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**NOTE AFTER FIRST PUBLICATION:**

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# Molecular geometry and TADF photophysics:

# the strange case of DMAC-py-TRZ

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## SUPPORTING INFORMATION

## General Methods

*General Synthetic Procedures*. The following starting materials were synthesized according to literature materials, **DMAC**.[1]All other reagents and solvents were obtained from commercial sources and used as received. Air-sensitive reactions were performed under a nitrogen atmosphere using Schlenk techniques, no special precautions were taken to exclude air or moisture during work-up and crystallisation. Flash column chromatography was carried out using silica gel (Silia-P from Silicycle, 60 Å, 40-63 μm). Analytical thin-layer-chromatography (TLC) was performed with silica plates with aluminum backings (250 μm with F-254 indicator). TLC visualization was accomplished by 254/365 nm UV lamp. HPLC analysis was conducted on a Shimadzu LC-40 HPLC system. HPLC traces were performed using a Shim-pack GIST 3μm C18 reverse phase analytical column. GCMS analysis was conducted using a Shimadzu QP2010SE GC-MS equipped with a Shimadzu SH-Rtx-1 column (30 m x 0.25 mm). $^{1}$H, $^{13}$C and $^{19}$F NMR spectra were recorded on a Bruker Advance spectrometer (500 MHz for $^{1}$H, 125 MHz for $^{13}$C, 471 MHz for $^{19}$F and 202 MHz for $^{31}$P). The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "q" for quartet, "m" for multiplet, and "br" for broad. $^{19}$F and $^{31}$P NMR spectra were recorded with proton decoupling. $^{1}$H and $^{13}$C NMR spectra were referenced residual solvent peaks with respect to TMS ($\delta$ = 0 ppm). Melting points were measured using open-ended capillaries on an Electrothermal 1101D Mel-Temp apparatus and are uncorrected. High-resolution mass spectrometry (HRMS) was performed by EPSRC National Mass Spectrometry Service Centre (NMSSC). Elemental analyses were performed by Mr. Stephen Boyer, London Metropolitan University or the School of Geosciences at the University of Edinburgh.

*Electrochemistry measurements*. Cyclic Voltammetry (CV) and Differential Pulse Voltammetry analyses were performed on an Electrochemical Analyzer potentiostat model 620D from CH Instruments. Sample of **DMAC-TRZ and DMAC-py-TRZ** were prepared in DCM that was degassed by sparging with DCM-saturated nitrogen gas for 10 minutes before measurements. All measurements were performed in 0.1 M DCM solution of tetrabutylammonium hexafluorophosphate, which was used as the supporting electrolyte. An $Ag/Ag^{+}$ electrode was used as the reference electrode while a glassy carbon electrode and a platinum wire were used as the working electrode and counter electrode, respectively. The redox potentials are reported relative to a saturated calomel electrode (SCE) with a ferrocene/ferrocenium ($Fc/Fc^{+}$) redox couple as the internal standard (0.46 V vs SCE for DCM [2]).

*Photophysical measurements*.–Optically dilute solutions of concentrations on the order of $10^{-5}$ M were prepared in HPLC grade methyl-cyclohexane, toluene, DCM, THF, and MeCN for absorption and emission analysis. Absorption spectra were recorded at room temperature on a Shimadzu UV-1800 double beam spectrophotometer with a 1 cm quartz cuvette. Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least five independent solutions at varying concentrations with absorbance ranging from $1.66 \times 10^{-5}$ to $1.93 \times 10^{-6}$ M.

For emission studies, aerated solutions were bubbled with compressed air for 5 minutes and spectra were taken using the same cuvette as for the absorption analysis. Degassed solutions were prepared via three freeze-pump-thaw cycles and spectra were taken using a home-made Schlenk quartz cuvette. Steady-state emission, excitation spectra and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980. Samples were excited at 340 nm for steady-state measurements and at 378 nm for time-resolved measurements. Photoluminescence quantum yields for solutions were determined using the optically dilute method [3] in which four sample solutions with absorbances of ca. 0.103, 0.065, 0.052 and 0.047 for **DMAC-py-TRZ**, and 0.098, 0.081, 0.061 and 0.041 for **DMAC-TRZ** at 360 nm were used. The Beer-Lambert law was found to remain linear at the concentrations of the solutions. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis with the Pearson regression factor ($R^2$) for the linear fit of the data set surpassing 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope obtained from the linear fit of these results. The equation $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$ was used to calculate the relative quantum yield of the sample, where ($\Phi_r$) is the absolute quantum yield of the external reference quinine sulfate ($\Phi_r$ = 54.6% in 1 *N* $H_2SO_4$).[4] A stands for the absorbance at the excitation wavelength, I is the integrated area under the corrected emission curve and n is the refractive index of the solvent. The subscripts "s" and "r" representing sample and reference, respectively. The experimental uncertainty in the emission quantum yields is conservatively estimated to be 10%, though we have found that statistically, we can reproduce $\Phi_{PL}$ values to 3% relative error. Thin-film $\Phi_{PL}$ measurements were performed using an integrating sphere in a Hamamatsu C9920-02 system. A xenon lamp coupled to a monochromator enabled excitation selectivity, chosen here to be 340 nm. The output was then fed into the integrating sphere via a fibre, exciting the sample. PL spectra were collected with a multimode fibre and detected with a back-thinned CCD. Doped thin films were prepared by mixing sample (10 wt%) and host material in Chlorobenzene

solution, followed by spin-casting on a quartz substrate. The $\Phi_{PL}$ of the films were then measured in air and by purging the integrating sphere with flowing $N_2$ gas. Time-resolved PL measurements of the thin films were carried out using the time-correlated single-photon counting technique. The samples were excited at 378 nm by a pulsed laser diode (Picoquant, model PLS 370) and were kept in a vacuum of $< 8 \times 10^{-4}$ mbar.

The singlet-triplet splitting energy, $\Delta E_{ST}$, was estimated by recording the prompt fluorescence spectra and phosphorescence emission at 77 K. The films were excited either by a Q-switched Nd:YAG laser emitting at 343 nm (Laser-export) or by a femtosecond optical parametric amplifier emitting at 320 nm (Orpheus-N, Light Conversion). Emission from the samples was focused onto a spectrograph (Chromex imaging, 250is spectrograph) and detected on a sensitive gated iCCD camera (Stanford Computer Optics, 4Picos) having a sub-nanosecond resolution. Prompt fluorescence spectra were measured 1 ns after the excitation of the femtosecond laser with iCCD exposure time of 100 ns. Phosphorescence spectra were measured 1 ms after the excitation of the Nd:YAG laser with iCCD exposure time of 8.5 ms.

Low-temperature emission measurements in 2-MeTHF and room temperature emission in polyTHF were collected with a FLS1000 Edinburgh fluorimeter, equipped with a gated PMT detector. Low-temperature measurements were performed using a liquid nitrogen cooled optical cryostat (OptistatDN, Oxford Instrument) equipped with temperature controller (ITC601, Oxford Instrument). 2-MeTHF was stored over molecular sieves for 1 night and filtered, and the sample was rapidly cooled down to 77 K to obtain transparent glasses.

*Fitting time-resolved luminescence measurements:* Time-resolved PL measurements were fitted to a sum of exponentials decay model with chi-squared ($\chi^2$) values between 1 and 2, using the EI FLS980 software. Each component of the decay is assigned a weight, ($w_i$), which is the contribution of the emission from each component to the total emission.

The average lifetime was then calculated using the following:

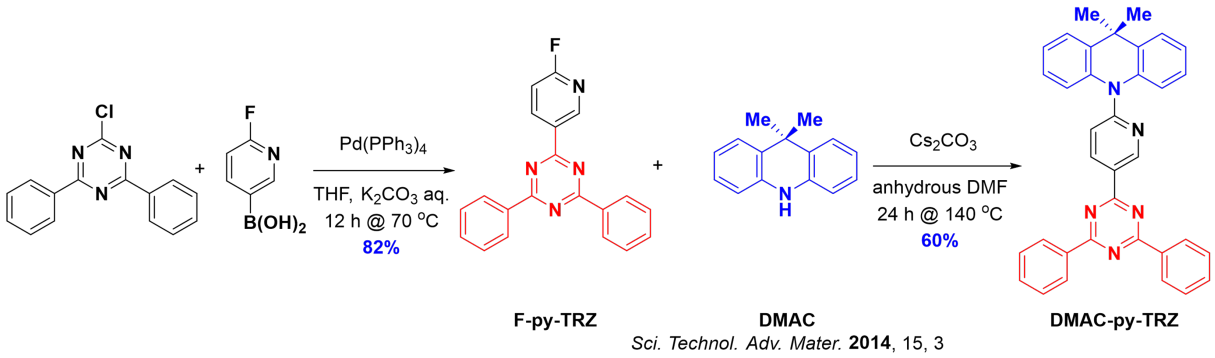
- Two exponential decay model:

$$\tau_{AVG} = \tau_1 w_1 + \tau_2 w_2$$

with weight defined as $w_1 = \frac{A1\tau_1}{A1\tau_1 + A2\tau_2}$ and $w_2 = \frac{A2\tau_2}{A1\tau_1 + A2\tau_2}$ where A1 and A2 are the preexponential-factors of each component.

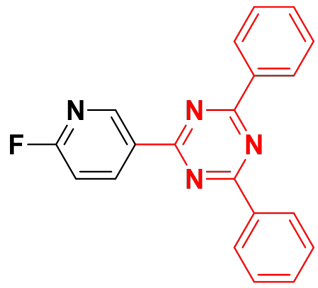
## Experimental Section

## Synthesis




*Sci. Technol. Adv. Mater.* **2014**, 15, 3

### 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (F-py-TRZ)



To a mixture of 2-chloro-4,6-diphenyl-1,3,5-triazine (1.30 g, 5.00 mmol, 1 equiv.) and (6-fluoropyridin-3-yl)boronic acid (0.78 g, 5.50 mmol, 1.1 equiv.) were added 40 mL of THF and 10 mL 2 M $K_2CO_3$ aqueous solution followed by bubbling with $N_2$ through the solution for 10 min and heating to reflux for 12 h under a $N_2$ atmosphere. The reaction was diluted with water, and the organic layer was extracted with dichloromethane (DCM) (3 × 50 mL). The organic phase was washed with brine, dried over $Na_2SO_4$ and concentrated under reduced pressure. The product was obtained as a white solid after recrystallization from THF (1.31 g). **Yield**: 80%. **$R_f$**: 0.81 (EtOAc: hexane = 1:4 on silica gel). **Mp**: 245-250 °C. **$^1$H NMR (500 MHz, $CDCl_3$) δ (ppm)**: 9.59-9.58 (d, 1H), 9.12-9.08 (m, 1H), 8.76-8.74 (m, 4H), 7.67 – 7.63 (m, 2H), 7.63 – 7.57 (m, 4H), 7.14-7.12 (m, 1H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ (ppm)**: 171.99, 169.38, 167.08, 165.13, 149.86, 149.73, 141.84, 141.77, 135.81, 133.07, 130.36, 130.32, 129.16, 128.91, 109.84, 109.54. **GC-MS retention time:** 12.024 min; **Mass Theoretical:** ($C_{20}H_{13}FN_4$) 328.35 g/mol; **Mass Found:** 328 g/mol.

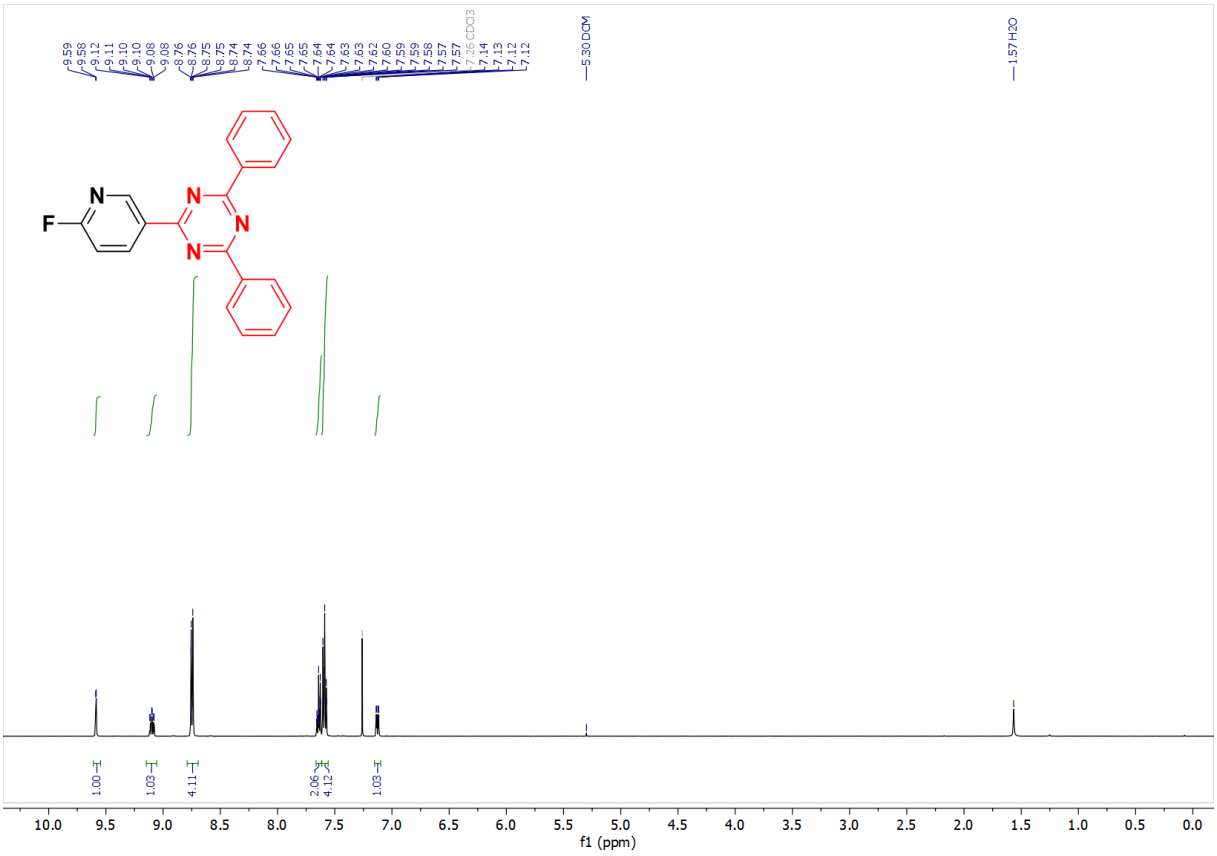



Figure **S1.** $^{1}$H NMR of **F-py-TRZ** in $CDCl_3$.

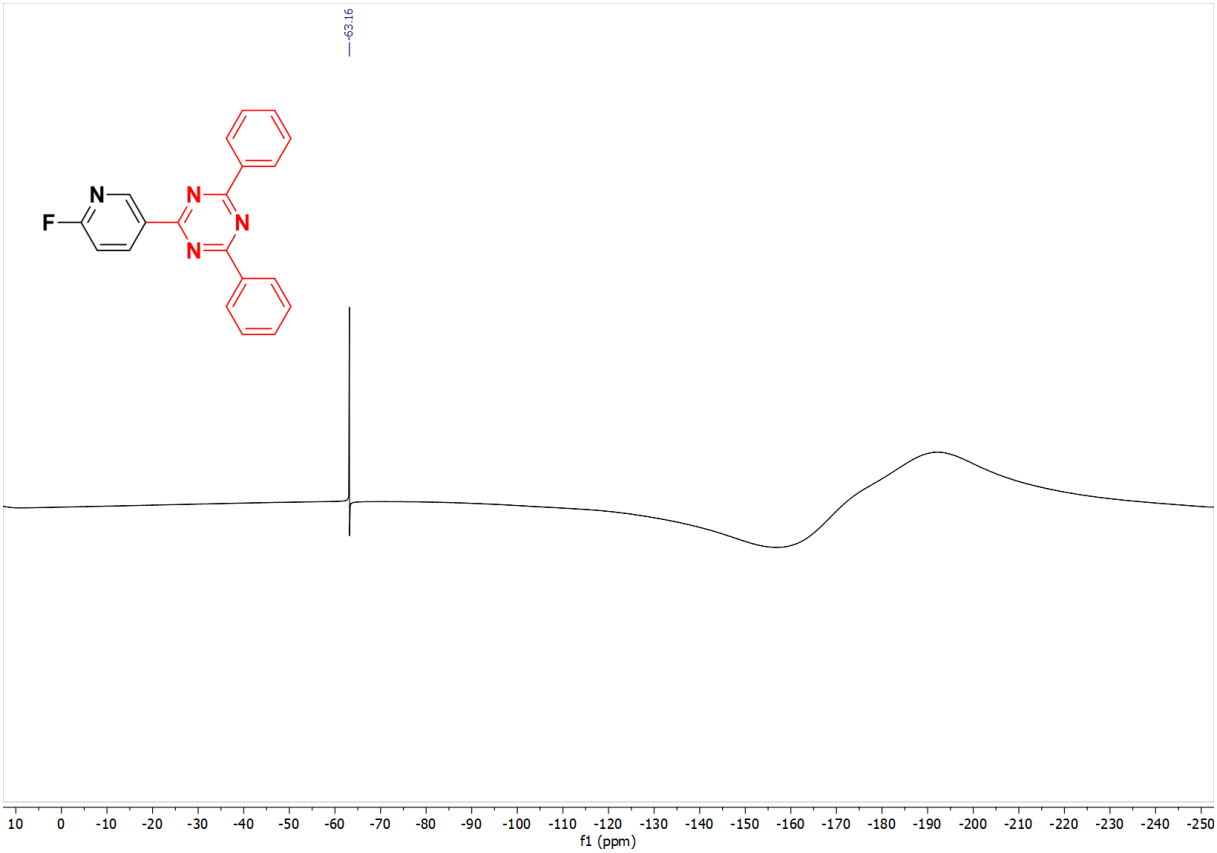



Figure **S2**. $^{19}$F NMR of **F-py-TRZ** in $CDCl_3$

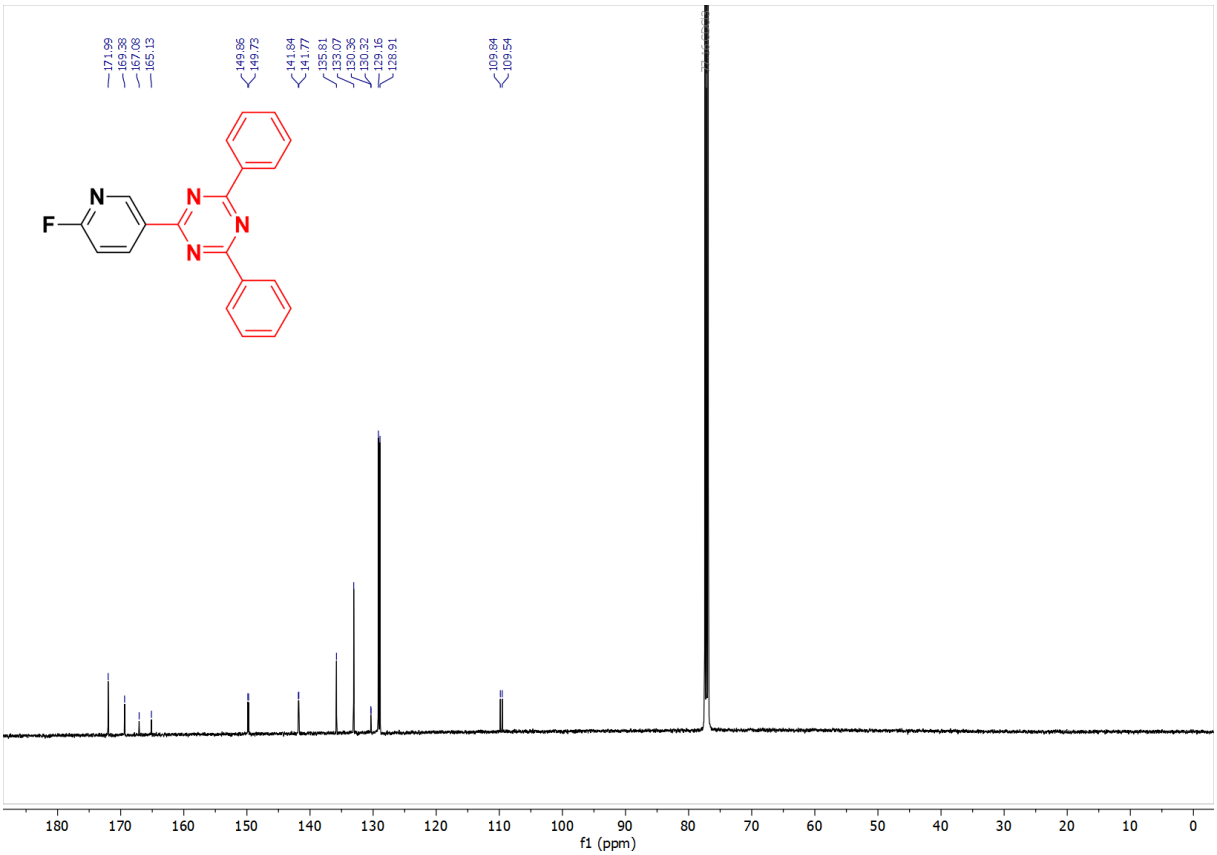
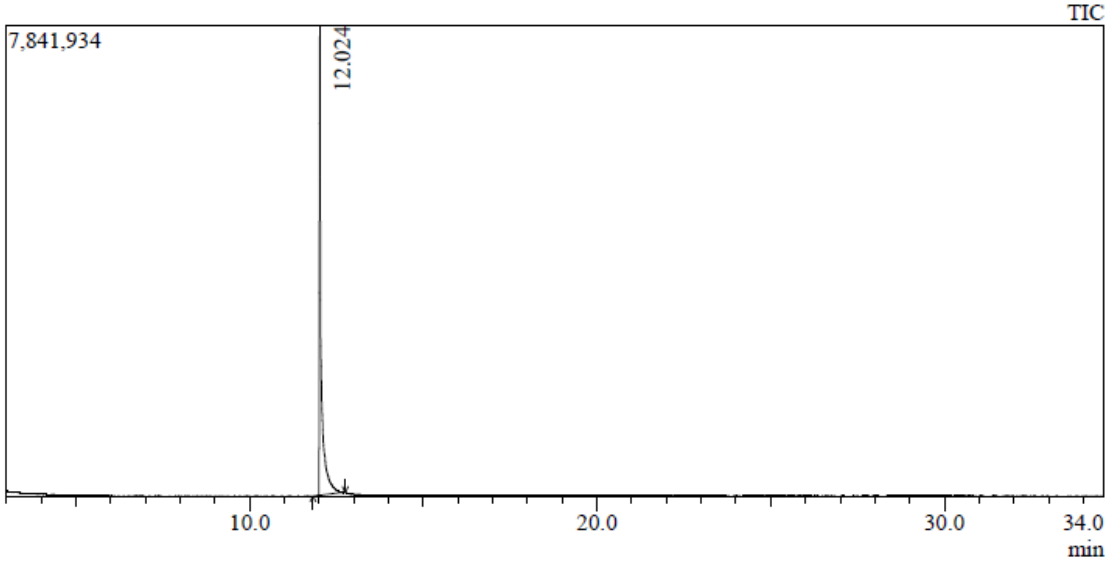



Figure **S3**. $^{13}C$ NMR of **F-py-TRZ** in $CDCl_3$.

