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Synthesis of Unexpected Dimethyl 2-(4-Chlorophenyl)-2,3-Dihydropyrrolo[2 ,1-*a*]Isoquinoline-1,3-Dicarboxylate via Hydrolysis/Cycloaddition/Elimination Cascades: Single Crystal X-Ray and Chemical Structure Insights

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Supplementary data

1. X-Ray single crystal measurements of 3

The crystal of **3** was immersed in cryo-oil, mounted in a loop, and measured at a temperature of 120 K. The X-ray diffraction data was collected on a Rigaku Oxford Diffraction Supernova diffractometer using Mo Kα radiation. The *CrysAlisPro* [1] software package was used for cell refinement and data reduction. A multi-scan absorption correction (*CrysAlisPro* [1]) was applied to the intensities before structure solution. The structure was solved by intrinsic phasing (*SHELXT* [2]) method. Structural refinement was carried out using *SHELXL* [3] software with *SHELXLE* [4] graphical user interface. Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.95-1.00 Å and U_{iso} = 1.2-1.5· U_{eq}(parent atom).

2. Hirshfeld surface analysis

The topology analyses were performed using Crystal Explorer 17.5 program [5].

3. Computational methods

All DFT calculations were performed using Gaussian 09 software package [6] utilizing B3LYP/6-31G(d,p) method. Natural charge calculations were performed using NBO 3.1 program as implemented in the Gaussian 09W package [7]. The self-consistent reaction filed (SCRF) method [8, 9] was used to model the solvent effects when calculated the optimized geometries in solution. Then the NMR chemical shifts for the protons and carbons were computed using GIAO method [10]. Also, the UV-Vis electronic spectra of the compound were calculated using TD-DFT method.

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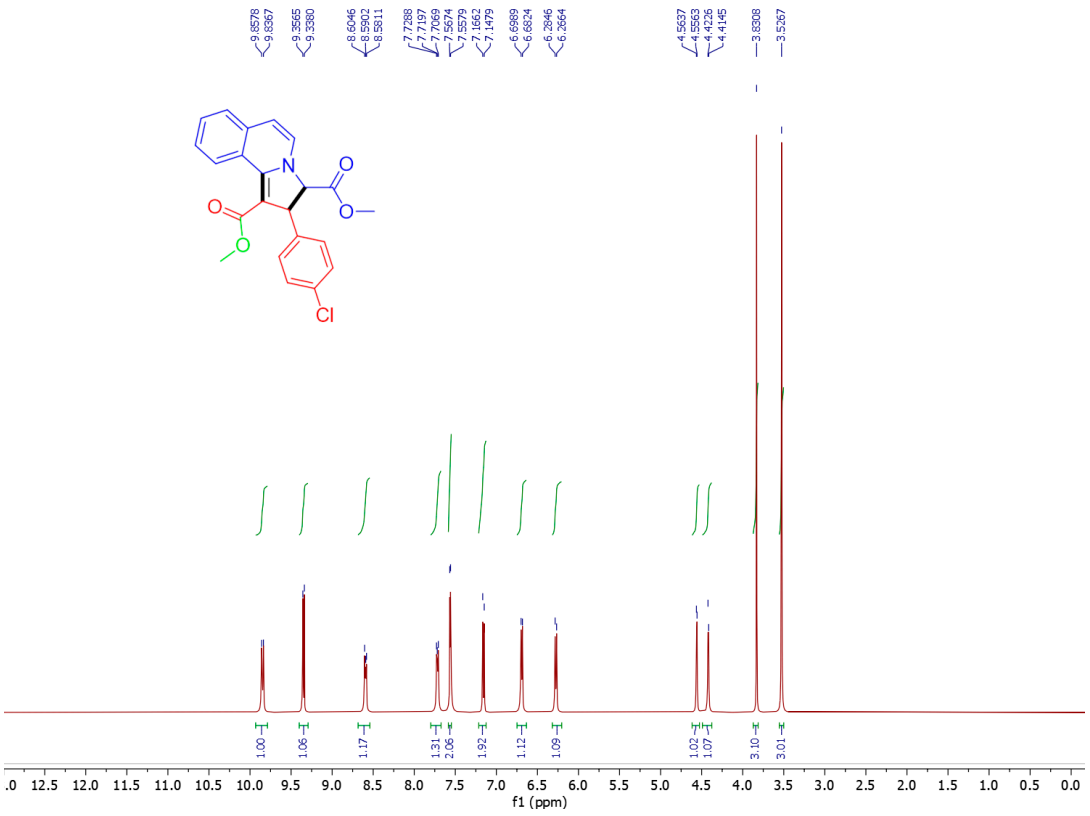

