

# 1,3-Bis[(+)-(S)-[1-(1-naphthyl)ethyl]-iminomethyl]benzene dichloromethane solvate

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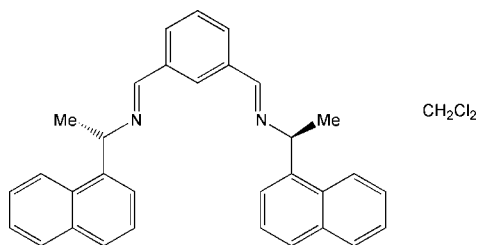
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.060;  $wR$  factor = 0.186; data-to-parameter ratio = 14.5.

In the title compound,  $\text{C}_{32}\text{H}_{28}\text{N}_2 \cdot \text{CH}_2\text{Cl}_2$ , the complete Schiff base and solvent molecules are both generated by crystallographic twofold axes, with the two C atoms of the former and the C atom of the latter lying on the rotation axis. The central benzene ring is substituted with two chiral groups including imine functionalities, with the common *E* configuration. The dihedral angle between the central benzene ring and the terminal naphthalene ring is  $45.42(9)^\circ$  and that between the two naphthalene rings is  $89.16(8)^\circ$ . The conformation of the Schiff base allows solvent molecules to fill the voids in the crystal, affording a stable 1:1 solvate, but the solvent interacts poorly with the Schiff base, as reflected by its rather high displacement parameters.

## Related literature

For solvent-free synthesis in organic chemistry, see: Jeon *et al.* (2005); Noyori (2005); Tanaka & Toda (2000). For related chiral Schiff bases synthesized using similar routes, see: Tovar *et al.* (2007).



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## Experimental

### Crystal data

$\text{C}_{32}\text{H}_{28}\text{N}_2 \cdot \text{CH}_2\text{Cl}_2$   
 $M_r = 525.49$   
 Orthorhombic,  $P2_12_12$   
 $a = 8.550(2)$  Å  
 $b = 20.706(6)$  Å  
 $c = 7.972(3)$  Å

$V = 1411.3(7)$  Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.25$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.40 \times 0.24 \times 0.20$  mm

### Data collection

Siemens P4 diffractometer  
 Absorption correction: gaussian  
 (XSCANS; Siemens, 1996)  
 $T_{\min} = 0.933$ ,  $T_{\max} = 0.954$   
 6308 measured reflections  
 2497 independent reflections

1428 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.060$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: 2.3%

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$   
 $wR(F^2) = 0.186$   
 $S = 1.06$   
 2497 reflections  
 172 parameters  
 H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.19$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.16$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1028 Friedel pairs  
 Flack parameter: 0.0 (2)

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2198).

## References

- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Jeon, S.-J., Li, H. & Walsh, P. J. (2005). *J. Am. Chem. Soc.* **127**, 16416–16425.  
 Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.  
 Noyori, R. (2005). *Chem. Commun.* pp. 1807–1811.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Siemens (1996). XSCANS. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Tanaka, K. & Toda, F. (2000). *Chem. Rev.* **100**, 1025–1074.  
 Tovar, A., Peña, U., Hernández, G., Portillo, R. & Gutiérrez, R. (2007). *Synthesis*, pp. 22–24.

**supplementary materials**

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## 1,3-Bis{(+)-(S)-[1-(1-naphthyl)ethyl]iminomethyl}benzene dichloromethane solvate

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### Comment

During the last few decades, a central objective in synthetic organic chemistry has been to develop greener and more economically competitive processes for the efficient synthesis of compounds with potential applications in diverse fields. In this context, the solvent-free approach is simple with amazing versatility because it reduces the use of organic solvents and minimizes the formation of other waste. Likewise, the reactions occur under mild conditions and usually require easier workup procedures and simpler equipment. Moreover, it may allow access to compounds that require harsh reaction conditions under traditional approaches or when the yields are too low to be of practical convenience (Jeon *et al.*, 2005; Noyori, 2005; Tanaka & Toda, 2000).

On the other hand, bisimines have lately attracted much attention, mostly due to their versatile coordination behavior and the interesting properties of their metal complexes. These compounds are particularly interesting since they can potentially act in a variety of coordination modes.

