Electronic Supplementary Material (ESI) for RSC Advances.

Crystal structure, spectroscopic characterization, NLO properties and Hirshfeld surface analysis of a piperonal chalcone derivative incorporating the pyrazolo[3,4-*b*]pyridine moiety

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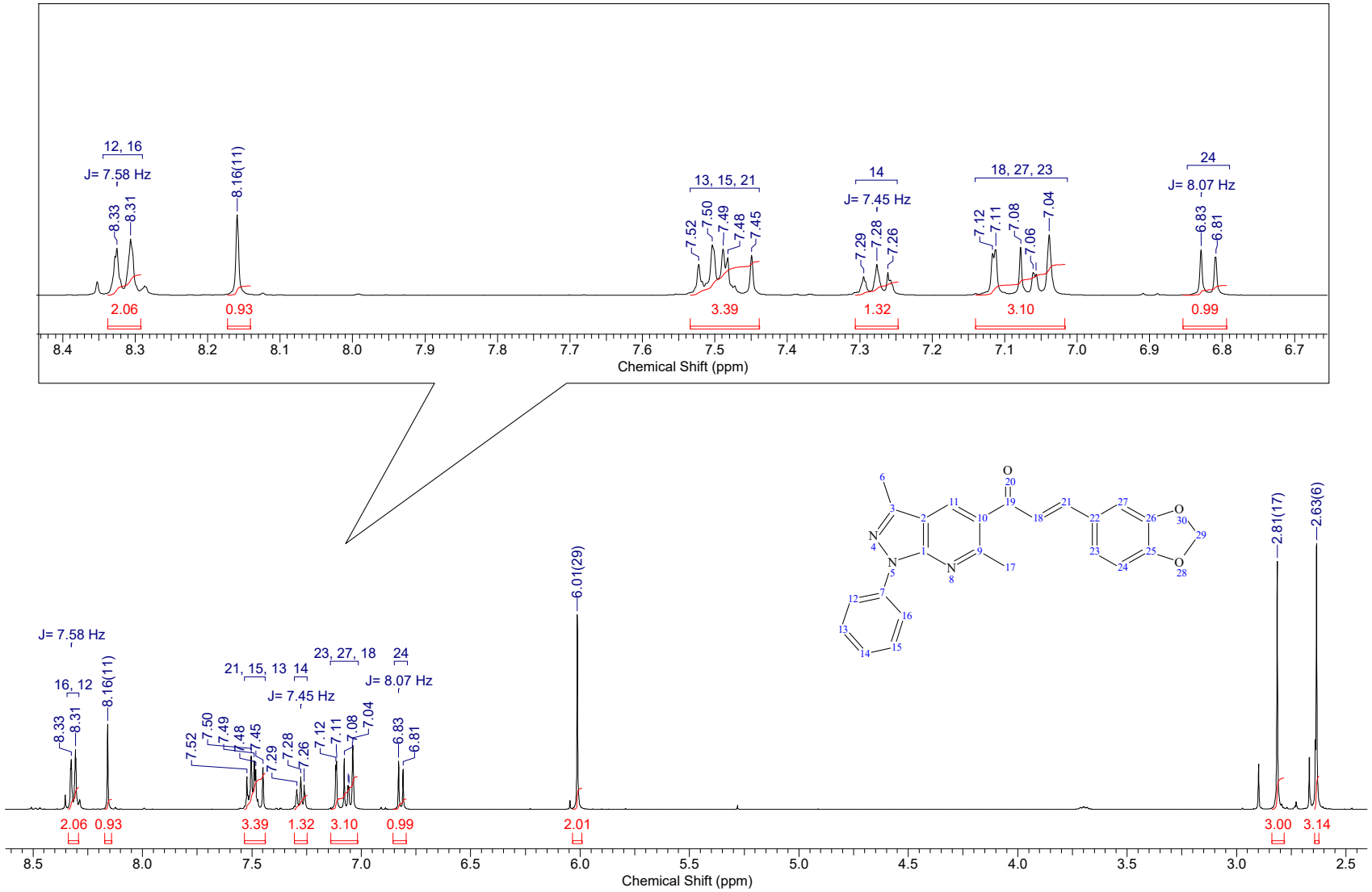


Figure SI-1. ^{1}H-NMR spectrum of (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(3,6-dimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl)prop-2-en-1-one (**6**) in $CDCl_3$.

