Chickpea Leaf Exudates: A green Bronsted acid type biosurfactant for bis(indole)methanes and bis(pyrazolyl)methanes synthesis

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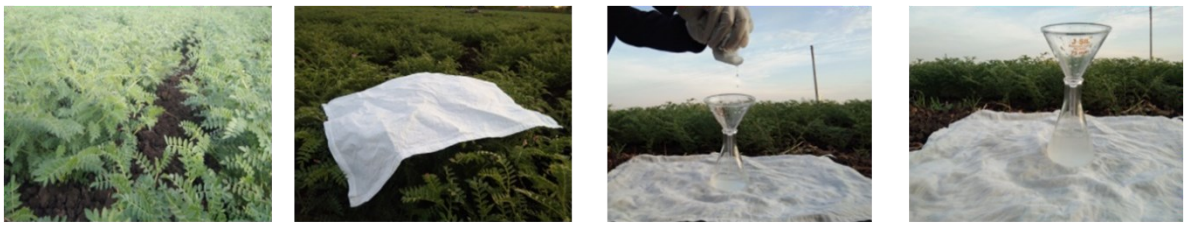
Electronic Supplemental Information (ESI)

1. Experimental section:

1.1 Collection of catalyst

For quantitative collection of *CLE* as a catalytic medium we consider growing period of newly cultivated chickpea crops. At first, for the purpose of exudates collection cultivated crops on various lands were selected and then exudates were collected manually using clean and soft cotton cloth by absorption-wringing process. It was observed that good quantity of exudates was obtained from chickpea crops of two months old (just before flowering stage). It was also observed that early morning (5.00 am to 6.00 am) period gave good collection of exudates (ESI). The pH of collected exudates was measured using pH-meter before use and it was found to be 1.1. The collected catalyst was stored several days at 5 ^{o}C.



(a) (b) (c) (d)

Fig. 1 (a) Cultivated *Chickpea crops* (b) absorption of *Chickpea exudates* by cotton cloth (c) wringing of *Chickpea exudates* (d) turbid *Chickpea leaf exudates*

1.2 General procedure for the synthesis of 3-((1H-indol-3-yl)(4-methoxyphenyl)methyl))-1*H*-indol

All the reactions were carried out under air atmosphere in pre-dried glassware. A mixtures of indoles (2.0 mmol), and aryl aldehydes (1.0 mmol) in solution of *CLE* (5.0 mL) and *iso*-PrOH (3.0 mL) were stirred at 60 ^{o}C in preheated oil bath till the completion of reaction as indicated by TLC (petroleum ether: ethyl acetate). After completion of reaction, 5.0 mL water was added in reaction mixture. The solid products were separated by simple filtration followed by washing with cold water 5.0 mL. The pure products were obtained by recrystallization with 96 % ethanol. All the products were confirmed by the spectroscopic method using NMR and FT-IR. The physical and spectroscopic data are in consistent with the proposed structures and are in harmony with the literature values.

1.3 General procedure for synthesis of 4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(4-methoxyphenyl)methyl)-3-methyl-1H-pyrazol-5-ol

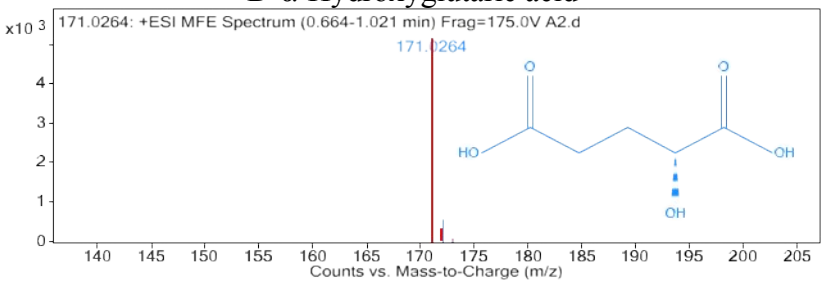
In a 25 mL round bottom flask aryl aldehyde (1.0 mmol), ethyl acetoacetate (2.0 mmol), hydrazine hydrate (2.0 mmol) were placed in solution of *CLE* (5.0 mL) in *iso*-PrOH (3.0 mL) and stirred at 60 ^{o}C in preheated oil bath till the completion of reaction as indicated by TLC (petroleum: ethyl acetate). After completion of reaction, 5.0 mL water was added in reaction mixture. The solid products were separated by simple filtration followed by washing with cold water 5.0 mL. The pure products were obtained by recrystallization with 96 % ethanol. Representative compounds were confirmed by physical constants and characterized by spectral analysis.

1.4 Recycle of catalyst

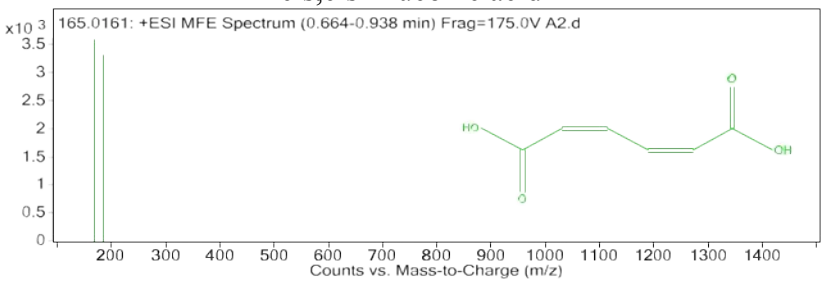
In order to investigate the recyclability and reusability of *CLE* catalyst, we synthesized compounds **3a** and **7a**. After completion of reaction, H_2O (5.0 mL) was added in reaction mixture and then it was filtered off. Whole filtrate containing *CLE* was concentrated under vacuum and directly used for the next cycle with fresh reactants for synthesis of **3a** and **7a** in *iso*-PrOH at 60^{o}C. The recovered catalyst was employed for further five successful recycles without significant lose of efficiency. However, reaction times were found to be increased while reuse of the recovered catalyst (Fig. **9**).

HPLC-MS spectra of all acids are present in *Chickpea Leaf Exudates*:

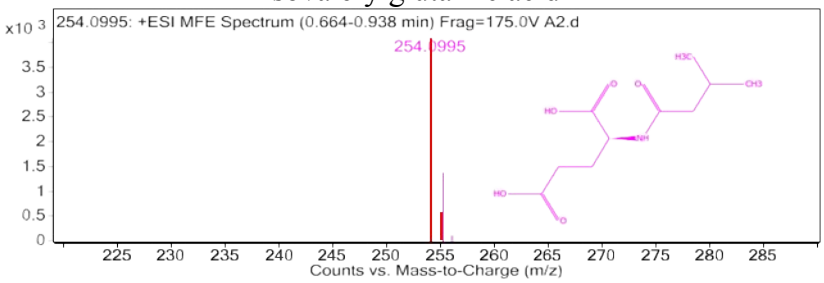
D-α-Hydroxyglutaric acid



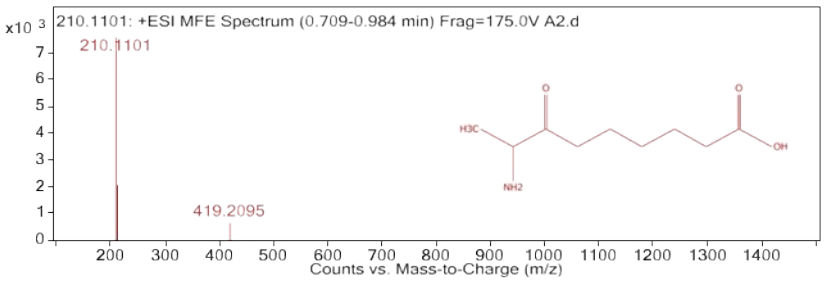
cis,cis-Muconic acid



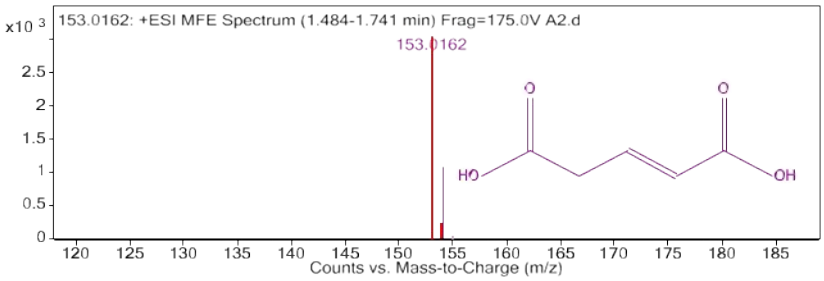
Isovalerylglutamic acid



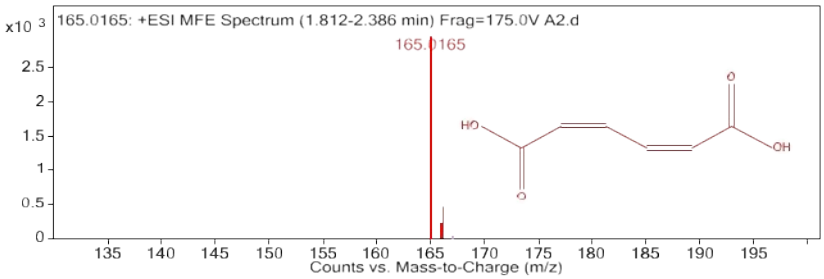
KAPA



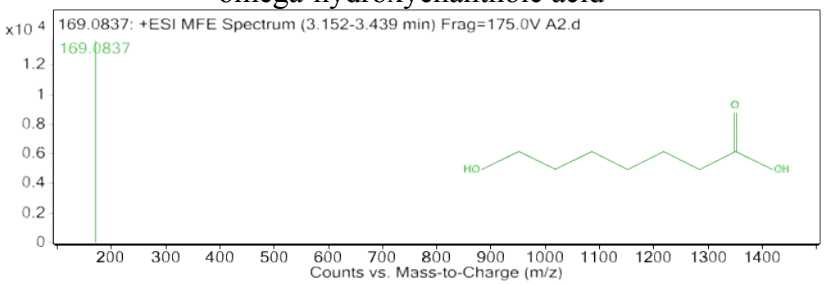
Glutaconic acid



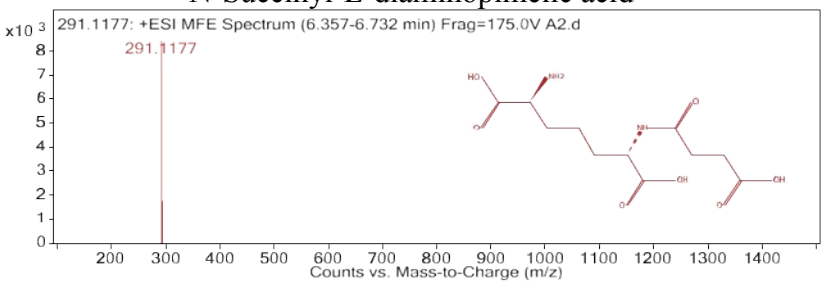
cis,cis-Muconic acid



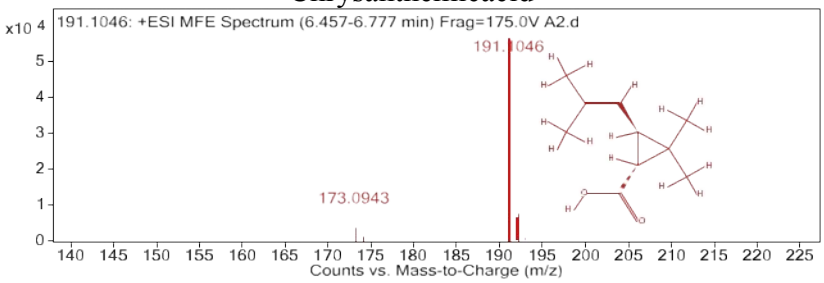
omega-hydroxyenanthoic acid



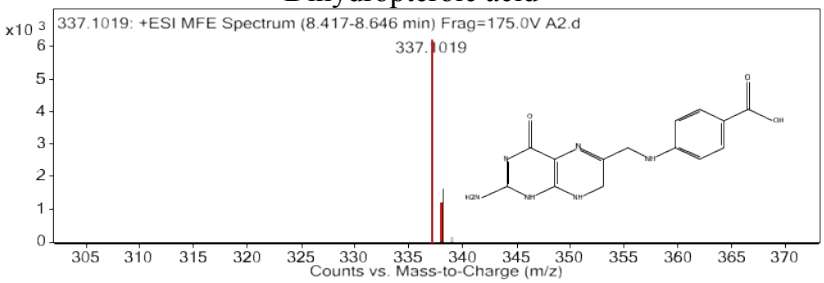
N-Succinyl-L-diaminopimelic acid



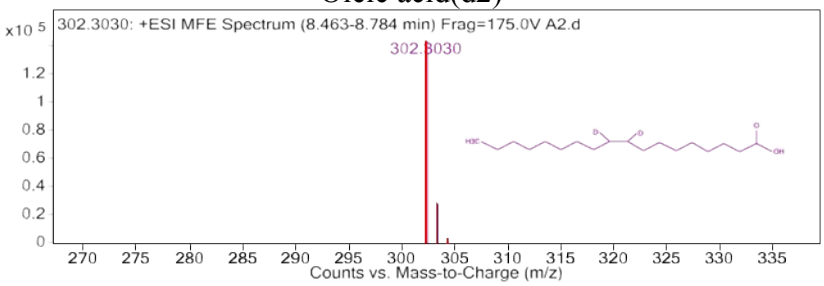
Chrysanthemicacid



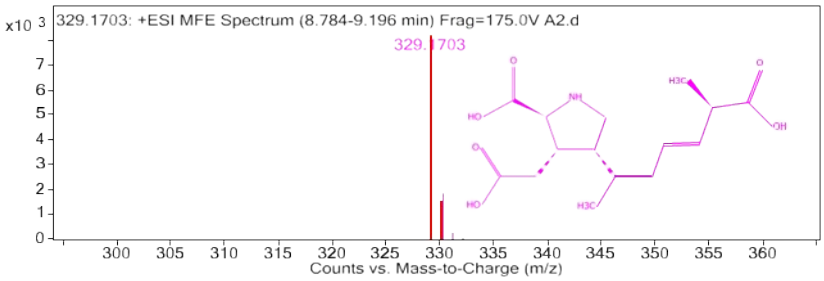
Dihydropteroic acid



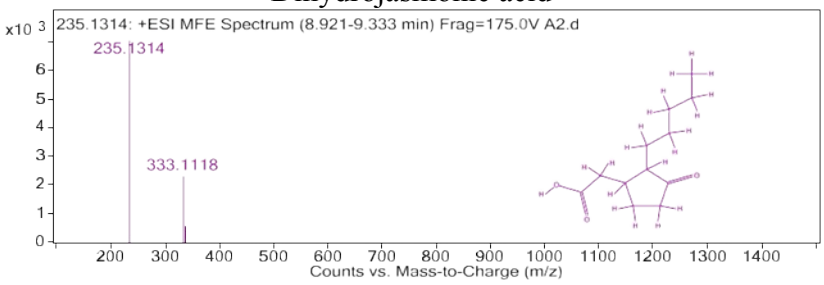
Oleic acid(d2)



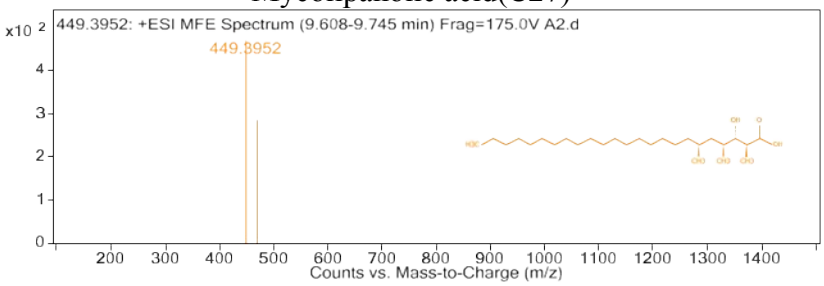
Domoic acid



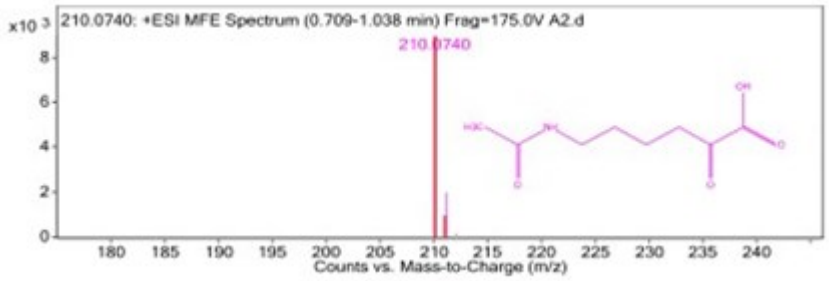
Dihydrojasmonic acid



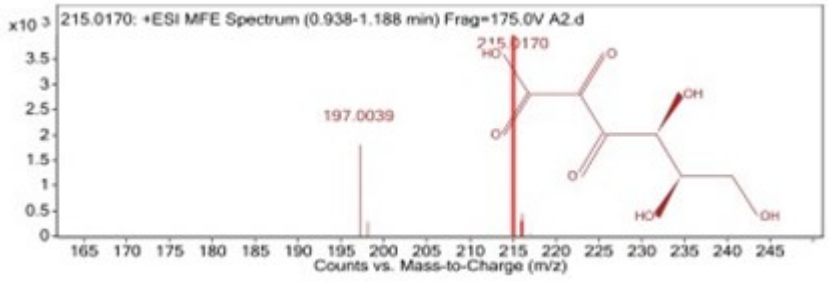
Mycolipanolic acid(C27)



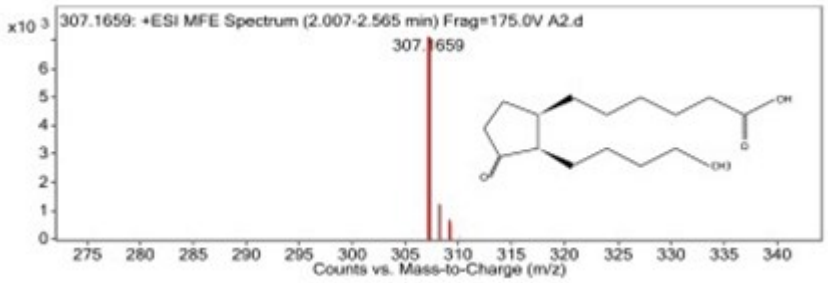
2-Keto-6-acetamidocaproate



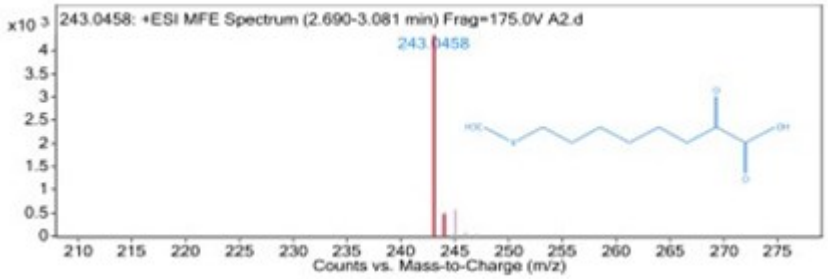
2,3-Dioxogulonic acid



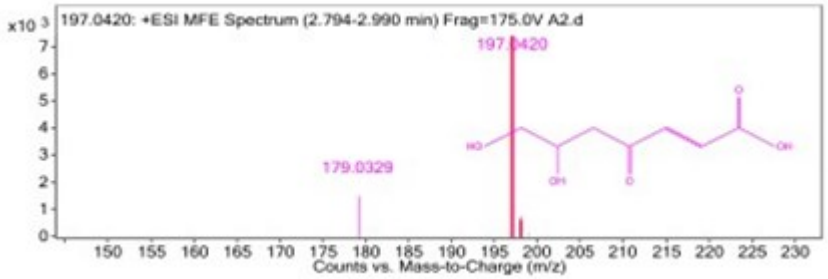
(1R,2R)-3-oxo-2-pentyl-cyclopentanehexanoic acid



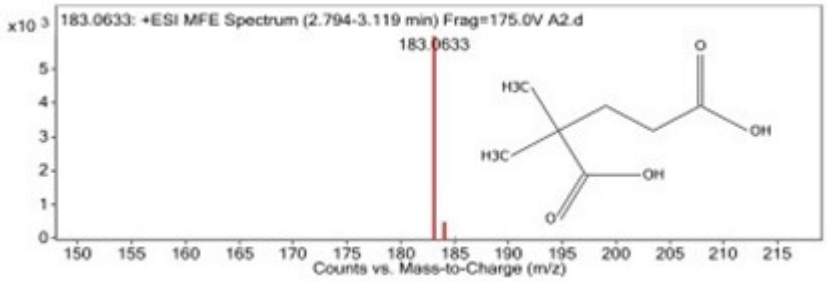
2-Oxo-8-methylthiooctanoic



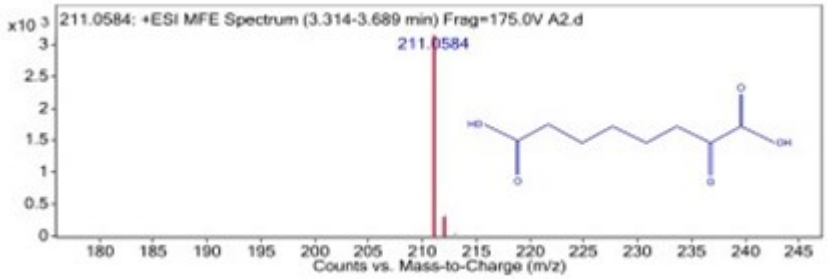
6,7-dihydroxy-4-oxo-2-heptenoic acid



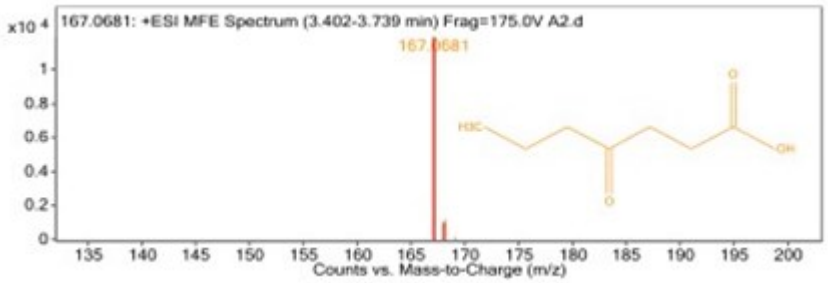
2,2-Dimethylglutaric acid



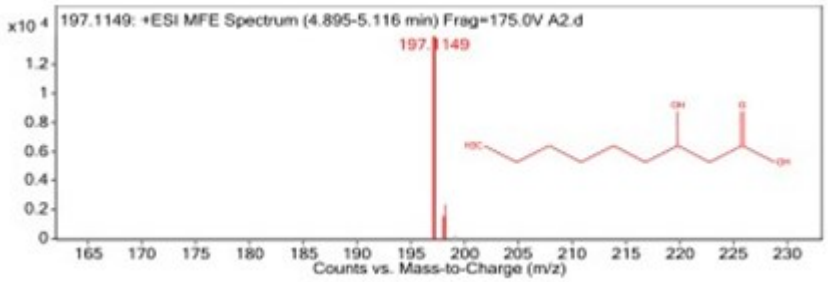
2-Oxosuberate



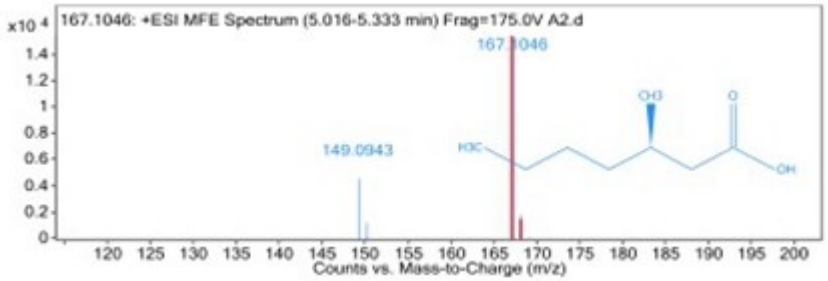
3-butyrl propionic acid



(+)-3-hydroxy pelargonic acid



3R-Methylheptanoic acid



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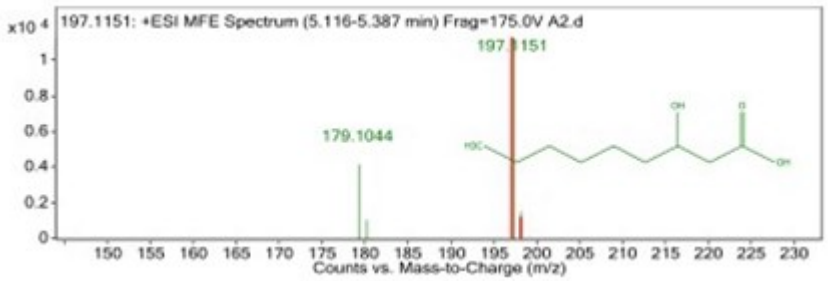
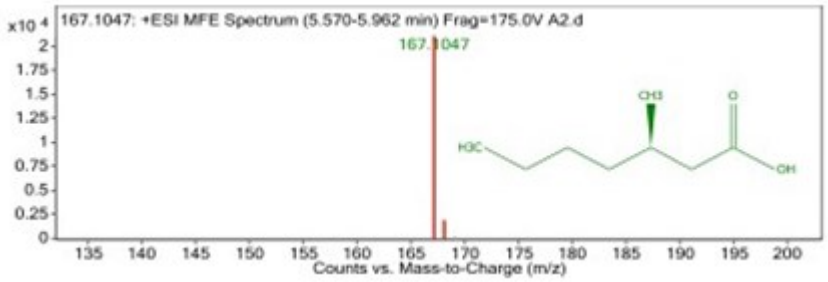
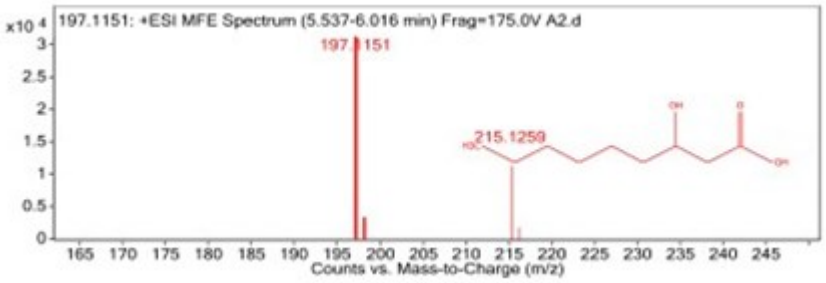


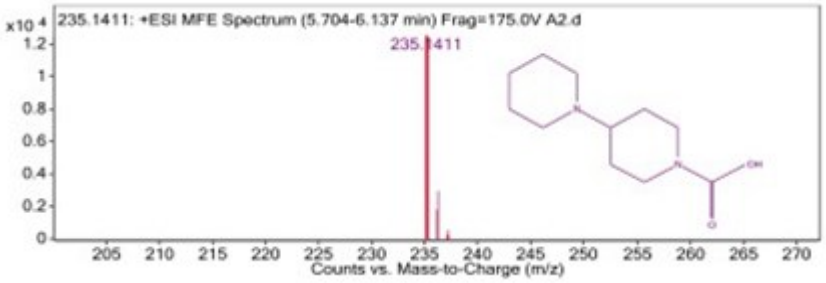
3R-Methylheptanoic acid



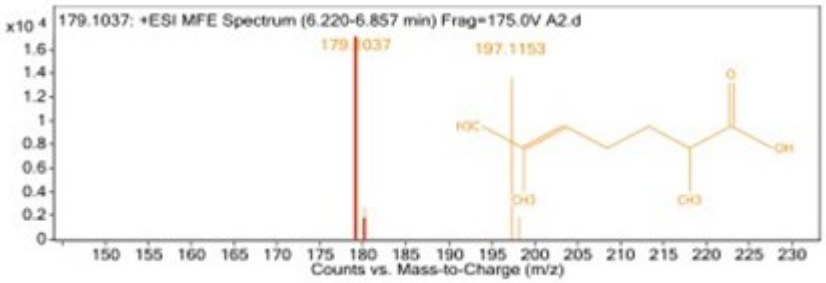
(+)-3-hydroxy pelargonic acid



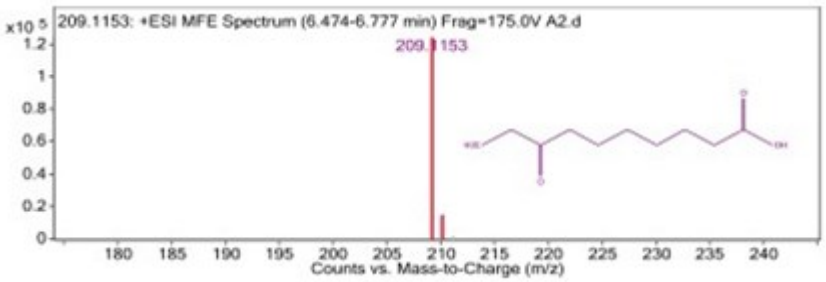
1,4'-Bipiperidine-1'- carboxylic acid



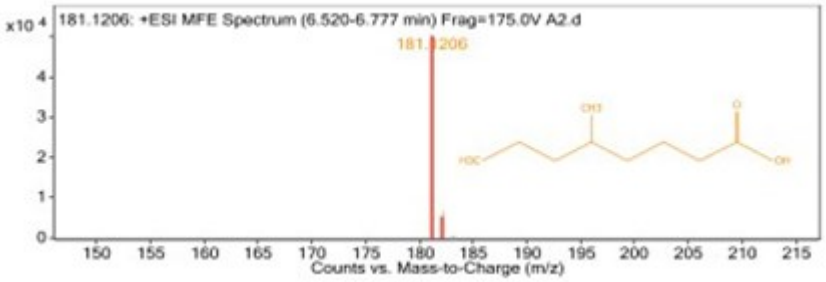
2,6-Dimethyl-5- heptenoic acid 156



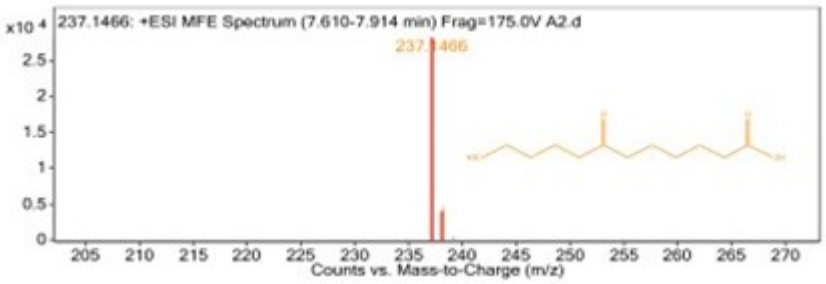
8-oxo capric acid 186



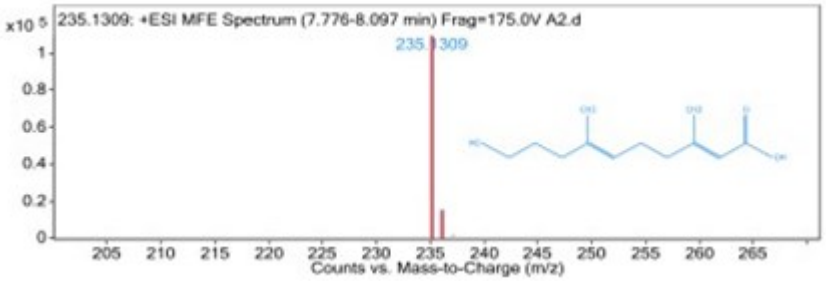
5-methyl-octanoic acid 158



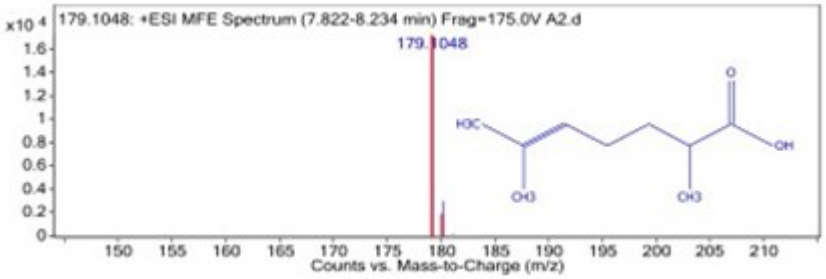
7-Oxododecanoic acid 214



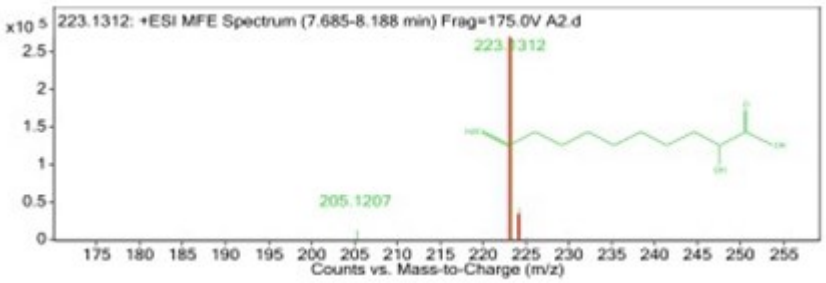
10-Hydroxy-3,7-dimethyl-2E,6E- decadienoic acid



