

Ethylenediamine: A Highly Effective Catalyst for One-Pot Synthesis of Aryl Nitroalkenes via Henry Reaction and Dehydration[†]

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Ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) was found to be a highly effective catalyst for the condensation of aryl aldehydes with nitromethane (or nitroethane). When 1%–2% (mol%) of ethylenediamine was used as the catalyst, the one-pot reaction of aryl aldehydes with nitromethane (or nitroethane) by refluxing for 3–10 h efficiently afforded various aryl nitroalkenes **1a**–**1y** in 85%–97% yields.

Keywords ethylenediamine, nitroalkene, nitromethane, nitroethane, aryl aldehyde

Introduction

Nitroalkenes are a kind of extremely important compounds because of the following two reasons. Firstly, nitroalkenes are an important “subunit” which exists in many biologically active molecules.^[1] Secondly, nitroalkenes are versatile intermediates and have found wide applications in organic transformations. For examples, they are excellent acceptors of Michael additions with various nucleophiles,^[2] they are useful dienophiles in the [4+2] cycloadditions;^[3] they can be used as substrates in stepwise or concerted [3+2] cycloadditions;^[4] and they can be reduced to afford some useful nitroalkanes and amines.^[5] Therefore, there is always a demand for more efficient, milder and convenient methods for the synthesis of nitroalkenes.

Generally, nitroalkenes can be obtained by an one-pot or a stepwise procedure via Henry reaction^[6] and the subsequent β -elimination/dehydration of nitroalcohols.^[7] Comparatively, the one-pot methods are obviously more convenient than the stepwise methods. In the literatures, amines,^[8] polymer-supported amines^[9] and ammonium salts^[10] have been explored as the catalyst for one-pot syntheses of nitroalkenes. However, these one-pot syntheses normally suffered from higher catalyst-loading (>20%),^[8,10] bad yields^[8,9a,9b] and inconvenient preparation of polymer-supported catalyst.^[9] It prompted us to reinvestigate the amine-catalyzed condensation of nitroalkanes with carbonyl compounds in order to develop a more efficient method for synthesis of nitroalkenes. We

then reexamined the efficacy of a variety of monoamines and diamines as the catalyst for one-pot synthesis of nitroalkenes via the condensation of nitroalkanes with carbonyl compounds. As a result, we found that ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) is a very effective catalyst for the condensation of nitromethane (or nitroethane) with various aryl aldehydes. Only low catalyst-loading (1%–2%) of ethylenediamine is needed, and yields of various aryl nitroalkenes are very good. Herein we want to report the details of the investigation in this article.

Results and Discussion

When a solution of 3,4-dimethoxy-benzaldehyde in nitromethane was heated to reflux in the presence of catalytic amount of an amine, both nitroalkene **1a** (Table 1) as the major product and the Michael adduct **2** (Scheme 1) as the minor product could be obtained. As can be seen from Table 1, we have tested eighteen amines to observe their effectiveness as a catalyst for the above model reaction. The tested amines include four diamines (Table 1, Entries 1–4), eight primary amines (Table 1, Entries 5–12), four secondary amines (Table 1, Entries 13–16) and two tertiary amines (Table 1, Entries 17, 18). It was found that primary amines worked well for the above model reaction to give nitroalkene **1a** in good yields (Table 1, Entries 1–12), and secondary amines also worked for the above model reaction to give nitroalkene **1a** in moderate yields (Table 1,

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Entries 13–16), whereas tertiary amines did not work at all (Table 1, Entries 17, 18). Diamines are obviously more active than monoamines. Among all the tested amines, ethylenediamine showed the best catalytic power for the model reaction. Only 1% (mol%) catalyst loading of ethylenediamine was needed to effectively catalyze the model reaction to afford nitroalkene **1a** in an excellent yield (Table 1, Entry 1).

Table 1 Reaction of 3,4-dimethoxy-benzaldehyde with nitromethane at reflux in the presence of various amine as a catalyst

Entry	Amine	Loa. ^a (equiv.)	t/h	Yield ^b /%
1		0.01	4	93
2		0.02	4	90
3		0.03	4	86
4		0.03	4	83
5		0.05	4	86
6		0.05	4	83
7		0.05	4	84
8		0.05	4	85
9		0.05	4	82
10		0.05	4	84
11		0.05	4	85
12		0.05	4	82
13		0.05	8	73
14		0.05	8	72
15		0.05	8	60
16		0.05	8	62

Entry	Amine	Loa. ^a (equiv.)	t/h	Yield ^b /%
17		0.10	12	0
18		0.10	12	0

^a Catalysis loading of an amine; ^b isolated yield.

