Synthesis

Mild and Efficient Reductive Deoxygenation of Epoxides to Olefins with Tin(II) Chloride/Sodium Iodide as a Novel Reagent

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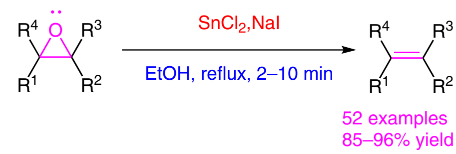

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Abstract A highly efficient and green protocol is reported for the reductive deoxygenation of organic epoxides to olefins using tin(II) chloride/sodium iodide as a novel reagent. The reaction gives an excellent yield (85–96%) in ethanol under reflux within 2–10 minutes, without affecting other functional groups. The advantages of our method are the use of inexpensive reagents, the eco-friendly and green reaction conditions, and the short reaction times and high yields.

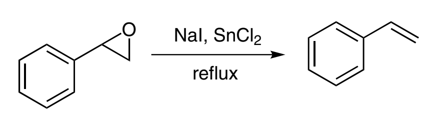
Key words deoxygenation, aliphatic and aromatic epoxides, alkenes, tin(II) chloride/sodium iodide

Epoxidation of organic compounds is well-known in organic and pharmaceutical syntheses as a means to obtain oxygen-containing intermediates.[1] In contrast, the reverse reaction (reductive deoxygenation) of epoxides to alkenes is little known; examples include the use of NaOH/TBAB,[2] $Mo(CO)_6$,[3] $CpTiCl_2$/Mg,[4] Ph_3P,[5] Na/Hg[6] and $NaBH_4$.[7] However, use of these catalysts has some drawbacks, such as low activity, low atom efficiency, tedious workup and moisture-sensitive reaction conditions.

Tin(II) chloride is used as a nontoxic, inexpensive and mild Lewis acid catalyst in diverse organic syntheses. It has mainly been used for the reduction of functional groups, such as nitrile and nitro groups, and as a catalyst in ring cyclization reactions to yield heterocycles (benzoxazoles, quinoxalines, benzimidazoles) and in the allylation of carbonyl compounds.[8] It has also been used as a Lewis acid catalyst for carbon–carbon bond formation, and in the Sonn–Müller reaction, the Stephen reduction,[9] the polymerization of L-lactide and transesterification reactions. Deoxygenation reactions of epoxides to olefins have been reported using $Co(salen)_2$/NaHg,[10] $(EtO)_2P(O)TeNa$,[11] LiI/Amberlyst-15,[12] $LReO_3/Ph_3P$,[13] $MoO(Et_2dtc)_2$[14] and $ZrCl_4$/NaI[1p] reagents, but these methods have drawbacks such as decreased functional group tolerance, lower versatility, low yields, long reaction times and tedious workup. Therefore, the development of simple and efficient reductive deoxygenation methods is of high interest.

In continuation of our interest in Lewis acid/base catalysis[15] and the importance of inexpensive, easily available, and stable catalysts for epoxide ring opening, herein we report a facile and eco-friendly protocol for the reductive deoxygenation of aliphatic and aromatic epoxides to olefins in the presence of a tin(II) chloride/sodium iodide ($SnCl_2$/NaI) combination as a highly efficient catalyst which affords the alkenes in excellent yield (up to 96%) within 2–10 minutes under reflux in ethanol.

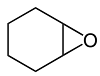
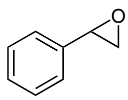
Table 1 Optimization of the Deoxygenation Reaction of Styrene Oxide with $SnCl_2$/NaI



Entry	NaI (equiv)	$SnCl_2$ (equiv)	Solvent	Temp	Time (min)	Yield[a] (%)
1	3	2	DMF	reflux	5	25
2	3	2	THF	reflux	5	10
3	1	2	EtOH	reflux	5	50
4	2	2	EtOH	reflux	5	60
5	**3**	**2**	**EtOH**	**reflux**	**5**	**96**
6	4	2	EtOH	reflux	5	70
7	3	2	NMP	reflux	5	20
8	3	2	DMSO	reflux	5	20

[a] Isolated yield.

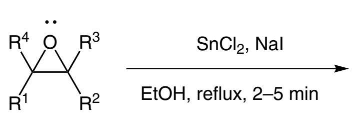
Table 2 Comparison of the $SnCl_2$/NaI Reagent and Reported Methods for the Deoxygenation of Epoxides to Olefins

Substrate	**$SnCl_2$/NaI** (min) [yield (%)]	Co(salen)$_2$/NaHg (h) [yield (%)]	$(EtO)_2P(O)TeNa$ (h) [yield (%)]	LiI/Amberlyst-15 (h) [yield (%)]	$LReO_3/Ph_3P$ (h) [yield (%)]	MoO/(Et$_2$dtc)$_2$ (h) [yield (%)]	$ZrCl_4$/NaI (min) [yield (%)]
	2–5 [95]	6 [95]	42 [88]	–	–	36 [92]	<15 [87]
	2–5 [95]	1 [95]	–	3 [85]	2 [32]	–	<15 [90]

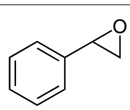
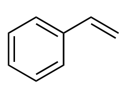
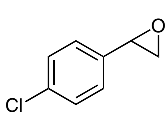
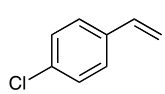
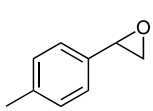
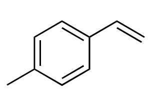
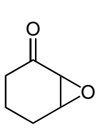
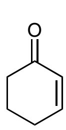
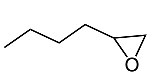
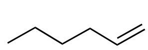
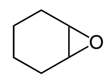
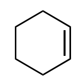
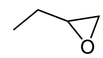
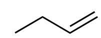
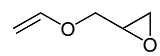
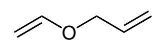
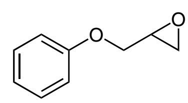
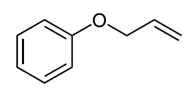
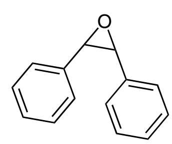
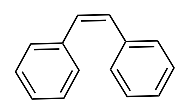
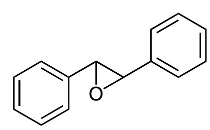
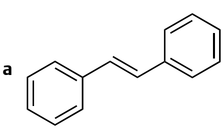
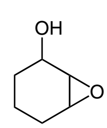
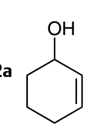
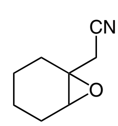
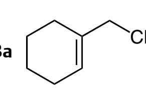
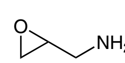
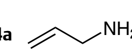
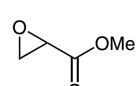
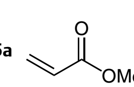
We optimized the deoxygenation reaction conditions for the reaction of styrene oxide (1 equiv) with the novel $SnCl_2$/NaI reagent by varying the molar ratios and the solvent. The product was obtained in excellent yield (96%) within 5 minutes in ethanol under reflux using $SnCl_2$ (2 equiv) and NaI (3 equiv) (Table 1, entry 5). When we increased or decreased the molar ratio of the $SnCl_2$/NaI reagent, or changed the solvent, lower yields were obtained (Table 1).

Our method overcomes the drawbacks of previous reported methods for the deoxygenation of epoxides to olefins: the advantages were highlighted when we compared the various methods (Table 2).

