crystals

MDPI

Supplementary Materials

One-Pot Synthesis, X-Ray Single Crystal and Molecular Insight of Enaminone-Based *β*-Morpholino-/ *N*-Methylpiperazinyl-/ Pyrrolidinylpropiophenone

Assem Barakat [1,2,*], Saied M. Soliman [2], Matti Haukka [3], Abdullah Mohammed Al-Majid [1], Mohammad Shahidul Islam [1], M. Ali[1] and Mohammed Rafi Shaik [1]

[1] Department of Chemistry, College of Science, King Saud University, P. O. Box 2455, Riyadh 11451, Saudi Arabia. Emails: amajid@ksu.edu.sa (A.M.A.M.); mislam@ksu.edu.sa (M.S.I.); maly.c@ksu.edu.sa (M.A); mrshaik@ksu.edu.sa (M.R.S.)

[2] Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426, Ibrahimia, Alexandria 21321, Egypt. saied1soliman@yahoo.com (S.M.S).

[3] Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland, email: matti.o.haukka@jyu.fi (M.H.).

* Correspondence: E-mail: ambarakat@ksu.edu.sa; Tel.: +966-11467-5901; Fax: +966-11467-5992.

Received: 20 March 2020; Accepted: 4 April 2020; Published: date

SUPPORTING INFORMATION

X-Ray structure determinations

The crystals of **1** and **2** were immersed in cryo-oil, mounted in a loop, and measured at a temperature of 170 K. The X-ray diffraction data were collected on a Bruker Kappa Apex II diffractometer using Mo Kα. The *Denzo-Scalepack* [1] software package was used for cell refinements and data reductions. The structures were solved by intrinsic phasing method using the *SHELXT* [2] software. A multi-scan absorption correction (*SADABS*[X3]) was applied to all data. Structural refinements were carried out using *SHELXL* [2] software. The crystal of **1** was solved as an inversion twin in space group $P2_12_12_1$. The BASF value was refined to 0.49532. Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C---H = 0.95–0.98 Å and U~iso~ = 1.2−1.5 U_{eq} (parent atom). The crystallographic details are summarized in Table **S1**.

References:

1. Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode, Academic Press, New York, pp. 307-326, 1997. In *Methods in Enzymology, Volume 276, Macromolecular Crystallography, Part A*, Carter, C. W., Sweet, J., Eds.; Academic Press: New York, USA, 1997; pp 307−326.
2. Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3–8.
3. Sheldrick, G. M. *SADABS - Bruker Nonius scaling and absorption correction -*, Bruker AXS, Inc.: Madison, Wisconsin, USA, **2012**.

Table S1. Crystal data and structure refinement for **1,** and **2**.

CCDC	1991661	1991662
Identification code	1	2
Empirical formula	$C_{13}H_{14}ClNO_2$	$C_{14}H_{17}ClN_2O$
Formula weight	251.70	264.74
Temperature	170(2) K	170(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions	a = 7.2256(2) Å α= 90°. b = 10.9717(3) Å β= 90°. c = 14.9867(3) Å γ = 90°.	a = 10.5001(3) Å α = 90°. b = 10.0923(3) Å β = 96.971(2)°. c = 13.1656(3) Å γ = 90°.
Volume	1188.10(5) $Å^3$	1384.85(7) $Å^3$
Z	4	4
Density (calculated)	1.407 Mg/m^3	1.270 Mg/m^3
Absorption coefficient	0.310 mm^{-1}	0.266 mm^{-1}
F(000)	528	560
Crystal size	0.447 x 0.281 x 0.200 mm^3	0.395 x 0.243 x 0.240 mm^3
Theta range for data collection	2.301 to 29.183°.	2.550 to 28.282°.
Index ranges	-9<=h<=9, -15<=k<=15, -20<=l<=20	-13<=h<=13, -13<=k<=13, -17<=l<=17
Reflections collected	23143	21197
Independent reflections	3196 [R(int) = 0.0313]	3431 [R(int) = 0.0326]
Completeness to theta = 25.242°	99.8 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.7192	0.7460 and 0.6994
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3196 / 0 / 155	3431 / 0 / 164
Goodness-of-fit on F^2	1.073	1.029
Final R indices [I > 2sigma(I)]	R1 = 0.0271, wR2 = 0.0683	R1 = 0.0487, wR2 = 0.0995
R indices (all data)	R1 = 0.0289, wR2 = 0.0696	R1 = 0.0625, wR2 = 0.1073
Absolute structure parameter	0.50(6)	n/a
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	0.251 and -0.188 e.$Å^{-3}$	0.266 and -0.401 e.$Å^{-3}$

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	5717(1)	10752(1)	6166(1)	30(1)
O(1)	6219(2)	4693(1)	6386(1)	30(1)
O(2)	5679(2)	1483(1)	2414(1)	34(1)
N(1)	6270(2)	2976(1)	3921(1)	23(1)
C(1)	6539(2)	7453(2)	5123(1)	23(1)

C(2)	6477(2)	8708(2)	5236(1)	25(1)
C(3)	5720(2)	9174(1)	6013(1)	21(1)
C(4)	5020(2)	8432(2)	6677(1)	24(1)
C(5)	5133(2)	7177(2)	6562(1)	23(1)
C(6)	5889(2)	6674(1)	5788(1)	19(1)
C(7)	6035(2)	5313(1)	5700(1)	21(1)
C(8)	5939(2)	4815(1)	4810(1)	22(1)
C(9)	6372(2)	3615(2)	4679(1)	22(1)
C(10)	5693(3)	3515(2)	3074(1)	28(1)
C(11)	4638(3)	2570(2)	2538(1)	35(1)
C(12)	6095(3)	953(2)	3255(1)	33(1)
C(13)	7233(3)	1811(1)	3827(1)	27(1)

Table S3. Bond lengths [Å] and angles [°] for **1**.

