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A Facile Access to functionalized Indenes and Fused Quinolines by Regioselective 5-*enolexo*-dig Michael Addition and Cyclization Reaction

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Herein we reported a facile approach to multi-substituted indenes and cyclopenta[*b*]quinolines under mild conditions. The reaction proceeds via Michael addition between commercially available cyanoacetate/malonic esters and *α,β*-unsaturated ketones. The synthetic methodology involves enolate mediated regio- and stereoselective intramolecular 5-*enolexo*-dig cyclization promoted by a catalytic base. The products formed stereoselectively *cis* in indenes and *trans*-isomers for cyclopenta[*b*]quinolines albeit presence of steric hindrance at a quaternary carbon substituted by active methylene compounds. The reaction pathway was investigated by isolating the reaction intermediate. This synthetic transformation was achieved with various aromatic and heteroaromatic Michael acceptors and desired products were obtained in high to excellent yields. The reaction is scalable up to grams level with only 10 mol% of base.

Introduction

Indenes[1] and fused quinolines[2] are an important core of many natural products and pharmaceutical drugs. These scaffolds show anti-HIV,[3] anti-cancer,[4] antidiabetic,[5] anti-inflammatory activity.[6] Particularly, cyclopentane ring fused quinolines showed inhibitory activity as AchE inhibitor implicated in Alzheimer's[7] disease and excellent MIC against *M. tuberculosis*.[8] These molecules are DNA intercalators and inhibit the enzymatic activity of topoisomerase I/II resulting in antitumor/anticancer agents[9] (Figure 1). In view of the importance of these scaffolds, various transformations have been reported for its synthesis in past two decades.[10] In particular, Jie Wu[11] (Scheme 1, eqn 1) and R. Sanz[12] had made enormous contributions to the synthesis of indenes by Michael addition and cycloisomerization cascade reactions using *o*-(alkynyl)styrenes. Jan Paradies[13] used metal free frustrated Lewis pair catalyst to achieve 5-*endo-dig* cyclization. Radical-mediated cyclization by I. V. Alabugin via 5-*exo*-dig[14a] as well as 5-*exo*-trig[14b] pathway developed to synthesize indene which would further recycle to 6-*endo*-trig by homoallylic ring expansion.[14c] Subsequently, domino coupling and C-H functionalization by gold catalyst[15] have also emerged as a method for preparation of indene derivatives. Recently, X. Xu[16] has demonstrated the synthesis of spiroindene derivatives using isocyanide by cycloaddition/iodocyclization strategy. In 2016, A. K. Verma group achieved Iodo-substituted indenes by 5-*endo*-dig cyclization using enediyne.[17]

Michael addition has an important role in C-C and C-N bond forming reactions to achieve the complex, diversified enantioselective structure. In 2015, O. Kwon[18] (Scheme 1, eqn 2), D. H. Dethe[19] and R. Balamurugan[20] developed Michael reaction to access the indene scaffolds.

Among previously reported strategies, radical annulation[21] Friedländer condensation,[22] Povarov reaction,[23] photocyclization[24] found to be an important tool for the synthesis of fused quinolines.

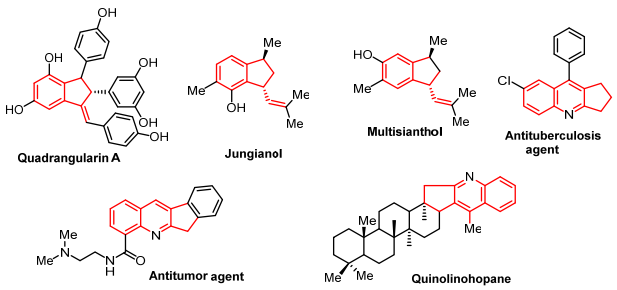

Figure 1 Selected examples of indene and fused quinoline containing natural compounds.

In 2016, L. Zhou[25] employed visible light mediated radical cyclization to assemble fused quinolines. Most recently, 2,3-disubstituted fused quinolines were synthesized via ketenimine or carbodiimide using α-diazo ketones.[26] In the continuation of our ongoing research towards the synthesis of *N*-heterocycles,[27] we successfully achieved the synthesis of highly functionalized indenes and fused quinolines by the tandem Michael addition followed 5-*enolexo*-dig cyclization. The previously presented methodologies to synthesize indenes and fused quinoline involve either harsh reaction conditions

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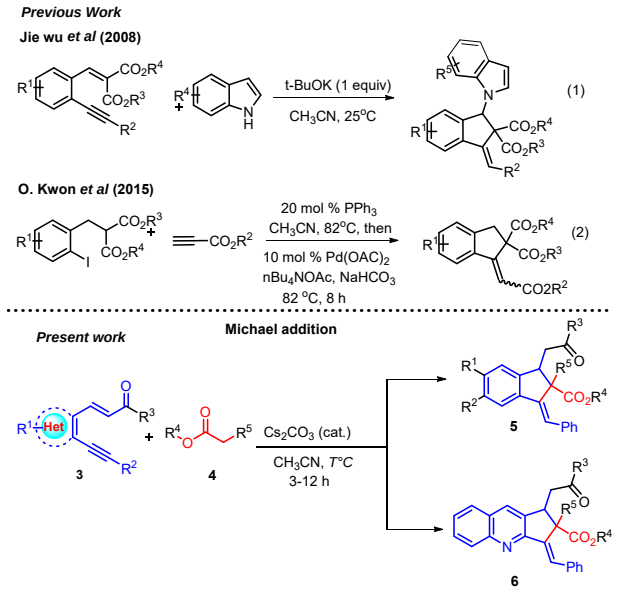
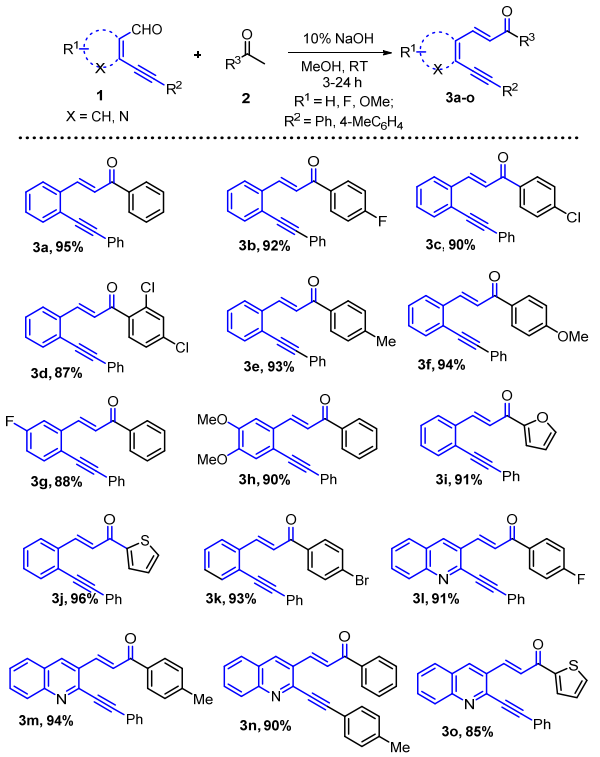


Scheme 1 Synthetic route to indenes and cyclopenta[*b*]quinolines.

or high loading of catalysts and bases. Therefore, we developed a highly regiospecific and stereoselective 5-*enol*exo-dig cyclization of the above compounds promoted by a catalytic base in mild conditions.



Scheme 2 Synthetic route to *o*-alkynylaromatic/heterocyclic chalcones. Reaction condition: **1** (5 mmol), **2** (5 mmol), 10% NaOH (1.5 mL), MeOH (15 mL) room temperature, 3-24 h.

The first enolate mediated 5-*enolexo*-dig cyclization was described by J. E. Baldwin *et* al.[28] The required "favored attack trajectories" for alkyne cyclization is well supported by experimental and theoretical calculations.[29] We observed selectively only *cis* product in case of indene and trans product for fused quinolines via regioselective 5-*enolexo*-dig cyclization. The pendant aryl group moves towards the quaternary carbon albeit the presence of steric hindrance which was confirmed by crystal analysis.[30]

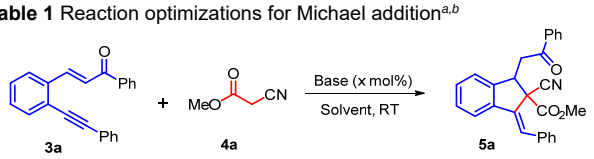
Results and discussion

Preparation of starting materials: To achieve our target moieties indenes and cyclopenta[*b*]quinolines, we synthesized **1** by standard Sonogashira cross-coupling reaction followed by Knoevenagel condensation reaction to delivered *o*-alkynylaromatic/heterocylic chalcones **3a-j** in good to excellent yield (Scheme 2).

Herein, we choose (*E*)-1-phenyl-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one (**3a**) and methyl cyanoacetate **4a** as a model substrate to intrigue the optimized conditions (Table 1).

The different bases were screened to optimize the reaction conditions. Initially, we used organic base DBU 0.5 equiv. and Lewis acid $AgNO_3$ (10 mol %) providing desired Michael adduct **5a** in 62% yield in 2 h at room temperature (Table 1, entry 1). The Similar reaction was carried out without Lewis acid to achieve the functionalized indene (entry 2). The use of strong base did not improve the yield (entry 3-5). The good yields were obtained with use of carbonate bases such as Na_2CO_3 and K_2CO_3 (entry 6-8), while $NaHCO_3$ delivered 63% yield (entry 9).