Sample Information

| | |
|---|---|
| Analyzed by | : Admin |
| Analyzed | : 08/03/2022 15:51:06 |
| Sample Type | : Unknown |
| Level # | : 1 |
| Sample Name | : F-py-TRZ |
| Sample ID | : |
| IS Amount | : [1]=1 |
| Sample Amount | : 1 |
| Dilution Factor | : 1 |
| Vial # | : 60 |
| Injection Volume | : 1.00 |
| Data File | : S:\Ettore\080322\F-py-TRZ.qgd |
| Org Data File | : S:\Ettore\080322\F-py-TRZ.qgd |
| Method File | : S:\standard method 1 for RTX-1 column 330 injection-long.qgm |
| Org Method File | : S:\standard method 1 for RTX-1 column 330 injection-long.qgm |
| Report File | : |
| Tuning File | : S:\auto tuning result\03022022.qgt |
| Modified by | : Admin |
| Modified | : 08/03/2022 16:25:43 |

Chromatogram F-py-TRZ S:\Ettore\080322\F-py-TRZ.qgd




Peak Report TIC

| Peak# | R.Time | Area | Area% | Height | A/H | Base m/z | Base Int. |
|---|---|---|---|---|---|---|---|
| 1 | 12.024 | 27141817 | 100.00 | 7807427 | 3.48 | 103.10 | 2762479 |
| | | 27141817 | 100.00 | 7807427 | | | |

Line#:1 R.Time:12.025(Scan#:1084)
MassPeaks:581
RawMode:Single 12.025(1084) BasePeak:103.10(3337273)
BG Mode:None Group 1 - Event 1 Scan

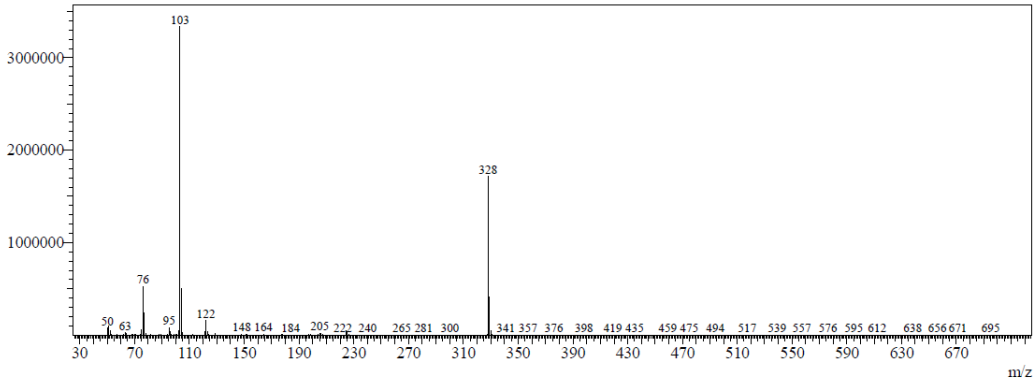
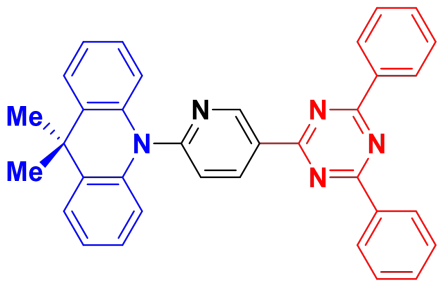



Figure **S4.** GC-MS trace of **F-py-TRZ**.

**10-(5-(4,6-diphenyl-1,3,5-triazin-2-yl)pyridin-2-yl)-9,9-dimethyl-9,10-dihydroacridine (DMAC-py-TRZ)**




To $Cs_2CO_3$ (1.03 g, 3 mmol, 3.1 equiv.) in a Schlenk flask was added DMAC (0.24 g, 1.1 mmol, 1.1 equiv.) and 10 mL of anhydrous DMF under $N_2$. The suspension was stirred for 30 min at room temperature. **F-py-TRZ** (0.33 g, 1.0 mmol, 1.0 equiv.,) was then added and the reaction was heated to reflux for 24 h. The reaction went from white to yellow/orange to dark red with increasing temperature. The reaction was diluted with water, and the organic layer was extracted with dichloromethane (DCM) (3× 50 mL). The organic phase was washed with brine, dried over $Na_2SO_4$ and concentrated under reduced pressure. The target product was obtained as a yellow solid after purification by column chromatography on silica gel using 5:1 hexane/DCM as eluent followed by recrystallization in THF/MeOH. (0.30 g). **Yield:** 60%. **$R_f$:** 0.81 (EtOAc: hexane = 1:4 on silica gel). **Mp**: 260-270 °C. **$^1$H NMR (500 MHz, $CDCl_3$) δ (ppm)**: 9.76 (d, 1H), 8.82-8.74 (m, 4H), 7.80-7.78 (m, 2H), 7.63 – 7.55 (m, 5H), 7.52-7.50 (m, 2H), 7.377.30 (m, 1H), 7.25 – 7.22 (m, 1H), 1.60 (s, 4H) **$^{13}$C NMR (125 MHz, $CDCl_3$) δ (ppm)**: 171.58, 170.22, 158.42, 150.44, 141.43, 140.13, 138.30, 136.30, 132.69, 129.06, 128.79, 126.18, 125.21, 125.06, 124.62, 124.05, 110.63, 37.94, 27.51. **HPLC retention time:** 5.039; **purity:** 99.98%; **HR-MS** (Xevo G2-XS QTof) **$[M+H]^+$ Calculated:** ($C_{35}H_{27}N_5$) 517.6400; **Found:** 518.2336.

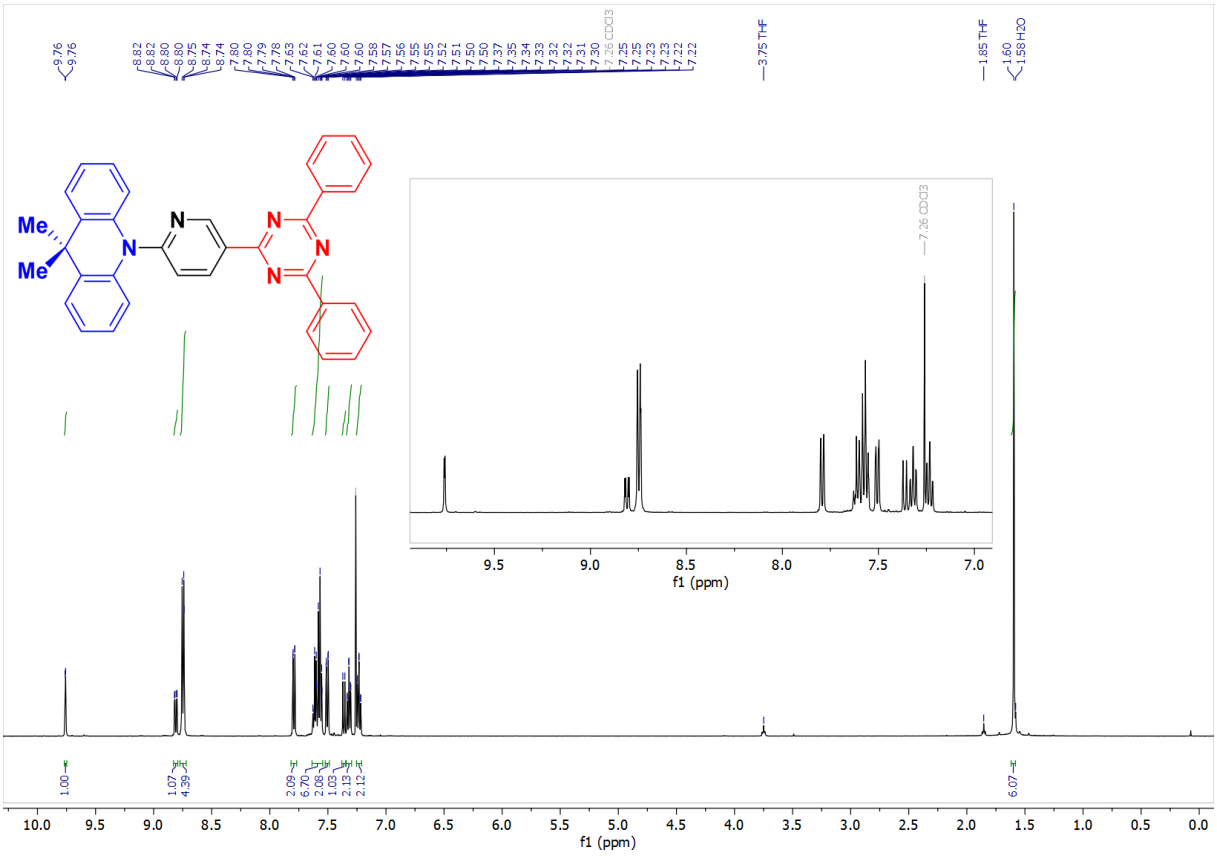



Figure **S5.** $^{1}$H NMR of **DMAC-py-TRZ** in $CDCl_3$.

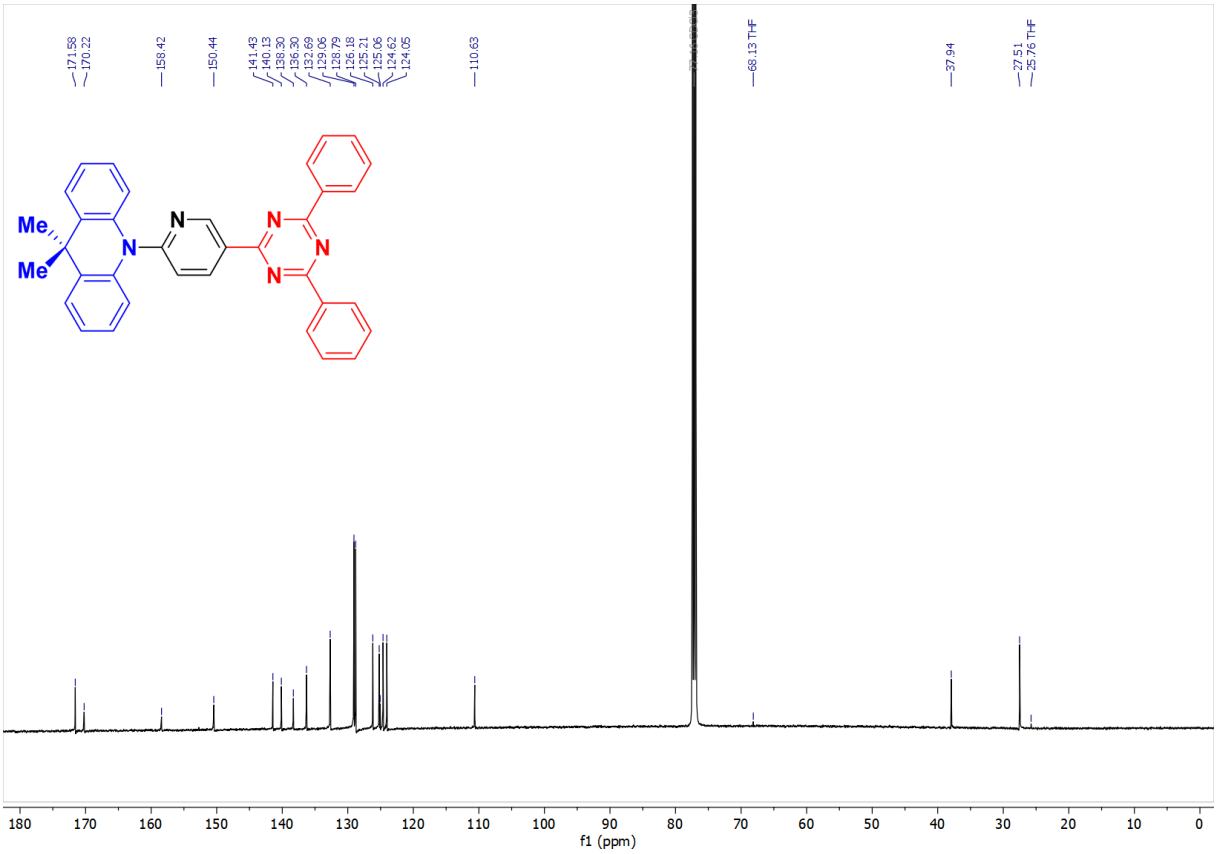


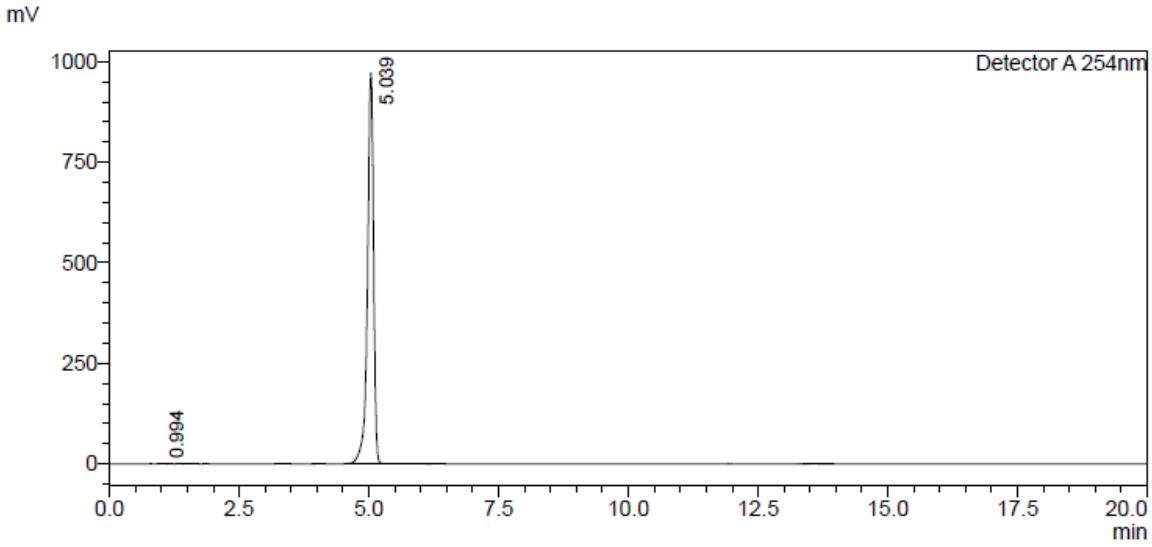

Figure **S6.** $^{13}$C NMR of **DMAC-py-TRZ** in $CDCl_3$.

# HPLC Trace Report31Aug2021

**<Sample Information>**

| | | | |
|---|---|---|---|
| Sample Name | : EC-2894-DMAC-py-TRZ | | |
| Sample ID | : | | |
| Method Filename | : 95% Acetonitrile 5 Water 20 mins.lcm | | |
| Batch Filename | : EC-2591-2713-2894-DMAC-py-TRZ-recryst-MeCN-95-try2.lcb | | |
| Vial # | : 1-5 | Sample Type | : Unknown |
| Injection Volume | : 10 uL | | |
| Date Acquired | : 31/08/2021 12:13:23 | Acquired by | : System Administrator |
| Date Processed | : 31/08/2021 12:33:26 | Processed by | : System Administrator |

**<Chromatogram>**




**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Area% | Area/Height | Width at 5% Height |
|---|---|---|---|---|---|---|
| 1 | 0.994 | 1528 | 485 | 0.019 | 3.152 | -- |
| 2 | 5.039 | 7924891 | 970451 | 99.981 | 8.166 | 0.305 |
| Total | | 7926419 | 970936 | 100.000 | | |

Figure **S7.** HPLC analysis report for **DMAC-py-TRZ**.

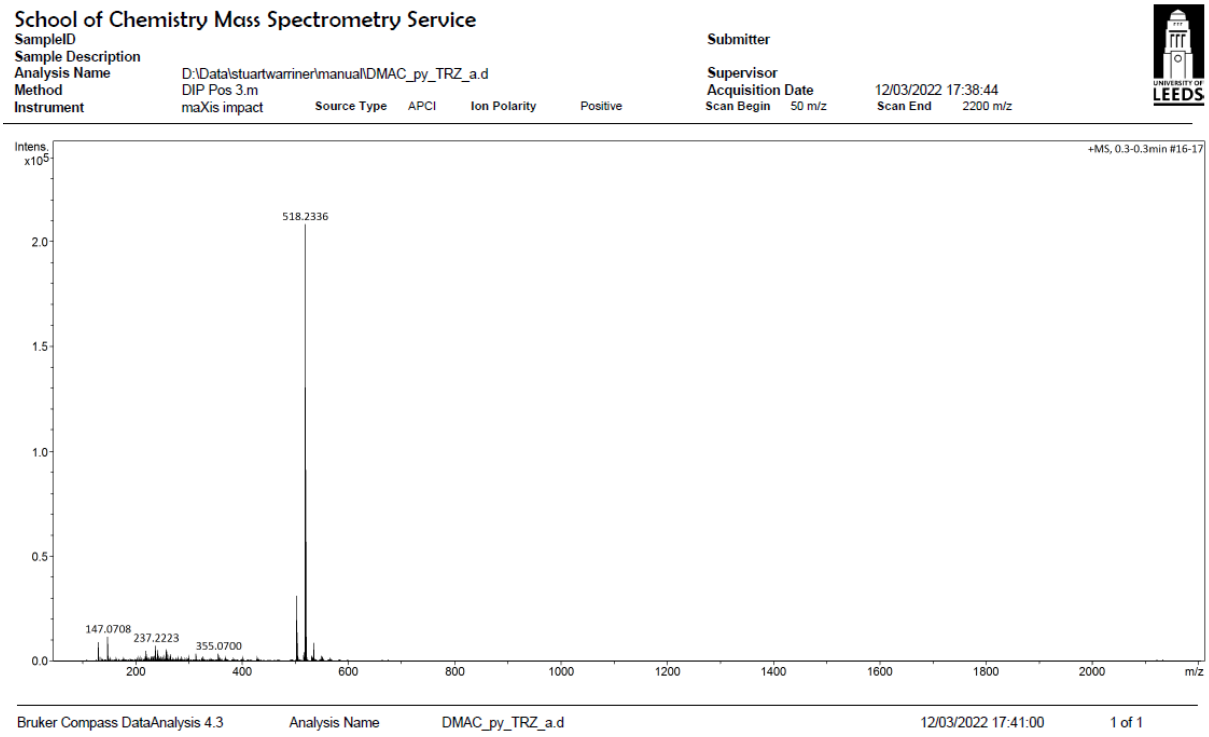



Figure **S8.** HRMS analysis report for **DMAC-py-TRZ**.

**Crystal structure**

**DMAC-py-TRZ**

**Data Collection**

A colourless prism crystal of $C_{38}H_{36}N_4O_2$ having approximate dimensions of 0.200 x 0.100 x 0.100 mm was mounted in a loop. All measurements were made on a Rigaku XtaLAB P100 diffractometer using multi-layer mirror monochromated Cu-Ka radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 9.13283(11) Å
b = 27.2082(2) Å b = 107.9900(13)°
c = 13.18180(16) Å
V = 3115.38(6) Å$^3$

For Z = 4 and F.W. = 580.73, the calculated density is 1.238 g/cm$^3$. The reflection conditions of:

h0l: l = 2n
0k0: k = 2n

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of -100 ± 1°C to a maximum 2q value of 136.6°.

**Data Reduction**

Of the 31449 reflections were collected, where 5667 were unique ($R_{int}$ = 0.0229). Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[5]

The linear absorption coefficient, m, for Cu-Ka radiation is 6.092 cm$^{-1}$. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.738 to 0.941. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.018550). [6]

**Structure Solution and Refinement**

The structure was solved by direct methods[7] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[8] on $F^2$ was based

on 5667 observed reflections and 402 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \; ||Fo| - |Fc|| \; / \; \Sigma \; |Fo| = 0.0564$$

$$wR2 = [ \; \Sigma \; ( \; w \; (Fo^2 - Fc^2)^2 \; ) / \; \Sigma \; w(Fo^2)^2]^{1/2} = 0.1413$$

The goodness of fit* was 1.12. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and -0.39 $e^-$/Å, respectively. [7]

*Goodness of fit is defined as:

$$[S\,w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$$

where: $N_o$ = number of observations
$N_v$ = number of variables

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4.[9] Anomalous dispersion effects were included in Fcalc;[10] the values for Df' and Df'' were those of Creagh and McAuley[11]. The values for the mass attenuation coefficients are those of Creagh and Hubbell.[12] All calculations were performed using the CrystalStructure[13] crystallographic software package except for refinement, which was performed using SHELXL Version 2018/3[8].

Experimental details

## A. Crystal Data

| | |
|---|---|
| Empirical Formula | $C_{38}H_{36}N_4O_2$ |
| Formula Weight | 580.73 |
| Crystal Color, Habit | colourless, prism |
| Crystal Dimensions | 0.200 X 0.100 X 0.100 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| Lattice Parameters | a = 9.13283(11) Å<br>b = 27.2082(2) Å<br>c = 13.18180(16) Å<br>β = 107.9900(13) °<br>V = 3115.38(6) Å$^3$ |
| Space Group | $P2_1/c$ (#14) |
| Z value | 4 |
| $D_{calc}$ | 1.238 g/cm$^3$ |
| $F_{000}$ | 1232.00 |
| μ(CuKα) | 6.092 cm$^{-1}$ |

B. Intensity Measurements

| | |
|---|---|
| Diffractometer | XtaLAB P100 |
| Radiation | CuKα (λ = 1.54184 Å)<br>multi-layer mirror monochromated |
| Temperature | -100.0°C |
| Detector Aperture | 83.8 x 33.5 mm |
| Data Images | 3982 exposures |
| Pixel Size | 0.172 mm |
| $2\theta_{max}$ | 136.6° |
| No. of Reflections Measured | Total: 31449<br>Unique: 5667 ($R_{int}$ = 0.0229) |
| Corrections | Lorentz-polarization<br>Absorption<br>(trans. factors: 0.738 - 0.941)<br>Secondary Extinction<br>(coefficient: 1.85500e-002) |

C. Structure Solution and Refinement

| | |
|---|---|
| Structure Solution | Direct Methods (SHELXT Version 2018/2) |
| Refinement | Full-matrix least-squares on $F^2$ |
| Function Minimized | $\Sigma$ w $(Fo^2 - Fc^2)^2$ |
| Least Squares Weights | $w = 1/ [ \sigma^2(Fo^2) + (0.0770 \cdot P)^2 + 0.7854 \cdot P ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$ |
| $2\theta_{max}$ cutoff | 136.6° |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (All reflections) | 5667 |
| No. Variables | 402 |
| Reflection/Parameter Ratio | 14.10 |
| Residuals: R1 (I>2.00s(I)) | 0.0564 |
| Residuals: R (All reflections) | 0.0571 |
| Residuals: wR2 (All reflections) | 0.1413 |
| Goodness of Fit Indicator | 1.121 |
| Max Shift/Error in Final Cycle | 0.005 |
| Maximum peak in Final Diff. Map | 0.29 $e^-/Å^3$ |
| Minimum peak in Final Diff. Map | -0.39 $e^-/Å^3$ |

**Table S1.** Atomic coordinates and $B_{iso}/B_{eq}$

| atom | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| O41 | 0.1125(2) | 0.53242(8) | 0.02043(17) | 7.91(5) |
| O42 | 0.40324(18) | 0.53301(6) | 0.01557(15) | 6.70(4) |
| N1 | 0.87448(13) | 0.67025(4) | 0.85205(10) | 3.05(2) |
| N24 | 0.30531(13) | 0.55040(4) | 0.53282(9) | 2.97(2) |
| N26 | 0.23761(13) | 0.46683(4) | 0.49053(9) | 3.01(2) |
| N28 | 0.46715(13) | 0.48661(4) | 0.62798(10) | 3.09(2) |
| C2 | 0.86471(15) | 0.68804(5) | 0.95008(11) | 2.74(2) |
| C3 | 0.73333(16) | 0.67846(5) | 0.98011(12) | 3.18(3) |
| C4 | 0.72070(18) | 0.69588(6) | 1.07545(12) | 3.50(3) |
| C5 | 0.83891(19) | 0.72329(6) | 1.14257(12) | 3.57(3) |
| C6 | 0.96857(17) | 0.73285(5) | 1.11304(12) | 3.25(3) |
| C7 | 0.98561(16) | 0.71610(5) | 1.01737(11) | 2.76(2) |
| C8 | 1.12447(16) | 0.73144(5) | 0.98341(11) | 2.97(3) |
| C9 | 1.13877(16) | 0.69915(5) | 0.89223(11) | 2.82(2) |
| C10 | 1.27510(17) | 0.69847(5) | 0.86597(12) | 3.43(3) |
| C11 | 1.29273(18) | 0.67112(6) | 0.78225(13) | 3.69(3) |
| C12 | 1.17088(18) | 0.64306(5) | 0.72162(12) | 3.49(3) |
| C13 | 1.03336(17) | 0.64289(5) | 0.74494(12) | 3.23(3) |
| C14 | 1.01558(16) | 0.67071(5) | 0.82997(11) | 2.78(2) |
| C15 | 1.1009(2) | 0.78520(5) | 0.94478(14) | 4.06(3) |
| C16 | 1.27382(19) | 0.72833(8) | 1.07786(14) | 4.49(4) |
| C17 | 0.75803(16) | 0.63651(5) | 0.79213(11) | 3.04(3) |
| C18 | 0.64376(16) | 0.65261(5) | 0.70309(11) | 2.96(3) |
| C19 | 0.53457(16) | 0.61955(5) | 0.64324(11) | 2.90(2) |
| C20 | 0.54155(16) | 0.57029(5) | 0.67265(11) | 2.91(3) |
| C21 | 0.65760(19) | 0.55460(6) | 0.76280(13) | 3.78(3) |
| C22 | 0.76522(19) | 0.58751(6) | 0.82240(13) | 3.88(3) |
| C23 | 0.43084(16) | 0.53395(5) | 0.60736(11) | 2.87(2) |
| C25 | 0.21315(16) | 0.51525(5) | 0.47561(11) | 2.85(2) |
| C27 | 0.36514(16) | 0.45461(5) | 0.56817(11) | 2.91(2) |
| C29 | 0.07363(16) | 0.53085(5) | 0.38987(11) | 3.12(3) |
| C30 | 0.04337(19) | 0.58031(6) | 0.36601(13) | 3.70(3) |
| C31 | -0.0879(2) | 0.59447(7) | 0.28679(14) | 4.39(3) |
| C32 | -0.1910(2) | 0.55953(7) | 0.23051(14) | 4.67(4) |
| C33 | -0.1626(2) | 0.51032(7) | 0.25298(14) | 4.52(3) |
| C34 | -0.03071(18) | 0.49586(6) | 0.33202(13) | 3.80(3) |
| C35 | 0.39853(17) | 0.40177(5) | 0.59082(11) | 3.01(3) |

