Synthesis and Applications of Tetrahydro-2-pyridinones via aza-Diels–Alder Reactions of Thio-substituted 1,3-Dienes with Arylsulfonyl Isocyanates

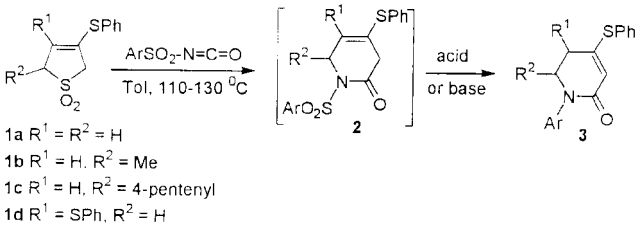
Shang-Shing P. Chou,* Chia-Cheng Hung

Department of Chemistry, Fu Jen Catholic University, Taipei, Taiwan 242, Republic of China
Fax +886(2)29041942; E-mail: chem1004@mails.fju.edu.tw

Received 23 July 2001; revised 28 August 2001

Abstract: The first aza-Diels–Alder reactions of arylsulfonyl isocyanates with thio-substituted 1,3-dienes via the 3-sulfolene precursors **1** gave the cyclized products **3** with complete control of chemo- and regioselectivity. The cyclized products **3a** and **5** underwent further reactions with nucleophiles and bases to give useful heterocyclic compounds. The *N*-tosyl group of the cyclic products could be selectively replaced by hydrogen or another substituent.

Key words: tetrahydropyridines, 2-pyridinones, aza-Diels–Alder reactions, thiosubstituted 1,3-dienes, arylsulfonyl isocyanates



Scheme 1

Reactions of dienes with compounds containing C=N double bonds to give six-membered aza-heterocycles have opened up a wide variety of opportunities for organic synthesis, in particular for the construction of alkaloids and other natural products.[1–3] In general, the use of strongly electron-deficient imines is a prerequivuisite. This can sometimes be accomplished by the attachment of an acyl[4] or a sulfonyl group[5–7] to the nitrogen. Although arylsulfonyl isocyanates have an electron-deficient C=N moiety, their aza-Diels–Alder reactions with dienes were rarely reported[8,9] because the [2+2] cycloaddition or electrophilic substitution predominates.[10–13]

It is well established that 3-sulfolenes are useful precursors to 1,3-dienes.[14,15] We have used this method to synthesize many sulfur-substituted dienes.[16–18] As an extension of our interest in the synthesis and reactions of sulfur-substituted dienes via 3-sulfolenes, we herein report the first aza-Diels–Alder reactions of thiosubstituted 1,3-butadienes with arylsulfonyl isocyanates to give the cyclized products with complete control of chemo- and regioselectivity.[19] The cyclized products could further undergo reactions with nucleophiles and bases to give useful heterocyclic compounds. The N-tosyl group of the cyclic products could also be selectively replaced by hydrogen or another substituent.

The thio-substituted 3-sulfolenes **1**[20,21] can undergo in situ thermal desulfonylation and subsequent cycloaddition with arylsulfonyl isocyanates to give the cyclized products **2** and **3** (Scheme 1). The results are summarized in Table 1.

The cycloaddition of thio-substituted 3-sulfolene **1a** with *p*-toulenesulfonyl isocyanate (PTSI) could be carried out in refluxing toluene to give the cyclized product **2a** and a small amount of the double bond-isomerized product **3a** (entry 1). Under this condition the diene was generated in situ from desulfonylation of the 3-sulfolene **1a**. In this reaction one equivalent of sodium bicarbonate was added to remove the sulfur dioxide generated and a catalytic amount of hydroquinone (HQ) was used to prevent polymerization of the diene. Since the ^{1}H NMR spectrum of the crude product did not show the presence of **3a**, its formation probably resulted from isomerization of **2a** during the silica gel chromatography. Indeed, when 10% of triethylamine was included in the eluent of chromatography, complete isomerization to product **3a** was achieved (entry 2). If the cycloaddition was carried out in the absence of $NaHCO_3$, only product **3a** was obtained (entry 3), no trace of **2a** being detected from the ^{1}H NMR spectrum of the crude product. Apparently, the sulfur dioxide generated from the reaction caused the isomerization of **2a** to **3a**. Thus, both acid and base catalyzed the isomerization of **2** to **3**. The cycloaddition of **1a** also proceeded with other arylsulfonyl isocyanates (entries 5–8). In all these reactions the C=N bond of the arylsulfonyl isocyanates acts as the dienophile to react with the diene chemo- and regioselectively.

Polar solvents cannot be used for the cycloaddition because they react with the isocyanates. It was found that toluene was a better solvent than THF (compare entry 2 with 4, 6 with 7). Furthermore, the presence of sodium bicarbonate increased the yield (compare entry 2 with 3, 5 and 7, 9 with 10). Under similar conditions, 3-sulfolene **1b**[16] and **1c**[22] reacted with PTSI to give the cyclized products **3d** and **3e** in 81% and 70% yield, respectively (entries 10 and 11). The cycloaddition reactions of bis(phenylthio)-substituted 3-sulfolene **1d**[21,23] with arylsulfonyl isocyanates were similar to those of **1a**, but required higher

Synthesis 2001, No. 16, 30 11 2001. Article Identifier:
1437-210X,E;2001,0,16,2450,2462,ftx,en;F06001SS.pdf.

ISSN 0039-7881

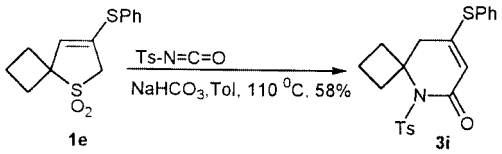
Table 1 Aza-Diels-Alder Reactions of 3-Sulfolenes **1** with Arylsulfonyl Isocyanates

Entry	1	Ar	Condition[a]	Product	Yield (%)
1[b,c]	**1a**	Ts (5 equiv)	110 °C, 4.5 h	**2a**	51[d]
2[b]	**1a**	Ts (3 equiv)	110 °C, 4.5 h	**3a**	71
3	**1a**	Ts (3 equiv)	110 °C, 4.5 h	**3a**	46
4[b,e]	**1a**	Ts (5 equiv)	110 °C, 4.5 h	**3a**	17
5	**1a**	$PhSO_2$ (5 equiv)	110 °C, 4 h	**3b**	30
6[b,e]	**1a**	$PhSO_2$ (5 equiv)	110 °C, 4.5 h	**3b**	23
7[b]	**1a**	$PhSO_2$ (5 equiv)	110 °C, 4.5 h	**3b**	50
8	**1a**	*p*-$ClPhSO_2$ (5 equiv)	110 °C, 4 h	**3c**	38
9	**1b**	Ts (5 equiv)	110 °C, 4.5 h	**3d**	62
10[b]	**1b**	Ts (5 equiv)	110 °C, 4.5 h	**3d**	81
11[b]	**1c**	Ts (5 equiv)	110 °C, 4.5 h	**3e**	70
12	**1d**	Ts (5 equiv)	130 °C, 8 h	**3f**	72
13[b]	**1d**	Ts (5 equiv)	130 °C, 8 h	**3f**	67
14	**1d**	$PhSO_2$ (5 equiv)	130 °C, 8 h	**3g**	73
15	**1d**	*p*-$ClPhSO_2$ (5 equiv)	130 °C, 8 h	**3h**	47

[a] Unless noted otherwise, a mixture of the 3-sulfolene **1**, the isocyanate and a catalytic amount of hydroquinone (HQ) was heated at 110 °C in toluene under nitrogen. If a higher temperature was needed, then a sealed tube was used. After workup the crude product was purified by silica gel column chromatography using hexane–EtOAc–Et_3N as eluent.
[b] One equivalent of anhydrous $NaHCO_3$ was also added.
[c] Triethylamine was not included in the eluent of the silica gel chromatography.
[d] Product **3a** was also obtained in 6% yield.
[e] THF was used as the solvent.

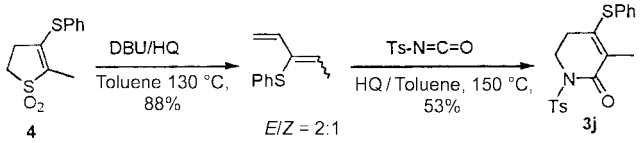
temperatures (entries 12–15). Furthermore, the presence of sodium bicarbonate caused a slight decrease of yield (compare entry 12 with 13). It should be noted that isoprene (5–10 equiv) reacted with PTSI under similar conditions to give the cyclized product **3** only in 5–7% yield. Obviously, the thio-substituent enhances the reactivity of the diene toward PTSI. We have also examined similar reactions with other monosubstituted dienes such as 2-trimethylsilyloxy-1,3-butadiene, 2-phenylsulfinyl-1,3-butadiene, 2-phenylsulfonyl-1,3-butadiene, or disubstituted dienes derived from **1** (R^1 = NHAc, SOPh, SO_2Ph, R^2 = H), but they all failed to undergo aza-Diels–Alder reactions with PTSI. It appears that the thiosubstituent on the diene strikes a balance of reactivity with PTSI: an electron-donating group is needed to increase the reactivity of cycloaddition, but too strong an electron-donating group (such as –OTMS and –NHAc) leads to other reaction pathways. It should also be noted that aryl, alkyl or acyl isocyanates did not undergo the aza-Diels–Alder reaction with thiosubstituted dienes.

It is interesting to note that the sterically hindered diene derived from 3-(phenylthio)-1-thia-spiro[4,3]oct-3-ene-1,1-dioxide (**1e**) reacted with PTSI to give the spiro bicyclic product **3i** in reasonable yield (Scheme 2).

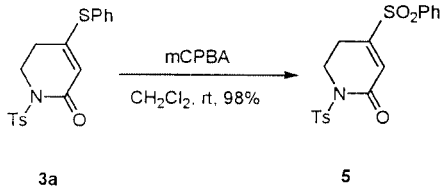


Scheme 2

Refluxing a toluene solution of 2-methyl-3-(phenylthio)-2-sulfolene (**4**)[24] and PTSI in the presence of DBU did not result in situ thermal desulfonylation and tandem cycloaddition, but only gave intractable materials. However, compound **4** could be desulfonylated by first heating with DBU at 130 °C to generate the diene, which could then undergo cycloaddition with PTSI to give the cyclized product **3j** (Scheme 3).



Scheme 3



Scheme 4

Although the thio-substituted 1,3-dienes are unsymmetrical, their aza-Diels–Alder reactions with arylsulfonyl isocyanates gave only one regioisomer, which was shown by spectroscopic methods to be the "*para*" adduct (with respect to the nitrogen). The regiochemistry is consistent with that predicted either by a concerted or stepwise mechanism.[1]

The cyclized products **3** all contain an interesting structure of an α,β-unsaturated lactam which also bears a phenylthio group at the β-position. The sulfide group in **3a** could be easily oxidized to the sulfone **5** by mCPBA (Scheme 4).

