Supporting information

β-Cyclodextrin catalysedC-C bond formation *via* C(sp^3)-H Functionalization of 2-Methyl azaarenes with Diones in aqueous medium

Atul Kumar* and Ratnakar Dutt Shukla

Medicinal and Process Chemistry Division, CSIR-Central Drug Research Institute (CDRI), Luck now, 226031, Academy of Scientific & Innovative Research (AcSIR) New Delhi India. E-mail:dratulsax@gmail.com

Fax: 91-522-26234051; Tel:91-522-2612411

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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-percoated 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 HRMS analyses. IR spectra were recorded on a Perkin-Elmer FT-IR RXI spectrophotometer and values reported in cm^{-1}. NMRspectra were recorded with 400 MHz spectrometers for ^{1}H NMR, 100 MHzfor^{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 spectra were obtained on a LCQ Advantage Ion trap mass spectrometer (Finnigan thermo fischer scientific).

Synthesis of β-cyclodextrin derivatives

O-p-toluenesulfonyl-β-cyclodextrin[1] (**β-CD-Ts**) and Mono-6-deoxy-6-(3-benzylimidazolium)-β -cyclodextrin (**β-CD-BIMOTs**) were synthesized by known method.[1]

Characterization of β-CD-Ts

White solid; Yield 58%; mp = 169-171°C; IR (KBr) max 3285, 2932, 1638, 1348, 1156.

Characterization of β-CD-BIMOTs

White solid; Yield 89%; mp = 206-208°C; IR (KBr) max 3282, 2936, 1648, 1158.

Representative experimental procedure for the synthesis of 3-hydroxy-3-(quinolin-2-ylmethyl) indolin-2-one:

2-Methyl-quinoline (1.2 mmol),isatin (1.0 mmol) and20 mol % β-cyclodextrin were taken in a 50 mL round bottom flask containing 5 mL water as a solvent. The reaction mixture was stirredat 80°C. The reaction was monitored by TLC. After completion of reaction,the reaction mixture was allowed to cool after attaining room temperature solid precipitate was appeared.The solid product was filtrated on sintered funnel and it was washed 3-4 times by water.The crude product was purified by 100-200 mesh silica gel column chromatography.

Recyclability of catalyst:

β-cyclodextrinbeing soluble in water comes in the filtrate. Theβ-cyclodextrin was recovered easily from filtrate by evaporating thewater under vacuum. The recovered β-cyclodextrinwas then successfully used for the next batch without any further purification and slight loss of catalytic activity was observed.

Characterisation data of all the synthesized compounds:

3-Hydroxy-3-(pyridin-2-ylmethyl)indolin-2-one (3a):

Light yellow solid; Yield 82%; mp = 167-169°C; IR (KBr) max 3365, 3014, 1748, 1620, 1598, 1374, 1215, 975, 657;^{1}H NMR (400 MHz; $CDCl_3$+DMSO-d^6): δ 10.17(s, 1H),8.17 (d, *J* = 8.48 Hz, 1H), 7.89 (d, *J* = 7.92 Hz, 1H), 7.79 (d, *J* = 8.32 Hz, 1H), 7.69 (t, *J* = 7.24 Hz, 1H), 7.54 (t, *J* = 7.40 Hz, 1H), 7.37 (d, *J* = 8.44 Hz, 1H), 7.10 (t, *J* = 7.48 Hz, 1H), 6.94 (d, *J* = 7.20 Hz, 1H),6.81 (t, *J* = 7.40 Hz, 1H), 6.68 (d, *J* = 7.60 Hz, 1H),6.36 (s, 1H), 3.53 (d, *J* = 13.48 Hz, 1H), 3.38 (d, *J* = 17.32 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$+DMSO-d^6):δ 178.8, 155.3, 147.0, 141.4, 137.8, 130.8, 129.1, 125.5, 124.4, 122.5, 121.8, 110.0, 75.9, 44.0;ESI-MS (m/z) = 241 $[M+H]^+$;Analysis Calcd.for $C_{14}H_{12}N_2O_2$:C, 74.47; H, 4.86; N, 9.65; Found: C, 74.41; H, 4.79; N, 9.69;ESI-HRMS Calcd. For$C_{14}H_{12}N_2O_2$: $[M+H]^+$, 241.0932, Found: m/z 241.0948.

3-Hydroxy-5-nitro-3-(pyridin-2-ylmethyl)indolin-2-one (3b):

Off white solid; Yield 85%; mp = 160-162°C; IR (KBr) max 3427, 3019, 2399, 1637, 1384, 1150, 929, 669, 627;^{1}H NMR (400 MHz; DMSO-d^6): δ 10.17(s, 1H),8.17 (d, *J* = 8.48 Hz, 1H), 7.89 (d, *J* = 7.92 Hz, 1H), 7.79 (d, *J* = 8.32 Hz, 1H), 7.69 (t, *J* = 7.24 Hz, 1H), 7.54 (t, *J* = 7.40 Hz, 1H), 7.37 (d, *J* = 8.44 Hz, 1H), 7.10 (t, *J* = 7.48 Hz, 1H), 6.94 (d, *J* = 7.20 Hz, 1H),6.81 (t, *J* = 7.40 Hz, 1H), 6.68 (d, *J* = 7.60 Hz, 1H),6.36 (s, 1H), 3.53 (d, *J* = 13.48 Hz, 1H), 3.38 (d, *J* = 17.32 Hz, 1H); ^{13}C NMR (100 MHz; DMSO-d^6):δ 179.4, 155.7, 148.9, 148.8, 142.2, 136.6, 132.4, 126.7, 124.9, 122.4, 120.7, 110.0, 75.8, 45.0;ESI-MS (m/z) = 286$[M+H]^+$;Analysis Calcd. for $C_{14}H_{11}N_3O_4$:C, 58.95; H, 3.89; N, 14.73; Found: C, 58.84; H, 3.96; N, 14.78; ESI-HRMS Calcd. for $C_{14}H_{11}N_3O_4$: $[M+H]^+$, 286.0783, Found: m/z 286.0796.

3-Hydroxy-1-methyl-3-(pyridin-2-ylmethyl)indolin-2-one (3c):

Light yellow solid; Yield 86%; mp = 134-136°C; IR (KBr) max 3400, 3019, 2399, 1760, 1720,1616, 1384, 1093, 929, 669;^{1}H NMR (400 MHz; $CDCl_3$+DMSO-d^6): δ 8.73(s, 1H),8.43 (s, 1H), 7.89 (s, 1H), 7.83 (d, *J* = 7.36 Hz, 1H), 7.34 (d, *J* = 6.48 Hz, 1H), 7.08-7.00 (m, 3H), 3.52 (d, *J* = 13.68 Hz, 1H), 3.40 (d, *J* = 13.68 Hz, 1H), 3.09 (s, 3H); ^{13}C NMR (100 MHz; $CDCl_3$+DMSO-d^6):δ 179.1, 157.6, 147.2, 142.3, 135.9, 131.7, 129.7, 129.3, 128.8, 128.1, 126.9, 126.4, 124.9, 123.2, 121.5, 109.8, 76.0, 46.0; ESI-MS (m/z) = 255$[M+H]^+$;Analysis Calcd.

for$C_{15}H_{14}N_2O_2$:C, 70.85; H, 5.55; N, 11.02; Found: C, 70.68; H, 5.64; N, 11.28;ESI-HRMS Calcd. for $C_{15}H_{14}N_2O_2$: $[M+H]^+$, 255.1089, Found: m/z 255.1094.

1-Benzyl-3-hydroxy-3-(pyridin-2-ylmethyl)indolin-2-one (3d):

White solid; Yield 85%; mp = 160-162°C; IR (KBr) max 3413, 3019, 1720, 1612, 1473, 1377, 1215, 1111, 669;^{1}H NMR (400 MHz; $CDCl_3$):8.62 (d, *J* = 4.08 Hz, 1H), 7.70 (t, *J* = 7.72 Hz, 1H), 7.51 (s, 1H), 7.36-7.26 (m, 5H), 7.19 (t, *J* = 7.64 Hz, 1H), 7.10 (d, *J* = 7.76 Hz, 1H), 6.95 (t, *J* = 7.44 Hz, 1H), 6.89 (dd, *J* = 7.36 Hz, 1H),6.72 (d, *J* = 7.84 Hz, 1H), 4.99 (d, *J* = 15.64 Hz, 1H),4.84 (d, *J* = 15.64 Hz, 1H), 3.43 (d, *J* = 14.72 Hz, 1H), 3.21 (d, *J* = 14.72 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$):δ 177.0, 157.5, 148.3, 142.1, 137.2, 135.7, 131.0, 129.3, 128.8, 127.6, 127.3, 126.7, 124.0, 122.8, 122.3, 109.3, 76.3, 43.7, 43.0;ESI-MS (m/z) = 331 $[M+H]^+$;Analysis Calcd. For$C_{21}H_{18}N_2O_2$:C, 76.34; H, 5.49; N, 8.48; Found: C, 76.38; H, 5.28; N, 8.53; ESI-HRMS Calcd. For$C_{21}H_{18}N_2O_2$: $[M+H]^+$, 331.1402, Found: m/z 331.1418.

3-Hydroxy-3-(quinolin-2-ylmethyl) indolin-2-one (3e):

Off White solid; Yield 82%; mp = 160-162°C; IR (KBr) max 3403, 3020, 1621, 1402, 1385, 1216, 1069, 669;^{1}H NMR (400 MHz; DMSO-d^6): δ 10.19(s, 1H),8.17 (d, *J* = 8.40 Hz, 1H), 7.88 (d, *J* = 7.48 Hz, 1H), 7.80 (d, *J* = 8.44 Hz, 1H), 7.69 (t, *J* = 8.28 Hz, 1H), 7.53 (t, *J* = 8.04 Hz, 1H), 7.36 (d, *J* = 8.48 Hz, 1H), 7.10 (t, *J* = 7.64 Hz, 1H), 6.96 (d, *J* = 7.28 Hz, 1H),6.81 (t, *J* = 7.52 Hz, 1H), 6.69 (d, *J* = 7.64 Hz, 1H),6.40 (s, 1H), 3.54 (d, *J* = 13.44 Hz, 1H), 3.40 (d, *J*= 13.48 Hz, 1H); ^{13}C NMR (100 MHz; DMSO-d^6):δ 179.1, 157.6, 147.2, 142.2, 135.9, 131.6, 129.7, 129.3, 128.8, 128.1, 126.9, 126.5, 124.9, 123.1, 121.6, 109.8, 76.1, 46.0;ESI-MS (m/z) = 291 $[M+H]^+$;Analysis Calcd. for $C_{18}H_{14}N_2O_2$:C, 74.47; H, 4.86; N, 9.65; Found: C, 74.42; H, 4.89; N, 9.59; ESI-HRMS Calcd. for $C_{18}H_{14}N_2O_2$: $[M+H]^+$, 291.1089, Found: m/z 291.1094.

3-Hydroxy-5-methyl-3-(quinolin-2-ylmethyl)indolin-2-one(3f):

Light Brown solid; Yield 84%;mp = 181-183°C;IR (KBr) max 3402, 3020, 1627, 1387, 1215, 670; ^{1}H NMR (400 MHz; DMSO-d^6):δ 10.07 (s, 1H), 8.20 (d, *J* = 8.40 Hz, 1H), 7.90 (d, *J* = 7.96Hz, 1H), 7.81 (d, *J* = 8.36Hz, 1H), 7.70 (t, *J* = 7.24 Hz, 1H), 7.55 (t, *J* = 7.68 Hz, 1H), 7.37 (d, *J* = 8.44 Hz, 1H),6.90 (d, *J* = 7.04 Hz, 1H),6.78(s, 1H),6.57 (d, *J* = 7.76 Hz, 1H),3.50 (d, *J* = 13.52 Hz, 1H), 3.38 (d, *J* = 13.40 Hz, 1H),2.11(s,3H); ^{13}CNMR (100 MHz; DMSO-d^6):δ179.0, 157.5, 146.7, 139.8, 136.4, 131.7, 130.3, 130.0, 129.5, 128.3, 128.2, 126.9, 126.6, 125.7, 123.3,

109.5, 76.1, 45.8, 21.1;ESI-MS (m/z) = 305 $[M+H]^+$;Analysis Calcd. for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20; Found: C, 74.86; H, 5.38; N, 9.26; ESI-HRMS Calcd. for$C_{19}H_{16}N_2O_2$: $[M+H]^+$, 305.1245, Found: m/z 305.1252.

3-Hydroxy-5-nitro-3-(quinolin-2-ylmethyl) indolin-2-one (3g):

Off white solid; Yield 84%;mp = 187-189°C; IR (KBr) max 3406, 3019, 2400, 1622,1403, 1385, 1215, 1069, 928, 669; ^{1}H NMR (400 MHz; DMSO-d^6):δ 10.93 (s, 1H), 8.22 (d, *J* =8.44 Hz, 1H), 8.10 (dd, *J* =8.60 Hz, 1H), 7.96 (d, *J* = 2.32 Hz, 1H), 7.88 (d, *J* = 8.12 Hz, 1H),7.66 (d, *J* =3.72 Hz,2H), 7.53-7.49 (m,1H), 7.40 (d, *J* =8.48 Hz,1H), 6.90 (d, *J* =8.64Hz,1H), 3.74 (d, *J* =14.32 Hz,1H), 3.55 (d, *J* =14.32 Hz, 1H);^{13}C NMR (100 MHz; DMSO-d^6):δ 179.0, 156.5, 149.0, 146.6, 141.8, 135.8, 132.6, 129.3, 128.0, 127.7, 126.3, 126.2, 126.1, 122.4, 120.0, 109.4, 74.9, 44.7;ESI-MS (m/z) = 336 $[M+H]^+$;AnalysisCalcd. for $C_{18}H_{13}N_3O_4$: C, 64.47; H, 3.91; N, 12.53; Found: C, 64.55; H, 3.85; N, 12.63; ESI-HRMS Calcd. for $C_{18}H_{13}N_3O_4$: $[M+H]^+$, 336.0940, Found: m/z 336.0952.

5-Chloro-3-hydroxy-3-(quinolin-2-ylmethyl)indolin-2-one (3h):

Dark brown solid; Yield 85%;mp = 188-190°C; IR (KBr) max 3431, 3019, 1650, 1384, 1216, 1119, 669, 619; ^{1}H NMR (400 MHz; DMSO-d^6):δ 10.36 (s, 1H), 8.25 (d, *J* =8.36 Hz, 1H), 7.94 (d, *J* =7.52 Hz, 1H), 7.80 (d, *J* = 8.44 Hz, 1H), 7.59(t, *J* = 8.08 Hz, 1H), 7.42 (d, *J* =8.48 Hz,1H), 7.19 (dd, *J* = 8.24 Hz, 1H), 7.09 (d, *J* =2.20 Hz,1H),6.74 (d, *J* =8.20 Hz,1H), 6.48 (s, 1H), 3.63 (d, *J* =13.76 Hz,1H), 3.49 (d, *J* =13.72 Hz, 1H); ^{13}C NMR (100 MHz; DMSO-d^6):δ 178.3, 156.7, 146.7, 140.1, 135.6, 133.4, 128.5, 128.2, 127.7, 126.3, 126.0, 125.0, 124.7, 122.6,110.6, 75.6, 45.1; ESI-MS (m/z) = 325 $[M+H]^+$;Analysis Calcd. for $C_{18}H_{13}ClN_2O_2$C, 66.57; H, 4.03; N, 8.63; Found: C, 66.75; H, 4.15; N, 8.86; ESI-HRMS Calcd. For$C_{18}H_{13}ClN_2O_2$: $[M+H]^+$, 325.0699, Found: m/z 235.0692.

5-Bromo-3-hydroxy-3-(quinolin-2-ylmethyl)indolin-2-one (3i):

Brown solid; Yield 82%;mp = 198-200°C; IR (KBr) max 3432, 3019, 1647, 1384, 1215, 1119, 669, 619; ^{1}H NMR (400 MHz; DMSO-d^6):δ 10.29 (s, 1H), 8.17 (d, *J* = 8.48 Hz, 1H), 7.86 (d, *J* = 8.04 Hz, 1H), 7.72 (d, *J* = 8.28 Hz, 1H), 7.66-7.62 (m, 1H), 7.50 (t, *J* = 7.52 Hz, 1H), 7.33 (d, *J* = 8.44 Hz, 1H), 7.24 (dd, *J* = 8.24 Hz, 1H), 7.12 (d, *J* = 1.72 Hz, 1H), 6.61 (d, *J* = 8.20 Hz, 1H), 6.39 (s, 1H), 3.55 (d, *J* = 13.80 Hz, 1H), 3.40 (d, *J* = 13.80 Hz, 1H); ^{13}C NMR (100 MHz;

DMSO-d^6):δ 178.2, 156.7, 146.7, 141.3, 135.6, 133.8, 131.3, 129.3, 128.2, 127.6, 127.4, 126.3, 126.0, 122.6, 112.7, 111.2, 75.5, 45.1;ESI-MS (m/z) = 369 $[M+H]^+$;AnalysisCalcd. For$C_{18}H_{13}BrN_2O_2$ C, 58.56; H, 3.55; N, 7.59; Found: C, 58.26; H, 3.37; N, 7.21; ESI-HRMS Calcd. For$C_{18}H_{13}BrN_2O_2$: $[M+H]^+$, 369.0194, Found: m/z 369.0188.

3-Hydroxy-5-iodo-3-(quinolin-2-ylmethyl) indolin-2-one (3j):

Light brown solid; Yield 84%;mp = 199-201°C;IR (KBr) max 3428, 3021, 1648, 1385, 1215, 1119, 669, 619; ^{1}H NMR (400 MHz; DMSO-d^6):δ 10.30 (s, 1H), 8.20 (d, *J* = 8.44 Hz, 1H), 7.90 (d, *J* = 8.04 Hz, 1H), 7.77 (d, *J* = 8.28 Hz, 1H), 7.70 (t, *J* = 8.44 Hz, 1H), 7.54 (t, *J* = 8.04 Hz, 1H), 7.43 (dd, *J* = 8.08 Hz, 1H), 7.37 (d, *J* = 8.44 Hz, 1H), 7.26 (d, *J* = 1.64 Hz, 1H), 6.55 (d, *J* = 8.08 Hz, 1H), 6.39 (s, 1H), 3.56 (d, *J* = 13.76 Hz, 1H), 3.39 (d, *J* = 13.84 Hz, 1H); ^{13}C NMR (100 MHz; DMSO-d^6):δ 178.0, 156.8, 146.7, 141.8, 137.2, 135.5, 134.0, 133.1, 129.3, 128.2, 127.6, 126.4, 126.0, 122.6, 111.7, 83.7, 75.4, 45.1; ESI-MS (m/z) = 417 $[M+H]^+$;Analysis Calcd. for $C_{18}H_{13}IN_2O_2$ C, 51.94; H, 3.15; N, 6.73; Found: C, 51.76; H, 3.37; N, 6.81; ESI-HRMS Calcd. for $C_{18}H_{13}IN_2O_2$: $[M+H]^+$, 417.0055, Found: m/z 417.0048.

