Synthesis of Optically Pure 1,2-Diaryl (and Alkylaryl)-1,2-Aminosulfides

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General Experimental Methods

Dry solvents and liquid reagents were distilled under argon just prior to use: THF was distilled from sodium and benzophenone ketyl, CH_2Cl_2 was dried over P_2O_5 and diisopropylamine over KOH. t-BuLi and n-BuLi (1.5 and 1.6M solutions in hexane, respectively) were purchased from commercial suppliers and used as received. All reaction vessels, after being flame-dried, were kept under argon. Reactions were monitored by TLC on commercially available precoated plates (Merck silica gel 60 F₂₅₄). Column chromatography was performed by using Silica Gel Merck 60 (230-400 mesh) and *Varian* SCX column. NMR spectra were obtained in CDCl_3 solutions at 300 and 75 MHz for ^1H and ^{13}C NMR, respectively (chemical shifts (δ) are given in ppm, and all coupling constants, J , are given in Hz. Mass spectra were measured by electron impact (EI, 70 eV) or FAB. Diastereoisomeric ratios were determined from integration of well-separated signals in the ^1H NMR spectra of the crude reaction mixtures (H-1, H-2 and SMe group for compounds **4**). Melting points were measured in open capillary tubes and they are uncorrected.

X-Ray of Structure 4a

Table 1. Crystal data and structure refinement for **4a**.

Identification code	4a	
Empirical formula	C ₃₃ H ₂₀ N O S ₃	
Formula weight	542.68	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.266(3) Å	$\alpha = 90^\circ$.
	b = 11.948(4) Å	$\beta = 90^\circ$.
	c = 27.816(10) Å	$\gamma = 90^\circ$.
Volume	2747.3(17) Å ³	
Z	8	
Density (calculated)	2.624 Mg/m ³	
Absorption coefficient	0.594 mm ⁻¹	
F(000)	2248	
Crystal size	0.16 x 0.22 x 0.25 mm ³	
Theta range for data collection	1.85 to 23.37°.	
Index ranges	-9<= <i>h</i> <=9, -13<= <i>k</i> <=13, -30<= <i>l</i> <=30	
Reflections collected	17815	
Independent reflections	3965 [R(int) = 0.0402]	
Completeness to theta = 23.37°	99.3 %	
Absorption correction	SADABS	
Max. and min. transmission	1.000000 and 0.798281	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3965 / 0 / 322	
Goodness-of-fit on F ²	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1093	
R indices (all data)	R1 = 0.0570, wR2 = 0.1155	
Absolute structure parameter	0.00(10)	
Largest diff. peak and hole	0.520 and -0.268 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4a**.
 $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-35(1)	6905(1)	2066(1)	55(1)
S(2)	-767(1)	10427(1)	1167(1)	72(1)
S(3)	4839(1)	8128(1)	1284(1)	79(1)
O(1)	-628(3)	7154(2)	1571(1)	67(1)
O(2)	8(5)	11243(3)	1495(1)	100(1)
N(1)	253(4)	9254(3)	1145(1)	60(1)
C(1)	1382(4)	7970(3)	2246(1)	45(1)
C(2)	1277(5)	8211(3)	2734(1)	59(1)
C(3)	2190(5)	9070(4)	2926(2)	65(1)
C(4)	3158(5)	9692(4)	2628(2)	66(1)
C(5)	3282(5)	9426(3)	2150(1)	58(1)
C(6)	2419(4)	8560(3)	1941(1)	44(1)
C(7)	2681(4)	8289(3)	1414(1)	50(1)
C(8)	2005(4)	9200(3)	1074(1)	51(1)
C(10)	5225(6)	6893(5)	1578(2)	109(2)
C(11)	1236(4)	5698(3)	2027(1)	48(1)
C(12)	1839(5)	5238(3)	2446(1)	57(1)
C(13)	2654(5)	4225(3)	2425(2)	64(1)
C(14)	2863(5)	3670(3)	2003(2)	62(1)
C(15)	2267(5)	4140(3)	1586(2)	68(1)
C(16)	1441(5)	5156(3)	1592(1)	59(1)
C(17)	3673(7)	2522(3)	1989(2)	90(2)
C(31)	2442(5)	9011(3)	555(1)	57(1)
C(32)	1805(6)	8108(4)	306(2)	79(1)
C(33)	2164(8)	7945(5)	-172(2)	105(2)
C(34)	3166(9)	8650(7)	-404(2)	123(3)
C(35)	3828(8)	9537(6)	-170(2)	112(2)
C(36)	3464(6)	9727(4)	314(2)	79(1)
C(41)	-300(5)	10934(3)	575(1)	60(1)
C(42)	-766(5)	10342(4)	177(1)	65(1)
C(43)	-334(6)	10733(4)	-273(2)	83(1)
C(44)	524(6)	11690(5)	-335(2)	92(2)
C(45)	965(8)	12290(5)	68(2)	96(2)
C(46)	540(6)	11923(4)	522(2)	78(1)
C(47)	1067(9)	12079(7)	-828(2)	155(3)

Table 3. Bond lengths [Å] and angles [°] for **4a**.

