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2- AND 3-PHENYLSULFONYLINDOLES – SYNTHETIC EQUIVALENTS OF UNSUBSTITUTED INDOLE IN N-ALKYLATION REACTIONS*

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The N-alkylation of 2- and 3-phenylsulfonylindoles under various conditions and the subsequent removal of the activating phenylsulfonyl group by reductive desulfonylation using Raney nickel leads to N-alkylindoles in high yield. 2-Phenylsulfonylindole readily undergoes the Mitsunobu reaction, while isomeric 3-phenylsulfonylindole is relatively inert under these conditions.

Keywords: indoles, N-alkylation, reduction desulfonylation, Mitsunobu reaction.

In medicinal chemistry, indole derivatives form one of the most important classes of heterocyclic compounds [1]. This importance is due to the wide distribution of the indole fragment in the structures of natural and synthetic biologically active compounds with a broad range of activities. An enormous variety of efficient synthetic methods for construction of the bicyclic indole system and its modifications is already known [2, 3]. Nevertheless, the search for new, reliable, and simple synthetic transformations for indole derivatives remains a subject of current research.

The direct N-alkylation of indole is clearly the most attractive method for obtaining N-alkyl derivatives. The initial generation of the indolyl anion is usually required for the success of this reaction. However, the ambident properties of the indolyl anion facilitate formation of N-alkylation, C-alkylation, and N,C-dialkylation products [2, 4, 5]. The selectivity of the reaction of the indolyl anion and the alkylating agent depends significantly on the nature of the cation, solvent, and structure of the alkylating agent. Although high selectivity for this reaction may be achieved by varying these factors, the problem of selective preparation of an indole N-alkylation product requires a specific solution in each concrete case [2, 6-8]. Special synthetic methods based on the use of phase-transfer catalysis [9-11], ionic liquids as the solvent [12, 13], other special solvents [14, 15], bases [16], and alkylating agents [17], as well as microwave irradiation have been proposed to resolve this problem. Furthermore, generation of the indolyl anion from an N-unsubstituted indole and indole derivatives lacking electron-withdrawing substituents requires the use of a stoichiometric amount of strong bases, which significantly limits the range of functional group tolerating the reaction conditions. It is also important to note

* Dedicated to Professor V. I. Minkin on the occasion of his seventieth birthday.

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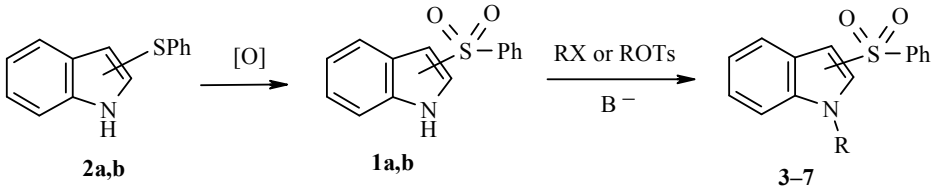
that elimination competes significantly with alkylation when secondary alkylating agents, especially halides, are used. This behavior is related to the high basicity of indolyl anions lacking electron-withdrawing substituents [2]. Indolyl anions with electron-withdrawing substituents at C-2 or C-3 undergo direct N-alkylation much more readily. Firstly, the use of weak inorganic or organic bases is usually sufficient for the generation of such indolyl anions. Secondly, electron-withdrawing substituents significantly reduce their basicity permitting the use of secondary alkylating agents. And thirdly, competing C-alkylation is not observed in reactions of indolyl anions with electron-withdrawing substituents [2]. These circumstances permitted us to propose a new general approach to the selective preparation of various N-substituted indoles based on the initial N-alkylation of indole derivatives containing an activating electron-withdrawing substituent at C-2 or C-3 with subsequent removal of this substituent to give the desired N-alkylation product. We proposed that the phenylsulfonyl group, which can be subsequently removed with ease by reductive desulfonylation, may be used as the activating electron-withdrawing group [19].



2a,b **1a,b** **3–7**

1 a 2-SO_2Ph, **b** 3-SO_2Ph; **2 a** 2-SPh, **b** 3-SPh

TABLE 1. Direct N-Alkylation of Indolylphenylsulfones **1a** and **1b**

Substrate	RX	Conditions*	Reaction time, h	Alkylation product	Yield, %*[2]
1a	MeI	A	4	**3a**	(12)
		A	8		(34)
		B	8		(45)
	Me_2CHI	A	12	**4a**	(<10)
		B	12		(35)
		C	18		(27)
	Phth$(CH_2)_3$Br*[3]	B	12	**5a**	(23)
		C	12		(<10)
1b	Me_2CHI	D	12	**4b**	90
		E	12		94
	Phth$(CH_2)_3$Br	A	12	**5b**	45
		C	12		60
		E	12		76
	$NCCH_2Br$	A	8	**6b**	65
		E	10		81
	$PhOCH_2CH_2Ts$	A	18	**7b**	72
		B	12		50
		E	8		80
		F	12		71

*A: K_2CO_3 (2 eq.), RX (2 eq.), acetone, reflux; B: NaH (1.1 eq.), RX (1.3 eq.), DMF, 25°C; C: K_2CO_3 (2 eq.), RX (2 eq.), DMF, 60°C; D: NaH (1.1 eq.), RX (1.3 eq.), DMF, 60°C; E: 1,8-diazabicyclo-[5.4.0]undec-7-ene (1.1 eq.), RX (1.1 eq.), DMF, 25°C; F: *t*-BuOH (1.1 eq.), RX (1.1 eq.), DMF, 25°C.

*[2]The yields determined by ^{1}H NMR spectroscopy are given in parentheses. The yields of the isolated reaction products are given by the numbers without parentheses.

*[3] Phth = phthalimido.

2-Phenylsulfonylindole (**1a**) and 3-phenylsulfonylindole (**1b**), which we propose for use as the synthetic equivalents of unsubstituted indole in N-alkylation reactions, may be obtained readily by oxidation of the corresponding sulfides **2a** [20] and **2b** [21] As described by Broggini et al. [22], the oxidation of indol-3-yl phenyl sulfide (**2b**) by 3-chloroperbenzoic acid leads to the corresponding sulfone **1b** in high yield. The use of the same reagent for oxidation of isomeric sulfide **2a** yielded corresponding sulfone **1a** in only 52% yield. OXONE® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) [23] proved the most efficient oxidizing agent for this reaction and the yield of sulfone **1b** was 94% in this case.

