DOI: 10.1002/ejoc.201000739

A Facile Synthesis of Substituted Indenones and Piperidine-2,6-diones from the Baylis–Hillman Acetates

Deevi Basavaiah*[a] and Dandamudi V. Lenin[a]

Keywords: Alkylation / Carbocycles / Cyclization / Baylis–Hillman reaction / Synthetic methods

Baylis–Hillman acetates were conveniently transformed into substituted indenone and piperidine-2,6-dione frameworks by treatment with (di)phenylacetonitrile followed by Friedel–Crafts cyclization or imide formation.

Introduction

The ind-2-en-1-one framework represents an important class of carbocyclic molecules, and many of these derivatives are found in important natural products.[1] Some of indenone derivatives are also known to be peroxisome proliferator-activated receptor γ (PPAR γ, drug used against type-2 diabetes) agonists,[2a,2b] estrogen receptor binding agents,[2c,2d] cyclooxygenase-2 inhibitors,[2e] and potent reversible inhibitors of 3CP.[2f] Due to their significant medicinal importance, the development of facile strategies to obtain such frameworks has become an attractive endeavor in synthetic organic and medicinal chemistry. In fact, several methodologies have been reported for their synthesis in recent years.[3] The piperidine-2,6-dione framework is another medicinally important skeleton present in several biologically active and natural products, such as: alonimid[4a,4b] (sedative and hypnotic activity), thalidomide[4c] (drug to prevent morning sickness of pregnant women), streptimidone[4d] (antibiotic), migrastatin[4e–4g] (antitumor agent), lactimidomycin[4h,4i] (antibiotic), and sesbanimide[4j,4k] (antitumor). Therefore, the development of facile strategies for the synthesis of these frameworks has become a challenging task in synthetic organic chemistry.[4c,4d,4f,4k,5] In a continuation of our interest in the synthesis of carbocyclic and heterocyclic molecules,[6] we herein report a facile, two-step protocol for synthesis of 2-substituted ind-2-en-1-one and 3,5-disubstituted piperidine-2,6-dione derivatives from the Baylis–Hillman (B-H) acetates.

In recent years, the B-H reaction has emerged as a powerful synthetic tool with which to provide diverse classes of multifunctional molecules, which are usually referred to as the Baylis–Hillman adducts. The products are formed by coupling at the α-position of activated alkenes with electrophiles under the influence of a catalyst or catalytic system, and the reaction can usually be performed in a one-pot, operationally simple procedure.[7] The B-H adducts have been successfully employed in various organic transformation methodologies and have also been used as synthons to obtain a number of natural products and biologically active molecules.[8]

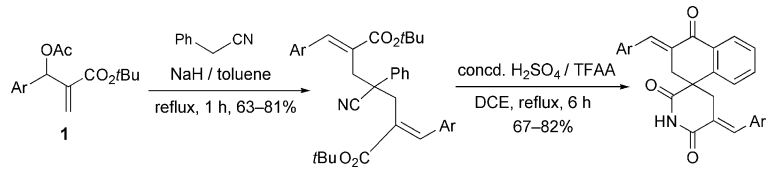
Results and Discussion

A few years ago, we successfully used B-H adducts as substrates in a number of Friedel–Crafts reactions to obtain various trisubstituted alkenes[9a,9b] and carbocylic/heterocyclic molecules.[9c–9e] Very recently we reported a facile, two-step protocol for the transformation of acetates (**1**) of the B-H adducts (obtained from aryl aldehydes and *tert*-butyl acrylate) into bis-(*E*)-benzylidene-tetralone-spiro-glutarimides.[5b] This strategy proceeds through bis-alkylation of benzyl cyanide with B-H acetates **1** followed by bis-cyclization involving a tandem intramolecular Friedel–Crafts reaction and imide formation (Scheme 1). From this experience, it occurred to us that it is possible to synthesize 2-arylmethylidene-4-cyanotetralone derivatives **3** by monoalkylation of benzyl cyanide with B-H acetates (**1**), followed by intramolecular Friedel–Crafts cyclization of the resulting (*E*)-alkylated products **2** according to the retrosynthetic strategy shown in Scheme 2. Similarly, the products **2** would be transformed into 3-arylmethylidene-5-phenylpiperidine-2,6-diones **4** by partial hydrolysis and cyclization (Scheme 2).

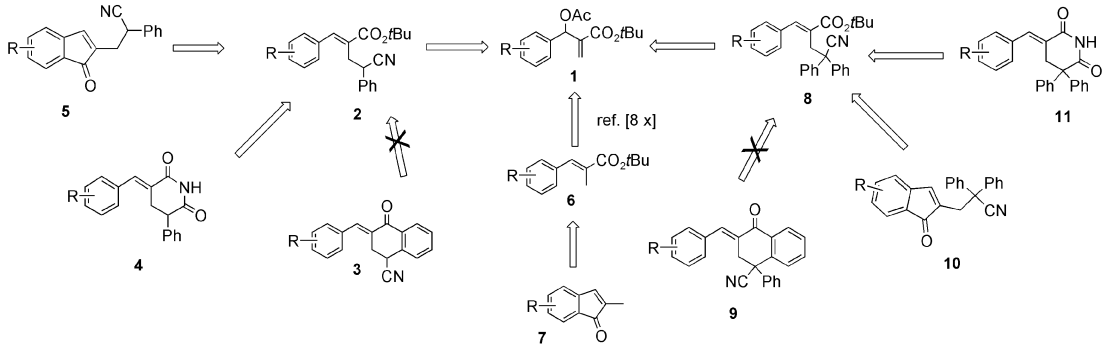
Accordingly, we performed the monoalkylaion of benzyl cyanide with *tert*-butyl 3-acetoxy-2-methylene-3-phenylpropanoate (**1a**) in the presence of *t*BuOK. Thus, treatment of benzyl cyanide (5 mmol) with **1a** (5 mmol) in the presence of *t*BuOK (5.5 mmol) in tetrahydrofuran (THF) at room temperature for 10 hours provided the required mono-alkylated product, (*E*)-*tert*-butyl 2-benzylidene-4-cyano-4-phenylbutanoate (**2a**), in 72% isolated yield (Table 1). We then performed the intramolecular Friedel–Crafts reaction of **2a** with trifluoroacetic acid (TFA)/trifluoroacetic anhydride

[a] School of Chemistry, University of Hyderabad, Hyderabad 500046, India
Fax: +91-40-23012460
E-mail: dbsc@uohyd.ernet.in

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000739.



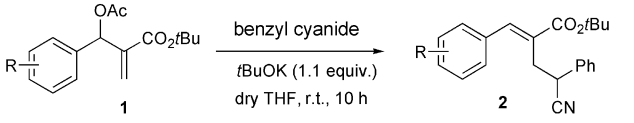
Scheme 1. Previously reported application of B-H adduct **1**.[5b]



Scheme 2. Retrosynthetic strategy.

(TFAA). To our surprise, we did not obtain the expected tetralone derivative **3a** (R = H), however, we were pleased to see the formation of the unexpected indenone derivative **5a** (R = H) [2-(2-cyano-2-phenylethyl)ind-2-en-1-one]. Thus, treatment of **2a** (0.5 mmol) with TFA (2.5 mmol)/TFAA (1 mmol) in dichloroethane (DCE; 3 mL) at reflux temperature for 5 hours provided 2-(2-phenyl-2-cyano)ethylind-2-en-1-one[10] (**5a**) in 38% isolated yield (Table 2). Although the yields were not that encouraging, this reaction was interesting in the sense that tetralone derivative **3a**, which was expected to form easily, did not form, whereas, the indenone derivative **5a**, which was not expected to form easily due to the *trans* orientation[11] of ester group and aryl group (*trans*-cinnamic ester derivative), was obtained in reasonably good yield.

Table 1. Synthesis of (*E*)-*tert*-butyl 2-arylmethylidene-4-cyano-4-phenylbutanoates **2a** and **2b**.[a][11]

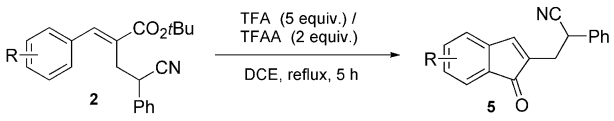


Entry	B-H acetate	R	Product[b]	Yield [%][c]
1	**1a**	H	**2a**	72
2	**1b**	4-*i*Pr	**2b**	80

[a] Reactions were carried out on a 5 mmol scale of B-H acetates **1a** and **1b**. [b] Obtained as colorless viscous liquids and well characterized. [c] Isolated yields based on B-H acetates **1a** and **1b**.

To understand the generality of this strategy, we transformed *tert*-butyl 3-acetoxy-2-methylene-3-(4-isopropylphenyl)propanoate (**1b**) into (*E*)-*tert*-butyl 2-(4-isopropylbenzylidene)-4-cyano-4-phenylbutanoate (**2b**) which, on treatment with TFA/TFAA, gave [2-(2-cyano-2-phenylethyl)-6-isopropylind-2-en-1-one] (**5b**) in 40% isolated yield (Table 2).[12]

Table 2. Synthesis of 2-(2-phenyl-2-cyano)ethylind-2-en-1-ones **5a** and **5b**.[a]



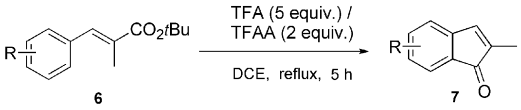
Entry	Substrate	R	Product[b]	R	Yield [%][c]
1	**2a**	H	**5a**	H	38
2	**2b**	4-*i*Pr	**5b**	6-*i*Pr	40

[a] Reactions were carried out on a 0.5 mmol scale of **2a** and **2b**. [b] Obtained as yellow solids and well characterized. [c] Isolated yields based on substrates **2a** and **2b**.