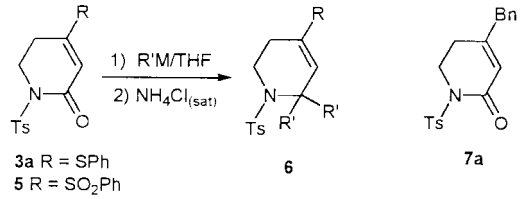
The lactams **3a** and **5** could react with various nucleophiles and bases to give addition, substitution, or elimination products. The sulfide-substituted lactam **3a** reacted with Grignard reagents, organolithium compounds and hydride reducing agents to give the double addition products **6** (Scheme 5). The results are summarized in Table 2. Decreasing the amount of nucleophiles and/or lowering the reaction temperatures still led to the double addition products, albeit in lower yields. The sulfone-substituted lactam **5** also yielded the double addition product **6g–i** with Grignard reagents (entries 12–16), but no identifiable products were obtained with organolithium reagents. When sulfone-substituted lactam **5** was reacted with a softer BnMgCl nucleophile, both the double addition product **6g** and substitution product **7a** were obtained (entries 12 and 13). Lowering the reaction temperature increased the amount of the substitution product **7a**.

The sulfide- and sulfone-substituted lactams **3a** and **5** also underwent substitution reactions (Scheme 6). The results are summarized in Table 3. Compound **3a** reacted

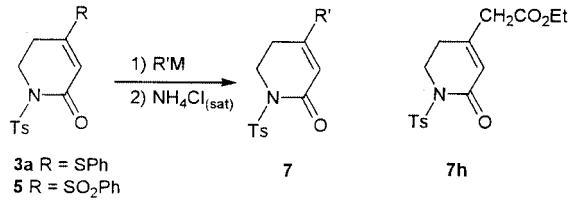
Table 2 Reactions of Lactams **3a** and **5** with Nucleophiles

Entry	**3a** or **5**	R'M	Condition	Product	Yield (%)
1	**3a**	MeLi (1.2 equiv)	THF, r.t., 1 h	**6a**	25[a]
2	**3a**	MeLi (4 equiv)	THF, r.t., 1 h	**6a**	66
3	**3a**	BuLi (4 equiv)	THF, r.t., 1 h	**6b**	60
4	**3a**	BnMgCl (1.2 equiv)	THF, r.t., 3 h	**6c**	44[a]
5	**3a**	BnMgCl (1.2 equiv)	THF, −70 °C, 4.5 h	**6c**	40[a]
6	**3a**	BnMgCl (4 equiv)	THF, r.t., 1 h	**6c**	68
7	**3a**	PhMgCl (1.2 equiv)	THF, −72 °C, 7 h	**6d**	23[a]
8	**3a**	PhMgCl (4 equiv)	THF, r.t., 1 h	**6d**	95
9	**3a**	Allyl–MgBr (1.1 equiv)	THF, r.t., 1 h	**6e**	15[a]
10	**3a**	Allyl–MgBr (4 equiv)	THF, r.t., 70 min	**6e**	91
11	**3a**	$LiAlH_4$ (2.5 equiv)	THF, r.t., 5 h	**6f**	23
12	**5**	BnMgCl (1.2 equiv)	THF, r.t., 3 h	**6g**	33[b]
13	**5**	BnMgCl (1.2 equiv)	THF, –70 °C, 4.5 h	**6g**	14[c]
14	**5**	PhMgCl (1.2 equiv)	THF, –72 °C, 7 h	**6h**	48[d]
15	**5**	PhMgCl (4 equiv)	THF, r.t., 1 h	**6h**	94
16	**5**	Allyl–MgBr (4 equiv)	THF, r.t., 1 h	**6i**	88

[a] Some of the starting material **3a** or **5** was also recovered.
[b] Substitution product **7a** was also obtained in 22% yield.
[c] Substitution product **7a** was also obtained in 34% yield.
[d] An inseparable mixture of **6h** and **5** (7:3) was obtained.



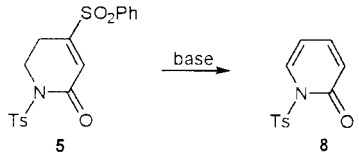
Scheme 5



Scheme 6

smoothly with organocopper reagents derived from Grignard reagents or organolithium compounds to give the substitution products **7a**–**d** (entries 1–5). However, its reaction with the organocopper reagent derived from Allyl–MgBr and CuI gave only the double addition product **6e** (entry 6). Attempted reactions of **3a** with weaker nucleophiles (NaN_3, NaCN or Et_2NH) led only to the recovered starting material. The sulfone-substituted lactam **5** also reacted with methylcopper reagent to give the substitution product **7b** (entry 7), although the yield was much lower than that obtained from **3a** (entry 1). On the other hand, compound **5** reacted efficiently with sodium azide, sodium cyanide, and dimethyl malonate anion to give the substitution products **7e**–**g** (entries 8–10), indicating its higher reactivity than **3a** toward nucleophiles. It should also be noted that lactam **5** reacted with the anion of ethyl acetoacetate to yield the deacetylated product **7h** (entry 11).

Reactions of lactam **5** with a variety of bases led to the elimination product **8** (Scheme 7), presumably via a series of double bond isomerization followed by elimination of the phenylsulfonyl group. The results are summarized in Table 4. Aliphatic and aromatic amines (entries 1–4) all gave the elimination product **8** in good yield. Inorganic salts (entries 5–8) varied in their efficiency for elimination. Enamine (entry 9) or the enolate derived from acetylacetone (entry 10) did not undergo the expected substitution reaction, but gave the elimination product **8** instead. It should be noted that treatment of the sulfide-substituted lactam **3a** with diethylamine under reflux or at 90 °C led only to recovered starting material.



Scheme 7

Following Parsons' method of using Bu_3SnH/AIBN to cleave the N-tosyl group of amides,[25] we prepared the lactams **9** in high yields (Scheme 8 and Table 5). Under this condition the ring substituents (PhS, $PhSO_2$, RCO_2Me, alkenyl, etc) were not affected.

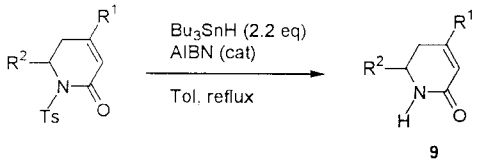
Table 3 Substitution Reactions of Lactams **3a** and **5** with Nucleophiles

Entry	**3a** or **5**	R'M	Condition	Product	Yield (%)
1	**3a**	BnMgCl (4 euiv), CuI (4 equiv)	THF, –78 °C, 8 h	**7a**	91
2	**3a**	MeLi (4 equiv), CuI (4 equiv)	THF, –78 °C, 3 h	**7b**	90
3	**3a**	MeLi (4 equiv), CuI (2 equiv)	THF, –78 °C, 3 h	**7b**	82
4	**3a**	BuLi (4 equiv), CuI (4 equiv)	THF, –78 °C, 3 h	**7c**	91
5	**3a**	PhMgBr (4 equiv), CuI (4 equiv)	THF, –78 °C, 8 h	**7d**	59[a]
6	**3a**	Allyl-MgBr (4 equiv), CuI (4 equiv)	THF, –78 °C 3 h	**6e**	66
7	**5**	MeLi (4 equiv), CuI (4 equiv)	THF, –78 °C–0°C	**7b**	47
8	**5**	NaN_3 (1.1 equiv)	DMF, 0 °C , 0.5 h	**7e**	76
9	**5**	NaCN (1.1 equiv)	DMF, 0 °C, 30 min	**7f**	93
10	**5**	$NaCH(CO_2Me)_2$ (2 equiv)	THF,–78 °C–r.t., 2 h	**7g**	63
11	**5**	$NaCHCOCH_3(CO_2Et)$ (2 equiv)	THF, r.t., 2 h	**7h**	35

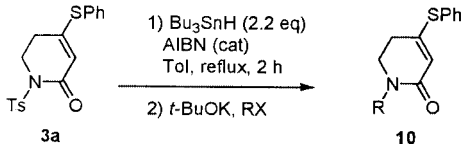
[a] An inseparable mixture of **7d** and **3a** (7:3) was obtained.

Table 4 Reactions of Lactam **5** with Bases to give **8**

Entry	Base	Condition	Yield (%)
1	Dimethylamine (40% aq, 4 equiv)	DMF, r.t., 1 h	76
2	Et_2NH (10 equiv)	THF, 90 °C, 6 h	65
3	Pyrrolidine (1.5 equiv)	DMF, r.t., 1 h	78
4	*N*-methylaniline (4 equiv)	DMF, r.t., 20 h	65
5	Sodium acetate (2 equiv)	DMF, r.t., 3.5 h	79
6	$NaNO_2$ (2 equiv)	DMF, r.t., 1 h	21
7	KF (10 equiv)	DMF, r.t., 5 h	89
8	KI (10 equiv)	DMF, r.t., 24 h	no reaction
9	1-(1-Pyrrolidino)cyclohexene (2 equiv)	CH_3CN, r.t., 70 min	35
10	Acetylacetone (4 equiv), LDA (4.4 equiv)	THF, 0 °C, 1.5 h	74



Scheme 8



Scheme 9

Table 5 N-Desulfonylation of Lactams

Entry	Compound	R^1	R^2	Product	Yield (%)
1	**3a**	SPh	H	**9a**	92
2	**3d**	SPh	Me	**9b**	98
3	**3e**	SPh	4-Pentenyl	**9c**	95
4	**6**	SO_2Ph	H	**9d**	87
5	**7a**	Bn	H	**9e**	84
6	**7b**	Me	H	**9f**	80
7	**7g**	$CH(CO_2Me)_2$	H	**9g**	77
8	**7h**	CH_2CO_2Me	H	**9h**	81

We have also found that following the treatment of lactam **3a** with Bu_3SnH/AIBN, direct addition of a mixture of *t*-BuOK and RX gave the *N*-substituted products **10** (Scheme 9 and Table 6). In most cases, the yields are fairly good since alkyl or acyl isocyanates do not undergo the aza-Diels–Alder reactions with thio-substituted dienes, the preparation of compounds **10** via this process constitutes an efficient way of constructing these molecules.

In summary, we have carried out the first aza-Diels–Alder reactions of arylsulfonyl isocyanates with thio-substituted 1,3-dienes via the 3-sulfolene precursors **1** to give the cyclized products **3** with complete control of chemo- and regioselectivity. The cyclized products **3a** and **5** could further undergo reactions with nucleophiles and bases to give useful heterocyclic compounds. The N-tosyl group of the cyclic products could also be selectively replaced by hydrogen or another substituent.