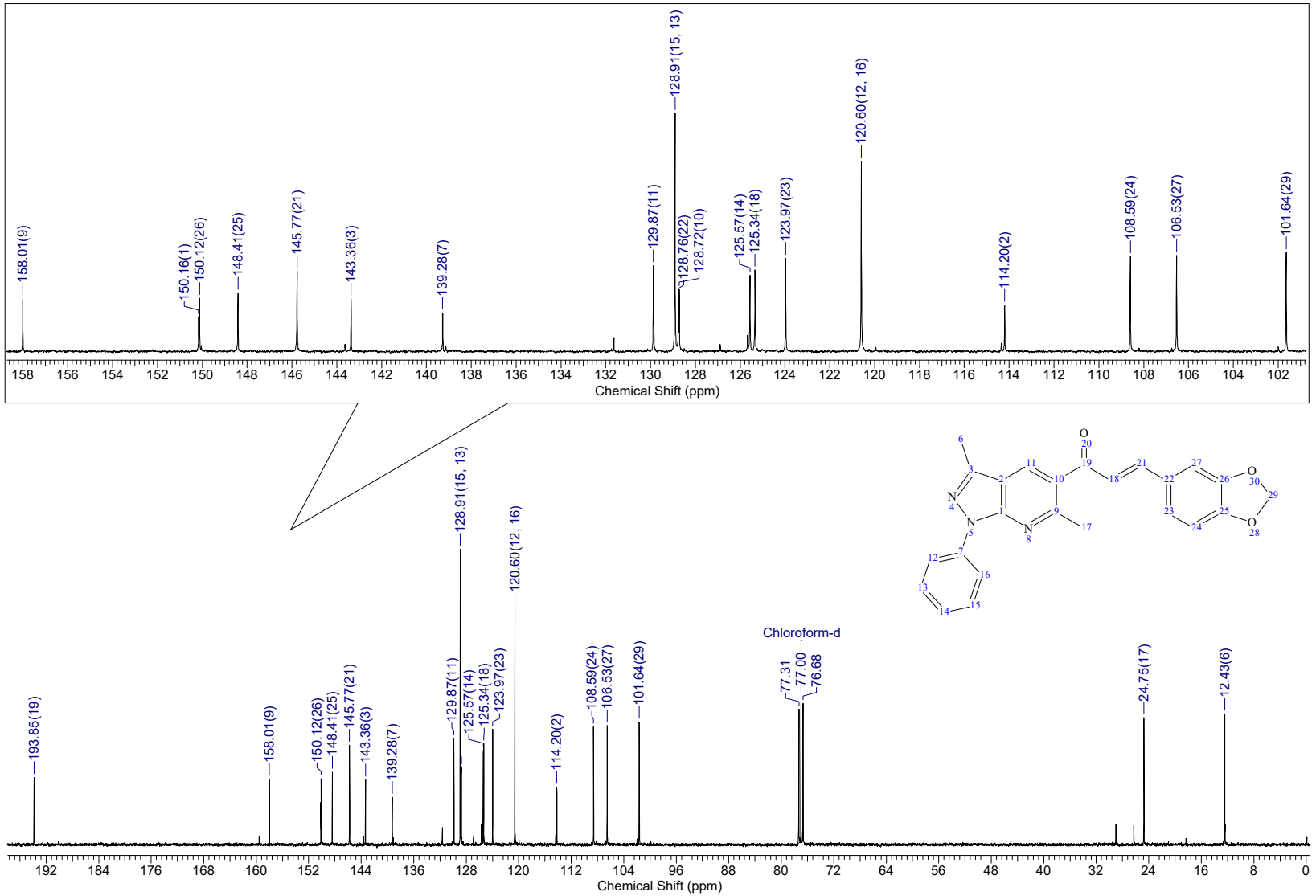


Figure SI-2. ^{13}C-NMR spectrum of (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(3,6-dimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl)prop-2-en-1-one (**6**) in $CDCl_3$.

Table SI-1. NMR data of (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(3,6-dimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl)prop-2-en-1-one (**6**) in $CDCl_3$.

Position	δ_C (ppm)	δ_H (ppm)
1	150.16 (C)	-
2	114.20 (C)	-
3	143.36 (C)	-
6	12.43 (CH_3)	2.63 (s)
7	139.28 (C)	-
9	158.01 (C)	-
10	128.72 (C)	-
11	129.87 (CH)	8.16 (s)
12	120.60 (CH)	8.32 (d, *J* = 7.6 Hz)
13	128.91 (CH)	7.52-7.45 (m)
14	125.57 (CH)	7.28 (t, *J* = 7.5 Hz)
15	128.91 (CH)	7.52-7.45 (m)
16	120.60 (CH)	8.32 (d, *J* = 7.6 Hz)
17	24.75 (CH_3)	2.81 (s)
18	125.34 (CH)	7.12-7.04 (m)
19	193.85 (C=O)	-
21	145.77 (CH)	7.52-7.45 (m)
22	128.76 (C)	-
23	123.97 (CH)	7.12-7.04 (m)
24	108.59 (CH)	6.82 (d, *J* = 8.0 Hz)
25	148.41 (C)	-
26	150.12 (C)	-
27	106.53 (CH)	7.12-7.04 (m)
29	101.64 (CH_2)	6.01 (s)

