RSC Advances

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

$FeCl_3$ catalysed multicomponent divergent synthesis of a library of indeno-fused heterocycles†

Cite this: *RSC Advances*, 2013, **3**, 3291

Sunil Rana,[a] Mike Brown[b] and Chhanda Mukhopadhyay*[a]

Received 9th November 2012,
Accepted 18th December 2012

DOI: 10.1039/c2ra23332k

www.rsc.org/advances

A simple, straightforward and versatile multicomponent synthetic protocol for indeno-fused heterocycles, namely diindeno[1,2-b:2′,1′-e]pyridine, indeno[1,2-b]quinoline and indeno[1,2-b]cyclopenta[e]pyridine derivatives, has been developed. The strategy involves the one pot three component reaction of enaminone, dialkyl but-2-ynedioate and 1,3-indanedione catalysed by $FeCl_3$ in acetonitrile under reflux. The presence of rotamers in the products with 2- and 3-substituted anilines as the amine component adds some interesting features to this expeditious domino reaction. In the course of the reaction, four new bonds (two C–C and two C–N bonds) and one stereocenter are formed in one operation. Mild reaction conditions, operational simplicity, wide substrate scope, product diversity and overall good yield make this reaction highly efficient for the library synthesis of indeno-fused heterocycles.

Introduction

The search for new multicomponent reactions (MCRs) involving domino processes leading to the formation of structurally important frameworks and drug molecules by pot, atom and step economic (PASE) methods is an active area of research in modern organic synthesis.[1] The remarkable features of MCRs that make them special are their ability to generate structurally diverse and complex compounds from simple starting materials without the isolation of intermediates, avoiding the tedious protection and deprotection of functional groups, thus minimizing both waste production and expenditure of human labor.[2] Consequently, these reactions are environmentally friendly, and often proceed with excellent stereoselectivities.[3] Therefore, the development of new MCRs is a continuous challenge to modern synthetic chemists.

The indenopyridine nucleus is the building block of the 4-azafluorenone group of alkaloids, represented by its smallest member, onychine.[4] Indenopyridine derivatives, having strong antispermatogenic activity are regularly designed for the development of male contraceptives.[5] Due to their antiproliferative activity, they are also potent anticancer agents.[6] These compounds are also used for the treatment of arteriosclerosis and hyperlipoproteinemia.[7] Besides these, many indenopyridine-containing compounds exhibit antihistamine,[8] adenosine A2a receptor antagonistic,[9] calcium modulating,[10] anti-inflammatory[11] and herbicidal activity.[12] On the other hand, indenoquinoline derivatives show a wide variety of biological activities such as antitumor,[13] anti-inflammatory,[14] antimalarial[15] and 5-HT-receptor binding activity.[16] Moreover, they also act as inhibitors for steroid reductase[17] and acetylcholinesterase inhibitors for the treatment of Alzheimer's disease.[18]

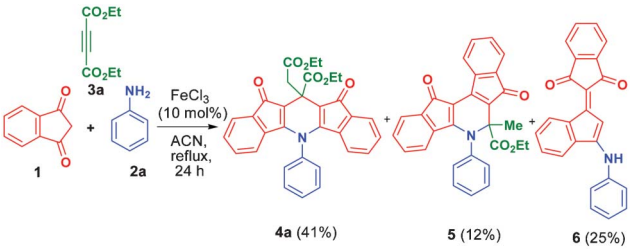
Apart from the Hantzsch-type synthesis,[19] there are only a few other methods available in the literature for the synthesis of indenopyridines.[20] Indenoquinoline compounds can be synthesized from Baylis–Hillman adducts,[21] by the imino Diels–Alder reaction,[22] the aza-Bergman cyclization,[23] and few other methods.[24] The paucity of efficient and general synthetic strategies for these heterocycles presents a challenge to modern organic chemists. In our approach, we have synthesized these two important heterocyclic cores by the coupling of enaminone, dialkyl acetylenedicarboxylate and 1,3-indanedione catalysed by $FeCl_3$. Over the past few years iron salts have been efficiently used as a catalyst for C–H functionalisation,[25] and C–C,[26] C–N,[27] C–O,[28] and C–S[29] bond formation in many organic syntheses. Several intra- and intermolecular cyclisation reactions are also facilitated by iron salts.[26a,30] These remarkable features of iron salts and our previous work on $FeCl_3$-catalysed double aminomethylation at the α-position of 1,3-dicarbonyl compounds[31] encouraged us to investigate these versatile transition metal salts as catalysts for the synthesis of various heterocyclic compounds.

Results and discussion

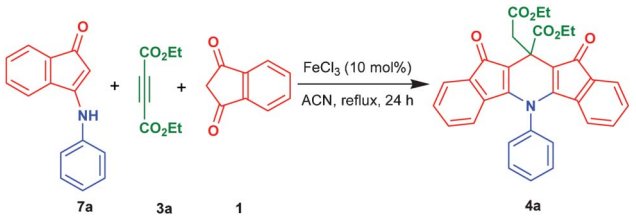
As a part of our continuing research into attaining high pot, atom and step economic reactions, we initially investigated the multicomponent reaction of diethyl acetylenedicarboxylate (1 eq.), aniline (1 eq.) and 1,3-indanedione (2 eq.) catalysed by

[a]Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata-700009, India. E-mail: cmukhop@yahoo.co.in; Tel: 91-33-23371104
[b]Bruker BioSpin, 2700 Technology Forest Drive, Woodlands, Texas 77381, USA

† Electronic supplementary information (ESI) available: all ^1H and ^{13}C NMR spectra. CCDC reference numbers 905874–905877. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ra23332k



Scheme 1 Pseudo four component reaction of 1,3-indanedione (2 mmol), diethyl acetylenedicarboxylate (1 mmol) and aniline (1 mmol).



Scheme 3 Three component reaction between enaminone (**7a**), 1,3-indanedione (**1**) and diethyl acetylenedicarboxylate (**3a**).

$FeCl_3$ in acetonitrile under reflux. We obtained **4a** (41% yield) as the major product, along with **5** and **6** as side products in significant quantities (isolated yields of 12% and 25%, respectively) (Scheme 1). Compound **6** is known and the characterization data are comparable with the literature values.[32] Compound **5** is unknown its structure was unequivocally confirmed by single crystal X-ray diffraction experiments (see Supplementary Information†) along with ^1H and ^{13}C NMR data.

The methodology required specific modification to avoid unwanted side products (**5** and **6**) and to increase the yield of the target molecule **4a**. After searching the literature we found that Shu-Jiang Tu and his group synthesised a similar type of indeno-fused heterocycle by the three component reaction of enaminone, 1,3-indanedione and aldehyde (Scheme 2).[24a] Inspired by their work, we modified our methodology and used enaminone **7a** (formed from aniline and 1,3-indanedione)[33] (1 eqv.), diethyl acetylenedicarboxylate (1 eqv.) and 1,3-indanedione (1 eqv.), maintaining the other reaction conditions the same as before (Scheme 3).

To our delight, after this modification, we obtained **4a** in 75% isolated yield; the side products **5** and **6** disappeared. This reaction differs from that of the previous group in terms of the use of dialkyl acetylenedicarboxylate in place of an aldehyde, which expands the scope of the synthesis of indeno-fused heterocycles. Another interesting feature is that here the cyclisation reaction occurs through the same carbon of the triple bond, which is a promising phenomenon for the further development of new cyclisation reactions. We then took the combination of reactants in Scheme 3 as model reaction to optimize the reaction conditions and attempted the reaction with various Lewis acids, but $FeCl_3$ (anhydrous) was found to be the best catalyst and was superior to $ZnCl_2$, $AlCl_3$, $FeBr_3$ (anhydrous forms) and other Lewis acids, as indicated by the results shown in Table 1. Only 10 mol% of $FeCl_3$ (anhydrous) was sufficient to obtain the maximum yield of the product in six hours, and further increasing the amount of catalyst and time did not improve the yields. A solvent screening experiment was also done and the result revealed that protonated solvents like ethanol and methanol decreased the yield of the product due to the formation of **6** in significant amounts. Among different non protic solvents like THF, ACN, toluene, DCM, DMF, DMSO and DCE, acetonitrile under reflux gave the maximum yield of **4a**. A stoichiometric ratio of enaminone : diethyl acetylenedicarboxylate : 1,3-indanedione (1 : 1.1 : 1.1) in the presence of 10 mol% $FeCl_3$ in refluxing acetonitrile was found to be the optimum conditions for the maximum yield of the desired product.

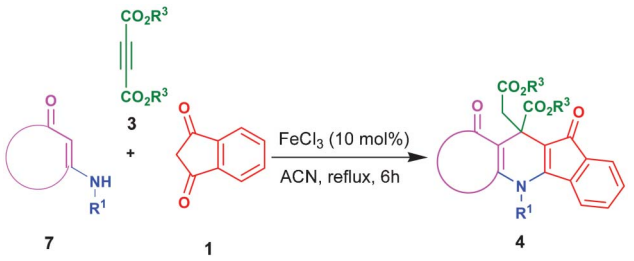
The initial observations showed us several options to synthesize a variety of indeno-fused compounds by simply varying the type of enaminone, formed from various cyclic-1,3-diketones and amines (Scheme 4, Table 2). Enaminones formed from six membered cyclic-1,3-diketones like 1,3-cyclohexanedione, 5-phenyl-1,3-cyclohexanedione and 3,3-dimethylcyclohexanedione gave access to indeno[1,2-b]quinoline derivatives, and the enaminone formed from 1,3-

Scheme 2 Synthesis of a similar type of indeno-quinoline derivatives.

Table 1 Choice of catalyst for the synthesis of ethyl-5,11-dihydro-10,12-dioxo-11-(ethoxycarbonyl)methyl-5-phenyl diindeno[1,2-b:,2′,1′-e]pyridine-11-carboxylate (**4a**)[a]

Entry	Catalyst (mol%)	Reaction time (h)	Isolated yield (%)
1	AcOH (10)	24	25
2	$H_3PW_{12}O_{40}$ (10)	24	29
3	SnO_2 (10)	24	21
4	4N HCl (1 ml)	24	10
5	4N H_2SO_4 (1 ml)	24	13
6	4N H_3PO_4 (1 ml)	24	22
7	TSOH (10)	24	60
8	anhyd. $FeCl_3$ (5)	24	59
9	anhyd. $FeCl_3$ (10)	24	75
10	anhyd. $FeCl_3$ (10)	6	75
11	anhyd. $FeCl_3$ (20)	24	74
12	$Fe(NO_3)_2$ (10)	24	55
13	anhyd. $FeBr_3$ (10)	24	60
14	anhyd. $AlCl_3$ (10)	24	41
15	$InCl_3$ (10)	24	62
16	anhyd. $ZnCl_2$ (10)	24	46
17	none	24	trace

[a] The reaction was performed using enaminone **1** (1mmol), diethyl acetylenedicarboxylate (1.1 mmol) and 1,3-indanedione (1.1 mmol) in 5 mL acetonitrile under reflux (80–82 °C).



Scheme 4 Versatile synthesis of diindeno[1,2-b:,2′,1′-e]pyridines and indeno[1,2-b]quinolines.

indanedione produced diindeno[1,2-b:2′,1′-e]pyridine derivatives.

Incorporating a number of aromatic and aliphatic amines in the enaminone part increased the versatility of the reaction. Aniline and substituted anilines with both electron withdrawing (Cl, Br, *etc.*) and donating groups (Me and OMe) at different positions of the phenyl ring gave good results for the yields of the products. The use of benzyl amine, *n*-butyl amine and 1-aminomethyl naphthalene further increased the scope of the reaction. Dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxylate were used as the dialkylbut-2-ynedioate part. In all the cases the yields of the reactions were moderate to good. With nitro-anilines the yields of the reaction were very low and we could not purify the products.

