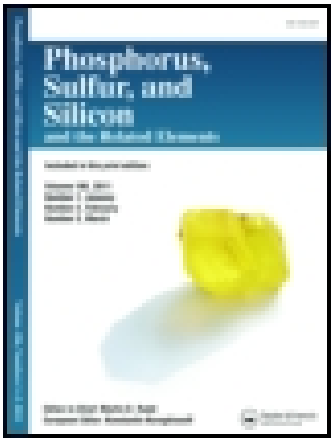

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KF/Al_2O_3 as an Efficient, Green, and Reusable Catalytic System for the Solvent-Free Synthesis of *N*-Alkyl Derivatives of Sulfonamides via Michael Reactions

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KF/Al_2O_3 efficiently catalyzes the microwave-assisted Michael addition of sulfonamides to α,β-unsaturated esters under solvent-free conditions to afford N-*alkyl derivatives of sulfonamides as biologically interesting compounds in high yields and in short reaction times. In this reaction,* N,N-*dialkylsulfonamides are also produced, but in very low yields.*

Keywords *N*-alkylsulfonamide; KF/Al_2O_3; Michael addition; microwave; solvent-free; sulfonamide

INTRODUCTION

In recent years, evolution of chemical reactions involving less hazardous, environmentally acceptable, and recyclable catalytic systems has gained considerable attention both in industrial and academia research.[1,2] KF/Al_2O_3 is one of the green catalytic systems that has been used in various organic transformations such as synthesis of pyrano[3,2-*c*]pyran derivatives,[2a] alkylation and arylation

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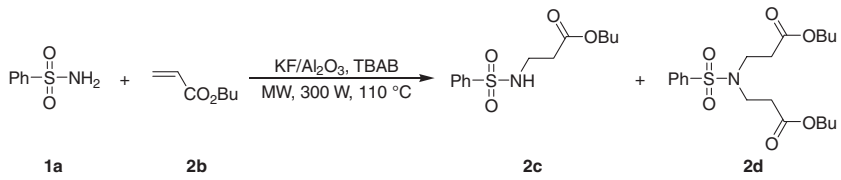
reactions,[2b–2d] hydrothilation of alkynes,[2e] cycloaddition of azomethine ylides,[2f] deformylation of *N*-arylformamides,[2g] conversion of aldehydes to nitriles,[2h] acetylation of amines, alcohols and phenols,[2i] synthesis of oxazolidinones,[2j] desilylation reactions,[2k] etc.[2l] Nevertheless, most of the existing processes in organic synthesis involve toxic and volatile organic solvents as reaction media, and these are environmentally unacceptable from a green chemistry viewpoint. One useful technique to solve this problem is the use of solvent-free conditions that makes synthesis simpler, saves energy, and prevents solvent waste, hazards, and toxicity.[3] Together with the removal of the solvent, nonconventional activation methods, mainly microwave irradiation, have been applied as powerful techniques to reduce reaction times and to increase yields.[3] Consequently, it is important to note that the combination of safe catalysis with the use of solventless technology under microwave irradiation represents a suitable way toward the so-called ideal synthesis.

N-Alkylsulfonamides are significant because of their biological activities including analgesic, anti-depressant, psychostimulant, anti-ulcer, anti-emetic, and anti-inflammatory properties.[4] Aza-Michael addition of sulfonamides to electrophilic alkenes can be used as a synthetic route toward *N*-alkylated sulfonamides. However, this reaction has not been extensively studied to date.[5] Reitz et al. have used Al_2O_3 to achieve Michael addition of sulfonamides to α,β-unsaturated ketones[5a]; however, this catalyst was not efficient when less reactive α,β -unsaturated esters were used.[5b] Furthermore, the reaction times are long and the yields are moderate. Gimbert et al. have carried out the Michael addition of sulfonamides to electrophilic alkenes in the presence of PBu_3.[5c] In this work, only *N*, *N*-dialkyl derivatives of sulfonamides were prepared in relatively long reaction times. Moreover, more recently, we have applied MgO/[bmim]Br,[5b] ZnO/[bmim]Br,[5d] and K_2CO_3[5e] for Michael addition of sulfonamides to α,β -unsaturated esters. These reports are associated with one or more of the following drawbacks: (i) the use of relatively expensive ionic liquids, (ii) moderate selectivity in the synthesis of *N*-alkyl and *N*, *N*-dialkylsulfonamides, and (iii) the necessity of a stoichiometric amount of catalyst.

