Construction of Porphyrin Based Photocatalyst Comprising Pyridinium Ionic Liquid Moiety for Metal-Free Visible Light-Assisted N-Arylation of Amines: Facile Approach to Afford Drug Intermediates

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Supporting information

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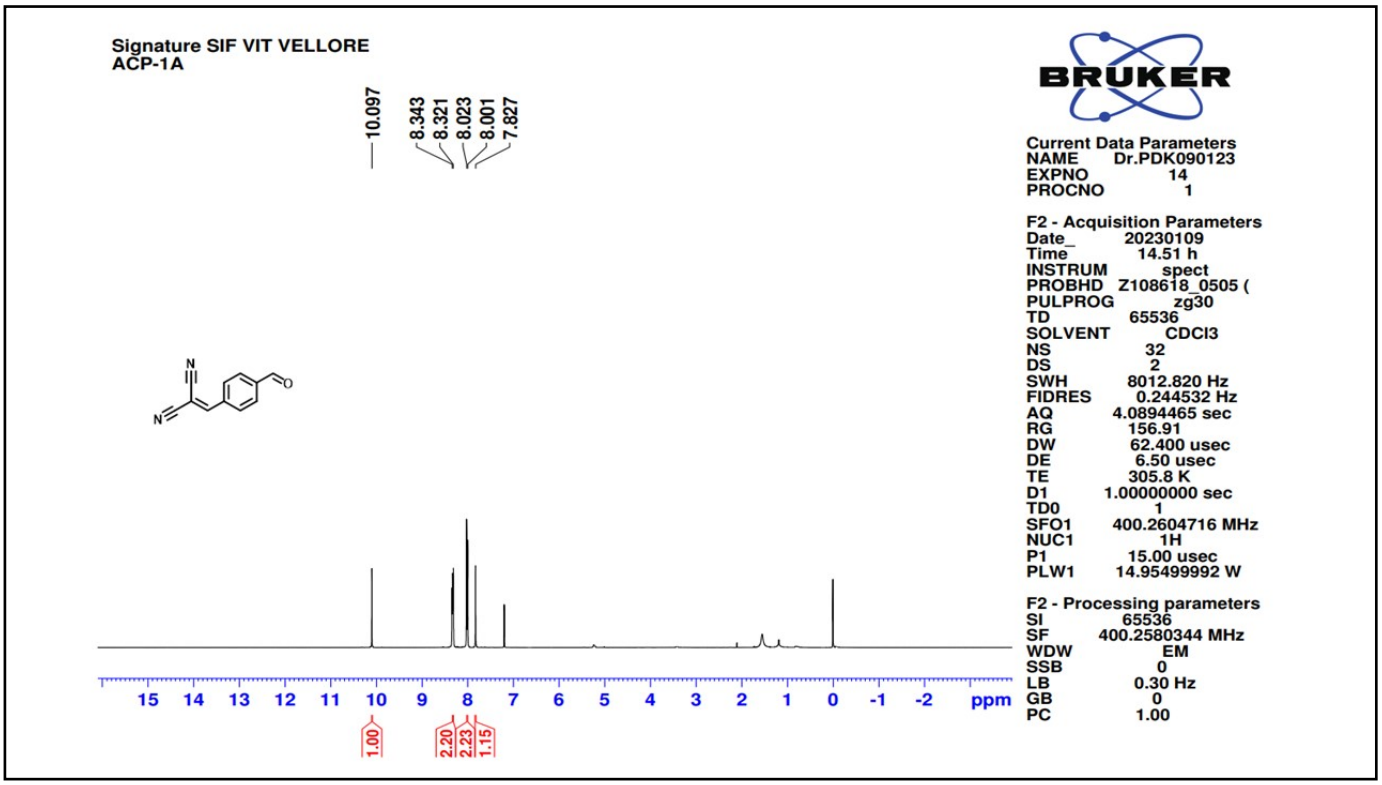


Fig S1. ^{1}H NMR spectrum of 2-(4-formylbenzylidene) malononitrile **(1A)**

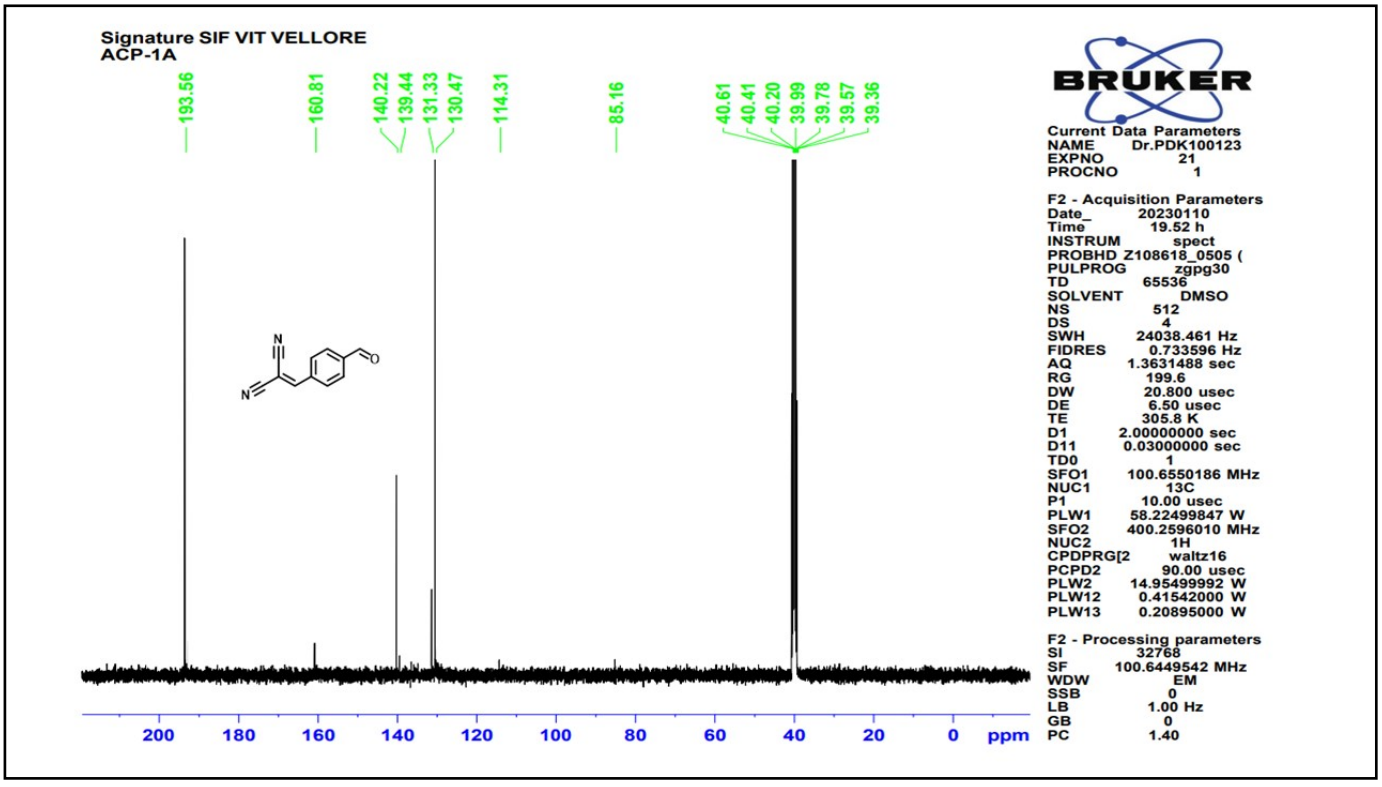


Fig S2. ^{13}C NMR spectrum of 2-(4-formylbenzylidene) malononitrile **(1A)**

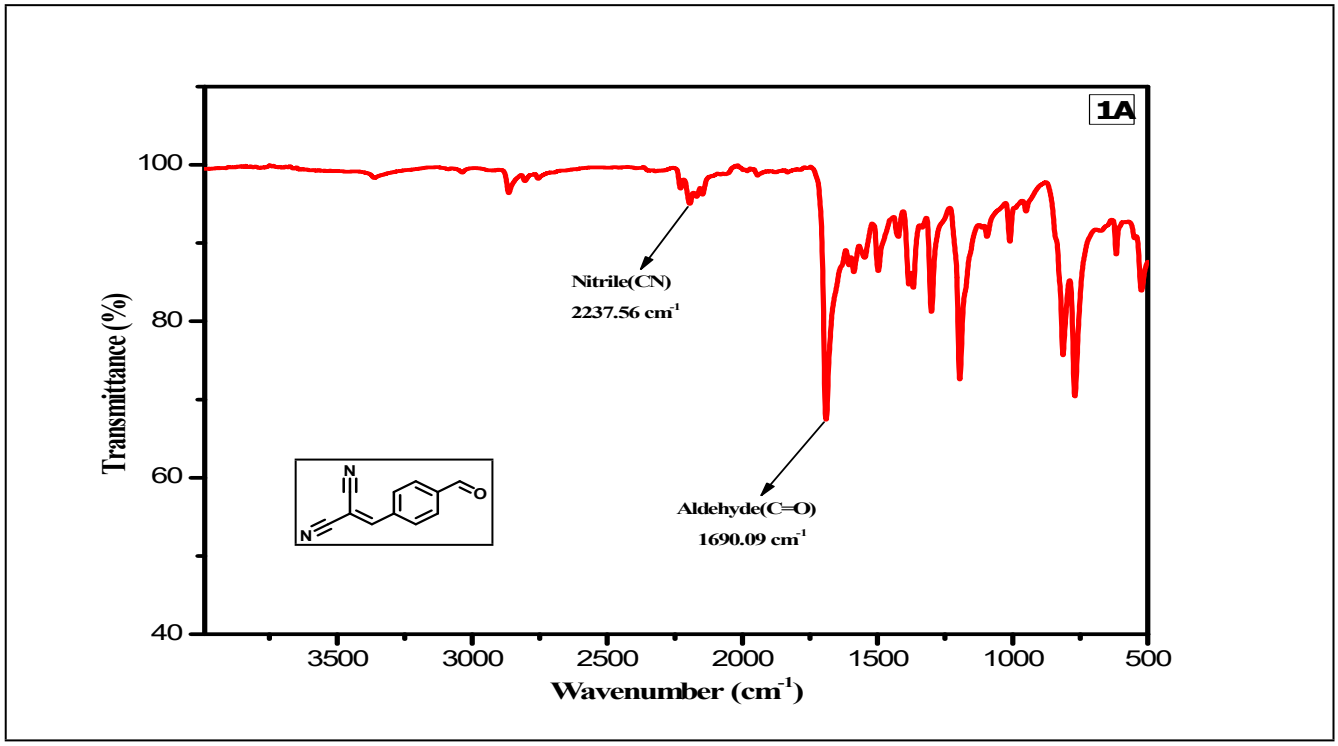


Fig. S3. FT-IR Spectrum of 2-(4-formyl benzylidene) malononitrile **(1A)**

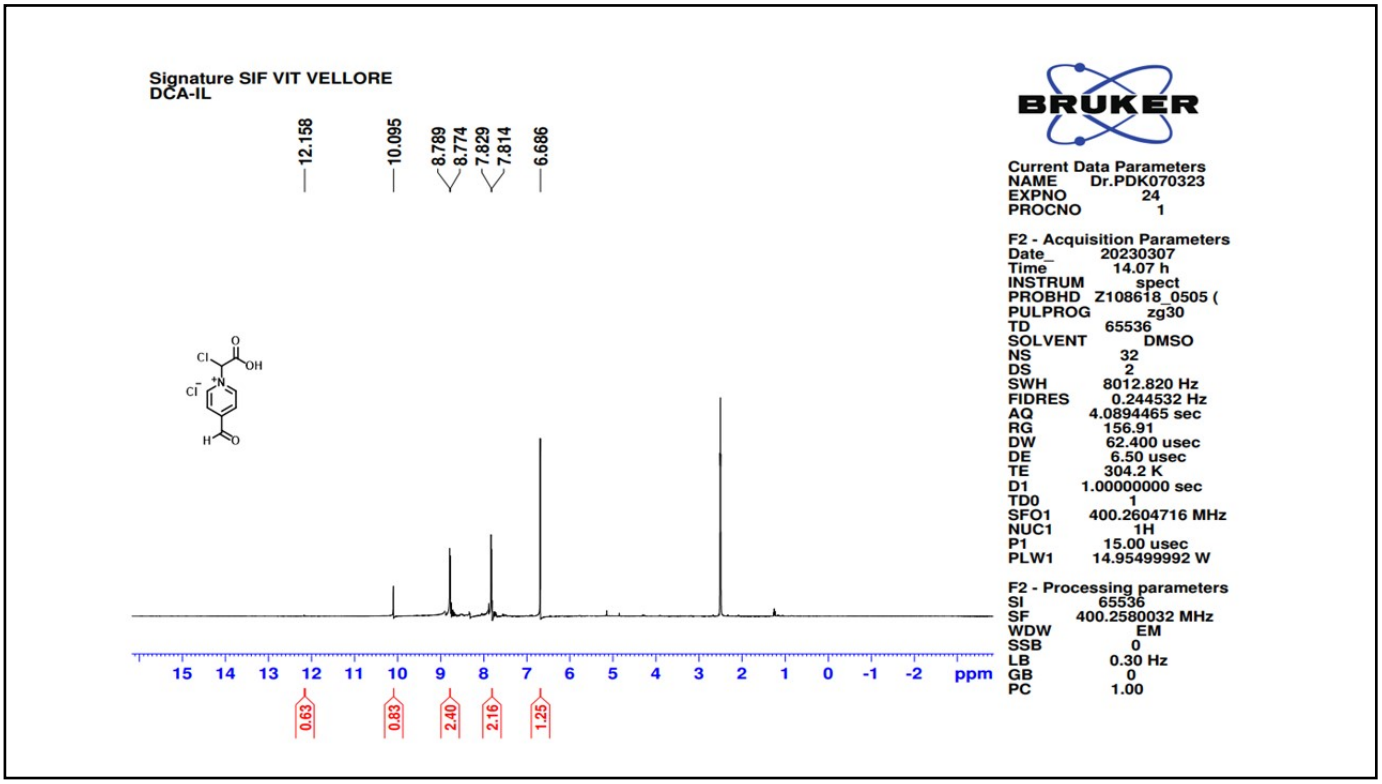


Fig S4. [1]H NMR spectrum of 1-(carboxychloromethyl)-4-formyl-pyridin-1-ium chloride **(1B)**

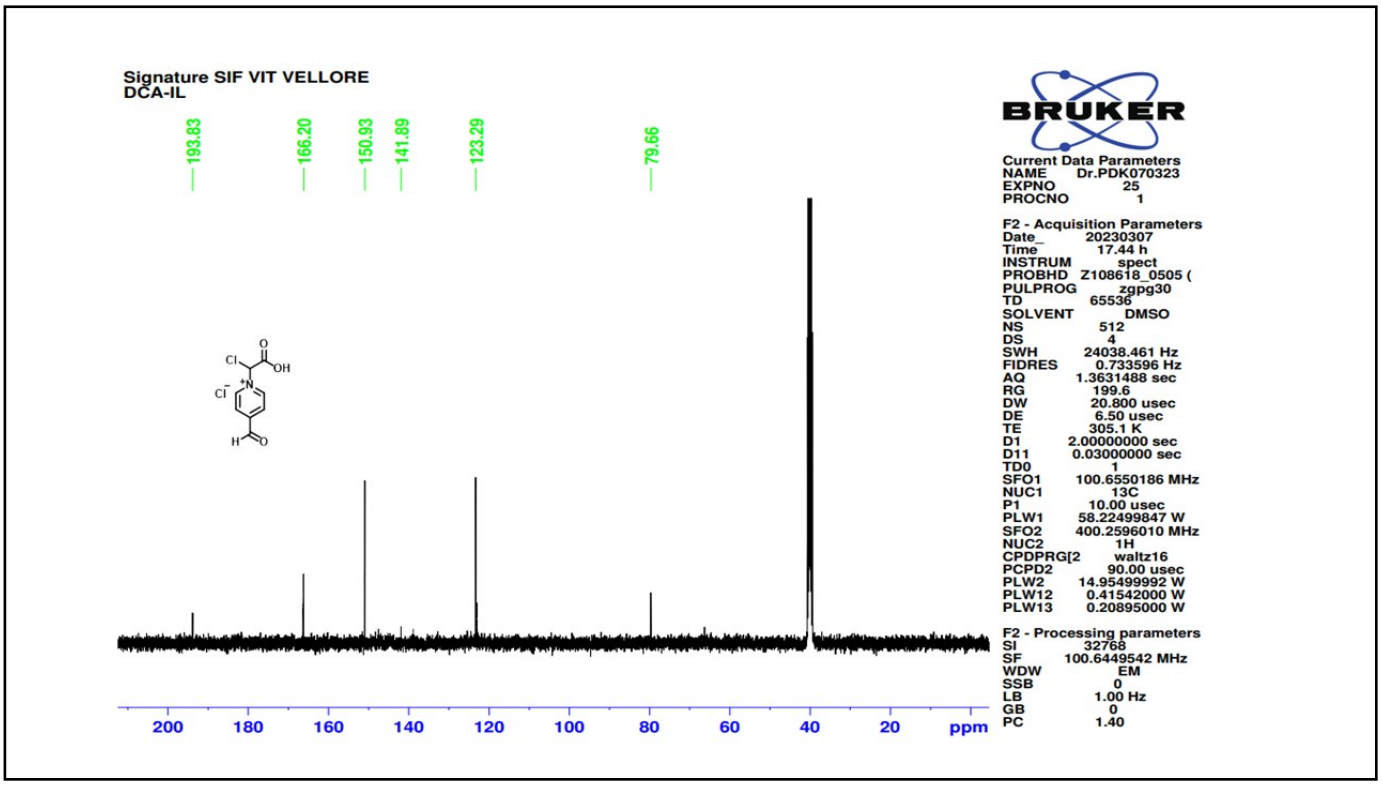


Fig S5. ^{13}CNMR spectrum of 1-(carboxychloromethyl)-4-formyl-pyridin-1-ium chloride **(1B)**

