

Electronic Supplementary Information (ESI)

**Trigonal molecular assembly system with dual light-driven functions of
phase transition and fluorescence switching**

*Ikue Abe, Mitsuo Hara, Takahiro Seki, Sung June Cho, Masaki Shimizu, Kazunori Matsuura,
Hae-Kap Cheong, Jin Young Kim, Jihun Oh, Jaehoon Jung, Mina Han**

Contents

Figure S1. DSC traces of 3BuAz.

Figure S2. Optimized C_3 -symmetric and asymmetric 3BuAz structures in THF.

Figure S3. SEM images and sphere size distribution as a function of concentration.

Figure S4. UV-vis absorption spectral changes of 3BuAz turbid suspension as a function of UV light irradiation time.

Figure S5. Photopatterning: (a) SEM, (b) OM, and corresponding (c) FOM images.

Figure S6. OM and corresponding FOM images of 3BuAz spheres before and after irradiation with UV light for 30 sec.

Figure S7. (Upper) Schematic illustration of GI-XRD measurements. (Lower) Two-dimensional GI-XRD images before and after UV light irradiation.

Figure S8. Crystal structure of 3BuAz.

Figure S9. Rietveld plot for 3BuAz.

Figure S10. ^1H NMR Spectrum of 3BuAz in CD_2Cl_2 .

Figure S11. ^{13}C NMR Spectrum of 3BuAz in CD_2Cl_2 .

Table 1. Crystallographic Data for 3BuAz.

Table 2. Final Atomic Coordinates and Displacement and Population Parameters for 3BuAz.

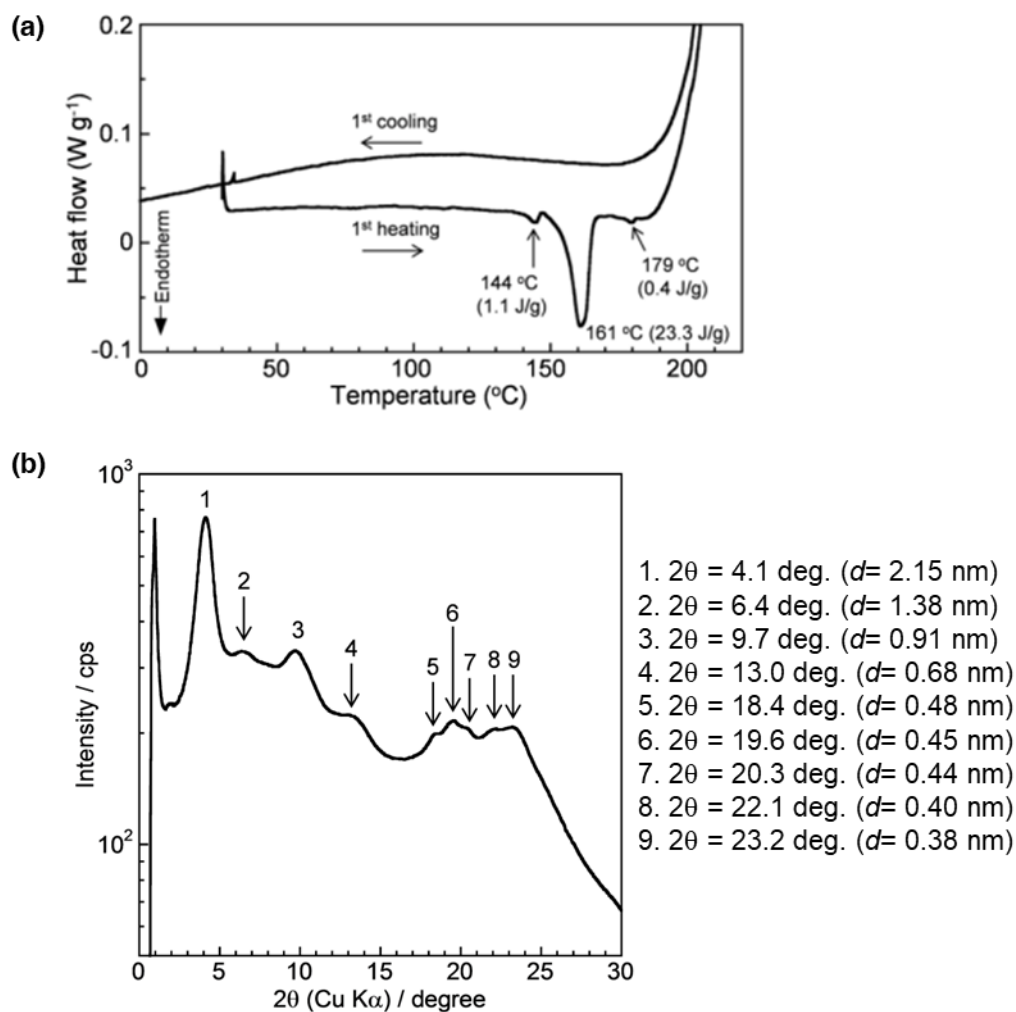


Figure S1. (a) DSC traces for the first heating and cooling cycles of 3BuAz at a rate of 2 °C/min. (b) XRD pattern of bulk sample taken at 25 °C.

