Electronic Supplementary Material (ESI) for New Journal of Chemistry.


**Supporting information**

# Anion Functionalized Ionic liquid From Artificial Sugar: A Sustainable Pathway for Diverse Bis-enol Derivatives

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**General remarks:**

**Chemical and Instrument:** All of the reagents purchased were of AR grade and used without further purification. Melting points were detected with a Stuart SMP30 Melting Point Measurer (Designed in UK) without correction; $^{1}H$ spectra were recorded on Jeol JNM ECX 500 MHz spectrometer in $CDCl_3$ and DMSO-$d_6$.

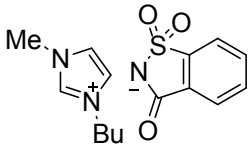
**Typical experimental procedure for the [Bmim]Sac[1]:** To a solution of 1-*n*-butyl-3-methylimidazolium bromide [Bmim]Br 26.7g (0.122 mol) in 100 mL acetone at room temperature, Sodium Saccharinate 25.0 g (0.122 mol) was added and stirred for about 30h. The reaction mixture was then filtered through a plug of Celite. The volatiles were removed under reduced pressure overnight and yield of 32.0 g (96%) of viscous oil was obtained.

**General procedure for the synthesis of Biscoumarin / Bispyranylmethane / Tetraketones:** In a 50 ml round bottom flask, mixture of substituted aldehyde (1.0 mmol), 4-hydroxy coumarin / 4-hydroxy-6-methyl-2-pyrone / dimedone / 1,3-cyclohexanedione (2.0 mmol) and Bmim(Sac) (10 mol%), was stirred at 80°C in water (2 ml) for time specified in Table 2. After completion of the reaction as monitored by TLC, the obtained solid precipitate was collected by filtration or the reaction mixture was extracted with ethyl acetate and water (in case of no precipitate). Then, the crude product was purified by recrystallization from EtOH.

**Reusability of the [Bmim]Sac:** The reusability of [Bmim]Sac was investigated from the reaction between benzaldehyde and 4-hydroxycoumarin as a model system. After completion of the reaction, precipitates separated out in the reaction mixture were filtered and aqueous layer containing catalyst was recovered under reduced pressure, dried, and reused for additional five times for subsequent reactions.

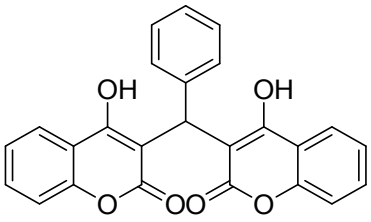
**Experimental data of all products:**

**[Bmim][Sac][1]:**



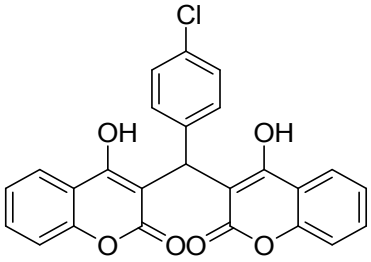
viscous oil (86%) $^1$H NMR (300 MHz, DMSO-$d_6$,) $\delta$ = 9.17 (s, 1H, ArH), 7.89 (d, $J$ = 5.4Hz, 1H, ArH), 7.78 (d, $J$ = 2.0Hz, 4H, ArH), 7.71(s, 1H, ArH), 4.18 (t, 2H, $J$ = 7.2Hz, $NCH_2$), 3.85(s, 3H, $CH_3$), 1.80 (m, 2H, $CH_2$), 1.28 (m, 2H, $CH_2$), 0.90 (t, 3H, $J$ = 7.3 Hz, $CH_3$); $^{13}$C NMR (75 MHz, DMSO$d_6$) $\delta$ = 164.7, 142.5, 136.5, 133.0, 131.5, 123.5, 122.2, 120.0, 48.4, 35.7, 31.3, 18.7, 13.2.

**3,3'-(Phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) 4a[2]:**



White solid, m. p. 230-232 °C; $^1$H NMR (500MHz, DMSO-$d_6$): δ = 6.21 (s, 1H, CH), 7.00-7.23(m, 8H, ArH), 7.44-7.48(m, 2H, ArH), 7.75-7.77 (m, 3H, ArH), Anal. Calcd. $C_{25}H_{16}O_6$: C, 72.81; H, 3.91. Found: C, 72.65; H, 3.97.

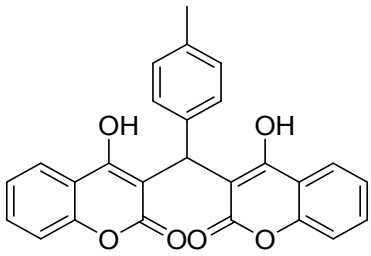
**3,3'-((4-Chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) 4b[2]**:



White solid, m. p. 242-245 °C; $^1$H NMR (500MHz, $CDCl_3$): δ = 6.03(s, 1H, CH), 7.14- 7.15 (m, 2H, ArH), 7.27-7.29 (d, $J$= 8.65Hz, 2H, ArH), 7.39-7.42 (m, 4H, ArH), 7.61-7.63 (m, 2H, ArH),

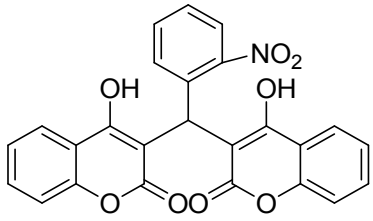
7.98-8.07 (m, 2H, ArH), 11.31 (brs, 1H, OH), 11.53 (brs, 1H, OH). Anal. Calcd. $C_{25}H_{15}ClO_6$: C, 67.20; H, 3.38. Found: C, 67.02; H, 3.51.

**3, 3'-(p-Tolylmethylene)bis(4-hydroxy-2H-chromen-2-one) 4c[2]:**



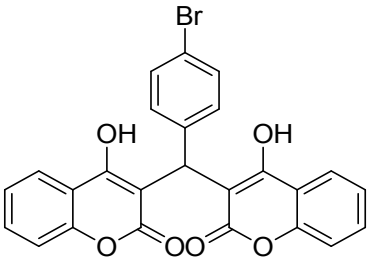

White solid, m. p. 263-265˚C; $^1$H NMR (500MHz, $CDCl_3$): δ = 2.32 (s, 3H, $CH_3$), 6.05 (s, 1H, CH), 7.08-7.12 (m, 4H, ArH), 7.39 (d, *J*= 8.30Hz, 4H, ArH), 7.59-7.63 (m, 2H, ArH), 7.96-8.05(m, 2H, ArH), 11.50 (brs, 2H, OH); Anal. Calcd. $C_{26}H_{18}O_6$: C, 73.23; H, 4.25. Found: C, 73.10; H, 4.30.

**3,3'-((2-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) 4d:**



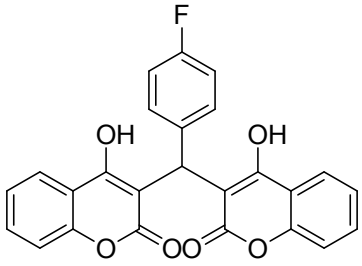

Pale yellow solid; m. p. 106-108˚C; $^1$H NMR (500 MHz, $CDCl_3$): δ= 6.61 (s, 1H, CH), 7.38-7.45 (m, 6H, ArH), 7.53-7.65 (m, 4H, ArH), 7.96-8.07 (m, 2H, ArH), 11.54 (br s, 2H, OH); Anal. Calcd. $C_{25}H_{15}NO_8$: C, 65.65; H, 3.31; N, 3.06. Found: C, 65.49; H, 3.49; N, 3.14.

**3,3'-((4-Bromophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) 4e[2]:**



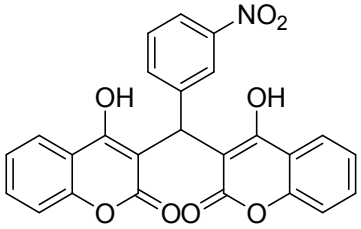
White solid, m. p. 260-262°C; $^1$H NMR (500MHz, $CDCl_3$): δ = 6.01 (s, 1H, CH), 7.08 (dd, *J* = 13.5Hz, 2H, ArH), 7.36-7.49 (m, 8H, ArH), 7.61-7.65 (m, 2H, ArH), 11.53 (brs, 2H, OH); Anal. Calcd. $C_{25}H_{15}BrO_6$: C, 61.12; H, 3.08. Found: C, 61.02; H, 3.17.

**3, 3'-((4-Fluorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) 4f:**



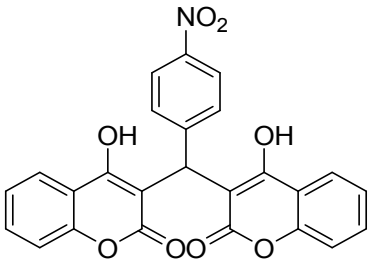

White solid, m. p. 213-216°C; $^1$H NMR (500MHz, $CDCl_3$): δ = 6.04 (s, 1H, CH), 6.98-7.02 (t, *J*= 8.7Hz, 2H, ArH), 7.16(dd, *J*= 5.2Hz, 2H, ArH), 7.36-7.41 (m, 4H, ArH), 7.61-7.64 (m, 2H, ArH), 7.98-8.07 (m, 2H, ArH), 11.31 (br s, 1H, OH); 11.53 (br s, 1H, OH); Anal. Calcd. $C_{25}H_{15}FO_6$: C, 69.77; H, 3.51. Found: C, 69.65; H, 3.62.

**3,3'-((3-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) 4g[4] :**



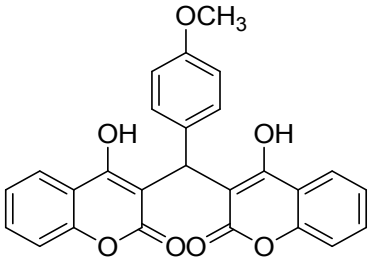

White solid, m. p. 125-127°C; $^1$H NMR (500 MHz, $CDCl_3$): δ= 6.12 (s, 1H, CH), 7.38-7.44 (m, 4H, ArH), 7.49-7.57 (m, 2H, ArH), 7.65-7.68 (m, 2H, ArH), 7.82-8.15 (m, 4H, ArH), 11.57(br s, 2H, OH); Anal. Calcd. $C_{25}H_{15}NO_8$: C, 65.65; H, 3.31; N, 3.06. Found: C, 65.53; H, 3.38; N, 3.11

**3,3'-((4-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) 4h[2]**:



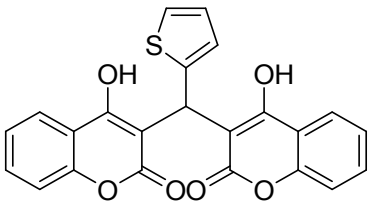

Yellow solid, m. p. 242-244 °C; $^1$H NMR (500MHz, $CDCl_3$): δ = 6.45 (s, 1H, CH), 7.32-7.44 (m, 4H, ArH), 7.47 (d, *J* = 8.4 Hz, 2H, ArH), 7.62 (d, *J* = 8.0 Hz, 2H, ArH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 8.13 (d, *J* = 8.8 Hz, 2H, ArH), 11.51 (brs, 2H, OH); Anal. Calcd. $C_{25}H_{15}NO_8$: C, 65.65; H, 3.31; N, 3.06. Found: C, 65.51; H, 3.39; N, 3.12.

**3,3'-((4-Methoxyphenyl)methylene)bis(4-hydroxy-2H chromen-2-one) 4i[2]:**



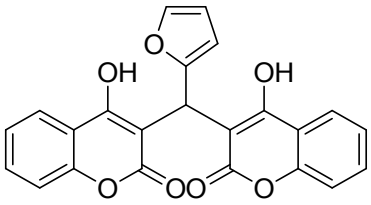

White solid, m. p. 228-230°C; $^1$H NMR (500MHz, $CDCl_3$): δ = 3.78 (s, 3H, $CH_3$), 6.03 (s, 1H, CH), 6.82 (d, *J* = 8.9 Hz, 2H, ArH), 7.10 (d, *J* = 8.2Hz, 2H, ArH), 7.38 (d, *J* = 8.2 Hz, 4H, ArH), 7.59-7.64 (m, 2H, ArH), 7.98-8.04 (m, 2H, ArH), 11.51 (brs, 2H, OH); Anal. Calcd. $C_{26}H_{18}O_7$: C, 70.58; H, 4.10. Found: C, 70.48; H, 4.18.

