Supporting information

Friedel-Crafts alkylation of indoles in Deep Eutectic Solvent

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General remarks:

All the reactions were carried out in oven-dried glassware. All the chemicals and reagents were purchased from commercial sources and were used without further purification. HPCL grade Acetonitrile (MERCK) was used for reaction. TLC (Thin Layer Chromatography) was performed on Merck-percolated silica gel 60-F_{254} and 100-200 mesh silica gel was used for column chromatography. The chromatographic solvents are mentioned as v/v ratios. All the synthesized compounds were fully characterized by ^{1}H, ^{13}C NMR, IR, and further confirmed through ESI-MS and ESI-HRMS analyses. IR spectra were recorded on a Perkin-Elmer FT-IR RXI spectrophotometer and values reported in cm^{-1}. NMR spectra were recorded with 300 and 400 MHz (based on availability of instruments) spectrometers for ^{1}H NMR, 75 and 100 MHz for ^{13}C NMR respectively. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H) or DMSO-d_6 (^{13}C) as internal standards. Integrals are in accordance with assignments; coupling constants

are given in Hz. ESI-MS and ESI-HRMS spectra were obtained on a LCQ Advantage Ion trap mass spectrometer (Finnigan thermo Fischer scientific).

Synthesis of deep eutectic solvent (DES)

Deep eutectic solvents were prepared by reported methods in literature.[1]

Representative experimental procedure for the synthesis of 3-hydroxy-3-(1H-indol-3-yl)indolin-2-one:

Indole (1.0 mmol) and isatin (1.0 mmol) were taken in a 50 mL round bottom flask containing 5 mL of DES. The reaction was stirred at room temperature. The reaction was monitored by TLC. After completion of reaction water was added. The DES being soluble in water comes in the water layer. The solid was separated by filtration. The crude product was purified by 100-200 mesh silica gel column chromatography.

Recycling of DES

Method 1: After completion of the reaction (monitored by TLC), the reaction mixture was diluted with water (10 mL) The DES being soluble in water comes in the water layer. Product was obtained by filtration. The DES was recovered easily from filtrate by evaporating the water at 80°C under vacuum. The recovered DES was then successfully used for the next batch and showing no significant loss of yield.

Method 2: After completion of reaction 2-Methyl THF was added to reaction mixture, product went to organic phase and DES settled down. Organic phase was separated and product was obtained by evaporating organic phase under vacuum and settled DES was used for next batch syntheses.

Characterisation data of all the synthesized compounds:

3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (3a):

White solid; Yield 89%; mp = 294-296 °C; IR (KBr) max 3404, 3051, 2931, 1711; ^{1}H NMR (400 MHz; DMSO-d^{6}): δ 10.98 (s, 1H), 10.34 (s, 1H), 7.37 (t, *J* = 8.56 Hz, 2H), 7.28-7.24 (m, 2H), 7.09 (d, *J* =2.52, 1H), 7.05 (t, *J* = 8.12 Hz, 1H), 6.98-6.94 (m, 1H), 6.92 (d, *J* = 7.56 Hz, 1H), 6.89-6.85 (m, 1H), 6.36 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^{6}): δ 178.9, 142.1, 137.3, 133.9, 129.5, 125.4, 125.2, 124.0, 122.1, 121.5, 120.8, 118.9, 115.9, 111.9, 110.1, 75.4; ESI-MS (m/z) = 265 $[M+H]^{+}$; Analysis Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60; Found: C, 72.74; H, 4.54; N, 10.56; ESI-HRMS Calcd. for $C_{16}H_{12}N_2O_2$: $[M+H]^{+}$, 265.0932, Found: m/z 265.0928.

3-hydroxy-1-methyl-3-(1H-indol-3-yl)indolin-2-one (3b):

White solid; Yield 94%; mp = 181-183°C; IR (KBr) max 3402, 3053, 2921, 1703; ^{1}H NMR (400 MHz; DMSO-d^{6}): δ 10.99 (s, 1H), 7.38-7.29 (m, 4H), 7.10-7.01 (m, 4H), 6.89 (t, *J* = 7.64 Hz, 1H), 6.42 (s, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz; DMSO-d^{6}): δ 177.0, 143.6, 137.3, 133.2, 129.6, 125.3, 124.8, 124.1, 122.8, 121.6, 120.8, 119.0, 115.6, 112.0, 109.0, 75.1, 26.4; ESI-MS (m/z) = 279 $[M+H]^{+}$; Analysis Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07; O, 11.50; Found: C, 73.32; H, 5.11; N, 10.02; O, 11.50; ESI-HRMS Calcd. for $C_{17}H_{14}N_2O_2$: $[M+H]^{+}$, 279.1089, Found: m/z 279.1094.

3,3-Di(1H-indol-3-yl)-1-methylindolin-2-one (3b^{I}):

Pale red solid, Yield 81%; mp = >300°C; IR (KBr) max 3423, 3020, 2247, 1598, 1567, 1404, 1385, 1104, 1042, 668, 518, 478; 1H NMR (300 MHz; DMSO-d^{6}): δ 10.96 (s, 2H), 7.36-7.27 (m, 4H), 7.18 (d, *J* = 7.80 Hz, 3H), 7.04 (t, *J* = 7.92 Hz, 3H), 6.85-6.77 (m, 4H), 3.27 (s, 3H); ^{13}C NMR (75 MHz; DMSO-d^{6}): δ 177.4, 143.2, 137.4, 134.2, 128.5, 126.1, 125.0, 124.8, 122.6, 121.5, 121.2, 118.8, 114.6, 112.1, 109.1, 52.6, 26.7; ESI-MS (m/z) = 378 $[M+H]^{+}$; Analysis Calcd. for $C_{25}H_{19}N_3O$: C, 79.55; H, 5.07; N, 11.13; Found: C, 79.62; H, 5.12; N, 11.19; ESI-HRMS Calcd. for $C_{25}H_{19}N_3O$: $[M+H]^{+}$, 378.1562, Found: m/z 378.1568.

3-hydroxy-5-nitro-3-(1H-indol-3-yl)indolin-2-one (3c):

white solid; Yield 92%; mp = 187-189°C; IR (KBr) max 3406, 3019, 2916, 1709; ^{1}H NMR (400 MHz; DMSO-d^{6}): δ 11.11 (s, 1H), 11.08 (s, 1H), 8.27 (dd, *J* = 8.64 Hz, 1H), 8.06 (d, *J* = 2.36 Hz, 1H), 7.51 (d, *J* = 7.96, 1H), 7.38 (d, *J* = 8.12 Hz, 1H), 7.13-7.11 (m, 2H), 7.09-7.05 (m, 1H), 6.96-6.92 (m, 1H), 6.74 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^{6}): δ 179.0, 148.6, 142.8, 137.4,

134.7, 126.9, 125.2, 124.4, 121.8, 120.7, 120.5, 119.3, 114.4, 112.2, 110.5, 75.0; ESI-MS (m/z) = 310 $[M+H]^+$; Analysis Calcd. for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.58; N, 13.59; Found: C, 62.21; H, 3.52; N, 13.53; ESI-HRMS Calcd. for $C_{16}H_{11}N_3O_4$: $[M+H]^+$, 310.0783, Found: m/z 310.0787.

5-Fluoro-3-hydroxy-3-(1 H -indol-3-yl)indolin-2-one (3d):

Dark brown solid; Yield 92%; mp = 196-198°C; IR (KBr) max 3420, 3348, 1731, 1614, 1476, 1174, 746; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.03 (s, 1H), 10.37 (s, 1H), 7.41 (dd, *J* = 15.24 Hz, 2H), 7.11 (m, 4H), 6.93-6.89 (m, 2H), 6.50 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 178.8, 159.7, 157.3, 138.3, 137.3, 135.7, 135.6, 125.2, 124.1, 121.6, 120.7, 119.1, 115.9, 115.6, 115.3, 112.8, 112.6, 112.0, 111.0, 110.9, 75.7; ESI-MS (m/z) = 283 $[M+H]^+$; Analysis Calcd. for $C_{16}H_{11}FN_2O_2$ C, 68.08; H, 3.93; N, 9.92; Found: C, 68.12; H, 3.98; N, 9.98; ESI-HRMS Calcd. for $C_{16}H_{11}FN_2O_2$: $[M+H]^+$, 283.0838, Found: m/z 283.0832.

5-Chloro-3-hydroxy-3-(1 H -indol-3-yl)indolin-2-one (3e):

Brown solid; Yield 91%; mp = 206-208 °C; IR (KBr) max 3422, 3357, 1731, 1620, 1476, 1178, 749; ^{1}H NMR (400 MHz; DMSO-d^6): δ; 11.04 (s, 1H), 10.50 (s, 1H), 7.38-7.34 (m, 2H), 7.33 (dd, *J* = 8.28 Hz, 1H), 7.21 (d, *J* = 2.16 Hz, 1H), 7.11 (d, *J* = 2.56 Hz, 1H), 7.07 (t, *J* = 7.56 Hz, 1H), 6.94-6.88 (m, 2H), 6.52 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 178.5, 141.0, 137.3, 135.9, 129.4, 126.1, 125.2, 125.1, 124.1, 121.7, 120.5, 119.1, 115.1, 112.1, 111.7, 75.5; ESI-MS (m/z) = 299 $[M+H]^+$; Analysis Calcd. for $C_{16}H_{11}ClN_2O_2$: C, 64.33; H, 3.71; N, 9.38; Found: C, 64.39; H, 3.78; N, 9.46; ESI-HRMS Calcd. for $C_{16}H_{11}ClN_2O_2$:$[M+H]^+$, 299.0543, Found: m/z 299.0549.

5-Bromo-3-hydroxy-3-(1 H -indol-3-yl)indolin-2-one (3f):

Light brown solid; Yield 90%; mp = 202-204°C; IR (KBr) max 3428, 3021, 1648, 1385, 1215, 1119, 669, 619; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.04 (s, 1H), 10.51 (s, 1H), 7.46 (dd, *J* = 8.24 Hz, 1H), 7.37 (t, *J* = 8.04 Hz, 3H), 7.11 (d, *J* = 2.48 Hz, 1H), 7.07 (t, *J* = 8.28 Hz, 1H), 6.92 (t, *J* = 9.04 Hz, 2H), 6.53 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 178.4, 141.4, 137.3, 136.3, 132.2, 127.8, 125.2, 124.1, 121.7, 120.5, 119.2, 115.2, 113.8, 112.3, 112.1, 75.4; ESI-MS (m/z) = 343 $[M+H]^+$; Analysis Calcd. for $C_{16}H_{11}BrN_2O_2$ C, 56.00; H, 3.23; N, 8.16; Found: C, 56.12;

H, 3.29; N, 8.11; ESI-HRMS Calcd. for $C_{16}H_{11}BrN_2O_2$: $[M+H]^+$, 343.9983, Found: m/z 343.9988.

3-hydroxy-5-Iodo-3-(1H-indol-3-yl)indolin-2-one (3g):

Light brown solid; Yield 88%; mp = 200-202°C; IR (KBr) max 3404, 3021, 1633, 1392, 1215, 669; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.04 (s, 1H), 10.50 (s, 1H), 7.45 (dd, *J* = 8.24 Hz, 1H), 7.37-7.32 (m, 3H), 7.11 (d, *J* = 2.44 Hz, 1H), 7.07 (t, *J* = 8.24 Hz, 1H), 6.92 (t, *J* = 8.36 Hz, 2H), 6.53 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 178.5, 141.5, 137.4, 136.5, 132.4, 128.0, 125.3, 124.2, 121.8, 120.6, 119.3, 115.3, 113.9, 112.4, 112.3, 75.6; ESI-MS (m/z) = 390 $[M+H]^+$; Analysis Calcd. for $C_{16}H_{11}IN_2O_2$ C, 49.25; H, 2.84; N, 7.18; Found: 49.29; H, 2.92; N, 7.11; ESI-HRMS Calcd. for $C_{16}H_{11}IN_2O_2$: $[M+H]^+$, 390.9899, Found: m/z 390.9892.

3-hydroxy-3-(2-methyl-1H-indol-3-yl)-1-methylindolin-2-one (3h):

White solid; Yield 85%; mp = 191-193°C; IR (KBr) max 3343, 1716, 1612, 1471, 1169, 749; ^{1}H NMR (400 MHz; DMSO-d^6): δ 10.89 (s, 1H), 7.66 (s, 1H), 7.37-7.33 (m, 1H), 7.26 (dd, *J* = 7.28 Hz, 1H), 7.22 (d, *J* = 7.84 Hz, 1H), 7.09 (d, *J* = 7.76 Hz, 1H), 7.03-7.00 (m, 1H), 6.94-6.89 (m, 2H), 6.76-6.72 (m, 1H), 6.34 (s, 1H), 3.19 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 177.3, 143.4, 135.3, 133.9, 129.6, 127.0, 124.9, 122.9, 120.3, 119.5, 118.7, 110.8, 109.7, 109.0, 76.0, 26.4, 13.7; ESI-MS (m/z) = 293 $[M+H]^+$; Analysis Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58; Found: C, 73.87; H, 5.57; N, 9.64; ESI-HRMS Calcd. for $C_{18}H_{16}N_2O_2$: $[M+H]^+$, 293. 1215, Found: m/z 293. 1218.

3- (5 -bromo -1H-indol-3-yl)-5-chloro -3-hydroxyindolin-2-one (3i):

Brown solid; Yield 88%; mp = 155-157°C; IR (KBr) max 3389, 1714, 1612, 1466, 1399, 1216, 1098, 832, 754, 665, 479; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.24 (s, 1H), 10.49 (s, 1H), 7.76 (s, 1H), 7.35 (m, 2H), 7.27-7.26 (m, 1H), 7.20-7.17 (m, 1H), 7.02 (t, *J* = 2.68 Hz, 1H), 6.94 (dd, *J* = 6.60 Hz, 1H), 6.58 (d, *J* = 3.08 Hz, 1H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 178.3, 141.0, 136.1, 135.3, 129.6, 127.3, 126.3, 125.6, 125.2, 124.2, 123.5, 115.0, 114.1, 111.8, 75.2; ESI-MS (m/z) =376 $[M+H]^+$; Analysis Calcd. for $C_{16}H_{10}BrClN_2O_2$ C, 50.89; H, 2.67; N, 7.42; Found: C, 50.81; H, 2.62; N, 7.48; ESI-HRMS Calcd. for $C_{16}H_{10}BrClN_2O_2$: $[M+H]^+$, 376.9585, Found: m/z 376.9589.

