
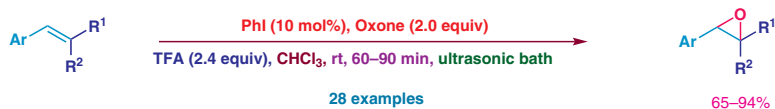


Hypervalent Iodine(III)-Catalyzed Epoxidation of β -Cyanostyrenes

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$R^1 = \text{CN, CO}_2\text{Et}; R^2 = \text{H, CN}; \text{Ar} = \text{Ph, 4-FC}_6\text{H}_4, 2\text{-ClC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 2,3\text{-(Cl)}_2\text{C}_6\text{H}_3, 3\text{-BrC}_6\text{H}_4, 4\text{-BrC}_6\text{H}_4, 4\text{-NCC}_6\text{H}_4, 3\text{-HOC}_6\text{H}_4, 4\text{-MeC}_6\text{H}_4, 3,4\text{-(MeO)}_2\text{C}_6\text{H}_3, 3,4,5\text{-(MeO)}_3\text{C}_6\text{H}_2, 2,3,4\text{-(MeO)}_3\text{C}_6\text{H}_2, 4\text{-(BnO)C}_6\text{H}_4, 3\text{-(HO)-4-(MeO)C}_6\text{H}_3, 1\text{-Naphthyl, 2-Naphthyl, 9-Anthryl}$

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Abstract A convenient approach for the synthesis of β -cyanoepoxides is illustrated by iodine(III)-catalyzed epoxidation of electron-deficient β -cyanostyrenes, wherein the active catalytic iodine(III) species was generated in situ. The epoxidation of β -cyanostyrenes was performed using 10 mol% PhI as precatalyst in the presence of 2.0 equivalents Oxone as an oxidant and 2.4 equivalents of TFA as an additive at room temperature under ultrasonic radiations. The β -cyanoepoxides were isolated in good to excellent yields in a short reaction time.

Key words epoxidation reaction, β -cyanostyrene, β -cyanoepoxide, iodobenzene, trifluoroacetic acid, Oxone

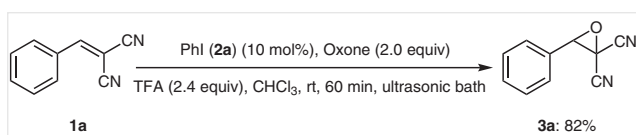
β -Cyanoepoxide systems are important architectures in synthetic and medicinal chemistry.¹ These scaffolds possess wide range of applications in organic transformations² such as 1,3-dipolar cycloadditions³ and regioselective nucleophilic addition reactions.^{2e,4} β -Cyanoepoxides are used as promising starting materials for the synthesis of various heterocyclic compounds which are enriched in numerous biological activities.⁵

In literature, different metal-based or organocatalytic approaches are published over the years for the synthesis of β -cyanoepoxides. The frequently used method for the synthesis of β -cyanoepoxides is the epoxidation of β -cyanostyrenes using different oxidizing agents. In 1981, Sekiya and co-workers were the first to report on the synthesis of β -cyanoepoxides through epoxidation of β -cyanostyrenes using molecular oxygen in the presence of a base, but this approach was associated with low yields.⁶ In 2003, Marechal's group developed the synthesis of β -cyanoepoxides in moderate yields by the epoxidation of β -cyanostyrenes using sodium hypochlorite as the source of oxygen.^{3d} Furthermore, Seeberger et al. developed a non-classical approach for the synthesis of functionalized β -cyanoepoxides featuring de-

aminative Mannich-type reaction of aliphatic amines with malononitrile using singlet oxygen produced in a continuous-flow photoreactor followed by the epoxidation with in situ generated peroxide species.⁷ Wang and co-workers developed a chemoenzymatic synthesis of β -cyanoepoxides through lipase-catalyzed Knoevenagel reaction of aromatic aldehydes with malononitrile followed by the epoxidation with urea-hydrogen peroxide (UHP) oxidant.⁸ In 2015, Lattanzi and co-workers employed organocatalyst cinchona-derived thiourea with cumyl hydroperoxide for the asymmetric epoxidation of β -cyanostyrenes to access enantioenriched β -cyanoepoxides under relatively mild reaction conditions.⁹ In 2018, Amrollahi and Mirhashemi reported the epoxidation of β -cyanostyrenes using catalytic amount of calcium hypochlorite for the synthesis of β -cyanoepoxides.¹⁰ However, the literature reported methods are associated with various drawbacks such as use of an expensive metal reagent, ligands, harsh reaction conditions, limited substrate scope, prolonged reaction time, and poor yields. Hence, there is still scope to develop a simple, clean, and efficient route for the synthesis of β -cyanoepoxides.

In the past two decades, the hypervalent iodine reagents have acquired wide attention in the field of synthetic organic chemistry due to their environmentally friendly nature, low toxicity, and simple handling.¹¹ These reagents act as a key replacement over toxic metal reagents because of their mild reaction condition and electrophilic nature.¹² Various iodine(III) reagents have been successfully used to achieve different organic transformations along with the epoxidation reactions.¹³ Recently, our research group reported an efficient metal-free approach for the epoxidation of β -cyanostyrenes to β -cyanoepoxides using iodine(III) reagents.¹⁴ In the current decade, various organic transformations have been successfully achieved using in situ generated hypervalent iodine reagents as active catalytic species.¹⁵

Herein, we describe a catalytic approach for the epoxidation of β -cyanostyrenes **1** using PhI (**2a**) as precatalyst in association with Oxone as terminal oxidant and trifluoroacetic acid (TFA) as an additive. The parent precursors **1** were prepared by Knoevenagel condensation of aromatic aldehydes with malonitrile or ethyl cyanoacetate in pyridine at 95 °C.^{16,17} The epoxidation of β -cyanostyrene **1a** was executed in CHCl₃ using 10 mol% of iodobenzene (**2a**) in the presence of 2.0 equivalents of Oxone and 2.4 equivalents of TFA at room temperature in ultrasonic bath. The epoxidation product was characterized as β -cyanoepoxide **3a** and obtained in 82% yield (Scheme 1).

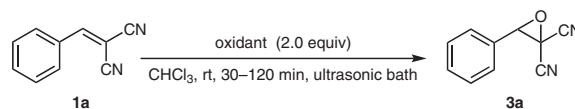


Scheme 1 Epoxidation of β -cyanostyrene **1a** using PhI (**2a**) as precatalyst

In the beginning, our efforts were emphasized to get the best reaction condition for the epoxidation of alkenes **1**, and β -cyanostyrene **1a** was selected as a model substrate. Herein, the oxidant plays a crucial role for in situ regeneration of catalytic iodine(III) active species by the oxidation of iodobenzene. Many of these commonly used oxidants have found to generate epoxide without the presence of any catalyst or additive. Hence selecting a suitable oxidant is important, as the oxidant should not react with the substrate or product. The progress of epoxidation reaction was examined with different oxidizing agent wherein both organic and inorganic oxidants were used. Initially, the epoxidation reaction was performed with *m*-chloroperbenzoic acid (*m*-CPBA) and the epoxide product **3a** was obtained in 65% yield (Table 1, entry 1). Epoxide product **3a** was obtained in 50% yield with the more common oxidant sodium perborate tetrahydrate (entry 2). Furthermore, the similar reaction was performed with Oxone wherein no product formation was observed (entry 3). Similarly, the reaction with sodium *meta*-periodate (NaIO₄) and potassium bromate (KBrO₃) resulted in no formation of product (entries 4 and 5). In addition, the use of hydrogen peroxide and peracetic acid led to no β -cyanoepoxide **3a** product but formation of few impurities was observed (entries 6 and 7). The same reaction using trifluoroacetic acid and Oxone led to no formation of product (entry 8). Additionally, the course of reaction was found unchanged when the Oxone was replaced with H₂O₂ (entry 9).

After observing that a series of oxidants (Table 1, entries 3–7) do not react with the substrate, it was decided to use them to reproduce the active catalytic iodine(III) species. Next, our efforts were directed towards the selection of

Table 1 Optimization of Oxidant-Based Epoxidation of β -Cyanostyrene **1a**

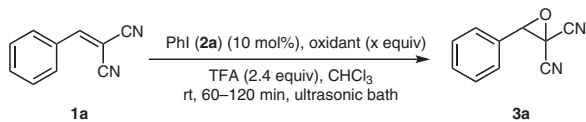


Entry	Oxidant	Time (min)	Yield (%)
1	<i>m</i> -CPBA	50	65
2	NaBO ₃ ·4H ₂ O	90	50
3	Oxone	120	–
4	NaIO ₄	120	–
5	KBrO ₃	120	–
6	H ₂ O ₂	120	–
7	Peracetic acid	120	–
8 ^a	Oxone + TFA	120	–
9 ^b	H ₂ O ₂ + TFA	120	–

^a Reaction conditions: Oxone (2.0 equiv), TFA (2.4 equiv).

^b Reaction conditions: H₂O₂ (2.0 equiv), TFA (2.4 equiv).

most suitable oxidant for the regeneration of iodine(III) active species to achieve the epoxidation of β -cyanostyrenes **1** to β -cyanoepoxides **3** successfully. In order to achieve the perfect oxidant, the epoxidation reaction of β -cyanostyrene **1a** was investigated with the above selected oxidants (Table 1, entries 3–7). Initially, inorganic oxidants Oxone, NaIO₄, and KBrO₃ were used for the iodine(III)-catalyzed epoxidation of β -cyanostyrene **1a** and the epoxide product **3a** was obtained in 82%, 70% and 68% yield, respectively (Table 2, entries 1–3). The desired product **3a** was isolated in 60% and 46% yield with hydrogen peroxide and peracetic acid, respectively (entries 4 and 5). Finally, the reaction was carried out using peracetic acid as oxidant without using any additive and the epoxide product **3a** was obtained in 35% yield (entry 6). Additionally, the stoichiometry of Oxone required for the efficient conversion of β -cyanostyrene to β -cyanoepoxide was also studied. An initial oxidant study demonstrated that using 2.0 and 2.4 equivalents of Oxone resulted in full conversion and the epoxide product **3a** was isolated in 82% yield in both the cases (entries 1 and 7). Furthermore, the epoxidation reaction was executed with 1.8 equivalents of Oxone and the epoxidation product **3a** was isolated in 70% yield along with unreacted starting material (entry 8). Finally, the epoxidation reaction was performed with stoichiometric amount of PhI (1.0 equiv) with Oxone (2.0 equiv) in CHCl₃ without using any additive, but the desired product **3a** did not form and all unreacted starting was recovered (entry 9).

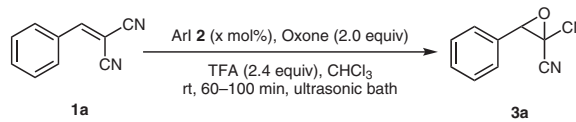
Table 2 Optimization of Oxidant for Iodine(III)-Catalyzed Epoxidation of β -Cyanostyrene **1a**^a

Entry	Oxidant (equiv)	Additive	Time (min)	Yield (%)
1	Oxone (2.0)	TFA	60	82
2	NaIO ₄ (2.0)	TFA	60	70
3	KBrO ₃ (2.0)	TFA	60	68
4	H ₂ O ₂ (2.0)	TFA	120	60
5	Peracetic acid (2.0)	TFA	120	46
6	Peracetic acid (2.0)	–	120	35
7	Oxone (2.4)	TFA	60	82
8	Oxone (1.8)	TFA	120	70
9 ^a	Oxone (2.0)	–	120	–

^a Reaction condition: PhI (1.0 equiv).

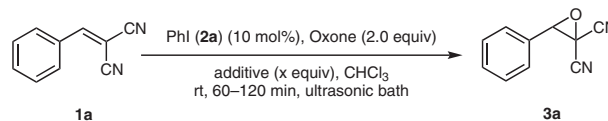
In addition, the screening of iodoarene-based precatalyst was carried out and the results are summarized in Table 3. The epoxidation product **3a** was obtained in 82% yield when 10 mol% of iodobenzene (**2a**) was used as precatalyst (Table 3, entry 1). The course of the reaction was quite similar with precatalyst 4-iodotoluene (**2b**) and the reaction product **3a** was isolated in 77% yield (entry 2). The epoxidation reaction could not work well with precatalyst 4-iodoanisole (**2c**) and the reaction product **3a** was observed in 55% yield only (entry 3). The complete conversion of starting material was observed but reaction was associated with the formation of some side products. More active precatalyst, iodopentafluorobenzene (**2d**) was also tested and the desired product **3a** was obtained in 85% yield (entry 4). The epoxide product **3a** was obtained in slightly higher yield with C₆F₅I (**2d**) compare to PhI (**2a**) but the latter one was preferred as precatalyst in further catalytic reactions as it is quite cheaper compared to iodopentafluorobenzene (**2d**). Further, the amount of precatalyst **2a** was also screened (entries 1, 5, and 6). The epoxidation of compound (**1a**) was examined with 5 mol% of precatalyst **2a** and the product **3a** was isolated in 67% yield (entry 5). The reaction product **3a** was obtained in 84% yield when reaction was performed with 12 mol% of iodobenzene (**2a**) (entry 6).

