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Studies on Development of Sufficiently Chemoselective N-Acylation Reagents: *N*-Acyl-*N*-(2,3,4,5,6-pentafluorophenyl)methanesulfonamides

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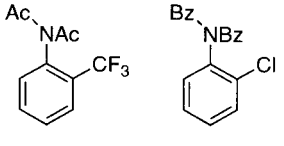
Abstract—A variety of storable *N*-acyl-*N*-(2,3,4,5,6-pentafluorophenyl)methanesulfonamides (**4a**–**e**) prepared from *N*-2,3,4,5,6-pentafluorophenylmethanesulfonamide (**3**), have been developed after systematic research on the structure–reactivity relationship and were found to serve as N-acylation reagents exhibiting sufficiently good chemoselectivity.

Introduction

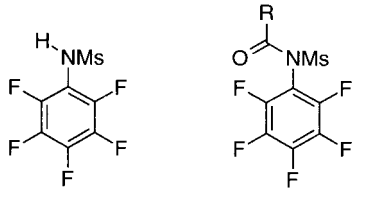
Chemoselective acylation of amino groups is an important reaction in synthetic operation[1] and is often required in organic synthesis. A variety of reagents have been developed by devising a leaving group for the above purpose,[2] and continuing efforts have been made in order to develop an ideally chemoselective reagent. It is reasonably assumed that a reagent bearing a bulky leaving group may satisfy such requirement.

Several years ago, we began studies to develop a new chemoselective N-acylation reagent employing the acyl-2-substituted anilide **A** as a leaving group, because the anilide **A** of **1** and **2** is expected to behave as a bulky leaving group (Fig. 1).[3] Recently, we have reported that *N*-acetyl-*N*-(2-trifluoromethylphenyl)acetamide[3a] (**1**) and *N*-benzoyl-(2-chlorophenyl)benzamide[3b] (**2**) serve as effective chemoselective N-acetylation and N-benzoylation reagents, respectively. Calculations of **1** and **2** by using the PM3 method[4] in the MOPAC package indicated that the 2-substituted phenyl group was placed almost perpendicular to the plane of N–C═O (Fig. 2). Therefore, sufficient steric bulkiness would be provided around the acyl carbonyl group.



1 **2**

As part of our program directed toward development of new N-acylation reagents, the present study was undertaken. In this paper, we would like to describe that a variety of storable *N*-acyl-*N*-(2,3,4,5,6-pentafluorophenyl)methanesulfonamides (**4a**–**e**) were prepared from *N*-2,3,4,5,6-pentafluorophenylmethanesulfonamide (**3**) under mild conditions and were found to serve as N-acylation reagents exhibiting sufficiently good chemoselectivity.

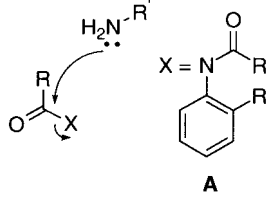


3

4a: RCO = Z
4b: RCO = Alloc (allyloxycarbonyl)
4c: RCO = Ac
4d: RCO = Bz
4e: RCO = Pv (pivaloyl)

First-Generation Reagents: *N*-Acyl-*N*-(2-fluorophenyl)methanesulfonamide[5] (13a, 13c and 13d)

At first, we planned to prepare the *N*-acyl-anilides **6** bearing



A

Figure 1. 2-Substituted anilide **A** as a leaving group.

Keywords: chemoselective N-acylation reagent; alkoxycarbonylation; sulfonamide; amine; protective group.

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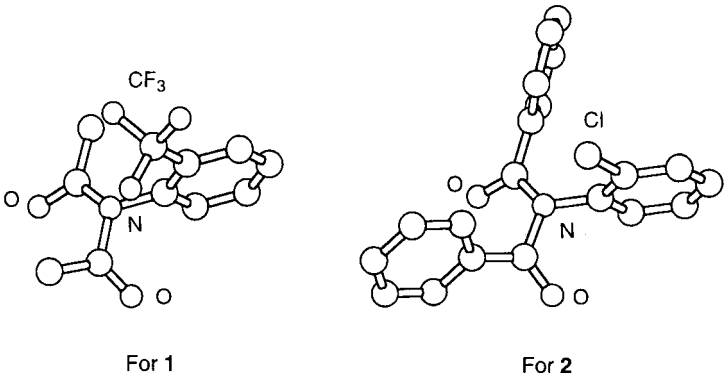
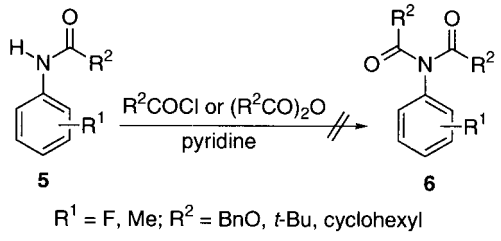


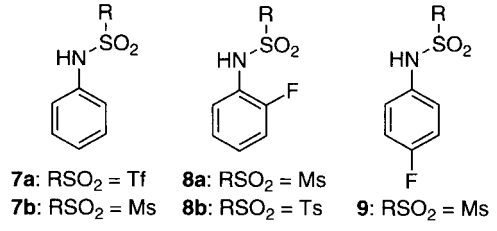
Figure 2. Calculated conformations of **1** and **2**.

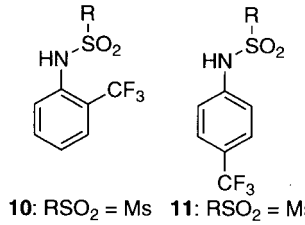
other acyl groups except for acetyl and benzoyl groups, under mild reaction conditions, acyl chloride or anhydride in pyridine.[6] However, after many experiments, our attempts proved to be unsuccessful (Scheme 1).



Scheme 1. Many attempts for preparation of various N-acyl-anilides **6**.

In an effort to overcome this problem, we decided to search for a versatile synthon to which various acyl groups could be introduced. We chose to focus on the use of sulfonamides **7**–**11** as a precursor of various N-acylation reagents to circumvent the low reactivity of **5**, since they were expected to have lower pK_a values than **5**. At first, introduction of a Z group into sulfonamides **7**–**11** was examined under mild reaction conditions, 4 equiv. of ZCl in pyridine (Table 1). After several experiments, we found that the *N*-Z-sulfonamides **13a**, **13b** and **14**–**16** could be prepared from the corresponding sulfonamides **8**–**11** bearing mesyl and tosyl groups in moderate to good yields (entries 3–7). In contrast, the use of trifluoromethanesulfonamide **7a** did not give any acylated product (entry 1).[7,8]





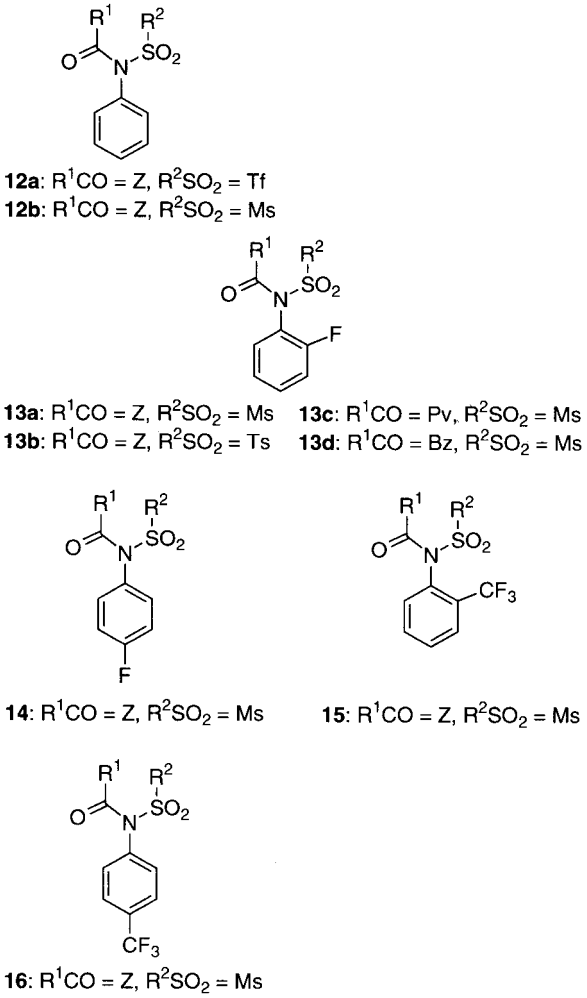
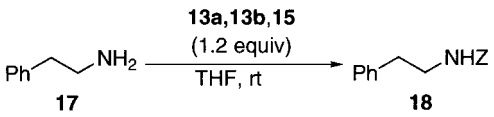


Table 1. Preparation of Z-sulfonamides **12**–**16** from **7**–**11** (all reactions were carried out with 4 equiv. of ZCl in pyridine at rt for 1 h)

Entry	Starting sulfonamide	Product (yield %)
1	**7a**	**12a** (0), **7a** (4)
2	**7b**	**12b** (–[a]), **7b** (41)
3	**8a**	**13a** (90)
4	**9**	**14** (39), **9** (45)
5	**10**	**15** (74)
6	**11**	**16** (21), **11** (64)
7	**8b**	**13b** (70)

[a] Formation of product **12b** along with significant amounts of inseparable impurities was observed.

Table 2. Acylation potentiality of *N*-Z-sulfonamides **13a**, **13b** and **15**



Entry	Z-Sulfonamide	Time (h)	Yield (%)
1	**13a**	18	95
2	**15**	120	80
3	**13b**	22	97

Table 3. Preparation of *N*-acyl-sulfonamides **13c** and **13d** from **8a** (all reactions were carried out with 2 equiv. of acyl chloride in pyridine at rt for 8 h)

Entry	Acyl chloride	Product: RCO	Yield (%)
1	PvCl	**13c**:Pv	84
2	BzCl	**13d**:Bz	92

Since the *N*-Z-sulfonamides **13a**, **13b** and **15** could be prepared in good yields, we chose them as the candidate for an N-benzyloxycarbonylation reagent. In order to evaluate their *N*-acyl-transfer potentiality, benzyloxycarbonylation of a typical primary amine, 2-phenylethylamine (**17**), with 1.2 equiv. of **13a**, **13b** and **15** was examined in THF at rt. The reaction was monitored by TLC and the results are shown in Table 2. All of them served as N-benzyloxycarbonylation reagents. The *N*-Z-methanesulfonamide **13a** containing a 2-fluoro group on the benzene ring was found to be the most reactive reagent (entry 1). The reactivity of the tosylamide **13b** was somewhat lower than that of **13a** (entry 3). The reaction of the *N*-Z-methanesulfonamide **15** containing a 2-trifluoromethyl group was very sluggish (entry 2). Taking the above results into consideration, **8a** was chosen as a promising precursor for various N-acylation reagents.