Figure S1. [1]HNMR spectrum for the synthesized compound **3.**

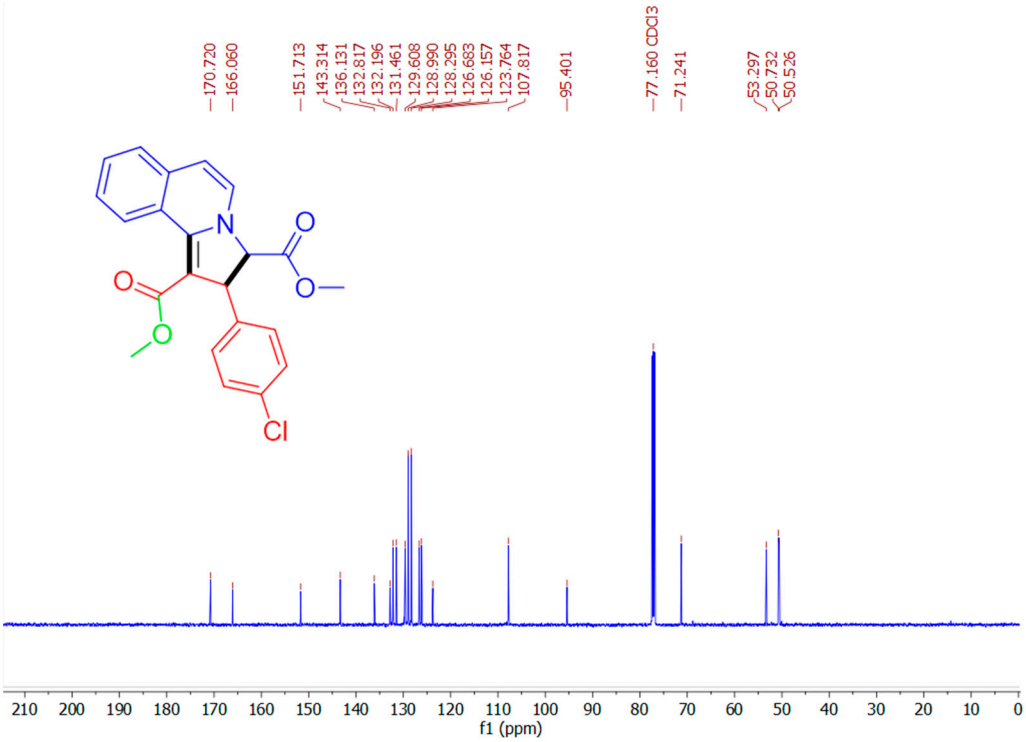

Figure S2. ^{13}C-NMR spectrum for the synthesized compound **3.**

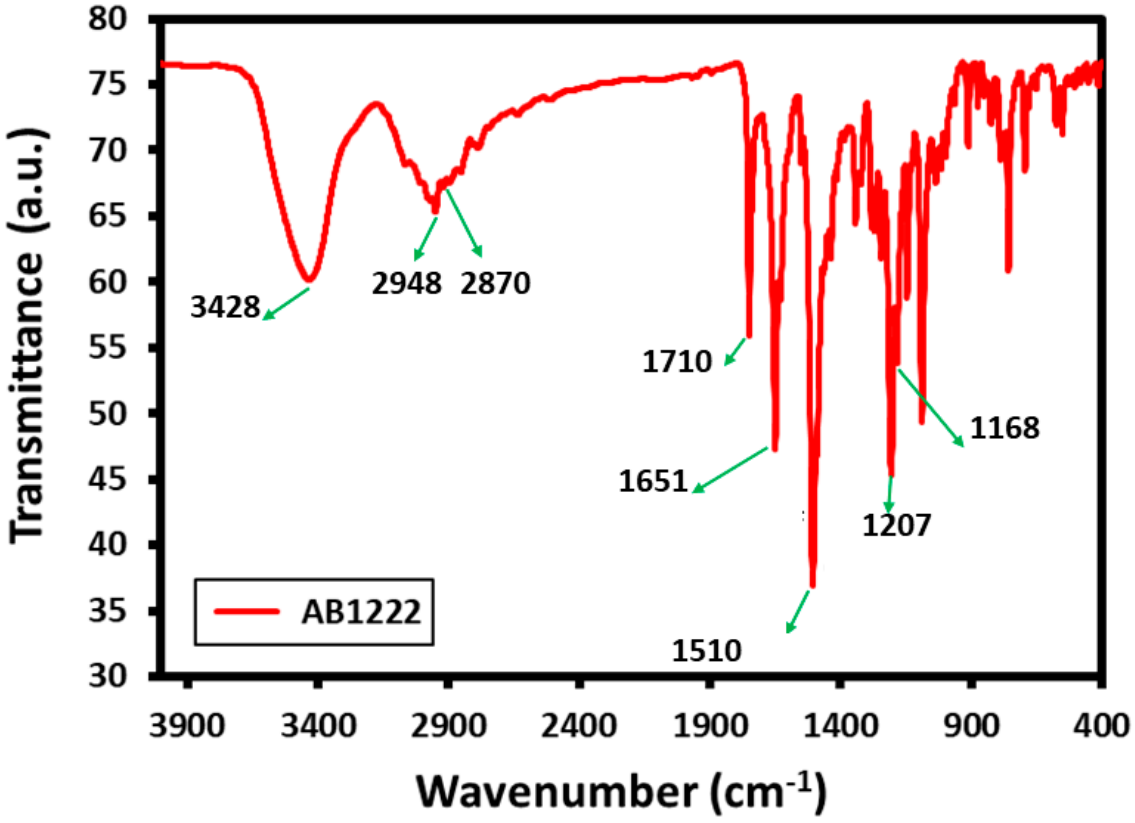

Figure S3. IR spectrum for the synthesized compound **3.**

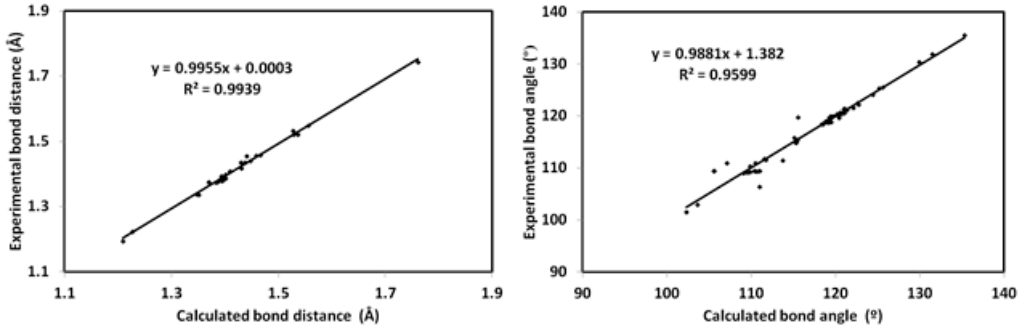

Figure S4. Correlations between the optimized and experimental geometric parameters.