S(1)-O(1)	1.493(3)
S(1)-C(11)	1.788(4)
S(1)-C(1)	1.800(4)
S(2)-O(2)	1.480(3)
S(2)-N(1)	1.637(3)
S(2)-C(41)	1.797(4)
S(3)-C(10)	1.717(5)
S(3)-C(7)	1.831(4)
N(1)-C(8)	1.463(5)
C(1)-C(2)	1.391(5)
C(1)-C(6)	1.397(5)
C(2)-C(3)	1.381(6)
C(3)-C(4)	1.370(6)
C(4)-C(5)	1.371(5)
C(5)-C(6)	1.384(5)
C(6)-C(7)	1.518(5)
C(7)-C(8)	1.547(5)
C(8)-C(31)	1.506(5)
C(11)-C(12)	1.382(5)
C(11)-C(16)	1.383(5)
C(12)-C(13)	1.386(5)
C(13)-C(14)	1.360(6)
C(14)-C(15)	1.379(6)
C(14)-C(17)	1.526(5)
C(15)-C(16)	1.392(5)
C(31)-C(36)	1.376(6)
C(31)-C(32)	1.385(6)
C(32)-C(33)	1.375(7)
C(33)-C(34)	1.346(9)
C(34)-C(35)	1.360(9)
C(35)-C(36)	1.397(7)
C(41)-C(42)	1.369(5)
C(41)-C(46)	1.378(6)
C(42)-C(43)	1.384(6)
C(43)-C(44)	1.357(7)
C(44)-C(45)	1.381(7)
C(44)-C(47)	1.515(6)
C(45)-C(46)	1.382(6)

O(1)-S(1)-C(11)	107.23(16)
O(1)-S(1)-C(1)	109.26(15)
C(11)-S(1)-C(1)	101.85(15)
O(2)-S(2)-N(1)	111.3(2)
O(2)-S(2)-C(41)	104.4(2)
N(1)-S(2)-C(41)	98.29(17)
C(10)-S(3)-C(7)	100.2(2)
C(8)-N(1)-S(2)	123.5(3)
C(2)-C(1)-C(6)	121.7(3)
C(2)-C(1)-S(1)	112.1(3)
C(6)-C(1)-S(1)	126.0(3)
C(3)-C(2)-C(1)	119.7(4)
C(4)-C(3)-C(2)	119.3(4)
C(3)-C(4)-C(5)	120.3(4)
C(4)-C(5)-C(6)	122.7(4)
C(5)-C(6)-C(1)	116.1(3)
C(5)-C(6)-C(7)	119.4(3)
C(1)-C(6)-C(7)	124.5(3)
C(6)-C(7)-C(8)	112.9(3)
C(6)-C(7)-S(3)	110.6(2)
C(8)-C(7)-S(3)	107.8(2)
N(1)-C(8)-C(31)	112.0(3)
N(1)-C(8)-C(7)	107.8(3)
C(31)-C(8)-C(7)	113.2(3)
C(12)-C(11)-C(16)	120.5(3)
C(12)-C(11)-S(1)	118.7(3)
C(16)-C(11)-S(1)	120.3(3)
C(11)-C(12)-C(13)	119.2(4)
C(14)-C(13)-C(12)	121.6(4)
C(13)-C(14)-C(15)	118.8(4)
C(13)-C(14)-C(17)	121.0(4)
C(15)-C(14)-C(17)	120.1(4)
C(14)-C(15)-C(16)	121.4(4)
C(11)-C(16)-C(15)	118.6(4)
C(36)-C(31)-C(32)	118.3(4)
C(36)-C(31)-C(8)	121.4(4)
C(32)-C(31)-C(8)	120.3(4)
C(33)-C(32)-C(31)	120.7(5)
C(34)-C(33)-C(32)	120.5(6)
C(33)-C(34)-C(35)	120.3(6)

