# Supplementary Materials

# Intermolecular halogen bond detected in racemic and optically pure N-C axially chiral 3-(2-halophenyl)quinazoline-4-thione derivatives

Ryosuke Matsui,[1] Erina Niijima,[1] Tomomi Imai,[1] Hiroyuki Kobayashi,[2] Akiko Hori,[2] Azusa Sato,[3] Yuko Nakamura[3] and Osamu Kitagawa*[1]

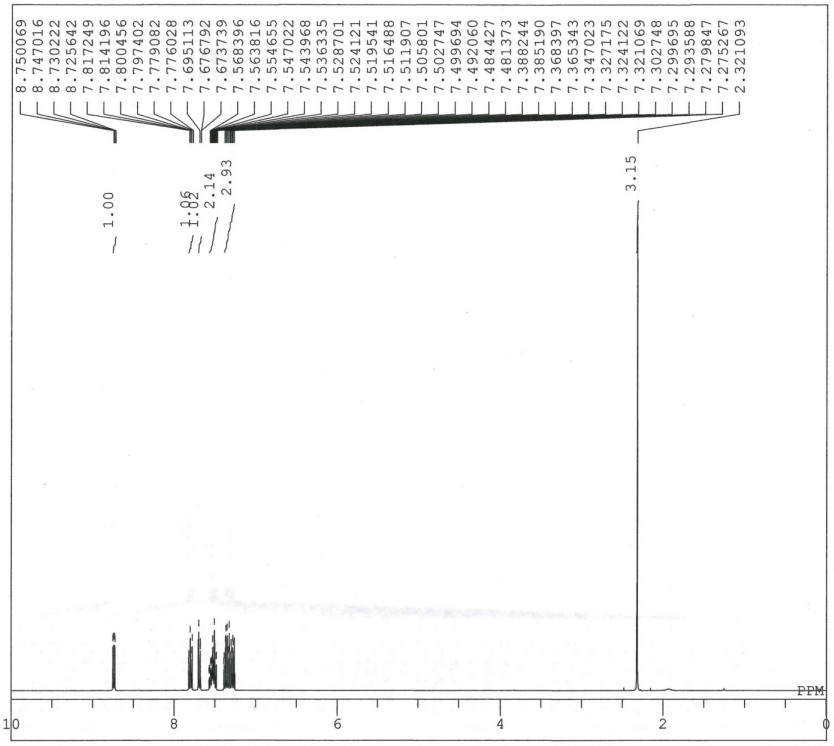
[1] Department of Applied Chemistry (Japanese Association of Bio-intelligence for Well-being), Shibaura institute of Technology, 3-7-5 Toyosu, Kohto-ku, Tokyo, 135-8548, Japan.

[2] Graduate School of Engineering and Science, Shibaura Institute of Technology, 307 Fukasaku, Minuma-ku, Saitama 337-8570, Japan.

[3] Division of Basic Sciences, Center for Medical and Nursing Education, Tokyo Women's Medical University, 8-1 Kawada-cho, Shinjuku-ku, 162-8666 Tokyo, Japan

AUTHOR E-MAIL ADDRESS: kitagawa@shibaura-it.ac.jp

**(Contents)**

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OBFRQ        399.78 MHz
OBSET          5.19 KHz
OBFIN          6.74 Hz
POINT         13107
FREQU       7999.88 Hz
SCANS            32
ACQTM         1.6384 sec
PD            5.0000 sec
PW1             5.17 usec
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CTEMP          16.9 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            34
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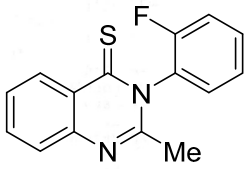
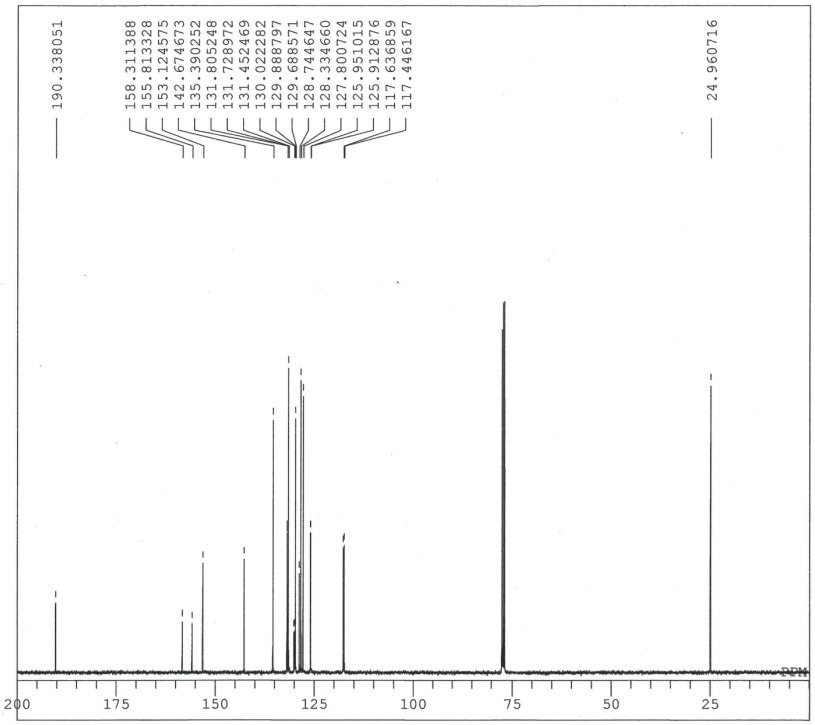



