Soluble precursors of 2,3-naphthalocyanine and phthalocyanine for use in thin film transistors

Atsuko Hirao,[a] Taiji Akiyama,[a] Tetsuo Okujima,*[a] Hiroko Yamada,[a,b] Hidemitsu Uno,[c] Yoshimasa Sakai,[d] Shinji Aramaki*[d] and Noboru Ono*[a]

[a] *Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama, 790-8577, Japan.*

[b] *PRESTO, Japan Science and Technology Agency, Japan.*

[c] *Department of Molecular Science, Integrated Center for Sciences, Ehime University, Matsuyama 790-8577, Japan*

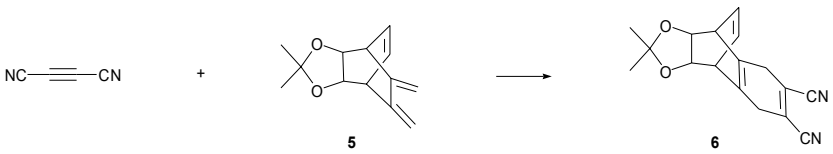
[d] *Mitsubishi Chemical Group Science and Technology Research Center, Inc., Yokohama, 227-8502, Japan.*

Supplementary Information

General and experimental details

General. Melting points were determined on a Yanaco micro melting point apparatus MP500D and are uncorrected. DI-EI and FAB mass spectra were measured on a JEOL JMS-700. MALDI-TOF mass spectra were measured on an Applied Biosystems Voyager de Pro. IR spectra were measured on a Horiba FT-720 Infrared Spectrophotometer. UV-vis spectra were measured on a JASCO V-570 spectrophotometer. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL AL-400 at 400 MHz (100 MHz). Gel permeation chromatography (GPC) was performed on a JAIGEL 2-H and a JAIGEL 1-H with $CHCl_3$. Elemental analyses were performed at Integrated Center for Sciences, Ehime University.

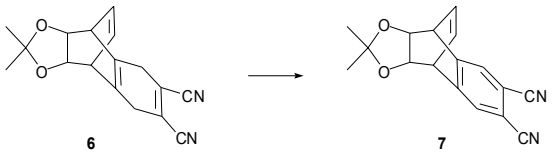
2,2-Dimethyl-4,9-ethano-3a,4,5,8,9,9a-hexahydronaphto[2,3-*d*][1,3]dioxole-6,7-dicabonitrile (6)



To a solution of dicyanoacetylene (0.33 g, 4.3 mmol) in dry CH_2Cl_2 (4 ml) was slowly added a solution of **5** (0.89 g, 4.4 mmol) at 0 ºC. The resulting mixture was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure, and the residue was washed with Et_2O and purified by recrystallization from $CHCl_3$/hexane to give **6** (0.56 g, 46%).

colorless crystals; mp 216-218 °C; MS (70 eV) *m*/*z* (relative intensity) 265 (M^+-Me, 13%), 223 (19), 193 (48), 100 (100), and 85 (97); IR (KBr disk) ν_{max} 2881 and 2229 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (m, 2H, $H_{10,11}$), 4.22 (m, 2H), 3.59 (m, 2H), 3.17 (s, 4H, $H_{5,8}$), 1.33 (s, 3H, 2-Me), and 1.25 (s, 3H, 2-Me); Anal. calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.61; H, 5.82; N, 9.89.

2,2-Dimethyl-4,9-ethano-3a,4,9,9a-tetrahydronaphto[2,3-*d*][1,3]dioxole-6,7-dicabonitrile (7)

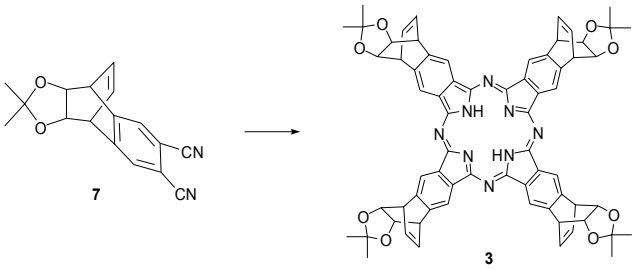


To a solution of **6** (0.19 g, 0.67 mmol) in $CHCl_3$ (40 ml) was added DDQ (0.68 g, 3.0 mmol). After an addition of 1,4-dioxane (20 ml), the resulting mixture was refluxed for 6 d. During that time, additional DDQ (0.60 g, 2.6 mmol) divided to 2 portions was added to the mixture. After removal of the solvent *in vacuo*, the residue was diluted with $CHCl_3$ and water. The organic layer was washed with water, brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was

purified by column chromatography on alumina with $CHCl_3$ to give **7** (0.18 g, 97%).

colorless crystals; MS (FAB) *m/z* 279 $[M+H]^+$; IR (KBr disk) ν_{max} 2233 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 2H, $H_{5,8}$), 6.50 (m, 2H, $H_{10,11}$), 4.32 (m, 2H, $H_{3a, 9a}$), 4.27 (m, 2H, $H_{4, 9}$), 1.40 (s, 3H, 2-Me), and 1.27 (s, 3H, 2-Me); Anal. calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.37; H, 5.11; N, 10.06.

Reaction of 7 with LiOBu.

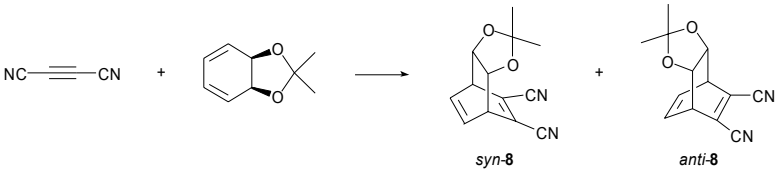


7 **3**

To Li wire (56 mg, 8.1 mmol) in a reaction vessel was added dry *n*-BuOH (8.0 ml) at room temperature under an Ar atmosphere. Li was dissolved at reflux. To this mixture was added **7** (0.50 g, 1.8 mmol) at room temperature. The resulting mixture was refluxed overnight. After an addition of MeOH/water (10 ml, v/v 1/1), the mixture was extracted with $CHCl_3$. The organic layer was washed with water, brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$/EtOAc (3/1) to give **3** (0.24 g, 47%)

deep green powder; mp > 300 °C (decomp); MS (MALDI-TOF) *m/z* 1115 (M^++1), 1015, 915, 815, and 715; ^1H NMR (400 MHz, $CDCl_3$) δ 8.35–8.67 (m, 8H), 6.87–7.35 (m, 8H), 4.62–5.22 (m, 16H), 1.25–1.77 (m, 24H), and -3.66–-4.46 (br, 2H); UV-vis ($CHCl_3$) λ_{max}, nm (log ε) 345 (4.94), 600 (4.51), 644 (4.75), 662 (5.21), and 699 (5.28); Anal. calcd for $C_{68}H_{58}N_8O_8 \cdot 1/2H_2O$: C, 72.65; H, 5.29; N, 9.97. Found: C, 72.71; H, 5.35; N, 9.89.