Introduction of other acyl groups, Pv and Bz groups, into **8a** was then examined under similar reaction conditions as described above, 2 equiv. of acyl chloride in pyridine (Table 3). As expected, **13c** and **13d** containing a 2-fluoro group could be prepared in good yields.[9]

With **13a**, **13c** and **13d**, acylation of several types of amines was examined in THF. The results are shown in Table 4. Primary, secondary and α-branched amines, **17**, **19** and **20** were all acylated, affording the corresponding acylated products in good yields (entries 1–6). A sterically hindered tertiary alkyl amine **21** was not acylated even in refluxing THF (entries 7 and 8). The substantial difference in the reaction rates between less-hindered and hindered amines prompted us to examine a chemoselective acylation of diamines. As shown in Table 5, less-hindered acylated products were obtained in good yields. However, in all cases, long reaction periods for the N-acylation of amines with **13a**, **13c** and **13d** were required.

Second-Generation Reagents: *N*-Acyl-*N*-(2,3,4,5,6-pentafluorophenyl)methanesulfonamides (4a–e)

In order to improve the low reactivity of **13a**, **13c** and **13d**, we focused on the preparation of the *N*-sulfonamides **4a** and **25**–**27** containing a stronger electron-withdrawing group on the benzene ring. Preparation of *N*-acyl-sulfonamides **4a** and **25**–**27** bearing a Z group was first examined under mild conditions, 4 equiv. of ZCl in pyridine. As shown in Table 6, a variety of storable *N*-Z-sulfonamides **4a**, **25** and **27** could be prepared from the corresponding sulfonamides **3**, **22** and **23** in good yields except **24**. From the viewpoint of synthetic yield, we chose the *N*-acylsulfonamides **4a**, **25** and **26** as the candidate for a second-generation reagent.

In order to evaluate the N-acyltransfer potentiality of **4a**, **25** and **26**, benzyloxycarbonylation of **17** was examined with 1.2 equiv. of **4a**, **25** and **26** in THF at rt. The results are shown in Table 7. The *N*-Z-sulfonamides **4a**, **25** and **26** containing 2,3,4,5,6-pentafluoro, 2,6-difluoro and

Table 4. Acylation of several amines with *N*-acyl-sulfonamides **13a**, **13c** and **13d** (all reactions were carried out with 1.2 equiv. of **13a**, **13c** and **13d** in THF)

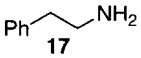
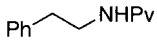
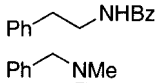
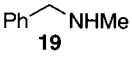
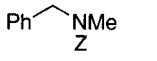
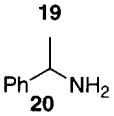
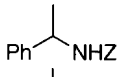
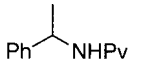
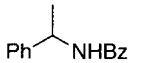
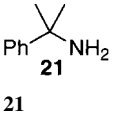
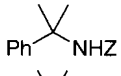
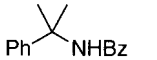
Entry	*N*-Acyl-sulfonamide	Amine	Conditions	Product	Yield (%)
1	**13c**		50°C, 20 h		72
2	**13d**	**17**	rt, 2 h		91
3	**13a**		rt, 36 h		93
4	**13a**		50°C, 20 h		90
5	**13c**	**20**	reflux, 24 h		77
6	**13d**	**20**	rt, 6 h		94
7	**13a**		reflux, 24 h		0
8	**13d**	**21**	reflux, 24 h		0

Table 5. Chemoselective acylation of diamines with *N*-acyl-sulfonamides **13a** and **13d** (all reactions were carried out with 1.0 equiv. of **13a** or **13d** in THF at 0°C for 24 h and were then left stirring at rt for 12 h)

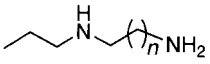
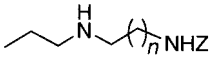
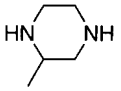
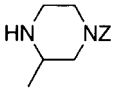
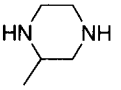
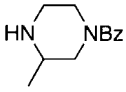
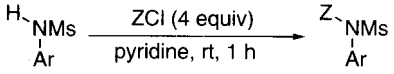
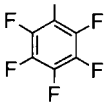
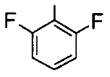
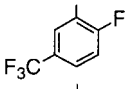
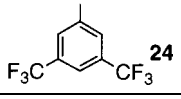
Entry	13a,d	Diamine	Product and Yield (%)	Entry	13a,d	Diamine	Product and Yield (%)
				3	**13a**		 91
1	**13a**	n=1	n=1:82%				
2	**13a**	2	2:86%	4	**13d**		 93

Table 6. Preparation of *N*-Z-sulfonamides **4a** and **25–27**



3,22-24 **4a,25-27**

Entry	Starting sulfonamide		Yield (%)[a]
1		**3**	**4a** (84)
2		**22**	**25** (89)
3		**23**	**26** (86)
4		**24**	**27** (32)[b]

[a] Yield after recrystallization (benzene–hexane).
[b] Starting sulfonamide **24** was recovered in 38% yield.

2-fluoro-5-trifluoromethyl groups, acylated the amine **17** in 99, 99 and 96% yields for 1.5, 7 and 7.5 h, respectively.[10]

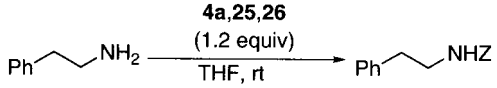
Since **4a** containing 2,3,4,5,6-pentafluoro groups was found to be the most reactive, the introduction of other acyl groups into **3** was examined (Table 8). Fortunately, the storable **4b–e** bearing various acyl groups, Alloc, Ac, Bz, and Pv groups, could be prepared in good yields. We were pleased to find that various acyl groups could be introduced into the sulfonamide **3** under mild conditions.

With **4a–e** bearing various acyl groups in hand, acylation of several types of amines was examined in THF (Table 9). Benzyloxycarbonylation using the Z-sulfonamide **4a** gave good results. Secondary amine **19** afforded the corresponding Z-product in 99% yield for 10 h at rt (entry 5). An α-branched amine **20** afforded the corresponding Z-product in 99% yield for 24 h at rt (entry 9). It took 48 h at 65°C for the conversion of a tertiary alkyl amine **21** into the corresponding Z-product in 64% yield (entry 14). Acylation using the Alloc- and Ac-sulfonamides **4b** and **4c** gave satisfactory results (entries 1,2,6,7,10,11,15 and 16). The Bz-sulfonamide **4d** was more reactive than the Z-, Alloc- and Ac-sulfonamides **4a–c** (for example: entry 12 vs. entries 9–11). Pivaloylation of amines **17** and **20** using **4e** was somewhat less reactive (entries 4 and 13). Thus, the acylsulfonamide **4a–e** containing a 2,3,4,5,6-pentafluorophenyl group provided much better reactivity than the first-generation reagents **13a**, **13c** and **13d**. The resulting leaving group **3** of **4a–e** was recovered in >90% yield for recycling by silica gel column.

Since apparent differences in the above reaction rates (Table 9) were observed, selective acylation using 1.0 equiv. of **4a–e** was tested with several diamines as shown in Table 10.[11] In all cases, only the less-hindered amino groups were acylated faster in good yields than **13a**, **13b** and **13c** (Tables 4 and 5).

As a result, our new reagents **4a–e** have several advantages as follows: (i) easy preparation of various acylation reagents **4a–e** prepared from a common substrate **3** under mild conditions; (ii) stability in air and easy handling; (iii) good selectivity in acylation. In a molecule with both less-

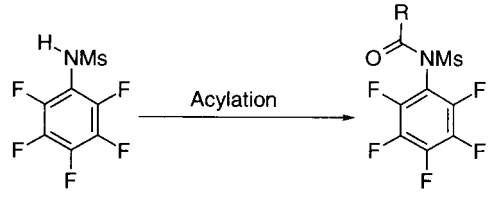
Table 7. Acylation potentiality of *N*-Z-sulfonamides **4a**, **25** and **26**



17 **18**

Entry	Sulfonamide	Time (h)	Yield (%)
1	**4a**	1.5	99
2	**25**	7	99
3	**26**	7.5	96

Table 8. Preparation of *N*-acylsulfonamide **4b–e**

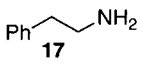
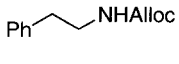
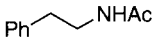
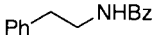
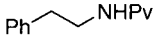
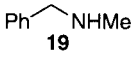
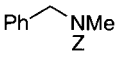
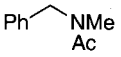
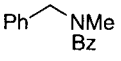
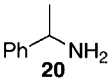
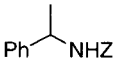
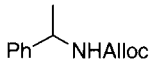
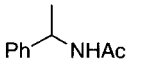
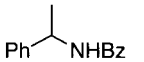
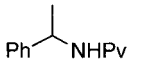
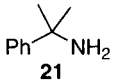
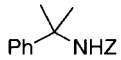
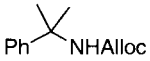
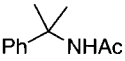
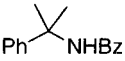


3 **4b-e**

Entry	Conditions	Yield (%)
1	AllocCl (4 equiv.), pyridine, rt, 1 h	**4b** (91)
2	Ac_2O (3 equiv.), pyridine, rt, 4 h	**4c** (94)
3	BzCl (2 equiv.), pyridine, rt, 8 h	**4d** (84[a])
4	PvCl (2 equiv.), pyridine, rt, 8 h	**4e** (94)

[a] Yield after recrystallization (benzene–hexane).

