

Supplementary Information

Experimental and DFT mechanistic insights on one-pot synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones under catalysis of DBU-based ionic liquids

Sara Fallah-Ghasemi Gildeh, Morteza Mehrdad,* Hossein Roohi, Khaterreh Ghauri, Sahar Fallah-Ghasemi Gildeh, and Kurosh Rad-Moghadam*

E-mail addresses: radmm@guilan.ac.ir (K. Rad-Moghadam); mehrdad@guilan.ac.ir (M. Mehrdad).

List of Contents

1. The optimized structures of [Bn-DBU][OAc] and [Bn-DBU][TFA] at B3LYP/SVP level of theory in gas phase	S1
2. The FT-IR spectra of the two synthesized DBU-based ILs, [Bn-DBU][CH ₃ CO ₂] and [Bn-DBU][CF ₃ CO ₂].....	S2
3. The H NMR spectra of the two synthesized DBU-based ILs, (1) [Bn-DBU][CH ₃ CO ₂] and [Bn-DBU][CF ₃ CO ₂].....	S3
4. The EDX spectra of fresh [Bn-DBU][TFA] (up) and [Bn-DBU][TFA] after 4 th recycling (below).....	S4
5. H NMR spectra of the some synthesized 1 <i>H</i> -pyrazolo[1,2- <i>b</i>]phthalazine-5,10-diones.....	S5
6. The optimized structures of the compounds (1), (2f), (3) and (4f) using DFT at B3LYP/SVP level of theory in gas phase for synthesis of 4f	S6
7. The optimized structures of the mechanistic proposal for the synthesis of 4f at B3LYP/SVP level theory in gas phase.....	S7
8. The optimized structures for synthesis of 4f with mechanism proposed at B3LYP/SVP level of theory in gas phase.....	S8

9. The approach of 5 to phthalhydrazide in its complexes with [Bn-DBU][AcO] and [Bn-DBU][TFA] ILs at B3LYP/SVP level of theory in gas phase.....S9

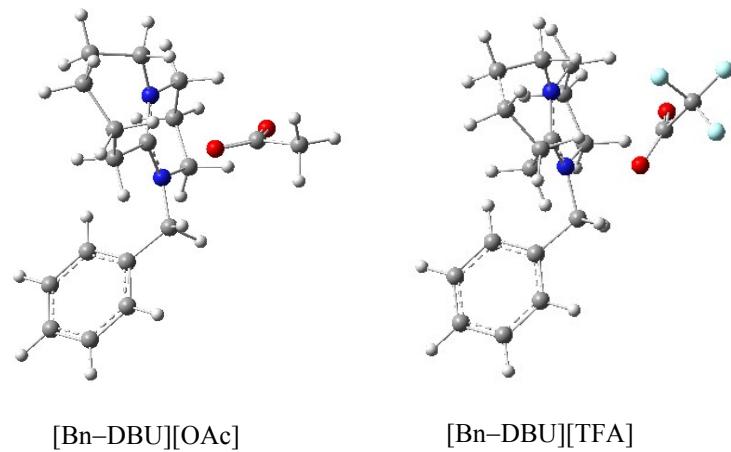


Fig. S1 The optimized structures of [Bn-DBU][OAc] and [Bn-DBU][TFA] at B3LYP/SVP level of theory in gas phase.