4,4-Dimethyl-3,5-dioxatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarbonitrile (8).



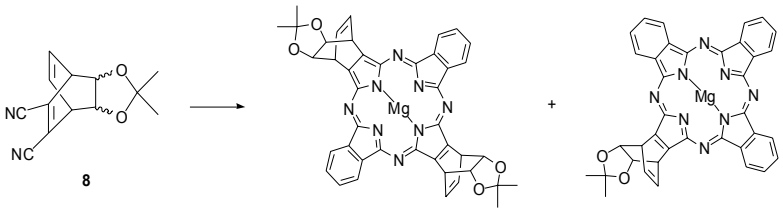
syn-**8** *anti*-**8**

To a degassed solution of dicyanoacetylene (1.1 g, 14 mmol) in $CHCl_3$ (3 ml) was added a solution of *cis*-5,6-isopropylidenedioxycyclohexa-1,3-diene (2.1 g, 14 mmol) in $CHCl_3$ (15 ml) at 0 ºC. The resulting mixture was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on alumina with $CHCl_3$ to give a mixture of *syn*- and *anti*-**8** (1.8 g, 57%). *Syn*- and *anti*-**8** were isolated by column chromatography on silica gel with hexane/EtOAc (1/3).

anti-**8**; colorless crystals; mp 181-182 ºC; MS (FAB) *m*/*z* 229 $[M+H]^+$; IR (KBr disk) ν_{max} 2223 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.39 (m, 2H, $H_{10,11}$), 4.38 (m, 2H), 4.24 (m, 2H), 1.33 (s, 3H, 4-Me), and 1.28 (s, 3H, 4-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.17, 129.96, 114.85, 113.37, 77.31, 46.39, 25.61 and 25.56; Anal. calcd for $C_{13}H_{12}N_2O_2 \cdot 1/6H_2O$: C, 67.52; H, 5.38; N, 12.11. Found: C, 67.66; H, 5.07; N, 12.12.

syn-**8**; colorless crystals; mp 201-202 °C; MS (FAB) *m*/*z* 229 $[M+H]^+$; IR (KBr disk) ν_{max} 2224 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.33 (m,2H, $H_{10,11}$), 4.34 (m, 2H), 4.25 (m, 2H), 1.41 (s, 3H, 4-Me), and 1.28 (s, 3H, 4-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.13, 130.11, 114.41, 114.21, 77.44, 46.28, 25.97 and 25.17; Anal. calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.53; H, 5.23; N, 12.34.

Reaction of 8 with $Mg(OBu)_2$.

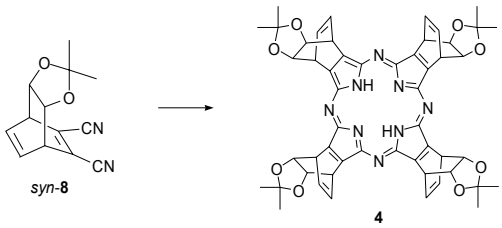


To a mixture of Mg turnings (12 mg, 0.51 mmol) and a small amount of iodine was added dry *n*-BuOH (15 ml) at room temperature under an Ar atmosphere. Mg was dissolved at reflux. To this mixture was added a mixture of *syn*- and *anti*-**8** (0.16 g, 0.72 mmol) at room temperature. The resulting mixture was refluxed for 1 d. After an addition of MeOH/water (30 ml, v/v 1/1), the mixture was extracted with $CHCl_3$. The organic layer was washed with water, brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on alumina with $CHCl_3$, recrystallization from MeOH/$CHCl_3$, and GPC to give **9**-Mg (32 mg, 24%) and **10**-Mg (13 mg, 11%).

9-Mg; blue powder; MS (MALDI-TOF) *m*/*z* 738 (M^++2), 638 and 538; ^1H NMR (400 MHz, DMSO-d_6) δ 9.44 (m, 2H), 9.38 (m, 2H), 8.30 (m, 4H), 7.04 (m, 4H), 5.61 (m, 4H), 4.72 (m, 2H), 4.80 (m, 2H), 1.52 (m, 6H), and 1.28 (m, 6H).

10-Mg; blue powder; MS (MALDI-TOF) *m*/*z* 638 (M^++2) and 538; ^1H NMR (400 MHz, DMSO-d_6) δ 9.44 (m, 4H), 9.38 (m, 2H), 8.31 (m, 2H), 8.25 (m, 4H), 7.07 (m, 2H), 5.65 (m, 2H), 4.79 (m, 2H), 1.53 (s, 3H), and 1.30 (s, 3H).

Reaction of *syn*-8 with Li(OBu).



To a mixture of Li wire (26 mg, 3.8 mmol; 33 mg, 4.8 mmol) and a small amount of iodine in reaction vessels (5 ml; 10 ml) was added dry *n*-BuOH (3.8 ml; 4.8 ml) at room temperature under an Ar atmosphere, respectively. Li was dissolved at reflux. To this mixture was added *syn*-**8** (0.19 g, 0.82 mmol; 0.23 g, 1.0 mmol) at room temperature. The resulting mixture was heated at 110 ºC for 1 d. After an addition of MeOH/water (20 ml, v/v 1/1), the combined mixture was extracted with $CHCl_3$. The organic layer was washed with water, brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on alumina with $CHCl_3$, column chromatography on silica gel with $CHCl_3$ and GPC to give **4** (4 mg, 2%)

purple powder; mp > 200 °C; MS (FAB) *m*/*z* 916 (M^++2), 816, 714, 614, and 514; UV-vis ($CHCl_3$) λ_{max}, nm (log ε) 343 (4.79), 552 (4.51), 624 (4.74), and 688 (4.05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (m, 8H), 6.00 (m, 8H), 5.05 (m, 8H), 0.98–1.26 (m, 12H), -1.13–-0.51 (m, 12H), and -3.09 (br, 2H, NH); HRMS calcd for $C_{52}H_{51}N_8O_8$ 915.3830, found 915.3831.

