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Nitrogen-containing Lewis bases catalyzed highly regio- and stereoselective reactions of allenyl acetates with isatin-derived oximes

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ABSTRACT

Different nitrogen-containing Lewis bases catalyzed reactions of highly reactive allenyl acetates with isatin-derived oximes afforded the corresponding oxime ethers or nitrone derivatives in good to high yields with high regio- and stereoselectivities.

1. Introduction

Oximes and their derivatives as useful synthons are widely utilized in organic synthesis,[1] since they can be easily transformed into ketones,[2] amides,[3] and nitriles.[4] They are also significant feedstocks to synthesize nitrogen-containing heterocyclic compounds by transition-metal[5] or Brønsted base[6] catalyzed cyclization. Meanwhile, oximes can be also used as ligands for oxime-derived palladacycles, which have been proved to be efficient and versatile in carbon–carbon coupling reactions.[7] On the other hand, 2-alkyl-2,3-butadienoates have attracted much attention and many interesting reaction outcomes have been explored due to their high reactivities.[8]

Moreover, the allylic alkylations of Morita–Baylis–Hillman (MBH) adducts catalyzed by Lewis bases have recently become an attractive strategy to construct a large variety of multifunctional compounds.[9] Based on these previous investigations, we intend to use a more reactive species to undergo the Lewis base catalyzed reactions. We found that the allenyl acetate shown in Fig. 1, which was first synthesized and used for the synthesis of (*E*)-α-ethynyl-α,β-unsaturated esters by Lee and co-workers in 2009,[10] may be the suitable substrate since it involves two highly active moieties. Recently, another investigation on the amine-catalyzed intermolecular formal [3+3] cycloaddition reaction using these substrates was reported by Tong and co-workers in 2012.[11] In order to make further investigations on the reactivities of these allenyl acetates, we decided to choose oximes and allenyl acetates as substrates to explore their reaction outcomes under the similar reaction conditions as reported by Kwon[8s] and our group[12] (Scheme 1).

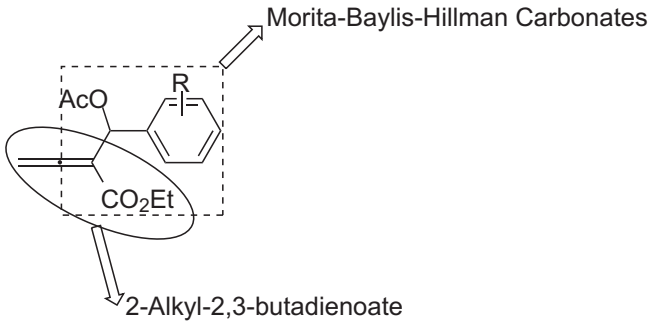

Fig. 1. Highly active allenyl acetates.

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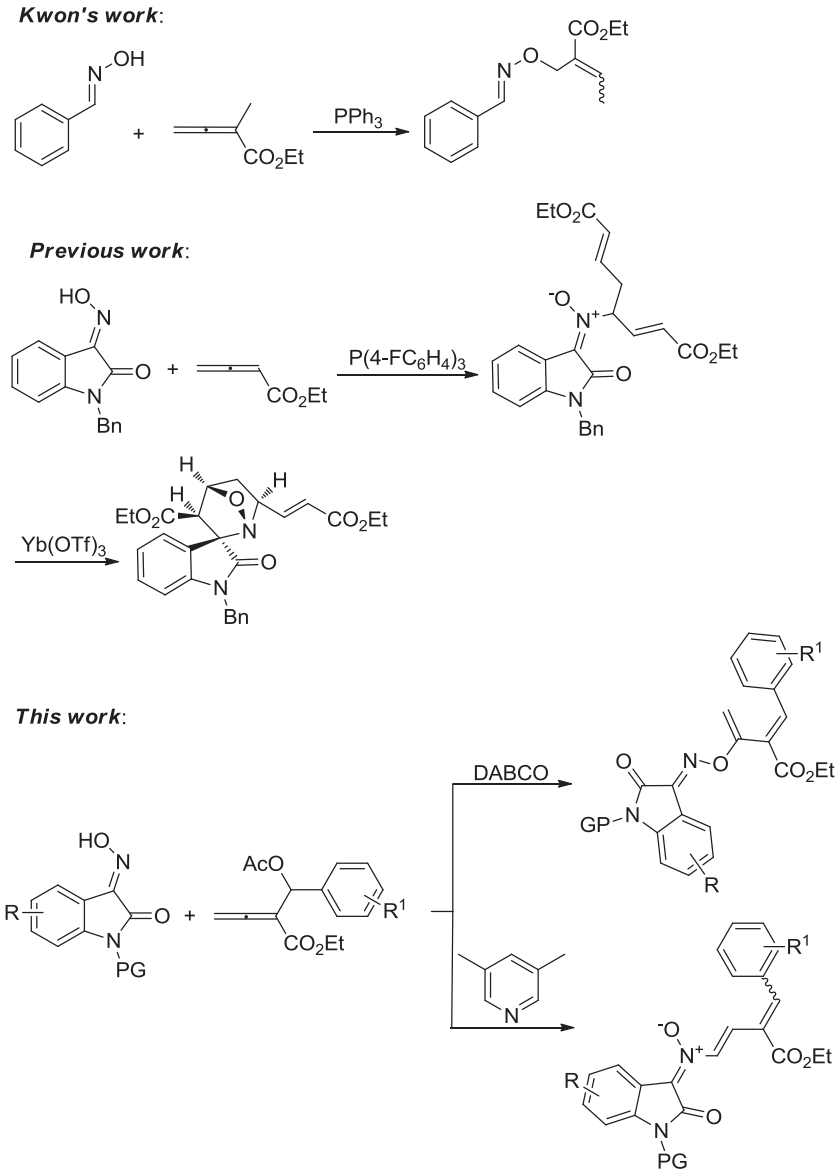
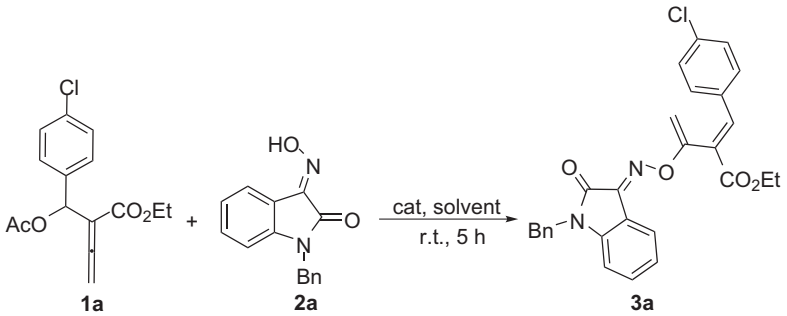


Scheme 1. Different Lewis bases catalyzed reactions of allenyl acetates with isatin-derived oximes.

2. Results and discussion

Previously, Kwon and co-workers have reported phosphine-catalyzed reaction of oximes with allenic esters, providing β′-umpolung addition products due to the nucleophilicity of the oximes[8s] and we have reported Lewis base ($P(4\text{-}FC_6H_4)_3$) catalyzed cascade reactions of isatin-derived oximes with allenic esters to furnish the corresponding nitrones, which could be further converted to bridged cycloadducts via intramolecular [3+2] cyclization catalyzed by Lewis acid [$Yb(OTf)_3$] (Scheme 1).[12] Therefore, we attempted to replace allenic esters with multifunctional allenyl acetates. We initially utilized allenyl acetate (**1a**) and (*E*)-1-benzyl-3-(hydroxyimino)-indolin-2-one (**2a**) as substrates to investigate their reaction behavior in THF at room temperature in the presence of Lewis base. The results are summarized in Table 1. Firstly, we found that the corresponding product **3a** was furnished in poor chemical yields using phosphorus-containing Lewis bases (PPh_3, $PhPMe_2$, $P(4\text{-}FC_6H_4)_3$) (Table 1, entries 1–3) as catalysts. Considering the different reactivities between phosphorus-containing and nitrogen-containing Lewis bases, we investigated the reactions in the presence of nitrogen-containing Lewis base, such as DABCO (1,4-diazabicyclo[2,2,2]octane). To our delight, the reaction was conducted in THF catalyzed by DABCO at room temperature for 5 h, affording highly regio- and stereoselective *E*-**3a** in 88% yield (Table 1, entry 4). Subsequently, other nitrogen-containing Lewis bases were also tested. Using Et_3N or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as catalyst, the yield of **3a** decreased to 67% and 31%, respectively (Table 1, entries 6 and 10). Meanwhile, if using pyridine as the catalyst, the yield decreased remarkably to 21% and a byproduct **4a** was obtained in 37% yield (Table 1, entry 5; for the structure of **4a**, see Table 3, entry 1). The reaction also proceeded fairly smoothly in the presence of DMAP (4-(*N*,*N*-dimethylamino) pyridine), affording *E*-**3a** in 62% yield. However, using 2,6-lutidine or imidazole as the Lewis base promoter under the standard conditions gave *E*-**3a** in 31% yield or 23% yield, respectively (Table 1, entries 8 and 9). Next, we used DABCO as the catalyst to examine the solvent effects. We found that THF was the best solvent (Table 1, entries 4 vs 11–14). Other solvents, such as toluene or DCM had a negative influence on the yield of **3a** (Table 1, entries 11 and 12). In MeCN and DMF, **3a** was only obtained in 33% and 41% yields,

Table 1
Optimization of the reaction conditions

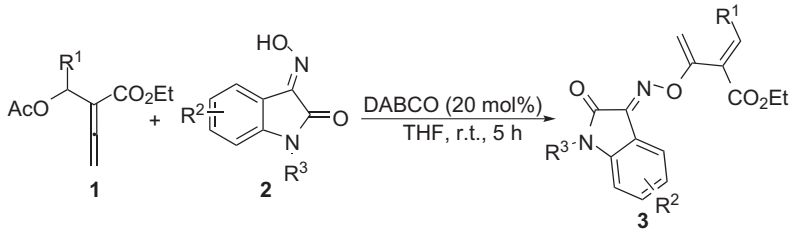


1a **2a** **3a**

Entry	Catalyst	Solvent	Yield[a] (%)
1	PPh_3	THF	21
2	$PhPMe_2$	THF	31
3	Tris(4-fluorophenyl)phosphine	THF	35
4	DABCO	THF	88
5	Pyridine	THF	21
6	Et_3N	THF	67
7	DMAP	THF	62
8	2,6-Lutidine	THF	31
9	Imidazole	THF	23
10	DBU	THF	31
11	DABCO	Toluene	51
12	DABCO	DCM	60
13	DABCO	MeCN	33
14	DABCO	DMF	41
15[b]	DABCO	THF	97
16[b,c]	DABCO	THF	90

[a] Isolated yield. Unless otherwise specified, **1a** (0.10 mmol), **2a** (0.10 mmol), and catalyst (0.02 mmol) were used.
[b] To a mixture of **2a** (0.10 mmol) and catalyst (0.02 mmol) in THF (1.0 mL) under Ar atmosphere was added the solution of **1a** (0.15 mmol in 1.0 mL THF) by syringe pump for 30 min.
[c] The catalyst loading was 10 mol %.

Table 2
DABCO catalyzed reactions of allenyl acetates with isatin-derived oximes

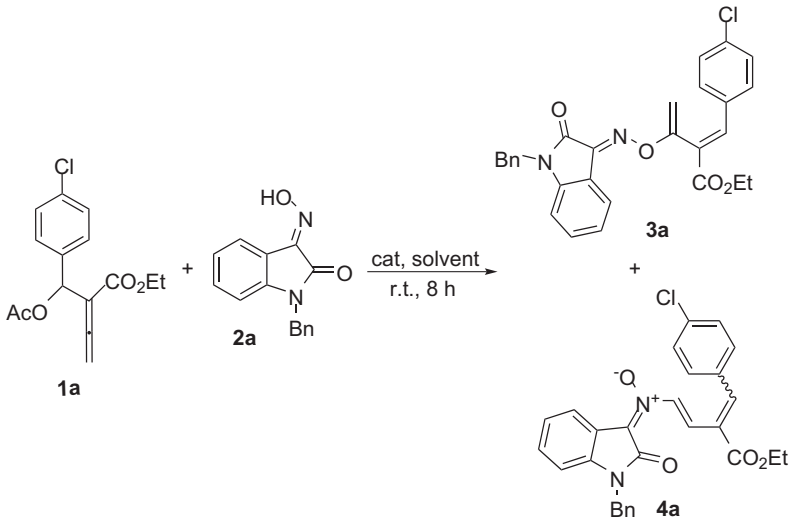


1 **2** **3**

Entry	R^1	R^2/R^3	Yield[a] (%)
1	3-BrC_6H_4 (**1b**)	H/Bn (**2a**)	**3b** (90)
2	4-$NO_2C_6H_4$ (**1c**)	H/Bn (**2a**)	**3c** (85)
3	2-$MeOC_6H_4$ (**1d**)	H/Bn (**2a**)	**3d** (83)
4	4-MeC_6H_4 (**1e**)	H/Bn (**2a**)	**3e** (92)
5	4-$CF_3C_6H_4$ (**1f**)	H/Bn (**2a**)	**3f** (87)
6	3-$MeOC_6H_4$ (**1g**)	H/Bn (**2a**)	**3g** (89)
7	3,4-$Cl_2C_6H_3$ (**1h**)	H/Bn (**2a**)	**3h** (96)
8	3,4,5-$MeO_3C_6H_2$ (**1i**)	H/Bn (**2a**)	**3i** (92)
9	2-Naphthyl (**1j**)	H/Bn (**2a**)	**3j** (94)
10	2-Thienyl (**1k**)	H/Bn (**2a**)	**3k** (90)
11	*n*-Heptyl (**1l**)	H/Bn (**2a**)	**3l** (42)
12	C_6H_5 (**1m**)	H/Bn (**2a**)	**3m** (88)
13	C_6H_5 (**1m**)	5-Br/Tr (**2b**)	**3n** (80)
14	4-ClC_6H_4 (**1a**)	6-Br/allyl (**2c**)	**3o** (82)
15	4-ClC_6H_4 (**1a**)	5-Br/allyl (**2d**)	**3p** (86)
16	3-BrC_6H_4 (**1b**)	5-Me/Bn (**2e**)	**3q** (83)
17	3-$MeOC_6H_4$ (**1g**)	7-Br/allyl (**2f**)	**3r** (90)
18	4-MeC_6H_4 (**1e**)	6-Me/allyl (**2g**)	**3s** (95)
19	2-Thienyl (**1k**)	H/allyl (**2h**)	**3t** (91)

[a] Isolated yield. Unless otherwise specified, to a mixture of **2** (0.10 mmol) and DABCO (0.02 mmol) in THF (1.0 mL) under Ar atmosphere was added the solution **1** (0.15 mmol in 1.0 mL THF) by syringe pump for 30 min.