3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one (3j):

White solid; Yield 87%; mp = >300°C; IR (KBr) max 3412, 3019, 2400, 1719, 1614, 1468, 669; ^{1}H NMR (400 MHz; DMSO-d^{6}): δ 11.19 (s, 1H), 10.34 (s, 1H), 7.73 (s, 1H), 7.34-7.16 (m, 4H), 7.03-6.91 (m, 3H), 6.43 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^{6}): δ 178.7, 142.1, 136.0, 133.3, 129.7, 127.4, 125.5, 125.2, 124.1, 123.6, 122.3, 115.7, 114.0, 111.2, 110.2, 75.1; ESI-MS (m/z) = 343 $[M+H]^{+}$; Analysis Calcd. for $C_{16}H_{11}BrN_2O_2$: C, 56.00; H, 3.23; N, 8.16; Found: C, 56.08; H, 3.29; N, 8.11; ESI-HRMS Calcd. for $C_{16}H_{11}BrN_2O_2$: $[M+H]^{+}$, 343.9983, Found: m/z 343.9988.

3-hydroxy-(5-methoxy-1H-indol-3-yl)indolin-2-one (3k):

White solid; Yield 86%; mp = 196-198°C; IR (KBr) max 3326, 1721, 1619, 1472, 1177, 760; ^{1}H NMR (400 MHz; DMSO-d^{6}): δ 10.81 (s, 1H), 10.30 (s, 1H), 7.28-7.21 (m, 3H), 7.01-6.99 (m, 1H), 6.97 (dd, *J* = 7.76 Hz, 1H), 6.92 (dd, *J*= 8.28 Hz, 1H), 6.84, (d, *J* = 2.44 Hz, 1H), 6.71 (dd, *J* = 8.80 Hz, 1H), 6.31 (s, 1H), 3.62 (s, 3H); ^{13}C NMR (400 MHz; DMSO-d^{6}): δ 178.9, 153.2, 142.1, 133.8, 132.4, 129.5, 125.8, 125.3, 124.7, 122.2, 115.5, 112.5, 111.3, 110.0, 103.1, 75.5, 55.6; ESI-MS (m/z) = 295 $[M+H]^{+}$; Analysis Calcd. for $C_{17}H_{14}N_2O_3$: C, 69.38 H, 4.79 N, 9.52. Found: C, 69.16 H, 4.75 N, 9.47; ESI-HRMS Calcd. for $C_{17}H_{14}N_2O_3$: $[M+H]^{+}$, 295.1038, Found: m/z 295.1032.

3-hydroxy-3-(2-methyl-1H-indol-3-yl)indolin-2-one (3l):

White solid; Yield 87%; mp = 176-178°C; IR (KBr) max 3504, 3395, 3209, 1708, 1621, 1469, 755; ^{1}H NMR (400 MHz; DMSO-d^{6}): 10.88 (s, 1H), 10.35 (s, 1H), 7.26-7.18 (m, 3H), 6.97-6.89 (m, 4H), 6.75-6.71 (m, 1H), 6.28 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz; DMSO-d^{6}): δ 179.1, 142.0, 135.3, 134.6, 133.9, 129.4, 127.1, 125.4, 122.1, 120.2, 119.6, 118.6, 110.7, 110.1, 109.9, 76.3, 13.7; ESI-MS (m/z) = 279 $[M+H]^{+}$; Analysis Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.31; H, 5.02; N, 10.01; ESI-HRMS Calcd. for $C_{17}H_{14}N_2O_2$: $[M+H]^{+}$, 279.1089, Found: m/z 279.1081.

3-(5-bromo-1H-indol-3-yl)-3-hydroxy-5-nitro-indolin-2-one (3m):

Light brown solid; Yield 89%; mp = 186-188°C; IR (KBr) max 3312, 2926, 1719, 1385, 755; ^{1}H NMR (400 MHz; DMSO-d^{6}): δ 11.32 (s, 1H), 11.06 (s, 1H), 8.29 (dd, *J* = 8.60 Hz, 1H), 8.11 (s, 1H), 7.93 (s, 1H), 7.36 (d, J = 9.00 Hz, 1H), 7.23 (dd, *J* = 8.68 Hz, 1H), 7.13 (d, *J* = 8.64 Hz,

1H), 7.04 (d, *J* = 2.56 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (400 MHz; DMSO-d^6): δ 178.7, 148.6, 142.8, 136.2, 134.1, 127.3, 127.1, 125.9, 124.4, 123.8, 120.7, 114.2, 111.9, 110.5, 74.8; ESI-MS (m/z) = 387 $[M+H]^+$; Analysis Calcd. for $C_{16}H_{10}BrN_3O_4$: C, 49.51; H, 2.60; N, 10.83; Found: C, 49.59; H, 2.68; N, 10.89; ESI-HRMS Calcd. for $C_{16}H_{10}BrN_3O_4$: $[M+H]^+$, 387.9888, Found: m/z 387.9881.

3-(5 -bromo-1H-indol-3-yl)-1-methyl-3-hydroxyindolin-2-one (3n):

White solid; Yield 88%; mp = 179-181°C; IR (KBr) max 3341, 1711, 1617, 1465, 1164, 749; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.21 (s, 1H), 7.77 (d, *J* = 1.88 Hz, 1H), 7.42-7.31 (m, 3H), 7.19 (dd, *J* = 8.64 Hz, 1H), 7.13-7.09 (m, 2H), 6.93 (d, *J* = 2.60 Hz, 1H), 6.48 (s, 1H), 3.14 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 176.9, 143.5, 136.0, 132.6, 129.8, 127.5, 125.7, 124.8, 124.2, 123.9, 123.0, 115.4, 114.0, 111.7, 109.1, 74.9, 26.4; ESI-MS (m/z) = 357 $[M+H]^+$; Analysis Calcd. for $C_{17}H_{13}BrN_2O_2$: C, 57.16; H, 3.67; N, 7.84; Found: C, 57.12; H, 3.63; N, 7.89; ESI-HRMS Calcd. for $C_{17}H_{13}BrN_2O_2$: 357.0194 $[M+H]^+$, Found: m/z 357.0198.

3-(5-bromo-1H-indol-3-yl)-1-ethyl-3-hydroxyindolin-2-one (3o):

Light brown solid; Yield 86%; mp = 183-185°C; IR (KBr) max 3349, 1718, 1609, 1473, 1166, 751; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.21 (s, 1H), 7.66 (s, 1H), 7.41-7.31 (m, 3H), 7.18-7.14 (m, 2H), 7.10 (t, *J* = 7.52 Hz, 1H), 7.01 (d, *J* = 2.56 Hz, 1H), 6.49 (s, 1H), 3.81-3.63 (m, 2H), 1.20 (t, *J* = 7.12 Hz, 3H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 176.5, 142.5, 136.0, 132.9, 129.8, 127.3, 125.6, 125.1, 124.1, 123.5, 122.8, 115.5, 114.1, 111.7, 109.1, 74.8, 34.5, 12.9; ESI-MS (m/z) = 371 $[M+H]^+$; Analysis Calcd. for $C_{18}H_{15}BrN_2O_2$: C, 58.24; H, 4.07; N, 7.55; Found: C, 58.29; H, 4.12; N, 7.62; ESI-HRMS Calcd. for $C_{18}H_{15}BrN_2O_2$: $[M+H]^+$, 371.0350, Found: m/z 371.0358.

2-hydroxy-2-(1H-indol-3-yl)acenaphthylen-1(2H)-one (4a):

White solid; Yield 88%; mp = 281-283°C; IR (KBr) max 3413, 1725, 1603, 1503, 1422, 1215, 831, 757; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.02 (s, 1H), 8.36 (dd, *J* = 8.08 Hz, 1H), 8.07 (d, *J* = 7.92 Hz, 1H), 7.96 (dd, *J* = 6.92 Hz, 1H), 7.89 (t, *J* = 8.08 Hz, 1H), 7.77 (t, *J* = 8.28 Hz, 1H), 7.67 (d, *J* = 6.44 Hz, 1H), 7.34 (d, *J* = 8.12 Hz, 1H), 7.13 (d, *J* = 8.08 Hz, 1H), 7.03-6.99 (m,

2H), 6.82-6.78 (m, 1H), 6.64 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 203.9, 143.2, 140.6, 137.3, 132.3, 131.1, 130.7, 129.5, 129.2, 125.6, 125.4, 124.3, 122.1, 121.6, 121.5, 120.9, 119.0, 116.2, 112.0, 79.3; ESI-MS (m/z) = 300 $[M+H]^+$; Analysis Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68; Found: C, 80.29; H, 4.46; N, 4.78; ESI-HRMS Calcd. for $C_{20}H_{13}NO_2$: $[M+H]^+$, 300.0980, Found: m/z 300.0988.

2-(5-bromo-1H-indol-3-yl)-2-hydroxyacenaphthylen-1(2H)-one (4b):

White solid; Yield 83%; mp = 276-278 °C; IR (KBr) max 3413, 1725, 1603, 1503, 1422, 1215, 831, 757; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.24 (s, 1H), 8.35 (d, *J* = 8.08 Hz, 1H), 8.08 (d, *J* = 8.16 Hz, 1H), 7.96 (d, *J* = 6.60 Hz, 1H), 7.88-7.79 (m, 2H), 7.76-7.73 (m, 2H), 7.36 (d, *J* = 8.64 Hz, 1H), 7.21 (dd, *J* = 8.60 Hz, 1H), 6.90 (d, *J* = 2.60 Hz, 1H), 6.77 (s, 1H): ^{13}C NMR (100 MHz; DMSO-d^6): δ 204.0, 143.3, 140.8, 137.5, 132.4, 131.2, 130.8, 129.7, 129.3, 125.7, 125.5, 124.4, 122.2, 121.6, 121.0, 119.1, 116.3, 112.1, 79.4; ESI-MS (m/z) = 378 $[M+H]^+$; Analysis Calcd. for $C_{20}H_{12}BrNO_2$: C, 63.51; H, 3.20; N, 3.70; Found: C, 63.58; H, 3.26; N, 3.78; ESI-HRMS Calcd. for $C_{20}H_{12}BrNO_2$: $[M+H]^+$, 378.0085, Found: m/z 300.0089.

1-hydroxy-1-(1H-indol-3-yl)aceanthrylen-2(1H)-one (5a):

White solid; Yield 87%; mp = 289-291 °C; IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619; ^{1}H NMR (400 MHz; DMSO-d^6): δ 11.02 (s, 1H), 9.07 (s, 1H), 8.99 (dd, *J* = 8.56 Hz, 1H), 8.39 (d, *J* = 8.56 Hz, 1H), 8.19 (d, *J* = 8.44 Hz, 1H), 7.85-7.81 (m, 1H), 7.76-7.69 (m, 2H), 7.66 (d, *J* = 6.16 Hz, 1H), 7.34 (d, *J* = 8.12 Hz, 1H), 7.12-7.09 (m, 1H), 6.78-6.74 (m, 1H), 6.68 (s, 1H); ^{13}C NMR (100 MHz; DMSO-d^6): δ 204.3, 143.4, 142.7, 137.3, 133.7, 133.4, 130.3, 129.9, 128.8, 128.4, 127.9, 126.9, 125.6, 124.2, 124.0, 123.4, 121.5, 121.0, 120.9, 118.9, 116.1, 112.0, 79.4; ESI-MS (m/z) = 350 $[M+H]^+$; Analysis Calcd. for $C_{24}H_{15}NO_2$: C, 82.50; H, 4.33; N, 4.01;Found: C, 82.58; H, 4.39; N, 4.12; ESI-HRMS Calcd. for $C_{24}H_{15}NO_2$: $[M+H]^+$, 350.1136, Found: m/z 350.1131.

