Electronic Supplementary Information

Chirality-dependent halogen bond in axially chiral quinazolin-4-one derivatives bearing *ortho*-halophenyl group

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(Contents)

Experimental Section

Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. In ^{1}H and ^{13}C NMR spectra, chemical shifts were expressed in δ (ppm) downfield from $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm), respectively. HRMS were recorded on a double focusing magnetic sector mass spectrometer using electron impact ionization. Column chromatography was performed on silica gel (75-150 mm). Medium-pressure liquid chromatography (MPLC) was performed on a 25 x 4 cm i. d. prepacked column (silica gel, 10 μm) with a UV detector. High-performance liquid chromatography (HPLC) was performed on a 25 x 0.4 cm i. d. chiral column with a UV detector.

3-(2-Bromophenyl)-2-methylquinazolin-4(3H)-one (1a). *Rac*-**1a** and *ent*-**1a** (99% ee) were prepared in accordance with the synthetic procedure that we previously reported.[1]

3-(2-Fluorophenyl)-2-methylquinazolin-4(3H)-one (1d). *Rac*-**1d** were prepared in accordance with the synthetic procedure that we previously reported.[2] The enantiomer of **1d** was separated through MPLC using a chiral AY-H column (25 X 1 cm, eluent: *n*-hexane/2-propanol = 1). **1d**: white solid; mp 97-99 °C (99% ee); 100-102 °C (racemate): $[\alpha]_D = +2.81$ (99% ee, c = 0.724, $CHCl_3$).

The synthesis of other 3-(2-halophenyl)-2-methylquinazolin-4(3H)-one derivatives *rac*-**1b**,**c** and their enantiomer separation were performed in accordance with following general procedure.

General procedure: Under N_2 atmosphere, to 2-chloroaniline (306 mg, 2.4 mmol) and *N*-acethyl anthranilic acid (358 mg, 2.0 mmol) in toluene (8.0 mL) was added PCl_3 (412 mg, 3.0 mmol), and the reaction mixture was stirred for 30 min at rt and for 7 h at 130 °C. The mixture was poured into water and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 3) gave *rac*-**1b** (378 mg, 65%). The enantiomers of **1b** were separated through MPLC using a chiral AY-H column (25 x 1 cm, eluent; *n*-hexane/2-propanol = 1).

3-(2-Chlorophenyl)-2-methylquinazolin-4(3H)-one (1b).[3] **1b**: white solid; mp 131-133 °C (99% ee); 130-131 °C (racemate): $[\alpha]_D = +102.25$ (99% ee, c = 0.454, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.27 (1H, d, *J* = 8.2 Hz), 7.77 (1H, m), 7.68 (1H, d, *J* = 8.2 Hz), 7.61 (1H, m), 7.45-7.49 (3H, m), 7.34 (1H, m), 2.22 (3H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 161.4, 153.6, 147.4, 135.3, 134.7, 132.5, 130.8, 130.7, 129.8, 128.4, 127.1, 126.8, 126.7, 120.5, 23.5. ^1H-NMR and ^{13}C-NMR spectra of **1b** coincided with those described in the literature[3] (*Rac*-**1b** is commercially available).

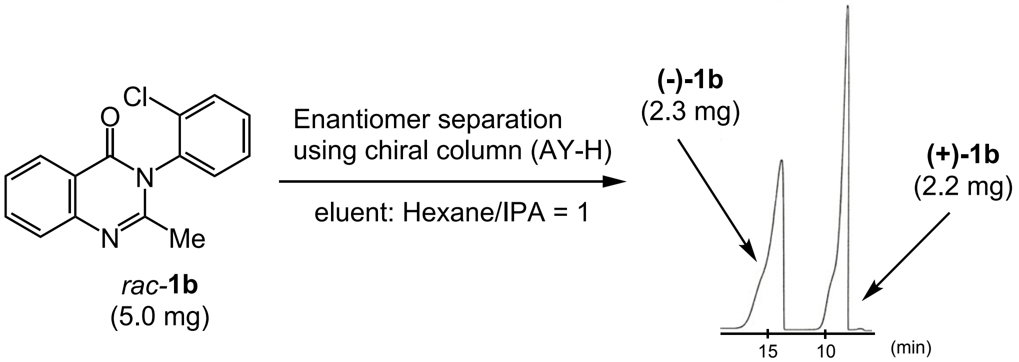
3-(2-Iodophenyl)-2-methylquinazolin-4(3H)-one (1c).[4] **1c**: white solid; mp 54-57 °C (99% ee); 132-133 °C (racemate): $[\alpha]_D = +172.4$ (99% ee, c = 0.420, $CHCl_3$); IR (neat) 1682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.29 (1H, d, *J* = 7.8 Hz), 8.01 (1H, td, *J* = 1.2, 8.0 Hz), 7.78 (1H, m), 7.70 (1H, d, *J* = 8.0 Hz), 7.54 (1H, tt, *J* = 1.4, 7.8 Hz), 7.46 (1H, tt, *J* = 1.4, 7.8 Hz), 7.34 (1H, dd, *J* = 1.0, 8.0 Hz), 7.21 (1H, tt, *J* = 1.8, 7.8 Hz), 2.21 (3H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 161.3, 153.4, 147.4, 140.6, 140.2, 134.8, 130.8, 130.0, 129.0, 127.2, 126.9, 126.7, 120.7, 98.9, 24.1; MS (*m/z*) 385 (MNa^+); HRMS. Calcd for $C_{15}H_{11}IN_2NaO$ (MNa^+) 384.98138. Found: 384.97883.