Table 3 Deoxygenation of Aliphatic and Aromatic Epoxides with $SnCl_2$/NaI



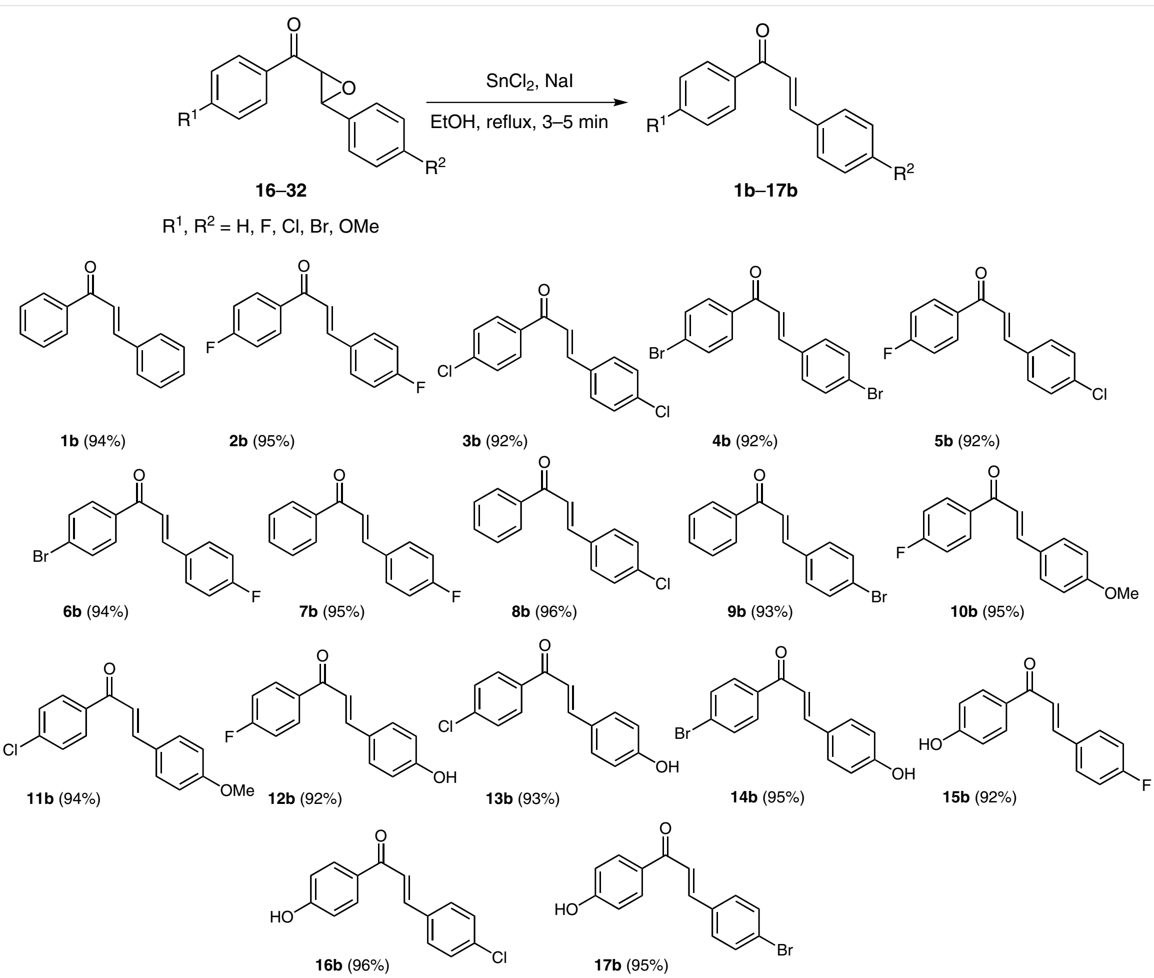
1–15 **1a–15a**

Entry	Epoxide	Time (min)	Product		Yield[a] (%)
1		2	**1a**		96[b]
2		4	**2a**		92
3		5	**3a**		90
4		5	**4a**		88
5		2	**5a**		85
6		3	**6a**		85
7		2	**7a**		88
8		3	**8a**		86
9		5	**9a**		90
10		5	**10a**		85
11		2	**11a**		95
12		3	**12a**		88
13		3	**13a**		85
14		3	**14a**		87
15		3	**15a**		85

[a] Isolated yield; all products were characterized by comparing their physical and chemical properties with authentic samples.[16]
[b] The volatile styrene was isolated by fractional distillation (see Supporting Information).

Under the optimal conditions, the $SnCl_2$/NaI reagent was explored with various aliphatic and aromatic epoxides. As shown in Table 3, the $SnCl_2$/NaI reagent surprisingly gave the products **1a**–**15a** in excellent yield (85–96%) within 2–5 minutes at reflux temperature; various aromatic (entries 1–3, 10 and 11), alicyclic (entries 4, 6, 12 and 13) and aliphatic (entries 5, 7–9, 14 and 15) epoxides were transformed to the corresponding alkenes in excellent yield. Carbonyl, hydroxy and nitrile groups in the deoxygenation of alicyclic epoxides (Table 3, entries 4, 12 and 13) and ether, amine and ester moieties in the aromatic and aliphatic epoxides (Table 3, entries 8, 9, 14 and 15) remained unaffected during the reaction. Our method is also highly stereospecific in nature; for example, the deoxygenation of *cis*-stilbene oxide gave *cis*-stilbene and *trans*-stilbene oxide gave *trans*-stilbene (Table 3, entries 10 and 11), while chemoselectivity was also observed (epoxide ring vs the hydroxy group; Table 3, entry 12). All products were characterized by comparing their physical and chemical properties with authentic samples.[16]

Under the optimal conditions, we converted various chalcone epoxides into chalcones **1b**–**17b** with the novel reagent $SnCl_2$/NaI in excellent yield (92–96%) within 5 minutes at reflux temperature in ethanol, without affecting carbonyl, hydroxy and halogen groups (Scheme 1). As an example, in the ^{1}H NMR spectrum of product **8b** the two characteristic doublet peaks at δ 4.25 and 4.06 ppm (J = 1.5–2 Hz) of the starting epoxide **23** (CHOCH) had disappeared, while two proton peaks for the CH=CH moiety appeared downfield, in the aromatic proton region (δ 6.5–8.0 ppm). In the ^{13}C NMR spectrum of **8b**, the disappearance of the characteristic peaks for the CHOCH group at δ 61.03 and 58.81 ppm and the appearance of two peaks in the downfield region at δ 122.41 and 116.20 ppm, with the carbonyl peak somewhat shifted downfield relative to the corresponding epoxide, indicated deoxygenation to the chalcone. Compounds **1b**–**17b** were further characterized by IR spectroscopy and GC-MS.