**2c**




```
DFILE  RM021 20210123 C NMR-1.a
COMNT
DATIM  2021-01-23 11:03:07
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU       25125.24 Hz
SCANS          1024
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             2.87 usec
IRNUC  1H
CTEMP          17.4 c
SLVNT  CDCL3
EXREF         77.01 ppm
BF             1.20 Hz
RGAIN            60
```

**Figure S1.** $^{1}$H-NMR and $^{13}$C-NMR spectra of compound **2c**.

# CheckCIF/PLATON report

***rac*-2a**

Structure factors have been supplied for datablock(s) en191206b_1_Pbca_a

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No syntax errors found. CIF dictionary Interpreting this report

**Table S1. Datablock: en191206b_1_Pbca_a**

Bond precision: C-C = 0.0030 A Wavelength=0.71073

| | | | |
|---|---|---|---|
| Cell: | a=13.9862(4) | b=11.8103(4) | c=16.7044(5) |
| | alpha=90 | beta=90 | gamma=90 |
| Temperature: | 100 K | | |

| | Calculated | Reported |
|---|---|---|
| Volume | 2759.25(15) | 2759.25(15) |
| Space group | P b c a | P b c a |
| Hall group | -P 2ac 2ab | -P 2ac 2ab |
| Moiety formula | C15 H11 Br N2 S | C15 H11 Br N2 S |
| Sum formula | C15 H11 Br N2 S | C15 H11 Br N2 S |
| Mr | 331.22 | 331.23 |
| Dx,g cm-3 | 1.595 | 1.595 |
| Z | 8 | 8 |
| Mu (mm-1) | 3.117 | 3.117 |
| F000 | 1328.0 | 1328.0 |
| F000’ | 1327.09 | |
| h,k,lmax | 16,14,19 | 16,14,19 |
| Nref | 2437 | 2435 |
| Tmin,Tmax | 0.502,0.746 | 0.500,0.760 |
| Tmin’ | 0.447 | |

Correction method= # Reported T Limits: Tmin=0.500 Tmax=0.760
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.026

R(reflections)= 0.0203( 2147) wR2(reflections)= 0.0496( 2435)

S = 1.030 Npar= 173

**Table S2.** The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

**Alert level C**

| | | | | |
|---|---|---|---|---|
| PLAT431_ALERT_2_C Short Inter HL..A Contact | Br1 | ..S1 | . | 3.41 Ang. |
| | | 1/2-x,1/2+y,z = | | 8_665 Check |

**Alert level G**

| | | |
|---|---|---|
| PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... | C9 | Check |
| PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . | Please | Do ! |
| PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still | 76% | Note |
| PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). | 1 | Note |
| PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File | 1 | Note |
| PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. | 13 | Info |

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
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## PLATON version of 18/12/2021; check.def file version of 18/12/2021