**Table S1.** Atomic coordinates and $B_{iso}/B_{eq}$ (continued)

| atom | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| C36 | 0.28492(18) | 0.36640(5) | 0.55072(13) | 3.47(3) |
| C37 | 0.3171(2) | 0.31724(6) | 0.57454(15) | 4.14(3) |
| C38 | 0.4615(2) | 0.30303(6) | 0.63764(15) | 4.36(3) |
| C39 | 0.5766(2) | 0.33787(6) | 0.67545(14) | 4.16(3) |
| C40 | 0.54490(18) | 0.38702(6) | 0.65279(12) | 3.53(3) |
| C41 | 0.1069(4) | 0.56877(16) | 0.0951(2) | 9.44(10) |
| C42 | 0.4227(3) | 0.57921(8) | -0.0218(2) | 6.78(6) |

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

**Table S2.** Atomic coordinates and $B_{iso}$ involving hydrogen atoms

| atom | x | y | z | $B_{iso}$ |
|---|---|---|---|---|
| H3 | 0.65172 | 0.65971 | 0.93429 | 3.818 |
| H4 | 0.63094 | 0.68906 | 1.09493 | 4.202 |
| H5 | 0.83094 | 0.73540 | 1.20826 | 4.279 |
| H6 | 1.04936 | 0.75158 | 1.15975 | 3.897 |
| H10 | 1.35949 | 0.71760 | 0.90732 | 4.121 |
| H11 | 1.38746 | 0.67159 | 0.76653 | 4.426 |
| H12 | 1.18163 | 0.62394 | 0.66404 | 4.193 |
| H13 | 0.94976 | 0.62368 | 0.70283 | 3.876 |
| H15A | 1.09188 | 0.80626 | 1.00287 | 4.877 |
| H15B | 1.00670 | 0.78769 | 0.88404 | 4.877 |
| H15C | 1.18917 | 0.79581 | 0.92287 | 4.877 |
| H16A | 1.26128 | 0.74684 | 1.13842 | 5.388 |
| H16B | 1.35908 | 0.74231 | 1.05689 | 5.388 |
| H16C | 1.29619 | 0.69386 | 1.09842 | 5.388 |
| H18 | 0.63953 | 0.68619 | 0.68262 | 3.557 |
| H19 | 0.45524 | 0.63066 | 0.58227 | 3.474 |
| H21 | 0.66278 | 0.52104 | 0.78345 | 4.542 |
| H22 | 0.84394 | 0.57663 | 0.88395 | 4.654 |
| H30 | 0.11361 | 0.60454 | 0.40453 | 4.442 |
| H31 | -0.10751 | 0.62835 | 0.27088 | 5.270 |
| H32 | -0.28153 | 0.56943 | 0.17627 | 5.610 |
| H33 | -0.23355 | 0.48633 | 0.21421 | 5.429 |
| H34 | -0.01112 | 0.46191 | 0.34697 | 4.559 |
| H36 | 0.18542 | 0.37602 | 0.50707 | 4.168 |
| H37 | 0.23947 | 0.29320 | 0.54729 | 4.968 |
| H38 | 0.48219 | 0.26935 | 0.65529 | 5.233 |
| H39 | 0.67703 | 0.32792 | 0.71682 | 4.990 |
| H40 | 0.62328 | 0.41088 | 0.67959 | 4.241 |
| H41A | 0.19136 | 0.59213 | 0.10309 | 11.325 |
| H41B | 0.11697 | 0.55329 | 0.16404 | 11.325 |
| H41C | 0.00831 | 0.58620 | 0.07009 | 11.325 |
| H41 | 0.15914 | 0.50761 | 0.05266 | 9.492 |
| H42A | 0.50011 | 0.57768 | -0.05928 | 8.136 |
| H42B | 0.45713 | 0.60208 | 0.03830 | 8.136 |
| H42C | 0.32470 | 0.59065 | -0.07108 | 8.136 |
| H42 | 0.44419 | 0.53213 | 0.08203 | 8.039 |

**Table S3.** Anisotropic displacement parameters

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| O41 | 0.0987(13) | 0.0977(13) | 0.1166(14) | -0.0039(10) | 0.0514(11) | -0.0039(11) |
| O42 | 0.0846(11) | 0.0596(9) | 0.1128(13) | 0.0042(7) | 0.0341(9) | 0.0198(8) |
| N1 | 0.0370(6) | 0.0349(6) | 0.0428(7) | -0.0060(5) | 0.0105(5) | -0.0090(5) |
| N24 | 0.0390(6) | 0.0312(6) | 0.0418(6) | -0.0041(5) | 0.0112(5) | -0.0055(5) |
| N26 | 0.0396(6) | 0.0306(6) | 0.0431(6) | -0.0028(5) | 0.0113(5) | -0.0052(5) |
| N28 | 0.0405(7) | 0.0307(6) | 0.0441(7) | -0.0034(5) | 0.0101(5) | -0.0048(5) |
| C2 | 0.0381(7) | 0.0247(6) | 0.0396(7) | 0.0018(5) | 0.0092(6) | -0.0002(5) |
| C3 | 0.0396(7) | 0.0315(7) | 0.0483(8) | -0.0019(5) | 0.0114(6) | -0.0016(6) |
| C4 | 0.0452(8) | 0.0393(8) | 0.0521(9) | 0.0021(6) | 0.0204(7) | 0.0023(6) |
| C5 | 0.0558(9) | 0.0388(8) | 0.0423(8) | 0.0034(6) | 0.0173(7) | -0.0020(6) |
| C6 | 0.0465(8) | 0.0320(7) | 0.0417(8) | -0.0015(6) | 0.0089(6) | -0.0037(6) |
| C7 | 0.0383(7) | 0.0242(6) | 0.0392(7) | 0.0017(5) | 0.0074(5) | 0.0004(5) |
| C8 | 0.0377(7) | 0.0297(7) | 0.0429(8) | -0.0032(5) | 0.0086(6) | -0.0041(5) |
| C9 | 0.0384(7) | 0.0269(6) | 0.0402(7) | 0.0002(5) | 0.0095(6) | 0.0022(5) |
| C10 | 0.0401(8) | 0.0390(8) | 0.0506(8) | -0.0026(6) | 0.0128(6) | -0.0001(6) |
| C11 | 0.0437(8) | 0.0454(8) | 0.0549(9) | 0.0044(6) | 0.0207(7) | 0.0029(7) |
| C12 | 0.0544(9) | 0.0358(7) | 0.0450(8) | 0.0073(6) | 0.0190(7) | -0.0000(6) |
| C13 | 0.0464(8) | 0.0312(7) | 0.0434(8) | -0.0004(6) | 0.0112(6) | -0.0034(6) |
| C14 | 0.0386(7) | 0.0265(6) | 0.0391(7) | 0.0010(5) | 0.0101(6) | 0.0014(5) |
| C15 | 0.0657(10) | 0.0290(7) | 0.0673(10) | -0.0056(7) | 0.0315(8) | -0.0030(7) |
| C16 | 0.0411(8) | 0.0729(12) | 0.0509(9) | -0.0017(8) | 0.0059(7) | -0.0167(8) |
| C17 | 0.0380(7) | 0.0347(7) | 0.0423(8) | -0.0059(6) | 0.0117(6) | -0.0079(6) |
| C18 | 0.0408(7) | 0.0296(7) | 0.0432(7) | -0.0032(5) | 0.0143(6) | -0.0045(5) |
| C19 | 0.0361(7) | 0.0334(7) | 0.0398(7) | -0.0011(5) | 0.0108(6) | -0.0047(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C20 | 0.0384(7) | 0.0314(7) | 0.0412(7) | -0.0035(5) | 0.0129(6) | -0.0057(6) |
| C21 | 0.0542(9) | 0.0315(7) | 0.0495(9) | -0.0059(6) | 0.0034(7) | 0.0003(6) |
| C22 | 0.0514(9) | 0.0370(8) | 0.0476(9) | -0.0045(6) | -0.0013(7) | -0.0016(6) |
| C23 | 0.0389(7) | 0.0311(7) | 0.0401(7) | -0.0034(5) | 0.0141(6) | -0.0038(5) |
| C25 | 0.0377(7) | 0.0313(7) | 0.0408(7) | -0.0024(5) | 0.0145(6) | -0.0052(5) |
| C27 | 0.0392(7) | 0.0319(7) | 0.0403(7) | -0.0032(5) | 0.0138(6) | -0.0049(5) |
| C29 | 0.0401(8) | 0.0372(7) | 0.0411(7) | -0.0005(6) | 0.0122(6) | -0.0062(6) |
| C30 | 0.0492(9) | 0.0376(8) | 0.0505(9) | 0.0028(6) | 0.0106(7) | -0.0044(6) |
| C31 | 0.0586(10) | 0.0478(9) | 0.0551(10) | 0.0127(8) | 0.0098(8) | 0.0004(7) |
| C32 | 0.0505(10) | 0.0698(12) | 0.0493(9) | 0.0127(8) | 0.0036(7) | -0.0017(8) |
| C33 | 0.0496(9) | 0.0600(11) | 0.0533(10) | -0.0049(8) | 0.0027(7) | -0.0109(8) |
| C34 | 0.0474(9) | 0.0420(8) | 0.0497(9) | -0.0036(7) | 0.0073(7) | -0.0073(7) |
| C35 | 0.0438(8) | 0.0309(7) | 0.0412(7) | -0.0010(6) | 0.0152(6) | -0.0044(5) |
| C36 | 0.0471(8) | 0.0333(7) | 0.0520(8) | -0.0038(6) | 0.0161(7) | -0.0071(6) |
| C37 | 0.0604(10) | 0.0319(8) | 0.0697(11) | -0.0071(7) | 0.0269(8) | -0.0087(7) |
| C38 | 0.0691(11) | 0.0303(8) | 0.0720(11) | 0.0066(7) | 0.0301(9) | 0.0015(7) |
| C39 | 0.0544(9) | 0.0429(9) | 0.0605(10) | 0.0090(7) | 0.0174(8) | 0.0044(7) |
| C40 | 0.0458(8) | 0.0376(8) | 0.0492(8) | -0.0010(6) | 0.0123(7) | -0.0020(6) |
| C41 | 0.0891(19) | 0.198(4) | 0.0699(16) | 0.006(2) | 0.0225(14) | -0.031(2) |
| C42 | 0.0812(15) | 0.0580(12) | 0.1149(19) | -0.0057(11) | 0.0249(14) | 0.0176(12) |

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

**Table S4.** Fragment Analysis

fragment: 1

| | |
|---|---|
| O(41) | C(41) |

fragment: 2

| | |
|---|---|
| O(42) | C(42) |

fragment: 3

| | | | | |
|---|---|---|---|---|
| N(1) | N(24) | N(26) | N(28) | C(2) |
| C(3) | C(4) | C(5) | C(6) | C(7) |
| C(8) | C(9) | C(10) | C(11) | C(12) |
| C(13) | C(14) | C(15) | C(16) | C(17) |
| C(18) | C(19) | C(20) | C(21) | C(22) |
| C(23) | C(25) | C(27) | C(29) | C(30) |
| C(31) | C(32) | C(33) | C(34) | C(35) |
| C(36) | C(37) | C(38) | C(39) | C(40) |

**Table S5. Bond lengths (Å)**

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| O41 | C41 | 1.407(4) | O42 | C42 | 1.382(3) |
| N1 | C2 | 1.408(2) | N1 | C14 | 1.406(2) |
| N1 | C17 | 1.4418(17) | N24 | C23 | 1.3358(16) |
| N24 | C25 | 1.3415(17) | N26 | C25 | 1.3405(17) |
| N26 | C27 | 1.3335(16) | N28 | C23 | 1.3369(17) |
| N28 | C27 | 1.3394(17) | C2 | C3 | 1.399(2) |
| C2 | C7 | 1.4085(18) | C3 | C4 | 1.381(2) |
| C4 | C5 | 1.384(2) | C5 | C6 | 1.381(3) |
| C6 | C7 | 1.394(2) | C7 | C8 | 1.528(2) |
| C8 | C9 | 1.527(2) | C8 | C15 | 1.5419(19) |
| C8 | C16 | 1.5391(19) | C9 | C10 | 1.392(2) |
| C9 | C14 | 1.4028(18) | C10 | C11 | 1.381(2) |
| C11 | C12 | 1.382(2) | C12 | C13 | 1.382(2) |
| C13 | C14 | 1.403(2) | C17 | C18 | 1.3791(17) |
| C17 | C22 | 1.387(2) | C18 | C19 | 1.3928(18) |

| | | | | | |
|---|---|---|---|---|---|
| C19 | C20 | 1.3912(19) | C20 | C21 | 1.3927(19) |
| C20 | C23 | 1.4843(18) | C21 | C22 | 1.381(2) |
| C25 | C29 | 1.4804(17) | C27 | C35 | 1.4808(19) |
| C29 | C30 | 1.390(2) | C29 | C34 | 1.395(2) |
| C30 | C31 | 1.380(2) | C31 | C32 | 1.382(2) |
| C32 | C33 | 1.378(3) | C33 | C34 | 1.384(2) |
| C35 | C36 | 1.394(2) | C35 | C40 | 1.393(2) |
| C36 | C37 | 1.385(2) | C37 | C38 | 1.379(2) |
| C38 | C39 | 1.389(2) | C39 | C40 | 1.381(2) |

**Table 6.** Bond lengths involving hydrogens (Å)

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| O41 | H41 | 0.840 | O42 | H42 | 0.840 |
| C3 | H3 | 0.950 | C4 | H4 | 0.950 |
| C5 | H5 | 0.950 | C6 | H6 | 0.950 |
| C10 | H10 | 0.950 | C11 | H11 | 0.950 |
| C12 | H12 | 0.950 | C13 | H13 | 0.950 |
| C15 | H15A | 0.980 | C15 | H15B | 0.980 |
| C15 | H15C | 0.980 | C16 | H16A | 0.980 |
| C16 | H16B | 0.980 | C16 | H16C | 0.980 |
| C18 | H18 | 0.950 | C19 | H19 | 0.950 |
| C21 | H21 | 0.950 | C22 | H22 | 0.950 |
| C30 | H30 | 0.950 | C31 | H31 | 0.950 |
| C32 | H32 | 0.950 | C33 | H33 | 0.950 |
| C34 | H34 | 0.950 | C36 | H36 | 0.950 |
| C37 | H37 | 0.950 | C38 | H38 | 0.950 |
| C39 | H39 | 0.950 | C40 | H40 | 0.950 |
| C41 | H41A | 0.980 | C41 | H41B | 0.980 |
| C41 | H41C | 0.980 | C42 | H42A | 0.980 |
| C42 | H42B | 0.980 | C42 | H42C | 0.980 |

**Table S7.** Bond angles (°)

| atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|
| C2 | N1 | C14 | 120.58(11) | C2 | N1 | C17 | 118.45(13) |
| C14 | N1 | C17 | 117.41(12) | C23 | N24 | C25 | 114.93(11) |
| C25 | N26 | C27 | 115.09(11) | C23 | N28 | C27 | 115.02(11) |
| N1 | C2 | C3 | 119.90(11) | N1 | C2 | C7 | 120.31(14) |
| C3 | C2 | C7 | 119.79(14) | C2 | C3 | C4 | 120.90(13) |
| C3 | C4 | C5 | 119.93(16) | C4 | C5 | C6 | 119.28(15) |
| C5 | C6 | C7 | 122.58(13) | C2 | C7 | C6 | 117.52(14) |
| C2 | C7 | C8 | 121.59(13) | C6 | C7 | C8 | 120.70(12) |
| C7 | C8 | C9 | 110.74(11) | C7 | C8 | C15 | 108.19(13) |
| C7 | C8 | C16 | 110.88(13) | C9 | C8 | C15 | 108.85(13) |
| C9 | C8 | C16 | 109.59(13) | C15 | C8 | C16 | 108.53(13) |
| C8 | C9 | C10 | 120.28(12) | C8 | C9 | C14 | 122.00(14) |
| C10 | C9 | C14 | 117.69(14) | C9 | C10 | C11 | 122.68(13) |
| C10 | C11 | C12 | 119.20(16) | C11 | C12 | C13 | 119.86(15) |
| C12 | C13 | C14 | 120.88(13) | N1 | C14 | C9 | 120.30(13) |
| N1 | C14 | C13 | 120.01(12) | C9 | C14 | C13 | 119.69(15) |
| N1 | C17 | C18 | 120.02(12) | N1 | C17 | C22 | 119.53(11) |
| C18 | C17 | C22 | 120.41(12) | C17 | C18 | C19 | 119.88(13) |
| C18 | C19 | C20 | 120.08(11) | C19 | C20 | C21 | 119.36(12) |
| C19 | C20 | C23 | 121.05(11) | C21 | C20 | C23 | 119.55(13) |
| C20 | C21 | C22 | 120.46(15) | C17 | C22 | C21 | 119.81(13) |
| N24 | C23 | N28 | 125.10(12) | N24 | C23 | C20 | 118.65(12) |
| N28 | C23 | C20 | 116.24(11) | N24 | C25 | N26 | 124.82(11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N24 | C25 | C29 | 117.87(12) | N26 | C25 | C29 |
| | | | 117.32(11) | | | |
| N26 | C27 | N28 | 125.00(12) | N26 | C27 | C35 |
| | | | 118.26(11) | | | |
| N28 | C27 | C35 | 116.74(11) | C25 | C29 | C30 |
| | | | 120.95(12) | | | |
| C25 | C29 | C34 | 120.21(12) | C30 | C29 | C34 |
| | | | 118.84(12) | | | |
| C29 | C30 | C31 | 120.48(14) | C30 | C31 | C32 |
| | | | 120.20(17) | | | |
| C31 | C32 | C33 | 120.08(15) | C32 | C33 | C34 |
| | | | 120.00(16) | | | |
| C29 | C34 | C33 | 120.40(15) | C27 | C35 | C36 |
| | | | 120.73(12) | | | |
| C27 | C35 | C40 | 119.90(13) | C36 | C35 | C40 |
| | | | 119.37(13) | | | |
| C35 | C36 | C37 | 119.98(13) | C36 | C37 | C38 |
| | | | 120.28(15) | | | |
| C37 | C38 | C39 | 120.12(15) | C38 | C39 | C40 |
| | | | 119.87(15) | | | |
| C35 | C40 | C39 | 120.33(14) | | | |

**Table S8.** Bond angles involving hydrogens (º)

| atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|
| C41 | O41 | H41 | 109.5 | C42 | O42 | H42 | 109.5 |
| C2 | C3 | H3 | 119.5 | C4 | C3 | H3 | 119.6 |
| C3 | C4 | H4 | 120.0 | C5 | C4 | H4 | 120.0 |
| C4 | C5 | H5 | 120.4 | C6 | C5 | H5 | 120.4 |
| C5 | C6 | H6 | 118.7 | C7 | C6 | H6 | 118.7 |
| C9 | C10 | H10 | 118.7 | C11 | C10 | H10 | 118.7 |
| C10 | C11 | H11 | 120.4 | C12 | C11 | H11 | 120.4 |
| C11 | C12 | H12 | 120.1 | C13 | C12 | H12 | 120.1 |
| C12 | C13 | H13 | 119.6 | C14 | C13 | H13 | 119.6 |
| C8 | C15 | H15A | 109.5 | C8 | C15 | H15B | 109.5 |
| C8 | C15 | H15C | 109.5 | H15A | C15 | H15B | 109.5 |
| H15A | C15 | H15C | 109.5 | H15B | C15 | H15C | 109.5 |
| C8 | C16 | H16A | 109.5 | C8 | C16 | H16B | 109.5 |
| C8 | C16 | H16C | 109.5 | H16A | C16 | H16B | 109.5 |
| H16A | C16 | H16C | 109.5 | H16B | C16 | H16C | 109.5 |
| C17 | C18 | H18 | 120.1 | C19 | C18 | H18 | 120.1 |
| C18 | C19 | H19 | 119.9 | C20 | C19 | H19 | 120.0 |
| C20 | C21 | H21 | 119.8 | C22 | C21 | H21 | 119.8 |
| C17 | C22 | H22 | 120.1 | C21 | C22 | H22 | 120.1 |
| C29 | C30 | H30 | 119.8 | C31 | C30 | H30 | 119.8 |
| C30 | C31 | H31 | 119.9 | C32 | C31 | H31 | 119.9 |
| C31 | C32 | H32 | 120.0 | C33 | C32 | H32 | 120.0 |
| C32 | C33 | H33 | 120.0 | C34 | C33 | H33 | 120.0 |
| C29 | C34 | H34 | 119.8 | C33 | C34 | H34 | 119.8 |
| C35 | C36 | H36 | 120.0 | C37 | C36 | H36 | 120.0 |
| C36 | C37 | H37 | 119.9 | C38 | C37 | H37 | 119.9 |
| C37 | C38 | H38 | 119.9 | C39 | C38 | H38 | 119.9 |
| C38 | C39 | H39 | 120.1 | C40 | C39 | H39 | 120.1 |
| C35 | C40 | H40 | 119.8 | C39 | C40 | H40 | 119.8 |
| O41 | C41 | H41A | 109.5 | O41 | C41 | H41B | 109.5 |
| O41 | C41 | H41C | 109.5 | H41A | C41 | H41B | 109.5 |
| H41A | C41 | H41C | 109.5 | H41B | C41 | H41C | 109.5 |
| O42 | C42 | H42A | 109.5 | O42 | C42 | H42B | 109.5 |
| O42 | C42 | H42C | 109.5 | H42A | C42 | H42B | 109.5 |
| H42A | C42 | H42C | 109.5 | H42B | C42 | H42C | 109.5 |

**Table S9.** Torsion Angles(°)
(Those having bond angles > 160 or < 20 degrees are excluded.)

| atom1 | atom2 | atom3 | atom4 | angle | atom1 | atom2 | atom3 | atom4 | angle |
|---|---|---|---|---|---|---|---|---|---|
| C2 | N1 | C14 | C9 | -15.47(18) | C2 | N1 | C14 | C13 | 164.94(10) |
| C14 | N1 | C2 | C3 | -167.08(10) | C14 | N1 | C2 | C7 | 13.91(17) |
| C2 | N1 | C17 | C18 | 104.27(15) | C2 | N1 | C17 | C22 | -78.10(16) |
| C17 | N1 | C2 | C3 | -8.89(17) | C17 | N1 | C2 | C7 | 172.09(10) |
| C14 | N1 | C17 | C18 | -96.85(15) | C14 | N1 | C17 | C22 | 80.77(17) |
| C17 | N1 | C14 | C9 | -173.87(10) | C17 | N1 | C14 | C13 | 6.53(17) |
| C23 | N24 | C25 | N26 | 1.6(2) | C23 | N24 | C25 | C29 | -178.63(13) |
| C25 | N24 | C23 | N28 | -0.8(2) | C25 | N24 | C23 | C20 | 178.44(13) |
| C25 | N26 | C27 | N28 | -1.3(2) | C25 | N26 | C27 | C35 | 178.86(13) |
| C27 | N26 | C25 | N24 | -0.7(2) | C27 | N26 | C25 | C29 | 179.61(13) |
| C23 | N28 | C27 | N26 | 2.1(2) | C23 | N28 | C27 | C35 | -178.11(13) |
| C27 | N28 | C23 | N24 | -1.0(2) | C27 | N28 | C23 | C20 | 179.82(13) |
| N1 | C2 | C3 | C4 | -179.46(10) | N1 | C2 | C7 | C6 | 179.66(10) |
| N1 | C2 | C7 | C8 | 4.69(18) | C3 | C2 | C7 | C6 | 0.65(18) |
| C3 | C2 | C7 | C8 | -174.32(11) | C7 | C2 | C3 | C4 | -0.44(19) |
| C2 | C3 | C4 | C5 | 0.1(2) | C3 | C4 | C5 | C6 | -0.0(2) |
| C4 | C5 | C6 | C7 | 0.3(2) | C5 | C6 | C7 | C2 | -0.6(2) |
| C5 | C6 | C7 | C8 | 174.45(12) | C2 | C7 | C8 | C9 | -19.22(16) |
| C2 | C7 | C8 | C15 | 99.99(13) | C2 | C7 | C8 | C16 | -141.11(11) |
| C6 | C7 | C8 | C9 | 165.97(11) | C6 | C7 | C8 | C15 | -74.82(14) |
| C6 | C7 | C8 | C16 | 44.08(16) | C7 | C8 | C9 | C10 | -164.49(10) |
| C7 | C8 | C9 | C14 | 17.75(16) | C15 | C8 | C9 | C10 | 76.69(14) |
| C15 | C8 | C9 | C14 | -101.06(14) | C16 | C8 | C9 | C10 | -41.85(17) |
| C16 | C8 | C9 | C14 | 140.39(13) | C8 | C9 | C10 | C11 | -177.98(11) |
| C8 | C9 | C14 | N1 | -1.63(19) | C8 | C9 | C14 | C13 | 177.97(10) |
| C10 | C9 | C14 | N1 | -179.44(11) | C10 | C9 | C14 | C13 | 0.16(18) |
| C14 | C9 | C10 | C11 | -0.13(19) | C9 | C10 | C11 | C12 | -0.1(2) |
| C10 | C11 | C12 | C13 | 0.3(2) | C11 | C12 | C13 | C14 | -0.3(2) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C12 | C13 | C14 | N1 | 179.66(11) | C12 | C13 | C14 | C9 | 0.06(19) |
| N1 | C17 | C18 | C19 | 177.77(13) | N1 | C17 | C22 | C21 | -177.39(14) |
| C18 | C17 | C22 | C21 | 0.2(3) | C22 | C17 | C18 | C19 | 0.2(2) |
| C17 | C18 | C19 | C20 | -0.6(2) | C18 | C19 | C20 | C21 | 0.6(2) |
| C18 | C19 | C20 | C23 | -177.18(13) | C19 | C20 | C21 | C22 | -0.2(3) |
| C19 | C20 | C23 | N24 | -13.8(2) | C19 | C20 | C23 | N28 | 165.50(14) |
| C21 | C20 | C23 | N24 | 168.44(15) | C21 | C20 | C23 | N28 | -12.3(2) |
| C23 | C20 | C21 | C22 | 177.60(14) | C20 | C21 | C22 | C17 | -0.2(3) |
| N24 | C25 | C29 | C30 | 3.2(2) | N24 | C25 | C29 | C34 | -176.33(13) |
| N26 | C25 | C29 | C30 | -177.09(13) | N26 | C25 | C29 | C34 | 3.4(2) |
| N26 | C27 | C35 | C36 | -14.7(2) | N26 | C27 | C35 | C40 | 165.22(13) |
| N28 | C27 | C35 | C36 | 165.44(13) | N28 | C27 | C35 | C40 | -14.6(2) |
| C25 | C29 | C30 | C31 | -179.24(14) | C25 | C29 | C34 | C33 | 178.92(14) |
| C30 | C29 | C34 | C33 | -0.6(3) | C34 | C29 | C30 | C31 | 0.3(3) |
| C29 | C30 | C31 | C32 | 0.2(3) | C30 | C31 | C32 | C33 | -0.3(3) |
| C31 | C32 | C33 | C34 | 0.0(3) | C32 | C33 | C34 | C29 | 0.4(3) |
| C27 | C35 | C36 | C37 | -178.62(14) | C27 | C35 | C40 | C39 | 179.20(13) |
| C36 | C35 | C40 | C39 | -0.8(2) | C40 | C35 | C36 | C37 | 1.4(3) |
| C35 | C36 | C37 | C38 | -0.2(3) | C36 | C37 | C38 | C39 | -1.6(3) |
| C37 | C38 | C39 | C40 | 2.2(3) | C38 | C39 | C40 | C35 | -1.0(3) |

