Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Solvent/Metal-Free Benzimidazolium-Based Carboxyl Functionalized Porphyrin Photocatalyst for Room-Temperature Alkylation of Amines under Irradiation of Visible Light

Subodh Uttamrao Raut[a], Kamlesh Rudreshwar Balinge[b], Shubham Avinash Deshmukh[a], Shital Haribhau Barange[a], Bhairav Chandroday Mataghare[a] and Pundlik Ramhau Bhagat[a]*

*(E-mail:*drprbhagat111@gmail.com)*

a. Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632014, India

b. Department of Chemistry, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Science, Saveetha University, Chennai, Tamil Nadu 602105, India

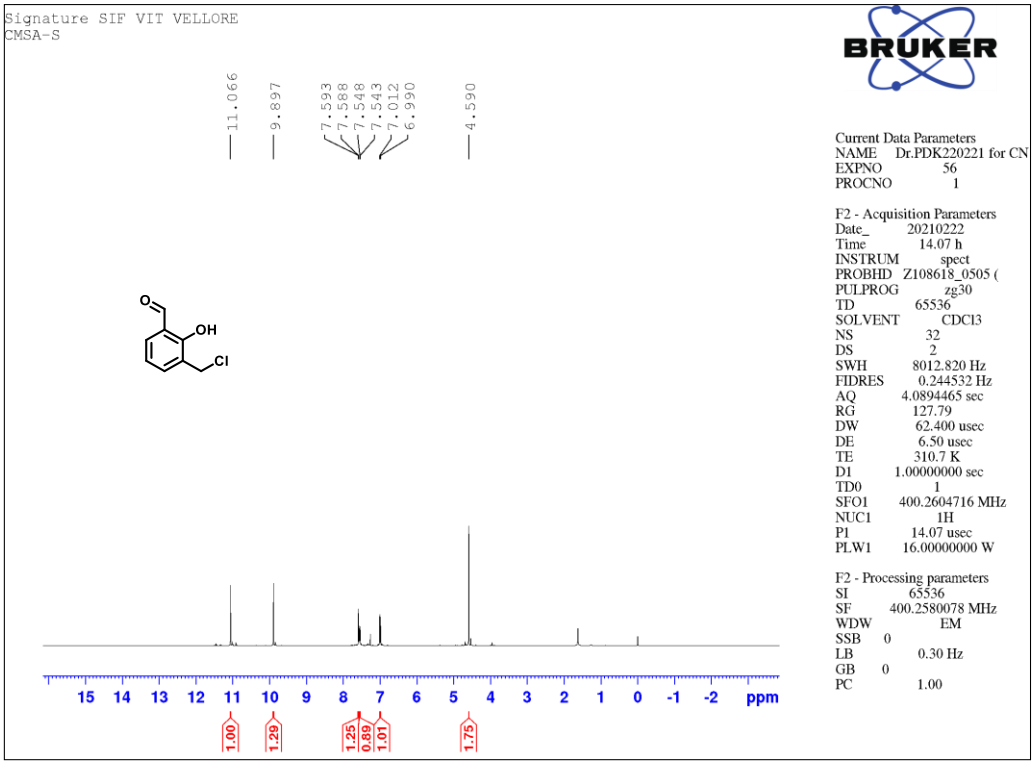


Fig.S1.^{1}H NMR Spectrum of compound 4B

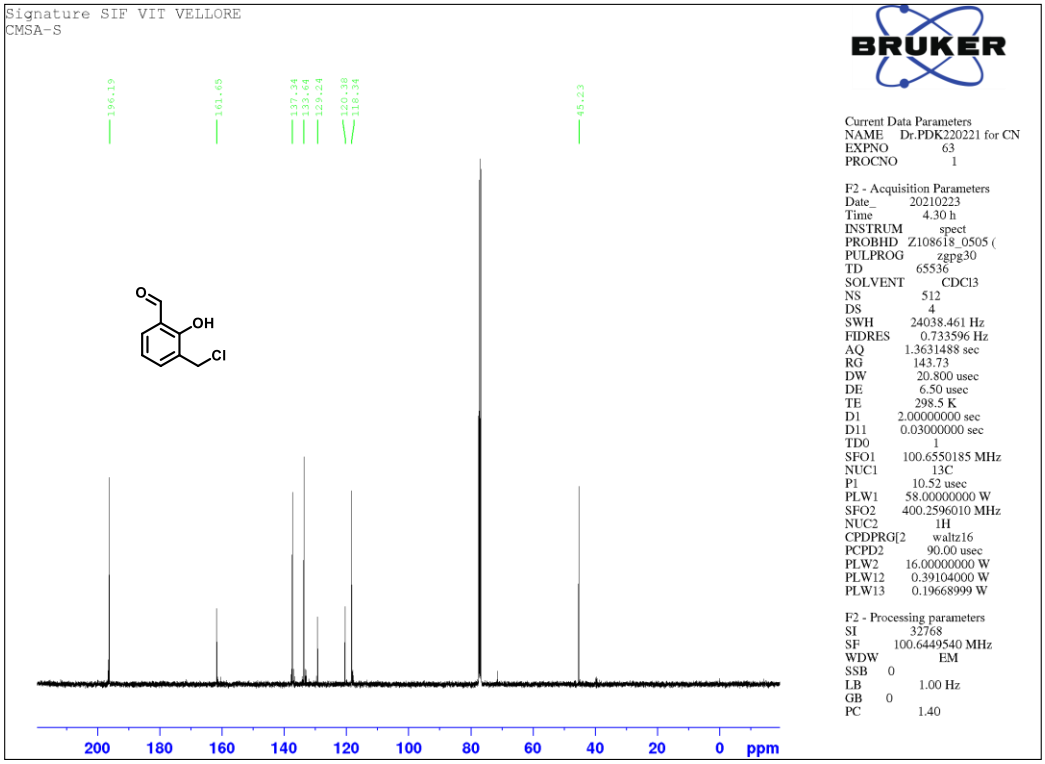


Fig.S2.^{13}C NMR Spectrum of compound 4B

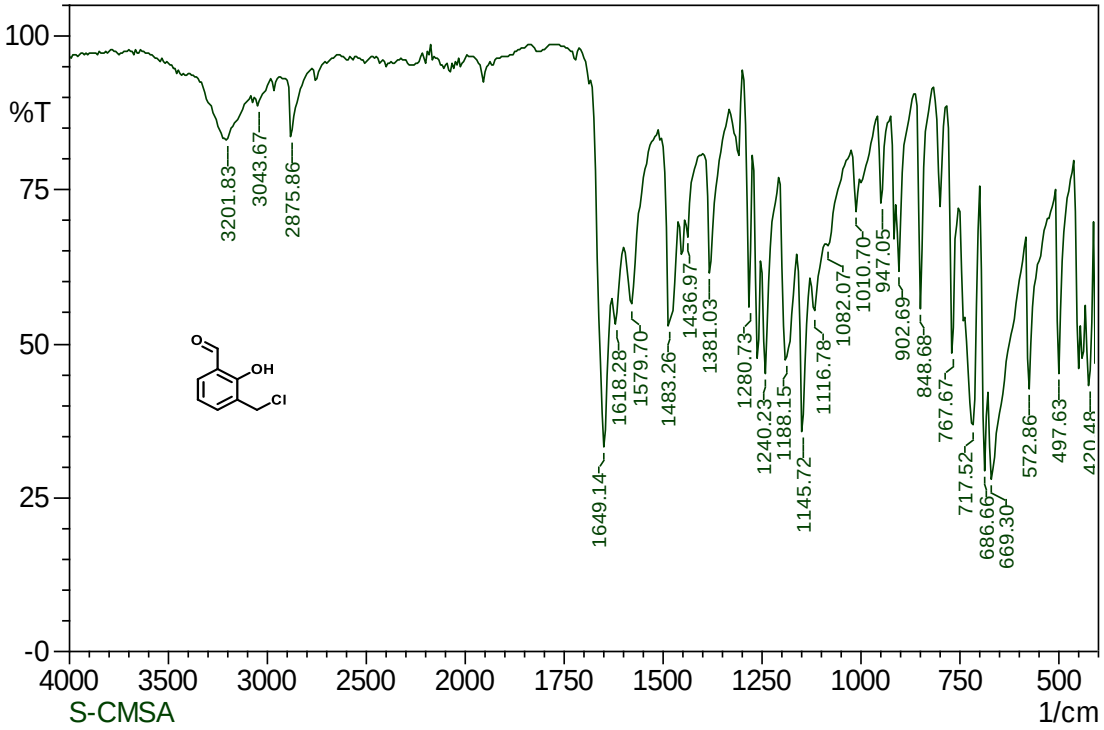


Fig.S3 FT-IR Spectrum of compound 4B

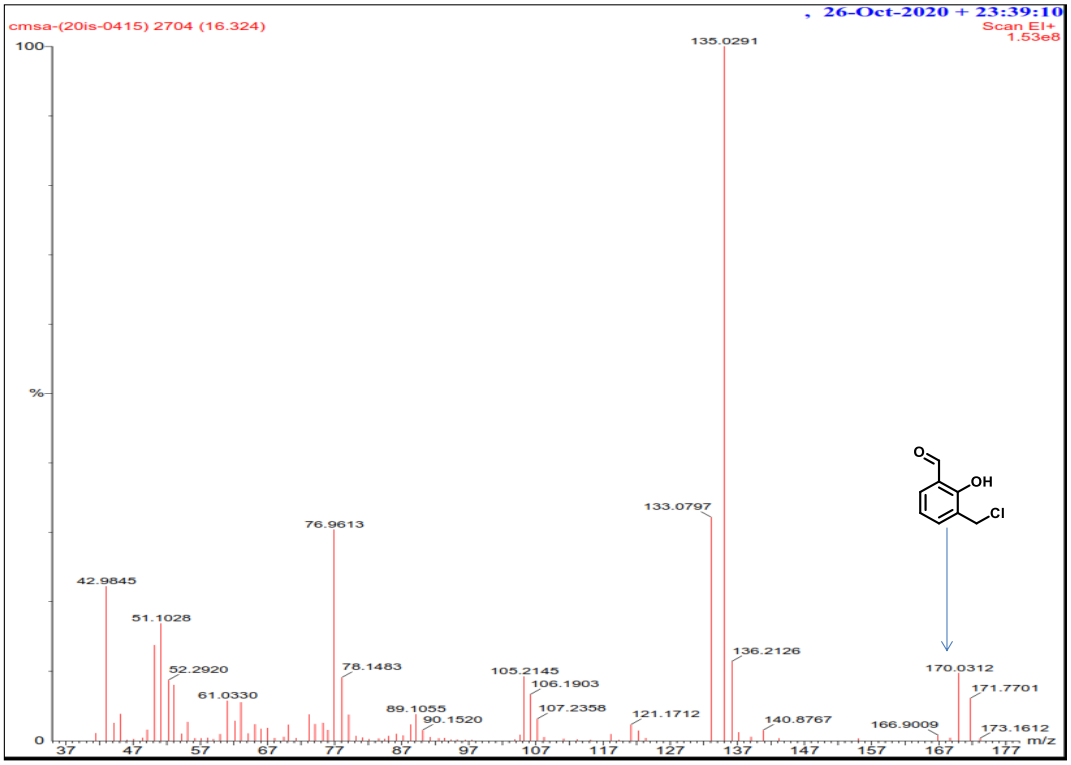


Fig.S4 GCMS Spectrum of compound 4B

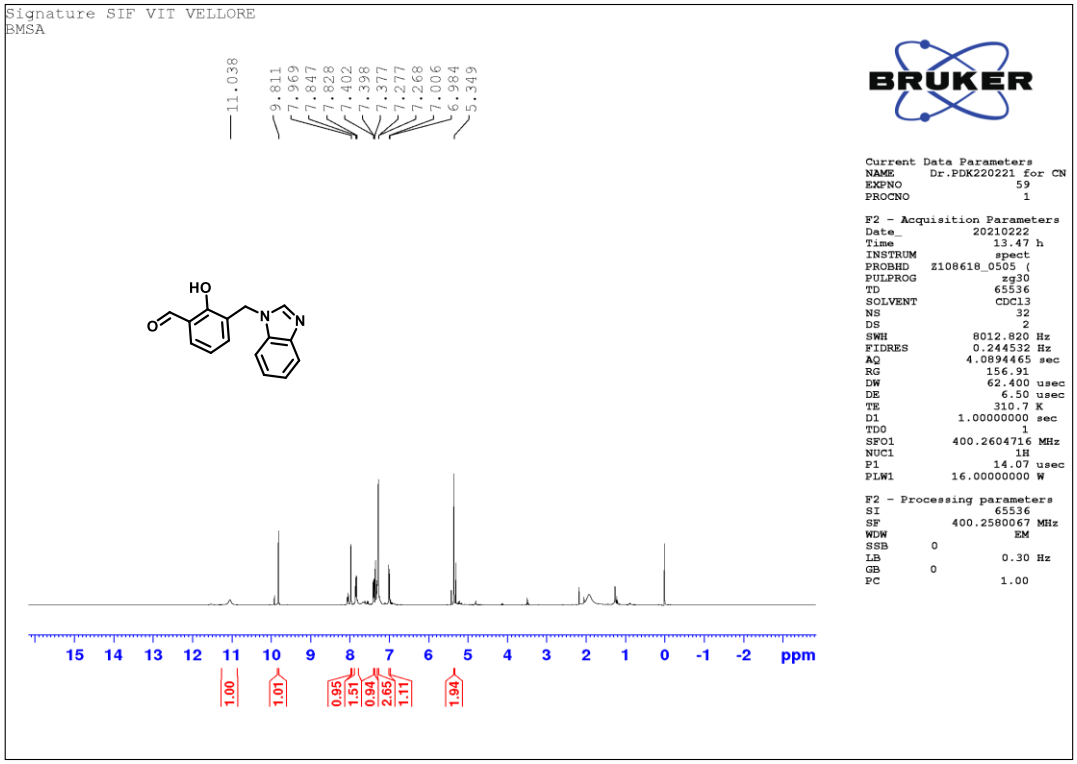


Fig.S5 ^{1}H NMR Spectrum of compound 4C

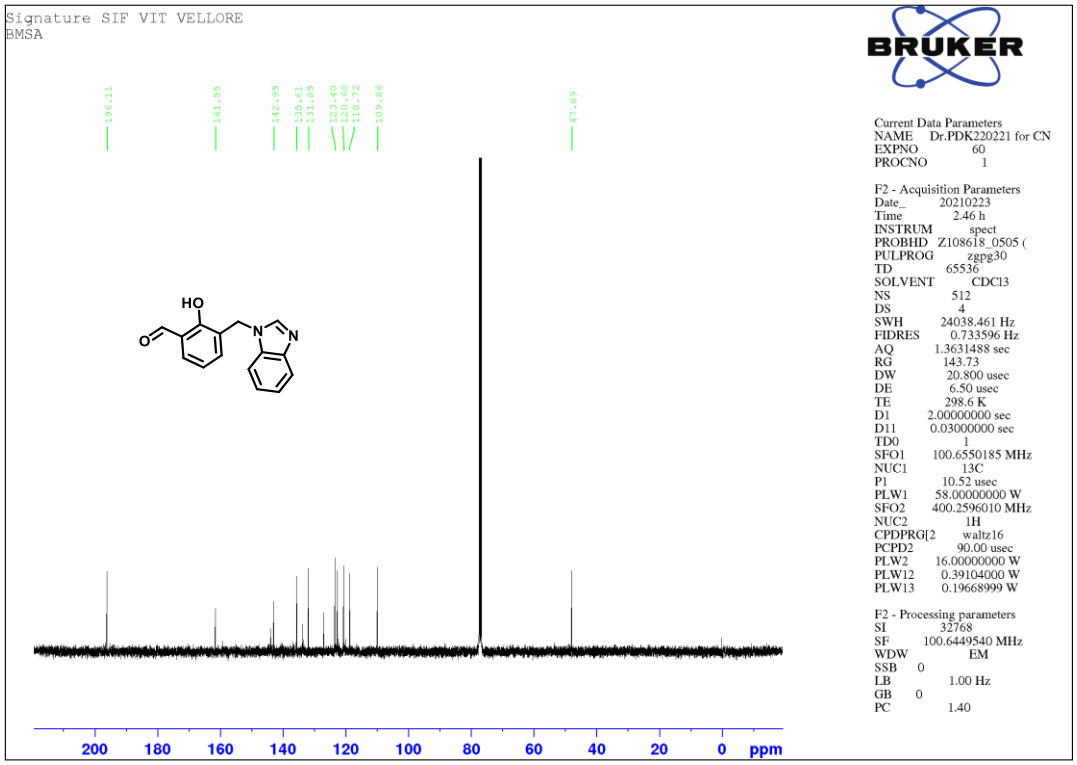