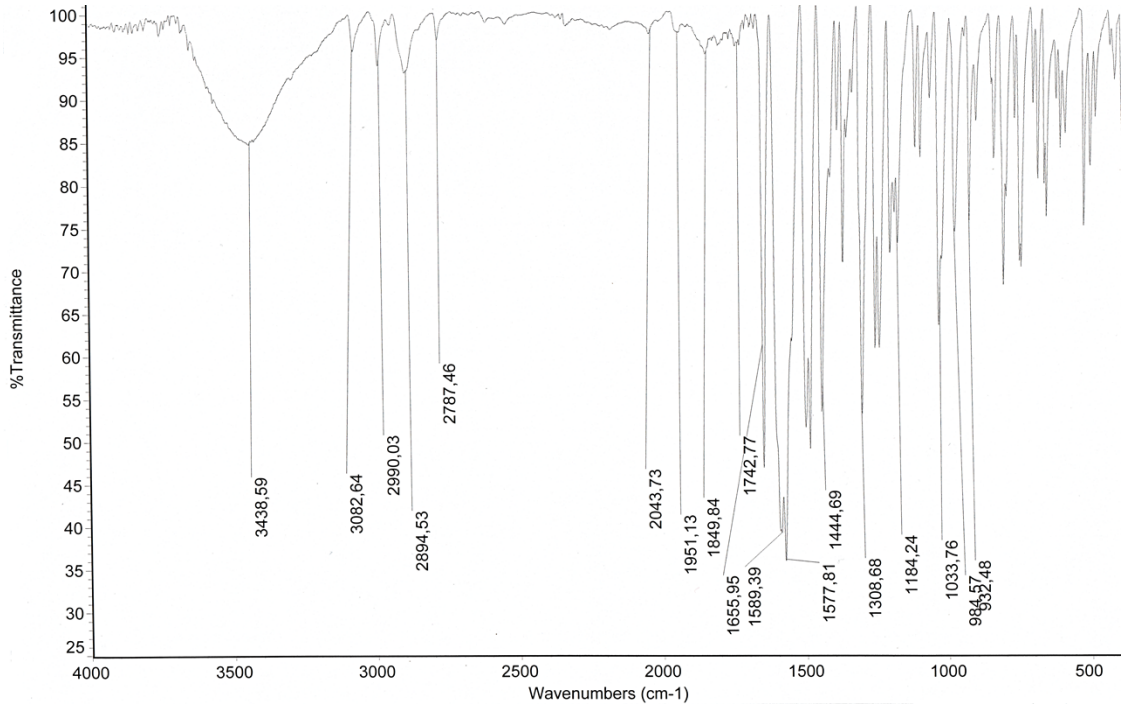


Figure SI-3. IR spectrum of (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(3,6-dimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl)prop-2-en-1-one (**6**).

Table SI-2. IR frequencies of (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(3,6-dimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl)prop-2-en-1-one (**6**).

Wavenumber (cm^{-1})	Intensity[†]	Assignment
3082	w	=C-H stretch
2990 and 2894	w	-C-H stretch
1655	s	C=O stretch
1589	s	C=N stretch
1577	s	C=C stretch
1444	s	-C-H bend
1308	s	C-O stretch
1033	m	C-O stretch
984	m	=C-H bend (in-plane)
754	m	=C-H bend (out-of-plane)

[†] Length of the peak (in the y-axis direction), s= strong, m= medium, w= weak.

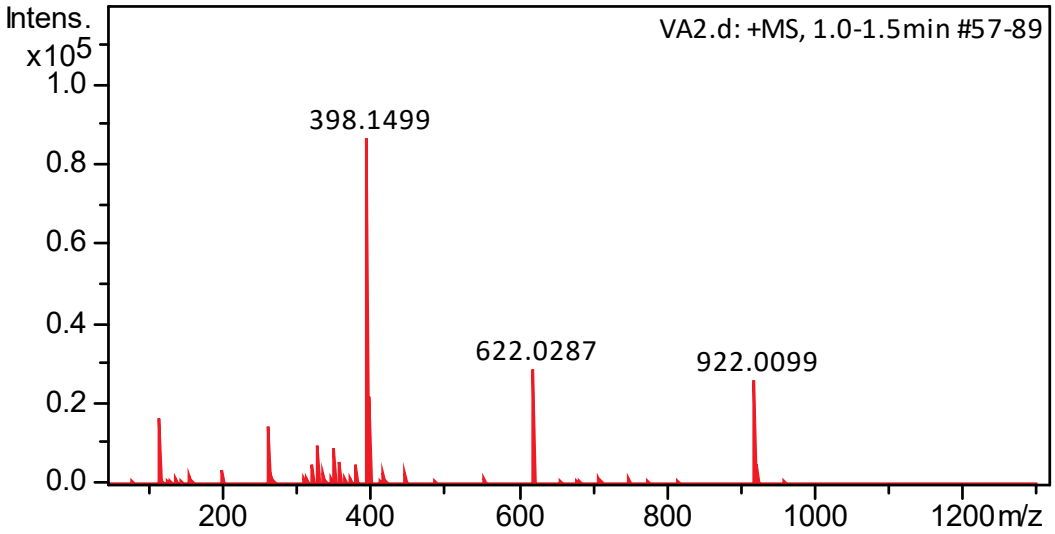


Figure SI-4. MS spectrum of (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-(3,6-dimethyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl)prop-2-en-1-one (**6**).

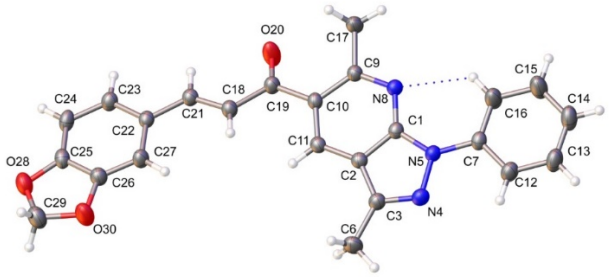
Table SI-3. Calculated and experimental ^{1}H chemical shift (ppm) values of compound **6**.