Cl(1)-C(3)	1.7466(15)
O(1)-C(7)	1.2403(19)
O(2)-C(12)	1.421(2)
O(2)-C(11)	1.422(2)
N(1)-C(9)	1.338(2)
N(1)-C(10)	1.460(2)
N(1)-C(13)	1.462(2)
C(1)-C(2)	1.387(2)
C(1)-C(6)	1.395(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.384(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.382(2)
C(4)-C(5)	1.390(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.397(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.502(2)
C(7)-C(8)	1.442(2)
C(8)-C(9)	1.367(2)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-C(11)	1.517(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.515(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(12)-O(2)-C(11)	109.80(14)
C(9)-N(1)-C(10)	122.80(13)
C(9)-N(1)-C(13)	120.91(15)

C(10)-N(1)-C(13)	113.98(14)
C(2)-C(1)-C(6)	120.66(15)
C(2)-C(1)-H(1)	119.7
C(6)-C(1)-H(1)	119.7
C(3)-C(2)-C(1)	118.82(15)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
C(4)-C(3)-C(2)	122.23(14)
C(4)-C(3)-Cl(1)	119.22(12)
C(2)-C(3)-Cl(1)	118.53(13)
C(3)-C(4)-C(5)	118.23(14)
C(3)-C(4)-H(4)	120.9
C(5)-C(4)-H(4)	120.9
C(4)-C(5)-C(6)	121.12(15)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(1)-C(6)-C(5)	118.90(14)
C(1)-C(6)-C(7)	121.53(14)
C(5)-C(6)-C(7)	119.54(14)
O(1)-C(7)-C(8)	124.31(14)
O(1)-C(7)-C(6)	118.64(14)
C(8)-C(7)-C(6)	117.05(13)
C(9)-C(8)-C(7)	119.15(15)
C(9)-C(8)-H(8)	120.4
C(7)-C(8)-H(8)	120.4
N(1)-C(9)-C(8)	127.90(16)
N(1)-C(9)-H(9)	116.1
C(8)-C(9)-H(9)	116.1
N(1)-C(10)-C(11)	109.09(14)
N(1)-C(10)-H(10A)	109.9
C(11)-C(10)-H(10A)	109.9
N(1)-C(10)-H(10B)	109.9
C(11)-C(10)-H(10B)	109.9
H(10A)-C(10)-H(10B)	108.3
O(2)-C(11)-C(10)	112.13(16)
O(2)-C(11)-H(11A)	109.2
C(10)-C(11)-H(11A)	109.2
O(2)-C(11)-H(11B)	109.2
C(10)-C(11)-H(11B)	109.2
H(11A)-C(11)-H(11B)	107.9
O(2)-C(12)-C(13)	111.24(14)
O(2)-C(12)-H(12A)	109.4
C(13)-C(12)-H(12A)	109.4
O(2)-C(12)-H(12B)	109.4
C(13)-C(12)-H(12B)	109.4
H(12A)-C(12)-H(12B)	108.0
N(1)-C(13)-C(12)	109.82(15)
N(1)-C(13)-H(13A)	109.7
C(12)-C(13)-H(13A)	109.7
N(1)-C(13)-H(13B)	109.7

C(12)-C(13)-H(13B)	109.7
H(13A)-C(13)-H(13B)	108.2

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic. Displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	35(1)	21(1)	35(1)	-7(1)	2(1)	1(1)
O(1)	43(1)	25(1)	22(1)	4(1)	2(1)	1(1)
O(2)	42(1)	28(1)	32(1)	-10(1)	-4(1)	3(1)
N(1)	28(1)	17(1)	22(1)	-1(1)	-1(1)	3(1)
C(1)	28(1)	22(1)	20(1)	-1(1)	6(1)	0(1)
C(2)	28(1)	22(1)	25(1)	0(1)	6(1)	-2(1)
C(3)	20(1)	18(1)	25(1)	-4(1)	-1(1)	1(1)
C(4)	25(1)	28(1)	18(1)	-5(1)	0(1)	2(1)
C(5)	26(1)	26(1)	16(1)	0(1)	1(1)	-1(1)
C(6)	19(1)	21(1)	18(1)	-1(1)	-1(1)	-1(1)
C(7)	20(1)	20(1)	22(1)	1(1)	2(1)	0(1)
C(8)	26(1)	20(1)	20(1)	1(1)	1(1)	0(1)
C(9)	22(1)	21(1)	22(1)	1(1)	2(1)	-1(1)
C(10)	36(1)	23(1)	24(1)	-2(1)	-5(1)	5(1)
C(11)	40(1)	34(1)	33(1)	-8(1)	-12(1)	8(1)
C(12)	41(1)	20(1)	37(1)	-6(1)	-3(1)	-1(1)
C(13)	31(1)	19(1)	30(1)	-3(1)	-1(1)	5(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(1)	7029	7122	4587	28
H(2)	6946	9237	4788	30
H(4)	4476	8771	7198	29
H(5)	4688	6652	7019	27
H(8)	5580	5314	4322	26
H(9)	6796	3182	5189	26
H(10A)	6792	3790	2736	33
H(10B)	4893	4231	3187	33
H(11A)	3469	2371	2850	42
H(11B)	4318	2916	1948	42
H(12A)	6789	185	3163	39
H(12B)	4928	753	3569	39
H(13A)	7433	1445	4423	32
H(13B)	8458	1944	3547	32

Table S6. Torsion angles [°] for **1.**

C(6)-C(1)-C(2)-C(3)	-1.5(3)
C(1)-C(2)-C(3)-C(4)	-0.2(3)
C(1)-C(2)-C(3)-Cl(1)	177.92(14)
C(2)-C(3)-C(4)-C(5)	1.7(3)
Cl(1)-C(3)-C(4)-C(5)	-176.39(13)
C(3)-C(4)-C(5)-C(6)	-1.6(3)
C(2)-C(1)-C(6)-C(5)	1.5(3)

C(2)-C(1)-C(6)-C(7)	-176.75(16)
C(4)-C(5)-C(6)-C(1)	0.0(3)
C(4)-C(5)-C(6)-C(7)	178.35(16)
C(1)-C(6)-C(7)-O(1)	149.14(17)
C(5)-C(6)-C(7)-O(1)	-29.1(2)
C(1)-C(6)-C(7)-C(8)	-31.2(2)
C(5)-C(6)-C(7)-C(8)	150.58(16)
O(1)-C(7)-C(8)-C(9)	-11.2(3)
C(6)-C(7)-C(8)-C(9)	169.12(15)
C(10)-N(1)-C(9)-C(8)	1.7(3)
C(13)-N(1)-C(9)-C(8)	163.39(17)
C(7)-C(8)-C(9)-N(1)	176.05(17)
C(9)-N(1)-C(10)-C(11)	-146.05(17)
C(13)-N(1)-C(10)-C(11)	51.1(2)
C(12)-O(2)-C(11)-C(10)	60.8(2)
N(1)-C(10)-C(11)-O(2)	-55.2(2)
C(11)-O(2)-C(12)-C(13)	-60.6(2)
C(9)-N(1)-C(13)-C(12)	145.05(16)
C(10)-N(1)-C(13)-C(12)	-51.8(2)
O(2)-C(12)-C(13)-N(1)	55.6(2)