Table 1 Reaction optimizations for Michael addition[a,b]



Entry	Base	Solvent	Time (h)	Yield (%)[c]
1[c]	DBU (50 mol%)	CH_3CN	2	62
2	DBU (50 mol%)	CH_3CN	2	62
3	*t*-BuOK (1 equiv)	CH_3CN	0.5	20
4	NaOH (50 mol%)	CH_3CN	3	65
5	NaH (1 equiv)	CH_3CN	1	68
6	K_2CO_3 (50 mol%)	CH_3CN	10	79
7	K_2CO_3 (1 equiv)	CH_3CN	8	80
8	Na_2CO_3 (1 equiv)	CH_3CN	7	78
9	$NaHCO_3$ (1 equiv)	CH_3CN	10	63
9	Cs_2CO_3 (10 mol%)	CH_3CN	3	84
10	**Cs_2CO_3 (15 mol%)**	**CH_3CN**	**3**	**85**
11	Cs_2CO_3 (20 mol%)	CH_3CN	3	84
12	Cs_2CO_3 (15 mol%)	DMA	3	73

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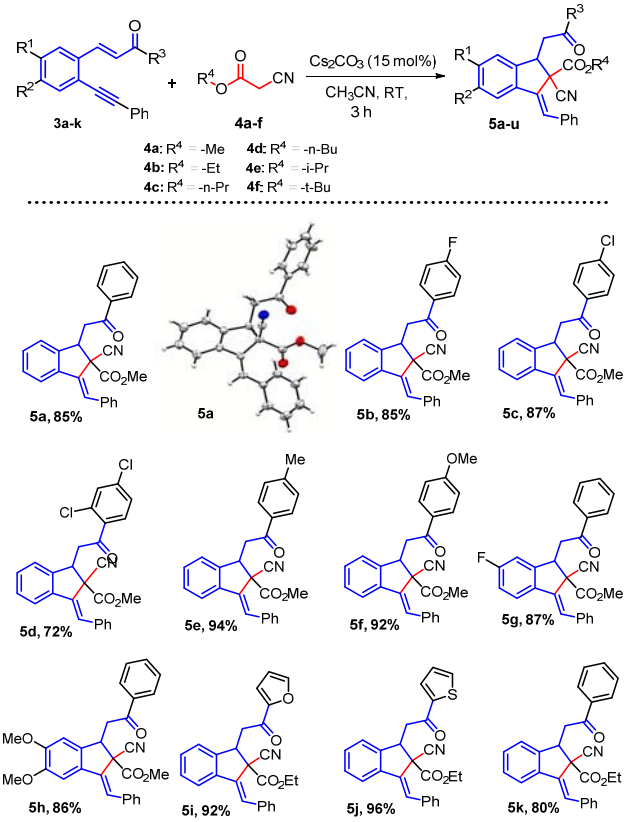
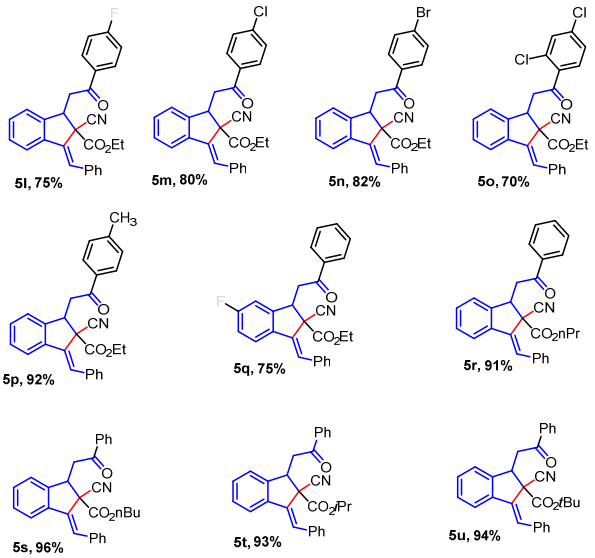
13	Cs_2CO_3 (15 mol%)	DMF	3	76
14	Cs_2CO_3 (15 mol%)	DMSO	4	79
15	Cs_2CO_3 (15 mol%)	THF	6	60
16	Cs_2CO_3 (15 mol%)	Dioxane	4	46
17	Cs_2CO_3 (15 mol%)	DCE	3	N. R.
18	Li_2CO_3 (15 ml%)	CH_3CN	2.5	68%

[a] Reaction condition: **3a** (0.5 mmol), **4a** (0.6 mmol), [b] Isolated yield based on **3a**, [c] $AgNO_3$ (10 mol %) used.

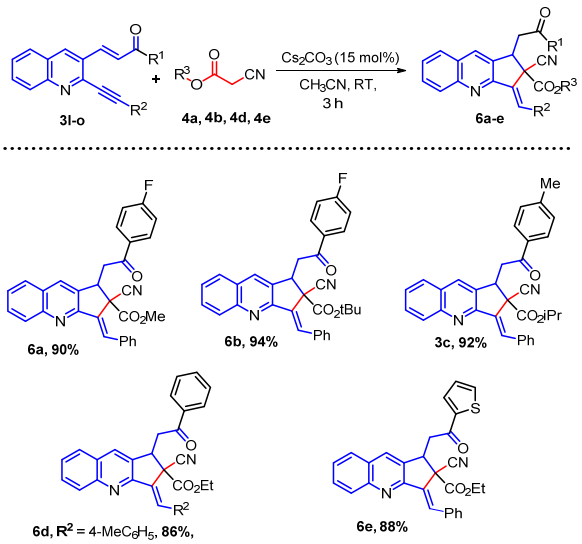
Interestingly, 15 mol% of Cs_2CO_3 produced indene **5a** (entry 10) in 85% yield and changing the quantity of Cs_2CO_3 did not affect the yield at all (entries 9 and 11). The same reaction in non-protic solvents such as DMA, DMF and DMSO gave **5a** in 73-79% yield (entry 12-14). The reaction in THF and Dioxane provided lower yield (entry 15 and 16). But the reaction completely failed in DCE (entry 17). Further there was no improvement in the reaction yield in the presence of Li_2CO_3 (entry 18). The structure of **5a** was confirmed by single crystal X-ray crystallographic analysis.[30]

The results of the optimized conditions (entry 10) encouraged us to study the substrate scope of Michael addition, with respect to *α,β*-unsaturated ketone and sterically featured cyanoacetates. The results are summarized in (Scheme 3). The aromatic chalcones bearing halogen substituents (**3b-c**) at *para*-position of phenyl ring proceed well with methyl cyanoacetate **4a** to afford **5b** and **5c** in 85 and 87% yield respectively. However, the substrate **3d** having 2, 4-dichloro substituent gave **5d** in 72% yield. Whereas chalcones **3e** and **3f** bearing electron donating groups gave **5e** and **5f** in excellent yields respectively. The substrate **3g**, containing fluoro substituent at R^1 position and electron donating groups such as methoxy group at R^1 and R^2 position of phenyl ring **3h** furnished **5g** and **5h** in 87 and 86% yield respectively. Interestingly, **5i** and **5j** were obtained in good yield by reacting ethyl cyanoacetate with 2-furan and 2-thienyl containing chalcones respectively.





Scheme 3 Substrate scope of Michael addition using different chalcones and cyanoacetates for the synthesis of Indenes. Reaction Condition: **3a-k** (0.5 mmol), **4a-f** (0.6 mmol), Cs_2CO_3 (15 mol %), CH_3CN (3 mL), 3 h, Isolated pure products yield.



Scheme 4 Substrate scope of Michael addition with heteroarenes chalcones for cyclopenta[*b*]quinolines. Reaction conditions: **3l-o** (0.5 mmol), **4** (0.6 mmol), Cs_2CO_3 (15 mol %), CH_3CN 3 mL, Isolated pure products yield.

Similarly, with ethyl cyanoacetate products **5k-q** obtained in 70-92% yield. Furthermore, steric nature of cyanoacetate was carefully

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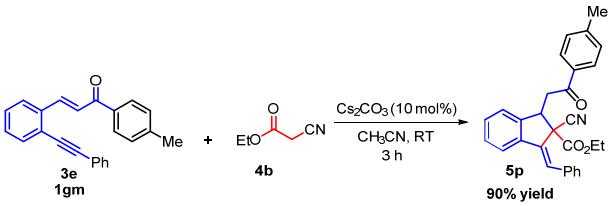
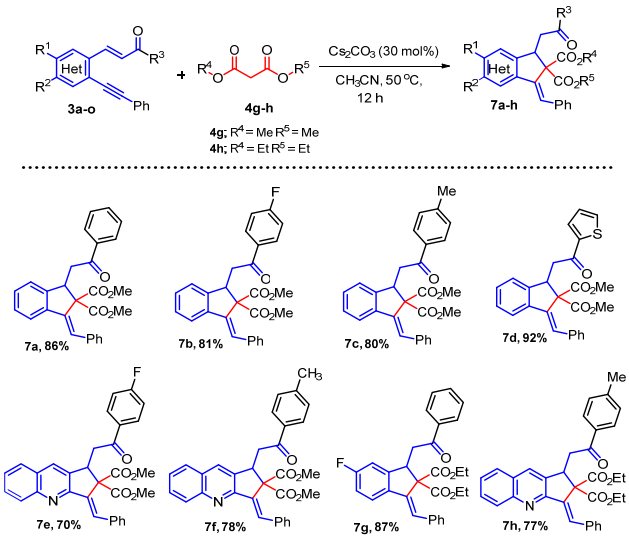
studied. The present synthetic pathway is well tolerated up to C4 aliphatic chains, such as n-propyl **4c** and n-butyl 4**d** delivered expected product **5r** and **5s** in excellent yields. The sterically hindered nucleophiles **4e** and **4f** also gave products **5t** and **5u** in similar yields respectively. The indenes formed by 5-*enolexo*-dig cyclization were selectively *Z*-isomers.

Due to the diverse utility of cyclopenta[*b*]quinolines in medicinal scaffolds, we evaluated the scope of quinolines based Michael acceptor **3l-o** (Scheme 4). To our surprise, these substrates well tolerated Michael addition cyclization cascade reactions. The electron withdrawing as well as electron donating heteroarene chalcones provides the product **6a-6c** in excellent yields. Interestingly, chalcones **3n** with substitution at alkyne with an electron donating group delivered the desired transformation in good yield. This Michael addition-cyclization reaction is feasible with substrate **3o** bearing 2-thienyl group as well. The *E*-isomers were formed with quinoline containing chalcones as substrate.



Scheme 5 Michael reaction at gram scale. Reaction conditions: **3e** (1gm scale), **4b** (1.2 equiv.), Cs_2CO_3 (10 mol %), 3 h, Isolated pure product yield.