**Table S10.** Possible hydrogen bonds

| Donor | H | Acceptor | D...A | D-H | H...A | D-H...A |
|---|---|---|---|---|---|---|
| O41 | H41 | O41 | 2.635(3) | 0.84 | 2.61 | 82.70 |
| O41 | H41 | O42 | 2.676(3) | 0.84 | 2.52 | 91.26 |

Symmetry Operators:

(1) -X,-Y+1,-Z

**Table S11**. Intramolecular contacts less than 3.60 Å

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| N1 | C8 | 2.9225(17) | N24 | C19 | 2.8566(17) |
| N24 | C27 | 2.6742(17) | N24 | C30 | 2.8233(18) |
| N26 | C23 | 2.6725(17) | N26 | C34 | 2.7986(17) |
| N26 | C36 | 2.8410(17) | N28 | C21 | 2.7742(19) |
| N28 | C25 | 2.6729(16) | N28 | C40 | 2.795(2) |
| C2 | C5 | 2.790(2) | C2 | C9 | 2.849(2) |
| C2 | C15 | 3.426(2) | C2 | C18 | 3.3975(18) |
| C2 | C22 | 3.193(2) | C3 | C6 | 2.7478(18) |
| C3 | C17 | 2.800(2) | C3 | C18 | 3.557(2) |
| C3 | C22 | 3.302(2) | C4 | C7 | 2.808(2) |
| C6 | C15 | 3.173(3) | C6 | C16 | 2.967(3) |
| C7 | C14 | 2.850(2) | C9 | C12 | 2.807(2) |
| C10 | C13 | 2.7442(19) | C10 | C15 | 3.194(2) |
| C10 | C16 | 2.912(3) | C11 | C14 | 2.790(2) |
| C13 | C17 | 2.776(2) | C13 | C18 | 3.438(2) |
| C13 | C22 | 3.295(3) | C14 | C15 | 3.446(2) |
| C14 | C18 | 3.3261(19) | C14 | C22 | 3.197(2) |
| C17 | C20 | 2.7771(18) | C18 | C21 | 2.772(2) |
| C19 | C22 | 2.7752(19) | C29 | C32 | 2.780(2) |
| C30 | C33 | 2.767(2) | C31 | C34 | 2.763(2) |
| C35 | C38 | 2.777(2) | C36 | C39 | 2.774(2) |
| C37 | C40 | 2.770(2) | | | |

**Table S12.** Intramolecular contacts less than 3.60 Å involving hydrogens

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| N1 | H3 | 2.600 | N1 | H13 | 2.604 |
| N1 | H15B | 3.396 | N1 | H18 | 2.612 |
| N1 | H22 | 2.611 | N24 | H19 | 2.553 |
| N24 | H30 | 2.503 | N26 | H34 | 2.471 |
| N26 | H36 | 2.538 | N28 | H21 | 2.451 |
| N28 | H40 | 2.478 | C2 | H4 | 3.275 |
| C2 | H6 | 3.255 | C2 | H15B | 3.238 |
| C2 | H18 | 3.490 | C2 | H22 | 3.144 |
| C3 | H5 | 3.253 | C3 | H22 | 3.331 |
| C4 | H6 | 3.237 | C5 | H3 | 3.249 |
| C6 | H4 | 3.245 | C6 | H15A | 2.894 |
| C6 | H15B | 3.480 | C6 | H16A | 2.617 |
| C6 | H16C | 3.236 | C7 | H3 | 3.285 |
| C7 | H5 | 3.286 | C7 | H15A | 2.667 |
| C7 | H15B | 2.670 | C7 | H15C | 3.338 |
| C7 | H16A | 2.665 | C7 | H16B | 3.364 |
| C7 | H16C | 2.772 | C8 | H6 | 2.676 |
| C8 | H10 | 2.662 | C9 | H11 | 3.285 |
| C9 | H13 | 3.281 | C9 | H15A | 3.345 |
| C9 | H15B | 2.681 | C9 | H15C | 2.679 |
| C9 | H16A | 3.350 | C9 | H16B | 2.728 |
| C9 | H16C | 2.657 | C10 | H12 | 3.244 |
| C10 | H15B | 3.510 | C10 | H15C | 2.925 |
| C10 | H16B | 2.674 | C10 | H16C | 3.013 |
| C11 | H13 | 3.248 | C12 | H10 | 3.235 |
| C13 | H11 | 3.253 | C13 | H22 | 3.400 |
| C14 | H10 | 3.249 | C14 | H12 | 3.279 |
| C14 | H15B | 3.268 | C14 | H18 | 3.409 |

| | | | | | |
|---|---|---|---|---|---|
| C14 | H22 | 3.195 | C15 | H6 | 3.148 |
| C15 | H10 | 3.150 | C15 | H16A | 2.728 |
| C15 | H16B | 2.637 | C15 | H16C | 3.351 |
| C16 | H6 | 2.671 | C16 | H10 | 2.615 |
| C16 | H15A | 2.687 | C16 | H15B | 3.352 |
| C16 | H15C | 2.677 | C17 | H3 | 2.445 |
| C17 | H13 | 2.418 | C17 | H19 | 3.256 |
| C17 | H21 | 3.253 | C18 | H3 | 3.032 |
| C18 | H13 | 2.904 | C18 | H22 | 3.257 |
| C19 | H21 | 3.261 | C20 | H18 | 3.269 |
| C20 | H22 | 3.265 | C21 | H13 | 3.547 |
| C21 | H19 | 3.263 | C22 | H3 | 2.838 |
| C22 | H13 | 2.817 | C22 | H18 | 3.258 |
| C23 | H19 | 2.670 | C23 | H21 | 2.638 |
| C25 | H30 | 2.661 | C25 | H34 | 2.652 |
| C27 | H36 | 2.664 | C27 | H40 | 2.644 |
| C29 | H31 | 3.261 | C29 | H33 | 3.269 |
| C30 | H32 | 3.250 | C30 | H34 | 3.257 |
| C31 | H33 | 3.249 | C32 | H30 | 3.249 |
| C32 | H34 | 3.248 | C33 | H31 | 3.248 |
| C34 | H30 | 3.258 | C34 | H32 | 3.250 |
| C35 | H37 | 3.264 | C35 | H39 | 3.264 |
| C36 | H38 | 3.253 | C36 | H40 | 3.265 |
| C37 | H39 | 3.255 | C38 | H36 | 3.253 |
| C38 | H40 | 3.255 | C39 | H37 | 3.256 |
| C40 | H36 | 3.265 | C40 | H38 | 3.254 |
| H3 | H4 | 2.325 | H3 | H18 | 3.363 |
| H3 | H22 | 3.058 | H4 | H5 | 2.339 |
| H5 | H6 | 2.317 | H6 | H15A | 2.671 |
| H6 | H16A | 2.044 | H6 | H16B | 3.503 |

| | | | | | |
|---|---|---|---|---|---|
| H6 | H16C | 3.054 | H10 | H11 | 2.317 |
| H10 | H15C | 2.681 | H10 | H16A | 3.522 |
| H10 | H16B | 2.084 | H10 | H16C | 2.828 |
| H11 | H12 | 2.339 | H12 | H13 | 2.327 |
| H13 | H18 | 3.244 | H13 | H22 | 3.114 |
| H15A | H16A | 2.548 | H15A | H16B | 2.901 |
| H15B | H16B | 3.542 | H15C | H16A | 3.021 |
| H15C | H16B | 2.440 | H15C | H16C | 3.551 |
| H18 | H19 | 2.343 | H19 | H30 | 3.349 |
| H21 | H22 | 2.329 | H21 | H40 | 3.268 |
| H30 | H31 | 2.325 | H31 | H32 | 2.330 |
| H32 | H33 | 2.328 | H33 | H34 | 2.331 |
| H34 | H36 | 3.286 | H36 | H37 | 2.333 |
| H37 | H38 | 2.326 | H38 | H39 | 2.339 |
| H39 | H40 | 2.330 | H41A | H41 | 2.387 |
| H41B | H41 | 2.049 | H41C | H41 | 2.592 |
| H42A | H42 | 2.420 | H42B | H42 | 2.003 |
| H42C | H42 | 2.538 | | | |

**Table S13.** Intermolecular contacts less than 3.60 Å

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| O41 | O41[1] | 2.635(3) | O41 | O42 | 2.676(3) |
| O41 | C41[1] | 3.468(4) | O41 | C42 | 3.306(4) |
| O42 | O41 | 2.676(3) | O42 | O42[2] | 2.639(3) |
| O42 | C41 | 3.335(4) | O42 | C42[2] | 3.431(3) |
| N24 | N28[3] | 3.5421(19) | N24 | C40[3] | 3.581(2) |
| N26 | C20[3] | 3.521(2) | N26 | C34[4] | 3.578(2) |
| N28 | N24[3] | 3.5421(19) | N28 | C23[3] | 3.548(2) |
| N28 | C25[3] | 3.585(2) | N28 | C33[4] | 3.592(3) |
| C11 | C19[5] | 3.564(2) | C11 | C42[6] | 3.527(3) |
| C16 | C39[7] | 3.597(2) | C19 | C11[8] | 3.564(2) |
| C19 | C35[3] | 3.375(2) | C19 | C36[3] | 3.465(3) |
| C20 | N26[3] | 3.521(2) | C20 | C27[3] | 3.596(2) |
| C23 | N28[3] | 3.548(2) | C23 | C27[3] | 3.404(2) |
| C25 | N28[3] | 3.585(2) | C25 | C34[4] | 3.451(3) |
| C27 | C20[3] | 3.596(2) | C27 | C23[3] | 3.404(2) |
| C27 | C32[4] | 3.511(3) | C27 | C33[4] | 3.547(3) |
| C31 | C36[4] | 3.367(3) | C31 | C41 | 3.580(4) |
| C32 | C27[4] | 3.511(3) | C33 | N28[4] | 3.592(3) |
| C33 | C27[4] | 3.547(3) | C34 | N26[4] | 3.578(2) |
| C34 | C25[4] | 3.451(3) | C35 | C19[3] | 3.375(2) |
| C36 | C19[3] | 3.465(3) | C36 | C31[4] | 3.367(3) |
| C39 | C16[7] | 3.597(2) | C40 | N24[3] | 3.581(2) |
| C41 | O41[1] | 3.468(4) | C41 | O42 | 3.335(4) |
| C41 | C31 | 3.580(4) | C42 | O41 | 3.306(4) |

| | | | | | |
|---|---|---|---|---|---|
| C42 | O42[2] | 3.431(3) | C42 | C11[9] | 3.527(3) |

Symmetry Operators:

(1) -X,-Y+1,-Z
(2) -X+1,-Y+1,-Z
(3) -X+1,-Y+1,-Z+1
(4) -X,-Y+1,-Z+1
(5) X+1,Y,Z
(6) X+1,Y,Z+1
(7) -X+2,-Y+1,-Z+2
(8) X-1,Y,Z
(9) X-1,Y,Z-1

**Table S14.** Intermolecular contacts less than 3.60 Å involving hydrogens

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| O41 | H21[1] | 3.120 | O41 | H22[2] | 2.824 |
| O41 | H22[1] | 3.200 | O41 | H41B[3] | 3.549 |
| O41 | H41C[3] | 3.499 | O41 | H41[3] | 2.606 |
| O41 | H42C | 3.027 | O41 | H42 | 2.884 |
| O42 | H21[1] | 3.245 | O42 | H32[4] | 3.161 |
| O42 | H33[3] | 2.992 | O42 | H41A | 3.007 |
| O42 | H41 | 2.522 | O42 | H42A[5] | 3.141 |
| O42 | H42[5] | 2.801 | N1 | H5[6] | 3.142 |
| N1 | H41C[7] | 3.580 | N24 | H12[8] | 3.079 |
| N24 | H34[9] | 3.532 | N24 | H40[1] | 3.241 |
| N26 | H13[1] | 3.577 | N28 | H33[9] | 3.487 |
| C2 | H37[10] | 3.019 | C2 | H41C[7] | 3.259 |
| C3 | H10[8] | 3.419 | C3 | H11[8] | 3.528 |
| C3 | H37[10] | 3.161 | C3 | H38[10] | 3.317 |
| C3 | H41C[7] | 3.489 | C3 | H42A[11] | 3.412 |
| C3 | H42B[11] | 3.531 | C4 | H10[8] | 3.410 |
| C4 | H16B[8] | 3.473 | C4 | H31[7] | 3.159 |
| C4 | H37[10] | 3.182 | C4 | H42B[11] | 3.438 |
| C5 | H15B[12] | 3.091 | C5 | H18[12] | 3.202 |
| C5 | H31[7] | 3.043 | C5 | H37[10] | 3.048 |
| C6 | H15B[12] | 3.525 | C6 | H37[10] | 2.880 |
| C7 | H37[10] | 2.876 | C7 | H41C[7] | 3.596 |
| C9 | H5[6] | 3.570 | C9 | H6[6] | 3.211 |
| C9 | H42C[7] | 3.365 | C10 | H3[4] | 3.441 |

| | | | | | |
|---|---|---|---|---|---|
| C10 | H6[6] | 3.166 | C10 | H16A[6] | 3.316 |
| C10 | H38[13] | 3.016 | C10 | H42B[7] | 3.531 |
| C10 | H42C[7] | 3.044 | C11 | H3[4] | 3.287 |
| C11 | H6[6] | 3.123 | C11 | H16A[6] | 2.885 |
| C11 | H19[4] | 3.575 | C11 | H38[13] | 3.317 |
| C11 | H42A[7] | 3.460 | C11 | H42C[7] | 2.875 |
| C12 | H6[6] | 3.091 | C12 | H15A[6] | 3.074 |
| C12 | H16A[6] | 3.379 | C12 | H34[1] | 3.208 |
| C12 | H42C[7] | 3.017 | C13 | H6[6] | 3.103 |
| C13 | H34[1] | 3.080 | C13 | H36[1] | 3.345 |
| C13 | H42C[7] | 3.316 | C14 | H5[6] | 3.205 |
| C14 | H6[6] | 3.167 | C14 | H42C[7] | 3.485 |
| C15 | H5[6] | 3.371 | C15 | H30[14] | 3.055 |
| C15 | H31[14] | 3.423 | C15 | H37[10] | 3.150 |
| C15 | H39[13] | 3.560 | C16 | H4[4] | 3.373 |
| C16 | H38[15] | 3.536 | C16 | H39[15] | 3.020 |
| C17 | H11[8] | 3.431 | C18 | H5[6] | 3.484 |
| C18 | H11[8] | 2.767 | C19 | H11[8] | 2.793 |
| C19 | H12[8] | 3.320 | C20 | H11[8] | 3.491 |
| C20 | H12[8] | 3.566 | C21 | H41B[1] | 3.544 |
| C21 | H41[1] | 3.011 | C21 | H42A[11] | 3.170 |
| C21 | H42[1] | 3.434 | C22 | H41C[7] | 3.334 |
| C22 | H41[1] | 3.031 | C22 | H42A[11] | 3.271 |
| C23 | H12[8] | 3.575 | C23 | H33[9] | 3.421 |
| C25 | H34[9] | 3.453 | C25 | H40[1] | 3.513 |

| | | | | | |
|---|---|---|---|---|---|
| C29 | H40[1] | 3.547 | C29 | H41B | 3.181 |
| C30 | H15A[16] | 3.533 | C30 | H36[9] | 3.277 |
| C30 | H40[1] | 3.289 | C30 | H41B | 3.031 |
| C31 | H15B[16] | 3.462 | C31 | H36[9] | 3.212 |
| C31 | H41B | 3.041 | C31 | H41C | 3.245 |
| C32 | H41B | 3.198 | C32 | H41C | 3.269 |
| C32 | H42[8] | 3.385 | C33 | H41B | 3.333 |
| C34 | H12[1] | 3.546 | C34 | H13[1] | 3.398 |
| C34 | H41B | 3.318 | C35 | H19[1] | 3.106 |
| C36 | H13[1] | 3.378 | C36 | H19[1] | 3.359 |
| C36 | H31[9] | 3.245 | C37 | H15A[17] | 3.568 |
| C37 | H15B[17] | 3.269 | C37 | H18[1] | 3.533 |
| C37 | H31[9] | 3.524 | C38 | H10[18] | 3.004 |
| C38 | H15C[18] | 3.525 | C38 | H16A[15] | 3.514 |
| C38 | H16C[15] | 3.501 | C39 | H10[18] | 3.554 |
| C39 | H15C[18] | 3.046 | C39 | H16A[15] | 3.359 |
| C39 | H16C[15] | 2.973 | C39 | H19[1] | 3.428 |
| C39 | H41A[1] | 3.580 | C40 | H19[1] | 3.135 |
| C40 | H30[1] | 3.436 | C40 | H41A[1] | 3.419 |
| C41 | H21[1] | 3.299 | C41 | H22[2] | 3.071 |
| C41 | H40[1] | 3.268 | C41 | H41[3] | 3.330 |
| C41 | H42C | 3.435 | C41 | H42 | 3.293 |
| C42 | H3[19] | 3.202 | C42 | H32[4] | 3.135 |
| C42 | H33[3] | 3.145 | C42 | H41A | 3.074 |
| C42 | H41 | 3.466 | C42 | H42[5] | 3.447 |

| | | | | | |
|---|---|---|---|---|---|
| H3 | C10[8] | 3.441 | H3 | C11[8] | 3.287 |
| H3 | C42[11] | 3.202 | H3 | H10[8] | 3.024 |
| H3 | H11[8] | 2.743 | H3 | H38[10] | 3.301 |
| H3 | H42A[11] | 2.642 | H3 | H42B[11] | 3.000 |
| H3 | H42C[11] | 3.511 | H4 | C16[8] | 3.373 |
| H4 | H10[8] | 3.013 | H4 | H16B[8] | 2.783 |
| H4 | H16C[8] | 3.075 | H4 | H18[12] | 3.579 |
| H4 | H31[7] | 3.224 | H4 | H32[7] | 3.443 |
| H4 | H42B[11] | 2.819 | H5 | N1[12] | 3.142 |
| H5 | C9[12] | 3.570 | H5 | C14[12] | 3.205 |
| H5 | C15[12] | 3.371 | H5 | C18[12] | 3.484 |
| H5 | H15B[12] | 2.458 | H5 | H18[12] | 2.712 |
| H5 | H31[7] | 3.032 | H5 | H37[10] | 3.591 |
| H5 | H37[20] | 3.561 | H6 | C9[12] | 3.211 |
| H6 | C10[12] | 3.166 | H6 | C11[12] | 3.123 |
| H6 | C12[12] | 3.091 | H6 | C13[12] | 3.103 |
| H6 | C14[12] | 3.167 | H6 | H12[12] | 3.590 |
| H6 | H15B[12] | 3.278 | H6 | H15C[12] | 3.548 |
| H6 | H37[10] | 3.353 | H6 | H39[15] | 3.325 |
| H10 | C3[4] | 3.419 | H10 | C4[4] | 3.410 |
| H10 | C38[13] | 3.004 | H10 | C39[13] | 3.554 |
| H10 | H3[4] | 3.024 | H10 | H4[4] | 3.013 |
| H10 | H16A[6] | 3.513 | H10 | H38[13] | 2.343 |
| H10 | H39[13] | 3.385 | H10 | H42B[7] | 3.564 |
| H10 | H42C[7] | 3.488 | H11 | C3[4] | 3.528 |

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|---|---|---|---|---|---|
| H11 | C17[4] | 3.431 | H11 | C18[4] | 2.767 |
| H11 | C19[4] | 2.793 | H11 | C20[4] | 3.491 |
| H11 | H3[4] | 2.743 | H11 | H16A[6] | 2.811 |
| H11 | H16B[6] | 3.571 | H11 | H18[4] | 2.873 |
| H11 | H19[4] | 2.907 | H11 | H38[13] | 2.966 |
| H11 | H42A[7] | 3.376 | H11 | H42C[7] | 3.243 |
| H12 | N24[4] | 3.079 | H12 | C19[4] | 3.320 |
| H12 | C20[4] | 3.566 | H12 | C23[4] | 3.575 |
| H12 | C34[1] | 3.546 | H12 | H6[6] | 3.590 |
| H12 | H15A[6] | 2.778 | H12 | H19[4] | 3.017 |
| H12 | H30[4] | 3.325 | H12 | H33[1] | 3.366 |
| H12 | H34[1] | 2.786 | H12 | H36[1] | 3.414 |
| H12 | H42C[7] | 3.450 | H13 | N26[1] | 3.577 |
| H13 | C34[1] | 3.398 | H13 | C36[1] | 3.378 |
| H13 | H34[1] | 2.529 | H13 | H36[1] | 2.659 |
| H15A | C12[12] | 3.074 | H15A | C30[14] | 3.533 |
| H15A | C37[10] | 3.568 | H15A | H12[12] | 2.778 |
| H15A | H19[14] | 3.593 | H15A | H30[14] | 2.787 |
| H15A | H31[14] | 3.520 | H15A | H36[10] | 3.135 |
| H15A | H37[10] | 2.913 | H15B | C5[6] | 3.091 |
| H15B | C6[6] | 3.525 | H15B | C31[14] | 3.462 |
| H15B | C37[10] | 3.269 | H15B | H5[6] | 2.458 |
| H15B | H6[6] | 3.278 | H15B | H30[14] | 3.076 |
| H15B | H31[14] | 2.751 | H15B | H36[10] | 3.531 |
| H15B | H37[10] | 2.675 | H15C | C38[13] | 3.525 |