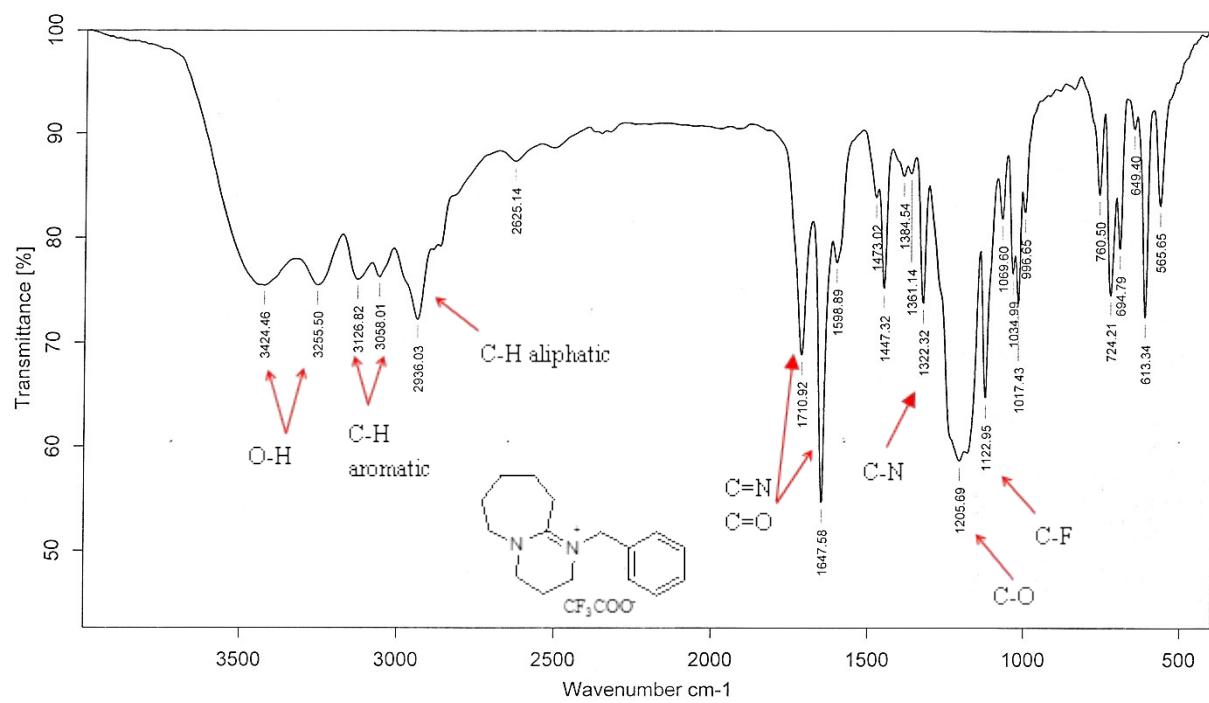
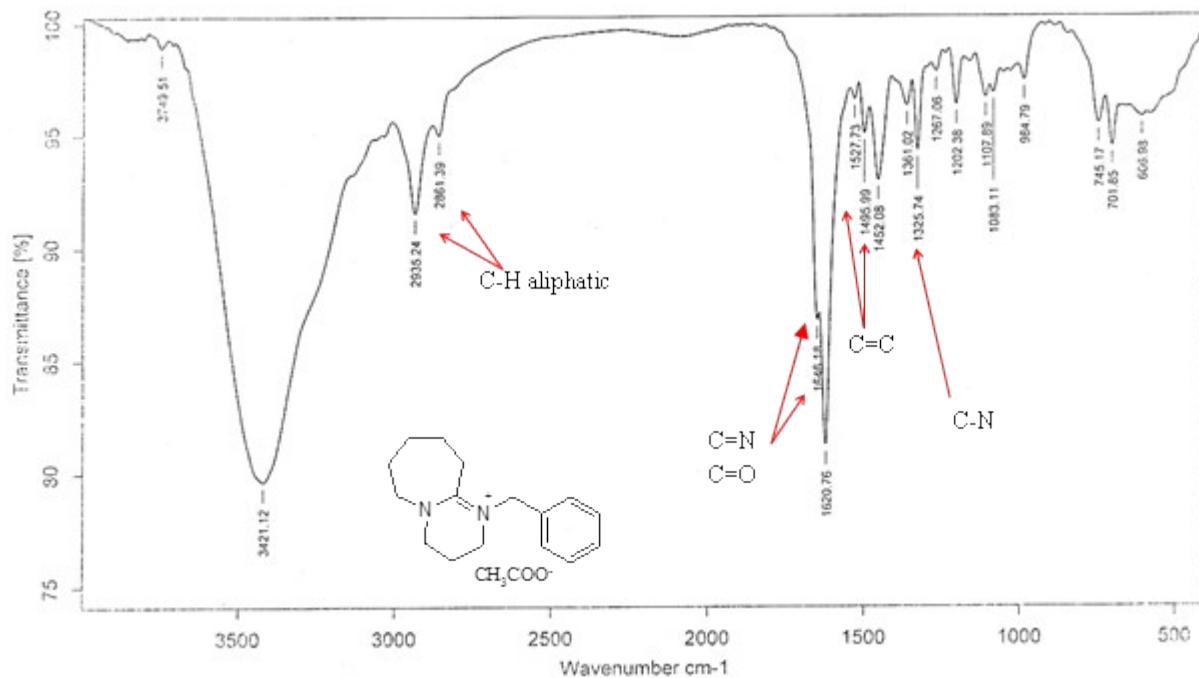
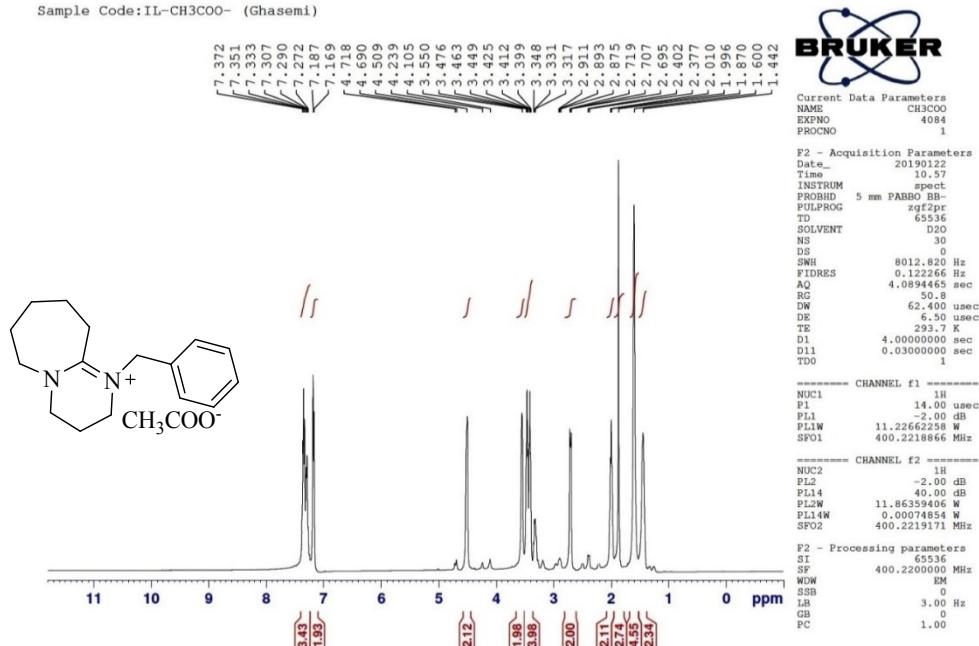


Fig. S2 The FT-IR spectra of the two synthesized DBU-based ILs, [Bn-DBU][CH₃CO₂] (up) [Bn-DBU][CF₃CO₂] (below).

Sample Code: IL-CH₃COO- (Ghasemi)



IL-CF₃-H
new experiment

Parameter	Value
1 Data File Name	D:\NMR\1397\07\09/ 97-09-20\97-09-20 fahlgasemri\IL-CF3-H.fid\fid
2 Title	IL-CF ₃ -H
3 Comment	new experiment
4 Origin	Varian
5 Owner	
6 Site	
7 Instrument	inova
8 Author	
9 Solvent	d2o
10 Temperature	23.0
11 Pulse Sequence	spdpd
12 Experiment	1D
13 Probe	ID
14 Number of Scans	8
15 Receiver Gain	30
16 Relaxation Delay	1.0000
17 Pulse Width	5.0000
18 Presaturation	
19 Frequency	
20 Acquisition Time	2.0492
21 Acquisition Date	2018-12-11T17:27:48
21 Modification Date	2018-12-11T17:28:12
22 Class	
23 Spectrometer Frequency	499.72
24 Spectral Width	7995.2
25 Lowest Frequency	-999.2
26 Nucleus	¹ H
27 Acquired Size	16384
28 Spectral Size	65536

