Supporting Information

A luminescent cadmium metal-organic frameworks for sensing of nitroaromatic explosives

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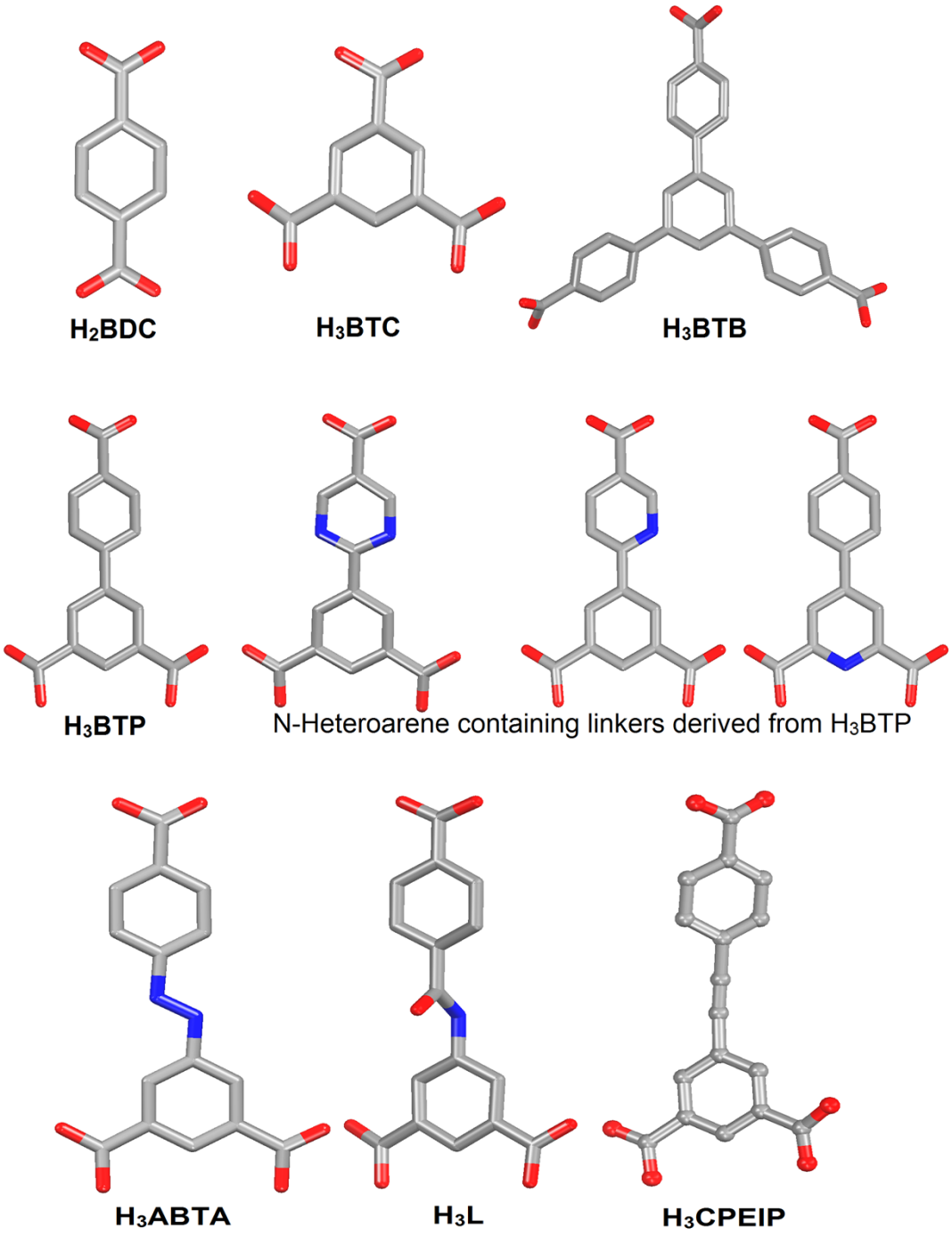
Fig. S1 Reported high symmetric aromatic polycarboxylates (H_2BDC[1] , H_3BTC[2] , H_3BTB[3]) and unsymmetrical aromatic polycarboxylate (H_3BTP[4], N-Heteroarene containing linkers derived from H_3BTP[5], H_3ABTA[6], 5-(4-carboxybenzoylamino)-isophthalic acid (H_3L)[7], and H_3CPEIP[8].



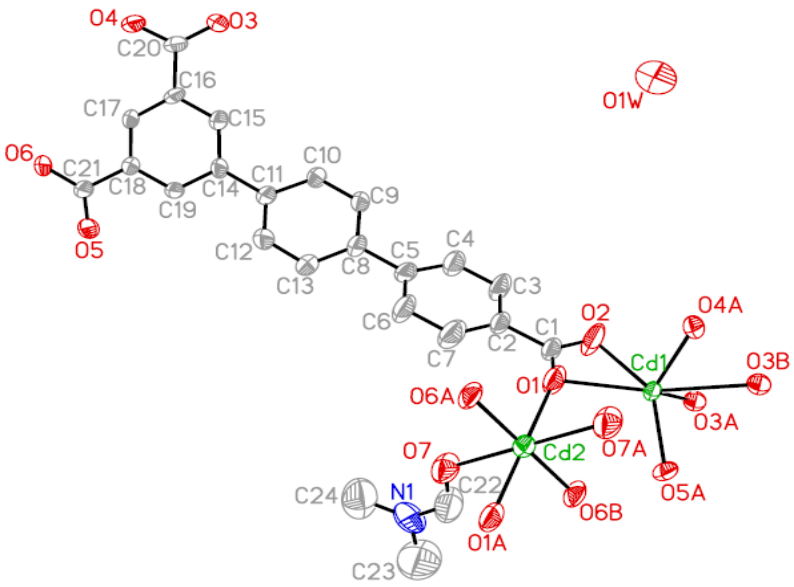


Fig. S2 Representation of the asymmetric unit of **1** showing ellipsoid at the50% probability level.

