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Three-component synthesis of cyclic β-aminoesters using CeO_2 nanoparticles as an efficient and reusable catalyst

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Abstract: CeO_2 nanoparticles were used as an efficient catalyst for the preparation of cyclic β-aminoesters by three-component reaction between primary amines, ethyl acetoacetate, and chalcones in ethanol. Atom economy, low catalyst loading, reusable catalyst, and high yields of products are some of the important features of this protocol.

Key words: Cyclic β-aminoesters, reusable catalyst, CeO_2 nanoparticles, chalcones, one-pot

1. Introduction

Aminoesters are important classes of organic compounds due to their wide range of biological and pharmacological activities. Aminoester-based compounds such as taxol and taxotere are a subunit in many natural products that have been investigated for screening of treating specific neoplasms.[1] A bioreducible linear poly(β-amino ester) has been designed to condense siRNA into nanoparticles and efficiently release it upon entering the cytoplasm.[2] A library of end-modified poly(β-amino ester)s have been reported as gene delivery vehicles.[3] Therefore, the development of novel, rapid, and clean synthetic routes towards focused libraries of such compounds is of great importance to both medicinal and synthetic chemists. A series of N-supported β-aminoesters have been designed via the aza-Baylis–Hillman reaction.[4] Recently, the synthesis of cyclic β-aminoesters via the three-component coupling of primary amines, β-ketoesters, and chalcones has been reported using MCRs in the presence of cerium(IV) ammonium nitrate (CAN) as catalyst.[5] However, some of the reported methods tolerate disadvantages including long reaction times and harsh reaction conditions. Therefore, to avoid these limitations, the exploration of an efficient, easily available catalyst with high catalytic activity and short reaction time for the preparation of β-aminoesters is still favored. The possibility of accomplishing multicomponent reactions under moderate conditions with a heterogeneous catalyst could improve their effectiveness from operating cost and ecological points of view. Nanoparticles can exhibit unique physical and chemical properties owing to their limited size and high surface areas. The high surface area of the nanoparticles is responsible for their catalytic activity. They decrease reaction times, impart greater selectivity, and can be easily recovered from the reaction mixture by simple filtration.[6–12] Among various nanoparticles, cerium nanoparticles have received considerable attention due to their unique properties and potential applications in various fields. CeO_2 has received much attention because of its many attractive properties, such as its unique UV absorption ability,[13] its ferromagnetism

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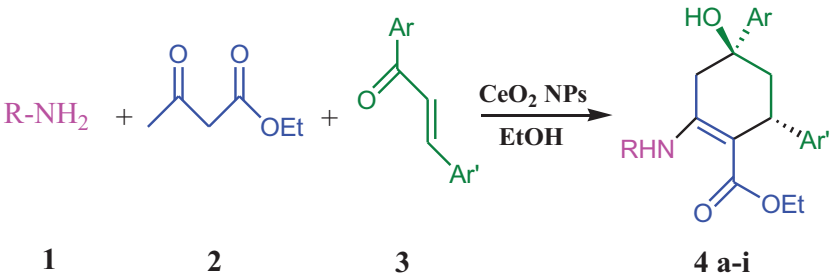
characteristics,[14] and as a major component of catalyst formulation for the dehydrogenation of ethylbenzene to styrene.[15] Recently, cerium nanoparticles were used as an expedient catalyst in many reactions including synthesis of cyclic ureas,[16] polyhydroquinolines,[17] and 1,4-disubstituted-1,2,3-triazoles.[18] Our research group has reported that CeO_2 nanoparticles act as an efficient heterogeneous catalyst for the direct synthesis of 4,6-disubstituted 2-alkylaminocyclohexene-1-carboxylic esters by the three-component reaction between primary amines, ethyl acetoacetate, and chalcones in ethanol as solvent (Scheme 1).



Scheme 1. Synthesis of 2-aminocyclohex-1-ene-1-carboxylic esters.

