Organometallic Reactions in Aqueous Media. Indium-Promoted Additions to 2-Pyridyl and Glyoxylic Acid Oxime Ethers

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Supporting Information

Contents:

Experimental procedures and characterizations for compounds: ethyl 2-{2-[2-(ethoxycarbonyl)-2-propenyl](methoxy)amino}-2-(2-pyridinyl)ethyl]acrylate (**9'**), (*syn*)-2-(1-Ammino-2-phenyl-butyl)pyridine, (*syn*)-2-(1-Ammino-2-ethoxycarbonyl-butyl)pyridine, **10b**, **16** and **17** S2-S4

ORTEP diagrams for compounds **16** and **17** S5

X-ray data for compound **16** S6-S13

X-ray data for compound **17** S14-S21

Ethyl 2-{2-[2-(ethoxycarbonyl)-2-propenyl](methoxy)amino}-2-(2-pyridinyl)ethyl]acrylate (9').

Following the general procedure for the allylation reaction (entry 7, Table 1), starting from oxime **I** and ethyl (2-bromomethyl)acrylate **4**, the title compound was obtained after 24 h in 53% yield as a colourless oil after chromatography on silica gel (light petroleum/Et₂O 3/7): ¹H NMR (200 MHz, CDCl₃) δ 8.6-8.5 (m, 1H), 7.7-7.6 (m, 1H), 7.4-7.3 (m, 1H), 7.15 (s, 1H), 6.20 (s, 1H), 6.05 (s, 1H), 5.75 (s, 1H), 5.45 (s, 1H), 4.42-4.10 (m, 5H), 3.53-3.41 (m, 7H), 3.11-2.91 (m, 2H), 1.30-1.13 (m, 6H); ¹³C NMR (50 MHz, CDCl₃) δ 167.0, 166.9, 158.8, 148.7, 137.6, 137.5, 136.0, 127.9, 127.1, 125.5, 124.6, 122.4, 70.2, 62.1, 60.6, 55.8, 33.8, 14.2; EI-MS (*m/e*): 331 (100), 285 (16.9), 249 (20.5), 217 (24.2), 204 (29.9), 189 (15.9), 144 (24.8), 143 (74.8), 130 (93.3), 118 (21.5), 106 (28.7), 92 (19.5), 78 (53.8), 69 (24.6); Anal. Calcd for C₁₉H₂₆N₂O₅: C, 62.98; H, 7.18; N, 7.73; Found: C, 63.07; H, 7.02; N, 7.81.

Ethyl 2-[(methoxyamino)(2-pyridinyl)methyl]-3-butenolate (10b): NaBH₃CN (4.0 mmol) was added to a solution of **10a** (1 mmol) and bromocresol green (5 mg) in THF (10 mL); the blue-green solution was acidified with a 1 M solution of *p*-TsOH in THF (pH ≈ 3.5, yellow solution) and then stirred at room temperature, maintaining the pH value around 3.5 (yellow solution) by means of additions of the *p*-TsOH solution. After 24 h the mixture was neutralised with saturated Na₂CO₃ and extracted with Et₂O; the organic layer was dried (MgSO₄), filtered and evaporated, affording a crude product containing **10a** and **10b** in a 55 : 45 ratio (¹H NMR); the two diastereoisomers were separated by chromatography on silica gel (light petroleum/Et₂O = 1:1), affording 0.42 mmol of **10a** and 0.35 mmol of **10b** as low melting solids. **10b**: ¹H NMR (300 MHz, CDCl₃) • 8.73 (d, 1H, *J* = 6.0 Hz), 8.07-8.01 (m, 1H), 7.76 (d, 1H, *J* = 8.1 Hz), 7.53-7.48 (m, 1H), 6.23 (br s, 1H), 5.74 (ddd, 1H, *J* = 17.1, 10.1, 9.3 Hz), 5.43 (d, 1H, *J* = 9.3 Hz), 5.1 (dd, 1H, *J* = 17.1, 0.9 Hz), 5.03 (dd, 1H, *J* = 10.2, 1.0 Hz), 4.15 (q, 2H, *J* = 7.1 Hz), 3.67 (apparent triplet, 1H), 3.41 (s, 3H), 1.21 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃) • 171.0, 158.0, 149.1, 141.3, 131.6, 127.2, 124.8, 121.1, 62.6, 61.8, 61.5, 52.7, 14.2;

EI-MS (*m/e*): 137 (100), 106 (12.2), 79 (21.4), 78 (7.2); Anal. Calcd for C₁₃H₁₈N₂O: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.28; H, 7.27; N, 11.15.

