Samarium(III) Triflate Catalyzed Conjugate Addition of Amines to Electron-Deficient Alkenes[1]

J. S. Yadav,* A. Ramesh Reddy, Y. Gopal Rao, A. V. Narsaiah, B. V. Subba Reddy

Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India
Fax +91(40)27160512

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Abstract: Amines undergo smooth nucleophilic addition to α,β-unsaturated compounds in the presence of a catalytic amount of samarium(III) triflate at ambient temperature to produce the corresponding β-amino compounds in excellent yields. This method is simple, convenient, and works efficiently under mild conditions.

Key words: amines, α,β-unsaturated compounds, conjugate addition, β-amino derivatives

The aza-Michael reaction is widely recognized as one of the most important C–N bond-forming reactions in organic synthesis.[2] β-Amino ketones are versatile building blocks for the synthesis of various complex natural products, antibiotics, β-amino alcohols, and chiral auxiliaries.[3] In recent years, the synthesis of β-amino acid derivatives with various substitution patterns in the carbon chain has become a field of increasing interest in organic synthesis. The most common method for the preparation of β-amino ketones is the Mannich reaction. However, the classical Mannich reaction often suffers from the drawbacks of long reaction times and harsh reaction conditions,[4] which limit its use in the synthesis of complex molecules. An alternative approach for the preparation of β-amino esters is the conjugate addition of amines to α,β-unsaturated ester derivatives. Generally, these reactions are performed under basic or acidic conditions;[5] however, to avoid the side reactions that are normally encountered in the presence of strong acid or base, a number of alternative methods have been developed.[6] In the past years, Lewis acids such as metal halides and metal triflates and microwave-accelerated reactions have been shown as the best promoters for these addition reactions, especially concerning simplicity, atom economy, and efficiency.[7] However, many of these methods involve the use of expensive catalysts, stoichiometric amounts of reagents, poor regioselectivity, and extended reaction times. Therefore, the introduction of a new and efficient protocol for the addition of amines to α,β-unsaturated compounds under mild and convenient conditions is still required. Samarium(III) triflate is well known in the literature as a mild, water-tolerant, and efficient Lewis acid catalyst for various organic transformations.[8]

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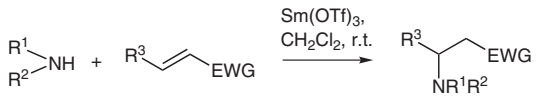
In continuation of our ongoing research program to develop various new synthetic methodologies[9] herein, we wish to disclose our results on conjugate addition of various amines to electron-deficient alkenes using 10 mol% of samarium(III) triflate under mild reaction conditions (Table 1).

In a typical experiment, benzylamine was treated with ethyl acrylate in dichloromethane in the presence of 10 mol% of samarium(III) triflate. The reaction went to completion within two hours and the product, ethyl 3-(benzylamino)propanoate (**3a**) was obtained in 96% yield. In a similar manner, the reaction of benzylamine with acrylonitrile gave the Michael product **3q** in 92% yield. The reaction proceeds smoothly with 10 mol% of the catalyst at room temperature and is completed within 2.5 hours. Encouraged by the results obtained with benzylamine, we turned our attention to various aliphatic, heterocyclic and aromatic amines. Interestingly, various α,β-unsaturated compounds such as ethyl acrylate, acrylonitrile, acrylamide, (*E*)-β-nitrostyrene, chalcone, and methyl vinyl ketone underwent 1,4-addition with a variety of amines to furnish the corresponding β-amino compounds. However, aromatic amines such as aniline and 1-aminonaphthalene failed to produce Michael adducts under these reaction conditions even after a long reaction time (10 h). The reactions are relatively faster with cyclic amines compared to acyclic amines. Similarly, acrylates react more rapidly than other unsaturated systems. In general, the reactions are completed in a short period (1.5–3.5 h) and the products are obtained in high yields ranging from 85% to 96%. In the absence of catalyst, the reactions are slow and the products are obtained in low yields. For example, treatment of pyrrolidine with β-nitrostyrene in the absence of catalyst furnished the corresponding 1,4-adduct **3r** in 20% yield after 24 hours whereas the same reaction in the presence of 10 mol% samarium(III) triflate within 2.5 hours gave the product in 89% yield. In all cases, the reactions proceed smoothly at ambient temperature to give the corresponding Michael adducts in excellent yields. The scope and generality of this process is illustrated with respect to various amines and α,β-unsaturated systems and the results are presented in Table 1.