Table 3
Optimization of the reaction conditions



Entry	**1A**/**2a**	Catalyst	Solvent	**2a** (M/mol L^{-1})	Yield[a] (%)	
					4a	**3a**
1	1.0/1.0	Pyridine	THF	0.10	37	21
2	1.5/1.0	3-Bromopyridine	THF	0.05	12	33
3	1.5/1.0	3,5-Dibromopyridine	THF	0.05	—	55
4	1.5/1.0	4-Methoxypyridine	THF	0.05	—	62
5	1.5/1.0	3,5-Dimethylpyridine	THF	0.05	41	28
6	1.0/1.0	Nicotinonitrile	THF	0.10	8	43
7	1.0/1.0	2-Chloro-5-(trifluo romethyl)pyridine	THF	0.10	—	47
8	1.0/1.0	pyridin-2-ol	THF	0.10	—	47
9	1.0/1.0	3,5-Dimethylpyridine	MeCN	0.10	14	45
10	1.0/1.0	3,5-dimethylpyridine	Toluene	0.10	84	4
11	1.0/1.0	3,5-Dimethylpyridine	DMF	0.10	Trace	70
12	1.0/1.0	3,5-Dimethylpyridine	DCM	0.10	58	20
13	1.0/1.0	3,5-Dimethylpyridine	1,4-Dioxane	0.10	76	8
14	1.0/1.0	3,5-Dimethylpyridine	EtOH	0.10	Trace	25
15	1.0/1.5	3,5-Dimethylpyridine	Toluene	0.15	90	—
16[b]	1.0/1.5	3,5-Dimethylpyridine	Toluene	0.15	85	—

[a] Isolated yield. The substrates were added in one pot manner. Unless otherwise specified, the catalyst loading was 20 mol %.
[b] The catalyst loading was 10 mol %.

respectively (Table 1, entries 13 and 14). Considering that **1a** can be easily converted to (*E*)-α-ethynyl-α,β-unsaturated ester,[10] we decided to change the order of adding substrates and increase the employed amount of **1a**. To a mixture of **2a** (0.10 mmol) and catalyst (0.02 mmol) in THF (1.0 mL) under argon atmosphere was added the solution of **1a** (0.15 mmol in 1.0 mL of THF) by a syringe pump for 30 min, and then the resulting mixture was stirred for 4.5 h, affording **3a** in 97% yield (Table 1, entry 15). Using 10 mol % of the catalyst loading afforded **3a** in 90% yield under identical conditions, suggesting that 20 mol % of catalyst should be used in this reaction process (Table 1, entry 16). Inorganic bases did not catalyze this reaction under the standard conditions.

Under these optimized conditions, we next examined the generality of this reaction using various allenyl acetates (**1**) and oximes (**2**). The results are presented in Table 2. A variety of allenyl acetates **1** having either electron-donating or withdrawing groups as substituents on the 2-, 3-, 4-position of benzene ring were examined, affording the corresponding oxime ethers **3** in high yields (83–92%) (Table 2, entries 1–6). Moreover, 3,4-disubstituted allenyl acetate **1h**, 3,4,5-trisubstituted allenyl acetate **1i**, and allenyl acetate **1m** having no substituent on the benzene ring also gave the corresponding products **3h**, **3i**, and **3m** in high yields (Table 2, entries 7–8, 12). When R^1 was a 2-naphthyl or a 2-thienyl group, the reactions also proceeded efficiently to furnish the corresponding products **3j** and **3k** in 94% and 90% yields, respectively (Table 2, entries 9 and 10). However, if R^1 was a *n*-heptyl group, the desired product **3l** was acquired in 42% yield (Table 2, entry 11). With oximes **2b**–**h** bearing different *N*-protecting groups and having a bromo, methyl or no substituent at the aromatic ring, the reactions proceeded smoothly to give the target products **3n**–**t** in good yields (80–95%) (Table 2, entries 13–19).

The structure of **3** has been unambiguously determined by X-ray diffraction of the analogue **3j**. The ORTEP drawing is shown in Fig. 2 and its CIF data of **3j** are presented in the Supplementary data.[13]

As aforementioned, byproduct **4a** was obtained if pyridine was used as the catalyst (Table 3, entry 1). Thus, we continued to optimize the reaction in order to obtain **4a** as a sole product. The results are summarized in Table 3. Initially, we examined the reaction outcomes by addition of the substrates in a one portion manner in the presence of various pyridine derivatives, such as 3-bromopyridine, 3,5-dibromopyridine, 4-methoxypyridine, 3,5-dimethylpyridine. We found that 3,5-dimethylpyridine gave **4a** in relatively high yield accompanying with **3a** (Table 3, entries 1–5). When using other pyridine derivatives, such as nicotinonitrile, 2-chloro-5-(trifluoromethyl)pyridine and pyridin-2-ol as the catalysts, the target product **4a** was hardly obtained under the standard conditions (Table 3, entries 6–8). Hence, we finally chose 3,5-dimethylpyridine as catalyst to examine the solvent effects. Upon screening of different solvents (MeCN, toluene, DMF, DCM, 1,4-dioxane, EtOH), we found the best solvent was toluene, affording **4a** in 84% yield along with trace amount of **3a** (0.10 M of **2a**) (Table

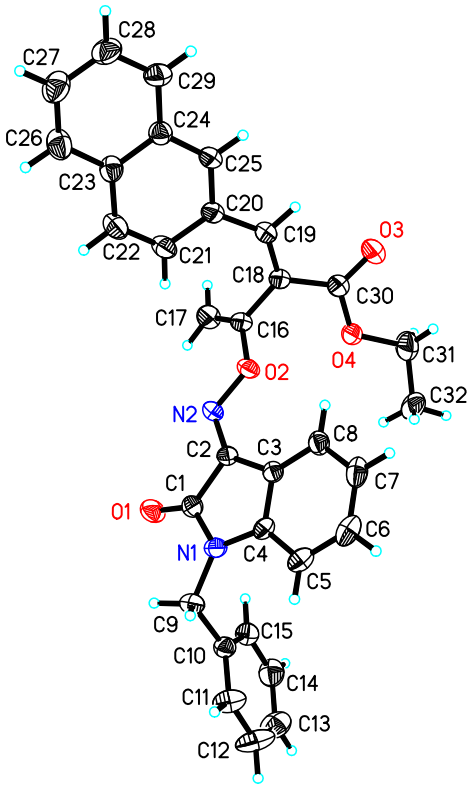


Fig. 2. ORTEP drawing of **3j**.

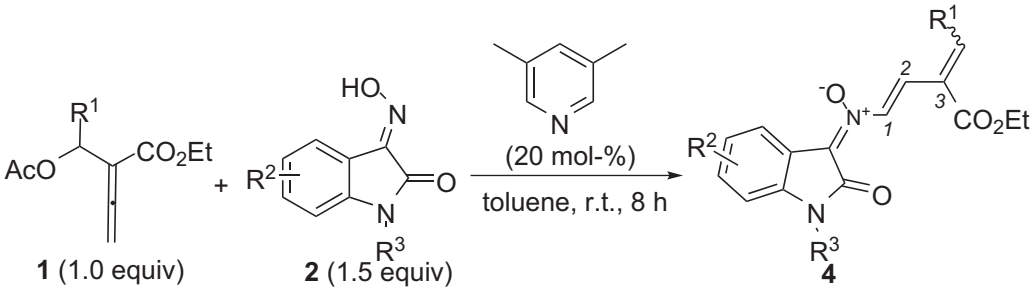
3, entries 9–14). To our delight, **4a** was afforded in 90% yield as the sole product upon increasing the employed amount of **2a** to 0.15 M (Table 3, entry 15). When the catalyst loading was reduced to 10 mol %, **4a** could be still obtained in 85% yield (Table 3, entry 16).

With these optimized conditions in hand, we next investigated the tolerance of various allenyl acetates **1** and oximes **2**. The results are presented in Table 4. When R^2=H, R^3=Bn or allyl group, we found that the corresponding products **4** were obtained in high yields with good stereoselectivities (high ratios of *E*/*Z*), regardless of whether allenyl acetates **1** have electron-donating or electron-withdrawing group at *ortho*, *meta*, *para* position on the benzene ring of R^1 (Table 4, entries 1–5 and 16–17). Meanwhile, 3,4,5-trisubstituted allenyl acetate, allenyl acetate having a heterocycle or a 2-naphthyl group also gave the desired products in high yields and high ratios of *E*/*Z* (Table 4, entries 7–9) except for substrate **1h** in which R^1 has a 3,4-disubstituted benzene ring and the desired product **4g** was formed in 79% yield (Table 4, entry 6). However, if R^1 was an aliphatic group (*n*-heptyl), the reaction only gave trace amount of **4k** (Table 4, entry 10). Moreover, regardless of an electron-donating or electron-withdrawing group was introduced at the 5-, 6-, or 7-position on the benzene ring of oximes or changing the *N*-protecting groups of oximes, the reactions also proceeded smoothly to produce the corresponding nitrones **4l**–**r** in good to high yields with good to excellent stereoselectivities (Table 4, entries 11–17).

The structures of the major and minor isomers of **4** have been also unambiguously determined by X-ray diffraction of analogue (1*E*,3*E*)-**4a** (major isomer) and (1*E*,3*Z*)-**4r** (minor product). Their ORTEP drawings are shown in Fig. 3 and Fig. 4, respectively, and the related CIF data are presented in the Supplementary data.[14]

Plausible mechanisms for these reactions are outlined in Scheme 2. Based on the earlier report proposed by Lee,[10] we propose the path **a** as a traditional reaction model to account for the formation of product **3**. DABCO is added to react with allenyl acetate, producing zwitterionic intermediate **A**, which was detected in NMR spectroscopic investigation by Lee and co-workers. Subsequently, deprotonation of pronucleophile forms negative oxygen ion **B**, which attacks intermediate **A** by passing through transition state **C** via S_N2-type displacement to furnish the corresponding

Table 4
3,5-Dimethylpyridine catalyzed reactions of allenyl acetates with isatin-derived oximes



Entry	R^1	R^2/R^3	Yield (%)[a] ((1*E*,3*E*)-**4**/(1*E*,3*Z*)-**4**)
1	3-BrC_6H_4 (**1b**)	H/Bn (**2a**)	**4b** 89 (6:1)
2	2-MeOC_6H_4 (**1d**)	H/Bn (**2a**)	**4c** 83 (50:1)
3	4-MeC_6H_4 (**1e**)	H/Bn (**2a**)	**4d** 90 (11:1)
4	4-$CF_3C_6H_4$ (**1f**)	H/Bn (**2a**)	**4e** 92 (13:1)
5	3-MeOC_6H_4 (**1g**)	H/Bn (**2a**)	**4f** 93 (14:1)
6	3,4-$Cl_2C_6H_3$ (**1h**)	H/Bn (**2a**)	**4g** 79 (4:1)
7	3,4,5-$MeO_3C_6H_2$ (**1i**)	H/Bn (**2a**)	**4h** 92 (>99:1)
8	2-Naphthyl (**1j**)	H/Bn (**2a**)	**4i** 96 (25:1)
9	2-Thienyl (**1k**)	H/Bn (**2a**)	**4j** 92 (9:1)
10	*n*-Heptyl (**1l**)	H/Bn (**2a**)	**4k** n.d.
11	3-BrC_6H_4 (**1b**)	5-Me/Bn (**2e**)	**4l** 88 (5:1)
12	2-Naphthyl (**1j**)	5-Me/Bn (**2e**)	**4m** 95 (8:1)
13	4-ClC_6H_4 (**1a**)	7-Br/allyl (**2f**)	**4n** 82 (7:1)
14	4-MeC_6H_4 (**1e**)	7-Br/allyl (**2f**)	**4o** 84 (18:1)
15	4-ClC_6H_4 (**1a**)	6-Me/allyl (**2g**)	**4p** 91 (8:1)
16	3-BrC_6H_4 (**1b**)	H/allyl (**2h**)	**4q** 94 (5:1)
17	3-MeOC_6H_4 (**1g**)	H/allyl (**2h**)	**4r** 95 (20:1)

[a] Isolated yield. The substrates were added in one portion manner.

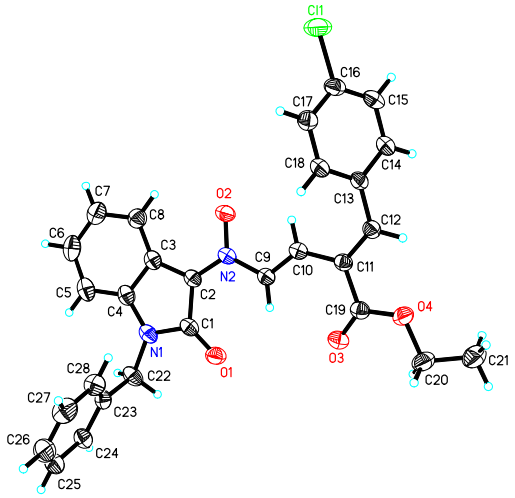


Fig. 3. ORTEP drawing of (1*E*,3*E*)-**4a**.

