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Cinchona alkaloid and di-*tert*-butyldicarbonate-DMAP promoted efficient synthesis of (*E*)-nitroolefins

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Nataraj Poomathi,[a] and Paramasivan T. Perumal*[a]

Synthesis of nitroolefins from aldehyde and olefin is generally limited by the formation of mixture of cis and trans compounds. Here we report an alternative, metal- free protocol for the synthesis of *β*-nitroolefins from arylidinemalononitrile using cinchona alkaloid along with di-*tert*-butyldicarbonate-DMAP in high yields with total selectivity.

Nitroolefins are prominent class of synthetic intermediates, which have found wide application in the preparation of variety of biorelevant compounds and pharmaceuticals.[1] These are widely used in different carbon-carbon bond-forming reactions like Michael reaction,[2] cycloaddition,[3] Morita-Baylis-Hillman reaction,[4] and for the generation of oximes,[5] hydroxylamines, nitroalkanes[6] and aliphatic amines. These are usually synthesized by Henry reaction, involving base mediated condensation of nitroalkanes with aldehyde or ketones followed by dehydration.[7a,b] An alternative and relatively simple approach relies upon readily available aldehyde, malononitrile and nitromethane as the strating materials, wherein anion formation and subsequent *β*-elimination of malononitrile lead to the desi-red nitroolefins in a stereoselective manner. This convenient and step economical process has drawn significant attention in recent decades.[7c,d] To date, a number of methods have been developed with different metal based and gaseous nitrating agents. [8] These methods while offering significant improvements in direct nitration of olefins often have several drawbacks. Problematic issues include the tendency to form an un-desired mixture of *E/Z* isomers,[8a,b] lack of functional group tolerance,[8e,g] and harsh reaction conditions among others.[8d,g] Although a number of methods[8h-s] for the synthesis of nitroolefins have been developed, more environmentally benign and efficient approaches are still needed to reduce the use of expensive catalysts, solvents and toxic reagents. Further, stereoselective synthesis of nitroolefins with an easy to handle metal free reagent is yet to be developed. Notably, from a practical aspect, metal-free synthesis[9] (Figure 1) are preferred, as the removal of metal contamination can render a process quite expensive.[10] In particular, preparation of nitrostyrene under metal-free conditions would be of great significance due to its close association with the pharmaceutical industry. To date, only a few synthetic methods using bifunctional catalysts have been reported, such as those applying transition metal catalyst and bifunctional catalyst.[11] To achieve the Michael addition of nitromethane to arylidinemalononitrile, we planned to use thiourea and cinchona alkaloid as a catalyst, where these catalyst systems are able to "intramolecularise" the reactions *via* simultaneous activation of two reaction partners.[12a-d] To our knowledge, no reports are available on the *β*-elimination of malononitrile using cinchona alkaloid and di-*tert*-butyldicarbonate leading to the desired nitroolefins. This has now been relished in the case of aromatic/heteroaromatic using malononitrile, nitromethane, di-*tert*-butyldicarbonate, DMAP and catalytic amount of cinchona alkaloid, This newly developed method is operationally simple, functional group tolerant, good yielding and scalable.

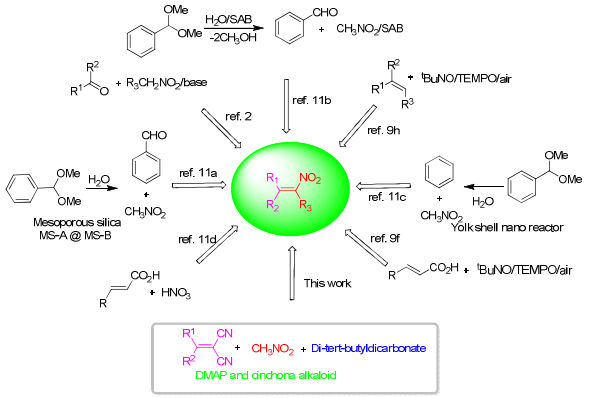


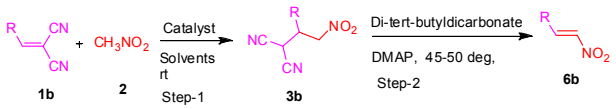
Figure 1 Metal-free strategy for the synthesis of *β*-nitroolefins.

Initially, a feasibility study of our hypothesis revealed that arylidinemalononitrile **1b**, nitromethane **2** was investigated using

[a] *Organic Chemistry Division, CSIR-Central Leather Research Institute, Adyar, Chennai-6000 20, India.*
Fax: +91-44-24911589; E-mail: ptperumal@gmail.com

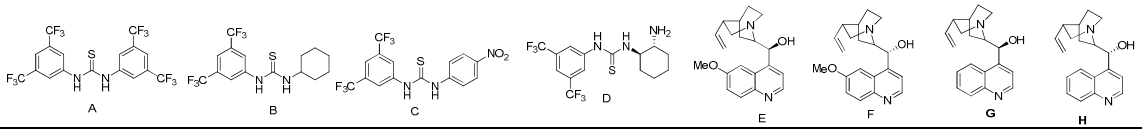
†Electronic Supplementary Information (ESI) available: Copies of ^{1}H NMR, and ^{13}C NMR spectra of all compounds and Experimental procedure. See DOI: 10.1039/x0xx00000x

Table 1 Optimization of the reaction conditions[c]



1b 2 3b 6b

Catalysts:



Entry	Catalyst (mol %)	Time (h)	Temp (°C)	Yield (%) DCM[a,b]	CH_3CN[a,b]	Toluene[a,b]	Dioxane[a,b]
1.	A (10)	4	50	--	--	--	--
2.	B (10)	4	50	--	--	--	--
3.	C (10)	4	50	--	--	--	--
4.	D (10)	4	50	55	45	72	35
5.	E (10)	4	50	65	35	62	25
6.	**F (10)**	**4**	50	78	40	**87**	35
7.	G (10)	4	50	60	35	70	25
8.	H (10)	4	50	68	37	75	26
9.	F (10)	7	50	77	40	87	30
10.	F (10)	10	50	77	40	87	30
11.	F (10)	10	rt	--	--	--	--
12.	--	10	50	30	30	30	25
13.	--	15	50	40	32	30	25
14.	F (10)	4	60	65	40	83	35
15.	F (10)	4	70	60	35	68	20
16.	F (5)	4	50	70	35	80	30
17.	F (15)	4	50	78	40	87	35
18.	F (25)	4	50	77	40	87	33

