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An efficient and convenient synthesis of *N*-substituted amides under heterogeneous condition using $Al(HSO_4)_3$ *via* Ritter reaction

ELNAZ KARIMIAN, BATOOL AKHLAGHINIA* and SARA S E GHODSINIA
Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran
e-mail: akhlaghinia@um.ac.ir

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Abstract. An efficient and inexpensive synthesis of *N*-substituted amides from the reaction of aliphatic and aromatic nitriles with various benzylic alcohols (secondary and tertiary) and *tert*-butyl alcohol by refluxing nitromethane *via* the Ritter reaction catalyzed by aluminum hydrogen sulfate [$Al(HSO_4)_3$] is described. The catalyst which is an air-stable, cost-effective solid acid could be readily recycled by filtration and reused four times without any significant loss of its activity.

Keywords. Aluminum hydrogen sulfate [$Al(HSO_4)_3$]; Ritter reaction; *N*-substituted amides; heterogeneous catalyst; nitriles; alcohols.

1. Introduction

The classical Ritter reaction as one of the most important carbon-nitrogen (C–N) bond-forming reaction offers a particularly atom-economical approach to the synthesis of amides. This reaction involves the reaction of a carbocation precursor (tertiary alcohol or substituted olefin), with nitriles in the presence of stoichiometric amount of a strong acid, typically H_2SO_4 and often together with a highly ionizing solvent such as AcOH.[1,2] However, the Ritter reaction requires stoichiometric amount of reagents, elevated temperatures, harsh reaction conditions, long reaction times and based on the structure of the reactants the reaction is accompanied by rearrangement and side products. Also, use of an excess amount of corrosive sulfuric acid is the main disadvantage of the classical Ritter reaction which has limited its applicability to compounds containing functional groups stable to acid. Despite this limitation, the Ritter reaction has found widespread use in synthesis. Over the years, due to the importance of amides as building blocks in organic and medicinal chemistry and to overcome the above mentioned limitations, several variations have been reported for the Ritter reaction to achieve higher yields with better chemo-selectivity under milder and environmentally acceptable conditions. These variations include the use of Nafion-H as a solid catalyst,[3–5] formic acid under reflux,[6] HBF_4Et_2O,[7] 2,4-dinitrobenzenesulfonic acid,[8] $HClO_4$-functionalized silica-coated nanoparticles,[9] sulfonic-acid functionalized silica,[10] P_2O_5/SiO_2,[11] $NaHSO_4/SiO_2$,[12,13] liquid HF,[14] TMS–CN/H_2SO_4 as a reagent for the synthesis of formamides,[15] *t*-BuOAc instead of *t*-BuOH as a carbocation precursor,[16] Tf_2O/ROH as an *in situ* source of ROTf,[17] pentafluorophenylammoniumtriflate (PFPAT),[18] trifluoromethanesulfonic acid (TfOH),[19] $Bi(OTf)_3$ and other metallic triflates,[20–23] metal complexes,[24] ionic liquids,[25,26] nitrosonium salt to effect the Ritter reaction of halides with nitriles,[27] using of gold (I) catalyst (this protocol is not suitable for solid nitrile for which the nitrile is used as the solvent),[28] silica-bonded *N*-propyl sulphamicacid),[29] nanocat-Fe-OSO_3H,[30] Amberlyst-(P-SO_3H),[31] $Ca(HSO_4)_2$,[32] $KAl(SO_4)_2.12H_2O$,[33] H_2SO_4/ball mill,[34] *o*-benzenedisulfonamide,[35] sulfated tungstate,[36] and $FeCl_3/AgSbF_6$[37] $Fe(ClO_4)_3$/silica gel,[38] 4,5,6,7-tetrachlorobenzo[*d*][1,3,2]dioxaborol-2-ol,[39] and *N*-Alkyl-4-boronopyridinium halides.[40] Although the modified methods offer better chemo-selectivity and milder, environmentally more acceptable conditions, some of them suffer from at least one of the following issues: limited availability of reagent, using hygroscopic reagents, low yield, tedious product isolation, longer reaction time and competing side reactions.

In this paper we wish to report a comprehensive study of the reactions between various organic nitriles and alcohols in the presence of catalytic amount of $Al(HSO_4)_3$ to provide *N*-substituted amides *via* Ritter fashion.

*For correspondence

2. Experimental

2.1 *General*

The purity determination of the products was accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra in $CDCl_3$ were recorded on Bruker Avance 400 and 300 MHz instruments. Mass spectra were recorded with a CH7A Varianmat Bremem instruments at 70 eV; in m/z (rel%), Elemental analyses were performed using Thermo Finnegan Flash EA 1112 Series instrument. The catalyst was prepared and purified by the method described in the literature.[41] All yields refer to isolated products after purification by recrystallization or thin layer chromatography.

2.2 *Preparation of aluminum hydrogen sulfate*

Anhydrous aluminum chloride (33.4 g, 0.25 mol) was placed into a 500 mL suction flask equipped with a constant-pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. Concentrated sulfuric acid (98%, 73.5 g, 0.75 mol) was added dropwise over a period of 1 h at room temperature during which HCl was evolved. After completion of the addition, the mixture was stirred for 30 min, while the residual HCl was eliminated by suction. Finally, a pale-brown solid material was obtained (77.0 g) and characterized according to the previously reported procedure.[41]

2.3 *Preparation of N-benzhydryl-2-phenylacetamide in the presence of $Al(HSO_4)_3$*

$Al(HSO_4)_3$ (0.5 mmol, 0.160 g) was added to a solution of phenylacetonitrile (1 mmol, 0.117 g) in nitromethane (2 mL) at 100°C. Benzhydrol (1 mmol, 0.184 g) was dissolved in nitromethane (2 mL) and added to the reaction mixture dropwise during 3 h. Progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by simple filtration. The concentrated residue was recrystallized from *n*-hexane to provide the corresponding amide (*N*-benzhydryl-2-phenylacetamide) as a white solid (0.295 g) with 98% isolated yield.