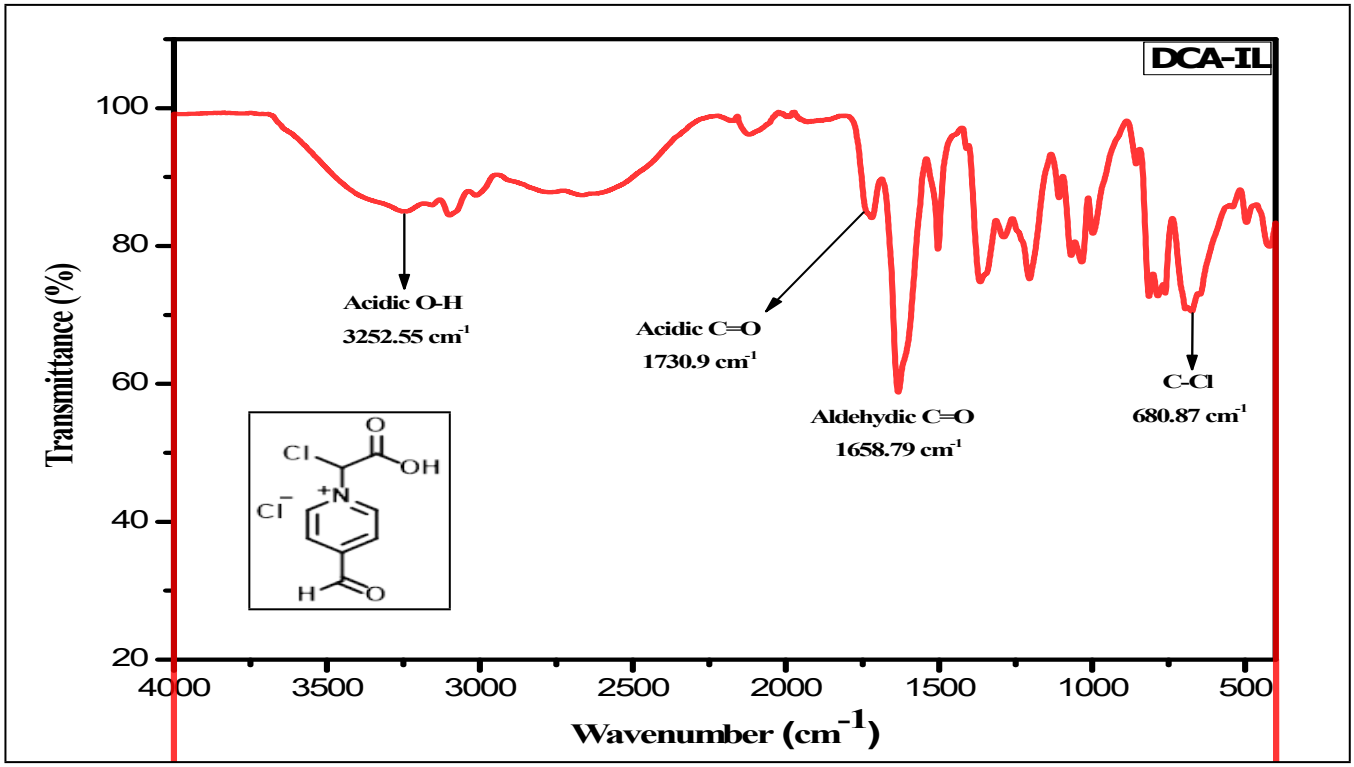


Fig S6. FT-IR spectrum of 1-(carboxychloromethyl)-4-formyl-pyridine-1-ium chloride **(1B)**