		M062X		TPSS		B3LYP	
Atom	**Experimental**	**Cal**	**Δx**	**Cal**	**Δx**	**Cal**	**Δx**
H6A	2.63	3.02	0,39	2.80	0,17	2.81	0,18
H6B	2.63	2.90	0,27	2.80	0,17	2.78	0,15
H6C	2.63	2.94	0,31	2.81	0,18	2.80	0,17
H11	8.16	9.55	1,39	8.49	0,33	8.68	0,52
H12	8.32	9.39	1,07	8.75	0,43	8.83	0,51
H13	7.49	8.56	1,07	7.74	0,25	7.80	0,31
H14	7.28	7.97	0,69	7.43	0,15	7.48	0,2
H15	7.49	8.51	1,02	7.69	0,2	7.76	0,27
H16	8.32	10.68	2,36	10.10	1,78	10.22	1,9
H17A	2.81	3.40	0,59	2.67	0,14	2.70	0,11
H17B	2.81	3.01	0,2	2.91	0,1	2.89	0,08
H17C	2.81	3.85	1,04	3.64	0,83	3.63	0,82
H18	7.08	8.72	1,64	7.71	0,63	7.77	0,69
H21	7.49	9.01	1,52	8.37	0,88	8.54	1,05
H23	7.08	7.87	0,79	7.24	0,16	7.30	0,22
H24	6.82	7.94	1,12	6.96	0,14	7.09	0,27
H27	7.08	8.17	1,09	7.43	0,35	7.61	0,53
H29A	6.01	5.89	0,12	6.07	0,06	5.92	0,09
H29B	6.01	6.40	0,39	6.43	0,42	6.30	0,29
	□		**0.90**		**0.39**		**0.44**

Table SI-4. Calculated and experimental ^{13}C chemical shift (ppm) values of compound **6**.

		M062X		TPSS		B3LYP	
Atom	**Experimental**	**Cal**	**Δx**	**Cal**	**Δx**	**Cal**	**Δx**
C1	150.16	169.49	19,33	150.01	0,15	157.21	7,05
C2	114.20	132.98	18,78	117.10	2,9	121.84	7,64
C3	143.36	165.46	22,1	144.59	1,23	151.96	8,6
C6	12.43	14.42	1,99	16.53	4,1	15.68	3,25
C7	139.28	161.53	22,25	142.04	2,76	148.71	9,43
C9	158.01	187.86	29,85	161.26	3,25	169.72	11,71
C10	128.72	150.34	21,62	128.74	0,02	134.82	6,1
C11	129.87	154.35	24,48	129.50	0,37	137.27	7,4
C12	120.60	138.52	17,92	118.08	2,52	123.86	3,26
C13	128.91	151.27	22,36	129.32	0,41	135.86	6,95
C14	125.57	146.14	20,57	124.57	1	130.66	5,09
C15	128.91	152.17	23,26	129.10	0,19	135.68	6,77
C16	120.60	139.68	19,08	118.70	1,9	124.43	3,83
C17	24.75	33.03	8,28	30.67	5,92	30.56	5,81
C18	125.34	141.67	16,33	121.23	4,11	126.87	1,53
C19	193.85	215.47	21,62	187.62	6,23	196.17	2,32
C21	145.77	173.37	27,6	147.45	1,68	156.97	11,2
C22	128.76	149.63	20,87	130.05	1,29	136.25	7,49
C23	123.97	150.86	26,89	130.30	6,33	136.93	12,96
C24	108.59	128.68	20,09	108.80	0,21	114.22	5,63
C25	148.41	171.00	22,59	153.11	4,7	159.17	10,76
C26	150.12	167.63	17,51	150.00	0,12	155.96	5,84
C27	106.53	123.09	16,56	103.55	2,98	109.43	2,9
C29	101.64	106.23	4,59	105.60	3,96	106.56	4,92
	□		**19.4**		**2.4**		**6.6**

Table SI-5. Cartesian coordinates of monomer optimized at M062X/6-311++g(d,p) level of theory.