2.3a *N-Benzhydrylbenzamide (table 2, entry 1)*: White crystal, yield 93%; M.p. 167-168°C (Lit. 168-169°C);[42] FT-IR (KBr): υ_{max}/cm^{-1} 3295 (N-H), 3060, 3029, 2925, 2855, 1653 (C=O), 1525, 1451, 1278, 985, 742, 702, 514; ^1H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.86-7.84 (m, 2H, PhCO), 7.57-7.29 (m, 13H, Ph), 6.75 (brd, 1H, J = 7.2 Hz, NH), 6.49 (d, 1H, J = 7.8 Hz, CHNH); MS(EI) m/z (%) 287 (17) [M^+], 104 (100) [M^+-$C_{13}H_{13}N$], 76 (80) [C_6H_4].

2.3b *N-Benzhydryl-4-ethoxybenzamide (table 2, entry 2)*: White solid, yield 95%, M.p. 178-180°C; FT-IR (KBr): υ_{max}/cm^{-1}3309 (N-H), 3057, 2973, 2930, 1637 (C=O), 1532, 1493, 1297, 1250, 1041, 849, 742, 696; ^1H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.80 (d, 2H, J = 8.7 Hz, Ph), 7.40-7.29 (m, 10H, Ph), 6.94 (d, 2H, J = 8.7 Hz, Ph), 6.61 (brd, 1H, J = 7.5 Hz, NH), 6.47 (d, 1H, J = 7.5 Hz, CHNH), 4.10 (q, 2H, J = 6.9 Hz, OCH_2CH_3), 1.46 (t, 3H, J = 7.2 Hz, OCH_2CH_3);^{13}C NMR(75 MHz, $CDCl_3$, 25°C) δ/ppm 166.03, 161.78, 141.65, 132.05, 128.88, 128.75, 127.53, 126.25, 114.28, 63.69, 57.39, 14.71. MS (EI) m/z (%) 331 (19) [M^+], 181 (72) [M^+-$C_9H_8O_2$], 120 (70) [M^+-$C_{14}H_{11}NO$], 76 (41) [C_6H_4], 28 (64) [M^+-C_2H_4]; Elemental analysis data (%) for ($C_{22}H_{21}NO$): C (79.62), H (7.23), N (5.43); found C (79.73), H (6.39), N (4.23).

2.3c *N-Benzhydryl-3,4,5-trimethoxybenzamide (table 2, entry 3)*: White solid, yield 90%, M.p. 200-201°C (Lit. 202-203°C);[43] FT-IR (KBr): υ_{max}/cm^{-1} 3291 (N-H), 3068, 3031, 3002, 2937, 2839, 1628 (C=O), 1581, 1534, 1495, 1337, 1234, 1126, 1004, 757, 698,607; ^1H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.41-7.29 (m, 10H, Ph), 7.06 (s, 2H, Ph), 6.69 (brd, 1H, J = 7.5 Hz, NH), 6.46 (d, 1H, J = 7.5 Hz, CHNH), 3.91 (s, 9H, OCH_3);.MS (EI) m/z (%) 377 (5) [M^+], 181 (46) [M^+-$C_{10}H_{12}O_4$], 167 (54)[M^+-$C_{14}H_{12}NO$], 77 (36) [C_6H_5], 28 (87) [M^+- ($C_9H_{11}O_3$+ $C_{13}H_{12}N$)].

2.3d *N-Benzhydryl-4-methylbenzamide (table 2, entry 4)*: White crystal, yield 85%, M.p. 176-177°C (Lit. 176-177°C);[6] FT-IR (KBr): υ_{max}/cm^{-1}3316 (N-H), 3088, 3060, 3027, 2929, 2851, 1636 (C=O), 1610, 1524, 1494, 1311, 1033, 752, 737, 701, 576. ^1H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.75 (d, 2H, J = 8.1 Hz, Ph), 7.41-7.25 (m, 12H, Ph), 6.71 (brd, 1H, J = 6.9 Hz, NH), 6.48 (d, 1H, J = 7.8 Hz, CHNH), 2.43 (s, 3H, CH_3Ph). MS (EI) m/z (%) 301 (5) [M^+], 182 (92) [M^+-C_8H_7O], 166 (100) [M^+-C_8H_9NO], 91 (42) [M^+-$C_{14}H_{12}NO$], 77 (80) [C_6H_5], 29 (75) [M^+-($C_{13}H_{12}N$+ C_7H_7)].

2.3e *N-Benzhydrylthiophene-2-carboxamide (table 2, entry 5)*: Light brown solid, yield 95%, M.p. 168-172°C (Lit. 161°C);[44] FT-IR (KBr): υ_{max}/cm^{-1} 3327 (N-H), 3084, 3023, 3002, 2917, 1620 (C=O), 1541, 1510, 1494, 1317, 860, 715, 699. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.58 (d, 1H, J = 2.9 Hz, thiophene), 7.52 (d, 1H, J = 4.4 Hz, thiophene), 7.41-7.29 (m, 10H, Ph), 7.10 (t, 1H, J = 3.8 Hz, thiophene), 6.59 (brd, 1H, J = 6.9 Hz, NH), 6.45 (d, 1H, J = 7.8 Hz, CHNH); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ/ppm 160.99, 141.28, 138.62, 130.27, 128.78, 128.35, 127.69, 127.65, 127.56, 57.38. MS (EI) m/z (%) 293 (5) [M^+], 181 (82) [M^+-C_5H_4OS], 166 (82) [M^+-C_5H_5NOS], 111 (100) [M^+-$C_{13}H_{12}N$], 83 (23) [M^+-C_4H_3S], 77 (83) [C_6H_5],28 (83) [M^+- (C_4H_3S+ $C_{13}H_{12}N$)]; Elemental analysis data (%) for ($C_{18}H_{15}NOS$): C (73.69), H (5.15), N (4.77), S (10.93); found (%): C (73.17), H (5.06), N (4.90), S (10.55).

