Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Introduction of *O*-sulfonated poly(vinylpyrrolidonium) hydrogen sulfate as an efficient, and reusable solid acid catalyst for some of the solvent-free multicomponent reactions

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Experimental

Material

Chemicals were purchased from Fluka, Merck, Aldrich and Southern Clay Products Chemical Companies. Yields refer to isolated products. Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy. The purity determination of the substrate and reaction monitoring were accomplished by TLC on silics-gel polygram SILG / UV 254 plates.

Instrumentation

The FT-IR spectra were run on a VERTEX 70 Bruker company **(**Germany). Thermogravimetric analyses (TGA) were performedon TG/DTA6300 Sll-Nonotechnology Company (Japan) (Samples were heated from 25 to 800 ^{o}C at ramp 10 ^{o}C min^{-1} under N_2atmosphere). Scanning election microphotographs (SEM) were obtained on a SEM-Philips XL30. The Wide-angle X-ray diffraction **(**XRD) measurements were performed at room temperature on a Siemens D-500 X-ray diffractometer (Germany), using Ni-filteredCo-Kα radiation (λ = 0.15418 nm). Elemental analyses of the samples were performed on a Vario EL III CHNOS Elemental Analyzer (Germany).

General procedure for the preparation of the [PVP-SO_3H]HSO_4 solid acid catalyst

Chlorosulfonic acid (1.2 mL, 18 mmol) was added to a suspension of powdered poly(vinylpyrrolidone) (2.0 g) [cross-linked poly(4-vinylpyridine) with MW > 1,000,000] in 10 mL dry CH_2Cl_2 over a period of 15 min. The mixture was stirred at room temperature for 3h and then the mixture was filtered. The solid residue was washed with ethyl acetate (20 mL) and dried at 80 ^oC to afford [PVP-SO_3H]Cl as a pale yellow powder.[50] The amount of chloride in [PVP-SO_3H]Cl was determined by potentiometric titration methods.[51] For this purpose, 0.5 g [PVP-SO_3H]Cl in 50 mL water was titrated with 0.l M $AgNO_3$. As shown in Fig. 1, the change happened at 15 mL of consumed $AgNO_3$. On the basis of these studies it can be concluded that [PVP-SO_3H]Cl has 3 mmol of Cl^- per gram of this reagent. After modulating of chloride, 3 g of [PVP-SO_3H]Cl was suspended in 20 mL of dry CH_2Cl_2. Then and under vigorous stirring, 9 mmol of concentrated H_2SO_4 (97%) was added drop wise to this mixture in an ice bath (0 ^oC) over a period of 15 min. The mixture was then warmed to room temperature and heated under reflux for 8 h. When the formed HCl was completely distilled off, the solution was cooled and CH_2Cl_2 was removed under vacuum to afford *O*-sulfonated poly(vinylpyrrolidonium) hydrogen sulfate ([PVP-SO_3H]HSO_4) as the brown solid product (4.8 gr).

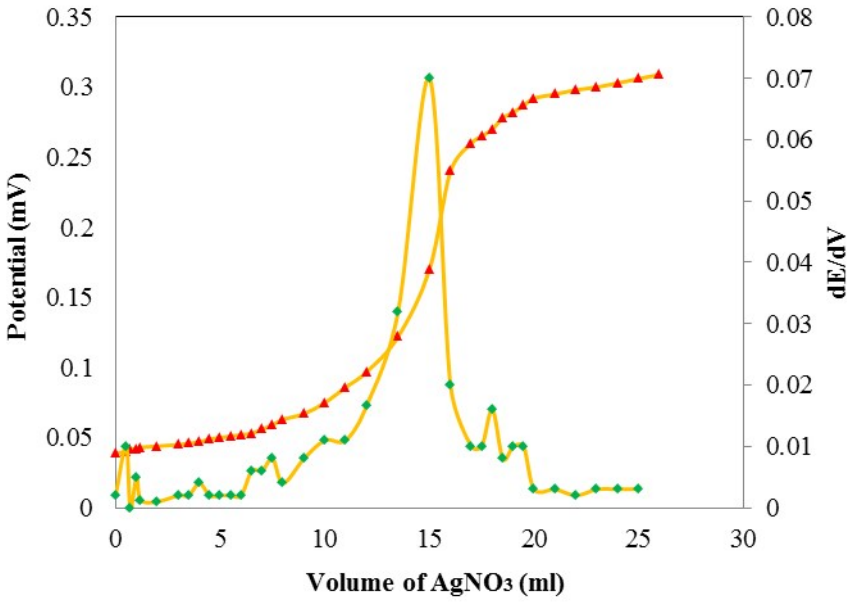


Fig. 1. Potentiometric titration curve of [PVP-SO_3H]Cl with $AgNO_3$.

Table 1. Elemental analysis data of the PVP (1), [PVP-SO_3H]Cl (2) and [PVP-SO_3H]HSO_4 (3) samples.

	Entry	PVP	[PVP-SO_3H]Cl	[PVP-SO_3H]HSO_4
Calcul. (%)	C	68.04	37.28	30.09
	H	10.71	6.26	5.37
	N	9.92	5.43	4.39
	Cl	—	13.75	—
Found (%)	C	67.89	35.42	25.57
	H	10.65	5.82	4.51
	N	10.12	5.10	3.63
	Cl	—	12.78	—
Conversion (%)		—	~ 95	~ 85

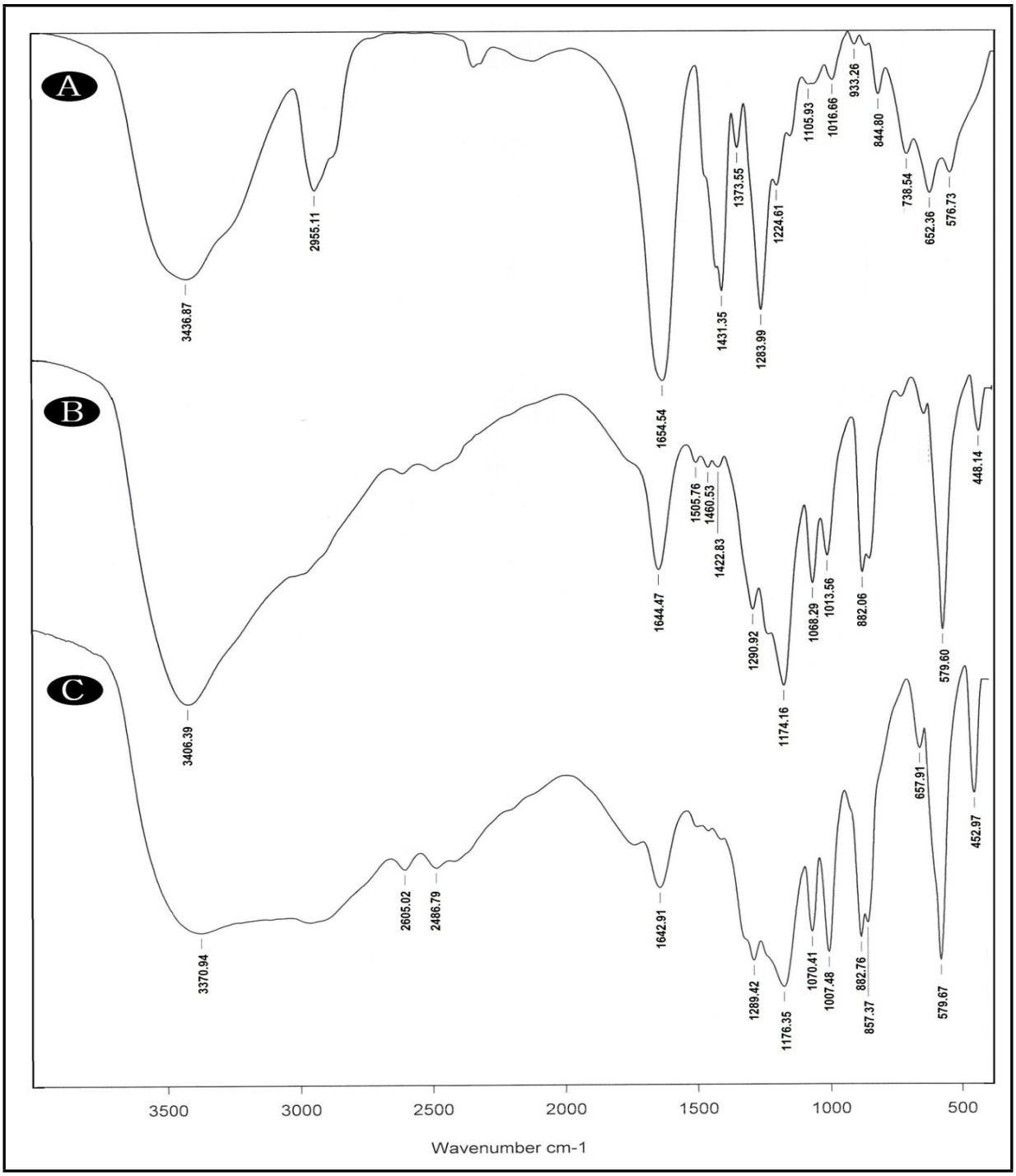


Fig. 2. FT-IR spectra of PVP (A), [PVP-SO_3H]Cl (B) and [PVP-SO_3H]HSO_4 (C).

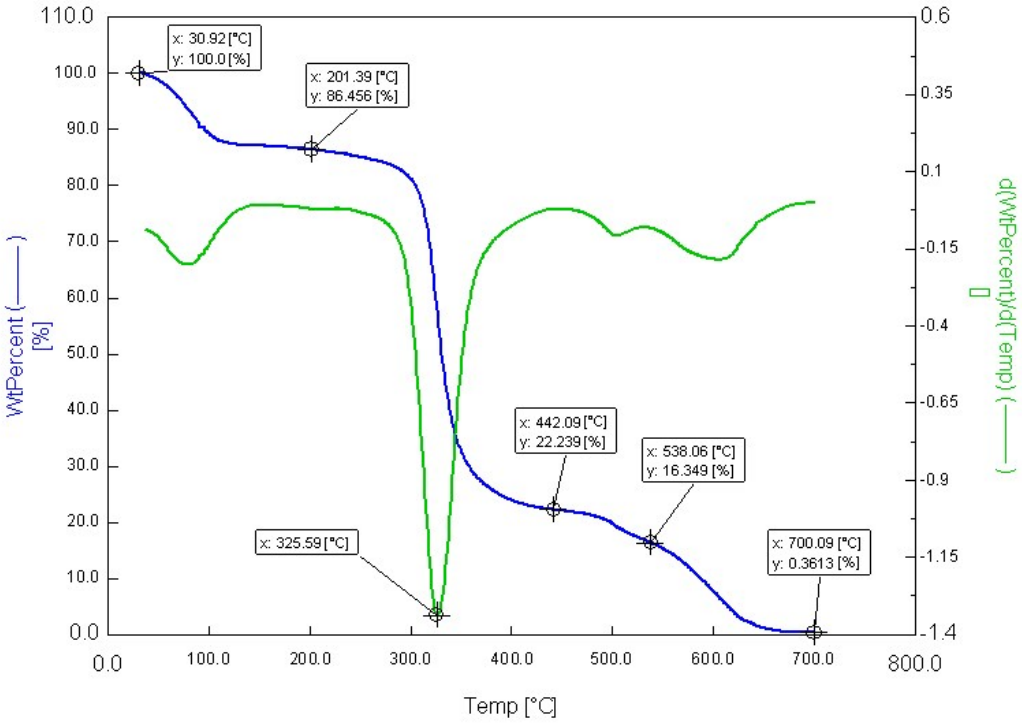


Fig. 3. TGA and DTGA curves for [PVP-SO_3H]HSO_4.