C(34)-C(35)-C(36)	120.1(6)
C(31)-C(36)-C(35)	120.0(5)
C(42)-C(41)-C(46)	119.9(4)
C(42)-C(41)-S(2)	120.4(3)
C(46)-C(41)-S(2)	119.7(3)
C(41)-C(42)-C(43)	119.0(4)
C(44)-C(43)-C(42)	122.3(4)
C(43)-C(44)-C(45)	118.2(4)
C(43)-C(44)-C(47)	121.9(5)
C(45)-C(44)-C(47)	119.9(5)
C(44)-C(45)-C(46)	120.7(5)
C(41)-C(46)-C(45)	119.8(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	44(1)	54(1)	65(1)	7(1)	3(1)	-2(1)
S(2)	83(1)	76(1)	57(1)	10(1)	17(1)	31(1)
S(3)	57(1)	86(1)	93(1)	10(1)	22(1)	14(1)
O(1)	59(2)	66(2)	77(2)	12(1)	-25(1)	-6(1)
O(2)	161(3)	87(2)	53(2)	-21(2)	5(2)	31(2)
N(1)	58(2)	60(2)	61(2)	17(2)	13(2)	9(2)
C(1)	43(2)	44(2)	48(2)	3(2)	0(2)	12(2)
C(2)	57(2)	64(2)	54(2)	6(2)	5(2)	20(2)
C(3)	78(3)	69(3)	49(2)	-8(2)	-17(2)	25(2)
C(4)	74(3)	55(2)	68(3)	-10(2)	-17(2)	9(2)
C(5)	61(2)	45(2)	66(3)	1(2)	-3(2)	-5(2)
C(6)	42(2)	40(2)	49(2)	2(2)	-6(2)	10(2)
C(7)	47(2)	51(2)	52(2)	-6(2)	7(2)	0(2)
C(8)	54(2)	51(2)	48(2)	2(2)	5(2)	3(2)
C(10)	70(3)	115(4)	143(5)	32(4)	4(3)	24(4)
C(11)	47(2)	43(2)	54(2)	6(2)	4(2)	-9(2)
C(12)	65(2)	58(2)	48(2)	5(2)	-3(2)	-2(2)
C(13)	66(3)	58(3)	68(3)	16(2)	-3(2)	0(2)
C(14)	58(2)	49(2)	79(3)	5(2)	11(2)	-4(2)
C(15)	80(3)	55(2)	68(3)	-6(2)	10(2)	-9(2)
C(16)	70(3)	52(2)	56(2)	6(2)	-4(2)	-10(2)
C(17)	96(4)	54(3)	118(4)	13(3)	22(3)	17(3)
C(31)	57(2)	64(2)	49(2)	-4(2)	4(2)	7(2)
C(32)	87(3)	79(3)	70(3)	-14(3)	-7(2)	12(3)
C(33)	127(5)	120(5)	68(3)	-36(3)	-19(3)	40(4)
C(34)	124(5)	189(8)	55(3)	-22(4)	11(3)	56(5)
C(35)	95(4)	173(6)	69(3)	30(4)	26(3)	11(5)
C(36)	76(3)	103(3)	56(3)	9(2)	17(2)	1(3)
C(41)	66(3)	52(2)	61(2)	6(2)	5(2)	9(2)
C(42)	74(3)	66(3)	57(2)	2(2)	-10(2)	2(2)
C(43)	93(4)	104(4)	51(3)	-4(2)	-15(2)	6(3)
C(44)	85(3)	127(4)	63(3)	29(3)	-11(3)	-12(3)
C(45)	105(4)	97(4)	87(4)	35(3)	-11(3)	-28(3)
C(46)	90(3)	72(3)	72(3)	4(2)	-15(2)	-3(3)
C(47)	135(5)	261(9)	71(4)	58(5)	-7(4)	-55(7)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4a**.

	x	y	z	U(eq)
H(1A)	-190(50)	8760(30)	1290(14)	72
H(2)	593	7796	2931	70
H(3)	2149	9226	3253	79
H(4)	3733	10297	2751	79
H(5)	3975	9846	1958	69
H(7)	2135	7580	1342	60
H(8)	2465	9921	1172	61
H(10A)	4734	6911	1890	164
H(10B)	6373	6796	1611	164
H(10C)	4785	6281	1396	164
H(12)	1699	5603	2738	68
H(13)	3068	3919	2707	77
H(15)	2420	3771	1295	81
H(16)	1036	5463	1309	71
H(17A)	3279	2109	1717	134
H(17B)	3425	2122	2279	134
H(17C)	4823	2614	1962	134
H(32)	1127	7607	464	94
H(33)	1712	7343	-336	126
H(34)	3406	8530	-727	147
H(35)	4524	10019	-332	134
H(36)	3913	10337	473	94
H(42)	-1363	9687	209	79
H(43)	-644	10326	-543	99
H(45)	1554	12948	34	115
H(46)	820	12342	791	94
H(47A)	2215	12202	-825	233
H(47B)	524	12764	-908	233
H(47C)	806	11518	-1062	233

4'g