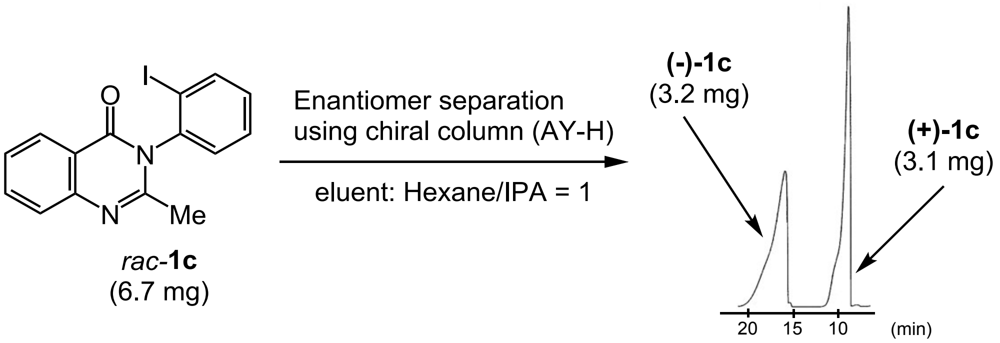
(References)

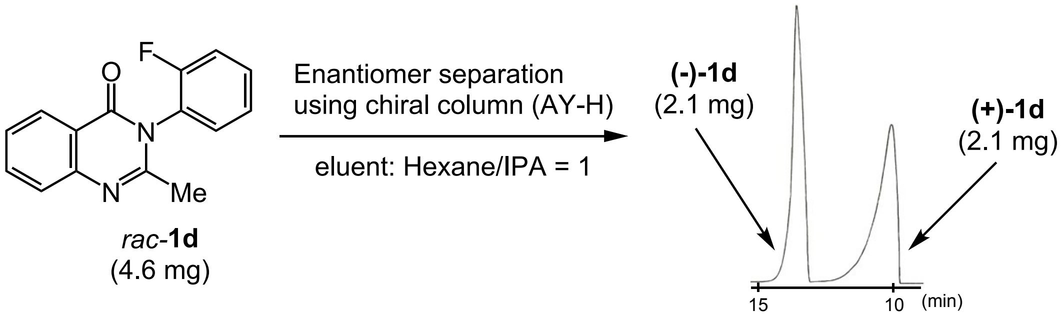
1) a) M. Hirai, S. Terada, H. Yoshida, K. Ebine, T. Hirata and O. Kitagawa, *Org. Lett.* 2016, **18**, 5700. b) S. Terada, M. Hirai, A. Honzawa, O. Kitagawa, A. Kamizela, A. Wzorek and V. A. Soloshonok, *Chem. Eur. J.* 2017, **23**, 14631.
2) A. Iida, M. Matsuoka, H. Hasegawa, N. Vanthuyne, D. Farran, C. Roussel, O. Kitagawa, *J. Org. Chem.* 2019, DOI: 10.1021/acs.joc.8b03043.
3) K. R. Arun, M. C. Uma, G. Sarheesh, J. C. Reddy, K. Rajender, *Adv. Syn. Catal.* 2011, **353**, 401.
4) J. F. Wolfe, T. L. Rathman, M. C. Sleevi, J. A. Campbell, T. D. Greenwood, *J. Med. Chem.* 1990, **33**, 161.

(Enantiomer Separation of **1b-d** through MPLC using a chiral AY-H column)

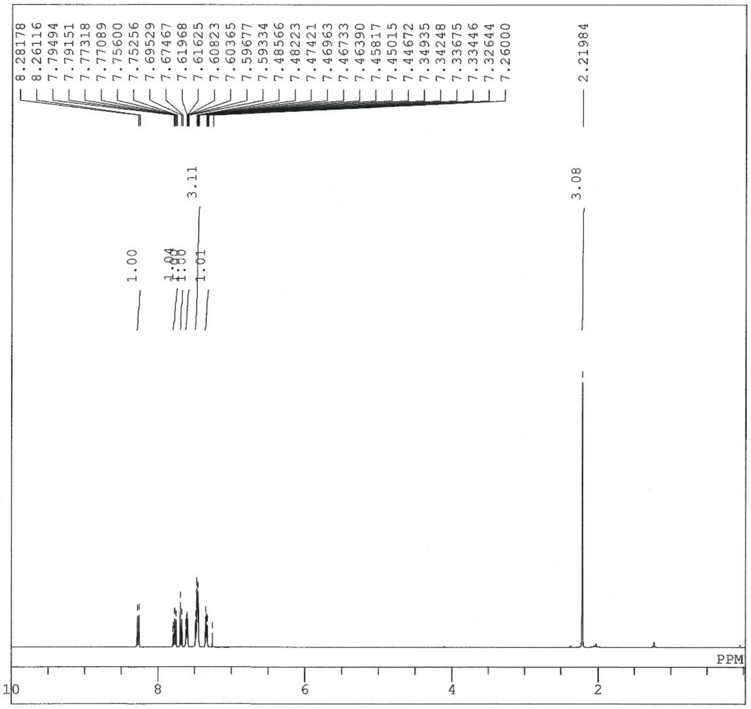
AY-H column (25 X 1 cm), eluent: *n*-hexane/2-propanol = 1, flow rate: 4.0 mL/min







Copies of ^{1}H- and ^{13}C-NMR spectra



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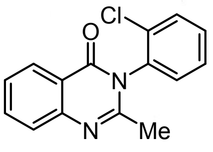
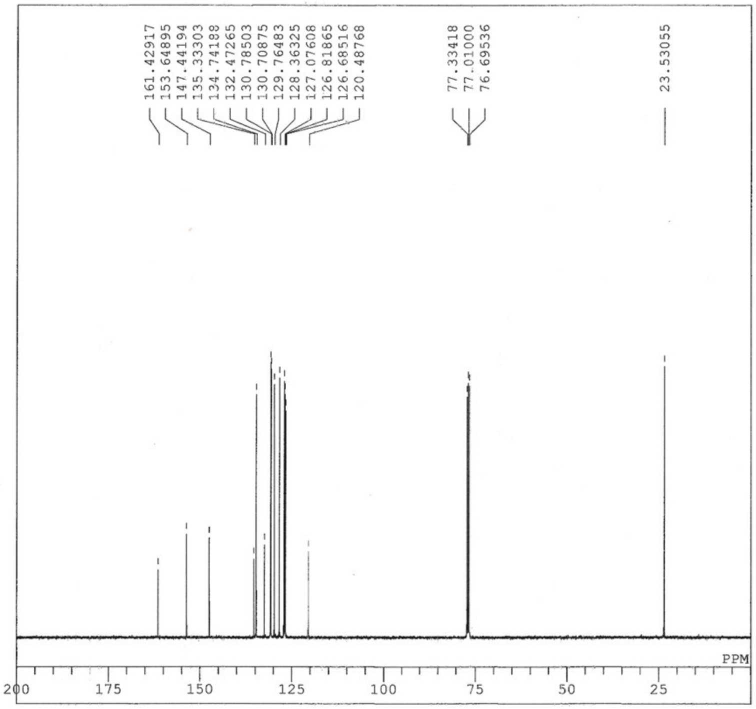


1b



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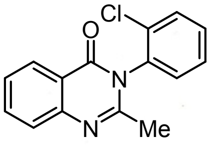