Table 9. Acylation of several amines with *N*-acylsulfonamides **4a–e** (all reactions were carried out with 1.2 equiv. of **4a–e** in THF)

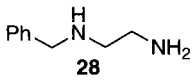
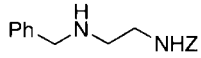
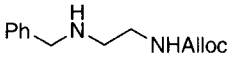
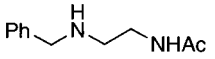
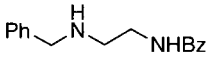
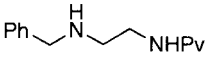
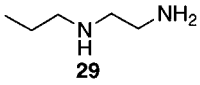
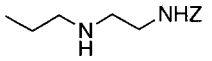
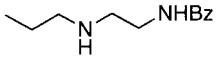
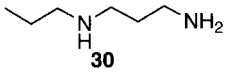
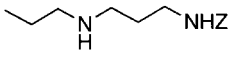
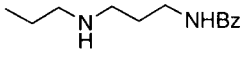
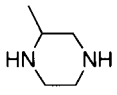
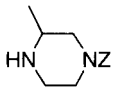
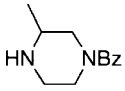
Entry	**4a-e**: RCO	Amine	Conditions	Product	Yield[a] (%)
1	**4b**: Alloc	 **17**	rt, 3.5 h		99
2	**4c**: Ac	**17**	rt, 50 min		95
3	**4d:** Bz	**17**	rt, 20 min		99
4	**4e:** Pv	**17**	rt, 4 h		76[b]
5	**4a**: Z	 **19**	rt, 10 h		99
6	**4b**: Alloc	**19**	rt, 24 h		99
7	**4c**: Ac	**19**	rt, 60 h		99
8	**4d:** Bz	**19**	rt, 1.5 h		99
9	**4a**: Z	 **20**	rt, 24 h		99
10	**4b**: Alloc	**20**	rt, 24 h		99
11	**4c**: Ac	**20**	rt, 4 h		99
12	**4d:** Bz	**20**	rt, 1.5 h		99
13	**4e:** Pv	**20**	rt, 48 h		62[b]
14	**4a**: Z	 **21**	65 °C, 48 h		64
15	**4b**: Alloc	**21**	65 °C, 48 h		68
16	**4c**: Ac	**21**	50 °C, 36 h		95
17	**4d:** Bz	**21**	65 °C, 48 h		93

[a] Average of two runs.
[b] ^{1}H NMR yield.

hindered amino and hindered amino groups, acyltransfer occurred only at the less-hindered amino group.

In summary, a variety of storable *N*-acyl-*N*-(2,3,4,5,6-pentafluorophenyl)methanesulfonamides (**4a–e**), which were prepared from 2,3,4,5,6-pentafluorophenylmethanesulfonamide (**3**) under mild conditions, were shown to be N-acylation reagents exhibiting sufficiently good chemoselectivity.

Table 10. Chemoselective acylation of several types of amines with *N*-acylsulfonamides **4a–e** (all reactions were carried out with 1.0 equiv. of **4a–e** in THF)

Entry	Amine	N-Acylsufonamide: RCO	Conditions	Product	Yield[a] (%)
1	 **28**	**4a**: Z	0 °C, 24 h		80
2	**28**	**4b**: Alloc	0 °C, 24 h		89
3	**28**	**4c**: Ac	0 °C, 24 h		92
4	**28**	**4d**: Bz	0 °C, 12 h		89
5	**28**	**4e**: Pv	0 °C, 36 h		82
6	 **29**	**4a**: Z	0 °C, 24 h		73
7	**29**	**4d**: Bz	0 °C, 12 h		92
8	 **30**	**4a**: Z	0 °C, 24 h		82
9	**30**	**4d**: Bz	0 °C, 12 h		91
10	 **31**	**4a**: Z	rt, 24 h		85
11	**31**	**4d**: Bz	0 °C, 18 h		90

[a] Average of two runs.

We believe that these new reagents **4a–e** can be widely used for selective protection of various polyamines.

Experimental

All melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were measured on a JASCO FT/IR-230 diffraction grating infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL GX-400 NMR spectrometer, operating at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR. ^{1}H NMR spectra were reported in δ units, parts per million (ppm) downfield from tetramethylsilane (δ=0) in $CDCl_3$ and residual DMSO (2.49 ppm) in DMSO-d_6. ^{13}C NMR spectra were reported in ppm relative to central $CDCl_3$ resonance (δ=77.00). Electron impact (EI) and FAB-MS were obtained from a JEOL JMS-DX-303 and JMS-HX110 instruments, respectively.

All starting amines and arylamines were commercially available. *N*-Phenylmethanesulfonamide (**7b**), and authentic samples of *N*-(2-phenylethyl)acetamide, *N*-(2-phenylethyl)-pivalamide and *N*-(1-phenylethyl)pivalamide are commercially available. All reagents were available from commercial sources and used without purification. In general, all reactions were carried out in dry solvents under argon atmosphere. The good purity of all isolated products was determined by ^{1}H NMR, TLC, melting point (for solid compounds) and elemental analysis (for new compounds). All yields (Tables 2, 4, 5 and 7–10) for the acylation of various amines with the *N*-acylsulfonamides

4a–e, **13a–d** and **25–27** referred to the average of two isolated yields. Pyridine was distilled under argon atmosphere from CaH_2 before use. THF was distilled under argon atmosphere from sodium/benzophenone ketyl before use. Silica gel column was performed on Kanto Chemical Silica gel 60 (spherical, 100–200 mm) unless otherwise mentioned.

PM3 calculations were performed with CAChe™ MOPAC (version 94.10).

General procedure A for preparation of *N*-arylmethanesulfonamide

To a stirred solution of arylamine in pyridine (0.6 M solution of arylamine) was gradually added methanesulfonyl chloride (1.5 equiv.) at 0°C. The reaction mixture was stirred for 12 h at 23°C and then concentrated directly using a rotary evaporator to afford the crude product as a mixture of *N*-mono- and di-mesylated arylamines. The following work-up was performed to convert the di-mesylated arylamine to mono-mesylated arylamine. The crude product was dissolved in a 2:1 mixture of THF and water (0.4 M solution of the starting arylamine), and then to this mixture was added NaOH (5 equiv. to the starting arylamine). The whole mixture was stirred for 1 h at 23°C, acidified with 15% aqueous HCl and extracted with EtOAc. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated to give the crude *N*-arylmethanesulfonamide.

General procedure B for preparation of *N*-arylmethanesulfonamide

To a stirred solution of arylamine in pyridine (0.6 M solution of arylamine) was gradually added methanesulfonyl chloride (2 equiv.) at 23°C. The reaction mixture was stirred for 6 h at 50°C, allowed to cool and then concentrated directly using a rotary evaporator to afford the crude product as a mixture of *N*-mono- and di-mesylated arylamines. The work-up was performed in the same manner as the procedure A.

***N*-(2-Fluorophenyl)methanesulfonamide (8a).** General procedure A was used with 2-fluoroaniline (1.34 g, 12.1 mmol). Purification by silica gel column (EtOAc–benzene=1:10) followed by recrystallization (EtOAc–hexane) afforded the analytically pure *N*-arylmethanesulfonamide **8a** (1.68 g, 73%) as colorless plates of mp 77–77.5°C. IR (nujol): ν=3254, 1612, 1597, 1499, 1466, 1408, 1324, 1254, 1156, 1101 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.04 (s, 3H), 6.75 (br s, 1H), 7.08–7.22 (m, 3H), 7.52–7.64 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=39.78, 115.65 (d, J=20.0 Hz), 123.42, 124.49 (d, J=12.5 Hz), 124.93 (d, J=4.2 Hz), 126.42 (d, J=7.5 Hz), 153.90 (d, J=243.5 Hz). EI-MS: m/z=189 (M^+), 110 (bp), 83. Anal. Calcd for $C_7H_8FNO_2S$: C, 44.44; H, 4.26; N, 7.40. Found: C, 44.51; H, 4.47; N, 7.44.

***N*-(4-Fluorophenyl)methanesulfonamide (9).** General procedure A was used with 4-fluoroaniline (1.20 mL, 12.7 mmol). Purification by silica gel column (EtOAc–benzene=1:10) followed by recrystallization (EtOAc–hexane) afforded the analytically pure *N*-arylmethanesulfonamide **9** (1.70 g, 71%) as colorless plates of mp 110–111°C. IR (nujol): ν=3243, 1508, 1319, 1146 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.99 (s, 3H), 6.84 (br s, 1H), 7.06 (dd, J=9.0, 9.0 Hz, 2H), 7.24 (dd, J=9.0, 4.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=39.08, 116.29 (d, J=22.5 Hz), 123.66 (d, J=8.3 Hz), 132.35 (d, J=2.5 Hz), 160.41 (d, J=245.1 Hz). EI-MS: m/z=189 (M^+), 110, 83 (bp). Anal. Calcd for $C_7H_8FNO_2S$: C, 44.44; H, 4.26; N, 7.40. Found: C, 44.49; H, 4.55; N, 7.40.

***N*-(2-Trifluoromethylphenyl)methanesulfonamide (10).** General procedure A was used with 2-trifluoromethylaniline (1.00 g, 6.20 mmol). Purification by silica gel column (EtOAc–benzene=1:5) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-arylmethanesulfonamide **10** (948 mg, 64%) as colorless needles of mp 84°C. IR (nujol): ν=3292, 1607, 1494, 1405, 1335, 1318, 1170, 1114 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.01 (s, 3H), 6.70 (br s, 1H), 7.33 (dd, J=8.3, 8.3 Hz, 1H), 7.60 (dd, J=8.3, 8.3 Hz, 1H), 7.66 (d, J=8.3 Hz, 1H), 7.83 (d, J=8.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ=40.08, 121.22 (q, J=29.2 Hz), 123.65 (q, J=271.8 Hz), 124.03, 125.43, 126.54 (q, J=3.8 Hz), 133.35, 134.10. EI-MS: m/z=239 (M^+), 219, 161 (bp), 141, 113. Anal. Calcd for $C_8H_8F_3NO_2S$: C, 40.17; H, 3.37; N, 5.86. Found: C, 40.38; H, 3.39; N, 5.87.