7-Fluoro-3-hydroxy-3-(quinolin-2-ylmethyl) indolin-2-one (3k):

Light brown solid; Yield 85%;mp = 179-181°C;IR (KBr) max 3404, 3021, 1633, 1392, 1215, 669;^{1}H NMR (400 MHz; DMSO-d^6):δ 10.69 (s, 1H),8.18 (d, *J* = 8.48 Hz, 1H), 7.88 (d, *J* = 8.08 Hz, 1H), 7.76 (d,*J* =8.32 Hz,1H), 7.69 (t, *J* = 8.36 Hz, 1H), 7.54 (t, *J* = 7.96 Hz, 1H),7.35(d,*J*=8.44 Hz,1H), 7.02 (t,*J*=9.60 Hz,1H), 6.87-6.80 (m, 2H), 6.47 (s, 1H), 3.58(d, *J*=13.84 Hz, 1H), 3.46(d, *J*=13.88 Hz, 1H); ^{13}C NMR (100 MHz; DMSO-d^6):δ 179.0, 157.2, 136.1, 134.8, 129.9, 129.3, 128.6, 128.1, 126.8, 126.6, 122.9, 122.5, 120.8, 116.4, 116.2, 76.1, 60.1, 45.8; ESI-MS (m/z) = 309 $[M+H]^+$;Analysis Calcd. for $C_{18}H_{13}FN_2O_2$ C, 70.12; H, 4.25; N, 9.09; Found: C, 70.36; H, 4.38; N, 9.22; ESI-HRMS Calcd. for$C_{18}H_{13}FN_2O_2$: $[M+H]^+$, 309.0995, Found: m/z 309.0998.

3-Hydroxy-1-methyl-3-(quinolin-2-ylmethyl) indolin-2-one(3l):

Brown solid; Yield 91%;mp = 144-146°C;IR (KBr) max 3393, 3185, 3020, 1718, 1615, 1402, 1216, 1091, 760, 669;^{1}H NMR(400 MHz; $CDCl_3$):δ 8.17 (d, *J* = 8.44 Hz, 1H), 8.13 (d, *J* = 8.48 Hz, 1H), 7.87 (d, *J* = 8.04 Hz, 1H),7.80(t, *J*=8.44 Hz, 1H),7.61 (t, *J*=8.04Hz, 1H), 7.30(dd,*J*=15.24 Hz, 1H), 7.21 (d, *J* = 8.36Hz, 1H), 6.93 (t, *J* = 7.48 Hz, 1H), 6.87 (t,*J*=7.72

Hz,2H), 3.60 (d, *J* = 15.04 Hz, 1H), 3.28 (d, *J* = 15.08 Hz, 1H),3.23(s,3H).^{13}C NMR (100 MHz; $CDCl_3$):δ 176.7, 158.6, 146.6, 143.0, 137.1, 131.2, 130.1, 129.4, 128.8, 127.7, 127.1, 126.6, 124.0, 122.8, 122.7, 108.3, 76.3, 43.2, 26.2;ESI-MS (m/z) = 305 $[M+H]^+$;Analysis Calcd. for $C_{19}H_{16}N_2O_2C$, 74.98; H, 5.30; N, 9.20; Found: C, 74.86; H, 5.27; N, 9.41; ESI-HRMS Calcd. For$C_{19}H_{16}N_2O_2$: $[M+H]^+$, 305.1245, Found: m/z 305.1256.

3-((6-Fluoroquinolin-2-yl) methyl)-3-hydroxy-1-methylindolin-2-one (3m):

Dark brown solid; Yield 89%; mp = 148-150°C; IR (KBr) max 3432, 3019, 1720, 1615, 1508, 1472, 1384, 1216, 1121, 770, 669, 619; ^{1}H NMR (400 MHz; $CDCl_3$):δH 8.11 (dd, *J* = 9.08 Hz, 2H),7.55 (t, *J* = 8.92 Hz, 1H), 7.47 (dd, *J* = 8.76 Hz, 1H), 7.30 (dd, *J*=15.08 Hz, 1H), 7.23 (d, *J* = 8.48 Hz, 1H), 6.95-6.89(m, 2H), 6.84 (d, *J* =7.76 Hz, 1H), 3.55 (d, *J* =14.92 Hz, 1H), 3.32 (d, *J* = 14.96 Hz, 1H), 3.21 (s, 3H);^{13}C NMR(100 MHz; $CDCl_3$):δ176.7, 161.6, 159.2, 157.8, 143.8, 143.1, 136.4, 136.4, 131.3, 131.2, 130.9, 129.5, 127.7, 127.6, 124.0, 123.5, 122.8, 120.4, 120.2, 110.8, 110.6, 108.4, 76.3, 43.3, 26.2;ESI-MS (m/z) = 323$[M+H]^+$;Analysis Calcd. For$C_{19}H_{15}FN_2O_2$: C, 70.80; H, 4.69; N, 8.69; Found: C, 70.54; H, 4.84; N, 8.59; ESI-HRMS Calcd. for$C_{19}H_{15}FN_2O_2$: $[M+H]^+$, 323.1151, Found: m/z 323.1164.

3-((6-Chloroquinolin-2-yl) methyl)-3-hydroxy-1-methylindolin-2-one (3n):

White solid; Yield 86%; mp = 152-154°C; IR (KBr) max 3381, 3016, 1718, 1614, 1470, 1384, 1217, 1092, 765; ^{1}H NMR (400 MHz; $CDCl_3$):δ 8.06 (t, *J* = 8.72 Hz, 2H), 7.83 (d, *J* = 2.24 Hz, 1H), 7.70 (d,*J* = 9.04 Hz, 1H),7.35 (s, 1H), 7.30 (t, *J* = 9.00 Hz, 1H), 7.23 (d, *J* = 8.40 Hz, 1H), 6.95-6.88 (m, 2H), 6.83 (d, *J* = 7.80 Hz, 1H), 3.55 (d, *J*= 14.96 Hz, 1H), 3.32 (d, *J*= 14.96 Hz, 1H), 3.20(s, 3H); ^{13}C NMR(100 MHz; $CDCl_3$):δ176.7, 158.8, 145.1, 143.1, 136.1, 132.3, 131.0, 130.9, 130.4, 129.5, 127.6, 126.4, 124.0, 123.6, 122.5, 108.4, 76.2, 43.4, 26.2;ESI-MS (m/z) = 339$[M+H]^+$;Analysis Calcd. For$C_{19}H_{15}ClN_2O_2$: C, 67.36; H, 4.46; N, 8.27; Found: C, 67.56; H, 4.36; N, 8.54; ESI-HRMS Calcd. For$C_{19}H_{15}ClN_2O_2$: $[M+H]^+$, 339.0856, Found: m/z 339.0848.

3-((8-Chloroquinolin-2-yl) methyl)-3-hydroxy-1-methylindolin-2-one(3o):

Light brown solid; Yield 84%; mp = 154-156°C; IR (KBr) max 3421, 3019, 2400, 1721, 1615, 1500, 1472, 1384, 1119, 928, 669, 619; (400 MHz; $CDCl_3$):δ8.20 (d,*J*=8.36 Hz, 1H), 7.91

(d,*J*=7.36 Hz, 1H), 7.80(d,*J*=8.04 Hz, 1H), 7.54 (t,*J*=7.88 Hz, 1H), 7.31 (s,1H), 7.28 (d, *J* = 5.32 Hz, 1H), 7.02 (d,*J*=7.04 Hz, 1H), 6.95 (t,*J*=7.44 Hz, 1H), 6.86 (d,*J*= 7.80 Hz, 1H),3.62 (d, *J* =15.48 Hz,1H), 3.38 (d, *J* = 15.48 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz; $CDCl_3$):δ 176.6, 159.6, 143.1, 142.8, 137.6, 132.9, 131.3, 130.1, 129.4, 128.3, 126.8, 126.6, 124.1, 123.4, 122.8, 108.3, 76.2, 42.8, 26.2;ESI-MS (m/z) = 339$[M+H]^+$;Analysis Calcd. for $C_{19}H_{15}ClN_2O_2$: C, 67.36; H, 4.46; N, 8.27; Found: C, 67.18; H, 4.54; N, 8.36;ESI-HRMS Calcd. for $C_{19}H_{15}ClN_2O_2$: $[M+H]^+$, 339.0856, Found: m/z 339.0862.

3-((6-Bromoquinolin-2-yl) methyl)-3-hydroxy-1-methylindolin-2-one(3p):

White solid; Yield 84%; mp = 151-153°C;IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619;^{1}H NMR (400 MHz; $CDCl_3$):δ 8.07 (d, *J* = 8.44 Hz, 1H), 8.02 (s, 1H), 8.00 (d, *J* = 8.96 Hz, 1H), 7.85 (dd,*J*=8.96Hz, 1H), 7.35 (s,1H),7.24 (d, *J* = 8.40 Hz, 1H), 6.95 (t,*J*= 7.36 Hz, 1H),6.90 (d, *J* = 7.28 Hz, 1H), 6.85 (d,*J*= 7.80 Hz, 1H),3.55 (d, *J* = 15.00 Hz, 1H), 3.32 (d, *J* = 14.96 Hz, 1H), 3.22 (s, 3H);^{13}C NMR (100 MHz; $CDCl_3$):δ 176.7, 159.0, 145.3, 143.1, 136.0, 133.6, 130.9, 130.5, 129.7, 129.5, 128.1, 124.0, 123.6, 122.8, 120.4, 108.4, 76.2, 43.4, 26.2;ESI-MS (m/z) = 383 $[M+H]^+$;AnalysisCalcd. for $C_{19}H_{15}BrN_2O_2$: C, 59.55; H, 3.95; N, 7.31; Found: C, 59.68; H, 3.86; N, 7.16;ESI-HRMS Calcd. for $C_{19}H_{15}BrN_2O_2$: $[M+H]^+$, 383.0350, Found: m/z 383.0363.

3-Hydroxy-3-(pyridin-2-ylmethyl)benzo[*b*]thiophen-2(*3H*)-one (4a):

Yellow solid; Yield 81%; mp = 161-163°C;IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619;^{1}H NMR (400 MHz; DMSO-d^6):δ 8.24 (d, *J* = 5.68 Hz, 1H), 8.09(dd,*J*= 8.64 Hz, 1H), 7.83 (d, *J* = 2.36 Hz, 1H), 7.61 (t,*J*=7.68Hz, 1H), 7.18(d,*J*= 7.80 Hz, 1H),7.13-7.10 (m, 1H), 6.87(d,*J*= 8.64 Hz, 1H),6.64 (s, 1H), 3.45 (d, *J* = 13.36 Hz, 1H), 3.29 (d, *J* = 13.36 Hz, 1H); ^{13}C NMR (100 MHz; DMSO-d^6):δ 179.2, 155.5, 148.6, 148.6, 142.0, 136.4, 132.2, 126.5, 124.7, 122.1, 120.4, 109.8, 75.5, 44.8;ESI-MS (m/z) = 258$[M+H]^+$;AnalysisCalcd. for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44; Found: C, 65.28; H, 4.39; N, 5.56;ESI-HRMS Calcd. for $C_{14}H_{11}NO_2S$: $[M+H]^+$, 258.0544, Found: m/z 258.0544.

3-Hydroxy-3-(quinolin-2-ylmethyl)benzo[*b*]thiophen-2(3*H*)-one (4b):

Yellow solid; Yield 87%; mp = 166-168°C;IR (KBr) max 3401, 3020, 2400, 1717, 1598, 1509, 1422, 1215, 1070, 927, 898, 670;^{1}H NMR (400 MHz; $CDCl_3$):δ 8.17 (d, *J* = 8.36 Hz, 1H), 8.13

(d,*J*=8.52 Hz, 1H), 7.87 (d, *J* = 8.12 Hz, 1H), 7.81 (t,*J*= 8.40Hz, 1H), 7.61 (t,*J*= 8.04 Hz, 1H), 7.37-7.32 (m, 2H), 7.23 (dd,*J*= 3.72 Hz, 2H), 7.18 (d, *J* = 8.36 Hz, 1H), 3.45 (d, *J* = 14.80 Hz, 1H), 3.40 (d, *J* = 14.84 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$):δ 205.1, 157.1, 146.6, 138.4, 137.5, 132.7, 130.3, 129.7, 128.7, 127.7, 127.2, 126.8, 126.7, 125.3, 123.4, 122.5, 85.0, 45.0;ESI-MS (m/z) = 308$[M+H]^+$;Analysis Calcd. for $C_{18}H_{13}NO_2S$: C, 70.34; H, 4.26; N, 4.56; Found: C, 70.42; H, 4.26; N, 4.45;ESI-HRMS Calcd. For$C_{18}H_{13}NO_2S$: $[M+H]^+$, 308.0701, Found: m/z 308.0714.

3-((6-Fluoroquinolin-2-yl)methyl)-3-hydroxybenzo[b]thiophen-2(3H)-one (4c):

Light yellow solid; Yield 88%; mp = 162-164°C;IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619;^{1}H NMR (400 MHz; DMSO-d^6):δ 8.19 (d, *J* = 8.44 Hz, 1H), 7.89 (d,*J* = 7.80 Hz, 1H), 7.77 (d, *J* = 8.36 Hz, 1H), 7.69 (t,*J*=8.32 Hz, 1H), 7.54 (t, *J* = 7.96 Hz1H),7.37 (d, *J* = 8.44 Hz, 1H), 6.93 (t, *J* = 9.60 Hz,1H),6.86 (dd, *J* = 8.28 Hz, 1H), 6.65 (dd, *J* = 8.40 Hz), 6.45 (s, 1H), 3.56 (d, *J* = 13.56 Hz, 1H), 3.42 (d, *J* = 13.60 Hz, 1H);^{13}C NMR(100 MHz; $CDCl_3$):δ 178.9, 157.3, 147.9, 147.2, 145.5, 136.0, 134.9, 129.8, 129.5, 129.3, 128.7, 128.1, 126.8, 126.5, 123.0, 122.4, 120.9, 120.8, 116.3, 116.2, 76.1, 76.0, 45.9ESI-MS (m/z) = 326$[M+H]^+$;AnalysisCalcd. for $C_{18}H_{12}FNO_2S$: C, 66.45; H, 3.72; N, 4.31; Found: C, 66.38; H, 3.94; N, 4.29;ESI-HRMS Calcd. for $C_{18}H_{12}FNO_2S$: $[M+H]^+$, 326.0606, Found: m/z 326.0626.

3-((4-Chloroquinolin-2-yl)methyl)-3-hydroxybenzo[b]thiophen-2(3H)-one (4d):

Light yellow solid; Yield 86%; mp = 164-166°C;IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619;^{1}H NMR (400 MHz; $CDCl_3$):δ 8.19 (d, *J* = 8.44 Hz, 1H), 7.89 (d, *J* = 7.80 Hz, 1H), 7.77 (d, *J* = 8.36 Hz, 1H), 7.69 (t,*J*=8.32 Hz, 1H), 7.54 (t, *J* = 7.96 Hz, 1H),7.37 (d, *J* = 8.44 Hz, 1H), 6.93-6.88 (m,1H),6.86 (dd, *J* = 8.28 Hz, 1H), 6.65 (dd, *J* = 8.40 Hz, 1H), 6.45 (s, 1H), 3.56 (d, *J* = 13.56 Hz, 1H), 3.43 (d, *J* = 13.60 Hz, 1H);^{13}C NMR (100 MHz; DMSO-d^6):δ 178.9, 158.0, 148.0, 142.2, 140.7, 131.5, 131.0, 129.4, 128.0, 124.9, 124.5, 123.8, 123.2, 121.6, 109.9, 75.9, 45.8;ESI-MS (m/z) = 342 $[M+H]^+$;AnalysisCalcd. For$C_{18}H_{12}ClNO_2S$: C, 63.25; H, 3.54; N, 4.10; Found: C, 63.52; H, 3.59; N, 4.08;ESI-HRMS Calcd. For$C_{18}H_{12}ClNO_2S$: $[M+H]^+$, 342.0311, Found: m/z 342.0324.

2-Hydroxy-2-(pyridin-2-ylmethyl)acenaphthylen-1(*2H*)-one (5a):

White solid; Yield 82%; mp = 161-163°C;IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619;^{1}H NMR (400 MHz; $CDCl_3$):δ 8.65 (d, *J* = 4.20 Hz, 1H), 8.14 (d, *J* = 8.12 Hz, 1H), 8.00 (dd,*J*=7.00Hz, 1H), 7.87(d, *J* = 8.36 Hz, 1H),7.77 (t, *J* = 8.00 Hz, 1H), 7.70 (t, *J* = 7.68 Hz, 2H),7.55 (t, *J* = 8.32 Hz, 1H), 7.33 (t, *J* = 6.92 Hz, 1H), 7.07 (dd, *J* = 15.40 Hz, 2H), 3.48 (d, *J* = 14.80 Hz, 1H), 3.19 (d, *J* = 14.80 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$):δ 203.6, 158.3, 148.3, 140.8, 140.7, 137.2, 131.9, 130.7, 130.6, 128.6, 128.3, 125.1, 124.6, 122.3, 122.2, 120.4, 80.0, 42.6;ESI-MS (m/z) = 276$[M+H]^+$;AnalysisCalcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09; Found: C, 78.76; H, 4.38; N, 5.13;ESI-HRMS Calcd. For$C_{18}H_{13}NO_2$: $[M+H]^+$, 276.0980, Found: m/z 276.0992.

2-Hydroxy-2-(quinolin-2-ylmethyl)acenaphthylen-1(2*H*)-one (5b):

White solid; Yield 88%; mp = 165-167°C;IR (KBr) max 3413, 1725, 1603, 1503, 1422, 1215, 1080, 831, 757;^{1}H NMR (400 MHz; $CDCl_3$):δ 8.17 (t, *J* = 8.20 Hz, 3H), 8.04 (d, *J* = 7.00 Hz, 1H), 7.96 (s, 1H), 7.89-7.76 (m, 4H), 7.63 (t,*J*=7.16Hz, 1H), 7.50 (t, *J* = 8.32 Hz, 1H),7.18 (d, *J* = 8.32 Hz, 1H), 7.09 (d, *J* = 6.92 Hz, 1H), 3.71 (d, *J* = 15.08 Hz, 1H), 3.35 (d, *J* = 15.08 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$):δ 203.3, 159.1, 146.7, 140.9, 140.8, 137.2, 131.9, 130.7, 130.2, 128.8, 128.6, 128.3, 127.7, 127.1, 126.6, 125.1, 122.8, 122.2, 120.6, 80.1, 43.0;ESI-MS (m/z) = 326$[M+H]^+$;Analysis Calcd. For$C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30; Found: C, 81.46; H, 4.71; N, 4.38;ESI-HRMS Calcd. For$C_{22}H_{15}NO_2$: $[M+H]^+$, 326.1136, Found: m/z 326.1128.

2-Hydroxy-2-(pyridin-2-ylmethyl)aceanthrylen-1(*2H*)-one (6a):

White solid; Yield 88%; mp = 184-186°C;IR (KBr) max 3399, 3010, 1708, 1627, 1384, 1215, 1067, 669;^{1}H NMR (400 MHz; $CDCl_3$):δ 9.17 (dd, *J* = 8.56 Hz, 1H), 8.71 (s, 1H), 8.67 (dd, *J* = 4.92 Hz, 1H), 8.18 (d, *J* = 8.52 Hz, 1H), 7.96 (d,*J*=8.64 Hz, 1H), 7.78 (t, *J* = 8.44 Hz, 1H), 7.71 (t, *J* = 7.68 Hz, 1H), 7.67 (t, *J* = 8.24 Hz, 1H), 7.51 (t, *J* = 8.64 Hz, 1H), 7.35 (t, *J* = 6.76 Hz, 1H),7.08 (d, *J* = 7.76 Hz, 1H), 7.05 (d, *J* = 6.52 Hz, 1H), 3.57 (d, *J* = 14.80 Hz, 1H), 3.25 (d, *J* = 14.80 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$):δ 203.5, 158.5, 148.2, 143.0, 140.9, 137.2, 133.5, 132.8, 129.3, 129.2, 128.5, 128.3, 127.7, 126.5, 125.2, 124.8, 124.7, 123.6, 122.3, 119.9, 80.0, 42.5;ESI-MS (m/z) = 326$[M+H]^+$;AnalysisCalcd. for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30;

Found: C, 81.46; H, 4.71; N, 4.38;ESI-HRMS Calcd. for$C_{22}H_{15}NO_2$: $[M+H]^+$, 326.1136, Found: m/z 326.1142.