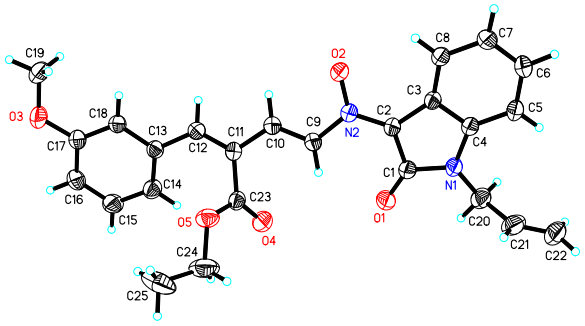


Fig. 4. ORTEP drawing of (1*E*,3*Z*)-**4r**.

product **3** and to regenerate the DABCO catalyst. During the experiments, we noticed that the yield of product **3a** had some relation with the nucleophilicity of catalyst. Thus, we plotted the correlation line between the yield of **3a** and the *N* (*N*: nucleophilicity parameter) parameters of several catalysts (shown in Fig. 5 or Fig. S1 in the Supplementary data and the *N* parameter of 2,6-Lutidine derived from 4-methylpyridine in DCM).[16a–g] It demonstrated that the yield of **3a** indeed had a linear correlation (R^2=0.98) with *N* parameters of catalysts. Therefore, this observation was in accordance with Mayr's findings[16c] that if the reaction was controlled by the rate of nucleophilic attack of the organocatalyst, the high nucleophilicity and nucleofugicity of DABCO is superior to that of 3,5-dimethylpyridine.

The formation of product **4** is proposed through path **b** in Scheme 2. In path **b**, the addition of 3,5-dimethylpyridine to allenyl acetate generates zwitterionic intermediate **D**, which gives negative oxygen ion **B** via deprotonation of pronucleophile. According to Mayr's work in 2007,[16c] 3,5-dimethylpyridine owned lower nucleophilicity, which implied that the ability of nucleofuge was worse than that of DABCO. Thus the following S_N2-type reaction may be difficult to occur in the reaction catalyzed by 3,5-dimethylpyridine. Instead of taking place S_N2-type reaction, the nitrogen of **B** attacks the carbon of terminal olefin in intermediate **D**, giving the corresponding intermediate **E**. Subsequently, the intermediate **E** undergoes the 1,2-proton shift to give intermediate **F**, which releases the catalyst 3,5-dimethylpyridine to form the product **4**. It has to point out here that the product **4** is obtained by addition of substrates in a one portion manner (for details, see Supplementary data), indicating that the high concentration of intermediate ammonium ions derived from the reactions of amines with electrophile benefits the formation of product. According to Mayr's report,[16c] the reactivity of 3,5-dimethylpyridine should be superior to that of DABCO in this type of the reaction.

In order to understand the detailed mechanism for the formation of product **4**, we have also theoretically investigated the reaction pathway **b**. All calculations have been performed at the mPW1K/6-31+G(d) level of theory with Gaussian 09 program.[17] The relative energies of all intermediates and transitional states along the suggested path **b** are shown in Scheme 3 (for details, see Supplementary data). Initially, the addition of catalyst 3,5-dimethylpyridine to compound **1** leads to the formation of intermediate **6**. Then, the oxime is bonded to intermediate **6** to give a complex **7**. The oxime is deprotonated to obtain the intermediate **9** via transition state **8** with an energy barrier of 0.5 kcal/mol. The nitrogen of oxime attacks the carbon of terminal olefin through transition state **10** with an energy barrier of 18.4 kcal/mol, affording the corresponding intermediate **11**. The intermediate **11** undergoes a 1,2-proton transfer by passing transition state **12** with an energy barrier of 47.3 kcal/mol, giving the intermediate **13**. Subsequently, the catalyst is eliminated through transition state **14**, leading to the product complex **15**. Cleavage of this complex to yield the separate components **4**, 3,5-dimethylpyridine, AcOH is endothermic by approximately 3 kcal/mol.

3. Conclusion

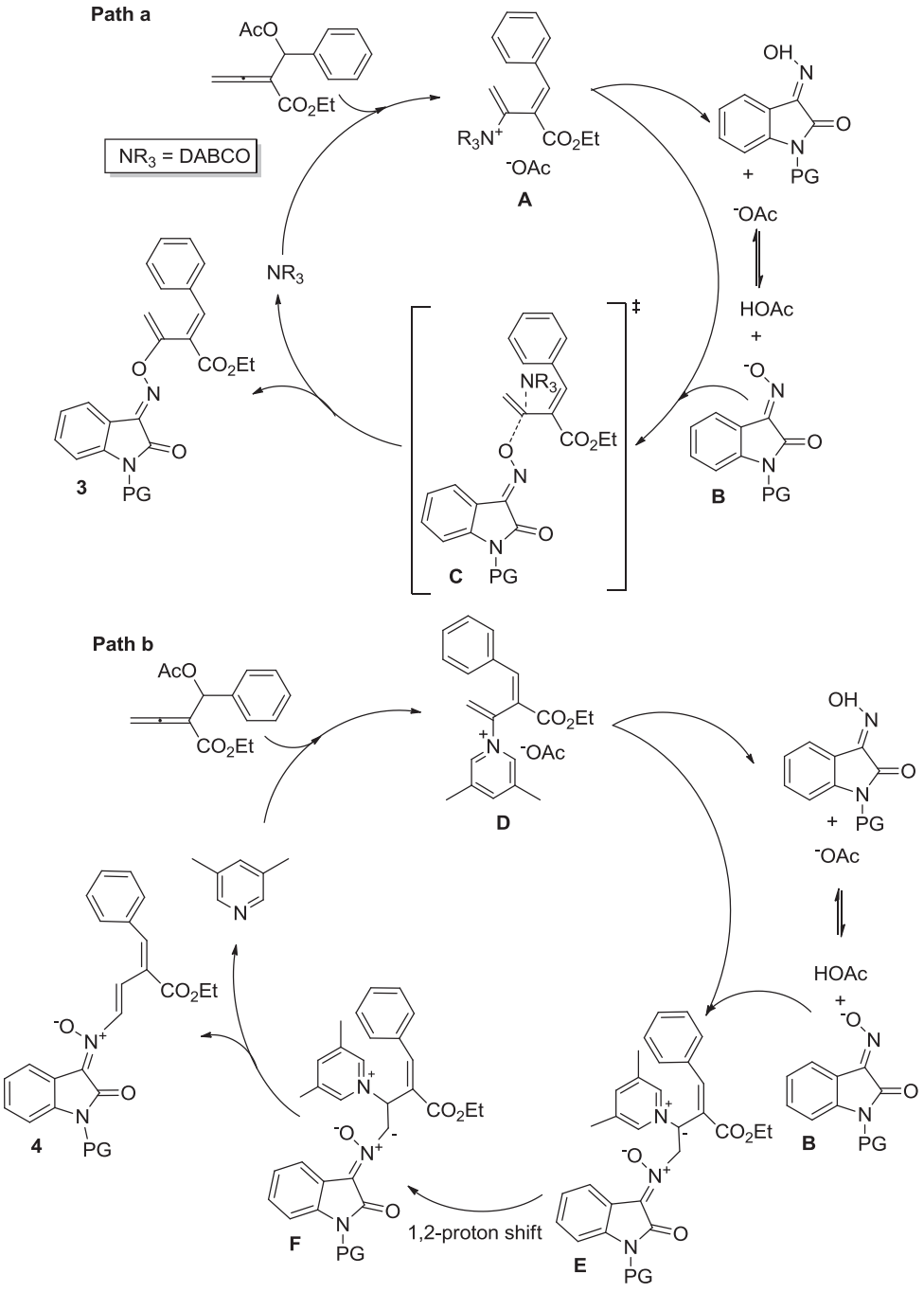
In summary, we have established novel and interesting reactions of allenyl acetates with isatin-derived oximes catalyzed by different nitrogen-containing Lewis bases, affording the corresponding oxime ethers or nitrones in good to high yields with high regio- and stereoselectivities. The steric and electronic factors of this reaction are not obvious but mainly depend on substrate **1**. For example, in Table 2 (entries 13–18) and Table 4 (entries 11–17), the yield and stereoselectivity of products **3** and **4** are better than those with withdrawing groups when an electron-donating group was introduced in substrate **1**. The mechanistic insights have been disclosed by control experiments and DFT calculations. Further studies on the mechanistic details of this catalytic system along with the properties of highly active allenyl acetates are currently underway in our laboratory.

4. Experimental section

4.1. General remarks

^{1}H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hertz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were recorded on a Perkin–Elmer PE-983 spectrometer with absorption in cm^{-1}. THF, toluene, and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN, DMF, and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. According to the previous literature,[10,15] Compounds **1a**–**m** were prepared. Among them, compounds **1a**, **1b**, **1g**, and **1m** were known compounds, the others were new compounds.

Compound **1d**. A yellow oil. IR (CH_2Cl_2): ν 2984, 1967, 1741, 1712, 1603, 1493, 1464, 1439, 1368, 1248, 1223, 1110, 1086, 1049, 1024, 972,



Scheme 2. Plausible reaction mechanisms.

856 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.32–7.25 (2H, m), 7.00 (1H, t, J=2.0 Hz), 6.93 (1H, t, J=7.2 Hz), 6.86 (1H, d, J=8.0 Hz), 5.19 (1H, dd, J_1=14.4 Hz, J_2=2.4 Hz), 5.13 (1H, dd, J_1=14.4 Hz, J_2=2.4 Hz), 4.19 (2H, q, J=6.8 Hz), 3.83 (3H, s), 2.09 (3H, s), 1.24 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.1, 169.5, 165.0, 156.5, 129.3, 127.4, 126.3, 120.2, 110.5, 101.9, 81.4, 66.8, 61.1, 55.5, 21.0, 14.1; MS (ESI) m/e 313.1 (M^++Na); HRMS (ESI) for $C_{16}H_{18}O_5$ (M^+): 290.1154, Found: 290.1146.

Compound **1e**. A yellow oil. IR (CH_2Cl_2): ν 2925, 2853, 1965, 1742, 1711, 1596, 1515, 1446, 1367, 1255, 1224, 1180, 1088, 1018, 972, 852, 789, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.30 (2H, d, J=8.0 Hz), 7.14 (2H, d, J=8.0 Hz), 6.55 (1H, t, J=2.4 Hz), 5.32 (1H, dd, J_1=14.4 Hz, J_2=2.8 Hz), 5.27 (1H, dd, J_1=14.4 Hz, J_2=2.4 Hz), 4.21–4.14 (2H, m), 2.33 (3H, s), 2.07 (3H, s), 1.23 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.2, 169.6, 164.8, 138.1, 135.1, 129.0, 127.3, 102.7, 82.0, 71.5, 61.2, 21.2, 21.0, 14.1; MS (ESI) m/e 297.1 (M^++Na); HRMS (ESI) for $C_{16}H_{18}O_4$ (M^+): 274.1205, Found: 274.1196.

Compound **1f**. A yellow oil. IR (CH_2Cl_2): ν 2987, 1967, 1935, 1746, 1712, 1621, 1420, 1369, 1324, 1254, 1224, 1124, 1066, 1017, 978, 856 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60 (2H, d, J=8.0 Hz), 7.52 (2H, d, J=8.0 Hz), 6.63 (1H, s), 5.34 (1H, dd, J_1=14.8 Hz, J_2=1.6 Hz), 5.27 (1H, dd, J_1=14.8 Hz, J_2=1.6 Hz), 4.22–4.16 (2H, m), 2.11 (3H, s), 1.25 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.5, 169.4, 164.6, 142.2, 130.4 (q, J=32.2 Hz), 127.5, 125.3 (q, J=3.8 Hz), 121.3 (q, J=272.4 Hz), 102.2, 82.4, 71.0, 61.5, 20.9, 14.1; ^{19}F

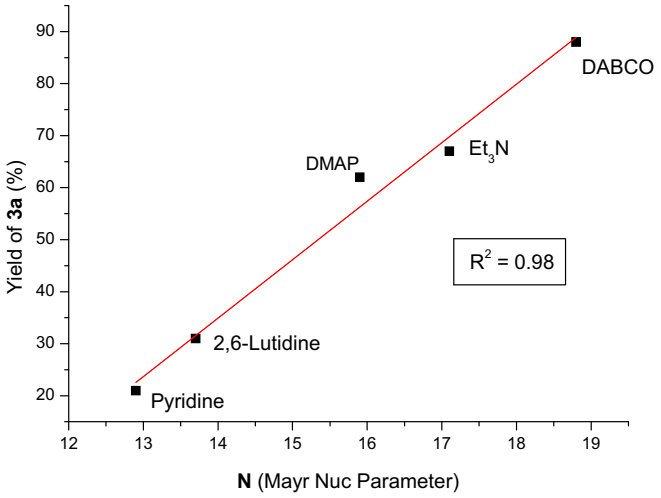


Fig. 5. Correlation of yield of **3a** (%) and ***N*** (Mayr Nuc Parameter).

NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ −62.7; MS (ESI) m/e 351.1 (M^++Na); HRMS (ESI) for $C_{16}H_{15}F_3O_4$ (M^+): 328.0922, Found: 328.0914.

Compound **1h**. A yellow oil. IR (CH_2Cl_2): ν 2923, 1712, 1604, 1520, 1430, 1348, 1324, 1136, 1136, 1097, 1077, 1027, 962, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.48 (1H, d, J=2.0 Hz), 7.41 (1H, d, J=8.0 Hz), 7.26–7.23 (1H, m), 6.52 (1H, t, J=2.4 Hz), 5.36 (1H, dd, J_1=14.8 Hz, J_2=2.4 Hz), 5.30 (1H, dd, J_1=14.8 Hz, J_2=2.4 Hz), 4.22–4.16 (2H, m), 2.10 (3H, s), 1.25 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.4, 169.3, 164.6, 138.5, 132.4, 132.3, 130.3, 129.1, 126.7, 102.0, 82.5, 70.4, 61.5, 20.9, 14.1; MS (ESI) m/e 351.1 (M^++Na); HRMS (ESI) for $C_{15}H_{14}Cl_2O_4$ (M^+): 328.0269, Found: 328.0262.

Compound **1i**. A yellow oil. IR (CH_2Cl_2): ν 2987, 2940, 1966, 1744, 1712, 1592, 1506, 1421, 1368, 1333, 1226, 1150, 1125, 1025, 1008, 859 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 6.63 (2H, s), 6.53 (1H, s), 5.34 (1H, dd, J_1=14.4 Hz, J_2=2.4 Hz), 5.29 (1H, dd, J_1=14.4 Hz, J_2=2.4 Hz), 4.23–4.17 (2H, m), 3.86 (6H, s), 3.83 (3H, s), 2.11 (3H, s), 1.25 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.2, 169.5, 164.8, 153.0, 137.9, 133.6, 104.4, 102.6, 82.1, 71.6, 61.3, 60.7, 56.0, 21.0, 14.1; MS (ESI) m/e 373.1 (M^++Na); HRMS (ESI) for $C_{18}H_{22}O_7$ (M^+): 350.1366, Found: 350.1360.