All the prepared compounds depicted in Table 2 were fully characterized by IR, ^{1}H NMR, ^{13}C NMR and CHN analyses. Finally, the structures of two representative compounds, one each from the diindeno[1,2-b:,2′,1′-e]pyridines and the indeno[1,2-b]quinolines, were unambiguously confirmed by single crystal X-ray diffraction experiments (entries **4c** and **4t**, Table 2), and their ORTEP diagrams are shown in Fig. 1 and Fig. 2 respectively.

Interestingly, in the case of the indeno[1,2-b]quinoline compounds, when 2- and 3-substituted anilines were used in the enaminone part, the ^{1}H NMR of the products showed a mixture of rotamers (rotational isomers), or more specifically atropisomers arising due to restricted rotation around a C–N bond (Fig. 1), and this phenomenon may have been overlooked by the previous group in the formation of similar types of heterocycles.[24a] Atropisomerism is common for biphenyl type systems.[34] The marked hydrogen (shown in a ring in Fig. 3) of the indane part generally appears as a doublet ($J \approx$ 7.5 Hz) at δ 5.00–5.50 ppm for the products formed with aniline or 4-substituted anilines. In the case of 2- and 3-substituted anilines, we obtain two closely spaced doublets for the marked hydrogen in the ^{1}H NMR spectrum (Fig. 4). Again, the methyl group of the aromatic amine appears as two singlets in both the ^{1}H and ^{13}C NMR spectra. This clearly indicates the presence of rotamers for products obtained from 2- and 3-substituted anilines. We were not able to separate the rotamers, which may be due to the fact that the interconversion between the rotamers occurs even at room temperature (25–27 °C). In case of diindeno[1,2-b:,2′,1′-e]pyridines, a rotameric mixture was obtained only with 2-methyl aniline.

Diastereoisomeric mixtures were obtained when 5-phenyl-1,3-cyclohexanedione was used as the enaminone part (entries **4m** and **4n**, Table 2) and the diastereomeric ratios were determined from the crude ^{1}H NMR spectra of the products.

After a number of interesting observations, we tried to increase the scope of the reaction by introducing the enaminone formed from 1,3-cyclopentanedione in this three component reaction under the same standardized reaction conditions. The expected product **9** was not obtained. Instead, we obtained **10** (Scheme 5) which was formed by the hydrolysis of the CO_2R^3 of the alkoxycarbonylmethyl moiety of **9**, followed by decarboxylation (shown in the mechanism).

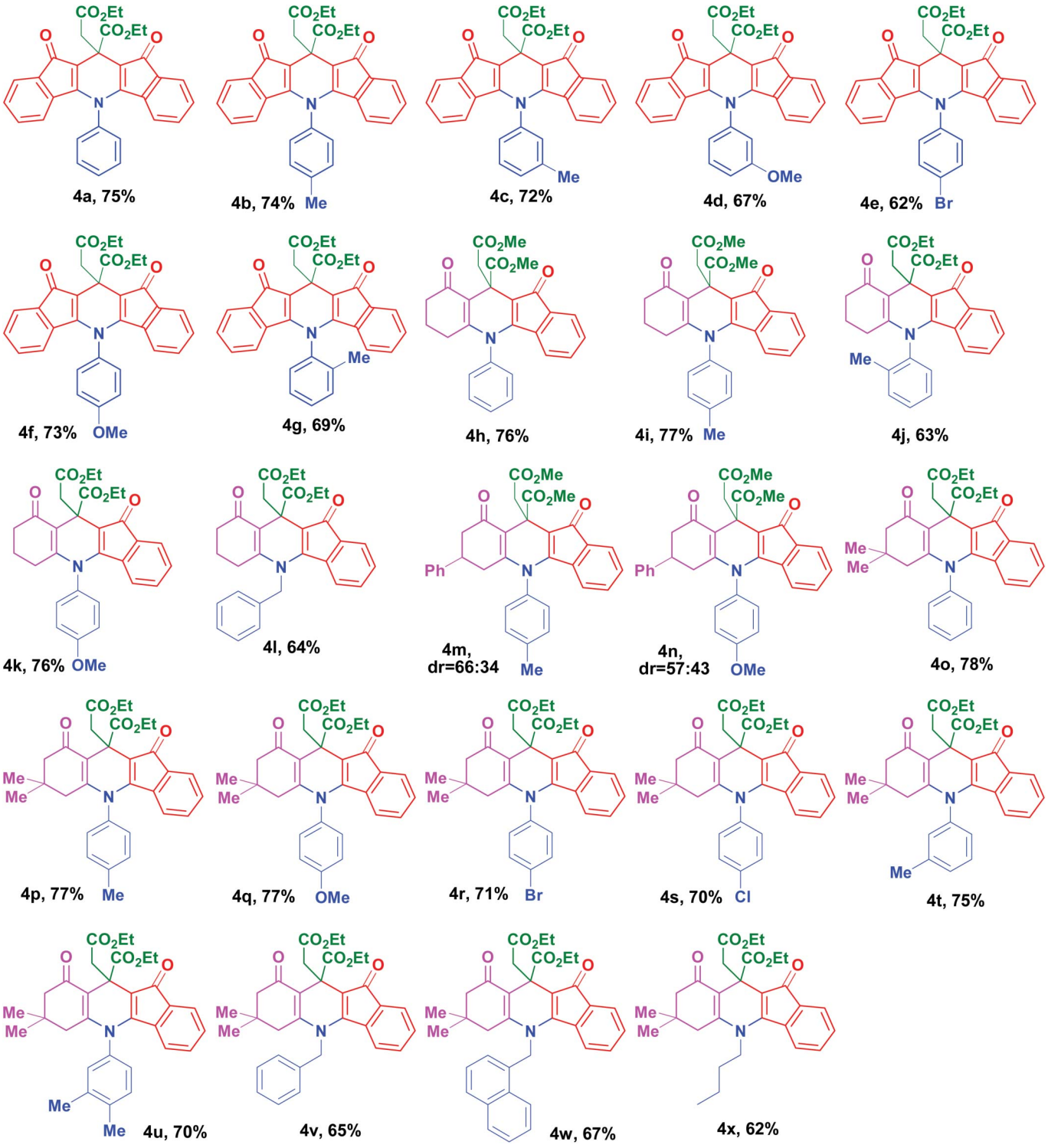
We attempted the reaction with six different enaminones (formed from six different amines) of 1,3-cyclopentanedione, but in all the cases the product **10** was obtained and we did not find traces of product **9**. Similarly, when 2- and 3-methyl anilines were used in the enaminone part, rotameric mixtures were obtained (entries **10f** and **10d**, Table 3) as before.

All six compounds prepared were fully characterized by ^{1}H NMR, ^{13}C NMR, IR and CHN analyses, and the structure of **10** was unequivocally confirmed by the single crystal X-ray diffraction experiment for one of the entries (**10a**) of Table 3, and the ORTEP plot is shown in Fig. 5.

A mechanistic rationale exhibiting a probable sequence of events for the indeno-fused heterocycles is given in Scheme 6. First, 1,3-indanedione in its enol form reacts with dialkyl acetylenedicarboxylate to form an intermediate (**A**). **A** then undergoes Michael addition with the enaminone followed by a condensation reaction, leading to cyclisation by the elimination of water to give the final product **4**. $FeCl_3$ may activate the triple bond by coordinating with it in the formation of the intermediate **A**. It also facilitates the Michael addition step, which is supported by the available literature.[26a,35] The formation of **10** may be visualized by the elimination of $-OR^3$ from the previously formed **4** to form the lactone **B**, which is then attacked by water to form **C**. Finally, a decarboxylation step occurs by the elimination of CO_2 to form the product **10**. We were not able to isolate the intermediates **A**, **B** or **C**, but these sequences of steps give a clear view of the mechanism of the reaction. In the formation of **10**, the generation of the intermediate **B** is crucial, and in case of the enaminone formed from 1,3-cyclopentanedione, **B** may be more stable than that formed from a six membered 1,3-diketone, which may be the reason for the formation of **10** only in the case of the enaminone formed from 1,3-cyclopentanedione. Similarly, the formation of the side product **5** in Scheme 1 may be visualized by the hydrolysis mechanism.

This new multicomponent reaction also suffers from limitations regarding the use of 1,3-indanedione, which is a specific component for this reaction. When other cyclic 1,3-diketones were used to substitute for indane-1,3-dione, the desired product was not obtained. Instead, a complex product mixture was obtained, from which no characteristic product could be separated. Nevertheless, this reaction is very

Table 2 Library synthesis of diindeno[1,2-b:,2′,1′-e]pyridines and indeno[1,2-b]quinolines[a]



[a] Compound numberings and percentage yields are shown in the table along with the structures.

promising as the coupling occurs through only one of the carbons of the triple bond, which is a significant phenomenon for the further development of new heterocycle libraries.

Conclusion

In summary, we have developed a simple and divergent multicomponent domino synthesis of diindeno[1,2-

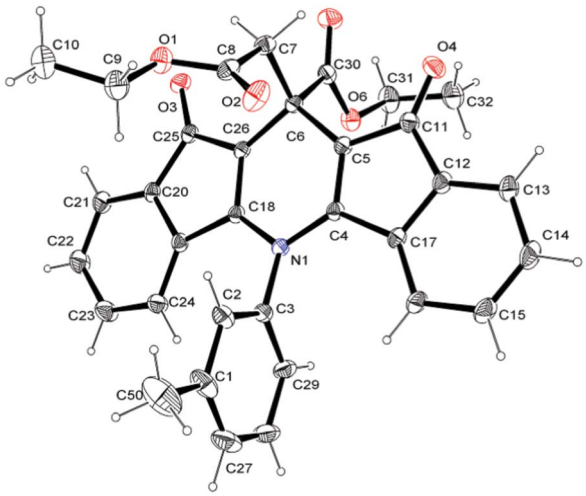


Fig. 1 ORTEP plot of a single crystal of the diindeno[1,2-b:,2′,1′-e]pyridine **4c** (Table 2) (CCDC 905876†) showing the crystallographic numbering.

b:2′,1′-e]pyridine, indeno[1,2-b]quinoline and indeno[1,2-b]cyclopenta[e]pyridine derivatives by the reaction of enaminone, dialkyl acetylenedicarboxylate and 1,3-indanedione catalyzed by $FeCl_3$ in acetonitrile under reflux in good yields. It is worth mentioning that in the course of these reactions, four new bonds (two C–C and two C–N) and one stereocenter are formed in one operation. Furthermore, the scope and limitations of this reaction were established, which enables further modifications leading to molecular diversity. Importantly, this method is suitable for library generation, which makes the methodology more attractive for organic synthesis.

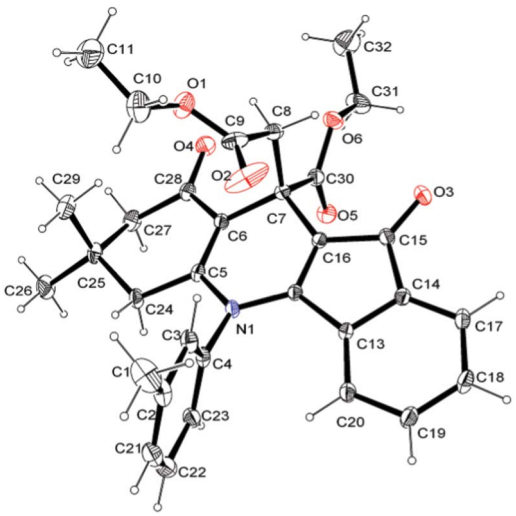


Fig. 2 ORTEP plot of a single crystal of the indeno[1,2-b]quinoline **4t** (Table 2) (CCDC 905875†) showing the crystallographic numbering.

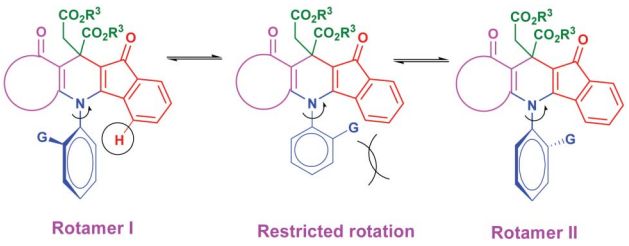


Fig. 3 Interconversion between rotamers.