***N*-(4-Trifluoromethylphenyl)methanesulfonamide (11).** General procedure A was used with 4-trifluoromethylaniline (1.13 g, 7.01 mmol). Purification by silica gel column (EtOAc–benzene=1:7) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-arylmethanesulfonamide **11** (1.14 g, 68%) as colorless fine needles of mp 128.5–130°C. IR (nujol): ν=3283, 1620, 1330, 1157, 1111 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.09 (s, 3H), 7.32 (d, J=8.5 Hz, 2H), 7.62 (d, J=8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=40.02, 118.99, 123.73 (q, J=271.0 Hz), 126.83 (q, J=32.5 Hz), 126.89 (q, J=3.3 Hz), 139.86. EI-MS: m/z=239 (M^+), 161, 140, 110, 83 (bp). Anal. Calcd for $C_8H_8F_3NO_2S$: C, 40.17; H, 3.37; N, 5.86. Found: C, 40.39; H, 3.56; N, 5.85.

***N*-(2,3,4,5,6-Pentafluorophenyl)methanesulfonamide (3).** General procedure B was used with 2,3,4,5,6-pentafluoroaniline (2.27 g, 12.4 mmol). Purification by silica gel column (EtOAc–benzene=1:9) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-arylmethanesulfonamide **3** (2.25 g, 69%) as colorless needles of mp 159–161°C. IR (nujol): ν=3222, 1530, 1515, 1341, 1330, 1165 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.25 (s). The signal of NH was not observed. EI-MS: m/z=261 (M^+), 182, 155 (bp), 117, 83. Anal. Calcd for $C_7H_4F_5NO_2S$: C, 32.19; H, 1.54; N, 5.36. Found: C, 32.21; H, 1.75; N, 5.36.

***N*-(2,6-Difluorophenyl)methanesulfonamide (22).** General procedure B was used with 2,6-difluoroaniline (1.45 g, 11.2 mmol). Purification by silica gel column (EtOAc–benzene=1:10) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-arylmethanesulfonamide **22** (1.11 g, 48%) as colorless fine needles of mp 149°C. IR (nujol): ν=3251, 1600, 1480, 1335,

1152 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.23 (s, 3H), 6.14 (br s, 1H), 6.94–7.07 (m, 2H), 7.18–7.30 (m, 1H). EI-MS: *m*/*z*=207 (M^+), 128 (bp), 149, 101. Anal. Calcd for $C_7H_7F_2NO_2S$: C, 40.58; H, 3.41; N, 6.76. Found: C, 40.76; H, 3.51; N, 6.72.

***N*-(2-Fluoro-5-trifluoromethylphenyl)methanesulfonamide (23).** General procedure B was used with 2-fluoro-5-trifluoromethylaniline (1.01 g, 5.64 mmol). Purification by silica gel column (EtOAc–benzene=1:10) followed by recrystallization (EtOAc–hexane) afforded the analytically pure *N*-arylmethanesulfonamide **23** (1.15 g, 79%) as colorless needles of mp 95.5–97.5°C. IR (nujol): ν=3251, 1609, 1523, 1427, 1411, 1335, 1167, 1121 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.10 (s, 3H), 6.35–7.10 (br, 1H), 7.27 (dd, *J*=9.0, 9.0 Hz, 1H), 7.45 (ddd, *J*=9.0, 4.6, 2.2 Hz, 1H), 7.88 (dd, *J*=7.3, 2.2 Hz, 1H). EI-MS: *m*/*z*=257 (M^+), 178 (bp), 151, 132, 101. Anal. Calcd for $C_8H_7F_4NO_2S$: C, 37.36; H, 2.74; N, 5.45. Found: C, 37.09; H, 2.83; N, 5.36.

***N*-[3,5-Bis(trifluoromethyl)phenyl]methanesulfonamide (24).** General procedure B was used with 3,5-bis(trifluoromethyl)aniline (2.40 g, 10.5 mmol). Purification by recrystallization (EtOAc–hexane) afforded the analytically pure *N*-arylmethanesulfonamide **24** (1.84 g, 57%) as colorless needles of mp 149–150°C. IR (nujol): ν=3237, 1624, 1472, 1432, 1375, 1362, 1147, 1124 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.14 (s, 3H), 7.31 (br s, 1H), 7.67 (s, 3H). EI-MS: *m*/*z*=307 (M^+), 287, 229 (bp), 208, 188, 132, 79. Anal. Calcd for $C_9H_7F_6NO_2S$: C, 35.19; H, 2.30; N, 4.56. Found: C, 35.24; H, 2.39; N, 4.64.

***N*-2-Fluorophenyl-4-toluenesulfonamide (8b).** To a stirred solution of 2-fluoroaniline (889 mg, 8.00 mmol) in pyridine (13.0 mL) was gradually added tosyl chloride (3.05 g, 16.0 mmol) at 0°C. The reaction mixture was stirred for 12 h at rt, and then concentrated directly using a rotary evaporator to afford the crude product. Purification by silica gel column (benzene) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-toluenesulfonamide **8b** (1.41 g, 67%) as colorless needles of mp 108–109°C. IR (nujol): ν=3250, 1597, 1499, 1417, 1337, 1255, 1166, 1092 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.38 (s, 3H), 6.74 (br s, 1H), 6.93–7.11 (m, 3H), 7.22 (d, *J*=8.5 Hz, 2H), 7.59 (ddd, *J*=8.0, 8.0, 2.2 Hz, 1H), 7.66 (d, *J*=8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=21.68, 115.27 (d, *J*=20.0 Hz), 123.09, 124.50, 124.58, 124.62, 125.92 (d, *J*=7.5 Hz), 127.05, 129.51, 135.73, 143.97, 153.68 (d, *J*=243.5 Hz). EI-MS: *m*/*z*=265 (M^+), 155, 111, 91 (bp). Anal. Calcd for $C_{13}H_{12}FNO_2S$: C, 58.85; H, 4.56; N, 5.28. Found: C, 59.14; H, 4.70; N, 5.23.

General procedure for benzyloxycarbonylation of *N*-arylsulfonamide

To a stirred solution of *N*-arylmethanesulfonamide in pyridine (0.5 M solution of substrate) was gradually added benzyloxycarbonyl chloride (4 equiv.) at 0°C. The reaction mixture was stirred at 23°C for 1 h and quenched by the addition of water. The whole mixture was extracted with ethyl acetate. The organic extracts were washed with water and brine, dried over Na_2SO_4, and concentrated using a rotary evaporator to afford the crude product.

***N*-Benzyloxycarbonyl-*N*-(2-fluorophenyl)methanesulfonamide (13a).** General procedure was used with the *N*-arylmethanesulfonamide **8a** (568 mg, 3.00 mmol). Purification by silica gel column (EtOAc–benzene=1:20) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-methanesulfonamide **13a** (872 mg, 90%) as colorless needles of mp 97–100°C. IR (nujol): ν=1737, 1497, 1448, 1346, 1155 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.42 (s, 3H), 5.21 (s, 2H), 7.12–7.42 (m, 9H). ^{13}C NMR ($CDCl_3$): δ=41.63, 69.63, 116.47, 116.67, 123.32, 123.45, 125.04, 125.08, 128.06, 128.88, 128.92, 131.74, 131.81, 132.54, 134.83, 152.46, 158.67 (d, *J*=250 Hz). EIMS: *m*/*z*=323 (M^+), 244, 199, 149, 109, 91 (bp). Anal. Calcd for $C_{15}H_{14}FNO_4S$: C, 55.72; H, 4.36; N, 4.33, Found: C, 55.87; H, 4.18; N, 4.39.

***N*-Benzyloxycarbonyl-*N*-(4-fluorophenyl)methanesulfonamide (14).** General procedure was used with the *N*-arylmethanesulfonamide **9** (567 mg, 3.00 mmol). Purification by silica gel column (EtOAc–benzene=1:40) afforded the desired product **14** (451 mg) accompanied by recovery of the unreacted starting material **9** (266 mg, 47%). Further purification of the desired product by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-methanesulfonamide **14** (381 mg, 39%) as colorless fine needles of mp 127–128°C. IR (nujol): ν=1734, 1508, 1351, 1223, 1156 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.43 (s, 3H), 5.22 (s, 2H), 7.07–7.14 (m, 2H), 7.18–7.26 (m, 4H), 7.30–7.37 (m, 3H). ^{13}C NMR ($CDCl_3$): δ=41.65, 69.21, 116.26, 116.48, 127.84, 128.10, 130.90, 131.11, 131.21, 134.52, 152.62, 162.86 (d, *J*=250 Hz). EIMS: *m*/*z*=323 (M^+), 279, 199, 91 (bp). Anal. Calcd for $C_{15}H_{14}FNO_4S$: C, 55.72; H, 4.36; N, 4.33, Found: C, 55.43; H, 4.36; N, 4.34.

