Supporting Information

An Unexpected Highly Stereoselective Double aza-Baylis-Hillman
Reaction of Sulfonated Imines with Phenyl Vinyl Ketone

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Table 1. Crystal data and structure refinement for cd22275.

Identification code	cd22275
Empirical formula	C32 H29 N O4 S
Formula weight	523.62
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.3996(8) Å alpha = 90 deg. b = 18.3652(11) Å beta = 90.9440(10) deg. c = 12.3047(8) Å gamma = 90 deg.
Volume	2801.7(3) Å ³
Z, Calculated density	4, 1.241 Mg/m ³
Absorption coefficient	0.152 mm ⁻¹
F(000)	1104
Crystal size	0.246 x 0.229 x 0.146 mm
Theta range for data collection	1.64 to 28.28 deg.
Limiting indices	-8<=h<=16, -22<=k<=24, -15<=l<=16
Reflections collected / unique	17117 / 6535 [R(int) = 0.0636]
Completeness to theta = 28.28	93.9 %
Absorption correction	Sadabs
Max. and min. transmission	1.00000 and 0.81749
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6535 / 4 / 448
Goodness-of-fit on F ²	0.892
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.0930
R indices (all data)	R1 = 0.1283, wR2 = 0.1126
Largest diff. peak and hole	0.192 and -0.239 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd22275. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S	3855(1)	1907(1)	2226(1)	57(1)
N	2789(2)	2424(1)	2248(2)	50(1)
O(1)	4040(2)	1635(1)	3303(1)	72(1)
O(2)	3666(2)	1408(1)	1355(2)	76(1)
O(3)	-279(2)	4336(1)	3079(2)	73(1)
O(4)	1945(2)	2347(1)	4886(1)	73(1)
C(1)	2782(2)	3074(1)	2972(2)	46(1)
C(2)	1649(2)	3157(1)	3418(2)	46(1)
C(3)	1576(2)	3838(1)	4147(2)	54(1)
C(4)	520(2)	3926(1)	4708(2)	49(1)
C(5)	-427(2)	4131(1)	4009(2)	51(1)
C(6)	1397(2)	2475(1)	4078(2)	50(1)
C(7)	443(3)	3889(2)	5773(3)	64(1)
C(8)	-1539(2)	4098(1)	4436(2)	46(1)
C(9)	-1905(2)	3534(2)	5084(2)	58(1)
C(10)	-2948(3)	3525(2)	5439(2)	69(1)
C(11)	-3645(3)	4077(2)	5185(3)	75(1)
C(12)	-3296(3)	4639(2)	4536(3)	72(1)
C(13)	-2267(2)	4643(1)	4155(2)	56(1)
C(14)	523(2)	1963(1)	3743(2)	51(1)
C(15)	642(3)	1233(2)	3983(2)	81(1)
C(16)	-167(4)	743(2)	3707(3)	103(1)
C(17)	-1105(4)	986(2)	3236(3)	97(1)
C(18)	-1235(3)	1697(2)	3016(3)	81(1)
C(19)	-414(3)	2188(2)	3238(2)	63(1)
C(20)	3217(2)	3752(1)	2435(2)	46(1)
C(21)	2807(3)	3986(2)	1456(2)	74(1)
C(22)	3241(3)	4582(2)	942(3)	95(1)
C(23)	4067(3)	4964(2)	1414(3)	89(1)
C(24)	4463(3)	4748(2)	2398(3)	80(1)
C(25)	4047(2)	4146(2)	2904(3)	64(1)
C(26)	4942(2)	2476(1)	1902(2)	49(1)
C(27)	4975(3)	2815(2)	901(2)	60(1)
C(28)	5795(3)	3278(2)	678(2)	67(1)
C(29)	6620(3)	3424(1)	1427(2)	66(1)
C(30)	6566(3)	3085(2)	2426(2)	63(1)
C(31)	5745(2)	2615(2)	2666(2)	57(1)
C(32)	7528(3)	3938(2)	1173(3)	115(1)

Table 3. Bond lengths [Å] and angles [deg] for cd22275.