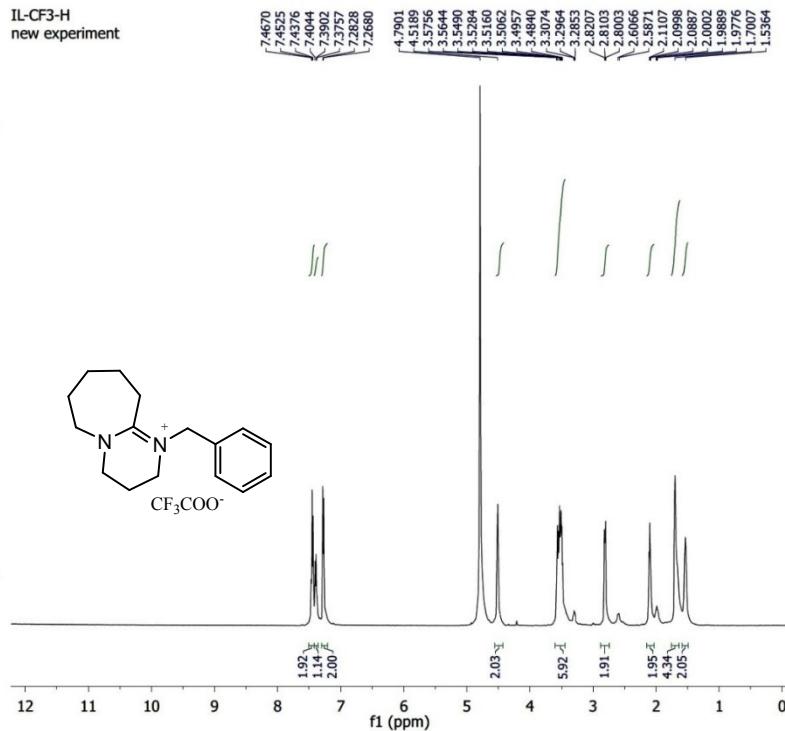
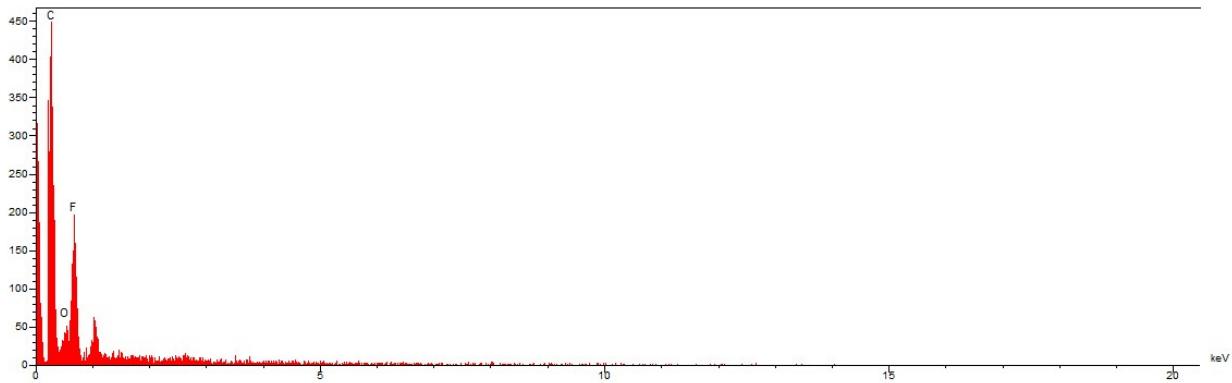
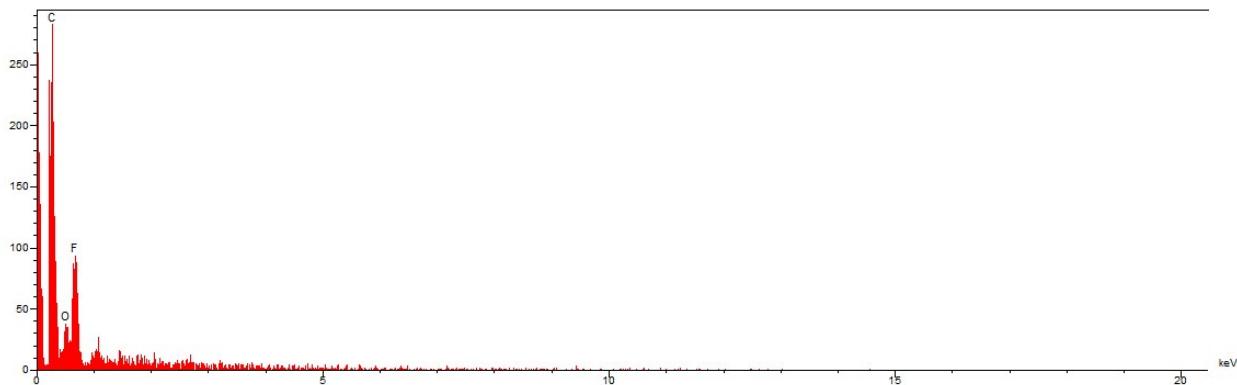


Fig. S3 The H NMR spectra of the two synthesized DBU-based ILs, (up) [Bn-DBU][CH₃CO₂], (below) [Bn-DBU][CF₃CO₂]