Compound **1j**. A yellow oil. IR (CH_2Cl_2): ν 3059, 2983, 1966, 1741, 1708, 1348, 1366, 1220, 1169, 1084, 1023, 980, 952, 857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.88 (1H, s), 7.85–7.81 (3H, m), 7.50 (1H, dd, J_1=8.4 Hz, J_2=1.6 Hz), 7.48–7.46 (2H, m), 6.77 (1H, t, J=2.0 Hz), 5.33 (1H, dd, J_1=14.8 Hz, J_2=2.4 Hz), 5.27 (1H, dd, J_1=14.8 Hz, J_2=2.4 Hz), 4.20–4.14 (2H, m), 2.12 (3H, s), 1.23 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.4, 169.6, 164.8, 135.4, 133.2, 133.0, 128.13, 128.10, 127.6, 126.5, 126.23, 126.16, 124.9, 102.6, 82.2, 71.7, 61.3, 21.0, 14.1; MS (ESI) m/e 333.1 (M^++Na); HRMS (ESI) for $C_{19}H_{18}O_4$ (M^+): 310.1205, Found: 310.1199.

Compound **1k**. A yellow oil. IR (CH_2Cl_2): ν 2961, 2928, 1967, 1741, 1711, 1445, 1367, 1258, 1222, 1093, 1022, 967, 856 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.27 (1H, d, J=5.2 Hz), 7.11 (1H, d, J=2.8 Hz), 6.96 (1H, dd, J_1=4.8, Hz, J_2=3.6 Hz), 6.85 (1H, d, J=1.6 Hz), 5.38 (2H, d, J=2.0 Hz), 4.24–4.17 (2H, m), 2.09 (3H, s), 1.25 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.9, 169.4, 164.5, 141.1, 126.7, 126.5, 125.9, 102.6, 82.7, 67.2, 61.4, 20.9, 14.1; MS (ESI) m/e 289.0 (M^++Na); HRMS (ESI) for $C_{13}H_{14}O_4S$ (M^+): 266.0613, Found: 266.0606.

Compound **1l**. A yellow oil. IR (CH_2Cl_2): ν 2927, 2857, 1971, 1743, 1715, 1465, 1368, 1230, 1021, 961, 855 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 5.58–5.55 (1H, m), 5.30 (2H, d, J=1.6 Hz), 4.21 (2H, q, J=7.2 Hz), 2.05 (3H, s), 1.28 (15H, t, J=7.2 Hz), 0.88 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.2, 170.1, 165.2, 101.9, 81.4, 70.1, 61.2, 33.4, 31.7, 29.2, 29.1, 25.4, 22.6, 21.0, 14.1, 14.0; MS (ESI) m/e 283.2 (M^++H); HRMS (ESI) for $C_{16}H_{26}O_4$ (M^+): 282.1831, Found: 282.1825.

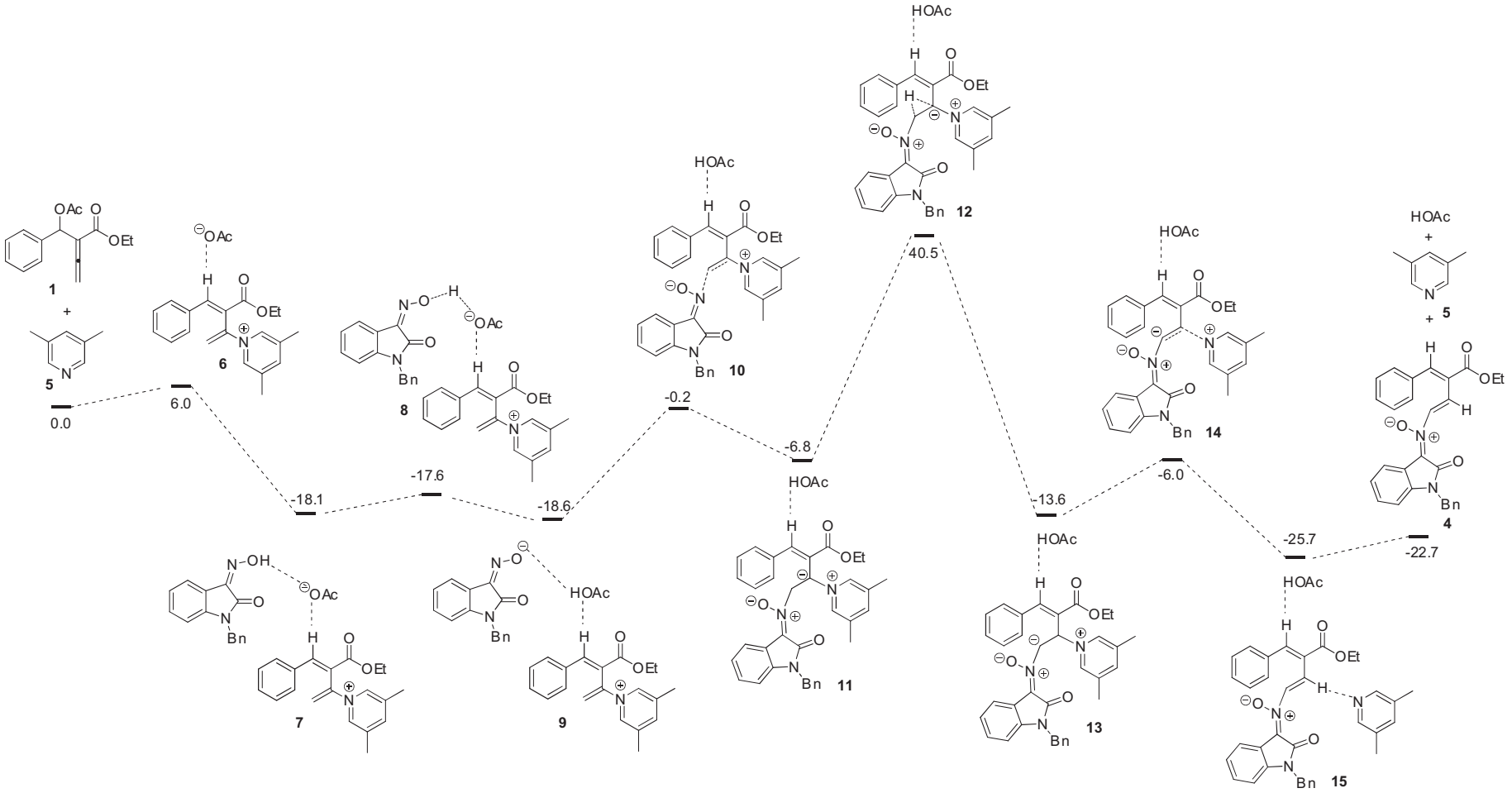
Reaction procedure for the preparation of product **3** has been summarized in the Supplementary data and the spectroscopic data are shown below.

4.1.1. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(4-chlorobenzylidene)but-3-enoate ***3a***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3a** (47 mg, 97% yield). A yellow solid. Mp for compound **3a**=56–58 °C; IR (CH_2Cl_2): ν 2925, 2854, 1712, 1661, 1606, 1490, 1465, 1348, 1306, 1181, 1161, 1092, 1075, 1051, 990, 948, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.84 (1H, s), 7.74 (1H, d, J=7.6 Hz), 7.57 (2H, d, J=8.4 Hz), 7.34–7.25 (8H, m), 6.93 (1H, t, J=7.6 Hz), 6.72 (1H, d, J=7.6 Hz), 5.53 (1H, d, J=2.4 Hz), 4.95 (2H, s), 4.67 (1H, d, J=2.4 Hz), 4.31 (2H, q, J=7.2 Hz), 1.31 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 163.2, 154.4, 146.1, 144.1, 142.8, 136.0, 135.1, 133.4, 132.3, 131.6, 128.9, 128.8, 128.7, 127.9, 127.4, 126.3, 123.1, 115.4, 109.6, 95.2, 61.5, 43.8, 14.2; MS (ESI) m/e 487.1 (M^++H); HRMS (ESI) for $C_{28}H_{23}ClN_2O_4$ (M^+): 486.1346, Found: 486.1332.

4.1.2. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(3-bromobenzylidene)but-3-enoate ***3b***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3b** (48 mg, 90% yield). A yellow solid. Mp for compound **3b**=60–63 °C; IR (CH_2Cl_2): ν 2925, 2886, 1716, 1606, 1495, 1465, 1379, 1348, 1249, 1184, 1050, 1028, 949, 844 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.80 (1H, s), 7.71–7.68 (2H, m), 7.59–7.57 (1H, m), 7.38–7.24 (7H, m), 7.15 (1H, t, J=8.0 Hz), 6.92 (1H, dt, J_1=8.0 Hz, J_2=0.8 Hz), 6.70 (1H, d, J=8.0 Hz), 5.55 (1H, d, J=6.4 Hz), 4.94 (2H, s), 4.70 (1H, d, J=6.8 Hz), 4.31 (2H, q, J=7.2 Hz), 1.31 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 163.1, 154.2, 146.0, 144.1, 142.1, 136.0, 135.1, 133.3, 133.1, 132.6, 129.9, 128.8, 128.6, 128.4, 127.8, 127.3, 123.1, 122.4, 115.3, 109.5, 95.7, 61.6, 43.7, 14.2; MS (ESI) m/e 548.1 (M^++NH_4); HRMS (ESI) for $C_{28}H_{23}BrN_2O_4$ (M^+): 530.0841, Found: 530.0831.

4.1.3. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(4-nitrobenzylidene)but-3-enoate ***3c***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3c** (42 mg, 85% yield). A yellow solid. Mp for compound **3c**=70–72 °C; IR (CH_2Cl_2): ν 2925, 2862, 1716, 1605, 1518, 1495, 1465, 1343, 1301, 1248, 1181, 1112, 1049, 947, 897, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.15 (2H, d, J=8.8 Hz), 7.91 (1H, s), 7.75 (2H, d, J=8.4 Hz), 7.72 (1H, dd, J_1=7.6 Hz, J_2=0.8 Hz), 7.33–7.26 (6H, m), 6.93 (1H, dt, J_1=7.6 Hz, J_2=0.8 Hz), 6.72 (1H, d, J=8.0 Hz), 5.52 (1H, d, J=6.4 Hz), 4.95 (2H, s), 4.69 (1H, d, J=2.4 Hz), 4.33 (2H, q, J=7.2 Hz), 1.32 (3H, t, J=7.2 Hz); 13C NMR ($CDCl_3$, 100 MHz): δ 165.5, 163.0, 154.0, 147.9, 146.2, 144.3, 141.0, 140.4, 135.0, 133.6, 130.8, 129.7, 128.9, 128.5, 127.9, 127.4, 123.6, 123.1, 115.3, 109.7, 96.4, 61.9, 43.8, 14.2; MS (ESI) m/e 515.2 (M^++NH_4); HRMS (ESI) for $C_{28}H_{23}N_3O_6$ (M^+): 497.1587, Found: 497.1575.

4.1.4. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(2-methoxybenzylidene)but-3-enoate ***3d***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3d** (40 mg, 83% yield). A yellow solid. Mp for compound **3d**=59–61 °C; IR (CH_2Cl_2): ν 2925, 2853, 1712, 1605, 1485, 1464, 1379, 1347, 1241, 1210, 1181, 1114, 1075, 1053, 991, 950, 845 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.22 (1H, s), 7.77 (1H, dd, J_1=7.6 Hz, J_2=2.8 Hz), 7.63 (1H, dd, J_1=7.6 Hz, J_2=1.2 Hz), 7.34–7.22 (7H, m), 6.92 (1H, dt, J_1=7.6 Hz, J_2=0.8 Hz), 6.85–6.82 (2H, m), 6.70 (1H, d, J=8.0 Hz), 5.47 (1H, d, J=6.4 Hz),



Gas-phase enthalpy profile(ΔH_{298} (kcal/mol)). Calculated at mPW 1K/6-31+G(d) level.

Scheme 3. The Reaction Energy Profile of Path **b**.

4.94 (2H, s), 4.64 (1H, d, J=6.4 Hz), 4.35 (2H, q, J=7.2 Hz), 3.87 (3H, s), 1.30 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 163.3, 158.0, 155.2, 145.7, 144.0, 139.6, 135.2, 133.1, 131.2, 130.2, 128.8, 128.7, 127.8, 127.3, 125.8, 123.2, 123.1, 120.4, 115.4, 110.4, 109.4, 107.9, 94.9, 61.2, 55.5, 43.6, 14.1; MS (ESI) m/e 500.2 (M^++NH_4); HRMS (ESI) for $C_{29}H_{26}N_2O_5$ (M^+): 482.1842, Found: 482.1833.

4.1.5. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(4-methylbenzylidene)but-3-enoate ***3e***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3e** (43 mg, 92% yield). A yellow solid. Mp for compound **3e**=66–68 °C; IR (CH_2Cl_2): ν 2983, 2924, 1711, 1660, 1605, 1496, 1465, 1348, 1293, 1199, 1179, 1075, 1051, 1014, 948, 845 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.88 (1H, s), 7.77–7.75 (1H, m), 7.56 (2H, d, J=8.0 Hz), 7.33–7.23 (6H, m), 7.12 (2H, d, J=8.0 Hz), 6.91 (1H, dt, J_1=7.6 Hz, J_2=0.8 Hz), 6.70 (1H, d, J=8.0 Hz), 5.53 (1H, d, J=2.4 Hz), 4.95 (2H, s), 4.70 (1H, d, J=2.4 Hz), 4.30 (2H, q, J=6.8 Hz), 2.29 (3H, s), 1.30 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.6, 163.3, 154.8, 145.9, 144.4, 144.0, 140.6, 135.1, 133.1, 130.9, 130.6, 129.2, 128.8, 128.7, 127.8, 127.3, 124.6, 123.1, 115.5, 109.4, 94.5, 61.3, 43.7, 21.4, 14.2; MS (ESI) m/e 484.2 (M^++NH_4); HRMS (ESI) for $C_{29}H_{26}N_2O_4$ (M^+): 466.1893, Found: 466.1880.