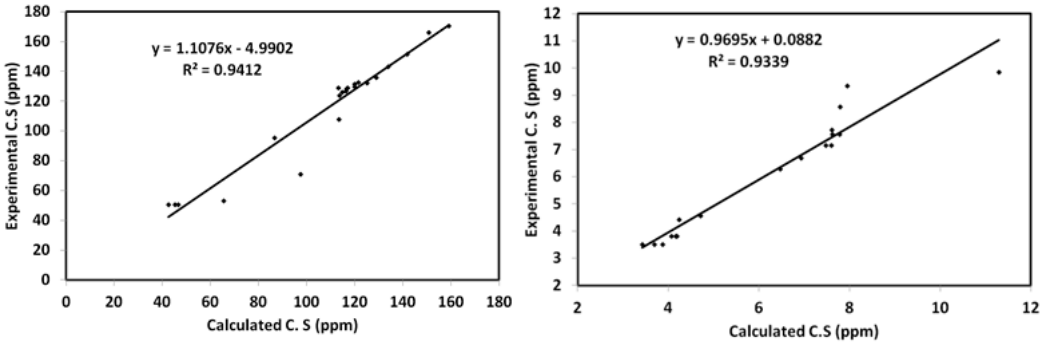

Figure S5. ^{1}H and ^{13}C NMR correlations between the calculated and experimental data.

Table S1. The calculated geometric parameters of **3**[a].

Parameter	Calc	Exp	Parameter	Calc	Exp
R(1-11)	1.761	1.743	A(1-11-9)	119.549	119.759
R(2-21)	1.347	1.338	A(1-11-12)	119.478	118.831
R(2-22)	1.441	1.455	A(21-2-22)	115.398	114.87
R(3-21)	1.209	1.194	A(2-21-3)	124.459	124.117
R(4-42)	1.372	1.37	A(2-21-19)	109.878	110.346
R(4-43)	1.43	1.436	A(2-22-23)	110.381	109.463
R(5-42)	1.227	1.223	A(2-22-24)	105.586	109.477
R(6-19)	1.458	1.457	A(2-22-25)	110.427	109.487
R(6-26)	1.37	1.376	A(3-21-19)	125.628	125.537
R(6-40)	1.397	1.382	A(42-4-43)	115.091	115.807
R(7-9)	1.395	1.387	A(4-42-5)	120.205	120.337
R(7-16)	1.399	1.39	A(4-42-41)	109.88	109.237
R(9-11)	1.393	1.386	A(4-43-44)	111.022	109.46
R(11-12)	1.394	1.378	A(4-43-45)	110.992	109.471
R(12-14)	1.394	1.392	A(4-43-46)	105.605	109.457
R(14-16)	1.401	1.387	A(5-42-41)	129.912	130.406
R(16-17)	1.528	1.521	A(42-5-38)	110.981	106.378
R(17-19)	1.556	1.549	A(19-6-26)	122.772	122.191
R(17-41)	1.527	1.532	A(19-6-40)	111.755	111.585
R(19-21)	1.536	1.522	A(6-19-17)	103.633	103.008
R(26-28)	1.351	1.336	A(6-19-20)	110.51	110.913
R(28-30)	1.438	1.436	A(6-19-21)	110.708	109.296
R(30-31)	1.409	1.408	A(26-6-40)	125.161	125.365
R(30-39)	1.431	1.418	A(6-26-27)	115.58	119.782