2.3f *N-Benzhydrylacetamide (table 2, entry 6)*: White solid, yield 95%, M.p. 109-110°C (Lit. 110-111°C);[45] FT-IR (KBr): υ_{max}/cm^{-1} 3259 (N-H), 3186, 3054, 3023, 2925, 1644 (C=O), 1544, 1493, 1450, 1370, 1288, 744, 699, 553, 469; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.39-7.24 (m, 10H, Ph), 6.29 (brd, 1H, J = 8.1 Hz, NH), 6.09 (d, 1H, J = 7.2 Hz, CHNH), 2.09 (s, 3H, CH_3CO); MS (EI) m/z (%) 225 (68) [M^+], 181 (88) [M^+-C_2H_4O], 147 (67) [M^+-C_6H_6], 106 (82) [M^+- (C_6H_5+ C_2H_3O)], 77 (72) [C_6H_5], 43 (72) [M^+-$C_{13}H_{12}N$].

2.3g *N-Benzhydrylpentanamide (table 2, entry 7)*: White solid, yield 90%, M.p. 115-117°C (Lit. 115-117°C);[43] FT-IR (KBr): υ_{max}/cm^{-1} 3249 (N-H), 3186, 3050, 3028, 2957, 2926, 2859, 1638 (C=O), 1542, 1493, 1451, 1269, 1118, 743, 698, 556. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.39-7.24 (m, 10H, Ph), 6.29 (d, 1H, J = 8.1 Hz, CHNH), 6.07 (brd, 1H, J = 7.5 Hz, NH), 2.28 (t, 2H, J = 7.8 Hz, CH_2CO), 1.68 (qn, 2H, J = 7.6 Hz, CH_2CH_2Et), 1.38 (sx, 2H, J = 7.5 Hz, $CH_2CH_2CH_3$), 0.94 (t, 3H, J = 7.5 Hz, CH_2CH_3); MS (EI) m/z (%) 267 (6) [M^+], 265 (97) [M^+-2H], 224 (14) [M^+-C_3H_7], 181 (97) [M^+-$C_5H_{10}O$], 166 (100) [M^+-$C_5H_{11}NO$], 106 (95) [M^+- (C_6H_5+ C_5H_9O)], 77 (72) [C_6H_5], 57 (80) [M^+-$C_{14}H_{12}NO$], 29 (90) [M^+-$C_{16}H_{16}NO$].

2.3h *N-Benzhydryl-2-phenylacetamide (table 2, entry 8)*: White solid, yield 98%, M.p. 161-162°C (Lit. 161-162°C);[46] FT-IR (KBr): υ_{max}/cm^{-1} 3296 (N-H), 3056, 3027, 2913, 2851, 1653 (C=O), 1524, 1493, 1449, 1052, 737, 702, 608; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.44-7.28 (m, 15H, Ph), 6.75 (brd, 1H, J = 7.2 Hz, NH), 5.45 (s, 1H, CHNH), 3.71 (s, 3H, CH_2CO); MS (EI) m/z (%) 301 (3) [M^+], 299 (59) [M^+-2H], 166 (100) [M^+-C_8H_9NO], 182 (93) [M^+-C_8H_7O], 105 (73) [M^+- (C_6H_5+ C_8H_7O)], 91 (59) [C_7H_7], 77 (69) [C_6H_5], 28 (73) [M^+- (C_7H_7+ $C_{13}H_{12}N$)].

2.3i *N-Benzhydryl-2-(3-methoxyphenyl) acetamide (table 2, entry 9)*: Brown solid, yield 92%, M.p. 124-126°C (Lit. 125-127°C);[47] FT-IR (KBr): υ_{max}/cm^{-1} 3287 (N-H), 3129, 3060, 3027, 2921, 2851, 1649 (C=O), 1602, 1533, 1494, 1460, 1236, 1048, 752, 696; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.37-7.25 (m, 10H, Ph), 7.14-7.09 (m, 4H, Ph), 6.46 (brs, 1H, NH), 6.23 (d, 1H, J = 8.4 Hz, CHNH), 3.77 (s, 3H, OCH_3Ph), 3.68 (s, 2H, CH_2CO); MS (EI) m/z (%) 331 (3) [M^+], 330 (32) [M^+-1H], 181 (44) [M^+-$C_9H_{10}O_2$], 166 (100) [M^+-$C_9H_{11}NO_2$], 91 (93) [M^+- ($C_{14}H_{12}NO$+ CH_3O)], 77 (44) [C_6H_5], 28 (91) [M^+- (C_8H_9O+ $C_{13}H_{12}N$)].

2.3j *N-(1-Phenylethyl)benzamide (table 2, entry 10)*: White solid, yield 85%, M.p. 102-104°C (Lit. 103-104°C);[36] FT-IR (KBr): υ_{max}/cm^{-1} 3346 (N-H), 3031, 2974, 2926, 1633 (C=O), 1521, 1489, 1275, 1013, 700, 647, 554; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.82-7.79 (m, 2H, PhCO), 7.56-7.32 (m, 8H, Ph), 6.36 (brd, 1H, J = 5.4 Hz, NH), 5.38 (qn, 2H, J = 7.2 Hz, CHNH), 1.65 (d, 3H, J = 6.9 Hz, CH_3CH); MS (EI) m/z (%) 225 (16) [M^+], 223 (93) [M^+-2H], 120 (30) [M^+-C_7H_5O], 105 (100) [M^+-$C_8H_{10}N$], 77 (93) [C_6H_5], 28 (93) [M^+- (C_6H_5+ $C_8H_{10}N$)].

