Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2013

SUPPORTING INFORMATION

Light gated reversible modulation of Cu^{2+} binding

Suman Pal, Joydev Hatai, K. Srikanth and Subhajit Bandyopadhyay*

Department of Chemical Sciences,
Indian Institute of Science Education and Research-Kolkata
India 741252

Email: sb1@iiserkol.ac.in

Contents

Numbering system used for NMR assignments S1

Overlay of ^{1}H NMR of **1**c and **1**o S1

Figure S1. ^{1}H NMR of **1**c and **1**o in DMSO-d_6.. ..... S1

Addition of metal salts to **1**c S2

Figure S2. Addition of perchlorate salts of different metals to **1c** S2

Figure S3. Overlay of Job's Plot with **1**c and **1**o. S2

Figure S4: Arhennius Plots for **1** and [**1**.Cu^{2+}]. S3

Figure S5: Eyring plots for **1** and [**1**.Cu^{2+}]. S4

Mass spectra of the **1**c-Cu(II) complex S5

Figure S6. Mass spectrum of **1**c-Cu(II) S5

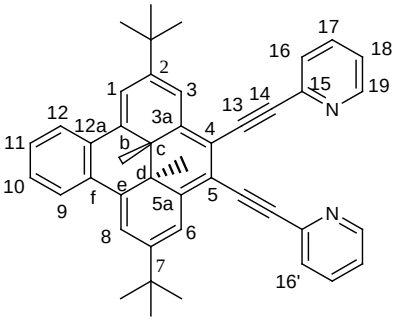
Figure S7. ^{1}H NMR of **2** S6

Figure S8. ^{1}H NMR spectrum of **1**c. S7

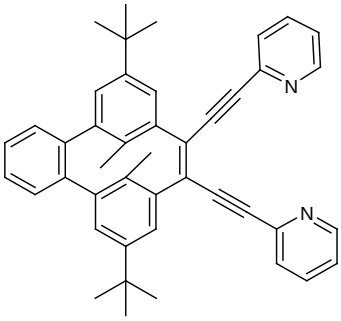
Figure S9. ^{13}C NMR spectra of **1**c S8

X-ray data S8

Numbering system used for NMR assignments



1c



1o

1c => Closed form of **1;** **1o** => Open form of **1**

Overlay of ^{1}H NMR of 1c and 1o

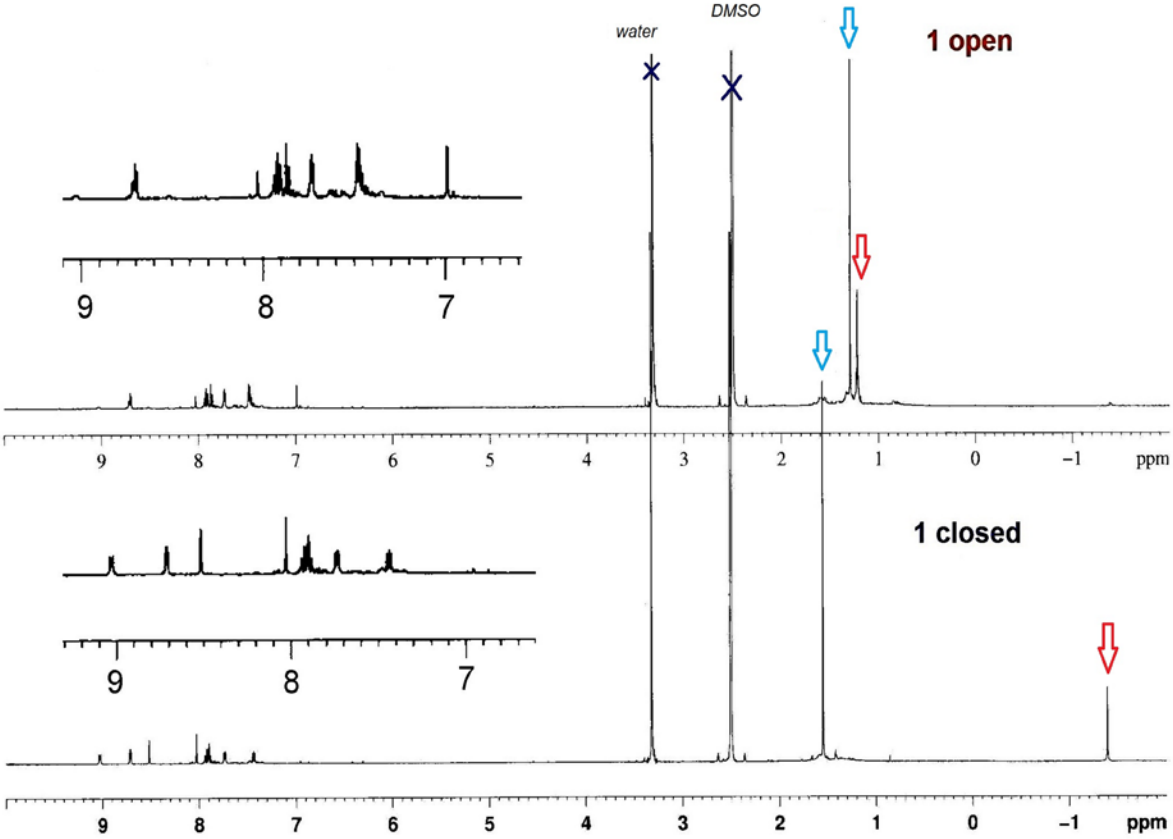


Figure S1. ^{1}H NMR of **1**c and **1**o in DMSO-d_6. The red arrow indicates the internal methyl and the blue arrow indicates the *t*-butyl protons.

Addition of metal salts to 1c

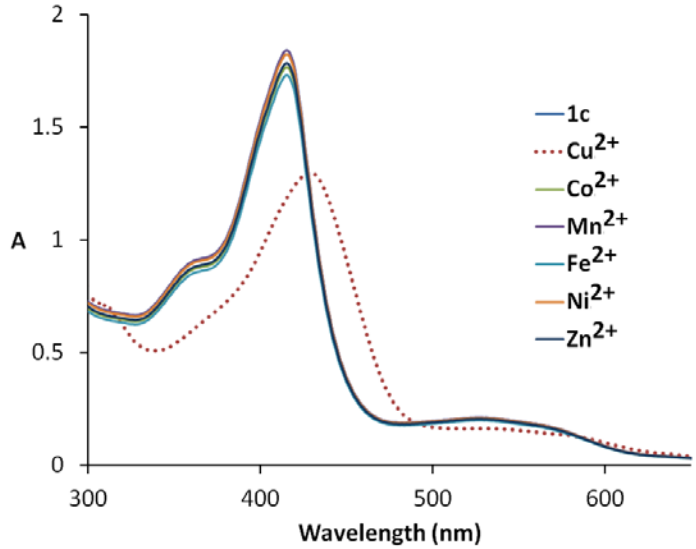


Figure S2. Addition of 3 equivalents of perchlorate salts of Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+} and Pd^{2+} to **1c** (3 x 10^{-5} M).