Table 6 N-Desulfonylation and Tandem Alkylation of Lactam **3a**

Entry	R	Reagent/Condition	Product	Yield (%)
1	Me	*t*-BuOK (4 equiv), MeI (4 equiv), r.t., 1.5 h	**10a**	82
2	Allyl	*t*-BuOK (8 equiv), Allyl-Br (8 equiv), r.t., 4 h	**10b**	69
3	Bn	*t*-BuOK (4 equiv), BnBr (4 equiv), r.t., 1.5 h	**10c**	90
4	Bz	*t*-BuOK (16 equiv), BzCl (16 equiv), r.t., 6 h	**10d**	84
5	Ac	*t*-BuOK (8 equiv), AcCl (8 equiv), r.t., 30 min	**10e**	90
6	CO_2Me	*t*-BuOK (4 equiv), MeO-COCl (4 equiv), r.t., 2 h, reflux, 3 h	**10f**	87
7	Cbz	*t*-BuOK (4 equiv), CbzCl (8 equiv), r.t., 24 h, Tol, reflux, 8 h	**10g**	65
8	Acryloyl	*t*-BuOK (4 equiv), H_2C=CHCOCl (4 equiv), r.t., 3 h	**10h**	24

Infrared spectra were recorded with an FT-IR spectrometer Analect RFX–65. ^{1}H and ^{13}C NMR spectra were measured for samples in $CDCl_3$ with an FT-NMR spectrometer Bruker AC–300 at 300 MHz and 75 MHz, respectively, with tetramethylsilane as the internal standard. Mass spectra were recorded with a spectrometer JEOL JMS-D-100. High resolution mass spectra were measured with a mass spectrometer JEOL TMS-HX 110. Melting points were measured with an apparatus Mel-Temp, and were uncorrected. The silica gel used for flash column chromatography was made by Merck (60 H). All reagents were of reagent grade and toluene was distilled from CaH_2 before use.

aza-Diels–Alder Reactions of Thio-substituted 1,3-Dienes with Arylsulfonyl Isocyanates; General Procedure

A mixture of the 3-sulfolene **1** (226 mg, 1 mmol), the isocyanate (5 mmol) and a catalytic amount of hydroquinone (10 mg, 0.1 mmol) was heated under N_2 in toluene (4 mL) at 110 °C for 4.5 h. If a higher temperature was needed, a sealed tube was used. The solvent was removed under vacum and to the reaction mixture was added a 5% aqueous NaOH solution (50 mL). This was extracted with CH_2Cl_2 (30 mL × 3), and the organic solution was dried (Na_2SO_4) and evaportated. The crude product was purified by silica gel column chromatography using hexane–EtOAc (8:1→ 4:1) with 5–10% of NEt_3 (except for making **2a**) as the eluent.

1-[(4-Methylphenyl)sulfonyl]-4-(phenylthio)-3,6-dihydro-2-pyridinone (2a)

White or pale yellow solid (185 mg, 51% yield); mp 66–68 °C.

IR (film): 3058, 2922, 1691, 1595,1474, 1461, 1440, 1386, 1356, 1293, 1257, 1187, 1167, 1146, 1088, 853, 705, 690 cm^{-1}.

^{1}H NMR: δ = 2.41 (3 H, s), 3.02 (2 H, d, *J* = 3.4 Hz), 4.50 (2 H, dd, *J* = 7.3, 3.4 Hz), 5.80 (1 H, br s), 7.29–7.37 (7 H, m), 7.92 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 21.5, 37.8, 47.5, 118.8, 128.6, 128.8, 129.1, 129.3, 129.4, 130.4, 133.1, 135.5, 145.1, 166.1.

EIMS (relative intensity) *m/z*: 359 (M^+, 15), 295 (28), 250 (36), 205 (17), 204 (94), 187 (13), 186 (93), 176 (18), 161 (34), 155 (36), 149 (11), 147 (24), 135 (15), 110 (12), 109 (34), 94 (10), 91 (100), 77 (10), 67 (11), 65 (34), 39 (13).

EI-HRMS (*m/z*): calcd for $C_{18}H_{17}NO_3S_2$, 359.0650; found, 359.0650.

1-[(4-Methylphenyl)sulfonyl]-4-(phenylthio)-5,6-dihydro-2-pyridinone (3a)

White or pale yellow solid (2.555 g, 71%); mp 105–106 °C.

IR (film): 3058, 2922, 2877, 1672, 1593, 1357, 1294, 1209, 1167, 1089, 900, 705, 688 cm^{-1}.

^{1}H NMR: δ = 2.38 (3 H, s), 2.67 (2 H, t, *J* = 6.3 Hz), 4.06 (2 H, t, *J* = 6.3 Hz), 5.13 (1 H, s), 7.27 (2 H, d, *J* = 8.2 Hz), 7.38–7.45 (5 H, m), 7.88 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 21.4, 29.5, 43.8, 113.9, 127.1, 128.2, 129.1, 129.8, 130.2, 135.1, 135.7, 144.4, 160.2, 161.5.

FAB-MS (relative intensity) *m/z*: 360 (M^++H, 100), 295 (3), 204 (6), 155 (11), 91 (21), 55 (12).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{18}H_{17}NO_3S_2$, 359.0650; found, 360.0690 (M^++H).

1-(Phenylsulfonyl)-4-(phenylthio)-5,6-dihydro-2-pyridinone (3b)

Pale yellow solid (347 mg, 50%); mp 103–104 °C.

IR (film): 3069, 2930, 2887, 1681, 1591, 1474, 1447, 1358, 1294, 1211, 1170, 1132, 1089, 902, 751, 731, 688, 662 cm^{-1}.

^{1}H NMR: δ = 2.69 (2 H, t, *J* = 6.3 Hz), 4.08 (2 H, t, *J* = 6.3 Hz), 5.14 (1 H, s), 7.38–7.60 (8 H, m), 8.02 (2 H, d, *J* = 7.8 Hz).

^{13}C NMR: δ = 29.7, 43.9, 114.1, 127.3, 128.3, 128.5, 129.8, 130.3, 133.4, 135.1, 138.9, 160.3, 161.5.

FAB-MS (relative intensity) *m/z*: 346 (M^++H, 100), 77 (10).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{17}H_{15}NO_3S_2$, 345.0493; found, 346.0565 (M^++H).

1-[(4-Chlorophenyl)sulfonyl]-4-(phenylthio)-5,6-dihydro-2-pyridinone (3c)

Pale yellow solid (144 mg, 38%); mp 151–152 °C.

IR (film): 3088, 3055, 2922, 2888, 1672, 1583, 1474, 1361, 1294, 1211, 1169, 1133, 1090, 901, 758, 673 cm^{-1}.

^{1}H NMR: δ = 2.70 (2 H, t, *J* = 6.3 Hz), 4.07 (2 H, t, *J* = 6.3 Hz), 5.14 (1 H, s), 7.41–7.47 (7 H, m), 7.95 (2 H, d, *J* = 6.8 Hz).

^{13}C NMR: δ = 29.8, 44.0, 114.0, 127.3, 128.9, 130.0, 130.5, 135.2, 137.4, 140.2, 138.9, 160.7, 161.5.

FAB-MS (relative intensity) *m/z*: 382 (42), 381 (21), 380 (M^++H, 100), 154 (11), 131 (11).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{18}H_{17}NO_3S_2$, 379.0104; found, 380.0184 (M^++H).

6-Methyl-1-[(4-methylphenyl)sulfonyl]-4-(phenylthio)-5,6-dihydro-2-pyridinone (3d)

Pale yellow solid (126 mg, 81%); mp 100–102 °C.

IR (film): 3055, 2977, 2928, 1671, 1595, 1381, 1352, 1319, 1224, 1166, 1090, 945, 705, 682 cm^{-1}.

^{1}H NMR: δ = 1.39 (3 H, d, *J* = 6.5 Hz), 2.30 (1 H, d, *J* = 17.1 Hz), 2.39 (3 H, s), 3.05 (1 H, dd, *J* = 17.1, 4.6 Hz), 4.96–5.01 (1 H, m), 5.16 (1 H, br s), 7.27 (2 H, d, *J* = 8.0 Hz), 7.39–7.46 (5 H, m), 7.93 (2 H, d, *J* = 8.0 Hz).

^{13}C NMR: δ = 19.5, 21.5, 35.9, 50.7, 113.3, 127.5, 128.8, 129.0, 129.9, 130.3, 135.2, 136.7, 144.3, 157.2, 160.6.

EI-MS (relative intensity) *m/z*: 373 (M^+, 1), 311 (7), 310 (22), 309 (100), 308 (15), 295 (12), 294 (61), 200 (53), 155 (12), 147 (17), 133 (34), 109 (26), 91 (79), 89 (12), 77 (11), 67 (17), 65 (34), 39 (15).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{19}H_{19}NO_3S_2$, 373.0806; found, 373.0788.

6-(4-Pentenyl)-1-[(4-methylphenyl)sulfonyl]-4-(phenylthio)-5,6-dihydro-2-pyridinone (3e)

Pale yellow solid (162 mg, 70%); mp 114–115 °C.

IR (film): 3071, 2924, 2859, 1670, 1595, 1440, 1347, 1223, 1185, 1166, 1088, 908, 886, 814, 751, 704, 691, 677, 659, 544 cm^{-1}.

^{1}H NMR: δ = 1.42–1.49 (2 H, m), 1.71–1.79 (2 H, m), 2.06–2.13 (2 H, m), 2.39 (3 H, s), 2.46 (1 H, d, *J* = 17.3 Hz), 2.94 (1 H, dd, *J* = 17.3, 3.7 Hz), 4.76–4.83 (1 H, m), 4.99–5.06 (2 H, m), 5.15 (1 H, br s), 5.72–5.86 (1 H, m), 7.26 (2 H, d, *J* = 8.1 Hz), 7.41–7.43 (5 H, m), 7.91 (2 H, d, *J* = 8.1 Hz).

^{13}C NMR: δ = 21.5, 25.5, 32.4, 33.0, 33.1, 55.0, 113.7, 115.2, 127.5, 128.9, 129.0, 129.9, 130.3, 135.2, 136.7, 137.8, 144.3, 157.2, 160.8.

FAB-MS (relative intensity) *m/z*: 428 (M^++H, 100), 294 (10), 204 (10), 155 (11), 91 (19).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{23}H_{25}NO_3S_2$, 427.1276, 428.1349 (M^++H).

Anal. Calcd for $C_{23}H_{25}NO_3S_2$: C, 64.61; H, 5.89. Found: C, 64.30; H, 5.96.

1-[(4-Methylphenyl)sulfonyl]-4,5-bis(phenylthio)-5,6-dihydro-2-pyridinone (3f)
Pale yellow solid (337 mg, 72%); mp 162–164 °C.

IR (film): 3057, 2921, 2871, 1673, 1581, 1474, 1454, 1439, 1378, 1356, 1321, 1283, 1224, 1168, 1089, 915, 751, 683 cm^{-1}.

^1H NMR δ = 2.36 (3 H, s), 3.84–3.93 (2 H, m), 4.49 (1 H, dd, *J* = 12.6, 2.8 Hz), 5.18 (1 H, s), 7.25 (2 H, d, *J* = 8.2 Hz), 7.31–7.44 (8 H, m), 7.56–7.59 (2 H, m), 7.95 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 21.3, 47.7, 48.2, 116.0, 127.2, 128.5, 128.9, 129.0, 129.2, 129.8, 130.2, 132.1, 134.2, 135.2, 135.7, 144.4, 159.0, 160.1.