Fig. S6 ^{13} CNMR Spectrum of compound 4C

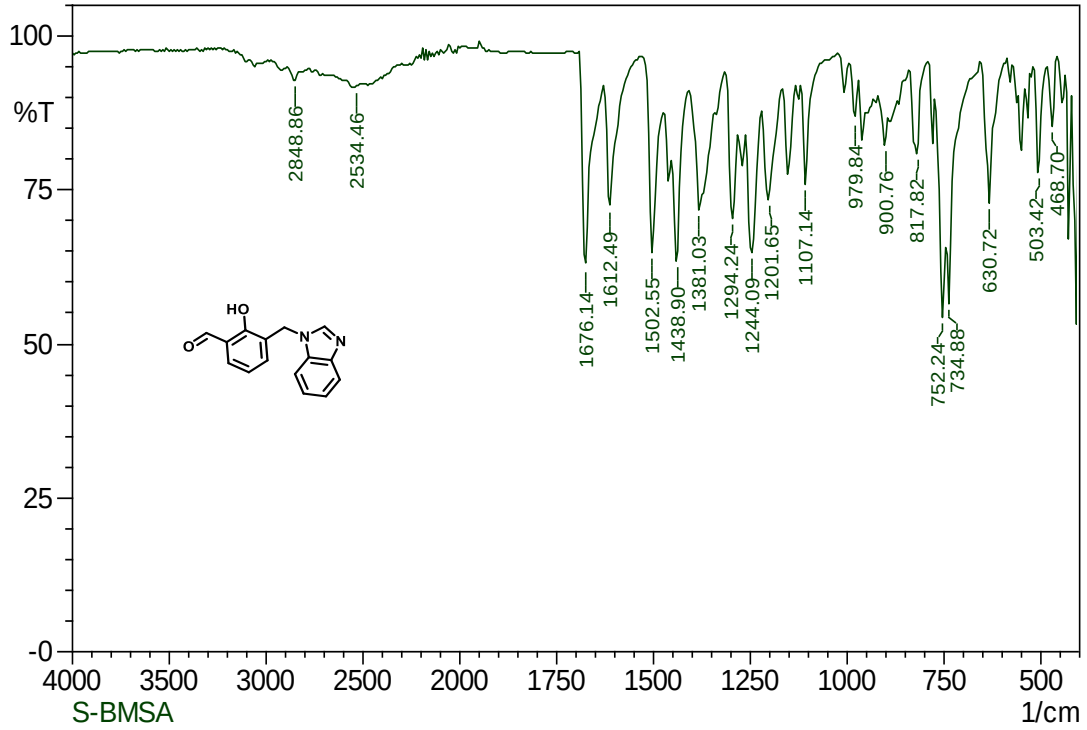


Fig.S7. FT-IR Spectrum of Compound 4C

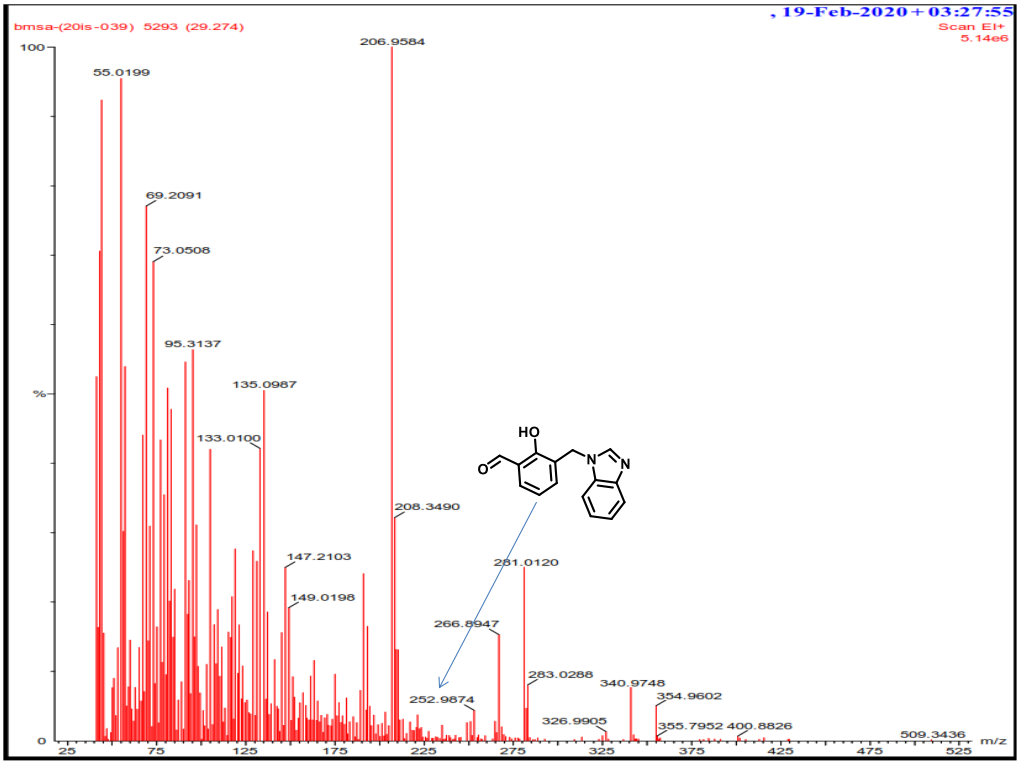


Fig.S8 GCMS Spectrum of compound 4C

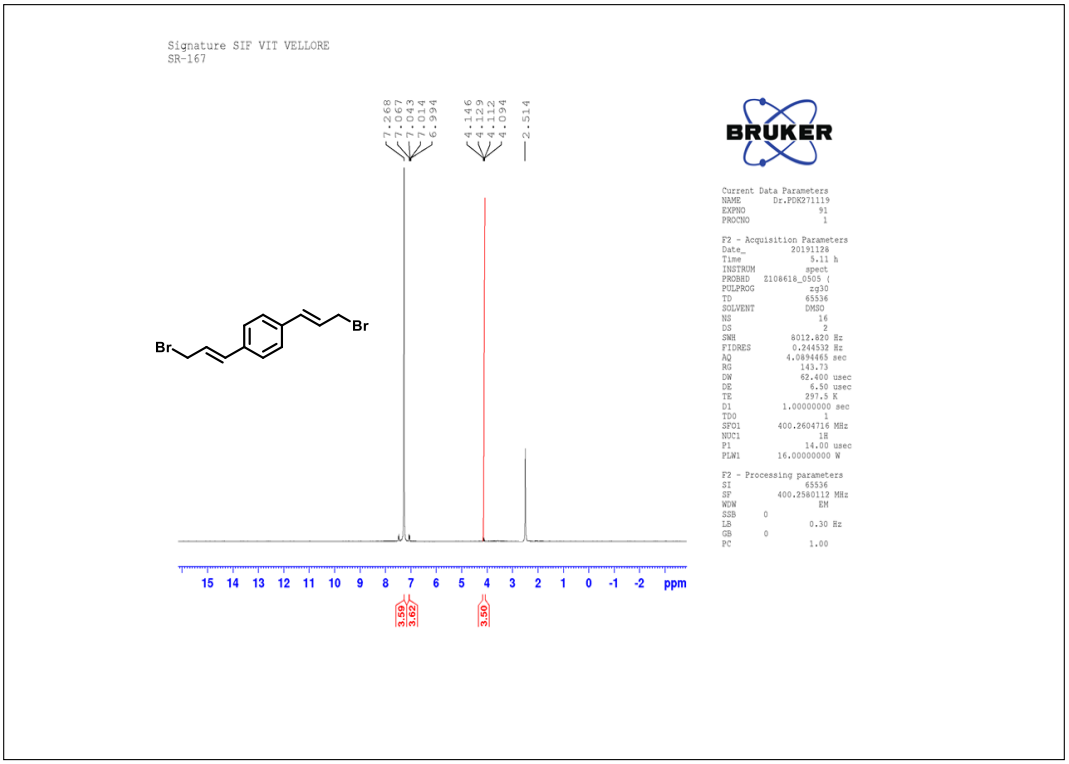


Fig.S9 ^{1}H NMR Spectrum of Compound 4D

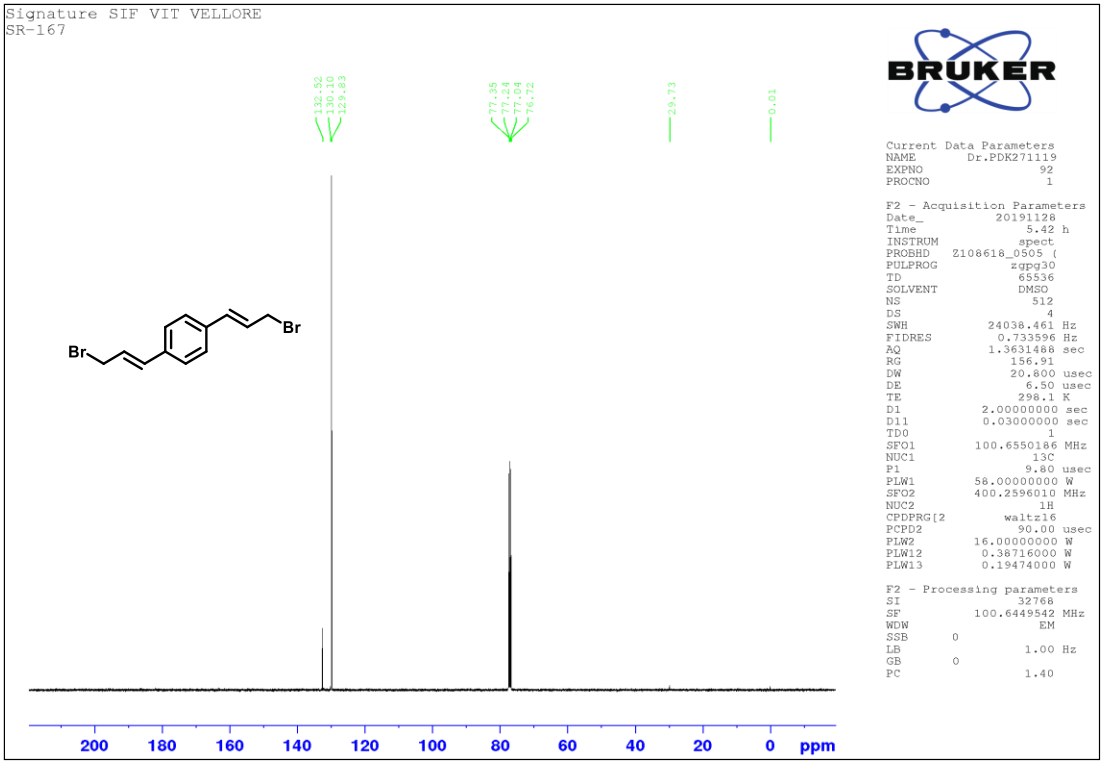


Fig.S10 ^{13} CNMR Spectrum of compound 4D

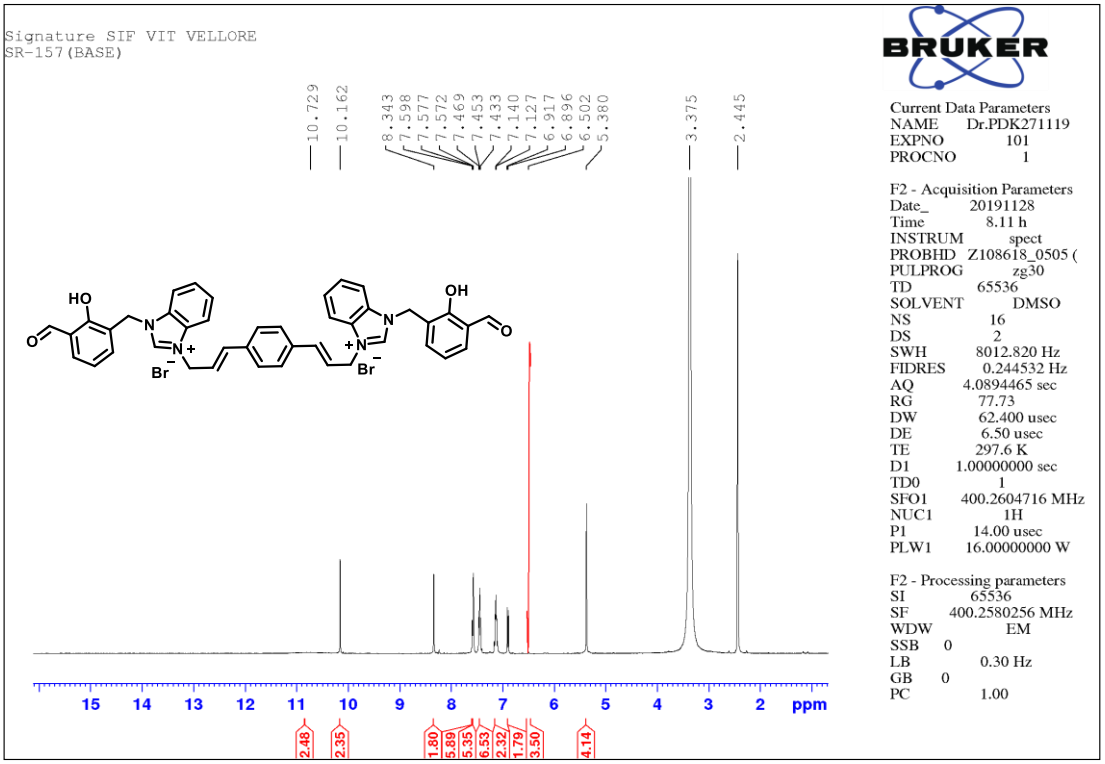


Fig.S11. ^{1}H NMR spectrum of compound 4E

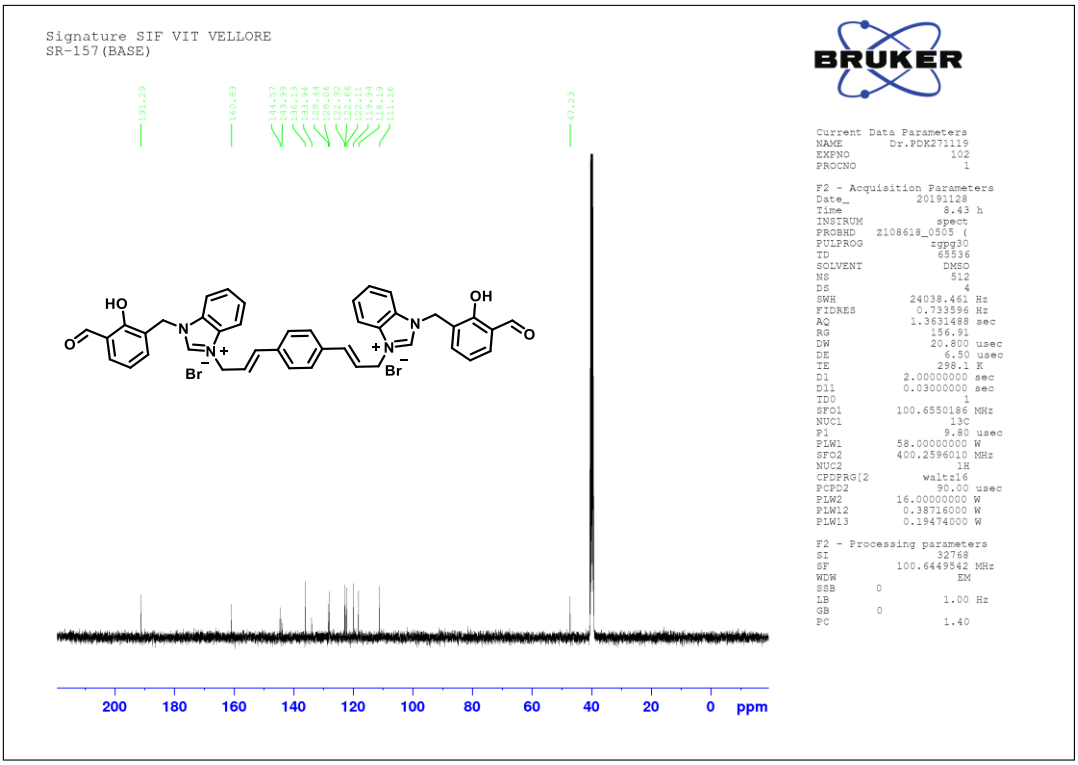


Fig.S12. ^{13} CNMR spectrum of compound 4E

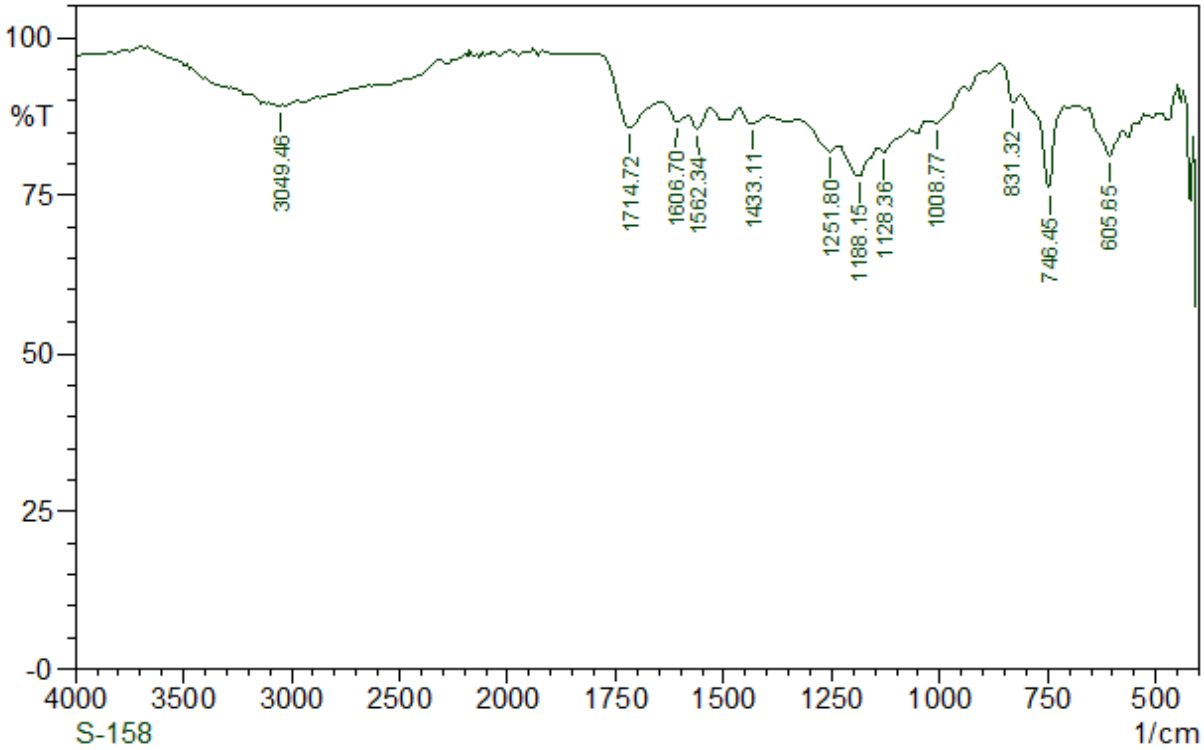


Fig.S13. .FT-IR spectrum of compound 4E

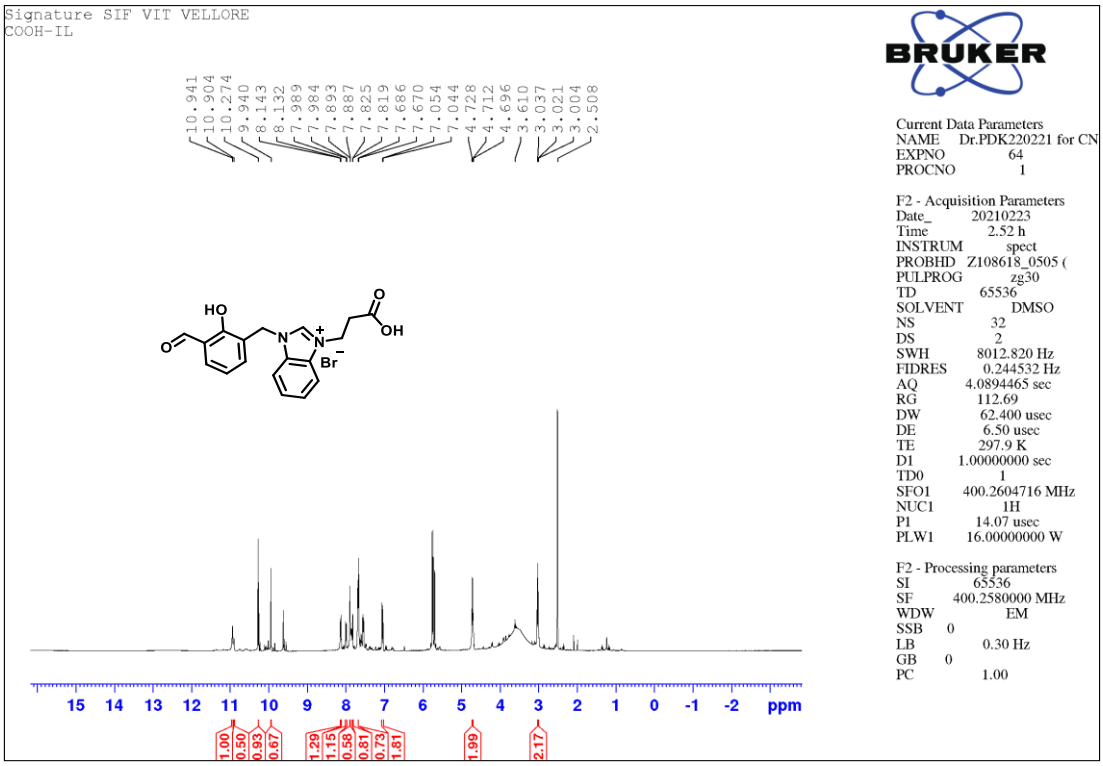


Fig.S14. ^{1}H NMR spectrum of compound 4F

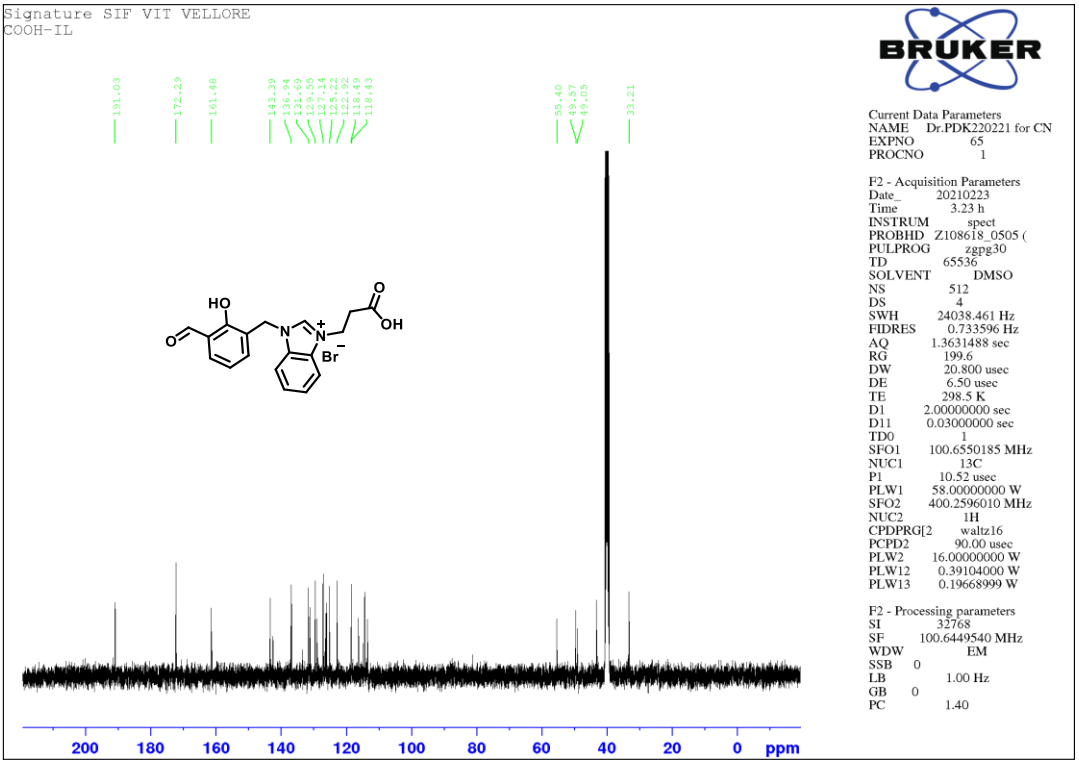


Fig.S15. ^{13}CNMR spectrum of compound 4F

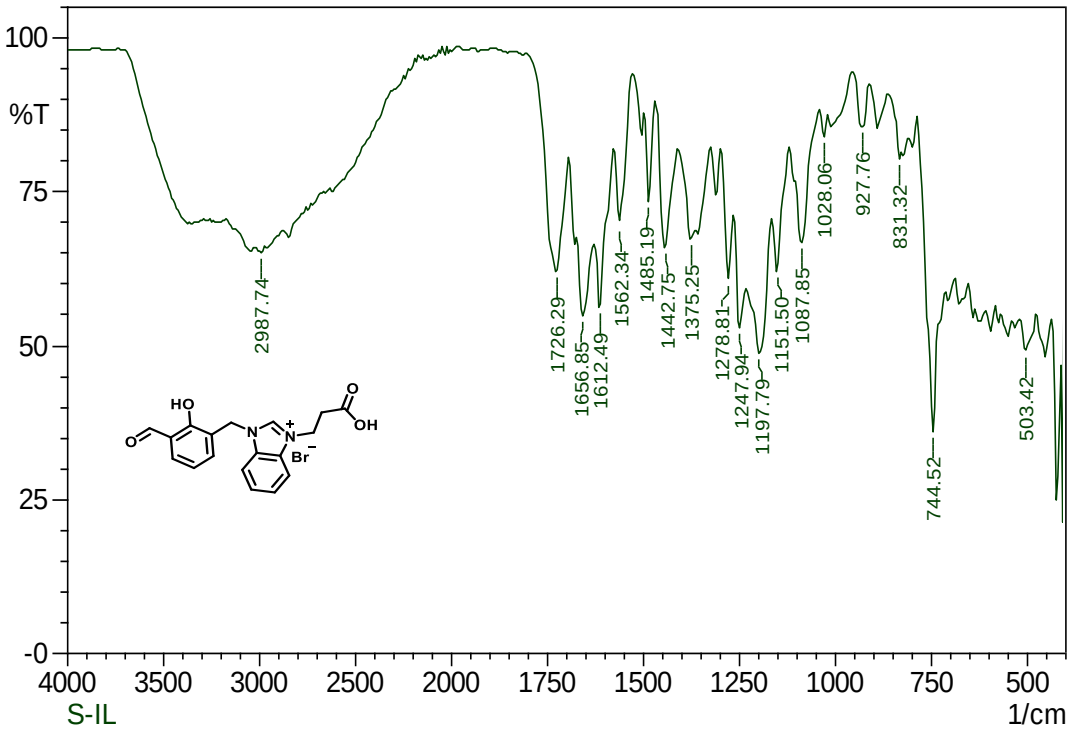


Fig.S16. FT-IR spectrum of compound 4F

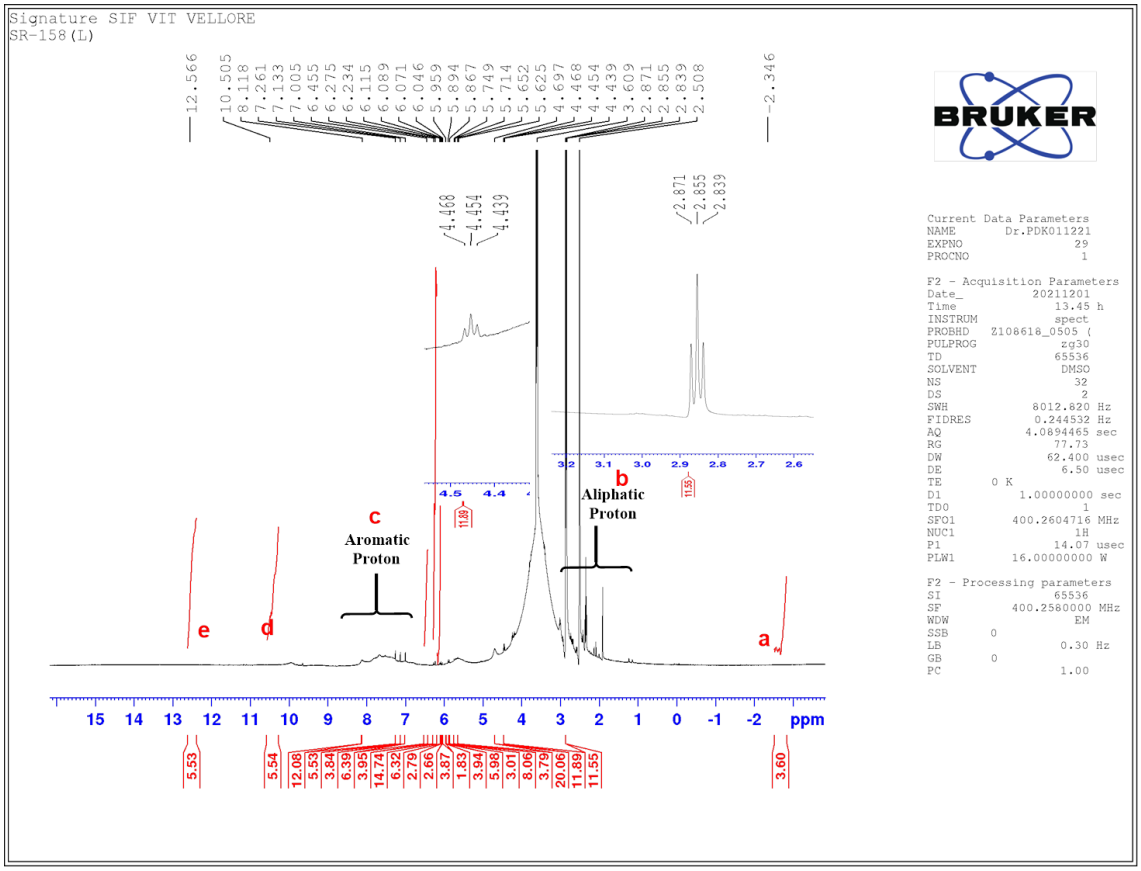


Fig.S17.[1]H NMR spectrum of Photocatalyst (MFBBCFPc)

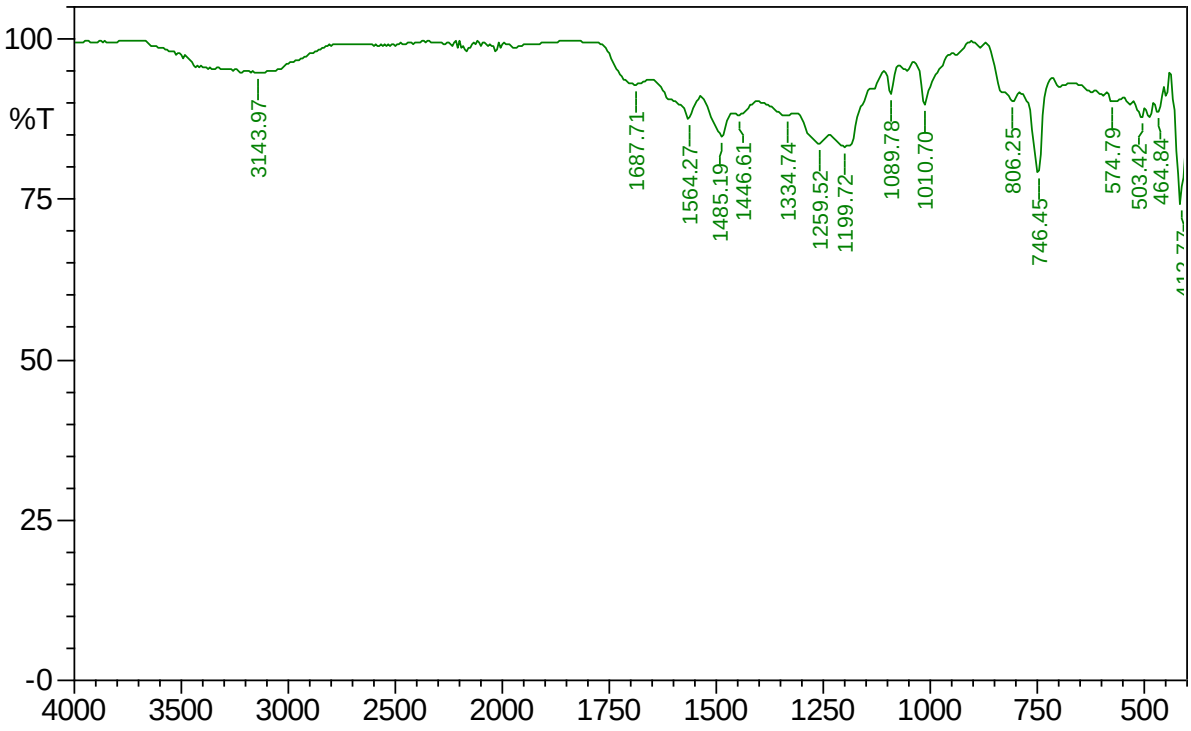


Fig.S18. .FT-IR spectrum of Photocatalyst (MFBBCFPc)

