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Cleavage and Reassembly of the C═O Bond of 2-Alkynylbenzaldehydes: A Metal-Free Access to Inden-1-ones

Tao Liu,[§] Tuanli Yao,* Feng Zhang,[§] Ying Ju, and Jiajing Tan*

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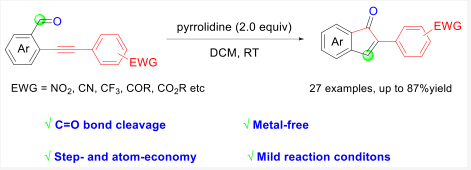
ABSTRACT: A metal-free approach to inden-1-ones from 2-alkynylbenzaldehydes mediated by pyrrolidine has been developed. The reaction proceeds under mild conditions in a step- and atom-economy process by cleaving the C═O bond and constructing new C−C as well as C═O bonds. Oxygen-18 and deuterium labeling experiments revealed an aza-Petasis−Ferrier rearrangement of an intermediate 1-amino-3-methylene-dihydroisobenzofuran.



INTRODUCTION

The indenone skeleton is ubiquitous in pharmaceutical and natural products, which exhibit various biological activities (Figure 1).[1] Indenone derivatives are also versatile synthetic precursors of many important aromatic and heterocyclic compounds.[2] A variety of methodologies for indenone synthesis have been reported, including dehydrohalogenation or dehydroxylation of the corresponding indanones,[3] cyclization of 1,3-diarylpropynones,[4] and aldol condensation of substituted *ortho*-aroylpropiophenones.[5] Although 2,3-disubstituted indenones could be prepared by transition-metal-catalyzed annulation of functionalized arenes with alkynes,[6] the intermolecular annulation often displayed a low regioselectivity when using unsymmetrical internal alkynes. Nevertheless, the Dong group recently developed an elegant and straightforward method to construct indenones from aryl iodides and unsaturated carboxylic anhydrides via Pd/norbornene (NBE) catalysis, which proved to be superior to previous methods in terms of regioselectivity and was successfully applied to the synthesis of pauciflorol F and acredinone A.[7]

During the past several years, 2-alkynyl aldehydes have emerged as a valuable synthon for the preparation of carbo- or heterocycles (Scheme 1).[8] In most of the previously reported reactions, a transition metal catalyst was indispensable to activate the alkyne motif and/or the aldehyde group. With regard to the synthesis of indenones from 2-alkynyl aldehydes, there were only two examples of the formation of indenone chelated iron complexes via a photolytic reaction of 2-alkynylbenzaldehydes and $Fe(CO)_5$.[9a] Moreover, a gold-catalyzed cyclization of cyclic 2-alkynylaldehyde derived acetals for the synthesis of indenone derivatives has been reported by Yamada and Sajiki.[9b] Despite the fact that the metal-free synthesis of 3-amino-1-indanones and 3-amino-1-indenones have been achieved by Wong[10a] and Verma,[10b] respectively, the direct cyclization of *ortho*-alkynyl aldehydes to generate indenones under metal-free conditions, to the best of our knowledge, has not yet been realized.[11]

Recently, we disclosed a base-catalyzed cyclization of *N*-*tert*-butyl-2-(1-alkynyl)benzaldimines for the synthesis of 3-amino-1-indenones, which was proposed to proceed through a cascade of 5-*exo*-*dig* cyclization of *N*-*tert*-butyl-2-(1-alkynyl)benzaldimines and thermal rearrangement of 3-methylene-2λ^2-isoindolin-1-ols.[12a] Inspired by our[12] and Wong's previous work,[10a] we proposed that, if an electron-deficient group was installed at the terminus of the alkyne, it might not only promote 5-*exo*-*dig* cyclization of 2-alkynyl aldehydes but also facilitate the elimination of the amino group from the *in situ* generated 3-amino-indanones, which should directly afford inden-1-ones as the final product.[13] Thus, we herein report our recent efforts in developing a metal-free synthesis of indenones from 2-alkynylbenzaldehydes by formal cleavage of a C═O bond and reassembly of new C−C and C═O bonds.

RESULTS AND DISCUSSION

We initiated our study by using ethyl 4-[(2-formylphenyl)-ethynyl]benzoate (**1a**) as the model substrate. In the presence of *N*,*N*-dimethylpyridin-4-amine (DMAP) or diethylamine (Et_2NH) in DCM at room temperature, cyclization product **2a** was not observed and **1a** was recovered in both cases (Table 1, entries 1 and 2). With pyrrolidine, we were pleased to observe a 70% isolated yield of **2a** with full conversion of **1a** (entry 3).[14] On the other hand, piperidine led to an incomplete reaction (entry 4). Switching the solvent to chloroform, acetonitrile, DMF, or THF led to lower yields of **2a**, and most of the transformations were incomplete even with prolonged

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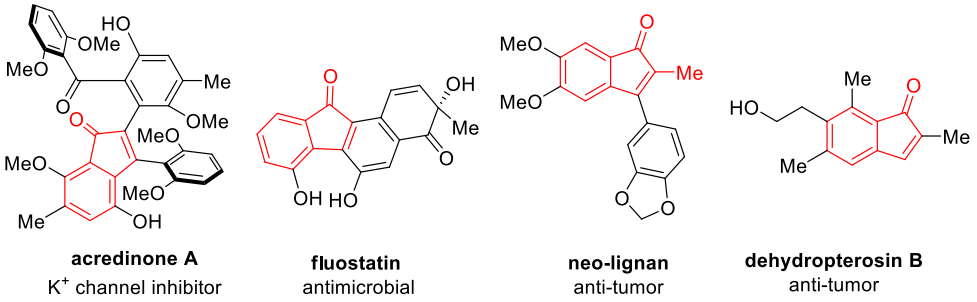
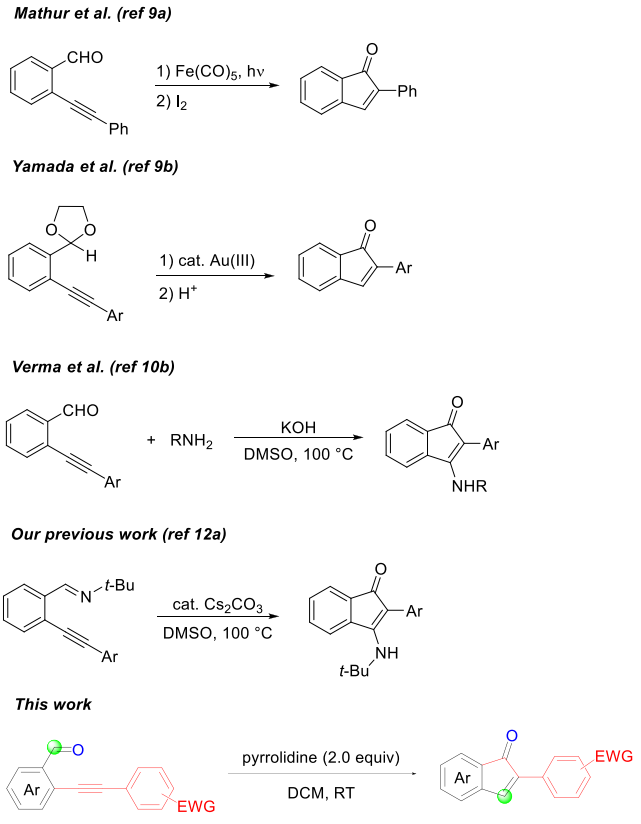


Figure 1. Natural products containing an indenone moiety.

Scheme 1. Synthesis of Inden-1-ones from 2-Alkynyl Aldehydes and Their Derivatives



reaction time (entries 5−8). When using 4.0 mL of DCM or employing 1.25 equiv of pyrrolidine, the reactions were incomplete even after elongated reaction time and **2a** was obtained in lower yields (entries 9 and 10). All efforts to develop a catalytic reaction by using a sub-stoichiometric quantity of pyrrolidine with different additives did not work (entries 11−15). Thus, the optimum reaction conditions were assumed to be the one displayed in Table 1, entry 3.

We next investigated the scope of substituents at the terminus of acetylenes (Table 2). When a phenyl group on the remote end of alkyne was substituted with electron-withdrawing substitutions such as ester, nitro, cyano, acyl, or CF_3 at the *para* position, the corresponding inden-1-one products **2a−e** were obtained in 50−87% yields. When the electro-withdrawing group was at the *meta* or *ortho* position, the reactions still proceeded smoothly to give inden-1-ones **2f−i** in good to excellent yields. Moreover, the electron-deficient pyridine ring, which often caused catalyst deactivation in transition metal catalysis, was amenable to give the expected inden-1-one **2j** in a 55% yield.[15] Disubstituted phenyl groups with at least one electron-withdrawing group could also be used to afford **2k−n** in good yields. Notably, these electron-deficient functionalities in the product could serve as a synthetic handle for further derivatization of these bicyclic products. In accordance with our working hypothesis, no desired product was formed when a phenyl, alkyl, or ester group is on the remote end of alkyne (not shown), demonstrating a certain limitation of our protocol.