Our results in a study of the direct N-alkylation of sulfones **1a** and **1b** using alkyl halides and sulfonates are given in Table 1. We varied the bases used for generating the indolyl anions and used primary and secondary alkylating agents. The corresponding N-alkylation products were obtained in high yield in virtually all cases of using indol-3-yl phenyl sulfone (**1b**) as the substrate. Under the same conditions, alkylation of the anion of indol-2-yl phenyl sulfone (**1a**) was more difficult to achieve. Complete conversion of the substrate was not observed for any of the proposed conditions, even upon significantly extending the reaction time.

N-Alkyl derivatives of indole may be obtained not only by direct alkylation but also by conjugate addition to Michael acceptors. We also studied the feasibility of using phenylsulfonylindoles **1a** and **1b** as substrates in such reactions.

The reactions of sulfones **1a** and **1b** with ethyl ether and acrylonitrile gave the corresponding N-alkylation products but the yields in the case of 2-phenylsulfonylindole **1a** were markedly lower (Table 2). The moderate reactivity of the anion of sulfone **1a** in direct alkylation reactions and conjugate addition is related to steric hindrance due to the phenylsulfonyl group near the nucleophilic site.

Another possible variant for the preparation of N-alkylated indole derivatives is based on the use of the Mitsunobu reaction [24]. When using the standard oxidation-reduction system containing diethyl azodicarboxylate and Ph_3P, indole derivatives containing electron-withdrawing groups such as C≡N [25], COR [26], CO_2R [26], and SO_2Ph [27] in the pyrrole fragment usually serve as the substrate. Bombur and Casi [28] have also reported the feasibility of alkylating 5-bromoindole under conditions of the Mitsunobu reaction by primary and secondary alcohols using cyanomethylenetrimethylphosphorane (CMMP) but the use of this oxidation-reduction system involves a number of experimental difficulties. We studied the possibility of N-alkylation of model indolyl sulfones **1a** and **1b** by primary and secondary alcohols using conditions of the

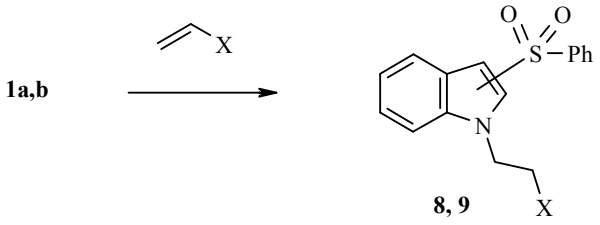


TABLE 2. N-Alkylation of Phenylsulfonylindoles **1a** and **1b** under Conjugate Addition Conditions

Substrate	X	Temperature, °C*	Reaction time, h	Alkylation products	Yield, %
1a	CN	25	8	**8a**	65
1b	CN	25	8	**8b**	82
	CO_2Me	25	12	**9b**	80
		69	10		92

* Reaction conditions: Triton B (8 mol%), CH_2=CHX (2.5 equiv.), THF.

Mitsunobu reaction and a standard oxidation-reduction system containing diisopropyl azodicarboxylate (DIAD) and Ph_3P (Table 3). Under these conditions, we discovered inverse reactivity of indolyl sulfones **1a** and **1b**. Indol-2-yl phenyl sulfone (**1a**) is readily alkylated both by primary and secondary alcohols. We should note that the alkylation of sulfone **1a** by 1-phenyl-2-butanol is accompanied by the formation of 18% 1-phenylbut-1-ene, which is the product of dehydration of the alcohol. On the other hand, the reaction of sulfone **1b** with 1-hexanol, a primary alcohol, gave the alkylation product in only 30% yield, while secondary alcohols proved unreactive relative to this substrate with yields of the alkylation products not exceeding 10%. The use of the oxidation-reduction system containing azodicarboxylic acid dipiperidide (ADDP) and tributylphosphine [29], which is usually more efficient for substrates with low NH-acidity, did not improve the yield. Such a significant difference in the behavior of isomeric indolyl sulfones in the Mitsunobu reaction is related, in our opinion, to the higher NH-acidity of indol-2-yl sulfone **1a** than for indol-3-yl sulfone **1b**.

An important feature of the Mitsunobu reaction is its stereospecificity [24]. This reaction proceeds with inversion of the configuration of the chiral alcohol used. This behavior makes the Mitsunobu reaction a reliable method for the preparation of nonracemic compounds using optically active secondary alcohols. Thus, we obtained the ethyl ester of (*R*)-1-(2-phenylsulfonylindol-1-yl)propionic acid as a pure enantiomer upon the alkylation of substrate **1a** by the ethyl ester of (*S*)-lactic acid.

In order to carry out the reductive desulfonylation of the resultant N-alkylated indolyl sulfones, we studied the feasibility of using various reducing systems. One such system containing magnesium and methanol, commonly used for this conversion [30, 31], proved unsuitable for the present problem. No significant

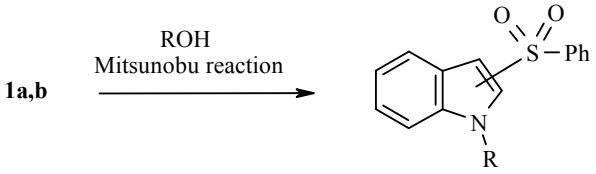


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TABLE 3. N-Alkylation of Phenylsulfonylindoles **1a** and **1b** under Conditions of the Mitsunobu Reaction

Substrate	ROH	Alkylation product	Conditions*	Yield, %*[2]
1a	$PhOCH_2CH_2OH$	**10a**	A	55
	n-$C_6H_{13}OH$	**11a**	A	90
	$Ph(CH_3)CHOH$	**12a**	A	68
	$PhCH_2CH(CH_2Me)OH$	**13a**	A	70*[3]
	(*R*,*S*)-$HOCH(Me)CO_2Et$	(*R*,*S*)-**14a**	A	68
	(*S*)-$HOCH(Me)CO_2Et$	(*R*)-**14a**	A	68
1b	*n*-$C_6H_{13}OH$	**11b**	A	25
			B	30
	$Ph(CH_3)CHOH$	**12b**	A	(<10)
			B	
	$PhCH_2(CH_2Me)CHOH$	**13b**	B	(<10)
	(*S*)-$HOCH(Me)CO_2Et$	(*R*)-**14b**	B	(<10)

* A: DIAD (1.5 eq.), Ph_3P (1.5 eq.), THF, 25°C, 24 h; B: ADDP (1.5 eq.), Bu_3P (1.5 eq.), THF, 48°C, 24 h.