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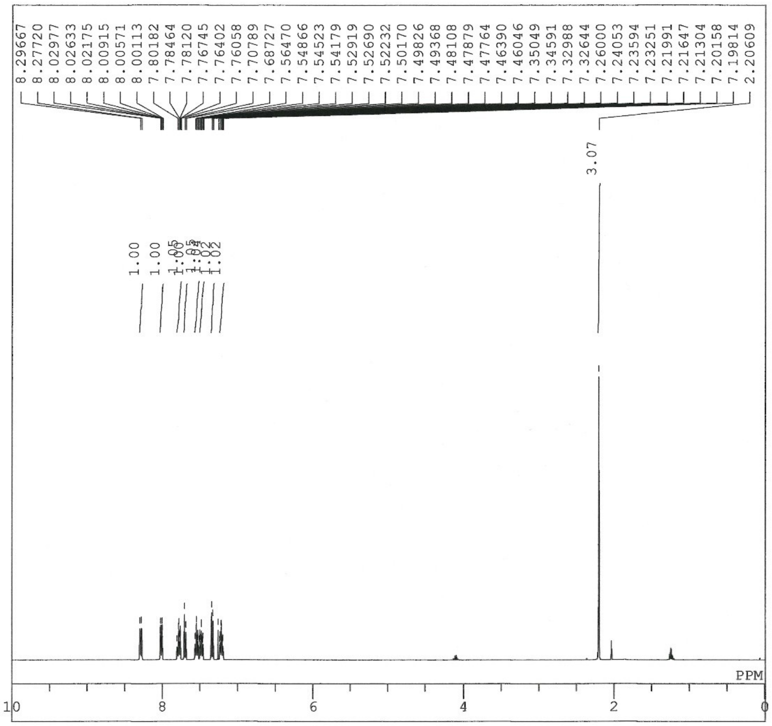

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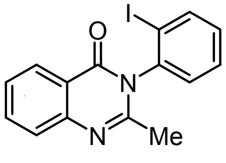
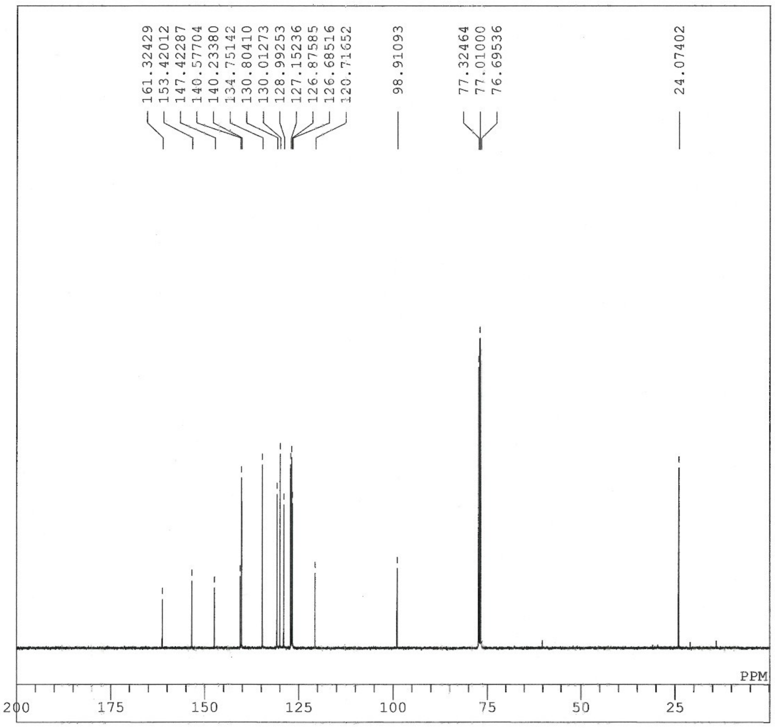


1c



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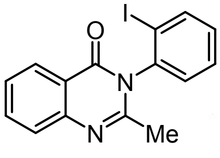


1c

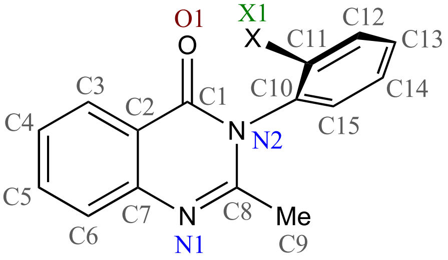
X-Ray single crystal data

The single crystal structures were determined by a Bruker D8 QUEST diffractometer with a graphite monochrometer and Mo*K*α radiation ($\lambda = 0.71073$ Å) generated at 50 kV and 1 mA. All the crystals were coated by paratone-N oil and measured at 100 K. SHELXT program was used for solving the structures. Refinement and further calculations were carried out using SHELXL. The crystal data and structure refinement of the racemic compounds, *rac*-**1a-d**, and the corresponding enantiomers, *ent*-**1a-c**, are summarized in Tables S1 and S2, respectively. All H atoms were placed in geometrically idealized positions and refined as riding, with aromatic C-H = 0.95 Å and aliphatic C-H = 0.98 Å [Uiso(H) = 1.2Ueq(C)]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

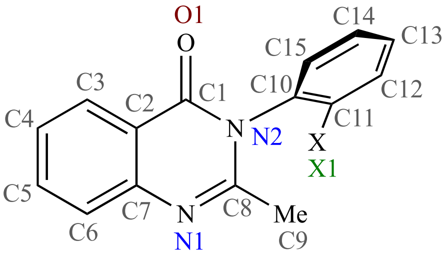
(1) Preparation of single crystals of **1b-d.**

1) *rac*-**1b**: The crystal was obtained by slow evaporation from CH_2Cl_2 and *n*-hexane (1:1) solution.
2) *rac*-**1c**: The crystal was obtained by slow evaporation from $CHCl_3$ and *n*-hexane (1:1) solution.
3) *rac*-**1d**: The crystal was obtained by slow evaporation from $CHCl_3$ and *n*-hexane (1:1) solution.
4) *ent*-**1b**: The crystal was obtained by slow evaporation from $CHCl_3$ and *n*-hexane (1:1) solution.
5) *ent*-**1c**: The crystal was obtained by slow evaporation from $CHCl_3$ and *n*-hexane (1:1) solution.
6) *ent*-**1d**: no single crystals were obtained from the examination of several solutions.

(2) Molecular structures with the numbering schemes, which were adapted by ref.6.