Continuing our work on the synthesis of chiral imines (Tovar *et al.*, 2007), we synthesized the title Schiff base under solvent-free conditions and report here its X-ray structure. The asymmetric unit contains one half-molecule and one half dichloromethane molecule, both placed on binary axis (Fig. 1). This arrangement is probably favored by the presence of a chiral center, C6, allowing to orient the substituents of the imine functionality towards the opposite faces of the central benzene core. The crystal is further stabilized by the inclusion of lattice solvent, resulting in a 1:1 solvate. Indeed, the shape of the Schiff base is suitable for the formation of a guest-host complex (Fig. 2). However, as no efficient hydrogen bonds are formed, the solvent molecule presents high displacement parameters, compared to the host (See Fig. 1).

### Experimental

Under solvent-free conditions, a mixture of benzene-1,3-dicarboxaldehyde (0.12 g, 0.9 mmol) and (*S*)-(-)-1-naphthylethylamine (0.32 g, 1.8 mmol) were mixed at 298 K, giving a white solid. The crude material was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>, affording colorless crystals of the title solvate (Yield: 98%; m.p. 343–345 K.  $[\alpha]_D^{25} = +253.7$  ( $c=1$ , CHCl<sub>3</sub>). IR and NMR data are consistent with the X-ray structure (see archived CIF).

### Refinement

All H atoms were placed in idealized positions and refined as riding to their carrier C atoms, with bond lengths fixed to 0.93 (aromatic CH), 0.96 (methyl CH<sub>3</sub>), 0.97 (methylene CH<sub>2</sub>) and 0.98 Å (methine CH). isotropic displacement parameters were calculated as  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{carrier atom})$  for the methyl group and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$  otherwise.

## Figures

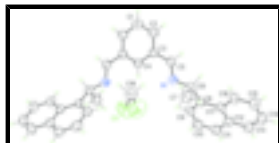


Fig. 1. Molecular structure of the title compound, with 30% probability level displacement ellipsoids for non-H atoms. Non-labeled atoms are generated through the symmetry operation  $2 - x, 1 - y, z$ .

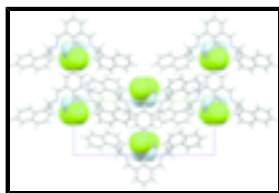


Fig. 2. A part of the crystal structure of the title compound along  $[100]$ , showing the lattice solvent molecules with a space-filling representation.

## 1,3-Bis{(+)-(S)-[1-(1-naphthyl)ethyl]iminomethyl}benzene dichloromethane solvate

### Crystal data

$C_{32}H_{28}N_2 \cdot CH_2Cl_2$

$M_r = 525.49$

Orthorhombic,  $P2_12_12$

Hall symbol: P 2 2ab

$a = 8.550 (2) \text{ \AA}$

$b = 20.706 (6) \text{ \AA}$

$c = 7.972 (3) \text{ \AA}$

$V = 1411.3 (7) \text{ \AA}^3$

$Z = 2$

$F_{000} = 552$

$D_x = 1.237 \text{ Mg m}^{-3}$

Melting point: 343 K

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 51 reflections

$\theta = 4.0\text{--}11.9^\circ$

$\mu = 0.25 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Prism, yellow

$0.40 \times 0.24 \times 0.20 \text{ mm}$

### Data collection

Siemens P4  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298 \text{ K}$

$2\theta/\omega$  scans

Absorption correction: gaussian  
(XSCANS; Siemens, 1996)

$T_{\min} = 0.933, T_{\max} = 0.954$

6308 measured reflections

2497 independent reflections

1428 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$

$\theta_{\max} = 25.0^\circ$

$\theta_{\min} = 2.0^\circ$

$h = -10 \rightarrow 10$

$k = -24 \rightarrow 24$

$l = -9 \rightarrow 9$

3 standard reflections

every 97 reflections

intensity decay: 2.3%

### Refinement

Refinement on  $F^2$

H-atom parameters constrained

Least-squares matrix: full  $w = 1/[\sigma^2(F_o^2) + (0.0833P)^2 + 0.2257P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $R[F^2 > 2\sigma(F^2)] = 0.060$   $(\Delta/\sigma)_{\max} < 0.001$   
 $wR(F^2) = 0.186$   $\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$   
 $S = 1.06$   $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$   
 2497 reflections Extinction correction: SHELXL97 (Sheldrick, 2008),  
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 172 parameters Extinction coefficient: 0.036 (6)  
 Primary atom site location: structure-invariant direct methods Absolute structure: Flack (1983), 1028 Friedel pairs  
 Secondary atom site location: difference Fourier map Flack parameter: 0.0 (2)  
 Hydrogen site location: inferred from neighbouring sites