*[2] The yields determined by GC/MS are given in parentheses. The yields of the isolated products in all the other cases are given without parentheses.

*[3] $PhCH{=}CHCH_2Me$ was also isolated in 18% yield.

conversion of the starting sulfones was noted even when using a large excess of magnesium (20 mol Mg per mol sulfone), carrying out the reaction at reflux, using ultrasonic radiation, replacing methanol by ethanol, and adding Hg^{2+} salts to the reaction mixture [19]. N-Alkylindole sulfones proved stable to the action of a commercial sample of Raney nickel [32]. On the other hand, the use of 3.5 g fresh-prepared Raney nickel catalyst per mmole substrate gave the reductive desulfonylation of N-alkylindole sulfones and the corresponding N-substituted indoles in high yield (Table 4) in virtually all cases. The reaction was carried out in ethanol or THF (depending on the solubility of the substrate) at reflux. The substrates with cyano (**6b, 8a, 8b**) and phthalimide groups (**5b)** undergo extensive reduction involving these groups.

Table 4 gives the yields of the N-alkylindoles calculated over the two steps involving N-alkylation of the sulfones and the subsequent reductive desulfonylation of these intermediates. Earlier studies on the synthesis of optically active β-amino acids using reductive desulfonylation by Raney nickel in one of the steps showed the lack of racemization of the chiral site on the nitrogen atom [33, 34]. Determination of the enantiomeric purity of the resultant indole **24** (>98% *ee*) using HPLC with a chiral stationary phase confirmed the lack of racemization during reductive desulfonylation.

This procedure for the preparation of 1-alkylindoles based on the N-alkylation of indolyl phenyl sulfones and subsequent reductive desulfonylation may be used for the synthesis of some 1-alkylindoles, which have previously been difficult to obtain, such as indole derivatives containing a chiral substituent at the nitrogen atom. Indeed, this simple and reliable procedure augments other methods for the synthesis of such compounds developed in our laboratory [25, 35, 36].

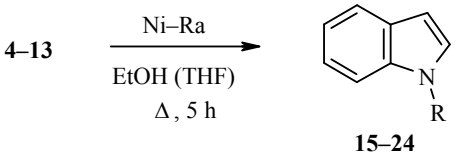

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TABLE 4. Reductive Desulfonylation of N-Alkyl-2- and N-Alkyl-3-phenylsulfonylindoles

Substrate	Reaction product	R	Solvent	Yield, %	Yield over two steps, %
4b	**15**	Me_2CH	EtOH	92	86
5b	**16**	$Phth(CH_2)_3$	THF	89*	68
6b	**17**	$NCCH_2$	THF	86*[2]	72
7b	**18**	$PhOCH_2CH_2$	EtOH	88	63
8a	**19**	$NCCH_2CH_2$	THF	93*[2]	71
8b	**19**	$NCCH_2CH_2$	THF	90*[2]	74
9b	**20**	$MeO_2CCH_2CH_2$	THF	84	77
10a	**18**	$PhOCH_2CH_2$	EtOH	85	26
11a	**21**	*n*-C_6H_{13}	EtOH	96	86
11b	**21**	*n*-C_6H_{13}	EtOH	93	28
12a	**22**	PhCHMe	EtOH	77	69
13a	**23**	$PhCH_2CHEt$	EtOH	81	57
(*R*,*S*)-**14a**	(*R*,*S*)-**24**	(*R*,*S*)-$MeCHCO_2Et$	EtOH	74	50
(*R*)-**14a**	(*R*)-**24**	(*R*)-$MeCHCO_2Et$	EtOH	74	49

* Yield of hexahydrophthalimide derivative.

*[2] Yield of the product of reduction of the nitrile group.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer for neat liquid compounds and for suspensions of solid compounds in vaseline. The ^{1}H and ^{13}C NMR spectra were taken on a Bruker AMX-400 spectrometer at 400 and 100 MHz, respectively, in DMSO-d_6. The chemical shifts are given relative to the residual signals of the solvent at 2.49 ppm. Chromato-mass-spectroscopic investigations were carried out using a gas chromatograph Carto Erba/Kratos Series (Ultra-1 column, 25 m, 0.25 mm HP), mass spectral detector ITD-700 (Finnigan MAT). The electron impact ionization voltage was 70 eV. The specific rotation values were measured on a Jasco DIP-360 polarimeter. The elemental analysis was carried out on a Carlo Erba EA1108 CHNS-O automatic CHN-microanalyzer. The reaction course was monitored by thin-layer chromatography on Sorbfil-UV plates using 6:1 hexane–ethyl acetate as the eluent and UV light for development. The chromatographic separation of the reaction mixtures was carried out by flash chromatography on a column packed with 0.040-0.063-mm Merck silica gel with elution by 10:1 hexane–ethyl acetate. The melting points were determined in open capillaries without correction. All the commercial reagents were used without prior purification.

Indol-2-yl Phenyl Sulfide (2a) [20] and **Indol-3-yl Phenyl Sulfide (2b)** [21] were prepared according to previously described by Hamel et al.

Indol-2-yl Phenyl Sulfone (1a). Aqueous OXONE® (40 ml 49.5%) was added dropwise to a solution of sulfide **2a** (2.24 g, 10 mmol) in methanol (40 ml) with stirring and cooling to 0°C. The suspension obtained was stirred at room temperature for 8 h, then, poured into ice water (50 ml) and the reaction mixture was extracted with four 75-ml portions of ethyl acetate. The combined extracts were washed with saturated aq. NaCl and dried over Na_2SO_4. The solvent was removed in vacuum. The residue was recrystallized from ethyl acetate to give 2.42 g (94%) **1a**; mp 149-152°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.13 (1H, t, *J* = 7.5, H-5); 7.23 (1H, s, H-3); 7.31 (1H, t, *J* = 8.3, H-6); 7.45 (1H, d, *J* = 8.1, H-7); 7.61-7.73 (4H, m, H-4, *m*-, *p*-H{$C_6H_5SO_2$}); 8.02 (2H, d, *J* = 7.4, *o*-H{$C_6H_5SO_2$}); 12.41 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 116.2, 120.2, 122.0, 123.6, 127.9, 128.8, 132.2 (2C), 129.9, 133.1 (2C), 135.4, 144.1, 147.2. Mass spectrum, *m/z* (I_{rel}, %): 257 $[M]^+$ (75), 193 (15), 132 (100), 104 (19), 89 (31), 77 (25). Found, %: C 65.49; H 4.28; N 5.50. $C_{14}H_{11}NO_2S$. Calculated, %: C 65.35; H 4.31; N 5.44.