**3,3'-(Thiophen-2-ylmethylene)bis(4-hydroxy-2H-chromen-2-one) 4j[2]:**



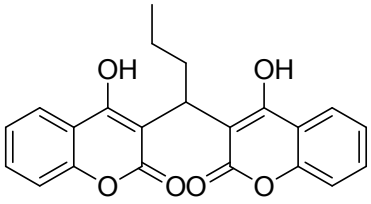

Yellow solid, m. p. 211-213 °C; $^1$H NMR (500MHz, DMSO-$d_6$): δ = 6.19 (s, 1H, CH), 6.85-6.94(m, 2H, ArH), 7.20(d, *J*= 5.0Hz, 1H, ArH), 7.39 (d, *J*= 8.2Hz, 4H, ArH), 7.61-7.62 (m, 2H, ArH), 8.00-8.06(m, 2H, ArH), 11.29 (br s, 1H, OH), 11.79 (br s, 1H, OH); Anal. Calcd. $C_{23}H_{14}O_6S$: C, 66.02; H, 3.37. Found: C, 66.09; H, 3.32.

**3,3'-(Furan-2-ylmethylene) bis(4-hydroxy-2H-chromen-2-one) 4k[2]:**



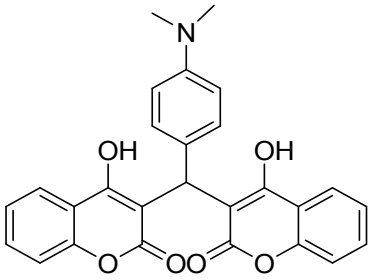
Off-white solid, m. p. 201-203°C; $^1$H NMR (500MHz, DMSO-$d_6$): δ = 5.96(m, 1H, FuranCH), 6.19 (s, 1H, CH), 6.26(m, 1H, FuranCH), 7.23-7.30 (m, 4H, ArH), 7.39 (m, 1H, ArH), 7.51-7.55 (m, 2H, ArH), 7.85 (d, *J* = 10.0 Hz, 2H, ArH); Anal. Calcd. $C_{23}H_{14}O_7$: C, 68.66; H, 3.51. Found: C, 68.54; H, 3.63.

**3,3'-(Butane-1,1-diyl)bis(4-hydroxy-2H-chromen-2-one) 4l[2]:**



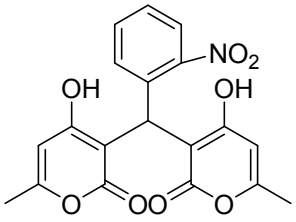
White solid, m. p. 119-123 °C; $^1$H NMR (500MHz, DMSO-$d_6$): δ = 0.90 (t, 3H, $CH_3$), 1.25-1.31 (m, 2H, $CH_2$), 2.13 (q, *J* = 7.2 Hz, 2H, $CH_2$), 4.96 (d, *J* = 8.0 Hz, 1H, CH), 7.38-7.41 (m, 4H, ArH), 7.63 (t, *J* = 7.2 Hz, 2H, ArH), 7.99 (d, *J* = 7.2 Hz, 2H, ArH), 11.97 (brs, 2H, OH); Anal. Calcd. $C_{22}H_{18}O_6$: C, 69.83; H, 4.79. Found: C, 69.74; H, 4.88.

**3,3'-((4-(Dimethylamino)phenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) 4m:**



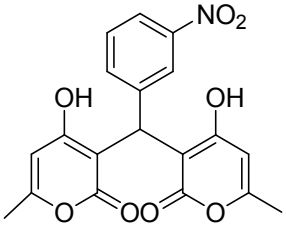
Pink solid, m. p. 223-225°C; $^1$H NMR (500MHz, DMSO-$d_6$): δ = 3.09 (s, 6H, 2x$CH_3$), 6.24 (s, 1H, CH), 7.18-7.24 (m, 6H, ArH), 7.46-7.48(m, 4H, ArH), 7.37(s, 2H, ArH), 7.76-7.77 (m, 2H, ArH).

**3,3'-((2-Nitrophenyl)methylene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) 4n:**



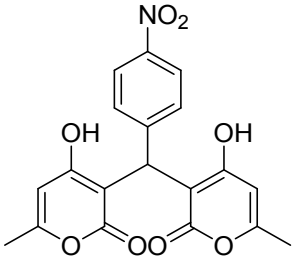
White solid, m. p. 224-226°C; $^1$H NMR (500MHz, DMSO-*d6*): δ = 2.10 (s, 6H, 2x$CH_3$), 5.89 (s, 2H, CH), 5.99 (s, 1H, CH), 7.19 (d, *J*= 7.9Hz, 1H, ArH), 7.33 (t, *J*= 7.6Hz, 1H, ArH), 7.46(t, *J*= 7.9Hz, 1H, ArH), 7.68(d, *J*= 8.8Hz, 1H, ArH), 11.25 (br s, 2H, OH); Anal. Calcd. $C_{19}H_{15}NO_8$: C, 59.22; H, 3.92. Found: C, 59.17; H, 3.97.

**3,3'-((3-Nitrophenyl)methylene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) 4o:**



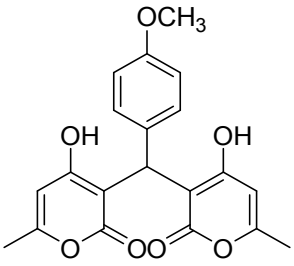
White solid, m. p. 202-204°C; $^1$H NMR (500MHz, $CDCl_3$): δ = 2.31 (s, 6H, $CH_3$), 5.78 (s, 1H, CH), 6.06 (m, 2H, CH), 7.49 (s, 2H, ArH), 7.99-8.10 (m, 3H, ArH), 10.99 (br s, 2H, OH). Anal. Calcd. $C_{19}H_{15}NO_8$: C, 59.22; H, 3.92. Found: C, 59.15; H, 3.98.

**3,3'-((4-Nitrophenyl)methylene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) 4p:**



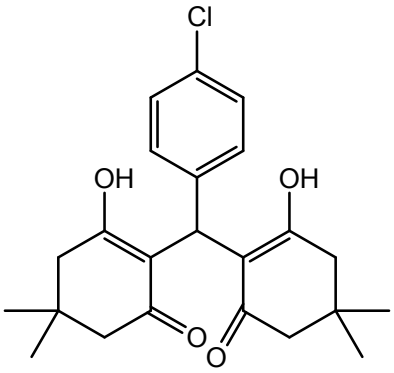
White solid, m. p. 234-236°C; $^1$H NMR (500MHz, $CDCl_3$): δ = 2.30 (s, 6H, 2x$CH_3$), 5.77 (s, 1H, CH), 6.05-6.14 (m, 2H, CH), 7.31 (d, *J*= 5.2Hz, 2H, ArH), 8.15 (d, *J*= 8.8Hz, 2H, ArH), 10.96 (br s, 2H, OH); Anal. Calcd. $C_{19}H_{15}NO_8$: C, 59.22; H, 3.92. Found: C, 59.13; H, 3.96.

**3,3'-(4-Methoxyphenyl)methylenebis(4-hydroxy-6-methyl-2H-pyran-2-one) 4q[3]** :



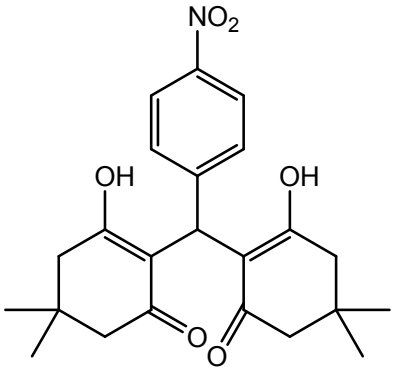

Yellow powder, m. p. 173-175°C; $^1$H NMR (500 MHz, DMSO-$d_6$) : δ = 2.07 (s, 6H, 2x$CH_3$), 3.69 (s, 3H, $OCH_3$), 5.63 (s, 2H, CH), 5.81 (s, 1H, CH), 6.71 (d, *J*=8.5 Hz, 2H, ArH), 6.89 (d, *J*= 8.5 Hz, 2H, ArH); Anal. Calcd. $C_{20}H_{18}O_7$: C, 64.86; H, 4.90. Found: C, 64.78; H, 4.98.

**2,2'-((4-Chlorophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) : 4r[5]**



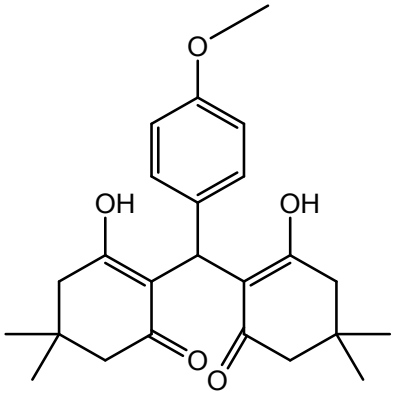

White solid, m. p. 140-142˚C; $^1$H NMR (500MHz, $CDCl_3$): δ= 1.08 (s, 6H, 2x$CH_3$), 1.20 (s, 6H, 2x$CH_3$), 2.27-2.46 (m, 8H, $CH_2$), 5.45 (s, 1H, CH), 6.99 (d, *J*= 7.85Hz, 2H, ArH), 7.23 (d, *J*= 8.65Hz, 2H, ArH), 11.86 (s, 1H, OH); Anal. Calcd. $C_{23}H_{27}ClO_4$: C, 68.56; H, 6.75. Found: C, 68.42; H, 6.87.

**2,2'-((4-Nitrophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone): 4s[6]**



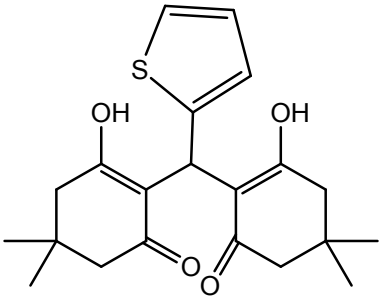

Yellow solid , m. p. 188-189˚C; $^1$H NMR (500 MHz, $CDCl_3$): δ= 1.10 (s, 6H, 2x$CH_3$), 1.22 (s, 6H, 2x$CH_3$), 2.27-2.49 (m, 8H, 4x$CH_2$), 5.53 (s, 1H, CH), 7.22 (t, *J*= 8.55Hz, 2H, ArH), 8.11 (d, *J* = 8.85 Hz, 2H, ArH ), 11.79 (br s, 2H, OH); Anal. Calcd. $C_{23}H_{27}NO_6$: C, 66.81; H, 6.58. Found: C, 66.72; H, 6.64.

**2,2'-((4-Methoxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) 4t[6] :**



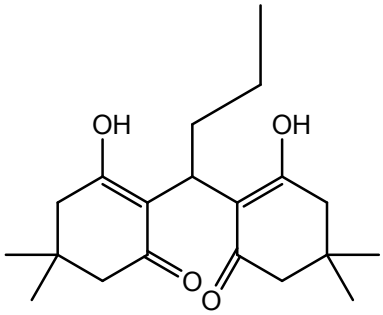

White solid, m. p. 140-142˚C; $^1$H NMR (500 MHz, $CDCl_3$): δ= 1.09 (s, 6H, 2x$CH_3$), 1.22 (s, 6H, 2x$CH_3$), 2.51-2.28 (m, 8H, 4x$CH_2$), 3.76 (s, 3H, $OCH_3$), 5.49 (s, 1H, CH), 6.80 (d, *J* = 8.7 Hz, 2H, ArH), 6.99 (d, *J* = 8.3 Hz, 2H, ArH), 11.94 (s, 2H, OH); Anal. Calcd. $C_{24}H_{30}O_5$: C, 72.34; H, 7.59. Found: C, 72.22; H, 7.67.