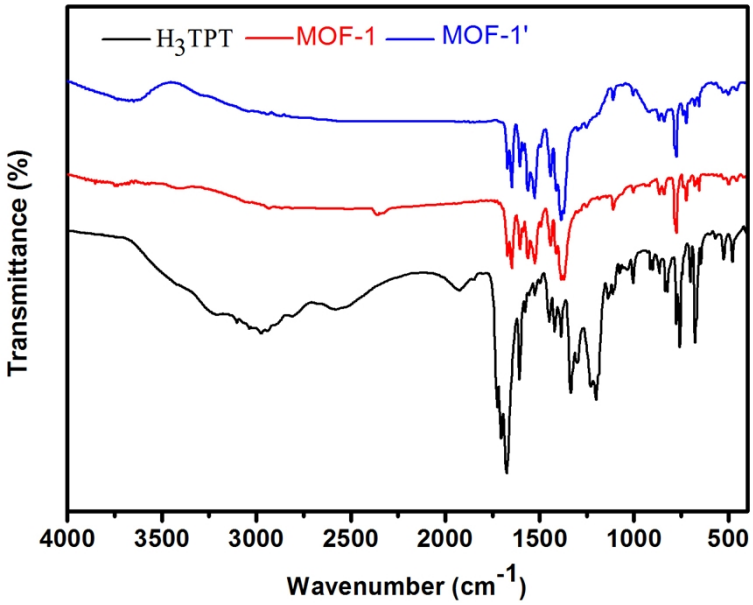


Fig. S3 Infra-red spectra of the H_3TPT, MOF-**1** and MOF-**1'**.

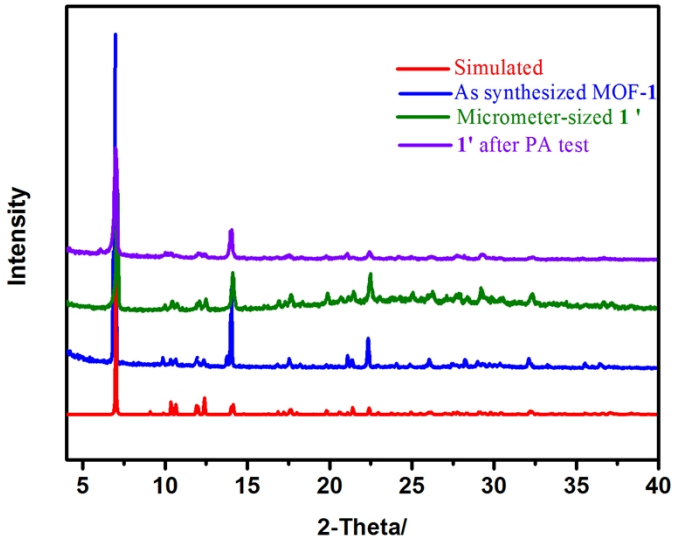


Fig. S4 PXRD patterns of the simulated pattern calculated from the single crystal X-ray data, the as-systhesized sample **1**, micrometer-sized **1'** and sample of **1'** after PA quenching and recovery test for five times.