Job's Plot

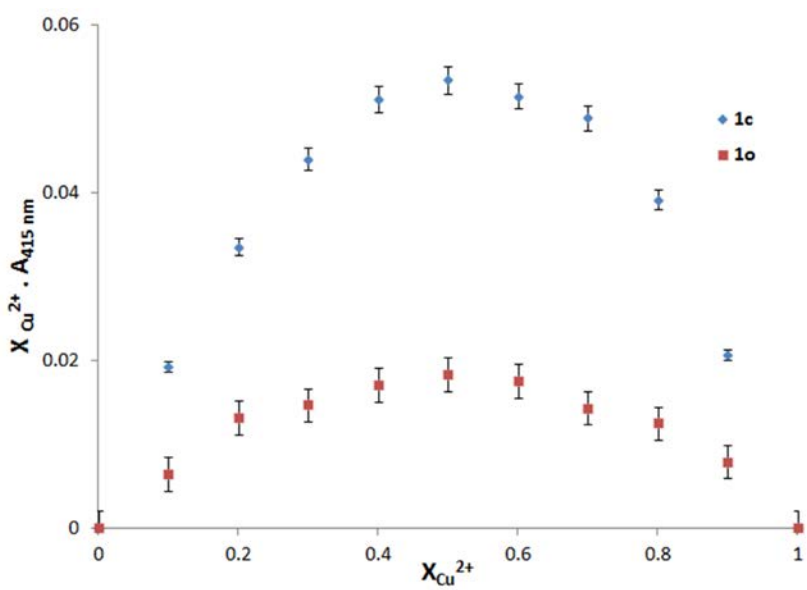
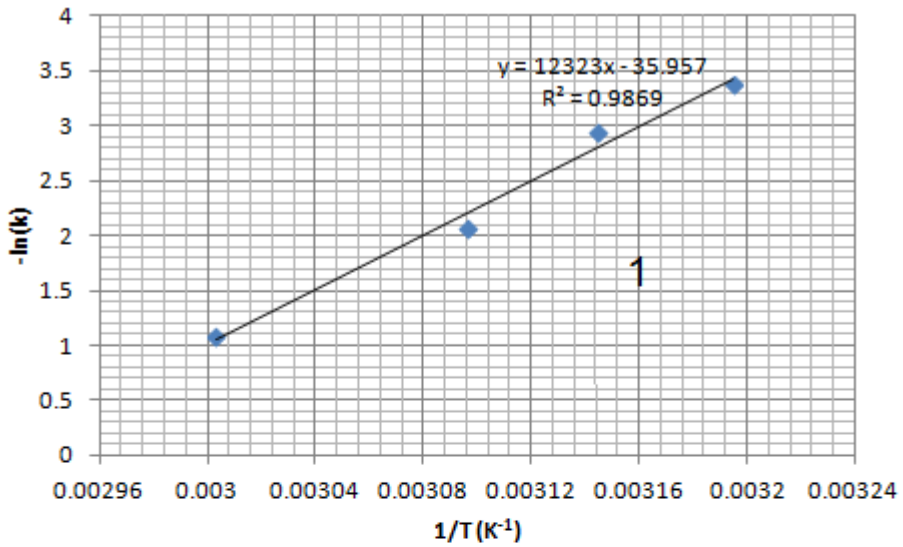


Figure S3. Overlay of Job's plot for the association of Cu^{2+} with **1**c and **1**o.

Arhennius and Eyring plots.