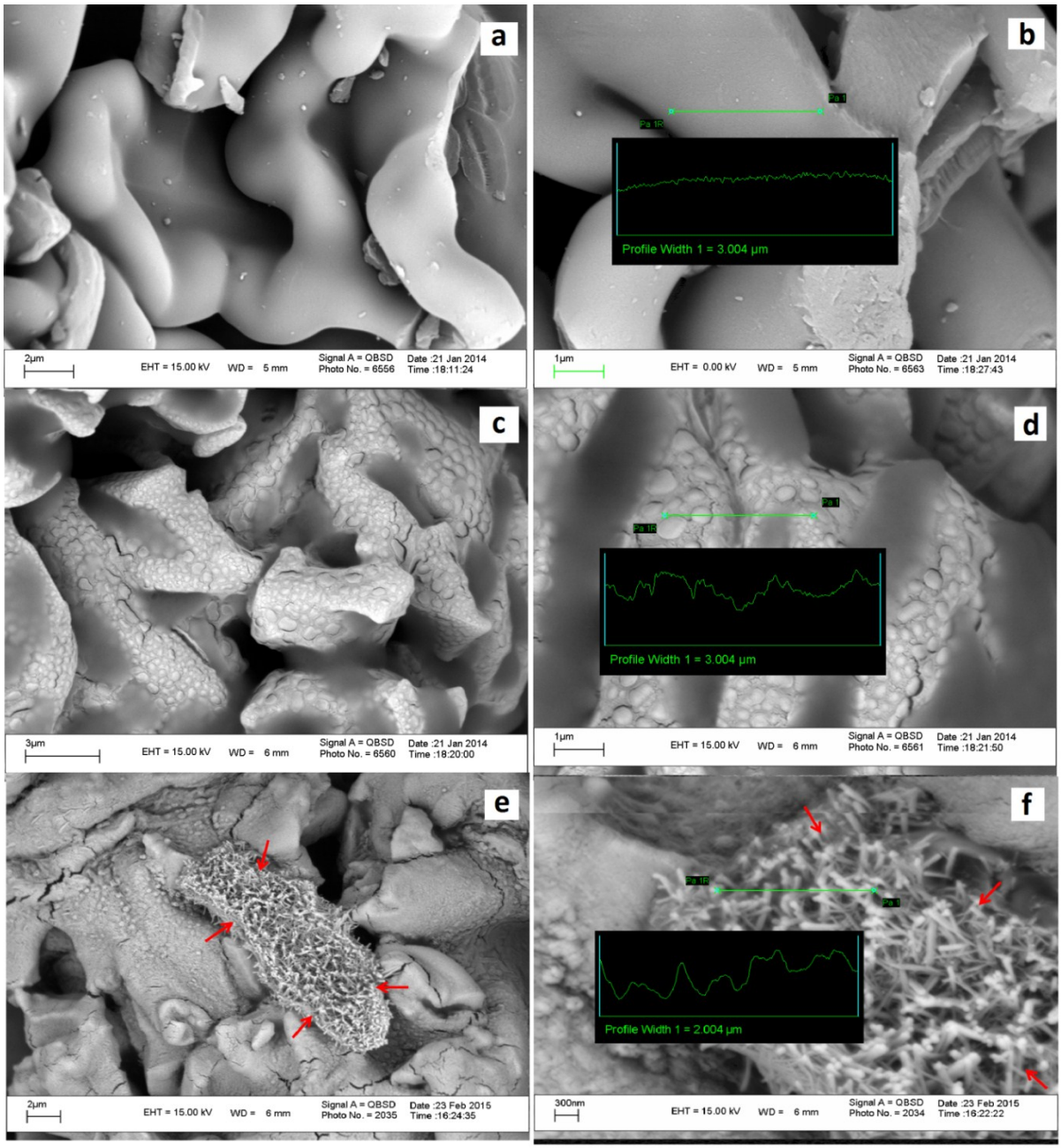


Fig. 4. SEM micrographs of PVP (a,b) [PVP-SO_3H]Cl (c,d) and [PVP-SO_3H]HSO_4 (e,f).

Table 2. Calculation of Hammett acidity function (H_0) for [PVP-SO_3H]Cl and [PVP-SO_3H]HSO_4.

Entry	Catalyst	A_{max}	$[I]_s$ %	$[IH^+]_s$ %	H_0
1	—	2.2086	100	0	0.99
2	[PVP-SO_3H] Cl	1.0025	45.39	54.61	0.90
3	[PVP-SO_3H] HSO_4	0.2318	10.49	89.51	0.058
4	Recovered catalyst	0.7384	33.43	66.56	0.69

Condition for UV-visible spectrum measurement: solvent: CCl_4, indicator: 4-nitroaniline (pK (I) aq= 0.99), 1.44×10−4 mol/L (10 mL); Catalyst: [PVP-SO_3H]Cl and [PVP-SO_3H]HSO_4 (5 mg), 25 °C.

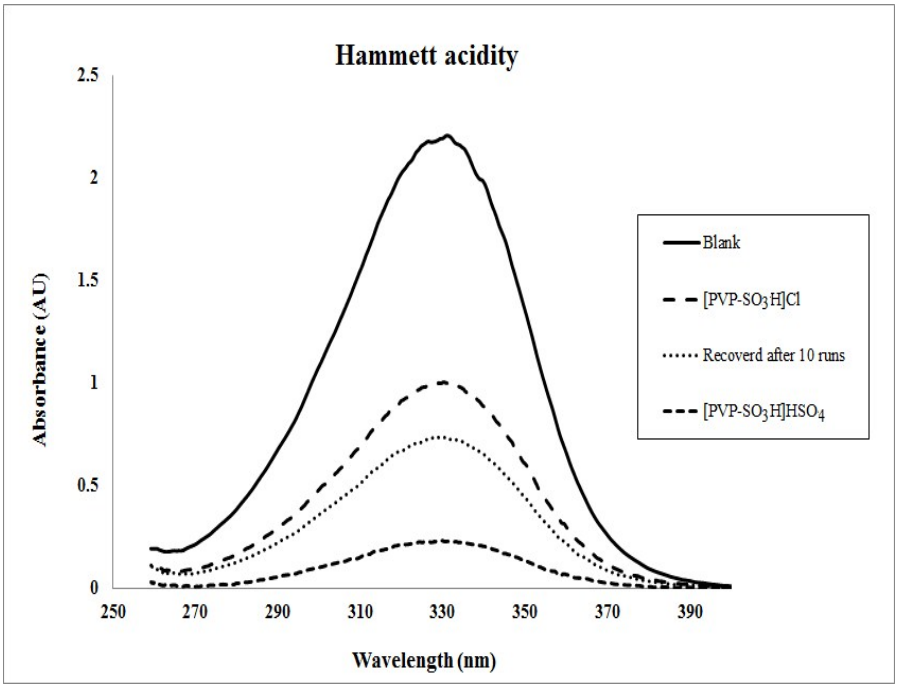


Fig. 5. Absorption spectra of 4-nitroaniline (indicator) [PVP-SO_3H]Cl and [PVP-SO_3H]HSO_4(catalyst) in CCl_4.

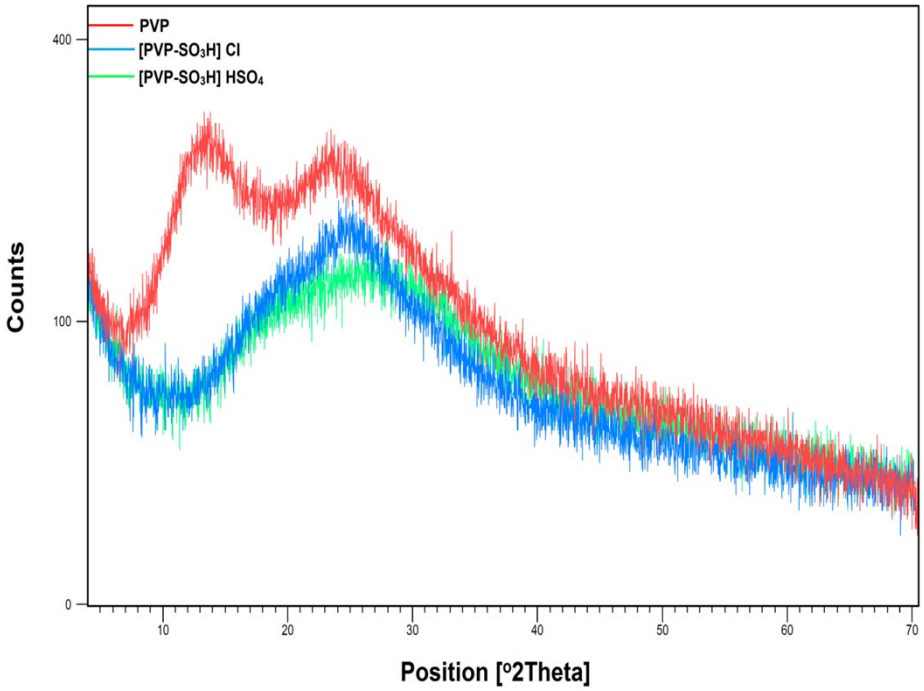


Fig. 6. XRD patterns of PVP in comparison with [PVP-SO_3H]Cl and [PVP-SO_3H]HSO_4.

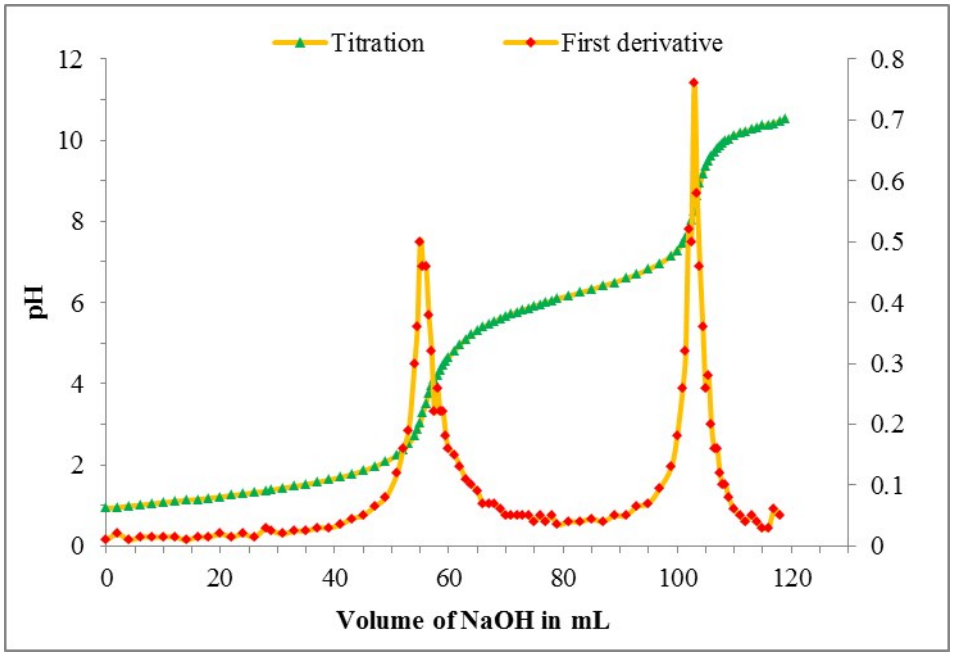
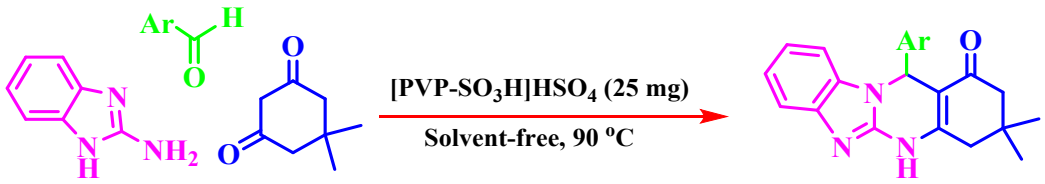


Fig. 7. pH meter titration curve of [PVP-SO_3H]HSO_4 with NaOH (0.05 M).

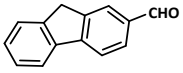
General procedure for the synthesis of tetrahydrobenzimidazo[2,1-b]quinazolin-1(2*H*)-one derivatives

A mixture of the requested aldehyde (1 mmol), 2-aminobenzimidazole (1 mmol), dimedone (1 mmol) and [PVP-SO_3H]HSO_4 (25 mg, 8.65 mol%) was heated in an oil bath (90 ^oC) under solvent-free conditions for the appropriate time. After completion of the reaction that monitored by TLC [*n*-hexane : ethylacetate(8:4)], EtOH was added and the catalyst was separated by filteration. Then water was added and the precipitated product was separated by filtration in high purity.



Scheme 1. Synthesis of tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-one derivatives catalyzed by [PVP-SO_3H]HSO_4.

Table 3. Preparation of tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-one derivatives using [PVP-SO_3H]HSO_4 as the catalyst.

Entry	Aldehyde	Time (min)	Yield (%)[a]	Melting point (°C)	
				Found	Reported [Ref.]
1A	C_6H_5–	12	94	>350	359-363 [20]
1B	2-Cl–C_6H_4–	16	92	340-342	>300 [30]
1C	3-Br–C_6H_5–	15	93	334-336	>300 [30]
1D	2-CH_3–C_6H_5–	25	92	334-336	>300 [30]
1E	3-Cl–C_6H_4–	12	94	340-342	>300 [30]
1F	3-CH_3O–C_6H_5–	13	94	320-322	>300 [31]
1G	3-NO_2–C6H5–	13	95	335-337	>300 [30]
1H	4-Cl–C_6H_4–	14	96	>350	>300 [20]
1I	4-Br–C_6H_4–	14	94	>350	>300 [20]
1J	4-CH_3O–C_6H_5–	10	94	340-342	>300 [20]
1K	4-NO_2–C_6H_5–	8	95	344-346	>300 [20]
1L	4-OH–C_6H_5–	25	93	332-334	330-332 [20]
1M	4-CH_3S–C_6H_4–	10	92	342-344	-
1N	4-CN–C_6H_5–	10	94	340-342	-
1O	4-CH_3–C_6H_5–	20	94	340-342	>300 [31]
1P	2-naphthyl–	15	93	344-346	-
1Q		15	92	347-349	-

[a] Isolated yield.