***N*-Benzyloxycarbonyl-*N*-(2-trifluoromethylphenyl)methanesulfonamide (15).** General procedure was used with the *N*-arylmethanesulfonamide **10** (749 mg, 3.13 mmol). Purification by silica gel column (EtOAc–benzene=1:20) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-methanesulfonamide **15** (865 mg, 74%) as colorless cubes of mp 98–100°C. IR (nujol): ν=1741, 1451, 1360, 1315, 1268, 1167 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.50 (s, 3H), 5.16 (d, *J*=12.3 Hz, 1H), 5.23 (d, *J*=12.3 Hz, 1H), 7.13–7.21 (m, 2H), 7.26–7.33 (m, 3H), 7.45 (d, *J*=7.7 Hz, 1H), 7.54 (dd, *J*=7.7, 7.7 Hz, 1H), 7.62 (dd, *J*=7.7, 7.7 Hz, 1H), 7.74 (d, *J*=7.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ=41.81, 69.43, 123.11 (q, *J*=274 Hz), 127.27, 127.31, 127.37, 127.42, 127.86, 128.02, 128.08, 128.17, 128.39, 128.54, 128.57, 128.68, 130.05, 132.39, 132.69, 133.02, 134.28, 152.33. EIMS: *m*/*z*=373 (M^+), 294, 234, 187, 91 (bp). Anal. Calcd for $C_{16}H_{14}F_3NO_4S$: C, 51.47; H, 3.78; N, 3.75, Found: C, 51.38; H, 3.76; N, 3.82.

***N*-Benzyloxycarbonyl-*N*-(4-trifluoromethylphenyl)methanesulfonamide (16).** General procedure was used with the *N*-arylmethanesulfonamide **11** (718 mg, 3.00 mmol). Purification by silica gel column (EtOAc–benzene=1:20) afforded the desired product **16** (423 mg) accompanied by recovery of the unreacted starting material **11** (460 mg, 64%). Further purification of the desired product by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-methanesulfonamide **16** (235 mg, 21%) as colorless needles of mp 148.5–150.5°C. IR (nujol): ν=1746, 1614,

1376, 1335, 1168, 1119 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.46 (s, 3H), 5.24 (s, 2H), 7.20–7.25 (m, 2H), 7.32–7.35 (m, 3H), 7.37 (d, J=8.8 Hz, 2H), 7.69 (d, J=8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=41.91, 69.47, 123.54 (q, J=272 Hz), 126.43, 126.47, 126.51, 128.01, 128.70, 128.77, 129.96, 131.55 (q, J=33.1 Hz), 134.33, 138.12, 152.24. EIMS: m/z=373 (M^+), 294, 249, 187, 149, 91, 63 (bp). Anal. Calcd for $C_{16}H_{14}F_3NO_4S$: C, 51.47; H, 3.78; N, 3.75, Found: C, 51.49; H, 3.82; N, 3.63.

***N*-Benzyloxycarbonyl-*N*-(2-fluorophenyl)-4-toluenesulfonamide (13b).** General procedure was used with the *N*-aryltoluenesulfonamide **8b** (796 mg, 3.00 mmol). Purification by silica gel column (EtOAc–benzene=1:40) afforded the desired product **13b** (914 mg) accompanied by recovery of the unreacted starting material **8b** (137 mg, 17%). Further purification of the desired product **13b** by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-toluenesulfonamide **13b** (842 mg, 70%) as colorless prisms of mp 103–104°C. IR (nujol): ν=1749, 1519, 1461, 1253, 1363, 1261, 1173 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.43 (s, 3H), 5.10 (s, 2H), 7.08–7.30 (m, 9H), 7.36–7.45 (m, 2H), 7.86 (d, J=8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=21.64, 68.94, 116.28, 116.48, 123.51, 123.65, 124.55, 124.59, 127.75, 128.33, 128.41, 129.08, 129.29, 131.26, 131.33, 131.97, 134.48, 135.67, 145.00, 151.38, 158.70 (d, J=252 Hz). EIMS: m/z=399 (M^+), 335, 291, 244, 200, 137, 91 (bp), 65. Anal. Calcd for $C_{21}H_{18}FNO_4S$: C, 63.14; H, 4.54; N, 3.51, Found: C, 63.24; H, 4.56; N, 3.60.

***N*-Benzyloxycarbonyl-*N*-(2,3,4,5,6-pentafluorophenyl)-methanesulfonamide (4a).** General procedure was used with the *N*-arylmethanesulfonamide **3** (742 mg, 2.84 mmol). Purification by silica gel column (EtOAc–benzene=1:20) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-methanesulfonamide **4a** (943 mg, 84%) as colorless needles of mp 98–100.5°C. IR (nujol): ν=1739, 1522, 1271, 1174, 993 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.46 (s, 3H), 5.29 (s, 2H), 7.27–7.41 (m, 5H). EIMS: m/z=395 (M^+), 351, 316, 256, 209, 181, 131, 107, 91, 79, 65 (bp). Anal. Calcd for $C_{15}H_{10}F_5NO_4S$: C, 45.58; H, 2.55; N, 3.54, Found: C, 45.65; H, 2.51; N, 3.61.

***N*-Benzyloxycarbonyl-*N*-(2,6-difluorophenyl)methanesulfonamide (25).** General procedure was used with the *N*-arylmethanesulfonamide **22** (624 mg, 3.01 mmol). Purification by silica gel column (EtOAc–benzene=1:20) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-methanesulfonamide **25** (914 mg, 89%) as colorless needles of mp 68–69°C. IR (nujol): ν=1736, 1597, 1476, 1362, 1244, 1162 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.46 (s, 3H), 5.26 (s, 2H), 7.00 (d, J=7.1 Hz, 1H), 7.02 (d, J=7.1 Hz, 1H), 7.20–7.43 (m, 6H). ^{13}C NMR ($CDCl_3$): δ=41.58, 69.59, 111.82, 111.86, 112.06, 112.90, 113.06, 127.71, 128.63, 131.22, 131.32, 131.41, 134.33, 151.43, 159.61 (dd, J=254, 3.7 Hz). EIMS: m/z=341 (M^+), 262, 217, 202, 155, 127, 107, 91 (bp), 77. Anal. Calcd for $C_{15}H_{13}F_2NO_4S$: C, 52.78; H, 3.84; N, 4.10, Found: C, 52.78; H, 3.78; N, 4.09.

***N*-Benzyloxycarbonyl-*N*-(2-fluoro-5-trifluoromethylphenyl)-methanesulfonamide (26).** General procedure was used with the *N*-arylmethanesulfonamide **23** (824 mg, 3.20 mmol). Purification by silica gel column (EtOAc–benzene=1:20) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-methanesulfonamide **26** (1.08 g, 86%) as colorless cubes of mp 89–91°C. IR (nujol): ν=1747, 1514, 1359, 1173, 1126 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.46 (s, 3H), 5.26 (s, 2H), 7.21–7.38 (m, 6H), 7.63–7.73 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=41.65, 69.74, 116.98, 117.18, 122.98 (q, J=272 Hz), 123.69, 123.84, 127.91, 128.68, 128.79, 129.78, 129.82, 134.15, 151.58, 160.28 (d, J=257 Hz). EIMS: m/z=391 (M^+), 312, 292, 252, 205, 177, 91 (bp). Anal. Calcd for $C_{16}H_{13}F_4NO_4S$: C, 49.11; H, 3.35; N, 3.58, Found: C, 49.12; H, 3.38; N, 3.62.

***N*-Benzyloxycarbonyl-*N*-[3,5-bis(trifluoromethyl)phenyl]-methanesulfonamide (27).** General procedure was used with the *N*-arylmethanesulfonamide **24** (931 mg, 3.03 mmol). Purification by silica gel column (EtOAc–benzene=1:40) afforded the desired product **27** (622 mg) accompanied by recovery of the unreacted starting material **24** (354 mg, 38%). Further purification of the desired product **27** by recrystallization (benzene–hexane) afforded the analytically pure *N*-Z-methanesulfonamide **27** (428 mg, 32%) as colorless fine needles of mp 142–143°C. IR (nujol): ν=1743, 1464, 1374, 1280, 1163, 1125 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.49 (s, 3H), 5.25 (s, 2H), 7.20–7.30 (m, 2H), 7.31–7.40 (m, 3H), 7.69 (s, 2H), 7.93 (s, 1H). EI-MS: m/z=441 (M^+), 422, 362, 302, 236, 188, 91 (bp), 79, 77, 65. Anal. Calcd for $C_{17}H_{13}F_6NO_4S$: C, 46.26; H, 2.97; N, 3.17. Found: C, 46.33; H, 3.12; N, 3.27.

***N*-Allyloxycarbonyl-*N*-(2,3,4,5,6-pentafluorophenyl)-methanesulfonamide (4b).** To a stirred solution of the *N*-arylmethanesulfonamide **3** (804 mg, 3.08 mmol) in pyridine (8.0 mL) was gradually added allyloxycarbonyl chloride (1.3 mL, 12.3 mmol) at 0°C. The reaction mixture was stirred at 23°C for 20 min and quenched by the addition of water. The whole mixture was extracted with ethyl acetate. The organic extracts were washed with water and brine, dried over Na_2SO_4, and concentrated using a rotary evaporator to afford the crude product. Purification by silica gel column (benzene) afforded the analytically pure *N*-Alloc-methanesulfonamide **4b** (968 mg, 91%) as a colorless solid of mp 47–48°C. IR (nujol): ν=1749, 1514, 1365, 1270, 1171 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.51 (s, 3H), 4.75 (ddd, J=5.9, 1.2, 1.2 Hz, 2H), 5.30 (br dd, J=1.2, 1.2 Hz, 1H), 5.33 (ddd, J=6.6, 1.2, 1.2 Hz, 1H), 5.88 (ddt, J=6.6, 5.9, 1.2 Hz, 1H). EIMS: m/z=345 (M^+), 222, 209, 181, 131, 79 (bp). Anal. Calcd for $C_{11}H_8F_5NO_4S$: C, 38.27; H, 2.33; N, 4.06, Found: C, 38.46; H, 2.45; N, 4.08.

General procedure for pivaloylation and benzoylation of *N*-arylmethanesulfonamide

To a stirred solution of *N*-arylmethanesulfonamide in pyridine (0.5 M solution of substrate) was gradually added acyl chloride (2 equiv.) at 0°C. The reaction mixture was stirred at 23°C for 8 h and quenched by the addition of water. The whole mixture was extracted with EtOAc. The organic extracts were washed with water and brine, dried over Na_2SO_4, and concentrated using a rotary evaporator to afford the crude product.