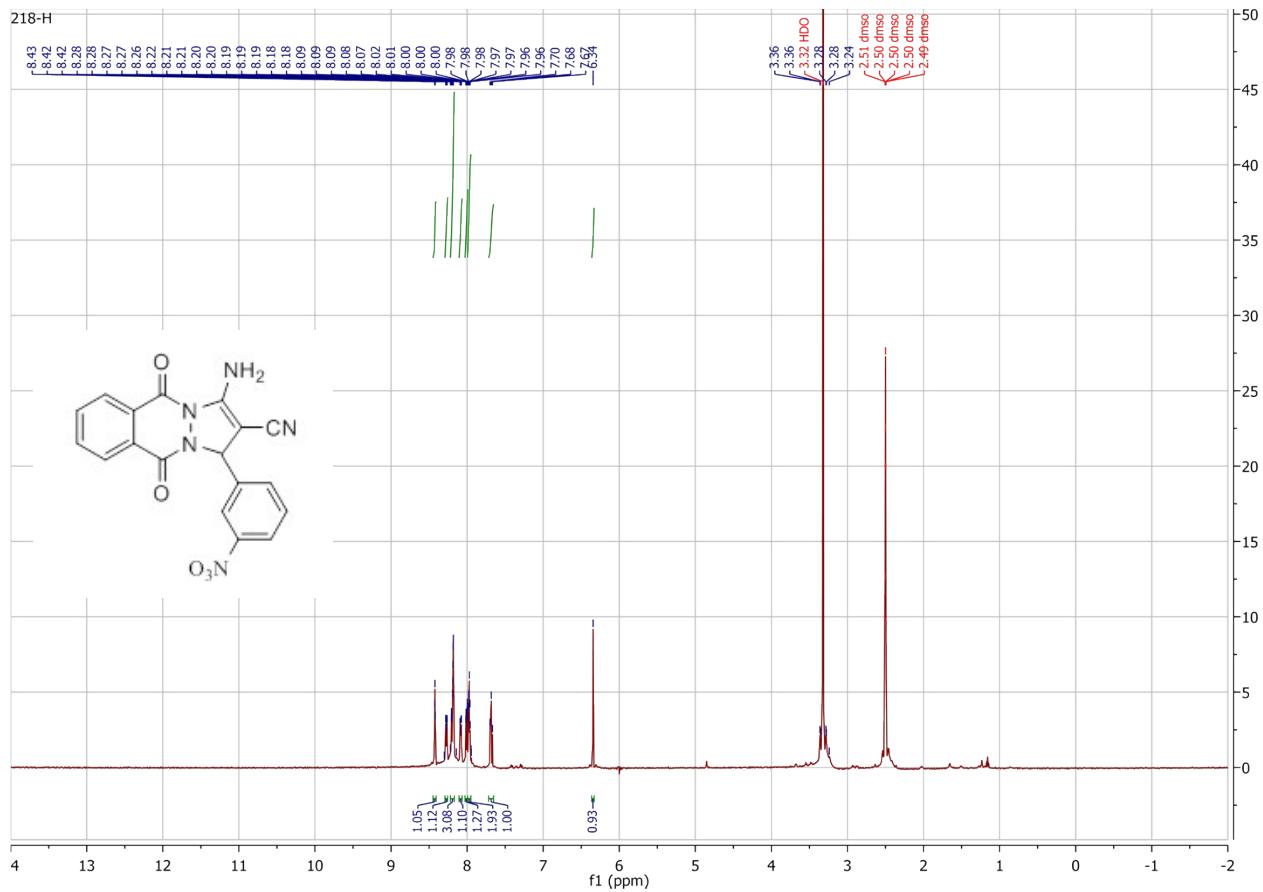


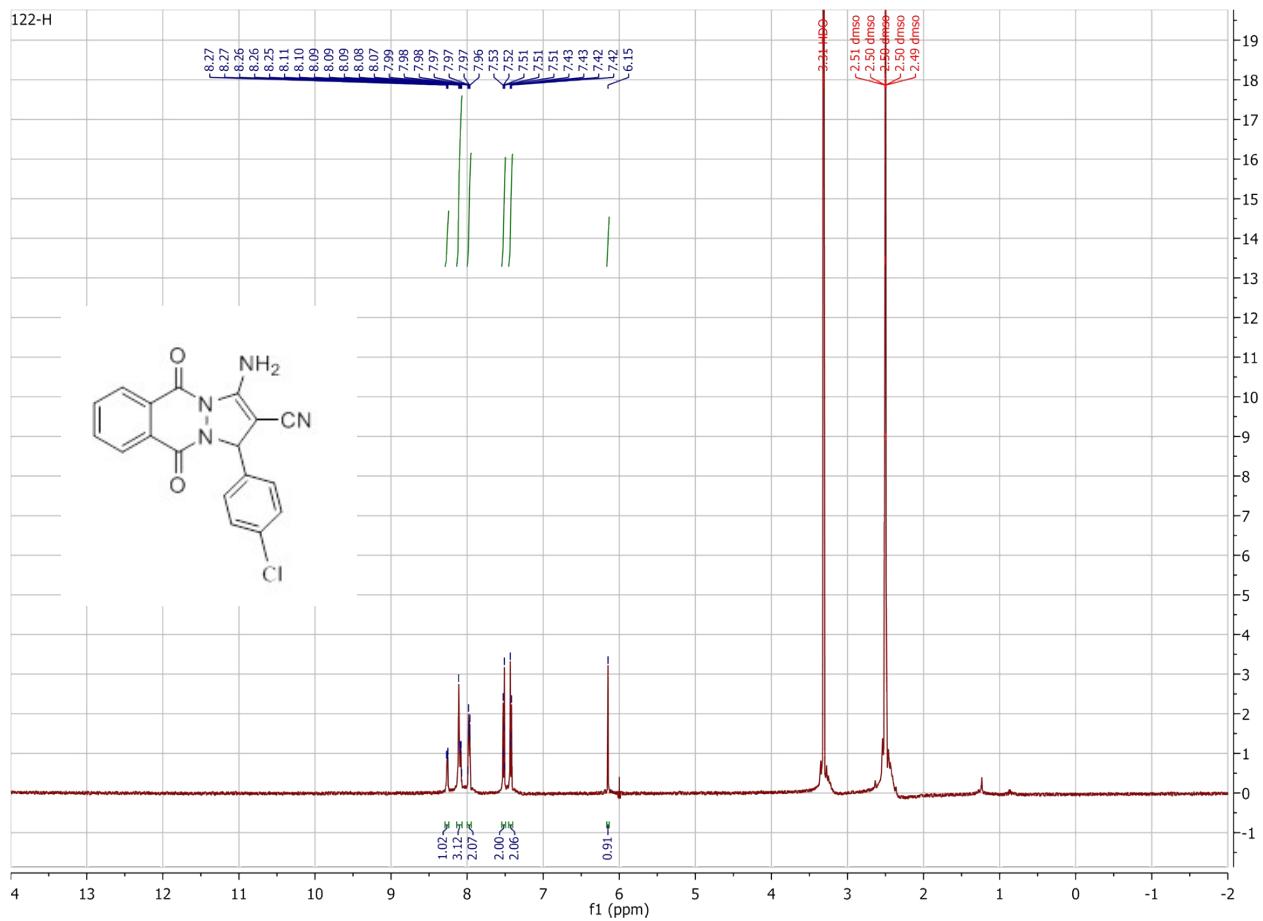
Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg	Class	LConf	HConf	Cat#
C	Ka	212.8	37.4548	0.8124	0.3900	64.16	72.74	0.6077		0.00	127.02	A	61.74	66.58	0.00
O	Ka	26.2	37.4548	0.0498	0.0239	11.73	9.98	0.2039		0.00	21.70	A	10.47	12.99	0.00
F	Ka	104.0	37.4548	0.1378	0.0661	24.11	17.28	0.2743		0.00	47.11	A	22.81	25.41	0.00
				1.0000	0.4800	100.00	100.00			0.00					0.00

