"Enhanced Visible-Light-Active Photocatalysts: Incorporating Bismuth Tungstate into Graphitic Carbon Nitride for Efficient Condensation Reaction"

Murugesan Shobika, Selvaraj Mohana Roopan*

Chemistry of Heterocycles & Natural Product Research Laboratory, Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632014, Tamil Nadu, India.

* Correspondence: mohanaroopan.s@vit.ac.in; Tel.: +0416-220-2313

Supporting Information

Table of Contents

Text S1. General Information (Materials):

Sodium tungstate dihydrate was procured from Thermo Fisher Scientific, while melamine was sourced from SDFCL. Furthermore, a range of additional chemicals, including bismuth nitrate hexahydrate, 1,3-cyclohexanedione, TEOF, and various amine, were acquired from Avra Synthesis Pvt. Ltd, India. These reagents were of analytical grade and were utilized in their original state without the need for further purification.

Text S2. Characterization Details

The as-prepared materials, including g-C_3N_4, Bi_2WO_6, and Bi_2WO_6/g-C_3N_4 composites with varying weight % ratios, were subjected to comprehensive characterization using a variety of physicochemical techniques. X-ray Photoelectron Spectroscopy (XPS) analyses were conducted at the Central Instrument Facility (CIF), Pondicherry University, Pondicherry, India, utilizing a Thermo Scientific instrument equipped with Al- Kα micro-focused monochromator with variable spot size covering an energy range of 100-4000 eV. The XPS setup was equipped with a dual beam source for charge compensation. Additionally, the analyser utilized was a 180° double focusing hemispherical analyser with a 128-channel detector. This technique allowed for the determination of elemental composition and chemical states within the materials. Structural elucidation of the as-prepared materials was carried out using a Bruker D8 Advance X-ray powder diffractometer, employing CuKα radiation (λ=1.54058) and a movable detector. The scanning range of 5°–90° as a function of the angle 2θ enabled the analysis of the crystalline phases present. Transmission Electron Microscope (TEM) analysis was performed on a Model FEI –TECNAI G2-20 TWIN, operating at 200 kV, to investigate the morphology and nanostructure of the synthesized materials at the microscopic level. Fourier Transform Infrared (FTIR) spectroscopy was conducted on a Shimadzu spectrophotometer using KBr pellets, covering the spectral range of 4000-400 cm^{-1}, to identify functional groups and chemical bonds present in the materials. UV-Vis diffuse reflection spectra were acquired using a Jasco V-670 spectrometer (Range: 190-3200 nm), providing insights into the optical properties and bandgap energies of the materials. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-700 spectrometer system, enabling the investigation of light emission properties, which are indicative of electronic transitions within the materials. The formation of organic compounds was confirmed through ^{1}H and ^{13}C NMR (Bruker 400MHz) spectroscopy, providing insights into molecular structure and composition. High-resolution mass

spectrometry (HR-MS) (XEVO-G2-XS-QTOF) (Waters, USA) determined precise molecular weights and molecular formulas, while gas chromatography-mass spectrometry (GC-MS) (Perkin Elmer Clarus 680 & 600) offered complementary data on compound purity and identity. This combined approach ensured accurate and reliable confirmation of compound formation.

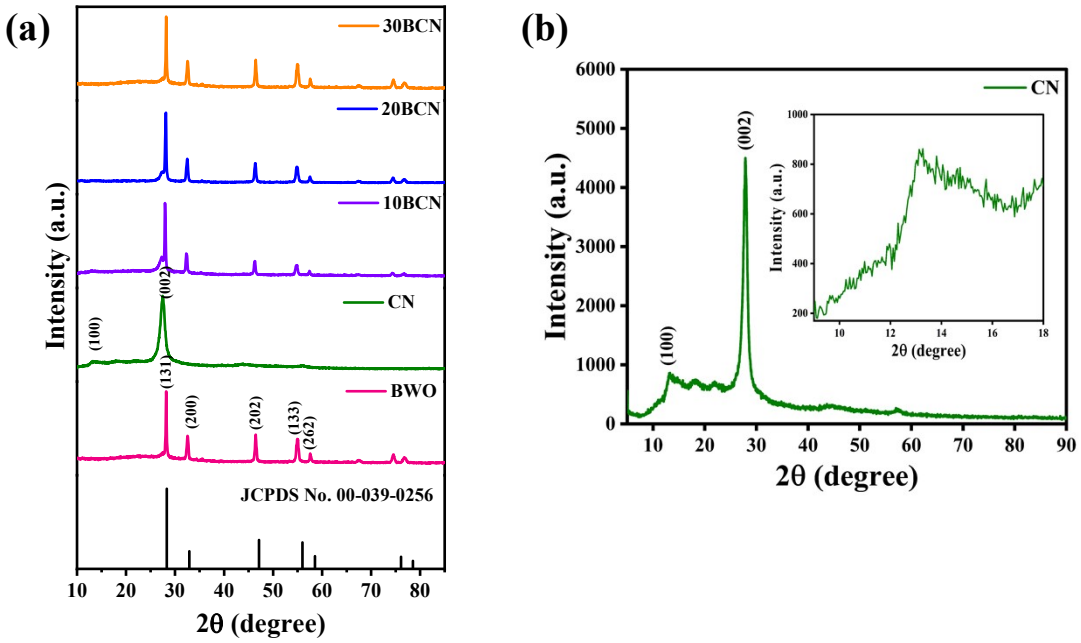


Fig. S1 (a) The XRD pattern of BWO, CN, 10BCN, 20BCN, and 30BCN; (b) The XRD pattern of CN and its enlarged image.

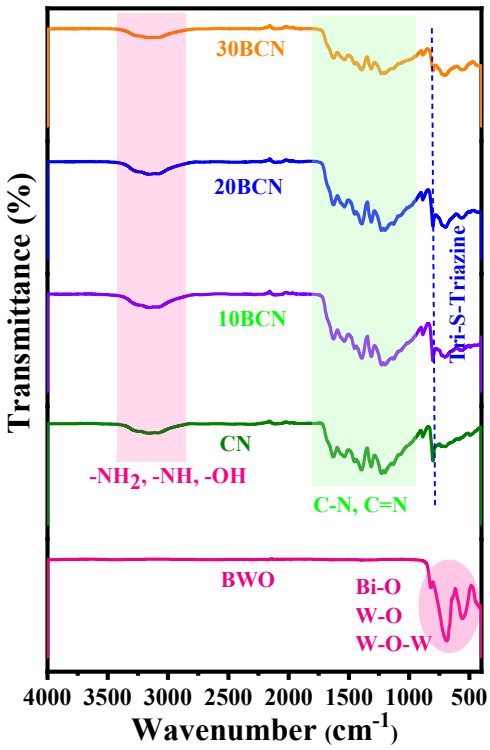


Fig. S2 FT−IR spectrum of BWO, CN, 10BCN, 20BCN, and 30BCN**.**

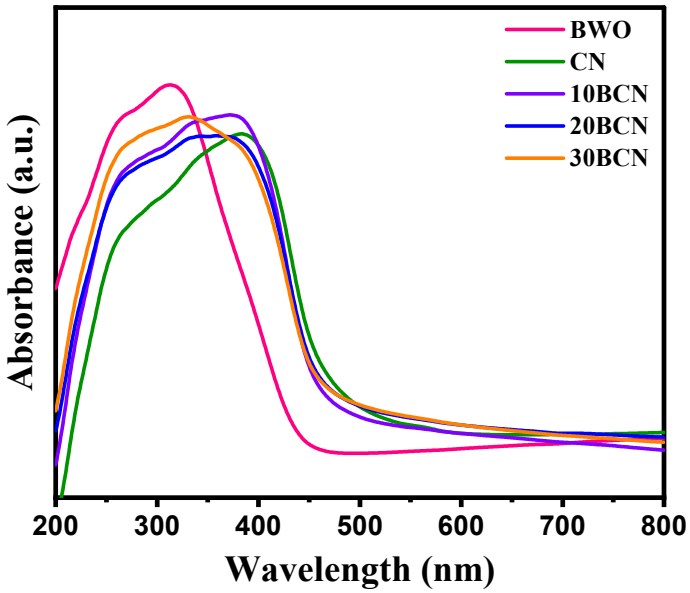


Fig. S3 UV-vis DRS spectra BWO, CN, 10BCN, 20BCN, and 30BCN.

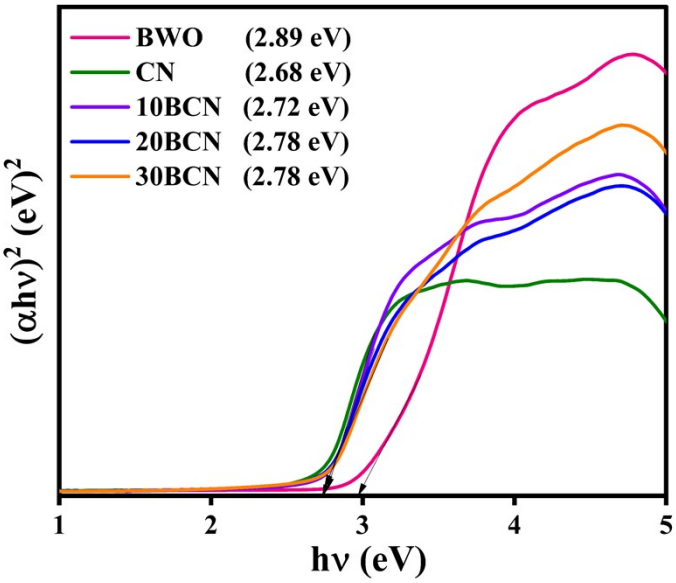


Fig. S4 Band gap spectra BWO, CN, 10BCN, 20BCN, and 30BCN.

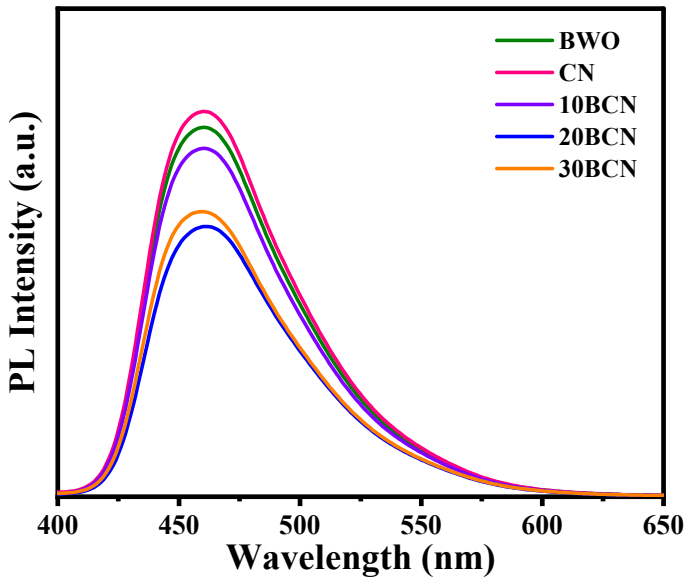


Fig. S5 PL Spectra of BWO, CN, 10BCN, 20BCN, and 30BC

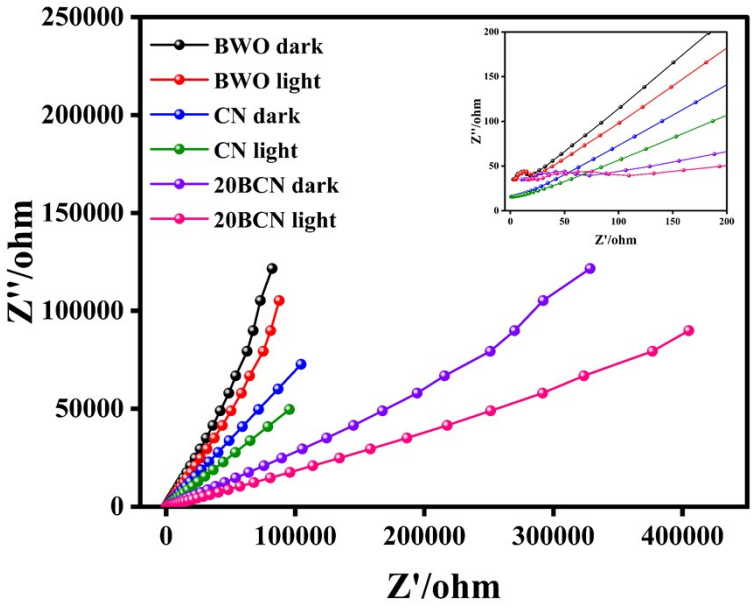


Fig. S6 EIS spectra BWO, CN and 20BCN with both light and dark condition

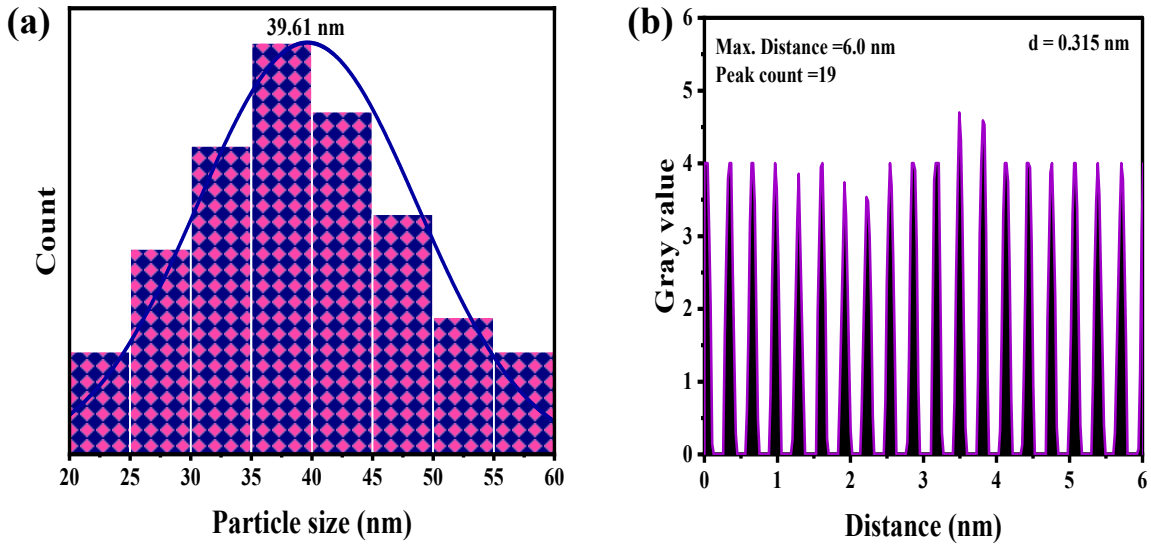


Fig. S7 (a) Histogram of particle sizes and (b) d-spacing calculation.

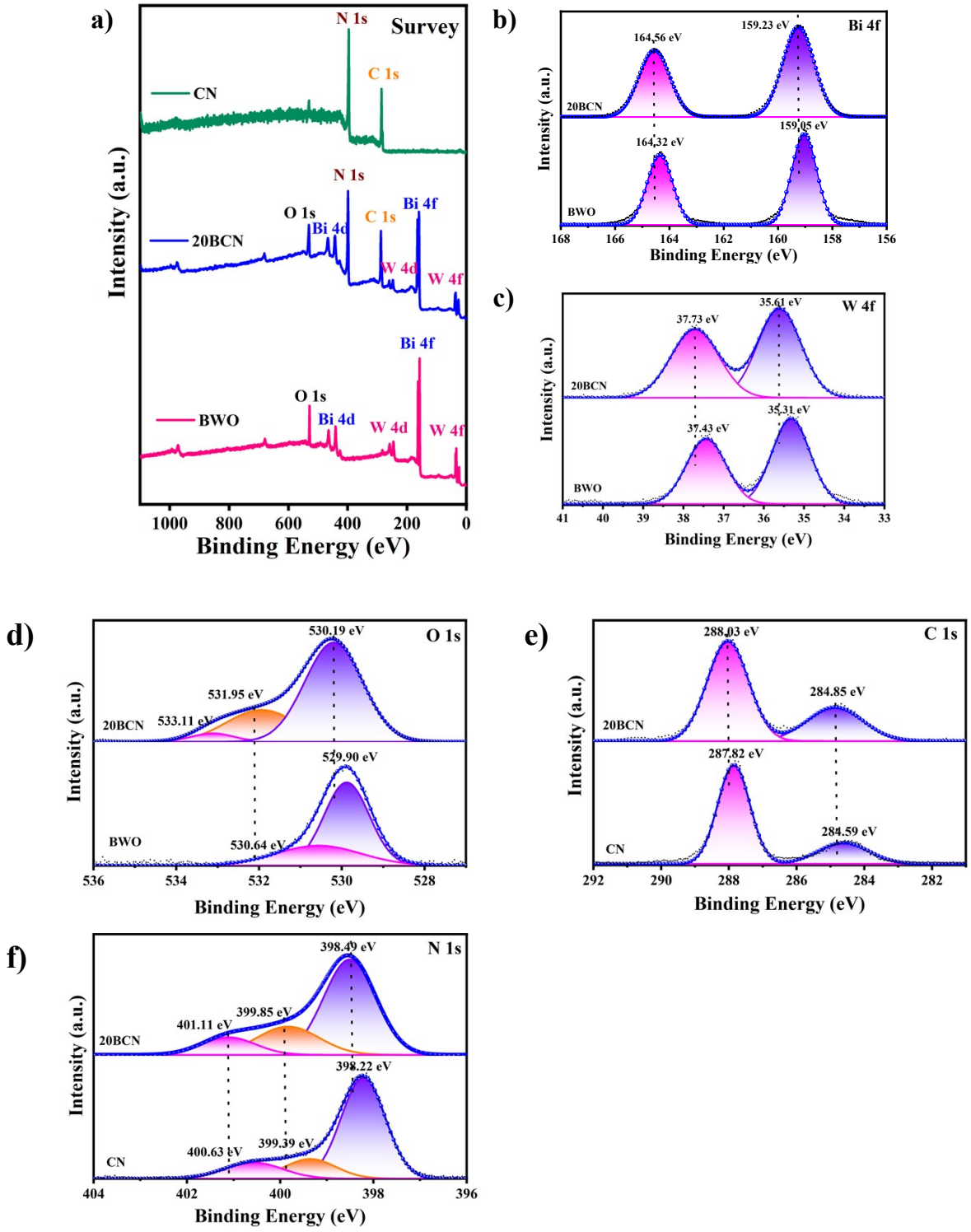


Fig. S8 XPS spectra of BWO, CN and 20BCN a) survey spectra and deconvoluted spectra of b) Bi 4f, c) W 4f, d) O 1s, e) C 1s and f) N 1s.

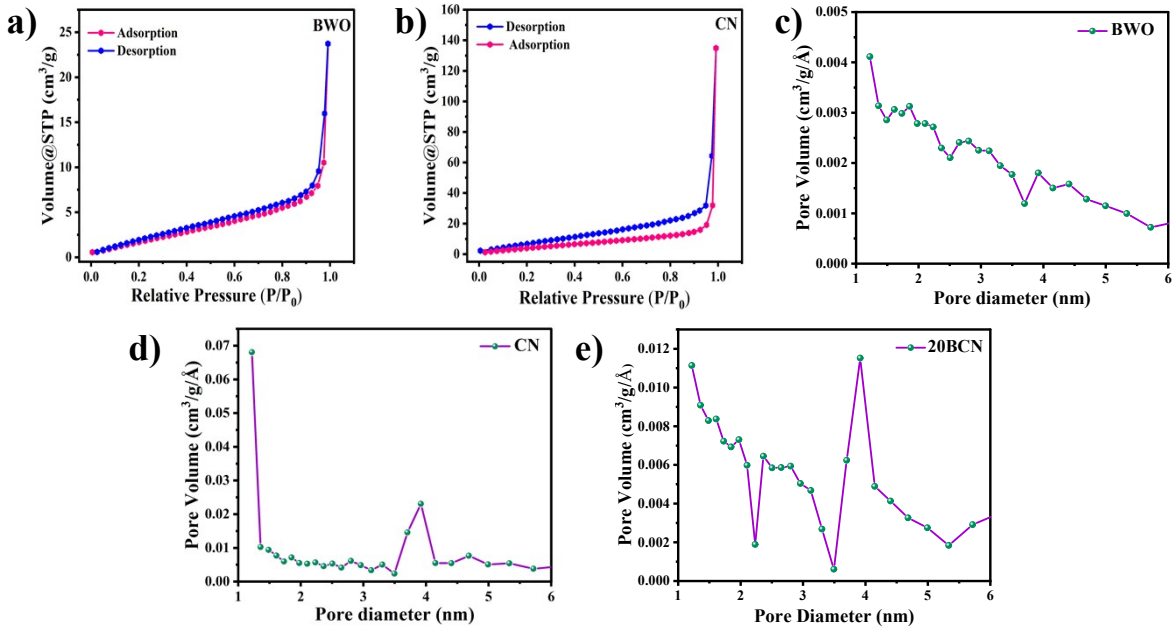


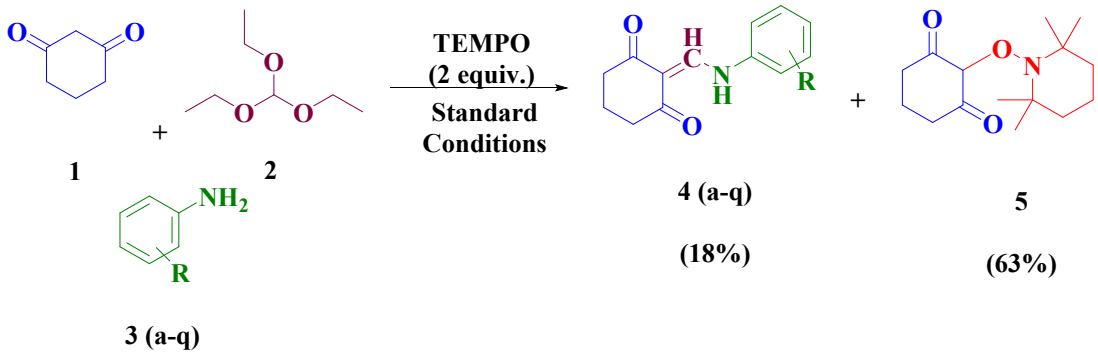
Fig. S9 N_2 adsorption-desorption isotherms of (a) BWO and (b) CN; Pore volume of (c) BWO, (d) CN and (e) 20BCN.