Indol-3-yl Phenyl Sulfone (1b) was obtained in 87% yield by the oxidation of sulfide **2b** by 3-chloroperbenzoic acid analogously to the procedure of Broggini [22], mp 147-149°C (ethanol) (mp 147°C (pentane–benzene) [22]). The ^{1}H NMR spectral data for this compound were identical to the results given by Broggini [22].

Alkylation of Sulfones 1a and 1b by Alkyl Halides and Sulfonates (General Method). A. K_2CO_3 (0.552 g, 4 mmol) was added to a solution of sulfone **1a** or **1b** (0.51 g, 2 mmol) in dry acetone (10 ml) and stirred for 30 min at 25°C. Then, alkylating agent (4 mmol) was added and the mixture was stirred at reflux (here and hereafter, the reaction time is indicated in Table 1) and cooled. The precipitate was filtered off and washed with 60 ml ethyl acetate. The combined organic extracts were washed with two 50-ml water portions and dried over Na_2SO_4. The solvent was removed in vacuum.

B. Suspension of NaH (60%, 88 mg, 2.2 mmol) in mineral oil was added in portions to a solution of sulfone **1a** or **1b** (0.51 g, 2 mmol) in dry DMF (15 ml) and stirred for 30 min at 25°C. Then, alkylating agent (2.6 mmol) was added and stirred at room temperature. The solvent was removed in vacuum. The precipitate was dissolved in ethyl acetate (50 ml), washed with two 50-ml water portions, and dried over Na_2SO_4. The solvent was removed in vacuum.

C. K_2CO_3 (0.552 g, 4 mmol) was added to a solution of sulfone **1a** or **1b** (0.51 g, 2 mmol) in dry DMF (15 ml) and stirred for 30 min at 25°C. Then, alkylating agent (4 mmol) was added and stirred at 60°C. After cooling, the solvent was removed in vacuum. The precipitate was dissolved in ethyl acetate (50 ml), washed with two 50-ml water portions, and dried over Na_2SO_4. The solvent was removed in vacuum.

D. Analogously to procedure B, the reaction mixture was stirred at 60°C.

E. A solution of sulfone **1a** or **1b** (0.51 g, 2 mmol) in DMF (5 ml) was added with stirring to a solution of diazabicycloundecene (0.32 g, 2.2 mmol) or diisopropylethylamine (0.19 g, 2 mmol) in DMF (10 ml) and stirred at room temperature for 1 h. Then, a solution of alkylating agent (2.2 mmol) in DMF (10 ml) was added dropwise. Stirring was continued at room temperature. The mixture was then poured into ice water (50 ml). The precipitate formed was filtered off, washed several times with ice water, and recrystallized from ethanol.

F. *t*-BuOK (0.49 g, 4.3 mmol) and alkylating agent (4.29 mmol) in DMF (5 ml) were added in portions to a solution of sulfone **1a** or **1b** (1 g, 3.9 mmol) in DMF (25 ml) and stirred at 25°C. The solvent was removed in vacuum. The residue was treated with 100 ml ice water. The precipitate formed was filtered off, washed with water, and recrystallized from ethanol.

1-Isopropyl-3-phenylsulfonylindole (4b), mp 148-151°C (ethanol). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.50 (6H, d, *J* = 6.0, CH_3); 4.84 (1H, sept, *J* = 6.0, CH); 7.17-7.35 (2H, m); 7.52-7.63 (3H, m); 7.69 (1H, d, *J* = 7.8, H-4); 7.99 (1H, d, *J* = 7.0, H-7); 8.35 (1H, s, H-2). Mass spectrum, *m/z* (I_{rel}, %): 299 $[M]^+$ (100), 284 $[M^+ - CH_3]$ (68), 257 $[M^+ - CH_3CH{=}CH_2]$ (13), 193 (17), 143 (20), 132 (32), 116 (16), 77 (20). Found, %: C 68.25; H 5.71; N 4.71. $C_{17}H_{17}NO_2S$. Calculated, %: C 68.20; H 5.72; N 4.68.

3-Phenylsulfonyl-1-(3-phthalimidopropyl)indole (5b), mp 200-202°C (ethanol). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.13 (2H, m, CH_2); 3.63 (2H, m, CH_2); 4.35 (2H, m, CH_2); 7.27 (2H, m); 7.59 (3H, m); 7.68 (1H, d, *J* = 7.9, H-4); 7.77 (1H, d, *J* = 7.9, H-7); 7.81-7.91 (4H, m); 7.97 (2H, d, *J* = 6.6, Phth); 8.36 (1H, s, H-2). Mass spectrum, *m/z* (I_{rel}, %): 444 $[M]^+$ (100), 284 (12), 270 (29), 160 (39), 143 (76), 130 (76), 77 (32). Found, %: C 67.57; H 4.49; N 6.34. $C_{25}H_{20}N_2O_4S$. Calculated, %: C 67.55; H 4.54; N 6.30.

1-Cyanomethyl-3-phenylsulfonylindole (6b), mp 148-151°C (ethanol). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 5.63 (2H, s, CH_2); 7.29-7.45 (2H, m); 7.54-7.66 (2H, m); 7.72 (1H, d, *J* = 8.4, H-4); 7.84 (1H, t, *J* = 7.8, H-6); 7.98 (2H, d, *J* = 8.1, *o*-$C_6H_5SO_2$); 8.00 (1H, d, *J* = 6.8, H-7); 8.34 (1H, s, H-2). Mass spectrum, *m/z* (I_{rel}, %): 296 $[M]^+$ (100), 257 $[M^+ - CHCN]$ (6), 203 (17), 192 (32), 171 (61), 103 (13), 77 (20). Found, %: C 64.87; H 4.04; N 9.43. $C_{16}H_{12}N_2O_2S$. Calculated, %: C 64.85; H 4.08; N 9.45.