Scheme 1 Deoxygenation of chalcone epoxides with $SnCl_2$/NaI

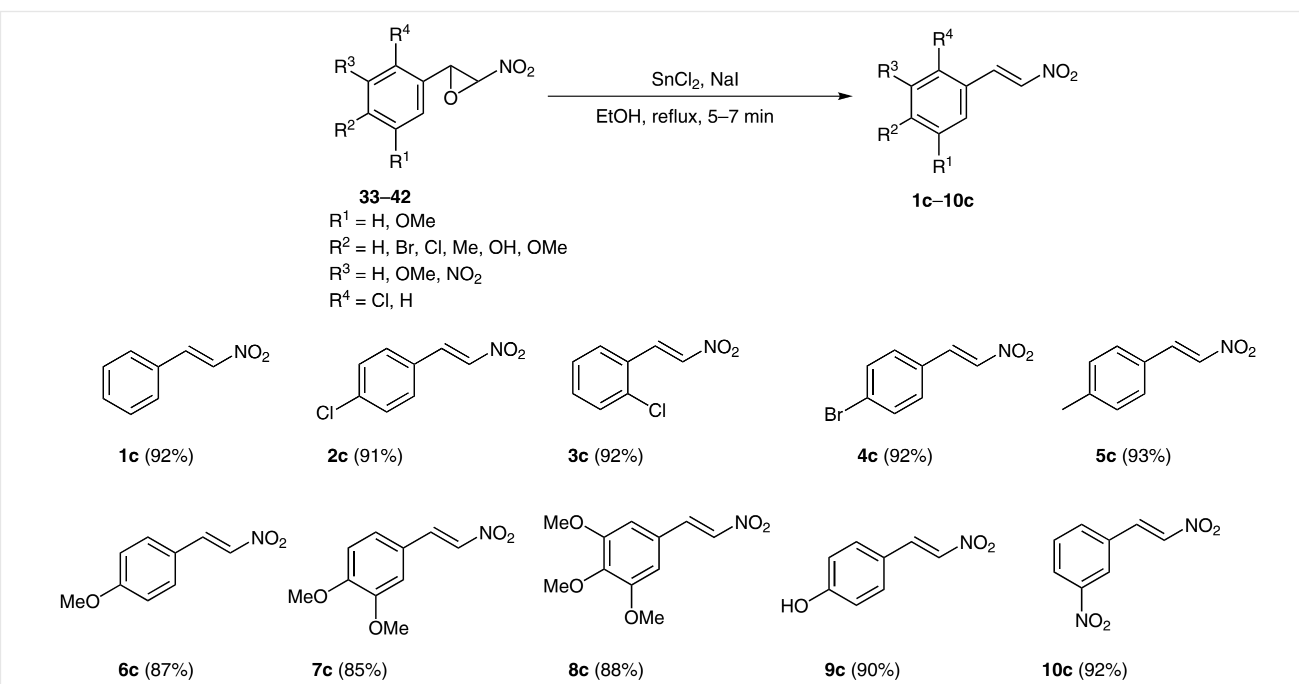
We performed the deoxygenation of various nitrostyrene epoxides with the novel reagent $SnCl_2$/NaI in ethanol to afford products **1c**–**10c** in excellent yield (85–93%) within 7 minutes at reflux temperature (Scheme 2). The products were characterized on the basis of spectroscopic analysis. For example, the ^1H NMR spectrum of product **2c** showed the absence of the two characteristic doublet peaks at δ 5.41 and 3.87 ppm (J = 2.5 Hz) due to the starting epoxide **34** (CHOCHN) and the appearance of peaks for CH=CHN in the aromatic region. Similarly, in the ^{13}C NMR spectrum of **2c**, the absence of the two characteristic peaks at δ 100.18 and 89.26 ppm for CHOCHN of the nitrostyrene epoxide, indicated deoxygenation to the corresponding nitrostyrene. Compounds **1c**–**10c** were further characterized by IR spectroscopy and GC-MS.

We also carried out the deoxygenation of hindered nitrochromene epoxides with the novel reagent $SnCl_2$/NaI in ethanol (Scheme 3). The deoxygenation products **1d**–**10d** were obtained in excellent yield (85–90%) within 10 minutes at reflux temperature, and were characterized spectroscopically. For example, the ^1H NMR spectrum of compound **2d** showed a characteristic singlet peak at δ 8.02 ppm corresponding to $CH=CNO_2$, and the absence of a peak at δ 3.82 ppm in the nitrochromene epoxide indicated the deoxygenation product. Similarly, in the ^{13}C NMR spectrum of **2d**, the characteristic peaks at δ 115.91 and 147.43 ppm of the $C=CNO_2$ carbons indicated deoxygenation to the nitrochromene epoxide. Compounds **1d**–**10d** were further characterized by IR spectroscopy and GC-MS.

In the deoxygenation reactions, a brown color was consistently observed, due to the generation of molecular iodine. Taking this observation into account, we propose a plausible reaction mechanism (Scheme 4). Thus, nucleophilic attack of the oxygen lone-pair electrons of the epoxide at tin(II) chloride liberates a chloride ion, which is followed by epoxide ring opening by iodide ion and removal of molecular iodine to give the corresponding olefin.

In conclusion, we have shown that tin(II) chloride/sodium iodide in ethanol is an efficient reagent for the eliminative deoxygenation reaction of epoxides to olefins in excellent yield (85–96%) within 2–10 minutes. This method is advantageous as inexpensive reagents are used in an eco-friendly and green reaction with high yields, short reaction times and high functional group tolerance.

Organic solvents were dried by standard methods; reagents (chemicals) were purchased from commercial sources, and used without further purification. All reactions were monitored by TLC using precoated silica gel aluminum plates. Visualization of TLC plates was accomplished with a UV lamp. Column chromatography was performed using silica gel 60–120 mesh size (RANKEM Limited) with PE–CH_2Cl_2 as eluent. Melting points were recorded on a Perfit apparatus and are uncorrected. All products were characterized by NMR and IR spectroscopy, and mass spectrometry. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 500 spectrometer operating at 500 MHz and 125 MHz, respectively. Chemical shifts are reported in parts per million (ppm, δ) downfield from TMS. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). IR spectra were recorded on a Thermo Nicolet



Scheme 2 Deoxygenation of nitrostyrene epoxides with $SnCl_2$/NaI

FT-IR spectrophotometer at r.t. GC-MS data were recorded on a Perkin-Elmer instrument using EtOAc as solvent between 80–180 °C oven temperature.

Chromene Epoxides 43–52; General Procedure

Aqueous 5 M NaOH (10 mL) was added dropwise to a stirred solution of a chromene (1.0 mmol) in THF–H_2O (2:1, 30 mL), and the mixture was further stirred for 10 min. Then, H_2O_2 (30 wt %, 15 mL) was added dropwise, and the mixture was further stirred at r.t. for 2 d (TLC monitoring). The reaction mixture was poured into H_2O (20–30 mL), and the resulting precipitate was collected by filtration, washed with H_2O and dried under reduced pressure. The product was recrystallized (EtOH) or subjected to silica gel column chromatography (petroleum ether–CH_2Cl_2, 8:2) to give the chromene epoxide **43–52** in 60–70% yield.

Characterization Data for Selected Synthesized Epoxides

2-Phenyloxirane (1)

Colorless oily liquid; yield: 115 mg (96%); bp 145 °C.

IR (KBr): 2994, 2888 (aromatic C–H str), 1622 (aromatic C=C str), 1263, 1096, 860, 745 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.24 (m, 5 H), 3.83 (t, J = 4.0 Hz, 1 H), 3.12 (t, J = 5.0 Hz, 1 H), 2.77 (dd, J = 7.0, 3.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.68, 128.61, 128.29, 125.59, 52.48, 51.35.

GC-MS: m/z = 120 [M$^+$] (C_8H_8O).