In this article, we report a simple method for the synthesis of *N*-alkylated sulfonamides via Michael addition of sulfonamides to α,β-unsaturated esters in the presence KF/Al_2O_3 (as a highly efficient, green, heterogeneous, and recyclable catalytic system) and tetrabutylammonium bromide (TBAB) under solvent-free and microwave irradiation conditions (Scheme 1). It is worth noting that this method has none at all of the above-mentioned disadvantages.



SCHEME 1

RESULTS AND DISCUSSION

To optimize the reaction conditions, we first studied the effect of different molar ratios of KF/Al_2O_3 on the Michael addition of benzenesulfonamide (2 mmol) to *n*-butyl acrylate (2.2 mmol) in the presence of TBAB (0.5 mmol) under solvent-free and microwave conditions (300 W, max. 110°C) (Scheme 1). The results are summarized in Table I. As can be seen from the data in Table I, the best molar ratio of KF/Al_2O_3 was 25 mol%. The model reaction was also examined in the presence of KF/TBAB as well as Al_2O_3/TBAB separately (Table II). As the data in Table II indicate, the selectivity of the reaction decreased remarkably when KF/TBAB was used. Moreover, Al_2O_3/TBAB afforded low yields of both *N*-alkyl and *N*, *N*-dialkylsulfonamides. In another study, the influence of TBAB on the reaction was investigated. The selectivity was decreased when TBAB was removed from the reaction media (Table II). Thus, TBAB has an essential effect on the selectivity of the reaction. The reaction of benzenesulfonamide with *n*-butyl acrylate was also examined in the presence of TBAB without KF/Al_2O_3; however, this reaction was not successful and compound **2c** was produced in trace yield (Table II).

TABLE I The Effect of Different Amounts of KF/Al_2O_3 on Reaction of Benzenesulfonamide with *n*-Butyl Acrylate in the Presence of TBAB Under Microwave Irradiation (300 W, Max. 110°C)

		Yield (%)[a]	
KF/Al_2O_3 (mol%)	Time (min)	*N*-Alkylated product **2c**	*N,N*-Dialkylated pruduct **2d**
15	15	79	5
25	9	92	6
40	8	71	18
60	6	62	23

[a]Isolated yield.

TABLE II Michael Addition of Benzenesulfonamide to *n*-Butyl Acrylate Using KF/TBAB, Al_2O_3/TBAB, KF/Al_2O_3 and TBAB Separately Under Microwave Irradiation (300 W, Max. 110°C)

		Yield (%)[a]	
Catalytic system	Time (min)	*N*-Alkylated product **2c**	*N,N*-Dialkylated pruduct **2d**
KF/TBAB	10	39	34
Al_2O_3/TBAB	15	33	5
KF/Al_2O_3[b]	17	43	31
TBAB[c]	20	Trace	—

[a]Isolated yield.
[b]This reaction was carried out in the absence of TBAB.
[c]This reaction was performed in the presence of TBAB without KF/Al_2O_3.

In order to select a suitable microwave power for the reaction, the Michael addition of benzenesulfonamide to *n*-butyl acrylate was examined in the presence of KF/Al_2O_3 and TBAB at different microwave powers (100–600 W) with controlled temperature (max. 110°C). The best results were observed at 300 W.

