Iodobenzene-Catalyzed Synthesis of Aryl Sulfonate Esters from Aminoquinolines *via* Remote Radical C-O Cross-Coupling

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Supporting Information

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1. General Information

All the chemicals were obtained commercially and used without any prior purification. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90°C) and ethyl acetate. ^{1}H, ^{13}C and ^{19}F NMR spectras were recorded on a Bruker Advance 500 spectrometer at ambient temperature with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. Melting points were determined on an X-5 Data microscopic melting point apparatus. The small-angle X-ray diffraction(SAXRD) data was taken on a German Bruker D4 X-ray diffractometer. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent 6530 QTOF mass spectrometer.

2. Experimental Section

General procedure for the synthesis of starting amides

To a 100 ml single neck flask charged with CH_2Cl_2 (30 mL) was added with 8-aminoquinoline (10 mmol), triethylamine (15 mmol) and stirred at room temperature for 5 min, then the reaction solution was cooled in an ice bath. The acid chloride (11 mmol) was added dropwise (if solid, it was dissolved with CH_2Cl_2). The reaction solution was stirring overnight. When it was completed (Monitored by TLC), the mixture was filtered through a pad of Celite, the solid was washed with CH_2Cl_2 (25 mL), and the organic layer was washed with 1 M $NaHCO_3$ aqueous solution (3 x 15 mL), then the organic layer was dried with Na_2SO_4, filtered, and *roto*-evaporated. The product was purified by silica gel column with PE/EtOAc(20/1).

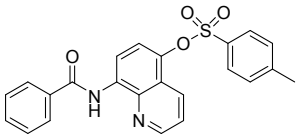
General procedure for the synthesis of compounds 3

A mixture of **1** (0.2 mmol), **2** (1.5 eq.) and $PhI(TFA)_2$ (2.0 eq.) in dioxane (1.0 mL) PhI (20 mol%), CH_3CO_3H (1.0 equiv), HFIP (1.0 mL) in 25 mL tube was stirred at room temperature under air atmosphere for 1 h. Monitored by TLC and after the reaction was completed, the solvent was removed under reduced pressure and the

residue was purified by silica gel column chromatography using PE/AcOEt as an eluent to afford the products aryl sulfonate esters 3.

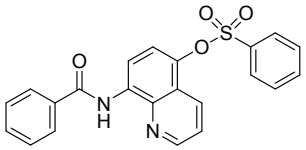
3. Characterization of the products

8-Benzamidoquinolin-5-yl 4-methylbenzenesulfonate(3a)



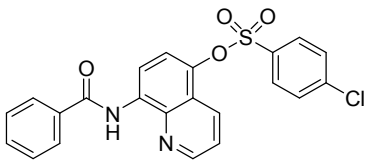
White solid, 93% yield, m.p. 161-162 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.65 (s, 1H), 8.86 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.79 (d, *J* = 8.6 Hz, 1H), 8.41 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.07 – 8.04 (m, 2H), 7.85 – 7.74 (m, 2H), 7.63 – 7.47 (m, 4H), 7.39 – 7.30 (m, 2H), 7.04 (d, *J* = 8.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.52, 148.96, 145.84, 139.72, 138.92, 134.87, 133.92, 132.20, 132.07, 131.53, 129.99, 128.88, 128.72, 127.31, 123.08, 122.23, 119.97, 115.41, 21.74. HRMS (ESI+): Calculated for $C_{23}H_{18}N_2O_4SH$: $[M+H]^+$ 419.1060, Found 419.1061.

8-Benzamidoquinolin-5-yl benzenesulfonate(3b)



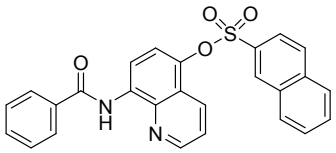
White solid, 94% yield, mp 93-94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.64 (s, 1H), 8.89 – 8.76 (m, 2H), 8.35 (dd, *J* = 8.5, 1.6 Hz, 1H), 8.10 – 8.00 (m, 2H), 7.89 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.73 – 7.63 (m, 1H), 7.62 – 7.50 (m, 5H), 7.48 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.08 (d, J = 8.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.49, 148.97, 139.57, 138.85, 135.20, 134.79, 134.56, 133.98, 132.08, 131.32, 129.38, 128.87, 128.63, 127.29, 122.94, 122.25, 120.02, 115.38. HRMS (ESI+): Calculated for $C_{22}H_{16}N_2O_4SH$: $[M+H]^+$ 405.0904, Found 405.0908.

8-Benzamidoquinolin-5-yl 4-chlorobenzenesulfonate(3c)



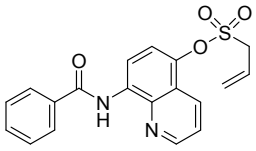
Brown solid, 92% yield, mp 177-178 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.65 (s, 1H), 8.87 (d, *J* = 3.1 Hz, 1H), 8.83 (d, *J* = 8.6 Hz, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.60-7.51 (m, 6H), 7.11 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.54, 149.07, 141.48, 139.39, 138.87, 134.75, 134.17, 133.64, 132.12, 131.23, 130.04, 129.76, 128.89, 127.31, 122.85, 122.37, 119.97, 115.40. HRMS (ESI+): Calculated for $C_{22}H_{15}ClN_2O_4SH$: $[M+H]^+$ 439.0514, Found 439.0519.

8-Benzamidoquinolin-5-yl naphthalene-2-sulfonate(3d)



Brown solid, 90% yield, mp 159-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.62 (s, 1H), 8.82 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.74 (d, *J* = 8.6 Hz, 1H), 8.46 – 8.39 (m, 2H), 8.05 – 8.01 (m, 2H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.95 – 7.88 (m, 3H), 7.71 – 7.67 (m, 1H), 7.62 (dd, *J* = 11.5, 4.5 Hz, 1H), 7.59 – 7.50 (m, 3H), 7.45 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.46, 149.00, 139.67, 138.93, 135.56, 134.79, 133.97, 132.06, 132.02, 131.85, 131.35, 130.72, 129.84, 129.78, 129.52, 128.86, 128.81, 128.06, 127.27, 123.00, 122.86, 122.26, 119.92, 115.30. HRMS (ESI+): Calculated for $C_{26}H_{18}N_2O_4SH$: $[M+H]^+$ 455.1060, Found 455.1065.

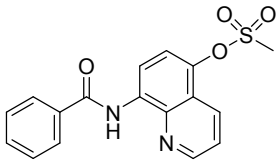
8-Benzamidoquinolin-5-yl prop-2-ene-1-sulfonate(3e)



White solid, 75% yield, mp 90-91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.68 (s, 1H), 8.92 (dd, *J* = 8.1, 5.0 Hz, 2H), 8.54 (d, *J* = 8.5 Hz, 1H), 8.21 – 7.96 (m, 2H), 7.66 – 7.52 (m, 5H), 7.48 (d, *J* = 8.6 Hz, 1H), 6.99-6.92 (m, 1H), 6.46 (dd, *J* = 15.1, 1.6 Hz, 1H), 1.97 (dd, *J* = 6.9, 1.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.57, 148.97, 147.47, 139.51, 138.90, 134.81, 133.93, 132.09, 131.73, 128.87, 127.34, 125.07,

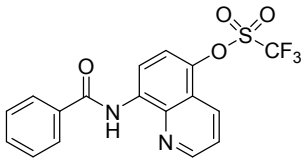
123.07, 122.37, 120.02, 115.73, 17.50. HRMS (ESI+): Calculated for $C_{19}H_{16}N_2O_4SH$: $[M+H]^+$ 369.0904, Found 369.0907.

8-Benzamidoquinolin-5-yl methanesulfonate(3f)



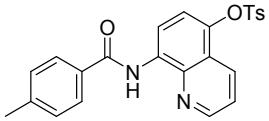
White solid, 95% yield, mp 181-182 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.68 (s, 1H), 8.96 (d, *J* = 8.6 Hz, 1H), 8.92 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.53 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.17 – 7.98 (m, 2H), 7.72 – 7.51 (m, 5H), 3.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.55, 149.18, 139.11, 139.09, 134.81, 134.27, 132.12, 131.37, 128.91, 127.35, 122.90, 122.59, 119.88, 115.63, 37.94. HRMS (ESI+): Calculated for $C_{17}H_{14}N_2O_4SH$: $[M+H]^+$ 343.0747, Found 343.0750.

8-Benzamidoquinolin-5-yl trifluoromethanesulfonate(3g)



White solid, 88% yield, mp 111-113 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.71 (s, 1H), 9.02 (d, *J* = 8.7 Hz, 1H), 8.99 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.46 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.12 – 8.07 (m, 2H), 7.69 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.63 – 7.56 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.57, 149.44, 138.96, 138.86, 135.17, 134.61, 132.23, 130.18, 128.93, 127.33, 123.24 (q, *J* = 273.4 Hz), 123.09, 119.68, 115.32, 114.05. HRMS (ESI+): Calculated for $C_{17}H_{11}F_3N_2O_4SH$: $[M+H]^+$ 397.0465, Found 397.0467.

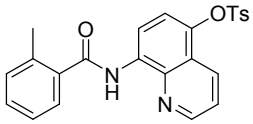
8-(4-methylbenzamido)quinolin-5-yl 4-methylbenzenesulfonate(3h)



White solid, 91% yield, mp 129-130 °C;^{1}H NMR (500 MHz, $CDCl_3$) δ 10.62 (s, 1H), 8.86 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.78 (d, *J* = 8.6 Hz, 1H), 8.40 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.49 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.36-7.31 (m, 4H), 7.03 (d, *J* = 8.6 Hz, 1H), 2.45 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.51, 148.89, 145.83, 142.64, 139.58, 138.85, 134.00, 132.15, 132.02, 131.53,

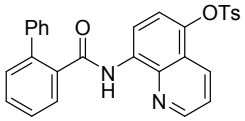
129.98, 129.54, 128.71, 127.33, 123.06, 122.18, 120.00, 115.35, 21.74, 21.55. HRMS (ESI+): Calculated for $C_{24}H_{20}N_2O_4SH$: $[M+H]^+$ 433.1217, Found 433.1219.

8-(2-methylbenzamido)quinolin-5-yl 4-methylbenzenesulfonate(3i)



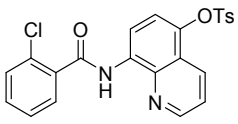
White solid, 92% yield, mp 128-129 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.92 – 8.66 (m, 2H), 8.39 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.37 – 7.28 (m, 4H), 7.04 (d, *J* = 8.6 Hz, 1H), 2.59 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.15, 148.94, 145.84, 139.70, 138.74, 136.75, 136.25, 134.02, 132.16, 131.46, 131.38, 130.53, 130.00, 128.67, 127.21, 126.07, 123.02, 122.20, 119.87, 115.26, 21.74, 20.19. HRMS (ESI+): Calculated for $C_{24}H_{20}N_2O_4SH$: $[M+H]^+$ 433.1217, Found 433.1219.

8-([1,1'-biphenyl]-2-ylcarboxamido)quinolin-5-yl 4-methylbenzenesulfonate(3j)



Yellow solid, 83% yield, mp 167-168 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.65 (d, *J* = 8.6 Hz, 1H), 8.52 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.31 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.89 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.56 (td, *J* = 7.5, 1.4 Hz, 1H), 7.51-7.46 (m, 4H), 7.37 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.85, 148.28, 145.79, 140.35, 139.95, 139.52, 138.38, 135.69, 133.75, 132.21, 131.24, 130.78, 130.72, 129.97, 129.27, 129.00, 128.65, 128.42, 127.70, 127.67, 122.78, 121.92, 119.75, 115.24, 21.73. HRMS (ESI+): Calculated for $C_{29}H_{22}N_2O_4SH$: $[M+H]^+$ 495.1373, Found 495.1378.

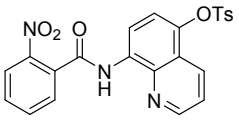
8-(2-chlorobenzamido)quinolin-5-yl 4-methylbenzenesulfonate(3k)



White solid, 80% yield, mp 183-184 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 8.80 (dd, *J* = 4.9, 3.3 Hz, 2H), 8.40 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 3H),

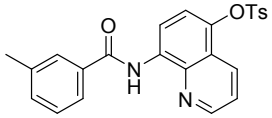
7.48 (dd, *J* = 8.5, 4.2 Hz, 2H), 7.43 (dd, *J* = 12.2, 6.7 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.90, 148.06, 144.86, 138.95, 137.81, 134.40, 132.67, 131.02, 130.72, 130.34, 130.12, 129.57, 129.11, 128.99, 127.67, 126.21, 122.00, 121.25, 118.79, 114.66, 20.74. HRMS (ESI+): Calculated for $C_{23}H_{17}ClN_2O_4SH$: $[M+H]^+$ 453.0671, Found 453.0678.

8-(2-nitrobenzamido)quinolin-5-yl 4-methylbenzenesulfonate(3l)



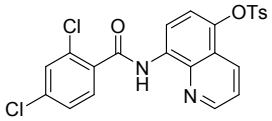
Yellow solid, 72% yield, mp 185-186 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.76 (s, 1H), 8.73 (d, *J* = 8.6 Hz, 1H), 8.41 (dd, *J* = 8.5, 1.6 Hz, 1H), 8.15 (s, 1H), 7.78 (s, 2H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 0.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.32, 149.07, 145.95, 140.24, 138.59, 133.91, 133.39, 131.98, 131.55, 131.00, 130.82, 130.07, 128.71, 128.58, 124.85, 124.79, 122.35, 121.78, 119.82, 115.92, 21.78. HRMS (ESI+): Calculated for $C_{23}H_{17}N_3O_6SH$: $[M+H]^+$ 464.0911, Found 464.0913.

8-(3-methylbenzamido)quinolin-5-yl 4-methylbenzenesulfonate(3m)



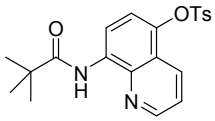
White solid, 89% yield, mp 166-167 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.87 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.79 (d, *J* = 8.6 Hz, 1H), 8.41 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.78, 148.86, 145.84, 139.65, 138.77, 134.84, 134.81, 133.90, 132.83, 132.14, 131.62, 129.98, 128.70, 128.69, 128.07, 124.24, 123.07, 122.18, 119.99, 115.54, 21.73, 21.46. HRMS (ESI+): Calculated for $C_{24}H_{20}N_2O_4SH$: $[M+H]^+$ 433.1217, Found 433.1219.

8-(2,4-dichlorobenzamido)quinolin-5-yl 4-methylbenzenesulfonate(3n)



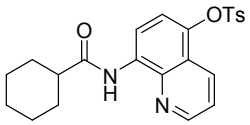
White solid, 75% yield, mp 196-197 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 8.81 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.77 (d, *J* = 8.6 Hz, 1H), 8.40 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.77 (dd, *J* = 8.3, 5.3 Hz, 3H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.49 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.39 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.79, 148.12, 144.88, 139.08, 138.25, 137.77, 136.30, 132.68, 132.47, 131.02, 130.39, 130.27, 129.40, 129.00, 127.65, 126.64, 122.00, 121.30, 118.78, 114.76, 20.74. HRMS (ESI+): Calculated for $C_{23}H_{16}Cl_2N_2O_4SH$: $[M+H]^+$ 487.0281, Found 487.0285.

8-Pivalamidoquinolin-5-yl 4-methylbenzenesulfonate(3o)



Yellow oil, 81% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.84 (d, *J* = 4.0 Hz, 1H), 8.66 (d, *J* = 8.6 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.49 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 1H), 2.47 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.33, 148.89, 145.78, 139.34, 138.91, 134.04, 132.15, 131.37, 129.96, 128.70, 122.96, 122.07, 119.92, 114.97, 40.37, 27.68, 21.73. HRMS (ESI+): Calculated for $C_{21}H_{22}N_2O_4SH$: $[M+H]^+$ 399.1373, Found 399.1379.

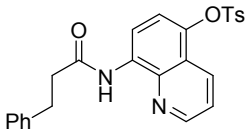
8-(cyclohexanecarboxamido)quinolin-5-yl 4-methylbenzenesulfonate(3p)



White solid, 88% yield, mp 122-123 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.80 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.64 (d, *J* = 8.6 Hz, 1H), 8.36 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 1H), 2.43 (s, 3H), 2.06 (dd, *J* = 13.6, 1.8 Hz, 2H), 1.94 – 1.81 (m, 2H),

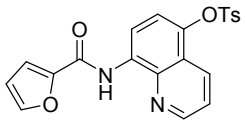
1.78 – 1.68 (m, 1H), 1.61 (ddd, *J* = 24.7, 12.4, 3.1 Hz, 2H), 1.45 – 1.27 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.88, 148.74, 145.77, 139.29, 138.54, 133.96, 132.12, 131.37, 129.94, 128.65, 122.92, 122.06, 119.90, 115.15, 46.81, 29.71, 25.75, 25.70, 21.70. HRMS (ESI+): Calculated for $C_{23}H_{24}N_2O_4SH$: $[M+H]^+$ 425.1530, Found 425.1534.

8-(3-phenylpropanamido)quinolin-5-yl 4-methylbenzenesulfonate(3q)



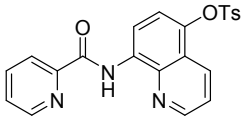
White solid, 87% yield, mp 115-116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.76 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.63 (d, *J* = 8.6 Hz, 1H), 8.36 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.45 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.33 – 7.26 (m, 6H), 7.23 – 7.17 (m, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 3.16 – 3.10 (m, 2H), 2.90 – 2.84 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.80, 148.67, 145.80, 140.60, 139.46, 138.31, 133.68, 132.17, 131.48, 129.96, 128.66, 128.58, 128.38, 126.30, 122.94, 122.09, 119.89, 115.34, 39.61, 31.38, 21.72. HRMS (ESI+): Calculated for $C_{25}H_{22}N_2O_4SH$: $[M+H]^+$ 447.1373, Found 447.1376.

8-(furan-2-carboxamido)quinolin-5-yl 4-methylbenzenesulfonate(3r)



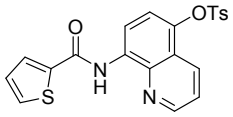
White solid, 91% yield, mp 161-162 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.87 (d, *J* = 4.1 Hz, 1H), 8.72 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.61 (s, 1H), 7.48 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.30 (dd, *J* = 9.0, 5.8 Hz, 3H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.58 (dd, *J* = 3.4, 1.7 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.33, 149.03, 148.07, 145.82, 144.72, 139.76, 138.72, 133.48, 132.15, 131.37, 129.96, 128.65, 123.01, 122.21, 119.87, 115.47, 115.44, 112.51, 21.70. HRMS (ESI+): Calculated for $C_{21}H_{16}N_2O_5SH$: $[M+H]^+$ 409.0853, Found 409.0858.

8-(nicotinamido)quinolin-5-yl 4-methylbenzenesulfonate(3s)



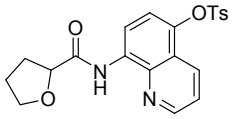
White solid, 83% yield, mp 184-185°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.19 (s, 1H), 8.95 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.87 (d, *J* = 8.6 Hz, 1H), 8.78 – 8.74 (m, 1H), 8.40 – 8.28 (m, 2H), 7.91 (td, *J* = 7.7, 1.6 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.77, 150.23, 149.32, 148.57, 145.76, 139.87, 139.47, 137.51, 133.80, 132.17, 131.07, 129.93, 128.67, 126.48, 123.04, 122.51, 122.11, 119.82, 115.51, 21.70. HRMS (ESI+): Calculated for $C_{22}H_{17}N_3O_4SH$: $[M+H]^+$ 420.1013, Found 420.1016.

8-(thiophene-2-carboxamido)quinolin-5-yl 4-methylbenzenesulfonate(3t)



White solid, 82% yield, mp 159-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.79 (d, *J* = 2.7 Hz, 1H), 8.62 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 3.7 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 5.0 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.12 – 7.10 (m, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.02, 147.97, 144.84, 138.63, 138.60, 137.58, 132.58, 130.99, 130.46, 130.23, 128.97, 127.67, 127.65, 126.93, 122.01, 121.25, 118.93, 114.27, 20.73. HRMS (ESI+): Calculated for $C_{21}H_{16}N_2O_4S_2H$: $[M+H]^+$ 425.0624, Found 425.0627.