^{1}H NMR spectra

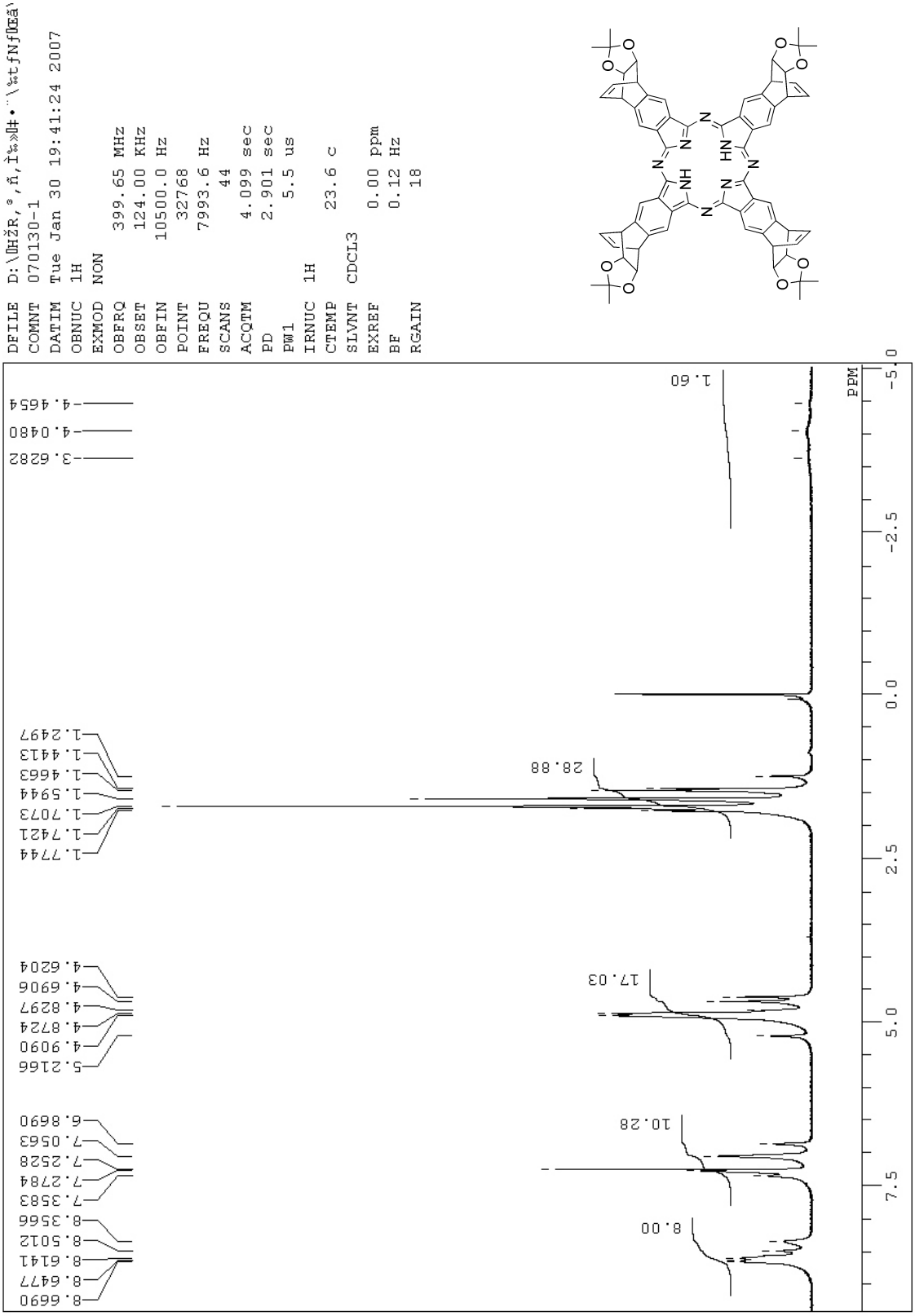


Fig. **S-1** ^{1}H NMR spectrum of **3** in $CDCl_3$.