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O	2.06653019	0.00000000	7.36614910
N	6.38985803	-1.85481766	-1.62879983
N	5.66305604	-1.05325576	-2.46217512
N	3.50736665	0.06652822	-2.36528812
C	4.47912063	-0.70135449	-1.86858728
C	4.47078378	-1.31215603	-0.60218529
C	5.71039431	-2.02342542	-0.52528450
C	6.23038506	-2.85368994	0.59942205
H	7.20261415	-3.26459676	0.33078559
H	5.54821327	-3.67793263	0.82046230
H	6.33942091	-2.25493832	1.50678316
C	6.19173136	-0.72744084	-3.74046521
C	2.44002463	0.24804516	-1.59770327
C	2.32689100	-0.31763064	-0.28764753
C	3.36149826	-1.09793309	0.20778576
H	3.29411316	-1.55413675	1.18992709
C	7.42028692	-1.27449972	-4.11692552
H	7.93961213	-1.93009079	-3.43326964
C	7.95459908	-0.96803624	-5.36048833
H	8.90783986	-1.39756166	-5.64529851
C	7.27968481	-0.12276476	-6.23547617
H	7.70103525	0.11205384	-7.20534697
C	6.05840085	0.41581721	-5.85007136
H	5.52027663	1.07542980	-6.52048041
C	5.50513507	0.12285112	-4.60821286
H	4.55583135	0.54387465	-4.31463495
C	1.35975975	1.11045870	-2.18897156
H	1.76484686	1.62266918	-3.05953214
H	0.98195028	1.83459423	-1.46656472
H	0.50769923	0.49667795	-2.48569252
C	1.23672889	-0.12213508	2.00793448
H	2.23592068	-0.07389695	2.42330354
C	1.08584231	-0.13379294	0.52747915
C	0.14559248	-0.12630484	2.78528560
H	-0.81407944	-0.15860573	2.27356697
C	0.09483242	-0.08906986	4.24593523
C	-1.15808550	-0.09259224	4.86383858
H	-2.04425444	-0.12332909	4.24070526
C	-1.30773807	-0.05394209	6.25568146
H	-2.28045651	-0.06241302	6.72872896
C	-0.15135851	-0.00720855	6.99548409
C	1.10658664	-0.00509443	6.39292586
C	1.26703601	-0.04674226	5.03498831
H	2.25680399	-0.04958665	4.59827253
C	1.37205941	0.31851579	8.56615951
H	1.46341879	1.39223077	8.76397420
H	1.76025277	-0.28489627	9.38298806

Table SI-6. Experimental and theoretical bond lengths (Å).

Distance	M062X	TPSS	B3LYP	Experimental
D (O20-C19)	1.215	1.238	1.225	1.231
D (O28-C25)	1.363	1.375	1.368	1.371
D (O28-C29)	1.425	1.447	1.436	1.434
D (O30-C26)	1.367	1.382	1.374	1.386
D (O30-C29)	1.423	1.441	1.432	1.430
D (N4-N5)	1.366	1.385	1.376	1.393
D (N4-C3)	1.307	1.326	1.314	1.323
D (N5-C1)	1.370	1.382	1.376	1.378
D (N5-C7)	1.421	1.427	1.423	1.426
D (N8-C1)	1.334	1.342	1.335	1.348
D (N8-C9)	1.327	1.343	1.334	1.342
D (C1-C2)	1.406	1.418	1.412	1.408
D (C2-C3)	1.431	1.433	1.432	1.434
D (C2-C11)	1.390	1.397	1.392	1.397
D (C3-C6)	1.492	1.498	1.494	1.500
D (C7-C12)	1.397	1.405	1.400	1.387
D (C7-C17)	1.395	1.405	1.400	1.377
D (C9-C10)	1.431	1.440	1.435	1.440
D (C9-C17)	1.503	1.509	1.506	1.512
D (C10-C11)	1.387	1.401	1.394	1.392
D (C10-C19)	1.496	1.500	1.499	1.504
D (C12-C13)	1.388	1.395	1.391	1.387
D (C13-C14)	1.391	1.400	1.394	1.370
D (C14-C15)	1.389	1.398	1.392	1.374
D (C15-C16)	1.391	1.398	1.393	1.394
D (C18-C19)	1.488	1.482	1.484	1.482
D (C18-C21)	1.340	1.357	1.348	1.339
D (C21-C22)	1.462	1.455	1.457	1.464
D (C22-C23)	1.397	1.412	1.405	1.396
D (C22-C27)	1.414	1.424	1.419	1.416
D (C23-C24)	1.400	1.404	1.401	1.399
D (C24-C25)	1.374	1.385	1.378	1.365
D (C25-C26)	1.395	1.401	1.396	1.390
D (C26-C27)	1.368	1.376	1.371	1.365

Table SI-7. Experimental and theoretical bond angles (°).