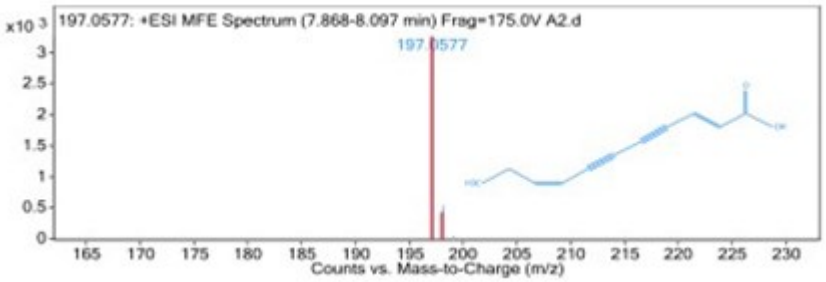
2,6-Dimethyl-5- heptenoic acid 156



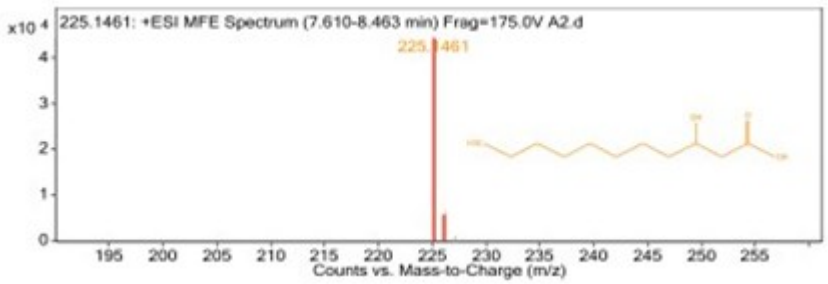
2-hydroxy-10- undecenoic acid 200



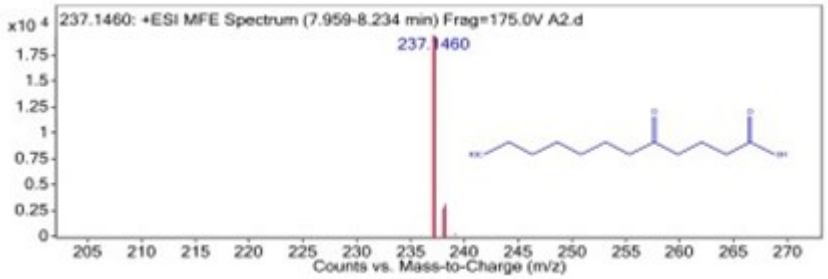
2E,8Z-Undecadiene- 4,6-diynoic acid 174



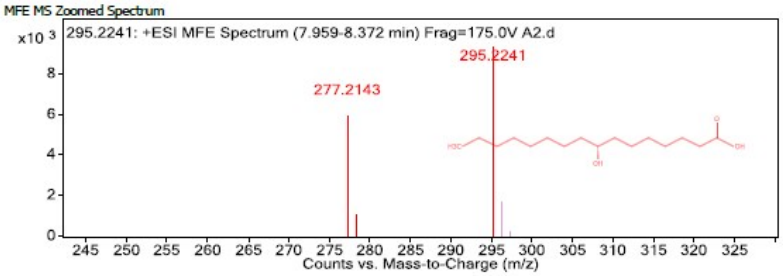
3-hydroxy-undecanoic acid 202



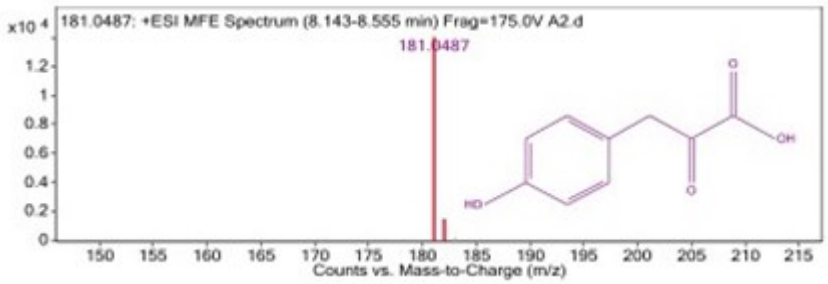
5-Oxododecanoic acid



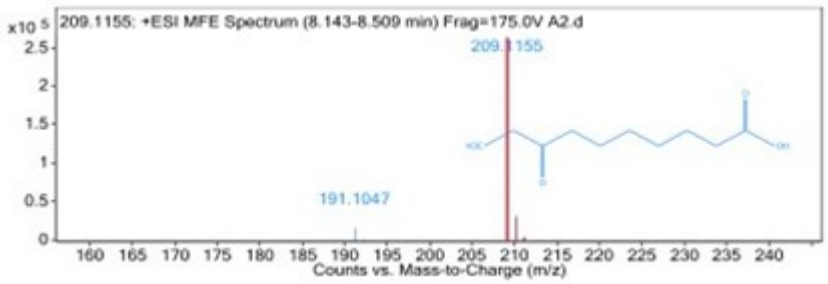
8S-hydroxy- hexadecanoic acid



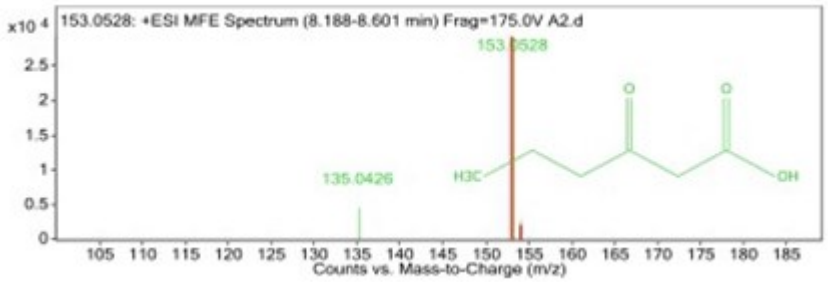
4- Hydroxyphenylpyruvic



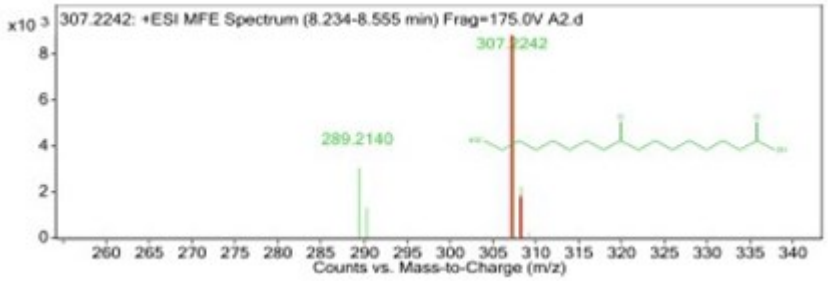
8-oxo capric acid



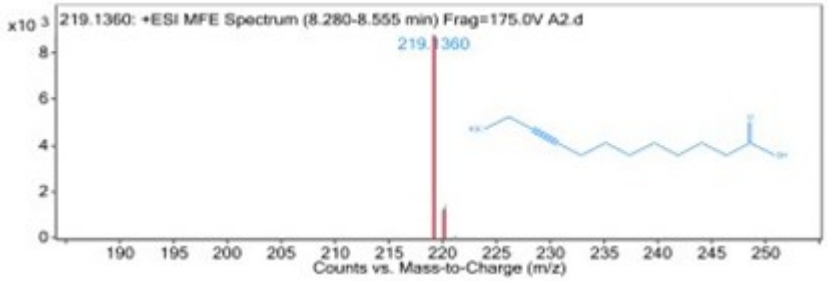
3-keto-n-caproic acid



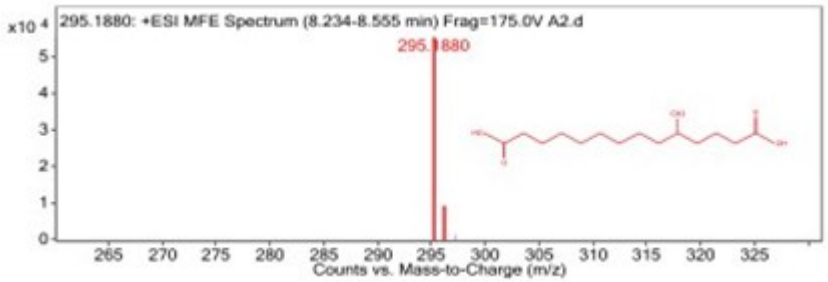
9-Keto heptadecylic acid



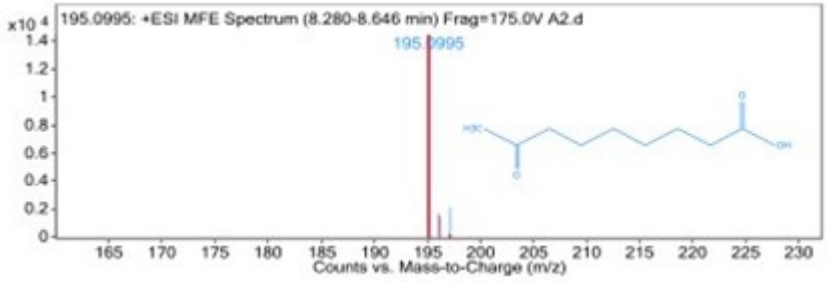
9-dodecynoic acid



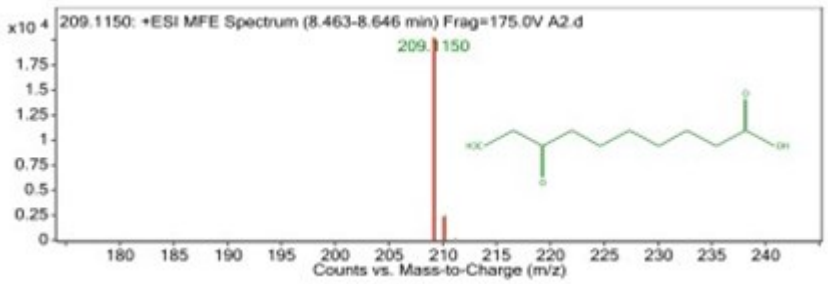
5-methyl- tetradecanedioic acid



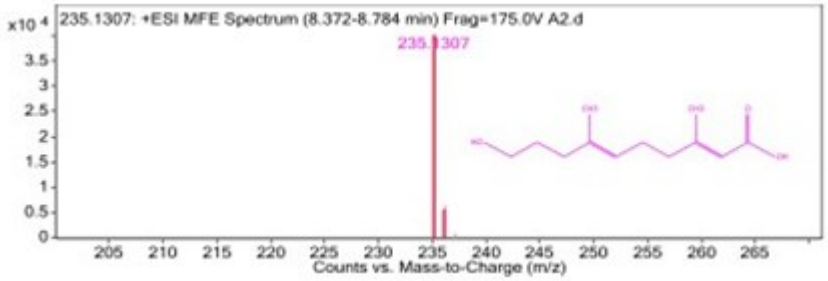
8-oxo-nonanoic acid



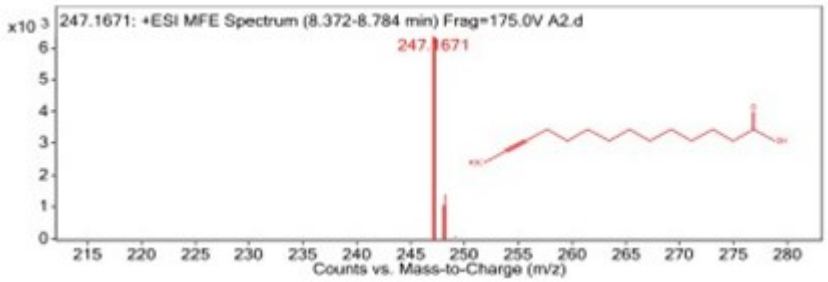
8-oxo capric acid



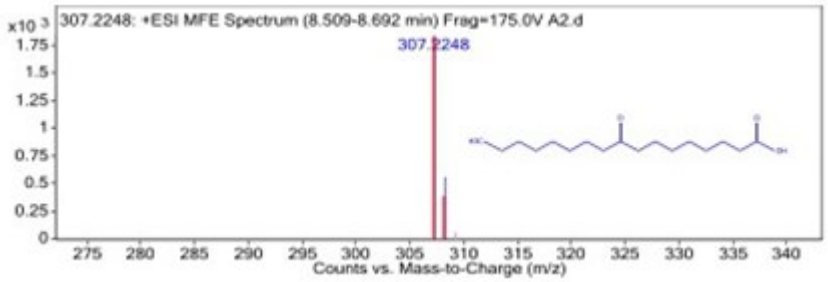
10-Hydroxy-3,7- dimethyl-2E,6E- decadienoic acid



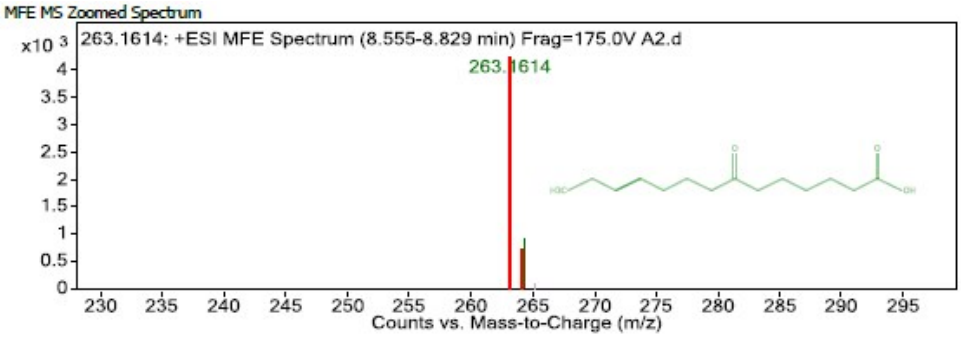
12-tetradecynoic acid



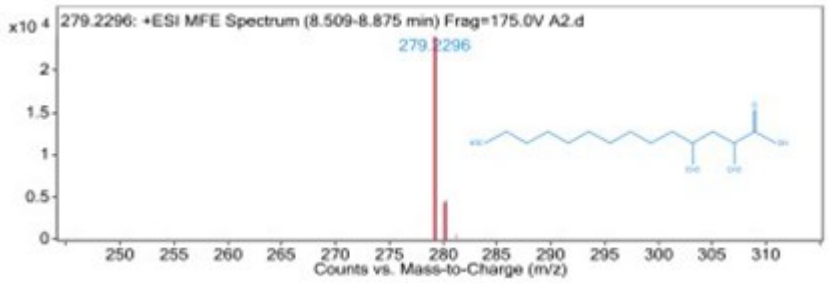
9-Keto heptadecylic acid



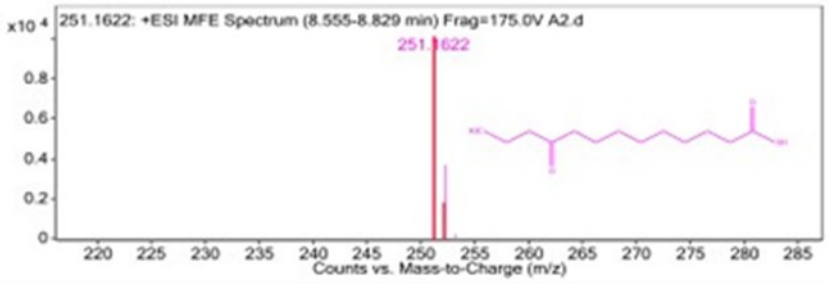
7-oxo-11E- Tetradecenoic acid



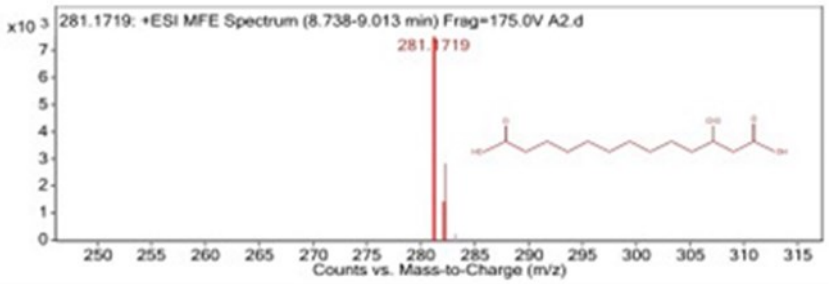
2,4-dimethyl-tetradecanoic acid



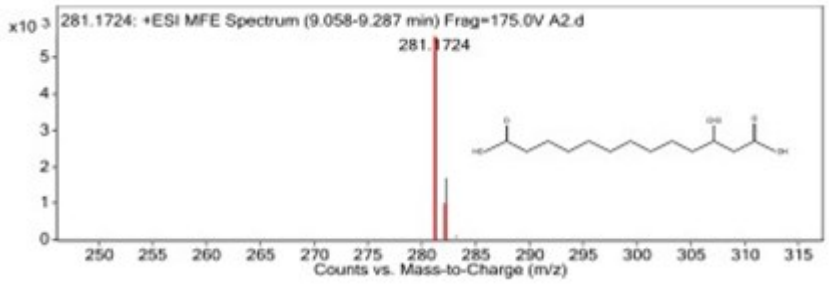
10-keto tridecanoic acid



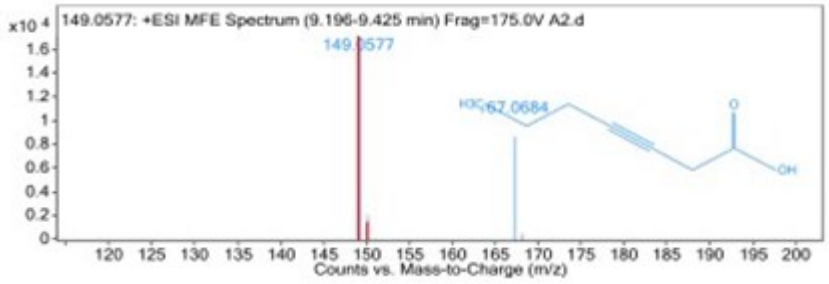
3-methyl-tridecanedioic acid



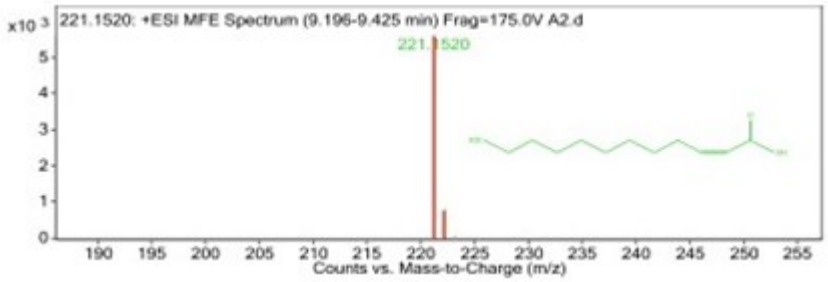
3-methyl-tridecanedioic acid



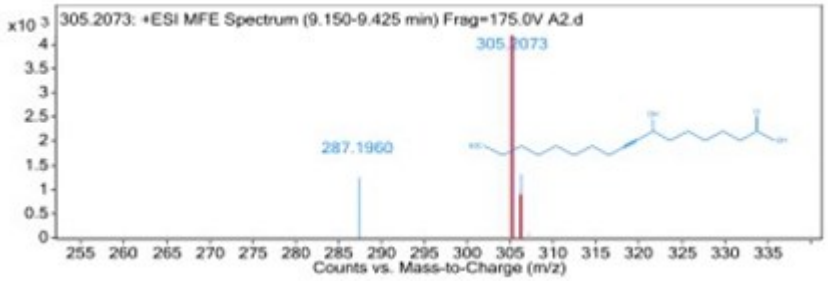
3-heptynoic acid



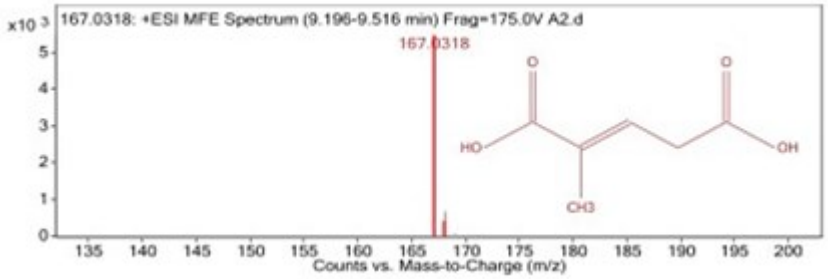
2Z-dodecenoic acid



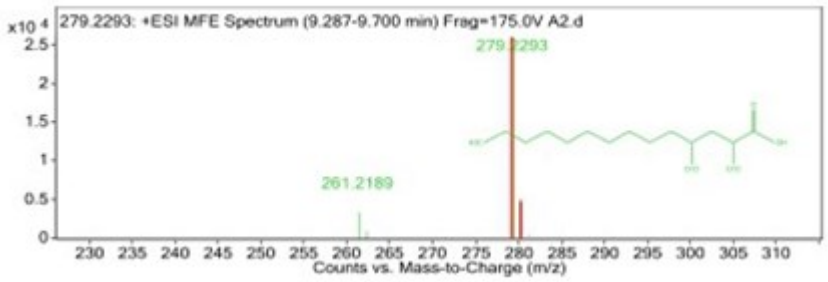
7-hydroxy-10-heptadecen-8-ynoic acid



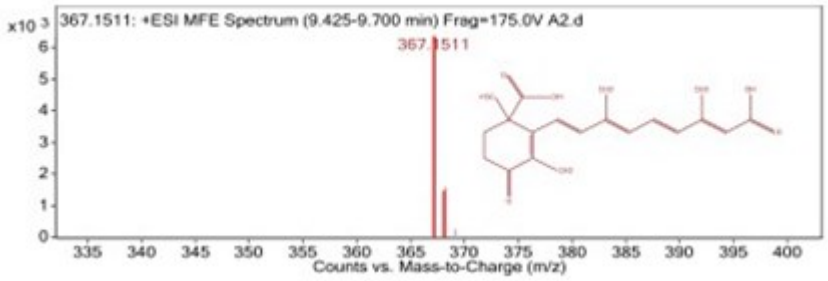
(E)-2-Methylglutaconic acid



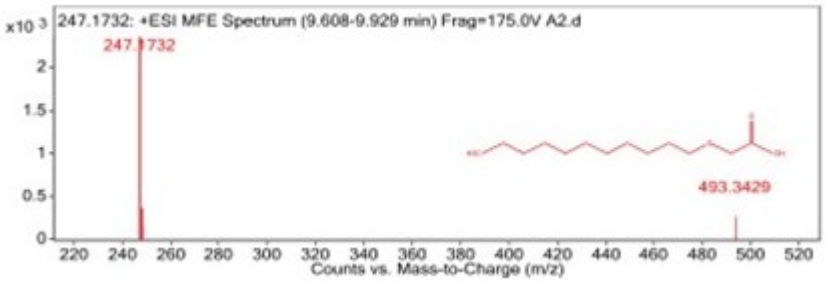
2,4-dimethyl- tetradecanoic acid



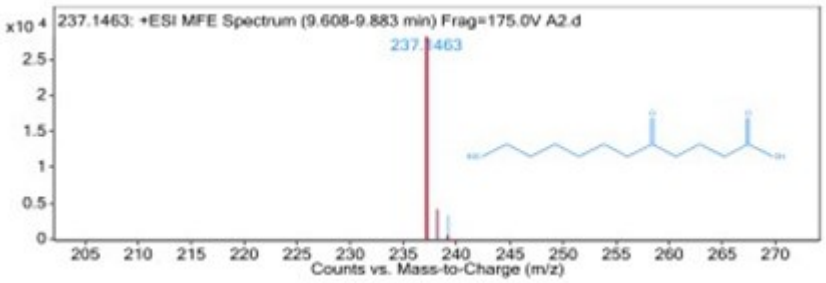
16-Hydroxy-4- carboxyretinoic acid



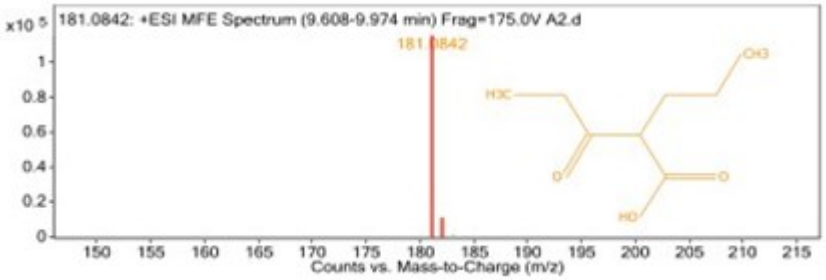
3-Thiatetradecanoic Acid



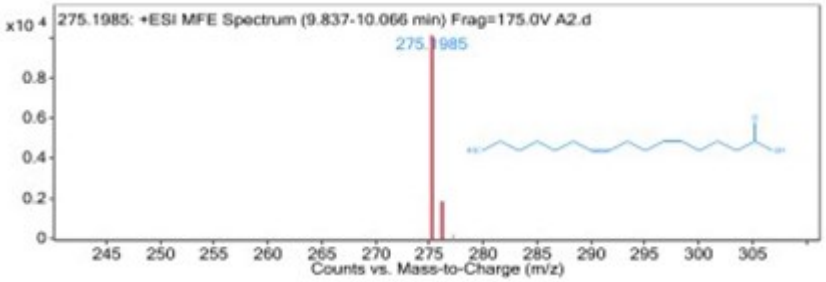
5-Oxododecanoic acid



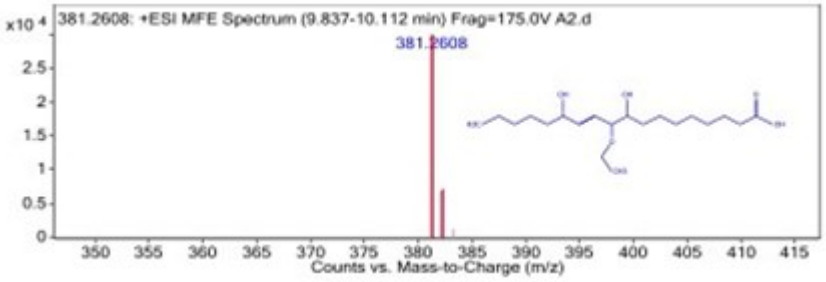
3-Oxovalproic acid



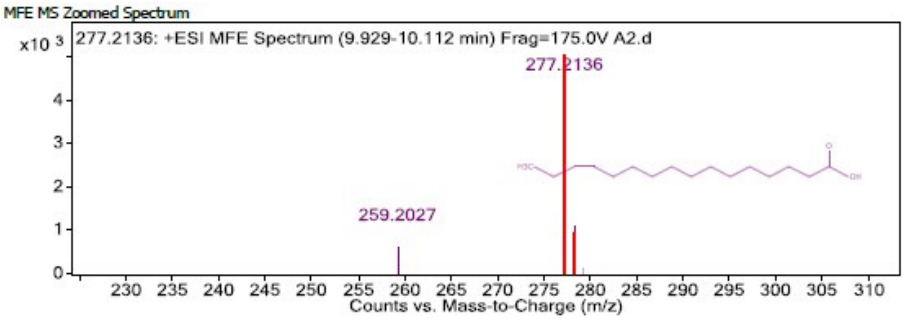
5Z,9Z-hexadecadienoic acid



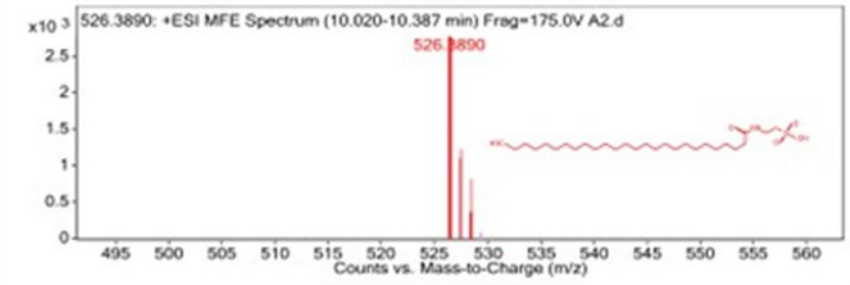
9,13-dihydroxy-10- ethoxy-11- octadecenoic acid