Table S7. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	844(1)	2886(1)	-622(1)	63(1)
O(1)	4087(1)	236(1)	3541(1)	43(1)
N(1)	6837(2)	2599(2)	5099(1)	44(1)
N(2)	8242(1)	4130(2)	6650(1)	40(1)
C(1)	2203(2)	1231(2)	2035(1)	34(1)
C(2)	1389(2)	1580(2)	1170(1)	38(1)
C(3)	1835(2)	2463(2)	489(1)	40(1)
C(4)	3047(2)	3008(2)	657(1)	39(1)
C(5)	3837(2)	2677(2)	1541(1)	34(1)
C(6)	3424(2)	1778(2)	2235(1)	31(1)
C(7)	4257(2)	1358(2)	3193(1)	32(1)
C(8)	5172(2)	2284(2)	3668(1)	35(1)
C(9)	5994(2)	1882(2)	4499(1)	34(1)
C(10)	7835(2)	1984(2)	5815(1)	40(1)
C(11)	8010(2)	2727(2)	6818(1)	41(1)
C(12)	8478(2)	4841(2)	7621(2)	64(1)
C(13)	7144(2)	4680(2)	6015(2)	55(1)
C(14)	6987(3)	4028(2)	4978(2)	69(1)

Table S8. Bond lengths [Å] and angles [°] for **2**.

Cl(1)-C(3)	1.7427(17)
O(1)-C(7)	1.2419(19)
N(1)-C(9)	1.328(2)
N(1)-C(10)	1.460(2)
N(1)-C(14)	1.462(2)
N(2)-C(13)	1.450(2)

N(2)-C(11)	1.458(2)
N(2)-C(12)	1.460(2)
C(1)-C(2)	1.384(2)
C(1)-C(6)	1.391(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.385(2)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.379(3)
C(4)-C(5)	1.385(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.393(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.507(2)
C(7)-C(8)	1.429(2)
C(8)-C(9)	1.369(2)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-C(11)	1.510(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.507(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900

C(9)-N(1)-C(10)	121.82(15)
C(9)-N(1)-C(14)	123.08(15)
C(10)-N(1)-C(14)	114.28(15)
C(13)-N(2)-C(11)	108.85(14)
C(13)-N(2)-C(12)	110.74(16)
C(11)-N(2)-C(12)	111.03(15)
C(2)-C(1)-C(6)	121.17(15)
C(2)-C(1)-H(1)	119.4
C(6)-C(1)-H(1)	119.4
C(1)-C(2)-C(3)	118.17(16)
C(1)-C(2)-H(2A)	120.9
C(3)-C(2)-H(2A)	120.9
C(4)-C(3)-C(2)	122.07(15)
C(4)-C(3)-Cl(1)	118.83(13)
C(2)-C(3)-Cl(1)	119.10(14)
C(3)-C(4)-C(5)	119.03(15)
C(3)-C(4)-H(4)	120.5
C(5)-C(4)-H(4)	120.5
C(4)-C(5)-C(6)	120.36(16)

C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(1)-C(6)-C(5)	119.17(15)
C(1)-C(6)-C(7)	118.35(14)
C(5)-C(6)-C(7)	122.48(14)
O(1)-C(7)-C(8)	123.64(15)
O(1)-C(7)-C(6)	118.05(15)
C(8)-C(7)-C(6)	118.29(14)
C(9)-C(8)-C(7)	118.74(15)
C(9)-C(8)-H(8)	120.6
C(7)-C(8)-H(8)	120.6
N(1)-C(9)-C(8)	128.62(16)
N(1)-C(9)-H(9)	115.7
C(8)-C(9)-H(9)	115.7
N(1)-C(10)-C(11)	110.76(15)
N(1)-C(10)-H(10A)	109.5
C(11)-C(10)-H(10A)	109.5
N(1)-C(10)-H(10B)	109.5
C(11)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
N(2)-C(11)-C(10)	110.78(14)
N(2)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11A)	109.5
N(2)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	108.1
N(2)-C(12)-H(12A)	109.5
N(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
N(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(2)-C(13)-C(14)	110.28(18)
N(2)-C(13)-H(13A)	109.6
C(14)-C(13)-H(13A)	109.6
N(2)-C(13)-H(13B)	109.6
C(14)-C(13)-H(13B)	109.6
H(13A)-C(13)-H(13B)	108.1
N(1)-C(14)-C(13)	109.50(17)
N(1)-C(14)-H(14A)	109.8
C(13)-C(14)-H(14A)	109.8
N(1)-C(14)-H(14B)	109.8
C(13)-C(14)-H(14B)	109.8
H(14A)-C(14)-H(14B)	108.2

Symmetry transformations used to generate equivalent atoms:

Table 9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2**. The anisotropic. Displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

Cl(1)	51(1)	101(1)	37(1)	21(1)	3(1)	16(1)
O(1)	45(1)	36(1)	47(1)	12(1)	0(1)	-5(1)
N(1)	49(1)	36(1)	45(1)	13(1)	-8(1)	-10(1)
N(2)	37(1)	40(1)	41(1)	1(1)	-2(1)	4(1)
C(1)	38(1)	34(1)	31(1)	2(1)	11(1)	2(1)
C(2)	33(1)	47(1)	34(1)	-1(1)	7(1)	4(1)
C(3)	40(1)	53(1)	27(1)	4(1)	8(1)	13(1)
C(4)	44(1)	43(1)	31(1)	7(1)	15(1)	7(1)
C(5)	35(1)	36(1)	33(1)	2(1)	11(1)	2(1)
C(6)	34(1)	31(1)	28(1)	-1(1)	9(1)	4(1)
C(7)	33(1)	34(1)	31(1)	3(1)	10(1)	3(1)
C(8)	39(1)	33(1)	34(1)	5(1)	6(1)	-1(1)
C(9)	34(1)	33(1)	38(1)	5(1)	9(1)	-2(1)
C(10)	32(1)	41(1)	46(1)	7(1)	2(1)	-1(1)
C(11)	38(1)	44(1)	41(1)	9(1)	2(1)	6(1)
C(12)	80(2)	56(1)	52(1)	-9(1)	-5(1)	13(1)
C(13)	51(1)	37(1)	72(1)	10(1)	-15(1)	1(1)
C(14)	94(2)	41(1)	61(1)	22(1)	-31(1)	-23(1)