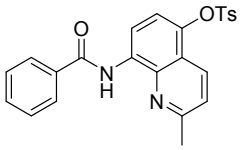
8-(tetrahydrofuran-2-carboxamido)quinolin-5-yl 4-methylbenzenesulfonate(3u)



White solid, 87% yield, mp 103-104 °C;^{1}H NMR (500 MHz, $CDCl_3$) δ 10.83 (s, 1H), 8.86 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.66 (d, *J* = 8.6 Hz, 1H), 8.35 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 1H), 4.59 (dd, *J* = 8.4, 5.7 Hz, 1H), 4.26 – 4.12 (m, 1H), 4.05 (d, *J* = 8.2 Hz, 1H), 2.44 (s, 3H), 2.42 – 2.36 (m, 1H), 2.29 – 2.18 (m, 1H), 1.98 (dd, J = 14.3, 7.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.23, 149.17, 145.78, 139.82, 138.94,

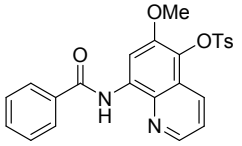
133.22, 132.15, 131.25, 129.94, 128.64, 122.99, 122.08, 119.73, 115.42, 79.09, 69.78, 30.42, 25.54, 21.70. HRMS (ESI+): Calculated for $C_{21}H_{20}N_2O_5SH$: $[M+H]^+$ 413.1166, Found 413.1168.

8-benzamido-2-methylquinolin-5-yl 4-methylbenzenesulfonate(3v)



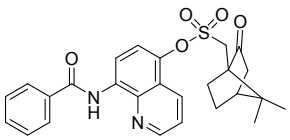
White solid, 80% yield, mp 127-128 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.73 (d, *J* = 8.6 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 6.8 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 1H), 2.77 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.40, 157.24, 144.74, 138.83, 137.37, 133.95, 132.18, 131.08, 130.97, 130.55, 128.93, 127.86, 127.69, 126.23, 122.10, 120.15, 117.84, 114.34, 24.34, 21.68. HRMS (ESI+): Calculated for $C_{24}H_{20}N_2O_4SH$: $[M+H]^+$ 433.1217, Found 433.1219.

8-Benzamido-6-methoxyquinolin-5-yl 4-methylbenzenesulfonate(3w)



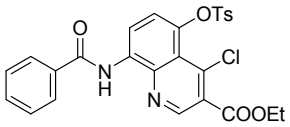
White solid, 95% yield, mp 145-146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.86 (s, 1H), 8.74 (d, *J* = 4.2 Hz, 1H), 8.46 (d, *J* = 7.1 Hz, 1H), 8.07 (d, *J* = 6.9 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 3.68 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.66, 148.70, 145.47, 144.18, 133.81, 133.57, 132.73, 132.59, 131.20, 129.97, 128.40, 127.92, 127.68, 126.26, 125.01, 123.44, 121.78, 103.32, 55.06, 21.68. HRMS (ESI+): Calculated for $C_{24}H_{20}N_2O_5SH$: $[M+H]^+$ 449.1166, Found 449.1168.

8-Benzamidoquinolin-5-yl((1R,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate(3y)



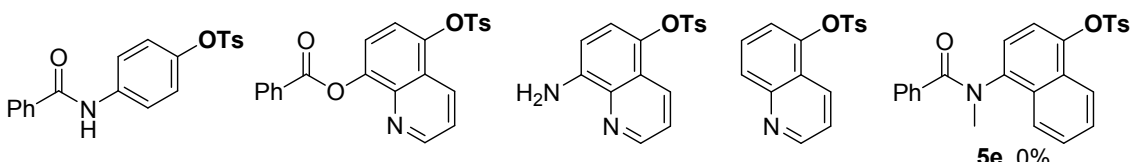
White solid, 88% yield, mp 124-125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.68 (s, 1H), 8.96 (d, *J* = 8.6 Hz, 1H), 8.90 (dd, *J* = 4.1, 1.2 Hz, 1H), 8.59 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.08 (d, *J* = 7.1 Hz, 2H), 7.64-7.55 (m, 5H), 4.00 (d, *J* = 14.9 Hz, 1H), 3.37 (d, *J* = 14.9 Hz, 1H), 2.65 – 2.53 (m, 1H), 2.50 – 2.40 (m, 1H), 2.17 (t, *J* = 4.5 Hz, 1H), 2.16 – 2.06 (m, 1H), 2.00 (d, *J* = 18.5 Hz, 1H), 1.82-1.76 (m, 1H), 1.52-1.46(m, 1H), 1.18 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_{33}$) δ 213.80, 165.38, 148.87, 139.03, 138.83, 134.73, 133.86, 131.93, 131.63, 128.74, 127.23, 123.01, 122.38, 119.80, 115.73, 58.15, 48.27, 47.93, 42.83, 42.37, 26.79, 25.15, 19.82, 19.63. HRMS (ESI+): Calculated for $C_{26}H_{26}N_2O_5SH$: $[M+H]^+$ 479.1635, Found 479.1638.

Ethyl 8-benzamido-4-chloro-5-(tosyloxy)quinoline-3-carboxylate(3z)



White solid, 65% yield, mp 168-170 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.96 (d, *J* = 1.9 Hz, 1H), 8.93 – 8.88 (m, 1H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.79 – 7.74 (m, 2H), 7.61 (d, *J* = 6.1 Hz, 1H), 7.56 (t, *J* = 6.8 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 1H), 4.54 – 4.48 (m, 2H), 2.47 (s, 3H), 1.49 – 1.44 (m, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 165.55, 164.56, 147.61, 145.88, 140.51, 140.41, 139.31, 134.55, 132.41, 132.30, 129.93, 128.96, 128.92, 127.84, 127.29, 127.21, 123.53, 120.87, 117.45, 62.52, 21.77, 14.22. HRMS (ESI+): Calculated for $C_{26}H_{21}ClN_2O_6SH$: $[M+H]^+$ 525.0882, Found 525.0885.

The exploration of the analogous substrates



5a, 0% **5b**, 0% **5c**, 0% **5d**, 0% **5e**, 0%

4. X-ray Crystal Data for 3y and 3z

Crystals of **3y** ($C_{26}H_{26}N_2O_5S$) and **3z** ($C_{26}H_{21}ClN_2O_6S$) were recrystallized from PE/AcOEt. The single faint yellow transparent granular crystal which was suitable for X-ray diffraction measurements was mounted on a glass fiber. Unit cell measurements and intensity data collections were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo Ka. The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL-97 program suite. Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. The obtained crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 1515409 (**3u**, CCDC NO.); 1515410 (**3v**, CCDC NO.) The crystallographic data and refinement parameters of them are listed in **Table S1-2**.

Table S1. Crystallographic data and structure refinement for **3y**

Empirical formula	$C_{26}H_{26}N_2O_5S$
Formula weight	478.55
Temperature, K	296.17
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	P21
Hall group	P 2yb
a, *b*, *c*, Å	8.7588(12), 15.745(2), 17.316(2)
α, *β*, *γ*, °	90.00, 99.308(2), 90.00
Volume, Å^3	2356.6(6)
Z	4
Calculated density, Mg/m^3	1.349
Absorption coefficient, mm^{-1}	0.178
F (000)	1008

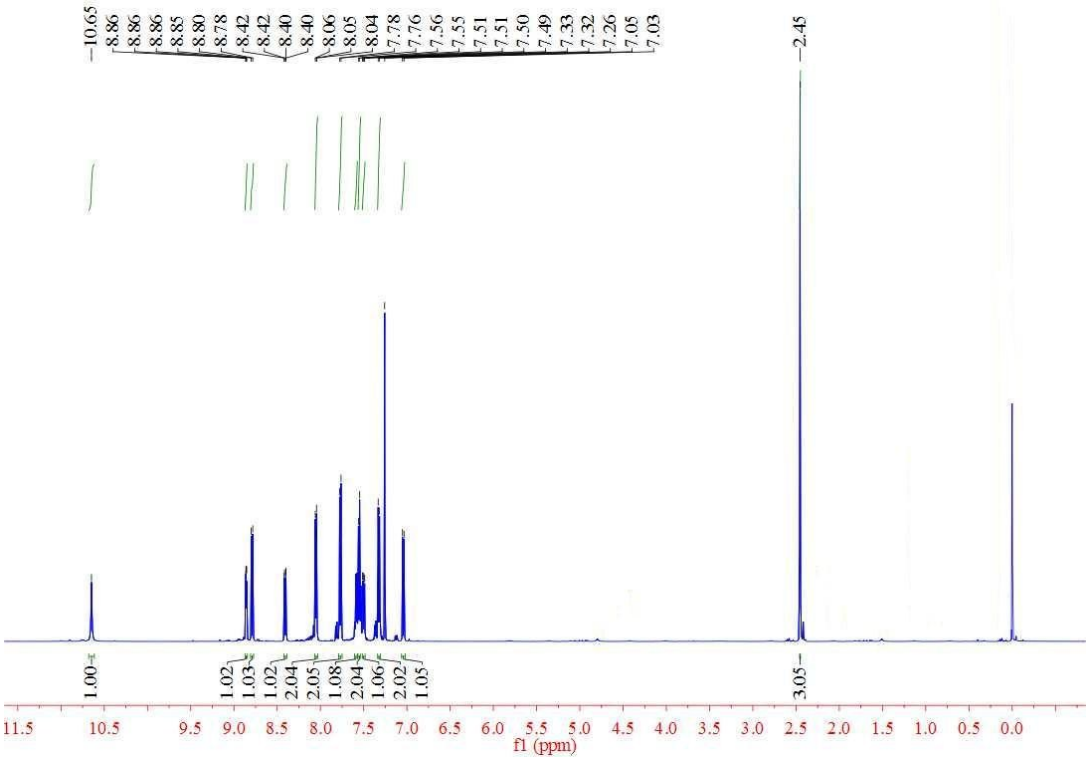
Theta range for data collection, ^{o}	1.19 to 25.10
Limiting indices	-10<=h<=10, -18<=k<=18, -20<=l<=20
Data / restraints / parameters	8330/1/613
Goodness of fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0455 , wR2 = 0.1190
R indices (all data)	R1 = 0.0643 , wR2 = 0.1417

Table S2. Crystallographic data and structure refinement for **3z**

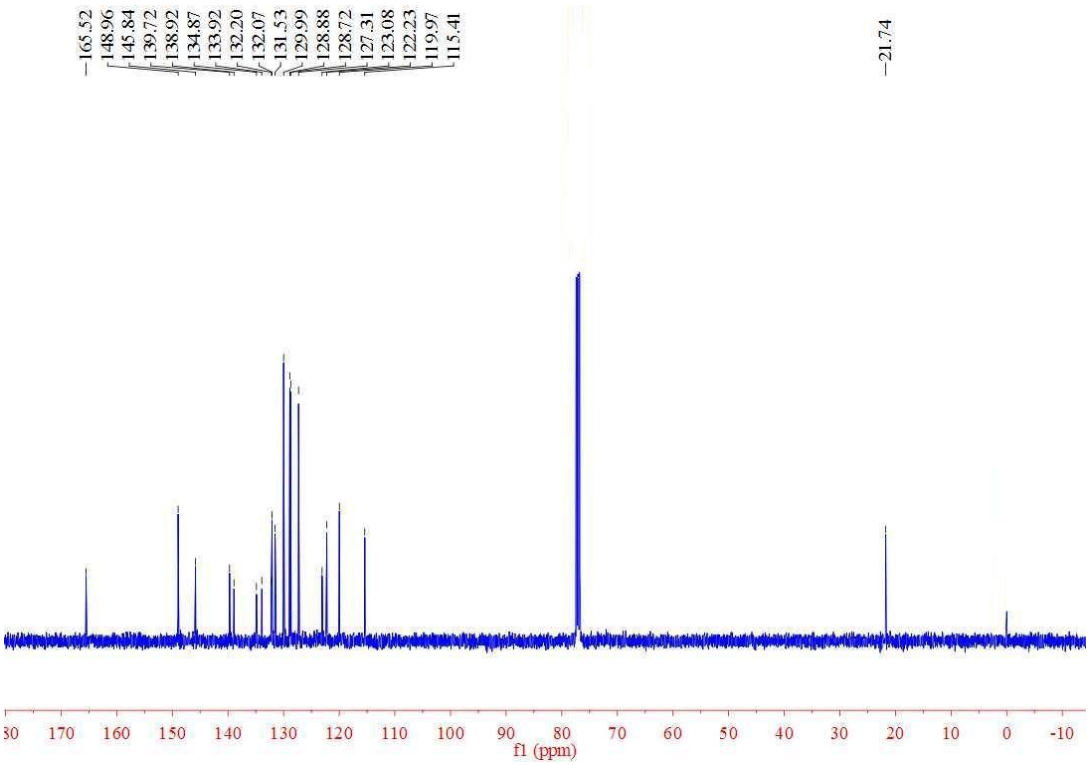
Empirical formula	$C_{26}H_{21}ClN_2O_6S$
Formula weight	524.96
Temperature, K	296
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	P21/n
Hall group	-P 2yn
a, *b*, *c*, Å	8.9158(9), 9.1950(9), 29.183(3)
α, β, γ, ^{o}	90.00, 95.779(2), 90.00
Volume, Å^3	2380.3(4)
Z	4
Calculated density, Mg/m^3	1.465
Absorption coefficient, mm^{-1}	0.295
F (000)	1088
Theta range for data collection, ^{o}	1.40 to 25.10
Limiting indices	-10<=h<=9, -10<=k<=10, -34<=l<=32
Data / restraints / parameters	4235/0/335
Goodness of fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1186
R indices (all data)	R1 = 0.0590, wR2 = 0.1385