After that, our aim was to find an appropriate additive. Initially, epoxidation of β -cyanostyrene **1a** was performed in chloroform with 10 mol% of iodobenzene (**2a**) as precatalyst and Oxone as an oxidant, but epoxidation reaction could not proceed (Table 4, entry 1). After that, the same reaction was attempted under similar reaction conditions but 2.4 equivalents of acetic acid was used as an additive. Although complete conversion was not observed, the desired product **3a** was obtained in 65% yield along with unreacted

Table 3 Optimization of Iodoarene-Based Precatalyst **2** for the Epoxidation of β -Cyanostyrene **1a**

Entry	Precatalyst (mol%)	Time (min)	Yield (%)
1	PhI (2a) (10)	60	82
2	4-MeC ₆ H ₄ I (2b) (10)	60	77
3	4-MeOC ₆ H ₄ I (2c) (10)	60	55
4	C ₆ F ₅ I (2d) (10)	60	85
5	PhI (2a) (5)	100	67
6	PhI (2a) (12)	60	84

starting material (entry 2). The epoxidation product **3a** was obtained in 82% yield when the additive acetic acid was replaced with TFA (entry 3). In addition, *p*-toluenesulfonic acid and trifluoromethanesulfonic acid were also used as additive but the catalytic reaction did not proceed and only unreacted starting material was observed (entries 4 and 5). In continuation, the amount of additive were also screened (entries 3, 6, and 7). The epoxidation of substrate **1a** was examined with 2.0 equivalents of TFA that led to incomplete conversion of starting substrate and the product **3a** was isolated in 67% yield (entry 6). The reaction product **3a** was gained in 83% yield when epoxidation of **1a** was performed with 2.8 equivalents of TFA (entry 7).

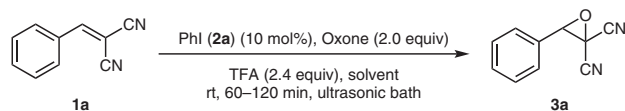
Table 4 Optimization of Additive for the Epoxidation of β -Cyanostyrene **1a**

Entry	Additive (equiv)	Time (min)	Yield (%)
1	–	120	–
2	AcOH (2.4)	120	65
3	TFA (2.4)	60	82
4	<i>p</i> -TSA (2.4)	120	–
5	CF ₃ SO ₃ H (2.4)	120	–
6	TFA (2.0)	120	67
7	TFA (2.8)	60	83

Furthermore, various polar and non-polar solvents were investigated in the epoxidation of β -cyanostyrene **1a** to β -cyanoepoxide **3a** (Table 5). Initially, the epoxidation reaction was executed in chloroform and the epoxide **3a** was obtained in 82% yield (Table 5, entry 1). The course of the

reaction was quite similar in acetonitrile and the desired product **3a** was obtained in 72% yield (entry 2). The epoxidation reaction proceeded well in THF and dichloromethane and the product **3a** was obtained in 70% and 68% yield, respectively (entries 3 and 4). The course of epoxidation reaction was also screened in polar and protic solvent such as methanol and 2,2,2-trifluoroethanol (TFE), and the reaction product **3a** was isolated in 56% and 70% yield, respectively (entries 5 and 6). Unlikely, the above reaction in polar solvents did not proceed in more polar solvents such as DMF and DMSO (entries 7 and 8). After that, the epoxidation of substrate **1a** was carried out in chloroform/water solvent combination; there was no product formation observed with all starting materials remaining unreacted (entry 9). During the reactions in the ultrasonic bath, the reaction temperature was maintained using a thermostat (at 27 °C), but the temperature was increased by 8.0 °C after the completion of reaction (60 min).

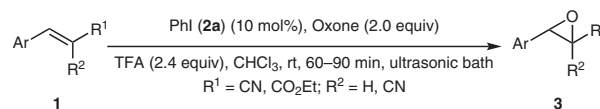
Table 5 Screening of Solvent for the Epoxidation of β -Cyanostyrene **1a**



Entry	Solvent	Time (min)	Yield (%)
1	CHCl ₃	60	82
2	MeCN	60	72
3	THF	60	70
4	CH ₂ Cl ₂	60	68
5	MeOH	120	56
6	TFE	120	70
7	DMF	120	–
8	DMSO	120	–
9	CHCl ₃ /H ₂ O (3:1)	120	–

After establishing optimal reaction conditions, a set of β -cyanostyrenes **1** were favorably oxidized to β -cyanoepoxides **3** in 65–94% yields (Table 6, entries 1–28). The epoxidation reaction proceeded smoothly with substrates having both electron-donating and -withdrawing moiety on the aromatic ring of β -cyanostyrenes **1**. It was observed that epoxides **3** were obtained in lower yield when electron-withdrawing group-bearing aromatic substituents were used as substrates (entries 2–7 and 14–20). Additionally, the epoxidation of more hindered substrates **1k**, **1l**, and **1a** resulted in the corresponding epoxides **3k**, **3l**, and **3a** in lower yields (entries 11, 12, and 27). Additionally, the reaction was identified to be applicable for substrate **1ab** possessing an ester group adjacent to double bond leading to epoxide **3ab**. All the synthesized compounds were characterized by spectroscopic analysis.

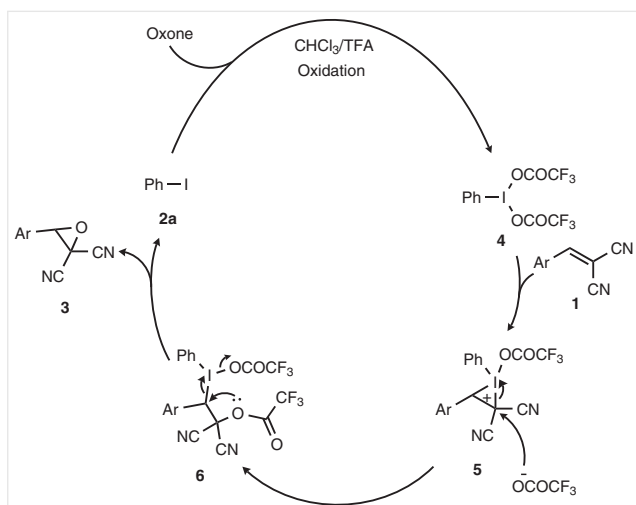
Table 6 The Extent of Epoxidation Reaction with Various β -Cyanostyrenes **1** to β -Cyanoepoxides **3** Using PhI (**2a**) as Precatalyst



Entry	Ar	R ¹	R ²	Time (min)	Yield (%)
1	Ph	CN	CN	60	82
2	4-FC ₆ H ₄	CN	CN	70	72
3	2-ClC ₆ H ₄	CN	CN	80	65
4	4-ClC ₆ H ₄	CN	CN	70	75
5	2,3-Cl ₂ C ₆ H ₃	CN	CN	90	70
6	3-BrC ₆ H ₄	CN	CN	80	77
7	4-BrC ₆ H ₄	CN	CN	80	78
8	4-MeC ₆ H ₄	CN	CN	60	80
9	3,4-(MeO) ₂ C ₆ H ₃	CN	CN	60	90
10	3,4,5-(MeO) ₃ C ₆ H ₂	CN	CN	60	92
11	2-Naphthyl	CN	CN	60	80
12	9-Anthryl	CN	CN	70	77
13	Ph	CO ₂ Et	CN	80	83
14	4-FC ₆ H ₄	CO ₂ Et	CN	90	75
15	2-ClC ₆ H ₄	CO ₂ Et	CN	90	66
16	4-ClC ₆ H ₄	CO ₂ Et	CN	80	77
17	3-BrC ₆ H ₄	CO ₂ Et	CN	80	79
18	4-BrC ₆ H ₄	CO ₂ Et	CN	80	80
19	4-NCC ₆ H ₄	CO ₂ Et	CN	90	72
20	3-HOC ₆ H ₄	CO ₂ Et	CN	80	74
21	4-MeC ₆ H ₄	CO ₂ Et	CN	60	84
22	3,4-(MeO) ₂ C ₆ H ₃	CO ₂ Et	CN	60	91
23	2,3,4-(MeO) ₃ C ₆ H ₂	CO ₂ Et	CN	60	93
24	3,4,5-(MeO) ₃ C ₆ H ₂	CO ₂ Et	CN	60	94
25	4-(BnO)C ₆ H ₄	CO ₂ Et	CN	60	90
26	3-(HO),4-(MeO)C ₆ H ₃	CO ₂ Et	CN	70	88
27	1-Naphthyl	CO ₂ Et	CN	60	77
28	Ph	CO ₂ Et	H	60	92

A proposed catalytic cycle for the epoxidation of β -cyanostyrenes **1** to β -cyanoepoxides **3** is illustrated in Scheme 2. The catalytic reaction begins with the in situ formation of active iodine(III) species **4** by oxidation of iodobenzene (**2a**) with Oxone. Furthermore, the iodine(III) species **4** activates the double bond of alkene **1** and form a three-membered iodonium intermediate **5**. The intermediate **5** then undergoes nucleophilic attack by trifluoroacetoxy anion, which leads to ring opening to form intermediate **6**. Moreover, the intermediate **6** undergoes intramolecular cyclization to accomplish β -cyanoepoxide **3** with the formation of iodobenzene (**2a**). Furthermore, the iodobenzene (**2a**) reoxidizes to active iodine(III) species **4** to continue the catalytic cycle.

Finally, the epoxidation of β -cyanostyrene **1a** was performed with $\text{PhI}(\text{OCOCF}_3)_2$ (2.0 equiv) in CHCl_3 , which resulted in the formation of β -cyanoepoxide **3a** in 83% yield. Notably, the reaction was found quite faster compared to in situ generated active catalytic iodine(III) species. This result support that the formation of iodine(III) intermediate **4** as active catalytic species during the formation of epoxides **3**.



Scheme 2 Proposed catalytic cycle for iodine(III)-catalyzed epoxidation of β -cyanostyrenes **1** to β -cyanoepoxides **3**

In conclusion, we have developed an iodine(III)-catalyzed synthesis of β -cyanoepoxides **3** in good to excellent yields by the epoxidation of β -cyanostyrenes **1** wherein iodine(III) active catalytic species was generated in situ by the oxidation of iodobenzene (**2a**) in the presence of Oxone as oxidant and trifluoroacetic acid as additive. Our method for the synthesis of β -cyanoepoxide **3** is very easy, efficient, and metal-free. Further investigations about this catalytic route are currently in progress.

Melting points were recorded with the melting point apparatus REMI DDMS 2545. IR spectra were recorded on Thermo Scientific Nicolet Nexus 470FT-IR spectrometer and band positions are reported in reciprocal centimeters. Samples were made as pellet with KBr and recorded. CHN data were recorded in Elementar VarioMICRO Select 15162036 Analyzer. ^1H NMR and ^{13}C NMR spectra were recorded on AV-400 Bruker using the solvents indicated with 400 and 100 MHz respectively. Mass spectra (m/z) were recorded under the conditions of electron ionization (EI). The reactions were carried out in 2.5 L ultrasonic bath (Model: CUB 2.5L, Citizon, India) with power dissipation as 50 W and frequency of 40 kHz was used for the synthesis. All the reactions were monitored by TLC that was performed on pre-coated sheets of silica gel 60 and column chromatography was performed with silica gel 60 (Avra synthesis Pvt. Ltd., 100–200 mesh). Hexane and EtOAc were used as eluting solvents and were bought from Avra Synthesis Pvt. Ltd. MeCN, THF, CH_2Cl_2 , DMF, DMSO, 1,4-dioxane, Et_2O , and MeOH of HPLC grade were used and dried with molecular sieves (4Å). All other purchased chemicals were used without further purification.

β -Cyanostyrenes **1**; General Procedure

β -Cyanostyrenes were prepared according to the reported procedure.¹⁸

A mixture of aromatic aldehyde (10.0 mmol), malononitrile or ethyl cyanoacetate (11.0 equiv), and pyridine (0.805 mL, 10.0 mmol) was heated at reflux temperature (95 °C) for 6–8 h. The progress of the reaction was monitored by TLC. After the completion of reaction, H_2O (10 mL) was added to the reaction mixture and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried (anhyd Na_2SO_4) and the solvent was evaporated under vacuum. Finally, the crude residue was purified by column chromatography using hexane as eluent and characterized as β -cyanostyrene **1**.