2.3k *4-Ethoxy-N-(1-phenylethyl) benzamide (table 2, entry 11)*: Light brown crystal, yield 90%, M.p. 145-146°C; FT-IR (KBr): υ_{max}/cm^{-1} 3318 (N-H), 3064, 3031, 2977, 2927, 2847, 1629 (C=O), 1533, 1505, 1306, 1259, 1180, 1042, 848, 698, 555. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.65 (d, 2H, J = 8.7 Hz, Ph) 7.34-7.19 (m, 5H, Ph), 6.84 (d, 2H, J = 8.7 Hz, Ph), 6.18 (brd, 1H, J = 7.2 Hz, NH), 5.26 (qn, 1H, J = 6.9 Hz, CHNH), 3.99 (q, 2H, J = 6.9 Hz, OCH_2CH_3), 1.52 (d, 3H, J = 6.9 Hz, $CHCH_3$), 1.35 (t, 3H, J = 6.9 Hz, CH_2CH_3); ^{13}C NMR(75 MHz, $CDCl_3$, 25°C) δ/ppm 166.13, 161.59, 143.33, 128.74, 128.72, 127.42, 126.61, 126.29, 114.20, 63.66, 49.11, 21.80, 14.72. MS (EI) m/z(%) 269 (8) [M^+], 268 (68) [M^+-1H], 223 (10) [M^+-C_2H_6O], 164 (71) [M^+-C_8H_9], 148 (100)

[M^+-C_8H_9O], 120 (80) [M^+-$C_9H_9O_2$], 77 (62) [C_6H_5], 28 (70) [M^+- ($C_8H_{10}N$+ C_8H_9O)]; Elemental analysis data (%) for ($C_{17}H_{19}NO_2$): C (75.81), H (7.11), N (5.20); found (%): C (76.92), H (7.23), N (5.43).

2.3l *3,4,5-Trimethoxy-N-(1-phenylethyl)benzamide (table 2, entry 12)*: White solid, yield 80%; M.p. 177-178°C (Lit. 177.5-178°C);[48] FT-IR (KBr): υ_{max}/cm^{-1} 3310 (N-H), 3064, 3031, 2962, 2925, 2854, 1628 (C=O), 1580, 1542, 1499, 1338, 1240, 1125, 1002, 853, 697, 583, 547; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.45-7.29 (m, 5H, Ph), 7.02 (s, 2H, Ph), 6.28 (brd, 1H, J = 7.5 Hz, NH), 5.36 (qn, 1H, J = 7.2 Hz, CHNH), 3.92 (s, 6H, OCH_3), 3.90 (s, 3H, OCH_3), 1.65 (d, 3H, J = 6.9 Hz, CH_3CH); MS (EI) m/z (%) 315 (4) [M^+], 167 (81) [M^+-$C_9H_{10}NO$], 119 (72) [M^+-$C_{10}H_{12}O_4$], 104 (50) [M^+-$C_{10}H_{13}NO_4$], 76 (46) [M^+-C_6H_4], 28 (95) [M^+- ($C_8H_{10}N$+ $C_9H_{11}O_3$)].

2.3m *4-Methyl-N-(1-phenylethyl) benzamide (table 2, entry 13)*: Pale yellow solid, yield 85%, M.p. 125-126°C (Lit. 127-128°C);[49] FT-IR (KBr): υ_{max}/cm^{-1} 3358 (N-H), 3031, 2974, 2921, 2851, 1632 (C=O), 1527, 1502, 1109, 754, 698, 593; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.70 (d, 2H, J = 8.1 Hz, Ph), 7.45-7.24 (m, 7H, Ph), 6.32 (brd, 1H, J = 6.9 Hz, NH), 5.37 (qn, 1H, J = 7.2 Hz, CHNH), 2.42 (s, 3H, CH_3Ph), 1.63 (d, 3H, J = 6.9 Hz, CH_3CH); MS (EI) m/z(%) 239 (6) [M^+], 238 (45) [M^+-1H], 119 (97) [M^+-$C_8H_{10}N$], 104 (31) [M^+-C_8H_9NO], 91 (60) [M^+-$C_9H_{10}NO$], 77 (18) [M^+-C_6H_5].

2.3n *N-(1-Phenylethyl)thiophene-2-carboxamide (table 2, entry 14)*: White crystal, yield 85%, M.p. 126-127°C (Lit. 127-128°C);[50] FT-IR (KBr): υ_{max}/cm^{-1} 3265 (N-H), 3080, 3031, 2975, 2929, 2864, 2827, 1622 (C=O), 1546, 1513, 1448, 1420, 1359, 1279, 1137, 826, 721, 696, 543;^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ/ppm 7.69-7.50 (m, 2H, thiophene), 7.42-7.23 (m, 5H, Ph), 7.07 (t, 1H, J = 3.8 Hz, thiophene), 6.23 (brs, 1H, NH), 5.33 (qn, 1H, J = 7.2 Hz, CHNH), 1.57 (d, 3H, J = 7.1 Hz, $CHCH_3$); MS (EI) m/z(%) 231 (17) [M^+], 230 (93) [M^+-1H], 215 (20) [M^+-CH_4], 154 (2) [M^+-C_7H_8NOS], 120 (43) [M^+-C_5H_4OS],111 (100) [M^+-$C_8H_{11}N$], 104 (50) [M^+-C_5H_6NOS], 83 (22) [M^+-$C_9H_{10}NO$], 77 (56) [C_6H_5].

2.3o *2-Phenyl-N-(1-phenylethyl)acetamide (table 2, entry 15)*: White solid, yield 75%, M.p. 97-99°C (Lit. 97-99°C);[51] FT-IR (KBr): υ_{max}/cm^{-1} 3319 (N-H), 3059, 3028, 2974, 2929, 2868, 1648 (C=O), 1531, 1495, 1244, 1135, 699; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.42-7.20 (m, 10H, Ph), 5.63 (brs, 1H, NH), 5.15 (qn, 1H, J = 7.2 Hz, CHNH), 3.62 (s, 2H, CH_2Ph), 1.42 (d, 3H, J = 6.9 Hz, CH_3CH); MS (EI) m/z(%) 239 (22) [M^+], 238 (85) [M^+-1H], 148 (10) [M^+-C_7H_7], 91 (52) [M^+-$C_9H_{10}NO$], 28(96) [M^+-($C_8H_{10}N$+ C_7H_7)].

2.3p *N-(tert-Butyl)benzamide (table 2, entry 16)*: White solid, yield 90%; M.p. 111-118°C (Lit. 111-118°C);[52] FT-IR (KBr): υ_{max}/cm^{-1} 3324 (N-H), 3068, 2965, 2937, 2770, 1636 (C=O), 1578, 1540, 1451, 1312, 1217, 1178, 1078, 1008, 719, 695, 579; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ/ppm 7.76-7.29 (m, 5H, Ph), 5.97 (brs, 1H, NH), 1.50 (s, 9H, $C(CH_3)_3$); MS (EI) m/z(%)177 (40) [M^+], 176 (77) [M^+-1H], 161 (34) [M^+-CH_4], 105 (100) [M^+-$C_4H_{10}N$], 77 (92) [C_6H_5], 29 (96) [M^+- ($C_4H_{10}N$+ C_6H_5)].