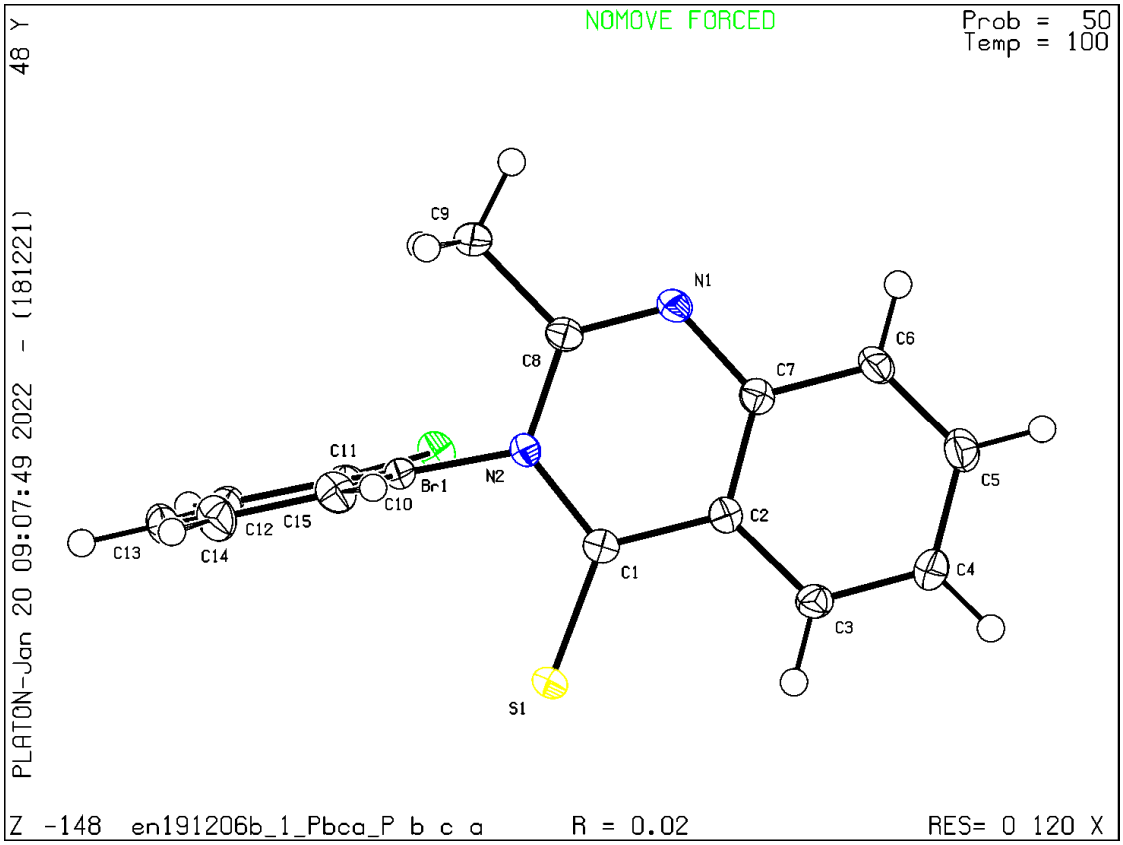


**Figure S2. Datablock en191206b_1_Pbca_a** - ellipsoid plot (**rac-2a**).

***rac*-2b**

Structure factors have been supplied for datablock(s) Pbca2_a

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No syntax errors found. CIF dictionary Interpreting this report

**Table S3. Datablock: Pbca2_a**

| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0020 A | Wavelength=0.71073 | |
| Cell: | a=14.1210(16) | b=11.5800(14) | c=16.6932(17) |
| | alpha=90 | beta=90 | gamma=90 |
| Temperature: | 100 K | | |

| | Calculated | Reported |
|---|---|---|
| Volume | 2729.7(5) | 2729.7(5) |
| Space group | P b c a | P b c a |
| Hall group | -P 2ac 2ab | -P 2ac 2ab |
| Moiety formula | C15 H11 Cl N2 S | C15 H11 Cl N2 S |
| Sum formula | C15 H11 Cl N2 S | C15 H11 Cl N2 S |
| Mr | 286.77 | 286.77 |
| Dx,g cm-3 | 1.396 | 1.396 |
| Z | 8 | 8 |
| Mu (mm-1) | 0.419 | 0.419 |
| F000 | 1184.0 | 1184.0 |
| F000’ | 1186.50 | |
| h,k,lmax | 16,13,19 | 16,13,19 |
| Nref | 2406 | 2403 |
| Tmin,Tmax | 0.875,0.899 | 0.700,0.900 |
| Tmin’ | 0.875 | |

Correction method= # Reported T Limits: Tmin=0.700 Tmax=0.900
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.023

R(reflections)= 0.0297( 2261) wR2(reflections)= 0.0840( 2403)