2-Hydroxy-2-(quinolin-2-ylmethyl) aceanthrylen-1(*2H*)-one (6b)

White solid; Yield 91%; mp = 198-200°C;IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619;^{1}H NMR (400 MHz; $CDCl_3$):δ9.20 (d, *J* = 8.52 Hz, 1H), 8.72 (s, 1H), 8.19 (dd, *J* = 8.28 Hz, 3H), 8.03 (s,1H), 7.95 (d, *J* = 8.68 Hz, 1H), 7.90 (d, *J* = 8.08 Hz, 1H), 7.83-7.75 (m, 2H), 7.68-7.60 (m, 2H), 7.46 (t,*J*=8.56 Hz, 1H), 7.21 (d, *J* = 8.32 Hz, 1H),7.06 (d, *J* = 6.60 Hz, 1H),3.79 (d, *J* = 15.08 Hz, 1H), 3.39 (d, *J* = 15.12 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$):δ 203.3, 159.5, 146.7, 143.1, 141.1, 137.1, 133.5, 132.8, 130.2, 129.3, 129.2, 128.4, 128.5, 128.4, 127.7, 127.1, 126.6, 126.5, 125.2, 124.9, 123.7, 122.8, 120.0, 80.1, 42.9;ESI-MS (m/z) = 376$[M+H]^+$;AnalysisCalcd. for $C_{26}H_{17}NO_2$: C, 83.18; H, 4.56; N, 3.73; Found: C, 83.46; H, 4.68; N, 3.52;ESI-HRMS Calcd. For$C_{26}H_{17}NO_2$: $[M+H]^+$, 376.1293, Found: m/z 376.1288.