2-(Phenylmethylene)propanedinitrile (**1a**)^{19–21}

White solid; yield: 1.34 g (8.69 mmol, 87%); mp 81–83 °C (Lit.¹⁴ mp 82–84 °C); $R_f = 0.4$ (EtOAc–hexane 1:49).

IR (KBr): 676, 753, 775, 957, 969, 999, 1100, 1149, 1163, 1297, 1316, 1334, 1372, 1449, 1566, 1588, 1735, 2222, 2925 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 7.43$ (t, $J = 7.6$ Hz, 2 H, ArH), 7.52 (tt, $J_1 = 1.2$ Hz, $J_2 = 7.6$ Hz, 1 H, ArH), 7.67 (s, 1 H, CH), 7.79 (d, $J = 7.6$ Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 82.8, 112.5, 113.6, 129.6, 130.7, 130.9, 134.6, 159.9$.

Anal. Calcd for $\text{C}_{10}\text{H}_6\text{N}_2$: C, 77.91; H, 3.92; N, 18.17. Found: C, 77.68; H, 3.93; N, 18.02.

2-[(4-Fluorophenyl)methylene]propanedinitrile (**1b**)¹⁹

White solid; yield: 1.46 g (8.48 mmol, 85%); mp 125–127 °C (Lit.¹⁹ mp 124–126 °C); $R_f = 0.4$ (EtOAc–hexane 1:49).

IR (KBr): 837, 937, 1170, 1217, 1302, 1365, 1417, 1509, 1573, 1594, 1737, 2230 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 7.12$ (dt, $J_1 = 2.0$ Hz, $J_2 = 8.4$ Hz, 2 H, ArH), 7.64 (s, 1 H, CH), 7.82–7.87 (m, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 82.3$ (d, $J = 2.0$ Hz), 112.4, 113.5, 117.1 (d, $J = 22.0$ Hz), 127.3 (d, $J = 3.0$ Hz), 133.3 (d, $J = 9.0$ Hz), 158.3, 165.8 (d, $J = 258.0$ Hz).

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{FN}_2$: C, 69.77; H, 2.67; N, 16.27. Found: C, 69.70; H, 2.62; N, 15.99.

2-[(2-Chlorophenyl)methylene]propanedinitrile (**1c**)²²

White solid; yield: 1.58 g (8.37 mmol, 84%); mp 94–96 °C (Lit.²² mp 97–98 °C); $R_f = 0.4$ (EtOAc–hexane 1:49).

IR (KBr): 698, 756, 960, 1038, 1050, 1131, 1215, 1371, 1439, 1463, 1585, 2224, 2231, 3049 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 7.31$ –7.36 (m, 1 H, ArH), 7.43–7.45 (m, 2 H, ArH), 8.06 (d, $J = 7.6$ Hz, 1 H, ArH), 8.16 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 85.7, 111.8, 113.1, 127.8, 129.0, 129.4, 130.6, 135.0, 136.4, 156.0$.

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{ClN}_2$: C, 63.68; H, 2.67; N, 14.85. Found: C, 63.70; H, 2.67; N, 14.80.

2-[(4-Chlorophenyl)methylene]propanedinitrile (**1d**)^{19,20,23}

White solid; yield: 1.57 g (8.12 mmol, 81%); mp 161–163 °C (Lit.¹⁴ mp 164–166 °C); $R_f = 0.4$ (EtOAc–hexane 1:49).

IR (KBr): 760, 794, 849, 935, 1008, 1015, 1216, 1365, 1412, 1492, 1584, 1677, 1738, 2226 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.45 (d, J = 8.8 Hz, 2 H, ArH), 7.66 (s, 1 H, CH), 7.78 (d, J = 8.8 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 83.4, 111.8, 113.6, 129.6, 131.9, 135.1, 141.1, 158.8.

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{ClN}_2$: C, 63.68; H, 2.82; N, 14.85. Found: C, 63.61; H, 2.67; N, 14.84.

2-[(2,3-Dichlorophenyl)methylene]propanedinitrile (1e)²⁴

White solid; yield: 1.71 g (7.66 mmol, 77%); mp 160–162 °C (Lit.¹⁴ mp 159–161 °C); R_f = 0.2 (EtOAc–hexane 1:49).

IR (KBr): 765, 784, 850, 930, 1020, 1220, 1370, 1420, 1510, 1590, 1670, 1740, 2230 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.23 (t, J = 8.0 Hz, 1 H, ArH), 7.52 (d, J = 8.0 Hz, 1 H, ArH), 7.83 (d, J = 8.0 Hz, 1 H, ArH), 8.08 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 87.3, 111.4, 112.7, 127.8, 131.0, 133.9, 134.8, 135.1, 156.0.

Anal. Calcd for $\text{C}_{10}\text{H}_4\text{Cl}_2\text{N}_2$: C, 53.85; H, 1.81; N, 12.56. Found: C, 53.81; H, 1.83; N, 12.49.

2-[(3-Bromophenyl)methylene]propanedinitrile (1f)²⁵

White solid; yield: 1.86 g (8.03 mmol, 80%); mp 110–112 °C (Lit.²⁵ mp 109–111 °C); R_f = 0.5 (EtOAc–hexane 1:49).

IR (KBr): 706, 815, 840, 937, 1070, 1077, 1214, 1359, 1410, 1488, 1583, 1741, 2225 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.31 (t, J = 8.0 Hz, 1 H, ArH), 7.60 (s, 1 H, ArH), 7.63 (d, J = 8.0 Hz, 1 H, ArH), 7.78 (d, J = 8.0 Hz, 1 H, ArH), 7.85 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 84.6, 111.9, 113.1, 123.6, 128.6, 131.1, 132.5, 137.2, 158.1.

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{BrN}_2$: C, 51.53; H, 2.16; N, 12.02. Found: C, 51.54; H, 2.10; N, 11.99.

2-[(4-Bromophenyl)methylene]propanedinitrile (1g)^{19,20}

White solid; yield: 1.91 g (8.14 mmol, 81%); mp 162–163 °C (Lit.¹⁹ mp 164–166 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 720, 859, 879, 941, 1030, 1092, 1242, 1290, 1370, 1408, 1470, 1577, 1737, 2226 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.56 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH), 7.60 (s, 1 H, CH), 7.65 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 83.4, 112.3, 113.4, 129.6, 129.9, 131.7, 133.1, 158.4.

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{BrN}_2$: C, 51.53; H, 2.16; N, 12.02. Found: C, 51.54; H, 2.10; N, 11.98.

2-[(4-Methylphenyl)methylene]propanedinitrile (1h)^{22,23}

Light yellow solid; yield: 1.41 g (8.38 mmol, 84%); mp 135–137 °C (Lit.²² mp 133–135 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 791, 812, 959, 1037, 1191, 1217, 1412, 1449, 1509, 1586, 1605, 1737, 2222 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 2.35 (s, 3 H, ArH), 7.22 (d, J = 8.4 Hz, 2 H, ArH), 7.61 (s, 1 H, CH), 7.70 (d, J = 8.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 21.9, 81.2, 112.8, 113.8, 128.5, 130.3, 130.9, 146.3, 159.7.

Anal. Calcd for $\text{C}_{11}\text{H}_8\text{N}_2$: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.26; H, 4.80; N, 16.60.

2-[(3,4-Dimethoxyphenyl)methylene]propanedinitrile (1i)

Yellow solid; yield: 1.75 g (8.24 mmol, 82%); mp 146–148 °C; R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 820, 849, 1015, 1142, 1204, 1216, 1263, 1365, 1422, 1443, 1468, 1505, 1512, 1564, 1727, 2221 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 3.82 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.84 (d, J = 8.4 Hz, 1 H, ArH), 7.27 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1 H, ArH), 7.53 (s, 1 H, CH), 7.56 (ds, J = 2.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 56.0, 56.2, 78.4, 110.8, 111.1, 113.5, 114.3, 124.2, 128.1, 149.5, 154.8, 159.1.

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.11; H, 4.69; N, 12.98.

2-[(3,4,5-Trimethoxyphenyl)methylene]propanedinitrile (1j)^{20,23}

Yellow solid; yield: 1.97 g (8.09 mmol, 81%); mp 143–145 °C (Lit.²³ mp 144–146 °C); R_f = 0.2 (EtOAc–hexane 1:49).

IR (KBr): 697, 750, 842, 938, 988, 1000, 1127, 1167, 1179, 1191, 1419, 1447, 1466, 1568, 1582, 1737, 2218 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 3.79 (s, 6 H, 2 × OCH_3), 3.87 (s, 3 H, OCH_3), 7.08 (s, 2 H, ArH), 7.55 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 56.4, 61.2, 80.6, 108.3, 113.2, 113.3, 125.9, 144.0, 153.3, 159.4.

Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$: C, 63.93; H, 4.95; N, 4.95. Found: C, 63.60; H, 4.94; N, 11.44.

2-(2-Naphthalenylmethylene)propanedinitrile (1k)^{21,26}

Yellow solid; yield: 1.69 g (8.31 mmol, 83%); mp 140–142 °C (Lit.²⁶ mp 142–144 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 730, 749, 763, 857, 882, 913, 937, 969, 1204, 1216, 1244, 1351, 1371, 1508, 1565, 1588, 1737, 2226 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.52–7.64 (m, 3 H, ArH), 7.87 (d, J = 8.8 Hz, 2 H, ArH), 8.02 (d, J = 8.8 Hz, 1 H, ArH), 8.20 (d, J = 8.8 Hz, 1 H, ArH), 8.58 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 85.1, 112.5, 113.8, 122.3, 125.4, 127.3, 127.5, 128.5, 128.6, 129.5, 131.1, 133.5, 134.9, 157.8.

Anal. Calcd for $\text{C}_{14}\text{H}_8\text{N}_2$: C, 82.33; H, 3.95; N, 13.72. Found: C, 81.78; H, 3.95; N, 13.71.

2-(9-Anthracenylmethylene)propanedinitrile (1l)²⁰

Orange solid; yield: 2.03 g (8.01 mmol, 80%); mp 204–206 °C (Lit.¹⁴ mp 205–206 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 717, 734, 896, 946, 1164, 1258, 1365, 1446, 1551, 1575, 2229 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.45 (dt, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 2 H, ArH), 7.55 (dt, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 2 H, ArH), 7.79 (dd, J_1 = 0.8 Hz, J_2 = 8.4 Hz, 2 H, ArH), 7.96 (d, J = 8.4 Hz, 2 H, ArH), 8.51 (s, 1 H, ArH), 8.80 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 92.3, 111.3, 112.9, 123.3, 123.8, 126.0, 128.3, 129.0, 129.5, 130.9, 132.4, 160.5.

Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{N}_2$: C, 85.02; H, 3.96; N, 11.02. Found: C, 84.70; H, 3.98; N, 11.03.

Ethyl (E)-2-Cyano-3-phenylacrylate (1m)²⁷

White solid; yield: 2.19 g (8.78 mmol, 88%); mp 49–51 °C (Lit.²¹ mp 50–52 °C); R_f = 0.5 (EtOAc–hexane 1:49).

IR (KBr): 763, 969, 995, 1103, 1149, 1160, 1292, 1324, 1366, 1430, 1583, 1733, 2221, 3025 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.31 (t, J = 6.8 Hz, 3 H, CH_3), 4.30 (q, J = 7.2 Hz, 2 H, CH_2), 7.33–7.52 (m, 3 H, ArH), 7.90 (d, J = 8.4 Hz, 2 H, ArH), 8.16 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.2, 62.8, 103.0, 115.5, 129.3, 131.1, 131.5, 133.3, 155.0, 162.5.

Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.33; H, 5.48; N, 6.92.

Ethyl (E)-2-Cyano-3-(4-fluorophenyl)acrylate (1n)²⁸

White solid; yield: 1.66 g (7.64 mmol, 76%); mp 96–97 °C (Lit.²⁸ mp 94–96 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 735, 835, 895, 1012, 1088, 1162, 1201, 1267, 1369, 1492, 1509, 1589, 1610, 1722, 1753, 2225, 2383, 2989, 3072 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.26–1.31 (m, 3 H, CH_3), 4.24–4.28 (m, 2 H, CH_2), 7.06–7.11 (m, 2 H, ArH), 7.91 (d, J = 8.4 Hz, 2 H, ArH), 8.09 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 62.7, 102.5, 115.4, 116.6 (d, J = 21.9 Hz), 127.8 (d, J = 3.0 Hz), 133.6 (d, J = 9.1 Hz), 153.3, 162.2, 166.6.

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{FNO}_2$: C, 65.75; H, 4.60; N, 6.39. Found: C, 65.73; H, 4.68; N, 6.35.