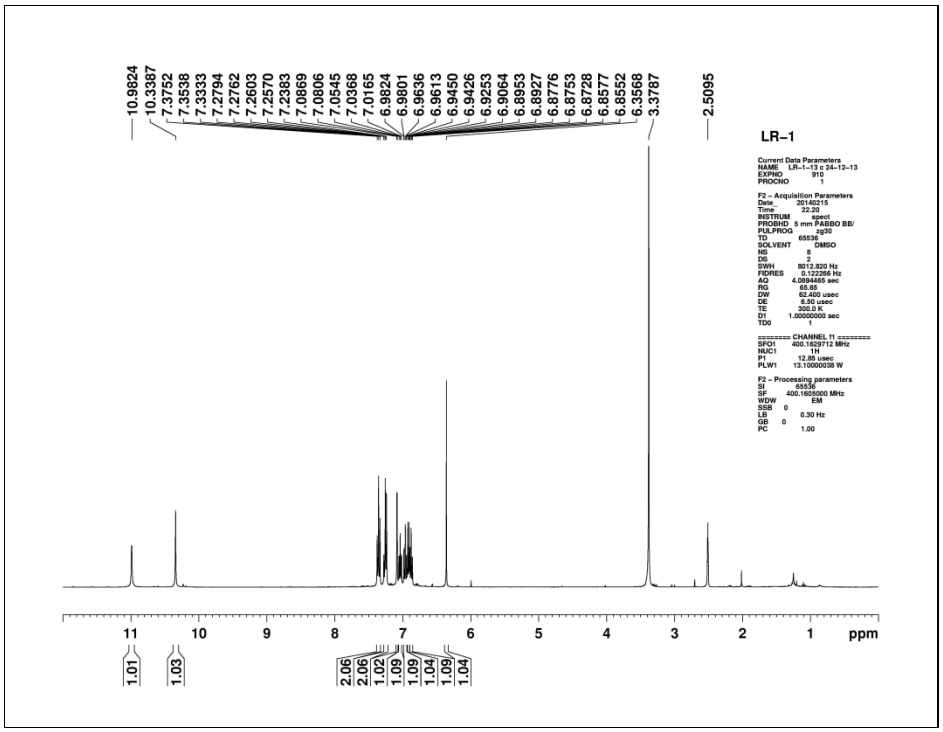

Figure 1: ^{1}H NMR of compound 3a

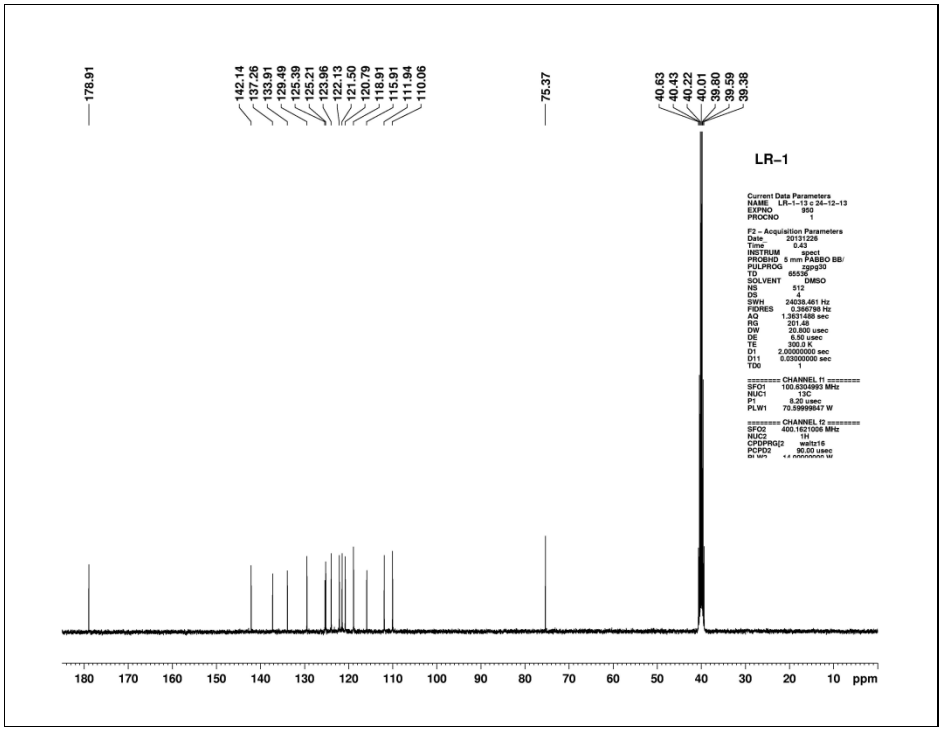

Figure 2: ^{13}C NMR of compound 3a

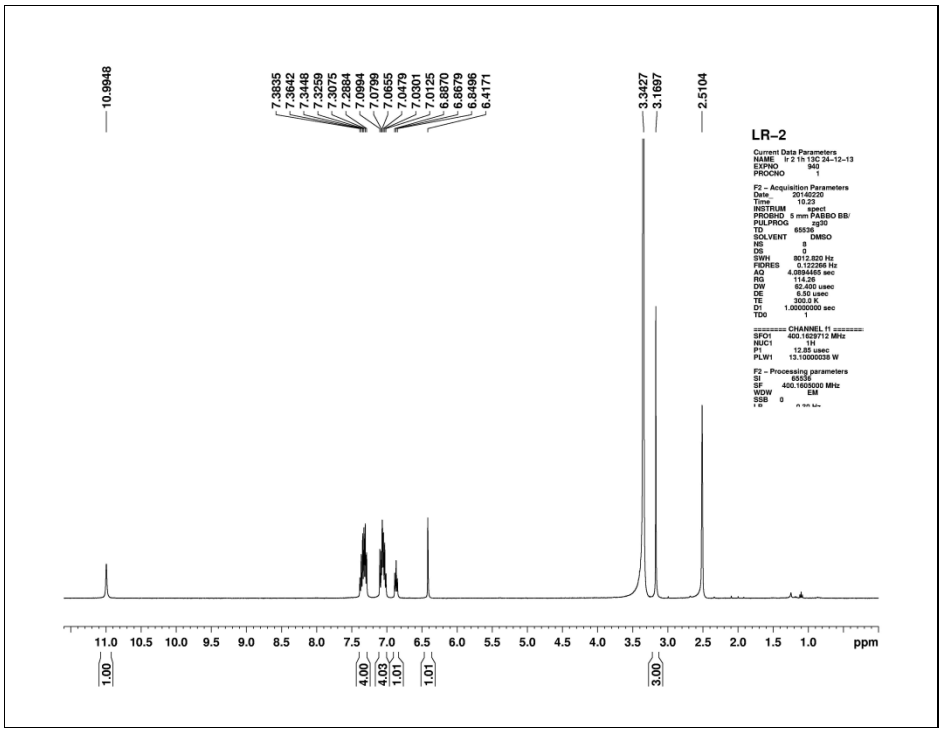

Figure 3: ^{1}H NMR of compound 3b

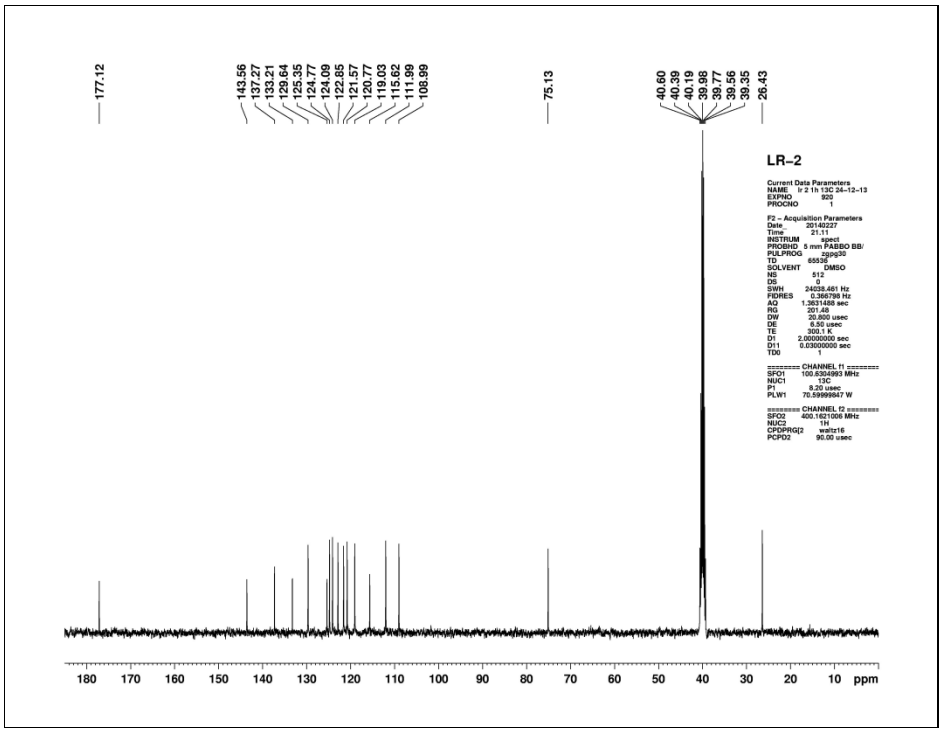

Figure 4: ^{13}C NMR of compound 3b

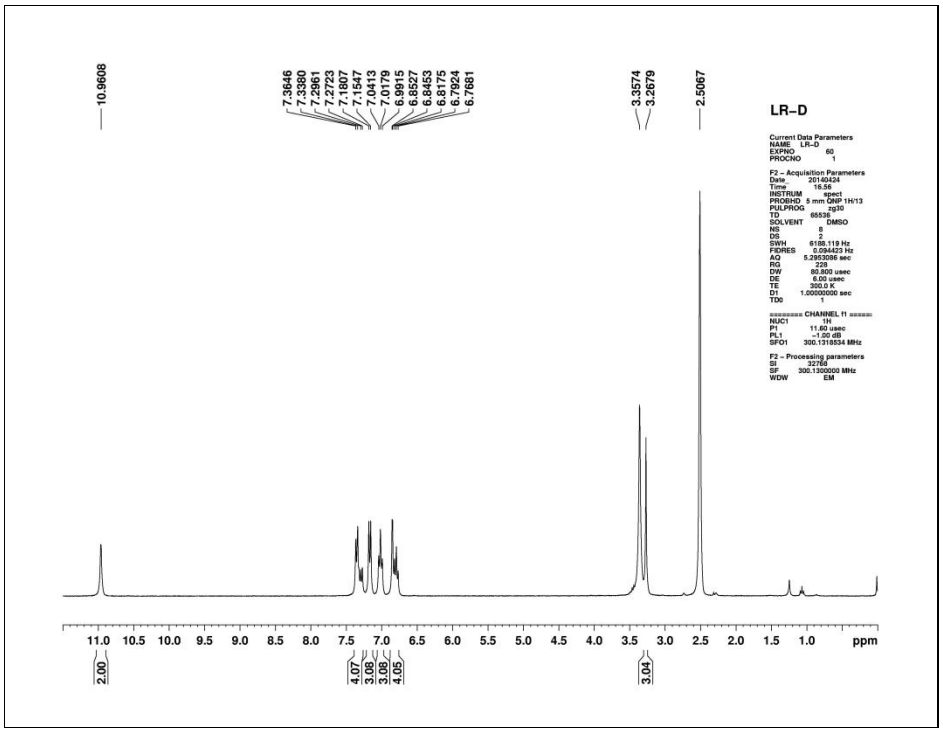

Figure 5: ^{1}H NMR of compound 3b^{I}

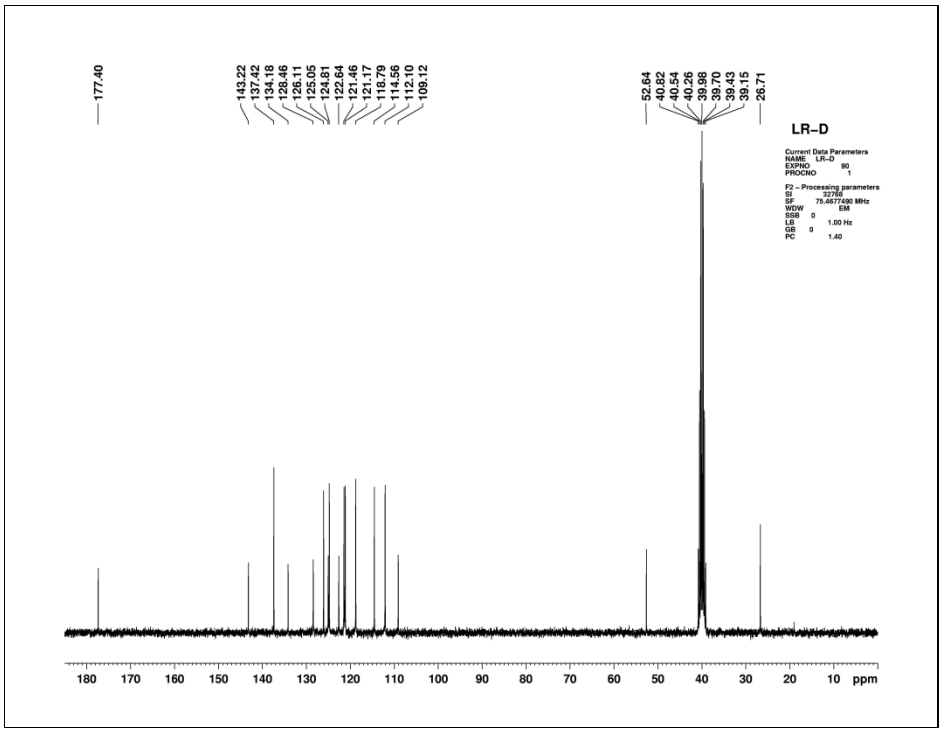

Figure 6: ^{13}C NMR of compound 3b^{I}

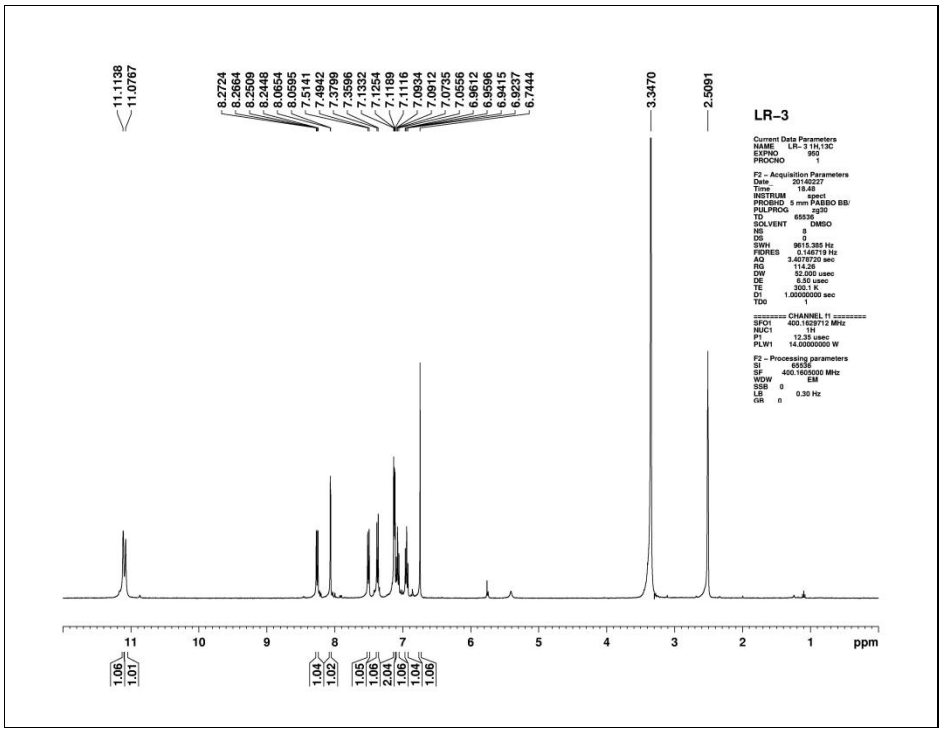