(*syn*)-2-(1-Amino-2-phenyl-butyl)pyridine. A Solution of **7** (0.6 mmol) in 2.5 mL of CH₃OH was slowly added to a suspension of Pd/C 10% (72 mg) in 1 mL of CH₃OH and then the mixture was hydrogenated under a positive H₂ pressure (3 Bar). After 48 h, the catalyst was removed by filtration on a celite pad and the solvent was concentrated under vacuum. Chromatography on silica gel (EtOAc/MeOH 9/1) afforded the title compound in 37% yield as a colourless oil: ¹H NMR (200 MHz, CDCl₃) • 8.60 (m, 1H), 7.70 (m, 1H), 7.40-7.15 (m, 7H), 4.10 (d, 1H, *J* = 8.9 Hz), 2.85 (dt, 1H, *J*_d = 10.1 Hz, *J*_t = 4.0 Hz), 1.95 (br s, 2H), 1.70-1.50 (m, 1H), 1.45-1.30 (m, 1H), 0.65 (t, 3H, *J* = 7.3 Hz); ¹³C NMR (50 MHz, CDCl₃) • 163.5, 149.4, 142.2, 136.5, 128.9, 128.6, 126.9, 122.8, 122.4, 62.6, 55.8, 26.0, 12.3; EI-MS (*m/e*) 107 (100), 80 (8). Anal. Calcd for C₁₅H₁₈N₂: C, 79.65; H, 7.96; N, 13.39. Found: C, 79.89; H, 7.98; N, 13.35.

(*syn*)-2-(1-Amino-2-ethoxycarbonyl-butyl)pyridine. Following the procedure used for (*syn*)-2-(1-Amino-2-phenyl-butyl)pyridine, starting from compound **10a** the title compound was obtained in 40% yield as a colourless oil: ¹H NMR (200 MHz, CDCl₃) δ 8.60 (m, 1H), 7.62 (m, 1H), 7.30-7.10 (m, 2H), 4.18 (q, 2H, *J* = 7.4 Hz), 4.08 (d, 1H, *J* = 8.7 Hz), 2.80 (m, 1H), 1.95 (br s, 2H), 1.70-1.50 (m, 1H), 1.35-1.25 (m, 1H), 1.25 (t, 3H, *J* = 7.1 Hz), 0.85 (t, 3H, *J* = 7.3 Hz); ¹³C NMR (50 MHz, CDCl₃) δ 175.1, 162.7, 122.4, 122.2, 136.6, 150.0, 60.3, 59.2, 54.7, 23.4, 14.4, 11.9; EI-MS (*m/e*) 107 (100), 80 (15). Anal. Calcd for C₁₂H₁₈N₂O₂: C, 64.86; H, 8.11; N, 12.61. Found: C, 65.05; H, 8.09; N, 12.65.

(*syn*)-2-(2-Phenyl-1-*p*-toluensulphonylamino-butyl)pyridine (16**).** Et₃N (0.22 mmol) and TsCl (0.22 mmol) were added to a stirred solution of (*syn*)-2-(1-Amino-2-phenyl-butyl)pyridine (0.2 mmol) in dry CH₂Cl₂. After 4 h the reaction was quenched with H₂O (1.5 mL) and extracted with EtOAc. The organic layer was washed with H₂O and brine, dried and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (light petroleum/Et₂O 6/4) affording the title compound as a white solid in 60% yield: mp = 144-146 °C; ¹H NMR (300 MHz,

CDCl₃) δ 8.30 (m, 1H), 7.57 (m, 1H), 7.55 (m, 2H), 7.20 (m, 3H), 7.05-7.00 (m, 3H), 6.95-6.85 (m, 3H), 5.70 (d, 1H, J = 7.5 Hz), 4.50 (t, 1H, J = 7.2 Hz), 2.90 (q, 1H, J = 7.2 Hz), 2.28 (s, 3H), 1.55 (quint, 2H, J = 7.5 Hz), 0.70 (t, 3H, J = 7.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 158.1, 148.3, 142.7, 139.3, 136.1, 129.0, 128.6, 128.2, 127.0, 126.8, 122.6, 122.1, 61.9, 53.5, 24.4, 21.3, 11.9; ESI-MS (m/e) 381 ($M + H^+$); Anal. Calcd for C₂₂H₂₄N₂O₂S: C, 69.44; H, 6.36; N, 7.36; S, 8.43. Found: C, 69.68; H, 6.18; N, 7.38; S, 8.40.