S = 1.054 Npar= 173

**Table S4**. The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

**Alert level C**

| | | | | | |
|---|---|---|---|---|---|
| PLAT230_ALERT_2_C Hirshfeld Test Diff for | S1 | --C1 | . | 6.1 | s.u. |
| PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. | | | 1 Check | | |

**Alert level G**

| | | |
|---|---|---|
| PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . | Please | Do ! |
| PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still | 88% | Note |
| PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). | 3 | Note |
| PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File | 3 | Note |
| PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged | Please | Check |
| PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. | 8 | Info |

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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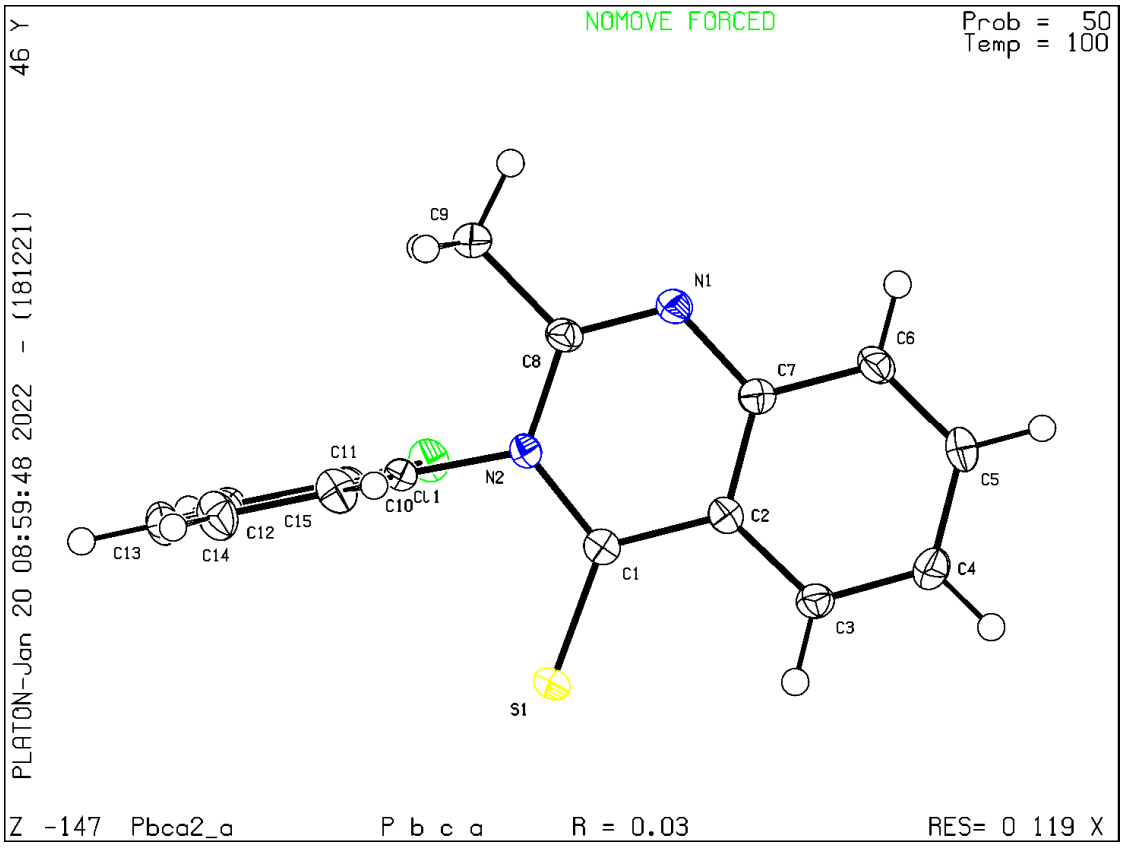


**Figure S3. Datablock Pbca2_a** - ellipsoid plot (**rac-2b**).

**(*P*)-2b**

Structure factors have been supplied for datablock(s) P21_a

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No syntax errors found. CIF dictionary Interpreting this report