EIMS (relative intensity) *m/z*: 467 (M^+, 9), 403 (51), 295 (23), 294 (82), 293 (29), 292 (51), 284 (27), 155 (41), 147 (47), 109 (58), 91 (100), 65 (50).

EI-HRMS (*m/z*): calcd for $C_{24}H_{21}NO_3S_3$, 467.0684; found, 467.0683.

1-(Phenylsulfonyl)-4,5-bis(phenylthio)-5,6-tetrahydro-2-pyridinone (3g)
Colorless viscous liquid (329 mg, 73%).

IR (film): 3059, 2924, 2871, 1681, 1581, 1474, 1448, 1359, 1321, 1282, 1224, 1170, 1089, 914, 884, 750, 735, 688 cm^{-1}.

^1H NMR: δ = 3.85& ndash;3.90 (1 H, m), 3.94 (1 H, d, *J* = 3.1 Hz), 4.51 (1 H, dd, *J* = 13, 3.1 Hz), 5.18 (1 H, s), 7.36–7.61 (13 H, m), 8.07 (2 H, dd, *J* = 7.5, 1.4 Hz).

^{13}C NMR: δ = 47.8, 48.3, 115.9, 127.2, 128.4, 128.5, 129.0, 129.3, 129.9, 130.3, 132.1, 133.5, 134.3, 135.2, 138.8, 159.3, 160.2.

EIMS (relative intensity) *m/z*: 453 (M^+, 18), 389 (34), 284 (22), 281 (22), 280 (88), 279 (28), 278 (54), 202 (22), 147 (40), 141 (46), 109 (32), 77 (100), 51 (20).

EI-HRMS (*m/z*): calcd for $C_{23}H_{19}NO_3S_3$, 453.0527; found, 453.0522.

1-[(4-Chlorophenyl)sulfonyl]-4,5-bis(phenylthio)-5,6-dihydro-2-pyridinone (3h)
Pale yellow liquid (227 mg, 47%).

IR (film): 3059, 2923, 2871, 1674, 1583, 1475, 1361, 1280, 1225, 1170, 1091, 915, 759, 735, 691 cm^{-1}.

^1H NMR: δ = 3.85–3.90 (1 H, m), 3.94 (1 H, d, *J* = 3.1 Hz), 4.50 (1 H, dd, *J* = 13.1, 3.1 Hz), 5.18 (1 H, s), 7.37–7.49 (10 H, m), 7.57–7.61 (2 H, m), 8.02 (2 H, dd, *J* = 6.8, 1.8 Hz).

^{13}C NMR: δ = 47.9, 48.3, 115.8, 127.2, 128.7, 129.1, 129.4, 130.0, 130.2, 130.5, 132.1, 134.3, 135.3, 137.2, 140.2, 159.8, 160.2.

EIMS (relative intensity) *m/z*: 487 (M^+, 14), 423 (32), 316 (19), 314 (63), 312 (36), 284 (21), 177 (17), 175 (46), 147 (47), 113 (33), 111 (100), 109 (78), 77 (16), 75 (23), 65 (23).

EI-HRMS (*m/z*): calcd for $C_{23}H_{18}ClNO_3S_3$, 487.0137; found: 487.0132.

5-[(4-Methylphenyl)sulfonyl]-8-(phenylthio)-5-azaspiro[3.5]non-7-en-6-one (3i)
Pale yellow liquid (48 mg, 58%).

IR (film): 3059, 2955, 1681, 1595, 1578, 1493, 1474, 1440, 1413, 1356, 1285, 1258, 1222, 1164, 1127, 1090, 966, 947, 852, 837, 814, 752, 705, 694, 667, 642, 561, 548 cm^{-1}.

^1H NMR: δ = 1.65–1.76 (2 H, m), 2.07–2.16 (2 H, m), 2.41 (3 H, s), 2.52–2.62 (2 H, m), 2.88 (2 H, br s), 5.29 (1 H, s), 7.30 (2 H, d, *J* = 8.2 Hz), 7.42–7.49 (5 H, m), 7.97 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 14.9, 21.5, 33.0, 40.7, 62.7, 114.6, 127.4, 129.4, 129.9, 130.3, 135.2, 139.0, 143.8, 160.2, 160.4, 162.9.

FABMS (relative intensity) *m/z*: 400 (M^++H, 100), 244 (12), 229 (23), 217 (13), 95 (13), 91 (29), 83 (12), 81 (13), 71 (11), 69 (19), 67 (12), 57 (23), 55 (27), 43 (20), 41 (17).

FAB-HRMS (*m/z*): calcd for $C_{21}H_{21}NO_3S_2$, 399.0963; found, 400.1039 (M^++H).

3-Methyl-1-[(4-methylphenyl)sulfonyl]-4-(phenylthio)-5,6-dihydro-2-pyridinone (3j)
Pale yellow brown solid (90 mg, 53%); mp 142–143 °C.

IR (film): 3057, 2922, 1671, 1596, 1473, 1439, 1383, 1355, 1305, 1250, 1167, 1099, 975, 861, 813, 750, 733, 704, 674, 615, 568, 544 cm^{-1}.

^1H NMR: δ = 1.93 (3 H, s), 2.32 (2 H, t, *J* = 6.3 Hz), 2.41 (3 H, s), 3.91 (2 H, t, *J* = 6.3 Hz), 7.30 (2 H, d, *J* = 8.2 Hz), 7.41–7.45 (5 H, m), 7.89 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 13.2, 21.5, 29.3, 43.3, 124.0, 128.4, 129.2, 129.3, 129.5, 129.6, 135.0, 136.1, 144.4, 151.0, 162.3.

AB-MS (relative intensity) *m/z*: 374 (M^++H, 100), 309 (9), 219 (9), 218 (8), 91 (9), 57 (10), 55 (9).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{19}H_{19}NO_3S_2$, 373.0806; found 374.0889, (M^++H).

Anal. Calcd for $C_{19}H_{19}NO_3S_2$: C, 61.10; H, 5.13. Found: C, 61.15; H, 5.19.

1-[(4-Methylphenyl)sulfonyl]-4-(phenylsulfonyl)-5,6-dihydro-2-pyridinone (5)
To a solution of **3a** (225 mg, 0.626 mmol) in CH_2Cl_2 at 0 °C was added a solution of *m*CPBA (50%, 540 mg, 1.565 mmol). After stirring at r.t.for 90 min, the mixture was diluted with CH_2Cl_2 (30 mL). This was washed with sequentially with 5% $Na_2S_2O_3$ (30 mL × 2) and 5% aq. $NaHCO_3$ (30 mL × 2). The organic solution was then dried (Na_2SO_4) and evaporated to give pure product (240 mg, 98%).

White solid; mp 152–153 °C.

IR (film): 3067, 2924, 2877, 1693, 1595, 1447, 1362, 1323, 1307, 1169, 1156, 1129, 1087, 1016, 884, 732, 704, 687 cm^{-1}.

^1H NMR: δ = 2.40 (3 H, s), 2.69 (2 H, t, *J* = 6.4 Hz), 4.07 (2 H, t, *J* = 6.4 Hz), 6.52 (1 H, s), 7.30 (2 H, d, *J* = 8.1 Hz), 7.55–7.61 (2 H, m), 7.69 (1 H, t, *J* = 7.2 Hz), 7.84-7.88 (4 H, m).

^{13}C NMR: δ = 21.5, 23.5, 43.7, 127.1, 128.5, 128.6, 129.4, 129.7, 134.7, 134.8, 136.6, 145.3, 154.2, 160.9.

FAB-MS (relative intensity) *m/z*: 392 (M^++H, 88), 165 (10), 155 (70), 154 (16), 152 (10), 139 (25), 136 (26), 91 (100), 89 (25), 77 (35).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{18}H_{17}NO_5S_2$, 391.0548; found, 392.0634, (M^++H).

Anal. Calcd for $C_{18}H_{17}NO_5S_2$: C, 55.23; H, 4.38. Found: C, 54.80; H, 4.19.

General Procedure for the Reaction of Lactams 3a and 5 with Grignard or Organolithium Reagents
To a solution of **3a** (210 mg, 0.58 mmol) in anhyd THF (5.8 mL) at r.t. was added dropwise MeLi (1.6 mL, 2.34 mmol, 1.5 M in Et_2O) and the resulting solution was stirred for 1 h. The reaction mixture was poured into sat. NH_4Cl solution and was extracted with CH_2Cl_2. The organic solution was dried (Na_2SO_4) and evaporated. The crude product was purified by silica gel column chromatography using hexane–EtOAc (8:1→2:1) with 5–10% of Et_3N as the eluent.

6,6-Dimethyl-1-[(4-methylphenyl)sulfonyl]-4-(phenylthio)-1,2,3,6-tetrahydropyridine (6a)
Pale yellow liquid (143 mg, 66%).

IR (film): 3070, 2971, 2926, 1475, 1439, 1323, 1157, 1094, 814, 744, 691, 662 cm^{-1}.

^1H NMR: δ = 1.40 (6 H, s), 2.41 (3 H, s), 2.62 (2 H, t, *J* = 6.0 Hz), 3.12 (2 H, d, *J* = 6.0 Hz), 5.95 (1 H, s), 7.19–7.28 (7 H, m), 7.73 (2 H, d, *J* = 8.0 Hz).

^{13}C NMR: δ = 21.4, 30.0, 31.6, 41.0, 72.1, 126.8, 127.1, 128.9, 129.4, 130.6, 132.2, 134.3, 137.0, 142.9, 143.5.

EIMS (relative intensity) *m/z*: 373 (M^+, 2), 358 (5), 265 (14), 264 (74), 205 (13), 203 (12), 184 (26), 178 (16), 177 (13), 155 (74), 110 (18), 109 (27), 108 (13), 92 (15), 91 (100), 77 (13), 65 (39), 59 (15), 43 (27).

EI-HRMS (*m/z*): calcd for $C_{20}H_{23}NO_2S_2$, 373.1170; found: 373.1172.

6,6-Dibutyl-1-[(4-methylphenyl)sulfonyl]-4-(phenylthio)-1,2,3,6-tetrahydropyridine (6b)
Pale yellow solid (166 mg, 60%); mp 93–95 °C.

IR (film): 2954, 2931, 2860, 1467, 1439, 1323, 1157, 1094, 813, 744, 691, 662 cm^{-1}.

^1H NMR: δ = 0.89 (6 H, t, *J* = 6.8 Hz), 1.25–1.41 (8 H, m), 1.53 (4 H, t, *J* = 7.6 Hz), 2.41 (3 H, s), 2.61 (2 H, t, *J* = 5.9 Hz), 3.13 (2 H, t, *J* = 5.9 Hz), 5.73 (1 H, s), 7.19–7.24 (5 H, m), 7.27 (2 H, d, *J* = 8.1 Hz), 7.74 (2 H, d, *J* = 8.1 Hz).

^{13}C NMR: δ = 13.9, 21.3, 22.9, 25.9, 30.3, 41.0, 42.5, 77.4, 126.8, 127.1, 128.9, 129.4, 130.9, 132.8, 134.6, 137.2, 141.4, 142.8.