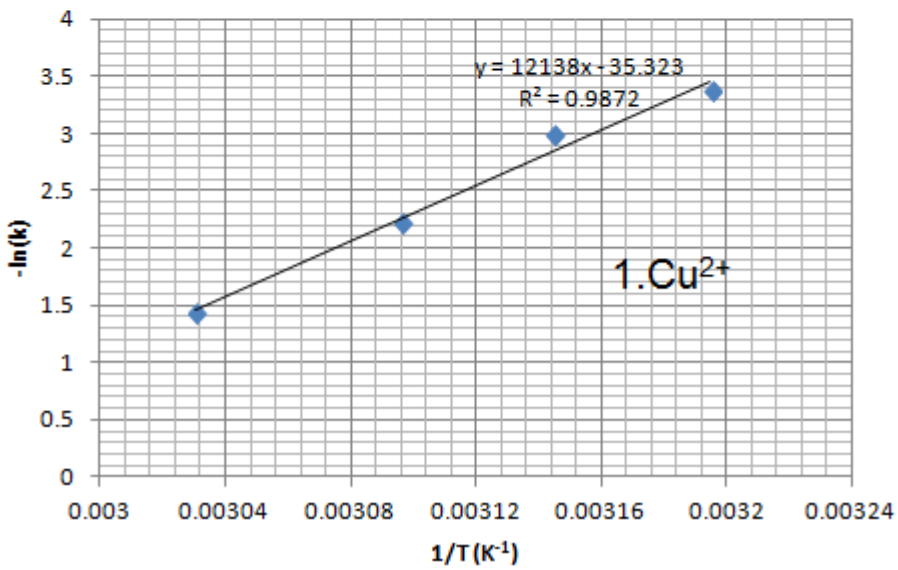


Figure S4: Arhennius Plots for **1** and **[1.Cu^{2+}].**

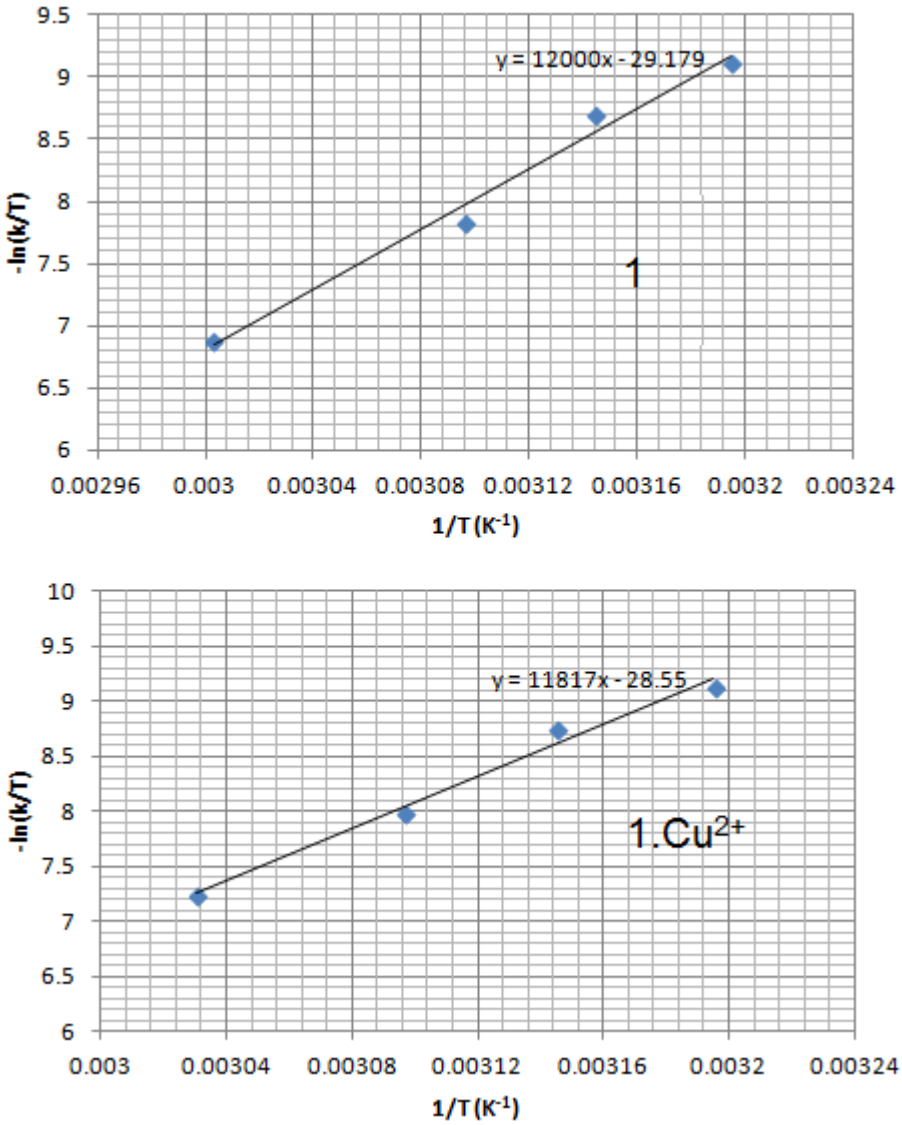


Figure S5: Eyring plots for **1** and [**1**.Cu^{2+}].

Mass spectra of the 1c-Cu^{II} complex

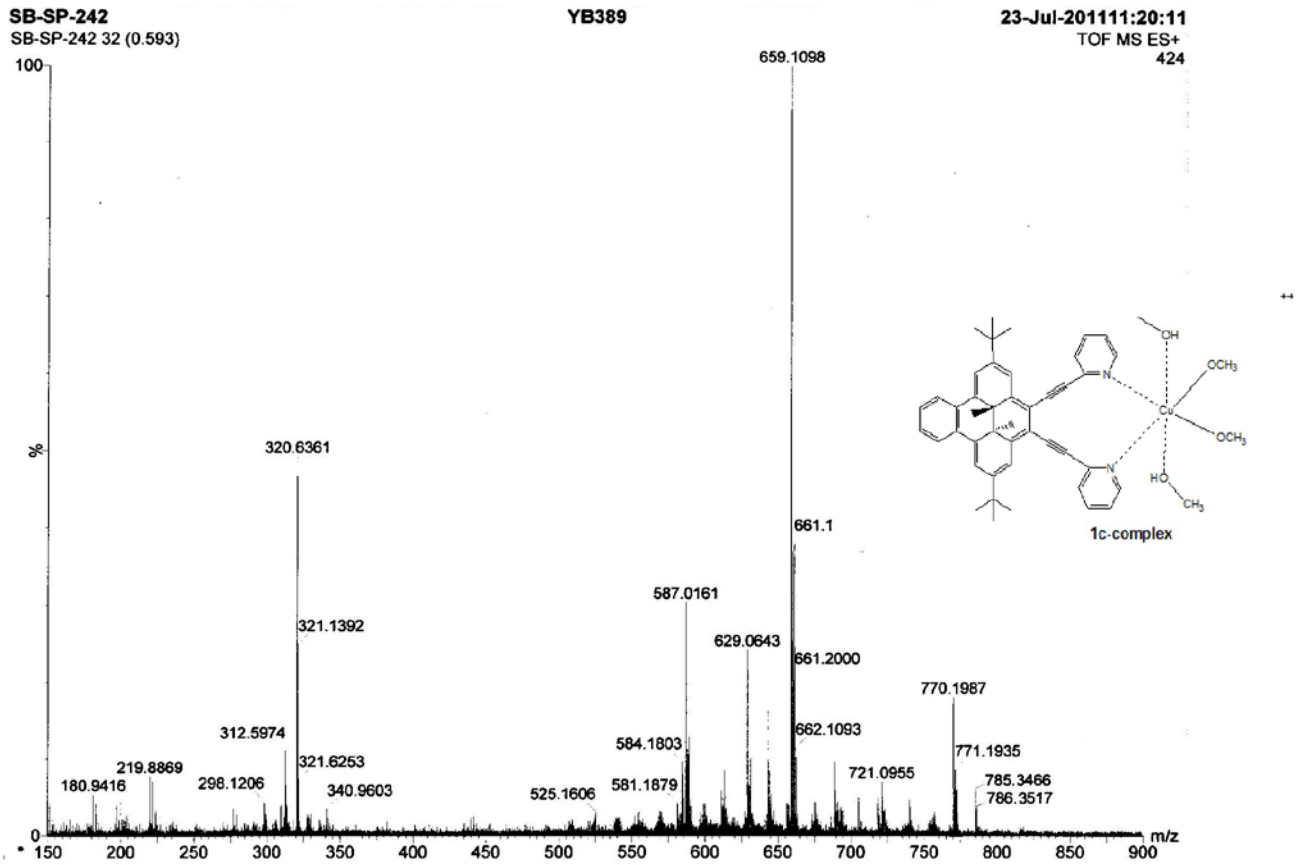


Figure S6. Mass spectrum of **1c-Cu^{II}** indicates association of four methanol molecules in the complex under the mass spectrometric conditions.