Figure 7: ^{1}H NMR of compound 3c

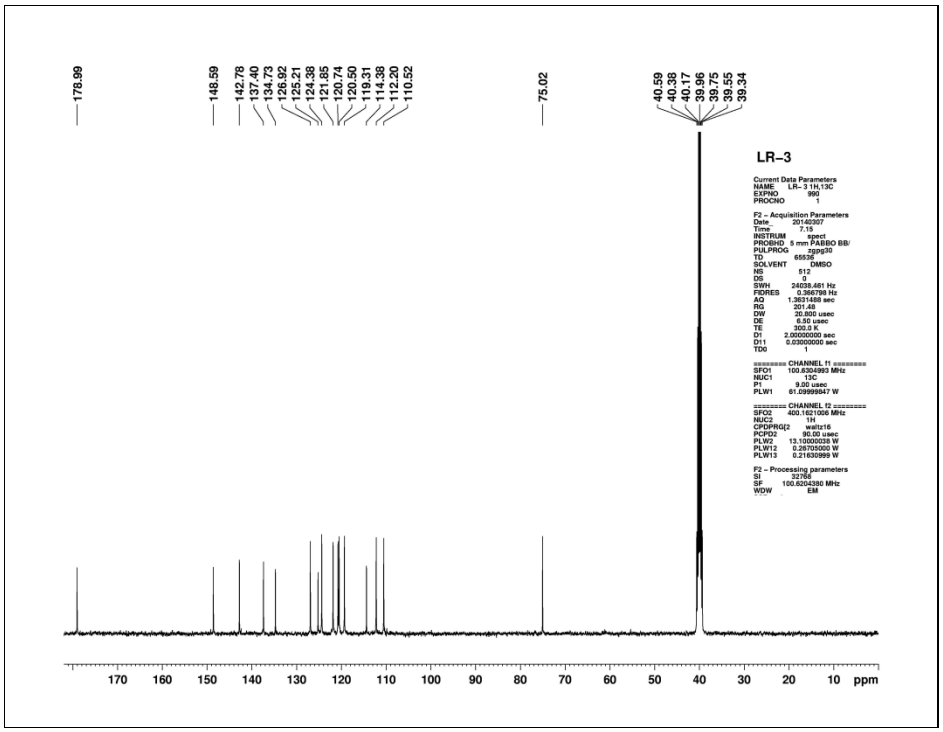

Figure 8: ^{13}C NMR of compound 3c

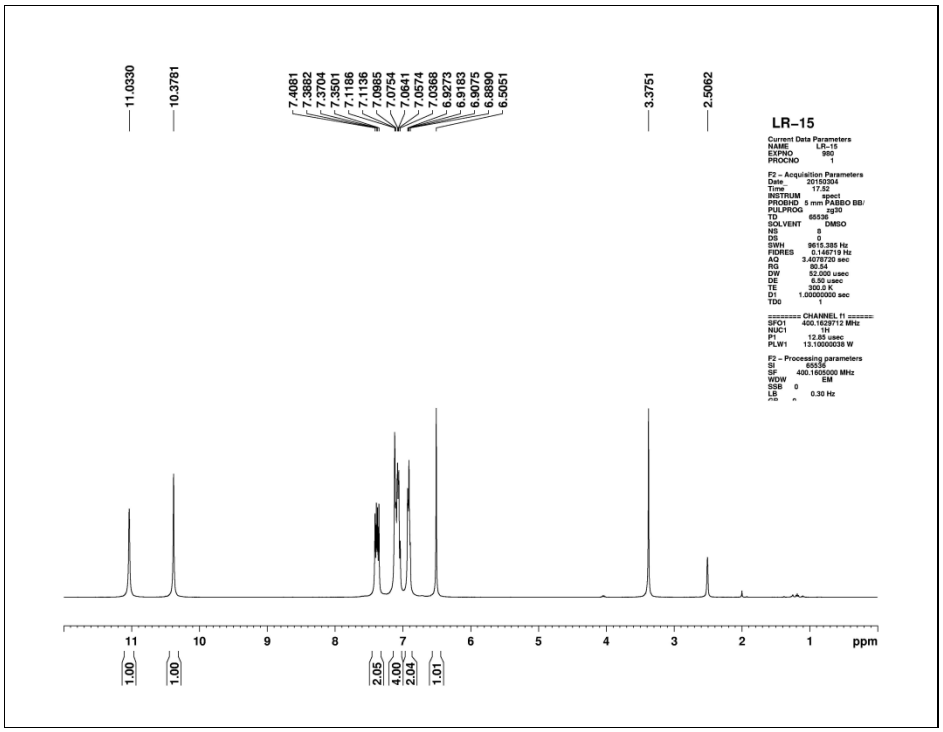

Figure 9: ^{1}H NMR of compound 3d

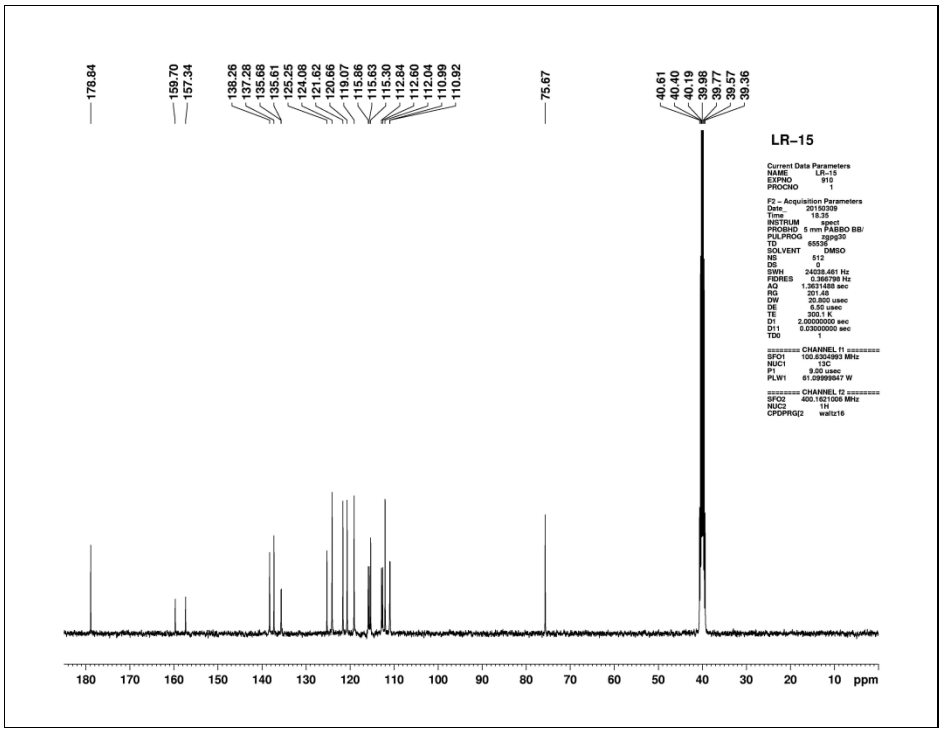

Figure 10: ^{13}C NMR of compound 3d

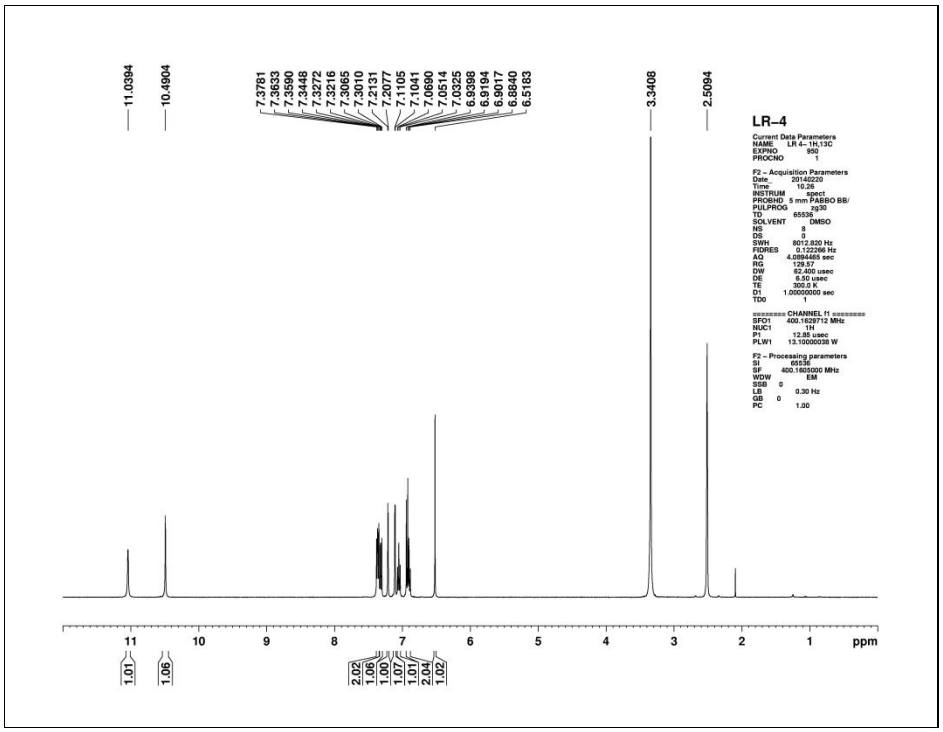

Figure 11: ^{1}H NMR of compound 3e

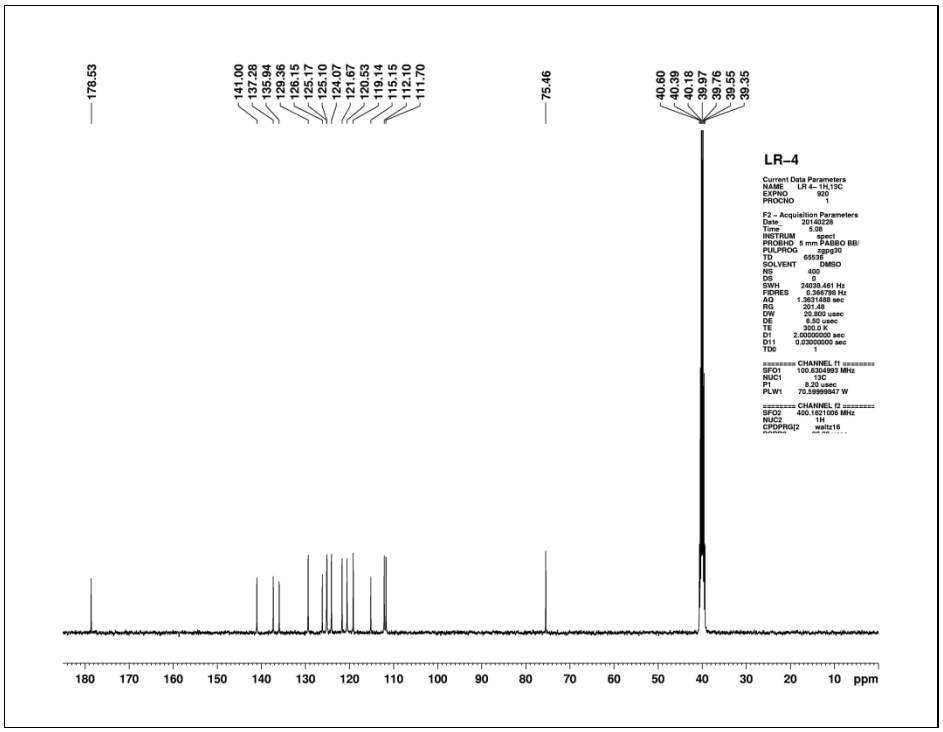

Figure12: ^{13}C NMR of compound 3e

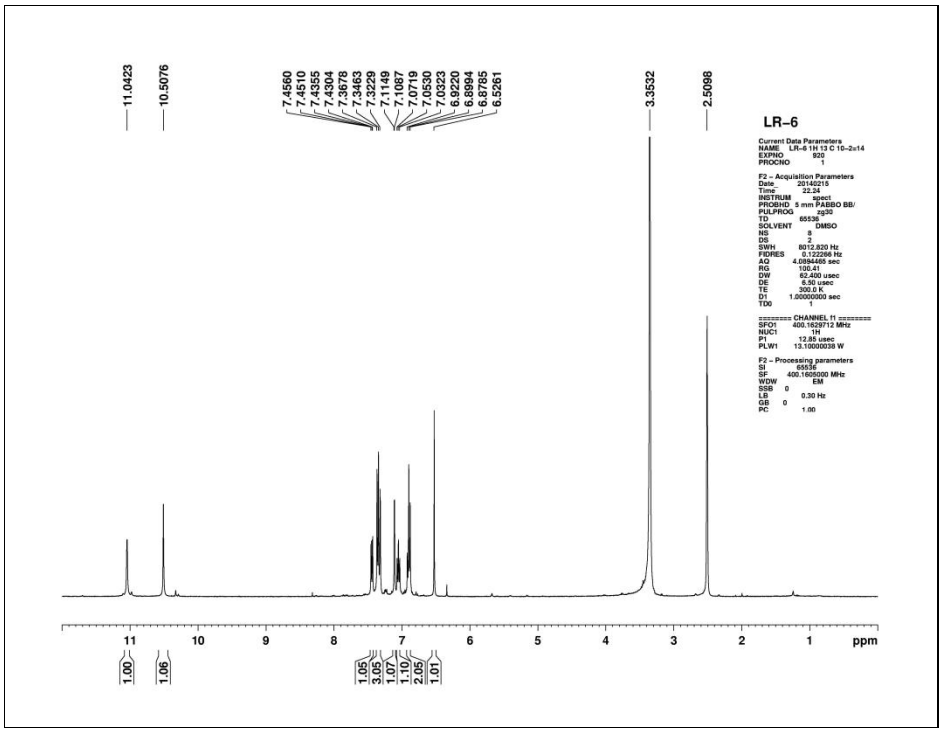

Figure 13: ^{1}H NMR of compound 3f

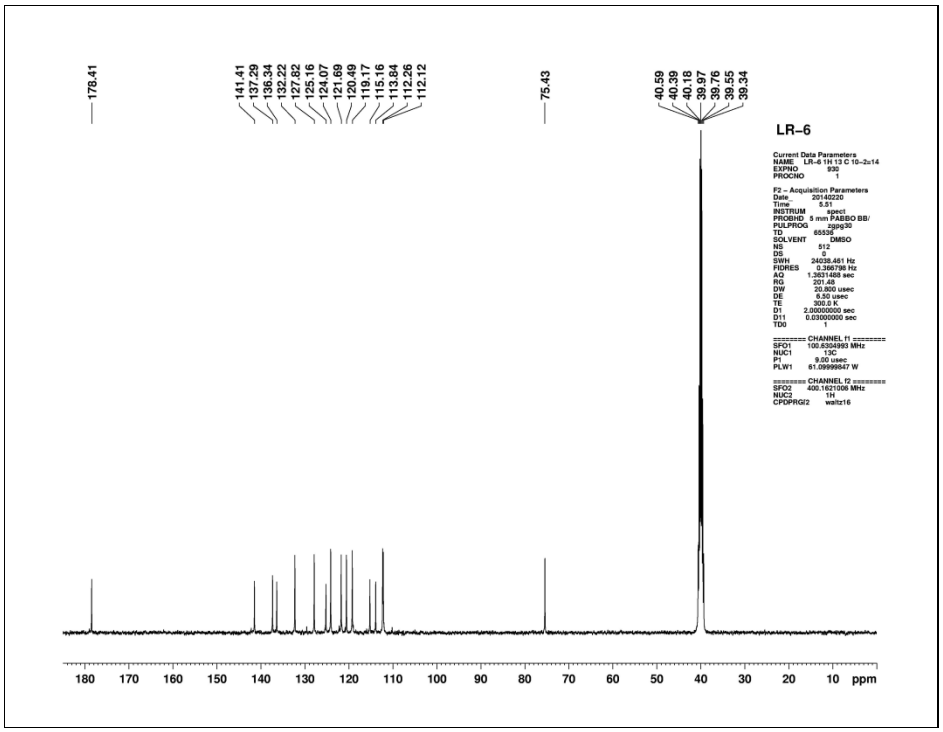