R(31-33)	1.384	1.373	A(6-26-28)	120.746	120.436
R(33-35)	1.401	1.398	A(6-40-39)	115.517	115.382
R(35-37)	1.387	1.377	A(6-40-41)	109.152	109.022
R(37-39)	1.41	1.408	A(9-7-16)	121.123	121.361
R(39-40)	1.466	1.458	A(7-9-11)	119.199	118.718
R(40-41)	1.393	1.393	A(7-16-14)	118.386	118.42
R(41-42)	1.448	1.441	A(7-16-17)	122.142	121.617
			A(9-11-12)	120.973	121.409
			A(11-12-14)	118.972	118.859
			A(12-14-16)	121.348	121.225
			A(14-16-17)	119.426	119.931
			A(16-17-19)	111.557	111.808
			A(16-17-41)	115.261	114.88
			A(19-17-41)	102.309	101.563
			A(17-19-21)	113.722	111.505
			A(17-41-40)	109.589	109.12
			A(17-41-42)	118.922	118.947
			A(20-19-21)	107.111	110.937
			A(26-28-30)	119.337	119.376
			A(28-30-31)	120.35	119.924
			A(28-30-39)	120.399	120.411
			A(31-30-39)	119.25	119.664
			A(30-31-33)	121.059	120.558
			A(30-39-37)	118.532	118.463
			A(30-39-40)	118.813	118.989
			A(31-33-35)	119.736	119.958
			A(33-35-37)	120.54	120.677
			A(35-37-38)	120.427	119.645
			A(35-37-39)	120.882	120.656
			A(37-39-40)	122.649	122.54
			A(39-40-41)	135.314	135.578
			A(40-41-42)	131.489	131.925

[a]Atom numbering refer to **Fig. 1 (main text)**

Table S2. The calculated natural charges of **3**[a].

Atom		Charge	Atom		Charge	Atom		Charge
Cl	1	-0.0116	C	17	-0.2659	H	32	0.2386
O	2	-0.5501	H	18	0.2848	C	33	-0.2110
O	3	-0.5817	C	19	-0.1311	H	34	0.2420
O	4	-0.5606	H	20	0.2817	C	35	-0.2435
O	5	-0.6441	C	21	0.8257	H	36	0.2439
N	6	-0.3782	C	22	-0.3350	C	37	-0.1877
C	7	-0.2191	H	23	0.2279	H	38	0.2835
H	8	0.2531	H	24	0.2301	C	39	-0.0850
C	9	-0.2445	H	25	0.2252	C	40	0.2655
H	10	0.2566	C	26	0.0261	C	41	-0.2553
C	11	-0.0454	H	27	0.2443	C	42	0.7894
C	12	-0.2468	C	28	-0.2927	C	43	-0.3292
H	13	0.2554	H	29	0.2498	H	44	0.2188
C	14	-0.2187	C	30	-0.0281	H	45	0.2203

	H	15	0.2445	C	31	-0.2294	H	46	0.2210
	C	16	-0.0336						

[a]Atom numbering refer to **Fig. 1(main text)**

Table S3. The calculated chemical shifts of **3**[a].

Atom		Calc	Exp.	Atom		Calc	Exp.
C	7	114.704	126.16	H	8	7.625	7.567
C	9	116.527	128.29	H	10	7.468	7.166
C	11	128.952	136.13	H	13	7.594	7.166
C	12	116.349	126.68	H	15	7.783	7.567
C	14	116.903	128.99	H	18	4.709	4.563
C	16	133.897	143.31	H	20	4.231	4.422
C	17	46.509	50.73	H	23	4.183	3.830
C	19	65.454	53.30	H	24	4.067	3.830
C	21	158.992	170.72	H	25	4.161	3.830
C	22	45.158	50.53	H	27	6.926	6.698
C	26	119.934	131.46	H	29	6.469	6.284
C	28	97.401	71.24	H	32	7.610	7.728
C	30	125.092	132.20	H	34	7.947	9.356
C	31	113.677	123.76	H	36	7.790	8.590
C	33	119.886	129.61	H	38	11.291	9.857
C	35	113.440	107.82	H	44	3.867	3.526
C	37	121.496	132.82	H	45	3.688	3.526
C	39	113.132	128.99	H	46	3.419	3.526
C	40	141.698	151.71				
C	41	86.573	95.40				
C	42	150.796	166.06				
C	43	42.543	50.53				

[a]Atom numbering refer to **Fig. 1(main text)**