(*syn*)-2-(2-Ethoxycarbonyl-1-*p*-toluensulphonylamino-butyl)pyridine (17). Following the procedure used for compound **16**, starting from (*syn*)-2-(1-Amino-2-ethoxycarbonyl-butyl)pyridine the title compound was obtained as a white solid in 70% yield: mp = 138-139 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.40 (m, 1H), 7.55 (m, 2H), 7.43 (m, 1H), 7.05 (m, 2H), 7.05-6.90 (m, 2H), 6.22 (d, 1H, J = 9.6 Hz), 4.59 (t, 1H, J = 7.5 Hz), 4.00 (q, 2H, J = 7.2 Hz), 2.78 (m, 1H), 2.30 (s, 3H), 1.64-1.50 (m, 1H), 1.35-1.20 (m, 1H), 1.20 (t, 3H, J = 6.9 Hz), 0.80 (t, 3H, J = 7.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 173.6, 157.8, 149.0, 142.8, 136.4, 129.1, 127.0, 122.4, 122.1, 60.6, 59.2, 52.5, 22.8, 21.4, 14.0, 11.6; ESI-MS (m/e) 377 ($M + H^+$); Anal. Calcd for C₁₉H₂₄N₂O₄S: C, 60.62; H, 6.43; N 7.44; S, 8.52. Found: C, 60.81; H, 6.41; N, 7.46; S, 8.49.

ORTEP diagram for (*syn*)-2-(2-Phenyl-1-*p*-toluensulphonylamino-butyl)pyridine (16):

ORTEP diagram for (*syn*)-2-(2-Ethoxycarbonyl-1-*p*-toluensulphonylamino-butyl)pyridine (17):

X-ray data for (*syn*)-2-(2-Phenyl-1-*p*-toluensulphonylamino-butyl)pyridine (16):

Table 1. Crystal data and structure refinement.

Empirical formula	C ₂₂ H ₂₄ N ₂ O ₂ S	
Formula weight	380.49	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/c$	
Unit cell dimensions	$a = 21.034(20)$ Å $b = 5.468(5)$ Å $c = 17.532(17)$ Å	$\alpha = 90^\circ$ $\beta = 102.828(15)^\circ$ $\gamma = 90^\circ$
Volume	1966(3) Å ³	
Z, Calculated density	4, 1.285 Mg/m ³	
Absorption coefficient	0.184 mm ⁻¹	
F(000)	808	
Crystal size	0.20 x 0.10 x 0.10 mm	
Theta range for data collection	1.99 to 25.00 deg.	
Limiting indices	-25 ≤ h ≤ 25, -6 ≤ k ≤ 6, -20 ≤ l ≤ 20	
Reflections collected / unique	13038 / 3471 [R(int) = 0.3081]	
Completeness to theta = 25.00	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9818 and 0.9641	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3471 / 0 / 245	
Goodness-of-fit on F ²	0.797	
Final R indices [I ≥ 2σ(I)]	R ₁ = 0.1027, wR ₂ = 0.2310	
R indices (all data)	R ₁ = 0.2934, wR ₂ = 0.2766	
Extinction coefficient	0.010(2)	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³).

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	3231(1)	7026(4)	2479(1)	47(1)
O(1)	3509(3)	6146(11)	3252(3)	66(2)
O(2)	2945(3)	9394(11)	2383(4)	59(2)
N(1)	2664(3)	5068(13)	2117(4)	50(2)
N(2)	2765(4)	3347(14)	604(4)	57(2)
C(1)	5428(4)	6880(20)	775(6)	86(4)
C(2)	4847(4)	6770(20)	1175(5)	54(3)
C(3)	4396(6)	8608(18)	1037(6)	72(3)
C(4)	3894(5)	8727(15)	1428(6)	55(3)
C(5)	3837(4)	6905(16)	1948(5)	42(2)
C(6)	4265(4)	5011(17)	2044(5)	52(2)
C(7)	4761(5)	4964(18)	1686(6)	59(3)
C(8)	2178(4)	5576(15)	1409(5)	43(2)
C(9)	2432(4)	5380(17)	683(5)	46(2)
C(10)	2320(4)	7121(18)	110(5)	53(2)
C(11)	2522(5)	6830(20)	-547(5)	62(3)
C(12)	2880(5)	4750(20)	-650(6)	64(3)
C(13)	2983(4)	3156(19)	-36(5)	59(3)
C(14)	1601(4)	3855(16)	1414(5)	50(2)
C(15)	1086(5)	4055(18)	674(5)	65(3)
C(16)	520(5)	2270(20)	601(6)	88(4)
C(17)	1345(4)	4172(16)	2146(5)	46(2)
C(18)	955(5)	6100(19)	2235(6)	66(3)
C(19)	714(5)	6370(20)	2893(9)	93(4)
C(20)	858(6)	4730(20)	3478(7)	87(4)
C(21)	1261(6)	2820(20)	3407(7)	89(4)
C(22)	1486(5)	2485(18)	2746(5)	59(3)

Table 3. Bond lengths [Å] and angles [deg].