We then turned our attention to varying the substitution on the aromatic ring of the aldehyde (Table 3). Both halides and electron-donating substituents were well tolerated on both the *meta* and *para* positions in **2o−v**. The single-crystal X-ray structure of **2q** provided the direct evidence of the cleavage of the carbonyl group.[16] The incorporation of the electron-donating methoxy group at the *para* position of aldehyde **1t** decelerated the reaction remarkably, and the cyclization occurred only at an elevated temperature. Sterically hindered aldehyde **1w** bearing both *ortho* and *meta* substitutions was also viable to afford inden-1-one **2w** in 75% yield. Besides, heterocyclic cyclopenta[*b*]quinolin-3-one **2x** and cyclopenta[*b*]pyridin-7-one **2y** were readily prepared under standard conditions with high efficiency. Benzaldehydes **1z** and **1z′**, both of which have an electron-withdrawing CF_3 group on the aromatic ring of the aldehyde, afforded a mixture of isomers **2z** and **2z′** through different mechanistic pathways (see Scheme 4). In each case, the major inden-1-one product is the one involving a cleavage of the carbonyl functionality.

Under standard reaction conditions, a gram-scale experiment was performed on **1a**, which proceeded with the same efficiency as the milligram-scale reaction (Scheme 2a). The synthetic utility of this method was further demonstrated by product derivatization including selective reduction, Michael addition, and hydrogenation (Scheme 2b). 1-Indanones **3** and **6**, as well as inden-1-ol **4**, were obtained from the corresponding inden-1-one **2** in good to excellent yields, respectively. Interestingly, when 2-(2-nitrophenyl)-1*H*-inden-1-one (**2f**) was subjected to Pd/C-catalyzed hydrogenation conditions, antioxidant 5,10-dihydroindeno[1,2-*b*]indole (DHII, **5**)[17] could be easily prepared in 73% yield. This one-pot transformation underwent a cascade of reduction of both the C=C bond and nitro group, intramolecular condensation, and isomerization.

To explore the mechanism of this reaction, we have performed a series of control experiments (Scheme 3a). The target product was not observed under standard reaction conditions, when *N*-(*p*-tolylsulfonyl)imine or (*R*,*E*)-*N*-(*tert*-

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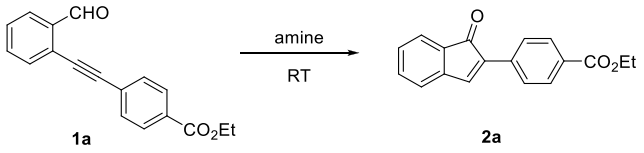
Table 1. Optimization of Reaction Conditions[a]

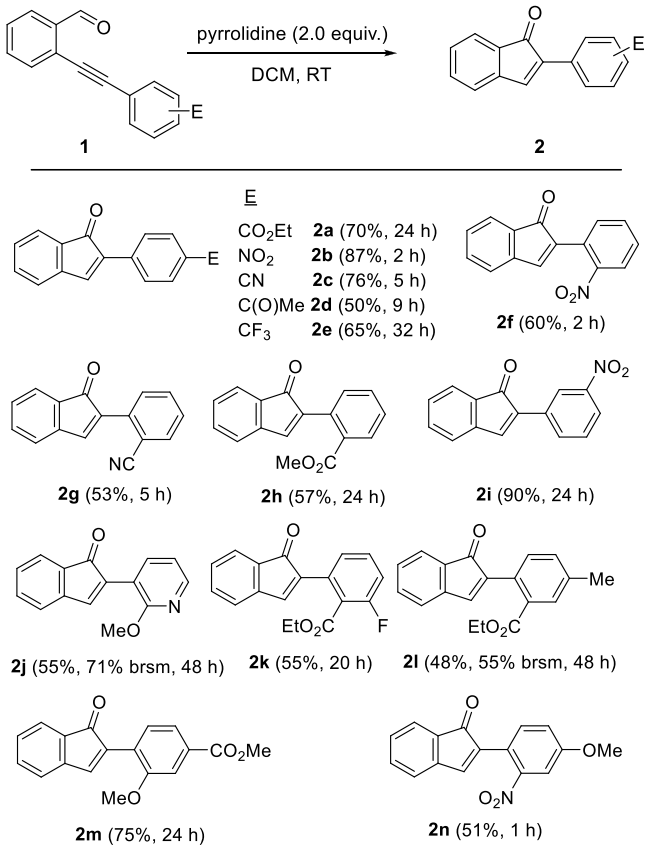


1a 2a

entry	amine (equiv)	solvent	additive (equiv)	time (h)	conv. (%)	yield (%)[b]
1	DMAP (2.0)	DCM		24	0	0
2	Et_2NH (2.0)	DCM		24	0	0
3	**pyrrolidine (2.0)**	**DCM**		**24**	**100**	**70**
4	piperidine (2.0)	DCM		32	51	39
5	pyrrolidine (2.0)	$CHCl_3$		31	96	62
6	pyrrolidine (2.0)	MeCN		9	100	56
7	pyrrolidine (2.0)	DMF		24	89	29
8	pyrrolidine (2.0)	THF		48	86	48
9[c]	pyrrolidine (2.0)	DCM		36	96	55
10	pyrrolidine (1.5)	DCM		32	90	42
11	pyrrolidine (0.5)	DCM	Et_3N (1.5)	32	0	0
12	pyrrolidine (0.5)	DCM	Cs_2CO_3 (1.5)	32	0	0
13	pyrrolidine (0.5)	DCM	DBU (1.5)	32	16	6
14[d]	pyrrolidine (0.5)	DCM	DBU (1.5)	32	35	10
15	pyrrolidine (0.5)	DCM	AcOH (0.4)	32	0	0

[a]Reaction conditions: **1a** (0.25 mmol) and amine (2.0 equiv), solvent (2.0 mL). [b]Isolated yield. [c]DCM (4.0 mL) used. [d]40 °C.

Table 2. Scope of the Substituents on the Acetylenes[a,b]



[a]Reaction conditions: **1** (0.25 mmol), pyrrolidine (2.0 equiv), DCM (2.0 mL). [b]Isolated yield.

butylsulfinyl)imine were used as analogues of aldehyde **1b**. The labeling experimental results could exclude the potential reaction pathway involving Michael addition of pyrrolidine to alkynes, as no incorporation of ^{18}O in indenone product **2c** was detected in LC-MS when running the reaction in the presence of 15 equiv of $H_2{}^{18}O$ in acetonitrile. Moreover, this labeling study could exclude the formation of an aminal intermediate generated by aldehyde and pyrrolidine in the reaction.[10a] With C1-deuterated aldehyde as the substrate (**1c-*d***), C3-deuterated indenone product (**2c-*d***) was obtained with a good level of deuterium retention either under standard conditions or in the presence of 10 equiv of water, further providing evidence to the proposed mechanistic pathway.