In conclusion, this article describes an efficient protocol for the conjugate addition of various amines to electron-deficient alkenes to produce β-amino compounds using a catalytic amount of samarium(III) triflate. This method avoids the use of special precautions like stringent reac-

Table 1 Conjugate Addition of Amines to Alkenes Catalyzed by Samarium(III) Triflate



1 2 3

Amine **1**		Alkene **2**		Product	Time	Yield
R^1	R^2	EWG	R^3		(h)	(%)
Bn	H	CO_2Et	H	**3a**	2.0	96
CH_2CH_2Ph	H	CO_2Et	H	**3b**	2.5	93
$-(CH_2)_2O(CH_2)_2-$		CO_2Et	H	**3c**	3.0	92
$-(CH_2)_2NPh(CH_2)_2-$		CO_2Et	H	**3d**	3.5	91
Et	Et	CO_2Et	H	**3e**	1.5	92
4-pyridylmethyl	Et	CO_2Et	H	**3f**	2.0	92
$-(CH_2)_4-$		CO_2Et	H	**3g**	1.5	90
CH(Me)Ph	H	CO_2Et	H	**3h**	2.5	88
$-(CH_2)_2NMe(CH_2)_2-$		CO_2Et	H	**3i**	2.5	89
CH(Pr)Ph	H	CO_2Et	H	**3j**	3.0	86
Bn	Me	CO_2Et	H	**3k**	2.5	89
$-(CH_2)_2O(CH_2)_2-$		CN	H	**3l**	3.0	90
Et	Et	CN	H	**3m**	2.0	89
$-(CH_2)_4-$		CN	H	**3n**	2.0	88
4-pyridylmethyl	Et	CN	H	**3o**	2.5	90
$-(CH_2)_2O(CH_2)_2-$		$CONH_2$	H	**3p**	3.0	85
Bn	H	CN	H	**3q**	2.5	92
$-(CH_2)_4-$		NO_2	Ph	**3r**	2.5	89
Bn	H	COPh	Ph	**3s**	3.5	86
Bn	H	COMe	H	**3t**	2.30	89
$-(CH_2)_4-$		$CONH_2$	H	**3u**	3.0	85
Bn	H	$CONH_2$	H	**3v**	3.5	87
4-pyridylmethyl	Et	NO_2	Ph	**3w**	3.0	86
$-(CH_2)_2O(CH_2)_2-$		NO_2	Ph	**3x**	2.5	88
4-pyridylmethyl	Et	COMe	H	**3y**	2.5	87

tion conditions, stoichiometric amounts of catalyst, and highly toxic reagents. The simple experimental procedure combined with easy of isolation of products makes this method a convenient and general strategy for the aza-Michael reaction.

Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^1H NMR spectra were recorded on a Gemini-200 spectrometer (200 MHz) in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. Column chromatography was performed using E. Merck 60–120 mesh silica gel.

2-Substituted Ethylamines 3; General Procedure

To a mixture of α,β-unsaturated compound **2** (2 mmol) and amine **1** (2 mmol) in CH_2Cl_2 (10 mL) was added $Sm(OTf)_3$ (0.2 mol%) at r.t. The resulting mixture was stirred at the same temperature for a specified period (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction as indicated by TLC, the mixture was diluted with CH_2Cl_2 (20 mL) and washed with H_2O and brine, and the organic layer was dried (anhyd Na_2SO_4) and concentrated under reduced pressure. Thus obtained crude products were purified by column chromatography (silica gel, 60–120 mesh, EtOAc–hexane, 2:8).

Ethyl 3-(Benzylamino)propanoate (3a)

IR (neat): 3254, 3041, 2968, 2837, 1728, 1612, 1591, 1504, 1472, 1355, 1286, 1131, 1058, 1016, 985, 867, 821, 794, 739 cm^{-1}.

^1H NMR: δ = 1.23 (t, *J* = 7.0 Hz, 3 H), 2.15 (br s, 1 H), 2.50 (t, *J* = 6.2 Hz, 2 H), 2.85 (t, *J* = 6.2 Hz, 2 H), 3.70 (s, 2 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 7.22–7.40 (m, 5 H).

MS (EI): *m/z* (%) = 207 (M^+, 25), 178 (18), 134 (100), 106 (31), 77 (56), 52 (15)

Ethyl 3-(Phenethylamino)propanoate (3b)

Colorless liquid.