Figure 14: ^{13}C NMR of compound 3f

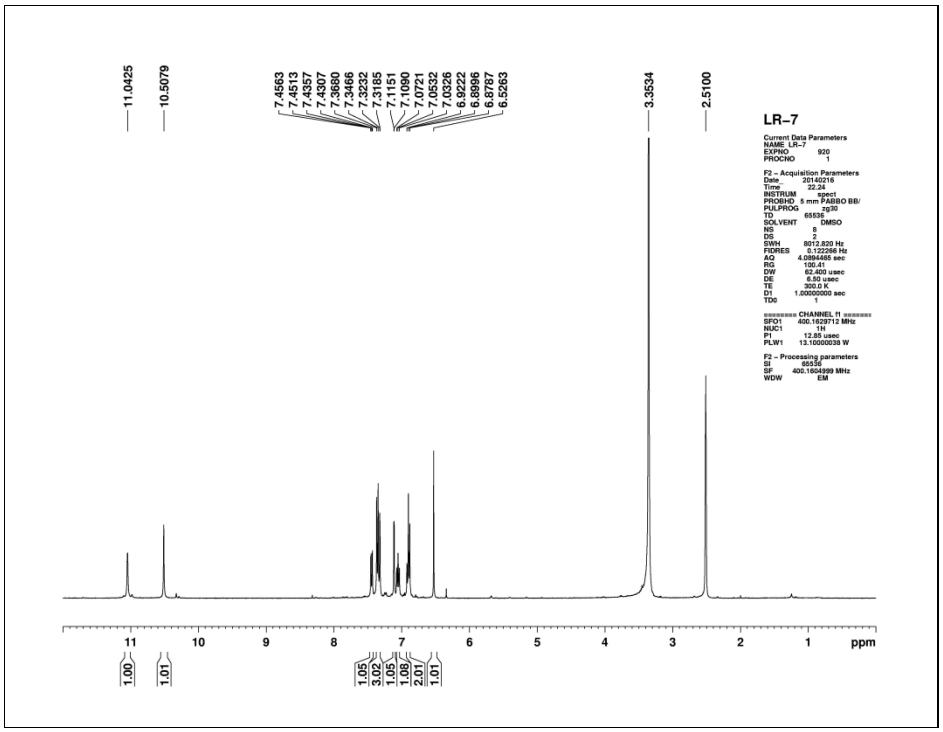

Figure 15: ^{1}H NMR of compound of 3g

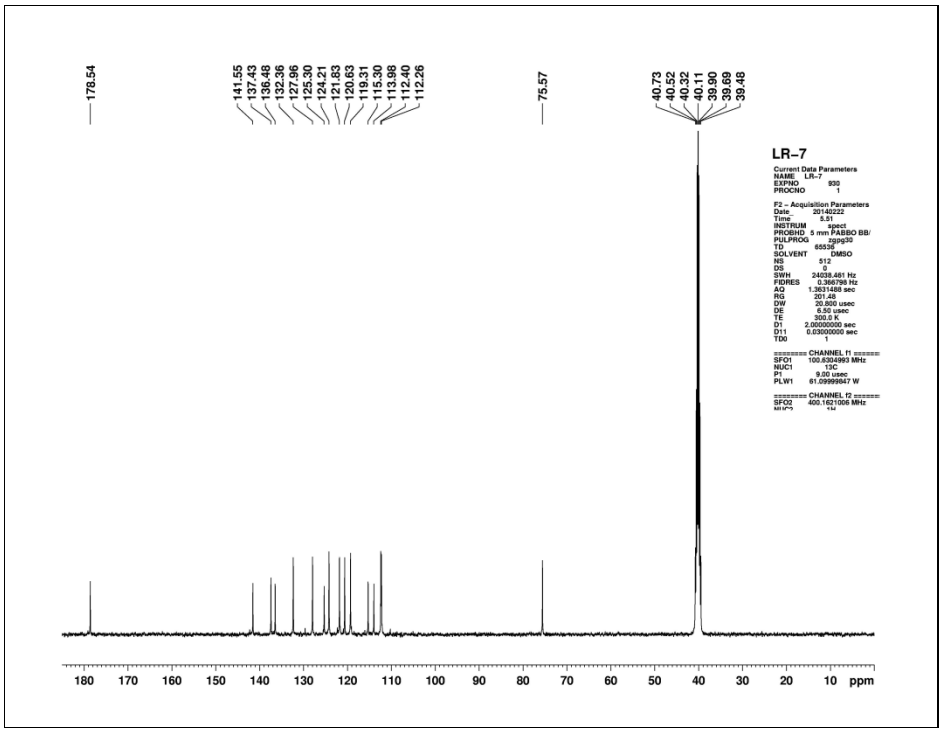

Figure 16: ^{13}C NMR of compound 3g

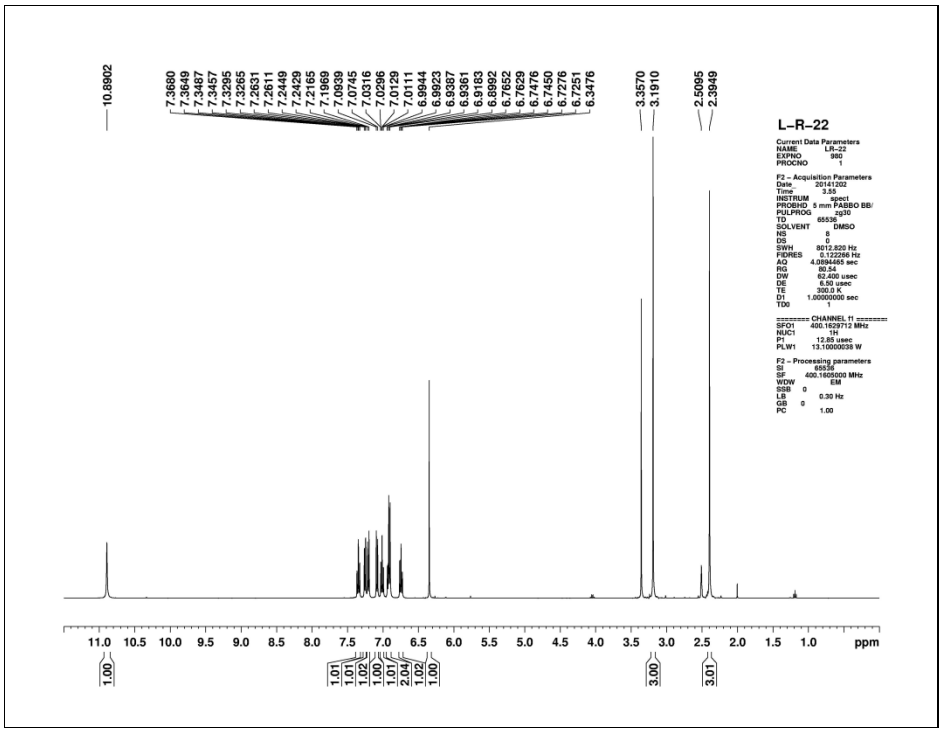

Figure 5: ^{1}H NMR of compound 3h

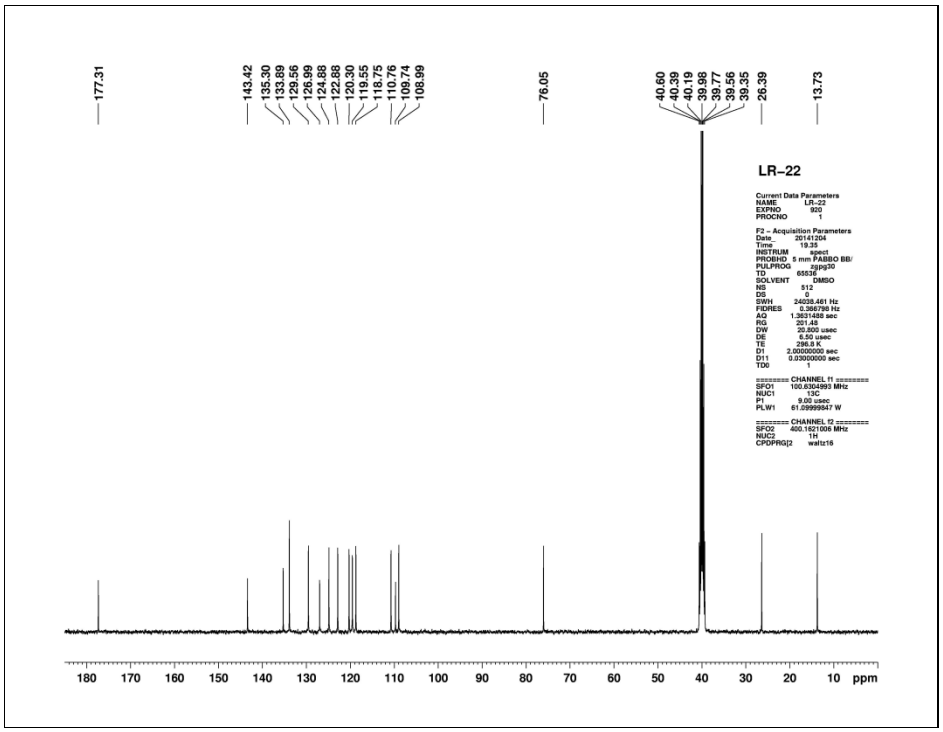

Figure 18: ^{13}C NMR of compound 3h

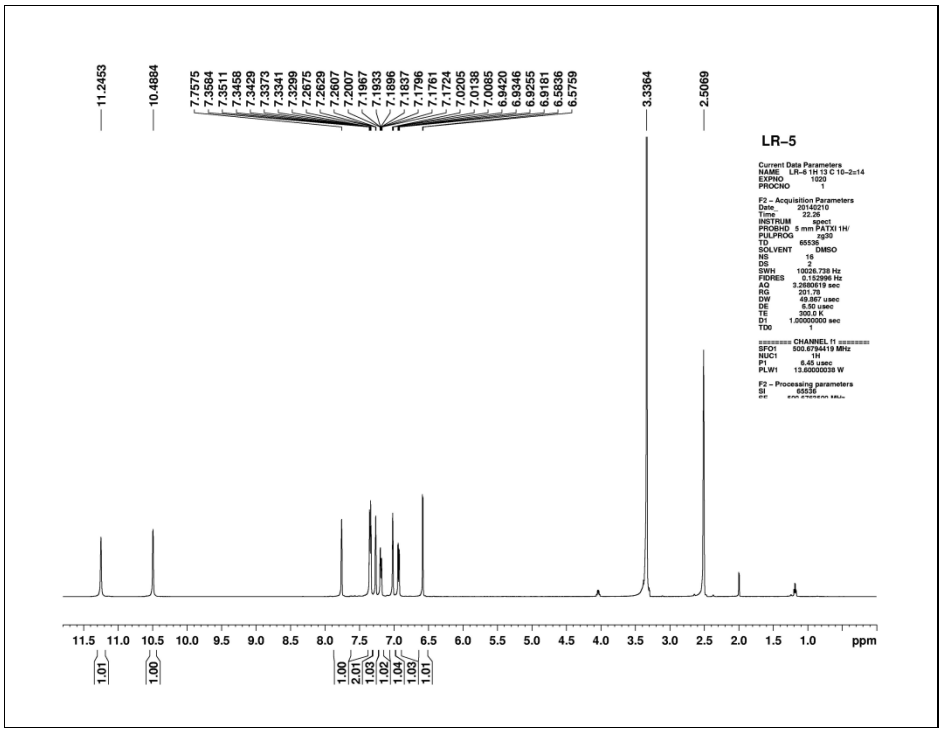

Figure 19: ^{1}H NMR of compound 3i

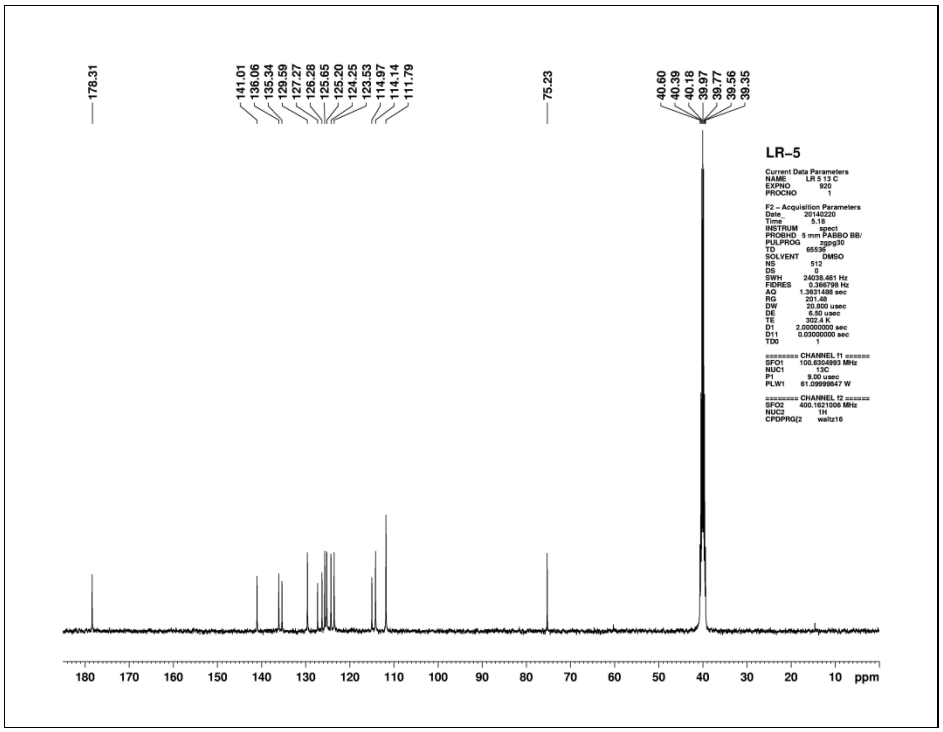

Figure 6: ^{13}C NMR of compound 3i

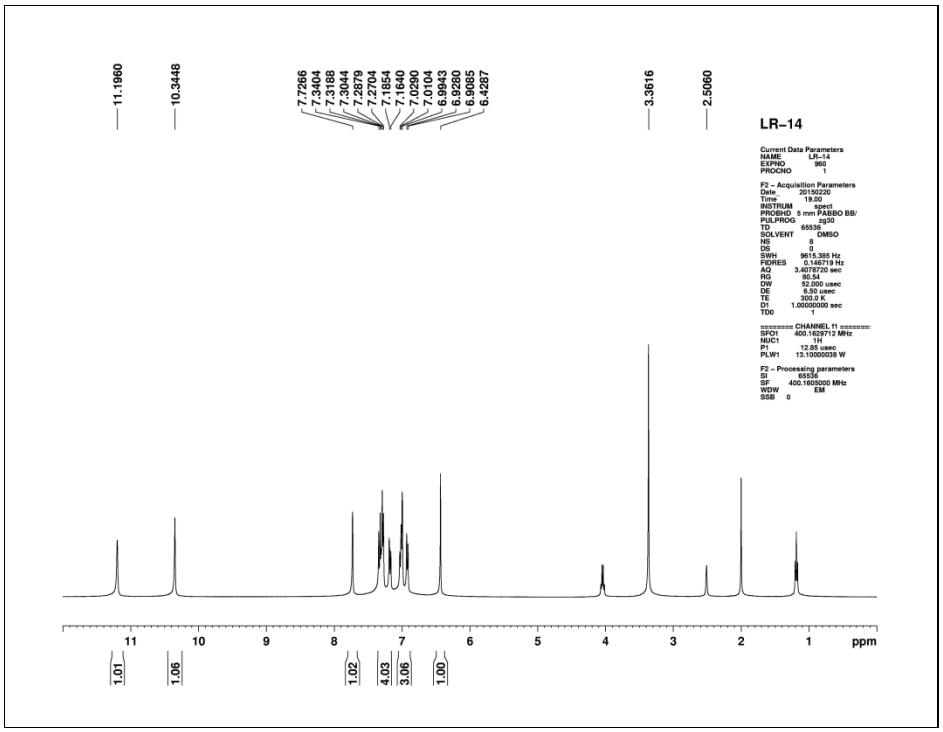