We have also performed the above model reaction under different catalyst loading of ethylenediamine (Figure 1). As can be seen from Figure 1, catalyst loading of ethylenediamine has a dramatic effect on the above model reaction, low catalyst loading (<2%) is crucial for affording a high yield (>90%) of the desired product **1a**. However, when catalyst loading is below 0.8% (0.008 equiv.), the reaction was not complete after refluxing for 4 h even though nitroalkene **1a** became the sole product. Notably, the yield of compound **1a** decreased as the catalyst loading increased. When catalyst loading increased to more than 10%, yield of nitroalkene **1a** dramatically decreased, and yield of the Michael adduct **2** as a side-product was gradually going up. When catalyst loading was more than 20% (mol%), the reaction became complicated, and only afforded the desired product **1a** in a low yield.

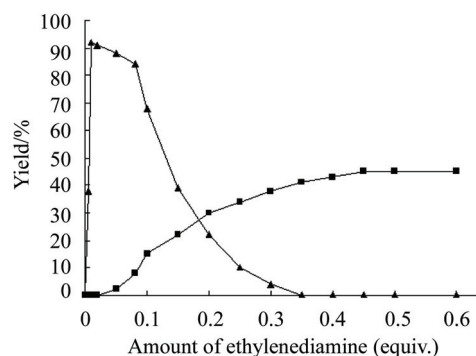
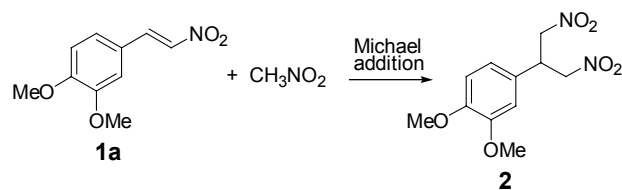


Figure 1 Diagram for the outcomes of reaction of 3,4-dimethoxybenzaldehyde with nitromethane after refluxing for 4 h with various catalyst loadings of ethylenediamine: ▲ represents an yield of nitroalkene **1a**; ■ represents an yield of Michael adduct **2**.

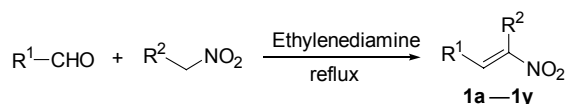
Scheme 1 Formation of by-product **2**



Based on the above study, we envisioned that the above ethylenediamine-catalyzed reaction might provide a general and highly efficient method for synthesis of nitroalkenes. We then attempted the condensation of

various aldehydes with nitromethane (or nitroethane) at reflux with 1%–2% (mol%) of ethylenediamine as the catalyst, and the results are summarized in Table 2.

Table 2 Ethylenediamine-catalyzed condensation of aldehydes with nitromethane or nitroethane at reflux^a



Entry	R ¹	R ²	t/h	1	Yield ^b /%
1	3,4-(OMe) ₂ -Ph	H	4	1a	93
2	3-OMe-4-OEt-Ph	H	4	1b	92
3	3,4-(OCH ₂ O)-Ph	H	4	1c	89
4	4-OMe-Ph	H	3	1d	90
5	3-OMe-Ph	H	4	1e	90
6	4-OEt-Ph	H	3	1f	92
7	3-OEt-Ph	H	4	1g	92
8	2-OEt-Ph	H	4	1h	87
9	4-OBn-Ph	H	3	1i	92
10	3-OMe-4-OH-Ph	H	3	1j	92
11	4-OH-Ph	H	3	1k	91
12	3-Indole	H	3	1l	93
13	4-F-Ph ^c	H	10	1m	85
14	2,4-(Cl) ₂ -Ph ^c	H	10	1n	87
15	3,4-(OMe) ₂ -Ph	Me	3	1o	94
16	3-OMe-4-OEt-Ph	Me	3	1p	97
17	3,4-(OCH ₂ O)-Ph	Me	3	1q	88
18	4-OEt-Ph	Me	3	1r	91
19	3-OEt-Ph	Me	4	1s	86
20	4-OBn-Ph	Me	3	1t	93
21	4-OH-Ph	Me	3	1u	93
22	3-OMe-4-OH-Ph	Me	3	1v	95
23	3-Indole	Me	3	1w	95
24	4-F-Ph ^c	Me	8	1x	86
25	2,4-(Cl) ₂ -Ph ^c	Me	8	1y	85

^aNitromethane or nitroethane was used as the solvent, and 1% or 2% (mol%) of ethylenediamine was used as the catalyst; ^b isolated yield; ^c 2% (mol%) of catalyst loading was needed due to the presence of electron-withdrawing groups.

As can be seen from Table 2, the reaction can be applicable to both electron-rich aryl aldehydes (Table 2, Entries 1–12, 15–23) and electron-deficient aryl aldehydes (Table 2, Entries 13, 14, 24, 25). Fourteen aryl aldehydes were tested for the reaction by using nitromethane as the solvent (Table 2, Entries 1–14), eleven aryl aldehydes were tested for the reaction by using nitroethane as the solvent (Table 2, Entries 15–25). All of these reactions worked very well, as a result, a total of twenty-five aryl nitroalkenes **1a–1y** were obtained in good to excellent yields (85%–97%). Reactions of

electron-deficient aryl aldehydes were obviously slower than electron-rich aryl aldehydes, and thus more catalyst loading (Table 2, Entries 13, 14, 24, 25) was needed. When 4-nitrobenzaldehyde and 3-nitrobenzaldehyde were used as the substrates, the reactions became very slow, only 25%–30% of conversion could be observed even after refluxing overnight.