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|---|---|---|---|---|---|
| H15C | C39[13] | 3.046 | H15C | H6[6] | 3.548 |
| H15C | H19[14] | 3.342 | H15C | H30[14] | 2.790 |
| H15C | H31[14] | 3.501 | H15C | H38[13] | 3.535 |
| H15C | H39[13] | 2.653 | H16A | C10[12] | 3.316 |
| H16A | C11[12] | 2.885 | H16A | C12[12] | 3.379 |
| H16A | C38[15] | 3.514 | H16A | C39[15] | 3.359 |
| H16A | H10[12] | 3.513 | H16A | H11[12] | 2.811 |
| H16A | H38[15] | 3.024 | H16A | H39[15] | 2.726 |
| H16B | C4[4] | 3.473 | H16B | H4[4] | 2.783 |
| H16B | H11[12] | 3.571 | H16B | H18[14] | 3.236 |
| H16B | H19[14] | 3.556 | H16C | C38[15] | 3.501 |
| H16C | C39[15] | 2.973 | H16C | H4[4] | 3.075 |
| H16C | H38[15] | 3.403 | H16C | H39[15] | 2.444 |
| H16C | H41A[7] | 2.936 | H16C | H42B[7] | 3.122 |
| H18 | C5[6] | 3.202 | H18 | C37[1] | 3.533 |
| H18 | H4[6] | 3.579 | H18 | H5[6] | 2.712 |
| H18 | H11[8] | 2.873 | H18 | H16B[16] | 3.236 |
| H18 | H37[1] | 3.576 | H18 | H38[10] | 3.520 |
| H19 | C11[8] | 3.575 | H19 | C35[1] | 3.106 |
| H19 | C36[1] | 3.359 | H19 | C39[1] | 3.428 |
| H19 | C40[1] | 3.135 | H19 | H11[8] | 2.907 |
| H19 | H12[8] | 3.017 | H19 | H15A[16] | 3.593 |
| H19 | H15C[16] | 3.342 | H19 | H16B[16] | 3.556 |
| H19 | H40[1] | 3.490 | H21 | O41[1] | 3.120 |
| H21 | O42[1] | 3.245 | H21 | C41[1] | 3.299 |

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|---|---|---|---|---|---|
| H21 | H41A[1] | 3.502 | H21 | H41B[1] | 2.785 |
| H21 | H41[1] | 2.398 | H21 | H42A[11] | 3.284 |
| H21 | H42[1] | 2.695 | H22 | O41[7] | 2.824 |
| H22 | O41[1] | 3.200 | H22 | C41[7] | 3.071 |
| H22 | H41A[7] | 3.596 | H22 | H41C[7] | 2.463 |
| H22 | H41[7] | 3.578 | H22 | H41[1] | 2.443 |
| H22 | H42A[11] | 3.446 | H30 | C15[16] | 3.055 |
| H30 | C40[1] | 3.436 | H30 | H12[8] | 3.325 |
| H30 | H15A[16] | 2.787 | H30 | H15B[16] | 3.076 |
| H30 | H15C[16] | 2.790 | H30 | H36[9] | 3.326 |
| H30 | H39[1] | 3.388 | H30 | H40[1] | 2.971 |
| H30 | H41B | 3.472 | H31 | C4[2] | 3.159 |
| H31 | C5[2] | 3.043 | H31 | C15[16] | 3.423 |
| H31 | C36[9] | 3.245 | H31 | C37[9] | 3.524 |
| H31 | H4[2] | 3.224 | H31 | H5[2] | 3.032 |
| H31 | H15A[16] | 3.520 | H31 | H15B[16] | 2.751 |
| H31 | H15C[16] | 3.501 | H31 | H36[9] | 3.221 |
| H31 | H41B | 3.484 | H31 | H41C | 3.342 |
| H32 | O42[8] | 3.161 | H32 | C42[8] | 3.135 |
| H32 | H4[2] | 3.443 | H32 | H41C | 3.386 |
| H32 | H42A[8] | 3.137 | H32 | H42B[8] | 2.667 |
| H32 | H42[8] | 2.632 | H33 | O42[3] | 2.992 |
| H33 | N28[9] | 3.487 | H33 | C23[9] | 3.421 |
| H33 | C42[3] | 3.145 | H33 | H12[1] | 3.366 |
| H33 | H42A[3] | 3.172 | H33 | H42C[3] | 2.769 |

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|---|---|---|---|---|---|
| H33 | H42[8] | 3.175 | H34 | N24[9] | 3.532 |
| H34 | C12[1] | 3.208 | H34 | C13[1] | 3.080 |
| H34 | C25[9] | 3.453 | H34 | H12[1] | 2.786 |
| H34 | H13[1] | 2.529 | H36 | C13[1] | 3.345 |
| H36 | C30[9] | 3.277 | H36 | C31[9] | 3.212 |
| H36 | H12[1] | 3.414 | H36 | H13[1] | 2.659 |
| H36 | H15A[17] | 3.135 | H36 | H15B[17] | 3.531 |
| H36 | H30[9] | 3.326 | H36 | H31[9] | 3.221 |
| H37 | C2[17] | 3.019 | H37 | C3[17] | 3.161 |
| H37 | C4[17] | 3.182 | H37 | C5[17] | 3.048 |
| H37 | C6[17] | 2.880 | H37 | C7[17] | 2.876 |
| H37 | C15[17] | 3.150 | H37 | H5[17] | 3.591 |
| H37 | H5[20] | 3.561 | H37 | H6[17] | 3.353 |
| H37 | H15A[17] | 2.913 | H37 | H15B[17] | 2.675 |
| H37 | H18[1] | 3.576 | H38 | C3[17] | 3.317 |
| H38 | C10[18] | 3.016 | H38 | C11[18] | 3.317 |
| H38 | C16[15] | 3.536 | H38 | H3[17] | 3.301 |
| H38 | H10[18] | 2.343 | H38 | H11[18] | 2.966 |
| H38 | H15C[18] | 3.535 | H38 | H16A[15] | 3.024 |
| H38 | H16C[15] | 3.403 | H38 | H18[17] | 3.520 |
| H39 | C15[18] | 3.560 | H39 | C16[15] | 3.020 |
| H39 | H6[15] | 3.325 | H39 | H10[18] | 3.385 |
| H39 | H15C[18] | 2.653 | H39 | H16A[15] | 2.726 |
| H39 | H16C[15] | 2.444 | H39 | H30[1] | 3.388 |
| H39 | H41A[1] | 3.170 | H40 | N24[1] | 3.241 |

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|---|---|---|---|---|---|
| H40 | C25[1] | 3.513 | H40 | C29[1] | 3.547 |
| H40 | C30[1] | 3.289 | H40 | C41[1] | 3.268 |
| H40 | H19[1] | 3.490 | H40 | H30[1] | 2.971 |
| H40 | H41A[1] | 2.843 | H40 | H41B[1] | 2.794 |
| H41A | O42 | 3.007 | H41A | C39[1] | 3.580 |
| H41A | C40[1] | 3.419 | H41A | C42 | 3.074 |
| H41A | H16C[2] | 2.936 | H41A | H21[1] | 3.502 |
| H41A | H22[2] | 3.596 | H41A | H39[1] | 3.170 |
| H41A | H40[1] | 2.843 | H41A | H42B | 2.824 |
| H41A | H42C | 2.912 | H41A | H42 | 2.910 |
| H41B | O41[3] | 3.549 | H41B | C21[1] | 3.544 |
| H41B | C29 | 3.181 | H41B | C30 | 3.031 |
| H41B | C31 | 3.041 | H41B | C32 | 3.198 |
| H41B | C33 | 3.333 | H41B | C34 | 3.318 |
| H41B | H21[1] | 2.785 | H41B | H30 | 3.472 |
| H41B | H31 | 3.484 | H41B | H40[1] | 2.794 |
| H41B | H41[3] | 3.580 | H41B | H42 | 3.525 |
| H41C | O41[3] | 3.499 | H41C | N1[2] | 3.580 |
| H41C | C2[2] | 3.259 | H41C | C3[2] | 3.489 |
| H41C | C7[2] | 3.596 | H41C | C22[2] | 3.334 |
| H41C | C31 | 3.245 | H41C | C32 | 3.269 |
| H41C | H22[2] | 2.463 | H41C | H31 | 3.342 |
| H41C | H32 | 3.386 | H41C | H41[3] | 3.153 |
| H41 | O41[3] | 2.606 | H41 | O42 | 2.522 |
| H41 | C21[1] | 3.011 | H41 | C22[1] | 3.031 |

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|---|---|---|---|---|---|
| H41 | C41[3] | 3.330 | H41 | C42 | 3.466 |
| H41 | H21[1] | 2.398 | H41 | H22[2] | 3.578 |
| H41 | H22[1] | 2.443 | H41 | H41B[3] | 3.580 |
| H41 | H41C[3] | 3.153 | H41 | H41[3] | 2.838 |
| H41 | H42C | 3.402 | H41 | H42 | 2.598 |
| H42A | O42[5] | 3.141 | H42A | C3[19] | 3.412 |
| H42A | C11[2] | 3.460 | H42A | C21[19] | 3.170 |
| H42A | C22[19] | 3.271 | H42A | H3[19] | 2.642 |
| H42A | H11[2] | 3.376 | H42A | H21[19] | 3.284 |
| H42A | H22[19] | 3.446 | H42A | H32[4] | 3.137 |
| H42A | H33[3] | 3.172 | H42A | H42[5] | 3.061 |
| H42B | C3[19] | 3.531 | H42B | C4[19] | 3.438 |
| H42B | C10[2] | 3.531 | H42B | H3[19] | 3.000 |
| H42B | H4[19] | 2.819 | H42B | H10[2] | 3.564 |
| H42B | H16C[2] | 3.122 | H42B | H32[4] | 2.667 |
| H42B | H41A | 2.824 | H42C | O41 | 3.027 |
| H42C | C9[2] | 3.365 | H42C | C10[2] | 3.044 |
| H42C | C11[2] | 2.875 | H42C | C12[2] | 3.017 |
| H42C | C13[2] | 3.316 | H42C | C14[2] | 3.485 |
| H42C | C41 | 3.435 | H42C | H3[19] | 3.511 |
| H42C | H10[2] | 3.488 | H42C | H11[2] | 3.243 |
| H42C | H12[2] | 3.450 | H42C | H33[3] | 2.769 |
| H42C | H41A | 2.912 | H42C | H41 | 3.402 |
| H42 | O41 | 2.884 | H42 | O42[5] | 2.801 |
| H42 | C21[1] | 3.434 | H42 | C32[4] | 3.385 |

| | | | | | |
|---|---|---|---|---|---|
| H42 | C41 | 3.293 | H42 | C42[5] | 3.447 |
| H42 | H21[1] | 2.695 | H42 | H32[4] | 2.632 |
| H42 | H33[4] | 3.175 | H42 | H41A | 2.910 |
| H42 | H41B | 3.525 | H42 | H41 | 2.598 |
| H42 | H42A[5] | 3.061 | H42 | H42[5] | 3.184 |

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1
(2) X-1,Y,Z-1
(3) -X,-Y+1,-Z
(4) X+1,Y,Z
(5) -X+1,-Y+1,-Z
(6) X,-Y+2,Z
(7) X+1,Y,Z+1
(8) X-1,Y,Z
(9) -X,-Y+1,-Z+1
(10) -X+1,Y+1/2,-Z+1/2+1
(11) X,Y,Z+1
(12) X,-Y+2,Z+1
(13) -X+2,Y+1/2,-Z+1/2+1
(14) X+1,-Y+2,Z+1
(15) -X+2,-Y+1,-Z+2
(16) X-1,-Y+2,Z
(17) -X+1,Y+1/2-1,-Z+1/2+1
(18) -X+2,Y+1/2-1,-Z+1/2+1
(19) X,Y,Z-1
(20) -X+1,-Y+1,-Z+2

**DMAC-TRZ**
**Data Collection**

A colorless platelet crystal of $C_{35}H_{27}N_5$ having approximate dimensions of 0.100 x 0.050 x 0.010 mm was mounted in a loop. All measurements were made on a Rigaku XtaLAB P100 diffractometer using multi-layer mirror monochromated Cu-Ka radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

a = 35.6867(10) Å
b = 18.671(5) Å
c = 8.1489(16) Å
V = 5429.7(18) Å$^3$

For Z = 8 and F.W. = 517.63, the calculated density is 1.266 g/cm$^3$. The reflection conditions of:

0kl: k = 2n
h0l: l = 2n
hk0: h = 2n

uniquely determine the space group to be:

Pbca (#61)

The data were collected at a temperature of -100 $\pm$ 1°C to a maximum 2q value of 136.1°.

**Data Reduction**

Of the 53594 reflections were collected, where 4924 were unique ($R_{int}$ = 0.0694); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).[14]

The linear absorption coefficient, μ, for Cu-Kα radiation is 5.939 cm$^{-1}$. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.754 to 0.994. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction[6] was applied (coefficient = 0.000980).

**Structure Solution and Refinement**

The structure was solved by direct methods[7] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[8] on $F^2$ was based

on 4924 observed reflections and 364 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \; ||Fo| - |Fc|| \; / \; \Sigma \; |Fo| = 0.0401$$

$$wR2 = [ \; \Sigma \; ( \; w \; (Fo^2 - Fc^2)^2 \; ) / \; \Sigma \; w(Fo^2)^2]^{1/2} = 0.1175$$

The goodness of fit* was 1.04. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.23 and -0.26 $e^-/Å^3$, respectively.

*Goodness of fit is defined as:

$$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$$

where: $N_o$ = number of observations
$N_v$ = number of variables

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4[9]. Anomalous dispersion effects were included in Fcalc[10]; the values for Df' and Df'' were those of Creagh and McAuley[11]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[12]. All calculations were performed using the CrystalStructure[13] crystallographic software package except for refinement, which was performed using SHELXL Version 2018/3[8].

Experimental details

## A. Crystal Data

| | |
|---|---|
| Empirical Formula | $C_{35}H_{27}N_5$ |
| Formula Weight | 517.63 |
| Crystal Color, Habit | colorless, platelet |
| Crystal Dimensions | 0.100 X 0.050 X 0.010 mm |
| Crystal System | orthorhombic |
| Lattice Type | Primitive |
| Lattice Parameters | a = 35.6867(10) Å<br>b = 18.671(5) Å<br>c = 8.1489(16) Å<br>V = 5429.7(18) Å$^3$ |
| Space Group | Pbca (#61) |
| Z value | 8 |
| $D_{calc}$ | 1.266 g/cm$^3$ |
| $F_{000}$ | 2176.00 |
| $\mu$(CuK$\alpha$) | 5.939 cm$^{-1}$ |

B. Intensity Measurements

| | |
|---|---|
| Diffractometer | XtaLAB P100 |
| Radiation | CuKα (λ = 1.54187 Å)<br>multi-layer mirror monochromated |
| Voltage, Current | 40kV, 30mA |
| Temperature | -100.0°C |
| Detector Aperture | 83.8 x 33.5 mm |
| Data Images | 3983 exposures |
| Pixel Size | 0.172 mm |
| $2\theta_{max}$ | 136.1° |
| No. of Reflections Measured | Total: 53594<br>Unique: 4924 ($R_{int}$ = 0.0694) |
| Corrections | Lorentz-polarization<br>Absorption<br>(trans. factors: 0.754 - 0.994)<br>Secondary Extinction<br>(coefficient: 9.80000e-004) |

C. Structure Solution and Refinement

| | |
|---|---|
| Structure Solution | Direct Methods (SHELXT Version 2018/2) |
| Refinement | Full-matrix least-squares on $F^2$ |
| Function Minimized | $\Sigma\ w\ (Fo^2 - Fc^2)^2$ |
| Least Squares Weights | $w = 1/\ [\ \sigma^2(Fo^2) + (0.0761 \cdot P)^2 + 0.5544 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$ |
| $2\theta_{max}$ cutoff | 136.1° |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (All reflections) | 4924 |
| No. Variables | 364 |
| Reflection/Parameter Ratio | 13.53 |
| Residuals: R1 (I>2.00σ(I)) | 0.0401 |
| Residuals: R (All reflections) | 0.0495 |
| Residuals: wR2 (All reflections) | 0.1175 |
| Goodness of Fit Indicator | 1.042 |
| Max Shift/Error in Final Cycle | 0.001 |
| Maximum peak in Final Diff. Map | 0.23 $e^-/Å^3$ |
| Minimum peak in Final Diff. Map | -0.26 $e^-/Å^3$ |

**Table S15.** Atomic coordinates and $B_{iso}/B_{eq}$

| atom | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| N1 | 0.35315(3) | 0.50418(6) | 0.45742(13) | 2.75(2) |
| N18 | 0.40003(3) | 0.44006(6) | 0.59632(16) | 3.82(2) |
| N24 | 0.50397(3) | 0.43057(5) | 0.82992(12) | 2.523(19) |
| N26 | 0.56064(3) | 0.48702(6) | 0.91070(12) | 2.81(2) |
| N28 | 0.51722(3) | 0.54957(5) | 0.74298(12) | 2.603(19) |
| C2 | 0.32577(4) | 0.45081(7) | 0.49687(15) | 2.78(2) |
| C3 | 0.33072(4) | 0.38039(7) | 0.44741(17) | 3.35(3) |
| C4 | 0.30319(4) | 0.33033(8) | 0.4807(2) | 4.05(3) |
| C5 | 0.27102(4) | 0.35066(9) | 0.5619(2) | 4.25(3) |
| C6 | 0.26589(4) | 0.42141(8) | 0.60902(18) | 3.77(3) |
| C7 | 0.29307(4) | 0.47303(7) | 0.57694(15) | 2.99(2) |
| C8 | 0.28957(4) | 0.55235(8) | 0.62473(17) | 3.29(3) |
| C9 | 0.30586(4) | 0.59660(7) | 0.48421(16) | 3.01(2) |
| C10 | 0.29127(4) | 0.66189(7) | 0.43067(19) | 3.75(3) |
| C11 | 0.30733(4) | 0.69910(8) | 0.3011(2) | 4.17(3) |
| C12 | 0.33756(4) | 0.67051(8) | 0.21769(19) | 3.86(3) |
| C13 | 0.35257(4) | 0.60568(8) | 0.26762(17) | 3.35(3) |
| C14 | 0.33759(4) | 0.57063(7) | 0.40278(15) | 2.77(2) |
| C15 | 0.31330(5) | 0.56522(9) | 0.78115(18) | 4.08(3) |
| C16 | 0.24875(4) | 0.57314(9) | 0.6598(2) | 4.43(3) |
| C17 | 0.38953(3) | 0.50112(7) | 0.52078(14) | 2.71(2) |
| C19 | 0.43430(4) | 0.43748(7) | 0.66566(18) | 3.39(3) |
| C20 | 0.45924(3) | 0.49429(6) | 0.66290(14) | 2.51(2) |
| C21 | 0.44759(4) | 0.55586(7) | 0.58128(16) | 3.13(2) |
| C22 | 0.41301(4) | 0.55897(7) | 0.50949(15) | 3.05(2) |
| C23 | 0.49549(3) | 0.49107(6) | 0.74803(13) | 2.31(2) |
| C25 | 0.53675(3) | 0.43168(6) | 0.90905(14) | 2.46(2) |
| C27 | 0.54931(3) | 0.54493(7) | 0.82742(14) | 2.61(2) |
| C29 | 0.54754(4) | 0.36694(7) | 1.00349(14) | 2.86(2) |
| C30 | 0.52275(4) | 0.30991(7) | 1.01993(16) | 3.42(3) |
| C31 | 0.53374(5) | 0.24886(9) | 1.1056(2) | 4.45(3) |
| C32 | 0.56927(5) | 0.24519(10) | 1.1731(2) | 5.30(4) |
| C33 | 0.59357(5) | 0.30179(11) | 1.1587(2) | 5.03(4) |
| C34 | 0.58289(4) | 0.36292(9) | 1.07577(16) | 3.74(3) |
| C35 | 0.57338(4) | 0.60954(7) | 0.83184(16) | 3.27(3) |
| C36 | 0.60613(4) | 0.61048(10) | 0.92601(19) | 4.42(3) |
| C37 | 0.62769(6) | 0.67236(12) | 0.9317(2) | 6.04(5) |
| C38 | 0.61732(7) | 0.73266(11) | 0.8457(3) | 6.34(5) |
| C39 | 0.58515(6) | 0.73182(9) | 0.7526(2) | 5.38(4) |
| C40 | 0.56316(5) | 0.67055(8) | 0.74502(19) | 4.05(3) |

$B_{eq} = 8/3\ p^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos g + 2U_{13}(aa^*cc^*)\cos b + 2U_{23}(bb^*cc^*)\cos a)$

**Table S16.** Atomic coordinates and $B_{iso}$ involving hydrogen atoms

| atom | x | y | z | $B_{iso}$ |
|---|---|---|---|---|
| H3 | 0.35288 | 0.36662 | 0.39104 | 4.020 |
| H4 | 0.30645 | 0.28194 | 0.44760 | 4.854 |
| H5 | 0.25226 | 0.31607 | 0.58573 | 5.101 |
| H6 | 0.24349 | 0.43483 | 0.66402 | 4.519 |
| H10 | 0.26988 | 0.68127 | 0.48403 | 4.496 |
| H11 | 0.29753 | 0.74437 | 0.26971 | 4.999 |
| H12 | 0.34798 | 0.69521 | 0.12656 | 4.627 |
| H13 | 0.37305 | 0.58527 | 0.20960 | 4.021 |
| H15A | 0.31216 | 0.61599 | 0.81126 | 4.891 |
| H15B | 0.33939 | 0.55169 | 0.75983 | 4.891 |
| H15C | 0.30338 | 0.53613 | 0.87133 | 4.891 |
| H16A | 0.23365 | 0.56588 | 0.56077 | 5.316 |
| H16B | 0.24760 | 0.62362 | 0.69244 | 5.316 |
| H16C | 0.23892 | 0.54320 | 0.74875 | 5.316 |
| H19 | 0.44172 | 0.39453 | 0.71908 | 4.065 |
| H21 | 0.46382 | 0.59610 | 0.57539 | 3.752 |
| H22 | 0.40533 | 0.60082 | 0.45235 | 3.658 |
| H30 | 0.49843 | 0.31258 | 0.97293 | 4.099 |
| H31 | 0.51689 | 0.20983 | 1.11769 | 5.337 |
| H32 | 0.57689 | 0.20319 | 1.22985 | 6.357 |
| H33 | 0.61785 | 0.29889 | 1.20602 | 6.039 |
| H34 | 0.59964 | 0.40231 | 1.06793 | 4.491 |
| H36 | 0.61357 | 0.56913 | 0.98561 | 5.299 |
| H37 | 0.64992 | 0.67308 | 0.99578 | 7.247 |
| H38 | 0.63230 | 0.77467 | 0.85070 | 7.610 |
| H39 | 0.57795 | 0.77338 | 0.69311 | 6.455 |
| H40 | 0.54103 | 0.67034 | 0.68020 | 4.857 |