2. Results and discussion

The catalyst was prepared by the co-precipitation technique using aqueous ammonia solution as the precipitating agent. The XRD patterns for CeO_2 nanoparticles are shown in Figure 1. The particle size of CeO_2 nanoparticles was investigated by XRD pattern. The crystallite size diameter (D) of the CeO_2 nanoparticles was calculated using the Debye–Scherrer equation ($D = K\lambda/\beta \cos\Theta$), where FWHM (full-width at half-maximum) is in radians, Θ is the position of the maximum of the diffraction peak, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the X-ray wavelength. The pattern agrees well with the reported pattern for CeO_2 nanoparticles (JCPDS No. 43-1002). The crystalline size was calculated from FWHM using Scherrer's formula and was observed to be 11 nm. The morphology and particle size of CeO_2 NPs were studied by scanning electron microscopy (SEM) as shown in Figure 2. The SEM images display particles with diameters in the size of nanometers.

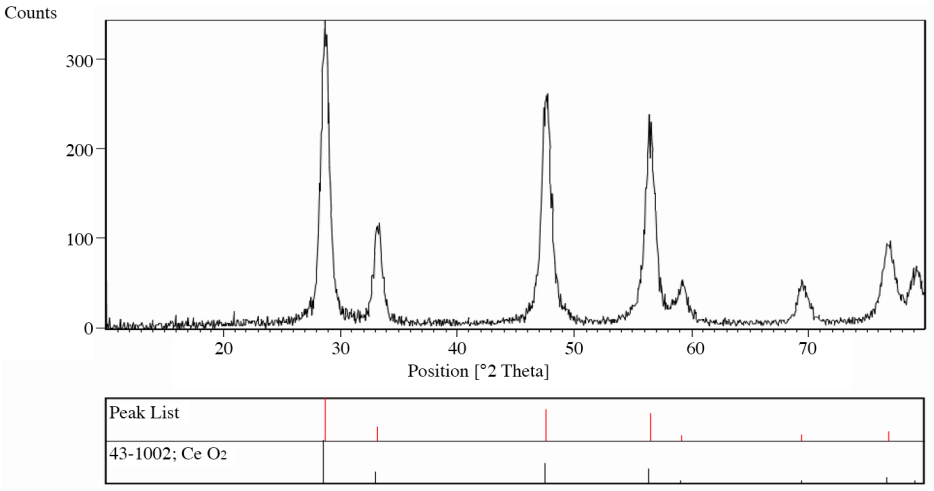


Figure 1. The XRD pattern of CeO_2 NPs.

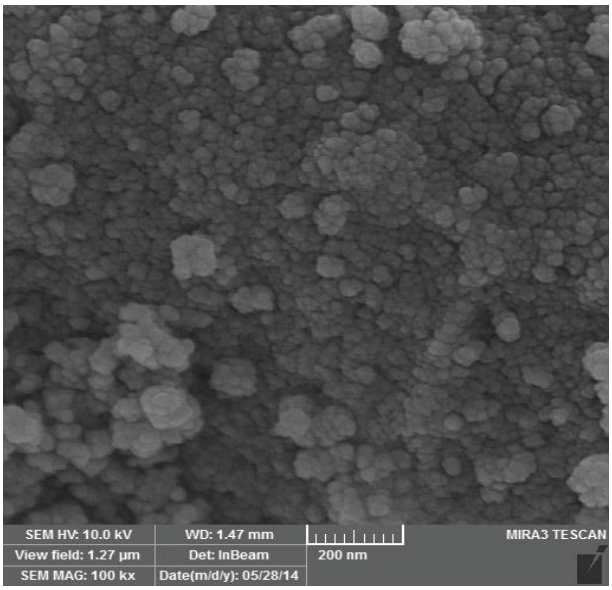


Figure 2. SEM images of CeO_2 NPs.