2.3q *N-(tert-Butyl)-4-ethoxybenzamide (table 2, entry 17)*: White solid, yield 93%, M.p. 100-105°C; FT-IR (KBr): υ_{max}/cm^{-1} 3354 (N-H), 3338, 3072, 2973, 2929, 2876, 2774, 1631 (C=O), 1607, 1545, 1506, 1451, 1318, 1255, 1217, 1178, 1119, 1046, 845, 768, 616;^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.69 (d, 2H, J = 8.7 Hz, Ph), 6.9 (d, 2H, J = 8.7 Hz, Ph), 5.91 (brs, 1H, NH), 4.08 (q, 2H, J = 6.9 Hz, OCH_2CH_3), 1.48-1.42 (m, 12H, $C(CH_3)_3$, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ/ppm 166.46, 161.25, 128.44, 128.00, 114.08, 63.60, 51.43, 28.96, 14.73.MS (EI) m/z(%) 221 (25) [M^+], 205 (46) [M^+-CH_4], 176 (45) [M^+-C_2H_5O], 164 (82) [M^+-C_4H_9], 148 (100) [M^+-$C_4H_{11}N$], 121(98) [M^+-$C_5H_{10}NO$], 57 (70) [C_4H_9], 30 (82) [C_2H_6]; Elemental analysis data (%) for ($C_{13}H_{19}NO_2$): C (70.56), H (8.65), N (6.33); found (%): C (71.21), H (8.36), N (6.97).

2.3r *N-(tert-Butyl)thiophene-2-carboxamide (table 2, entry 18)*: White solid, yield 90%, M.p. 147-148°C (Lit. 148°C);[16] FT-IR (KBr): υ_{max}/cm^{-1} (N-H), 3174, 3092, 3067, 2968, 2932, 2843, 1619 (C=O), 1539, 1511, 1453, 1363, 1308, 1217, 1110, 833, 745, 730, 448; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ/ppm 7.47-7.43 (m, 2H, thiophene), 7.07 (t, 1H, J = 3.6 Hz, thiophene), 5.84 (brs, 1H, NH), 1.49 (s, 9H, $C(CH_3)_3$); MS (EI) m/z(%)183 (16) [M^+], 182 (75) [M^+-1H], 167 (75) [M^+-CH_4], 126 (76) [M^+-C_4H_9O], 110 (100) [M^+-$C_4H_{10}N$], 82 (60) [M^+-$C_5H_{11}NO$], 57 (62) [M^+-C_5H_4NOS], 28 (76) [M^+- ($C_4H_{10}N$+ C_4H_3S)].

2.3s *2-Phenyl-N-tritylacetamide (table 2, entry 19)*: White solid, yield 85%, M.p. 187-188°C (Lit. 187-188°C);[53] ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.43-7.23 (m, 14H, Ph), 7.16-7.09 (m, 6H, Ph), 6.60 (brs, 1H, NH), 3.66 (s, 2H, $\underline{CH_2}CO$); MS (EI) m/z (%)377 (31) [M^+], 181(89) [M^+-(C_8H_8O, C_6H_5)], 164 (83), 90 (78) [M^+-$C_{20}H_{17}NO$], 28 (79) [M^+-($C_{19}H_{16}N$+ C_7H_7)].

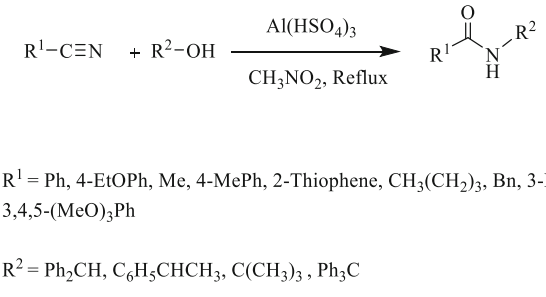
2.3t *N-Tritylpentanamide (table 2, entry 20)*: White solid, yield 90%, M.p. 183-184°C(Lit.184-185°C);[54] ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ/ppm 7.36-7.22 (m, 15H, Ph), 6.59 (brs, 1H, NH), 2.31 (t, 2H, J = 7.8 Hz, $\underline{CH_2}CO$), 1.66 (qn, 2H, J = 7.6 Hz, $CH_2\underline{CH_2}Et$), 1.38 (sx, 2H, J = 7.5 Hz, $CH_2\underline{CH_2}CH_3$), 0.94 (t, 3H, J = 7.5 Hz, $CH_2\underline{CH_3}$); MS (EI) m/z (%) 343 (2) [M^+], 76 (29) [M^+-$C_{18}H_{21}NO$], 43 (49) [M^+-$C_{21}H_{18}NO$], 57 (68) [M^+-$C_{20}H_{16}NO$], 28 (100) [M^+- ($C_{19}H_{16}N$ + C_4H_9)].

3. Results and Discussion

Recently, we have reported thealkylation of 1,3-dicarbonyl compounds and synthesis of unsymmetrical ethers in the presence of $Fe(HSO_4)_3$.[55,56] In the course of our study, with the aim of finding efficient and cost-effective catalysts,[57] we found out that*N*-substituted amides were easily formed from the reaction of aliphatic and aromatic nitriles with various benzylic alcohols (secondary and tertiary) and *tert*-butyl alcohol in the presence of $Al(HSO_4)_3$ *via* the Ritter reaction pathway (scheme 1).