**Table S5. Datablock: P21_a**

| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0041 A | Wavelength=0.71073 | |
| Cell: | a=8.3918(7) | b=16.9928(15) | c=10.0448(10) |
| | alpha=90 | beta=111.646 | gamma=90 |
| Temperature: | 100 K | | |

| | Calculated | Reported |
|---|---|---|
| Volume | 1331.4(2) | 1331.4(2) |
| Space group | P 21 | P 21 |
| Hall group | P 2yb | P 2yb |
| Moiety formula | C15 H11 Cl N2 S | C15 H11 Cl N2 S |
| Sum formula | C15 H11 Cl N2 S | C15 H11 Cl N2 S |
| Mr | 286.77 | 286.77 |
| Dx,g cm-3 | 1.431 | 1.431 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.429 | 0.429 |
| F000 | 592.0 | 592.0 |
| F000’ | 593.25 | |
| h,k,lmax | 9,20,11 | 9,20,11 |
| Nref | 4690 [2431] | 4472 |
| Tmin,Tmax | 0.897,0.934 | 0.770,0.940 |
| Tmin’ | 0.873 | |

Correction method= # Reported T Limits: Tmin=0.770 Tmax=0.940
AbsCorr = MULTI-SCAN

Data completeness= 1.84/0.95 Theta(max)= 25.026

R(reflections)= 0.0256( 4381) wR2(reflections)= 0.0631( 4472)

S = 1.060 Npar= 345

**Table S6**. The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

**Alert level C**

| | | | |
|---|---|---|---|
| PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ..... | | 7.03 | Note |
| PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... | 0.00407 | | Ang. |
| PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= | 0.595 | 4 | Report |

**Alert level G**

| | | | |
|---|---|---|---|
| PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... | | C24 | Check |
| PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . | | Please | Do ! |
| PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still | | 96% | Note |
| PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File | | 2 | Note |
| PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. | | 2 | Info |

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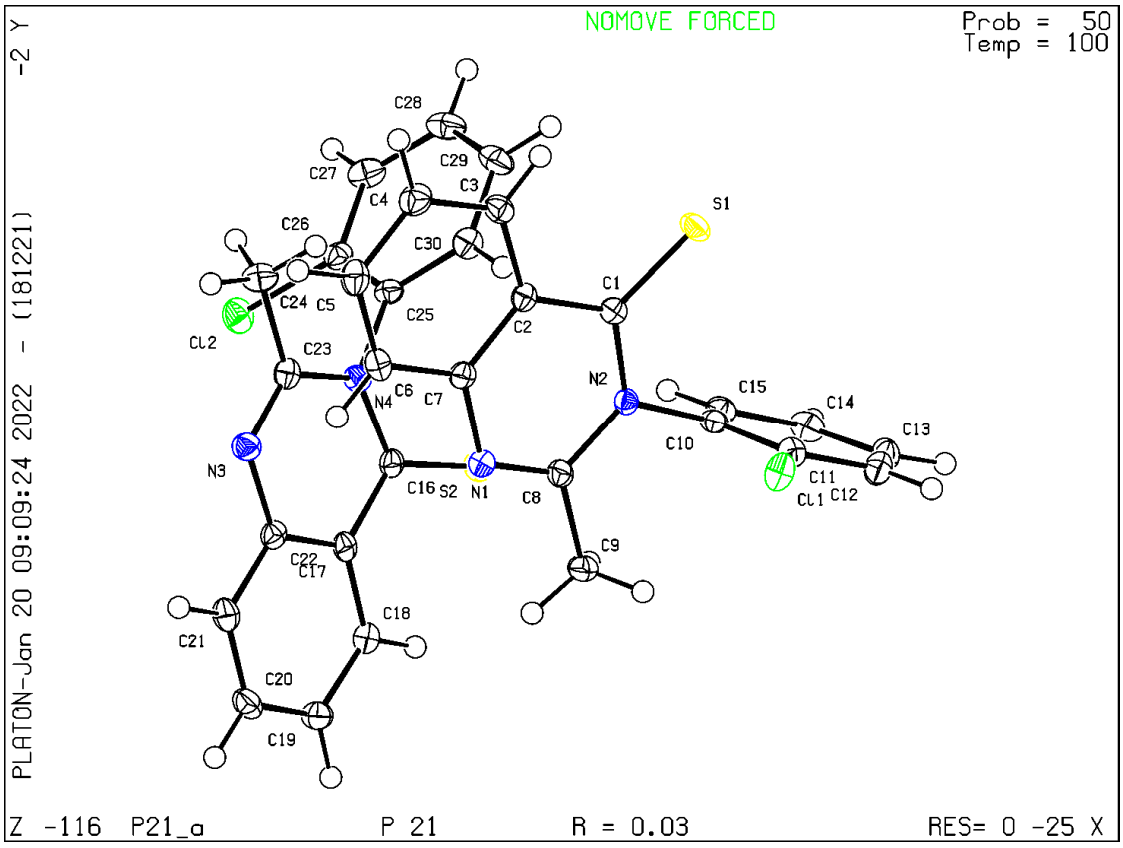