(P)-**1a**



(M)-**1a**

ref.6) M. Hirai, S. Terada, H. Yoshida, K. Ebine, T. Hirata and O. Kitagawa, *Org. Lett*. **2016**, *18,* 5700.

(3) Crystal Data of *rac*-**1a-d**.

Three racemic crystals *rac*-**1b-d** were measured and the crystal data and structures of *rac*-**1a-d** were summarized in Table S1 and Figures S1-4, respectively.

Table S1 Crystal data of *rac*-**1a-d**.

	rac-**1a** (ref.7)	*rac*-**1b**	*rac*-**1c**	*rac*-**1d**
Chemical formula	$C_{15}H_{11}BrN_2O$	$C_{15}H_{11}ClN_2O$	$C_{15}H_{11}IN_2O$	$C_{15}H_{11}FN_2O$
Description, color	block, colorless	block, colorless	block, colorless	block, colorless
Crystal size	0.178x0.111x0.051	0.187x0.073x0.041	0.880x0.176x0.130	0.780x0.422x0.322
Formula weight	315.17	270.71	362.16	254.26
T [K]	90	100	100	100
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1$/c	$P2_1$/c	Iba2	$P2_1$/c
a [Å]	17.6787(10)	17.616(3)	15.8947(3)	6.4513(3)
b [Å]	5.5608(3)	5.6004(10)	21.2266(4)	7.9032(3)
c [Å]	13.0283(7)	12.779(2)	8.08590(10)	23.1654(9)
α [°]	90	90	90	90
β [°]	97.8320(10)	98.051(6)	90	96.1070(10)
γ [°]	90	90	90	90
V [Å^3]	1268.84(12)	1248.2(4)	2728.11(8)	1174.41(8)
Z	4	4	8	4
D_c [g cm^{-3}]	1.650	1.440	1.763	1.438
F(000)	632	560	1408	528
R_{int}	0.0157	0.0788	0.0223	0.0355
Flack			0.010(9)	
Reflections measured	5869	10023	15044	12721
Reflections independent	2243	2194	2347	2074
GOF	1.095	1.107	1.081	1.103
R [$(I) > 2\sigma(I)$]	0.0181	0.0572	0.0134	0.0387
wR (F_o^2)	0.0481	0.1317	0.0333	0.0977
CCDC No.	1561609	1897963	1897966	1897964

ref.7) S. Terada, M. Hirai, A. Honzawa, O. Kitagawa, A. Kamizela, A. Wzorek and V. A. Soloshonok, *Chem. Eur. J.* **2017**, *23*, 14631.

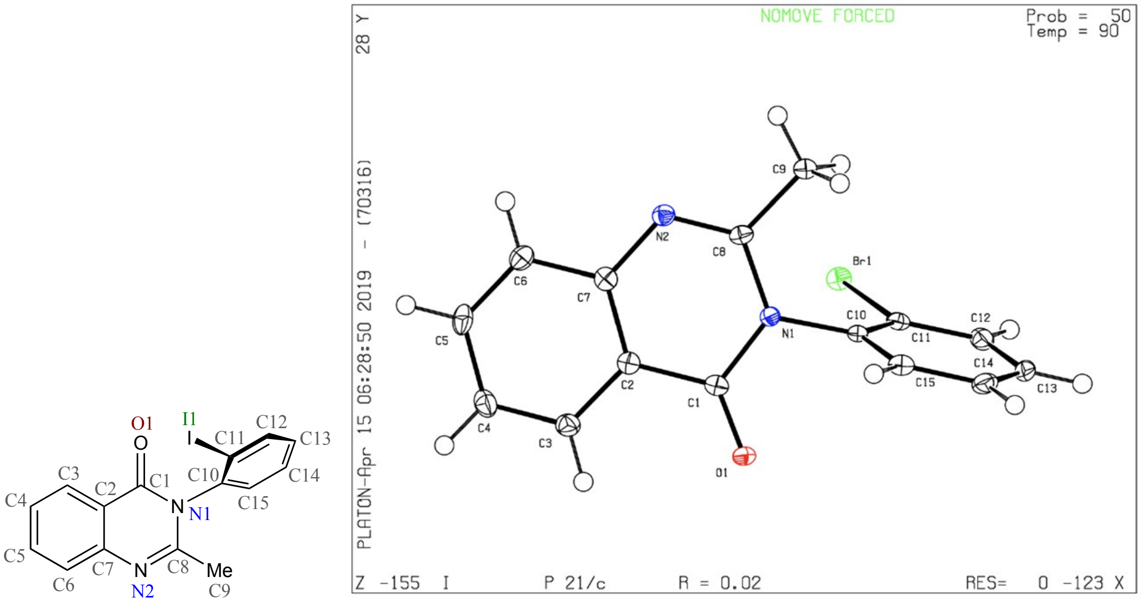


Fig. S1 Crystal structure of *rac*-**1a** at 90 K with 50% probability thermal ellipsoids (from ref.7). The numbering schemes of N1 and N2 are opposite to other crystals (we did not change the numbering because of the previously reported structure).

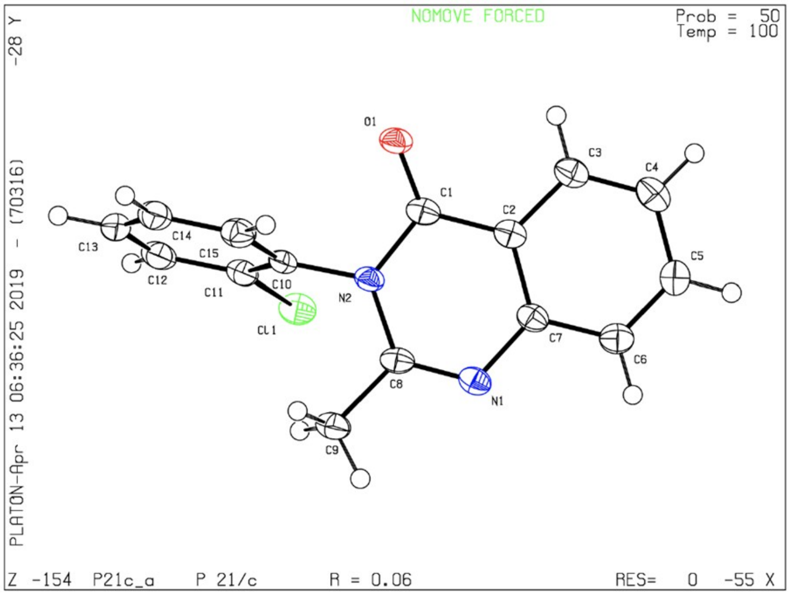


Fig. S2 Crystal structure of *rac*-**1b** at 100 K with 50% probability thermal ellipsoids. The numbering schemes were adapted to the first report of *ent*-**1a** by ref.6.