The spectral data of the selected compounds:

3,3-Dimethyl-12-(4-thiomethyl-phenyl)-3,4,5,12-tetrahydrobenzimidazo [2,1-*b*]quinazolin-1(2*H*)-one (1M): White solid, Yield: 87 %, M.p. 342-344 ^{o}C; FT-IR (KBr) ν_{max} = 3418, 3148, 2954, 1671, 1568, 1375, 1262, 744 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.07 (6H, s, CH_3), 2.15 (4H, s, CH_2), 2.40 (3H, s, SCH_3), 6.12 (1H, s), 6.93 (2H, d, J = 8.0 Hz), 7.03 (2H, d, J = 7.6 Hz), 7.07-7.11 (2H, m), 7.25-7.28 (2H, m), 7.65 (1H, s, NH) ppm.; ^{13}C NMR (DMSO-d_6, 100 Mz): δ = 15.8, 28.8, 30.3, 31.6, 48.8, 111.8, 114.8, 122.1, 126.1, 128.1, 132.7, 133,1, 142.8, 152.5 ppm.

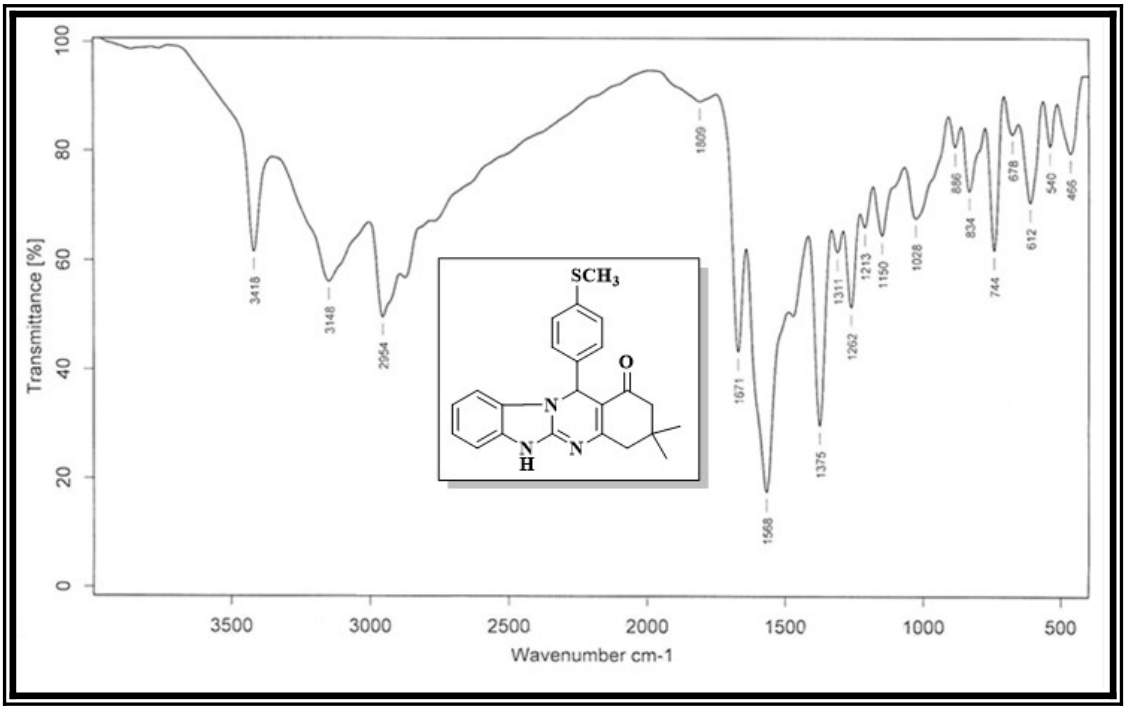


Fig. 8. FT-IR of 3,3-Dimethyl-12-(4-thiomethyl-phenyl)-3,4,5,12-tetrahydrobenzimidazo [2,1-*b*]quinazolin-1(2*H*)-one

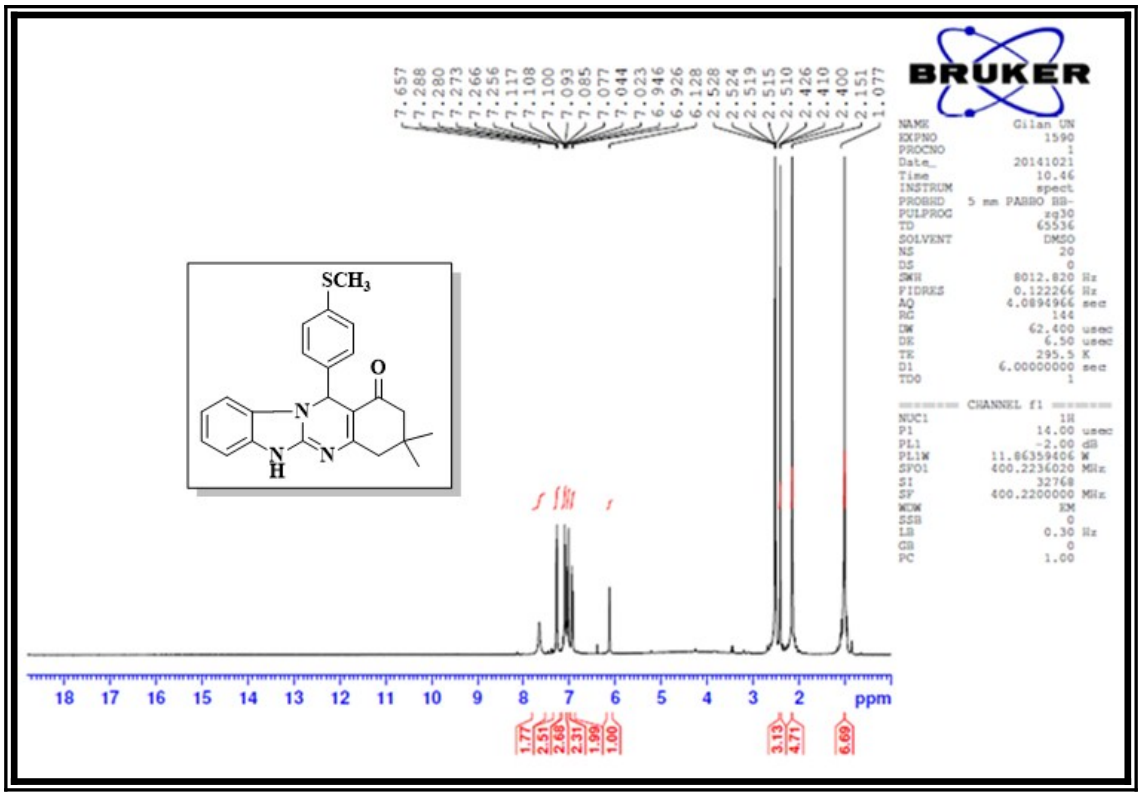


Fig. 9. [1]H NMR of 3,3-Dimethyl-12-(4-thiomethyl-phenyl)-3,4,5,12-tetrahydrobenzimidazo [2,1-*b*]quinazolin-1(2*H*)-one.

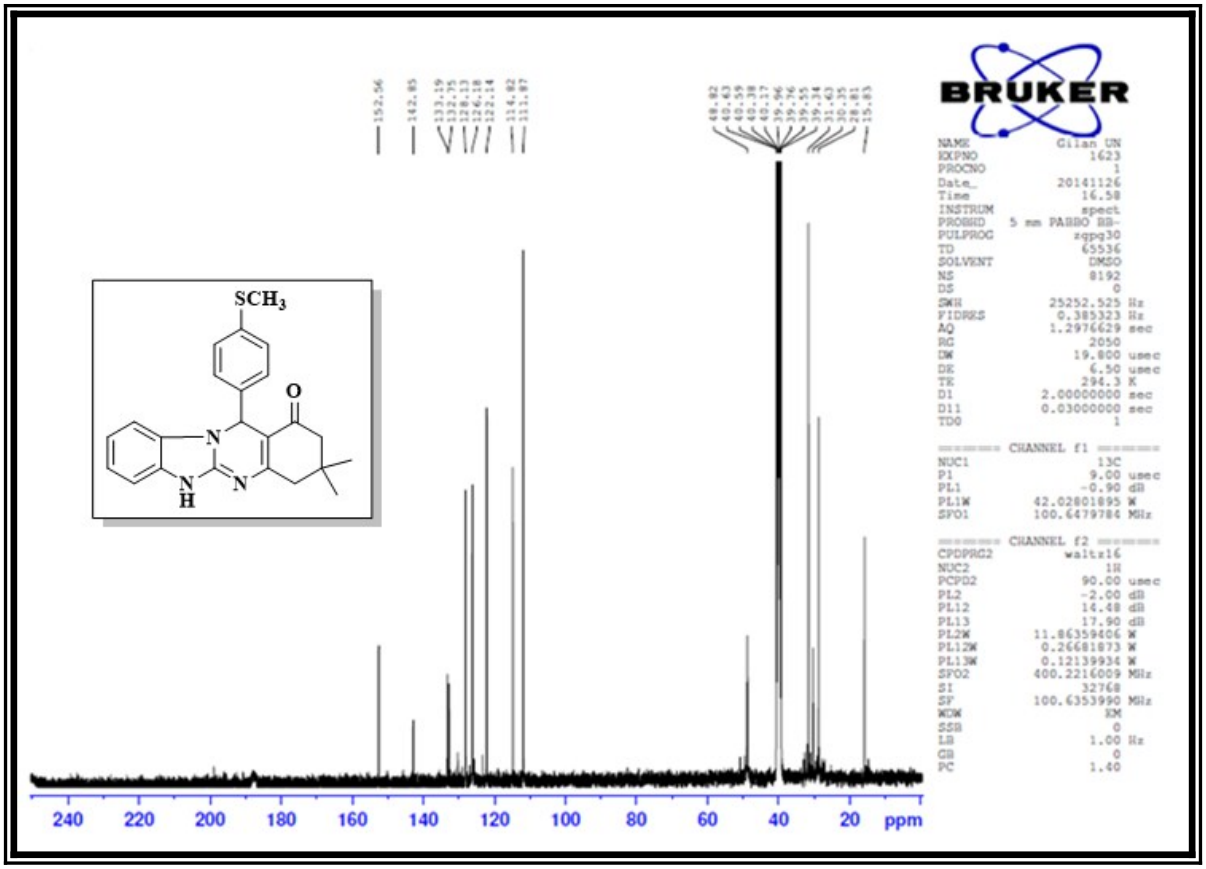


Fig. 10. ^{13}C NMR of 3,3-Dimethyl-12-(4-thiomethyl-phenyl)-3,4,5,12-tetrahydrobenzimidazo [2,1-*b*]quinazolin-1(2*H*)-one.

3,3-Dimethyl-12-(4-cyano-phenyl)-3,4,5,12-tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-one (1N): White solid, Yield: 92%, M.p. 340-342 ^{o}C; FT-IR (KBr) ν_{max} = 3425, 3045, 2962, 2227,1567, 1448,1358, 1264, 748 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.92 (3H, s, CH_3), 1.07 (3H, s,CH_3), 2.07 (1H, d, J = 16.0 Hz), 2.28 (1H, d, J = 16.0 Hz), 2.67-2.69 (2H,m), 6.56 (1H, s), 6.98 (1H, td, J_1= 8.0 Hz, J_2 = 0.8 Hz), 7.08 (1H, td, J_1 = 8.2 Hz, J_2 = 0.8 Hz), 7.41 (1H, d, J= 8.0 Hz), 7.24 (1H, d, J = 8.0 Hz), 7.54 (2H, dd, J_1= 5.0 Hz, J_2 = 1.6 Hz), 7.75 (2H, dd, J_1 = 5.0 Hz, J_2 = 1.6 Hz), 11.26 (1H, s, NH) ppm.; ^{13}C NMR (DMSO-d_6, 100 Mz): Sample solubility was too low for ^{13}C NMR.

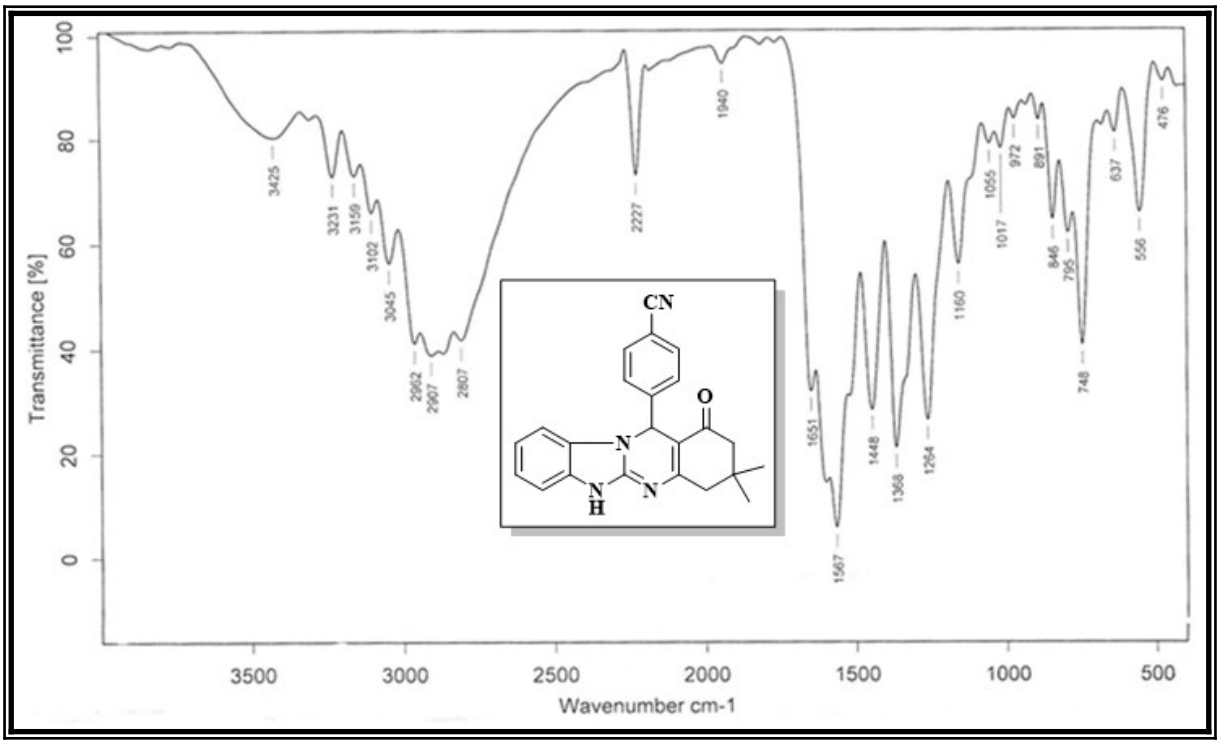


Fig. 11. FT-IR of 3,3-Dimethyl-12-(4-cyano-phenyl)-3,4,5,12-tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-one.