EIMS (relative intensity) *m/z*: 457 (M^+, 3), 418 (28), 248 (12), 247 (71), 235 (43), 209 (23), 184 (42), 177 (11), 163 (28), 155 (79), 110 (11), 92 (10), 91 (100), 85 (88), 65 (13), 57 (32), 41 (15).

EI-HRMS (*m/z*): calcd for $C_{26}H_{35}NO_2S_2$, 457.2109; found, 457.2104.

6,6-Dibenzyl-1-[(4-methylphenyl)sulfonyl]-4-(phenylthio)-1,2,3,6-tetrahydropyridine (6c)
Pale yellow solid (100 mg, 68%); mp 116–117 °C.

IR (film): 3059, 3027, 2922, 2860, 1598, 1494, 1474, 1453, 1439, 1322, 1304, 1235, 1156, 1119, 1032, 1023, 814, 744, 701, 662, 566, 550 cm^{-1}.

^1H NMR: δ = 1.98 (2 H, t, *J* = 6.0 Hz), 2.40 (3 H, s), 2.76 (2 H, t, *J* = 6.0 Hz), 2.87 (2 H, d, *J* = 13.5 Hz), 2.94 (2 H, d, *J* = 13.5 Hz), 5.79 (1 H, s), 6.98-7.00 (2 H, m), 7.17–7.30 (15 H, m), 7.50 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 21.4, 29.5, 40.8, 48.5, 77.6, 126.8, 127.1, 128.1, 128.8 (x2), 129.4, 130.7, 131.6, 133.5, 134.0, 136.2, 136.8, 137.9, 142.8.

FAB-MS (relative intensity) *m/z*: 526 (M^++H, 40), 452 (12), 355 (27), 281 (18), 269 (10), 184 (27), 155 (47), 91 (100).

FAB-HRMS (*m/z*): calcd for $C_{32}H_{31}NO_2S_2$, 525.1796; found, 526.1884 (M^++H).

1-[(4-Methylphenyl)sulfonyl]-6,6-diphenyl-4-(phenylthio)-1,2,3,6-tetrahydropyridine (6d)
Pale yellow liquid (236 mg, 95%).

IR (film): 3057, 3026, 2924, 2860, 1597, 1582, 1491, 1474, 1446, 1326, 1304, 1158, 1120, 1093, 1022, 1001, 813, 747, 701, 666, 634, 550 cm^{-1}.

^1H NMR: δ = 2.40 (3 H, s), 2.42 (2 H, t, *J* = 6.2 Hz), 3.06 (2 H, t, *J* = 6.2 Hz), 6.52 (1 H, s), 7.22–7.34 (17 H, m), 7.65 (2 H, d, *J* = 8.0 Hz).

^{13}C NMR: δ = 21.4, 30.8, 41.0, 79.3, 126.2, 127.1, 127.3, 127.5, 128.3, 129.1, 129.4, 131.9, 133.5, 137.1, 140.2, 140.3, 143.0, 146.8.

FAB-MS (relative intensity) *m/z*: 498 (M^++H, 30), 327 (23), 218 (10), 217 (27), 206 (15), 205 (66), 184 (75), 183 (17), 178 (10), 177 (13), 167 (13), 155 (63), 149 (36), 105 (100), 102 (11), 91 (45), 77 (18).

FAB-HRMS (*m/z*): calcd for $C_{30}H_{27}NO_2S_2$, 497.1483; found, 498.1556 (M^++H).

6,6-Diallyl-1-[(4-methylphenyl)sulfonyl]-4-(phenylthio)-1,2,3,6-tetrahydropyridine (6e)
Colorless liquid (169 mg, 91%).

IR (film): 3072, 2976, 2925, 1475, 1438, 1322, 1304, 1157, 1094, 918, 814, 745, 691, 663 cm^{-1}.

^1H NMR: δ = 2.33 (4 H, d, *J* = 6.3 Hz), 2.41 (3 H, s), 2.60 (2 H, t, *J* = 5.9 Hz), 3.12 (2 H, t, *J* = 5.9 Hz), 5.09-5.18 (4 H, m), 5.73–5.87 (3 H, m), 7.20–7.28 (7 H, m), 7.72 (2 H, d, *J* = 7.9 Hz).

^{13}C NMR: δ = 21.3, 30.3, 41.1, 46.4, 75.8, 119.6, 127.1, 128.9, 129.4, 129.4, 131.2, 132.7, 133.9, 134.0, 137.1, 139.6, 142.9.

EI-MS (relative intensity) *m/z*: 425 (M^+, 0.1), 403 (10), 402 (43), 360 (10), 232 (10), 231 (69), 219 (30), 189 (15), 184 (51), 177 (45), 163 (24), 155 (88), 110 (16), 109 (18), 91 (100), 77 (12), 69 (26), 67 (18), 65 (29), 41 (40), 39 (16)

EI-HRMS (*m/z*): calcd for $C_{24}H_{27}NO_2S_2$, 425.1483; found, 425.1470.

1-[(4-Methylphenyl)sulfonyl]-4-(phenylthio)-1,2,3,6-tetrahydro-pyridine (6f)
To a solution of **3a** (194 mg, 0.54 mmol) in anhyd THF (5.8 mL) at r.t. was added $LiAlH_4$ (95%, 13 mg, 0.34 mmol). After stirring for 5 h, saturated NaCl solution was slowly added, and was extracted with CH_2Cl_2. The organic solution was dried (Na_2SO_4) and evaporated. The crude product was purified by silica gel column chromatography using hexane–EtOAc (8:1→2:1) with 5–10% of Et_3N as the eluent.

White solid (42 mg, 23%); mp 91–93 °C.

IR (film): 3055, 2922, 2850, 1596, 1474, 1439, 1339, 1304, 1239, 1165, 1099, 1057, 1023, 945, 815, 745, 719, 692, 651, 595 cm^{-1}.

^1H NMR: δ = 2.29 (2 H, br s), 2.43 (3 H, s), 3.21 (2 H, t, *J* = 5.6 Hz), 3.67 (2 H, d, *J* = 3.1 Hz), 5.74 (1 H, t, *J* = 3.1 Hz), 7.26–7.33 (7 H, m), 7.66 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 21.4, 29.7, 43.3, 45.7, 123.5, 127.5, 127.6, 129.1, 129.6, 131.6, 131.8, 132.7, 133.5, 143.6.

EIMS (relative intensity) *m/z*: 345 (M^+, 10), 326 (23), 316 (9), 266 (13), 251 (8), 237 (16), 236 (100), 217 (22).

EI-HRMS (*m/z*): calcd for $C_{18}H_{19}NO_2S_2$, 345.0857; found, 345.0852.

6,6-Dibenzyl-1-[(4-methylphenyl)sulfonyl]-4-(phenylsulfonyl)-1,2,3,6-tetrahydropyridine (6g)
Pale yellow liquid (89 mg, 33%).

IR (film): 3060, 3028, 2922, 1598, 1494, 1446, 1453, 1439, 1324, 1291, 1148, 1121, 1092, 1023, 814, 733, 704, 688, 662, 616, 569, 550 cm^{-1}.

^1H NMR: δ = 2.03 (2 H, t, *J* = 6.7 Hz), 2.39 (3 H, s), 2.54 (2 H, t, *J* = 6.7 Hz), 2.97 (4 H, s), 6.97 (1 H, s), 7.15 (10 H, br s), 7.24 (3 H, d, *J* = 8.1 Hz), 7.36–7.44 (2 H, t, *J* = 7.4 Hz), 7.51 (2 H, d, *J* = 7.4 Hz), 7.57 (2 H, d, *J* = 8.1 Hz).

^{13}C NMR: δ = 21.4, 25.8, 41.8, 47.9, 77.8, 126.8, 126.9, 127.8, 128.2, 129.0, 129.4, 130.4, 133.1, 135.4, 136.9, 138.6, 138.9, 143.0, 145.4.

FAB-MS (relative intensity) *m/z*: 558 (M^++H, 57), 484 (25), 364 (10), 184 (22), 155 (38), 154 (18), 137 (10), 136 (15), 107 (10), 102 (26), 92 (10), 91 (100), 77 (11), 57 (10), 55 (11).

FAB-HRMS (*m/z*): calcd for $C_{32}H_{31}NO_4S_2$, 557.1694; found, 558.1780 (M^++H).

1-[(4-Methylphenyl)sulfonyl]-6,6-diphenyl-4-(phenylsulfonyl)-1,2,3,6-tetrahydropyridine (6h)

Yellow liquid (247mg, 94%).

IR (film): 3060, 3028, 2926, 1597, 1492, 1446, 1326, 1303, 1152, 1091, 1074, 814, 749, 732, 700, 662, 554 cm^{-1}.

^1H NMR: δ = 2.37 (3 H, s), 2.67 (2 H, t, *J* = 7.0 Hz), 3.03 (2 H, t, *J* = 7.0 Hz), 7.19 (2 H, d, *J* = 7.8 Hz), 7.26 (11 H, br s), 7.41 (2 H, d, *J* = 7.6 Hz), 7.51–7.57 (3 H, m), 7.65 (2 H, d, *J* = 7.8 Hz).

^{13}C NMR: δ = 21.3, 26.7, 42.0, 80.0, 126.4, 126.9, 127.8, 127.9, 128.4, 129.1, 129.4, 133.3, 136.6, 138.3, 138.6, 143.0, 144.6, 146.5.

FAB-MS (relative intensity) *m/z*: 530 (M^++H, 16), 388 (12), 217 (18), 206 (19), 205 (100), 184 (54), 183 (17), 167 (13), 155 (53), 139 (12), 118 (19), 105 (55), 102 (22), 91 (41), 77 (22).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{30}H_{27}NO_4S_2$. 529.1381; found, 530.1456 (M^++H).

6,6-Diallyl-1-[(4-methylphenyl)sulfonyl]-4-(phenylsulfonyl)-1,2,3,6-tetrahydropyridine (6i)

Colorless liquid (177 mg, 88%).

IR (film): 3073, 2977, 2925, 1446, 1325, 1303, 1157, 1081, 997, 920, 814, 737, 689, 662 cm^{-1}.

^1H NMR: δ = 2.36 (4 H, d, *J* = 7.3 Hz), 2.40 (3 H, s), 2.65 (2 H, t, *J* = 6.7 Hz), 3.06 (2 H, t, *J* = 6.7 Hz), 5.10 (4 H, d, *J* = 12.2 Hz), 5.65–5.79 (2 H, m), 6.83 (1 H, s), 7.27 (2 H, d, *J* = 8.0 Hz), 7.46–7.51 (2 H, m), 7.59 (1 H, d, *J* = 7.1 Hz), 7.69 (2 H, d, *J* = 8.0 Hz), 7.76 (2 H, d, *J* = 7.2 Hz).

^{13}C NMR: δ = 21.3, 26.2, 42.3, 45.7, 76.2, 120.0, 127.0, 127.9, 129.1, 129.5, 131.8, 133.3, 136.9, 138.8, 138.9, 143.1, 146.0.