(3-(4-Chlorophenyl)oxiran-2-yl)(phenyl)methanone (23)

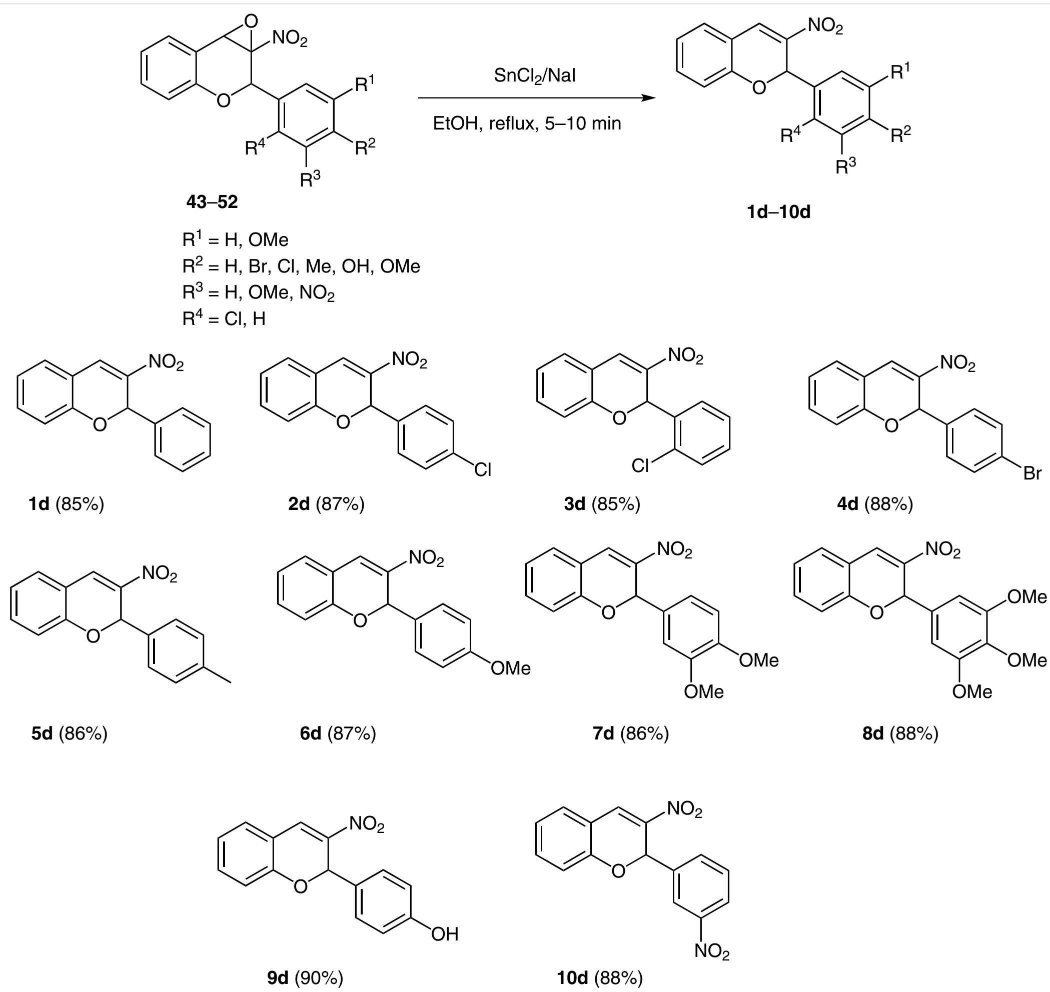
White solid; yield: 247 mg (96%); mp 155 °C.

IR (KBr): 2933, 2877 (aromatic C–H str), 1598 (aromatic C=C str), 1266, 1085, 866, 731 cm^{-1}.

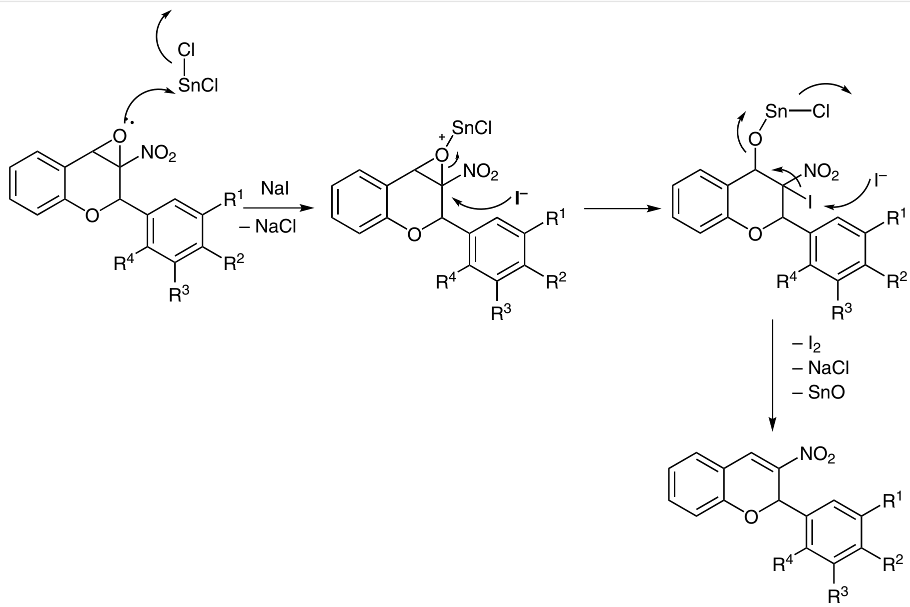
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (dd, J = 8.5, 1.5 Hz, 2 H), 7.62 (d, J = 7.5 Hz, 1 H), 7.49 (t, J = 8.5 Hz, 2 H), 7.37 (t, J = 7.0 Hz, 2 H), 7.30 (dd, J = 8.5, 2.5 Hz, 2 H), 4.25 (d, J = 1.5 Hz, 1 H), 4.06 (d, J = 1.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.83, 135.44, 134.23, 134.11, 129.13, 129.04, 128.45, 127.22, 61.03, 58.81.

GC-MS: m/z = 258 [M$^+$] ($C_{15}H_{11}ClO_2$).



Scheme 3 Deoxygenation of nitrochromene epoxides with $SnCl_2$/NaI



Scheme 4 Plausible mechanism for the deoxygenation of epoxide to olefin with $SnCl_2$/NaI

2-(4-Chlorophenyl)-3-nitrooxirane (34)

Yellow oily liquid; yield: 189 mg (95%); bp 150–152 °C.

IR (KBr): 3118, 3057, 1516, 1339 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.5 Hz, 2 H), 7.26 (d, *J* = 8.5 Hz, 2 H), 5.41 (d, *J* = 2.5 Hz, 1 H), 3.87 (d, *J* = 2.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.00, 132.98, 128.93, 127.36, 100.18, 89.26.

GC-MS: *m/z* = 199 [M^+] ($C_8H_6ClNO_3$).

2-(4-Chlorophenyl)-1a-nitro-1a,7b-dihydro-2*H*-oxireno[2,3-*c*]chromene (44)

Brown oily liquid; yield: 196 mg (65%); bp 160–163 °C.

IR (KBr): 3070, 2925, 1642, 1513, 1329, 1108 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (dd, *J* = 7.0, 2.0 Hz, 2 H), 7.21 (t, *J* = 7.5 Hz, 1 H), 7.11–6.97 (m, 3 H), 6.94 (dd, *J* = 6.5, 2.0 Hz, 2 H), 5.29 (s, 1 H), 3.82 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.61, 134.77, 129.92, 128.99, 128.72, 128.59, 127.21, 122.34, 121.94, 116.91, 111.47, 89.87, 60.67.

GC-MS: *m/z* = 303 [M^+] ($C_{15}H_{10}ClNO_4$).