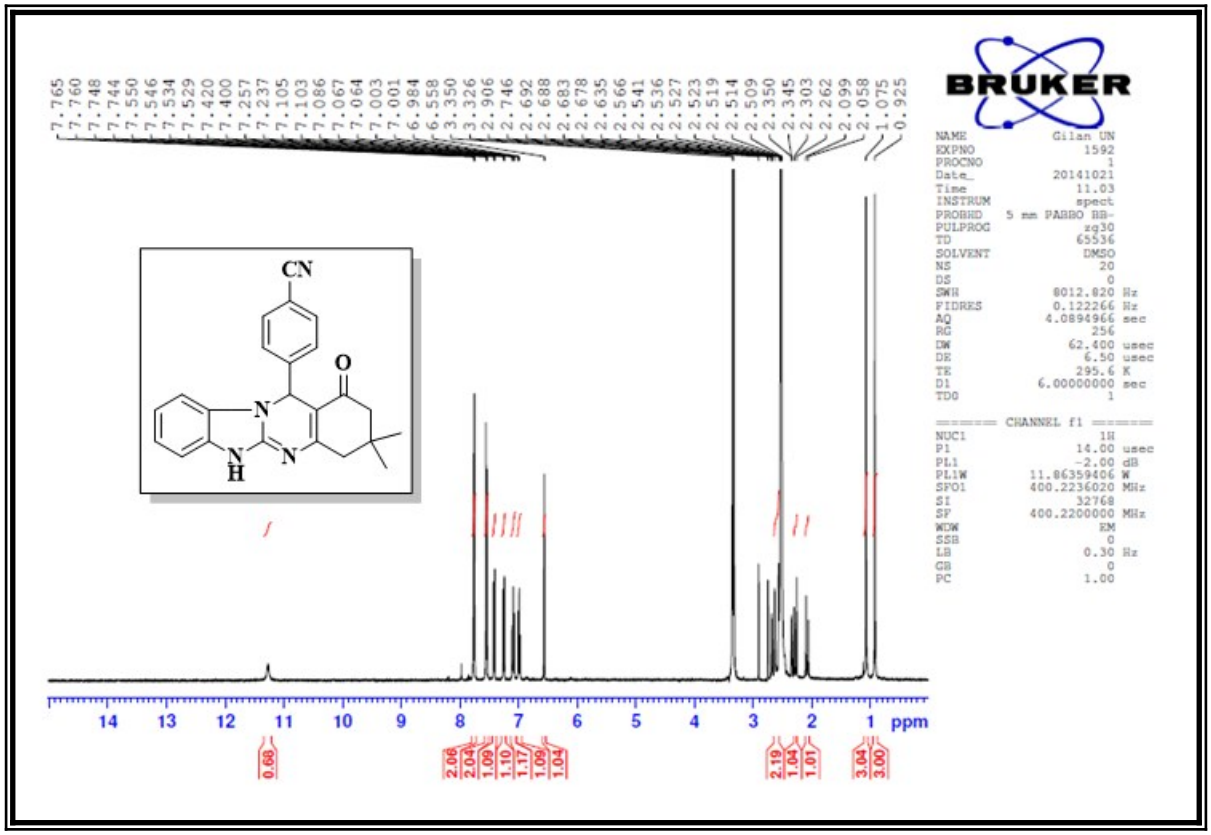


Fig. 12. [1]H NMR of 3,3-Dimethyl-12-(4-cyano-phenyl)-3,4,5,12-tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-one.

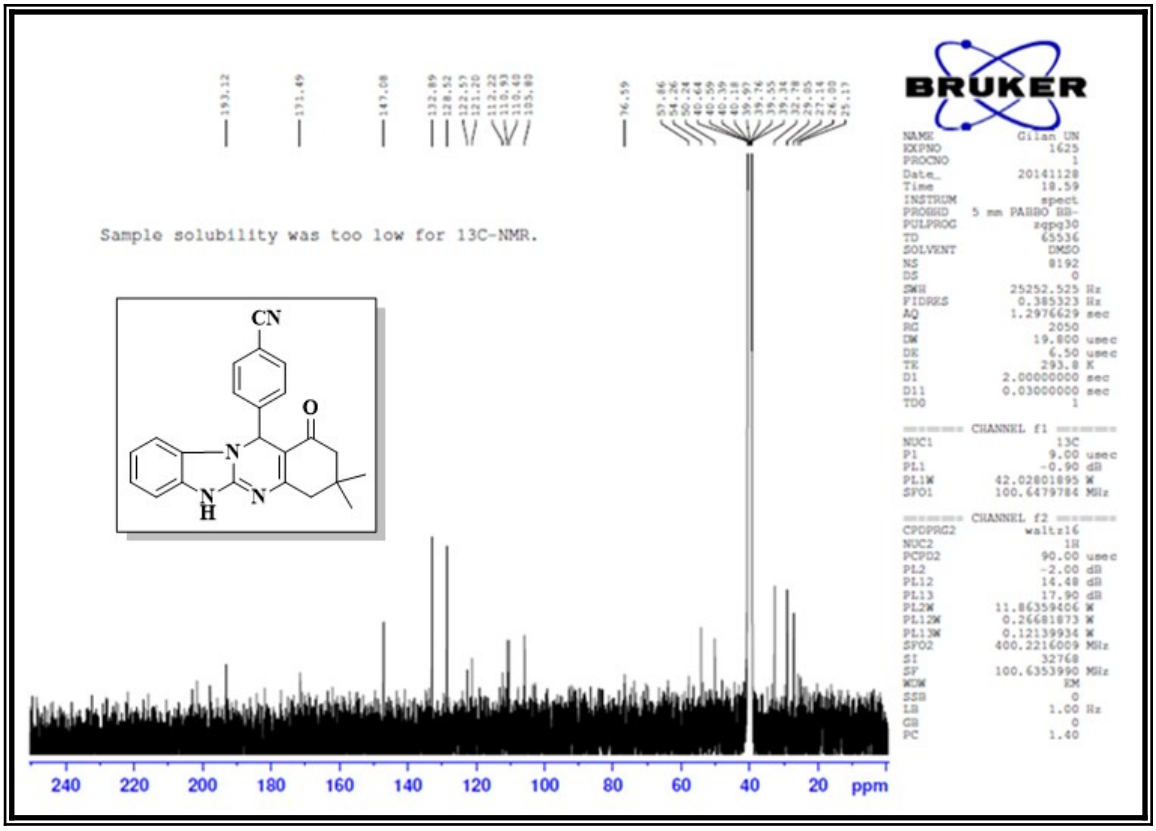


Fig. 13. ^{13}C NMR of 3,3-Dimethyl-12-(4-cyano-phenyl)-3,4,5,12-tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-one.

3,3-Dimethyl-12-(2-naphthyl)-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-one (1P): White solid, Yield: 89%, M.p. 344-346 ^{o}C; FT-IR (KBr) ν_{max} = 3443, 3050, 2964,1575, 1370, 1261, 746 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.94 (3H, s, CH_3), 1.08 (3H, s, CH_3), 2.04 (1H, d, J = 16.0 Hz), 2.29 (1H, d, J = 16.0 Hz), 2.67- 274 (2H, m), 6.60 (1H, s), 6.93 (1H, t, J = 7.6 Hz), 7.03 (1H, t, J = 7.6 Hz), 7.31 (2H,m), 7.38 (1H, d, J = 8.0 Hz), 7.49 (2H, m), 7.80 (2H, t, J = 7.6 Hz), 7.92 (1H, d, J = 7.6), 8.04 (1H, s), 11.19 (1H, s, NH) ppm.; ^{13}C NMR (DMSO-d_6, 100 Mz): Sample solubility was too low for ^{13}C NMR.

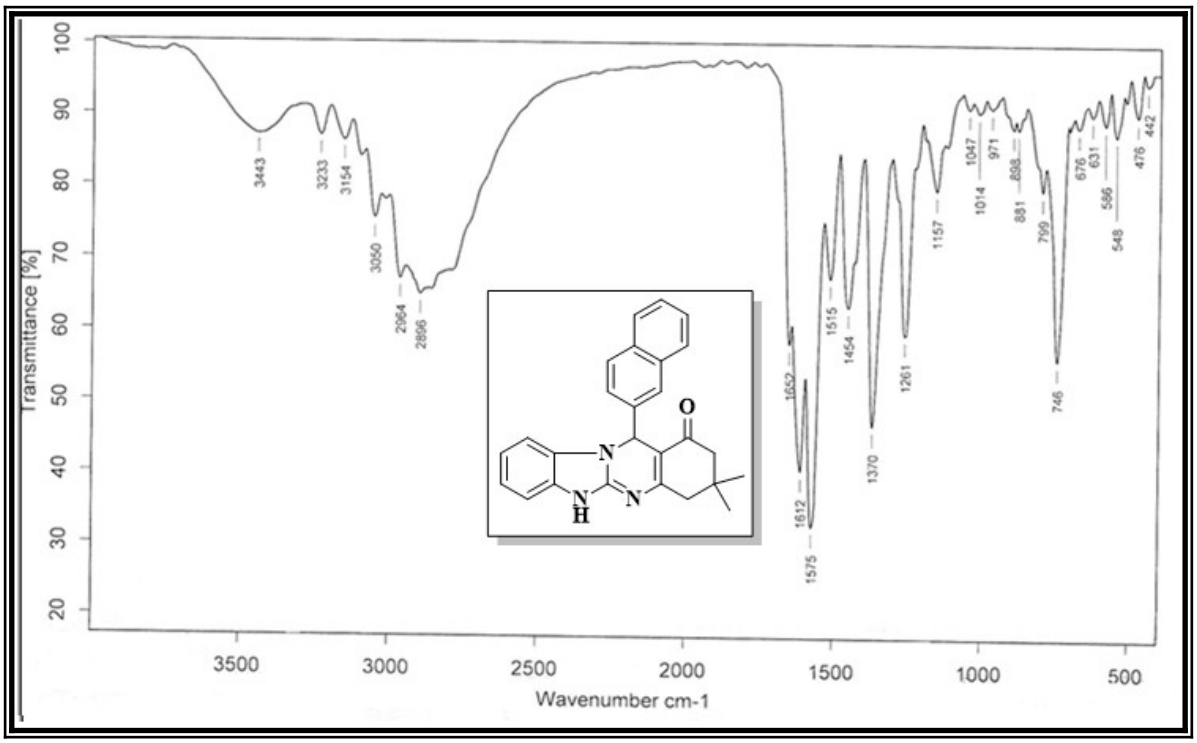


Fig. 14. FT-IR of 3,3-Dimethyl-12-(2-naphthyl)-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-one.