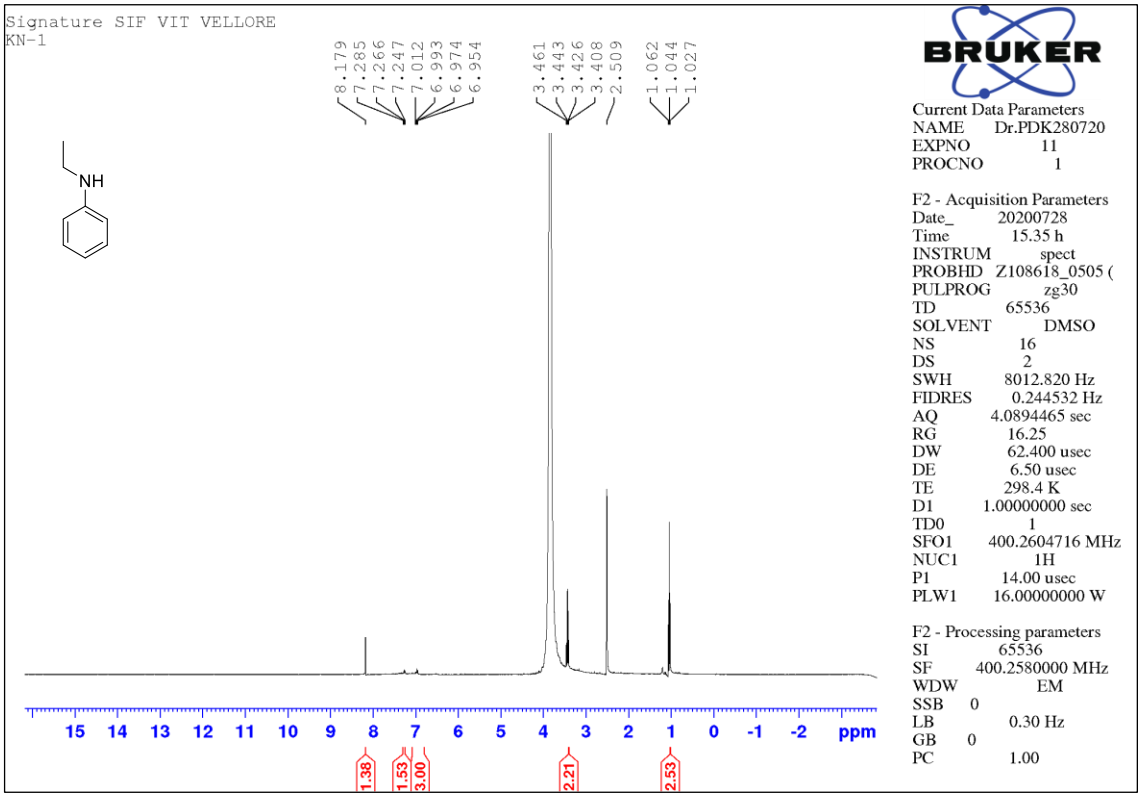


Fig.S19 ^{1}H NMR spectrum of N-ethyl aniline (**D1**)

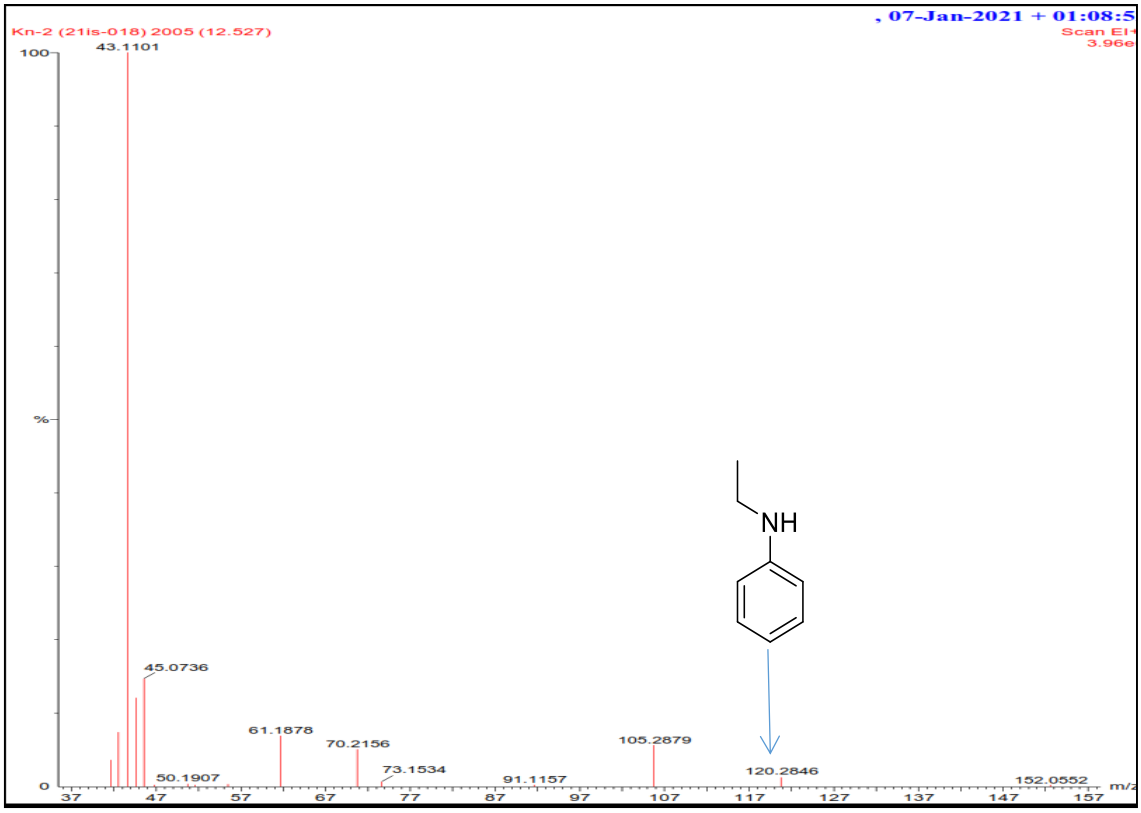


Fig.S20 GCMS spectrum of N-ethyl aniline (**D1**)

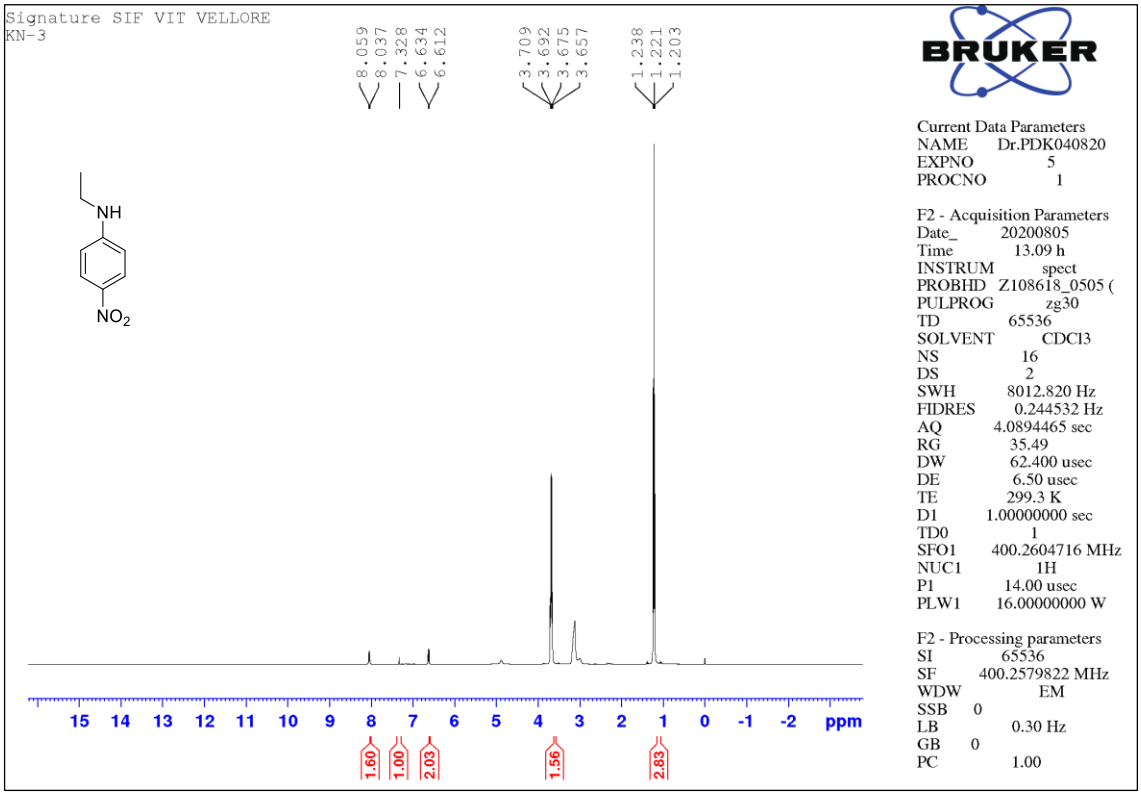


Fig.S21. ^{1}H NMR spectrum of N-ethyl-4-nitroaniline **(D2)**

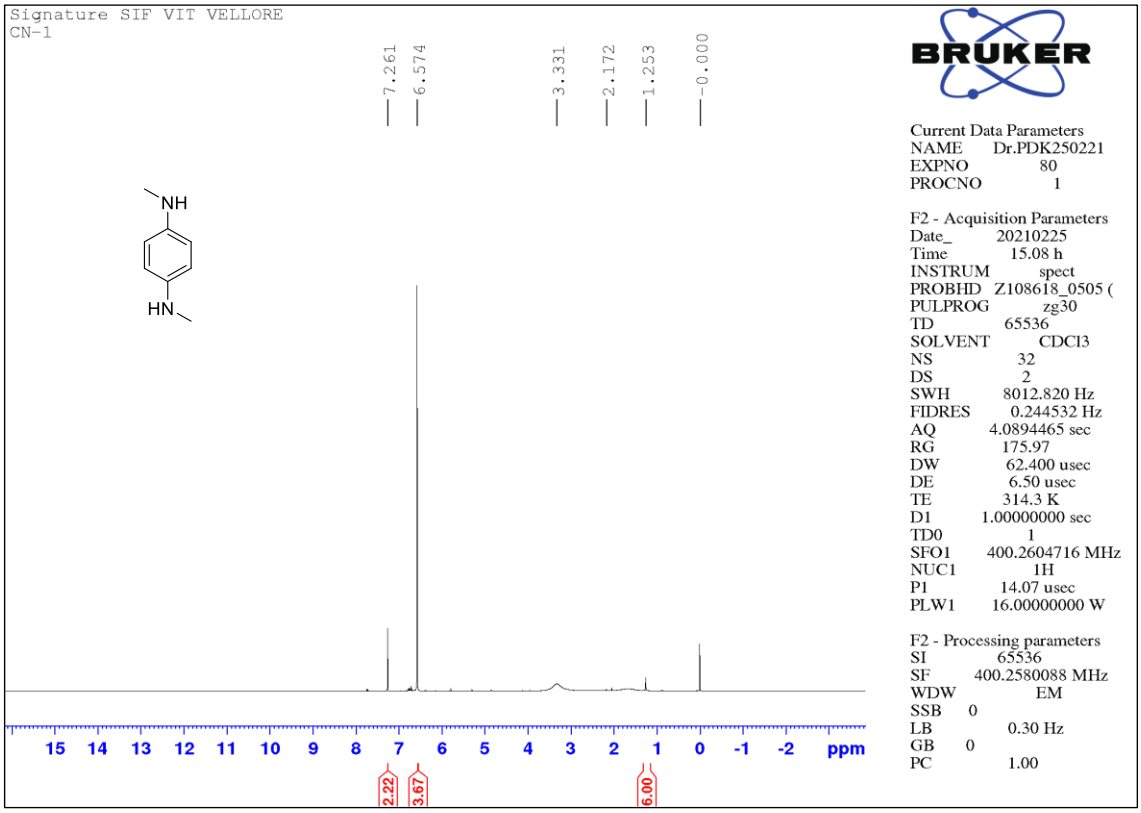


Fig.S22 ^{1}H NMR spectrum of N^{1}, N^{4}-dimethylbenzene-1, 4-diamine **(D3)**

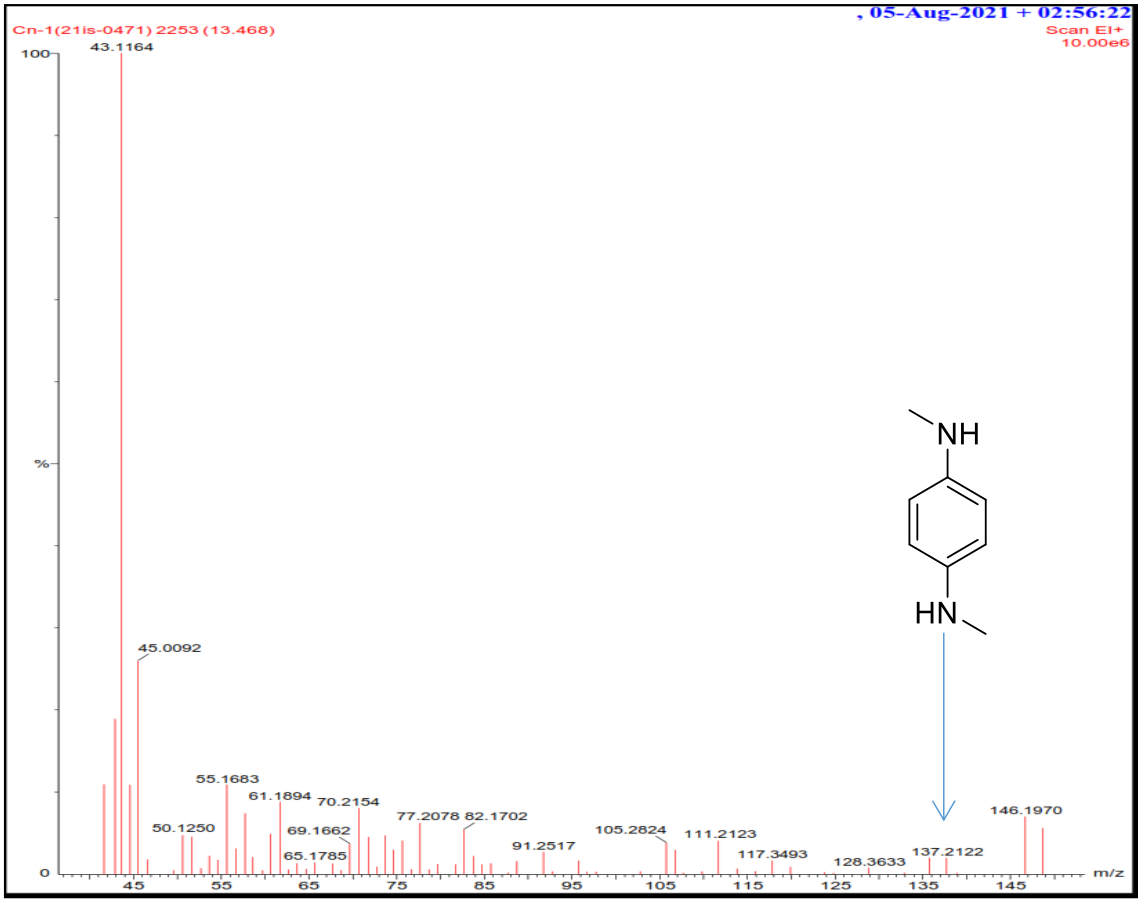


Fig.S23 GCMS spectrum of N^1, N^4-dimethylbenzene-1, 4-diamine **(D3)**

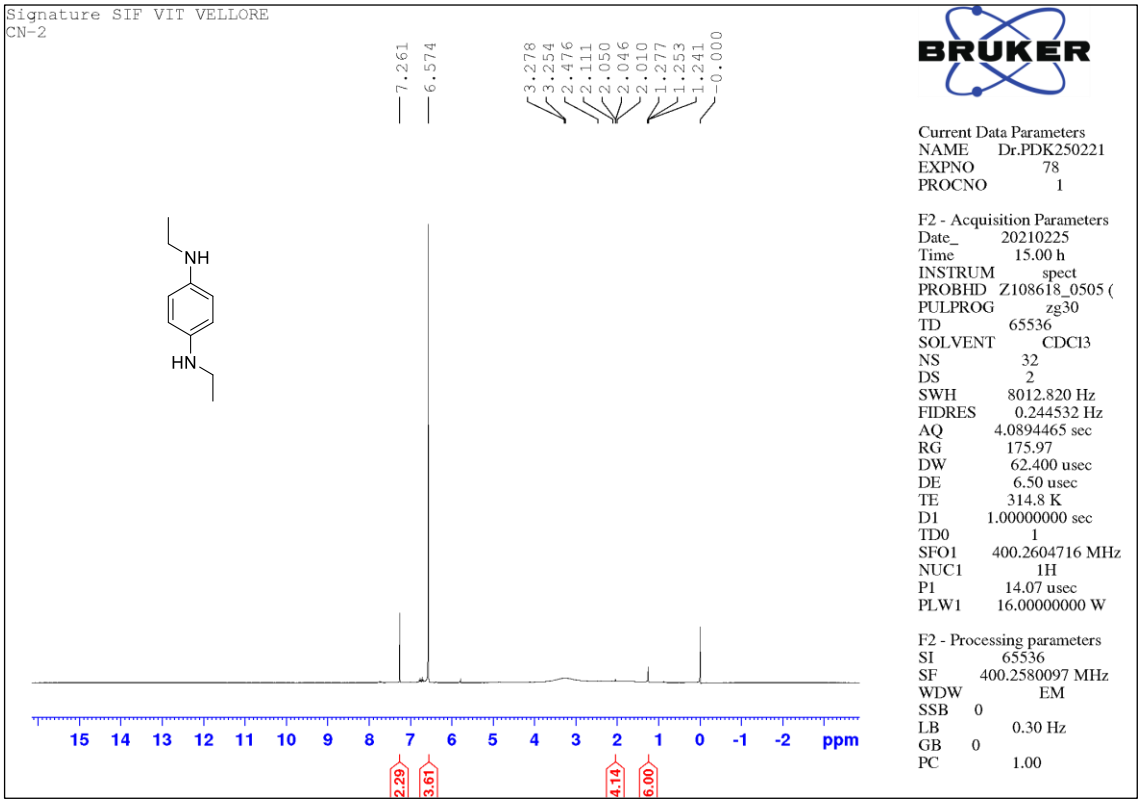


Fig.S24 ^{1}H NMR spectrum of N^1, N^4-diethylbenzene-1,4-diamine **(D4)**

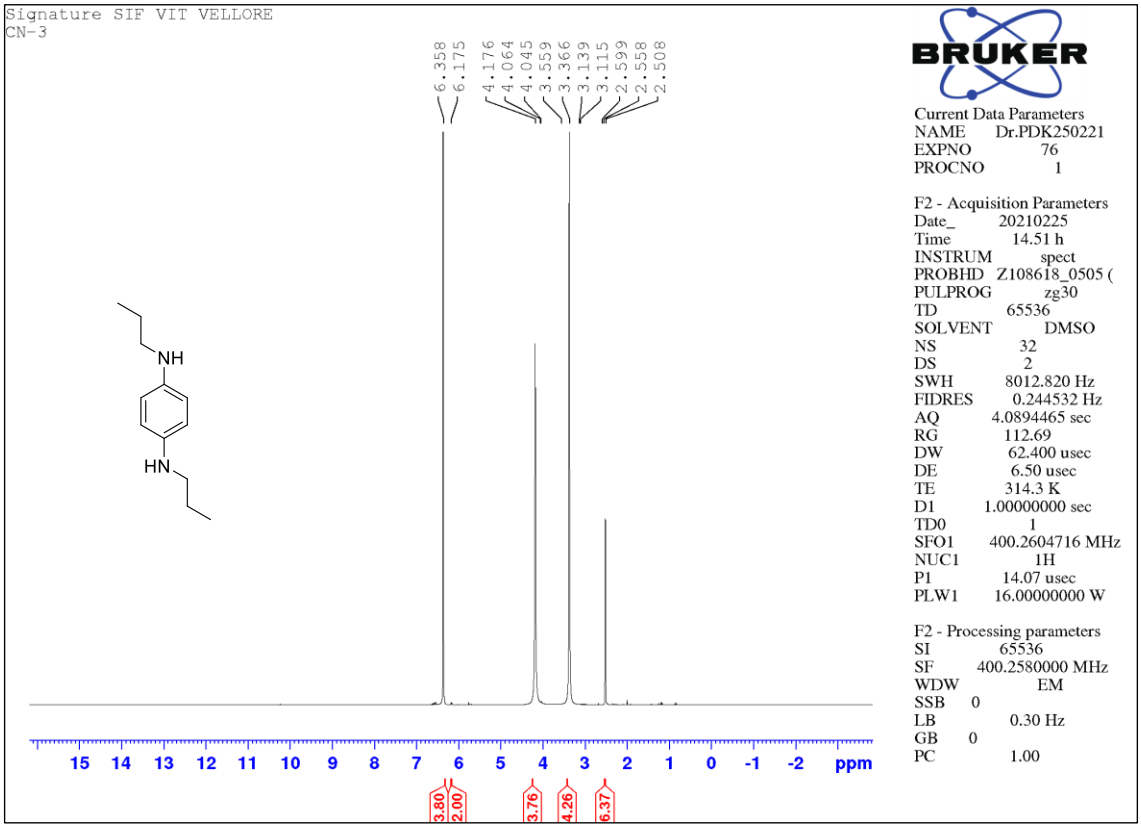


Fig.S25 ^{1}H NMR spectrum of N^1, N^4-dipropylbenzene-1, 4-diamine **(D5)**

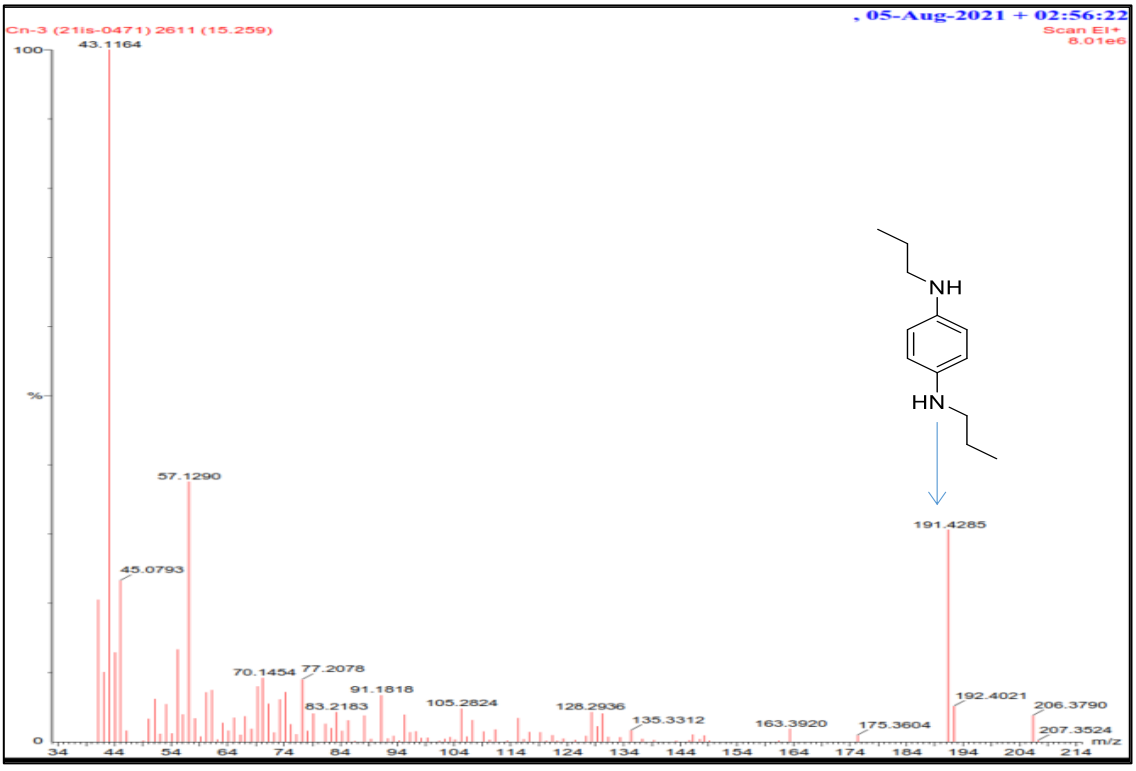
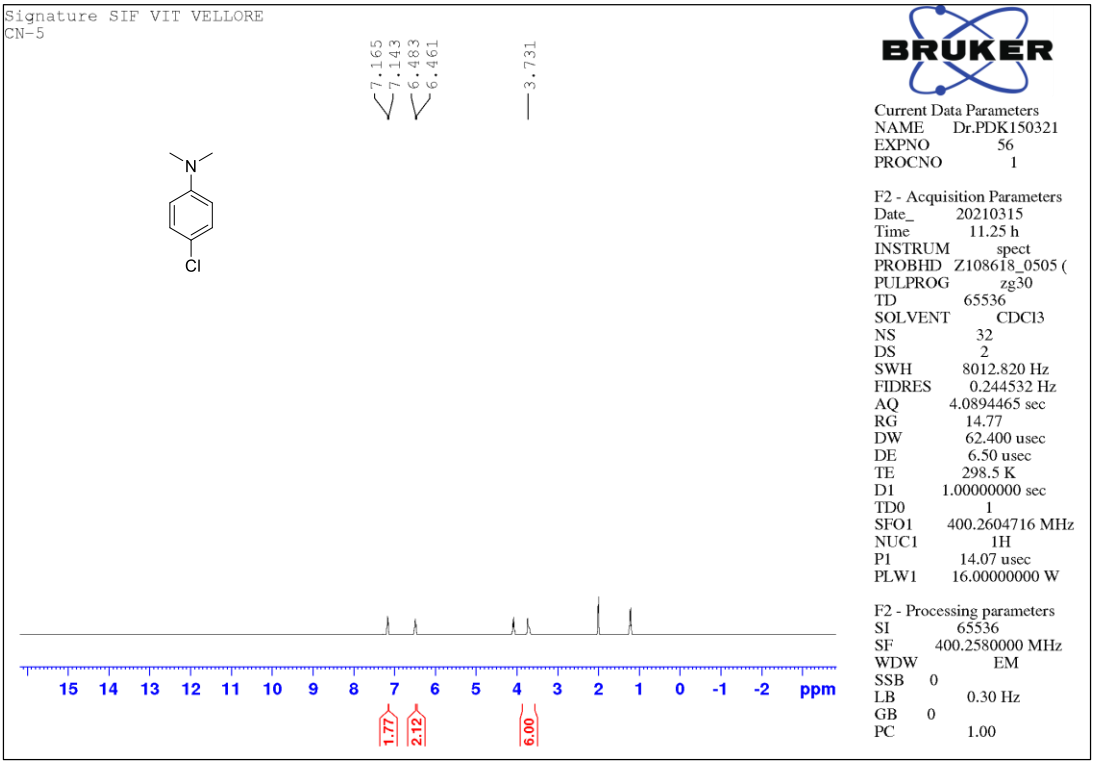