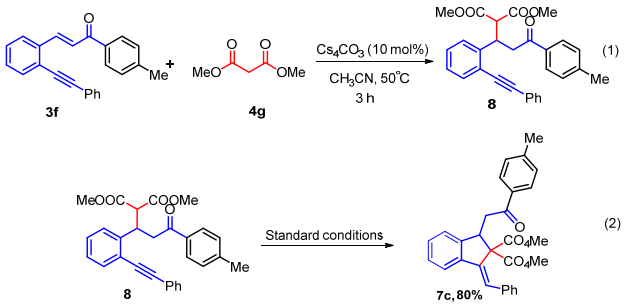
To demonstrate the rationality of present methodology, we conducted the reaction in gram scale (Scheme 5). The reaction delivered desired Michael product **5p** in 90% yield with the 10 mol% of Cs_2CO_3.



Scheme 6 Substrate scope of Michael addition with Malonic esters. Reaction condition: **3a-o** (0.5 mmol), **4** (0.6 mmol), Cs_2CO_3 (30 mol %), CH_3CN (3 ml), 50 °C, 12 h, Isolated products yield.

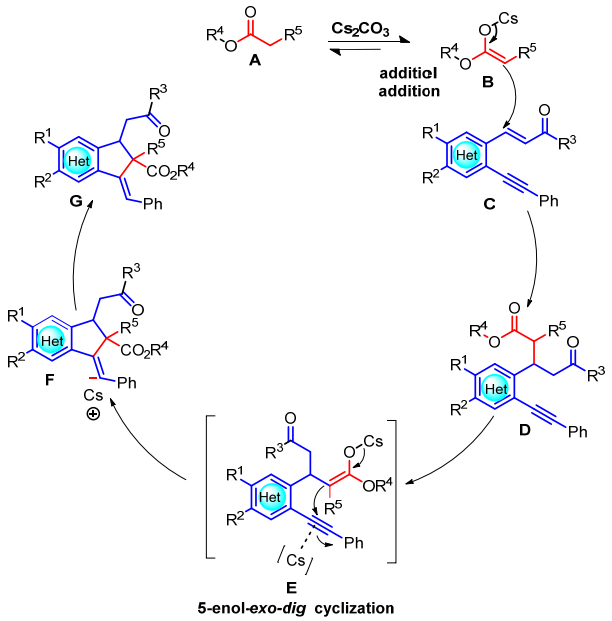
To Next, we elaborate the substrate scope with malonic esters (Scheme 6). The dimethyl and diethyl malonate **4g** and **4h** smoothly react with diverse *o*-alkynylaromatic/heterocylic chalcones to yield the products **7a-h** in good to excellent yields.

To investigate the reaction mechanism, we conducted a few control experiments. We isolated the intermediate of reaction such as Michael product **8** (Scheme 7 eqn 1). When this intermediate subjected to standard conditions, it delivered the 5-*enolexo*-dig cyclized product **7c** in 80% yield (Scheme 6, eqn 2). Based on the evidence from the control experiments and result and discussion we proposed a plausible reaction mechanism (Scheme 8).



Scheme 7 Control experiment for elucidation of mechanisms.

Base abstracts a proton from the active methylene compound '**A**' and generates enolate '**B**', which subsequently attacks at the *β*-position of chalcone furnishing Michael addition product '**D**'. Further removal of an active proton from the intermediates '**D**' generates enolate '**E**'. The base could be involved in activation of the alkyne.[31] This enolate attacks the LUMO of alkyne by an obtuse angle at a π*-system[29] which leads to 5-*enolexo*-dig cyclization gives the intermediates '**F**' which on protonation furnished the desired product '**G**'. The nucleophilic attack onto alkynes is favoring the *trans*-addition which resulted in the *Z*-isomers in case of indenes and *E*-isomers for fused quinolines.[32]



Scheme 8 Plausible reaction mechanism of Michael addition.

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Conclusions

In summary, we have developed an expeditious, cost-efficient method for the synthesis of highly substituted indenes and cyclopenta[*b*]quinolines using aromatic/heteroaromatic chalcones as building blocks. The reaction was completed using a catalytic amount of base in air using mild conditions. The stereochemistry of products did not change in the presence of different cations such as Na^+ or K^+ and at variable temperatures. The exclusive 5-*enolexo*-dig cyclization of *o*-alkynyl aromatic *α,β*-unsaturated ketones yielded highly regioselective product. The stereochemically single products were obtained suggesting kinetically controlled reactions according to Baldwin's rules. The mechanistic pathway of reaction has been described by isolating the intermediate. The presence of cyano and ester group will facilitate the further synthetic elaboration of the above compounds to synthesize complex scaffolds.

Experimental section

General Information

The solvents used for reactions were dried and distilled before use by standard methods. All the reagents used were commercially available and used without further purification. ^1H and ^{13}C NMR of compounds were recorded on JEOL spectrometer using 400 MHz and 100 MHz frequency respectively. The HRMS (m/z) of synthesized compounds were recorded on Mass Q-TOF LC/MS mass spectrometer. Melting points were measured using Buchi-B-540 instrument and are uncorrected. For the monitoring and visualization of reactions, TLC coated on silica gel plates (silica gel 60, F_{254}) was used.

General procedure for the synthesis of *α,β*-unsaturated ketones/Chalcones (*3a-o*):

To the 25 mL RB flask added 2-bromo-benzaldehyde **1** (5 mmol) followed by 10 ml methanol and acetophenone **2** (5 mmol). The 10% NaOH (1.5 mL) was added dropwise for 15 min. at 0°C. The reaction mixture was allowed to stir at room temperature for 3-24 h. After completion of reaction as indicated by TLC, the reaction mixture was poured onto 50 gm of crushed ice to precipitate the reaction mixture. The precipitate formed was washed with dist. water (2 X 10 mL) and a cold ethanol solution (5 mL) and dried to yield the desired product. Alternatively, methanol was evaporated under reduced pressure and extracted with ethyl acetate (2 X 50 mL). The combined organic layer was washed with distilled water (2 x 10 mL) and finally with brine solution (10 mL). The separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was purified by chromatography on silica gel using ethyl acetate/hexane as the eluent to yield the **3a-o** as the desired product.

General procedure for the synthesis of indenes and cyclopenta[*b*]quinolines (5a-7h):

To the 10 mL RB flask was added *α,β*-unsaturated ketone **3** (0.5 mmol), Cs_2CO_3 (15–30 mol%), and cyanoacetates/malonic esters **4** (0.6 mmol) and allowed to stir at room temperature or heat at 50 °C for 3 to 12 h. After completion of the reaction indicated by TLC, it was diluted with 10 mL of sat. NH_4Cl solution (in case of malonic ester 10 mL of dilute HCl was added). Extraction with ethyl acetate (2 x 50 mL) and distilled water (2 x 10 mL) was carried out. Finally, a combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by chromatography on silica gel using ethyl acetate/hexane as the eluent to yield the **5a-7h** as desired products.

***(E)*-1-Phenyl-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one (3a).** Yellow oil; (1.46 gm, 95% yield); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 16.0 Hz, 1H), 8.1 (d, *J* = 7.4 Hz, 2H), 7.79-7.76 (m, 1H), 7.67 - 7.51 (m, 5H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.40-7.35 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.4, 143.0, 138.1, 136.1, 132.9, 132.6, 131.6, 129.8, 128.6, 128.4, 128.3, 128.2, 126.7, 124.3, 124.1, 122.7, 95.7, 87.1 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{16}O$ $(M+H)^+$ 309.1279, found 309.1277.

***(E)*-1-(4-Fluorophenyl)-3-(2-(phenylethynyl) phenyl) prop-2-e-1-one (3b).** Pale yellow solid; (1.50 gm, 92% yield); mp 87- 88°C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 16.0Hz, 1H), 8.05-8.09 (m, 2H), 7.76-7.74 (m, 1H), 7.64-7.59 (m, 2H), 7.54-7.51 (m, 2H), 7.40-7.35 (m, 5H), 7.12 ppm (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.5, 165.5 (d, *J* = 252.6 Hz), 143.1, 135.9, 134.4, 132.9, 131.5, 131.1, 131.0, 129.9, 128.6 (d, *J* = 17.1 Hz), 128.4, 126.8, 124.3, 123.6, 122.6, 115.6 (d, *J* = 20.9 Hz), 95.8, 87.1 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{15}FO$ $(M+H)^+$ 327.1185, found 327.1182.

***(E)*-1-(4-Chlorophenyl)-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one (3c).** Pale yellow solid; (1.53 gm, 90% yield); mp 109.1-112.1°C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 15.2 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.77-7.74 (m, 1H), 7.62-7.56 (m, 2H), 7.52-7.50 (m, 2H), 7.44-7.36 ppm (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 143.5, 139.0, 136.4, 135.8, 132.9, 131.5, 130.0, 129.9, 128.8, 128.7, 128.5, 128.4, 126.7, 124.4, 123.7, 122.6, 95.8, 87.0 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{15}ClO$ $(M+H)^+$ 343.0889, found 343.0888

***(E)*-1-(2,4-Dichlorophenyl)-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one (3d).** Yellow solid; (1.64 gm, 87% yield); mp 146-148°C; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 16.0 Hz, 1H), 7.68-7.66 (m, 1H), 7.51-7.49 (m, 1H), 7.38-7.37 (m, 1H), 7.36-7.28 (m, 6H), 7.24-7.22 (m, 3H), 7.07-7.03 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.7, 145.7, 137.2, 136.5, 135.2, 132.7, 132.3, 131.4, 130.6, 130.2, 130.0, 128.8, 128.6, 128.4, 127.4, 127.1, 126.1, 124.7, 122.3, 95.9, 86.4 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{14}Cl_2O$ $(M+H)^+$ 377.0500, found 377.0505.