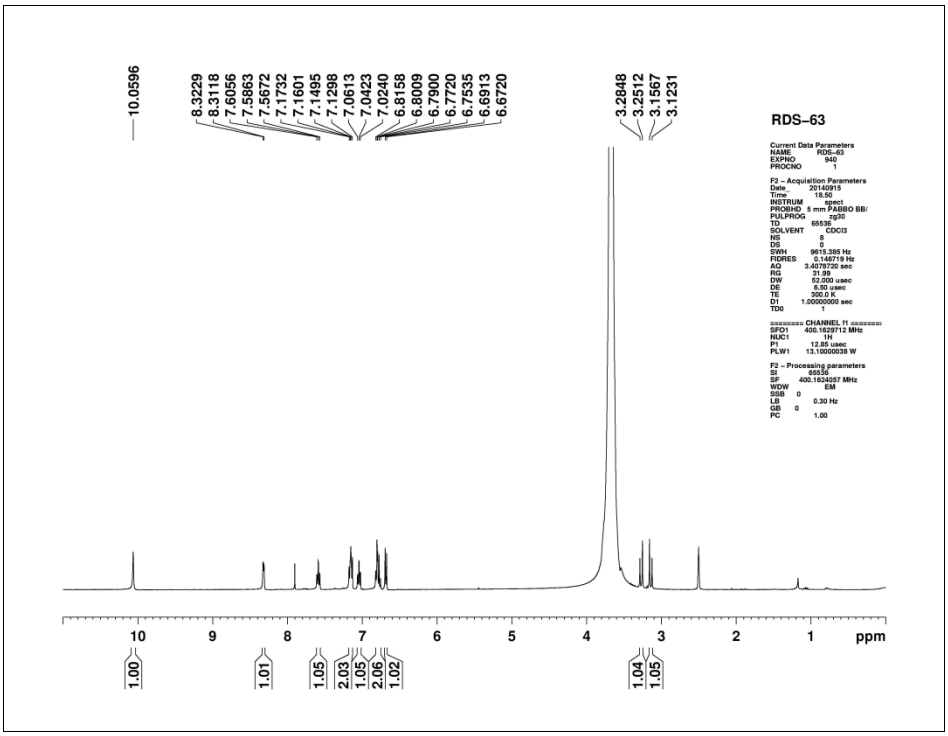

Figure 1: ^{1}H NMR ofcompound 3a

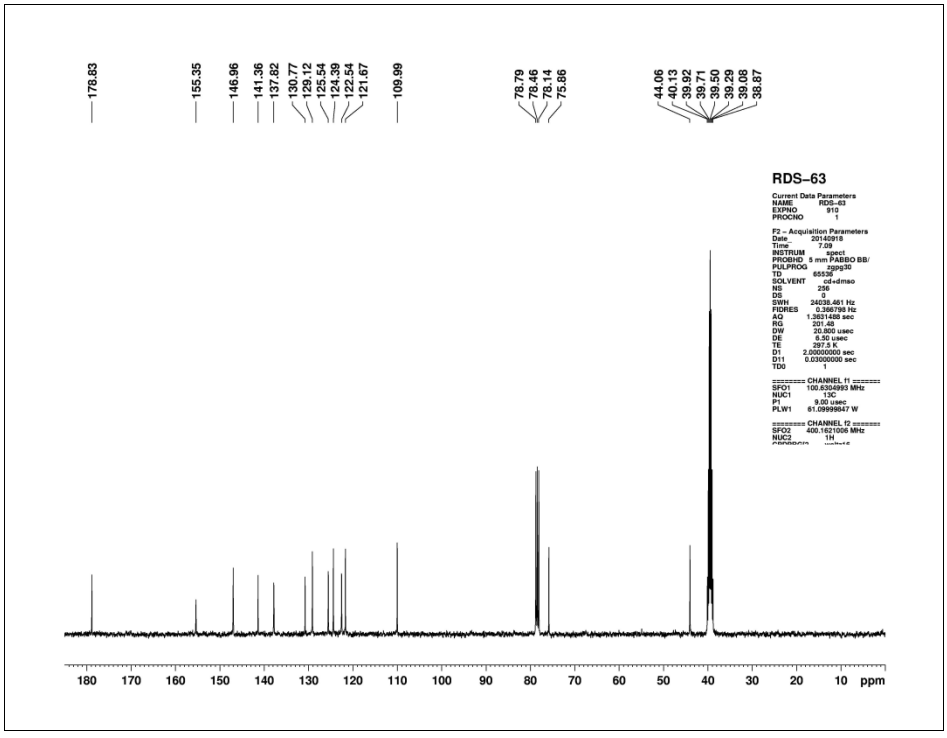

Figure 2: ^{13}C NMR of compound 3a

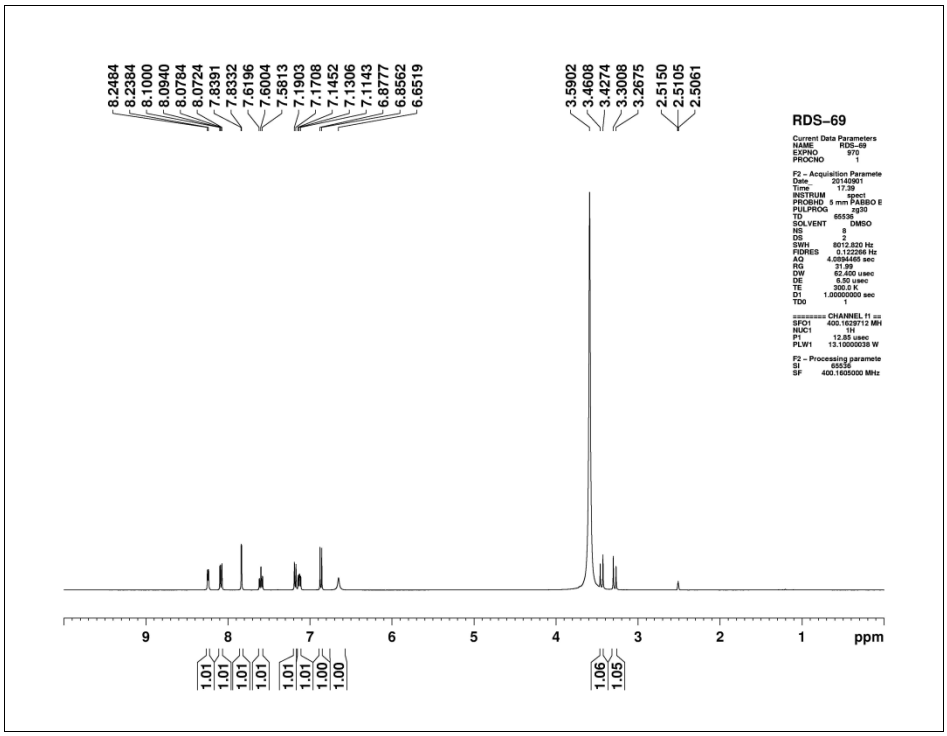

Figure 3: ^{1}H NMR of compound 3b

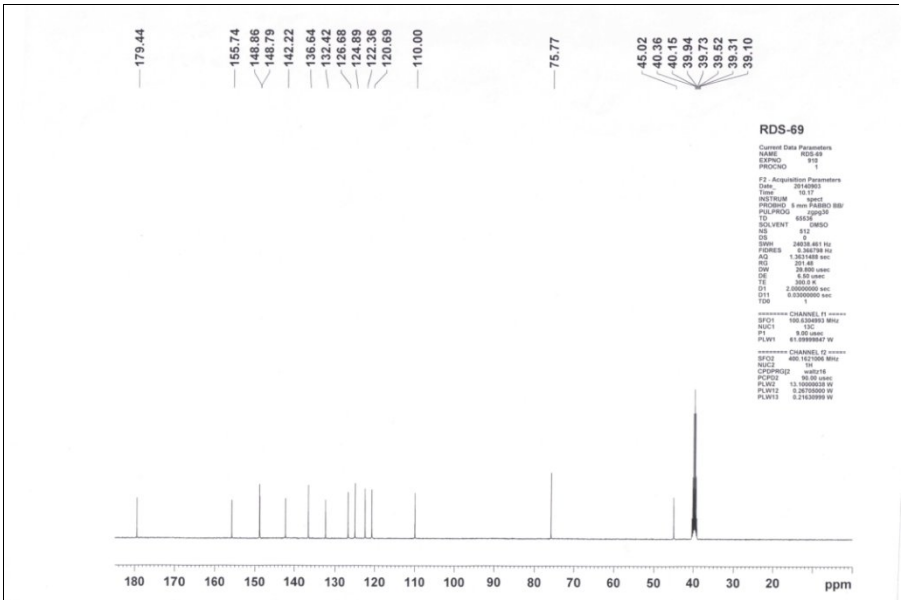

Figure 4: ^{13}C NMRof compound 3b

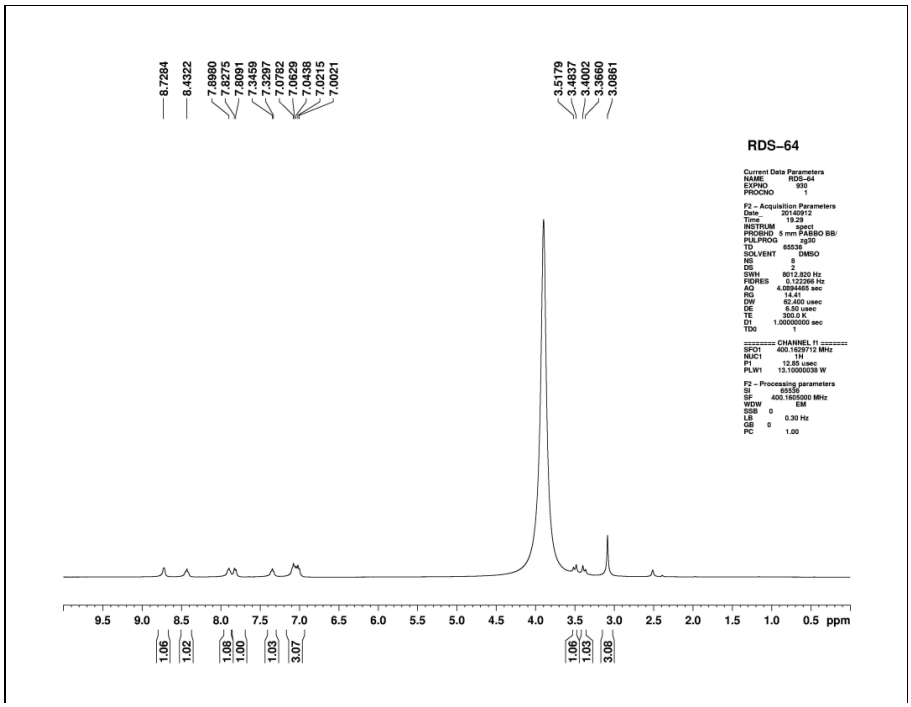

Figure 5: ^{1}H NMR of compound 3c

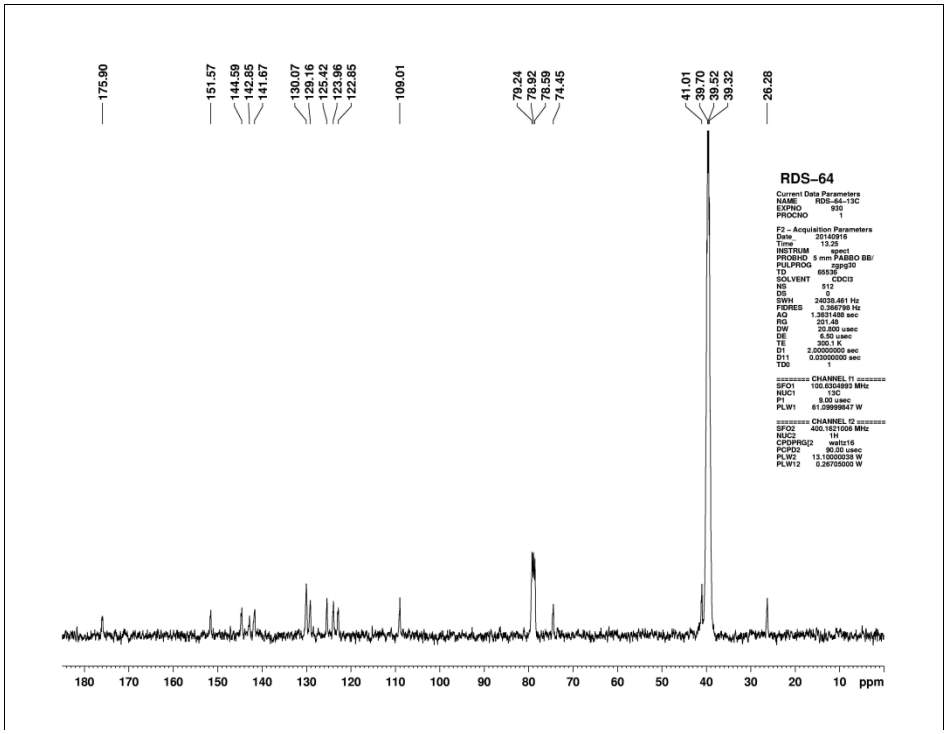

Figure 6:^{13}C NMR of compound 3c

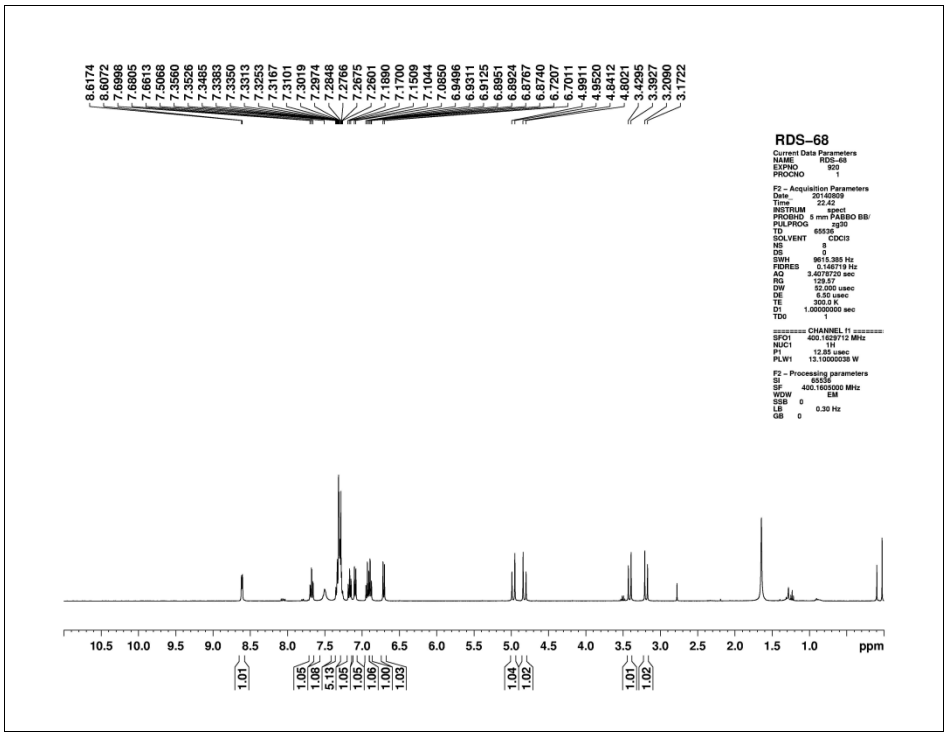

Figure 7: ^{1}H NMR of compound 3d

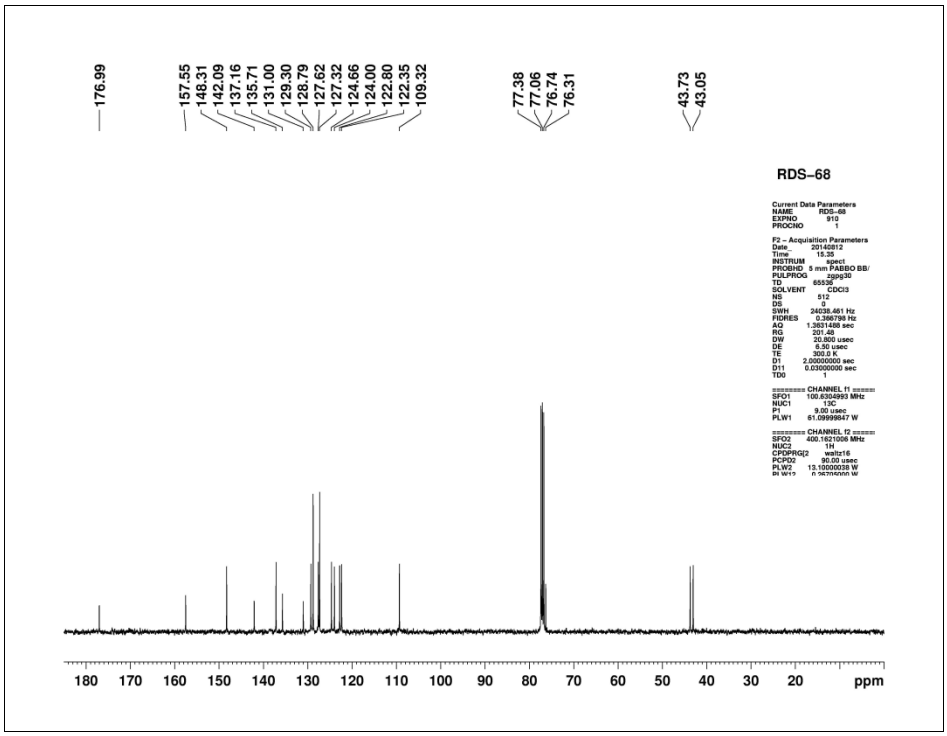

Figure 8: ^{13}C NMR of compound 3d

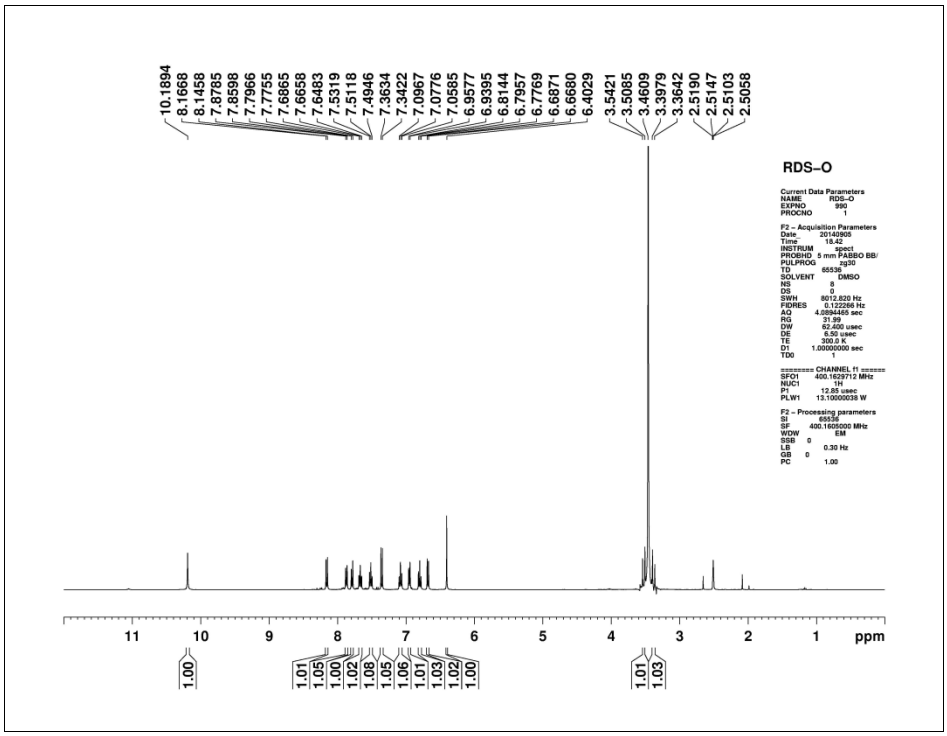

Figure 9: ^{1}H NMR of compound 3e

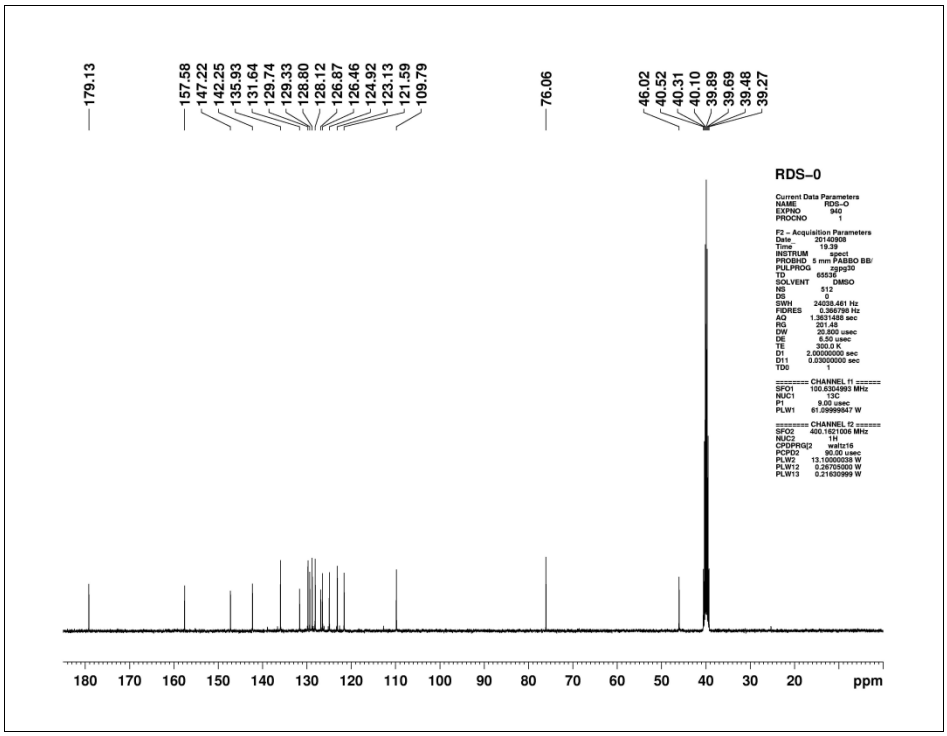

Figure 10: ^{13}C NMR of compound 3e

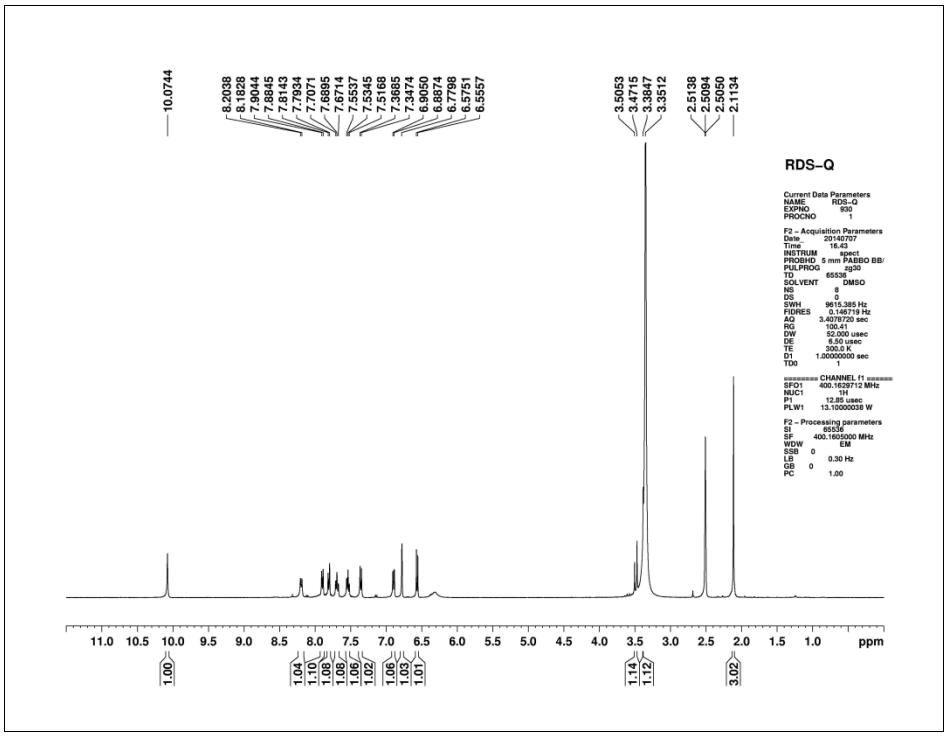

Figure 11: ^{1}H NMR of compound of 3f

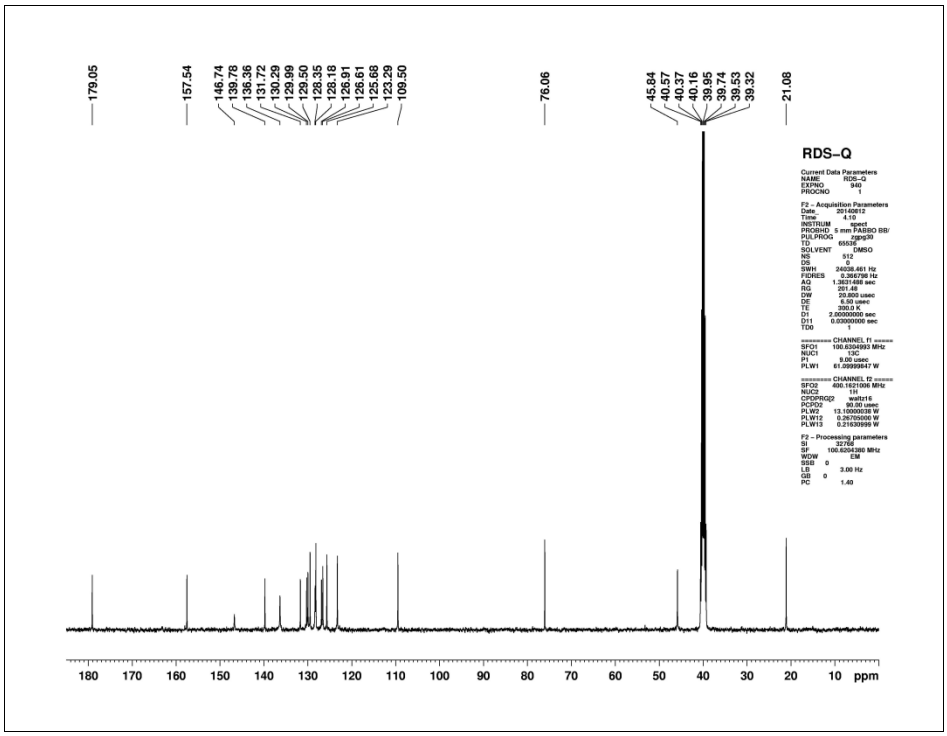

Figure 12: ^{13}C NMR of compound 3f