5. Copies of ^{1}H and ^{13}C NMR Spectra

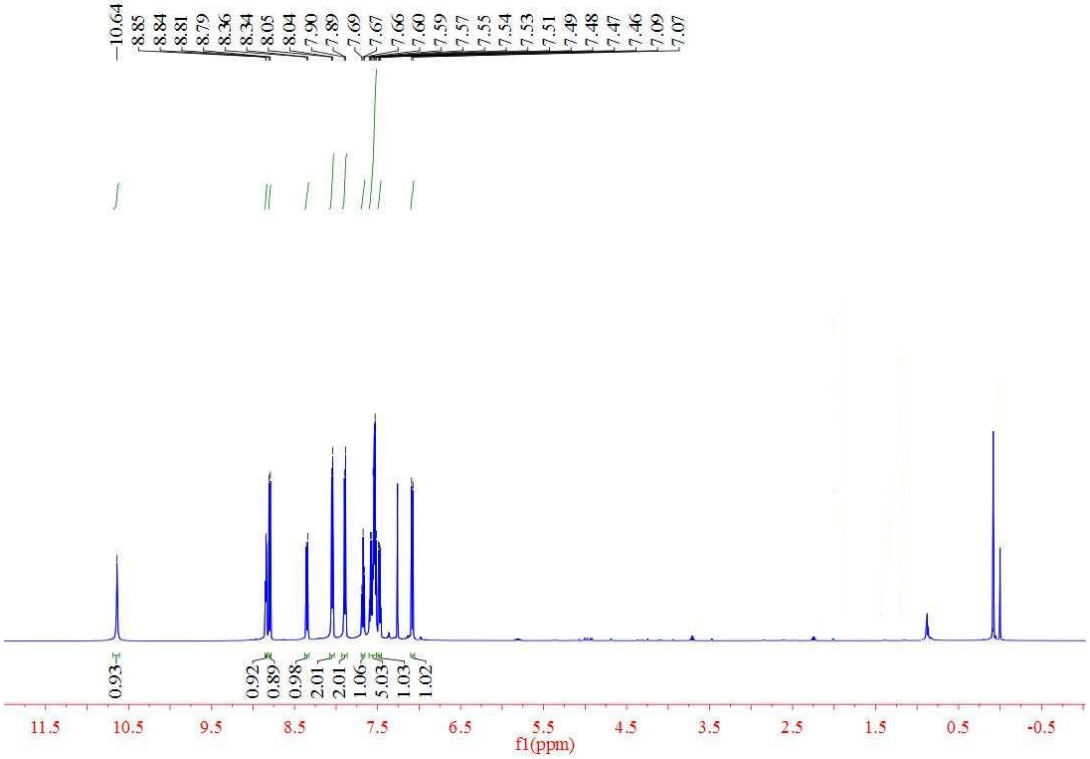
3a, ^{1}H NMR



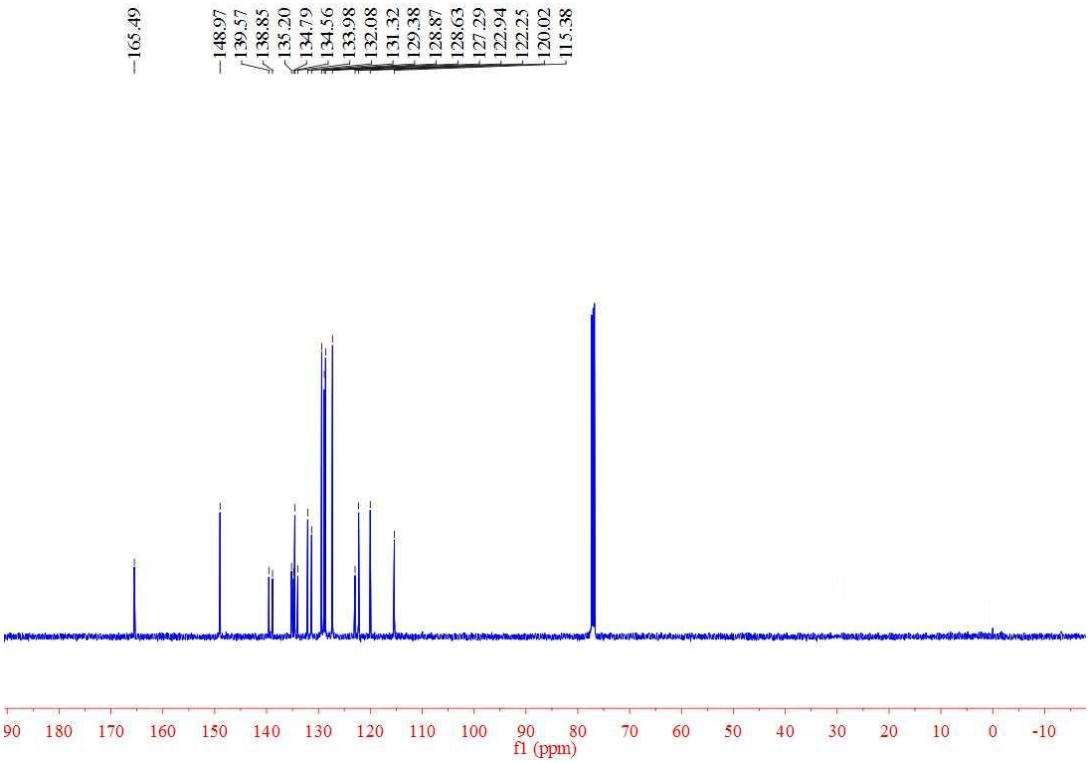
3a, ^{13}C NMR



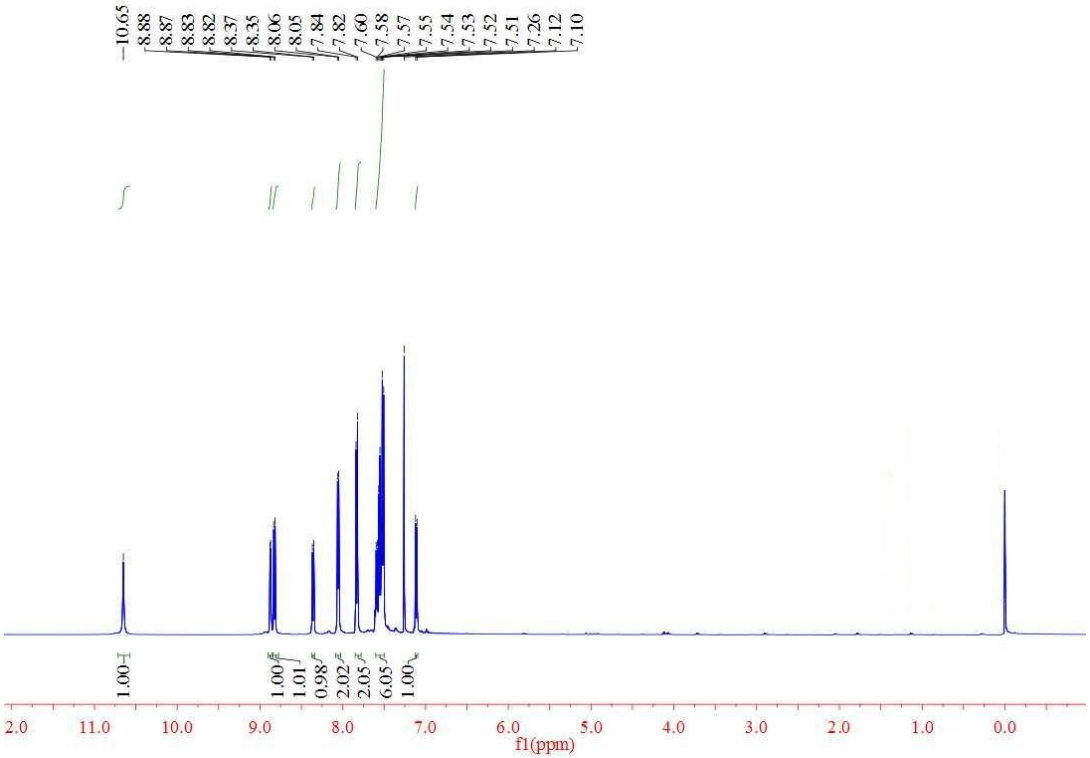
3b, ^{1}H NMR



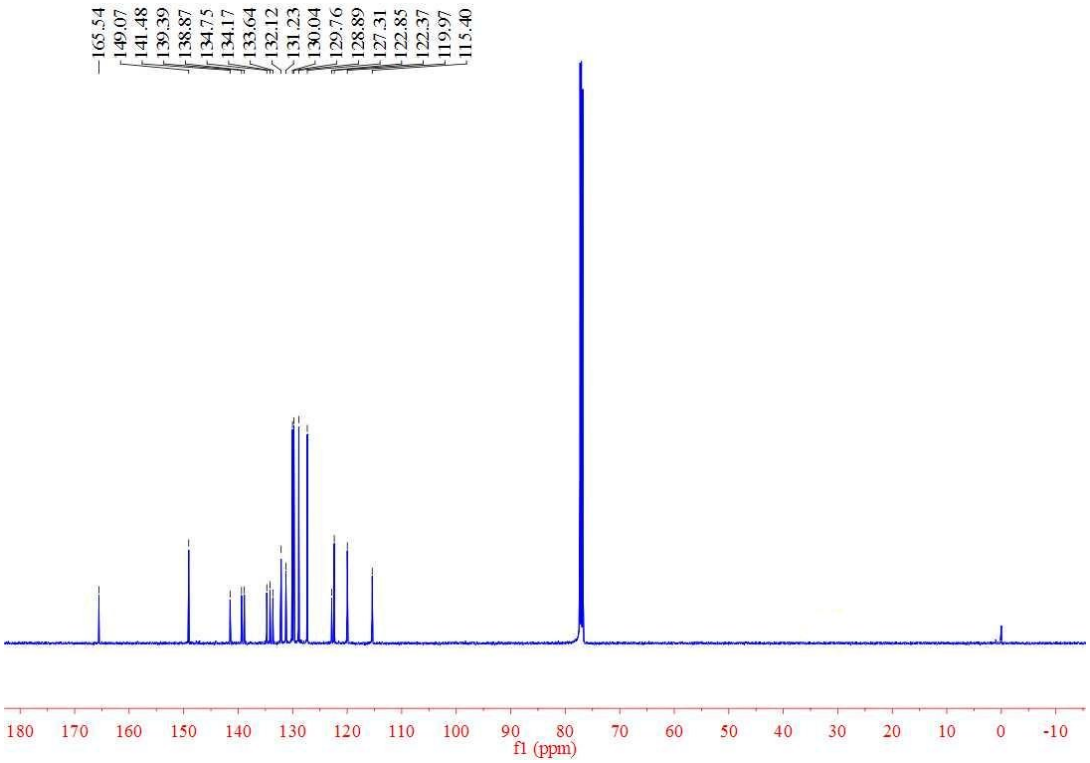
3b, ^{13}C NMR



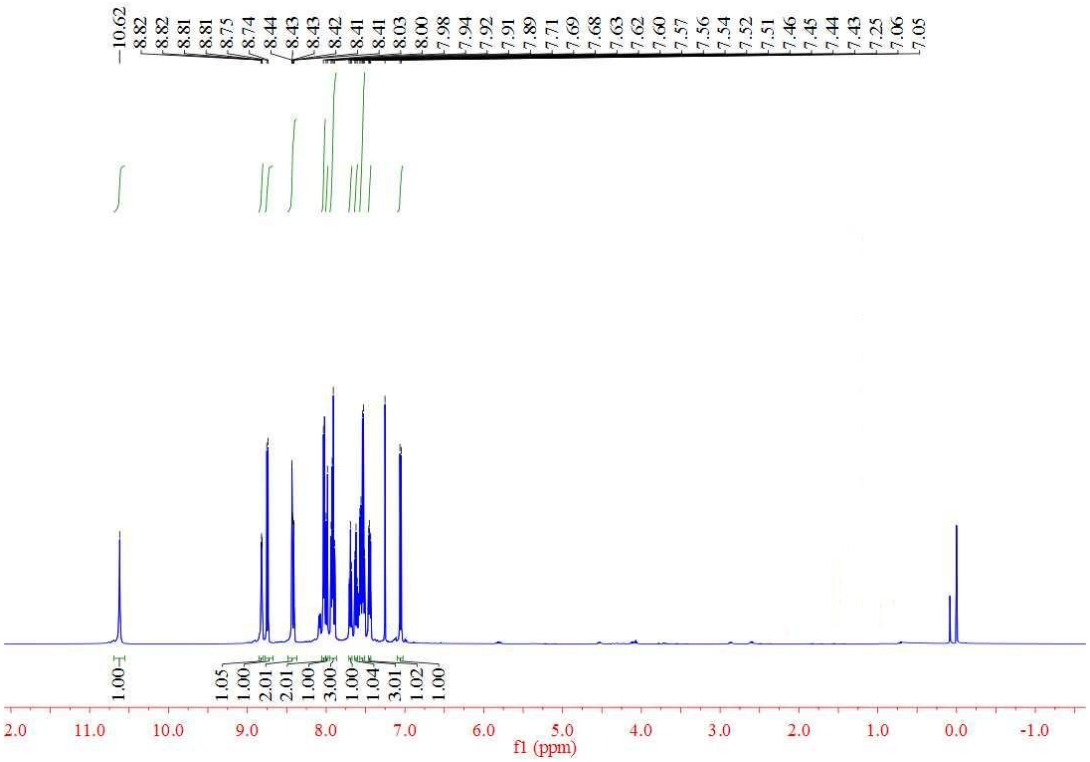
3c, ^{1}H NMR



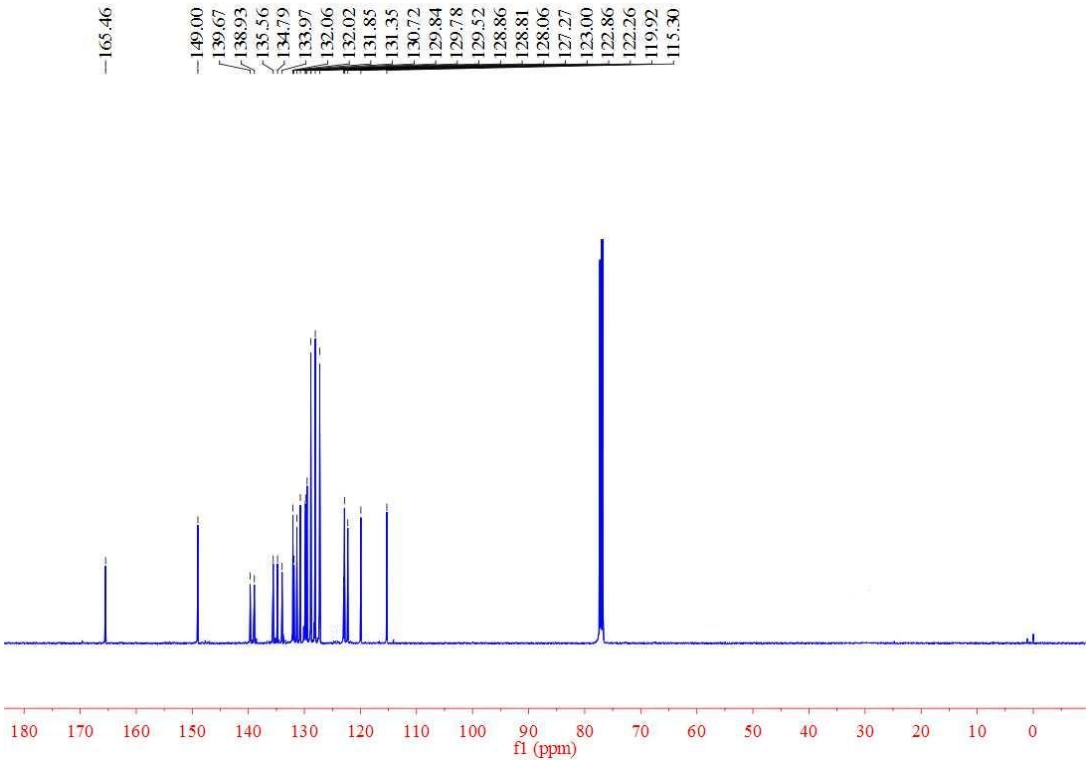
3c, ^{13}C NMR



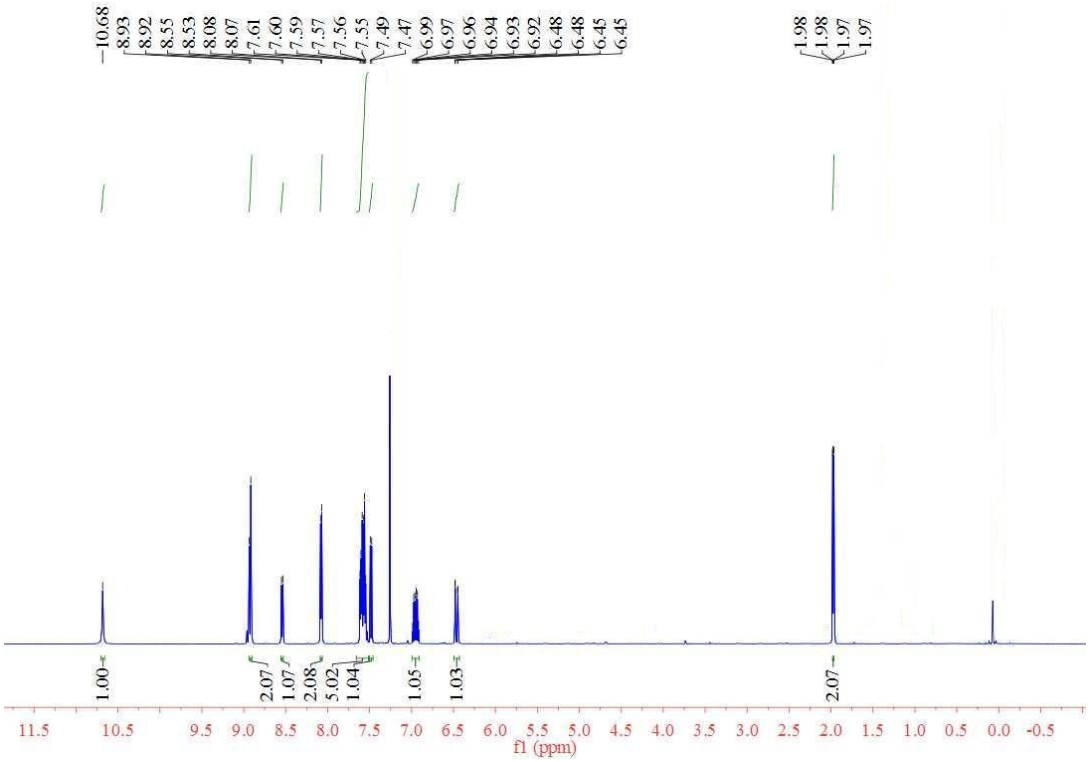
3d, ^{1}H NMR



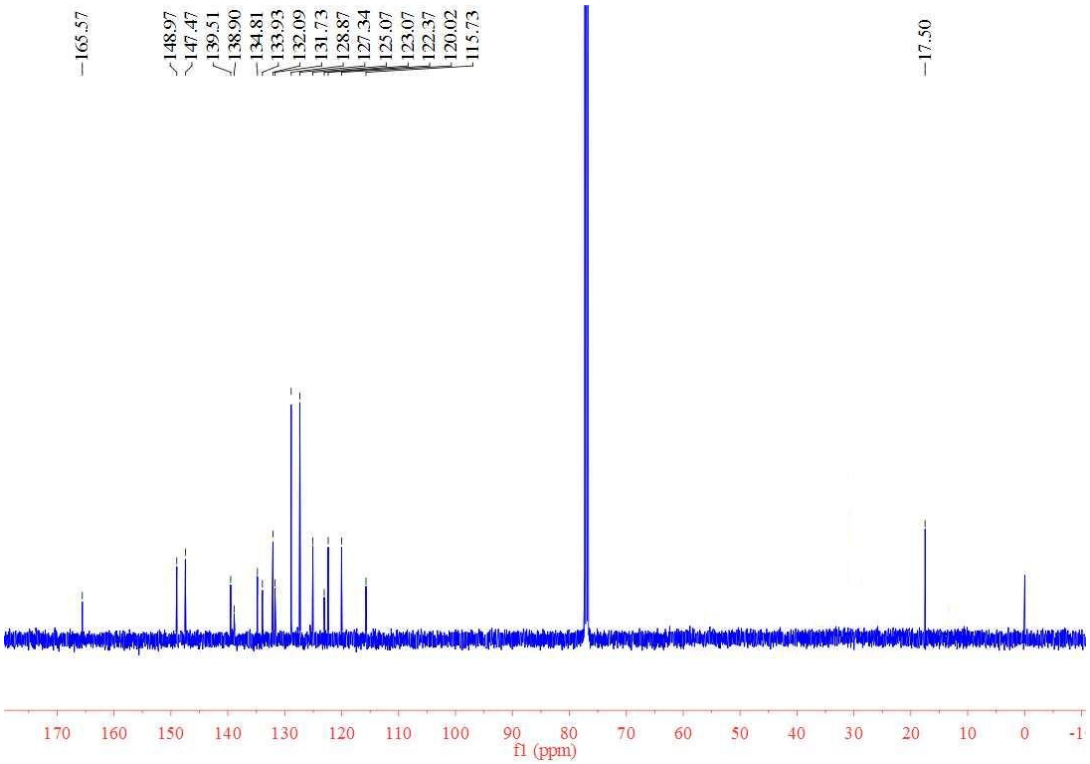
3d, ^{13}C NMR