Figure 21: ^{1}H NMR of compound 3j

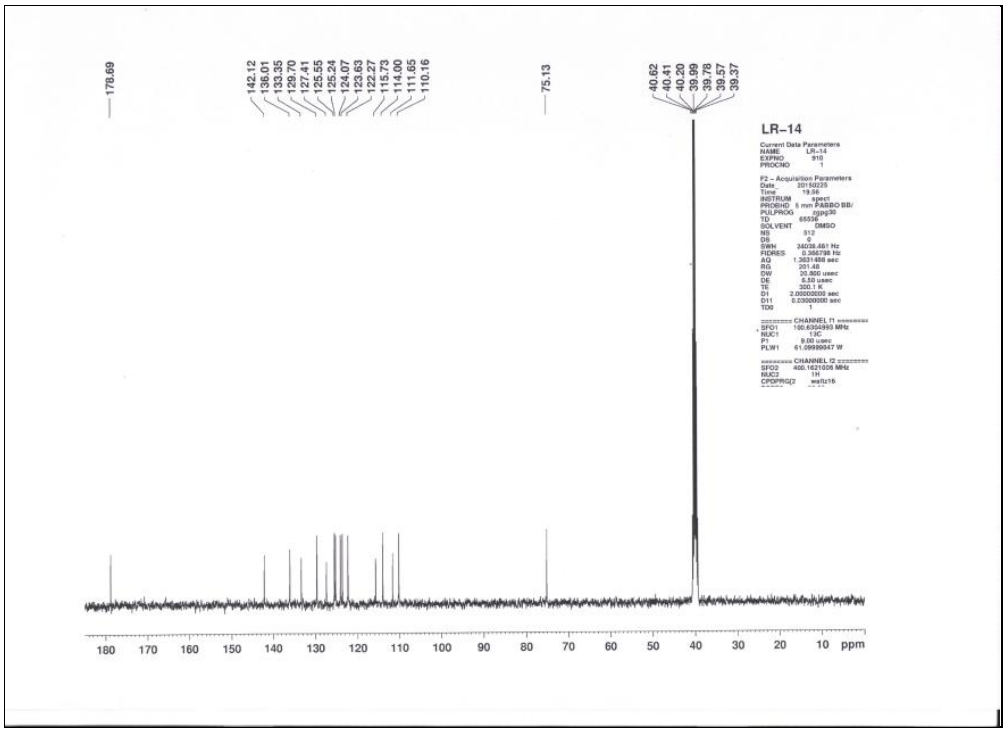

Figure 72: ^{13}C NMR of compound 3j

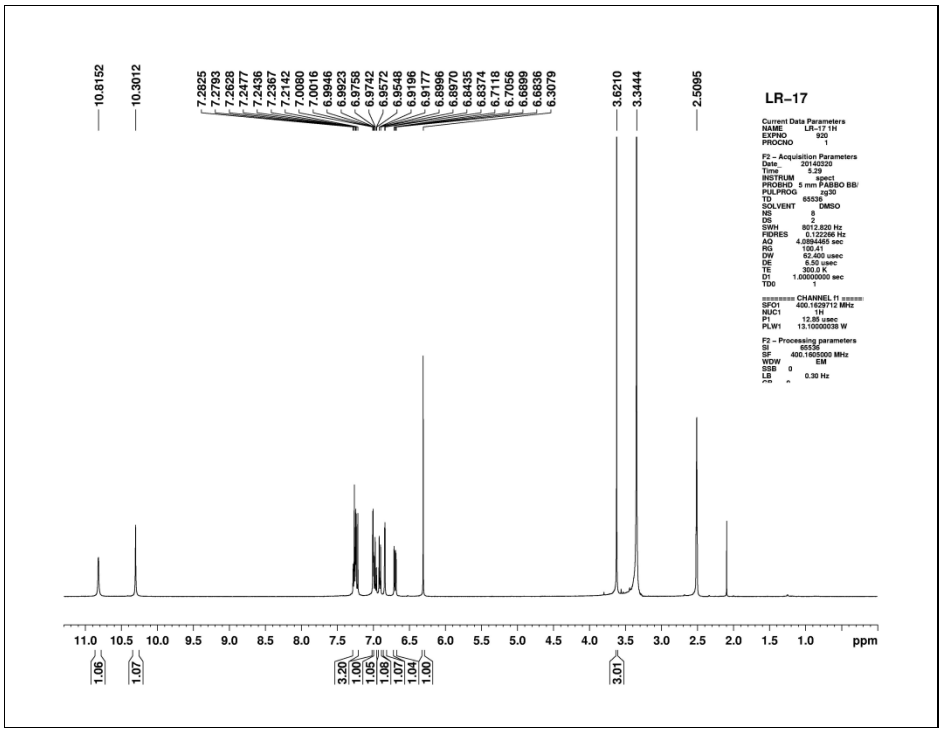

Figure 23: ^{1}H NMR of compound 3k

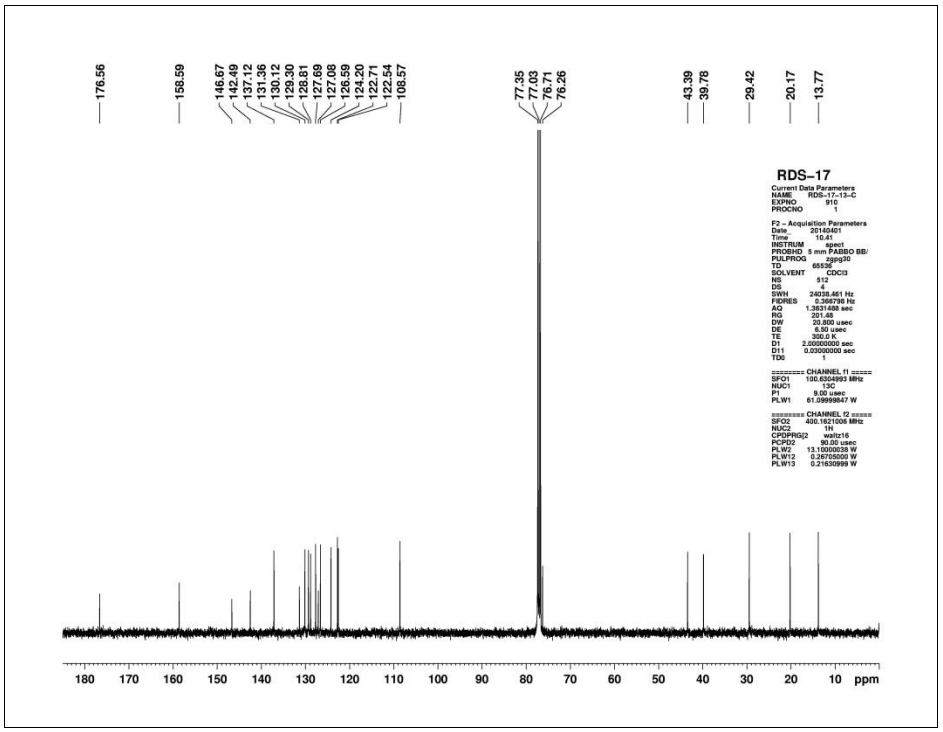

Figure 24:^{13}C NMR of compound 3k

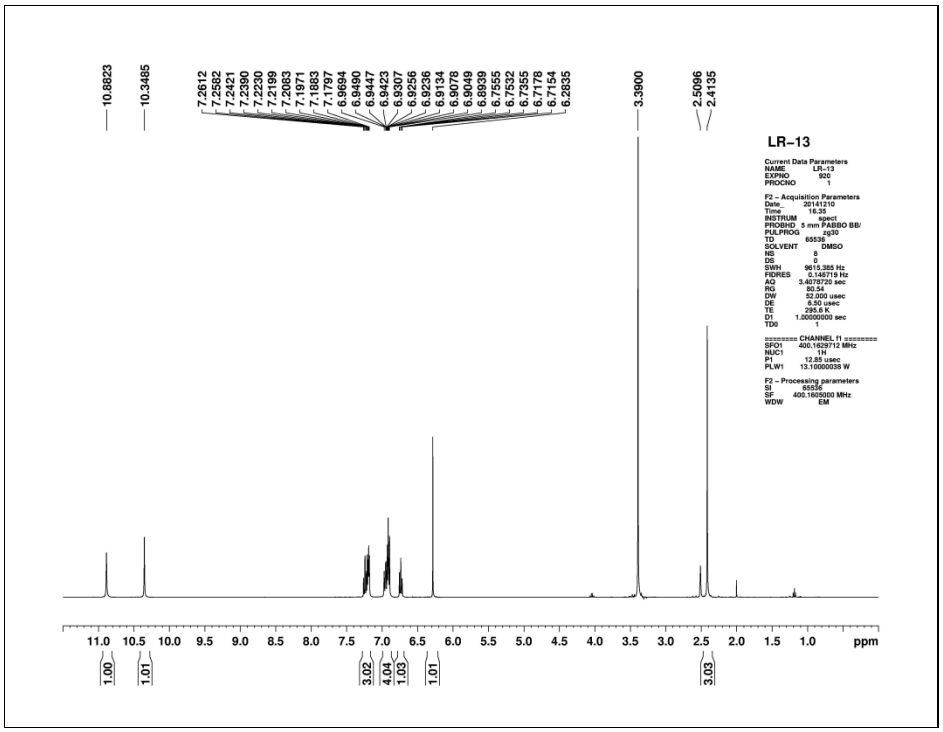

Figure 25: ^{1}H NMR of compound 3l

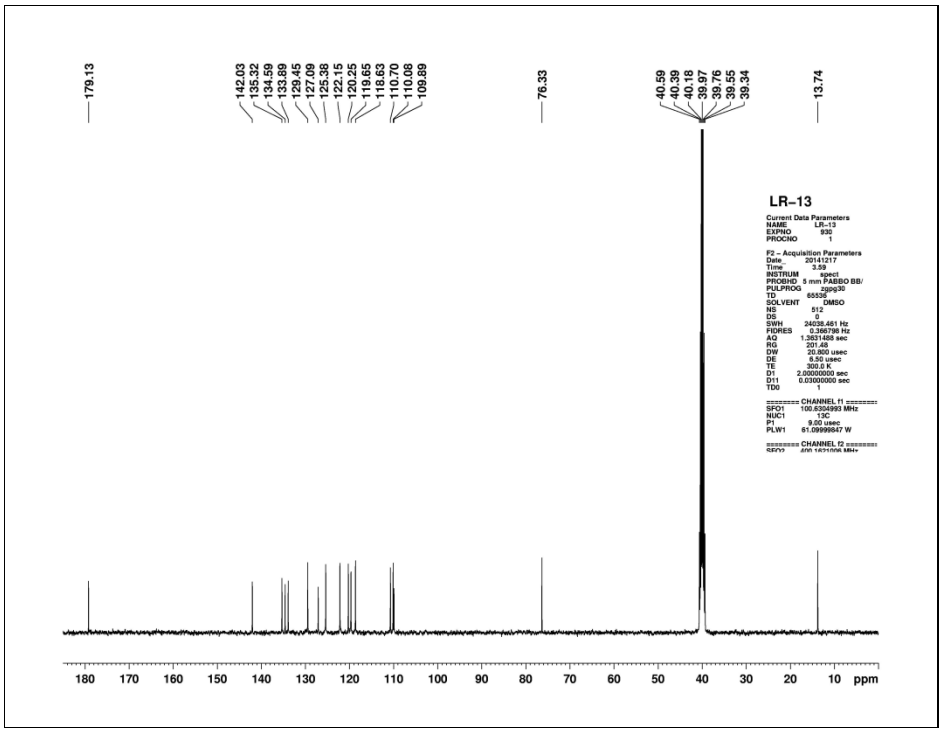

Figure 26: ^{13}C NMR of compound 3l

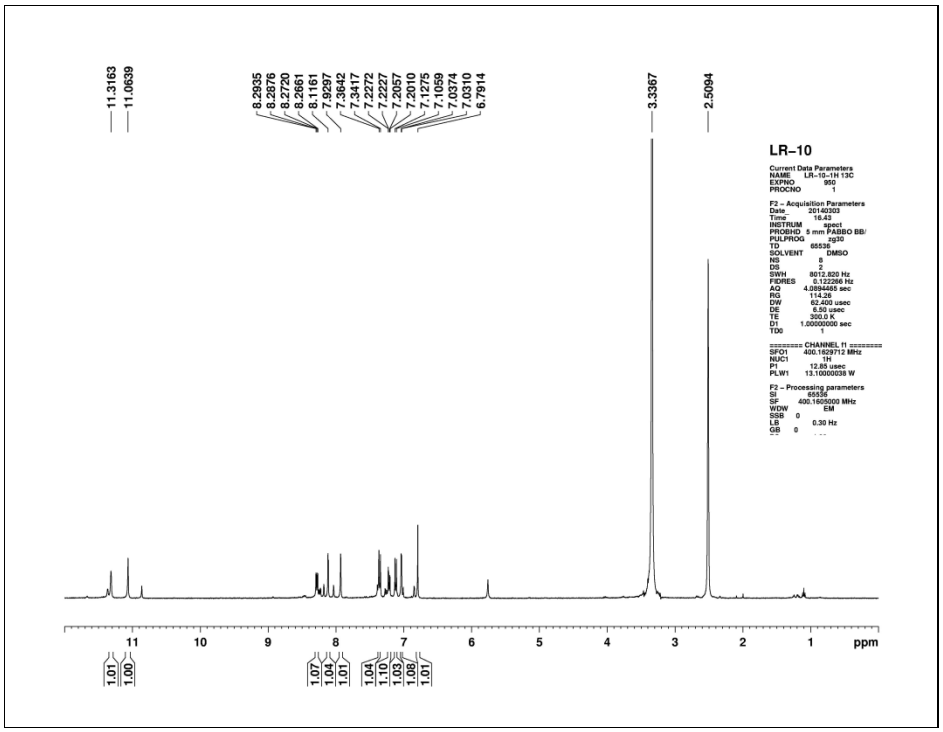

Figure 27: ^{1}H NMR of compound 3m