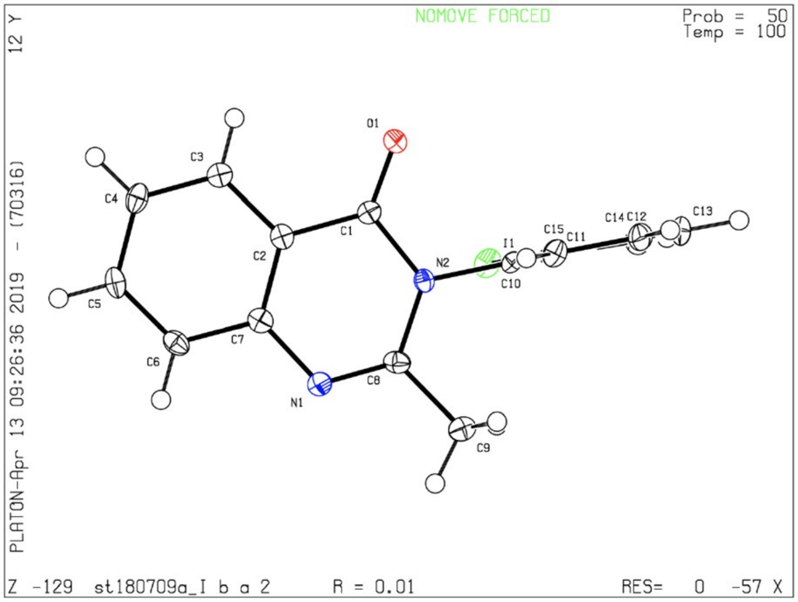


Fig. S3 Crystal structure of *rac*-**1c** at 100 K with 50% probability thermal ellipsoids.

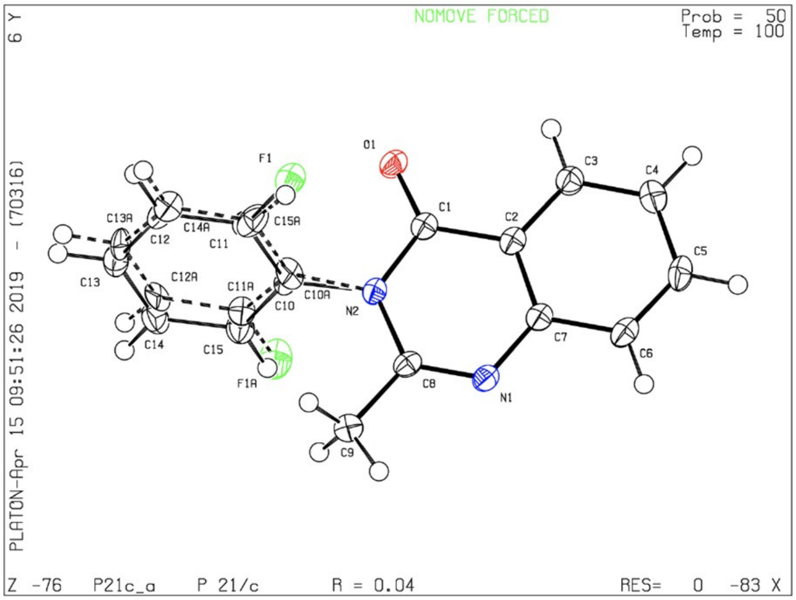


Fig. S4 Crystal structure of *rac*-**1d** at 100 K with 50% probability thermal ellipsoids. The site occupancy factor of the major structure (solid line) is 0.796(3) and the corresponding minor structure (dashed line) is 0.204(3).

(4) Crystal Data of *ent*-**1a-c**.

Three racemic crystals *ent*-**1b** and *ent*-**1c** were measured, and the crystal data and structures of *ent*-**1a-c** were summarized in Table S2 and Figures S5-7, respectively.

Table S2 Crystal data of *ent*-**1a-c**.

	ent-**1a** (ref.6)	*ent*-**1b**	*ent*-**1c**
Chemical formula	$C_{15}H_{11}BrN_2O$	$C_{15}H_{11}ClN_2O$	$C_{15}H_{11}IN_2O$
Description, color	block, colorless	block, colorless	block, colorless
Crystal size	0.120x0.070x0.060	0.629x0.410x0.361	0.214x0.190x0.173
Formula weight	315.17	270.71	362.16
T [K]	90	100	100
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1$	$P2_1$
a [Å]	7.5938(3)	8.8518(2)	10.8013(2)
b [Å]	10.3102(4)	15.3215(3)	15.1552(3)
c [Å]	16.6572(7)	10.3543(3)	12.7524(3)
α [°]	90	90	90
β [°]	90	113.2740(10)	94.8710(10)
γ [°]	90	90	90
V [Å^3]	1304.15(9)	1290.01(5)	2079.98(7)
Z	4	4	6
D_c [g cm^{-3}]	1.605	1.394	1.735
$F(000)$	632	560	1056
R_{int}	0.0194	0.0212	0.0301
Flack	0.017(3)	-0.011(13)	-0.019(8)
Reflections measured	12544	14814	23993
Reflections independent	2276	4513	7181
GOF	1.070	1.055	1.074
$R [(I) > 2\sigma(I)]$	0.0137	0.0221	0.0181
$wR (F_o^2)$	0.0350	0.0565	0.0373
CCDC No.	1492721	1897962	1897965

ref.6) M. Hirai, S. Terada, H. Yoshida, K. Ebine, T. Hirata and O. Kitagawa, *Org. Lett*. **2016**, *18,* 5700.