4.1.6. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(4-(trifluoromethyl)benzylidene)but-3-enoate ***3f***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3f** (45 mg, 87% yield). A yellow solid. Mp for compound **3f**=55–57 °C; IR (CH_2Cl_2): ν 2927, 2858, 1723, 1607, 1466, 1349, 1323, 1253, 1168, 1125, 1092, 1067, 1016, 950, 844 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.89 (1H, s), 7.70 (3H, dd, J_1=7.6 Hz, J_2=2.4 Hz), 7.54 (2H, d, J=8.4 Hz), 7.33–7.23 (6H, m), 6.90 (1H, t, J=8.0 Hz), 6.70 (1H, d, J=8.0 Hz), 5.50 (1H, d, J=6.0 Hz), 4.93 (2H, s), 4.65 (1H, d, J=6.8 Hz), 4.31 (2H, q, J=6.8 Hz), 1.30 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.9, 163.1, 154.2, 146.1, 144.1, 142.2, 137.4, 135.1, 133.4, 131.2 (q, J_{C-F}=32.4 Hz), 130.3, 128.8, 128.7, 128.6, 128.3, 127.8, 127.3, 125.3 (q, J_{C-F}=3.7 Hz), 123.7 (q, J_{C-F}=270.7 Hz), 123.1, 115.3, 109.6, 95.7, 61.7, 43.7, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ −63.0; MS (ESI) m/e 538.2 (M^++NH_4); HRMS (ESI) for $C_{29}H_{23}F_3N_2O_4$ (M^+): 520.1610, Found: 520.1597.

4.1.7. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(3-methoxybenzylidene)but-3-enoate ***3g***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3g** (43 mg, 89% yield). A yellow solid. Mp for compound **3g**=53–55 °C; IR (CH_2Cl_2): ν 2980, 2935, 2850, 1713, 1605, 1465, 1379, 1348, 1294, 1233, 1161, 1184, 1075, 1050, 948, 848 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.88 (1H, s), 7.76 (1H, d, J=8.0 Hz), 7.34–7.21 (9H, m), 6.92 (1H, t, J=8.0 Hz), 6.85–6.82 (1H, m), 6.70 (1H, d, J=8.0 Hz), 5.54 (1H, d, J=2.0 Hz), 4.94 (2H, s), 4.69 (1H, d, J=2.8 Hz), 4.31 (2H, q, J=7.2 Hz), 3.74 (3H, s), 1.31 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 163.2, 159.3, 154.7, 146.0, 144.2, 144.0, 135.1, 135.0, 133.2, 129.4, 128.8, 128.7, 127.8, 127.3, 125.9, 123.2, 123.1, 116.4, 115.4, 114.7, 109.5, 95.1, 61.4, 55.2, 43.7, 14.2; MS (ESI) m/e 500.2 (M^++NH_4); HRMS (ESI) for $C_{29}H_{26}N_2O_5$ (M^+): 482.1842, Found: 482.1831.

4.1.8. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(3,4-dichlorobenzylidene)but-3-enoate ***3h***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3h** (50 mg, 96% yield). A yellow solid. Mp for **3h**=57–59 °C; IR (CH_2Cl_2): ν 2928, 1724, 1655, 1607, 1496, 1466, 1378, 1348, 1248, 1184, 1157, 1092, 1075, 1029, 949, 844 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.77 (1H, s), 7.70 (1H, dd, J_1=7.6 Hz, J_2=1.2 Hz), 7.65 (1H, d, J=2.0 Hz), 7.50–7.48 (1H, m), 7.36–7.25 (7H, m), 6.92 (1H, dt, J_1=7.6 Hz, J_2=1.2 Hz), 6.71 (1H, d, J=8.0 Hz), 5.55 (1H, d, J=2.8 Hz), 4.95 (2H, s), 4.71 (1H, d, J=2.4 Hz), 4.31 (2H, q, J=7.2 Hz), 1.31 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 163.1, 154.0, 146.1, 144.2, 141.1, 135.1, 133.9, 133.8, 133.4, 132.6, 132.0, 130.4, 129.0, 128.8, 128.5, 127.8, 127.7, 127.3, 123.1, 115.3, 109.6, 96.0, 61.7, 43.7, 14.2; MS (ESI) m/e 538.1 (M^++NH_4); HRMS (ESI) for $C_{28}H_{22}Cl_2N_2O_4$ (M^+): 520.0957, Found: 520.0944.

4.1.9. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(3,4,5-trimethoxybenzylidene)but-3-enoate ***3i***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3i** (50 mg, 92% yield). A yellow solid. Mp for compound **3i**=62–64 °C; IR (CH_2Cl_2): ν 2937, 2837, 1727, 1659, 1606, 1578, 1505, 1465, 1348, 1246, 1184, 1126, 1075, 1053, 949, 842 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.83 (1H, s), 7.74 (1H, d, J=7.6 Hz), 7.33–7.23 (6H, m), 7.00 (2H, s), 6.91 (1H, t, J=7.6 Hz), 6.70 (1H, d, J=8.0 Hz), 5.59 (1H, d, J=2.4 Hz), 4.94 (2H, s), 4.76 (1H, d, J=2.4 Hz), 4.33 (2H, q, J=7.2 Hz), 3.80 (6H, s), 3.77 (3H, s), 1.33 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 163.0, 154.9, 152.8, 146.1, 144.1, 144.0, 139.7, 135.0, 133.3, 129.0, 128.8, 128.6, 127.8, 127.2, 124.6, 123.0, 115.3, 109.5, 107.9, 95.3, 61.3, 60.7, 56.1, 43.7, 14.2; MS (ESI) m/e 560.2 (M^++NH_4); HRMS (ESI) for $C_{31}H_{30}N_2O_7$ (M^+): 542.2053, Found: 542.2041.

4.1.10. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(naphthalen-2-ylmethylene)but-3-enoate ***3j***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3j** (47 mg, 94% yield). A yellow solid. Mp for compound **3j**=135–138 °C; IR (CH_2Cl_2): ν 2979, 2931, 1727, 1660, 1607, 1496, 1466, 1379, 1349, 1240, 1206, 1126, 1075, 949, 858 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.07 (1H, s), 8.04 (1H, s), 7.84–7.80 (2H, m), 7.74–7.71 (3H, m), 7.47–7.44 (2H, m), 7.32–7.25 (2H, m), 7.19 (1H, dt, J_1=7.6 Hz, J_2=1.2 Hz), 6.80 (1H, t, J=8.0 Hz), 6.66 (1H, d, J=8.0 Hz), 5.58 (1H, d, J=2.4 Hz), 4.93 (2H, s), 4.72 (1H, d, J=2.4 Hz), 4.33 (2H, q, J=7.2 Hz), 1.33 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 163.2, 154.8, 146.0, 144.3, 144.0, 135.1, 133.8, 133.1, 132.9, 131.8, 131.5, 128.8, 128.6, 128.58, 128.0, 127.8, 127.6, 127.3, 126.4, 126.3, 125.8, 123.0, 115.4, 109.4, 95.3, 61.4, 43.7, 14.3; MS (ESI) m/e 520.2 (M^++NH_4); HRMS (ESI) for $C_{32}H_{26}N_2O_4$ (M^+): 502.1893, Found: 502.1880.

4.1.11. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-(thiophen-2-ylmethylene)but-3-enoate ***3k***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3k** (41 mg, 90% yield). A yellow solid. Mp for compound **3k**=124–126 °C; IR (CH_2Cl_2): ν 2924, 2854, 1725, 1705, 1658, 1604, 1495, 1465, 1379, 1349, 1250, 1021, 1178, 1075, 1047, 948, 857 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.07 (1H, s), 7.85 (1H, d, J=7.2 Hz), 7.44–7.43 (2H, m), 7.34–7.24 (6H, m), 7.03 (1H, t, J=4.4 Hz), 6.94 (1H, t, J=8.0 Hz), 6.70 (1H, d, J=7.6 Hz), 5.68 (1H, d, J=2.4 Hz), 4.95 (2H, s), 4.85 (1H, d, J=2.4 Hz), 4.30 (2H, q, J=7.2 Hz), 1.29 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 163.2, 154.1, 145.9, 144.1, 137.1, 135.1, 134.7, 133.2, 131.7, 128.8, 127.7, 127.3, 127.1, 123.1, 122.0, 115.5, 109.5, 95.9, 61.3, 43.7, 14.3; MS (ESI) m/e 476.2 (M^++NH_4); HRMS (ESI) for $C_{26}H_{22}N_2O_4S$ (M^+): 458.1300, Found: 458.1288.

4.1.12. (E)-Ethyl 2-(1-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy) vinyl)dec-2-enoate ***3l***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3l** (20 mg, 42% yield). A yellow oil. IR (CH_2Cl_2): ν 2925, 2854, 1722, 1607, 1466, 1379, 1349, 1250, 1217, 1182, 1051, 952, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.92 (1H, d, J=7.2 Hz), 7.33–7.26 (6H, m), 7.16 (1H, t, J=7.6 Hz), 7.00 (1H, dt, J_1=7.6 Hz, J_2=0.8 Hz), 6.72 (1H, d, J=7.6 Hz), 5.50 (1H, d, J=2.0 Hz), 4.95 (2H, s), 4.53 (1H, d, J=2.0 Hz), 4.23 (2H, q, J=7.2 Hz), 2.39 (2H, dd, J_1=15.2 Hz, J_2=7.2 Hz), 1.48 (2H, m), 1.34–1.23 (11H, m), 0.88–0.81 (3H, m); ^{13}C

NMR ($CDCl_3$, 100 MHz): δ 165.9, 163.5, 154.2, 150.4, 145.5, 144.1, 135.2, 133.2, 128.8, 128.7, 128.1, 127.8, 127.4, 123.2, 115.6, 109.6, 94.7, 61.0, 43.7, 31.7, 29.9, 29.3, 29.0, 28.6, 22.6, 14.2, 14.0; MS (ESI) m/e 492.3 (M^++NH_4); HRMS (ESI) for $C_{29}H_{34}N_2O_4$ (M^+): 474.2519, Found: 474.2510.

4.1.13. (E)-Ethyl 3-((E)-1-benzyl-2-oxoindolin-3-ylideneaminooxy)-2-benzylidenebut-3-enoate ***3m***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3m** (40 mg, 88% yield). A yellow solid. Mp for compound **3m**=68–71 °C; IR (CH_2Cl_2): ν 2925, 2853, 1716, 1607, 1495, 1466, 1378, 1349, 1254, 1183, 1077, 1051, 1029, 951, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.91 (1H, s), 7.75 (1H, dd, J_1=7.6 Hz, J_2=0.8 Hz), 7.66–7.64 (2H, m), 7.33–7.23 (9H, m), 6.91 (1H, dt, J_1=7.6 Hz, J_2=1.2 Hz), 6.70 (1H, d, J=8.0 Hz), 5.53 (1H, d, J=2.4 Hz), 4.95 (2H, s), 4.67 (1H, d, J=2.0 Hz), 4.31 (2H, q, J=7.2 Hz), 1.31 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 163.3, 154.6, 146.0, 144.3, 144.1, 135.2, 133.8, 133.2, 130.4, 130.0, 128.8, 128.7, 128.5, 127.8, 127.4, 125.8, 123.1, 115.5, 109.5, 94.7, 61.4, 43.7, 14.2; MS (ESI) m/e 470.2 (M^++NH_4); HRMS (ESI) for $C_{28}H_{24}N_2O_4$ (M^+): 452.1736, Found: 452.1723.

4.1.14. (E)-Ethyl 2-benzylidene-3-((E)-2-oxo-1-tritylindolin-3-ylideneaminooxy)but-3-enoate ***3n***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3n** (55 mg, 80% yield). A yellow solid. Mp for compound **3n**=51–54 °C; IR (CH_2Cl_2): ν 2923, 2853, 1732, 1596, 1491, 1448, 1366, 1261, 1188, 1125, 1079, 1050, 1013, 952, 812 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.89 (1H, s), 7.82 (1H, d, J=2.0 Hz), 7.60 (1H, d, J=6.8 Hz), 7.45–7.41 (6H, m), 7.31–7.21 (12H, m), 7.06 (1H, dd, J_1=8.8 Hz, J_2=2.0 Hz), 6.14 (1H, d, J=8.8 Hz), 5.47 (1H, d, J=2.0 Hz), 4.66 (1H, d, J=2.0 Hz), 4.33 (2H, q, J=7.2 Hz), 1.32 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 163.2, 154.6, 144.8, 144.3, 143.8, 141.2, 134.2, 133.8, 130.4, 129.9, 129.2, 128.4, 128.3, 127.8, 127.2, 125.6, 117.6, 117.5, 115.5, 95.4, 75.1, 61.5, 14.3; MS (ESI) m/e 700.2 (M^++NH_4); HRMS (ESI) for $C_{40}H_{31}BrN_2O_4$ (M^+): 682.1467, Found: 682.1464.

4.1.15. (E)-Ethyl 3-((E)-1-allyl-6-bromo-2-oxoindolin-3-ylideneaminooxy)-2-(4-chlorobenzylidene)but-3-enoate ***3o***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3o** (38 mg, 82% yield). A yellow solid. Mp for compound **3o**=110–113 °C; IR (CH_2Cl_2): ν 2926, 2850, 1721, 1602, 1486, 1429, 1367, 1336, 1262, 1185, 1090, 1061, 1013, 929, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.83 (1H, s), 7.56 (3H, t, J=8.8 Hz), 7.28 (2H, d, J=8.4 Hz), 7.10 (1H, dd, J_1=8.0 Hz, J_2=1.6 Hz), 6.97 (1H, d, J=1.2 Hz), 5.86–5.79 (1H, m), 5.50 (1H, d, J=2.4 Hz), 5.30 (1H, s), 5.26 (1H, d, J=9.2 Hz), 4.68 (1H, d, J=2.4 Hz), 4.36 (2H, d, J=5.2 Hz), 4.31 (2H, q, J=7.2 Hz), 1.31 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 162.6, 154.4, 145.2, 142.8, 136.1, 132.2, 131.6, 130.3, 129.5, 128.8, 128.7, 127.8, 126.2, 126.1, 118.4, 114.0, 113.0, 95.6, 61.5, 42.4, 14.2; MS (ESI) m/e 532.1 (M^++NH_4); HRMS (ESI) for $C_{24}H_{20}N_2O_4BrCl$ (M^+): 514.0295, Found: 514.0280.