The efficiency and capacity of the solvent-free procedure, in comparison to solution condition, was also studied. For this purpose, a mixture of benzenesulfonamide (2 mmol), KF/Al_2O_3 (25 mol%), TBAB (0.5 mmol), and *n*-butyl acrylate (2.2 mmol) was irradiated in a microwave oven (300 W, max. 110°C) in different solvents (2 mL) (Table III). As it

TABLE III Comparative the Reaction of Benzenesulfonamide with *n*-Butyl Acrylate in the Presence of KF/Al_2O_3 and TBAB Under Solution Conditions Versus the Solvent-Free Method

		Yield (%)[a]	
Solvent	Time (min)	N-Alkylated product **2c**	N,N-Dialkylated product **2d**
Solvent-free	9	92	6
DMF	9	81	13
DMSO	9	40	29
o-Xylene	15	27	10

[a]Isolated yield.

can be seen from the data in Table III, the solvent-free method afforded higher yield and selectivity.

To demonstrate the effectiveness of microwave irradiation with respect to conventional heating, the reaction between benzenesulfonamide (2 mmol) and *n*-butyl acrylate (2.2 mmol) in the presence of KF/Al_2O_3 (25 mol%) and TBAB (0.5 mmol) was examined in an oil bath (110°C). However, the reaction was not complete under these conditions after 8 h, and the Michael adducts **2c** and **2d** were obtained in 65% and 13%, respectively. The results were not improved by increasing the reaction time and the temperature. Therefore, microwave irradiation is essential to promote this reaction.

After optimization of the reaction conditions, sulfonamides were reacted with structurally diverse α,β -unsaturated esters. The results are displayed in Table IV. As the data in Table IV demonstrate, all reactions proceeded efficiently, and the desired Michael adducts were obtained in high yields and in short reaction times. In addition, the selectivity was excellent in all reactions. It has been observed that the type of alkoxy group (-OR) in the α,β -unsaturated esters does not significantly affect the yields, the selectivities, or the reaction times (Table IV, entries 1–8). When benzenesulfonamide was added to sterically hindered α,β -unsaturated esters (ethyl methacrylate and ethyl crotonate), the yields decreased and the reaction times increased (Table IV, entries 9–12). Nevertheless, in these reactions the selectivity increased. Interestingly, Michael addition of benzenesulfonamide as well as naphthalene-2-sulfonamide to ethyl crotonate afforded only monosubstituted product (Table IV, entries 11 and 12). Furthermore, the type of sulfonamide had no significant effect on the reaction results.

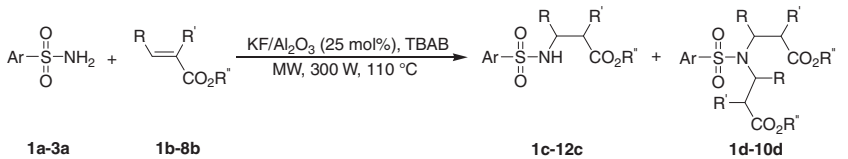
The interesting behavior of the KF/Al_2O_3 system lies in the fact that it can be reused after simple washing with warm $CHCl_3$, thus rendering the process more economical. The yields of compounds **2c** and **2d** (model compounds) in the second, third, and fourth uses of the KF/Al_2O_3 were almost as high as in the first use.

In summary, we have developed an efficient method for the synthesis of *N*-alkylsulfonamides via Michael reactions. This new strategy has several advantages, such as high yields, high selectivity, short reaction times, low cost, simple experimental as well as straightforward isolation, and finally, agreement with the green chemistry protocol.

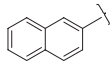
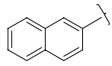
EXPERIMENTAL

All chemicals were purchased from Merck or Fluka Chemical Companies. All reactions were carried out using a laboratory microwave oven

TABLE IV Synthesis of *N*-Alkylsulfonamides via Michael Addition Reaction Using KF/Al_2O_3 and TBAB Under Microwave Irradiation (300 W, 110°C)