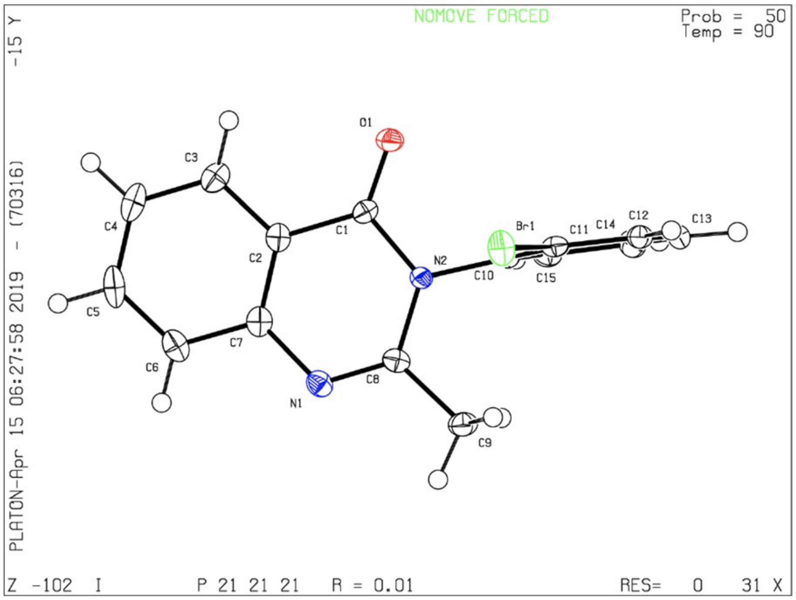


Fig. S5 Crystal structure of *ent*-**1a** at 90 K with 50% probability thermal ellipsoids (ref.6).

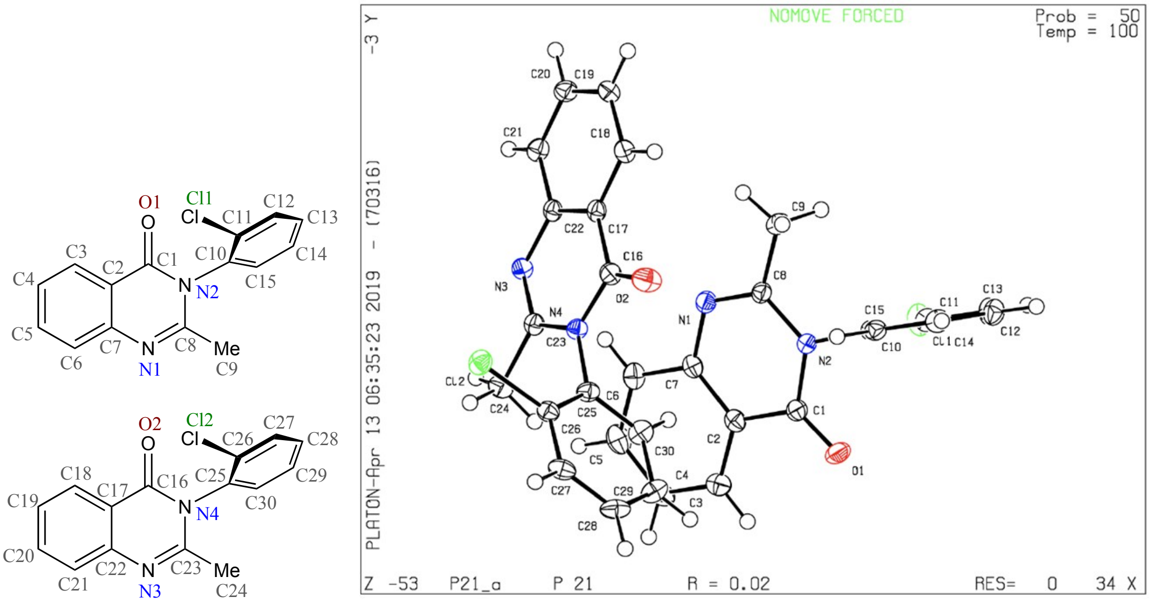


Fig. S6 Crystal structure of *ent*-**1b** at 100 K with 50% probability thermal ellipsoids. Flack parameter of the crystal is -0.011(13).

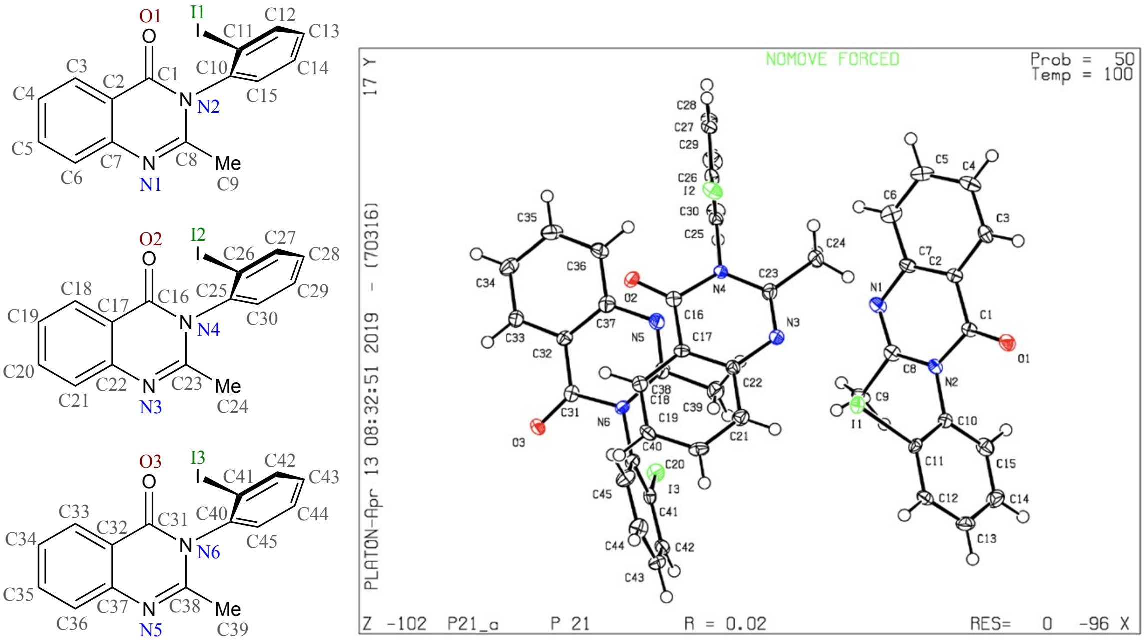


Fig. S7 Crystal structure of *ent*-**1b** at 100 K with 50% probability thermal ellipsoids. Flack parameter of the crystal is -0.019(8).

(5) Intramolecular distances of *rac*-**1a-d** and *ent*-**1a-c.**

Table S3. The bond lengths of *rac*-**1a-d**.