On the basis of these investigations, a plausible mechanism is proposed (Scheme 4). Initially, the nucleophilic addition of pyrrolidine to aldehyde **1** generates hemiaminal **I**. In pathway **A**, 5-*exo-dig* cyclization of the hydroxy group generates intermediate **II**.[13b] The cyclization is facilitated by electron-deficient groups at the terminus of the triple bond. Next, the corresponding 1-amino-3-methylene-dihydroisobenzofuran **II** undergoes fragmentation, followed by cyclization of the enolate onto the iminium ion, to form 3-amino-1-indanone **IV** (aza-Petasis−Ferrier rearrangement). Subsequent elimination of pyrrolidine under basic conditions eventually affords inden-1-one **2** (carbonyl-cleavage product). In pathway **B**, 5-*exo-dig* cyclization of the amino group and fragmentation of **V** generates intermediate **VI**. Intramolecular nucleophilic addition of the enamine to the aldehyde, followed by a hydride shift to the iminium ion, produces 3-amino-1-indanone **VIII**,[18] which is then converted to inden-1-one **2′** (non-carbonyl-cleavage product) via elimination of pyrrolidine. Normally, pathway **A** dominates the reaction and affords inden-1-one **2** (carbonyl-cleavage product) exclusively. When an electron-withdrawing CF_3 group is on the aromatic ring of the aldehyde (such as **1z** and **1z′**), the alkyne is sufficiently polarized. As such, pathway **B** (5-*exo-dig* cyclization of the amino group) can compete with pathway **A** (5-*exo-dig* cyclization of the hydroxy group), which leads to

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Table 3. Scope of the Substituents on the Aromatic Ring of Aldehyde[a]

Entry	Aldehyde	Product(s)	% Yield[b]
1[c]	R = F (**1o**)	**2o**	43
2[c]	Cl (**1p**)	**2p**	70
3[c]	OMe (**1q**)	**2q** (CCDC 1983775)	64
4[c]	R = F (**1r**)	**2r**	55
5[c]	Me (**1s**)	**2s**	60 (68)
6[c,d]	OMe (**1t**)	**2t**	49 (56)
7[e]	R = NO_2 (**1u**)	**2u**	58
8	CO_2Et (**1v**)	**2v**	55
9	**1w**	**2w**	75
10	**1x**	**2x**	64
11	**1y**	**2y**	75
12	**1z**	**2z** (2z + 2z' = 47 + 20)	
13	**1z′**	**2z′** (2z′ + 2z = 51 + 12)	

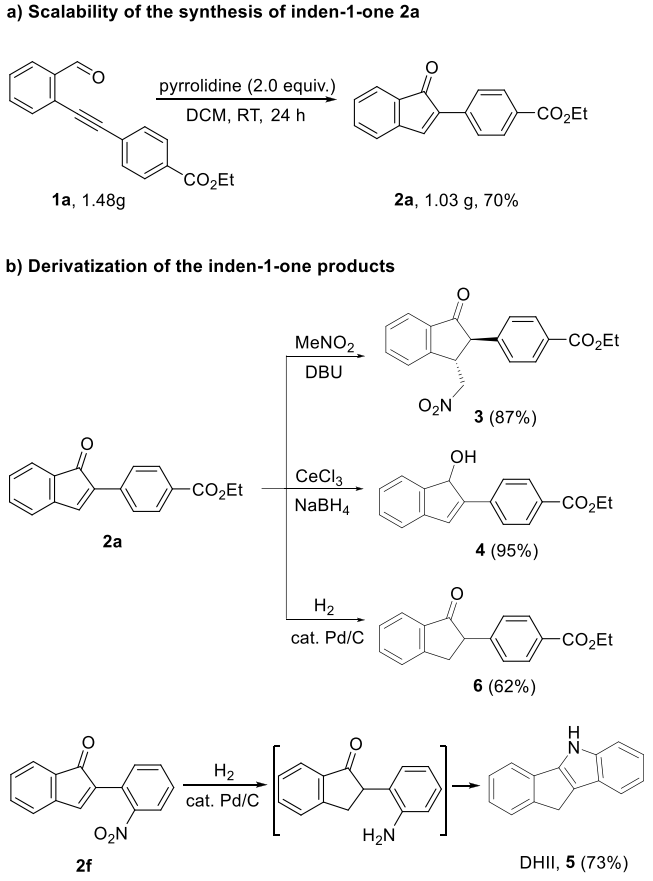
[a]Reaction conditions: **1** (0.25 mmol), pyrrolidine (2.0 equiv), DCM (2.0 mL), 24 h. [b]Isolated yield. The yield in parentheses is based on the recovery of **1**. [c]48 h. [d]40 °C. [e]6 h.

the formation of inden-1-one **2′** (non-carbonyl-cleavage product) as a minor product.

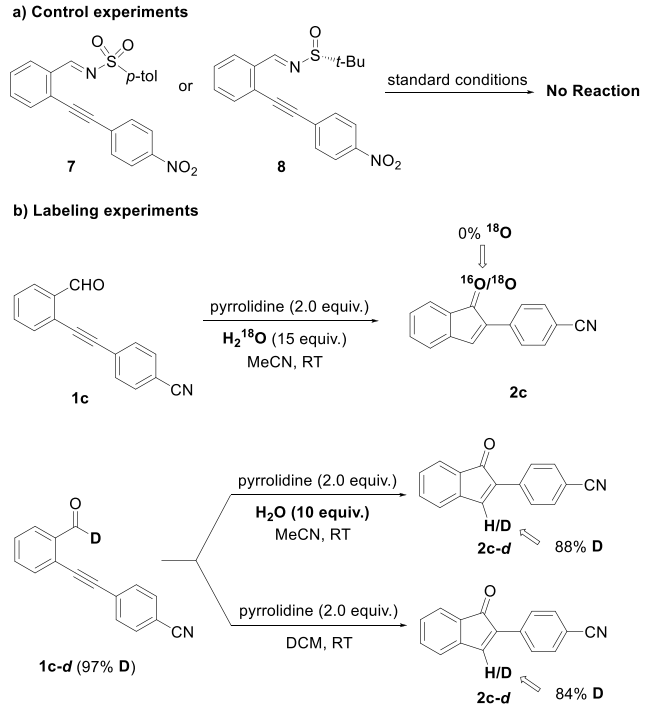
CONCLUSIONS

In summary, we have developed a metal-free, pyrrolidine-mediated synthesis of inden-1-ones from 2-alkynylbenzaldehydes under mild reaction conditions in good to excellent yields by cleaving the C═O bond and constructing new C−C and C═O bonds. The synthetic utility of this "cut and sew" protocol is further demonstrated by the gram-scale synthesis and derivatization of the inden-1-one products. The preliminary mechanistic study reveals an aza-Petasis−Ferrier

Scheme 2. Scalability Study and Derivatization of the Inden-1-one Products



Scheme 3. Mechanistic Studies



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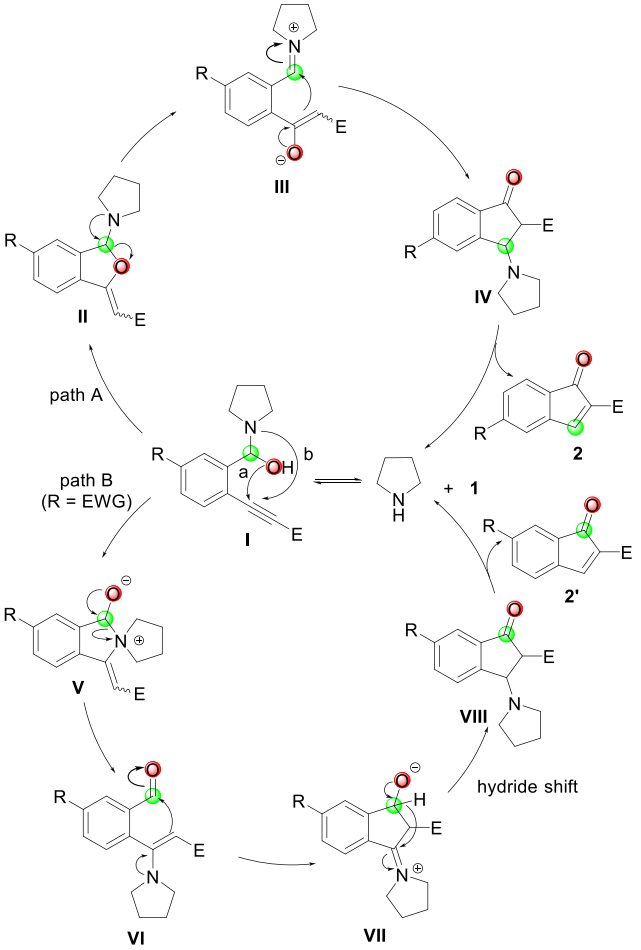
Scheme 4. Proposed Mechanism



rearrangement of the corresponding 1-amino-3-methylenedihydroisobenzofuran intermediate. Further investigations are currently undergoing in our group.

EXPERIMENTAL SECTION

General Information. NMR spectra were recorded on a Bruker AM 400 MHz spectrometer and calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$ (^1H): δ = 7.26 ppm; $CDCl_3$ (^{13}C): δ = 77.16 ppm). High-resolution mass analysis was performed using a Bruker maXis impact q-TOF Mass Spectrometer or a Thermo Scientific Q Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer. The crystal data for **2q** were collected at 169.97(10) K with a Rigaku XtaLAB Synergy four-circle diffractometer under Cu Kα radiation (λ = 1.54184 Å). Melting points were determined on a Stanford Research Systems OptiMelt apparatus. The infrared (IR) spectra were acquired as thin films using a universal ATR sampling accessory on a Bruker Vertex 80 FT-IR spectrometer, and the absorption frequencies are reported in cm^{-1}. Flash chromatography separations were carried out using silica gel columns. The new compounds were characterized by ^1H NMR, $^{13}C\{^1H\}$ NMR, HRMS, and IR. The structures of known compounds were further confirmed by comparing their ^1H NMR data with those of the literature. All reagents and solvents were used as received from commercial sources without further purification. Compounds **1a**,[19] **1b**,[20] **1c**,[21] **1d**,[22] **1e**,[21] **1f**,[23] **1g**,[24] **1h**,[25] **1i**,[26] **1o–t**,[12a] **1v**,[12a] **1w**,[12a] **1y,z′**,[12a] and **7**[29] were prepared by following the literature procedure.