1a-3a **1b-8b** **1c-12c** **1d-10d**

Entry	Ar	R	R′	R″	Product[a]	Time (min)	Yield (%)[b]
1[c]	C_6H_5	H	H	CH_3CH_2	**1c**	9	89
					1d		6
2	C_6H_5	H	H	$CH_3(CH_2)_2CH_2$	**2c**	9	92
					2d		6
3	C_6H_5	H	H	$CH_3(CH_2)_4CH_2$	**3c**	10	91
					3d		6
4	C_6H_5	H	H	$C_6H_5CH_2$	**4c**	11	90
					4d		6
5	C_6H_5	H	H	$C_6H_5CH_2CH_2$	**5c**	12	89
					5d		5
6	C_6H_5	H	H	$C_6H_5CH{=}CHCH_2$	**6c**	13	90
					6d		5
7	*p*-$CH_3C_6H_4$	H	H	$CH_3(CH_2)_2CH_2$	**7c**	12	92
					7d		5
8		H	H	$CH_3(CH_2)_4CH_2$	**8c**	10	91
					8d		6
9	C_6H_5	H	CH_3	CH_3CH_2	**9c**	18	81
					9d		4
10	*p*-$CH_3C_6H_4$	H	CH_3	CH_3CH_2	**10c**	18	85
					10d		4
11[d]	C_6H_5	CH_3	H	CH_3CH_2	**11c**	24	77
12[d]		CH_3	H	CH_3CH_2	**12c**	24	74

[a]All known compounds were identified by comparison of their spectral data with those in the authentic samples.

[b]Isolated yield.

[c]In this reaction, the α,β -unsaturated esters/sulfonamide (mol/mol) ratio was 1.3:1.

[d]This reaction was performed at 120°C (300 W).

(MW 3000, Landgraf Company, Germany). The ^1H NMR (250 MHz) and ^{13}C NMR (62.5 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer. Mass spectra were recorded on a Shimadzu GC MS-QP 1000 EX apparatus. Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Procedure for the Preparation of the KF/Al_2O_3 Catalytic System

A mixture of KF (0.291 g, 5 mmol) and Al_2O_3 (0.510, 5 mmol) was ground vigorously to give the KF/Al_2O_3 catalytic system as a white powder (0.801 g).

General Procedure for the Synthesis of *N*-Alkyl Derivatives of Sulfonamides via Michael Reaction

A well-ground mixture of sulfonamide (2 mmol), KF/Al_2O_3 (0.080 g, 0.5 mmol, 25 mol%), and TBAB (0.161 g, 0.5 mmol) was placed in a microwave vessel, and then α,β -unsaturated ester (2.2 mmol) was added and mixed carefully with a small rod. The resulting mixture was irradiated in a microwave oven at 300 W (max. 110°C) for the times reported in Table IV. Subsequently, the reaction mixture was cooled to room temperature and suspended in chloroform (60 mL), filtered, the filtrate washed with water (2 × 50 mL), and then dried over anhydrous $MgSO_4$. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel eluting with EtOAc:*n*-hexane (1:3). After isolation of the products, the remaining KF/Al_2O_3 was dried and used for the next run under identical reaction conditions.

Ethyl 3-(Phenylsulfonamido)propanoate (1c)

Colorless oil (Lit.[5b] oil); ^{1}H NMR ($CDCl_3$): δ 1.16 (t, 3H, $J = 7.0$ Hz, CH_3), 2.48 (t, 2H, $J = 5.0$ Hz, CH_2CO), 3.15 (t, 2H, $J = 5.0$ Hz, CH_2N), 4.02 (q, 2H, $J = 7.0$ Hz, CH_2O), 5.56 (s, 1H, NH), 7.42-7.52 (m, 3H, 3,4,5-H_{Ph}), 7.80 (m, 2H, 2,6-H_{Ph}).

Diethyl 3,3′-(Phenylsulfonylazanediyl)dipropanoate (1d)

Colorless oil (Lit.[5b] oil); ^{1}H NMR ($CDCl_3$): δ 1.22 (t, 6H, $J = 7.1$ Hz, $2CH_3$), 2.59 (t, 4H, $J = 5.0$ Hz, $2CH_2CO$), 3.45 (t, 4H, $J = 5.0$ Hz, CH_2NCH_2), 4.08 (q, 4H, $J = 7.1$ Hz, $2CH_2O$), 7.46-7.57 (m, 3H, 3,4,5-H_{Ph}), 7.87 (m, 2H, 2,6-H_{Ph}).

