Synthesis of novel diesters of carbohydrate-derived 5-(chloromethyl)furfural as potential fuel oxygenates and surfactants of renewable origin

Sandeep Kumar Yadav[1] and Saikat Dutta[1*]

[1] Department of Chemistry, National Institute of Technology Karnataka (NITK), Surathkal, Mangalore-575025, Karnataka, India.

* Corresponding author. E-mail: sdutta@nitk.edu.in

Number of pages: 66

Number of figures: 105

The calculations for Atom Economy (AE), Carbon Economy (CE), and Product Mass Intensity (PMI) for ethyl 5-(acetoxymethyl)furan-2-carboxylate **1a**.

Atom economy (AE): It is a calculation of how many atoms of the reactants present in the final product. The ideal value of AE factor is 100%.

$$Atom\ economy\ (\%) = \frac{MW\ of\ product}{\Sigma\ (MW\ of\ reactants)} \times 100$$

$$= \frac{212.20}{144.55 + 108.57 + 46.07 + 161.24} \times 100\%$$

$$= \frac{212.20}{460.43} \times 100\%$$

$$= 46\%$$

Carbon economy (CE): Carbon Economy is a calculation which shows the total number of carbon present in the product compared to how much carbon was used to create the product.

$$Carbon\ Economy\ (\%) = \frac{No\ of\ carbon\ atoms\ in\ product}{\Sigma(No\ of\ carbon\ atoms\ in\ reactants)} \times 100\%$$

$$= \frac{10}{10} \times 100\%$$

$$= 100\%$$

Product mass intensity (PMI): PMI is defined as the total mass of the input materials (reactants) including solvent in a chemical reaction divided by the mass of product.

$$PMI = \frac{\Sigma(Mass\ of\ reactants\ including\ solvent)}{Mass\ of\ the\ product}$$

$$= \frac{(Mass\ of\ reactants\ for\ Step\ 1 + Mass\ of\ reagents\ for\ Step\ 2)}{Mass\ of\ the\ product}$$

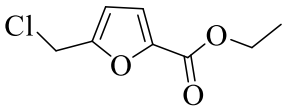
$$= \frac{\begin{pmatrix} Mass\ of\ CMF + Mass\ of\ TBHC + Mass\ of\ EtOH + Mass\ of\ EtOAc + Mass\ of\ Na2SO4 + \\ + Mass\ of\ Silica\ Gel + Mass\ of\ pet\ ether + Mass\ of\ EtOAc) + (Mass\ of\ TEAA + Mass\ of\ EtOAc \\ + Mass\ of\ Na2SO4 + Mass\ of\ Silica\ Gel) \end{pmatrix}}{Mass\ of\ the\ product}$$

$$= \frac{\begin{pmatrix} (0.3 + 0.675 + 1.5 * 0.789 + 1.5 * 0.902 + 0.1 + 7.5 + 1.5 * 0.64 + 1.5 * 0.902) \\ + (0.1 + 2 + 0.415 + 10 * 0.902) \end{pmatrix}}{0.310}$$

$$= \frac{(13.424 + 11.535)}{0.310}$$

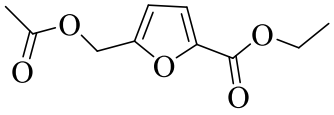
$$= 80.5$$

Ethyl 5-(chloromethyl)furan-2-carboxylate (**1**): Light yellow liquid (2.563 g, 83%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, *J* = 3.6 Hz), 6.47 (d, 1H, *J* = 3.6 Hz), 4.59 (s, 2H), 4.35 (q, 2H, *J* = 6.8 Hz), 1.36 (t, 3H, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.6, 154.2, 118.7, 111.5, 61.3, 36.8, 14.4. FTIR (cm^{-1}): 2982, 2959, 2918, 2850, 1715, 1534, 1297, 1265, 1210, 1153, 1016.



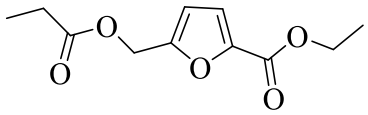
1

Ethyl 5-(acetoxymethyl)furan-2-carboxylate (**1a**): Yellow liquid (0.310 g, 85%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, *J* = 3.4 Hz), 6.47 (d, 1H, *J* = 3.4 Hz), 5.06 (s, 2H), 4.34 (q, 2H, *J* = 7.1 Hz), 2.06 (s, 3H), 1.35 (t, 3H, *J* = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.5, 158.7, 153.4, 145.1, 118.5, 112.3, 61.2, 58.0, 20.8, 14.4. FTIR (cm^{-1}): 2958, 2926, 2855, 1746, 1726, 1600, 1462, 1375, 1300, 1231, 1024.



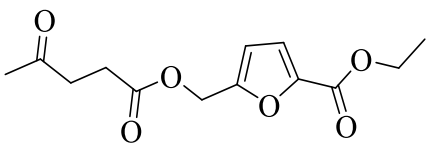
1a

Ethyl 5-((propionyloxy)methyl)furan-2-carboxylate (**1b**): Yellow liquid (0.268 g, 80%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.26 (d, 1H, *J* = 3.6 Hz), 6.62 (d, 1H, *J* = 3.6 Hz), 5.23 (s, 2H), 4.50 (q, 2H, *J* = 7.2 Hz), 2.50 (q, 2H, *J* = 7.6 Hz), 1.51 (t, 3H, *J* = 7.2 Hz), 1.28 (t, 3H, *J* = 7.6 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 173.8, 158.5, 153.5, 145.0, 118.4, 112.0, 61.1, 57.8, 27.3, 14.3, 8.9. FTIR (cm^{-1}): 3132, 2983, 2922, 2852, 1728, 1599, 1532, 1298, 1210, 1170, 1137, 1018. HRMS (ESI) calculated for $C_{11}H_{24}O_5$ $[M+Na]^+$ 249.0733, found 249.0739.



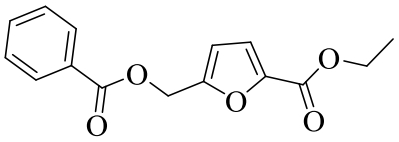
1b

Ethyl 5-(((4-oxopentanoyl)oxy)methyl)furan-2-carboxylate (**1c**): Yellow liquid (0.226 g, 88%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, J = 3.6 Hz), 6.47 (d, 1H, *J* = 3.6 Hz), 5.08 (s, 2H), 4.34 (q, 2H, *J* = 7.2 Hz), 2.74 (t, 2H, *J* = 6.4 Hz), 2.59 (t, 2H, *J* = 6.4 Hz), 2.16 (s, 3H), 1.35 (t, 3H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 2026.5, 172.3, 158.7, 153.3, 145.1, 118.6, 112.2. 61.2, 58.2, 37.9, 29.9, 27.9, 14.4. FTIR (cm^{-1}): 2987, 2956, 2920, 2851, 1722, 1539, 1526, 1368, 1302, 1212, 1152, 1023. HRMS (ESI) calculated for $C_{13}H_{16}O_6$ $[M+Na]^+$ 291.0839, found 291.0843.



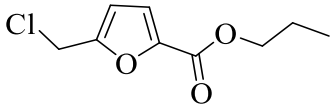
1c

Ethyl 5-((benzoyloxy)methyl)furan-2-carboxylate (**1d**): Yellow liquid (0.236 g, 84%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.04 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.58-7.54 (m, 1H), 7.43 (t, 2H, J = 8.0 Hz), 7.14 (d, 1H, J = 3.6 Hz), 6.58 (d, 1H, J = 3.6 Hz), 5.34 (s, 2H), 4.37 (q, 2H, J = 7.2 Hz), 1.37 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.1, 158.7, 153.6, 145.2, 133.4, 129.9, 129.6, 128.5, 118.6, 112.5, 61.2, 58.4, 14.4. FTIR (cm^{-1}): 3132, 2982, 2935, 1716, 1530, 1450, 1390, 1261, 1209, 1173, 1095, 1061, 709. HRMS (ESI) calculated for $C_{15}H_{14}O_5$ $[M+H]^+$ 275.0914, found 275.0918.



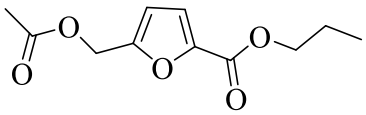
1d

Propyl 5-(chloromethyl)furan-2-carboxylate (**2**): Light yellow liquid (2.238 g, 82%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.26 (d, 1H, J = 3.6 Hz), 6.64 (d, 1H, J = 3.6 Hz), 4.75 (s, 2H), 4.41 (t, 2H, J = 6.8 Hz), 1.97-1.88 (m, 2H), 1.15 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.6, 154.2, 145.2, 118.6, 111.4, 66.8, 36.8, 22.1, 10.4. FTIR (cm^{-1}): 2964, 2922, 2853, 1720, 1527, 1298, 1210, 1160, 1054. HRMS (ESI) calculated for $C_9H_{11}ClO_3$ $[M+H]^+$ 203.0469, found 203.0469.



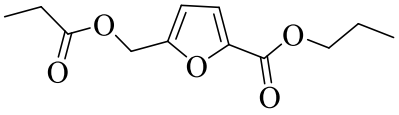
2

Propyl 5-(acetoxymethyl)furan-2-carboxylate (**2a**): Yellow liquid (0.290 g, 85%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (d, 2H, J = 3.6 Hz), 6.48 (d, 1H, J = 3.6 Hz), 5.07 (s, 2H), 4.25 (t, 2H, J = 6.8 Hz), 2.08 (s, 3H), 1.80-1.70 (m, 2H), 0.98 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.5, 158.8, 153.5, 145.1, 118.5, 112.3, 66.7, 58.0, 22.2, 20.8, 10.4. FTIR (cm^{-1}): 2970, 2939, 2881, 1744, 1715, 1525, 1375, 1207, 1133, 1020, 760. HRMS (ESI) calculated for $C_{11}H_{14}O_5$ $[M+Na]^+$ 249.0733, found 249.0733.