S-O(2)	1.4268(16)
S-O(1)	1.4310(16)
S-N	1.628(2)
S-C(26)	1.757(3)
N-C(1)	1.490(3)
N-H(29)	0.826(15)
O(3)-C(5)	1.222(3)
O(4)-C(6)	1.218(2)
C(1)-C(20)	1.513(3)
C(1)-C(2)	1.524(3)
C(1)-H(1)	0.947(17)
C(2)-C(6)	1.527(3)
C(2)-C(3)	1.542(3)
C(2)-H(2)	0.996(17)
C(3)-C(4)	1.499(3)
C(3)-H(3)	0.99(2)
C(3)-H(4)	0.91(2)
C(4)-C(7)	1.316(4)
C(4)-C(5)	1.493(3)
C(5)-C(8)	1.484(3)
C(6)-C(14)	1.489(3)
C(7)-H(5)	0.94(2)
C(7)-H(6)	0.97(2)
C(8)-C(9)	1.388(3)
C(8)-C(13)	1.388(3)
C(9)-C(10)	1.373(4)
C(9)-H(7)	0.933(19)
C(10)-C(11)	1.365(4)
C(10)-H(8)	0.97(2)
C(11)-C(12)	1.378(4)
C(11)-H(9)	0.97(3)
C(12)-C(13)	1.366(4)
C(12)-H(10)	0.912(15)
C(13)-H(11)	0.99(2)
C(14)-C(19)	1.372(3)
C(14)-C(15)	1.380(3)
C(15)-C(16)	1.385(4)
C(15)-H(12)	1.00(2)
C(16)-C(17)	1.366(5)
C(16)-H(13)	0.957(17)
C(17)-C(18)	1.343(5)
C(17)-H(14)	0.959(17)
C(18)-C(19)	1.382(4)
C(18)-H(15)	0.96(3)
C(19)-H(16)	0.941(19)
C(20)-C(21)	1.369(3)
C(20)-C(25)	1.376(3)
C(21)-C(22)	1.377(4)
C(21)-H(17)	0.93(2)
C(22)-C(23)	1.362(4)
C(22)-H(18)	0.93(3)
C(23)-C(24)	1.358(4)
C(23)-H(19)	0.97(3)
C(24)-C(25)	1.374(4)
C(24)-H(20)	0.92(3)
C(25)-H(21)	0.91(2)
C(26)-C(27)	1.381(3)
C(26)-C(31)	1.382(3)
C(27)-C(28)	1.357(4)
C(27)-H(22)	0.94(2)