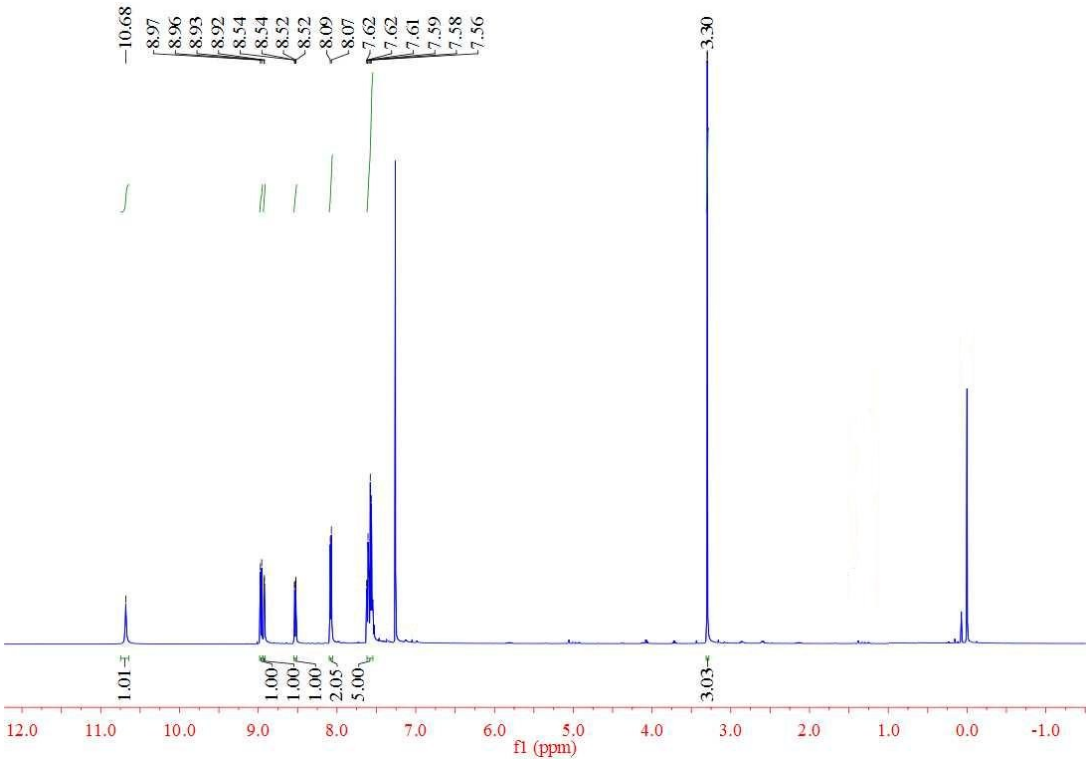
3e, ^{1}H NMR



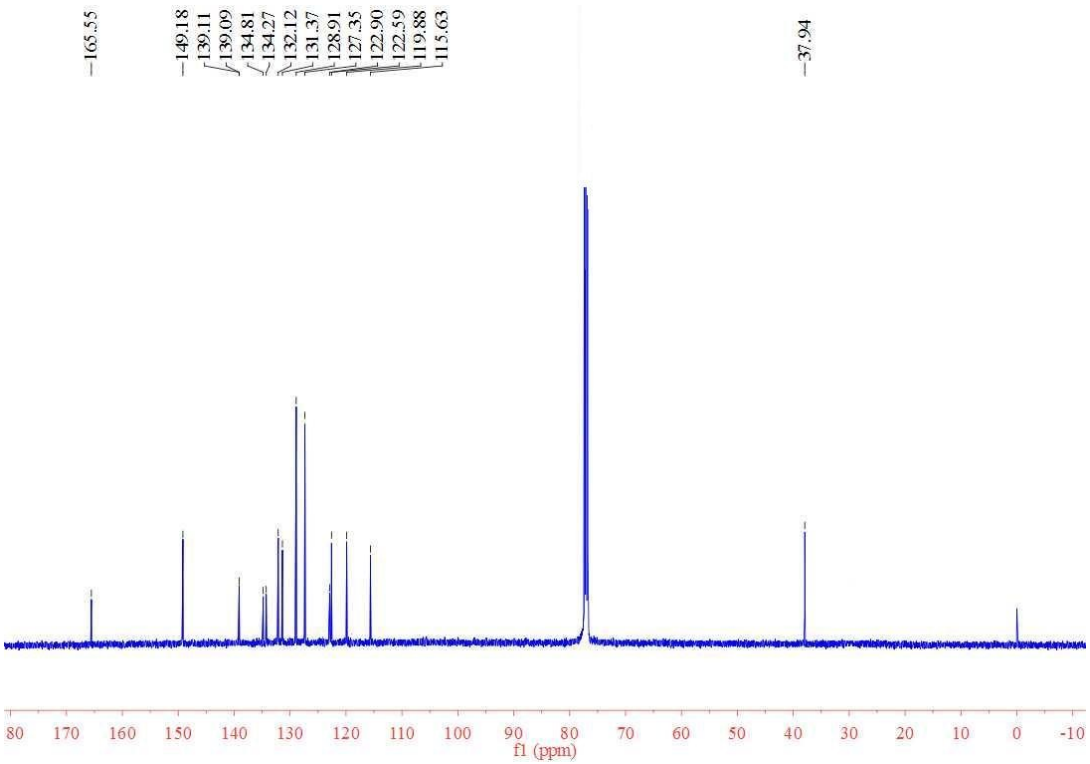
3e, ^{13}C NMR



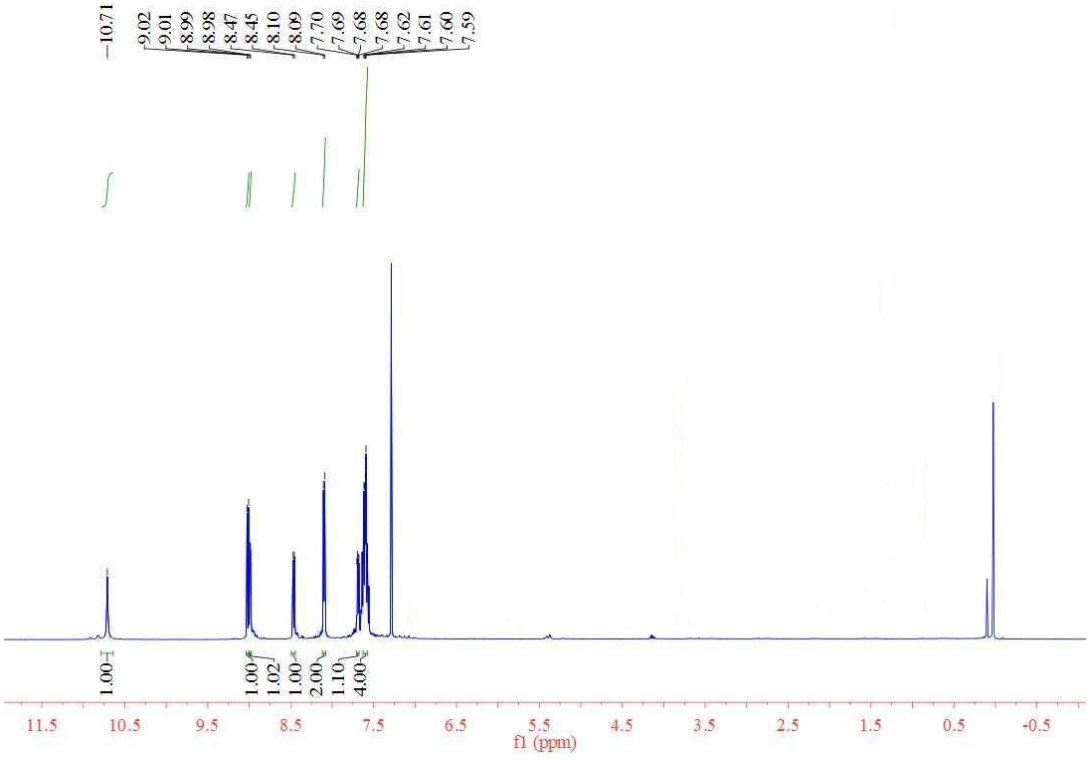
3f, ^{1}H NMR



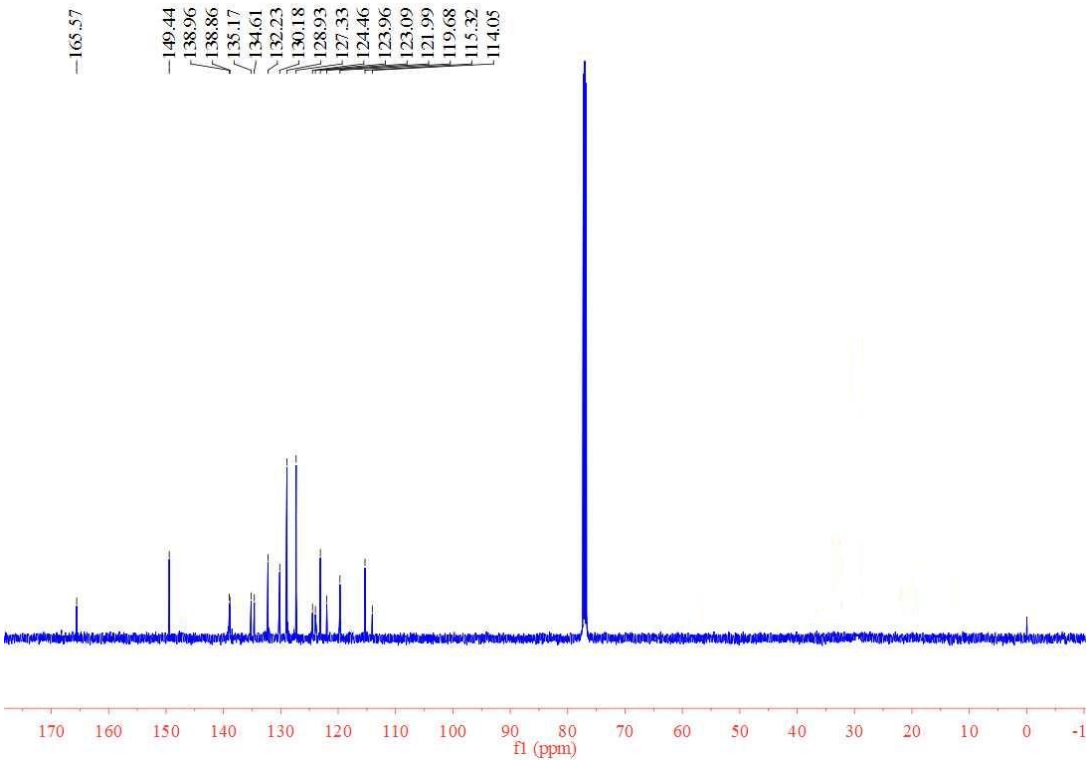
3f, ^{13}C NMR



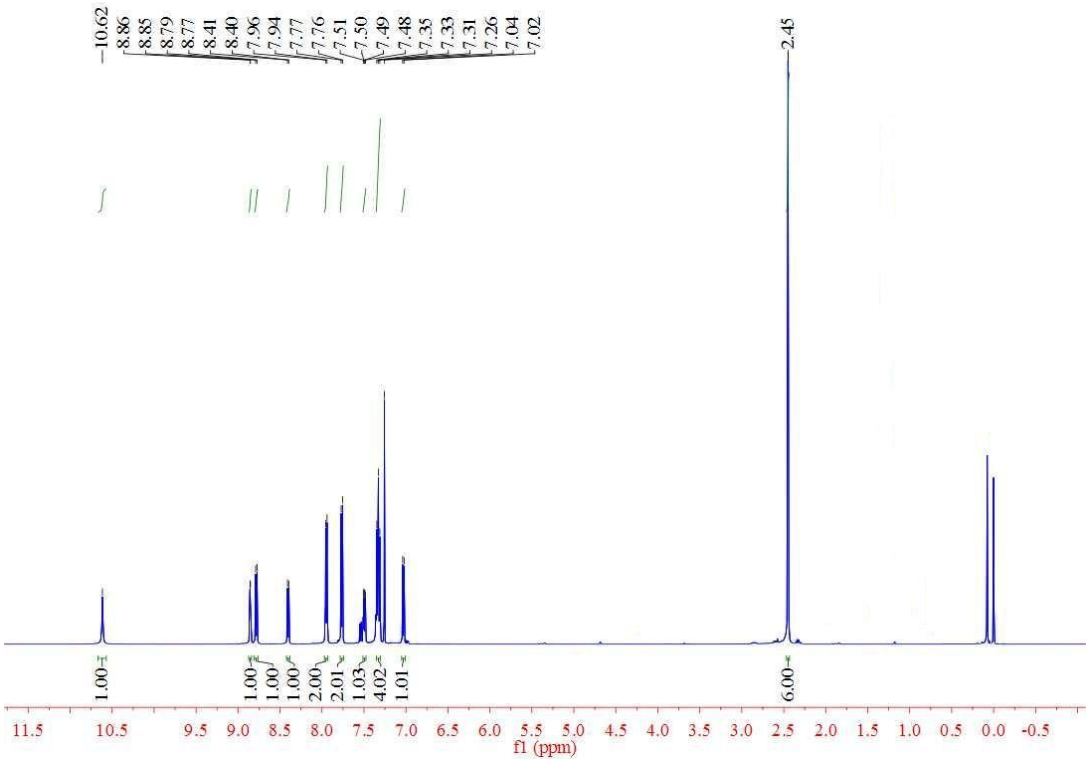
3g, ^{1}H NMR



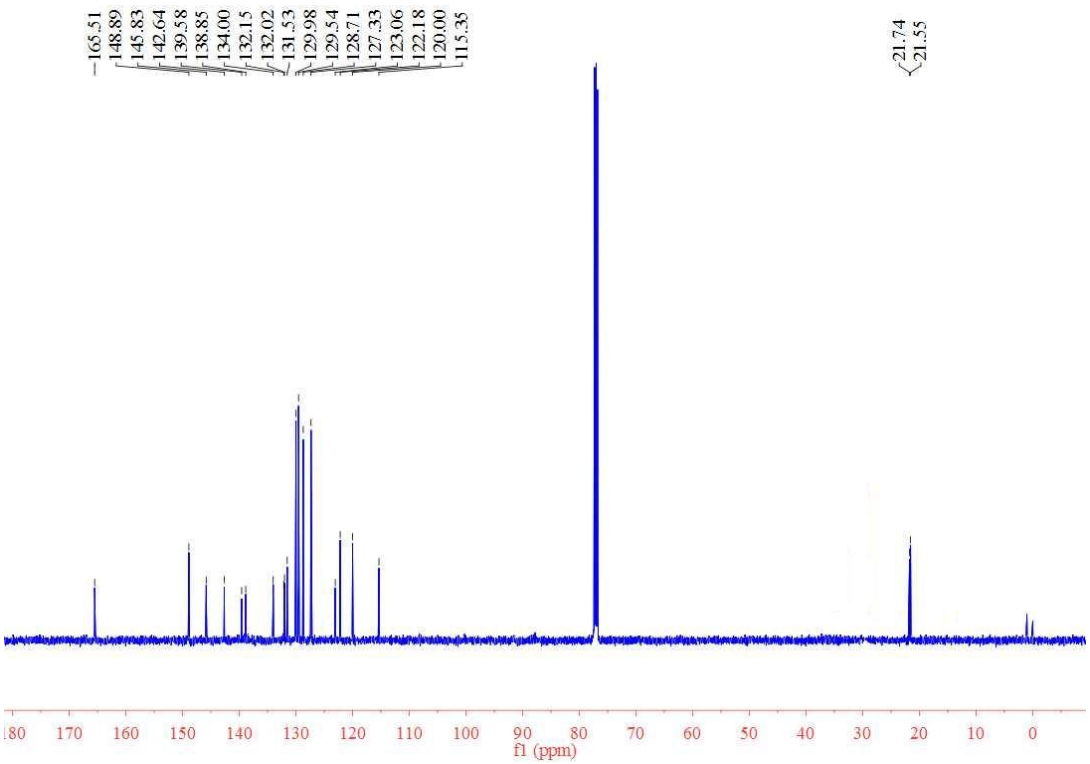
3g, ^{13}C NMR



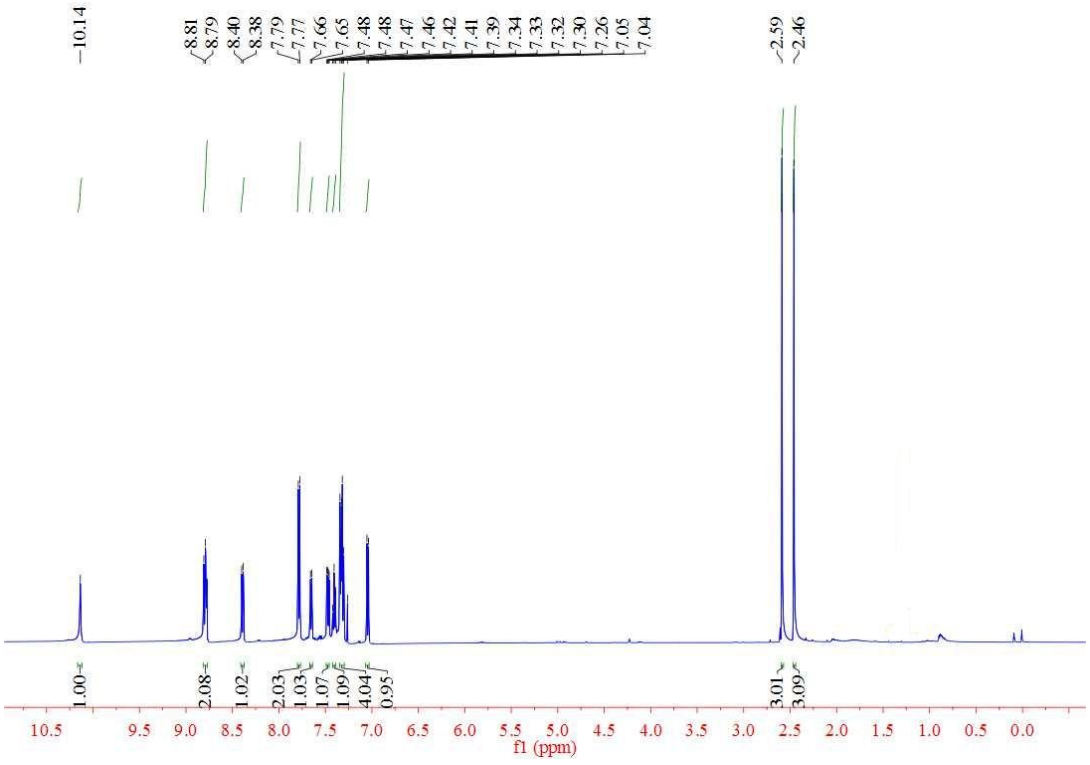
3h, ^{1}H NMR



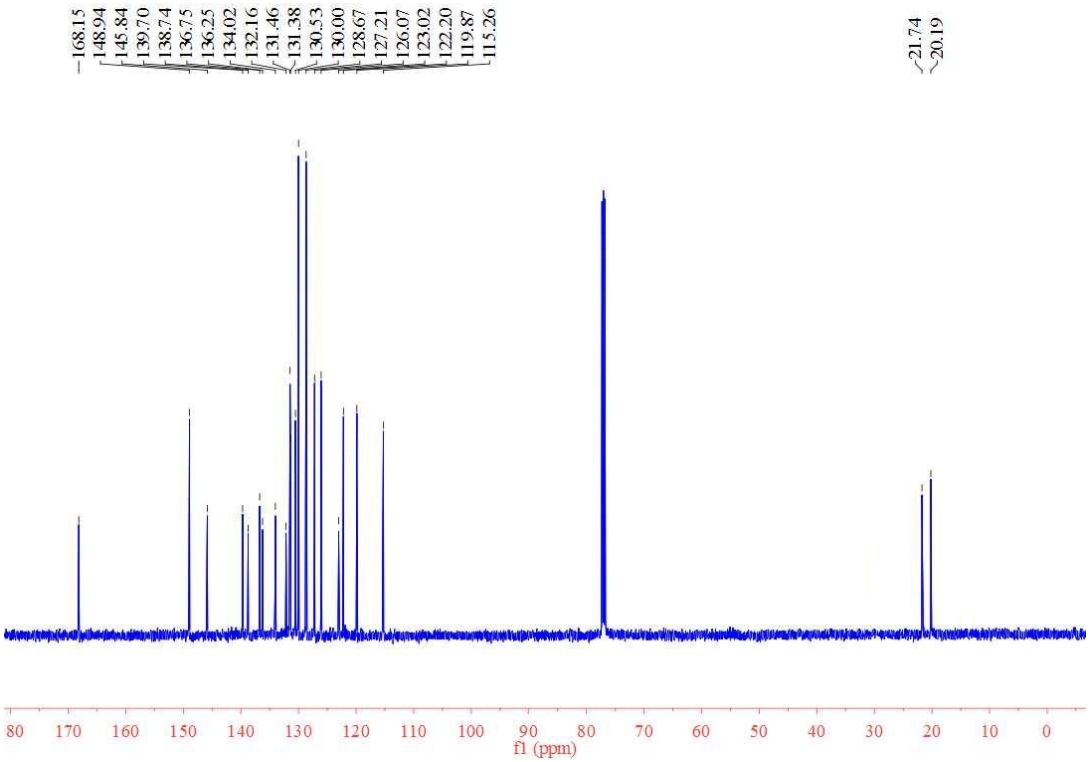
3h, ^{13}C NMR



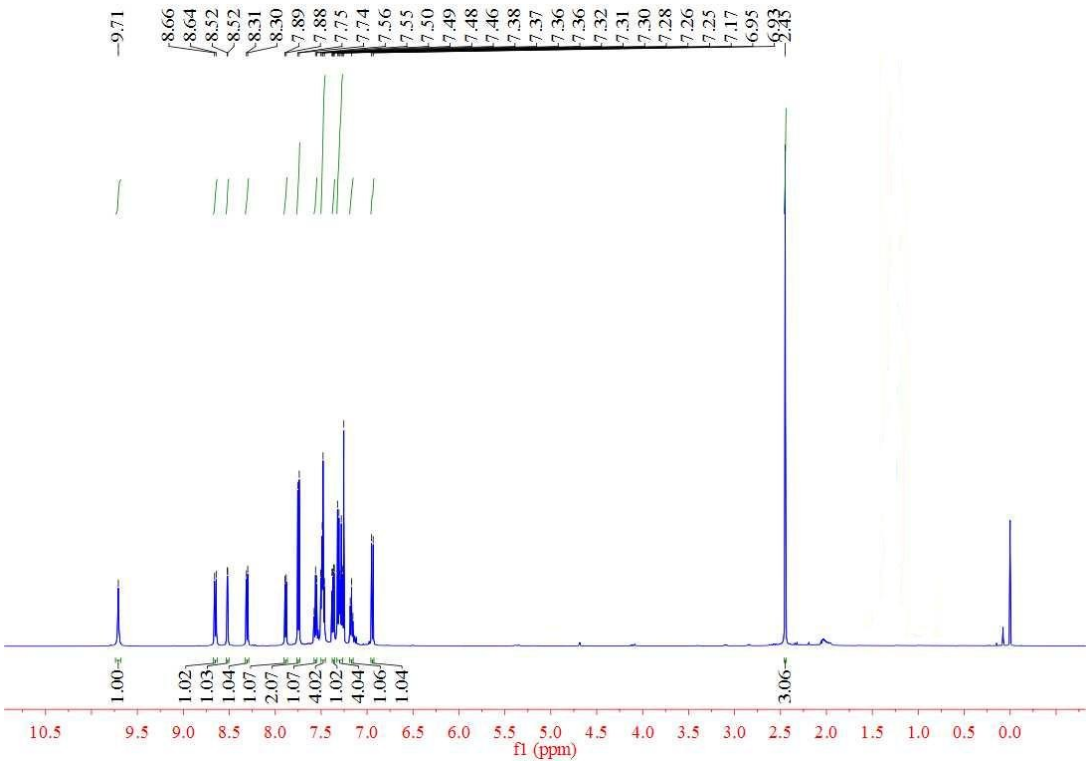
3i, ^{1}H NMR



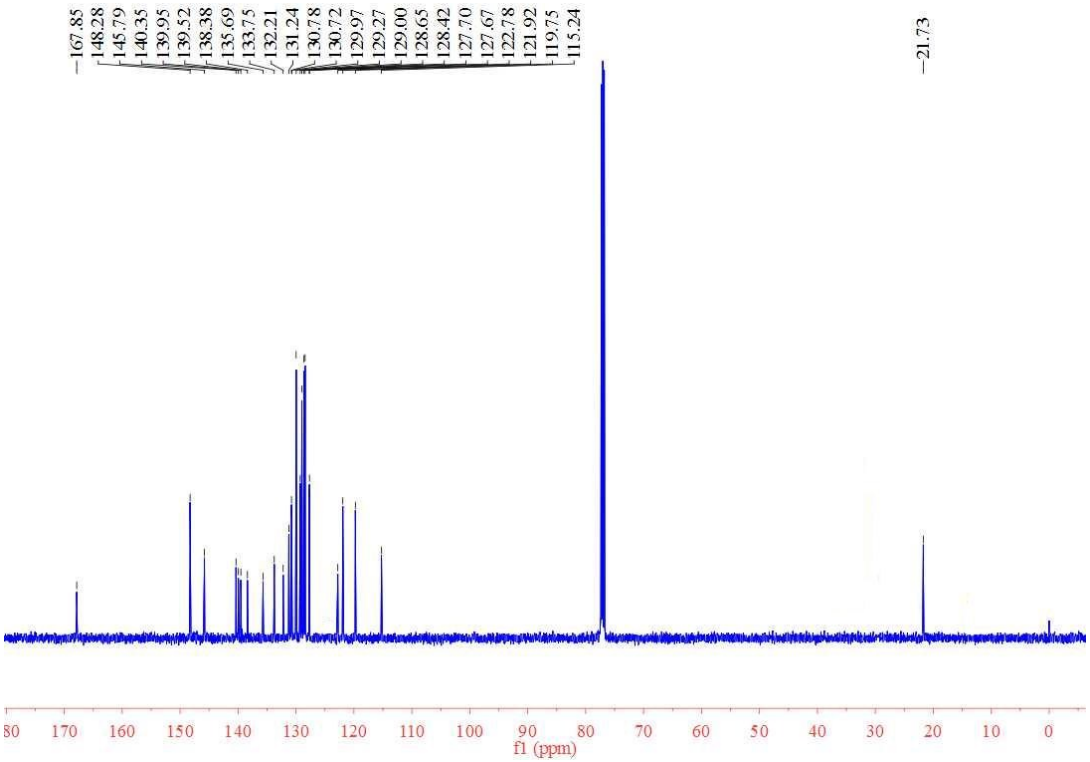