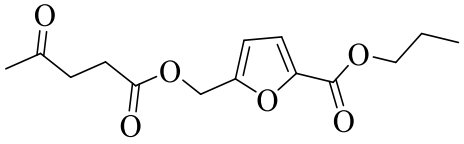
2a

Propyl 5-((propionyloxy)methyl)furan-2-carboxylate (**2b**): Yellow liquid (0.196 g, 79%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, J = 3.6 Hz), 6.47 (d, 1H, J = 3.6 Hz), 5.08 (s, 2H), 4.24 (t, 2H, J = 6.8 Hz), 2.35 (q, 2H, J = 7.6 Hz), 1.79-1.70 (m, 2H), 1.12 (t, 3H, J = 7.6 Hz), 0.97 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 174.0, 158.8, 153.7, 145.1, 118.5, 112.1, 66.7, 57.9, 27.4, 22.2, 10.4, 9.0. FTIR (cm^{-1}): 2971, 2943, 2882, 1717, 1524, 1293, 1270, 1132, 1081, 761. HRMS (ESI) calculated for $C_{12}H_{16}O_5$ $[M+Na]^+$ 263.0890, found 263.0897.



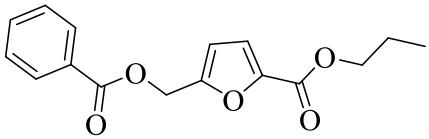
2b

Propyl 5-(((4-oxopentanoyl)oxy)methyl)furan-2-carboxylate (**2c**): Yellow liquid (0.231 g, 87%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, J = 3.6 Hz), 6.47 (d, 1H, J = 3.6 Hz), 5.08 (s, 2H), 4.24 (t, 2H, J = 6.8 Hz), 2.74 (t, 2H, J = 6.8 Hz), 2.59 (t, 2H, J = 6.8 Hz), 2.16 (s, 3H), 1.79-1.70 (m, 2H), 0.97 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 206.5, 172.3, 158.8, 153.4, 145.1, 118.5, 112.2, 66.7, 58.2, 37.9, 29.9, 27.7, 22.1, 10.4. FTIR (cm^{-1}): 2956, 2919, 2871, 2852, 1722, 1599, 1461, 1398, 1377, 1210, 1151, 1083, 817. HRMS (ESI) calculated for $C_{14}H_{18}O_6$ $[M+Na]^+$ 305.0996, found 305.1069.



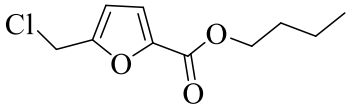
2c

Propyl 5-((benzoyloxy)methyl)furan-2-carboxylate (**2d**): Yellow liquid (0.266 g, 84%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.04 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.57-7.53 (m, 1H), 7.42 (t, 2H, J = 7.7 Hz), 7.14 (d, 2H, J = 3.6 Hz), 6.58 (d, 2H, J = 3.6 Hz), 5.34 (s, 2H), 4.26 (t, 2H, J = 6.8 Hz), 1.80-1.71 (m, 2H), 0.99 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.1, 158.8, 153.6, 145.2, 133.4, 129.9, 129.6, 128.5, 118.6, 112.5, 66.7, 58.4, 22.2, 10.5. FTIR (cm^{-1}): 2969, 2880, 1715, 1536, 1451, 1366, 1295, 1135, 1090, 1068, 760. HRMS (ESI) calculated for $C_{16}H_{16}O_5$ $[M+Na]^+$ 311.0890, found 311.0899.



2d

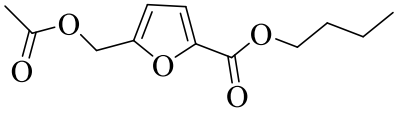
Butyl 5-(chloromethyl)furan-2-carboxylate (**3**): Light yellow liquid (3.401 g, 85%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.26 (d, 1H, J = 3.6 Hz), 6.64 (d, 1H, J = 3.6 Hz), 4.76 (s, 2H), 4.46 (t, 2H, J = 6.8 Hz), 1.92-1.84 (m, 2H), 1.65-1.55 (m, 2H), 1.12 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.6, 154.2, 145.2, 118.6, 111.4, 65.1, 36.8, 30.8, 19.2, 13.8. FTIR (cm^{-1}): 2960, 2930, 2873, 1717, 1521, 1464, 1296, 1210, 1158, 1060, 1018, 760. HRMS (ESI) calculated for $C_{10}H_{13}ClO_3$ $[M+H]^+$ 217.0626, found 217.0637.



3

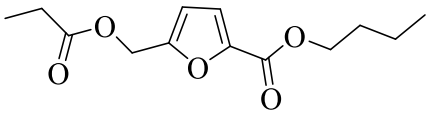
Butyl 5-(acetoxymethyl)furan-2-carboxylate (**3a**): Yellow liquid (0.252 g, 84%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, J = 3.6 Hz), 6.48 (d, 1H, J = 3.6 Hz), 5.07 (s, 2H), 4.29 (t, 2H, J = 6.8 Hz), 2.08 (s, 3H), 1.75-1.68 (m, 2H), 1.48-1.38 (m, 2H), 0.95 (t, 3H, J =

7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.5, 158.8, 153.5, 145.2, 118.5, 112.3, 65.1, 58.0, 30.8, 20.9, 19.2, 13.8. FTIR (cm^{-1}): 2960, 2937, 2875, 1744, 1716, 1599, 1536, 1464, 1295, 1223, 1207, 1020, 762. HRMS (ESI) calculated for $C_{12}H_{16}O_5$ $[M+Na]^+$ 263.0890, found 263.0893.



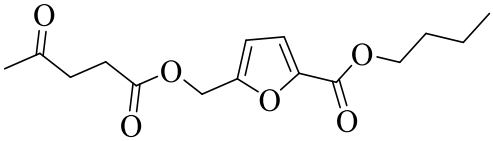
3a

Butyl 5-((propionyloxy)methyl)furan-2-carboxylate (**3b**): Yellow liquid (0.182 g, 79%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, *J* = 3.6 Hz), 6.47 (d, 1H, *J* = 3.6 Hz), 5.08 (s, 2H), 4.29 (t, 2H, *J* = 6.8 Hz), 2.35 (q, 2H, *J* = 7.6 Hz), 1.74-1.67 (m, 2H), 1.47-1.38 (m, 2H), 1.13 (t, 3H, *J* = 7.6 Hz), 0.95 (t, 3H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 174.0, 158.8, 153.6, 145.1, 118.5, 112.1, 65.0, 57.9, 30.8, 27.4, 19.2, 13.8, 9.0. FTIR (cm^{-1}): 2961, 2937, 2875, 1729, 1719, 1536, 1462, 1295, 1135, 1081, 1017, 762. HRMS (ESI) calculated for $C_{13}H_{18}O_5$ $[M+Na]^+$ 277.1046, found 277.1057.



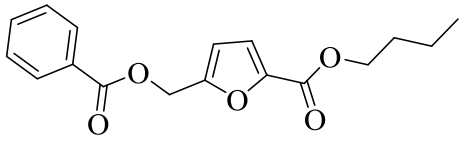
3b

Butyl 5-(((4-oxopentanoyl)oxy)methyl)furan-2-carboxylate (**3c**): Yellow liquid (0.240 g, 87%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.09 (d, 1H, *J* = 3.6 Hz), 6.48 (d, 1H, *J* = 3.6 Hz), 5.08 (s, 2H), 4.29 (t, 2H, *J* = 6.8 Hz), 2.75 (t, 2H, *J* = 6.8 Hz), 2.60 (t, 2H, *J* = 6.8 Hz), 2.17 (s, 3H), 1.74-1.67 (m, 2H), 1.47-1.38 (m, 2H), 0.95 (t, 3H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 206.5, 172.3, 158.8, 153.4, 145.1, 118.5, 112.2, 65.1, 58.2, 37.9, 30.9, 29.9, 27.9, 19.2, 13.8. FTIR (cm^{-1}): 2961, 2937, 2875, 1714, 1524, 1295, 1207, 1136, 1020, 762. HRMS (ESI) calculated for $C_{15}H_{20}O_6$ $[M+Na]^+$ 319.1152, found 319.1158.



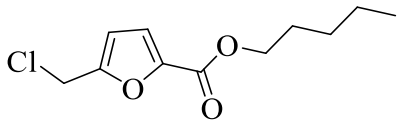
3c

Butyl 5-((benzoyloxy)methyl)furan-2-carboxylate (**3d**): Yellow liquid (0.0.242 g, 83%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.05 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 7.58-7.54 (m, 1H), 7.43 (t, 2H, *J* = 7.6 Hz), 7.14 (d, 2H, *J* = 3.6 Hz), 6.58 (d, 2H, *J* = 3.6 Hz), 5.35 (s, 2H), 4.31 (t, 2H, *J* = 6.4 Hz), 1.76-1.69 (m, 2H), 1.49-1.39 (m, 2H), 0.96 (t, 3H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm):166.2, 158.9, 153.6, 145.2, 133.4, 130.0, 129.6, 128.5, 118.6, 112.5, 65.1, 58.5, 30.9, 19.3, 13.8. FTIR (cm^{-1}): 2957, 2921, 2872, 1718, 1461, 1267, 1143, 1098, 1024, 711. HRMS (ESI) calculated for $C_{17}H_{18}O_5$ $[M+Na]^+$ 325.1046, found 325.1053.



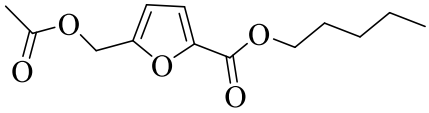
3d

pentyl 5-(chloromethyl)furan-2-carboxylate (**4**): Light yellow liquid (2.167 g, 85%), ^{1}H-NMR ($CDCl_3$, 800 MHz) δ (ppm): 7.26 (d, 1H, *J* = 3.2 Hz), 6.63 (d, 1H, *J* = 3.2 Hz), 4.75 (s, 2H), 4.45 (t, 2H, *J* = 7.2 Hz), 1.91-1.88 (m, 2H), 155-1.51 (m, 4H), 1.07 (t, 3H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 200 MHz) δ (ppm):158.7, 154.2, 145.3, 118.7, 111.5, 65.4, 36.8, 28.5, 28.1, 22.4, 14.1. FTIR (cm^{-1}): 2957, 2932, 2867, 1722, 1528, 1463, 1298, 1157, 1123, 1018, 762. HRMS (ESI) calculated for $C_{11}H_{15}ClO_3$ $[M+Na]^+$ 253.0602, found 253.0638.



