, 909, 816, 592, 534 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.29 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.77–7.75 (m, 2 H), 7.61 (ddd, *J* = 7.0, 5.1, 1.8 Hz, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 7.5 Hz, 1 H), 7.42–7.36 (m, 4 H), 7.33 (s, 1 H), 7.31–7.28 (m, 2 H), 7.23 (dt, *J* = 7.4, 1.1 Hz, 1 H), 5.76 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 177.3, 156.2, 153.2, 145.2, 143.7, 142.7, 133.6, 133.5, 128.7, 128.5, 128.1, 127.6, 127.0, 125.9, 125.2, 123.8, 123.4, 122.4, 120.9, 118.8, 118.1, 46.6.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{15}BrNaO_2$: 437.0148; found: 437.0152.

3-(3-Bromo-2-phenyl-1*H*-inden-1-yl)-6-methyl-4*H*-chromen-4-one (6cb)

Yield: 59 mg (80%, reaction time = 5 h); white solid; mp 172–175 °C.

IR ($CHCl_3$): 3057, 2926, 1641, 1622, 1574, 1483, 1243, 1046, 807, 696, 604 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.08 (s, 1 H), 7.76 (d, *J* = 7.4 Hz, 2 H), 7.53 (d, *J* = 7.6 Hz, 1 H), 7.46 (d, *J* = 7.5 Hz, 1 H), 7.42–7.35 (m, 4 H), 7.30–7.27 (m, 2 H), 7.24–7.18 (m, 2 H), 5.77 (s, 1 H), 2.45 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 177.4, 154.5, 153.1, 145.2, 143.7, 142.6, 135.2, 134.9, 133.5, 128.7, 128.5, 128.1, 127.6, 127.0, 125.2, 123.44, 123.4, 122.2, 120.9, 118.7, 117.8, 46.6, 20.9.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{25}H_{17}BrNaO_2$: 451.0304; found: 451.0304.

6-Bromo-3-(3-bromo-2-phenyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6cc)

Yield: 72.2 mg (85%, reaction time = 5.5 h); white solid; mp 110–112 °C.

IR ($CHCl_3$): 3064, 2925, 1641, 1620, 1483, 1320, 1160, 935, 746, 696, 604 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 2.3 Hz, 1 H), 7.75 (s, 1 H), 7.73 (s, 1 H), 7.69 (dd, *J* = 8.9, 2.4 Hz, 1 H), 7.53 (d, *J* = 7.6 Hz, 1 H), 7.44–7.42 (m, 1 H), 7.40–7.36 (m, 3 H), 7.33–7.29 (m, 2 H), 7.23–7.19 (m, 2 H), 5.72 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.0, 154.9, 153.3, 144.8, 143.4, 142.6, 136.6, 133.3, 128.7, 128.5, 128.2, 127.7, 127.0, 125.0, 123.3, 122.7, 120.9, 120.0, 119.0, 118.6, 46.5.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{14}Br_2NaO_2$: 514.9253; found: 514.9248.

3-(3-Bromo-2-phenyl-1*H*-inden-1-yl)-6-fluoro-4*H*-chromen-4-one (6cd)

Yield: 61.1 mg (82%, reaction time = 3.5 h); white solid; mp 190–193 °C.

IR ($CHCl_3$): 3064, 2923, 2850, 1637, 1580, 1478, 1458, 1264, 1129, 939, 828, 731, 693, 594 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 7.9, 2.5 Hz, 1 H), 7.75 (d, *J* = 7.6 Hz, 2 H), 7.53 (d, *J* = 7.6 Hz, 1 H), 7.46–7.42 (m, 1 H), 7.40–7.36 (m, 3 H), 7.34–7.29 (m, 4 H), 7.26–7.22 (m, 1 H), 5.73 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.6, 159.5 (d, $^1J_{C-F}$ = 247.3 Hz), 153.4, 152.4, 144.9, 143.5, 142.7, 133.4, 128.6 (d, $^2J_{C-F}$ = 15.4 Hz), 128.2, 127.7, 127.1, 124.9 (d, $^3J_{C-F}$ = 7.1 Hz), 123.4, 122.1, 121.9, 121.85, 121.0, 120.3 (d, $^3J_{C-F}$ = 8.0 Hz), 119.0, 110.7 (d, $^2J_{C-F}$ = 23.8 Hz), 46.5.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.8.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{15}BrFO_2$: 435.0216; found: 435.0218.

3-(3-Bromo-2-phenyl-1*H*-inden-1-yl)-6-nitro-4*H*-chromen-4-one (6ce)

Yield: 64.1 mg (81%, reaction time = 3.5 h); white solid; mp 180–184 °C.

IR ($CHCl_3$): 3080, 2924, 2857, 1649, 1628, 1529, 1465, 1345, 1321, 1262, 746, 696, 592 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.16 (d, *J* = 2.6 Hz, 1 H), 8.44 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.74 (d, *J* = 7.5 Hz, 2 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.48–7.44 (m, 2 H), 7.42–7.37 (m, 4 H), 7.32–7.27 (d, *J* = 7.4 Hz, 1 H), 7.25–7.23 (m, 1 H), 5.71 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.0, 158.9, 153.5, 144.8, 144.4, 143.0, 142.7, 133.2, 128.7, 128.6, 128.3, 128.0, 127.9, 127.2, 123.74, 123.7, 123.3, 122.8, 121.2, 119.9, 119.4, 46.4.