EIMS (relative intensity) *m/z*: 457 (M^+, 0.1), 435 (9), 434 (37), 274 (11), 184 (34), 155 (70), 125 (23), 109 (13), 92 (10), 91 (100), 77 (15), 67 (16), 65 (15), 41 (27), 39 (10).

EI-HRMS (*m/z*): calcd for $C_{24}H_{27}NO_4S_2$, 457.1381; found, 457.1353.

General Procedure for the Reaction of Lactams 3a and 5 with Organocopper Reagents

To a mixture of CuI (382 mg, 2 mmol) in anhyd THF (5 mL) at –78 °C was added dropwise BnMgCl (1 mL, 2 mmol, 2 M in THF) and the solution was stirred for 0.5 h. To the mixture was added a solution of **3a** (180 mg, 0.5 mmol) in THF (5 mL) at –78 °C and stirred for 8 h. The reaction mixture was poured into saturated NH_4Cl solution and was extracted with CH_2Cl_2. The organic solution was dried (Na_2SO_4) and evaporated. The crude product was purified by silica gel column chromatography using hexane–EtOAc (4:1→2:1) with 5–10% of Et_3N as the eluent.

4-Benzyl-1-[(4-methylphenyl)sulfonyl]-5,6-dihydro-2-pyridinone (7a)

White solid (156 mg, 91%); mp 71–72 °C.

IR (film): 3060, 3027, 2923, 1685, 1637, 1596, 1494, 1466, 1453, 1420, 1376, 1353, 1319, 1290, 1229, 1185, 1167, 1120, 1089, 940, 814, 705, 691, 641, 543 cm^{-1}.

^1H NMR: δ = 2.41 (3 H, s), 2.41–2.43 (2 H, m), 3.48 (2 H, s), 3.97 (2 H, t, *J* = 6.5 Hz), 5.62 (1 H, s), 7.10 (2 H, d, *J* = 7.4 Hz), 7.24–7.33 (5 H, m), 7.90 (2 H, d, *J* = 8.3 Hz).

^{13}C NMR: δ = 21.5, 28.4, 42.9, 43.9, 120.8, 127.1, 128.4, 128.7, 128.9 (x 2), 129.2, 135.9, 144.5, 158.8, 163.2.

FAB-MS (relative intensity) *m/z*: 342 (M^++H, 100), 155 (16), 102 (14), 91 (38).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{19}H_{19}NO_3S$, 341.1086; found, 342.1173 (M^++H).

4-Methyl-1-[(4-methylphenyl)sulfonyl]-5,6-dihydro-2-pyridinone (7b)

White solid (120 mg, 90%); mp 104–106 °C.

IR (film): 2924, 1685, 1593, 1386, 1351, 1312, 1167, 1090, 952, 899, 706, 691 cm^{-1}.

^1H NMR: δ = 1.94 (3 H, s), 2.41 (3 H, s), 2.46 (2 H, t, *J* = 6.4 Hz), 4.03 (2 H, t, *J* = 6.4 Hz), 5.63 (1 H, s), 7.30 (2 H, d, *J* = 8.1 Hz), 7.91 (2 H, d, *J* = 8.1 Hz).

^{13}C NMR: δ = 21.5, 22.8, 30.3, 43.7, 120.6, 128.4, 129.2, 136.1, 144.4, 156.6, 163.2.

FAB-MS (relative intensity) m/z 267 (16), 266 (M^++H, 100), 155 (16), 91 (28), 81 FAB-HRMS (NBA) (*m/z*): calcd for $C_{13}H_{15}NO_3S$, 265.0773; found, 266.0854 (M^++H).

4-Butyl-1-[(4-methylphenyl)sulfonyl]-5,6-dihydro-2-pyridinone (7c)

Colorless liquid (111 mg, 91%).

IR (film): 2956, 2930, 2871, 1685, 1638, 1596, 1492, 1466, 1380, 1353, 1289, 1227, 1168, 1126, 1089, 934, 900, 862, 814, 706, 691, 640, 545 cm^{-1}.

^1H NMR; δ = 0.89 (3 H, t, *J* = 7.1 Hz), 1.24–1.48 (4 H, m), 2.19 (2 H, t, *J* = 7.1 Hz), 2.41 (3 H, s), 2.46 (2 H, t, *J* = 6.5 Hz), 4.01 (2 H, t, *J* = 6.5 Hz), 5.61 (1 H, s), 7.30 (2 H, d, *J* = 8.1 Hz), 7.91 (2 H, d, *J* = 8.1 Hz).

^{13}C NMR: δ = 13.6, 21.5, 22.1, 28.5, 28.9, 36.1, 43.8, 119.4, 128.3, 129.2, 136.0, 144.4, 160.7, 163.4.

EIMS (relative intensity) *m/z*: 307 (M^+, 4), 244 (17), 243 (100), 242 (30), 120 (62), 119 (41), 91 (36), 82 (20), 65 (18), 41 (18), 39 (15), 27 (12).

EI-HRMS (*m/z*): calcd for $C_{16}H_{21}NO_3S$, 307.1242; found, 307.1265.

4-Azido-1-[(4-methylphenyl)sulfonyl]-5,6-dihydro-2-pyridinone (7e)

To a solution of **5** (255 mg, 0.65 mmol) in DMF (6.5 mL) at 0 °C was added NaN_3 (51 mg, 0.72 mmol) and. The reaction mixture was stirred for 0.5 h and was poured into saturated NaCl solution and was extracted with CH_2Cl_2. The organic solution was dried (Na_2SO_4) and evaporated. The crude product was purified by silica gel column chromatography using hexane–EtOAc (8:1→2:1) with 5–10% of Et_3N as the eluent.

White solid (145 mg, 76%); mp 106–108 °C (decomp).

IR (film): 3066, 2922, 2113, 1676, 1617, 1376, 1352, 1312, 1204, 1166, 1089, 705, 688 cm^{-1}.

^1H NMR: δ = 2.42 (3 H, s), 2.56 (2 H, t, *J* = 6.3 Hz), 4.08 (2 H, t, *J* = 6.3 Hz), 5.49 (1 H, s), 7.31 (2 H, d, *J* = 8.2 Hz), 7.91 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 21.5, 27.3, 43.0, 107.6, 128.4, 129.3, 135.8, 144.7, 156.1, 162.7.

FAB-MS (relative intensity) *m/z*: 293 (M^++H, 15), 267 (23), 265 (46), 237 (13), 155 (74), 139 (26), 91 (100), 77 (14), 70 (18).

FAB-HRMS (NBA) *m/z*: calcd for $C_{12}H_{12}N_4O_3S$, 292.0630; found, 293.0721 (M^++H).

1-[(4-Methylphenyl)sulfonyl]-6-oxo-1,2,3,6-tetrahydro-4-pyridinyl cyanide (7f)
A similar procedure was used as for **7e**.

Pale yellow solid (80 mg, 93%); mp 123–124 °C.

IR (film): 3072, 2923, 2852, 2255, 2224, 1689, 1595, 1355, 1314, 1170, 1088, 911, 814, 705, 688 cm^{-1}.

^1H NMR: δ = 2.44 (3 H, s), 2.75 (2 H, t, *J* = 6.4 Hz), 4.13 (2 H, t, *J* = 6.4 Hz), 5.40 (1 H, s), 7.34 (2 H, d, *J* = 8.2 Hz), 7.91 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 21.6, 27.1, 43.3, 115.3, 126.1, 128.6, 129.5, 134.8, 135.3, 145.5, 160.0.

FAB-MS (relative intensity) *m/z*: 277 (M^++H, 32), 155 (32), 136 (23), 107 (20), 105 (20), 97 (25), 95 (35), 93 (21), 91 (63), 85 (22), 83 (37), 81 (43), 79 (27), 77 (24), 73 (22), 71 (41), 69 (71), 67 (42), 57 (100), 55 (86), 43 (71), 41 (60), 29 (20).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{13}H_{12}N_2O_3S$, 276.0569; found, 277.0666 (M^++H).

Dimethyl 2-{1-[(4-Methylphenyl)sulfonyl]-6-oxo-1,2,3,6-tetrahydro-4-pyridinyl}malonate (7g)
To a mixture of NaH (71 mg, 1.5 mmol) in anhyd THF (5 mL) at 0 °C was added dimethyl malonate (0.11 mL, 1 mmol) and was stirred for 0.5 h. To the mixture was added a solution **5** (194 mg, 0.5 mmol) in THF (5 mL) at –78 °C. The solution was slowly warmed to r.t. The reaction mixture was poured into saturated ammonium chloride solution and was extracted with CH_2Cl_2. The organic solution was dried (Na_2SO_4) and evaporated. The crude product was purified by silica gel column chromatography using hexane–EtOAc (8:1→ 4:1) with 5–10% of NEt_3 as the eluent.

Colorless liquid (119 mg, 63%).

IR (film): 2955, 1738, 1690, 1435, 1354, 1305, 1210, 1187, 1168, 1126, 1089, 706, 690 cm^{-1}.

^1H NMR: δ = 2.42 (3 H, s), 2.69 (2 H, t, *J* = 6.3 Hz), 3.76 (6 H, s), 4.06 (2 H, t, *J* = 6.3 Hz), 4.26 (1 H, s), 5.81 (1 H, s), 7.31 (2 H, d, *J* = 8.2 Hz), 7.91 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR: δ = 21.4, 27.2, 43.9, 53.0, 57.3, 124.7, 128.3, 129.2, 135.5, 144.7, 149.4, 162.1, 166.0.

EIMS (relative intensity) *m/z*: 381 (M^+, 0.2), 318 (16), 317 (83), 316 (43), 294 (14), 226 (10), 198 (10), 186 (16), 170 (14), 166 (11), 155 (16), 139 (10), 138 (18), 120 (27), 119 (30), 91 (100), 89 (10), 65 (35), 59 (42).

EI-HRMS (*m/z*): calcd for $C_{17}H_{19}NO_7S$, 381.0882; found, 381.0887.

Ethyl 2-{1-[(4-Methylphenyl)sulfonyl]-6-oxo-1,2,3,6-tetrahydro-4-pyridinyl}acetate (7h)
A similar procedure was used as for **7g**.

Colorless liquid (47 mg, 35%).

IR (film): 2981, 2924, 1733, 1686, 1595, 1466, 1353, 1286, 1214, 1186, 1168, 1125, 1089, 1028, 959, 893, 814, 706, 690 cm^{-1}.

^1H NMR: δ = 1.26 (3 H, t, *J* = 7.1 Hz), 2.42 (3 H, s), 2.59 (2 H, t, *J* = 6.4 Hz), 3.21 (2 H, s), 4.06 (2 H, t, *J* = 6.4 Hz), 4.15 (2 H, q, *J* = 7.1 Hz), 5.73 (1 H, s), 7.31 (2 H, d, *J* = 8.3 Hz), 7.91 (2 H, d, *J* = 8.3 Hz).

^{13}C NMR: δ = 14.0, 21.5, 28.8, 41.6, 43.8, 61.4, 123.1, 128.4, 129.3, 135.8, 144.7, 151.7, 162.7, 168.7.