Deoxygenation of Aliphatic and Aromatic Epoxides 1–15, Chalcone Epoxides 16–32, Nitrostyrene Epoxides 33–42 and Nitrochromene Epoxides 43–52 with Tin(II) Chloride/Sodium Iodide; General Procedure

To a solution of an epoxide (1 mmol) and NaI (3 mmol) in absolute EtOH (5 mL), $SnCl_2$ (2 mmol) was added in several portions. The mixture was stirred at reflux temperature and the progress of the reaction was monitored by TLC. After 2–10 min the reaction mixture was poured into ice–water (a precipitate was obtained), and the mixture was stirred for 10 min. The solid was collected by filtration and dried to give the pure product **2a**–**15a**, **1b**–**17b**, **1c**–**10c** and **1d**–**10d** in 85–96% yield.

Styrene (1a)

Colorless oily liquid; yield: 99 mg (96%); bp 145 °C.

IR (KBr): 3106, 2908, 2839, 1498, 1309 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2 H), 7.35–7.31 (m, 2 H), 7.27–7.24 (m, 1 H), 6.73 (m, 1 H), 5.78 (d, *J* = 1.5 Hz, 1 H), 5.26 (d, *J* = 1.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.63, 136.95, 128.61, 127.89, 126.29, 125.58, 113.91.

GC-MS: *m/z* = 104 [M^+] (C_8H_8).

(*E*)-Chalcone (1b)

Yellow solid; yield: 195 mg (94%); mp 55–57 °C.

IR (KBr): 2935, 2877 (aromatic C–H str), 1585 (aromatic C=C str), 1266, 1088, 862, 733 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2 H), 7.38 (d, *J* = 8.5 Hz, 4 H), 7.30 (d, *J* = 8.5 Hz, 4 H), 7.12 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.70, 144.98, 138.28, 134.96, 132.91, 130.67, 129.07, 128.73, 128.61, 128.56, 122.15.

GC-MS: *m/z* = 208 [M^+] ($C_{15}H_{12}O$).

(*E*)-1,3-Bis(4-fluorophenyl)prop-2-en-1-one (2b)

Yellow solid; yield: 231 mg (95%); mp 56–58 °C.

IR (KBr): 2922, 2875 (aromatic C–H str), 1595 (aromatic C=C str), 1266, 1089, 858, 731 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 1 H), 7.58–7.49 (m, 3 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 6.98 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.47, 165.40, 162.90, 143.65, 138.18, 132.98, 130.50, 130.41, 128.75, 128.57, 128.20, 121.82, 116.35, 116.13.

GC-MS: *m/z* = 244 [M^+] ($C_{15}H_{10}F_2O$).

(*E*)-1,3-Bis(4-chlorophenyl)prop-2-en-1-one (3b)

Yellow solid; yield: 253 mg (92%); mp 56–57 °C.

IR (KBr): 2920 (aromatic C–H str), 1592 (aromatic C=C str), 1406, 1336, 1233, 1125, 1091, 771 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.5 Hz, 2 H), 7.77–7.61 (m, 3 H), 7.46 (d, *J* = 8.5 Hz, 1 H), 7.14–7.09 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.66, 142.59, 136.27, 133.66, 131.56, 130.77, 129.60, 129.29, 122.41, 118.60, 118.19.

GC-MS: *m*/*z* = 278, 276 [M$^+$] ($C_{15}H_{10}Cl_2O$).

(*E*)-1,3-Bis(4-bromophenyl)prop-2-en-1-one (4b)

Yellow solid; yield: 334 mg (92%); mp 55–59 °C.

IR (KBr): 2992, 2886 (aromatic C–H str), 1620 (aromatic C=C str), 1262, 1095, 860, 743 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 9.0 Hz, 2 H), 7.75–7.61 (m, 3 H), 7.45 (d, *J* = 9.0 Hz, 1 H), 7.14–7.08 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.69, 144.98, 138.29, 134.96, 132.91, 130.67, 129.07, 128.74, 128.61, 128.56, 122.16.

GC-MS: *m*/*z* = 366, 364 [M$^+$] ($C_{15}H_{10}Br_2O$).

(*E*)-3-(4-Chlorophenyl)-1-(4-fluorophenyl)prop-2-en-1-one (5b)

Yellow solid; yield: 239 mg (92%); mp 58–59 °C.

IR (KBr): 2931, 2873 (aromatic C–H str), 1597 (aromatic C=C str), 1263, 1081, 860, 737 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.5 Hz, 2 H), 7.74 (d, *J* = 15.5 Hz, 1 H), 7.57 (d, *J* = 8.5 Hz, 2 H), 7.51 (d, *J* = 16.0 Hz, 1 H), 7.38 (d, *J* = 8.5 Hz, 2 H), 6.98 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.69, 161.14, 142.67, 134.07, 132.24, 131.54, 130.78, 130.44, 129.82, 124.64, 122.49, 116.20.

GC-MS: *m*/*z* = 260 [M$^+$] ($C_{15}H_{10}ClFO$).

(*E*)-1-(4-Bromophenyl)-3-(4-fluorophenyl)prop-2-en-1-one (6b)

Yellow solid; yield: 285 mg (94%); mp 60–62 °C.

IR (KBr): 2951, 2880 (aromatic C–H str), 1607 (aromatic C=C str), 1271, 1107, 843, 729 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.5 Hz, 2 H), 7.93–7.75 (m, 1 H), 7.74 (d, *J* = 15.5 Hz, 2 H), 7.57 (d, *J* = 8.5 Hz, 1 H), 7.39–7.30 (m, 2 H), 6.98 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.70, 160.07, 144.98, 138.28, 134.96, 132.91, 130.67, 129.07, 128.73, 128.61, 122.16.

GC-MS: *m*/*z* = 306, 304 [M$^+$] ($C_{15}H_{10}BrFO$).

(*E*)-3-(4-Fluorophenyl)-1-phenylprop-2-en-1-one (7b)

Yellow solid; yield: 214 mg (95%); mp 60–62 °C.

IR (KBr): 2923, 2887 (aromatic C–H str), 1593 (aromatic, C=C str), 1466, 1336, 1263, 1120, 1087, 741 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.0 Hz, 2 H), 7.72 (d, *J* = 15.5 Hz, 1 H), 7.55–7.49 (m, 5 H), 7.26 (d, *J* = 7.0 Hz, 1 H), 6.98 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.66, 161.13, 142.59, 136.27, 133.65, 131.56, 130.76, 129.60, 129.29, 122.40, 116.20.

GC-MS: *m*/*z* = 226 [M$^+$] ($C_{15}H_{11}FO$).

(*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (8b)

Yellow solid; yield: 232 mg (96%); mp 56–57 °C.

IR (KBr): 2992, 2886 (aromatic C–H str), 1620 (aromatic C=C str), 1262, 1095, 860, 743 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9.0 Hz, 2 H), 7.78–7.56 (m, 4 H), 7.53–7.51 (m, 3 H), 7.48–7.26 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.66, 142.59, 136.27, 133.65, 131.57, 130.77, 129.60, 129.29, 122.41, 116.20.

GC-MS: *m*/*z* = 242 [M$^+$] ($C_{15}H_{11}ClO$).

(*E*)-3-(4-Bromophenyl)-1-phenylprop-2-en-1-one (9b)

Yellow solid; yield: 265 mg (93%); mp 55–57 °C.

IR (KBr): 2951, 2880 (aromatic C–H str), 1607 (aromatic C=C str), 1271, 1107, 843, 729 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (t, *J* = 8 Hz, 2 H), 7.72 (d, *J* = 8 Hz, 3 H), 7.56–7.50 (m, 3 H), 7.27 (d, *J* = 7.5 Hz, 1 H), 6.99 (d, *J* = 7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.00, 143.45, 138.09, 133.45, 133.05, 129.69, 129.35, 128.77, 128.59, 122.52, 120.35.

