Synthesis of 2-(1-Aryl-2-nitroethyl)-3-arylaminoacrylates via Domino Reaction of Arylamines, Methyl Propiolate, and Nitrostyrenes

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Abstract: An efficient synthetic protocol for 2-(1-aryl-2-nitroethyl)-3-arylaminoacrylates was successfully developed by the one-pot domino reaction of arylamines, methyl propiolate, and nitrostyrenes. The reaction involves the formation of β-enamino ester and its sequential Michael addition to nitrostyrene.

Key words: domino reaction, β-enamino ester, electron-deficient alkyne, nitrostyrene, acrylate

β-Enaminones and β-enamino esters represent important building blocks for the synthesis of a wide variety of heterocycles and pharmaceutical compounds.[1–4] They are readily generated by the direct condensation of β-dicarbonyl compounds with primary and secondary amines.[5] On the other hand, the addition of aliphatic and aromatic amines to activated alkynes having carbonyl groups is also a convenient method for preparation of β-enaminones and β-enamino esters.[6] The obtained β-enaminones and β-enamino esters by this method could react further with sequential addition of nucleophilic or electrophilic reagents to give versatile N,O-heterocycles.[7–9] We have developed several successful new domino reactions by using the in situ formed β-enamino esters derived from the reactions of arylamine with electron-deficient alkynes.[10] Very recently Balalaie and co-workers have reported the synthesis of tetrasubstituted pyrroles by $FeCl_3$-catalyzed three-component reaction of primary amines, dialkyl acetylenedicarboxylates, and β-nitrostyrene derivatives.[11]The publication of this work prompted us to disclose our own findings in this field. Herein, we report the one-pot domino reaction of arylamines, methyl propiolate, and nitrostyrenes for the efficient synthesis of the 2-(1-aryl-2-nitroethyl)-3-arylaminoacrylates.

The desired β-enamino ester was prepared in situ by the reaction of 4-methoxyaniline with methyl propiolate in ethanol at room temperature for overnight according to the previously established reaction conditions.[10] Then, nitrostyrene was added and the resulting mixture was stirred at room temperature for additional 24 hours. After work-up, the polysubstituted acrylate **1a** was obtained in 72% yield. The polysubstituted acrylate obviously comes from the Michael addition of the in situ formed β-enamino ester to nitrostyrene. No further reactions and cyclization processes were observed by prolonging the reaction to several days at room temperature. Trying to carry out the reaction at elevated temperature produces a very complicated mixture due to the decomposition of the polysubstituted acrylate **1a**. The preparation of 2-substituted 3-aminoacrylate and 1-substituted 2-aminoalk-1-enyl ketone derivatives by the reaction of 3-aminoacrylate and alk-1-enyl-2-aminoketone derivatives with nitroethylenes has been already reported.[12] In order to explore the generality and scope of this domino reaction, other nitrostyrenes were used in the reaction under the same conditions. The results are summarized in Table 1. All of the reactions proceeded smoothly to afford the corresponding 2-(1-aryl-2-nitroethyl)-3-arylaminoacrylates **1a–q** in satisfactory yields (70–86%). The substituents with different electronic effects on aromatic aldehydes showed marginal effect to the reactivity. Arylamines with an electron-donating alkyl or methoxy and with the weak electron-withdrawing chloro group reacted efficiently to give the expected products. Arylamines bearing strong electron-withdrawing groups such as nitro group can not react with methyl propiolate to give the desired intermediate β-enamino ester, hence they could not be used in this domino reaction.

The structures of the 2-(1-aryl-2-nitroethyl)-3-arylaminoacrylates **1a–q** were characterized by elemental analyses, ^{1}H and ^{13}C NMR, MS, and IR spectra, and were further confirmed by single-crystal X-ray diffraction performed on the two compounds **1d** and **1g** (Figure 1).[13] The ^{1}H NMR spectra of compounds **1a–q** usually show one triplet and two sets of dd peaks for the $CHAr^1CH_2NO_2$ unit, while the sign of the vinyl proton is usually overlapped with the peaks of protons of the aromatic groups. For example, in the ^{1}H NMR spectrum of **1a**, the one proton of $CHAr^1$ unit shows a triplet at 4.65 ppm with J = 7.8 Hz. The two dd peaks at 4.98 and 4.88 ppm are typical signals of two diasterotopic protons of methylene group (CH_2NO_2). In the single crystal structures of compounds **1d** and **1g**, an intramolecular N–H···O hydrogen bond was formed between the amino group and ester carbonyl group; thus, the arylamino group and the ester group exist in *cis*-position on the C=C double bond. The ^{1}H NMR spectra and the single crystal structures all indicated that the prepared acrylate derivatives **1a–q** exist in the thermodynamically stable *Z*-configuration (arylamino group and the ester group in *cis*-position on the C=C double bond), in which intramolecular hydrogen bonding is possible. It