***(E)*-3-(2-(Phenylethynyl)phenyl)-1-(p-tolyl)prop-2-en-1-one (3e).** Yellow solid; (1.49 gm, 93% yield); mp 95.6-98.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.34 (d, *J* = 16.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.77-7.75 (m, 1H), 7.65-7.58 (m, 2H), 7.54-7.52 (m, 2H), 7.37-7.33 (m, 5H), 7.25 (d, *J* = 8.4 Hz, 2H), 2.40 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.7, 143.4, 142.5, 136.2, 135.5, 132.9, 131.6, 129.7, 129.2, 128.7, 128.6, 128.5, 128.3, 126.6, 124.2, 124.1, 122.7, 95.7, 87.1, 21.6 ppm; HRMS (ESI) m/z calcd for $C_{24}H_{18}O$ $(M+H)^+$, 323.1436, found 323.1455.

***(E)*-1-(4-Methoxyphenyl)-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one (3f).** Yellow solid; (1.82 gm, 94% yield); 79.6-83.3 mp 79.6-84.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 16.0 Hz, 1H), 8.03

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(d, *J* = 8.4 Hz, 2H), 7.78-7.75 (m, 1H), 7.63 (d, *J* = 16.0 Hz, 1H), 7.62-7.59 (m, 1H), 7.56-7.55 (m, 2H), 7.39-7.36 (m, 5H), 6.94 (d, *J* = 9.1 Hz, 2H), 3.86 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.3, 163.2, 142.0, 136.3, 132.9, 131.6, 130.9, 130.8, 129.6, 128.6, 128.5, 128.3, 126.7, 124.1, 123.9, 122.7, 113.7, 95.6, 87.2, 55.4 ppm; HRMS (ESI) *m/z* calcd for $C_{24}H_{18}O_2(M+H)^+$ 339.1385, found 339.1364.

***(E)*-3-(5-Fluoro-2-(phenylethynyl)phenyl)-1-phenylprop-2-en-1-one (3g).** Yellow solid; (0.98 gm, 88% yield); mp 84.1-87.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 16.0 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.62-7.60 (m, 1H), 7.59-7.57 (m, 2H), 7.54-7.44 (m, 5H), 7.37-7.34 (m, 3H), 7.10 ppm (td, *J* = 8.4, 3.0, Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.6, 162.2 (d, *J* = 248.8 Hz), 141.6, 138.3,138.2, 137.8, 134.7 (d, *J* = 7.6 Hz), 132.8, 131.5, 128.6, 128.5 (d, *J* = 6.6 Hz), 128.3, 124.9, 122.5, 120.5, 117.3 (d, *J* = 22.8 Hz), 113.1 (d, *J* = 22.8 Hz), 95.4, 86.1 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{15}FO$ $(M+H)^+$ 327.1185, found 327.1184.

***(E)*-3-(4,5-Dimethoxy-2-(phenylethynyl)phenyl)-1-phenylprop-2-en-1-one (3h).** Yellow solid; (1.65 gm, 90% yield); mp 147.1-140.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 16.0 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.58-7.55 (m, 1H), 7.49-7.45 (m, 5H), 7.35-7.33 (m, 3H), 7.20 (s, 1H), 7.05 (s, 1H), 3.98 (s, 3H), 3.95 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.6, 150.7, 149.5, 143.3, 138.4, 132.3, 131.4, 129.5, 128.5, 128.4, 128.3, 122.8, 122.2, 118.1, 114.4, 108.4, 94.7, 87.1, 56.0, 55.9 ppm; HRMS (ESI) *m/z* calcd for $C_{25}H_{20}O_3$ $(M+H)^+$ 369.1490 found 369.1480.

(*E*)-1-(Furan-2-yl)-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one (3i). Pale yellow solid; (1.35 gm, 91% yield); mp 84.5-87.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 16.0 Hz, 1H), 7.70-7.67 (m, 1H), 7.55-7.51 (m, 5H), 7.32-7.24 (m, 6H), 6.49-6.48 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.1, 153.6, 146.4, 141.9, 135.9, 132.9, 131.6, 129.9, 128.6, 128.4, 128.3, 126.8, 124.4, 122.8, 122.7, 117.5, 112.5, 95.8, 87.1 ppm; HRMS (ESI) *m/z* calcd for $C_{21}H_{14}O_2$ $(M+H)^+$ 299.1072 found 299.1065.

***(E)*-3-(2-(Phenylethynyl)phenyl)-1-(thiophen-2-yl)prop-2-en-1-one (3j).** Pale yellow solid; (1.50 gm, 96% yield); mp 134.5-137.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (d, *J* = 16.0 Hz, 1H), 7.85 (d, *J* = 3.8 Hz, 1H), 7.77-7.75 (m, 1H),7.66 (d, *J* = 4.5 Hz,1H), 7.61-7.54 (m, 4H), 7.39 -7.35 (m, 5H), 7.14 ppm (t, *J* = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 182.2, 145.4, 142.0, 135.8, 133.9, 132.9, 131.9, 131.6, 129.9, 128.6, 128.5, 128.4, 128.2, 126.6, 124.4, 123.3, 122.7, 95.8, 87.1 ppm; HRMS (ESI) *m/z* calcd for $C_{21}H_{14}OS$ $(M+H)^+$ 315.0843 found 315.0860.

***(E)*-1-(4-Bromophenyl)-3-(2-(phenylethynyl)phenyl)prop-2-en-1-one (3k).** Pale yellow solid; (1.80 gm, 93% yield); 108.1-111.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 16.0 Hz, 1H), 7.85 (d, *J* = 9.9 Hz, 2H), 7.76-74 (m, 1H), 7.61-7.49 (m, 6H), 7.39-7.36 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.3, 143.6, 136.8, 135.8, 132.9, 131.8, 131.5, 130.1, 128.7, 128.5, 128.4, 127.6, 126.7, 124.4, 123.6, 122.6, 95.9, 87.0 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{15}BrO$ $(M+H)^+$ 387.0385 found 387.0380.

***(E)*-1-(4-Fluorophenyl)-3-(2-(phenylethynyl)quinolin-3-yl)prop-2-en-1-one (3l).** Pale yellow solid; (2.14 gm, 91% yield); mp 160.1-163.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (s, ^{1}H), 8.46 (d, *J* = 15.6 Hz, 1H), 8.14-8.08 (m, 3H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.80-7.74 (m, 2H), 7.69-7.67 (m, 2H), 7.59 (t, *J* = 8.4 Hz, 1H), 7.44-7.40 (m, 3H), 7.16 ppm (t, *J* = 11.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 188.7, 165.5 (d, *J* = 253.6 Hz), 148.4, 143.3, 141.0, 134.1(d, *J* = 2.8 Hz), 133.9, 132.2, 131.3, 131.2, 131.1, 129.5, 129.4, 129.1, 128.4, 127.9 (d, *J* = 20.9 Hz), 126.8, 124.9, 121.5, 115.8 (d, *J* = 21.9 Hz), 94.9, 87.2 ppm; HRMS (ESI) *m/z* calcd for $C_{26}H_{16}FNO$ $(M+H)^+$ 378.1294, found 378.1274.

***(E)*-3-(2-(Phenylethynyl)quinolin-3-yl)-1-(p-tolyl)prop-2-en-1-one (3m).** Colourless solid; (1.75 gm, 94% yield); mp 135.2-139.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (s, ^{1}H), 8.46 (d, *J* = 16.0 Hz, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.78-7.74 (m, 2H), 7.69-7.67 (m, 2H), 7.58 (t, *J* = 8.4 Hz, 1H), 7.42-7.36 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.43 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.9, 148.3, 143.7, 143.4, 140.3, 135.2, 133.7, 132.3, 131.0, 129.6, 129.4, 129.3, 129.0, 128.7, 128.4, 128.0, 127.7, 126.8, 125.4, 121.6, 94.9, 87.2, 21.6 ppm; HRMS (ESI) *m/z* calcd for $C_{27}H_{19}NO$ $(M+H)^+$ 374.1544, found 374.1543.

***(E)*-1-Phenyl-3-(2-(p-tolylethynyl)quinolin-3-yl)prop-2-en-1-one (3n).** Colourless solid; (1.69 53 gm, 90% yield); mp 185.5-188.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 8.37 (d, *J* = 16.0 Hz,1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 6.8 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70-7.67 (m, 2H), 7.55-7.48 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H); 2.32 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.5, 148.4, 143.5, 140.9, 139.9, 137.8, 133.8, 132.8, 132.2, 131.1, 129.5, 129.2, 129.0, 128.7, 128.6, 128.0, 127.6, 126.7, 125.4, 118.5, 95.4, 86.8, 21.6 ppm; HRMS (ESI) *m/z* calcd for $C_{27}H_{19}NO$ $(M+H)^+$, 374.1544, found 374.1542.

***(E)*-3-(2-(Phenylethynyl)quinolin-3-yl)-1-(thiophen-2-yl)prop-2-en-1-one (3o).** Pale yellow solid; (1.55 gm, 85% yield); mp 163.1-165.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.54-8.49 (m, 2H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 3.8 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.77-7.65 (m, 5H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.42-7.39 (m, 3H), 7.17 ppm (t, *J* = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 181.6, 148.4, 145.1, 143.4, 139.9, 134.3, 133.8, 132.3, 132.1, 131.1, 129.5, 129.4, 129.1, 128.4, 128.3, 128.0, 127.8, 126.8, 124.8, 121.6, 95.0, 87.2 ppm; HRMS(ESI) *m/z* calcd for $C_{24}H_{16}NOS$ $(M+H)^+$, calculated 366.0925, found 366.0952.

(*Z*)-Methyl-1-benzylidene-2-cyano-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-indene-2-carboxylate (5a). Colorless solid; (179 mg, 85% yield); mp 153.1-156.2 °C; 1H NMR (400 MHz, CDCl3) δ = 8.03 (d, *J* = 7.8 Hz, 2H), 7.62-7.58 (m, 2H), 7.51-7.47 (m, 4H), 7.40-7.20 (m, 6H), 7.21-7.19 (m, 1H), 4.61 (t, *J* = 6.0 Hz, 1H), 3.86-3.70 (m, 2H), 3.36 ppm (s, 3H); 13C NMR (100 MHz, CDCl3) δ = 197.1, 167.6, 142.1, 138.8, 138.4, 136.1, 134.9, 133.6, 129.7, 128.8, 128.7, 128.6, 128.3, 128.1, 128.0, 125.6, 123.7, 121.0, 117.4, 57.0, 53.2, 48.8, 41.1 ppm; HRMS (ESI) *m/z* calcd for $C_{27}H_{21}NO_3$ $(M+NH_4)^+$ 425.1865, found 425.1869.