Although these reactions are quite interesting due to the unexpected transformation of *trans*-cinnamic esters into ind-2-en-1-one derivatives, the low yields of the products were disappointing. From these results, it occurred to us that it should be possible to transform *trans*-cinnamic acids/esters into indenone derivatives using TFA/TFAA. Accordingly, we directed our attention to the conversion of (2*E*)-*tert*-butyl 3-phenyl-2-methylprop-2-enoate (**6a**) into 2-methylind-2-en-1-one (**7a**) by treatment with TFA/TFAA. The required *trans* ester **6a** was prepared by treatment of *tert*-butyl 3-acetoxy-2-methylene-3-phenylpropanoate (**1a**) with sodium borohydride following the procedure developed in our laboratory.[8x] We then examined the Friedel–Crafts cyclization of *trans* ester **6a** into 2-methylind-2-en-1-one (**7a**) using TFA/TFAA. The best results were obtained when (2*E*)-*tert*-butyl 3-phenyl-2-methylprop-2-enoate (**6a**; 1.0 mmol) was heated to reflux for 5 h in DCE (3 mL) in the presence of TFA (5 mmol) and TFAA (2 mmol), thus providing the expected 2-methylind-2-en-1-one (**7a**) in 18% isolated yield.[12] To understand the general nature of this reaction strategy, we extended this methodology to another B-H acetate, *tert*-butyl 3-acetoxy-2-methylene-3-(4-isoprop-

ylphenyl)propanoate (**1b**). Treatment of **1b** with $NaBH_4$ following the known methodology[8x] gave the *trans*-cinnamic ester (**6b**). Subsequent treatment of **6b** with TFA/TFAA provided the desired 6-isopropyl-2-methylind-2-en-1-one (**7b**) in 20% isolated yield (Table 3). Comparison of yields obtained for **5a** and **5b** (38 and 40%) with those of **7a** and **7b** (18 and 20%) clearly indicates that *trans*-cinnamic esters **2a** and **2b**, containing sterically bulky phenylcyanomethyl groups at the α-position, provided better yields of indenone derivatives in comparison to those of **6a** and **6b**, which contain a simple methyl group at the α-position.

Table 3. Synthesis of 2-methylind-2-en-1-ones **7a** and **7b**.[a]



6 7

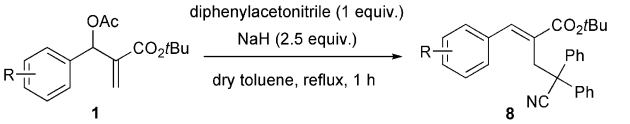
Entry	Substrate	R	Product[b]	R	Yield [%][c]
1	**6a**	H	**7a**	H	18
2	**6b**	4-*i*Pr	**7b**	6-*i*Pr	20

[a] Reactions were carried out on a 1 mmol scale of **6a** and **6b**. [b] Obtained as yellow viscous liquids and well characterized. [c] Isolated yields based on substrates **6a** and **6b**).

With a view to further understanding the influence of steric factors in the formation of ind-2-en-1-one derivatives, we selected (*E*)-*tert*-butyl 2-benzylidene-4-cyano-4,4-diphenylbutanoate (**8a**) as a substrate for intramolecular Friedel–Crafts cyclization. The required *trans*-cinnamic ester (**8a**) was obtained by treatment of **1a** (2 mmol) with diphenylacetonitrile (2 mmol) in anhydrous toluene (5 mL) in the presence of NaH (5 mmol), in 81% isolated yield (Table 4). The Friedel–Crafts cyclization of **8a** was performed with TFA/TFAA in DCE for 5 h at reflux temperature to provide 2-(2-cyano-2,2-diphenylethyl)ind-2-en-1-one (**10a**) in 66% isolated yield (Table 5).[14] This result fascinated us because *trans*-cinnamic ester **8a**, containing the sterically more hindered diphenylcyanomethyl group, provided superior yields of the indenone derivative (**10a**). To understand the generality of this methodology, we subjected a representative class of B-H acetates (**1b**–**g**) to this reaction strategy. The resulting alkylated *trans*-cinnamic esters (**8b**–**g**) were obtained in 75–83% isolated yields (Table 4) which, on intramolecular Friedel–Crafts reaction using TFA/TFAA, furnished the required indenone derivatives, 2-(2-cyano-2,2-diphenylethyl)ind-2-en-1-ones (**10a**–**g**), in 60–70% isolated yields (Table 5).[14] The structures of compounds **8d** and **10a** were further confirmed by single-crystal X-ray data analysis.[13]

To understand the applicability of this strategy to the naphthalene framework, we prepared (*E*)-*tert*-butyl 4-cyano-2-(naphth-1-ylmethylidene)-4,4-diphenylbutanoate (**8h**) from *tert*-butyl 3-acetoxy-2-methylene-3-(naphth-1-yl)-propanoate (**1h**) in 76% yield by using the reaction with diphenylacetonitrile in the prersence of NaH. Subsequent treatment of **8h** with TFA/TFAA gave the expected indenone derivative, 12-(2-cyano-2,2-diphenylethyl)tricyclo-

Table 4. Synthesis of (*E*)-*tert*-butyl 2-arylmethylidene-4-cyano-4,4-diphenylbutanoates **8a**–**g**.[a],[11]

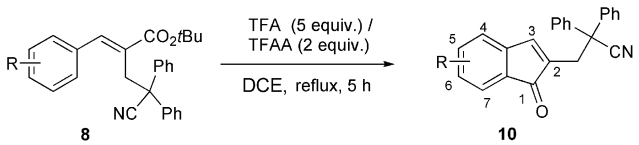


1 8

Entry	B-H acetate	R	Product[b]	Yield [%][c]
1	**1a**	H	**8a**	81
2	**1b**	4-*i*Pr	**8b**	83
3	**1c**	3-Me	**8c**	78
4	**1d**	4-Et	**8d**[d]	79
5	**1e**	4-Me	**8e**	75
6	**1f**	3-Br	**8f**	80
7	**1g**	2-Me	**8g**	77

[a] All reactions were carried out on a 2 mmol scale of B-H acetates **1a**–**g**. [b] Obtained as colorless solids and well characterized. [c] Isolated yields based on B-H acetates **1a**–**g**. [d] The structure of this molecule was further confirmed by single-crystal X-ray data analysis.[13]

Table 5. Synthesis of 2-(2-cyano-2,2-diphenylethyl)ind-2-en-1-ones **10a**–**g**.[a]



8 10

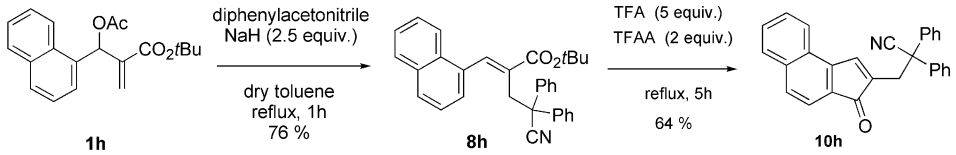
Entry	Substrate	R	Product[b]	R	Yield [%][c]
1	**8a**	H	**10a**[d]	H	66
2	**8b**	4-*i*Pr	**10b**	6-*i*Pr	63
3	**8c**	3-Me	**10c**	5-Me	64
4	**8d**	4-Et	**10d**	6-Et	70
5	**8e**	4-Me	**10e**	6-Me	60
6	**8f**	3-Br	**10f**	5-Br	66
7	**8g**	2-Me	**10g**	4-Me	62

[a] All reactions were carried out on a 0.5 mmol scale of **8a**–**g**. [b] Obtained as yellow solids and well characterized. [c] Isolated yields based on substrates **8a**–**g**. [d] The structure of this molecule was also confirmed by single-crystal X-ray data analysis.[13]

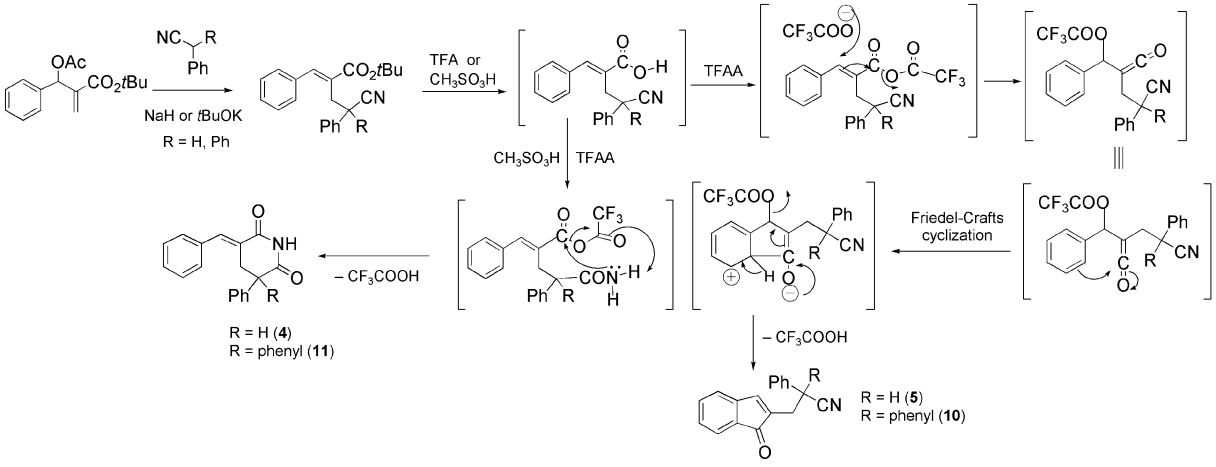
[8.3.0.$0^{2,7}$]trideca-1(10),2(7),3,5,8,12-hexaene-11-one (**10h**) in 64% isolated yield (Scheme 3).