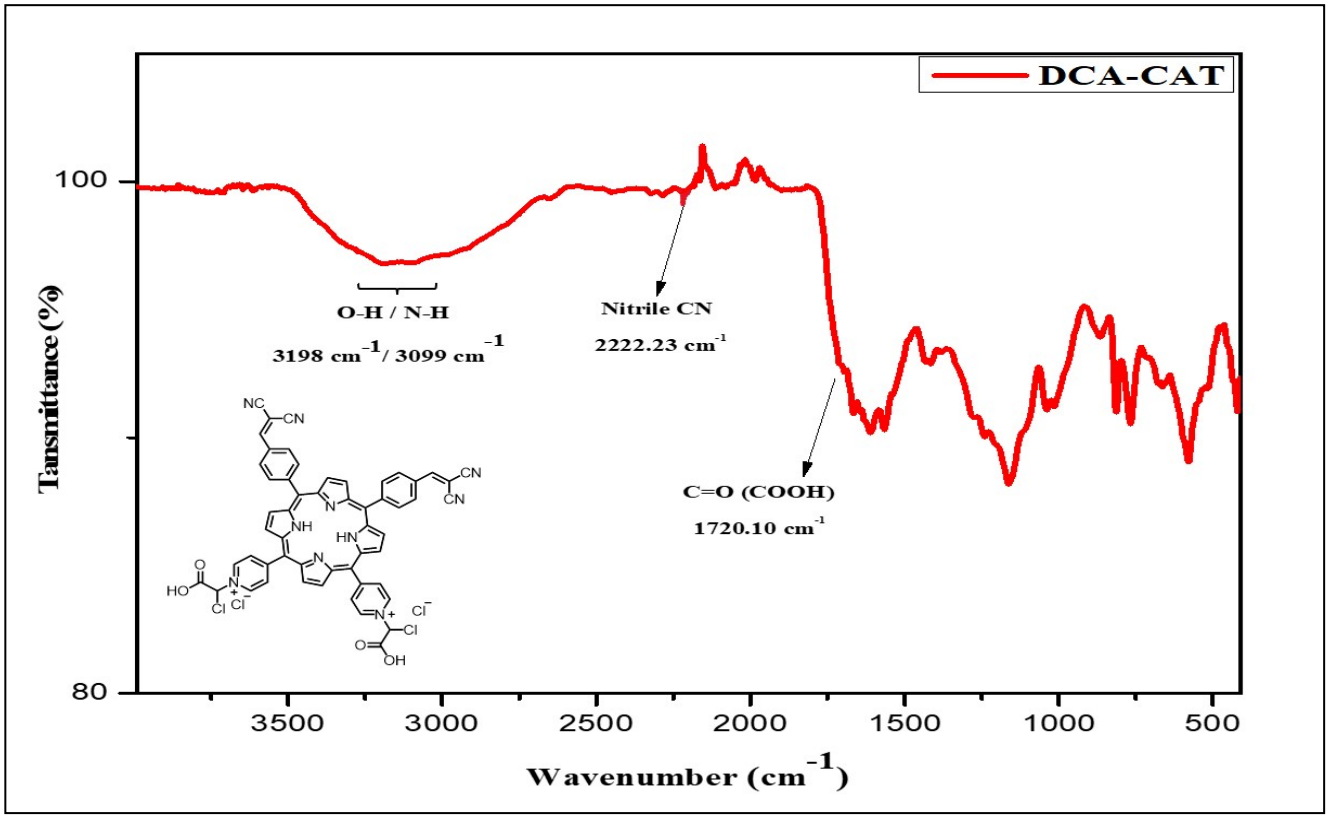


Fig S7. FT-IR Spectrum of PBILFPc Photocatalyst

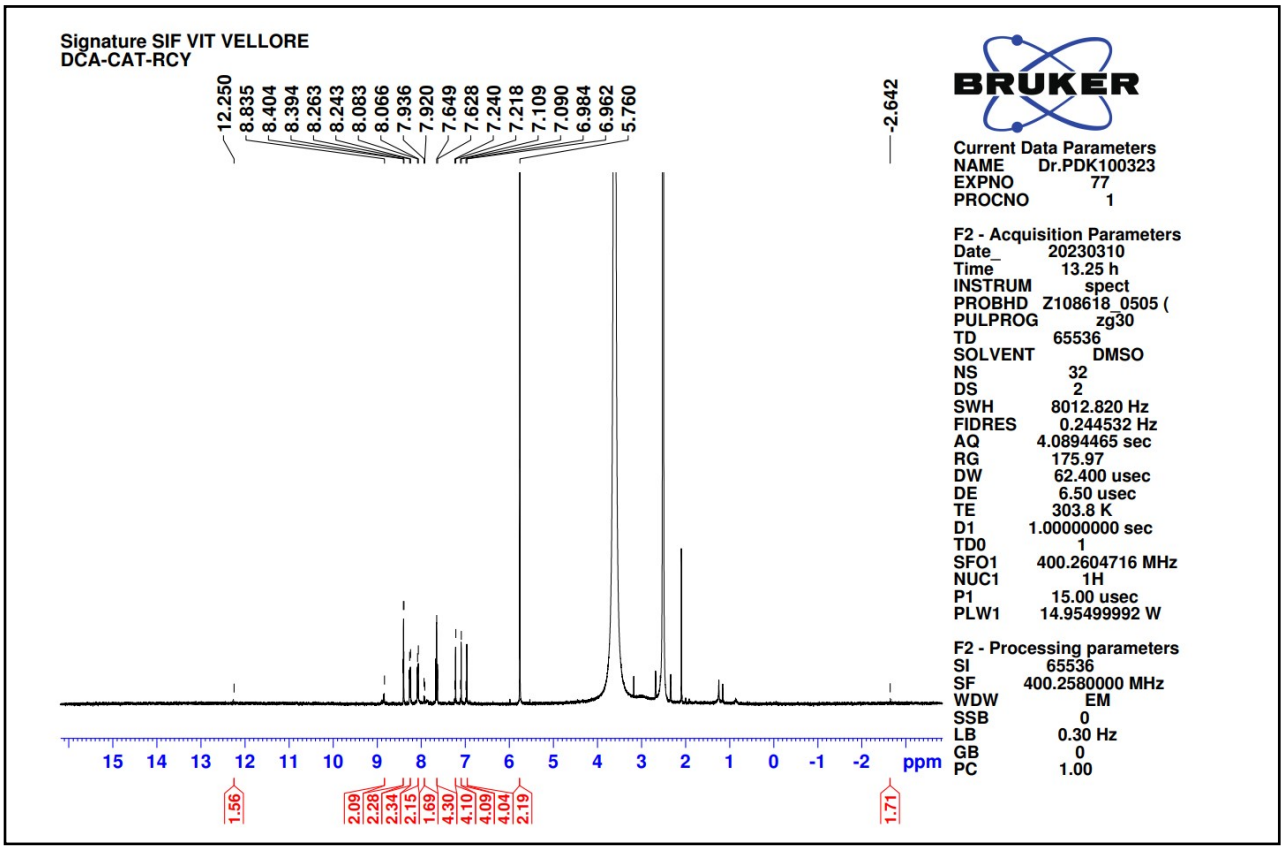


Fig S8. [1]H NMR spectrum of Recycled PBILFPc Photocatalyst

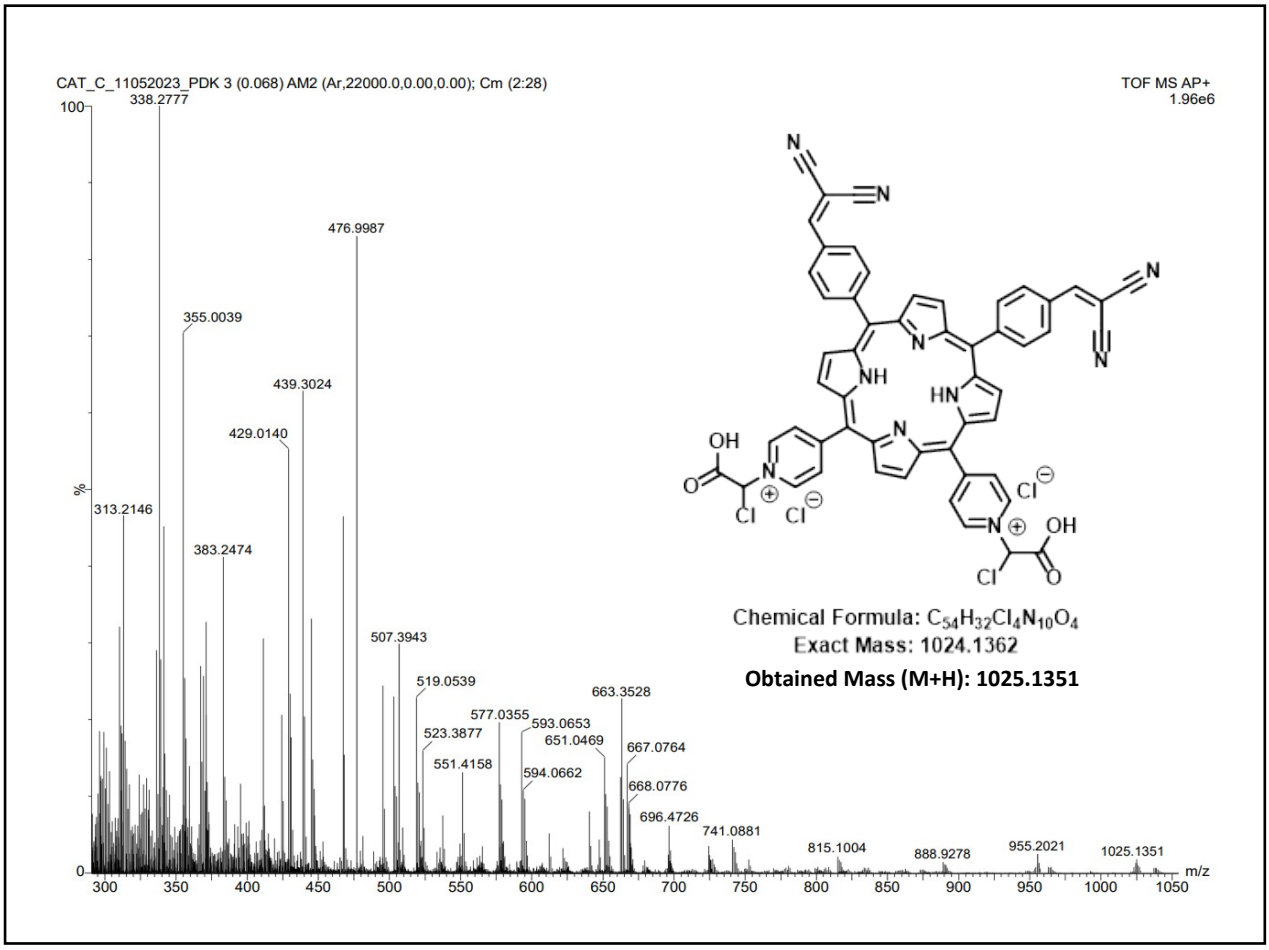


Fig S9. HRMS (M + H)+ Spectrum of PBILFPc Photocatalyst

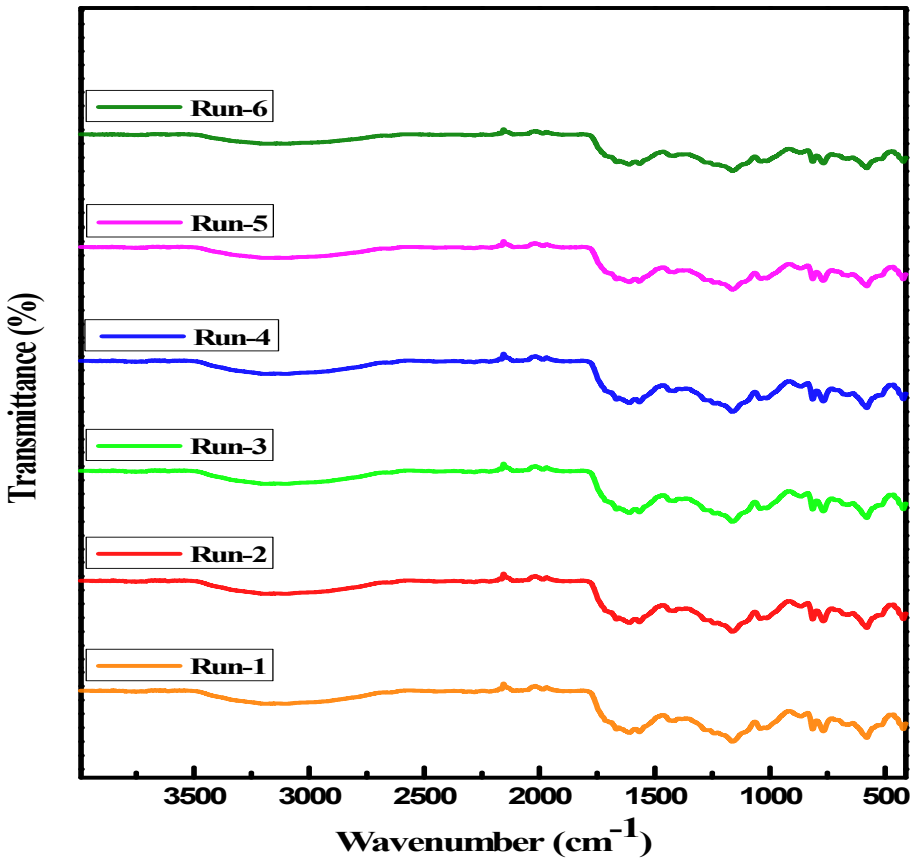


Fig S10. Comparative FT-IR Spectrum of PBILFPc Photocatalyst upto 6th Run

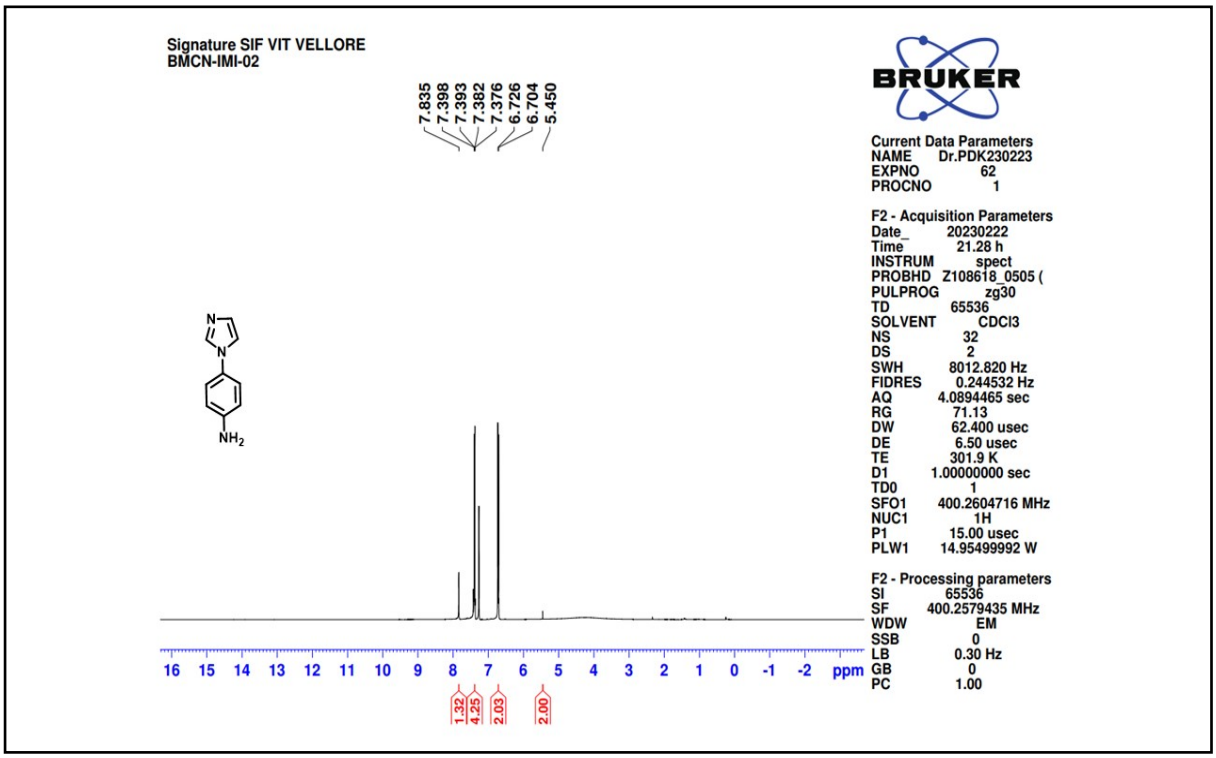


Fig S11. ^{1}H NMR spectrum of 4-(1H-imidazol-1-yl)aniline **(A2)**

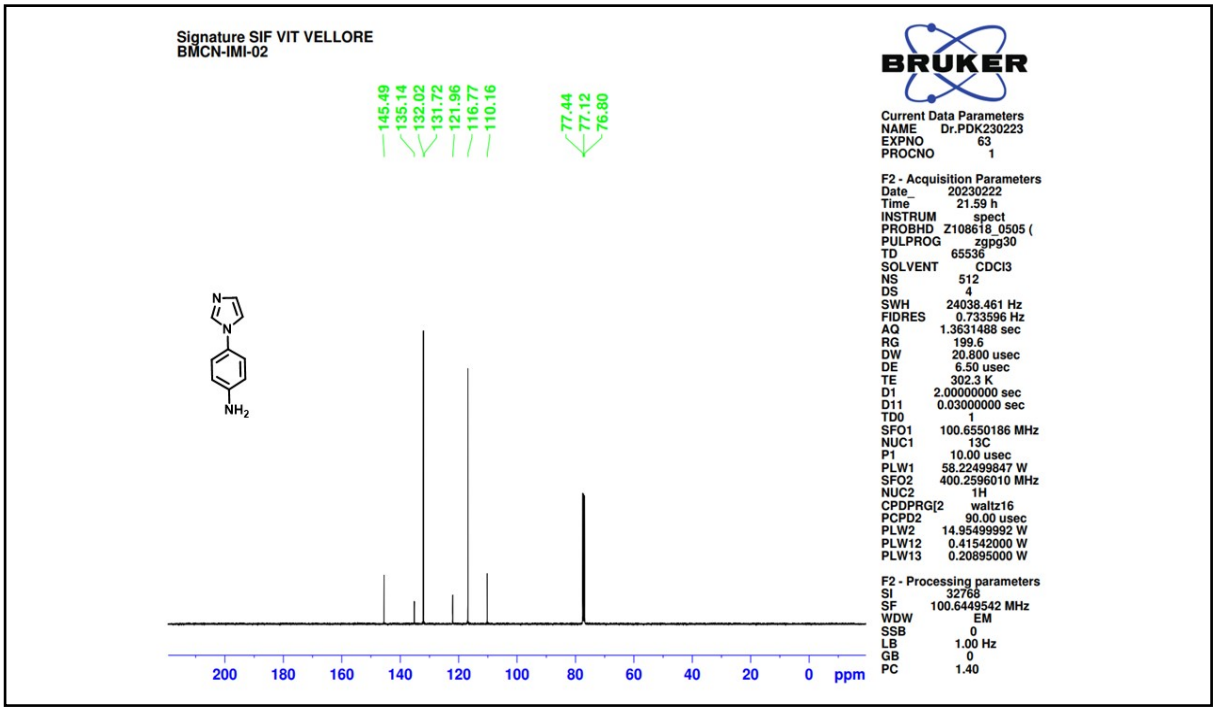


Fig S12. ^{13}C NMR spectrum of 4-(1H-imidazol-1-yl)aniline **(A2)**

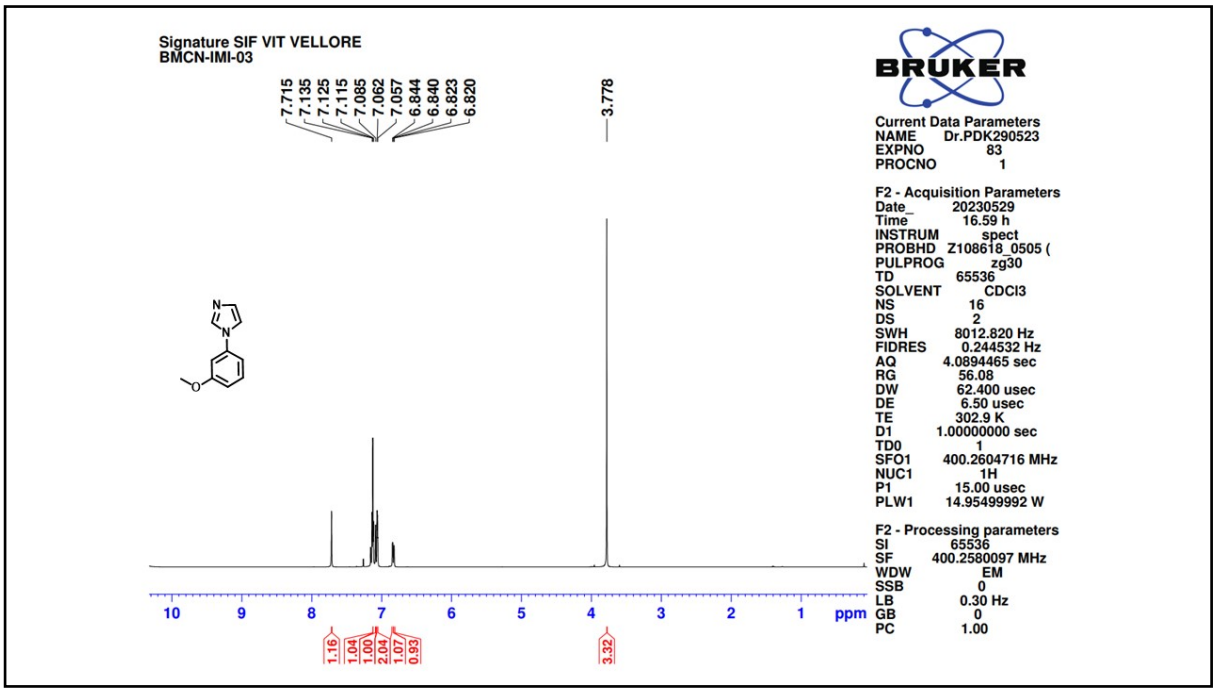


Fig S13. ^{1}H NMR spectrum of 1-(3-methoxyphenyl)-1H-imidazole **(A3)**

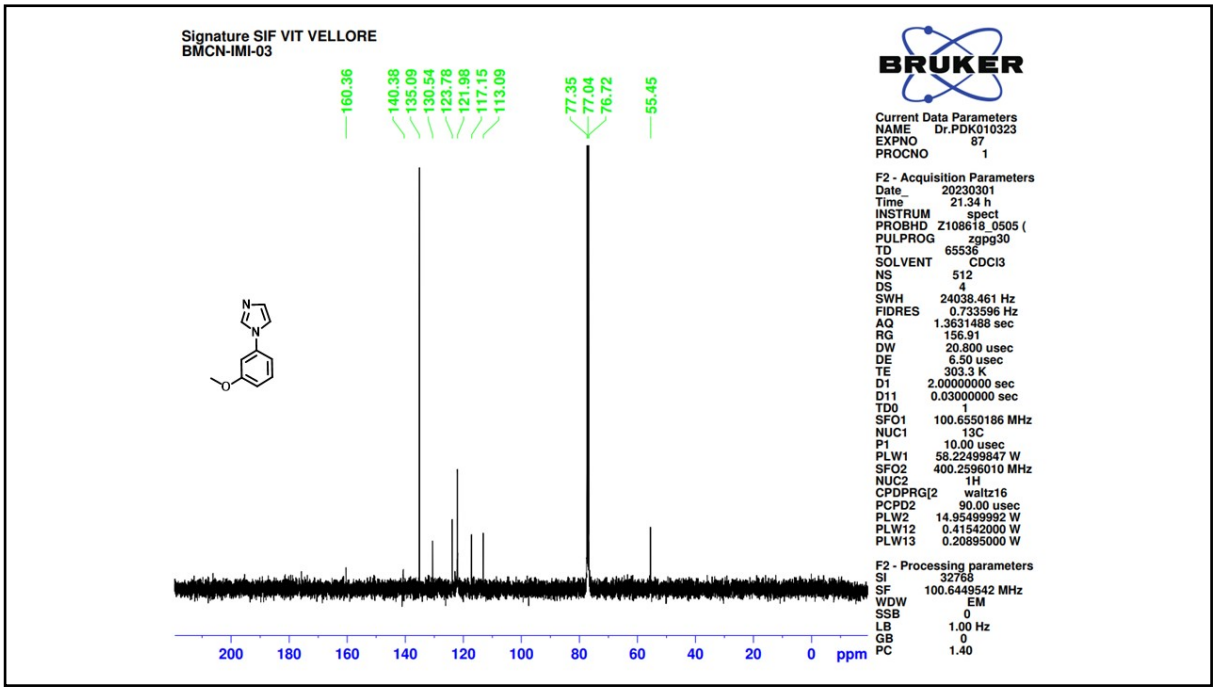


Fig S14. ^{13}C NMR spectrum of 1-(3-methoxyphenyl)-1H-imidazole **(A3)**