S(1)-O(2)	1.422(6)
S(1)-O(1)	1.434(6)
S(1)-N(1)	1.623(7)
S(1)-C(5)	1.739(8)
N(1)-C(8)	1.449(9)
N(2)-C(13)	1.307(10)
N(2)-C(9)	1.338(10)
C(1)-C(2)	1.540(12)
C(2)-C(3)	1.367(13)
C(2)-C(7)	1.372(12)
C(3)-C(4)	1.381(13)
C(4)-C(5)	1.374(11)
C(5)-C(6)	1.357(11)
C(6)-C(7)	1.332(11)
C(8)-C(9)	1.490(11)
C(8)-C(14)	1.537(11)
C(9)-C(10)	1.366(11)
C(10)-C(11)	1.323(11)
C(11)-C(12)	1.396(13)
C(12)-C(13)	1.366(12)
C(14)-C(15)	1.498(11)
C(14)-C(17)	1.508(11)
C(15)-C(16)	1.523(12)
C(17)-C(18)	1.366(12)
C(17)-C(22)	1.381(11)
C(18)-C(19)	1.366(14)
C(19)-C(20)	1.346(15)
C(20)-C(21)	1.365(14)
C(21)-C(22)	1.358(12)
O(2)-S(1)-O(1)	119.4(4)
O(2)-S(1)-N(1)	107.4(4)
O(1)-S(1)-N(1)	105.0(4)
O(2)-S(1)-C(5)	108.2(4)
O(1)-S(1)-C(5)	107.4(4)
N(1)-S(1)-C(5)	109.1(4)
C(8)-N(1)-S(1)	121.8(6)
C(13)-N(2)-C(9)	116.5(8)
C(3)-C(2)-C(7)	117.2(9)
C(3)-C(2)-C(1)	118.8(10)
C(7)-C(2)-C(1)	124.0(10)
C(2)-C(3)-C(4)	121.7(9)
C(5)-C(4)-C(3)	118.9(8)
C(6)-C(5)-C(4)	118.9(8)
C(6)-C(5)-S(1)	120.4(7)
C(4)-C(5)-S(1)	120.7(7)
C(7)-C(6)-C(5)	121.5(9)

C(6)-C(7)-C(2)	121.7(9)
N(1)-C(8)-C(9)	113.5(7)
N(1)-C(8)-C(14)	106.6(7)
C(9)-C(8)-C(14)	113.2(7)
N(2)-C(9)-C(10)	120.8(8)
N(2)-C(9)-C(8)	116.4(8)
C(10)-C(9)-C(8)	122.9(8)
C(11)-C(10)-C(9)	121.4(9)
C(10)-C(11)-C(12)	119.7(10)
C(13)-C(12)-C(11)	114.5(9)
N(2)-C(13)-C(12)	126.9(10)
C(15)-C(14)-C(17)	113.7(7)
C(15)-C(14)-C(8)	111.7(7)
C(17)-C(14)-C(8)	111.4(7)
C(14)-C(15)-C(16)	115.3(8)
C(18)-C(17)-C(22)	117.5(9)
C(18)-C(17)-C(14)	121.5(9)
C(22)-C(17)-C(14)	121.0(9)
C(17)-C(18)-C(19)	121.6(10)
C(20)-C(19)-C(18)	120.6(11)
C(19)-C(20)-C(21)	118.5(11)
C(22)-C(21)-C(20)	121.5(11)
C(21)-C(22)-C(17)	120.1(10)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
S(1)	42(1)	51(1)	45(1)	-4(1)	4(1)	1(1)
O(1)	83(5)	72(5)	42(4)	4(3)	15(3)	12(4)
O(2)	52(4)	51(4)	75(4)	-10(4)	14(3)	9(3)
N(1)	43(4)	52(5)	50(4)	12(4)	2(4)	-13(4)
N(2)	72(5)	46(5)	54(5)	13(4)	19(4)	8(4)
C(1)	59(7)	107(9)	99(8)	-2(8)	32(6)	-27(7)
C(2)	27(5)	76(7)	56(6)	-29(6)	5(4)	-6(5)
C(3)	102(9)	51(7)	72(7)	15(6)	39(7)	6(6)
C(4)	66(7)	34(6)	68(6)	3(5)	22(6)	5(5)
C(5)	28(5)	43(5)	55(5)	-8(5)	7(4)	-5(5)
C(6)	43(6)	64(7)	50(5)	6(5)	13(5)	5(5)
C(7)	46(6)	46(6)	77(7)	5(6)	-3(5)	-9(5)
C(8)	45(5)	38(5)	46(5)	8(4)	6(4)	-3(4)
C(9)	32(5)	54(6)	51(6)	15(5)	9(4)	0(5)
C(10)	55(6)	53(6)	55(6)	17(5)	23(5)	5(5)
C(11)	68(7)	68(7)	51(6)	9(6)	17(5)	-11(6)
C(12)	56(7)	88(8)	50(6)	1(7)	14(5)	-12(6)
C(13)	75(7)	67(7)	43(5)	3(6)	27(5)	14(6)
C(14)	41(5)	49(6)	60(6)	-1(5)	13(5)	-6(4)
C(15)	70(7)	79(7)	46(6)	-5(5)	13(5)	-23(6)
C(16)	56(7)	103(9)	102(8)	-11(7)	8(6)	-33(7)
C(17)	53(6)	38(5)	47(5)	-12(5)	9(5)	-14(5)
C(18)	74(7)	63(7)	66(7)	19(6)	24(6)	4(6)
C(19)	77(8)	68(9)	149(12)	-4(9)	60(9)	24(6)
C(20)	88(9)	99(10)	82(8)	19(8)	36(7)	14(8)
C(21)	89(9)	106(10)	80(8)	9(8)	35(7)	22(8)
C(22)	68(6)	62(7)	53(6)	5(6)	24(5)	12(5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for p21c.