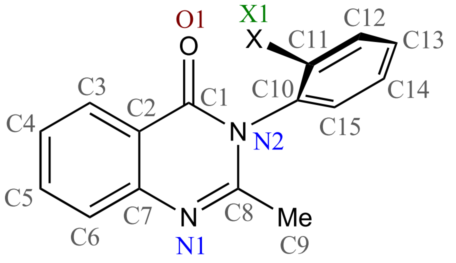
	rac-**1a** (ref.7)	*rac*-**1b**	*rac*-**1c**	*rac*-**1d**
X1—C11	1.9028 (18)	1.739 (4)	2.101 (3)	1.335 (3)
C1—O1	1.223 (2)	1.232 (4)	1.215 (4)	1.2253 (18)
C1—N2 (N1 for **1a**)	1.407 (2)	1.400 (4)	1.410 (4)	1.404 (2)
C1—C2	1.464 (3)	1.452 (5)	1.457 (4)	1.460 (2)
C2—C7	1.405 (3)	1.402 (5)	1.397(4)	1.403 (2)
C2—C3	1.404 (3)	1.408 (5)	1.406 (4)	1.394 (2)
C3—C4	1.380 (3)	1.372 (5)	1.380 (4)	1.382 (2)
C3—H3	0.9500	0.9500	0.9500	0.9500
C4—C5	1.401 (3)	1.397 (5)	1.401 (5)	1.399 (2)
C4—H4	0.9500	0.9500	0.9500	0.9500
C5—C6	1.382 (3)	1.368 (5)	1.378 (4)	1.373 (2)
C5—H5	0.9500	0.9500	0.9500	0.9500
C6—C7	1.405 (3)	1.404 (5)	1.402 (4)	1.406 (2)
C6—H6	0.9500	0.9500	0.9500	0.9500
C7—N1 (N2 for **1a**)	1.396 (2)	1.397 (4)	1.399 (4)	1.386 (2)
C8—N1 (N2 for **1a**)	1.292 (2)	1.297 (4)	1.293 (5)	1.290 (2)
C8—N2 (N1 for **1a**)	1.402 (2)	1.399 (4)	1.386 (5)	1.4028 (19)
C8—C9	1.496 (2)	1.496 (5)	1.500 (4)	1.494 (2)
C9—H9A	0.9800	0.9800	0.9800	0.9800
C9—H9B	0.9800	0.9800	0.9800	0.9800
C9—H9C	0.9800	0.9800	0.9800	0.9800
C10—C15	1.386 (3)	1.384 (5)	1.380 (5)	1.3900
C10—C11	1.394 (3)	1.395 (5)	1.394 (4)	1.3900
C10—N2 (N1 for **1a**)	1.444 (2)	1.434 (4)	1.444 (4)	1.458 (3)
C11—C12	1.385 (3)	1.384 (5)	1.391 (5)	1.3900
C12—C13	1.390 (3)	1.383 (5)	1.383 (6)	1.3900
C12—H12	0.9500	0.9500	0.9500	0.9500
C13—C14	1.385 (3)	1.381 (5)	1.389 (4)	1.3900
C13—H13	0.9500	0.9500	0.9500	0.9500
C14—C15	1.386 (3)	1.382 (5)	1.398 (5)	1.3900
C14—H14	0.9500	0.9500	0.9500	0.9500
C15—H15	0.9500	0.9500	0.9500	0.9500

Table S4. Selected bond lengths of *ent*-**1a-c**.

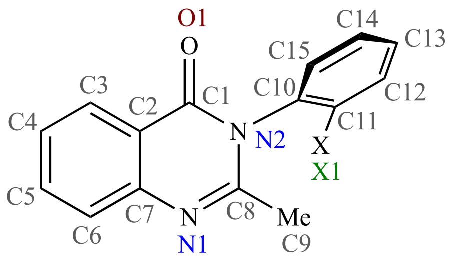
	ent-**1a** (ref.6)	*ent*-**1b**	*ent*-**1c**
X1—C11	1.901 (2)	1.732 (2)	2.105 (4)
C1—O1	1.219 (3)	1.214 (3)	1.215 (5)
C1—N2	1.402 (3)	1.408 (3)	1.407 (5)
C1—C2	1.466 (3)	1.461 (3)	1.465 (6)
C2—C7	1.393 (3)	1.398 (3)	1.401 (6)
C2—C3	1.402 (3)	1.400 (3)	1.398 (6)
C3—C4	1.380 (3)	1.378 (3)	1.368 (6)
C3—H3	0.9500	0.9500	0.9500
C4—C5	1.399 (4)	1.396 (3)	1.399 (7)
C4—H4	0.9500	0.9500	0.9500
C5—C6	1.375 (3)	1.381 (3)	1.375 (7)
C5—H5	0.9500	0.9500	0.9500
C6—C7	1.412 (3)	1.404 (3)	1.398 (6)
C6—H6	0.9500	0.9500	0.9500
C7—N1	1.398 (3)	1.397 (3)	1.394 (6)
C8—N1	1.294 (3)	1.296 (3)	1.295 (6)
C8—N2	1.396 (3)	1.393 (3)	1.384 (6)
C8—C9	1.493 (3)	1.493 (3)	1.501 (6)
C9—H9A	0.9800	0.9800	0.9800
C9—H9B	0.9800	0.9800	0.9800
C9—H9C	0.9800	0.9800	0.9800
C10—C11	1.389 (3)	1.381 (3)	1.393 (6)
C10—C15	1.388 (3)	1.393 (3)	1.381 (6)
C10—N2	1.449 (3)	1.442 (2)	1.445 (5)
C11—C12	1.379 (3)	1.384 (3)	1.395 (6)
C12—C13	1.390 (3)	1.383 (3)	1.394 (6)
C12—H12	0.9500	0.9500	0.9500
C13—C14	1.384 (3)	1.387 (3)	1.380 (7)
C13—H13	0.9500	0.9500	0.9500
C14—C15	1.388 (3)	1.390 (3)	1.387 (7)
C14—H14	0.9500	0.9500	0.9500
C15—H15	0.9500	0.9500	0.9500

For crystals of *ent*-**1b** and **1c**, the bond lengths of one molecule (C1-15, N1-2, O1, X1) are summarized here.