**Table S17.** Anisotropic displacement parameters

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0315(5) | 0.0363(6) | 0.0368(6) | 0.0023(4) | -0.0003(4) | 0.0042(4) |
| N18 | 0.0420(7) | 0.0425(7) | 0.0607(8) | 0.0004(5) | -0.0078(6) | -0.0003(6) |
| N24 | 0.0342(5) | 0.0295(5) | 0.0322(5) | 0.0020(4) | 0.0011(4) | 0.0010(4) |
| N26 | 0.0351(6) | 0.0381(6) | 0.0335(5) | 0.0016(4) | 0.0008(4) | -0.0042(4) |
| N28 | 0.0364(6) | 0.0294(5) | 0.0331(5) | -0.0001(4) | 0.0046(4) | -0.0021(4) |
| C2 | 0.0338(6) | 0.0374(7) | 0.0343(6) | 0.0007(5) | -0.0016(5) | 0.0051(5) |
| C3 | 0.0390(7) | 0.0384(7) | 0.0499(8) | 0.0055(6) | 0.0004(6) | 0.0046(6) |
| C4 | 0.0510(9) | 0.0347(7) | 0.0681(10) | 0.0018(6) | -0.0041(7) | 0.0081(7) |
| C5 | 0.0489(8) | 0.0475(8) | 0.0651(9) | -0.0092(7) | 0.0022(7) | 0.0150(7) |
| C6 | 0.0401(7) | 0.0560(9) | 0.0471(8) | -0.0026(7) | 0.0071(6) | 0.0078(6) |
| C7 | 0.0376(7) | 0.0440(7) | 0.0322(6) | 0.0013(6) | 0.0001(5) | 0.0034(5) |
| C8 | 0.0387(7) | 0.0480(8) | 0.0384(7) | 0.0046(6) | 0.0018(5) | -0.0065(6) |
| C9 | 0.0373(7) | 0.0368(7) | 0.0403(7) | 0.0011(5) | -0.0075(5) | -0.0065(5) |
| C10 | 0.0452(8) | 0.0375(7) | 0.0597(9) | 0.0067(6) | -0.0122(7) | -0.0110(6) |
| C11 | 0.0585(9) | 0.0318(7) | 0.0679(10) | -0.0027(6) | -0.0259(8) | 0.0053(7) |
| C12 | 0.0506(8) | 0.0434(8) | 0.0525(8) | -0.0111(6) | -0.0160(6) | 0.0127(6) |
| C13 | 0.0407(7) | 0.0443(8) | 0.0424(7) | -0.0051(6) | -0.0058(6) | 0.0060(6) |
| C14 | 0.0350(6) | 0.0333(6) | 0.0368(7) | 0.0004(5) | -0.0073(5) | 0.0010(5) |
| C15 | 0.0564(9) | 0.0595(10) | 0.0389(8) | 0.0019(7) | -0.0004(6) | -0.0082(7) |
| C16 | 0.0454(8) | 0.0646(10) | 0.0583(9) | 0.0085(7) | 0.0086(7) | -0.0109(8) |
| C17 | 0.0331(6) | 0.0407(7) | 0.0292(6) | 0.0055(5) | 0.0017(5) | -0.0011(5) |
| C19 | 0.0371(7) | 0.0366(7) | 0.0550(8) | 0.0017(5) | -0.0060(6) | 0.0011(6) |
| C20 | 0.0344(6) | 0.0330(6) | 0.0279(6) | 0.0036(5) | 0.0027(5) | -0.0021(5) |
| C21 | 0.0394(7) | 0.0415(7) | 0.0379(7) | 0.0035(6) | 0.0027(5) | 0.0077(6) |
| C22 | 0.0356(7) | 0.0446(7) | 0.0356(7) | 0.0070(5) | -0.0005(5) | 0.0131(6) |
| C23 | 0.0330(6) | 0.0281(6) | 0.0266(5) | 0.0029(5) | 0.0048(4) | -0.0017(4) |
| C25 | 0.0324(6) | 0.0342(6) | 0.0269(6) | 0.0056(5) | 0.0041(5) | -0.0032(5) |
| C27 | 0.0338(6) | 0.0342(6) | 0.0312(6) | 0.0001(5) | 0.0053(5) | -0.0067(5) |
| C29 | 0.0419(7) | 0.0392(7) | 0.0277(6) | 0.0113(6) | 0.0058(5) | 0.0011(5) |
| C30 | 0.0502(8) | 0.0394(7) | 0.0402(7) | 0.0103(6) | 0.0085(6) | 0.0056(6) |
| C31 | 0.0677(10) | 0.0454(8) | 0.0559(9) | 0.0154(8) | 0.0211(8) | 0.0169(7) |
| C32 | 0.0690(11) | 0.0736(12) | 0.0587(10) | 0.0367(10) | 0.0221(8) | 0.0351(9) |
| C33 | 0.0536(9) | 0.0861(13) | 0.0515(9) | 0.0261(9) | 0.0064(7) | 0.0288(9) |
| C34 | 0.0446(8) | 0.0620(9) | 0.0356(7) | 0.0133(7) | 0.0016(6) | 0.0085(6) |
| C35 | 0.0442(7) | 0.0403(7) | 0.0398(7) | -0.0089(6) | 0.0118(6) | -0.0127(6) |
| C36 | 0.0523(9) | 0.0655(10) | 0.0499(8) | -0.0186(8) | 0.0042(7) | -0.0162(7) |
| C37 | 0.0727(12) | 0.0926(15) | 0.0642(11) | -0.0452(11) | 0.0082(9) | -0.0275(11) |
| C38 | 0.1008(15) | 0.0681(13) | 0.0720(12) | -0.0526(12) | 0.0287(11) | -0.0303(10) |
| C39 | 0.0907(13) | 0.0413(9) | 0.0723(11) | -0.0224(9) | 0.0309(10) | -0.0159(8) |
| C40 | 0.0593(9) | 0.0383(8) | 0.0562(9) | -0.0094(7) | 0.0162(7) | -0.0085(6) |

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

**Table S18.** Bond lengths (Å)

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| N1 | C2 | 1.4321(18) | N1 | C14 | 1.4304(17) |
| N1 | C17 | 1.3983(15) | N18 | C17 | 1.3487(17) |
| N18 | C19 | 1.3481(18) | N24 | C23 | 1.3464(15) |
| N24 | C25 | 1.3359(15) | N26 | C25 | 1.3396(16) |
| N26 | C27 | 1.3391(17) | N28 | C23 | 1.3402(15) |
| N28 | C27 | 1.3388(15) | C2 | C3 | 1.3865(19) |
| C2 | C7 | 1.3999(19) | C3 | C4 | 1.383(2) |
| C4 | C5 | 1.378(2) | C5 | C6 | 1.388(2) |
| C6 | C7 | 1.392(2) | C7 | C8 | 1.536(2) |
| C8 | C9 | 1.527(2) | C8 | C15 | 1.549(2) |
| C8 | C16 | 1.534(2) | C9 | C10 | 1.3955(19) |
| C9 | C14 | 1.399(2) | C10 | C11 | 1.387(2) |
| C11 | C12 | 1.383(2) | C12 | C13 | 1.385(2) |
| C13 | C14 | 1.3882(19) | C17 | C22 | 1.3701(18) |
| C19 | C20 | 1.3848(18) | C20 | C21 | 1.3917(17) |
| C20 | C23 | 1.4691(15) | C21 | C22 | 1.367(2) |
| C25 | C29 | 1.4838(17) | C27 | C35 | 1.4813(18) |
| C29 | C30 | 1.3908(19) | C29 | C34 | 1.394(2) |
| C30 | C31 | 1.393(2) | C31 | C32 | 1.384(2) |
| C32 | C33 | 1.372(3) | C33 | C34 | 1.380(3) |
| C35 | C36 | 1.398(2) | C35 | C40 | 1.390(2) |
| C36 | C37 | 1.389(3) | C37 | C38 | 1.377(3) |
| C38 | C39 | 1.377(3) | C39 | C40 | 1.389(2) |

**Table S19.** Bond lengths involving hydrogens (Å)

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| C3 | H3 | 0.950 | C4 | H4 | 0.950 |
| C5 | H5 | 0.950 | C6 | H6 | 0.950 |
| C10 | H10 | 0.950 | C11 | H11 | 0.950 |
| C12 | H12 | 0.950 | C13 | H13 | 0.950 |
| C15 | H15A | 0.980 | C15 | H15B | 0.980 |
| C15 | H15C | 0.980 | C16 | H16A | 0.980 |
| C16 | H16B | 0.980 | C16 | H16C | 0.980 |
| C19 | H19 | 0.950 | C21 | H21 | 0.950 |
| C22 | H22 | 0.950 | C30 | H30 | 0.950 |
| C31 | H31 | 0.950 | C32 | H32 | 0.950 |
| C33 | H33 | 0.950 | C34 | H34 | 0.950 |
| C36 | H36 | 0.950 | C37 | H37 | 0.950 |
| C38 | H38 | 0.950 | C39 | H39 | 0.950 |
| C40 | H40 | 0.950 | | | |

**Table S20.** Bond angles (°)

| atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|
| C2 | N1 | C14 | 114.11(11) | C2 | N1 | C17 | 121.48(11) |
| C14 | N1 | C17 | 120.72(11) | C17 | N18 | C19 | 118.27(11) |
| C23 | N24 | C25 | 115.03(10) | C25 | N26 | C27 | 115.18(10) |
| C23 | N28 | C27 | 115.24(10) | N1 | C2 | C3 | 120.51(12) |
| N1 | C2 | C7 | 117.85(11) | C3 | C2 | C7 | 121.52(13) |
| C2 | C3 | C4 | 119.56(13) | C3 | C4 | C5 | 119.98(14) |
| C4 | C5 | C6 | 120.32(14) | C5 | C6 | C7 | 121.01(13) |
| C2 | C7 | C6 | 117.59(12) | C2 | C7 | C8 | 118.14(12) |
| C6 | C7 | C8 | 124.27(13) | C7 | C8 | C9 | 107.49(11) |
| C7 | C8 | C15 | 108.28(12) | C7 | C8 | C16 | 111.61(12) |
| C9 | C8 | C15 | 108.97(12) | C9 | C8 | C16 | 111.37(12) |
| C15 | C8 | C16 | 109.05(12) | C8 | C9 | C10 | 124.40(13) |
| C8 | C9 | C14 | 118.44(12) | C10 | C9 | C14 | 117.16(12) |
| C9 | C10 | C11 | 121.41(13) | C10 | C11 | C12 | 120.21(14) |
| C11 | C12 | C13 | 119.66(14) | C12 | C13 | C14 | 119.75(13) |
| N1 | C14 | C9 | 117.85(11) | N1 | C14 | C13 | 120.42(12) |
| C9 | C14 | C13 | 121.64(12) | N1 | C17 | N18 | 117.45(11) |
| N1 | C17 | C22 | 120.72(12) | N18 | C17 | C22 | 121.81(11) |
| N18 | C19 | C20 | 123.29(12) | C19 | C20 | C21 | 116.65(11) |
| C19 | C20 | C23 | 121.80(11) | C21 | C20 | C23 | 121.50(11) |
| C20 | C21 | C22 | 120.62(12) | C17 | C22 | C21 | 119.33(12) |
| N24 | C23 | N28 | 124.68(10) | N24 | C23 | C20 | 117.79(10) |
| N28 | C23 | C20 | 117.49(10) | N24 | C25 | N26 | 125.04(10) |
| N24 | C25 | C29 | 117.71(10) | N26 | C25 | C29 | 117.26(10) |
| N26 | C27 | N28 | 124.82(11) | N26 | C27 | C35 | 118.04(10) |
| N28 | C27 | C35 | 117.12(11) | C25 | C29 | C30 | 120.57(12) |
| C25 | C29 | C34 | 119.85(12) | C30 | C29 | C34 | 119.58(13) |
| C29 | C30 | C31 | 119.71(14) | C30 | C31 | C32 | 119.85(16) |
| C31 | C32 | C33 | 120.46(17) | C32 | C33 | C34 | 120.29(16) |
| C29 | C34 | C33 | 120.08(15) | C27 | C35 | C36 | 120.55(13) |
| C27 | C35 | C40 | 120.20(13) | C36 | C35 | C40 | 119.24(14) |
| C35 | C36 | C37 | 119.45(16) | C36 | C37 | C38 | 120.97(19) |
| C37 | C38 | C39 | 119.7(2) | C38 | C39 | C40 | 120.34(17) |
| C35 | C40 | C39 | 120.30(16) | | | | |

**Table S21.** Bond angles involving hydrogens (°)

| atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|
| C2 | C3 | H3 | 120.2 | C4 | C3 | H3 | 120.2 |
| C3 | C4 | H4 | 120.0 | C5 | C4 | H4 | 120.0 |
| C4 | C5 | H5 | 119.8 | C6 | C5 | H5 | 119.8 |
| C5 | C6 | H6 | 119.5 | C7 | C6 | H6 | 119.5 |
| C9 | C10 | H10 | 119.3 | C11 | C10 | H10 | 119.3 |
| C10 | C11 | H11 | 119.9 | C12 | C11 | H11 | 119.9 |
| C11 | C12 | H12 | 120.2 | C13 | C12 | H12 | 120.2 |
| C12 | C13 | H13 | 120.1 | C14 | C13 | H13 | 120.1 |
| C8 | C15 | H15A | 109.5 | C8 | C15 | H15B | 109.5 |
| C8 | C15 | H15C | 109.5 | H15A | C15 | H15B | 109.5 |
| H15A | C15 | H15C | 109.5 | H15B | C15 | H15C | 109.5 |
| C8 | C16 | H16A | 109.5 | C8 | C16 | H16B | 109.5 |
| C8 | C16 | H16C | 109.5 | H16A | C16 | H16B | 109.5 |
| H16A | C16 | H16C | 109.5 | H16B | C16 | H16C | 109.5 |
| N18 | C19 | H19 | 118.4 | C20 | C19 | H19 | 118.3 |
| C20 | C21 | H21 | 119.7 | C22 | C21 | H21 | 119.7 |
| C17 | C22 | H22 | 120.3 | C21 | C22 | H22 | 120.3 |
| C29 | C30 | H30 | 120.1 | C31 | C30 | H30 | 120.1 |
| C30 | C31 | H31 | 120.1 | C32 | C31 | H31 | 120.1 |
| C31 | C32 | H32 | 119.8 | C33 | C32 | H32 | 119.8 |
| C32 | C33 | H33 | 119.9 | C34 | C33 | H33 | 119.9 |
| C29 | C34 | H34 | 120.0 | C33 | C34 | H34 | 120.0 |
| C35 | C36 | H36 | 120.3 | C37 | C36 | H36 | 120.3 |
| C36 | C37 | H37 | 119.5 | C38 | C37 | H37 | 119.5 |
| C37 | C38 | H38 | 120.2 | C39 | C38 | H38 | 120.1 |
| C38 | C39 | H39 | 119.8 | C40 | C39 | H39 | 119.8 |
| C35 | C40 | H40 | 119.9 | C39 | C40 | H40 | 119.8 |

**Table S22.** Torsion Angles(O)

(Those having bond angles > 160 or < 20 degrees are excluded.)

| atom1 | atom2 | atom3 | atom4 | angle | atom1 | atom2 | atom3 | atom4 | angle |
|---|---|---|---|---|---|---|---|---|---|
| C2 | N1 | C14 | C9 | 41.08(15) | C2 | N1 | C14 | C13 | -135.56(11) |
| C14 | N1 | C2 | C3 | 136.89(11) | C14 | N1 | C2 | C7 | -39.08(14) |
| C2 | N1 | C17 | N18 | 11.46(16) | C2 | N1 | C17 | C22 | -166.90(10) |
| C17 | N1 | C2 | C3 | -64.64(15) | C17 | N1 | C2 | C7 | 119.39(12) |
| C14 | N1 | C17 | N18 | 168.53(10) | C14 | N1 | C17 | C22 | -9.84(16) |
| C17 | N1 | C14 | C9 | -117.57(12) | C17 | N1 | C14 | C13 | 65.79(15) |
| C17 | N18 | C19 | C20 | -0.1(2) | C19 | N18 | C17 | N1 | -176.59(11) |
| C19 | N18 | C17 | C22 | 1.75(18) | C23 | N24 | C25 | N26 | -0.32(16) |
| C23 | N24 | C25 | C29 | 179.24(8) | C25 | N24 | C23 | N28 | -0.30(15) |
| C25 | N24 | C23 | C20 | -177.99(9) | C25 | N26 | C27 | N28 | -1.68(16) |
| C25 | N26 | C27 | C35 | 176.63(9) | C27 | N26 | C25 | N24 | 1.24(16) |
| C27 | N26 | C25 | C29 | -178.33(9) | C23 | N28 | C27 | N26 | 1.15(16) |
| C23 | N28 | C27 | C35 | -177.17(9) | C27 | N28 | C23 | N24 | -0.09(15) |
| C27 | N28 | C23 | C20 | 177.61(9) | N1 | C2 | C3 | C4 | -177.25(10) |
| N1 | C2 | C7 | C6 | 177.45(10) | N1 | C2 | C7 | C8 | -2.97(16) |
| C3 | C2 | C7 | C6 | 1.52(18) | C3 | C2 | C7 | C8 | -178.90(11) |
| C7 | C2 | C3 | C4 | -1.43(19) | C2 | C3 | C4 | C5 | 0.3(2) |
| C3 | C4 | C5 | C6 | 0.7(2) | C4 | C5 | C6 | C7 | -0.6(2) |
| C5 | C6 | C7 | C2 | -0.5(2) | C5 | C6 | C7 | C8 | 179.94(12) |
| C2 | C7 | C8 | C9 | 39.58(15) | C2 | C7 | C8 | C15 | -78.00(13) |
| C2 | C7 | C8 | C16 | 161.97(10) | C6 | C7 | C8 | C9 | -140.87(12) |
| C6 | C7 | C8 | C15 | 101.55(14) | C6 | C7 | C8 | C16 | -18.48(17) |
| C7 | C8 | C9 | C10 | 142.38(12) | C7 | C8 | C9 | C14 | -37.75(15) |
| C15 | C8 | C9 | C10 | -100.49(14) | C15 | C8 | C9 | C14 | 79.38(14) |
| C16 | C8 | C9 | C10 | 19.84(18) | C16 | C8 | C9 | C14 | -160.29(11) |
| C8 | C9 | C10 | C11 | -179.50(11) | C8 | C9 | C14 | N1 | -0.60(18) |
| C8 | C9 | C14 | C13 | 176.00(11) | C10 | C9 | C14 | N1 | 179.29(11) |
| C10 | C9 | C14 | C13 | -4.11(19) | C14 | C9 | C10 | C11 | 0.62(19) |
| C9 | C10 | C11 | C12 | 2.5(2) | C10 | C11 | C12 | C13 | -2.2(2) |
| C11 | C12 | C13 | C14 | -1.2(2) | C12 | C13 | C14 | N1 | -179.03(12) |
| C12 | C13 | C14 | C9 | 4.5(2) | N1 | C17 | C22 | C21 | 176.07(10) |
| N18 | C17 | C22 | C21 | -2.22(18) | N18 | C19 | C20 | C21 | -0.97(19) |
| N18 | C19 | C20 | C23 | 176.36(11) | C19 | C20 | C21 | C22 | 0.48(17) |
| C19 | C20 | C23 | N24 | 0.03(16) | C19 | C20 | C23 | N28 | -177.83(10) |
| C21 | C20 | C23 | N24 | 177.23(10) | C21 | C20 | C23 | N28 | -0.63(16) |
| C23 | C20 | C21 | C22 | -176.85(10) | C20 | C21 | C22 | C17 | 1.04(18) |
| N24 | C25 | C29 | C30 | -5.46(16) | N24 | C25 | C29 | C34 | 174.19(9) |
| N26 | C25 | C29 | C30 | 174.14(9) | N26 | C25 | C29 | C34 | -6.21(16) |
| N26 | C27 | C35 | C36 | -2.57(17) | N26 | C27 | C35 | C40 | 178.86(10) |
| N28 | C27 | C35 | C36 | 175.87(10) | N28 | C27 | C35 | C40 | -2.70(17) |
| C25 | C29 | C30 | C31 | 178.41(10) | C25 | C29 | C34 | C33 | -177.66(10) |
| C30 | C29 | C34 | C33 | 1.99(19) | C34 | C29 | C30 | C31 | -1.24(18) |
| C29 | C30 | C31 | C32 | -0.3(2) | C30 | C31 | C32 | C33 | 1.1(2) |
| C31 | C32 | C33 | C34 | -0.4(3) | C32 | C33 | C34 | C29 | -1.2(2) |
| C27 | C35 | C36 | C37 | -178.26(11) | C27 | C35 | C40 | C39 | 178.25(11) |
| C36 | C35 | C40 | C39 | -0.3(2) | C40 | C35 | C36 | C37 | 0.3(2) |
| C35 | C36 | C37 | C38 | -0.1(3) | C36 | C37 | C38 | C39 | -0.1(3) |
| C37 | C38 | C39 | C40 | 0.0(3) | C38 | C39 | C40 | C35 | 0.2(3) |

**Table S23.** Intramolecular contacts less than 3.60 Å

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| N1 | C8 | 2.7957(18) | N1 | C15 | 3.2063(19) |
| N1 | C19 | 3.5801(18) | N18 | C2 | 2.7785(18) |
| N18 | C3 | 2.9718(18) | N18 | C21 | 2.7514(18) |
| N24 | C19 | 2.8267(18) | N24 | C27 | 2.6791(16) |
| N24 | C30 | 2.8146(17) | N26 | C23 | 2.6774(15) |
| N26 | C34 | 2.794(2) | N26 | C36 | 2.822(2) |
| N28 | C21 | 2.8151(18) | N28 | C25 | 2.6762(16) |
| N28 | C40 | 2.7911(19) | C2 | C5 | 2.756(2) |
| C2 | C9 | 2.815(2) | C2 | C13 | 3.573(2) |
| C2 | C15 | 3.182(2) | C3 | C6 | 2.770(2) |
| C3 | C14 | 3.579(2) | C3 | C17 | 3.1374(19) |
| C4 | C7 | 2.801(2) | C6 | C15 | 3.470(2) |
| C6 | C16 | 2.928(2) | C7 | C14 | 2.8034(19) |
| C7 | C17 | 3.5120(18) | C9 | C12 | 2.811(2) |
| C9 | C17 | 3.4903(18) | C10 | C13 | 2.766(2) |
| C10 | C15 | 3.469(2) | C10 | C16 | 2.922(2) |
| C11 | C14 | 2.758(2) | C13 | C17 | 3.1316(19) |
| C13 | C22 | 3.049(2) | C14 | C15 | 3.204(2) |
| C14 | C22 | 2.837(2) | C17 | C20 | 2.7470(15) |
| C19 | C22 | 2.7096(19) | C29 | C32 | 2.771(2) |
| C30 | C33 | 2.773(2) | C31 | C34 | 2.770(2) |
| C35 | C38 | 2.785(3) | C36 | C39 | 2.773(3) |
| C37 | C40 | 2.760(3) | | | |

**Table S24.** Intramolecular contacts less than 3.60 Å involving hydrogens

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| N1 | H3 | 2.625 | N1 | H13 | 2.622 |
| N1 | H15B | 2.665 | N1 | H22 | 2.593 |
| N18 | H3 | 2.740 | N18 | H15B | 3.287 |
| N18 | H22 | 3.228 | N24 | H19 | 2.491 |
| N24 | H30 | 2.500 | N26 | H34 | 2.466 |
| N26 | H36 | 2.508 | N28 | H21 | 2.500 |
| N28 | H40 | 2.463 | C2 | H4 | 3.252 |
| C2 | H6 | 3.251 | C2 | H15B | 2.894 |
| C2 | H15C | 3.534 | C3 | H5 | 3.248 |
| C4 | H6 | 3.252 | C5 | H3 | 3.250 |
| C6 | H4 | 3.257 | C6 | H15C | 3.309 |
| C6 | H16A | 2.959 | C6 | H16C | 2.719 |
| C7 | H3 | 3.286 | C7 | H5 | 3.273 |
| C7 | H15A | 3.352 | C7 | H15B | 2.667 |
| C7 | H15C | 2.698 | C7 | H16A | 2.742 |
| C7 | H16B | 3.380 | C7 | H16C | 2.722 |
| C8 | H6 | 2.761 | C8 | H10 | 2.757 |
| C9 | H11 | 3.280 | C9 | H13 | 3.287 |
| C9 | H15A | 2.699 | C9 | H15B | 2.679 |
| C9 | H15C | 3.352 | C9 | H16A | 2.713 |
| C9 | H16B | 2.731 | C9 | H16C | 3.369 |
| C9 | H22 | 3.560 | C10 | H12 | 3.259 |
| C10 | H15A | 3.303 | C10 | H16A | 2.927 |
| C10 | H16B | 2.737 | C11 | H13 | 3.252 |

| | | | | | |
|---|---|---|---|---|---|
| C12 | H10 | 3.253 | C12 | H22 | 3.346 |
| C13 | H11 | 3.250 | C13 | H22 | 2.412 |
| C14 | H10 | 3.247 | C14 | H12 | 3.258 |
| C14 | H15A | 3.553 | C14 | H15B | 2.932 |
| C14 | H22 | 2.515 | C15 | H10 | 3.600 |
| C15 | H16A | 3.362 | C15 | H16B | 2.685 |
| C15 | H16C | 2.699 | C16 | H6 | 2.589 |
| C16 | H10 | 2.588 | C16 | H15A | 2.699 |
| C16 | H15B | 3.360 | C16 | H15C | 2.692 |
| C17 | H3 | 3.022 | C17 | H13 | 3.040 |
| C17 | H15B | 2.809 | C17 | H19 | 3.169 |
| C17 | H21 | 3.220 | C19 | H21 | 3.228 |
| C20 | H22 | 3.256 | C21 | H19 | 3.222 |
| C22 | H13 | 2.872 | C22 | H15B | 3.329 |
| C23 | H19 | 2.643 | C23 | H21 | 2.665 |
| C25 | H30 | 2.662 | C25 | H34 | 2.648 |
| C27 | H36 | 2.669 | C27 | H40 | 2.648 |
| C29 | H31 | 3.266 | C29 | H33 | 3.261 |
| C30 | H32 | 3.260 | C30 | H34 | 3.265 |
| C31 | H33 | 3.248 | C32 | H30 | 3.261 |
| C32 | H34 | 3.243 | C33 | H31 | 3.248 |
| C34 | H30 | 3.267 | C34 | H32 | 3.243 |
| C35 | H37 | 3.264 | C35 | H39 | 3.265 |
| C36 | H38 | 3.263 | C36 | H40 | 3.265 |
| C37 | H39 | 3.238 | C38 | H36 | 3.262 |

| | | | | | |
|---|---|---|---|---|---|
| C38 | H40 | 3.254 | C39 | H37 | 3.236 |
| C40 | H36 | 3.266 | C40 | H38 | 3.257 |
| H3 | H4 | 2.336 | H4 | H5 | 2.327 |
| H5 | H6 | 2.328 | H6 | H15C | 3.316 |
| H6 | H16A | 2.611 | H6 | H16B | 3.536 |
| H6 | H16C | 2.144 | H10 | H11 | 2.326 |
| H10 | H15A | 3.297 | H10 | H16A | 2.589 |
| H10 | H16B | 2.162 | H10 | H16C | 3.538 |
| H11 | H12 | 2.333 | H12 | H13 | 2.339 |
| H13 | H22 | 2.307 | H15A | H16A | 3.591 |
| H15A | H16B | 2.503 | H15A | H16C | 2.990 |
| H15B | H16B | 3.583 | H15B | H16C | 3.590 |
| H15B | H22 | 3.558 | H15C | H16A | 3.592 |
| H15C | H16B | 2.959 | H15C | H16C | 2.511 |
| H19 | H30 | 3.274 | H21 | H22 | 2.317 |
| H21 | H40 | 3.200 | H30 | H31 | 2.346 |
| H31 | H32 | 2.331 | H32 | H33 | 2.317 |
| H33 | H34 | 2.327 | H34 | H36 | 3.225 |
| H36 | H37 | 2.336 | H37 | H38 | 2.322 |
| H38 | H39 | 2.326 | H39 | H40 | 2.334 |