Table S1

Sample Code	Surface area (m^2/g)	Pore Volume (cm^3/g)	Average pore diameter (nm)
BWO	18.711	0.041	1.220
CN	99.481	0.187	1.218
20BCN	58.883	0.152	3.917

Radical Scavenging Study

Free radical trapping study by TEMPO



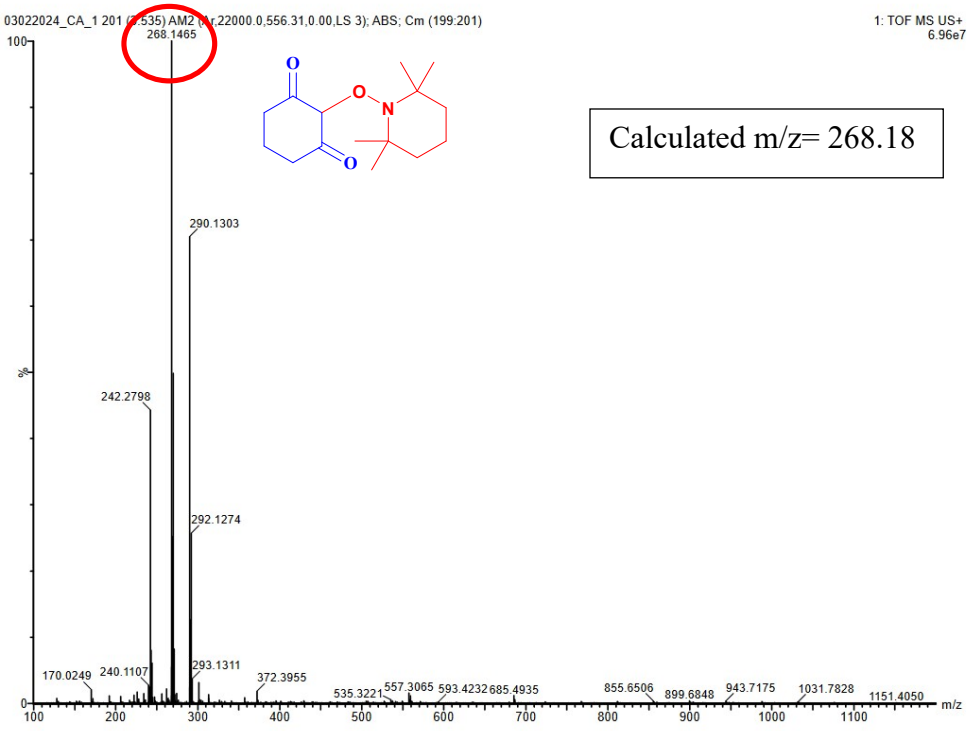
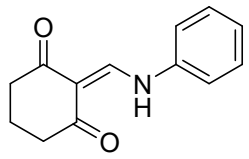
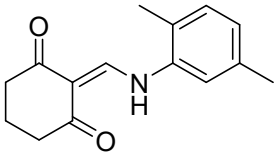


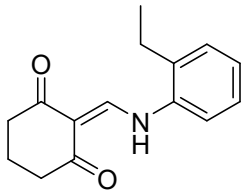
Fig. S10 HR-MS data of compound 5.

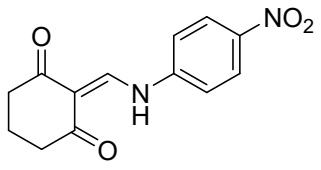
Spectral and analytical characterization of the 2-((arylamino)methylene)cyclohexane-1,3-dione derivatives (4a-q).

1	**2-((phenylamino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{13}NO_2$ 215.0946 Yellow solid/ crystal 116-118	
FT-IR, ν/cm^{-1}	3474-3249 (NH); 3057(CH aromatic); 2944 (CH_2); 1661,1659 (2C=O); 1596 (C=C); 1455 (C-C stretch in aromatic ring).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.87-1.94 (qu, *J*= 6.4 Hz, 2H), 2.41-2.44 (t, *J*= 6.4 Hz, 2H), 2.50-2.52 (t, *J*= 6.4 Hz, 2H), 7.24-7.27 (t, *J*= 6.8 Hz, 1H), 7.41-7.50 (m, 4H), 8.49-8.52 (d, *J*= 13.6 Hz, 1H), 12.67-12.71 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.6, 37.7, 38.0, 110.1, 119.0, 126.6, 130.3, 139.0, 150.8, 195.9, 200.0.	
GC-MS	Calculated 215.0946	Found 215.252

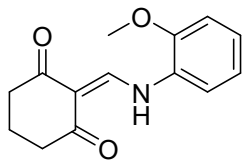
2	**2-(((2,5-dimethylphenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{15}H_{17}NO_2$ 243.1259 Brown solid 134-135	
FT-IR, ν/cm^{-1}	3591-3508 (NH); 3248 (CH aromatic); 2948 (CH_2), 1661,1659 (2C=O); 1592 (C=C); 1469 (C-C stretch in aromatic ring).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.88-1.95 (qu, *J*= 6.4 Hz, 2H), 2.27 (s, 3H), 2.31 (s, 3H) 2.41-2.45 (t, *J*= 6.4 Hz, 2H), 2.50-2.51 (t, *J*= 6.4 Hz, 2H), 6.98-7.00 (d, *J*= 7.6 Hz, 1H), 7.17-7.19 (d, *J*= 8 Hz, 1H), 7.43 (s, 1H) 8.55-8.58 (d, *J*= 13.2 Hz, 1H), 13.02-13.05 (d, *J*= 13.2 Hz, 1H).	

^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	16.9, 19.7, 21.0, 37.6, 37.8, 110.3, 117.2, 124.9, 127.2, 131.4, 137.1, 137.6, 150.8, 195.8, 200.5.	
HR-MS ((ESI +ve) *m/z* $[M+H]^+$)	Calculated 243.1259	Found 244.1345

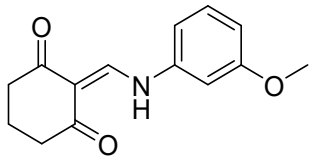
3	**2-(((2-ethylphenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{15}H_{17}NO_2$ 243.1259 Brownish yellow solid 69-70	
FT-IR, ν/cm^{-1}	3359-3194 (NH); 3071 (CH aromatic); 2960 (CH_2), 1670,1668 (2C=O); 1575 (C=C); 1473 (C-C stretch in aromatic ring).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.19-1.22 (t, *J*= 7.2 Hz, 3H), 1.89-1.95 (qu, *J*= 6.4 Hz, 2H), 2.41-2.45 (t, *J*= 6.4 Hz, 2H), 2.52-2.55 (t, *J*= 6.4 Hz, 2H), 2.66-2.72 (q, *J*= 7.6 Hz, 2H), 7.22-7.24 (t, *J*= 7.6 Hz, 1H), 7.30-7.34 (t, *J*= 8 Hz, 2H), 7.57-7.59 (d, *J*= 8 Hz, 1H), 8.54-8.57 (d, *J*= 13.2 Hz, 1H), 13.18-13.21 (d, *J*= 13.2 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	14.4, 19.7, 24.2, 37.6, 37.8, 110.4, 117.5, 126.9, 128.1, 130.0, 134.1, 136.8, 151.4, 195.8, 200.7.	
HR-MS ((ESI +ve) *m/z* $[M+H]^+$)	Calculated 243.1259	Found 244.1342

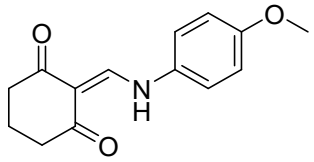
4	**2-(((4-nitrophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{12}N_2O_4$ 260.0797 Yellow solid 176-177	
FT-IR, ν/cm^{-1}	3464-3272 (NH); 3074 (CH aromatic); 2960 (CH_2), 1670,1668 (2C=O); 1579 (C=C); 1501 (C-C stretch in aromatic ring).	

^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.89-1.96 (qu, *J*= 6.8 Hz, 2H), 2.46-2.49 (t, *J*= 6.8 Hz, 2H), 2.53-2.56 (t, *J*= 6.8 Hz, 2H), 7.74-7.76 (d, *J*= 9.2 Hz, 2H), 8.23-8.26 (d, *J*= 9.2 Hz, 2H), 8.51-8.55 (d, *J*= 13.2 Hz, 1H), 12.60-12.63(d, *J*= 13.2 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.3, 37.8, 38.2, 111.6, 119.4, 125.8, 144.7,144.9, 149.9, 196.2, 200.6.	
GC-MS	Calculated 260.0797	Found 260.179

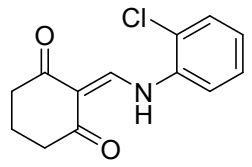
5	**2-(((2-methoxyphenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (^{o}C)**	$C_{14}H_{15}NO_3$ 245.1052 Yellow solid 119-120	
FT-IR, ν/cm^{-1}	3337-3195 (NH); 3067 (CH aromatic); 2942 (CH_3); 2874 (CH_2), 1660,1658 (2C=O); 1602 (C=C); 1491 (C-C stretch in aromatic ring).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.87-1.94 (qu, *J*= 6.8 Hz, 2H), 2.41-2.44 (t, *J*= 6.8 Hz, 2H), 2.49-2.52 (t, *J*= 6.8 Hz, 2H), 3.92 (s, 3H), 7.05-7.07 (t, *J*= 1.2 Hz, 1H), 7.15-7.17 (d, *J*= 1.2 Hz, 1H), 7.21-7.25 (t, *J*= 1.2 Hz, 1H), 7.644-7.646 (d, *J*= 0.8 Hz, 1H) 8.55-8.59 (d, *J*= 13.6 Hz, 1H), 12.96-13.00 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.6, 37.7, 38.0, 55.3, 56.6, 110.4, 112.5, 116.5, 121.8, 127.1, 127.6, 149.4, 149.4, 195.8, 200.1.	
HR-MS ((ESI +ve) *m/z* [M+H]$^{+}$)	Calculated 245.1052	Found 246.1140

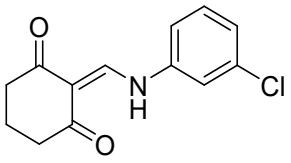
6	**2-(((3-methoxyphenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour**	$C_{14}H_{15}NO_3$ 245.1052 Yellow solid	

Melting point (°C)	68-70	
FT-IR, ν/cm^{-1}	3633-3480 (NH); 3082 (CH aromatic); 2954 (CH_3); 2874 (CH_2), 1662,1660 (2C=O); 1573 (C=C); 1500 (C-C stretch in aromatic ring).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.87-1.94 (qu, *J*= 6.4 Hz, 2H), 2.41-2.44 (t, *J*= 6.4 Hz, 2H), 2.48-2.51 (t, *J*= 6.4 Hz, 2H), 3.80 (s, 3H), 6.82-6.83 (dd, *J*= 8 Hz, 1H), 7.01-7.03 (dd, *J*= 8 Hz, 1H), 7.08-7.09 (t, *J*= 2.4 Hz, 1H), 7.31-7.35 (t, 1H) 8.48-8.52 (d, *J*= 14 Hz, 1H), 12.64-12.67 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.6, 37.7, 38.0, 55.3, 55.9, 104.6, 110.1, 110.9, 112.6, 131.1, 140.3, 150.9, 160.8, 195.9, 200.1.	
GC-MS	Calculated 245.1052	Found 245.227

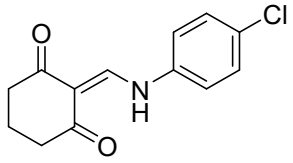
7	**2-(((4-methoxyphenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{14}H_{15}NO_3$ 245.1052 Yellow solid 117-118	
FT-IR, ν/cm^{-1}	3460-3239 (NH); 3079 (CH aromatic); 2945 (CH_3); 2854 (CH_2), 1659,1658 (2C=O); 1588 (C=C); 1519 (C-C stretch in aromatic ring).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.88-1.93 (qu, *J*= 6.4 Hz, 2H), 2.39-2.42 (t, *J*= 6.4 Hz, 2H), 2.46-2.50 (t, *J*= 6.4 Hz 2H), 3.76 (s, 3H), 6.98-7.00 (d, *J*= 8.8 Hz, 2H), 7.42-7.45 (d, *J*= 8.8 Hz, 2H), 8.39-8.42 (d, *J*= 13.6 Hz, 1H), 12.71-12.74 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.7, 37.6, 37.9, 55.3, 109.6, 115.4, 132.2, 150.9, 158.1, 195.7, 199.6.	
GC-MS	Calculated	Found

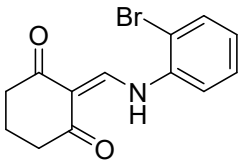
	245.1052	245.2268

8	**2-(((2-chlorophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{12}ClNO_2$ 249.0557 Brown solid 141-142	
FT-IR, ν/cm^{-1}	3420-3299 (NH); 3066 (CH aromatic); 2952 (CH_2), 1665,1664 (2C=O); 1587 (C=C); 1487 (C-C stretch in aromatic ring); 720 (C-Cl).	
^{1}H-NMR (400 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	1.90-1.96 (qu, *J*= 6.8 Hz, 2H), 2.44-2.47 (t, *J*= 6.4 Hz, 2H), 2.53-2.57 (t, *J*= 6 Hz, 2H), 7.27-7.29 (t, *J*= 8 Hz, 1H), 7.42-7.46 (t, *J*= 8 Hz, 1H), 7.59-7.61 (dd, *J*= 8 Hz, 1H), 7.84-7.86 (dd, *J*= 8 Hz, 1H), 8.59-8.62 (d, *J*= 13.2 Hz, 1H), 13.19-13.22 (d, *J*= 13.2 Hz 1H).	
^{13}C-NMR (100 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	19.4, 37.7, 38.0, 111.1, 118.3, 123.5, 127.4, 129.3, 130.4, 135.8, 150.2, 195.9, 201.0.	
GC-MS	Calculated 249.0557	Found 249.191

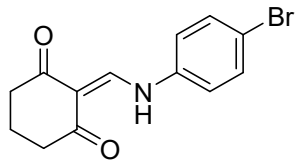
9	**2-(((3-chlorophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{12}ClNO_2$ 249.0557 Brown Crystal 73-74	
FT-IR, ν/cm^{-1}	3487-3316 (N-H); 3167 (C-H aromatic); 2935 (CH_2), 1670,1668 (2C=O); 1568 (C=C); 1417 (C-C stretch in aromatic ring); 723 (C-Cl).	
^{1}H-NMR (400 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	1.87-1.94 (qu, *J*= 6.8 Hz, 2H), 2.42-2.45 (t, *J*= 6.4 Hz, 2H), 2.49-2.52 (t, *J*= 6 Hz, 2H), 7.28-7.30 (d, *J*= 7.2 Hz, 1H), 7.41-7.47 (m, *J*= 8.4 Hz, 2H), 7.69 (s, 1H), 8.46-8.49 (d, *J*= 13.6 Hz,	

	1H), 12.57-12.60 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.5, 37.7, 38.1, 110.6, 117.8, 119.1, 126.1, 131.7, 134.6, 140.7, 150.9, 195.9, 200.1.	
GC-MS	Calculated 249.0557	Found 249.191

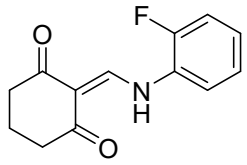
10	**2-(((4-chlorophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{12}ClNO_2$ 249.0557 Brown crystal 156-157	
FT-IR, ν/cm^{-1}	3449-3235 (NH); 3073 (CH aromatic); 2945 (CH_2), 1663,1661 (2C=O); 1570 (C=C); 1496 (C-C stretch in aromatic ring); 740 (C-Cl).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.87-1.94 (qu, *J*= 6.4 Hz, 2H), 2.41-2.44 (t, *J*= 6.8 Hz, 2H), 2.49-2.50 (t, *J*= 6 Hz, 2H), 7.46-7.48 (d, *J*= 8.8 Hz, 2H), 7.53-7.55 (d, *J*= 8.8 Hz, 2H), 8.44-8.47 (d, *J*= 13.6 Hz, 1H), 12.60-12.63 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.5, 37.7, 38.0, 110.4, 120.9, 130.0, 130.5, 138.2, 150.8, 195.9, 200.0.	
GC-MS	Calculated 249.0557	Found 249.1908

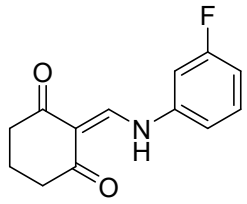
11	**2-(((2-bromophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{12}BrNO_2$ 293.0051 Brown Crystal 166-167	

FT-IR, ν/cm^{-1}	3455-3202 (NH); 3074 (CH aromatic); 2941 (CH_2), 1668,1666 (2C=O); 1588 (C=C); 1403 (C-C stretch in aromatic ring); 669 (C-Br).	
^{1}H-NMR (400 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	1.90- 1.96 (qu, *J*= 6.4 Hz, 2H), 2.44-2.47 (t, *J*= 6.4 Hz, 2H), 2.53-2.55 (t, *J*= 6.4 Hz, 2H), 7.18-7.21 (t, *J*= 8 Hz, 1H), 7.46-7.50 (t, *J*= 8 Hz, 1H), 7.73-7.75 (dd, *J*= 8.4 Hz, 1H), 7.79-7.81 (d, *J*= 8.4 Hz, 1H), 8.56-8.59 (d, *J*= 13.2 Hz, 1H), 13.11-13.14 (d, *J*= 12.8 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	19.4, 37.7, 38.0, 111.0, 113.9, 118.6, 127.8, 129.8, 133.7, 137.2, 150.3, 195.9, 200.8.	
HR-MS ((ESI +ve) *m/z* [M+H]$^+$)	Calculated 293.0051	Found 294.0133

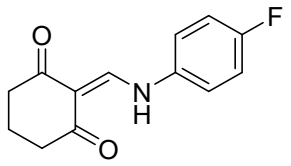
12	**2-(((4-bromophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (^{o}C)**	$C_{13}H_{12}BrNO_2$ 293.0051 Yellow solid 172-173	
FT-IR, ν/cm^{-1}	3422-3377 (NH); 3074 (CH aromatic); 2944 (CH_2), 1658,1656 (2C=O); 1562 (C=C); 1501 (C-C stretch in aromatic ring); 658 (C-Br).	
^{1}H-NMR (400 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	1.87-1.94 (qu, *J*= 6.8 Hz, 2H), 2.41-2.44 (t, *J*= 6 Hz, 2H), 2.50-2.51 (t, *J*= 6.4 Hz, 2H), 7.46-7.49 (d, *J*= 8.8 Hz, 2H), 7.59-7.61 (d, *J*= 8.8 Hz, 2H), 8.44-8.47 (d, *J*= 13.6 Hz, 1H), 12.58-12.62 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	19.5, 37.7, 38.0, 110.4, 118.6, 121.2, 132.9, 138.6, 150.7, 195.9, 200.1.	
HR-MS ((ESI +ve) *m/z* [M+H]$^+$)	Calculated 293.0051	Found 294.0141

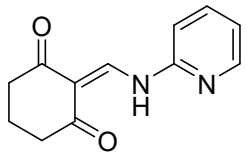
13	**2-(((2-fluorophenyl)amino)methylene)cyclohexane-1,3-dione**

Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{12}FNO_2$ 233.0852 Yellow solid 115-117	
FT-IR, ν/cm^{-1}	3470-3334 (NH); 3062 (CH aromatic); 2946 (CH_2), 1667 (2C=O); 1574 (C=C); 1506 (C-C stretch in aromatic ring); 1323 (C-F).	
^{1}H-NMR (400 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	1.89- 1.95 (qu, *J*= 6.4 Hz, 2H), 2.43-2.46 (t, *J*= 6 Hz, 2H), 2.52-2.53 (t, *J*= 6.4 Hz, 2H), 7.26-7.29 (m, 2H), 7.37-7.40 (m, 1H), 7.79-7.83 (m, 1H), 8.56-8.59 (d, *J*= 13.2 Hz, 1H), 12.98-13.02 (d, *J*= 13.2 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	19.5, 37.7, 38.0, 110.9, 116.5, 116.7, 119.0, 126.1, 127.1, 127.2, 127.4, 150.9, 151.8, 154.3, 195.9, 201.0.	
HR-MS ((ESI +ve) *m/z* [M+H]$^+$)	Calculated 233.0852	Found 234.0933

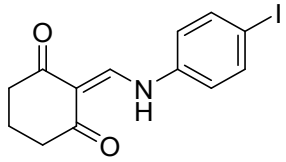
14	**2-(((3-fluorophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{12}FNO_2$ 233.0852 Yellow solid 125-126	
FT-IR, ν/cm^{-1}	3428-3295 (NH); 3046 (CH aromatic); 2960 (CH_2), 1661 (2C=O); 1570 (C=C); 1455 (C-C stretch in aromatic ring); 1323 (C-F).	
^{1}H-NMR (400 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	1.88- 1.94 (qu, *J*= 6.4 Hz, 2H), 2.42-2.45 (t, *J*= 6.4 Hz, 2H), 2.50-2.51 (t, *J*= 6.4 Hz, 2H), 7.05-7.09 (dt, *J*= 8.4 Hz, 1H), 7.31-7.33 (dd, *J*= 8 Hz, 1H), 7.42-7.46 (m, 1H), 7.48-7.50 (m, 1H), 8.47-8.50 (d, *J*= 13.6 Hz, 1H), 12.60-13.64 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d$_6$, Me$_4$Si) (ppm): δ	19.5, 37.7, 38.1, 106.4, 106.6, 110.5, 112.9, 113.1, 115.1, 131.8, 131.9, 140.9, 141.0, 150.9, 162.0, 164.4, 196.0, 200.2.	

HR-MS ((ESI +ve) *m/z* $[M+H]^+$)	Calculated 233.0852	Found 234.0929

15	**2-(((4-fluorophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{13}H_{12}FNO_2$ 233.0852 Brown solid 133-134	
FT-IR, ν/cm^{-1}	3487-3338 (NH); 3076 (CH aromatic); 2952 (CH_2), 1668,1666 (2C=O); 1590 (C=C); 1511 (C-C stretch in aromatic ring); 1323 (C-F).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.87- 1.93 (qu, *J*= 6.8 Hz, 2H), 2.41-2.44 (t, *J*= 6 Hz, 2H), 2.50-2.51 (t, *J*= 6.4 Hz, 2H), 7.25-7.29 (t, *J*= 8.8 Hz, 2H), 7.54-7.57 (m, 2H), 8.41-8.44 (d, *J*= 13.6 Hz, 1H), 12.64-12.67 (d, *J*= 13.6 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.6, 37.6, 38.0, 110.1, 116.8, 117.0, 121.2, 121.3, 135.7, 151.4, 159.3, 161.7,195.9, 199.9.	
HR-MS ((ESI +ve) *m/z* $[M+H]^+$)	Calculated 233.0852	Found 234.0938

16	**2-((pyridin-2-ylamino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (°C)**	$C_{12}H_{12}N_2O_2$ 216.0899 Yellow solid 104-106	
FT-IR, ν/cm^{-1}	3479-3356 (NH); 3176 (CH aromatic); 2946 (CH_2), 1664,1662 (2C=O); 1594 (C=C); 1540 (C-C stretch in aromatic ring).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.89- 1.95 (qu, *J*= 6.4 Hz, 2H), 2.44-2.49 (t, *J*= 6.4 Hz, 2H), 2.50-2.51 (t, *J*= 6.4 Hz, 2H), 7.26-7.28 (m, 1H), 7.52-7.54 (d, *J*= 8 Hz, 1H), 7.85-7.89 (dt, *J*= 8 Hz, 1H), 8.42-8.43 (dd, *J*= 4.8 Hz, 1H), 9.05-9.08 (d, *J*= 12 Hz, 2H), 12.42-12.45 (d, *J*= 13.2 Hz, 1H).	