	x	y	z	U(eq)
H(1N)	2652	3692	2351	60
H(1A)	5703	5480	926	129
H(1B)	5674	8344	932	129
H(1C)	5270	6882	217	129
H(3)	4427	9808	672	86
H(4)	3599	10020	1340	66
H(6)	4210	3716	2367	62
H(7)	5056	3674	1785	71
H(8)	2025	7257	1444	52
H(10)	2098	8541	184	63
H(11)	2425	8004	-940	74
H(12)	3035	4480	-1099	77
H(13)	3235	1786	-77	71
H(14)	1773	2185	1429	60
H(15A)	1289	3803	235	78
H(15B)	914	5706	635	78
H(16A)	214	2543	114	133
H(16B)	307	2525	1026	133
H(16C)	681	626	618	133
H(18)	851	7258	1838	79
H(19)	448	7697	2936	111
H(20)	686	4887	3921	104
H(21)	1384	1735	3821	107
H(22)	1735	1113	2698	71

Table 6. Torsion angles [deg] for p21c.

O(2)-S(1)-N(1)-C(8)	38.6(8)
O(1)-S(1)-N(1)-C(8)	166.7(6)
C(5)-S(1)-N(1)-C(8)	-78.4(7)
C(7)-C(2)-C(3)-C(4)	3.6(15)
C(1)-C(2)-C(3)-C(4)	-174.5(9)
C(2)-C(3)-C(4)-C(5)	-2.1(15)
C(3)-C(4)-C(5)-C(6)	-1.9(13)
C(3)-C(4)-C(5)-S(1)	177.8(8)
O(2)-S(1)-C(5)-C(6)	168.5(7)
O(1)-S(1)-C(5)-C(6)	38.4(8)
N(1)-S(1)-C(5)-C(6)	-74.9(8)
O(2)-S(1)-C(5)-C(4)	-11.2(8)
O(1)-S(1)-C(5)-C(4)	-141.3(6)
N(1)-S(1)-C(5)-C(4)	105.4(7)
C(4)-C(5)-C(6)-C(7)	4.5(13)
S(1)-C(5)-C(6)-C(7)	-175.2(7)
C(5)-C(6)-C(7)-C(2)	-3.0(14)
C(3)-C(2)-C(7)-C(6)	-1.0(13)
C(1)-C(2)-C(7)-C(6)	176.9(9)
S(1)-N(1)-C(8)-C(9)	75.2(9)
S(1)-N(1)-C(8)-C(14)	-159.5(6)
C(13)-N(2)-C(9)-C(10)	1.2(12)
C(13)-N(2)-C(9)-C(8)	179.3(7)
N(1)-C(8)-C(9)-N(2)	49.4(10)
C(14)-C(8)-C(9)-N(2)	-72.3(9)
N(1)-C(8)-C(9)-C(10)	-132.5(8)
C(14)-C(8)-C(9)-C(10)	105.8(9)
N(2)-C(9)-C(10)-C(11)	1.8(13)
C(8)-C(9)-C(10)-C(11)	-176.2(8)
C(9)-C(10)-C(11)-C(12)	-2.7(13)
C(10)-C(11)-C(12)-C(13)	0.7(13)
C(9)-N(2)-C(13)-C(12)	-3.4(14)
C(11)-C(12)-C(13)-N(2)	2.5(14)
N(1)-C(8)-C(14)-C(15)	-175.1(7)
C(9)-C(8)-C(14)-C(15)	-49.6(10)
N(1)-C(8)-C(14)-C(17)	56.4(9)
C(9)-C(8)-C(14)-C(17)	-178.1(7)
C(17)-C(14)-C(15)-C(16)	-57.3(11)
C(8)-C(14)-C(15)-C(16)	175.5(8)
C(15)-C(14)-C(17)-C(18)	-49.6(11)
C(8)-C(14)-C(17)-C(18)	77.7(10)
C(15)-C(14)-C(17)-C(22)	128.9(9)
C(8)-C(14)-C(17)-C(22)	-103.7(9)
C(22)-C(17)-C(18)-C(19)	0.3(14)
C(14)-C(17)-C(18)-C(19)	178.9(9)
C(17)-C(18)-C(19)-C(20)	0.2(17)
C(18)-C(19)-C(20)-C(21)	1.5(19)
C(19)-C(20)-C(21)-C(22)	-3.8(19)