***(Z)*-Methyl-1-benzylidene-2-cyano-3-(2-(4-fluorophenyl)-2-oxoethyl)-2,3-dihydro-1H-indene-2-carboxylate (5b).** Colorless solid; (187 mg, 85% yield); mp 152.5-155.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08-8.04 (m, 2H), 7.62-7.60 (m, 1H), 7.48-7.46 (m, 2H), 7.40-7.30 (m, 6H), 7.20-7.14 (m, 3H), 4.62-4.58 (m, 1H), 3.83-3.66 (m, 2H), 3.36 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.5, 167.6, 166.0 (d, *J* = 254.5 Hz), 142.0, 138.8, 138.3, 134.9, 132.6 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 9.5 Hz), 129.7, 128.8, 128.7, 128.2, 128.0, 125.7, 123.6, 121.1, 117.4, 115.8 (d, *J* = 21.9 Hz), 56.9, 53.2, 48.8, 41.0 ppm; HRMS (ESI) *m/z* calcd for $C_{27}H_{20}FNO_3$ $(M+NH_4)^+$ 443.1771, found 443.1768.

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***(Z)*-Methyl-1-benzylidene-3-(2-(4-chlorophenyl)-2-oxoethyl)-2-cyano-2,3-dihydro-1H-indene-2-carboxylate (5c).** Colorless solid; (200 mg, 87% yield); mp 128.7-131.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06-8.02 (m, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.46-744 (m, 2H), 738-7.29 (m, 6H), 7.18-7.11 (m, 3H), 4.58 (t, *J* = 6.8 Hz, 1H), 3.81-3.64 (m, 2H), 3.31 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.0, 167.6, 141.9, 140.1, 138.8, 138.3, 134.9, 134.5, 129.7, 129.6, 129.0, 128.8, 128.7, 128.3, 128.0, 125.7, 123.6, 121.1, 117.4, 56.9, 53.2, 48.8, 41.1 ppm; HRMS (ESI) *m/z* calcd for $C_{27}H_{20}ClNO_3$ $(M+NH_4)^+$ 459.1475, found 459.1477.

***(Z)*-Methyl-1-benzylidene-2-cyano-3-(2-(2,4-dIchlorophenyl-2-oxo-ethyl)-2,3-dihydro-1H-indene-2-carboxylate (5d).** Colorless white solid; (171 mg, 72% yield); mp 132.3-135.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (t, *J* = 8.4 Hz, 2H), 7.46-7.44 (m, 3H), 7.39-7.29 (m, 7H), 7.24-7.20 (m, 1H), 4.57 (t, *J* = 6.0 Hz, 1H), 3.74-3.72 (m, 2H), 3.36 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.7, 167.7, 141.5, 138.8, 138.2, 138.0, 136.3, 134.7, 132.1, 130.7, 130.5, 129.8, 128.8, 128.3, 128.0, 127.5, 125.8, 123.5, 121.1, 117.3, 56.7, 53.3, 48.9, 45.4 ppm; HRMS (ESI) *m/z* calcd for $C_{27}H_{19}C_2lNO_3$ $(M+NH_4)^+$ 493.1085, found 493.1097.

***(Z)*-Methyl-1-benzylidene-2-cyano-3-(2-oxo-2-(p-tolyl)ethyl)- 2,3-dihydro-1H-indene-2-carboxylate (5e).** Colorless solid; (199 mg, 94% yield); mp 138.7-142.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.4 Hz, 2H), 7.61-7.59 (m, 1H), 7.49-7.47 (m, 2H), 7.39-7.29 (m, 8H), 7.20-7.18 (m, 1H), 4.61 (t, *J* = 6.0Hz, 1H), 3.82-3.72 (m, 2H), 3.35 (s, 3H), 2.41 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.6, 167.6, 144.5, 142.2, 138.8, 138.4, 134.9, 133.7, 129.7, 129.3, 128.7, 128.6, 128.2, 127.9, 125.5, 123.7, 121.0, 117.4, 57.0, 53.1, 48.8, 40.9, 21.6 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}NO_3$ $(M+Na)^+$ 444.1575, found 444.1592.

***(Z)*-Methyl-1-benzylidene-2-cyano-3-(2-(4-methoxyphenyl)-2-ox -oethyl)-2,3-dihy dro-1H-indene-2-carboxylate (5f).** Pale yellow solid; (201 mg, 92% yield); mp 112.2-115.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 6.8 Hz, 1H), 7.47-7.45 (m, 2H), 7.39-7.28 (m, 6H), 7.20-7.18 (m, 1H), 6.94 (d, *J* = 8.2 Hz, 2H), 4.60 (t, *J* = 6.1 Hz, 1H), 3.86 (s, 3H), 3.79-3.64 (m, 2H), 3.34 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.4, 167.6, 163.8, 142.3, 138.8, 138.4, 134.9, 130.5, 129.7, 129.2, 128.7, 128.5, 128.2, 127.9, 125.5, 123.7, 121.0, 117.5, 113.8, 57.0, 55.4, 53.1, 48.9, 40.6 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}NO_4$ $(M+NH_4)^+$ 460.1524, found 460.1526.

***(Z)*-Methyl-1-benzylidene-2-cyano-5-fluoro-3-(2-oxo-2-phenylet -hyl)-2,3-dihydro-1H-indene-2-carboxylate (5g).** Colorless solid; (185 mg, 87% yield); mp 164.5-166.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.4 Hz, 2H), 7.62-7.54 (m, 2H), 7.50-7.44 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.32-7.28 (m, 1H), 7.21 (s, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.91-6.89 (m, 1H), 4.57 (t, *J* = 6.0 Hz, 1H), 3.85-3.64 (m, 2H), 3.35 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.7, 167.4, 163.8 (d, *J* = 254.6 Hz), 144.4, 144.3, 137.1, 135.9, 134.7, 133.7, 128.7, 128.3, 128.2 , 128.1, 125.3, 122.6, 122.5, 117.2, 116.2 (d, *J* = 22.8 Hz), 111.0 (d, *J* = 22.8 Hz), 57.2, 53.3, 48.5, 40.9 ppm; HRMS (ESI) *m/z* calcd for $C_{27}H_{20}FNO_3$ $(M+NH_4)^+$ 443.1771, found 443.1750

***(Z)*-Methyl-1-benzylidene-2-cyano-5,6-dimethoxy-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-indene-2-carboxylate (5h).** Colorless solid; (200 mg, 86% yield); mp 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.6 Hz, 2H), 7.60-7.58 (m, 1H), 7.51-7.45 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30-7.28 (m, 1H), 7.09 (s, 1H), 7.04 (s, 1H), 6.67 (s, 1H), 4.53 (t, *J* = 6.1 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 3.82 (dd, J_1 = 18.3, J_2 = 7.6 Hz, 1H), 3.66 (dd, J_1 = 19.1, J_2 = 6.2 Hz, 1H), 3.38 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.3, 167.7, 151.2, 150.1, 138.4, 136.2, 135.1, 135.0, 133.6, 131.2, 128.7, 128.7, 128.2, 128.1, 127.6, 123.0, 117.5, 105.9, 103.0, 57.0, 56.1, 53.2, 48.6, 41.4 ppm; HRMS (ESI) *m/z* calcd for $C_{29}H_{25}NO_5$ $(M+NH_4)^+$ 485.2076, found 485.2064.

***(Z)*-Ethyl-1-benzylidene-2-cyano-3-(2-(furan-2-yl)-2-oxoethyl)-2,-3 -dihydro-1H-indene-2-carboxylate (5i).** Colorless solid; (203 mg, 92% yield); mp 139.4-142.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (s, 1H), 7.60 (d, *J* = 6.8 Hz, 1H), 7.49-7.47 (m, 2H), 7.39-7.27 (m, 7H), 7.20-7.18 (m, 1H), 6.58-6.56 (m, 1H), 4.58 (t, *J* = 6.8 Hz, 1H), 3.85-3.78 (m, 1H), 3.75-3.66 (m, 2H), 3.62-3.56 (m, 1H), 0.99 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.7 166.9, 152.0, 146.9, 141.9, 139.0, 137.8, 135.1, 129.7, 128.8, 128.7, 128.3, 128.0, 125.5, 123.7, 121.0, 118.0, 117.3, 112.4, 62.9, 57.2, 48.4, 40.5, 13.3 ppm; HRMS (ESI) *m/z* calcd for $C_{26}H_{21}NO_4$ $(M+NH_4)^+$ 429.1814, found 429.1805.

***(Z)*-Ethyl-1-benzylidene-2-cyano-3-(2-oxo-2-(thiophen-2-yl)ethyl-)-2,3-dihydro-1H-indene-2-carboxylate (5j).** Colorless solid; (205 mg, 96% yield); mp 155.6-157.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 3.4 Hz, 1H), 7.69 (d, *J* = 4.5 Hz, 1H), 7.60 (d, *J* = 6.8 Hz, 1H), 7.49-7.47 (m, 2H), 7.38-7.25 (m, 6H), 7.19-7.15 (m, 2H), 4.61 (t, *J* = 6.9 Hz, 1H), 3.84-3.62 (m, 4H), 0.98 ppm (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.6, 166.9, 143.3, 141.9, 139.0, 137.8, 135.1, 134.4, 132.7, 129.7, 128.7, 128.6, 128.3, 128.0, 125.5, 123.7, 121.0, 117.4, 62.9, 57.2, 48.8, 41.3, 13.3 ppm; HRMS (ESI) *m/z* calcd for $C_{26}H_{21}NO_3$ $(M+NH_4)^+$ 445.1585, found 445.1582.