Experimental section

General information

^1H and ^{13}C spectra were obtained on a Bruker 300 MHz instrument at 300 MHz and 75 MHz respectively. DEPTQ-135 experiments were performed on a Bruker 300 MHz instrument at 75 MHz. Chemical shifts are reported in parts per million (ppm) downfield from an internal TMS (trimethylsilane) reference. Coupling constants (*J*) are reported in hertz (Hz), and spin multiplicities are represented by the symbols s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), dt (doublet of triplet) and m (multiplet). IR spectra were recorded on a Perkin Elmer Spectrophotometer RX/FT-IR system. Band positions are reported in reciprocal centimeters (cm^{-1}). The CHN analyses were carried out on a 2400 Series II CHNS Analyzer, Perkin Elmer USA. X-ray diffraction was done on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo Kα (λ = 0.71073 Å) radiation. Melting points were determined on an electrical melting point apparatus with an open capillary. The progress of the reaction was checked by TLC using 300–400 mesh silica gel. Column chromatography was performed using 60–120 mesh silica gel. All the available reagents were purchased from commercial

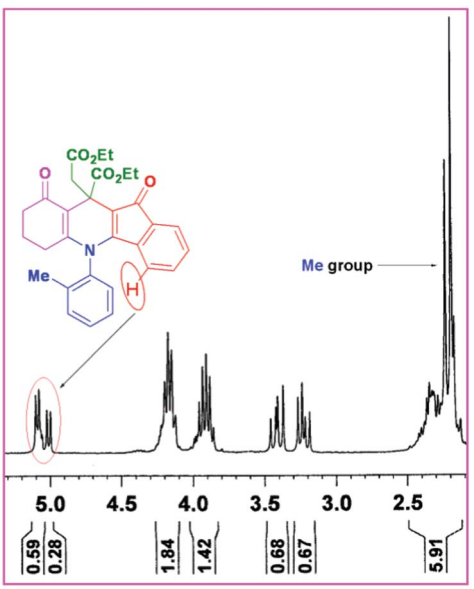
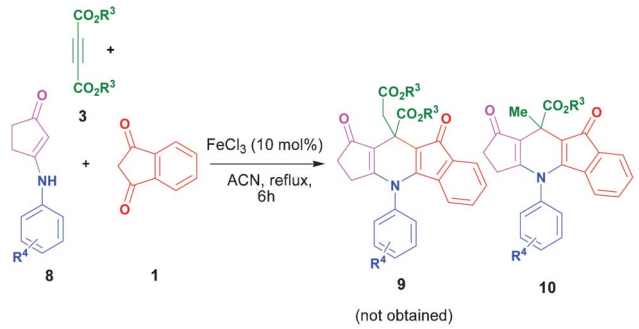


Fig. 4 Presence of rotamers in the ^1H NMR spectrum of **4j**.



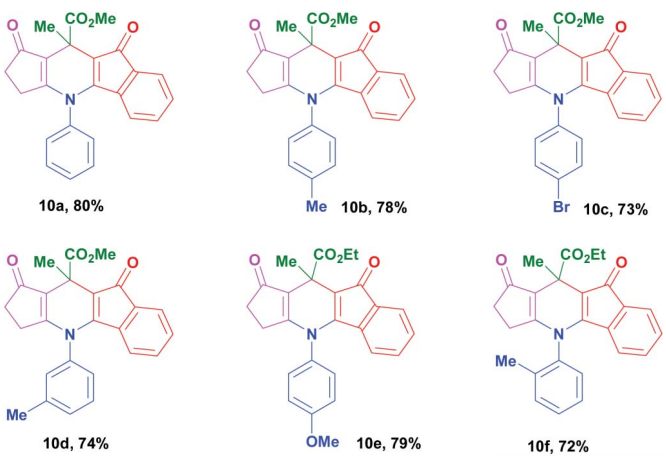
Scheme 5 Three component reaction of enaminone (formed from 1,3-pentanedione and aromatic amine), dialkyl acetylenedicarboxylate and 1,3-indanedione.

sources and were used without purification. Enaminones were prepared according to the standard literature procedures. All the solvents used during the reactions were distilled for purity.

General procedure for the synthesis of indeno-pyridine, indeno-quinoline and indeno-cyclopenta-pyridine derivatives

Enaminone (1 mmol), dialkyl acetylenedicarboxylate (1.1 mmol), 1,3-indanedione (1.1 mmol), anhyd. $FeCl_3$ (0.1 mmol) and acetonitrile (5 ml) were added to a 25 ml round bottomed flask fitted with a refluxing condenser with a calcium chloride guard tube, and the resulting mixture was refluxed for 6 h in an oil bath. After the completion of the reaction as indicated by TLC, acetonitrile was removed by rotary evaporation under vacuum. To the crude mixture 20 ml water was added and product was extracted with 20 ml dichloromethane to remove $FeCl_3$. Dichloromethane was removed by rotary evaporation under reduced pressure. The crude product was then purified by column chromatography using silica gel (60–120 mesh) with 15% ethyl acetate in petroleum ether (60°–80 °C) as the eluent.

Table 3 Synthesis of indeno[1,2-b]cyclopenta[e]pyridine derivatives[a]



[a] Compound numberings and percentage yields are shown in the table along with the structures.

Ethyl-5,11-dihydro-10,12-dioxo-11-(ethoxycarbonyl)methyl-5-phenyl diindeno[1,2-b:2′,1′-e]pyridine-11-carboxylate (4a)

(Table 2, entry 1): Yield 75% (389 mg); red solid; m.p.: 202–204 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2984, 1728, 1687, 1623, 1455, 1383, 1194, 1021, 848, 761, 714; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.80–7.62 (5H, m, ArH), 7.41 (2H, d, J = 6.9 Hz, ArH), 7.16 (2H, t, J = 7.5 Hz, ArH), 6.93 (2H, t, J = 7.5 Hz, ArH), 5.48 (2H, d, J = 7.5 Hz, ArH), 4.28 (2H, q, J = 7.2 Hz, OCH_2), 3.98 (2H, q, J = 7.2 Hz, OCH_2), 3.46 (2H, s, CH_2), 1.29 (3H, t, J = 7.2 Hz, CH_3), 1.00 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 171.6, 171.2, 156.4, 138.7, 136.6, 133.3, 131.8, 131.2, 130.1, 129.7, 121.9, 121.3, 112.0, 62.1, 59.9, 42.8, 38.2, 14.1, 14.0; Anal. calcd. for $C_{32}H_{25}NO_6$; C: 73.98; H: 4.85; N: 2.70. Found: C: 74.23; H: 4.76; N: 2.71%.

Ethyl-5,11-dihydro-10,12-dioxo-11-(ethoxycarbonyl)methyl-5-(4-methylphenyl) diindeno[1,2-b:2′,1′-e]pyridine-11-carboxylate (4b)

(Table 2, entry 2): Yield 74% (394 mg); red solid; m.p.: 164–166 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2980, 1738, 1727, 1692, 1582, 1385, 1354, 1207, 1011, 852; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.65 (2H, d, J = 7.5 Hz, ArH), 7.55–7.47 (4H, m, ArH), 7.25 (2H, t, J = 7.5 Hz, ArH), 7.03 (2H, t, J = 7.5 Hz, ArH), 5.62 (2H, d, J = 7.5 Hz, ArH), 4.36 (2H, q, J = 7.2 Hz, OCH_2), 4.05 (2H, q, J = 7.2 Hz, OCH_2), 3.54 (2H, s, CH_2), 2.68 (3H, s, CH_3), 1.38 (3H, t, J = 7.2 Hz, CH_3), 1.08 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 171.7, 171.2, 156.5, 141.5, 136.6, 136.0, 133.4, 131.7, 130.6, 129.6, 121.8, 121.4, 111.9, 62.1, 59.9, 42.8, 38.2, 21.6, 14.1, 14.0; Anal. calcd. for $C_{33}H_{27}NO_6$; C: 74.28; H: 5.10; N: 2.63. Found: C: 74.52; H: 5.03; N: 2.70%.

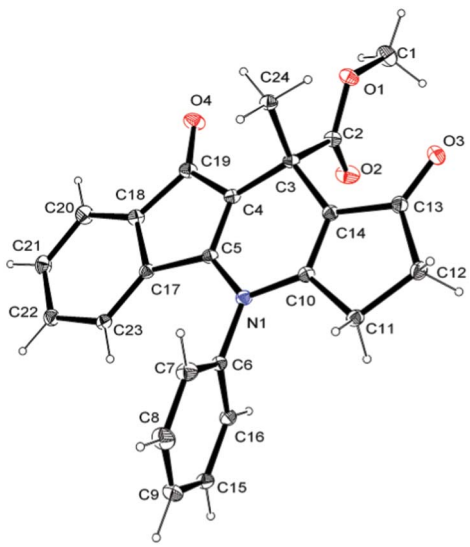
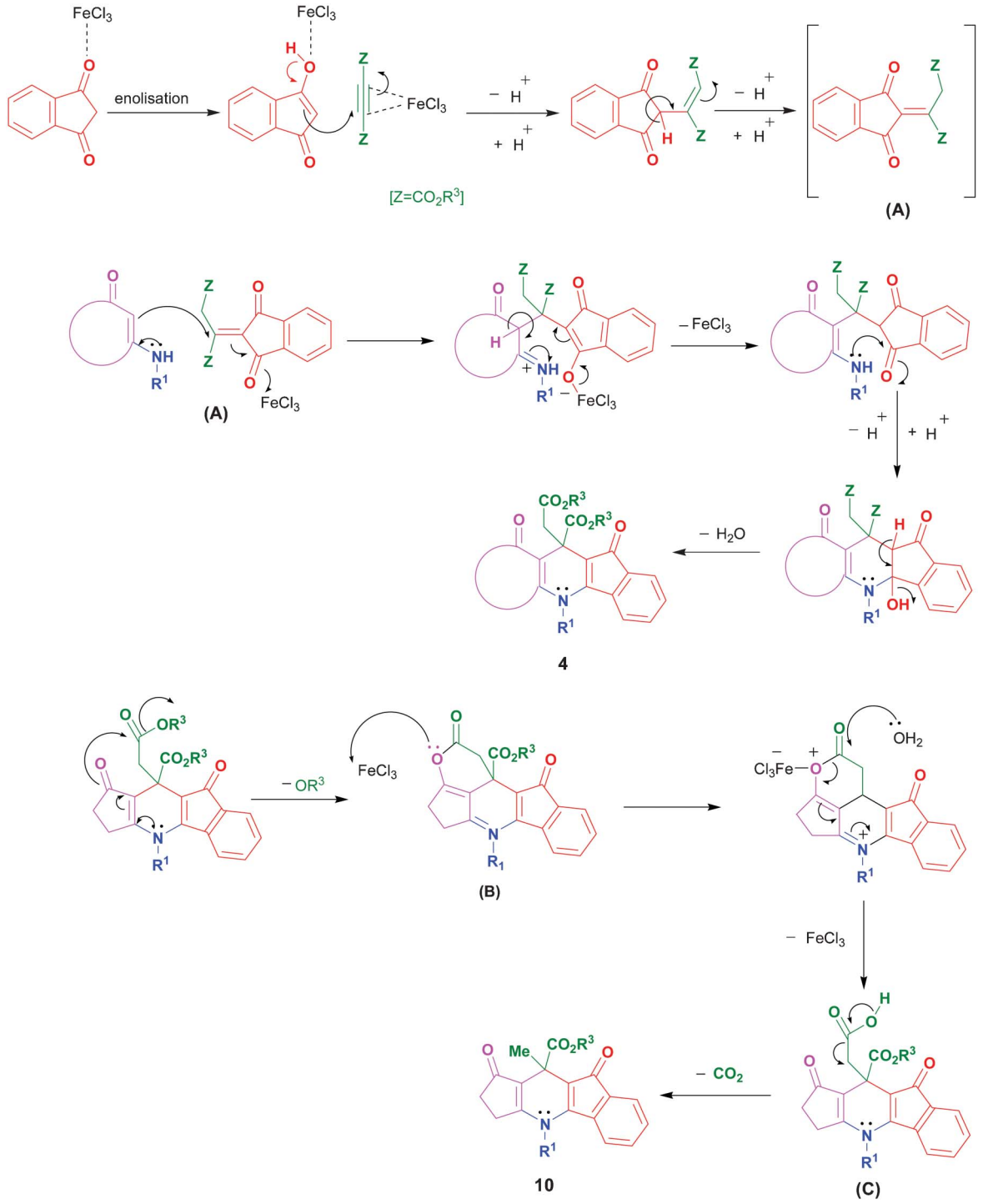


Fig. 5 ORTEP plot of a single crystal of the indeno[1,2-b]cyclopenta[e]pyridine **10a** (Table 3) (CCDC 905874†) showing the crystallographic numbering.