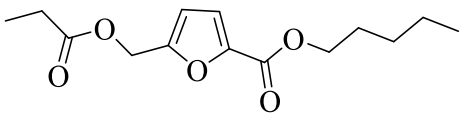
4

Pentyl 5-(acetoxymethyl)furan-2-carboxylate (**4a**): Yellow liquid (0.296 g, 84%), ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.27 (d, 1H, *J* = 3.6 Hz), 6.65 (d, 1H, *J* = 3.6 Hz), 5.24 (s, 2H), 4.44 (t, 2H, *J* = 6.9 Hz), 2.24 (s, 3H), 1.93-1.85 (m, 2H), 1.56-1.50 (m, 4H), 1.07 (t, 3H, *J* = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 170.5, 158.8, 153.5, 145.2, 118.5, 112.3, 65.4, 58.0, 28.5, 28.1, 22.4, 20.9, 14.1. FTIR (cm^{-1}): 2958, 2934, 2871, 1744, 1718, 1535, 1376, 1296, 1208, 1136, 1021, 762. HRMS (ESI) calculated for $C_{13}H_{18}O_5$ $[M+K]^+$ 293.0786, found 293.0789.



4a

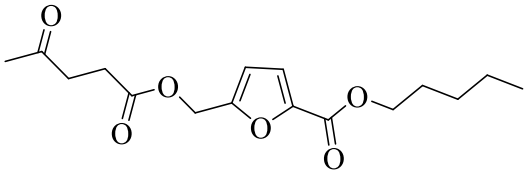
Pentyl 5-((propionyloxy)methyl)furan-2-carboxylate (**4b**): Yellow liquid (0.212 g, 80%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.26 (d, 1H, *J* = 3.6 Hz), 6.63 (d, 1H, *J* = 3.6 Hz), 5.23 (s, 2H), 4.43 (t, 2H, *J* = 6.8 Hz), 2.51 (q, 2H, *J* = 7.6 Hz), 1.90-1.84 (m, 2H), 1.56-1.50 (m, 4H), 1.28 (t, 3H, *J* = 7.6 Hz), 1.05 (t, 3H, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm):174.1, 158.8, 153.6, 145.1, 118.5, 112.2, 65.4, 57.9, 28.5, 28.1, 27.4, 22.4, 14.1, 9.1. FTIR (cm^{-1}): 2958, 2934, 2869, 1733, 1532, 1462, 1297, 1209, 1139, 962, 763. HRMS (ESI) calculated for $C_{14}H_{20}O_5$ $[M+H]^+$ 269.1384, found 269.1389.



4b

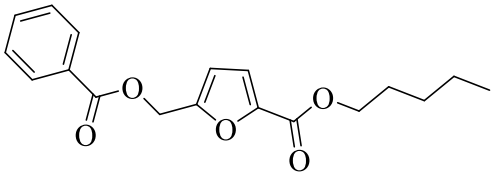
Pentyl 5-(((4-oxopentanoyl)oxy)methyl)furan-2-carboxylate(**4c**): Yellow liquid (0.245 g, 88%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (d, 1H, *J* = 3.6 Hz), 6.49 (d, 1H, *J* = 3.6 Hz), 5.10 (s, 2H), 4.29 (t, 2H, *J* = 6.8 Hz), 2.76 (t, 2H, *J* = 6.4 Hz), 2.61 (t, 2H, *J* = 6.4 Hz), 2.18 (s, 3H), 1.77-1.71 (m, 2H), 1.40-1.36 (m, 4H), 0.92 (t, 3H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100

MHz) δ (ppm):206.5, 172.3, 158.8, 153.4, 145.1, 118.6, 112.3, 65.4, 58.3, 37.9, 30.0, 28.5, 28.1, 27.9, 22.4, 14.1. FTIR (cm^{-1}): 2958, 2928, 2859, 1717, 1533, 1297, 1208, 1141, 1021, 763. HRMS (ESI) calculated for $C_{16}H_{22}O_6$ $[M+Na]^+$ 333.1309, found 333.1315.



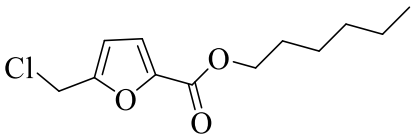
4c

pentyl 5-((benzoyloxy)methyl)furan-2-carboxylate(**4d**): Yellow liquid (0.233 g, 84%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.05 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.58-7.54 (m, 1H), 7.43 (t, 2H, J = 8.0 Hz), 7.14 (d, 1H, J = 3.6 Hz), 6.58 (d, 1H, J = 3.6 Hz), 5.35 (s, 2H), 4.30 (t, 2H, J = 6.8 Hz), 1.78-1.71 (m, 2H), 1.40-1.36 (m, 4H), 0.91 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.1, 158.8, 153.6, 145.2, 133.4, 129.9, 129.6, 128.5, 118.6, 112.5, 65.4, 58.4, 28.5, 28.1, 22.4, 14.1. FTIR (cm^{-1}): 2959, 2927, 2865, 1726, 1458, 1300, 1267, 1142, 1101, 1069, 762. HRMS (ESI) calculated for $C_{18}H_{20}O_5$ $[M+Na]^+$ 339.1203, found 339.1208.



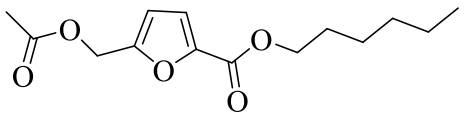
4d

Hexyl 5-(chloromethyl)furan-2-carboxylate (**5**): Light yellow liquid (2.620 g, 86%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, J = 3.6 Hz), 6.48 (d, 1H, J = 3.6 Hz), 4.59 (s, 2H), 4.30 (t, 2H, J = 6.8 Hz), 1.77-1.70 (m, 2H), 1.42-1.25 (m, 6H), 0.89 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.7, 154.2, 145.3, 118.7, 115.5, 65.5, 36.9, 31.5, 28.8, 25.7, 22.7, 14.1. FTIR (cm^{-1}): 2957, 2930, 2860, 1723, 1529, 1299, 1212, 1160, 1019, 762. HRMS (ESI) calculated for $C_{12}H_{17}ClO_3$ $[M+H]^+$ 245.0939, found 245.0937.



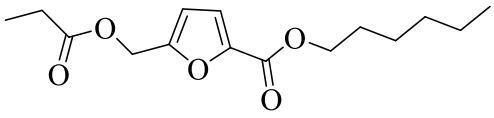
5

Hexyl 5-(acetoxymethyl)furan-2-carboxylate (**5a**): Yellow liquid (0.308 g, 85%), ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.26 (d, 1H, J = 3.3 Hz), 6.65 (d, 1H, J = 3.3 Hz), 5.24 (s, 2H), 4.44 (t, 3H, J = 6.9 Hz), 2.24 (s, 3H), 1.93-1.84 (m, 2H), 1.58-1.44 (m, 6H), 1.04 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 170.5, 158.8, 153.5, 145.2, 118.5, 112.3, 65.4, 58.0, 31.5, 28.7, 25.6, 22.6, 20.9, 14.1. FTIR (cm^{-1}): 2957, 2931, 2860, 1745, 1718, 1598, 1375, 1296, 1208, 1021, 812, 762. HRMS (ESI) calculated for $C_{14}H_{20}O_5$ $[M+K]^+$ 307.0942, found 307.0952.



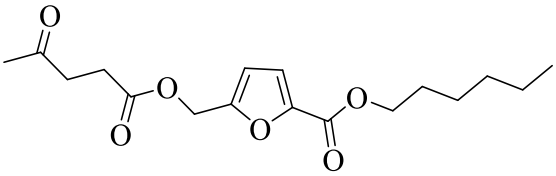
5a

Hexyl 5-((propionyloxy)methyl)furan-2-carboxylate (**5b**): Yellow liquid (0.185 g, 78%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (d, 1H, *J* = 3.6 Hz), 6.48 (d, 1H, *J* = 3.6 Hz), 5.09 (s, 2H), 4.29 (t, 2H, *J* = 6.8 Hz), 2.36 (q, 2H, *J* = 7.6 Hz), 1.76-1.69 (m, 2H), 1.42-1.25 (m, 6H), 1.14 (t, 3H, *J* = 7.6 Hz), 0.89 (t, 3H, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 174.0, 158.8, 153.7, 145.1, 118.5, 112.2, 65.4, 57.9, 31.5, 28.8, 27.5, 25.7, 22.6, 14.1, 9.1. FTIR (cm^{-1}): 2956, 2928, 2857, 1732, 1719, 1462, 1296, 1208, 1138, 1018, 762. HRMS (ESI) calculated for $C_{15}H_{22}O_5$ $[M+Na]^+$ 305.1359, found 305.1363.



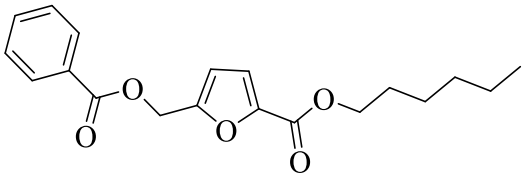
5b

Hexyl 5-(((4-oxopentanoyl)oxy)methyl)furan-2-carboxylate (**5c**): Yellow liquid (0.239 g, 89%), ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.27 (d, 1H, *J* = 3.6 Hz), 6.65 (d, 1H, *J* = 3.6 Hz), 5.25 (s, 2H), 4.44 (t, 2H, *J* = 6.8 Hz), 2.92 (t, 2H, *J* = 6.2 Hz), 2.76 (t, 2H, *J* = 6.2 Hz), 2.34 (s, 3H), 1.93-1.84 (m, 2H), 1.58-1.45 (m, 6H), 1.05 (t, 3H, *J* = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 206.5, 172.3, 158.8, 153.4, 145.1, 118.5, 112.2, 65.3, 58.2, 37.9, 31.5, 29.9, 28.7, 27.9, 25.6, 22.6, 14.1. FTIR (cm^{-1}): 2957, 2930, 2860, 1715, 1536, 1296, 1208, 1139, 992, 763. HRMS (ESI) calculated for $C_{17}H_{24}O_6$ $[M+H]^+$ 325.1646, found 325.1647.