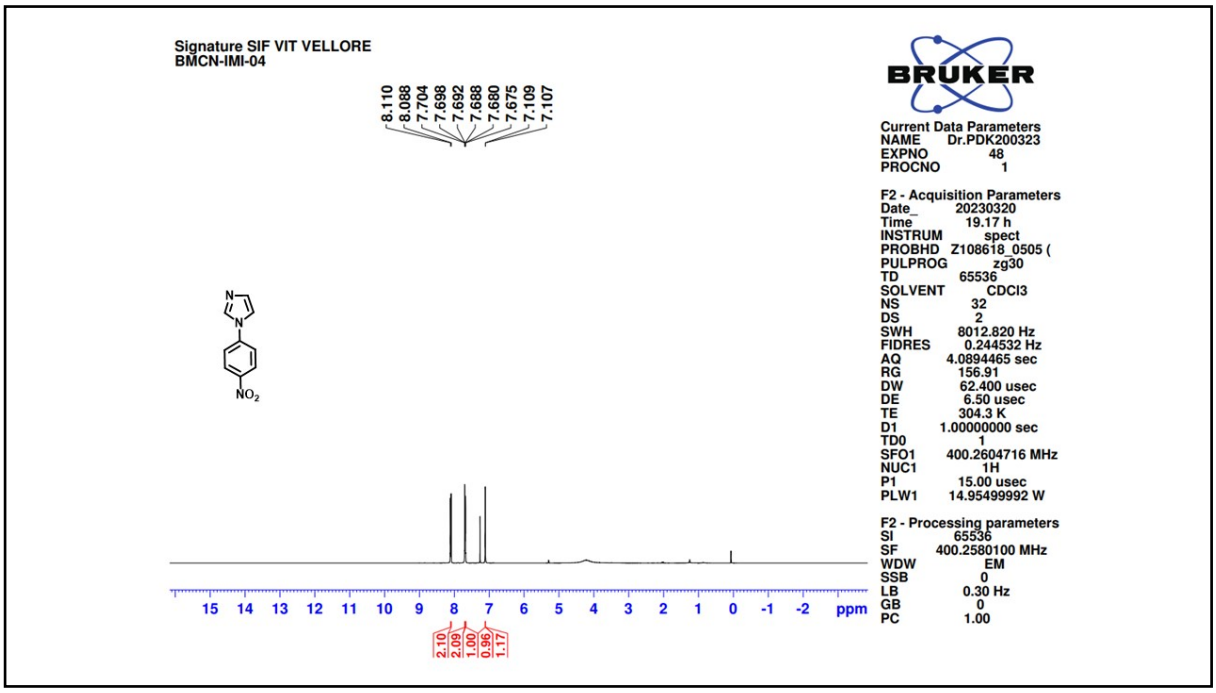


Fig S15. ^{1}H NMR spectrum of 1-(4-nitrophenyl)-1H-imidazole **(A4)**

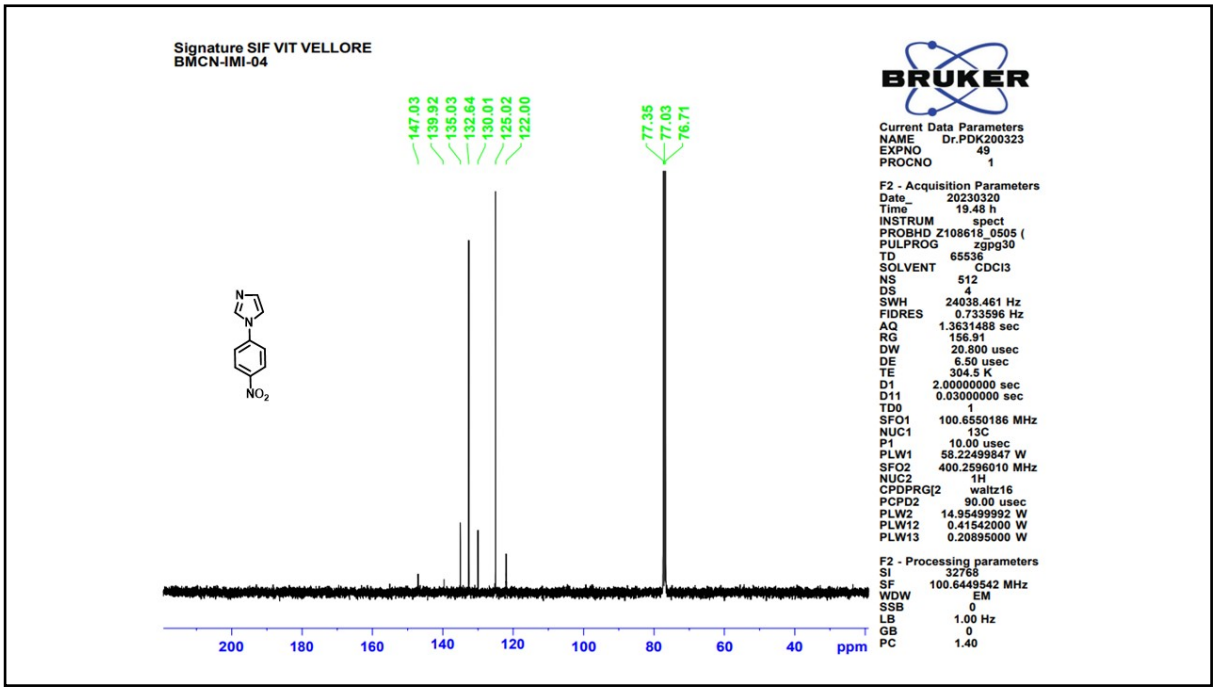


Fig S16. ^{13}C NMR spectrum of 1-(4-nitrophenyl)-1H-imidazole **(A4)**

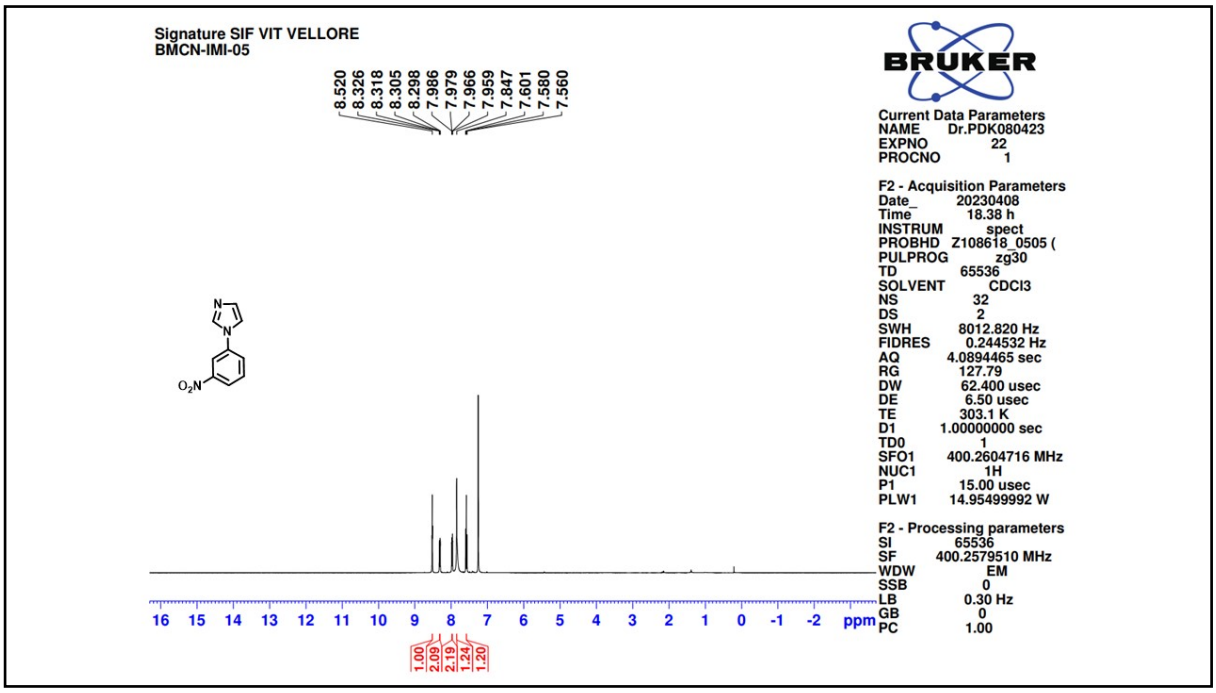


Fig S17. ^{1}H NMR spectrum of 1-(3-nitrophenyl)-1H-imidazole **(A5)**

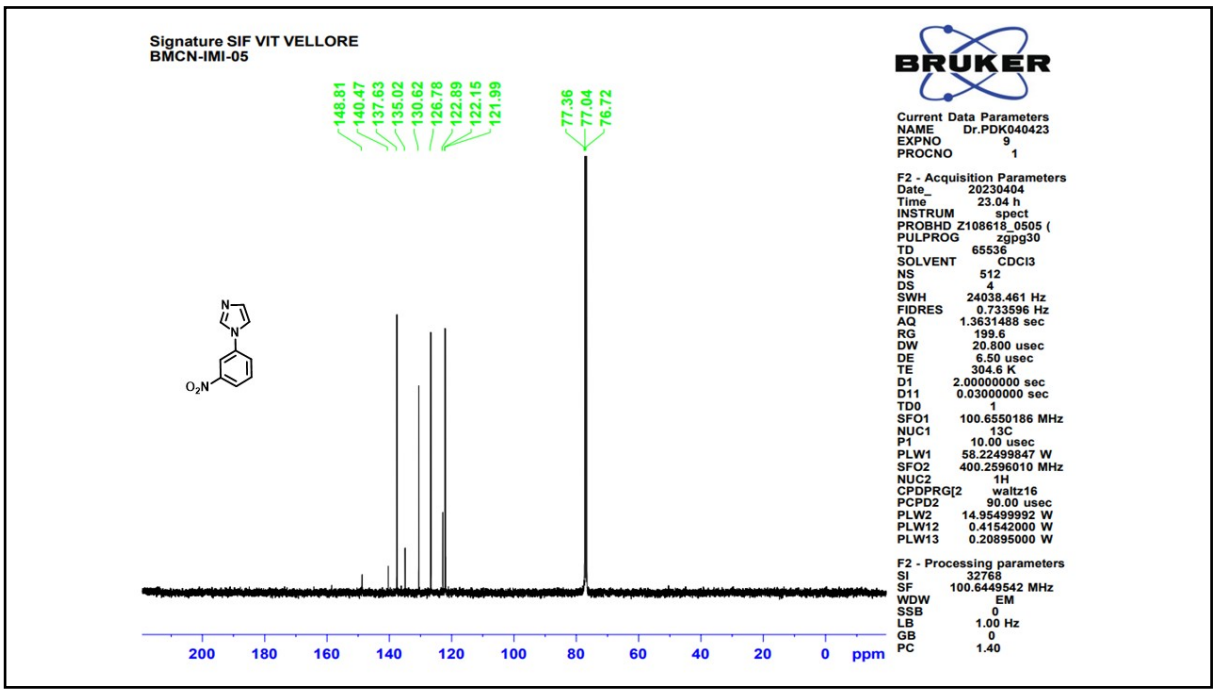


Fig S18. ^{13}C NMR spectrum of 1-(3-nitrophenyl)-1H-imidazole **(A5)**

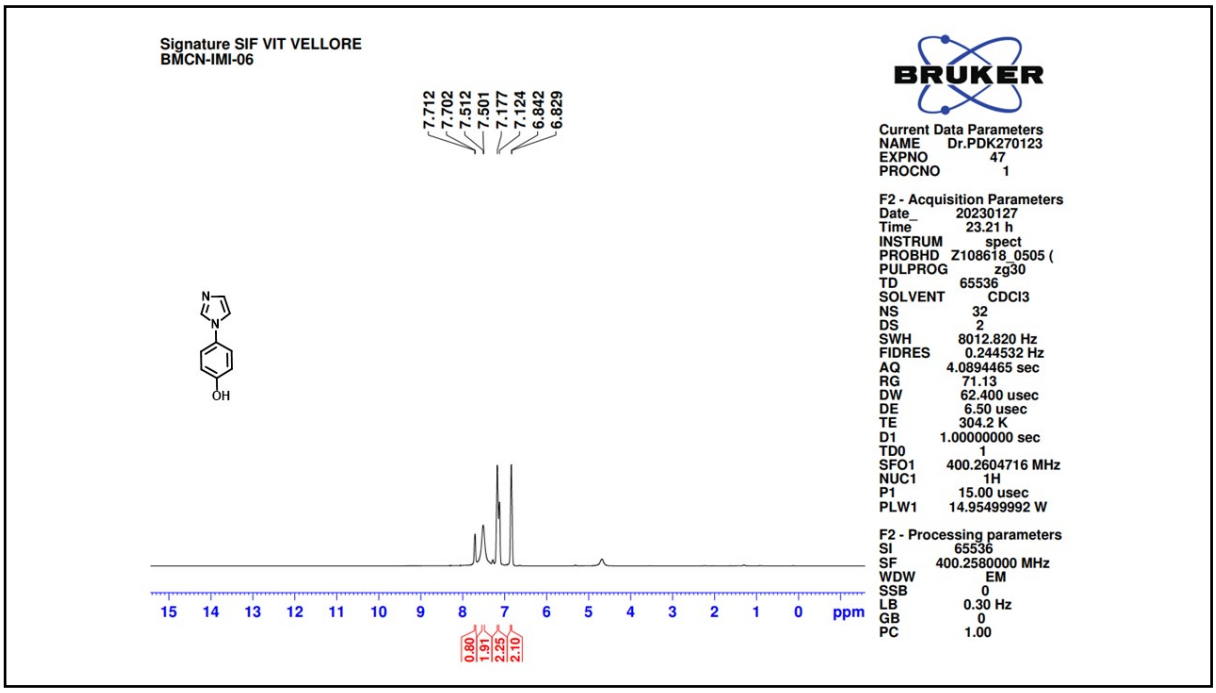


Fig S19. ^{1}H NMR spectrum of 4-(1H-imidazol-1-yl)phenol **(A6)**

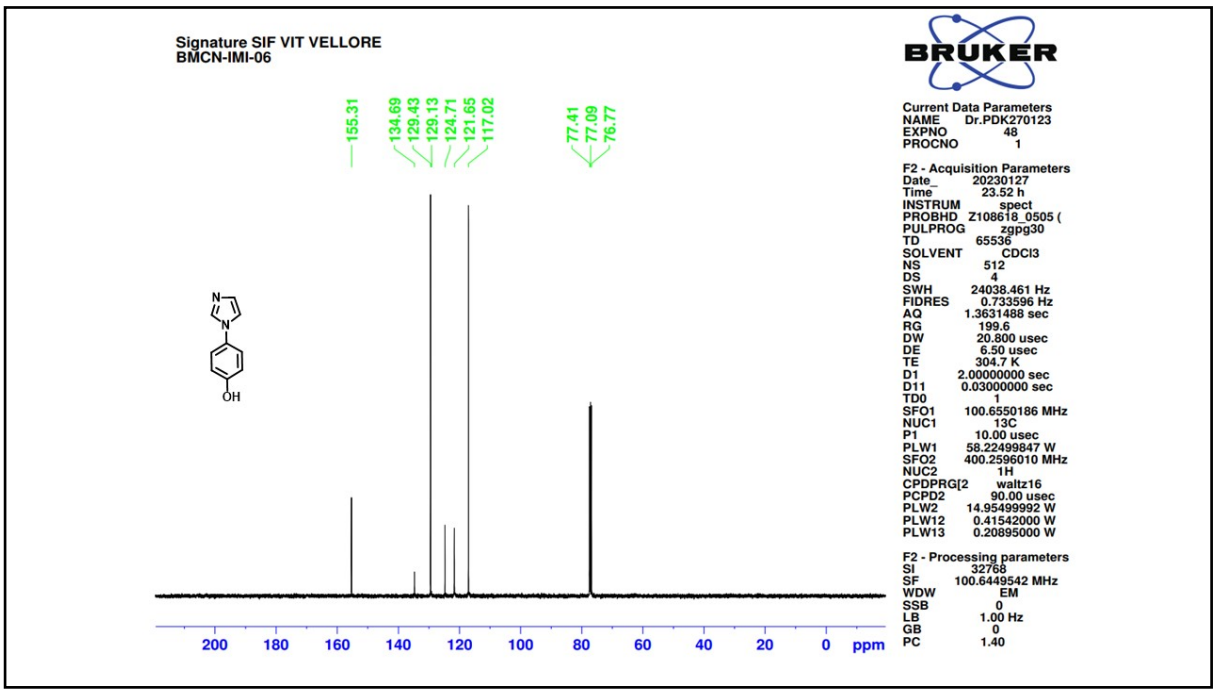


Fig S20. ^{13}C NMR spectrum of 4-(1H-imidazol-1-yl)phenol **(A6)**

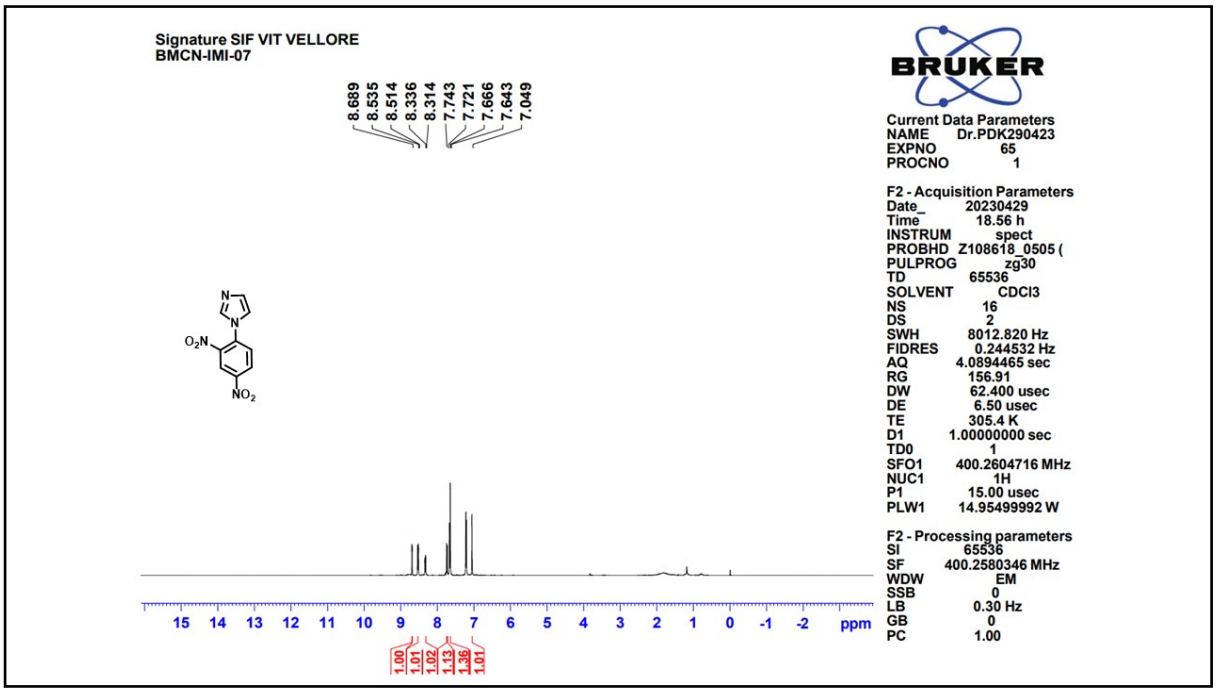


Fig S21. ^{1}H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-imidazole **(A7)**