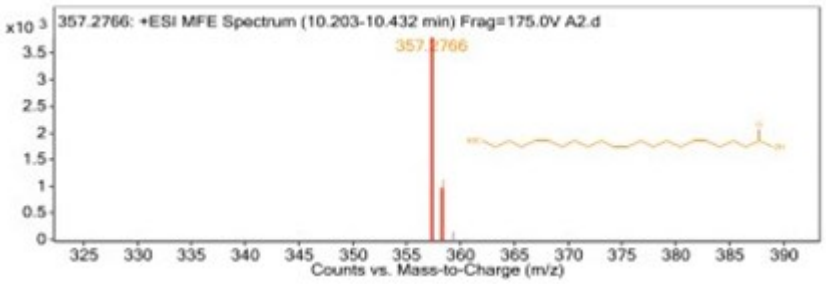
13Z-hexadecenoic acid



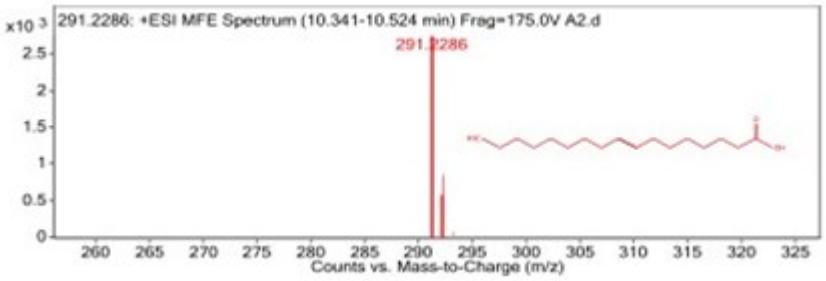
2-hexacosanamidoethanesulfonic acid



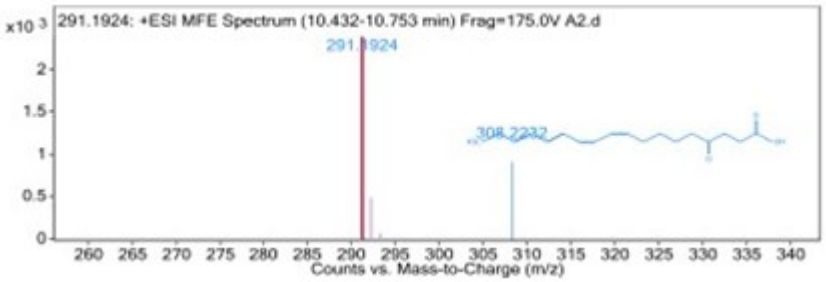
5Z,11Z,17Z-docosatrienoic acid



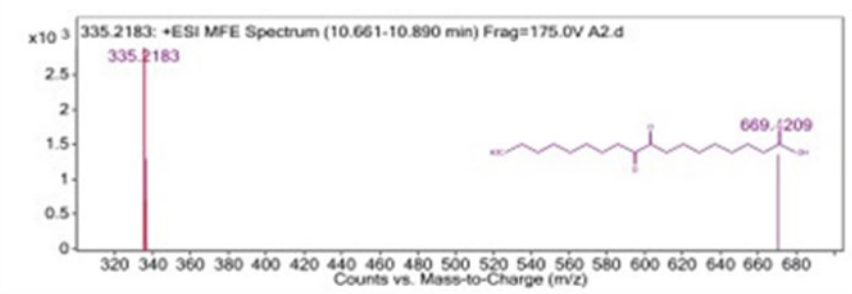
8E-heptadecenoic acid



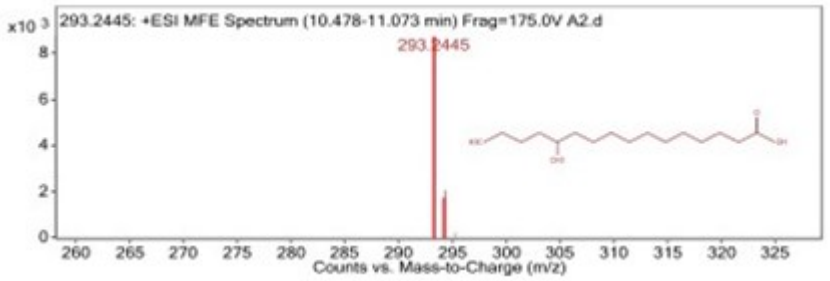
4-oxo-9Z,11Z,13E,15E- octadecatetraenoic acid



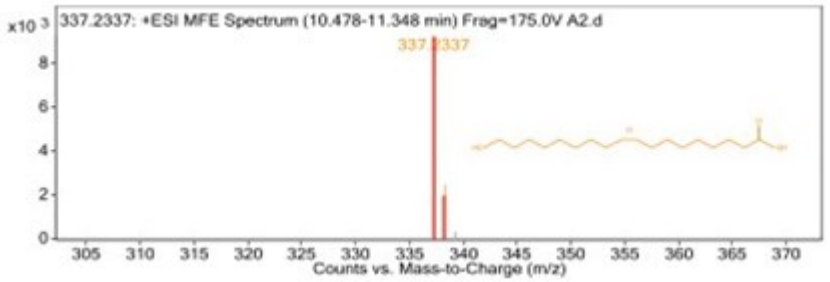
9,10-dioxo- octadecanoic acid



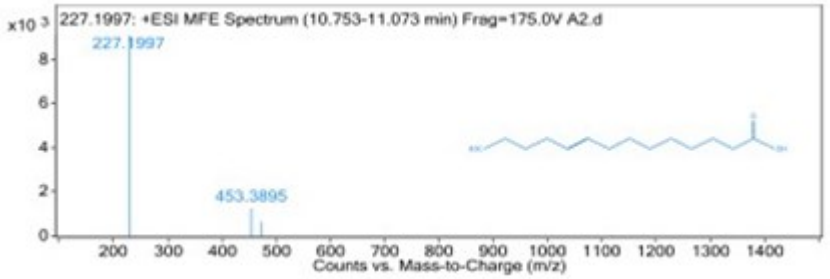
12-methyl-hexadecanoic acid



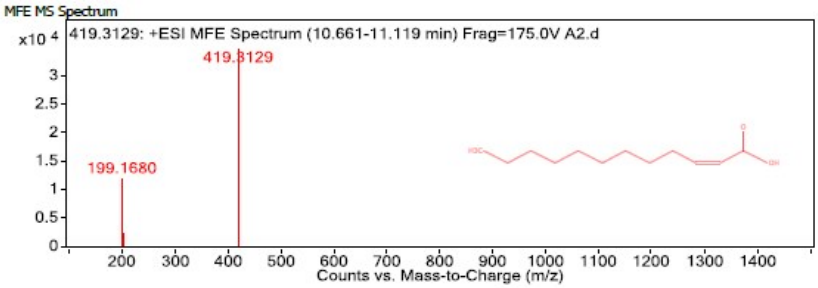
18-hydroxy-9S,10R- epoxy-stearic acid



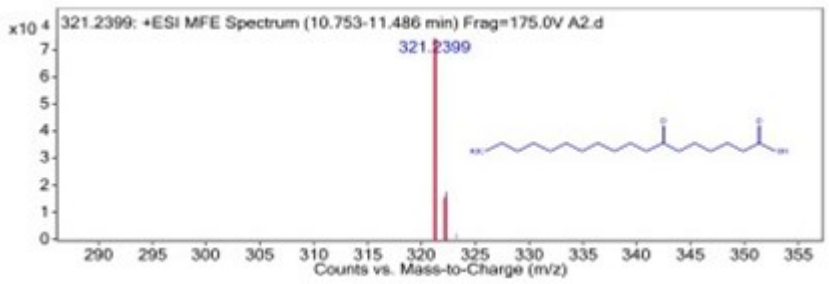
9E-tetradecenoic acid



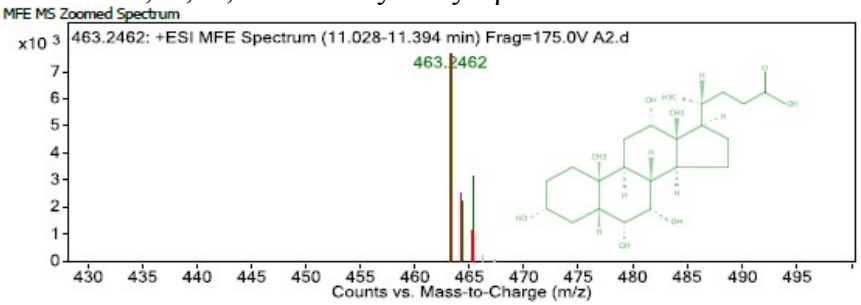
2Z-dodecenoic acid



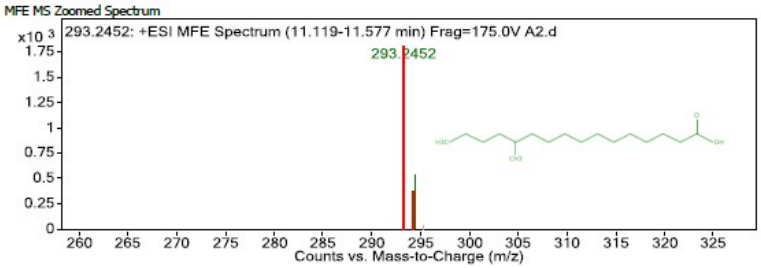
7-keto-stearic acid



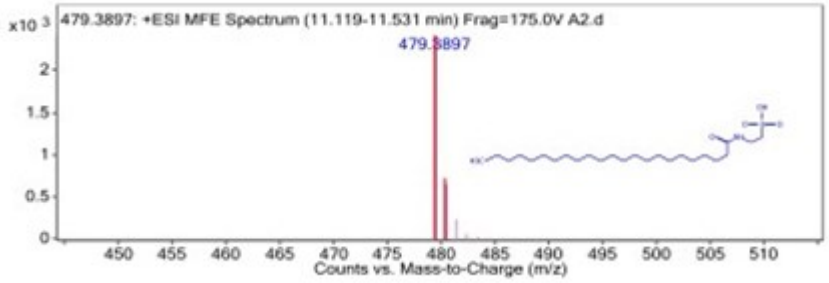
3α,6α,7α,12α-Tetrahydroxy-5β-cholan-24-oic Acid



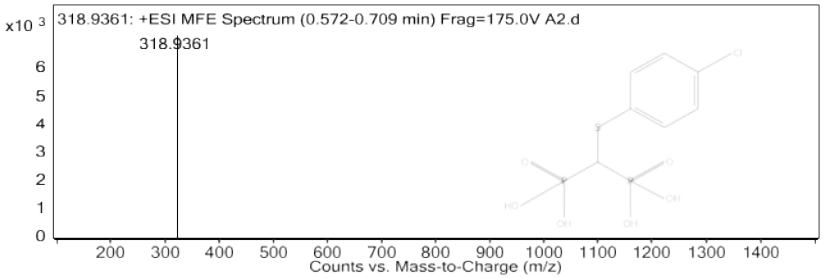
12-methyl-hexadecanoic acid



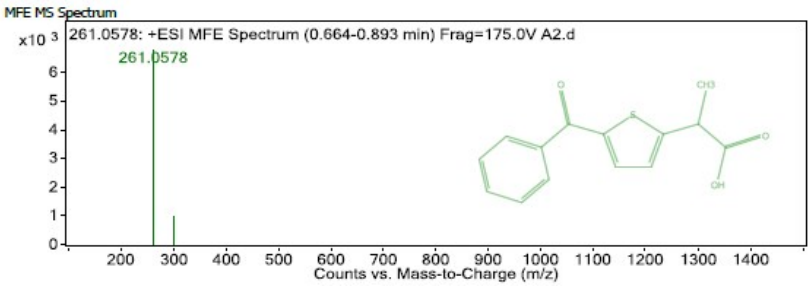
2-Tricosanamidoethanes ulfonic acid



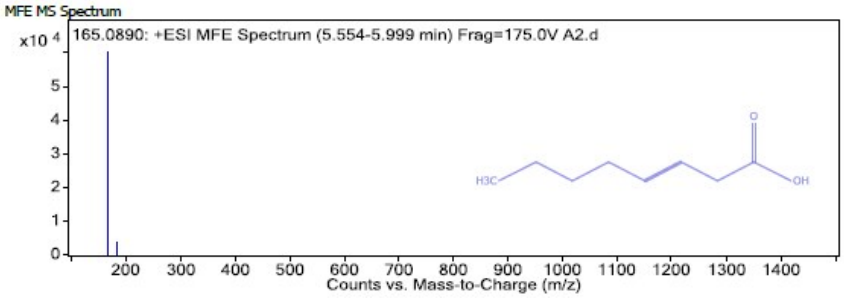
Tiludronic acid



Tiaprofenic acid

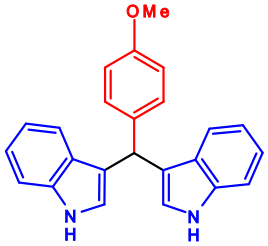


trans-β-octenoic acid



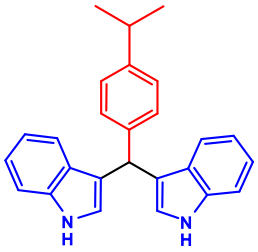
Spectroscopic data and copies of FT-IR, ^{1}H NMR & ^{13}C NMR of isolated compounds:

3, 3`-(4-Methoxyphenyl)methylenebisindole **(table 2, entry 3a)**



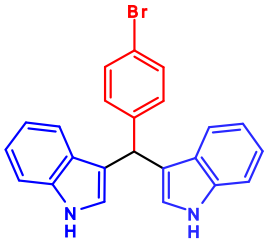
FTIR ν_{max} = 3399, 3052, 2929, 2835, 1606, 1505, 1450, 1420, 1340, 1302, 1015, 739 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (s, 2H, -NH), 7.31-7.39 (m, 4H, Ar-H), 7.25 (s, 1H, Ar-H), 7.23 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.14 (ddd, *J* = 8.1 Hz, 7.0 Hz & 1.1 Hz, 2H, Ar-H), 6.98 (ddd, *J* = 8.1 Hz, 7.0 Hz & 1.1 Hz, 2H, Ar-H), 6.8 (m, 2H, Ar-H), 6.61 (dd, *J* = 2.5 Hz & 1.1 Hz, 2H, Ar-H), 5.82 (s, 1H, -CH), 3.76 (s, 3H, -OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 136.6, 136.2, 129.5, 127.0, 123.4, 121.8, 120.0, 119.9, 119.1, 113.5, 110.9, 55.2, 39.3 ppm.

3, 3`-(4-Isopropylphenyl)methylenebisindole **(table 2, entry 3b)**



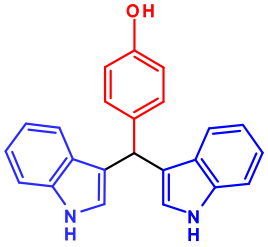
FTIR ν_{max} = 3402, 3051, 2956, 2838, 1606, 1548, 1453, 1244, 1089, 795, 745, 597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7 (s, 2H, -NH), 7.38 (d, *J* = 4.5 Hz, 2H, Ar-H), 7.30 (d, *J* = 4.5 Hz, 2H, Ar-H), 7.23 (d, *J* = 3.0 Hz, 2H, Ar-H), 7.09-7.17 (m, 4H, Ar-H), 6.9-7.01 (m, 2H, Ar-H), 6.60 (d, *J* = 1.5 Hz, 2H, Ar-H), 5.8 (s, 1H, -CH), 2.8 (m, 1H, -CH), 1.21 (d, 6H, -CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 145.4, 141.2, 136.6, 128.4, 127.0, 126.3, 123.5, 121.5, 121.8, 119.9, 119.1, 110.9, 54.1, 36.4, 22.4 ppm.

3,3'-((4-Bromophenyl)methylene)bis(1H-indole **(table 2, entry 3c)**



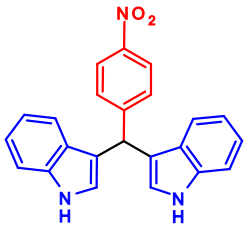
FTIR ν_{max} = 3402, 3058, 2924, 2854, 1617, 1457, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.9 (s, 2H, -NH), 7.45 (d, J = 2.2 Hz, 2H, Ar-H), 7.43 (d, J = 8Hz, 2H, Ar-H), 7.35 (d, J = 8.1Hz, 2H, Ar-H), 7.0 (ddd, J = 8.0 Hz, 6.9 Hz & 1.1 Hz, 2H, Ar-H), 6.62 (d, J = 2.3 Hz, 2H, Ar-H), 5.83 (s, 1H, -CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 136.6, 131.2, 130.5, 126.8, 123.6, 122.1, 119.9, 119.8, 119.3, 119.0, 111.0, 39.6 ppm.

3, 3`-(4-Hydroxyphenyl)methylenebisindole **(table 2, entry 3d)**



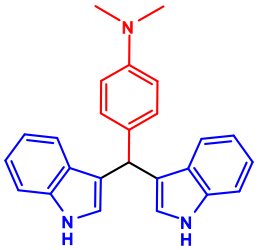
FTIR ν_{max} = 3435, 3398, 3051, 2838, 1605, 1508, 1171, 1086, 1046, 792, 744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 10.4 (brs, 1H, -OH), 9.36 (s, 2H, -NH), 7.25-7.35 (m, 4H, Ar-H), 6.86-7.08 (m, 4H, Ar-H), 6.84 (d, J = 8.2 Hz, 2H, Ar-H), 6.67-6.82 (d, J = 8.2 Hz, 2H, Ar-H), 6.60 (s, 2H, Ar-H), 5.69 (s, 1H, -CH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 154.1, 134.2, 131.7, 131.0, 127.3, 123.5, 122.6, 121.2, 118.4, 114.8, 113.5, 110.7, 57.7 ppm.

3, 3`-(4-Nitrophenyl)methylenebisindole **(table 2, entry 3e)**



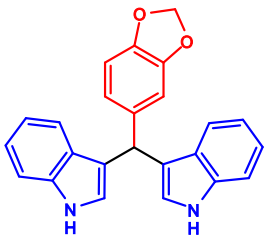
FTIR ν_{max} = 3429, 3055, 1599, 1519, 1457, 1359 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ 10.2 (s, 2H, -NH), 8.01 (dd, J = 8.3 Hz & 2.7 Hz, 2H, Ar-H), 7.48 (dd, J = 8.4 Hz, 2H, Ar-H), 7.36 (dd, J = 8 Hz, 2H, Ar-H), 7.19 (d, J = 7.1 Hz, 2H, Ar-H), 6.98-7.03 (m, 2H, Ar-H), 6.6-6.8 (m, 4H, Ar-H), 5.88 (s, 1H, -CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 137.1, 127.6, 128.0, 127.2, 126.7, 125.1, 121.8, 119.9, 118.1, 111.7, 110.9, 31.6 ppm.

3, 3`-(P-dimethylaminophenyl)methylenebisindole **(table 2, entry 3f)**



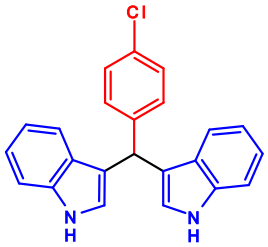
FTIR ν_{max} = 3402, 3049, 2956, 1652, 1595, 1451, 1420, 1228, 1166, 1088, 1011, 931, 849, 742cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 2H, -NH), 7.41 (d, J = 7.9 Hz, 2H, Ar-H), 7.34 (d, J = 7.9 Hz, 2H, Ar-H), 7.13-7.25 (m, 4H, Ar-H), 7.00 (d, J = 8.3 Hz, 2H, Ar-H), 6.66 (d, J = 8.4 Hz, 4H, Ar-H), 5.8 (s, 1H, -CH), 3.9 (s, 6H, $-NCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 136.7, 132.3, 129.2, 127.2, 123.5, 121.7, 120.4, 120.0, 119.0, 112.6, 110.9, 110.9, 40.8, 40.0, 39.1 ppm.

3,3'-(benzo[d][1,3]dioxol-5-ylmethylene)bis(1H-indole) **(table 2, entry 3g)**



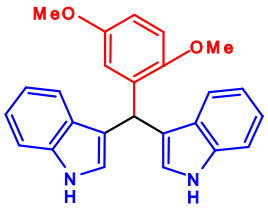
FTIR ν_{max} = 3410, 3055, 1485, 1336, 1242, 1093, 1037, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): = δ 7.8 (brs, 2H, -NH), 7.25-7.34 (m, 4H, Ar-H), 7.08-7.20 (m, 2H, Ar-H), 6.91-6.93 (m, 2H, Ar-H), 6.72-6.78 (m, 2H, Ar-H), 6.58-6.68 (m, 3H, Ar-H), 5.6 (s, 2H, $-OCH_2-$), 3.2 (s, 1H, -CH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): = δ 147.8, 145.8, 138.2, 136.7, 126.7, 123.5, 121.1, 121.0, 119.7, 119.2, 119.0, 110.8, 110.4, 108.0, 101.8, 39.3 ppm.

3, 3`-(4-Chlorophenyl)methylenebisindole **(table 2, entry 3h)**



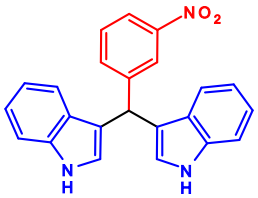
FTIR ν_{max} = 3420, 3054, 1499, 1460, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (brs, 2H, -NH), 7.34 (d, *J* = 8.1 Hz, 4H, Ar-H), 7.25 (d, *J* = 5.1 Hz, 4H, Ar-H), 7.13 (m, *J* = 7.7 Hz, 2H, Ar-H), 6.99 (m, 2H, Ar-H), 6.55 (s, 2H, Ar-H), 5.8 (s, 1H, -CH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 146.0, 136.2, 133.2, 129.5, 129.4, 127.6, 123.4, 121.8, 120.7, 119.6, 119.0, 112.3, 40.2 ppm.

3, 3`-(2, 5 dimethoxyphenyl)methylenebisindole **(table 2, entry 3i)**



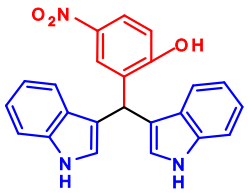
FTIR ν_{max} = 3410, 2838, 1512, 1466, 1241, 1088, 848 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.8 (s, 2H, -NH), 7.39 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.26 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.11 (t, *J* = 7.5 Hz, 2H, Ar-H), 6.97 (t, *J* =7.5 Hz, 2H, Ar-H), 6.85 (d, *J* = 8.7 Hz, 1H, Ar-H), 6.73 (d, *J* = 3.1 Hz, 1H, Ar-H), 6.69 (dd, *J* = 8.7 Hz & 5.6 Hz, 1H, Ar-H), 6.5 (s, 2H, Ar-H), 6.3 (s, 1H, -CH), 3.76 (s, 3H, $-OCH_3$), 3.62 (s, 3H, $-OCH_3$) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 153.4, 151.4, 136.7, 133.9, 127.2, 123.5, 121.7, 119.9, 119.3, 118.9, 116.7, 111.8, 110.9, 110.6, 56.6, 55.5, 32.1 ppm.

3, 3`-(3-Nitrophenyl)methylenebisindole **(table 2, entry 3j)**



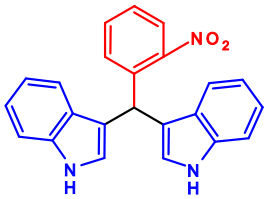
FTIR ν_{max} = 3402, 2957, 2839, 1669, 1589, 1366, 1248, 1165, 796, 742, 591cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (brs, 1H, -NH), 8.05 (s, 1H, NH), 7.97 (s, 2H, Ar-H), 7.68 (d, *J* = 7.4 Hz, 1H, Ar-H), 7.33-7.46 (m, 4H, Ar-H), 7.17-7.26 (m, 3H, Ar-H), 7.03 (m, *J* = 7.4 Hz, 2H, Ar-H), 6.63 (s, 2H, Ar-H), 6.0 (s, 1H, -CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+DMSO): δ 147.6, 146.6, 136.4, 134.4, 128.5, 126.0, 123.5, 122.6, 120.8, 120.5, 118.5, 118.1, 116.6, 111.0, 39.2 ppm.

3, 3`-(2-Hydroxyl, 5-Nitrophenyl)methylenebisindole **(table 2, entry 3k)**



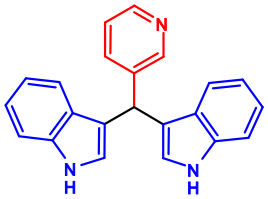
FTIR ν_{max} = 3426, 3312, 3047, 1590, 1531, 1460, 1363 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 10.4 (brs, 1H, -OH), 9.9 (s, 2H, -NH), 7.82-7.87 (m, 2H, Ar-H), 7.47-7.48 (m, 4H, Ar-H), 7.27 (d, *J* = 7.2 Hz, 2H, Ar-H), 6.80-7.02 (m, 3H, Ar-H), 6.63 (s, 2H, Ar-H), 6.2 (s, 1H, -CH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 150.0, 140.9, 136.5, 127.4, 125.8, 125.4, 122.9, 122.4, 120.4, 119.5, 119.1, 116.7, 112.1, 111.0, 49.8 ppm.

3, 3`-(2-Nitrophenyl)methylenebisindole **(table 2, entry 3l)**



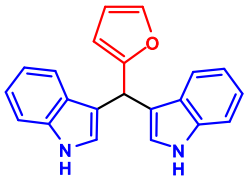
FTIR ν_{max} = 3413, 3055, 1521, 1456, 1352, 1095 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.0 (brs, 2H, -NH), 7.82 (m, 2H, Ar-H), 7.32-7.42 (m, 2H, Ar-H), 7.14 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.28 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.08-7.17 (m, 4H, Ar-H), 6.66 (s, 2H, Ar-H), 6.7 (s, 1H, -CH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 150.0, 138.5, 136.1, 132.5, 130.7, 128.2, 127.7, 124.4, 124.0, 121.9, 120.1, 120.0, 118.7, 111.2, 35.7 ppm.

3,3'-((3-pyridyl)methylene)bis(1H-indole) **(table 2, entry 3m)**



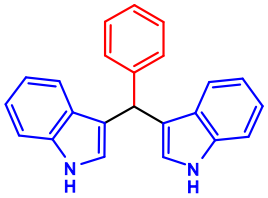
FTIR ν_{max} = 3448, 3029, 2780, 1677, 1699, 904, 718 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.1 (brs, 2H, -NH); 8.60-8.61 (m, 1H, Ar-H,), 8.37-8.39 (m, 1H, Ar-H), 7.25-7.37 (m, 6H, Ar-H), 7.02-7.06 (m, 2H, Ar-H), 6.84-6.88 (m, 4H, Ar-H), 5.9 (s, 1H, -CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 137.8, 137.8, 132.7, 130.9, 128.0, 127.4, 124.8, 121.7, 119.5, 118.7, 112.4, 33.6 ppm.

3-[(Furan-2-yl)(1H-indol-3-yl)methyl]-1H-indole **(table 2, entry 3n)**



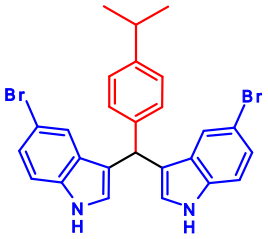
FTIR ν_{max} = 742, 783, 1008, 1454, 3053, 3412 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.9 (brs, 2H, -NH), 7.48 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.35-6.96 (m, 7H, Ar-H), 6.83 (s, 2H, Ar-H), 6.28 (s, H, Ar-H), 6.0 (s, 1H, Ar-H), 5.93 (s, 1H, -CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 141.8, 136.3, 126.4, 122.1, 120.8, 118.8, 117.1, 115.6, 111.4, 110.2, 105.7, 33.6 ppm.

3, 3`-Phenylmethylenebisindole **(table 2, entry 3o)**



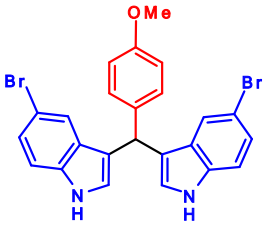
FTIR ν_{max} = 3412, 3056, 1616, 1455, 1417, 1337, 1093, 1010, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (brs, 2H, -NH), 7.25-7.32 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.19-7.24 (m, 2H, Ar-H), 7.17-7.19 (m, 4H, Ar-H), 7.11-7.16 (m, 3H, Ar-H), 6.97 (ddd, *J* = 8.0 Hz, 6.7 Hz & 1.3 Hz, 2H, Ar-H), 6.5 (dd, *J* = 2.4 Hz & 1.3 Hz, 2H, Ar-H), 5.8 (s, 1H, -CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 136.2, 128.9, 127.8, 127.6, 127.5, 124.1, 123.8, 122.7, 120.5, 119.9, 119.5, 111.7, 40.7 ppm.

5-bromo-3-((5-bromo-1H-indol-3-yl)(4-isopropylphenyl)methyl)-1H-indole **(table 2, entry 3p)**



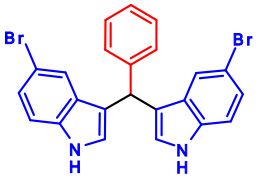
FTIR ν_{max} = 3400, 3100, 2841, 1679, 581 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 2H, -NH), 7.76 (s, 2H, Ar-H), 7.28 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.25 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.22 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.18 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.48 (s, 2H, Ar-H), 5.7 (s, 1H, -CH), 2.8-2.9 (m, 1H, -CH), 1.26 (d, *J* = 6.9 Hz, $-CH_3$, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 134.8, 133.2, 128.3, 127.4, 126.5, 123.8, 122.1, 121.7, 116.3, 112.7, 111.6, 38.4, 32.5, 22.8 ppm.

5-bromo-3-((5-bromo-1H-indol-3-yl)(4-methoxyphenyl)methyl)-1H-indole **(table 2, entry 3q)**



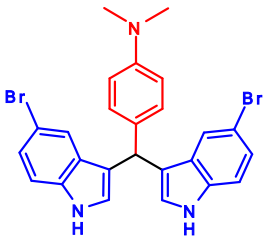
FTIR ν_{max} = 3400, 3100, 2840, 1681, 580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.0 (s, 2H, -NH), 7.45 (s, 2H, Ar-H), 7.22-7.25 (m, 2H, Ar-H), 7.21 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.18 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.4 Hz, 2H, Ar-H) 6.61 (s, Ar-H, 2H), 5.68 (s, 1H, -CH), 3.78 (s, 3H, $-OCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 134.6, 133.3, 129.2, 128.4, 125.8, 124.5, 123.5, 120.3, 117.7, 111.8, 108.6, 55.6, 40.3 ppm.