Bond angle	M062X	TPSS	B3LYP	Experimental
A(O20-C19- C10)	121.2	120.9	121.0	121.3
A(O20- C19- C18)	121.5	121.6	121.6	119.6
A(C25-O28- C29)	105.0	104.9	105.5	105.7
A(O28- C25- C24)	129.0	128.3	128.7	128.5
A(O28- C25- C26)	109.2	109.8	109.6	110.4
A(O28- C29- O30)	107.0	107.4	107.2	108.3
A(C26-O30- C29)	105.0	104.9	105.5	105.9
A(O30- C26- C25)	109.0	109.5	109.3	109.1
A(O30- C26- C27)	128.6	128.1	128.4	127.9
A(N5- N4-C3)	108.3	107.7	108.2	107.5
A(N4- N5-C1)	110.3	110.2	110.0	110.0
A(N4- N5-C7)	119.0	118.8	119.0	118.4
A(N4- C3-C2)	109.9	110.2	110.0	110.3
A(N4- C3-C6)	121.8	120.7	121.3	121.2
A(C1- N5- C7)	130.7	131.0	130.9	131.6
A(N5- C1-N8)	128.0	127.6	128.1	127.3
A(N5- C1- C2)	106.5	106.5	106.6	106.9
A(N5- C7-C12)	118.7	118.8	119.0	119.2
A(N5- C7-C16)	121.1	120.9	121.1	121.3
A(C1- N8-C9)	116.7	116.5	117.1	116.0
A(N8- C1- C2)	125.5	125.9	125.3	125.8
A(N8- C9- C10)	122.6	122.6	122.4	123.2
A(C1- C2- C3)	105.0	105.3	105.2	105.4
A(C1- C2-C11)	117.6	117.1	117.4	117.3
A(C3- C2- C11)	137.4	137.6	137.4	137.2
A(C2- C3- C6)	128.3	129.1	128.7	128.6
A(C2- C11- C10)	118.3	118.7	118.8	119.1
A(C12- C7- C16)	120.3	120.3	120.0	119.5
A(C7- C12-C13)	119.6	119.5	119.7	120.2
A(C7- C16-C15)	119.2	119.2	119.4	119.5
A(C10- C9-C17)	122.0	122.5	122.4	122.7
A(C9- C10- C11)	119.4	119.1	119.0	118.6
A(C9- C10- C19)	121.0	121.3	121.4	121.6
A(C11- C10- C19)	119.5	119.5	119.6	119.7
A(C10- C19- C18)	117.3	117.6	117.5	119.0
A(C12- C13-C14)	120.7	120.8	120.8	120.4
A(C13- C14- C15)	119.2	119.2	119.1	119.4
A(C14- C15- C16)	121.0	121.0	121.0	121.0
A(C19- C18-C21)	119.6	120.2	120.5	121.9
A(C18- C21- C22)	127.4	128.0	128.1	127.9
A(C21-C22-C23)	118.2	118.1	118.2	118.6
A(C21- C22- C27)	122.0	122.5	122.5	122.1
A(C23- C22- C27)	119.8	119.4	119.3	119.3
A(C22- C23- C24)	122.4	122.6	122.5	122.5
A(C22-C27- C26)	117.2	117.3	117.5	117.1
A(C23- C24- C25)	116.5	116.5	116.7	117.1
A(C24 - C25- C26)	121.8	121.8	121.7	121.1
A(C25- C26- C27)	122.3	122.4	122.3	123.0

Table SI-8. Experimental dihedral Angles (°).

A	B	C	D	Angle	A	B	C	D	Angle
O28	C25	C26	O30	-0.4(3)	C9	C10	C19	C18	-163.4(2)
O28	C25	C26	C27	178.9(2)	C11	C2	C3	N4	177.1(2)
O30	C26	C27	C22	-179.7(2)	C11	C2	C3	C6	-2.9(4)
N4	N5	C1	N8	179.99(19)	C11	C10	C19	O20	-156.4(2)
N4	N5	C1	C2	0.7(2)	C11	C10	C19	C18	20.7(3)
N4	N5	C7	C12	-1.5(3)	C12	C7	C16	C15	0.2(4)
N4	N5	C7	C16	179.0(2)	C12	C13	C14	C15	-0.2(5)
N5	N4	C3	C2	-0.3(2)	C13	C14	C15	C16	-0.2(5)
N5	N4	C3	C6	179.8(2)	C14	C15	C16	C7	0.2(5)
N5	C1	C2	C3	-0.8(2)	C16	C7	C12	C13	-0.6(4)
N5	C1	C2	C11	-178.11(17)	C17	C9	C10	C11	-176.9(2)
N5	C7	C12	C13	179.8(2)	C17	C9	C10	C19	7.1(3)
N5	C7	C16	C15	179.8(3)	C18	C21	C22	C23	-179.8(2)
N8	C1	C2	C3	179.9(2)	C18	C21	C22	C27	-1.6(4)
N8	C1	C2	C11	2.6(3)	C19	C10	C11	C2	175.00(19)
N8	C9	C10	C11	1.1(3)	C19	C18	C21	C22	176.1(2)
N8	C9	C10	C19	-174.81(19)	C21	C18	C19	O20	-0.9(4)
C1	N5	C7	C12	-178.0(2)	C21	C18	C19	C10	-178.0(2)
C1	N5	C7	C16	2.4(4)	C21	C22	C23	C24	178.5(2)
C1	N8	C9	C10	0.6(3)	C21	C22	C27	C26	-178.9(2)
C1	N8	C9	C17	178.8(2)	C22	C23	C24	C25	-0.1(3)
C1	C2	C3	N4	0.7(2)	C23	C22	C27	C26	-0.7(3)
C1	C2	C3	C6	-179.4(2)	C23	C24	C25	O28	-179.5(2)
C1	C2	C11	C10	-0.6(3)	C23	C24	C25	C26	0.4(4)
C3	N4	N5	C1	-0.3(2)	C24	C25	C26	O30	179.7(2)
C3	N4	N5	C7	-177.54(19)	C24	C25	C26	C27	-1.0(4)
C3	C2	C11	C10	-176.8(2)	C25	O28	C29	O30	-7.2(3)
C7	N5	C1	N8	-3.2(4)	C25	C26	C27	C22	1.1(4)
C7	N5	C1	C2	177.5(2)	C26	O30	C29	O28	7.0(3)
C7	C12	C13	C14	0.6(4)	C27	C22	C23	C24	0.3(3)
C9	N8	C1	N5	178.3(2)	C29	O28	C25	C24	-175.4(3)
C9	N8	C1	C2	-2.5(3)	C29	O28	C25	C26	4.7(3)
C9	C10	C11	C2	-1.0(3)	C29	O30	C26	C25	-4.1(3)
C9	C10	C19	O20	19.4(3)	C29	O30	C26	C27	176.6(3)