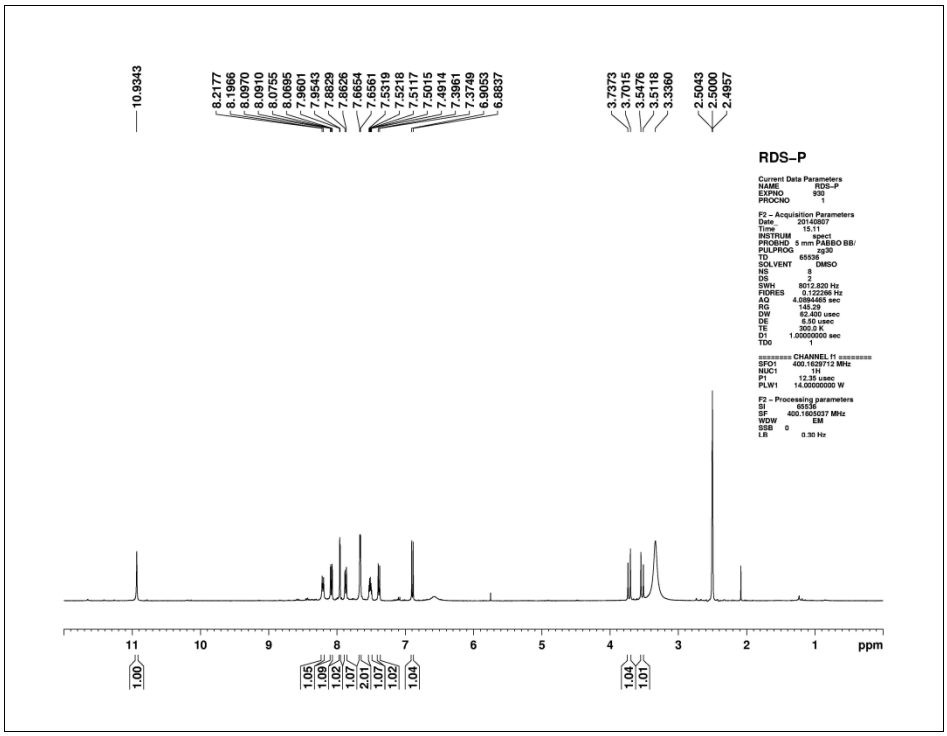

Figure 13: ^{1}H NMR of compound 3g

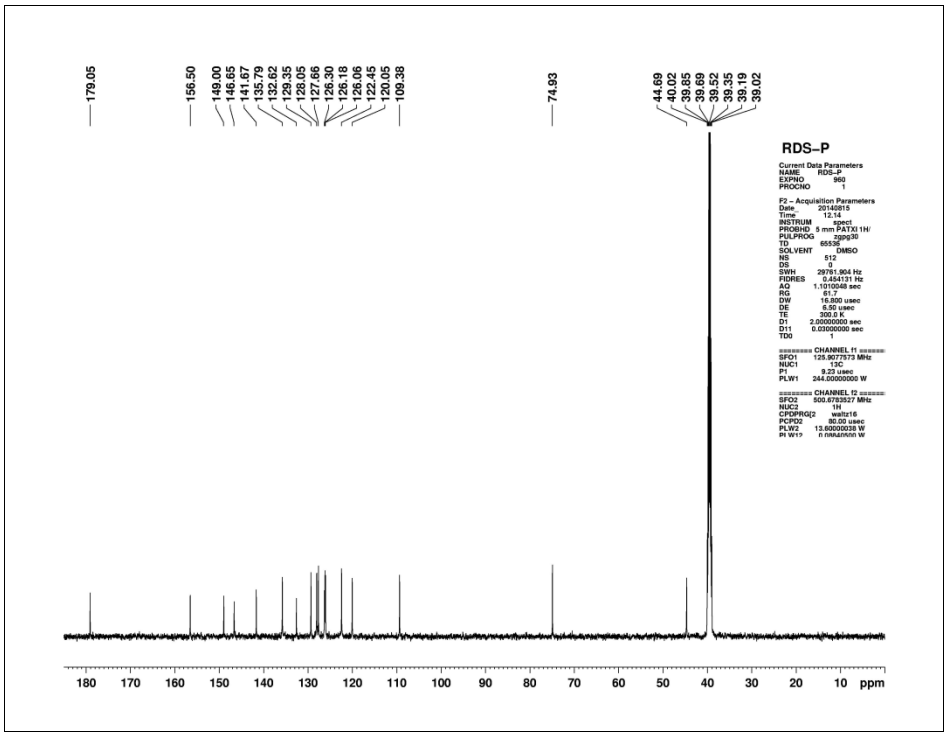

Figure 14: ^{13}C NMR of compound 3g

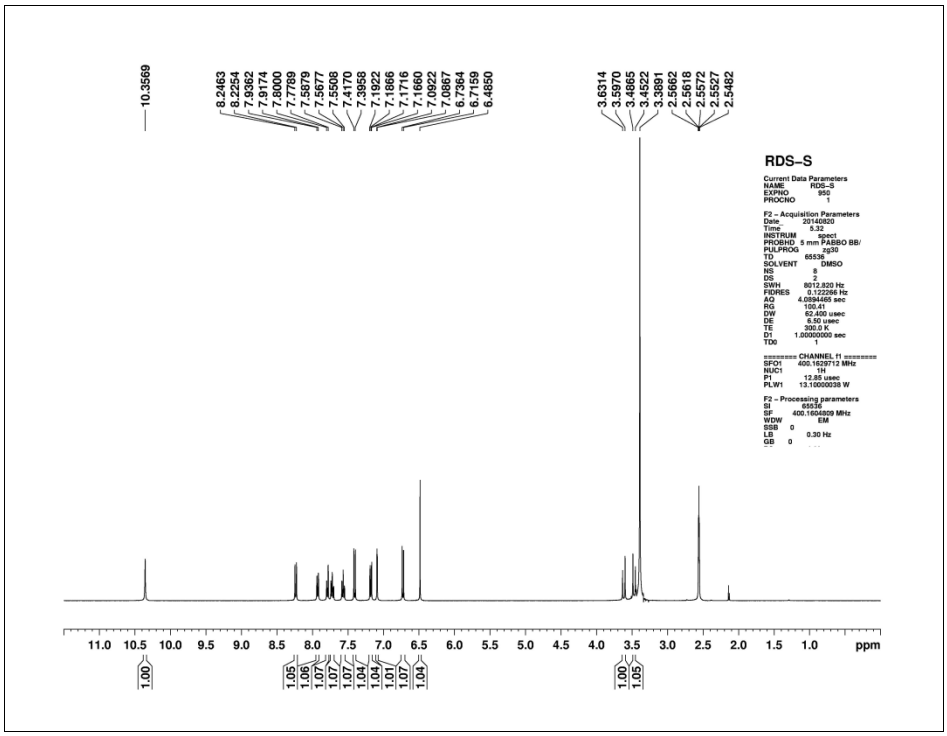

Figure 15: ^{1}H NMR of compound 3h

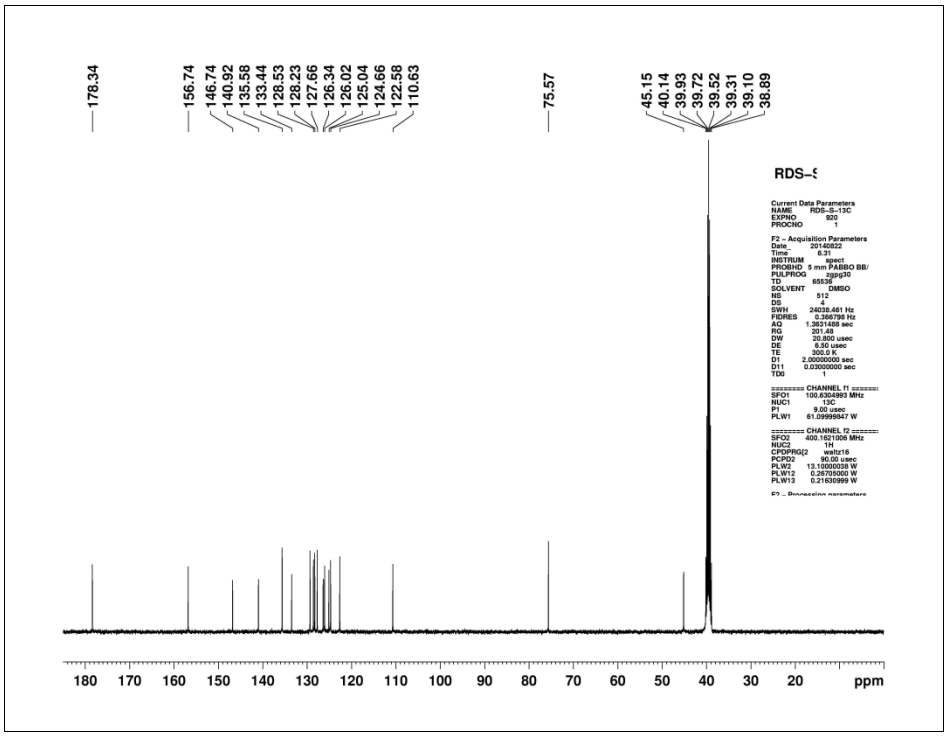

Figure 16: ^{13}C NMR of compound 3h

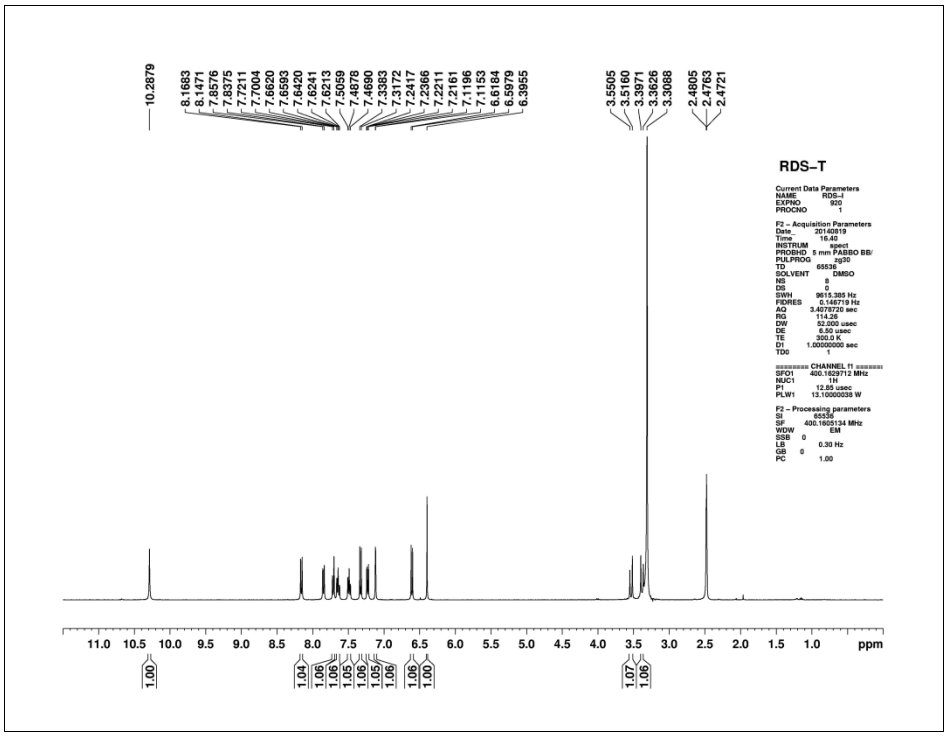

Figure 17: ^{1}H NMR of compound 3i

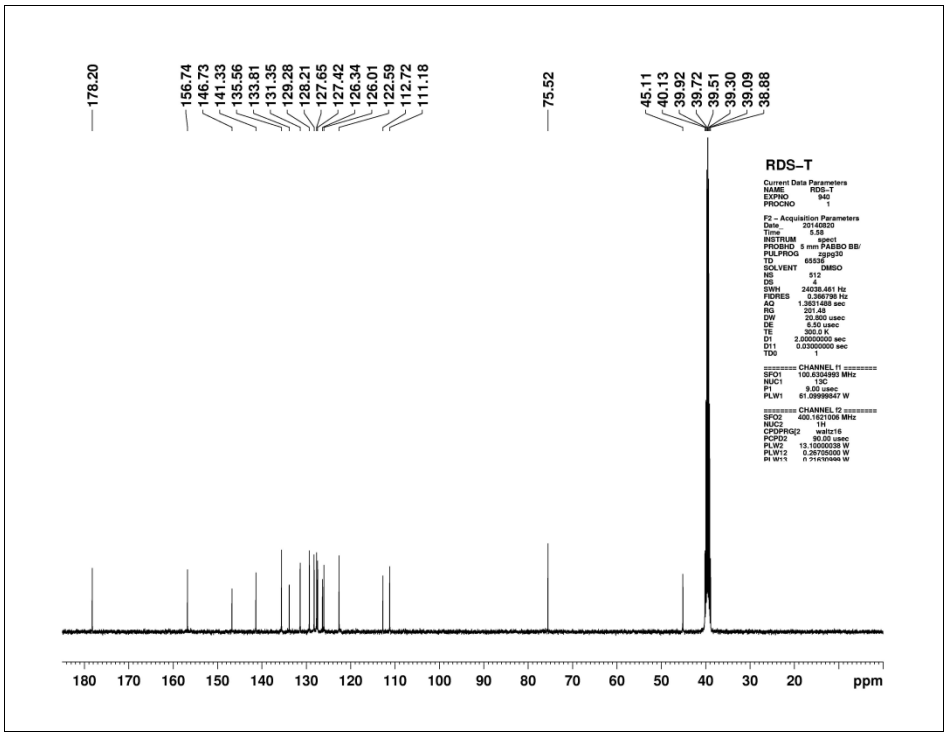

Figure 18: ^{13}C NMR of compound 3i

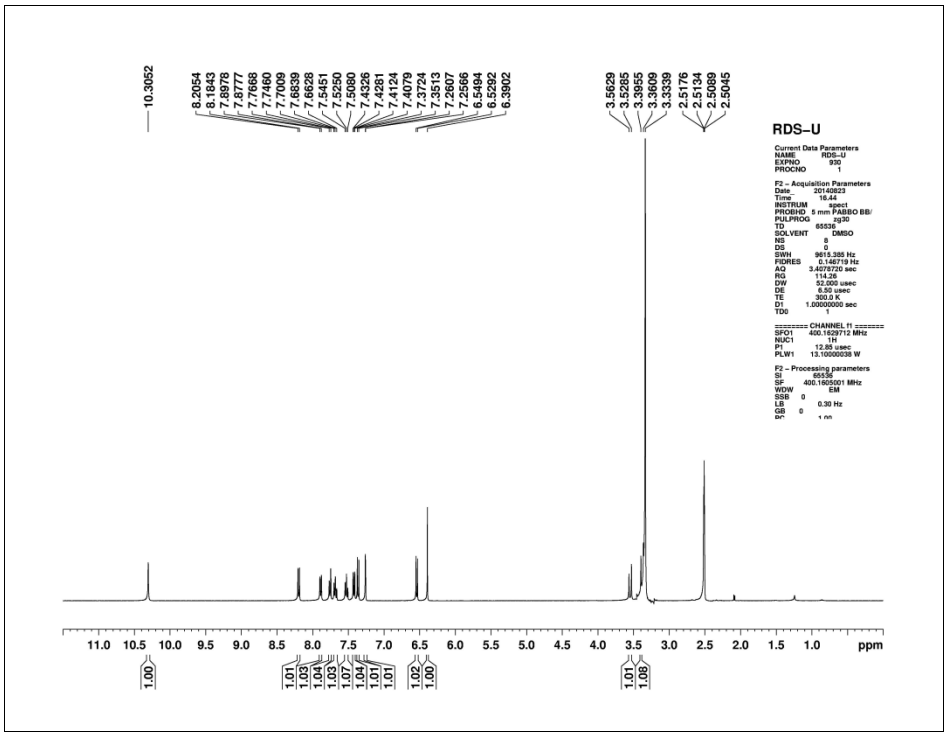

Figure 19: ^{1}H NMR of compound 3j

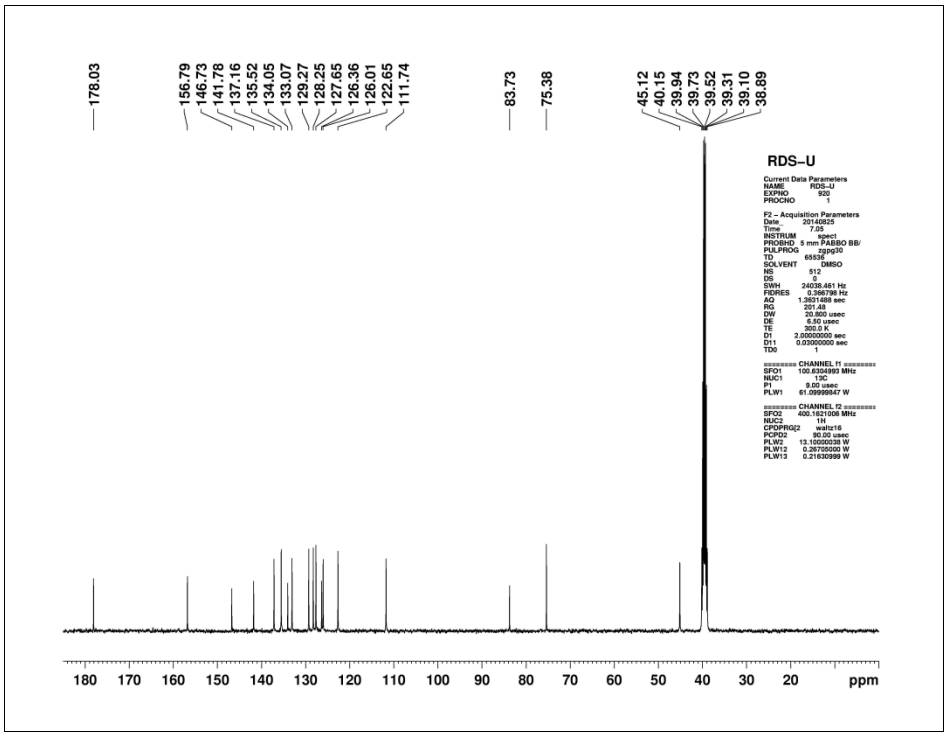

Figure 20:^{13}C NMR of compound 3j

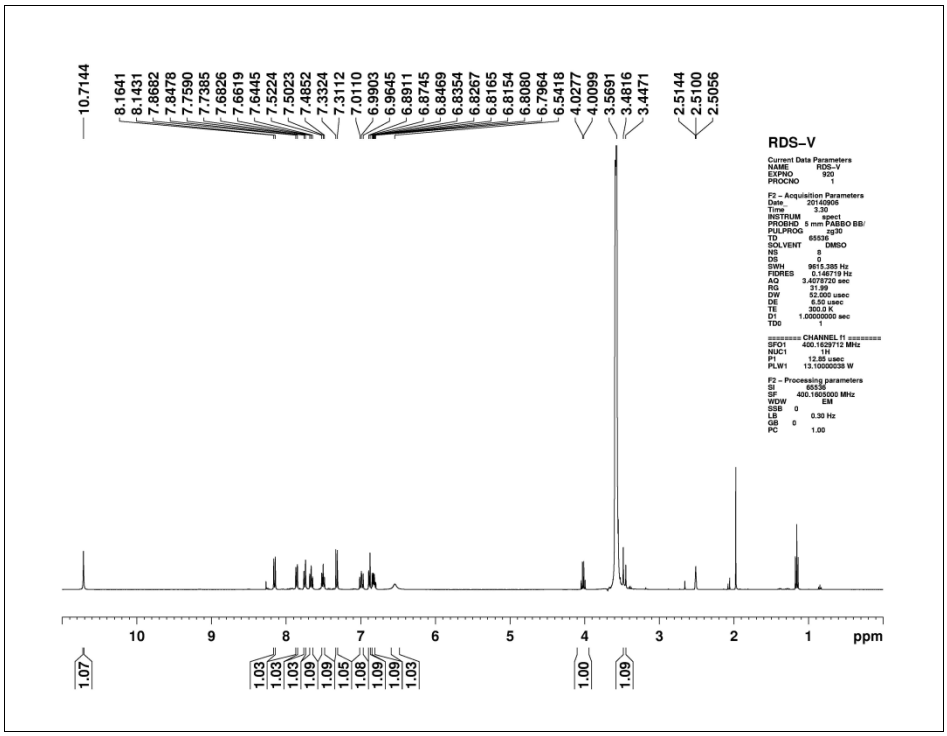

Figure 21: ^{1}H NMR of compound 3k

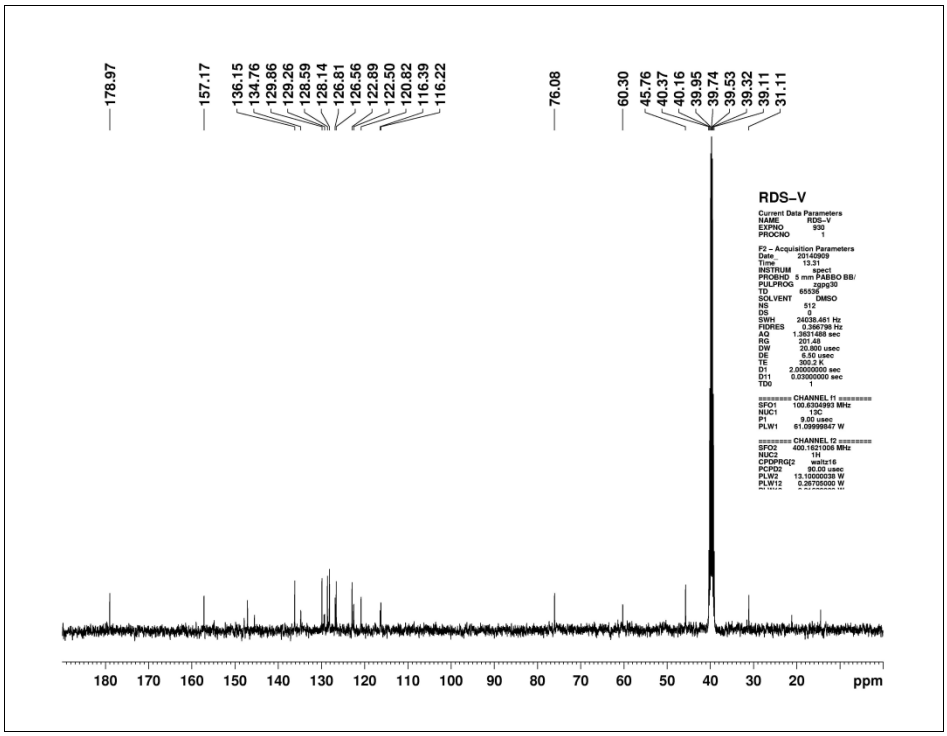

Figure 22: ^{13}C NMR of compound 3k

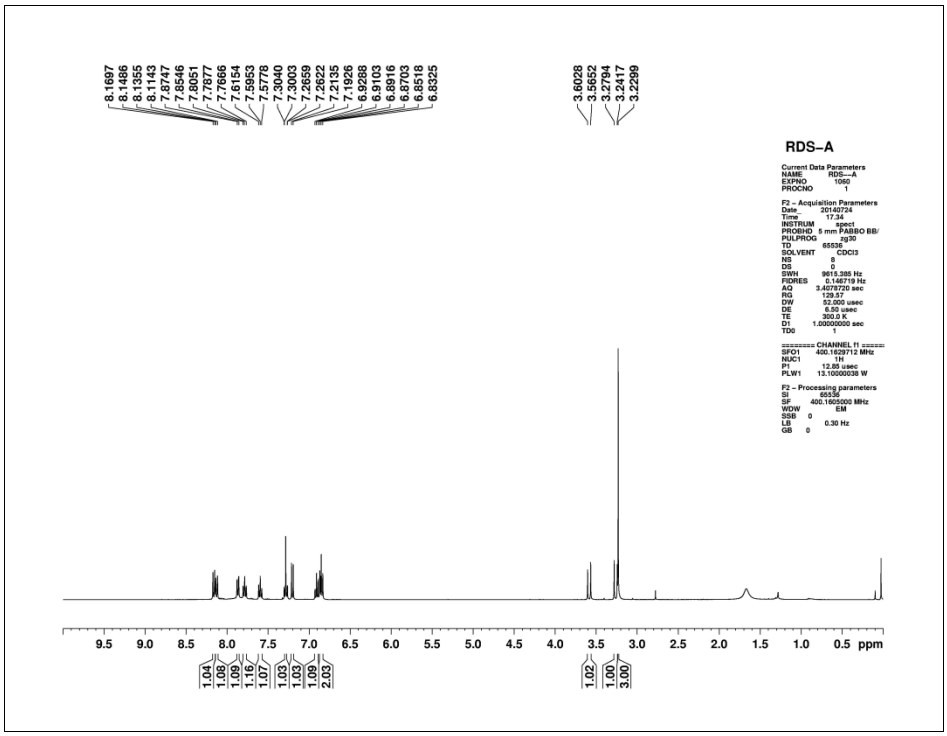

Figure 23: ^{1}H NMR of compound 3l

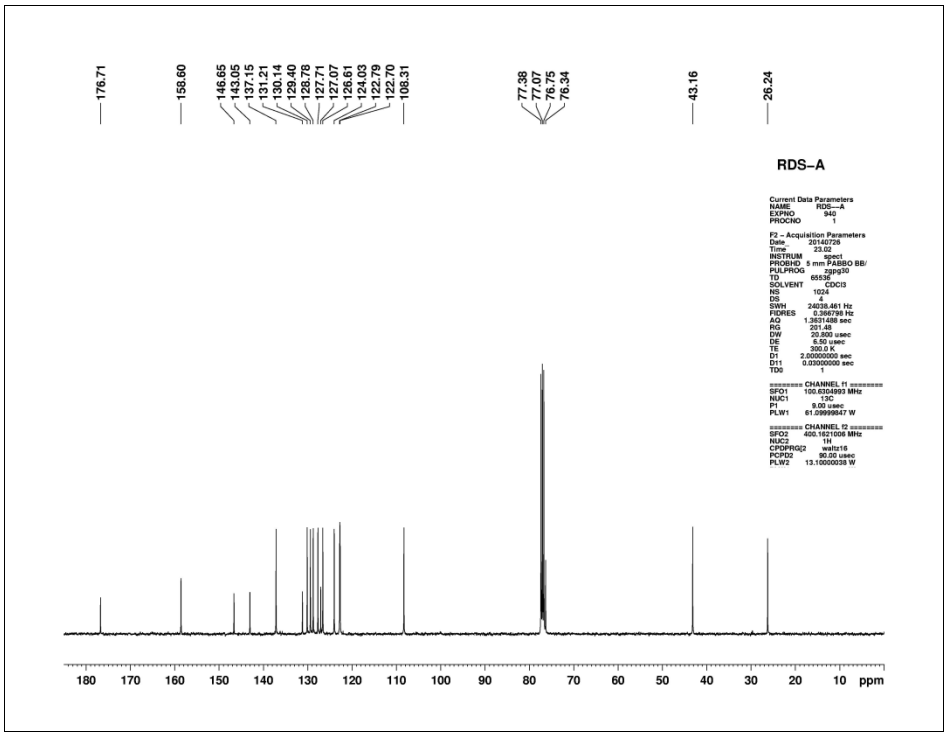

Figure 24: ^{13}C NMR of compound 3l