HRMS (ESI-TOF): *m*/*z* $[M + K]^+$ calcd for $C_{24}H_{14}BrKNO_4$: 497.9738; found: 497.9740.

3-(3-Bromo-2-phenyl-1*H*-inden-1-yl)-4*H*-benzo[*h*]chromen-4-one (6cf)

Yield: 65.6 mg (82%, reaction time = 8 h); white solid; mp 68–70 °C.

IR ($CHCl_3$): 3065, 2979, 2928, 1642, 1462, 1442, 1379, 1254, 1046, 914, 698, 570 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (t, *J* = 8.8 Hz, 2 H), 7.87 (d, *J* = 8.2 Hz, 1 H), 7.81 (d, *J* = 7.7 Hz, 2 H), 7.75 (d, *J* = 8.8 Hz, 1 H), 7.64 (t, *J* = 7.8 Hz, 1 H), 7.57–7.52 (m, 4 H), 7.42–7.36 (m, 3 H), 7.29–7.27 (m, 1 H), 7.23–7.22 (m, 1 H), 5.84 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 177.1, 153.7, 152.3, 145.1, 143.6, 142.7, 135.7, 133.5, 129.3, 128.7, 128.6, 128.2, 128.0, 127.7, 127.1, 127.0, 125.4, 124.0, 123.8, 123.5, 122.1, 121.0, 120.8, 120.1, 118.9, 46.7.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{17}BrNaO_2$: 489.0287; found: 489.0286.

3-(3-Bromo-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-4*H*-benzo[*h*]-chromen-4-one (6cg)

Yield: 71.3 mg (84%, reaction time = 6.5 h); white solid; mp 172–174 °C.

IR ($CHCl_3$): 2985, 2938, 1642, 1447, 1374, 1243, 1048, 914, 738, 609 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.24 (dd, *J* = 8.1, 2.3 Hz, 2 H), 7.87 (d, *J* = 8.1 Hz, 1 H), 7.76 (d, *J* = 8.8 Hz, 1 H), 7.69 (d, *J* = 8.3 Hz, 2 H), 7.64 (dt, *J* = 7.3, 1.3 Hz, 1 H), 7.56 (dt, *J* = 7.6, 1.1 Hz, 1 H), 7.51 (s, 1 H), 7.40 (d, *J* = 7.7 Hz, 1 H), 7.32 (s, 1 H), 7.20–7.16 (m, 3 H), 5.79 (s, 1 H), 2.35 (s, 3 H), 2.29 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 177.3, 153.8, 152.4, 145.3, 142.4, 140.2, 138.0, 137.0, 135.7, 130.7, 129.3, 129.27, 128.6, 128.3, 128.0, 127.1, 125.4, 124.3, 124.2, 123.9, 122.1, 120.9, 120.5, 120.1, 118.1, 46.3, 21.4, 21.2.

HRMS (ESI-TOF): *m*/*z* [M + K]$^+$ calcd for $C_{30}H_{21}BrKO_2$: 531.0357; found: 531.0353.

2-(3-Bromo-2-phenyl-1*H*-inden-1-yl)-1*H*-benzo[*f*]chromen-1-one (6ch)

Yield: 70.4 mg (88%, reaction time = 2.5 h); white solid; mp 88–90 °C.

IR ($CHCl_3$): 3064, 2981, 2925, 1642, 1461, 1442, 1400, 1244, 1046, 792, 698, 575 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (dd, *J* = 8.1, 2.5 Hz, 2 H), 7.85–7.81 (m, 3 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.61 (dt, *J* = 7.5, 1.0 Hz, 1 H), 7.56–7.50 (m, 4 H), 7.42–7.37 (m, 3 H), 7.28–7.27 (m, 1 H), 7.23 (dt, *J* = 7.5, 0.8 Hz, 1 H), 5.84 (s, 1 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.1, 153.7, 152.3, 145.1, 143.6, 142.6, 135.6, 133.5, 129.3, 128.7, 128.5, 128.1, 127.9, 127.6, 127.1, 127.0, 125.4, 123.9, 123.8, 123.4, 122.0, 120.9, 120.7, 120.0, 118.9, 46.6.

HRMS (ESI-TOF): *m*/*z* [M + K]$^+$ calcd for $C_{28}H_{17}BrKO_2$: 503.0043; found: 503.0038.

3-(3-Bromo-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-4*H*-chromen-4-one (6ci)

Yield: 61 mg (80%, reaction time = 5.5 h); white solid; mp 184–186 °C.

IR ($CHCl_3$): 3054, 2918, 2854, 1631, 1465, 1393, 1351, 907, 816, 710, 590 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 7.0 Hz, 1 H), 7.65–7.62 (m, 3 H), 7.43–7.38 (m, 2 H), 7.32–7.27 (m, 3 H), 7.19–7.16 (m, 3 H), 5.70 (s, 1 H), 2.34 (s, 3 H), 2.31 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.5, 156.2, 153.3, 145.3, 142.5, 140.2, 137.9, 137.0, 133.6, 130.7, 129.2, 128.6, 128.3, 126.0, 125.2, 124.1, 123.9, 122.8, 120.5, 118.12, 118.1, 46.3, 21.5, 21.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{19}BrNaO_2$: 467.0443; found: 467.0444.

3-(3-Bromo-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-6-methyl-4*H*-chromen-4-one (6cj)

Yield: 65.3 mg (83%, reaction time = 6 h); white solid; mp 228–230 °C.