***N*-Pivaloyl-*N*-(2-fluorophenyl)methanesulfonamide (13c).** General procedure was used with the *N*-arylmethanesulfonamide **8a** (602 mg, 3.18 mmol). Purification by silica gel column (EtOAc–benzene=1:20) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-Pv-methanesulfonamide **13c** (729 mg, 84%) as colorless cubes of mp 102–103°C. IR (nujol): ν=1695, 1494, 1350, 1172, 1116, 968 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.06 (s, 9H), 3.39 (s, 3H), 7.14–7.27 (m, 2H), 7.42–7.49 (m, 2H). EIMS: *m*/*z*=273 (M^+), 216, 189 (bp), 172, 151, 137. Anal. Calcd for $C_{12}H_{16}FNO_3S$: C, 52.73; H, 5.90; N, 5.13, Found: C, 52.57; H, 5.78; N, 5.18.

***N*-Pivaloyl-*N*-phenylmethanesulfonamide (32).** General procedure was used with *N*-phenylmethanesulfonamide (**7b**) (514 mg, 3.00 mmol). Purification by silica gel column (EtOAc–benzene=1:20) afforded the analytically pure *N*-Pv-methanesulfonamide **32** (222 mg, 29%) as colorless solid of mp 121–124°C accompanied by recovery of the unreacted starting material **7b** (293 mg, 57%). IR (nujol): ν=1695, 1349, 1119 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.07 (s, 9H), 3.29 (s, 3H), 7.32–7.36 (m, 2H), 7.42–7.47 (m, 3H). ^{13}C NMR ($CDCl_3$): δ=28.73, 40.22, 43.95, 129.23, 129.69, 130.03, 135.73, 182.16. EIMS: *m*/*z*=171 (MH^+-Pv), 149, 119, 92, 85, 57 (bp). Anal. Calcd for $C_{12}H_{17}NO_3S$: C, 56.45; H, 6.71; N, 5.49, Found: C, 56.16; H, 6.81; N, 5.41.

***N*-Pivaloyl-*N*-(4-fluorophenyl)methanesulfonamide (33).** General procedure was used with the *N*-arylmethanesulfonamide **9** (588 mg, 3.11 mmol). Purification by silica gel column (EtOAc–benzene=1:40) afforded the analytically pure *N*-Pv-methanesulfonamide **33** (204 mg, 24%) as a colorless solid of mp 88–90°C and the unreacted starting material **9** (406 mg, 69%). IR (nujol): ν=1693, 1506, 1353, 1218, 1168, 1124 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.08 (s, 9H), 3.29 (s, 3H), 7.11–7.18 (m, 2H), 7.29–7.36 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=28.72, 40.34, 43.86, 116.37 (d, *J*=23.3 Hz), 131.64 (d, *J*=3.3 Hz), 131.87 (d, *J*=8.3 Hz), 162.93 (d, *J*=251.0 Hz), 181.78. EIMS: *m*/*z*=273 (M^+), 189 (bp), 137, 110, 85, 57. Anal. Calcd for $C_{12}H_{16}FNO_3S$: C, 52.73; H, 5.90; N, 5.13, Found: C, 53.02; H, 5.98; N, 5.00.

***N*-Pivaloyl-*N*-(2,3,4,5,6-pentafluorophenyl)methanesulfonamide (4e).** General procedure was used with the *N*-arylmethanesulfonamide **3** (799 mg, 3.06 mmol). Purification by silica gel column (benzene–hexane=1:1) afforded the analytically pure *N*-Pv-methanesulfonamide **4e** (992 mg, 94%) as a colorless solid. Recrystallization (benzene–hexane) afforded colorless needles of mp 94–95°C. IR (nujol): ν=1715, 1706, 1521, 1506, 1362, 1180, 1110, 1036 cm^{-1}. ^1H NMR ($CDCl_3$): δ=1.14 (s, 9H), 3.47 (s, 3H). EIMS: *m*/*z*=345 (M^+), 261, 209, 183, 131, 85, 57 (bp). Anal. Calcd for $C_{12}H_{12}F_5NO_3S$: C, 41.74; H, 3.50; N, 4.06, Found: C, 41.95; H, 3.61; N, 4.14.

***N*-Benzoyl-*N*-(2-fluorophenyl)methanesulfonamide (13d).** General procedure was used with the *N*-arylmethanesulfonamide **8a** (825 mg, 3.16 mmol). Purification by silica gel column (EtOAc–benzene=1:20) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-Bz-methanesulfonamide **13d** (852 mg, 92%) as colorless prisms of mp 105–106°C. IR (nujol): ν=1712, 1492, 1351, 1247, 1169 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.51 (s, 3H). 6.95–7.02 (m, 1H), 7.13–7.38 (m, 5H), 7.46–7.52 (m, 3H). EIMS: *m*/*z*=293 (M^+), 185, 139, 105, 77 (bp). Anal. Calcd for $C_{14}H_{12}FNO_3S$: C, 57.33; H, 4.12; N, 4.78, Found: C, 57.44; H, 3.91; N, 4.80.

***N*-Benzoyl-*N*-(2,3,4,5,6-pentafluorophenyl)methanesulfonamide (4d).** General procedure was used with the *N*-arylmethanesulfonamide **3** (868 mg, 3.32 mmol). Purification by silica gel column (benzene–hexane=1:1) followed by recrystallization (benzene–hexane) afforded the analytically pure *N*-Bz-methanesulfonamide **4d** (1.02 g, 84%) as colorless prisms of mp 105–106°C. IR (nujol): ν=1717, 1508, 1447, 1362, 1320, 1260, 1172, 1157 cm^{-1}. ^1H NMR ($CDCl_3$): δ=3.57 (s, 3H), 7.32–7.38 (m, 2H), 7.44–7.51 (m, 3H). EIMS: *m*/*z*=365 (M^+), 238, 105 (bp), 77. Anal. Calcd for $C_{14}H_8F_5NO_3S$: C, 46.03; H, 2.21; N, 3.84, Found: C, 46.02; H, 2.34; N, 3.72.

***N*-Acetyl-*N*-(2,3,4,5,6-pentafluorophenyl)methanesulfonamide (4c).** To a stirred solution of the *N*-arylmethanesulfonamide **3** (807 mg, 3.09 mmol) in pyridine (8.0 mL) was gradually added acetic anhydride (0.87 mL, 9.27 mmol) at 0°C. The reaction mixture was stirred at 23°C for 4 h and directly concentrated using a rotary evaporator to afford the crude product. Purification by silica gel column (EtOAc–benzene=1:20) afforded the analytically pure *N*-Ac-methanesulfonamide **4c** (881 mg, 94%) as a colorless oil. IR (neat): ν=1728, 1519, 1367, 1237, 1169, 1055 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.15 (s, 3H), 3.49 (s, 3H). EIMS: *m*/*z*=303 (M^+), 261, 183 (bp), 131, 79. Anal. Calcd for $C_9H_6F_5NO_3S$: C, 35.65; H, 2.00; N, 4.62, Found: C, 35.62; H, 2.15; N, 4.65.

Typical procedure for acylation of amine with the Z-sulfonamide 4a corresponding to entry 1 in Table 7

To a stirred solution of 2-phenylethylamine (**17**) (0.11 mL, 0.900 mmol) in THF (3.00 mL) was added the *N*-Z-methanesulfonamide **4a** (427 mg, 1.08 mmol) at 23°C. The reaction mixture was stirred for 1.5 h at the same temperature and concentrated using a rotary evaporator. The residue was purified by silica gel[†] column (benzene) to give benzyl *N*-(2-phenylethyl)carbamate (**18**) (227 mg, 99%) as a colorless solid. Successive elution of the silica gel column with EtOAc recovered the sulfonamide **3** (257 mg, 91%).

Benzyl *N*-(2-phenylethyl)carbamate (18). The physical data shown below were comparable to those reported.[12] A colorless solid of mp 66–67.5°C. Reported mp 56–58°C. IR (nujol): ν=3326, 1677 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.81 (t, *J*=6.8 Hz, 2H), 3.46 (dt, *J*=6.8, 6.8 Hz, 2H), 4.76 (br s), 5.09 (s, 2H), 7.17–7.38 (m, 10H). ^{13}C NMR ($CDCl_3$): δ=36.17, 42.29, 66.66, 126.37, 127.95, 128.36, 128.48, 128.62, 136.41, 138.51, 156.06. EI-MS: *m*/*z*=255 (M^+), 194, 164, 146, 120, 91 (bp).

Physical data of the other acylated amines were shown below.

[†] NH-type silica gel Chromatorex NHDM1020, which was purchased from Fuji Silysia Chemical Ltd, was used.

Benzyl *N*-(1-phenylethyl)carbamate. A colorless oil. IR (neat): ν=3328, 1701, 1689 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.48 (d, J=6.8 Hz, 3H), 4.86 (br s, 1H), 4.99–5.10 (m, 1H), 5.05 (d, J=12.2 Hz, 1H), 5.11 (d, J=12.2 Hz, 1H), 7.20–7.40 (m, 10H). ^{13}C NMR ($CDCl_3$): δ=22.59, 50.78, 66.73, 125.76, 127.17, 127.94, 128.33, 128.48, 136.31, 155.31. EI-MS: m/z=255 (M^+), 240, 196, 163, 106 (bp). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.50; H, 6.87; N, 5.55.

Benzyl *N*-benzyl-*N*-methylcarbamate. The physical data shown below were comparable to those reported.[2d] A colorless oil. IR (neat): ν=1704 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.87 and 2.90 (s, 3H), 4.50 (s, 2H), 5.18 (s, 2H), 7.15–7.43 (m, 10H). EI-MS: m/z=255 (M^+), 210, 163, 121 (bp), 89.

Benzyl *N*-cumylcarbamate. A colorless solid of mp 63–64°C. IR (nujol): ν=3276, 1704 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.67 (s, 3H×2), 5.02 (s, 2H), 5.17 (br s, 1H), 7.21–7.41 (m, 10H). EI-MS: m/z=269 (M^+), 254, 210, 119, 108, 91 (bp). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.80; H, 7.26; N, 5.31.