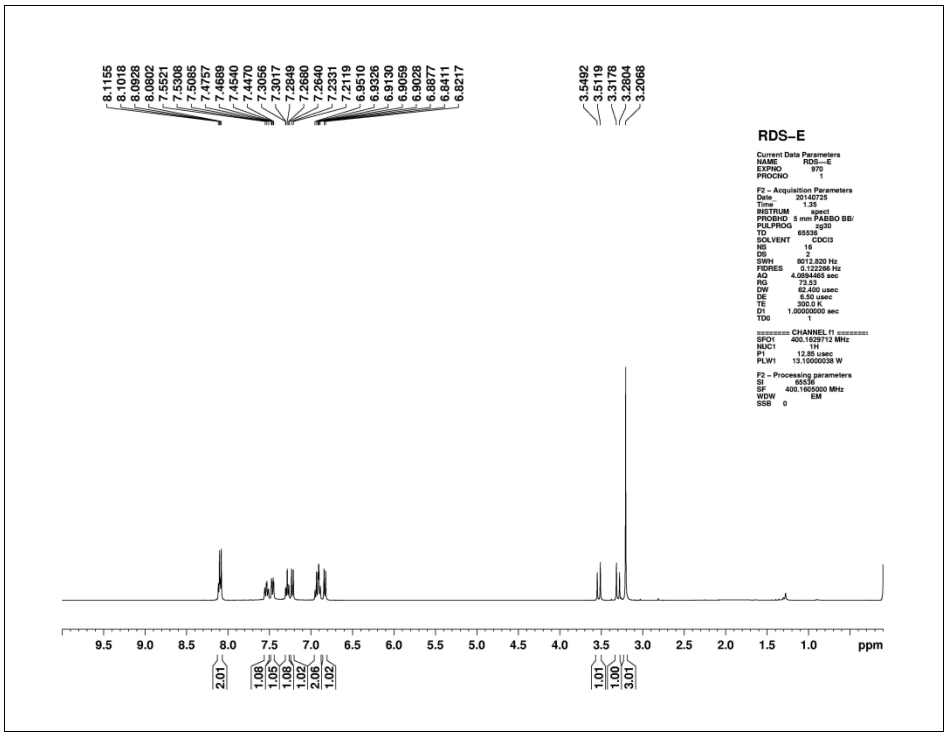

Figure 25: ^{1}H NMR of compound 3m

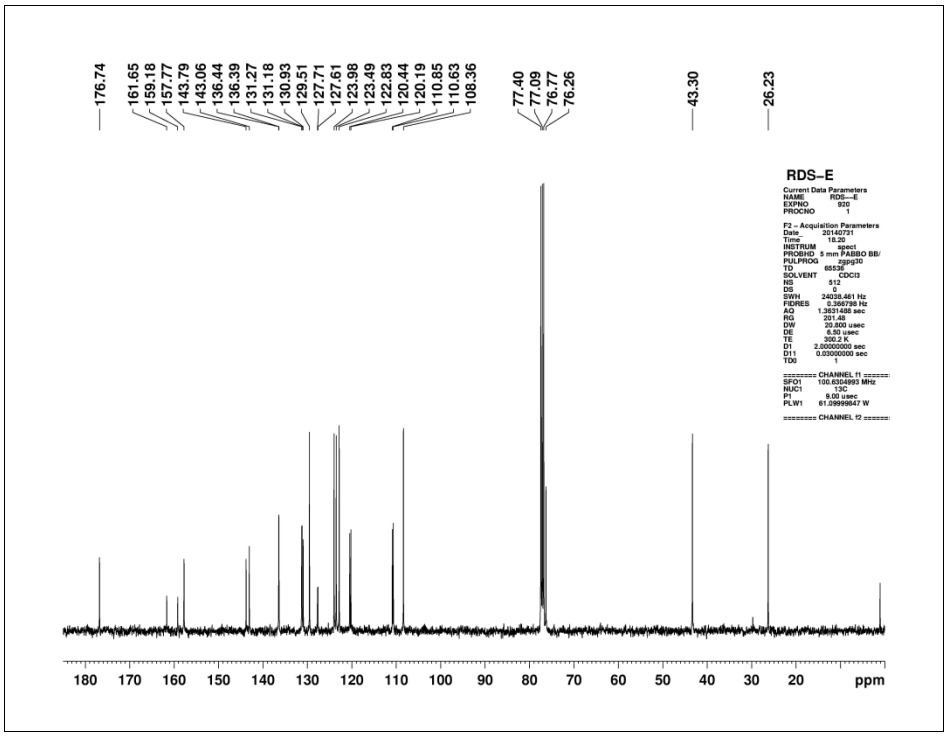

Figure 26: ^{13}C NMR of compound 3m

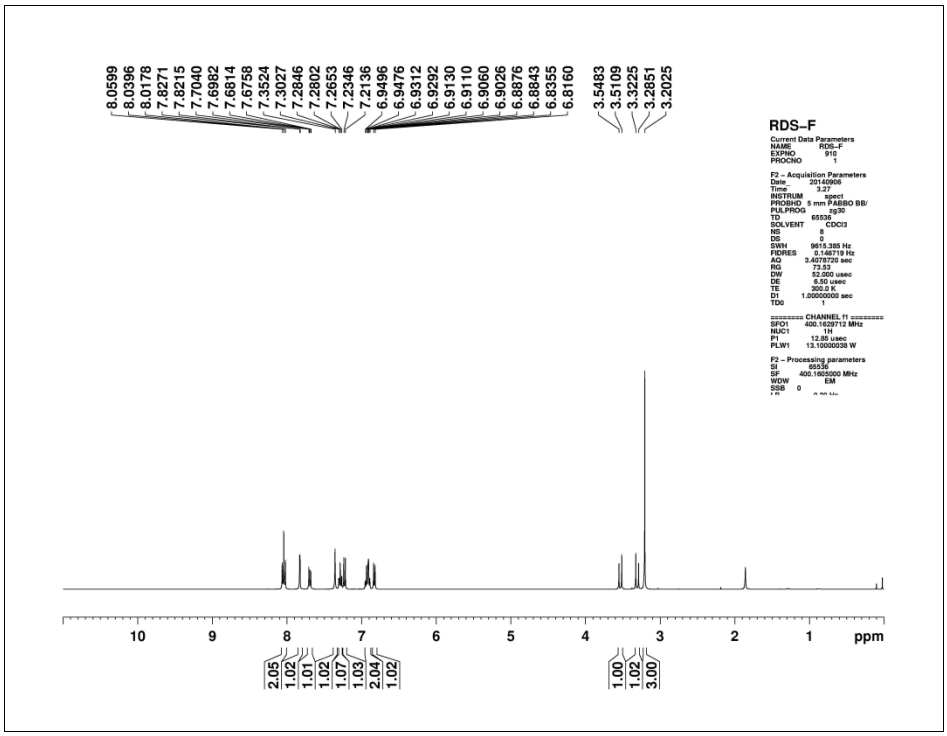

Figure 27: ^{1}H NMR of compound 3n

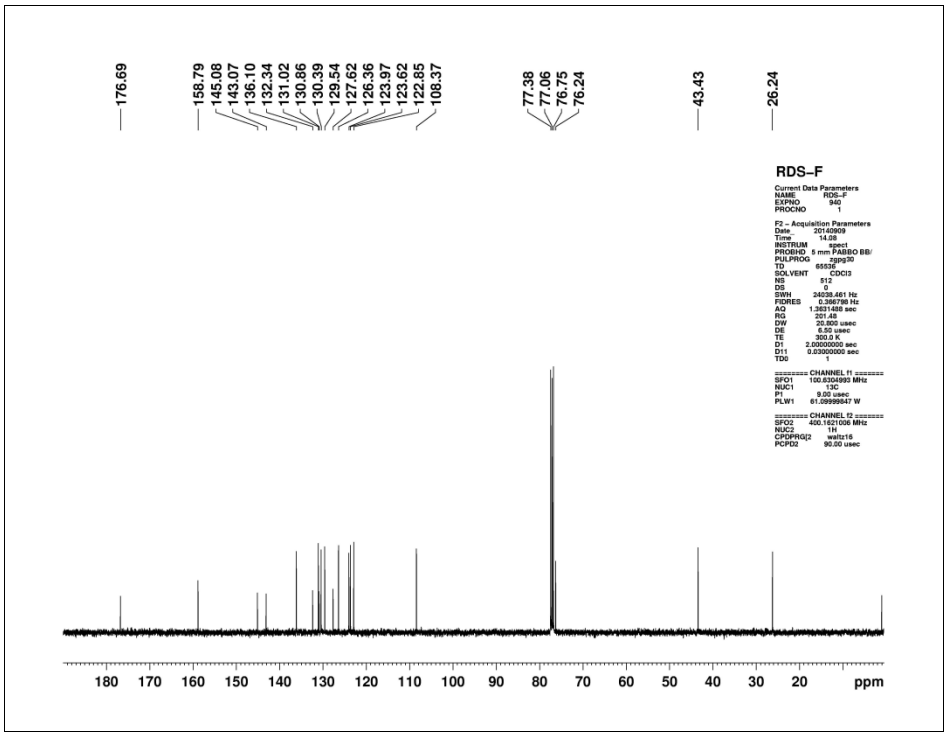

Figure 28: ^{13}C NMR of compound 3n

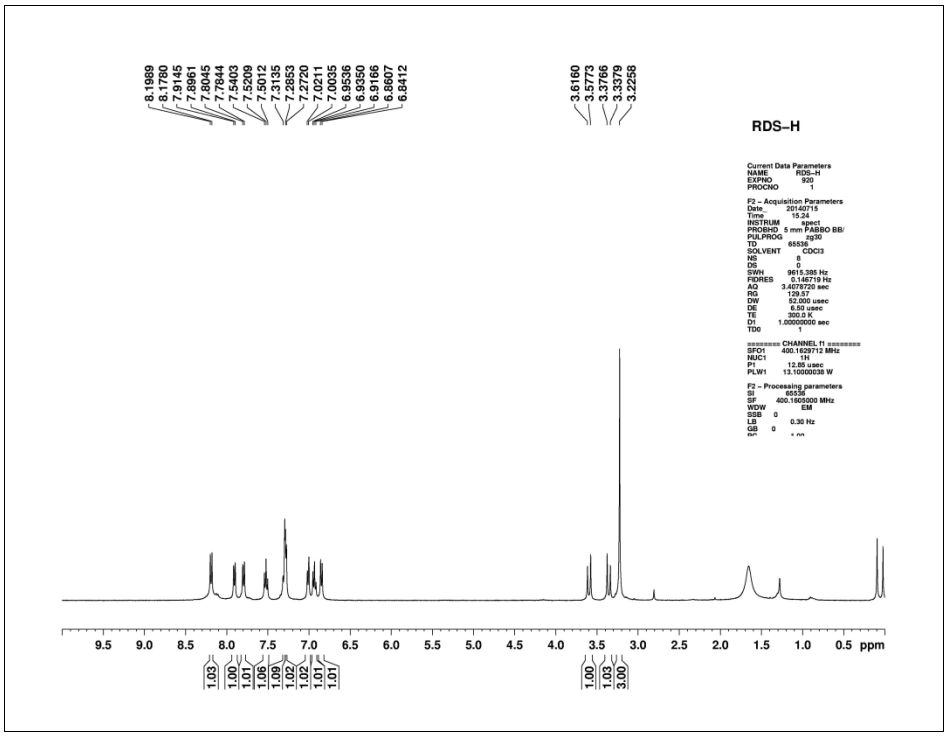

Figure 29: ^{1}H NMR of compound 3o

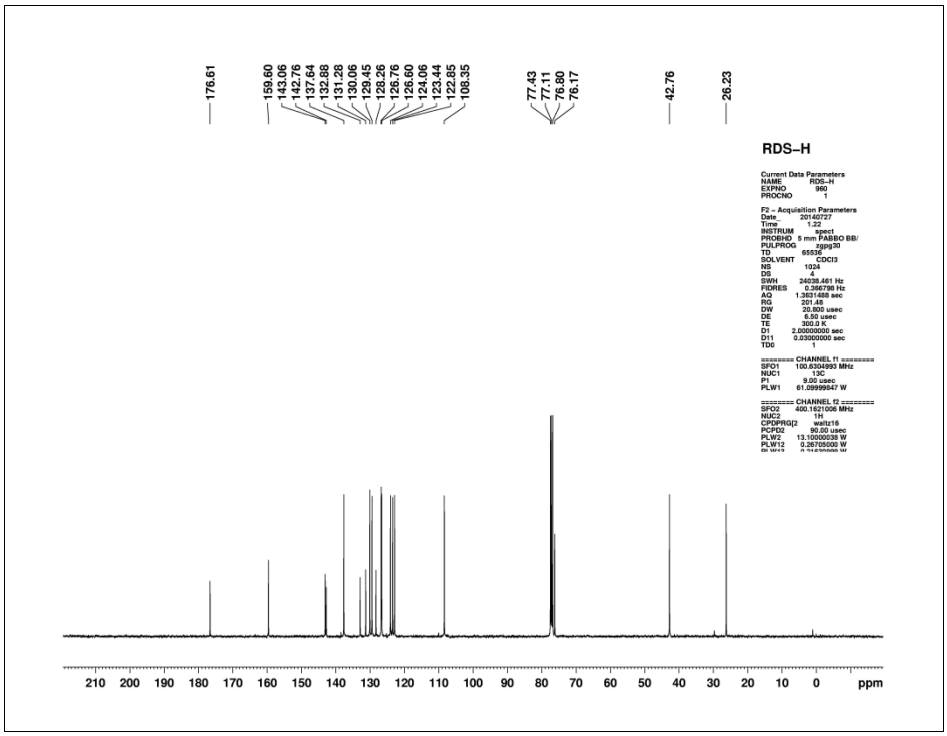

Figure 30: ^{13}C NMR of compound 3o

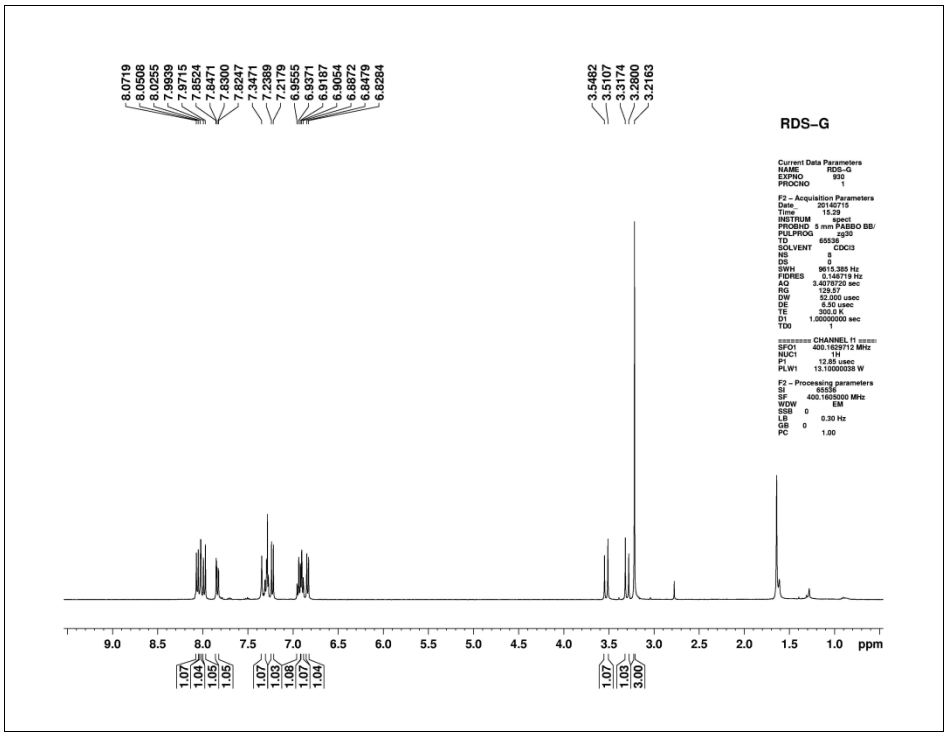

Figure 31: ^{1}H NMR of compound 3p

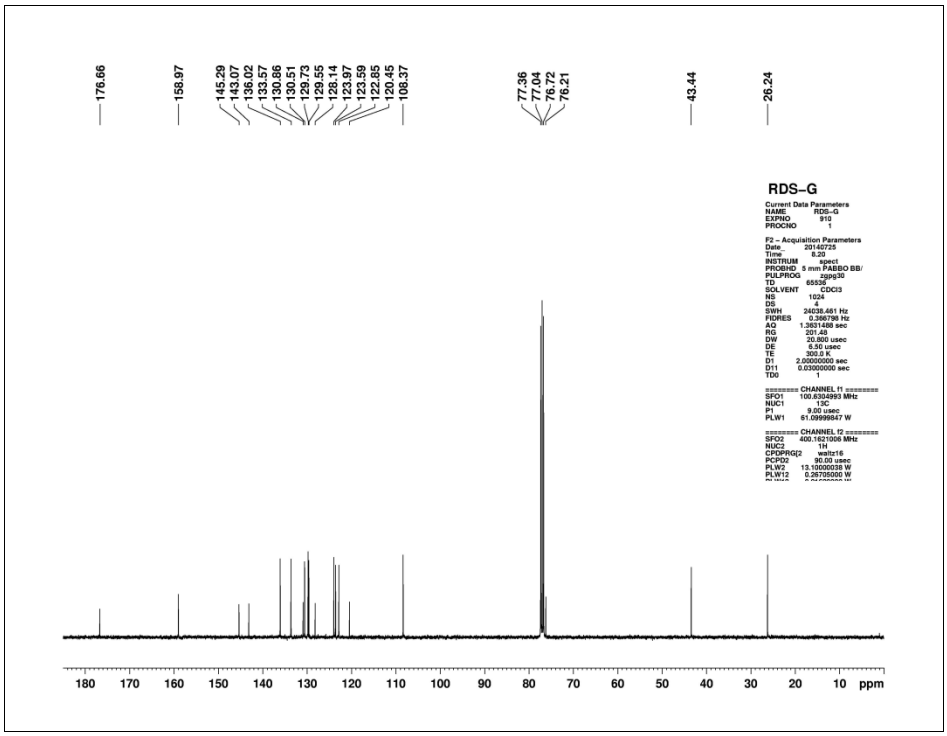

Figure 32: ^{13}C NMR of compound 3p

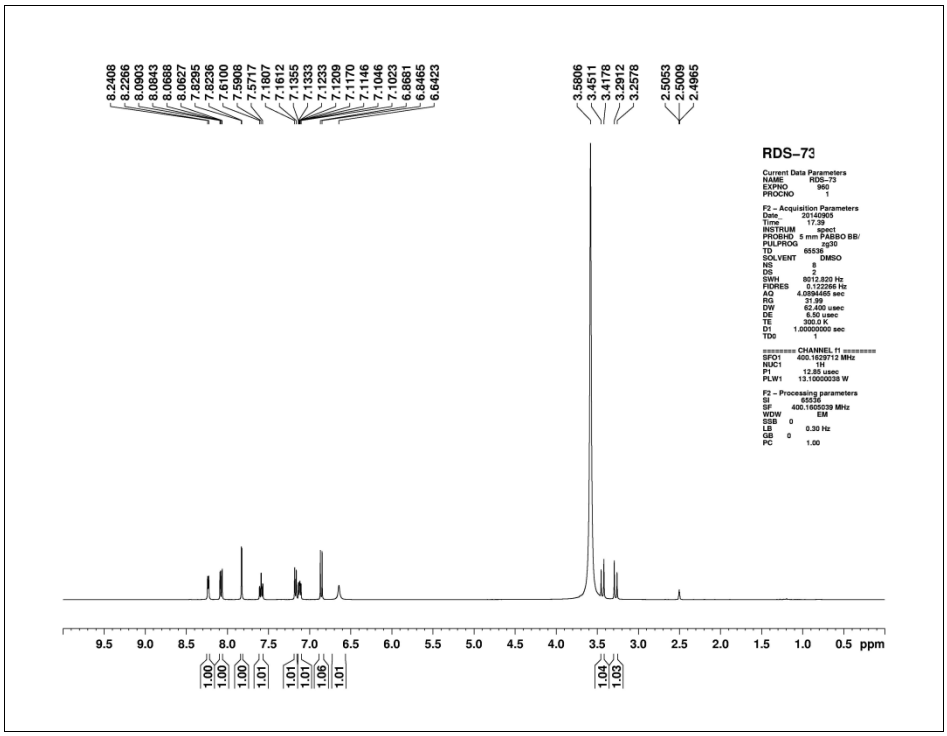

Figure 33: ^{1}H NMR of compound 4a

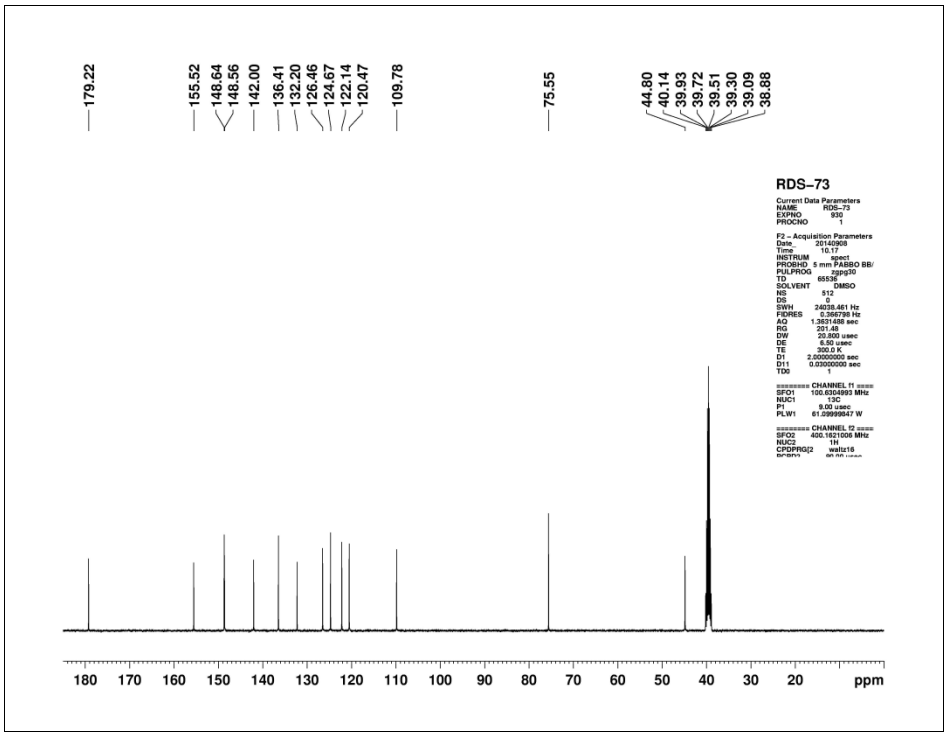

Figure 34: ^{13}C NMR of compound 4a

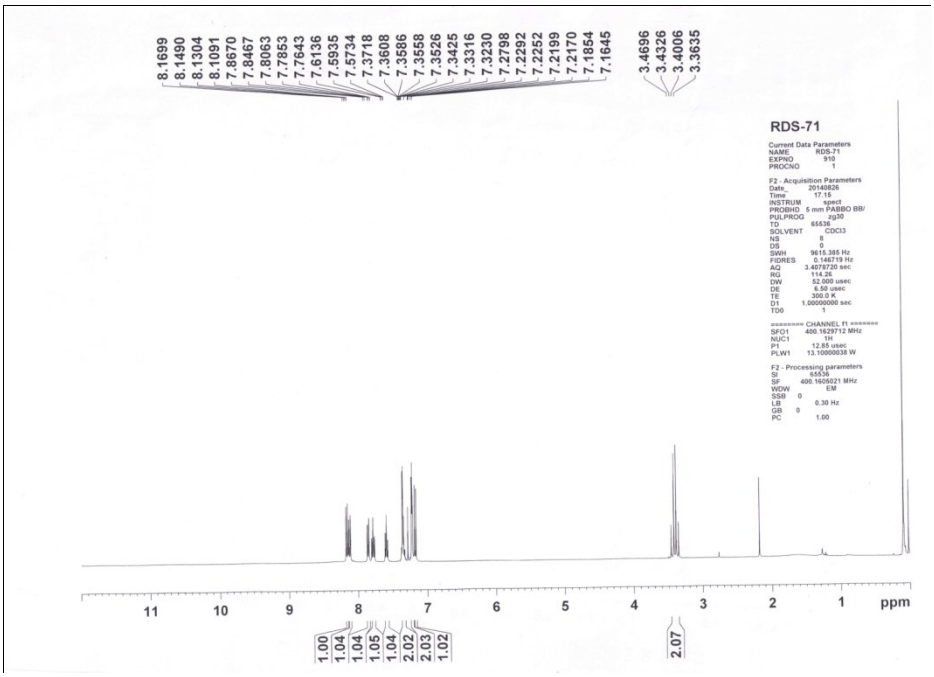

Figure 35: ^{1}H NMR of compound 4b

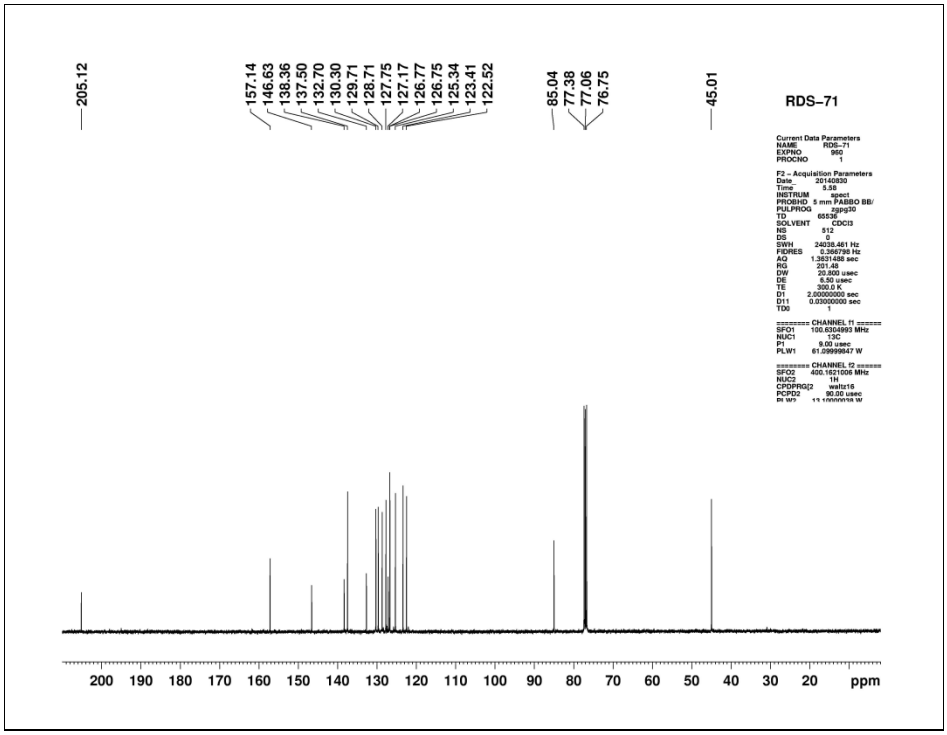

Figure 36: ^{13}C NMR of compound 4b