Butyl 3-(Phenylsulfonamido)propanoate (2c)

Colorless oil (Lit.[5b] oil); ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, $J = 6.5$ Hz, CH_3), 1.34 (m, 2H, CH_3CH_2), 1.56 (m, 2H, $CH_3CH_2CH_2$), 2.51 (t, 2H, $J = 5.0$ Hz, CH_2CO), 3.19 (t, 2H, $J = 5.0$ Hz, CH_2N), 4.03 (t, 2H, $J = 7.0$ Hz, CH_2O), 5.68 (s, 1H, NH), 7.48–7.57 (m, 3H, 3,4,5-H_{Ph}), 7.79 (m, 2H, 2,6-H_{Ph}).

Dibutyl 3,3′-(Phenylsulfonylazanediyl)dipropanoate (2d)

Colorless oil (Lit.[5b] oil); ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 6H, $J = 6.5$ Hz, $2CH_3$), 1.33 (m, 4H, $2CH_3CH_2$), 1.56 (m, 4H, $2CH_3CH_2CH_2$), 2.63 (t,

4H, $J = 5.1$ Hz, $2CH_2CO$), 3.45 (t, 4H, $J = 5.1$ Hz, CH_2NCH_2), 4.06 (t, 4H, $J = 6.9$ Hz, $2CH_2O$), 7.51–7.60 (m, 3H, 3,4,5-H_{Ph}), 7.82 (m, 2H, 2,6-H_{Ph}).

Hexyl 3-(Phenylsulfonamido)propanoate (3c)

Colorless oil (Lit.[5d] oil); ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, $J = 6.7$ Hz, CH_3), 1.28–1.34 (m, 6H, CH_3CH_2, $CH_3CH_2CH_2$ and $CH_3(CH_2)_2CH_2$), 1.57 (m, 2H, $CH_3(CH_2)_3CH_2$), 2.56 (t, 2H, $J = 5.1$ Hz, CH_2CO), 3.16 (t, 2H, $J = 5.1$ Hz, CH_2N), 4.09 (t, 2H, $J = 6.9$ Hz, CH_2O), 5.63 (s, 1H, NH), 7.41–7.48 (m, 3H, 3,4,5-H_{Ph}), 7.78 (m, 2H, 2,6-H_{Ph}).

Dihexyl 3,3′-(Phenylsulfonylazanediyl)dipropanoate (3d)

Colorless oil (Lit.[5d] oil); ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 6H, $J = 6.6$ Hz, $2CH_3$), 1.26–1.32 (m, 12H, $2CH_3CH_2$, $2CH_3CH_2CH_2$ and $2CH_3(CH_2)_2CH_2$), 1.58 (m, 4H, $2CH_3(CH_2)_3CH_2$), 2.61 (t, 4H, $J = 5.0$ Hz, 2O=CCH_2), 3.41 (t, 4H, $J = 5.0$ Hz, CH_2NCH_2), 4.05 (t, 4H, $J = 6.9$ Hz, $2CH_2O$), 7.43–7.50 (m, 3H, 3,4,5-H_{Ph}), 7.74 (m, 2H, 2,6-H_{Ph}).

Benzyl 3-(Phenylsulfonamido)propanoate (4c)

Pale yellow oil (Lit.[5e] oil); ^{1}H NMR ($CDCl_3$): δ 2.65 (t, 2H, $J = 5.1$ Hz, CH_2CO), 3.17 (t, 2H, $J = 5.1$ Hz, CH_2N), 5.00 (s, 2H, CH_2O), 5.71 (s, 1H, NH), 7.26–7.31 (m, 5H, H_{PhC}), 7.45–7.51 (m, 3H, 3,4,5-H_{PhS}), 7.82 (m, 2H, 2,6-H_{PhS}).

Dibenzyl 3,3′-(Phenylsulfonylazanediyl)dipropanoate (4d)

Pale yellow oil (Lit.[5e] oil); ^{1}H NMR ($CDCl_3$): δ 2.58 (t, 4H, $J = 5.0$ Hz, $2CH_2CO$), 3.36 (t, 4H, $J = 5.0$ Hz, CH_2NCH_2), 5.00 (s, 4H, $2CH_2O$), 7.22–7.25 (m, 10H, H_{PhC}), 7.39–7.48 (m, 3H, 3,4,5-H_{PhS}), 7.72 (m, 2H, 2,6-H_{PhS}).