1-Phenyloxyethyl-3-phenylsulfonylindole (7b), mp 164-166°C (ethanol). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.32 (2H, t, *J* = 5.0); 4.69 (2H, t, *J* = 5.0); 6.83 (2H, d, *J* = 7.8, *o*-C_6H_5O); 6.91 (1H, t, *J* = 7.8, *p*-C_6H_5O); 7.20-7.35 (4H, m); 7.51-7.63 (3H, m); 7.70-7.82 (2H, m); 7.96 (2H, d, *J* = *o*-$C_6H_5SO_2$); 8.31 (1H, s, H-2). Mass spectrum, *m/z*, (I_{rel}, %): 377 $[M]^+$ (90), 284 $[M^+ - OPh]$ (9), 270 $[M^+ - CH_2OPh]$ (100), 236 (15), 206 (13), 143 (47), 129 (23), 77 (65). Found, %: C 69.99; H 5.04; N 3.73. $C_{22}H_{19}NO_3S$. Calculated, %: C 70.00; H 5.07; N 3.71.

Alkylation of Sulfones 1a and 1b Under Conjugate Addition Reaction Conditions (General Method). Two drops of Triton B® (40% in methanol) were added to a solution of sulfone **1a** or **1b** (0.51 g, 2 mmol) in dry THF (20 ml). Then, a solution of methyl acrylate (or acrylonitrile) (5 mmol) in THF (5 ml) was added dropwise with stirring. The solution was stirred at either 25 or 69°C (reaction time indicated in Table 2). Then, 10 ml 10% aq. acetic acid was added and the product was concentrated in vacuum. The residue was treated with water. The liquid was decanted and the product was recrystallized from ethanol.

1-(2-Cyanoethyl)-3-phenylsulfonylindole (8a), mp 146-148°C (ethanol). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.86 (2H, t, *J* = 6.7, CH_2); 4.66 (2H, t, *J* = 6.9, CH_2); 7.22 (1H, t, *J* = 7.3, H-5); 7.42 (1H, t, *J* = 7.8, H-6); 7.46 (1H, s, H-3); 7.67 (2H, t, *J* = 7.7, *m*-$C_6H_5SO_2$); 7.72-7.89 (3H, m); 8.01 (2H, t, *J* = 7.2, *o*-$C_6H_5SO_2$). Mass spectrum, *m/z* (I_{rel}, %): 310 $[M]^+$ (100), 270 $[M^+ - CO_2CN]$ (62), 222 (32), 204 (38), 178 (20), 91 (51), 77 (26). Found, %: C 65.77; H 4.54; N 8.98. $C_{17}H_{14}N_2O_2S$. Calculated, %: C 65.79; H 4.55; N 9.03.

1-(2-Cyanoethyl)-3-phenylsulfonylindole (8b), mp 179-181°C (ethanol). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.14 (2H, t, *J* = 6.7, CH_2); 4.62 (2H, t, *J* = 6.7, CH_2); 7.29 (2H, m); 7.53-7.65 (3H, m); 7.72-7.82 (2H, m); 7.97 (2H, d, *J* = 6.7, *o*-$C_6H_5SO_2$); 8.38 (1H, s, H-2). Mass spectrum, *m/z* (I_{rel}, %): 310 $[M]^+$ (84), 270 $[M^+ - CO_2CN]$ (100), 206 (14), 185 (10), 129 $[M^+ - SO_2Ph - CH_2CN]$ (16), 77 [Ph] (23). Found, %: C 65.84; H 4.49; N 9.05. $C_{17}H_{14}N_2O_3S$. Calculated, %: C 65.81; H 4.52; N 9.01.

Methyl Ester of 3-(3-Phenylsulfonylindol-1-yl)propionic Acid (9b), mp 159-161°C (ethanol). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.93 (2H, t, *J* = 7.7, CH_2); 3.55 (3H, s, CH_3); 4.56 (2H, t, *J* = 7.7, CH_2); 7.19-7.34 (2H, m); 7.53-7.63 (2H, m); 7.66 (1H, d, *J* = 8.5, H-4); 7.77 (1H, d, *J* = 7.8, H-7); 7.96 (2H, d, *J* = 7.4, *o*-$C_6H_5SO_2$); 8.25 (1H, s, H-2). Mass spectrum, *m/z* (I_{rel}, %): 343 $[M]^+$ (100), 270 [M^+ - CO_2Me] (66), 206 (20), 143 (13), 128 (12), 77 (19). Found, %: C 63.00; H 4.90; N 4.06. $C_{18}H_{17}NO_4S$. Calculated, %: C 62.96; H 4.99; N 4.08.

Alkylation of Sulfones 1a and 1b Under Conditions of the Mitsunobu Reaction (General Method). Triphenylphosphine (0.76 g, 3 mmol) and ethanol (3 mmol) were added consecutively in an argon atmosphere to a solution of sulfone **1a** or **1b** (0.51 g, 2 mmol) in dry THF (50 ml). Then, a solution of diisopropyl ester of azodicarboxylic acid (0.6 g, 3 mmol) in THF (20 ml) was added dropwise with stirring and cooling to 0°C and stirred for 24 h at 25°C. The solvent was removed in vacuum and the residue was subjected to chromatography.

1-(2-Phenyloxyethyl)-2-phenylsulfonylindole (10a), mp 155-157°C (ethanol). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.02 (2H, t, *J* = 5.2, CH_2); 4.75 (2H, t, *J* = 5.4, CH_2); 6.64 (2H, d, *J* = 7.8, *o*-C_6H_5O); 6.88 (1H, t, *J* = 7.4, *m*-C_6H_5O); 7.19 (1H, t, *J* = 7.5, H-5); 7.34-7.50 (2H, m); 7.61-7.78 (7H, m); 8.00 (2H, d, *J* = 7.8, *o*-$C_6H_5SO_2$). Mass spectrum, *m/z* (I_{rel}, %): 377 $[M]^+$ (81), 284 [M^+ - OPh] (79), [270 [M^+ - CH_2OPh] (67), 236 (47), 204 (43), 143 (100), 91 (52), 77 (8). Found, %: C 69.99; H 5.09; N 3.69. $C_{22}H_{19}NO_3S$. Calculated, %: C 70.00; H 5.07; N 3.71.

1-Hexyl-2-phenylsulfonylindole (11a), mp 58-60°C (hexane). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.81 (3H, t, *J* = 6.9, CH_3); 1.34-1.38 (8H, m, $(CH_2)_4$); 4.28 (2H, t, *J* = 7.4, CH_2); 7.18 (1H, t, *J* = 7.5, H-5); 7.37 (1H, t, *J* = 7.8, H-6); 7.42 (1H, s, H-3); 7.56 (2H, d, *J* = 8.6, *o*-$C_6H_5SO_2$); 7.66-7.96 (5H, m). Mass spectrum, *m/z* (I_{rel}, %): 341 $[M]^+$ (30), 270 (13), 200 [M^+ - SO_2Ph] (100), 130 (48), 91 (20), 77 (13). Found, %: C 70.40; H 6.71; N 4.14. $C_{20}H_{21}NO_2S$. Calculated, %: C 70.35; H 6.79; N 4.10.