4.1.16. (E)-Ethyl 3-((E)-1-allyl-5-bromo-2-oxoindolin-3-ylideneaminooxy)-2-(4-chlorobenzylidene)but-3-enoate ***3p***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3p** (40 mg, 86% yield). A yellow solid. Mp for compound **3p**=86–88 °C; IR (CH_2Cl_2): ν 2925, 2854, 1724, 1606, 1489, 1463, 1449, 1335, 1259, 1171, 1090, 1041, 954, 799 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.84 (1H, s), 7.78 (1H, dd, J_1=6.8 Hz, J_2=1.2 Hz), 7.55 (2H, t, J=8.4 Hz), 7.49 (1H, dd, J_1=8.0 Hz, J_2=1.2 Hz), 7.28 (2H, d, J=8.8 Hz), 6.82 (1H, t, J=8.0 Hz), 6.01–5.95 (1H, m), 5.52 (1H, d, J=2.8 Hz), 5.26–5.16 (2H, m), 4.83 (2H, dd, J_1=2.8 Hz, J_2=2.0 Hz), 4.70 (1H, d, J=2.8 Hz), 4.31 (2H, q, J=7.2 Hz), 1.30 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 163.4, 154.4, 144.5, 142.9, 141.5, 139.0, 136.1, 132.4, 132.2, 131.6, 128.8, 127.8, 126.1, 124.3, 123.3, 121.7, 118.2, 116.9. 102.8, 95.8, 61.5, 43.1, 14.2; MS (ESI) m/e 532.1 (M^++NH_4); HRMS (ESI) for $C_{24}H_{20}N_2O_4BrCl$ (M^+): 514.0295, Found: 514.0283.

4.1.17. (E)-Ethyl 3-((E)-1-benzyl-5-methyl-2-oxoindolin-3-ylideneaminooxy)-2-(3-bromobenzylidene)but-3-enoate ***3q***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3q** (45 mg, 83% yield). A yellow solid. Mp for compound **3q**=60–63 °C; IR (CH_2Cl_2): ν 2924, 1716, 1661, 1614, 1593, 1481, 1454, 1339, 1250, 1187, 1154, 1093, 1074, 1050, 954, 907, 855 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.80 (1H, s), 7.70 (1H, s), 7.59 (1H, d, J=8.0 Hz), 7.45 (1H, s), 7.36–7.26 (6H, m), 7.15 (1H, t, J=8.0 Hz), 7.05 (1H, dd, J_1=8.0 Hz, J_2=0.8 Hz), 6.57 (1H, d, J=8.4 Hz), 5.57 (1H, d, J=2.4 Hz), 4.92 (2H, s), 4.72 (1H, d, J=2.4 Hz), 4.32 (2H, q, J=7.6 Hz), 2.18 (3H, s), 1.32 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 163.2, 154.1, 146.2, 141.9, 141.8, 136.0, 135.2, 133.6, 133.1, 132.6, 132.5, 129.9, 129.1, 128.8, 128.4, 127.7, 127.3, 122.3, 115.2, 109.3, 95.8, 61.6, 43.7, 20.9, 14.2; MS (ESI) m/e 562.1 (M^++NH_4); HRMS (ESI) for $C_{29}H_{25}BrN_2O_4$ (M^+): 544.0998, Found: 544.0998.

4.1.18. (E)-Ethyl 3-((E)-1-allyl-7-bromo-2-oxoindolin-3-ylideneaminooxy)-2-(3-methoxybenzylidene)but-3-enoate ***3r***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3r** (46 mg, 90% yield). A yellow oil; IR (CH_2Cl_2): ν 2961, 2928, 1735, 1713, 1598, 1466, 1441, 1366, 1336, 1260, 1234, 1172, 1098, 1050, 1017, 955, 847 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.88 (1H, s), 7.78 (1H, d, J=7.6 Hz), 7.46 (1H, d, J=7.6 Hz), 7.27–7.18 (3H, m), 6.85–6.79 (2H, m), 6.00–5.94 (1H, m), 5.54 (1H, d, J=2.4 Hz), 5.22–5.14 (2H, m), 4.82 (2H, t, J=2.4 Hz), 4.73 (1H, d, J=2.4 Hz), 4.31 (2H, q, J=7.2 Hz), 3.74 (3H, s), 1.31 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 163.3, 159.3, 154.6, 144.4, 144.3, 141.4, 138.8, 134.9, 132.3, 129.4, 127.8, 125.7, 124.2. 123.1, 118.1, 116.7, 116.4, 114.7, 102.6, 95.7, 61.4, 55.2, 43.0, 14.2; MS (ESI) m/e 528.1 (M^++NH_4); HRMS (ESI) for $C_{25}H_{23}N_2O_5Br$ (M^+): 510.0790, Found: 510.0781.

4.1.19. (E)-Ethyl 3-((E)-1-allyl-6-methyl-2-oxoindolin-3-ylideneaminooxy)-2-(3-methylbenzylidene)but-3-enoate ***3s***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3s** (41 mg, 95% yield). A yellow solid. Mp for compound **3s**=83–85 °C; IR (CH_2Cl_2): ν 2961, 2923, 2855, 1731, 1614, 1482, 1443, 1366, 1342, 1258, 1181, 1093, 1053, 1017, 955, 799 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.88 (1H, s), 7.56 (2H, d, J=8.0 Hz), 7.54 (1H, s), 7.14–7.10 (3H, m), 6.69 (1H, d, J=8.0 Hz), 5.86–5.78 (1H, s), 5.52 (1H, d, J=2.4 Hz), 5.27–5.22 (2H, m), 4.67 (1H, d, J=2.4 Hz), 4.36–4.35 (2H, m), 4.31 (2H, q, J=7.2 Hz), 2.29 (3H, s), 2.19 (3H, s), 1.31 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.6, 162.9, 154.8, 146.1, 144.2, 141.9, 140.5, 133.5, 132.5, 131.0, 130.9, 130.6, 129.2, 129.15, 124.6, 117.8, 115.3, 109.1, 94.5, 61.2, 42.2, 21.4, 20.9, 14.2; MS (ESI) m/e 448.2 (M^++NH_4); HRMS (ESI) for $C_{26}H_{26}N_2O_4$ (M^+): 430.1893, Found: 430.1899.

4.1.20. (E)-Ethyl 3-((E)-1-allyl-2-oxoindolin-3-ylideneaminooxy)-2-(thiophen-2-ylmethylene)but-3-enoate ***3t***. Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **3t** (37 mg, 91% yield). A yellow solid. Mp for compound **3t**=153–154 °C; IR (CH_2Cl_2): ν 2981, 2925, 1727, 1704, 1604, 1465, 1420, 1348, 1250, 1199, 1179, 1046, 988, 947, 856 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.07 (1H, s), 7.85 (1H, dd, J_1=7.6 Hz, J_2=0.4 Hz), 7.44–7.43 (2H, m), 7.34 (1H, dt, J_1=8.0 Hz, J_2=1.2 Hz), 7.03 (1H, t, J=8.0 Hz), 6.97 (1H, dt, J_1=7.6 Hz, J_2=0.8 Hz), 6.81 (1H, d, J=7.6 Hz), 5.87–5.80 (1H, m), 5.66 (1H, d, J=2.4 Hz), 5.29–5.23 (2H, m), 4.83 (1H, d, J=2.4 Hz), 4.39–4.37 (2H, m), 4.29 (2H, d, J=7.2 Hz), 1.29 (3H, t, J=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 162.8, 154.1, 145.9, 144.1, 137.2, 137.1, 134.7, 133.2, 131.7, 130.8, 128.8, 127.1, 123.1, 122.0, 117.9, 115.4, 109.4, 95.8, 61.2,

42.2, 14.2; MS (ESI) m/e 426.1 (M^++NH_4); HRMS (ESI) for $C_{22}H_{20}N_2O_4S$ (M^+): 408.1144, Found: 408.1160.

Reaction procedure for the preparation of product **4** also has been summarized in the Supplementary data and the spectroscopic data are shown below.

*4.1.21. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-4-(4-chlorophenyl)-3-(ethoxycarbonyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4a**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4a** (44 mg, 90% overall yield in a stereoselective ratio=33:1 ((1*E*,3*E*)-**4a**/(1*E*,3*Z*)-**4a**)). A red solid. Mp for compound **4a**=166–167 °C; IR (CH_2Cl_2): ν 2961, 1710, 1691, 1606, 1526, 1464, 1414, 1382, 1347, 1259, 1088, 1012, 863 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ ((1*E*,3*E*)-**4a**) 10.04 (1H, d, *J*=13.2 Hz), 8.46 (1H, d, *J*=7.2 Hz), 7.94 (1H, s), 7.89 (1H, d, *J*=13.2 Hz), 7.45–7.37 (4H, m), 7.33–7.26 (6H, m), 7.07 (1H, t, *J*=8.0 Hz), 6.74 (1H, d, *J*=7.6 Hz), 5.00 (2H, s), 4.42 (2H, q, *J*=7.2 Hz), 1.44 (3H, t, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ ((1*E*,3*E*)-**4a**) 165.8, 160.4, 144.9, 141.1, 136.9, 136.0, 135.5, 133.5, 133.1, 132.3, 131.6, 129.1, 128.8, 127.8, 127.3, 126.7, 125.9, 123.7, 123.2, 118.5, 108.9, 61.8, 43.7, 14.2; MS (ESI) m/e 504.2 (M^++NH_4); HRMS (ESI) for $C_{28}H_{23}N_2O_4Cl$ (M^+): 486.1346, Found: 486.1335.

*4.1.22. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-4-(3-bromophenyl)-3-(ethoxycarbonyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4b**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4b** (47 mg, 89% overall yield in a stereoselective ratio=6:1 ((1*E*,3*E*)-**4b**/(1*E*,3*Z*)-**4b**)). A red solid. Mp for compound **4b**=156–158 °C; IR (CH_2Cl_2): ν 2924, 2854, 1714, 1690, 1605, 1557, 1495, 1463, 1380, 1346, 1261, 1228, 1202, 1175, 1118, 964, 859 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 10.04 (1H, d, *J*=13.2 Hz), 9.40 (0.15H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4b**), 8.46 (0.15H, d, *J*=7.2 Hz, (1*E*,3*Z*)-**4b**), 8.45 (1H, d, *J*=7.2 Hz), 7.90 (1H, s), 7.87 (1H, d, *J*=13.2 Hz), 7.64 (0.15H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4b**), 7.58 (1H, s), 7.54 (1H, d, *J*=7.6 Hz), 7.46 (0.15H, d, *J*=6.8 Hz, (1*E*,3*Z*)-**4b**), 7.40 (1H, d, *J*=8.0 Hz), 7.35–7.22 (9H, m), 7.05 (1H, d, *J*=7.6 Hz), 6.73 (1H, d, *J*=7.6 Hz), 6.72 (0.15H, d, *J*=7.6 Hz, (1*E*,3*Z*)-**4b**), 4.99 (2H, s), 4.97 (0.30H, s, (1*E*,3*Z*)-**4b**), 4.42 (2H, q, *J*=7.2 Hz), 4.41 (0.30H, q, *J*=7.2 Hz, (1*E*,3*Z*)-**4b**), 1.44 (3H, t, *J*=7.2 Hz), 1.33 (0.50H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4b**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 160.4, 144.4, 141.1, 137.1, 136.6, 135.5, 133.5, 132.9, 132.6, 132.2, 130.3, 130.0, 128.8, 128.6, 127.7, 127.5, 127.3, 127.2, 125.8, 123.4, 123.1, 122.8, 118.5, 108.8, 61.8, 43.7, 14.2; MS (ESI) m/e 531.1 (M^++H); HRMS (ESI) for $C_{28}H_{23}N_2O_4Br$ (M^+): 530.0841, Found: 530.0835.

*4.1.23. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-(2-methoxyphenyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4c**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4c** (40 mg, 83% overall yield in a stereoselective ratio=50:1 ((1*E*,3*E*)-**4c**/(1*E*,3*Z*)-**4c**)). A red solid. Mp for compound **4c**=201–203 °C; IR (CH_2Cl_2): ν 2923, 2852, 1712, 1697, 1604, 1524, 1457, 1345, 1249, 1177, 1097, 1025, 971, 855 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ ((1*E*,3*E*)-**4c**) 10.06 (1H, d, *J*=13.2 Hz), 8.45 (1H, dd, J_1=7.6 Hz, J_2=0.8 Hz), 8.22 (1H, s), 7.91 (1H, dd, J_1=13.2 Hz, J_2=0.8 Hz), 7.42–7.24 (9H, m), 7.04 (1H, dt, J_1=8.4 Hz, J_2=0.4 Hz), 6.94 (1H, d, *J*=8.0 Hz), 6.72 (1H, d, *J*=7.6 Hz), 5.00 (2H, s), 4.42 (2H, q, *J*=7.2 Hz), 3.89 (3H, s), 1.44 (3H, t, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ ((1*E*,3*E*)-**4c**) 166.1, 160.4, 158.1, 143.4, 140.9, 136.1, 135.6, 133.1, 131.9, 131.60, 131.57, 128.8, 127.7, 127.3, 125.8, 125.7, 125.0, 123.8, 123.0, 120.7, 118.6, 110.7, 108.8, 61.5, 55.6, 43.7, 14.2; MS (ESI) m/e 483.2 (M^++H); HRMS (ESI) for $C_{29}H_{26}N_2O_5$ (M^+): 482.1842, Found: 482.1835.