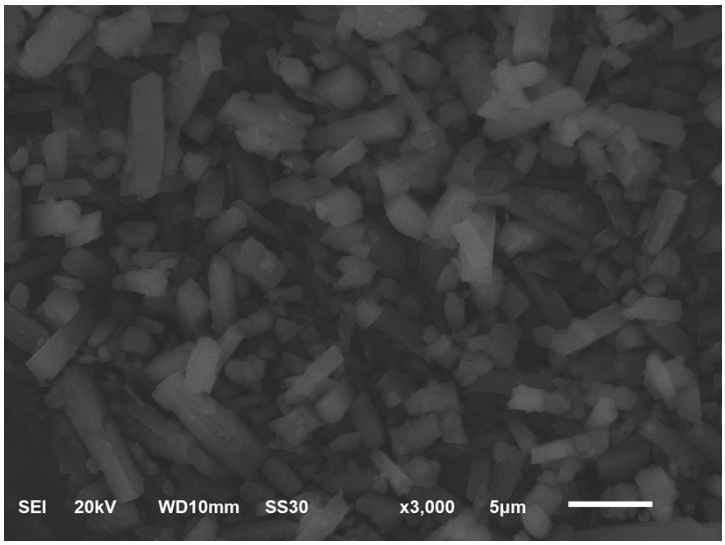


Fig. S5 The SEM image of micrometer-sized **1'**

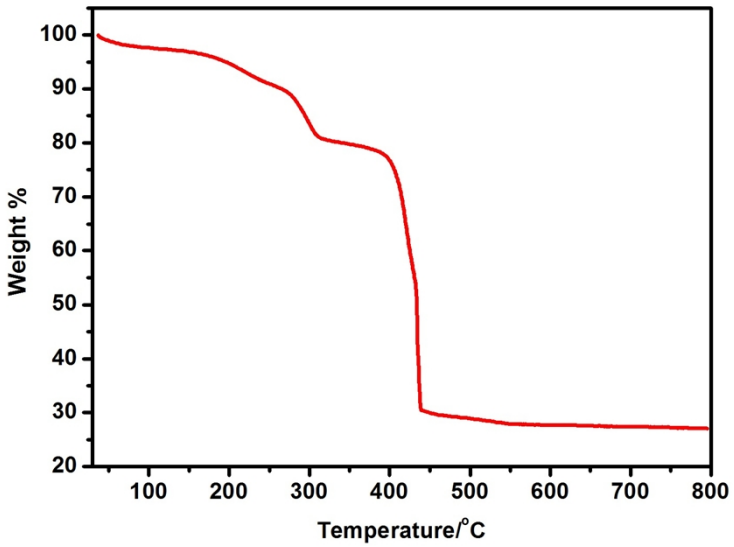


Fig. S6 The TGA curve of **1**

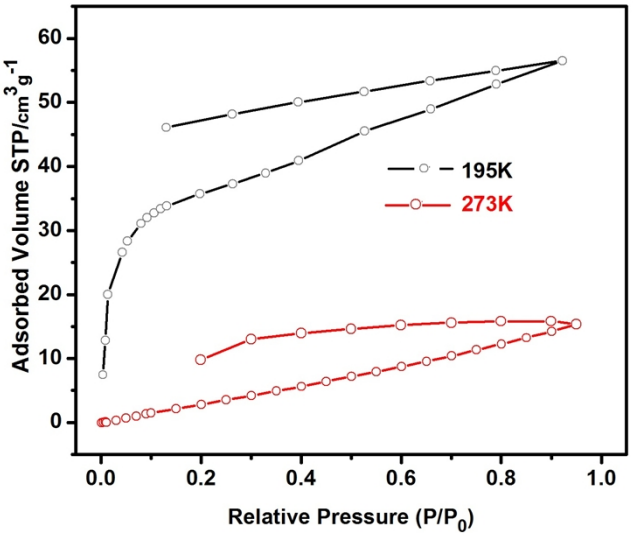


Fig. S7 CO_2 adsorption-desorption isotherms measured at 195 K and 273 K.

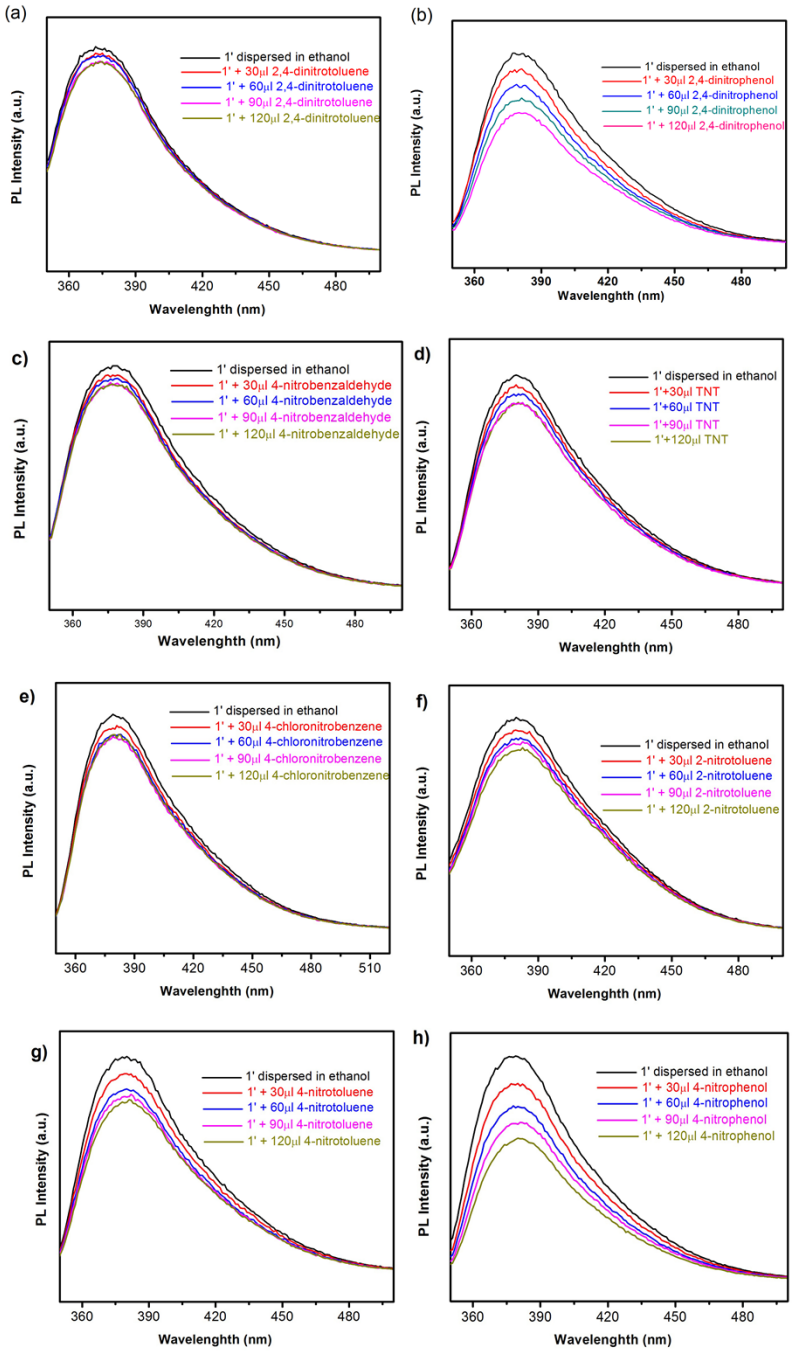


Fig. S8 Fluorescence titrations of 0.5mg **1'** dispersed in 2mL ethanol solution with the addition of different volume of 0.001M solution of nitromethane (a), 2, 4-dinitrophenol (DNP) (b), 4- nitrobenzaldehyde (c), 2, 4, 6-trinitrotoluene (TNT) (d), 4-chloronitrobenzene (e), 2-nitrotoluene (f), 4-nitrotoluene (g), and 4- nitrophenol (h) in ethanol. Excited at 334 nm and fluorescence emission was recorded from 350 nm to 500 nm. The slit width for both excitation and emission was 1.5 nm.

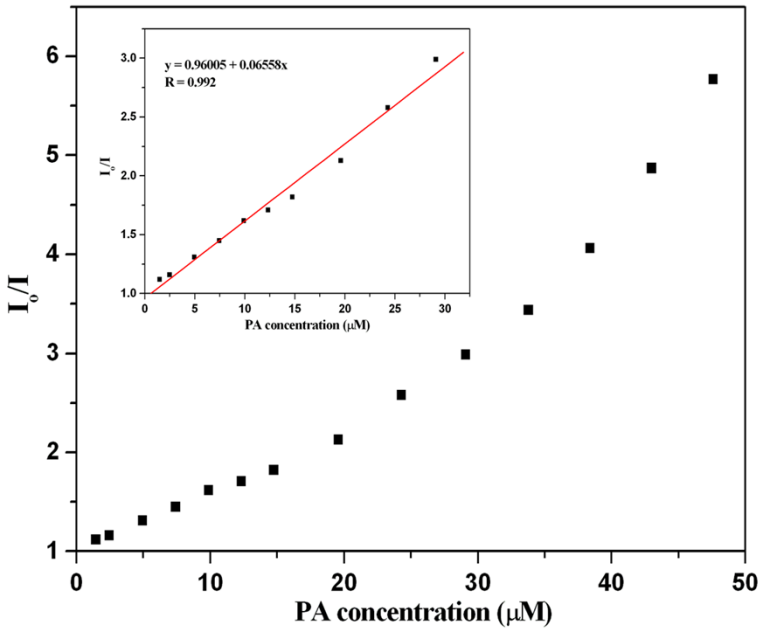


Fig. S9 Plot of I_o/I versus PA concentration in ethanol for **1'**.