Fig.S26 GCMS Spectrum of N1,N4-Dipropylbenzene-1,4-diamine **(D5)**



FigS.27 ^{1}H NMR spectrum of 4-chloro-N, N-dimethyl aniline **(D6)**

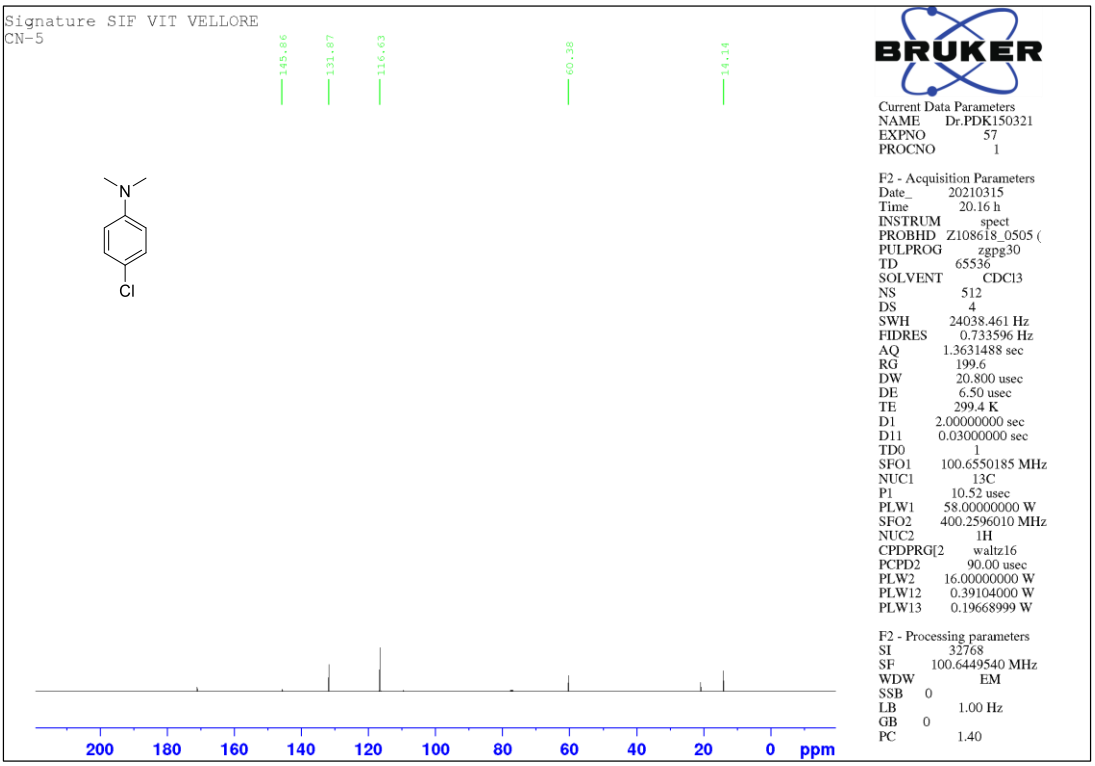


Fig. S28 ^{13} CNMR spectrum of 4-chloro-N, N-dimethyl aniline **(D6)**

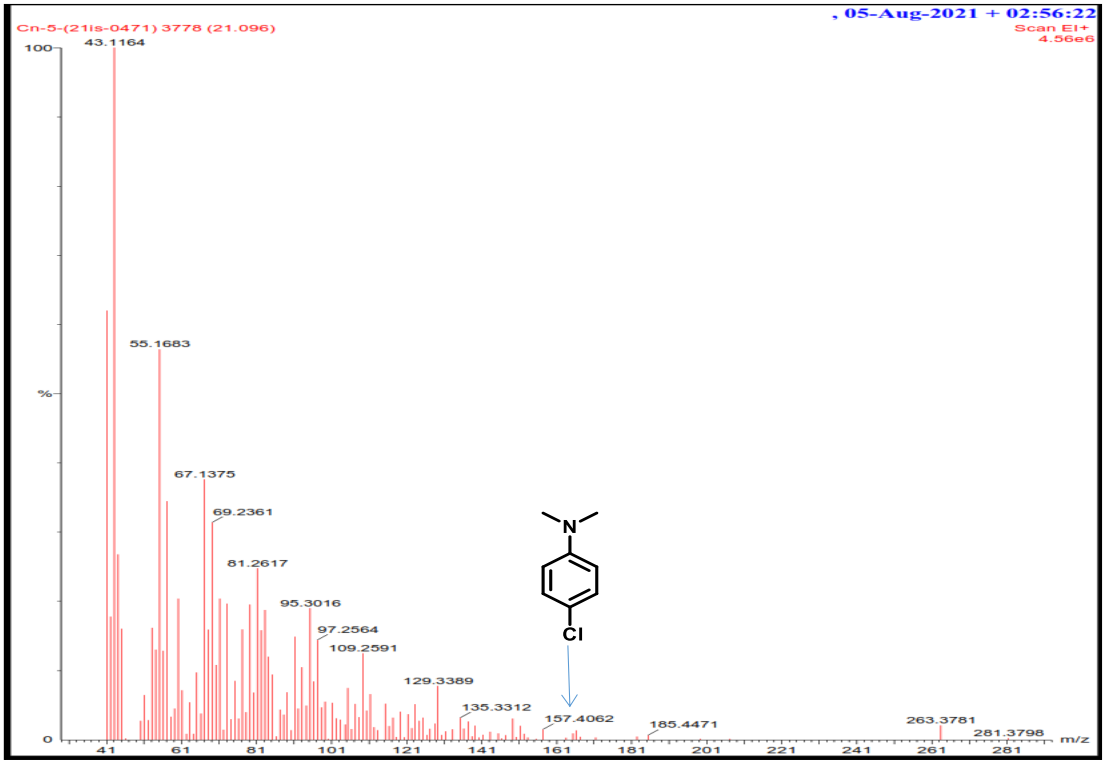


Fig.S29 GCMS spectrum of 4-chloro-N, N-dimethyl aniline **(D6)**

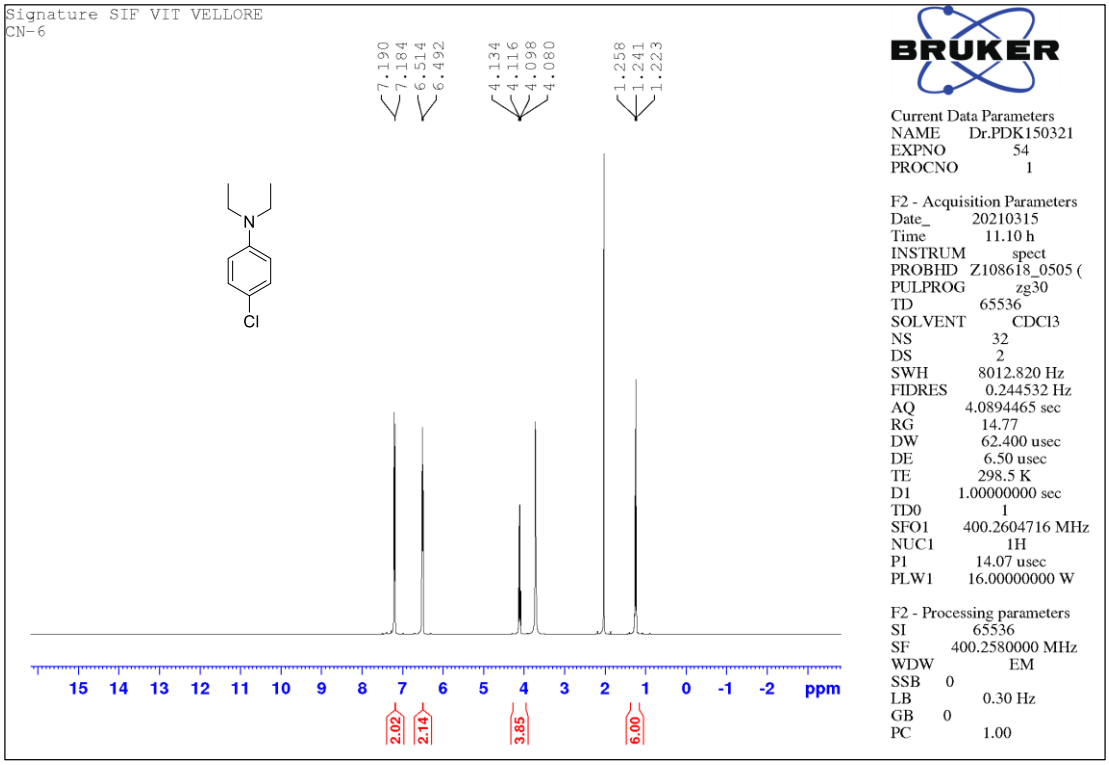


Fig. S30 ^{1}H NMR spectrum of 4-chloro-N,N-diethylaniline **(D7)**

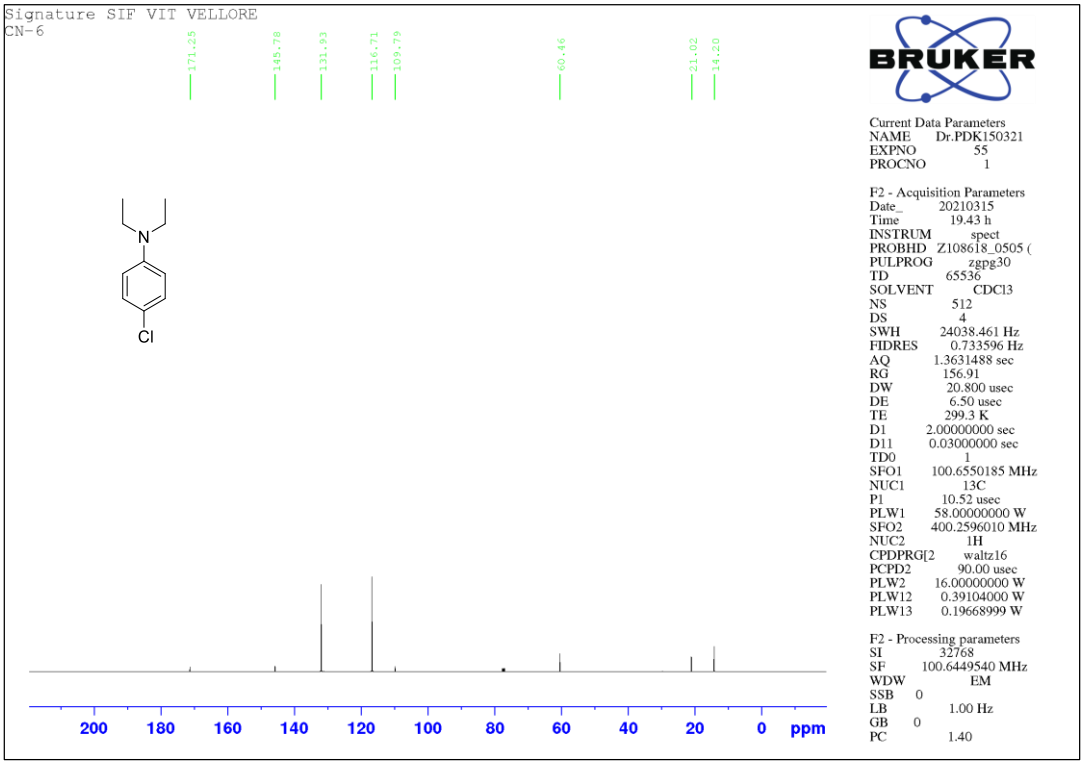


Fig. S31 [13] CNMR spectrum of 4-chloro-N,N-diethylaniline **(D7)**

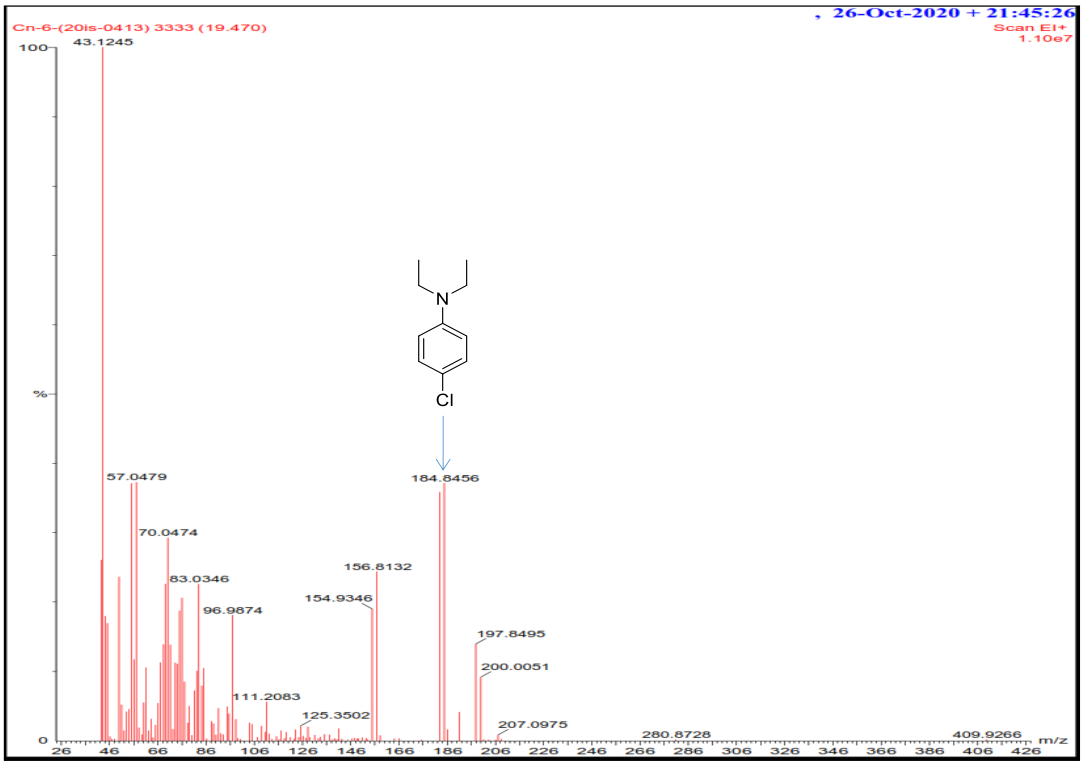


Fig. S32 GCMS spectrum of 4-chloro-N,N-diethylaniline **(D7)**

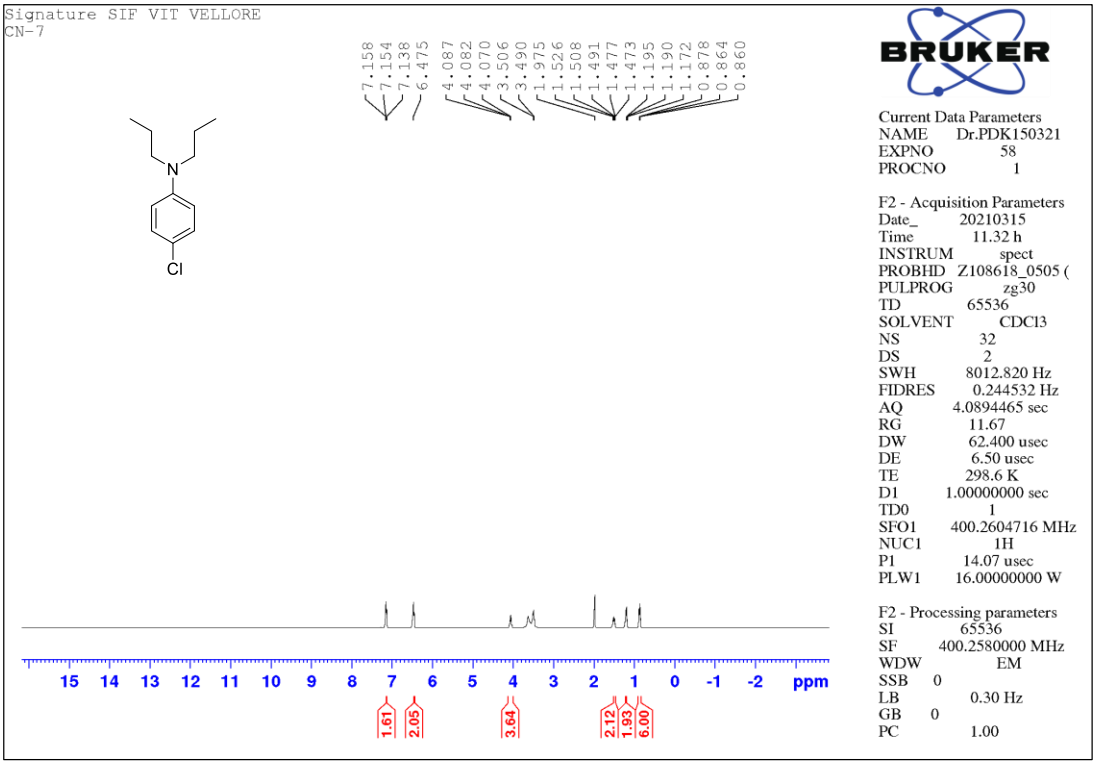


Fig. S33 ^{1}H NMR spectrum of 4-chloro-N,N-dipropylaniline **(D8)**

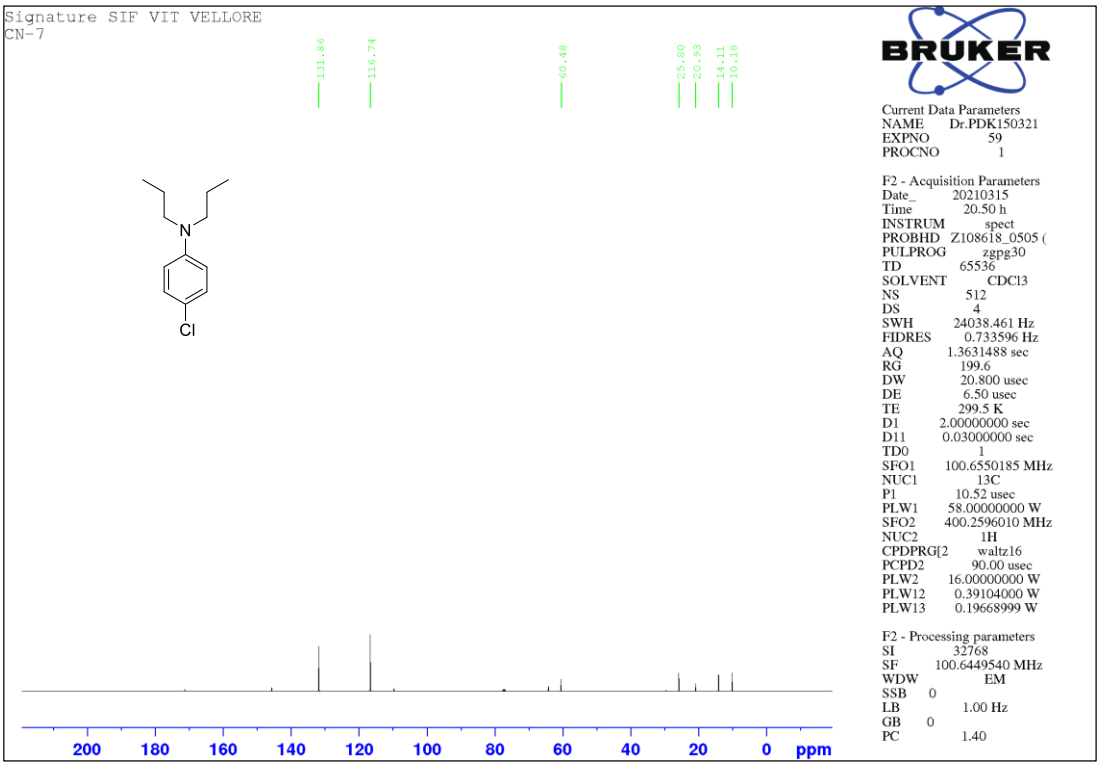


Fig. S34 ^{13}C NMR spectrum of 4-chloro-N,N-dipropylaniline **(D8)**

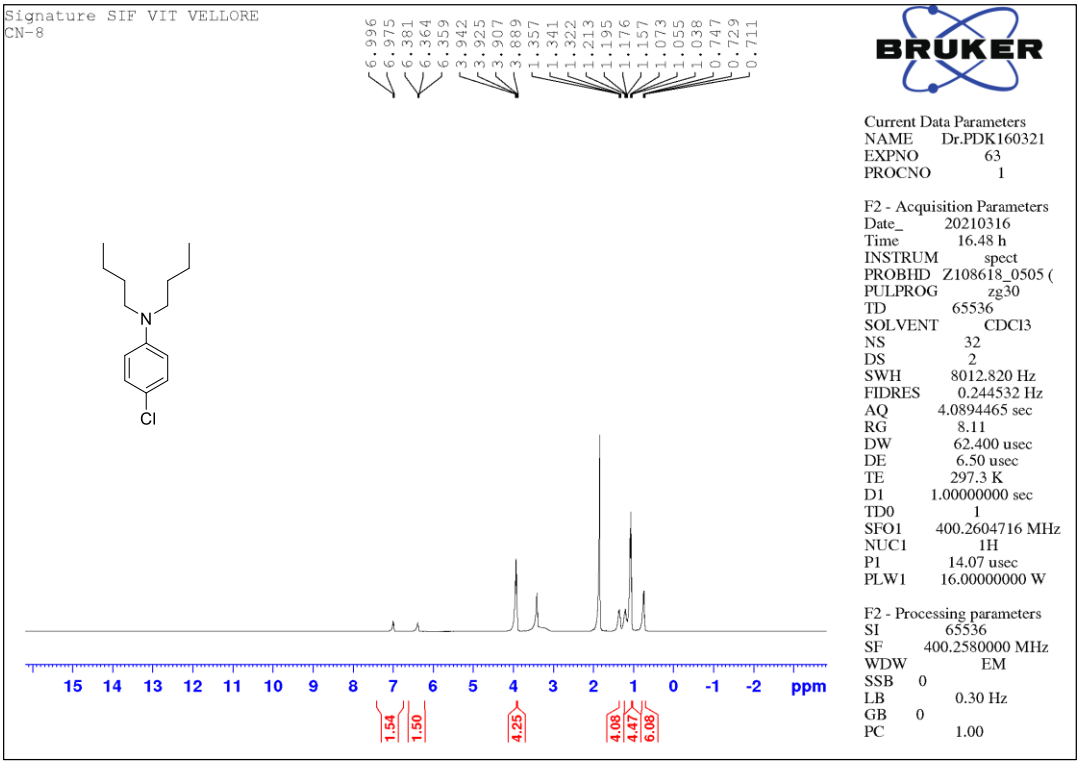


Fig. S35 ^{1}H NMR spectrum of 4-chloro-N, N-dibutylaniline **(D9)**

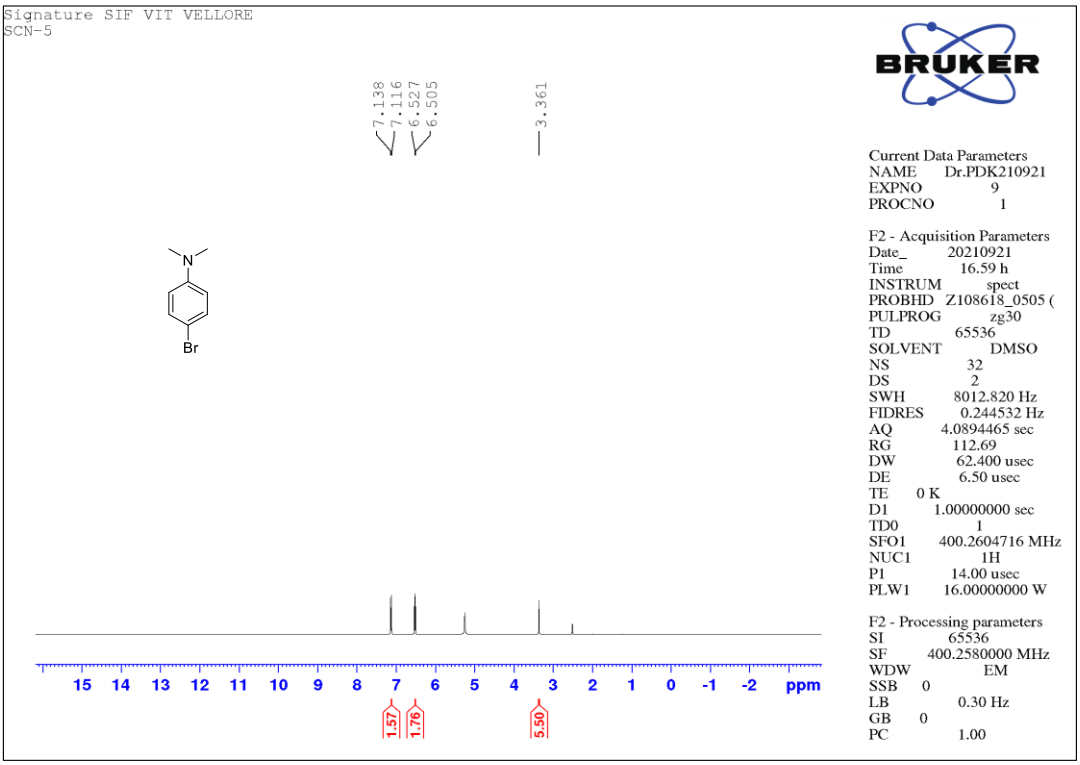


Fig. S36 ^{1}H NMR spectrum of 4-bromo-N,N-dimethylaniline **(D10)**

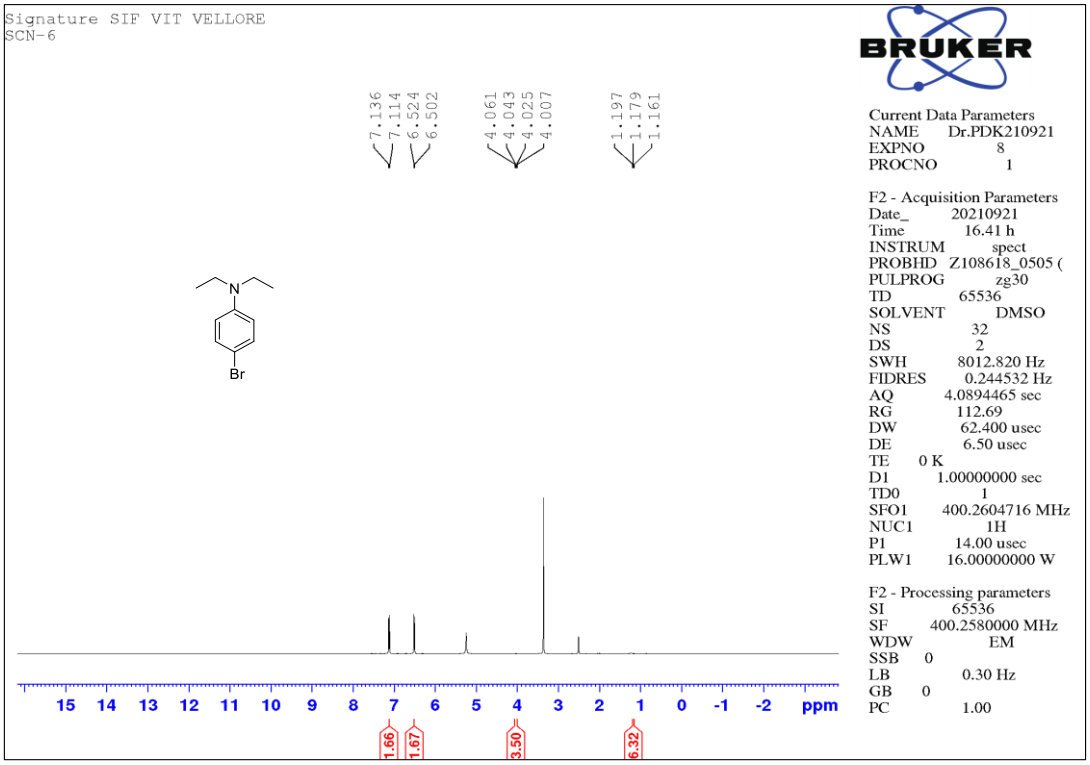


Fig.S37 ^{1}H NMR spectrum of 4-bromo-N,N-diethylaniline **(D11)**

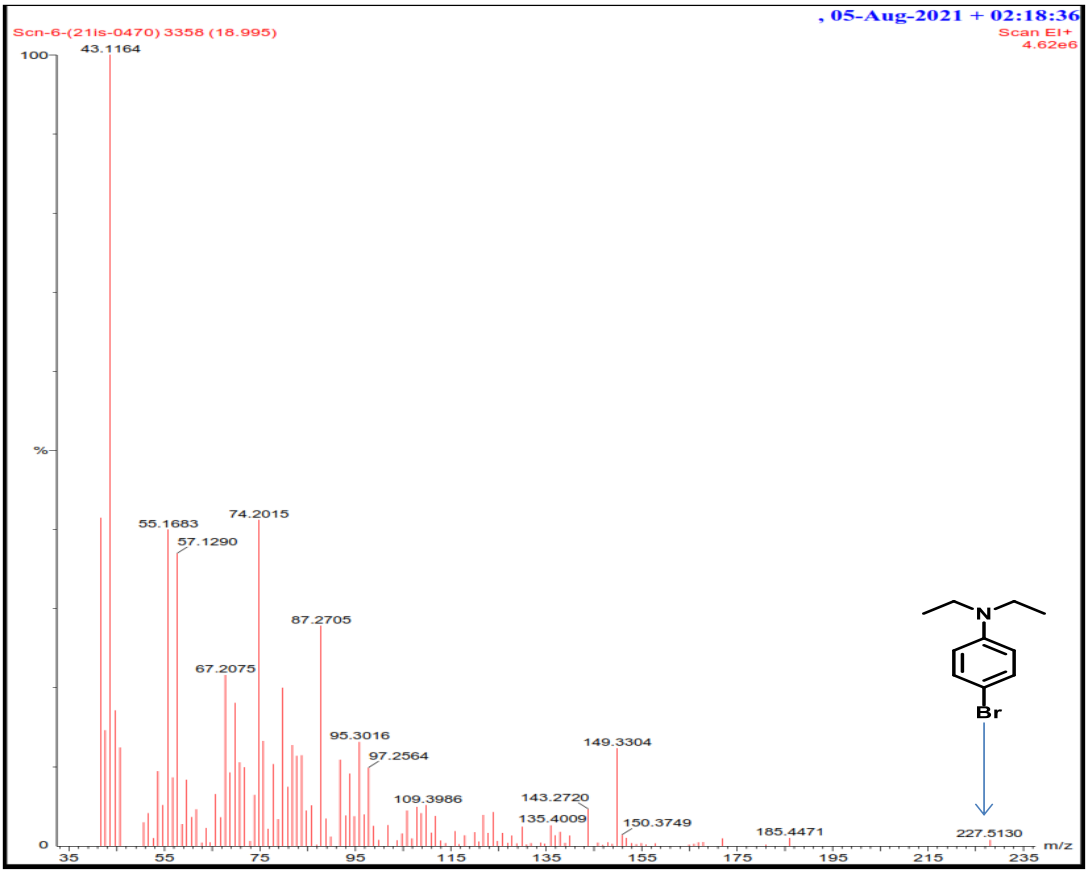


Fig. S38 GCMS spectrum of 4-bromo-N,N-diethylaniline **(D11)**

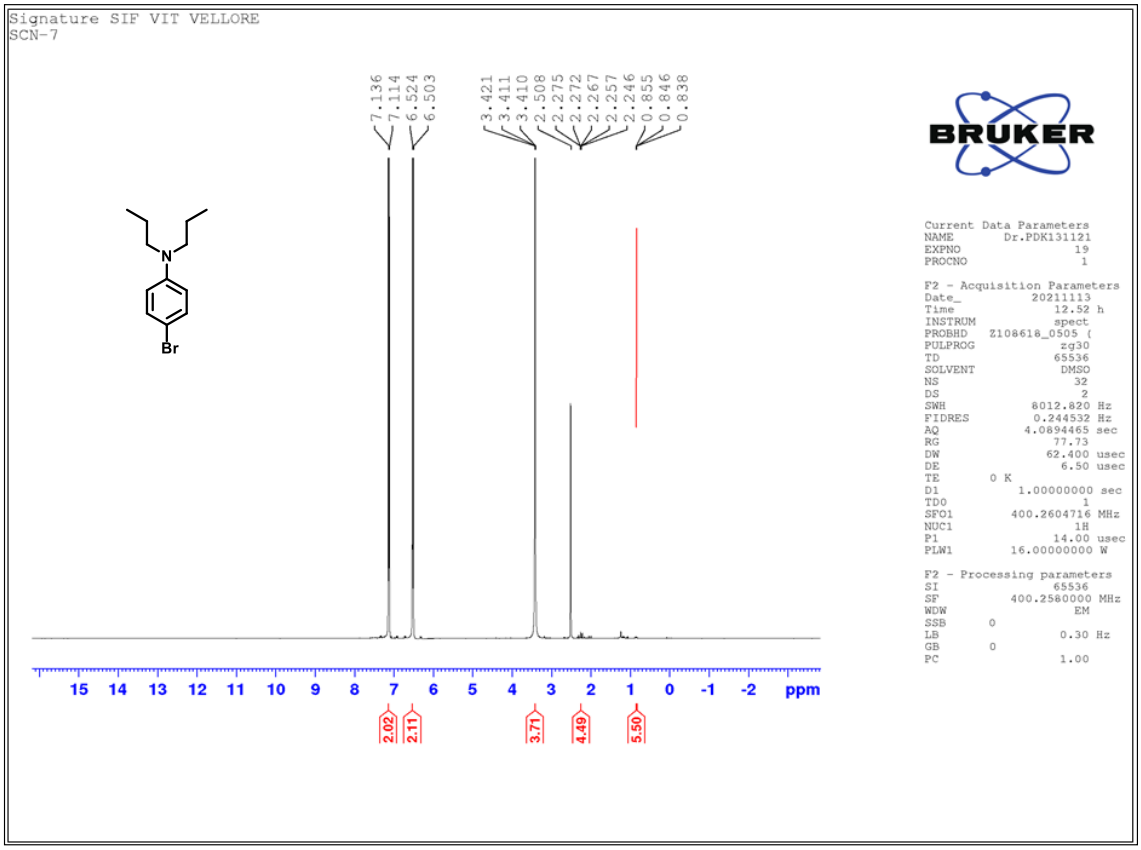


Fig.S39 [1]H NMR 4-bromo-N, N-dipropylaniline **(D12)**

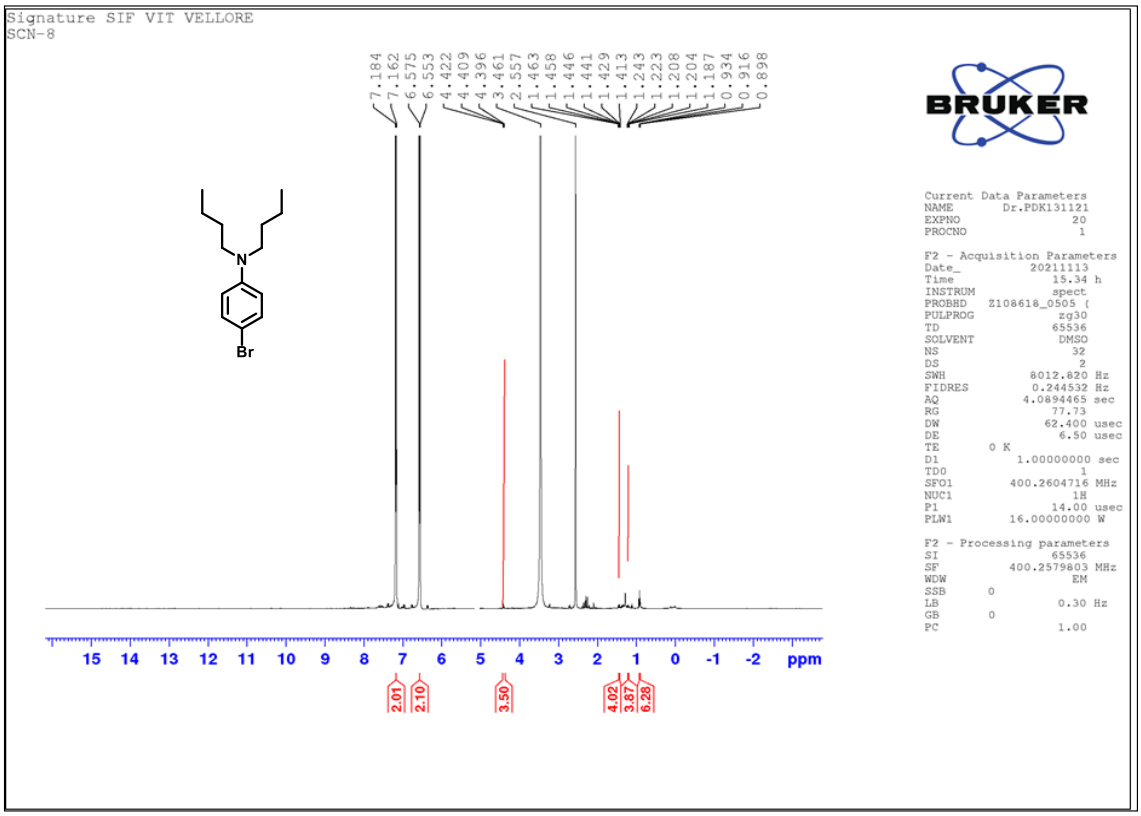