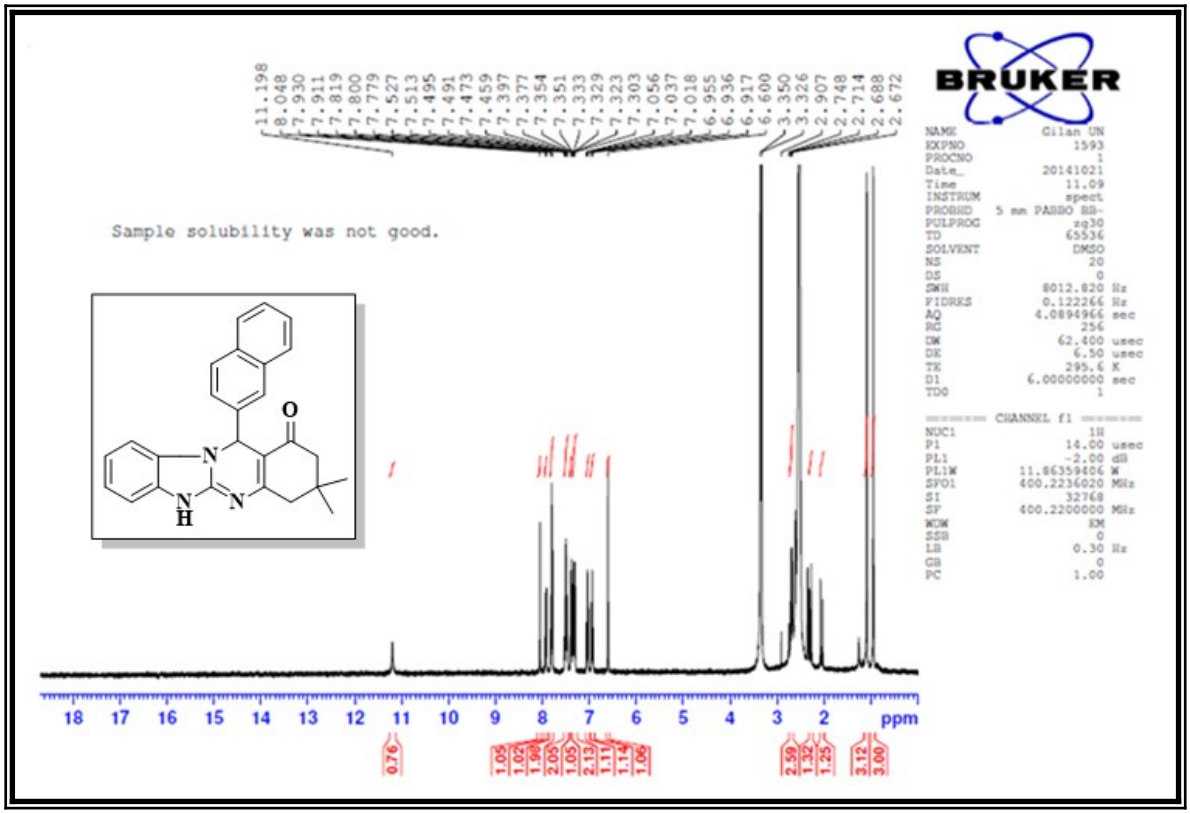


Fig. 15. [1]H NMR of 3,3-Dimethyl-12-(2-naphthyl)-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-one.

12-(2-Fluorenyl)-3,3-dimethyl-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-one (1Q): White solid, Yield: 89%, M.p. 347-349 ^{o}C; FT-IR (KBr) ν_{max} = 3431, 3047, 3229, 2908, 1575, 1372, 1264, 741 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.96 (3H, s, CH_3), 1.08 (3H, s, CH_3), 2.07 (1H, d, J = 16.0 Hz), 2.28 (1H, d, J = 16.0 Hz), 2.65-2.69 (2H, m), 3.85 (2H, s, CH_2), 6.50 (1H,s), 6.96 (1H, td, J_1 = 7.2 Hz, J_2 = 1.2 Hz), 7.05 (1H, td, J_1 = 7.2 Hz, J_2 = 1.2 Hz), 7.28 (1H, td, J_1= 7.2 Hz, J_2 = 1.2 Hz), 7.31 (2H, d, J = 7.6 Hz), 7.38 (2H, d, J = 7.6 Hz), 7.54 (1H, d, J = 7.2 Hz), 7.54 (1H, s), 7.78 (1H, d, J = 7.6 Hz), 7.81 (1H, d, J = 7.2 Hz), 11.1 (1H, s, NH) ppm.; ^{13}C NMR (DMSO-d_6, 100 Mz): Sample solubility was too low for ^{13}C NMR.

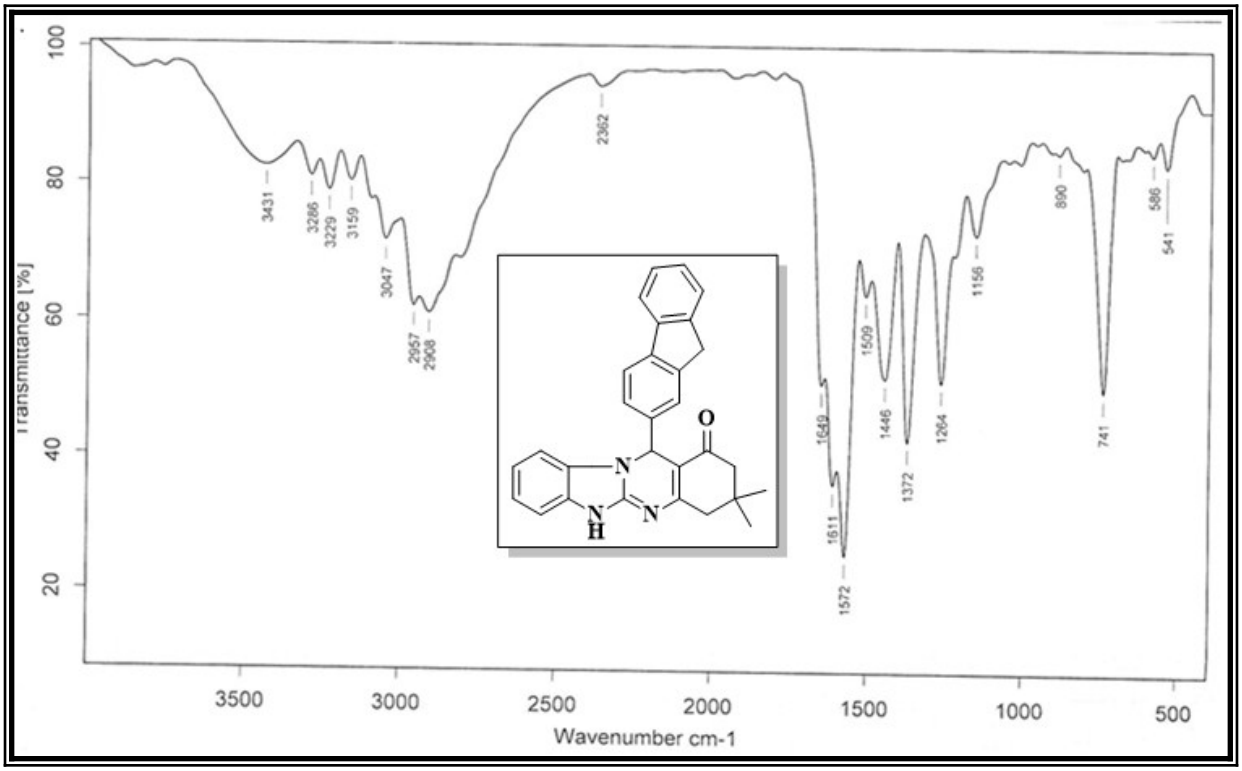


Fig. 16. FT-IR of 12-(2-Fluorenyl)-3,3-dimethyl-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-one.

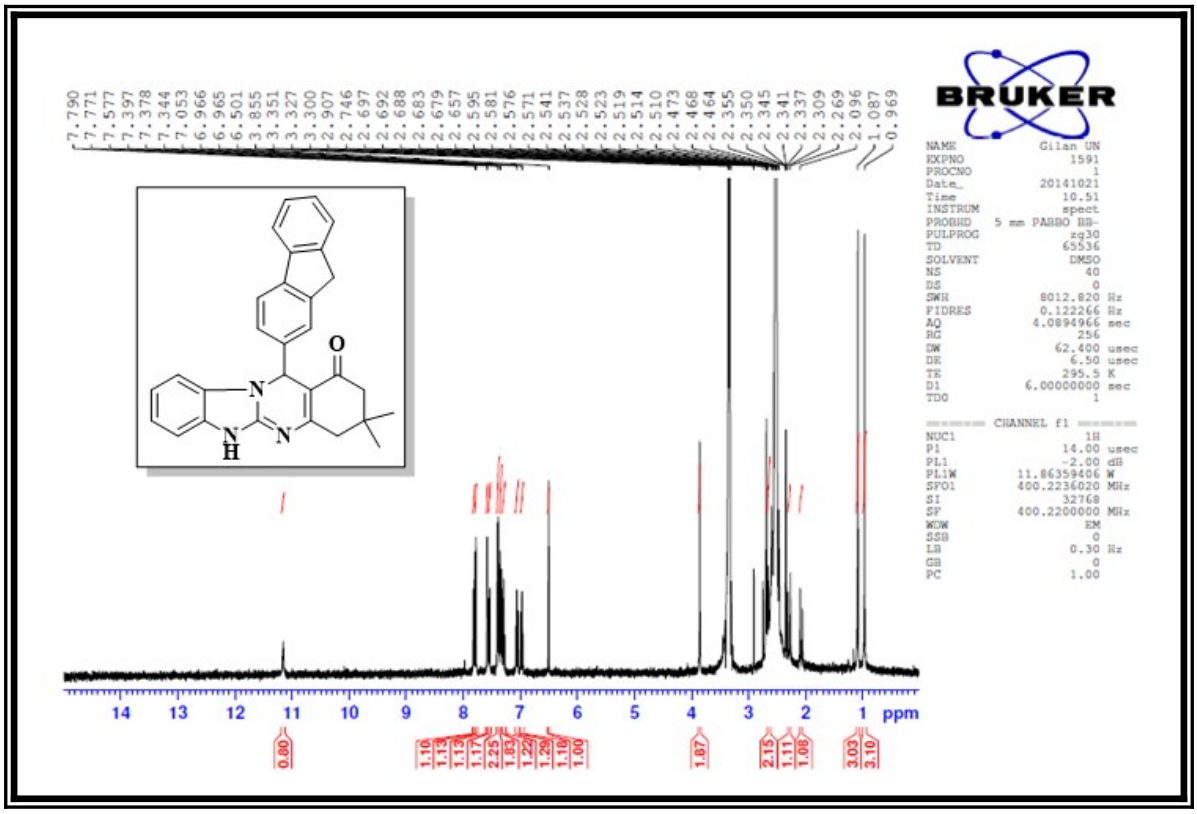
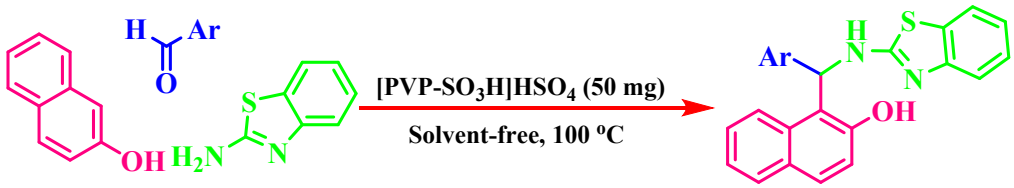


Fig. 17. 1H NMR of 12-(2-Fluorenyl)-3,3-dimethyl-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-one.

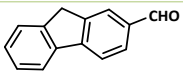
General procedure for the preparation of 1-(benzothiazolylamino)phenylmethyl-2-naphthols

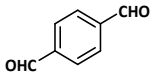
A mixture of the aldehyde (1 mmol), 2-aminobenzothiazole (1 mmol), 2-naphthol (1 mmol) and [PVP-SO_3H]HSO_4 (50 mg, 17.3 mol %) was heated in an oil bath (100 ^oC) under solvent-free conditions for the appropriate time (Table 1). After completion of the reaction that monitored by TLC [*n*-hexane : ethylacetate (8:2)], ethyl acetate (10 mL) was added and the catalyst was separated by filteration. In continue the solvent was evaporated, and the requested product was purified by recrystallization from aqueous ethanol.



Scheme 3. [PVP-SO_3H]HSO_4 catalyzed the synthesis of 1-(benzothiazolylamino)-phenylmethyl-2-naphthols derivatives.

Table 4. Preparation of 1-(benzothiazolylamino)phenylmethyl-2-naphthol derivatives catalyzed by [PVP-SO_3H]HSO_4 under solvent-free conditions.

Entry	Aldehyde	Time (min)	Yield (%)[a]	Melting point (°C)	
				Found	Reported [Ref.]
2A	C_6H_5–	6	94	201-203	202-204 [37]
2B	2-Cl–C_6H_4–	6	90	188-190	187-189 [37]
2C	2-CH_3O–C_6H_5–	4	92	170-172	168-170 [37]
2D	2-NO_2–C_6H_4–	6	93	218-220	215-216 [37]
2E	3-Br–C_6H_5–	4	92	203-205	203-205 [37]
2F	3-CH_3O–C_6H_5–	6	91	184-186	184-186 [37]
2G	3-NO_2–C6H5–	6	93	190-192	191-194 [33]
2H	3-CH_3–C_6H_5–	6	95	187-188	189-191 [55]
2I	4-Cl–C_6H_4–	4	94	208-210	209-210 [32]
2J	4-Br–C_6H_4–	4	93	211-213	200-202 [37]
2K	4-CH_3O–C_6H_5–	5	95	172-174	172-173 [36]
2L	4-NO_2–C_6H_5–	5	92	186-188	187-189 [37]
2M	2-naphthyl–	5	95	197-199	197-199 [60]
2N		5	92	194-196	195-197 [60]
2O	2-pyridyl–	10	92	191-193	-
2P	3-pyridyl–	6	93	187-188	189-190 [37]
2Q	4-pyridyl–	5	89	209-211	210-212 [37]

2R		6	88	214-216	215-217 [60]

[a] Isolated yields.