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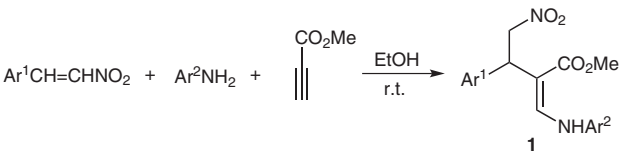
Table 1 Synthesis of Polysubstituted Acrylates via Domino Reactions



Entry	Product	Ar^1	Ar^2	Yield (%)
1	**1a**	Ph	4-$MeOC_6H_4$	72
2	**1b**	4-MeC_6H_4	4-$MeOC_6H_4$	81
3	**1c**	4-*t*-BuC_6H_4	4-$MeOC_6H_4$	82
4	**1d**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	86
5	**1e**	4-FC_6H_4	4-$MeOC_6H_4$	71
6	**1f**	4-ClC_6H_4	4-$MeOC_6H_4$	80
7	**1g**	4-BrC_6H_4	4-$MeOC_6H_4$	70
8	**1h**	4-MeC_6H_4	Ph	81
9	**1i**	Ph	4-MeC_6H_4	77
10	**1j**	4-MeC_6H_4	4-MeC_6H_4	80
11	**1k**	4-$MeOC_6H_4$	4-MeC_6H_4	83
12	**1l**	3-$MeOC_6H_4$	4-MeC_6H_4	80
13	**1m**	4-ClC_6H_4	4-MeC_6H_4	79
14	**1n**	4-BrC_6H_4	4-MeC_6H_4	73
15	**1o**	4-MeC_6H_4	3-MeC_6H_4	76
16	**1p**	4-MeC_6H_4	4-ClC_6H_4	72
17	**1q**	4-*t*-BuC_6H_4	4-ClC_6H_4	78

also means that this domino reaction is a highly stereoselective reaction.

In summary, we have developed a domino reaction of arylamines, methyl propiolate, and nitrostyrenes, and found an efficient and stereoselective protocol for the preparation of 2-(1-aryl-2-nitroethyl)-3-arylaminoacrylates in good yields. This protocol has the advantages of mild reaction conditions, easily accessible starting materials, and easy purification of the products, which makes it a useful and attractive method for the synthesis of the polysubstituted acrylates. The potential uses of the reaction in synthetic and medicinal chemistry might be quite significant.

All reactions were monitored by TLC. Melting points were taken on a hot-plate microscope apparatus. IR spectra were obtained on a Bruker Tensor 27 spectrometer (KBr disc). NMR spectra were recorded with a Bruker AV-600 spectrometer with DMSO-d_6 as solvent and TMS as internal standard (600 and 150 MHz for ^1H and ^{13}C NMR spectra, respectively). Elemental analyses were obtained on Thermo Flash 2000 instrument. HPLC/MS analyses were carried out using a Fennigan LCQ Deca XP MAX instrument. Aromatic aldehydes, arylamines, nitromethane, methyl propiolate, and other reagents are commercial reagents and used as received. Solvents were purified by standard techniques.