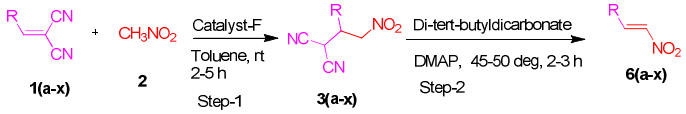
[a]The reaction was performed with arylidinemalononitile **1b** (0.1 mmol), nitromethane **2** (0.5 mmole), catalyst, di-*tert*-butyldicarbonate (0.2 mmol) and DMAP (0.02 mmol) in 2 mL of solvents at 45-50 deg.[b] Isolated yields. [c]*E/Z* ratio is approximately >97/3 for all the synthesized products except entry 6, 8-17 in table 1(*E/Z* ratio: 99>1). It was determined by NMR analysis of the crude products.

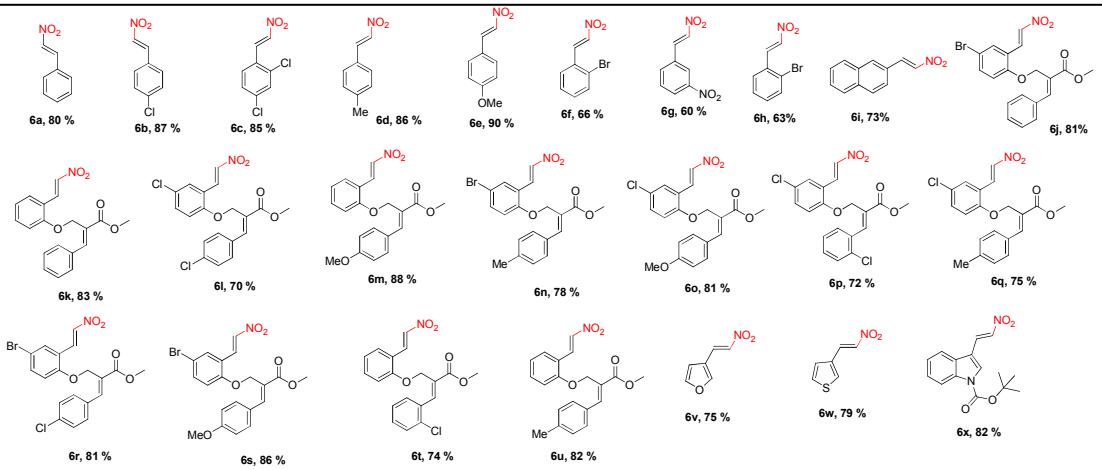
various bases, such as TEA, DABCO, Piperidine , DBU and DMAP with di-*tert* butyldicarbonate using catalyst A-H. Although product **6b** can be generated in the presence of all of these bases except entry 1, 2 and 3, only DMAP resulted in a high chemical yield using catalyst F in toluene at 45-50 deg to furnish the desired product **6b** in 87 % yield (Table 1, entry 6). Next, several bifunctional catalysts with different solvents such as CH_3CN, DCM, toluene and dioxane, were evaluated for their efficacy in this cascade reaction (Table 1, entries 1-18) and cinchona alkaloid F was found to be the most promising catalyst for this cascade reaction (Table 1, entry 6). The results showed that toluene was optimal choice (Table 1, entry 6). However, in the absence of catalyst, the cascade process did not proceed significantly, even in toluene (Table 1, entry 12, 13). Finally, we examined the effect of the catalyst concentration on this cascade reaction. The results revealed that decreasing the amount of catalyst F from 10 to 5 mol % led to an decrease in the yield from 87 to 80 % (Table 1, entry 16), whereas by increasing the amount of catalyst F from 10 to 25 mol %, the yield of the product could not be improved significantly (Table 1, entry 17, 18). We found that 2 equiv of di-*tert*-butyldicarbonate and 10 mol % of catalyst F in toluene at 50 °C could provide *β*-nitrostyrene in an excellent 90 % isolated yield with complete *E*-selectivity (Table 2, 6e). With the reaction conditions optimized, the substrate scope was then investigated to show the generality of this cascade reaction (Table 2). In most cases, the reactions afforded the corresponding nitroolefins product with moderate to good yields (65-90 %). The structural variation of alkylidenemalononitrile **1** could be well tolerated in this reaction irrespective of the electronic nature or the positions of the substituent on the aromatic ring, compared with the 4-methoxy benzaldehyde (6e, 90 %) gave excellent yields of the desired nitro product.

It is noteworthy that this cascade process could also be successfully extended to several 2-formylphenoxy-methyl-3-phenylacrylate derivatives (Table 2, **6j-6u** with including those containing Cl, Br, Me and OMe) under the optimized conditions in good yields (70-90 %). The scope of the reaction was further studied with various heterocyclic compounds under optimized conditions. Oxgen, sulphur and nitrogen based heterocycles such as furan, thiophene and indole gave the nitro products (Table 2, **6(v-x)**) in 75, 79 and 82 % isolated yield, respectively**.** Unfortunately alkylidinemalononitrile (e.g 2-butylidinemalononitrile) did not form the desired nitroolefin product under the reaction conditions.