For all of the reactions of aryl aldehydes with nitromethane (or nitroethane), more thermodynamic stable *trans* (*E*)-nitroalkenes **1a–1y** were obtained, and ¹H NMR spectra showed that there was almost no contamination of less stable *cis* (*Z*)-isomers.

It is worthy to note that the above reaction can not be applicable to aliphatic aldehydes and ketones. It was observed that ethylenediamine-catalyzed condensation of aliphatic aldehydes with nitromethane (or nitroethane) was complicated, affording desired alkyl nitroalkenes in low yields. Ethylenediamine-catalyzed condensation of ketones with nitromethane (or nitroethane) did not work at all even after refluxing for 24 h.

Conclusions

In conclusion, ethylenediamine was found to be a highly effective catalyst for the condensation of aryl aldehydes with nitromethane or nitroethane. Low catalyst loading (1–2 mol%) of ethylenediamine was found to be very crucial for high-yielding synthesis of aryl nitroalkenes. The above ethylenediamine-catalyzed reaction of aryl aldehydes with nitromethane (or nitroethane) might provide a general and efficient method for the synthesis of *trans* (*E*)-aryl nitroalkenes.

Experimental

General methods

¹H and ¹³C NMR spectra were acquired on a Bruker AM-500 (or AM-400) instrument. Chemical shifts were given on the delta scale as parts per million (ppm) with tetramethylsilane (TMS) as the internal standard. IR spectra were recorded on a Nicolet Magna IR-550 spectrometer. MS spectra were recorded on a Shimadzu GC-MS 2010 or a Mariner Mass Spectrum equipment. Melting points were determined on a Mel-TEMP II melting point apparatus. All reagents and solvents were analytically pure, and were used as such as received from the chemical suppliers.

Typical procedure for the ethylenediamine-catalyzed condensation of nitromethane (or nitroethane) with an aryl aldehyde

3,4-Dimethoxy-benzaldehyde (3.325 g, 20.01 mmol) was dissolved in nitromethane (15 mL). A fresh solution of ethylenediamine (0.2 mL, 1 mol/L) was injected by a syringe. The resulting solution was then heated to reflux, and stirring was continued at reflux for around 4 h. The reaction was monitored by TLC (EtOAc/hexane = 1 : 5). After the reaction was complete, the nitromethane was removed by vacuum distillation to give yellowish crys-

tals as crude product, which was then triturated in aqueous methanol (CH₃OH/H₂O=1 : 1, 10 mL). Pale yellow crystals were collected on a Buchner funnel by suction, and rinsed with small amount of aqueous methanol (CH₃OH/H₂O=1 : 1). After drying overnight in a warm air, nitroalkene **1a** (3.896 g, 18.62 mmol) was obtained in 93% yield.

Characterization data of compounds **1a**–**1y** and **2**

(E)-1,2-Dimethoxy-4-(2-nitrovinyl)benzene (1a) Pale yellow crystals, m.p. 140–141 °C (lit.^[1c] 142–144 °C). ¹H NMR (500 MHz, CDCl₃) δ: 3.94 (s, 3H), 3.95 (s, 3H), 6.92 (d, *J*=8.3 Hz, 1H), 7.01 (d, *J*=1.7 Hz, 1H), 7.18 (dd, *J*₁=8.3 Hz, *J*₂=1.7 Hz, 1H), 7.54 (d, *J*=13.6 Hz, 1H), 7.97 (d, *J*=13.6 Hz, 1H); IR (KBr film) *v*: 3130, 3000, 1635, 1600, 1525, 1495, 1340, 1260, 1225, 1160, 1145, 1015, 980, 805, 605 cm⁻¹; MS (EI) *m/z* (%): 209 (100) [M]⁺, 194 (2), 178 (6), 162 (48), 147 (16), 133 (7), 119 (11), 91 (10), 77 (8).

(E)-1-Ethoxy-2-methoxy-4-(2-nitrovinyl)benzene (1b) Yellow crystals, m.p. 148–149 °C. ¹H NMR (400 MHz, CDCl₃) δ: 1.50 (t, *J*=7.0 Hz, 3H), 3.92 (s, 3H), 4.16 (t, *J*=7.0 Hz, 2H), 6.90 (d, *J*=8.3 Hz, 1H), 7.01 (s, 1H), 7.15 (d, *J*=8.3 Hz, 1H), 7.53 (d, *J*=13.5 Hz, 1H), 7.96 (d, *J*=13.5 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ: 152.28, 149.68, 139.46, 135.04, 124.68, 122.56, 112.25, 110.49, 64.55, 56.05, 14.59; IR (KBr film) *v*: 3126, 2981, 1629, 1598, 1516, 1499, 1477, 1337, 1265, 1232, 1168, 1145, 1046, 1030, 981, 803, 617. MS (EI) *m/z* (%): 223 (100) [M]⁺, 224 (11), 195 (7), 176 (11), 149 (11), 148 (49), 133 (18), 117 (6), 105 (7), 89 (11), 77 (7). Anal. calcd for C₁₁H₁₃NO₄: C 59.19, H 5.87, N 6.27; found C 59.34, H 5.98, N 6.04.