These results, to some extent, suggest that the reaction pathway may not proceed through isomerization of the *trans*-cinnamic esters into the *cis* derivatives, and probably involves the reorganization of the *trans* double bond so that the five-membered ring formation providing indenone derivatives **5a**, **5b**, and **10a**–**h**, becomes easier (which is otherwise difficult to form) than the formation of the six-membered ring (providing the tetralone derivatives **3** and **9**). On this basis, a plausible mechanism involving formation of a ketene-type transition state through Michael addition of a trifluoroacetoxide anion onto the *trans*-cinnamic ester derivative, is presented in Scheme 4.

We then turned our attention towards the synthesis of piperidine-2,6-dione frameworks (**4**) from the *trans* esters **2**. We selected (*E*)-*tert*-butyl 2-benzylidene-4-cyano-4-phenylbutanoate (**2a**) as a substrate. The best results in this direc-



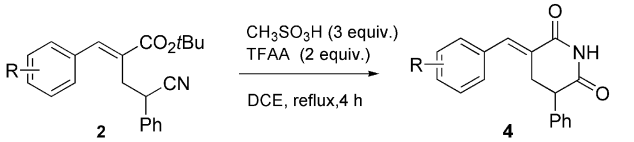
Scheme 3. Synthesis of **10h**.



Scheme 4. Plausible mechanism for the formation of substituted ind-2-en-1-one and piperidine-2,6-dione derivatives.

tion were obtained when **2a** (0.5 mmol) was treated with methanesulfonic acid (CH_3SO_3H; 1.5 mmol) and TFAA (1 mmol) in DCE at reflux temperature for 4 h, thus providing the desired (*E*)-3-benzylidene-5-phenylpiperidine-2,6-dione (**4a**) in 70% isolated yield. Similarly, we transformed (*E*)-*tert*-butyl 2-(3-methylbenzylidene)-4-cyano-4-phenylbutanoate (**2c**) into the piperidine-2,6-dione derivative (**4b**) in 75% isolated yield (Table 6).

Table 6. Synthesis of (*E*)-3-arylmethylidene-5-phenylpiperidine-2,6-diones **4a** and **4b**.[a]

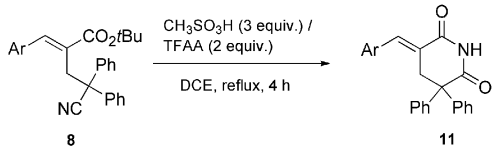


Entry	Substrate	R	Product[b]	Yield [%][c]
1	**2a**	H	**4a**	70
2	**2c**	3-Me	**4b**	75

[a] Reactions were carried out on a 0.5 mmol scale of **2a** and **2c**. [b] Obtained as colorless solids and well characterized. [c] Isolated yields based on substrates **2a** and **2c**.

Encouraged by these results, we extended the same strategy to the more hindered *trans* ester (*E*)-*tert*-butyl 2-benzylidene-4-cyano-4,4-diphenylbutanoate (**8a**). In this case also, treatment of **8a** (0.5 mmol) with CH_3SO_3H (1.5 mmol) and TFAA (1 mmol) in DCE at reflux temperature for 4 h furnished (*E*)-3-benzylidene-5,5-diphenylpiperidine-2,6-dione (**11a**) in 85% isolated yield. To understand the generality of this methodology, we successfully transformed *trans* esters **8b**–**h** into the corresponding piperidine-2,6-dione derivatives **11b**–**h** in 75–86% yields (Table 7). The structure of **11a** was further confirmed by single-crystal X-ray data analysis.[13] A plausible mechanism for the transformation of **8a**–**h** into **11a**–**h** is presented in Scheme 4.

Table 7. Synthesis of (*E*)-3-arylmethylidene-5,5-diphenylpiperidine-2,6-diones **11a**–**h**.[a]



Entry	Substrate	Ar	Product[b]	Yield [%][c]
1	**8a**	Ph	**11a**[d]	85
2	**8b**	4-*i*PrC_6H_4	**11b**	86
3	**8c**	3-MeC_6H_4	**11c**	81
4	**8d**	4-EtC_6H_4	**11d**	77
5	**8e**	4-MeC_6H_4	**11e**	80
6	**8f**	3-BrC_6H_4	**11f**	82
7	**8g**	2-MeC_6H_4	**11g**	75
8	**8h**	1-naphthyl	**11h**	79

[a] All reactions were carried out on a 0.5 mmol scale of substrates **8a**–**h**. [b] Obtained as colorless solids and well characterized. [c] Isolated yields based on substrates **8a**–**h**. [d] The structure of this compound was also confirmed by single-crystal X-ray data analysis.[13]

Conclusions

Baylis–Hillman acetates have been transformed into 2-substituted ind-2-en-1-one derivatives in a two-step protocol. This transformation proceeds through an unusual conversion of *trans*-cinnamic esters into the ind-2-en-1-one

frameworks. The yields of the indenone derivatives depend on the steric bulk of the substituent at the α-position of the ester group of *trans*-cinnamic esters. We have also developed a simple two-step strategy to transform the B-H acetates into substituted piperidine-2,6-dione derivatives.

Experimental Section

General Remarks: Melting points were recorded with a Superfit (India) capillary melting point apparatus. Infrared spectra were recorded with a JASCO FT/IR 5300 spectrophotometer; spectra were calibrated against polystyrene absorption at 1601 cm^{-1}. Solid samples were recorded as KBr plates. ^1H and ^{13}C NMR spectra were recorded with a Bruker AVANCE-400 spectrometer. ^1H NMR (400 MHz) spectra were recorded in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard. ^{13}C NMR (100 MHz) spectra were measured in $CDCl_3$ with the central peak of the solvent triplet (δ = 77.10 ppm) as internal standard. Elemental analyses were recorded with a Thermo-Finnigan Flash EA 1112 analyzer. Mass spectra were recorded with a Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction data were collected at 298 K with a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-K_α fine-focus sealed tube (λ = 0.71073 Å).

(*E*)-*tert*-Butyl 2-Benzylidene-4-cyano-4-phenylbutanoate (2a): To a stirred solution of benzyl cyanide (5 mmol, 0.577 mL) and *t*BuOK (5.5 mmol, 0.616 g) in anhydrous THF (10 mL), was added *tert*-butyl 3-acetoxy-2-methylene-3-phenylpropanoate (**1a**; 5 mmol, 1.380 g) slowly at r.t. After stirring for 10 h at r.t., the reaction mixture was diluted with diethyl ether (5 mL) and washed with water (2 × 5 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL) and the combined organic layer was dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue thus obtained was purified by column chromatography (silica gel; EtOAc/hexanes, 3%) to provide **2a** as a colorless viscous liquid (72%, 1.20 g). IR (Neat): $\tilde{\nu}$ = 2245, 1714, 1631 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 9 H), 2.95 and 3.15 [d ABq, *J* = 13.6, 7.2 (8.8) Hz, 2 H], 4.35 (t, *J* = 8.4 Hz, 1 H), 7.18–7.42 (m, 10 H), 7.81 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.13, 33.70, 36.19, 81.51, 120.42, 127.33, 128.08, 128.50, 128.61, 128.98, 129.52, 135.02, 135.39, 142.75, 166.27 ppm. LCMS: *m*/*z* = 334 [M + H]$^+$.

(*E*)-*tert*-Butyl 2-(4-Isopropylbenzylidene)-4-cyano-4-phenylbutanoate (2b): Yield 80%. IR (Neat): $\tilde{\nu}$ = 2241, 1712, 1631 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (d, *J* = 6.8 Hz, 6 H), 1.56 (s, 9 H), 2.84–3.03 (m, 2 H), 3.12–3.24 (m, 1 H), 4.26 (t, *J* = 8.0 Hz, 1 H), 7.04–7.42 (m, 9 H), 7.78 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.90, 28.20, 33.79, 33.97, 36.28, 81.42, 120.58, 126.71, 127.43, 128.15, 128.97, 129.04, 132.49, 135.54, 142.82, 149.67, 166.53 ppm; In addition, peaks at δ = 21.41, 128.70, 128.85, 129.34, 132.10, 138.79 ppm with low intensity indicate that **2b** was contaminated with 5% impurity. The material was used as such in the next step.

(*E*)-*tert*-Butyl 4-Cyano-2-(3-methylbenzylidene)-4-phenylbutanoate (2c): Yield 73%. IR (Neat): $\tilde{\nu}$ = 2241, 1695, 1631 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 9 H), 2.33 (s, 3 H), 2.95 and 3.15 [d ABq, *J* = 13.6, 7.6 (8.8) Hz, 2 H], 4.26 (t, *J* = 8.0 Hz, 1 H), 6.94 (s, 1 H), 7.00 (d, *J* = 7.6 Hz, 1 H), 7.12 (d, *J* = 7.6 Hz, 1 H), 7.20–7.40 (m, 6 H), 7.77 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.37, 28.16, 33.80, 36.21, 81.47, 120.51, 125.66, 127.41, 128.06, 128.41, 128.99, 129.30, 134.99, 135.47, 138.13, 142.97, 166.38 ppm. LCMS: *m*/*z* = 348 [M + H]$^+$.

