Gold and BINOL-Phosphoric Acid Catalyzed Enantioselective Hydroamination/*N*-Sulfonyliminium Cyclization Cascade

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Experimental

(10b)

Crystal data

$C_{16}H_{17}BrN_2O{\cdot}CHCl_3$	V = 1918.80 (5) Å^3
M_r = 452.60	Z = 4
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 11.0236 (2) Å	μ = 2.57 mm^{-1}
b = 12.9544 (2) Å	T = 150 K
c = 13.4366 (2) Å	0.62 × 0.38 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer	4361 independent reflections
Absorption correction: Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	4092 reflections with $I > 2.0\sigma(I)$
T_{min} = 0.17, T_{max} = 0.46	R_{int} = 0.087
56832 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034	H-atom parameters constrained
$wR(F^2)$ = 0.083	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
S = 1.00	$\Delta\rho_{min}$ = −0.44 e Å^{-3}
4361 reflections	Absolute structure: Flack (1983), 1893 Friedel-pairs
255 parameters	Flack parameter: −0.007 (8)
162 restraints	

Table 1

Selected geometric parameters (Å, º)

Br1—C2	1.889 (3)	N13—C14	1.489 (3)
C2—C3	1.391 (4)	N13—C19	1.349 (3)

C2—C10	1.384 (4)	C14—C15	1.534 (3)
C3—N4	1.374 (3)	C14—C16	1.536 (3)
C3—C7	1.416 (4)	C16—C17	1.516 (4)
N4—C5	1.385 (3)	C17—C18	1.520 (4)
C5—C6	1.374 (3)	C18—C19	1.507 (4)
C5—C14	1.502 (3)	C19—O20	1.244 (3)
C6—C7	1.429 (4)	C21—Cl22	1.738 (3)
C6—C11	1.499 (4)	C21—Cl23	1.746 (3)
C7—C8	1.415 (4)	C21—Cl24	1.743 (3)
C8—C9	1.371 (5)	C25—Cl26	1.740 (5)
C9—C10	1.399 (5)	C25—Cl27	1.743 (5)
C11—C12	1.527 (4)	C25—Cl28	1.744 (5)
C12—N13	1.477 (3)		
Br1—C2—C3	119.8 (2)	C12—N13—C14	116.3 (2)
Br1—C2—C10	121.2 (2)	C12—N13—C19	119.0 (2)
C3—C2—C10	119.0 (3)	C14—N13—C19	124.7 (2)
C2—C3—N4	130.7 (2)	C5—C14—N13	105.81 (19)
C2—C3—C7	121.0 (2)	C5—C14—C15	110.8 (2)
N4—C3—C7	108.3 (2)	N13—C14—C15	110.0 (2)
C3—N4—C5	108.0 (2)	C5—C14—C16	109.1 (2)
N4—C5—C6	110.2 (2)	N13—C14—C16	110.1 (2)
N4—C5—C14	122.6 (2)	C15—C14—C16	111.0 (2)
C6—C5—C14	127.2 (2)	C14—C16—C17	111.1 (2)
C5—C6—C7	106.6 (2)	C16—C17—C18	108.3 (2)
C5—C6—C11	121.9 (2)	C17—C18—C19	115.2 (2)
C7—C6—C11	131.5 (2)	C18—C19—N13	120.3 (2)
C6—C7—C3	106.8 (2)	C18—C19—O20	118.8 (2)
C6—C7—C8	134.0 (3)	N13—C19—O20	120.9 (3)
C3—C7—C8	119.2 (3)	Cl22—C21—Cl23	110.61 (6)
C7—C8—C9	118.5 (3)	Cl22—C21—Cl24	110.54 (6)
C8—C9—C10	122.1 (3)	Cl23—C21—Cl24	110.61 (6)
C9—C10—C2	120.1 (3)	Cl26—C25—Cl27	110.58 (6)
C6—C11—C12	108.2 (2)	Cl26—C25—Cl28	110.60 (6)
C11—C12—N13	110.4 (2)	Cl27—C25—Cl28	110.59 (6)

Table 2

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H161···O20^{i}	0.96	2.33	3.229 (4)	155 (1)
C21—H211···C7	0.97	2.55	3.511 (4)	170 (1)
C25—H211···C7	1.11	2.55	3.517 (4)	145 (1)
C25—H251···C7	0.98	2.60	3.517 (4)	157 (1)
N4—H41···O20^{i}	0.84	1.99	2.809 (4)	166 (1)

Symmetry code: (i) −*x*+1/2, −*y*+1, *z*+1/2.