(E)-5-(2-Nitrovinyl)benzo[d][1,3]dioxole (1c) Yellow crystals, m.p. 159–160 °C. ¹H NMR (500 MHz, CDCl₃) δ: 6.07 (s, 2H), 6.88 (d, *J*=7.6 Hz, 1H), 7.00 (s, 1H), 7.09 (d, *J*=7.6 Hz, 1H), 7.48 (d, *J*=13.5 Hz, 1H), 7.93 (d, *J*=13.5 Hz, 1H); IR (KBr film) *v*: 3180, 2920, 1630, 1600, 1495, 1450, 1340, 1270, 1245, 1100, 1030, 970, 915, 810, 725 cm⁻¹; MS (EI) *m/z* (%): 193 (100) [M]⁺, 176 (2), 150 (6), 146 (78), 133 (5), 117 (11), 89 (38), 63 (17).

(E)-1-Methoxy-4-(2-nitrovinyl)benzene (1d) Yellow crystals, m.p. 86–87 °C. ¹H NMR (500 MHz, CDCl₃) δ: 3.87 (s, 3H), 6.96 (d, *J*=8.6 Hz, 1H), 7.51 (d, *J*=8.6 Hz, 1H), 7.53 (d, *J*=13.5 Hz, 1H), 7.98 (d, *J*=13.5 Hz, 1H); IR (KBr film) *v*: 3150, 2920, 2830, 1630, 1602, 1515, 1340, 1250, 1170, 1040, 960, 730, 705 cm⁻¹; MS (EI) *m/z* (%): 179 (56) [M]⁺, 162 (5), 148 (3), 132 (100), 121 (17), 103 (7), 89 (30), 77 (24), 63 (19).

(E)-1-Methoxy-3-(2-nitrovinyl)benzene (1e) Yellow crystals, m.p. 93–94 °C. ¹H NMR (400 MHz, CDCl₃) δ: 3.85 (s, 3H), 6.99–7.08 (m, 2H), 7.14 (d, *J*=7.8 Hz, 1H), 7.36 (dd, *J*₁=1.1 Hz, *J*₂=7.8 Hz, 1H), 7.57 (d, *J*=13.7 Hz, 1H), 7.96 (d, *J*=13.7 Hz, 1H); IR (KBr film) *v*: 3112, 1638, 1579, 1515, 1433, 1345, 1275, 1244, 1162, 1045, 965, 840, 784 cm⁻¹; MS (EI) *m/z* (%): 179 (100) [M]⁺, 180 (10), 162 (6), 148 (4), 132 (27),

118 (11), 102 (10), 90 (12), 89 (11), 77 (10), 63 (5).

(E)-1-Ethoxy-4-(2-nitrovinyl)benzene (1f) Yellow crystals, m.p. 115–116 °C. ¹H NMR (400 MHz, CDCl₃) δ: 1.44 (t, *J*=7.0 Hz, 3H), 4.09 (q, *J*=7.0 Hz, 2H), 6.94 (d, *J*=7.9 Hz, 2H), 7.49 (d, *J*=7.9 Hz, 1H), 7.52 (d, *J*=13.6 Hz, 1H), 7.97 (d, *J*=13.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 162.43, 139.15, 134.89, 131.23, 122.33, 115.36, 63.89, 14.64; IR (KBr film) *v*: 3106, 1629, 1601, 1518, 1495, 1339, 1311, 1252, 1177, 1045, 970, 918, 841, 805, 588 cm⁻¹; MS (EI) *m/z* (%): 193 (100) [M]⁺, 194 (12), 164 (2), 148 (11), 146 (50), 119 (19), 118 (79), 107 (17), 96 (7), 91 (22), 77 (6), 65 (14). Anal. calcd for C₁₀H₁₁NO₃: C 62.17, H 5.74, N 7.25; found C 62.39, H 5.57, N 7.31.

(E)-1-Ethoxy-3-(2-nitrovinyl)benzene (1g) Yellow crystals, m.p. 104–105 °C. ¹H NMR (400 MHz, CDCl₃) δ: 1.44 (t, *J*=7.0 Hz, 3H), 4.07 (q, *J*=7.0 Hz, 2H), 7.01–7.06 (m, 2H), 7.12 (d, *J*=7.7 Hz, 1H), 7.28–7.37 (m, 1H), 7.56 (d, *J*=13.6 Hz, 1H), 7.96 (d, *J*=13.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 159.51, 139.12, 137.26, 131.29, 130.40, 121.64, 118.46, 114.57, 63.74, 14.72; IR (KBr film) *v*: 3112, 1632, 1601, 1501, 1486, 1356, 1275, 1246, 1180, 1048, 980, 790 cm⁻¹; MS (EI) *m/z* (%): 193 (100) [M]⁺, 194 (10), 164 (6), 146 (15), 138 (8), 118 (54), 110 (10), 91 (25), 89 (19), 77 (11), 65 (21). Anal. calcd for C₁₀H₁₁NO₃: C 62.17, H 5.74, N 7.25; found C 62.37, H 5.61, N 7.39.