*4.1.24. (1E,3E,NE)-N-(1-benzyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-p-tolylbuta-1,3-dien-1-amine oxide (1E,3E)-**4d**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4d** (42 mg, 90% overall yield in a stereoselective ratio=11:1 ((1*E*,3*E*)-**4d**/(1*E*,3*Z*)-**4d**)). A red solid. Mp for compound **4d**=141–143 °C; IR (CH_2Cl_2): ν 2923, 2854, 1711, 1690, 1604, 1520, 1464, 1346, 1263, 1204, 1177, 1136, 1097, 1027, 962, 857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 10.04 (1H, d, *J*=13.2 Hz), 9.36 (0.09H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4d**), 8.46 (1H, d, *J*=7.2 Hz), 7.99 (2H, d, *J*=6.8 Hz), 7.67 (0.09H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4d**), 7.38 (2H, d, *J*=8.0 Hz), 7.32–7.24 (9H, m), 7.05 (1H, t, *J*=7.6 Hz), 6.72 (1H, d, *J*=7.6 Hz), 4.99 (2H, s), 4.97 (0.18H, s, (1*E*,3*Z*)-**4d**), 4.42 (2H, q, *J*=7.2 Hz), 2.40 (3H, s), 2.36 (0.27H, s, (1*E*,3*Z*)-**4d**), 1.44 (3H, t, *J*=7.2 Hz), 1.34 (0.27H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4d**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 160.4, 146.9, 140.9, 140.4, 136.3, 135.6, 133.2, 132.0, 131.9, 130.5, 129.5, 129.3, 128.8, 127.7, 127.3, 127.2, 125.7, 125.3, 124.6, 123.0, 118.6, 108.8, 61.6, 43.7, 21.5, 14.2; MS (ESI) m/e 467.2 (M^++H); HRMS (ESI) for $C_{29}H_{26}N_2O_4$ (M^+): 466.1893, Found: 466.1885.

*4.1.25. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-(4-(trifluoromethyl)phenyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4e**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4e** (48 mg, 92% overall yield in a stereoselective ratio=13:1 ((1*E*,3*E*)-**4e**/(1*E*,3*Z*)-**4e**)). A red solid. Mp for compound **4e**=196–198 °C; IR (CH_2Cl_2): ν 2926, 2858, 1715, 1690, 1606, 1496, 1464, 1348, 1323, 1227, 1122, 1067, 1016, 968, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 10.05 (1H, d, *J*=13.2 Hz), 9.44 (0.07H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4e**), 8.44 (1H, d, *J*=7.6 Hz), 7.98 (1H, s), 7.86 (2H, d, *J*=13.2 Hz), 7.72 (2H, d, *J*=8.0 Hz), 7.56 (2H, d, *J*=8.0 Hz), 7.32–7.26 (6H, m), 7.06 (1H, t, *J*=7.6 Hz), 6.73 (1H, d, *J*=8.0 Hz), 4.99 (2H, s), 4.98 (0.14H, s, (1*E*,3*Z*)-**4e**), 4.44 (2H, q, *J*=7.2 Hz), 1.46 (3H, t, *J*=7.2 Hz), 1.30 (0.21H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4e**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 160.4, 144.2, 141.2, 138.1, 137.2, 135.4, 133.7, 132.4, 131.2 (q, *J*=32.6 Hz), 130.3, 129.0, 128.8, 128.2, 127.7, 127.3, 127.2, 125.9, 125.7 (q, *J*=3.5 Hz), 123.8 (q, *J*=270.5 Hz), 123.2, 108.9, 62.0, 43.7, 14.2; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ −62.83, −62.85; MS (ESI) m/e 521.2 (M^++H); HRMS (ESI) for $C_{29}H_{23}F_3N_2O_4$ (M^+): 520.1610, Found: 520.1602.

*4.1.26. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-(3-methoxyphenyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4f**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4f** (45 mg, 93% overall yield in a stereoselective ratio=14:1 ((1*E*,3*E*)-**4f**/(1*E*,3*Z*)-**4f**)). A red solid. Mp for compound **4f**=123–125 °C; IR (CH_2Cl_2): ν 2925, 2853, 1712, 1690, 1605, 1571, 1494, 1463, 1346, 1246, 1135, 1118, 1097, 1077, 1027, 963, 866 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ ((1*E*,3*E*)-**4f**) 10.03 (1H, d, *J*=13.6 Hz), 8.46 (1H, d, *J*=7.6 Hz), 7.99 (1H, d, *J*=12.4 Hz), 7.39–7.25 (7H, m), 7.05 (1H, t, *J*=8.0 Hz), 6.97 (1H, d, *J*=8.0 Hz), 6.73 (1H, d, *J*=8.0 Hz), 4.99 (2H, s), 4.42 (2H, q, *J*=7.2 Hz), 3.84 (3H, s), 1.45 (3H, t, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ ((1*E*,3*E*)-**4f**) 166.0, 160.4, 159.6, 146.5, 141.0, 136.5, 135.6, 133.3, 132.0, 129.8, 128.8, 127.7, 127.3, 126.4, 124.3, 123.1, 122.9, 118.6, 116.0, 115.2, 108.8, 61.7, 55.3, 43.7, 14.2; MS (ESI) m/e 483.2 (M^++H); HRMS (ESI) for $C_{29}H_{26}N_2O_5$ (M^+): 482.1842, Found: 482.1832.

*4.1.27. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-4-(3,4-dichlorophenyl)-3-(ethoxycarbonyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4g**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4g** (41 mg, 79% overall yield in a stereoselective ratio=4:1 ((1*E*,3*E*)-**4g**/(1*E*,3*Z*)-**4g**)). A red solid. Mp for compound **4g**=211–213 °C; IR (CH_2Cl_2): ν 2962, 1718, 1689, 1607, 1522, 1465, 1350, 1259, 1089, 1017, 863 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 10.03 (1H, d, *J*=13.2 Hz), 9.42 (0.25H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4g**), 8.46 (1H, d, *J*=6.8 Hz), 7.86–7.84 (1H, m), 7.84–7.82 (0.25H, m), 7.56

(0.25H, s, (1*E*,3*Z*)-**4g**), 7.55–7.53 (1H, m), 7.44 (0.25H, d, *J*=8.4 Hz, (1*E*,3*Z*)-**4g**), 7.36–7.23 (9H, m), 7.10–7.05 (1H, m), 6.74 (1H, d, *J*=8.0 Hz), 6.73 (0.25H, d, *J*=8.0 Hz, (1*E*,3*Z*)-**4g**), 5.00 (2H, s), 4.98 (0.50H, s, (1*E*,3*Z*)-**4g**), 4.42 (2H, q, *J*=7.2 Hz), 4.31 (0.50H, q, *J*=7.2 Hz, (1*E*,3*Z*)-**4g**), 1.44 (3H, t, *J*=7.2 Hz), 1.35 (0.75H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4g**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.5, 160.4, 143.1, 141.1, 137.3, 135.5, 134.6, 134.0, 133.7, 132.4, 131.9, 130.8, 129.2, 128.8, 127.9, 127.8, 127.3, 127.2, 125.9, 123.2, 123.0, 118.5, 108.9, 61.9, 43.7, 14.2; MS (ESI) m/e 521.1 (M^++H); HRMS (ESI) for $C_{28}H_{22}Cl_2N_2O_4$ (M^+): 520.0957, Found: 520.0954.

*4.1.28. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-(3,4,5-trimethoxyphenyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4h**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4h** (50 mg, 92% overall yield in a stereoselective ratio=>99:1 ((1*E*,3*E*)-**4h**/(1*E*,3*Z*)-**4h**)). A red solid. Mp for compound **4h**=193–195 °C; IR (CH_2Cl_2): ν 2927, 1711, 1692, 1606, 1520, 1464, 1431, 1346, 1333, 1257, 1178, 1125, 1098, 1005, 966, 858 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ ((1*E*,3*E*)-**4h**) 10.02 (1H, d, *J*=13.2 Hz), 8.46 (1H, d, *J*=7.6 Hz), 8.10 (1H, d, *J*=13.2 Hz), 7.94 (1H, s), 7.32–7.25 (6H, m), 7.06 (1H, t, *J*=7.6 Hz), 6.74 (3H, d, *J*=6.0 Hz), 5.00 (2H, s), 4.42 (2H, q, *J*=7.2 Hz), 3.93 (3H, s), 3.91 (6H, s), 1.45 (3H, t, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ ((1*E*,3*E*)-**4h**) 166.0, 160.5, 153.2, 146.4, 140.9, 139.7, 136.3, 135.6, 133.2, 132.0, 130.0, 128.8, 127.7, 127.8, 127.3, 125.7, 125.4, 124.6, 123.1, 118.6, 108.8, 108.0, 61.6, 61.0, 56.2, 43.7, 14.2; MS (ESI) m/e 543.2 (M^++H); HRMS (ESI) for $C_{31}H_{30}N_2O_7$ (M^+): 542.2053, Found: 542.2043.

*4.1.29. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-(naphthalen-2-yl)buta-1,3-dien-1-amine oxide (1E,3E)-**4i**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4i** (48 mg, 96% overall yield in a stereoselective ratio=25:1 ((1*E*,3*E*)-**4i**/(1*E*,3*Z*)-**4i**)). A red solid. Mp for compound **4i**=181–182 °C; IR (CH_2Cl_2): ν 2924, 2854, 1713, 1693, 1607, 1521, 1496, 1464, 1381, 1347, 1225, 1177, 1097, 1077, 969, 859 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ ((1*E*,3*E*)-**4i**) 10.09 (1H, d, *J*=13.2 Hz), 8.45 (1H, d, *J*=7.6 Hz), 8.17 (1H, s), 8.07 (1H, d, *J*=13.2 Hz), 7.96 (1H, s), 7.90 (2H, d, *J*=8.4 Hz), 7.85 (1H, d, *J*=7.6 Hz), 7.59–7.50 (3H, m), 7.32–7.23 (6H, m), 7.04 (1H, t, *J*=7.6 Hz), 6.72 (1H, d, *J*=7.6 Hz), 4.99 (2H, s), 4.45 (2H, q, *J*=7.2 Hz), 1.47 (3H, t, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 160.4, 146.7, 141.0, 136.7, 135.6, 133.6, 133.3, 133.0, 132.2, 132.0, 131.0, 128.8, 128.5, 127.7, 127.4, 127.3, 127.0, 126.7, 126.2, 125.7, 124.4, 123.1, 118.6, 108.8, 61.7, 43.7, 14.2; MS (ESI) m/e 503.2 (M^++H); HRMS (ESI) for $C_{32}H_{26}N_2O_4$ (M^+): 502.1893, Found: 502.1882.

*4.1.30. (1E,3E,NE)-N-(1-Benzyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-(thiophen-2-yl)buta-1,3-dien-1-amine oxide (1E,3E)-**4j**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4j** (42 mg, 92% overall yield in a stereoselective ratio=9:1 ((1*E*,3*E*)-**4j**/(1*E*,3*Z*)-**4j**). A red solid. Mp for compound **4j**=188–191 °C; IR (CH_2Cl_2): ν 2910, 2862, 1689, 1607, 1519, 1463, 1415, 1346, 1261, 1024, 1095, 1016, 959, 858 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.09 (1H, d, *J*=13.2 Hz), 8.53 (1H, d, *J*=7.6 Hz), 8.31 (1H, d, *J*=7.6 Hz), 8.07 (1H, s), 7.85 (0.12H, d, *J*=7.6 Hz, (1*E*,3*Z*)-**4j**), 7.63 (1H, d, *J*=5.2 Hz), 7.45 (1H, d, *J*=3.6 Hz), 7.32–7.25 (7H, m), 7.17 (1H, t, *J*=3.6 Hz), 7.07 (1H, t, *J*=3.6 Hz), 6.93 (0.12H, t, *J*=3.6 Hz, (1*E*,3*Z*)-**4j**), 6.73 (1H, d, *J*=7.6 Hz), 4.99 (2H, s), 4.94 (0.24H, s, (1*E*,3*Z*)-**4j**), 4.41 (2H, q, *J*=7.2 Hz), 4.29 (0.24H, q, *J*=7.2 Hz, (1*E*,3*Z*)-**4j**), 1.44 (3H, t, *J*=7.2 Hz), 1.29 (0.36H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4j**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.9, 160.4, 141.0, 138.0, 137.9, 136.6, 135.5, 134.6, 133.3, 132.4, 132.1, 128.8, 128.1, 127.7, 127.3, 125.9, 123.9, 123.1, 122.2, 118.6, 108.8, 61.9, 43.7, 14.2; MS (ESI) m/e 459.1 (M^++H); HRMS (ESI) for $C_{26}H_{22}N_2O_4S$ (M^+): 458.1300, Found: 458.1292.

*4.1.31. (1E,3E,NE)-N-(1-Benzyl-5-methyl-2-oxoindolin-3-ylidene)-4-(3-bromophenyl)-3-(ethoxycarbonyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4l**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4l** (48 mg, 88% overall yield in a stereoselective ratio=5:1 ((1*E*,3*E*)-**4l**/(1*E*,3*Z*)-**4l**). A red solid. Mp for compound **4l**=155–157 °C; IR (CH_2Cl_2): ν 2979, 2853, 1715, 1689, 1522, 1482, 1376, 1327, 1265, 1219, 1183, 1105, 1075, 1026, 908, 803 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.04 (1H, d, *J*=13.2 Hz), 9.41 (0.20H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4l**), 8.31 (1H, s), 7.89 (1H, s), 7.87 (2H, d, *J*=13.6 Hz), 7.63 (0.20H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4l**), 7.58 (1H, s), 7.54 (1H, d, *J*=8.0 Hz), 7.47 (0.20H, d, *J*=8.0 Hz, (1*E*,3*Z*)-**4l**), 7.41 (1H, d, *J*=7.6 Hz), 7.36–7.23 (7H, m, (1*E*,3*E*)-**4l** & (1*E*,3*Z*)-**4l**), 7.08 (1H, d, *J*=8.0 Hz), 6.99 (0.20H, s, (1*E*,3*Z*)-**4l**), 6.61 (1H, d, *J*=8.0 Hz), 6.60 (0.20H, d, *J*=8.0 Hz, (1*E*,3*Z*)-**4l**), 4.97 (2H, s), 4.95 (0.40H, s), 4.42 (2H, q, *J*=7.2 Hz), 4.41 (0.40H, q, *J*=7.2 Hz, (1*E*,3*Z*)-**4l**), 2.33 (0.60H, s, (1*E*,3*Z*)-**4l**), 2.31 (3H, s), 1.44 (3H, t, *J*=7.2 Hz), 1.29 (0.60H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4l**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 160.4, 144.3, 139.0, 137.0, 136.7, 135.6, 133.8, 133.0, 132.8, 132.7, 132.5, 130.3, 128.8, 128.5, 127.7, 127.5, 127.2, 127.1, 126.4, 123.2, 122.8, 118.5, 108.7, 61.8, 43.7, 21.0, 14.2; MS (ESI) m/e 545.1 (M^++H); HRMS (ESI) for $C_{29}H_{25}N_2O_4Br$ (M^+): 544.0998, Found: 544.0989.