Table S10. Hydrogen coordinates (× 10^4) and isotropic, displacement parameters (Å^2 × 10^3) for 2.

	x	y	z	U(eq)
H(1)	1923	608	2501	40
H(2A)	547	1224	1046	46
H(4)	3335	3603	174	46
H(5)	4665	3064	1674	41
H(8)	5210	3161	3413	42
H(9)	5955	969	4668	41
H(10A)	8654	1980	5513	48
H(10B)	7598	1054	5938	48
H(11A)	7231	2625	7165	49
H(11B)	8743	2347	7267	49
H(12A)	7738	4736	8001	96
H(12B)	8608	5784	7488	96
H(12C)	9245	4481	8025	96
H(13A)	7265	5646	5936	66
H(13B)	6360	4541	6350	66
H(14A)	6224	4394	4556	83
H(14B)	7750	4210	4626	83

Table S11. Torsion angles [°] for **2**.

C(6)-C(1)-C(2)-C(3)	1.8(2)
C(1)-C(2)-C(3)-C(4)	-0.9(3)
C(1)-C(2)-C(3)-Cl(1)	178.39(13)
C(2)-C(3)-C(4)-C(5)	-0.8(3)
Cl(1)-C(3)-C(4)-C(5)	179.86(13)
C(3)-C(4)-C(5)-C(6)	1.7(2)
C(2)-C(1)-C(6)-C(5)	-1.0(2)
C(2)-C(1)-C(6)-C(7)	179.74(15)

C(4)-C(5)-C(6)-C(1)	-0.8(2)
C(4)-C(5)-C(6)-C(7)	178.43(15)
C(1)-C(6)-C(7)-O(1)	28.0(2)
C(5)-C(6)-C(7)-O(1)	-151.22(15)
C(1)-C(6)-C(7)-C(8)	-150.18(15)
C(5)-C(6)-C(7)-C(8)	30.6(2)
O(1)-C(7)-C(8)-C(9)	6.3(2)
C(6)-C(7)-C(8)-C(9)	-175.60(14)
C(10)-N(1)-C(9)-C(8)	-166.41(17)
C(14)-N(1)-C(9)-C(8)	2.6(3)
C(7)-C(8)-C(9)-N(1)	-174.05(17)
C(9)-N(1)-C(10)-C(11)	-139.68(17)
C(14)-N(1)-C(10)-C(11)	50.4(2)
C(13)-N(2)-C(11)-C(10)	60.79(19)
C(12)-N(2)-C(11)-C(10)	-177.07(16)
N(1)-C(10)-C(11)-N(2)	-53.87(19)
C(11)-N(2)-C(13)-C(14)	-63.1(2)
C(12)-N(2)-C(13)-C(14)	174.56(18)
C(9)-N(1)-C(14)-C(13)	138.04(19)
C(10)-N(1)-C(14)-C(13)	-52.2(3)
N(2)-C(13)-C(14)-N(1)	58.1(3)

Atom numbering refer to figure S1

Table 12. The calculated geometric parameters of the studied compounds.

Parameter	Calc.	Exp.	Parameter	Calc.	Exp.
	1			**2**	
R(1-9)	1.759	1.747	R(1-9)	1.759	1.743
R(2-15)	1.236	1.240	R(2-15)	1.237	1.242
R(3-23)	1.420	1.422	R(3-18)	1.356	1.328
R(3-26)	1.421	1.421	R(3-20)	1.463	1.460
R(4-18)	1.358	1.338	R(3-33)	1.460	1.462
R(4-20)	1.461	1.460	R(4-23)	1.461	1.458
R(4-29)	1.464	1.462	R(4-26)	1.456	1.460
R(5-7)	1.394	1.387	R(4-30)	1.460	1.450
R(5-14)	1.402	1.395	R(5-7)	1.391	1.384
R(7-9)	1.394	1.384	R(5-14)	1.403	1.391
R(9-10)	1.396	1.382	R(7-9)	1.396	1.385
R(10-12)	1.391	1.390	R(9-10)	1.394	1.379
R(12-14)	1.403	1.397	R(10-12)	1.394	1.385
R(14-15)	1.508	1.502	R(12-14)	1.402	1.393
R(15-16)	1.462	1.442	R(14-15)	1.509	1.507
R(16-18)	1.362	1.367	R(15-16)	1.460	1.429
R(20-23)	1.530	1.517	R(16-18)	1.363	1.369
R(26-29)	1.527	1.515	R(20-23)	1.527	1.510
			R(30-33)	1.530	1.506
A(1-9-7)	119.4	118.5	A(1-9-7)	119.5	119.1

A(1-9-10)	119.5	119.2	A(1-9-10)	119.3	118.8
A(2-15-14)	118.7	118.6	A(2-15-14)	118.6	118
A(2-15-16)	122.4	124.3	A(2-15-16)	122.6	123.6
A(23-3-26)	110.7	109.8	A(18-3-20)	120.3	121.8
A(3-23-20)	111.7	112.1	A(18-3-33)	122.6	123.1
A(3-23-24)	110.1	109.2	A(3-18-16)	129.2	128.6
A(3-23-25)	106.8	109.2	A(20-3-33)	114.5	114.3
A(3-26-27)	106.8	109.4	A(3-20-23)	110.8	110.8
A(3-26-28)	110.3	109.4	A(3-33-30)	110.6	109.5
A(3-26-29)	110.7	111.2	A(23-4-26)	112	111
A(18-4-20)	122.4	122.8	A(23-4-30)	110.1	108.8
A(18-4-29)	120.1	120.9	A(4-23-20)	110.1	110.8
A(4-18-16)	129.1	127.9	A(26-4-30)	111.9	110.8
A(4-18-19)	114.6	116.1	A(4-30-33)	110.9	110.3
A(20-4-29)	114.6	114	A(7-5-14)	121.3	121.2
A(4-20-21)	110.3	109.9	A(5-7-9)	118.9	118.2
A(4-20-22)	109.2	109.9	A(5-14-12)	118.5	119.2
A(4-20-23)	109.9	109.1	A(5-14-15)	117.4	118.3
A(4-29-26)	110.1	109.8	A(7-9-10)	121.2	122.1
A(4-29-30)	108.9	109.7	A(9-10-12)	119.1	119
A(4-29-31)	110.1	109.7	A(10-12-14)	121.1	120.4
A(7-5-14)	121.1	120.7	A(12-14-15)	124.1	122.5
A(5-7-9)	119.1	118.8	A(14-15-16)	118.8	118.3
A(5-14-12)	118.5	118.9	A(15-16-18)	118	118.7
A(5-14-15)	124.1	121.5			
A(7-9-10)	121.2	122.2			
A(9-10-12)	119	118.2			
A(10-12-14)	121.3	121.1			
A(12-14-15)	117.4	119.6			
A(14-15-16)	118.9	117.0			
A(15-16-18)	118.0	119.1			

Atom numbering refer to figure S1

Table S13 Natural charge populations at the different atomic sites of the studied conformers.