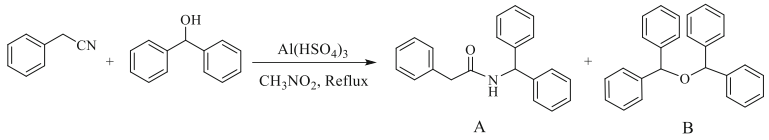
At first, the reaction between phenylacetonitrile and benzhydrol was chosen as model reaction. Then in order to optimize the reaction conditions, in a set of experiments the model reaction was carried out in different reaction conditions (table 1). To prove the catalytic activity of $Al(HSO_4)_3$ in the Ritter reaction, in the absence of any catalyst, performing the model reaction in solvent free condition and also in nitromethane (at room temperature and reflux) has not led to formation of the desired product (table 1, entry 1,4,5). Applying 0.5 mmol of catalyst in nitromethane and in solvent free conditions has not produced *N*-benzhydryl-2-phenylacetamide (table 1, entries 2 and 3). Based on our previous reports,[55,56] in the present study, we also found that in the presence of $Al(HSO_4)_3$, the rate of addition of benzhydrol plays an important role in the yield of *N*-benzhydryl-2-phenylacetamide. Quick addition of benzhydrol leads to the formation of excess amount of symmetrical ether which was obtained from self-condensation of benzhydrol. To minimize self-condensation of benzhydrol in all of the following reactions, addition of benzhydrol should be performed dropwise, which consumes more time. In this manner, *N*-benzhydryl-2-phenylacetamide was obtained as the desired product. By applying 1/1 molar ratio of phenyl acetonitrile/benzhydrol and using 0.5 mmol of $Al(HSO_4)_3$, maximum yield of the desired product was obtained by refluxing nitromethane without formation of any by-product (table 1, entry 6). It is important to note that the yield of the reaction was not increased by applying other molar ratios of reactants, whilst symmetrical ether as by-product was produced considerably (table 1, entries 7-8). To investigate the effect of catalyst loading, formation of*N*-benzhydryl-2-phenylacetamide was carried out by refluxing nitromethane in the presence of different amounts of $Al(HSO_4)_3$. Additional amounts of catalyst did not have any influence on the reaction rate while lower amount of catalyst diminished the reaction rate concomitant with formation of by-product (table 1, entries 9-10). In an effort to develop better reaction conditions, different solvents were screened for the preparation of *N*-benzhydryl-2-phenylacetamide from the reaction of phenylacetonitrile with benzhydrol in the presence of 0.5 mmol of $Al(HSO_4)_3$. No product was obtained when the reaction was performed by refluxing in H_2O and EtOH (table 1, entries 11-12). Refluxing in solvents, such as 1,2-dichloroethane, $CHCl_3$, 1,4-dioxane, DMF and toluene gave the desired product in low yield along with formation of considerable amounts of by-product (table 1, entries 13-17). As shown in table 1, under the optimized reaction conditions (table 1, entry 6) and in the presence of Al ($HSO_4)_3$/silica, *N*-benzhydryl-2-phenylacetamide was produced in low yield after long reaction time with the formation of symmetrical ether (table 1, entry 18).

To show the general application of the protocol and with the optimal conditions at hand (table 1, entry 6), the substrate scope of the Ritter reaction in the presence



Scheme 1. Synthesis of *N*-substituted amides in the presence of $Al(HSO_4)_3$.

Table 1. Synthesis of *N*-benzhydryl-2-phenylacetamide in the presence of $Al(HSO_4)_3$ under different reaction conditions.



Entry	Molar ratio of phenyl acetonitrile/ benzhydrol (mmol)	Catalyst (mmol)	Solvent	Temperature (°C)	Time (h)	Conversion[a] (%)	Selectivity A/B
1	1/1	0	None	r.t	24	0	0/0
2	1/1	0.5	None	r.t	24	0	0/0
3	1/1	0.5	CH_3NO_2	r.t	24	0	0/15
4	1/1	0	CH_3NO_2	r.t	24	0	0/0
5	1/1	0	CH_3NO_2	Reflux	24	0	0/15
6	1/1	0.5	CH_3NO_2	Reflux	3	>98	>98
7	1/1.5	0.5	CH_3NO_2	Reflux	3	70	80/ 20
8	1/2	0.5	CH_3NO_2	Reflux	3	60	40/60
9	1/1	0.4	CH_3NO_2	Reflux	3	85	90/ 10
10	1/1	0.6	CH_3NO_2	Reflux	3	>98	>98
11	1/1	0.5	H_2O	Reflux	3	0	0/0
12	1/1	0.5	C_2H_5OH	Reflux	3	0	0/0
13	1/1	0.5	DCE	Reflux	3	80	90/ 10
14	1/1	0.5	$CHCl_3$	Reflux	3	80	80/ 20
15	1/1	0.5	1,4-Dioxan	Reflux	4	50	50/ 50
16	1/1	0.5	DMF	Reflux	4	50	50/ 50
17	1/1	0.5	Toluene	Reflux	4	60	80/ 20
18[b]	1/1	0.05g	CH_3NO_2	Reflux	24	24	70/30

[a]The corresponding data refer to the conversion of phenyl acetonitrile.
[b]The reaction was performed in the presence of $Al(HSO_4)_3$/Silica.

of $Al(HSO_4)_3$ was investigated. Different *N*-substituted amides were obtained from the reaction of aromatic, heteroaromatic and aliphatic nitriles with secondary and tertiary benzylic alcohols and tertiary butyl alcohol with good to excellent yields (table 2). Also, all the reactions proceeded well in short reaction times with high selectivity without formation of any by-products. From this Table, it is clear that, in the presence of $Al(HSO_4)_3$ the reaction of benzhydrol was completed in short reaction time than 1-phenylethanol due to more stability of the corresponding carbocation (compare entries 1-9 with entries 10-15). This result led us to conclude that the more stable carbocation improved the reaction rate. Comparatively owing to the steric hindrance, tertiary butyl alcohol and tertiary benzylic alcohol reacted more slowly than benzhydrol and 1-phenyethanol (table 2, entries 16-20). With effective conditions established for the Ritter reaction, we next investigated the ability of $Al(HSO_4)_3$ to catalyze the formation of *N*-substituted amides from the reaction of organic nitriles with primary benzylic alcohols. Even after a long period of time, organic nitriles did not react with primary benzylic alcohols under optimized reaction conditions. Comparatively, low activity of primary benzylic alcohols towards organic nitriles in the presence of $Al(HSO_4)_3$ is attributed to the low stability of the corresponding primary benzylic cation. Also, we tried to expand the scope of the Ritter reaction for organic nitriles with secondary and primary aliphatic alcohols, but the catalyst was ineffective in these reactions even when excess amounts of catalyst (1 mmol of catalyst) were used.

