Supporting Information

Highly Efficient aza-Baylis-Hillman Reaction of *N*-Tosylated Imines with MVK, Acrolein, and Phenyl Acrylate or α -Naphthyl Acrylate: Lewis Base Effects and A Convenient Method to Synthesize α,β -Unsaturated β -Amino Carbonyl Compounds

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General Remarks. Unless otherwise stated, all reactions were carried out under argon atmosphere. All solvents were distilled before use. Commercially available reagents were used without further purification. Infrared spectra were measured on a spectrometer (Perkin-Elmer-983). ^1H -NMR and ^{13}C -NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI method. All solid compounds reported in this paper gave satisfactory CHN microanalyses. Melting points are uncorrected.

Table 1. Crystal data and structure refinement for cd22430.

Identification code	cd22430
Empirical formula	C18 H18 N O4 S Cl
Formula weight	379.84
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.679(4) Å alpha = 97.700(10) deg. b = 8.422(5) Å beta = 91.157(10) deg. c = 14.216(8) Å gamma = 90.604(9) deg.
Volume	910.8(8) Å ³
Z, Calculated density	2, 1.385 Mg/m ³
Absorption coefficient	0.346 mm ⁻¹
F(000)	396
Crystal size	0.456 x 0.266 x 0.203 mm
Theta range for data collection	2.44 to 24.99 deg.
Limiting indices	-9<=h<=9, -10<=k<=9, -12<=l<=16
Reflections collected / unique	4540 / 3155 [R(int) = 0.0636]
Completeness to theta = 24.99	98.5 %
Absorption correction	Sadabs
Max. and min. transmission	1.00000 and 0.40409
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3155 / 0 / 244
Goodness-of-fit on F ²	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0942, wR2 = 0.2726
R indices (all data)	R1 = 0.1374, wR2 = 0.2958
Extinction coefficient	0.017(8)
Largest diff. peak and hole	0.737 and -0.333 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd22430. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S	2052(2)	2310(2)	7839(1)	54(1)
O(1)	7734(7)	3668(6)	10577(3)	64(1)
O(2)	6730(6)	1503(6)	9672(3)	63(1)
O(3)	2597(7)	726(5)	7477(3)	66(1)
O(4)	483(6)	2536(7)	8333(4)	73(2)
N(1)	3556(7)	3079(8)	8564(4)	54(1)
Cl	6940(4)	10112(3)	6298(2)	100(1)
C(1)	5395(9)	3057(9)	8275(5)	51(2)
C(2)	6541(8)	3900(7)	9037(4)	47(2)
C(3)	7233(9)	5363(8)	9055(4)	49(2)
C(4)	7033(8)	6557(8)	8395(4)	50(2)
C(5)	8413(11)	7619(9)	8341(6)	71(2)
C(6)	8362(12)	8721(9)	7712(6)	79(2)
C(7)	6950(12)	8774(8)	7127(5)	67(2)
C(8)	5529(11)	7806(9)	7194(5)	68(2)
C(9)	5574(9)	6683(9)	7808(5)	61(2)
C(10)	7065(8)	3043(8)	9844(5)	49(2)
C(11)	7198(12)	545(9)	10404(5)	74(2)
C(12)	1981(9)	3446(8)	6902(4)	52(2)
C(13)	2783(10)	2950(10)	6045(5)	67(2)
C(14)	2816(11)	3935(11)	5356(5)	77(2)
C(15)	2132(11)	5476(11)	5499(6)	77(2)
C(16)	1342(11)	5950(10)	6344(7)	79(2)
C(17)	1274(11)	4951(9)	7032(5)	68(2)
C(18)	2235(14)	6549(14)	4748(7)	112(4)

Table 3. Bond lengths [Å] and angles [deg] for cd22430.