3i, ^{13}C NMR



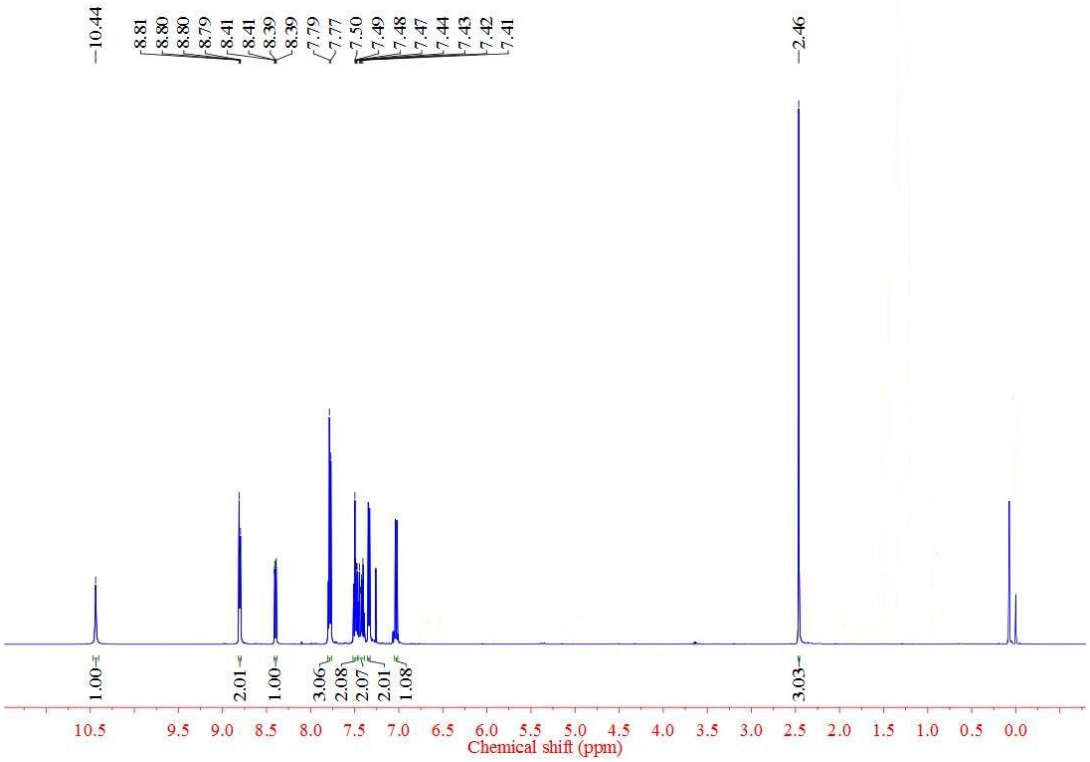
3j, ^{1}H NMR



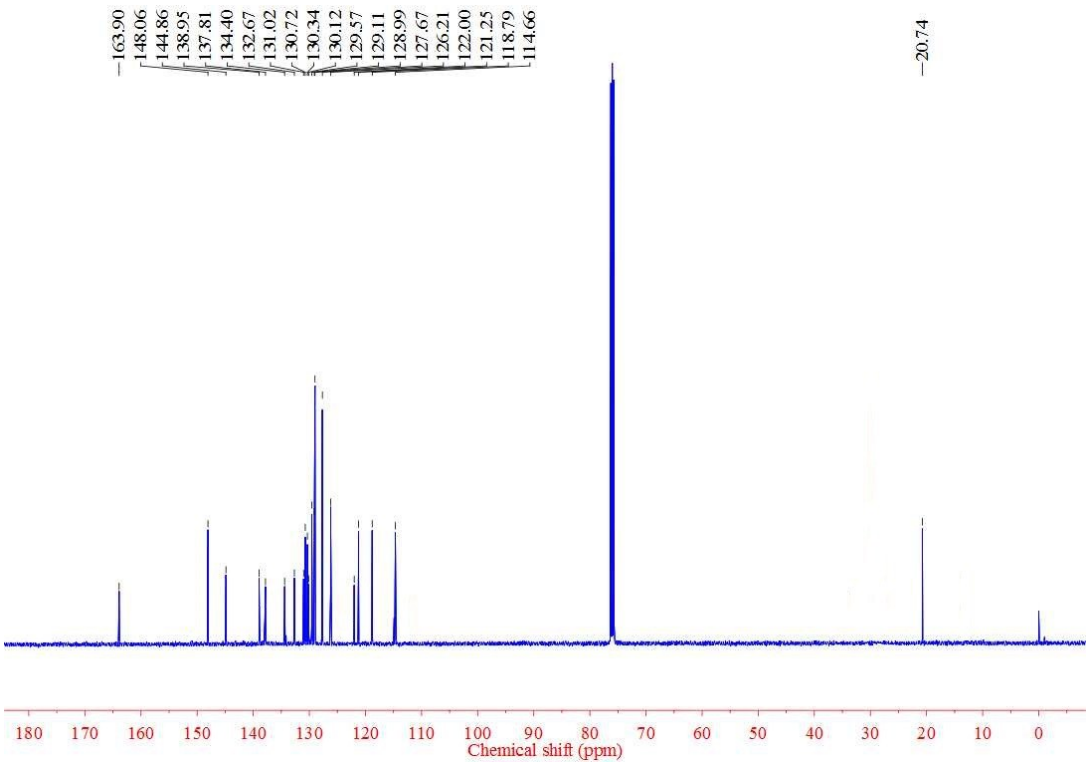
3j, ^{13}C NMR



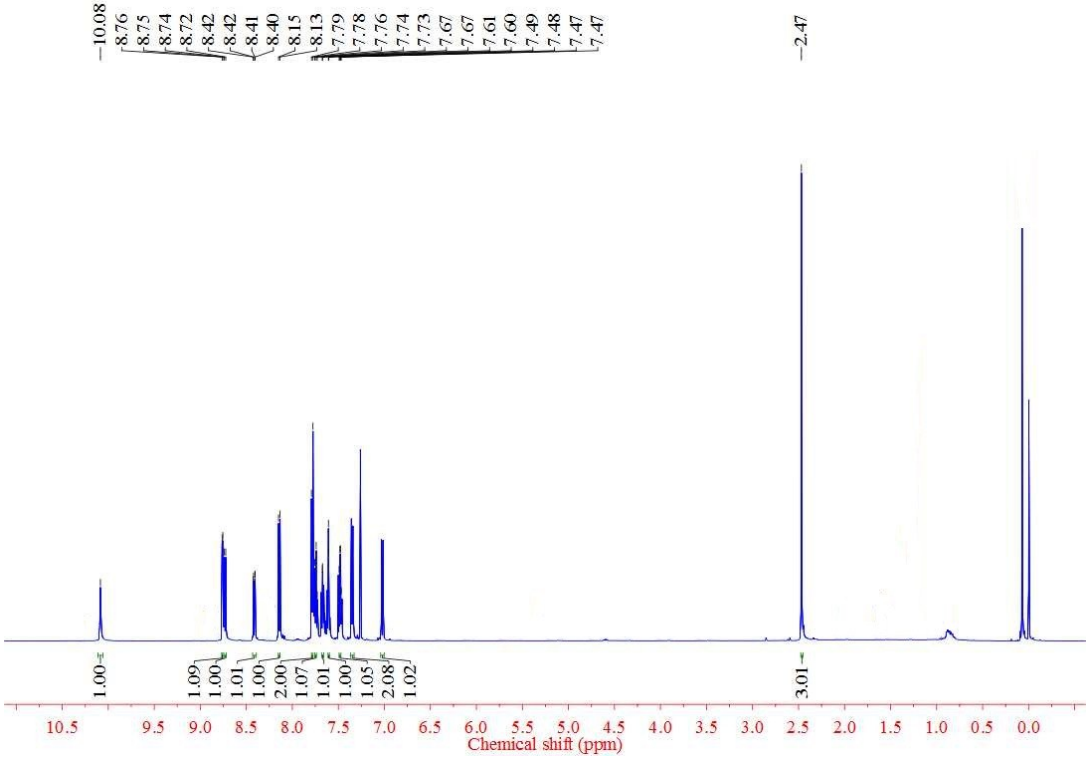
3k, ^{1}H NMR



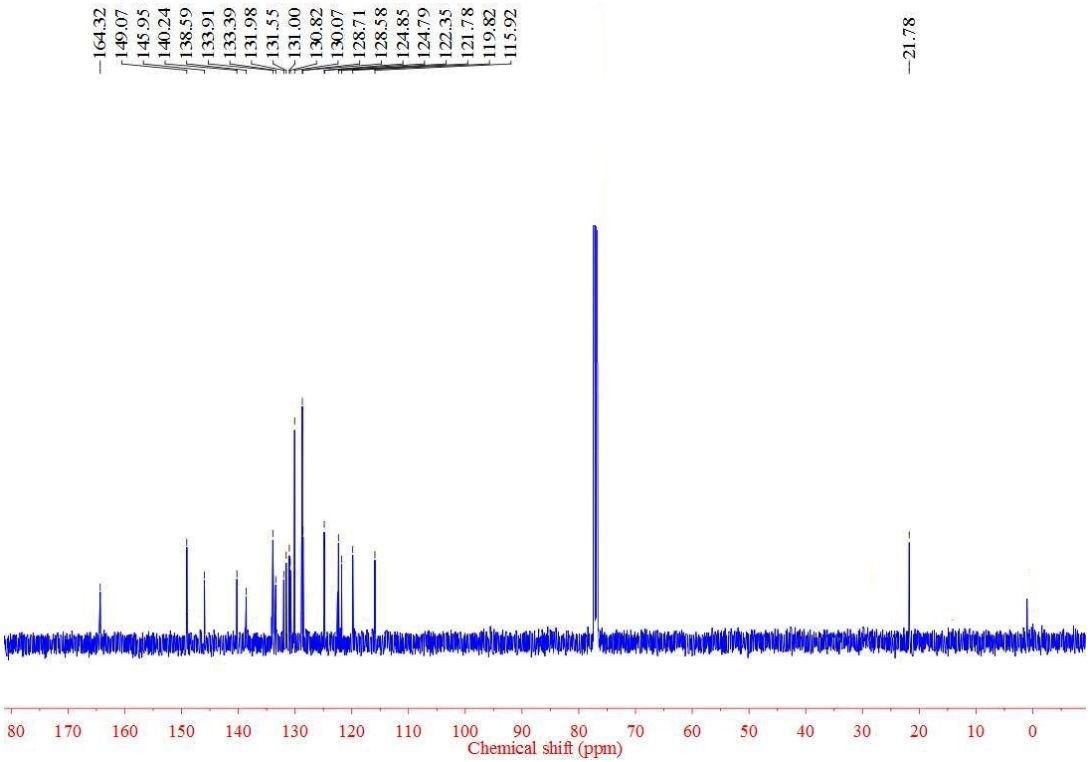
3k, ^{13}C NMR



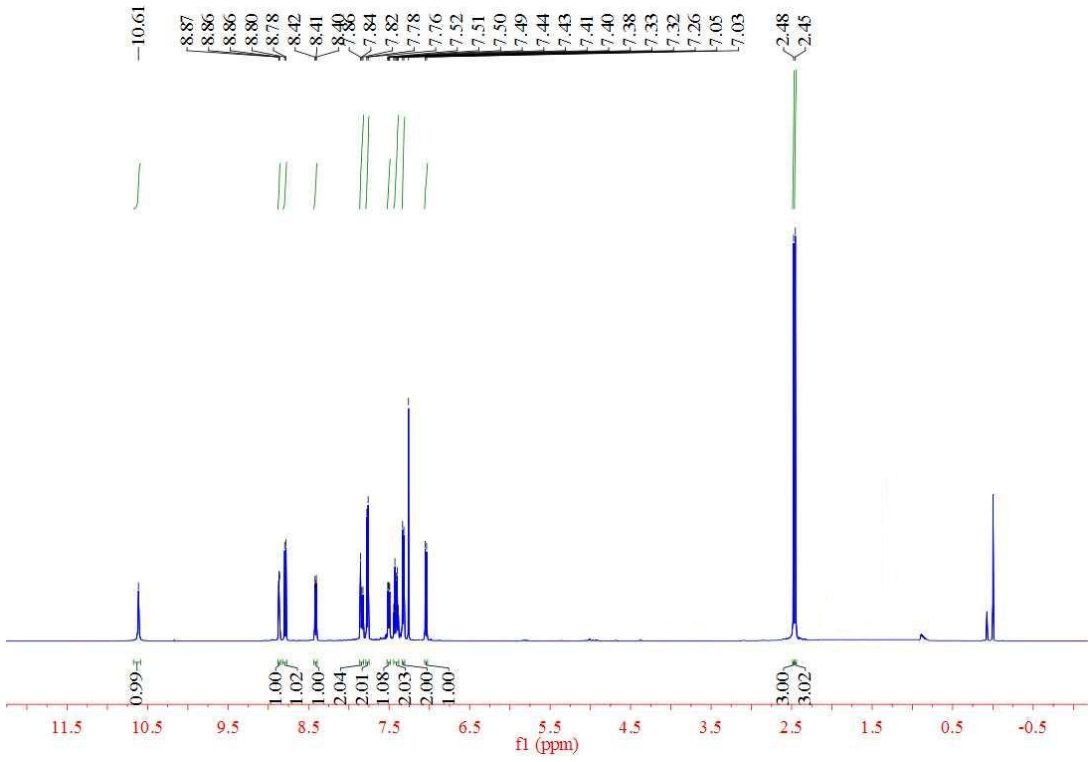
3l, ^{1}H NMR



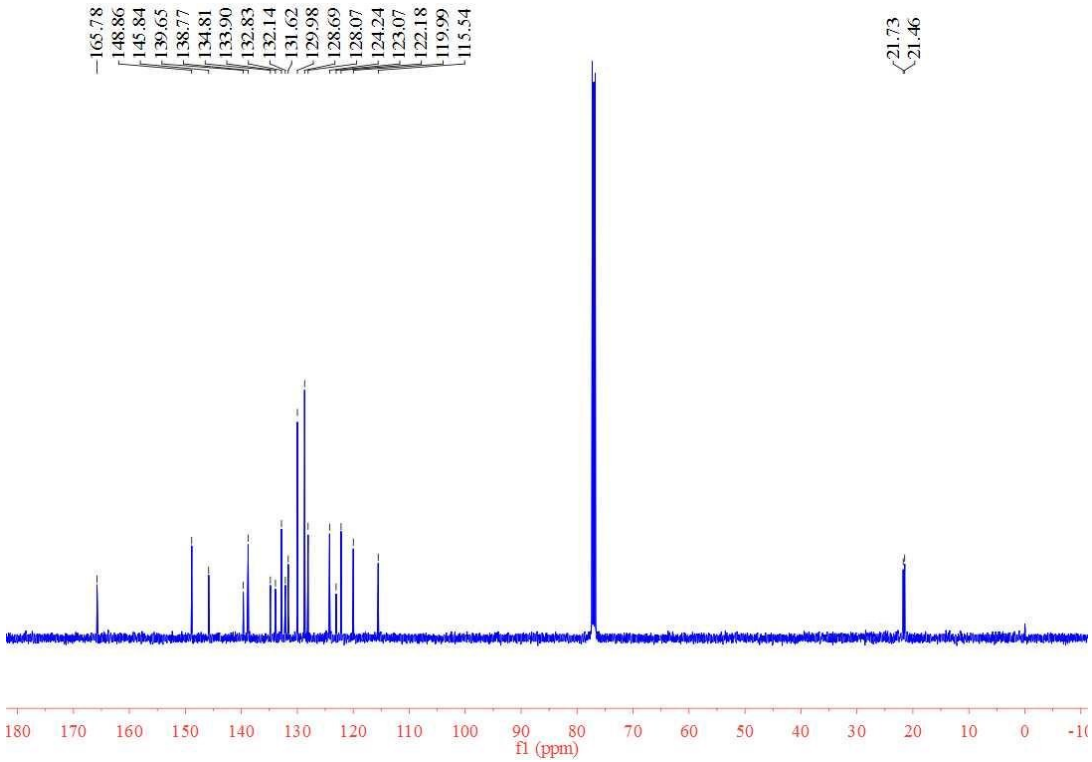
3l, ^{13}C NMR



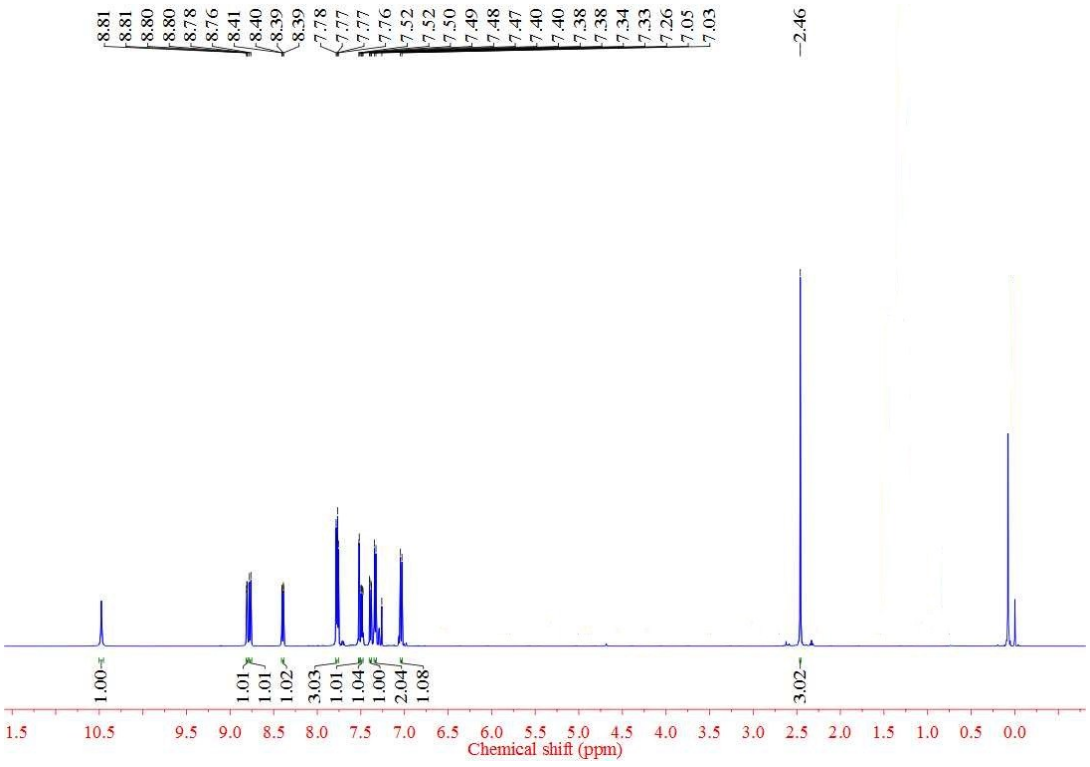
3m, ^{1}H NMR



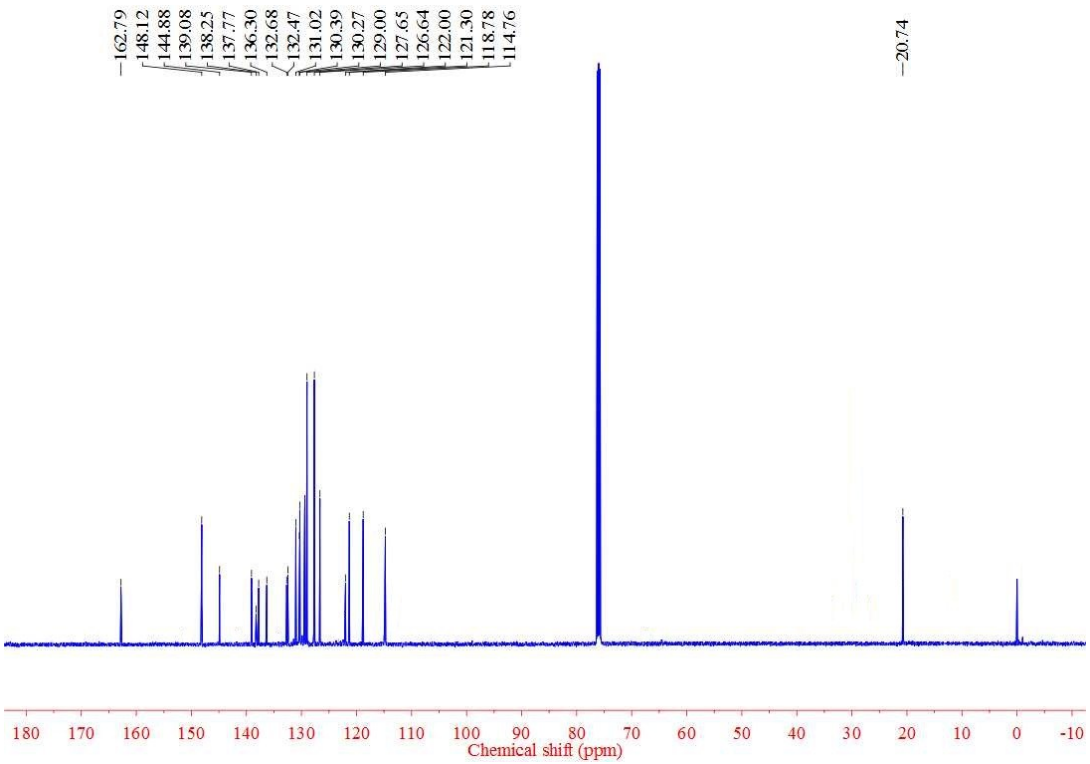
3m, ^{13}C NMR



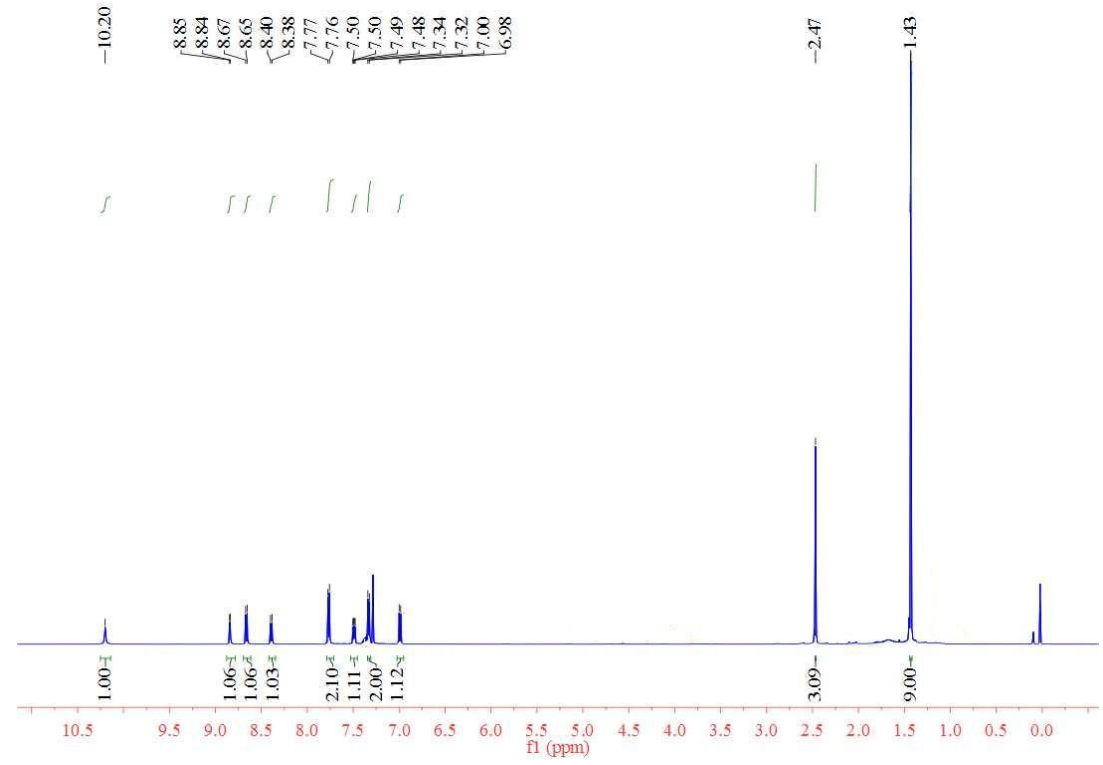