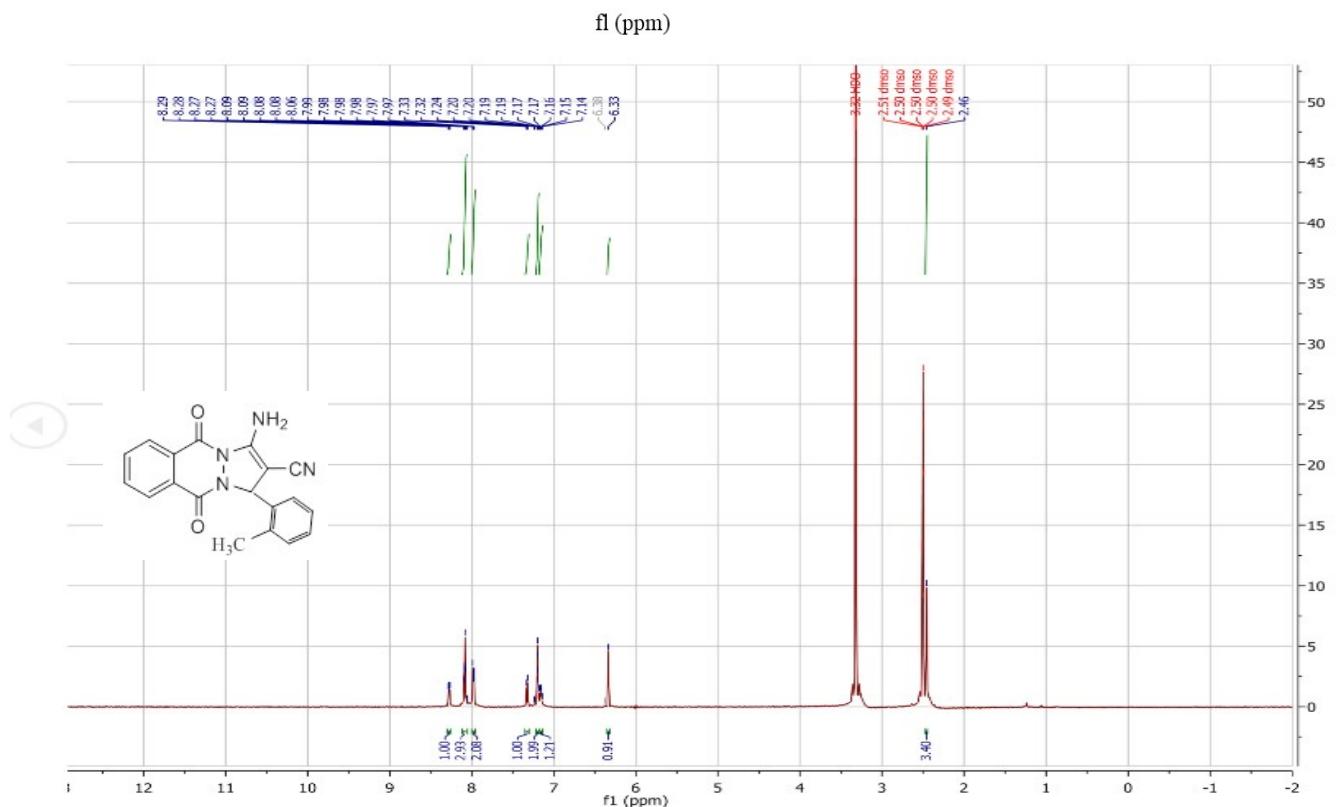


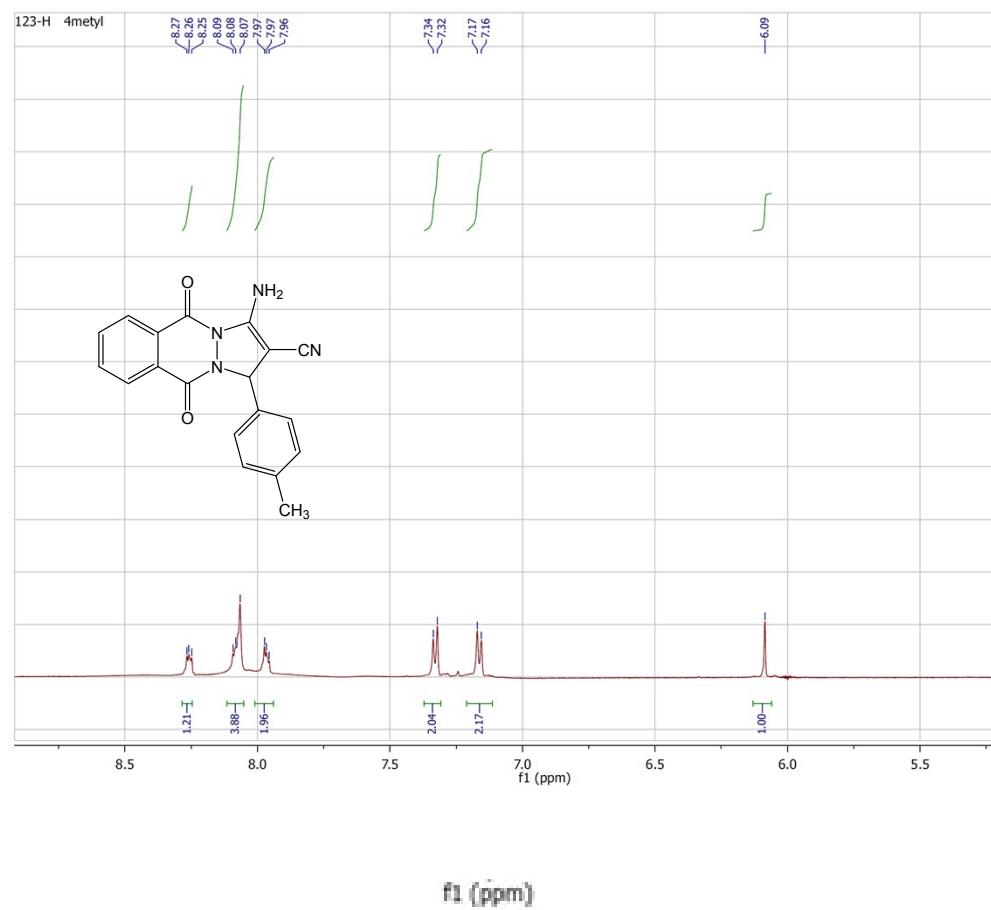
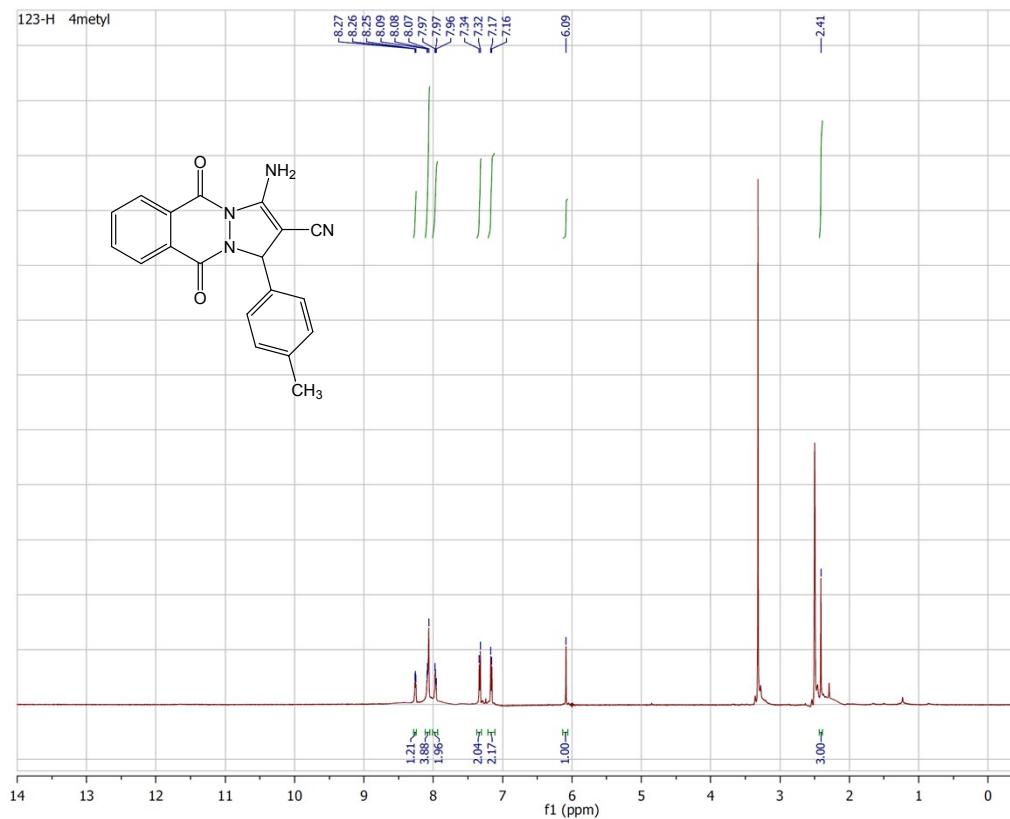
Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg	Class	LConf	HConf	Cat#
C	Ka	188.9	16.0765	0.8502	0.4328	67.56	75.46	0.6404		0.00	466.40	A	64.58	70.55	0.00
O	Ka	21.1	16.0765	0.0472	0.0240	12.41	10.40	0.1937		0.00	16.81	A	10.76	14.05	0.00
F	Ka	65.7	16.0765	0.1026	0.0522	20.03	14.14	0.2608		0.00	30.55	A	18.52	21.53	0.00
				1.0000	0.5091	100.00	100.00			0.00					0.00

Fig. S4 The EDX spectra of fresh [Bn-DBU][TFA] (up) and [Bn-DBU][TFA] after 4th recycling (below)