IR ($CHCl_3$): 3027, 2921, 2854, 1641, 1621, 1484, 1320, 1166, 909, 816, 787, 594 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.64 (d, *J* = 8.2 Hz, 2 H), 7.43–7.37 (m, 2 H), 7.29–7.27 (m, 2 H), 7.21–7.15 (m, 4 H), 5.71 (s, 1 H), 2.46 (s, 3 H), 2.34 (s, 3 H), 2.31 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.5, 154.5, 153.2, 145.4, 142.5, 140.2, 137.9, 136.9, 135.1, 134.8, 130.7, 129.2, 128.5, 128.2, 125.2, 124.1, 123.5, 122.5, 120.4, 118.0, 117.9, 46.3, 21.4, 21.2, 20.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}BrO_2$: 457.0798; found: 457.0799.

3-(3-Bromo-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-6-fluoro-4*H*-chromen-4-one (6ck)

Yield: 68.2 mg (86%, reaction time = 4 h); white solid; mp 250–252 °C.

IR ($CHCl_3$): 3061, 2921, 2854, 1635, 1613, 1476, 1454, 1390, 1265, 1129, 817, 593 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (t, *J* = 7.5 Hz, 1 H), 7.64 (t, *J* = 7.7 Hz, 2 H), 7.42–7.33 (m, 4 H), 7.27–7.26 (m, 1 H), 7.22–7.16 (m, 3 H), 5.68 (s, 1 H), 2.36–2.31 (m, 6 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 176.8, 159.6 (d, $^1J_{C\text{-}F}$ = 248.6 Hz), 153.5, 152.5, 145.1, 142.3, 140.2, 138.0, 137.0, 130.6, 129.3, 128.5, 128.4, 124.9 (d, $^3J_{C\text{-}F}$ = 7.3 Hz), 124.1, 122.3, 121.9 (d, $^3J_{C\text{-}F}$ = 10.2 Hz), 120.6, 120.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 118.2, 110.7 (d, $^2J_{C\text{-}F}$ = 23.7 Hz), 46.2, 21.5, 21.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}BrFO_2$: 461.0547; found: 461.0552.

6-Bromo-3-(3-bromo-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-4*H*-chromen-4-one (6cl)

Yield: 64.7 mg (72%, reaction time = 6 h); white solid; mp 184–186 °C.

IR ($CHCl_3$): 2921, 2854, 1641, 1621, 1483, 1432, 1320, 1166, 909, 817, 787, 594 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 2.2 Hz, 1 H), 7.68 (dd, *J* = 8.9, 2.4 Hz, 1 H), 7.62 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 7.9 Hz, 1 H), 7.31 (s, 1 H), 7.24 (s, 1 H), 7.21–7.16 (m, 4 H), 5.66 (s, 1 H), 2.35 (s, 3 H), 2.32 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 176.2, 155.0, 153.4, 145.0, 142.2, 140.2, 138.0, 137.1, 136.6, 130.6, 129.3, 128.6, 128.5, 128.4, 125.1, 124.1, 123.1, 120.6, 120.1, 118.6, 118.3, 46.2, 21.5, 21.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}Br_2O_2$: 520.9746; found: 520.9739.

3-(3-Bromo-2-(4-bromophenyl)-1*H*-inden-1-yl)-6-methyl-4*H*-chromen-4-one (6cm)

Yield: 63.8 mg (73%, reaction time = 2.5 h); white solid; mp 160–164 °C.

IR ($CHCl_3$): 1640, 1622, 1483, 1458, 1319, 1158, 910, 819, 732, 606 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (s, 1 H), 7.73 (d, *J* = 7.7 Hz, 1 H), 7.64–7.61 (m, 1 H), 7.53–7.50 (m, 2 H), 7.48 (d, *J* = 8.5 Hz, 1 H), 7.44–7.41 (m, 2 H), 7.39–7.35 (m, 2 H), 7.31–7.28 (m, 1 H), 7.25–7.19 (m, 1 H), 5.72 (s, 1 H), 2.46 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 177.2, 154.5, 153.2, 142.8, 142.6, 135.4, 135.0, 132.4, 131.7, 130.7, 130.2, 128.7, 127.7, 127.2, 125.2, 123.4, 122.3, 121.9, 121.0, 119.3, 117.9, 46.6, 20.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{16}Br_2NaO_2$: 528.9409; found: 528.9401.

3-(3-Bromo-2-ethyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6cn)

Yield: 53.7 mg (85%, reaction time = 5 h); pale yellow oil.

IR ($CHCl_3$): 2966, 2923, 1644, 1621, 1483, 1459, 1339, 1318, 1160, 1139, 935, 817, 727, 597 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 7.1 Hz, 1 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.47–7.41 (m, 2 H), 7.39–7.31 (m, 4 H), 7.17 (t, *J* = 7.1 Hz, 1 H), 5.18 (s, 1 H), 2.72 (sextet, *J* = 7.4 Hz, 1 H), 2.21 (sextet, *J* = 6.9 Hz, 1 H), 1.14 (t, *J* = 7.5 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.3, 156.3, 153.0, 149.3, 145.0, 142.8, 133.7, 128.0, 127.4, 126.0, 125.3, 123.8, 123.2, 122.2, 119.9, 118.2, 118.0, 45.5, 21.7, 13.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{15}BrNaO_2$: 389.0147; found: 389.0143.