Fig. S40 [1]H NMR spectrum of 4-bromo-N, N-dibutylaniline **(D13)**

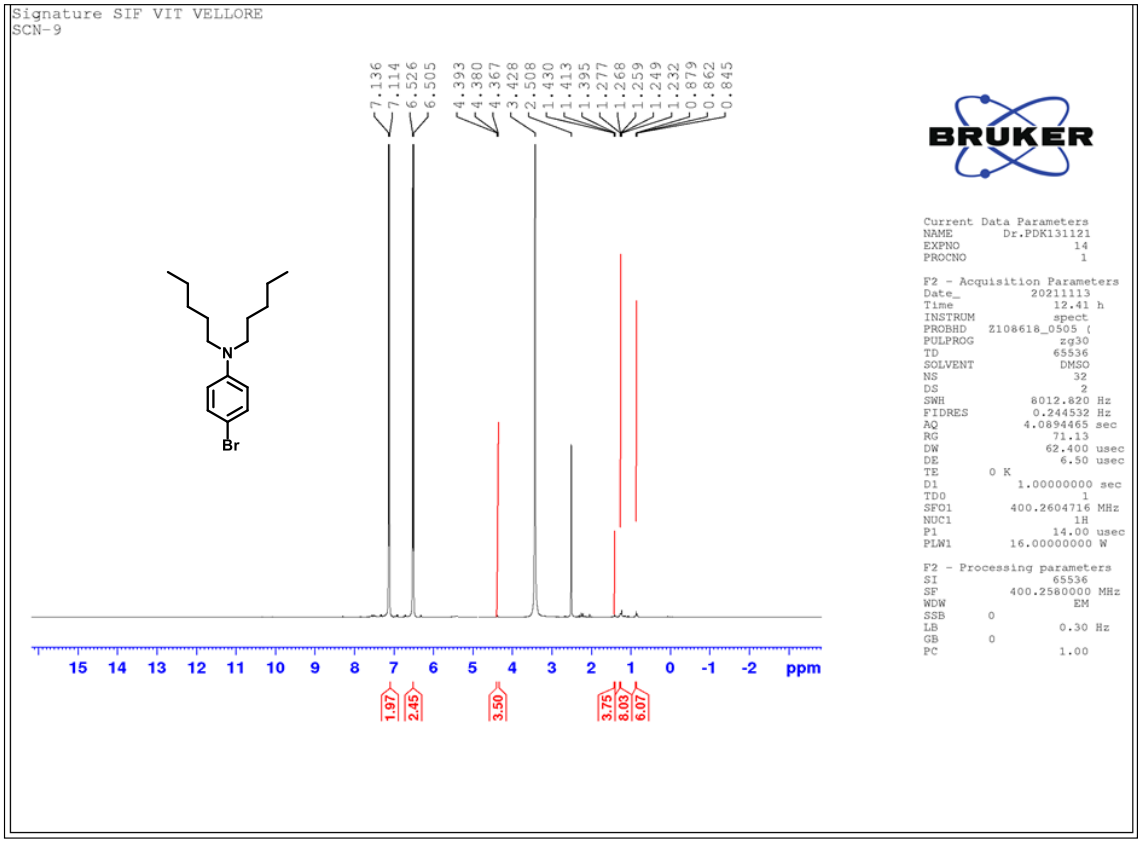


Fig. S41 ^{1}H NMR spectrum of 4-bromo-N, N-dipentylaniline **(D14)**

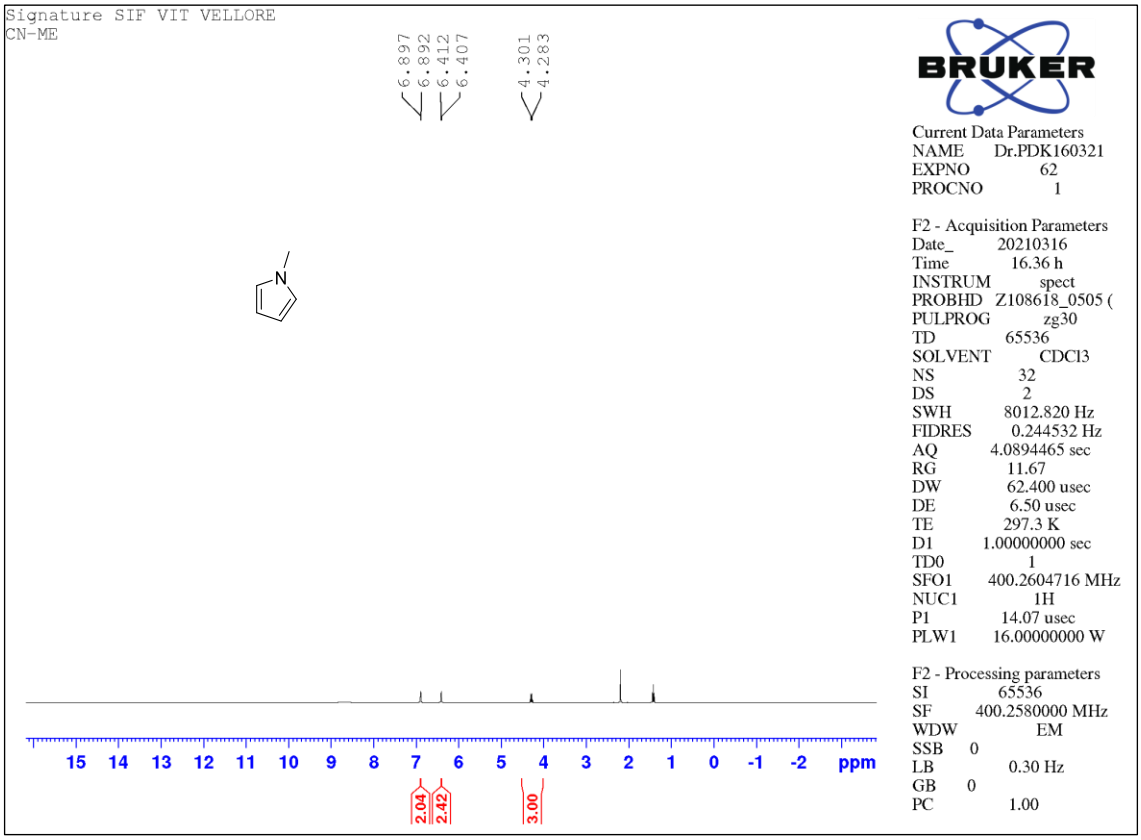


Fig. S42 ^{1}H NMR spectrum of 1-methyl-1H-pyrrole **(D15)**

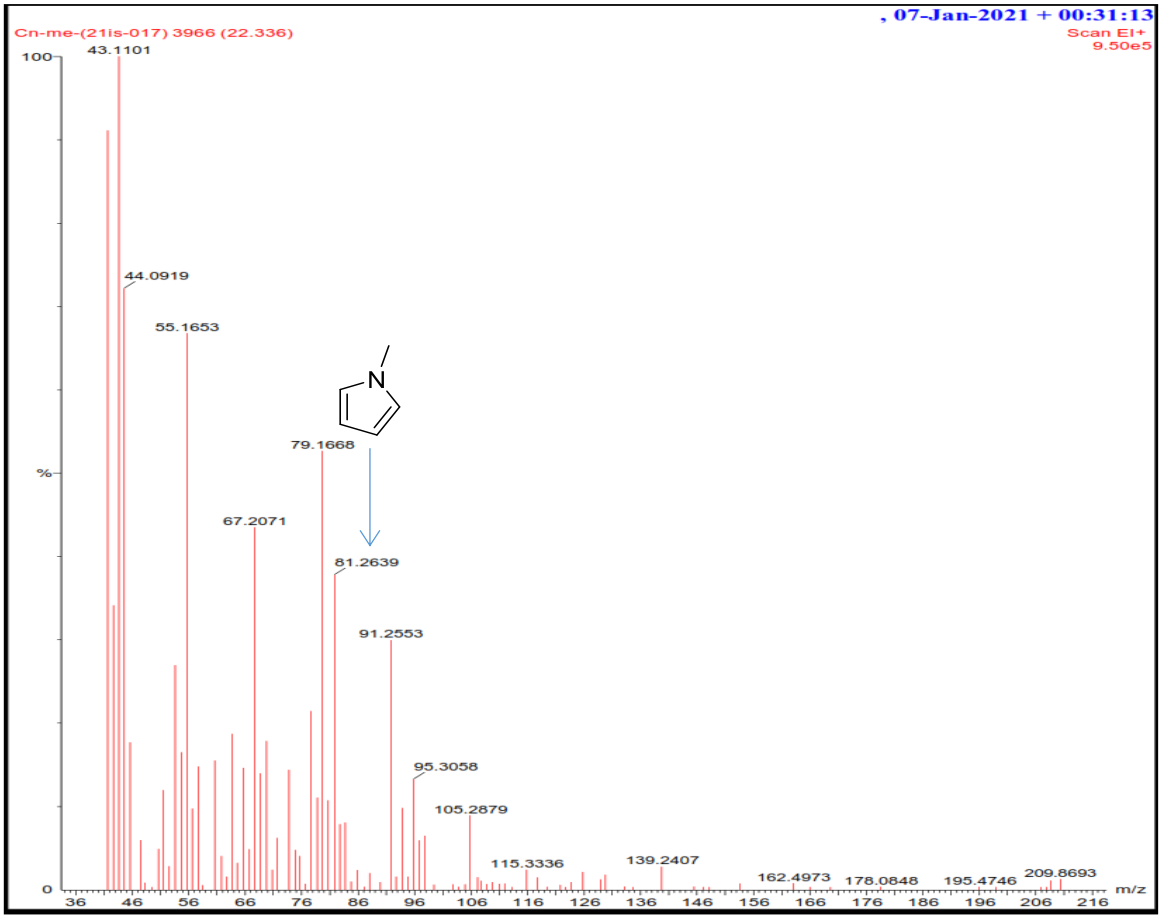


Fig. S43 GCMS spectrum of 1-methyl-1H-pyrrole **(D15)**

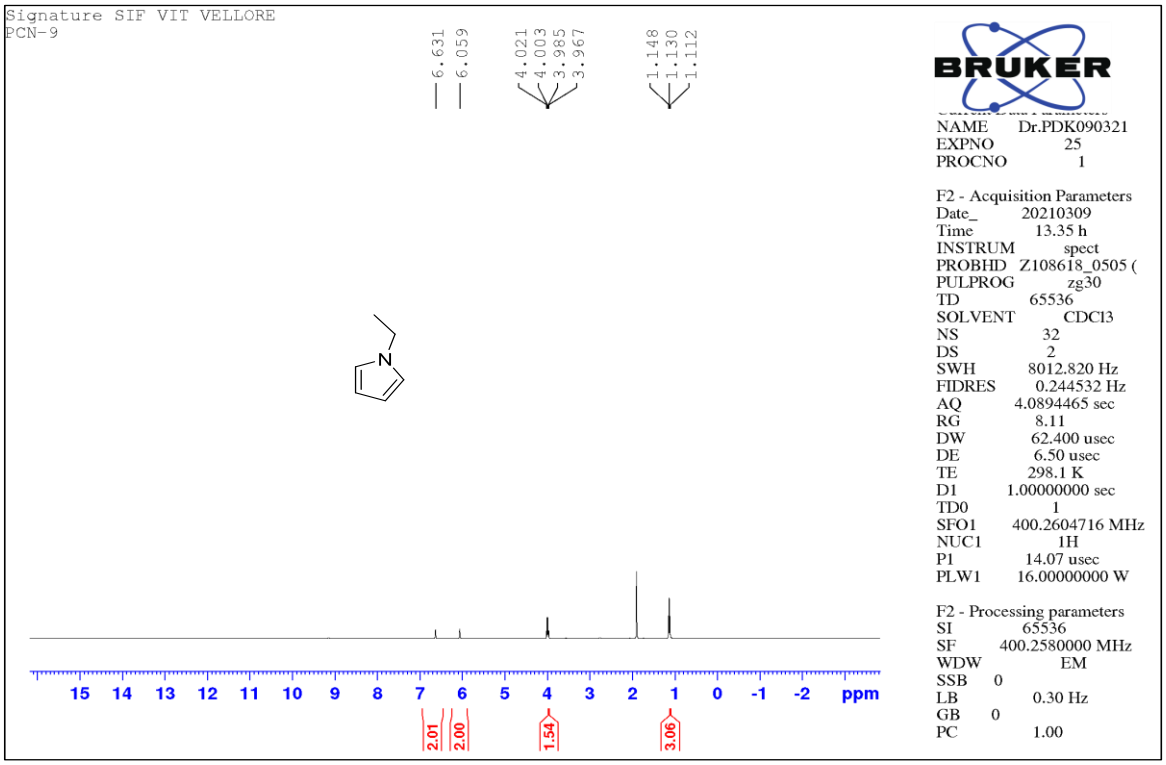


Fig. S44 ^{1}H NMR spectrum of 1-ethyl-1H-pyrrole **(D16)**

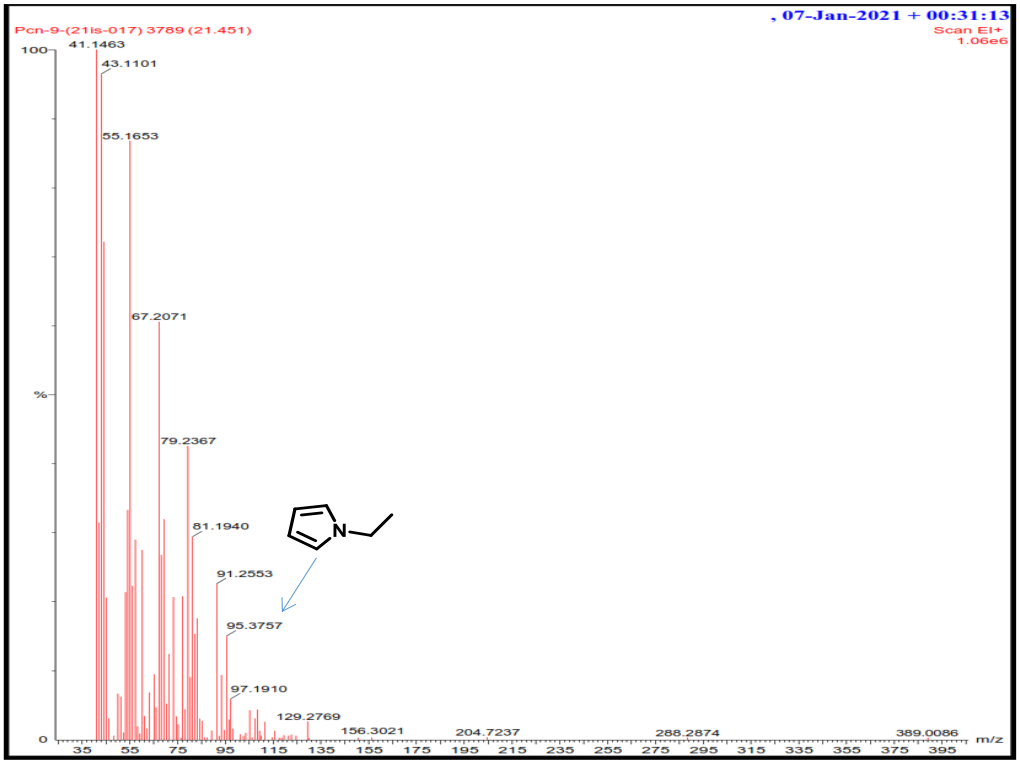


Fig. S45 GCMS spectrum of 1-ethyl-1H-pyrrole **(D16)**

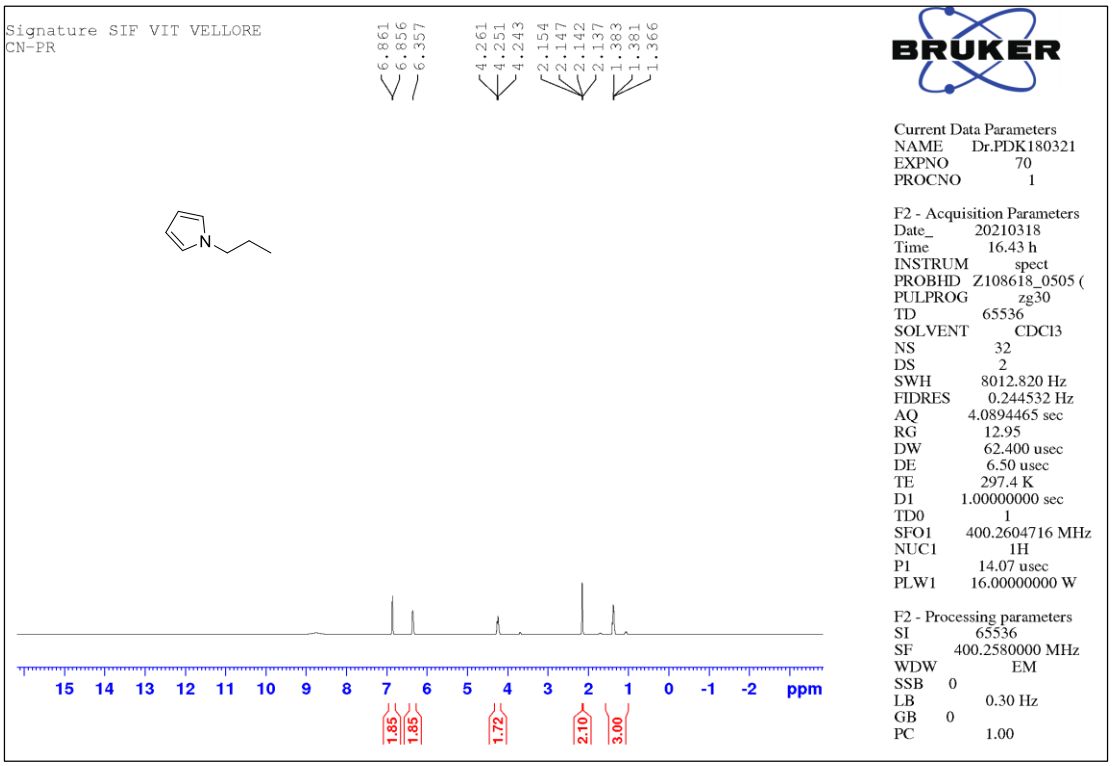


Fig. S46 ^{1}HNMR spectrum of 1-Propyl l-1H-pyrrole **(D17)**

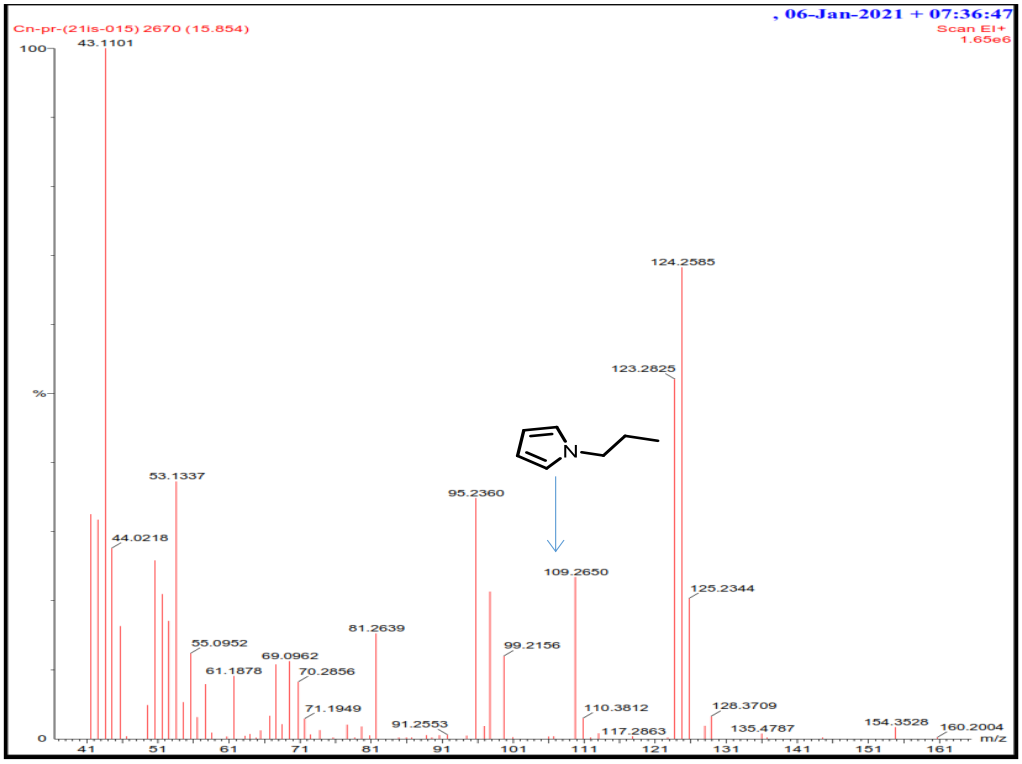


Fig. S47 GCMS spectrum of 1-Propyl l-1H-pyrrole **(D17)**

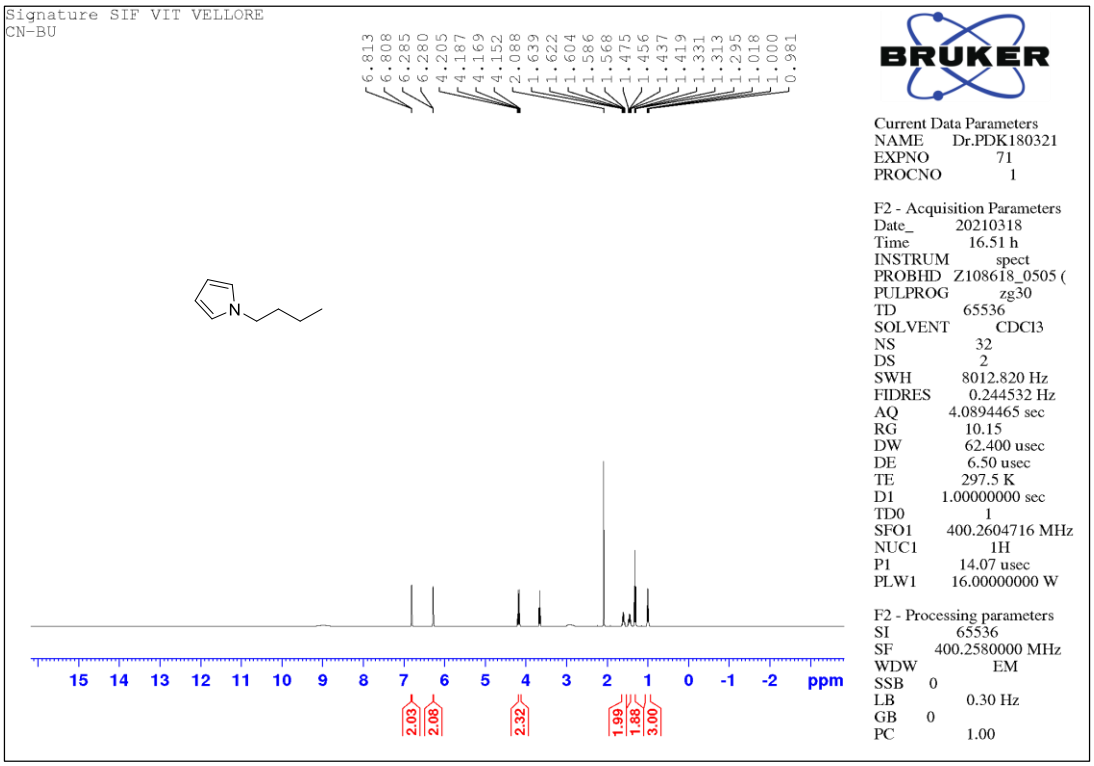


Fig. S48 ^{1}H NMR spectrum of 1-Butyl l-1H-pyrrole **(D18)**

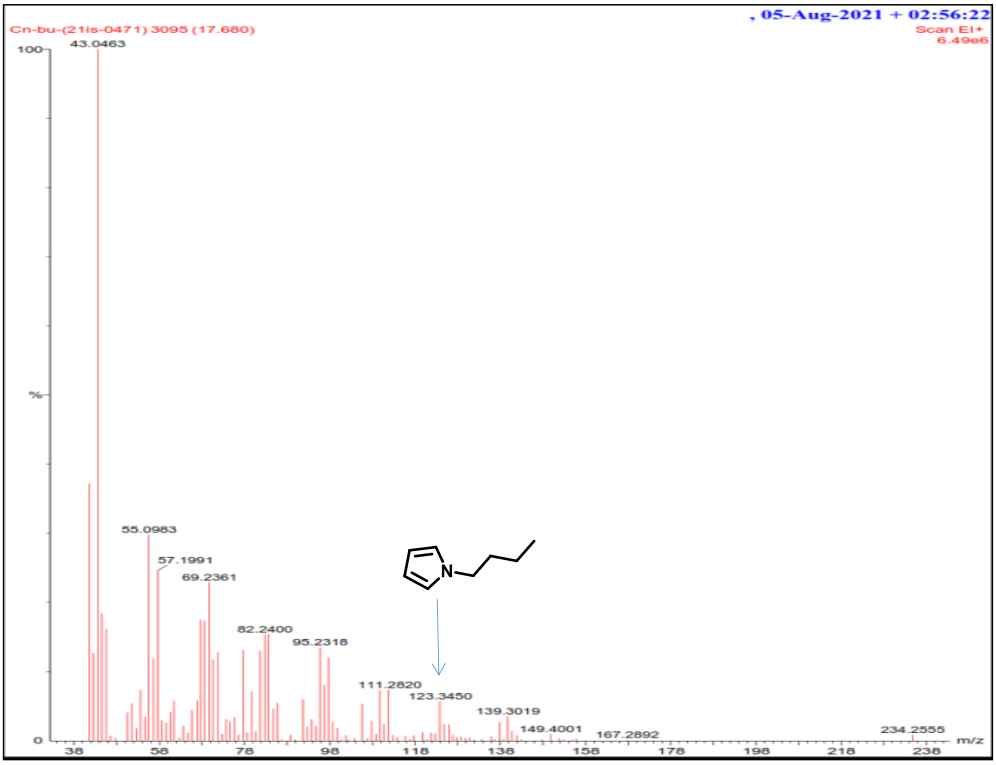


Fig. S49 GCMS spectrum of 1-Butyl l-1H-pyrrole **(D18)**

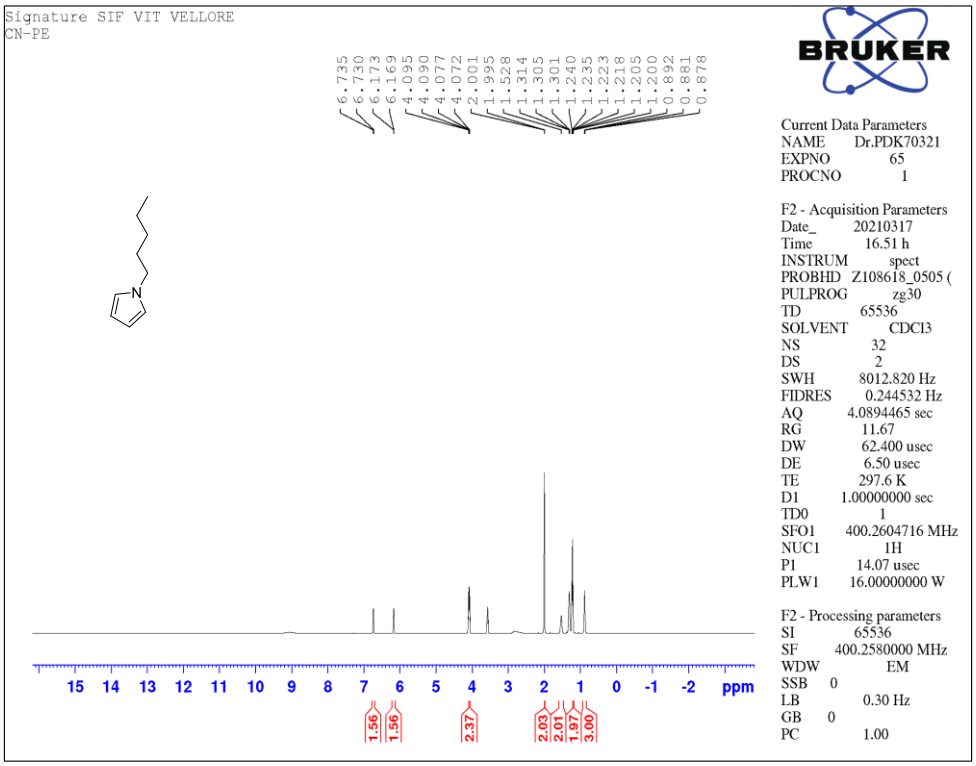


Fig.S50 ^{1}H NMR spectrum of 1-pentyl-1H-pyrrole **(D19)**

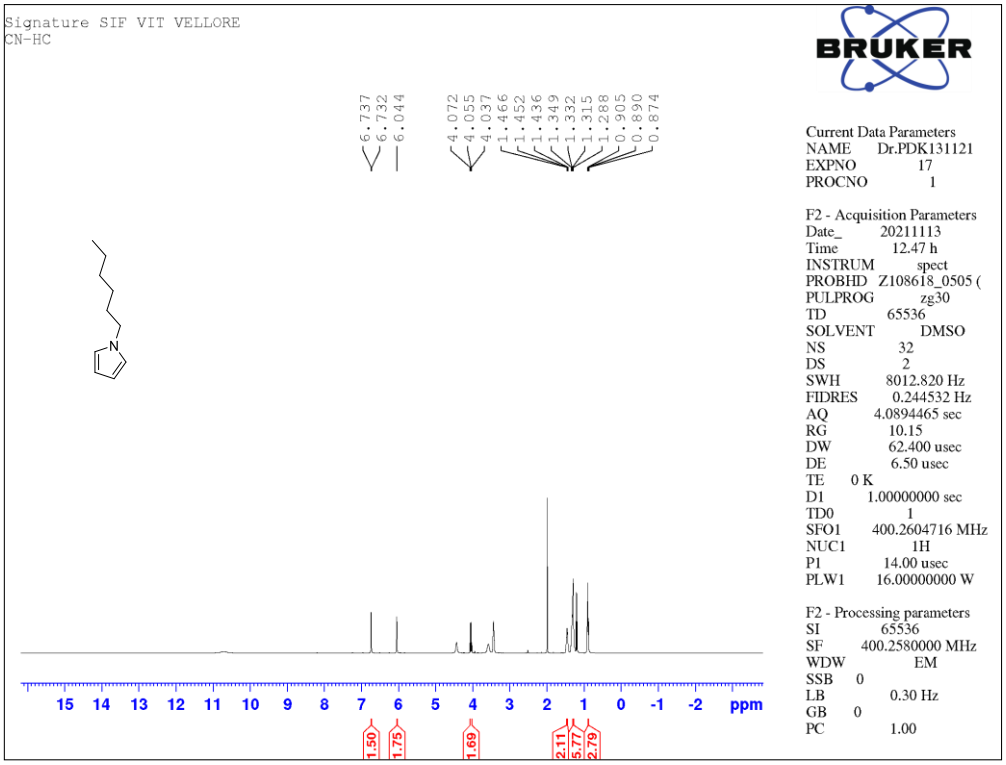


Fig.S51 ^{1}H NMR spectrum of 1-hexyl-1H-pyrrole **(D20)**

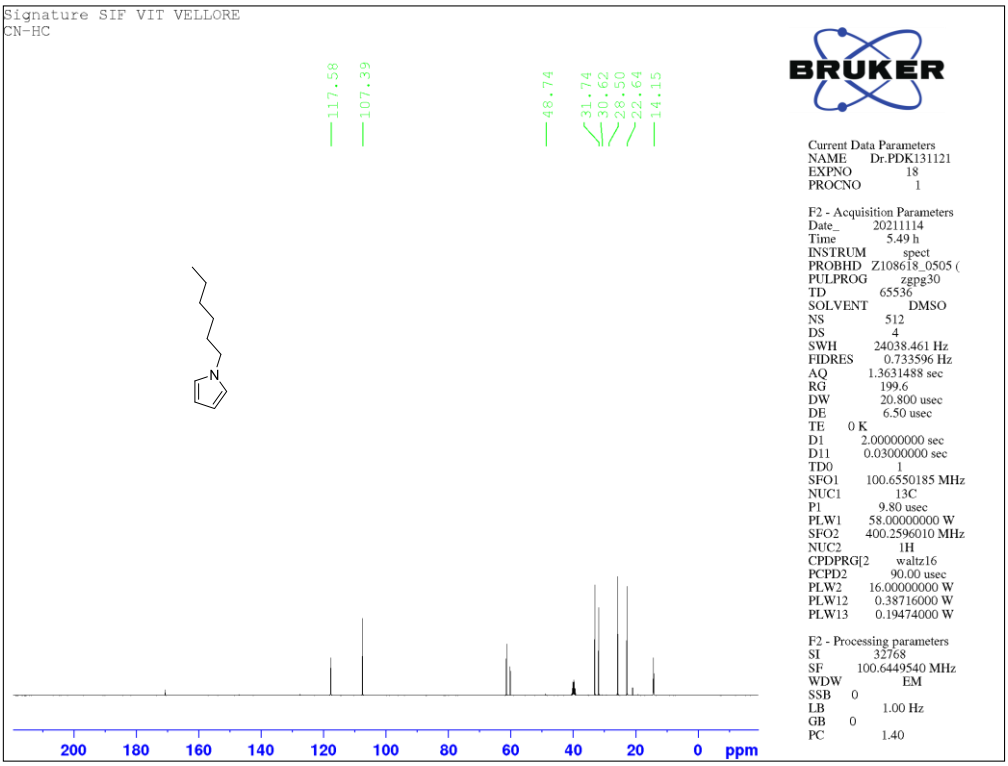


Fig.S52 ^{13} CNMR spectrum of 1-hexyl-1H-pyrrole **(D20)**

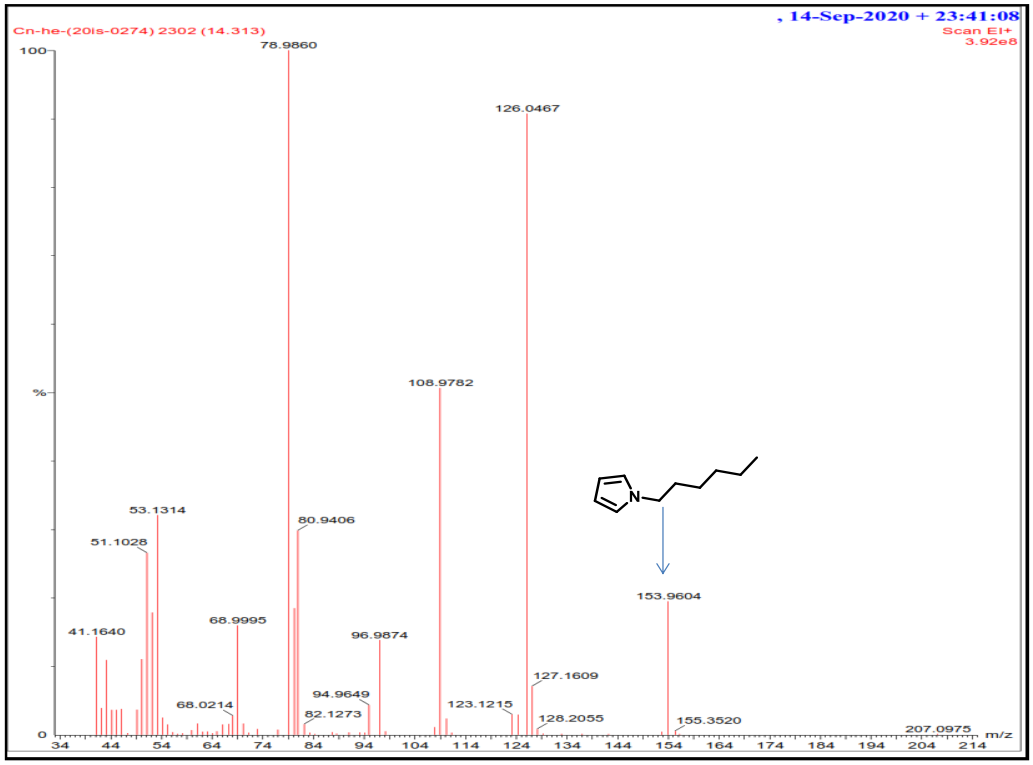


Fig.S53 [13] GCMS spectrum of 1-hexyl-1H-pyrrole **(D20)**

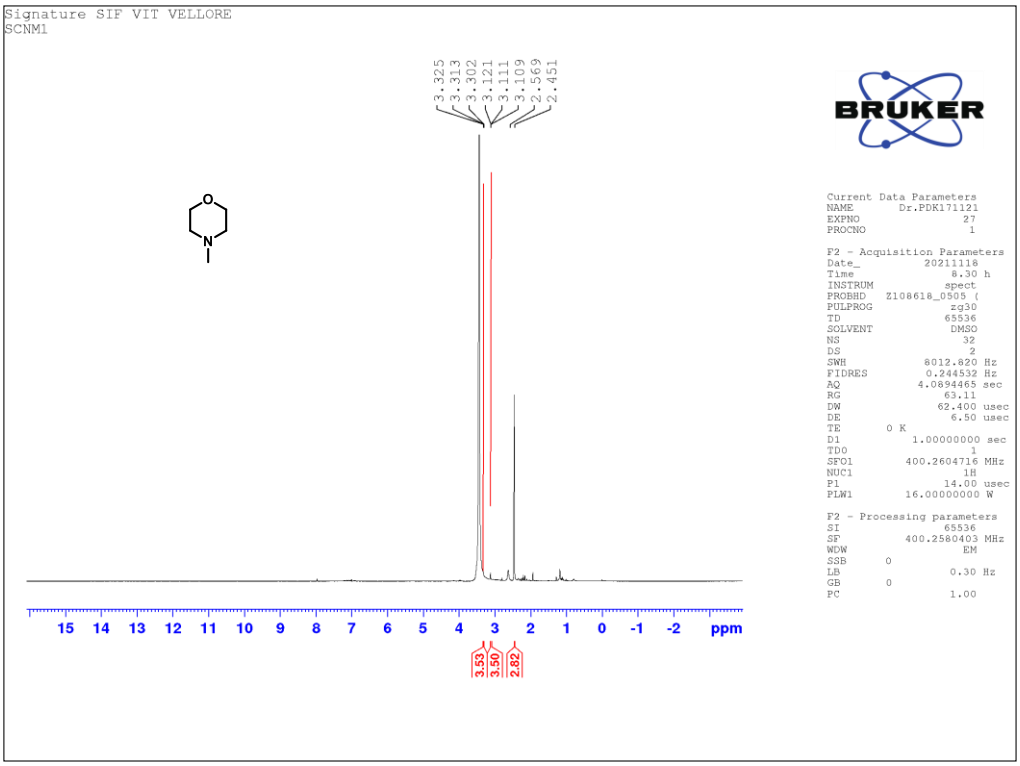


Fig.S54 [1]H NMR spectrum of 4-methylmorpholine **(D21)**

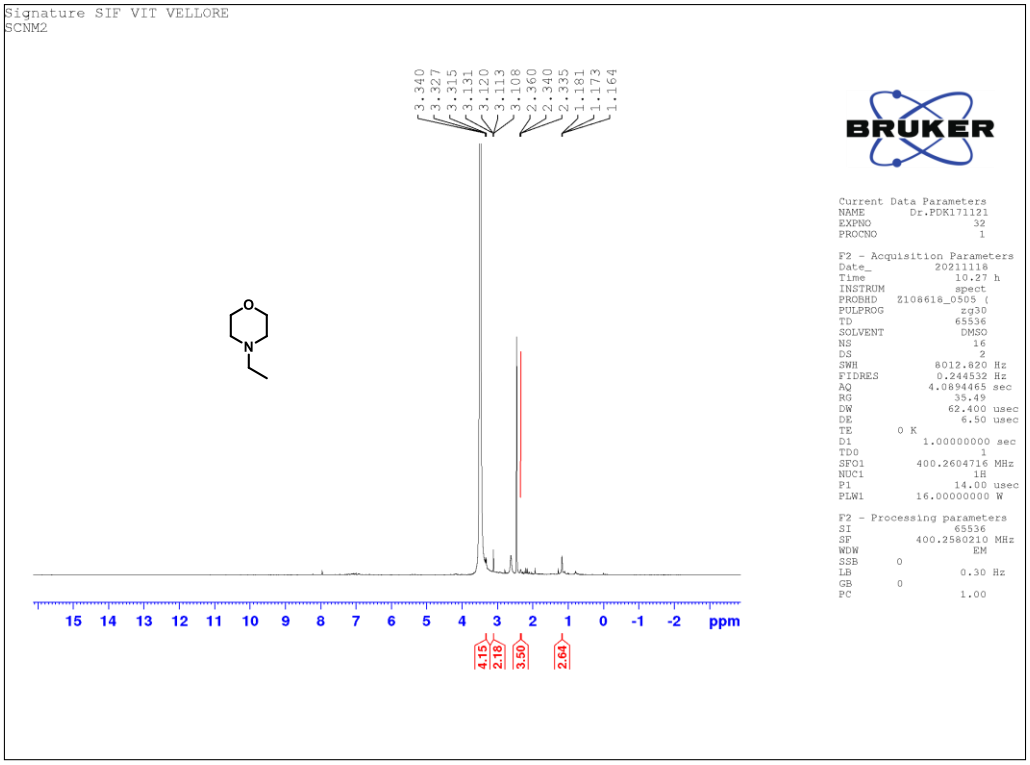