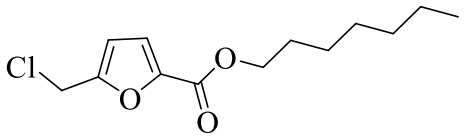
5c

Hexyl 5-((benzoyloxy)methyl)furan-2-carboxylate (**5d**): Yellow liquid (0.254 g, 85%), ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.05 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.59-7.53 (m, 1H), 7.43 (t, 2H, *J* = 7.4 Hz), 7.14 (d, 1H, *J* = 3.4 Hz), 6.58 (d, 1H, *J* = 3.4 Hz), 5.35 (s, 2H), 4.30 (t, 2H, *J* = 6.8 Hz), 1.78-1.69 (m, 2H), 1.45-1.29 (m, 6H), 0.89 (t, 3H, *J* = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 166.2, 158.8, 153.6, 145.2, 133.4, 129.9, 129.6, 128.5, 118.6, 112.5, 65.4, 58.4, 31.5, 28.8, 25.7, 22.6, 14.1. FTIR (cm^{-1}): 2957, 2931, 2859, 1718, 1466, 1296, 1263, 1138, 1093, 1068, 762. HRMS (ESI) calculated for $C_{19}H_{22}O_5$ $[M+NH_4]^+$ 348.1805, found 348.1839.



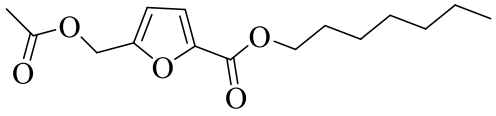
5d

Heptyl 5-(chloromethyl)furan-2-carboxylate (**6**): Light yellow liquid (2.396 g, 89%), ^{1}H-NMR ($CDCl_3$, 800 MHz) δ (ppm):7.26 (d, 1H, *J* = 3.2 Hz), 6.64 (d, 1H, *J* = 3.2 Hz), 4.75 (s, 2H), 4.45 (t, 2H, *J* = 7.2 Hz), 1.91-1.87 (m, 2H), 1.56-1.53 (m 2H), 1.51-1.47 (m, 2H), 1.46-1.43 (m, 4H), 1.04 (t, 3H, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 200 MHz) δ (ppm):158.6, 154.1, 145.2, 118.6, 111.4, 65.4, 36.8, 31.8, 29.0, 28.7, 25.9, 22.6, 14.1. FTIR (cm^{-1}): 2553, 2927, 2859, 1730, 1462, 1298, 1159, 1224, 762. HRMS (ESI) calculated for $C_{13}H_{19}ClO_3$ $[M+K]^+$ 297.0654, found 297.0665.



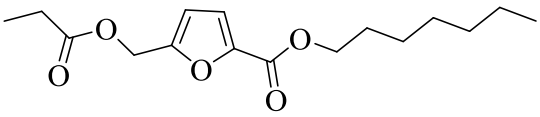
6

Heptyl 5-(acetoxymethyl)furan-2-carboxylate (**6a**): Yellow liquid (0.284 g, 86%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (d, 1H, *J* = 3.6 Hz), 6.49 (d, 1H, *J* = 3.6 Hz), 5.08 (s, 2H), 4.29 (t, 2H, *J* = 6.8 Hz), 2.09 (s, 3H), 1.77-1.70 (m, 2H), 1.42-1.29 (m, 8H), 0.88 (t, 3H, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.6, 158.8, 153.5, 145.2, 118.5, 112.3, 65.4, 58.0, 31.8, 29.0, 28.8, 26.0, 22.7, 20.9, 14.2. FTIR (cm^{-1}): 2956, 2928, 2857, 1745, 1719, 1295, 1208, 1020, 762. HRMS (ESI) calculated for $C_{15}H_{22}O_5$ $[M+K]^+$ 321.1099, found 321.1113.



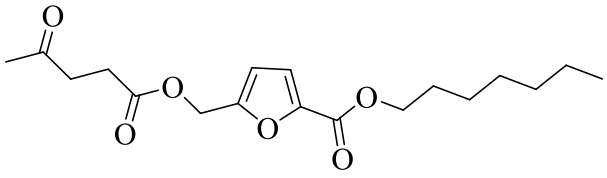
6a

Heptyl 5-((propionyloxy)methyl)furan-2-carboxylate (**6b**): Yellow liquid (0.209 g, 80%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (d, 1H, *J* = 3.6 Hz), 6.49 (d, 1H, *J* = 3.6 Hz), 5.09 (s, 2H), 4.29 (t, 2H, *J* = 6.8 Hz), 2.37 (q, 2H, *J* = 7.6 Hz), 1.77-1.70 (m, 2H), 1.42-1.25 (m, 8H), 1.14 (t, 3H, *J* = 7.6 Hz), 0.88 (t, 3H, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 174.1, 158.9, 153.6, 145.1, 118.5, 112.2, 65.4, 57.9, 31.5, 29.8, 28.7, 27.5, 25.7, 22.6, 14.1, 9.1. FTIR (cm^{-1}): 2956, 2928, 2857, 1716, 1524, 1295, 1139, 950, 763. HRMS (ESI) calculated for $C_{16}H_{24}O_5$ $[M+Na]^+$ 319.1516, found 319.1523.



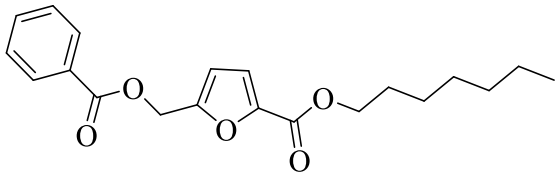
6b

Heptyl 5-(((4-oxopentanoyl)oxy)methyl)furan-2-carboxylate (**6c**): Yellow liquid (0.220 g, 89%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (d, 1H, *J* = 3.4 Hz), 6.49 (d, 1H, *J* = 3.4 Hz), 5.09 (s, 2H), 4.28 (t, 2H, *J* = 6.8 Hz), 2.76 (t, 2H, *J* = 6.8 Hz), 2.61 (d, 2H, *J* = 6.8 Hz), 2.18 (s, 3H), 1.74-1.69 (m, 2H), 1.41-1.24 (m, 8H), 0.88 (t, 3H, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 206.6, 172.4, 158.8, 153.4, 145.1, 118.6, 112.3, 65.4, 58.2, 37.9, 31.8, 30.0, 29.0, 28.8, 27.9, 26.0, 22.7, 14.2. FTIR (cm^{-1}): 2958, 2928, 2858, 1718, 1537, 1353, 1261, 1141, 950, 762. HRMS (ESI) calculated for $C_{18}H_{26}O_6$ $[M+Na]^+$ 361.1622, found 361.1622.



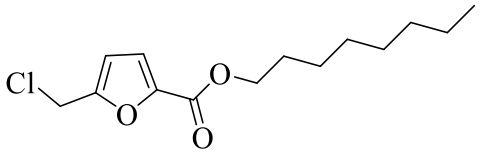
6c

Heptyl 5-((benzoyloxy)methyl)furan-2-carboxylate (**6d**): Yellow liquid (0.201 g, 83%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.04 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.58-7.54 (m, 1H), 7.43 (t, 2H, J = 6.9 Hz), 7.14 (d, 1H, J = 3.4 Hz), 6.59 (d, 1H, J = 3.4 Hz), 5.34 (s, 2H), 4.29 (t, 2H, J = 6.8 Hz), 1.77-1.70 (m, 2H), 1.41-1.24 (m, 8H), 0.87 (t, 3H, J = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.2, 158.9, 153.6, 145.2, 133.4, 129.9, 129.6, 128.5, 118.6, 112.5, 65.4, 58.4, 31.8, 29.0, 28.8, 26.0, 22.7, 14.2. FTIR (cm^{-1}): 2955, 2928, 2857, 1720, 1452, 1296, 1264, 1209, 1064, 762. HRMS (ESI) calculated for $C_{20}H_{24}O_5$ $[M+H]^+$ 345.1697, found 345.1698.



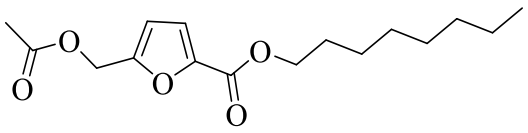
6d

Octyl 5-(chloromethyl)furan-2-carboxylate (**7**): Light yellow liquid (2.802 g, 89%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, J = 3.6 Hz), 6.48 ((d, 1H, J = 3.6 Hz), 4.59 (s, 2H), 4.29 (t, 2H, J = 6.8 Hz), 1.77-1.69 (m, 2H), 1.43-1.25 (m, 10H), 0.87 (t, 3H, J = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.7, 154.2, 145.2, 118.6, 111.5, 65.4, 36.8, 31.9, 29.3, 29.3, 28.8, 26.0, 22.8, 14.2. FTIR (cm^{-1}): 2955, 2925, 2855, 1720, 1466, 1267, 1159, 1055, 762. HRMS (ESI) calculated for $C_{16}H_{21}ClO_3$ $[M+H]^+$ 273.1252, found 273.1253.



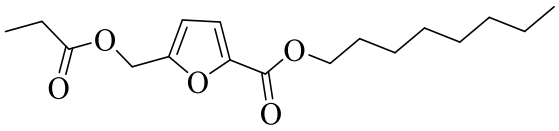
7

Octyl 5-(acetoxymethyl)furan-2-carboxylate (**7a**): Yellow liquid (0.243 g, 85%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (d, 1H, J = 3.4 Hz), 6.49 (d, 1H, J = 3.4 Hz), 5.08 (s, 2H), 4.29 (t, 2H, J = 6.8 Hz), 2.09 (s, 3H), 1.77-1.70 (m, 2H), 1.42-1.25 (m, 10H), 0.87 (t, 3H, J = 6.6 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.6, 158.8, 153.5, 145.2, 118.5, 112.3, 65.4, 58.0, 31.9, 29.3, 29.3, 28.8, 26.0, 22.8, 20.9, 14.2. FTIR (cm^{-1}): 2955, 2926, 2857, 1743, 1726, 1297, 1212, 1140, 763. HRMS (ESI) calculated for $C_{16}H_{24}O_5$ $[M+Na]^+$ 319.1516, found 319.1517.