GC-MS: *m*/*z* = 288, 286 [M$^+$] ($C_{15}H_{11}BrO$).

(*E*)-1-(4-Fluorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (10b)

Yellow solid; yield: 243 mg (95%); mp 59–61 °C.

IR (KBr): 2931, 2873 (aromatic C–H str), 1597 (aromatic C=C str), 1263, 1081, 860, 737 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.5 Hz, 2 H), 7.74 (d, *J* = 15.5 Hz, 1 H), 7.58–7.49 (m, 3 H), 7.38 (d, *J* = 8.5 Hz, 2 H), 6.98 (d, *J* = 8.5 Hz, 2 H), 3.88 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.47, 165.40, 162.90, 143.65, 138.18, 132.98, 131.18, 130.50, 130.41, 128.75, 128.57, 128.20, 121.82, 116.35, 116.33, 55.47.

GC-MS: *m*/*z* = 256 [M$^+$] ($C_{16}H_{13}FO_2$).

(*E*)-1-(4-Chlorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (11b)

Yellow solid; yield: 255 mg (94%); mp 58–60 °C.

IR (KBr): 2950 (aromatic C–H str), 1582 (aromatic C=C str), 1389, 1275, 1059, 854, 723 (C–Cl str) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 9.0 Hz, 2 H), 7.73 (d, *J* = 9 Hz, 1 H), 7.57 (d, *J* = 8.5 Hz, 3 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 6.98 (d, *J* = 8.5 Hz, 2 H), 3.83 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.52, 161.94, 145.41, 137.29, 131.95, 130.46, 130.06, 127.72, 127.45, 119.15, 114.55, 55.55.

GC-MS: *m*/*z* = 272 [M$^+$] ($C_{16}H_{13}ClO_2$).

(*E*)-1-(4-Fluorophenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one (12b)

Yellow solid; yield: 222 mg (92%); mp 60–62 °C.

IR (KBr): 3426 (OH str), 2923 (aromatic C–H str), 1591 (aromatic C=C str), 1417, 1395, 1282, 1170, 1092 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8 Hz, 2 H), 7.77 (d, *J* = 15.5 Hz, 1 H), 7.63 (t, *J* = 8.5 Hz, 2 H), 7.47 (d, *J* = 16 Hz, 1 H), 7.11 (t, *J* = 8.5 Hz, 2 H), 6.95 (d, *J* = 8.5 Hz, 2 H), 6.25 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 187.5, 164.68, 162.67, 141.94, 132.02, 131.52, 131.45, 129.53, 122.46, 116.42, 116.25.

GC-MS: *m*/*z* = 242 [M$^+$] ($C_{15}H_{11}FO_2$).

(*E*)-1-(4-Chlorophenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one (13b)

Yellow solid; yield: 239 mg (93%); mp 58–62 °C.

IR (KBr): 3452 (OH str), 2963 (aromatic C–H str), 1599 (aromatic C=C str), 1451, 1419, 1262, 1021, 933, 868, 799, 704 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2 H), 7.77 (d, *J* = 15.5 Hz, 1 H), 7.64–7.58 (m, 2 H), 7.46 (d, *J* = 15.5 Hz, 1 H), 7.10 (t, *J* = 8.5 Hz, 2 H), 6.95 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 187.24, 162.41, 141.68, 131.76, 131.26, 131.19, 129.27, 122.20, 116.16, 115.99.

GC-MS: *m*/*z* = 258 [M^+] ($C_{15}H_{11}ClO_2$).

(*E*)-1-(4-Bromophenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one (14b)

Yellow solid; yield: 286 mg (95%); mp 60–63 °C.

IR (KBr): 3408 (OH str), 2917 (aromatic C–H str), 1589 (aromatic C=C str), 1489, 1415, 1288, 1177, 1091, 1014, 929, 701 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2 H), 7.77 (d, *J* = 15.5 Hz, 1 H), 7.63 (m, 2 H), 7.46 (d, *J* = 15.5 Hz, 1 H), 7.10 (t, *J* = 8.5 Hz, 2 H), 6.95 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 186.98, 162.15, 141.42, 131.51, 131.00, 130.93, 129.02, 121.95, 115.91, 115.74, 115.31.

GC-MS: *m*/*z* = 304, 302 [M^+] ($C_{15}H_{11}BrO_2$).

(*E*)-3-(4-Fluorophenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (15b)

Yellow solid; yield: 222 mg (92%); mp 60–62 °C.

IR (KBr): 3415 (OH str), 2931, 2873 (aromatic C–H str), 1681 (C=O str), 1597 (aromatic C=C str), 1263, 1081, 860, 737 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2 H), 7.77 (d, *J* = 15.5 Hz, 1 H), 7.62 (dd, *J* = 6, 13.5 Hz, 2 H), 7.46 (d, *J* = 15.5 Hz, 1 H), 7.10 (t, *J* = 8 Hz, 2 H), 6.95 (d, *J* = 8.5 Hz, 2 H), 6.24 (br s, 1 H; D_2O exchangeable).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 187.50, 164.68, 162.67, 141.94, 132.02, 131.52, 131.45, 129.53, 122.46, 116.42, 116.25.

GC-MS: *m*/*z* = 242 [M^+] ($C_{15}H_{11}FO_2$).

(*E*)-3-(4-Chlorophenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (16b)

Yellow solid; yield: 247 mg (96%); mp 61–64 °C.

IR (KBr): 3408 (OH str), 2928, 2876 (aromatic C–H str), 1684 (C=O str), 1598 (aromatic C=C str), 1268, 1085, 864, 735 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2 H), 7.76 (d, *J* = 15.5 Hz, 1 H), 7.63–7.61 (m, 2 H), 7.45 (d, *J* = 16 Hz, 1 H), 7.10 (t, *J* = 8.5 Hz, 2 H), 6.94 (d, *J* = 8.5 Hz, 2 H), 6.2 (br s, 1 H; D_2O exchangeable).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 187.20, 162.37, 141.64, 131.72, 131.22, 131.15, 129.23, 122.16, 116.12, 115.95.

GC-MS: *m*/*z* = 258 [M^+] ($C_{15}H_{11}ClO_2$).

(*E*)-3-(4-Bromophenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (17b)

Yellow solid; yield: 286 mg (95%); mp 61–63 °C.

IR (KBr): 3410 (OH str), 2926, 2875 (aromatic C–H str), 1686 (C=O str), 1599 (aromatic C=C str), 1265, 1078, 862, 730 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8 Hz, 2 H), 7.77 (d, *J* = 15.5 Hz, 1 H), 7.63 (t, *J* = 8 Hz, 2 H), 7.46 (d, *J* = 15.5 Hz, 1 H), 7.10 (t, *J* = 8.5 Hz, 2 H), 6.95 (d, *J* = 8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 186.88, 162.05, 141.32, 131.41, 130.90, 130.83, 128.92, 121.85, 115.81, 115.21.

GC-MS: *m*/*z* = 304, 302 [M^+] ($C_{15}H_{11}BrO_2$).

[(*E*)-2-Nitrovinyl]benzene (1c)

Yellow solid; yield: 137 mg (92%); mp 55–57 °C.