Initially, we carried out the MCR between butyl amine, ethyl acetoacetate, and chalcone at room temperature as a model reaction in the presence of different catalysts. Meanwhile, we observed the effect of different solvents on the progress of the reaction. Ethanol was found to be the best solvent, in which the product was obtained in good yield. We examined several catalysts for this multicomponent synthesis. From the results, reported in Table 1, it is evident that CeO_2 nanoparticles are the best catalyst among those tested. The model reactions were carried out in the presence of various catalysts, such as ZrO_2, CuO, $InCl_3$, and CAN. When the reaction was carried out using CAN and CeO_2 NPs as the catalyst, the product was obtained in moderate to good yield. The reaction works well for different chalcones and primary amine. The substituents with electron-withdrawing properties reacted faster than substituents with electron-donor properties at both aromatic rings (Table 2).

Table 1. Optimization of reaction condition using different catalysts.[a]

Entry	Solvent	Catalyst	mol%	Time (h)	Yield %[b]
1	*n*-Hexane	ZrO_2	4	45	12
2	CH_2Cl_2	$InCl_3$	3	35	15
3	H_2O	CuO	4	33	23
4	CH_3CN	CAN	5	30	58
5	EtOH	CAN	5	30	62
6	EtOH	Nd_2O_3	2	15	55
7	EtOH	CeO_2 bulk	5	12	60
8	CH_3CN	CeO_2 NPs	4	6	67
9	EtOH	CeO_2 NPs	2	5	72
10	EtOH	CeO_2 NPs	4	5	85
11	EtOH	CeO_2 NPs	6	5	85

[a] *n*-Butyl amine (3.9 mmol), ethyl acetoacetate (3 mmol), chalcone (3.3 mmol)
[b] Isolated yield

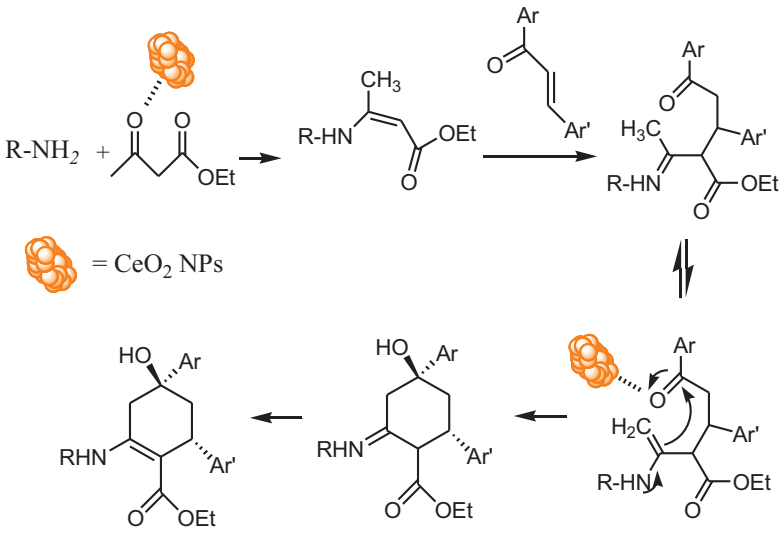
Table 2. Synthesis of 2-aminocyclohex-1-ene-1-carboxylic esters at room temperature in ethanol.

Entry	product	R	Ar'	Ar	Time (h)	Yield %[a]	mp (°C) [ref.]
1	**4a**	*n*Bu	C_6H_5	C_6H_5	5	85	98–99 [5]
2	**4b**	*n*Bu	C_6H_5	4-Cl-C_6H_4	4.5	84	117–118 [5]
3	**4c**	H	C_6H_5	C_6H_5	7	73	140–141 [5]
4	**4d**	H	C_6H_5	4-Cl- C_6H_4	6.5	75	146–147 [5]
5	**4e**	H	4-F-C_6H_4	C_6H_5	7	72	168–171
6	**4f**	*n*Bu	4-F-C_6H_4	C_6H_5	6	80	126–129
7	**4g**	*n*Bu	4-Me-C_6H_4	C_6H_5	7.5	71	135–137
8	**4h**	*n*Bu	C_6H_5	4-Me-C_6H_4	7.5	70	107–109
9	**4i**	H	4-Me-C_6H_4	C_6H_5	9	68	173–175