General Procedure for the Synthesis of 2-Alkynylbenzaldehydes. To a solution of aryl halide (1.0 mmol, 1.0 equiv) in MeCN (6.7 mL) were added $PdCl_2(PPh_3)_2$ (0.05 mmol, 0.05 equiv), 2-ethynylbenzaldehyde (1.3 mmol, 1.3 equiv), and Et_3N (3.0 equiv). The resulting mixture was heated in an oil bath at 80 °C under argon. The progress of the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction was diluted with ethyl acetate (20 mL), washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate).

*2-((2-Methoxypyridin-3-yl)ethynyl)benzaldehyde (**1j**).* This product was obtained as an amorphous coloress solid (0.178 g, 75%) by using 3-iodo-2-methoxypyridine (0.235 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.170 g, 1.3 mmol). R_f = 0.36 (PE/EtOAc = 10:1); mp 96–98 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.14 (dd, J = 5.0, 1.7 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.74 (dd, J = 7.4, 1.7 Hz, 1H), 7.62 (d, J = 7.3 Hz, 1H), 7.55 (td, J = 7.6, 1.1 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 6.91–6.86 (m, 1H), 4.02 (s, 3H);$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.1, 165.7, 149.0, 143.3, 137.9, 135.7, 134.9, 130.7, 129.0, 128.5, 118.4, 108.5, 93.0, 92.1, 56.0; IR (neat) 1693, 1577, 1467, 1399 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{12}NO_2$ 238.0863; found 238.0857.

*Ethyl 2-Fluoro-6-((2-formylphenyl)ethynyl)benzoate (**1k**).* This product was obtained as a yellow oil (0.258 g, 87%) by using ethyl 2-fluoro-6-iodobenzoate (0.294 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.170 g, 1.3 mmol). R_f = 0.49 (PE/EtOAc = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.63–7.56 (m, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.43–7.39 (m, 2H), 7.18–7.10 (m, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.9, 164.5, 160.0 (C-F, 1 $J_{C\text{-}F}$ = 254.5 Hz), 136.4, 134.0, 133.6, 131.9 (C-F, 3 $J_{C\text{-}F}$ = 9.1 Hz), 129.5, 128.9 (C-F, 4 $J_{C\text{-}F}$ = 3.0 Hz), 127.5, 126.2, 124.0 (C-F, 2 $J_{C\text{-}F}$ = 17.2 Hz), 123.1 (C-F, 3 $J_{C\text{-}F}$ = 5.1 Hz), 117.2 (C-F, 2 $J_{C\text{-}F}$ = 22.2 Hz), 92.7 (C-F, 4 $J_{C\text{-}F}$ = 4.0 Hz), 89.7, 62.4, 14.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.47 to −112.54 (m, 1F); IR (neat) 1731, 1698, 1597, 1456, 1269 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{14}FO_3$297.0921; found 297.0915.

*Ethyl 2-((2-Formylphenyl)ethynyl)-5-methylbenzoate (**1l**).* This product was obtained as a colorless oil (0.267 g, 91%) by using ethyl 2-iodo-5-methylbenzoate (0.290 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.169 g, 1.3 mmol). R_f = 0.43 (PE/EtOAc = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.76 (s, 1H), 7.62 (d, J = 7.2 Hz, 1H), 7.53–7.50 (m, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 7.9 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.7, 166.0, 139.2, 136.2, 134.2, 133.8, 133.3, 132.7, 131.9, 131.2, 128.7, 127.3, 127.0, 119.9, 95.3, 89.0, 61.4, 21.4, 14.4; IR (neat) 1696, 1593, 1497, 1290 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{19}H_{17}O_3$ 293.1172; found 293.1164.

*Methyl 4-((2-Formylphenyl)ethynyl)-3-methoxybenzoate (**1m**).* This product was obtained as an amorphous colorless solid (0.147 g, 50%) by using methyl 4-iodo-3-methoxybenzoate (0.292 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.169 g, 1.3 mmol). R_f = 0.28 (PE/EtOAc = 10:1); mp 122–124 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.64–7.58 (m, 2H), 7.57–7.48 (m, 3H), 7.41 (t, J = 7.5 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.3, 166.5, 160.3, 136.1, 133.9, 133.2, 133.1, 131.8, 129.0, 127.2, 126.8, 121.9, 116.4, 111.4, 92.2, 91.7, 56.2, 52.6; IR (neat) 2949, 1722, 1688, 1403, 1292 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{15}O_4$ 295.0965; found 295.0969.

*2-((4-Methoxy-2-nitrophenyl)ethynyl)benzaldehyde (**1n**).* This product was obtained as an amorphous yellow solid (0.280 g, 99%) by using 1-iodo-4-methoxy-2-nitrobenzene (0.279 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.170 g, 1.3 mmol). R_f = 0.16 (PE/EtOAc = 10:1); mp 112–114 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.69–7.54 (m, 4H), 7.45 (t, J = 7.6 Hz, 1H), 7.15 (dd, J = 8.7, 2.6 Hz, 1H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.9, 160.3, 150.4, 136.4, 136.0, 134.0, 133.8, 129.4, 127.5, 126.4, 120.2, 110.1, 109.9,

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91.6, 90.9, 56.3; IR (neat) 1689, 1589, 1526, 1463, 1345 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calculated for $C_{16}H_{12}NO_4$ 282.0761; found 282.0754.

*6-((4-Nitrophenyl)ethynyl)benzo[d][1,3]dioxole-5-carbaldehyde (**1u**).* This product was obtained as an amorphous yellow solid (0.245 g, 83%) by using 1-iodo-4-nitrobenzene (0.249 g, 1.0 mmol) and 6-ethynylbenzo[*d*][1,3]dioxole-5-carbaldehyde (0.169 g, 1.3 mmol). R_f = 0.26 (PE/EtOAc = 1:1); mp 219−221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 8.26−8.22 (m, 2H), 7.69−7.64 (m, 2H), 7.38 (s, 1H), 7.04 (s, 1H), 6.11 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 189.5, 152.7, 149.7, 147.6, 132.8, 132.5, 129.4, 124.0, 122.2, 112.4, 106.7, 102.9, 93.1, 90.1; IR (neat) 1676, 1596, 1516, 1474, 1344 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calculated for $C_{16}H_{10}NO_5$ 296.0553; found 296.0551.

*Ethyl 4-((3-Formylquinolin-2-yl)ethynyl)benzoate (**1x**).* This product was obtained as an amorphous colorless solid (0.285g, 87%) by using ethyl 4-iodobenzoate (0.276 g, 1.0 mmol) and 2-ethynylquinoline-3-carbaldehyde (0.236 g, 1.3 mmol). R_f = 0.34 (PE/EtOAc = 10:1); mp 156−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.77 (s, 1H), 8.79 (s, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.90 (t, *J* = 7.1 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.67 (t, *J* = 7.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.6, 166.0, 150.3, 143.5, 137.6, 133.4, 132.4, 131.5, 129.9, 129.8, 129.6, 129.1, 128.7, 126.7, 125.9, 94.3, 88.0, 61.6, 14.5; IR (neat) 1716, 1595, 1550, 1399, 1281 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calculated for $C_{21}H_{16}NO_3$ 330.1125; found 330.1122.

Procedure for the Synthesis of Ethyl (*S,E*)-4-((2-(((*tert*-Butylsulfinyl)imino)methyl)phenyl)ethynyl)benzoate (8). To a solution of (*S,E*)-2-methyl-*N*-(2-((trimethylsilyl)ethynyl)-benzylidene)propane-2-sulfinamide (0.61 g, 2.0 mmol, 1.0 equiv) in MeOH (4.0 mL) and DCM (4.0 mL) was added K_2CO_3 (1.1 g, 8.0 mmol, 4.0 equiv). The resulting mixture was heated in an oil bath at 80 °C under argon. The progress of the reaction was monitored by TLC analysis to establish its completion. The completed reaction was quenched with water (20 mL), extracted with ethyl acetate (20 mL), washed with brine (20 mL), dried ($MgSO_4$), and concentrated. The crude product is used as is in the next step.