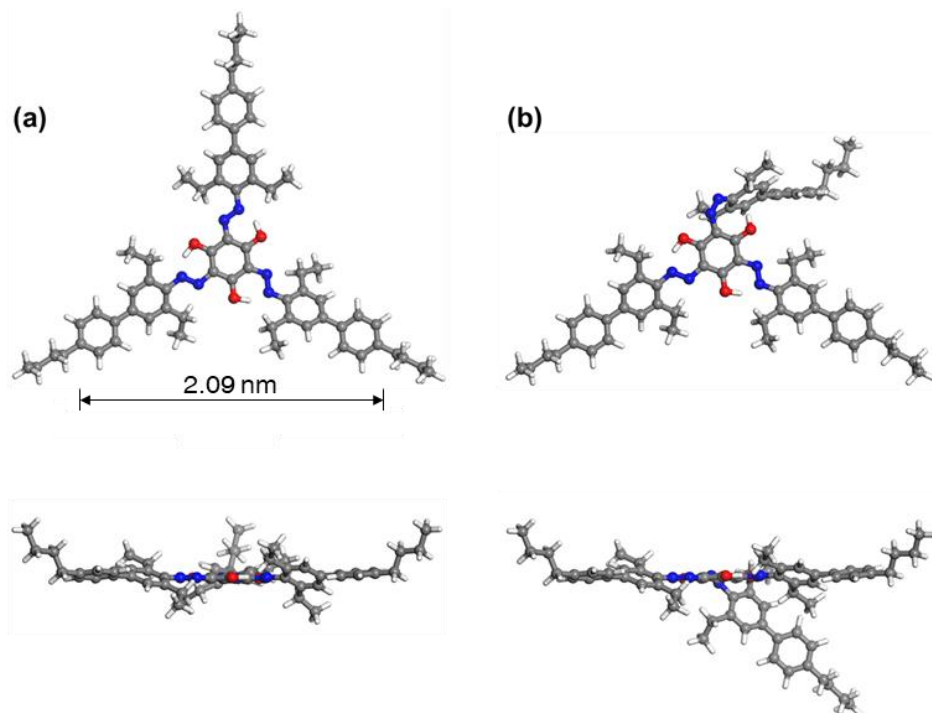


Figure S2. Top and side views for the optimized geometries of (a) C_3 -symmetric 3BuAz (with three trans azo groups) and (b) asymmetric 3BuAz (with two trans and one cis azo groups). The geometry optimizations were performed using B3LYP/6-31G(d,p)^{S1} implemented in Gaussian09 software package.^{S2} The influence of solvent (THF) on the molecular structure was considered using SCRF-SMD^{S3} solvation model. The trans to cis structural isomerization of one azo group leads to the instability of 23.1 kcal/mol in (b) with respect to (a). The lateral size of (a) is measured by the distance between the carbon atoms of flexible butyl groups connecting to the outer benzene rings.

References

- [S1] C. Adamo and V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.
- [S2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford CT, **2009**.
- [S3] A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378.