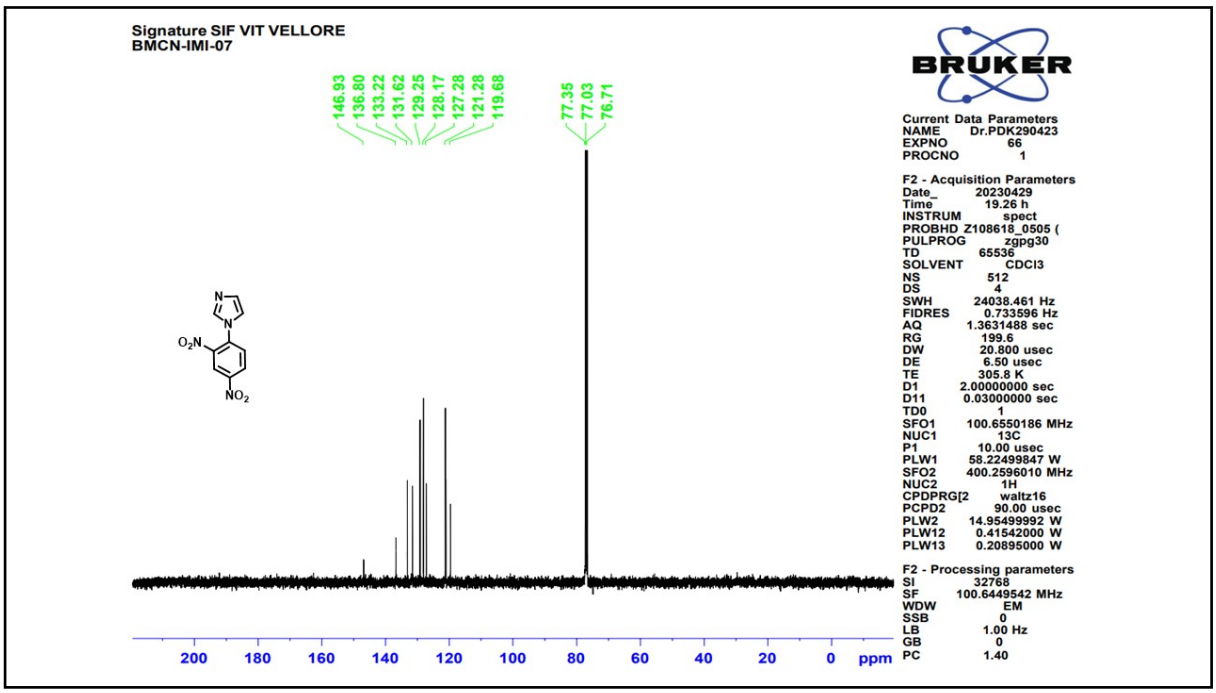


Fig S22. ^{13}C NMR spectrum of 1-(2,4-dinitrophenyl)-1H-imidazole **(A7)**

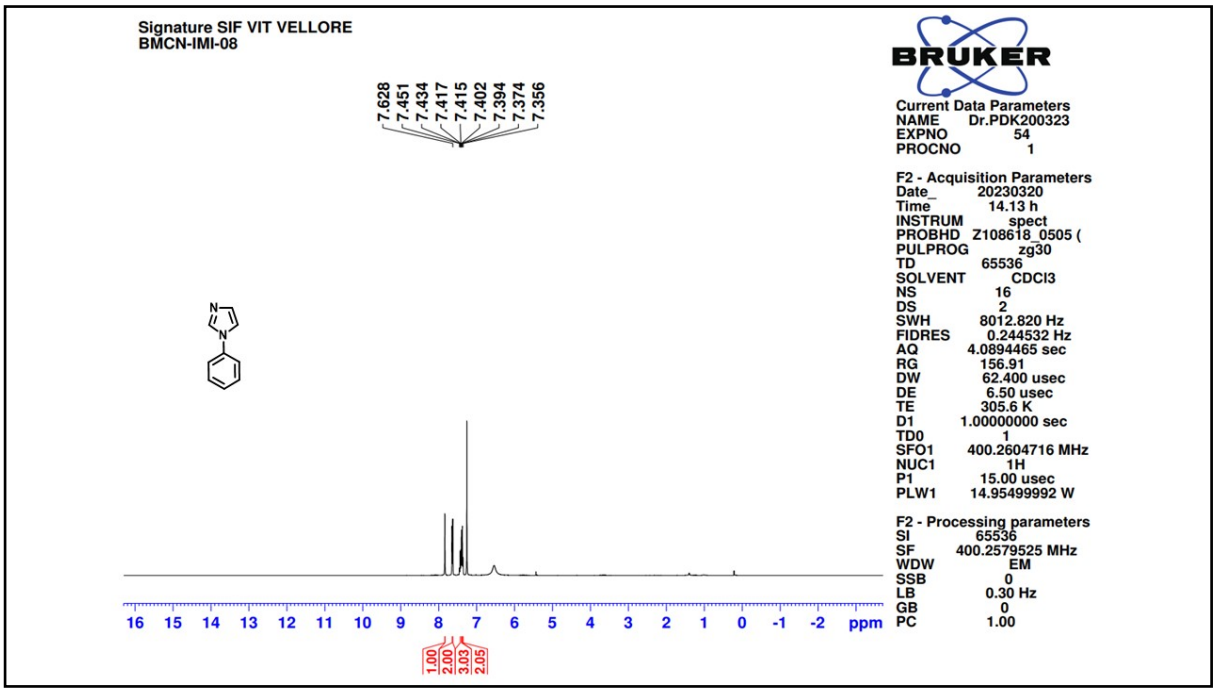


Fig S23. ^{1}H NMR spectrum of 1-phenyl-1H-imidazole **(A8)**

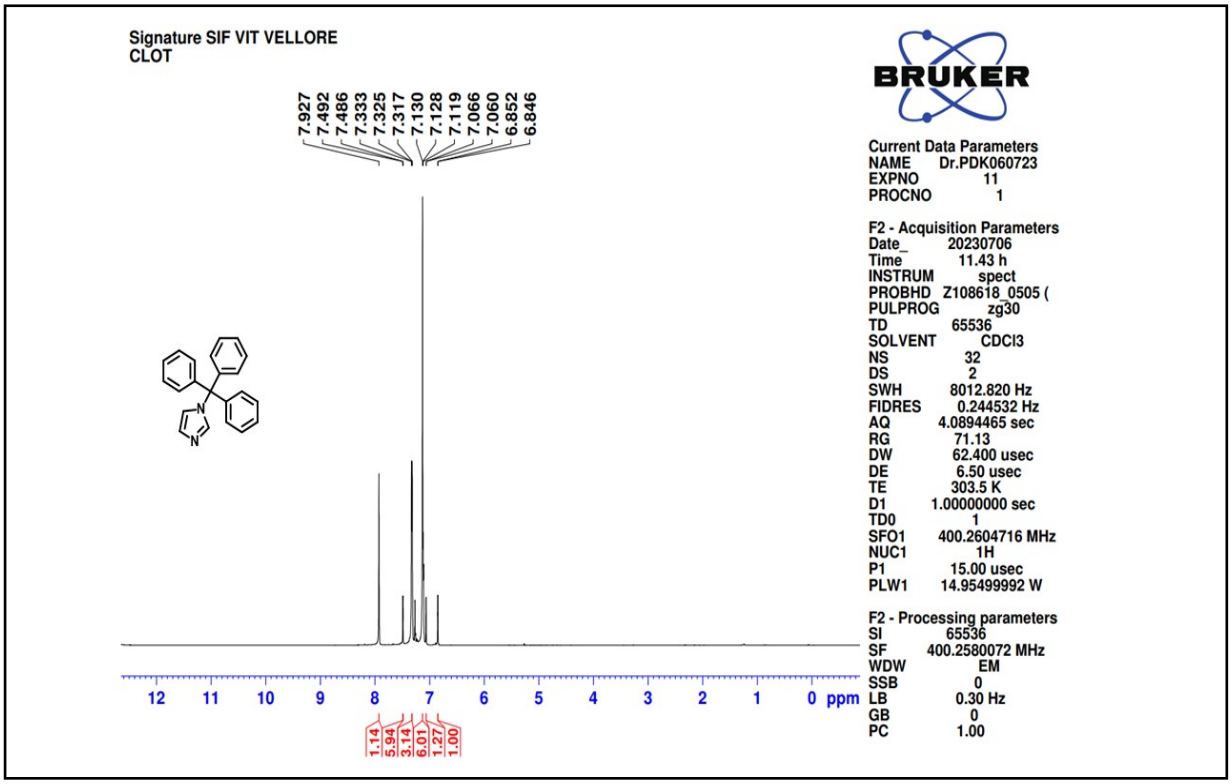


Fig S24. ^{1}H NMR spectrum of 1-trityl-1H-imidazole **(A9)**

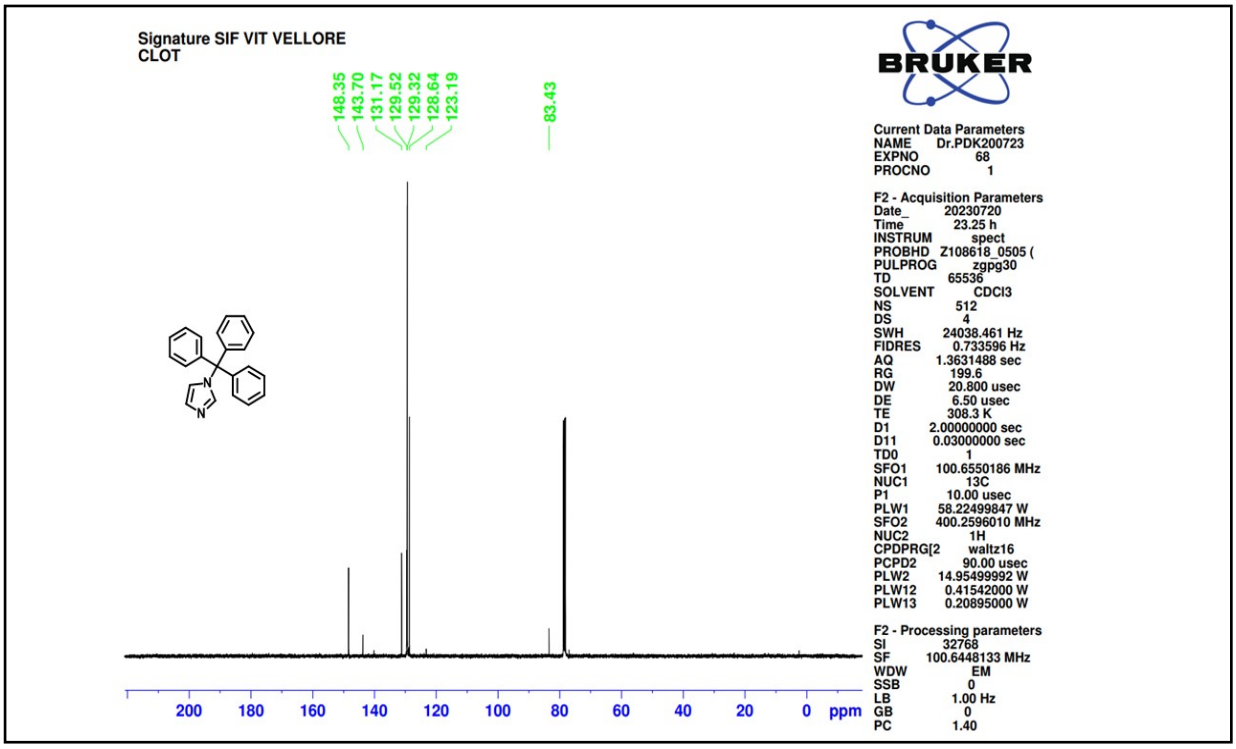


Fig S25. ^{13}C NMR spectrum of 1-trityl-1H-imidazole **(A9)**

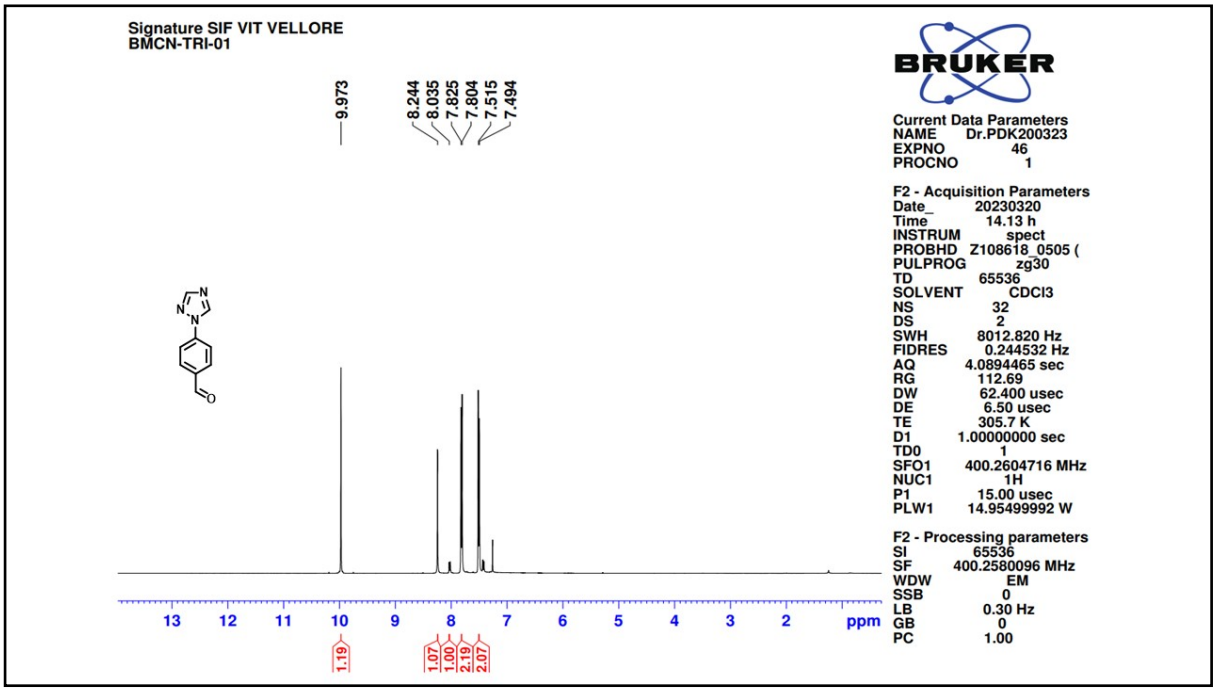


Fig S26. ^{1}H NMR spectrum of 4-(1H-1,2,4-triazol-1-yl)benzaldehyde **(A10)**

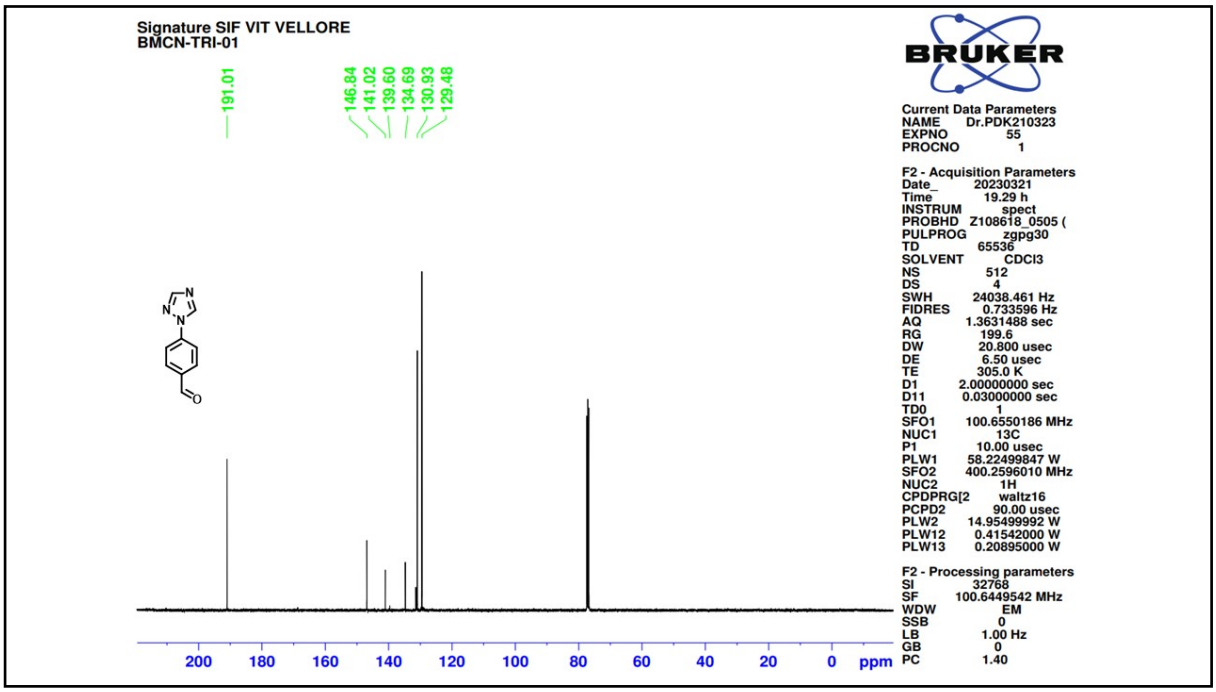


Fig S27. ^{13}C NMR spectrum of 4-(1H-1,2,4-triazol-1-yl)benzaldehyde **(A10)**

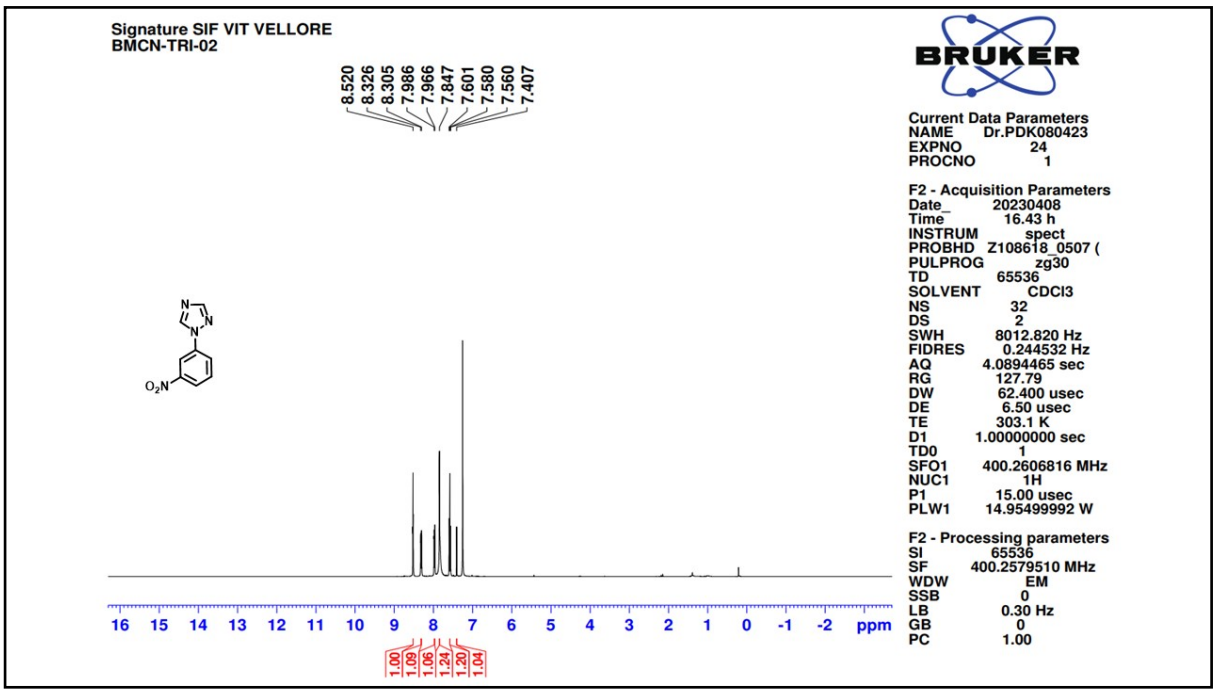


Fig S28. ^{1}H NMR spectrum of 1-(3-nitrophenyl)-1H-1,2,4-triazole **(A11)**

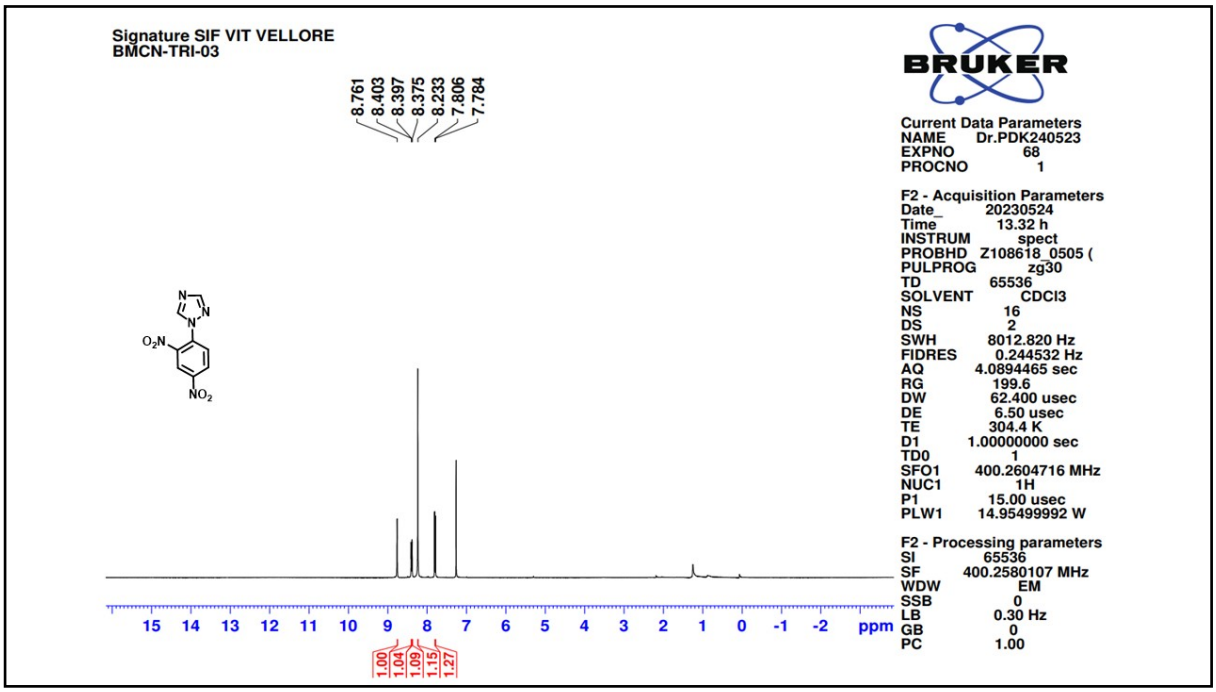


Fig S29. ^{1}H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-1,2,4-triazole **(A12)**