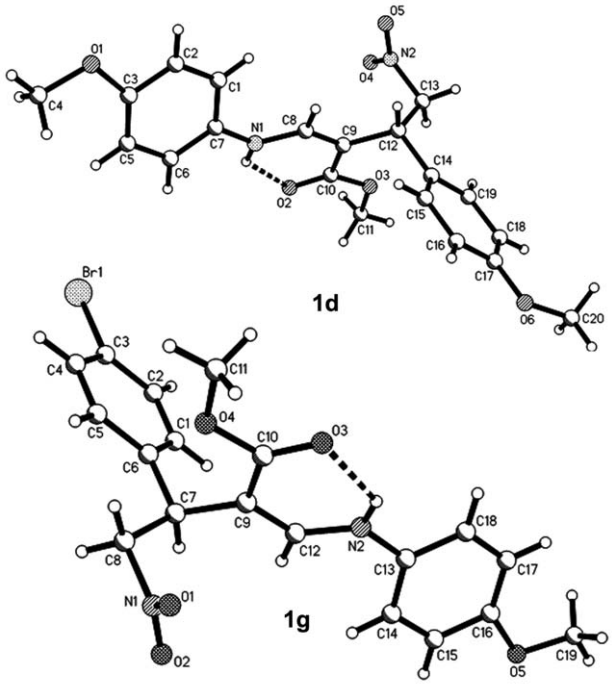


Figure 1 Molecular structures of compounds **1d**,**g**

Domino Reaction of Arylamines, Methyl Propiolate, and Nitrostyrenes; General Procedure

A mixture of arylamine (2.0 mmol) and methyl propiolate (0.168 g, 2.0 mmol) in EtOH (5 mL) was stirred at r.t. overnight. Then, nitrostyrene (2.0 mmol) was added and the solution was stirred at r.t. for an additional 24 h. The resulting precipitate was collected by filtration and washed with cold EtOH to give the pure product (Table 1).

Methyl 2-(2-Nitroethyl-1-phenyl)-3-(4-methoxyphenylamino)acrylate (1a)

Yield: 0.510 g (72%); yellow solid; mp 97–98 °C.

IR (KBr): 3212, 2940, 2837, 1676, 1629, 1545, 1513, 1447, 1378, 1315, 1217, 1129, 1031, 943, 824, 775 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 9.98 (d, *J* = 12.6 Hz, 1 H, NH), 7.33 (t, *J* = 7.8 Hz, 2 H, ArH), 7.26 (d, *J* = 7.2 Hz, 3 H, ArH), 7.05 (d, *J* = 13.2 Hz, 1 H, CH), 6.83–6.79 (m, 4 H, ArH), 4.98 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 7.9 Hz, 1 H, CH), 4.88 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 8.2 Hz, 1 H, CH), 4.65 (t, *J* = 7.8 Hz, 1 H, CH), 3.75 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.2, 155.9, 145.0, 139.1, 134.1, 128.8, 127.6, 127.3, 117.5, 115.0, 96.2, 78.1, 55.6, 51.0, 44.3.

MS: *m*/*z* (%) = 379.38 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{20}N_2O_5$: C, 64.04; H, 5.66; N, 7.86. Found: C, 63.85; H, 5.80; N, 7.51.

Methyl 2-[1-(4-Methylphenyl)-2-nitroethyl]-3-(4-methoxyphenylamino)acrylate (1b)

Yield: 0.598 g (81%); yellow solid; mp 129–130 °C.

IR (KBr): 3302, 3010, 2953, 2838, 1672, 1619, 1546, 1515, 1454, 1374, 1298, 1218, 1038, 952, 821 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.97 (d, *J* = 12.0 Hz, 1 H, NH), 7.14 (br s, 4 H, ArH), 7.05 (d, *J* = 12.6 Hz, 1 H, CH), 6.84–6.80 (m, 4 H, ArH), 4.96 (dd, $^3J_{HH}$ = 12.3 Hz, $^2J_{HH}$ = 7.9 Hz, 1 H, CH), 4.85 (dd, $^3J_{HH}$ = 12.3 Hz, $^2J_{HH}$ = 8.4 Hz, 1 H, CH), 4.62 (t, *J* = 7.8 Hz, 1 H, CH), 3.76 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 2.32 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.3, 155.9, 144.9, 137.0, 135.9, 134.2, 129.5, 127.4, 117.4, 115.0, 96.3, 78.3, 55.6, 51.0, 43.9, 21.0.

MS: *m*/*z* (%) = 393.28 ([M + Na], 100).

Anal. Calcd for $C_{20}H_{22}N_2O_5$: C, 64.85; H, 5.99; N, 7.56. Found: C, 64.70; H, 6.36; N, 7.29.