Atom		**1**	**Atom**		**2**
Cl	1	-0.0045	Cl	1	-0.0062
O	2	-0.6060	O	2	-0.6083
O	3	-0.5728	N	3	-0.4280
N	4	-0.4338	N	4	-0.5092
C	5	-0.2013	C	5	-0.1810
H	6	0.2391	H	6	0.2674
C	7	-0.2558	C	7	-0.2536
H	8	0.2557	H	8	0.2569
C	9	-0.0318	C	9	-0.0323
C	10	-0.2532	C	10	-0.2561
H	11	0.2574	H	11	0.2553
C	12	-0.1802	C	12	-0.2019
H	13	0.2677	H	13	0.2394
C	14	-0.1263	C	14	-0.1247
C	15	0.5138	C	15	0.5124
C	16	-0.4520	C	16	-0.4553
H	17	0.2217	H	17	0.2213

	C	18	0.0869		C	18	0.0894
	H	19	0.2492		H	19	0.2485
	C	20	-0.2965		C	20	-0.2631
	H	21	0.2327		H	21	0.2325
	H	22	0.2512		H	22	0.2512
	C	23	-0.1242		C	23	-0.2790
	H	24	0.2070		H	24	0.2061
	H	25	0.2405		H	25	0.2458
	C	26	-0.1258		C	26	-0.4806
	H	27	0.2406		H	27	0.1978
	H	28	0.2068		H	28	0.2328
	C	29	-0.2896		H	29	0.2330
	H	30	0.2520		C	30	-0.2771
	H	31	0.2313		H	31	0.2456
					H	32	0.2063
					C	33	-0.2696
					H	34	0.2505
					H	35	0.2339

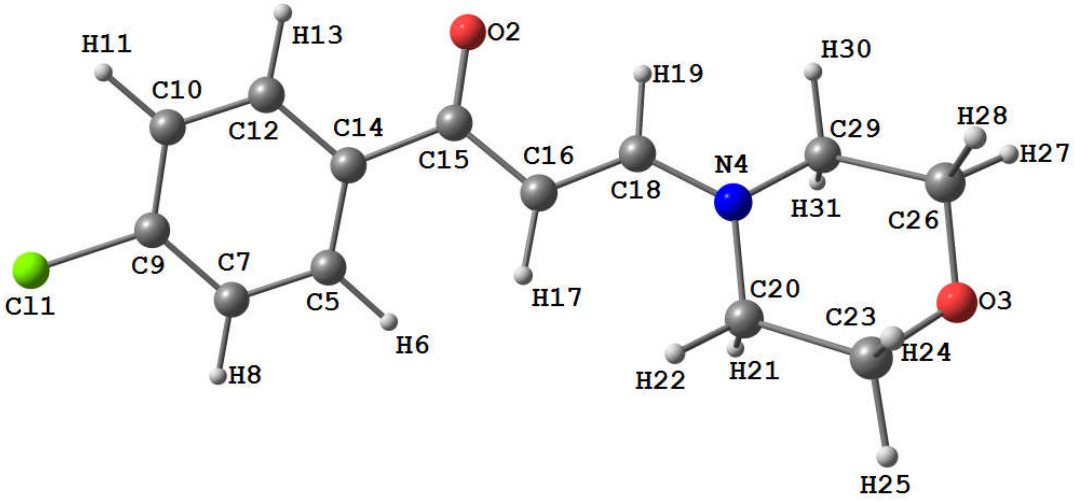
Atom numbering refer to figure S1

Table S14. The calculated and experimental chemical shifts (ppm) for the studied compounds.

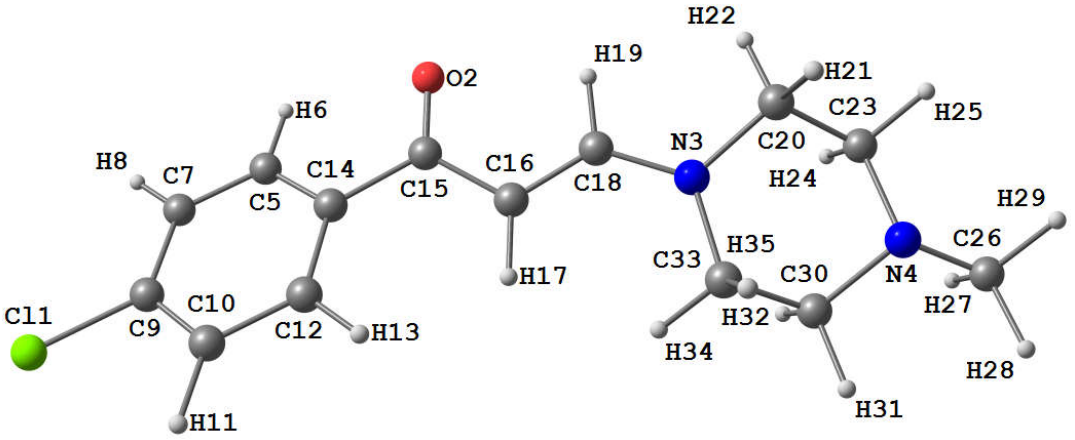
1		**calc**	**Exp**	**1**		**calc**	**exp**
C	5	116.0311	129.213	H	6	8.0932	7.932
C	7	115.7201	128.211	H	8	7.6124	7.492
C	9	133.0427	138.657	H	11	7.6544	7.492
C	10	116.2274	128.211	H	13	8.3406	7.932
C	12	117.7694	129.213	H	17	6.1787	6.080
C	14	127.0229	135.705	H	19	7.744	7.715
C	15	170.1034	184.844	H	21	3.4323	3.465
C	16	80.0674	90.841	H	22	3.5617	3.465
C	18	138.6107	153.209	H	24	3.8353	3.637
C	20	37.6916	65.377	H	25	4.1075	3.637
C	23	57.7637	66.096	H	27	4.0672	3.637
C	26	58.6574	66.096	H	28	3.9102	3.637
C	29	45.6261	65.377	H	30	3.3177	3.465
				H	31	3.8523	3.465
2		**calc**	**exp**			**calc**	**exp**
C	5	117.7107	129.129	H	6	8.3197	7.847
C	7	116.1467	128.173	H	8	7.6558	7.406
C	9	132.9159	138.749	H	11	7.6146	7.406
C	10	115.6853	128.173	H	13	8.087	7.847
C	12	115.9801	129.129	H	17	6.1592	5.790
C	14	127.3179	135.614	H	19	7.7585	7.716
C	15	170.1116	184.752	H	21	3.8127	2.272
C	16	80.0635	90.573	H	22	3.4443	2.272
C	18	138.3561	153.041	H	24	2.458	2.413
C	20	46.2339	53.654	H	25	2.7809	2.413
C	23	46.4877	55.069	H	27	2.2183	3.267
C	26	37.251	45.579	H	28	2.5584	3.267
C	30	45.5512	55.069	H	29	2.5381	3.267
C	33	37.6145	53.654	H	31	2.8289	2.413