Scheme 6 Plausible mechanism for the formation of indeno-fused heterocycles.

Ethyl-5,11-dihydro-10,12-dioxo-11-(ethoxycarbonyl)methyl-5-(3-methylphenyl) diindeno[1,2-b:2′,1′-e]pyridine-11-carboxylate (4c)

(Table 2, entry 3): Yield 72% (384 mg); red solid; m.p.: 196–198 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2985, 1738, 1689, 1581, 1452, 1385, 1219, 1030, 925, 849, 764, 717, 520; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.52–7.43 (4H, m, ArH), 7.34 (2H, d, J = 7.2 Hz, ArH), 7.10 (2H, t, J = 7.5 Hz, ArH), 6.87 (2H, t, J = 7.5 Hz, ArH), 5.45 (2H, d, J = 7.5 Hz, ArH), 4.21 (2H, q, J = 7.2 Hz, OCH_2), 3.91 (2H, q, J = 7.2 Hz, OCH_2), 3.40 (2H, s, CH_2), 2.43 (3H, s, CH_3), 1.22 (3H, t, J = 7.2 Hz, CH_3), 0.95 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 171.6, 171.2, 156.4, 141.5, 138.5, 136.6, 133.4, 131.8, 131.7, 129.6, 127.0, 121.8, 121.4, 111.9, 62.1, 59.9, 42.8, 38.1, 21.3, 14.1, 14.0; Anal. calcd. for

$C_{33}H_{27}NO_6$; C: 74.28; H: 5.10; N: 2.63. Found: C: 74.48; H: 5.02; N: 2.56%.

Ethyl-11-hydro-10,12-dioxo-11-(ethoxycarbonyl)methyl-5-(3-methoxyphenyl)-5*H*-diindeno[1,2-b:2′,1′-e]pyridine-11-carboxylate (4d)

(Table 2, entry 4): Yield 67% (368 mg); red solid; m.p.: 178–180 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2978, 1732, 1698, 1627, 1601, 1583, 1488, 1384, 1353, 1231, 1035, 849, 766; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.51 (1H, t, J = 8.1 Hz, ArH), 7.39 (2H, d, J = 7.2 Hz, ArH), 7.30–7.12 (5H, m, ArH), 6.94 (2H, t, J = 7.5 Hz, ArH), 5.59 (2H, d, J = 6.0 Hz, ArH), 4.26 (2H, q, J = 7.2 Hz, OCH_2), 3.94 (2H, q, J = 7.2 Hz, OCH_2), 3.85 (3H, s, OMe), 3.38 (2H, s, CH_2), 1.27 (3H, t, J = 7.2 Hz, CH_3), 0.98 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 171.2, 156.3, 139.5, 136.5, 133.3, 131.8, 129.7, 122.2, 121.8, 121.4, 115.2, 111.9, 62.1, 59.9, 55.8, 42.9, 38.2, 14.1, 14.0; Anal. calcd. for $C_{33}H_{27}NO_7$; C: 72.12; H: 4.95; N: 2.55. Found: C: 72.25; H: 4.86; N: 2.48%.

Ethyl-5-(4-bromophenyl)-11-hydro-10,12-dioxo-11-(ethoxycarbonyl)methyl-5*H*-diindeno[1,2-b:2′,1′-e]pyridine-11-carboxylate (4e)

(Table 2, entry 5): Yield 62% (371 mg); red solid; m.p.: 182–184 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2970, 1726, 1693, 1611, 1580, 1490, 1385, 1361, 1222, 1018, 838, 706; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.79 (2H, d, J = 8.4 Hz, ArH), 7.62 (2H, d, J = 8.4 Hz, ArH), 7.42 (2H, d, J = 7.5 Hz, ArH), 7.19 (2H, t, J = 7.5 Hz, ArH), 7.00 (2H, t, J = 7.5 Hz, ArH), 5.57 (2H, d, J = 7.5 Hz, ArH), 4.27 (2H, q, J = 7.2 Hz, OCH_2), 3.96 (2H, q, J = 7.2 Hz, OCH_2), 3.45 (2H, s, CH_2), 1.29 (3H, t, J = 7.2 Hz, CH_3), 1.00 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.8, 171.2, 156.3, 137.8, 136.5, 133.4, 133.2, 131.9, 131.8, 129.9, 125.4, 122.1, 121.2, 62.2, 60.0, 42.7, 38.1, 14.2, 14.0; Anal. calcd. for $C_{32}H_{24}BrNO_6$; C: 64.22; H: 4.04; N: 2.34. Found: C: 64.49; H: 4.00; N: 2.26%.

Ethyl-11-hydro-10,12-dioxo-11-(ethoxycarbonyl)methyl-5-(4-methoxyphenyl)-5*H*- diindeno[1,2-b:2′,1′-e]pyridine-11-carboxylate (4f)

(Table 2, entry 6): Yield 73% (401 mg); red solid; m.p.: 160–162 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2970, 1738, 1692, 1645, 1607, 1577, 1480, 1375, 1333, 1253, 1027, 840; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.59 (2H, d, J = 7.8 Hz, ArH), 7.42 (2H, d, J = 6.9 Hz, ArH), 7.18 (2H, t, J = 7.5 Hz, ArH), 7.11 (2H, d, J = 7.8 Hz, ArH), 6.97 (2H, dt, J = 7.2 Hz and 1.2 Hz, ArH), 5.60 (2H, d, J = 7.5 Hz, ArH), 4.28 (2H, q, J = 7.2 Hz, OCH_2), 4.00–3.92 (5H, m, OCH_2 and OMe), 3.45 (2H, s, CH_2), 1.29 (3H, t, J = 7.2 Hz, CH_3), 1.00 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 191.0, 171.2, 161.3, 157.0, 136.7, 133.4, 131.8, 131.2, 131.0, 129.7, 123.1, 121.9, 121.5, 115.1, 112.0, 62.1, 60.0, 55.8, 42.8, 38.2, 14.2, 14.0; Anal. calcd. for $C_{33}H_{27}NO_7$; C: 72.12; H: 4.95; N: 2.55. Found: C: 72.37; H: 4.88; N: 2.49%.

Ethyl-11-hydro-10,12-dioxo-11-(ethoxycarbonyl)methyl-5-(2-methylphenyl)-5*H*- diindeno[1,2-b:2′,1′-e]pyridine-11-carboxylate (4g)

(Table 2, entry 7): Yield 69% (368 mg); red solid; m.p.: 176–178 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2986, 1731, 1690, 1627, 1583, 1455, 1387, 1192, 1022, 907, 850, 756, 714; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.08 (2H, d, J = 7.8 Hz, ArH), 7.98–7.82 (4H, m, ArH), 7.59 (2H, t, J = 7.5 Hz, ArH), 7.35 (2H, t, J = 7.5 Hz, ArH), 5.88 (2H, d, J = 7.5 Hz, ArH), 4.66 (2H, q, J = 7.2 Hz, OCH_2), 4.40 (2H, q, J = 7.2 Hz, OCH_2), 3.94 (2H, s, CH_2), 2.74 (3H, s, CH_3), 1.67 (3H, t, J = 7.2 Hz, CH_3), 1.44 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 171.2, 156.1, 138.6, 137.6, 136.4, 133.4, 132.0, 131.4, 131.3, 130.1, 129.8, 127.7, 121.9, 120.6, 112.2, 62.0, 59.9, 43.0, 37.7, 17.4, 14.1, 14.0; Anal. calcd. for $C_{33}H_{27}NO_6$; C: 74.28; H: 5.10; N: 2.63. Found: C: 74.51; H: 5.00; N: 2.56%.

Methyl-10-[(methoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-9,11-dioxo-5-phenyl-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4h)

(Table 2, entry 8): Yield 76% (348 mg); red solid; m.p.: 204–206 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2943, 1723, 1688, 1655, 1634, 1588, 1557, 1513, 1398, 1239, 1176, 1078, 908, 794; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.70–7.50 (5H, m, ArH), 7.37 (1H, d, J = 6.9 Hz, ArH), 7.13 (1H, t, J = 7.5 Hz, ArH), 6.87 (1H, t, J = 7.5 Hz, ArH), 5.18 (1H, d, J = 7.5 Hz, ArH), 3.80 (3H, s, CO_2Me), 3.57 (3H, s, CO_2Me), 3.38 (1H, d, J = 15.9 Hz, CH_aH_b), 3.27 (1H, d, J = 15.9 Hz, CH_bH_a), 2.45–1.80 (6H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.2, 191.1, 173.5, 172.1, 155.5, 154.5, 138.7, 136.6, 133.3, 131.4, 130.2, 129.9, 129.6, 121.5, 121.0, 115.8, 109.6, 52.7, 51.1, 43.8, 38.9, 36.8, 27.8, 21.0; Anal. calcd. for $C_{27}H_{23}NO_6$; C: 70.89; H: 5.07; N: 3.06. Found: C: 71.01 H: 4.99; N: 3.00%.

Methyl-10-[(methoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-9,11-dioxo-5-*p*-tolyl-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4i)

(Table 2, entry 9): Yield 77% (363 mg); red solid; m.p.: 216–218 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2943, 1723, 1688, 1655, 1634, 1588, 1557, 1398, 1239, 1176, 1078, 908, 794; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.50–7.30 (5H, m, ArH), 7.10 (1H, t, J = 7.5 Hz, ArH), 6.86 (1H, t, J = 7.5 Hz, ArH), 5.25 (1H, d, J = 7.5 Hz, ArH), 3.76 (3H, s, CO_2Me), 3.53 (3H, s, CO_2Me), 3.34 (1H, d, J = 15.6 Hz, CH_aH_b), 3.23 (1H, d, J = 15.9 Hz, CH_bH_a), 2.50 (3H, s, Me), 2.45–2.15 (4H, m, CH_2), 2.10–1.80 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.2, 191.1, 173.5, 172.1, 155.7, 154.8, 140.5, 136.6, 135.9, 133.3, 131.5, 130.8, 130.2, 129.6, 129.5, 129.3, 121.4, 121.2, 115.8, 109.5, 52.6, 51.1, 43.8, 39.0, 36.8, 27.8, 21.4, 21.0; Anal. calcd. for $C_{28}H_{25}NO_6$; C: 71.33; H: 5.34; N: 2.97. Found: C: 71.53 H: 5.27; N: 2.93%.

Ethyl-10-[(ethoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-9,11-dioxo-5-*o*-tolyl-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4j)

(Table 2, entry 10): Yield 63% (315 mg); red viscous liquid; ν_{max} (KBr) (cm^{-1}) 2930, 1747, 1728, 1689, 1652, 1456, 1397, 1353, 1232, 1081, 719; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.50–7.43 (1H, m, ArH), 7.40–7.29 (4H, m, ArH), 7.06 (1H, t, J = 7.5 Hz, ArH), 6.85–6.75 (1H, m, ArH), 5.09 (0.68H, d, J = 7.5 Hz, ArH), 5.00 (0.32H, d, J = 7.5 Hz, ArH), 4.25–4.13 (2H, m, OCH_2), 3.45–3.25 (2H, m, CH_2), 3.95–3.85 (2H, m, OCH_2), 2.45–2.15 (6H, m, Me and CH_2), 2.00–1.80 (3H, m, CH_2), 1.30–1.20 (3H, m, CH_3), 1.01 (3H, t, J = 6.9 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.0, 191.0, 173.1, 172.8, 171.8, 171.6, 155.0, 153.9, 153.8, 138.2, 137.9, 137.6, 137.4, 136.2, 133.3, 131.6, 131.4, 130.5, 130.0,

129.8, 129.7, 129.6, 129.4, 127.6, 127.5, 121.38, 121.31, 120.2, 120.1, 116.4, 116.3, 109.6, 61.5, 61.4, 59.7, 59.6, 44.7, 44.3, 38.4, 36.94, 36.86, 26.8, 21.2, 21.1, 21.0, 17.5, 17.3, 14.1, 14.0; Anal. calcd. for $C_{30}H_{29}NO_6$; C: 72.13; H: 5.85; N: 2.80. Found: C: 72.31 H: 5.77; N: 2.75%.