IR (neat): 3430, 3027, 2930, 2852, 1730, 1601, 1457, 1375, 1253, 1171, 1121, 1030, 748, 699, 638, 580 cm^{-1}.

^1H NMR: δ = 1.23 (t, *J* = 6.5 Hz, 3 H), 2.15 (s, 1 H), 2.47 (t, *J* = 6.0 Hz, 2 H), 2.75–2.95 (m, 6 H), 4.10 (q, *J* = 6.0 Hz, 4 H), 7.12–7.30 (m, 5 H).

MS (EI): *m/z* (%) = 221 (95), 220 (10), 209 (20), 208 (100), 205 (10), 160 (12) 140 (10), 102 (10), 88 (10), 73 (13).

Ethyl 3-(4-Phenylpiperazin-1-yl)propanoate (3d)

IR (neat): 3444, 2975, 2821, 1930, 1732, 1618, 1599, 1500, 1455, 1380, 1231, 1056, 1015, 927, 864, 760, 694 cm^{-1}.

^1H NMR: δ = 1.26 (t, *J* = 7.0 Hz, 3 H), 2.45–2.55 (m, 8 H), 2.68 (t, *J* = 7.5 Hz, 2 H), 3.48 (s, 2 H), 4.12 (q, *J* = 7.0 Hz, 2 H), 7.18–7.30 (m, 5 H).

MS (EI): *m/z* (%) = 262 (M^+, 40), 233 (21), 189 (100), 161 (15), 119 (26), 91 (10), 84 (36), 77 (85), 65 (14), 52 (12), 42 (20).

Ethyl 3-{*N*-Ethyl-*N*-[(pyridine-4-yl)methyl]amino}propanoate (3f)

Brown liquid.

IR (neat): 3440, 3051, 2943, 2837, 1728, 1645, 1605, 1573, 1461, 1339, 1258, 1169, 1108, 1071, 968, 842, 741 cm^{-1}.

^1H NMR: δ = 1.08 (t, *J* = 6.5 Hz, 3 H), 1.26 (t, *J* = 6.5 Hz, 3 H), 2.40–2.60 (m, 4 H), 2.81 (t, *J* = 6.0 Hz, 2 H), 3.60 (s, 2 H), 4.15 (q, *J* = 6.5 Hz, 2 H), 7.24 (d, *J* = 6.0 Hz, 2 H), 8.58 (d, *J* = 6.0 Hz, 2 H).

MS (EI): *m/z* (%) = 236 (M^+, 15), 207 (18), 163 (100), 135 (32), 134 (20), 106 (45) 78 (25), 53 (15), 40 (10).

Ethyl 3-(Pyrrolidin-1-yl)propanoate (3g)

Light red liquid.

IR (neat): 3432, 2928, 1727, 1630, 1518, 1458, 1343, 1216, 1163, 1108, 1024, 961, 845, 761, 732 cm^{-1}.

^1H NMR: δ = 1.30 (t, *J* = 7.5 Hz, 3 H), 1.78–1.88 (m, 4 H), 2.48–2.60 (m, 6 H), 2.82 (t, *J* = 7.5 Hz, 2 H), 4.15 (q, *J* = 7.5 Hz, 2 H).

MS (EI): *m/z* (%) = 171 (M^+, 20), 142 (25), 98 (100), 70 (15), 46 (10).

Ethyl 3-(1-Phenylethylamino)propanoate (3h)
Liquid.

IR (neat): 3446, 3062, 3027, 2973, 2929, 2863, 1731, 1451, 1373, 1256, 1182, 1121, 1029, 953, 861, 760 cm^{-1}.

^1H NMR: δ = 1.25 (t, *J* = 6.5 Hz, 3 H), 1.32 (d, *J* = 6.0 Hz, 3 H), 1.85 (br s, 1 H), 2.42 (t, *J* = 6.0 Hz, 2 H), 2.60–2.80 (m, 2 H), 3.75 (q, *J* = 6.5 Hz, 1 H), 4.12 (q, *J* = 6.5 Hz, 2 H), 7.15–7.30 (m, 5 H).

MS (EI): *m/z* (%) = 221 (M^+, 10), 207 (80), 179 (10), 161 (12), 135 (20), 119 (55), 106 (100), 92 (25), 78 (32), 51 (40), 43 (35).

Ethyl 3-(4-Methylpiperazin-1-yl)propanoate (3i)
Light yellow liquid.