C(20)-C(21)-C(22)-C(17)	4.4(17)
C(18)-C(17)-C(22)-C(21)	-2.6(14)
C(14)-C(17)-C(22)-C(21)	178.8(9)

X-ray data for (*syn*)-2-(2-Ethoxycarbonyl-1-*p*-toluensulphonylamino-butyl)pyridine (17):

Table 1. Crystal data and structure refinement.

Identification code	p1b		
Empirical formula	C19 H24 N2 O4 S		
Formula weight	376.46		
Temperature	293(2) K		
Wavelength	0.71073 Å		
Crystal system, space group	Triclinic, P-1		
Unit cell dimensions	a = 8.7860(15) Å b = 10.3755(19) Å c = 11.722(2) Å	alpha = 98.147(5) deg. beta = 99.969(4) deg. gamma = 107.255(5) deg.	
Volume	983.7(3) Å³		
Z, Calculated density	2, 1.271 Mg/m³		
Absorption coefficient	0.190 mm⁻¹		
F(000)	400		
Crystal size	0.50 x 0.10 x 0.10 mm		
Theta range for data collection	1.80 to 25.00 deg.		
Limiting indices	-10<=h<=10, -12<=k<=12, -13<=l<=13		
Reflections collected / unique	8781 / 3454 [R(int) = 0.0617]		
Completeness to theta = 25.00	99.8 %		
Absorption correction	Empirical		
Max. and min. transmission	0.9812 and 0.9110		
Refinement method	Full-matrix least-squares on F²		
Data / restraints / parameters	3454 / 0 / 238		
Goodness-of-fit on F²	0.927		
Final R indices [I>2sigma(I)]	R1 = 0.0992, wR2 = 0.2490		

R indices (all data) R1 = 0.1580, wR2 = 0.2782

Largest diff. peak and hole 1.150 and -0.310 e.Å⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³).

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	11882(2)	3644(2)	2170(1)	47(1)
O(1)	13107(5)	4972(4)	2509(3)	67(1)
O(2)	12304(5)	2423(4)	2269(3)	64(1)
O(3)	11476(5)	879(5)	-1025(4)	76(1)
O(4)	11875(5)	2584(5)	-2027(4)	72(1)
N(1)	11082(5)	3522(4)	782(3)	39(1)
N(2)	7927(5)	3831(4)	162(4)	43(1)
C(1)	6225(9)	3342(10)	4529(7)	109(3)
C(2)	7723(7)	3470(8)	4017(5)	64(2)
C(3)	8365(9)	2400(7)	3924(6)	73(2)
C(4)	9673(7)	2474(6)	3401(5)	60(2)
C(5)	10343(6)	3621(6)	2968(4)	45(1)
C(6)	9760(7)	4702(6)	3084(5)	57(2)
C(7)	8441(8)	4606(7)	3607(5)	68(2)
C(8)	9603(5)	2366(5)	152(4)	36(1)
C(9)	8067(5)	2622(5)	368(4)	36(1)
C(10)	6595(6)	4103(6)	371(5)	54(2)
C(11)	5410(6)	3244(6)	770(5)	57(2)
C(12)	5548(6)	2014(6)	965(5)	53(1)
C(13)	6896(6)	1683(5)	757(5)	44(1)
C(14)	9594(6)	2140(5)	-1170(4)	43(1)
C(15)	8056(7)	1011(6)	-1926(5)	59(2)
C(16)	7925(10)	775(9)	-3225(6)	95(2)
C(17)	11078(6)	1775(6)	-1372(5)	48(1)
C(18)	13268(10)	2301(11)	-2365(8)	117(3)
C(19)	12989(14)	1784(12)	-3588(9)	145(4)

Table 3. Bond lengths [Å] and angles [deg].