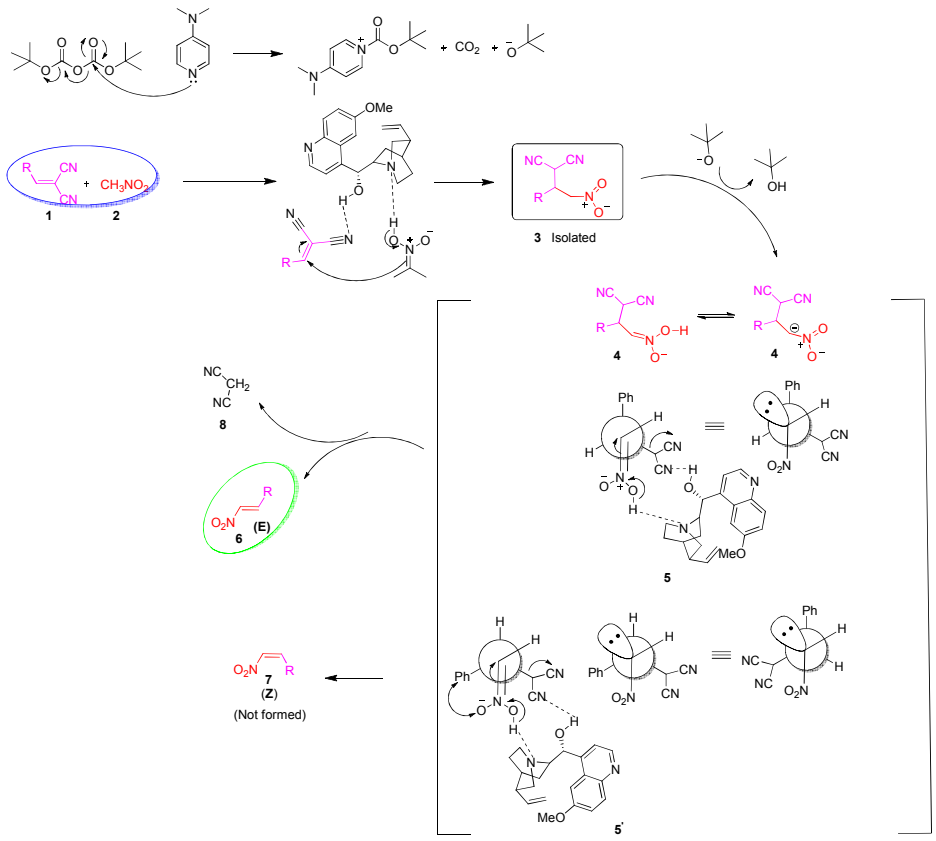
To demonstrate the scalability of the *β*-elimination of malononitrile method, 4-chlorobenzaldehyde was reacted in a 6

Table 2 Substrate scope of the arylidinemalononitriles, 2-formylphenoxy-methyl-3-phenylacrylates and heterocyclic compound in the metal-free synthesis of *β*-nitroolefins[a,b]





[a]Unless otherwise noted, the reactions in step-1 were performed with arylidinemalononitile/2-formylphenoxy-methyl-3-phenylacrylates/heterocyclic compounds **1** (0.1 mmol), nitromethane 2 (0.5 mmole) and catalyst-F (10 mol %). In step-2, the reactions were performed with di-tert-butyldicarbonate (0.2 mmol) and DMAP (0.02 mmol) in 2 mL of toluene. Yield refers to the column purified products. [b] E/Z ratio is >99/1 for all the synthesized products. It was determined by NMR analysis of the crude product



Scheme 1 Plausible reaction mechanism for the metal-free synthesis of *β*-nitroolefins **6**

mmol scale. In this experiment, the desired nitrostyrene product was isolated in preoperatively useful yield (87 %). The structures of all the nitroolefins **6(a-u)** and **6(v-x)** are deduced by their satisfactory spectral (^{1}H NMR, ^{13}C NMR and EI-HRMS) studies. The structures of the compounds **6t** have been further confirmed by X-ray analysis[13] (Figure 2).

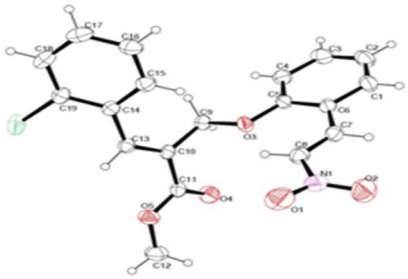


Figure 2 ORTEP diagram of compound **6t**

On the basis of the above results a plausible mechanism for the formation of *β*-nitroolefins is proposed in scheme 1. The first step is the generation of *tert*-butoxide from DMAP and di-*tert*-butyldicarbonate, and which has been proposed previously by our group.[12e] Cinchona catalyst F containing hydrogen bond donors and a tertiary amine moiety, where the amine could be oriented in such a way as to cooperatively bind a single proton from the nitromethane and the hydroxyl group could activate arylidinemalononitrile **1** electrophilically *via* hydrogen bonding that would result in efficient assembly of the nitromethane and the arylidinemalononitrile followed by smooth Michael addition and consecutive protonation led to the 2-(2-nitro-1-phenylethyl)malononitrile intermediate **3**. We have isolated intermediate **3u** in table 1, which was fully characterized by NMR spectroscopy.[14] Next, in the presence of the generated *tert*-butoxide, intermediate **3** can be deprotonated to furnish cabanion **4,** which could be possible two conformations **5** and **5'**, stabilized by an hydrogen bonding with catalyst F. The conformations of which are nearly ideal for the subsequent E2 or E1cb reaction process for stereo electronic reasons as depicted in Newman projection 5 and 5', however intermediate 5' suffers from severe steric and more dipole repulsion between Phenyl, nitro, cyano groups and catalyst F so out of two possible pathways involving **4**, preferential formation of energetically more favourable conformation of intermediate **5** over **5'**, followed by *β*-elimination of malononitrile to afford the desired nitro product **6** and recycles malononitrile **8** in scheme **1**. The presence of a single isomer is probably the tertiary amine and hydroxyl group in cinchona alkaloid would activate the nitro group (intermediate-4) through hydrogen bonding, thus the synergistic interactions would ensure high stereoselectivity in this transformation.[15]

According to the above plausible reaction mechanism and the experimental results, this protocol offers greatly improved the overall yield and E/Z selectivity, is this due to the participation of organocatalyst and Boc-anhydride/DMAP combination provides a better elimination protocol compared to other conventional base-mediated conditions, without cinchona alkaloid, the overall yield of the product was found to be very low and E/Z selectivity also reduced[16] which provided further support to the proposed mechanism. Finally, the absolute (*E*) configuration was obtained in accordance with X-ray crystal structure analysis.