1-Hexyl-3-phenylsulfonylindole (11b), mp 72-74°C (hexane). IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.80 (3H, t, *J* = 5.7, CH_3); 1.21-1.79 (8H, m, $(CH_2)_4$); 4.26 (2H, t, *J* = 6.8, CH_2); 7.20-7.32 (4H, m); 7.52-7.65 (4H, m); 7.89 (1H, d, *J* = 7.8, H-4); 8.30 (1H, s, H-2). Mass spectrum, *m/z* (I_{rel}, %): 341 $[M]^+$ (100), 270 (25), 200 (19), 130 (50), 77 (31). Found, %: C 0.36; H 6.76; N 4.16. $C_{20}H_{23}NO_2S$. Calculated, %: C 70.35; H 6.79; N 4.10.

1-(1-Phenylet-2-yl)-2-phenylsulfonyl)indole (12a), amorphous compound. IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.57 (3H, d, *J* = 7.1, CH_3); 6.17 (1H, q, *J* = 7.1, CH); 6.88-7.01 (2H, m); 7.06-7.11 (2H, m); 7.19-7.27 (3H, m); 7.51 (1H, s, H-3); 7.64 (2H, t, *J* = 7.8, $C_6H_5SO_2$); 7.71-7.79 (3H, m); 8.01 (2H, d, *J* = 8.1, $C_6H_5SO_2$). Mass spectrum, *m/z* (I_{rel}, %): 361 $[M]^+$ (21), 257 [M^+ - $PhCH{=}CH_2$] (90), 219 (23), 132 (45), 105 ($PhCH{=}CH_2$] (100), 77 (23). Found, %: C 73.10; H 5.26; N 3.90. $C_{22}H_{19}NO_2S$. Calculated, %: C 73.10; H 5.30; N 3.88.

1-(1-Phenylbut-2-yl)-3-phenylsulfonylindole (13a) was obtained as an amorphous compound. IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.10 (3H, t, *J* = 7.4, CH_3); 1.56 (1H, m); 2.11 (1H, m); 2.95 (1H, m); 3.25 (1H, m); 4.85 (1H, m); 7.06 (2H, d, *J* = 6.8, *o*-C_6H_5); 7.15-7.27 (4H, m); 7.38 (1H, t, *J* = 7.8, H-5); 7.43 (1H, s, H-2); 7.62-7.68 (2H, m); 7.74 (1H, m); 7.81 (1H, d, *J* = 7.8, H-7); 7.86-7.95 (3H, m). Mass spectrum, *m/z* (I_{rel}, %): 389 $[M]^+$ (15), 298 [M^+ - $PhCH_2$] (85), 157 [M^+ - $PhCH_2$ – SO_2Ph] (100), 92 (32), 77 (8). Found, %: C 74.00; H 5.88; N 3.59. $C_{24}H_{23}NO_2S$. Calculated, %: C 74.00; H 5.95; N 3.60.

Ethyl Ester of (*R,S*)-2-(3-Phenylsulfonylindol-1-yl)propionic Acid ((*R,S*)-14a)) was obtained as an amorphous compound. IR spectrum, ν, cm^{-1}: 1100-1300 (SO_2), 1740 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.9 (3H, t, *J* = 7.1, $CH_2C\underline{H}_3$); 1.48 (3H, d, *J* = $CHC\underline{H}_3$); 3.93-3.99 (2H, m, OCH_2); 5.65 (1H, m, CH); 7.20 (1H, t, *J* = 7.8, H-5); 7.27 (1H, d, *J* = 7.7, H-4); 7.36 (1H, t, *J* = 7.5, H-6); 7.50 (1H, s, H-3); 7.64 (2H, t, *J* = 7.1, *m*-$C_6H_5SO_4$); 7.73 (3H, m); 7.79 (1H, d, *J* = 7.8, H-7). Mass spectrum, *m/z* (I_{rel}, %): 357 $[M]^+$ (30), 284 (M^+ - CO_2Et] (84), 216 (12), 143 [M^+ - SO_2Ph^+ - CO_2Et] (100), 115 [M^+ - SO_2Ph^+ - $MeCHCO_2Et$] (12), 77 (12). Found, %: C 63.89; H 5.29; N 3.89. $C_{19}H_{19}NO_4S$. Calculated, %: C 63.85; H 5.36; N 3.92.

Ethyl Ester of (*R*)-2-(3-Phenylsulfonylindol-1-yl)propionic Acid ((*R*)-14a) was obtained as an amorphous compound from the ethyl ester of (*S*)-lactic acid, $[\alpha]_D^{25}$ -17° (neat), >98% *ee*. $[\alpha]_D^{25}$ -2.5° (*c* = 1.2, ethanol). Found, %: C 63.91; H 5.33; N 3.94. $C_{19}H_{19}NO_4S$. Calculated, %: 63.85; H 5.36; N 3.92.

Reductive Desulfonylation of N-Alkyl-2- and N-Alkyl-3-phenylsulfonylindoles (General Method). Fresh-prepared raney nickel [37] (3.5 g) was added to a solution of N-alkyl-2- or N-alkyl-3-phenyl-sulfonylindole (1 mmol) in ethanol or THF (25 ml) (see Table 4). The resultant mixture was stirred at reflux until the starting sulfone was completely consumed. The catalyst was filtered off and the solvent was removed in vacuum. The residue was dissolved in 20 ml ethyl acetate, washed with two 30-ml water portions, dried over Na_2SO_4, concentrated, and subjected to chromatography.

1-Isopropylindole (15) was obtained in 92% yield (0.146 g) as a light-yellow viscous liquid. The ^{1}H NMR spectral parameters of this product were in accord with the data of Botta [38].