Fig.S55 [1]H NMR spectrum of 4-Ethyl morpholine **(D22)**

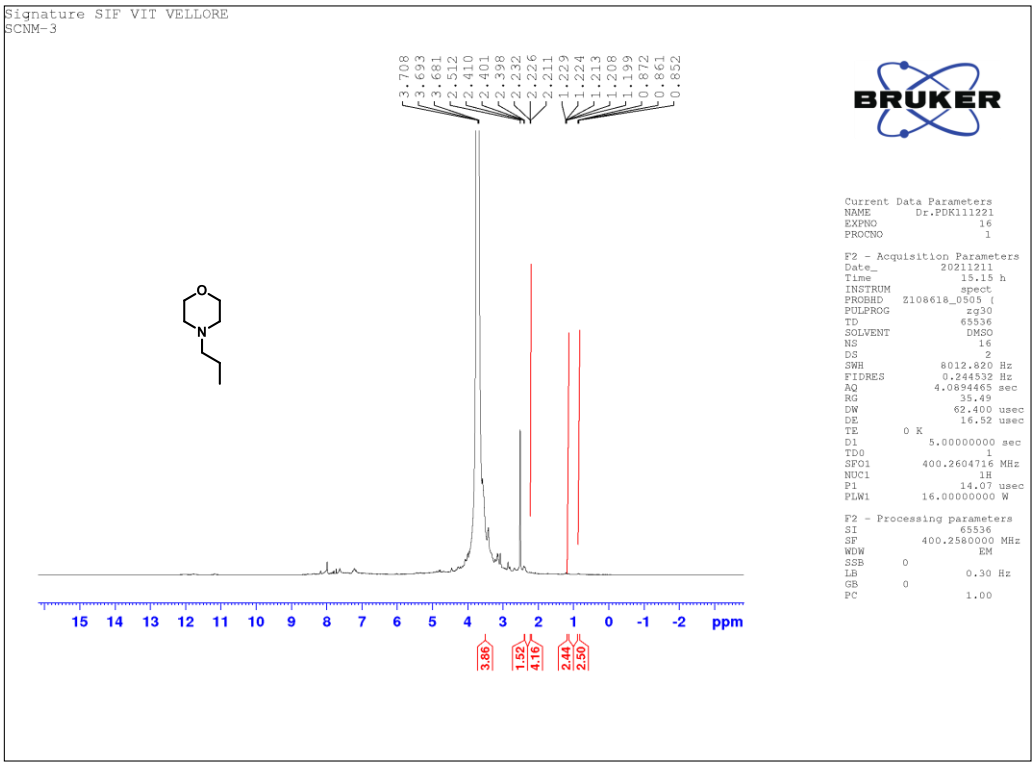


Fig.S56 [1]H NMR spectrum of 4-Propyl morpholine **(D23)**

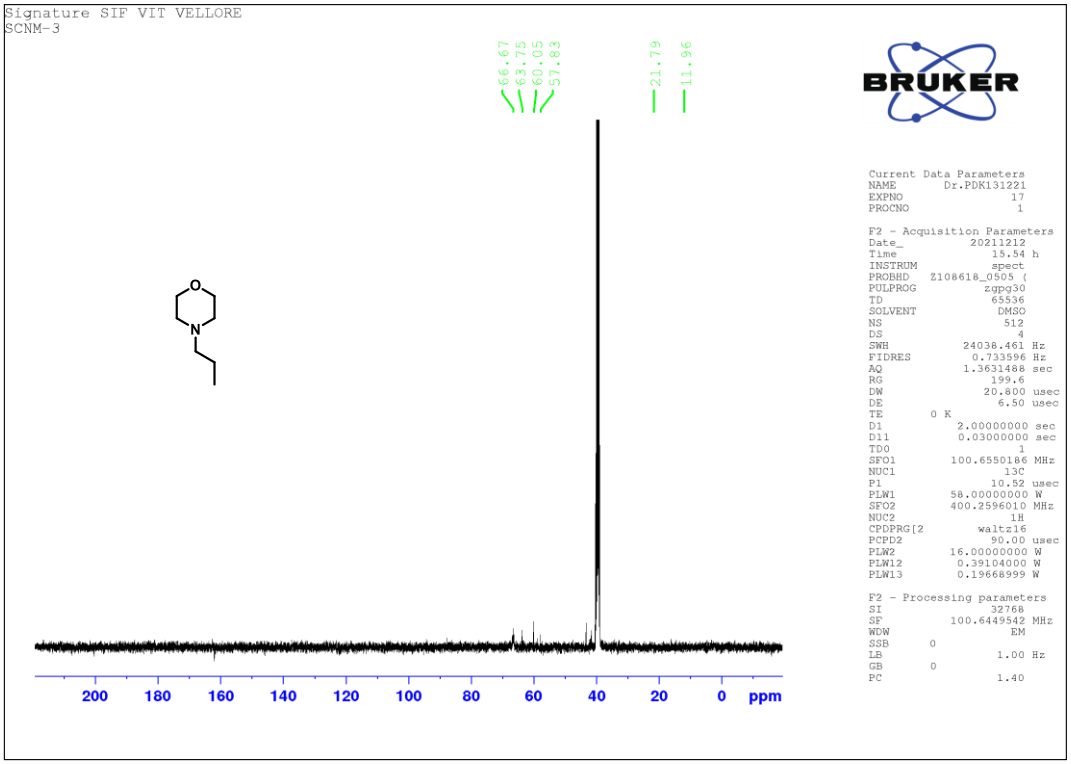


Fig.S57 ^{13} CNMR spectrum of 4-propylmorpholine **(D23)**

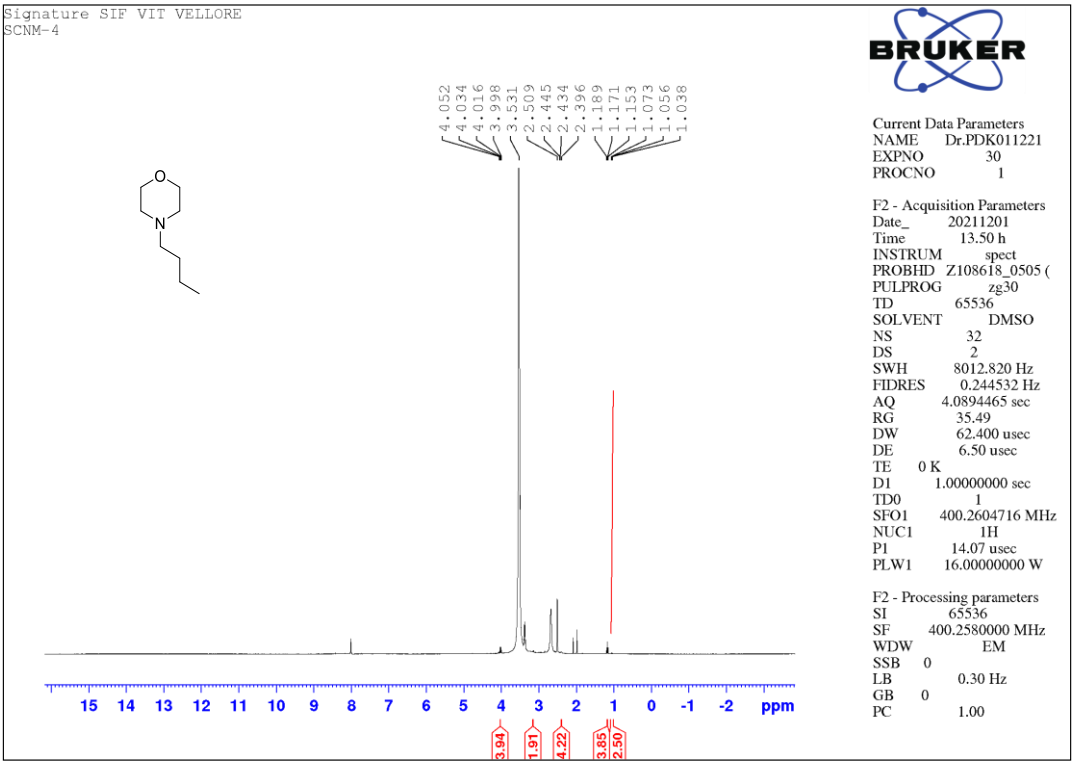


Fig. S58 ^{1}H NMR spectrum of 4-butylmorpholine **(D24)**

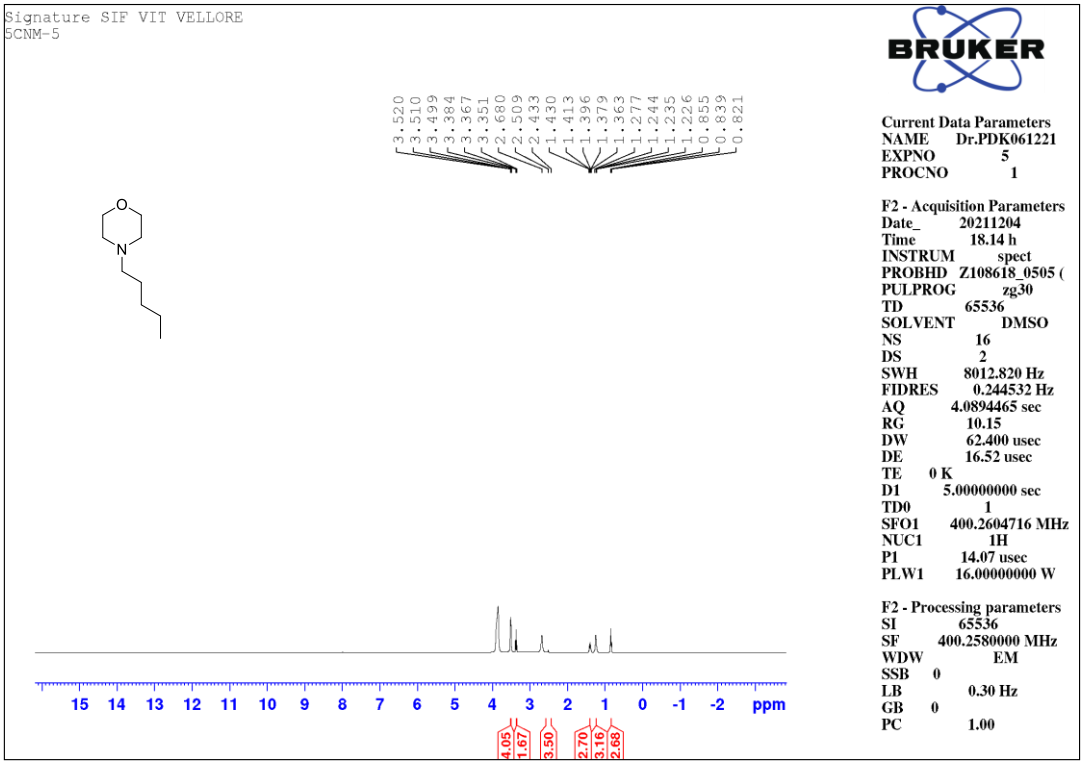


Fig. S59 ^{1}H NMR spectrum of 4-pentylmorpholine **(D25)**

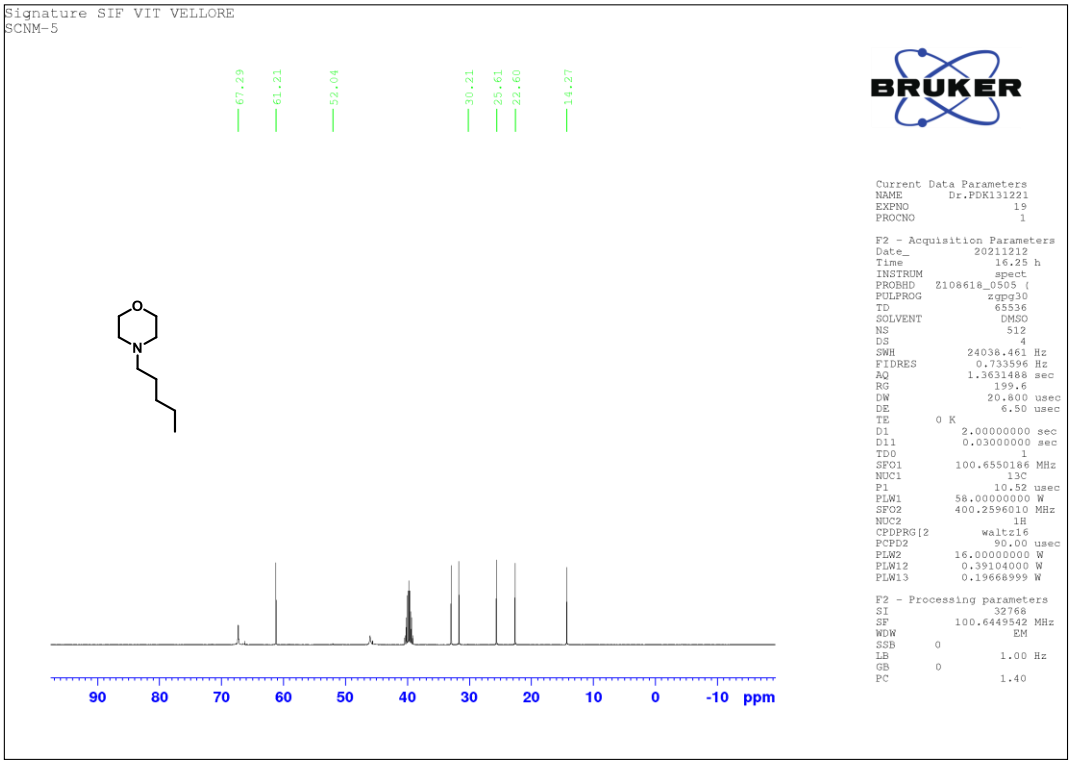


Fig. S60 ^{13}C NMR spectrum of 4-pentylmorpholine **(D25)**

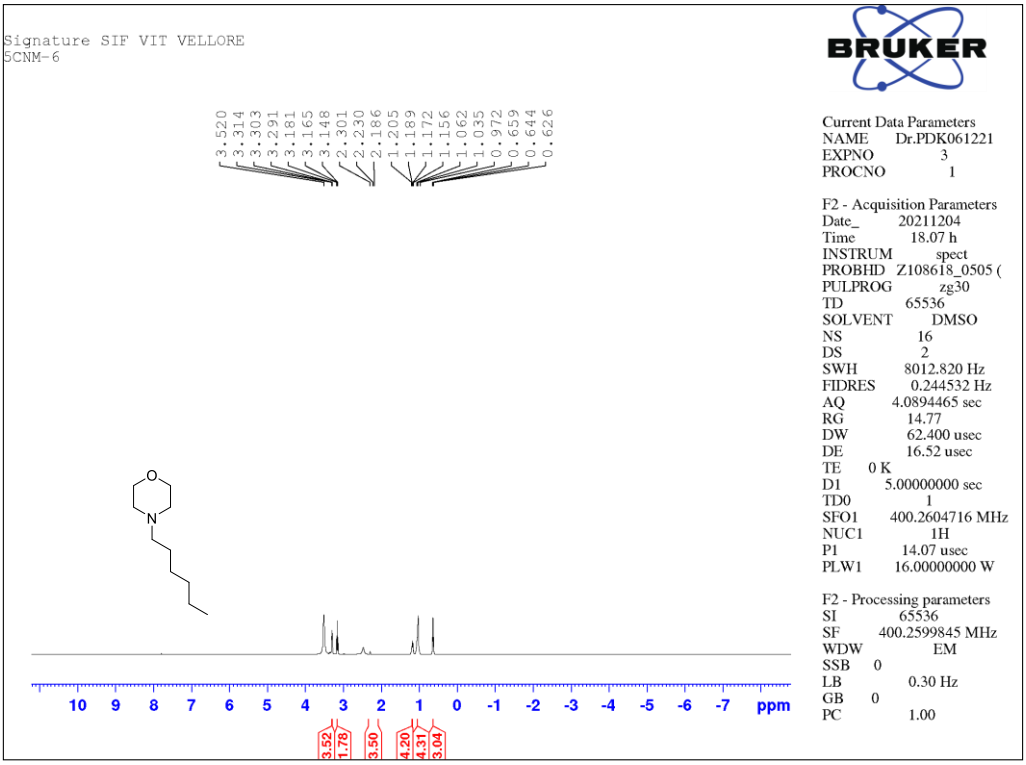


Fig. S61 ^{1}H NMR spectrum of 4-hexylmorpholine **(D26)**

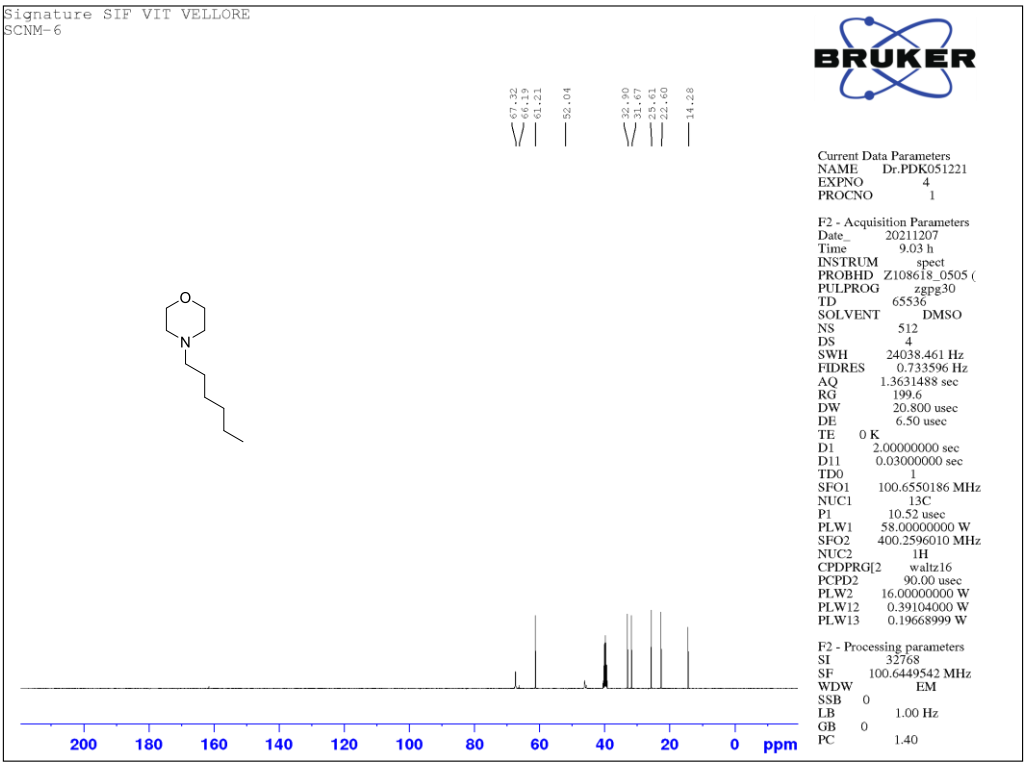


Fig. S62 ^{13}C NMR spectrum of 4-hexylmorpholine **(D26)**

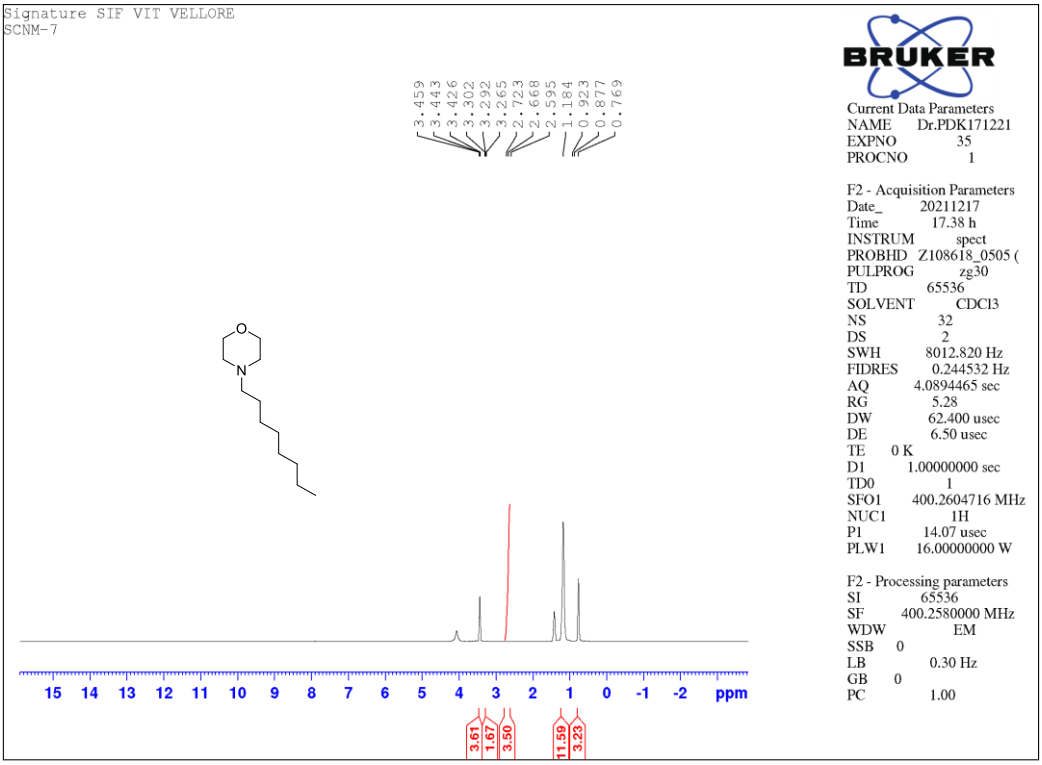


Fig. S63 ^{1}H NMR spectrum of 4-octylmorpholine **(D27)**

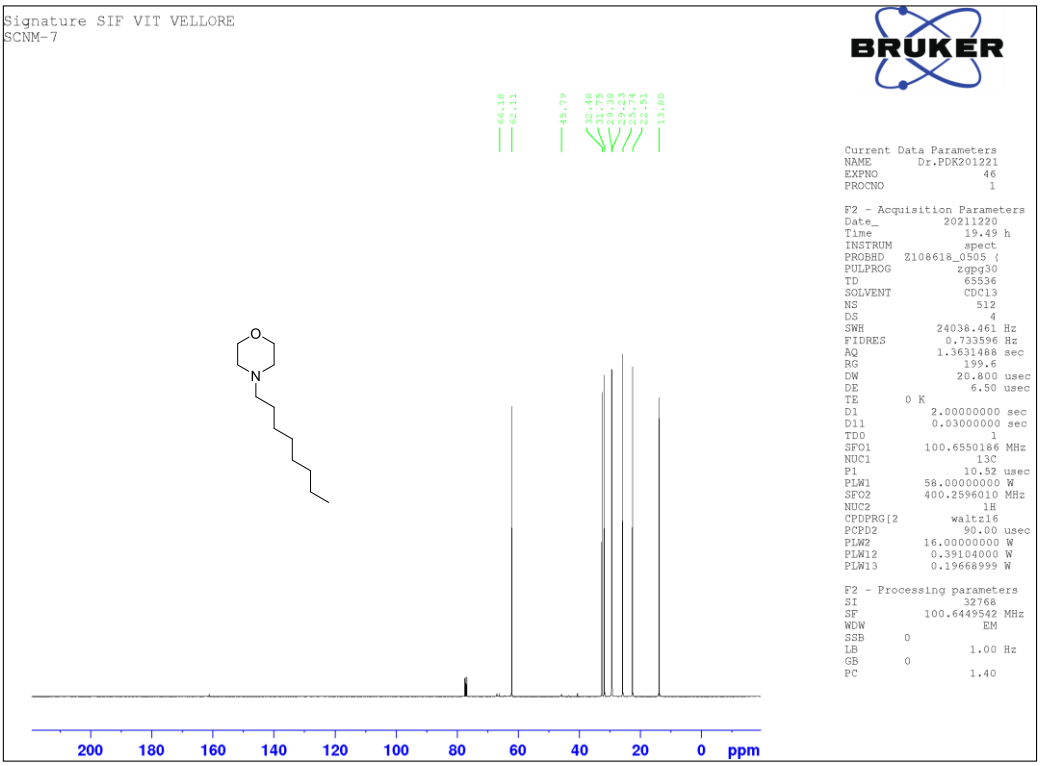


Fig. S64 ^{13}C NMR spectrum of 4-octylmorpholine **(D27)**

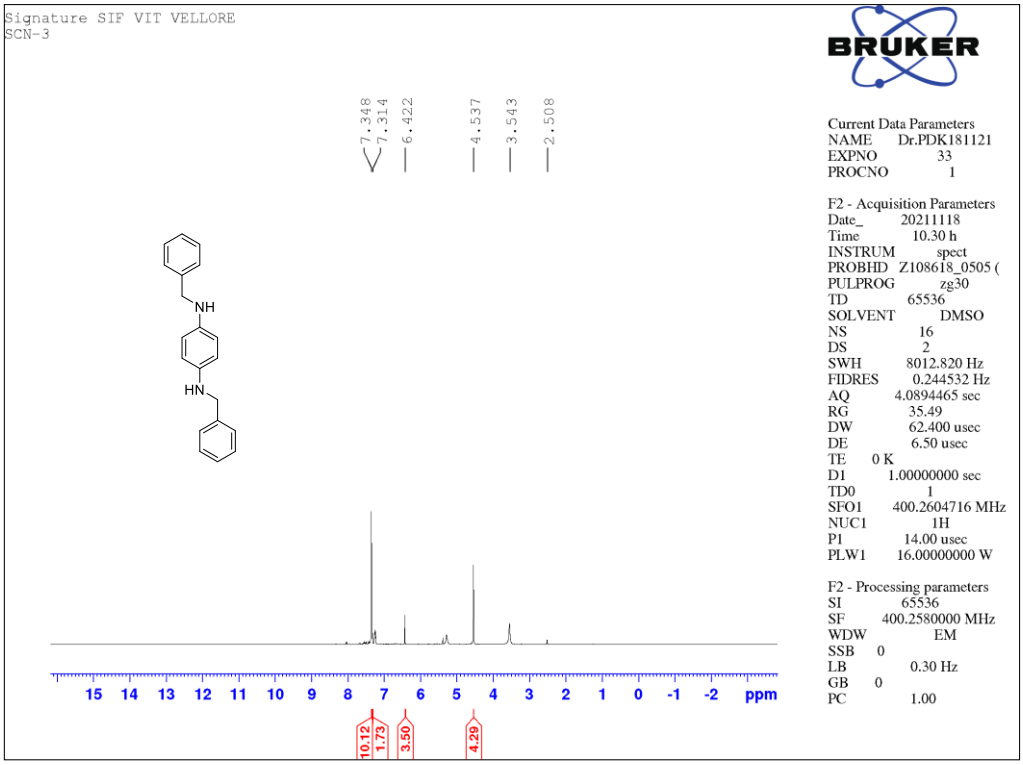


Fig. S65 ^{1}H NMR spectrum of N^1, N^4-dibenzylbenzene-1,4-diamine **(D28)**

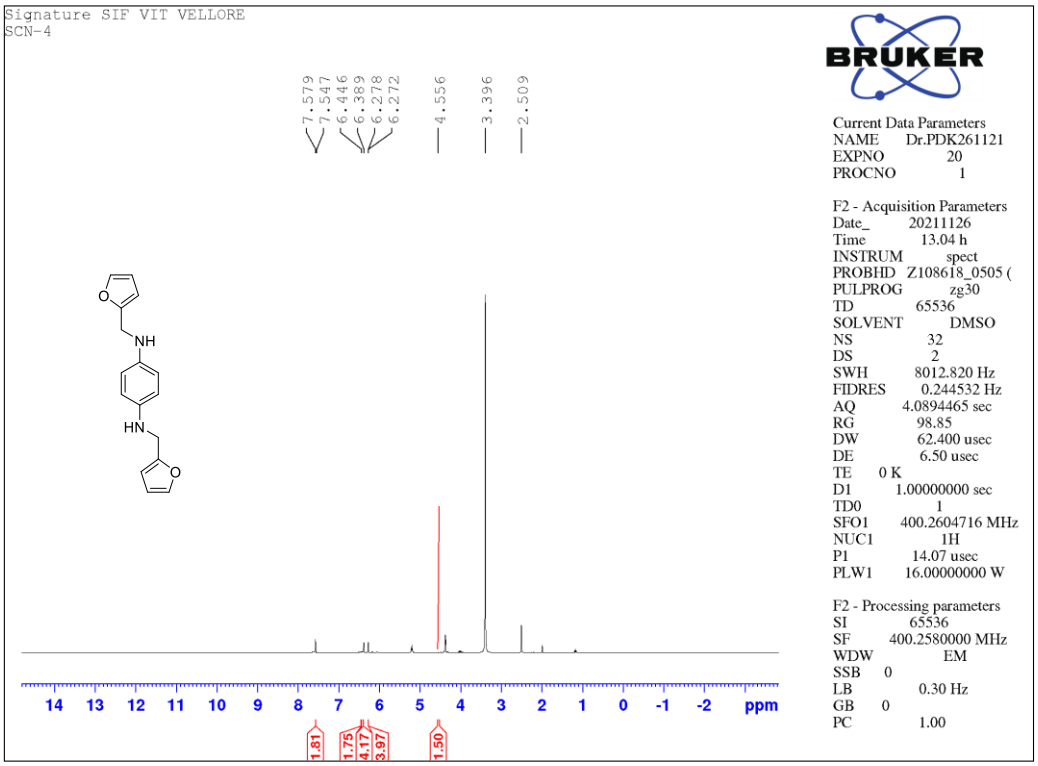


Fig. S66 ^{1}H NMR spectrum of N^1,N^4-bis(furan-2-ylmethyl)benzene-1,4-diamine**(D29)**

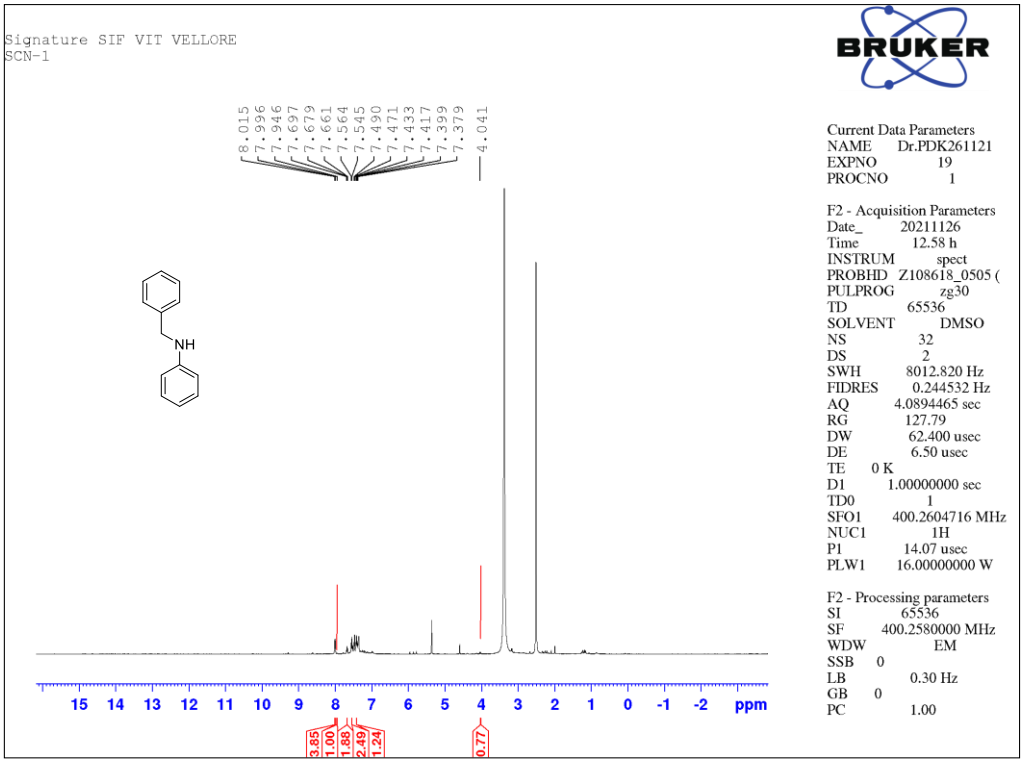


Fig. S67 ^{1}H NMR spectrum of N-benzylaniline **(D30)**

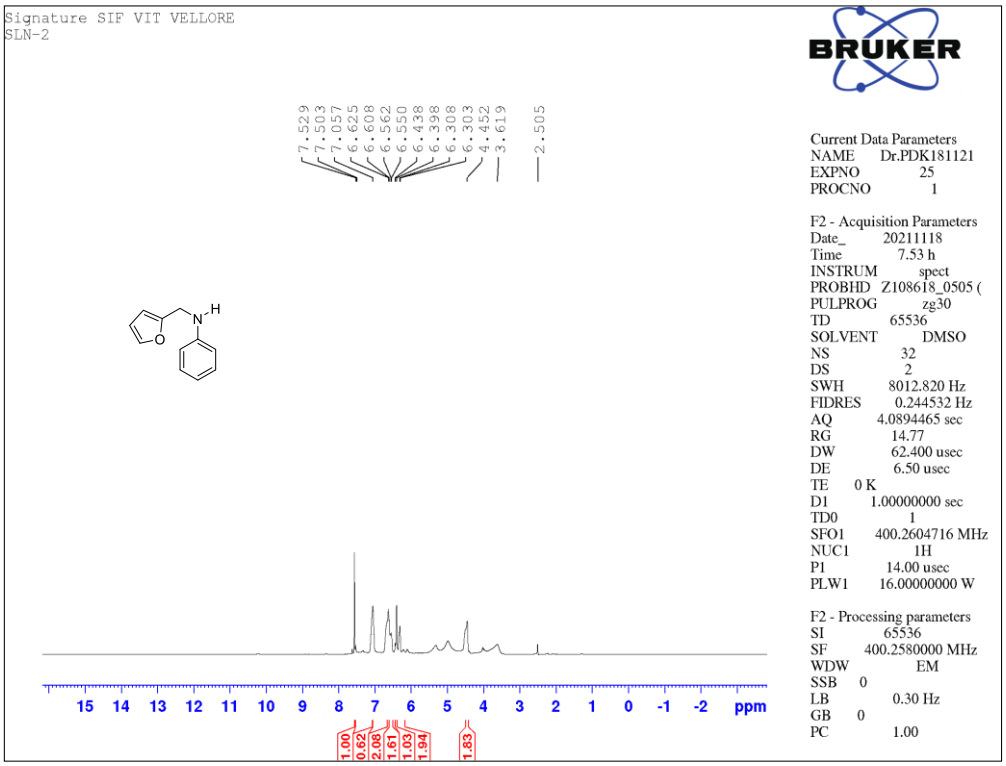


Fig. S68 ^{1}H NMR spectrum of N-(furan-2-ylmethyl) aniline **(D31)**

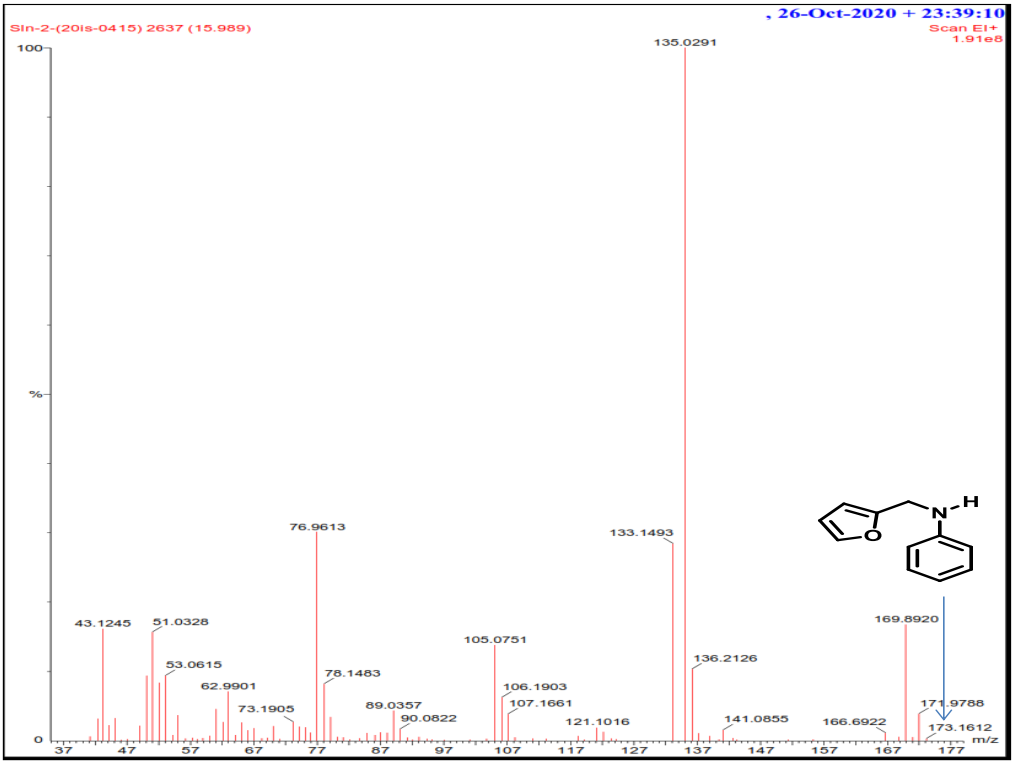


Fig. S69 [1]GCMS spectrum of N-(furan-2-ylmethyl) aniline **(D31)**