Ethyl (E)-3-(2-Chlorophenyl)-2-cyanoacrylate (1o)²⁹

White solid; yield: 1.80 g (7.68 mmol, 77%); mp 54–56 °C (Lit.²⁹ mp 56–57 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 789, 826, 1020, 1076, 1100, 1202, 1282, 1310, 1370, 1414, 1452, 1481, 1510, 1567, 1620, 1730, 1761, 2220, 2410, 2900 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.28 (t, J = 7.2 Hz, 3 H, CH_3), 4.28 (q, J = 7.2 Hz, 2 H, CH_2), 7.23–7.29 (m, 1 H, ArH), 7.30–7.38 (m, 2 H, ArH), 8.09 (d, J = 7.6 Hz, 1 H, ArH), 8.53 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 62.9, 114.7, 127.5, 129.7, 129.8, 130.3, 133.7, 136.3, 150.8, 161.7.

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{ClNO}_2$: C, 61.16; H, 4.28; N, 5.94. Found: C, 61.20; H, 4.29; N, 5.90.

Ethyl (E)-3-(4-Chlorophenyl)-2-cyanoacrylate (1p)^{27,29,30}

White crystalline solid; yield: 1.92 g (8.21 mmol, 82%); mp 49–51 °C (Lit.³⁰ mp 50–52 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 797, 831, 1010, 1019, 1077, 1093, 1198, 1286, 1309, 1364, 1410, 1445, 1478, 1490, 1613, 1650, 1721, 1754, 2223, 2957, 2989, 3036 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.32 (t, J = 7.2 Hz, 3 H, CH_3), 4.31 (q, J = 7.2 Hz, 2 H, CH_2), 7.39 (d, J = 8.8 Hz, 2 H, ArH), 7.85 (d, J = 8.4 Hz, 2 H, ArH), 8.11 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 62.9, 103.5, 115.3, 129.7 (2 C), 129.9, 132.2 (2 C), 139.6, 153.4, 162.2.

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{ClNO}_2$: C, 61.16; H, 4.28; N, 5.94. Found: C, 61.12; H, 4.30; N, 5.99.

Ethyl (E)-3-(3-Bromophenyl)-2-cyanoacrylate (1q)

White solid; yield: 2.23 g (8.02 mmol, 80%); mp 90–92 °C; R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 680, 693, 772, 789, 895, 967, 1019, 1075, 1096, 1161, 1199, 1261, 1371, 1476, 1552, 1571, 1605, 1780, 2223, 2988 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.30 (t, J = 7.2 Hz, 3 H, CH_3), 4.29 (q, J = 7.2 Hz, 2 H, CH_2), 7.28 (t, J = 8.0 Hz, 1 H, ArH), 7.56 (dd, J_1 = 0.8 Hz, J_2 = 7.2 Hz, 1 H, ArH), 7.87 (d, J = 8.0 Hz, 1 H, ArH), 7.92 (s, 1 H, ArH), 8.06 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.2, 62.9, 104.6, 114.9, 123.2, 128.9, 130.8, 133.3, 133.8, 135.9, 153.0, 161.9.

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{BrNO}_2$: C, 51.45; H, 3.60; N, 5.00. Found: C, 51.42; H, 3.62; N, 5.02.

Ethyl (E)-3-(4-Bromophenyl)-2-cyanoacrylate (1r)²⁹

White solid; yield: 2.31 g (8.34 mmol, 83%); mp 92–94 °C (Lit.²⁹ mp 90–92 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 693, 791, 896, 968, 1007, 1019, 1095, 1160, 1200, 1262, 1370, 1392, 1444, 1476, 1553, 1571, 1607, 1780, 2223, 2988 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.32 (t, J = 7.2 Hz, 3 H, CH_3), 4.31 (q, J = 6.8 Hz, 2 H, CH_2), 7.56 (d, J = 8.4 Hz, 2 H, ArH), 7.77 (d, J = 8.8 Hz, 2 H, ArH), 8.09 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.2, 62.9, 103.7, 115.2, 128.2, 130.3, 132.2 (2 C), 132.7 (2 C), 153.5, 162.2.

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{BrNO}_2$: C, 51.45; H, 3.60; N, 5.00. Found: C, 51.47; H, 3.62; N, 5.02.

Ethyl (E)-2-Cyano-3-(4-cyanophenyl)acrylate (1s)²⁸

White crystalline solid; yield: 1.92 g (8.51 mmol, 85%); mp 132–134 °C (Lit.²⁸ mp 134–136 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 840, 930, 970, 1090, 1140, 1250, 1370, 1431, 1480, 1560, 1650, 1759, 2221, 2939, 2991, 3031 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.34 (t, J = 7.2 Hz, 3 H, CH_3), 4.34 (q, J = 7.2 Hz, 2 H, CH_2), 7.73 (d, J = 8.4 Hz, 2 H, ArH), 7.99 (d, J = 8.4 Hz, 2 H, ArH), 8.18 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 63.3, 106.8, 114.6, 115.9, 117.7, 131.0 (2 C), 132.9 (2 C), 135.3, 152.2, 161.5.

Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.07; H, 4.50; N, 12.32.

Ethyl (E)-2-Cyano-3-(3-hydroxyphenyl)acrylate (1t)²⁷

White solid; yield: 1.69 g (7.79 mmol, 78%); mp 84–86 °C (Lit.²⁷ mp 85–87 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 762, 971, 992, 1120, 1153, 1175, 1291, 1361, 1390, 1430, 1450, 1581, 1650, 1790, 2220, 3030, 3610 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.29 (t, J = 7.2 Hz, 3 H, CH_3), 4.28 (q, J = 7.2 Hz, 2 H, CH_2), 6.99 (dd, J_1 = 1.6 Hz, J_2 = 6.4 Hz, 1 H, ArH), 7.24 (t, J = 8.0 Hz, 1 H, ArH), 7.32 (d, J = 8.0 Hz, 1 H, ArH), 7.48 (s, 1 H, ArH), 8.09 (s, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 63.0, 102.6, 115.5, 116.6, 121.2, 124.2, 130.5, 132.5, 155.6, 156.7, 162.8.

Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_3$: C, 66.35; H, 5.10; N, 6.46. Found: C, 66.33; H, 5.14; N, 6.46.

Ethyl (E)-2-Cyano-3-(4-methylphenyl)acrylate (1u)^{29,31}

White solid; yield: 1.84 g (8.62 mmol, 86%); mp 90–92 °C (Lit.³¹ mp 89–90 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 1001, 1095, 1129, 1161, 1219, 1257, 1336, 1370, 1423, 1464, 1506, 1578, 1749, 2221, 2965 cm^{-1} .

¹H NMR (400 MHz, CDCl₃): δ = 1.28 (t, *J* = 7.2 Hz, 3 H, CH₃), 2.30 (s, 3 H, CH₃), 4.25 (q, *J* = 7.2 Hz, 2 H, CH₂), 7.17 (d, *J* = 8.0 Hz, 2 H, ArH), 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 8.07 (s, 1 H, CH).

¹³C NMR (100 MHz, CDCl₃): δ = 13.1, 20.8, 61.5, 100.5, 114.7, 127.8, 128.9 (2 C), 130.2 (2 C), 143.6, 153.8, 161.6.

Anal. Calcd for C₁₃H₁₃NO₂: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.53; H, 6.06; N, 6.52.

Ethyl (*E*)-2-Cyano-3-(3,4-dimethoxyphenyl)acrylate (**1v**)²⁷

White solid; yield: 2.27 g (8.66 mmol, 87%); mp 148–150 °C (Lit.²⁷ mp 150–151 °C); *R*_f = 0.3 (EtOAc–hexane 1:49).

IR (KBr): 1023, 1079, 1167, 1240, 1250, 1340, 1390, 1420, 1479, 1509, 1590, 1750, 1860, 2090, 2221, 3010 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.32 (t, *J* = 7.2 Hz, 3 H, CH₃), 3.87 (s, 3 H, OCH₃), 3.89 (s, 3 H, OCH₃), 4.29 (q, *J* = 7.2 Hz, 2 H, ArH), 6.87 (d, *J* = 8.4 Hz, 1 H, ArH), 7.39 (dd, *J*₁ = 2.4 Hz, *J*₂ = 6.0 Hz, 1 H, ArH), 7.73 (s, 1 H, ArH), 8.07 (s, 1 H, CH).

¹³C NMR (100 MHz, CDCl₃): δ = 14.2, 56.0, 56.5, 62.4, 99.4, 110.9, 111.7, 116.3, 124.6, 127.9, 149.3, 153.7, 154.5, 163.0.

Anal. Calcd for C₁₄H₁₅NO₄: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.33; H, 5.78; N, 5.41.

Ethyl (*E*)-2-Cyano-3-(2,3,4-trimethoxyphenyl)acrylate (**1w**)

Yellow solid; yield: 2.23 g (7.71 mmol, 77%); mp 100–102 °C; *R*_f = 0.2 (EtOAc–hexane 1:49).

IR (KBr): 771, 836, 954, 1007, 1036, 1090, 1125, 1160, 1190, 1250, 1340, 1371, 1423, 1470, 1509, 1584, 1609, 1747, 2220, 2940, 2976 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.32 (t, *J* = 7.2 Hz, 3 H, CH₃), 3.79 (s, 3 H, OCH₃), 3.88 (s, 3 H, OCH₃), 3.91 (s, 3 H, OCH₃), 4.29 (q, *J* = 6.8 Hz, 2 H, ArH), 6.71 (d, *J* = 9.2 Hz, 1 H, ArH), 8.12 (d, *J* = 8.8 Hz, 1 H, ArH), 8.53 (s, 1 H, CH).

¹³C NMR (100 MHz, CDCl₃): δ = 14.2, 56.2, 60.9, 62.1, 62.4, 100.2, 107.7, 116.4, 118.7, 125.0, 141.9, 149.0, 154.9, 158.5, 163.1.

Anal. Calcd for C₁₅H₁₇NO₅: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.87; H, 5.84; N, 4.84.

Ethyl (*E*)-2-Cyano-3-(3,4,5-trimethoxyphenyl)acrylate (**1x**)³¹

Yellow solid; yield: 2.44 g (8.41 mmol, 84%); mp 79–81 °C (Lit.³¹ mp 78–80 °C); *R*_f = 0.2 (EtOAc–hexane 1:49).

IR (KBr): 770, 833, 946, 1006, 1024, 1091, 1126, 1159, 1186, 1219, 1255, 1334, 1370, 1421, 1463, 1505, 1578, 1604, 1748, 2217, 2938, 2972 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.21 (t, *J* = 7.2 Hz, 3 H, CH₃), 4.15 (q, *J* = 7.2 Hz, 2 H, CH₂), 6.32 (d, *J* = 16.0 Hz, 1 H, CH), 7.23–7.26 (m, 3 H, ArH), 7.37–7.41 (m, 2 H, ArH), 7.58 (d, *J* = 16.0 Hz, 1 H, CH).

¹³C NMR (100 MHz, CDCl₃): δ = 13.3, 59.4, 117.2, 126.9 (2 C), 127.8 (2 C), 129.1, 133.4, 143.5, 165.9.

Anal. Calcd for C₁₅H₁₇NO₅: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.83; H, 5.88; N, 4.82.

Ethyl (*E*)-2-Cyano-3-(4-benzoyloxyphenyl)acrylate (**1y**)³²

White solid; yield: 2.67 g (8.66 mmol, 87%); mp 78–80 °C (Lit.³² mp 80–81 °C); *R*_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 610, 790, 851, 1027, 1218, 1260, 1336, 1370, 1398, 1513, 1780, 2212, 2937, 2973 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.17–1.27 (m, 3 H, CH₃), 4.11–4.25 (m, 2 H, CH₂), 5.01 (s, 2 H, CH₂), 6.91–7.30 (m, 7 H, ArH), 7.84–8.04 (m, 3 H, ArH).

¹³C NMR (100 MHz, CDCl₃): δ = 14.2, 24.7, 62.4, 70.3, 99.6, 115.6 (2 C), 116.2, 124.6, 127.5 (2 C), 128.3, 128.8 (2 C), 133.6 (2 C), 135.9, 154.2, 162.9 (d, *J* = 10.1 Hz).

Anal. Calcd for C₁₉H₁₇NO₃: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.23; H, 5.59; N, 4.52.

Ethyl (*E*)-2-Cyano-3-(3-hydroxy-4-methoxyphenyl)acrylate (**1z**)²⁷

White solid; yield: 1.97 g (8.02 mmol, 80%); mp 100–102 °C (Lit.²⁷ mp 101–103 °C); *R*_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 759, 969, 980, 1123, 1150, 1180, 1300, 1380, 1429, 1432, 1459, 1587, 1649, 1653, 1740, 2221, 3020, 3609 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.31 (t, *J* = 7.2 Hz, 3 H, CH₃), 3.90 (s, 3 H, OCH₃), 4.29 (q, *J* = 7.2 Hz, 2 H, CH₂), 6.86 (d, *J* = 8.4 Hz, 1 H, ArH), 7.49 (dd, *J*₁ = 2.0 Hz, *J*₂ = 6.4 Hz, 1 H, ArH), 7.56 (s, 1 H, ArH), 8.04 (s, 1 H, CH).