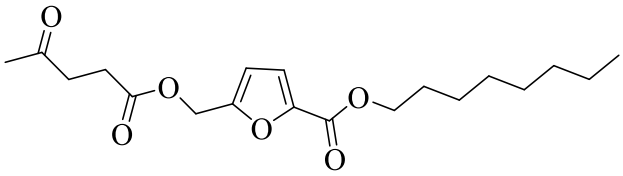
7a

Octyl 5-((propionyloxy)methyl)furan-2-carboxylate (**7b**): Yellow liquid (0.190 g, 81%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (d, 1H, *J* = 3.6 Hz), 6.49 (d, 1H, *J* = 3.6 Hz), 5.09 (s, 2H), 4.28 (t, 2H, *J* = 6.8 Hz), 2.36 (q, 2H, *J* = 7.6 Hz), 1.76-1.68 (m, 2H), 1.41-1.24 (m, 10H), 1.14 (t, 3H, *J* = 7.6 Hz), 0.87 (t, 3H, *J* = 6.6 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 174.1, 158.9, 153.6, 145.1, 118.6, 112.3, 65.4, 57.9, 31.9, 29.3, 29.3, 28.8, 27.5, 26.0, 22.8, 14.2, 9.1. FTIR (cm^{-1}): 2954, 2927, 2857, 1734, 1463, 1296, 1139, 1018, 762. HRMS (ESI) calculated for $C_{17}H_{26}O_5$ $[M+Na]^+$ 333.1672, found 333.1675.



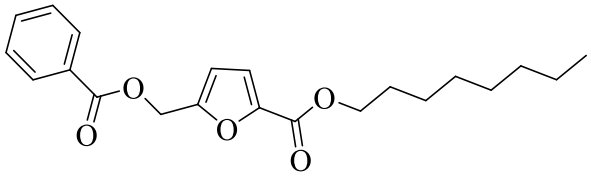
7b

Octyl 5-(((4-oxopentanoyl)oxy)methyl)furan-2-carboxylate (**7c**): Yellow liquid (0.278 g, 90%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (d, 1H, *J* = 3.6 Hz), 6.48 (d, 1H, *J* = 3.6 Hz), 5.08 (s, 2H), 4.27 (t, 2H, *J* = 6.8 Hz), 2.75 (t, 2H, *J* = 6.8 Hz), 2.60 (t, 2H, *J* = 3.6 Hz), 2.17 (s, 3H), 1.77-1.68 (m, 2H), 1.41-1.22 (m, 10H), 0.86 (t, 3H, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 206.6, 172.3, 158.8, 153.4, 145.1, 118.6, 112.3, 65.4, 58.2, 37.9, 31.9, 29.9, 29.3, 29.3, 28.8, 27.9, 26.0, 22.7, 14.2. FTIR (cm^{-1}): 2955, 2925, 2855, 1719, 1296, 1208, 1140, 1021, 762. HRMS (ESI) calculated for $C_{19}H_{28}O_6$ $[M+H]^+$ 353.1959, found 353.1956.



7c

Octyl 5-((benzoyloxy)methyl)furan-2-carboxylate (**7d**): Yellow liquid (0.216 g, 84%), ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.04 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.58-7.54 (m, 1H), 7.43 (t, 3H, *J* = 7.6 Hz), 7.14 (d, 1H, *J* = 3.6 Hz), 6.59 (d, 1H, *J* = 3.6 Hz), 5.34 (s, 2H), 4.29 (t, 2H, *J* = 6.8 Hz), 1.77-1.70 (m, 2H), 1.42-1.23 (m, 10H), 0.87 (t, 3H, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.2, 158.9, 153.6, 145.2, 133.4, 129.9, 129.6, 128.5, 118.6, 112.5, 65.4, 58.4, 31.9, 29.3, 29.3, 28.8, 26.0, 22.8, 14.2. FTIR (cm^{-1}): 2954, 2926, 2856, 1720, 1452, 1297, 1264, 1095, 1069, 710. HRMS (ESI) calculated for $C_{21}H_{26}O_5$ $[M+H]^+$ 359.1853, found 359.1858.



7d

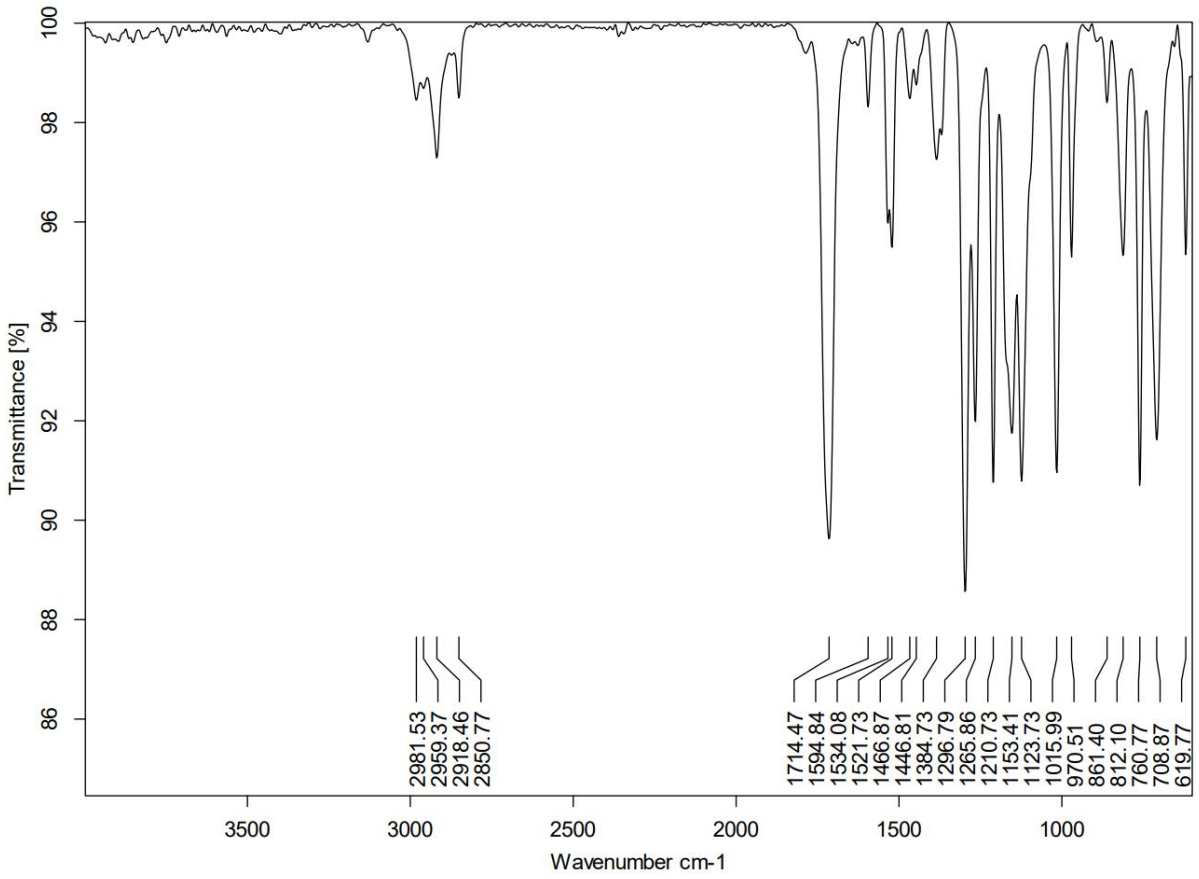


Figure S1. The FTIR spectrum of **1**.

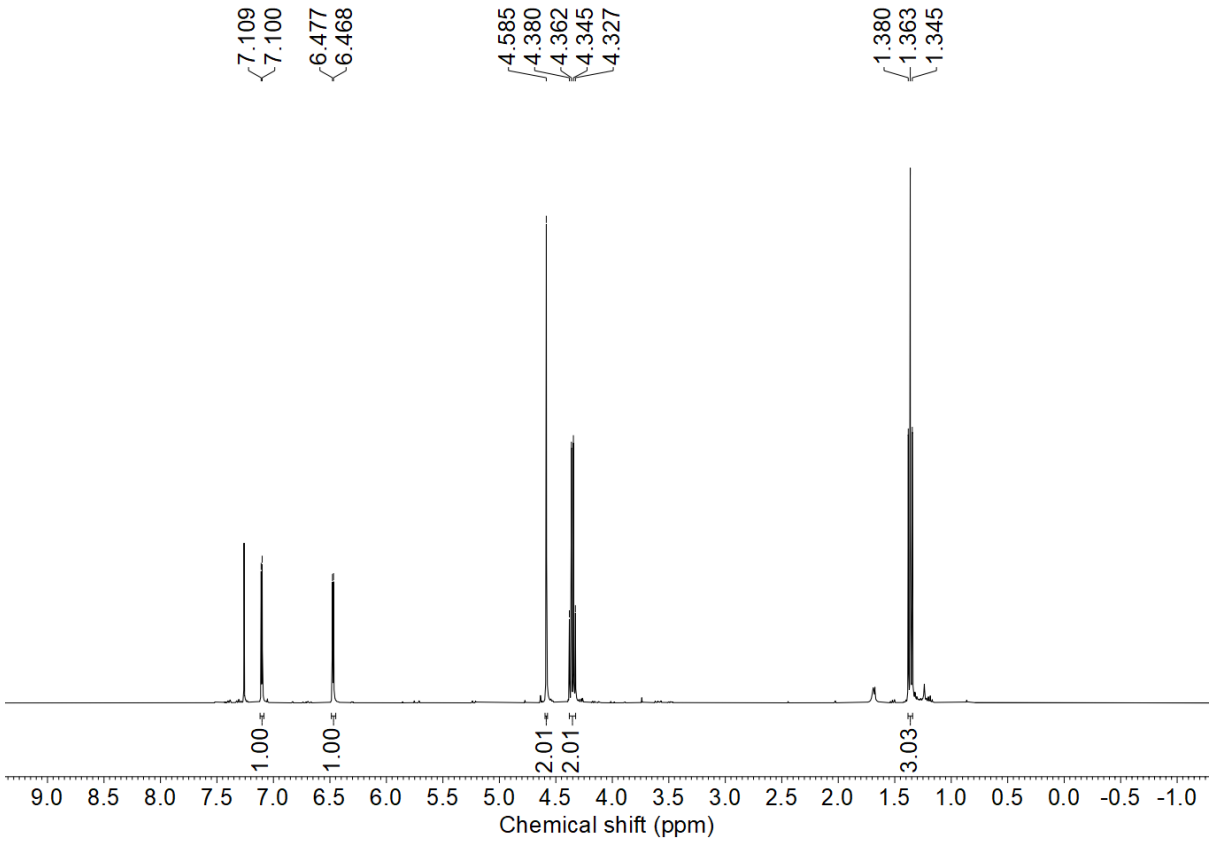


Figure S2. The ^{1}H-NMR spectrum of **1**.