Conclusions

In summary, we have described an easy, efficient and metal-free general route to aromatic *β*-nitrostyrens with total *E*-selectivity has been discovered under mild conditions. The substrate scope of the arylidinemalononitrile bearing aromatic and heterocyclic moieties was explored and *E*-nitro compounds were obtained selectively. The process is practical, avoiding multistep and expensive purification procedure. Further studies are in progress to broaden the potentiality of the procedure and to better clarify the reaction pathway.

Experimental Section

General procedure for the synthesis of Arylidinemalononitriles and (*E*)-methyl-2-((4-chloro-2-(2,2di-cyanovinyl)-phenoxy)-methyl)-3-(4-methoxy-phenyl)-acrylate derivatives:

Aldehyde (1 mmol), malononitrile (1 mmol) in ethanol (3 mL) and catalytic amount of water were charged in a 25 mL round bottomed flask and the resulting solution was stirred for 3-5 h at room temperature. The consumption of the starting material was monitored by TLC. The precipitated solid was filtred and washed with ethanol (5-7 mL), dried under vacuum to obtain pure **1a-x** in good yields (78-89 %). The identities of products were confirmed by NMR giving good agreement with the assigned structures.

General procedure for the preparation of *E*-nitroolefin derivatives:

A mixture of arylidine/heteroarylidinemalononitriles/(E)-methyl 2-((4-chloro-2-(2,2-di-cyanovinyl)-phenoxy)-methyl)-3-(4-methox-yphenyl)-acrylate derivatives 1(a-x) (0.1 mmol), nitromethane 2 (0.5 mmol) in toluene (3 mL) and catalytic amount of cinchona alkaloid F (10 mol %) were charged in a 25 mL round bottomed flask and the resulting solution was stirred for 2-5 h at room temperature. The consumption of the starting material was monitored by TLC. After completition of the reaction, DMAP (0.020 mmol) and di-*tert*-butyldicarbonate (2.0 equiv) was then added to a stirred solution of corresponding crude product 3. After stirring the reaction at 45-50 deg. for 2-3 hrs followed by TLC, the solvent was removed under reduced pressure and the residue was purified by column chromatography on siliga gel (3:97 % ethylacetate and petether) to afford pure products 6(a-x) in average to good yields 65-90 %.

The identities of products 6(a-x) were confirmed by NMR and EI-HRMS, giving good agreement with the assigned structures.

6a: (*E*)-(2-nitrovinyl) benzene: Isolated as yellow solid, 80 %, m.p: 57-58°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.93 (1 H, d, *J* = 13.7), 7.51 (1 H, d, *J* = 13.7), 7.49 – 7.45 (2 H, m), 7.44 – 7.34 (3 H, m) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 139.08, 137.15, 132.16, 130.10, 129.42, 129.16 ppm. EI-HRMS: Anal. Calcd for $C_8H_7NO_2$: 149.0477, Found: 149.0472. Elemental analysis: Anal. Calcd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39; O, 21.45 %. Found: C, 64.36; H, 4.79; N, 9.33; O, 21.49 %.

6b: (*E*)-1-chloro-4-(2-nitrovinyl) benzene: Isolated as yellow solid, 87 %, m.p: 111-112°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.96 (1 H, d, *J* = 13.7), 7.57 (1 H, d, *J* = 13.7), 7.53 – 7.47 (2 H, m), 7.47 – 7.40 (2 H, m) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 138.36, 137.71, 137.45, 130.29, 129.79, 128.55 ppm. EI-HRMS: Anal. Calcd for $C_8H_6ClNO_2$: 183.0087, Found: 183.0083. Elemental analysis: Anal. Calcd for $C_8H_6ClNO_2$: C, 52.34; H, 3.29; Cl, 19.31; N, 7.63; O, 17.43 %. Found: C, 52.30; H, 3.25; Cl, 19.38; N, 7.68; O, 17.37 %.

6c: (*E*)-2,4-dichloro-1-(2-nitrovinyl)benzene: Isolated as yellow solid, 85 %, m.p: 118-119°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.33 (1 H, d, *J* = 13.7), 7.58 (1 H, d, *J* = 13.7), 7.55 – 7.49 (2 H, m), 7.34 (1 H, dd, *J* = 8.4, 1.9) ppm. ^{13}C NMR δ_C (101 MHz, $CDCl_3$) 139.05, 138.49, 136.68, 133.99, 130.69, 129.29, 128.04, 127.12 ppm. EI-HRMS: Anal. Calcd for $C_8H_5Cl_2NO_2$: 216.9697, Found: 216.9695. Elemental analysis: Anal. Calcd for $C_8H_5Cl_2NO_2$: C, 44.07; H, 2.31; Cl, 32.52; N, 6.42; O, 14.68 %. Found: C, 44.0; H, 2.37; Cl, 32.45; N, 6.35; O, 14.61 %.

6d: (*E*)-1-methyl-4-(2-nitrovinyl) benzene: Isolated as yellow solid, 86 %, m.p: 105-106°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 7.98 (1 H, d, *J* = 13.6), 7.56 (1 H, d, *J* = 13.6), 7.44 (2 H, d, *J* = 8.1), 7.25 (2 H, d, *J* = 8.0), 2.41 (3 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 143.14, 139.20, 136.31, 130.17, 129.22, 127.31, 21.68 ppm. EI-HRMS: Anal. Calcd for $C_9H_9NO_2$: 163.0633, Found: 163.0630. Elemental analysis: Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58; O, 19.61 %. Found: C, 66.20; H, 5.60; N, 8.51; O, 19.69 %.