***(Z)*-Ethyl-1-benzylidene-2-cyano-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-indene-2-carboxylate (5k).** Colorless solid; (168 mg, 80% yield); mp 146-148°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05-8.03 (m, 2H), 7.61-7.60 (m, 2H), 7.51-7.47 (m, 4H), 7.39-7.27 (m, 6H), 7.20-7.18 (m, 1H), 4.63 (t, *J* = 6.8 Hz, 1H), 3.88-3.81 (m, 2H), 3.75-3.69 (m, 2H), 1.00 ppm (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.0, 167.1, 142.2, 139.0, 138.0, 136.2, 135.1, 133.5, 129.6, 128.8, 128.7, 128.5, 128.3, 128.1, 128.0, 125.5, 123.7, 121.0, 62.8, 57.2, 48.8, 41.0, 13.4 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}NO_3$ $(M+NH_4)^+$ 439.2021, found 439.2021.

***(Z)*-Ethyl-1-benzylidene-2-cyano-3-(2-(4-fluorophenyl)-2-oxoethyl)-2,3-dihydro-1H-indene-2-carboxylate (5l).** Colorless solid; (165 mg, 75% yield); mp 117.8-120.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08-8.05 (m, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.49-7.47 (m, 2H), 7.39-7.29 (m, 6H), 7.19-7.14 (m, 3H), 4.62 (t, *J* = 6.0 Hz, 1H), 3.88-3.77 (m, 2H), 3.74-3.64 (m, 2H), 1.00 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) = δ 195.4, 167.2, 165.9 (d, *J* = 238.3 Hz), 142.0, 139.0, 137.9, 135.0, 132.6 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 8.5 Hz), 129.7, 128.8, 128.6, 128.3, 128.0, 125.6, 123.6, 121.0, 117.4, 115.8, (d, *J* = 21.9 Hz), 62.8, 57.1, 48.8, 40.9, 13.3 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{22}FNO_3$ $(M+NH_4)^+$ 457.1927, found 457.1918.

***(Z)*-Ethyl-1-benzylidene-3-(2-(4-chlorophenyl)-2-oxoethyl)-2-cyano-2,3-dihydro-1H-indene-2-carboxylate (5m).** Colorless solid; (179 mg, 80% yield); mp 137.1-140.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91(d, *J* = 9.1 Hz, 2H), 7.55-7.53 (m, 1H), 7.42-7.39 (m, 4H), 7.32-7.18 (m, 6H), 7.12-7.10 (m, 1H), 4.54 (t, *J* = 6.8 Hz, 1H), 3.80-3.70 (m, 2H), 3.67-3.56 (m, 2H), 0.94 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.8, 167.1, 142.0, 140.1, 139.0, 137.9, 135.0, 134.5, 129.7, 129.6, 129.0, 128.8, 128.6, 128.3, 128.0, 125.6, 123.6,

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121.1, 117.4, 62.9,57.1, 48.8, 41.0, 13.4 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{22}ClNO_3$ $(M+NH_4)^+$ 473.1632, found 473.1616.

***(Z)*-Ethyl-1-benzylidene-3-(2-(4-bromophenyl)-2-oxoethyl)-2-cyano-2,3-dihydro-1H-indene-2-carboxylate (5n).** Colorless solid; (205 mg, 82% yield); mp 138.5-141.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 8.4 Hz, 2H), 7.65-7.60 (m, 3H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.39-7.29 (m, 6H), 7.19-7.17 (m, 1H), 4.61 (t, *J* = 5.3 Hz, 1H), 3.88-3.76 (m, 2H), 3.72-3.62 (m, 2H), 1.00 ppm (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.0, 167.1, 142.0, 139.0, 137.9, 135.0, 134.9, 132.0, 129.6, 128.9, 128.8, 128.6, 128.3, 128.0, 125.6, 123.6, 121.1, 117.4, 62.9, 57.1, 48.7, 41.0, 13.4 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{22}BrNO_3$ $(M+Na)^+$ 522.0680, found 522.0689.

***(Z)*-Ethyl-1-benzylidene-2-cyano-3-(2-(2,4-dichlorophenyl)-2-oxoethyl)-2,3-di hydro-1H-indene-2-carboxylate (5o).** Colorless solid; (165 mg, 70% yield); mp 106.7-109.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56-7.52 (m, 2H), 7.42-7.40 (m, 3H), 7.33-7.28 (m, 5H), 7.25-7.14 (m, 3H), 4.52 (t, *J* = 6.8 Hz, 1H), 3.83-3.79 (m, 1H), 3.68-3.62 (m, 3H), 0.97 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) = δ 198.6, 167.2, 141.7, 139.0, 137.9, 136.4, 134.9, 132.1, 130.7, 130.5, 129.7, 128.9, 128.7, 128.3, 128.1, 127.5, 125.8, 123.5, 121.1, 117.3, 63.0, 56.9, 48.9, 45.4, 13.4 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{21}Cl_2NO_3$ $(M+NH_4)^+$ 507.1242, found 507.1251.

(*Z*)-Ethyl1-benzylidene-2-cyano-3-(2-oxo-2-(p-tolyl)ethyl)-2,3-dihydro-1H-inden e-2-carboxylate (5p). Colorless solid; (200 mg, 92% yield); mp 146-148°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 6.8 Hz, 1H), 7.50-7.48 (m, 2H), 7.39-7.33 (m, 3H), 7.31-7.27 (m, 5H), 7.19-7.17 (m, 1H), 4.62 (t, *J* = 6.4 Hz, 1H), 3.87-3.77 (m, 2H), 3.74-3.66 (m, 2H), 2.42 (s, 3H), 0.99 ppm (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.5, 167.1, 144.5, 142.2, 139.0, 138.0, 135.1, 133.7, 129.6, 129.3, 128.8, 128.5, 128.3, 128.3, 128.0, 125.5, 123.7, 121.0, 117.5, 62.8, 57.2, 48.8, 40.9, 21.6, 13.4 ppm; HRMS (ESI) *m/z* calcd for $C_{29}H_{25}NO_3$ $(M+Na)^+$ 458.1732, found 458.1742.

***(Z)*-Ethyl-1-benzylidene-2-cyano-5-fluoro-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-indene-2-carboxylate (5q).** Colourless solid; (167 mg, 75%), mp 121-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08-8.05 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.49-7.47 (m, 2H), 7.39-7.29 (m, 6H), 7.19-7.13 (m, 3H), 4.62 (t, *J* = 6.8 Hz, 1H), 3.88-3.82 (m, 2H), 3.81-3.64 (m, 2H), 1.00 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.4, 166.8, 163.8 (d, *J* = 248.8 Hz), 144.5, 144.4, 136.8, 136.0, 135.0, 134.9, 133.7, 128.7, 128.2 (d, *J* = 19.0 Hz), 128.0, 125.2, 122.5, 122.4, 117.2, 116.1 (d, *J* = 22.8 Hz), 111.1 (d, *J* = 23.8 Hz), 63.0, 57.4, 48.5, 40.9, 13.3 ppm; HRMS (ESI) m/z calcd for $C_{28}H_{22}FNO_3$ $(M+NH_4)^+$ 457.1927, found 457.1918.

***(Z)*-Propyl-1-benzylidene-2-cyano-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-inde ne-2-carboxylate (5r).** Colorless solid; (200 mg, 91% yield); mp 163.5-166.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.0 Hz, 2H), 7.62-7.58 (m, 2H), 7.51-7.47 (m, 4H), 7.41-7.27 (m, 6H), 7.20-7.19 (m, 1H), 4.64 (t, *J* = 6.0 Hz, 1H), 3.88-3.68 (m, 3H), 3.60-3.54 (m, 1H), 1.58-1.39 (m, 2H), 0.79 ppm (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.9, 167.1, 142.2, 139.0, 138.0, 136.2, 135.0, 133.5, 129.6, 128.8, 128.7, 128.6, 128.3, 128.1, 127.9, 125.5, 123.7, 121.0, 117.4, 68.3, 57.2, 48.8, 41.1, 21.2, 10.2 ppm; HRMS (ESI) *m/z* calcd for $C_{29}H_{25}NO_3$ $(M+NH_4)^+$ 453.2178, found 453.2174.

(*Z*)-Butyl-1-benzylidene-2-cyano-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-inden e-2-carboxylate (5s). Colorless solid; (215 mg, 96% yield); mp 141.2-143.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.0 Hz, 2H), 7.62-7.58 (m, 2H), 7.51-7.47 (m, 4H), 7.39-7.29 (m, 6H), 7.20-7.18 (m, 1H), 4.63 (t, *J* = 6.0 Hz, 1H), 3.87-3.79 (m, 2H), 3.73-3.67 (m, 1H), 3.64-3.58 (m, 1H), 1.41-1.32 (m, 2H), 1.31-1.18 (m, 2H), 0.82 ppm (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.9, 167.1, 142.3, 139.0, 138.0, 136.2, 135.0, 133.5, 129.6, 128.8, 128.7, 128.6, 128.3, 128.2, 128.0, 125.5, 123.7, 121.0, 117.4, 66.6, 57.2, 48.8, 41.1, 29.8, 18.8, 13.5 ppm; HRMS (ESI) *m/z* calcd for $C_{30}H_{27}NO_3$ $(M+NH_4)^+$ 467.2334, found 467.2332.

***(Z)*-Isopropyl-1-benzylidene-2-cyano-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-indene-2-carboxylate (5t).** Colorless solid; (203 mg, 93% yield); mp 146-148°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 7.6 Hz, 2H), 7.62-7.60 (m, 2H), 7.53-7.48 (m, 4H), 7.40-7.28 (m, 6H), 7.18-7.16 (m, 1H), 4.73-4.63 m, 2H), 3.88-3.66(m, 2H), 1.04-1.02 (m, 3H), 0.88-0.87 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.8, 166.5, 142.3, 139.2, 137.2, 136.2, 135.1, 133.6, 129.6, 128.9, 128.7, 128.5, 128.4, 128.2, 128.1, 125.4, 123.8, 121.0, 117.5, 57.5, 48.9, 41.2, 21.2, 20.8 ppm; HRMS (ESI) *m/z* calcd for $C_{29}H_{25}NO_3$ $(M+NH_4)^+$ 453.2178, found 453.2174.