**Figure S4**. **Datablock P21_a** - ellipsoid plot [(*P*)-**2b**].

***rac*-2c**

Structure factors have been supplied for datablock(s) hk201126b

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No syntax errors found. CIF dictionary Interpreting this report

**Table S7. Datablock: hk201126b**

| | | | | |
|---|---|---|---|---|
| Bond precision: | C-C = 0.0030 A | | Wavelength=0.71073 | |
| Cell: | a=13.3633(19) | b=14.1656(18) | c=14.7771(18) | |
| | alpha=90 | beta=114.812(4) | gamma=90 | |
| Temperature: | 100 K | | | |
| | Calculated | | Reported | |
| Volume | 2539.1(6) | | 2539.1(6) | |
| Space group | C 2/c | | C 2/c | |
| Hall group | -C 2yc | | -C 2yc | |
| Moiety formula | C15 H11 F N2 S | | C15 H11 F | N2 S |
| Sum formula | C15 H11 F N2 S | | C15 H11 F | N2 S |
| Mr | 270.32 | | 270.32 | |
| Dx,g cm-3 | 1.414 | | 1.414 | |
| Z | 8 | | 8 | |
| Mu (mm-1) | 0.253 | | 0.253 | |
| F000 | 1120.0 | | 1120.0 | |
| F000’ | 1121.43 | | | |
| h,k,lmax | 15,16,17 | | 15,16,17 | |
| Nref | 2247 | | 2245 | |
| Tmin,Tmax | 0.937,0.955 | | 0.830,0.960 | |
| Tmin’ | 0.930 | | | |

Correction method= # Reported T Limits: Tmin=0.830 Tmax=0.960
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.024

R(reflections)= 0.0352( 2010) wR2(reflections)= 0.1121( 2245)

S = 1.124 Npar= 173

**Table S8**. The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

**Alert level C**

| | | | |
|---|---|---|---|
| PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= | 0.595 | 3 | Report |
| PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. | 1 Check | | |

**Alert level G**

| | | |
|---|---|---|
| PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . | Please Do | ! |
| PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still | 76% | Note |
| PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged | Please | Check |
| PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. | 3 | Info |

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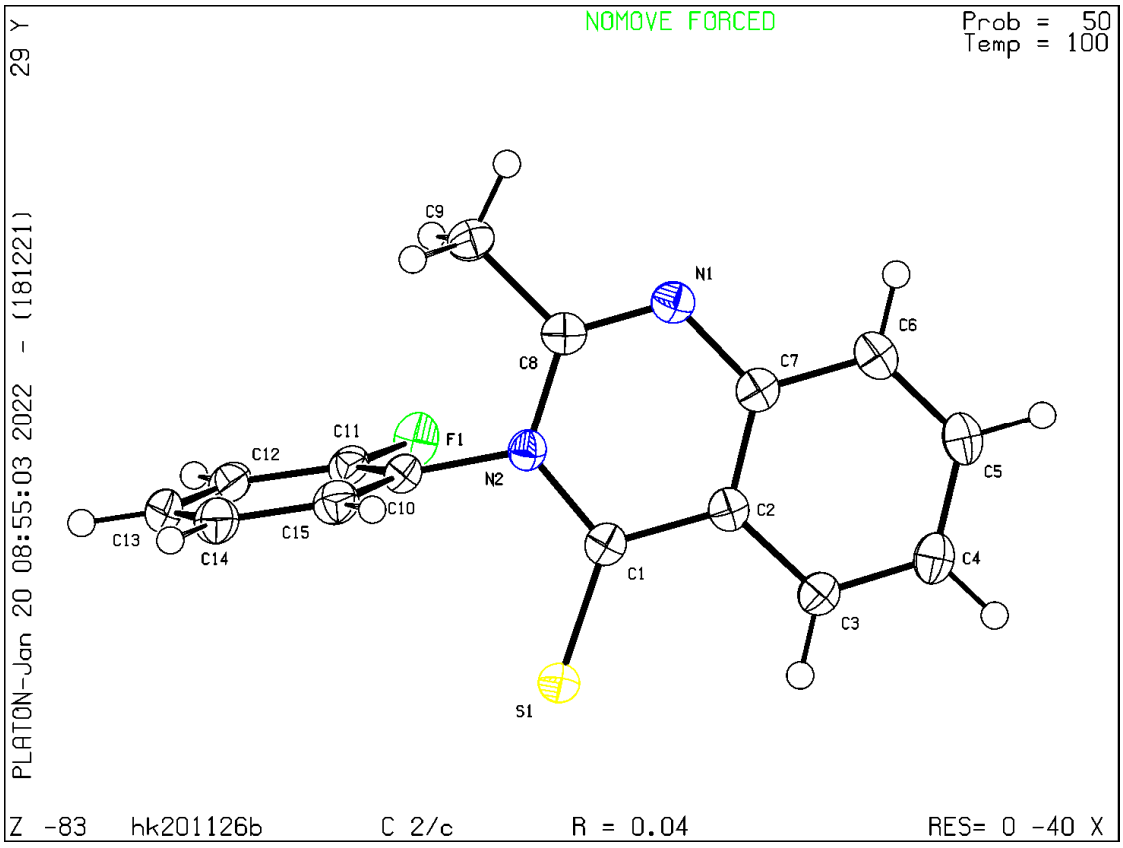