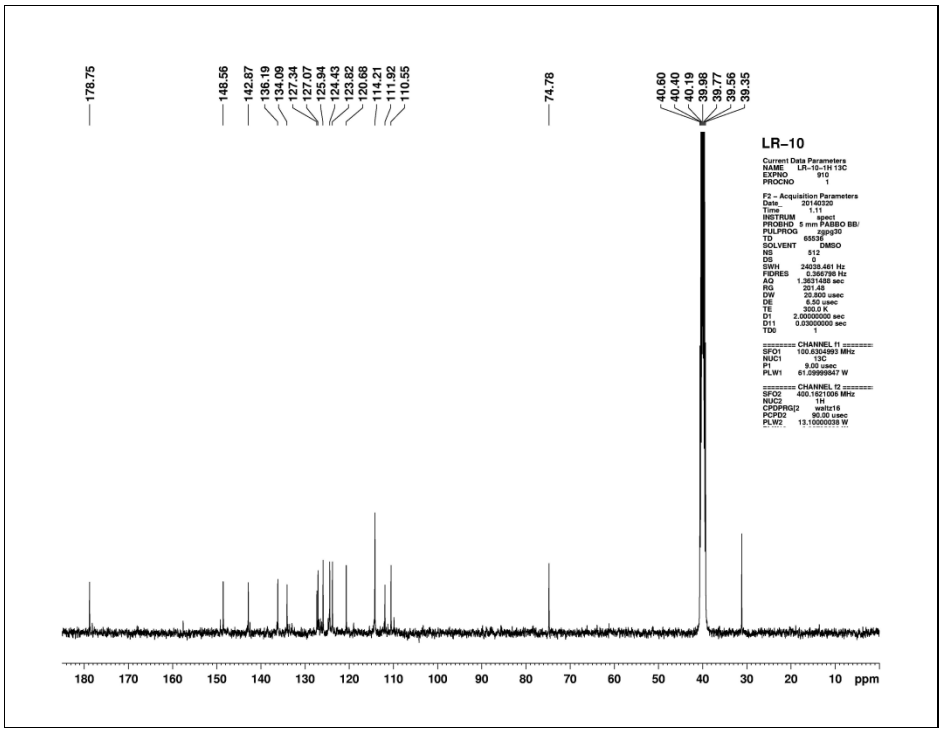

Figure 28: ^{13}C NMR of compound 3m

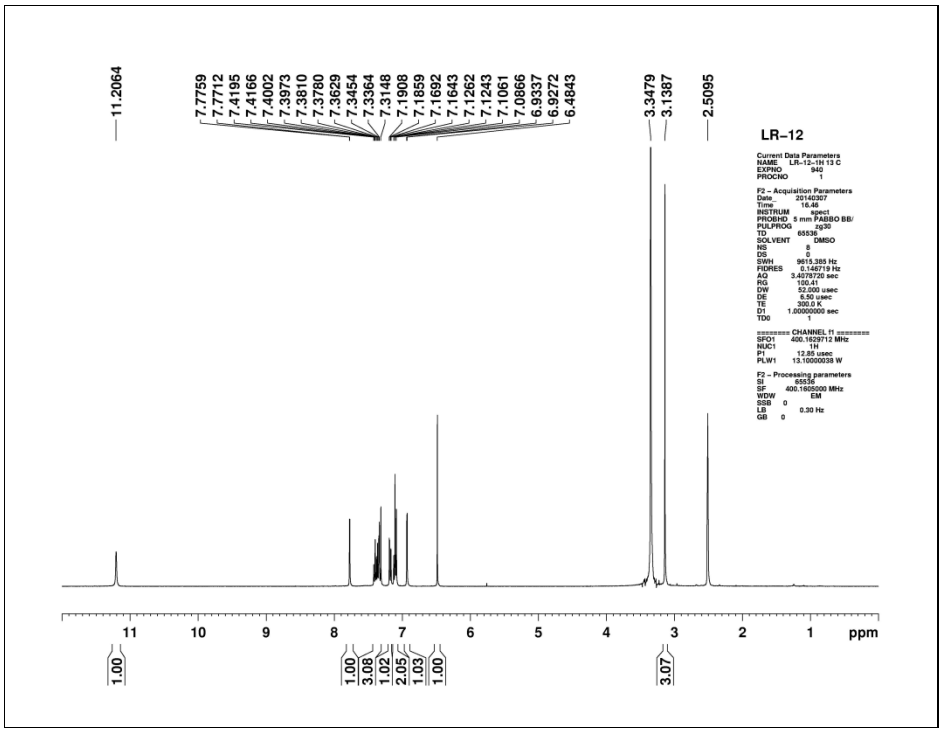

Figure 29: ^{1}H NMR of compound 3n

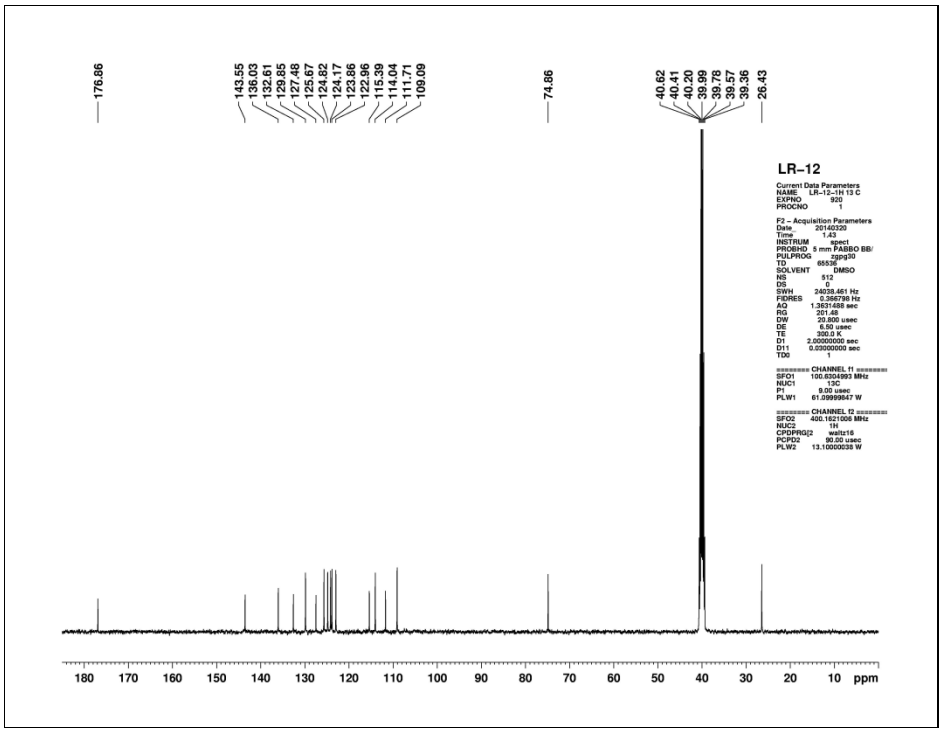

Figure 30: ^{13}C NMR of compound 3n

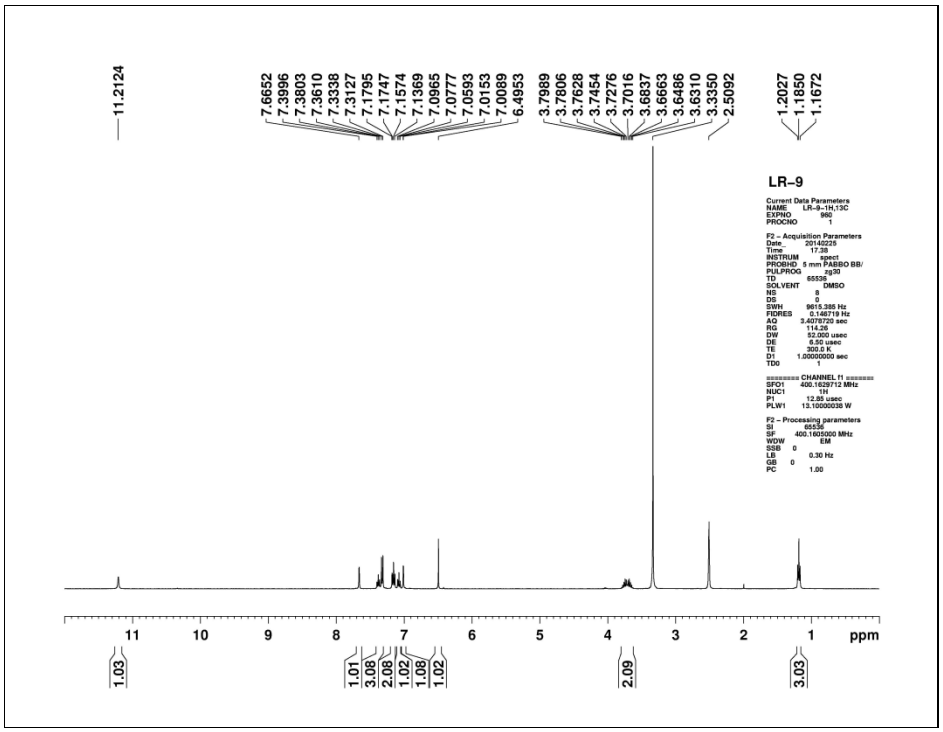

Figure 31: ^{1}H NMR of compound 3o

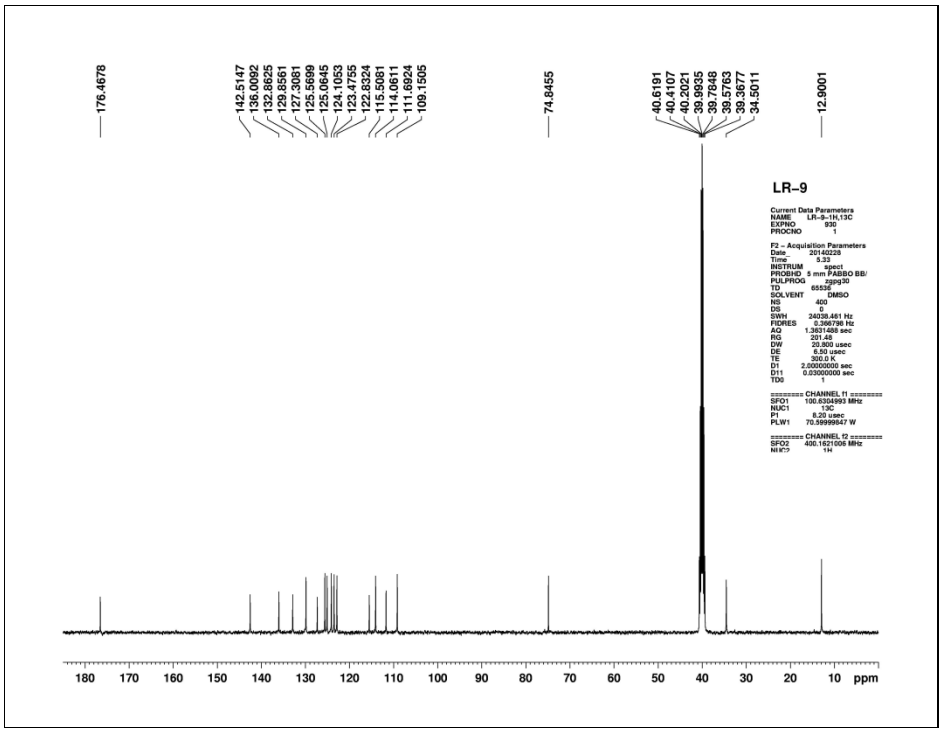

Figure 32: ^{13}C NMR of compound 3o

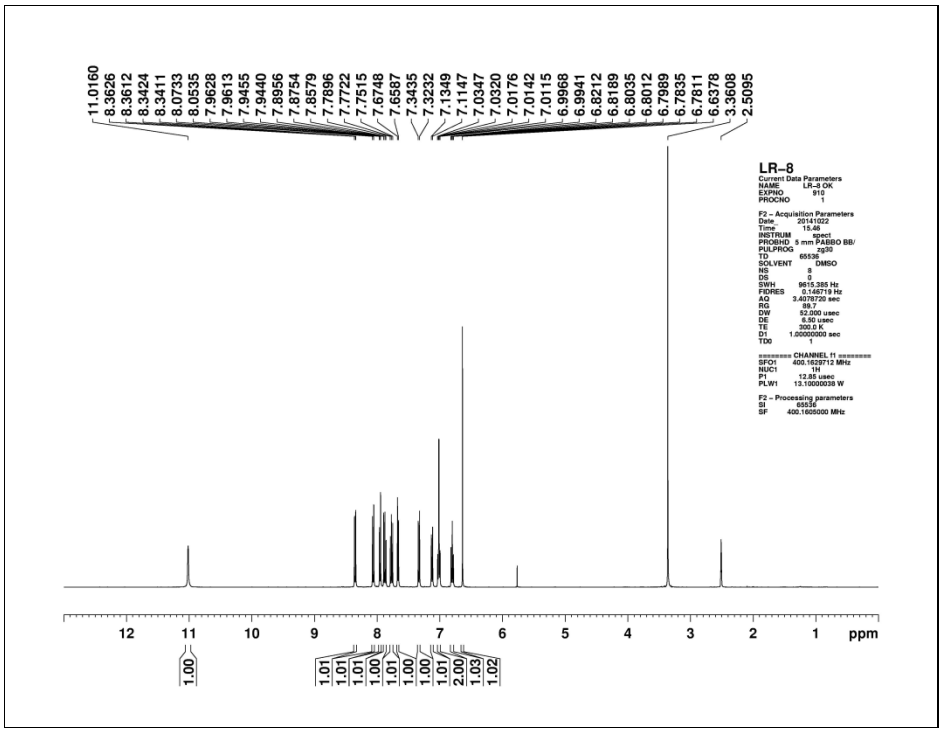

Figure 33: ^{1}H NMR of compound 4a

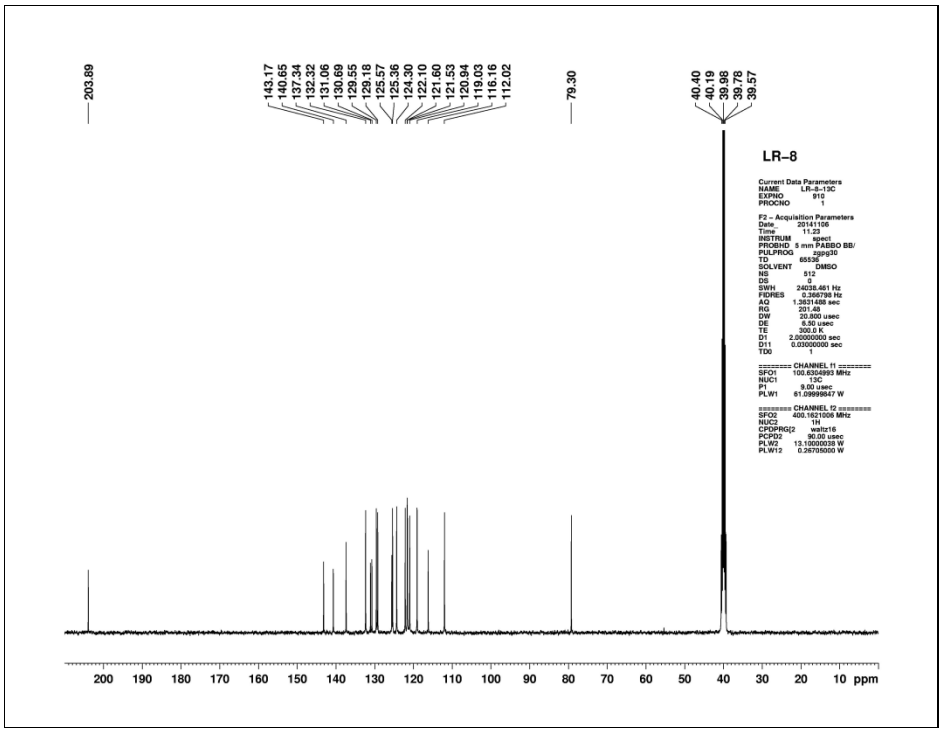

Figure 34: ^{13}C NMR of compound 4a