(6) Intramolecular angles of *rac*-**1a-d** and *ent*-**1a-c.**



(P)-**1a**



(M)-**1a**

Table S5. Selected bond angles and torsion angles of *rac*-**1a-c**.

	rac-**1a** (ref.7)	*rac*-**1b**	*rac*-**1c**	*rac*-**1d**
O1—C1—N2 (N1 for **1a**)	120.87 (16)	120.4 (3)	121.1 (3)	120.60 (13)
C1—N2—C10 (N1 for **1a**)	116.57 (14)	117.2 (3)	117.0 (2)	116.96 (18)
C15—C10—N2 (N1 for **1a**)	119.51 (16)	120.0 (3)	119.0 (3)	122.0 (2)
C11—C10—N2 (N1 for **1a**)	120.90 (15)	120.8 (3)	120.3 (3)	118.0 (2)
C12—C11—**X1**	119.42 (14)	120.0 (3)	119.7 (2)	120.5 (2)
C10—C11—**X1**	120.10 (13)	119.7 (3)	121.4 (2)	119.5 (2)
N1—C8—N2	123.27 (16)	123.4 (3)	124.2 (3)	123.22 (14)
N2—C8—C9 (N1 for **1a**)	119.77 (15)	117.0 (3)	118.5 (3)	117.68 (13)
O1—C1—N2—C10 (N1 for **1a**)	6.0 (2)	5.9 (4)	−3.3 (4)	1.2 (2)
C11—C10—N2—C1 (N1 for **1a**)	101.7 (2)	100.8 (4)	−90.9 (3)	−70.5 (3)

Table S6. Selected bond angles and torsion angles of *ent*-**1a-c**.

	ent-**1a** (ref.6)	*ent*-**1b**	*ent*-**1c**
O1—C1—N2 (N1 for **1a**)	120.83 (19)	120.49 (19)	121.3 (4)
C1—N2—C10 (N1 for **1a**)	117.41 (18)	115.32 (16)	1.215 (5)
C15—C10—N2 (N1 for **1a**)	118.77 (19)	120.51 (18)	120.0 (4)
C11—C10—N2 (N1 for **1a**)	121.67 (19)	119.56 (18)	120.3 (4)
C12—C11—**X1**	119.56 (17)	119.94 (15)	119.1 (3)
C10—C11—**X1**	119.37 (16)	119.49 (16)	120.4 (3)
N1—C8—N2	123.5 (2)	123.08 (18)	123.5 (4)
N2—C8—C9 (N1 for **1a**)	116.93 (18)	117.70 (18)	117.7 (4)
O1—C1—N2—C10 (N1 for **1a**)	-2.0 (3)	5.4 (3)	3.5 (6)
C11—C10—N2—C1 (N1 for **1a**)	89.1 (2)	80.9 (2)	102.5 (5)

(7) Intermolecular weak interactions of *rac*-**1a-d** and *ent*-**1a-c.**

Table S7. Intermolecular distances of *rac*-**1a-d** from PRATON (ref.8).. The π-planes were assigned as C_4N_2 (C_g of six membered ring of N1-C7-C2-C1-N2-C8), C_6 (C_g of six membered ring of C2-C3-C4-C5-C6-C7), Ph (C_g of six membered ring of C10-C11-C12-C13-C14-C15), $C_{10}N_2$ (C_g of ten membered ring of C1-C2-C3-C4-C5-C6-C7-N1-C8-N2).

	rac-**1a** (ref.7)	*rac*-**1b**	*rac*-**1c**	*rac*-**1d**
π···π	*not observed*	*not observed*	*not observed*	C_4N_2···C_6 3.7797(9) Å C_6···C_6 3.8142(9) Å
C-H···π	C9-H9C···$C_{10}N_2$ 3.7253(19) Å	C9-H9C···$C_{10}N_2$ 3.725(4) Å	C6-H6···$C_{10}N_2$ 3.559(3) Å	C14-H14···$Ph_{dis.}$ 3.779(7) Å C14A-H14A···Ph 3.673(12) Å C14A-H14A···$Ph_{dis.}$ 3.724(13) Å
C-Hal···π	C11-Br1···Ph 3.7569(8) Å	C11-Cl1···Ph 3.7983(19) Å	C11-I1···Ph 3.8307(13) Å	*not observed*
Hal···O	Br1···O1 3.145(1) Å	Cl1···O1 3.209(2) Å	I1···O1 3.129(2) Å	*not observed*
C-H···X	*not observed*	*not observed*	C14-H14···N1 3.466(4) Å	C4-H4···F1A 3.7797(9) Å C6-H6···F1 3.191(2) Å C9-H9A···O1 3.3703(18) Å C12-H12···O1 3.308(3) Å
Others				

ref.8) A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148.

Table S8. Intermolecular distances of *ent*-**1a-c** from PRATON (ref.8). The π-planes were assigned as C_4N_2 (C_g of six membered ring of N1-C7-C2-C1-N2-C8), C_6 (C_g of six membered ring of C2-C3-C4-C5-C6-C7), Ph (C_g of six membered ring of C10-C11-C12-C13-C14-C15), C_8N_2 (C_g of ten membered ring of C1-C2-C3-C4-C5-C6-C7-N1-C8-N2).

	ent-**1a** (ref.6)	*ent*-**1b**	*ent*-**1c**
π···π	*not observed*	*not observed*	C_6···C_6 3.922(3) Å
C-H···π	C9-H9C···C_6 3.680(3) Å C9-H9C···$C_{10}N_2$ 3.415(3) Å	C14-H14··· C_4N_2 3.811(2) Å C14-H14··· C_8N_2 3.635(2) Å C15-H15··· C_6 3.642(2) Å C20-H20··· Ph 3.765(3) Å C30-H30··· C_4N_2 3.675(3) Å C30-H30··· C_8N_2 3.532(2) Å	C5-H5···C_6 3.629(5) Å
C-Hal···π	*not observed*	C26-Cl2··· C_4N_2 3.8388(9) Å C26-Cl2··· C_6 3.7165(11) Å C26-Cl2··· C_8N_2 3.5829(8) Å	C41-I3···Ph 3.8141(18) Å
Hal···O	*not observed*	*not observed*	I3···O1: 3.298(3) Å
C-H···X	C13-H13···O1 3.297(3) Å	C13-H13···N1 3.289(3) Å C20-H20···O2 3.175(3) Å	C15-H15···O3 3.387(6) Å C19-H19···I3 3.912(4) Å
Others	Br1···C6 3.343 Å		C16-O2··· C_4N_2 3.984(4) Å C31-O3··· C_4N_2 3.457(3) Å I1···N3: 3.015 Å I2···N1: 3.298 Å

ref.8) A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148.