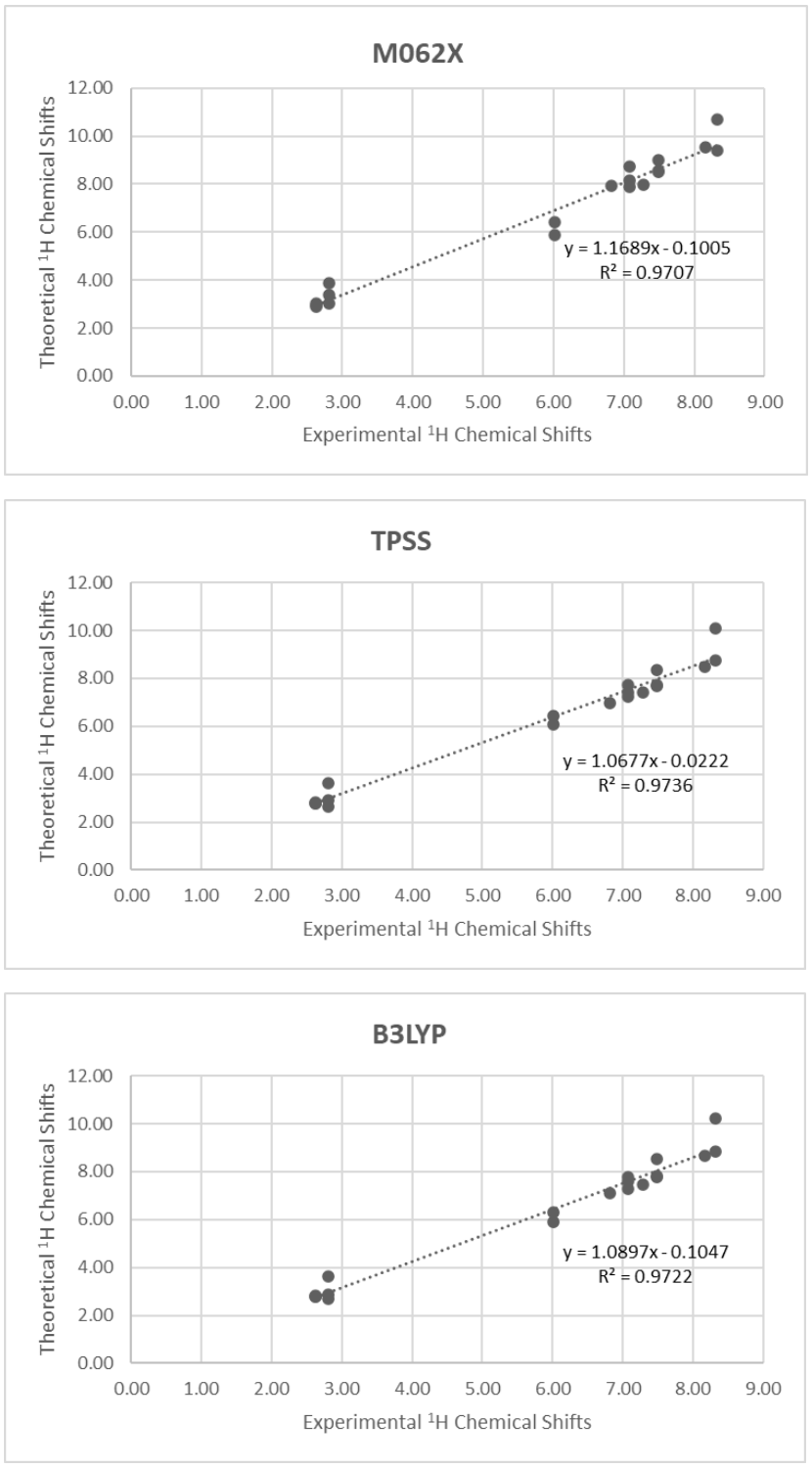

Figure SI-5. Correlation graphs between experimental and theoretical ^{1}H NMR chemical shift values of the title compound.