FAB-MS (relative intensity) *m/z*: 338 (M^++H, 100), 155 (34), 139 (13), 102 (34), 91 (58), 57 (12), 41 (12), 39 (10), 29 (12).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{16}H_{19}NO_5S$, 337.0984; found, 338.1051 (M^++H).

1-[(4-Methylphenyl)sulfonyl]-2-pyridinone (8)
To a solution of **5** (185 mg, 0.47 mmol) in DMF (4.6 mL) at r.t. was added pyrrolidine (50 mg, 0.7 mmol). After stirring for 1 h, the reaction mixture was poured into saturated NaCl solution and was extracted with CH_2Cl_2. The organic solution was dried (Na_2SO_4) and evaporated. The crude product was purified by silica gel column chromatography using hexane–EtOAc (8:1→2:1) with 5–10% of Et_3N as the eluent.

Pale yellow solid (92 mg, 78%); mp 128–130 °C.

IR (film): 2924, 1685, 1593, 1386, 1351, 1312, 1167, 1090, 952, 899, 706, 691 cm^{-1}.

^1H NMR: δ = 2.43 (3 H, s), 6.22–6.27 (1 H, m), 6.40 (1 H, d, *J* = 9.3 Hz), 7.27–7.31 (1 H, m), 7.34 (2 H, d, *J* = 8.3 Hz), 7.99 (2 H, d, *J* = 8.3 Hz), 8.08 (1 H, dd, *J* = 7.4, 1.7 Hz).

^{13}C NMR: δ = 21.6, 106.1, 123.4, 129.4, 129.8, 131.6, 133.4, 141.0, 146.1, 160.0.

EI-MS (relative intensity) *m/z*: 250 (18), 249 (M^+, 3), 186 (19), 185 (100), 184 (85), 157 (45), 156 (12), 155 (27), 91 (73), 65 (16), 39 (22).

EI-HRMS (*m/z*): calcd for $C_{12}H_{11}NO_3S$, 249.0460; found, 249.0464.

Anal. Calcd for $C_{12}H_{11}NO_3S$: C, 57.82; H, 4.45. Found: C, 57.81; H, 4.64.

General Procedure for Desulfonylation of Lactams
To a mixture of the lactam (0.50 mmol) and AIBN (0.10 mmol) in degassed toluene (10 mL) was added Bu_3SnH (1.1 mmol). This was heated at reflux under N_2 for 2 h. During this period another two portions of AIBN (0.10 mmol each) were added in 30 min interval. The solvent was then evaporated under vacuum and the crude product was purified by silica gel column chromatography using hexane–EtOAc (2:1→1:1) with 5–10% of NEt_3 as the eluent to give the desulfonylated product.

4-(Phenylthio)-5,6-dihydro-2-pyridinone (9a)
While solid (95 mg, 92%); mp 112–113 °C.

IR (film): 3298, 3203, 3073, 3043, 2922, 2851, 1667, 1591, 1479, 1439, 1409, 1339, 1244, 1210, 1125, 1013, 839, 768, 748, 706, 691, 639 cm^{-1}.

^1H NMR: δ = 2.51 (2 H, t, *J* = 6.7 Hz), 3.44 (2 H, t, *J* = 6.7 Hz), 5.27 (1 H, s), 6.25 (1 H, br s), 7.43–7.51 (5 H, m).

^{13}C NMR: δ = 28.8, 39.5, 114.5, 128.1, 129.7, 129.9, 135.2, 155.6, 166.0.

FAB-MS (relative intensity) *m/z*: 206 (M^++H, 100), 204 (11), 77 (3), 39 (3), 30 (8).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{11}H_{11}NOS$, 205.0561; found, 206.0641 (M^++H).

Anal. Calcd for $C_{11}H_{11}NOS$: C, 64.36; H, 5.40. Found: C, 64.22; H, 5.50.

6-Methyl-4-(phenylthio)-5,6-dihydro-2-pyridinone (9b)
While solid (63 mg, 98%); mp 180–181 °C.

IR (film): 3183, 3053, 2962, 2926, 1666, 1586, 1474, 1444, 1403, 1333, 1305, 1102, 1022, 838, 810, 777, 754, 704, 692, 608, 541, 509, 498 cm^{-1}.

^1H NMR: δ = 1.23 (3 H, d, *J* = 6.3 Hz), 2.31–2.41 (2 H, m), 3.67–3.75 (1 H, m), 5.24 (1 H, s), 6.61 (1 H, br s), 7.39–7.48 (5 H, m).

^{13}C NMR: δ = 20.6, 36.3, 46.6, 114.1, 128.2, 129.7, 129.8, 135.2, 154.7, 166.2.

FAB-MS (relative intensity) *m/z*: 220 (M^++H, 100), 219 (21), 218 (25), 204 (14), 177 (9), 154 (9), 136 (9), 44 (10).

FAB-HRMS (*m/z*): calcd for $C_{12}H_{13}NOS$, 219.0718; found, 220.0801 (M^++H).

6-(4-Pentenyl)-4-(phenylthio)-5,6-dihydro-2-pyridinone (9c)
Pale yellow solid (58 mg, 95%); mp 126–127 °C.

IR (film): 3185, 3072, 2936, 2852, 1654, 1584, 1472, 1459, 1402, 1341, 910, 850, 754, 691, 500 cm^{-1}.

^{1}H NMR: δ = 1.41–1.62 (4 H, m), 2.03–2.09 (2 H, m), 2.28–2.50 (2 H, m), 3.55–3.61 (1 H, m), 4.95–5.03 (2 H, m), 5.26 (1 H, s), 5.69–5.83 (1 H, m), 6.25 (1 H, br s), 7.40–7.50 (5 H, m).

^{13}C NMR: δ = 24.4, 33.2, 34.2, 34.5, 50.7, 114.3, 115.0, 128.2, 129.7, 129.8, 135.2, 137.8, 154.6, 165.9.

FABMS (relative intensity) *m/z*: 274 (M^++H, 100), 272 (15), 204 (18), 98 (8).

FAB-HRMS (NBA) (*m/z*):calcd for $C_{16}H_{19}NOS$, 273.1187; found, 274.1268 (M^++H).

4-(Phenylsulfonyl)-,5,6-dihydro-2-pyridinone (9d)
White solid (103 mg, 87%); mp 157–159 °C.

IR (film): 3227, 3056, 3073, 2921, 1674, 1620, 1480, 1445, 1345, 1309, 1155, 1089, 996, 755, 686, 649, 584, 560 cm^{-1}.

^{1}H NMR: δ = 2.56 (2 H, td, *J* = 6.7, 1.2 Hz), 3.47 (2 H, td, *J* = 6.7, 2.6 Hz), 6.63 (1 H, d, *J* = 1.2 Hz), 6.77 (1 H, br s), 7.60 (2 H, t, *J* = 7.4 Hz), 7.71 (1 H, t, *J* = 7.4 Hz), 7.91 (1 H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 22.3, 39.4, 127.4, 128.5, 129.6, 134.4, 137.2, 151.8, 164.0.

FAB-MS (relative intensity) *m/z*:238 (M^++H, 100), 236 (9), 154 (19), 137 (15), 136 (17).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{11}H_{11}NO_3S$, 237.0460; found, 238.0539 (M^++H).

Anal. Calcd for $C_{11}H_{11}NO_3S$: C, 55.68; H, 4.67. Found: C, 55.64; H, 4.68.

4-Benzyl-5,6-dihydro-2-pyridinone (9e)
White solid (69 mg, 84%); mp. 124–125 °C.

IR (film): 3218, 3060, 3024, 2944, 2843, 1666, 1623, 1600, 1483, 1450, 1403, 1372, 1337, 1139, 997, 870, 753, 701, 667, 618 cm^{-1},

^{1}H NMR: δ = 2.23 (2 H, t, *J* = 7.1 Hz), 3.35 (2 H, td, *J* = 7.1, 2.5 Hz), 3.49 (2 H, s), 5.69 (1 H, s), 6.47 (1 H, br s), 7.15–7.33 (5 H, m).

^{13}C NMR: δ = 27.3, 39.4, 43.2, 120.4, 126.8, 128.6, 128.9, 136.8, 155.1, 167.2.

FAB-MS (relative intensity) *m/z*: 188 (M^++H, 100), 186 (13), 91 (10), 81 (10), 69 (15), 67 (11), 57 (16), 55 (25), 43 (18), 41 (17).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{12}H_{13}NO$, 187.0997; found, 188.1072 (M^++H).

4-Methyl-5,6-dihydro-2-pyridinone (9f)
White solid (42 mg, 80%); mp 112–113 °C.

IR (film): 2932, 2855, 1676, 1623, 1482, 1449, 1379, 1362, 1336, 1154, 1109, 995, 856, 748 cm^{-1}.

^{1}H NMR: δ = 1.96 (3 H, s), 2.28 (2 H, t, *J* = 7.1 Hz), 3.41 (2 H, td, *J* = 7.1, 2.6 Hz), 5.69 (1 H, s), 6.76 (1 H, br s).

^{13}C NMR: δ = 22.9, 29.0, 39.2, 119.8, 152.9, 167.4.

FAB-MS (relative intensity) *m/z*: 112 (M^++H, 100), 110 (10), 109 (10), 107 (10), 105 (11), 95 (20), 93 (14), 91 (15), 83 (15), 81 (27), 79 (13), 71 (12), 69 (28), 67 (19), 57 (27), 55 (41), 43 (27), 41 (26).

FAB-HRMS (NBA) (*m/z*): calcd for C_8H_9NO, 111.0684; found, 112.0754 (M^++H).

Dimethyl 2-(6-Oxo-1,2,3,6-tetrahydro-4-pyridinyl)malonate (9g)
Light yellow liquid (32 mg, 77%).

IR (film): 3245, 2955, 2922, 2855, 1735, 1678, 1624, 1482, 1436, 1371, 1320, 1274, 1202, 1152, 1106, 1020, 1000, 750 cm^{-1}.

^{1}H NMR: δ = 2.52 (2 H, t, *J* = 6.9 Hz), 3.46 (2 H, td, *J* = 6.9, 2.5 Hz), 3.77 (6 H, s), 4.27 (1 H, s), 5.88 (1 H, s), 6.18 (1 H, br s).

^{13}C NMR: δ = 26.1, 39.6, 53.0, 58.0, 124.9, 146.1, 165.7, 166.7.

FAB-MS (relative intensity) *m/z*: 228 (M^++H, 100), 136 (11), 95 (10), 91 (11), 81 (13), 69 (20), 67 (14), 57 (20), 55 (30), 43 (21), 41 (22).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{10}H_{13}NO_5$, 227.0794; found, 228.0884 (M^++H).

Ethyl 2-(6-Oxo-1,2,3,6-tetrahydro-4-pyridinyl)acetate (9h)
Light yellow liquid (33 mg, 81%).

IR (film): 3246, 2980, 2933, 1731, 1676, 1624, 1481, 1334, 1250, 1211, 1177, 1151, 1106, 1027, 749 cm^{-1}.