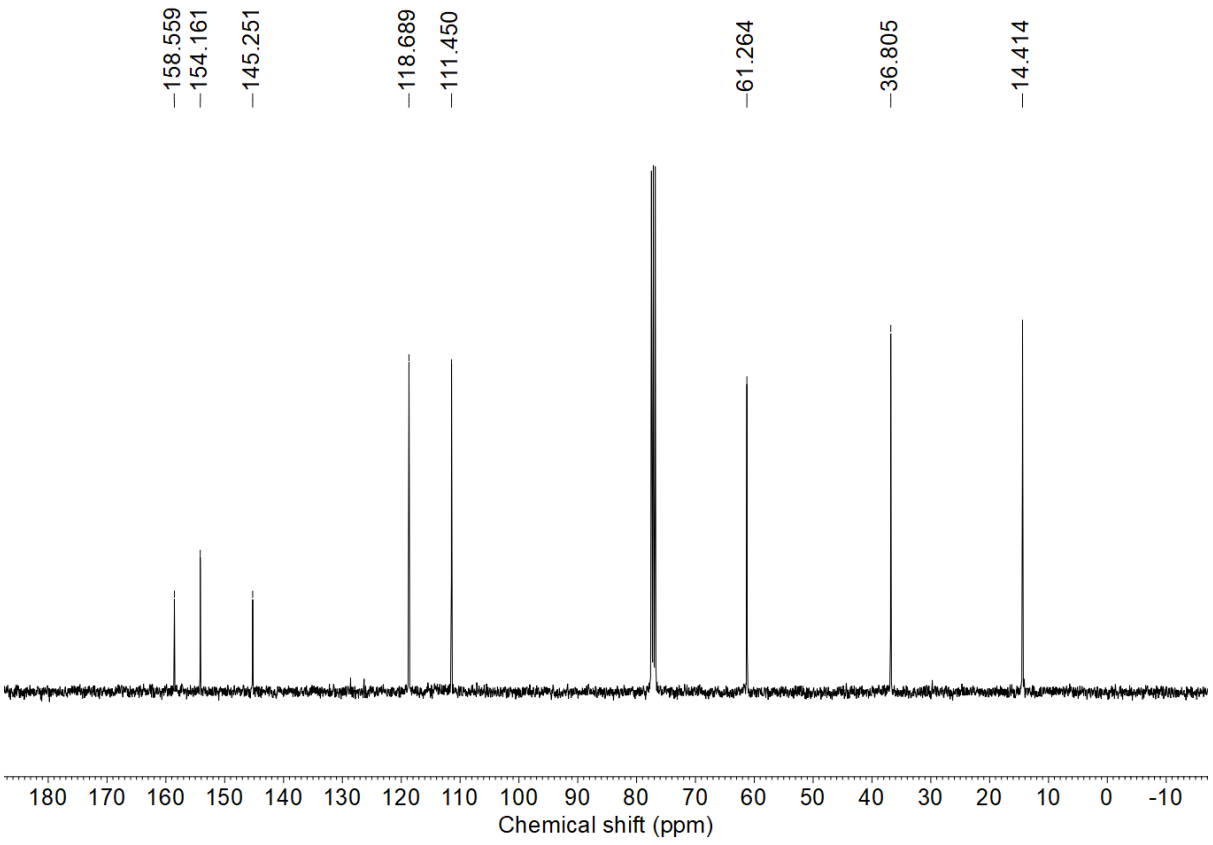


Figure S3. The ^{13}C-NMR spectrum of **1**.

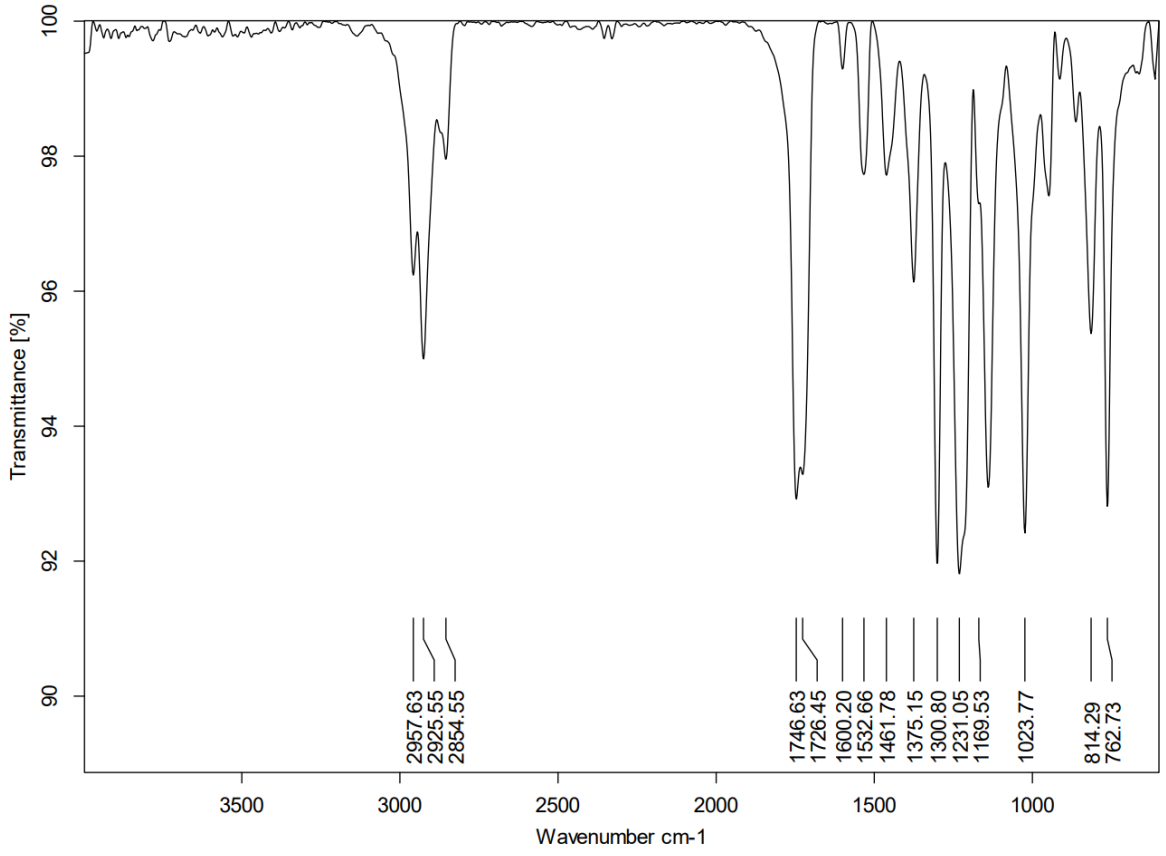


Figure S4. The FTIR spectrum of **1a**.

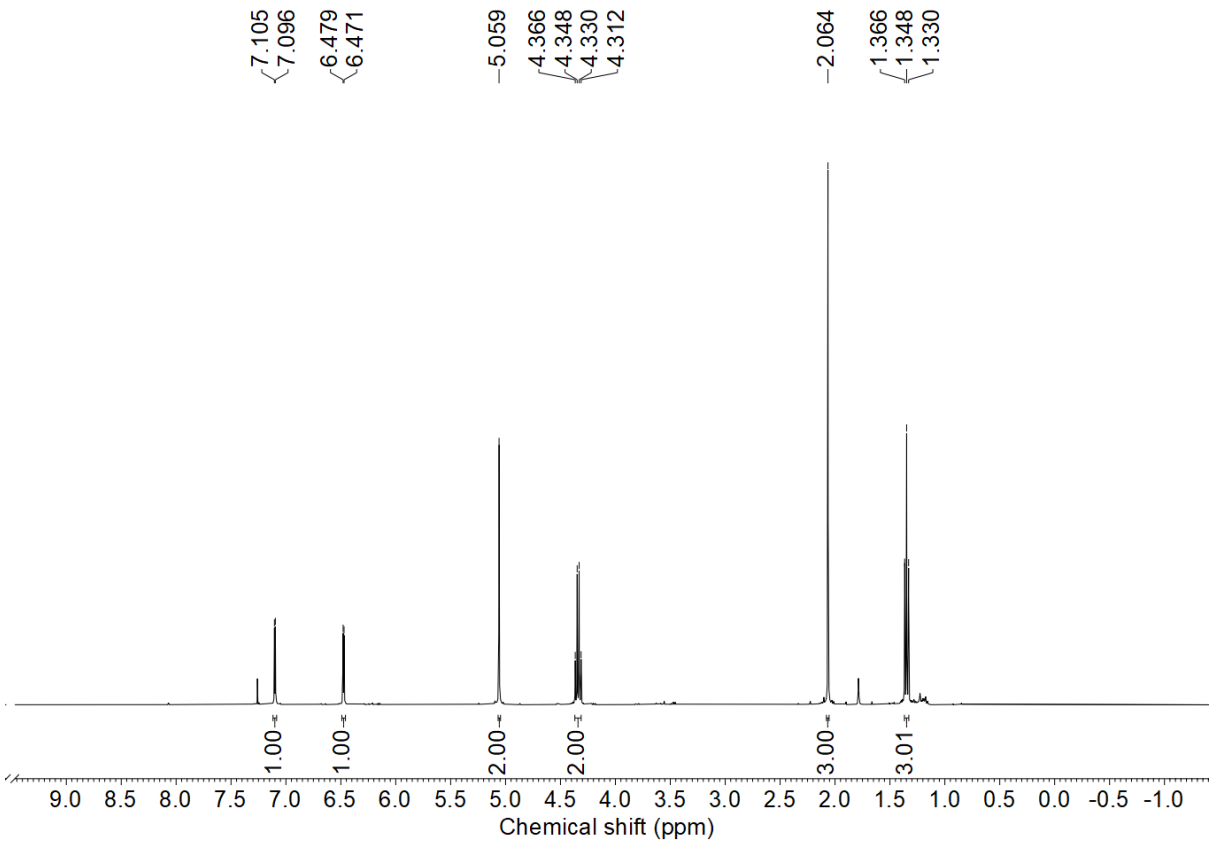


Figure S5. The ^{1}H-NMR spectrum of **1a**.