2-(2-Cyano-2-phenylethyl)ind-2-en-1-one (5a): To a stirred solution of (*E*)-*tert*-butyl 2-benzylidene-4-cyano-4-phenylbutanoate (**2a**; 0.5 mmol, 0.167 g) in DCE (3 mL), were added TFA (2.5 mmol, 0.285 g, 0.19 mL) and TFAA (1 mmol, 0.210 g, 0.14 mL) at r.t. The reaction mixture was heated to reflux for 5 h and then allowed to cool to r.t. The reaction mixture was poured into aqueous K_2CO_3 and extracted with diethyl ether (2 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, the solvent was evaporated and the residue, thus obtained, was purified by column chromatography (ethyl acetate/hexanes, 5%) to provide **5a** as a yellow solid (38%, 0.049 g); m.p. 116–117 °C. IR (KBr): $\tilde{\nu}$ = 2237, 1711, 1651, 1604 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.86 (d, *J* = 7.6 Hz, 2 H), 4.13 (t, *J* = 7.6 Hz, 1 H), 7.01 (d, *J* = 7.2 Hz, 1 H), 7.16–7.22 (m, 1 H), 7.30–7.48 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.65, 36.70, 120.31, 122.31, 123.08, 127.35, 128.46, 128.89, 129.26, 130.38, 134.23, 134.39, 135.08, 143.99, 146.34, 197.49 ppm. LCMS *m*/*z* = 260 [M + H]$^+$. $C_{18}H_{13}NO$ (259.31): calcd. C 83.37, H 5.05, N 5.40; found C 83.45, H 5.11, N 5.51.

2-(2-Cyano-2-phenylethyl)-6-isopropylind-2-en-1-one (5b): Yield 40%; m.p. 66–68 °C. IR (KBr): $\tilde{\nu}$ = 2241, 1705, 1606 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.4 Hz, 6 H), 2.75–2.95 (m, 3 H), 4.12 (t, *J* = 7.2 Hz, 1 H), 6.90 (d, *J* = 7.2 Hz, 1 H), 7.09–7.48 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.71, 31.66, 34.13, 36.73, 120.34, 121.71, 122.17, 127.35, 128.40, 129.22, 130.80, 131.72, 133.85, 135.13, 141.51, 146.55, 150.32, 197.87 ppm. LCMS: *m*/*z* = 302 [M + H]$^+$. $C_{21}H_{19}NO$ (301.39): calcd. C 83.69, H 6.35, N 4.65; found C 83.65, H 6.39, N 4.77.

2-Methylind-2-en-1-one (7a): To a stirred solution of (2*E*)-*tert*-butyl 2-methyl-3-phenylprop-2-enoate[15] (**6a**; 1.0 mmol, 0.218 g) in DCE (3 mL), was added TFA (5 mmol, 0.570 g, 0.38 mL) and TFAA (2 mmol, 0.420 g, 0.28 mL) at r.t. The reaction mixture was heated to reflux for 5 h and then allowed to cool to r.t. The reaction mixture was poured into aqueous K_2CO_3 and extracted with diethyl ether (2 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, the solvent was evaporated and the residue, thus obtained, was purified by column chromatography (ethyl acetate/hexanes, 2%) to provide **7a**[3k,3l] as a yellow viscous liquid[16] (18%, 0.026 g). IR (Neat): $\tilde{\nu}$ = 1712, 1606 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 3 H), 6.92 (d, *J* = 7.2 Hz, 1 H), 7.08–7.19 (m, 2 H), 7.22–7.30 (m, 1 H), 7.36 (d, *J* = 6.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.07, 121.14, 122.62, 127.88, 130.79, 133.84, 136.24, 143.35, 144.95, 198.81 ppm. LCMS: *m*/*z* = 145 [M + H]$^+$.

6-Isopropyl-2-methylind-2-en-1-one (7b): Yield 20%. IR (Neat): $\tilde{\nu}$ = 1712, 1616 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 7.2 Hz, 6 H), 1.85 (s, 3 H), 2.85 (sept, *J* = 7.2 Hz, 1 H), 6.83 (d, *J* = 7.2 Hz, 1 H), 7.08–7.15 [m, 2 H, with a doublet at δ = 7.10 (*J* = 7.2 Hz, 1 H) and a singlet at δ = 7.09 (1 H)], 7.28 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.06, 23.76, 34.07, 120.97, 121.29, 131.23, 131.30, 135.76, 142.48, 143.50, 149.17, 199.20 ppm. LCMS: *m*/*z* = 187 [M + H]$^+$. $C_{13}H_{14}O$ (186.25): calcd. C 83.83, H 7.58; found C 83.75, H 7.65.

(*E*)-*tert*-Butyl 2-Benzylidene-4-cyano-4,4-diphenylbutanoate (8a): To a stirred suspension of oil-free NaH (5 mmol, 0.120 g) in anhydrous toluene (5 mL), were added successively diphenylacetonitrile (2 mmol, 0.386 g) and *tert*-butyl 3-acetoxy-2-methylene-3-phenylpropanoate (**1a**; 2 mmol, 0.552 g) at r.t. The reaction mixture was heated to reflux for 1 h under an N_2 atmosphere and then allowed to cool to 0 °C and the excess NaH was carefully quenched by slow addition of water. The reaction mixture was extracted with diethyl

ether (2 × 10 mL) and the combined organic layer was dried with anhydrous Na_2SO_4. The solvent was removed and the residue, thus obtained, was subjected to column chromatography (ethyl acetate/hexanes, 5%) to provide a solid, which was crystallized from ethyl acetate/hexanes (3%) at 0 °C to afford **8a** as a colorless crystalline solid (81%, 0.660 g); m.p. 78–80 °C. IR (KBr): $\tilde{\nu}$ = 2243, 1705, 1631 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9 H), 3.82 (s, 2 H), 6.97–7.05 (m, 2 H), 7.15–7.32 (m, 13 H), 7.67 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.02, 34.81, 51.21, 81.46, 121.70, 127.39, 127.79, 127.88, 128.32, 128.52, 128.62, 129.73, 135.34, 139.99, 142.40, 166.94 ppm. LCMS: *m*/*z* = 410 [M + H]$^+$.

(*E*)-*tert*-Butyl 4-Cyano-2-(4-isopropylbenzylidene)-4,4-diphenylbutanoate (8b): Yield 83%; m.p. 90–92 °C. IR (KBr): $\tilde{\nu}$ = 2237, 1701, 1622 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.8 Hz, 6 H), 1.44 (s, 9 H), 2.85 (sept, *J* = 6.8 Hz, 1 H), 3.83 (s, 2 H), 6.94 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 7.15–7.32 (m, 10 H), 7.64 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.89, 28.03, 33.88, 34.90, 51.27, 81.32, 121.74, 126.40, 127.42, 127.77, 128.48, 128.79, 132.75, 140.11, 142.55, 148.83, 167.12 ppm. LCMS: *m*/*z* = 452 [M + H]$^+$.

(*E*)-*tert*-Butyl 4-Cyano-2-(3-methylbenzylidene)-4,4-diphenylbutanoate (8c): Yield 78%; m.p. 82–84 °C. IR (KBr): $\tilde{\nu}$ = 2245, 1703, 1601 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 9 H), 2.22 (s, 3 H), 3.81 (s, 2 H), 6.68 (s, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 6.98 (d, *J* = 7.6 Hz, 1 H), 7.05–7.12 (m, 1 H), 7.17–7.31 (m, 10 H), 7.64 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.28, 27.98, 34.85, 51.15, 81.37, 121.68, 125.34, 127.33, 127.62, 128.09, 128.41, 128.63, 129.33, 129.44, 135.18, 137.74, 139.99, 142.59, 166.95 ppm. LCMS: *m*/*z* = 422 [M – H]$^+$.

(*E*)-*tert*-Butyl 4-Cyano-2-(4-ethylbenzylidene)-4,4-diphenylbutanoate (8d): Yield 79%; m.p. 84–86 °C. IR (KBr): $\tilde{\nu}$ = 2224, 1699, 1624 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.6 Hz, 3 H), 1.43 (s, 9 H), 2.57 (q, *J* = 7.6 Hz, 2 H), 3.83 (s, 2 H), 6.95 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 7.15–7.36 (m, 10 H), 7.66 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.47, 28.00, 28.62, 34.85, 51.25, 81.29, 121.76, 127.40, 127.77, 127.84, 128.49, 128.81, 132.60, 140.08, 142.57, 144.28, 167.10 ppm. LCMS: *m*/*z* = 438 [M + H]$^+$.

Crystal data for 8d:[13] $C_{30}H_{31}NO_2$ (437.56), colorless crystal plates, crystal dimensions: 0.38 × 0.32 × 0.22 mm^3, crystal system: monoclinic; lattice type: primitive; lattice parameters: *a* = 10.7663(9) Å, *b* = 19.0208 (16) Å, *c* = 14.8036 (9) Å, *α* = 90.00°, *β* = 122.66(4)°, *γ* = 90.00°; *V* = 2252.1 (3) Å^3; space group: p 2 (1)/c; *Z* = 4; $D_{calcd.}$ = 1.139 g/cm^3; *F*(000) = 936; *λ* (Mo-K_α) = 0.71073 Å; *R* (*I* ≥ 2σ_1) = 0.0791, *wR*^{2} = 0.2130.

(*E*)-*tert*-Butyl 4-Cyano-2-(4-methylbenzylidene)-4,4-diphenylbutanoate (8e): Yield 75%; m.p. 112–114 °C. IR (KBr): $\tilde{\nu}$ = 2233, 1701, 1639 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9 H), 2.29 (s, 3 H), 3.82 (s, 2 H), 6.95 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 7.18–7.40 (m, 10 H), 7.64 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.22, 27.98, 34.90, 51.27, 81.22, 121.75, 127.39, 127.74, 128.48, 128.76, 128.92, 129.02, 132.38, 137.96, 140.10, 142.47, 167.04 ppm. LCMS: *m*/*z* = 422 [M – H]$^+$.

(*E*)-*tert*-Butyl 2-(3-Bromobenzylidene)-4-cyano-4,4-diphenylbutanoate (8f): Yield 80%; m.p. 121–122 °C. IR (KBr): $\tilde{\nu}$ = 2235, 1701, 1635 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 9 H), 3.77 (s, 2 H), 6.83–6.98 (m, 2 H), 7.00–7.09 (m, 1 H), 7.10–7.35 (m, 11 H), 7.56 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.07, 34.80, 51.08, 81.96, 121.52, 122.57, 126.74, 127.40, 127.95, 128.56, 129.77, 130.74, 131.02, 131.34, 137.45, 139.75, 140.66, 166.56 ppm. LCMS: *m*/*z* = 488 [M + H]$^+$, 490 [M + 2 + H]$^+$.