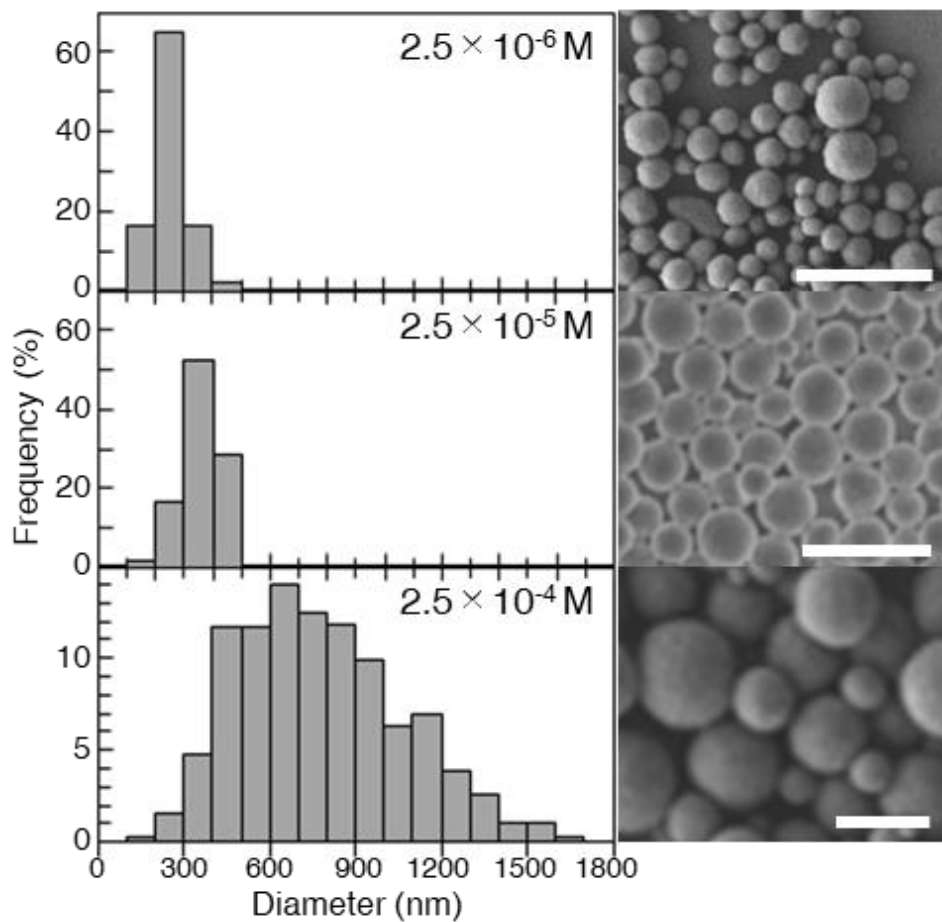


Figure S3. SEM images and sphere size distribution obtained from 2.5×10^{-6} M, 2.5×10^{-5} M, and 2.5×10^{-4} M THF-H₂O mixtures (1:3, v/v). Scale bar: 1 μ m.

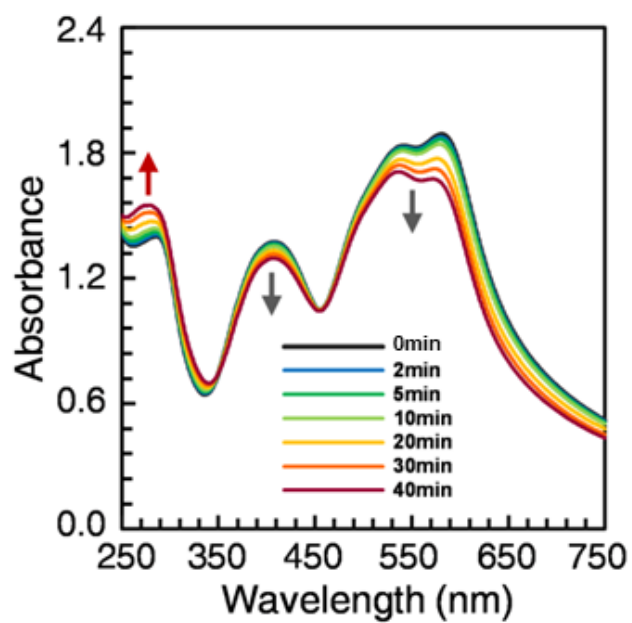


Figure S4. UV-vis absorption spectral changes of 3BuAz turbid suspension (5×10^{-5} M THF-H₂O, 1/5, v/v) as a function of UV light irradiation time.

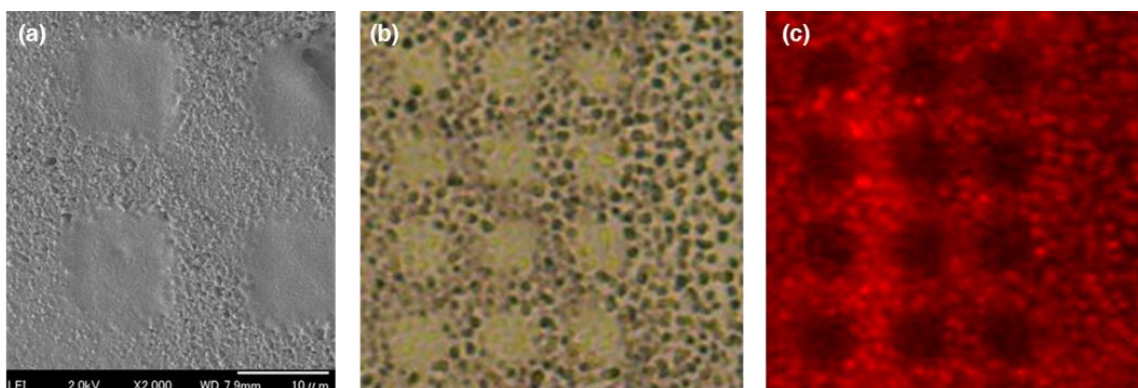


Figure S5. (a) SEM, (b) OM, and corresponding (c) FOM images taken after irradiation with UV light through a square-pattern photomask for 20 min.

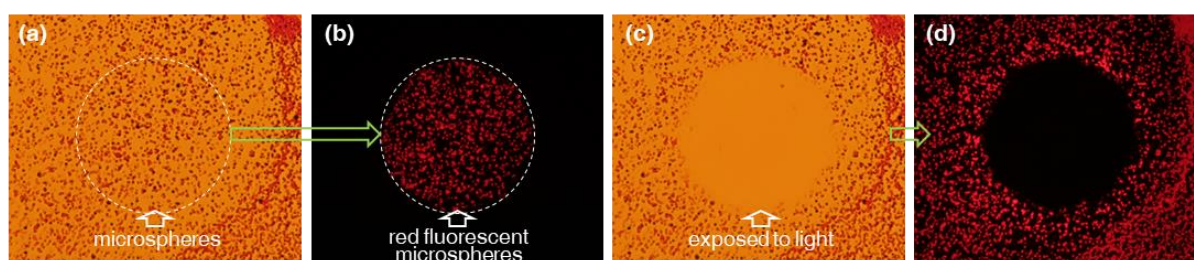


Figure S6. (a, c) OM and corresponding (b, d) FOM images of 3BuAz spheres before and after irradiation with UV light for 30 sec. The dark region in (d) corresponds to the UV-exposed isotropic state.