6e: (*E*)-1-methoxy-4-(2-nitrovinyl) benzene: Isolated as yellow solid, 90 %, m.p: 90-92°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 7.96 (1 H, d, *J* = 13.6), 7.52 (1 H, d, *J* = 6.0), 7.51–7.48 (2 H, m), 6.99–6.92 (2 H, m), 3.86 (3 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 162.99, 139.07, 135.02, 131.21, 122.55, 114.95, 55.55 ppm. EI-HRMS: Anal. Calcd for $C_9H_9NO_3$: 179.0582, Found: 179.0580. Elemental analysis: Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82; O, 26.79 %. Found: C, 60.39; H, 5.01; N, 7.75; O, 26.73 %.

6f: (*E*)-1-bromo-2-(2-nitrovinyl) benzene: Isolated as yellow solid, 66 %, m.p: 140-142°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.40 (1 H, d, *J* = 13.7), 7.69 (1 H, dd, *J* = 7.8, 1.4), 7.63 – 7.49 (2 H, m), 7.44–7.26 (2 H, m) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 138.89, 137.60, 134.04, 132.92, 130.41, 128.49, 128.08, 126.35 ppm. EI-HRMS: Anal. Calcd for $C_8H_6BrNO_2$: 226. 9582 Found: 226.9581. Elemental analysis: Anal. Calcd for $C_8H_6BrNO_2$: C, 42.13; H, 2.65; Br, 35.04; N, 6.14; O, 14.03 %. Found: C, 42.19; H, 2.69; Br, 35.01; N, 6.19; O, 14.07 %.

6g: (*E*)-1-nitro-3-(2-nitrovinyl) benzene Isolated as yellow solid, 60 %, m.p: 127-128°C, ^{1}H NMR δ_H (500 MHz,) 8.28–8.09 (3 H, m), 7.61 (1 H, dd, *J* = 4.9, 2.2). ppm. ^{13}C NMR δ_C (125 MHz, $CDCl_3$) 126.66, 126.39, 130.88, 131.97, 134.67, 148.95 ppm. EI-HRMS: Anal. Calcd for $C_8H_6N_2O_4$: 194.0328 Found: 194.0327. Elemental analysis: Anal. Calcd for $C_8H_6N_2O_4$: C, 49.49; H, 3.12; N, 14.43; O, 32.96 %. Found: C, 49.43; H, 3.17; N, 14.39; O, 32.91 %.

6h: (*E*)-1-bromo-4-(2-nitrovinyl) benzene: Isolated as yellow solid, 63 %, m.p: 143-145°C, δ_H (500 MHz,) 7.94 (1 H, d, *J* = 13.7), 7.58 (3 H, t, *J* = 10.8), 7.41 (2 H, d, *J* = 8.4) ppm. ^{13}C NMR δ_C (125 MHz, $CDCl_3$) 127.01, 129.13, 130.60, 132.95, 137.64,138.09 ppm. EI-HRMS: Anal. Calcd for $C_8H_6BrNO_2$: 226.9582 Found: 226.9580. Elemental analysis: Anal. Calcd for $C_8H_6BrNO_2$: C, 42.13; H, 2.65; Br, 35.04; N, 6.14; O, 14.03 %. Found: C, 42.09; H, 2.60; Br, 35.09; N, 6.10; O, 13.03 %.

6i: (*E*)-2-(2-nitrovinyl)naphthalene: Isolated as yellow solid, 73 %, m.p: 128-130°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.79 (1 H, d, *J* = 13.4), 8.09 (1 H, d, *J* = 8.4), 7.98 (1 H, d, *J* = 8.2), 7.94 – 7.85 (1 H, m), 7.71 (1 H, d, *J* = 7.2), 7.66 – 7.54 (3 H, m), 7.53 – 7.46 (1 H, m) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 138.50, 136.09, 133.79, 132.58, 131.59, 129.09, 127.76, 126.98, 126.82, 126.41, 125.43, 122.98 ppm. EI-HRMS: Anal. Calcd for $C_{12}H_9NO_2$: 199.0633, Found: 199.0632. Elemental analysis: Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03; O, 16.06 %. Found: C, 72.30; H, 4.47; N, 6.05; O, 16.01 %.

6j: (*E*)-methyl 2-((4-bromo-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-phenylacrylate: Isolated as yellow solid, 81 %, m.p: 98-100°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.11 (1 H, s), 7.99 (1 H, d, *J* = 13.7), 7.71 (1 H, d, *J* = 13.7), 7.58 (1 H, d, *J* = 2.4), 7.51 (1 H, d, *J* = 2.5), 7.39 (5 H, s), 6.88 (1 H, d, *J* = 8.9), 4.99 (2 H, s), 3.89 (3 H, s). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.19, 157.14, 146.43, 139.11, 135.62, 134.12, 134.07, 133.57, 129.95, 129.40, 128.92, 126.08, 121.63, 114.77, 113.73, 64.07, 52.59 ppm. EI-HRMS: Anal. Calcd for $C_{19}H_{16}BrNO_5$: 417.0212, Found: 417.0210. Elemental analysis: Anal. Calcd for $C_{19}H_{16}BrNO_5$: C, 54.56; H, 3.86; Br, 19.10; N, 3.35; O, 19.13 %. Found: C, 54.51; H, 3.82; Br, 18.70; N, 3.31; O, 18.15 %.

6k:(*E*)-methyl-2-((2-((E)-2-nitro-vinyl)-phenoxy)-methyl)-3-phenyl-acrylate: Isolated as yellow solid, 83 %, m.p: 127-130°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.11 (1 H, t, *J* = 6.8), 7.78 (1 H, d, *J* = 13.6), 7.50 – 7.40 (2 H, m), 7.39 – 7.36 (1 H, m), 7.05 (1 H, t, *J* = 7.5), 6.99 (1 H, d, *J* = 8.4), 5.01 (1 H, s), 3.89 (2 H, s). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.34, 158.28, 146.22, 138.34, 135.28, 134.19, 133.38, 132.34, 129.84, 129.48, 128.88, 126.40, 121.62, 119.70, 112.96, 63.67, 52.55 ppm. EI-HRMS: Anal. Calcd for $C_{19}H_{17}NO_5$: 339.1107, Found: 339.1105. Elemental analysis: Anal. Calcd for

$C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13; O, 23.57 %. Found: C, 67.17; H, 5.01; N, 4.19; O, 23.51 %.