¹³C NMR (100 MHz, CDCl₃): δ = 14.2, 56.2, 62.5, 100.0, 110.8, 115.9, 116.5, 125.1, 125.8, 145.9, 151.1, 154.6, 163.1.

Anal. Calcd for C₁₃H₁₃NO₂: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.13; H, 5.35; N, 5.70.

Ethyl (*E*)-2-Cyano-3-(naphthalen-1-yl)acrylate (**1aa**)³³

White solid; yield: 2.05 g (8.21 mmol, 82%); mp 79–81 °C (Lit.³³ mp 80–81 °C); *R*_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 730, 780, 938, 1022, 1081, 1097, 1129, 1160, 1219, 1255, 1335, 1370, 1467, 1507, 1602, 1717, 1750, 2222, 2967 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.31 (t, *J* = 7.2 Hz, 3 H, CH₃), 4.31 (q, *J* = 7.2 Hz, 2 H, CH₂), 7.40–7.49 (m, 3 H, ArH), 7.76 (d, *J* = 8.4 Hz, 1 H, ArH), 7.87 (t, *J* = 7.6 Hz, 2 H, ArH), 8.17 (d, *J* = 7.2 Hz, 1 H, ArH), 8.95 (s, 1 H, CH).

¹³C NMR (100 MHz, CDCl₃): δ = 14.2, 62.8, 105.8, 115.4, 122.8, 125.4, 126.8, 127.8, 128.2, 128.3, 129.2, 131.7, 133.4, 133.5, 152.7, 162.3.

Anal. Calcd for C₁₆H₁₃NO₂: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.43; H, 5.28; N, 5.58.

Ethyl (*E*)-Cinnamate (**1ab**)

(*E*)-Ethyl cinnamate was prepared according to reported procedure.³⁴

To a solution of cinnamic acid (1.48 g, 10 mmol) in CH₂Cl₂ (25 mL) was added SOCl₂ (1.0 mL, 15 mmol) and DMF (80 μL, 0.95 mmol) and the mixture was stirred at rt for 1 h. The consumption of acid was monitored by using TLC. The unreacted SOCl₂ was removed under reduced pressure and CH₂Cl₂ (20 mL) was added followed by addition of EtOH (2.0 mL, 20 mmol) with stirring at rt for 3 h. After the completion of reaction, H₂O (10 mL) was added to the reaction mixture and extracted with CH₂Cl₂ (3 × 10 mL) and the combined organic layers were dried (anhyd Na₂SO₄). The solvent was evaporated under vacuum and the crude product was purified by column chromatography using hexane as eluent and characterized as ethyl (*E*)-cinnamate (**1ab**); colorless oil; yield: 1.50 g (8.52 mmol, 85%); bp 49–51 °C/760 Torr (Lit.³⁵ bp 50–51 °C/760 Torr); *R*_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 990, 1002, 1140, 1220, 1360, 1430, 1550, 1670, 1736, 1860, 2080 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.22 (t, *J* = 7.2 Hz, 3 H, CH₃), 4.15 (q, *J* = 7.2 Hz, 2 H, OCH₂), 6.32 (d, *J* = 16.0 Hz, 1 H, CH), 7.19–7.29 (m, 3 H, ArH), 7.36–7.40 (m, 2 H, ArH), 7.58 (d, *J* = 16.0 Hz, 1 H, CH).

^{13}C NMR (100 MHz, CDCl_3): δ = 13.3, 59.4, 117.2, 126.9 (2C), 127.8 (2C), 129.1, 133.4, 143.5, 165.9.

GC-MS: m/z (%) = 176 ($[\text{M}^+$], 90), 174 (20), 158 (45), 148 (80), 146 (60), 131 (100), 130 (50), 127 (34), 117 (40), 103 (100), 101 (41), 91 (50), 77 (90), 63 (20), 51 (50).

Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2$: C, 74.98; H, 6.86. Found: C, 74.96; H, 6.88.

β -Cyanooxepoxides **3**; General Procedure

A mixture of β -cyanostyrene **1** (1.0 mmol, 1.0 equiv), PhI (**2a**; 10 μL , 10 mol%), TFA (185 μL , 2.4 mmol, 2.4 equiv), and Oxone (2.0 equiv) in CHCl_3 (5 mL) was irradiated in ultrasonic bath at rt for 60–90 min. The sequel of reaction was monitored by TLC. After completion of reaction, H_2O (5 mL) was added to the reaction mixture and extracted with CH_2Cl_2 (3 \times 5 mL). The combined organic layers were dried (anhyd Na_2SO_4) and concentrated under vacuum. The crude products were purified by column chromatography on silica gel using EtOAc-hexane (1:49) and isolated products were characterized as β -cyanooxepoxides **3** by spectroscopic analysis.

Phenyl-2,2-oxiranedicarbonitrile (**3a**)^{9,36}

White solid; yield: 139 mg (0.82 mmol, 82%); mp 52–54 C (Lit.³⁶ mp 54–56 C); R_f = 0.6 (hexane).

IR (KBr): 725, 744, 840, 886, 1000, 1045, 1158, 1190, 1228, 1267, 1378, 1516, 1610, 1914, 2122 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 4.56 (s, 1 H, CH), 7.30 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH), 7.34–7.39 (m, 3 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 41.7, 65.8, 110.1, 111.6, 126.8, 127.5, 129.1, 131.4.

GC-MS: m/z (%) = 171 ($[\text{M}^+ + 1]$, 17), 170 ($[\text{M}^+]$, 40), 142 (38), 116 (15), 113 (100), 105 (25), 90 (50), 92 (30), 78 (15).

Anal. Calcd for $\text{C}_{10}\text{H}_6\text{N}_2\text{O}$: C, 70.58; H, 3.55; N, 16.46. Found: C, 70.20; H, 3.53; N, 16.45.

(4-Fluorophenyl)-2,2-oxiranedicarbonitrile (**3b**)¹⁰

White solid; yield: 135 mg (0.72 mmol, 72%); mp 78–80 C (Lit.¹⁴ mp 76–78 C); R_f = 0.4 (hexane).

IR (KBr): 727, 747, 831, 890, 1015, 1055, 1162, 1188, 1238, 1273, 1378, 1513, 1609, 1911, 2121, 2259 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 4.59 (s, 1 H, CH), 7.08 (t, J = 8.8 Hz, 2 H, ArH), 7.31 (t, J = 8.8 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 40.7, 64.3, 109.1, 110.5, 115.6 (d, J = 22.2 Hz), 122.3 (d, J = 3.1 Hz), 128.0 (d, J = 8.9 Hz), 163.9 (d, J = 251.0 Hz).

GC-MS: m/z (%) = 188 (30), 160 (22), 133 (85), 108 (100), 107 (50), 95 (44), 75 (35).

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{FN}_2\text{O}$: C, 63.83; H, 2.68; N, 14.89. Found: C, 63.22; H, 2.91; N, 14.85.

(2-Chlorophenyl)-2,2-oxiranedicarbonitrile (**3c**)¹⁴

White solid; yield: 133 mg (0.65 mmol, 65%); mp 50–52 C (Lit.¹⁴ mp 51–53 C); R_f = 0.4 (hexane).

IR (KBr): 684, 699, 718, 830, 857, 1011, 1045, 1191, 1377, 1425, 1513, 1573, 1926, 2112, 2258, 2344 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 4.84 (s, 1 H, CH), 7.21 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1 H, ArH), 7.27 (dt, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1 H, ArH), 7.31 (dt, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1 H, ArH), 7.35 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 40.9, 63.6, 109.7, 111.1, 126.4, 127.1, 127.4, 129.9, 132.2, 133.9.

GC-MS: m/z (%) = 206 ($[\text{M}^+]$, 8), 204 (24), 169 (15), 141 (95), 140 (25), 139 (24), 89 (100), 75 (24), 49 (25).

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{ClN}_2\text{O}$: C, 58.70; H, 2.46; N, 13.69. Found: C, 58.76; H, 2.51; N, 13.73.

(4-Chlorophenyl)-2,2-oxiranedicarbonitrile (**3d**)⁹

White solid; yield: 153 mg (0.75 mmol, 75%); mp 127–129 C (Lit.⁹ mp 125–126 C); R_f = 0.4 (hexane).

IR (KBr): 683, 693, 715, 827, 866, 1011, 1044, 1189, 1378, 1425, 1512, 1571, 1927, 2107, 2348, 2393 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 4.59 (s, 1 H, CH), 7.27 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH), 7.36 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 41.6, 65.1, 109.8, 111.3, 125.9, 128.1, 129.6, 137.8.

GC-MS: m/z (%) = 206 ($[\text{M}^+ + 2]$, 32), 205 ($[\text{M}^+ + 1]$, 11), 204 ($[\text{M}^+]$, 10), 149 (12), 142 (22), 141 (98), 139 (100), 111 (54), 75 (48), 50 (42).

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{ClN}_2\text{O}$: C, 58.70; H, 2.46; N, 13.69. Found: C, 58.76; H, 3.04; N, 13.69.

(2,3-Dichlorophenyl)-2,2-oxiranedicarbonitrile (**3e**)

White solid; yield: 167 mg (0.70 mmol, 70%); mp 127–129 C; R_f = 0.4 (hexane).

IR (KBr): 690, 720, 830, 861, 1015, 1050, 1190, 1375, 1430, 1515, 1930, 2110, 2350, 2390 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 4.82 (s, 1 H, CH), 7.11 (d, J = 7.6 Hz, 1 H, ArH), 7.21 (t, J = 8.0 Hz, 1 H, ArH), 7.48 (d, J = 8.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 39.8, 62.5, 108.5, 109.9, 124.3, 127.1, 127.7, 131.0, 131.9, 132.9.

GC-MS: m/z (%) = 241 ($[\text{M}^+ + 2]$, 11), 240 ($[\text{M}^+ + 1]$, 8), 239 ($[\text{M}^+]$, 60), 237 (100), 142 (22), 141 (98), 139 (70), 111 (54), 75 (48), 50 (42).

Anal. Calcd for $\text{C}_{10}\text{H}_4\text{Cl}_2\text{N}_2\text{O}$: C, 50.24; H, 1.69; N, 11.72. Found: C, 50.26; H, 1.73; N, 11.03.

(3-Bromophenyl)-2,2-oxiranedicarbonitrile (**3f**)⁹

White solid; yield: 191 mg (0.77 mmol, 77%); mp 115–117 C (Lit.⁹ mp 115–116 C); R_f = 0.3 (hexane).

IR (KBr): 747, 760, 800, 912, 1065, 1120, 1262, 1279, 1381, 1520, 1630, 1920, 2119, 2250 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 4.57 (s, 1 H, CH), 7.24 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH), 7.53 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 41.5, 64.7, 109.8, 111.2, 123.2, 125.2, 129.7, 129.9, 130.7, 134.6.

GC-MS: m/z (%) = 250 ($[\text{M}^+ + 3]$, 10), 249 ($[\text{M}^+ + 2]$, 90), 248 ($[\text{M}^+ + 1]$, 18), 247 ($[\text{M}^+]$, 90), 219 (45), 180 (25), 166 (43), 140 (50).

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{BrN}_2\text{O}$: C, 48.22; H, 2.02; N, 11.25. Found: C, 48.45; H, 2.29; N, 11.28.

(4-Bromophenyl)-2,2-oxiranedicarbonitrile (**3g**)¹⁰

White solid; yield: 194 mg (0.78 mmol, 78%); mp 116–118 C (Lit.¹⁰ mp 118–119 C); R_f = 0.4 (hexane).

IR (KBr): 724, 750, 827, 891, 1115, 1054, 1173, 1195, 1239, 1277, 1382, 1518, 1613, 1921, 2124, 2252 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 4.57 (s, 1 H, CH), 7.19 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH), 7.53 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 41.4, 65.1, 109.8, 111.2, 126.0, 126.4, 128.3, 132.5.

GC-MS: m/z (%) = 250 ($[\text{M}^+ + 3]$, 24), 249 ($[\text{M}^+ + 2]$, 13), 248 ($[\text{M}^+ + 1]$, 22), 247 ($[\text{M}^+]$, 100), 221 (30), 187 (40), 181 (32), 174 (41), 144 (80), 117 (20).