[a]Isolated yield

We also investigated recycling of the CeO_2 NPs as catalyst in ethanol for the preparation of product **4a**. The results showed that CeO_2 NPs can be reused several times without noticeable loss of catalytic activity (run 1 85%, run 2 84%, run 3 83%, run 4 81%, run 5 81%).

The mechanism of these domino reactions is proposed in Scheme 2. Moreover, the present reaction CeO_2 NPs may act as Lewis solid acids. The increased surface area due to small particle size increased reactivity. The reaction proceeded with complete selectivity in favor of the diastereoisomer having a *cis*-arrangement for the aryl substituents at C-4 and C-6, with both substituents placed in an equatorial position.



Scheme 2. Proposed reaction pathway for the synthesis of 2-aminocyclohex-1-ene-1-carboxylic esters.

We have developed a straightforward method for the synthesis of 2-aminocyclohex-1-ene-1-carboxylic esters at room temperature in good to excellent yields in the presence of CeO_2 nanoparticles as a reusable and efficient catalyst.

3. Experimental

3.1. Chemicals and apparatus

All organic materials were purchased commercially from Sigma-Aldrich and Merck and were used without further purification. All melting points are uncorrected and were determined in a capillary tube on a Boetius melting

point microscope. FT-IR spectra were recorded with KBr pellets using a Nicolet Magna 550 IR spectrometer. NMR spectra were recorded on a Bruker 400 MHz spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Powder X-ray diffraction (XRD) was carried out on a Philips X'pert diffractometer. Microscopic morphology of products was visualized by SEM (MIRA 3 TESCAN).

3.2. Preparation of CeO_2 nanoparticles

Nano CeO_2 was prepared according to the method reported in the literature with some modification.[19] CeO_2 nanoparticles were prepared by a co-precipitation procedure with postannealing in air. Briefly, 3 g of highly pure $Ce(NO_3)_3.6H_2O$ was dissolved in a mixture of 50 mL of deionized water and 20 mL of alcohol. Then the adequate amount of aqueous ammonia solution (28 wt%) was added to the above solution until the pH value reached 8. Next the mixture was stirred for 4 h at room temperature and then dried at 80 °C for 6 h. After, the solid was treated at 700 °C for 2 h to obtain the CeO_2 nanoparticles.

3.3. General procedure for the synthesis of 2-aminocyclohex-1-ene-1-carboxylic esters

A solution of amine (3.9 mmol) and ethyl acetoacetate (3 mmol) in ethanol (4 mL) and CeO_2 nanoparticles (4 mol%) as catalyst was stirred for 15 min at room temperature. Chalcone (3.3 mmol) was then added to the stirred solution and the stirring was continued for the time periods specified. After completion of the reaction, as indicated by TLC, the mixture was dissolved in CH_2Cl_2 (20 mL), filtered, and the heterogeneous catalyst was recovered, washed with water and brine, dried (anhydrous Na_2SO_4), and the solvent was evaporated under reduced pressure. Pure products were obtained by column chromatography on neutral alumina, eluting with an n-hexane-ethyl acetate mixture (90:10 v/v).