6l: (*E*)-methyl 2-((4-chloro-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(4-chlorophenyl)acrylate: Isolated as yellow solid, 70 %, m.p: 135-137°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 7.98–7.87 (1 H, m), 7.62 (1 H, d, *J* = 13.7), 7.37 (1 H, d, *J* = 2.5), 7.32–7.22 (3 H, m), 6.87 (1 H, d, *J* = 8.9), 4.88 (1 H, s), 3.81 (2 H, s). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 166.95, 156.49, 145.02, 139.06, 136.18, 133.51, 132.80, 132.47, 131.04, 130.69, 129.23, 126.85, 126.61, 121.11, 114.38, 64.02, 52.67 ppm. EI-HRMS: Anal. Calcd for C_{19} H_{15} Cl_2 NO_5: 407.0327, Found: 407.0325. Elemental analysis: Anal. Calcd for $C_{19}H_{15}Cl_2NO_5$: C, 55.90; H, 3.70; Cl, 17.37; N, 3.43; O, 19.60 %. Found: C, 55.85; H, 3.66; Cl, 17.31; N, 3.49; O, 19.55 %.

6m: (*E*)-methyl-3-(4-methoxy-phenyl)-2-((2-((E)-2-nitro-vinyl)-phenoxy)-methyl)-acrylate: Isolated as yellow solid, 88 %, m.p: 108-110°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.24–8.01 (1 H, m), 7.77 (1 H, d, *J* = 13.6), 7.52–7.35 (2 H, m), 7.09–6.98 (1 H, m), 6.90 (1 H, d, *J* = 8.8), 5.04 (1 H, s), 3.87 (1 H, s), 3.81 (1 H, s). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.67, 161.12, 158.36, 146.17, 138.31, 135.30, 133.42, 132.34, 131.67, 126.66, 123.78, 121.57, 119.70, 114.40, 112.99, 63.82, 55.38, 52.42 ppm. EI-HRMS: Anal. Calcd for C_{20} H_{19} NO_6: 369.1212, Found: 369.1211. Elemental analysis: Anal. Calcd for $C_{20}H_{19}NO_6$: C, 65.03; H, 5.18; N, 3.79; O, 25.99 %. Found: C, 64.06; H, 5.12; N, 3.72; O, 26.06 %.

6n: (*E*)-methyl 2-((4-bromo-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(p-tolyl)acrylate: Isolated as yellow solid, 78 %, m.p: 123-140°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.14–7.92 (1 H, m), 7.71 (1 H, d, *J* = 13.6), 7.58 (1 H, d, *J* = 2.4), 7.50 (1 H, dd, *J* = 8.8, 2.5), 7.33–7.25 (1 H, m), 7.20 (1 H, d, *J* = 8.0), 6.90 (1 H, d, *J* = 8.9), 5.00 (1 H, s), 3.88 (2 H, s), 2.36 (2 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.36, 157.19, 146.61, 140.53, 139.11, 135.62, 134.15, 133.61, 131.22, 129.67, 129.58, 125.03, 121.62, 114.77, 113.66, 64.14, 52.52, 21.41ppm. EI-HRMS: Anal. Calcd for C_{20} H_{18} Br NO_5: 431.0368, Found: 431.0366. Elemental analysis: Anal. Calcd for $C_{20}H_{18}BrNO_5$: C, 55.57; H, 4.20; Br, 18.48; N, 3.24; O, 18.51 %. Found: C, 55.51; H, 4.17; Br, 18.43; N, 3.29; O, 18.43 %.

6o: (*E*)-methyl 2-((4-chloro-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(4-methoxyphenyl)acrylate: Isolated as yellow solid, 81 %, m.p: 140-142°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.08–7.96 (1 H, m), 7.71 (1 H, d, *J* = 13.7), 7.44 (1 H, d, *J* = 2.6), 7.39 (1 H, dd, *J* = 8.9, 2.7), 7.00 (1 H, d, *J* = 8.9), 6.91 (1 H, d, *J* = 8.8), 5.03 (1 H, s), 3.87 (1 H, s), 3.82 (2 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.57, 161.20, 156.74, 146.37, 139.11, 133.72, 132.76, 131.63, 131.18, 126.59, 126.53, 123.45, 121.13, 114.44, 114.42, 64.30, 55.40, 52.46 ppm. EI-HRMS: Anal. Calcd for C_{20} H_{18} Cl NO_6: 403.0823, Found: 403.0822. Elemental analysis: Anal. Calcd for $C_{20}H_{18}ClNO_6$: C, 59.49; H, 4.49; Cl, 8.78; N, 3.47; O, 23.77 %. Found: C, 59.43; H, 4.42; Cl, 8.74; N, 3.54; O, 23.70 %.

6p:(*E*)-methyl2-((4-chloro-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(2-chloro-phenyl)-acrylate: Isolated as yellow solid, 72 %, m.p: 136-138°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.15 (1 H, s), 7.97 (1 H, d, *J* = 13.7), 7.69 (1 H, d, *J* = 13.7), 7.47 – 7.39 (2 H, m), 7.33 (3 H, ddd, *J* = 8.6, 5.4, 2.0), 7.29–7.22 (1 H, m), 6.86 (1 H, d, *J* = 8.9), 4.91 (2 H, s), 3.91 (3 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 166.60, 156.47, 142.93, 139.03, 134.25, 133.54, 132.86, 132.71, 130.93, 130.85, 129.98, 129.90, 128.18, 127.02, 126.73, 121.12, 114.47, 64.34, 52.71ppm. EI-HRMS: Anal. Calcd for C_{19} H_{15} Cl_2 NO_5: 407.0327, Found: 407.0325. Elemental analysis: Anal. Calcd for $C_{19}H_{15}Cl_2NO_5$: C, 55.90; H, 3.70; Cl, 17.37; N, 3.43; O, 19.60 %. Found: C, 55.84; H, 3.64; Cl, 17.31; N, 3.49; O, 19.53 %.