3n, ^{1}H NMR



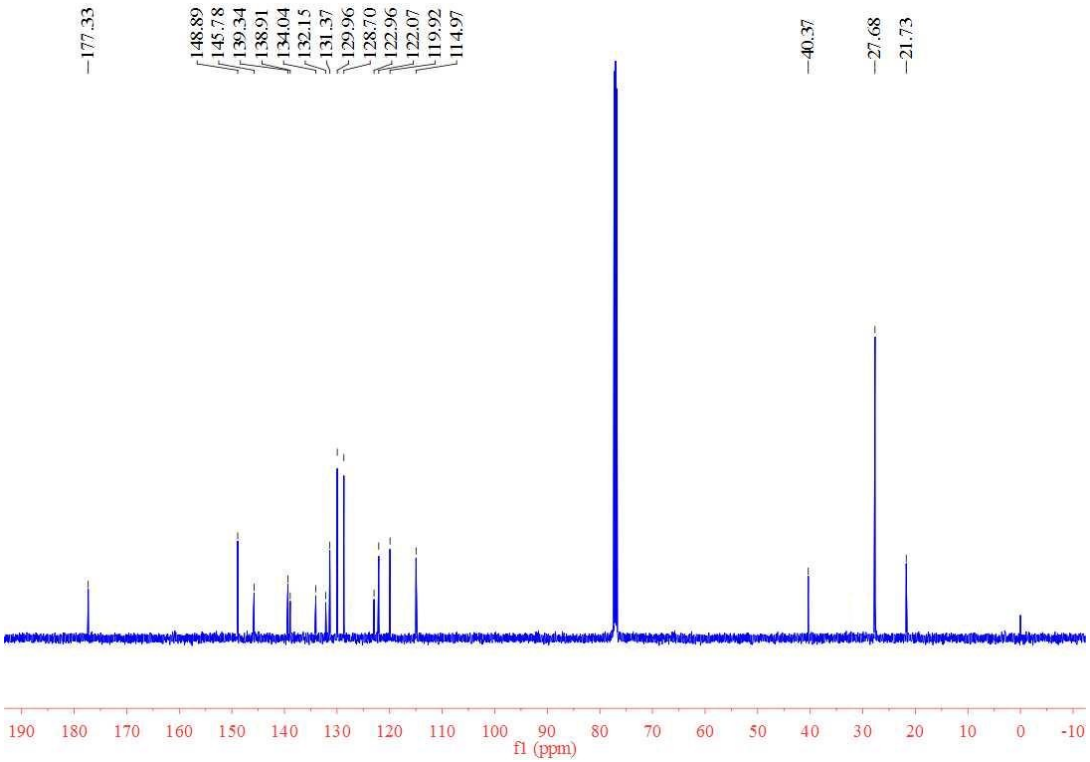
3n, ^{13}C NMR



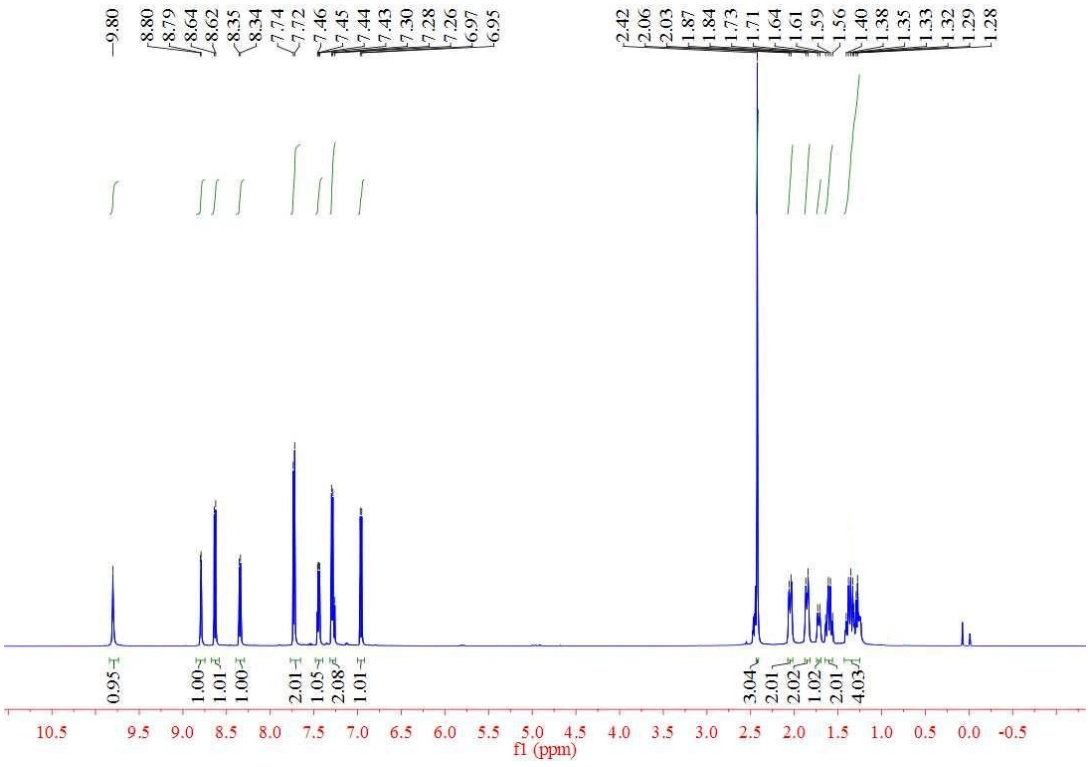
3o, ^{1}H NMR



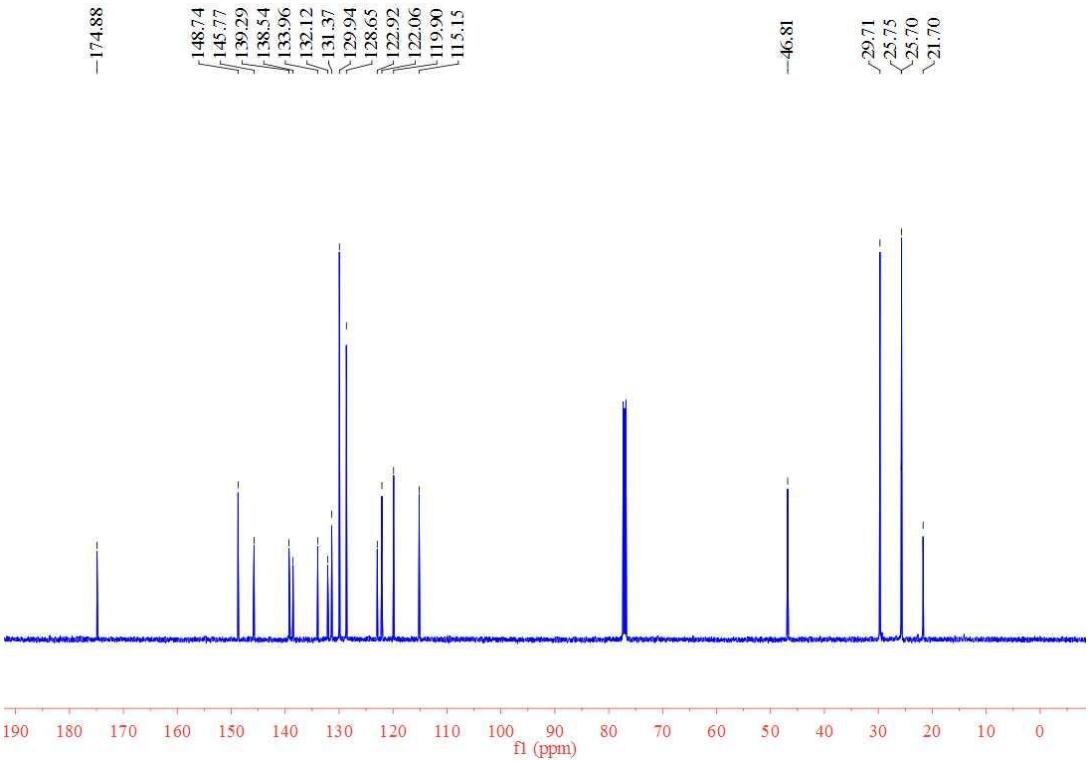
3o, ^{13}C NMR



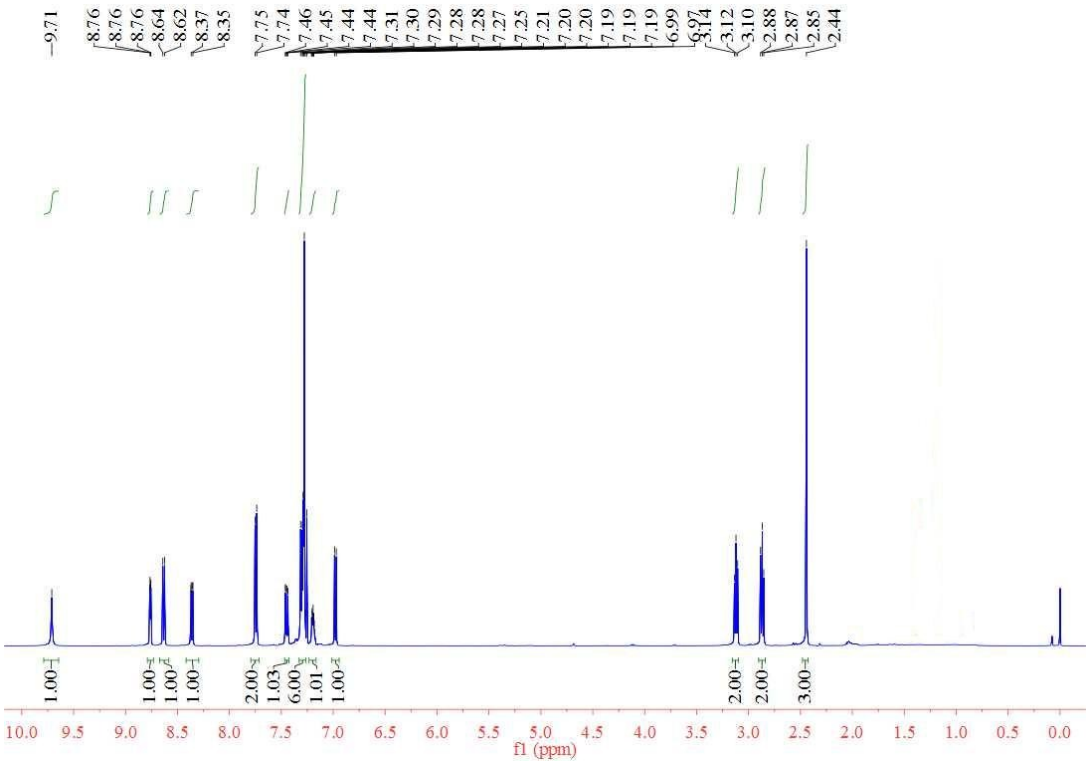
3p, ^{1}H NMR



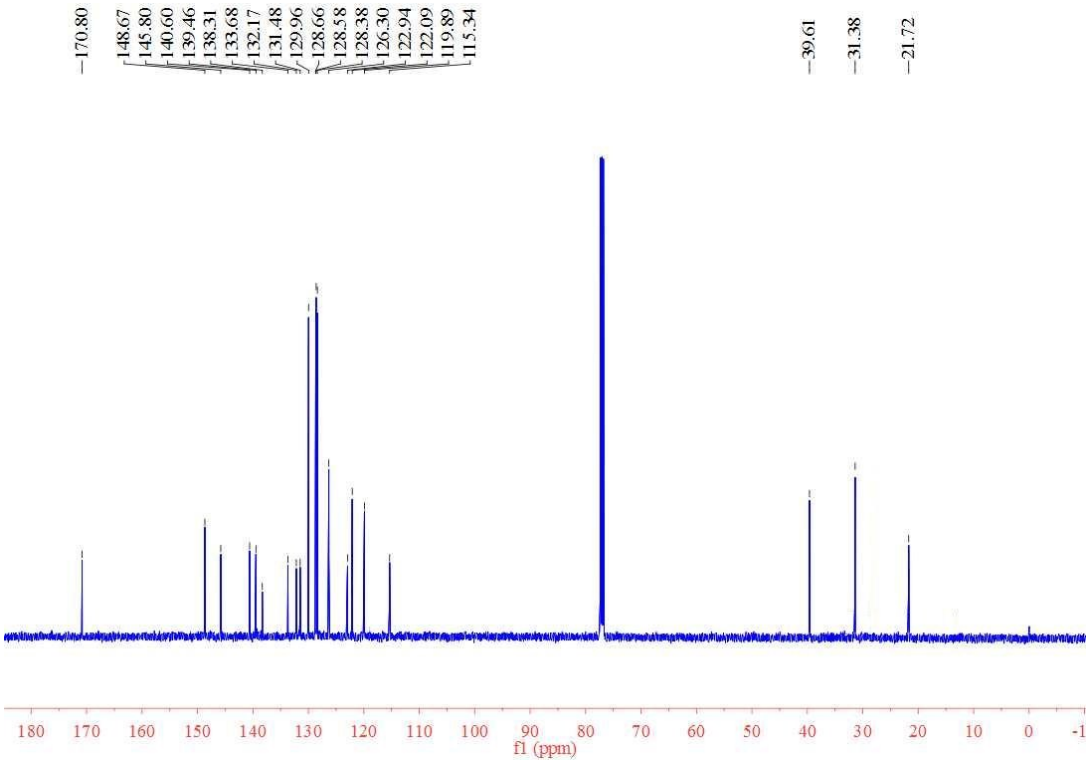
3p, ^{13}C NMR



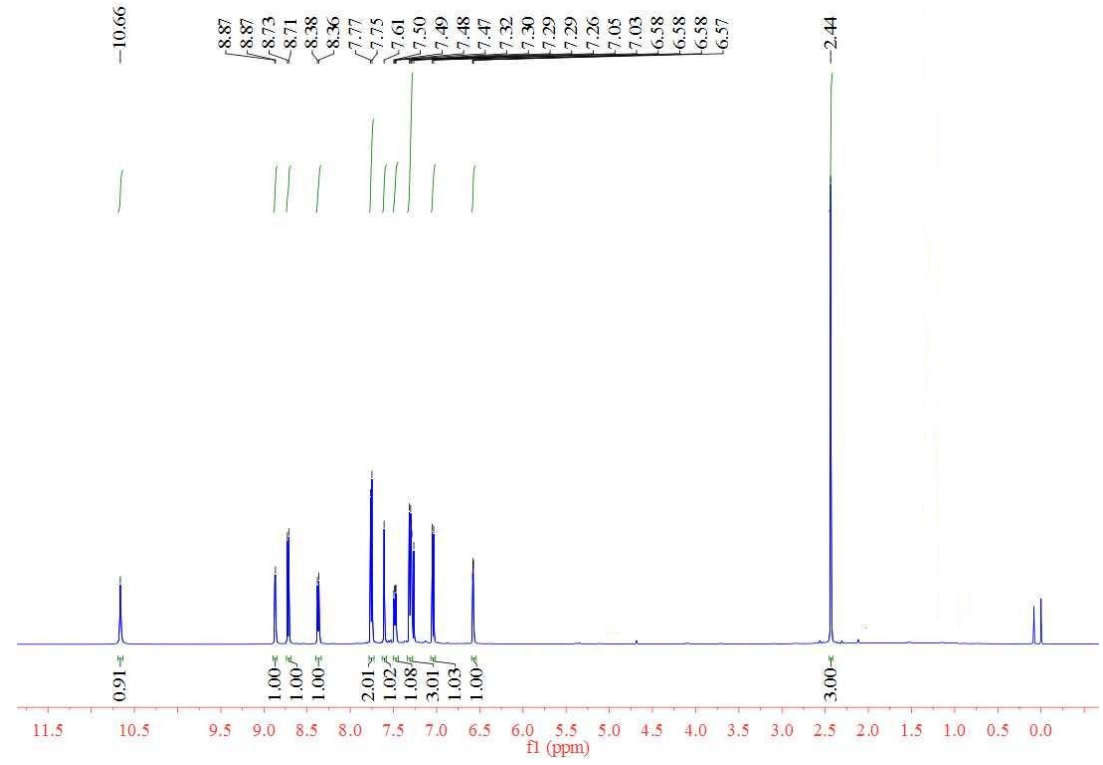
3q, ^{1}H NMR



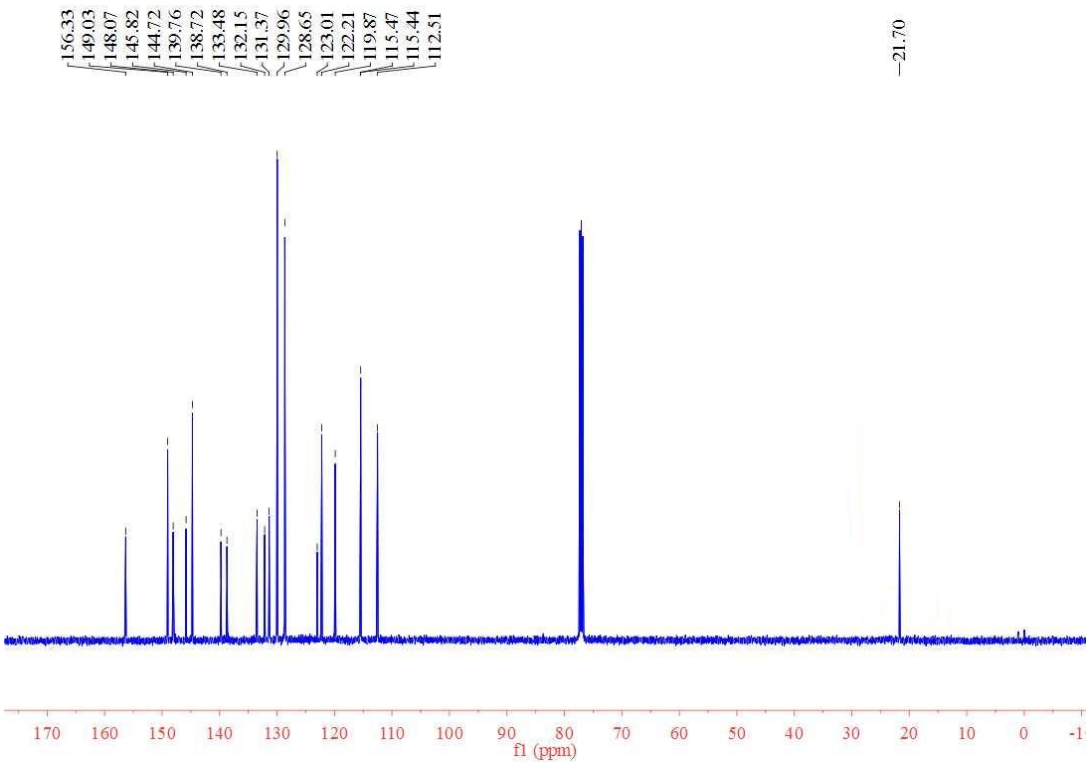
3q, ^{13}C NMR



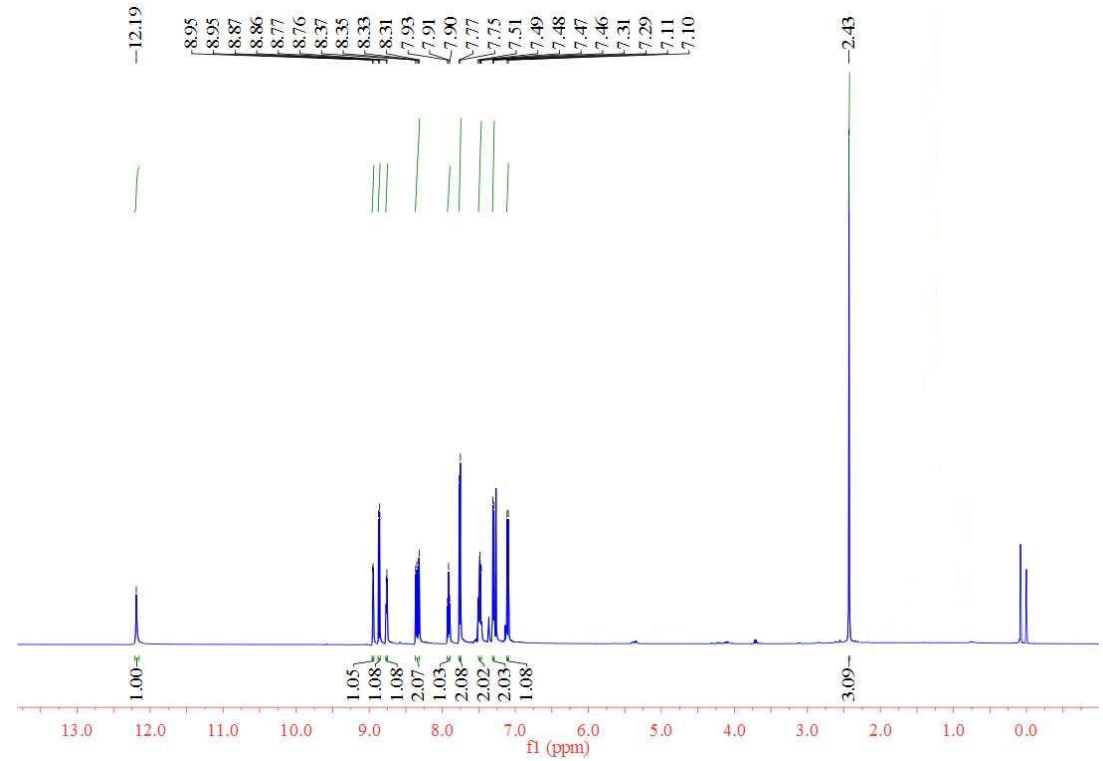
3r, ^{1}H NMR



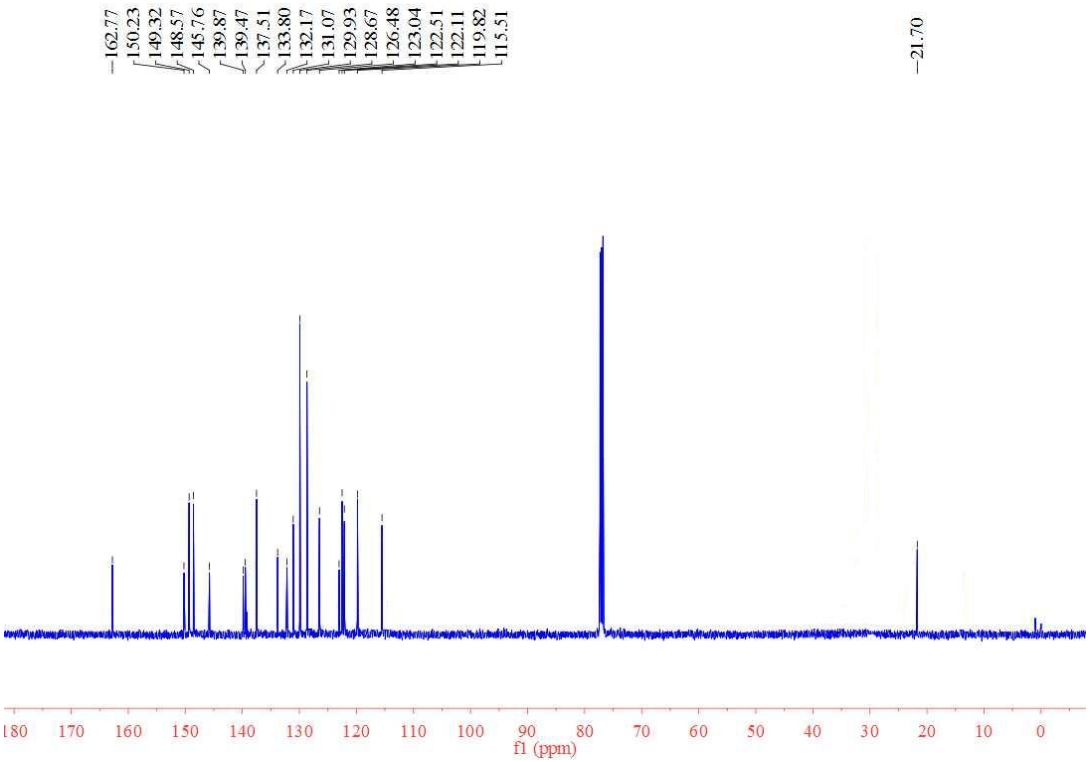