**2,2'-(Thiophen-2-ylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone)4u:**



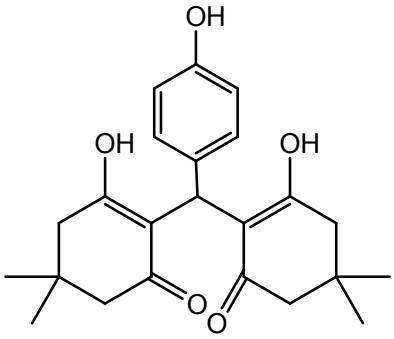

White solid, m. p. 112-114˚C, $^1$H NMR (500 MHz, $CDCl_3$): δ= 1.09 (s, 6H, 2x$CH_3$), 1.20 (s, 6H, 2x$CH_3$), 2.25-2.39 (m, 8H, $CH_2$), 5.61 (s, 1H, CH), 6.62 (d,1H, *J*= 3.2Hz, ArH), 6.85 (t, 1H, *J*= 5.0Hz, ArH), 7.11 (d, 1H, *J*= 5.2Hz, ArH), 12.31 (s, 2H, OH). Anal. Calcd. $C_{21}H_{26}O_4S$: C, 67.35; H, 7.00. Found: C, 67.20; H, 7.19.

**2,2'-(Butane-1,1-diyl)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone)4v:**



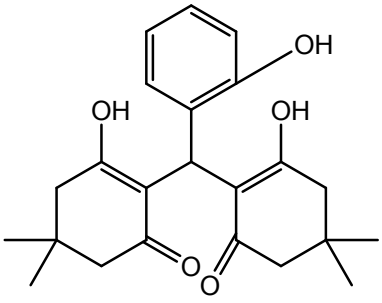

White solid, m. p. 99-102 ˚C $^1$H NMR (500 MHz, $CDCl_3$): δ= 0.84-1.05 (t, 3H, $CH_3$), 1.06 (s, 6H, 2x$CH_3$), 1.09 (s, 6H, 2x$CH_3$), 1.17-1.20 (m, 2H, $CH_2$), 1.95-1.99 (m, 2H, $CH_2$), 2.25-2.27 (m, 8H, 4x$CH_2$), 3.90-3.94 (m, 1H, CH), 12.48 (s, 1H, OH). Anal. Calcd. $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.69; H, 9.20.

**2,2'-((4-Hydroxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone): 4w**



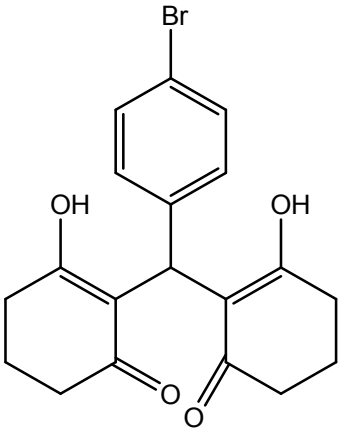
White solid, m. p. 194-196˚C; $^1$H NMR (500 MHz, $CDCl_3$): δ= 0.98 (s, 6H, 2x$CH_3$), 1.08 (s, 6H, 2x$CH_3$), 2.15-2.28 (m, 4H, 2x$CH_2$), 2.45 (s, 4H, 2x$CH_2$), 4.65 (s, 1H, CH), 6.54 (d, *J* = 8.55Hz, 2H, ArH), 7.07 (d, *J* = 8.6 Hz, 2H, ArH). Anal. Calcd. $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.70; H, 7.51.

**2,2'-((2-Hydroxyphenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone): 4x**



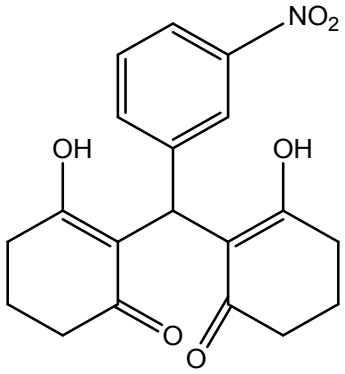

White solid, m. p. 120-133˚C; $^1$H NMR (500 MHz, $CDCl_3$): δ= 0.97 (s, 6H, 2x$CH_3$), 1.01 (s, 3H, $CH_3$), 1.11 (s, 3H, $CH_3$), 1.90-1.99 (m, 2H, $CH_2$), 2.28-2.60 (m, 6H, 3x$CH_2$ ), 4.65 (s,1H, CH), 6.97-7.03 (m, 3H, ArH), 7.12-7.16 (m, 1H, ArH), 10.47(s, 1H, OH).Anal. Calcd. $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.72; H, 7.48.

**2,2'-((4-Bromophenyl)methylene)bis(3-hydroxycyclohex-2-enone): 4y[7]**



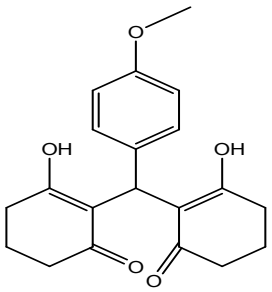

White solid; m. p. 226-228˚C; $^1$H NMR (400 MHz, $CDCl_3$): δ= 1.96-2.07 (m, 4H, $CH_2$), 2.33-2.50 (m, 4H, $CH_2$), 2.52-2.69 (m, 4H, $CH_2$), 5.39 (s, 1H, CH), 6.98 (d, 2H, *J* = 8.0 Hz, ArH ), 7.38 (t, 2H, *J* =7.8 Hz, ArH ), 12.32 (br s, 2H, OH); Anal. Calcd. $C_{19}H_{19}BrO_4$: C, 58.33; H, 4.89. Found: C, 58.23; H, 4.95.

**2,2'-((3-Nitrophenyl)methylene)bis(3-hydroxycyclohex-2-enone): 4z**[7]




Sand yellow solid, m. p. 205-207˚C; $^1$HNMR (500 MHz, $CDCl_3$): δ= 2.04-2.12 (m, 4H, $CH_2$), 2.35-2.55 (m, 4H, $CH_2$), 2.58-2.73 (m, 4H, $CH_2$), 5.49 (s, 1H, CH), 7.41-7.47 (m, 2H, ArH), 7.97 (s, 1H, ArH), 8.05 (d, *J* = 8.0 Hz, 1H, ArH), 12.31 (br s, 2H, OH); Anal. Calcd. $C_{19}H_{19}NO_6$: C, 63.86; H, 5.36; N, 3.92. Found: C, 63.72; H, 5.39; N, 3.97.

**2,2'-((4-Methoxyphenyl)methylene)bis(3-hydroxycyclohex-2-enone): 4a'**[7]




Light yellow solid, m. p. 192-194˚C; $^1$H NMR (500 MHz, $CDCl_3$): δ= 1.93-2.68 (m, 4H, 2x$CH_2$), 2.32-2.51 (m, 4H, 2x$CH_2$), 2.52-2.69 (m, 4H, 2x$CH_2$), 3.78 (s, 3H, $OCH_3$), 5.43 (s, 1H, CH), 6.81 (d, *J* = 8.8 Hz, 2H, ArH), 7.01 (t, *J*=8.4Hz, 2H, ArH), 12.36 (br s, 2H, OH); Anal. Calcd. $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.02; H, 6.59