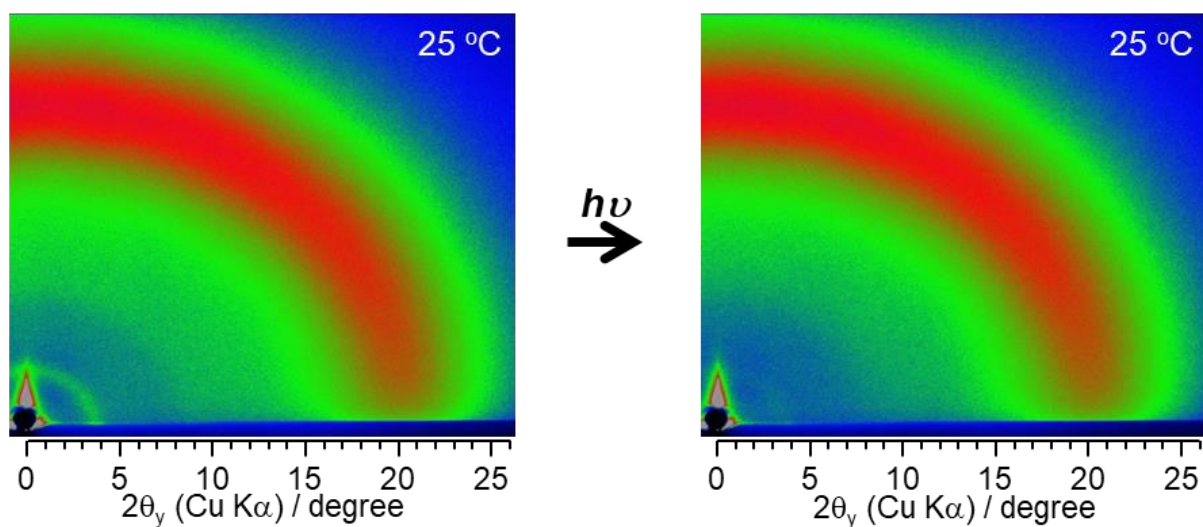
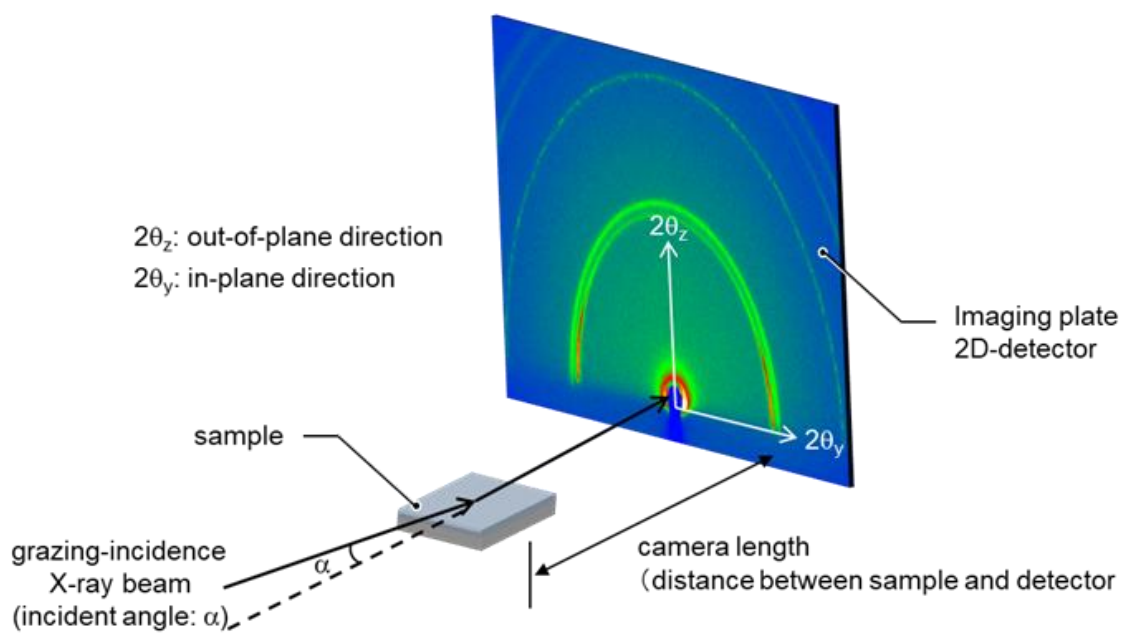


Figure S7. (Upper) Schematic illustration of grazing incidence X-ray diffraction (GI-XRD) measurements. (Lower) Two-dimensional GI-XRD images before and after UV light irradiation.