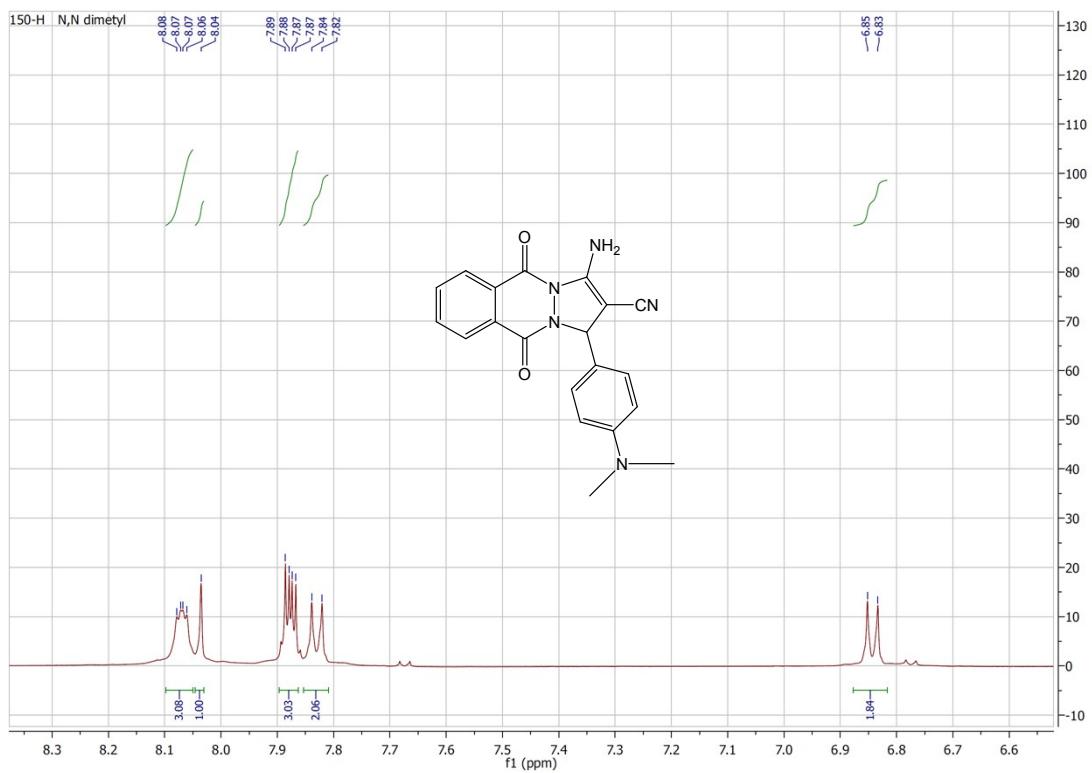
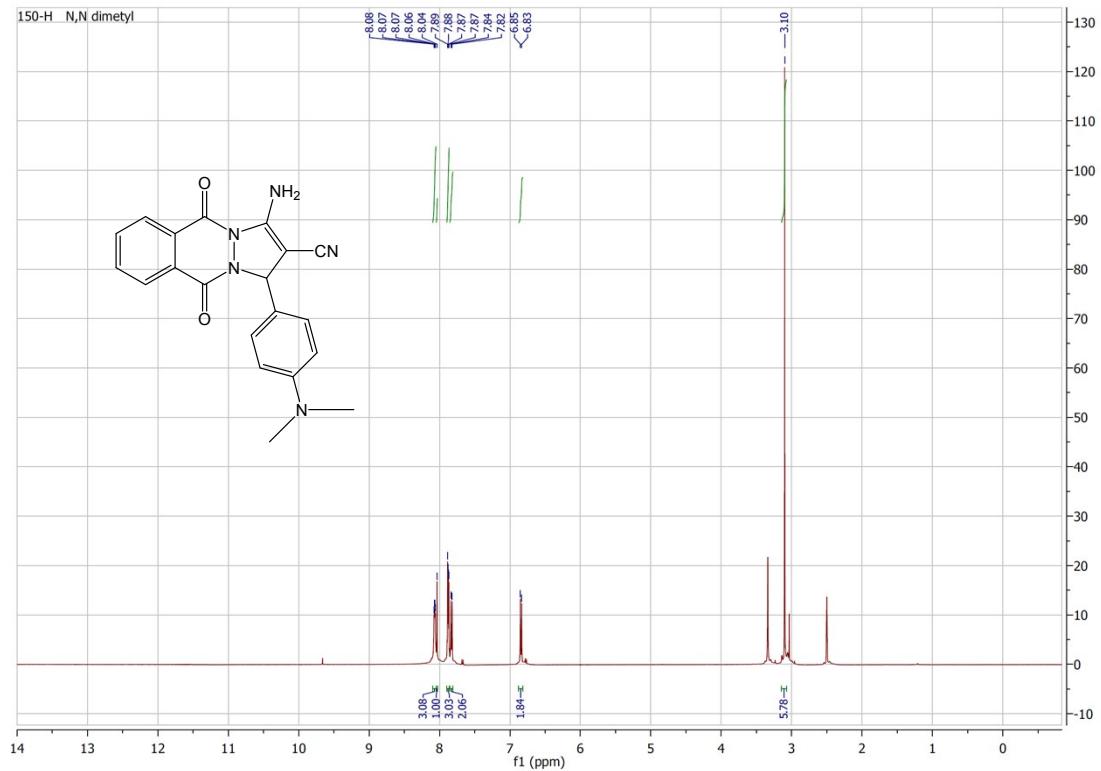


Fig. S5 H NMR spectra of the synthesized 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones

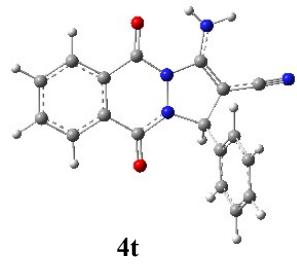


Fig. S6 The optimized structures of **4t** using DFT at B3LYP/SVP level of theory in gas phase

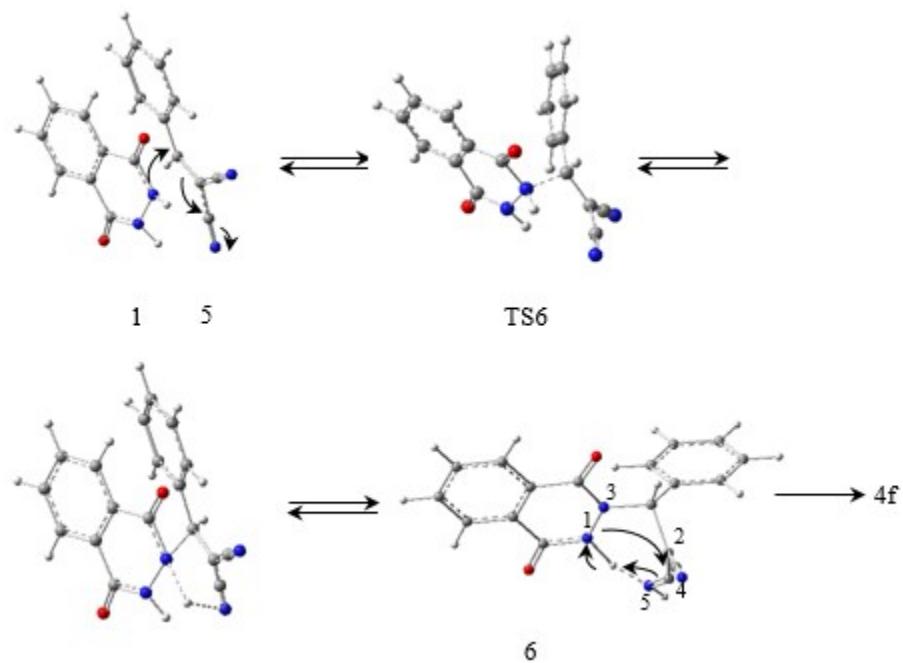


Fig. S7 The optimized structures of mechanistic proposal for the synthesis of **4t** at B3LYP/SVP level theory in gas phase.