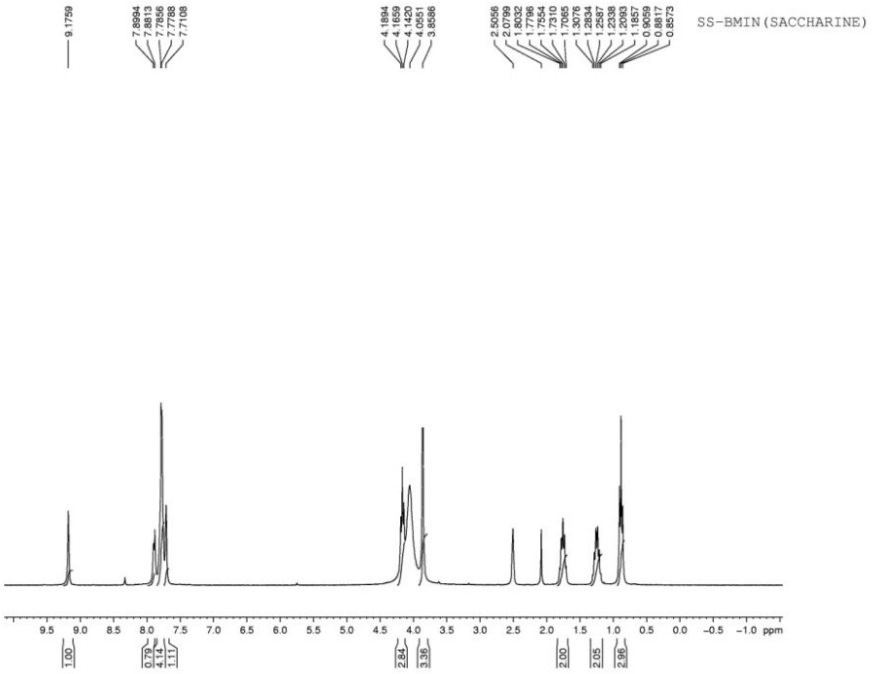



Fig 1.1H NMR of **[Bmim]Sac**

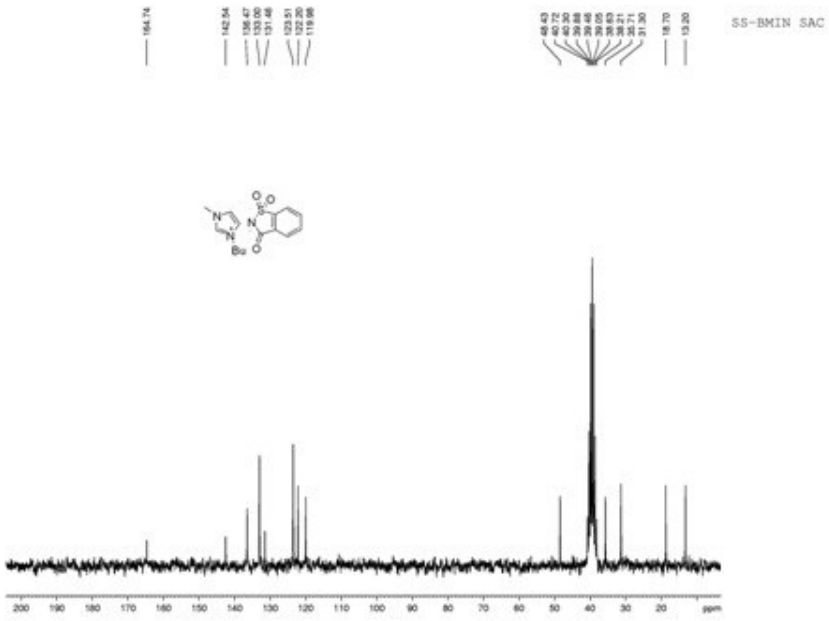



Fig 2. $^{13}$C NMR of **[Bmim]Sac**

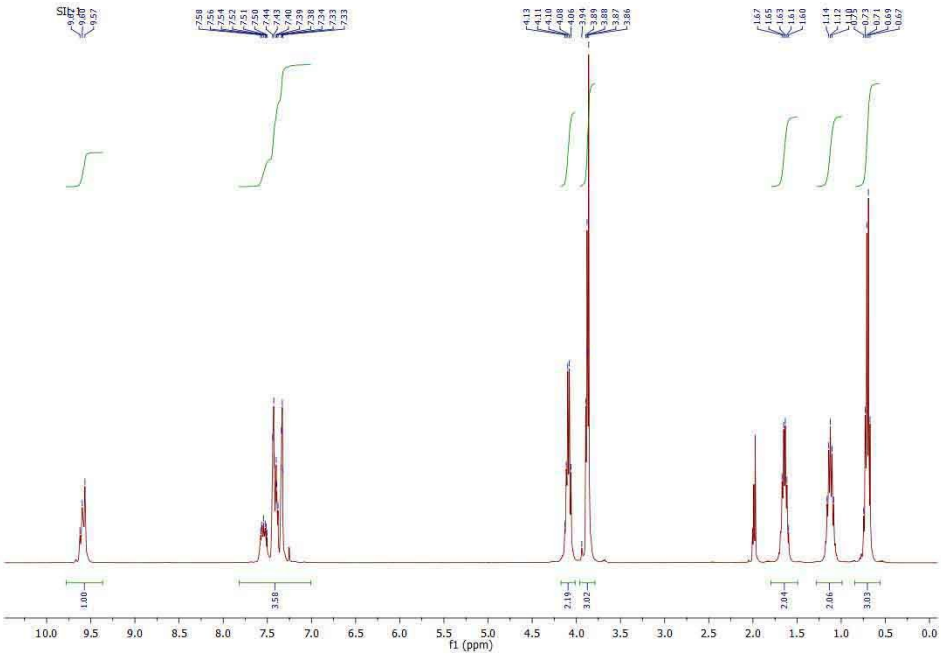



Fig 3.[1]H NMR of **[Bmim]Sac recovered after 3th cycle**

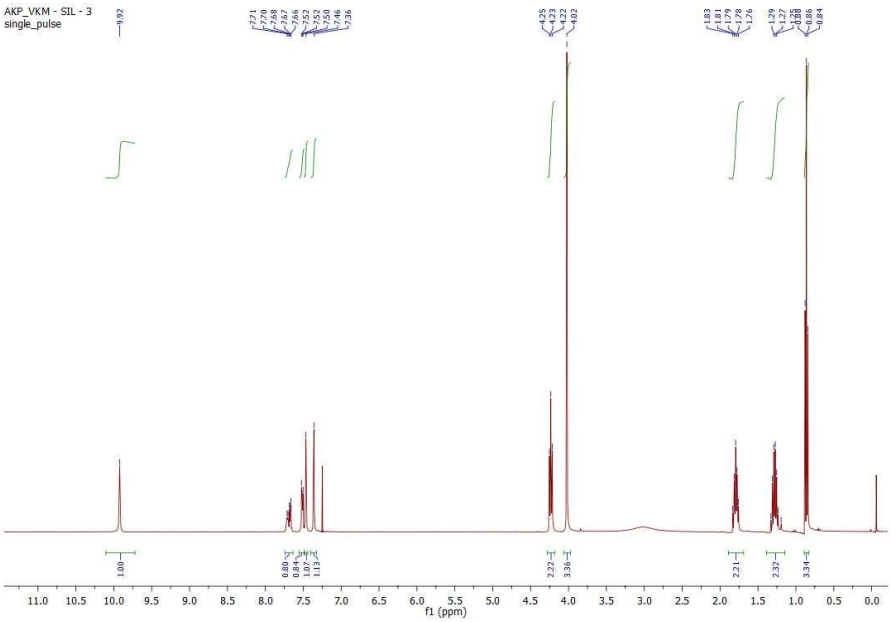



Fig 4.[1]H NMR of **[Bmim]Sac recovered after 5th cycle**

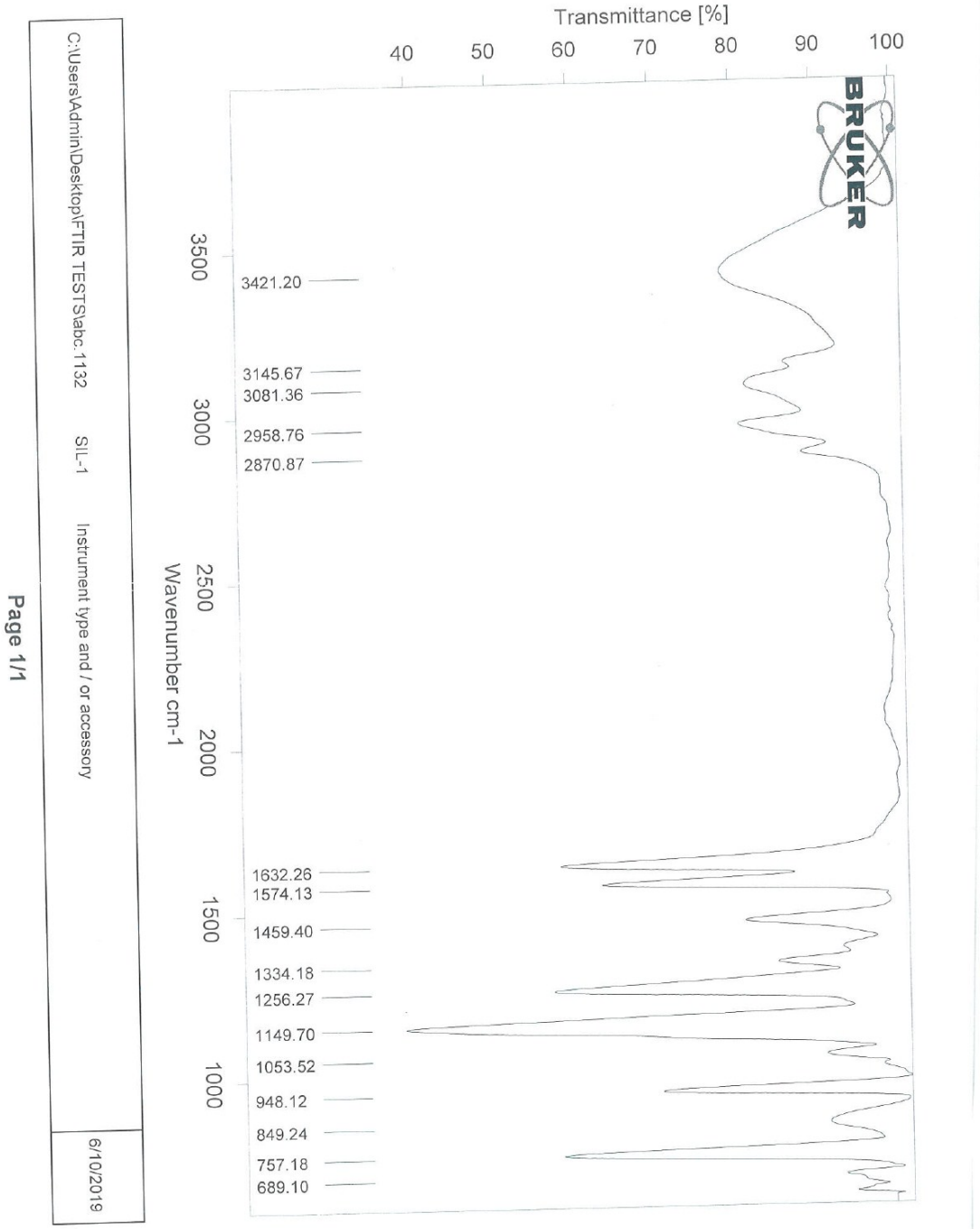



Fig 5. IR of **[Bmim]Sac**

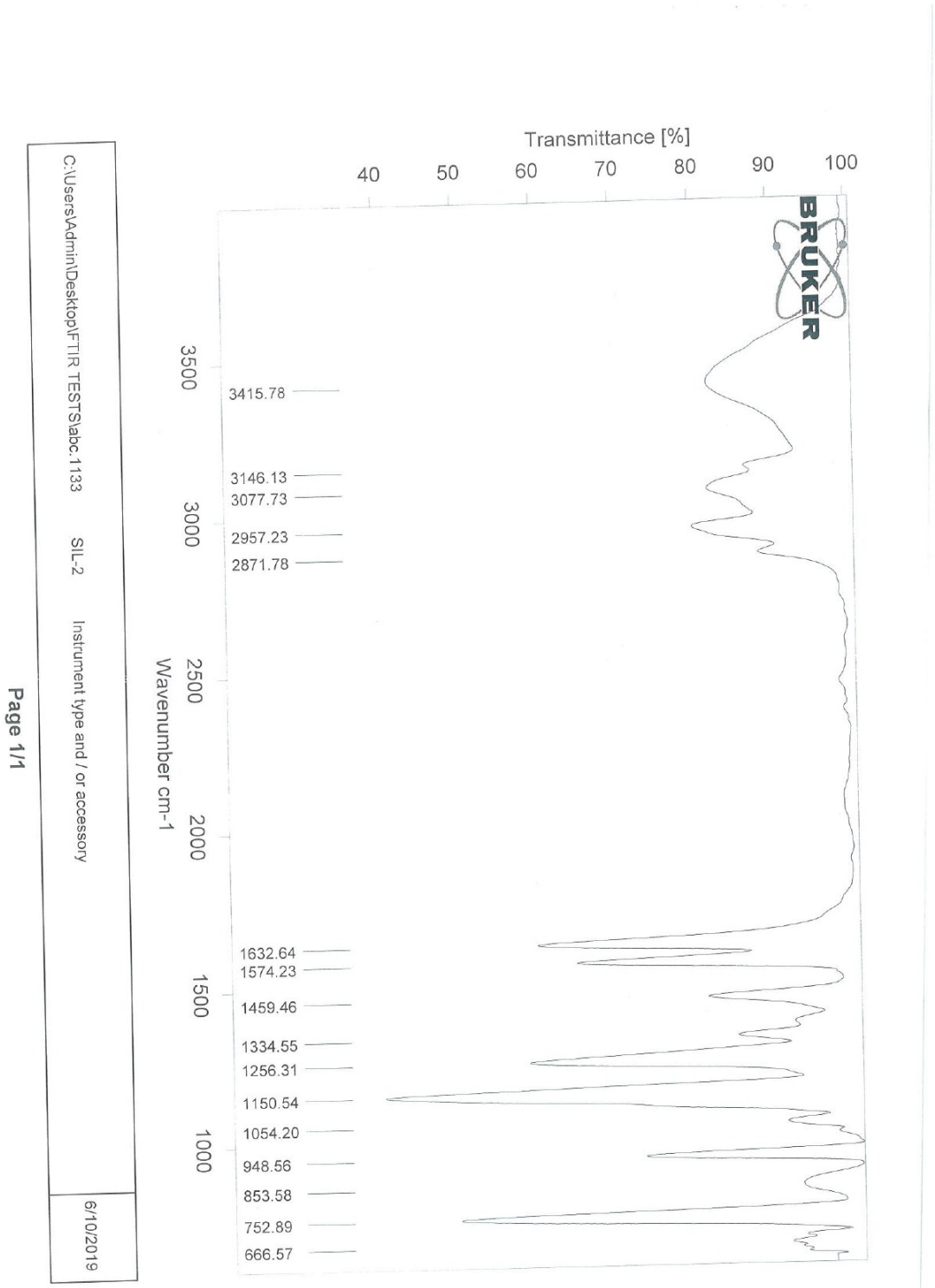



Fig 6.IR of **[Bmim]Sac recovered after 5$^{th}$ cycle**

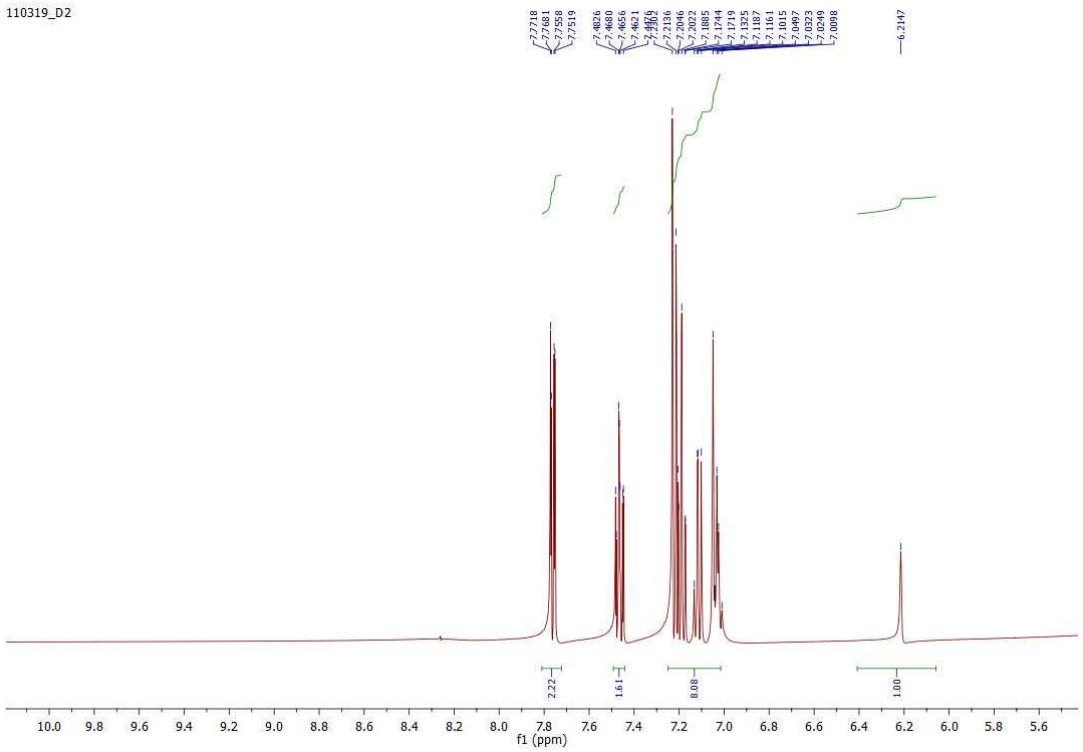