5-bromo-3-((5-bromo-1H-indol-3-yl)(phenyl)methyl)-1H-indole **(table 2, entry 3r)**



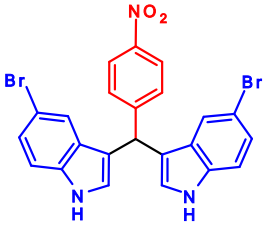
FTIR ν_{max} = 3405, 2910, 2370, 1718, 1560, 1441, 1217,1099, 872, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.0 (s, 2H, -NH), 7.52 (d, *J* = 2.1 Hz, 2H, Ar-H), 7.50 (m, Ar-H, 3H), 7.20-7.30 (m, 6H, Ar-H), 6.64 (d, *J* = 2.1 Hz, 2H, Ar-H), 5.75 (s, 1H, -CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 135.2, 129.7, 129.1, 128.7, 126.8, 123.9, 121.5, 121.3, 116.0, 113.3, 112.8, 55.3 ppm.

4-(bis(5-bromo-1H-indol-3-yl)methyl)-N,N-dimethylbenzenamine **(table 2, entry 3s)**



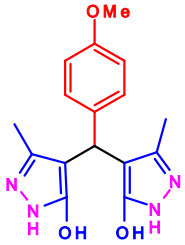
FTIR ν_{max} = 3415, 3142, 2856, 2903, 1679, 581 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.0 (s, 2H, -NH), 7.74 (m, 2H, Ar-H), 7.49 (m, 2H, Ar-H), 7.12-7.26 (d, *J* = 7.5 Hz, 1H, Ar-H), 6.64-6.71 (m, 5H, Ar-H), 6.49 (s, 1H, Ar-H), 5.7 (s, 1H, Ar-H), 3.08 (d, $-NCH_3$, 3H), 2.92 (s, $-NCH_3$, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 135.5, 130.2, 129.9, 128.9, 127.1, 121.9, 121.4, 117.3, 114.1, 113.3, 112.5, 55.2, 40.2 ppm.

5-bromo-3-((5-bromo-1H-indol-3-yl)(4-nitrophenyl)methyl)-1H-indole **(table 2, entry 3t)**



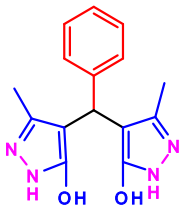
FTIR ν_{max} = 3390, 3167, 2822, 2900, 1686, 1534, 1330, 587 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$):δ 8.15 (s, 2H, -NH), 8.08 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.42- 7.45 (m, Ar-H, 4H), 7.24-7.29 (m, 4H, Ar-H), 6.65 (s, 2H, Ar-H), 5.85 (s, 1H, -CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 144.1, 135.3, 130.2, 129.7, 128.7, 121.9, 121.6, 121.3, 116.2, 113.1, 112.3, 54.9 ppm.

4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(4-methoxyphenyl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7a)**



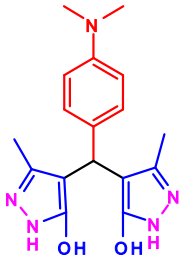
FTIR ν_{max} = 3661, 3261, 2624, 2361, 1589, 1508, 1234, 1020, 788, 740 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 10.2-12.5 (brs, 4H, -NH,-OH), 7.00-7.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.74-6.77 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.79 (s, 1H, -CH,), 3.67 (s, 3H, $-OCH_3$), 2.05 (s, 6H, $2CH_3$) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 161.1, 157.2, 139.6, 135.3, 128.4, 113.1, 104.5, 54.9, 31.9, 10.4 ppm.

4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(phenyl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7b)**



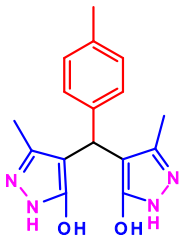
FTIR ν_{max} = 3051, 2908, 2723, 2528, 1626, 1531, 1492, 1380, 1202 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 11.26 (brs, 4H, -NH,-OH), 7.19-7.27 (m, 2H, Ar-H), 7.07-7.18 (m, 3H, Ar-H), 4.84 (s, 1H, -CH), 2.07 (s, 6H, CH_3) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 161.4, 143.8, 140.5, 128.3, 127.9, 126.0, 104.3, 33.2, 10.9 ppm.

4-((4-(dimethylamino)phenyl)(5-hydroxy-3-methyl-1H-pyrazol-4-yl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7c)**



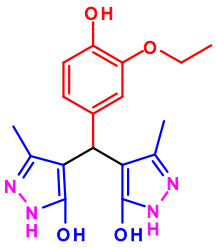
FTIR ν_{max} = 3639, 3106, 2362, 2324, 1699, 1511, 1467, 1124, 786, 745 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 11.36 (brs, 4H, -NH, -OH), 6.92 (d, *J* = 7.5 Hz, 2H, Ar-H), 6.56 (d, *J* = 7.5 Hz, 2H, Ar-H), 4.67 (s, 1H, -CH), 2.79 (s, $-NCH_3$, 3H,), 2.64 (s, $-NCH_3$, 3H), 2.04 (s, 6H, $2CH_3$) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 161.0, 148.6, 139.7, 131.5, 127.9, 112.3, 104.6, 46.5, 26.7, 10.5 ppm.

4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(p-tolyl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7d)**



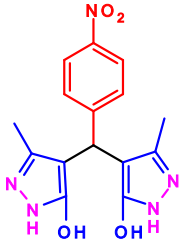
FTIR ν_{max} = 3449, 3124, 2920, 2729, 1703, 1600, 1516, 1464, 1393 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 9.5-12.5 (brs, 4H, -OH, -NH), 6.99 (d, J = 8.0 Hz, 4H, Ar-H), 4.75 (s, 1H, -CH), 2.21 (s, 6H, CH_3), 2.05 (s, 3H, -CH_3) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 161.3, 141.2, 140.3, 133.9, 127.9, 127.1, 105.5, 32.2, 21.6, 10.8 ppm.

4-((3-ethoxy-4-hydroxyphenyl)(5-hydroxy-3-methyl-1H-pyrazol-4-yl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7e)**



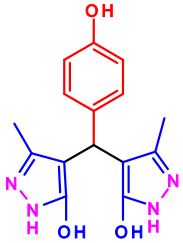
FTIR ν_{max} = 3616, 2992, 2364, 1703, 1604, 1511, 1427, 1262, 1202, 1125, 1041, 825, 752 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 11.23 (brs, 4H, -NH, -OH), 8.54 (brs, 1H -OH), 6.71 (m, 1H, Ar-H), 6.60 (d, J = 8.4 Hz, Ar-H) 6.49 (d, 1H, J = 8.4 Hz, Ar-H), 4.68 (s, 1H, -CH), 3.84 (q, 2H, J = 6.9 Hz, -OCH_2), 2.03 (s, 6H, 2x CH_3,), 1.25 (t, J = 6.9 Hz, 3H, -CH_2-) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 148.1, 142.8, 139.2, 135.1, 122.1, 120.1, 116.3, 114.3, 63.9, 25.3, 14.7, 10.4 ppm.

4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(4-nitrophenyl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7f)**



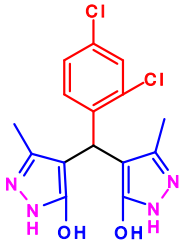
FTIR ν_{max} = 3420, 2961, 1602, 1510, 1444, 1345, 1178, 881, 802, 772 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 11.36 (brs, 4H, -NH, -OH), 8.0 (d, J = 8.2 Hz, 2H, Ar-H), 7.5 (d, J = 8.2 Hz, 2H, Ar-H), 4.99 (s, 1H, -CH), 2.10 (s, 6H, 2CH_3) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 160.4, 151.4, 148.1, 138.0, 127.2, 125.5, 104.3, 33.3, 11.8 ppm.

4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(4-hydroxyphenyl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7g)**



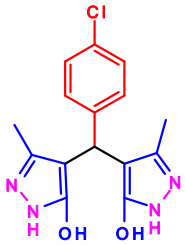
FTIR ν_{max} = 3267, 1559, 1514, 1467, 1401, 1174, 872, 788, 730 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 11.7 (brs, 4H, -NH, -OH), 9.04 (s, 1H, -OH), 6.91 (d, J = 8.4 Hz, 2H, Ar-H), 6.59 (d, J = 8.4 Hz, 2H, Ar-H), 4.70 (s, 1H, -CH), 2.06 (s, 6H, 2CH_3) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 161.4, 155.5, 139.2, 135.4, 130.4, 116.0, 115.7, 25.3, 11.8 ppm.

4-((2,4-dichlorophenyl)(5-hydroxy-3-methyl-1H-pyrazol-4-yl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7h)**



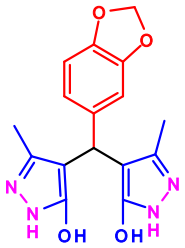
FTIR ν_{max} = 3578, 3095, 2362, 2118, 1699, 1469, 1348, 1212, 783, 693 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 7.21 (d, 1H, J = 4.8 Hz, Ar-H), 6.83 (dd, J = 8.4 Hz & J = 4.8 Hz, 1H, Ar-H), 6.58 (d, J = 7.2 Hz, 1H, Ar-H), 4.96 (s, 1H, -CH), 2.08 (s, 6H, 2CH_3) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 155.7, 139.2, 136.1, 135.8, 132.6, 131.4, 130.2, 125.9, 116.3, 22.4, 11.7 ppm.

4-((4-chlorophenyl)(5-hydroxy-3-methyl-1H-pyrazol-4-yl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7i)**



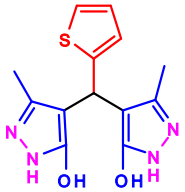
FTIR ν_{max} = 3225, 3089, 2975, 1604, 1540, 1496, 1302 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 11.0 (brs, 4H, -NH, -OH), 7.27 (d, J = 8.4 Hz, 2H, Ar-H), 7.13 (d, J = 8.4 Hz, 2H, Ar-H), 4.80 (s, 1H, -CH), 2.05 (s, 6H, $2CH_3$) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 158.2, 144.3, 136.3, 129.8, 129.3, 127.5, 108.5, 33.6, 11.9 ppm.

4-((benzo[d][1,3]dioxol-6-yl)(5-hydroxy-3-methyl-1H-pyrazol-4-yl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7j)**



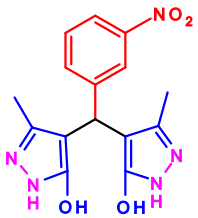
FTIR ν_{max} = 3614, 3320, 3141, 2886, 2360, 1593, 1489, 1230, 1027, 753, 662 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 9.8-12.3 (brs, 4H, -NH,-OH), 6.56-6.64 (m, 3H, Ar-H), 5.91 (s, 2H, -O-CH_2-O-), 4.70 (s, 1H, -CH), 2.06 (s, 6H, $2CH_3$) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 148.6, 145.4, 139.1, 135.0, 131.2, 122.4, 120.2, 108.0, 107.4, 100.5, 32.5, 10.3 ppm.

4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(thiophen-2-yl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7k)**



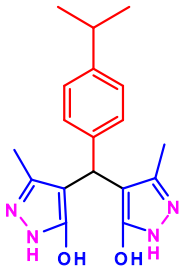
FTIR ν_{max} = 3580, 3112, 2926, 1607, 1482 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 11.36 (brs, 4H, -NH, -OH), 7.30 (d, J = 5.2 Hz, 1H, Ar-H), 7.05 (m, 1H, Ar-H), 6.55 (m, 1H, Ar-H), 5.27 (s, 1H, CH), 2.24 (s, 6H, CH_3) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 159.9, 136.8, 135.4, 134.9, 125.6, 118.4, 101.1, 30.8, 11.3 ppm.

4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(3-nitrophenyl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7l)**



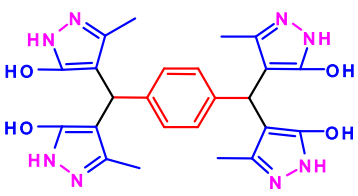
FTIR ν_{max} = 3419, 2961, 1603, 1515, 1444, 1343, 1178, 881, 806, 773 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 10.4-12.2 (brs, 4H, -NH, -OH), 8.02 (dd, 1H, J = 7.6 Hz & 4.0 Hz, Ar-H), 7.95 (d, J = 7.6 Hz, 1H, Ar-H), 7.55-7.58 (m, 2H, Ar-H), 4.81 (s, 1H, -CH), 2.06 (s, 6H, 2-CH_3) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 148.2, 139.2, 139.0, 135.7, 135.2, 129.6, 124.2, 118.2, 116.4, 25.9, 11.4 ppm.

4-((5-hydroxy-3-methyl-1H-pyrazol-4-yl)(4-isopropylphenyl)methyl)-3-methyl-1H-pyrazol-5-ol **(table 4, entry 7m)**



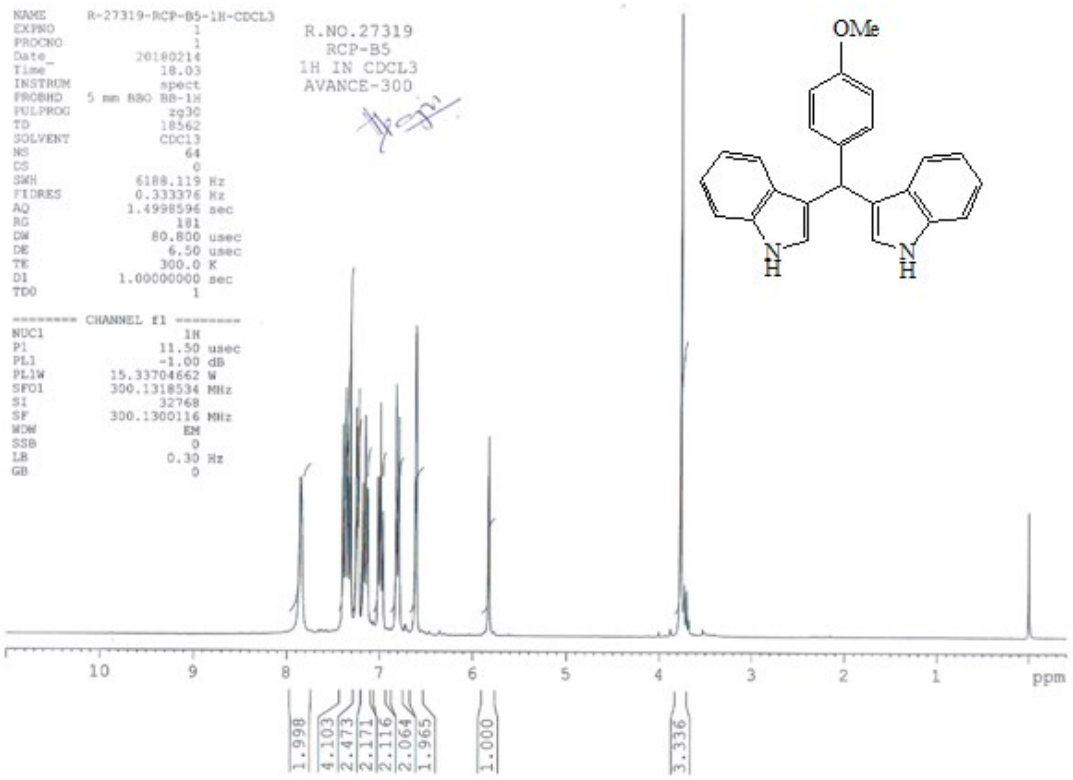
FTIR ν_{max} = 3276, 2954, 2360, 1599, 1506, 1445, 1202, 754, 609 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 10.7-12.2 (brs, 4H, -NH, -OH), 7.01-7.07 (m, 2H, Ar-H), 4.74 (s, 1H, -CH), 2.79 (m, 1H, -$CH(CH_3)$), 2.07 (s, 6H, 2-CH_3), 1.14 (d, 6H, 2 -CH_3) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 145.6, 139.02, 135.8, 135.3, 128.6, 126.2, 116.3, 36.4, 25.4, 23.5, 11.8 ppm.

4,4',4",4"'-(1,4-phenylenebis (methanetriyl)) tetrakis (3-methyl-1H-pyrazol-5-ol) **(table 4, entry 7n)**

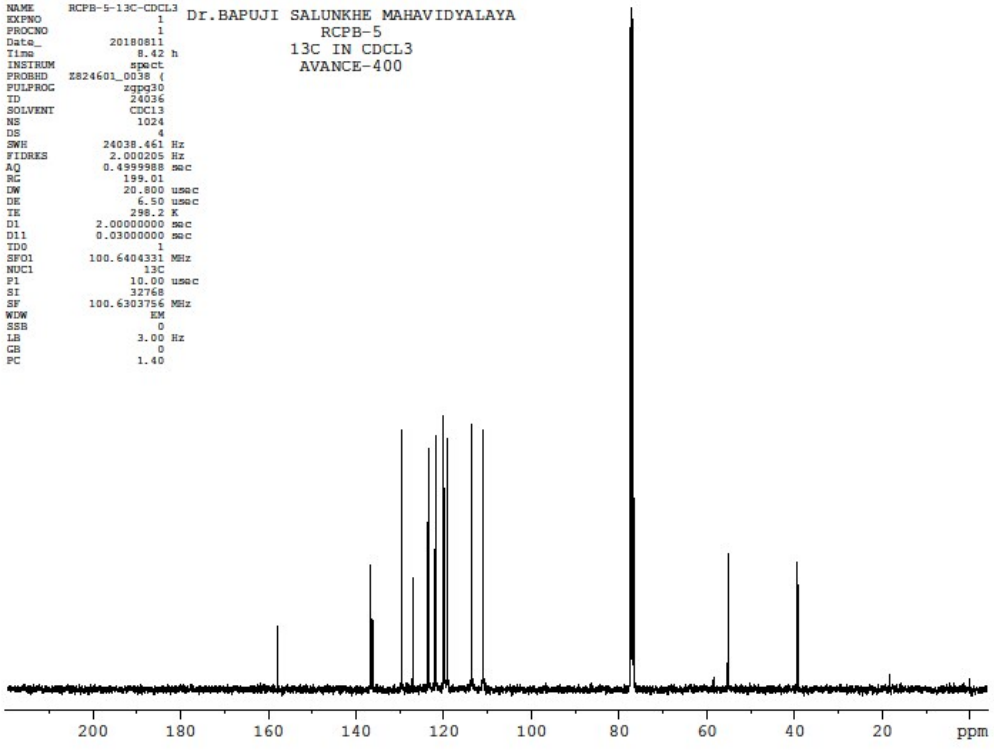


FTIR ν_{max} = 3615, 3260, 2885, 2360, 1687, 1505, 1122, 868, 735, 601 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 10.6-12.4 (brs, 8H, -NH, -OH), 6.95 (s, 4H, Ar-H), 4.68 (s, 2H, -CH), 2.05 (s, 12H, $-CH_3$) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 139.3, 135.1, 135.0, 129.2, 116.4, 25.4, 11.8 ppm.

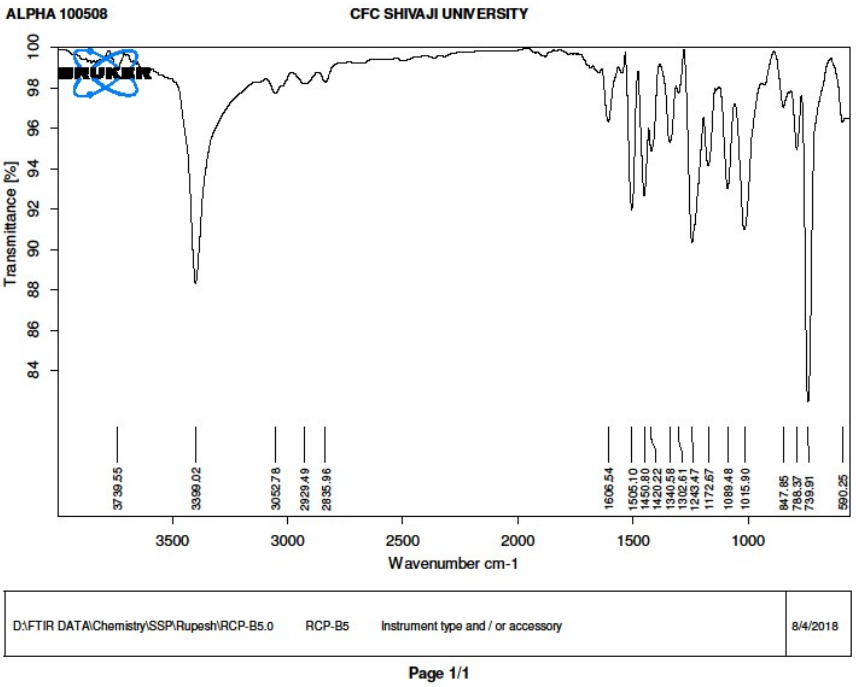
Spectral characterization of selected compounds