(15a)

Crystal data

$C_{21}H_{21}BrN_2O_2S$	V = 1920.19 (3) Å^3
M_r = 445.38	Z = 4
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.4507 (1) Å	μ = 2.27 mm^{-1}
b = 16.2752 (2) Å	T = 150 K
c = 11.5043 (1) Å	0.50 × 0.30 × 0.15 mm
β = 101.0903 (5)°	

Data collection

Nonius KappaCCD diffractometer	8412 independent reflections
Absorption correction: Multi-scan *DENZO/SCALEPACK* (Otwinowski & Minor, 1997)	7894 reflections with $I > 2.0\sigma(I)$
T_{min} = 0.54, T_{max} = 0.71	R_{int} = 0.063
35947 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029	H-atom parameters constrained
$wR(F^2)$ = 0.064	$\Delta\rho_{max}$ = 1.11 e Å^{-3}
S = 0.99	$\Delta\rho_{min}$ = −0.93 e Å^{-3}
8412 reflections	Absolute structure: Flack (1983), 3898 Friedel-pairs
488 parameters	Flack parameter: 0.010 (4)
1 restraint	

Table 3

Selected geometric parameters (Å, º)

Br1—C2	1.900 (2)	Br28—C29	1.901 (2)
C2—C3	1.385 (3)	C29—C30	1.386 (4)
C2—C7	1.392 (4)	C29—C34	1.381 (4)
C3—C4	1.389 (3)	C30—C31	1.387 (4)
C4—C5	1.393 (3)	C31—C32	1.392 (4)
C4—C8	1.521 (3)	C32—C33	1.388 (3)
C5—C6	1.390 (4)	C33—C34	1.401 (3)
C6—C7	1.383 (4)	C33—C35	1.514 (3)
C8—N9	1.449 (3)	C35—N36	1.460 (3)
N9—C10	1.384 (3)	N36—C37	1.384 (3)
N9—C17	1.397 (3)	N36—C40	1.395 (3)
C10—C11	1.394 (3)	C37—C38	1.406 (3)
C10—C15	1.416 (3)	C37—C54	1.404 (3)
C11—C12	1.384 (4)	C38—C39	1.432 (3)
C12—C13	1.401 (4)	C38—C51	1.410 (3)
C13—C14	1.382 (4)	C39—C40	1.368 (3)
C14—C15	1.396 (3)	C39—C49	1.500 (3)
C15—C16	1.437 (3)	C40—C41	1.519 (3)
C16—C17	1.367 (3)	C41—N42	1.497 (3)