3.4. Spectral data

Ethyl 2-(butylamino)-4-hydroxy-4,6-diphenylcyclohex-1-enecarboxylate (4a): mp 97–100 °C (lit.[5] mp 98–99 °C); IR (KBr): (υ_{max}/cm^{-1}) 3445.6, 3269.5, 3019.7, 1628.5, 1594.5, 1449.0, ^{1}H NMR ($CDCl_3$, 400 MHz): 0.88 (t, J = 6.9 Hz, 3H), 1.06 (t, J= 7.2 Hz, 3H), 1.09 (m, 2H), 1.27 (m, 2H), 2.28 (dd, J = 14.0, 12.0 Hz, 1H), 2.39 (dd, J = 14.0, 6.9 Hz, 1H), 2.49 (m, 1H), 2.80 (m, 1H), 3.13 (dd, J= 12, 6.9 Hz, 1H), 3.61 (m, 2H), 4.08 (q, 2H, OCH_2), 6.59 (bs, 1H, NH), 7.50 (bs, 1H, OH), 7.24–7.55 (m, 10 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.1, 14.4, 20.6, 32.9, 39.9, 41.7, 42.9, 46.2, 58.9, 72.3, 91.6, 124.9, 125.7, 127.1, 127.8, 128.5, 128.8, 146.9, 150.1, 157.9, 170.9. Anal. Calcd for $C_{25}H_{31}NO_3$: C, 76.30; H, 7.94; N, 3.56. Found: C, 76.41; H, 7.85; N, 3.61.

Ethyl 2-(butylamino)-4-(4-chlorophenyl)-4-hydroxy-6-phenylcyclohex-1-enecarbox-ylate (4b): mp 118-119 °C (lit.[5] mp 117–118 °C); IR (KBr): (υ_{max}/cm^{-1}) 3431.1, 3276.8, 3024.6, 2932.1, 1625.1, 1592.5, 1452.1, 1095.1. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.80 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H), 1.08 (m, 2H), 1.30 (m, 2H), 2.27 (dd, J = 13.7, 11.0 Hz, 1H), 2.38 (dd, J = 13.7, 6.8 Hz, 1H), 2.46 (m, 1H), 2.75 (m, 1H), 3.12 (dd, J= 11.0, 6.8 Hz, 1H), 3.53 (m, 2H), 4.08 (q, 2H, OCH_2), 6.59 (bs, 1H, NH), 7.50 (brs, 1H, OH), 7.24–7.55 (m, 9 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.1, 14.3, 20.7, 32.8, 39.9, 41.5, 42.9, 45.9, 59.1, 71.9, 91.6, 125.7, 126.7, 127.1, 128.6, 128.9, 133.6, 145.6, 149.7, 157.6, 170.8. Anal. Calcd for $C_{25}H_{30}ClNO_3$: C, 70.16; H, 7.07; N, 3.27. Found: C, 70.11; H, 6.96; N, 3.31.

Ethyl 2-amino-4-hydroxy-4,6-diphenylcyclohex-1-enecarboxylate (4c): mp 140–141 °C (lit.[5] mp 140–141 °C); IR (KBr): (υ_{max}/cm^{-1}) 3473.1, 3329.5, 2983.2, 2924.5, 1655.3, 1609.6, 1532.1, 1360.3,

1065.8, ^{1}H NMR ($CDCl_3$, 400 MHz): 0.92 (t, J = 7.2 Hz, 3H), 2.00 (dd, J = 13.7, 11.2 Hz, 1H), 2.27–2.35 (m, 2H), 2.41 (m, 1H), 3.01 (m, 1H), 3.73–4.00 (m, 2H), 6.20 (bs, 2H), 7.12–7.48 (m, 10H), 7.50 (bs, 1H, OH), ^{13}C NMR ($CDCl_3$, 100 MHz): 14.1, 39.9, 45.4, 46.7, 59.4, 72.6, 94.9, 124.9, 125.8, 127.4, 127.9, 128.6, 128.8, 146.5, 149.2, 154.7, 170.2. Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.62; H, 6.82; N, 4.11.