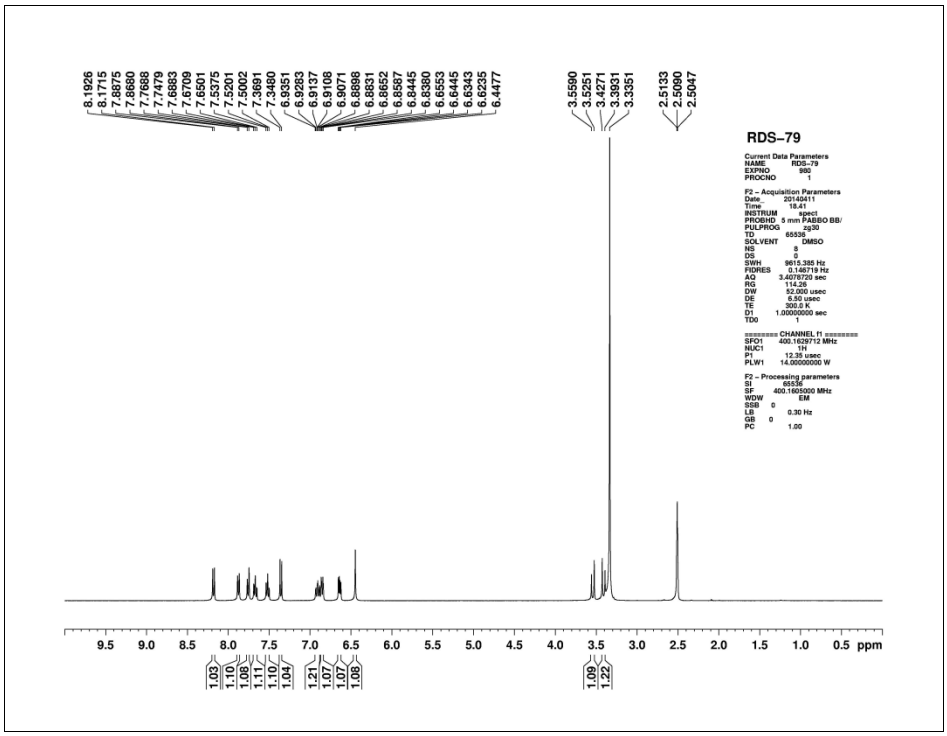

Figure 37: ^{1}H NMR of compound 4c

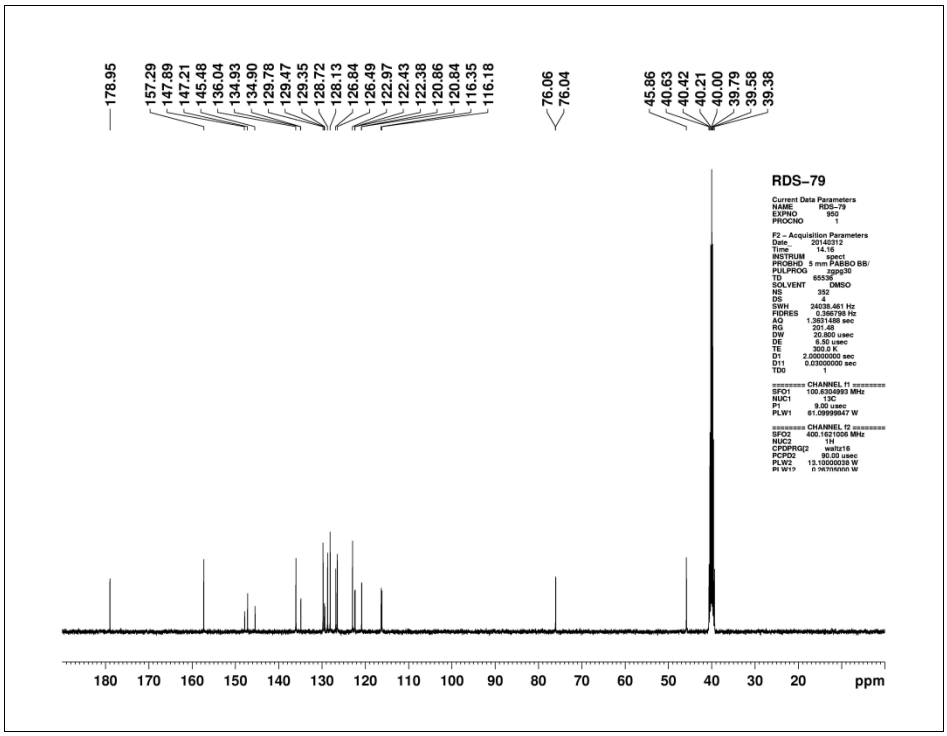

Figure 38: ^{13}C NMR of compound 4c

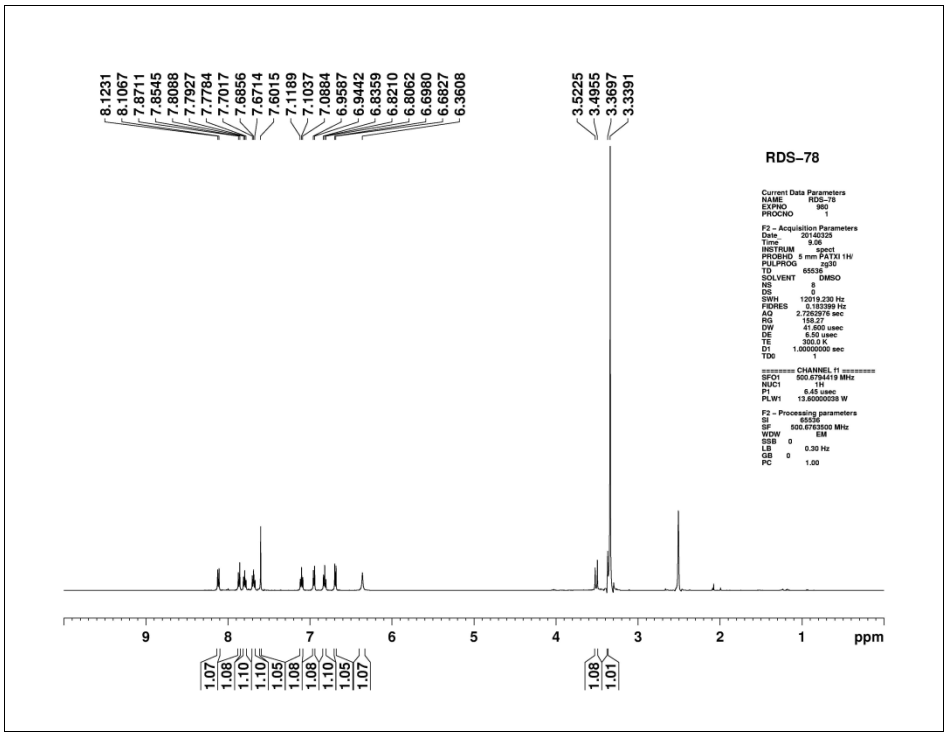

Figure 39: ^{1}H NMR of compound 4d

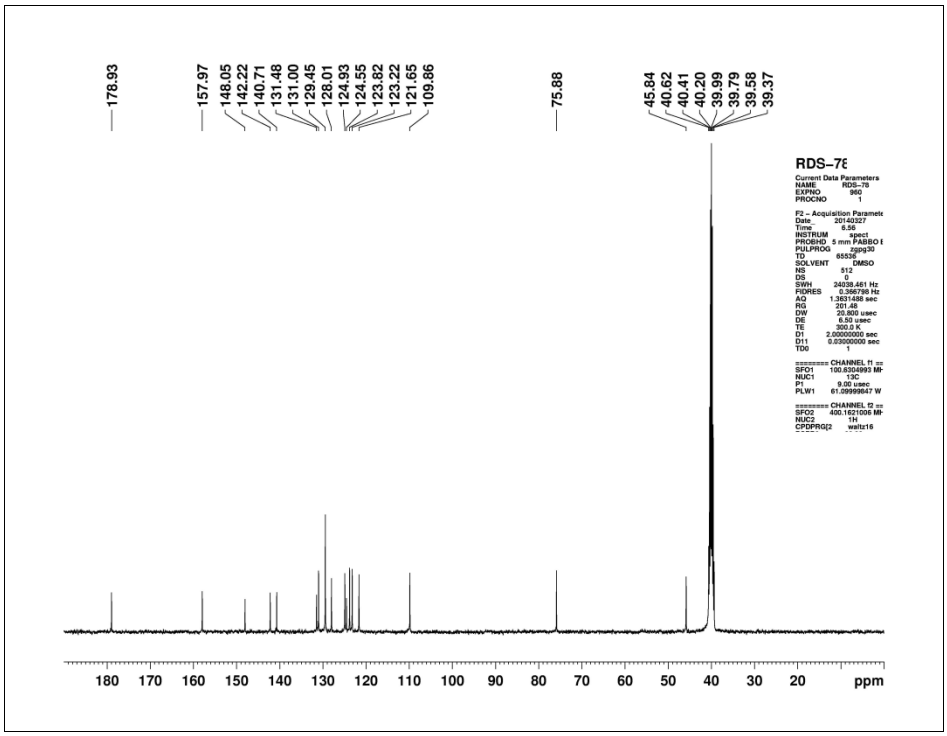

Figure 40: ^{13}C NMR of compound 4d

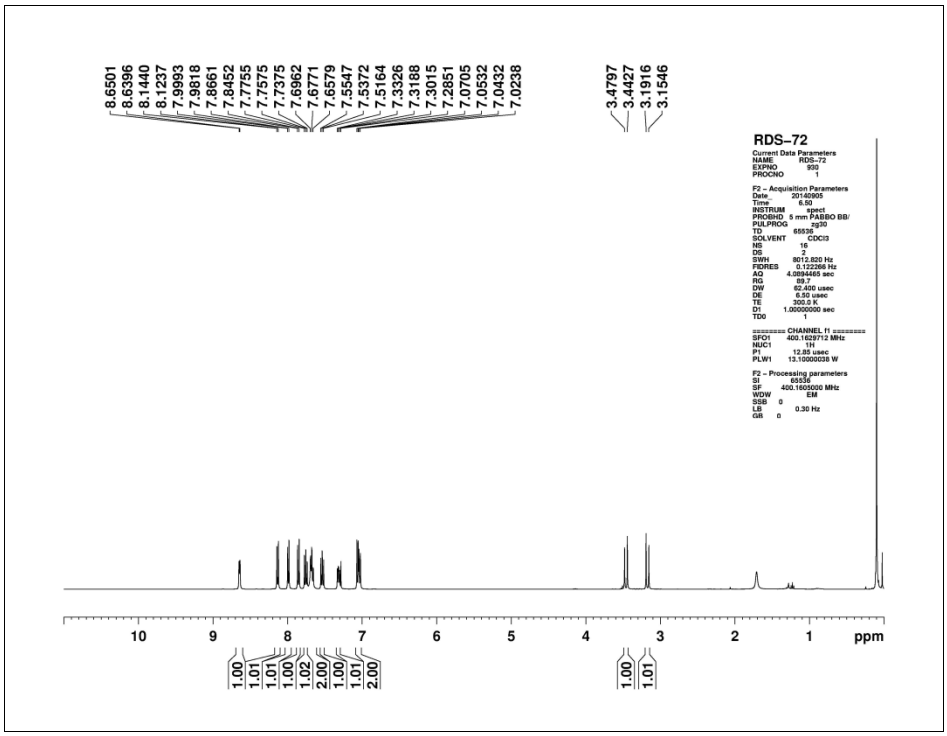

Figure 41: ^{1}H NMR of compound 5a

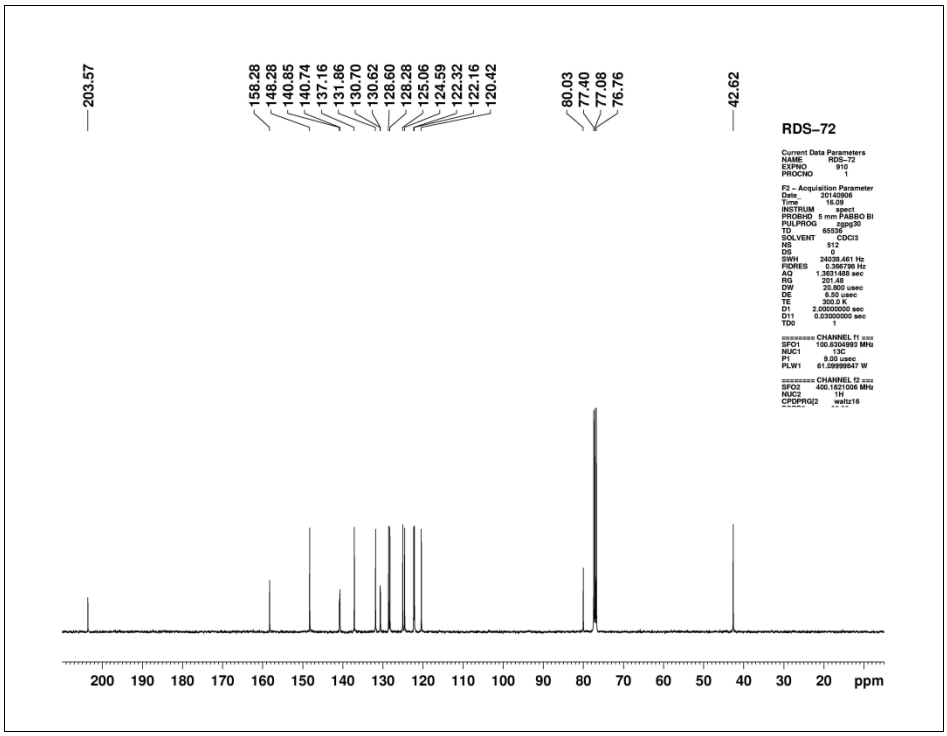

Figure 42: ^{13}C NMR of compound 5a

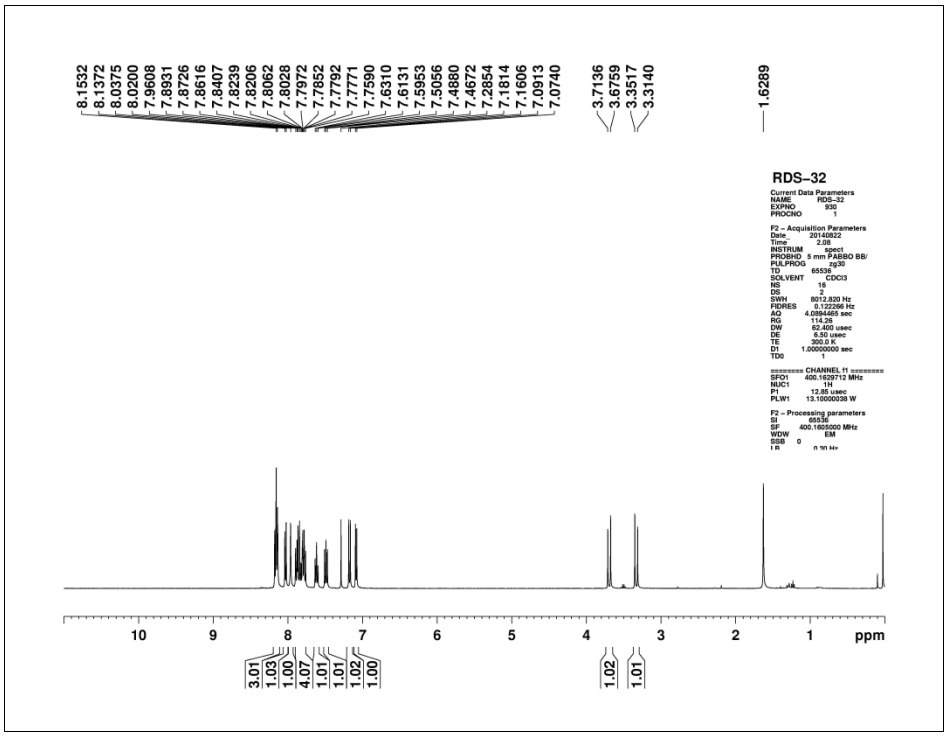

Figure 43: ^{1}H NMR of compound 5b

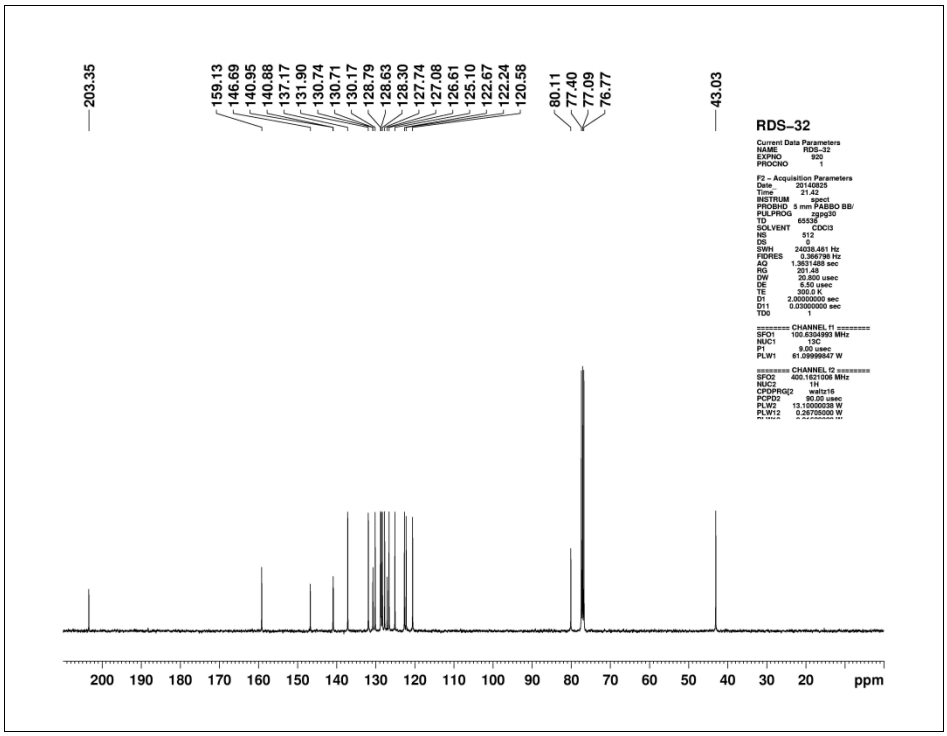

Figure 44: ^{13}C NMR of compound 5b

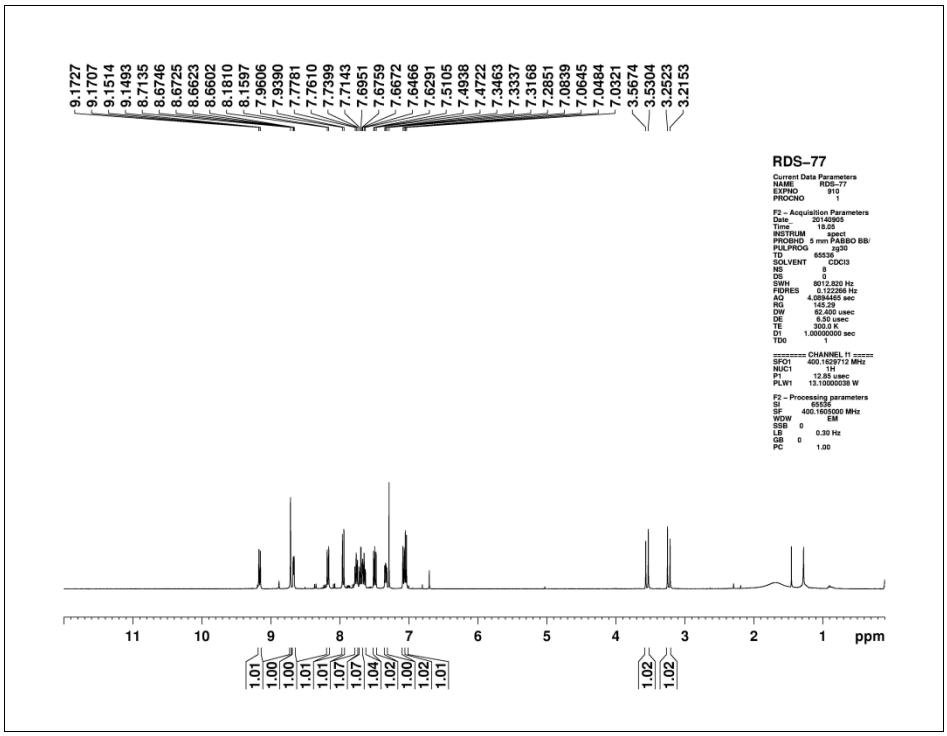

Figure 45: ^{1}H NMR of compound 6a

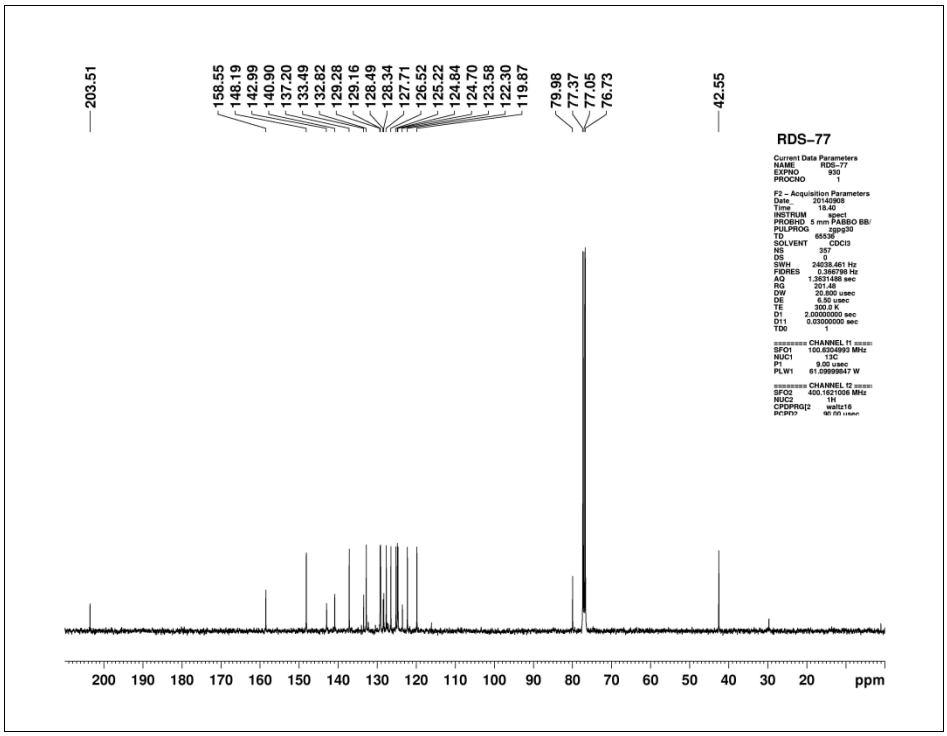

Figure 46: ^{13}C NMR of compound 6a

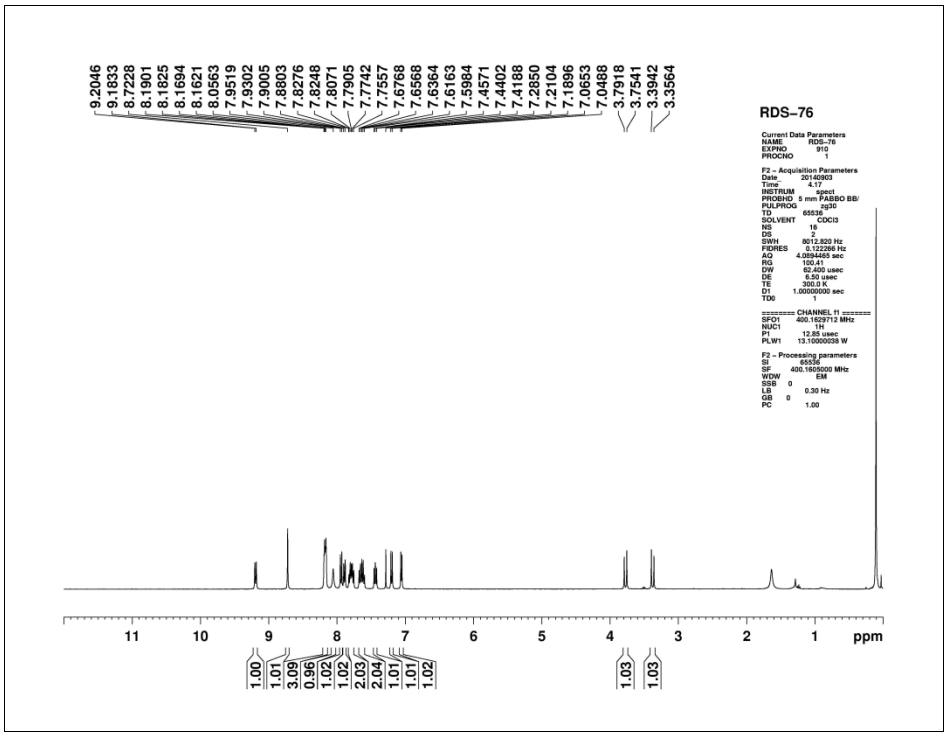

Figure 47: ^{13}C NMR of compound 6b

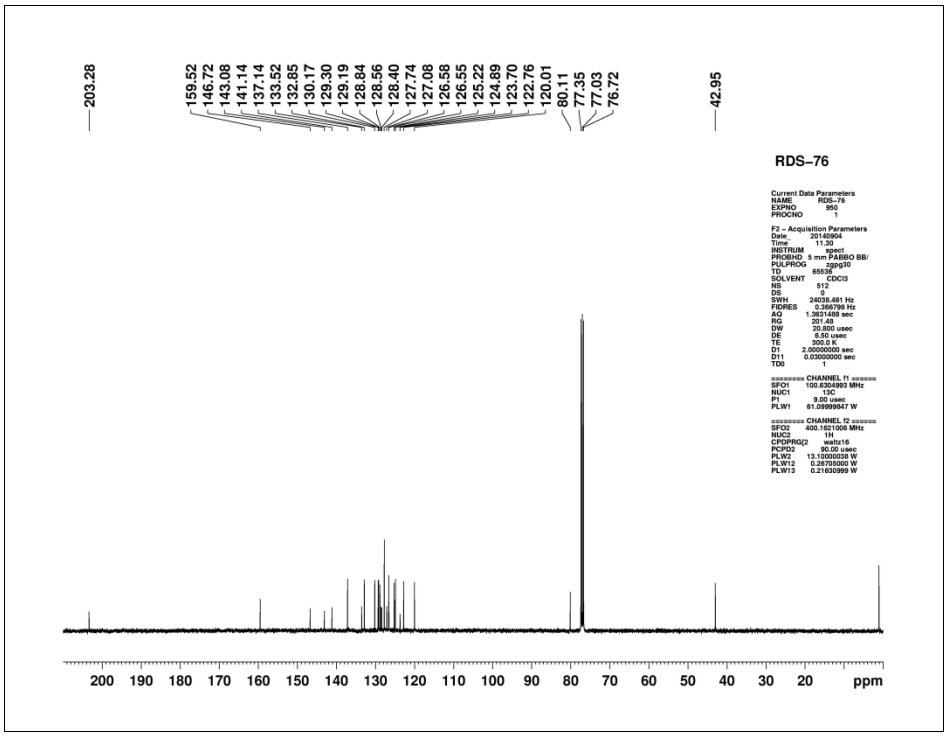

Figure 48: ^{13}C NMR of compound 6b