IR (neat): 3418, 2936, 2800, 1735, 1508, 1459, 1410, 1372, 1287, 1206, 1183, 1115, 1088, 1010, 961, 836, 795, 742 cm^{-1}.

^1H NMR: δ = 1.25 (t, *J* = 6.5 Hz, 3 H), 2.25 (s, 3 H), 2.38–2.55 (m, 10 H), 2.68 (t, *J* = 6.0 Hz, 2 H), 4.15 (q, *J* = 6.5 Hz, 2 H).

MS (EI): *m/z* (%) = 200 (M^+, 100), 171 (12), 127 (40), 99 (10), 84 (10), 56 (10).

Ethyl 3-(*N*-Phenyl-*N*-propylamino)propanoate (3j)
Colorless liquid.

IR (neat): 3432, 3051, 2942, 2839, 1730, 1605, 1570, 1462, 1378, 1259, 1170, 1125, 1034, 952, 840, 739 cm^{-1}.

^1H NMR: δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.35 (t, *J* = 7.0 Hz, 3 H), 1.50–1.70 (m, 2 H), 2.36–2.42 (m, 2 H), 2.60–2.70 (m, 2 H), 3.55 (t, *J* = 6.0 Hz, 1 H), 4.10 (q, *J* = 7.0 Hz, 2 H), 7.20–7.35 (m, 5 H).

MS (EI): *m/z* (%) = 249 (M^+, 100), 220 (22), 176 (45), 148 (24), 119 (15), 104 (10), 77 (62), 51 (20).

Ethyl 3-(*N*-Benzyl-*N*-methylamino)propanoate (3k)
Colorless liquid.

IR (neat): 3424, 3052, 2926, 2843, 1735, 1587, 1458, 1386, 1212, 1123, 1029, 745, 700, 604 cm^{-1}.

^1H NMR: δ = 1.27 (t, *J* = 7.5 Hz, 3 H), 2.18 (s, 3 H), 2.50 (t, *J* = 7.5 Hz, 2 H), 2.72 (t, *J* = 7.5 Hz, 2 H), 3.50 (s, 2 H), 4.12 (q, *J* = 7.5 Hz, 2 H), 7.15–7.30 (m, 5 H).

MS (EI): *m/z* (%) = 222 (M^+, 100), 216 (20), 194 (12), 149 (10), 134 (20), 121 (12), 92 (15), 77 (15), 66 (10), 51 (35).

Ethyl 3-(Morpholin-4-yl)propanoate (3l)
IR (neat): 2841, 1722, 1615, 1592, 1506, 1463, 1410, 1376, 1230, 1108, 1036, 1005, 981, 912, 871, 824, 766, 742, 691 cm^{-1}.

^1H NMR: δ = 1.30 (t, *J* = 7.0 Hz, 3 H), 2.45–2.52 (m, 6 H), 2.68 (t, *J* = 6.8 Hz, 2 H), 3.70 (t, *J* = 4.5 Hz, 4 H), 4.20 (q, *J* = 7.0 Hz, 2 H).

MS (EI): *m/z* (%) = 187 (M^+, 18), 158 (22), 114 (100), 86 (15), 58 (30).

3-{*N*-Ethyl-*N*-[(pyridin-4-yl)methyl]amino}propanenitrile (3o)
Liquid.

IR (neat): 3445, 3056, 2927, 2350, 1637, 1416, 1217, 1080, 761 cm^{-1}.

^1H NMR: δ = 1.10 (t, *J* = 6.0 Hz, 3 H), 2.40 (t, *J* = 6.0 Hz, 2 H), 2.60 (q, *J* = 6.0 Hz, 2 H), 2.80 (t, *J* = 6.0 Hz, 2 H), 3.60 (s, 2 H), 7.30 (d, *J* = 7.0 Hz, 2 H), 8.58 (d, *J* = 7.0 Hz, 2 H).

MS (EI): *m/z* (%) = 189 (M^+, 10), 149 (100), 141 (15), 121 (10), 111 (15), 106 (30), 92 (60), 83 (20), 70 (25), 65 (18), 57 (50), 51 (12), 43 (45).

1-(2-Nitro-1-phenylethyl)pyrrolidine (3r)
Thick syrup.

IR (KBr): 3430, 3052, 2947, 2841, 1635, 1568, 1510, 1495, 1420, 1371, 1267, 1215, 1173, 1121, 1085, 1006, 953, 861, 739 cm^{-1}.