(*E*)-*tert*-Butyl 4-Cyano-2-(2-methylbenzylidene)-4,4-diphenylbutanoate (8g): Yield 77%; m.p. 108–110 °C. IR (KBr): $\tilde{\nu}$ = 2239, 1709, 1599 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, 9 H), 1.94 (s, 3 H), 3.80 (s, 2 H), 6.97–7.27 (m, 14 H), 7.67 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.83, 28.01, 34.32, 51.20, 81.42, 121.44, 125.48, 127.15, 127.63, 127.74, 128.05, 128.45, 129.92, 130.16, 134.63, 137.35, 139.82, 141.85, 166.87 ppm. LCMS: *m*/*z* = 422 [M – H]$^+$.

(*E*)-*tert*-Butyl 4-Cyano-2-(naphth-1-ylmethylidene)-4,4-diphenylbutanoate (8h): Yield 76%; m.p. 116–118 °C. IR (KBr): $\tilde{\nu}$ = 2229, 1699, 1631 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 9 H), 3.82 (s, 2 H), 6.82–7.19 (m, 11 H), 7.22–7.49 (m, 3 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 8.11 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.15, 35.19, 51.08, 81.85, 121.53, 125.04, 125.42, 126.05, 127.01, 127.29, 128.12, 128.28, 128.49, 131.23, 131.48, 132.76, 133.39, 139.71, 141.03, 166.90 ppm. LCMS: *m*/*z* = 460 [M + H]$^+$.

2-(2-Cyano-2,2-diphenylethyl)ind-2-en-1-one (10a): To a stirred solution of (*E*)-*tert*-butyl 2-benzylidene-4-cyano-4,4-diphenylbutanoate (**8a**; 0.5 mmol, 0.205 g) in DCE (3 mL), were added TFA (2.5 mmol, 0.285 g, 0.19 mL) and TFAA (1 mmol, 0.210 g, 0.14 mL) at r.t. The reaction mixture was heated at reflux for 5 h and then allowed to cool to r.t. The reaction mixture was poured into aqueous K_2CO_3 and extracted with diethyl ether (2 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, the solvent was evaporated and the residue, thus obtained, was purified by column chromatography (ethyl acetate/hexanes, 5%) to provide **10a** as a yellow solid (66%, 0.110 g); m.p. 148–150 °C. IR (KBr): $\tilde{\nu}$ = 2235, 1709, 1599 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (d, *J* = 0.8 Hz, 2 H), 6.95 (d, *J* = 7.2 Hz, 1 H), 7.10–7.18 (m, 1 H), 7.23–7.48 (m, 13 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.57, 51.44, 122.25, 122.40, 123.01, 127.08, 128.22, 128.70, 128.97, 129.84, 133.62, 134.00, 139.35, 144.24, 146.48, 196.85 ppm. LCMS: *m*/*z* = 336 [M + H]$^+$, 334 [M – H]$^+$. $C_{24}H_{17}NO$ (335.40): calcd. C 85.94, H 5.11, N 4.18; found C 85.79, H 5.06, N 4.05.

Crystal Data for 10a:[13] $C_{24}H_{17}NO$ (335.39), yellow block-shaped crystals, crystal dimensions: 0.36 × 0.24 × 0.18 mm^3; crystal system: triclinic; lattice type: primitive; lattice parameters: *a* = 9.3189(11) Å, *b* = 10.0476(12) Å, *c* = 10.1708(12) Å, *α* = 95.696(2)°, *β* = 107.552(2)°, *γ* = 92.075(2)°; *V* = 901.30(18) Å^3; space group: $p\bar{1}$; *Z* = 2; $D_{calcd.}$ = 1.236 g/cm^3; *F*(000) = 352; *λ* (Mo-K_α) = 0.71073 Å; *R* (*I* ≥ 2σ_1) = 0.0716, *wR*^{2} = 0.1586.

2-(2-Cyano-2,2-diphenylethyl)-6-isopropylind-2-en-1-one (10b): Yield 63%; m.p. 146–148 °C. IR (KBr): $\tilde{\nu}$ = 2220, 1705, 1614 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, *J* = 6.8 Hz, 6 H), 2.85 (sept, *J* = 6.8 Hz, 1 H), 3.36 (d, *J* = 1.6 Hz, 2 H), 6.85 (d, *J* = 7.2 Hz, 1 H), 7.08–7.13 (m, 1 H), 7.23–7.39 (m, 8 H), 7.40–7.47 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.67, 33.55, 34.06, 51.46, 121.62, 122.09, 122.39, 127.05, 128.15, 128.92, 130.25, 131.51, 133.05, 139.40, 141.77, 146.71, 150.09, 197.26 ppm. LCMS: *m*/*z* = 378 [M + H]$^+$. $C_{27}H_{23}NO$ (377.48): calcd. C 85.91, H 6.14, N 3.71; found C 85.87, H 6.09, N 3.78.

2-(2-Cyano-2,2-diphenylethyl)-5-methylind-2-en-1-one (10c): Yield 64%; m.p. 138–140 °C. IR (KBr): $\tilde{\nu}$ = 2220, 1701, 1620 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 3.36 (s, 2 H), 6.76 (d, *J* = 7.2 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 7.10–7.16 (m, 1 H), 7.20 (s, 1 H), 7.23–7.38 (m, 6 H), 7.39–7.48 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.13, 33.45, 51.31, 120.07, 122.40, 126.36, 127.04, 128.12, 128.91, 131.85, 133.21, 133.37, 137.80, 139.40, 144.52, 145.26, 197.81 ppm. LCMS: *m*/*z* = 350 [M + H]$^+$. $C_{25}H_{19}NO$ (349.43): calcd. C 85.93, H 5.48, N 4.01; found C 86.10, H 5.51, N 4.07.

2-(2-Cyano-2,2-diphenylethyl)-6-ethylind-2-en-1-one (10d): Yield 70%; m.p. 122–124 °C. IR (KBr): $\tilde{\nu}$ = 2220, 1709, 1604 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, J = 7.6 Hz, 3 H), 2.57 (q, J = 7.6 Hz, 2 H), 3.36 (s, 2 H), 6.84 (d, J = 7.2 Hz, 1 H), 7.08 (d, J = 7.6 Hz, 1 H), 7.19 (s, 1 H), 7.23–7.38 (m, 7 H), 7.39–7.48 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.26, 28.68, 33.46, 51.42, 122.06, 122.36, 122.99, 127.01, 128.12, 128.88, 130.17, 132.73, 132.88, 139.33, 141.57, 145.31, 146.71, 197.17 ppm. LCMS: m/z = 364 $[M + H]^+$. $C_{26}H_{21}NO$ (363.46): calcd. C 85.92, H 5.82, N 3.85; found C 85.96, H 5.79, N 3.71.

2-(2-Cyano-2,2-diphenylethyl)-6-methylind-2-en-1-one (10e): Yield 60%; m.p. 141–142 °C. IR (KBr): $\tilde{\nu}$ = 2220, 1705, 1620 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 3.36 (d, J = 1.2 Hz, 2 H), 6.83 (d, J = 7.2 Hz, 1 H), 7.03–7.09 (m, 1 H), 7.15 (s, 1 H), 7.27–7.38 (m, 7 H), 7.40–7.46 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.32, 33.51, 51.48, 122.00, 122.41, 124.15, 127.07, 128.15, 128.91, 130.16, 132.84, 133.79, 138.89, 139.38, 141.39, 146.71, 197.14 ppm. LCMS: m/z = 350 $[M + H]^+$, 382 $[M + H + MeOH]^+$. $C_{25}H_{19}NO$ (349.43): calcd. C 85.93, H 5.48, N 4.01; found C 85.97, H 5.39, N 4.07.

5-Bromo-2-(2-cyano-2,2-diphenylethyl)ind-2-en-1-one (10f): Yield 66%; m.p. 168–170 °C. IR (KBr): $\tilde{\nu}$ = 2220, 1714, 1601 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.39 (s, 2 H), 7.11 (s, 1 H), 7.18 (d, J = 7.6 Hz, 1 H), 7.25–7.46 (m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.65, 51.41, 122.28, 124.14, 125.76, 127.08, 128.35, 128.40, 128.81, 129.06, 131.41, 135.09, 139.20, 145.12, 146.11, 195.46 ppm. LCMS (m/z): 414 $[M + H]^+$, 416 $(M + 2 + H)^+$. $C_{24}H_{16}BrNO$ (414.30): calcd. C 69.58, H 3.89, N 3.38; found C 69.48, H 3.82, N 3.45.

2-(2-Cyano-2,2-diphenylethyl)-4-methylind-2-en-1-one (10g): Yield 62%; m.p. 116–119 °C. IR (KBr): $\tilde{\nu}$ = 2239, 1703, 1621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3 H), 3.37 (s, 2 H), 6.98–7.04 (m, 1 H), 7.06 (d, J = 7.6 Hz, 1 H), 7.15 (d, J = 6.8 Hz, 1 H), 7.21–7.46 (m, 11 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.95, 33.53, 51.56, 120.70, 122.41, 127.12, 128.18, 128.57, 128.91, 129.75, 131.53, 132.82, 135.85, 139.39, 142.09, 144.90, 197.15 ppm. LCMS: m/z = 350 $[M + H]^+$. $C_{25}H_{19}NO$ (349.43): calcd. C 85.93, H 5.48, N 4.01; found C 85.96, H 5.41, N 4.10.