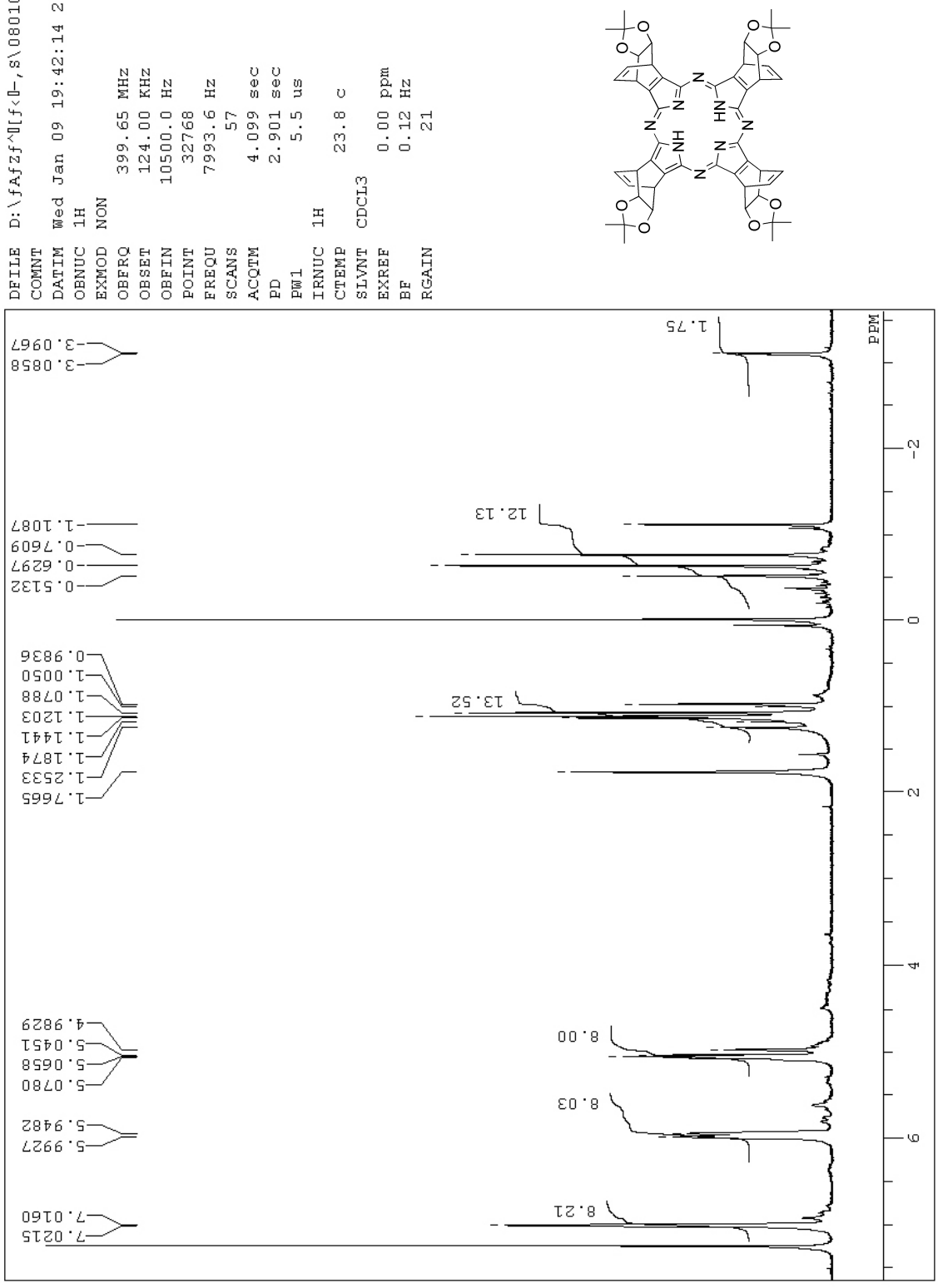


Fig. **S-2** ^{1}H NMR spectrum of **4** in $CDCl_3$.

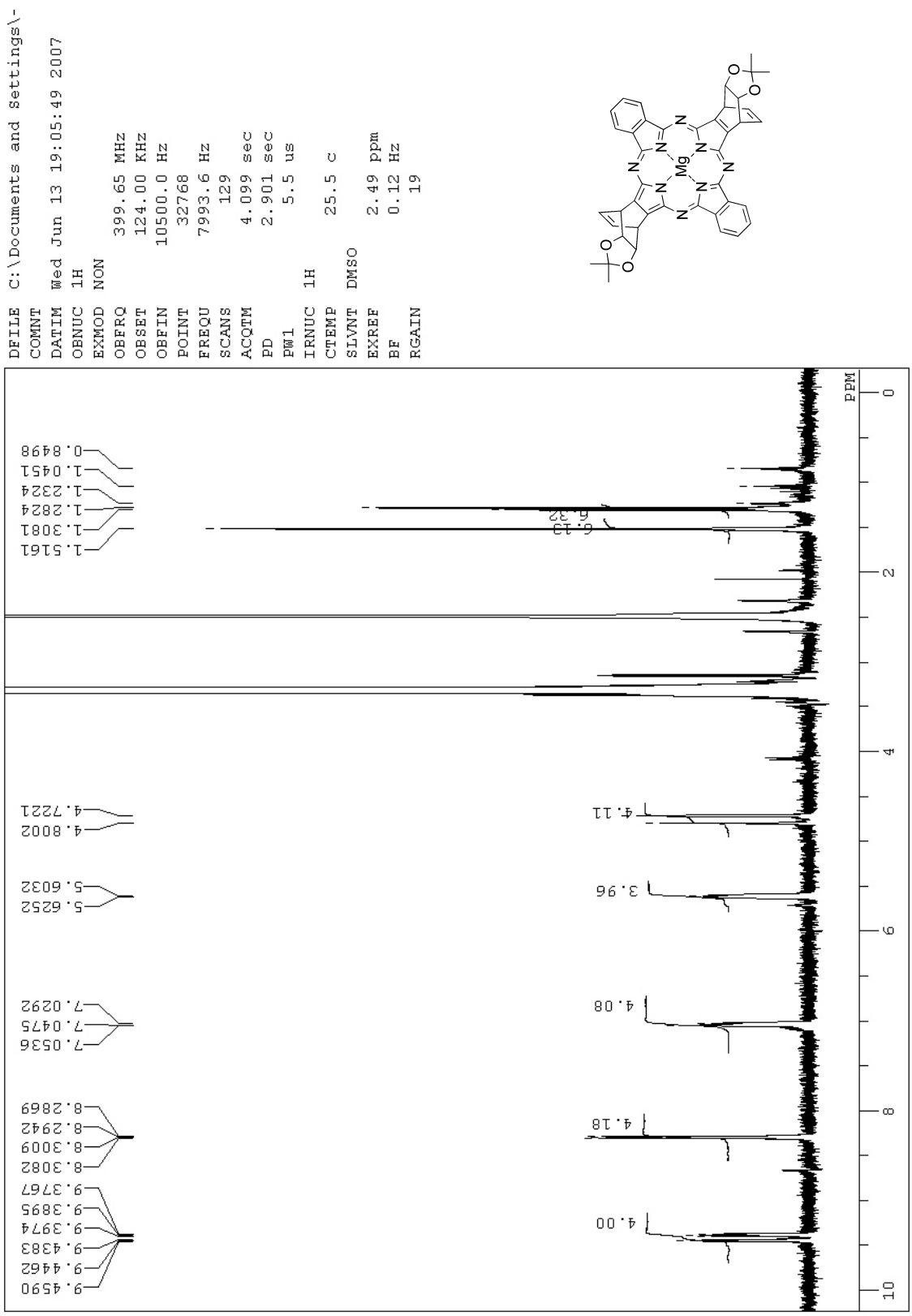


Fig. **S-3** ^{1}H NMR spectrum of **9**-Mg in DMSO-d_6.