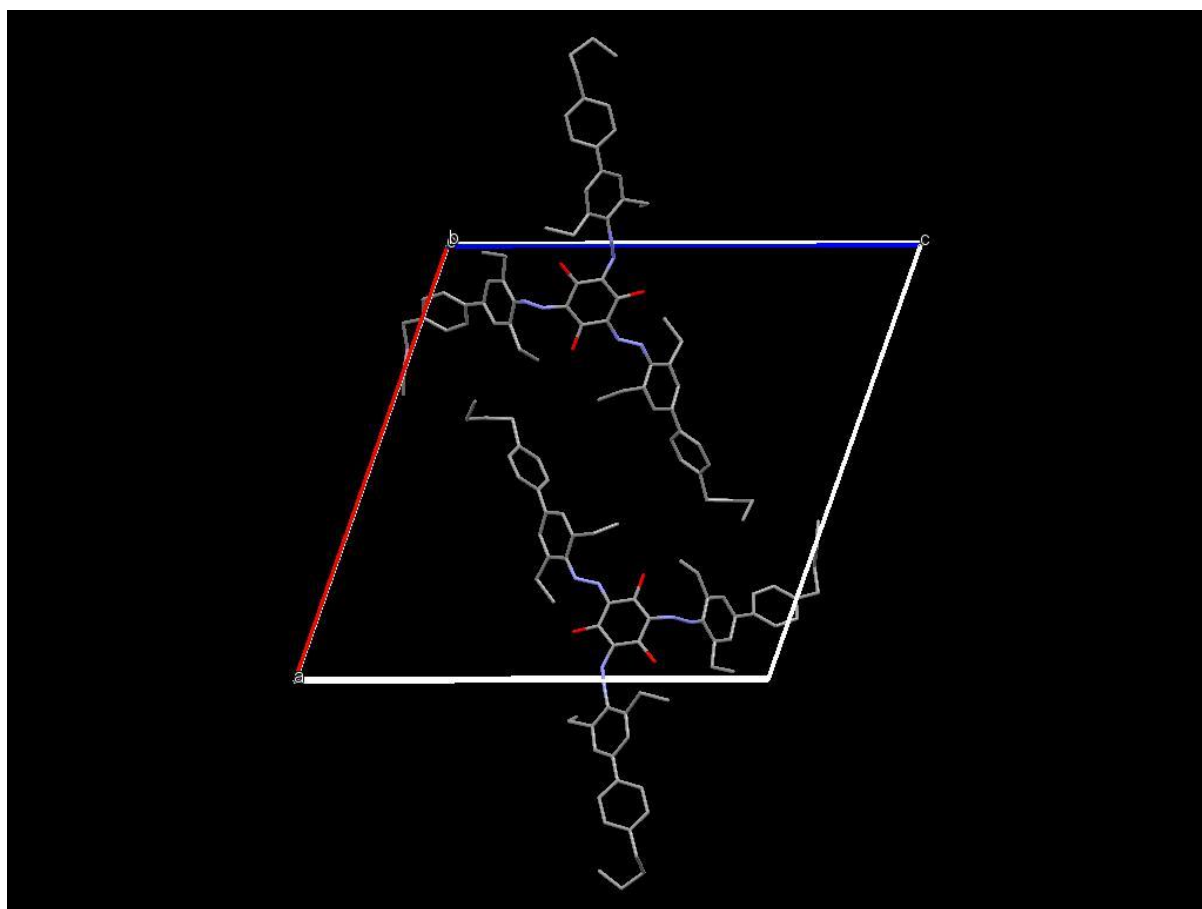


Figure S8. Crystal structure of 3BuAz

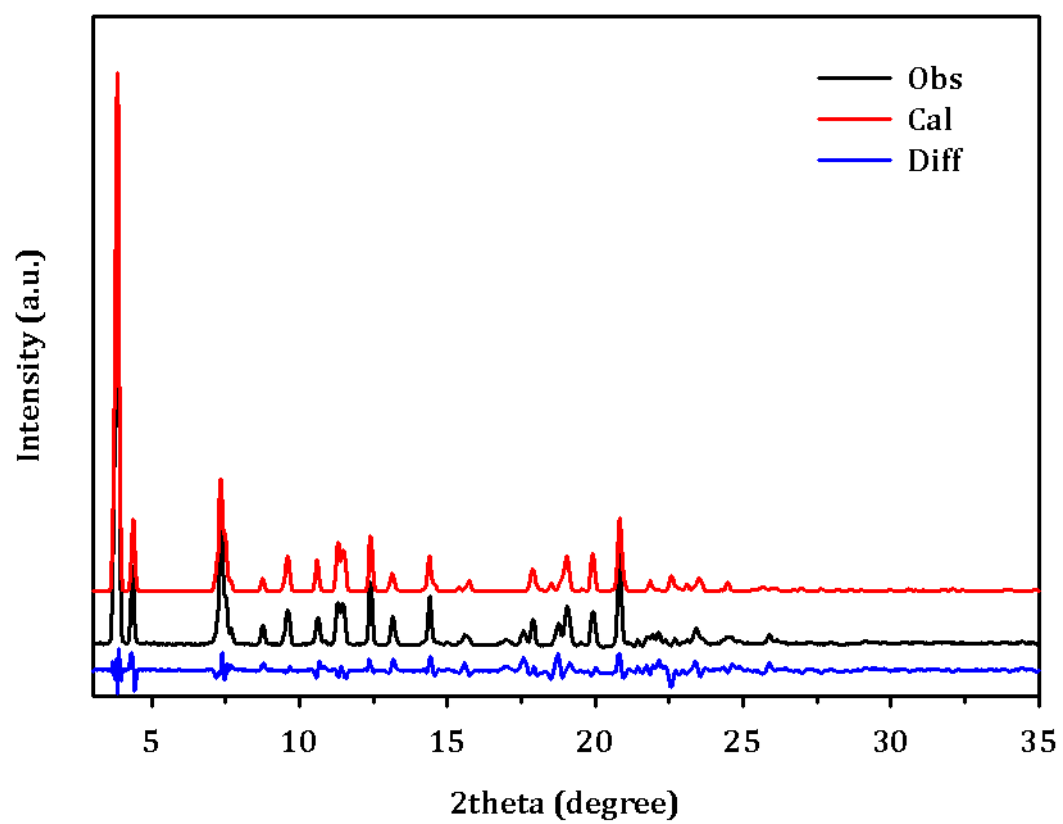