C16—C26	1.495 (3)	C41—C47	1.554 (3)
C17—C18	1.515 (3)	C41—C50	1.529 (3)
C18—N19	1.493 (3)	N42—S43	1.642 (2)
C18—C24	1.557 (3)	N42—C48	1.475 (3)
C18—C27	1.526 (3)	S43—O44	1.442 (2)
N19—S20	1.637 (2)	S43—O45	1.436 (2)
N19—C25	1.475 (3)	S43—C46	1.765 (3)
S20—O21	1.432 (2)	C46—C47	1.517 (4)
S20—O22	1.4389 (19)	C48—C49	1.528 (4)
S20—C23	1.768 (3)	C51—C52	1.372 (4)
C23—C24	1.525 (4)	C52—C53	1.409 (4)
C25—C26	1.522 (3)	C53—C54	1.384 (4)
Br1—C2—C3	118.66 (18)	Br28—C29—C30	119.17 (19)
Br1—C2—C7	119.59 (18)	Br28—C29—C34	118.45 (19)
C3—C2—C7	121.7 (2)	C30—C29—C34	122.4 (2)
C2—C3—C4	119.4 (2)	C29—C30—C31	118.1 (2)
C3—C4—C5	119.7 (2)	C30—C31—C32	120.5 (2)
C3—C4—C8	117.6 (2)	C31—C32—C33	120.8 (2)
C5—C4—C8	122.8 (2)	C32—C33—C34	119.0 (2)
C4—C5—C6	119.9 (2)	C32—C33—C35	123.6 (2)
C5—C6—C7	121.1 (2)	C34—C33—C35	117.4 (2)
C2—C7—C6	118.2 (2)	C33—C34—C29	119.2 (2)
C4—C8—N9	113.68 (19)	C33—C35—N36	113.44 (19)
C8—N9—C10	121.95 (19)	C35—N36—C37	121.92 (19)
C8—N9—C17	128.4 (2)	C35—N36—C40	130.2 (2)
C10—N9—C17	108.04 (18)	C37—N36—C40	107.90 (19)
N9—C10—C11	129.7 (2)	N36—C37—C38	108.5 (2)
N9—C10—C15	108.5 (2)	N36—C37—C54	129.4 (2)
C11—C10—C15	121.9 (2)	C38—C37—C54	122.1 (2)
C10—C11—C12	117.1 (2)	C37—C38—C39	106.6 (2)
C11—C12—C13	121.7 (2)	C37—C38—C51	118.8 (2)
C12—C13—C14	121.0 (2)	C39—C38—C51	134.6 (2)
C13—C14—C15	118.7 (2)	C38—C39—C40	107.6 (2)
C10—C15—C14	119.5 (2)	C38—C39—C49	129.2 (2)
C10—C15—C16	106.2 (2)	C40—C39—C49	123.2 (2)
C14—C15—C16	134.1 (2)	N36—C40—C39	109.4 (2)
C15—C16—C17	107.8 (2)	N36—C40—C41	124.8 (2)
C15—C16—C26	128.5 (2)	C39—C40—C41	125.7 (2)
C17—C16—C26	123.4 (2)	C40—C41—N42	107.20 (18)
N9—C17—C16	109.5 (2)	C40—C41—C47	113.02 (19)
N9—C17—C18	124.5 (2)	N42—C41—C47	103.86 (18)
C16—C17—C18	125.7 (2)	C40—C41—C50	111.70 (19)
C17—C18—N19	107.40 (18)	N42—C41—C50	108.67 (19)
C17—C18—C24	112.60 (19)	C47—C41—C50	111.9 (2)
N19—C18—C24	104.89 (19)	C41—N42—S43	113.44 (15)
C17—C18—C27	112.3 (2)	C41—N42—C48	117.98 (19)
N19—C18—C27	108.10 (19)	S43—N42—C48	119.11 (17)
C24—C18—C27	111.1 (2)	N42—S43—O44	110.06 (13)
C18—N19—S20	113.29 (15)	N42—S43—O45	110.16 (12)

C18—N19—C25	120.05 (18)	O44—S43—O45	116.07 (14)
S20—N19—C25	119.29 (16)	N42—S43—C46	95.66 (11)
N19—S20—O21	109.75 (12)	O44—S43—C46	107.95 (13)
N19—S20—O22	109.60 (11)	O45—S43—C46	115.04 (14)
O21—S20—O22	116.58 (13)	S43—C46—C47	101.51 (17)
N19—S20—C23	95.05 (11)	C41—C47—C46	106.6 (2)
O21—S20—C23	108.72 (13)	N42—C48—C49	111.8 (2)
O22—S20—C23	115.00 (13)	C48—C49—C39	109.4 (2)
S20—C23—C24	100.68 (17)	C38—C51—C52	119.1 (2)
C23—C24—C18	107.68 (19)	C51—C52—C53	121.5 (2)
N19—C25—C26	111.43 (19)	C52—C53—C54	120.8 (2)
C25—C26—C16	107.9 (2)	C37—C54—C53	117.6 (2)

Table 4

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H121···O44^{i}	0.94	2.54	3.390 (4)	152
C23—H232···O44^{ii}	0.98	2.51	3.347 (4)	143
C35—H351···O21	0.96	2.55	3.430 (4)	152
C46—H461···O22^{iii}	0.97	2.50	3.282 (4)	137

Symmetry codes: (i) $x+1$, y, $z-1$; (ii) $x+1$, y, z; (iii) $-x+1$, $y-1/2$, $-z+1$.

For both compounds, data collection: *COLLECT* (Nonius, 2001).; cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997). Program(s) used to solve structure: Superflip (Palatinus & Chapuis, 2007) for (10b); *SIR92* (Altomare *et al.*, 1994) for (15a). For both compounds, program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS* (Betteridge *et al.*, 2003).

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