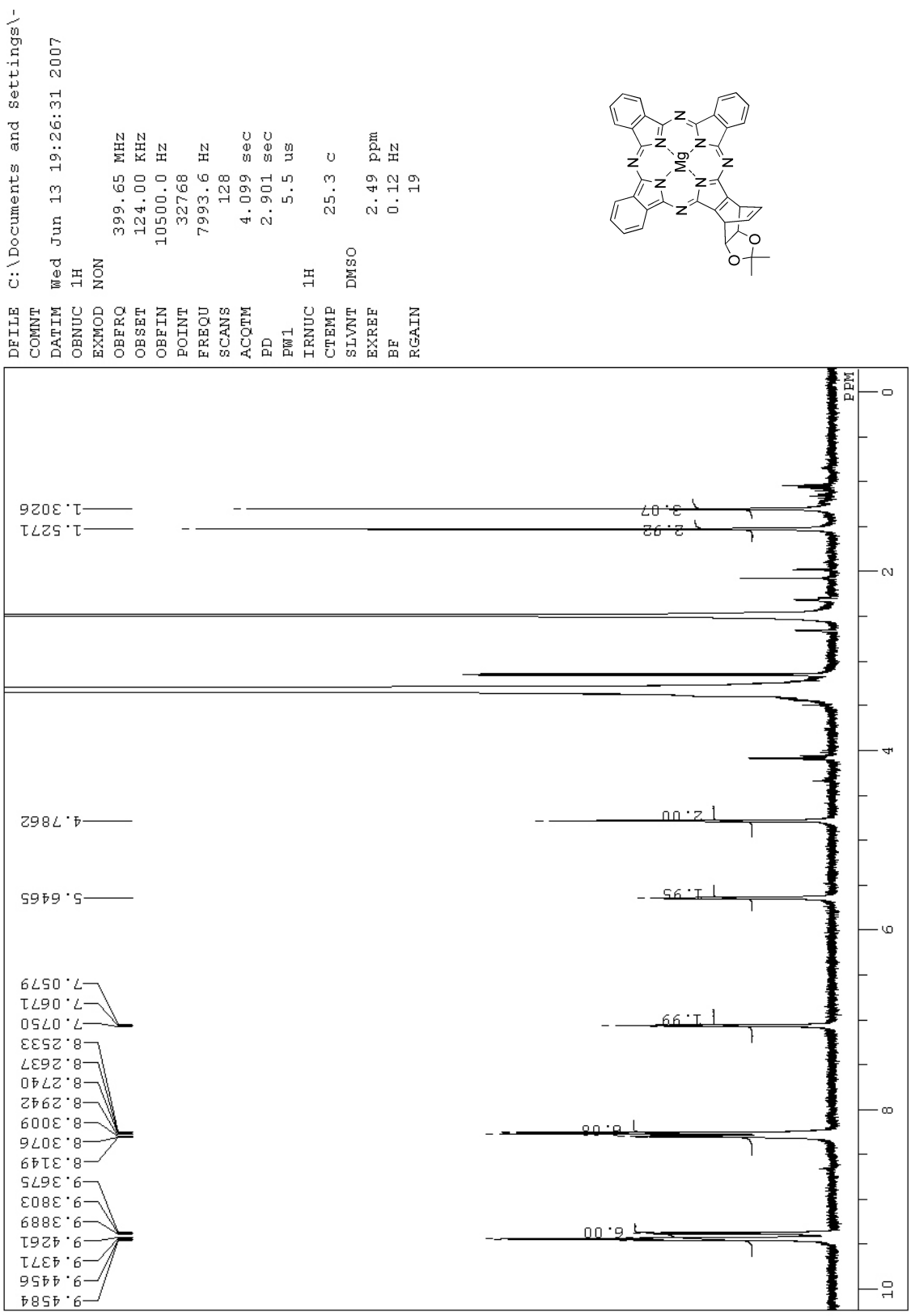


Fig. **S-4** ^{1}H NMR spectrum of **10**-Mg in DMSO-d_6.

UV-vis absorption spectra

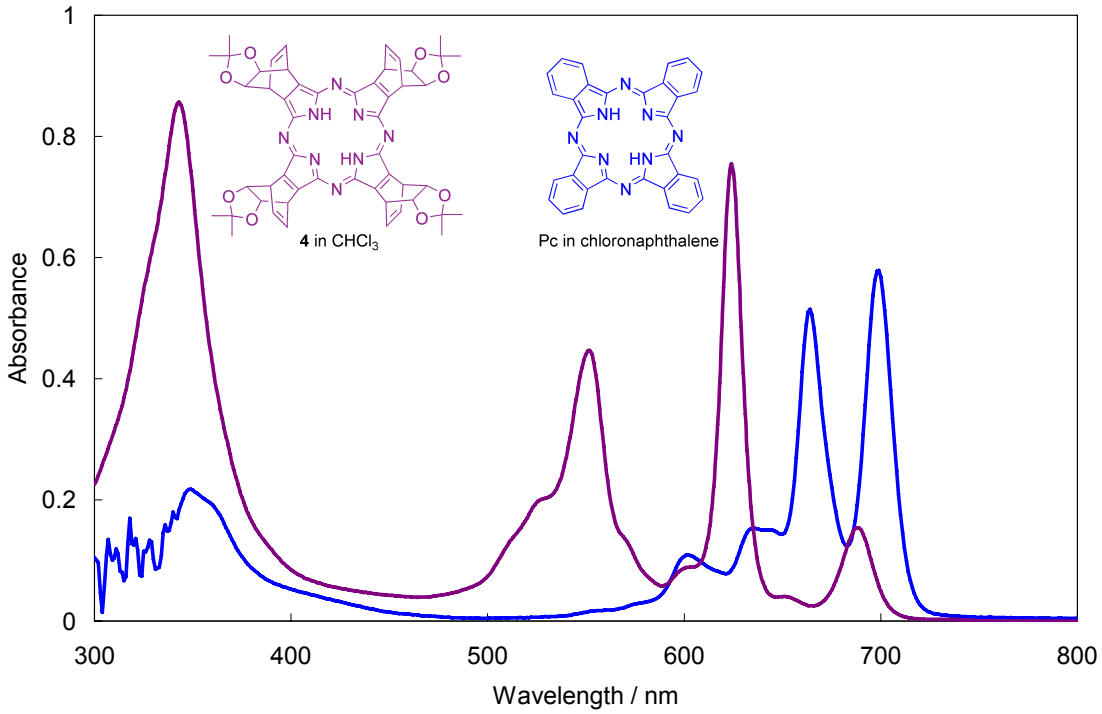


Fig. **S-5** UV-vis absorption spectra of **4** and Pc.