(E)-1-Ethoxy-2-(2-nitrovinyl)benzene (1h) Yellow crystals, m.p. 38–39 °C. ¹H NMR (400 MHz, CDCl₃) δ: 1.53 (t, *J*=7.0 Hz, 3H), 4.17 (q, *J*=7.0 Hz, 2H), 6.92–7.04 (m, 2H), 7.39–7.47 (m, 2H), 7.90 (d, *J*=13.6 Hz, 1H), 8.14 (d, *J*=13.6 Hz, 1H); IR (KBr film) *v*: 3110, 2985, 1628, 1599, 1509, 1450, 1341, 1252, 1040, 966, 756 cm⁻¹; MS (EI) *m/z* (%): 193 (31) [M]⁺, 194 (4), 176 (2), 164 (2), 148 (7), 131 (5), 119 (11), 118 (100), 91 (20), 89 (20), 77 (8), 63 (11).

(E)-1-Benzyloxy-4-(2-nitrovinyl)benzene (1i) Yellow crystals, m.p. 119–120 °C. ¹H NMR (400 MHz, CDCl₃) δ: 5.12 (s, 2H), 7.02 (d, *J*=8.9 Hz, 2H), 7.31–7.45 (m, 5H), 7.46–7.52 (m, 3H), 7.96 (d, *J*=13.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 162.11, 139.00, 136.05, 135.15, 131.25, 128.78, 128.37, 127.54, 122.80, 115.80, 70.26; IR (KBr film) *v*: 3106, 1626, 1598, 1512, 1491, 1341, 1307, 1246, 1175, 1003, 969, 828, 753, 619 cm⁻¹; MS (EI) *m/z* (%): 255 (7) [M]⁺, 134 (1), 117 (1), 92 (7), 91 (100), 89 (2), 65 (4), 63 (1), 51 (1). Anal. calcd for C₁₅H₁₃NO₃: C 70.58, H 5.13, N 5.49; found C 70.36, H 5.41, N 5.32.

(E)-2-Methoxy-4-(2-nitrovinyl)phenol (1j) Yellow crystals, m.p. 163–164 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ: 3.90 (s, 3H), 6.92 (d, *J*=8.2 Hz, 1H), 7.29 (dd, *J*₁=8.2 Hz, *J*₂=1.8 Hz, 1H), 7.45 (d, *J*=1.8 Hz, 1H), 7.89 (d, *J*=13.5 Hz, 1H), 7.99 (d, *J*=13.5 Hz, 1H); IR (KBr film) *v*: 3475, 3050, 2580, 1605, 1520, 1490, 1360, 1295, 1160, 1015, 975, 940, 815, 575 cm⁻¹; MS (EI) *m/z* (%): 195 (100) [M]⁺, 178 (4), 164 (3), 148 (55), 133 (28), 117 (10), 105 (12), 89 (19), 78 (11), 63 (6).

(E)-4-(2-Nitrovinyl)phenol (1k) Yellow crystals, m.p. 165–166 °C. $^1\text{H NMR}$ (500 MHz, acetone- d_6) δ : 6.96 (d, $J=8.6$ Hz, 2H), 7.71 (d, $J=8.6$ Hz, 2H), 7.85 (d, $J=13.5$ Hz, 1H), 8.03 (d, $J=13.5$ Hz, 1H); IR (KBr film) ν : 3365, 3050, 2510, 1598, 1485, 1340, 1280, 1255, 1160, 970, 825, 560 cm^{-1} ; MS (EI) m/z (%): 165 (67) $[\text{M}]^+$, 148 (9), 135 (2), 118 (100), 107 (15), 91 (26), 77 (9), 65 (28).

(E)-3-(2-Nitrovinyl)-1H-indole (1l) Orange crystals, m.p. 170–171 °C. $^1\text{H NMR}$ (500 MHz, acetone- d_6) δ : 7.25–7.36 (m, 2H), 7.56–7.62 (m, 1H), 7.93 (d, $J=13.4$ Hz, 1H), 7.95–8.02 (m, 1H), 8.16 (s, 1H), 8.40 (d, $J=13.4$ Hz, 1H); IR (KBr film) ν : 3410, 3126, 2981, 2520, 1629, 1598, 1517, 1499, 1478, 1336, 1265, 1144, 925, 800, 745 cm^{-1} ; MS (EI) m/z (%): 188 (100) $[\text{M}]^+$, 171 (8), 156 (3), 145 (27), 141 (70), 130 (13), 115 (91), 104 (10), 89 (17), 77 (7), 63 (10). Anal. calcd for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2$: C 63.82, H 4.28, N 14.89; found C 63.66, H 4.41, N 15.12.