To a solution of 1-iodo-4-nitrobenzene (0.249 g, 1.0 mmol, 1.0 equiv) in MeCN (4.6 mL) were added $PdCl_2(PPh_3)_2$ (0.035 g, 0.05 mmol, 0.05 equiv), (*S,E*)-*N*-(2-ethynylbenzylidene)2-methylpropane-2-sulfinamide (0.350 g, 1.5 mmol, 1.5 equiv), and Et_3N (3.0 equiv). The resulting mixture was heated in an oil bath at 80 °C under argon. The progress of the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction was diluted with ethyl acetate (20 mL), washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate). This product was obtained as an amorphous brown solid (0.337 g, 95%). R_f = 0.26 (PE/EtOAc = 10:1); mp 117−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 2H), 8.12−8.08 (m, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.64 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.56−7.44 (m, 2H), 1.28 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.4, 147.5, 135.1, 133.2, 132.7, 132.2, 129.8, 129.6, 127.8, 124.5, 123.9, 94.3, 90.9, 58.2, 22.9; IR (neat) 1593, 1519, 1343, 1268, 1082 cm^{-1};HRMS (ESI) *m/z*: $[M + H]^+$ calculated for $C_{19}H_{19}N_2O_3S$ 355.1111; found 355.1103.

Procedure for the Synthesis of 4-((2-(Formyl-*d*)phenyl)-ethynyl)benzonitrile (1c-*d*). To a solution of 2-iodobenzaldehyde-*α*-*d*[30] (0.139 g, 0.6 mmol, 1.0 equiv) in MeCN (1.0 mL) were added $PdCl_2(PPh_3)_2$ (0.0085 g, 0.012 mmol, 0.02 equiv), 4-ethynylbenzonitrile (0.092 g, 0.72 mmol, 1.2 equiv), Et_3N (3.0 mL), and CuI (0.0012 g, 0.006 mmol, 0.01 equiv). The resulting mixture was heated in an oil bath at 55 °C under argon for 2 h. The progress of the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction was diluted with ethyl acetate (40 mL), washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate) to afford **1c-*d*** as an amorphous colorless solid (0.125 g, 90%): R_f = 0.23 (PE/EtOAc = 10:1); mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 0.03H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.69−7.57 (m, 6H), 7.50 (t, *J* = 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ190.8 (t, $J_{C\text{-}D}$ = 27.9 Hz), 136.3, 134.1, 133.7, 132.4, 129.7, 128.1, 127.4, 125.6, 118.5, 112.6, 94.3, 89.4 (one carbon missing due to overlap); IR (neat) 2229, 1685, 1559, 1541, 1457 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calculated for $C_{16}H_9DNO$ 233.0820; found 233.0819.

General Procedure for Pyrrolidine-Mediated Synthesis of Inden-1-ones. To a solution of 2-alkynylbenzaldehyde (0.25 mmol, 1.0 equiv) in DCM (2.0 mL) was added pyrrolidine (0.5 mmol, 2.0 equiv), and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by TLC analysis to establish its completion. The reaction was concentrated, and the residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate).

*Ethyl 4-(1-Oxo-1H-inden-2-yl)benzoate (**2a**).* This product was obtained as an amorphous orange solid (0.048 g, 70%) by using ethyl 4-((2-formylphenyl)ethynyl)benzoate (0.069 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.55 (PE/EtOAc = 5:1); mp 112−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.7, 166.5, 144.6, 143.6, 135.8, 135.4, 134.5, 131.3, 130.2, 130.0, 129.5, 127.2, 123.5, 122.7, 61.3, 14.5; IR (neat) 1709, 1603, 1456, 1274 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calculated for $C_{18}H_{15}O_3$ 279.1016; found 279.1008.

*2-(4-Nitrophenyl)-1H-inden-1-one (**2b**).* This product was obtained as an amorphous yellow solid (0.055 g, 87%) by using 2-((4-nitrophenyl)ethynyl)benzaldehyde (0.063 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol), and the spectral data were consistent with the literature.[27] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9.0 Hz, 2H), 7.98 (d, *J* = 9.0 Hz, 2H), 7.85 (s, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H).

*4-(1-Oxo-1H-inden-2-yl)benzonitrile (**2c**).* This product was obtained as an amorphous red solid (0.044 g, 76%) by using 4-((2-formylphenyl)ethynyl)benzonitrile (0.059 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.36 (PE/EtOAc = 5:1); mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.78 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.2, 145.5, 143.2, 136.0, 134.7, 134.4, 132.5, 131.1, 130.0, 127.8, 123.6, 123.0, 119.0, 111.8; IR (neat) 2226, 1701, 1601, 1452 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calculated for $C_{16}H_{10}NO$ 232.0757; found 232.0752.

*(4-Acetylphenyl)-1H-inden-1-one (**2d**).* This product was obtained as an amorphous orange solid (0.031 g, 50%) by using 2-((4-acetylphenyl)ethynyl)benzaldehyde (0.062 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.33 (PE/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 1H), 2.60 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.9, 196.6, 144.8, 143.6, 136.6, 136.1, 135.2, 134.5, 131.3, 129.6, 128.8, 127.5, 123.5, 122.7, 26.9; IR (neat) 1711, 1675, 1600, 1454, 1357 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calculated for $C_{17}H_{13}O_2$ 249.0910; found 249.0906.

*2-(4-(Trifluoromethyl)phenyl)-1H-inden-1-one (**2e**).* This product was obtained as an amorphous orange solid (0.044 g, 65%) by using 2-((4-(trifluoromethyl)phenyl)ethynyl)benzaldehyde (0.068 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.49 (PE/EtOAc = 10:1); mp 125−127 °C; ^{1}H NMR (400 MHz, CDCl3) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.74 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H); $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$) δ 196.5, 144.6,

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143.6,135.1, 135.0, 134.6, 131.2, 130.3 (C-F, 2 J_{C-F} = 32.3 Hz), 129.6, 127.7, 125.7 (C-F, 3 J_{C-F} = 4.0 Hz), 124.3 (C-F, 1 J_{C-F} = 273.7 Hz), 123.6, 122.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.70 (s, 3F); IR (neat) 1713, 1601, 1460, 1112 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{10}F_3O$ 275.0678; found 275.0676.

*2-(2-Nitrophenyl)-1H-inden-1-one (**2f**).* This product was obtained as an amorphous orange solid (0.038 g, 60%) by using 2-((2-nitrophenyl)ethynyl)benzaldehyde (0.063 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.32 (PE/EtOAc = 5:1); mp 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.57−7.42 (m, 4H), 7.38 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.1, 148.8, 144.0, 143.6, 136.9, 134.4, 133.2, 131.2, 130.6, 129.5, 129.3, 126.9, 124.8, 123.9, 122.8; IR (neat) 1710, 1601, 1518, 1457, 1350 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{10}NO_3$ 252.0655; found 252.0647.

*2-(1-Oxo-1H-inden-2-yl)benzonitrile (**2g**).* This product was obtained as an amorphous orange solid (0.030g, 53%) by using 2-((2-formylphenyl)ethynyl)benzonitrile (0.057 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.48 (PE/EtOAc = 5:1); mp 191−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 7.1 Hz, 1H), 7.44−7.38 (m, 2H), 7.28 (t, J = 7.3 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.8, 147.8, 143.5, 134.7, 134.5, 134.2, 133.4, 132.9, 130.5, 130.3, 130.0, 128.5, 123.7, 123.4, 118.8, 111.0; IR (neat) 2221, 1711, 1598, 1454 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{10}NO$ 232.0757; found 232.0752.

*Methyl 2-(1-Oxo-1H-inden-2-yl)benzoate (**2h**).* This product was obtained as an orange oil (0.038 g, 57%) by using methyl 2-((2-formylphenyl)ethynyl)benzoate (0.066 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.32 (PE/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.46 (d, J = 7.1 Hz, 1H), 7.44−7.39 (m, 2H), 7.37−7.33 (m, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 7.1 Hz, 1H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.6, 168.0, 144.5, 142.4, 140.4, 134.3, 132.5, 132.2, 131.0, 130.4, 130.2, 128.8, 128.7, 123.6, 122.4, 52.4 (one carbon missing due to overlap); IR (neat) 1716, 1599, 1444, 1271 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{17}H_{13}O_3$ 265.0859; found 265.0854.