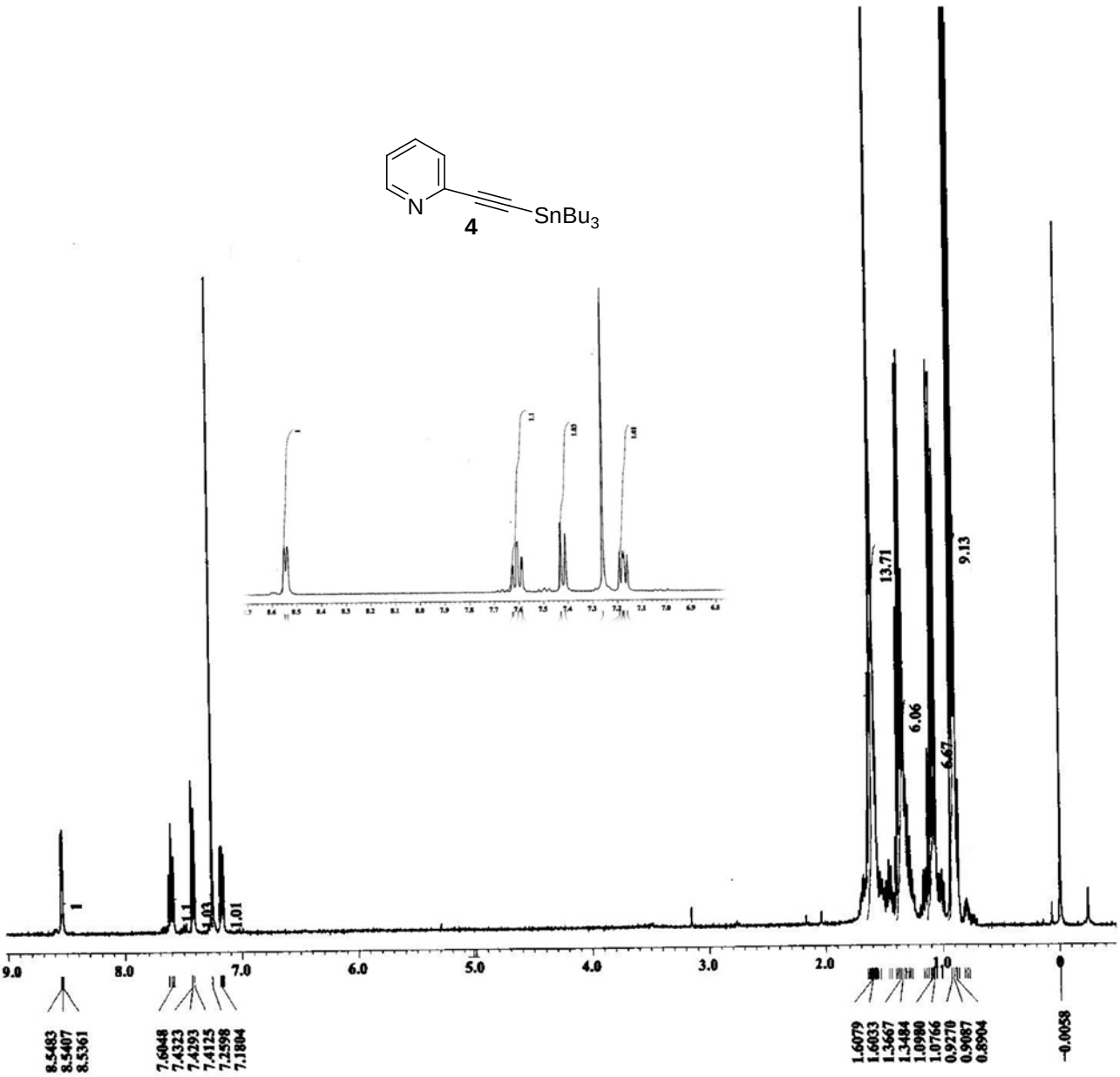


Figure S7. ^{1}H NMR of **4**

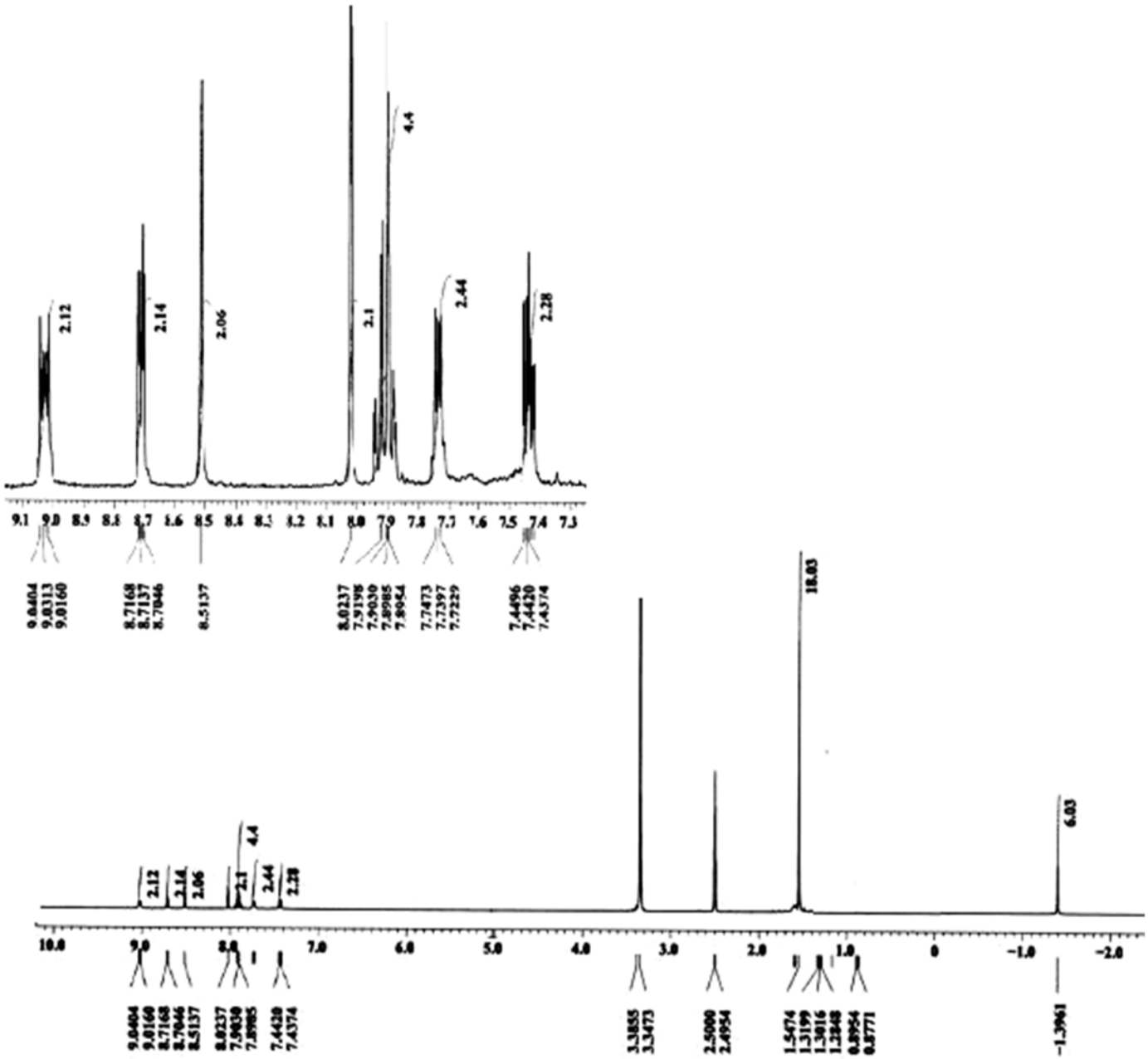


Figure S8. ^{1}H NMR spectrum of **1**c.