^{1}H NMR spectral evidence for association of β-CD with 2-methylazaarene and Diones

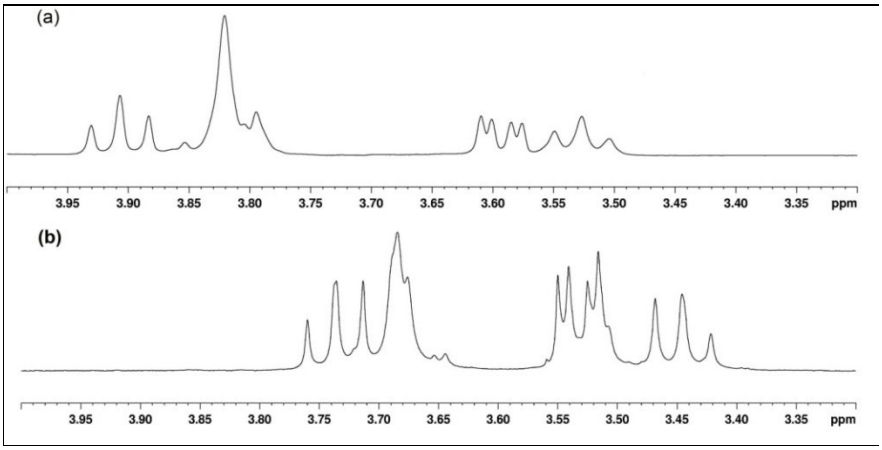

Fig.49: ^{1}H NMR spectra of (a) β-CD and (b) β-CD complex with 2-methylquinoline and isatin after 2 h

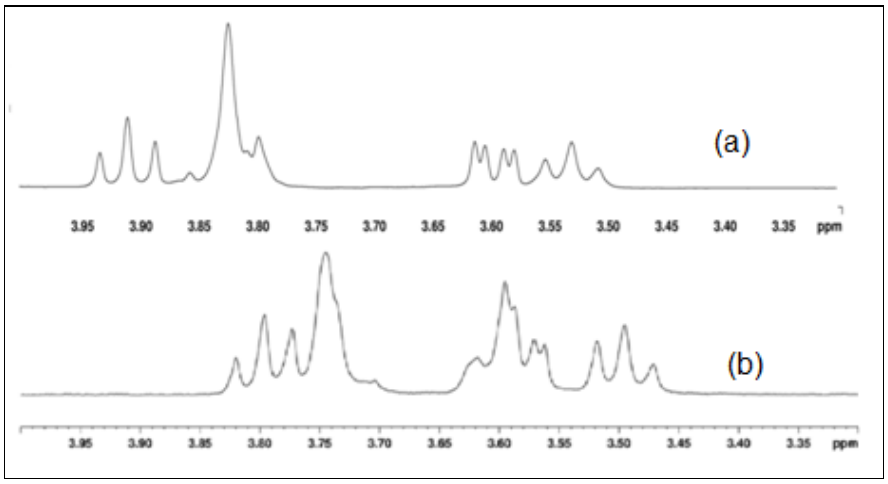

Fig.50: ^{1}H NMR spectra of (a) β-CD and (b) β-CD complex with 2-methylquinoline and 1-methylisatin after 2 h

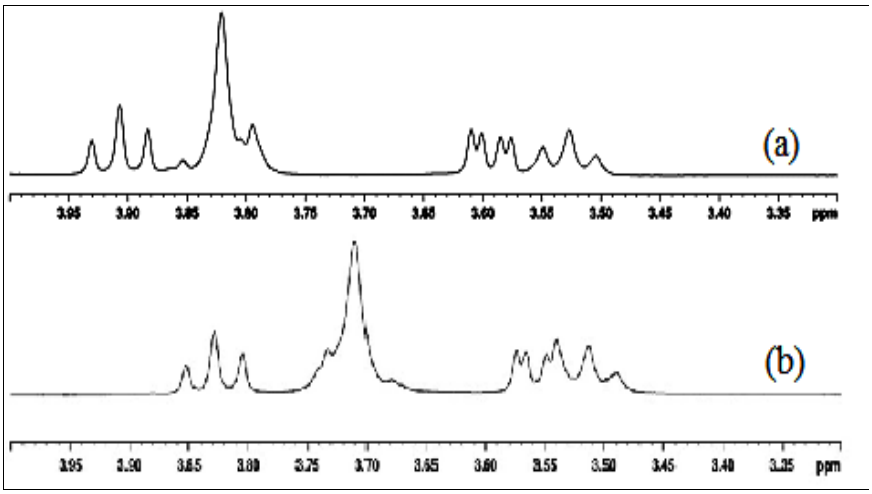

Fig.51: ^{1}H NMR spectra of (a) β-CD and (b) β-CD complex with 2-methylquinoline and benzo[*b*]thiophene-2, 3-dione after 2 h

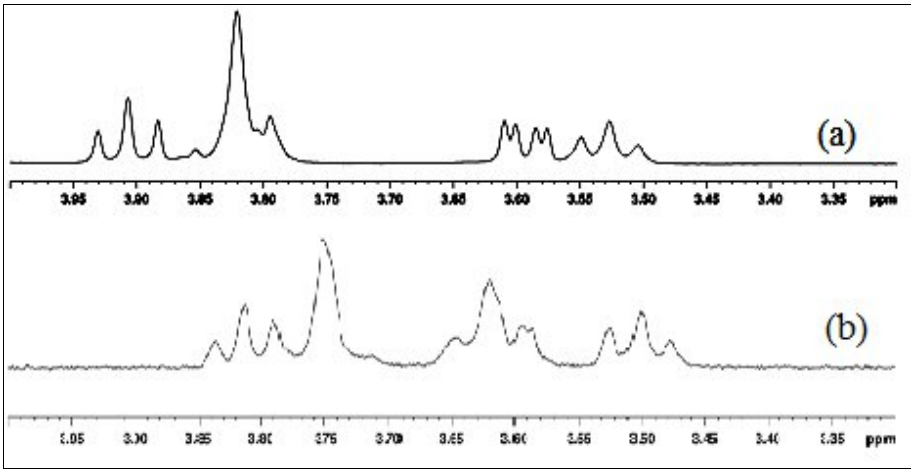

Fig.52: ^{1}H NMR spectra of (a) β-CD and (b) β-CD complex with 2-methylquinoline and acenaphthylene-1, 2-dione after 2 h

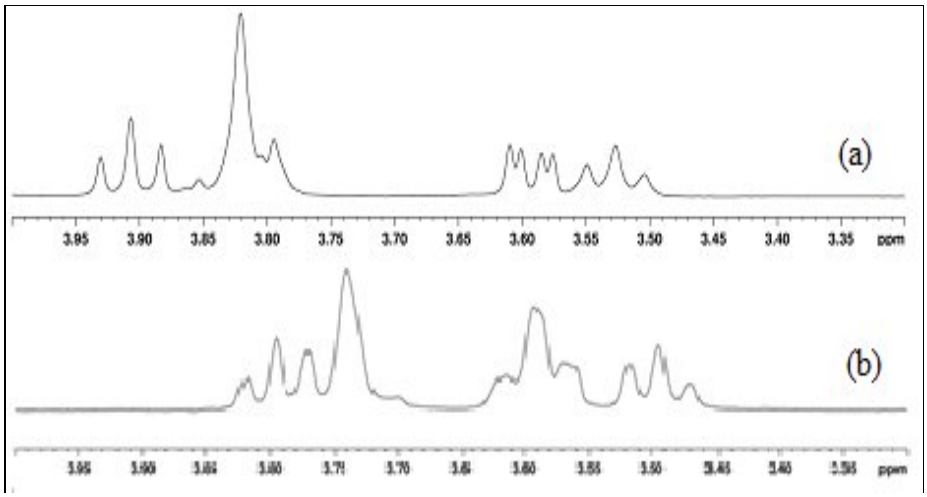

Fig.53: ^{1}H NMR spectra of (a) β-CD and (b) β-CD complex with 2-methylquinoline and aceanthrylene-1, 2-dione after 2 h

References

1. M. Raoov, S. Mohamad and Mhd. R.Abas, *Int. J. Mol. Sci*. 2014, **15**, 100-119.