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.8943 (5)	0.38124 (15)	1.0214 (4)	0.0789 (10)
C1	1.0000	0.5000	1.5231 (7)	0.0904 (19)
H1A	1.0000	0.5000	1.6398	0.108*
C2	0.9506 (5)	0.4463 (2)	1.4376 (5)	0.0800 (12)
H2A	0.9166	0.4102	1.4968	0.096*
C3	0.9508 (4)	0.44531 (18)	1.2633 (5)	0.0660 (10)
C4	1.0000	0.5000	1.1777 (7)	0.0682 (14)
H4A	1.0000	0.5000	1.0611	0.082*
C5	0.9004 (5)	0.38667 (18)	1.1771 (5)	0.0711 (10)
H5A	0.8711	0.3514	1.2420	0.085*
C6	0.8370 (5)	0.32020 (18)	0.9537 (5)	0.0747 (11)
H6A	0.8222	0.2897	1.0464	0.090*
C7	0.6791 (5)	0.3332 (2)	0.8717 (6)	0.0947 (14)
H7A	0.6077	0.3499	0.9539	0.142*
H7B	0.6383	0.2937	0.8262	0.142*
H7C	0.6918	0.3642	0.7832	0.142*
C8	0.9507 (5)	0.29178 (16)	0.8309 (5)	0.0646 (9)
C9	1.0643 (5)	0.32880 (18)	0.7563 (5)	0.0760 (11)
H9A	1.0740	0.3720	0.7868	0.091*
C10	1.1656 (6)	0.3034 (2)	0.6361 (6)	0.0924 (14)
H10A	1.2430	0.3295	0.5899	0.111*
C11	1.1527 (6)	0.2419 (2)	0.5865 (5)	0.0851 (12)
H11A	1.2184	0.2263	0.5028	0.102*
C12	1.0413 (5)	0.20049 (19)	0.6592 (5)	0.0751 (11)
C13	1.0297 (6)	0.1351 (2)	0.6116 (6)	0.0911 (13)
H13A	1.0960	0.1188	0.5293	0.109*
C14	0.9225 (6)	0.0957 (2)	0.6848 (7)	0.0973 (15)
H14A	0.9158	0.0527	0.6524	0.117*
C15	0.8233 (5)	0.1194 (2)	0.8073 (7)	0.0909 (14)
H15A	0.7514	0.0919	0.8578	0.109*
C16	0.8295 (5)	0.18255 (17)	0.8549 (6)	0.0749 (11)

## supplementary materials

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H16A	0.7615	0.1975	0.9371	0.090*
C17	0.9380 (4)	0.22579 (17)	0.7812 (5)	0.0652 (9)
C18	0.5000	0.5000	0.8916 (9)	0.123 (3)
H18A	0.4641	0.5349	0.9629	0.148*
Cl1	0.6505 (3)	0.52641 (11)	0.7706 (3)	0.1852 (10)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.102 (3)	0.0685 (19)	0.067 (2)	-0.0018 (18)	0.003 (2)	0.0003 (16)
C1	0.099 (5)	0.115 (5)	0.057 (3)	0.000 (4)	0.000	0.000
C2	0.084 (3)	0.090 (3)	0.066 (2)	0.004 (3)	0.008 (2)	0.008 (2)
C3	0.062 (2)	0.076 (2)	0.060 (2)	0.0110 (19)	0.0047 (19)	0.0017 (19)
C4	0.073 (3)	0.075 (3)	0.056 (3)	0.015 (3)	0.000	0.000
C5	0.073 (2)	0.070 (2)	0.070 (3)	0.008 (2)	0.007 (2)	0.008 (2)
C6	0.085 (3)	0.070 (2)	0.069 (2)	-0.001 (2)	0.003 (2)	0.0066 (19)
C7	0.080 (3)	0.099 (3)	0.105 (3)	0.016 (3)	0.008 (3)	0.000 (3)
C8	0.069 (2)	0.064 (2)	0.060 (2)	0.0002 (18)	0.003 (2)	0.0087 (17)
C9	0.085 (3)	0.072 (2)	0.071 (2)	-0.006 (2)	0.005 (2)	0.009 (2)
C10	0.091 (3)	0.100 (3)	0.086 (3)	-0.005 (3)	0.026 (3)	0.022 (3)
C11	0.082 (3)	0.102 (3)	0.072 (3)	0.013 (3)	0.011 (2)	0.003 (2)
C12	0.071 (2)	0.081 (2)	0.073 (2)	0.010 (2)	-0.014 (2)	-0.004 (2)
C13	0.089 (3)	0.090 (3)	0.095 (3)	0.020 (3)	-0.019 (3)	-0.019 (3)
C14	0.097 (3)	0.076 (3)	0.120 (4)	0.012 (3)	-0.030 (4)	-0.010 (3)
C15	0.078 (3)	0.075 (3)	0.120 (4)	-0.005 (2)	-0.024 (3)	0.007 (3)
C16	0.066 (2)	0.072 (2)	0.087 (3)	-0.004 (2)	-0.004 (2)	0.002 (2)
C17	0.059 (2)	0.069 (2)	0.068 (2)	0.0022 (18)	-0.007 (2)	0.0072 (18)
C18	0.192 (10)	0.094 (5)	0.084 (4)	-0.003 (5)	0.000	0.000
Cl1	0.1454 (16)	0.208 (2)	0.202 (2)	-0.0442 (14)	0.0100 (17)	0.0547 (16)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