In our experiments, completion of the reaction was confirmed by the disappearance of the organic nitriles and then amide formation on TLC, followed by the disappearance of nitrile CN stretching frequency at 2260-2220 cm^{-1} in the Fourier transform infrared (FT-IR) spectrum. The resulting *N*-substituted amides, after purification *via* either re-crystallization or thin layer chromatography were characterized using FT-IR, NMR, and mass spectrometry (MS). Absorption bands at 3354-3249 and 1653-1619 cm^{-1} corresponding to NH, and CO groups of *N*-substituted amides, respectively, confirmed the formation of the desired products. In the ^1H NMR spectra, the NH proton of *N*-substituted amides was appeared at 6.75-5.63 ppm. In the ^{13}C NMR spectra, signals around 166.46-160.99 ppm were assigned to the carbonyl carbon atom of *N*-substituted amides. Most of the products obtained were known compounds and characterized by comparison of

Table 2. Synthesis of structurally different *N*-substituted amides in the presence of $Al(HSO_4)_3$.

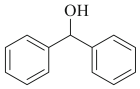
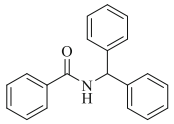
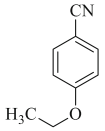
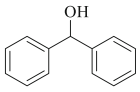
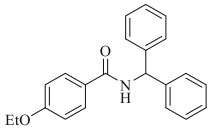
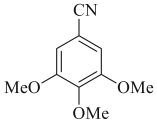
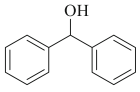
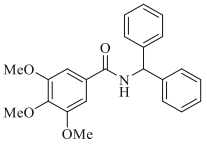
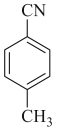
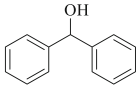
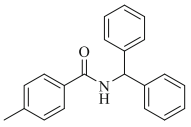
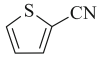
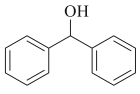
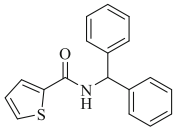
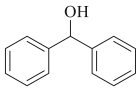
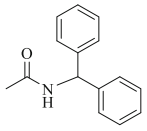
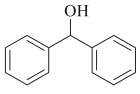
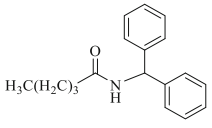
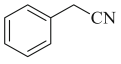
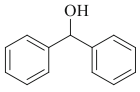
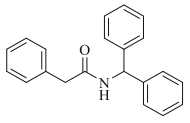
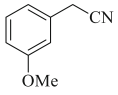
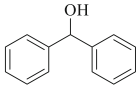
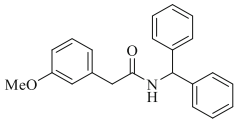
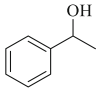
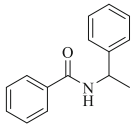
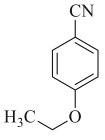
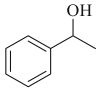
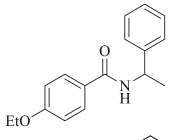
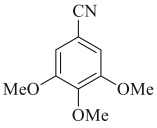
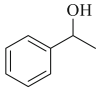
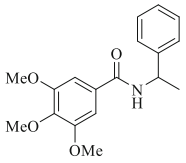
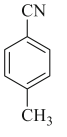
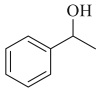
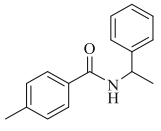
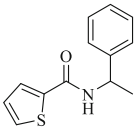
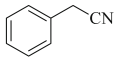
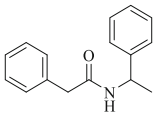
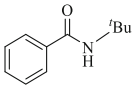
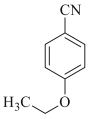
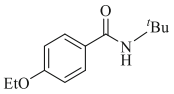
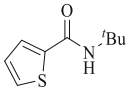
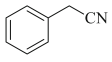
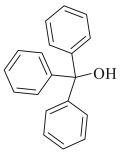
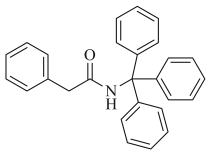
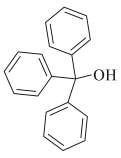
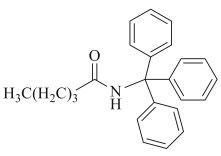
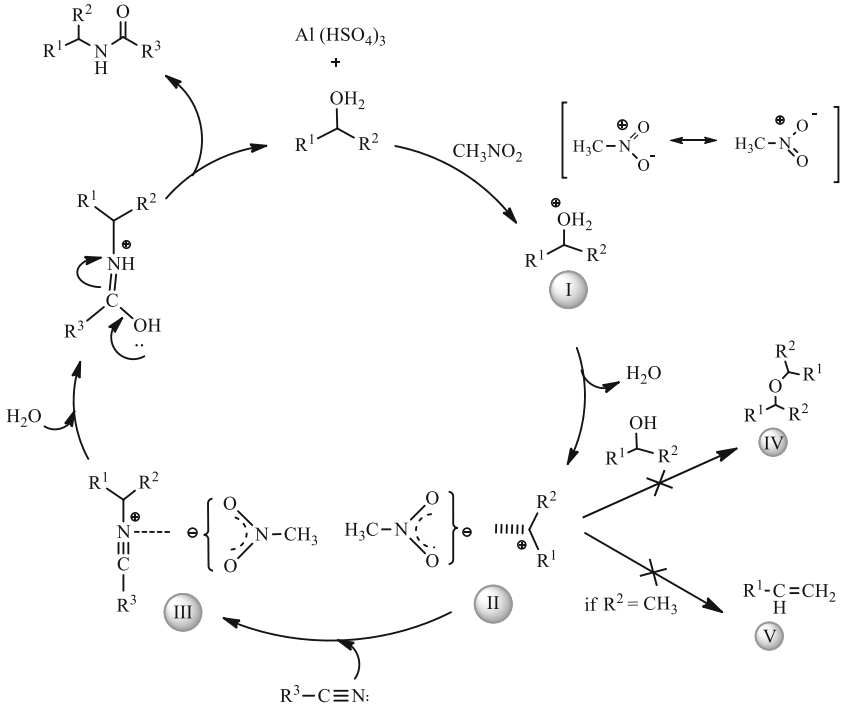
Entry	Nitrile	Alcohol	Product	Time (h)	Isolated yield (%)
1				2	93
2				2	95
3				2	90
4				2	85
5				1	95
6	CH_3CN			2	95
7	$CH_3(CH_2)_2CN$			2	90
8				3	98
9				1.5	92
10				2.5	85
11				2	90
12				2.5	80
13				3	85