Phenethyl 3-(Phenylsulfonamido)propanoate (5c)

Pale yellow oil (Lit.[5b] oil); ^{1}H NMR ($CDCl_3$): δ 2.48 (t, 2H, $J = 5.2$, CH_2CO), 2.88 (t, 2H, $J = 6.8$ Hz, CH_2Ph), 3.14 (t, 2H, $J = 5.2$ Hz, CH_2N), 4.24 (t, 2H, $J = 6.8$ Hz, CH_2O), 5.43 (s, 1H, NH), 7.15–7.28 (m, 5H, H_{PhC}), 7.47–7.52 (m, 3H, 3,4,5-H_{PhS}), 7.81–7.86 (m, 2H, 2,6-H_{PhS}).

Diphenethyl 3,3′-(Phenylsulfonylazanediyl)dipropanoate (5d)

Pale yellow oil (Lit.[5b] oil); ^{1}H NMR ($CDCl_3$): δ 2.51 (t, 4H, $J = 5.2$ Hz, $2CH_2CO$), 2.82 (t, 4H, $J = 6.9$ Hz, $2CH_2Ph$), 3.30 (t, 4H, $J = 5.2$ Hz, CH_2NCH_2), 4.19 (t, 4H, $J = 6.9$ Hz, $2CH_2O$), 7.10-7.19 (m, 10H, H_{PhC}), 7.42–7.45 (m, 3H, 3,4,5-H_{PhS}), 7.7–7.82 (m, 2H, 2,6-H_{PhS}).

Cinnamyl 3-(Phenylsulfonamido)propanoate (6c)

Pale yellow oil (Lit.[5e] oil); ^{1}H NMR ($CDCl_3$): δ 2.55 (t, 2H, $J = 5.2$ Hz, CH_2CO), 3.19 (t, 2H, $J = 5.2$ Hz, CH_2N), 4.69 (m, 2H, CH_2O), 5.50 (s, 1H, NH), 6.23 (m, 1H, =C*H*CH_2), 6.63 (d, 1H, $J = 15.7$ Hz, =CHPh), 7.29–7.35 (m, 5H, H_{PhC}), 7.45–7.50 (m, 3H, 3,4,5-H_{PhS}), 7.95 (m, 2H, 2,6-H_{PhS}).

Dicinnamyl 3,3′-(Phenylsulfonylazanediyl)dipropanoate (6d)

Pale yellow oil (Lit.[5e] oil); ^{1}H NMR ($CDCl_3$): δ 2.51 (t, 4H, $J = 5.1$ Hz, $2CH_2CO$), 3.41 (t, 4H, $J = 5.1$ Hz, CH_2NCH_2), 4.73 (m, 4H, $2CH_2O$), 6.15 (m, 2H, 2=C*H*CH_2), 6.54 (d, 2H, $J = 15.7$ Hz, 2=C*H*Ph), 7.28–7.36 (m, 10H, H_{PhC}), 7.41–7.47 (m, 3H, 3,4,5-H_{PhS}), 7.94 (m, 2H, 2,6-H_{PhS}).

Butyl 3-(4-Methylphenylsulfonamido)propanoate (7c)

Pale yellow oil (Lit.[5d] oil); ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $J = 6.8$ Hz, CH_3CH_2), 1.33 (m, 2H, CH_3CH_2), 1.56 (m, 2H, $CH_3CH_2CH_2$), 2.40 (s, 3H, CH_3Ar), 2.51 (t, 2H, $J = 5.3$ Hz, CH_2CO), 3.16 (t, 2H, $J = 5.3$ Hz, CH_2N), 4.04 (t, 2H, $J = 7.0$ Hz, CH_2O), 5.76 (s, 1H, NH), 7.33 (d, 2H, $J = 7.9$ Hz, 3,5-H_{Ar}), 7.72 (d, 2H, $J = 7.9$ Hz, 2,6-H_{Ar}).