6q: (*E*)-methyl 2-((4-chloro-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(p-tolyl)acrylate: Isolated as yellow solid, 75 %, m.p: 149-151°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.09–7.94 (1 H, m), 7.72 (1 H, d, *J* = 13.7), 7.43 (1 H, d, *J* = 2.6), 7.37 (1 H, dd, *J* = 8.9, 2.6), 7.30 (1 H, d, *J* = 8.1), 7.20 (1 H, d, *J* = 8.0), 6.95 (1 H, d, *J* = 8.9), 5.00 (1 H, s), 3.88 (2 H, s), 2.36 (2 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 167.38, 156.71, 146.59, 140.52, 139.12, 133.71, 132.72, 131.23, 131.19, 129.67, 129.58, 126.58, 125.07, 121.13, 114.40, 64.21, 52.51, 21.41ppm. EI-HRMS: Anal. Calcd for C_{20} H_{18} Cl NO_5: 387.0874, Found: 387.0873. Elemental analysis: Anal. Calcd for $C_{20}H_{18}ClNO_5$: C, 61.94; H, 4.68; Cl, 9.14; N, 3.61; O, 20.63 %. Found: C, 61.99; H, 4.61; Cl, 9.19; N, 3.52; O, 20.55 %.

6r: (*E*)-methyl 2-((4-bromo-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(4-chlorophenyl)acrylate: Isolated as yellow solid, 81 %, m.p: 133-135°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.06–7.96 (1 H, m), 7.69 (1 H, d, *J* = 13.7), 7.59 (1 H, d, *J* = 2.4), 7.52 (1 H, dd, *J* = 8.8, 2.4), 7.41–7.30 (2 H, m), 6.89 (1 H, d, *J* = 8.9), 4.95 (1 H, s), 3.89 (2 H, s) ppm. ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 166.93, 156.97, 145.06, 139.06, 136.21, 135.70, 134.02, 133.42, 132.45, 130.68, 129.24, 126.57, 121.60, 114.73, 113.95, 63.94, 52.68 ppm. EI-HRMS: Anal. Calcd for C_{19} H_{15} Br Cl NO_5: 450.9822, Found: 450.9820. Elemental analysis: Anal. Calcd for $C_{19}H_{15}BrClNO_5$: C, 50.41; H, 3.34; Br, 17.65; Cl, 7.83; N, 3.09; O, 17.67 %. Found: C, 50.35; H, 3.30; Br, 17.69; Cl, 7.88; N, 3.02; O, 17.61 %.

6s: (*E*)-methyl 2-((4-bromo-2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(4-methoxyphenyl)acrylate: Isolated as yellow solid, 81 %, m.p: 148-150°C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.05 (1 H, s), 7.99 (1 H, d, *J* = 13.7), 7.70 (1 H, d, *J* = 13.6), 7.57 (1 H, d, *J* = 2.4), 7.51 (1 H, dd, *J* = 8.8, 2.4), 7.38 (2 H, d, *J* = 8.7), 6.92 (3 H, dd, *J* = 16.2, 8.8), 5.02 (2 H, s), 3.87 (3 H, s), 3.82 (3 H, s) ppm. ^{13} C NMR: δ_C (100 MHz, $CDCl_3$) 167.55, 161.20, 157.22, 146.37, 139.08, 135.67, 134.12, 133.61, 131.64, 126.51, 123.41, 121.61, 114.81, 114.45, 113.66, 64.24, 55.40, 52.46 ppm. EI-HRMS: Anal. Calcd for C_{20} H_{18} Br NO_6: 447.0317, Found: 447.0315. Elemental analysis: Anal. Calcd for $C_{20}H_{18}BrNO_6$: C, 53.59; H, 4.05; Br, 17.83; N, 3.12; O, 21.42 %. Found: C, 53.51; H, 4.01; Br, 17.89; N, 3.05; O, 21.35 %.

6t:(*E*)-methyl-3-(2-chloro-phenyl)-2-((2-((E)-2-nitrovinyl)-phenoxy)-methyl)-acrylate: Isolated as yellow solid, 86 %, m.p: 125-128°C, ^{1}HNMR δ_H (400 MHz, $CDCl_3$) 8.16 (1 H, s), 8.08 (1 H, d, *J* = 13.6), 7.75 (1 H, d, *J* = 13.6), 7.49–7.36 (4 H, m), 7.32 (1 H, m), 7.26–7.20 (1 H, m), 7.04 (1 H, t, *J* = 7.6), 6.92 (1 H, d, *J* = 8.4),

4.92 (2 H, s), 3.92 (3 H, s) ppm. ^{13} C NMR: δ_C (100 MHz, $CDCl_3$) 166.72, 156.52, 142.71, 141.53, 135.12, 134.88, 133.33, 132.05, 131.78, 130.74, 130.09, 129.83, 128.89, 128.46, 128.00, 126.99, 125.12, 121.69, 113.84, 113.03, 63.88, 49.48 ppm. EI-HRMS: Anal. Calcd for C_{19} H_{16} Cl NO_5: 373.0717, Found: 373.0715. Elemental analysis: Anal. Calcd for $C_{19}H_{16}ClNO_5$: C, 61.05; H, 4.31; Cl, 9.48; N, 3.75; O, 21.40 %. Found: C, 61.0; H, 4.25; Cl, 9.42; N, 3.70; O, 21.33 %.