Methyl 2-[1-(4-*tert*-Butylphenyl)-2-nitroethyl]-3-(4-methoxyphenylamino)acrylate (1c)
Yield: 0.678 g (82%); white solid; mp 122–124 °C.

IR (KBr): 3297, 2959, 1670, 1620, 1551, 1513, 1445, 1372, 1293, 1216, 1031, 948, 828, 787 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.96 (d, *J* = 12.0 Hz, 1 H, NH), 7.34 (d, *J* = 7.8 Hz, 2 H, ArH), 7.18 (d, *J* = 8.4 Hz, 2 H, ArH), 7.05 (d, *J* = 13.2 Hz, 1 H, CH), 6.83–6.79 (m, 4 H, ArH), 4.99 (dd, $^3J_{HH}$ = 12.4 Hz, $^2J_{HH}$ = 8.1 Hz, 1 H, CH), 4.86 (dd, $^3J_{HH}$ = 12.4 Hz, $^2J_{HH}$ = 8.1 Hz, 1 H, CH), 4.62 (t, *J* = 7.8 Hz, 1 H, CH), 3.76 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 1.30 (s, 9 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.3, 155.9, 150.2, 145.0, 136.0, 134.2, 127.2, 125.7, 117.4, 115.0, 96.3, 78.3, 55.6, 51.0, 44.0, 34.5, 31.3.

MS: *m*/*z* (%) = 435.44 ([M + Na], 100).

Anal. Calcd for $C_{23}H_{28}N_2O_5$: C, 66.97; H, 6.84; N, 6.79. Found: C, 66.63; H, 6.57; N, 6.63.

Methyl 2-[1-(4-Methoxyphenyl)-2-nitroethyl]-3-(4-methoxyphenylamino)acrylate (1d)
Yield: 0.662 g (86%); light yellow solid; mp 116–118 °C.

IR (KBr): 3299, 2951, 2837, 1670, 1618, 1549, 1512, 1453, 1371, 1302, 1217, 1032, 951, 830, 778 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.96 (d, *J* = 12.6 Hz, 1 H, NH), 7.18 (d, *J* = 8.4 Hz, 2 H, ArH), 7.03 (d, *J* = 12.6 Hz, 1 H, CH), 6.87 (d, *J* = 9.0 Hz, 2 H, ArH), 6.83–6.79 (m, 4 H, ArH), 4.95 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 7.6 Hz, 1 H, CH), 4.82 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 8.5 Hz, 1 H, CH), 4.62 (t, *J* = 7.8 Hz, 1 H, CH), 3.78 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.2, 158.7, 155.9, 144.8, 134.1, 130.9, 128.7, 117.4, 115.0, 114.9, 114.2, 96.5, 78.4, 55.6, 55.3, 51.0, 43.6.

MS: *m*/*z* (%) = 409.41 ([M + Na], 100).

Anal. Calcd for $C_{20}H_{22}N_2O_6$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.15; H, 6.06; N, 7.11.

Methyl 2-[1-(4-Fluorophenyl)-2-nitroethyl]-3-(4-methoxyphenylamino)acrylate (1e)
Yield: 0.534 g (71%); white solid; mp 78–80 °C.

IR (KBr): 3210, 2944, 2836, 1674, 1629, 1550, 1512, 1447, 1376, 1317, 1225, 1129, 1033, 997, 947, 828, 780 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.97 (d, *J* = 12.6 Hz, 1 H, NH), 7.24–7.22 (m, 2 H, ArH), 7.05–7.01 (m, 3 H, ArH, CH), 6.83–6.81 (m, 4 H, ArH), 4.96 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 7.8 Hz, 1 H, CH), 4.85 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 8.4 Hz, 1 H, CH), 4.62 (t, *J* = 7.8 Hz, 1 H, CH), 3.76 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0, 161.1, 156.0, 144.9, 134.8, 134.0, 129.1, 129.0, 117.5, 115.7, 115.6, 115.0, 96.1, 78.2, 55.6, 51.1, 43.7.

MS: *m*/*z* (%) = 397.54 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{19}FN_2O_5$: C, 60.96; H, 5.12; N, 7.48. Found: C, 60.73; H, 5.40; N, 7.39.