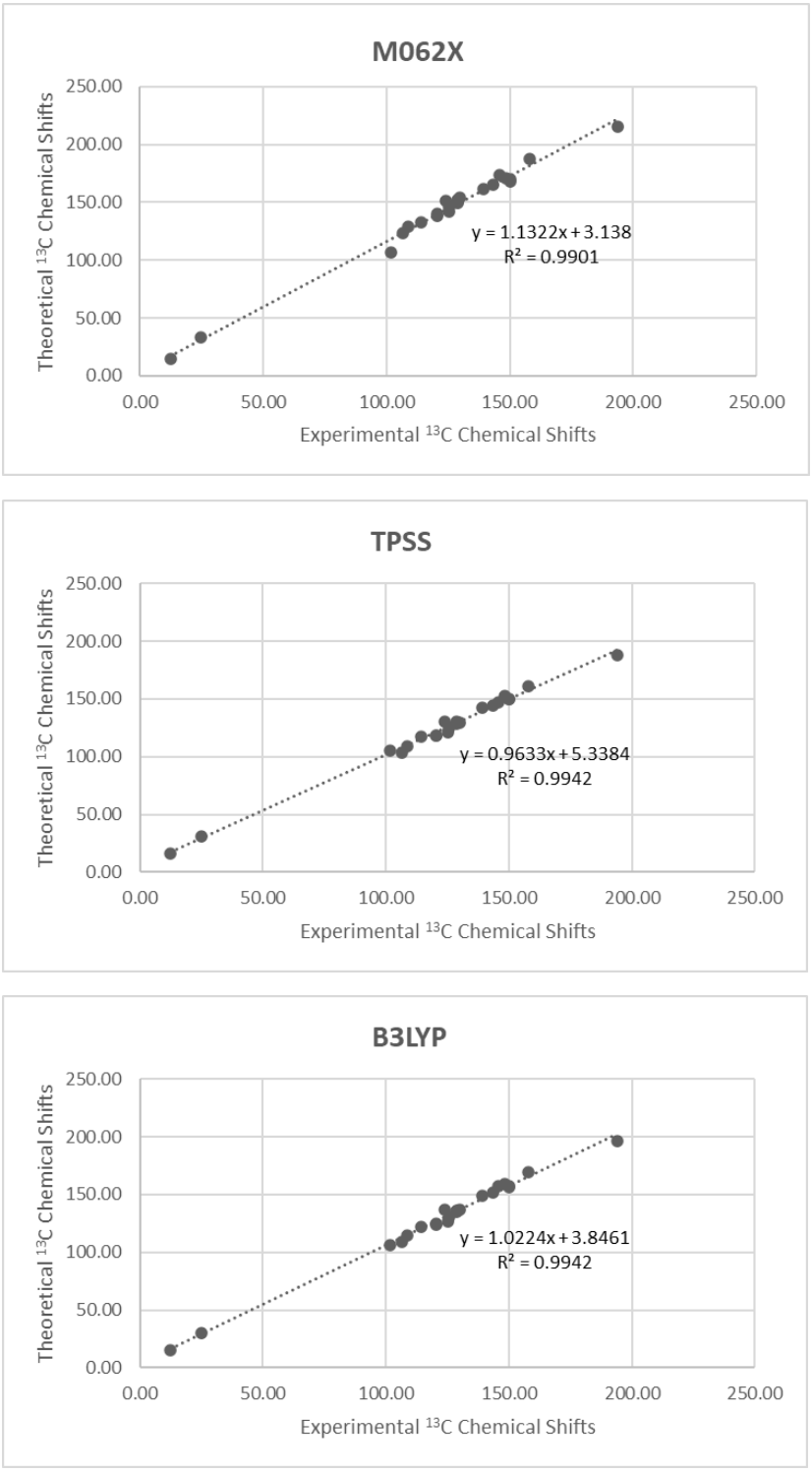

Figure SI-6. Correlation graphs between experimental and theoretical ^{13}C NMR chemical shift values of the title compound.

Table SI-9. Dipole moment, polarizability, and hyperpolarizability values obtained at CAM-B3LYP/6-311++g(d,p) level of theory.

Title compound

Dipole moment (Debye)

μx	μy	μz	μ
-4,237100	-2,530250	0,845993	5,007

polarizability (10**-24 esu)

αxx	αxy	αyy	αxz	αyz	αzz	<α>
79,269500	0,103276	46,703700	2,275300	0,294936	26,510400	50,827867

hyperpolarizability (10**-30 esu)

βxxx	βxxy	βyxy	βyyy	βxxz	βyxz	βyyz	βzxz	βzyz	βzzz	<β>
19,689400	17,495600	0,102002	0,453853	-2,402840	-0,282915	-0,798313	0,804725	0,212376	0,599606	27,4642393

Second dipole hyperpolarizability (10**-36 esu)

Υxxxx	Υxxyx	Υxxyy	Υyxyy	Υyyyy	Υxxzx	Υxxzy	Υyxzy	Υyyzy	Υxxzz	Υyxzz	Υyyzz	Υzxzz	Υzyzz	Υzzzz	<Υ>
502,871000	17,556800	43,325000	-3,849380	29,559200	-6,054570	-6,105900	-0,925067	0,532152	15,850000	0,393220	7,578540	0,570437	0,351177	21,059000	137,39926

UREA

Dipole moment (Debye)

μx	μy	μz	μ
0,000184	-3,875030	0,000000	3,875

polarizability (10**-24 esu)

αxx	αxy	αyy	αxz	αyz	αzz	<α>
5,250520	-0,000141	5,695470	0,044968	0,000099	3,548960	4,83165

hyperpolarizability (10**-30 esu)

βxxx	βxxy	βyxy	βyyy	βxxz	βyxz	βyyz	βzxz	βzyz	βzzz	<β>
-0,000030	0,432433	0,000151	-0,572009	0,000032	0,024244	-0,000054	0,000037	-0,273526	0,000063	0,41381331

Second dipole hyperpolarizability ((10**-36 esu))

Υxxxx	Υxxyx	Υxxyy	Υyxyy	Υyyyy	Υxxzx	Υxxzy	Υyxzy	Υyyzy	Υxxzz	Υyxzz	Υyyzz	Υzxzz	Υzyzz	Υzzzz	<Υ>
4,361840	-0,000168	1,401950	-0,000194	2,108040	0,060824	0,000063	-0,076203	0,000197	0,760435	-0,000020	0,778058	-0,104961	0,000000	2,356410	2,9414352