Table 2. (continued)

Entry	Nitrile	Alcohol	Product	Time (h)	Isolated yield (%)
14				1.5	85
15				3	75
16				3	90
17				3	93
18				2.5	90
19				3	85
20	$CH_3(CH_2)_3CN$			3	90



Scheme 2. Proposed mechanism for Ritter reaction in the presence of $Al(HSO_4)_3$.

their melting points with those of the reported compounds. Complete characterization of novel compounds are also reported in this paper.

The suggested Ritter reaction mechanism was published in 1948.[1] Based on the Ritter reaction mechanism, we suggest that, initially the Brønsted acid catalyzed the reaction with fast generation of the protonated species **I** *via* the protonation of hydroxyl group of alcohol which was followed by generation of the corresponding stable benzylic carbocation **II**. This idea is supported by performing the reaction in the absence of catalyst. Without any catalyst, the Ritter reaction did not proceed even after a long period of time (table 1, entry 1). Nucleophilic attack of organic nitrile to benzylic carbocation **II** produced the nitrilium ion **III**. The positive sites of benzylic carbocation **II** and nitrilium ion **III** can interact with the negative oxygen of the solvent which stabilized these two intermediates, while the other reacting components cannot interact with solvent. As the more stabilized intermediate was obtained faster, CH_3NO_2 was chosen as a suitable solvent in the present study. Hydrolysis of **III** affords the corresponding *N*−substituted amide and releases the proton which re-enters to the catalytic cycle. Because of dropwise addition of benzylic alcohol to the reaction mixture, the formation of any symmetric ether **IV** as by-product was prohibited. Also, dehydration of **II**, which leads to alkene **V**, did not happen in the Ritter reaction in the presence of $Al(HSO_4)_3$. Further studies to elucidate the details of the mechanism are ongoing (scheme 2).

Catalyst re-usability was assessed in the reaction of phenylacetonitrile with benzhydrol. To this end, the reaction was stopped after 3 h (*i.e.*, at 100% conversion of phenylacetonitrile) and the catalyst removed by filtration and washed with acetone and 1,2-dichloroethane several times. Table 3 shows the results obtained after six re-use cycles. These results by themselves suggest that the heterogeneous catalyst was used for 4 successive times in the new experiments without any significant impact on yields of productswith purity similar to that obtained in the first run.

Table 3. Synthesis of *N*-benzhydryl-2-phenylacetamide in the presence of reused $Al(HSO_4)_3$.

Run	Time (h)	Conversion (%)	Isolated yield (%)
1	3	>98	96
2	3	>98	95
3	3	>98	93
4	3	>98	92
5a	3/4.5	85/90	80/85
6a	3/6	70/80	65/75

[a]The second number in the third and fourth columns correspond to conversion and yield after 4.5 and 6 h.

Table 4. Ritter reaction of benzhydrol with phenyl acetonitrile under optimized conditions in the presence of other catalysts.

Entry	Catalyst	Time (h)	Conversion (%)	Selectivity Amide/Ether
1	$FeCl_3.6H_2O$	3	70	60/40
2	$Fe(NO_3)_3.9H_2O$	3	50	50/50
3	$CuCl_2.2H_2O$	24	0	0
4	$NiCl_2.6H_2O$	24	0	0
5	$ZnCl_2$	4	20	20/80
6	$MnCl_2.2H_2O$	24	0	0
7	$AlCl_3$	24	0	0
8	Al_2O_3	24	0	0
9	$Al(HSO_4)_3$	3	>98	>98

To show the efficiency of $Al(HSO_4)_3$ in Ritter reaction, the model reaction in the presence of $Al(HSO_4)_3$ was compared with various metal salt catalysts such as $FeCl_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $ZnCl_2$, $MnCl_2.2H_2O$, $AlCl_3$ and Al_2O_3(table 4). Performing the reaction in the presence of $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $MnCl_2.2H_2O$, $AlCl_3$ and Al_2O_3 did not produce the desired product in quantitative yield (table 4, entries 3, 4, 6, 7, 8). Comparatively, Ritter reaction in the presence of $FeCl_3.6H_2O$, $Fe(NO_3)_3.9H_2O$ and $ZnCl_2$ produced *N*-benzhydryl-2-phenylacetamide in low yield concomitant with the formation of by-products in considerable yield (table 4, entries 1, 2, 5).

4. Conclusions

In conclusion, we have described that $Al(HSO_4)_3$ (as an air-stable, cost-effective and reusable solid acid) catalyzes the Ritter reaction of organic nitriles with benzylic alcohols (secondary and tertiary) as well as the Ritter reaction of organic nitriles with tertiary butyl alcohol, respectively. In contrast to the existing methods using potentially hazardous catalysts/additives, the present method (an inexpensive and eco-friendly process which allows the preparation of various *N*-substituted amides that can be useful synthons), offers the following advantages: (i) $Al(HSO_4)_3$ is easy to prepare from commercially available aluminum chloride and sulfuric acid, (ii) $Al(HSO_4)_3$ as a heterogeneous catalyst is recyclable without any significant impact on the yields of the products, (iii) short reaction times, (iv) ease of product isolation/purification, (v) no side reactions and (vi) low cost and simplicity in process handling.

Supplementary Information (SI)

Supplementary Information is available at www.ias.ac.in/chemsci.

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