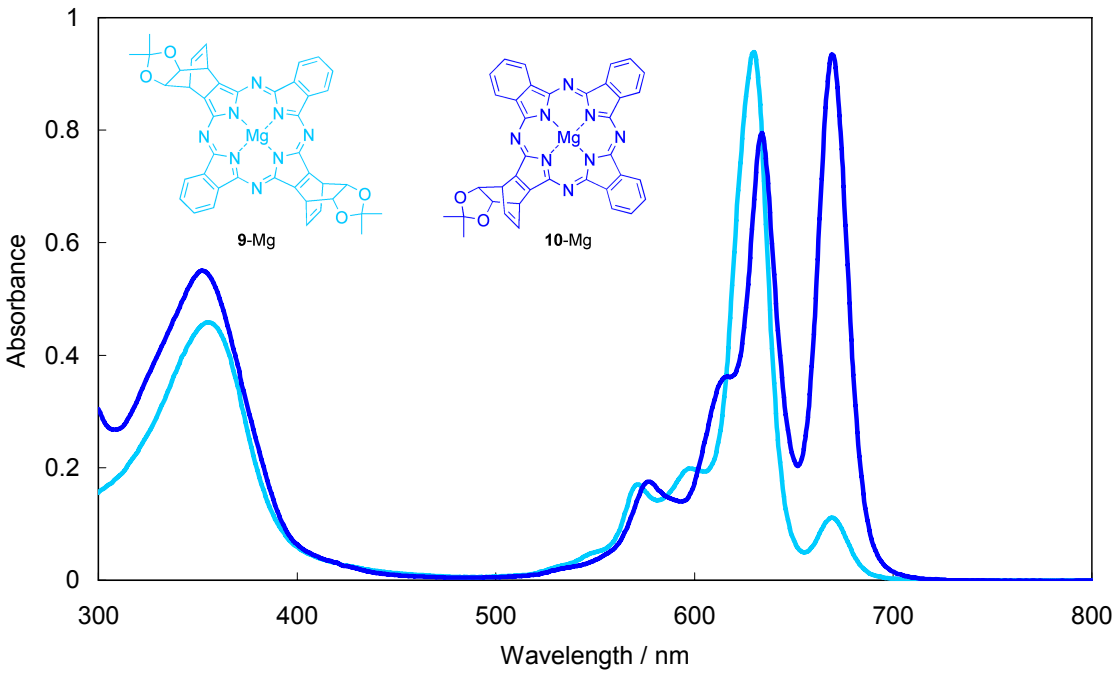


Fig. **S-6** UV-vis absorption spectra of **9**-Mg and **10**-Mg in $CHCl_3$.

TGA

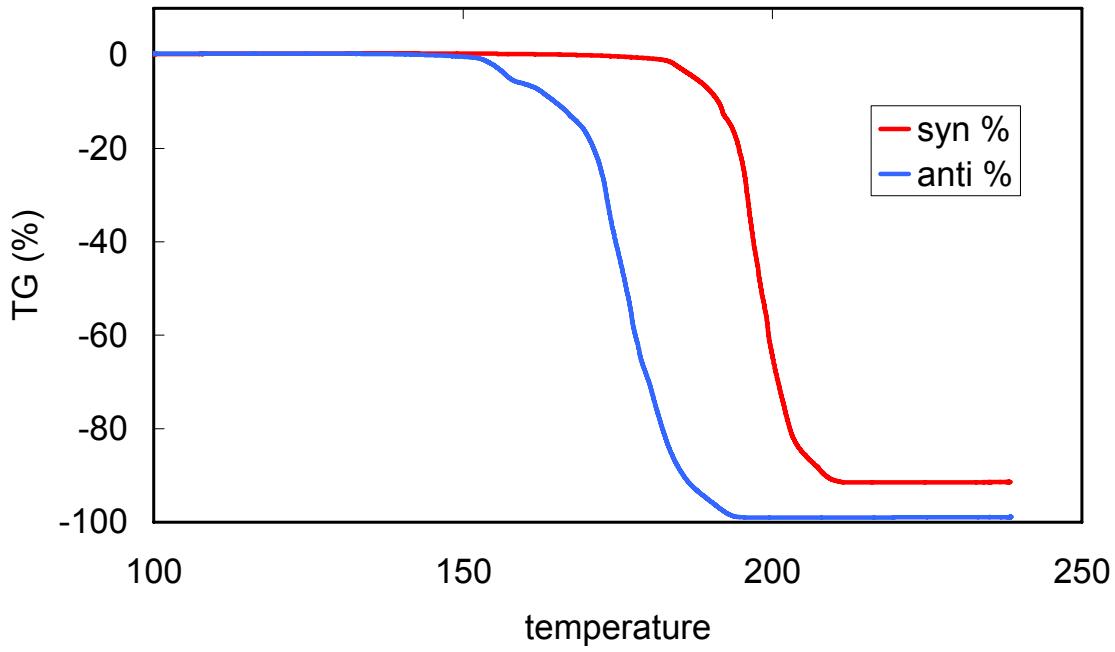


Fig. **S-7** TGA of *syn*- and *anti*-**8**.