1-((Benzo[d]thiazol-2-ylamino)(pyridin-2-yl)methyl)naphthalen-2-ol (2O) : White solid, Yield: 91%, M.p. 191-193 ^{o}C; FT-IR (KBr) ν_{max} = 3381, 1526, 1444, 1332, 1267, 1201, 1046, 745 cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 7.00 (s, 1H), 7.02-7.80 (m, 15H), 8.80 (s, 1H), 10.28 (br, 1H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 21.7, 119.3, 121.4, 121.4, 122.9, 123.7, 123.7, 125.9, 126.0, 126.8, 126.9, 127.1, 127.4, 127.5, 128.4, 128.5, 129.1, 130.0, 131.2, 132.6, 137.5, 143.0, 152.6, 153.6, 166.8 ppm.

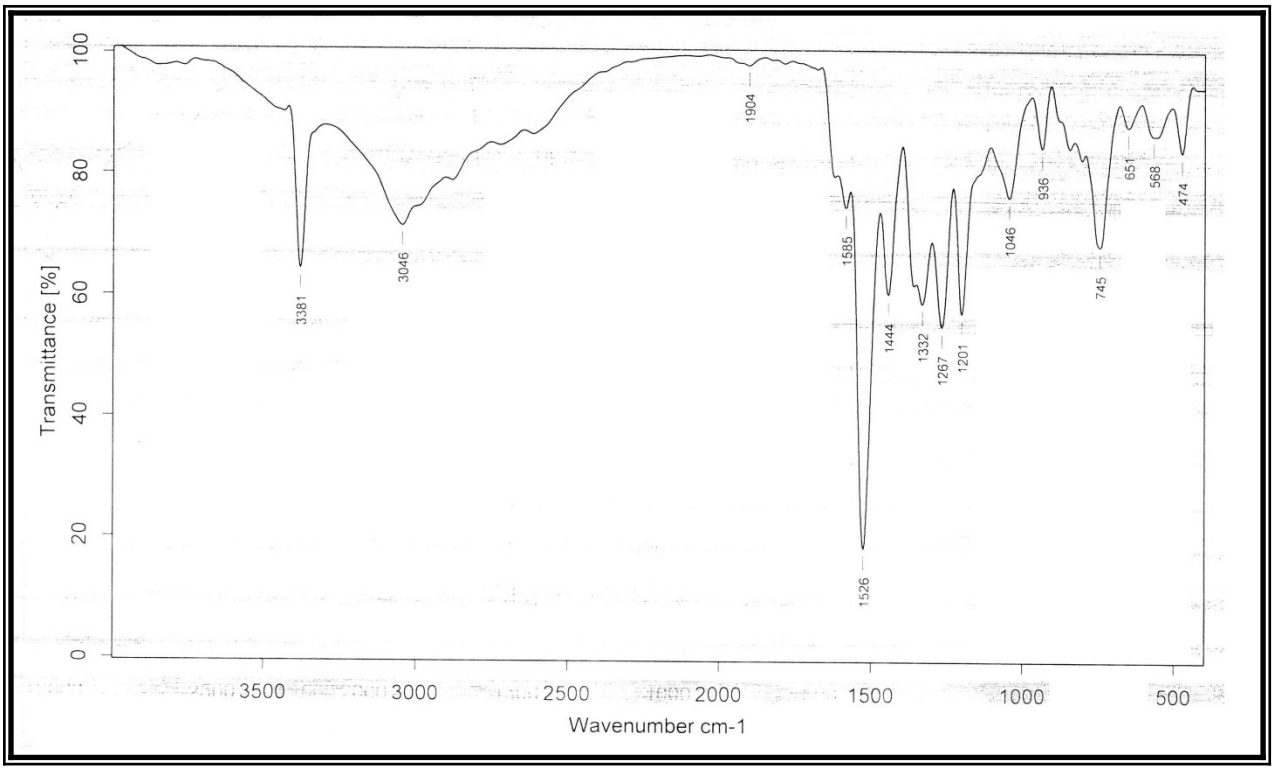


Fig. 18. FT-IR of 1-((Benzo[d]thiazol-2-ylamino)(pyridin-2-yl)methyl)naphthalen-2-ol.

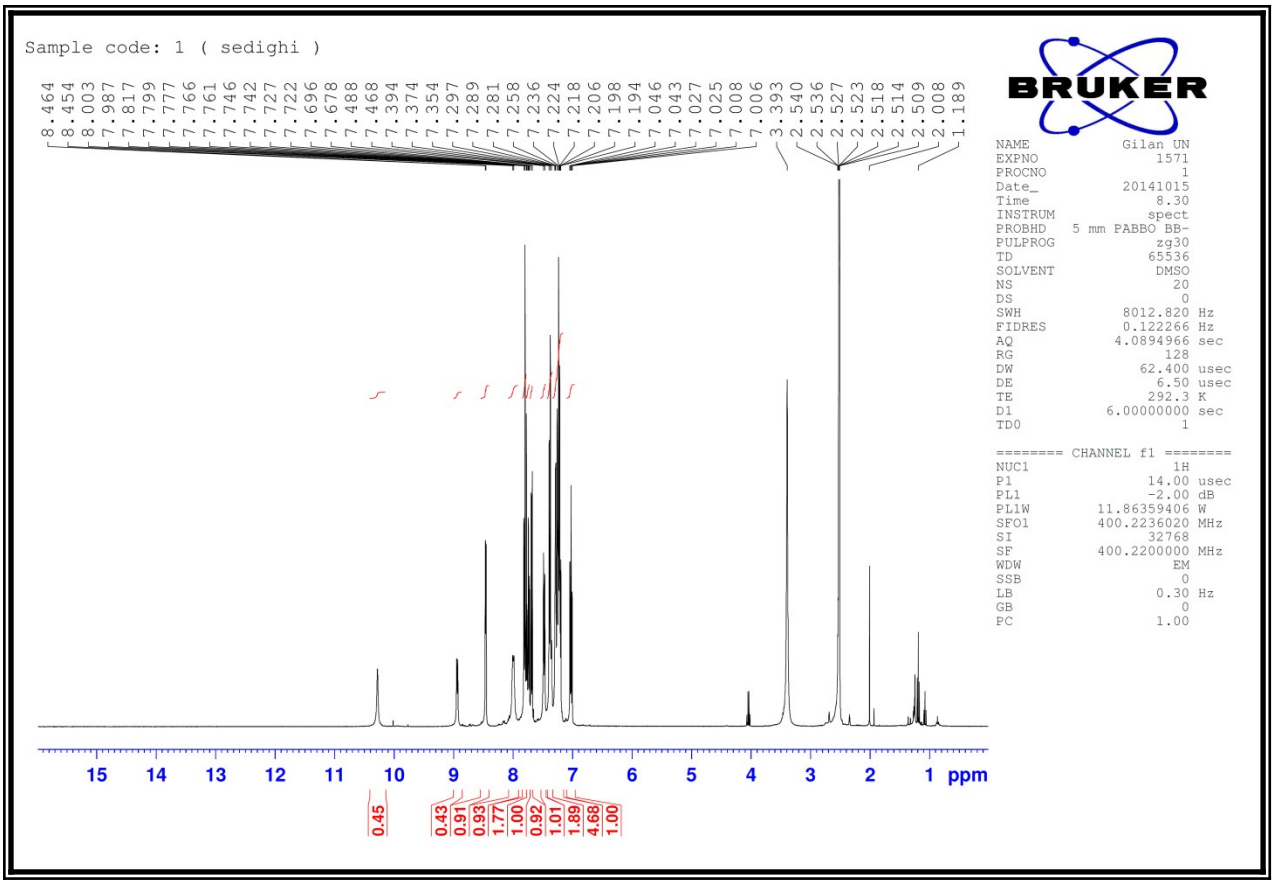
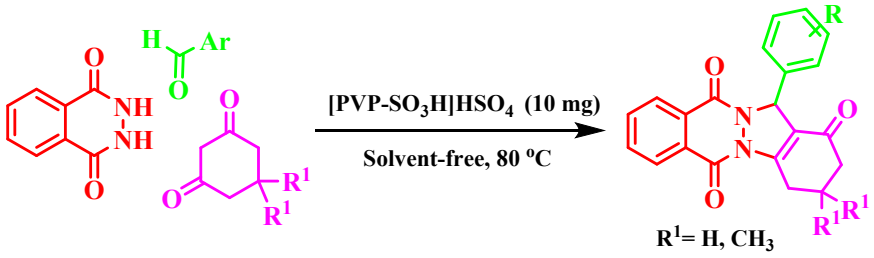


Fig. 19. ^{1}H NMR of 1-((Benzo[d]thiazol-2-ylamino)(pyridin-2-yl)methyl)naphthalen-2-ol.

General procedure for the preparation of 2*H*-indazolo[2,1-b]phthalazine-1,6,11(13*H*)-triones

A mixture of the requested aldehyde (1 mmol), dimedone and/ or 1,3-cyclohexadione (1 mmol), phthalhydrazide (1 mmol) and [PVP-SO_3H]HSO_4 (10 mg, 3.46 mol%) was heated in an oil bath (80 ^oC) under solvent-free conditions for the appropriate time. After completion of the reaction that monitored by TLC [*n*-hexane : ethylacetate(8:2)], EtOH was added and the catalyst was separated by filteration. Then water was added and the precipitated product was separated by filtration in high purity.



Scheme 4. [PVP-SO_3H]HSO_4 catalyzed the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-triones derivatives.

Table 5. Preparation of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-triones derivatives using [PVP-SO_3H]HSO_4 as the catalyst.

Entry	Aldehyde	R	Time (min)	Yield (%)[a]	Melting point (°C)	
					Found	Reported [ref.]
3A	C_6H_5–	CH_3	10	90	202-203	205-207 [61]
3B	2-Cl–C_6H_4–	CH_3	18	89	254-257	262-264 [61]
3C	2-CH_3O–C_6H_5–	CH_3	17	88	245-247	242-243 [44]
3D	2-NO_2–C_6H_4–	CH_3	20	91	235-238	236-238 [43]
3E	2-OH–C_6H_4–	CH_3	20	90	180-182	184-188 [39d]
3F	3-CH_3O–C_6H_5–	CH_3	12	93	198-200	206-208 [43]
3G	3-NO_2–C6H5–	CH_3	13	94	268-270	270-271 [61]
3H	4-Cl–C_6H_4–	CH_3	8	96	257-259	262-264 [61]
3I	4-Br–C_6H_4–	CH_3	8	95	252-256	258-260 [61]
3J	4-CH_3O–C_6H_5–	CH_3	12	94	215-217	220-221 [61]
3K	4-NO_2–C_6H_5–	CH_3	15	93	217-220	220-222 [61]
3L	C_6H_5–	H	8	95	220-222	222-224 [39c]
3M	2-Cl–C_6H_4–	H	15	93	232-234	-
3N	2-NO_2–C_6H_4–	H	18	92	248-250	-
3O	3-NO_2–C6H5–	H	12	92	222-224	228-230 [39c]
3P	4-Cl–C_6H_4–	H	6	93	250-255	----[39c]
3Q	4-Br–C_6H_4–	H	6	94	270-274	279-282 [39d]

3R	4-CH_3O–C_6H_5–	H	8	94	250-254	254-255 [39c]
3S	4-NO_2–C_6H_5–	H	25	87	240-245	252-254 [43]
3T	4-CN–C_6H_5–	H	30	93	284-285	>280 [45]
3U	4-CH_3–C_6H_5–	H	5	90	237-240	244-246 [39c]
3V	4-OH–C_6H_4–	H	15	93	259-261	265-266 [39c]
3W	4-$(CH_3)_2N$-C_6H_4–	H	17	85	248-251	256-258 [39c]

[a]Isolated yield.

13-(2-Chlorophenyl)-2,3,4,13-tetrahydro-1*H*-indazolo[1,2-b]phthalazine-1,6,11-trione (3M): White solid, Yield: 93%, M.p. 232-234 ^{o}C; FT-IR (KBr): ν_{max} = 3075, 2959, 1658, 1526, 1357, 1311, 1267, 1139, 1017, 701 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.13-2.14 (m, 2H, CH_2), 2.32-2.36 (m, 2H, CH_2), 3.29-3.45 (m, 2H, CH_2), 6.61 (s, 1H, CH), 7.27-7.31 (m, 2H, Ar-H), 7.39-7.41 (m, 2H, Ar-H), 7.52-7.54 (m, 1H, Ar-H), 7.09-8.00 (m, 2H, Ar-H), 8.08-8.10 (m, 1H, Ar-H), 8.28-8.30 (m, 1H, Ar-H) ppm.