12-(2-Cyano-2,2-diphenylethyl)tricyclo[8.3.0.0^{2,7}]trideca-1(10),2(7),-3,5,8,12-hexaen-11-one (10h): Yield 64%; m.p. 184–186 °C. IR (KBr): $\tilde{\nu}$ = 2220, 1712, 1620 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.45 (s, 2 H), 7.27–7.41 (m, 6 H), 7.42–7.53 (m, 7 H), 7.65 (d, J = 8.0 Hz, 1 H), 7.73–7.82 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.55, 51.58, 119.25, 122.46, 123.21, 125.38, 126.65, 127.12, 127.17, 128.22, 128.25, 128.47, 128.80, 128.94, 132.08, 137.37, 139.33, 142.48, 143.48, 197.76 ppm. LCMS: m/z = 386 $[M + H]^+$. $C_{28}H_{19}NO$ (385.46): calcd. C 87.25, H 4.97, N 3.63; found C 87.16, H 5.02, N 3.71.

(*E*)-3-Benzylidene-5-phenylpiperidine-2,6-dione (4a): To a stirred solution of (*E*)-*tert*-butyl 2-benzylidene-4-cyano-4-phenylbutanoate (**2a**; 0.5 mmol, 0.167 g) in DCE (3 mL), were added CH_3SO_3H (1.5 mmol, 0.144 g, 0.098 mL) and TFAA (1 mmol, 0.210 g, 0.14 mL) at r.t. The reaction mixture was heated to reflux for 4 h and then allowed to cool to r.t. The reaction mixture was poured into aqueous K_2CO_3 and extracted with EtOAc (2 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, the solvent was evaporated and the residue, thus obtained, was purified by column chromatography (ethyl acetate/hexanes, 25%) to provide **4a** as a colorless solid (70%, 0.098 g); m.p. 172–174 °C. IR (KBr): $\tilde{\nu}$ = 3150–2900 (multiple bands), 1714, 1687, 1616 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.15–3.27 (m, 1 H), 3.30–3.42 (m, 1 H), 3.80–3.92 (m, 1 H), 7.21 (d, J = 6.8 Hz, 2 H), 7.28–7.48 (m, 8 H), 7.96 (s, 1 H), 8.09 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.62, 47.68, 125.87, 127.87, 128.15, 128.73, 128.91, 129.45, 129.83, 134.40, 136.85, 140.97, 166.67, 172.64 ppm. LCMS: m/z = 278 $[M + H]^+$, 310 $[M + H + MeOH]^+$. $C_{18}H_{15}NO_2$ (277.32): calcd. C 77.96, H 5.45, N 5.05; found C 77.85, H 5.41, N 5.14.

(*E*)-3-(3-Methylbenzylidene)-5-phenylpiperidine-2,6-dione (4b): Yield 75%; m.p. 162–164 °C. IR (KBr): $\tilde{\nu}$ = 3200–2900 (multiple bands), 1720, 1697, 1626 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 3.14–3.26 (m, 1 H), 3.28–3.42 (m, 1 H), 3.80–3.90 (m, 1 H), 7.08–7.42 (m, 9 H), 7.93 (s, 1 H), 8.10 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.49, 30.66, 47.79, 125.65, 126.88, 127.92, 128.20, 128.65, 128.97, 130.34, 130.55, 134.41, 136.95, 138.53, 141.32, 166.66, 172.69 ppm. LCMS: m/z = 292 $[M + H]^+$, 324 $[M + H + MeOH]^+$. $C_{19}H_{17}NO_2$ (291.35): calcd. C 78.33, H 5.88, N 4.81; found C 78.45, H 5.93, N 4.76.

(*E*)-3-Benzylidene-5,5-diphenylpiperidine-2,6-dione (11a): To a stirred solution of **8a** (0.5 mmol, 0.205 g) in DCE (3 mL), were added CH_3SO_3H (1.5 mmol, 0.144 g, 0.098 mL) and TFAA (1 mmol, 0.210 g, 0.14 mL) at r.t. The reaction mixture was heated to reflux for 4 h and then allowed to cool to r.t. and poured into aqueous K_2CO_3 and extracted with EtOAc (2 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4, the solvent was evaporated and the residue, thus obtained, was purified by column chromatography (ethyl acetate/hexanes, 25%) to provide **11a** as a colorless solid (85%, 0.150 g); m.p. 218–221 °C. IR (KBr): $\tilde{\nu}$ = 3150–2900 (multiple bands), 1714, 1685, 1608 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.64 (s, 2 H), 6.95–7.08 (m, 4 H), 7.19–7.52 (m, 11 H), 7.85 (s, 1 H), 8.32 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, 50% $[D_6]$DMSO in $CDCl_3$): δ = 34.34, 55.59, 125.84, 126.51, 126.69, 127.23, 127.66, 127.90, 133.02, 137.66, 139.16, 164.76, 172.80 ppm. LCMS: m/z = 354 $[M + H]^+$. $C_{24}H_{19}NO_2$ (353.42): calcd. C 81.56, H 5.42, N 3.96; found C 81.48, H 5.48, N 4.05.

Crystal Data for 11a:[13] $C_{24}H_{19}NO_2$ (353.40), colorless crystals, block-shaped, crystal dimensions: 0.28 × 0.20 × 0.18 mm^3; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 7.2161(6) Å, b = 18.4306(16) Å, c = 13.8854(12) Å, α = 90.00°, β = 98.373(2)°, γ = 90.00°; V = 1827.0(3) $Å^3$; space group: $P2(1)/c$; Z = 4; $D_{calcd.}$ = 1.285 g/cm^3; $F(000)$ = 744; λ (Mo-K_α) = 0.71073 Å; R ($I \geq 2\sigma_1$) = 0.0404, wR^2 = 0.0859.

(*E*)-3-(4-Isopropylbenzylidene)-5,5-diphenylpiperidine-2,6-dione (11b): Yield 86%; m.p. 207–208 °C. IR (KBr): $\tilde{\nu}$ = 3150–2920 (multiple bands), 1710, 1685, 1624 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (d, J = 6.8 Hz, 6 H), 2.95 (sept, J = 6.8 Hz, 1 H), 3.66 (d, J = 1.2 Hz, 2 H), 7.00–7.10 (m, 4 H), 7.22–7.37 (m, 10 H), 7.83 (s, 1 H), 8.18 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.78, 34.04, 36.54, 57.44, 125.38, 126.95, 127.66, 128.23, 128.45, 129.90, 132.02, 140.27, 141.29, 150.65, 166.40, 174.15 ppm. LCMS: m/z = 396 $[M + H]^+$. $C_{27}H_{25}NO_2$ (395.50): calcd. C 82.00, H 6.37, N 3.54; found C 82.15, H 6.30, N 3.61.

(*E*)-3-(3-Methylbenzylidene)-5,5-diphenylpiperidine-2,6-dione (11c): Yield 81%; m.p. 207–208 °C. IR (KBr): $\tilde{\nu}$ = 3150–2925 (multiple bands), 1699, 1685, 1618 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 3.63 (d, J = 1.6 Hz, 2 H), 6.98–7.18 (m, 4 H), 7.11–7.38 (m, 10 H), 7.81 (s, 1 H), 8.27 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.50, 36.39, 57.55, 126.09, 126.57, 127.72, 128.23, 128.48, 128.70, 130.27, 130.33, 134.52, 138.56, 140.15, 141.55, 166.29, 174.14 ppm. LCMS: m/z = 368 $[M + H]^+$. $C_{25}H_{21}NO_2$ (367.45): calcd. C 81.72, H 5.76, N 3.81; found C 81.65, H 5.71, N 3.92.

(*E*)-3-(4-Ethylbenzylidene)-5,5-diphenylpiperidine-2,6-dione (11d): Yield 77%; m.p. 186–188 °C. IR (KBr): $\tilde{\nu}$ = 3140–2915 (multiple

bands), 1716, 1682, 1620 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.2 Hz, 3 H), 2.68 (q, J = 7.2 Hz, 2 H), 3.65 (s, 2 H), 6.98–7.07 (m, 4 H), 7.22–7.37 (m, 10 H), 7.83 (s, 1 H), 8.13 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.17, 28.71, 36.50, 57.39, 125.41, 127.58, 128.17, 128.30, 128.38, 129.83, 131.88, 140.26, 141.20, 145.98, 166.50, 174.16 ppm. LCMS: m/z = 382 $[M + H]^+$. $C_{26}H_{23}NO_2$ (381.47): calcd. C 81.86, H 6.08, N 3.67; found C 81.92, H 6.13, N 3.58.

(*E*)-3-(4-Methylbenzylidene)-5,5-diphenylpiperidine-2,6-dione (11e): Yield 80%; m.p. 228–230 °C. IR (KBr): $\tilde{\nu}$ = 3150–2925 (multiple bands), 1712, 1682, 1625 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 3.65 (s, 2 H), 6.98–7.07 (m, 4 H), 7.22–7.35 (m, 10 H), 7.82 (s, 1 H), 8.06 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, 50% $[D_6]$DMSO in $CDCl_3$): δ = 19.81, 34.48, 55.51, 124.74, 124.98, 125.84, 126.55, 126.70, 127.99, 128.07, 130.12, 137.74, 139.25, 164.81, 172.80 ppm. LCMS: m/z = 368 $[M + H]^+$. $C_{25}H_{21}NO_2$ (367.45): calcd. C 81.72, H 5.76, N 3.81; found C 81.57, H 5.82, N 3.76.