Allyl *N*-(2-phenylethyl)carbamate. A colorless oil. IR (neat): ν=3338, 1701 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.81 (t, J=6.8 Hz, 2H), 3.45 (dt, J=6.8, 6.8 Hz, 2H), 4.55 (d, J=5.4 Hz, 2H), 4.76 (br s, 1H), 5.20 (d, J=10.5 Hz, 1H), 5.28 (d, J=16.8 Hz, 1H), 5.90 (ddd, J=16.8, 10.5, 5.4 Hz, 1H), 7.13–7.36 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=36.21, 42.24, 65.47, 117.46, 126.35, 128.47, 128.61, 132.77, 138.54, 155.93. EI-MS: m/z=205 (M^+), 164, 114, 105, 91 (bp). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 70.40; H, 7.53; N, 6.94.

Allyl *N*-(1-phenylethyl)carbamate. A colorless solid of mp 43–44°C. IR (nujol): ν=3319, 1689 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.48 (d, J=6.8 Hz, 3H), 4.50–4.61 (m, 2H), 4.77–4.91 (br, 1H), 5.01 (br s, 1H), 5.19 (br d, J=10.3 Hz, 1H), 5.28 (br d, J=16.6 Hz, 1H), 5.82–5.98 (m, 1H), 7.22–7.38 (m, 5H). EI-MS: m/z=205 (M^+), 190, 164 (bp), 146, 120, 105, 91. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 70.42; H, 7.54; N, 6.87.

Allyl *N*-benzyl-*N*-methylcarbamate. A colorless oil. IR (neat): ν=1702 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.86 and 2.89 (s, 3H), 4.48 (d, J=10.3 Hz, 1H), 4.50 (d, J=10.3 Hz, 1H), 4.61–4.69 (m, 2H), 5.16–5.37 (m, 2H), 5.88–6.03 (br, 1H), 7.18–7.39 (m, 5H). EI-MS: m/z=205 (M^+), 164, 120, 91 (bp). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 70.50; H, 7.43; N, 6.85.

Allyl *N*-cumylcarbamate. A colorless oil. IR (neat): ν=3344, 1718, 1707 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.67 (s, 3H×2), 4.48 (d, J=4.6 Hz, 2H), 5.12–5.38 (m, 3H), 5.89 (br s, 1H), 7.18–7.47 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=23.87, 55.26, 65.08, 117.39, 124.63, 126.54, 128.19, 132.83, 146.72, 154.02. EI-MS: m/z=219 (M^+, bp), 178, 161, 146, 142, 117, 98. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.45; H, 7.87; N, 6.28.

***N*-(2-Phenylethyl)acetamide.** The physical data shown below were identical with those of the commercially available *N*-(2-phenylethyl)acetamide and were comparable to those reported.[13] A colorless solid of mp 53–54°C. Reported mp 50.5–52°C. IR (nujol): ν=3287, 1638 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.93 (s, 3H), 2.82 (t, J=6.8 Hz, 2H), 3.51 (dt, J=6.8, 6.8 Hz, 2H), 5.58 (br s, 1H), 7.16–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=23.39, 35.71, 40.71, 126.34, 128.46, 128.54, 138.68, 169.75. EI-MS: m/z=163 (M^+), 104 (bp), 91.

***N*-(1-Phenylethyl)acetamide.** The physical data shown below were comparable to those reported.[14] Colorless needles (benzene–hexane), mp 79–80°C. Reported mp 76°C. IR (KBr): ν=3450, 1648 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.49 (d, J=6.8 Hz, 3H), 1.98 (s, 3H), 5.13 (dq, J=6.8, 6.8 Hz, 1H), 5.73 (br s, 1H), 7.23–7.40 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=21.82, 23.60, 48.85, 126.05, 127.24, 128.53, 142.96, 168.76. FAB-MS: m/z=164 (MH^+).

***N*-Benzyl-*N*-methylacetamide.** The physical data as shown below were comparable to those reported.[15] A colorless oil. IR (neat): ν=1646 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.16 (s, 3H), 2.92 and 2.94 (s, 3H), 4.53 and 4.59 (s, 2H), 7.16–7.40 (m, 5H). EI-MS: m/z=163 (M^+, bp), 148, 120, 106, 91, 77.

***N*-Cumylacetamide.** Colorless needles (benzene–hexane), mp 108–109°C. IR (nujol): ν=3337, 3304, 1654 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.69 (s, 3H×2), 1.95 (s, 3H), 5.79 (br s, 1H), 7.19–7.44 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=24.44, 29.16, 55.95, 124.57, 126.48, 128.20, 146.65, 168.80. EI-MS: m/z=178 (MH^+), 177 (M^+), 162, 120 (bp), 91. Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90, Found: C, 74.71; H, 8.80; N, 7.97.

***N*-(2-Phenylethyl)benzamide.** The physical data shown below were comparable to those reported.[13] Colorless needles (EtOAc–hexane), mp 122–123°C. Reported mp 118–120.5°C. IR (nujol): ν=3343, 1639 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=2.94 (t, J=6.8 Hz, 2H), 3.73 (dt, J=6.8, 6.8 Hz, 2H), 6.11 (br s, 1H), 7.20–7.51 (m, 8H), 7.65–7.72 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=35.81, 41.20, 41.23, 126.44, 126.64, 126.68, 128.39, 128.56, 128.66, 131.22, 134.51, 138.75, 167.20, 167.25. EI-MS: m/z=225 (M^+), 105, 84 (bp).

***N*-(1-Phenylethyl)benzamide.** The physical data shown below were comparable to those reported.[16] Colorless needles (benzene–hexane), mp 128.5–129°C. Reported mp 124°C. IR (nujol): ν=3356, 1633 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.61 (d, J=7.0 Hz, 3H), 5.34 (dt, J=7.0, 7.0 Hz, 1H), 6.24–6.40 (br, 1H), 7.24–7.51 (m, 8H), 7.74–7.79 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=21.85, 49.27, 126.10, 126.76, 127.31, 128.39, 128.59, 131.29, 134.44, 142.93, 166.29. FAB-MS: m/z=226 (MH^+).

***N*-Benzyl-*N*-methylbenzamide.** The physical data shown below were comparable to those reported.[3b] A colorless oil. IR (neat): ν=1633 cm^{-1}. ^{1}H NMR (DMSO-d_6, 90°C): δ=2.87 (s, 3H), 4.59 (s, 2H), 7.22–7.48 (m, 10H). FAB-MS: m/z=226 (MH^+).

***N*-Cumylbenzamide.** The physical data shown below were comparable to those reported.[17] Colorless needles (benzene–hexane) of mp 168–169°C. Reported mp 156–158°C. IR

(nujol): ν=3258, 1635 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.83 (s, 3H×2), 6.39 (br s, 1H), 7.22–7.51 (m, 8H), 7.73–7.78 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=29.26, 56.35, 124.59, 126.64, 126.67, 128.36, 128.39, 131.15, 135.29, 146.62, 166.16. FAB-MS: m/z=240 (MH^+).

Typical procedure for chemoselective acylation of diamine with the *N*-Z-sulfonamide 4a corresponding to entry 1 in Table 10

To a stirred solution of *N*-benzylethylenediamine (68 μL, 0.450 mmol) in THF (1.5 mL) was added the *N*-Z-sulfonamide **4a** (178 mg, 0.450 mmol) at 0°C. The reaction mixture was stirred for 24 h at the same temperature, quenched by the addition of piperidine (0.05 mL) and directly concentrated using a rotary evaporator. The residue was purified by silica gel column (EtOAc) to give *N*-benzyl-*N′*-benzyloxycarbonylethylenediamine (102 mg, 80%) as a colorless oil together with the sulfonamide **3** (108 mg, 92%).

***N*-Benzyl-*N′*-benzyloxycarbonylethylenediamine.** The physical data shown below were comparable to those reported.[2w] A colorless oil. IR (neat): ν=3332, 1714 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.76 (br s, 1H), 2.76 (t, J=5.9 Hz, 2H), 3.30 (dt, J=5.9, 5.9 Hz, 2H), 3.77 (s, 2H), 5.10 (s, 2H), 5.26 (br s, 1H), 7.21–7.39 (m, 10H). ^{13}C NMR ($CDCl_3$): δ=40.82, 48.40, 53.57, 66.64, 126.88, 127.89, 127.93, 128.28, 128.33, 136.46, 139.91, 156.29. EI-MS: m/z=285 (MH^+), 284 (M^+), 194, 149, 133, 132, 118 (bp), 107, 105, 91, 89.

The physical data of the other acylated diamines are shown below.

***N*-Benzyloxycarbonyl-*N′*-propylethylenediamine.** A pale yellow oil. IR (neat): ν=3325, 1714 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=0.90 (t, J=7.3 Hz, 3H), 1.47 (tq, J=7.3, 7.3 Hz, 2H), 1.56 (br s, 1H), 2.55 (t, J=7.3 Hz, 2H), 2.74 (t, J=5.6 Hz, 2H), 3.29 (dt, J=5.6, 5.6 Hz, 2H), 5.10 (s, 2H), 5.31 (br s, 1H), 7.28–7.39 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=11.80, 23.21, 40.79, 48.83, 51.37, 66.54, 127.83, 127.87, 128.10, 128.27, 136.44, 156.29. EI-MS: m/z=237 (MH^+), 236 (M^+), 207, 149, 91, 72 (bp). Anal. Calcd for $C_{13}H_{20}N_2O_2$: C, 66.07; H, 8.53; N, 11.85. Found: C, 66.35; H, 8.76; N, 11.60.

***N*-Benzyloxycarbonyl-*N′*-propyl-1,3-propanediamine.** A pale yellow oil. IR (neat): ν=3334, 1713, 1701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 50°C): δ=0.91 (t, J=7.1 Hz, 3H), 1.31 (br s, 1H), 1.48 (tq, J=7.1, 7.1 Hz, 2H), 1.66 (tt, J=6.6, 6.6 Hz, 2H), 2.54 (t, J=7.1 Hz, 2H), 2.68 (t, J=6.6 Hz, 2H), 3.25–3.32 (br, 2H), 5.09 (s, 2H), 5.70 (br s, 1H), 7.26–7.40 (m, 5H). EI-MS: m/z=250 (M^+), 222, 149 (bp), 134, 120, 91. Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.16; H, 8.85; N, 11.19. Found: C, 67.34; H, 8.91; N, 10.79.