***(Z)*-tert-Butyl-1-benzylidene-2-cyano-3-(2-oxo-2-phenylethyl)-2,-3-di hydro-1H-indene-2-carboxylate (5u):** Colorless solid; (211 mg, 94% yield); mp 146-148°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 8.0 Hz, 2H), 7.61-7.55 (m, 4H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.36-7.27 (m, 4H), 7.16-7.14 (m, 1H), 4.65 (t, *J* = 6.8 Hz, 1H), 3.85-3.65 (m, 2H), 1.15 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.9, 165.8, 142.6, 139.4, 137.1, 136.3, 135.4, 133.6, 129.5, 129.0, 128.7, 128.6, 128.4, 128.2, 128.0, 125.3, 123.9, 120.9, 117.7, 84.3, 57.9, 48.9, 41.6, 27.1 ppm; HRMS (ESI) *m/z* calcd for $C_{30}H_{27}NO_3$ $(M+Na)^+$ 472.1888, found 472.1872.

***(E)*-Methyl-3-benzylidene-2-cyano-1-(2-(4-fluorophenyl)-2-oxoethyl)-2,3-dihydro-1H-cyclo-penta[*b*]quinoline-2-carboxylate (6a).** Colorless solid; (214 mg, 90% yield); mp 162-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 8.14-8.09 (m, 3H), 7.95 (s, 1H), 7.78-7.73 (m, 2H), 7.60-7.58 (m, 2H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.38-7.37 (m, 1H), 7.21-7.16 (m, 2H), 4.70 (t, *J* = 6.8 Hz, 1H), 3.94-3.79 (m, 2H), 3.44 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.1, 167.4, 164.8, 157.4, 149.0, 135.5, 134.4, 133.6, 132.4, 131.5, 131.2, 130.9 (d, *J* = 9.5 Hz), 130.0, 129.3, 129.2, 128.8, 128.4, 128.2, 127.8, 126.8, 118.8, 116.0 (d, *J* = 21.9Hz), 55.3, 53.5, 46.1, 41.4 ppm; HRMS (ESI) *m/z* calcd for $C_{30}H_{21}FN_2O_3$ $(M+H)^+$ 477.1614, found 477.1629.

***(E)*-Butyl-3-benzylidene-2-cyano-1-(2-(4-fluorophenyl)-2-oxoethyl)-2,3-dihydro-1H-cyclo-penta[b]quinoline-2-carboxylate (6b):** Colorless solid; (243 mg, 94% yield); mp 145.1-148.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (s, 1H), 8.14-8.10 (m, 3H), 7.95 (s, 1H), 7.78-7.71 (m, 2H), 7.62-7.60 (m, 2H), 7.54-7.50 (m, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.36-7.34 (m, 1H), 7.20 (t, *J* = 9.1 Hz, 2H), 4.70 (t, *J* = 6.8 Hz, 1H), 3.96-3.85 (m, 2H), 3.81-3.73 (m, 2H), 1.41-1.33 (m, 2H), 1.28-1.16 (m, 2H), 0.81 ppm (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.0, 166.9, 166.1 (d, *J* = 255.5 Hz), 157.6, 149.0, 135.1, 134.5, 133.8, 132.5, 132.4, 131.3, (d, *J* = 30.2 Hz), 131.0 (d, *J* = 9.5 Hz), 130.0, 129.4, 129.2, 128.9, 128.4, 128.2, 127.8, 126.7, 116.7, 116.5 (d, *J* = 21.9 Hz), 67.0, 55.5, 46.1, 41.5, 29.8, 18.8, 13.5 ppm; HRMS (ESI) *m/z* calcd for $C_{33}H_{27}FN_2O_3$ $(M+H)^+$ 519.2084, found 519.2075.

***(E)*-Isopropyl-3-benzylidene-2-cyano-1-(2-oxo-2-(p-tolyl)ethyl)-2,-3-dihydro-1H-cyclo-penta[*b*]quinoline-2-carboxylate (6c).** Colorless solid; (230 mg, 92% yield); mp 179.5-183.8 °C; ^{1}H NMR (400 MHz,

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$CDCl_3$) δ = 8.19 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.92 (s, 1H), 7.76-7.69 (m, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37-7.31 (m, 3H), 4.80-4.76 (m, 1H), 4.70 (t, *J* = 8.0 Hz, 1H), 3.96-3.78 (m, 2H), 2.45 (s, 3H), 1.08 (d, *J* = 6.1 Hz, 3H), 0.85 ppm (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.2, 166.3, 157.8, 148.9, 144.8, 134.7, 134.6, 134.1, 133.5, 131.4, 131.1, 129.8, 129.6, 129.5, 129.2, 129.0, 128.6, 128.4, 128.2, 127.8, 126.6, 116.9, 71.6, 55.8, 46.2, 41.5, 21.7, 21.2, 20.7 ppm; HRMS (ESI) *m/z* calcd for $C_{33}H_{28}N_2O_3$ $(M+H)^+$ 501.2178, found 501.2145.

***(E)*-Ethyl-2-cyano-3-(4-methylbenzylidene)-1-(2-oxo-2-phenyle thyl)-2,3-dihydro-1H-cyclo-penta[*b*]quinoline-2-carboxylate (6d).** Colorless solid; (210 mg, 86 % yield); mp 132.1-134.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 8.13-8.09 (m, 3H), 7.93 (s, 1H), 7.77-7.69 (m, 2H), 7.65-7.62 (m, 1H), 7.55-7.49 (m, 5H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.71 (t, *J* = 6.8 Hz, 1H), 4.00-3.90 (m, 3H), 3.85-3.79 (m, 1H), 2.39 (s, 3H), 1.04 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.7, 167.0, 157.9, 149.0, 139.2, 136.0, 134.1, 133.9, 133.8, 131.7, 131.5, 131.3, 129.9, 129.5, 129.2, 128.8, 128.3, 128.2, 127.8, 126.6, 116.8, 63.2, 55.6, 46.1, 41.7, 21.4, 13.4 ppm; HRMS (ESI) *m/z* calcd for $C_{32}H_{26}N_2O_3(M+H)^+$ 487.2021, found 487.2004.

***(E)*-Ethyl-3-benzylidene-2-cyano-1-(2-oxo-2-(thiophen-2-yl)ethyl)-2,3-dihydro-1H-cyclo-penta[*b*]quinoline-2-carboxylate (6e).** Colorless solid; (211 mg, 88 % yield); mp 163-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.96 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.78-7.76 (m, 1H), 7.73-7.69 (m, 2H), 7.61-7.59 (m, 2H), 7.53-7.49 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.37-7.35 (m, 1H), 7.19-7.17 (m, 1H), 4.68 (t, *J* = 5.3 Hz, 1H), 3.92-3.85 (m, 2H), 3.83-3.73 (m, 2H), 1.00 ppm (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.3, 166.7, 157.5, 149.0, 143.0. 135.1, 134.7, 134.6, 133.6, 133.0,131.4, 131.3, 129.9, 129.3, 129.2, 128.9, 128.4, 128.2, 127.8, 126.7, 116.7, 63.3, 55.5, 46.0, 41.7, 13.4 ppm; HRMS (ESI) *m/z* calcd for $C_{29}H_{22}N_2O_3S$ $(M+H)^+$ 479.1429, found 479.1401.

***(Z)*-Dimethyl1-benzylidene-3-(2-oxo-2-phenylethyl)-1H-Inde ne-2,2(3H)-dicarbo xylate (7a).** Pale Yellow solid; (189 mg, 86% yield); mp 64-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.2 Hz, 2H) 7.57 (d, *J* = 7.6 Hz, 1H), 7.52-7.47 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.31-7.25 (m, 5H), 7.23-7.27 (m, 2H), 4.97-4.94 (m, 1H). 3.67 (s, 3H), 3.60 (dd, J_1 = 19.3, J_2 = 9.1 Hz, 1H), 3.18-3.12 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.7, 170.2, 168.6, 144.3, 140.5, 139.0, 136.5, 130.2, 129.0, 128.4, 128.3, 127.9, 125.9, 124.0, 120.8, 67.8, 53.4, 52.2, 47.9, 42.7 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{25}O_5$ $(M+H)^+$ 441.1702, found 441.1723.

***(Z)*-Dimethyl1-benzylidene-3-(2-(4-fluorophenyl)-2-oxoethy)-1H-indene-2,2(3H)-dicarboxylate (7b).** Pale Yellow solid; (186 mg, 81% yield); mp 61-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92-7.88 (m, 2H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.32-7.28 (m, 4H), 7.24-7.20 (m, 2H), 7.16-7.13 (m, 1H), 7.05 (t, *J* = 8.0 Hz, 2H), 4.96-4.93 (m, 1H), 3.68 (s, 3H), 3.58 (dd, J_1 = 19.0, J_2 = 9.1 Hz, 1H), 3.16 (s, 3H), 3.10 ppm (dd, J_1 = 18.3, J_2 = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.2, 170.2, 168.7, 165.7 (d, *J* = 266.0 Hz), 144.2, 140.5, 139.0, 136.2, 132.9, 130.6, 130.5, 129.0, 128.3, 128.0, 127.4, 126.1, 124.0, 120.8, 115.5 (d, *J* = 21.9 Hz), 67.8, 53.2, 52.3, 48.0, 42.7 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}FO_5$ $(M+H)^+$ 459.1607, found 459.1626.

***(Z)*-Dimethyl-1-benzylidene-3-(2-oxo-2-(p-tolyl)ethyl)-1H-indene-2,2(3H)-dicarb oxylate (7c).** Pale Yellow solid; (182 mg, 80% yield); mp 68-71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.31-7.27 (m, 5H), 7.22-7.17 (m, 4H), 4.97-4.94 (m, 1H), 3.67 (s, 3H), 3.56 (dd, J_1 = 18.3, J_2 = 9.6 Hz, 1H), 3.17 (s, 3H), 3.14-3.09 (m, 1H), 2.36 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.3, 170.3, 168.6, 144.4, 143.8, 140.5, 139.1, 136.2, 134.0, 129.1, 129.0,128.3, 128.0, 127.9, 127.8, 127.3, 125.9, 124.0,120.7, 67.8, 53.1, 52.2, 48.0, 42.6, 21.5 ppm; HRMS (ESI) *m/z* calcd for $C_{29}H_{26}O_5$ $(M+H)^+$ 455.1858, found 455.1873.