^1H NMR: δ = 2.10–2.30 (m, 4 H), 2.70–2.90 (m, 4 H), 4.15 (dd, *J* = 6.0, 2.0 Hz, 1 H), 4.35 (dd, *J* = 6.0, 2.0 Hz, 1 H), 4.90 (t, *J* = 7.0 Hz, 1 H), 7.20–7.55 (m, 5 H).

MS (EI): *m/z* (%) = 220 (20), 174 (10), 160 (100), 90 (25), 77 (15), 65 (10), 51 (22).

3-(Benzylamino)-1,3-diphenylpropan-1-one (3s)
Colorless liquid.

IR (neat): 3338, 3060, 3028, 2924, 2853, 1682, 1643, 1603, 1493, 1450, 1336, 1283, 1214, 1178, 1075, 1022, 981, 855, 750 cm^{-1}.

^1H NMR: δ = 3.25–3.35 (m, 1 H), 3.55–3.70 (m, 1 H), 4.25–4.35 (m, 1 H), 4.70 (s, 2 H), 7.20–7.50 (m, 10 H), 7.55–8.05 (m, 5 H).

MS (EI): *m/z* (%) = 317 (15), 316 (40), 315 (M^+, 10), 308 (15), 299 (32), 298 (100), 224 (18), 210 (15), 147 (15), 119 (25), 77 (18), 51 (20).

***N*-Ethyl-2-nitro-1-phenyl-*N*-[(pyridin-4-yl)methyl]ethanamine (3w)**
Low-melting solid.

IR (KBr): 3334, 3078, 3049, 2930, 2846, 1681, 1625, 1605, 1573, 1510, 1495, 1415, 1341, 1280, 1215, 1169, 1072, 1015, 980, 873, 739 cm^{-1}.

^1H NMR: δ = 1.05 (t, *J* = 6.5 Hz, 3 H), 2.40 (q, *J* = 6.5 Hz, 2 H), 3.60 (s, 2 H), 4.35 (dd, *J* = 6.0, 20 Hz, 1 H), 4.55 (dd, *J* = 6.0, 20 Hz, 1 H), 5.05 (t, *J* = 6.5 Hz, 1 H), 7.20–7.60 (m, 7 H), 8.50 (d, *J* = 6.0 Hz, 2 H).

MS (EI): *m/z* (%) = 285 (M^+, 18), 239 (20), 225 (100), 196 (15), 119 (10), 106 (45), 92 (25), 78 (10), 77 (55), 65 (10), 53 (15), 51 (20).

4-(2-Nitro-1-phenylethyl)morpholine (3x)
Light red solid; mp 51–52 °C.

IR (KBr): 3426, 3032, 2922, 2854, 1634, 1560, 1493, 1452, 1366, 1276, 1227, 1112, 1035, 1002, 868, 741 cm^{-1}.

^1H NMR: δ = 2.30–2.55 (m, 4 H), 3.50–3.70 (4 H), 4.30 (dd, *J* = 6.5, 2.0 Hz, 1 H), 4.50 (dd, *J* = 6.5, 2.0 Hz, 1 H), 4.95 (t, *J* = 7.5 Hz, 1 H), 7.20–7.60 (m, 5 H).

MS (EI): *m/z* (%) = 237 (60), 236 (M^+, 20), 235 (10), 197 (35), 177 (10), 176 (90), 169 (12), 161 (10), 132 (15), 131 (100), 90 (15), 77 (12), 65 (18), 51 (20).

4-{*N*-Ethyl-*N*-[(pyridin-4-yl)methyl]amino}butan-2-one (3y)
Light yellow liquid.

IR (neat): 3438, 3053, 2937, 1718, 1678, 1615, 1583, 1506, 1459, 1351, 1292, 1210, 1172, 1105, 1083, 1015, 973, 847, 734 cm^{-1}.

^1H NMR: δ = 1.10 (t, *J* = 6.5 Hz, 3 H), 2.10 (s, 3 H), 2.40 (q, *J* = 6.5 Hz, 2 H), 2.65 (t, *J* = 6.0 Hz, 2 H), 2.70 (t, *J* = 6.0 Hz, 2 H), 3.60 (s, 2 H), 7.24 (d, *J* = 6.0 Hz, 2 H), 8.58 (d, *J* = 6.0 Hz, 2 H).

MS (EI): *m/z* (%) = 206 (M^+, 25), 177 (10), 163 (100), 135 (30), 134 (12), 106 (62), 92 (15), 78 (20), 53 (10).

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