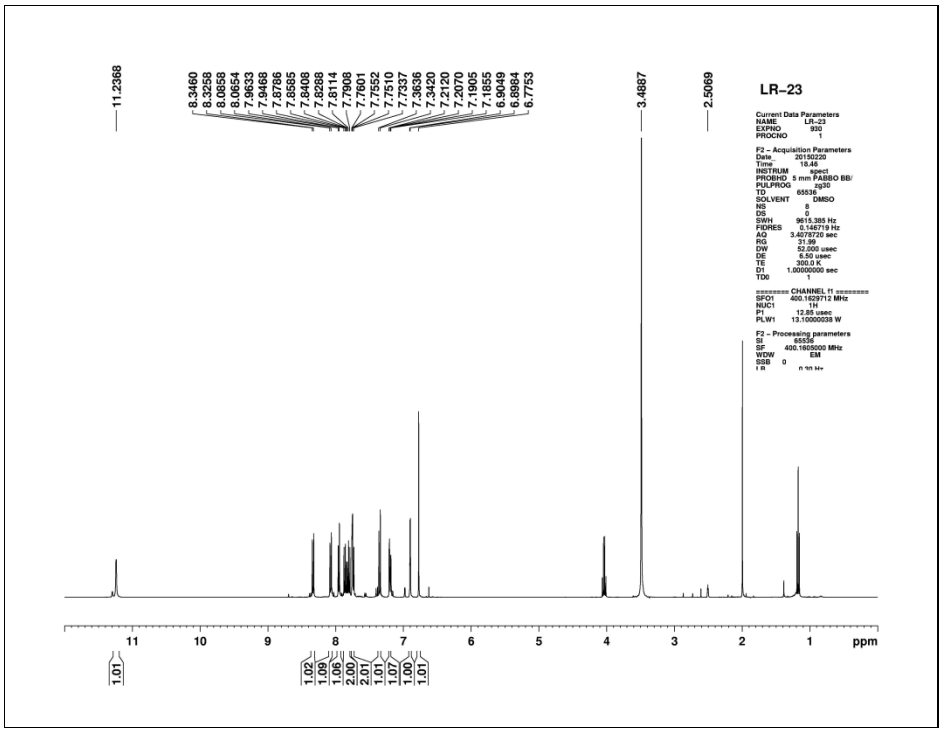

Figure 35: ^{13}C NMR of compound 4b

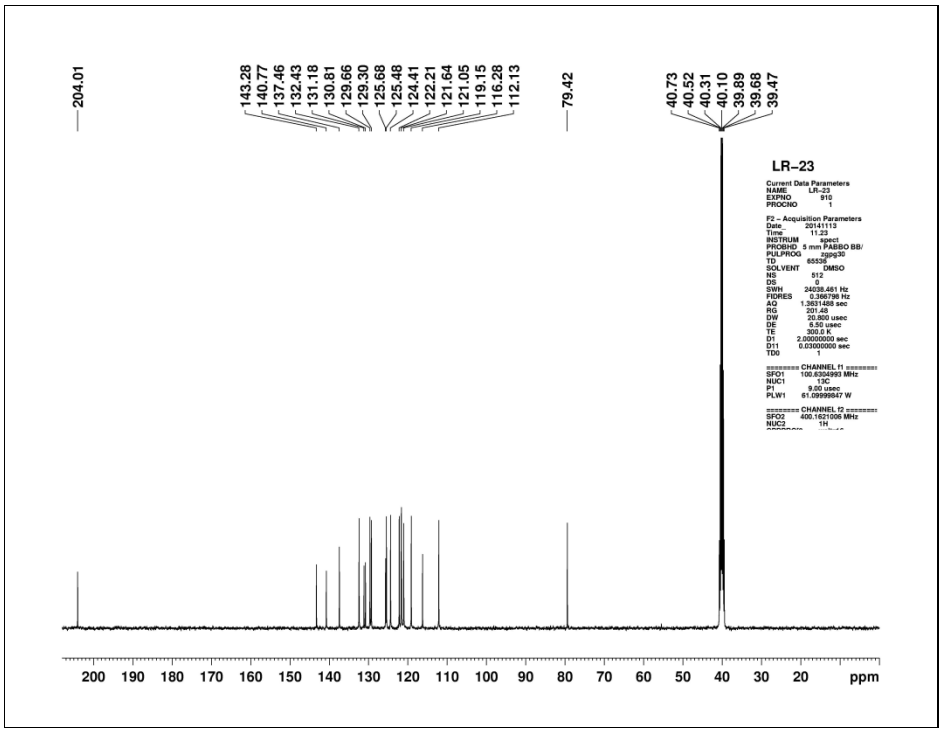

Figure 36: ^{13}C NMR of compound 4b

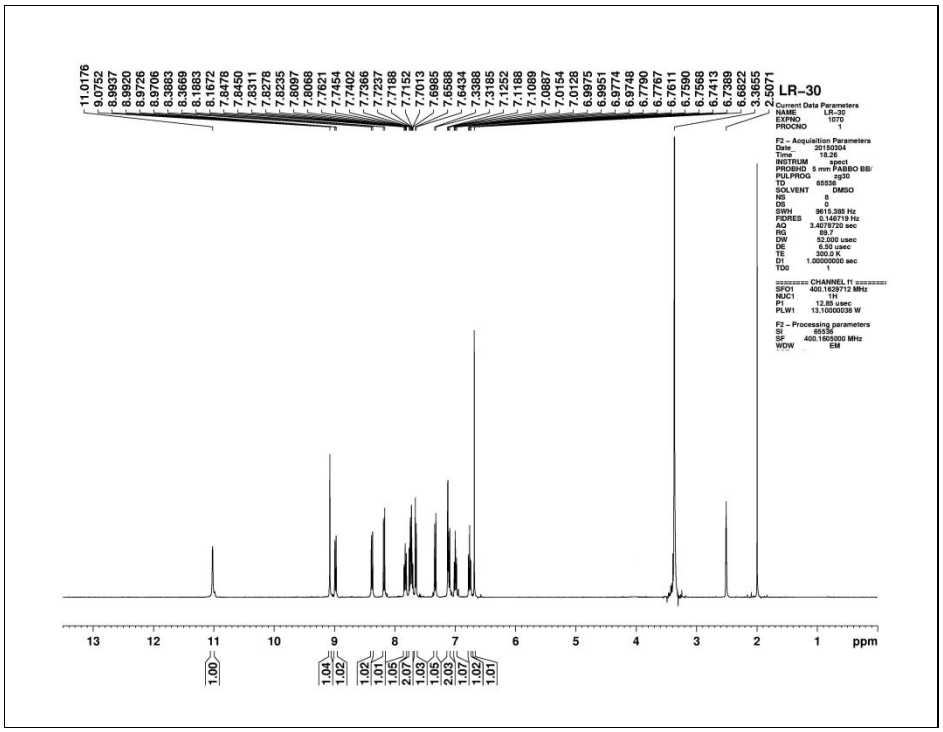

Figure 37: ^{1}H NMR of compound 5a

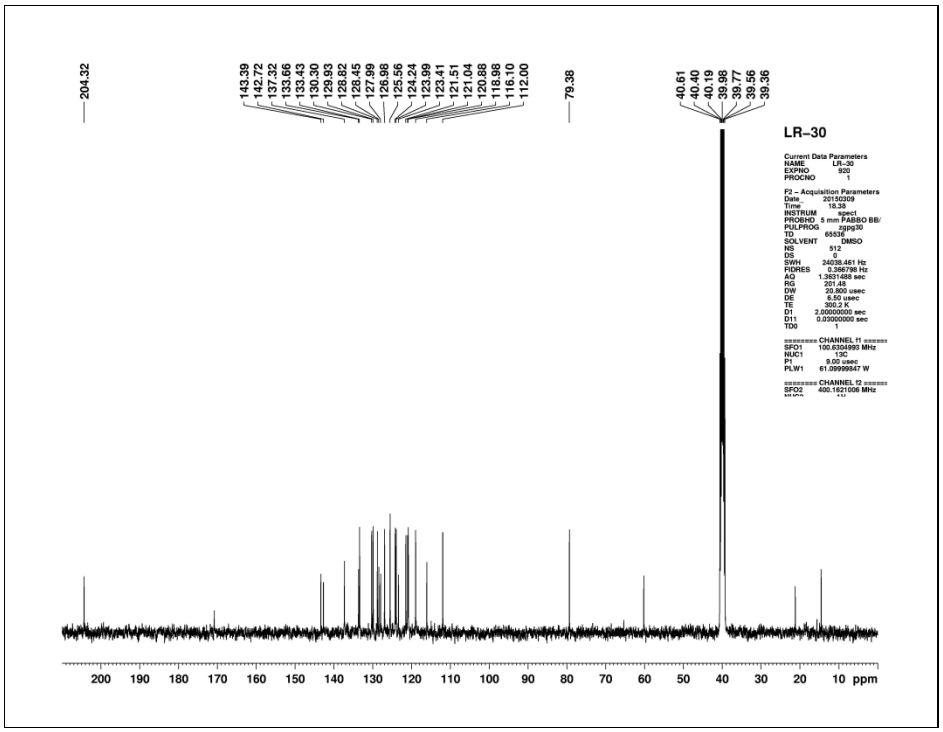

Figure 38: ^{13}C NMR of compound 5a

References:

1. (a) Q. Zhang, K. D O. Vigier, S. Royer and F. Jerome, *Chem. Soc. Rev*., **2012**, 41, 7108–7146; (b) E. Durand, J. Lecomte and P. Villeneuve; *Eur. J. Lipid Sci. Technol*. **2013**, 115, 379–385.