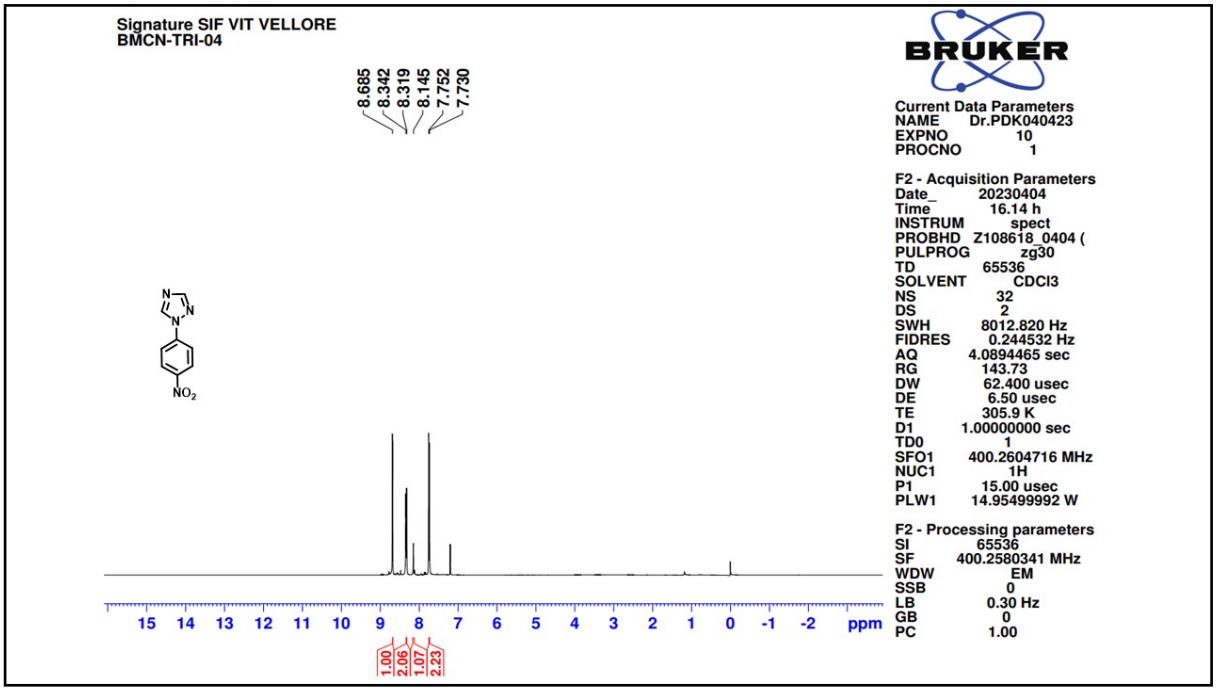


Fig S30. ^{1}H NMR spectrum of 1-(4-nitrophenyl)-1H-1,2,4-triazole **(A13)**

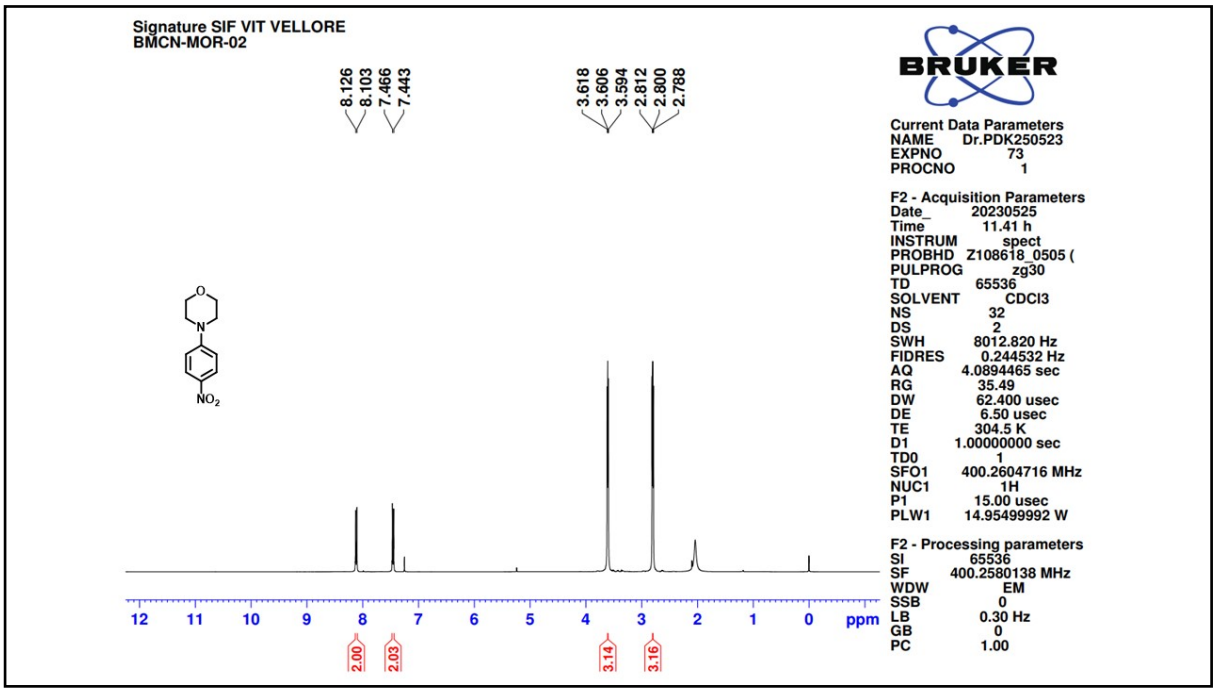


Fig S31. ^{1}H NMR spectrum of 4-(4-nitrophenyl)morpholine **(A14)**

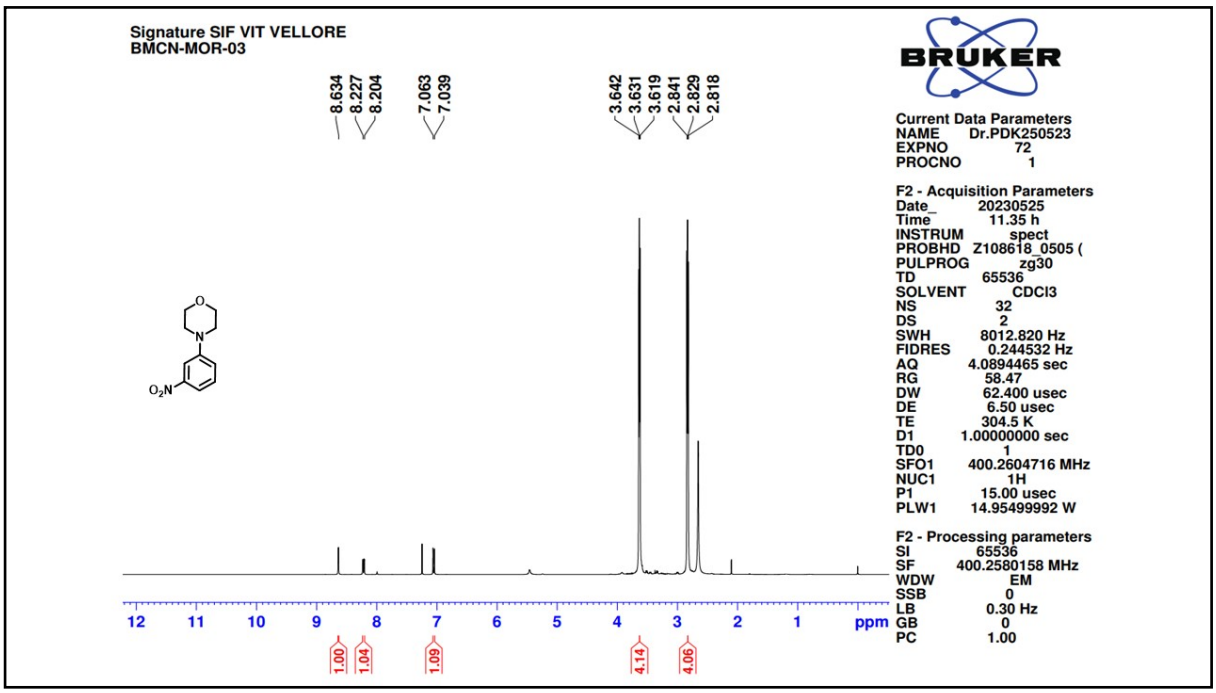


Fig S32. ^{1}H NMR spectrum of 4-(3-nitrophenyl)morpholine **(A15)**

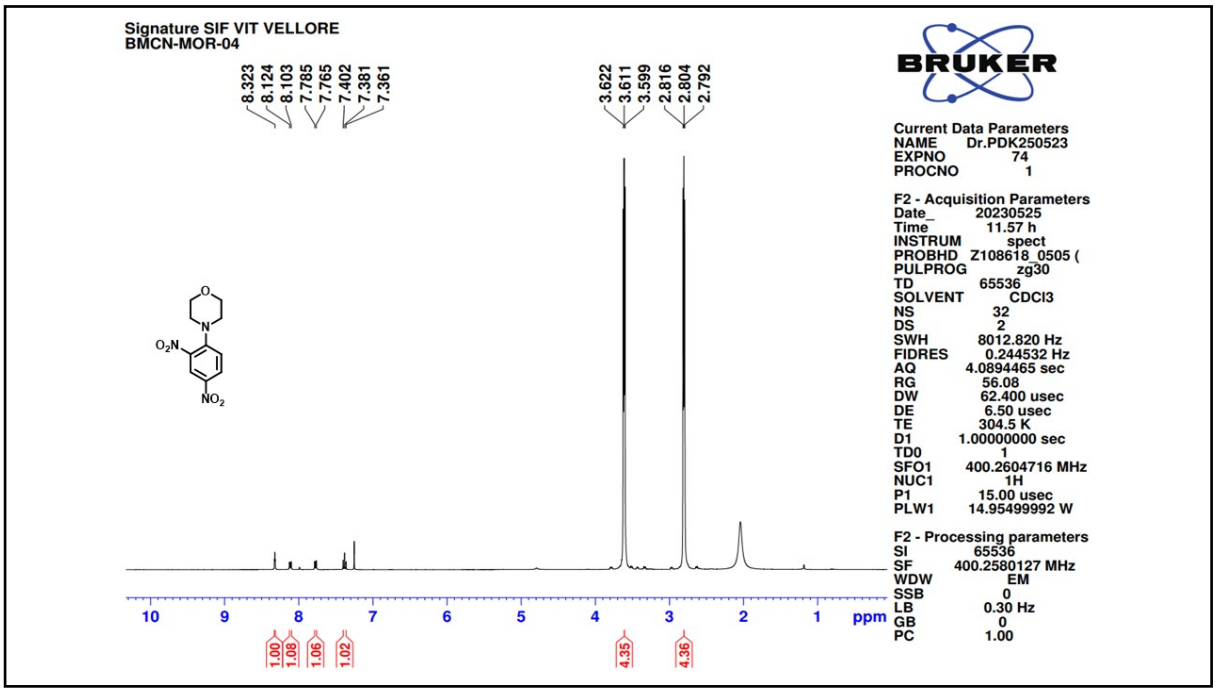


Fig S33. ^{1}H NMR spectrum of 4-(2,4-dinitrophenyl)morpholine **(A16)**

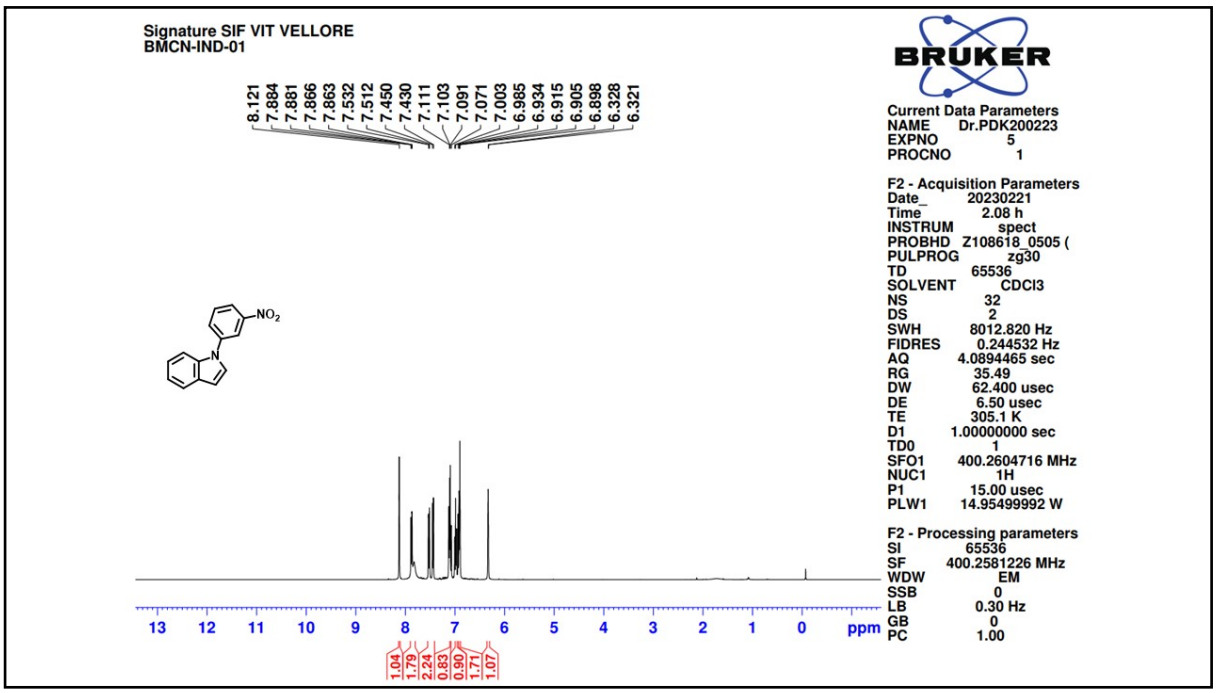


Fig S34. ^{1}H NMR spectrum of 1-(3-nitrophenyl)-1H-indole **(A17)**

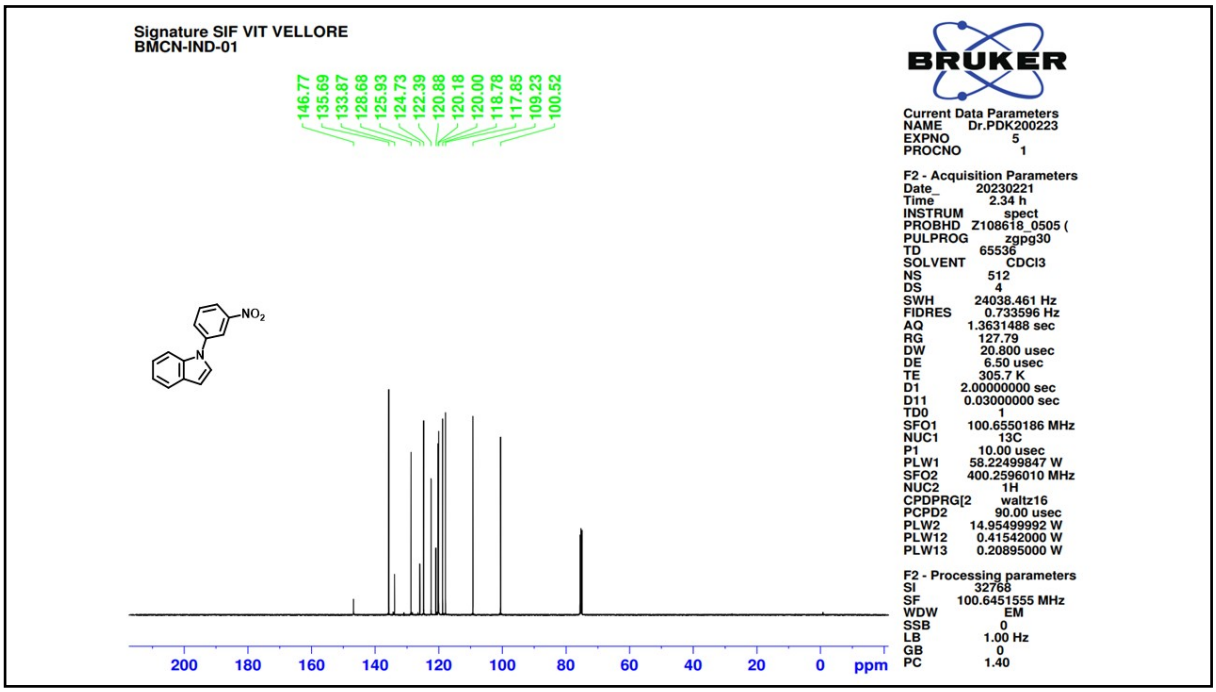


Fig S35. ^{1}H NMR spectrum of 1-(3-nitrophenyl)-1H-indole **(A17)**

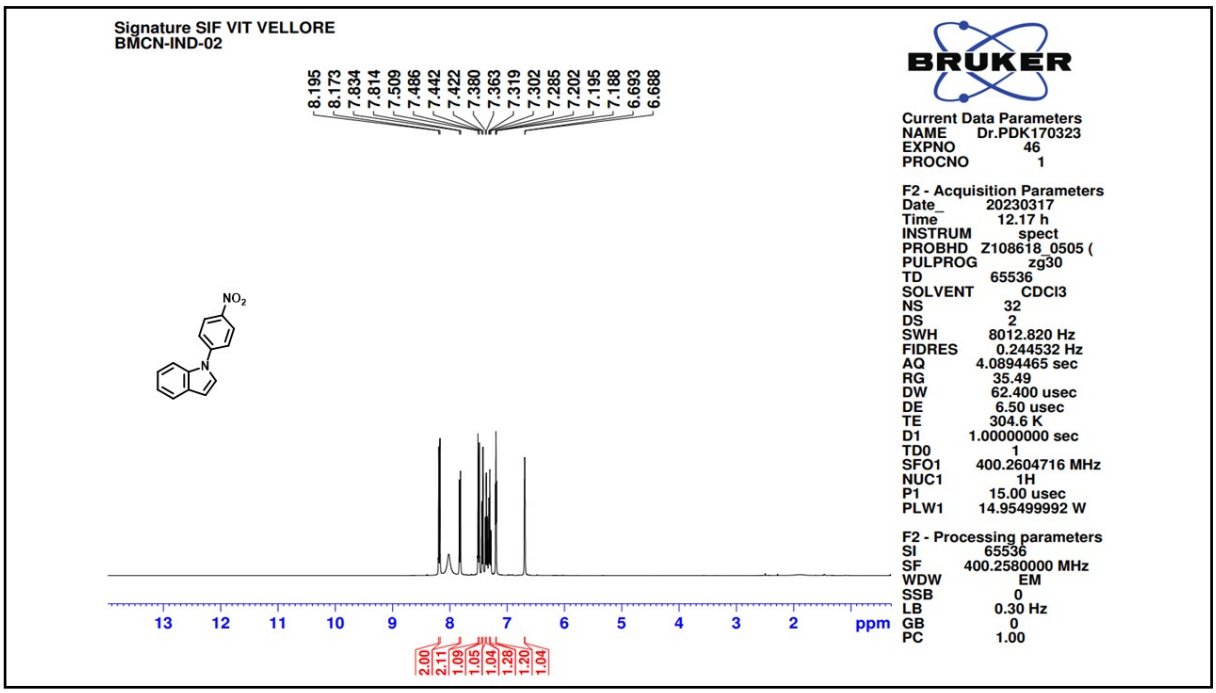


Fig S36. ^{1}H NMR spectrum of 1-(4-nitrophenyl)-1H-indole **(A18)**

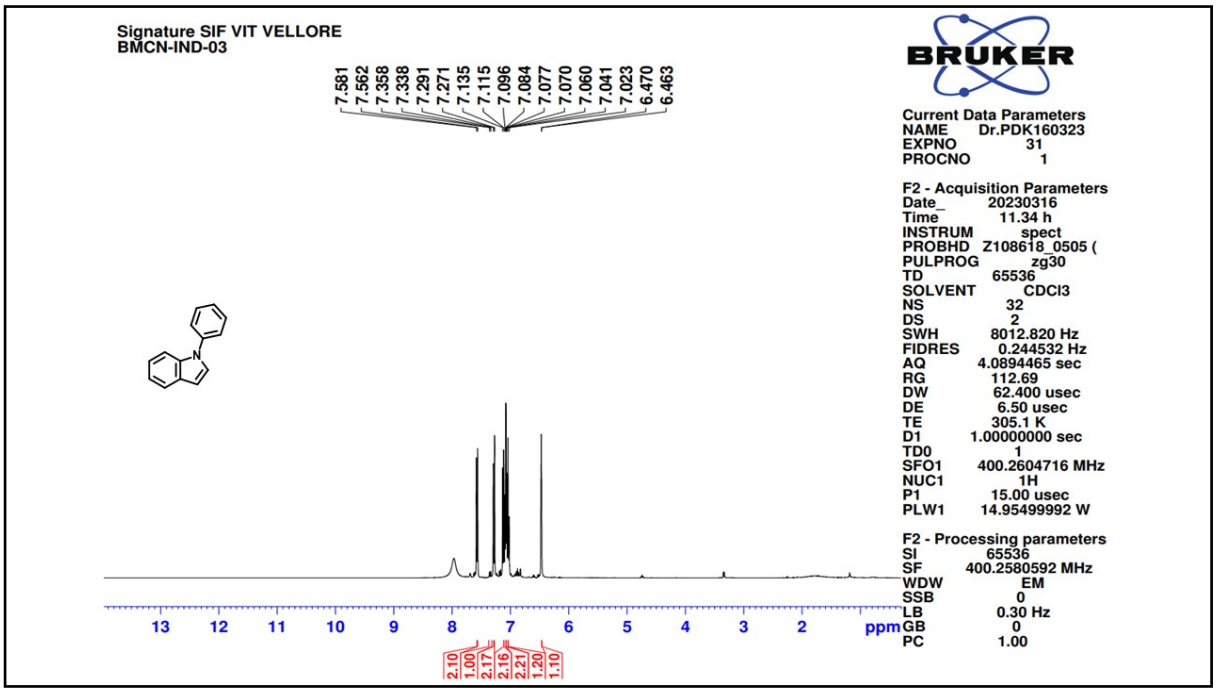


Fig S37. [1]H NMR spectrum of 1-phenyl-1H-indole **(A19)**

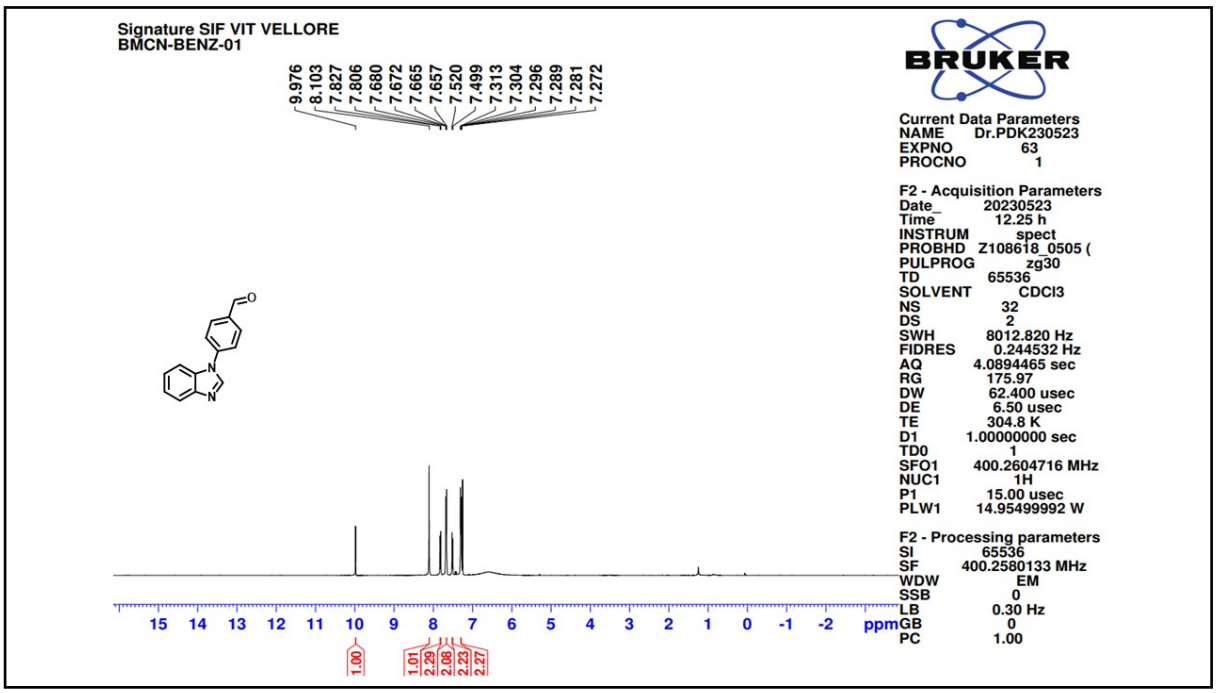


Fig S38. [1]H NMR spectrum of 4-(1H-benzo[d]imidazol-1-yl)benzaldehyde **(A20)**

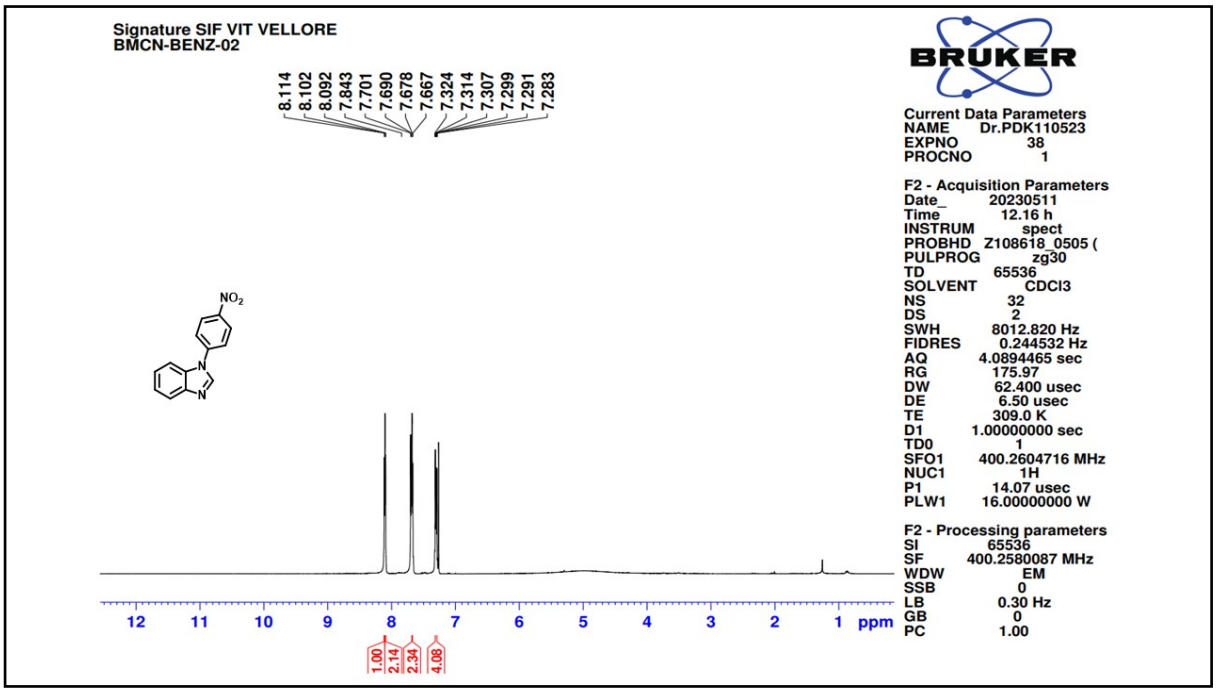


Fig S39. ^{1}H NMR spectrum of 1-(4-nitrophenyl)-1H-benzo[d]imidazole **(A21)**

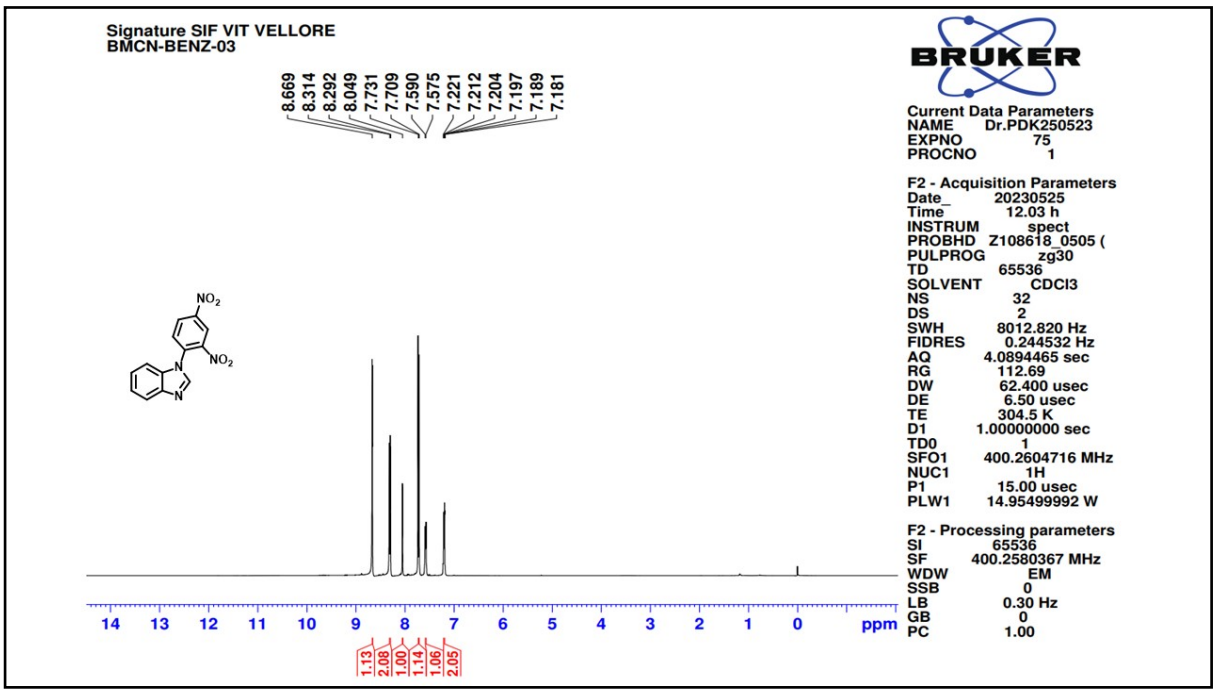


Fig S40. ^{1}H NMR spectrum of 1-(2,4-dinitrophenyl)-1H-benzo[d]imidazole **(A22)**