(*E*)-3-(3-Bromobenzylidene)-5,5-diphenylpiperidine-2,6-dione (11f): Yield 82%; m.p. 138–140 °C. IR (KBr): $\tilde{\nu}$ = 3150–2945 (multiple bands), 1715, 1690, 1614 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.58 (s, 2 H), 6.97–7.05 (m, 4 H), 7.20–7.32 (m, 8 H), 7.41 (s, 1 H), 7.51 (d, J = 7.6 Hz, 1 H), 7.73 (s, 1 H), 8.61 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.14, 57.57, 122.92, 127.77, 127.81, 127.85, 128.15, 128.56, 130.35, 132.12, 132.34, 136.59, 139.43, 139.94, 165.85, 173.89 ppm. LCMS: m/z = 432 $[M + H]^+$, 434 $[M + 2 + H]^+$. $C_{24}H_{18}BrNO_2$ (432.32): calcd. C 66.68, H 4.20, N 3.24; found C 66.57, H 4.26, N 3.29.

(*E*)-3-(2-Methylbenzylidene)-5,5-diphenylpiperidine-2,6-dione (11g): Yield 75%; m.p. 182–184 °C. IR (KBr): $\tilde{\nu}$ = 3150–2925 (multiple bands), 1716, 1682, 1622 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 3 H), 3.52 (d, J = 1.6 Hz, 2 H), 6.94–7.01 (m, 4 H), 7.13 (d, J = 7.6 Hz, 1 H), 7.18–7.38 (m, 9 H), 7.86 (s, 1 H), 8.18 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.80, 36.30, 57.68, 125.86, 126.84, 127.69, 128.12, 128.47, 128.86, 129.40, 130.44, 133.59, 137.64, 140.06, 140.80, 166.27, 174.17 ppm. LCMS: m/z = 368 $[M + H]^+$. $C_{25}H_{21}NO_2$ (367.45): calcd. C 81.72, H 5.76, N 3.81; found C 81.65, H 5.81, N 3.88.

(*E*)-3-(Naphth-1-ylmethylidene)-5,5-diphenylpiperidine-2,6-dione (11h): Yield 79%; m.p. 158–160 °C. IR (KBr): $\tilde{\nu}$ = 3150–2920 (multiple bands), 1722, 1685, 1624 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.54 (s, 2 H), 6.92 (d, J = 7.6 Hz, 4 H), 7.08–7.61 (m, 10 H), 7.71 (d, J = 8.4 Hz, 1 H), 7.86–7.98 (m, 2 H), 8.13 (br. s, 1 H), 8.35 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.85, 57.59, 124.70, 125.13, 126.61, 126.83, 126.99, 127.66, 128.16, 128.34, 128.47, 128.67, 129.84, 131.44, 131.69, 133.57, 139.90, 140.03, 166.02, 174.22 ppm. LCMS: m/z = 404 $[M + H]^+$. $C_{28}H_{21}NO_2$ (403.48): calcd. C 83.35, H 5.25, N 3.47; found C 83.24, H 5.31, N 3.55.

Supporting Information (see also the footnote on the first page of this article): ^1H and ^{13}C NMR spectra for all the indenones **5a**, **5b**, **7a**, **7b**, and **10a**–**h** and piperidine-2,6-diones **4a**, **4b**, and **11a**–**h**. ORTEP diagrams of compound **8d** (Figure S1), **10a** (Figure S2), and **11a** (Figure S3).

Acknowledgments

We thank the Department of Science and Technology (DST) (New Delhi) for funding this project. D. V. L. thanks the University Grants Commission (UGC) (New Delhi) for his fellowship. We thank UGC (New Delhi) for support and for providing some instrumental facilities. We thank the National Single-Crystal X-ray facility, funded by DST. We thank Prof. S. Pal, School of Chemistry, University of Hyderabad for helpful discussions regarding the X-ray crystal structures.

[1] a) L. M. X. Lopes, M. Yoshida, O. R. Gottlieb, *Phytochemistry* **1984**, *23*, 2021–2024; b) M. A. Ernst-Russell, C. L. L. Chai, J. H. Wardlaw, J. A. Elix, *J. Nat. Prod.* **2000**, *63*, 129–131.

[2] a) J. H. Ahn, M. S. Shin, S. H. Jung, S. K. Kang, K. R. Kim, S. D. Rhee, W. H. Jung, S. D. Yang, S. J. Kim, J. R. Woo, J. H. Lee, H. G. Cheon, S. S. Kim, *J. Med. Chem.* **2006**, *49*, 4781–4784; b) J. H. Ahn, M. S. Shin, S. H. Jung, J. A. Kim, H. M. Kim, S. H. Kim, S. K. Kang, K. R. Kim, S. D. Rhee, S. D. Park, J. M. Lee, J. H. Lee, H. G. Cheon, S. S. Kim, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5239–5244; c) G. M. Anstead, S. R. Wilson, J. A. Katzenellenbogen, *J. Med. Chem.* **1989**, *32*, 2163–2171; d) G. M. Anstead, R. J. Altenbach, S. R. Wilson, J. A. Katzenellenbogen, *J. Med. Chem.* **1988**, *31*, 1316–1326; e) C. H. Park, X. Siomboing, S. Yous, B. Gressier, M. Luyckx, P. Chavatte, *Eur. J. Med. Chem.* **2002**, *37*, 461–468; f) S. H. Reich, T. Johnson, M. B. Wallace, S. E. Kephart, S. A. Fuhrman, S. T. Worland, D. A. Matthews, T. F. Hendrickson, F. Chan, J. Meador III, R. A. Ferre, E. L. Brown, D. M. DeLisle, A. K. Patick, S. L. Binford, C. E. Ford, *J. Med. Chem.* **2000**, *43*, 1670–1683.

[3] a) T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Kagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, N. Chatani, T. Nishioka, *Org. Lett.* **2009**, *11*, 1777–1780; b) D. Mal, S. R. De, *Org. Lett.* **2009**, *11*, 4398–4401; c) H. Shimizu, M. Murakami, *Synlett* **2008**, 1817–1820; d) C.-C. Liu, R. P. Korivi, C.-H. Cheng, *Chem. Eur. J.* **2008**, *14*, 9503–9506; e) H. Tsukamoto, Y. Kondo, *Org. Lett.* **2007**, *9*, 4227–4230; f) J. Petrignet, T. Roisnel, R. Gree, *Chem. Eur. J.* **2007**, *13*, 7374–7384; g) B. Chen, X. Xie, J. Lu, Q. Wang, J. Zhang, S. Tang, X. She, X. Pan, *Synlett* **2006**, 259–262; h) T. Miura, M. Murakami, *Org. Lett.* **2005**, *7*, 3339–3341; i) A. V. Vasilyev, S. Walspurger, P. Pale, J. Sommer, *Tetrahedron Lett.* **2004**, *45*, 3379–3381; j) D. C. Harrowven, N. A. Newman, C. A. Knight, *Tetrahedron Lett.* **1998**, *39*, 6757–6760; k) R. Aumann, J. Schroder, H. Heinen, *Chem. Ber.* **1990**, *123*, 1369–1374; l) R. J. Murray, N. H. Cromwell, *J. Org. Chem.* **1976**, *41*, 3540–3545.

[4] a) *Dictionary of Drugs* (Eds.: J. Elks, C. R. Ganellin), Chapman and Hall, London, **1990**, 1st ed., p. 32 (A-00142); b) A. A. Carr, D. R. Meyer, *Ger. Pat.* 1971, 2,035,636; *Chem. Abstr.* **1971**, *74*, 99895h; c) S. M. Capitosti, T. P. Hansen, M. L. Brown, *Org. Lett.* **2003**, *5*, 2865–2867; d) H. Kondo, T. Oritani, H. Kiyota, *Eur. J. Org. Chem.* **2000**, 3459–3462; e) C. Gaul, J. T. Njardarson, D. Shan, D. C. Dorn, K.-D. Wu, W. P. Tong, X.-Y. Huang, M. A. S. Moore, S. J. Danishefsky, *J. Am. Chem. Soc.* **2004**, *126*, 11326–11337; f) C. Gaul, J. T. Njardarson, S. J. Danishefsky, *J. Am. Chem. Soc.* **2003**, *125*, 6042–6043; g) S. Reymond, J. Cossy, *Eur. J. Org. Chem.* **2006**, 4800–4804; h) K. Sugawara, Y. Nishiyama, S. Toda, N. Komiyama, M. Hatori, T. Moriyama, Y. Sawada, H. Kamei, M. Konishi, T. Oki, *J. Antibiot.* **1992**, *45*, 1433–1441; i) J. Ju, S. R. Rajski, S.-K. Lim, J.-w. Seo, N. R. Peters, F. M. Hoffmann, B. Shen, *J. Am. Chem. Soc.* **2009**, *131*, 1370–1371; j) R. G. Powell, C. R. Smith Jr., D. Weisleder, *J. Am. Chem. Soc.* **1983**, *105*, 3739–3741; k) R. H. Schlessinger, J. L. Wood, *J. Org. Chem.* **1986**, *51*, 2621–2623.

[5] a) D. Basavaiah, D. V. Lenin, B. Devendar, *Tetrahedron Lett.* **2009**, *50*, 3538–3542; b) D. Basavaiah, R. J. Reddy, *Org. Biomol. Chem.* **2008**, *6*, 1034–1039; c) V. Singh, G. P. Yadav, P. R. Maulik, S. Batra, *Tetrahedron* **2006**, *62*, 8731–8739; d) M. J. Lee, S. C. Kim, J. N. Kim, *Bull. Korean Chem. Soc.* **2006**, *27*, 140–142; e) H.-W. Chen, R.-T. Hsu, M.-Y. Chang, N.-C. Chang, *Org. Lett.* **2006**, *8*, 3033–3035; f) P.-P. Sun, M.-Y. Chang, M.-Y. Chiang, N.-C. Chang, *Org. Lett.* **2003**, *5*, 1761–1763; g) J. B. P. Dordevic, M. D. Ivanovic, V. D. Kiricojevic, *Tetrahedron Lett.* **2005**, *46*, 2611–2614; h) M. J. Wanner, G. J. Koomen, *Tetrahedron Lett.* **1992**, *33*, 1513–1516.