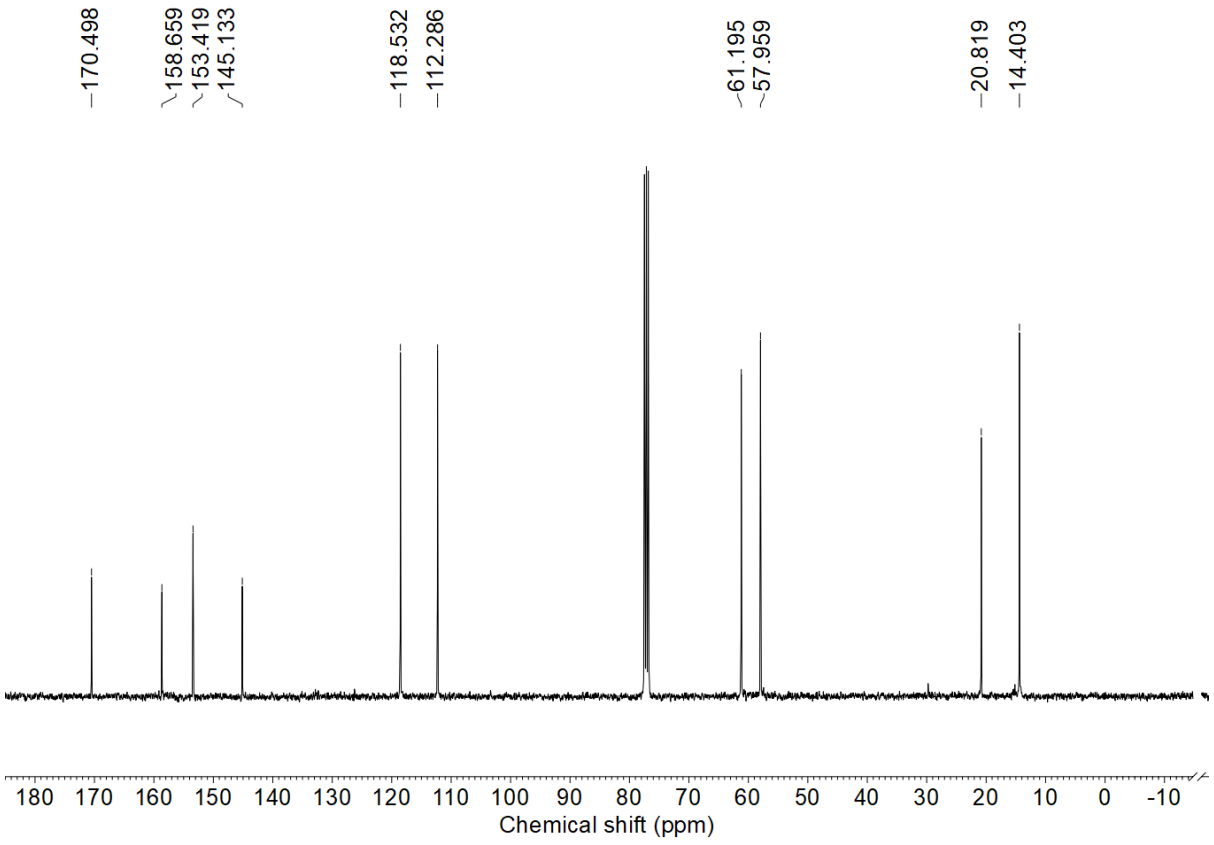


Figure S6. The ^{13}C-NMR spectrum of **1a**.

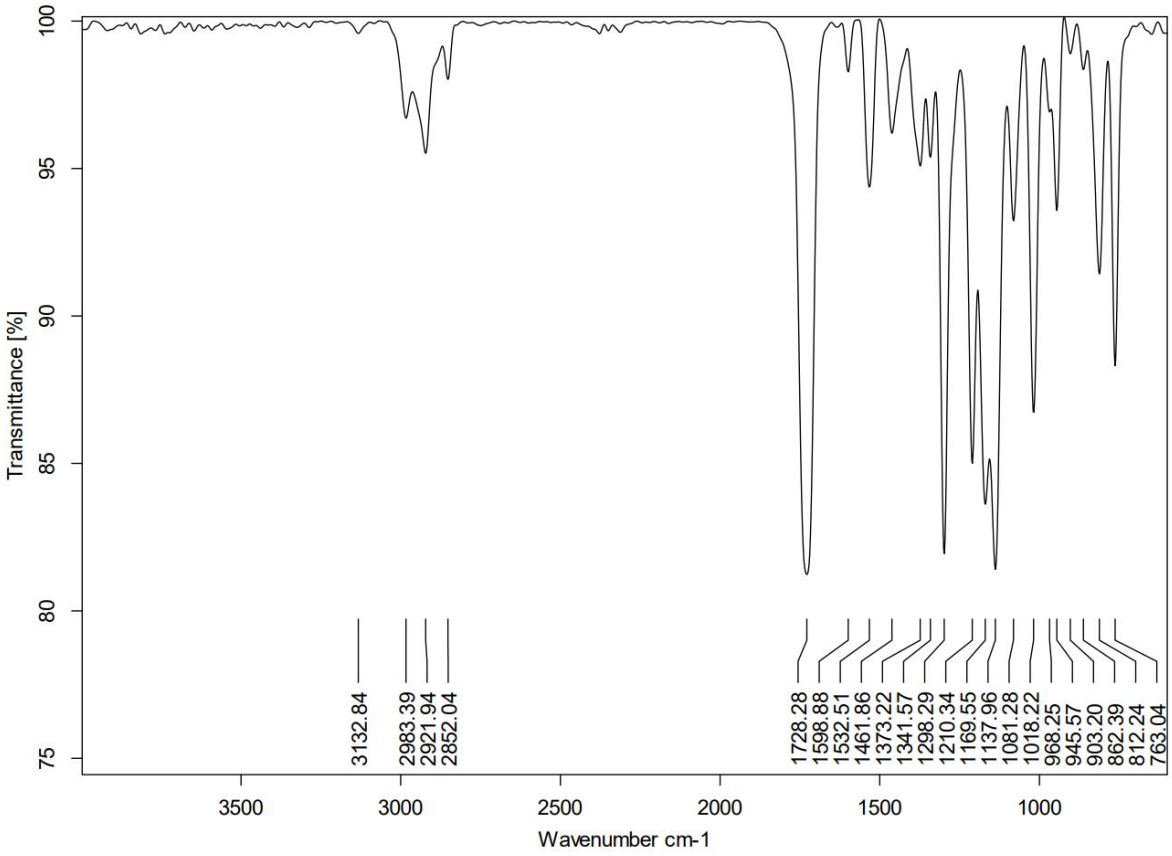


Figure S7. The FTIR spectrum of **1b**.

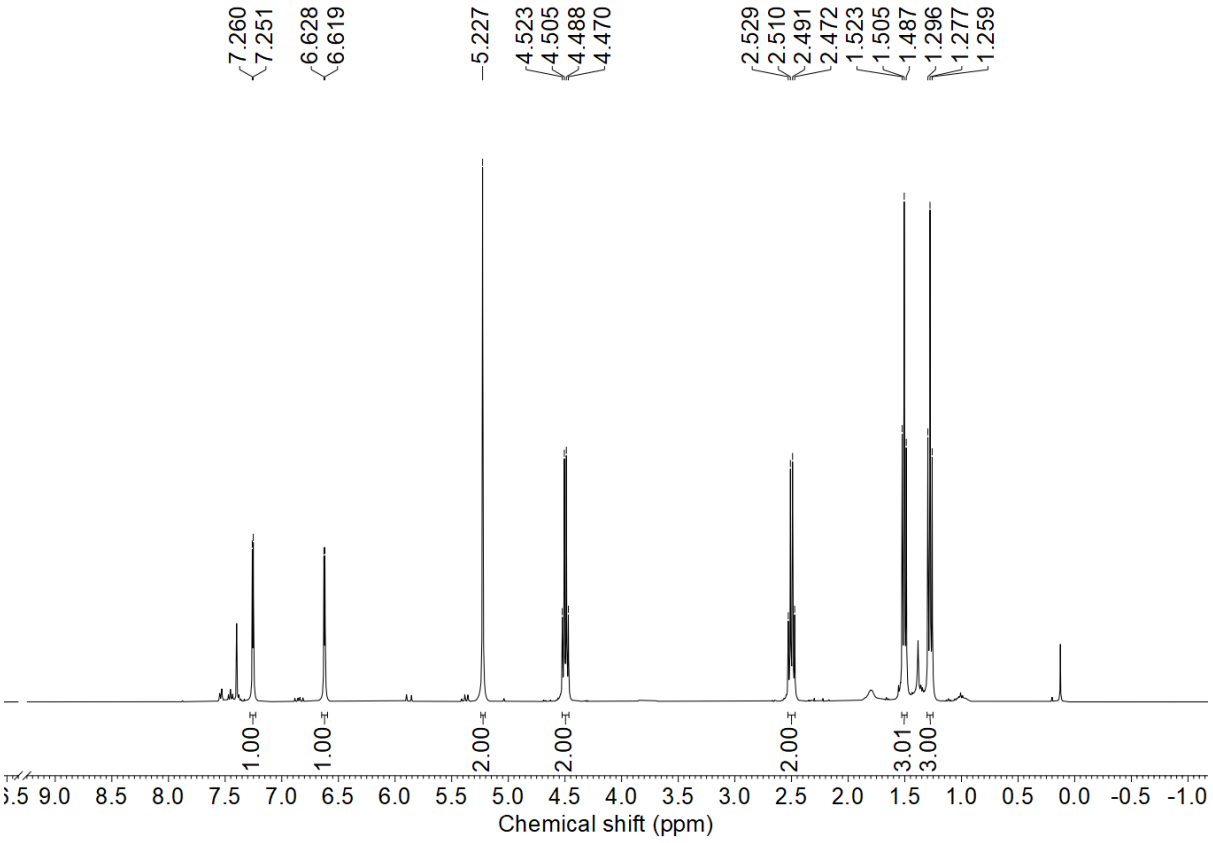


Figure S8. The ^{1}H-NMR spectrum of **1b**.