Anal. Calcd for $\text{C}_{10}\text{H}_5\text{BrN}_2\text{O}$: C, 48.22; H, 2.02; N, 11.25. Found: C, 48.45; H, 2.28; N, 11.26.

(4-Methylphenyl)-2,2-oxiranedicarbonitrile (3h)¹⁰

White solid; yield: 154 mg (0.80 mmol, 80%); mp 60–62 °C (Lit.¹⁰ mp 63–65 °C); R_f = 0.5 (hexane).

IR (KBr): 765, 816, 893, 1161, 1179, 1201, 1273, 1530, 1754, 1854, 1874, 2224, 2225, 2923 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 2.28 (s, 3 H, CH_3), 4.56 (s, 1 H, CH), 7.14–7.20 (m, 4 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 20.2, 40.8, 65.1, 109.3, 110.6, 123.5, 125.7, 128.8, 129.9.

GC-MS: m/z (%) = 185 ($[\text{M}^+ + 1]$, 14), 184 ($[\text{M}^+]$, 100), 158 (23), 156 (26), 155 (40), 151 (60), 129 (55), 127 (100), 102 (37).

Anal. Calcd for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}$: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.11; H, 4.38; N, 15.10.

(3,4-Dimethoxyphenyl)-2,2-oxiranedicarbonitrile (3i)¹⁴

White solid; yield: 207 mg (0.90 mmol, 90%); mp 144–146 °C (Lit.¹⁴ mp 142–144 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 732, 779, 821, 849, 967, 1015, 1037, 1142, 1157, 1167, 1193, 1271, 1453, 1467, 1505, 1566, 1580, 2221, 2312, 2831, 2963 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 3.87 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 6.89 (d, J = 8.4 Hz, 1 H, ArH), 7.31 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1 H, ArH), 7.57 (s, 1 H, ArH), 7.61 (d, J = 2.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 56.1, 56.3, 78.6, 110.8, 111.1, 113.6, 114.4, 124.3, 128.2, 149.6, 154.9, 159.1.

GC-MS: m/z (%) = 231 ($[\text{M}^+ + 1]$, 14), 230 ($[\text{M}^+]$, 100), 202 (36), 176 (15), 173 (100), 165 (24), 150 (55), 138 (32), 136 (35).

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_3$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.60; H, 4.55; N, 12.15.

(3,4,5-Trimethoxyphenyl)-2,2-oxiranedicarbonitrile (3j)¹⁴

White solid; yield: 239 mg (0.92 mmol, 92%); mp 96–98 °C (Lit.¹⁴ mp 95–97 °C); R_f = 0.3 (EtOAc–hexane 1:49).

IR (KBr): 701, 764, 832, 844, 1126, 1152, 1241, 1333, 1453, 1461, 1641, 2230, 2838, 3002 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 3.80 (s, 9 H, $3 \times \text{OCH}_3$), 4.56 (s, 1 H, CH), 6.54 (s, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 41.6, 56.3, 60.9, 66.0, 103.7, 110.2, 111.4, 122.3, 140.4, 153.8.

GC-MS: m/z (%) = 261 ($[\text{M}^+ + 1]$, 15), 260 ($[\text{M}^+]$, 65), 232 (32), 206 (20), 204 (100), 196 (25), 180 (52), 168 (30), 166 (38).

Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 59.60; H, 4.87; N, 11.00.

3-(2-Naphthalenyl)-2,2-oxiranedicarbonitrile (3k)⁹

White solid; yield: 176 mg (0.80 mmol, 80%); mp 129–131 °C (Lit.⁹ mp 127–129 °C); R_f = 0.3 (hexane).

IR (KBr): 761, 775, 893, 1060, 1083, 1196, 1266, 1342, 1368, 1512, 1597, 1725, 2234, 2929 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 5.18 (s, 1 H, CH), 7.43–7.48 (m, 2 H, ArH), 7.55 (t, J = 7.6 Hz, 1 H, ArH), 7.61 (t, J = 7.6 Hz, 1 H, ArH), 7.86 (s, 1 H, ArH), 7.87–7.96 (m, 2 H, ArH)

^{13}C NMR (100 MHz, CDCl_3): δ = 41.4, 64.3, 110.0, 111.6, 121.3, 123.7, 124.3, 125.1, 126.9, 127.9, 129.4, 130.6, 131.5, 133.3.

GC-MS: m/z (%) = 221 ($[\text{M}^+ + 1]$, 17), 220 ($[\text{M}^+]$, 89), 192 (34), 166 (18), 163 (100), 155 (22), 140 (56), 144 (30), 127 (35).

Anal. Calcd for $\text{C}_{14}\text{H}_8\text{N}_2\text{O}$: C, 76.35; H, 3.66; N, 12.72. Found: C, 76.05; H, 3.67; N, 12.78.

(9-Anthracenyl)-2,2-oxiranedicarbonitrile (3l)¹⁴

White solid; yield: 208 mg (0.77 mmol, 77%); mp 97–99 °C (Lit.¹⁴ mp 96–98 °C); R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 765, 779, 896, 1064, 1090, 1199, 1268, 1340, 1362, 1509, 1600, 1742, 2238, 2930 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 5.46 (s, 1 H, CH), 7.49 (t, J = 8.0 Hz, 2 H, ArH), 7.70–7.77 (m, 2 H, ArH), 8.02 (t, J = 7.6 Hz, 2 H, ArH), 8.22–8.31 (m, 2 H, ArH), 8.54 (s, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 40.5, 54.6, 108.9, 110.8, 123.4, 125.7, 127.2, 129.5, 131.1, 133.5, 134.0, 183.4.

GC-MS: m/z (%) = 271 ($[\text{M}^+ + 1]$, 20), 270 ($[\text{M}^+]$, 95), 243 (30), 216 (22), 214 (100), 205 (20), 190 (52), 192 (32), 177 (38).

Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}$: C, 79.99; H, 3.73; N, 10.36. Found: C, 79.63; H, 3.69; N, 10.34.

Ethyl 2-Cyano-3-phenyloxirane-2-carboxylate (3m)³⁷

Colorless oil; yield: 180 mg (0.83 mmol, 83%); bp 352–354 °C/760 Torr (Lit.³⁸ 355–357 °C/760 Torr); R_f = 0.6 (EtOAc–hexane 1:49).

IR (KBr): 694, 725, 743, 838, 886, 1042, 1158, 1160, 1253, 1370, 1396, 1452, 1758, 2250, 2932, 2984 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.31 (dt, J_1 = 2.8 Hz, J_2 = 7.2 Hz, 3 H, CH_3), 4.31 (tq, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 2 H, CH_2), 4.44 (s, 1 H, CH), 7.30–7.39 (m, 5 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.0, 53.4, 64.1, 64.5, 112.9, 126.8, 128.8, 130.4, 162.7.

GC-MS: m/z (%) = 218 ($[\text{M}^+ + 1]$, 14), 217 ($[\text{M}^+]$, 90), 189 (40), 163 (18), 160 (100), 152 (22), 137 (52), 139 (36), 125 (20).

Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.33; H, 5.18; N, 6.43.

Ethyl 2-Cyano-3-(4-fluorophenyl)oxirane-2-carboxylate (3n)

Colourless solid; yield: 176 mg (0.75 mmol, 75%); mp 156–158 °C; R_f = 0.4 (hexane).

IR (KBr): 684, 740, 768, 833, 869, 980, 1008, 1034, 1044, 1179, 1201, 1211, 1283, 1365, 1438, 1487, 1492, 1568, 1609, 1801, 2215, 2979 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.24 (t, J = 7.2 Hz, 3 H, CH_3), 4.24 (tq, J_1 = 1.6 Hz, J_2 = 6.8 Hz, 2 H, CH_2), 4.41 (s, 1 H, CH), 6.98–7.04 (m, 2 H, ArH), 7.28–7.35 (m, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 13.9, 53.4, 63.9 (d, J = 36.4 Hz), 113.0, 115.9 (d, J = 22.0 Hz), 125.9 (d, J = 3.0 Hz), 128.9 (d, J = 8.7 Hz), 162.5, 162.6, 165.1.

GC-MS: m/z (%) = 237 ($[M^+ + 2]$, 20), 236 ($[M^+ + 1]$, 15), 235 ($[M^+]$, 90), 219 (43), 207 (32), 190 (43), 178 (50), 153 (65), 150 (32), 134 (17), 125 (90), 109 (67), 108 (23), 97 (23), 85 (32).

Anal. Calcd for $C_{12}H_{10}FNO_3$: C, 61.28; H, 4.29; N, 5.95. Found: C, 61.33; H, 4.32; N, 5.93.

Ethyl 2-Cyano-3-(2-chlorophenyl)oxirane-2-carboxylate (3o)

White solid; yield: 166 mg (0.66 mmol (66%)); mp 125–127 °C; R_f = 0.4 (hexane).

IR (KBr): 667, 732, 767, 838, 896, 1010, 1061, 1080, 1110, 1163, 1222, 1270, 1378, 1434, 1446, 1529, 1580, 1760, 2217, 2968 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ = 1.18–1.32 (m, 3 H, CH_3), 4.30–4.35 (m, 2 H, CH_2), 4.68 (s, 1 H, CH), 7.26–7.36 (m, 4 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 52.7, 62.3, 64.3, 112.6, 127.3 (2 C), 128.7, 129.6, 131.3, 133.6, 162.3.

GC-MS: m/z (%) = 253 ($[M^+ + 2]$, 16), 252 ($[M^+ + 1]$, 24), 251 ($[M^+]$, 100), 248 (40), 247 (90), 231 (17), 206 (26), 171 (36), 143 (25), 132 (47), 105 (30), 77 (42), 51 (20).

Anal. Calcd for $C_{12}H_{10}ClNO_3$: C, 57.27; H, 4.01; N, 5.57. Found: C, 57.30; H, 4.04; N, 5.60.

Ethyl 3-(4-Chlorophenyl)-2-cyanooxirane-2-carboxylate (3p)

White solid; yield: 193 mg (0.77 mmol, 77%); mp 70–72 °C; R_f = 0.2 (hexane).

IR (KBr): 681, 734, 771, 841, 890, 1007, 1054, 1073, 1094, 1162, 1201, 1219, 1287, 1374, 1438, 1477, 1491, 1571, 1598, 1753, 2223, 2970 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.2 Hz, 3 H, CH_3), 4.29 (tq, J_1 = 1.2 Hz, J_2 = 6.8 Hz, 2 H, CH_2), 4.42 (s, 1 H, CH), 7.26–7.36 (m, 4 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 53.3, 63.7, 64.3, 112.9, 128.2 (2 C), 128.5, 129.1 (2 C), 136.4, 162.4.

GC-MS: m/z (%) = 253 ($[M^+ + 2]$, 27), 252 ($[M^+ + 1]$, 18), 251 ($[M^+]$, 85), 235 (34), 222 (90), 205 (75), 193 (16), 179 (40), 169 (32), 150 (43), 141 (94), 124 (21), 113 (32), 89 (46), 77 (51), 63 (40).

Anal. Calcd for $C_{12}H_{10}ClNO_3$: C, 57.27; H, 4.01; N, 5.57. Found: C, 57.30; H, 4.06; N, 5.54.

Ethyl 2-Cyano-3-(3-bromophenyl)oxirane-2-carboxylate (3q)

White solid; yield: 233 mg (0.79 mmol, 79%); mp 155–157 °C; R_f = 0.3 (hexane).

IR (KBr): 681, 693, 733, 772, 787, 854, 918, 1006, 1054, 1112, 1161, 1219, 1285, 1373, 1393, 1438, 1476, 1571, 1598, 1680, 1752, 2219, 2990 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (td, J_1 = 0.8 Hz, J_2 = 6.0 Hz, 3 H, CH_3), 4.26 (td, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 2 H, CH_2), 4.40 (s, 1 H, CH), 7.18–7.28 (m, 2 H, ArH), 7.44–7.49 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 53.3, 63.4, 64.4, 112.7, 122.8, 125.3, 129.9, 130.5, 132.3, 133.5, 162.3.

GC-MS: m/z (%) = 297 ($[M^+ + 3]$, 14), 296 ($[M^+ + 2]$, 10), 295 ($[M^+ + 1]$, 26), 294 ($[M^+]$, 100), 268 (29), 249 (52), 222 (41), 212 (59), 184 (92), 163 (18), 142 (30), 89 (91), 84 (48), 65 (20).

Anal. Calcd for $C_{12}H_{10}BrNO_3$: C, 48.67; H, 3.40; N, 4.73. Found: C, 48.70; H, 3.41; N, 4.75.

Ethyl 2-Cyano-3-(4-bromophenyl)oxirane-2-carboxylate (3r)

White solid; yield: 235 mg (0.80 mmol, 80%); mp 117–119 °C; R_f = 0.4 (hexane).