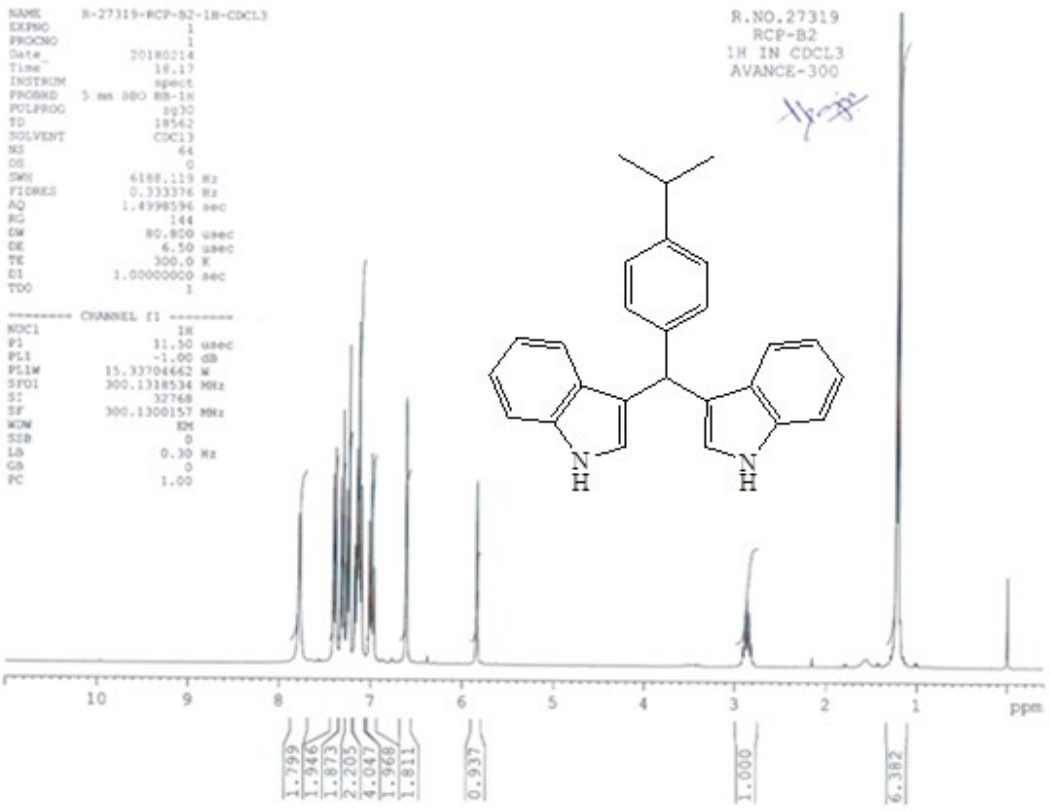
^{1}H NMR spectrum of compound 3a



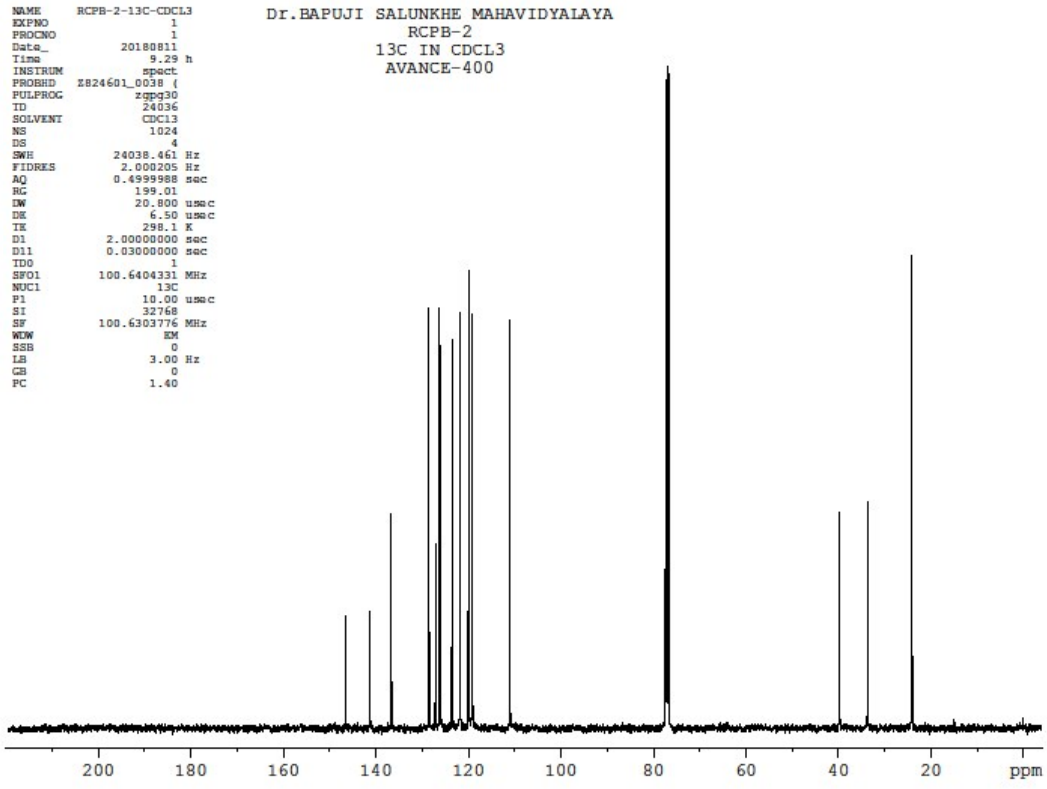
^{13}C NMR spectrum of compound 3a



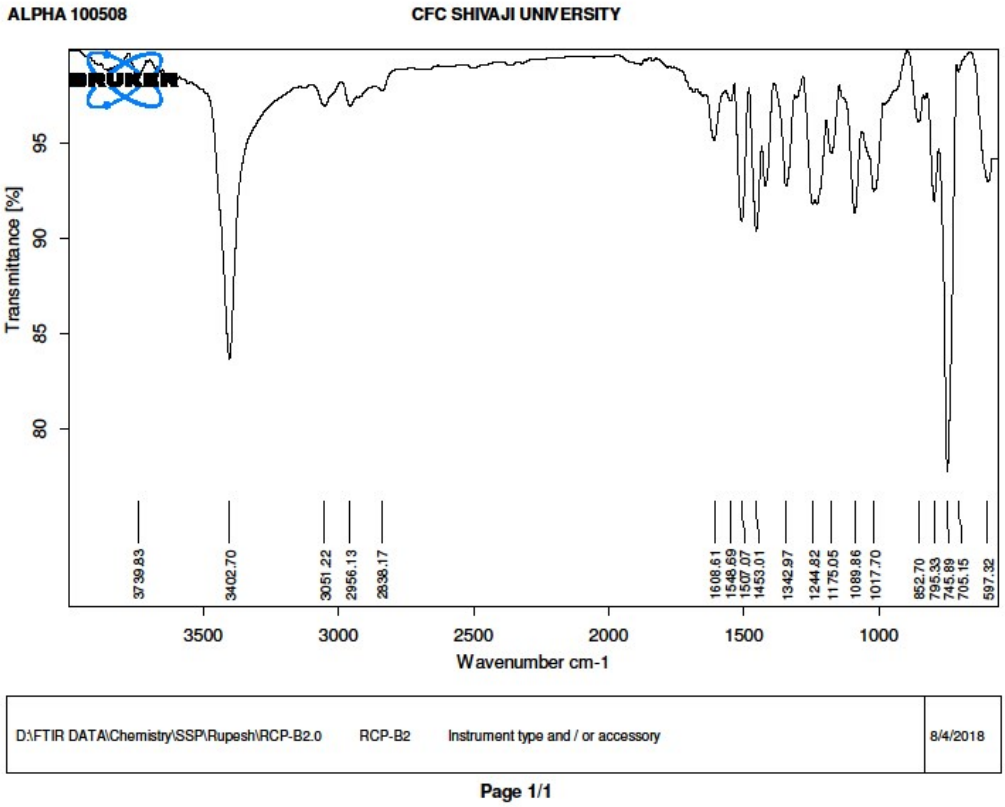
FT-IR spectrum of compound 3a



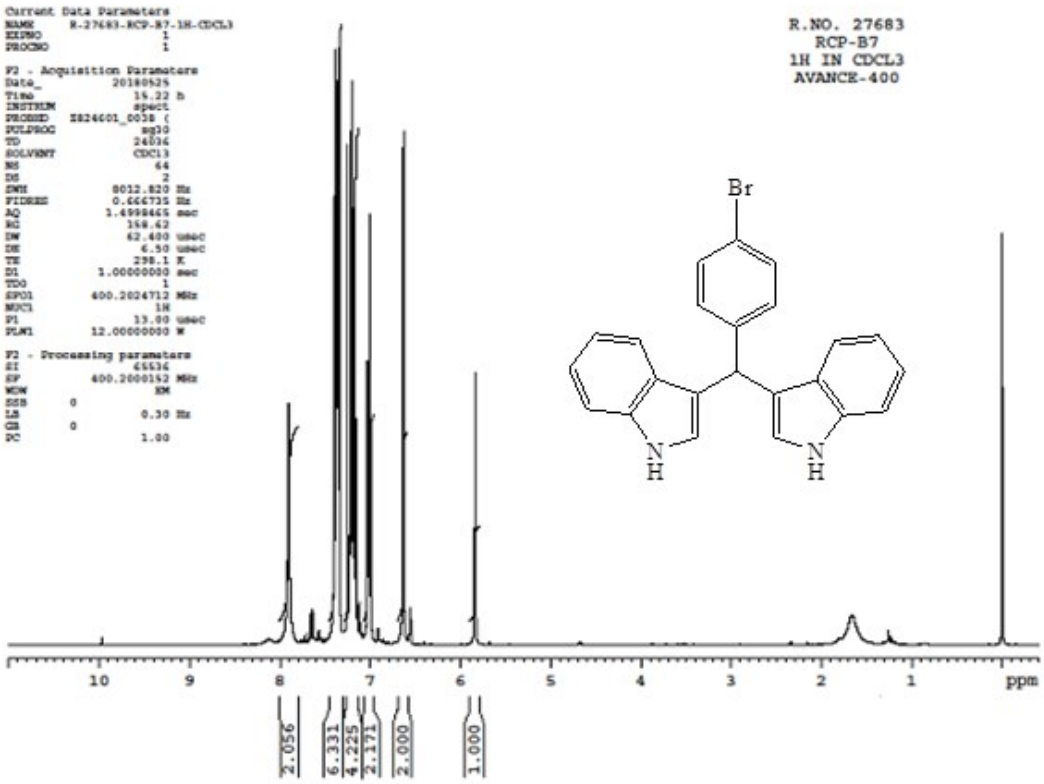
^{1}H NMR spectrum of compound 3b



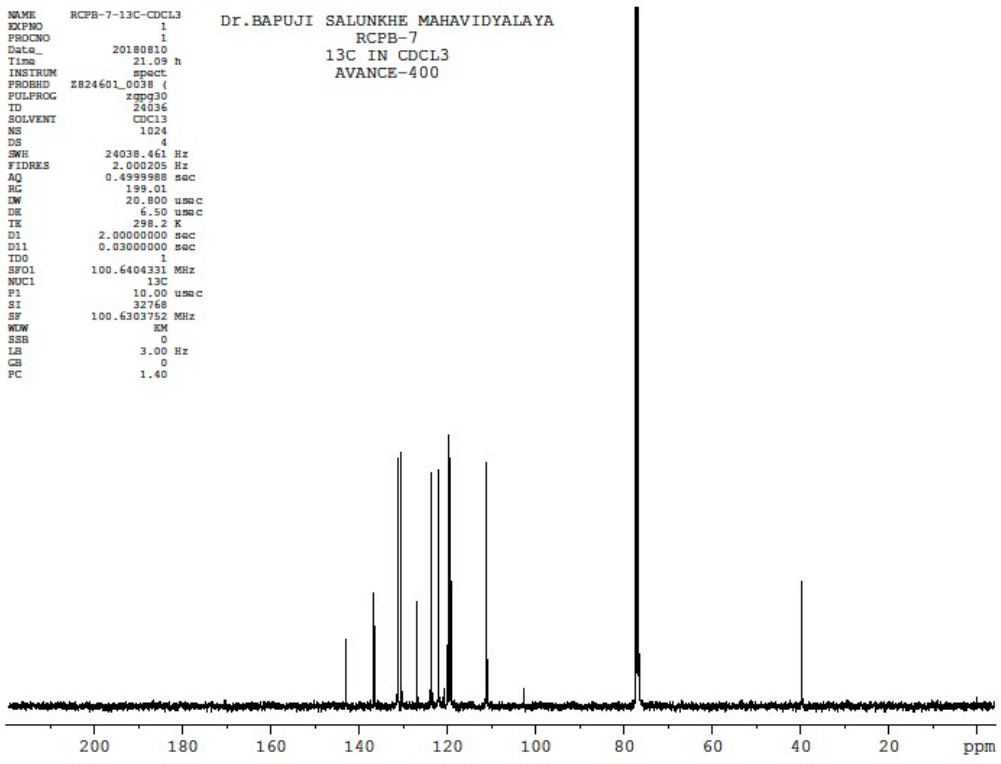
^{13}C NMR spectrum of compound 3b



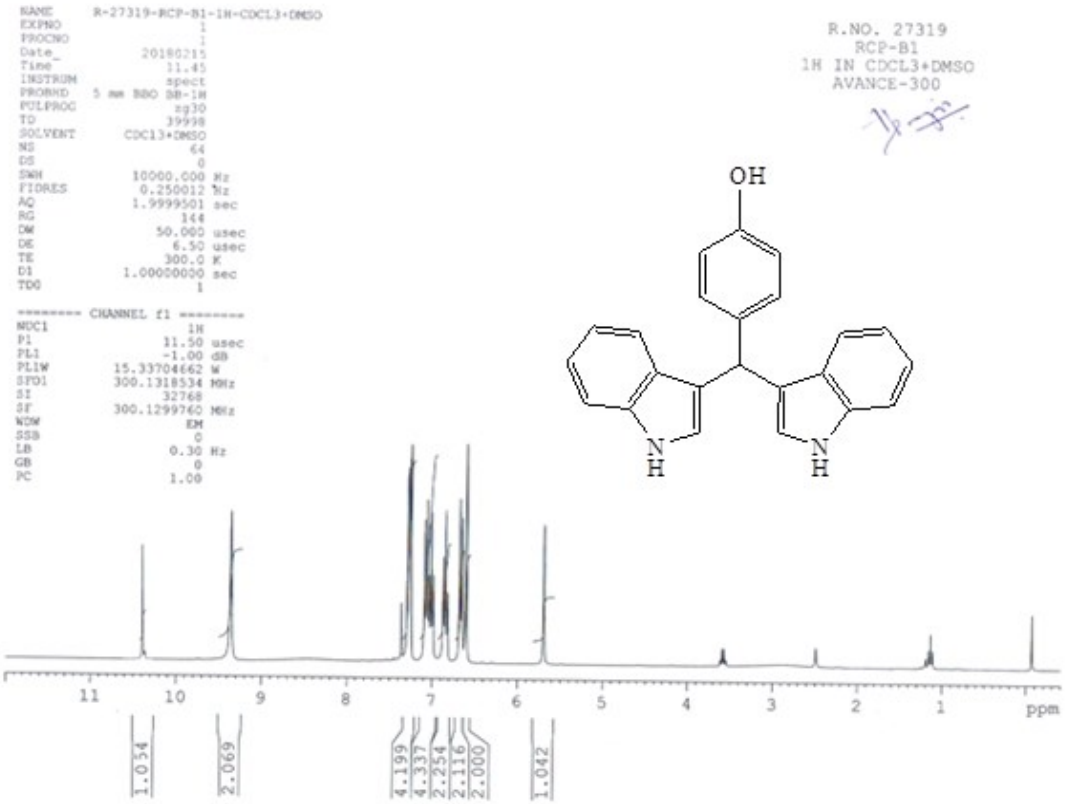
FT-IR spectrum of compound 3b



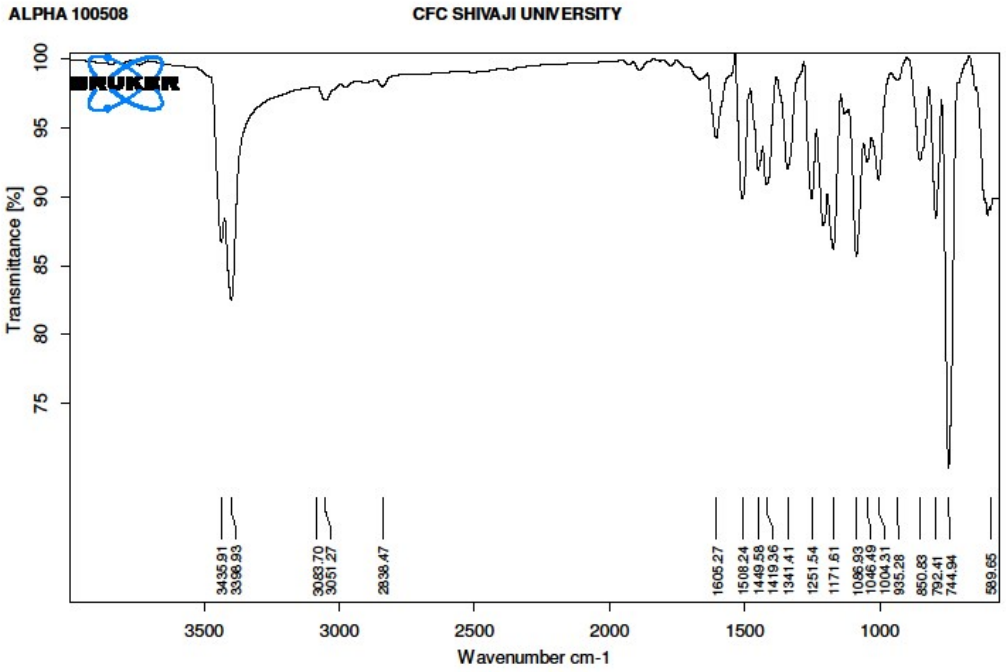
^{1}H NMR spectrum of compound 3c



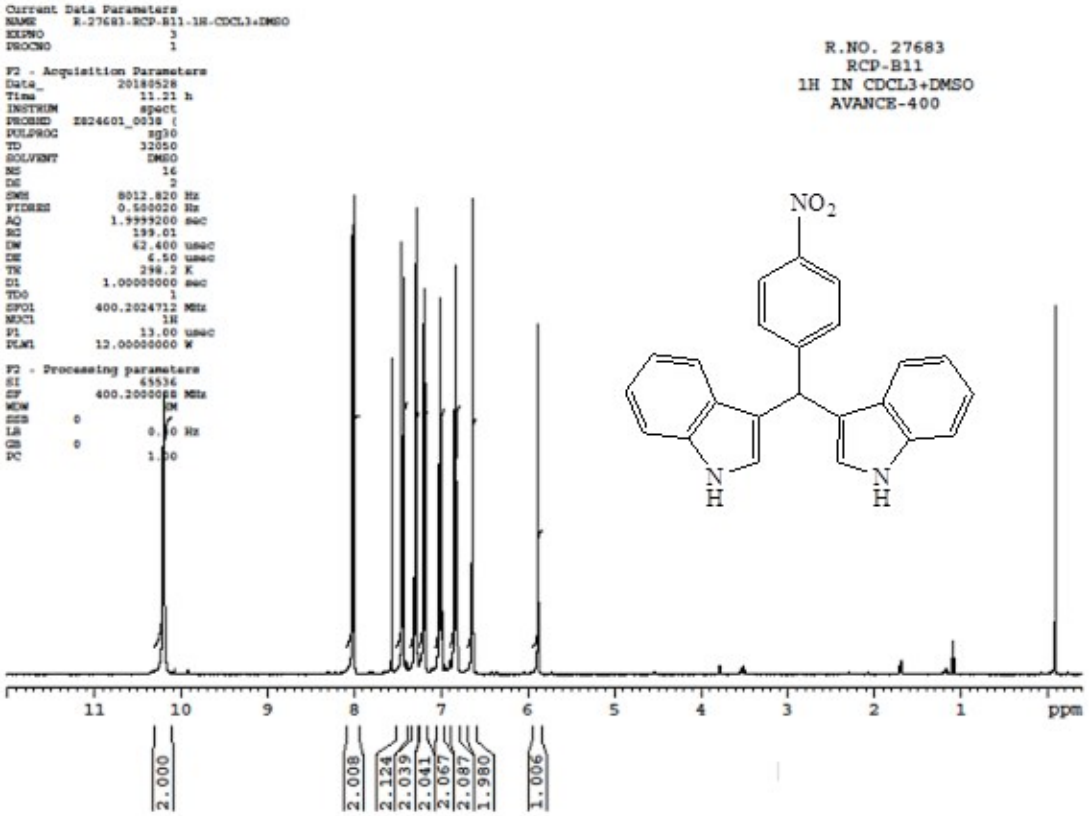
^{13}C NMR spectrum of compound 3c



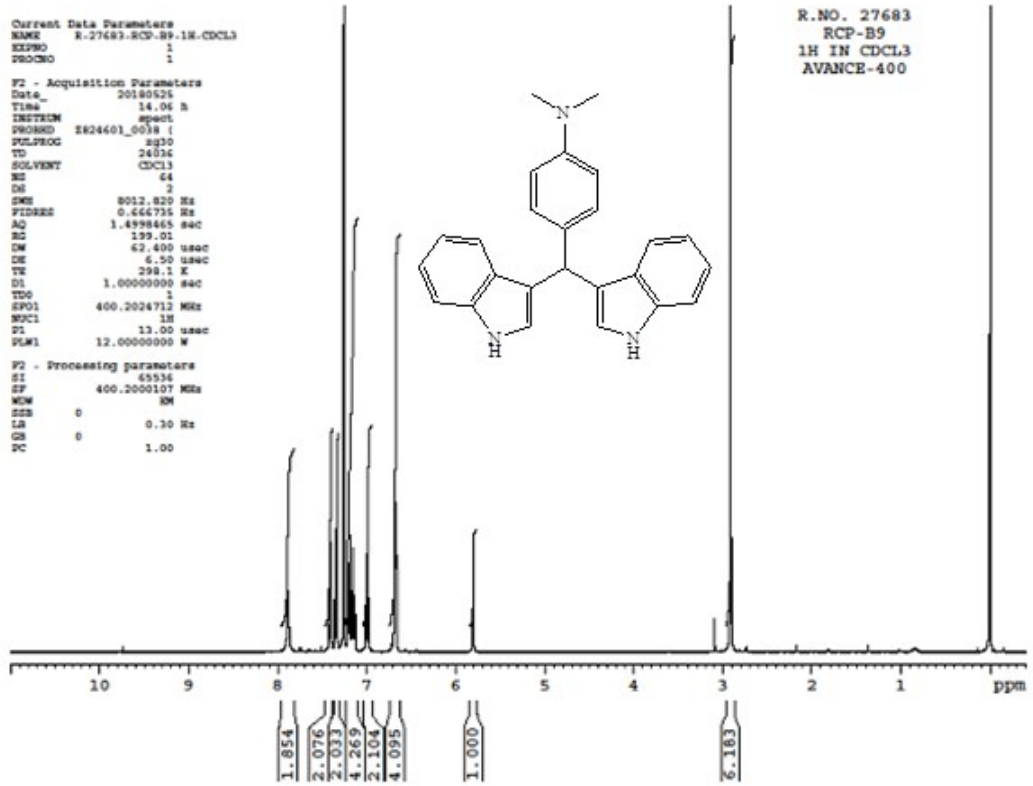
^{1}H NMR spectrum of compound 3d



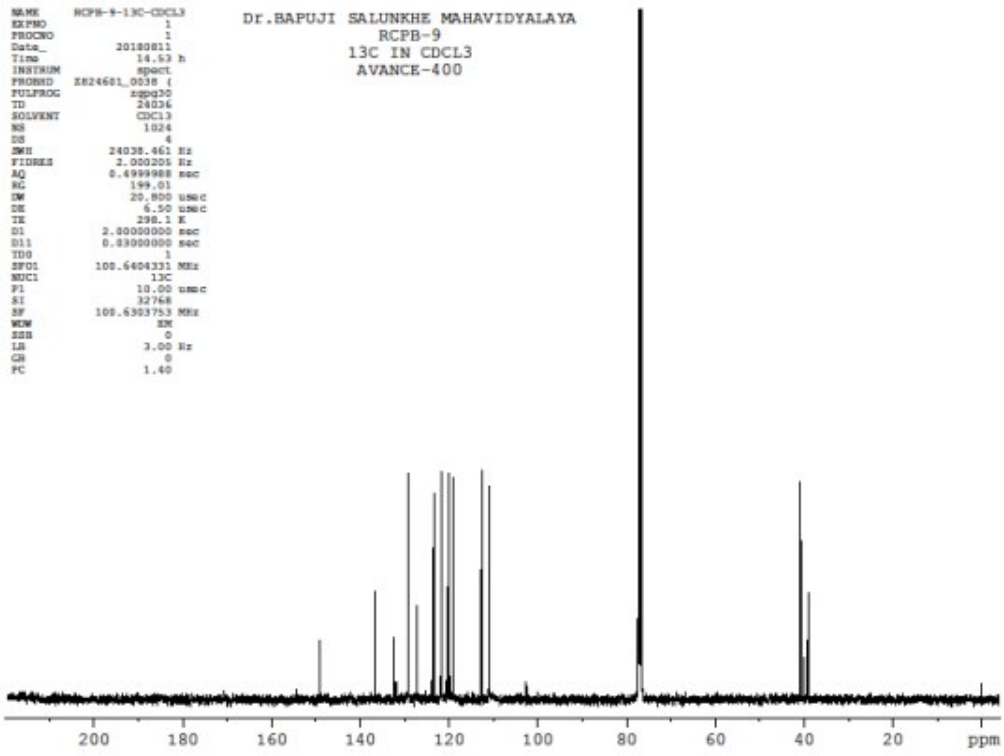
FT-IR spectrum of compound 3d



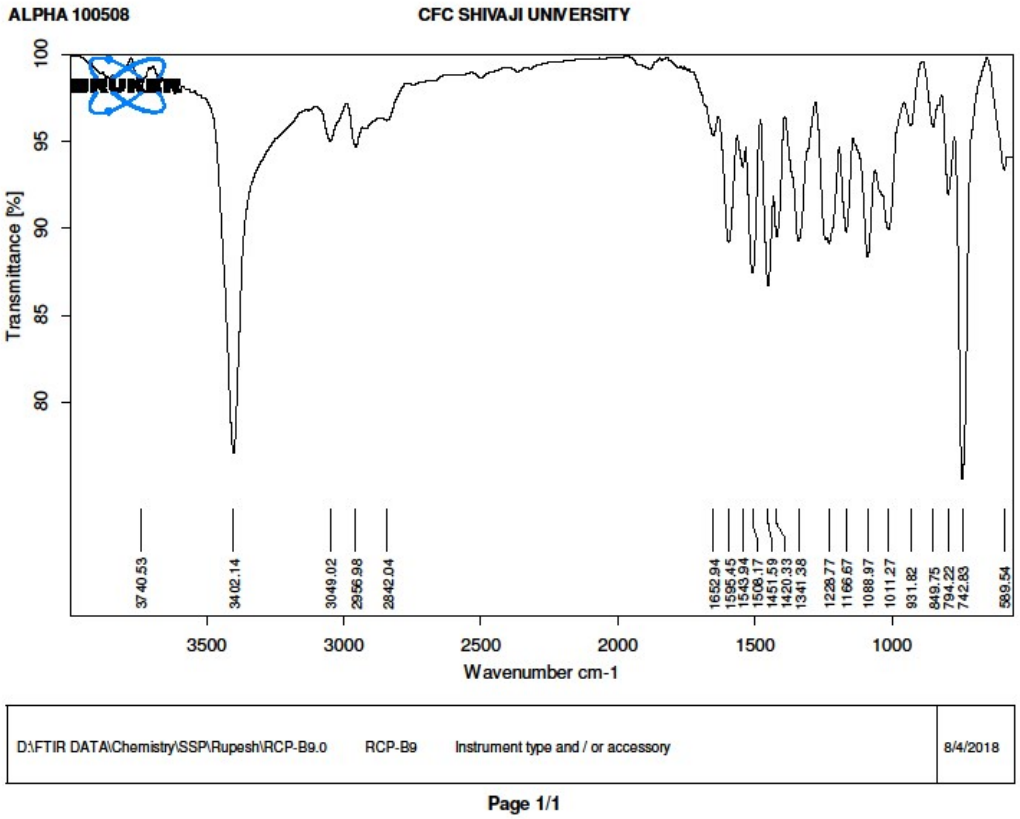
^{1}H NMR spectrum of compound 3e



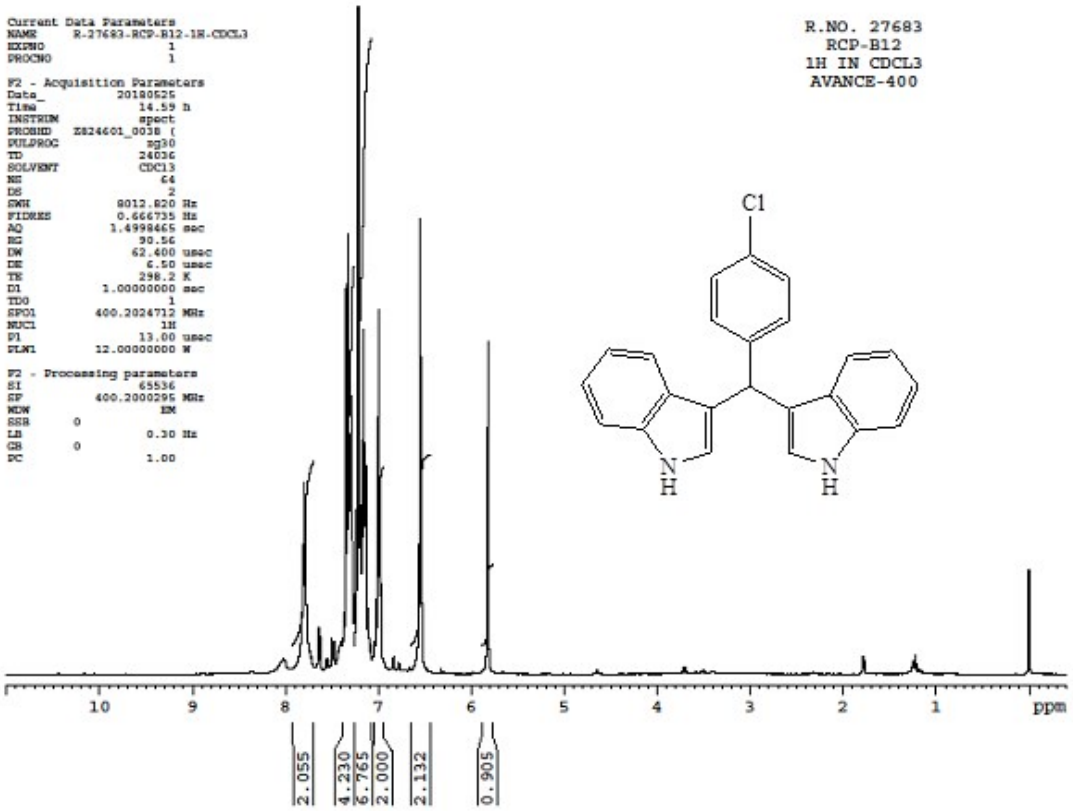
^{1}H NMR spectrum of compound 3f