*(3-Nitrophenyl)-1H-inden-1-one (**2i**).* This product was obtained as an amorphous orange solid (0.056 g, 90%) by using 2-((3-nitrophenyl)ethynyl)benzaldehyde (0.062 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.46 (PE/EtOAc = 5:1); mp 149−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.22−8.13 (m, 2H), 7.82 (s, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 7.1 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 7.1 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.1, 148.7, 144.9, 143.3, 134.7, 134.1, 133.3, 133.2, 131.1, 129.9, 129.8, 123.7, 123.1, 123.0, 122.1; IR (neat) 1709, 1596, 1526, 1447, 1348 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{10}NO_3$ 252.0655; found 252.0649.

*(2-Methoxypyridin-3-yl)-1H-inden-1-one (**2j**).* This product was obtained as an orange oil (0.033 g, 55%) by using 2-((2-methoxypyridin-3-yl)ethynyl)benzaldehyde (0.059 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol), and **1j** (0.014 g) was recovered. R_f = 0.51 (PE/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 7.6, 1.8 Hz, 1H), 8.10 (s, 1H), 8.07 (dd, J = 4.9, 1.7 Hz, 1H), 7.42 (d, J = 7.1 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.94 (dd, J = 7.5, 4.9 Hz, 1H), 4.03 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.8, 161.9, 147.0, 145.7, 144.7, 138.3, 134.4, 130.8, 130.1, 129.1, 123.2, 122.6, 117.1, 115.2, 53.8; IR (neat) 1710, 1585, 1443, 1370 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{15}H_{12}NO_2$ 238.0863; found 238.0856.

*Ethyl 2-Fluoro-6-(1-oxo-1H-inden-2-yl)benzoate (**2k**).* This product was obtained as a yellow oil (0.041 g, 55%) by using ethyl 2-fluoro-6-((2-formylphenyl)ethynyl)benzoate (0.074 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.28 (PE/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.46 (d, J = 7.0 Hz, 1H), 7.44−7.39 (m, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.21 (d, J = 7.9 Hz, 1H), 7.15−7.07 (m, 2H), 4.28 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.4, 165.4, 160.6 (C-F, 1 J_{C-F} = 254.5 Hz), 144.9, 144.0, 137.5 (C-F, 4 J_{C-F} = 3.0 Hz), 134.5, 132.9 (d, 3 J_{C-F} = 3.0 Hz), 132.0 (C-F,3 J_{C-F} = 10.1 Hz), 130.7, 129.3, 125.5 (C-F, 4 J_{C-F} = 3.0 Hz), 123.7, 122.7, 121.3 (C-F, 2 J_{C-F} = 15.2 Hz), 116.5 (C-F, 2 J_{C-F} = 22.2 Hz), 62.0, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.76 to −112.84 (m, 1F); IR (neat) 1717, 1598, 1457, 1262 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{14}FO_3$ 297.0921; found 297.0913.

*Ethyl 5-Methyl-2-(1-oxo-1H-inden-2-yl)benzoate (**2l**).* This product was obtained as a yellow oil (0.035 g, 48%) by using ethyl 2-((2-formylphenyl)ethynyl)-5-methylbenzoate (0.073 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol), and **1l** (0.010 g) was recovered. R_f = 0.44 (PE/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.45 (d, J = 7.1 Hz, 1H), 7.37 (s, 1H), 7.36−7.29 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.5, 175.4, 152.2, 149.4, 148.1, 146.4, 141.8, 140.4, 138.7, 138.6, 137.7, 137.1, 136.3, 131.1, 129.8, 68.9, 28.9, 21.9 (one carbon missing due to overlap); IR (neat) 1717, 1599, 1449, 1281 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{19}H_{17}O_3$ 293.1172; found 293.1162.

*Methyl 3-Methoxy-4-(1-oxo-1H-inden-2-yl)benzoate (**2m**).* This product was obtained as an amorphous orange solid (0.056 g, 75%) by using methyl 4-((2-formylphenyl)ethynyl)-3-methoxybenzoate (0.076 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.52 (PE/EtOAc = 5:1); mp 149−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.66 (dd, J = 8.1, 1.4 Hz, 1H), 7.58 (d, J = 1.3 Hz, 1H), 7.44 (d, J = 7.1 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.1 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.3, 167.0, 158.2, 148.1, 144.5, 134.3, 131.5, 130.6, 130.38, 130.36, 129.3, 125.0, 123.2, 122.6, 122.0, 111.6, 55.9, 52.5; IR (neat) 1711, 1598, 1451, 1291, 1269 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{15}O_4$ 295.0965; found 295.0959.

*2-(4-Methoxy-2-nitrophenyl)-1H-inden-1-one (**2n**).* This product was obtained as an amorphous orange solid (0.037 g, 51%) by using 2-((4-methoxy-2-nitrophenyl)ethynyl)benzaldehyde (0.070 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.32 (PE/EtOAc = 5:1); mp 161−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 2.6 Hz, 1H), 7.45 (s, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.39−7.33 (m, 2H), 7.24−7.18 (m, 1H), 7.15 (dd, J = 8.5, 2.6 Hz, 1H), 7.11 (d, J = 7.3 Hz, 1H), 3.88 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.6, 160.3, 149.6, 144.3, 142.9, 136.8, 134.5, 132.2, 130.7, 129.2, 123.9, 122.7, 119.8, 119.1, 109.8, 56.2; IR (neat) 1601, 1530, 1448, 1353, 1269 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{12}NO_4$ 282.0761; found 282.0754.

*Ethyl 4-(5-Fluoro-1-oxo-1H-inden-2-yl)benzoate (**2o**).* This product was obtained as an amorphous orange solid (0.032 g, 43%) by using ethyl 4-((4-fluoro-2-formylphenyl)ethynyl)benzoate (0.074 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol), and **1o** (0.005 g) was recovered. R_f = 0.42 (PE/EtOAc = 10:1); mp 168−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.66 (s, 1H), 7.46 (dd, J = 7.9, 5.1 Hz, 1H), 6.91−6.80 (m, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.8, 167.0 (C-F, 1 J_{C-F} = 255.5 Hz), 166.4, 146.7 (C-F, 3J_{C-F} = 10.1 Hz), 142.1 (C-F, 4 J_{C-F} = 3.0 Hz), 136.9, 135.4, 130.6, 130.0, 127.4, 127.1 (C-F, 4 J_{C-F} = 3.0 Hz), 125.4 (C-F, 3J_{C-F} = 10.1 Hz), 115.0 (C-F, 2 J_{C-F} = 23.2 Hz), 111.3 (C-F, 2 J_{C-F} = 25.3 Hz), 61.3, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −103.47 to −103.56 (m, 1F); IR (neat) 1709, 1603, 1467, 1278 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{18}H_{14}FO_3$ 297.0921; found 297.0914.

*Ethyl 4-(5-Chloro-1-oxo-1H-inden-2-yl)benzoate (**2p**).* This product was obtained as an amorphous orange solid (0.055 g, 70%) by using ethyl 4-((4-chloro-2-formylphenyl)ethynyl)benzoate

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(0.078 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.45 (PE/EtOAc = 5:1); mp 166−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.68 (s, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.08 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.9, 166.2, 145.3, 142.7, 140.4, 136.5, 135.1, 130.4, 129.8, 129.2, 128.8, 127.2, 124.2, 123.1, 61.1, 14.4; IR (neat) 1709, 1600, 1450, 1279 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{18}H_{14}ClO_3$ 313.0626; found 313.0622.

*Ethyl 4-(5-Methoxy-1-oxo-1H-inden-2-yl)benzoate (**2q**).* This product was obtained as a crystalline red solid (0.049 g, 64%) by using ethyl 4-((2-formyl-4-methoxyphenyl)ethynyl)benzoate (0.077 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol), and **1q** (0.004 g) was recovered. R_f = 0.41 (PE/EtOAc = 5:1); mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.62 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 2.1 Hz, 1H), 6.62 (dd, J = 8.0, 2.1 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.2, 166.5, 165.1, 146.2, 142.4, 136.8, 136.0, 130.2, 129.9, 127.3, 125.4, 124.0, 111.4, 111.0, 61.2, 55.9, 14.5; IR (neat) 1709, 1595, 1479, 1279 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{19}H_{17}O_4$ 309.1121; found 309.1112.