3-(3-Bromo-2-ethyl-1*H*-inden-1-yl)-6-methyl-4*H*-chromen-4-one (6co)

Yield: 54.4 mg (83%, reaction time = 6 h); pale yellow oil.

IR ($CHCl_3$): 2965, 2927, 2871, 1644, 1621, 1483, 1459, 1318, 1160, 1045, 816, 727, 542 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1 H), 7.48 (d, *J* = 7.7 Hz, 1 H), 7.38–7.30 (m, 5 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 5.18 (s, 1 H), 2.71 (sextet, *J* = 7.3 Hz, 1 H), 2.48 (s, 3 H), 2.21 (sextet, *J* = 6.8 Hz, 1 H), 1.13 (t, *J* = 7.5 Hz, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 177.4, 154.7, 152.9, 149.5, 145.1, 142.8, 135.3, 135.0, 127.4, 126.0, 125.3, 123.5, 123.2, 121.9, 119.9, 117.9, 117.87, 45.5, 21.7, 21.0, 13.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{17}BrNaO_2$: 403.0304; found: 403.0305.

6-Bromo-3-(3-bromo-2-pentyl-1*H*-inden-1-yl)-4*H*-chromen-4-one (6cp)

Yield: 67.2 mg (80%, reaction time = 5.5 h); pale yellow oil.

IR ($CHCl_3$): 2959, 2928, 2856, 1647, 1622, 1605, 1461, 1435, 1335, 1149, 933, 818, 725, 600 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.44 (s, 1 H), 7.75 (dd, *J* = 8.9, 2.5 Hz, 1 H), 7.39–7.29 (m, 5 H), 7.17 (dt, *J* = 7.2, 1.2 Hz, 1 H), 5.12 (s, 1 H), 2.70–2.64 (m, 1 H), 2.16 (septet, *J* = 5.2 Hz, 1 H), 1.58–1.48 (m, 2 H), 1.34–1.27 (m, 4 H), 0.85 (t, *J* = 6.7 Hz, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 176.0, 155.1, 153.1, 147.8, 144.8, 142.7, 136.7, 128.7, 127.5, 126.1, 125.1, 123.2, 122.6, 120.13, 120.0, 119.0, 118.8, 45.7, 31.5, 28.4, 28.2, 22.4, 13.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{21}Br_2O_2$: 488.9883; found: 488.9883.

3-(3-Bromo-2-butyl-1*H*-inden-1-yl)-6-fluoro-4*H*-chromen-4-one (6cq)

Yield: 59.7 mg (84%, reaction time = 6 h); pale yellow oil.

IR ($CHCl_3$): 2959, 2928, 2856, 1647, 1622, 1606, 1461, 1435, 1335, 1149, 933, 725, 600 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 6.7 Hz, 1 H), 7.44–7.42 (m, 1 H), 7.41–7.39 (m, 1 H), 7.37–7.29 (m, 4 H), 7.17 (dt, *J* = 7.3, 1.4 Hz, 1 H), 5.12 (s, 1 H), 2.73–2.65 (m, 1 H), 2.16 (septet, *J* = 5.2 Hz, 1 H), 1.54–1.45 (m, 2 H), 1.39–1.30 (m, 2 H), 0.89 (t, *J* = 7.3 Hz, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 176.6, 159.7 (d, $^1J_{C-F}$ = 248.1 Hz), 153.1, 152.6, 147.8, 145.0, 142.7, 127.5, 126.1, 124.9 (d, $^3J_{C-F}$ = 7.4 Hz), 123.2, 122.0 (d, $^2J_{C-F}$ = 25.8 Hz), 121.7, 120.3 (d, $^3J_{C-F}$ = 8.0 Hz), 120.0, 118.9, 110.8 (d, $^2J_{C-F}$ = 23.7 Hz), 45.7, 30.9, 27.9, 22.5, 13.8.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.7.

HRMS (ESI-TOF): *m*/*z* [M + K]$^+$ calcd for $C_{22}H_{18}BrFKO_2$: 451.0106; found: 451.0106.

3-(3-Bromo-2-(2-bromoethyl)-1*H*-inden-1-yl)-4*H*-chromen-4-one (6cr)

Yield: 61.3 mg (80%, reaction time = 5.5 h); white semisolid.

IR ($CHCl_3$): 3077, 2925, 2857, 1639, 1610, 1479, 1463, 1317, 909, 824, 668 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 7.9 Hz, 1 H), 7.72–7.67 (m, 1 H), 7.48–7.43 (m, 3 H), 7.40–7.36 (m, 2 H), 7.31 (d, *J* = 7.2 Hz, 1 H), 7.23 (dt, *J* = 7.4, 0.9 Hz, 1 H), 5.17 (s, 1 H), 3.65–3.55 (m, 2 H), 3.25 (quint, *J* = 6.7 Hz, 1 H), 2.76 (septet, *J* = 7.3 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 177.1, 156.3, 153.4, 144.6, 144.3, 142.5, 133.9, 127.7, 126.7, 126.1, 125.5, 123.7, 123.3, 121.7, 121.3, 120.5, 118.2, 46.1, 31.7, 30.1.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{14}Br_2NaO_2$: 468.9233; found: 468.9238.