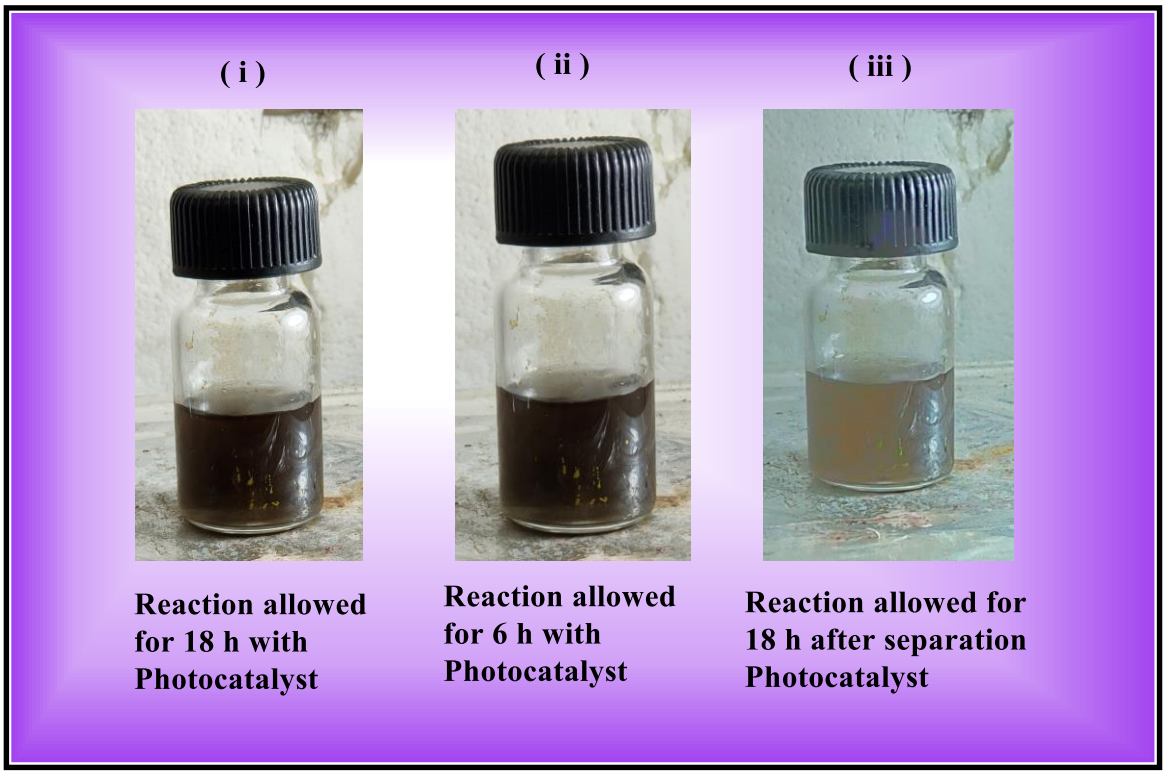


Fig. S70 Leaching test of photocatalyst under optimized conditions

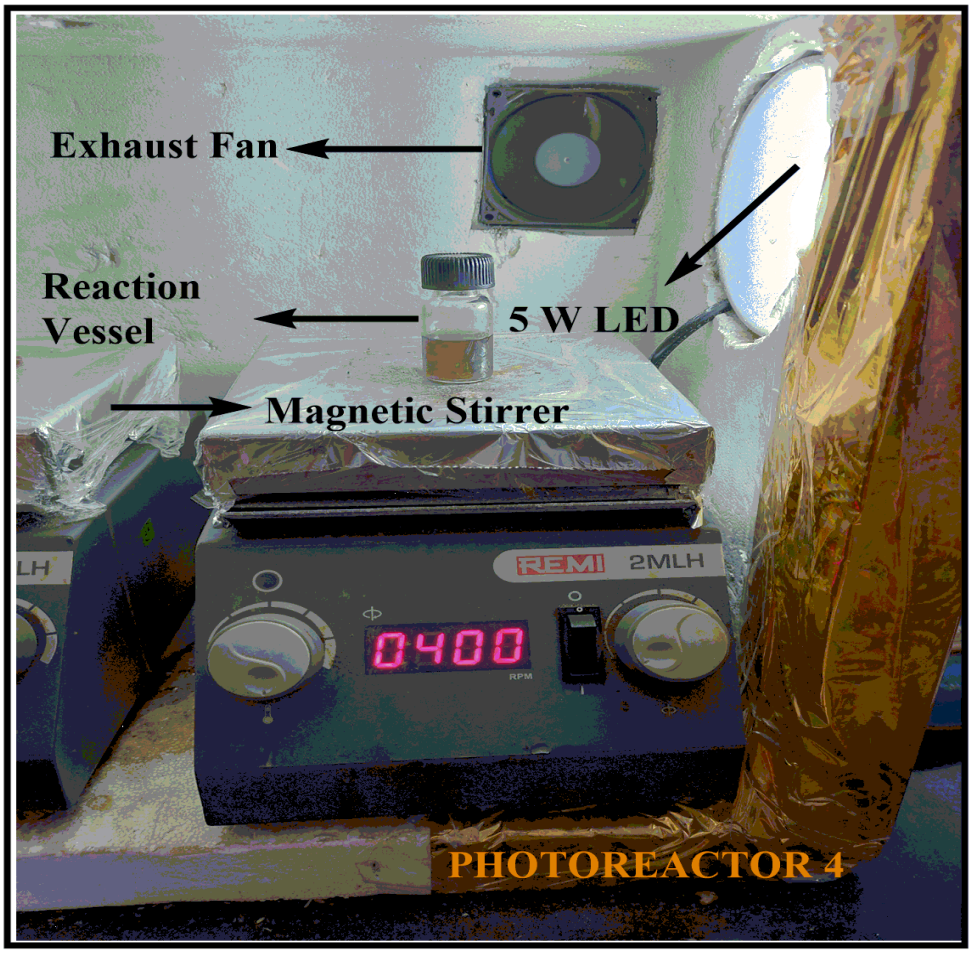


Fig. S71 Home-made Photocatalytic Reactor

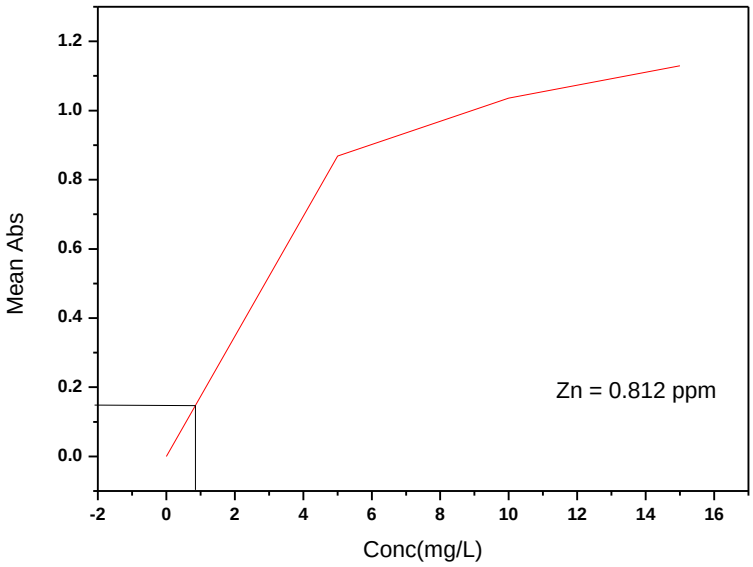


Fig. S72. Atomic absorption spectroscopy of Zn

Table S1. Comparison of binding energies of different metals in XPS

Sr.no	Porphyrin based catalyst	Range of binding energies in XPS	References
1.	Zn-TESP	Zn $2p_{3/2}$ B.E range 1020-1025 eV	Killian, M. S., Gnichwitz, J. F., Hirsch, A., Schmuki, P., & Kunze, J. (2010). ToF-SIMS and XPS studies of the adsorption characteristics of a Zn-porphyrin on TiO_2. *Langmuir*, *26*(5), 3531-3538.
2.	Platinum complex/Zn-porphyrin	Pt $4f_{7/2}$ B.E range 70-73 eV	Polzonetti, G., Ferri, A., Russo, M. V., Iucci, G., Licoccia, S., & Paolesse, R. (1999). Platinum complex/Zn-porphyrin macrosystem assemblies: Electronic structure and conformational investigation by x-ray photoelectron spectroscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, *17*(3), 832-839.
3.	Porphyrin-based porous polyimide polymer/Pd nanoparticle	Pd $3d_{5/2}$ B.E range 335-345 eV	Zhu, W., Wang, X., Li, T., Shen, R., Hao, S. J., Li, Y., ... & Gu, Z. G. (2018). Porphyrin-based porous polyimide polymer/Pd nanoparticle composites as efficient catalysts for Suzuki–Miyaura coupling reactions. Polymer Chemistry, 9(12), 1430-1438.