**Figure 7.** $^{1}H$ NMR of **4a** in $CDCl_3$

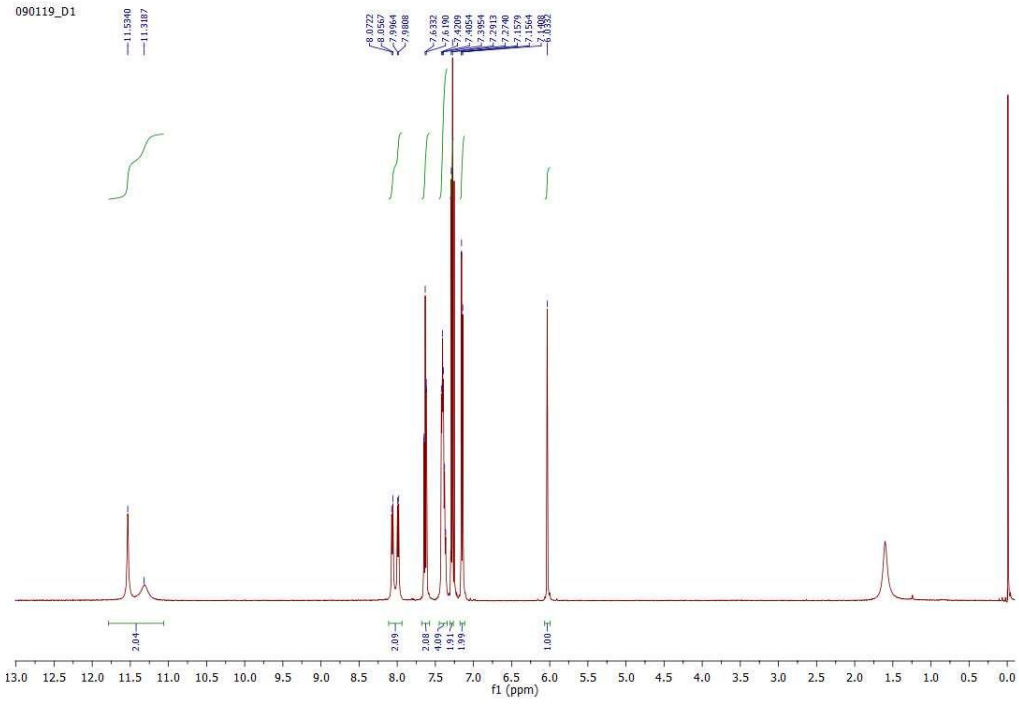



**Figure 8.** $^{1}H$ NMR of 4b **8** in $CDCl_3$

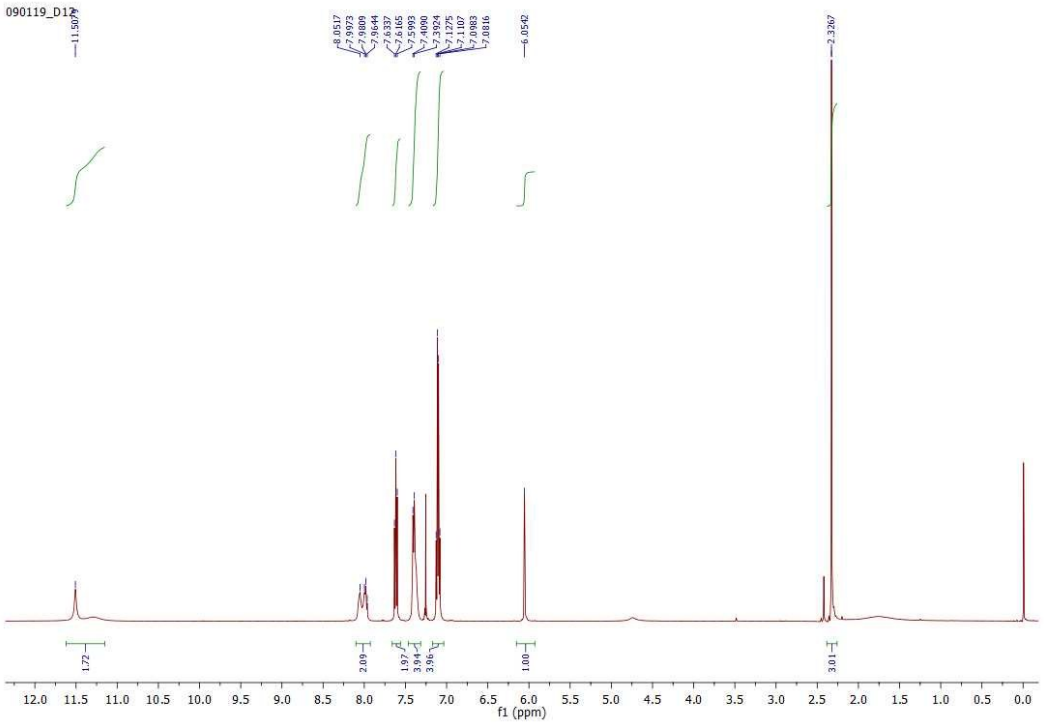



**Figure 9.** $^{1}H$ NMR of **4c** in $CDCl_3$

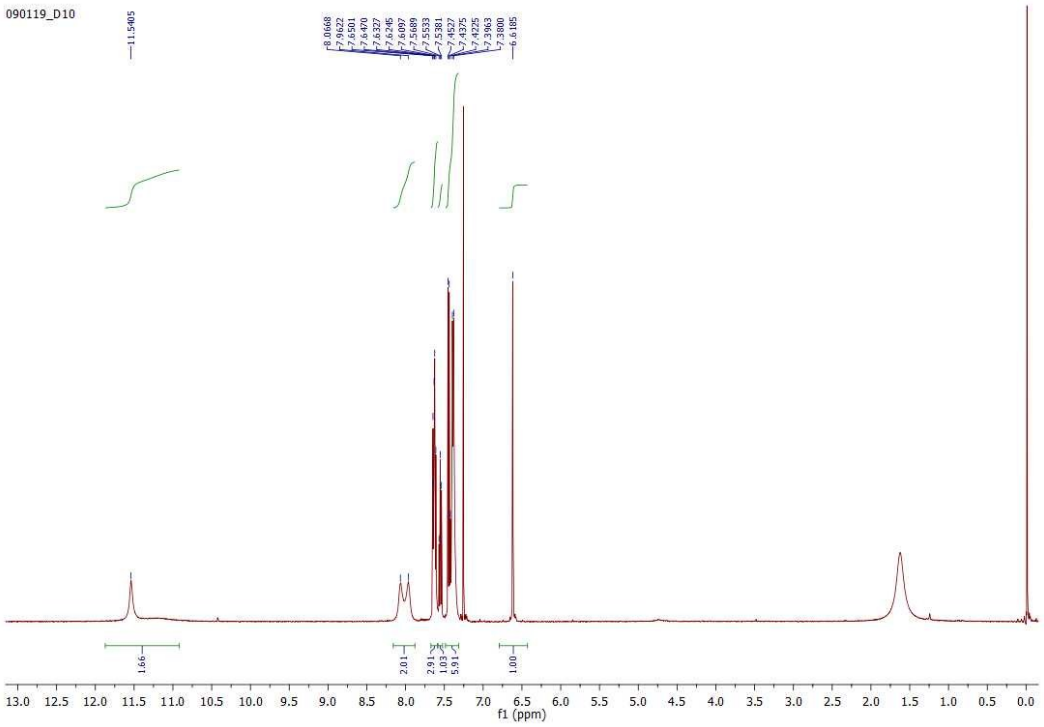



**Figure 10.** $^{1}H$ NMR of **4d** in $CDCl_3$

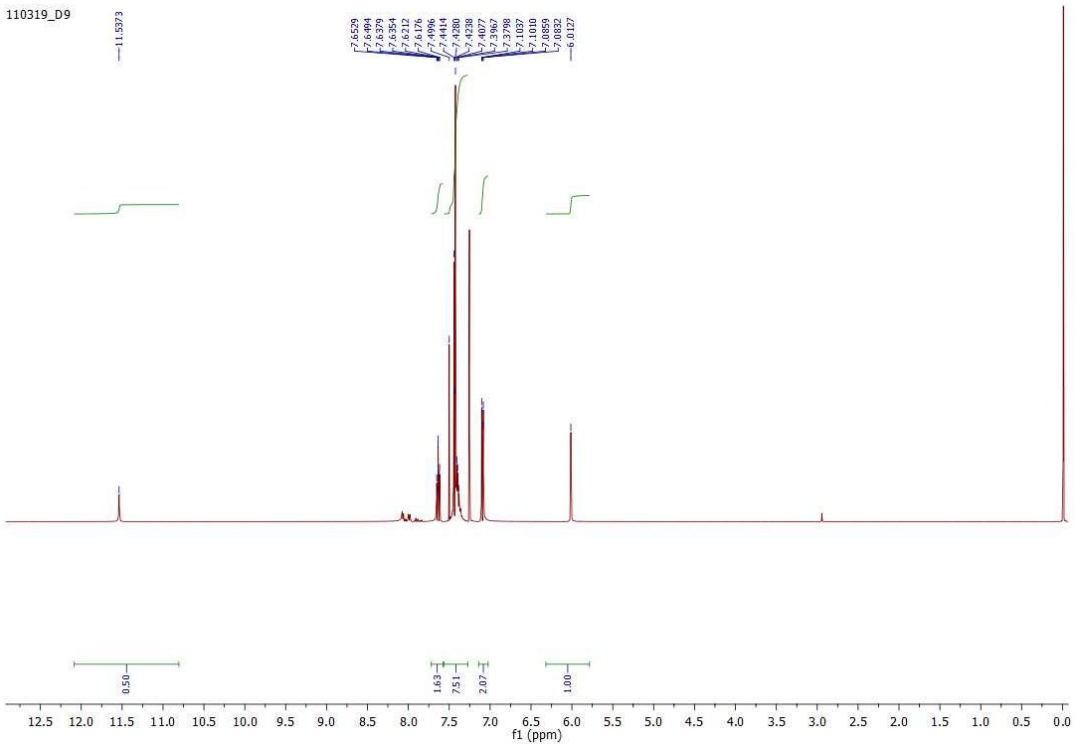



**Figure 11.** $^{1}$H NMR of **4e** in $CDCl_3$

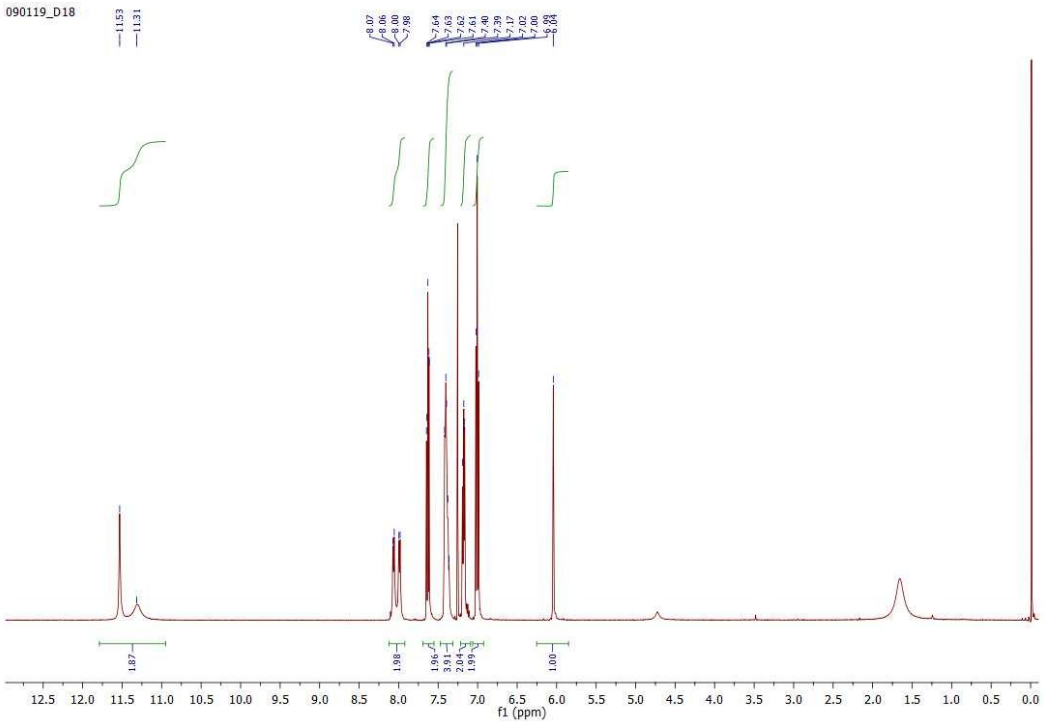



**Figure 12.** $^{1}$H NMR of **4f** in $CDCl_3$

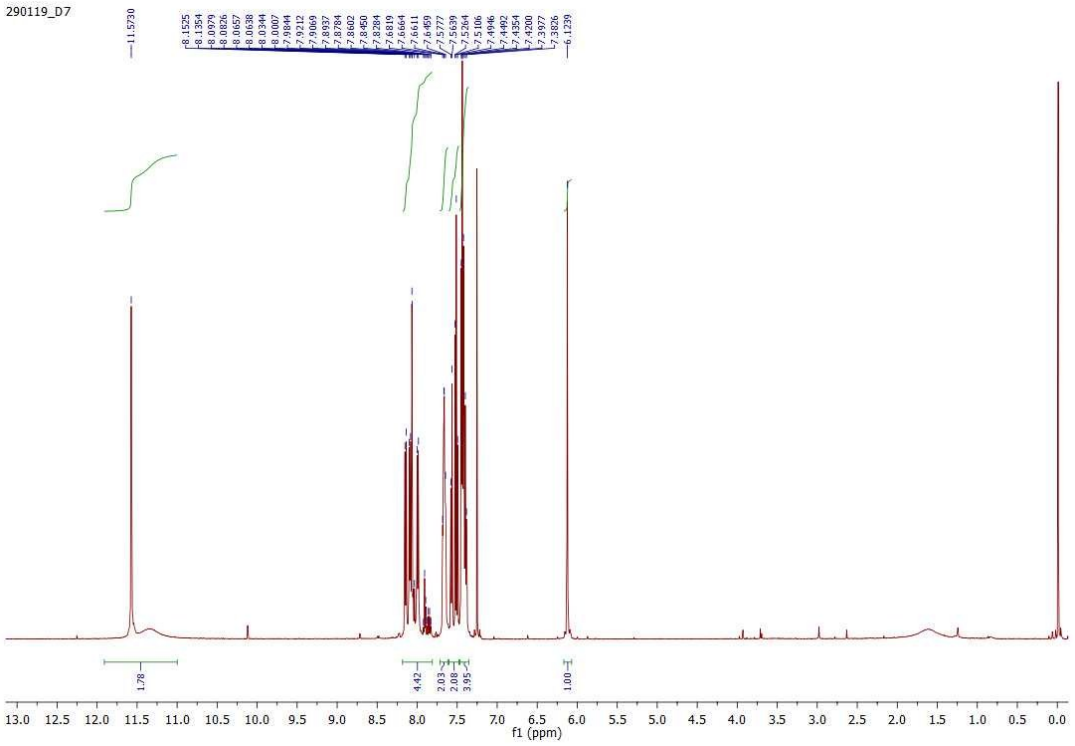



**Figure 13.** $^{1}H$ NMR of **4g** in $CDCl_3$

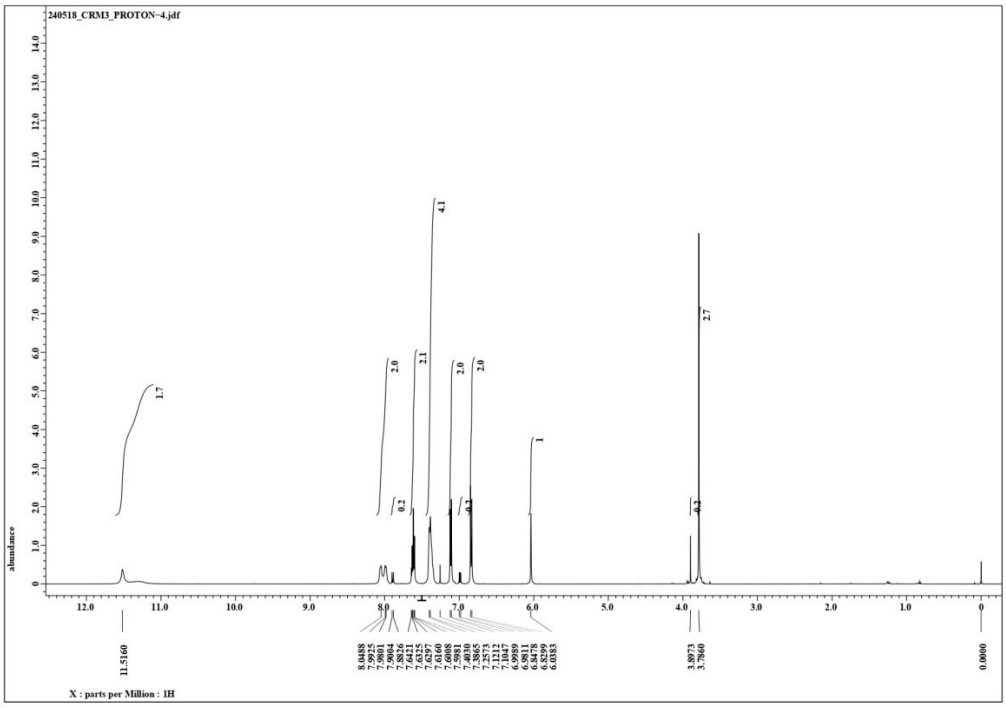