**Figure S5. Datablock hk201126b** - ellipsoid plot (**rac-2c**).

Hirshfeld Surface analysis

HS analysis showing intermolecular interactions for sulfur and halogen substituents.

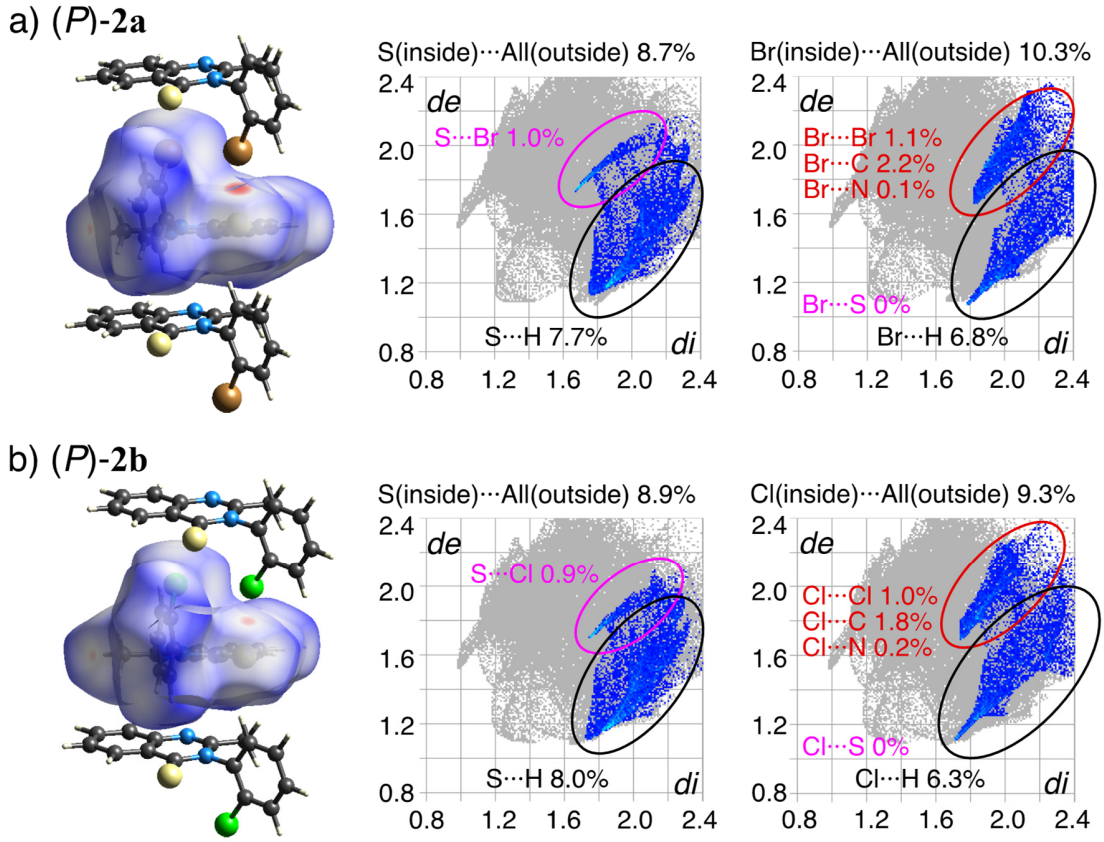


**Figure S6**. The HS mapped with $d_{norm}$ and the fingerprint plots of enantiomer a) (*P*)-**2a** and b) (*P*)-**2b** showing the $d_e$ and $d_i$ of 0.8-2.4 Å for remarkable interactions [0.5 isovalue of molecular weight function w(r)].