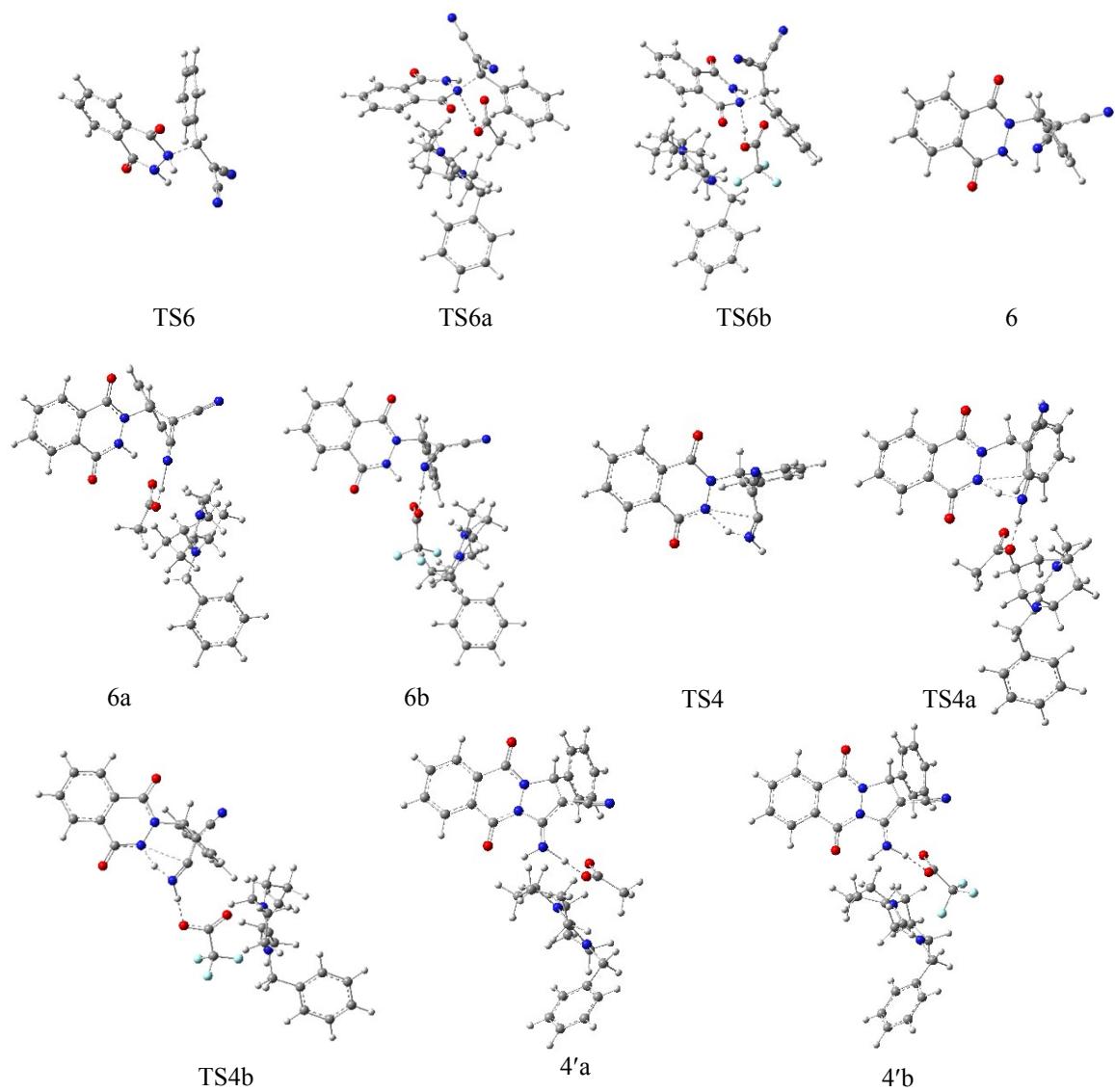


Fig. S8 The optimized structures for synthesis of **4t** with mechanism proposed at B3LYP/SVP level of theory in gas phase.

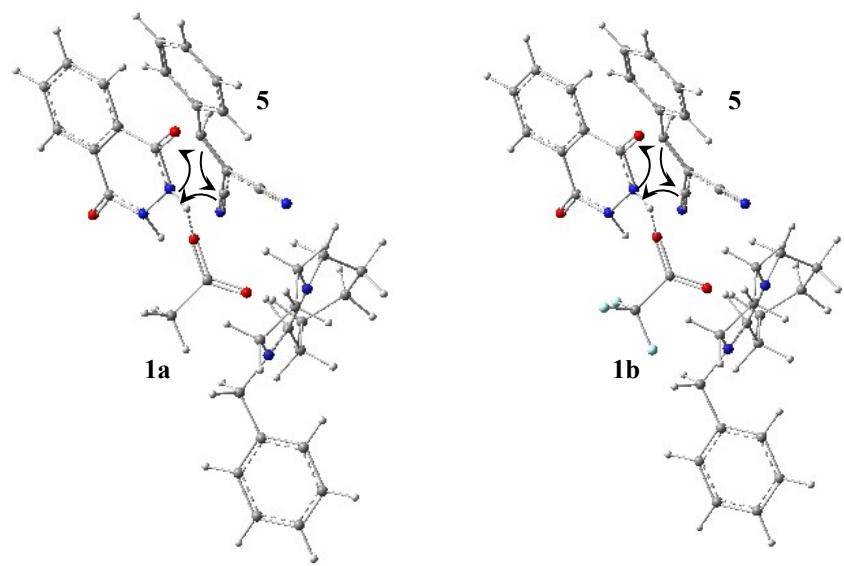


Fig. S9 The approach of **5** to phthalhydrazide in its complexes with [Bn-DBU][AcO] and [Bn-DBU][TFA] ILs at B3LYP/SVP level of theory in gas phase.