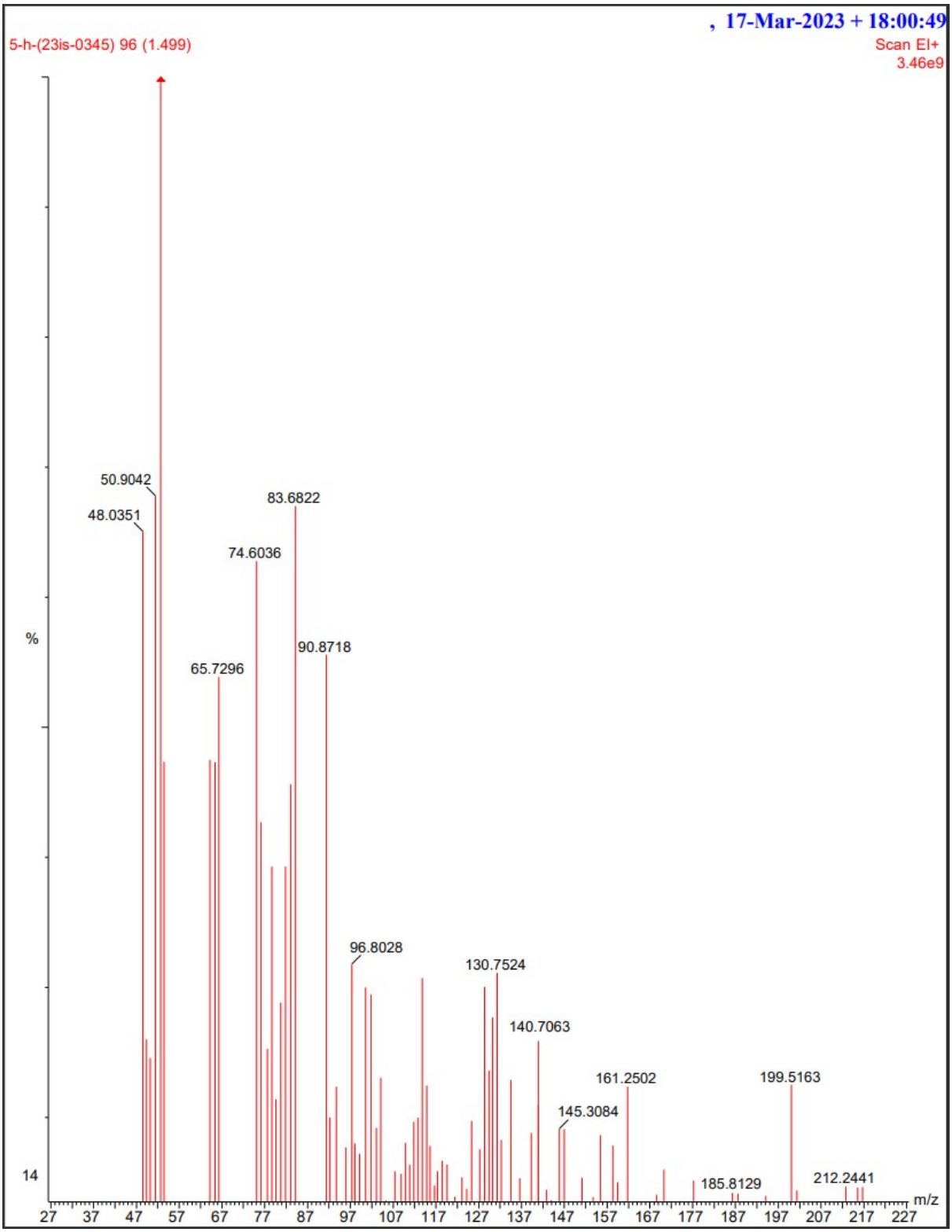


Fig S41. GCMS spectrum of Reaction Mixture after 5 hours

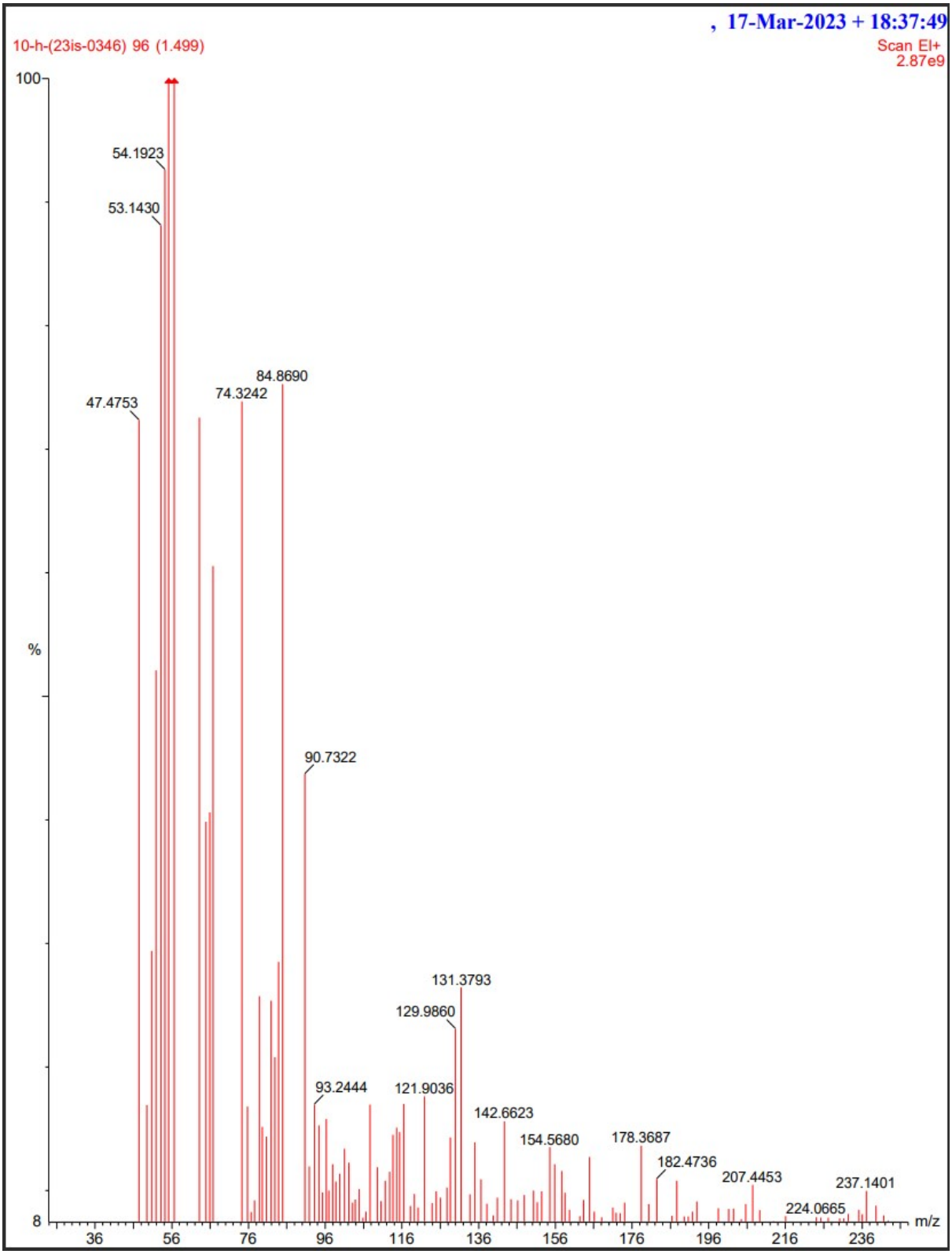


Fig S42. GCMS spectrum of Reaction Mixture after 10 hours

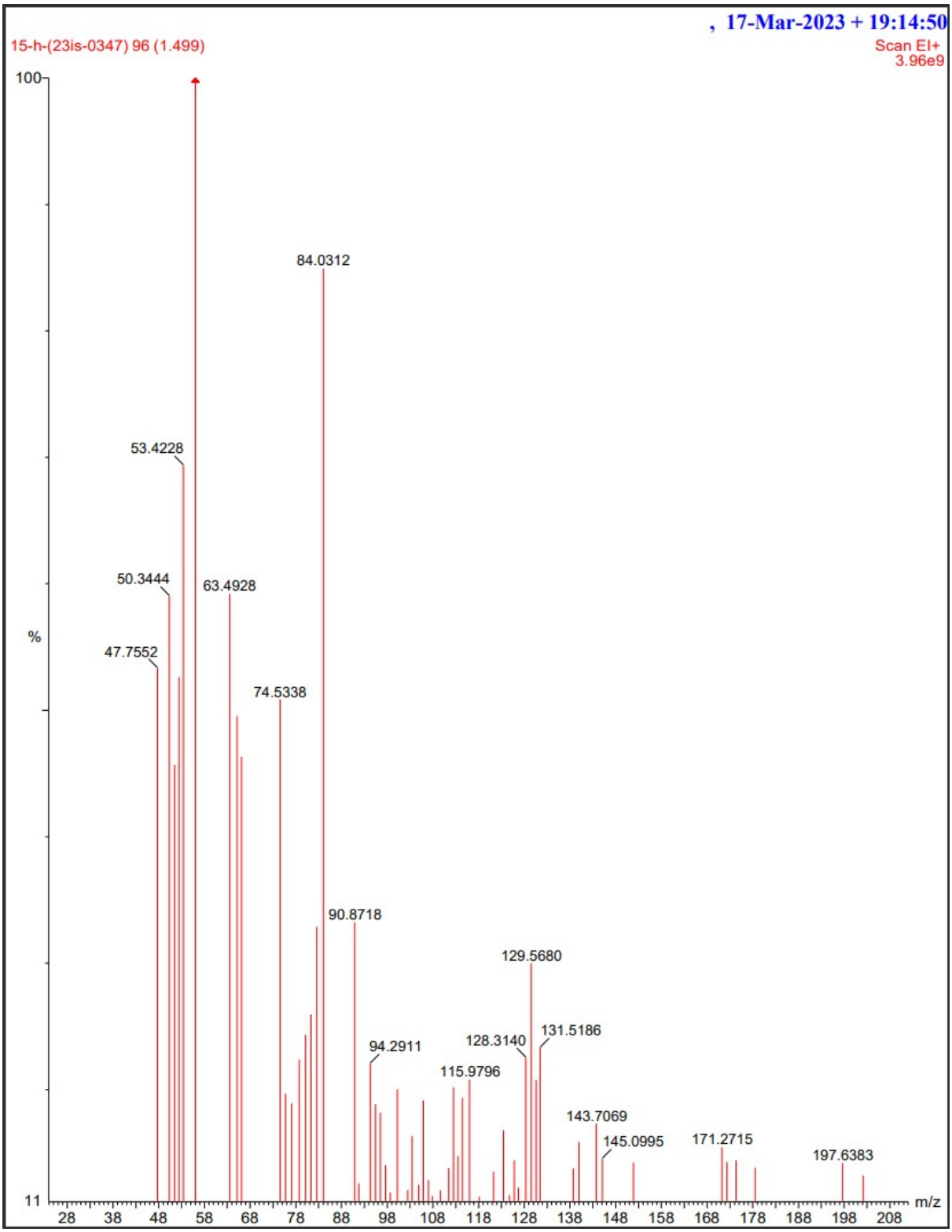


Fig S43. GCMS spectrum of Reaction Mixture after 15 hours

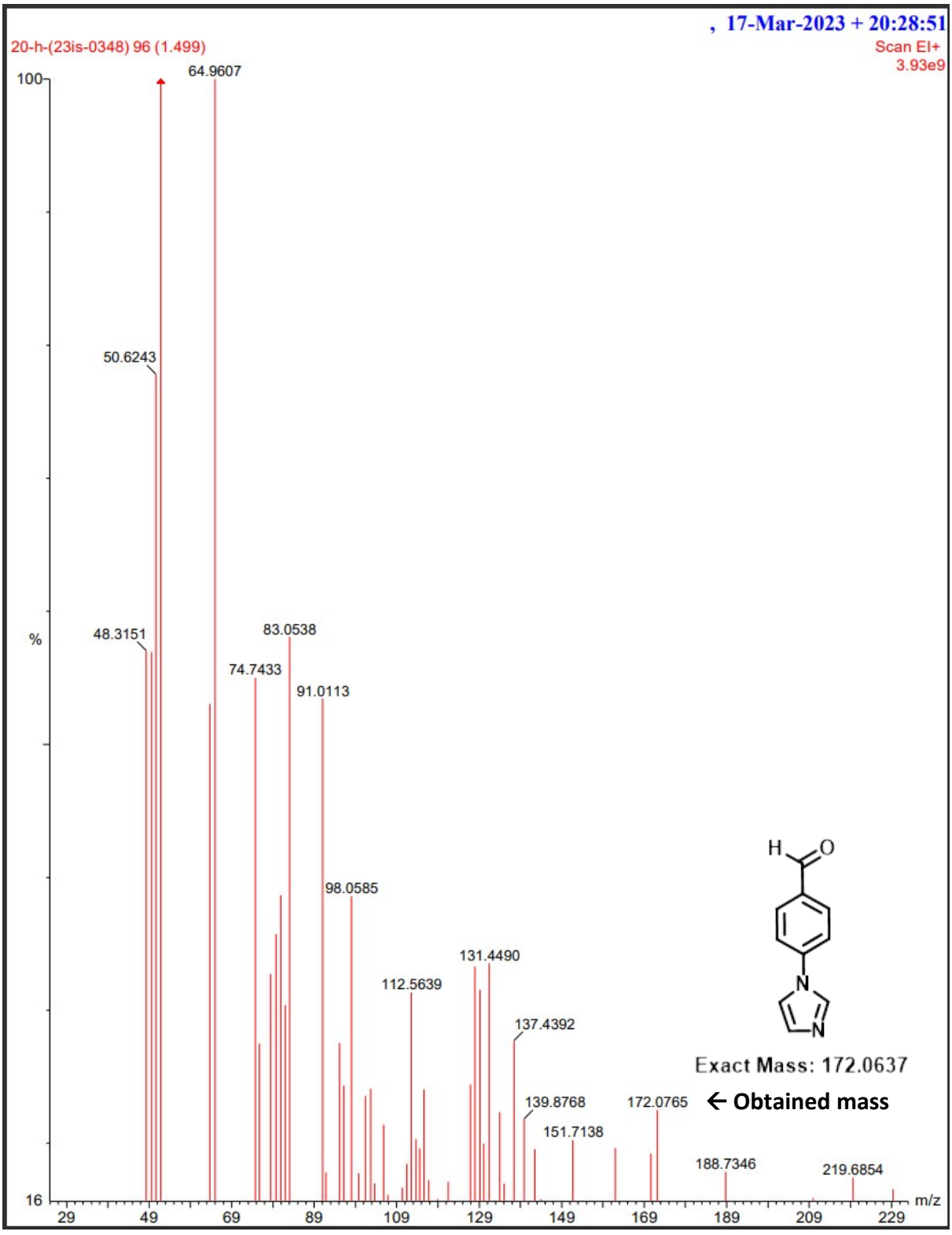


Fig S44. GCMS spectrum of Reaction Mixture after 20 hours

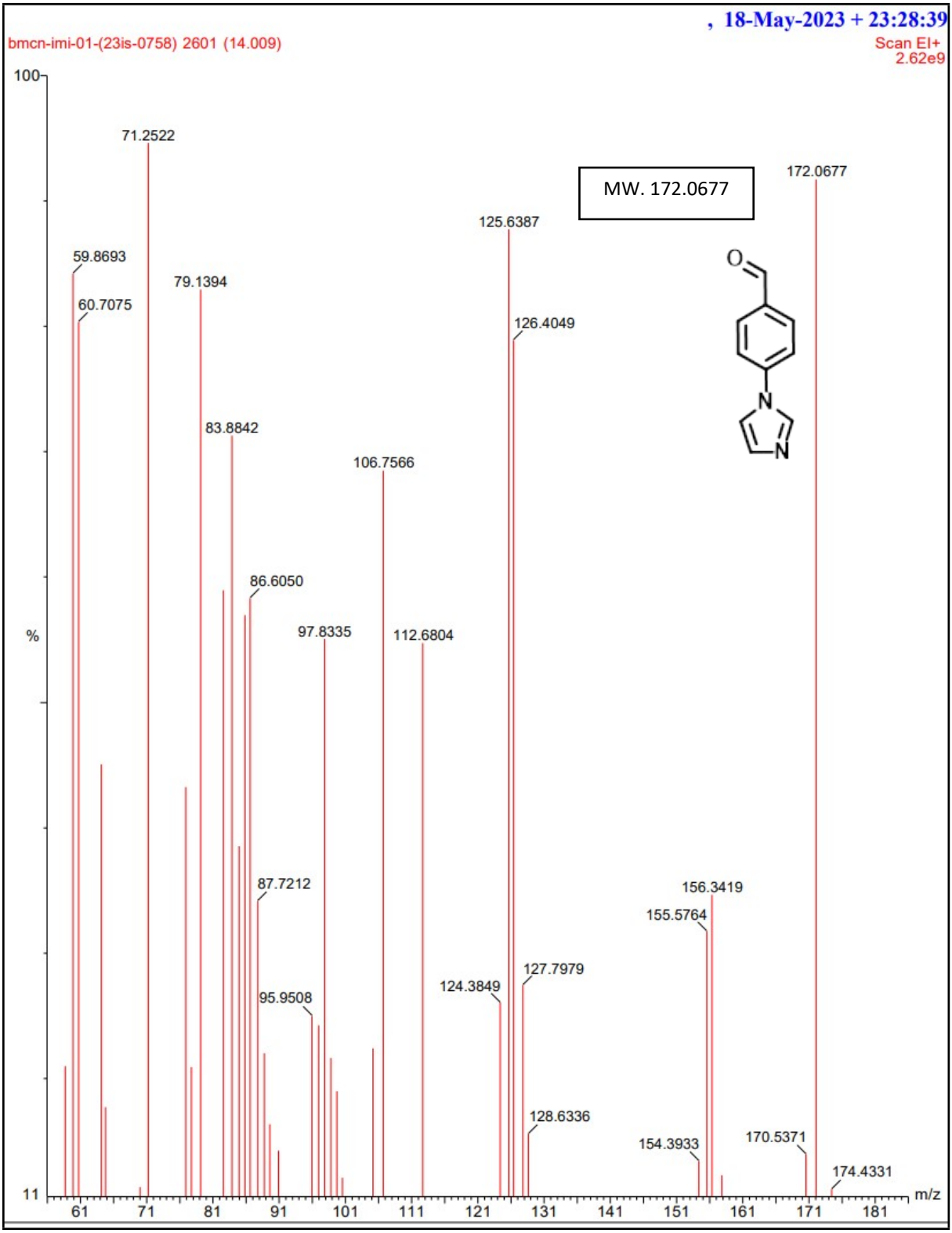


Fig S45. GCMS spectrum of 4-(1H-imidazol-1-yl)benzaldehyde [BMCN-IMI-01]**A1**

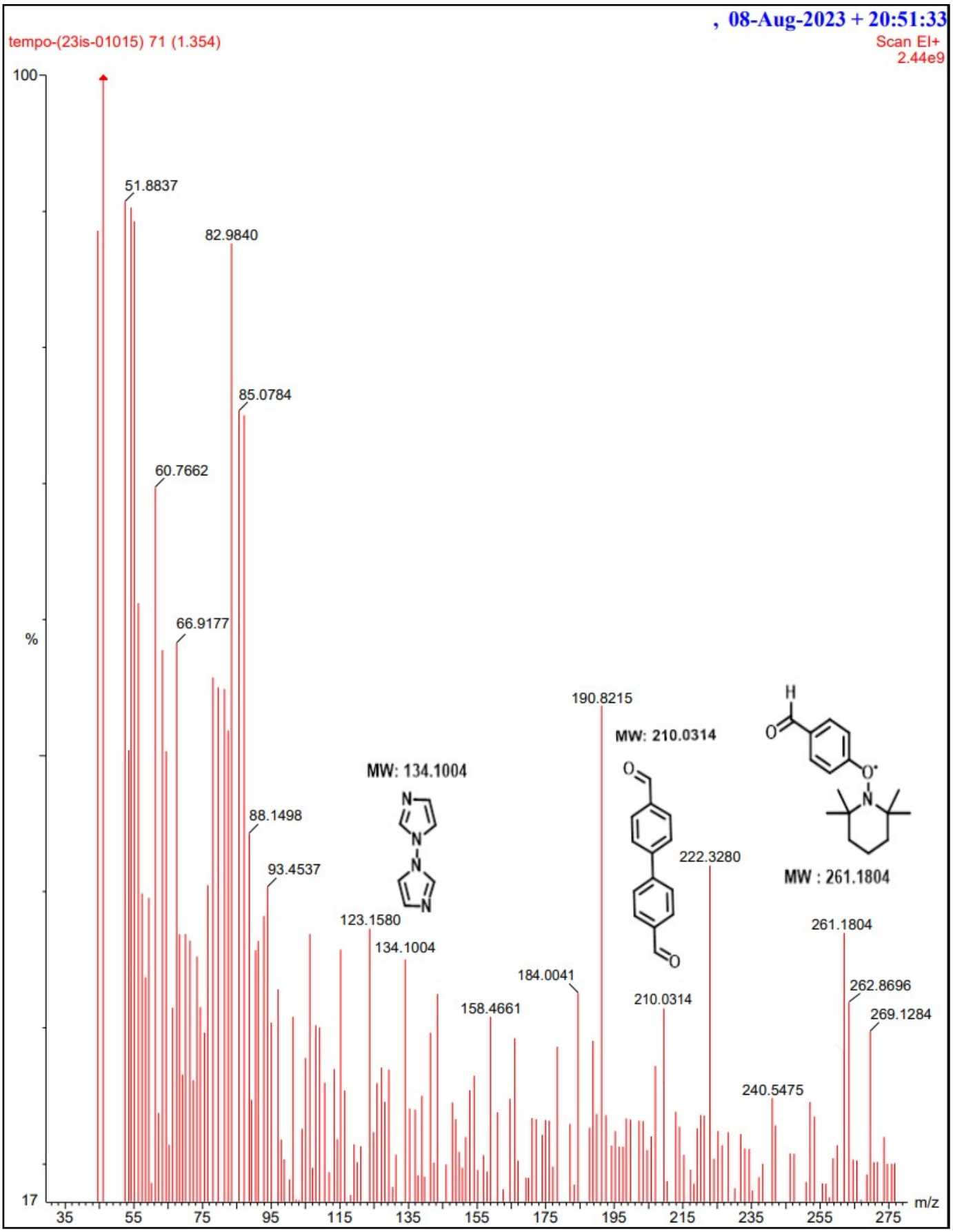
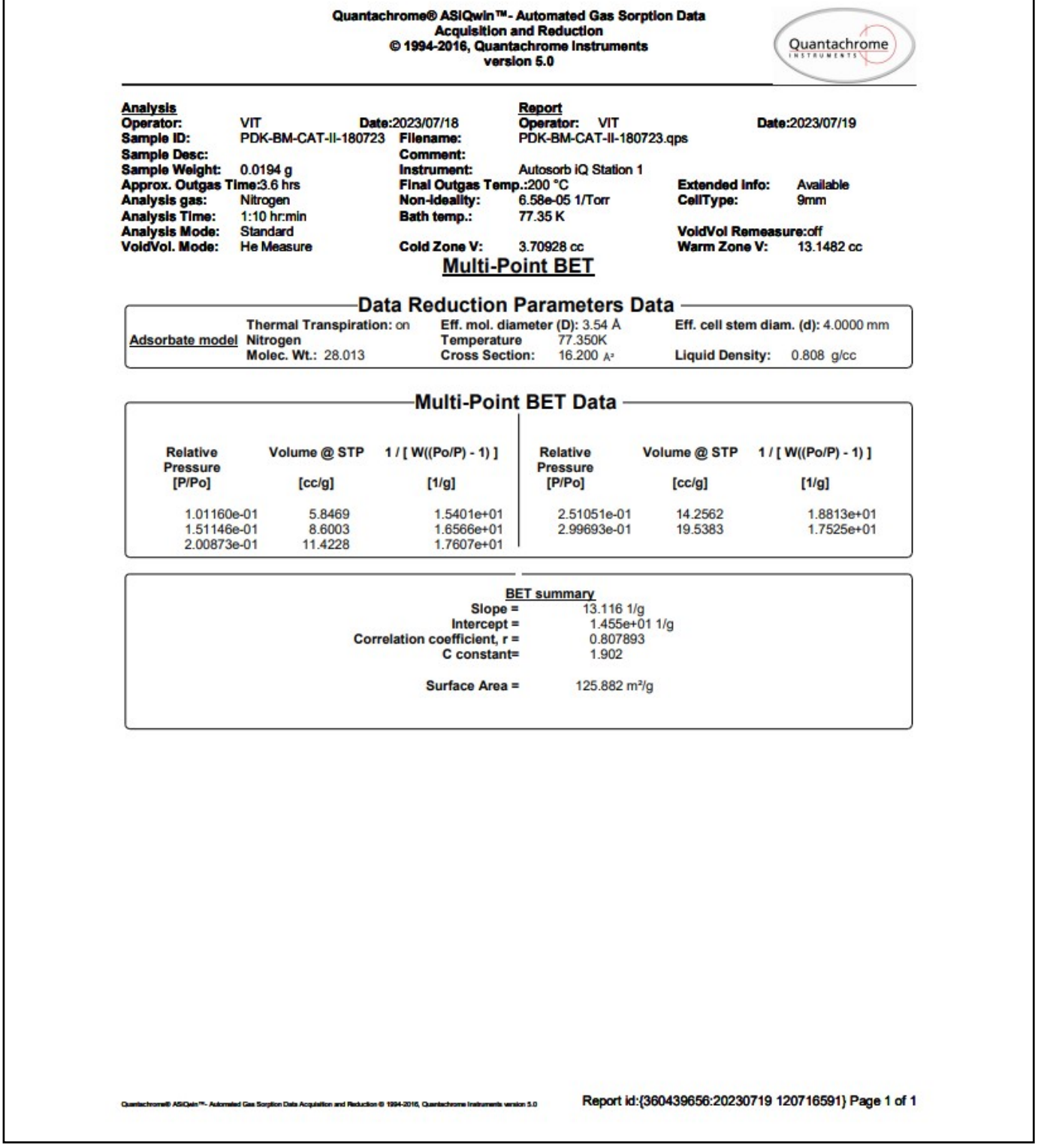


Fig S46. GCMS spectrum of Aryl radical with TEMPO

Time (h)	A* Under Optimized Reaction conditions	B	C
0	R1 + R2 + 20 mg PBILFPc + ACN 10 mL	R1 + R2 + 20 mg PBILFPc + ACN 10 mL	R1 + R2 + 20 mg PBILFPc + ACN 10 mL
5	**Reaction continued**	**Reaction works up to know the yield of the product at 5 h**	**Photocatalyst removed by filtration and continued reaction under 5 W LED for 20 h**
10	**Reaction continued**		**Reaction continued**
15	**Reaction continued**		**Reaction continued**
20	**Reaction continued**		**Reaction continued**
	Product Yield = 91 %	**Product Yield = 31%**	**Product Yield = 31 %**

Fig S47. Leaching Test of PBILFPc Photocatalyst.



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Quantachrome INSTRUMENTS

Analysis				Report			
Operator:	VIT	Date:	2023/07/18	Operator:	VIT	Date:	2023/07/19
Sample ID:	PDK-BM-CAT-II-180723	Filename:		PDK-BM-CAT-II-180723.qps			
Sample Desc:		Comment:					
Sample Weight:	0.0194 g	Instrument:		Autosorb iQ Station 1			
Approx. Outgas Time:	3.6 hrs	Final Outgas Temp.:		200 °C	Extended Info:		Available
Analysis gas:	Nitrogen	Non-ideality:		6.58e-05 1/Torr	CellType:		9mm
Analysis Time:	1:10 hr:min	Bath temp.:		77.35 K			
Analysis Mode:	Standard				VoidVol Remeasure:		off
VoidVol. Mode:	He Measure	Cold Zone V:		3.70928 cc	Warm Zone V:		13.1482 cc

Multi-Point BET

Data Reduction Parameters Data

	Thermal Transpiration: on	Eff. mol. diameter (D): 3.54 Å		Eff. cell stem diam. (d): 4.0000 mm	
Adsorbate model	Nitrogen	Temperature	77.350K		
	Molec. Wt.: 28.013	Cross Section:	16.200 Å²	Liquid Density:	0.808 g/cc

Multi-Point BET Data

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)] [1/g]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)] [1/g]
1.01160e-01	5.8469	1.5401e+01	2.51051e-01	14.2562	1.8813e+01
1.51146e-01	8.6003	1.6566e+01	2.99693e-01	19.5383	1.7525e+01
2.00873e-01	11.4228	1.7607e+01			

BET summary

Slope =	13.116 1/g
Intercept =	1.455e+01 1/g
Correlation coefficient, r =	0.807893
C constant=	1.902
Surface Area =	125.882 m²/g

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Fig S48. BET Surface Area of PBILFPc Photocatalyst.

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Analysis				Report			
Operator:	VIT	**Date:**	2023/07/18	**Operator:**	VIT	**Date:**	2023/07/19
Sample ID:	PDK-BM-CAT-II-180723	**Filename:**		PDK-BM-CAT-II-180723.qps			
Sample Desc:		**Comment:**					