8-(2-Aryl-3-halo-1*H*-inden-1-yl)-2*H*-chromen-2-ones 8a–8f; General Procedure

Compounds **8a–8f** were prepared by following a similar procedure as described for compounds **6aa–6ah**, using BBr_3 or BCl_3 (2.5 equiv) instead of $BF_3{\cdot}OEt_2$ and 0.172 mmol each of **7** and **4**.

8-(3-Chloro-2-phenyl-1*H*-inden-1-yl)-2*H*-chromen-2-one (8a)

Yield: 60.5 mg (95%, reaction time = 4 h); white solid; mp 126–130 °C.

IR ($CHCl_3$): 2923, 2850, 1735, 1602, 1490, 1400, 1267, 1076, 918, 868, 665, 534 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.72–7.70 (m, 3 H), 7.56 (d, *J* = 7.5 Hz, 1 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.32–7.29 (m, 2 H), 7.27–7.25 (m, 2 H), 7.22–7.19 (m, 2 H), 6.96 (t, *J* = 7.0 Hz, 1 H), 6.84 (s, 1 H), 6.50 (d, *J* = 8.9 Hz, 1 H), 6.04 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.5, 152.1, 144.0, 141.9, 141.5, 133.0, 130.4, 129.1, 128.5, 128.4, 127.8, 127.6, 127.3, 127.0, 126.8, 124.6, 123.6, 119.7, 119.1, 116.5, 47.8.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{15}ClNaO_2$: 393.0653; found: 393.0647.

8-(3-Chloro-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-2*H*-chromen-2-one (8b)

Yield: 63.8 mg (93%, reaction time = 4.5 h); white solid; mp 139–142 °C.

IR ($CHCl_3$): 2854, 1734, 1602, 1490, 1400, 1266, 1076, 914, 699, 578, 538 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.8 Hz, 1 H), 7.62 (d, *J* = 7.8 Hz, 2 H), 7.43 (d, *J* = 7.7 Hz, 1 H), 7.24 (d, *J* = 7.5 Hz, 1 H), 7.18 (d, *J* = 7.7 Hz, 1 H), 7.11 (d, *J* = 8 Hz, 2 H), 7.06 (s, 1 H), 6.95 (t, *J* = 6.8 Hz, 1 H), 6.86 (s, 1 H), 6.50 (d, *J* = 8.7 Hz, 1 H), 5.99 (s, 1 H), 2.32 (s, 3 H), 2.27 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.5, 152.0, 145.2, 143.9, 140.4, 139.4, 137.5, 136.8, 130.4, 130.2, 129.0, 128.3, 128.27, 128.25, 127.7, 126.7, 124.6, 124.3, 119.2, 119.1, 116.3, 47.3, 21.4, 21.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{20}ClO_2$: 399.1146; found: 399.1138.

8-(3-Bromo-2-phenyl-1*H*-inden-1-yl)-2*H*-chromen-2-one (8c)

Yield: 64.3 mg (90%, reaction time = 10 h); white solid; mp 110–112 °C.

IR ($CHCl_3$): 3067, 1734, 1602, 1574, 1488, 1402, 1175, 918, 621, 578 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.69 (m, 3 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.40 (t, *J* = 7.0 Hz, 1 H), 7.32–7.29 (m, 2 H), 7.25–7.19 (m, 4 H), 6.95 (t, *J* = 6.8 Hz, 1 H), 6.82 (s, 1 H), 6.47 (d, *J* = 10.4 Hz, 1 H), 6.01 (s, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.4, 152.1, 145.3, 143.9, 143.1, 133.7, 129.3, 128.7, 128.2, 127.9, 127.7, 127.0, 126.9, 126.8, 124.6, 123.5, 120.9, 119.1, 118.9, 117.0, 116.4, 49.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{15}BrNaO_2$: 437.0148; found: 437.0140.

8-(3-Bromo-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-2*H*-chromen-2-one (8d)

Yield: 67.1 mg (88%, reaction time = 11 h); white solid; mp 145–148 °C.

IR ($CHCl_3$): 2922, 1735, 1602, 1491, 1258, 1075, 733, 618 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 6.7 Hz, 1 H), 7.60 (d, *J* = 8 Hz, 2 H), 7.41 (d, *J* = 7.7 Hz, 1 H), 7.24 (d, *J* = 7.5 Hz, 1 H), 7.19 (d, *J* = 7.7 Hz, 1 H), 7.10 (d, *J* = 7.9 Hz, 2 H), 7.03 (s, 1 H), 6.96 (t, *J* = 7.0 Hz, 1 H), 6.84 (s, 1 H), 6.49 (d, *J* = 8.8 Hz, 1 H), 5.96 (s, 1 H), 2.32 (s, 3 H), 2.27 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.5, 152.0, 144.2, 143.9, 143.2, 140.6, 137.6, 136.8, 130.9, 130.5, 129.0, 128.4, 128.3, 127.5, 126.7, 124.6, 124.2, 120.5, 119.0, 118.2, 116.3, 48.7, 21.4, 21.2.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{20}BrO_2$: 443.0641; found: 443.0634.

8-(3-Chloro-2-phenyl-1*H*-inden-1-yl)-6-methyl-2*H*-chromen-2-one (8e)

Yield: 53.1 mg (79%, reaction time = 5 h); yellow solid; mp 105–108 °C.