3r, ^{13}C NMR



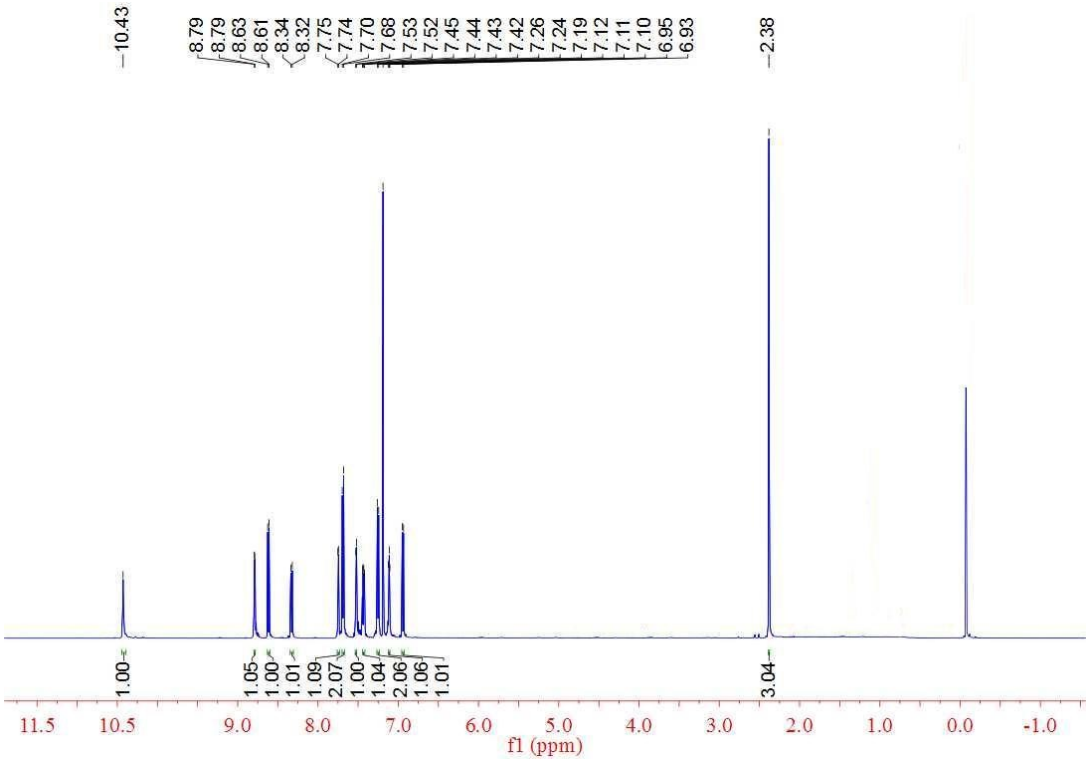
3s, ^{1}H NMR



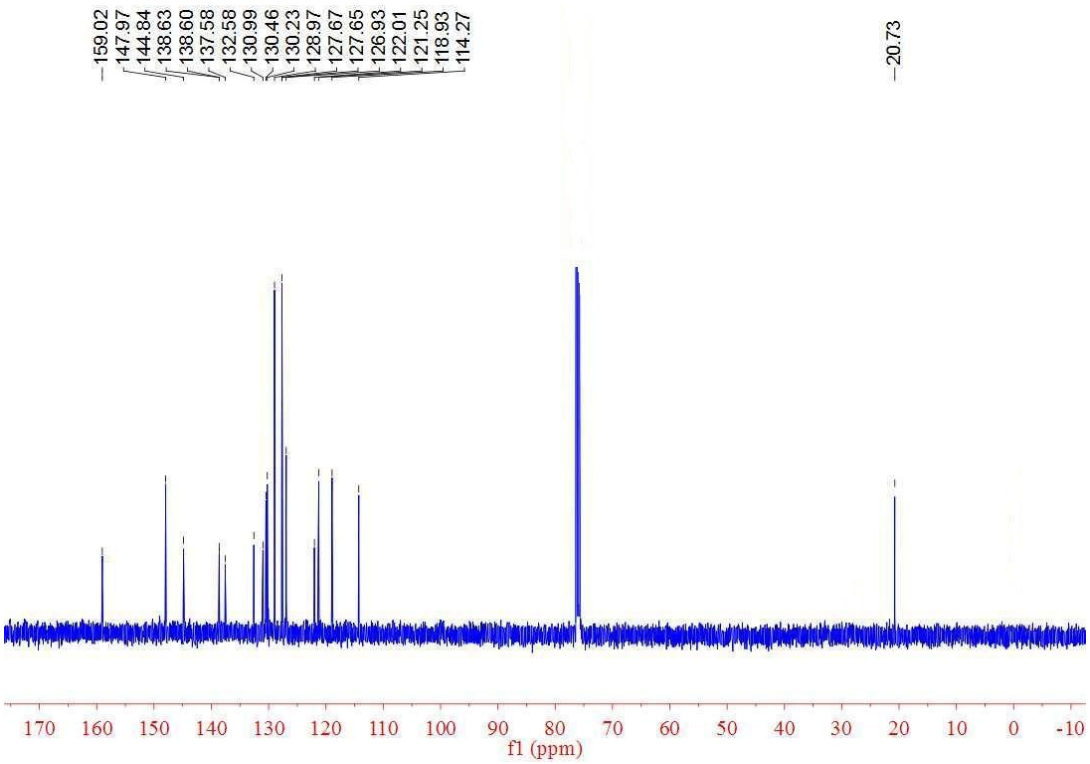
3s, ^{13}C NMR



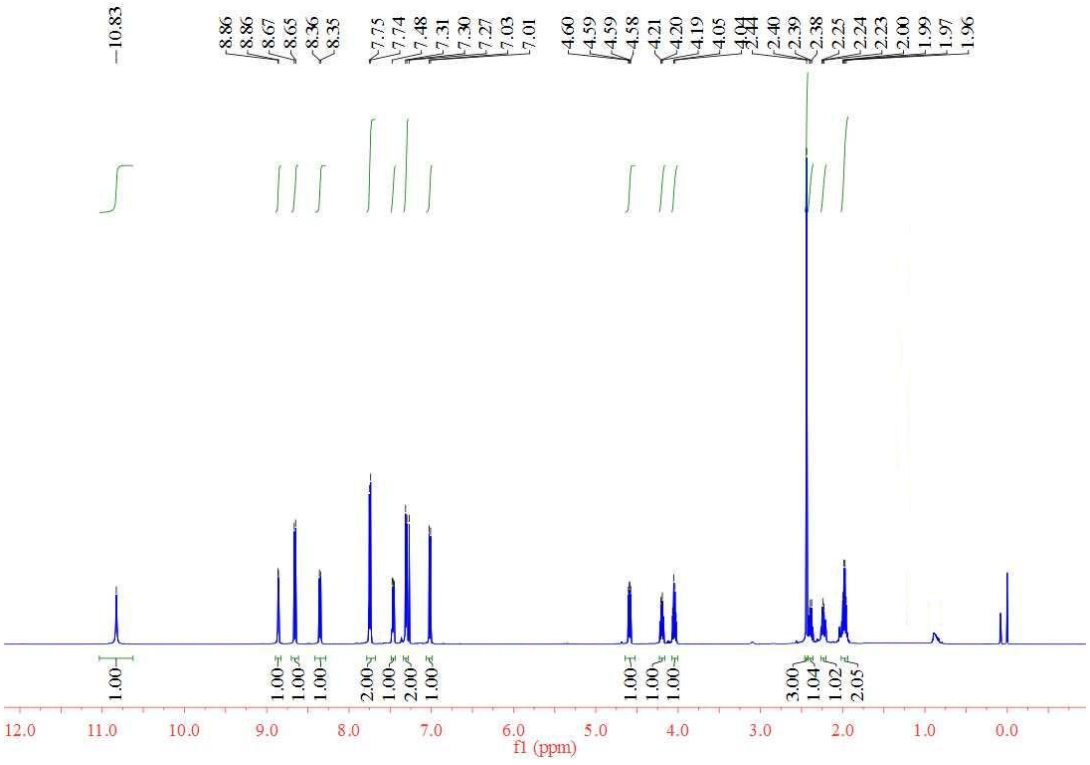
3t, ^{1}H NMR



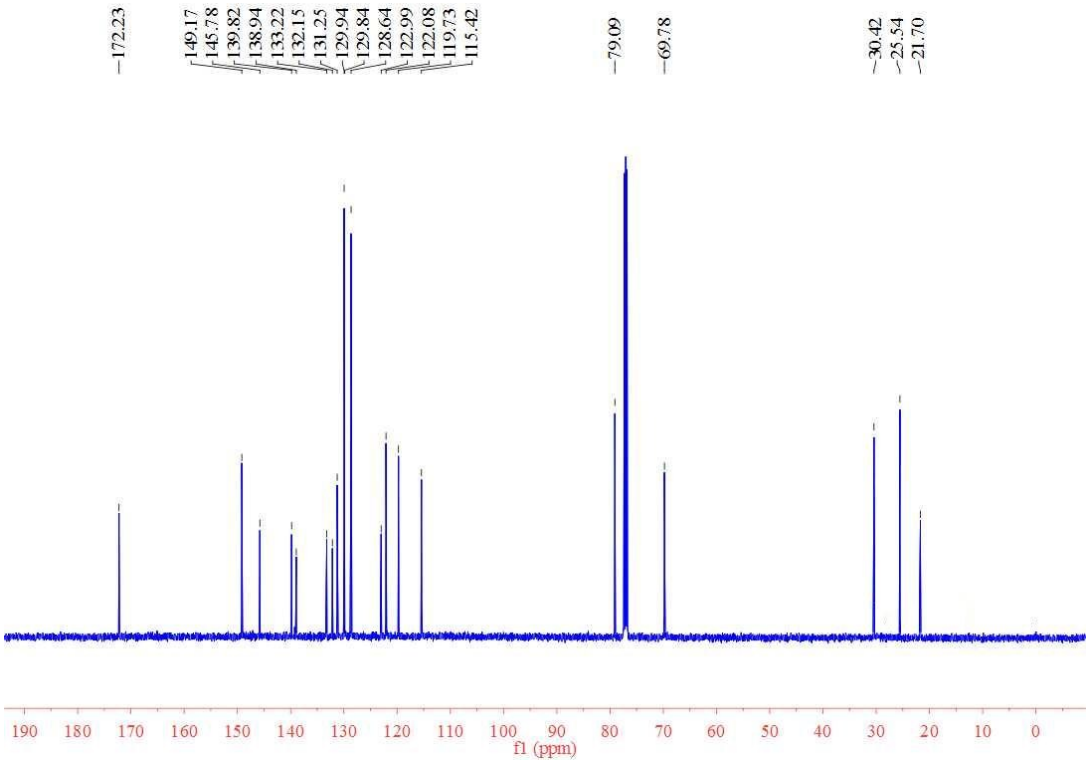
3t, ^{13}C NMR



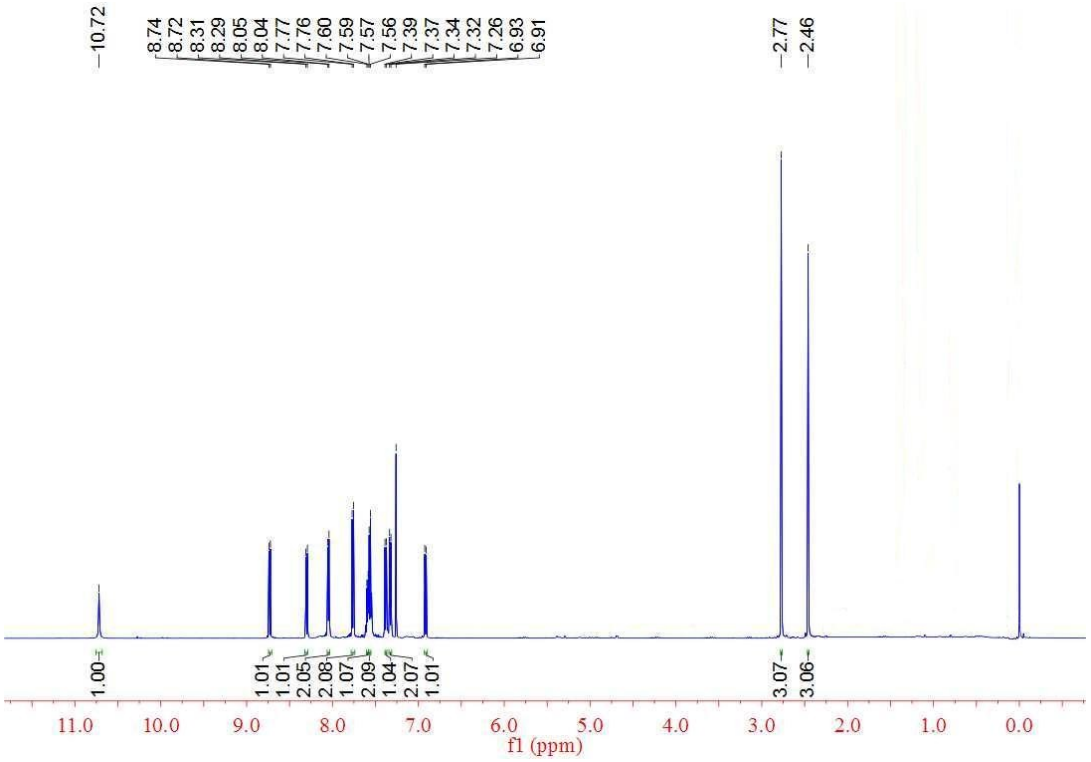
3u, ^{1}H NMR



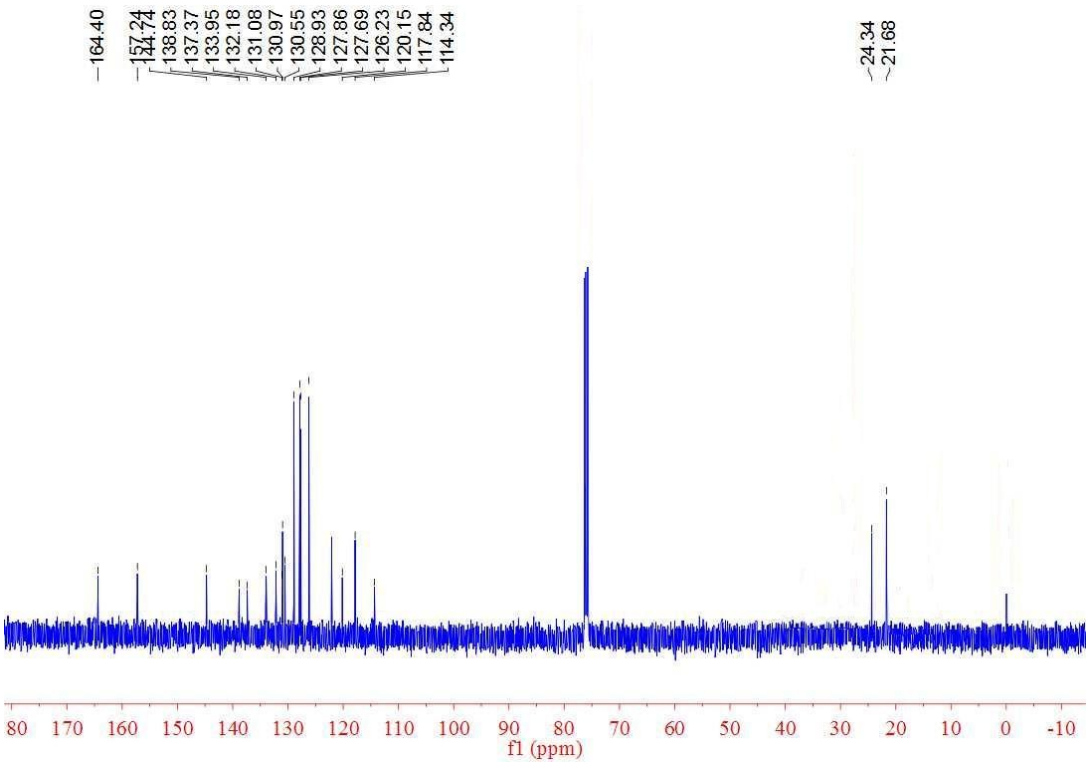
3u, ^{13}C NMR



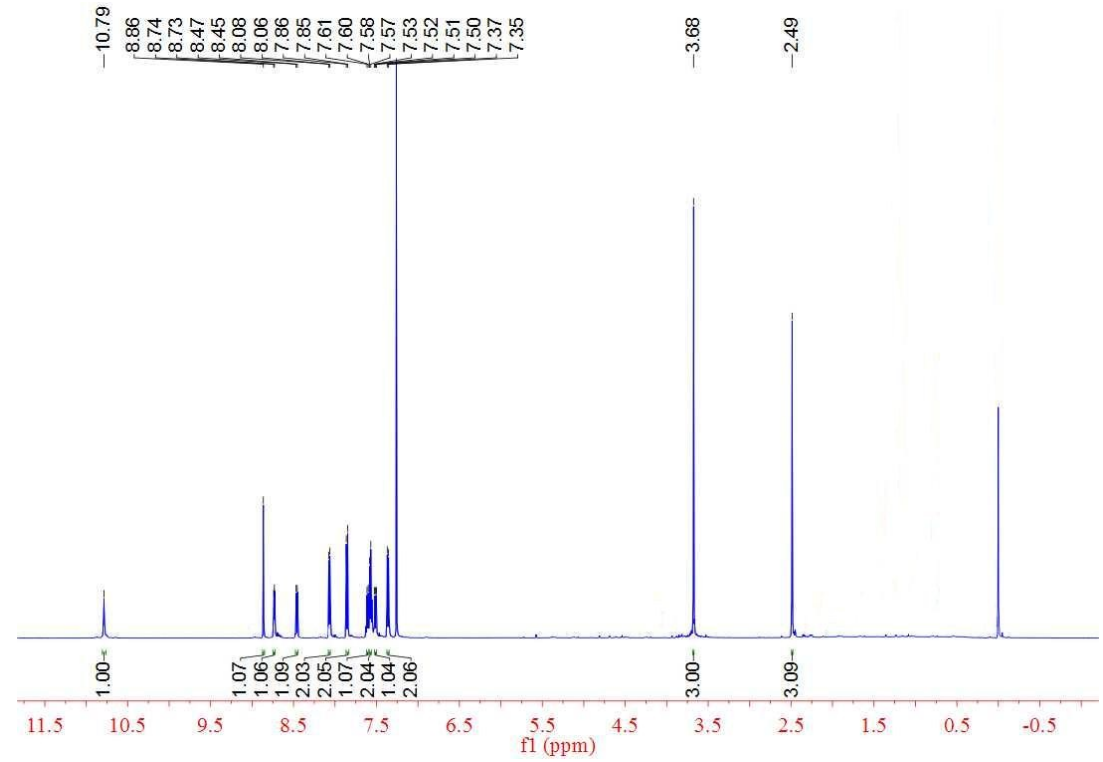
3v, ^{1}H NMR



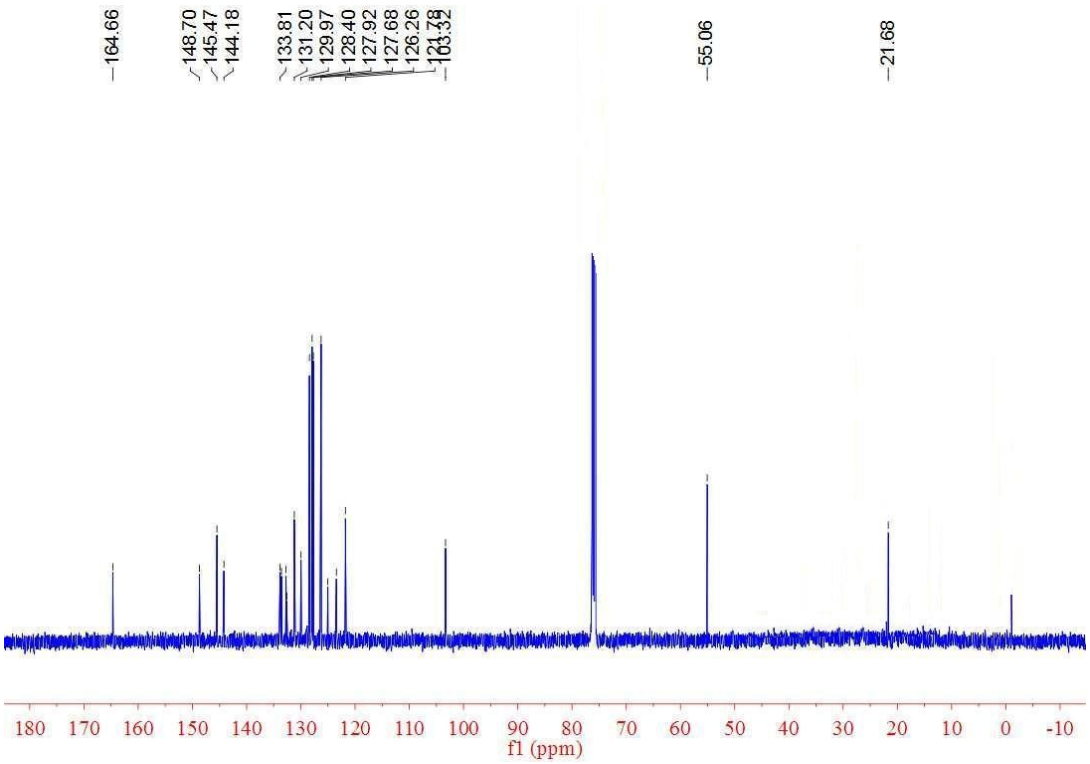
3v, ^{13}C NMR



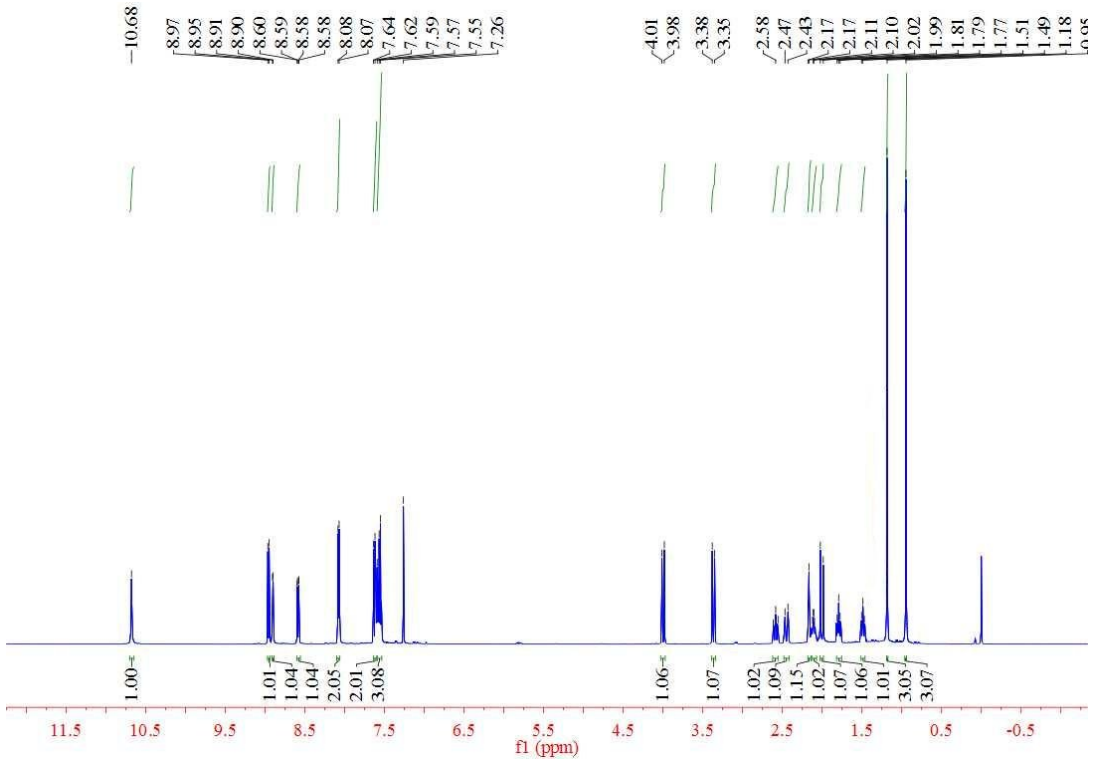