C(28)-C(29)	1.392(4)
C(28)-H(23)	0.95(2)
C(29)-C(30)	1.379(4)
C(29)-C(32)	1.507(4)
C(30)-C(31)	1.372(4)
C(30)-H(24)	0.95(2)
C(31)-H(25)	0.93(2)
C(32)-H(26)	0.9600
C(32)-H(27)	0.9600
C(32)-H(28)	0.9600
O(2)-S-O(1)	119.51(11)
O(2)-S-N	105.31(11)
O(1)-S-N	107.85(12)
O(2)-S-C(26)	109.20(12)
O(1)-S-C(26)	107.81(11)
N-S-C(26)	106.44(10)
C(1)-N-S	119.37(16)
C(1)-N-H(29)	111.9(15)
S-N-H(29)	111.2(16)
N-C(1)-C(20)	113.1(2)
N-C(1)-C(2)	108.06(19)
C(20)-C(1)-C(2)	114.4(2)
N-C(1)-H(1)	107.5(11)
C(20)-C(1)-H(1)	108.0(11)
C(2)-C(1)-H(1)	105.3(12)
C(1)-C(2)-C(6)	107.95(19)
C(1)-C(2)-C(3)	110.7(2)
C(6)-C(2)-C(3)	109.9(2)
C(1)-C(2)-H(2)	108.6(11)
C(6)-C(2)-H(2)	110.0(10)
C(3)-C(2)-H(2)	109.6(10)
C(4)-C(3)-C(2)	114.6(2)
C(4)-C(3)-H(3)	108.6(14)
C(2)-C(3)-H(3)	107.2(13)
C(4)-C(3)-H(4)	109.6(15)
C(2)-C(3)-H(4)	105.3(13)
H(3)-C(3)-H(4)	111.5(19)
C(7)-C(4)-C(5)	121.1(3)
C(7)-C(4)-C(3)	122.1(3)
C(5)-C(4)-C(3)	116.5(2)
O(3)-C(5)-C(8)	119.9(2)
O(3)-C(5)-C(4)	119.2(2)
C(8)-C(5)-C(4)	120.8(2)
O(4)-C(6)-C(14)	119.9(2)
O(4)-C(6)-C(2)	118.4(2)
C(14)-C(6)-C(2)	121.7(2)
C(4)-C(7)-H(5)	121.6(15)
C(4)-C(7)-H(6)	117.2(14)
H(5)-C(7)-H(6)	121(2)
C(9)-C(8)-C(13)	117.6(3)
C(9)-C(8)-C(5)	123.3(2)
C(13)-C(8)-C(5)	119.1(2)
C(10)-C(9)-C(8)	120.7(3)
C(10)-C(9)-H(7)	121.7(13)
C(8)-C(9)-H(7)	117.5(13)
C(11)-C(10)-C(9)	120.9(3)
C(11)-C(10)-H(8)	123.0(16)
C(9)-C(10)-H(8)	115.9(16)
C(10)-C(11)-C(12)	119.0(3)
C(10)-C(11)-H(9)	120.2(15)
C(12)-C(11)-H(9)	120.8(15)
C(13)-C(12)-C(11)	120.4(3)
C(13)-C(12)-H(10)	118.7(17)