IR ($CHCl_3$): 2924, 1732, 1625, 1606, 1583, 1429, 1295, 1110, 878, 655, 593 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.6 Hz, 2 H), 7.87 (d, *J* = 8.8 Hz, 1 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.63 (t, *J* = 7.3 Hz, 1 H), 7.57–7.54 (m, 2 H), 7.50–7.44 (m, 4 H), 6.86 (s, 1 H), 6.70 (d, *J* = 8.1 Hz, 1 H), 6.26 (s, 1 H), 2.34 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.7, 150.2, 145.2, 143.9, 141.8, 141.6, 134.3, 133.1, 131.0, 128.9, 128.5, 128.3, 127.7, 127.5, 126.9, 126.8, 123.6, 119.6, 118.9, 116.3, 47.7, 20.5.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{25}H_{17}ClNaO_2$: 407.0809; found: 407.0802.

8-(3-Bromo-6-methyl-2-(*p*-tolyl)-1*H*-inden-1-yl)-6-methyl-2*H*-chromen-2-one (8f)

Yield: 69.1 mg (88%, reaction time = 6 h); yellow solid; mp 78–80 °C.

IR ($CHCl_3$): 2922, 1732, 1623, 1606, 1459, 1395, 1286, 1156, 1106, 914, 790, 666, 614 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.1 Hz, 2 H), 7.40 (d, *J* = 7.7 Hz, 1 H), 7.30–7.25 (m, 1 H), 7.18 (d, *J* = 7.7 Hz, 1 H), 7.09 (d, *J* = 7.9 Hz, 2 H), 7.01 (d, *J* = 5.5 Hz, 2 H), 6.60 (s, 1 H), 6.48–6.42 (m, 1 H), 5.91 (s, 1 H), 2.32 (s, 3 H), 2.27 (s, 3 H), 2.11 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 160.9, 150.3, 144.4, 143.9, 140.7, 137.6, 136.8, 134.3, 131.2, 131.1, 129.0, 128.5, 128.3, 127.1, 126.9, 124.3, 120.5, 118.9, 118.2, 116.4, 48.7, 21.5, 21.2, 20.6.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{27}H_{21}BrNaO_2$: 479.0617; found: 479.0609.

2-(Hydroxymethyl)cyclohex-2-en-1-one (15)[16]

To a stirred mixture of 36% aq HCHO (0.45 mL, 5.20 mmol, 5.0 equiv) and cyclohex-2-enone (100 mg, 1.040 mmol, 1.0 equiv) was added DMAP (38 mg, 0.312 mmol, 0.3 equiv). The resulting mixture was stirred at room temperature. After consumption of the starting material (2 d), the reaction was quenched with 1.5 N HCl until pH 4. The mixture was extracted with CH_2Cl_2 (3 × 3 mL) and the combined organic layers were washed successively with sat. aq $NaHCO_3$ solution and brine. Solvents were removed through vacuum and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 3:2) to afford **15** (92 mg, 70%) as a pale yellow oil.

IR ($CHCl_3$): 2929, 2869, 1670, 1391, 1173, 1068, 910, 543 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.92 (t, *J* = 3.8 Hz, 1 H), 4.21 (s, 2 H), 2.59 (s, 1 H), 2.44–2.36 (m, 4 H), 1.99 (quint, *J* = 6.6 Hz, 2 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.6, 146.9, 138.2, 61.8, 38.1, 25.6, 22.6.

6-Oxocyclohex-1-ene-1-carbaldehyde (10e)[17]

To a stirred solution of 2-(hydroxymethyl)cyclohex-2-en-1-one (**15**; 50 mg, 0.396 mmol, 1.0 equiv) in EtOAc (3 mL) was added IBX (166 mg, 0.594 mmol, 1.5 equiv) under N_2 atmosphere. The resulting suspension was refluxed for 5 h (TLC monitoring). The reaction mixture was cooled to room temperature and filtered through a sintered glass funnel. The filter cake was washed with EtOAc (3 × 2 mL). The combined filtrate was concentrated and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 7:3) to afford **10e** (39.3 mg, 80%) as a green oil.

IR ($CHCl_3$): 2924, 2854, 1714, 1460, 1267, 1068, 822, 669 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.07 (s, 1 H), 7.81 (t, *J* = 4.1 Hz, 1 H), 2.63–2.58 (m, 2 H), 2.55–2.51 (m, 2 H), 2.07 (quint, *J* = 7.1 Hz, 2 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 197.9, 189.2, 157.8, 135.0, 38.0, 26.4, 21.8.

LRMS (ESI-TOF): *m*/*z* $[M + K]^+$ calcd for $C_7H_8KO_2$: 163.0155; found: 163.0735.

2,2-Difluoro-6-methyl-4-phenyl-2*H*-1,3,2-dioxaborinin-1-ium-2-uide (12)

To a mixture of benzoylacetone (**11**; 50 mg, 0.308 mmol, 1.0 equiv) and alkyne **4a** (55 mg, 0.308 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added $BF_3{\cdot}OEt_2$ (0.215 mL, 0.77 mmol, 2.5 equiv) at room temperature. The mixture was stirred for 7 h at which time TLC indicated consumption of **11**. The reaction was then quenched with a few drops of sat. aq $Na_2S_2O_3$ solution. The solvent was removed through vacuum and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to afford **12** (38.4 mg, 60%) as a cream-coloured solid; mp 120–123 °C.[11]

IR ($CHCl_3$): 1542, 1440, 1357, 1116, 1069, 707, 680, 575 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.6 Hz, 2 H), 7.68 (t, *J* = 7.4 Hz, 1 H), 7.52 (t, *J* = 7.7 Hz, 2 H), 6.60 (s, 1 H), 2.41 (s, 3 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 192.6, 182.8, 135.4, 131.1, 129.1, 129.0, 97.5, 24.7.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –138.6.