Ethyl 2-amino-4-(4-chlorophenyl)-4-hydroxy-6-phenylcyclohex-1-enecarboxylate (4d): mp 146–147 °C (lit.[5] mp 146–147 °C); IR (KBr): (υ_{max}/cm^{-1}) 3489.5, 3446.2, 3310.3, 2981.5, 2945.6, 1664.4, 1612.3, 1542.0, 1492.5, 1366.8, 1065.7; ^{1}H NMR ($CDCl_3$, 400 MHz): 0.82 (t, J = 7.2 Hz, 3H),1.97 (dd, J = 13.7, 11.2 Hz, 1H), 2.25–2.41 (m, 3H), 2.99 (m, 1H), 3.75–4.00 (m, 2H), 6.20 (bs, 2H), 7.13–7.45 (m, 9H), 7.50 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$, 100 MHz): 14.1, 39.9, 45.2, 46.6, 59.3, 72.4, 94.8, 125.9, 126.6, 127.3, 128.6, 128.9, 133.6, 145.2, 148.9, 154.5, 170.2. Anal. Calcd for $C_{21}H_{22}ClNO_3$: C, 67.83; H, 5.96; N, 3.77. Found: C, 67.71; H, 5.91; N, 3.82.

Ethyl 2-amino-6-(4-fluorophenyl)-4-hydroxy-4-phenylcyclohex-1-enecarboxylate (4e): mp 168–171 °C. IR (KBr): (υ_{max}/cm^{-1}) 3485.5, 3447.2, 3310.3, 1628.5, 1594.5, 1449.0, ^{1}H NMR ($CDCl_3$, 400 MHz): 0.92 (t, J= 7.2 Hz, 3H), 2.21 (m, 1H), 2.36 (m, 2H), 2.43 (m, 1H), 3.11 (m, 1H), 3.75–4.00 (q, J= 7.2 Hz, 2H), 6.22 (bs, 2H), 6.93 (bs, 1H, OH), 7.21–7.87 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 14.2, 39.9, 45.6, 46.8, 59.6, 72.8, 94.9, 124.9, 125.9, 127.5, 127.9, 128.7, 128.9, 146.5, 149.4, 154.9, 170.3. Anal. Calcd for $C_{21}H_{22}FNO_3$: C, 70.97; H, 6.24; N, 3.94; Found: C, 70.91; H, 6.15; N, 3.89.

Ethyl 2-(butylamino)-6-(4-fluorophenyl)-4-hydroxy-4-phenylcyclohex-1-enecarbox-ylate (4f): mp 126–129 °C. IR (KBr): (υ_{max}/cm^{-1}) 3430.0, 3276.5, 3022.4, 2931.1, 1623.2, 1593.5, 1094.2; ^{1}H NMR ($CDCl_3$, 400 MHz): 0.69 (t, J = 7.0 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H), 1.09 (m, 2H), 1.43 (m, 2H), 2.30 (dd, J = 13.7, 11.0 Hz, 1H), 2.38 (dd, J = 13.7, 6.8 Hz, 1H), 2.46 (m, 1H), 2.77 (m, 1H), 3.12 (dd, J= 11.0, 6.8 Hz, 1H), 3.20 (m, 2H), 4.04 (q, J = 7.0, 2H, OCH_2), 6.59 (bs, 1H, NH), 7.40 (bs, 1H, OH), 7.24–7.49 (m, 9 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.0, 14.2, 20.5, 32.6, 39.9, 41.4, 42.9, 45.9, 59.2, 71.9, 91.8, 125.8, 126.6, 127.1, 128.5, 128.7, 133.6, 145.5, 149.5, 157.4, 170.5. Anal. Calcd for $C_{25}H_{30}FNO_3$: C, 72.97; H, 7.35; N, 3.40; Found: C, 72.89; H, 7.29; N, 3.31.