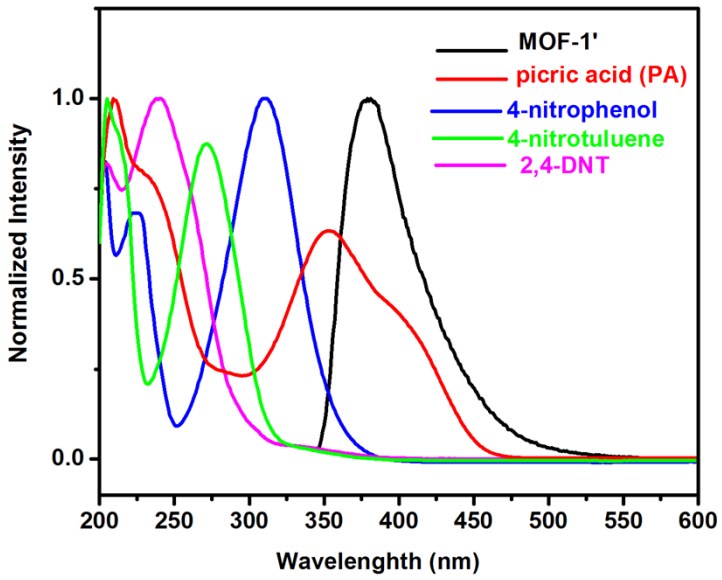


Fig. S10 Spectral overlaps between the absorption spectra of analytes with the concentration of 1.0×10^{-3} M and the emission spectra of **1'** in ethanol (2.06×10^{-4} M).

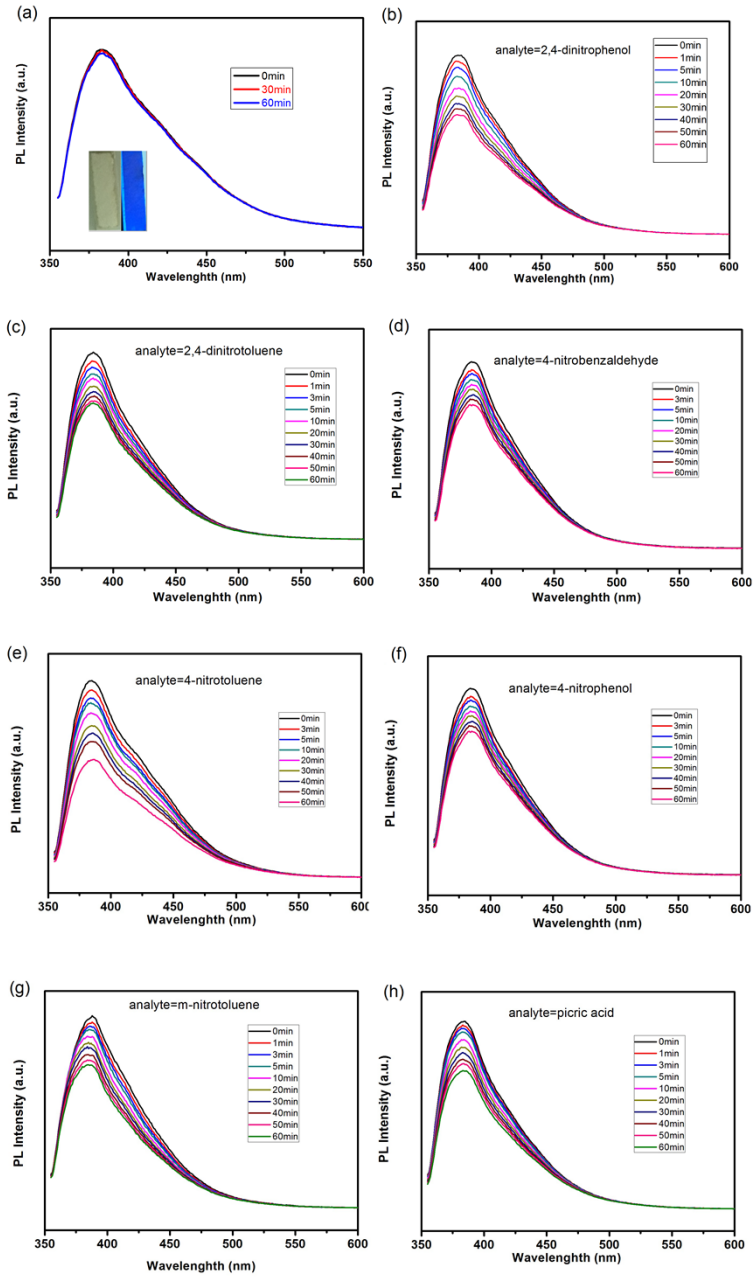


Fig. S11 (a) The luminescent spectra of **1'** on double-sided tape at different time, and the photographs of the layer of **1'** under the sunlight and the UV light (inset). The vapor sensing of **1'** for 2,4-dinitrophenol (b), 2,4-dinitrotoluene (c), 4-nitrobenzaldehyde (d), 4-nitrotoluene (e), 4- nitrophenol (f), m-nitrotoluene (g), and picric acid (h).