***(Z)*-Dimethyl1-benzylidene-3-(2-oxo-2-(thiophen-2-yl)ethyl)-1,3-dihydro-2H-in dene-2,2-dicarboxylate (7d).** Pale yellow solid; (200 mg, 93% yield); mp 60-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60-7.56 (m, 3H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.32-7.25 (m, 5H), 7.23-7.20 (m, 2H), 7.06-7.03 (m, 1H), 4.94-4.91 (m, 1H), 3.65 (s, 3H), 3.49 (dd, J_1 = 17.5, J_2 = 8.4 Hz, 1H), 3.21 (s, 3H), 3.13 ppm (dd, J_1 = 17.5, J_2 = 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.6, 170.1, 168.6, 144.1, 143.7, 140.5, 138.9, 136.2, 133.4, 131.9, 129.0, 128.5, 128.4, 128.2, 128.0, 127.4, 126.0, 124.1, 120.8, 67.8, 53.1, 52.2, 47.9, 43.1 ppm; HRMS (ESI) *m/z* calcd for $C_{26}H_{22}O_5S$ $(M+H)^+$ 447.1266, found 447.1276.

***(E)*-Dimethyl-3-benzylidene-1-(2-(4-fluorophenyl)-2-oxoethyl)-1-H-cyclopenta[*b*]quinoline-2,2(3H)-dicarboxylate (7e).** Colorless solid; (185 mg, 87% yield); mp 149-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 8.10 (d, *J* = 9.1 Hz, 1H), 7.98-7.95 (m, 2H), 7.91 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 6.8 Hz, 2H), 7.47 (t, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 6.8 Hz, 2H), 7.31 7.29 (m, 1H), 7.10 (t, *J* = 8.4 Hz, 2H), 4.98 (t, *J* = 6.0 Hz, 1H), 3.65-3.59 (m, 1H), 3.57 (s, 3H), 3.39 (s, 3H), 3.38-3.32 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.8, 169.5, 168.4, 159.4, 148.6, 136.4, 135.9, 135.7, 132.8, 132.7, 131.1, 130.9, 130.7, 130.6, 129.4, 129.1, 128.3, 128.2, 128.0, 127.7, 126.2, 115.8, 115.6, 66.3, 53.0, 52.3, 45.4, 41.9 ppm; HRMS (ESI) *m/z* calcd for $C_{31}H_{24}FNO_5$ $(M+H)^+$ 510.1716, found 510.1710.

***(E)*-Dimethyl-3-benzylidene-1-(2-oxo-2-(p-tolyl)ethyl)-1H-cyclop - enta[*b*]quinoline-2,2(3H)-dicarboxylate (7f).** Colorless solid; (196 mg, 78% yield); mp 175.2-178.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (s,1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 6.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.37 (t, *J* = 8.4 Hz, 2H), 7.31-7.29 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.99 (t, *J* = 6.8 Hz, 1H), 3.63-3.59 (m, 1H), 3.57 (s, 3H), 3.41-3.34 (m, 1H), 3.39 (s, 3H), 2.39 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.0, 169.5, 168.4, 159.5, 148.6, 144.2, 136.4, 136.2, 135.7, 133.9, 131.0, 129.3, 129.2, 129.2, 129.1, 128.4, 128.1, 128.0, 127.8, 126.1, 66.3, 52.9, 52.5, 45.4, 41.8, 21.6 ppm; HRMS (ESI) *m/z* calcd for $C_{32}H_{28}NO_5$ $(M+H)^+$ 506.1967, found 506.1973.

***(Z)*-Diethyl-1-benzylidene-5-fluoro-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (7g).** Yellow solid; (200mg, 87% yield); mp 78-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 9.6 Hz, 2H), 7.56-7.51 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 6.8 Hz, 2H), 7.24-7.22 (m, 1H), 7.18 (s, 1H), 7.00-6.98 (m, 2H), 4.92 (t, *J* = 6.8 Hz, 1H), 4.16-4.07 (m, 2H), 3.71-3.67 (m, 1H), 3.62-3.55 (m, 2H), 3.20 (dd, J_1 = 19.1, J_2 = 6.0 Hz, 1H), 1.17 (t, *J* = 6.8 Hz, 3H), 0.88 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.2, 169.4, 168.0, 163.3 (d, *J* = 245.9 Hz), 146.7 (d, *J* = 7.6 Hz), 137.6, 136.6, 136.3 (d, *J* = 13.3 Hz), 133.1, 128.6, 128.2, 128.0, 127.9, 127.9, 127.3, 125.5, 122.0 (d, J = 34.3 Hz), 115.1 (d, *J* = 23.8 Hz), 111.2 (d, *J*

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= 22.8 Hz), 68.3, 62.1, 61.7, 47.5, 42.2, 13.7, 13.3 ppm; HRMS (ESI) *m/z* calcd for $C_{30}H_{31}FO_5$ $(M+H)^+$ 487.1921, found 487.1903.

***(E)*-Diethyl-3-benzylidene-1-(2-oxo-2-(p-tolyl)ethyl)-1H-cyclopenta[*b*]quinoline-2,2(3H)-dicarboxylate (7h).** Yellow solid; (210 mg, 77% yield); mp 62-65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (s,1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.73-7.70 (m, 3H), 7.66 (t, *J* = 6.8 Hz, 1H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.38-7.34 (m, 2H), 7.31-7.28 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 4.95 (t, *J* = 7.6 Hz, 1H), 4.03-4.39 (m, 2H), 3.95-3.91 (m, 1H), 3.84-3.8 (m, 1H), 3.60 (dd, J_1 = 18.3, J_2 = 6.0 Hz, 1H), 3.44 (dd, J_1 = 18.3, J_2 = 7.6 Hz, 1H), 2.39 (s, 3H), 1.03 (t, *J* = 7.6 Hz, 3H), 0.98 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.0, 169.0, 168.0, 157.7, 148.5, 144.2,136.4,136.1, 135.9, 133.9, 131.0, 130.9,129.6, 129.3, 129.2, 129.0, 128.4, 128.2, 128.1, 127.9, 127.8, 126.0, 66.5, 62.1, 61.9, 45.3, 41.7, 21.6, 13.6, 13.5 ppm; HRMS (ESI) *m/z* calcd for $C_{34}H_{31}NO_5$ $(M+H)^+$ 534.2280, found 534.2320.

Experimental procedure for control experiments:

Step 1 (Scheme 6, eqn 1)

To the 10 mL RB flask was added *α,β*-unsaturated ketone 3f (0.5 mmol), Cs_2CO_3 (10 mol%), and dimethylmalonic esters 4g (0.6 mmol) and allowed to stirred at heat at 50 °C for 3 h. It was diluted with 10 mL of dilute HCl. The reaction mixture was extraction with ethyl acetate (2 x 50 mL) and distilled water (2 x 10 mL). Finally, combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by chromatography on silica gel using ethyl acetate/hexane as the eluent to yield the **8** as desired products.

Step 2 (Scheme 6, eqn 2)

To the 10 mL RB flask was added Michael adduct **8** (0.5 mmol) and Cs_2CO_3 (15 mol%), allowed to stirred at heat at 50 °C for 3-6 h. After completion of reaction indicated by TLC, it was diluted with 10 mL of dilute HCl. The reaction mixture was extraction with ethyl acetate (2 x 50 mL) and distilled water (2 x 10 mL). Finally, combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by chromatography on silica gel using ethyl acetate/hexane as the eluent to yield the **7c** as desired products in 80% yield.

Dimethyl2-(3-oxo-1-(2-(phenylethynyl)phenyl)-3-(p-tolyl)propyl)-malonate (8). Pale yellow oil; (182 mg, 80 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.4 Hz, 2H), 7.56-7.54 (m, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.36-7.34 (m, 3H), 7.32-7.30 (m, 1H), 7.23-7.16 (m, 4H), 4.80-4.73 (m, 1H), 4.28 (d, *J* = 8.0 Hz, 1H), 3.81-3.77 (m, 1H), 3.68 (s, 3H), 3.65-3.60 (m, 1H), 3.56 (s, 3H), 2.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.3, 168.8, 168.3, 143.7, 141.8, 134.2, 132.8, 131.5, 129.2, 129.1, 128.4, 128.3, 128.2, 128.2, 126.9, 123.1, 122.5, 94.6, 87.4, 55.3, 52.5, 52.4, 40.2, 39.1, 21.5 ppm; HRMS (ESI) *m/z* calcd for $C_{29}H_{26}O_5$ $(M+H)^+$ 455.1858, found 455.1891.

Conflicts of interest

The authors declare no conflict of interest.

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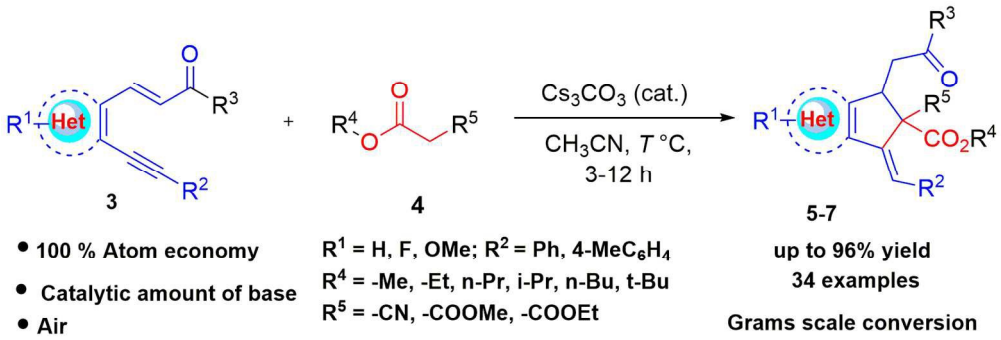

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