Ethyl-10-[(ethoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-5-(4-methoxyphenyl)-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4k)

(Table 2, entry 11): Yield 76% (392 mg); red solid; m.p.: 150–152 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2973, 1739, 1681, 1654, 1634, 1557, 1508, 1400, 1356, 1302, 1228, 1211, 1084, 858; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.20–7.04 (3H, m, ArH), 6.90–6.75 (3H, m, ArH), 6.70–6.60 (1H, m, ArH), 5.07 (1H, d, J = 7.2 Hz, ArH), 4.10–3.90 (2H, m, OCH_2), 3.80–3.64 (5H, m, OCH_2 and OCH_3), 3.08 (1H, d, J = 15.0 Hz, CH_aH_b), 2.93 (1H, d, J = 15.0 Hz, CH_bH_a), 2.25–1.85 (4H, m, CH_2), 1.80–1.50 (2H, m, CH_2), 1.02 (3H, t, J = 7.2 Hz, CH_3), 0.82 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 195.9, 190.8, 172.7, 171.5, 160.4, 155.6, 154.7, 136.5, 133.1, 131.3, 130.9, 130.5, 130.4, 129.3, 121.1, 115.7, 115.0, 114.5, 109.4, 61.1, 59.6, 55.5, 43.8, 38.9, 36.6, 27.5, 20.7, 13.93, 13.87; Anal. calcd. for $C_{30}H_{29}NO_7$; C: 69.89; H: 5.67; N: 2.72;. Found: C: 70.01; H: 5.59; N: 2.66%.

Ethyl-10-[(ethoxycarbonyl)methyl]-5-benzyl-6,7,8,9,10,11-hexahydro-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4l)

(Table 2, entry 12): Yield 64% (320 mg); red solid; m.p.: 186–188 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2978, 1731, 1717, 1684, 1647, 1587, 1450, 1412, 1360, 1324, 1033, 924, 721; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.45–7.25 (6H, m, ArH), 7.12 (1H, t, J = 7.5 Hz, ArH), 6.99 (1H, t, J = 7.5 Hz, ArH), 6.79 (1H, d, J = 7.2 Hz, ArH), 5.15 (2H, s, benzylic CH_2), 4.21–4.11 (2H, m, OCH_2), 3.95–3.84 (2H, m, OCH_2), 3.32 (1H, d, J = 15.0 Hz, CH_aH_b), 3.14 (1H, d, J = 15.0 Hz, CH_bH_a), 2.55–2.25 (4H, m, CH_2), 1.95–1.80 (2H, m, CH_2), 1.24 (3H, t, J = 7.2 Hz, CH_3), 0.96 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 195.7, 190.7, 173.1, 171.8, 157.0, 155.1, 136.4, 136.1, 133.6, 131.8, 129.9, 129.5, 128.1, 125.3, 121.9, 121.2, 117.2, 110.8, 61.5, 59.7, 50.9, 44.3, 38.8, 36.6, 26.2, 21.2, 14.1, 14.0; Anal. calcd. for $C_{30}H_{29}NO_6$; C: 72.13; H: 5.85; N: 2.80. Found: C: 72.37 H: 5.79; N: 2.73%.

Methyl-10-[(methoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-9,11-dioxo-7-phenyl-5-*p*-tolyl-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4m) (crude product)

(Table 2, entry 13): dr = 66 : 34; red sticky mass; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.35–7.00 (11H, m, ArH), 6.80 (1H, t, J = 7.5 Hz, ArH), 5.22 (0.33H, d, J = 8.1 Hz, ArH), 5.12 (0.67H, d, J = 8.1 Hz, ArH), 3.90–3.10 (9H, m, CH, CH_2 and 2 × CO_2Me), 2.70–2.20 (7H, m, 2 × CH_2 and CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 195.3, 191.0, 173.4, 172.0, 154.1, 142.4, 140.6, 136.6, 135.7, 133.2, 131.5, 131.4, 130.9, 130.7, 130.4, 130.2, 129.6, 129.4, 129.3, 129.0, 128.9, 128.7, 127.5, 127.0, 126.7, 126.6, 121.4, 121.2, 117.5, 115.5, 52.9, 52.7, 52.6, 51.1, 43.9, 43.8, 43.6, 43.4, 39.2, 39.1, 38.0, 35.2, 34.6, 21.3, 21.1.

Methyl-10-[(methoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-5-(4-methoxyphenyl)-9,11-dioxo-7-phenyl-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4n) (crude product)

(Table 2, entry 14): dr = 57 : 43; red sticky mass; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.40–6.90 (12H, m, ArH), 5.29 (0.43H, d, J = 7.2 Hz, ArH), 5.21 (0.57H, d, J = 7.2 Hz, ArH), 3.90–3.70 (6H, m, 2 × CO_2Me), 3.52 (1.59H, s, OMe), 3.45 (1.41H, s, OMe), 3.40–3.10 (2H, m, CH_2), 2.65–2.30 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 195.5, 195.3, 191.0, 173.3, 172.0, 160.6, 156.0, 154.4, 154.1, 142.3, 136.6, 136.5, 133.2, 131.5, 130.8, 130.7, 130.6, 130.3, 129.6, 129.5, 128.9, 128.7, 128.6, 127.1, 127.0, 126.7, 126.6, 126.5, 121.4, 121.2, 116.0, 115.5, 115.3, 114.8, 114.7, 55.6, 52.7, 52.6, 51.1, 43.8, 43.7, 43.6, 39.3, 39.1, 39.0, 38.0, 35.2, 34.6.

Ethyl-10-[(ethoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-7,7-dimethyl-9,11-dioxo-5-phenyl-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4o)

(Table 2, entry 15): Yield 78% (401 mg); red solid; m.p.: 128–130 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2964, 1737, 1687, 1642, 1586, 1457, 1400, 1359, 1216, 1083, 1025, 893, 715; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.65–7.40 (5H, m, ArH), 7.33 (1H, d, J = 6.9 Hz, ArH), 7.08 (1H, t, J = 7.2 Hz, ArH), 6.82 (1H, t, J = 7.2 Hz, ArH), 5.12 (1H, d, J = 7.2 Hz, ArH), 4.30–4.15 (2H, m, OCH_2), 3.98–3.90 (2H, m, OCH_2), 3.42 (1H, d, J = 15.9 Hz, CH_aH_b), 3.23 (1H, d, J = 15.9 Hz, CH_bH_a), 2.30–2.13 (3H, m, CH_2), 1.96 (1H, d, J = 17.4 Hz, CH_2), 1.28 (3H, t, J = 7.2 Hz, CH_3), 1.10–0.90 (9H, m, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.1, 191.0, 172.9, 171.8, 155.6, 152.6, 138.8, 136.6, 133.3, 131.3, 130.3, 130.2, 130.0, 129.9, 129.6, 129.5, 121.3, 120.9, 115.1, 61.5, 59.8, 50.4, 44.0, 41.2, 38.7, 32.2, 28.8, 27.2, 14.1; Anal. calcd. for $C_{31}H_{31}NO_6$; C: 72.50; H: 6.08; N: 2.73. Found: C: 72.71 H: 6.11; N: 2.86%.

Ethyl-10-[(ethoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-7,7-dimethyl-9,11-dioxo-5-*p*-tolyl-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4p)

(Table 2, entry 16): Yield 77% (406 mg); red solid; m.p.: 172–174 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2960, 1734, 1725, 1680, 1638, 1589, 1558, 1514, 1403, 1362, 1304, 1237, 1173, 1032, 896; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.40–7.25 (5H, m, ArH), 7.07 (1H, t, J = 7.5 Hz, ArH), 6.83 (1H, t, J = 7.5 Hz, ArH), 5.20 (1H, d, J = 7.5 Hz, ArH), 4.30–4.13 (2H, m, OCH_2), 3.98–3.88 (2H, m, OCH_2), 3.41 (1H, d, J = 15.6 Hz, CH_aH_b), 3.21 (1H, d, J = 15.6 Hz, CH_bH_a), 2.49 (3H, s, CH_3), 2.30–2.10 (3H, m, CH_2), 1.96 (1H, d, J = 17.4 Hz, CH_2), 1.26 (3H, t, J = 7.2 Hz, CH_3), 1.05–0.92 (9H, m, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.2, 191.0, 172.9, 171.8, 155.8, 153.0, 140.5, 136.7, 136.1, 133.4, 131.4, 130.9, 130.3, 129.5, 121.3, 121.1, 115.1, 109.5, 61.4, 59.8, 50.4, 44.0, 41.2, 38.7, 32.2, 28.8, 27.3, 21.4, 14.1, 14.0; Anal. calcd. for $C_{32}H_{33}NO_6$; C: 72.85; H: 6.30; N: 2.65. Found: C: 72.99 H: 6.21; N: 2.58%.

Ethyl-10-[(ethoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-5-(4-methoxyphenyl)-7,7-dimethyl-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4q)

(Table 2, entry 17): Yield 77% (419 mg); red solid; m.p.: 124–126 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2958, 1745, 1734, 1683, 1648,

1634, 1559, 1555, 1510, 1409, 1361, 1247, 898, 724; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.35–7.25 (3H, m, ArH), 7.10–6.95 (3H, m, ArH), 6.82 (1H, t, J = 7.5 Hz, ArH), 5.24 (1H, d, J = 7.2 Hz, ArH), 4.28–4.10 (2H, m, OCH_2), 3.94–3.82 (5H, m, OCH_2 and OCH_3), 3.36 (1H, d, J = 15.6 Hz, CH_aH_b), 3.17 (1H, d, J = 15.6 Hz, CH_bH_a), 2.24–2.07 (3H, m, CH_2), 1.93 (1H, d, J = 17.7 Hz, CH_2), 1.23 (3H, t, J = 7.2 Hz, CH_3), 1.00–0.85 (9H, m, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.2, 191.0, 172.9, 171.8, 160.4, 156.1, 153.3, 136.6, 133.3, 131.4, 131.1, 130.9, 130.8, 129.5, 121.1, 115.1, 115.0, 114.7, 109.4, 61.4, 59.8, 50.3, 43.8, 41.1, 38.6, 32.1, 28.8, 27.2, 14.0; Anal. calcd. for $C_{32}H_{33}NO_7$; C: 70.70; H: 6.12; N: 2.58. Found: C: 70.95 H: 6.07; N: 2.50%.