Figure S9. Rietveld plot for 3BuAz.

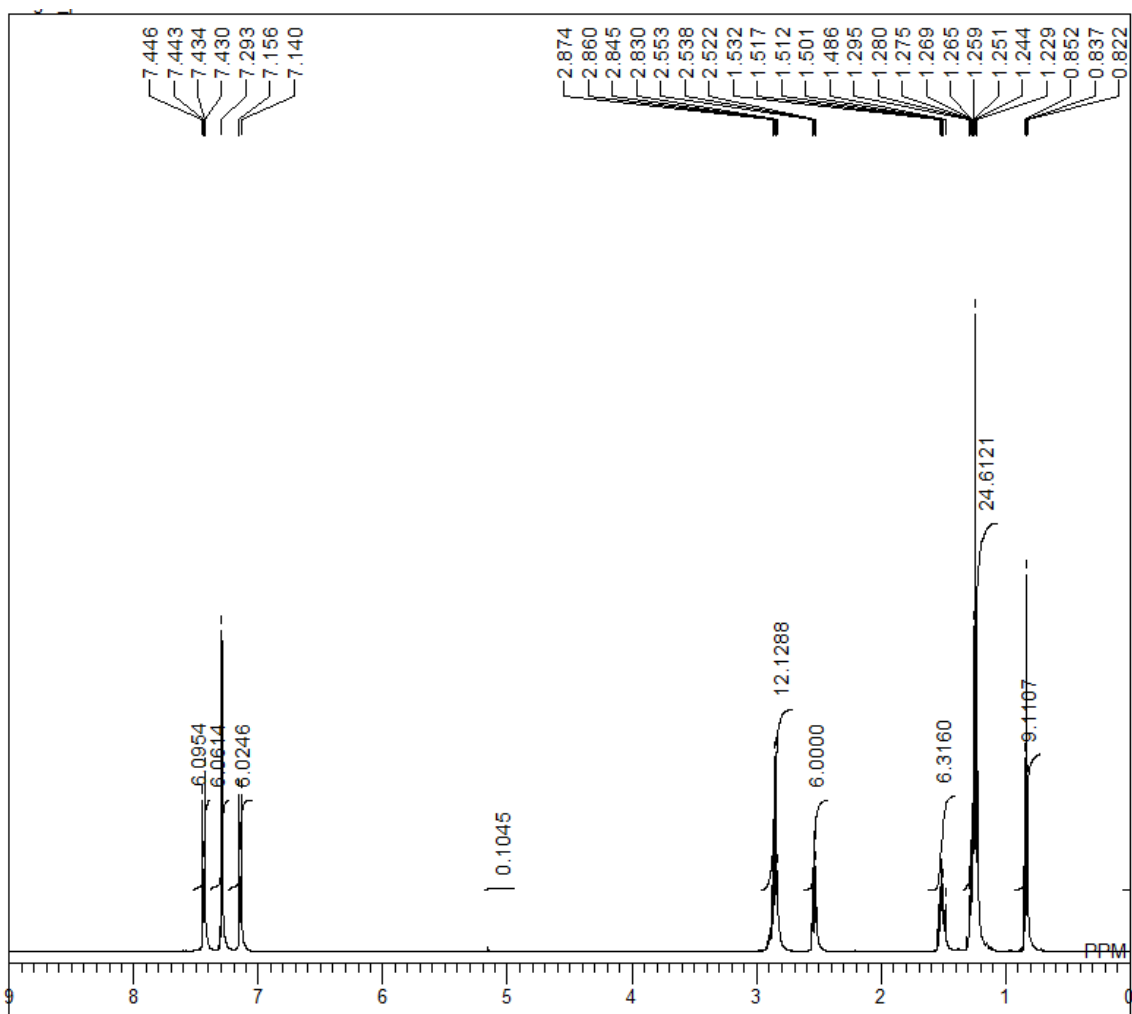


Figure S10. ^1H NMR Spectrum of 3BuAz in CD_2Cl_2 .