X-ray crystallographic data

syn-8 (CCDC No. 692988)

checkCIF/PLATON report (full structural check)

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: __060705Polar

Bond precision: C-C = 0.0028 A Wavelength=0.71070

Cell: a=13.640(2) b=10.8311(17) c=17.021(3)
alpha=90 beta=109.834(1) gamma=90

Temperature: 298 K

	Calculated	Reported
Volume	2365.5(7)	2365.6(7)
Space group	C 2/m	C 1 2/m 1
Hall group	-C 2y	-C 2y
Moiety formula	C13 H12 N2 O2	C13 H12 N2 O2
Sum formula	C13 H12 N2 O2	C13 H12 N2 O2
Mr	228.25	228.25
Dx,g cm-3	1.282	1.282
Z	8	8
Mu (mm-1)	0.088	0.088
F000	960.0	960.0
F000'	960.43	
h,k,lmax	17,14,22	17,14,22
Nref	2853	2819
Tmin,Tmax	0.983,0.991	0.890,0.991
Tmin'	0.983	

Correction method= AbsCorr=MULTI-SCAN

Data completeness= Ratio = 0.988 Theta(max)= 27.480

R(reflections)= 0.0605(2223) wR2(reflections)= 0.1617(2819)

S = 1.110 Npar= 168

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 C9 -- C10 .. 5.57 su
PLAT371_ALERT_2_C Long C(sp2)-C(sp1) Bond C1 - C2 ... 1.43 Ang.
PLAT371_ALERT_2_C Long C(sp2)-C(sp1) Bond C9 - C10 ... 1.43 Ang.

Alert level G

PLAT793_ALERT_4_G Check the Absolute Configuration of C3 ..... S
PLAT793_ALERT_4_G Check the Absolute Configuration of C4 ..... R
PLAT793_ALERT_4_G Check the Absolute Configuration of C11 ..... R
PLAT793_ALERT_4_G Check the Absolute Configuration of C12 ..... S

0 **ALERT level A** = In general: serious problem
0 **ALERT level B** = Potentially serious problem
3 **ALERT level C** = Check and explain
4 **ALERT level G** = General alerts; check

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Publication of your CIF

A full structural check has been run on your CIF. This includes checks on:

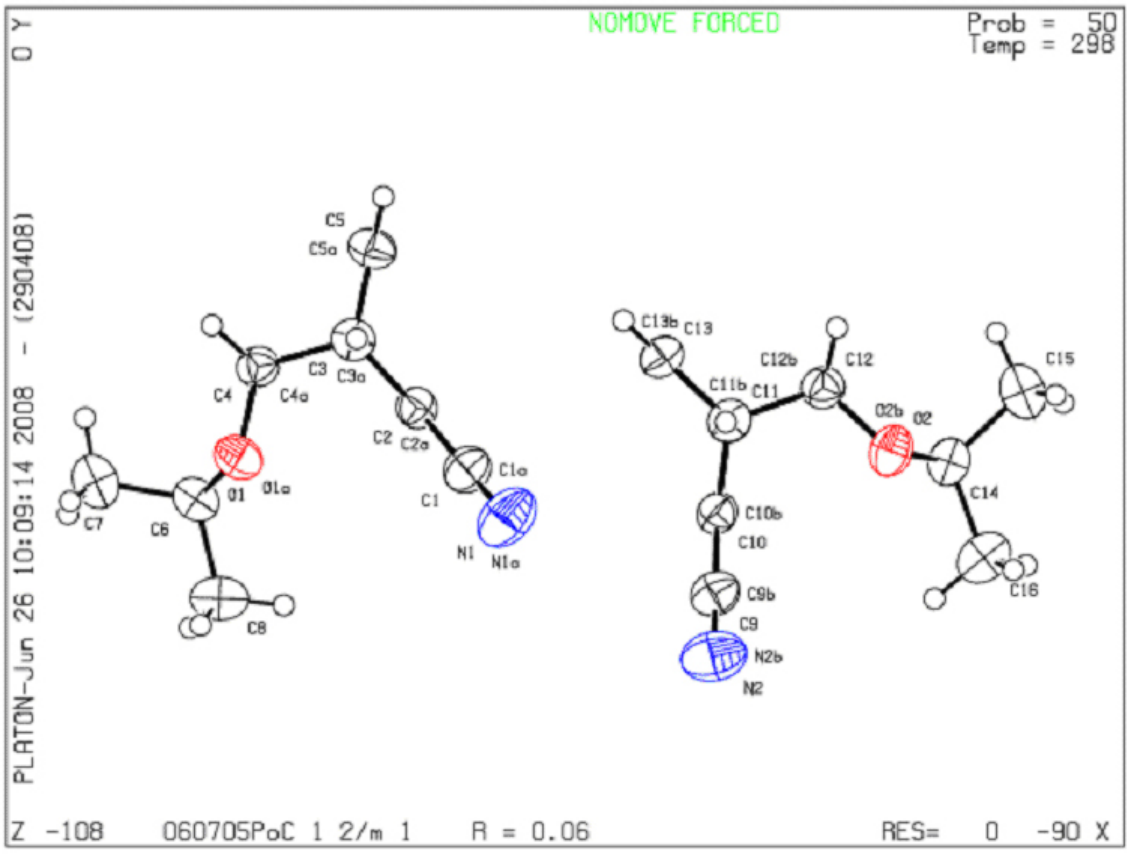
- CIF syntax and construction
- Cell and geometry details
- Space-group symmetry
- Anisotropic displacement parameters

These full checks give an indication of potential problems with your CIF. Please note that if you intend to submit your CIF for publication in Acta Crystallographica Section C or E, you must make sure that full publication checks are run on the final version of the CIF prior to submission.

If you intend to submit to another section of Acta Crystallographica, Journal of Applied Crystallography or Journal of Synchrotron Radiation, you should make sure that at least basic structural checks are run on the final version of your CIF prior to submission.

To submit your CIF for publication in an IUCr journal click here.