**Figure 14.** $^{1}H$ NMR of **4i** in $CDCl_3$

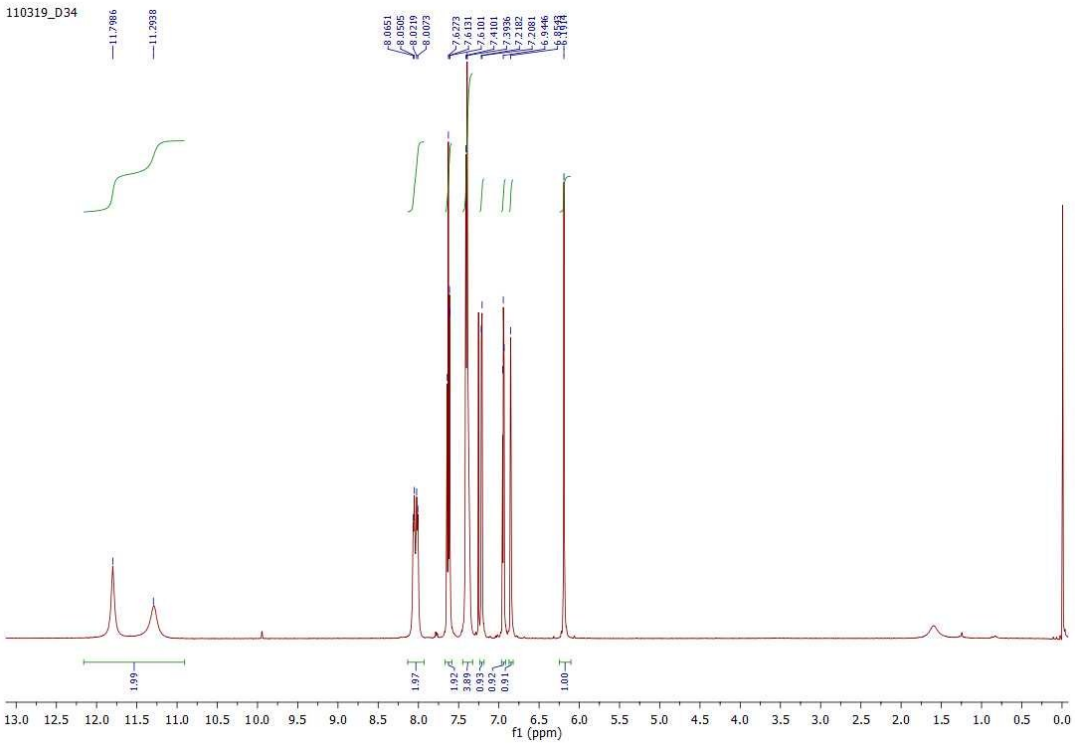



**Figure 15.** $^{1}$H NMR of **4j** in $CDCl_3$

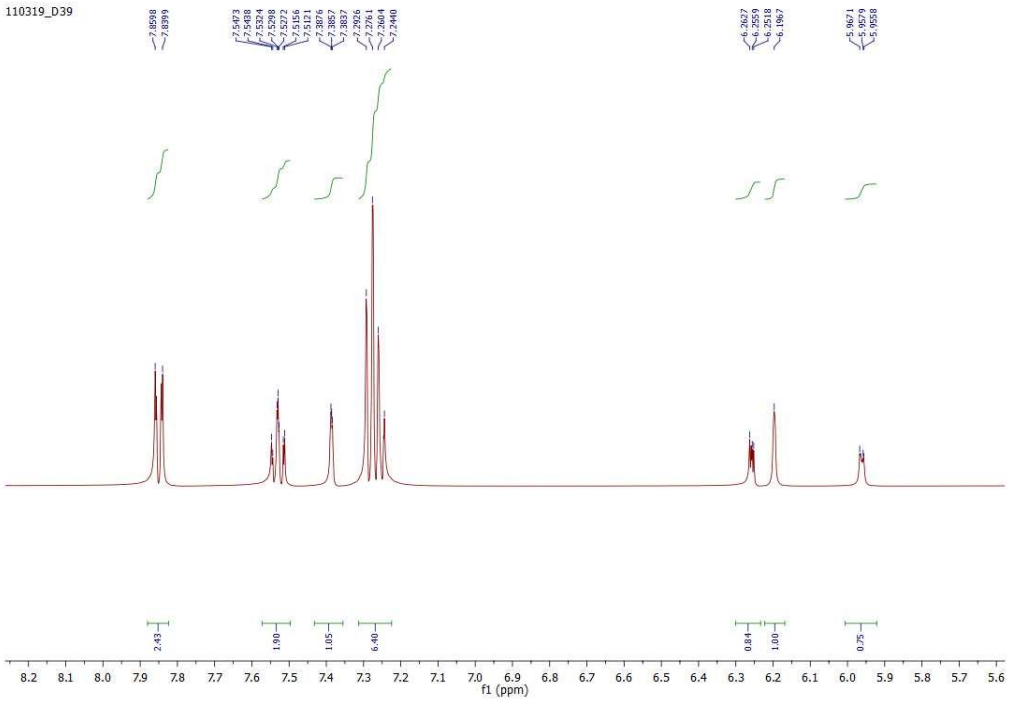



**Figure 16.** $^{1}$H NMR of **4k** in DMSO-$d_6$

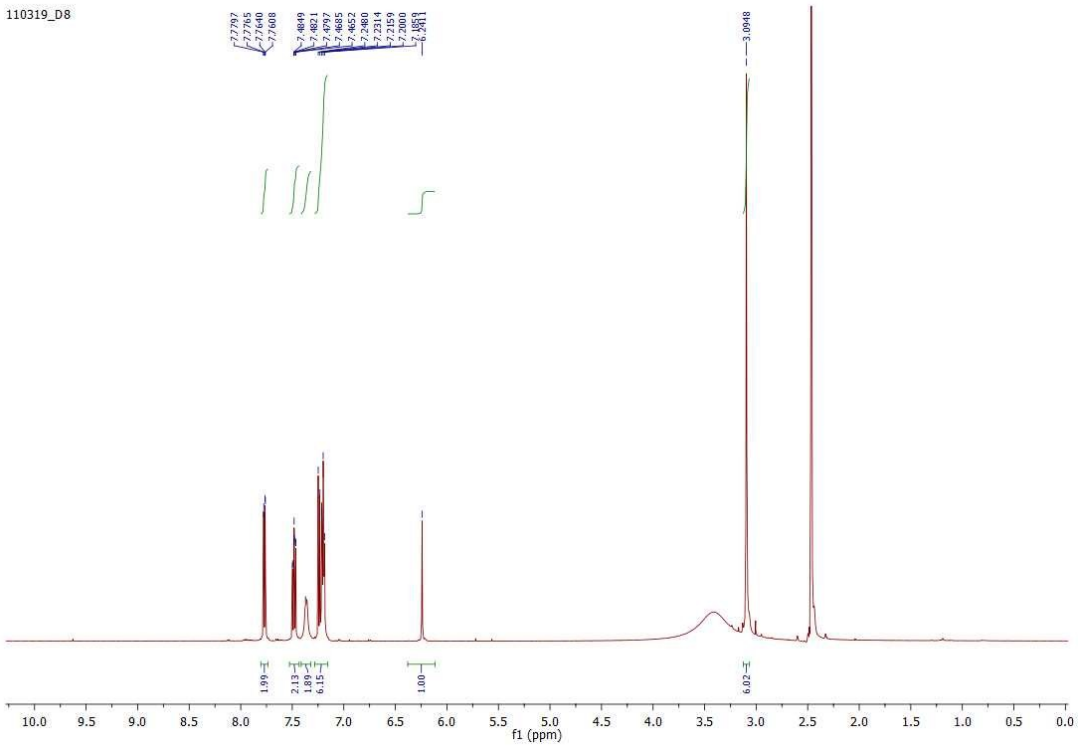



**Figure 17.** $^{1}$H NMR of **4m** in DMSOd$_6$

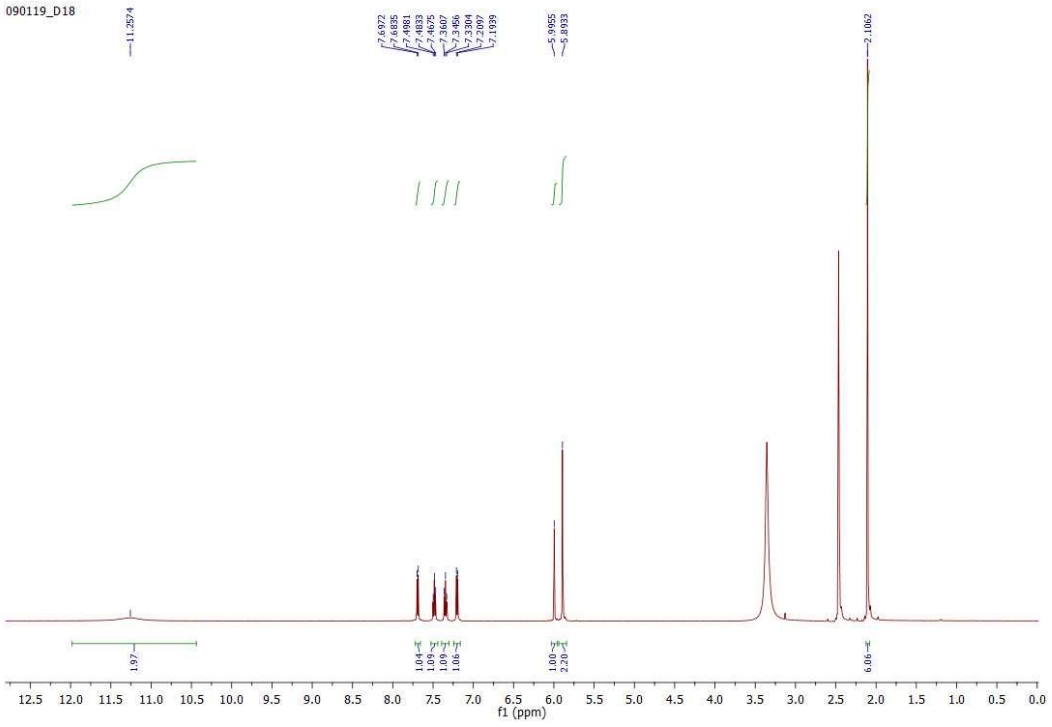



**Figure 18.** $^{1}$H NMR of **4n** in DMSO-d$_6$

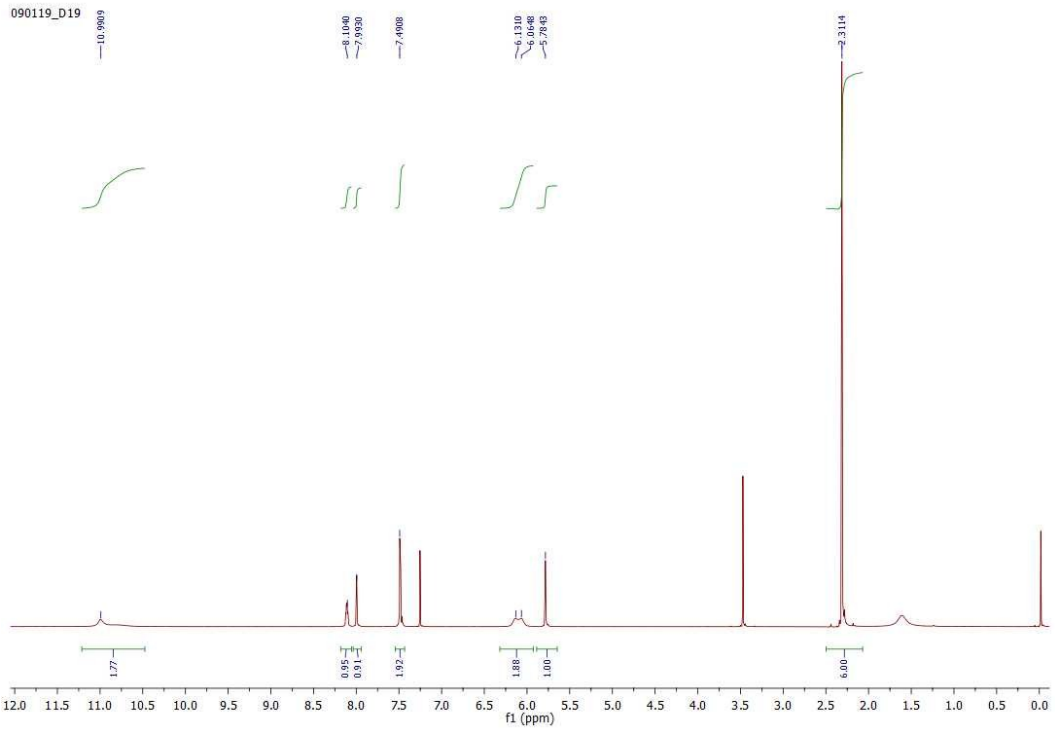



**Figure 19.** $^{1}H$ NMR of **4o** in $CDCl_3$

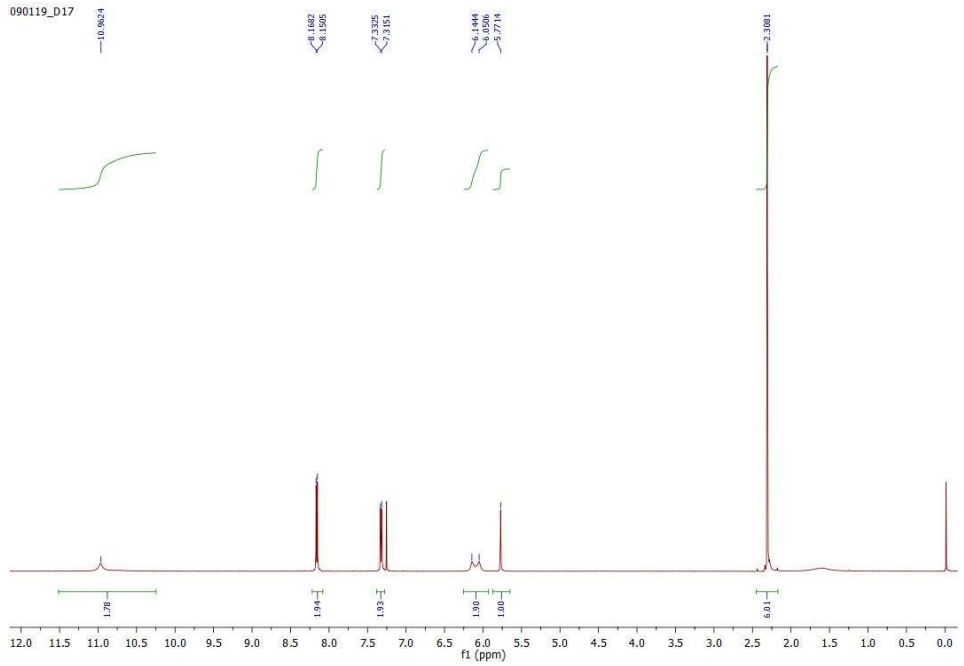



**Figure 20.** $^{1}H$ NMR of **4p** in $CDCl_3$

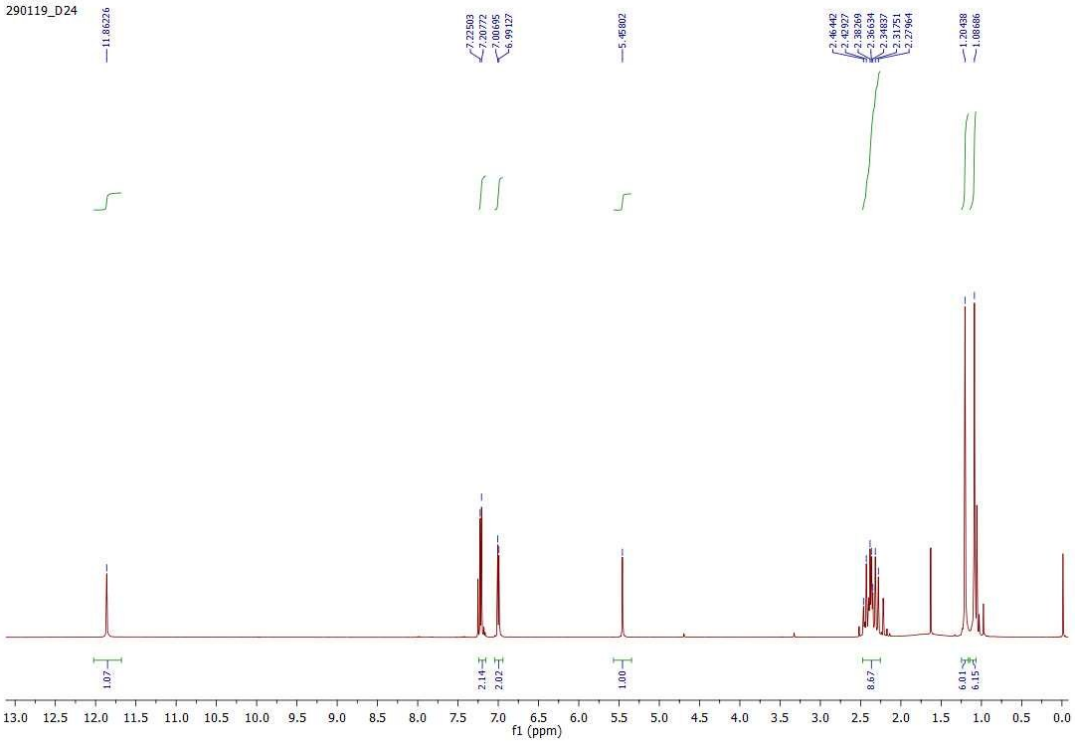