Dibutyl 3,3′-(Tosylazanediyl)dipropanoate (7d)

Pale yellow oil (Lit.[5d] oil); ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 6H, $J = 6.9$ Hz, $2CH_3CH_2$), 1.32 (m, 4H, $2CH_3CH_2$), 1.57 (m, 4H, $2CH_3CH_2CH_2$), 2.42 (s, 3H, CH_3Ar), 2.63 (t, 4H, $J = 5.2$ Hz, $2CH_2CO$), 3.43 (t, 4H, $J = 5.2$ Hz, CH_2NCH_2), 4.02 (t, 4H, $J = 7.0$ Hz, $2CH_2O$), 7.31 (d, 2H, $J = 7.9$ Hz, 3,5-H_{Ar}), 7.72 (d, 2H, $J = 7.9$ Hz, 2,6-H_{Ar}).

Hexyl 3-(Naphthalene-2-sulfonamido)propanoate (8c)

Pale yellow oil; ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $J = 6.7$ Hz, CH_3), 1.31–1.38 (m, 6H, CH_3CH_2, $CH_3CH_2CH_2$ and $CH_3(CH_2)_2CH_2$), 1.60 (m, 2H, $CH_3(CH_2)_3CH_2$), 2.58 (t, 2H, $J = 5.0$ Hz, CH_2CO), 3.18 (t, 2H, $J = 5.0$ Hz, CH_2N), 4.11 (t, 2H, $J = 6.8$ Hz, OCH_2), 5.56 (s, 1H, NH), 7.54–7.65 (m, 4H, H_{Ar}), 7.85–7.95 (m, 3H, H_{Ar}); ^{13}C NMR ($CDCl_3$): δ 13.9, 22.4, 25.8, 28.5, 31.2, 34.3, 38.5, 65.8, 123.1, 126.5, 126.9, 127.3, 127.5, 127.7, 128.3, 129.0, 129.2, 131.9, 172.3; MS (m/z): 363 (M^+); Anal. calcd. for $C_{19}H_{25}NO_4S$: C, 62.78; H, 6.93; N, 3.85. Found: C, 62.97; H, 7.16; N, 3.72.

Dihexyl 3,3′-(Naphthalene-2-sulfonylazanediyl)dipropanoate (8d)

Pale yellow oil, ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 6H, $J = 6.7$ Hz, $2CH_3$), 1.28–1.33 (m, 12H, $2CH_3CH_2$, $2CH_3CH_2CH_2$ and $2CH_3(CH_2)_2CH_2$),

1.56 (m, 4H, $2CH_3(CH_2)_3CH_2$), 2.57 (t, 4H, $J = 5.1$ Hz, $2CCH_2O$), 3.44 (t, 4H, $J = 5.1$ Hz, $2CH_2N$), 4.10 (t, 4H, $J = 6.7$ Hz, $2OCH_2$), 7.50–7.59 (m, 4H, H_{Ar}), 7.82–7.93 (m, 3H, H_{Ar}); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.4, 28.6, 30.9, 33.5, 43.7, 65.1, 122.8, 126.6, 127.1, 127.4, 127.7, 127.9, 128.4, 129.3, 129.4, 131.5, 171.8; MS (*m/z*): 418 (M^+ -$C_6H_{13}O$); Anal. calcd. for $C_{28}H_{41}NO_6S$: C, 64.71; H, 7.95; N, 2.70. Found: C, 64.90; H, 7.78; N, 2.94.

Ethyl 2-Methyl-3-(phenylsulfonamido)propanoate (9c)

Pale yellow oil (Lit.[5b] oil); ^1H NMR ($CDCl_3$): δ 1.17–1.26 (m, 6H, $2CH_3$), 2.73 (m, 1H, CHCO), 3.14–3.20 (m, 2H, CH_2N), 4.12 (q, 2H, $J =$ 7.0 Hz, CH_2O), 5.65 (s, 1H, NH), 7.55–7.64 (m, 3H, 3,4,5-H_{Ph}), 7.93 (m, 2H, 2,6-H_{Ph}).