S-O(4)	1.409(5)
S-O(3)	1.434(5)
S-N(1)	1.604(6)
S-C(12)	1.742(6)
O(1)-C(10)	1.206(8)
O(2)-C(10)	1.309(8)
O(2)-C(11)	1.441(7)
N(1)-C(1)	1.479(8)
N(1)-H(10)	0.98(6)
C1-C(7)	1.735(7)
C(1)-C(2)	1.481(9)
C(1)-H(1)	0.97(5)
C(1)-H(2)	1.01(7)
C(2)-C(3)	1.334(9)
C(2)-C(10)	1.486(8)
C(3)-C(4)	1.470(9)
C(3)-H(3)	1.02(6)
C(4)-C(5)	1.390(10)
C(4)-C(9)	1.397(9)
C(5)-C(6)	1.373(10)
C(5)-H(5)	0.9300
C(6)-C(7)	1.358(12)
C(6)-H(6)	0.9300
C(7)-C(8)	1.368(11)
C(8)-C(9)	1.370(9)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(17)	1.375(10)
C(12)-C(13)	1.392(10)
C(13)-C(14)	1.366(10)
C(13)-H(13)	0.9300
C(14)-C(15)	1.397(12)
C(14)-H(14)	0.9300
C(15)-C(16)	1.369(11)
C(15)-C(18)	1.491(11)
C(16)-C(17)	1.375(10)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
O(4)-S-O(3)	120.2(3)
O(4)-S-N(1)	105.8(3)
O(3)-S-N(1)	106.9(3)
O(4)-S-C(12)	108.1(3)
O(3)-S-C(12)	108.2(3)
N(1)-S-C(12)	106.9(3)
C(10)-O(2)-C(11)	117.3(5)
C(1)-N(1)-S	120.5(4)
C(1)-N(1)-H(10)	100(3)
S-N(1)-H(10)	119(3)
N(1)-C(1)-C(2)	111.2(5)
N(1)-C(1)-H(1)	113(3)
C(2)-C(1)-H(1)	108(3)
N(1)-C(1)-H(2)	107(4)
C(2)-C(1)-H(2)	115(4)

H(1)-C(1)-H(2)	103(5)
C(3)-C(2)-C(1)	126.0(6)
C(3)-C(2)-C(10)	115.4(6)
C(1)-C(2)-C(10)	118.6(6)
C(2)-C(3)-C(4)	131.2(6)
C(2)-C(3)-H(3)	117(3)
C(4)-C(3)-H(3)	112(3)
C(5)-C(4)-C(9)	117.7(6)
C(5)-C(4)-C(3)	117.4(6)
C(9)-C(4)-C(3)	124.9(6)
C(6)-C(5)-C(4)	121.1(8)
C(6)-C(5)-H(5)	119.5
C(4)-C(5)-H(5)	119.5
C(7)-C(6)-C(5)	119.8(8)
C(7)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(6)-C(7)-C(8)	120.8(7)
C(6)-C(7)-C1	119.4(7)
C(8)-C(7)-C1	119.8(7)
C(7)-C(8)-C(9)	119.9(7)
C(7)-C(8)-H(8)	120.1
C(9)-C(8)-H(8)	120.1
C(8)-C(9)-C(4)	120.7(7)
C(8)-C(9)-H(9)	119.7
C(4)-C(9)-H(9)	119.7
O(1)-C(10)-O(2)	122.8(6)
O(1)-C(10)-C(2)	124.8(6)
O(2)-C(10)-C(2)	112.4(6)
O(2)-C(11)-H(11A)	109.5
O(2)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
O(2)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(17)-C(12)-C(13)	118.0(6)
C(17)-C(12)-S	119.8(5)
C(13)-C(12)-S	121.9(5)
C(14)-C(13)-C(12)	120.0(7)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(15)	121.8(8)
C(13)-C(14)-H(14)	119.1
C(15)-C(14)-H(14)	119.1
C(16)-C(15)-C(14)	117.6(7)
C(16)-C(15)-C(18)	121.5(9)
C(14)-C(15)-C(18)	120.9(9)
C(15)-C(16)-C(17)	120.7(8)
C(15)-C(16)-H(16)	119.6
C(17)-C(16)-H(16)	119.6
C(16)-C(17)-C(12)	121.8(7)
C(16)-C(17)-H(17)	119.1
C(12)-C(17)-H(17)	119.1
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd22430.
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	64(1)	51(1)	50(1)	16(1)	-8(1)	-7(1)
O(1)	89(4)	60(3)	43(3)	10(2)	-21(2)	-2(3)
O(2)	82(3)	52(3)	56(3)	18(2)	-15(2)	-7(2)
O(3)	92(4)	44(3)	62(3)	8(2)	-17(3)	-7(2)
O(4)	60(3)	90(4)	71(3)	22(3)	1(3)	-20(3)
N(1)	58(3)	67(4)	39(3)	18(3)	-2(2)	8(3)
Cl	169(3)	65(1)	74(1)	37(1)	28(2)	5(1)
C(1)	55(4)	58(5)	43(4)	12(3)	-1(3)	2(3)
C(2)	55(4)	48(4)	38(3)	11(3)	-2(3)	-2(3)
C(3)	57(4)	51(4)	40(3)	9(3)	1(3)	4(3)
C(4)	58(4)	45(4)	45(4)	6(3)	2(3)	-3(3)
C(5)	74(5)	64(5)	78(5)	23(4)	-9(4)	-8(4)
C(6)	91(6)	56(5)	95(6)	23(4)	14(5)	-14(4)
C(7)	99(6)	41(4)	64(5)	15(3)	13(4)	8(4)
C(8)	80(5)	65(5)	62(5)	28(4)	-4(4)	-1(4)
C(9)	60(4)	64(5)	63(4)	26(4)	-3(4)	-10(3)
C(10)	51(4)	47(4)	50(4)	15(3)	0(3)	-2(3)
C(11)	106(6)	51(4)	70(5)	26(4)	-29(4)	-8(4)
C(12)	63(4)	50(4)	45(4)	12(3)	-9(3)	-1(3)
C(13)	82(5)	69(5)	48(4)	10(4)	-13(4)	-1(4)
C(14)	93(6)	88(6)	49(4)	13(4)	-7(4)	-17(5)
C(15)	73(5)	87(6)	78(6)	38(5)	-21(4)	-11(5)
C(16)	89(6)	63(5)	92(6)	33(5)	-9(5)	8(4)
C(17)	87(5)	68(5)	51(4)	19(4)	4(4)	10(4)
C(18)	109(8)	146(10)	96(7)	78(7)	-14(6)	-10(7)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd22430.