1-Benzyloxycarbonyl-3-methylpiperazine. A colorless oil. IR (neat): ν=3322, 1697 cm^{-1}. ^{1}H NMR (DMSO-d_6, 90°C): δ=0.95 (d, J=6.2 Hz, 3H), 2.39–2.63 (m, 4H), 2.75–2.83 (m, 2H), 3.77–3.83 (m, 2H), 5.08 (s, 2H), 7.28–7.38 (m, 5H). EI-MS: m/z=234 (M^+), 233, 134, 91 (bp), 78. Anal. Calcd for $C_{13}H_{17}N_2O_2$: C, 66.93; H, 7.34; N, 12.01. Found: C, 67.11; H, 7.76; N, 11.97.

***N*-Allyloxycarbonyl-*N′*-benzylethylenediamine.** A pale yellow oil. IR (neat): ν=3331, 1714 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.51 (s, 1H), 2.77 (t, J=5.9 Hz, 2H), 3.29 (dt, J=5.9, 5.9 Hz, 2H), 3.78 (s, 2H), 4.56 (br d, J=5.4 Hz, 2H), 5.16–5.27 (br, 1H), 5.20 (ddt, J=10.5, 1.2, 1.2 Hz, 1H), 5.92 (ddt, J=17.3, 1.2, 1.2 Hz, 1H), 5.92 (ddt, J=17.3, 10.5, 5.4 Hz, 1H), 7.22–7.36 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=40.78, 48.42, 53.58, 65.50, 117.44, 126.90, 127.90, 128.29, 132.81, 139.90, 156.17. EI-MS: m/z=235 (MH^+), 234 (M^+), 204, 164, 143, 120, 106, 91 (bp), 65. Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.51; H, 7.81; N, 11.72.

***N*-Acetyl-*N′*-benzylethylenediamine.** A colorless solid of mp 55–57°C. IR (nujol): ν=3301, 3281, 1633 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.59 (br s, 1H), 1.97 (s, 3H), 2.77 (t, J=5.9 Hz, 2H), 3.33 (dt, J=11.5, 5.9 Hz, 2H), 3.78 (s, 2H), 6.10 (br s, 1H), 7.23–7.37 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=23.37, 39.23, 48.03, 53.54, 126.94, 127.89, 128.30, 139.85, 169.93. EI-MS: m/z=193 (MH^+), 192 (M^+), 133, 132, 120, 91 (bp). Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.43; H, 8.55; N, 14.43.

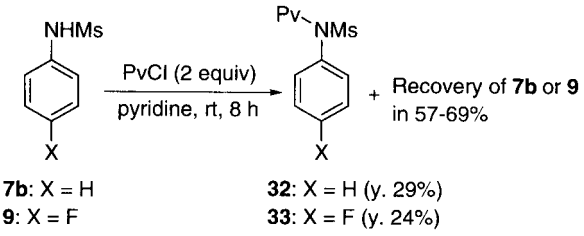
***N*-Benzyl-*N′*-benzoylethylenediamine.** Colorless plates (benzene–hexane) of mp 60–61°C. IR (nujol): ν=3352, 3309, 1631 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.97 (s, 1H), 2.81 (dd, J=5.9, 5.9 Hz, 2H), 3.47 (dd, J=5.9, 5.9 Hz, 2H), 3.74 (s, 2H), 6.80 (br s, 1H), 7.15–7.45 (m, 8H), 7.65–7.74 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=39.56, 47.88, 53.52, 126.77, 126.98, 127.95, 128.34, 131.16, 134.49, 139.93, 167.25. EI-MS: m/z=255 (MH^+), 254 (M^+), 132 (bp), 106, 77. Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.78; H, 7.25; N, 10.99.

***N*-Benzoyl-*N′*-propylethylenediamine.** The physical data shown below were identical with those reported.[3b] A pale yellow oil. IR (neat): ν=3300, 1644 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.90 (t, J=7.3 Hz, 3H), 1.48 (tq, J=7.3, 7.3 Hz, 2H), 1.57 (br s, 1H), 2.58 (t, J=7.3 Hz, 2H), 2.83 (t, J=5.9 Hz, 2H), 3.49 (d, J=5.9 Hz, 1H), 3.52 (d, J=5.9 Hz, 1H), 6.98 (br s, 1H), 7.36–7.49 (m, 3H), 7.76–7.80 (m, 2H). FAB-MS: m/z=207 (MH^+).

***N*-Benzoyl-*N′*-propyl-1,3-propanediamine.** The physical data shown below were identical with those reported.[3b] A pale yellow oil. IR (nujol): ν=3457, 3291, 1644 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=0.93 (t, J=7.3 Hz, 3H), 1.55 (tq, J=7.3, 7.3 Hz, 2H), 1.57 (br s, 1H), 1.77 (tt, J=5.9, 5.9 Hz, 2H), 2.60 (t, J=7.3 Hz, 2H), 2.83 (t, J=5.9 Hz, 2H), 3.57 (br d, J=5.9 Hz, 1H), 3.59 (br d, J=5.9 Hz, 1H), 7.38–7.50 (m, 3H), 7.78–7.83 (m, 2H), 8.31 (br s, 1H). FAB-MS: m/z=221 (MH^+).

1-Benzoyl-3-methylpiperazine. The physical data shown below were identical with those reported.[3b] A pale yellow oil. IR (nujol): ν=3308, 1623 cm^{-1}. ^{1}H NMR (DMSO-d_6, 100°C):δ=0.93 (d, J=6.2 Hz, 3H), 2.09 (br s, 1H), 2.49–2.70 (m, 4H), 2.80–3.00 (m, 3H), 7.29–7.43 (m, 5H). FAB-MS: m/z=205 (MH^+).

***N*-Benzyl-*N′*-pivaloylethylenediamine.** A pale yellow oil. IR (neat): ν=3342, 1643 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.19



Scheme 2.

(s, 9H), 2.77 (t, J=5.9 Hz, 2H), 3.33 (dt, J=5.9, 5.9 Hz, 2H), 3.79 (s, 2H), 6.28 (br s, 1H), 7.21–7.37 (m, 5H). The signal of benzylic NH was not observed. ^{13}C NMR ($CDCl_3$): δ=27.67, 38.70, 39.03, 47.89, 53.40, 126.89, 127.87, 128.26, 139.96, 178.24. EI-MS: m/z=235 (MH^+), 234 (M^+), 149, 133, 120, 91 (bp), 57. Anal. Calcd for $C_{14}H_{22}N_2O$: C, 71.76; H, 9.46; N, 11.95. Found: C, 72.02; H, 9.60; N, 11.84.

Acknowledgements

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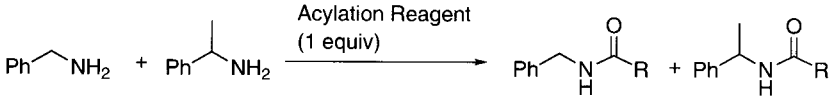
6. Preparation of **6** with BuLi and R^2COCl (R^2CO=Z, cyclohexylcarbonyl and pivaloyl) in THF were also unsuccessful.
7. Benzyloxycarbonylation of *N*-phenyltrifluoromethanesulfonamide (**7a**) under ZCl in pyridine gave an *N*-benzylation product without formation of the desired Z-sulfonamide **12a**. A similar result has been reported in the benzyloxycarbonylation of *N*-(4-trifluoromethylphenyl)trifluoromethanesulfonamide by Yasuhara, Nagaoka and Tomioka: see, Ref. 2w.

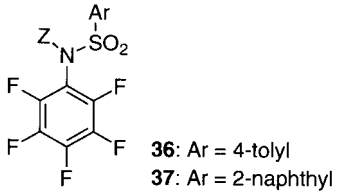
Table 11. Competition acylation



Entry	Acylation reagent	Conditions	Yield (%) **34**+**35**	Selectivity[a] **34**:**35**
1	**4a**	THF, 0°C, 12 h	89	8:1
2	**13a**	THF, rt, 18 h	90	8:1
3	ZCl	Et_3N, THF, 0°C, 1 h	92	3:1
4	**4d**	THF, 0°C, 3 h	86	5:1
5	**13d**	THF, 0°C, 48 h	89	10:1
6	Bz_2O	THF, 0°C, 1 h	92	5:1
7	BzCN[b]	CH_2Cl_2, 0°C, 12 h	97	5:1
8	Bz_2NOMe[c]	THF, 0°C, 12 h	88	3:1
9	**4c**	THF, 0°C, 10 h	86	9:1
10	Ac_2O	Et_3N, CH_2Cl_2,0°C, 1 h	91	1:1

[a] Determined by ^{1}H NMR analysis.
[b] Ref. 2k.
[c] Ref. 2m.

8. *N*-acetyl-*N*-phenyltrifluoromethanesulfonamide has been reported to behave as an acetylation reagent: Hendrickson, J. B.; Bergeron, R. *Tetrahedron Lett.* **1973**, 4607–4610.
9. In this case, the use of other sulfonamides **7b** and **9** gave less satisfactory results (Scheme 2).
10. The *N*-Z-sulfonamide **27** acylated 2-(phenylethyl)amine (**17**) in 98% yield for 4 h at rt.
11. The selectivity in the acylation of a 1:1 mixture of a less hindered amine and a hindered amine was also investigated with **13a**, **13d**,**4a** and **4d**. The observed selectivity in the acylation with **13a**, **13d**,**4a** and **4d** was not at all inferior to the currently reagents (entries 3, 6–8 and 10), as shown in Table 11 . The above competition acylation with the use of **36** and **37** instead of **4a** gave the same selectivity.



36: Ar = 4-tolyl
37: Ar = 2-naphthyl

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