^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.3, 37.8, 38.2, 110.9, 114.2, 121.8, 139.8, 148.1, 149.1, 150.5, 196.6, 200.4.	
GC-MS	Calculated 216.0899	Found 216.225

17	**2-(((4-iodophenyl)amino)methylene)cyclohexane-1,3-dione**	
Molecular Formula **Molecular Weight (g/mol)** **Colour** **Melting point (^{o}C)**	$C_{13}H_{12}INO_2$ 340.9913 Brownish green solid 153-154	
FT-IR, ν/cm^{-1}	3405-3295 (NH); 3087 (CH aromatic); 2922 (CH_2), 1668, 1666 (2C=O); 1594 (C=C); 1506 (C-C stretch in aromatic ring); 545 (C-F).	
^{1}H-NMR (400 MHz, DMSO-d_6, Me_4Si) (ppm): δ	1.87- 1.93 (qu, *J*= 6.4 Hz, 2H), 2.41-2.44 (t, *J*= 6 Hz, 2H), 2.50-2.51 (t, *J*= 6.4 Hz, 2H), 7.32-7.34 (d, *J*= 8.8 Hz, 2H), 7.73-7.76 (d, *J*= 8.8 Hz, 2H), 8.44-8.47 (d, *J*= 12.4 Hz, 1H), 12.57-12.60 (d, *J*= 13.2 Hz, 1H).	
^{13}C-NMR (100 MHz, DMSO-d_6, Me_4Si) (ppm): δ	19.5, 37.7, 38.0, 91.1, 110.4, 121.3, 138.7, 139.0, 150.5, 195.9, 200.1.	
HR-MS ((ESI +ve) *m/z* [M+H]$^+$)	Calculated 340.9913	Found 341.9991