3w, ^{1}H NMR



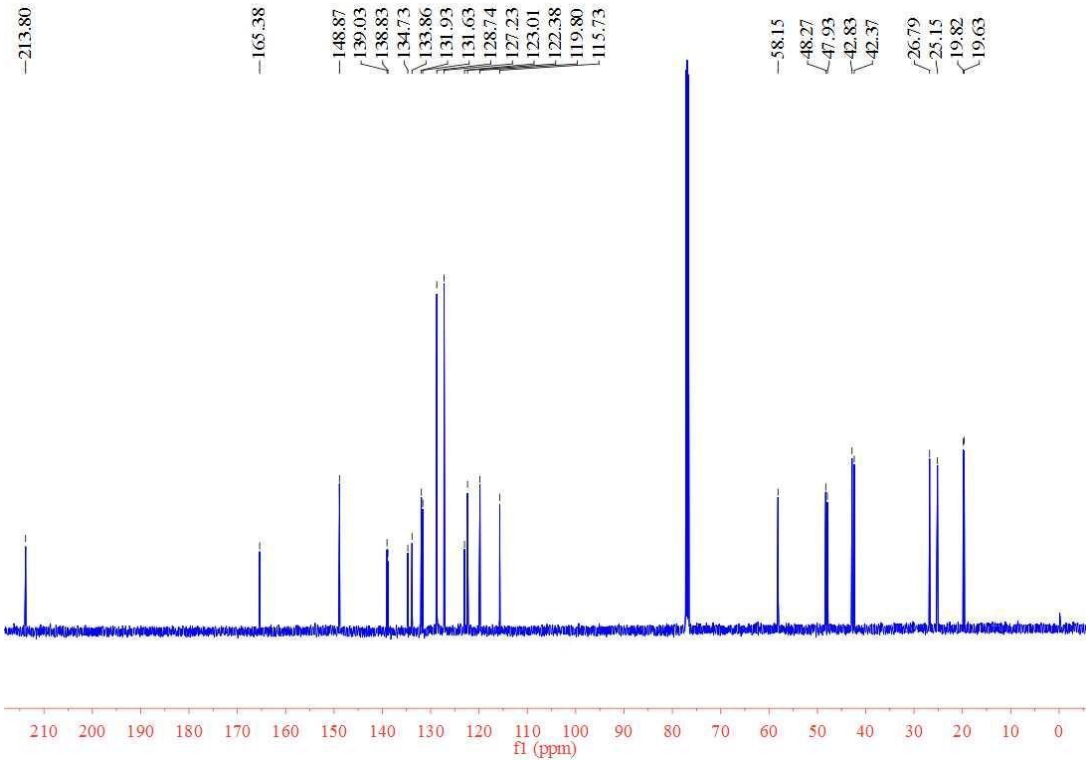
3w, ^{13}C NMR



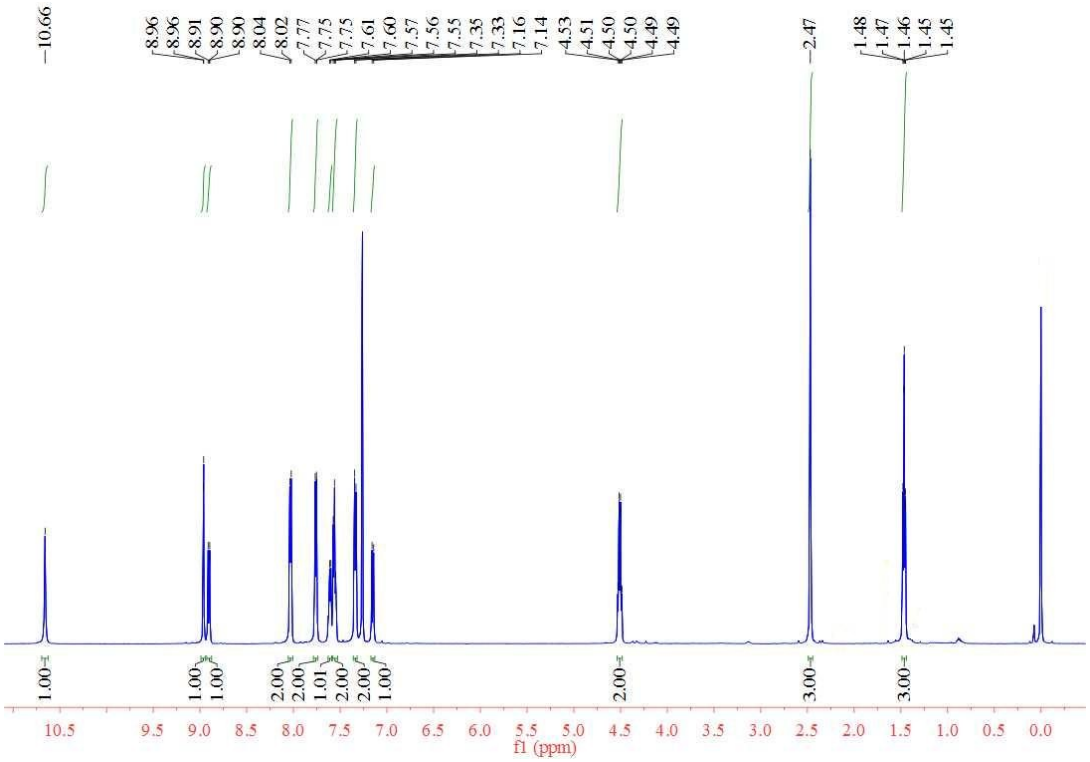
3y, ^{1}H NMR



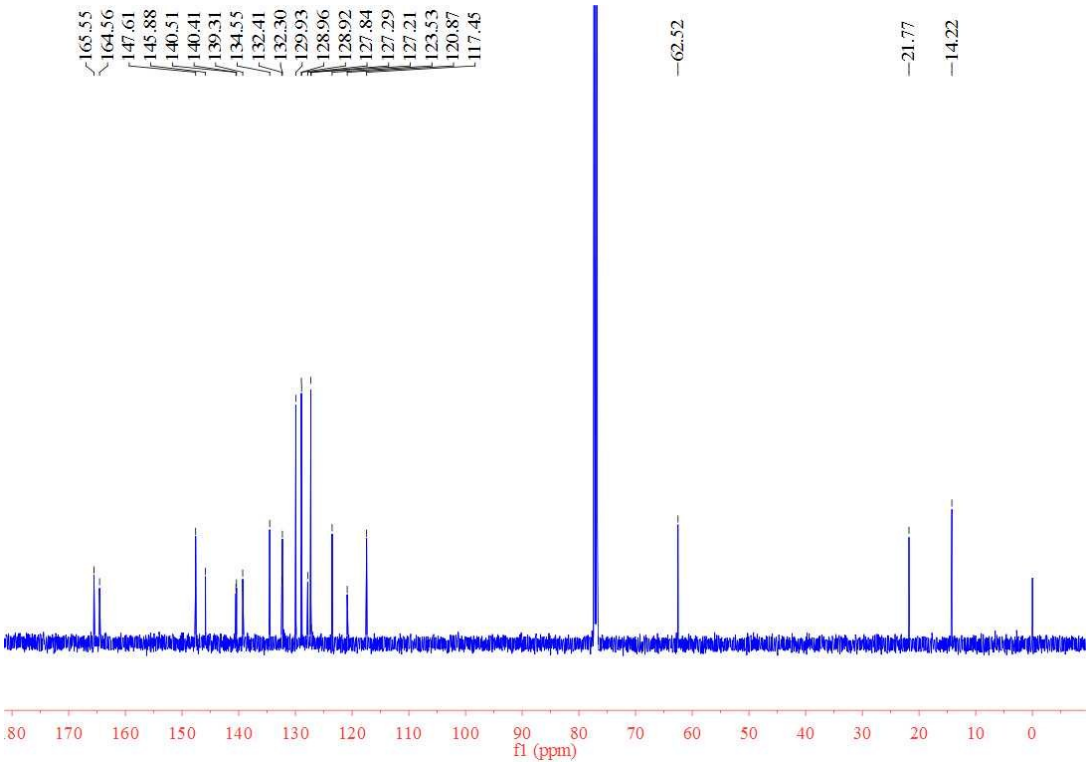
3y, ^{13}C NMR



3z, ^{1}H NMR



3z, ^{13}C NMR


165.55
164.56
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132.30
129.93
128.96
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127.84
127.29
127.21
123.53
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62.52
21.77
14.22
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)