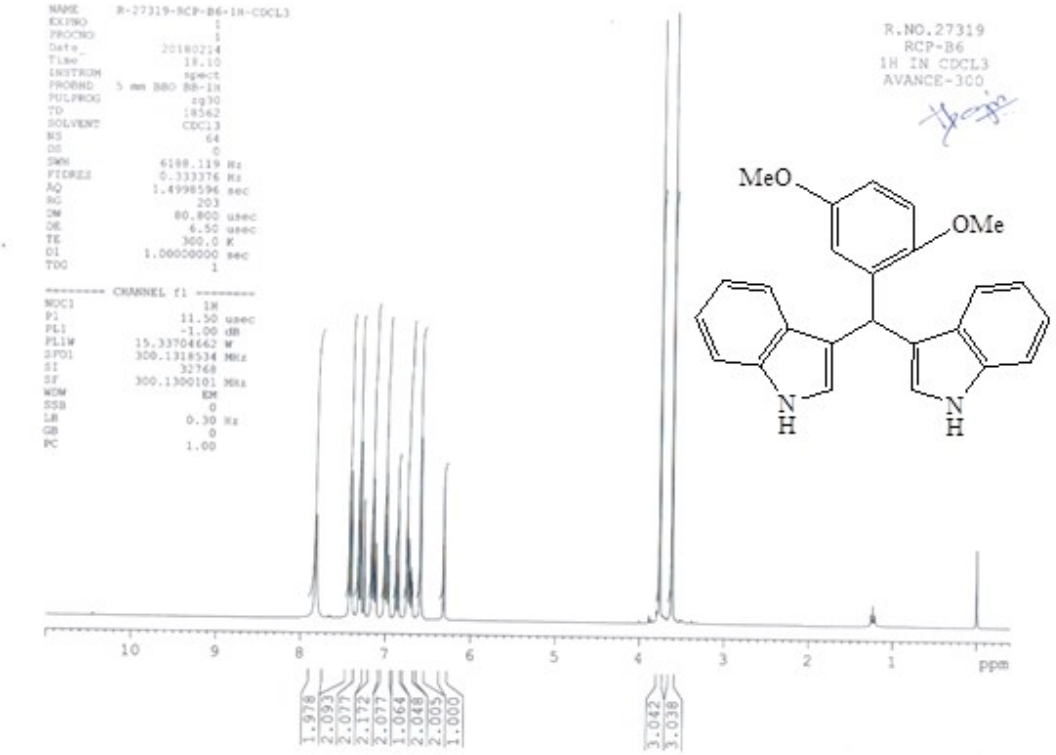
^{13}C NMR spectrum of compound 3f



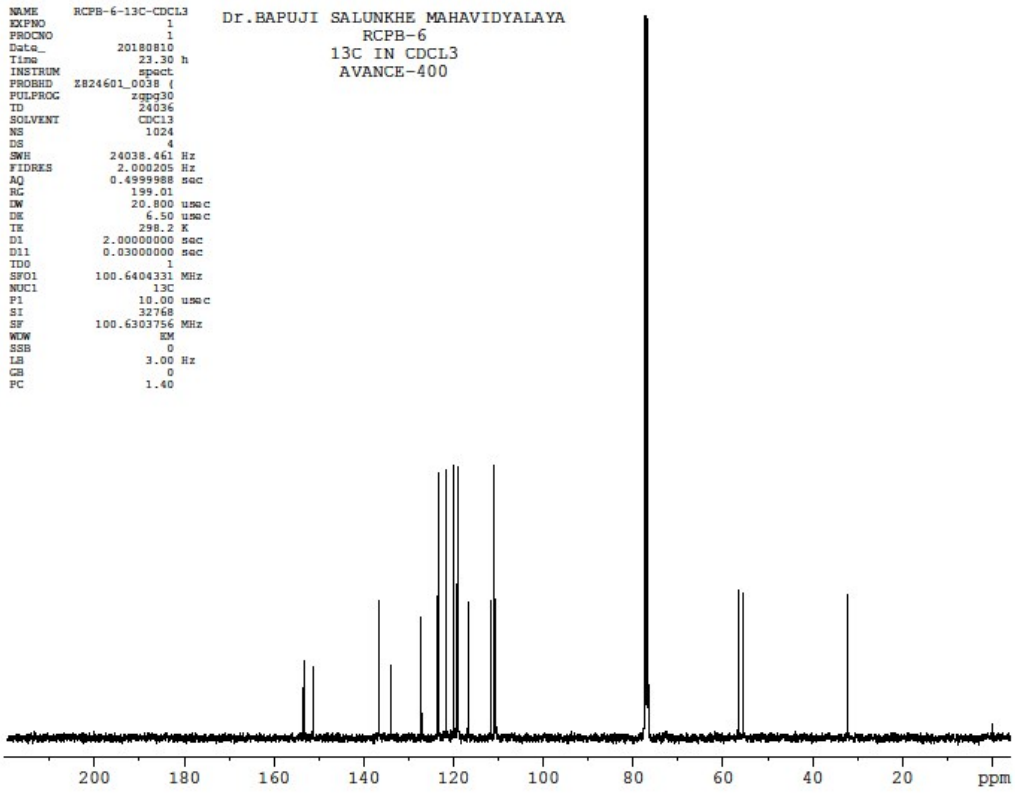
FT-IR spectrum of compound 3f



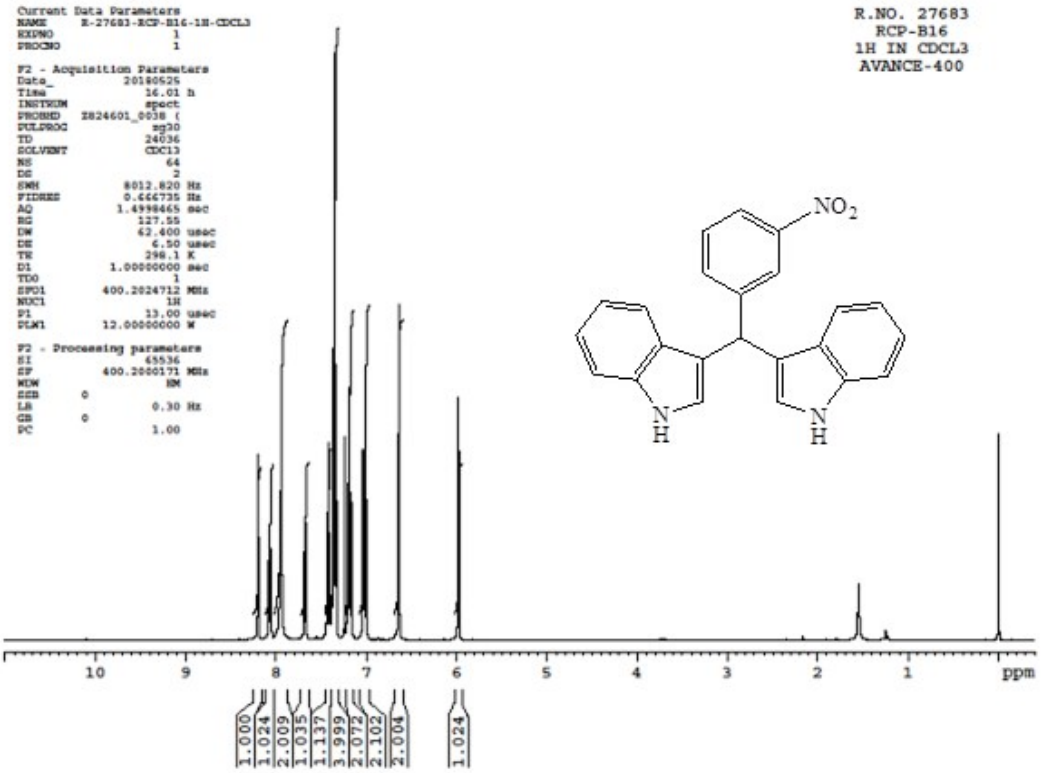
^{1}H NMR spectrum of compound 3h



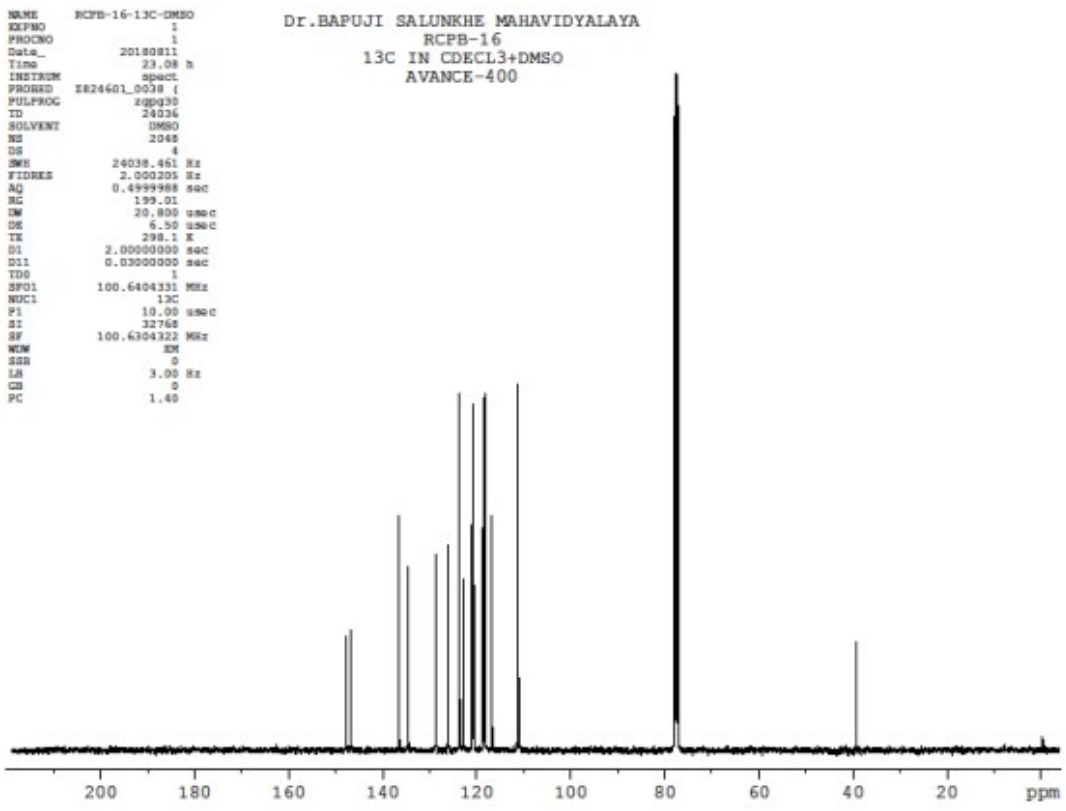
^{1}H NMR spectrum of compound 3i



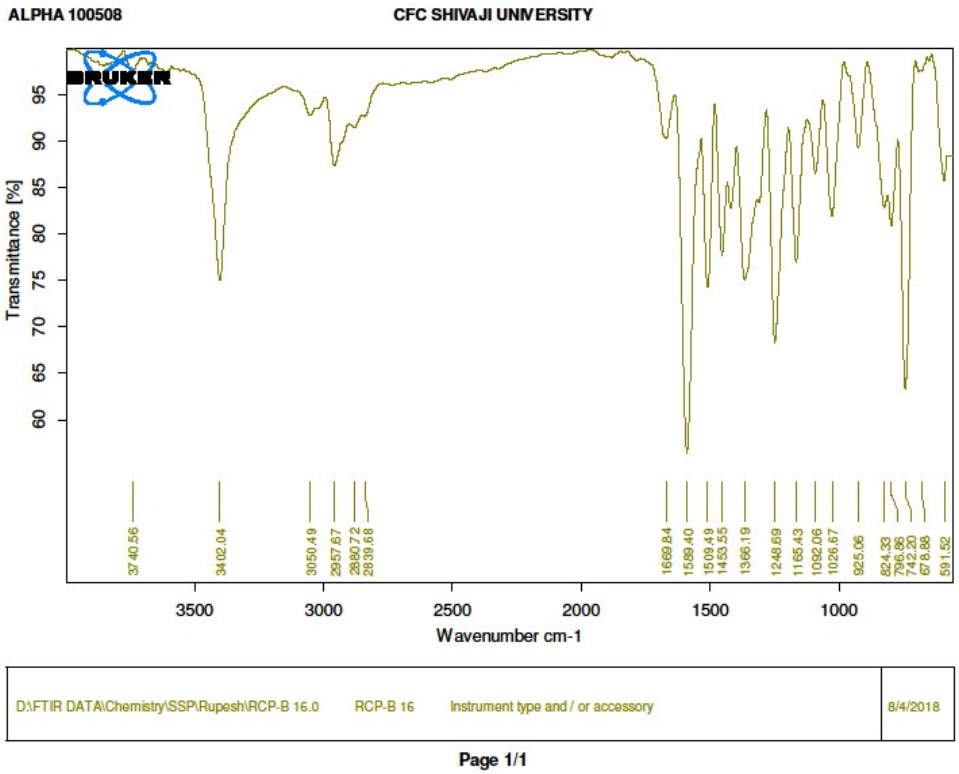
^{13}C NMR spectrum of compound 3i



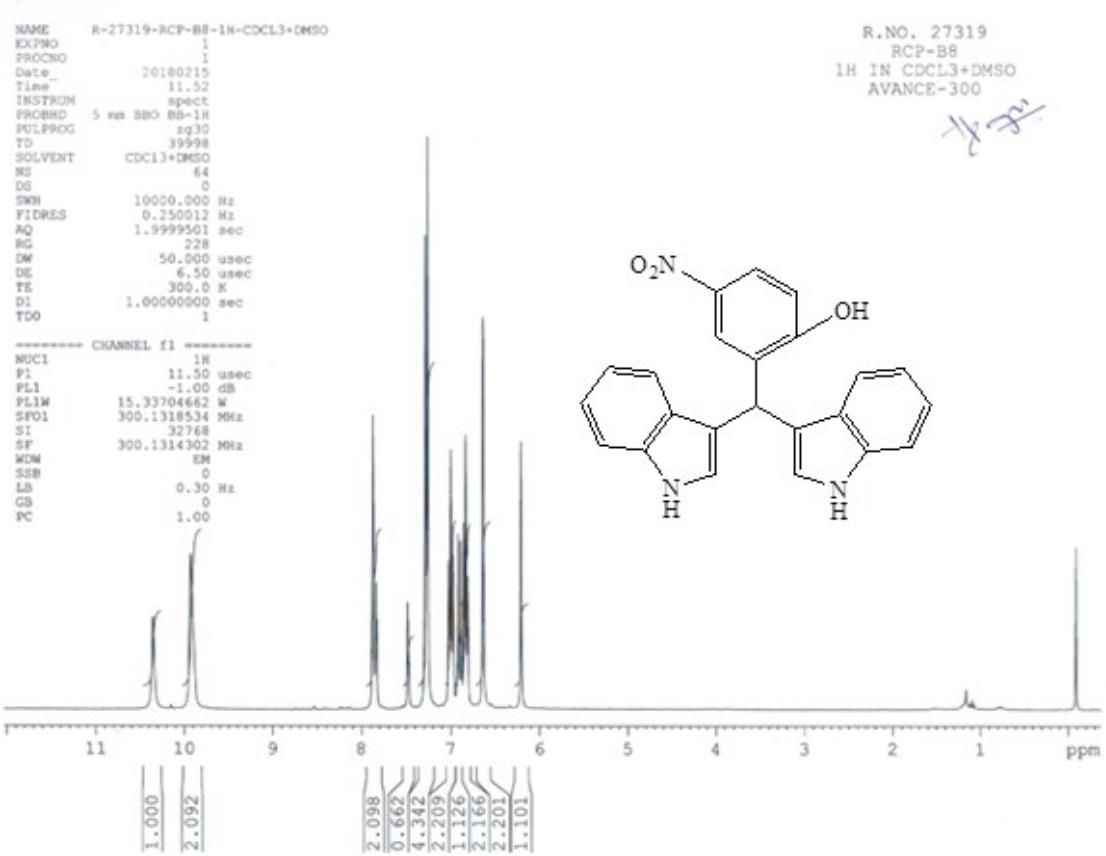
^{1}H NMR spectrum of compound 3j



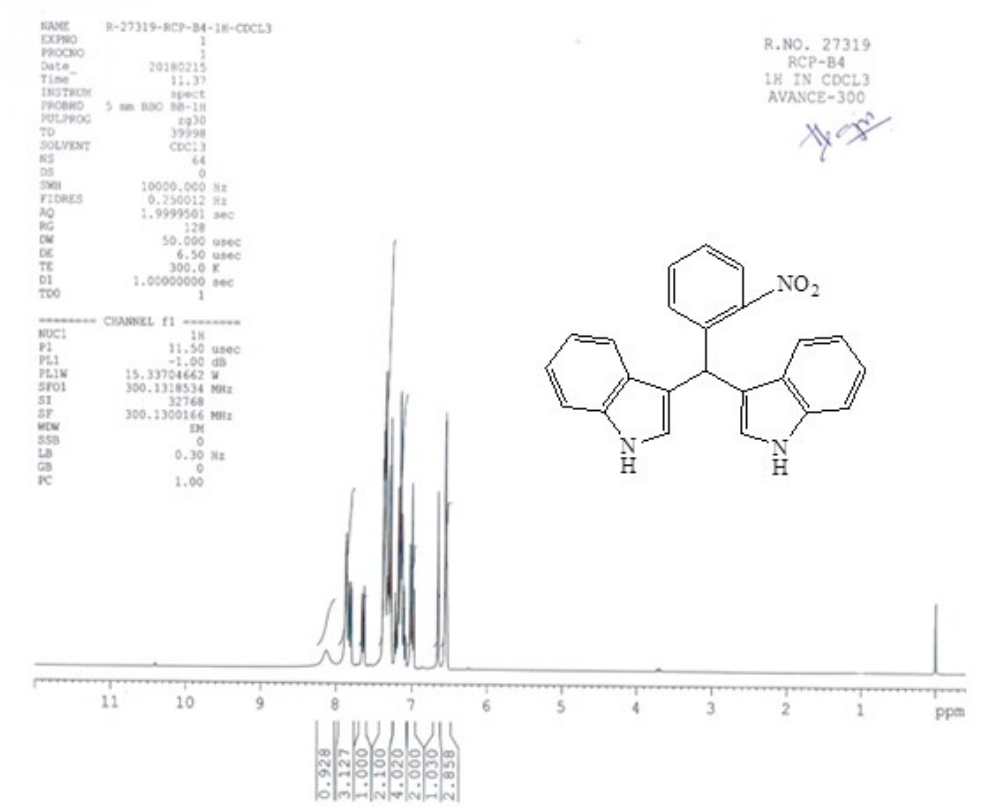
^{13}C NMR spectrum of compound 3j



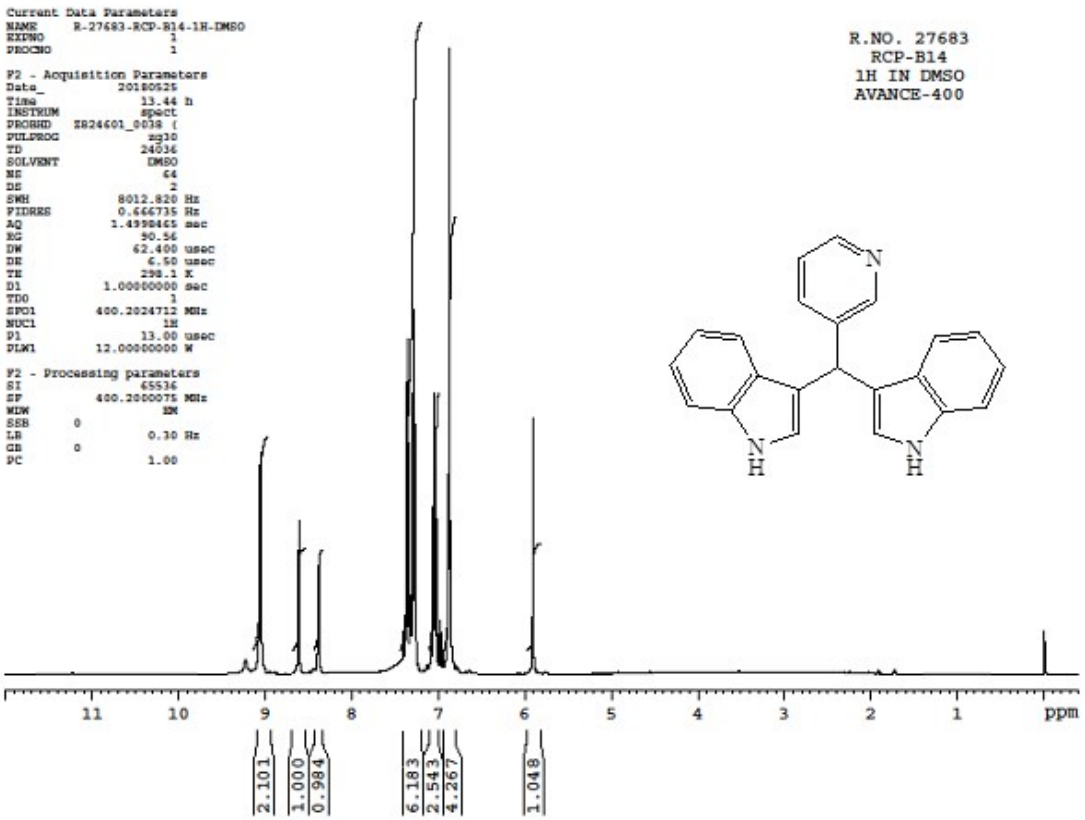
FT-IR spectrum of compound 3j



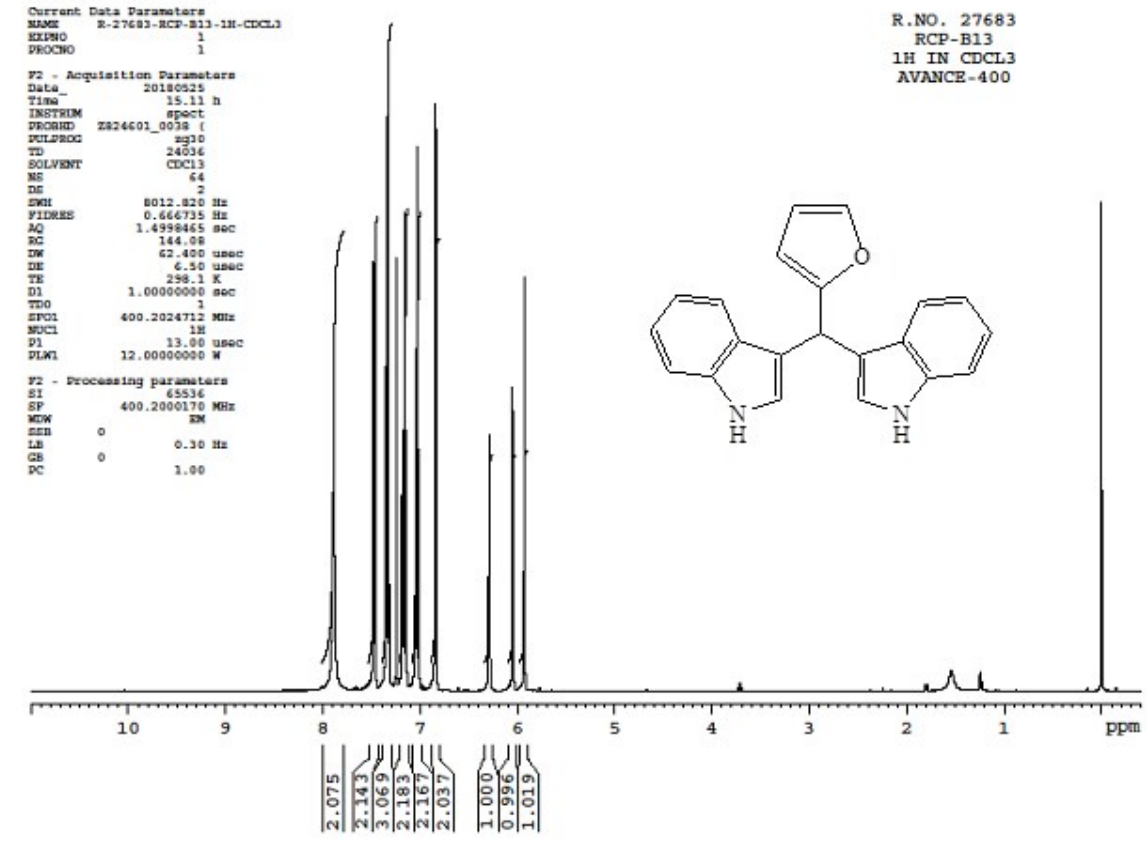
^{1}H NMR spectrum of compound 3k



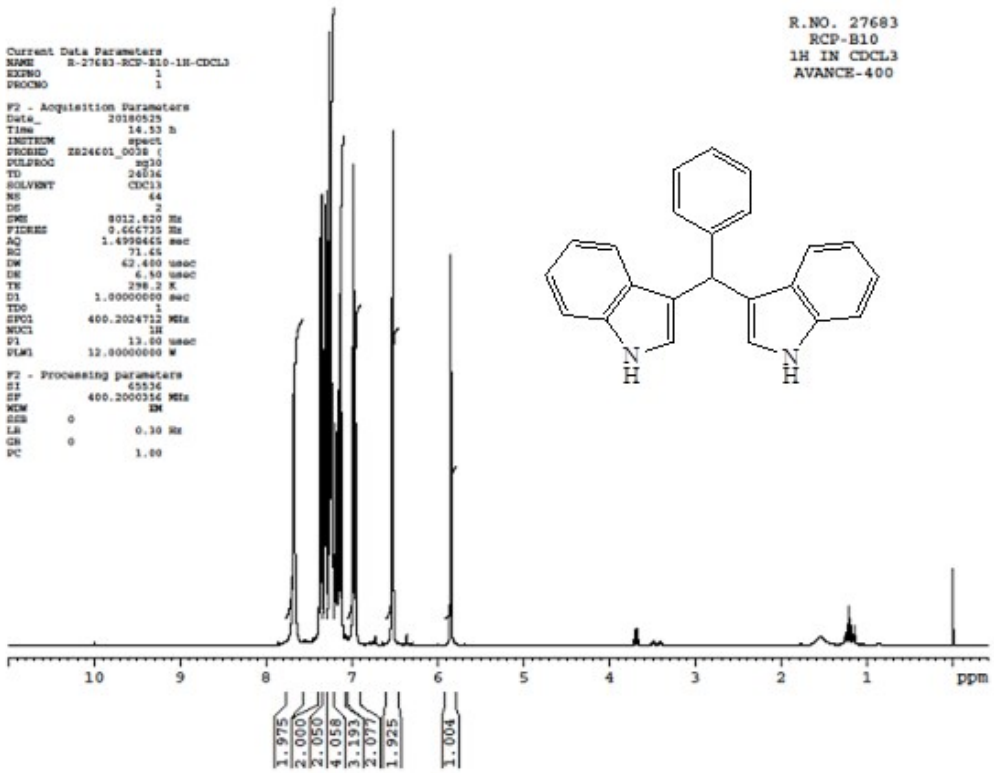
^{1}H NMR spectrum of compound 3l



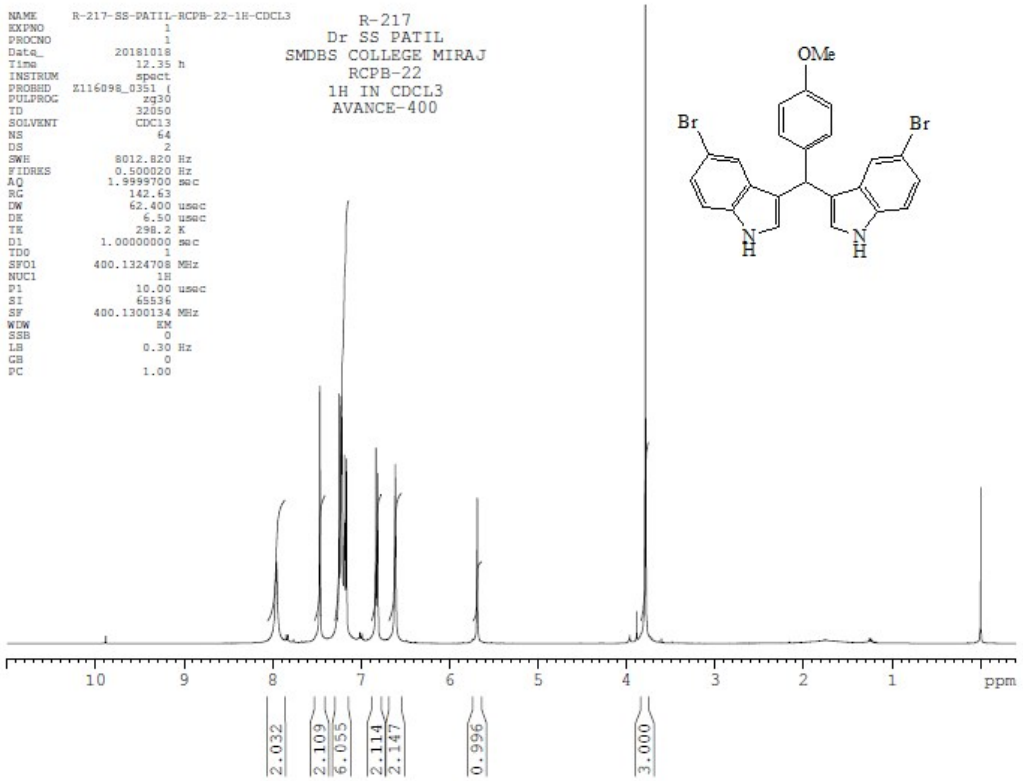
^{1}H NMR spectrum of compound 3m



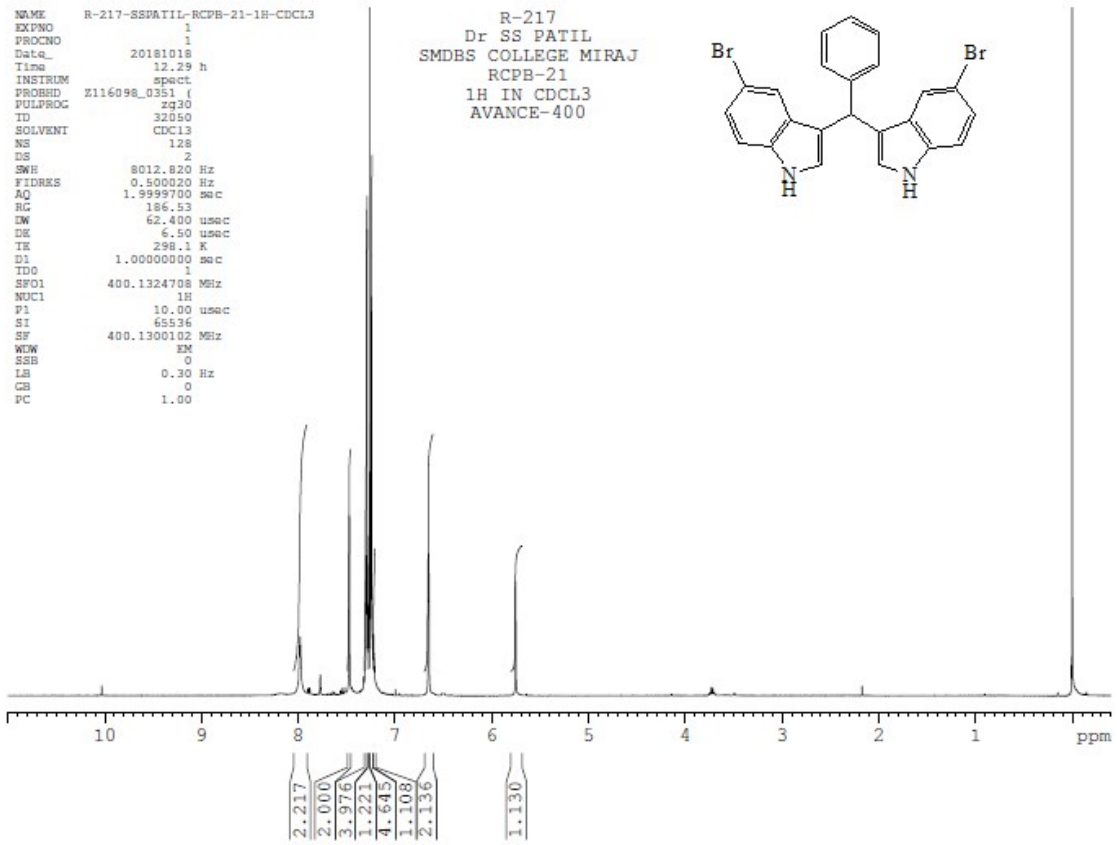
^{1}H NMR spectrum of compound 3n



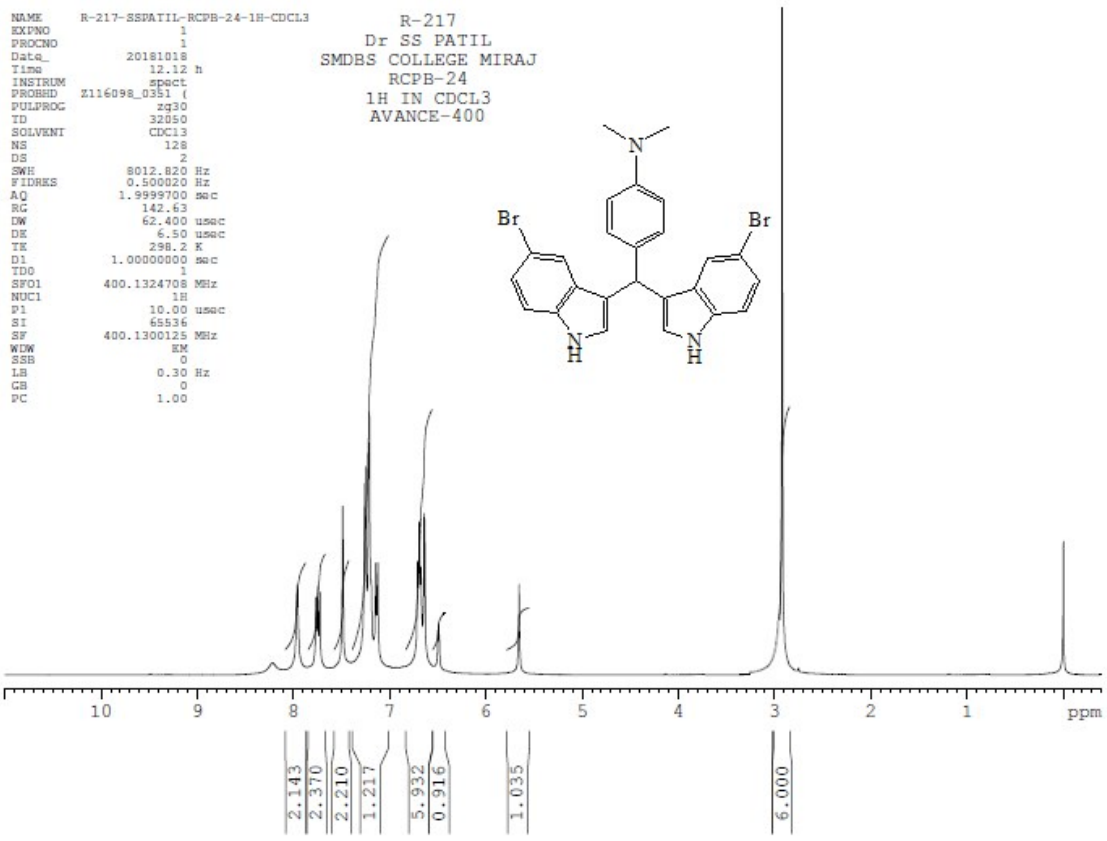