N1—C5	1.248 (5)	C9—C10	1.395 (6)
N1—C6	1.459 (5)	C9—H9A	0.9300
C1—C2	1.371 (5)	C10—C11	1.338 (6)
C1—C2 <sup>i</sup>	1.371 (5)	C10—H10A	0.9300
C1—H1A	0.9300	C11—C12	1.407 (6)
C2—C3	1.390 (5)	C11—H11A	0.9300
C2—H2A	0.9300	C12—C13	1.410 (6)
C3—C4	1.387 (4)	C12—C17	1.414 (5)
C3—C5	1.460 (5)	C13—C14	1.359 (7)
C4—C3 <sup>i</sup>	1.387 (4)	C13—H13A	0.9300
C4—H4A	0.9300	C14—C15	1.384 (7)
C5—H5A	0.9300	C14—H14A	0.9300
C6—C8	1.500 (5)	C15—C16	1.363 (5)
C6—C7	1.524 (6)	C15—H15A	0.9300
C6—H6A	0.9800	C16—C17	1.416 (5)
C7—H7A	0.9600	C16—H16A	0.9300

C7—H7B	0.9600	C18—C11 <sup>ii</sup>	1.699 (5)
C7—H7C	0.9600	C18—C11	1.699 (5)
C8—C9	1.373 (5)	C18—H18A	0.9698
C8—C17	1.427 (5)		
C5—N1—C6	117.4 (3)	C8—C9—C10	121.8 (4)
C2—C1—C2 <sup>i</sup>	120.4 (6)	C8—C9—H9A	119.1
C2—C1—H1A	119.8	C10—C9—H9A	119.1
C2 <sup>i</sup> —C1—H1A	119.8	C11—C10—C9	120.7 (4)
C1—C2—C3	120.6 (4)	C11—C10—H10A	119.7
C1—C2—H2A	119.7	C9—C10—H10A	119.7
C3—C2—H2A	119.7	C10—C11—C12	121.0 (4)
C4—C3—C2	118.7 (4)	C10—C11—H11A	119.5
C4—C3—C5	122.5 (4)	C12—C11—H11A	119.5
C2—C3—C5	118.8 (4)	C11—C12—C13	121.5 (4)
C3—C4—C3 <sup>i</sup>	121.1 (5)	C11—C12—C17	118.7 (4)
C3—C4—H4A	119.4	C13—C12—C17	119.8 (4)
C3 <sup>i</sup> —C4—H4A	119.4	C14—C13—C12	120.5 (5)
N1—C5—C3	123.7 (4)	C14—C13—H13A	119.7
N1—C5—H5A	118.1	C12—C13—H13A	119.7
C3—C5—H5A	118.1	C13—C14—C15	120.3 (4)
N1—C6—C8	111.3 (3)	C13—C14—H14A	119.9
N1—C6—C7	107.6 (3)	C15—C14—H14A	119.9
C8—C6—C7	111.3 (3)	C16—C15—C14	120.8 (5)
N1—C6—H6A	108.8	C16—C15—H15A	119.6