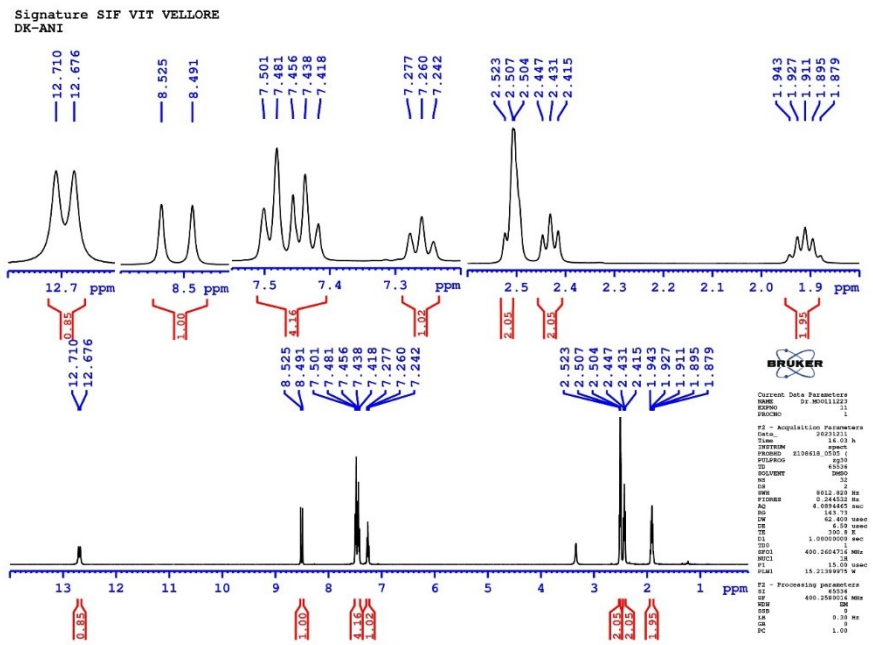


Fig. S11 [1]H NMR spectra of **4a**

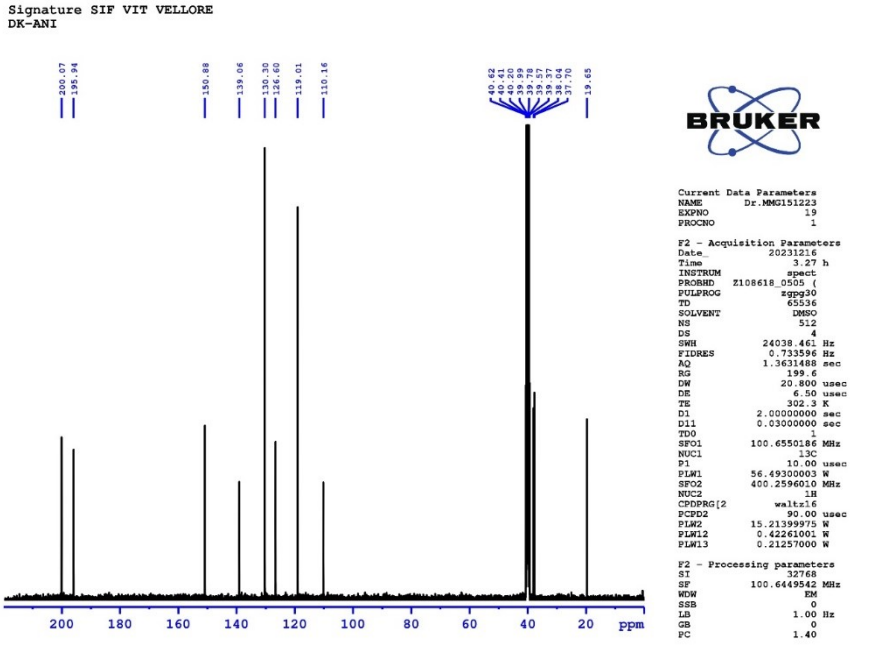


Fig. S12 [13]C NMR spectra of **4a**

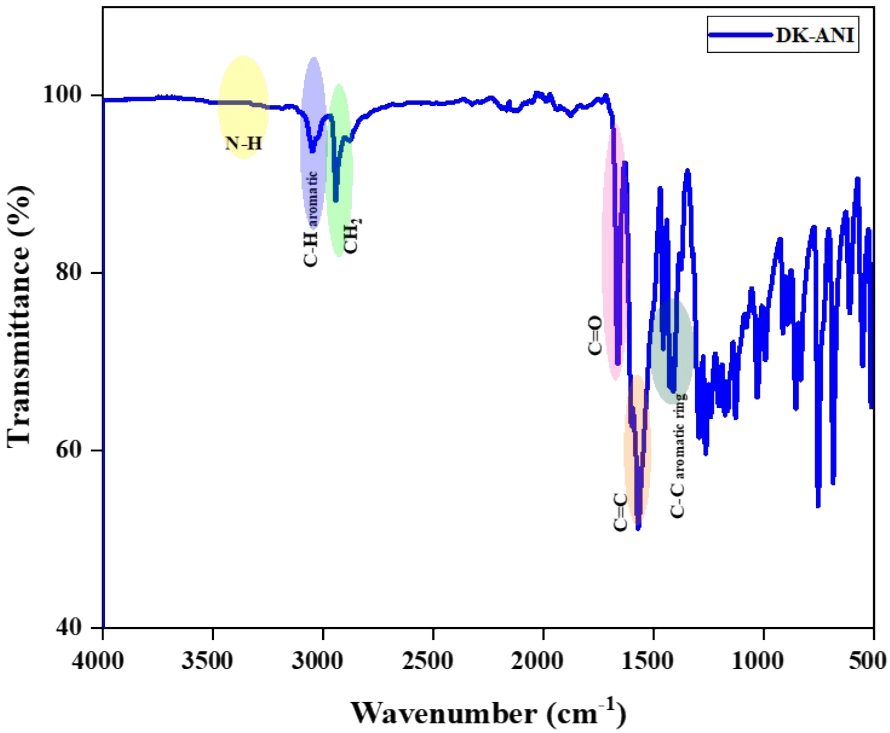


Fig. S13 FT-IR spectra of **4a**

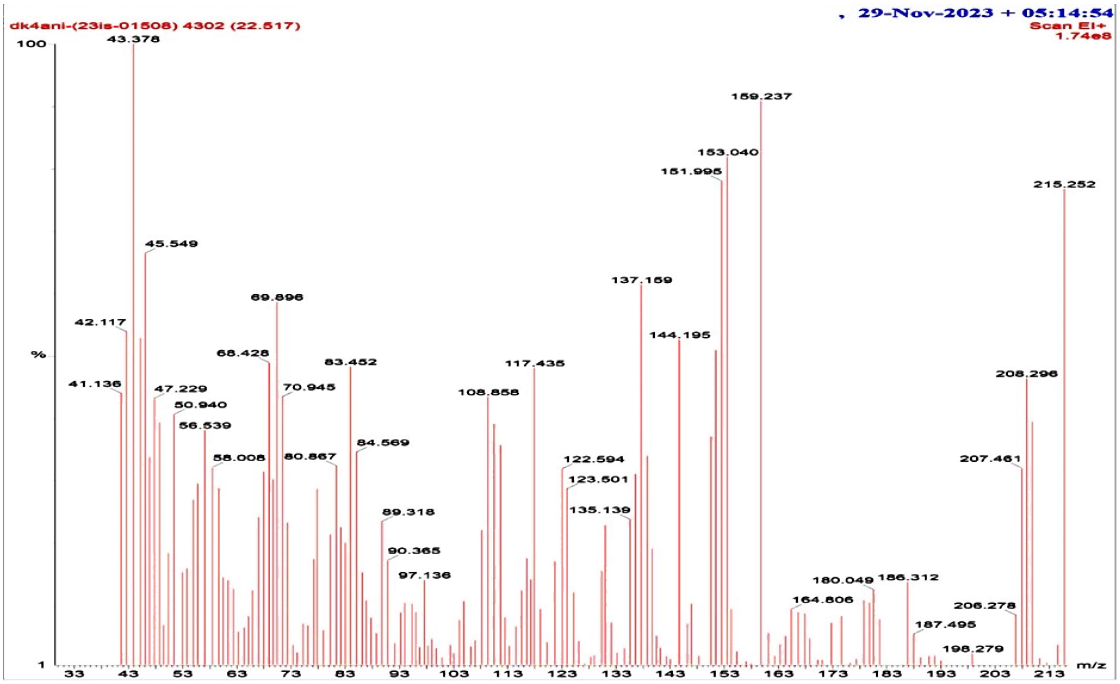


Fig. S14 GC-MS spectra of **4a**

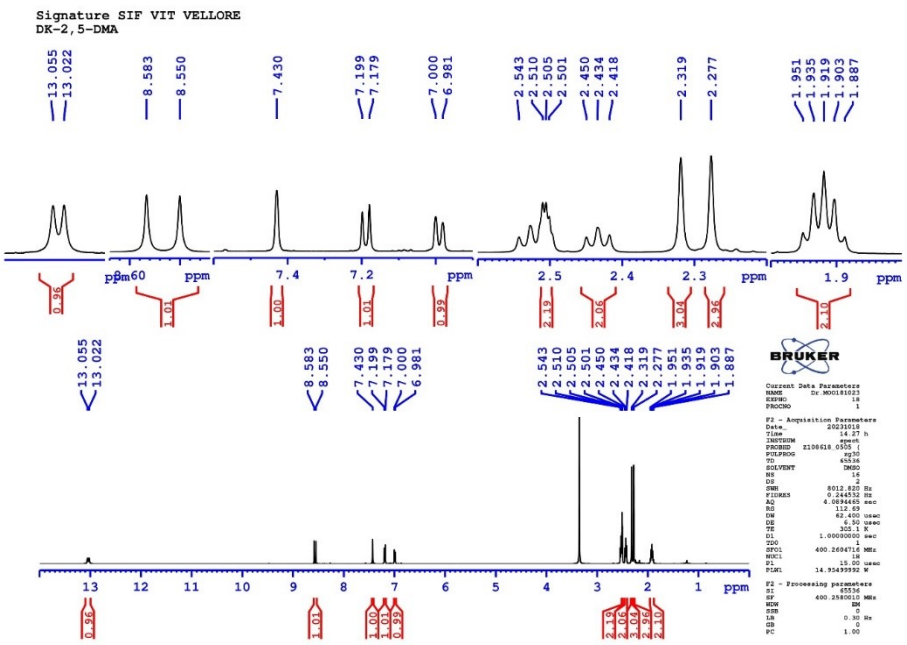


Fig. S15 ^{1}H NMR spectra of **4b**

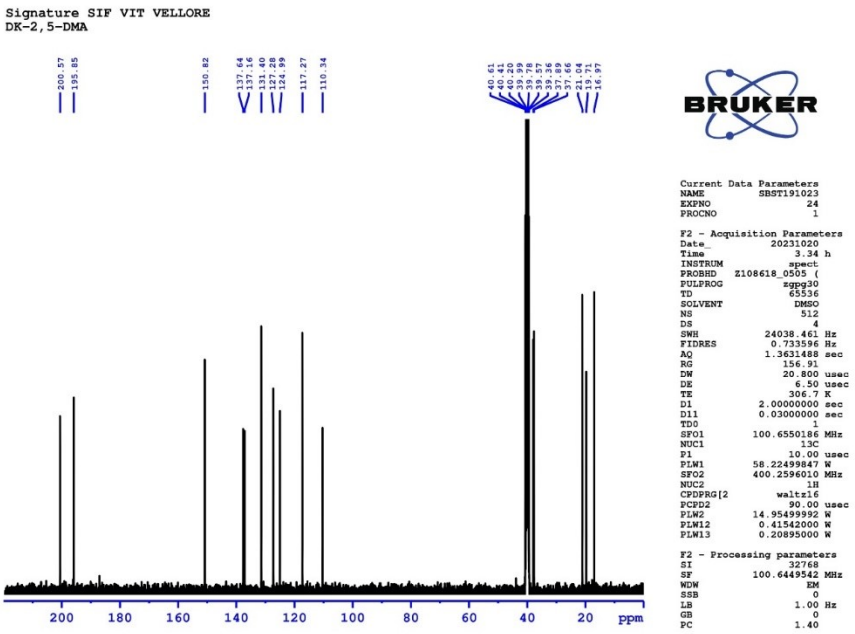


Fig. S16 ^{13}C NMR spectra of **4b**

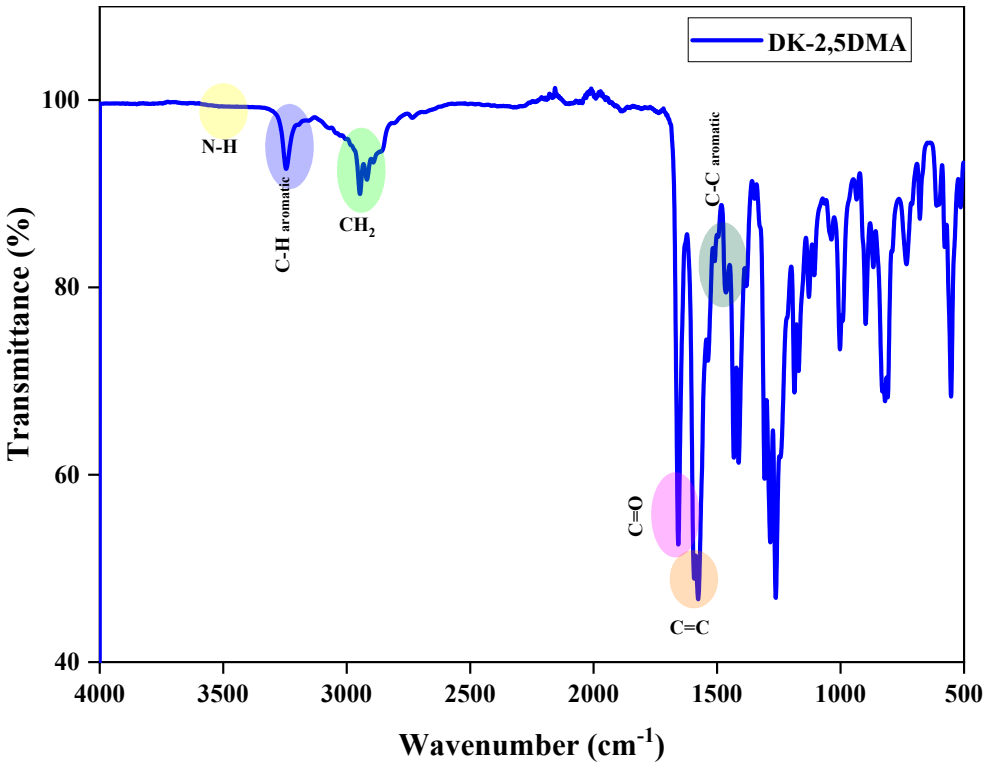


Fig. S17 FT-IR spectra of **4b**

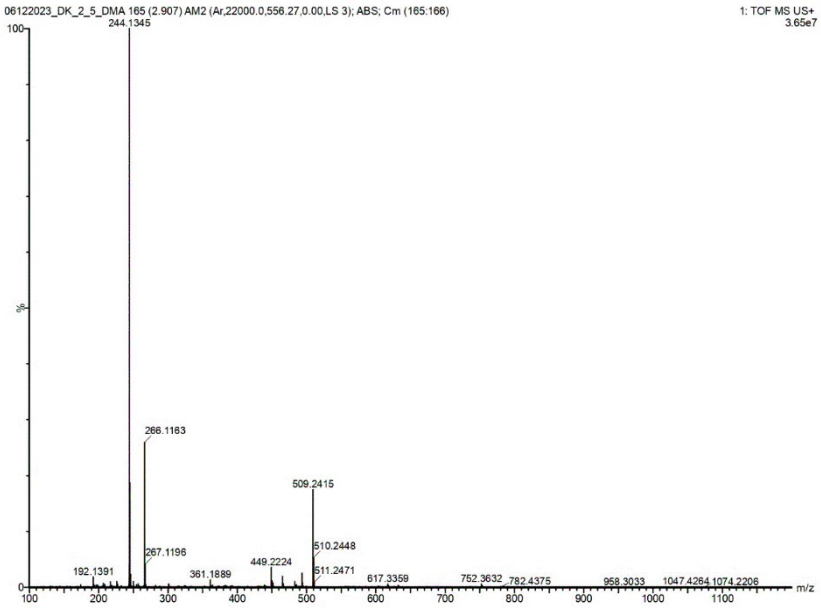


Fig. S18 HR-MS spectra of **4b**

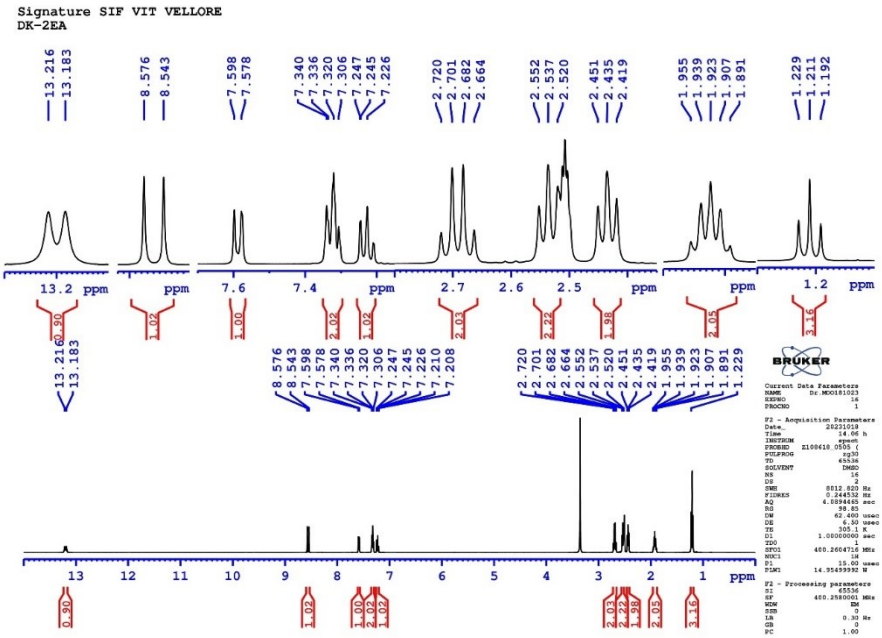


Fig. S19 ^{1}H NMR spectra of **4c**

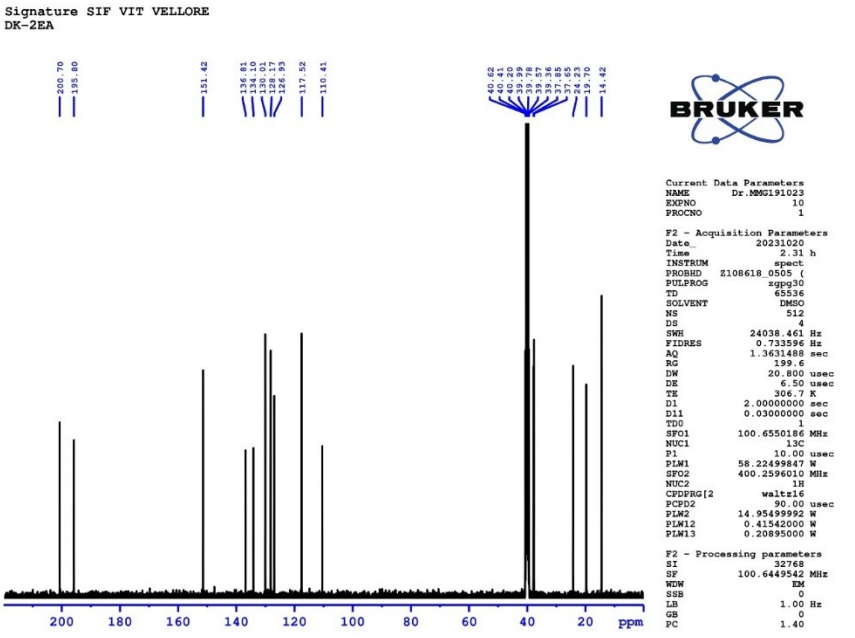


Fig. S20 ^{13}C NMR spectra of **4c**

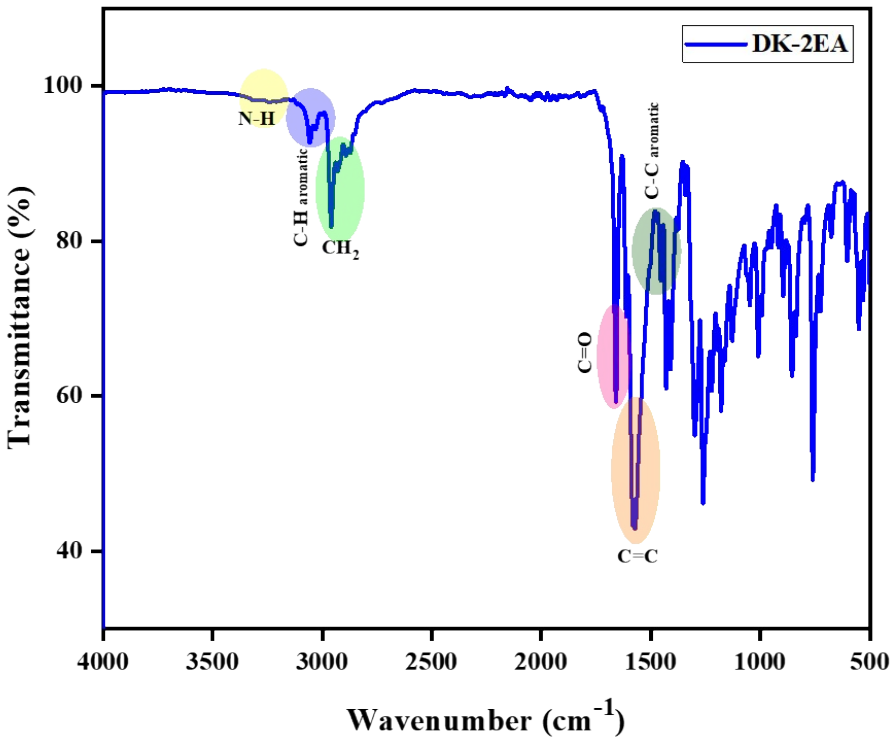


Fig. S21 FT-IR spectra of **4c**

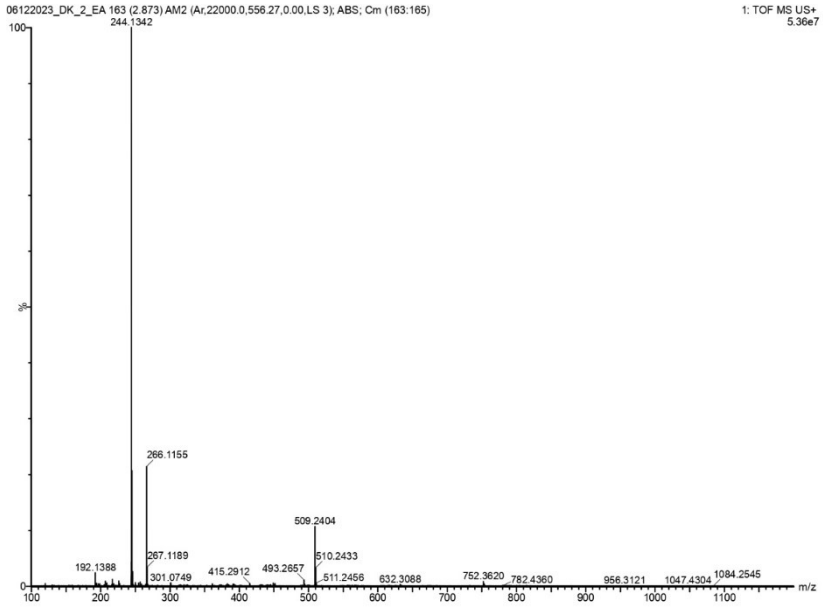


Fig. S22 HR-MS spectra of **4c**