*Ethyl 4-(6-Fluoro-1-oxo-1H-inden-2-yl)benzoate (**2r**).* This product was obtained as an amorphous orange solid (0.041 g, 55%) by using ethyl 4-((5-fluoro-2-formylphenyl)ethynyl)benzoate (0.074 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.50 (PE/EtOAc = 5:1); mp 159−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.72 (s, 1H), 7.17 (dd, J = 7.0, 2.1 Hz, 1H), 7.08−6.97 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.1 (C-F, 4 $J_{C\text{-}F}$ = 1.3 Hz), 166.4, 163.9 (C-F, 1 $J_{C\text{-}F}$ = 252.5 Hz), 144.3 (C-F, 5 $J_{C\text{-}F}$ = 3.0 Hz), 139.1 (C-F, 5 $J_{C\text{-}F}$ = 4.0 Hz), 135.9 (C-F, 4 $J_{C\text{-}F}$ = 5.1 Hz), 135.5, 133.6 (C-F, 3 $J_{C\text{-}F}$ = 7.1 Hz), 130.3, 130.0, 127.1, 123.7 (C-F, 3$J_{C\text{-}F}$ = 8.1 Hz), 119.8 (C-F, 2 $J_{C\text{-}F}$ = 23.2 Hz), 112.2 (C-F, 2 $J_{C\text{-}F}$ = 25.3 Hz), 61.3, 14.5; IR (neat) 1709, 1603, 1477, 1277 cm^{-1}; ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.22 to −110.39 (m, 1F); HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{18}H_{14}FO_3$ 297.0921; found 297.0916.

*Ethyl 4-(6-Methyl-1-oxo-1H-inden-2-yl)benzoate (**2s**).* This product was obtained as an amorphous red solid (0.044 g, 60%) by using ethyl 4-((2-formyl-5-methylphenyl)ethynyl)benzoate (0.073 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol), and **1s** (0.009 g) was recovered. R_f = 0.63 (PE/EtOAc = 5:1); mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.72 (s, 1H), 7.28 (s, 1H), 7.14 (d, J = 7.3 Hz, 1H), 6.98 (d, J = 7.3 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.0, 166.6, 144.9, 140.8, 140.0, 136.1, 134.7, 134.4, 131.7, 130.0, 129.9, 127.1, 124.6, 122.5, 61.2, 21.7, 14.6; IR (neat) 1711, 1593, 1447, 1367, 1275 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{19}H_{17}O_3$ 293.1172; found 293.1166.

*Ethyl 4-(6-Methoxy-1-oxo-1H-inden-2-yl)benzoate (**2t**).* This product was obtained as an amorphous purple solid (0.038 g, 49%) by using ethyl 4-((2-formyl-5-methoxyphenyl)ethynyl)-benzoate (0.077 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol), and **1t** (0.010 g) was recovered. R_f = 0.39 (PE/EtOAc = 5:1); mp 115−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.70 (s, 1H), 7.04 (s, 1H), 6.97 (d, J = 7.9 Hz, 1H), 6.75 (dd, J = 7.9, 2.1 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.4, 166.6, 161.5, 145.6, 136.1, 135.3, 134.2, 133.5, 129.9, 129.7, 126.8, 123.6, 117.0, 111.4, 61.2, 56.0, 14.5; IR (neat) 1711, 1594, 1484, 1280 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{19}H_{17}O_4$ 309.1121; found 309.1114.

*6-(4-Nitrophenyl)-5H-indeno[5,6-d][1,3]dioxol-5-one (**2u**).* This product was obtained as an amorphous purple solid (0.043 g, 58%) by using 6-((4-nitrophenyl)ethynyl)benzo[d][1,3]dioxole-5-carbaldehyde (0.074 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.31 (PE/DCM = 1:1); mp 199−201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.7 Hz, 2H), 7.65 (s, 1H), 7.00 (s, 1H), 6.66 (s, 1H), 6.04 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.6, 152.6, 148.8, 147.3, 144.6, 139.7, 138.0, 133.3, 127.6, 125.3, 124.1, 106.1, 105.3, 102.6; IR (neat) 1655, 1587, 1513, 1470, 1396, 1334 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{16}H_{10}NO_5$ 296.0553; found 296.0552.

*Ethyl 4-(5-Oxo-5H-indeno[5,6-d][1,3]dioxol-6-yl)benzoate (**2v**).* This product was obtained as an amorphous purple solid (0.045 g, 55%) by using ethyl 4-((6-formylbenzo[d][1,3]dioxol-5-yl)ethynyl)-benzoate (0.080 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.43 (DCM); mp 187−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.54 (s, 1H), 6.97 (s, 1H), 6.61 (s, 1H), 6.01 (s, 2H), 4.36 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.3, 166.6, 152.4, 148.2, 143.0, 140.1, 135.9, 134.6, 129.94, 129.87, 126.9, 125.3, 105.9, 105.0, 102.4, 61.2, 14.6; IR (neat) 2921, 1709, 1603, 1470 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{19}H_{15}O_5$ 323.0914; found 323.0906.

*Ethyl 4-(6-Oxo-6H-indeno[4,5-d][1,3]dioxol-7-yl)benzoate (**2w**).* This product was obtained as an amorphous orange solid (0.061 g, 75%) by using ethyl 4-((4-formylbenzo[d][1,3]dioxol-5-yl)ethynyl)-benzoate (0.081 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.37 (PE/EtOAc = 5:1); mp 174−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.56 (s, 1H), 6.92 (dd, J = 7.5, 0.6 Hz, 1H), 6.35 (d, J = 7.5 Hz, 1H), 5.84 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.1, 166.5, 154.2, 141.6, 138.1, 136.6, 136.0, 130.2, 129.9, 127.2, 126.4, 122.0, 119.9, 106.6, 102.5, 61.3, 14.6; IR (neat) 1711, 1601, 1460, 1279 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{19}H_{15}O_5$ 323.0914; found 323.0905.

*Ethyl 4-(3-Oxo-3H-cyclopenta[b]quinolin-2-yl)benzoate (**2x**).* This product was obtained as an amorphous red solid (0.053 g, 64%) by using ethyl 4-((3-formylquinolin-2-yl)ethynyl)benzoate (0.082 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.29 (DCM); mp 239−241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.3 Hz, 1H), 8.11−8.08 (m, 3H), 7.98 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 7.1 Hz, 1H), 7.74 (s, 1H), 7.67 (td, J = 7.6, 1.5 Hz, 1H), 7.58 (td, J = 7.5, 1.2 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.1, 166.4, 153.4, 148.4, 144.4, 138.4, 135.1, 133.3, 132.1, 131.0, 130.4, 130.1, 129.6, 129.5, 129.0, 127.8, 127.3, 61.4, 14.6; IR (neat) 1711, 1591, 1445, 1274 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{21}H_{16}NO_3$ 330.1125; found 330.1117.

*Ethyl 4-(7-Oxo-7H-cyclopenta[b]pyridin-6-yl)benzoate (**2y**).* This product was obtained as an amorphous orange solid (0.052 g, 75%) by using ethyl 4-((3-formylpyridin-2-yl)ethynyl)benzoate (0.070 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.28 (DCM/MeOH = 100:1); mp 140−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 5.1 Hz, 1H), 8.05 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.82 (s, 1H), 7.45 (d, J = 7.4 Hz, 1H), 7.23−7.19 (m, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.3, 166.4, 151.3, 149.8, 142.2, 139.2, 134.9, 134.8, 130.8, 130.1, 129.1, 127.3, 126.9, 61.4, 14.5; IR (neat) 1720, 1603, 1443, 1280 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{17}H_{14}NO_3$ 280.0968; found 280.0961.

*Ethyl 4-(1-Oxo-5-(trifluoromethyl)-1H-inden-2-yl)benzoate (**2z**).* This product was obtained as an amorphous orange solid (0.041 g, 47%) by using ethyl 4-((2-formyl-4-(trifluoromethyl)phenyl)-ethynyl)benzoate (0.087 g, 0.25 mmol) and pyrrolidine (0.036 g, 0.5 mmol). R_f = 0.61 (PE/EtOAc = 5:1); mp 156−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 7.80 (s, 1H), 7.57−7.52 (m, 2H), 7.33 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.2, 166.4, 144.4, 143.4, 136.8, 136.0 (C-F, 2 $J_{C\text{-}F}$ = 32.3 Hz), 135.0, 133.8, 130.8, 130.1, 127.5, 127.0 (C-F, 3 $J_{C\text{-}F}$ = 4.0 Hz), 123.6 (C-F, 1 $J_{C\text{-}F}$ = 274.7 Hz), 123.3, 119.2 (C-F, 3 $J_{C\text{-}F}$ = 4.0 Hz), 61.4, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.36 (s, 3F); IR (neat) 1711, 1602, 1431, 1280 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{19}H_{14}F_3O_3$ 347.0890; found 347.0886.