S(1)-O(1)	1.425(4)
S(1)-O(2)	1.436(4)
S(1)-N(1)	1.627(4)
S(1)-C(5)	1.770(5)
O(3)-C(17)	1.186(6)
O(4)-C(17)	1.343(6)
O(4)-C(18)	1.445(8)
N(1)-C(8)	1.472(6)
N(2)-C(10)	1.336(6)
N(2)-C(9)	1.347(6)
C(1)-C(2)	1.518(9)
C(2)-C(7)	1.358(9)
C(2)-C(3)	1.385(9)
C(3)-C(4)	1.381(9)
C(4)-C(5)	1.371(7)
C(5)-C(6)	1.363(7)
C(6)-C(7)	1.387(8)
C(8)-C(9)	1.506(6)
C(8)-C(14)	1.532(7)
C(9)-C(13)	1.382(6)
C(10)-C(11)	1.354(7)
C(11)-C(12)	1.364(8)
C(12)-C(13)	1.378(7)
C(14)-C(17)	1.507(7)
C(14)-C(15)	1.528(7)
C(15)-C(16)	1.486(8)
C(18)-C(19)	1.409(12)
O(1)-S(1)-O(2)	120.7(3)
O(1)-S(1)-N(1)	104.3(2)
O(2)-S(1)-N(1)	107.7(2)
O(1)-S(1)-C(5)	108.9(2)
O(2)-S(1)-C(5)	106.7(2)
N(1)-S(1)-C(5)	107.8(2)
C(17)-O(4)-C(18)	117.5(6)
C(8)-N(1)-S(1)	120.7(3)
C(10)-N(2)-C(9)	116.6(4)
C(7)-C(2)-C(3)	118.2(6)
C(7)-C(2)-C(1)	121.4(7)
C(3)-C(2)-C(1)	120.4(7)
C(4)-C(3)-C(2)	120.9(6)
C(5)-C(4)-C(3)	119.5(6)
C(6)-C(5)-C(4)	120.5(5)
C(6)-C(5)-S(1)	119.9(4)
C(4)-C(5)-S(1)	119.4(4)
C(5)-C(6)-C(7)	119.1(6)
C(2)-C(7)-C(6)	121.8(6)

N(1)-C(8)-C(9)	111.8(4)
N(1)-C(8)-C(14)	108.2(4)
C(9)-C(8)-C(14)	111.2(4)
N(2)-C(9)-C(13)	122.8(4)
N(2)-C(9)-C(8)	115.2(4)
C(13)-C(9)-C(8)	122.1(4)
N(2)-C(10)-C(11)	124.0(5)
C(10)-C(11)-C(12)	119.2(5)
C(11)-C(12)-C(13)	119.0(5)
C(12)-C(13)-C(9)	118.4(5)
C(17)-C(14)-C(15)	109.0(4)
C(17)-C(14)-C(8)	110.1(4)
C(15)-C(14)-C(8)	112.9(4)
C(16)-C(15)-C(14)	116.0(5)
O(3)-C(17)-O(4)	124.2(5)
O(3)-C(17)-C(14)	124.9(5)
O(4)-C(17)-C(14)	110.8(5)
C(19)-C(18)-O(4)	113.0(7)

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

	U11	U22	U33	U23	U13	U12
S(1)	34(1)	61(1)	45(1)	11(1)	12(1)	14(1)
O(1)	48(2)	72(3)	56(3)	0(2)	13(2)	-10(2)
O(2)	68(3)	90(3)	60(3)	29(2)	23(2)	55(2)
O(3)	72(3)	71(3)	111(4)	30(3)	45(3)	46(3)
O(4)	62(3)	99(3)	69(3)	31(2)	40(2)	24(2)
N(1)	32(2)	44(2)	45(3)	11(2)	13(2)	13(2)
N(2)	35(2)	46(3)	57(3)	19(2)	19(2)	18(2)
C(1)	65(5)	190(9)	71(5)	10(5)	35(4)	36(5)
C(2)	51(4)	97(5)	37(3)	7(3)	13(3)	15(4)
C(3)	81(5)	81(5)	57(4)	26(3)	30(3)	11(4)
C(4)	65(4)	63(4)	58(4)	24(3)	24(3)	21(3)
C(5)	43(3)	60(3)	28(3)	8(2)	11(2)	12(3)
C(6)	63(4)	62(4)	53(4)	13(3)	21(3)	28(3)
C(7)	74(4)	87(5)	61(4)	12(3)	18(3)	53(4)
C(8)	30(2)	42(3)	42(3)	15(2)	16(2)	13(2)
C(9)	30(2)	36(3)	43(3)	10(2)	13(2)	9(2)
C(10)	44(3)	64(4)	72(4)	30(3)	26(3)	29(3)
C(11)	40(3)	75(4)	71(4)	29(3)	28(3)	27(3)
C(12)	37(3)	62(4)	63(4)	23(3)	28(3)	7(3)
C(13)	38(3)	41(3)	56(3)	18(2)	18(2)	9(2)
C(14)	49(3)	44(3)	42(3)	9(2)	17(2)	20(2)
C(15)	45(3)	67(4)	51(3)	-15(3)	7(3)	14(3)
C(16)	84(5)	120(7)	58(5)	-9(4)	7(4)	18(5)
C(17)	44(3)	51(3)	52(3)	6(3)	22(2)	17(3)
C(18)	69(5)	201(10)	95(6)	28(6)	55(5)	46(6)
C(19)	172(11)	176(10)	119(8)	3(7)	88(8)	85(9)