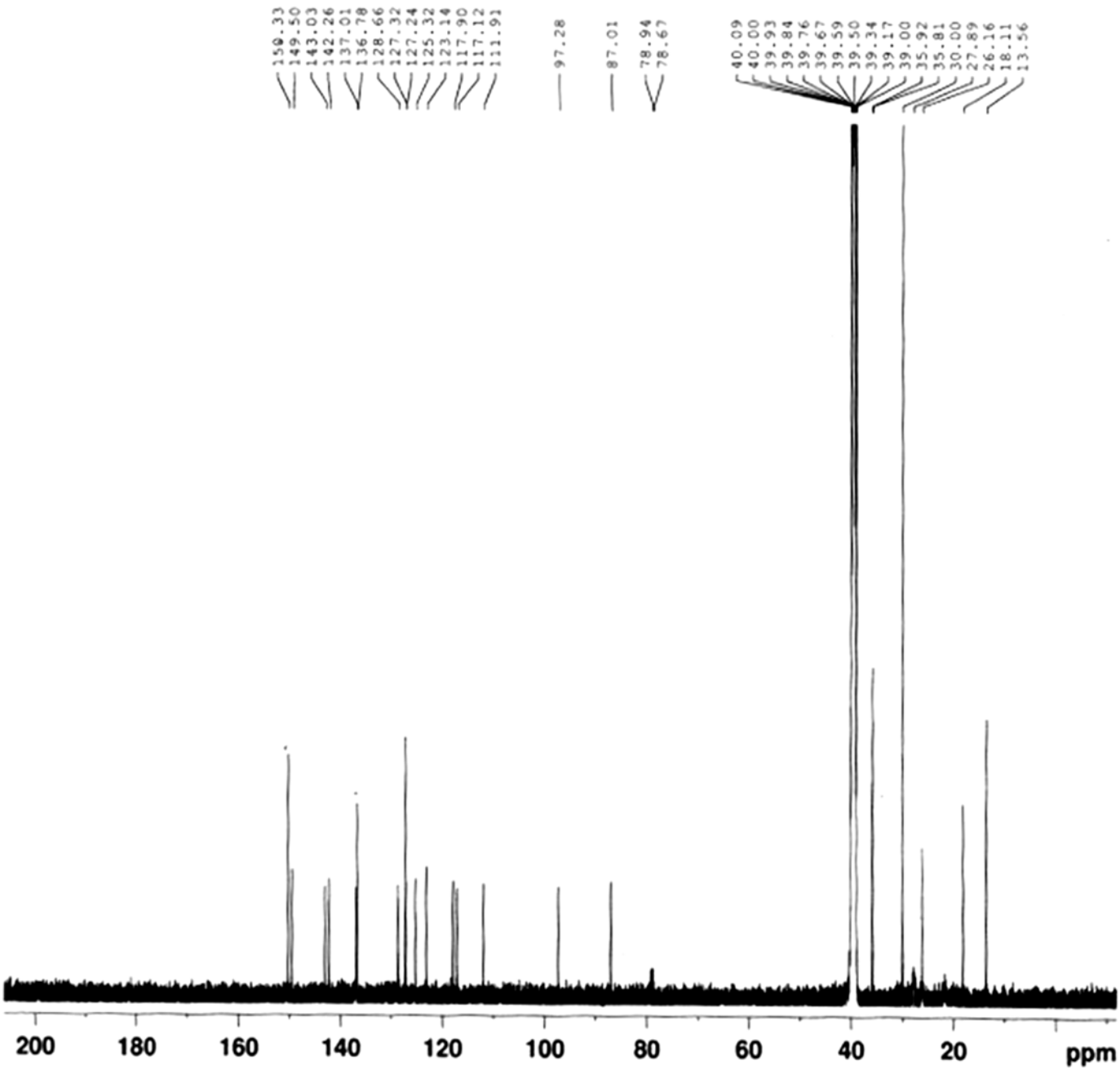
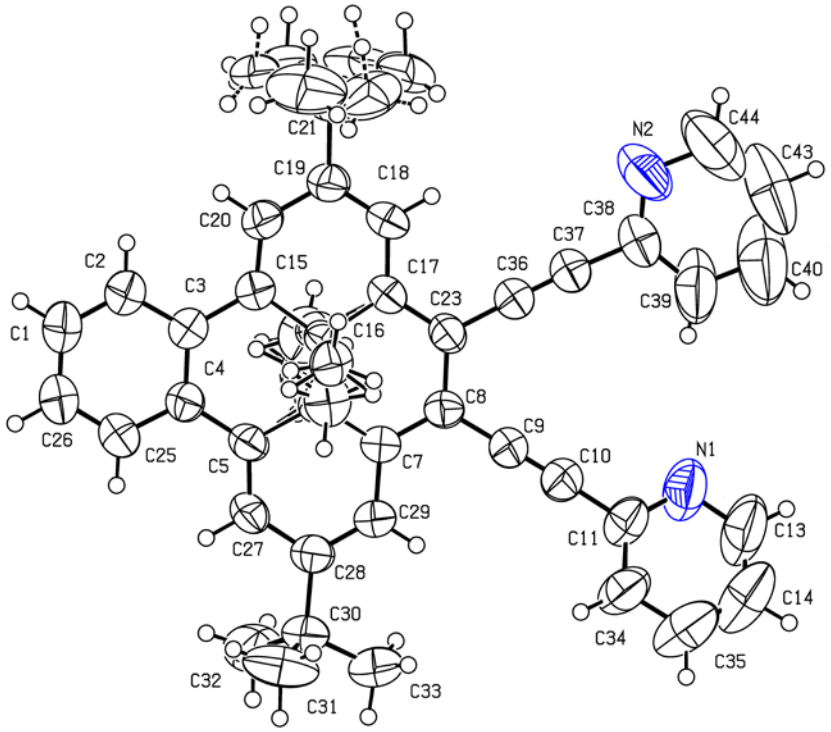


Figure S9. ^{13}C NMR spectra of **1**c

X-ray diffraction studies

Single crystal data of **1** were collected on a Bruker's KAPPA APEX II CCD Duo diffractometer using Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 100 K. Systematically absent reflections led to the identification of space group P2(1)/c for **2**. Of total 25920 reflections for the complex, 2546 with [I >

2r(I)] were used for structure solutions. The structure was solved by direct methods, and the structure solution and refinement were based on $|F^2|$. All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions when possible and given isotropic U values 1.2 times that of the atom to which they are bonded. The final differences Fourier map showed the maximum and minimum peak heights at 0.16 and -0.18 e$Å^{-3}$ for **2** with no chemical significance. All calculations were carried out using SHELXL-97 [1] and ORTEP-32 [2]. ORTEP diagram is drawn by using PLATON 1.10 [3]. The crystal data and data collection parameters are listed in Table 1.