Ethyl-10-[(ethoxycarbonyl)methyl]-5-(4-bromophenyl)-6,7,8,9,10,11-hexahydro-7,7-dimethyl-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4r)

(Table 2, entry 18): Yield 71% (421 mg); red solid; m.p.: 198–200 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2957, 1726, 1684, 1727, 1648, 1638, 1560, 1489, 1363, 1228, 820; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.70–7.61 (2H, m, ArH), 7.36 (1H, d, J = 7.2 Hz, ArH), 7.28 (2H, d, J = 7.2 Hz, ArH), 7.06 (1H, t, J = 7.5 Hz, ArH), 6.85 (1H, t, J = 7.5 Hz, ArH), 5.23 (1H, d, J = 7.5 Hz, ArH), 4.27–4.09 (2H, m, OCH_2), 3.93–3.82 (2H, m, OCH_2), 3.35 (1H, d, J = 16.2 Hz, CH_aH_b), 3.18 (1H, d, J = 16.2 Hz, CH_bH_a), 2.22 (1H, d, J = 15.9 Hz, CH_2), 2.13 (1H, d, J = 15.9 Hz, CH_2), 2.09 (1H, d, J = 17.4 Hz, CH_2), 1.87 (1H, d, J = 17.4 Hz, CH_2), 1.22 (3H, t, J = 7.2 Hz, CH_3), 1.00–0.85 (9H, m, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.0, 190.9, 172.8, 171.8, 155.3, 152.3, 137.8, 136.5, 133.6, 133.2, 132.9, 131.7, 131.5, 129.7, 124.3, 121.6, 120.8, 115.3, 110.0, 61.5, 59.8, 50.3, 43.8, 41.3, 38.6, 32.2, 28.9, 27.1, 14.1, 14.0; Anal. calcd. for $C_{31}H_{30}BrNO_6$; C: 62.84; H: 5.10; N: 2.36. Found: C: 63.03 H: 5.05; N: 2.29%.

Ethyl-10-[(ethoxycarbonyl)methyl]-5-(4-chlorophenyl)-6,7,8,9,10,11-hexahydro-7,7-dimethyl-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4s)

(Table 2, entry 19): Yield 70% (384 mg); red solid; m.p.: 208–210 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2958, 1738, 1721, 1687, 1644, 1589, 1493, 1589, 1493, 1399, 1362, 1226, 1157, 1085, 1017, 854; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.55–7.40 (3H, m, ArH), 7.34 (1H, d, J = 7.8 Hz, ArH), 7.28 (1H, d, J = 6.9 Hz, ArH), 7.06 (1H, t, J = 7.5 Hz, ArH), 6.84 (1H, t, J = 7.5 Hz, ArH), 5.23 (1H, d, J = 7.5 Hz, ArH), 4.25–4.10 (2H, m, OCH_2), 3.93–3.84 (2H, m, OCH_2), 3.35 (1H, d, J = 16.2 Hz, CH_aH_b), 3.17 (1H, d, J = 16.2 Hz, CH_bH_a), 2.21 (1H, d, J = 16.2 Hz, CH_2), 2.13 (1H, d, J = 16.2 Hz, CH_2), 2.09 (1H, d, J = 17.4 Hz, CH_2), 1.88 (1H, d, J = 17.4 Hz, CH_2), 1.21 (3H, t, J = 7.2 Hz, CH_3), 1.00–0.85 (9H, m, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.0, 190.9, 172.8, 171.8, 155.4, 152.4, 137.3, 136.5, 136.4, 133.2, 131.5, 131.4, 131.2, 130.7, 129.9, 129.7, 121.6, 120.8, 115.3, 110.0, 61.5, 59.8, 50.3, 43.8, 41.3, 38.6, 32.2, 28.9, 27.1, 14.1; Anal. calcd. for $C_{31}H_{30}ClNO_6$; C: 67.94; H: 5.52; N: 2.56. Found: C: 68.20 H: 5.46; N: 2.48%.

Ethyl-10-[(ethoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-7,7-dimethyl-9,11-dioxo-5-*m*-tolyl-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4t)

(Table 2, entry 20): Yield 75% (396 mg); red solid; m.p.: 148–150 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2950, 1729, 1644, 1588, 1458, 1360, 1238, 1081, 1028, 901, 722; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.50–7.40 (2H, m, ArH), 7.32 (1H, d, J = 6.9 Hz, ArH), 7.26–7.22 (2H, m, ArH), 7.08 (1H, t, J = 7.2 Hz, ArH), 6.83 (1H, t, J = 7.5 Hz, ArH), 5.16–5.12 (1H, m, ArH), 4.28–4.14 (2H, m, OCH_2), 4.00–3.91 (2H, m, OCH_2), 3.42 (1H, d, J = 15.9 Hz, CH_aH_b), 3.23 (1H, dd, J = 15.6 Hz and 4.2 Hz, CH_bH_a), 2.50–2.41 (3H, m, Me), 2.30–2.10 (3H, m, CH_2), 1.99 (1H, d, J = 17.4 Hz, CH_2), 1.27 (3H, t, J = 6.9 Hz, CH_3), 1.10–0.94 (9H, m, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.1, 191.0, 172.9, 171.8, 155.7, 152.7, 140.7, 140.0, 138.6, 136.7, 133.4, 131.4, 131.0, 130.3, 130.0, 129.5, 129.4, 126.9, 121.3, 121.1, 115.0, 109.5, 61.4, 59.8, 50.4, 44.0, 41.2, 38.7, 32.3, 28.9, 28.6, 27.4, 27.2, 21.4, 14.1; Anal. calcd. for $C_{32}H_{33}NO_6$; C: 72.85; H: 6.30; N: 2.65. Found: C: 73.08 H: 6.22; N: 2.56%.

Ethyl-10-[(ethoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-7,7-dimethyl-5-(3,4-dimethylphenyl)-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4u)

(Table 2, entry 21): Yield 70% (379 mg); red viscous liquid; ν_{max} (KBr) (cm^{-1}) 2958, 1725, 1708, 1681, 1634, 1589, 1499, 1360, 1215, 718; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.29–7.21 (2H, m, ArH), 7.18–7.00 (3H, m, ArH), 6.80 (1H, t, J = 7.5 Hz, ArH), 5.20–5.10 (1H, m, ArH), 4.22–4.10 (2H, m, OCH_2), 3.95–3.85 (2H, m, OCH_2), 3.38 (1H, d, J = 15.6 Hz, CH_aH_b), 3.15 (1H, d, J = 15.6 Hz, CH_bH_a), 2.38–1.90 (10H, m, 2 × CH_3 and 2 × CH_2), 1.26–1.15 (3H, m, CH_3), 1.00–0.85 (9H, m, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 196.1, 195.8, 190.9, 174.1, 172.8, 171.7, 155.8, 153.0, 150.6, 139.0, 138.9, 138.3, 136.7, 136.6, 136.0, 133.4, 133.3, 131.3, 131.1, 130.5, 130.3, 129.4, 129.3, 126.9, 121.1, 121.0, 114.9, 109.2, 61.3, 60.9, 59.7, 50.5, 50.3, 43.9, 41.5, 41.0, 40.9, 38.6, 32.2, 32.1, 28.7, 28.5, 27.4, 27.1, 24.4, 19.8, 19.6, 14.0, 13.9; Anal. calcd. for $C_{33}H_{35}NO_6$; C: 73.18; H: 6.51; N: 2.59. Found: C: 73.29 H: 6.44; N: 2.51%.

Ethyl-10-[(ethoxycarbonyl)methyl]-5-benzyl-6,7,8,9,10,11-hexahydro-7,7-dimethyl-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4v)

(Table 2, entry 22): Yield 65% (343 mg); red solid; m.p.: 180–182 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2953, 1739, 1715, 1680, 1644, 1589, 1552, 1453, 1411, 1374, 1028, 720; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.45–7.30 (6H, m, ArH), 7.13 (1H, t, J = 7.5 Hz, ArH), 7.00 (1H, t, J = 7.5 Hz, ArH), 6.78 (1H, d, J = 7.5 Hz, ArH), 5.30–5.10 (2H, m, CH_2), 4.25–4.09 (2H, m, OCH_2), 3.95–3.85 (2H, m, OCH_2), 3.41 (1H, d, J = 15.6 Hz, CH_aH_b), 3.19 (1H, d, J = 15.6 Hz, CH_aH_b), 2.40–2.25 (2H, m, CH_2), 1.97 (2H, s, CH_2), 1.23 (3H, t, J = 6.9 Hz, CH_3), 1.00–0.88 (9H, m, 3 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 195.8, 190.7, 172.8, 171.9, 157.2, 153.4, 136.5, 136.1, 133.6, 131.8, 129.9, 129.5, 128.1, 125.3, 125.2, 121.9, 121.3, 116.2, 110.7, 61.5, 59.8, 50.7, 50.2, 44.2, 39.6, 38.4, 32.4, 27.8, 14.1; Anal. calcd. for $C_{32}H_{33}NO_6$; C: 72.85; H: 6.30; N: 2.65. Found: C: 73.04 H: 6.22; N: 2.59%.

Ethyl-10-[(ethoxycarbonyl)methyl]-6,7,8,9,10,11-hexahydro-7,7-dimethyl-5-[(naphthalen-1-yl)methyl]-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4w)

(Table 2, entry 23): Yield 67% (387 mg); red solid; m.p.: 220–222 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2960, 1732, 1684, 1654, 1634, 1590, 1557, 1414, 1368, 1326, 1024, 794; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.95 (1H, d, J = 7.2 Hz, ArH), 7.87 (1H, d, J = 8.1 Hz, ArH), 7.82 (1H, d, J = 8.1 Hz, ArH), 7.61 (2H, t, J = 7.2 Hz, ArH),

7.55–7.40 (2H, m, ArH), 7.31 (1H, d, J = 6.9 Hz, ArH), 7.03 (1H, t, J = 7.5 Hz, ArH), 6.77 (1H, t, J = 7.5 Hz, ArH), 6.49 (1H, d, J = 7.5 Hz, ArH), 5.65–5.50 (2H, m, NCH_2), 4.30–4.10 (2H, m, OCH_2), 4.00–3.90 (2H, m, OCH_2), 3.46 (1H, d, J = 15.9 Hz, CH_aH_b), 3.25 (1H, d, J = 15.9 Hz, CH_bH_a), 2.45–2.35 (2H, m, CH_2), 2.19 (2H, s, CH_2), 1.24 (3H, t, J = 7.2 Hz, CH_3), 0.99 (3H, t, J = 7.2 Hz, CH_3), 0.95–0.85 (6H, m, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 195.8, 190.7, 172.8, 172.0, 157.2, 153.3, 135.9, 133.8, 133.5, 131.8, 131.4, 129.7, 129.4, 129.1, 128.9, 128.8, 127.2, 126.6, 125.9, 123.6, 121.7, 121.3, 121.1, 116.3, 110.7, 61.4, 59.7, 50.2, 49.1, 44.2, 39.2, 38.3, 32.4, 29.6, 21.7, 14.0; Anal. calcd. for $C_{36}H_{35}NO_6$; C: 74.85; H: 6.11; N: 2.42. Found: C: 75.02 H: 6.07; N: 2.35%.

Ethyl-10-[(ethoxycarbonyl)methyl]-5-butyl-6,7,8,9,10,11-hexahydro-7,7-dimethyl-9,11-dioxo-5*H*-indeno[1,2-b]quinoline-10-carboxylate (4x)

(Table 2, entry 24): Yield 62% (306 mg); red viscous liquid; ν_{max} (KBr) (cm^{-1}) 2960, 1716, 1677, 1657, 1626, 1455, 1403, 1324, 1157, 1068, 895; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.41–7.37 (6H, m, ArH), 7.26–7.17 (3H, m, ArH), 4.17–4.11 (2H, m, OCH_2), 3.91–3.80 (4H, m, OCH_2 and NCH_2), 3.31 (1H, d, J = 15.3 Hz, CH_aH_b), 3.10 (1H, d, J = 15.3 Hz, CH_bH_a), 2.55–2.40 (2H, m, CH_2), 2.21 (2H, s, CH_2), 1.85–1.70 (2H, m, CH_2), 1.50–1.35 (2H, m, CH_2), 1.18 (3H, t, J = 7.2 Hz, CH_3), 1.08 (6H, s, 2 × CH_3), 0.99–0.90 (6H, m, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 195.8, 190.6, 172.8, 171.7, 156.5, 152.6, 136.6, 133.8, 131.8, 129.9, 121.9, 121.0, 116.0, 110.7, 61.3, 59.7, 49.9, 46.6, 44.0, 40.1, 38.4, 33.3, 32.4, 28.5, 28.0, 19.7, 14.0, 13.7; Anal. calcd. for $C_{29}H_{35}NO_6$; C: 70.57; H: 7.15; N: 2.84. Found: C: 70.74 H: 7.08; N: 2.77%.