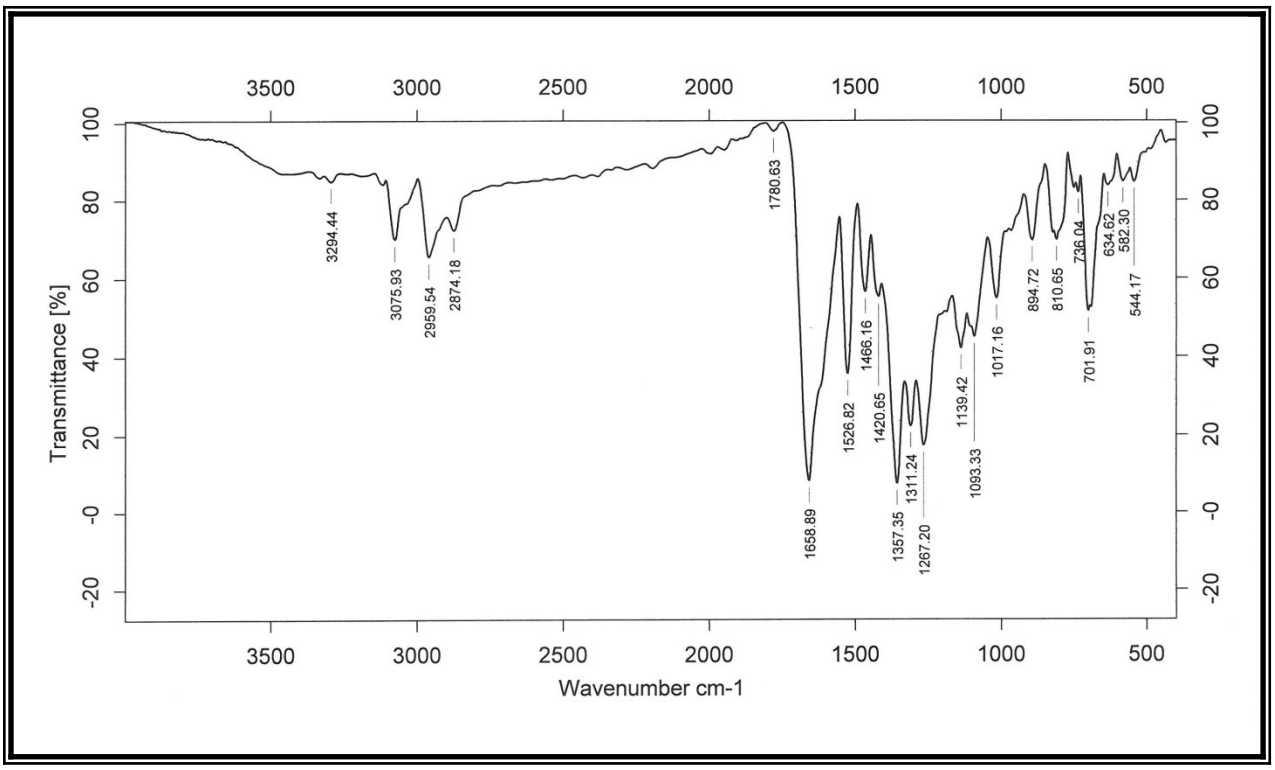


Fig. 20. FT-IR of 13-(2-Chlorophenyl)-2,3,4,13-tetrahydro-1*H*-indazolo[1,2-b]phthalazine-1,6,11-trione.

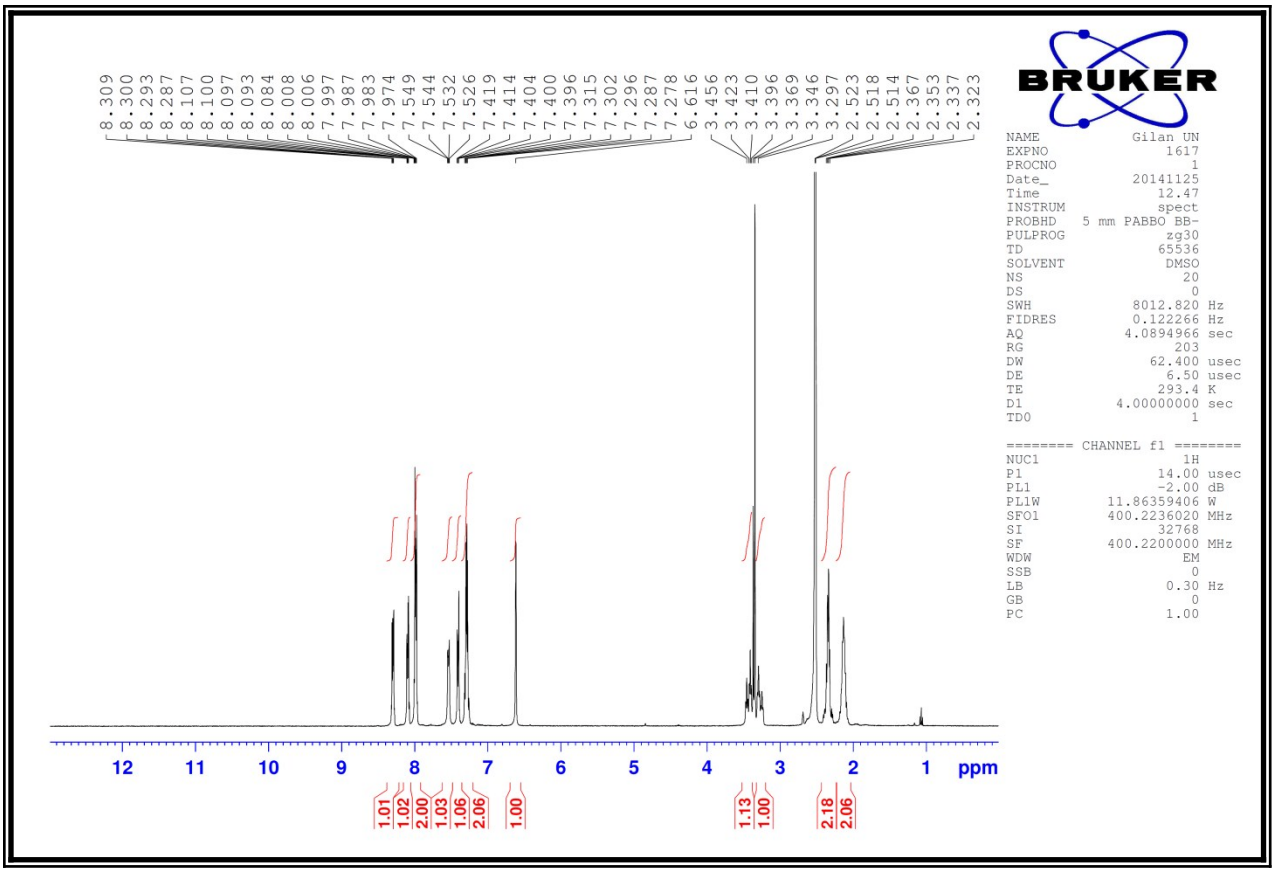


Fig. 21. ^{1}H NMR of 13-(2-Chlorophenyl)-2,3,4,13-tetrahydro-1*H*-indazolo[1,2-b]phthalazine-1,6,11-trione.

13-(2-Nitrophenyl)-2,3,4,13-tetrahydro-1*H*-indazolo[1,2-b]phthalazine-1,6,11-trione (3N): White solid, Yield: 92%, M.p. 248-250 ^{o}C; FT-IR (KBr): ν_{max} = 2954, 1660, 1524, 1364, 1271, 698 cm^{-1}.; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.10-2.17 (m, 2H, CH_2), 2.33-2.36 (m, 2H, CH_2), 3.24-3.45 (m, 2H, CH_2), 7.18 (s, 1H, CH), 7.52-7.56 (1H, td, J_1 = 7.2 Hz, J_2 = 1.2 Hz), 7.61-7.65 (1H, td, J_1 = 7.2 Hz, J_2 = 1.2 Hz), 7.70-7.72 (2H, dd, J_1= 8.0 Hz, J_2 = 1.2 Hz), 7.97-8.01 (m, 3H, Ar-H), 8.07-8.11 (m, 1H, Ar-H), 8.27-8.29 (m, 1H, Ar-H) ppm.; ^{13}C NMR (DMSO-d_6, 100 MHz,) : δ 192.75, 155.87, 154.40, 154.21, 149.28, 135.07, 134.37, 134.13, 131.80, 131.25, 129.78, 129.61, 133.538, 132.547, 132.393, 132.108, 125.427, 63.976, 39.559, 27.569, 25.566 ppm.

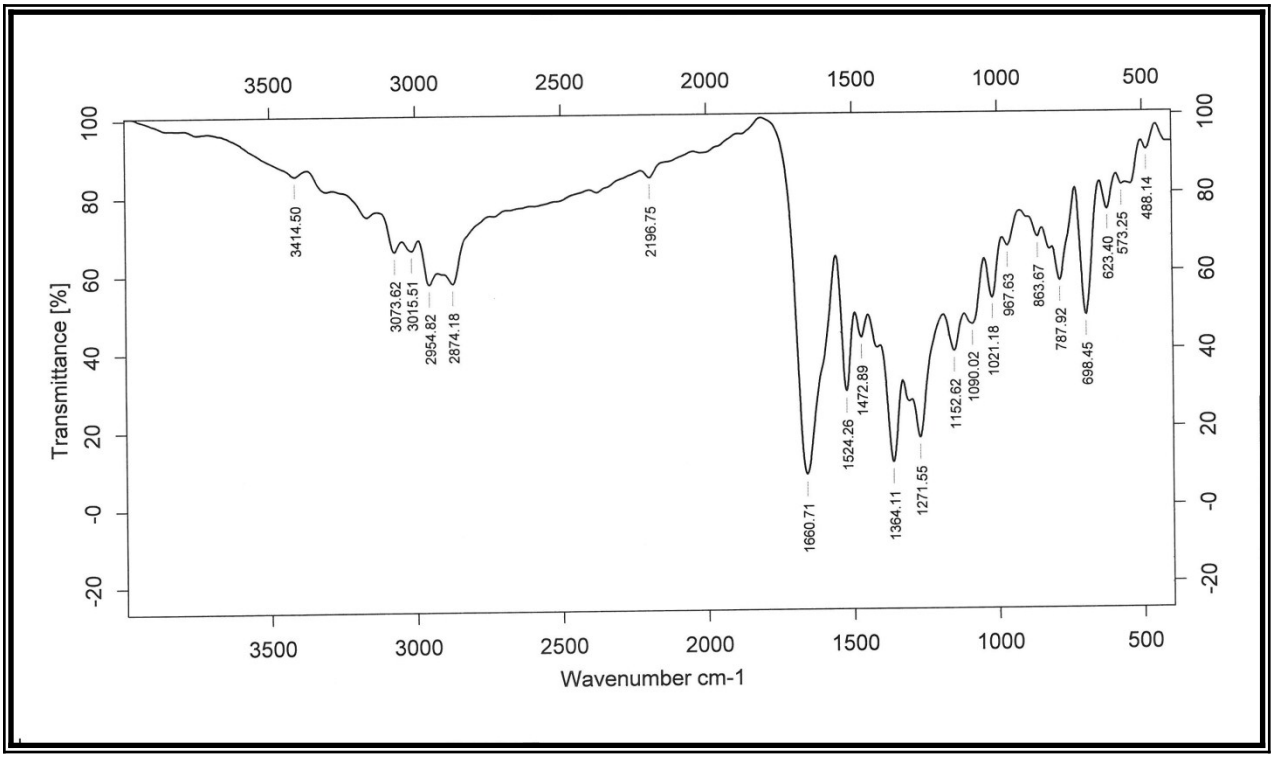


Fig. 22. FT-IR of 13-(2-Nitrophenyl)-2,3,4,13-tetrahydro-1*H*-indazolo[1,2-b]phthalazine-1,6,11-trione.

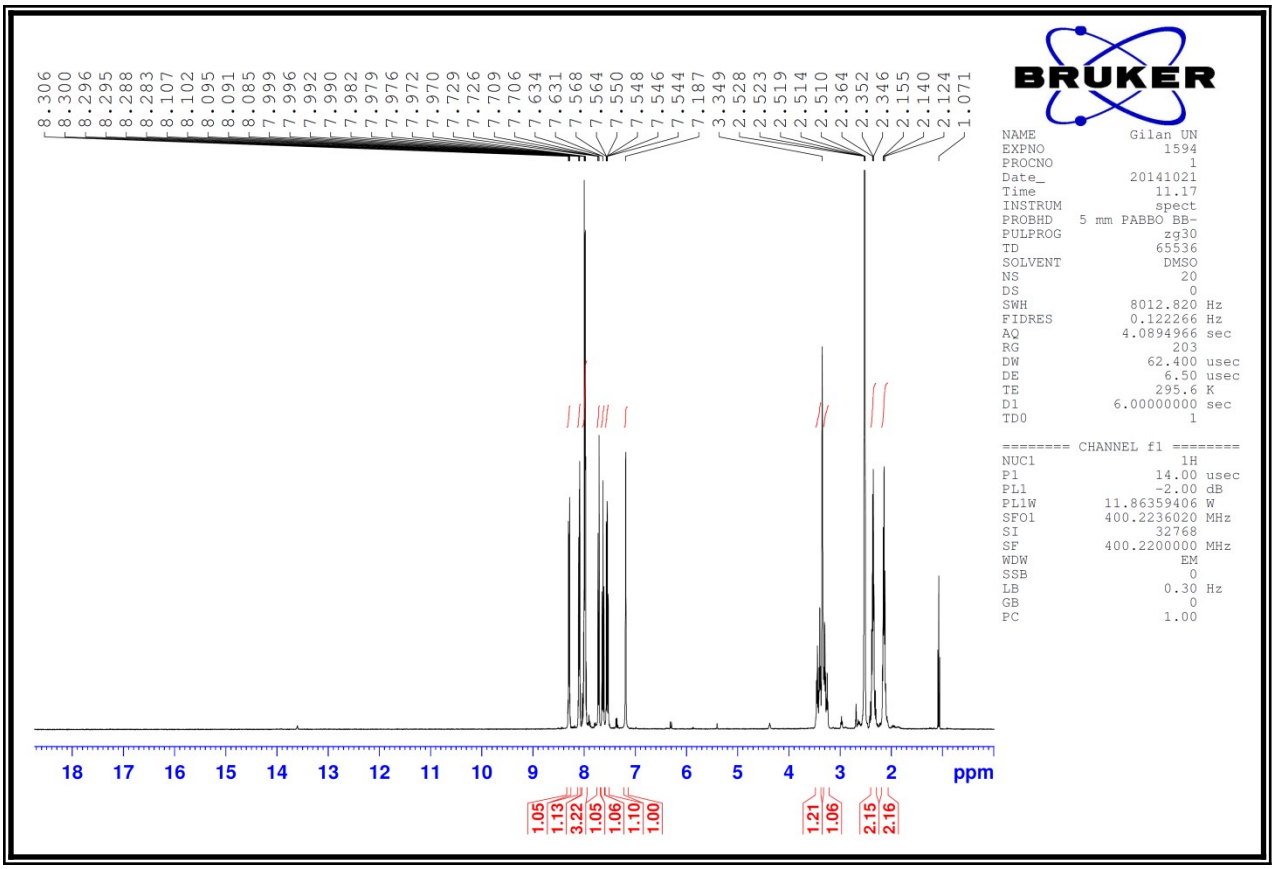


Fig. 23. [1]H NMR of 13-(2-Nitrophenyl)-2,3,4,13-tetrahydro-1*H*-indazolo[1,2-b]phthalazine-1,6,11-trione.