PLATON version of 29/04/2008; check.def file version of 22/04/2008
Datablock __060705Polar - ellipsoid plot



Download CIF editor (enCIFer) from the CCDC
Test a new CIF entry

***anti*-8 (CCDC No. 692987)**

checkCIF/PLATON report (full structural check)

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Datablock: __LessPolar

Bond precision: C-C = 0.0044 A Wavelength=0.71070
Cell: a=6.7368(14) b=9.5154(15) c=10.4950(15)
alpha=114.705(17) beta=95.44(2) gamma=102.56(2)
Temperature: 298 K

	Calculated	Reported
Volume	583.3(2)	583.3(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C13 H12 N2 O2	C13 H12 N2 O2
Sum formula	C13 H12 N2 O2	C13 H12 N2 O2
Mr	228.25	228.25
Dx,g cm-3	1.300	1.300

Z	2	2
Mu (mm-1)	0.090	0.090
F000	240.0	240.0
F000'	240.11	
h,k,lmax	8,12,13	8,12,13
Nref	2680	2639
Tmin,Tmax	0.991,0.995	0.784,0.995
Tmin'	0.973	

Correction method= AbsCorr=MULTI-SCAN

Data completeness= Ratio = 0.985 Theta(max)= 27.480

R(reflections)= 0.0782(1445) wR2(reflections)= 0.2465(2639)

S = 1.041 Npar= 157

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

ABSTM02_ALERT_3_C The ratio of expected to reported Tmax/Tmin(RR') is < 0.90
Tmin and Tmax reported: 0.784 0.995
Tmin(prime) and Tmax expected: 0.973 0.995
RR(prime) = 0.805
Please check that your absorption correction is appropriate.

PLAT371_ALERT_2_C Long C(sp2)-C(sp1) Bond C4 - C12 ... 1.43 Ang.

PLAT371_ALERT_2_C Long C(sp2)-C(sp1) Bond C5 - C13 ... 1.42 Ang.

PLAT061_ALERT_4_C Tmax/Tmin Range Test RR' too Large 0.81

Alert level G

PLAT793_ALERT_4_G Check the Absolute Configuration of C2 ..... S

PLAT793_ALERT_4_G Check the Absolute Configuration of C3 ..... S

PLAT793_ALERT_4_G Check the Absolute Configuration of C6 ..... R

PLAT793_ALERT_4_G Check the Absolute Configuration of C7 ..... R

---

0 **ALERT level A** = In general: serious problem
0 **ALERT level B** = Potentially serious problem
4 **ALERT level C** = Check and explain
4 **ALERT level G** = General alerts; check

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Publication of your CIF

A full structural check has been run on your CIF. This includes checks on:

- CIF syntax and construction
- Cell and geometry details
- Space-group symmetry

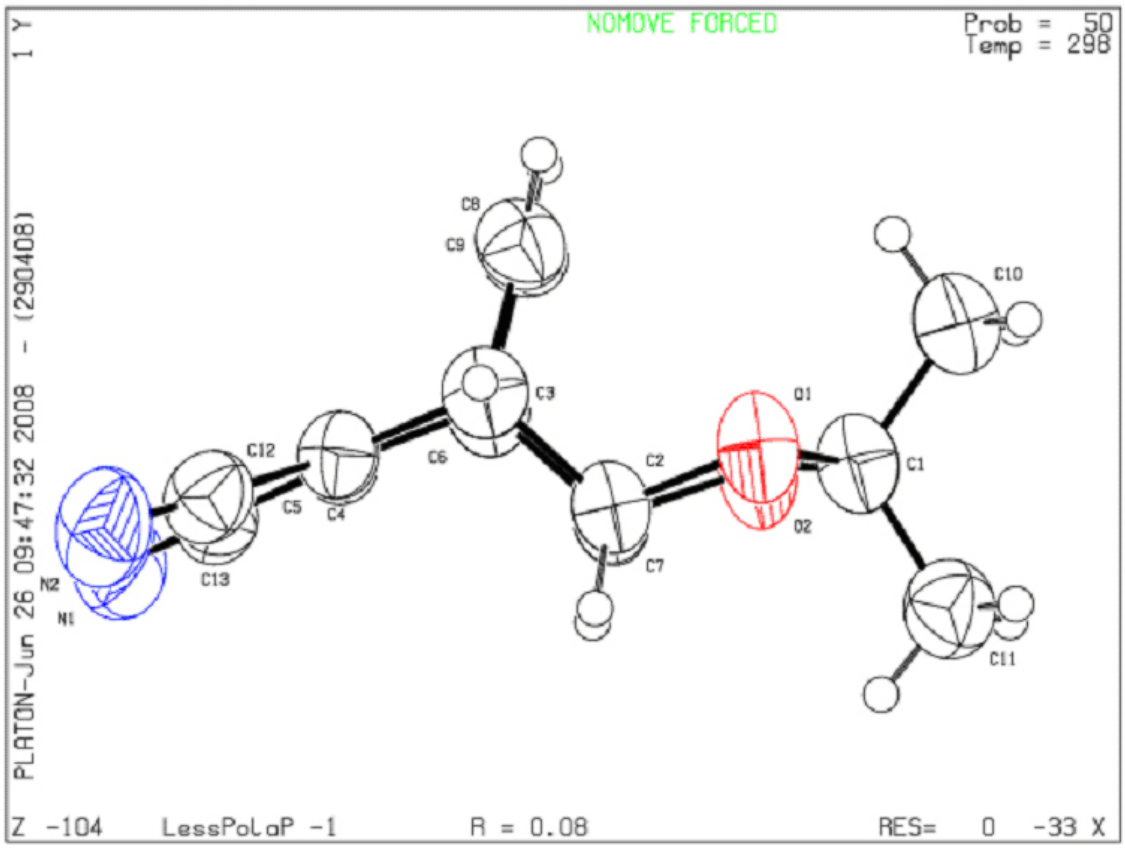
- Anisotropic displacement parameters

These full checks give an indication of potential problems with your CIF. Please note that if you intend to submit your CIF for publication in Acta Crystallographica Section C or E, you must make sure that full publication checks are run on the final version of the CIF prior to submission.

If you intend to submit to another section of Acta Crystallographica, Journal of Applied Crystallography or Journal of Synchrotron Radiation, you should make sure that at least basic structural checks are run on the final version of your CIF prior to submission.

To submit your CIF for publication in an IUCr journal click here.

PLATON version of 29/04/2008; check.def file version of 22/04/2008
Datablock __LessPolar - ellipsoid plot



Download CIF editor (enCIFer) from the CCDC
Test a new CIF entry