		H	32	2.3713	2.413
		H	34	3.7292	2.272
		H	35	3.3585	2.272

Atom numbering refer to figure S1



1



2

Figure S1. Atom numbering of the optimized structures of conformers A and B (**See Table S12**).

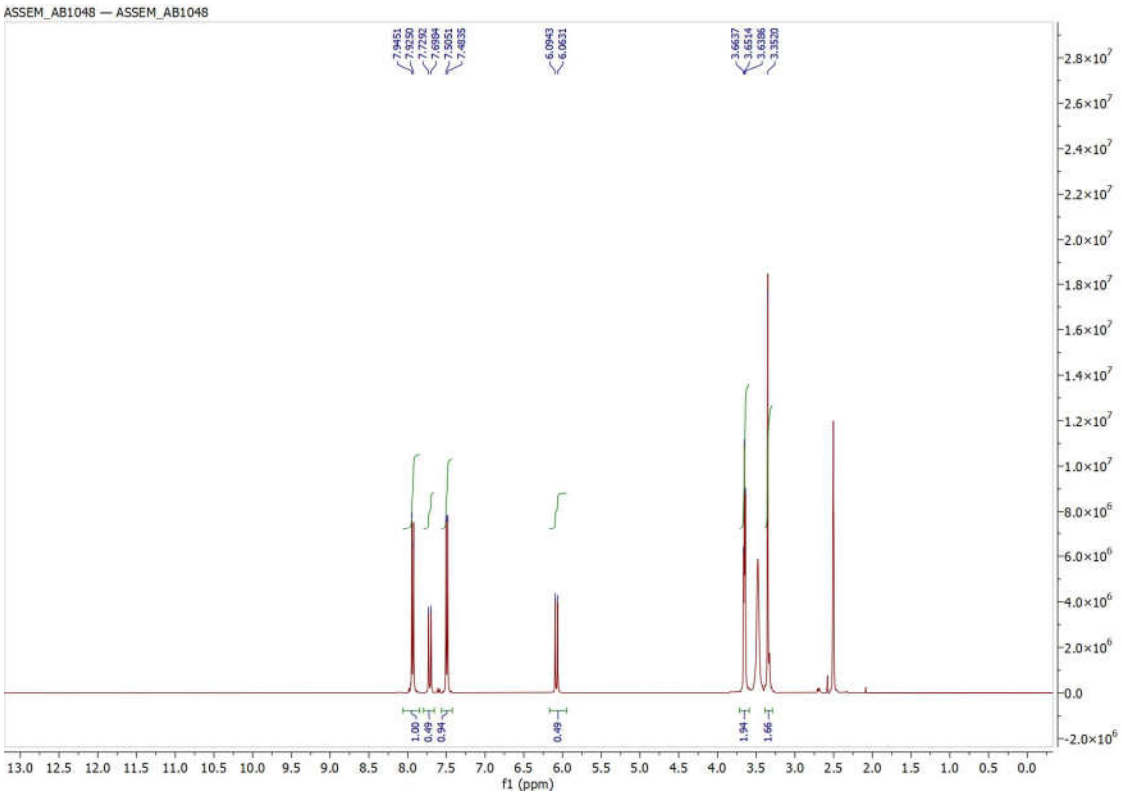