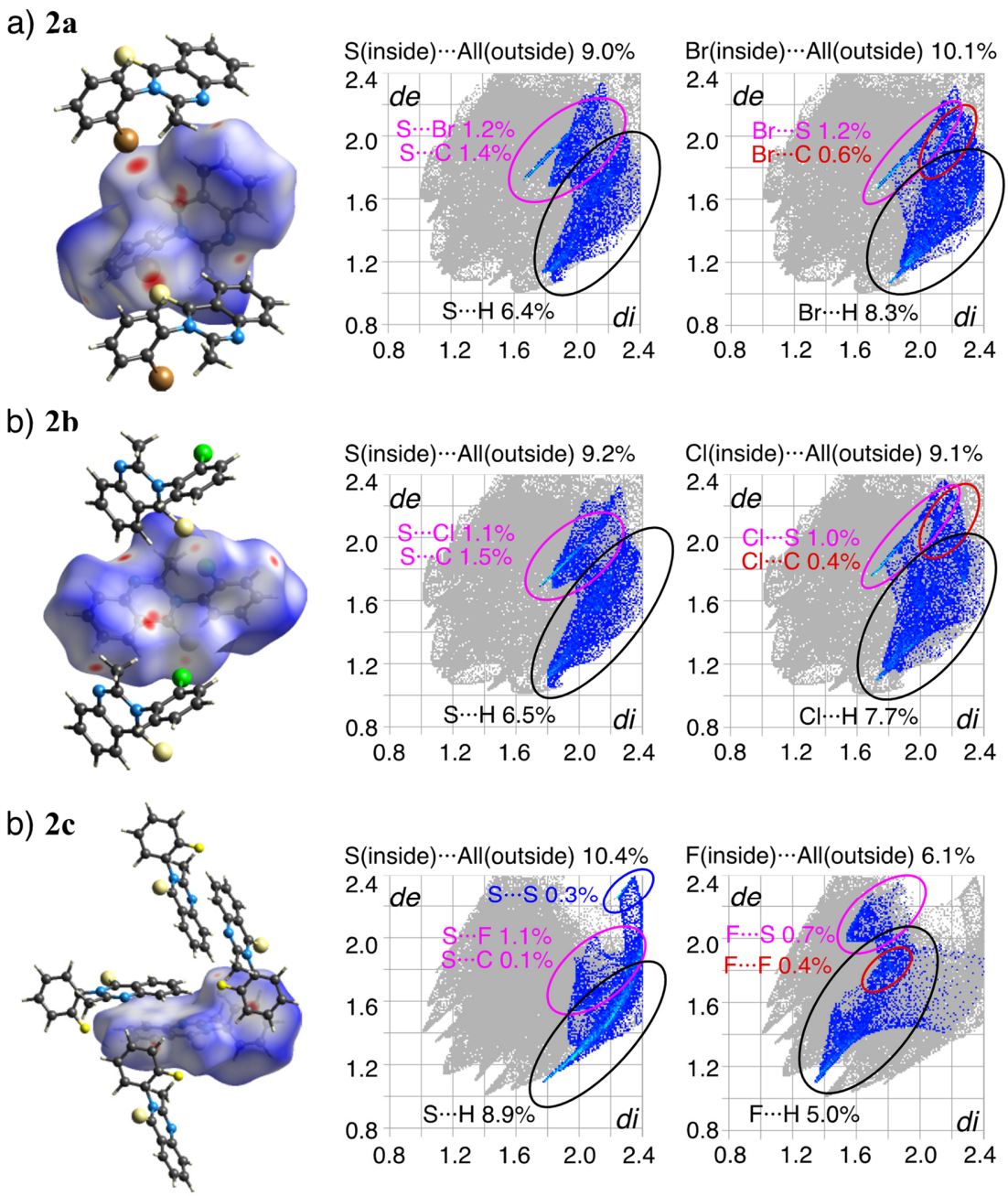


**Figure S7**. The HS mapped with $d_{norm}$ and the fingerprint plots of racemic a) racemic **2a**, b) racemic **2b**, and c) racemic **2c** showing the $d_e$ and $d_i$ of 0.8-2.4 Å for remarkable interactions [0.5 isovalue of molecular weight function w(r)].