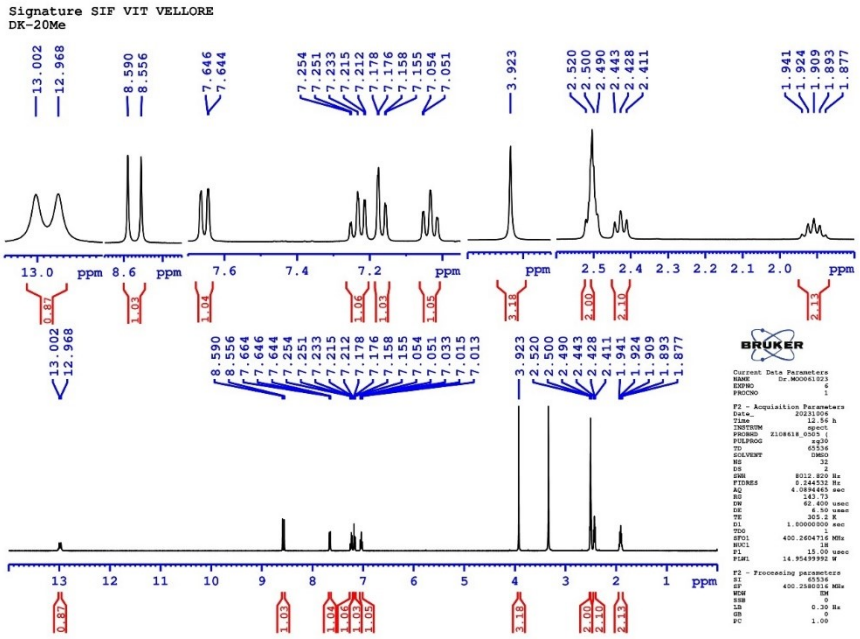


Fig. S23 ^{1}H NMR spectra of **4d**

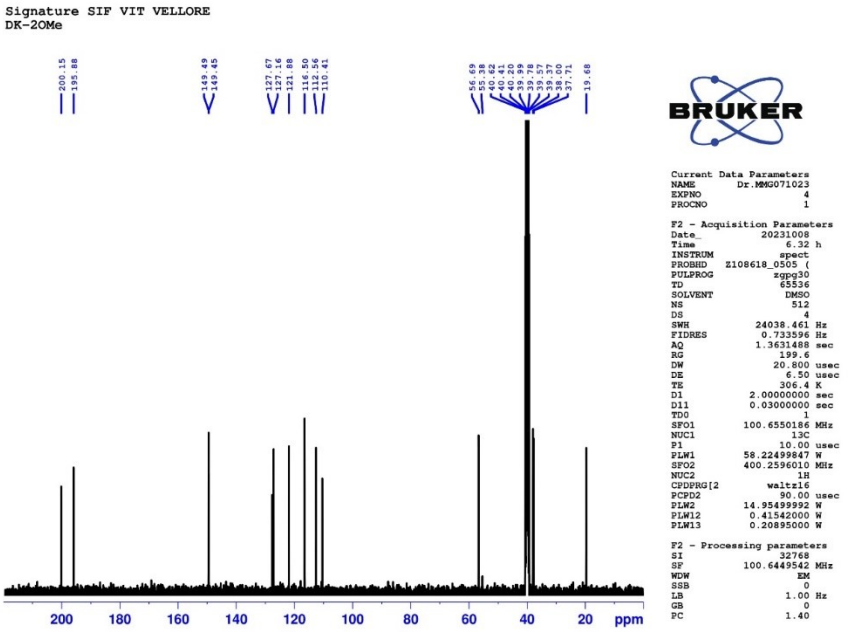


Fig. S24 ^{13}C NMR spectra of **4d**

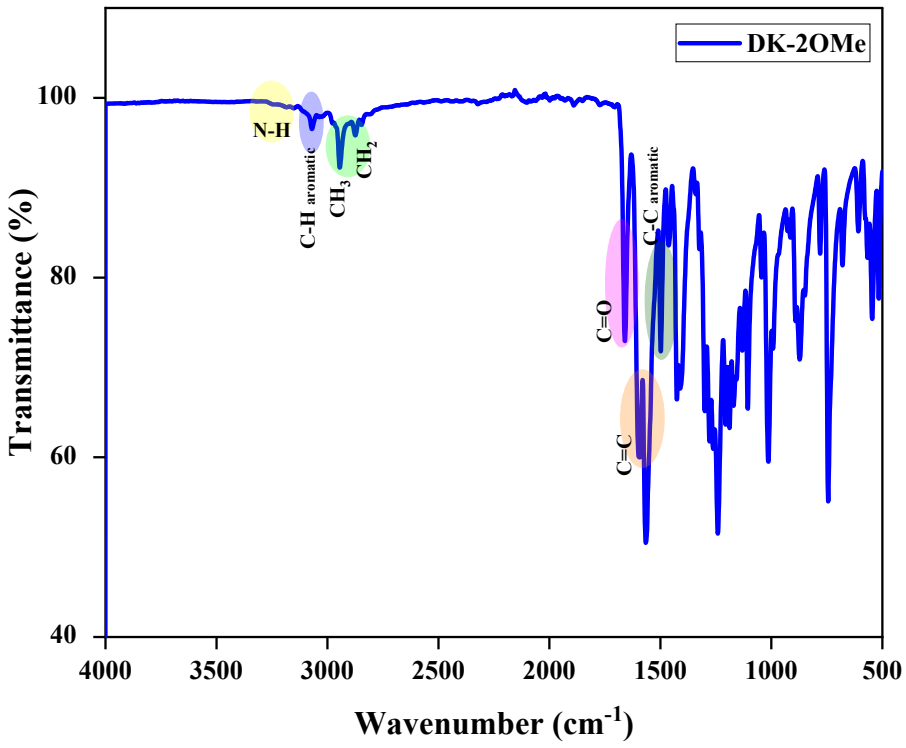


Fig. S25 FT-IR spectra of **4d**

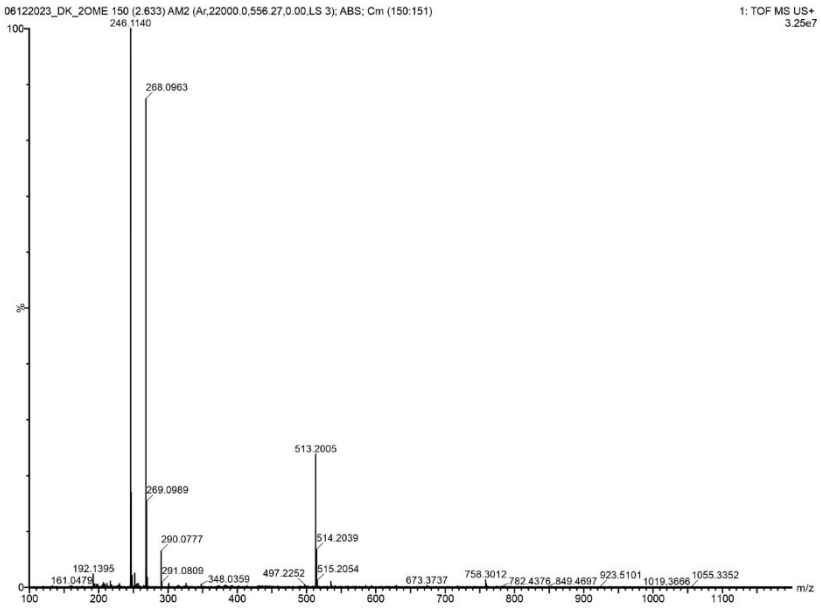


Fig. S26 HR-MS spectra of **4d**

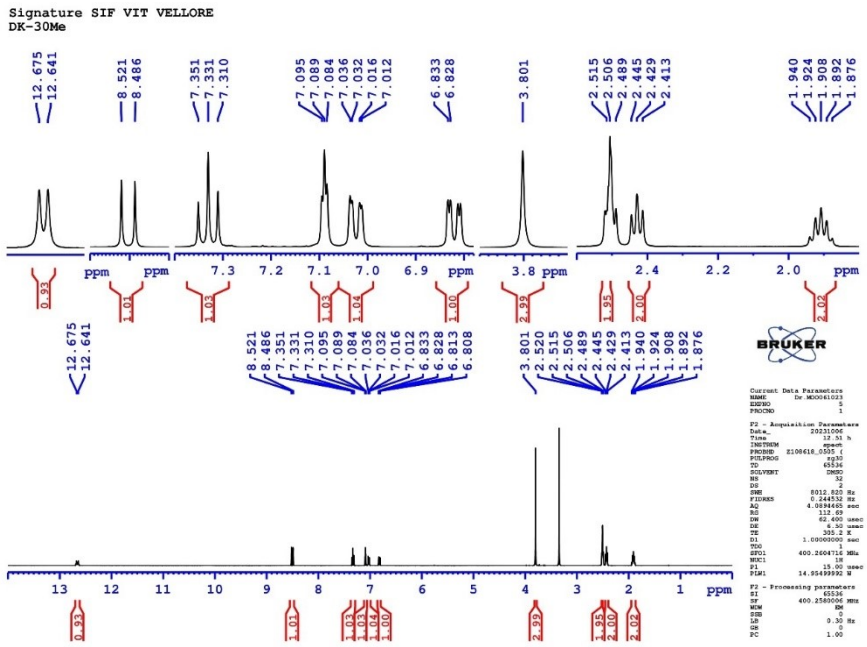


Fig. S27 ^{1}H NMR spectra of **4e**

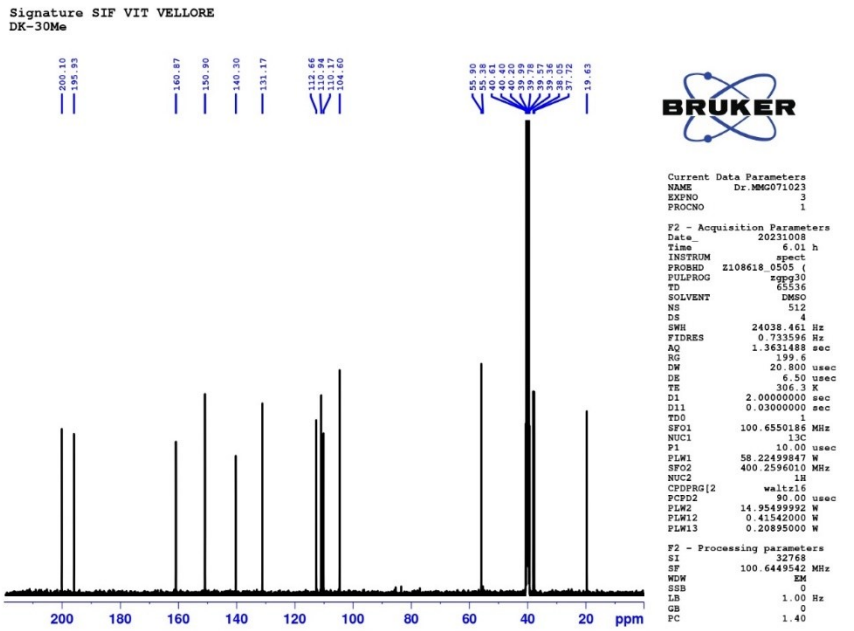


Fig. S28 ^{13}C NMR spectra of **4e**

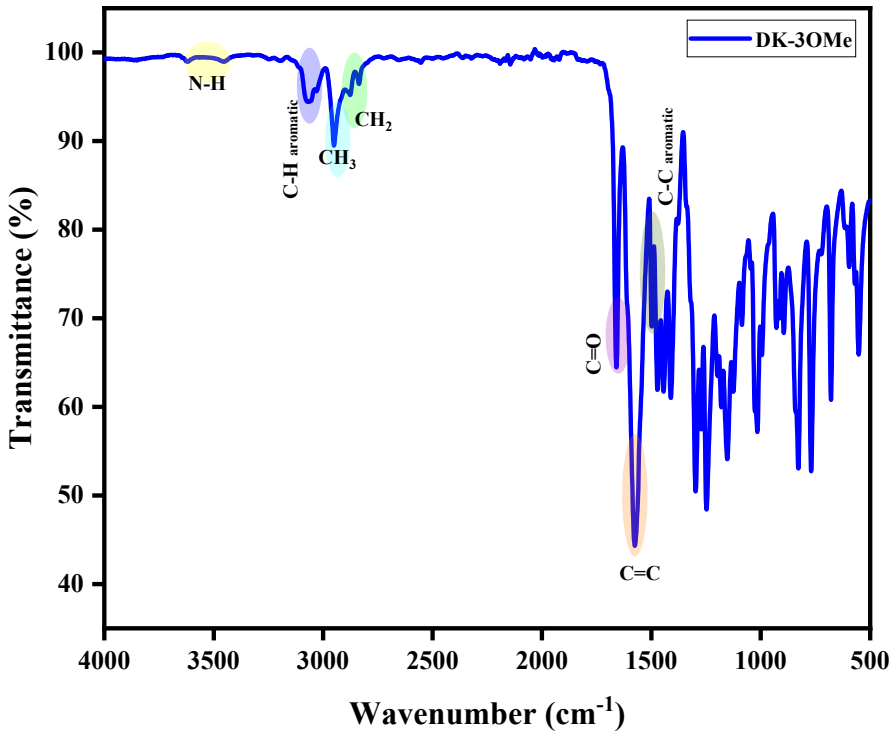


Fig. S29 FT-IR spectra of **4e**

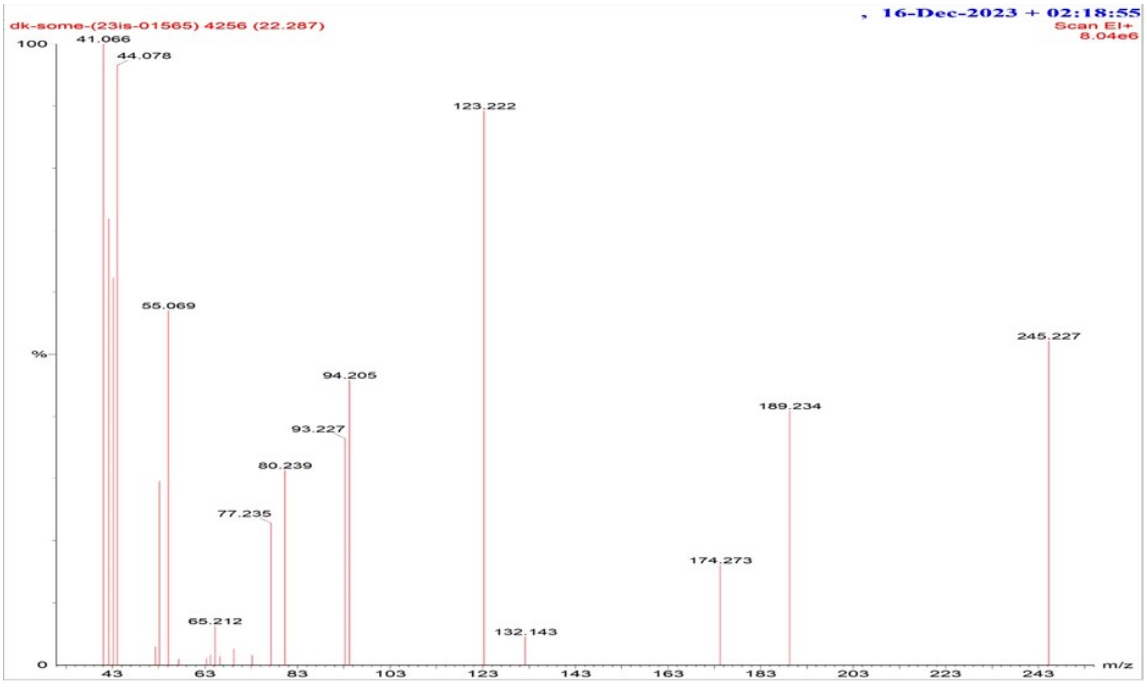


Fig. S30 GC-MS spectra of **4e**

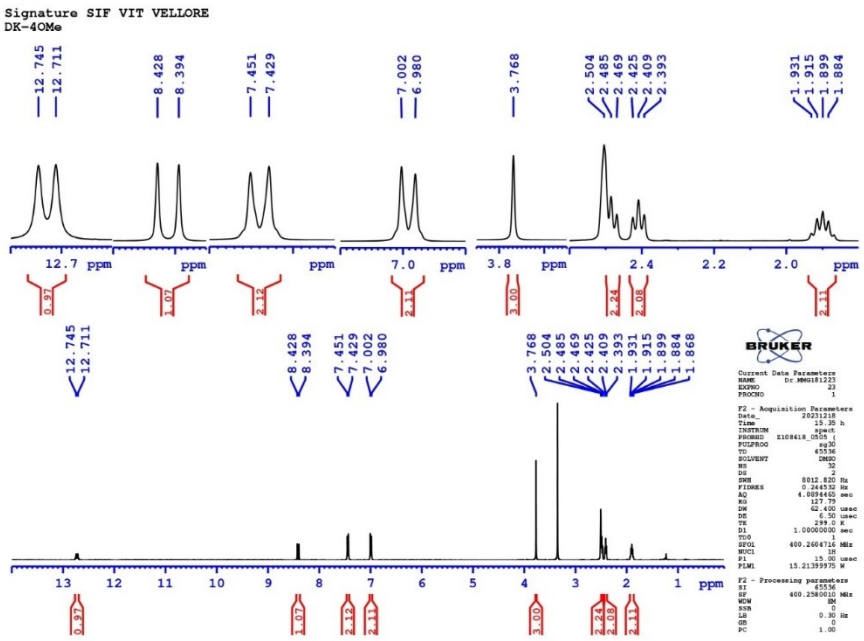


Fig. S31 [1]H NMR spectra of **4f**

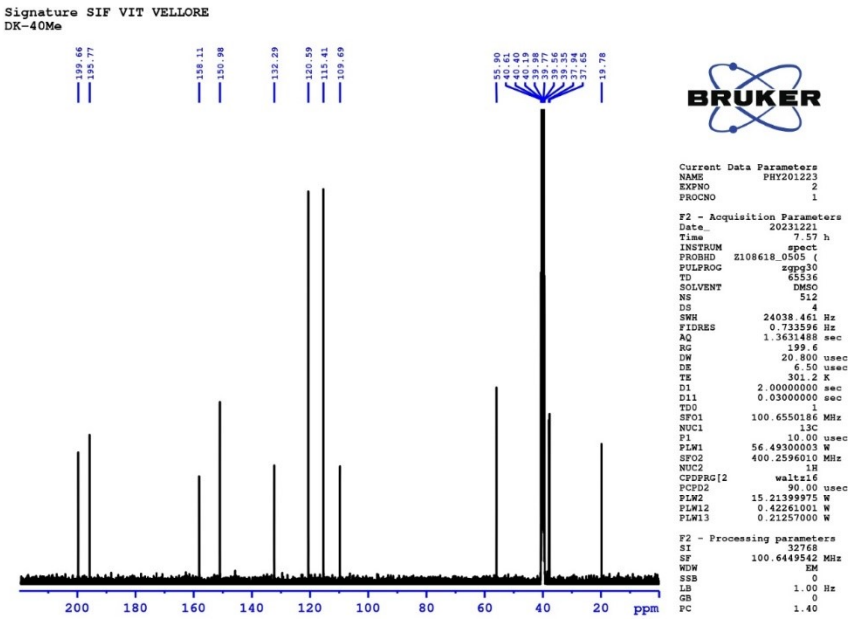


Fig. S32 [13]C NMR spectra of **4f**

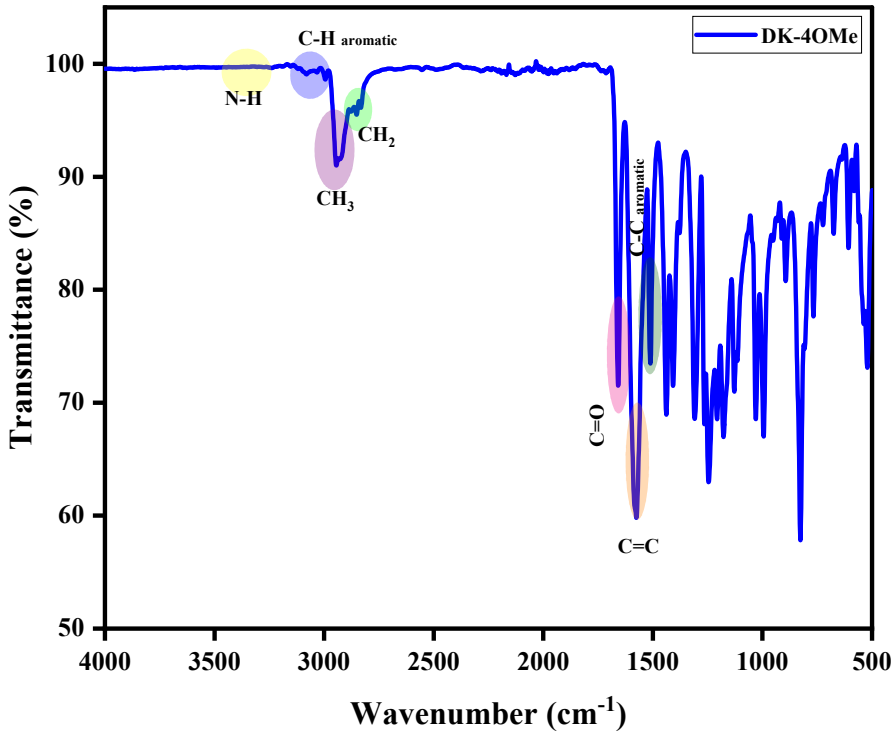


Fig. S33 FT-IR spectra of **4f**

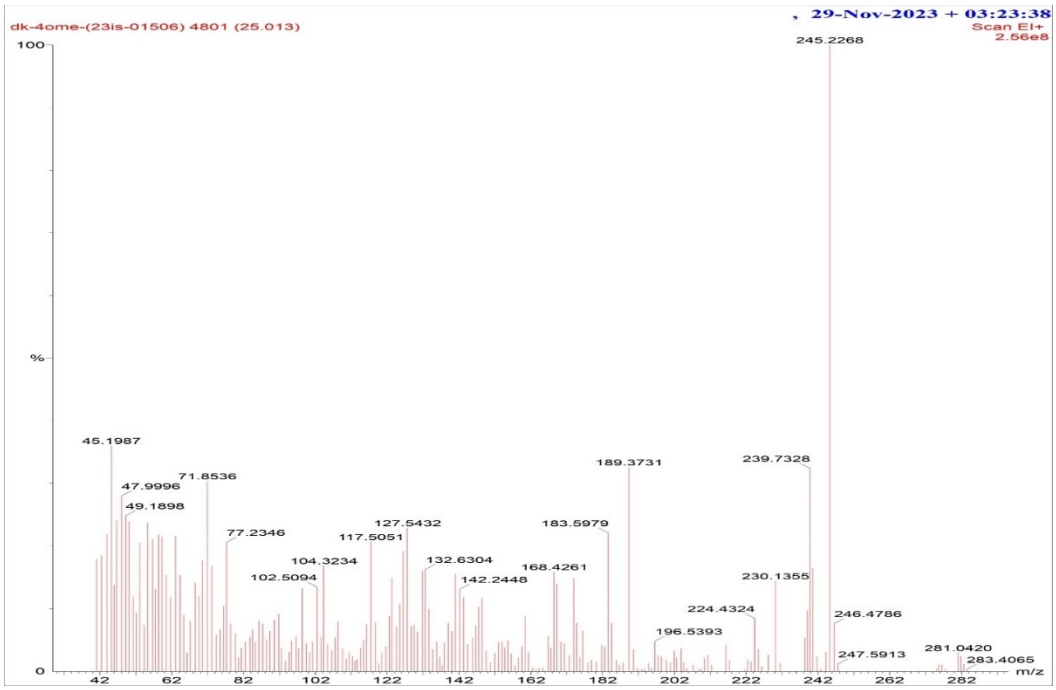


Fig. S34 GC-MS spectra of **4f**