Structure of **1**

Molecular structure of **1** is shown in the above figure and it showing the atom labeling and displacement ellipsoids at the 50% probability level. For clarity hydrogen atoms are not labeled. The unit cell contains four molecules, and there is an inversion centre. In the crystal structure there is no hydrogen bond, only few short contact interactions are present like Van der Waals or some non specific interaction. A very weak interaction of N of one molecule with H—C of the other molecule containing same ring like N2…H44—C44 with distance 2.646 Å.

[1] SMART (version 5.625) and SHELX-TL (version 6.12); Bruker AXS Inc.: Madison, WI, **2000**.
[2] G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, **1999**.
[3] A. L. Spek, Acta Cryst., **2009**, D65, 148.

Table 1 Crystal data and structure refinement for **1**

Parameters	Crystal data
Chemical formula	C44 H40 N2
Formula weight	596.78
T (K)	100(2)
Crystal system	Monoclinic
Space group	P2(1)/c
a (Å)	18.414(3)
b (Å)	9.8998(12)
c (Å)	22.545(4)
α (°)	90.00
β (°)	104.963(7)
γ (°)	90.00
Vol ($Å^3$)	3970.5(10)
Z	4
Θ range	2.26 – 22.01
ρ (gcm^{-3})	0.998
μ (mm^{-1})	0.057
Range *h*	-20 to +20
Range *k*	-11 to +10
Range *l*	-25 to +25
F (000)	1272
Crystal size (mm)	0.0417 x 0.0292 x 0.0072
Reflns collected	25920
Independent reflns	6085
Obsd reflns	2546
R_1 (reflections)	0.0632
wR_2 (reflections)	0.1578

Table 2. Bond lengths [Å] and angles [°] for **1**

Table 2a - Bond Distances (Angstrom)

N1	-C11	1.327(5)	C10	-C11	1.448(4)
N1	-C13	1.352(6)	C11	-C34	1.363(5)
N2	-C38	1.306(6)	C13	-C14	1.333(8)
N2	-C44	1.394(10)	C14	-C35	1.345(8)
C1	-C2	1.363(5)	C15	-C16	1.531(6)
C1	-C26	1.379(6)	C15	-C16D	1.546(6)
C2	-C3	1.404(4)	C15	-C20	1.352(4)
C3	-C4	1.402(4)	C16	-C16D	0.771(7)
C3	-C15	1.463(4)	C16	-C17	1.534(6)
C4	-C5	1.455(4)	C16	-C24	1.594(10)
C4	-C25	1.403(5)	C16D	-C17	1.549(6)
C5	-C6	1.532(6)	C16D	-C45D	1.589(12)
C5	-C6D	1.537(6)	C17	-C18	1.412(4)
C5	-C27	1.344(4)	C17	-C23	1.386(4)
C6	-C6D	0.757(7)	C18	-C19	1.359(4)
C6	-C7	1.545(6)	C19	-C20	1.436(5)

C6	-C16	1.493(8)	C19	-C21	1.518(4)
C6	-C16D	1.274(8)	C21	-C46	1.476(8)
C6	-C45	1.595(12)	C21	-C47	1.526(7)
C6D	-C7	1.539(6)	C21	-C48	1.564(8)
C6D	-C16	1.318(8)	C21	-C46D	1.574(17)
C6D	-C16D	1.515(8)	C21	-C47D	1.458(15)
C6D	-C24D	1.595(10)	C21	-C48D	1.539(16)
C7	-C8	1.374(4)	C23	-C36	1.424(4)
C7	-C29	1.421(4)	C24	-C24D	0.725(13)
C8	-C9	1.426(4)	C25	-C26	1.362(5)
C8	-C23	1.444(4)	C27	-C28	1.447(4)
C9	-C10	1.184(4)	C28	-C29	1.357(5)
C28	-C30	1.524(5)	C25	-H25	0.9500
C30	-C31	1.508(6)	C26	-H26	0.9500
C30	-C32	1.524(5)	C27	-H27	0.9500
C30	-C33	1.525(6)	C29	-H29	0.9500
C34	-C35	1.379(6)	C31	-H31A	0.9800
C36	-C37	1.192(5)	C31	-H31B	0.9800

C37	-C38	1.429(5)	C31	-H31C	0.9800
C38	-C39	1.366(7)	C32	-H32A	0.9800
C39	-C40	1.351(9)	C32	-H32B	0.9800
C40	-C43	1.345(14)	C32	-H32C	0.9800
C43	-C44	1.356(12)	C33	-H33A	0.9800
C45	-C45D	0.724(14)	C33	-H33B	0.9800
C1	-H1	0.9500	C33	-H33C	0.9800
C2	-H2	0.9500	C34	-H34	0.9500
C13	-H13	0.9500	C35	-H35	0.9500
C14	-H14	0.9500	C39	-H39	0.9500
C18	-H18	0.9500	C40	-H40	0.9500
C20	-H20	0.9500	C43	-H43	0.9500
C24	-H24A	0.9800	C44	-H44	0.9500
C24	-H24B	0.9800	C45	-H45A	0.9800
C24	-H24C	0.9800	C45	-H45B	0.9800
C24	-H24D	0.8600	C45	-H45C	0.9800
C24	-H24F	0.8900	C45	-H45D	0.8700
C24D	-H24A	0.6900	C45	-H45F	0.8900

C24D	-H24C	0.9900	C45D	-H45A	0.8700
C24D	-H24D	0.9800	C45D	-H45C	0.8200
C24D	-H24E	0.9800	C45D	-H45D	0.9800
C24D	-H24F	0.9800	C45D	-H45E	0.9800
C45D	-H45F	0.9800	C47D	-H47E	0.9800
C46	-H46A	0.9800	C47D	-H47F	0.9800
C46	-H46B	0.9800	C47D	-H47D	0.9800
C46	-H46C	0.9800	C48	-H48C	0.9800
C46D	-H46E	0.9800	C48	-H48A	0.9800
C46D	-H46F	0.9800	C48	-H48B	0.9800
C46D	-H46D	0.9800	C48D	-H48D	0.9800
C47	-H47C	0.9800	C48D	-H48E	0.9800
C47	-H47A	0.9800	C48D	-H48F	0.9800
C47	-H47B	0.9800			

Table 2b - Bond Angles (Degrees)

C11	-N1	-C13	116.0(3)	C16	-C6	-C16D	31.1(3)
C38	-N2	-C44	115.4(5)	C16	-C6	-C45	108.3(5)
C2	-C1	-C26	119.9(3)	C16D	-C6	-C45	77.2(5)