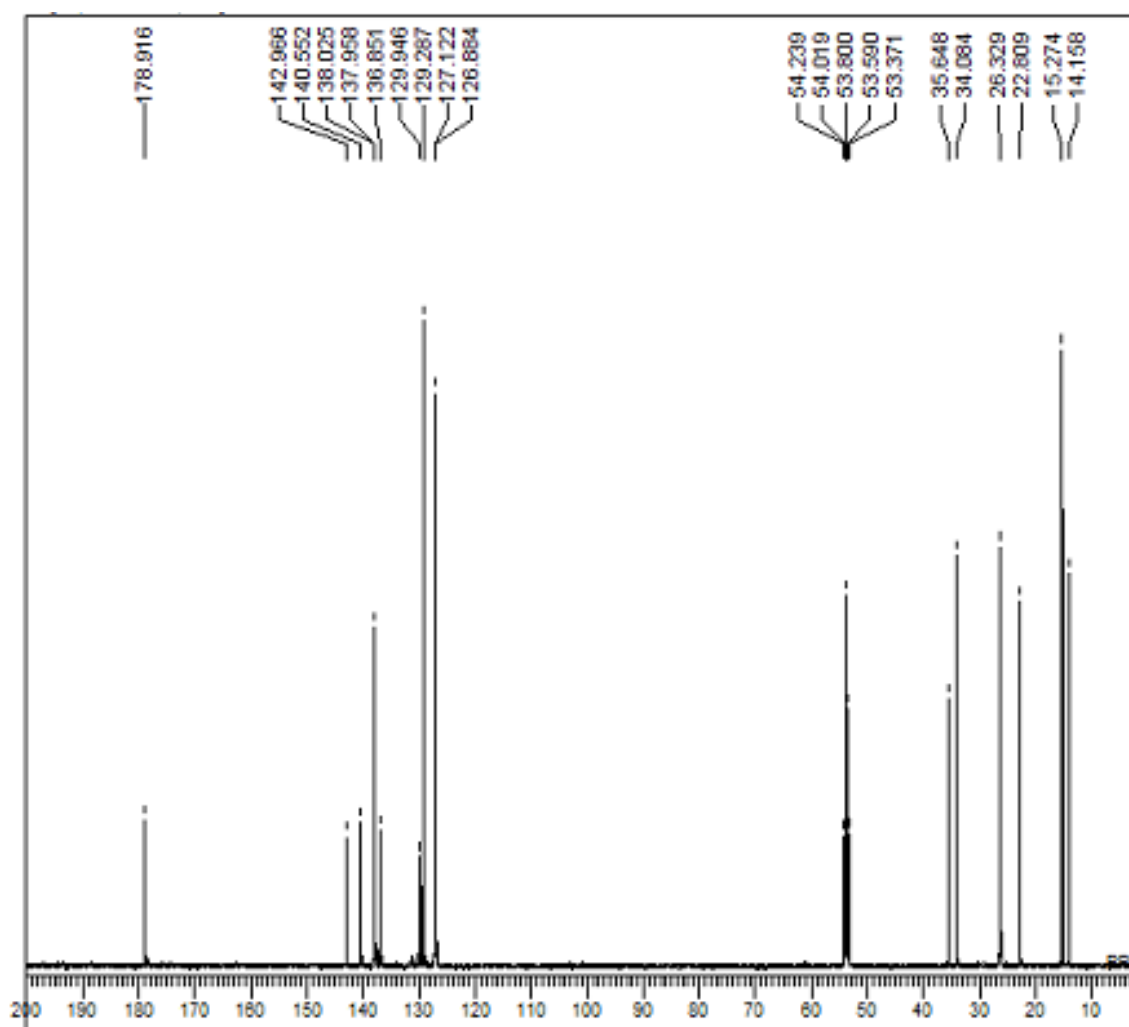


Figure S11. ^{13}C NMR Spectrum of 3BuAz in CD_2Cl_2 .

Table S1. Crystallographic Data for 3BuAz

material	3BuAz
Unit cell	
Composition	
Refined structure	C132 N12 O6
symmetry	monoclinic
space group	P 2 ₁
<i>a</i> , Å	25.049(12)
<i>b</i> , Å	5.0772(13)
<i>c</i> , Å	24.428(14)
α , °	90
β , °	109.56(3)
γ , °	90
cell volume, Å ³	2927(2)
No. Observation	1651
No. Parameters	33
No. Restraints	0
No. Constraints	1
R _p , %	1.60
R _{wp} , %	2.41
GOF	0.37

Table S2. Final Atomic Coordinates and Displacement and Population Parameters for 3BuAz