Ethyl 2-(butylamino)-4-hydroxy-4-phenyl-6-*p*-tolylcyclohex-1-enecarboxylate (4g): mp 135–137 °C. IR (KBr): (υ_{max}/cm^{-1}) 3423.0, 3275.5, 3021.8, 2932.7, 1625.8, 1594.7, 1095.6; ^{1}H NMR ($CDCl_3$, 400 MHz): 0.73 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.5 Hz, 3H), 1.14 (m, 2H), 1.46 (m, 2H), 2.31 (s, 3H, CH_3), 2.33 (dd, J = 13.8, 11.0 Hz, 1H), 2.38 (dd, J = 13.8, 7.0 Hz, 1H), 2.46 (m, 1H), 2.78 (m, 1H), 3.14 (dd, J= 11.0, 7.0 Hz, 1H), 3.24 (m, 2H), 4.05 (q, J = 7.0, 2H, OCH_2), 6.64 (bs, 1H, NH), 7.45 (bs, 1H, OH), 7.20–7.75 (m, 9 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.0, 14.3, 20.5, 22.4, 32.8, 39.9, 41.4, 42.9, 45.9, 59.4, 71.9, 91.8, 126.1, 126.6, 127.4, 128.6, 128.9, 133.7, 145.7, 149.8, 157.7, 170.5. Anal. Calcd for $C_{26}H_{33}NO_3$: C, 76.62; H, 8.16; N, 3.44; Found: C, 76.68; H, 8.26; N, 3.31.

Ethyl 2-(butylamino)-4-(4-methylphenyl)-4-hydroxy-6-phenylcyclohex-1-enecarbox-ylate (4h): mp 107–109 °C. IR (KBr): (υ_{max}/cm^{-1}) 3429.2, 3278.4, 3024.7, 2933.9, 1627.3, 1592.4, 1452.2, 1091.4; ^{1}H NMR ($CDCl_3$, 400 MHz): 0.82 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H), 1.09 (m, 2H), 1.32 (m, 2H), 2.29 (dd, J = 13.8, 11.0 Hz, 1H), 2.35 (s, 3H, CH_3), 2.39 (dd, J = 13.8, 6.8 Hz, 1H), 2.48 (m, 1H), 2.78 (m, 1H), 3.15 (dd, J= 11.0, 6.8 Hz, 1H), 3.57 (m, 2H), 4.09 (q, 2H, OCH_2), 6.61 (bs, 1H, NH), 7.55 (brs, 1H, OH), 7.28–7.50 (m, 9 H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.1, 14.4, 20.8, 23.2, 32.7, 39.8, 41.6,

42.9, 46.0, 59.2, 71.9, 91.7, 125.8, 126.6, 127.3, 128.7, 128.9, 133.8, 145.7, 149.8, 157.7, 170.8. Anal. Calcd for $C_{26}H_{33}NO_3$: C, 76.62; H, 8.16; N, 3.44; Found: C, 76.71; H, 8.29; N, 3.31.

Ethyl 2-amino-6-(4-methylphenyl)-4-hydroxy-4-phenylcyclohex-1-enecarboxylate (4i): mp 173–175 °C. IR (KBr): (υ_{max}/cm^{-1}) 3488.2, 3453.6, 3312.1, 1627.3, 1599.6, 1445.6; ^{1}H NMR ($CDCl_3$, 400 MHz): 0.93 (t, J= 7.2 Hz, 3H), 2.23 (m, 1H), 2.33 (s, 3H, CH_3), 2.38 (m, 2H), 2.46 (m, 1H), 3.12 (m, 1H), 3.78 (q, J= 7.4 Hz, 2H), 6.32 (bs, 2H), 7.02 (bs, 1H, OH), 7.23–7.92 (m, 9H); ^{13}C NMR ($CDCl_3$,100 MHz): 14.2, 24.1, 39.9, 45.7, 46.8, 59.7, 72.8, 94.9, 125.1, 125.8, 127.6, 127.9, 128.8, 128.9, 146.7, 149.7, 154.9, 170.4. Anal. Calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99; Found: C, 75.09; H, 7.06; N, 3.83.

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