*4.1.32. (1E,3E,NE)-N-(1-Benzyl-5-methyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-(naphthalen-2-yl)buta-1,3-dien-1-amine oxide (1E,3E)-**4m**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4m** (49 mg, 95% overall yield in a stereoselective ratio=8:1 ((1*E*,3*E*)-**4m**/(1*E*,3*Z*)-**4m**)). A red solid. Mp for compound **4m**=198–200 °C; IR (CH_2Cl_2): ν 2923, 2854, 1712, 1686, 1614, 1519, 1481, 1453, 1367, 1326, 1182, 1122, 1104, 1025, 955, 858 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.09 (1H, d, *J*=13.2 Hz), 9.43 (0.12H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4m**), 8.33 (0.12H, s, (1*E*,3*Z*)-**4m**), 8.30 (1H, s), 8.16 (1H, s), 8.07 (1H, d, *J*=12.8 Hz), 7.96 (1H, s), 7.92–7.79 (3H, m), 7.72 (0.12H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4m**), 7.59–7.49 (3H, m), 7.33–7.22 (6H, m, (1*E*,3*E*)-**4m** & (1*E*,3*Z*)-**4m**), 7.06 (1H, d, *J*=8.0 Hz), 6.60 (1H, d, *J*=8.0 Hz), 4.97 (2H, s), 4.95 (0.24H, s, (1*E*,3*Z*)-**4m**), 4.45 (2H, q, *J*=7.2 Hz), 2.33 (0.24H, s, (1*E*,3*Z*)-**4m**), 2.29 (3H, s), 1.47 (3H, t, *J*=7.2 Hz), 1.31 (0.36H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4m**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 160.5, 146.5, 138.9, 136.7, 135.7, 133.6, 133.5, 133.0, 132.7, 132.6, 132.3, 131.0, 128.8, 128.5, 127.7, 127.4, 127.3, 127.2, 127.0, 126.7, 126.4, 126.3, 124.2, 118.6, 108.6, 61.7, 43.7, 20.9, 14.2; MS (ESI) m/e 517.2 (M^++H); HRMS (ESI) for $C_{33}H_{28}N_2O_4$ (M^+): 516.2049, Found: 516.2037.

*4.1.33. (1E,3E,NE)-N-(1-Allyl-7-bromo-2-oxoindolin-3-ylidene)-4-(4-chlorophenyl)-3-(ethoxycarbonyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4n**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4n** (42 mg, 82% overall yield in a stereoselective ratio=7:1 ((1*E*,3*E*)-**4n**/(1*E*,3*Z*)-**4n**). A red solid. Mp for compound **4n**=144–146 °C; IR (CH_2Cl_2): ν 2925, 2853, 1715, 1694, 1614, 1518, 1466, 1438, 1412, 1330, 1279, 1166, 1089, 1012, 951, 907, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.01 (1H, d, *J*=13.2 Hz), 9.37 (0.14H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4n**), 8.55 (1H, d, *J*=7.6 Hz), 7.95 (1H, s), 7.85 (1H, d, *J*=13.2 Hz), 7.62 (0.14H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4n**), 7.48–7.38 (5H, m, (1*E*,3*E*)-**4n** & (1*E*,3*Z*)-**4n**), 7.30 (1H, d, *J*=25.6 Hz), 6.98–6.93 (1H, m), 6.04–5.94 (1H, m), 5.20 (1H, d, *J*=10.8 Hz), 5.14 (1H, d, *J*=17.2 Hz), 4.89–4.87 (2H, m), 4.41 (2H, q, *J*=7.2 Hz), 1.43 (3H, t, *J*=7.2 Hz), 1.32 (0.42H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4n**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 160.6, 145.4, 138.1, 137.6, 137.1, 136.1, 133.0, 132.7, 132.3, 131.6, 130.3, 129.1, 128.8, 126.6, 124.7, 124.3, 124.2, 121.5, 116.6, 102.1, 61.8, 43.0, 14.2; MS (ESI) m/e 515.0

(M^++H); HRMS (ESI) for $C_{24}H_{20}BrClN_2O_4$ (M^+): 514.0295, Found: 514.0286.

*4.1.34. (1E,3E,NE)-N-(1-Allyl-7-bromo-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-p-tolylbuta-1,3-dien-1-amine oxide (1E,3E)-**4o**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4o** (38 mg, 84% overall yield in a stereoselective ratio=18:1 ((1*E*,3*E*)-**4o**/(1*E*,3*Z*)-**4o**)). A red solid. Mp for compound **4o**=118–120 °C; IR (CH_2Cl_2): ν 2923, 2853, 1693, 1602, 1590, 1517, 1438, 1412, 1329, 1204, 1127, 1085, 1019, 948, 878 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 10.02 (1H, d, *J*=13.2 Hz), 9.34 (0.06H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4o**), 8.57 (1H, dd, J_1=8.0 Hz, J_2=0.8 Hz), 8.01 (1H, s), 7.95 (1H, d, *J*=13.2 Hz), 7.64 (0.06H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4o**), 7.46 (1H, dd, J_1=8.0 Hz, J_2=0.8 Hz), 7.37 (1H, d, *J*=8.0 Hz), 7.27 (1H, d, *J*=8.0 Hz), 7.17 (0.12H, d, *J*=8.0 Hz, (1*E*,3*Z*)-**4o**), 6.94 (1H, t, *J*=8.0 Hz), 6.03–5.96 (1H, m), 5.19 (1H, dd, J_1=8.0 Hz, J_2=0.8 Hz), 5.14 (1H, dd, J_1=8.0 Hz, J_2=0.8 Hz), 4.89–4.88 (2H, m), 4.41 (2H, q, *J*=7.2 Hz), 2.41 (3H, s), 2.37 (0.18H, s, (1*E*,3*Z*)-**4o**), 1.43 (3H, t, *J*=7.2 Hz), 1.33 (0.18H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4o**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 160.7, 147.4, 140.6, 137.9, 137.4, 136.5, 132.7, 132.0, 131.9, 130.6, 129.6, 125.3, 125.2, 124.6, 124.1, 121.6, 116.6, 102.1, 102.0, 61.6, 43.0, 21.5, 14.2; MS (ESI) m/e 495.1 (M^++H); HRMS (ESI) for $C_{25}H_{23}BrN_2O_4$ (M^+): 494.0841, Found: 494.0833.

*4.1.35. (1E,3E,NE)-N-(1-Allyl-6-methyl-2-oxoindolin-3-ylidene)-4-(4-chlorophenyl)-3-(ethoxycarbonyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4p**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4p** (41 mg, 91% overall yield in a stereoselective ratio=8:1 ((1*E*,3*E*)-**4p**/(1*E*,3*Z*)-**4p**)). A red solid. Mp for compound **4p**=165–166 °C; IR (CH_2Cl_2): ν 2922, 2853, 1713, 1692, 1588, 1521, 1486, 1445, 1377, 1341, 1306, 1265, 1123, 1089, 1012, 965, 908, 851 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 9.94 (1H, d, *J*=13.2 Hz), 9.29 (0.12H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4p**), 8.32 (1H, d, *J*=7.6 Hz), 7.90 (1H, s), 7.86 (1H, d, *J*=13.2 Hz), 7.60 (0.12H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4p**), 7.44–7.32 (4H, m), 6.89 (1H, d, *J*=8.0 Hz), 6.63 (1H, s), 5.89–5.82 (1H, m), 5.26–5.22 (2H, m), 4.44–4.37 (4H, m), 2.39 (3H, s), 1.77 (0.36H, s, (1*E*,3*Z*)-**4p**), 1.43 (3H, t, *J*=7.2 Hz), 1.32 (0.36H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4p**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8, 160.3, 144.5, 143.6, 141.4, 136.7, 135.8, 133.5, 133.1, 131.5, 131.1, 129.0, 126.8, 125.8, 123.8, 123.0, 117.6, 116.0, 109.6, 61.7, 42.1, 22.6, 14.2; MS (ESI) m/e 451.1 (M^++H); HRMS (ESI) for $C_{25}H_{23}ClN_2O_4$ (M^+): 450.1346, Found: 450.1335.

*4.1.36. (1E,3E,NE)-N-(1-Allyl-2-oxoindolin-3-ylidene)-4-(3-bromophenyl)-3-(ethoxycarbonyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4q**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4q** (45 mg, 94% overall yield in a stereoselective ratio=5:1 ((1*E*,3*E*)-**4q**/(1*E*,3*Z*)-**4q**)). A red solid. Mp for compound **4q**=117–119 °C; IR (CH_2Cl_2): ν 3115, 2979, 1691, 1645, 1604, 1556, 1463, 1377, 1343, 1267, 1186, 1104, 1092, 965, 923, 861 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 9.99 (1H, d, *J*=13.2 Hz), 9.35 (0.20H, d, *J*=13.2 Hz, (1*E*,3*Z*)-**4q**), 8.45 (1H, d, *J*=7.6 Hz), 7.89 (1H, s), 7.85 (1H, d, *J*=7.6 Hz), 7.62 (0.20H, d, *J*=8.0 Hz, (1*E*,3*Z*)-**4q**), 7.58 (1H, s), 7.54 (1H, d, *J*=8.0 Hz), 7.46 (0.20H, d, *J*=8.0 Hz, (1*E*,3*Z*)-**4q**), 7.41–7.23 (3H, m), 7.08 (1H, t, *J*=8.0 Hz), 6.82 (1H, d, *J*=8.0 Hz), 5.90–5.81 (1H, m), 5.26 (1H, d, *J*=6.4 Hz), 5.22 (1H, s), 4.44–4.39 (4H, m), 1.44 (3H, t, *J*=7.2 Hz), 1.32 (0.60H, t, *J*=7.2 Hz, (1*E*,3*Z*)-**4q**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 160.0, 144.3, 141.4, 137.0, 136.6, 133.8, 133.6, 132.9, 132.6, 132.2, 131.1, 131.0, 130.3, 130.0, 128.6, 127.5, 125.8, 123.3, 123.1, 122.8, 118.4, 117.8, 108.7, 61.8, 42.2, 14.2; MS (ESI) m/e 481.1 (M^++H); HRMS (ESI) for $C_{24}H_{21}BrN_2O_4$ (M^+): 480.0685, Found: 480.0674.

*4.1.37. (1E,3E,NE)-N-(1-Allyl-2-oxoindolin-3-ylidene)-3-(ethoxycarbonyl)-4-(3-methoxyphenyl)buta-1,3-dien-1-amine oxide (1E,3E)-**4r**.* Following the general procedure, the mixture was purified by column chromatography using silica gel to give the target product **4r** (41 mg, 95% overall yield in a stereoselective ratio=20:1 ((1*E*,3*E*)-**4r**/(1*E*,3*Z*)-**4r**)). A red solid. Mp for ((1*E*,3*E*)-**4r**)=50–53 °C; mp for ((1*E*,3*Z*)-**4r**)=48–51 °C; IR (CH_2Cl_2): ν 3116, 2925, 2853, 1712, 1692, 1604, 1572, 1519, 1430, 1378, 1344, 1289, 1175, 1117, 1022, 964, 930, 865 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ ((1*E*,3*E*)-**4r**) 9.98 (1H, d, *J*=13.2 Hz), 8.45 (1H, d, *J*=7.6 Hz), 7.97 (1H, d, *J*=13.2 Hz), 7.968 (1H, s), 7.36 (2H, q, *J*=9.2 Hz), 7.07 (2H, dd, J_1=12.0 Hz, J_2=7.6 Hz), 6.97 (2H, d, *J*=6.4 Hz), 6.82 (1H, d, *J*=8.0 Hz), 5.90–5.81 (1H, m), 5.25 (1H, d, *J*=6.8 Hz), 5.22 (1H, s), 4.45–4.39 (4H, m), 3.84 (3H, s), 1.44 (3H, t, *J*=7.2 Hz); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ ((1*E*,3*Z*)-**4r**) 9.33 (1H, d, *J*=13.2 Hz), 8.48 (1H, d, *J*=8.4 Hz), 7.65 (1H, d, *J*=13.2 Hz), 7.38–7.28 (2H, m), 7.23–7.21 (2H, m), 7.11 (1H, t, *J*=7.6 Hz), 7.04 (1H, s), 7.00–6.89 (2H, m), 6.85–6.80 (1H, m), 5.89–5.81 (1H, m), 5.28–5.22 (2H, m), 4.43–4.37 (4H, m), 3.81 (3H, s), 1.32 (3H, t, *J*=8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ ((1*E*,3*E*)-**4r**) 166.0, 160.0, 159.6, 146.4, 141.0, 136.4, 135.9, 133.3, 132.0, 131.1, 129.8, 126.4, 125.7, 124.2, 123.0, 122.8, 118.5, 117.7, 115.9, 115.2, 108.7, 61.6, 55.3, 42.2, 14.2; ^{13}C NMR ($CDCl_3$, 100 MHz): δ ((1*E*,3*Z*)-**4r**) 167.4, 160.0, 159.5, 144.2, 141.1, 140.7, 135.9, 133.2, 132.2, 131.1, 130.6, 129.4, 128.7, 126.0, 123.1, 118.4, 118.0, 117.8, 115.5, 108.8, 95.1, 61.9, 55.2, 42.3, 14.2; MS (ESI) m/e ((1*E*,3*E*)-**4r**) 433.2 (M^++H); HRMS (ESI) for $C_{25}H_{24}N_2O_5$ (M^+): 432.1685, Found: 432.1680; MS (ESI) m/e ((1*E*,3*Z*)-**4r**) 450.2 (M^++NH_4); HRMS (ESI) for $C_{25}H_{24}N_2O_5$ (M^+): 432.1685, Found: 432.1683.

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Supplementary data

The ^1H and ^{13}C NMR spectroscopic data and charts of the compounds and X-ray crystal data of **3j**, (1*E*,3*E*)-**4a**, (1*E*,3*Z*)-**4r** are included in the Supplementary data. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2013.02.070.

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