^{1}H NMR spectrum of compound 3o



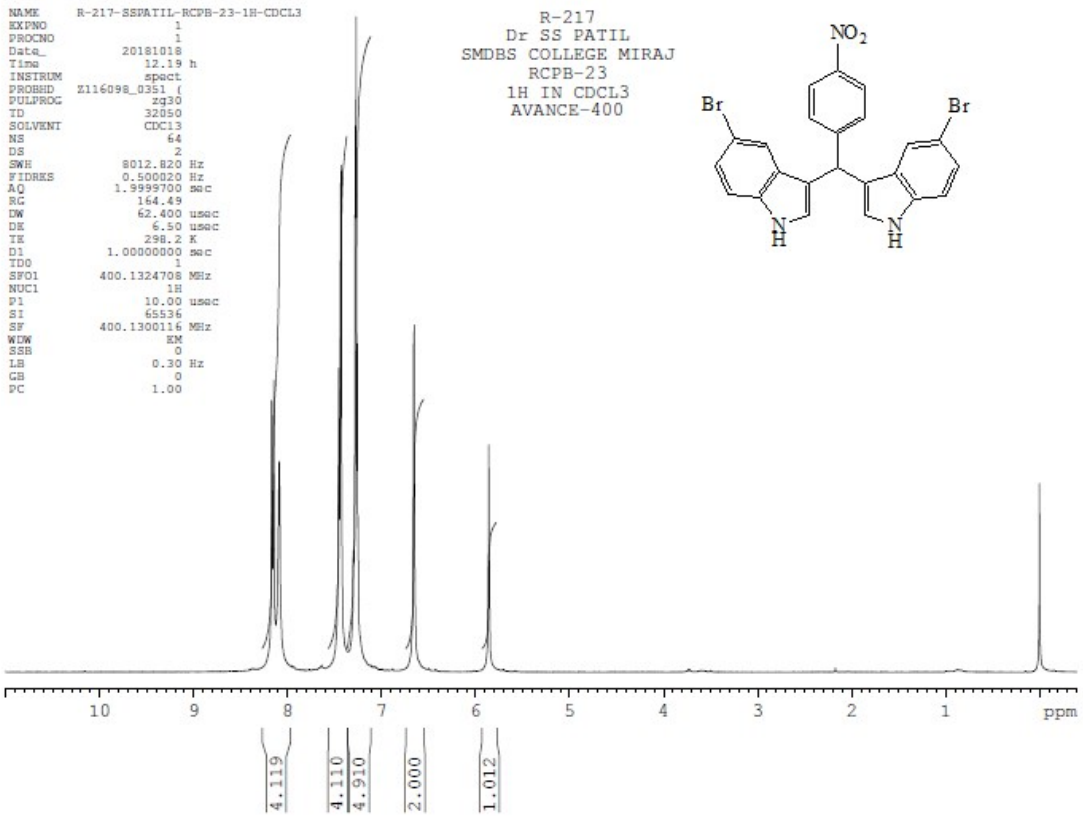
^{1}H NMR spectrum of compound 3q



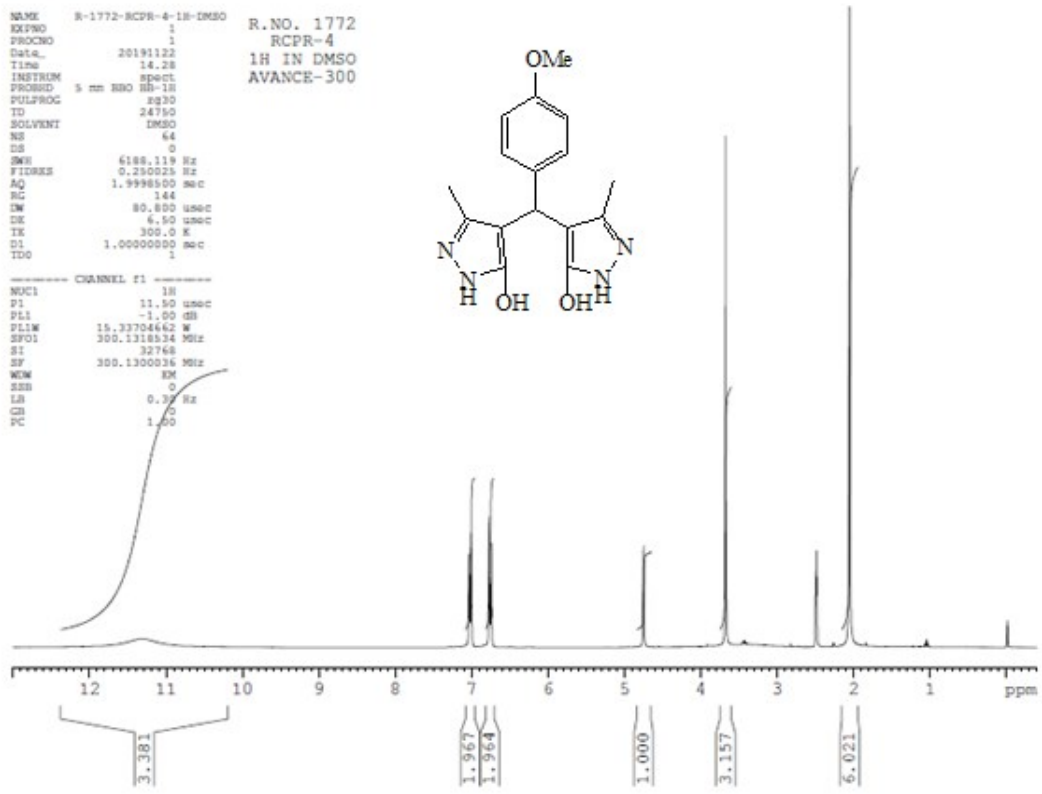
^{1}H NMR spectrum of compound 3r



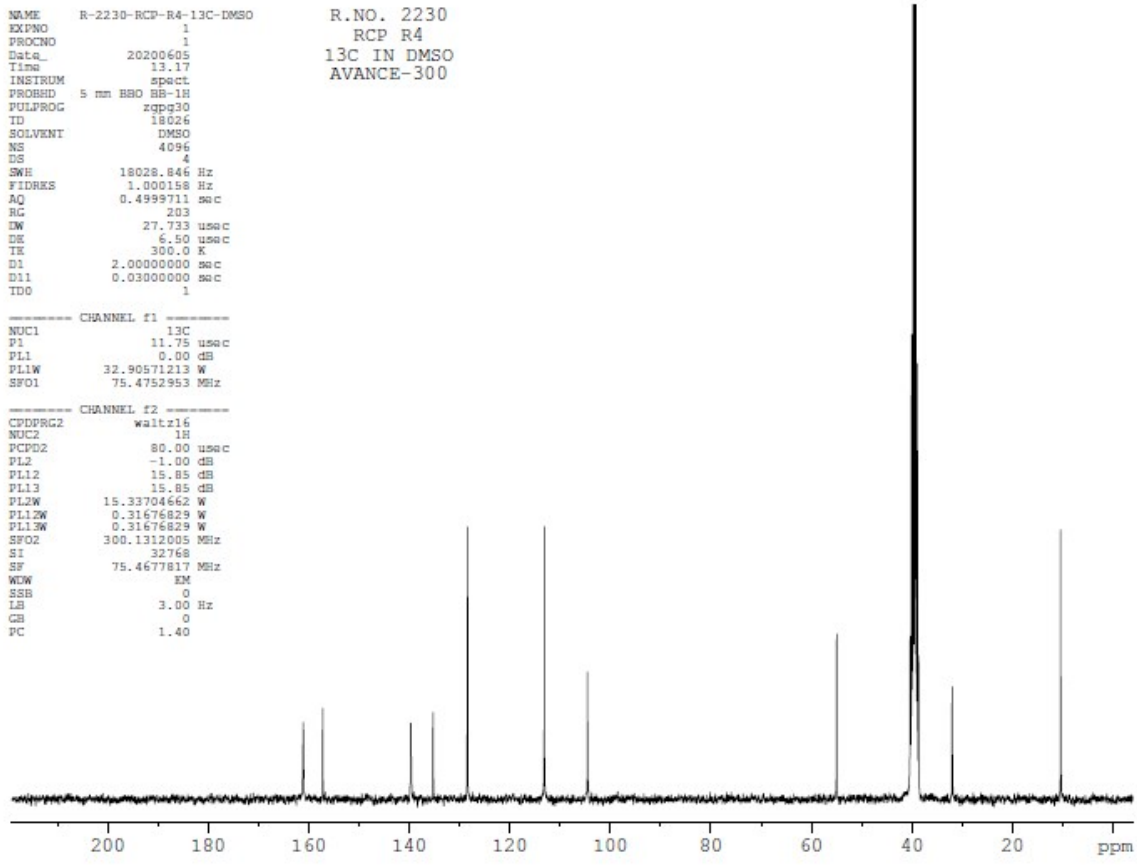
^{1}H NMR spectrum of compound 3Sk



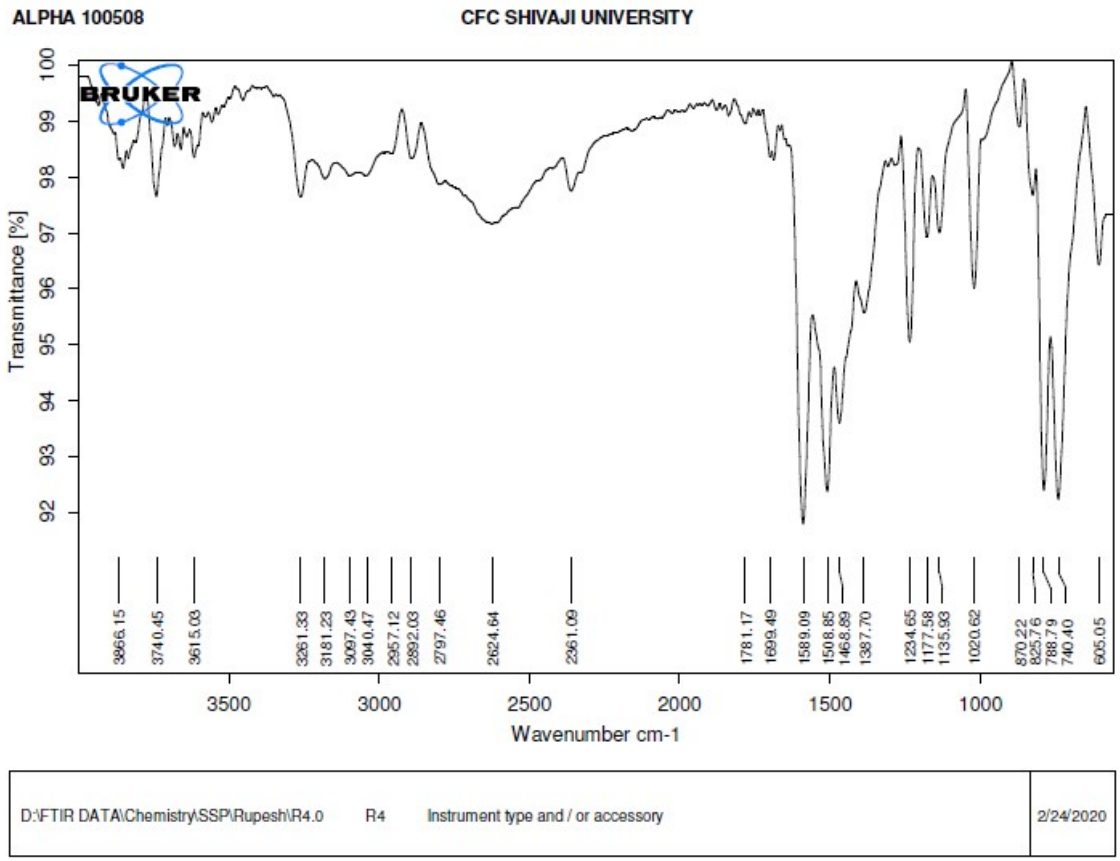
^{1}H NMR spectrum of compound 3t



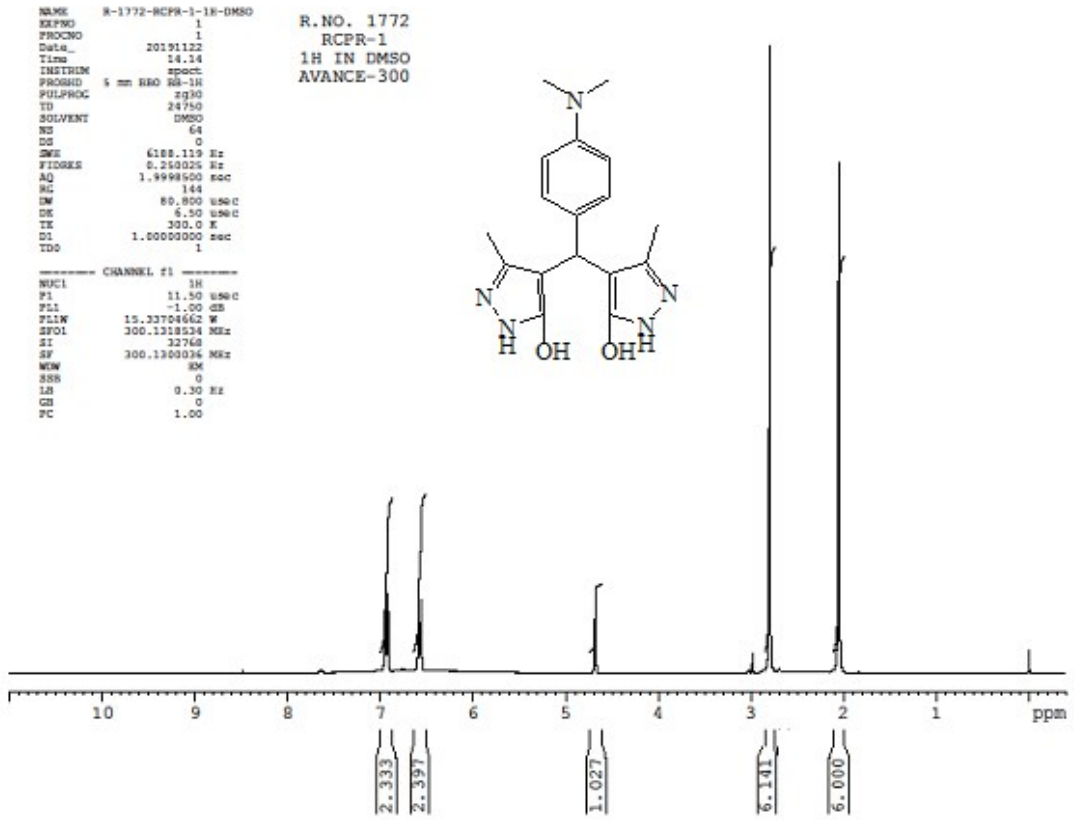
^{1}H NMR spectrum of compound 7a



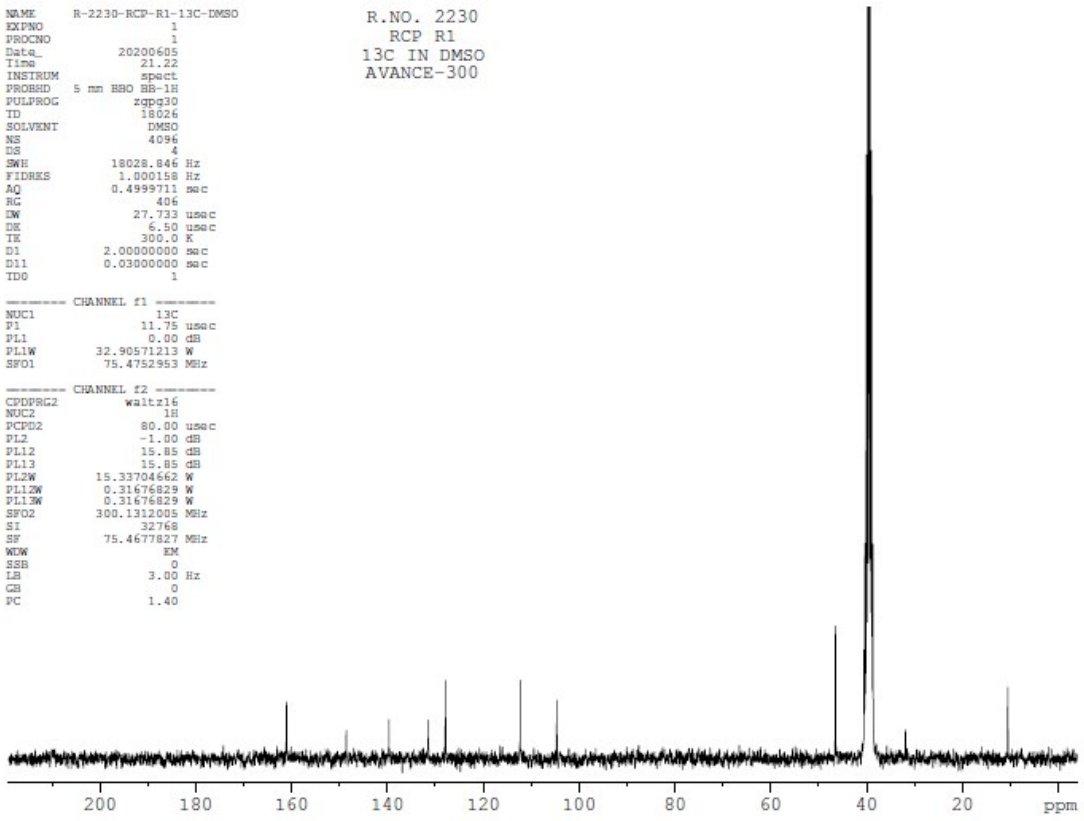
^{13}C NMR spectrum of compound 7a



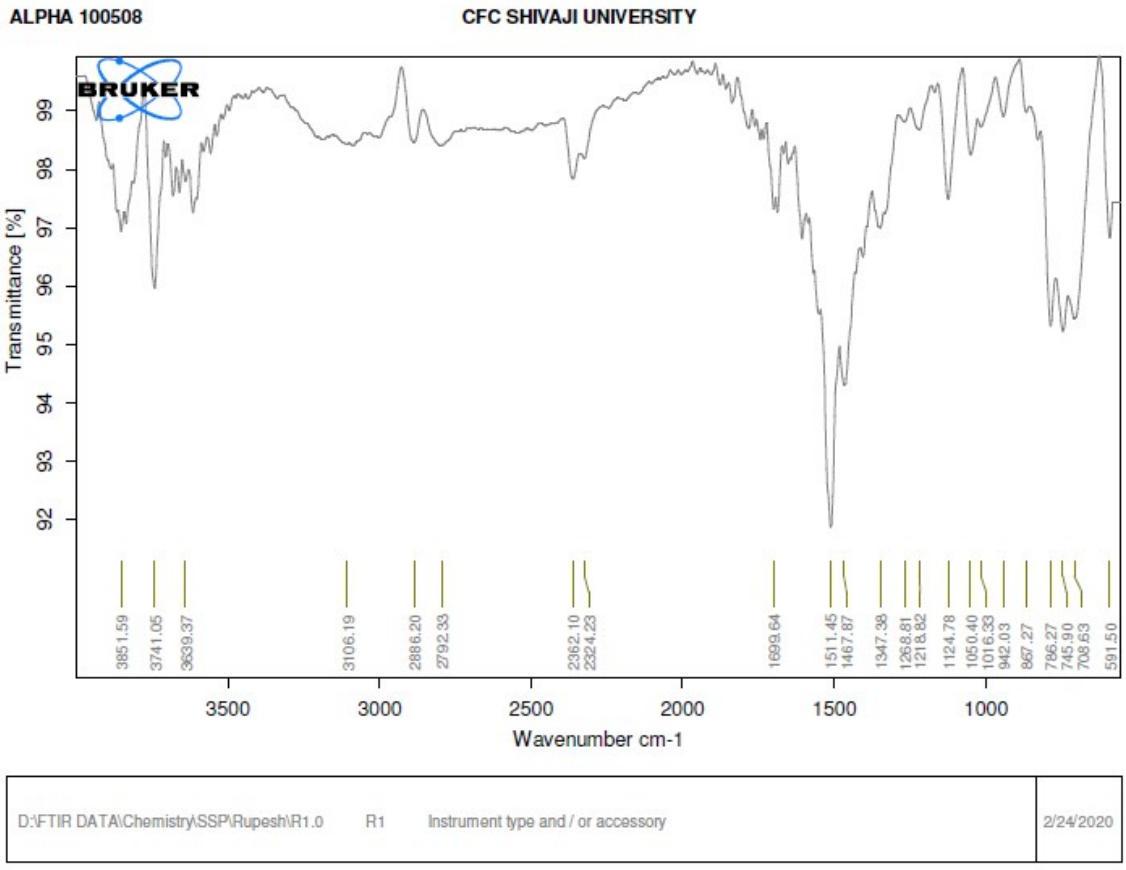
FT-IR spectrum of compound 7a



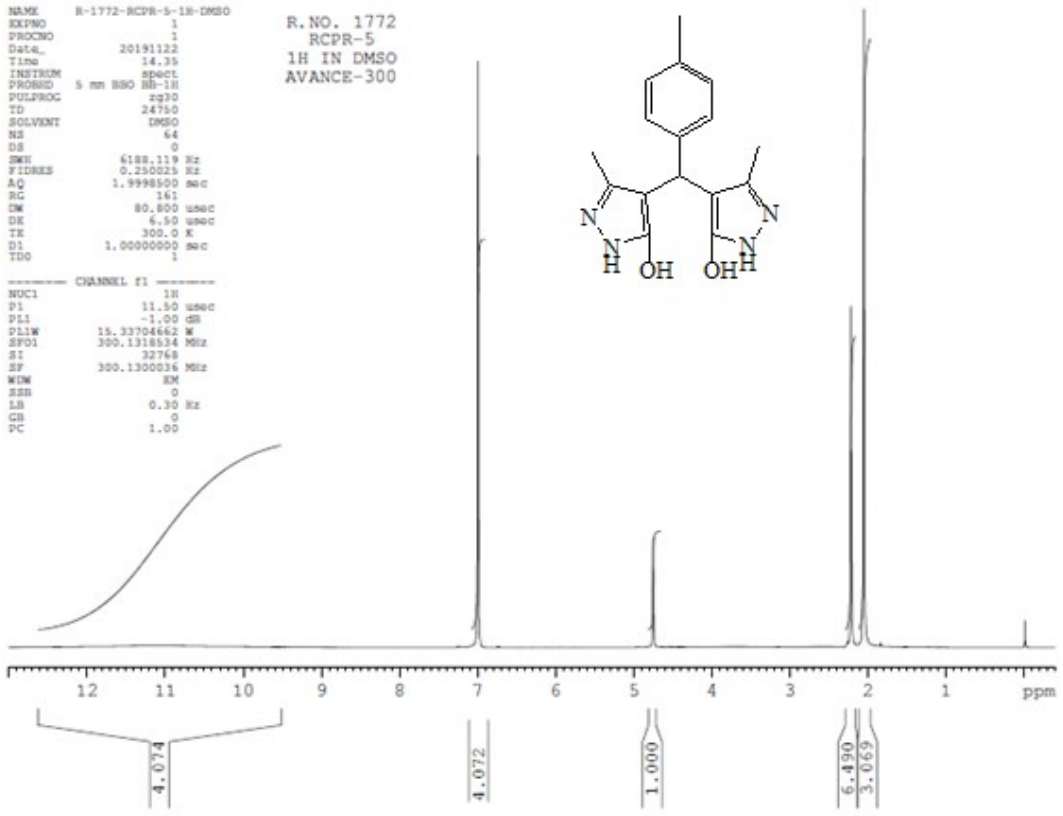
^{1}H NMR spectrum of compound 7c



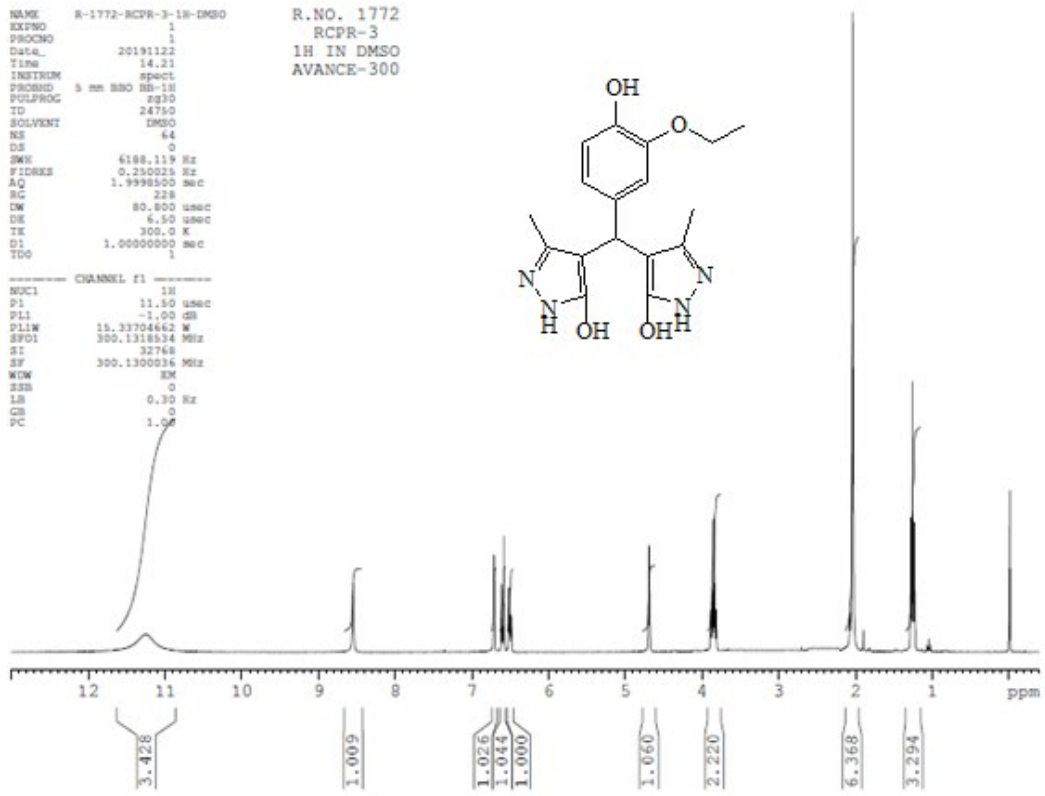
^{13}C NMR spectrum of compound 7c



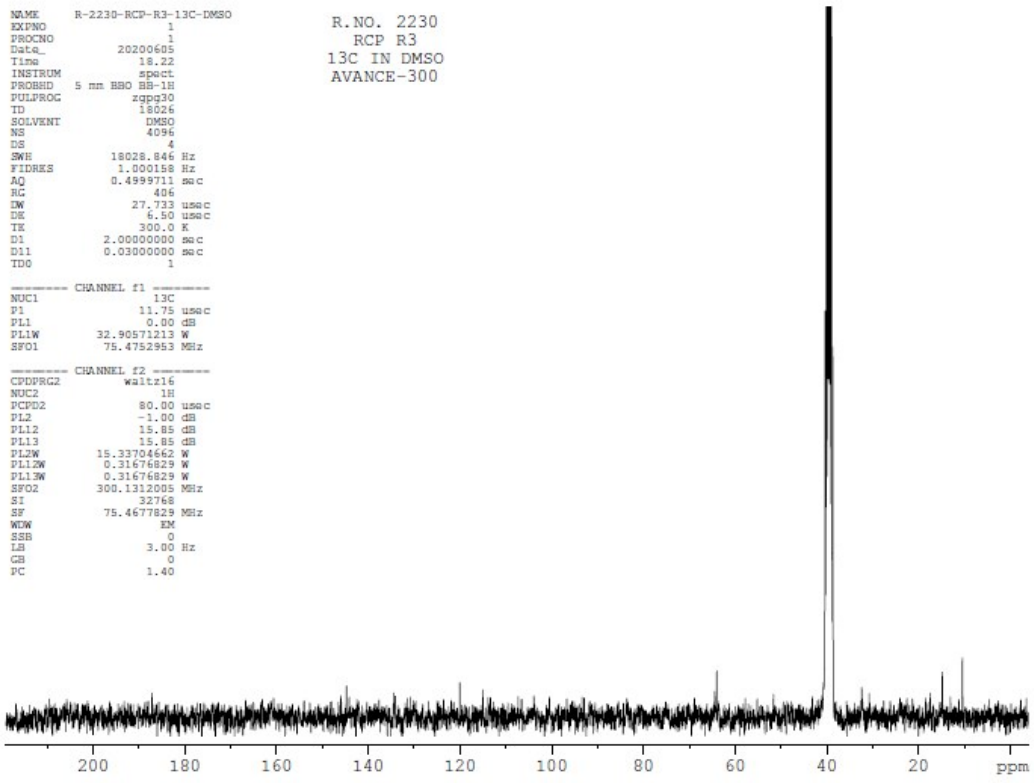
FT-IR spectrum of compound 7c



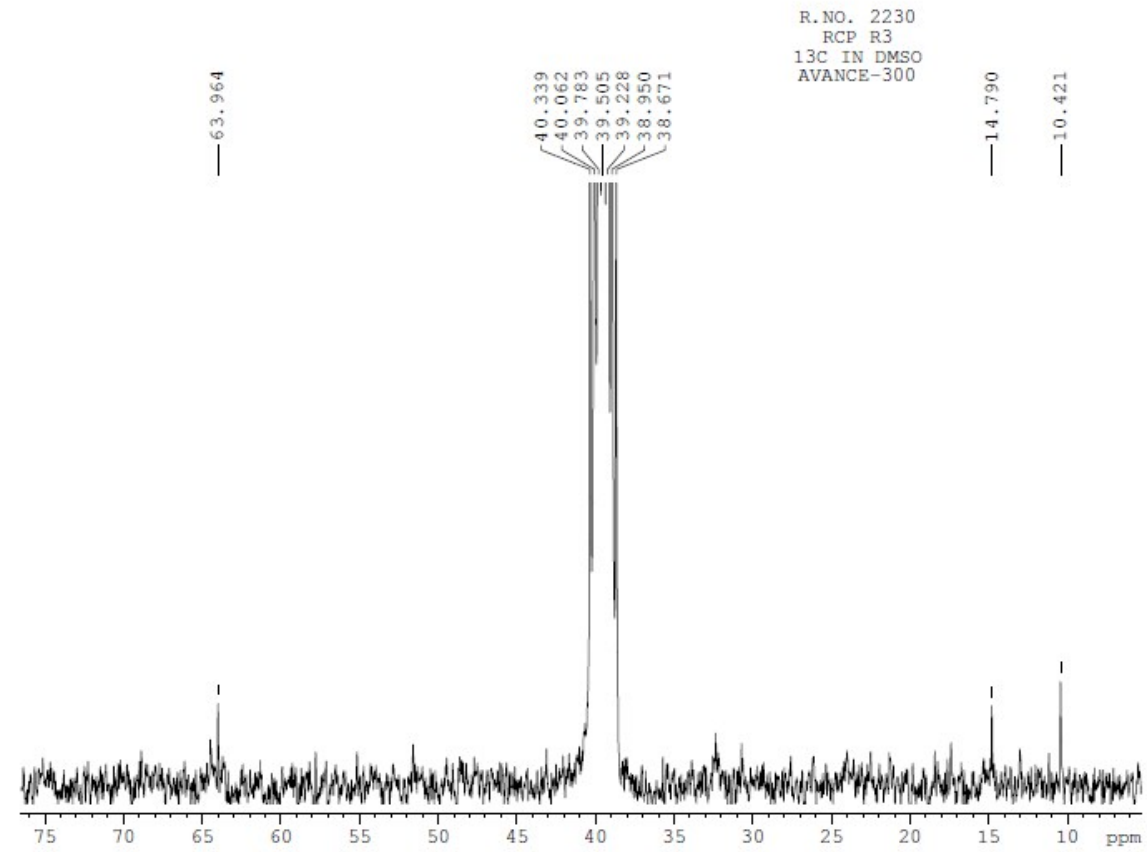
^{1}H NMR spectrum of compound 7d

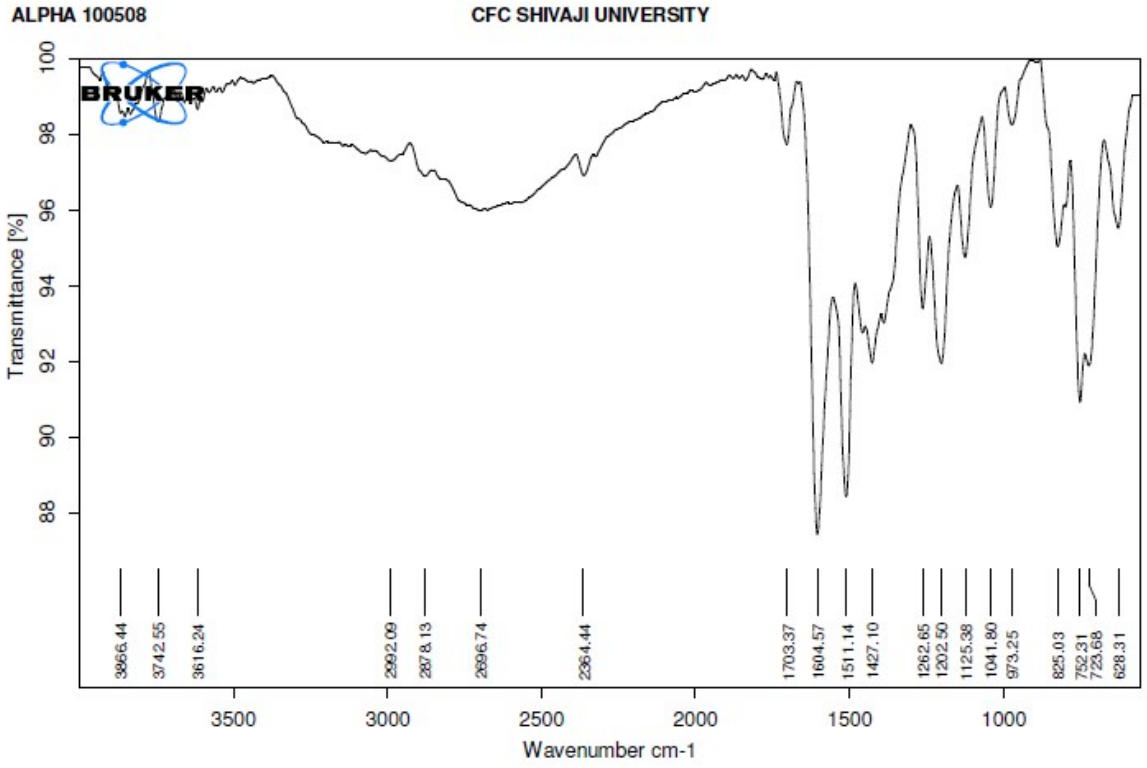