[6] a) D. Basavaiah, K. R. Reddy, *Tetrahedron* **2010**, *66*, 1215–1219; b) D. Basavaiah, K. Aravindu, K. Santosh Kumar, K. R. Reddy, *Eur. J. Org. Chem.* **2010**, 1843–1848; c) D. Basavaiah, B. Devendar, K. Aravindu, A. Veerendhar, *Chem. Eur. J.* **2010**, *16*, 2031–2035; d) D. Basavaiah, B. Devendar, D. V. Lenin, T. Satyanarayana, *Synlett* **2009**, 411–416; e) D. Basavaiah, K. Aravindu, *Org. Lett.* **2007**, *9*, 2453–2456; f) D. Basavaiah, K. R. Reddy, *Org. Lett.* **2007**, *9*, 57–60; g) D. Basavaiah, R. J. Reddy, J. S. Rao, *Tetrahedron Lett.* **2006**, *47*, 73–77; h) D. Basavaiah, J. S. Rao, R. J. Reddy, A. J. Rao, *Chem. Commun.* **2005**, 2621–2623; i) D. Basavaiah, D. S. Sharada, A. Veerendhar, *Tetrahedron Lett.* **2004**, *45*, 3081–3083; j) D. Basavaiah, T. Satyanarayana, *Chem. Commun.* **2004**, 32–33; k) D. Basavaiah, J. S. Rao, R. J. Reddy, *J. Org. Chem.* **2004**, *69*, 7379–7382; l) D. Basavaiah, A. J. Rao, *Tetrahedron Lett.* **2003**, *44*, 4365–4368; m) D. Basavaiah, R. M. Reddy, N. Kumaragurubaran, D. S. Sharada, *Tetrahedron* **2002**, *58*, 3693–3697.

[7] For leading reviews on the Baylis–Hillman reaction, see: a) S. Gowrisankar, H. S. Lee, S. H. Kim, K. Y. Lee, J. N. Kim, *Tetrahedron* **2009**, *65*, 8769–8780; b) V. Declerck, J. Martinez, F. Lamaty, *Chem. Rev.* **2009**, *109*, 1–48; c) V. Singh, S. Batra, *Tetrahedron* **2008**, *64*, 4511–4574; d) D. Basavaiah, K. V. Rao, R. J. Reddy, *Chem. Soc. Rev.* **2007**, *36*, 1581–1588; e) G. Masson, C. Housseman, J. Zhu, *Angew. Chem. Int. Ed.* **2007**, *46*, 4614–4628; f) D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811–891; g) E. Ciganek, in: *Organic Reactions* (Ed.: L. A. Paquette), Wiley, New York, **1997**, vol. 51, pp. 201–350; h) D. Basavaiah, P. Dharma Rao, R. Suguna Hyma, *Tetrahedron* **1996**, *52*, 8001–8062; i) S. E. Drewes, G. H. P. Roos, *Tetrahedron* **1988**, *44*, 4653–4670.

[8] a) M. C. Redondo, M. Ribagorda, M. C. Carreno, *Org. Lett.* **2010**, *12*, 568–571; b) G. W. Amarante, H. M. S. Milagre, B. G. Vaz, B. R. V. Ferreira, M. N. Eberlin, F. Coelho, *J. Org. Chem.* **2009**, *74*, 3031–3037; c) B. Alcaide, P. Almendros, T. M. del Campo, M. T. Quiros, *Chem. Eur. J.* **2009**, *15*, 3344–3346; d) M. Bakthadoss, G. Sivakumar, D. Kannan, *Org. Lett.* **2009**, *11*, 4466–4469; e) X.-Y. Guan, Y. Wei, M. Shi, *J. Org. Chem.* **2009**, *74*, 6343–6346; f) E. Tarsis, A. Gromova, D. Lim, G. Zhou, D. M. Coltart, *Org. Lett.* **2008**, *10*, 4819–4822; g) Y. Shang, Z. Feng, L. Yuan, S. Wang, *Tetrahedron* **2008**, *64*, 5779–5783; h) S. A. M. Winbush, D. J. Mergott, W. R. Roush, *J. Org. Chem.* **2008**, *73*, 1818–1829; i) Z.-Y. Lei, G.-N. Ma, M. Shi, *Eur. J. Org. Chem.* **2008**, 3817–3820; j) J. M. Sorbetti, K. N. Clary, D. A. Rankic, J. E. Wulff, M. Parvez, T. G. Back, *J. Org. Chem.* **2007**, *72*, 3326–3331; k) R. Robiette, V. K. Aggarwal, J. N. Harvey, *J. Am. Chem. Soc.* **2007**, *129*, 15513–15525; l) Z. Shafiq, L. Liu, Z. Liu, D. Wang, Y.-J. Chen, *Org. Lett.* **2007**, *9*, 2525–2528; m) M. Dadwal, R. Mohan, D. Panda, S. M. Mobin, I. N. N. Namboothiri, *Chem. Commun.* **2006**, 338–340; n) J. Xu, Y. Guan, S. Yang, Y. Ng, G. Peh, C.-H. Tan, *Chem. Asian J.* **2006**, *1*, 724–729; o) C. E. Aroyan, M. M. Vasbinder, S. J. Miller, *Org. Lett.* **2005**, *7*, 3849–3851; p) T. Turki, J. Villieras, H. Amri, *Tetrahedron Lett.* **2005**, *46*, 3071–3072; q) M. E. Krafft, T. F. N. Haxell, *J. Am. Chem. Soc.* **2005**, *127*, 10168–10169; r) G. W. Kabalka, B. Venkataiah, G. Dong, *J. Org. Chem.* **2004**, *69*, 5807–5809; s) D. Chen, C. Timmons, J. Liu, A. Headley, G. Li, *Eur. J. Org. Chem.* **2004**, 3330–3335; t) H. Kinoshita, S. Kinoshita, Y. Munechika, T. Iwamura, S.-i. Watanabe, T. Kataoka, *Eur. J. Org. Chem.* **2003**, 4852–4861; u) P. T. Kaye, M. A. Musa, X. W. Nocanda, R. S. Robinson, *Org. Biomol. Chem.* **2003**, *1*, 1133–1138; v) D. Basavaiah, A. J. Rao, *Chem. Commun.* **2003**, 604–605; w) D. Basavaiah, B. Sreenivasulu, A. J. Rao, *J. Org. Chem.* **2003**, *68*, 5983–5991; x) D. Basavaiah, M. Krishnamacharyulu, R. Suguna Hyma, P. K. S. Sarma, N. Kumaragurubaran, *J. Org. Chem.* **1999**, *64*, 1197–1200; y) D. Basavaiah, R. Suguna Hyma, K. Padmaja, M. Krishnamacharyulu, *Tetrahedron* **1999**, *55*, 6971–6976; z) D. Basavaiah, V. V. L. Gowriswari, P. K. S. Sarma, P. Dharma Rao, *Tetrahedron Lett.* **1990**, *31*, 1621–1624.

[9] a) D. Basavaiah, M. Krishnamacharyulu, R. Suguna Hyma, S. Pandiaraju, *Tetrahedron Lett.* **1997**, *38*, 2141–2144; b) D. Basavaiah, S. Pandiaraju, K. Padmaja, *Synlett* **1996**, 393–395; c) D. Basavaiah, M. Bakthadoss, G. Jayapal Reddy, *Synthesis* **2001**, 919–923; d) D. Basavaiah, R. M. Reddy, *Tetrahedron Lett.* **2001**, *42*, 3025–3027; e) D. Basavaiah, M. Bakthadoss, S. Pandiaraju, *Chem. Commun.* **1998**, 1639–1640.

[10] We also isolated approximately 20–30 mg of an unknown impure product in the 0.5 mmol scale reaction. Although there was no significant formation of the tetralone derivatives, the presence of some minor amounts of such derivatives is not ruled out because the yields of the indenone derivatives was only 38–40%.

[11] Chemical shifts of the β-vinyl protons *cis* to the carbonyl group (ketone, ester, acid, and amide) were well differentiated from those of corresponding β-vinyl protons *trans* to the carbonyl group in the ^{1}H NMR spectrum of trisubstituted alkenes. The vinylic β-protons *cis* to the carbonyl group appear downfield in comparison with those of vinylic β-protons *trans* to the carbonyl group.[5a,9a,9b,9d,9e] See also: L. M. Jackman, S. Sternhell, *Applications of nuclear magnetic resonance spectroscopy in organic chemistry*, 2nd ed., Pergamon, Oxford, **1969**, vol. 5; S. W. Tobey, *J. Org. Chem.* **1969**, *34*, 1281–1298].

[12] We also isolated approximately 30–40% of the *trans*-cinnamic acid (in addition to the desired indenone derivative).

[13] Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union road, Cambridge CB2 1EZ, UK, for compounds **8d** (CCDC-775027), **10a** (CCDC-775028), and **11a** (CCDC-776461).

[14] In this case also the formation of minor amounts of the tetralone derivative cannot be ruled out because the yields of the products were not quantitative.

[15] This compound was prepared by reduction of *tert*-butyl 3-acetoxy-2-methylene-3-phenylpropanoate with $NaBH_4$ in *t*BuOH following the known procedure developed by our research group.[8x] Compound **7a** is known in the literature and its spectroscopic data (IR, ^{1}H NMR, and ^{13}C NMR) are also reported.[3k,3l] Our data is in agreement with those reported in the literature.

[16] Literature report[3l] indicates that **7a** is a low melting solid (44–46 °C). Since yields of the compound were very low, we did not attempt to obtain the compound as a solid.

Received: May 21, 2010
Published Online: August 24, 2010