2-[3-(1H-Indol-1-yl)propyl]hexahydro-1H-isoindole-1,3(2H)-dione (16) was obtained in 89% yield (0.27 g) as an amorphous compound. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.25-1.43 (4H, m); 1.50-1.79 (4H, m); 1.87-1.91 (2H, m); 2.87-2.94 (2H, m); 3.66-3.42 (2H, m); 4.15-4.12 (2H, m); 6.43 (1H, d, *J* = 3.1, H-3); 7.04 (1H, t, *J* = 8.4, H-5); 7.12 (1H, t, *J* = 8.4, H-6); 7.40 (1H, d, *J* = 3.1, H-2); 7.44 (1H, d, *J* = 8.1, H-7); 7.54 (1H, d, *J* = 7.8, H-4). Mass spectrum, *m/z* (I_{rel}, %): 310 $[M]^+$ (76), 194 (15), 157 $[M^+ - RH]$ (17), 144 $[M^+ - RCH_2]$ (22), 130 $[M^+ - RCH_2CH_2]$ (100), 117 $[M^+ - RCH_2CH_2CH_2]$ (15), 103 $[R=N(CO_2)_2C_6H_{10}]$ (6). Found, %: C 73.58; H 7.09; N 9.01. $C_{19}H_{22}N_2O_2$. Calculated, %: C 73.52; H 7.14; N 9.03.

1-(2-Aminoethyl)indole (17) was obtained in 86% yield (0.140 g) as a light-yellow viscous liquid. The ^{1}H NMR spectral parameters of this product were in accord with the data of Cuardo [39].

1-(2-Phenyloxylethyl)indole (18) was obtained in 88% yield (0.21 g) as a colorless viscous liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.29 (2H, t, *J* = 5.3, CH_2); 4.58 (2H, t, *J* = 5.3, CH_2); 6.86-6.95 (4H, m); 7.03 (1H, t, *J* = 7.5, H-5); 7.12-7.18 (2H, m); 7.43 (1H, d, *J* = 3.2, H-2); 7.55 (2H, t, *J* = 7.7, *m*-C_6H_5O); 7.60 (1H, t, *J* = 7.6, H-6). Mass spectrum, *m/z* (I_{rel}, %): 237 $[M]^+$ (47), 144 $[M^+ - PhO]$ (10), 130 $[M^+ - CH_2OPh]$ (100), 103 (8), 89 (9), 77 (15). Found, %: C 81.01; H 6.33; N 5.91. $C_{16}H_{15}NO$. Calculated, %: C 80.98; H 6.37; N 5.90.

1-(3-Aminopropyl)indole (19) was obtained in 93% yield (0.25 g) as a colorless viscous liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.14 (2H, t, *J* = 7.1, CH_2); 1.99-2.15 (2H, m, CH_2); 4.28 (2H, t, *J* = 6.8, CH_2); 6.45 (1H, m, H-3); 7.03 (1H, t, *J* = 7.2, H-5); 7.13 (1H, m, H-4); 7.39 (1H, d, *J* = 2.8, H-2); 7.47-7.58 (2H, m, H-6, H-7). Mass spectrum, *m/z* (I_{rel}, %): 172 $[M^+ - H_2]$ (2), 158 $[M^+ - NH_2]$ (3), 131 (100), 117 (15), 58 (23), 44 (17). Found, %: C 75.85; H 8.13; N 16.11. $C_{11}H_{14}N_2$. Calculated, %: C 75.82; H 8.10; N 16.08.

Methyl Ester of 3-(Indol-1-yl)propionic Acid (20) was obtained in 86% yield (0.17 g) as a light-yellow viscous liquid. The ^{1}H NMR spectral parameters of this product were in accord with the data of Bennasar [40].

1-Hexylindole (21) was obtained in 96% yield (0.20 g) as a light-yellow viscous liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.85-1.24 (9H, m); 1.74 (2H, m); 4.13 (2H, m); 6.41 (1H, d, *J* = 2.8, H-3); 7.00 (1H, t, *J* = 7.8, H-5); 7.11 (1H, t, *J* = 7.2, H-6); 7.35 (1H, d, *J* = 3.2, H-2); 7.45 (1H, d, *J* = 7.1, H-7); 7.53 (1H, d, *J* = 7.15, H-4). Mass spectrum, *m/z* (I_{rel}, %): 201 $[M]^+$ (38), 130 $[M^+ - C_5H_{11}]$ (100), 117 $[M^+ - C_6H_{12}]$ (10). Found, %: C 83.57; H 9.48; N 6.91. $C_{14}H_{19}N$. Calculated, %: C 83.53; H 9.51; N 6.96.

1-(1-Phenylethyl)indole (22) was obtained in 77% yield (0.17 g) as a light-yellow viscous liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.95 (3H, d, *J* = 7.1, CH_3); 5.70 (1H, q, *J* = 7.1, CH); 6.59 (1H, d, *J* = 3.2, H-3); 7.08-7.18 (4H, m); 7.22-7.34 (5H, m); 7.66 (1H, d, *J* =7.1, H-7). Mass spectrum, *m/z* (I_{rel}, %): 221 $[M]^+$ (79), 117 $[M^+ - PhCH{=}CH_2]$ (100), 105 $[CH_2{=}CHPh]$ (96), 89 (35). Found, %: C 86.80; H 6.88; N 6.35. $C_{16}H_{15}N$. Calculated, %: C 86.84; H 6.83; N 6.33.

1-(1-Phenylbut-2-yl)indole (23) was obtained in 81% yield (0.20 g) as a light-yellow viscous liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.79 (3H, t, *J* = 7.1, CH_3); 1.97 (2H, m); 3.16 (2H, m); 4.45 (1H, m, CH); 6.53 (1H, d, *J* = 3.2, H-3); 7.00 (2H, d, *J* = 6.3, H-7); 7.06-7.35 (7H, m); 7.63 (1H, d, *J* = 7.8, H-4). Mass

spectrum, *m/z* (I_{rel}, %): 249 $[M]^+$ (12), 158 $[M^+ - PhCH_2]$ (100), 117 $[M^+ - MeCH_2CH\text{-}CHPh]$ (17), 91 $[PhCH_2]$ (12). Found, %: C 86.71; H 7.57; N 5.68. $C_{18}H_{19}N$. Calculated, %: C 86.75; H 7.63; N 5.62.