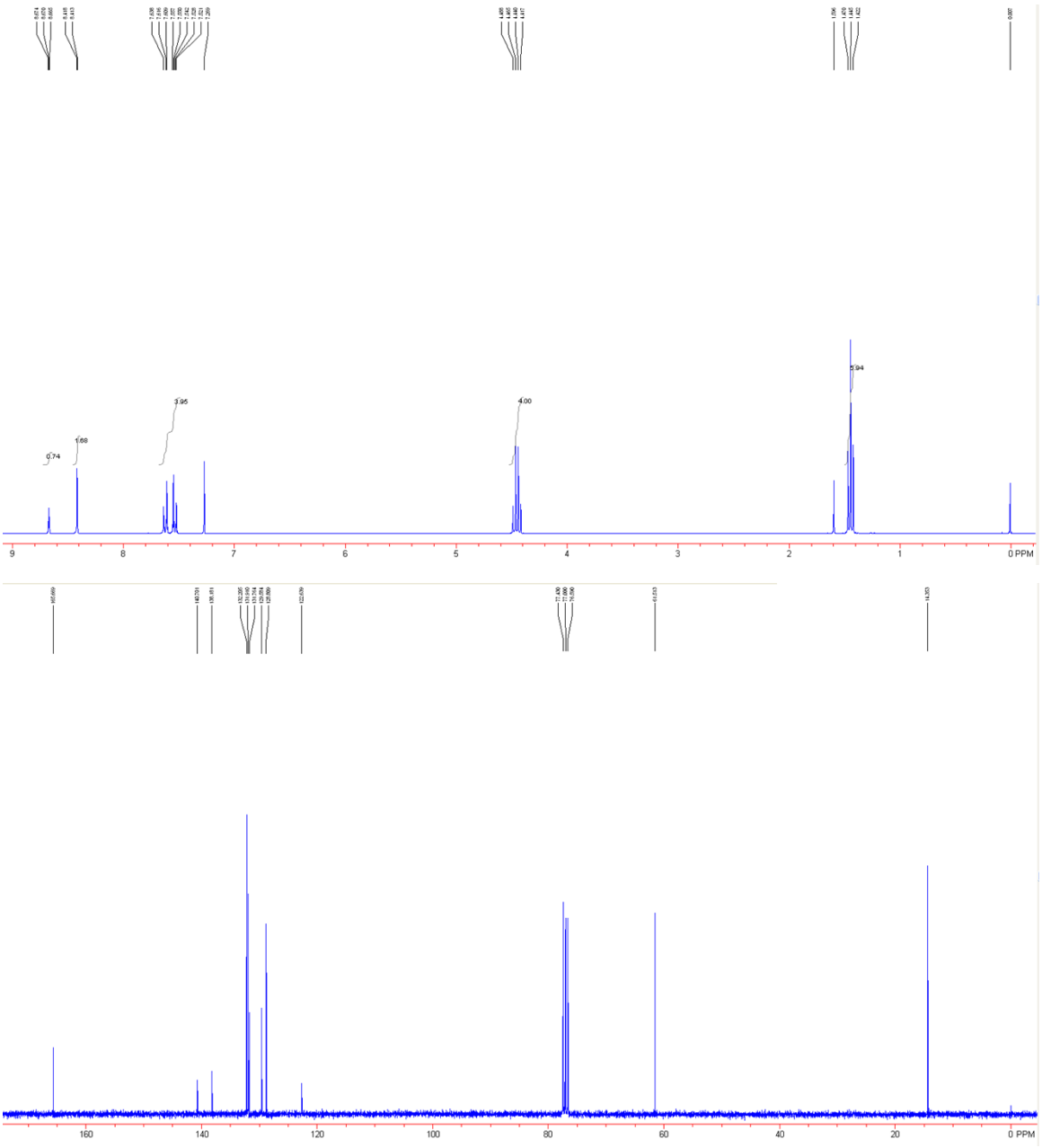


Fig. 12 The ^{1}H and ^{13}C NMR spectra of **M1**

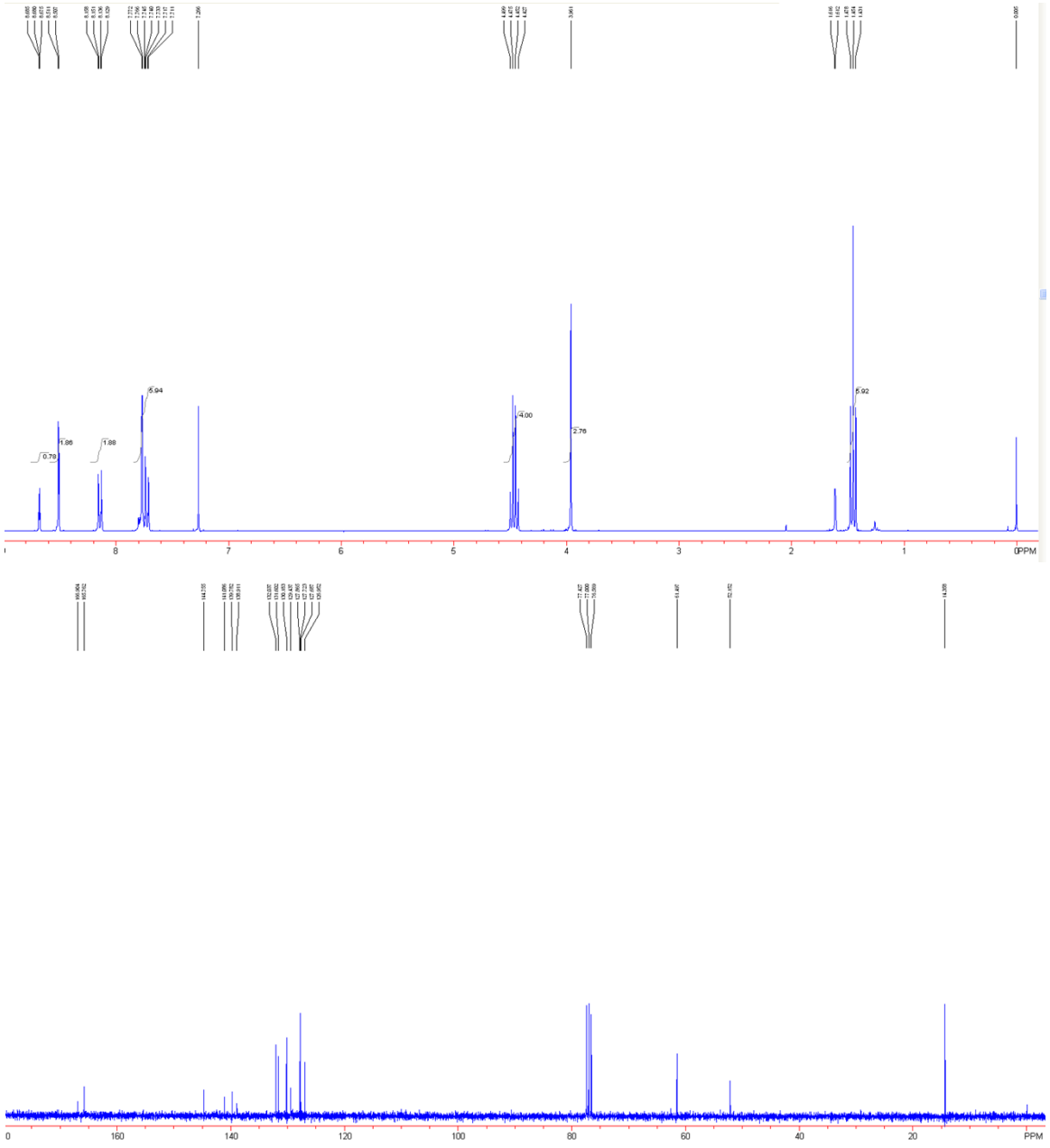


Fig. 13 The ^{1}H and ^{13}C NMR spectra of **M2**

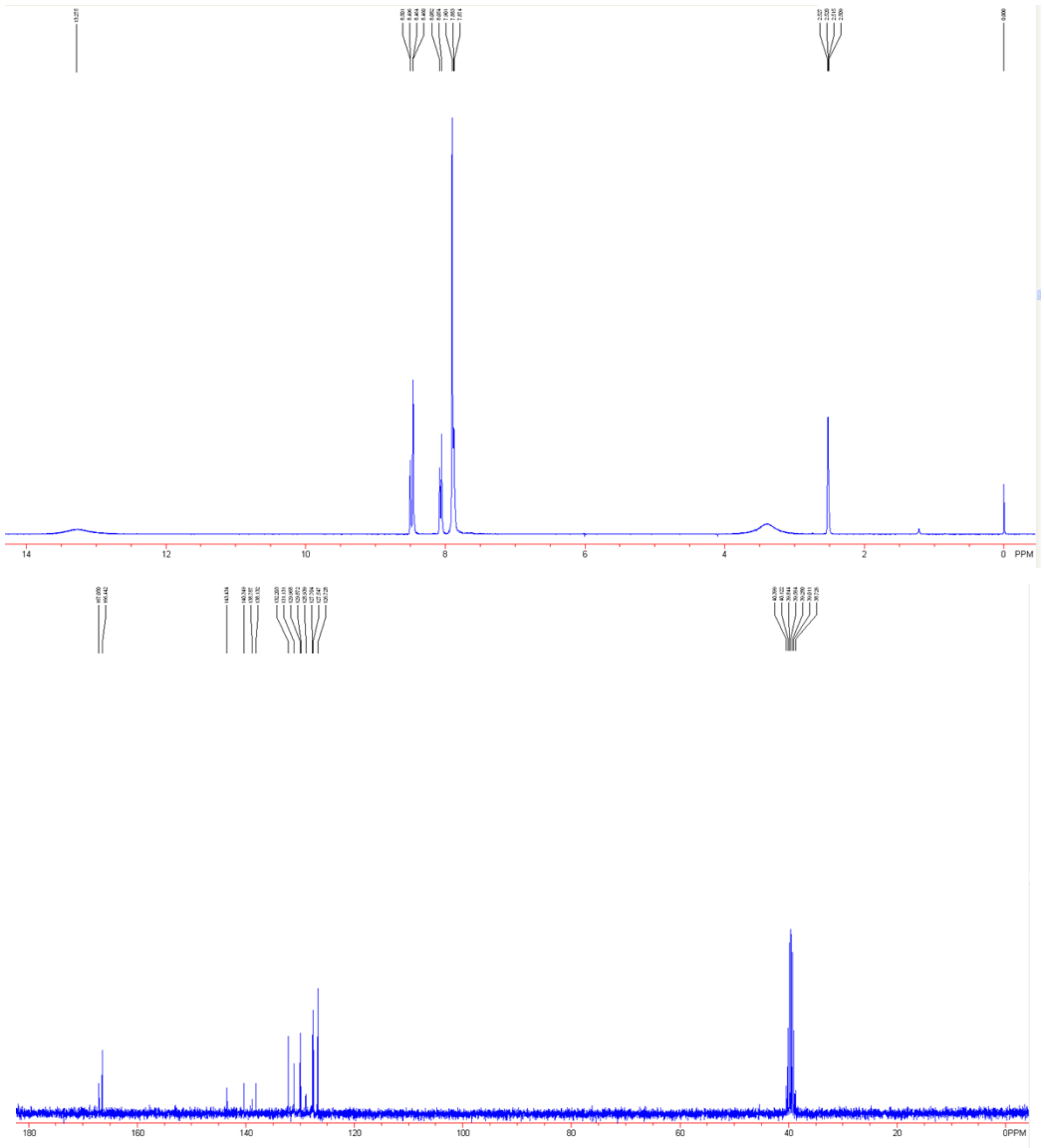


Fig. S14 The ^{1}H and ^{13}C NMR spectra of H_3TPT

Table S1. Crystal Data and Structure Refinement for **1**

Empirical formula	$C_{48}\ H_{37}\ Cd_3\ N_2\ O_{14.5}$
Formula weight	1211.04
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/c
Unit cell dimensions	a = 19.524(4) Å α = 90° b = 10.049(2) Å β= 95.409(4)° c = 25.359(5) Å γ = 90°
Volume	4953.2(17) $Å^3$
Z	2
Absorption coefficient	1.343 mm^{-1}
F (000)	2392
Theta range for data collection	1.61 to 28.21°
Limiting indices	-25≤ h≤25, -13≤k≤9, -29≤l≤33
Reflections collected / unique	17595 / 6090
R_{int}	0.1021
Completeness to theta = 28.21	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7751 and 0.7476
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6090 / 7 / 311
Goodness-of-fit on F^2	1.013
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0704, wR_2 = 0.1698
R indices (all data)	R_1 = 0.1487, wR_2 = 0.2050
Largest diff. peak and hole	1.612 and -1.183 e. $Å^{-3}$