Methyl-10-methyl-6,7,8,9,10-pentahydro-8,10-dioxo-5-phenyl-5*H*-indeno[1,2-b]cyclopenta[e]pyridine-10-carboxylate (10a)

(Table 3, entry 1): Yield 80% (308 mg); red solid; m.p.: 218–220 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 1728, 1694, 1683, 1589, 1557, 1455, 1361, 1309, 1263, 1099, 898; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.70–7.45 (5H, m, ArH), 7.39 (1H, d, J = 6.9 Hz, ArH), 7.16 (1H, t, J = 7.5 Hz, ArH), 6.92 (1H, dt, J = 7.5 Hz and 0.9 Hz, ArH), 5.45 (1H, d, J = 7.5 Hz, ArH), 3.78 (3H, s, CO_2Me), 2.50–2.30 (4H, m, ArH), 1.77 (3H, s, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 173.3, 165.6, 154.9, 137.6, 136.1, 133.4, 131.5, 130.4, 130.0, 129.7, 129.0, 128.9, 122.4, 121.6, 121.1, 114.5, 52.7, 40.9, 34.1, 25.0, 23.0; Anal. calcd. for $C_{24}H_{19}NO_4$; C: 74.79; H: 4.97; N: 3.63. Found: C: 74.98; H: 4.90; N: 3.56%.

Methyl-10-methyl-6,7,8,9,10-pentahydro-8,10-dioxo-5-(4-methylphenyl)-5*H*-indeno[1,2-b]cyclopenta[e]pyridine-10-carboxylate (10b)

(Table 3, entry 2): Yield 78% (312 mg); red solid; m.p.: 210–212 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 1727, 1688, 1642, 1591, 1557, 1395, 1372, 1262, 1140; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.40–7.25 (5H, m, ArH), 7.09 (1H, t, J = 7.5 Hz, ArH), 6.87 (1H, t, J = 7.5 Hz, ArH), 5.45 (1H, J = 7.5 Hz, ArH), 3.70 (3H, s, CO_2Me), 2.45 (3H, s, Me), 2.40–2.20 (4H, m, CH_2), 1.69 (3H, s, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 173.4, 165.8, 155.1, 140.7, 136.2, 134.9, 133.4, 131.5, 130.6, 129.6, 128.6, 128.5, 122.3, 121.6, 121.1, 114.4, 52.6, 40.9, 34.0, 24.9, 23.0, 21.3; Anal. calcd. for $C_{25}H_{21}NO_4$; C: 75.17; H: 5.30; N: 3.51. Found: C: 75.31; H: 5.26; N: 3.45%.

Methyl-10-methyl-6,7,8,9,10-pentahydro-8,10-dioxo-5-(4-bromophenyl)-5*H*-indeno[1,2-b]cyclopenta[e]pyridine-10-carboxylate (10c)

(Table 3, entry 3): Yield 73% (339 mg); red solid; m.p.: 236–238 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 1752, 1688, 1645, 1591, 1553, 1492, 1393, 1371, 1097, 1067, 825; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.75 (2H, d, J = 9.0 Hz, ArH), 7.45–7.35 (3H, m, ArH), 7.21 (1H, t, J = 7.5 Hz, ArH), 7.01 (1H, t, J = 7.5 Hz, ArH), 5.59 (1H, d, J = 7.5 Hz, ArH), 3.79 (3H, s, CO_2Me), 2.50–2.42 (2H, m, CH_2), 2.39–2.34 (2H, m, CH_2), 1.77 (3H, s, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.8, 173.3, 165.0, 154.5, 136.7, 136.0, 133.4, 133.3, 131.7, 130.6, 130.5, 129.9, 124.6, 122.7, 121.9, 120.9, 114.9, 52.8, 41.0, 34.0, 25.0, 23.0; Anal. calcd. for $C_{24}H_{18}BrNO_4$; C: 62.08; H: 3.91; N: 3.02. Found: C: 62.22; H: 3.87; N: 2.96%.

Methyl-10-methyl-6,7,8,9,10-pentahydro-8,10-dioxo-5-(3-methylphenyl)-5*H*-indeno[1,2-b]cyclopenta[e]pyridine-10-carboxylate (10d)

(Table 3, entry 4): Yield 74% (296 mg); red solid; m.p.: 242–244 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 2931, 1748, 1692, 1644, 1592, 1557, 1392, 1372, 1309, 1232, 884; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.55–7.25 (5H, m, ArH), 7.16 (1H, t, J = 7.5 Hz, ArH), 6.94 (1H, t, J = 7.5 Hz, ArH), 5.49 (1H, d, J = 7.2 Hz, ArH), 3.77 (3H, s, CO_2Me), 2.55–2.35 (7H, m, 2 × CH_2 and CH_3), 1.85–1.75 (3H, m, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 173.3, 165.7, 155.0, 140.4, 137.4, 136.1, 133.4, 131.5, 131.1, 129.7, 129.6, 129.4, 129.3, 125.9, 125.7, 122.3, 121.6, 121.1, 114.4, 52.6, 40.9, 34.0, 24.9, 23.1, 22.9, 21.2; Anal. calcd. for $C_{25}H_{21}NO_4$; C: 75.17; H: 5.30; N: 3.51. Found: C: 75.34; H: 5.26; N: 3.47%.

Ethyl-10-methyl-6,7,8,9,10-pentahydro-8,10-dioxo-5-(4-methoxyphenyl)-5*H*-indeno[1,2-b]cyclopenta[e]pyridine-10-carboxylate (10e)

(Table 3, entry 5): Yield 79% (339 mg); red solid; m.p.: 202–204 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 1727, 1683, 1640, 1592, 1552, 1374, 1305, 1252, 1104, 895; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.40–7.30 (3H, m, ArH), 7.15 (1H, t, J = 7.5 Hz, ArH), 7.10–7.02 (2H, m, ArH), 6.95 (1H, dt, J = 7.5 Hz and 0.9 Hz, ArH), 5.56 (1H, d, J = 7.5 Hz, ArH), 4.23 (2H, q, J = 7.2 Hz, OCH_2), 3.93 (3H, s, OMe), 2.45–2.34 (4H, m, CH_2), 1.73 (3H, s, Me), 1.26 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 172.8, 166.0, 160.6, 155.3, 136.2, 133.4, 131.5, 130.0, 129.9, 129.8, 129.5, 122.4, 121.4, 121.1, 114.9, 114.4, 61.3, 55.6, 41.0, 34.0, 24.9, 22.8, 14.0; Anal. calcd. for $C_{26}H_{23}NO_5$; C: 72.71; H: 5.40; N: 3.26. Found: C: 72.88; H: 5.36; N: 3.19%.

Ethyl-10-methyl-6,7,8,9,10-pentahydro-8,10-dioxo-5-(2-methylphenyl)-5*H*-indeno[1,2-b]cyclopenta[e]pyridine-10-carboxylate (10f)

(Table 3, entry 6): Yield 72% (298 mg); red solid; m.p.: 174–176 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 1721, 1687, 1645, 1591, 1552, 1454, 1393, 1368, 1240, 1098, 891; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.60–7.50 (1H, m, ArH), 7.49–7.40 (4H, m, ArH), 7.18 (1H, t, J = 7.5 Hz, ArH), 6.93 (1H, t, J = 7.5 Hz, ArH), 5.45 (1H, d, J = 7.5 Hz, ArH), 4.24 (2H, q, J = 7.2 Hz, OCH_2), 2.50–2.40 (3H, m, CH_2), 2.28 (3H, s, Me), 2.25–2.10 (1H, m, CH_2), 1.77 (3H, s,

CH_3), 1.26 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 190.9, 172.7, 165.4, 155.1, 137.7, 136.6, 136.1, 133.4, 131.8, 131.7, 130.7, 129.8, 129.0, 127.6, 122.7, 121.7, 120.1, 114.4, 61.5, 41.3, 34.1, 24.7, 22.1, 17.2, 14.1; Anal. calcd. for $C_{26}H_{23}NO_4$; C: 75.53; H: 5.61; N: 3.39. Found: C: 75.75; H: 5.57; N: 3.35%.

5,6,7,12-tetrahydro-6-methyl-7,12-dioxo-5-phenylindeno[1,2,3,2-bcd]pyridine-6-carboxylate (6)

Yield 12% (54 mg); black solid; m.p.: 186–188 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 1728, 1681, 1638, 1589, 1556, 1421, 1370, 1352, 1242, 1007, 879; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 8.57 (1H, d, J = 6.9 Hz, ArH), 7.60–7.18 (10H, m, ArH), 6.95 (1H, t, J = 7.2 Hz, ArH), 5.33 (1H, d, J = 7.5 Hz, ArH), 4.15–4.05 (2H, m, OCH_2), 1.83 (3H, s, CH_3), 1.12 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 191.6, 186.3, 170.1, 167.1, 150.6, 139.1, 138.6, 138.2, 135.3, 133.7, 132.9, 132.4, 131.7, 130.5, 130.12, 130.08, 129.8, 129.7, 128.9, 126.2, 123.3, 121.9, 121.2, 114.2, 103.3, 70.4, 62.4, 21.6, 14.0; Anal. calcd. for $C_{29}H_{21}NO_4$; C: 77.84; H: 4.73; N: 3.13. Found: C: 78.03; H: 4.68; N: 3.07%.

2-[3-(phenylamino)-1*H*-inden-1-ylidene]-2*H*-indene-1,3-dione (7)[31]

Yield 25% (87 mg); deep blue solid; m.p.: 214–216 °C (EtOAc); ν_{max} (KBr) (cm^{-1}) 3042, 1700.8, 1634, 1587, 1481, 1449, 1351, 1326, 1092, 1001, 746; ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 10.72 (1H, brs, NH), 9.20–9.15 (1H, m, ArH), 7.95–7.30 (13H, m, ArH); Anal. calcd. for $C_{24}H_{15}NO_2$; C: 82.50; H: 4.33; N: 4.01. Found: C: 82.74; H: 4.26; N: 3.94%. We were not able to take the ^{13}C NMR spectrum of compound **6** due to its poor solubility in the NMR solvent.

Acknowledgements

One of the authors (SR) thanks the Council of Scientific and Industrial Research, New Delhi, for his fellowship (SRF). We acknowledge the grant received from UGC funded Major project, F. No. 37-398/2009 (SR) dated 11-01-2010.

References

1 (*a*) A. Dömling, W. Wang and K. Wang, *Chem. Rev.*, 2012, **112**, 3083; (*b*) Q. Zhu, H. Jiang, J. Li, S. Liu, C. Xia and M. Zhang, *J. Comb. Chem.*, 2009, **11**, 685; (*c*) M. Misra, S. K. Pandey, V. P. Pandey, J. Pandey, R. Tripathi and R. P. Tripathi, *Bioorg. Med. Chem.*, 2009, **17**, 625; (*d*) H. Bienaymé, C. Hulme, G. Oddon and P. Schmitt, *Chem.–Eur. J.*, 2000, **6**, 3321.

2 (*a*) C. C. A. Cariou, G. J. Clarkson and M. Shipman, *J. Org. Chem.*, 2008, **73**, 9762; (*b*) S. M. Kupchan, Y. Komoda, W. A. Court, G. J. Thomas, R. M. Smith, A. Karim, C. J. Gilmore, R. C. Haltivanger and R. F. Bryan, *J. Am. Chem. Soc.*, 1972, **94**, 1354; (*c*) R. W. Armstrong, A. P. Combs, P. A. Tempest, S. D. Brown and T. A. Keating, *Acc. Chem. Res.*, 1996, **29**, 123 (*d*) L. Zhou, D. S. Bohle, H. F. Jiang and C. J. Li, *Synlett.*, 2009, 937; (*e*) G. Ren, J. Zhang, Z. Duan, M. Cui and Y. Wu, *Aust. J. Chem.*, 2009, **62**, 75; (*f*) C. Boominathan, M. Nagaraj, R. Muthusubramanian and R.V. Krishnakumar, *Tetrahedron*, 2011, **67**, 6057.