IR (KBr): 3106, 3042, 1508, 1341 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 14 Hz, 1 H), 7.59 (d, *J* = 14 Hz, 1 H), 7.57–7.53 (m, 2 H), 7.52–7.48 (m, 1 H), 7.43–7.32 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.54, 136.27, 131.54, 130.77, 129.62, 124.36.

GC-MS: *m*/*z* = 150, 149 [M^+] (100%) ($C_8H_7NO_2$), 148, 132, 125, 104, 92, 74, 60.

1-Chloro-4-[(*E*)-2-nitrovinyl]benzene (2c)

Yellow solid; yield: 166 mg (91%); mp 115–116 °C.

IR (KBr): 3099, 3025, 1590, 1398 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 13.5 Hz, 1 H), 7.58 (d, *J* = 13.5 Hz, 1 H), 7.52–7.51 (m, 2 H), 7.47–7.45 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.30, 136.65, 133.00, 130.92, 129.62, 129.29.

GC-MS: *m*/*z* = 185, 183 [M^+] ($C_8H_6ClNO_2$), 149, 148, 136, 125, 102 (100%), 74, 73.

1-Chloro-2-[(*E*)-2-nitrovinyl]benzene (3c)

Brown solid; yield: 168 mg (92%); mp 40–42 °C.

IR (KBr): 3116, 3056, 1516, 1338 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 13.6 Hz, 1 H), 7.51 (d, *J* = 13.6 Hz, 1 H), 7.47–7.45 (m, 2 H), 6.91–6.89 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.52, 136.27, 133.62, 131.54, 130.77, 129.62, 129.30, 124.36.

GC-MS: *m*/*z* = 185, 183 [M^+] ($C_8H_6ClNO_2$), 149, 148, 136, 125, 102 (100%), 74, 73.

1-Bromo-4-[(*E*)-2-nitrovinyl]benzene (4c)

Light yellow solid; yield: 208 mg (92%); mp 148–150 °C.

IR (KBr): 3102, 3052, 1507, 1331 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 14 Hz, 1 H), 7.60–7.58 (m, 2 H), 7.57 (d, *J* = 14 Hz, 1 H), 7.42–7.40 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.54, 136.27, 133.61, 131.54, 130.71, 129.62, 122.37.

GC-MS: *m*/*z* = 229, 227 [M^+] ($C_8H_6BrNO_2$), 226, 182 (100%), 180, 178, 175.

1-Methyl-4-[(*E*)-2-nitrovinyl]benzene (5c)

Yellow solid; yield: 151 mg (93%); mp 100–102 °C.

IR (KBr): 3110, 3056, 2916, 1496, 1336 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 13.5 Hz, 1 H), 7.57 (d, *J* = 13.5 Hz, 1 H), 7.45–7.43 (m, 2 H), 7.26–7.25 (m, 2 H), 2.41 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.10, 139.54, 136.27, 133.62, 131.54, 130.77, 129.62, 23.10.

GC-MS: m/z = 168, 163 [M$^+$] ($C_9H_9NO_2$), 146, 114, 102, 80 (100%).

1-Methoxy-4-[(*E*)-2-nitrovinyl]benzene (6c)

Yellow solid; yield: 155 mg (87%); mp 86–88 °C.

IR (KBr): 3104, 2904, 2838, 1495, 1307 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, J = 13.5 Hz, 1 H), 7.57 (d, J = 13.5 Hz, 1 H), 7.38–7.35 (m, 1 H), 7.15–7.13 (m, 1 H), 7.05–7.03 (m, 2 H), 3.85 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.12, 139.54, 136.27, 130.77, 122.36, 115.19, 57.45.

GC-MS: m/z = 179 [M$^+$] ($C_9H_9NO_3$), 132, 118, 103, 89 (100%).

1,2-Dimethoxy-4-[(*E*)-2-nitrovinyl]benzene (7c)

Yellow solid; yield: 177 mg (85%); mp 138–140 °C.

IR (KBr): 3128, 2958, 2923, 1500, 1334 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, J = 13.5 Hz, 1 H), 7.53 (d, J = 13.5 Hz, 1 H), 7.18–7.16 (m, 1 H), 7.00–6.91 (m, 2 H), 3.95 (s, 3 H), 3.90 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.87, 149.10, 138.54, 135.27, 122.36, 121.12, 115.89, 115.06, 57.87.

GC-MS: m/z = 209 [M$^+$] ($C_{10}H_{11}NO_4$), 163, 162, 147, 119, 77 (100%).

1,2,3-Trimethoxy-5-[(*E*)-2-nitrovinyl]benzene (8c)

Yellow solid; yield: 210 mg (88%); mp 115–116 °C.

IR (KBr): 3104, 2935, 2832, 1503, 1323 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, J = 13.6 Hz, 1 H), 7.53 (d, J = 13.6 Hz, 1 H), 6.75 (s, 2 H), 3.91 (s, 3 H), 3.90 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.12, 143.62, 137.12, 136.65, 129.87, 106.00, 61.17, 55.76.

GC-MS: m/z = 239 [M$^+$] ($C_{11}H_{13}NO_5$), 191, 176, 149, 120, 63 (100%), 53.

4-[(*E*)-2-Nitrovinyl]phenol (9c)

Yellow solid; yield: 148 mg (90%); mp 162–164 °C.

IR (KBr): 3370, 3108, 1483, 1339 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, J = 13.6 Hz, 1 H), 7.51 (d, J = 13.6 Hz, 1 H), 7.47–7.45 (m, 2 H), 6.91–6.89 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.87, 140.11, 139.52, 130.77, 123.12, 115.10.

GC-MS: m/z = 166, 165 [M$^+$] ($C_8H_7NO_3$), 148, 118 (100%), 91, 65.

1-Nitro-3-[(*E*)-2-nitrovinyl]benzene (10c)

Light brown solid; yield: 178 mg (92%); mp 120–122 °C.

IR (KBr): 3100, 2832, 1522, 1349 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, J = 13.7 Hz, 1 H), 7.56 (d, J = 13.7 Hz, 1 H), 7.50–7.48 (m, 2 H), 7.44–7.43 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.13, 140.10, 139.54, 136.27, 133.61, 130.71, 122.35, 122.12.

GC-MS: m/z = 194 [M$^+$] ($C_8H_6N_2O_4$), 147, 108, 102 (100%), 89, 76, 63.

3-Nitro-2-phenyl-2*H*-chromene (1d)

Yellow solid; yield: 215 mg (85%); mp 98–100 °C.

IR (KBr): 3071, 1646, 1507, 1328, 1215 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.38–7.36 (m, 2 H), 7.33–7.30 (m, 5 H), 7.01–6.98 (m, 1 H), 6.87–6.85 (m, 1 H), 6.58 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.61, 146.47, 141.96, 141.35, 134.47, 130.03, 129.03, 128.85, 127.34, 127.12, 122.96, 122.60, 117.43, 107.37, 79.79.

GC-MS: m/z = 253 [M$^+$] ($C_{15}H_{11}NO_3$), 236, 207, 178 (100%), 152, 89, 77, 63.

2-(4-Chlorophenyl)-3-nitro-2*H*-chromene (2d)

Yellow solid; yield: 249 mg (87%); mp 150 °C.

IR (KBr): 3076, 2923, 1639, 1495, 1323, 1214 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.35–7.27 (m, 6 H), 6.99 (t, J = 7.5 Hz, 1 H), 6.86 (d, J = 8 Hz, 1 H), 6.57 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.96, 147.43, 145.11, 139.90, 128.84, 128.80, 127.33, 126.58, 122.91, 122.55, 117.43, 115.91, 79.47.