[b] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2=[\sum[\ w\ (F_o^2-F_c^2)^2]\ /\ \sum[\ w\ (F_o^2)^2]]^{1/2}$.

Table. S2 Selected bond lengths [Å] and angles [°] for **1**.

Bond lengths / Å

Cd(1)-O(5)#1	2.180(3)	C(6)-H(6)	0.93
Cd(1)-O(4)#2	2.270(3)	C(7)-H(7)	0.93
Cd(1)-O(3)#3	2.308(3)	C(8)-C(13)	1.376(7)
Cd(1)-O(2)	2.354(4)	C(8)-C(9)	1.394(7)
Cd(1)-O(1)	2.363(4)	C(9)-C(10)	1.371(7)
Cd(1)-O(3)#2	2.529(3)	C(9)-H(9)	0.93
Cd(2)-O(6)#4	2.215(3)	C(10)-C(11)	1.403(7)
Cd(2)-O(6)#1	2.215(3)	C(10)-H(10)	0.93
Cd(2)-O(7)	2.289(4)	C(11)-C(12)	1.373(7)
Cd(2)-O(7)#5	2.289(4)	C(11)-C(14)	1.484(6)
Cd(2)-O(1)	2.293(4)	C(12)-C(13)	1.374(7)
Cd(2)-O(1)#5	2.294(4)	C(12)-H(12)	0.93
O(1)-C(1)	1.244(6)	C(13)-H(13)	0.93
O(2)-C(1)	1.245(6)	C(14)-C(19)	1.396(6)

O(3)-C(20)	1.255(6)	C(14)-C(15)	1.402(7)
O(3)-Cd(1)#6	2.308(3)	C(15)-C(16)	1.391(6)
O(3)-Cd(1)#7	2.529(3)	C(15)-H(15)	0.93
O(4)-C(20)	1.253(6)	C(16)-C(17)	1.370(6)
O(4)-Cd(1)#7	2.270(3)	C(16)-C(20)	1.499(6)
O(5)-C(21)	1.233(6)	C(17)-C(18)	1.385(6)
O(5)-Cd(1)#8	2.180(3)	C(17)-H(17)	0.93
O(6)-C(21)	1.256(5)	C(18)-C(19)	1.387(6)
O(6)-Cd(2)#4	2.215(3)	C(18)-C(21)	1.506(6)
O(7)-C(22)	1.244(8)	C(19)-H(19)	0.93
C(1)-C(2)	1.488(6)	C(22)-N(1)	1.317(8)
C(2)-C(3)	1.377(7)	C(22)-H(22)	0.93
C(2)-C(7)	1.378(8)	N(1)-C(24)	1.369(6)
C(3)-C(4)	1.379(7)	N(1)-C(23)	1.433(10)
C(3)-H(3)	0.93	C(23)-H(23A)	0.96
C(4)-C(5)	1.396(7)	C(23)-H(23B)	0.96
C(4)-H(4)	0.93	C(23)-H(23C)	0.96
C(5)-C(6)	1.381(7)	C(24)-H(24A)	0.96
C(5)-C(8)	1.499(7)	C(24)-H(24B)	0.96
C(6)-C(7)	1.402(7)	C(24)-H(24C)	0.96

Bond angles / °

O(5)#1-Cd(1)-O(4)#2	128.21(12)	C(4)-C(5)-C(8)	121.6(4)
O(5)#1-Cd(1)-O(3)#3	85.13(12)	C(5)-C(6)-C(7)	119.9(5)
O(4)#2-Cd(1)-O(3)#3	111.10(12)	C(5)-C(6)-H(6)	120
O(5)#1-Cd(1)-O(2)	137.65(15)	C(7)-C(6)-H(6)	120
O(4)#2-Cd(1)-O(2)	93.66(15)	C(2)-C(7)-C(6)	121.0(5)
O(3)#3-Cd(1)-O(2)	84.98(12)	C(2)-C(7)-H(7)	119.5
O(5)#1-Cd(1)-O(1)	103.27(14)	C(6)-C(7)-H(7)	119.5
O(4)#2-Cd(1)-O(1)	103.26(14)	C(13)-C(8)-C(9)	117.9(5)
O(3)#3-Cd(1)-O(1)	127.89(12)	C(13)-C(8)-C(5)	120.7(5)
O(2)-Cd(1)-O(1)	54.24(13)	C(9)-C(8)-C(5)	121.4(5)
O(5)#1-Cd(1)-O(3)#2	85.43(11)	C(10)-C(9)-C(8)	121.6(5)
O(4)#2-Cd(1)-O(3)#2	54.11(11)	C(10)-C(9)-H(9)	119.2
O(3)#3-Cd(1)-O(3)#2	77.04(12)	C(8)-C(9)-H(9)	119.2
O(2)-Cd(1)-O(3)#2	131.65(14)	C(9)-C(10)-C(11)	121.1(5)
O(1)-Cd(1)-O(3)#2	153.68(13)	C(9)-C(10)-H(10)	119.4
O(5)#1-Cd(1)-C(1)	123.53(14)	C(11)-C(10)-H(10)	119.4
O(4)#2-Cd(1)-C(1)	98.73(13)	C(12)-C(11)-C(10)	115.4(4)
O(3)#3-Cd(1)-C(1)	107.67(13)	C(12)-C(11)-C(14)	123.0(4)
O(2)-Cd(1)-C(1)	27.14(14)	C(10)-C(11)-C(14)	121.6(4)
O(1)-Cd(1)-C(1)	27.12(13)	C(11)-C(12)-C(13)	124.7(5)
O(3)#2-Cd(1)-C(1)	150.62(13)	C(11)-C(12)-H(12)	117.7