IR (KBr): 681, 693, 734, 771, 842, 854, 889, 1006, 1055, 1161, 1287, 1374, 1476, 1571, 1753, 2216, 2990 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.2 Hz, 3 H, CH_3), 4.28 (td, J_1 = 1.6 Hz, J_2 = 6.8 Hz, 2 H, CH_2), 4.40 (s, 1 H, CH), 7.21 (d, J = 8.0 Hz, 2 H, ArH), 7.48 (d, J = 8.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 53.3, 63.8, 64.2, 112.8, 124.8, 128.4 (2 C), 129.0, 132.1 (2 C), 162.4.

GC-MS: m/z (%) = 297 ($[M^+ + 3]$, 9), 296 ($[M^+ + 2]$, 15), 295 ($[M^+ + 1]$, 23), 294 ($[M^+]$, 100), 268 (28), 250 (43), 222 (40), 212 (53), 184 (80), 158 (17), 143 (50), 89 (90), 85 (54), 63 (43).

Anal. Calcd for $C_{12}H_{10}BrNO_3$: C, 48.67; H, 3.40; N, 4.73. Found: C, 48.70; H, 3.43; N, 4.78.

Ethyl 2-Cyano-3-(4-cyanophenyl)oxirane-2-carboxylate (3s)

White solid; yield: 174 mg (0.72 mmol, 72%); mp 165–167 °C; R_f = 0.4 (hexane).

IR (KBr): 689, 732, 740, 756, 876, 890, 987, 1012, 1089, 1111, 1140, 1198, 1211, 1257, 1298, 1356, 1390, 1416, 1465, 1589, 1632, 1665, 1790, 2212, 2789, 3001 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ = 1.16–1.34 (m, 3 H, CH_3), 4.32–4.52 (m, 3 H, CH, CH_2), 7.48–7.69 (m, 4 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 53.2, 63.2, 64.6, 112.3, 114.3, 117.9, 127.6 (2C), 132.6 (2C), 134.9, 161.9.

GC-MS: m/z (%) = 243 ($[M^+ + 1]$, 20), 242 ($[M^+]$, 100), 226 (40), 213 (50), 197 (54), 181 (23), 169 (34), 160 (54), 141 (49), 127 (18), 115 (23), 104 (32), 88 (16), 83 (45), 64 (42).

Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.50; H, 4.20; N, 11.52.

Ethyl 2-Cyano-3-(3-hydroxyphenyl)oxirane-2-carboxylate (3t)

Colourless solid; yield: 172 mg (0.74 mmol, 74%); mp 122–124 °C; R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 680, 687, 740, 760, 779, 920, 1009, 1060, 1110, 1160, 1215, 1284, 1376, 1391, 1440, 1475, 1572, 1599, 1682, 1757, 2231, 2991 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.2 Hz, 3 H, CH_3), 4.32 (tq, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 2 H, CH_2), 4.39 (s, 1 H, CH), 6.81–6.86 (m, 2 H, ArH), 6.91 (d, J = 7.6 Hz, 1 H, ArH), 7.21 (t, J = 8.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 53.2, 64.3, 112.9, 113.4, 117.7, 119.0, 119.1, 130.2, 131.4, 156.3, 162.8.

GC-MS: m/z (%) = 234 ($[M^+ + 1]$, 21), 233 ($[M^+]$, 60), 232 (70), 204 (28), 186 (60), 151 (90), 131 (43), 123 (80), 95 (70), 77 (80).

Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.83; H, 4.78; N, 6.03.

Ethyl 2-Cyano-3-(4-methylphenyl)oxirane-2-carboxylate (3u)

Colourless solid; yield: 194 mg (0.84 mmol, 84%); mp 162–164 °C; R_f = 0.4 (hexane).

IR (KBr): 649, 690, 712, 770, 842, 884, 912, 1026, 1141, 1169, 1267, 1323, 1378, 1454, 1590, 1738, 2239, 2790, 2879 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.2 Hz, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 4.25 (tq, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 2 H, CH_2), 4.38 (s, 1 H, CH), 7.12 (d, J = 8.0 Hz, 2 H, ArH), 7.21 (d, J = 8.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 13.9, 21.4, 53.5, 64.1, 64.6, 113.2, 126.7 (2 C), 126.9, 129.5 (2 C), 140.5, 162.8.

GC-MS: m/z (%) = 232 ($[\text{M}^+ + 1]$, 12), 231 ($[\text{M}^+]$, 80), 229 (20), 215 (30), 203 (43), 185 (60), 186 (70), 174 (40), 157 (30), 149 (70), 121 (90), 119 (60), 103 (55), 91 (50), 78 (42).

Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.50; H, 5.68; N, 6.07.

Ethyl 2-Cyano-3-(3,4-dimethoxyphenyl)oxirane-2-carboxylate (3v)

Colourless solid; yield: 252 mg (0.91 mmol, 91%); mp 66–68 °C; R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 640, 740, 758, 776, 867, 926, 1008, 1069, 1120, 1167, 1231, 1280, 1376, 1398, 1436, 1470, 1568, 1609, 1687, 1760, 2997 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.32 (t, J = 7.2 Hz, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 4.25–4.37 (m, 2 H, CH_2), 4.39 (s, 1 H, CH), 6.83–6.86 (m, 3 H, ArH), 6.96 (dd, J_1 = 2.0 Hz, J_2 = 6.4 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 13.9, 53.4, 55.7 (d, J = 1.8 Hz), 62.5, 64.1, 64.7, 109.1, 111.1, 113.2, 120.2, 121.9, 149.3, 150.8, 162.8.

GC-MS: m/z (%) = 279 ($[\text{M}^+ + 2]$, 10), 278 ($[\text{M}^+ + 1]$, 18), 277 ($[\text{M}^+]$, 90), 261 (34), 220 (41), 194 (36), 169 (18), 160 (100), 152 (22), 138 (52), 107 (37), 76 (60).

Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.63; H, 5.43; N, 5.07.

Ethyl 2-Cyano-3-(2,3,4-trimethoxyphenyl)oxirane-2-carboxylate (3w)

White solid; yield: 285 mg (0.93 mmol, 93%); mp 109–111 °C; R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 698, 756, 779, 867, 894, 1011, 1060, 1070, 1109, 1165, 1205, 1224, 1289, 1376, 1440, 1470, 1489, 1573, 1590, 1765, 1879, 2989 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.32 (t, J = 6.8 Hz, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.29 (q, J = 7.2 Hz, 2 H, CH_2), 6.71 (d, J = 9.2 Hz, 1 H, ArH), 8.12 (d, J = 9.2 Hz, 1 H, ArH), 8.52 (s, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.2, 56.2, 60.9, 62.1, 62.3, 100.2, 107.7, 116.4, 118.7, 125.0, 141.9, 149.0, 154.9, 158.5, 163.1.

GC-MS: m/z (%) = 309 ($[\text{M}^+ + 2]$, 22), 308 ($[\text{M}^+ + 1]$, 25), 307 ($[\text{M}^+]$, 100), 279 (40), 250 (55), 232 (90), 217 (60), 203 (70), 195 (40), 181 (30), 152 (20), 120 (19), 91 (26), 79 (40).

Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.64; H, 5.54; N, 4.53.

Ethyl 2-Cyano-3-(3,4,5-trimethoxyphenyl)oxirane-2-carboxylate (3x)

White solid; yield: 288 mg (0.94 mmol, 94%); mp 84–86 °C; R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 672, 744, 776, 869, 891, 1011, 1061, 1067, 1087, 1176, 1203, 1221, 1280, 1376, 1440, 1470, 1499, 1570, 1601, 1760, 2966 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.29–1.33 (m, 3 H, CH_3), 3.76–3.80 (m, 9 H, 3 \times OCH_3), 4.31 (tq, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 2 H, CH_2), 4.38 (s, 1 H, CH), 6.57 (s, 2 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 13.9, 53.3, 56.2 (2 C), 60.8, 64.2, 64.6, 103.8 (2 C), 113.1, 125.0, 139.5, 153.5 (2 C), 162.6.

GC-MS: m/z (%) = 309 ($[\text{M}^+ + 2]$, 20), 308 ($[\text{M}^+ + 1]$, 26), 307 ($[\text{M}^+]$, 100), 291 (40), 276 (30), 261 (90), 245 (40), 234 (50), 217 (55), 203 (40), 181 (30), 168 (20), 150 (21), 125 (43), 110 (26), 79 (30), 66 (16).

Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.67; H, 5.59; N, 4.60.

Ethyl 3-[4-(Benzyloxy)phenyl]-2-cyanooxirane-2-carboxylate (3y)

Colorless solid; yield: 290 mg (0.90 mmol, 90%); mp 135–137 °C; R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 673, 747, 787, 845, 898, 1011, 1023, 1041, 1087, 1145, 1209, 1267, 1301, 1375, 1434, 1498, 1534, 1776, 2976 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.26–1.33 (m, 3 H, CH_3), 4.27–4.40 (m, 3 H, CH_2 , CH), 4.87–5.01 (m, 2 H, ArH), 6.91–7.32 (m, 9 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.0, 53.5, 64.1, 64.7, 70.2, 115.19 (2 C), 116.0 (d, J = 3.6 Hz), 121.9, 127.6 (2 C), 128.2, 128.4 (2 C), 128.7 (2 C), 136.5, 160.5, 162.9.

GC-MS: m/z (%) = 325 ($[\text{M}^+ + 2]$, 10), 324 ($[\text{M}^+ + 1]$, 20), 323 ($[\text{M}^+]$, 90), 307 (42), 278 (56), 240 (34), 189 (40), 163 (18), 160 (21), 152 (22), 149 (80), 137 (52), 139 (36), 121 (20).

Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.56; H, 5.28; N, 4.34.

Ethyl 2-Cyano-3-(3-hydroxy-4-methoxyphenyl)oxirane-2-carboxylate (3z)

Colorless solid; yield: 217 mg (0.88 mmol, 88%); mp 107–109 °C; R_f = 0.4 (EtOAc–hexane 1:49).

IR (KBr): 640, 681, 734, 747, 781, 845, 1028, 1071, 1079, 1096, 1189, 1203, 1223, 1297, 1367, 1420, 1434, 1498, 1575, 1589, 1712, 2932 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.31 (t, J = 7.2 Hz, 3 H, CH_3), 3.91 (s, 3 H, OCH_3), 4.29 (q, J = 7.2 Hz, 2 H, CH_2), 6.87 (d, J = 8.4 Hz, 1 H, CH), 7.45 (dd, J_1 = 2.0 Hz, J_2 = 6.4 Hz, 1 H, ArH), 7.56 (s, 1 H, ArH), 8.05 (s, 1 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.2, 56.2, 62.5, 100.1, 110.7, 115.9, 116.5, 125.1, 125.7, 145.9, 151.0, 154.6, 163.1.

GC-MS: m/z (%) = 265 ($[\text{M}^+ + 2]$, 8), 264 ($[\text{M}^+ + 1]$, 21), 263 ($[\text{M}^+]$, 100), 247 (60), 202 (40), 176 (30), 169 (16), 165 (80), 151 (40), 141 (55), 114 (39), 76 (31).

Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.30; H, 5.00; N, 5.35.

Ethyl 2-Cyano-3-(1-naphthyl)oxirane-2-carboxylate (3aa)

White solid; yield: 205 mg (0.77 mmol, 77%); mp 152–154 °C; R_f = 0.3 (hexane).

IR (KBr): 657, 719, 770, 798, 865, 889, 970, 1006, 1067, 1119, 1158, 1172, 1208, 1260, 1290, 1386, 1440, 1480, 1499, 1590, 1611, 1689, 1787, 2890 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.28–1.35 (m, 3 H, CH_3), 4.32–4.39 (m, 2 H, CH_2), 5.01 (s, 1 H, CH), 7.42–7.51 (m, 4 H, ArH), 7.75–7.84 (m, 3 H, ArH).

^{13}C NMR (100 MHz, CDCl_3): δ = 14.0, 53.2, 62.8, 64.3, 112.9, 121.7, 124.2, 125.3, 126.1, 126.5, 127.3, 129.2, 130.6, 130.9, 133.9, 162.9.

GC-MS: m/z (%) = 269 ($[\text{M}^+ + 2]$, 16), 268 ($[\text{M}^+ + 1]$, 25), 267 ($[\text{M}^+]$, 70), 266 (30), 251 (40), 240 (20), 221 (70), 206 (30), 194 (80), 178 (40), 167 (50), 155 (50), 139 (90), 127 (43), 113 (21), 101 (24), 77 (17), 63 (24).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.93; H, 4.88; N, 5.20.

Ethyl 3-Phenylloxirane-2-carboxylate (3ab)³⁸

Colorless oil; yield: 177 mg (0.92 mmol, 92%); bp 132–134 °C/760 Torr (Lit.³⁸ 130–132 °C/760 Torr); R_f = 0.6 (hexane).