^{1}H NMR: δ = 1.27 (3 H, t, *J* = 7.1 Hz), 2.41 (2 H, t, *J* = 6.9 Hz), 3.22 (2 H, s), 3.45 (2 H, td, *J* = 6.9, 2.6 Hz), 4.17 (2 H, q, *J* = 7.1 Hz), 5.80 (1 H, s), 6.44 (1 H, br s).

^{13}C NMR: δ = 14.0, 27.6, 39.4, 42.1, 61.1, 122.7, 148.1, 166.5, 169.3.

FAB-MS (relative intensity) *m/z*: 184 (M^++H, 100), 183 (10), 182 (24), 138 (12), 111 (16), 110 (13), 55 (13), 41 (10).

FAB-HRMS (NBA) (*m/z*): calcd for $C_9H_{13}NO_3$,183.0895; found, 184.0985 (M^++H).

General Procedure for N-Desulfonylation and Tandem Alkylation of Lactam 3a
The same general procedure was used as for the preparation of **9** except for the following. After compound **3a** was reacted with Bu_3SnH/AIBN at reflux for 2 h, the reaction mixture was cooled to r.t. The alkyl halide or the acyl chloride (2.0 mmol) and *t*-BuOK (2.0 mmol) were then added sequentially. The reaction conditions as shown in Table 6 were followed. The solvent was then removed under vacuum. The crude product was purified by silica gel column chromatography using hexane–EtOAc (4:1→1:1) with 5–10% of Et_3N as the eluent.

1-Methyl-4-(phenylthio)-5,6-dihydro-2-pyridinone (10a)
Light yellow solid (90 mg, 82%); mp 78–80 °C.

IR (film): 3055, 2927, 2855, 1649, 1593, 1489, 1439, 1399, 1350, 1332, 1279, 1246, 1200, 1147, 1064, 1023, 999, 969, 926, 853, 769, 750, 705, 692, 646 cm^{-1}.

^{1}H NMR: δ = 2.53 (2 H, t, *J* = 7.0 Hz), 2.94 (3 H, s), 3.42 (2 H, t, *J* = 7.0 Hz), 5.33 (1 H, s), 7.39–7.48 (5 H, m).

^{13}C NMR: δ = 28.8, 34.1, 47.4, 115.8, 128.5, 129.7, 129.8, 135.1, 152.6, 164.0.

FAB-MS (relative intensity) *m/z*: 220 (M^++H, 100), 218 (19), 44(8), 42 (4).

FABHRMS (NBA) (*m/z*): calcd for $C_{12}H_{13}NOS$, 219.0718; found, 220.0799 (M^++H).

Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.97. Found: C, 65.45; H, 6.13.

1-Allyl-4-(phenylthio)-5,6-dihydro-2-pyridinone (10b)
Light yellow liquid (85 mg, 69%).

IR (film): 3075, 2925, 2835, 1649, 1593, 1474, 1440, 1415, 1352, 1336, 1296, 1242, 1215, 1178, 1088, 1068, 1024, 993, 971, 922, 853, 767, 749, 705, 692 cm^{-1}.

^{1}H NMR: δ = 2.51 (2 H, t, *J* = 6.9 Hz), 3.38 (2 H, t, *J* = 6.9 Hz), 3.99 (2 H, d, *J* = 5.8 Hz), 5.14–5.20 (2 H, m), 5.35 (1 H, s), 5.69–5.82 (1 H, m), 7.38–7.51 (5 H, m).

^{13}C NMR: δ = 28.9, 44.5, 48.4, 115.6, 117.2, 128.4, 129.7, 129.8, 133.2, 135.1, 152.9, 163.6.

FABMS (relative intensity) *m/z*:246 (M^++H, 100), 245 (7), 244 (23), 70 (17), 41 (15).

FABHRMS (NBA) (*m/z*): calcd for $C_{12}H_{13}NOS$, 245.0874; found, 246.0958 (M^++H).

1-Benzyl-4-(phenylthio)-5,6-dihydro-2-pyridinone (10c)
Pale yellow liquid (133 mg, 90%).

IR (film): 3059, 2928, 2922, 2855, 1645, 1592, 1493, 1474, 1439, 1355, 1314, 1242, 1151, 1124, 1086, 1074, 1027, 968, 853, 749, 731, 695, 596 cm^{-1}.

^{1}H NMR: δ = 2.44 (2 H, t, *J* = 6.7 Hz), 3.31 (2 H, t, *J* = 6.7 Hz), 4.57 (2 H, s), 5.40 (1 H, s), 7.22–7.50 (10 H, m).

^{13}C NMR: δ = 28.8, 44.4, 49.2, 115.4, 127.2, 127.8, 128.3, 129.3, 129.7, 130.6, 135.1, 137.3, 152.9, 163.7.

FAB-MS (relative intensity) *m/z*: 296 (M^++H, 100), 295 (9), 294 (17), 91 (44).

FAB-HRMS (NBA) *m/z*: calcd for $C_{18}H_{17}NOS$, 295.1031; found, 296.1111 (M^++H).

1-Benzoyl-4-(phenylthio)-5,6-dihydro-2-pyridinone (10d)
Pale yellow solid (130 mg, 84%); mp 134–136 °C.

IR (film): 3058, 2928, 2888, 1676, 1590, 1466, 1440, 1379, 1307, 1215, 1176, 1114, 1048, 1023, 987, 935, 855, 795, 772, 750, 729, 702, 691, 639 cm^{-1}

^{1}H NMR: δ = 2.73 (2 H, t, *J* = 6.3 Hz), 4.03 (2 H, t, *J* = 6.3 Hz), 5.30 (1 H, s), 7.33–7.56 (10 H, m).

^{13}C NMR: δ = 29.4, 43.3, 114.5, 127.5, 127.9, 128.2, 130.0, 130.4, 131.4, 135.3, 136.1, 161.2, 163.9, 173.5.

FAB-MS (relative intensity) *m/z*: 310 (M^++H, 45), 309 (4), 308 (4), 106 (9), 105 (100), 77 (14).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{18}H_{16}NO_2S$, 309.0823; found, 310.0896 (M^++H).

1-Acetyl-4-(phenylthio)-5,6-dihydro-2-pyridinone (10e)
Pale yellow liquid (112 mg, 90%).

IR (film): 3055, 2922, 2855, 1678, 1594, 1368, 1312, 1273, 1217, 1151, 1062, 1025, 982, 933, 855, 749, 691 cm^{-1}.

^{1}H NMR: δ = 2.50 (3 H, s), 2.55 (2 H, t, *J* = 6.3 Hz), 4.01 (2 H, t, *J* = 6.3 Hz), 5.32 (1 H, s), 7.44–7.53 (5 H, m).

^{13}C NMR: δ = 27.0, 29.1, 40.8, 115.0, 127.6, 129.9, 130.3, 135.3, 160.9, 163.9, 172.9.

FAB-MS (relative intensity) *m/z*: 248 (M^++H, 100), 247 (9), 246 (9), 207 (10), 206 (70), 205 (11), 204 (25), 102 (10), 77 (11), 43 (15).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{13}H_{13}NO_2S$, 247.0667; found, 248.0739 (M^++H).

Methyl 6-oxo-4-(phenylthio)-1,2,3,6-tetrahydro-1-pyridinecarboxylate (10f)
Pale yellow solid (114 mg, 87%); mp 88–90 °C.

IR (film): 3057, 3002, 2952, 2850, 1763, 1714, 1682, 1595, 1474, 1439, 1388, 1321, 1206, 1096, 1025, 941, 855, 773, 752, 705, 692, 637, 505 cm^{-1}.

^{1}H NMR: δ = 2.57 (2 H, t, *J* = 6.1 Hz), 3.84 (3 H, s), 3.98 (2 H, t, *J* = 6.1 Hz), 5.33 (1 H, s), 7.42–7.51 (5 H, m).

^{13}C NMR: δ = 29.0, 43.6, 53.6, 115.1, 127.4, 129.8, 130.1, 135.1, 154.4, 159.6, 161.8.

FAB-MS (relative intensity) *m/z*: 264 (M^++H, 100), 232 (47), 206 (6), 91 (5), 77 (5);.

FAB-HRMS (*m/z*): calcd for $C_{13}H_{13}NO_3S$, 263.0616; found, 264.0701 (M^++H).

Benzyl 6-oxo-4-(phenylthio)-1,2,3,6-tetrahydro-1-pyridinecarboxylate (10g)
Pale yellow liquid (111 mg, 65%).

IR (film): 3060, 3031, 2940, 2890, 1761, 1711, 1689, 1595, 1379, 1318, 1288, 1204, 1158, 1098, 1025, 939, 856, 771, 749, 694 cm^{-1}.

^{1}H NMR: δ = 2.55 (2 H, t, *J* = 6.1 Hz), 3.97 (2 H, t, *J* = 6.1 Hz), 5.27 (2 H, s), 5.33 (1 H, s), 7.32–7.47 (10 H, m).

^{13}C NMR: δ = 29.2, 43.7, 68.3, 115.4, 127.6, 127.8, 128.1, 128.4, 129.9, 130.3, 135.2, 135.4, 153.8, 159.5, 162.0.

FAB-MS (relative intensity) *m/z*: 340 (M^++H, 65), 296 (16), 232 (14), 91 (100), 57 (14), 55 (13), 43 (10), 41 (11).

FAB-HRMS (NBA) (*m/z*): calcd for $C_{19}H_{17}NO_3S$, 339.0929; found, 340.1006 (M^++H).

1-Acryloyl-4-(phenylthio)-5,6-dihydro-2-pyridinone (10h)
Pale yellow liquid (31 mg, 24%).

IR (film): 3058, 2955, 2927, 1676, 1593, 1403, 1380, 1315, 1215, 1191, 1015, 936, 855, 750, 691 cm^{-1}.

^{1}H NMR: δ = 2.60 (2 H, td, *J* = 6.4, 0.8 Hz), 4.03 (2 H, t, *J* = 6.4 Hz), 5.34 (1 H, d, *J* = 0.8 Hz), 5.71 (1 H, dd, *J* = 10.3, 1.7 Hz), 6.36 (1 H, dd, *J* = 16.7, 1.7 Hz), 7.02 (1 H, dd, *J* = 16.7, 10.3 Hz), 7.45–7.53 (5 H, m).

^{13}C NMR: δ = 29.2, 41.4, 114.8, 127.5, 128.2, 130.0, 130.4, 131.5, 135.3, 161.5, 164.0, 168.4.

FAB-MS (relative intensity) *m/z*: 260 (M^++H, 100), 259 (13), 257 (10), 206 (58), 204 (19), 197 (11), 189 (11), 174 (20), 154 (18), 137 (12), 136 (19), 114 (24), 91 (11), 77 (11), 55 (25.

FAB-HRMS (*m/z*): calcd for $C_{14}H_{13}NO_2S$, 259.0667; found, 260.0738 (M^++H).

Acknowledgement

Financial support of this work by the National Science Council of the Republic of China is gratefully acknowledged (NSC 89-2113-M-030-005).

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