4.	Fe (III) Porphyrin surface anchored TiO_2	Fe $2p_{3/2}$ B.E 710 eV	ArunaKumari, M. L., & Devi, L. G. (2015). New insights into the origin of the visible light photocatalytic activity of Fe (III) porphyrin surface anchored TiO_2. Environmental Science: Water Research & Technology, 1(2), 177-187.
5.	MFBBCFPc	No evidence of metal B.E with respect to Zn/ Pt/ Pd/ Fe observed in MFBBCFPc photocatalyst	Present work (Fig.6 (a) XPS survey of MFBBCFPc, (b) High resolution of O1s of MFBBCFPc, (c) High resolution of N1s of MFBBCFPc, (d) High resolution of C1s of MFBBCFPc, (e) High resolution of Br3d of MFBBCFPc)

Table S2. Elemental ID and Quantification obtained from XPS data

Name	***Peak BE***	***FWHM eV***	***Area (P) CPS.eV***	***Atomic %***	***Q***
C1s	285.53	1.75	895404.71	67.88	1
O1s	532.95	3.27	318090.56	9.98	1
N1s	400.95	3.49	171619.32	8.39	1
Br3d	68.83	2.97	43531.69	1.06	1
Si2p ???	102.96	4.01	11327.96	0.86	1
S2p ???	169.59	2.00	10906.55	0.41	1
Br3d	67.91	2.02	5675.21	0.14	1
C1s	284.87	1.73	116234.76	8.81	1
N1s	400.44	2.99	22530.84	1.10	1
O1s	532.49	2.72	43977.98	1.38	1

Table S3. Atomic absorption spectroscopy of Zn

Sample ID	Conc mg/L	Mean Abs
Std 1	5	0.8688
Std 2	10	1.0359
Std 3	15	1.294
SR-158	X	0.1461

X = 0.812 mg/L

Table S4. ICP-OES of CN-35 and MFBBCFPC

SOPHISTICATED ANALYTICAL INSTRUMENT FACILITY IIT MADRAS, CHENNAI-36 PERKIN ELMER OPTIMA 5300 DV ICP-OES		
Sample code	**Element symbol and Wavelength (nm)**	**Concn.in ppm µg/ml (or) mg/litre**
CN-35	Fe 238.204	0.070 mg/L
	Pd 340.458	BDL
	Ru 240.272	0.002 mg/L
	Zn 206.200	0.020 mg/L
MFBBCFPC	Fe 238.204	0.912 mg/L
	Pd 340.458	BDL
	Ru 240.272	0.013 mg/L
	Zn 206.200	0.678 mg/L