Sample Weight:	0.0194 g	**Instrument:**		Autosorb iQ Station 1			
Approx. Outgas Time:	3.6 hrs	**Final Outgas Temp.:**		200 °C	**Extended Info:**		Available
Analysis gas:	Nitrogen	**Non-ideality:**		6.58e-05 1/Torr	**CellType:**		9mm
Analysis Time:	1:10 hr:min	**Bath temp.:**		77.35 K			
Analysis Mode:	Standard				**VoidVol Remeasure:**		off
VoidVol. Mode:	He Measure	**Cold Zone V:**		3.70928 cc	**Warm Zone V:**		13.1482 cc

Isotherm

Data Reduction Parameters Data

	Thermal Transpiration: on	**Eff. mol. diameter (D):** 3.54 Å		**Eff. cell stem diam. (d):** 4.0000 mm	
Adsorbate model	**Nitrogen**	**Temperature**	77.350K		
	Molec. Wt.: 28.013	**Cross Section:**	16.200 A^2	**Liquid Density:**	0.808 g/cc

Isotherm Data

Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]
5.14290e-02	3.0293	7.50562e-01	51.9415	5.99838e-01	49.4972
1.01160e-01	5.8469	8.00023e-01	55.4085	5.49707e-01	46.1393
1.51146e-01	8.6003	8.48867e-01	59.0659	4.99487e-01	42.6190
2.00873e-01	11.4228	9.01418e-01	62.8823	4.49537e-01	39.2034
2.51051e-01	14.2562	9.49482e-01	66.3261	3.99568e-01	35.3820
2.99693e-01	19.5383	9.94247e-01	91.9689	3.49602e-01	31.5638
3.50258e-01	23.6354	9.93438e-01	89.6739	2.99576e-01	27.6544
4.00412e-01	27.3751	9.50859e-01	70.4747	2.49551e-01	23.7072
4.50805e-01	30.7916	8.99781e-01	67.5018	1.99747e-01	19.5642
5.00173e-01	34.3641	8.50510e-01	64.6092	1.49557e-01	15.3359
5.50398e-01	37.9283	8.00176e-01	61.6616	9.96401e-02	11.1639
6.00149e-01	41.4892	7.50897e-01	58.6172	5.16977e-02	6.8480
6.50263e-01	45.0035	7.00484e-01	55.5266		
7.00302e-01	48.6208	6.49412e-01	52.7108		

Fig S49. BET Isotherm Parameters of PBILFPc Photocatalyst.

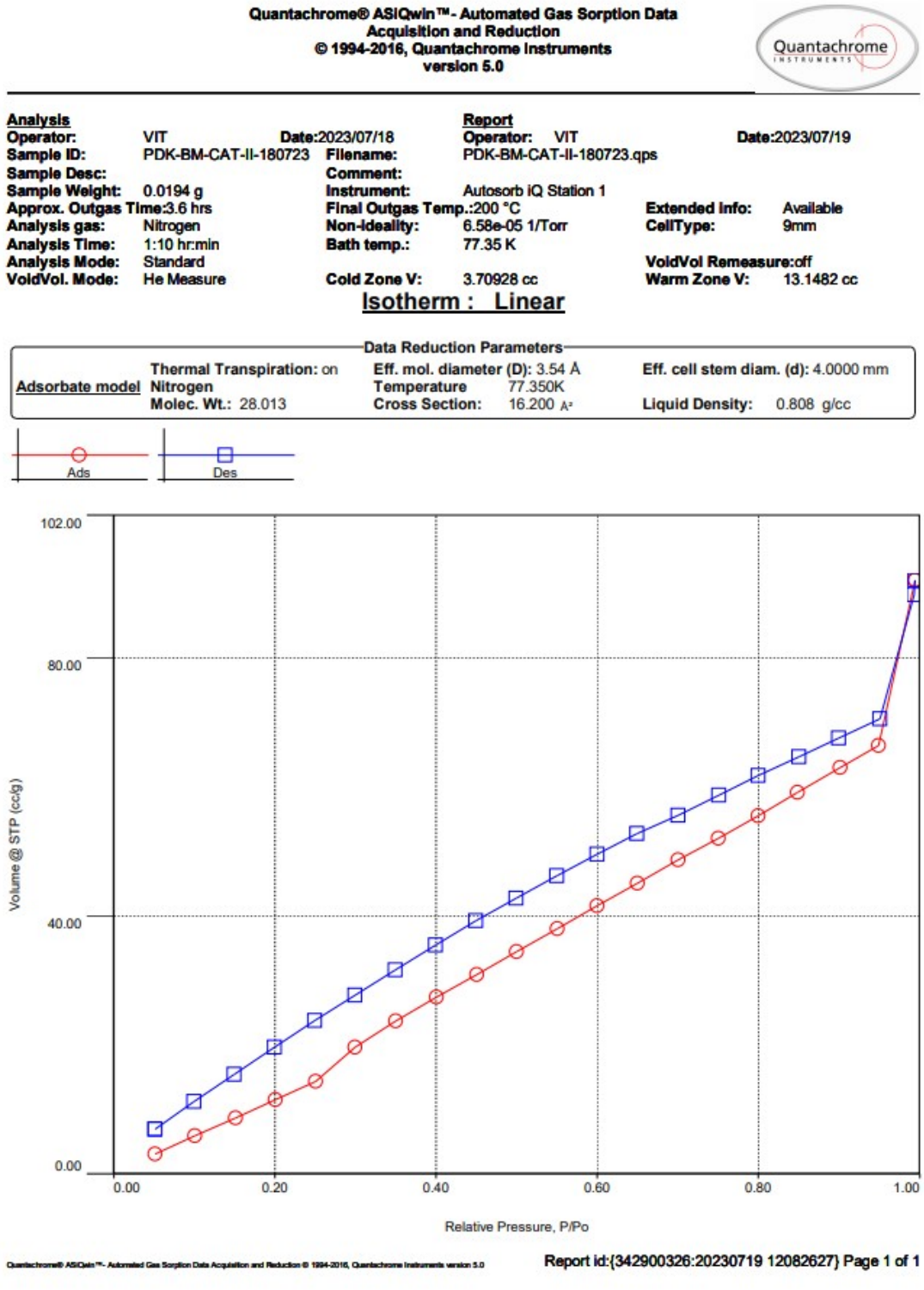

Fig S50. BET Adsorption/Desorption Isotherm of PBILFPc Photocatalyst.

TON & TOF Calculation as per the reviewer's suggestion

The TON of the photocatalyst was found to be 9,33,333 and TOF is 46,666. The detailed calculation are as follows:

Molecular Weight of the Photocatalyst = 1026.071

Quantity of Photocatalyst utilized for the reaction 20mg = 0.02g

Moles of Photocatalyst = (0.02/1026.071) x 100 =

= 0.00195

For TON = (Optimized time of reaction x yield of reaction) / moles of Photocatalyst

= (20 x 91) / 0.00195

= 9,33,333.33

For TOF = TON / Reaction Time

= 9,33,333.33 / 20

=46,666.67 h^{-1}

Preparation of Stock Solution for UV-visible and Fluorescence Spectroscopy

A 1mM Stock solution of PBILFPc Photocatalyst was prepared.

A standard working concentration of $2x10^{-5}$ M was used for UV-visible and Fluorescence spectroscopy studies.

$$W = \frac{NEV}{1000} =$$ (10^{-3} x 1026.071 x 10) / 1000

W = 10.26 x 10^{-3} g

W = 10 mg in 10mL DMSO

Stock = 10^{-3} M in DMSO (10mL)

Note: Due to the heterogeneous nature of the Photocatalyst, it is difficult for us to properly dissolve it in DMSO, we gave gentle heating and sonication to the stock solution, and after we took it for analysis.

Now Working Concentration

Stock Solution : Working Solution

N1V1 = N2V2

10^{-3} x 40µL = N2 x 2mL

N2 = (10^{-3} x 40x10^{-3}mL) / 2

N2 = 2 x 10^{-5} M