C1	-C2	-C3	122.2(3)	C5	-C6D	-C6	75.4(5)
C2	-C3	-C4	118.0(3)	C5	-C6D	-C7	110.4(3)
C2	-C3	-C15	121.0(3)	C5	-C6D	-C16	120.9(4)
C4	-C3	-C15	121.0(3)	C5	-C6D	-C16D	107.9(3)
C3	-C4	-C5	120.7(3)	C5	-C6D	-C24D	109.5(5)
C3	-C4	-C25	118.2(3)	C6	-C6D	-C7	76.2(6)
C5	-C4	-C25	121.1(3)	C6	-C6D	-C16	87.7(7)
C4	-C5	-C6	115.4(3)	C6	-C6D	-C16D	57.1(6)
C4	-C5	-C6D	116.0(3)	C6	-C6D	-C24D	169.2(8)
C4	-C5	-C27	123.9(3)	C7	-C6D	-C16	119.8(5)
C6	-C5	-C6D	28.5(3)	C7	-C6D	-C16D	106.9(4)
C6	-C5	-C27	118.8(3)	C7	-C6D	-C24D	109.9(4)
C6D	-C5	-C27	118.3(3)	C16	-C6D	-C16D	30.6(3)
C5	-C6	-C6D	76.1(6)	C16	-C6D	-C24D	81.5(5)
C5	-C6	-C7	110.3(4)	C16D	-C6D	-C24D	112.1(5)
C5	-C6	-C16	110.5(4)	C6	-C7	-C6D	28.4(3)
C5	-C6	-C16D	122.9(5)	C6	-C7	-C8	116.6(3)
C5	-C6	-C45	108.6(5)	C6	-C7	-C29	119.0(3)

C6D	-C6	-C7	75.4(5)	C6D	-C7	-C8	117.5(3)
C6D	-C6	-C16	61.9(6)	C6D	-C7	-C29	118.2(3)
C6D	-C6	-C16D	93.0(7)	C8	-C7	-C29	122.5(3)
C6D	-C6	-C45	170.2(8)	C7	-C8	-C9	120.6(3)
C7	-C6	-C16	109.1(3)	C7	-C8	-C23	120.8(3)
C7	-C6	-C16D	120.8(4)	C9	-C8	-C23	118.5(3)
C7	-C6	-C45	110.0(5)	C8	-C9	-C10	177.5(4)
C9	-C10	-C11	176.1(3)	C6	-C16D	-C15	120.9(5)
N1	-C11	-C10	117.6(3)	C6	-C16D	-C16	90.4(7)
N1	-C11	-C34	123.0(3)	C6	-C16D	-C17	120.8(4)
C10	-C11	-C34	119.5(3)	C6	-C16D	-C45D	82.8(5)
N1	-C13	-C14	124.1(5)	C6D	-C16D	-C15	108.5(4)
C13	-C14	-C35	119.4(5)	C6D	-C16D	-C16	60.5(6)
C3	-C15	-C16	115.9(3)	C6D	-C16D	-C17	107.9(3)
C3	-C15	-C16D	115.1(3)	C6D	-C16D	-C45D	112.8(5)
C3	-C15	-C20	124.4(3)	C15	-C16D	-C16	74.4(5)
C16	-C15	-C16D	29.0(3)	C15	-C16D	-C17	109.5(3)
C16	-C15	-C20	118.0(3)	C15	-C16D	-C45D	109.0(5)

C16D	-C15	-C20	118.4(3)	C16	-C16D	-C17	74.4(5)
C6	-C16	-C6D	30.4(3)	C16	-C16D	-C45D	173.2(8)
C6	-C16	-C15	108.6(3)	C17	-C16D	-C45D	109.2(5)
C6	-C16	-C16D	58.6(6)	C16	-C17	-C16D	29.0(3)
C6	-C16	-C17	108.6(4)	C16	-C17	-C18	118.3(3)
C6	-C16	-C24	107.5(5)	C16	-C17	-C23	116.8(3)
C6D	-C16	-C15	121.2(4)	C16D	-C17	-C18	118.7(3)
C6D	-C16	-C16D	89.0(7)	C16D	-C17	-C23	115.9(3)
C6D	-C16	-C17	120.4(5)	C18	-C17	-C23	123.2(3)
C6D	-C16	-C24	77.1(5)	C17	-C18	-C19	122.9(3)
C15	-C16	-C16D	76.6(5)	C18	-C19	-C20	118.2(3)
C15	-C16	-C17	111.1(4)	C18	-C19	-C21	122.6(3)
C15	-C16	-C24	110.4(5)	C20	-C19	-C21	119.2(3)
C16D	-C16	-C17	76.6(6)	C15	-C20	-C19	124.3(3)
C16D	-C16	-C24	166.0(8)	C19	-C21	-C46	110.6(4)
C17	-C16	-C24	110.6(4)	C19	-C21	-C47	107.8(4)
C6	-C16D	-C6D	29.9(3)	C19	-C21	-C48	111.4(3)
C19	-C21	-C46D	113.2(7)	C14	-C35	-C34	118.8(4)

C19	-C21	-C47D	111.3(8)	C23	-C36	-C37	178.9(3)
C19	-C21	-C48D	105.5(6)	C36	-C37	-C38	176.5(3)
C46	-C21	-C47	114.2(5)	N2	-C38	-C37	117.3(4)
C46	-C21	-C48	107.5(5)	N2	-C38	-C39	124.6(4)
C47	-C21	-C48	105.2(4)	C37	-C38	-C39	118.1(4)
C46D	-C21	-C47D	109.2(9)	C38	-C39	-C40	119.7(6)
C46D	-C21	-C48D	104.0(11)	C39	-C40	-C43	117.5(8)
C47D	-C21	-C48D	113.5(13)	C40	-C43	-C44	121.6(7)
C8	-C23	-C17	120.8(3)	N2	-C44	-C43	121.0(7)
C8	-C23	-C36	119.2(3)	C6	-C45	-C45D	104.3(14)
C17	-C23	-C36	120.0(3)	C16D	-C45D	-C45	95.5(13)
C16	-C24	-C24D	104.9(11)	C2	-C1	-H1	120.00
C6D	-C24D	-C24	96.6(11)	C26	-C1	-H1	120.00
C4	-C25	-C26	122.5(3)	C1	-C2	-H2	119.00
C1	-C26	-C25	119.2(3)	C3	-C2	-H2	119.00
C5	-C27	-C28	124.4(3)	N1	-C13	-H13	118.00
C27	-C28	-C29	118.0(3)	C14	-C13	-H13	118.00
C27	-C28	-C30	118.6(3)	C13	-C14	-H14	120.00