C8—C6—H6A	108.8	C14—C15—H15A	119.6
C7—C6—H6A	108.8	C15—C16—C17	121.1 (4)
C6—C7—H7A	109.5	C15—C16—H16A	119.4
C6—C7—H7B	109.5	C17—C16—H16A	119.4
H7A—C7—H7B	109.5	C12—C17—C16	117.4 (4)
C6—C7—H7C	109.5	C12—C17—C8	119.9 (3)
H7A—C7—H7C	109.5	C16—C17—C8	122.7 (4)
H7B—C7—H7C	109.5	C11 <sup>ii</sup> —C18—C11	110.8 (4)
C9—C8—C17	117.9 (4)	C11 <sup>ii</sup> —C18—H18A	109.4
C9—C8—C6	121.5 (3)	C11—C18—H18A	109.4
C17—C8—C6	120.5 (3)		
C2 <sup>i</sup> —C1—C2—C3	0.4 (3)	C10—C11—C12—C13	-178.1 (4)
C1—C2—C3—C4	-0.9 (6)	C10—C11—C12—C17	2.7 (6)
C1—C2—C3—C5	178.7 (3)	C11—C12—C13—C14	179.2 (4)
C2—C3—C4—C3 <sup>i</sup>	0.4 (3)	C17—C12—C13—C14	-1.6 (6)
C5—C3—C4—C3 <sup>i</sup>	-179.1 (4)	C12—C13—C14—C15	0.0 (7)
C6—N1—C5—C3	-178.2 (4)	C13—C14—C15—C16	1.0 (7)
C4—C3—C5—N1	-1.5 (6)	C14—C15—C16—C17	-0.3 (6)
C2—C3—C5—N1	179.0 (4)	C11—C12—C17—C16	-178.6 (4)
C5—N1—C6—C8	-126.4 (4)	C13—C12—C17—C16	2.2 (5)
C5—N1—C6—C7	111.4 (4)	C11—C12—C17—C8	-1.5 (5)
N1—C6—C8—C9	-19.0 (5)	C13—C12—C17—C8	179.3 (4)

## supplementary materials

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C7—C6—C8—C9	101.1 (4)	C15—C16—C17—C12	-1.3 (6)
N1—C6—C8—C17	164.5 (3)	C15—C16—C17—C8	-178.3 (4)
C7—C6—C8—C17	-75.4 (4)	C9—C8—C17—C12	0.3 (5)
C17—C8—C9—C10	-0.3 (6)	C6—C8—C17—C12	177.0 (3)
C6—C8—C9—C10	-176.9 (4)	C9—C8—C17—C16	177.2 (3)
C8—C9—C10—C11	1.5 (7)	C6—C8—C17—C16	-6.1 (5)
C9—C10—C11—C12	-2.7 (7)		

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



Fig. 1

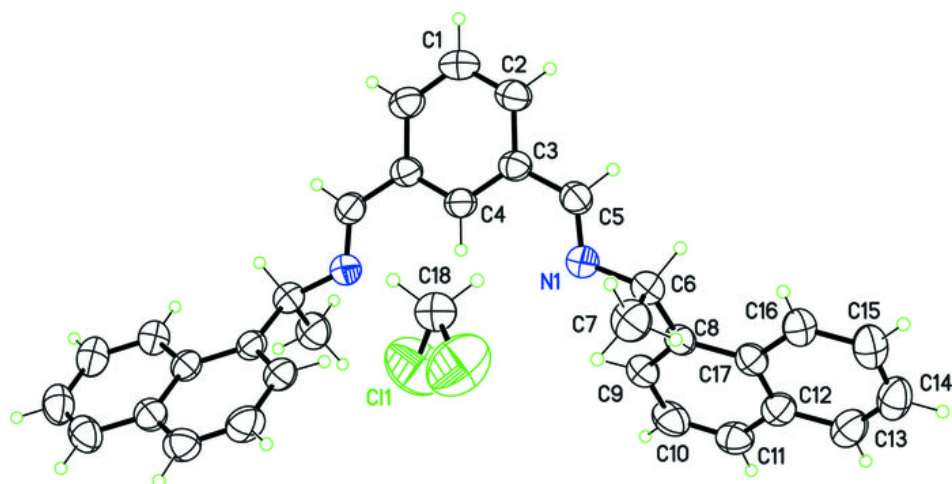


Fig. 2