HRMS (ESI-TOF): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_9BF_2NaO_2$: 233.0558; found: 233.0554.

Funding Information

This work was supported by the Science and Engineering Research Board (SERB) New Delhi, Grant No. EMR/2017/000499.

Acknowledgment

A.K. thanks the Indian Institute of Technology Bombay for a research fellowship.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690881.

References

(1) For examples, see: (a) Adesanya, S. A.; Nia, R.; Martin, M.-T.; Boukamcha, N.; Montagnac, A.; Païs, M. *J. Nat. Prod.* **1999**, *62*, 1694. (b) Huang, K.-S.; Wang, Y.-H.; Li, R.-L.; Lin, M. *Phytochemistry* **2000**, *54*, 875. (c) Yu, H.; Kim, I. J.; Folk, J. E.; Tian, X.; Rothman, R. B.; Baumann, M. H.; Dersch, C. M.; Flippen-Anderson, J. L.; Parrish, D.; Jacobson, A. E.; Rice, K. C. *J. Med. Chem.* **2004**, *47*, 2624. (d) Clegg, N. J.; Paruthiyil, S.; Leitman, D. C.; Scanlan, T. S. *J. Med. Chem.* **2005**, *48*, 5989. (e) Majetich, G.; Shimkus, J. M. *J. Nat. Prod.* **2010**, *73*, 284. (f) Liedtke, A. J.; Crews, B. C.; Daniel, C. M.; Blobaum, A. L.; Kingsley, P. J.; Ghebreselasie, K.; Marnett, L. J. *J. Med. Chem.* **2012**, *55*, 2287. (g) Vilums, M.; Heuberger, J.; Heitman, L. H.; Ijzerman, A. P. *Med. Res. Rev.* **2015**, *35*, 1097.

(2) For examples, see: (a) Dyrager, C.; Möllers, L. N.; Kjäll, L. K.; Alao, J. P.; Diner, P.; Wallner, F. K.; Sunnerhagen, P.; Grøtli, M. *J. Med. Chem.* **2011**, *54*, 7427. (b) Gaspar, A.; Matos, M. J.; Garrido, J.; Uriarte, E.; Borges, F. *Chem. Rev.* **2014**, *114*, 4960. (c) Keri, R. S.; Budagumpi, S.; Pai, R. K.; Balakrishna, R. G. *Eur. J. Med. Chem.* **2014**, *78*, 340. (d) Silva, C. F. M.; Pinto, D. C. G. A.; Silva, A. M. S. *ChemMedChem.* **2016**, *11*, 2252. (e) Reis, J.; Gaspar, A.; Milhazes, N.; Borges, F. *J. Med. Chem.* **2017**, *60*, 7941. (f) Li, F.; Wu, J.-J.; Wang, J.; Yang, X.-L.; Cai, P.; Liu, Q.-H.; Kong, L.-Y.; Wang, X.-B. *Bioorg. Med. Chem.* **2017**, *25*, 3815.

(3) For examples, see: (a) Meunier, B. *Acc. Chem. Res.* **2008**, *41*, 69. (b) Decker, M. *Curr. Med. Chem.* **2011**, *18*, 1464. (c) Lödige, M.; Hiersch, L. *Int. J. Med. Chem.* **2015**, doi: 10.1155/2015/458319. (d) Bérubé, G. *Expert Opin. Drug Discovery* **2016**, *11*, 281. (e) Agarwal, D.; Gupta, R. D.; Awasthi, S. K. *Antimicrob. Agents Chemother.* **2017**, *61*, 1.

(4) For some informative reviews, see: (a) Denmark, S. E. *Compr. Org. Synth.* **1991**, *5*, 751. (b) Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429. (c) Tius, M. A. *Eur. J. Org. Chem.* **2005**, 2193. (d) Nakanishi, W.; West, F. G. *Curr. Opin. Drug Discovery Dev.* **2009**, *12*, 732. (e) Shimada, N.; Stewart, C.; Tius, M. A. *Tetrahedron* **2011**, *67*, 5851. (f) Spencer, W. T. III.; Vaidya, T.; Frontier, A. J. *Eur. J. Org. Chem.* **2013**, 3621. (g) Di Grandi, M. J. *Org. Biomol. Chem.* **2014**, *12*, 5331. (h) Wenz, D. R.; Read de Alaniz, J. *Eur. J. Org. Chem.* **2015**, 23. (i) Vinogradov, M. G.; Turova, O. V.; Zlotin, S. G. *Org. Biomol. Chem.* **2017**, *15*, 8245.