C(11)-C(12)-H(10)	120.8(17)
C(12)-C(13)-C(8)	121.2(3)
C(12)-C(13)-H(11)	124.3(12)
C(8)-C(13)-H(11)	114.5(12)
C(19)-C(14)-C(15)	118.4(3)
C(19)-C(14)-C(6)	122.8(2)
C(15)-C(14)-C(6)	118.7(3)
C(14)-C(15)-C(16)	120.3(3)
C(14)-C(15)-H(12)	116.6(13)
C(16)-C(15)-H(12)	122.7(13)
C(17)-C(16)-C(15)	120.0(3)
C(17)-C(16)-H(13)	121.9(19)
C(15)-C(16)-H(13)	118.0(19)
C(18)-C(17)-C(16)	120.1(4)
C(18)-C(17)-H(14)	120.2(17)
C(16)-C(17)-H(14)	119.7(17)
C(17)-C(18)-C(19)	120.6(4)
C(17)-C(18)-H(15)	123.9(17)
C(19)-C(18)-H(15)	115.5(17)
C(14)-C(19)-C(18)	120.5(3)
C(14)-C(19)-H(16)	119.1(14)
C(18)-C(19)-H(16)	120.3(14)
C(21)-C(20)-C(25)	117.9(3)
C(21)-C(20)-C(1)	120.8(2)
C(25)-C(20)-C(1)	121.3(2)
C(20)-C(21)-C(22)	120.7(3)
C(20)-C(21)-H(17)	120.0(14)
C(22)-C(21)-H(17)	119.2(14)
C(23)-C(22)-C(21)	120.6(3)
C(23)-C(22)-H(18)	120.6(19)
C(21)-C(22)-H(18)	118.6(19)
C(24)-C(23)-C(22)	119.3(4)
C(24)-C(23)-H(19)	117.3(16)
C(22)-C(23)-H(19)	123.3(16)
C(23)-C(24)-C(25)	120.3(3)
C(23)-C(24)-H(20)	121.1(18)
C(25)-C(24)-H(20)	118.5(18)
C(24)-C(25)-C(20)	121.2(3)
C(24)-C(25)-H(21)	122.4(15)
C(20)-C(25)-H(21)	116.5(14)
C(27)-C(26)-C(31)	119.5(3)
C(27)-C(26)-S	120.3(2)
C(31)-C(26)-S	120.1(2)
C(28)-C(27)-C(26)	119.7(3)
C(28)-C(27)-H(22)	123.7(15)
C(26)-C(27)-H(22)	116.6(15)
C(27)-C(28)-C(29)	122.1(3)
C(27)-C(28)-H(23)	122.8(14)
C(29)-C(28)-H(23)	115.1(14)
C(30)-C(29)-C(28)	117.2(3)
C(30)-C(29)-C(32)	121.0(3)
C(28)-C(29)-C(32)	121.8(3)
C(31)-C(30)-C(29)	121.5(3)
C(31)-C(30)-H(24)	121.2(15)
C(29)-C(30)-H(24)	117.1(15)
C(30)-C(31)-C(26)	119.9(3)
C(30)-C(31)-H(25)	122.1(14)
C(26)-C(31)-H(25)	117.9(14)
C(29)-C(32)-H(26)	109.5
C(29)-C(32)-H(27)	109.5
H(26)-C(32)-H(27)	109.5
C(29)-C(32)-H(28)	109.5
H(26)-C(32)-H(28)	109.5
H(27)-C(32)-H(28)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd22275. 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	63(1)	46(1)	61(1)	-5(1)	-8(1)	12(1)
N	53(1)	48(1)	48(1)	-6(1)	-11(1)	10(1)
O(1)	82(1)	62(1)	70(1)	18(1)	-10(1)	11(1)
O(2)	86(2)	53(1)	89(1)	-27(1)	-12(1)	14(1)
O(3)	69(1)	90(1)	59(1)	19(1)	11(1)	10(1)
O(4)	89(2)	70(1)	58(1)	7(1)	-29(1)	-8(1)
C(1)	45(2)	49(1)	45(2)	-5(1)	-13(1)	4(1)
C(2)	45(2)	46(1)	45(2)	-5(1)	-12(1)	0(1)
C(3)	53(2)	51(2)	57(2)	-9(1)	0(2)	0(2)
C(4)	52(2)	43(1)	53(2)	-7(1)	3(1)	-8(1)
C(5)	57(2)	40(1)	55(2)	-3(1)	3(2)	-3(1)
C(6)	55(2)	51(2)	45(2)	-6(1)	-3(1)	4(1)
C(7)	57(2)	74(2)	61(2)	-6(2)	2(2)	-9(2)
C(8)	46(2)	40(1)	52(2)	-4(1)	-2(1)	-6(1)
C(9)	53(2)	55(2)	66(2)	4(1)	-8(2)	-3(2)
C(10)	63(2)	78(2)	66(2)	10(2)	1(2)	-22(2)
C(11)	48(2)	99(3)	79(2)	-8(2)	8(2)	-3(2)
C(12)	60(2)	64(2)	93(3)	-11(2)	-7(2)	8(2)
C(13)	58(2)	42(2)	69(2)	-3(1)	-1(2)	-7(2)
C(14)	63(2)	52(2)	39(1)	-5(1)	1(1)	-9(2)
C(15)	114(3)	62(2)	65(2)	9(2)	-20(2)	-20(2)
C(16)	171(4)	67(2)	70(2)	10(2)	-12(3)	-43(3)
C(17)	120(4)	109(3)	63(2)	-13(2)	8(2)	-59(3)
C(18)	59(2)	100(3)	82(2)	-27(2)	3(2)	-16(2)
C(19)	65(2)	58(2)	67(2)	-15(2)	-2(2)	-5(2)
C(20)	45(2)	43(1)	50(2)	-8(1)	-4(1)	5(1)
C(21)	96(3)	46(2)	79(2)	3(2)	-30(2)	1(2)
C(22)	138(4)	61(2)	84(3)	18(2)	-22(3)	-1(2)
C(23)	111(3)	52(2)	105(3)	9(2)	12(3)	-9(2)
C(24)	73(3)	64(2)	101(3)	-6(2)	-5(2)	-18(2)
C(25)	65(2)	63(2)	63(2)	-2(2)	-9(2)	-7(2)
C(26)	54(2)	50(1)	45(2)	-5(1)	-5(1)	11(1)
C(27)	70(2)	65(2)	44(2)	-8(1)	-14(2)	12(2)
C(28)	90(3)	65(2)	46(2)	5(2)	-7(2)	4(2)
C(29)	79(2)	68(2)	52(2)	0(1)	-3(2)	-3(2)
C(30)	65(2)	70(2)	55(2)	-3(2)	-15(2)	-1(2)
C(31)	63(2)	66(2)	41(2)	1(1)	-9(2)	12(2)
C(32)	135(3)	123(3)	88(3)	23(2)	-11(2)	-52(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd22275.