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*Ethyl 4-(1-Oxo-6-(trifluoromethyl)-1H-inden-2-yl)benzoate (**2z′**).* This product was obtained as an amorphous orange solid (0.044 g, 51%) by using ethyl 4-((2-formyl-5-(trifluoromethyl)phenyl)-ethynyl)benzoate (0.086 g, 0.25 mmol) and pyrrolidine (0.035 g, 0.5 mmol). R_f = 0.49 (PE/EtOAc = 5:1); mp 166−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.79 (s, 1H), 7.69 (s, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 8.6 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.8, 166.4, 146.9, 143.1, 137.4, 135.0, 131.8 (q, 3 J_{C-F} = 4.0 Hz), 131.63, 131.59 (C-F, 2 J_{C-F} = 32.3 Hz), 130.9, 130.1, 127.5, 123.8 (C-F, 1 J_{C-F} = 270.7 Hz), 122.5, 120.2 (C-F, 3J_{C-F} = 3.0 Hz), 61.4, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.90 (s, 3F); IR (neat) 1711, 1608, 1445, 1281 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{19}H_{14}F_3O_3$ 347.0890; found 347.0886.

*trans-Ethyl 4-(1-(Nitromethyl)-3-oxo-2,3-dihydro-1H-inden-2-yl)benzoate (**3**).* To a solution of **2a** (0.0557 g, 0.2 mmol, 1.0 equiv) in $MeNO_2$ (2.0 mL) was added DBU (0.003 g, 0.02 mmol, 0.1 equiv). The resulting mixture was stirred at room temperature for 2 h. The completed reaction was concentrated, and the residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate). This product was obtained as a yellow oil (0.059 g, 87%). R_f = 0.22 (PE/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 7.9 Hz, 1H), 7.75−7.69 (m, 1H), 7.56−7.52 (m, 2H), 7.18 (d, J = 8.3 Hz, 2H), 4.85 (dd, J = 12.9, 5.7 Hz, 1H), 4.71 (dd, J = 12.9, 7.9 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 4.23−4.17 (m, 1H), 3.82 (d, J = 4.2 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.1, 166.3, 150.7, 142.6, 136.2, 136.1, 130.5, 130.1, 129.9, 128.3, 125.4, 125.3, 78.1, 61.2, 58.1, 46.0, 14.5; IR (neat) 1715, 1602, 1551, 1463, 1370, 1278 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{19}H_{18}NO_5$ 340.1179; found 340.1179.

*Ethyl 4-(1-Hydroxy-1H-inden-2-yl)benzoate (**4**).* To a solution of **2a** (0.0557g, 0.2 mmol, 1.0 equiv) in MeOH (4.6 mL) was added $CeCl_3{\cdot}7H_2O$ (0.082 g, 0.22 mmol, 1.1 equiv). After stirring at 0 °C for 10 min, $NaBH_4$ (0.0083 g, 0.22 mmol, 1.1 equiv) was added and the mixture was stirred at the same temperature for 3 min. After warming-up to room temperature, the reaction was further stirred for 10 min. The reaction was quenched with satd. NaCl (5 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate). This product was obtained as an amorphous colorless solid (0.053 g, 95%). R_f = 0.34 (PE/EtOAc = 5:1); mp 99−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 7.1 Hz, 1H), 7.32−7.26 (m, 2H), 7.26−7.20 (m, 1H), 7.13 (s, 1H), 5.48 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.06 (s, 1H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 147.7, 145.7, 141.7, 138.3, 130.1, 129.4, 129.1, 126.9, 126.5, 123.9, 121.9, 76.5, 61.2, 14.5; IR (neat) 3211, 1714, 1595, 1461, 1280 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{18}H_{17}O_3$ 281.1172; found 281.1165.

*5,10-Dihydroindeno[1,2-b]indole (**5**).* To a solution of **2f** (0.0503 g, 0.2 mmol, 1.0 equiv) in EtOAc (2.0 mL) was added Pd/C (10 wt %, 0.0213 mg, 0.02 mmol, 0.1 equiv). The reaction mixture was stirred under H_2 (1 atm, balloon) at room temperature for 18 h. The suspension was diluted with EtOAc (6 mL) and filtered through a short pad of Celite. The filtrate was concentrated, and the residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate = 5:1). This product was obtained as an amorphous colorless solid (0.030 g, 73%), and the spectral data were consistent with the literature.[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.66−7.60 (m, 1H), 7.53 (d, J = 7.4 Hz, 1H), 7.50−7.40 (m, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.23−7.12 (m, 3H), 3.72 (s, 2H).

*Ethyl 4-(1-Oxo-2,3-dihydro-1H-inden-2-yl)benzoate (**6**).* To a solution of **2a** (0.0557 g, 0.2 mmol, 1.0 equiv) in EtOAc (2.0 mL) was added Pd/C (10 wt %, 21.3 mg, 0.02 mmol, 0.1 equiv). The reaction mixture was stirred under H_2 (1 atm, balloon) at room temperature for 0.5 h. The suspension was diluted with EtOAc (10 mL) and filtered through a short pad of Celite. The filtrate was concentrated, and the residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate). This product was obtained as a colorless oil (0.035 g, 62%). R_f = 0.23 (PE/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 7.7 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 4.33 (q, J = 7.0 Hz, 2H), 3.94 (dd, J = 8.4, 4.1 Hz, 1H), 3.69 (dd, J = 17.5, 8.4 Hz, 1H), 3.25 (dd, J = 17.5, 4.0 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.4, 166.6, 153.7, 144.9, 136.2, 135.5, 130.3, 129.4, 128.12, 128.09, 126.7, 124.8, 61.1, 53.5, 35.7, 14.5; IR (neat) 1713, 1602, 1462, 1274 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{18}H_{17}O_3$ 281.1172; found 281.1170.

Labeling Experiments. To a solution of 2-alkynylbenzaldehyde **1c** (0.0289 g, 0.125 mmol, 1.0 equiv) in dried MeCN (1.5 mL) were added $H_2{}^{18}O$ (0.0338 g, 1.88 mmol, 15 equiv) and pyrrolidine (0.0178 g, 0.25 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 4 h. The reaction was concentrated and the residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate) to afford **2c** (0.0185 g, 64%). No incorporation of ^{18}O in indenone **2c** was observed in LC-MS.

To a solution of deuterated 2-alkynylbenzaldehyde **1c-*d*** (0.023 g, 0.10 mmol, 1.0 equiv) in MeCN (0.8 mL) were added H_2O (0.018 g, 1.88 mmol, 10 equiv) and pyrrolidine (0.014 g, 0.20 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 5 h. The reaction was concentrated and the residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate) to afford **2c-*d*** (0.0093 g, 40%). ^{1}H NMR showed 88% of deuteration in **2c-*d***.

To a solution of deuterated 2-alkynylbenzaldehyde **1c-*d*** (0.023 g, 0.10 mmol, 1.0 equiv) in DCM (0.8 mL) was added pyrrolidine (0.014 g, 0.20 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 5 h. The reaction was concentrated and the residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate) to afford **2c-*d*** (0.012 g, 52%) as an amorphous red solid. ^{1}H NMR showed 84% of deuteration in **2c-*d***. R_f = 0.31 (PE/EtOAc = 5:1); mp 146−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.76 (s, 0.16H), 7.64 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 7.1 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.25 (t, J = 7.3 Hz, 1H), 7.12 (d, J = 7.1 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.1, 145.4, 145.1 (t, J_{C-D} = 25.8 Hz), 143.3, 143.2, 136.0, 134.6, 134.5, 134.4, 132.5, 131.2, 130.0, 127.8, 123.6, 123.0, 119.0, 111.9; IR (neat) 2361, 1699, 1559, 1398 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{16}H_9DNO$ 233.0820; found 233.0819.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00780.

Copies of ^{1}H, ^{19}F, and ^{13}C{^{1}H} NMR data and X-ray crystal data for **2q** (PDF)

Accession Codes

CCDC 1983775 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Tuanli Yao − *Key Laboratory of Chemical Additives for China National Light Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and*

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Technology, Xi'an 710021, China; orcid.org/0000-0003-2905-6596; Email: yaotuanli@sust.edu.cn

Jiajing Tan − *Department of Organic Chemistry, College of Chemistry, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*; Email: tanjj@mail.buct.eud.cn

Authors

Tao Liu − *Key Laboratory of Chemical Additives for China National Light Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China*

Feng Zhang − *Key Laboratory of Chemical Additives for China National Light Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China*

Ying Ju − *Key Laboratory of Chemical Additives for China National Light Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c00780

Author Contributions

[§]T.L. and F.Z. contributed equally.

Notes

The authors declare no competing financial interest.

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