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

	x	y	z	U(eq)
H(100)	11020(60)	4340(50)	660(40)	47
H(1A)	5950	4171	4532	164
H(1B)	6454	3201	5324	164
H(1C)	5322	2572	4054	164
H(3)	7910	1623	4218	88
H(4)	10095	1750	3342	71
H(6)	10241	5493	2815	68
H(7)	8037	5339	3679	82
H(8)	9659	1533	435	43
H(10)	6475	4932	235	65
H(11)	4513	3490	909	68
H(12)	4744	1407	1235	63
H(13)	7015	847	875	53
H(14)	9647	3005	-1433	52
H(15A)	8008	153	-1671	70
H(15B)	7109	1241	-1770	70
H(16A)	6942	27	-3614	143
H(16B)	8856	549	-3397	143
H(16C)	7893	1595	-3503	143
H(18A)	14201	3144	-2138	140
H(18B)	13538	1637	-1934	140
H(19A)	13955	1628	-3763	217
H(19B)	12730	2440	-4019	217
H(19C)	12092	931	-3813	217

Table 6. Torsion angles [deg].

O(1)-S(1)-N(1)-C(8)	-171.3(3)
O(2)-S(1)-N(1)-C(8)	59.2(4)
C(5)-S(1)-N(1)-C(8)	-55.6(4)
C(7)-C(2)-C(3)-C(4)	-1.6(9)
C(1)-C(2)-C(3)-C(4)	176.4(6)
C(2)-C(3)-C(4)-C(5)	0.0(9)
C(3)-C(4)-C(5)-C(6)	2.0(8)
C(3)-C(4)-C(5)-S(1)	-173.8(5)
O(1)-S(1)-C(5)-C(6)	44.6(5)
O(2)-S(1)-C(5)-C(6)	176.5(4)
N(1)-S(1)-C(5)-C(6)	-68.0(5)
O(1)-S(1)-C(5)-C(4)	-139.6(4)
O(2)-S(1)-C(5)-C(4)	-7.7(5)
N(1)-S(1)-C(5)-C(4)	107.8(4)
C(4)-C(5)-C(6)-C(7)	-2.3(8)
S(1)-C(5)-C(6)-C(7)	173.5(4)
C(3)-C(2)-C(7)-C(6)	1.3(9)
C(1)-C(2)-C(7)-C(6)	-176.7(6)
C(5)-C(6)-C(7)-C(2)	0.6(9)
S(1)-N(1)-C(8)-C(9)	82.9(5)
S(1)-N(1)-C(8)-C(14)	-154.3(3)
C(10)-N(2)-C(9)-C(13)	1.1(7)
C(10)-N(2)-C(9)-C(8)	-178.5(4)
N(1)-C(8)-C(9)-N(2)	52.2(5)
C(14)-C(8)-C(9)-N(2)	-68.9(5)
N(1)-C(8)-C(9)-C(13)	-127.4(5)
C(14)-C(8)-C(9)-C(13)	111.4(5)
C(9)-N(2)-C(10)-C(11)	-0.1(8)
N(2)-C(10)-C(11)-C(12)	-0.7(10)
C(10)-C(11)-C(12)-C(13)	0.3(9)
C(11)-C(12)-C(13)-C(9)	0.7(8)
N(2)-C(9)-C(13)-C(12)	-1.5(8)
C(8)-C(9)-C(13)-C(12)	178.2(5)
N(1)-C(8)-C(14)-C(17)	61.2(5)
C(9)-C(8)-C(14)-C(17)	-175.6(4)
N(1)-C(8)-C(14)-C(15)	-176.7(4)
C(9)-C(8)-C(14)-C(15)	-53.5(6)
C(17)-C(14)-C(15)-C(16)	-59.9(7)
C(8)-C(14)-C(15)-C(16)	177.4(5)
C(18)-O(4)-C(17)-O(3)	2.5(9)
C(18)-O(4)-C(17)-C(14)	-176.0(5)
C(15)-C(14)-C(17)-O(3)	-71.7(7)
C(8)-C(14)-C(17)-O(3)	52.7(7)
C(15)-C(14)-C(17)-O(4)	106.9(5)
C(8)-C(14)-C(17)-O(4)	-128.8(5)
C(17)-O(4)-C(18)-C(19)	111.3(9)

Table 7. Hydrogen bonds [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(100)...N(2)#1	0.89(5)	2.28(5)	3.049(6)	145(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z