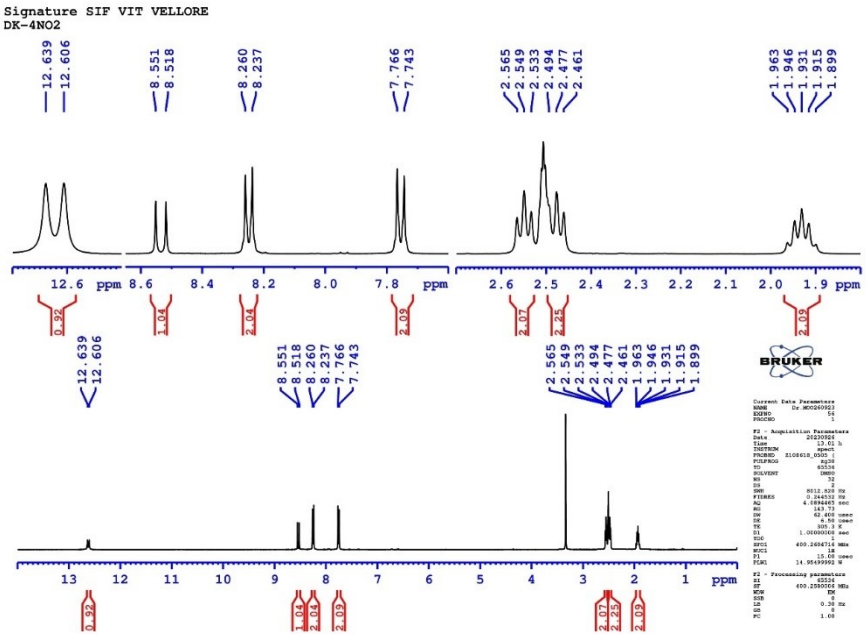


Fig. S35 ^{1}H NMR spectra of **4g**

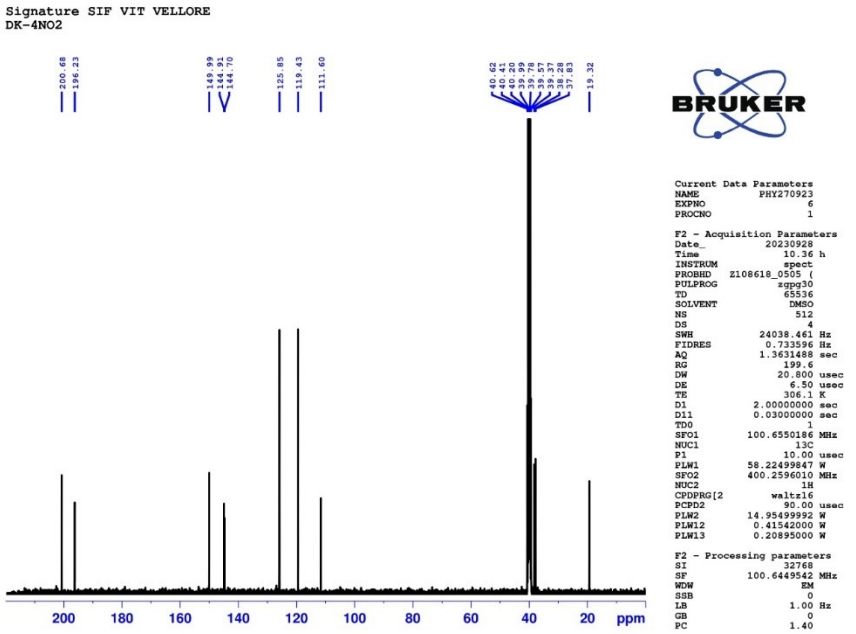


Fig. S36 ^{13}C NMR spectra of **4g**

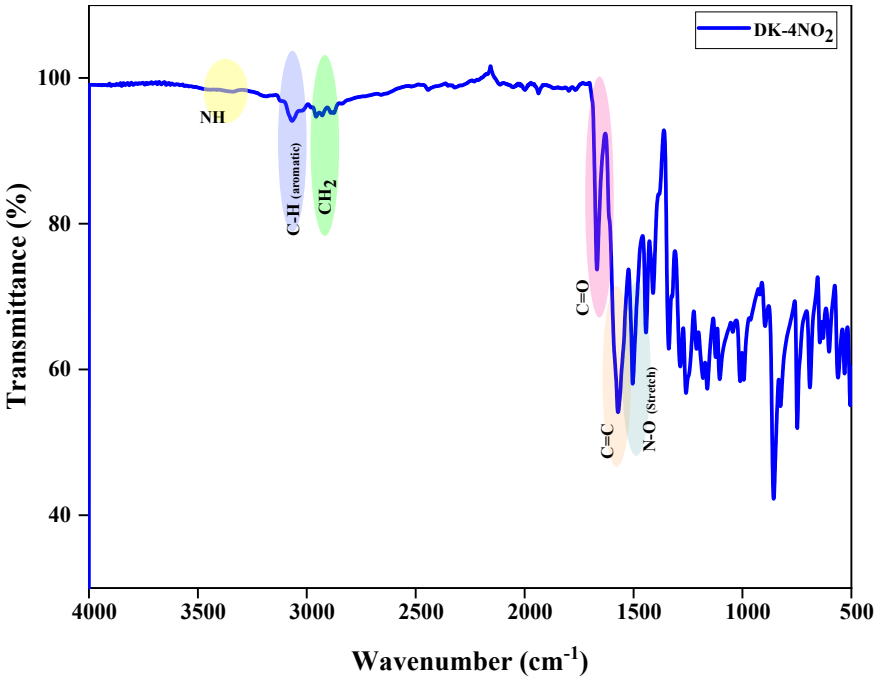


Fig. S37 FT-IR spectra of **4g**

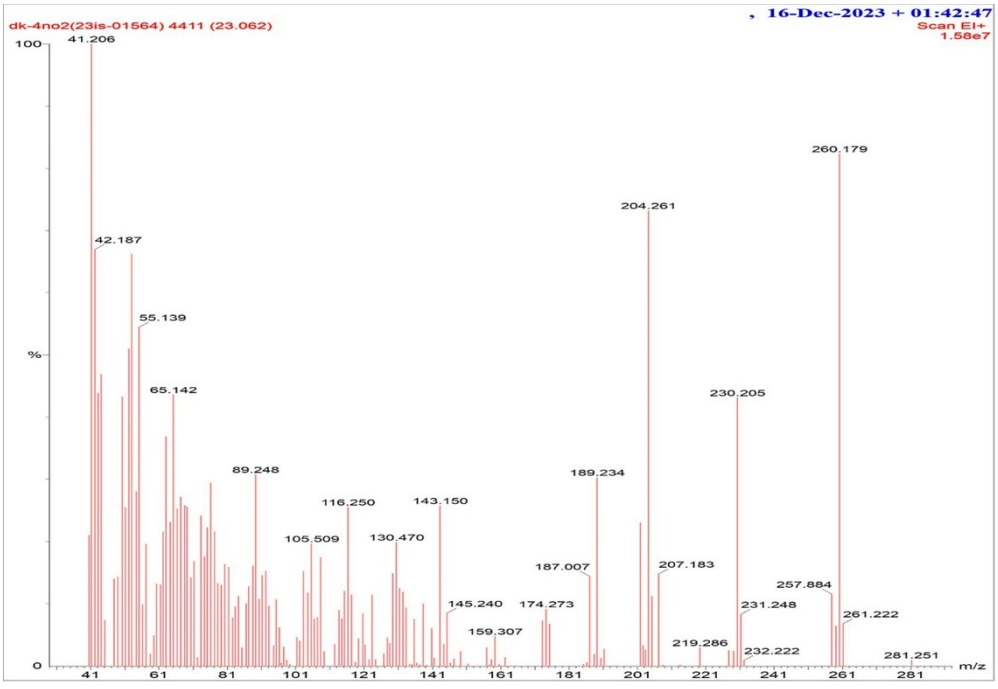


Fig. S38 GC-MS spectra of **4g**

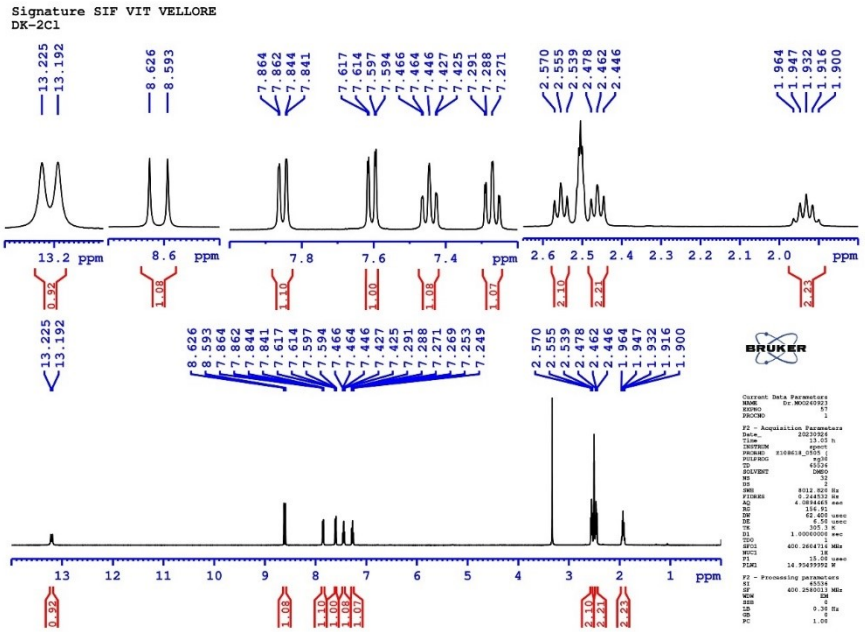


Fig. S39 ^{1}H NMR spectra of **4h**

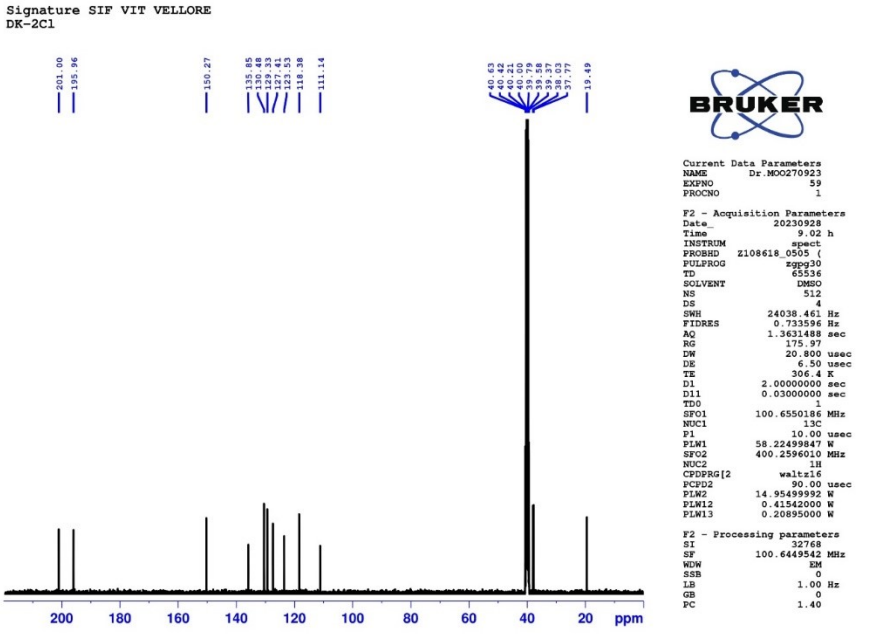


Fig. S40 ^{13}C NMR spectra of **4h**

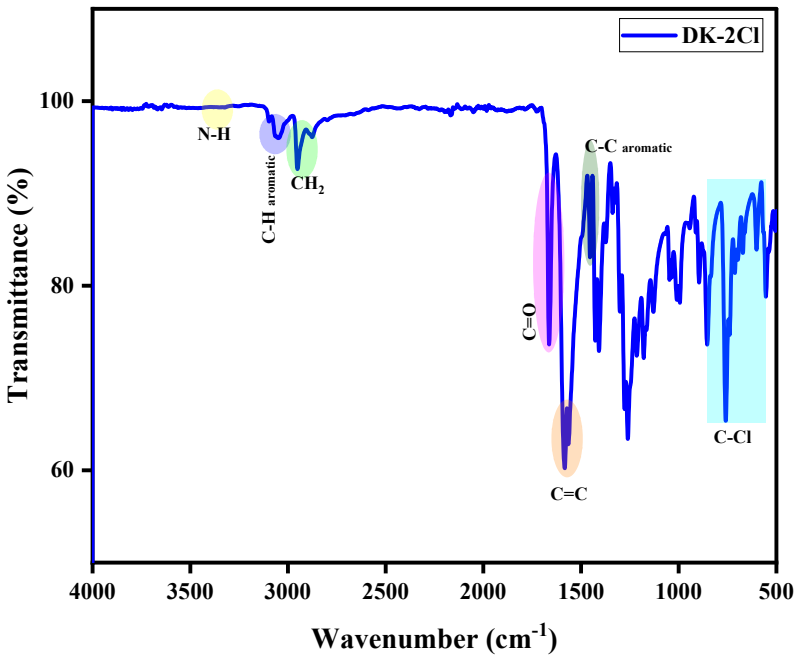


Fig. S41 FT-IR spectra of **4h**

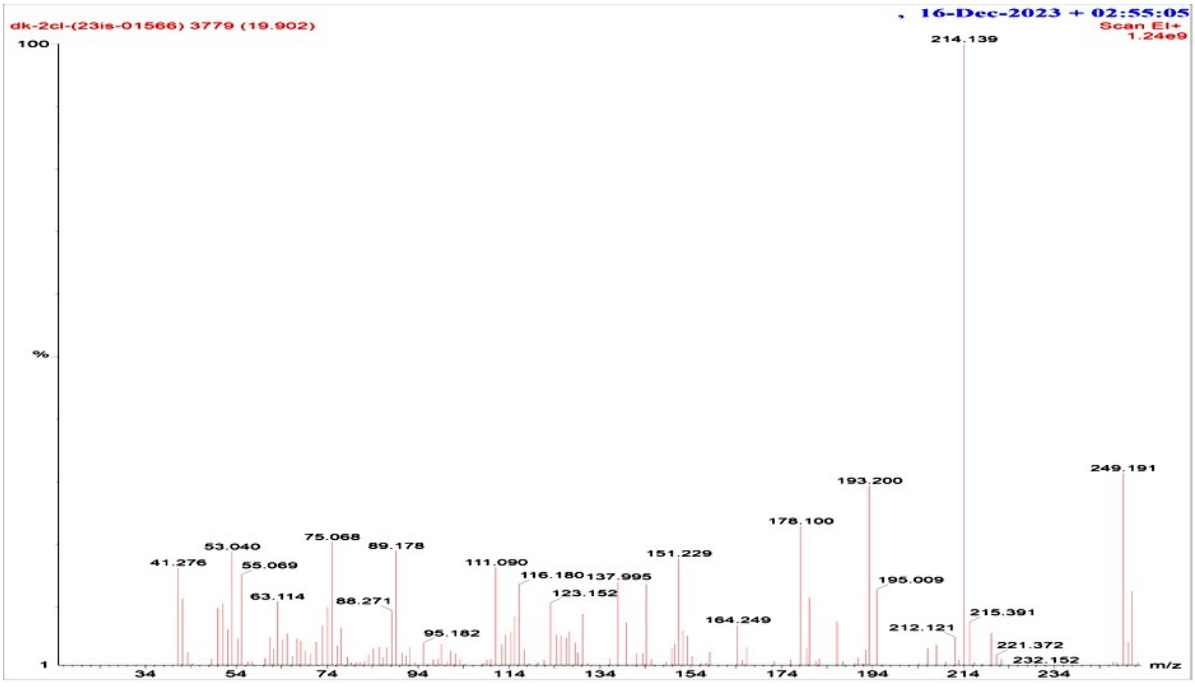


Fig. S42 GC-MS spectra of **4h**

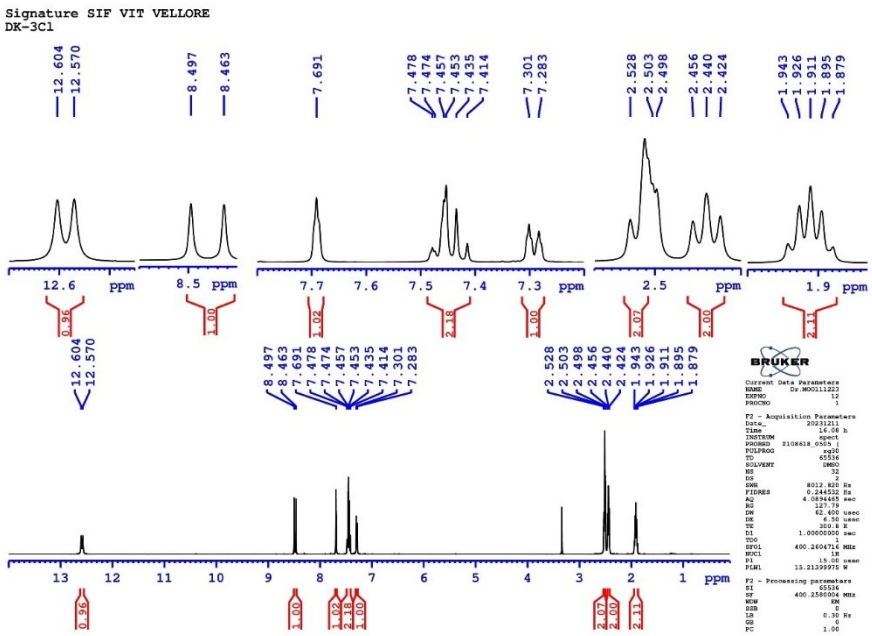


Fig. S43 [1]H NMR spectra of **4i**

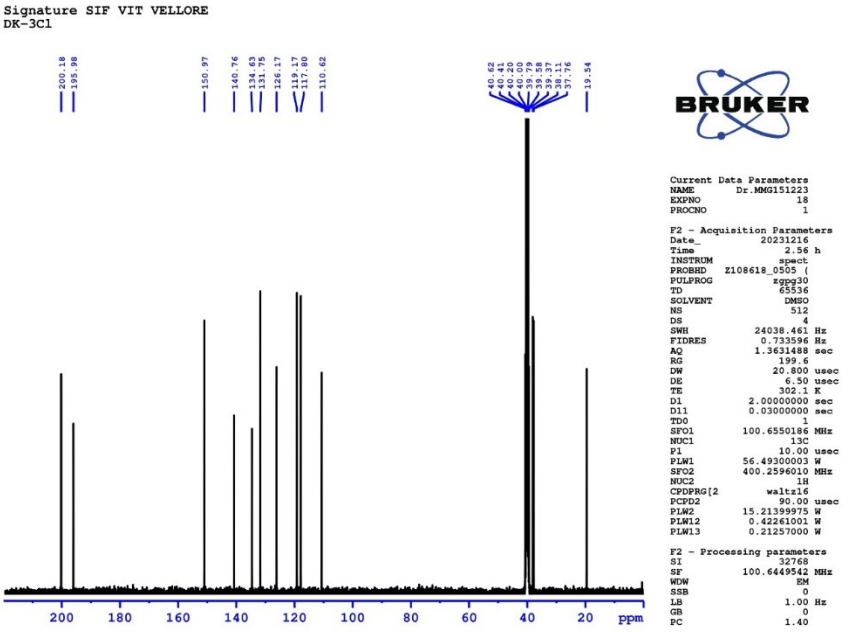


Fig. S44 [13]C NMR spectra of **4i**

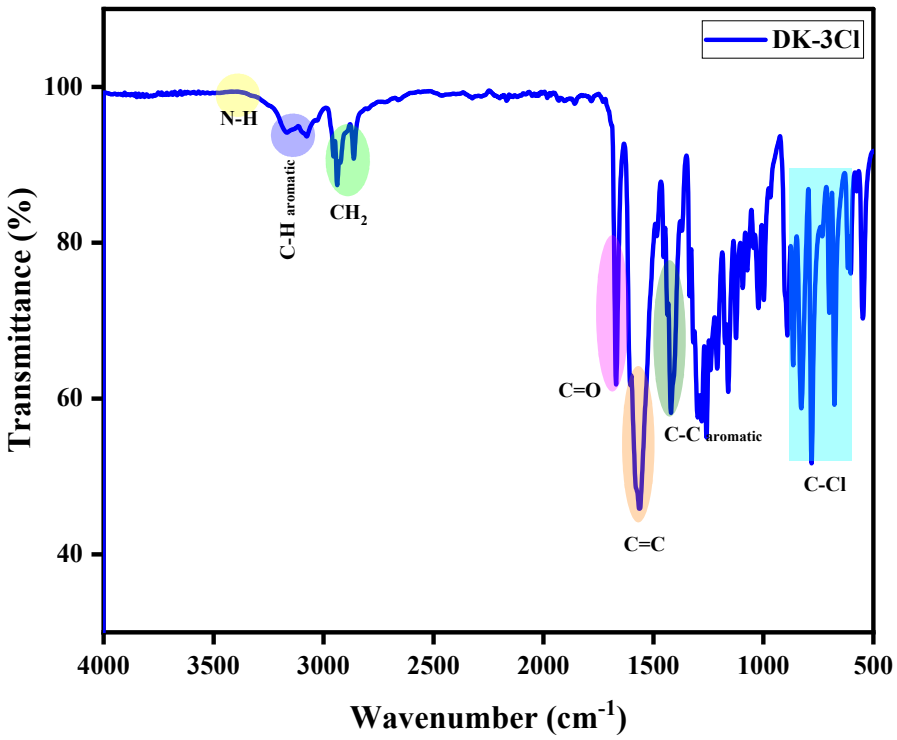


Fig. S45 FT-IR spectra of **4i**

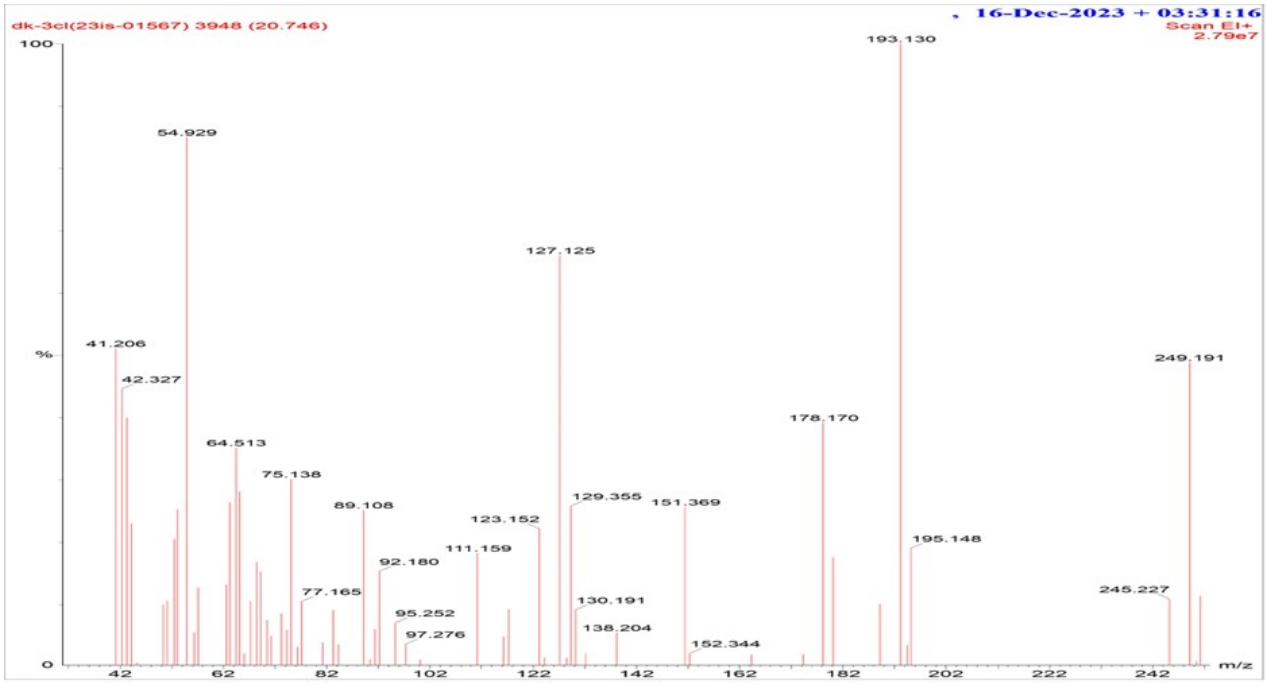
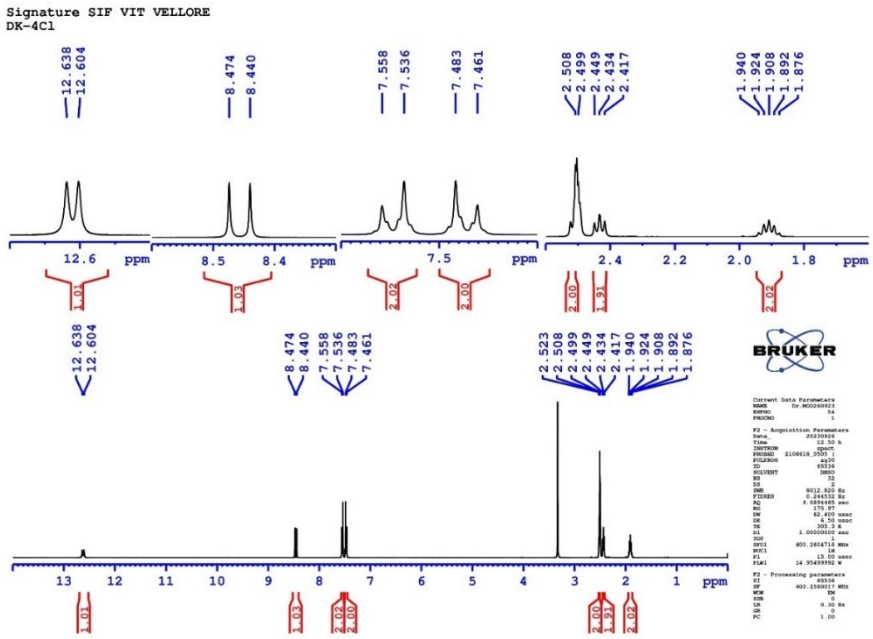