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}, 10^2 \times \text{\AA}^2$
C1	0.8429(10)	0.329(2)	0.6825(11)	1.12(10)
C2	0.8933(10)	0.288(3)	0.6736(12)	1.26(11)
C3	0.8989(10)	0.351(3)	0.6218(12)	1.36(11)
C4	0.8522(10)	0.4354(18)	0.5775(12)	1.27(11)
C5	0.8019(11)	0.4808(15)	0.5860(12)	1.12(11)
C6	0.7970(10)	0.4194(12)	0.6393(12)	1.06(10)
N7	0.8602(11)	0.424(3)	0.5275(12)	1.32(11)
N8	0.8438(13)	0.591(5)	0.4888(13)	1.34(13)
C9	0.8178(14)	0.667(6)	0.4363(14)	1.28(14)
C10	0.8370(15)	0.597(8)	0.3927(13)	1.32(15)
C11	0.8137(17)	0.699(9)	0.3386(15)	1.25(18)
C12	0.7710(19)	0.870(10)	0.3253(16)	1.1(2)
C13	0.7525(19)	0.947(9)	0.3692(17)	1.13(19)
C14	0.7754(17)	0.846(7)	0.4236(16)	1.20(16)
C15	0.7595(17)	0.981(6)	0.4717(18)	1.23(17)
C16	0.6955(18)	1.019(7)	0.4550(19)	1.04(18)
C17	0.8911(13)	0.440(8)	0.4033(13)	1.50(15)
C18	0.8790(12)	0.151(7)	0.4110(12)	1.34(14)
C19	0.743(2)	0.936(12)	0.2703(18)	1.0(2)
C20	0.686(2)	0.960(13)	0.2529(18)	0.8(2)
C21	0.655(2)	1.001(15)	0.1974(19)	0.6(3)
C22	0.680(3)	1.024(16)	0.1567(19)	0.6(3)
C23	0.738(2)	1.014(15)	0.1739(19)	0.9(3)
C24	0.769(2)	0.975(13)	0.2306(18)	1.1(3)
C25	0.646(3)	1.116(19)	0.097(2)	0.4(4)
C26	0.619(3)	0.88(2)	0.0579(19)	0.1(4)
C27	0.654(3)	0.80(2)	0.0213(18)	0.2(4)
C28	0.715(3)	0.735(19)	0.0612(16)	0.5(3)
O29	0.7536(12)	0.559(4)	0.5409(13)	1.02(12)
N30	0.7475(11)	0.475(3)	0.6420(13)	0.96(11)
C31	0.6826(9)	0.089(5)	0.6308(13)	0.69(13)
N32	0.7061(10)	0.314(4)	0.6288(12)	0.81(12)
C33	0.6892(10)	-0.044(5)	0.6821(13)	0.66(13)
C34	0.6568(12)	-0.254(6)	0.6828(15)	0.58(15)

C35	0.6173(12)	-0.349(8)	0.6365(16)	0.54(17)
C36	0.6109(12)	-0.224(8)	0.5854(15)	0.54(17)
C37	0.6423(10)	-0.009(7)	0.5825(14)	0.61(14)
C38	0.6289(11)	0.132(8)	0.5251(14)	0.59(15)
C39	0.5801(11)	0.324(10)	0.5155(15)	0.56(18)
C40	0.7292(10)	0.045(5)	0.7407(12)	0.72(12)
C41	0.7738(12)	-0.171(5)	0.7664(12)	0.70(13)
C42	0.5804(15)	-0.537(9)	0.6420(19)	0.5(2)
C43	0.5968(17)	-0.714(9)	0.686(2)	0.5(2)
C44	0.5588(19)	-0.854(10)	0.703(2)	0.5(3)
C45	0.5032(19)	-0.824(12)	0.675(2)	0.5(3)
C46	0.4859(17)	-0.651(12)	0.630(2)	0.5(3)
C47	0.5246(15)	-0.511(11)	0.614(2)	0.5(2)
C48	0.461(2)	-1.008(13)	0.687(3)	0.6(4)
C49	0.489(2)	-1.131(13)	0.747(3)	0.6(4)
C50	0.498(2)	-0.919(13)	0.793(3)	0.6(4)
C51	0.514(2)	-1.052(14)	0.851(3)	0.5(4)
O52	0.8415(10)	0.285(4)	0.7381(11)	1.04(11)
O53	0.9473(10)	0.297(4)	0.6077(12)	1.54(12)
N54	0.9299(10)	0.164(5)	0.7170(12)	1.28(12)
N55	0.9832(11)	0.188(7)	0.7300(13)	1.46(13)
C56	1.0186(12)	0.079(9)	0.7758(14)	1.46(15)
C57	1.0203(13)	0.188(10)	0.8281(14)	1.41(16)
C58	1.0588(15)	0.097(12)	0.8785(15)	1.39(19)
C59	1.0952(15)	-0.094(13)	0.8798(16)	1.4(2)
C60	1.0920(14)	-0.204(12)	0.8284(17)	1.5(2)
C61	1.0567(13)	-0.117(10)	0.7776(15)	1.52(18)
C62	0.9775(13)	0.385(9)	0.8348(13)	1.36(15)
C63	0.9342(13)	0.242(9)	0.8554(12)	1.10(14)
C64	1.0657(12)	-0.240(9)	0.7255(16)	1.63(18)
C65	1.0127(11)	-0.222(7)	0.6732(15)	1.52(15)
C66	1.1291(17)	-0.191(15)	0.9316(18)	1.4(3)
C67	1.1791(18)	-0.075(17)	0.9611(19)	1.5(3)
C68	1.215(2)	-0.187(19)	1.009(2)	1.5(4)
C69	1.202(2)	-0.413(19)	1.030(2)	1.2(4)
C70	1.152(2)	-0.532(17)	1.000(2)	1.1(3)

C71	1.1161(19)	-0.418(15)	0.9520(19)	1.1(3)
C72	1.236(2)	-0.50(2)	1.092(2)	1.1(4)
C73	1.294(3)	-0.60(2)	1.094(3)	1.2(5)
C74	1.333(2)	-0.38(2)	1.093(3)	1.6(5)
C75	1.328(3)	-0.16(2)	1.135(2)	1.5(5)