**Table S25.** Intermolecular contacts less than 3.60 Å

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| N24 | N26[1] | 3.4859(15) | N24 | N28[1] | 3.5808(15) |
| N24 | C27[1] | 3.4090(16) | N26 | N24[1] | 3.4859(15) |
| N26 | C20[1] | 3.5635(16) | N26 | C23[1] | 3.4516(15) |
| N28 | N24[1] | 3.5808(15) | N28 | C20[2] | 3.5094(16) |
| N28 | C21[2] | 3.5262(17) | N28 | C25[1] | 3.4457(16) |
| N28 | C29[1] | 3.4698(17) | N28 | C30[1] | 3.5568(17) |
| C3 | C37[2] | 3.566(3) | C5 | C11[3] | 3.533(2) |
| C11 | C5[4] | 3.533(2) | C20 | N26[1] | 3.5635(16) |
| C20 | N28[2] | 3.5094(16) | C21 | N28[2] | 3.5262(17) |
| C21 | C23[2] | 3.4778(18) | C21 | C34[1] | 3.361(2) |
| C23 | N26[1] | 3.4516(15) | C23 | C21[2] | 3.4778(18) |
| C23 | C25[1] | 3.3486(16) | C25 | N28[1] | 3.4457(16) |
| C25 | C23[1] | 3.3486(16) | C27 | N24[1] | 3.4090(16) |
| C29 | N28[1] | 3.4698(17) | C29 | C32[5] | 3.497(2) |
| C30 | N28[1] | 3.5568(17) | C30 | C31[5] | 3.572(2) |
| C30 | C32[5] | 3.435(2) | C31 | C30[6] | 3.572(2) |
| C32 | C29[6] | 3.497(2) | C32 | C30[6] | 3.435(2) |
| C34 | C21[1] | 3.361(2) | C37 | C3[2] | 3.566(3) |
| C37 | C39[7] | 3.513(3) | C38 | C39[7] | 3.570(3) |
| C39 | C37[8] | 3.513(3) | C39 | C38[8] | 3.570(3) |

Symmetry Operators:

(1) -X+1,-Y+1,-Z+2
(2) -X+1,-Y+1,-Z+1
(3) -X+1/2,-Y+1,Z+1/2
(4) -X+1/2,-Y+1,Z+1/2-1
(5) X,-Y+1,Z
(6) X,-Y+1,Z+1

(7) X,-Y+2,Z+1

(8) X,-Y+2,Z

**Table S26.** Intermolecular contacts less than 3.60 Å involving hydrogens

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| N18 | H36[1] | 3.445 | N18 | H38[2] | 3.325 |
| N24 | H21[3] | 3.532 | N24 | H31[4] | 3.174 |
| N26 | H13[3] | 2.895 | N26 | H22[3] | 3.594 |
| N28 | H30[1] | 3.507 | C2 | H16C[5] | 3.071 |
| C3 | H16B[5] | 3.483 | C3 | H16C[5] | 3.291 |
| C3 | H38[2] | 2.889 | C4 | H16B[5] | 3.089 |
| C4 | H16C[5] | 3.377 | C4 | H37[2] | 3.385 |
| C4 | H38[2] | 2.875 | C5 | H10[6] | 3.541 |
| C5 | H11[7] | 3.464 | C5 | H16B[5] | 3.120 |
| C5 | H16C[5] | 3.250 | C6 | H15C[5] | 3.239 |
| C6 | H16B[5] | 3.530 | C6 | H16C[5] | 3.014 |
| C7 | H16C[5] | 2.924 | C9 | H6[5] | 3.202 |
| C10 | H5[5] | 3.238 | C10 | H5[8] | 3.507 |
| C10 | H6[5] | 3.086 | C10 | H11[9] | 3.278 |
| C11 | H5[5] | 2.772 | C11 | H6[5] | 3.285 |
| C11 | H15A[10] | 3.458 | C11 | H33[11] | 3.256 |
| C12 | H5[5] | 3.390 | C12 | H6[5] | 3.525 |
| C12 | H15A[12] | 3.581 | C12 | H32[11] | 3.143 |
| C12 | H33[11] | 2.943 | C12 | H34[3] | 3.505 |
| C13 | H32[11] | 3.107 | C13 | H34[3] | 3.226 |
| C14 | H6[5] | 3.488 | C15 | H33[1] | 3.533 |
| C15 | H34[1] | 3.396 | C19 | H36[1] | 3.318 |
| C19 | H39[2] | 3.302 | C19 | H40[3] | 3.574 |
| C20 | H34[1] | 3.599 | C21 | H31[11] | 3.536 |

| | | | | | |
|---|---|---|---|---|---|
| C21 | H34[1] | 3.409 | C22 | H32[11] | 3.344 |
| C22 | H34[1] | 3.547 | C23 | H21[3] | 3.421 |
| C25 | H13[3] | 3.376 | C25 | H32[4] | 3.244 |
| C27 | H30[1] | 3.553 | C29 | H13[3] | 3.441 |
| C29 | H21[1] | 3.524 | C29 | H32[4] | 2.790 |
| C30 | H31[4] | 3.305 | C30 | H32[4] | 3.063 |
| C30 | H40[1] | 3.360 | C31 | H21[2] | 3.212 |
| C31 | H22[2] | 3.548 | C31 | H30[13] | 3.444 |
| C31 | H32[4] | 3.543 | C31 | H40[1] | 3.527 |
| C32 | H12[2] | 3.501 | C32 | H22[2] | 3.022 |
| C33 | H12[2] | 3.372 | C33 | H12[3] | 3.124 |
| C33 | H21[1] | 3.539 | C33 | H32[4] | 3.546 |
| C34 | H12[3] | 3.160 | C34 | H13[3] | 2.969 |
| C34 | H15B[1] | 3.468 | C34 | H21[1] | 3.383 |
| C34 | H32[4] | 3.085 | C35 | H3[3] | 3.228 |
| C35 | H30[1] | 3.349 | C36 | H3[3] | 3.000 |
| C36 | H19[1] | 3.360 | C36 | H39[9] | 3.233 |
| C37 | H3[3] | 2.815 | C37 | H4[11] | 3.268 |
| C37 | H38[9] | 3.559 | C37 | H39[9] | 2.952 |
| C38 | H3[11] | 3.462 | C38 | H3[3] | 2.879 |
| C38 | H4[11] | 3.329 | C38 | H37[10] | 3.547 |
| C38 | H39[9] | 3.162 | C39 | H3[3] | 3.105 |
| C39 | H19[11] | 3.194 | C39 | H37[10] | 3.588 |
| C40 | H3[3] | 3.269 | C40 | H30[1] | 3.196 |
| H3 | C35[3] | 3.228 | H3 | C36[3] | 3.000 |

| | | | | | |
|---|---|---|---|---|---|
| H3 | C37[3] | 2.815 | H3 | C38[2] | 3.462 |
| H3 | C38[3] | 2.879 | H3 | C39[3] | 3.105 |
| H3 | C40[3] | 3.269 | H3 | H36[3] | 3.506 |
| H3 | H37[3] | 3.240 | H3 | H38[2] | 2.767 |
| H3 | H38[3] | 3.335 | H4 | C37[2] | 3.268 |
| H4 | C38[2] | 3.329 | H4 | H10[6] | 3.323 |
| H4 | H16B[5] | 3.340 | H4 | H37[2] | 2.602 |
| H4 | H38[2] | 2.738 | H4 | H38[3] | 3.436 |
| H5 | C10[7] | 3.238 | H5 | C10[6] | 3.507 |
| H5 | C11[7] | 2.772 | H5 | C12[7] | 3.390 |
| H5 | H10[7] | 3.341 | H5 | H10[6] | 2.765 |
| H5 | H11[7] | 2.584 | H5 | H11[6] | 3.403 |
| H5 | H12[7] | 3.599 | H5 | H15A[5] | 3.449 |
| H5 | H16B[5] | 3.397 | H6 | C9[7] | 3.202 |
| H6 | C10[7] | 3.086 | H6 | C11[7] | 3.285 |
| H6 | C12[7] | 3.525 | H6 | C14[7] | 3.488 |
| H6 | H10[7] | 3.424 | H6 | H15C[5] | 2.963 |
| H6 | H16A[7] | 3.334 | H6 | H16C[5] | 3.466 |
| H10 | C5[8] | 3.541 | H10 | H4[8] | 3.323 |
| H10 | H5[5] | 3.341 | H10 | H5[8] | 2.765 |
| H10 | H6[5] | 3.424 | H10 | H11[9] | 2.885 |
| H11 | C5[5] | 3.464 | H11 | C10[10] | 3.278 |
| H11 | H5[5] | 2.584 | H11 | H5[8] | 3.403 |
| H11 | H10[10] | 2.885 | H11 | H15A[10] | 2.680 |
| H11 | H16B[10] | 3.106 | H11 | H33[11] | 3.193 |

| | | | | | |
|---|---|---|---|---|---|
| H12 | C32[11] | 3.501 | H12 | C33[11] | 3.372 |
| H12 | C33[3] | 3.124 | H12 | C34[3] | 3.160 |
| H12 | H5[5] | 3.599 | H12 | H15A[12] | 3.229 |
| H12 | H32[11] | 2.929 | H12 | H33[11] | 2.664 |
| H12 | H33[3] | 2.974 | H12 | H34[3] | 3.053 |
| H13 | N26[3] | 2.895 | H13 | C25[3] | 3.376 |
| H13 | C29[3] | 3.441 | H13 | C34[3] | 2.969 |
| H13 | H32[11] | 2.878 | H13 | H34[3] | 2.474 |
| H13 | H36[3] | 3.327 | H15A | C11[9] | 3.458 |
| H15A | C12[14] | 3.581 | H15A | H5[7] | 3.449 |
| H15A | H11[9] | 2.680 | H15A | H12[14] | 3.229 |
| H15A | H33[1] | 2.964 | H15A | H34[1] | 3.316 |
| H15B | C34[1] | 3.468 | H15B | H33[1] | 3.192 |
| H15B | H34[1] | 2.728 | H15B | H36[1] | 3.494 |
| H15C | C6[7] | 3.239 | H15C | H6[7] | 2.963 |
| H15C | H16A[7] | 2.785 | H16A | H6[5] | 3.334 |
| H16A | H15C[5] | 2.785 | H16A | H16C[5] | 3.402 |
| H16B | C3[7] | 3.483 | H16B | C4[7] | 3.089 |
| H16B | C5[7] | 3.120 | H16B | C6[7] | 3.530 |
| H16B | H4[7] | 3.340 | H16B | H5[7] | 3.397 |
| H16B | H11[9] | 3.106 | H16C | C2[7] | 3.071 |
| H16C | C3[7] | 3.291 | H16C | C4[7] | 3.377 |
| H16C | C5[7] | 3.250 | H16C | C6[7] | 3.014 |
| H16C | C7[7] | 2.924 | H16C | H6[7] | 3.466 |
| H16C | H16A[7] | 3.402 | H19 | C36[1] | 3.360 |

| | | | | | |
|---|---|---|---|---|---|
| H19 | C39[2] | 3.194 | H19 | H31[4] | 3.417 |
| H19 | H36[1] | 3.185 | H19 | H38[2] | 3.508 |
| H19 | H39[2] | 2.474 | H19 | H40[3] | 3.526 |
| H21 | N24[3] | 3.532 | H21 | C23[3] | 3.421 |
| H21 | C29[1] | 3.524 | H21 | C31[11] | 3.212 |
| H21 | C33[1] | 3.539 | H21 | C34[1] | 3.383 |
| H21 | H31[11] | 2.731 | H21 | H32[11] | 3.507 |
| H22 | N26[3] | 3.594 | H22 | C31[11] | 3.548 |
| H22 | C32[11] | 3.022 | H22 | H31[11] | 3.489 |
| H22 | H32[11] | 2.502 | H22 | H33[1] | 3.456 |
| H30 | N28[1] | 3.507 | H30 | C27[1] | 3.553 |
| H30 | C31[4] | 3.444 | H30 | C35[1] | 3.349 |
| H30 | C40[1] | 3.196 | H30 | H31[4] | 2.998 |
| H30 | H32[4] | 3.442 | H30 | H39[2] | 3.130 |
| H30 | H40[2] | 3.255 | H30 | H40[1] | 3.174 |
| H31 | N24[13] | 3.174 | H31 | C21[2] | 3.536 |
| H31 | C30[13] | 3.305 | H31 | H19[13] | 3.417 |
| H31 | H21[2] | 2.731 | H31 | H22[2] | 3.489 |
| H31 | H30[13] | 2.998 | H31 | H40[2] | 3.272 |
| H31 | H40[1] | 3.463 | H32 | C12[2] | 3.143 |
| H32 | C13[2] | 3.107 | H32 | C22[2] | 3.344 |
| H32 | C25[13] | 3.244 | H32 | C29[13] | 2.790 |
| H32 | C30[13] | 3.063 | H32 | C31[13] | 3.543 |
| H32 | C33[13] | 3.546 | H32 | C34[13] | 3.085 |
| H32 | H12[2] | 2.929 | H32 | H13[2] | 2.878 |

| | | | | | |
|---|---|---|---|---|---|
| H32 | H21[2] | 3.507 | H32 | H22[2] | 2.502 |
| H32 | H30[13] | 3.442 | H32 | H34[13] | 3.483 |
| H33 | C11[2] | 3.256 | H33 | C12[2] | 2.943 |
| H33 | C15[1] | 3.533 | H33 | H11[2] | 3.193 |
| H33 | H12[2] | 2.664 | H33 | H12[3] | 2.974 |
| H33 | H15A[1] | 2.964 | H33 | H15B[1] | 3.192 |
| H33 | H22[1] | 3.456 | H34 | C12[3] | 3.505 |
| H34 | C13[3] | 3.226 | H34 | C15[1] | 3.396 |
| H34 | C20[1] | 3.599 | H34 | C21[1] | 3.409 |
| H34 | C22[1] | 3.547 | H34 | H12[3] | 3.053 |
| H34 | H13[3] | 2.474 | H34 | H15A[1] | 3.316 |
| H34 | H15B[1] | 2.728 | H34 | H32[4] | 3.483 |
| H36 | N18[1] | 3.445 | H36 | C19[1] | 3.318 |
| H36 | H3[3] | 3.506 | H36 | H13[3] | 3.327 |
| H36 | H15B[1] | 3.494 | H36 | H19[1] | 3.185 |
| H37 | C4[11] | 3.385 | H37 | C38[9] | 3.547 |
| H37 | C39[9] | 3.588 | H37 | H3[3] | 3.240 |
| H37 | H4[11] | 2.602 | H37 | H38[9] | 3.116 |
| H37 | H39[9] | 3.191 | H38 | N18[11] | 3.325 |
| H38 | C3[11] | 2.889 | H38 | C4[11] | 2.875 |
| H38 | C37[10] | 3.559 | H38 | H3[11] | 2.767 |
| H38 | H3[3] | 3.335 | H38 | H4[11] | 2.738 |
| H38 | H4[3] | 3.436 | H38 | H19[11] | 3.508 |
| H38 | H37[10] | 3.116 | H38 | H39[9] | 3.515 |
| H39 | C19[11] | 3.302 | H39 | C36[10] | 3.233 |

| | | | | | |
|---|---|---|---|---|---|
| H39 | C37[10] | 2.952 | H39 | C38[10] | 3.162 |
| H39 | H19[11] | 2.474 | H39 | H30[11] | 3.130 |
| H39 | H37[10] | 3.191 | H39 | H38[10] | 3.515 |
| H40 | C19[3] | 3.574 | H40 | C30[1] | 3.360 |
| H40 | C31[1] | 3.527 | H40 | H19[3] | 3.526 |
| H40 | H30[11] | 3.255 | H40 | H30[1] | 3.174 |
| H40 | H31[11] | 3.272 | H40 | H31[1] | 3.463 |

Symmetry Operators:

(1) -X+1,-Y+1,-Z+2
(2) -X+1,Y+1/2-1,-Z+1/2+1
(3) -X+1,-Y+1,-Z+1
(4) X,-Y+1,Z
(5) -X+1/2,-Y+1,Z+1/2-1
(6) -X+1,Y,Z
(7) -X+1/2,-Y+1,Z+1/2
(8) -X+1,Y+1,Z
(9) X,-Y+2,Z+1
(10) X,-Y+2,Z
(11) -X+1,Y+1/2,-Z+1/2+1
(12) X,Y,Z-1
(13) X,-Y+1,Z+1
(14) X,Y,Z+1

**DFT Calculations**

All calculations are performed with Gaussian 16 B.01[15] (M062X/6-31 G(d))[16] in the gas phase. Excited state calculation with TD-DFT calculation (Tamm-Dancoff approximation).[17] The four adjacent atoms (as marked in **Figure S9a** and **S9b**) are defined to estimate the dihedral angle between the DMAC and the bridging aryl in **DMAC-TRZ** and **DMAC-py-TRZ**. To perform relaxed scan calculations, this angle was frozen, while the molecule was otherwise allowed to relax towards the ground-state equilibrium structure.

*a. Rigid dihedral angle scan of each of **DMAC-TRZ** and **DMAC-py-TRZ***

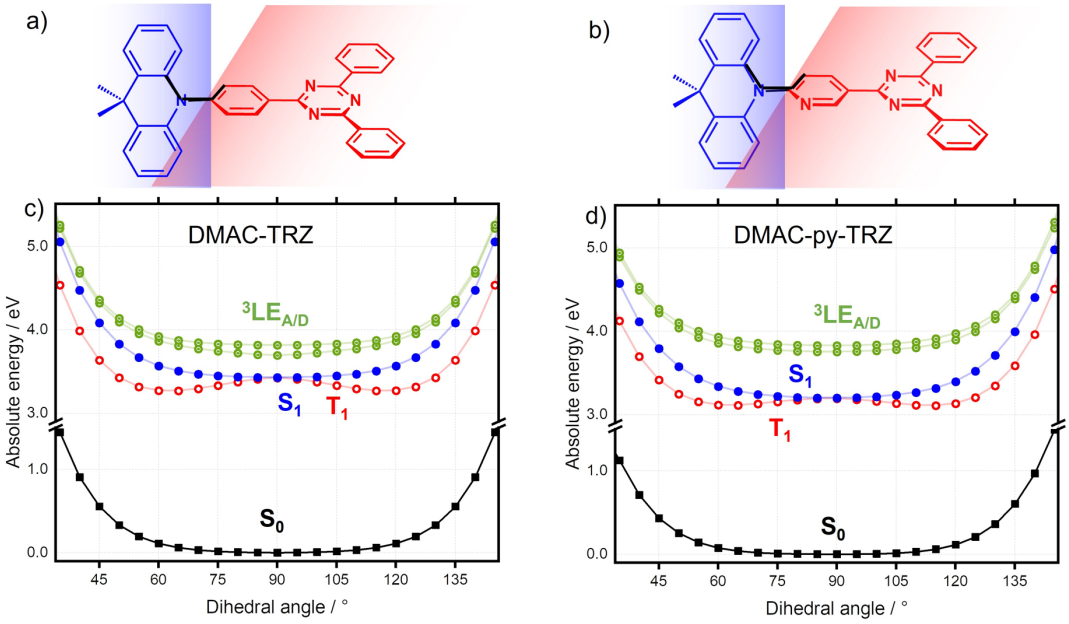
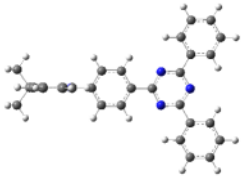



Figure **S9**. Sketch of a) **DMAC-TRZ** and b) **DMAC-py-TRZ** showing four adjacent atoms to define the dihedral angle of the dihedral rigid scan of interest. Energies of ground (black), lowest energy singlet (blue), lowest energy triplet (red) and two higher energy triplet (green) states.

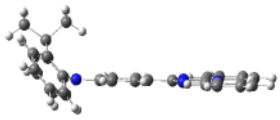
*b. Optimized geometry of $S_0$ (bent and orthogonal), $S_1$ and $T_1$ for both **DMAC-TRZ** and **DMAC-py-TRZ**.*

**DMAC-TRZ**

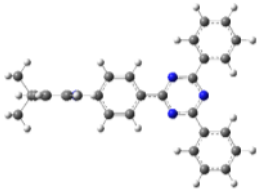
a. $S_0$: Orthogonal (angle = 90°)



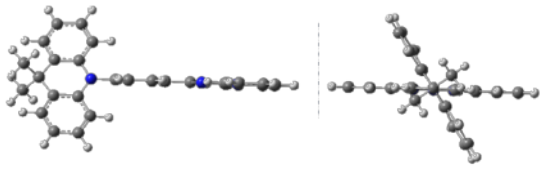
b. $S_0$: bent (angle = 10°)



c. $S_1$: Optimized (angle = 90°)



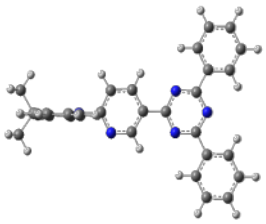
d. $T_1$: Orthogonal (angle = 60°)



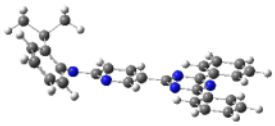
Different side view

**DMAC-py-TRZ**

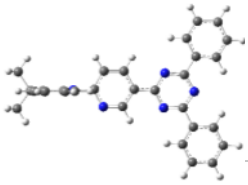
e. $S_0$: Orthogonal (angle = 90°)



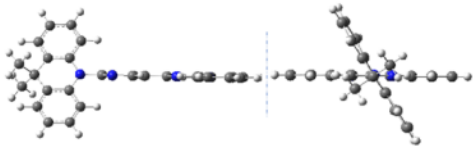
f. $S_0$: bent (angle = 10°)



g. $S_1$: Optimized (angle = 90°)

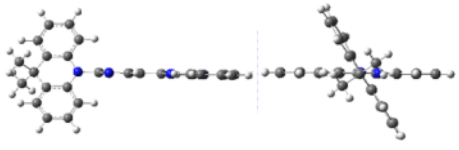


h. $T_1$: (dihedral angle = 60°) Obtained from orthogonal starting geometry



Different side view

i. $T_1$: (dihedral angle = 30°) Obtained from bent starting geometry



Different side view

Figure **S10.** Optimized geometries (bent and orthogonal) of the ground state ($S_0$), first singlet excited state ($S_1$), first triplet-excited state ($T_1$) for both **DMAC-TRZ** and **DMAC-py-TRZ**. All geometries are obtained at the M06-2X/6-31g(d) level of theory.