Methyl 2-[1-(4-Chlorophenyl)-2-nitroethyl]-3-(4-methoxyphenylamino)acrylate (1f)
Yield: 0.620 g (80%); light yellow solid; mp 100–102 °C.

IR (KBr): 3297, 2952, 1671, 1619, 1549, 1514, 1452, 1371, 1298, 1219, 1104, 1035, 951, 825 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.97 (d, *J* = 12.6 Hz, 1 H, NH), 7.29 (d, *J* = 8.4 Hz, 2 H, ArH), 7.19 (d, *J* = 8.4 Hz, 2 H, ArH), 7.06 (d, *J* = 12.6 Hz, 1 H, CH), 6.84 (br s, 4 H, ArH), 4.95 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 7.8 Hz, 1 H, CH), 4.85 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 8.2 Hz, 1 H, CH), 4.59 (t, *J* = 7.8 Hz, 1 H, CH), 3.76 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0, 156.0, 144.9, 137.8, 133.9, 133.1, 128.9, 117.6, 115.0, 95.8, 77.9, 55.6, 51.1, 43.9.

MS: *m*/*z* (%) = 413.20 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{19}ClN_2O_5$: C, 58.39; H, 4.90; N, 7.17. Found: C, 58.53; H, 5.27; N, 6.87.

Methyl 2-[1-(4-Bromophenyl)-2-nitroethyl]-3-(4-methoxyphenylamino)acrylate (1g)
Yield: 0.606 g (70%); light yellow solid; mp 138–140 °C.

IR (KBr): 3296, 2952, 1671, 1619, 1550, 1514, 1452, 1371, 1298, 1223, 1035, 950, 825 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.98 (d, *J* = 12.6 Hz, 1 H, NH), 7.46 (d, *J* = 8.4 Hz, 2 H, ArH), 7.14 (d, *J* = 8.4 Hz, 2 H, ArH), 7.06 (d, *J* = 12.6 Hz, 1 H, CH), 6.86–6.83 (m, 4 H, ArH), 4.96 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 7.9 Hz, 1 H, CH), 4.88 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 8.2 Hz, 1 H, CH), 4.57 (t, *J* = 7.8 Hz, 1 H, CH), 3.78 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0, 156.0, 145.0, 138.3, 133.9, 131.9, 129.2, 121.2, 117.6, 115.0, 95.7, 77.9, 55.6, 51.1, 44.0.

MS: *m*/*z* (%) = 458.57 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{19}BrN_2O_5$: C, 52.43; H, 4.40; N, 6.44. Found: C, 52.28; H, 4.76; N, 6.21.

Methyl 2-[1-(4-Methylphenyl)-2-nitroethyl]-3-phenylaminoacrylate (1h)
Yield: 0.554 g (81%); white solid; mp 124–126 °C.

IR (KBr): 3292, 2952, 1673, 1594, 1545, 1506, 1439, 1373, 1307, 1231, 1197, 1148, 996, 944, 829, 751 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.06 (d, *J* = 12.0 Hz, 1 H, NH), 7.27 (t, *J* = 7.8 Hz, 2 H, ArH), 7.16–7.14 (m, 5 H, ArH, CH), 6.99 (t, *J* = 7.2 Hz, 1 H, ArH), 6.86 (d, *J* = 7.8 Hz, 1 H, ArH), 4.96 (dd, $^3J_{HH}$ = 12.4 Hz, $^2J_{HH}$ = 7.9 Hz, 1 H, CH), 4.85 (dd, $^3J_{HH}$ = 12.4 Hz, $^2J_{HH}$ = 8.4 Hz, 1 H, CH), 4.64 (t, *J* = 7.8 Hz, 1 H, CH), 3.74 (s, 3 H, OCH_3), 2.32 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.2, 143.8, 140.5, 137.1, 135.8, 129.8, 129.7, 129.5, 127.5, 127.1, 123.0, 115.8, 115.6, 97.6, 78.2, 51.2, 43.9, 21.0.

MS: *m*/*z* (%) = 363.59 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{20}N_2O_4$: C, 67.05; H, 5.92; N, 8.23. Found: C, 66.84; H, 6.22; N, 8.20.

Methyl 2-(2-Nitroethyl-1-phenyl)-3-(4-methylphenylamino)acrylate (1i)
Yield: 0.522 g (77%); white solid; mp 104–106 °C.