Figure S2. [1]HNMR (DMSO-d_6) of **1.**

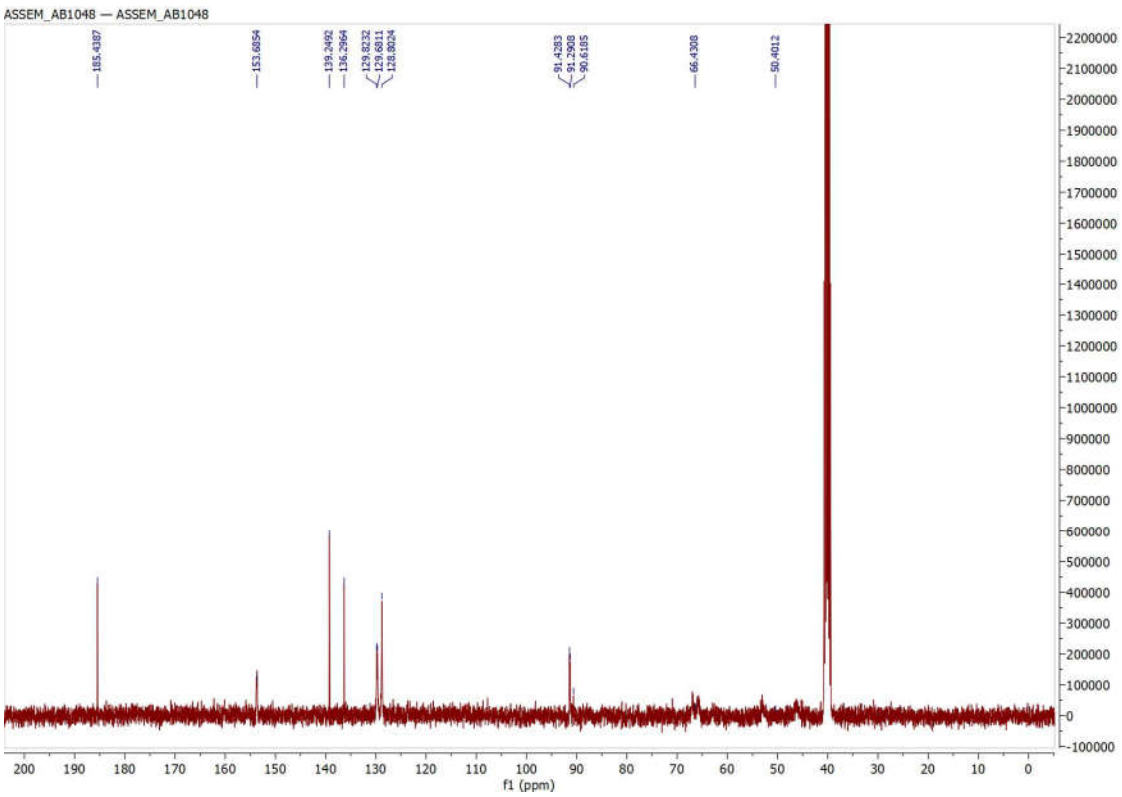


Figure S3. [13]CNMR (DMSO-d_6) of **1.**

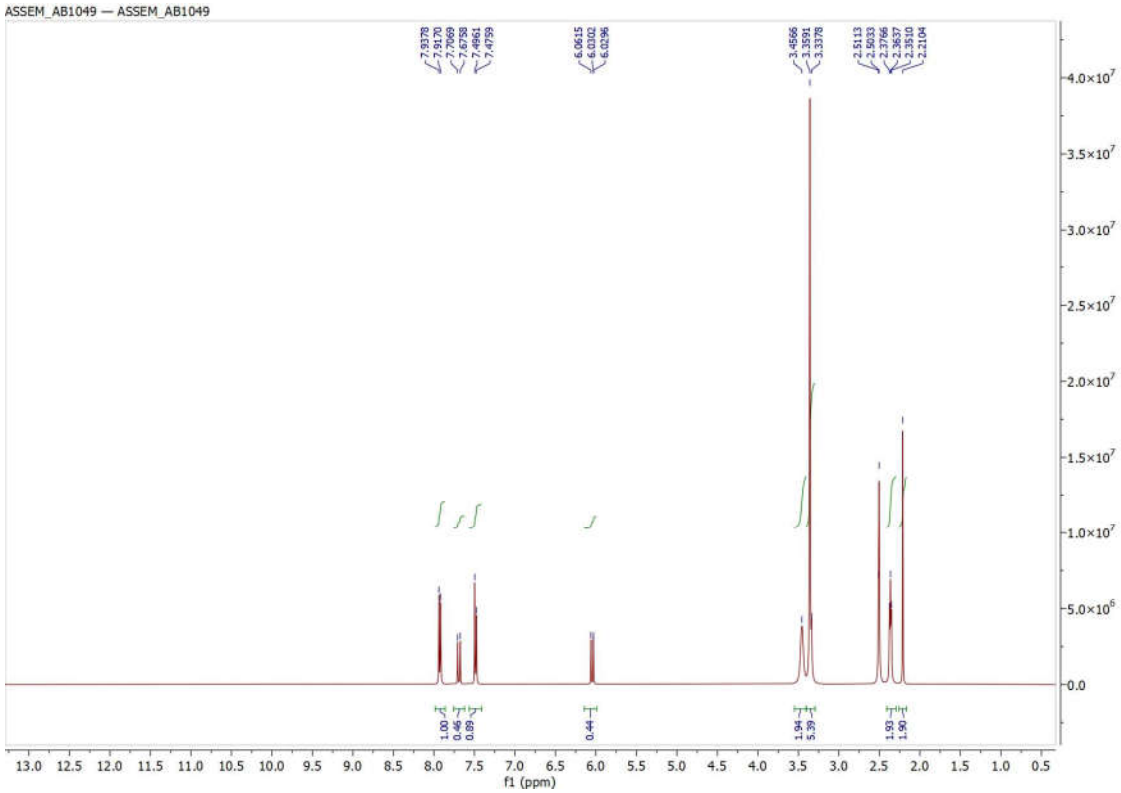


Figure S4. [1]HNMR (DMSO-d_6) of **2.**