*c. Molecular Orbitals of **DMAC-TRZ** vs **DMAC-py-TRZ***

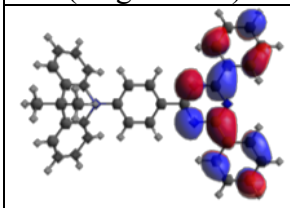
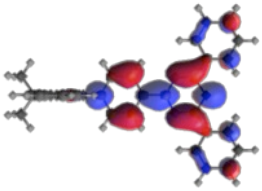
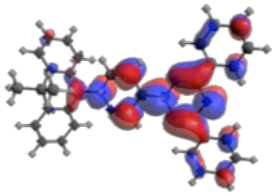
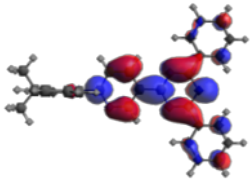
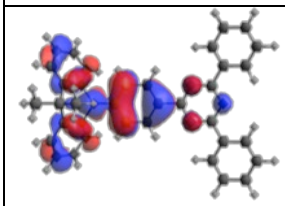
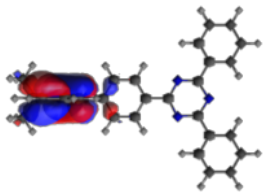
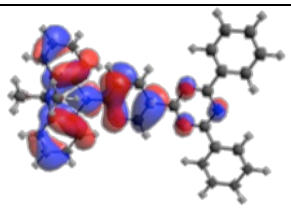
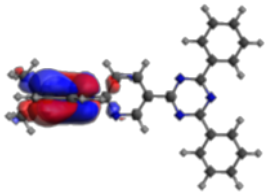
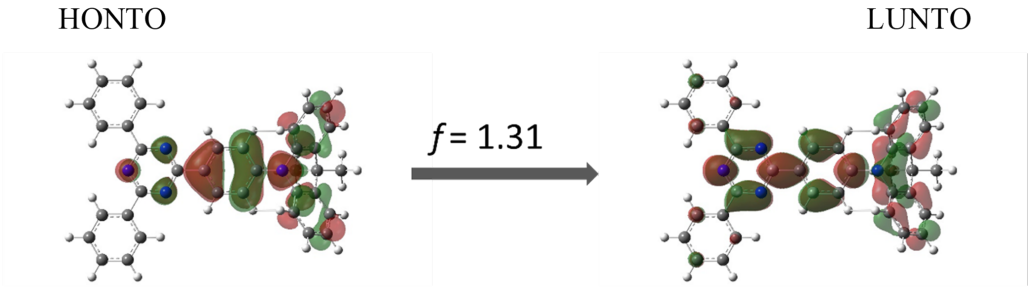
| a. **DMAC-TRZ** | | b. **DMAC-py-TRZ** | |
|---|---|---|---|
| Bent (Angle = 10°) | Orthogonal (Angle = 90°) | Bent (Angle = 10°) | Orthogonal (Angle = 90°) |
|  LUMO |  LUMO |  LUMO |  LUMO |
| | | | |
|  HOMO |  HOMO |  HOMO |  HOMO |

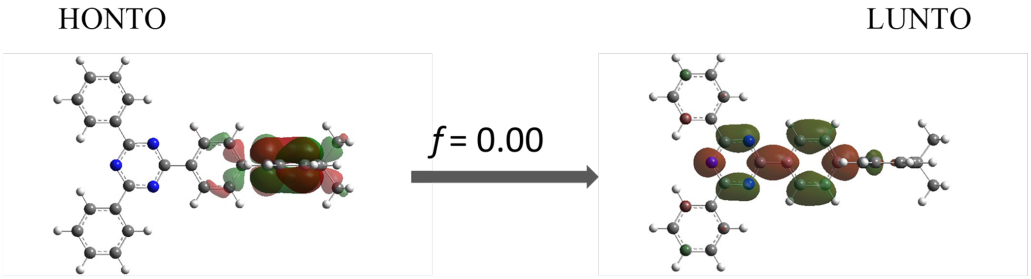
Figure **S11**. Molecular orbitals (HOMO and LUMO) of a) **DMAC-TRZ** and b) **DMAC-py-TRZ** for both bent and orthogonal geometries

*d. Natural transition orbitals of **DMAC-TRZ** and **DMAC-py-TRZ***

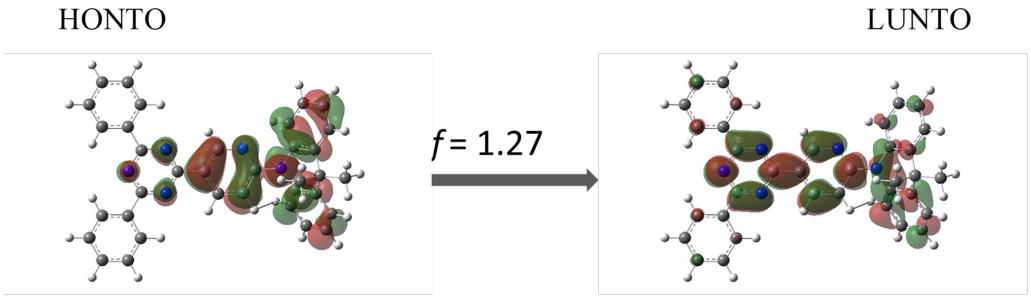
a. **DMAC-TRZ:** Bent (Angle = 10º)




b. **DMAC-TRZ:** Orthogonal (Angle = 90º)




c. **DMAC-py-TRZ:** Bent (Angle = 10º)




d. **DMAC-py-TRZ:** Orthogonal (Angle = 90º)

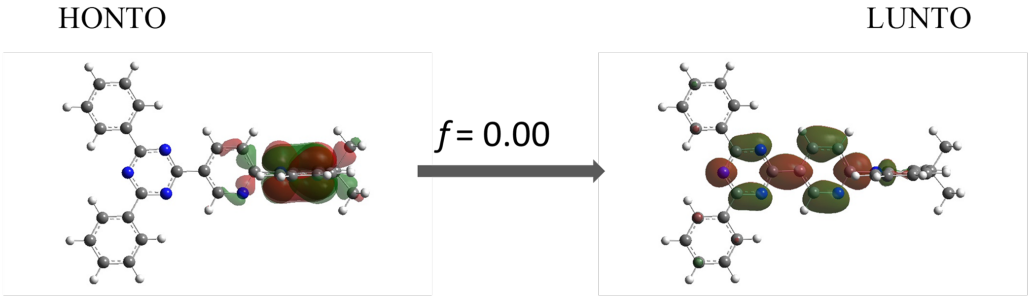



Figure **S12**. Natural transition orbitals and oscillator strength (*f*) related to the $S_0$-$S_1$ transition of **DMAC-TRZ** for both a) bent b) orthogonal geometries and of **DMAC-py-TRZ** for both c) bent d) orthogonal geometries shown.

Table **S27.** Absorption and emission data of **DMAC-py-TRZ** in different solvents.

| **Solvent** | $\lambda_{abs}/nm$ | $\lambda_{PL}/nm$ | $\Delta\nu/cm^{-1}$ |
|---|---|---|---|
| Cyclohexane | 370 | 472 | 5840 |
| Toluene | 370 | 550 | 8845 |
| Chloroform | 370 | 573 | 9575 |
| DMSO | 368 | 675 | 12212 |
| 2MeTHF (298 K) | 370 | 596 | 10192 |
| 2MeTHF (77 K) | 370 | 404 | 2275 |

Spectroscopic data: absorption wavelength ($\lambda_{abs}$), emission wavelength ($\lambda_{PL}$) and Stokes shift ($\Delta\nu$) in different solvents

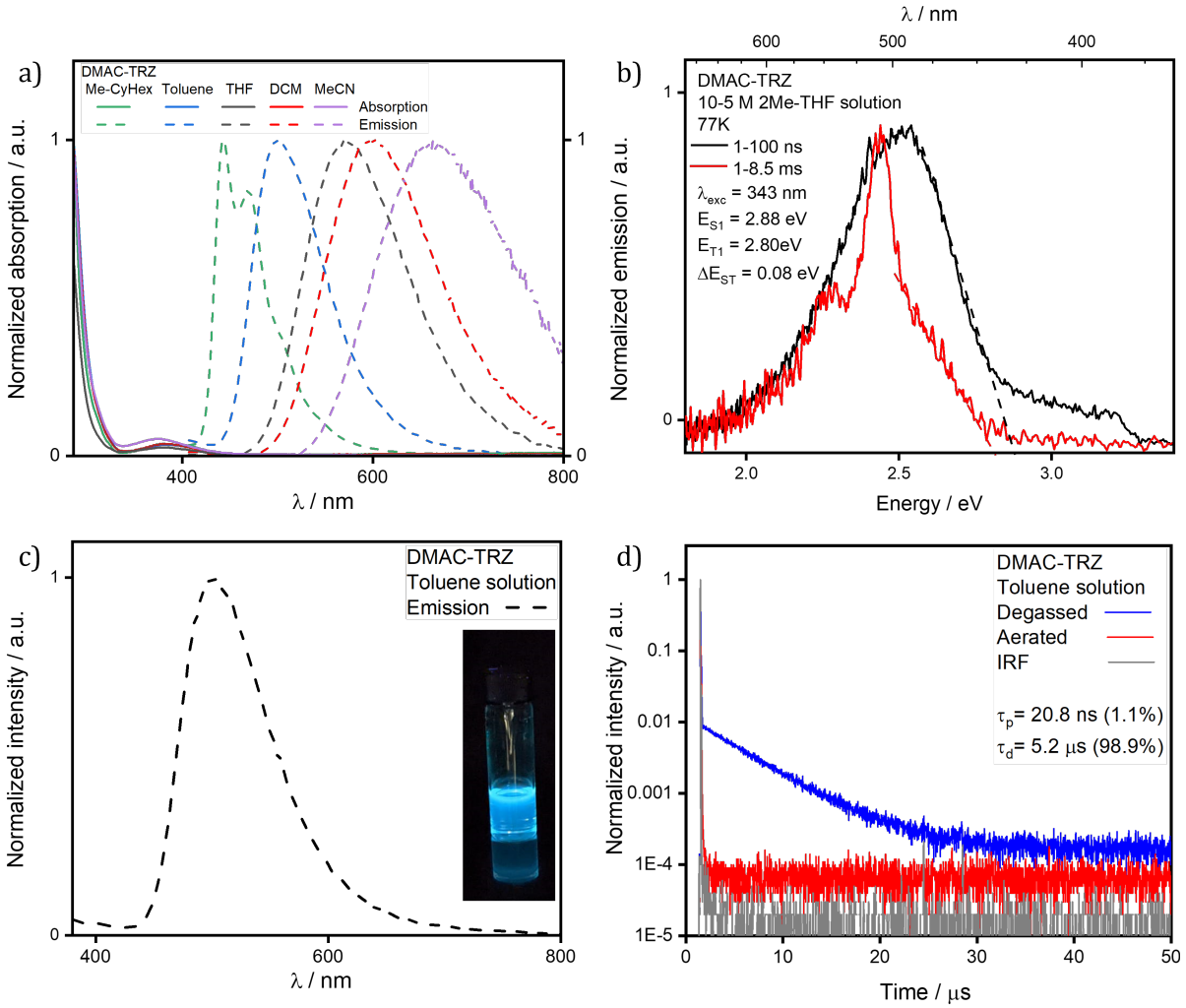



Figure **S13.** a) Ground and excited state solvatochromism study of **DMAC-TRZ** ($\lambda_{exc}$, = 340 nm); b) Prompt fluorescence and phosphorescence spectra at 77 K in $10^{-5}$ M 2-MeTHF glass ($\lambda_{exc}$ = 343 nm, prompt and delayed fluorescence spectra were obtained over the 1–100 ns and 1–8.5 ms time ranges, respectively); c) emission spectrum of **DMAC-py-TRZ** (toluene, $10^{-5}$

M solutions, $\lambda_{exc}$ = 340 nm); d) time-resolved photoluminescence decay of degassed and aerated solutions of **DMAC-py-TRZ** (toluene, $10^{-5}$ M solutions, $\lambda_{exc}$ = 378 nm).

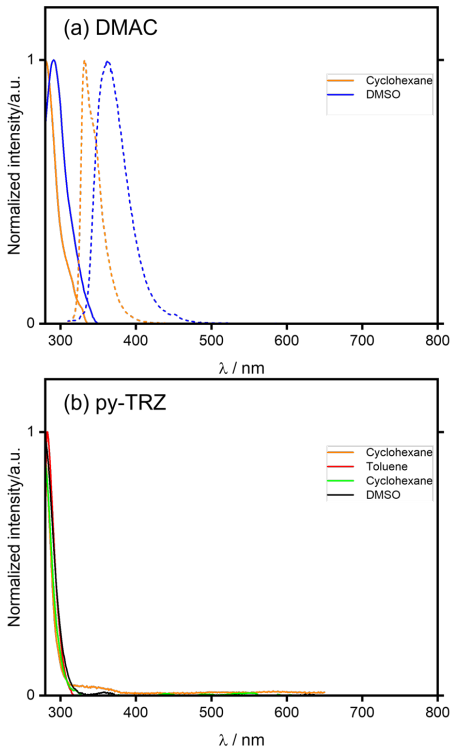



Figure **S14**. Steady-state absorption (continuous lines) and emission (dotted lines) spectra of (a) **DMAC**, (b) **py-TRZ** in different solvents. Emission spectra for excitation at 300 nm.

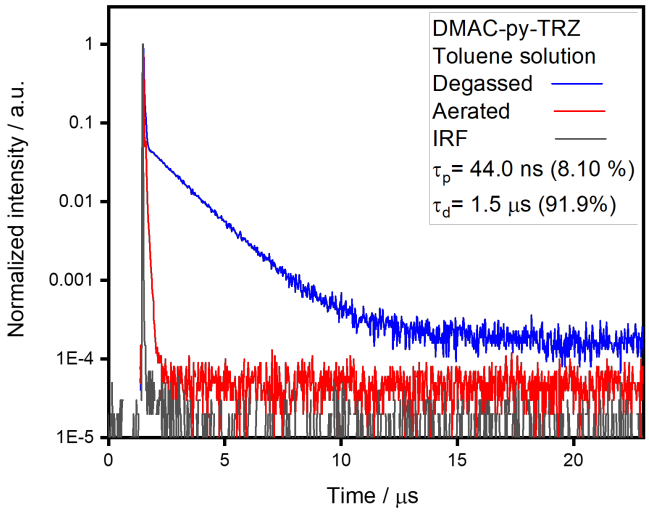


Figure **S15**. Time-resolved PL decay of degassed and aerated solutions of **DMAC-py-TRZ** (Toluene, $10^{-5}$ M solutions, $\lambda_{exc}$ = 378 nm).

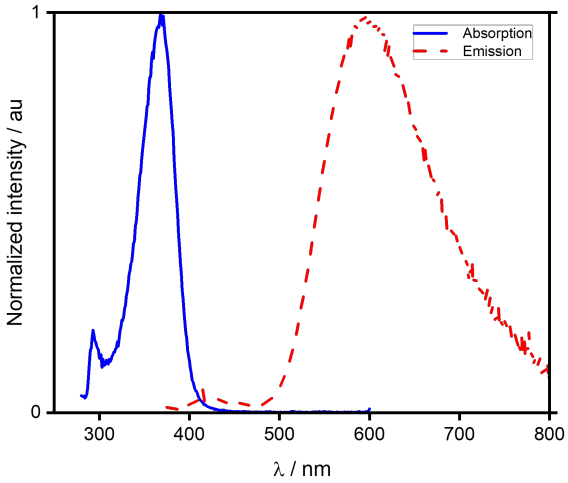



Figure **S16**. Absorption (blue dashed line) and emission (red continuous line, $\lambda_{ecc}$=370 nm) spectra of **DMAC-py-TRZ** in 2-MeTHF at room temperature.

Table **28**. Additional photophysical data of DMAC-TRZ and DMAC-py-TRZ in matrices.

| Material | Environment | $\lambda_{PL}$ / nm[a] | $\Phi_{PL}$ $N_2$ (air)[b] / % | $\tau_p$, $\tau_d$ [c] / ns; µs | $S_1$[d] / eV | $T_1$[e] / eV |
|---|---|---|---|---|---|---|
| **DMAC-TRZ** | mCP 10 wt% | 499 | 47 (45) | 22.9; 15.3 | 2.83 | 2.81 |
| | PMMA 10 wt% | 523 | 18 (15) | 41.6; 17.0 | 2.85 | 2.74 |
| **DMAC-py-TRZ** | mCP 10 wt% | 496 | 57 (54) | 24.9; 5.3 | 2.76 | 2.71 |
| | PMMA 10 wt% | 516 | 64 (58) | 26.0; 4.7 | 2.76 | 2.74 |

[a] measured at room temperature. [b] $\lambda_{exc}$ = 340 nm, obtained using an integrating sphere. [c] $\tau_p$ (prompt lifetime) and $\tau_d$ (delayed lifetime) were obtained from the transient PL decay of degassed doped film, $\lambda_{exc}$ = 378 nm. [d] $S_1$ was obtained from the onset of the prompt fluorescence measured at 77 K, obtained in the 1–100 ns time range. [e] $T_1$ was obtained from the onset of the phosphorescence spectrum measured at 77 K, obtained in the 1–8.5 ms time range.

The $S_1$ and $T_1$ energies in Table **S28** are estimated from the onsets of fluorescence and phosphorescence spectra, respectively. Data in Fig. **7** (main text) demonstrate quite unambiguously that self-absorption heavily affects the spectra measured in matrices down to 1% concentration. This self-absorption issue is particularly problematic in **DMAC-py-TRZ** samples due to the large extinction coefficient of the bent form that is responsible for the sizable absorbance values in low-concentration thin films.

*f. Spectroscopic analysis of **DMAC-py-TRZ** in viscous solvent (polyTHF)*

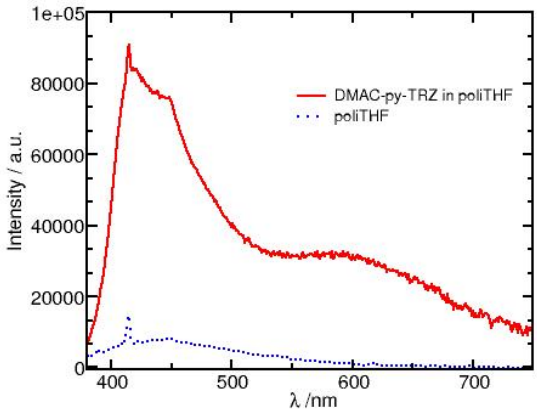



Figure **S17**. PL spectrum (red line) of **DMAC-py-TRZ** dissolved in polyTHF ($\lambda_{exc}$=370nm). The blue dotted line is the emission spectrum of the pure solvent.

*g. Additional DFT/TD-DFT data for **DMAC-TRZ** and **DMAC-py-TRZ***

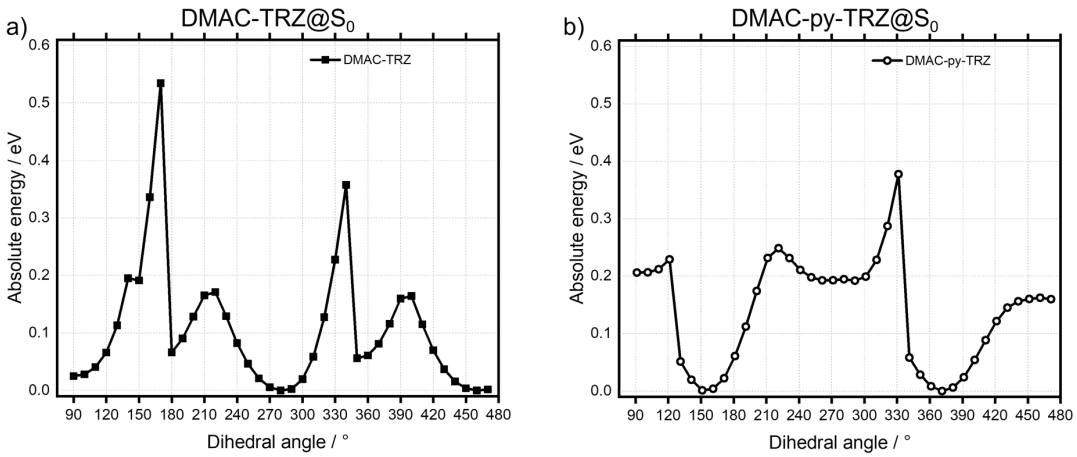



Figure **S18**. Full relaxed dihedral angle scan of **DMAC-TRZ** and **DMAC-py-TRZ** at the $S_0$ geometry.

These scans were obtained from the redundant coordinate scan calculation available in Gaussian 16.B01 software. In this case, we optimized every angle starting from the previously optimized geometry starting from a 90$^o$ dihedral angle at gaps of 10$^o$. The main issue using this approach is that scans lack symmetry during a full 360$^o$ rotation. In the main text's approach, we first changed the dihedral angle starting from an identical geometry (orthogonal in our case) and run optimization at each angle. In this case, scans are symmetric at every 0-90$^o$ range, so the full ranges are not shown in main text. However, the conclusion about both conformers stays the same using either approache.

*h. UV-VIS absorption spectra of **DMAC-TRZ** and **DMAC-py-TRZ***

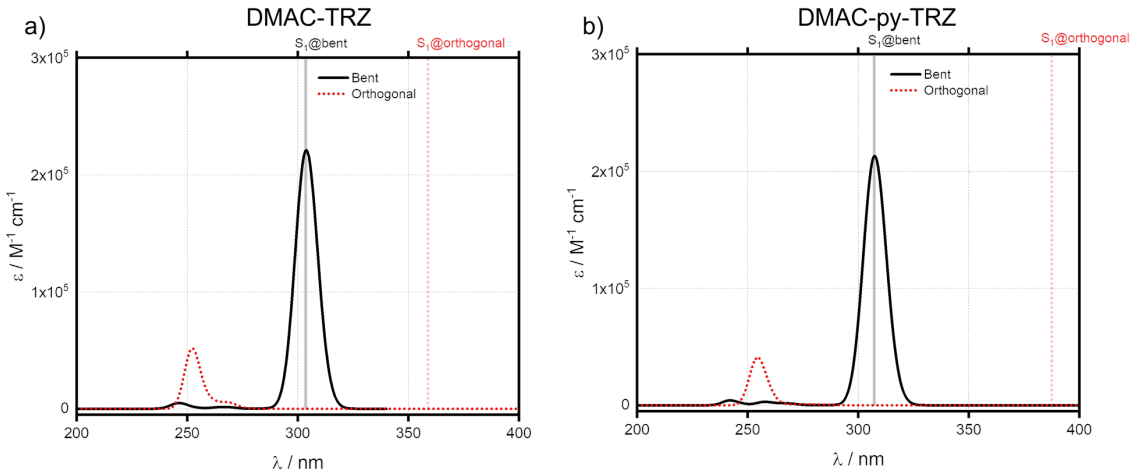



Figure **S139**. UV-VIS absorption spectra of a) **DMAC-TRZ** and b) **DMAC-py-TRZ** for orthogonal (red) and bent (black) geometry at the M062X/6-31G(d) level.

*i. Excited-state energies for **DMAC-TRZ** and **DMAC-py-TRZ***

Table **S29**. $S_1$ , $T_1$ and $\Delta E_{ST}$ energies of **DMAC-TRZ** and **DMAC-py-TRZ** calculated in the gas phase at the TDA-DFT- M062X/6-31G(d) level.

| | | **$S_1$ / eV** | **$T_1$ / eV** | **$\Delta E_{ST}$ / eV** |
|---|---|---|---|---|
| **DMAC-TRZ** | Orthogonal | 3.452 | 3.444 | 0.008 |
| | Bent | 4.081 | 3.239 | 0.842 |
| **DMAC-py-TRZ** | Orthogonal | 3.197 | 3.188 | 0.009 |
| | Bent | 4.034 | 3.248 | 0.786 |

## References


(1) Takahashi, T.; Shizu, K.; Yasuda, T.; Togashi, K.; Adachi, C. Donor–Acceptor-Structured 1,4-Diazatriphenylene Derivatives Exhibiting Thermally Activated Delayed Fluorescence: Design and Synthesis, Photophysical Properties and OLED Characteristics. *Sci. Technol. Adv. Mater.* **2014**, *15* (3), 034202.

(2) Connelly, N. G., and Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96* (2), 877–910.

(3) Crosby, G. A.; Demas, J. N. Measurement of Photoluminescence Quantum Yields. Review. *J. Phys. Chem.* **1971**, *75* (8), 991–1024. https://doi.org/10.1021/j100678a001.

(4) Melhuish, W. H. Quantum Efficiencies of Fluorescence of Organic Substan Ces: Effect of Solvent and Concentration of the Fluorescent Solute. *J. Phys. Chem.* **1961**, *65* (2), 229–235. https://doi.org/10.1021/j100820a009.

(5) Corporation, R. CrysaAlisPro: Data Collection and Processing Software. Tokyo, Japan 2015, pp 196–8666.

(6) F.R. Ahmed. Larson, A.C. (1970), Crystallographic Computing. Copenhagen 1970, pp 291–294.

(7) Sheldrick, G. M. SHELXT Version 2018/2. Acta Cryst. A70, C1437 2014.

(8) Sheldrick, G. M. SHELXL Version 2018/3. Acta Cryst. A64 2008, pp 112–122.

(9) *International Tables for Crystallography*, A.J.C. Wil.; Kluwer Academic Publishers, Dordrecht, Netherlands, 1992.

(10) Ibers, J. A. & Hamilton, W. C. No Title. *Acta Crystallogr.,* **1964**, *781* (17).

(11) Creagh, D. C. & McAuley, W. . *International Tables for Crystallography*, A.J.C. Wil.; Kluwer Academic Publishers, Boston, 1992.

(12) Creagh, D. C. & Hubbell, J. H. *International Tables for Crystallography*, A.J.C. Wil.; Kluwer Academic Publishers, Boston, 1992.

(13) CrystalStructure 4.3: Crystal Structure Analysis Package. Rigaku Corporation: Tokyo, Japan pp 196–8666.

(14) Corporation, R. CrystalClear: Data Collection and Processing Software. Tokyo, Japan pp 196–8666.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. a.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. a.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, a. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, a. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. a.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. a.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, a. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. G16_C01. 2016, p Gaussian 16, Revision C.01, Gaussian, Inc., Wallin.

(16) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem. Acc.* **2008**, *120* (1–3), 215–241. https://doi.org/10.1007/s00214-007-0310-x.

(17) Hirata, S.; Head-Gordon, M. Time-Dependent Density Functional Theory within the Tamm-Dancoff Approximation. *Chem. Phys. Lett.* **1999**, *314* (3–4), 291–299. https://doi.org/10.1016/S0009-2614(99)01149-5.