^{1}H NMR spectrum of compound 7e



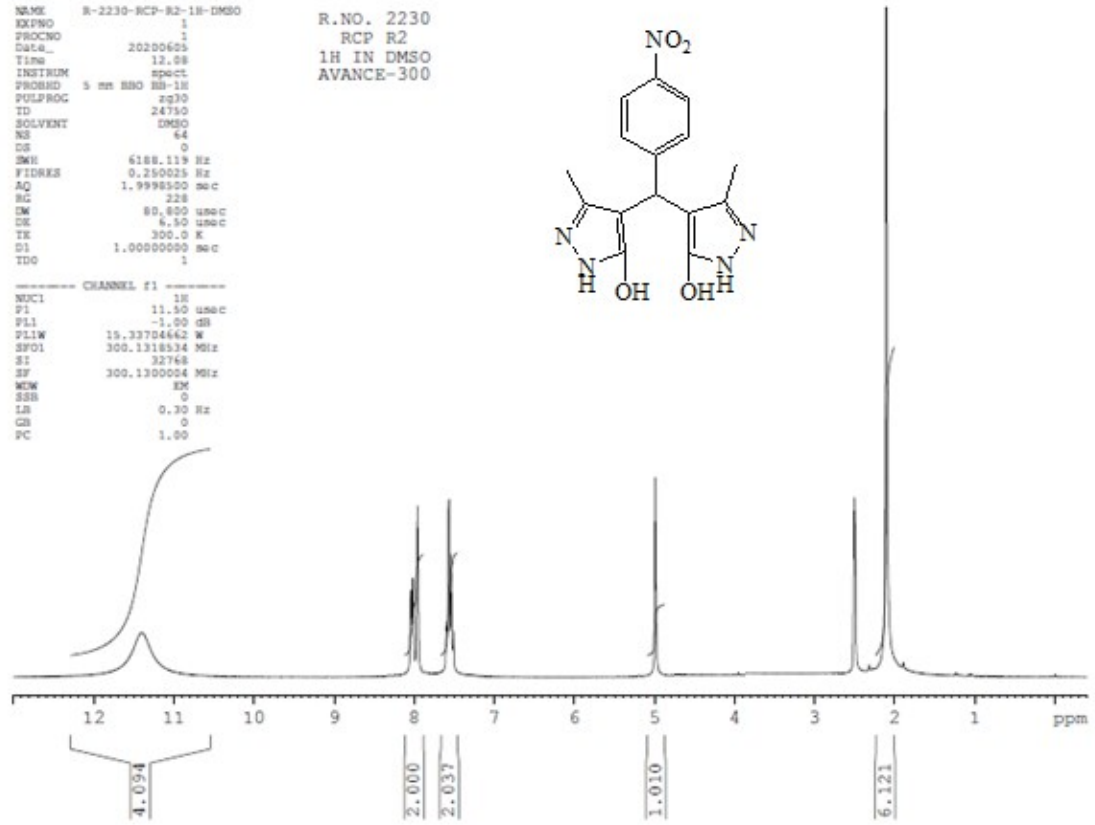
^{13}C NMR spectrum of compound 7e



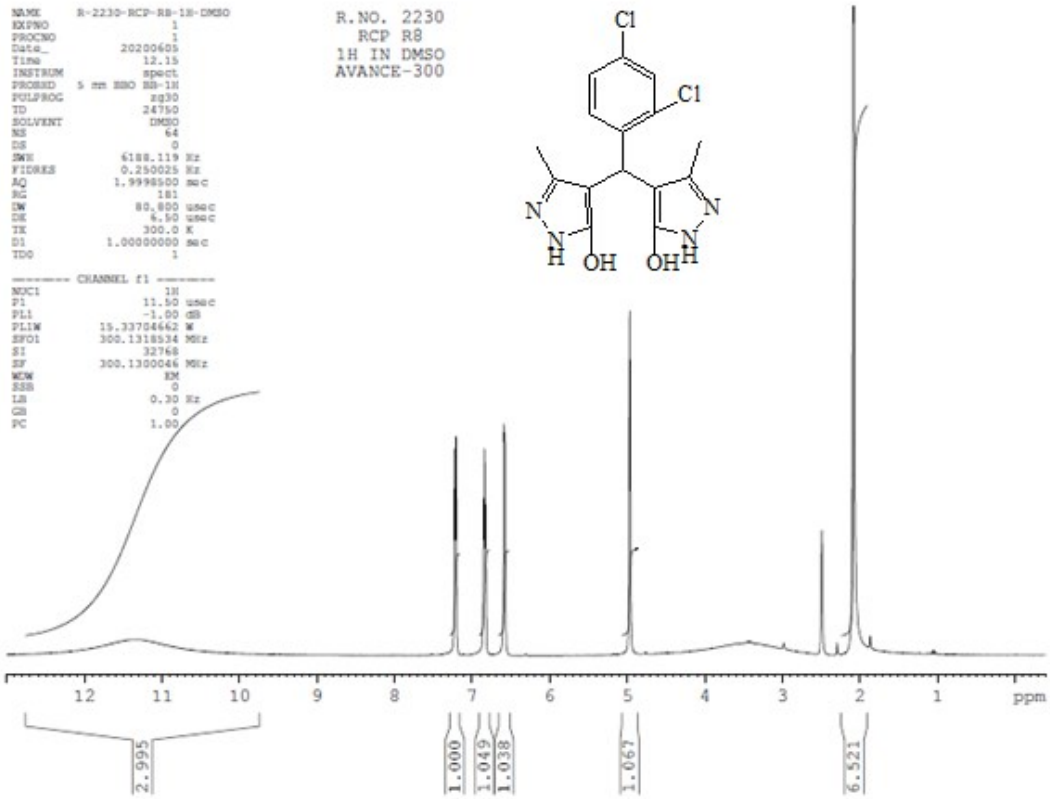


D:\FTIR DATA\Chemistry\SSP\Rupesh\R3.0	R3	Instrument type and / or accessory	2/24/2020

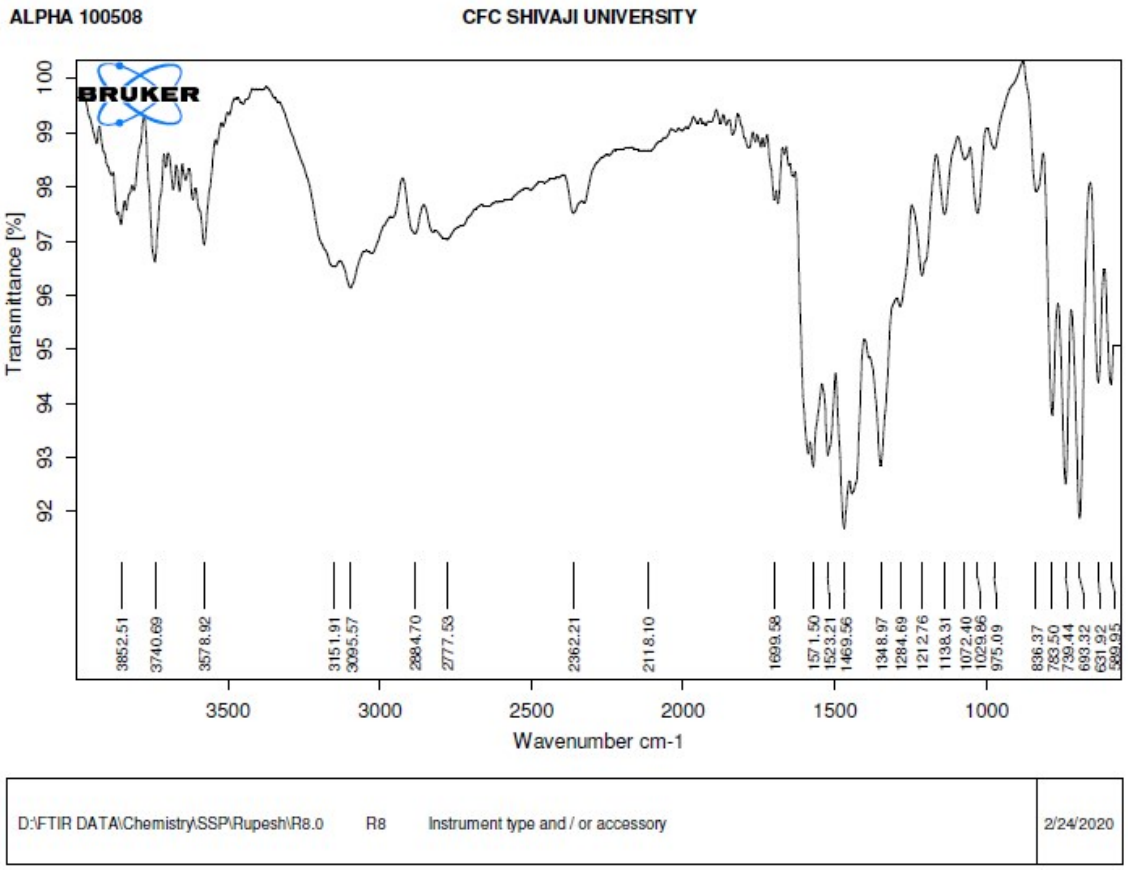
FT-IR spectrum of compound 7e



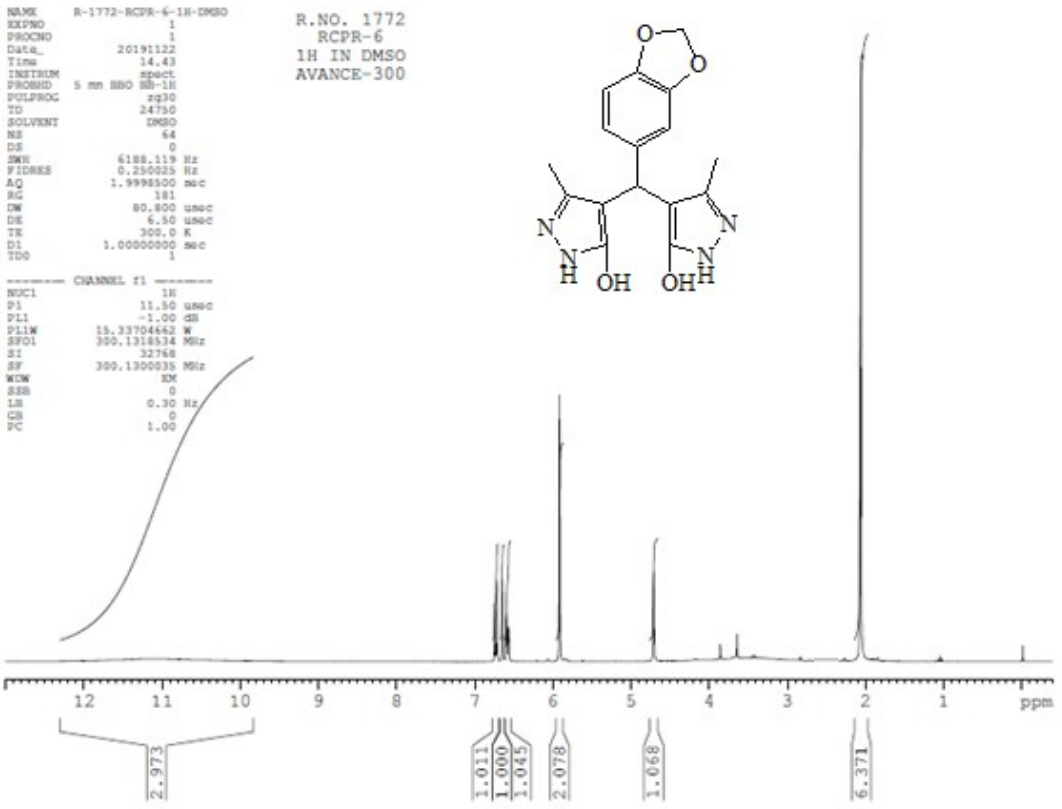
^{1}H NMR spectrum of compound 7f



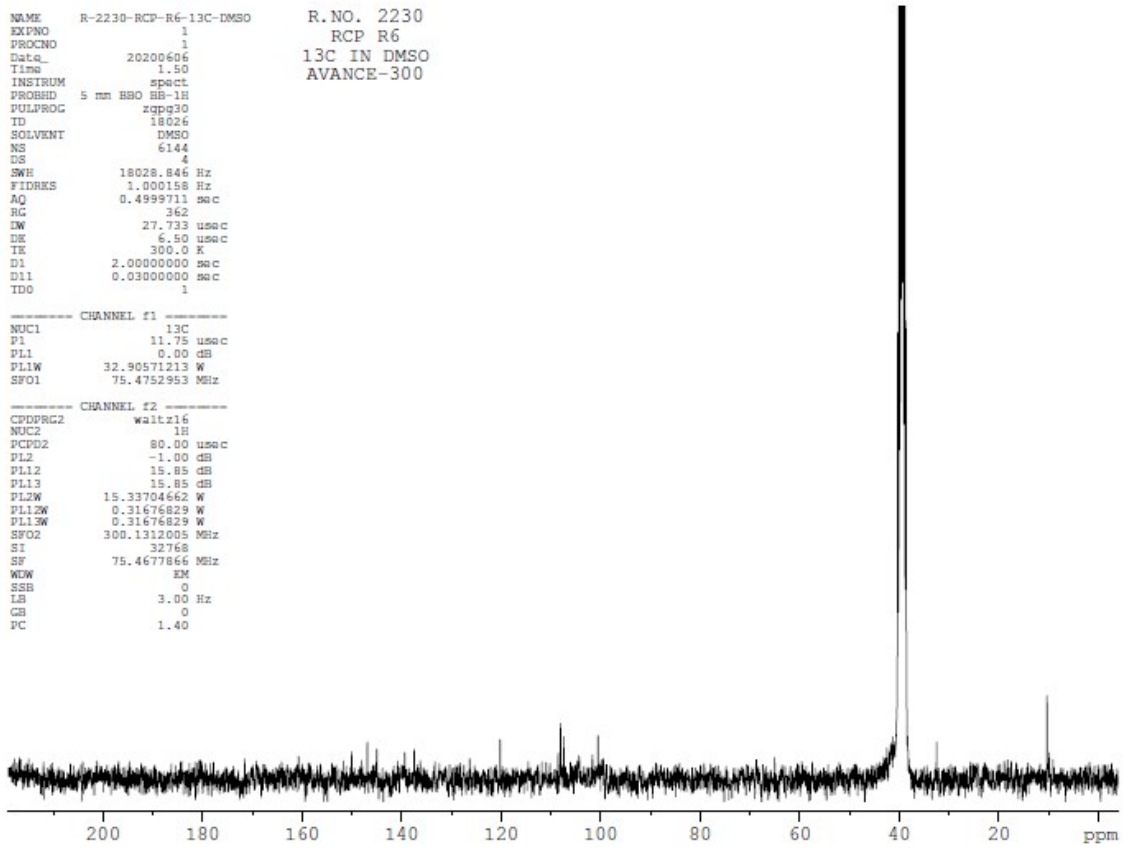
^{1}H NMR spectrum of compound 7h



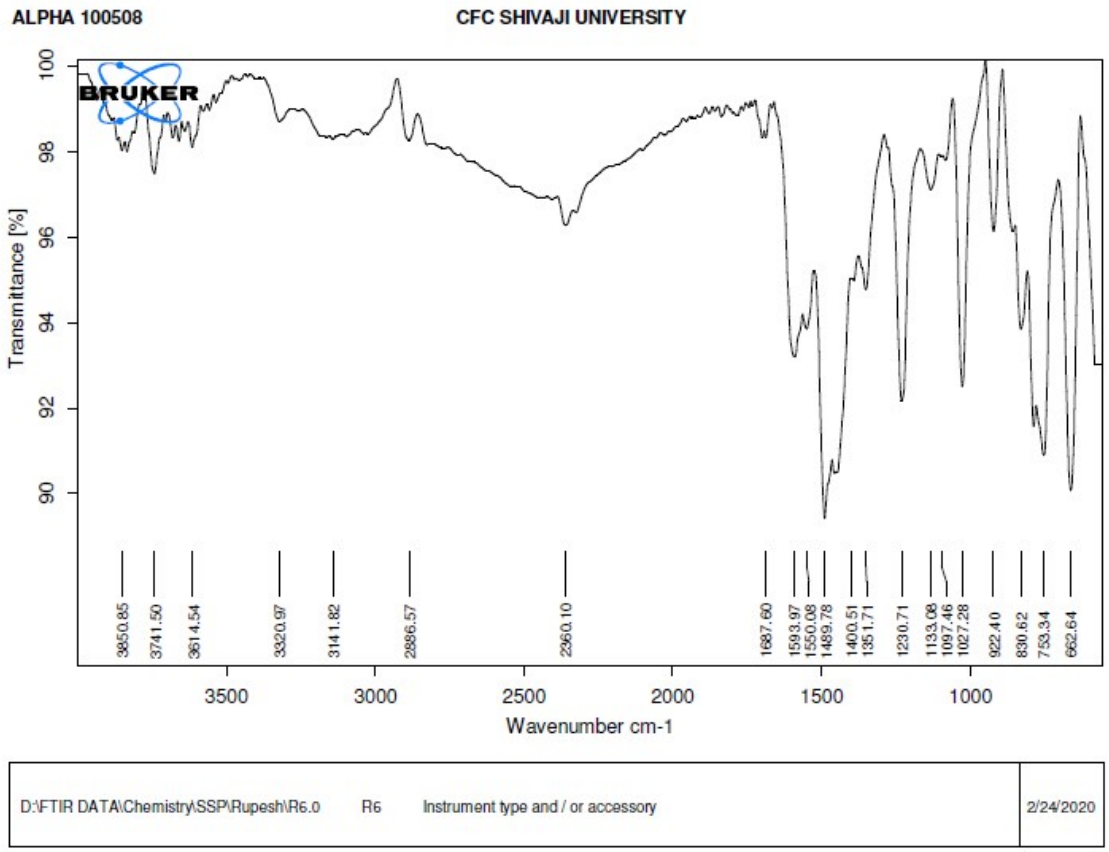
FT-IR spectrum of compound 7h



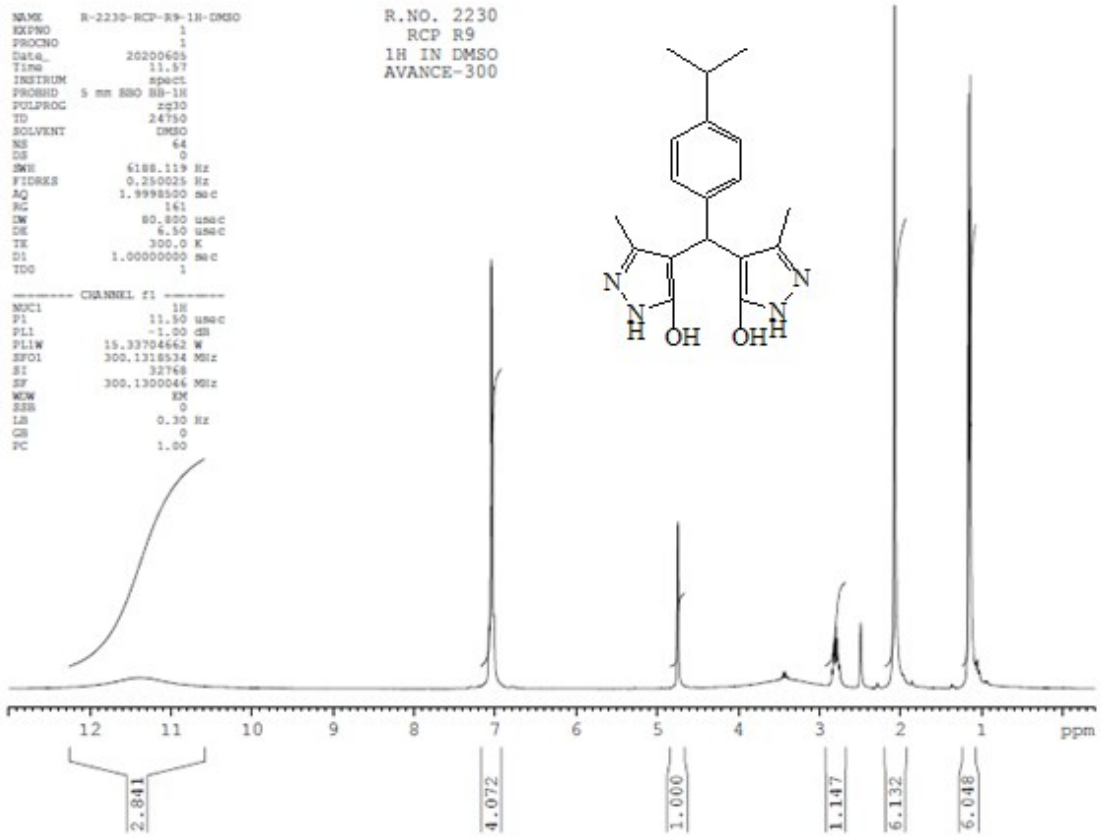
^{1}H NMR spectrum of compound 7j



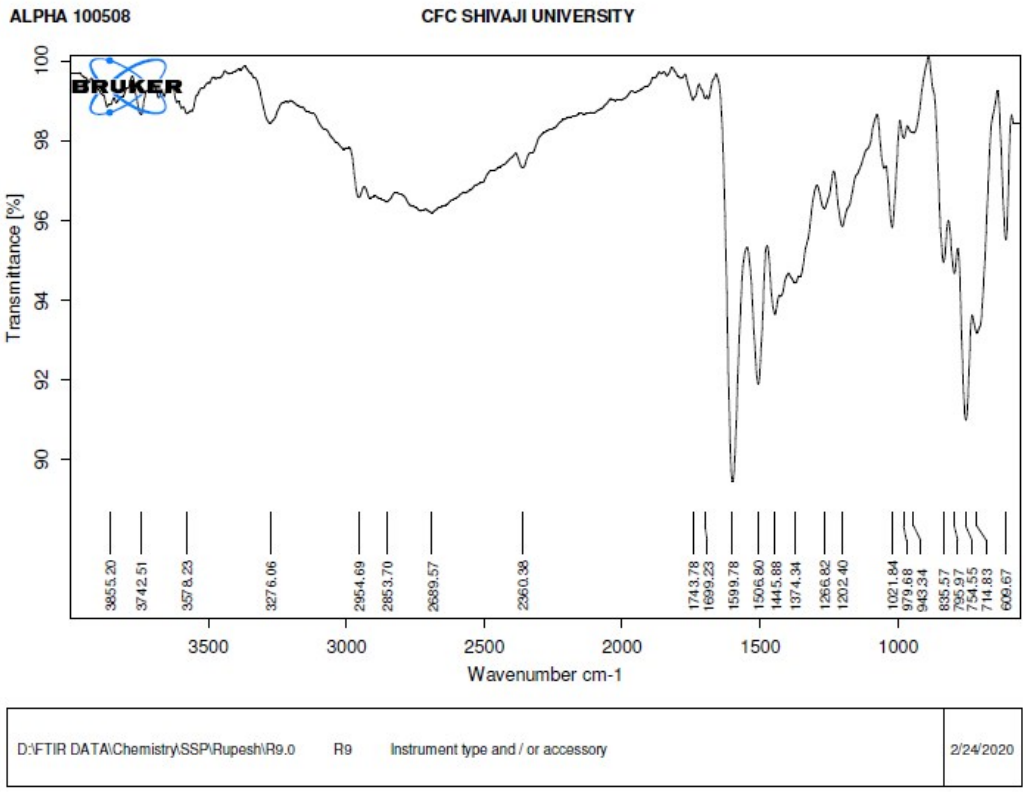
^{13}C NMR spectrum of compound 7j



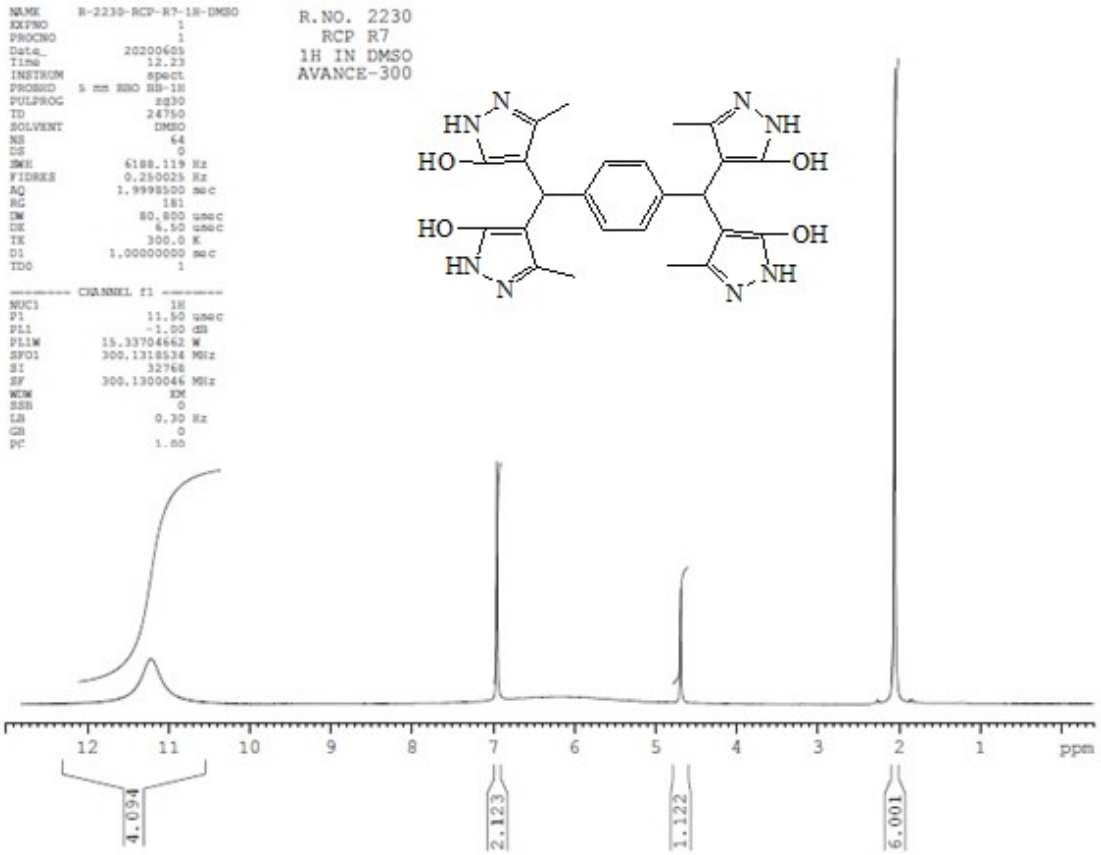
FT-IR spectrum of compound 7j



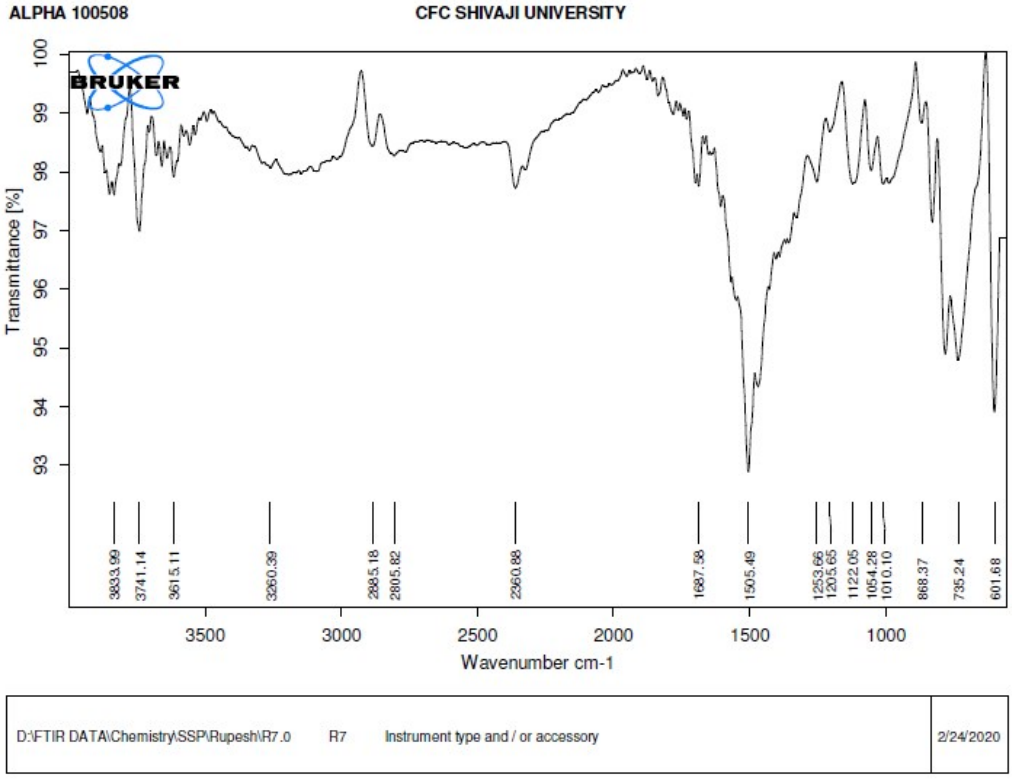
^{1}H NMR spectrum of compound 7m



FT-IR spectrum of compound 7m



^{1}H NMR spectrum of compound 7n



FT-IR spectrum of compound 7n