GC-MS: m/z = 287 [M$^+$] ($C_{15}H_{10}ClNO_3$), 270, 257, 241 (100%), 205, 178, 89, 77, 63.

2-(2-Chlorophenyl)-3-nitro-2*H*-chromene (3d)

Yellow solid; yield: 243 mg (85%); mp 90–92 °C.

IR (KBr): 3069, 2923, 1644, 1511, 1327, 1107 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.48 (dd, J = 1, 9.5 Hz, 1 H), 7.34 (dd, J = 2, 8 Hz, 1 H), 7.32–7.27 (m, 3 H), 7.19 (dd, J = 2, 8 Hz, 1 H), 7.07 (s, 1 H), 7.00 (dt, J = 1, 9.1 Hz, 1 H), 6.82 (d, J = 8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.61, 146.74, 144.99, 139.94, 134.77, 129.92, 128.99, 128.72, 128.59, 127.21, 122.34, 121.94, 116.91, 114.47, 79.59.

GC-MS: m/z = 289, 287 [M$^+$] ($C_{15}H_{10}ClNO_3$), 270, 257, 241, 205, 176, 146 (100%), 89, 76, 63.

2-(4-Bromophenyl)-3-nitro-2*H*-chromene (4d)

Yellow solid; yield: 291 mg (88%); mp 162 °C.

IR (KBr): 3078, 2923, 1639, 1496, 1323, 1065 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 8.19 (d, J = 8.5 Hz, 1 H), 8.13 (s, 1 H), 7.71 (d, J = 8 Hz, 1 H), 7.52 (t, J = 8 Hz, 1 H), 7.36 (t, J = 7.5 Hz, 2 H), 7.05 (t, J = 7.5 Hz, 1 H), 6.90 (d, J = 8.5 Hz, 1 H), 6.66 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.36, 146.74, 144.02, 141.16, 133.48, 132.27, 128.94, 128.72, 127.36, 124.24, 123.16, 122.48, 117.41, 79.11.

GC-MS: m/z = 333, 331 [M$^+$] ($C_{15}H_{10}BrNO_3$), 287, 285, 205 (100%), 176, 146, 89, 76, 63.

3-Nitro-2-*p*-tolyl-2*H*-chromene (5d)

Yellow solid; yield: 229 mg (86%); mp 136–138 °C.

IR (KBr): 3078, 2924, 1646, 1506, 1321, 1114 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (s, 1 H), 7.32–7.28 (m, 2 H), 7.25–7.24 (m, 2 H), 7.11 (d, J = 8 Hz, 2 H), 6.98 (dt, J = 1, 7.5 Hz, 1 H), 6.84 (dd, J = 1, 7.5 Hz, 1 H), 6.54 (s, 1 H), 2.30 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.68, 148.83, 145.95, 140.06, 131.42, 129.70, 128.80, 127.32, 127.05, 122.86, 122.59, 117.42, 79.71, 21.56.

GC-MS: m/z = 267 [M$^+$] ($C_{16}H_{13}NO_3$), 250, 237, 221 (100%), 178, 146, 91, 77, 65.

2-(4-Methoxyphenyl)-3-nitro-2*H*-chromene (6d)

Yellow solid; yield: 246 mg (87%); mp 158–160 °C.

IR (KBr): 2945, 1645, 1507, 1326, 1179 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.31 (d, J = 7.5 Hz, 2 H), 7.30–7.28 (s, 2 H), 7.02–6.96 (m, 1 H), 6.85–6.80 (m, 3 H), 6.52 (s, 1 H), 3.75 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.78, 153.74, 146.82, 143.94, 128.81, 128.55, 127.34, 126.41, 122.87, 122.62, 117.43, 114.42, 107.42, 79.54, 56.34.

GC-MS: m/z = 283 [M$^+$] ($C_{16}H_{13}NO_4$), 266, 253, 237 (100%), 222, 194, 165, 91, 89, 69.

2-(3,4-Dimethoxyphenyl)-3-nitro-2*H*-chromene (7d)

Yellow solid; yield: 269 mg (86%); mp 86–88 °C.

IR (KBr): 2931, 1645, 1517, 1334, 1145 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.33–7.29 (m, 2 H), 7.01–6.98 (m, 1 H), 6.92 (d, J = 2.05 Hz, 1 H), 6.87–6.84 (m, 2 H), 6.74 (d, J = 8.5 Hz, 1 H), 6.51 (s, 1 H), 3.82 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.67, 150.27, 149.31, 144.79, 141.99, 128.84, 127.35, 126.69, 122.95, 122.61, 119.97, 117.47, 111.20, 109.78, 107.35, 79.77, 57.02.

GC-MS: m/z = 314, 313 [M$^+$] ($C_{17}H_{15}NO_5$), 267 (100%), 251, 223, 177, 122, 91, 77, 63.

3-Nitro-2-(3,4,5-trimethoxyphenyl)-2*H*-chromene (8d)

Yellow solid; yield: 301 mg (88%); mp 130–132 °C.

IR (KBr): 2941, 2832, 1576, 1507, 1329, 1128 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.34 (t, J = 7.5 Hz, 2 H), 7.01 (t, J = 7.5 Hz, 1 H), 6.89 (d, J = 8 Hz, 1 H), 6.56 (s, 2 H), 6.51 (s, 1 H), 3.79 (s, 6 H), 3.75 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.59, 147.49, 145.59, 139.13, 129.75, 128.87, 127.33, 123.05, 122.55, 117.46, 107.20, 104.11, 79.93, 56.87.

GC-MS: m/z = 344, 343 [M$^+$] ($C_{18}H_{17}NO_6$), 313, 297, 207 (100%), 191, 168, 91, 77, 63.

4-(3-Nitro-2*H*-chromen-2-yl)phenol (9d)

Yellow solid; yield: 242 mg (90%); mp 144–146 °C.

IR (KBr): 3069, 2954, 1650, 1515, 1391, 1187 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (s, 1 H), 7.64 (s, 1 H), 7.60–7.57 (m, 2 H), 7.34–7.32 (m, 2 H), 7.29–7.26 (m, 2 H), 7.11–7.09 (m, 2 H), 6.90–6.87 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.38, 147.18, 144.74, 142.09, 136.00, 132.98, 129.31, 128.93, 128.46, 127.36, 123.14, 122.49, 117.40, 79.06.

GC-MS: m/z = 269 [M$^+$] ($C_{15}H_{11}NO_4$), 252, 236, 223 (100%), 165, 131, 89, 77, 65.

3-Nitro-2-(3-nitrophenyl)-2*H*-chromene (10d)

Yellow solid; yield: 262 mg (88%); mp 160–162 °C.

IR (KBr): 3074, 1649, 1520, 1395, 1070 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42–8.41 (m, 1 H), 8.35–8.33 (m, 1 H), 8.32 (s, 1 H), 8.21 (dd, J = 1, 8 Hz, 1 H), 8.06–8.03 (m, 1 H), 7.88 (d, J = 8, 1 Hz, 1 H), 7.77 (d, J = 8 Hz, 1 H), 7.70–7.66 (m, 2 H), 7.61 (t, J = 8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.00, 148.59, 144.68, 142.16, 136.67, 133.14, 130.15, 129.12, 127.40, 124.89, 123.49, 122.34, 122.13, 117.44, 78.56.

GC-MS: m/z = 299, 298 [M$^+$] ($C_{15}H_{10}N_2O_5$), 283, 252, 205 (100%), 176, 130, 102, 76, 63.

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Supporting Information

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