Fig. S46 GC-MS spectra of **4i**



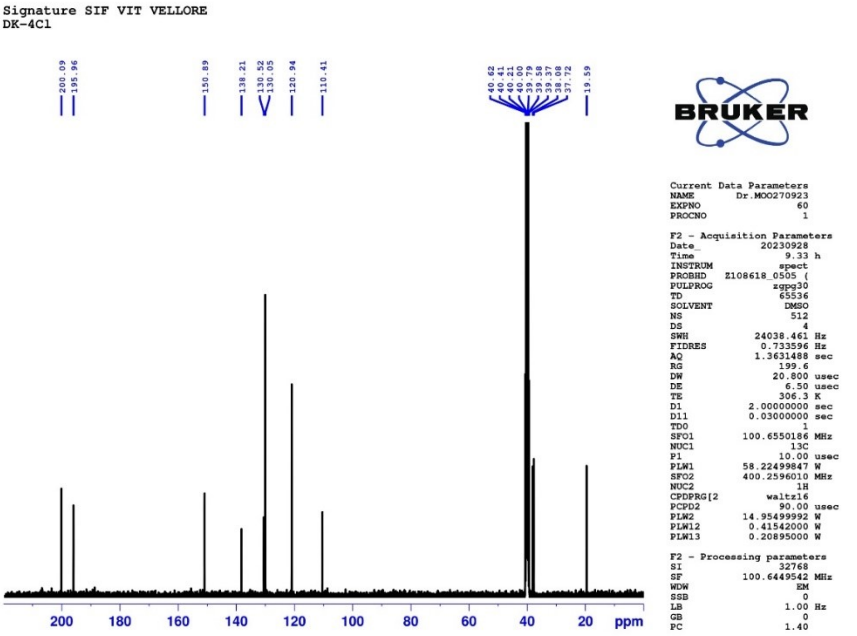


Fig. S47 ^{1}H NMR spectra of **4j**

Fig. S48 ^{13}C NMR spectra of **4j**

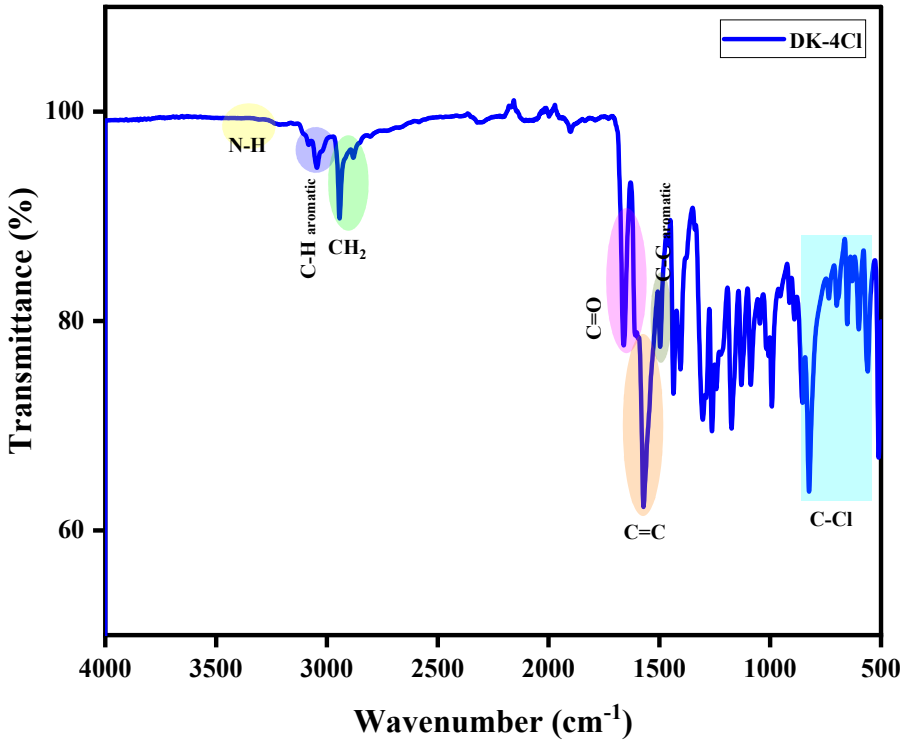


Fig. S49 FT-IR spectra of **4j**

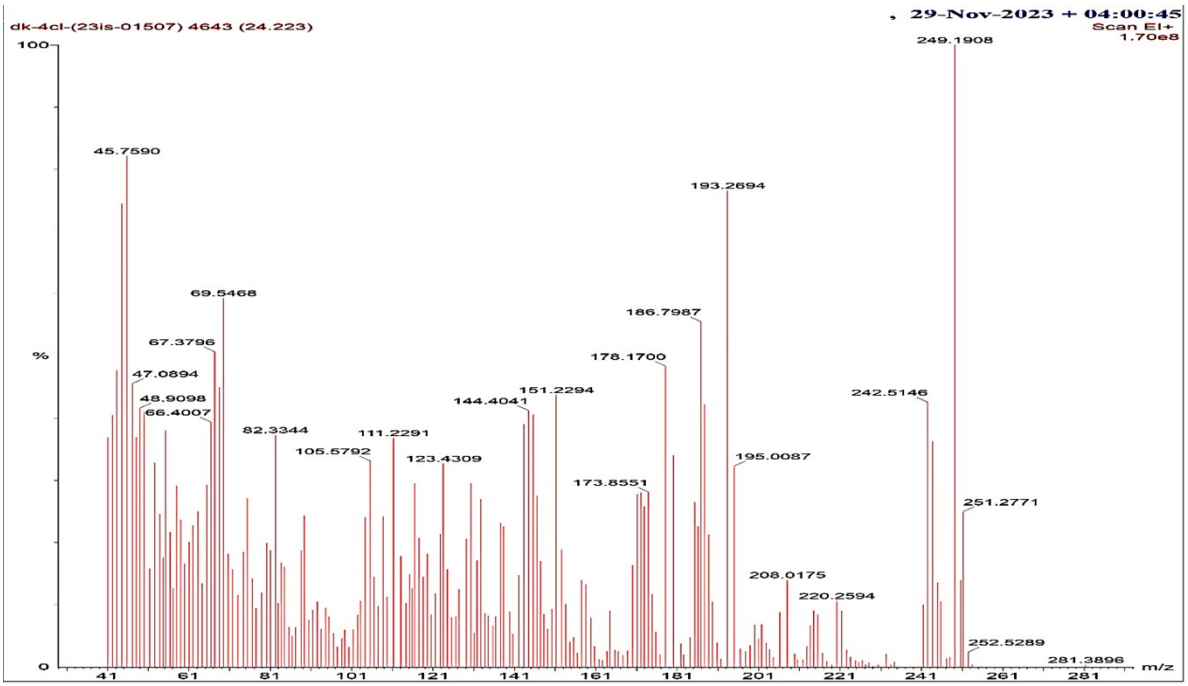


Fig. S50 GC-MS spectra of **4j**

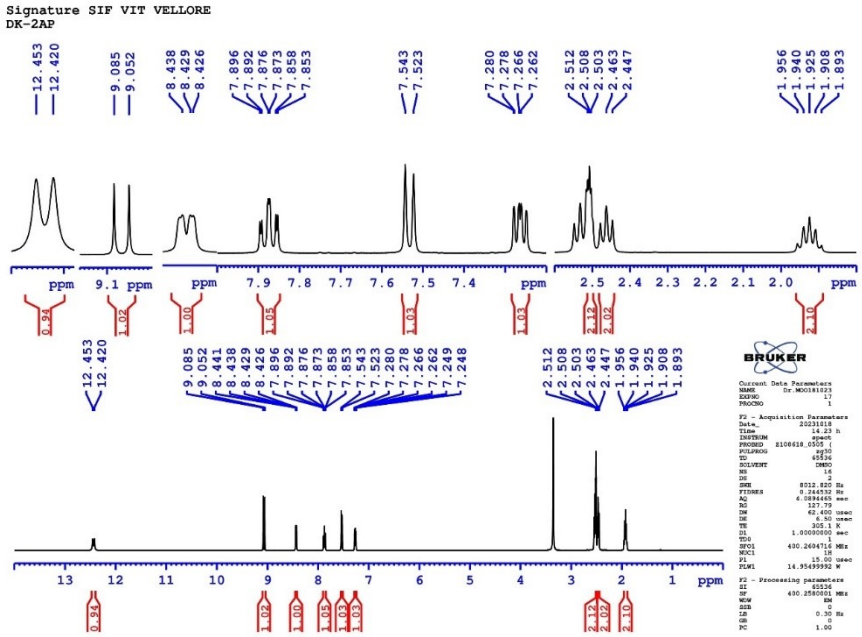


Fig. S51 ^{1}H NMR spectra of **4k**

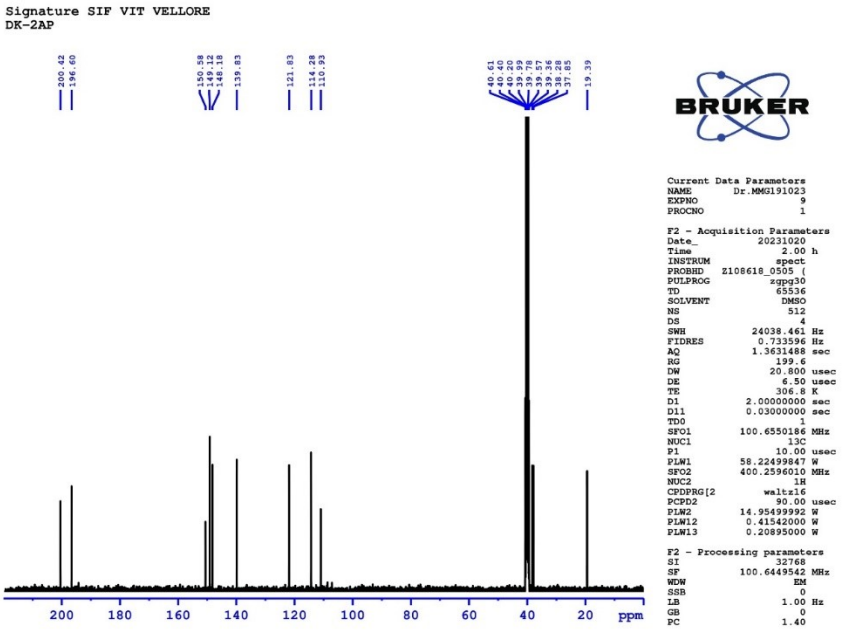


Fig. S52 ^{13}C NMR spectra of **4k**

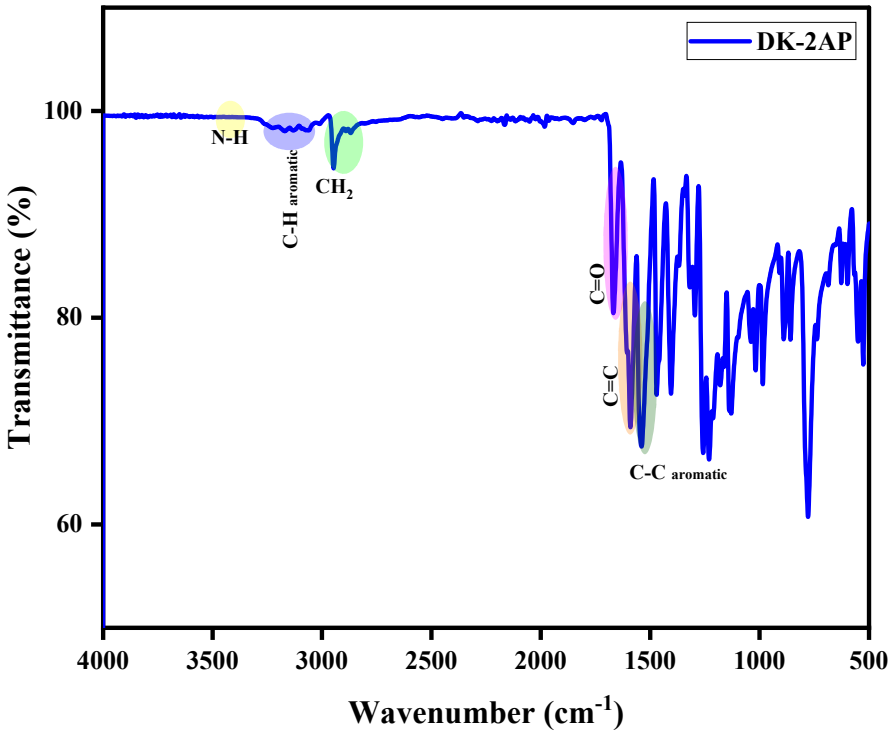


Fig. S53 FT-IR spectra of **4k**

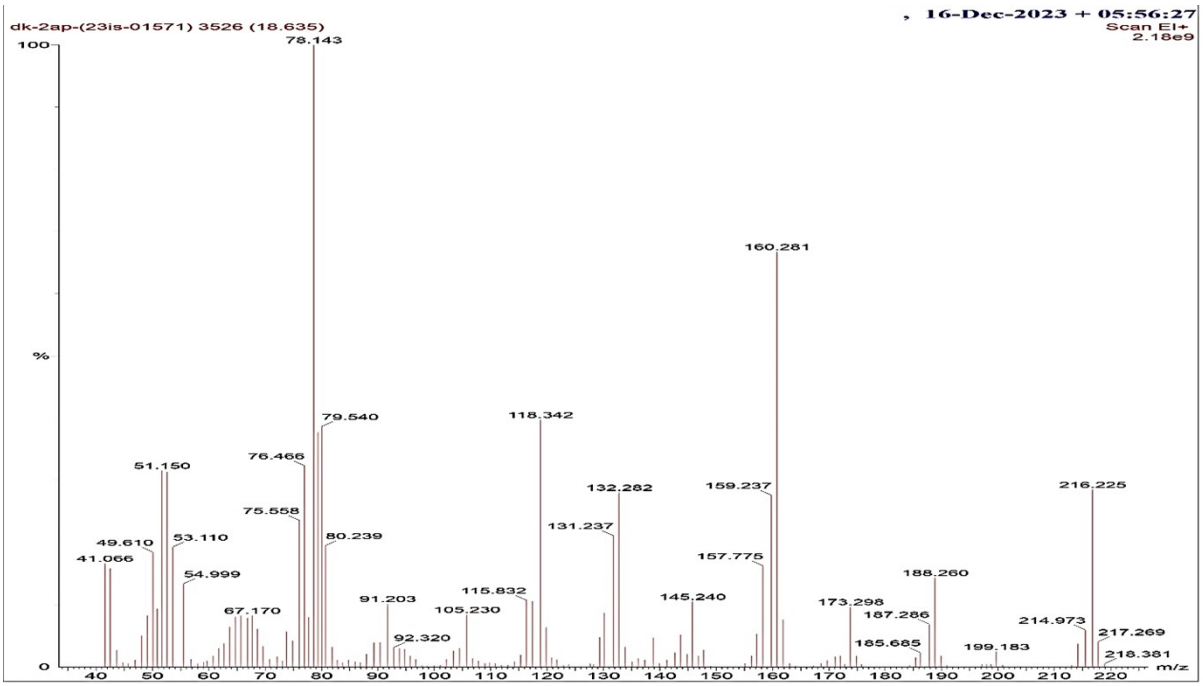


Fig. S54 GC-MS spectra of **4k**

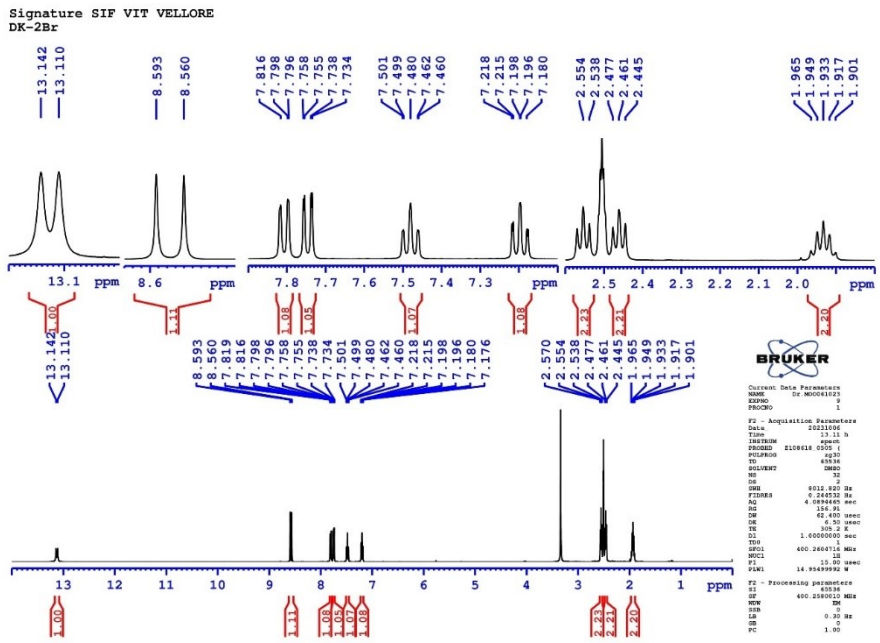


Fig. S55 ^{1}H NMR spectra of **4l**

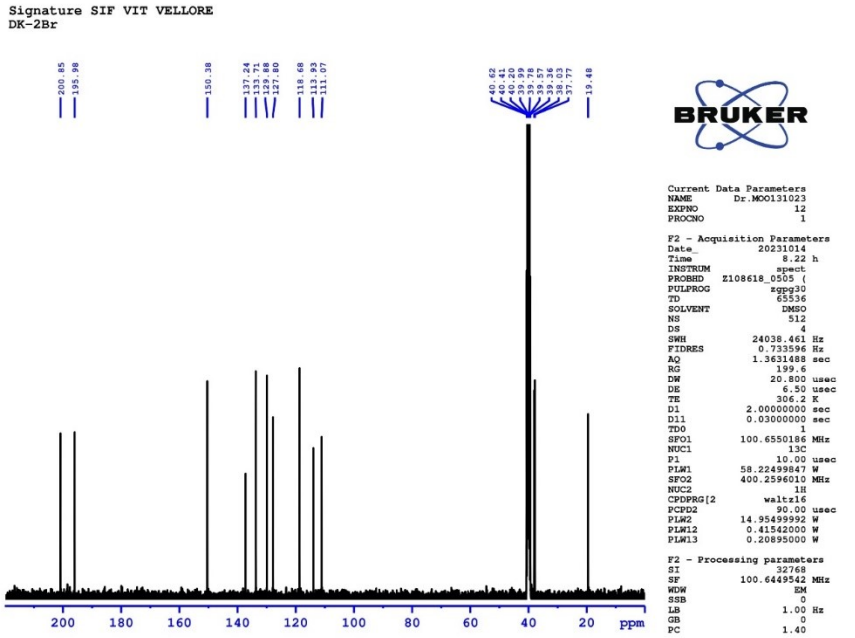


Fig. S56 ^{13}C NMR spectra of **4l**

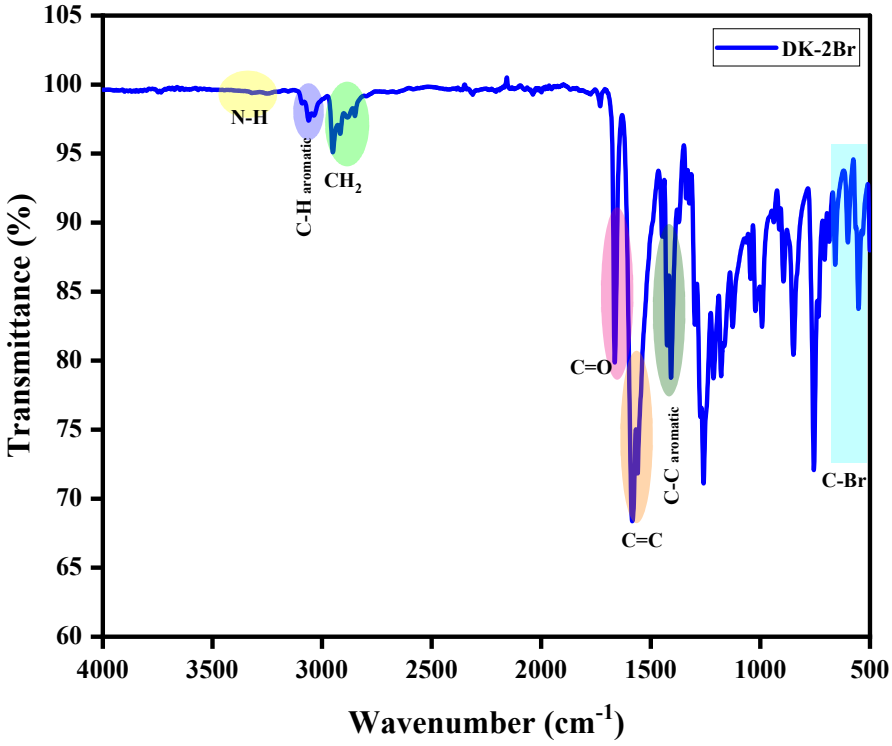


Fig. S57 FT-IR spectra of **4l**

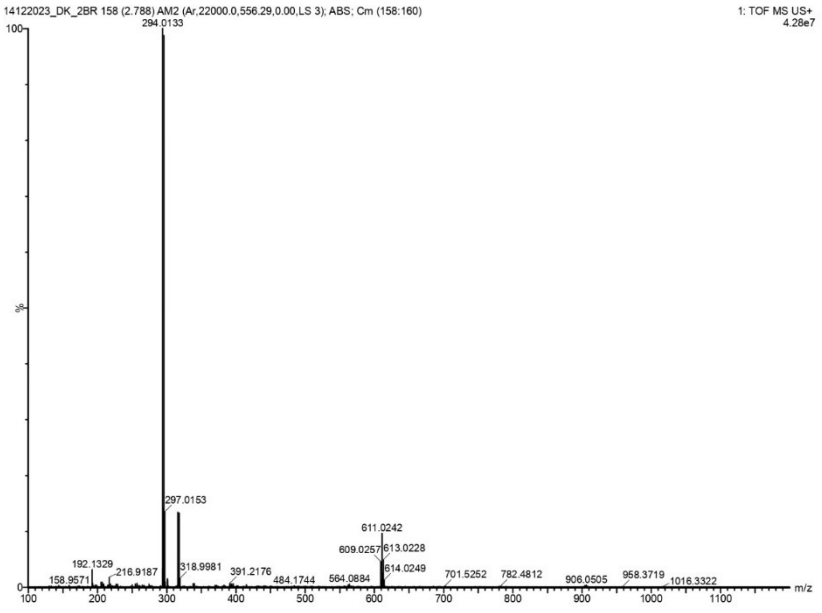


Fig. S58 HR-MS spectra of **4l**

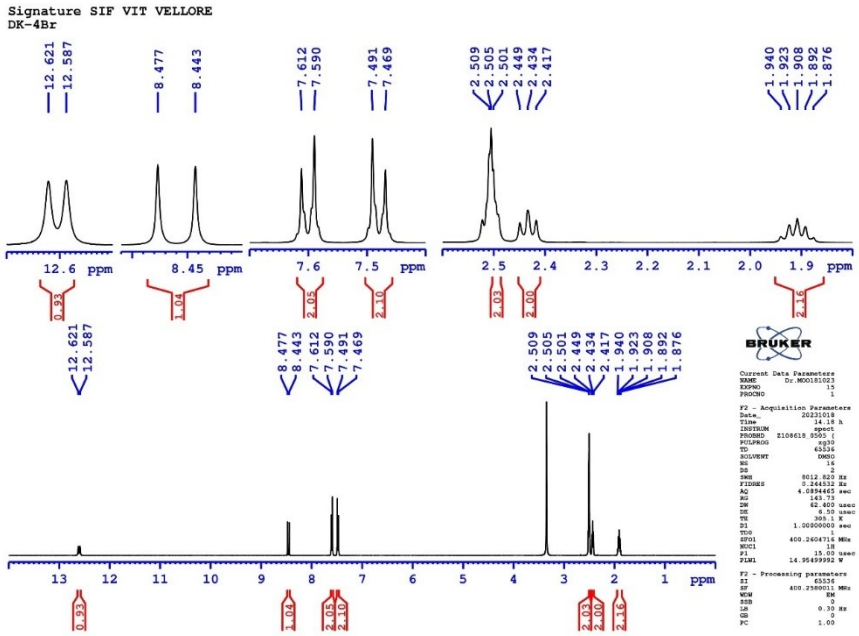


Fig. S59 [1]H NMR spectra of **4m**

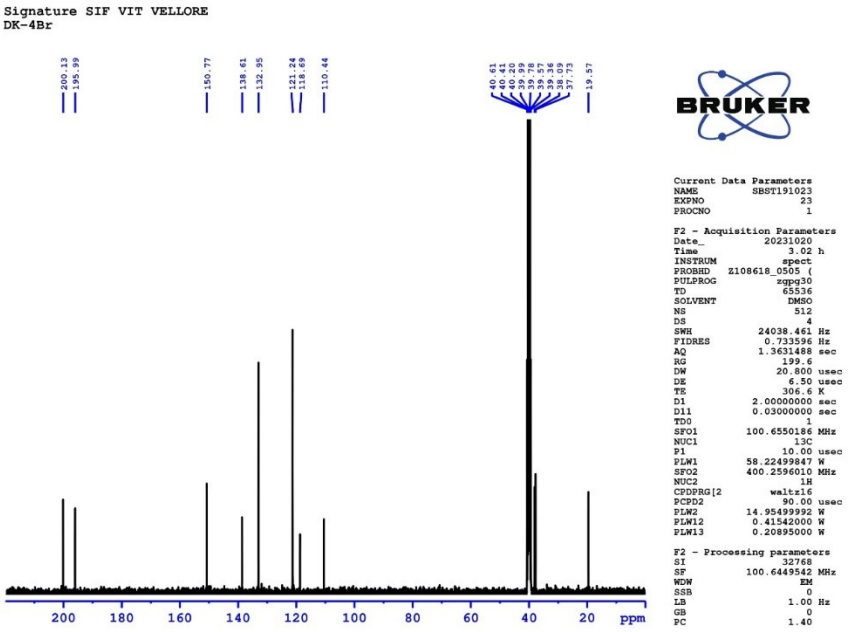


Fig. S60 [13]C NMR spectra of **4m**

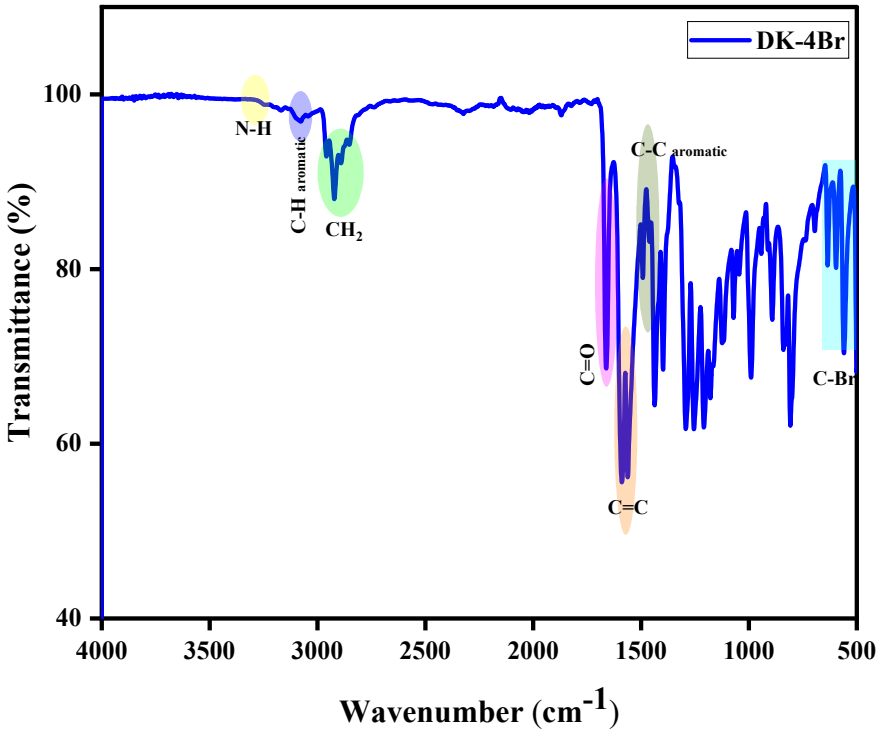


Fig. S61 FT-IR spectra of **4m**

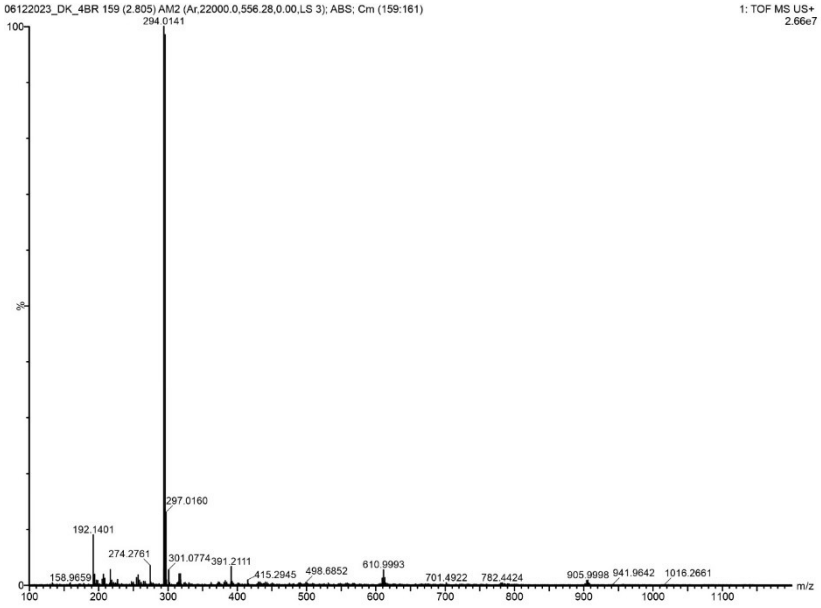


Fig. S62 HR-MS spectra of **4m**