IR (KBr): 690, 732, 778, 844, 898, 1011, 1043, 1058, 1086, 1170, 1205, 1223, 1290, 1357, 1443, 1472, 1495, 1575, 1597, 1762, 2989 cm^{-1} .

¹H NMR (400 MHz, $CDCl_3$): δ = 1.17–1.25 (m, 3 H, CH_3), 4.10–4.17 (m, 2 H, CH_2), 6.28–6.36 (m, 1 H, CH), 7.23–7.40 (m, 5 H, ArH), 7.53–7.61 (m, 1 H, ArH).

¹³C NMR (100 MHz, $CDCl_3$): δ = 14.3, 60.5, 118.3, 128.1 (2 C), 128.9 (2 C), 130.2, 134.5, 144.6, 166.9.

GC-MS: m/z (%) = 193 ($[M^+ + 1]$, 17), 192 ($[M^+]$, 90), 189 (40), 162 (26), 159 (70), 146 (52), 120 (39), 94 (30).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.73; H, 6.30.

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Supporting Information

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References

- Robert, A.; Baudy-Floc'h, M.; Le Grel, P.; Foucaud, A. *Trends Org. Chem.* **1995**, *5*, 37; and references cited therein.
- (a) Hamza-Reguig, S.; Bentabed-Ababsa, G.; Domingo, L. R.; Rios-Gutierrez, M.; Philippot, S.; Fontanay, S.; Duval, R. E.; Ruchaud, S.; Bach, S.; Roisnel, T.; Mongin, F. *J. Mol. Struct.* **2018**, *1157*, 276. (b) Serrar, H.; Boukhris, S.; Hassikou, A.; Souizi, A. *J. Heterocycl. Chem.* **2015**, *52*, 1269. (c) Pan, J.; Zhang, W.; Zhang, J.; Lu, S. *Tetrahedron Lett.* **2007**, *48*, 2781. (d) Grigoropoulou, G.; Clark, J. H.; Elings, J. A. *Green Chem.* **2003**, *5*, 1. (e) Seifi, M.; Sheibani, H. *ARKIVOC* **2013**, (iv), 191.
- (a) Bentabed-Ababsa, G.; Hamza-Reguig, S.; Derdour, A.; Domingo, L. R.; Saez, J. A.; Roisnel, T.; Dorcet, V.; Nassare, E.; Mongin, F. *Org. Biomol. Chem.* **2012**, *10*, 8434. (b) Tagliapietra, S.; Cravotto, G.; Gaudino, E. C.; Visentin, S.; Mussi, V. *Synlett* **2012**, 23, 1459. (c) Domingo, L. R.; Saez, J. A. *J. Org. Chem.* **2011**, *76*, 373. (d) Volmajer, J.; Toplak, R.; Bittner, S.; Le Marechala, A. M. *ARKIVOC* **2003**, (xiv), 49. (e) Bentabed-Ababsa, G.; Derdour, A.; Roisnel, T.; Saez, J. A.; Perez, P.; Chamorro, E.; Domingo, L. R.; Mongin, F. *J. Org. Chem.* **2009**, *74*, 2120. (f) Bentabed, G.; Rahmouni, M.; Mongin, F.; Derdour, A.; Hamelin, J.; Bazureau, J. P. *Synth. Commun.* **2007**, *37*, 2935.
- (a) Majcen-Le Marechal, A.; Le Grel, P.; Robert, A.; Biskup, J.; Ferk, V.; Toplak, R. *ARKIVOC* **2001**, 119. (b) Roger, F.; Le Pironnec, M.-G.; Guerro, M.; Gougeon, P.; Gall, P.; Le Grel, P.; Baudy-Floc'h, M. *Synthesis* **1999**, 1341. (c) Boukhris, S.; Souizi, A. *Tetrahedron Lett.* **2000**, *41*, 2559. (d) Amanetoullah, A. O.; Chaabouni, M. M.; Baklouti, A. *Synth. Commun.* **1996**, *26*, 1155.
- (a) Guillemet, M.; Robert, A.; Baudy-Floc'h, M. *Tetrahedron Lett.* **1995**, *36*, 547. (b) Majcen-Le Marechal, A.; Robert, A.; Leban, I. *J. Chem. Soc., Perkin Trans. 1* **1993**, 351. (c) Majcen-Le Marechal, A.; Robert, A.; Leban, I. *Tetrahedron* **1990**, *46*, 451. (d) Souizi, A.; Robert, A. *C. R. Acad. Sci. Paris, Ser. 2* **1982**, *295*, 571. (e) Robert, A.; Le Marechal, A. *J. Chem. Soc., Chem. Commun.* **1978**, 447. (f) Ferrey, M.; Robert, A.; Foucaud, A. *C. R. Acad. Sci. Paris, Ser. C* **1973**, *277*, 1153.
- Sekiya, M.; Suzuki, K.; Nanjo, K. *Chem. Pharm. Bull.* **1981**, *29*, 336.
- Seeberger, P. H.; Gilmore, K.; Ushakov, D. B. *Chem. Commun.* **2014**, 50, 12649.
- Wang, L.; Wang, Z.; Li, F.; Zhang, X.; Yang, F. *Eur. J. Org. Chem.* **2016**, 1251.
- Lattanzi, A.; Vidal-Albalat, A.; Meninno, S. *Org. Lett.* **2015**, *17*, 4348.
- Amrollahi, M. A.; Mirhashemi, F. *Tetrahedron Lett.* **2018**, *59*, 2661.
- (a) Graham, K. M.; Jasmin, E. *Tetrahedron Lett.* **2018**, *59*, 2965. (b) Chen, Q.; Gao, G.-L. *Curr. Organocatal.* **2017**, *4*, 33.
- (a) Akira, N.; Hodaka, K.; Junki, T.; Akira, I.; Tomohiro, M.; Yasuyoshi, M. *Org. Biomol. Chem.* **2018**, *16*, 541. (b) Kitamura, T.; Mizuno, S.; Muta, K.; Oyamada, J. *J. Org. Chem.* **2018**, *83*, 2773. (c) Fujita, M. *Tetrahedron Lett.* **2017**, *58*, 4409. (d) Mizar, P.; Wirth, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 5993. (e) Singh, F. V.; Wirth, T. *Synthesis* **2013**, *45*, 2499; and references are cited therein. (f) Kajiyama, D.; Saitoh, T.; Yamaguchi, S.; Nishiyama, S. *Synthesis* **2012**, *44*, 1667. (g) Wardrop, D. J.; Yermolina, M. V.; Bowen, E. G. *Synthesis* **2012**, *44*, 1199. (h) Singh, F. V.; Wirth, T. *Org. Lett.* **2011**, *13*, 6504. (i) Du, X.; Chen, H.; Chen, Y.; Chen, J.; Liu, Y. *Synlett* **2011**, 1010. (j) Wang, H.; Fan, R. *J. Org. Chem.* **2010**, *75*, 6994. (k) Moriarty, R. M.; Tyagi, S.; Kinch, M. *Tetrahedron* **2010**, *66*, 5801. (l) Bose, S. S.; Idrees, M. *Synthesis* **2010**, 393. (m) Pardo, L. M.; Tellitu, I.; Domínguez, E. *Synthesis* **2010**, 971.
- (a) Jiang, X.; Zhu, W.; Yang, L.; Zheng, Z.; Yu, C. *Eur. J. Org. Chem.* **2019**, 2268. (b) Shu, S.; Li, Y.; Jiang, J.; Ke, Z.; Liu, Y. *J. Org. Chem.* **2019**, *84*, 458. (c) Ghosh, M. K.; Rajkiewicz, A. A.; Kalek, M. *Synthesis* **2019**, *51*, 359. (d) Xing, L.; Zhang, Y.; Du, Y. *Curr. Org. Chem.* **2019**, *23*, 14. (e) Dohi, T.; Sasa, H.; Dochi, M.; Yasui, C.; Kita, Y. *Synthesis* **2019**, *51*, 1185. (f) Jain, N.; Hein, J. E.; Ciufolini, M. A. *Synlett* **2019**, *30*, 1222. (g) Xing, B.; Ni, C.; Hu, J. *Angew. Chem. Int. Ed.* **2018**, *57*, 9896.
- Singh, F. V.; Mangaonkar, S. R.; Kole, P. B. *Synth. Commun.* **2018**, *48*, 2169.
- Singh, F. V.; Wirth, T. *Chem. Asian J.* **2014**, *9*, 950; and references cited therein.
- Ushakov, D. B.; Gilmore, K.; Seeberger, P. H. *J. Org. Chem.* **1997**, *62*, 7512.
- Denmark, S. E.; Edwards, M. G. *J. Org. Chem.* **2006**, *71*, 7293.
- Singh, F. V.; Rehbein, J.; Wirth, T. *ChemistryOpen* **2012**, *1*, 245.
- Jimenez, D. E. Q.; Ferreira, I. M.; Birolli, W. G.; Fonseca, L. P.; Porto, A. L. M. *Tetrahedron* **2016**, *72*, 7317.
- Sen, B.; Akdere, E. H.; Savk, A.; Gultekin, E.; Parali, O.; Goksu, H.; Sen, F. *Appl. Catal., B* **2018**, *225*, 148.
- Ferreira, J. M. G. O.; de Resende Filho, J. B. M.; Batista, P. K.; Teotonio, E. E. S.; Vale, J. A. *J. Braz. Chem. Soc.* **2018**, *29*, 1382.
- Jiang, W.; Yang, J.; Liu, Y.-Y.; Song, S.-Y.; Ma, J.-F. *Inorg. Chem.* **2017**, *56*, 3036.

- (23) Lolak, N.; Kuyuldar, E.; Burhan, H.; Goksu, H.; Akocak, S.; Sen, F. *ACS Omega* **2019**, *4*, 6848.
- (24) Kharas, G. B.; Russell, S. M.; Cisler, R.; Capen, T. L.; Chlupsa, E. A.; Debellis, L. A.; Duke, J. T. A.; Frazier, C. B.; Gora, A.; Kamenetsky, E.; Kurani, A. S.; Kuta, D. L.; Madison, A. L.; Miramon, P. J. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2008**, *45*, 261.
- (25) Kharas, G. B.; Russell, S. M.; Ward, D. R.; Doshi, R. M.; Hijazin, M. Y.; Korkofigas, E.; Kuzenkova, N.; Leung, B.; Martinez, H.; Merchant, F. A.; Meschbach, N. T.; Opiola, E. S. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2008**, *45*, 133.
- (26) Filho, J. B. M. R.; Pires, G. P.; Ferreira, J. M. G. O.; Teotonio, E. E. S.; Vale, J. A. *Catal. Lett.* **2017**, *147*, 167.
- (27) Mitra, A. K.; De, A.; Karchaudhuri, N. *Synth. Commun.* **1999**, *29*, 2731.
- (28) Meng, D.; Qiao, Y.; Wang, X.; Wen, W.; Zhao, S. *RSC Adv.* **2018**, *8*, 30180.
- (29) Wan, J.-P.; Jing, Y.; Liu, Y.; Sheng, S. *RSC Adv.* **2014**, *4*, 63997.
- (30) Panja, S. K.; Dwivedi, N.; Saha, S. *RSC Adv.* **2015**, *5*, 65626.
- (31) Wang, H.; Li, L.; Bai, X.-F.; Deng, W. H.; Zheng, Z.-J.; Yang, K.-F.; Xu, L.-W. *Green Chem.* **2013**, *15*, 2349.
- (32) Wiles, C.; Watts, P.; Haswell, S. J.; Pombo-Villar, E. *Tetrahedron* **2005**, *61*, 10757.
- (33) Yu, Y.-Q.; Wang, Z.-L. *J. Chin. Chem. Soc.* **2013**, *60*, 288.
- (34) Dev, K.; Maurya, R. *RSC Adv.* **2015**, *5*, 13102.
- (35) Zhang, Y.; Wen, X.; Shi, Y.; Yue, R.; Bai, L.; Liu, Q.; Ba, X. *Ind. Eng. Chem. Res.* **2019**, *58*, 1142.
- (36) Mayer, R. J.; Tokuyasu, T.; Mayer, P.; Gomar, J.; Sabelle, S.; Mennucci, B.; Mayr, H.; Ofial, A. R. *Angew. Chem. Int. Ed.* **2017**, *56*, 13279.
- (37) Mennino, S.; Zullo, L.; Overgaard, J.; Lattanzi, A. *Adv. Synth. Catal.* **2017**, *359*, 913.
- (38) Miao, C.; Yan, X.; Xu, D.; Xia, C.; Sun, W. *Adv. Synth. Catal.* **2017**, *359*, 476.