IR (KBr): 3295, 3022, 2956, 1674, 1617, 1549, 1445, 1371, 1303, 1200, 1150, 997, 950, 820, 780 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.01 (d, *J* = 12.6 Hz, 1 H, NH), 7.34–7.32 (m, 2 H, ArH), 7.26–7.23 (m, 3 H, ArH), 7.11 (d, *J* = 12.6 Hz, 1 H, CH), 7.06 (d, *J* = 7.8 Hz, 2 H, ArH), 6.76 (d, *J* = 7.8 Hz, 2 H, ArH), 4.98 (dd, $^3J_{HH}$ = 12.6 Hz, $^2J_{HH}$ = 7.8 Hz, 1 H, CH), 4.88 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 7.2 Hz, 1 H, CH), 4.66 (t, *J* = 7.8 Hz, 1 H, CH), 3.73 (s, 3 H, OCH_3), 2.27 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.1, 144.4, 139.0, 138.1, 132.7, 130.2, 128.8, 127.6, 127.4, 115.9, 96.8, 78.1, 51.1, 44.3, 20.7.

MS: *m*/*z* (%) = 363.46 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{20}N_2O_4$: C, 67.05; H, 5.92; N, 8.23. Found: C, 66.91; H, 6.03; N, 7.84.

Methyl 2-[1-(4-Methylphenyl)-2-nitroethyl]-3-(4-methylphenylamino)acrylate (1j)
Yield: 0.568 g (80%); white solid; mp 126–128 °C.

IR (KBr): 3298, 2950, 1673, 1617, 1545, 1445, 1372, 1304, 1200, 1151, 1051, 999, 948, 812 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.0 (d, *J* = 12.6 Hz, 1 H, NH), 7.14 (br s, 4 H, ArH), 7.11 (d, *J* = 12.6 Hz, 1 H, CH), 7.07 (d, *J* = 7.8 Hz, 2 H, ArH), 6.76 (d, *J* = 8.4 Hz, 2 H, ArH), 4.96 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 7.8 Hz, 1 H, CH), 4.85 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 8.4 Hz, 1 H, CH), 4.63 (t, *J* = 7.8 Hz, 1 H, CH), 3.74 (s, 3 H, OCH_3), 2.32 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.2, 144.3, 138.1, 137.0, 135.9, 132.6, 130.2, 129.5, 127.4, 115.9, 96.9, 78.3, 51.1, 43.9, 21.0, 20.7.

MS: *m*/*z* (%) = 377.39 ([M + Na], 100).

Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.53; H, 6.47; N, 7.5.

Methyl 2-[1-(4-Methoxyphenyl)-2-nitroethyl]-3-(4-methylphenylamino)acrylate (1k)
Yield: 0.614 g (83%); white solid; mp 120–122 °C.

IR (KBr): 3296, 2951, 1670, 1615, 1546, 1513, 1449, 1371, 1303, 1235, 1199, 1152, 1032, 848, 826, 778 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.99 (d, *J* = 11.4 Hz, 1 H, NH), 7.18 (d, *J* = 7.2 Hz, 2 H, ArH), 7.10–7.06 (m, 3 H, ArH, CH), 6.87 (d, *J* = 7.2 Hz, 2 H, ArH), 6.76 (d, *J* = 7.2 Hz, 2 H, ArH), 4.96–4.93 (m, 1 H, CH), 4.84–4.81 (m, 1 H, CH), 4.62 (t, *J* = 7.2 Hz, 1 H, CH), 3.78 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 2.27 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.2, 158.8, 144.2, 138.1, 132.6, 130.8, 130.2, 128.7, 128.4, 115.8, 115.7, 114.4, 114.2, 97.0, 78.4, 55.3, 51.1, 43.6, 20.7.

MS: *m*/*z* (%) = 393.22 ([M + Na], 100).

Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 64.85; H, 5.99; N, 7.56. Found: C, 64.79; H, 6.27; N, 7.44.

Methyl 2-[1-(3-Methoxyphenyl)-2-nitroethyl)-3-(4-methylphenylamino)acrylate (1l)
Yield: 0.589 g (80%); white solid; mp 98–100 °C.