O(5)#1-Cd(1)-C(20)#2	108.73(13)	C(13)-C(12)-H(12)	117.7
O(4)#2-Cd(1)-C(20)#2	27.00(13)	C(12)-C(13)-C(8)	119.2(5)
O(3)#3-Cd(1)-C(20)#2	93.10(13)	C(12)-C(13)-H(13)	120.4
O(2)-Cd(1)-C(20)#2	112.85(16)	C(8)-C(13)-H(13)	120.4
O(1)-Cd(1)-C(20)#2	129.65(15)	C(19)-C(14)-C(15)	118.1(4)
O(3)#2-Cd(1)-C(20)#2	27.22(12)	C(19)-C(14)-C(11)	120.2(4)
C(1)-Cd(1)-C(20)#2	124.49(14)	C(15)-C(14)-C(11)	121.7(4)
O(6)#4-Cd(2)-O(6)#1	180.00(18)	C(16)-C(15)-C(14)	121.1(4)
O(6)#4-Cd(2)-O(7)	91.84(13)	C(16)-C(15)-H(15)	119.5
O(6)#1-Cd(2)-O(7)	88.15(13)	C(14)-C(15)-H(15)	119.5
O(6)#4-Cd(2)-O(7)#5	88.15(13)	C(17)-C(16)-C(15)	119.1(4)
O(6)#1-Cd(2)-O(7)#5	91.85(13)	C(17)-C(16)-C(20)	121.2(4)
O(7)-Cd(2)-O(7)#5	180.000(1)	C(15)-C(16)-C(20)	119.8(4)
O(6)#4-Cd(2)-O(1)	92.98(14)	C(16)-C(17)-C(18)	121.5(4)
O(6)#1-Cd(2)-O(1)	87.02(14)	C(16)-C(17)-H(17)	119.2
O(7)-Cd(2)-O(1)	100.63(14)	C(18)-C(17)-H(17)	119.2
O(7)#5-Cd(2)-O(1)	79.37(14)	C(17)-C(18)-C(19)	119.1(4)
O(6)#4-Cd(2)-O(1)#5	87.02(14)	C(17)-C(18)-C(21)	119.7(4)
O(6)#1-Cd(2)-O(1)#5	92.98(14)	C(19)-C(18)-C(21)	121.2(4)
O(7)-Cd(2)-O(1)#5	79.37(14)	C(18)-C(19)-C(14)	121.0(4)
O(7)#5-Cd(2)-O(1)#5	100.63(14)	C(18)-C(19)-H(19)	119.5
O(1)-Cd(2)-O(1)#5	180.00(13)	C(14)-C(19)-H(19)	119.5
C(1)-O(1)-Cd(2)	157.2(4)	O(4)-C(20)-O(3)	122.2(4)
C(1)-O(1)-Cd(1)	92.9(3)	O(4)-C(20)-C(16)	117.1(4)
Cd(2)-O(1)-Cd(1)	106.18(14)	O(3)-C(20)-C(16)	120.6(4)
C(1)-O(2)-Cd(1)	93.3(3)	O(4)-C(20)-Cd(1)#7	55.4(2)
C(20)-O(3)-Cd(1)#6	124.7(3)	O(3)-C(20)-Cd(1)#7	67.2(2)
C(20)-O(3)-Cd(1)#7	85.6(3)	C(16)-C(20)-Cd(1)#7	170.1(3)
Cd(1)#6-O(3)-Cd(1)#7	102.96(12)	O(5)-C(21)-O(6)	126.4(4)
C(20)-O(4)-Cd(1)#7	97.6(3)	O(5)-C(21)-C(18)	117.8(4)
C(21)-O(5)-Cd(1)#8	124.4(3)	O(6)-C(21)-C(18)	115.9(4)
C(21)-O(6)-Cd(2)#4	133.1(3)	O(7)-C(22)-N(1)	123.6(6)
C(22)-O(7)-Cd(2)	119.1(4)	O(7)-C(22)-H(22)	118.2
O(1)-C(1)-O(2)	119.5(4)	N(1)-C(22)-H(22)	118.2
O(1)-C(1)-C(2)	121.4(4)	C(22)-N(1)-C(24)	130.8(7)
O(2)-C(1)-C(2)	119.1(4)	C(22)-N(1)-C(23)	116.6(6)
O(1)-C(1)-Cd(1)	60.0(3)	C(24)-N(1)-C(23)	112.5(7)
O(2)-C(1)-Cd(1)	59.6(2)	N(1)-C(23)-H(23A)	109.5
C(2)-C(1)-Cd(1)	174.5(3)	N(1)-C(23)-H(23B)	109.5
C(3)-C(2)-C(7)	119.6(5)	H(23A)-C(23)-H(23B)	109.5
C(3)-C(2)-C(1)	121.1(4)	N(1)-C(23)-H(23C)	109.5
C(7)-C(2)-C(1)	119.3(4)	H(23A)-C(23)-H(23C)	109.5
C(2)-C(3)-C(4)	119.3(5)	H(23B)-C(23)-H(23C)	109.5
C(2)-C(3)-H(3)	120.4	N(1)-C(24)-H(24A)	109.5

C(4)-C(3)-H(3)	120.4	N(1)-C(24)-H(24B)	109.5
C(3)-C(4)-C(5)	122.4(5)	H(24A)-C(24)-H(24B)	109.5
C(3)-C(4)-H(4)	118.8	N(1)-C(24)-H(24C)	109.5
C(5)-C(4)-H(4)	118.8	H(24A)-C(24)-H(24C)	109.5
C(6)-C(5)-C(4)	117.8(5)	H(24B)-C(24)-H(24C)	109.5
C(6)-C(5)-C(8)	120.6(5)		

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