	x	y	z	U(eq)
H(5)	9386	7583	8737	85
H(6)	9293	9429	7687	95
H(8)	4534	7910	6824	81
H(9)	4624	5997	7833	73
H(11A)	8442	459	10442	112
H(11B)	6683	-504	10256	112
H(11C)	6779	1044	11003	112
H(13)	3297	1949	5942	80
H(14)	3308	3569	4776	92
H(16)	846	6959	6453	95
H(17)	736	5303	7602	81
H(18A)	1091	6916	4609	168
H(18B)	2705	5970	4184	168
H(18C)	2978	7453	4968	168
H(1)	5580(70)	3550(60)	7700(40)	34(14)
H(2)	5680(80)	1900(80)	8070(40)	54(18)
H(3)	8020(70)	5780(60)	9620(40)	34(14)
H(10)	3470(70)	4200(80)	8850(40)	40

Table 6. Torsion angles [deg] for cd22430.

O(4)-S-N(1)-C(1)	-179.8(5)
O(3)-S-N(1)-C(1)	50.9(6)
C(12)-S-N(1)-C(1)	-64.8(6)
S-N(1)-C(1)-C(2)	177.2(5)
N(1)-C(1)-C(2)-C(3)	-103.7(7)
N(1)-C(1)-C(2)-C(10)	79.6(7)
C(1)-C(2)-C(3)-C(4)	3.1(11)
C(10)-C(2)-C(3)-C(4)	179.9(6)
C(2)-C(3)-C(4)-C(5)	-151.9(7)
C(2)-C(3)-C(4)-C(9)	26.8(11)
C(9)-C(4)-C(5)-C(6)	-1.8(11)
C(3)-C(4)-C(5)-C(6)	177.0(7)
C(4)-C(5)-C(6)-C(7)	-0.5(12)
C(5)-C(6)-C(7)-C(8)	3.9(12)
C(5)-C(6)-C(7)-C1	-177.2(6)
C(6)-C(7)-C(8)-C(9)	-5.0(12)
C1-C(7)-C(8)-C(9)	176.1(6)
C(7)-C(8)-C(9)-C(4)	2.6(11)
C(5)-C(4)-C(9)-C(8)	0.7(10)
C(3)-C(4)-C(9)-C(8)	-178.0(6)
C(11)-O(2)-C(10)-O(1)	-0.1(10)
C(11)-O(2)-C(10)-C(2)	179.5(6)
C(3)-C(2)-C(10)-O(1)	16.1(10)
C(1)-C(2)-C(10)-O(1)	-166.8(6)
C(3)-C(2)-C(10)-O(2)	-163.4(6)
C(1)-C(2)-C(10)-O(2)	13.6(8)
O(4)-S-C(12)-C(17)	39.7(7)
O(3)-S-C(12)-C(17)	171.4(6)
N(1)-S-C(12)-C(17)	-73.9(7)
O(4)-S-C(12)-C(13)	-147.2(6)
O(3)-S-C(12)-C(13)	-15.5(7)
N(1)-S-C(12)-C(13)	99.3(6)
C(17)-C(12)-C(13)-C(14)	-1.5(11)
S-C(12)-C(13)-C(14)	-174.7(6)
C(12)-C(13)-C(14)-C(15)	3.0(12)
C(13)-C(14)-C(15)-C(16)	-3.1(12)
C(13)-C(14)-C(15)-C(18)	178.0(8)
C(14)-C(15)-C(16)-C(17)	1.7(13)
C(18)-C(15)-C(16)-C(17)	-179.3(8)
C(15)-C(16)-C(17)-C(12)	-0.4(13)
C(13)-C(12)-C(17)-C(16)	0.2(12)
S-C(12)-C(17)-C(16)	173.6(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd22430 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
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Figure 1. The ORTEP draw of **12**.