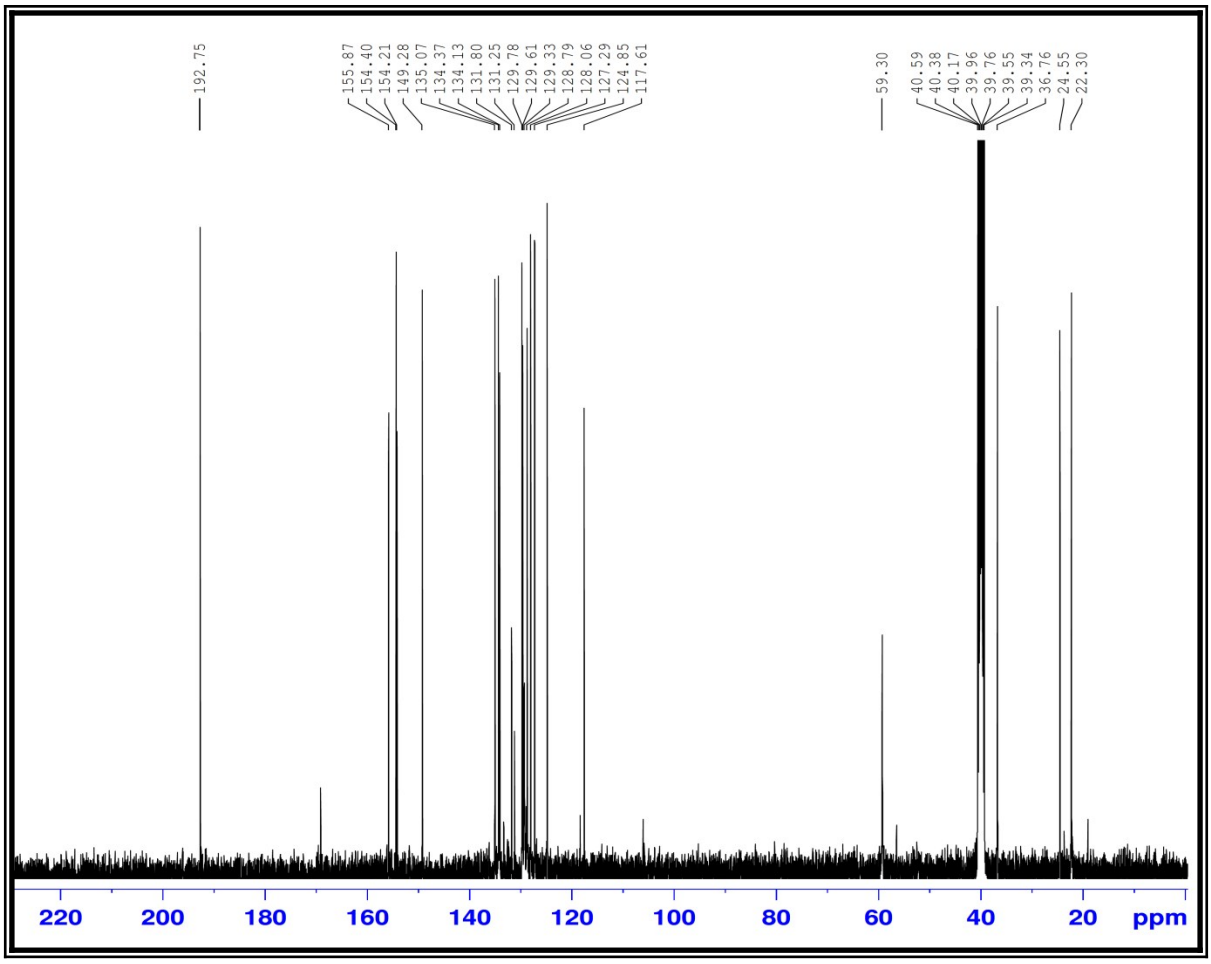


Fig. 24. ^{13}C NMR of 13-(2-Nitrophenyl)-2,3,4,13-tetrahydro-1*H*-indazolo[1,2-b]phthalazine-1,6,11-trione.

4-(1,6,11-Trioxo-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-b]phthalazin-13-yl)benzonitrile (3T): White solid, Yield: 93%, M.p. 284-285 ^{o}C; FT-IR (KBr): ν_{max} = 2953, 2658, 1472, 1361, 1306, 1262, 835, 698 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.11-2.13 (m, 2H, CH_2), 2.33-2.36 (m, 2H, CH_2), 3.21-3.26 (m, 2H, CH_2), 6.35 (s, 1H, CH), 7.71-7.73 (d, J =8 Hz, 2H, Ar-H), 7.79-7.81 (d, J = 8 Hz, 2H, Ar-H), 7.97-8.01 (m, 2H, Ar-H), 8.09-8.11 (m, 1H, Ar-H), 8.28-8.30 (m, 1H, Ar-H) ppm.

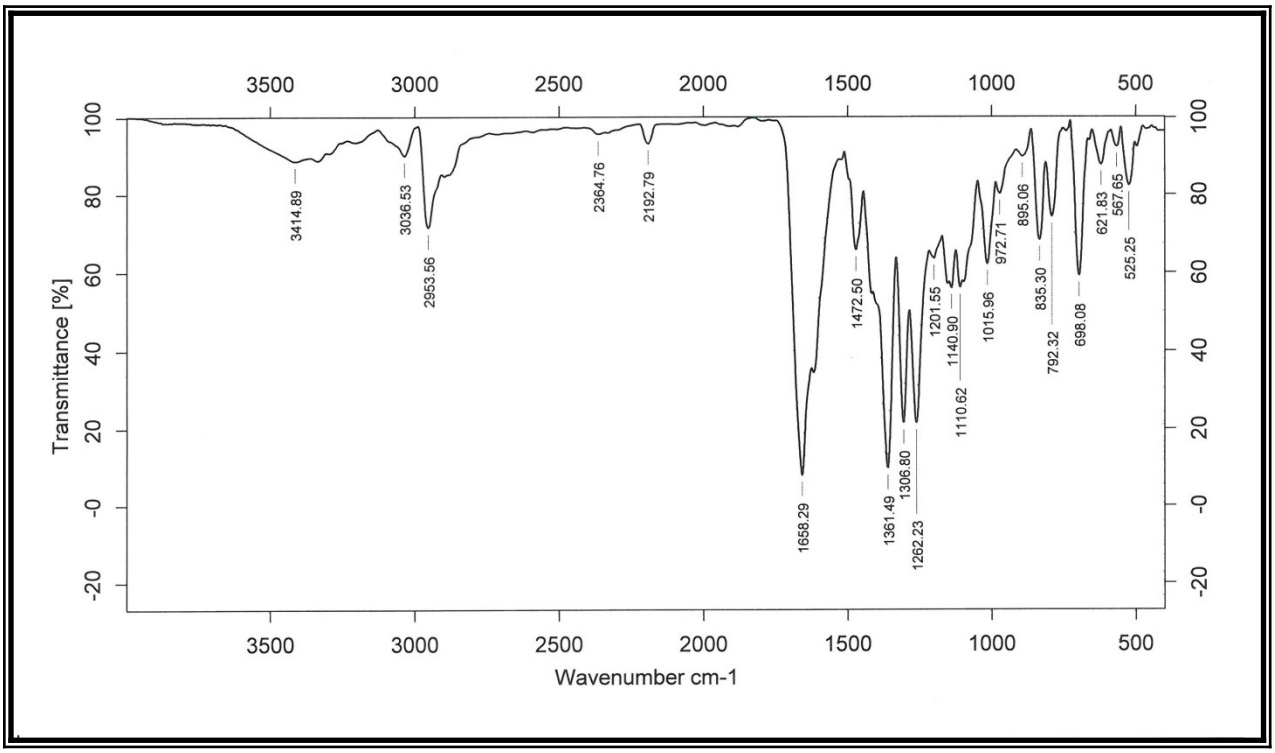


Fig. 25. FT-IR of 4-(1,6,11-Trioxo-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-b]phthalazin-13-yl)benzonitrile.

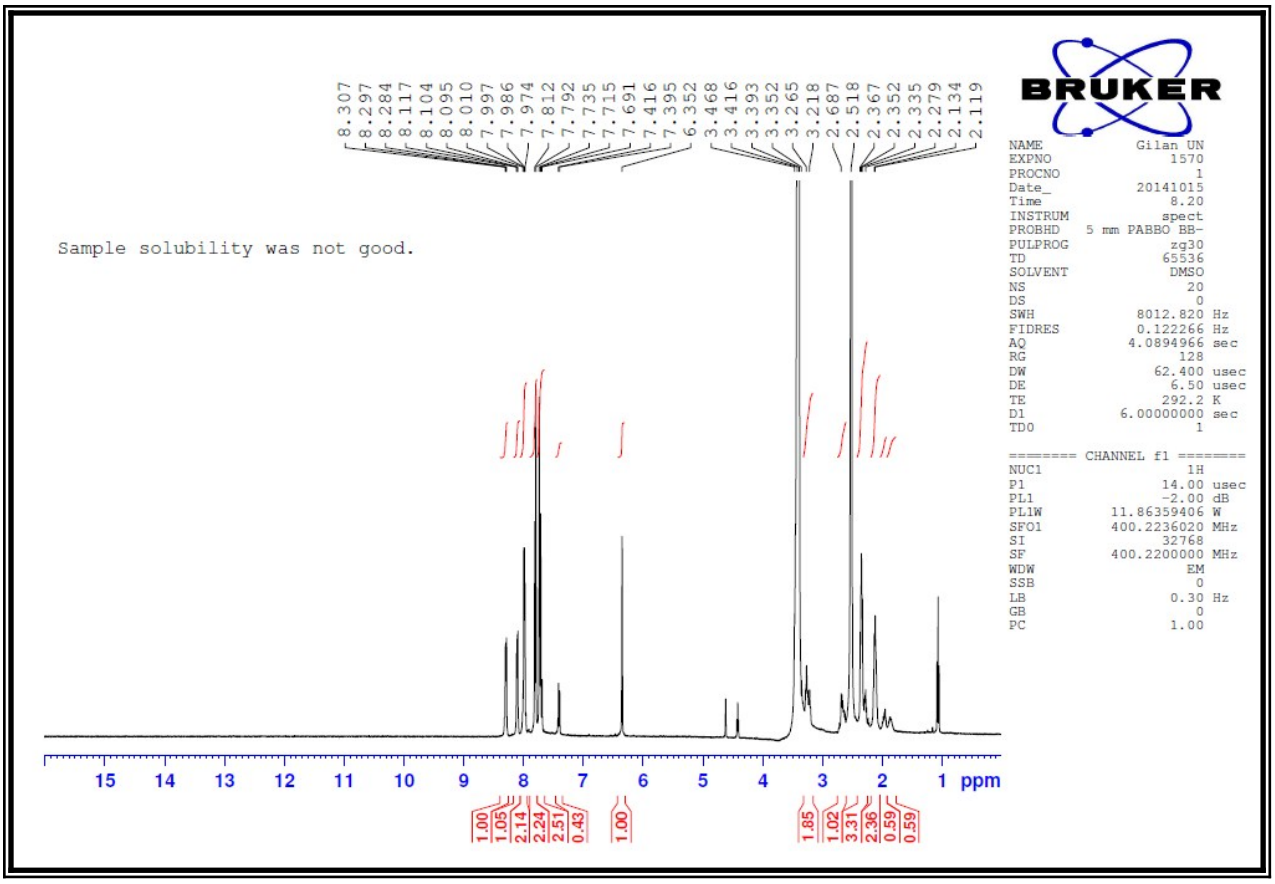


Fig. 26. [1]H NMR of 4-(1,6,11-Trioxo-2,3,4,6,11,13-hexahydro-1*H*-indazolo[1,2-b]phthalazin-13-yl)benzonitrile.