3 (*a*) C. Mukhopadhyay, S. Rana, R. J. Butcher and A. M. Schmiedekamp, *Tetrahedron Lett.*, 2011, **52**, 5835; (*b*) V. P. Mehta, S. G. Modha, E. Ruijter, K. V. Hecke, L. V. Meervelt, C. Pannecouque, J. Balzarini, R. V. A. Orru and E. V. Eycken, *J. Org. Chem.*, 2011, **76**, 2828; (*c*) V. Cerulli, L. Banfi, A. Basso, V. Rocca and R. Riva, *Org. Biomol. Chem.*, 2012, **10**, 1255; (*d*) A. Scala, M. Cordaro, F. Risitano, I. Colao, A. Venuti, M. T. Sciortino, P. Primerano and G. Grassi, *Mol. Diversity*, 2012, **16**, 325; (*e*) S. Muthusamy, J. Krishnamurthi and E. Suresh, *Chem. Commun.*, 2007, 861; (*f*) M. Paravidino, R. S. Bon, R. Scheffelaar, D. J. Vugts, A. Znabet, R. F. Schmitz, F. J. J. de Kanter, M. Lutz, A. L. Spek, M. B. Groen and R. V. A. Orru, *Org. Lett.*, 2006, **8**, 5369.

4 (*a*) J. Zhang, A.-R. O. El-Shabrawy, M. A. El-Shanawany, P. L. Schiff and D. J. Slatkin, *J. Nat. Prod.*, 1987, **50**, 800; (*b*) G. J. Arango, D. Cortes, B. K. Cassels, A. Cavé and C. Mérienne, *Phytochemistry*, 1987, **26**, 2093.

5 (*a*) S. A. Hild, B. J. Attardi and J. Reel, *Biol. Reprod.*, 2004, **71**, 348; (*b*) C. E. Cook, M. C. Wani, J. M. Jump, Y.-W. Lee, P. A. Fail, S. A. Anderson, Y.-Q. Gu and V. Petrow, *J. Med. Chem.*, 1995, **38**, 753; (*c*) C. L.-T. Chang, H. P. Fung, Y.-F. Lin, C.-Y. Kuo and C.-W. Chien, *Biol. Pharm. Bull.*, 2002, **25**, 1097; (*d*) C. E. Cook, J. M. Jump, P. Zhang, J. R. Stephens, Y.-W. Lee, P. A. Fail and S. A. Anderson, *J. Med. Chem.*, 1997, **40**, 2111.

6 M. Manpadi, P. Y. Uglinskii, S. K. Rastogi, K. M. Cotter, Y.-S. C. Wong, L. A. Anderson, A. J. Ortega, S. V. Slambrouck, W. F. A. Steelant, S. Rogelj, P. Tongwa, M. Y. Antipin, I. V. Magedov and A. Kornienko, *Org. Biomol. Chem.*, 2007, **5**, 3865.

7 A. Brandes, M. Loegers, G. Schmidt, R. Angerbauer, C. Schmeck, K.-D. Bremm, H. Bischoff, D. Schmidt and J. Schuhmacher, *Ger. Offen. DE 19627430 A1 19980115*, 1998.

8 J. Augstein, A. L. Ham and P. R. Leeming, *J. Med. Chem.*, 1972, **15**, 466.

9 (*a*) G. R. Heintzelman, K. M. Averill, J. H. Dodd, K. T. Demarest and Y. Tang, P. F. Jackson, *PCT Int. Appl. WO 2003088963*, 2003; (*b*) G. R. Heintzelman, K. M. Averill, J. H. Dodd, K. T. Demarest, Y. Tang and P. F. Tang, *U. S. Pat. Appl. Publ. US 2004082578*, 2004.

10 C. Safak, R. Simsek, Y. Altas, S. Boydag and K. Erol, *Boll. Chim. Farm.*, 1997, **136**, 665.

11 K. Cooper, M. J. Fray, P. E. Cross and K. Richardson, *Eur. Pat. Appl. EP 299727 A1 19890118*, 1989.

12 C. Rentzea, N. Meyer, J. Kast, P. Plath, H. Koenig, Al. Harreus, U. Kardorff, M. Gerber and H. Walter, *Ger. Offen DE 4301426*, 1994.

13 M. Yamato, Y. Takeuchi, K. Hashigaki, Y. Ikeda, M.-R. Chang, K. Takeuchi, M. Matsushima, T. Tsuruo, T. Tashiro, S. Tsukagoshi, Y. Yamashita and H. Nakanoe, *J. Med. Chem.*, 1989, **32**, 1295.

14 M. A. Quraishi, V. R. Thakur and S. N. Dhawan, *Indian J. Chem. Sect. B.*, 1989, **28B**, 891.

15 B. Venugopalan, C. P. Bapat, E. P. Desouza and N. J. DeSouza, *Indian J. Chem. Sect. B.*, 1992, **31B**, 35.

16 M. Anzino, A. Cappelli, S. Vomero, A. Cagnotto and M. Skorupska, *Med. Chem. Res.*, 1993, **3**, 44.

17 J. R. Brooks, C. Berman, M. Hichens, R. L. Primka, G. F. Reynolds and G. H. Rasmusson, *Proc. Soc. Exp. Biol. Med.*, 1982, **169**, 67.

18 A. Rampa, A. Bisi, F. Belluti, S. Gobbi, P. Valenti, V. Andrisano, V. Cavrini, A. Cavalli and M. Recanatini, *Bioorg. Med. Chem.*, 2000, **8**, 497.

19 (*a*) A. Hantzsch, *Justus Liebigs Ann. Chem.*, 1882, **215**, 1; (*b*) P. K. Tapaswi and C. Mukhopadhyay, *Arkivoc*, 2011, **x**, 287; (*c*) S. Tu, B. Jiang, H. Jiang, Y. Zhang, R. Jia, J. Zhang, Q. Shao, C. Li, D. Zhou and L. Cao, *Tetrahedron*, 2007, **63**, 5406; (*d*) S. Samai, G. C. Nandi, R. Kumar and M. S. Singh, *Tetrahedron Lett.*, 2009, **50**, 7096; (*e*) S. Paul and A. R. Das, *Tetrahedron Lett.*, 2012, **53**, 2206.

20 (*a*) Z. Chamas, O. Dietz, E. Aubert, Y. Fort and V. Mamane, *Org. Biomol. Chem.*, 2010, **8**, 4815; (*b*) V. V. Kouznetsov, C. O. Puentes, A. R. R. Bohórquez, S. A. Zacchino, M. Sortino, M. Gupta, Y. Vázquez, A. Bahsas and J. Amaro-Luis, *Lett. Org. Chem.*, 2006, **3**, 300; (*c*) R. Ghahremanzadeh, G. I. Shakibaei, S. Ahadi and A. Bazgir, *J. Comb. Chem.*, 2010, **12**, 191; (*d*) M. T. DuPriest, C. L. Schmidt, D. Kuzmich and S. B. Williams, *J. Org. Chem.*, 1986, **51**, 2021; (*e*) R. Ghahremanzadeh, S. Ahadi, G. I. Shakibaei and A. Bazgir, *Tetrahedron Lett.*, 2010, **51**, 499.

21 C. G. Lee, K. Y. Lee, S. GowriSankar and J. N. Kim, *Tetrahedron Lett.*, 2004, **45**, 7409.

22 G. Babu and P. T. Perumal, *Tetrahedron Lett.*, 1998, **39**, 3225.

23 X. Lu, J. L. Petersen and K. K. Wang, *Org. Lett.*, 2003, **5**, 3277.

24 (*a*) S.-J. Tu, B. Jiang, J.-Y. Zhang, R.-H. Jia, Y. Zhang and C.-S. Yao, *Org. Biomol. Chem.*, 2006, **4**, 3980; (*b*) C.-H. Tseng, Y.-L. Chen, P.-J. Lu, C.-N. Yang and C.-C. Tzeng, *Bioorg. Med. Chem.*, 2008, **16**, 3153; (*c*) X. Bu and L. W. Deady, *Synth. Commun.*, 1999, **29**, 4223.

25 (*a*) N. Yoshikai, A. Mieczkowski, A. Matsumoto, L. Ilies and E. Nakamura, *J. Am. Chem. Soc.*, 2010, **132**, 5568; (*b*) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Rev.*, 2011, **111**, 1293; (*c*) R. Li, S. R. Wang and W. Lu, *Org. Lett.*, 2007, **9**, 2219; (*d*) J. Gao, Q.-W. Song, L.-N. He, Z.-Z. Yang and X.-Y. Dou, *Chem. Commun.*, 2012, **48**, 2024.

26 (*a*) C. Bolm, J. Legros, J. L. Paih and L. Zani, *Chem. Rev.*, 2004, **104**, 6217; (*b*) T. Hatakeyama, N. Nakagawa and M. Nakamura, *Org. Lett.*, 2009, **11**, 4496; (*c*) M. Carril, A. Correa and C. Bolm, *Angew. Chem., Int. Ed.*, 2008, **47**, 4862.

27 (*a*) A. Correa and C. Bolm, *Angew. Chem., Int. Ed.*, 2007, **46**, 8862; (*b*) A. Correa, S. Elmore and C. Bolm, *Chem.–Eur. J.*, 2008, **14**, 3527; (*c*) A. Correa and C. Bolm, *Adv. Synth.Catal.*, 2008, **350**, 391; (*d*) B. Anxionnat, A. Guérinot, S. Reymond and J. Cossy, *Tetrahedron Lett.*, 2009, **50**, 3470; (*e*) A. K. Bhattacharya, K. C. Rana, D. S. Raut, V. P. Mhaindarkar and M. I. Khan, *Org. Biomol. Chem.*, 2011, **9**, 5407.

28 O. Bistri, A. Correa and C. Bolm, *Angew. Chem., Int. Ed.*, 2008, **47**, 586.

29 A. Correa, M. Carril and C. Bolm, *Angew. Chem., Int. Ed.*, 2008, **47**, 2880.

30 (*a*) T. Sengupta, K. S. Gayen, P. Pandit and D. K. Maiti, *Chem.–Eur. J.*, 2012, **18**, 1905; (*b*) Y.-Y. Han, W.-Y. Han, X. Hou, X.-M. Zhang and W.-C. Yuan, *Org. Lett.*, 2012, **14**, 4054; (*c*) X. Xu, X. Xu, H. Li, X. Xie and Y. Li, *Org. Lett.*, 2010, **12**, 100; (*d*) S. Maiti, S. Biswas and U. Jana, *J. Org. Chem.*, 2010, **75**, 1674; (*e*) C. Christoffers, *Tetrahedron Lett.*, 1998, **39**, 7083; (*f*) J. M. Takacs, P. W. Newsometh and C. Kuehnt, *Tetrahedron*, 1990, **46**, 5507.

31 C. Mukhopadhyay, S. Rana and R. J. Butcher, *Tetrahedron Lett.*, 2011, **52**, 4153.

32 J. Irick, *J. Chem. Eng. Data*, 1971, **16**, 118.

33 M. Regitz and H. Schwall, *Justus Liebigs Ann. Chem.*, 1969, **728**, 99.

34 (*a*) G. Bringmann, A. J. P. Mortimer, P. A. Keller, M. J. Gresser, J. Garner and M. Breuning, *Angew. Chem., Int. Ed.*, 2005, **44**, 5384; (*b*) S. Reichert and B. Breit, *Org. Lett.*, 2007, **9**, 899; (*c*) J. Clayden, W. J. Moran, P. J. Edwards and S. R. LaPlante, *Angew. Chem., Int. Ed.*, 2009, **48**, 6398.

35 (*a*) A. M. Chibiryaev, N. D. Kimpe and A.V. Tkachev, *Tetrahedron Lett.*, 2000, **41**, 8011; (*b*) J. Comelles, M. M. Mañas and A. Vallribera, *Arkivoc*, 2005, **ix**, 207; (*c*) V. R. Choudhary, D. K. Dumbre and S. K. Patil, *RSC Adv.*, 2012, **2**, 7061.