(5) For examples, see: (a) Weinreb, S. M.; Auerbach, J. *J. Am. Chem. Soc.* **1975**, *97*, 2503. (b) Kim, S.-H.; Cha, J. K. *Synthesis* **2000**, 2113. (c) Li, W.-D. Z.; Wang, Y.-Q. *Org. Lett.* **2003**, *5*, 2931. (d) He, W.; Huang, J.; Sun, X.; Frontier, A. J. *J. Am. Chem. Soc.* **2007**, *129*, 498. (e) He, W.; Huang, J.; Sun, X.; Frontier, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 300. (f) Williams, D. R.; Robinson, L. A.; Nevill, C. R.; Reddy, J. P. *Angew. Chem. Int. Ed.* **2007**, *46*, 915. (g) Bitar, A. Y.; Frontier, A. J. *Org. Lett.* **2009**, *11*, 49. (h) Bhattacharya, C.; Bonfante, P.; Deagostino, A.; Kapulnik, Y.; Larini, P.; Occhiato, E. G.; Prandi, C.; Venturello, P. *Org. Biomol. Chem.* **2009**, *7*, 3413. (i) Carlsen, P. N.; Mann, T. J.; Hoveyda, A. H.; Frontier, A. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 9334. (j) Grant, T. N.; Rieder, C. J.; West, F. G. *Chem. Commun.* **2009**, 5676. (k) Malona, J. A.; Cariou, K.; Frontier, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 7560. (l) Churruca, F.; Fousteris, M.; Ishikawa, Y.; von Wantoch Rekowski, M.; Hounsou, C.; Surrey, T.; Giannis, A. *Org. Lett.* **2010**, *12*, 2096. (m) Vaidya, T.; Eisenberg, R.; Frontier, A. J. *ChemCatChem* **2011**, *3*, 1531. (n) Magnus, P.; Freund, W. A.; Moorhead, E. J.; Rainey, T. *J. Am. Chem. Soc.* **2012**, *134*, 6140. (o) Zhou, Z.; Tius, M. A. *Angew. Chem. Int. Ed.* **2015**, *54*, 6037.

(6) (a) Alachouzos, G.; Frontier, A. J. *Angew. Chem. Int. Ed.* **2017**, *56*, 15030. (b) Alachouzos, G.; Frontier, A. J. *J. Am. Chem. Soc.* **2019**, *141*, 118. (c) Holt, C.; Alachouzos, G.; Frontier, A. J. *J. Am. Chem. Soc.* **2019**, *141*, 5461.

(7) Ghavtadze, N.; Fröhlich, R.; Bergander, K.; Würthwein, E.-U. *Synthesis* **2008**, 3397.

(8) (a) Viswanathan, G. S.; Li, C.-J. *Tetrahedron Lett.* **2002**, *43*, 1613. (b) Zhou, X.; Zhang, H.; Xie, X.; Li, Y. *J. Org. Chem.* **2008**, *73*, 3958. (c) Yeh, M.-C. P.; Lin, M.-N.; Hsu, C.-H.; Liang, C.-J. *J. Org. Chem.* **2013**, *78*, 12381. (d) Strom, K. R.; Impastato, A. C.; Moy, K. J.; Landreth, A. J.; Snyder, J. K. *Org. Lett.* **2015**, *17*, 2126.

(9) (a) Ye, S.; Gao, K.; Zhou, H.; Yang, X.; Wu, J. *Chem. Commun.* **2009**, 5406. (b) Sanz, R.; Martínez, A.; García-García, P.; Fernández-Rodríguez, M. A.; Rashid, M. A.; Rodríguez, F. *Chem. Commun.* **2010**, *46*, 7427. (c) Johansson Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062.

(10) Sultana, S.; Maezono, S. M. B.; Akhtar, M. S.; Shim, J. J.; Wee, Y. J.; Kim, S. H.; Lee, Y. R. *Adv. Synth. Catal.* **2018**, *360*, 751.

(11) CCDC 1945920 (**6ae**), CCDC 1945839 (**6bb**), CCDC 1945927 (**6bi**), CCDC 1945916 (**6bm**), CCDC 1945936 (**6cm**), CCDC 1945919 (**8e**) and CCDC 1946265 (**12**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures. See the Supporting Information (SI) for structures.

(12) (a) He, W.; Sun, X.; Frontier, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 14278. (b) Nie, J.; Zhu, H.-W.; Cui, H.-F.; Hua, M.-Q.; Ma, J.-A. *Org. Lett.* **2007**, *9*, 3053. (c) Xi, Z.-G.; Zhu, L.; Luo, S.; Cheng, J.-P. *J. Org. Chem.* **2013**, *78*, 606. (d) Zhu, L.; Xi, Z.-G.; Lv, J.; Luo, S. *Org. Lett.* **2013**, *15*, 4496. (e) Zhu, Y.-P.; Cai, Q.; Jia, F.-C.; Liu, M.-C.; Gao, Q.-H.; Meng, X.-G.; Wu, A.-X. *Tetrahedron* **2014**, *70*, 9536. (f) Carmichael, R. A.; Sophanpanichkul, P.; Chalifoux, W. A. *Org. Lett.* **2017**, *19*, 2592.

(13) During the completion and submission of our work a conceptionally similar paper appeared; see: Sultana, S.; Lee, Y. R. *Adv. Synth. Catal.* **2020**, *362*, 927.

(14) Dückert, H.; Khedkar, V.; Waldmann, H.; Kumar, K. *Chem. Eur. J.* **2011**, *17*, 5130.

(15) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796.

(16) Shairgojray, B. A.; Dar, A. A.; Bhat, B. A. *Tetrahedron Lett.* **2013**, *54*, 2391.

(17) Adary, E. M.; Chang, C.-W.; D' Auria, D. T.; Nguyen, P. M.; Polewacz, K.; Reinicke, J. A.; Seo, H.; Berger, G. O. *Tetrahedron Lett.* **2015**, *56*, 386.