(E)-1-Fluoro-4-(2-nitrovinyl)benzene (1m) Pale yellow crystals, m.p. 101–102 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.12–7.18 (m, 2H), 7.51–7.62 (m, 3H), 7.99 (d, $J=13.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 166.21, 163.68, 137.89, 136.87, 131.39, 131.30, 126.36, 126.33, 116.89, 116.67; IR (KBr film) ν : 3113, 1639, 1592, 1507, 1422, 1342, 1231, 1162, 963, 831, 520 cm^{-1} ; MS (EI) m/z (%): 167 (43) $[\text{M}]^+$, 150 (9), 137 (4), 121 (16), 120 (100), 109 (40), 101 (88), 95 (21), 84 (11), 75 (31), 63 (5). Anal. calcd for $\text{C}_8\text{H}_6\text{FNO}_2$: C 57.49, H 3.62, N 8.38; found C 57.36, H 3.81, N 8.19.

(E)-2,4-Dichloro-1-(2-nitrovinyl)benzene (1n) Yellow crystals, m.p. 108–109 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.34 (dd, $J_1=2.0$ Hz, $J_2=8.5$ Hz, 1H), 7.52 (d, $J=2.0$ Hz, 1H), 7.54 (d, $J=8.5$ Hz, 1H), 7.58 (d, $J=13.7$ Hz, 1H), 8.15 (d, $J=13.7$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 139.03, 138.47, 136.66, 133.97, 130.64, 129.32, 128.05, 127.09; IR (KBr film) ν : 3105, 1633, 1587, 1501, 1469, 13587, 1340, 1278, 1105, 971, 816, 786 cm^{-1} ; MS (EI) m/z (%): 217 (50) $[\text{M}]^+$, 218 (5), 184 (33), 182 (100), 172 (47), 170 (71), 154 (30), 152 (87), 136 (53), 99 (44), 83 (7), 75 (16). Anal. calcd for $\text{C}_8\text{H}_5\text{Cl}_2\text{NO}_2$: C 44.07, H 2.31, N 6.42; found C 44.31, H 2.43, N 6.25.

(E)-1,2-Dimethoxy-4-(2-nitroprop-1-enyl)benzene (1o) Yellow crystals, m.p. 73–74 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 2.50 (s, 3H), 3.92 (s, 3H), 3.94 (s, 3H), 6.91–6.98 (m, 2H), 7.14 (dd, $J_1=8.3$ Hz, $J_2=1.5$ Hz, 1H), 8.07 (s, 1H); IR (KBr film) ν : 3128, 2926, 1645, 1600, 1525, 1340, 1284, 1118, 1035, 982, 926, 845, 820, 605 cm^{-1} ; MS (EI) m/z (%): 223 (100) $[\text{M}]^+$, 224 (12), 208 (3), 192 (13), 176 (75), 161 (32), 146 (30), 131 (37), 119 (23), 115 (21), 103 (22), 91 (27), 77 (18), 65 (13).

(E)-1-Ethoxy-2-methoxy-4-(2-nitroprop-1-enyl)benzene (1p) Yellow crystals, m.p. 111–112 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 1.50 (t, $J=7.0$ Hz, 3H), 2.49 (s, 3H), 3.91 (s, 3H), 4.16 (q, $J=7.0$ Hz, 2H), 6.94 (d, $J=8.4$ Hz, 1H), 6.97 (s, 1H), 7.07 (d, $J=8.4$ Hz, 1H), 8.06 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ :

150.22, 149.28, 145.77, 133.91, 124.80, 124.06, 113.40, 112.31, 64.44, 56.05, 14.66, 14.17; IR (KBr film) ν : 2989, 2938, 1649, 1599, 1523, 1498, 1299, 1265, 1141, 1031, 913, 796, 615 cm^{-1} ; MS (EI) m/z (%): 237 (100) $[\text{M}]^+$, 238 (11), 222 (1), 206 (3), 190 (23), 163 (11), 162 (51), 147 (26), 131 (25), 103 (40), 91 (16), 77 (13). Anal. calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_4$: C 60.75, H 6.37, N 5.90; found C 60.54, H 6.48, N 6.13.

(E)-5-(2-Nitroprop-1-enyl)benzo[d][1,3]dioxole (1q) Yellow crystals, m.p. 98–99 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 2.46 (s, 3H), 6.05 (s, 2H), 6.85 (d, $J=8.1$ Hz, 1H), 6.95 (s, 1H), 6.98 (dd, $J_1=8.1$ Hz, $J_2=1.0$ Hz, 1H), 8.02 (s, 1H); IR (KBr film) ν : 3180, 2975, 2920, 1665, 1598, 1525, 1455, 1418, 1328, 1260, 1025, 995, 920, 825 cm^{-1} ; MS (EI) m/z (%): 207 (67) $[\text{M}]^+$, 176 (16), 160 (73), 149 (20), 131 (23), 119 (2), 103 (100), 102 (50), 92 (16), 77 (60), 63 (30).