Ethyl Ester of (*R,S*)-2-(Indol-2-yl)propionic Acid ((*R,S*)-24) was obtained in 74% yield (0.16 g). IR spectrum, ν, cm^{-1}: 1740 (CO). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, t, *J* = 7.7, $OCH_2C\underline{H}_3$); 1.73 (3H, d, *J* = 7.9, $CHC\underline{H}_3$); 4.12 (2H, m, $OC\underline{H}_2CH_3$); 5.76 (1H, m, $C\underline{H}CH_3$); 6.49 (1H, d, *J* = 3.1, H-3); 7.08 (2H, m); 7.42 (2H, m); 7.55 (1H, d, *J* = 7.8, H-4). Mass spectrum, *m/z* (I_{rel}, %): 217 $[M]^+$ (18), 144 $[M^+ - CO_2Et]$ (100), 117 (10), 89 (10), 43 (58). Found, %: C 71.93: H 6.88; N 6.48. $C_{13}H_{15}NO_2$. Calculated, %: C 71.87; H 6.96; N 6.45.

Ethyl Ester of (*R*)-2-(Indol-1-yl)propionic Acid ((*R*)-24) was obtained in 74% yield (0.16 g) as a light-yellow, viscous liquid, $[\alpha]_D^{25}$ -13.5° (ethanol, 3.2). Found, %: C 71.91; H 6.93; N 6.42. $C_{13}H_{15}NO_2$. Calculated, %: C 71.87; H 6.96; N 6.45.

REFERENCES

1. D. A. Horton, G. T. Bourne, and M. L. Smythe, *Chem. Rev.*, **103**, 893 (2003).
2. R. J. Sundberg, *Indoles*, Academic Press, San Diego (1996).
3. G. R. Humphrey and J. T. Kuethe, *Chem. Rev.*, **106**, 2875 (2006).
4. K. Sukata, *Bull. Chem. Soc. Jpn.*, **56**, 280 (1983).
5. W. C. Guda and D. J. Mathre, *J. Org. Chem.*, **45**, 3172 (1980).
6. M. G. Reinecke, J. F. Sebastian, H. W. Jonson, Jr., and C. Pyun, *J. Org. Chem.*, **37**, 3066 (1972).
7. B. Cardillo, G. Casnati, A. Pochini, and A. Ricca, *Tetrahedron*, **23**, 3771 (1967).
8. G. M. Rubottom and J. C. Chabala, *Synthesis*, 566 (1972).
9. E. Santaniello, C. Farach, and F. Pointi, *Synthesis,* 617 (1979).
10. A. Barco, S. Benetti, and G. P. Pollini, *Synthesis*, 124 (1976).
11. V. Bocchi, G. Casnati, and A. Dossena, *Synthesis*, 414 (1976).
12. Y. R. Jorapur, J. M. Jeong, and D. Y. Chi, *Tetrahedron Lett.*, **47**, 2435 (2006).
13. G. Vavilina, A. Zicmanis, S. Drozdova, P. Mekss, and M. Klavins, *Khim. Geterotsikl. Soedin.*, 676 (2008). [*Chem. Heterocycl. Comp.*, **44**, 530 (2008)].
14. H. Normant and T. Cuvigny, *Bull. Soc. Chim. Fr.*, 1866 (1965).
15. D. M. Fink, *Synlett*, 2396 (2004).
16. S. Hayat, Atta-ur-Rathman, M. I. Choudhary, K. M. Khan, W. Schumann, and E. Bayer, *Tetrahedron*, **50**, 9951 (2001).
17. T. Kunieda and B. Witkop, *J. Org. Chem.*, **35**, 3981 (1970).
18. D. Bogdal, J. Pielichowski, and K. Jaskot, *Heterocycles*, **45**, 715 (1991).
19. C. Najera and M. Yus, *Tetrahedron*, **55**, 10547 (1999).
20. P. Hamel, Y. Girard, and J. Atkinson, *J. Org. Chem.*, **57**, 2695 (1992).
21. J. Atkinson, P. Hamel, and Y. Girard, *Synth. Commun.*, 480 (1988).
22. G. Broggini, D. Diliddo, and G. Zecchi, *J. Heterocycl. Chem.*, **28**, 89 (1991).
23. B. M. Trost and D. P. Curran, *Tetrahedron Lett.*, **22**, 1289 (1981).
24. K. C. Kumara Swamy, N. N. Bhuvan Kumar, E. Balaraman, and K. V. P. Pavan Kumar, *Chem. Rev.*, **109**, 2551 (2009).
25. N. E. Golantsov, A. V. Karchava, Z. A. Starikova, F. M. Dolgushin, and M. A. Yurovskaya, *Khim. Geterotsikl. Soedin.*, 1540 (2005). [*Chem. Heterocycl. Comp.*, **41**, 1290 (2005)].
26. S. S. Bhagwat and C. Guck, *Tetrahedron Lett.*, **35**, 3477 (1994).
27. S. Caddick, C. L. Shering, and S. N. Wadman, *Tetrahedron Lett.*, **56**, 469 (2006).
28. A. Bombur and G. Casi, *Tetrahedron Lett.*, **43**, 2187 (2002).
29. T. Tsunoda and T. Yamanya, *Tetrahedron Lett.,* **34**, 1640 (1993).

30. G. H. Lee, I. K. Youn, E. B. Choi, H. K. Lee, G. H. Yon, H. C. Yang, and C. S. Pak, *Curr. Org. Chem.*, **8**, 1263 (2004).
31. A. C. Brown and L. A. Carpino, *J. Org. Chem.*, **50**, 1749 (1985).
32. G. H. Lee, E. B. Choi, E. Lee, and C. S. Pak, *Tetrahedron Lett.*, **28**, 4541 (1993).
33. W. A. Bonner, *J. Am. Chem. Soc.*, **74**, 1034 (1952).
34. R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).
35. A. V. Kurkin, D. S. Belov, and M. A. Yurovskaya, *Khim. Geterotsikl. Soedin.*, 1391 (2008). [*Chem. Heterocycl. Comp.*, **44**, 1123 (2008)].
36. A. V. Karchava, M. A. Yurovskaya, T. R. Wagner, B. L. Zybailov, and Y. G. Bundel, *Tetrahedron: Asymmetry*, **6**, 2895 (1995).
37. L. W. Covert and H. Adkins, *J. Am. Chem. Soc.*, **54**, 4116 (1932).
38. M. Botta, F. De Angelis, and R. Nicoletti, *J. Heterocycl. Chem.*, **16**, 501 (1979).
39. A. M. Cuardo, M. P. Matia, J. L. Garsia, J. J. Vaquero, and J. Alvares-Builla, *Synth. Commun.*, **21**, 535 (1991).
40. M.-L. Bennasar, E. Zulaica, B. A. Sufi, and J. Bosch, *Tetrahedron*, **52**, 8601 (1996).