	x	y	z	U(eq)
H(26)	7292	4431	1276	173
H(27)	7739	3872	432	173
H(28)	8132	3840	1649	173
H(1)	3228(15)	2968(9)	3584(15)	37(6)
H(2)	1130(15)	3202(9)	2796(14)	34(5)
H(3)	1691(19)	4267(12)	3675(18)	67(8)
H(4)	2118(18)	3788(11)	4651(17)	52(7)
H(5)	-210(20)	3994(12)	6125(19)	64(9)
H(6)	1086(19)	3756(11)	6180(18)	55(8)
H(7)	-1420(17)	3161(10)	5255(16)	44(7)
H(8)	-3160(20)	3095(13)	5840(20)	84(9)
H(9)	-4370(20)	4082(12)	5485(19)	71(8)
H(10)	-3748(17)	5010(10)	4343(19)	69(9)
H(11)	-1982(16)	5014(10)	3654(16)	46(7)
H(12)	1361(19)	1077(12)	4269(19)	65(8)
H(13)	-50(20)	240(10)	3880(20)	110(11)
H(14)	-1666(19)	646(13)	3060(20)	106(11)
H(15)	-1870(20)	1899(14)	2670(20)	95(11)
H(16)	-485(17)	2678(11)	3029(17)	50(7)
H(17)	2230(18)	3739(11)	1126(17)	52(7)
H(18)	3000(20)	4695(15)	240(20)	104(11)
H(19)	4430(20)	5358(14)	1060(20)	92(10)
H(20)	5040(20)	4981(14)	2720(20)	91(10)
H(21)	4305(19)	3983(11)	3559(19)	62(8)
H(22)	4409(19)	2709(11)	411(19)	65(8)
H(23)	5848(18)	3529(12)	2(19)	64(8)
H(24)	7150(20)	3164(12)	2923(19)	76(9)
H(25)	5683(18)	2402(11)	3351(19)	61(8)
H(29)	2576(18)	2523(11)	1626(14)	56(8)

Table 6. Torsion angles [deg] for cd22275.