Diethyl 3,3′-(Phenylsulfonylazanediyl)bis(2-methylpropanoate) (9d)

Pale yellow oil (Lit.[5b] oil); ^1H NMR ($CDCl_3$): δ 1.09–1.19 (m, 12H, $4CH_3$), 2.78 (m, 2H, 2CHCO), 3.22–3.27 (m, 4H, CH_2NCH_2), 4.03 (q, 4H, $J = 7.0$ Hz, $2CH_2O$), 7.44–7.53 (m, 3H, 3,4,5-H_{Ph}), 7.75 (m, 2H, 2,6-H_{Ph}).

Ethyl 2-Methyl-3-(4-methylphenylsulfonamido)propanoate (10c)

Pale yellow oil; ^1H NMR ($CDCl_3$): δ 1.24–1.30 (m, 6H, $2CH_3$), 2.48 (s, 3H, CH_3Ar), 2.78 (m, 1H, CHCO), 3.16–3.19 (m, 2H, CH_2N), 4.08 (q, 2H, $J = 7.1$ Hz, CH_2O), 5.72 (s, 1H, NH), 7.29 (d, 2H, $J = 7.9$ Hz, 3,5-H_{Ar}), 7.74 (d, 2H, $J = 7.9$ Hz, 2,6-H_{Ar}); ^{13}C NMR ($CDCl_3$): δ 14.2, 14.6, 19.6, 39.2, 44.7, 64.2, 127.8, 129.5, 136.4, 142.7, 171.5; MS (*m/z*): 285 (M^+); Anal. calcd. for $C_{13}H_{19}NO_4S$: C, 54.72; H, 6.71; N, 4.91. Found: C, 54.51; H, 6.96; N, 4.76.

Diethyl 3,3′-(Tosylazanediyl)bis(2-methylpropanoate) (10d)

Pale yellow oil; ^1H NMR ($CDCl_3$): δ 1.15–1.23 (m, 12H, $4CH_3$), 2.43 (s, 3H, CH_3Ar), 2.74 (m, 2H, 2CHCO), 3.18–3.24 (m, 4H, CH_2NCH_2), 4.07 (q, 4H, $J = 7.0$ Hz, $2CH_2O$), 7.30 (d, 2H, $J = 7.9$ Hz, 3,5-H_{Ar}), 7.75 (d, 2H, $J = 7.9$ Hz, 2,6-H_{Ar}); ^{13}C NMR ($CDCl_3$): δ 14.0, 14.9, 19.4, 40.1, 51.2, 63.9, 128.0, 130.1, 136.1, 143.1, 172.3; MS (*m/z*): 399 (M^+); Anal. calcd. for $C_{19}H_{29}NO_6S$: C, 57.12; H, 7.32; N, 3.51. Found: C, 56.95; H, 7.08; N, 3.32.

Ethyl 3-(Phenylsulfonamido)butanoate (11c)

Pale yellow solid; mp 61–63°C (Lit.[5e] mp 60–62°C); ^{1}H NMR ($CDCl_3$): δ 1.14–1.23 (m, 6H, $2CH_3$), 2.38–2.43 (m, 2H, CH_2CO), 3.68 (m, 1H, CHN), 4.04 (q, 2H, $J = 7.1$ Hz, CH_2O), 5.39 (s, 1H, NH), 7.49–7.59 (m, 3H, 3,4,5-H_{Ph}), 7.89 (m, 2H, 2,6-H_{Ph}).

Ethyl 3-(Naphthalene-2-sulfonamido)butanoate (12c)

Buff oil (Lit.[5b] buff oil); ^{1}H NMR ($CDCl_3$): δ 1.07–1.12 (m, 6H, $2CH_3$), 2.31–2.35 (m, 2H, CH_2CO), 3.67 (m, 1H, CHN), 3.99 (q, 2H, $J = 7.0$ Hz, CH_2O), 5.38 (s, 1H, NH), 7.52–7.57 (m, 4H, H_{Ar}), 7.79–7.90 (m, 3H, H_{Ar}).

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