IR (KBr): 2947, 1674, 1617, 1546, 1441, 1378, 1304, 1221, 1125, 1051, 1007, 937, 862, 777 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.01 (d, *J* = 12.6 Hz, 1 H, NH), 7.27–7.25 (m, 1 H, ArH), 7.12 (d, *J* = 12.6 Hz, 1 H, CH), 7.08 (d, *J* = 8.4 Hz, 2 H, ArH), 6.85 (d, *J* = 7.8 Hz, 1 H, ArH), 6.80 (br s, 2 H, ArH), 6.77 (d, *J* = 8.4 Hz, 2 H, ArH), 4.96 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 7.8 Hz, 1 H, CH), 4.88 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 8.3 Hz, 1 H, CH), 4.64 (t, *J* = 7.8 Hz, 1 H, CH), 3.79 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 2.28 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.1, 159.9, 144.4, 140.6, 138.0, 132.7, 130.2, 129.8, 119.6, 115.9, 113.9, 112.4, 96.6, 78.1, 55.3, 51.1, 44.2, 20.7.

MS: *m*/*z* (%) = 393.24 ([M + Na], 100).

Anal. Calcd for $C_{20}H_{22}N_2O_5$: C, 64.85; H, 5.99; N, 7.56. Found: C, 64.65; H, 6.10; N, 7.67.

Methyl 2-[1-(4-Chlorophenyl)-2-nitroethyl]-3-(4-methylphenylamino)acrylate (1m)
Yield: 0.590 g (79%); light yellow solid; mp 116–118 °C.

IR (KBr): 3298, 2951, 1674, 1613, 1548, 1447, 1370, 1305, 1277, 1197, 1149, 1003, 945, 823, 784 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.01 (d, *J* = 12.6 Hz, 1 H, NH), 7.31 (d, *J* = 9.6 Hz, 2 H, ArH), 7.20 (d, *J* = 8.4 Hz, 2 H, ArH), 7.11 (d, *J* = 13.2 Hz, 1 H, CH), 7.09 (d, *J* = 8.4 Hz, 2 H, ArH), 4.96 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 7.8 Hz, 1 H, CH), 4.86 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 8.3 Hz, 1 H, CH), 4.60 (t, *J* = 7.8 Hz, 1 H, CH), 3.73 (s, 3 H, OCH_3), 2.29 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.9, 144.3, 137.9, 137.8, 133.2, 132.9, 130.3, 128.9, 128.8, 116.0, 96.3, 77.9, 51.1, 43.9, 20.7.

MS: *m*/*z* (%) = 397.35 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{19}ClN_2O_4$: C, 60.88; H, 5.11; N, 7.47. Found: C, 60.67; H, 6.32; N, 7.29.

Methyl 2-[1-(4-Bromophenyl)-2-nitroethyl]-3-(4-methylphenylamino)acrylate (1n)
Yield: 0.607 g (73%); white solid; mp 135–136 °C.

IR (KBr): 3298, 2951, 1673, 1614, 1548, 1517, 1485, 1445, 1370, 1304, 1228, 1196, 1150, 1072, 1003, 945, 870, 821, 784 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.0 (d, *J* = 12.6 Hz, 1 H, NH), 7.46 (d, *J* = 8.4 Hz, 2 H, ArH), 7.15–7.11 (m, 3 H, ArH, CH), 7.09 (d, *J* = 8.4 Hz, 2 H, ArH), 6.79 (d, *J* = 7.8 Hz, 2 H, ArH), 4.96 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 7.8 Hz, 1 H, CH), 4.86 (dd, $^3J_{HH}$ = 12.7 Hz, $^2J_{HH}$ = 8.2 Hz, 1 H, CH), 4.56 (t, *J* = 7.8 Hz, 1 H, CH), 3.73 (s, 3 H, OCH_3), 3.29 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.9, 144.3, 138.2, 137.9, 133.0, 131.9, 130.3, 129.2, 121.2, 116.0, 96.2, 77.9, 51.1, 44.0, 20.7.

MS: *m*/*z* (%) = 441.04 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{19}BrN_2O_4$: C, 54.43; H, 4.57; N, 6.68. Found: C, 54.30; H, 4.71; N, 6.35.