**Figure 21.** $^{1}$H NMR of **4r** in $CDCl_3$

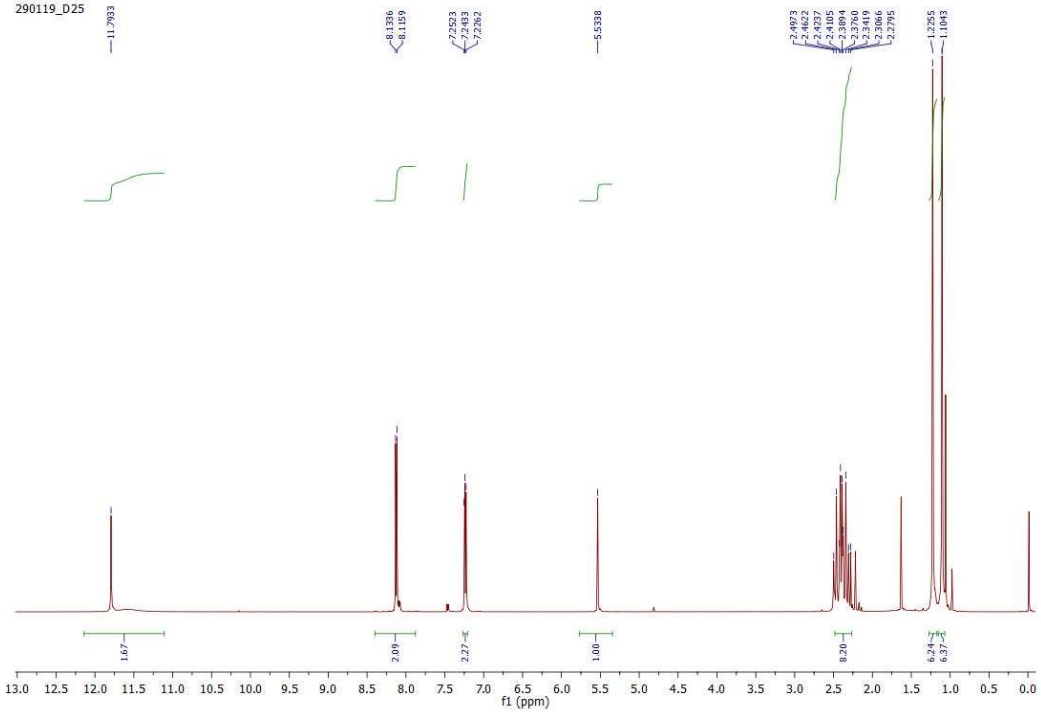



**Figure 22.** $^{1}$H NMR of **4s** in $CDCl_3$

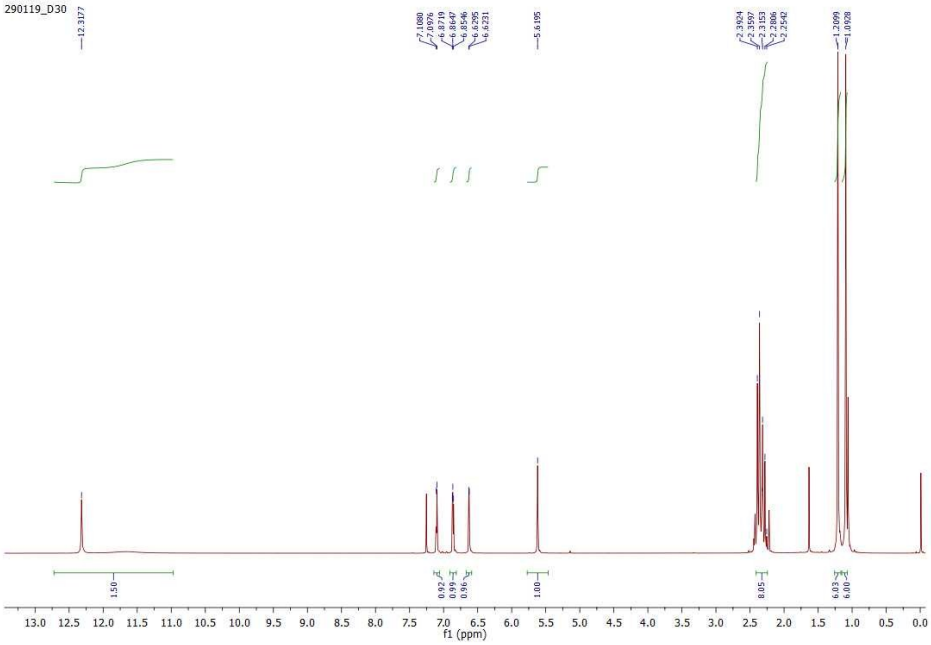



**Figure 23.** $^{1}$H NMR of **4u** in $CDCl_3$

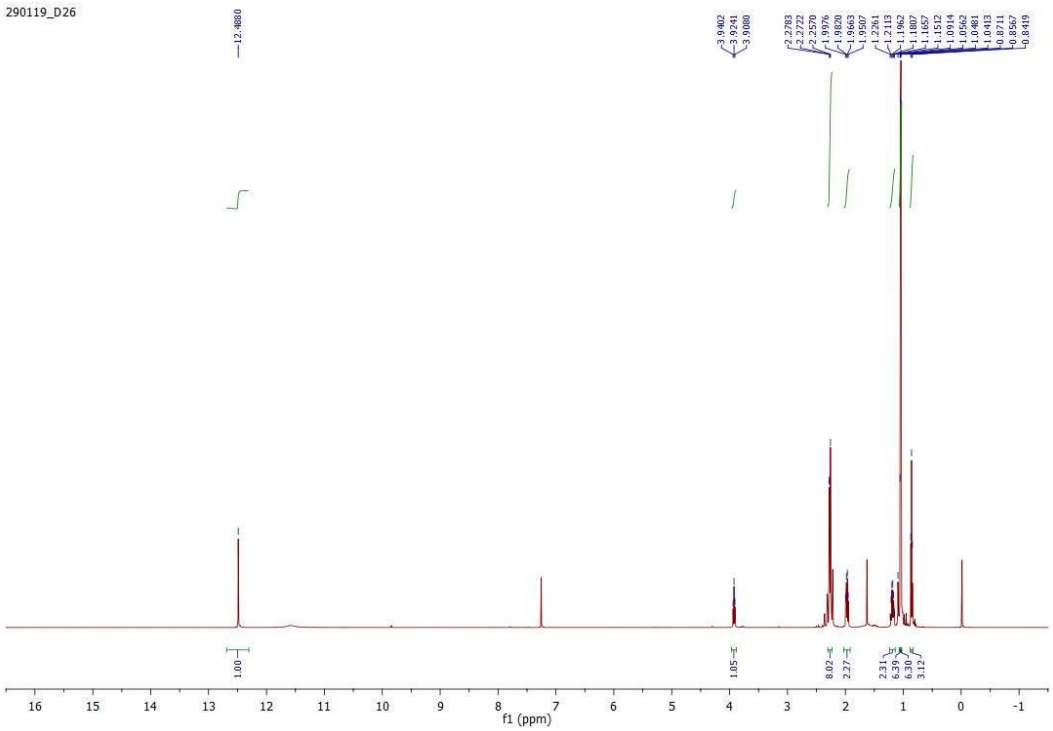



**Figure 24** $^{1}$H NMR of **4v** in $CDCl_3$

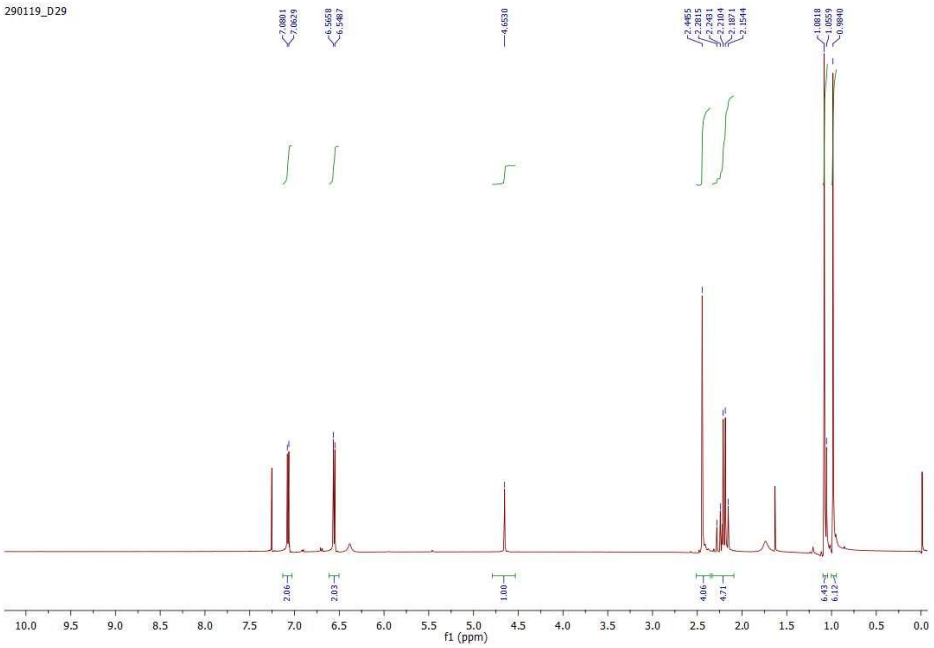



**Figure 25.** $^{1}H$ NMR of **4w** in $CDCl_3$

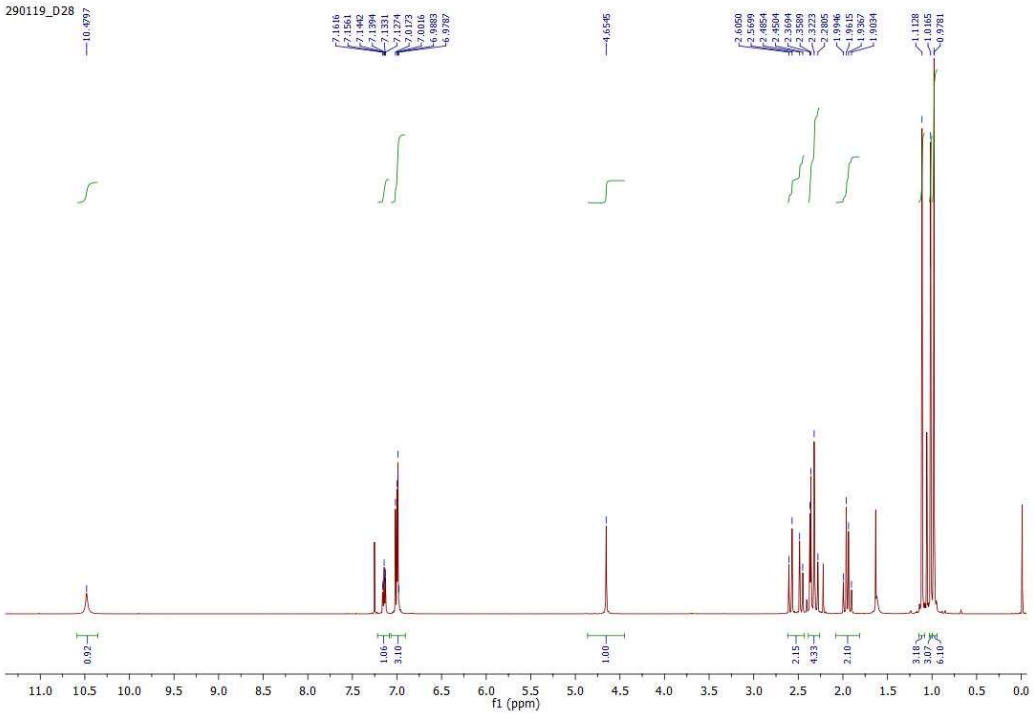



**Figure 26.** $^{1}H$ NMR of **4x** in $CDCl_3$

**References:**


1. A. Kumar, S. Srivastava, G. Gupta, P. Kumar, J. Sarkar, *RSC Adv*, **2013**, *3*, 3548-3552;
2. C. Yang, W.-Q. Su, and D-Z. Xu, *RSC Adv*., **2016**, *6*, 99656.
3. M. Proud, V. Sridharan, *Tetrahedron Letters,* **2015**, *56,* 6614-6616.
4. R. Rezaei, F. Moezzi, M.M. Doroodmand, *Chinese Chemical Letters* **2014**, 25, 183–186X.
5. Gerd Kaupp,* M. Reza Naimi-Jamal and Jens Schmeyers, Tetrahedron **2003,** 59, 3753–3760.
6. Tsai-Wen Chung, Bharat D. Narhe, Chun-Cheng Lin, Chung-Ming Sun *Org. Lett.*, **2015**, *17* (21), 5368–5371
7. Jian-Jun Yu, Li-Min Wang,* Jin-Qian Liu, Feng-Lou Guo, Ying Liu and Ning Jiao, ***Green Chem.***, 2010,**12**, 216-219