C29	-C28	-C30	123.4(3)	C35	-C14	-H14	120.00
C7	-C29	-C28	122.7(3)	C17	-C18	-H18	119.00
C28	-C30	-C31	108.0(3)	C19	-C18	-H18	119.00
C28	-C30	-C32	109.9(3)	C15	-C20	-H20	118.00
C28	-C30	-C33	111.4(3)	C19	-C20	-H20	118.00
C31	-C30	-C32	110.8(4)	C16	-C24	-H24A	109.00
C31	-C30	-C33	109.0(3)	C16	-C24	-H24B	109.00
C32	-C30	-C33	107.7(3)	C16	-C24	-H24C	109.00
C11	-C34	-C35	118.8(4)	C16	-C24	-H24D	112.00
C16	-C24	-H24F	111.00	H24A	-C24D	-H24E	88.00
C24D	-C24	-H24A	45.00	H24A	-C24D	-H24F	27.00
C24D	-C24	-H24B	143.00	H24C	-C24D	-H24D	10.00
C24D	-C24	-H24C	70.00	H24C	-C24D	-H24E	103.00
C24D	-C24	-H24D	76.00	H24C	-C24D	-H24F	119.00
C24D	-C24	-H24F	74.00	H24D	-C24D	-H24E	110.00
H24A	-C24	-H24B	110.00	H24D	-C24D	-H24F	109.00
H24A	-C24	-H24C	109.00	H24E	-C24D	-H24F	109.00
H24A	-C24	-H24D	114.00	C4	-C25	-H25	119.00

H24A	-C24	-H24F	29.00	C26	-C25	-H25	119.00
H24B	-C24	-H24C	109.00	C1	-C26	-H26	120.00
H24B	-C24	-H24D	102.00	C25	-C26	-H26	120.00
H24B	-C24	-H24F	82.00	C5	-C27	-H27	118.00
H24C	-C24	-H24D	7.00	C28	-C27	-H27	118.00
H24C	-C24	-H24F	130.00	C7	-C29	-H29	119.00
H24D	-C24	-H24F	132.00	C28	-C29	-H29	119.00
C6D	-C24D	-H24A	103.00	C30	-C31	-H31A	109.00
C6D	-C24D	-H24C	107.00	C30	-C31	-H31B	110.00
C6D	-C24D	-H24D	110.00	C30	-C31	-H31C	110.00
C6D	-C24D	-H24E	110.00	H31A	-C31	-H31B	109.00
C6D	-C24D	-H24F	110.00	H31A	-C31	-H31C	109.00
C24	-C24D	-H24A	88.00	H31B	-C31	-H31C	110.00
C24	-C24D	-H24C	67.00	C30	-C32	-H32A	109.00
C24	-C24D	-H24D	58.00	C30	-C32	-H32B	109.00
C24	-C24D	-H24E	154.00	C30	-C32	-H32C	109.00
C24	-C24D	-H24F	61.00	H32A	-C32	-H32B	110.00
H24A	-C24D	-H24C	143.00	H32A	-C32	-H32C	109.00

H24A	-C24D	-H24D	134.00	H32B	-C32	-H32C	109.00
C30	-C33	-H33A	109.00	H45A	-C45	-H45B	110.00
C30	-C33	-H33B	109.00	H45A	-C45	-H45C	110.00
C30	-C33	-H33C	109.00	H45A	-C45	-H45D	123.00
H33A	-C33	-H33B	109.00	H45A	-C45	-H45F	15.00
H33A	-C33	-H33C	109.00	H45B	-C45	-H45C	110.00
H33B	-C33	-H33C	110.00	H45B	-C45	-H45D	89.00
C11	-C34	-H34	121.00	H45B	-C45	-H45F	96.00
C35	-C34	-H34	121.00	H45C	-C45	-H45D	21.00
C14	-C35	-H35	121.00	H45C	-C45	-H45F	121.00
C34	-C35	-H35	121.00	H45D	-C45	-H45F	131.00
C38	-C39	-H39	120.00	C16D	-C45D	-H45A	107.00
C40	-C39	-H39	120.00	C16D	-C45D	-H45C	103.00
C39	-C40	-H40	121.00	C16D	-C45D	-H45D	109.00
C43	-C40	-H40	121.00	C16D	-C45D	-H45E	109.00
C40	-C43	-H43	119.00	C16D	-C45D	-H45F	109.00
C44	-C43	-H43	119.00	C45	-C45D	-H45A	75.00
N2	-C44	-H44	119.00	C45	-C45D	-H45C	78.00

C43	-C44	-H44	120.00	C45	-C45D	-H45D	59.00
C6	-C45	-H45A	109.00	C45	-C45D	-H45E	155.00
C6	-C45	-H45B	109.00	C45	-C45D	-H45F	61.00
C6	-C45	-H45C	109.00	H45A	-C45D	-H45C	141.00
C6	-C45	-H45D	114.00	H45A	-C45D	-H45D	123.00
C6	-C45	-H45F	110.00	H45A	-C45D	-H45E	98.00
C45D	-C45	-H45A	60.00	H45A	-C45D	-H45F	14.00
C45D	-C45	-H45B	146.00	H45C	-C45D	-H45D	21.00
C45D	-C45	-H45C	55.00	H45C	-C45D	-H45E	95.00
C45D	-C45	-H45D	75.00	H45C	-C45D	-H45F	129.00
C45D	-C45	-H45F	74.00	H45D	-C45D	-H45E	110.00
H45D	-C45D	-H45F	109.00	H47B	-C47	-H47C	110.00
H45E	-C45D	-H45F	109.00	C21	-C47D	-H47D	110.00
C21	-C46	-H46A	109.00	H47D	-C47D	-H47E	109.00
C21	-C46	-H46B	109.00	H47D	-C47D	-H47F	109.00
C21	-C46	-H46C	109.00	H47E	-C47D	-H47F	109.00
H46A	-C46	-H46B	110.00	C21	-C47D	-H47E	110.00
H46A	-C46	-H46C	110.00	C21	-C47D	-H47F	110.00

H46B	-C46	-H46C	110.00	H48B	-C48	-H48C	109.00
H46D	-C46D	-H46E	109.00	H48A	-C48	-H48B	109.00
H46D	-C46D	-H46F	110.00	H48A	-C48	-H48C	110.00
H46E	-C46D	-H46F	110.00	C21	-C48	-H48A	110.00
C21	-C46D	-H46E	109.00	C21	-C48	-H48B	109.00
C21	-C46D	-H46F	109.00	C21	-C48	-H48C	110.00
C21	-C46D	-H46D	109.00	C21	-C48D	-H48D	109.00
H47A	-C47	-H47B	109.00	C21	-C48D	-H48E	109.00
H47A	-C47	-H47C	109.00	C21	-C48D	-H48F	109.00
C21	-C47	-H47A	109.00	H48D	-C48D	-H48E	110.00
C21	-C47	-H47B	109.00	H48D	-C48D	-H48F	110.00