(E)-1-Ethoxy-4-(2-nitroprop-1-enyl)benzene (1r) Pale yellow crystals, m.p. 74–75 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 1.45 (t, $J=7.0$ Hz, 3H), 2.47 (s, 3H), 4.09 (q, $J=7.0$ Hz, 2H), 6.94 (d, $J=8.4$ Hz, 1H), 6.96 (d, $J=8.8$ Hz, 2H), 7.41 (d, $J=8.8$ Hz, 2H), 8.06 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 160.56, 145.55, 133.69, 132.14, 124.51, 114.94, 63.72, 14.69, 14.11; IR (KBr film) ν : 2983, 1645, 1605, 1519, 1495, 1392, 1300, 1260, 1180, 1097, 984, 919, 845, 587, 529 cm^{-1} ; MS (EI) m/z (%): 207 (86) $[\text{M}]^+$, 208 (10), 191 (2), 177 (3), 161 (15), 160 (100), 149 (6), 133 (83), 132 (83), 131 (69), 121 (39), 105 (56), 77 (57), 63 (15). Anal. calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_3$: C 63.76, H 6.32, N 6.76; found C 63.39, H 6.57, N 6.54.

(E)-1-Ethoxy-3-(2-nitroprop-1-enyl)benzene (1s) Pale yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 1.44 (t, $J=7.0$ Hz, 3H), 2.44 (s, 3H), 4.06 (q, $J=7.0$ Hz, 2H), 6.93 (s, 1H), 6.95 (d, $J=7.8$ Hz, 2H), 6.99 (d, $J=7.8$ Hz, 1H), 7.35 (t, $J=7.9$ Hz, 1H), 8.06 (s, 1H); IR (KBr film) ν : 2989, 2940, 1658, 1597, 1575, 1529, 1442, 1388, 1333, 1274, 1169, 1048, 955, 795, 695 cm^{-1} ; MS (EI) m/z (%): 207 (100) $[\text{M}]^+$, 208 (10), 192 (2), 178 (2), 162 (15), 160 (13), 150 (8), 133 (11), 132 (20), 131 (28), 105 (21), 121 (17), 103 (19), 77 (14).

(E)-1-(Benzyloxy)-4-(2-nitroprop-1-enyl)benzene (1t) Yellow crystals, m.p. 144–145 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 2.45 (s, 3H), 5.11 (s, 2H), 7.03 (d, $J=8.7$ Hz, 2H), 7.31–7.44 (m, 7H), 8.05 (s, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ : 160.27, 145.83, 136.29, 133.56, 132.13, 128.74, 128.27, 127.50, 125.00, 115.37, 70.17, 14.14; IR (KBr film) ν : 2941, 1645, 1602, 1517, 1495, 1386, 1294, 1255, 1178, 1169, 1003, 979, 928, 762, 705, 620 cm^{-1} ; MS (EI) m/z (%): 269 (9) $[\text{M}]^+$, 270 (2), 223 (1), 178 (1), 115 (2), 103 (2), 92 (6), 91 (100), 77 (1), 65 (4). Anal. calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C 71.36, H 5.61, N 5.20; found C 71.53, H 5.47, N 5.36.

(E)-4-(2-Nitroprop-1-enyl)phenol (1u) Yellow crystals, m.p. 123–124 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 2.48 (s, 3H), 5.70 (s, 1H), 6.94 (d, $J=8.7$ Hz, 2H), 7.38 (d, $J=8.7$ Hz, 2H), 8.08 (s, 1H); IR (KBr film) ν : 3300, 2926, 1650, 1600, 1532, 1435, 1288, 1200,

1180, 1190, 988, 835, 525 cm^{-1} ; MS (EI) m/z (%): 179 (61) $[\text{M}]^+$, 162 (7), 149 (4), 132 (100), 133 (20), 131 (69), 121 (33), 115 (21), 103 (36), 89 (7), 77 (36), 63 (9).

(E)-2-Methoxy-4-(2-nitroprop-1-enyl)phenol (1v) Pale yellow crystals, m.p. 99–101 °C. ^1H NMR (500 MHz, CDCl_3) δ : 2.47 (s, 3H), 3.93 (s, 3H), 6.16 (s, 1H), 6.95 (d, $J=1.4$ Hz, 1H), 6.98 (d, $J=8.3$ Hz, 1H), 7.04 (dd, $J_1=8.3$ Hz, $J_2=1.4$ Hz, 1H), 8.04 (s, 1H); IR (KBr film) ν : 3525, 3015, 2950, 1645, 1545, 1500, 1500, 1288, 1178, 1025, 998, 845, 502 cm^{-1} ; MS (EI) m/z (%): 209 (100) $[\text{M}]^+$, 210 (12), 192 (8), 178 (3), 163 (17), 162 (89), 147 (54), 131 (26), 119 (24), 103 (82), 91 (45), 77 (22), 65 (16).