6u: (*E*)-methyl 2-((2-((E)-2-nitrovinyl)phenoxy)methyl)-3-(p-tolyl)acrylate: Isolated as yellow solid, 82 %, m.p: 118-120^{o}C, ^{1}HNMR (400 MHz, $CDCl_3$) δ_H 8.10 (1 H, d, *J* = 14.8), 7.77 (1 H, d, *J* = 13.6), 7.44 (1 H, dd, *J* = 18.4, 8.0), 7.32 (1 H, d, *J* = 7.8), 7.25 (1 H, t, *J* = 7.5), 7.18 (2 H, d, *J* = 7.4), 7.03 (1 H, dd, *J* = 17.7, 8.1), 5.02 (1 H, s), 3.88 (2 H, s), 2.35 (3 H, s) ppm. ^{13} NMR: δ_C (100 MHz, $CDCl_3$) 167.50, 158.34, 146.36, 140.36, 138.34, 135.27, 133.35, 132.32, 131.35, 129.64, 129.62, 129.05, 128.23, 125.41, 125.31, 121.57, 119.72, 112.99, 63.76, 52.46, 21.39 ppm. EI-HRMS: Anal. Calcd for C_{20} H_{19} NO_5: 353.1263, Found: 353.1260. Elemental analysis: Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96; O, 22.64 %. Found: C, 67.91; H, 5.48; N, 3.90; O, 22.60 %.

6v: (*E*)-3-(2-nitrovinyl) furan : Isolated as yellow solid, 75 %, m.p: 74-76^{o}C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 7.94 (1 H, d, *J* = 13.5), 7.84–7.83 (1 H, m), 7.52 (1 H, t, *J* = 1.3), 7.41 (1 H, s), 7.37 (1 H, s), 7.26 (1 H, s), 6.57 (1 H, d, *J* = 1.9). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 147.29, 145.37, 136.74, 129.53, 118.21, 107.25 ppm. EI-HRMS: Anal. Calcd for C_6 H_6 NO_3: 139.0269, Found: 139.0267. Elemental analysis: Anal. Calcd for $C_6H_6NO_3$: C, 51.80; H, 3.62; N, 10.07; O, 34.50 %. Found: C, 51.74; H, 3.67; N, 10.01; O, 34.45 %.

6w: (*E*)-3-(2-nitrovinyl) thiophene: Isolated as yellow solid, 89 %, m.p: 87-90^{o}C, ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 8.15 (1 H, d, *J* = 13.4), 7.57 (1 H, d, *J* = 4.9), 7.51–7.43 (2 H, m), 7.15 (1 H, dd, *J* = 5.1, 3.7). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 135.39, 134.62, 133.79, 132.09, 131.63, 128.90 ppm. EI-HRMS: Anal. Calcd for $C_6H_5NO_2S$: 155.0041, Found: 155.0040. Elemental analysis: Anal. Calcd for $C_6H_5NO_2S$: C, 46.44; H, 3.25; N, 9.03; O, 20.62; S, 20.66 %. Found: C, 46.40; H, 3.21; N, 9.09; O, 20.55; S, 20.60 %.

6x:(*E*)-tert-butyl-3-(2-nitro-vinyl)-1H-indole-1-carboxylate: Isolated as yellow solid, 89 %, ^{1}H NMR : δ_H (400 MHz, $CDCl_3$) 8.23 (1 H, d, *J* = 8.1), 8.17 (1 H, d, *J* = 13.7), 8.03 (1 H, s), 7.78 (1 H, d, *J* = 13.7), 7.71 (1 H, dd, *J* = 7.2, 0.8), 7.41 (2 H, dtd, *J* = 20.7, 7.4, 1.2), 1.70 (9 H, s) ppm. ^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 148.63, 136.40, 135.79, 132.19, 131.58, 126.85, 125.97, 124.26, 120.20, 115.93, 112.51, 85.58, 28.10 ppm. EI-HRMS: Anal. Calcd for C_{15} H_{16} N_2 O_4: 288.1110, Found: 288.1109. Elemental analysis: Anal. Calcd for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.59; N, 9.72; O, 22.20; %. Found: C, 62.42; H, 5.53; N, 9.79; O, 22.14; %.

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13 Crystal data for product **6t** (CCDC-:1051895, Figure 2): $C_{19}H_{16}ClNO_5$, crystallised in the monoclinic, space group P 2(1)/n with the following unit cell parameters a = 9.0038(2) A alpha = 90 deg., b = 13.6511(3) A beta = 102.1556(12) deg., c = 14.6295(4) A gamma = 90 deg:

14 **3u**:(***E***)**-methyl-2-((2-(1,1-di-cyano-3-nitro-propan-2-yl)-phenoxy)-methyl)-3-(p-tolyl)-acrylate:** Isolated as yellow gelly semi solid, 95 %, ^{1}H NMR (400 MHz, $CDCl_3$) 8.00 (1H, s), 7.36–7.22 (3H, m), 7.19 (3H, t, *J* = 8.0), 6.97 (1H, t, *J* = 7.5), 6.87 (1H, d, *J* = 8.3), 4.96 (1H, dd, *J* = 13.7, 9.0), 4.89 (2H, s), 4.78 (1H, dd, *J* = 13.7, 5.3), 4.61 (3H, s), 4.24 (1H, dd, *J* = 14.3, 8.7), 3.82 (3H, s), 2.32 (3H, s) ppm. ^{13} C NMR: δ_C (100 MHz, $CDCl_3$) 167.64, 155.71, 146.51, 140.76, 131.46, 131.10, 130.10, 129.91, 129.53, 125.09, 122.16, 120.47, 112.85, 111.18, 111.15, 74.24, 63.70, 52.60, 24.77, 21.44 ppm.

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16 See supporting information.

Abstract:

Synthesis of nitroolefins from aldehyde and olefin is generally limited by the formation of mixture of cis and trans compounds. Here we report an alternative, metal- free protocol for the synthesis of *β*-nitroolefins from arylidinemalanonitrile using bifunctional cinchona alkaloid along with di-*tert*-butyldicarbonate-DMAP in high yields with total selectivity