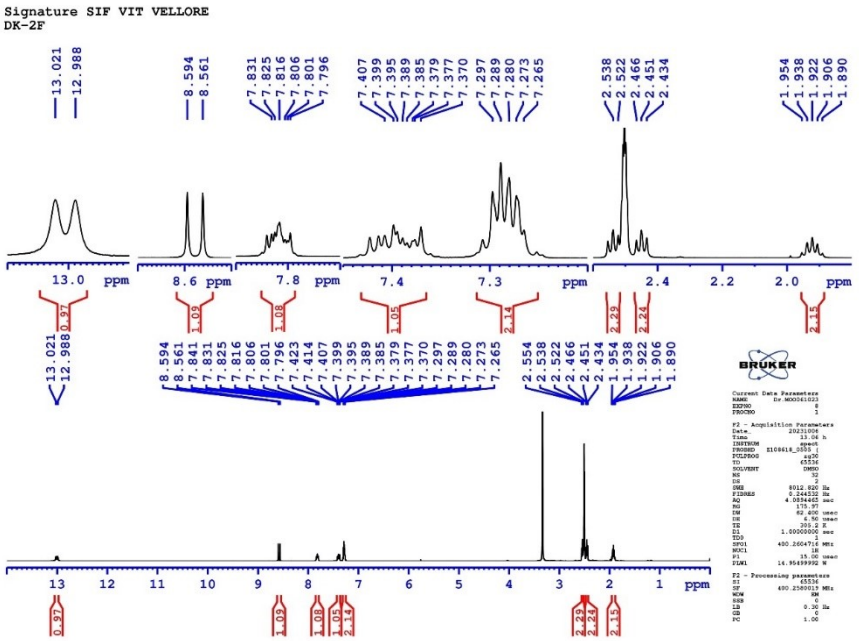


Fig. S63 ^{1}H NMR spectra of **4n**

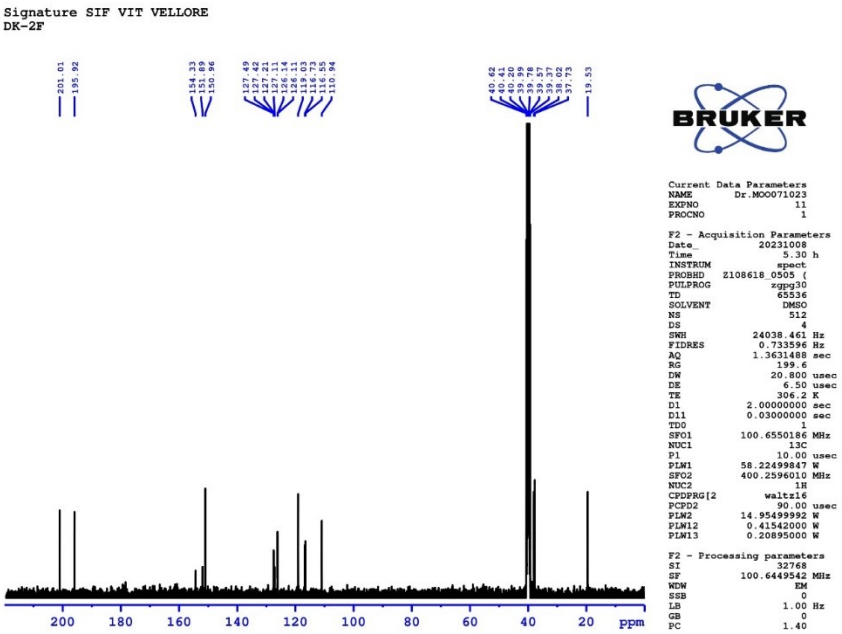


Fig. S64 ^{13}C NMR spectra of **4n**

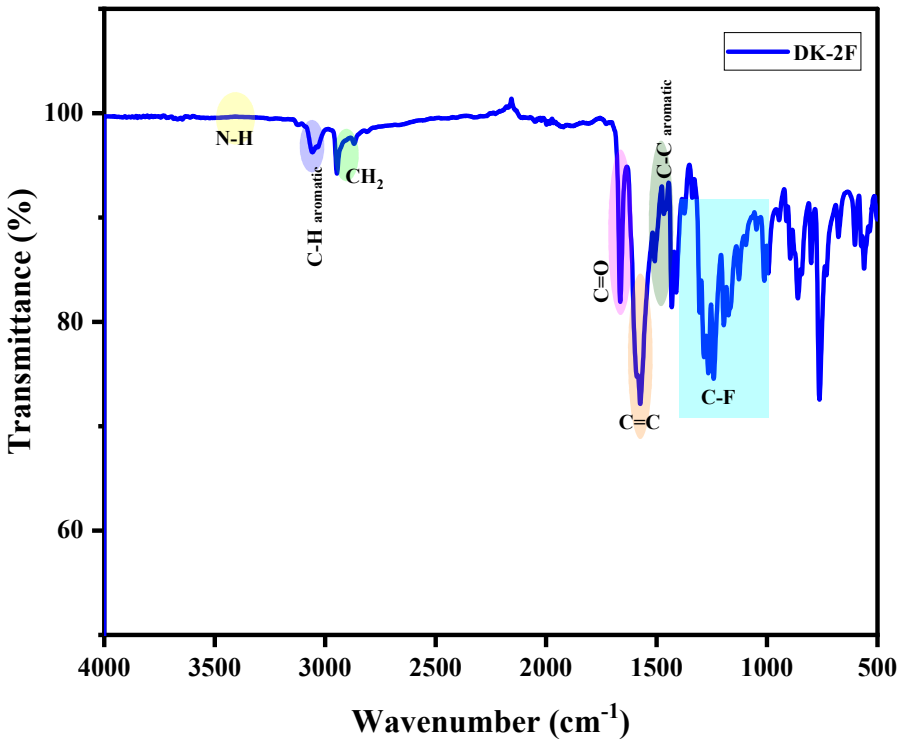


Fig. S65 FT-IR spectra of **4n**

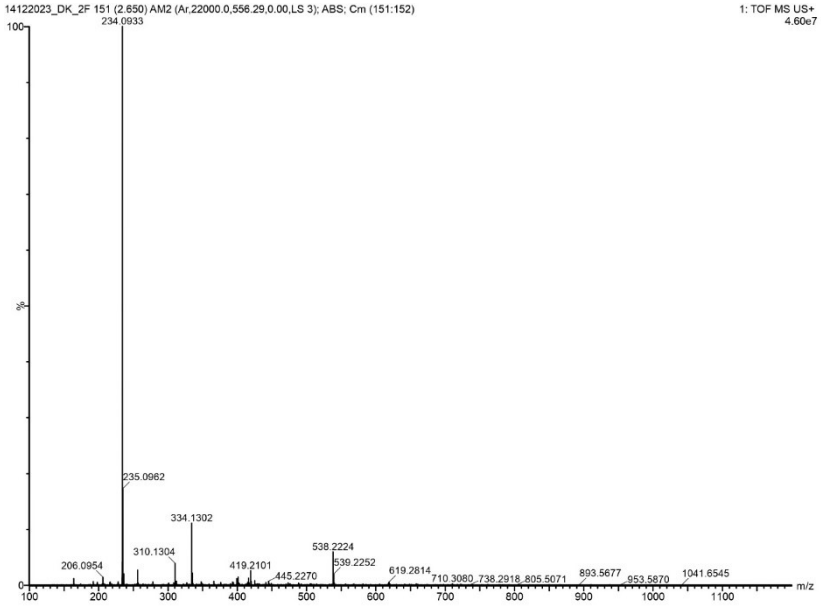


Fig. S66 HR-MS spectra of **4n**

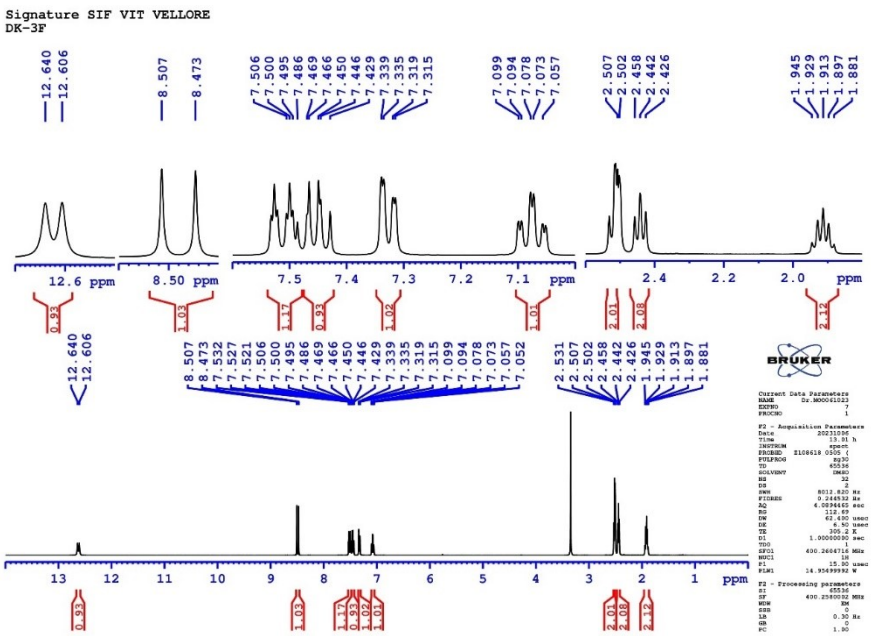


Fig. S67 ^{1}H NMR spectra of **4o**

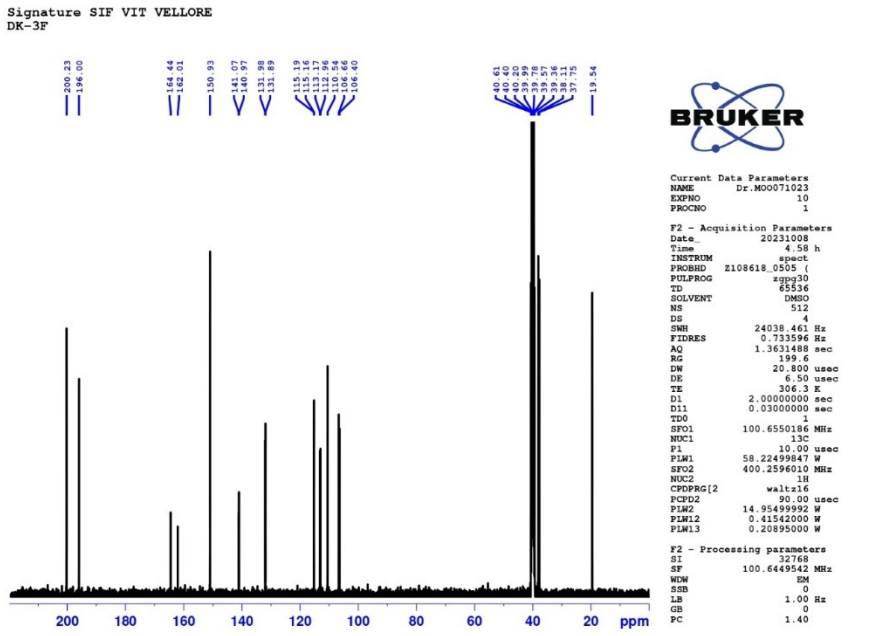


Fig. S68 ^{13}C NMR spectra of **4o**

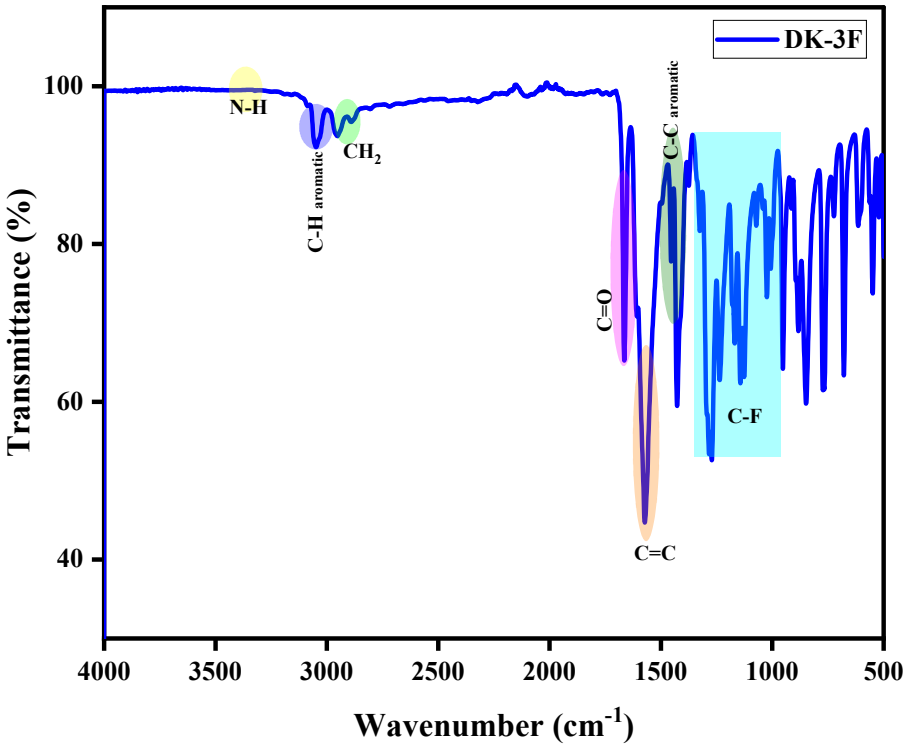


Fig. S69 FT-IR spectra of **4o**

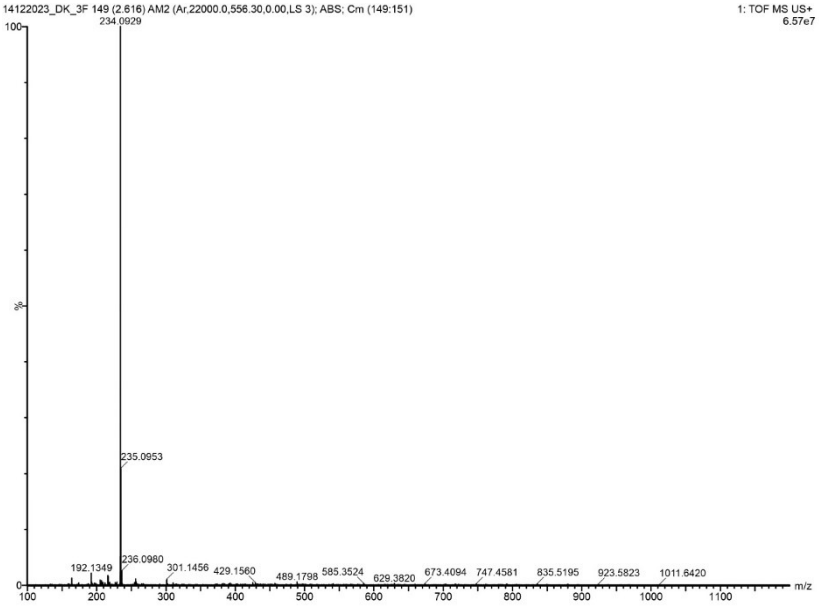


Fig. S70 HR-MS spectra of **4o**

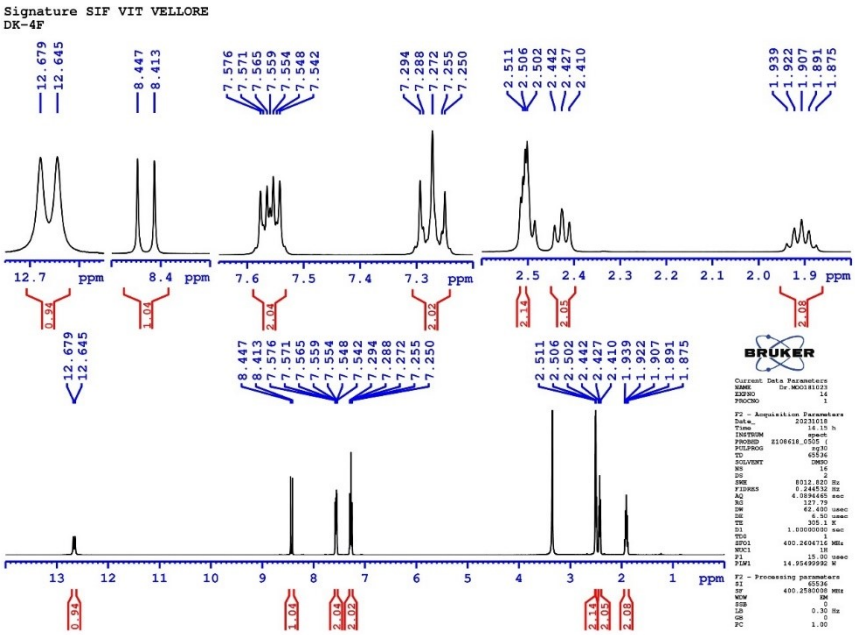


Fig. S71 ^{1}H NMR spectra of **4p**

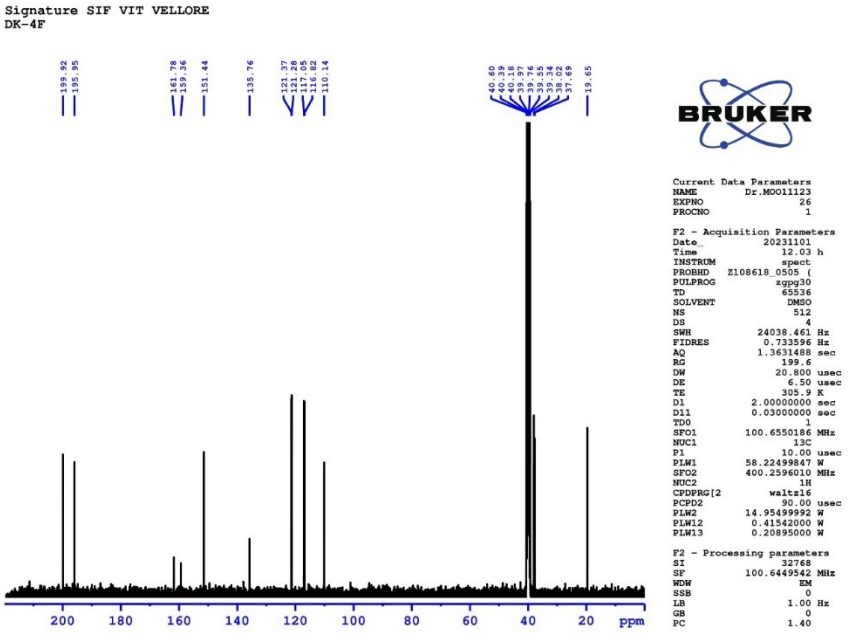


Fig. S72 ^{13}C NMR spectra of **4p**

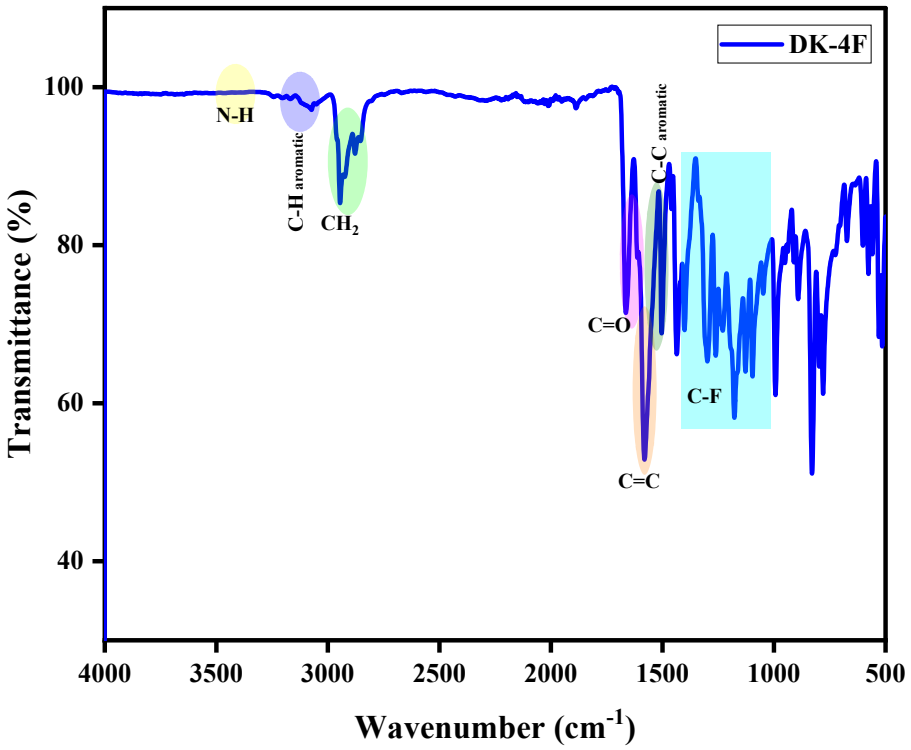


Fig. S73 FT-IR spectra of **4p**

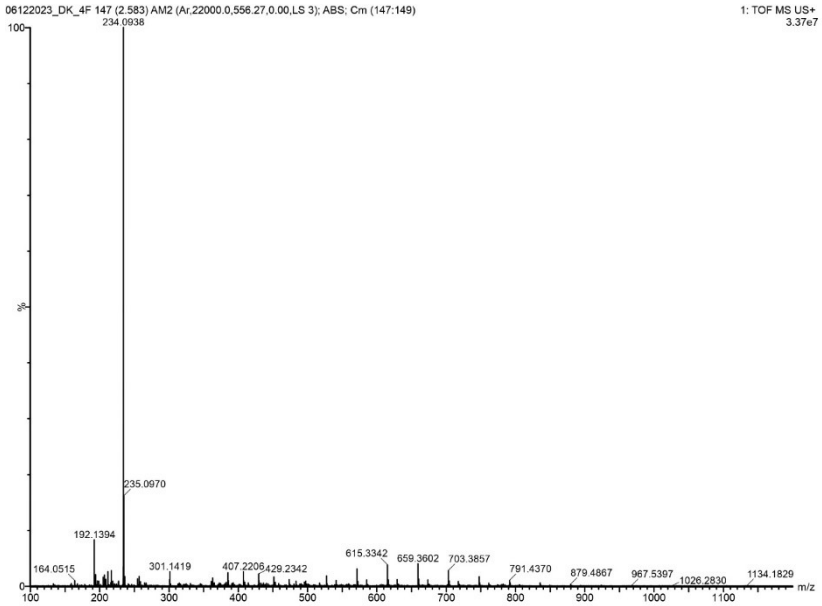


Fig. S74 HR-MS spectra of **4p**

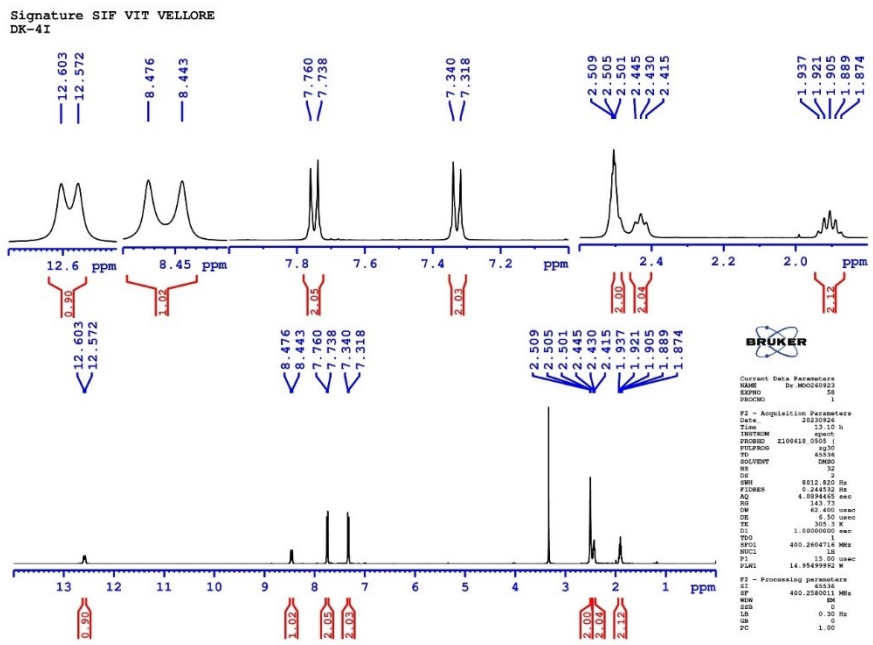


Fig. S75 ^{1}H NMR spectra of **4q**

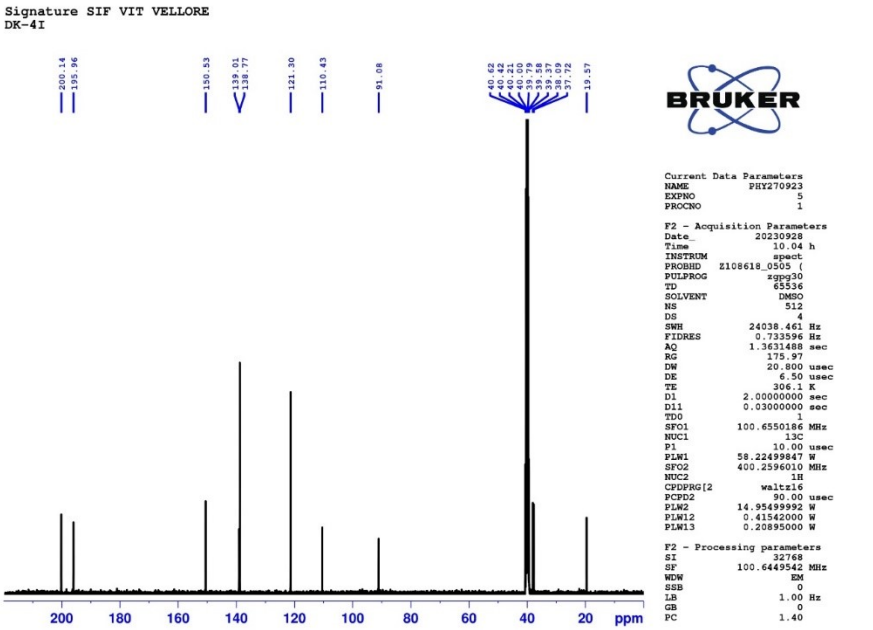


Fig. S76 ^{13}C NMR spectra of **4q**

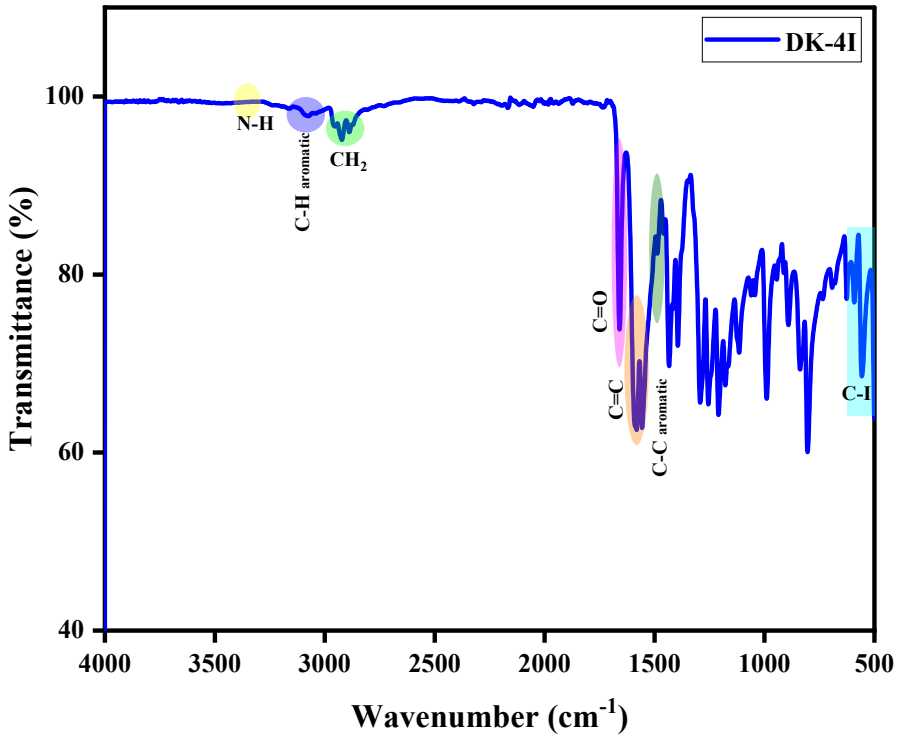


Fig. S77 FT-IR spectra of **4q**

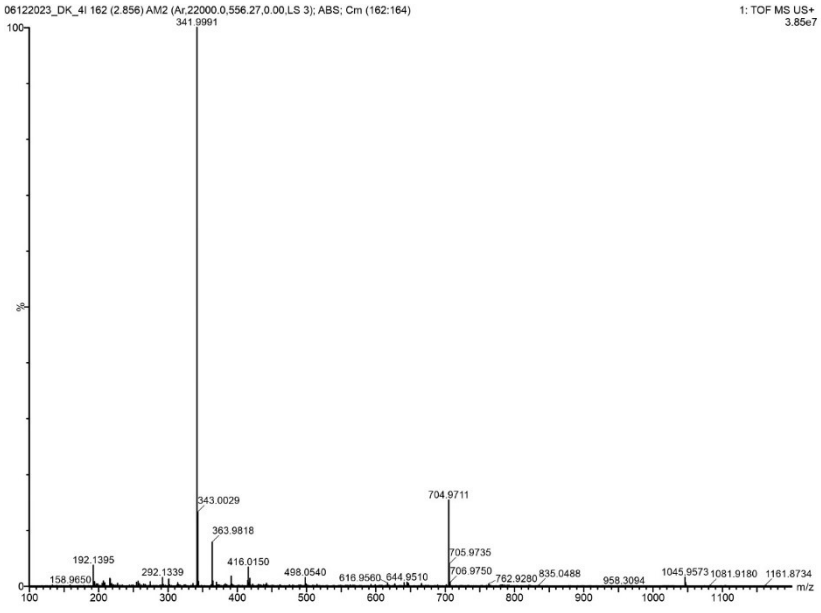


Fig. S78 HR-MS spectra of **4q**