(E)-3-(2-Nitroprop-1-enyl)-1H-indole (1w) Orange crystals, m.p. 188–190 °C. ^1H NMR (500 MHz, CDCl_3) δ : 2.54 (s, 3H), 7.27–7.36 (m, 2H), 7.47 (d, $J=8.0$ Hz, 1H), 7.58 (d, $J=2.4$ Hz, 1H), 7.83 (d, $J=7.8$ Hz, 1H), 8.53 (s, 1H), 8.75 (d, $J=2.4$ Hz, 1H); IR (KBr film) ν : 3400, 3100, 1630, 1575, 1475, 1322, 1280, 1220, 1105, 965, 750 cm^{-1} ; MS (EI) m/z (%): 202 (100) $[\text{M}]^+$, 203 (15), 185 (6), 172 (10), 157 (22), 156 (27), 155 (79), 145 (44), 128 (63), 117 (26), 104 (17), 77 (18), 63 (12). Anal. calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2$: C 65.34, H 4.98, N 13.85; found C 65.52, H 5.07, N 13.96.

(E)-1-Fluoro-4-(2-nitroprop-1-enyl)benzene (1x) Pale yellow crystals, m.p. 64–66 °C. ^1H NMR (400 MHz, CDCl_3) δ : 2.45 (s, 3H), 7.16 (t, $J=8.6$ Hz, 2H), 7.45 (dd, $J_1=5.3$ Hz, $J_2=8.6$ Hz, 2H), 8.05 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 164.67, 162.16, 147.52, 132.45, 132.11, 132.02, 128.54, 128.51, 116.30, 116.08, 13.96; IR (KBr film) ν : 3083, 1651, 1492, 1518, 1500, 1382, 1315, 1229, 1163, 980, 846, 535 cm^{-1} ; MS (EI) m/z (%): 181 (26) $[\text{M}]^+$, 164 (4), 133 (100), 135 (17), 134 (46), 123 (24), 115 (38), 109 (42), 96 (5), 83 (11), 75 (7), 63 (6). Anal. calcd for $\text{C}_9\text{H}_8\text{FNO}_2$: C 59.67, H 4.45, N 7.73; found C 59.63, H 4.30, N 7.86.

(E)-2,4-Dichloro-1-(2-nitroprop-1-enyl)benzene (1y) Yellow crystals, m.p. 83–84 °C. ^1H NMR (400 MHz, CDCl_3) δ : 2.33 (s, 3H), 7.28 (d, $J=8.8$ Hz, 1H), 7.35 (dd, $J_1=2.0$ Hz, $J_2=8.4$ Hz, 1H), 7.51 (d, $J=2.0$ Hz, 1H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 149.56, 136.32, 135.59, 130.95, 129.8, 129.97, 129.49, 127.42, 13.96 (s); IR (KBr film) ν : 3108, 1659, 1588, 1526, 1472, 1390, 1321, 1213, 1110, 1052, 984, 911, 866, 847, 773, 558 cm^{-1} ; MS (EI) m/z (%): 231 (19) $[\text{M}]^+$, 235 (2), 233 (12), 198 (20), 196 (62), 186 (15), 184 (24), 168 (30), 166 (100), 150 (41), 149 (69), 115 (73), 99 (5), 75 (9), 63 (7). Anal. calcd for $\text{C}_9\text{H}_7\text{Cl}_2\text{NO}_2$: C 46.58, H 3.04, N 6.04; found C 46.48, H 3.15, N 6.12.

4-(1,3-Dinitropropan-2-yl)-1,2-dimethoxybenzene (2) White crystals, m.p. 92–93 °C. ^1H NMR (400 MHz, CDCl_3) δ : 3.85 (s, 3H), 3.87 (s, 3H), 4.22–4.28 (m, 1H), 4.70–4.80 (m, 1H), 6.70 (d, $J=2.0$ Hz, 1H), 6.76 (dd, $J_1=2.0$ Hz, $J_2=7.8$ Hz, 1H), 6.84 (d, $J=7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 149.56, 149.45, 126.36, 119.39, 111.74, 110.61, 76.92, 56.01, 55.91, 41.51; IR (KBr film) ν : 3025, 2942, 1565, 1522,

1378, 1263, 1242, 1146, 1020, 863, 811, 653 cm^{-1} ; MS (EI) m/z (%): 270 (100) $[\text{M}]^+$, 250 (4), 223 (38), 194 (35), 178 (53), 164 (54), 151 (26), 146 (39), 131 (14), 121 (16), 103 (26), 91 (42), 77 (27), 63 (7).

Supporting Information

Copies of spectra of ^1H NMR of compounds **1a–1y** and **2**. Copies of spectra of ^{13}C NMR of compounds **1b**, **1f**, **1g**, **1i**, **1m**, **1n**, **1p**, **1r**, **1t**, **1x**, **1y** and **2**.

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