O(2)-S-N-C(1)	-171.90(18)
O(1)-S-N-C(1)	59.4(2)
C(26)-S-N-C(1)	-56.0(2)
S-N-C(1)-C(20)	88.9(2)
S-N-C(1)-C(2)	-143.38(18)
N-C(1)-C(2)-C(6)	61.6(2)
C(20)-C(1)-C(2)-C(6)	-171.51(19)
N-C(1)-C(2)-C(3)	-178.1(2)
C(20)-C(1)-C(2)-C(3)	-51.1(3)
C(1)-C(2)-C(3)-C(4)	-174.5(2)
C(6)-C(2)-C(3)-C(4)	-55.3(3)
C(2)-C(3)-C(4)-C(7)	114.7(3)
C(2)-C(3)-C(4)-C(5)	-71.2(3)
C(7)-C(4)-C(5)-O(3)	161.8(2)
C(3)-C(4)-C(5)-O(3)	-12.3(3)
C(7)-C(4)-C(5)-C(8)	-17.4(3)
C(3)-C(4)-C(5)-C(8)	168.5(2)
C(1)-C(2)-C(6)-O(4)	63.2(3)
C(3)-C(2)-C(6)-O(4)	-57.6(3)
C(1)-C(2)-C(6)-C(14)	-115.3(2)
C(3)-C(2)-C(6)-C(14)	123.8(2)
O(3)-C(5)-C(8)-C(9)	139.5(2)
C(4)-C(5)-C(8)-C(9)	-41.3(3)
O(3)-C(5)-C(8)-C(13)	-38.7(3)
C(4)-C(5)-C(8)-C(13)	140.5(2)
C(13)-C(8)-C(9)-C(10)	-0.6(4)
C(5)-C(8)-C(9)-C(10)	-178.8(2)
C(8)-C(9)-C(10)-C(11)	-1.5(4)
C(9)-C(10)-C(11)-C(12)	1.9(5)
C(10)-C(11)-C(12)-C(13)	-0.1(5)
C(11)-C(12)-C(13)-C(8)	-2.0(4)
C(9)-C(8)-C(13)-C(12)	2.3(4)
C(5)-C(8)-C(13)-C(12)	-179.4(2)
O(4)-C(6)-C(14)-C(19)	147.5(3)
C(2)-C(6)-C(14)-C(19)	-34.0(4)
O(4)-C(6)-C(14)-C(15)	-30.2(4)
C(2)-C(6)-C(14)-C(15)	148.4(3)
C(19)-C(14)-C(15)-C(16)	0.7(4)
C(6)-C(14)-C(15)-C(16)	178.4(3)
C(14)-C(15)-C(16)-C(17)	-2.8(5)
C(15)-C(16)-C(17)-C(18)	1.7(6)
C(16)-C(17)-C(18)-C(19)	1.6(5)
C(15)-C(14)-C(19)-C(18)	2.5(4)
C(6)-C(14)-C(19)-C(18)	-175.1(3)
C(17)-C(18)-C(19)-C(14)	-3.7(5)
N-C(1)-C(20)-C(21)	53.5(3)
C(2)-C(1)-C(20)-C(21)	-70.8(3)
N-C(1)-C(20)-C(25)	-125.5(2)
C(2)-C(1)-C(20)-C(25)	110.2(3)
C(25)-C(20)-C(21)-C(22)	2.4(4)
C(1)-C(20)-C(21)-C(22)	-176.7(3)
C(20)-C(21)-C(22)-C(23)	-2.0(5)
C(21)-C(22)-C(23)-C(24)	0.3(5)
C(22)-C(23)-C(24)-C(25)	1.0(5)
C(23)-C(24)-C(25)-C(20)	-0.6(5)
C(21)-C(20)-C(25)-C(24)	-1.1(4)
C(1)-C(20)-C(25)-C(24)	178.0(3)
O(2)-S-C(26)-C(27)	48.6(2)
O(1)-S-C(26)-C(27)	179.90(19)
N-S-C(26)-C(27)	-64.6(2)

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O(2)-S-C(26)-C(31)	-134.46(19)
O(1)-S-C(26)-C(31)	-3.2(2)
N-S-C(26)-C(31)	112.3(2)
C(31)-C(26)-C(27)-C(28)	0.2(4)
S-C(26)-C(27)-C(28)	177.1(2)
C(26)-C(27)-C(28)-C(29)	0.4(4)
C(27)-C(28)-C(29)-C(30)	-1.0(4)
C(27)-C(28)-C(29)-C(32)	179.9(3)
C(28)-C(29)-C(30)-C(31)	1.1(4)
C(32)-C(29)-C(30)-C(31)	-179.9(3)
C(29)-C(30)-C(31)-C(26)	-0.6(4)
C(27)-C(26)-C(31)-C(30)	-0.1(4)
S-C(26)-C(31)-C(30)	-177.0(2)

Symmetry transformations used to generate equivalent atoms:

S//

Table 7. Hydrogen bonds for cd22275 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

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