Methyl 2-[1-(4-Methylphenyl)-2-nitroethyl)-3-(3-methylphenylamino)acrylate (1o)
Yield: 0.540 g (76%); white solid; mp 105–106 °C.

IR (KBr): 3300, 2919, 1673, 1619, 1586, 1546, 1500, 1439, 1368, 1307, 1208, 1151, 997, 950, 828, 776 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.00 (d, *J* = 12.0 Hz, 1 H, NH), 7.17–7.14 (m, 6 H, ArH, CH), 6.81 (d, *J* = 7.2 Hz, 1 H, =CH), 6.69–6.66 (m, 2 H, ArH), 4.97 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 7.9 Hz, 1 H, CH), 4.86 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 8.3 Hz, 1 H, CH), 4.62 (t, *J* = 7.8 Hz, 1 H, CH), 3.74 (s, 3 H, OCH_3), 2.32 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.1, 143.9, 140.4, 139.7, 137.0, 135.9, 129.5, 129.4, 127.4, 123.9, 116.6, 112.8, 97.3, 78.3, 51.1, 44.0, 21.5, 21.0.

MS: *m*/*z* (%) = 377.33 ([M + Na], 100).

Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.44; H, 6.50; N, 7.65.

Methyl 2-[1-(4-Methylphenyl)-2-nitroethyl)-3-(4-chlorophenylamino)acrylate (1p)
Yield: 0.537 g (72%); white solid; mp 142–144 °C.

IR (KBr): 3304, 2950, 1675, 1624, 1548, 1502, 1452, 1372, 1317, 1227, 1198, 1152, 1001, 944, 823 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.06 (d, *J* = 12.0 Hz, 1 H, NH), 7.23 (d, *J* = 8.4 Hz, 2 H, ArH), 7.14 (br s, 4 H, ArH), 7.07 (d, *J* = 12.0 Hz, 1 H, CH), 6.78 (d, *J* = 8.4 Hz, 2 H, ArH), 4.98–4.95 (m, 1 H, CH), 4.87–4.83 (m, 1 H, CH), 4.62 (t, *J* = 7.8 Hz, 1 H, CH), 3.75 (s, 3 H, OCH_3), 2.33 (s, 3 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.1, 143.4, 139.1, 135.5, 129.7, 129.6, 127.9, 127.4, 116.9, 98.4, 78.2, 51.3, 43.9, 21.0.

MS: *m*/*z* (%) = 397.59 ([M + Na], 100).

Anal. Calcd for $C_{19}H_{19}ClN_2O_4$: C, 60.88; H, 5.11; N, 7.47. Found: C, 60.73; H, 5.45; N, 7.50.

Methyl 2-[1-(4-*tert*-Butylphenyl)-2-nitroethyl]-3-(4-chlorophenylamino)acrylate (1q)

Yield: 0.645 g (78%); white solid; mp 148–150 °C.

IR (KBr): 3404, 3289, 2960, 1669, 1626, 1551, 1500, 1438, 1371, 1227, 1151, 1104, 1005, 940, 823, 786 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.05 (d, *J* = 12.6 Hz, 1 H, NH), 7.35 (d, *J* = 8.4 Hz, 2 H, ArH), 7.22 (d, *J* = 8.4 Hz, 2 H, ArH), 7.18 (d, *J* = 8.4 Hz, 2 H, ArH), 7.07 (d, *J* = 12.0 Hz, 1 H, CH), 6.78 (d, *J* = 8.4 Hz, 2 H, ArH), 4.99 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 8.2 Hz, 1 H, CH), 4.88 (dd, $^3J_{HH}$ = 12.5 Hz, $^2J_{HH}$ = 7.9 Hz, 1 H, CH), 4.62 (t, *J* = 7.8 Hz, 1 H, CH), 3.75 (s, 3 H, OCH_3), 1.30 (s, 9 H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.1, 150.4, 143.4, 139.1, 135.6, 129.7, 127.9, 127.2, 125.8, 116.9, 98.4, 78.1, 51.2, 44.0, 34.5, 31.3.

MS: *m*/*z* (%) = 439.36 ([M + Na], 100).

Anal. Calcd for $C_{22}H_{25}ClN_2O_4$: C, 63.38; H, 6.04; N, 6.72. Found: C, 63.27; H, 6.51; N, 6.49.

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