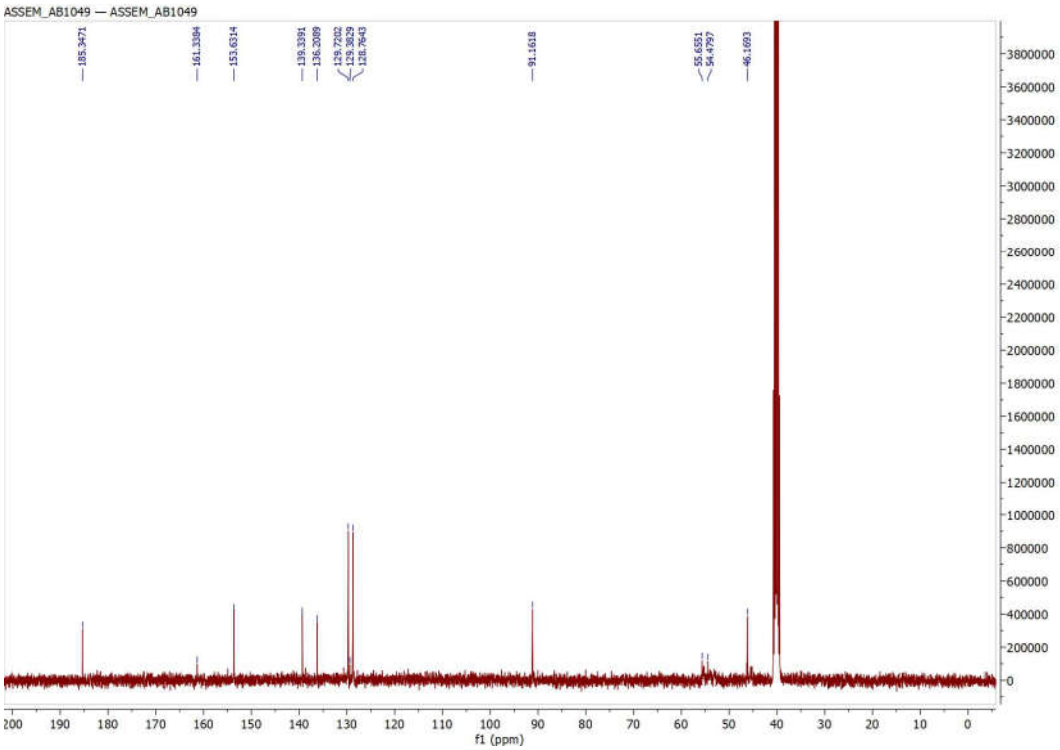


Figure S5. [13]CNMR (DMSO-d_6) of **2.**

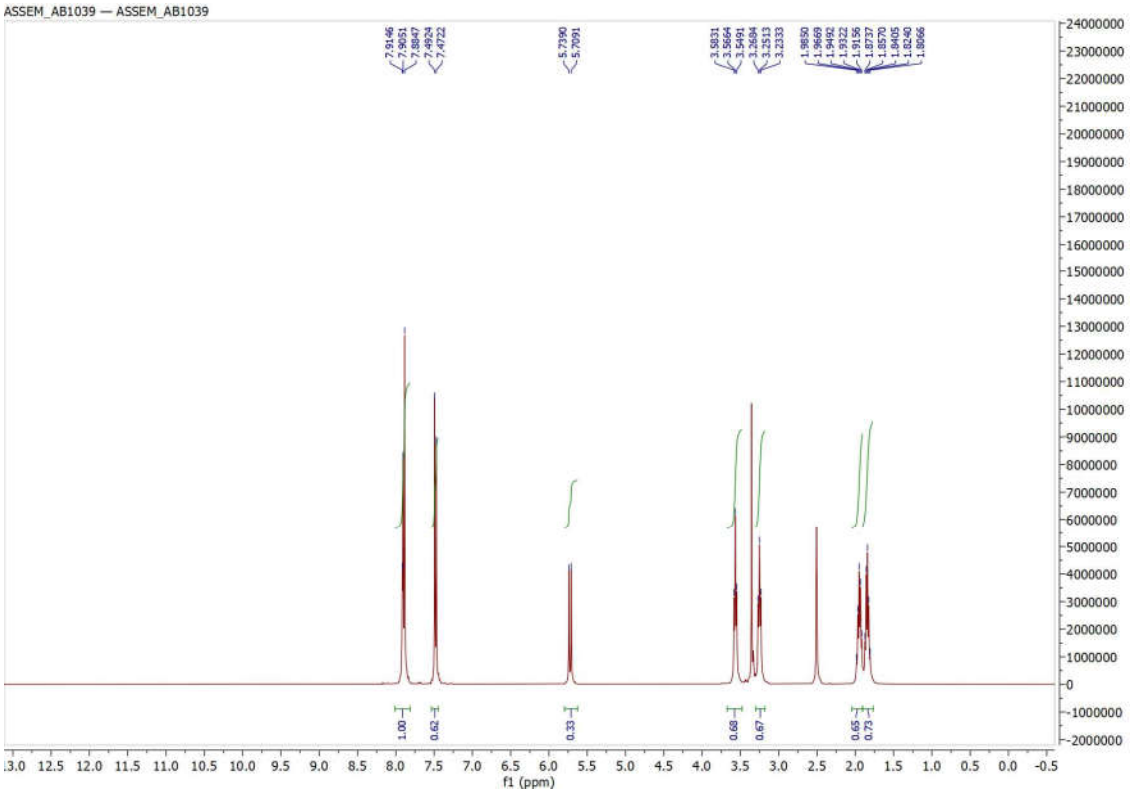


Figure S6. [1]HNMR (DMSO-d_6) of **3.**

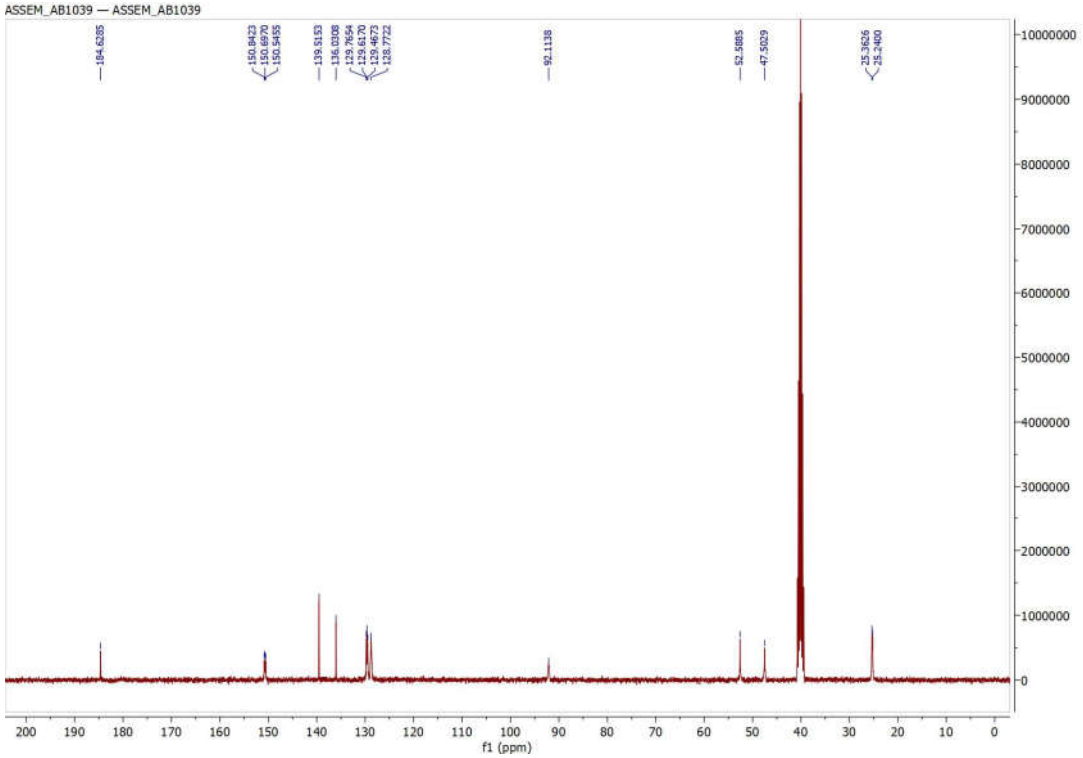


Figure S7. [13]CNMR (DMSO-d_6) of **3.**