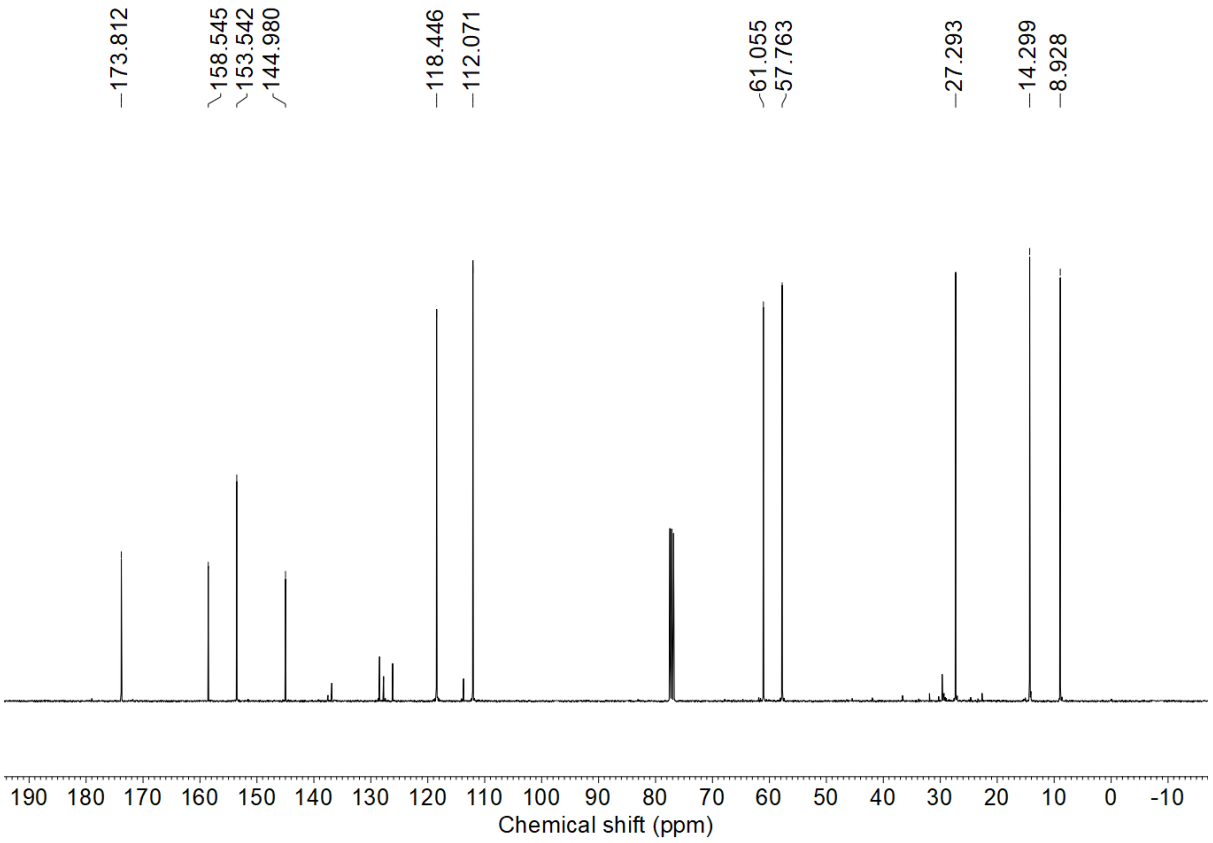


Figure S9. The ^{13}C-NMR spectrum of **1b**.

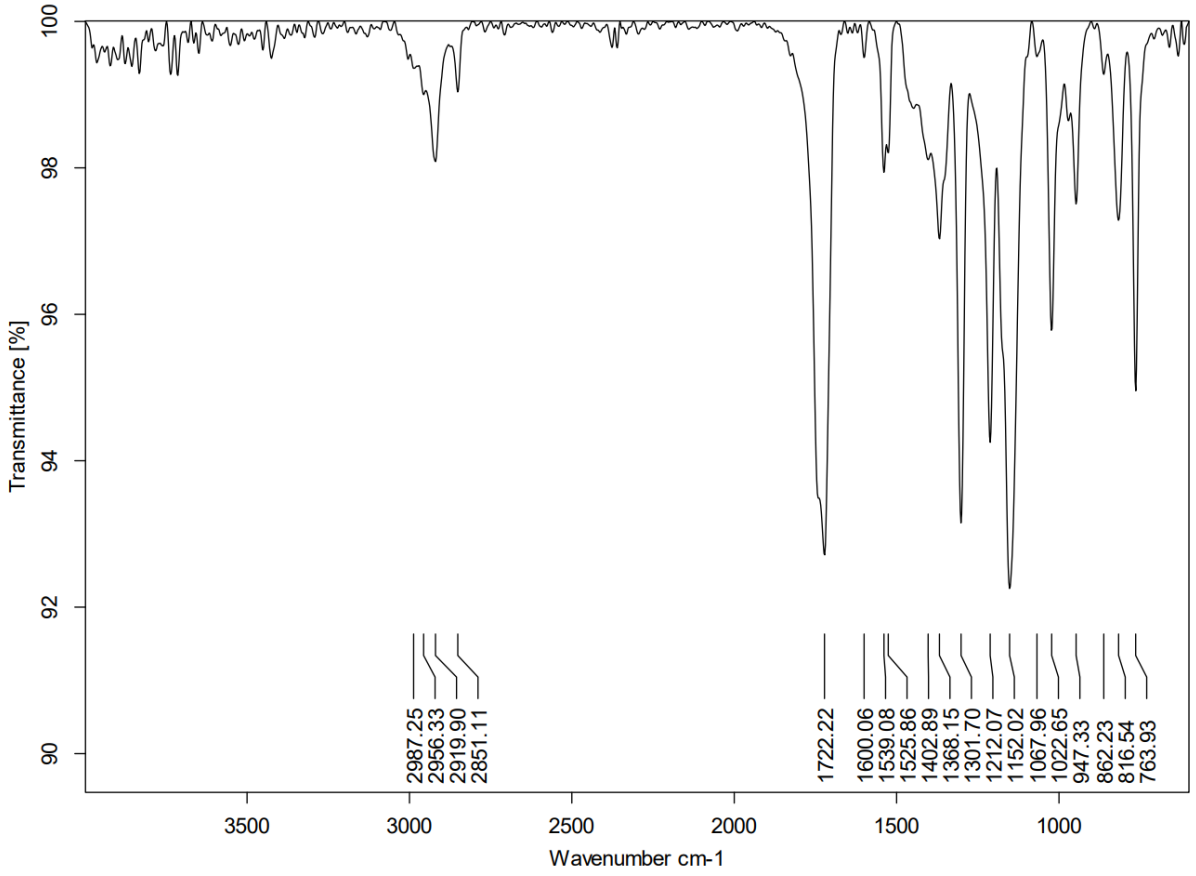


Figure S10. The FTIR spectrum of **1c**.

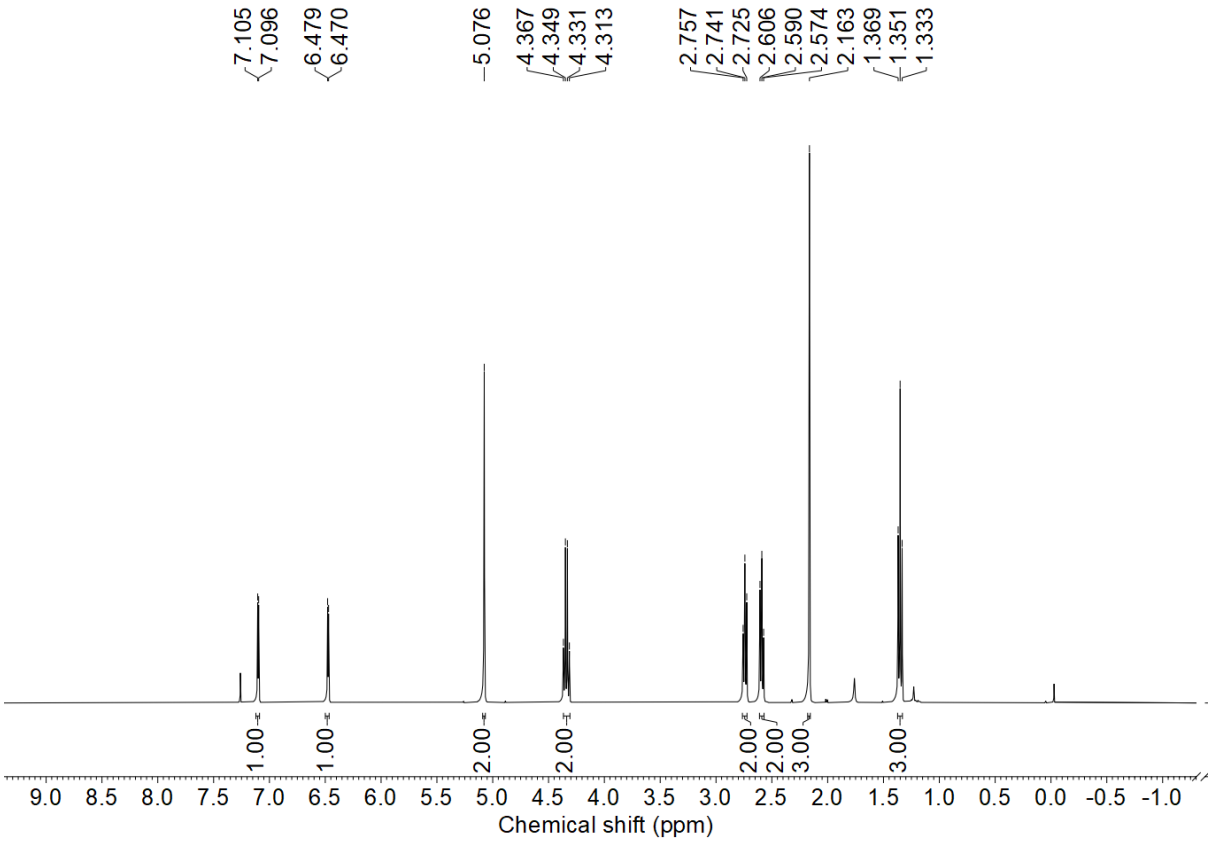


Figure S11. The ^{1}H-NMR spectrum of **1c**.

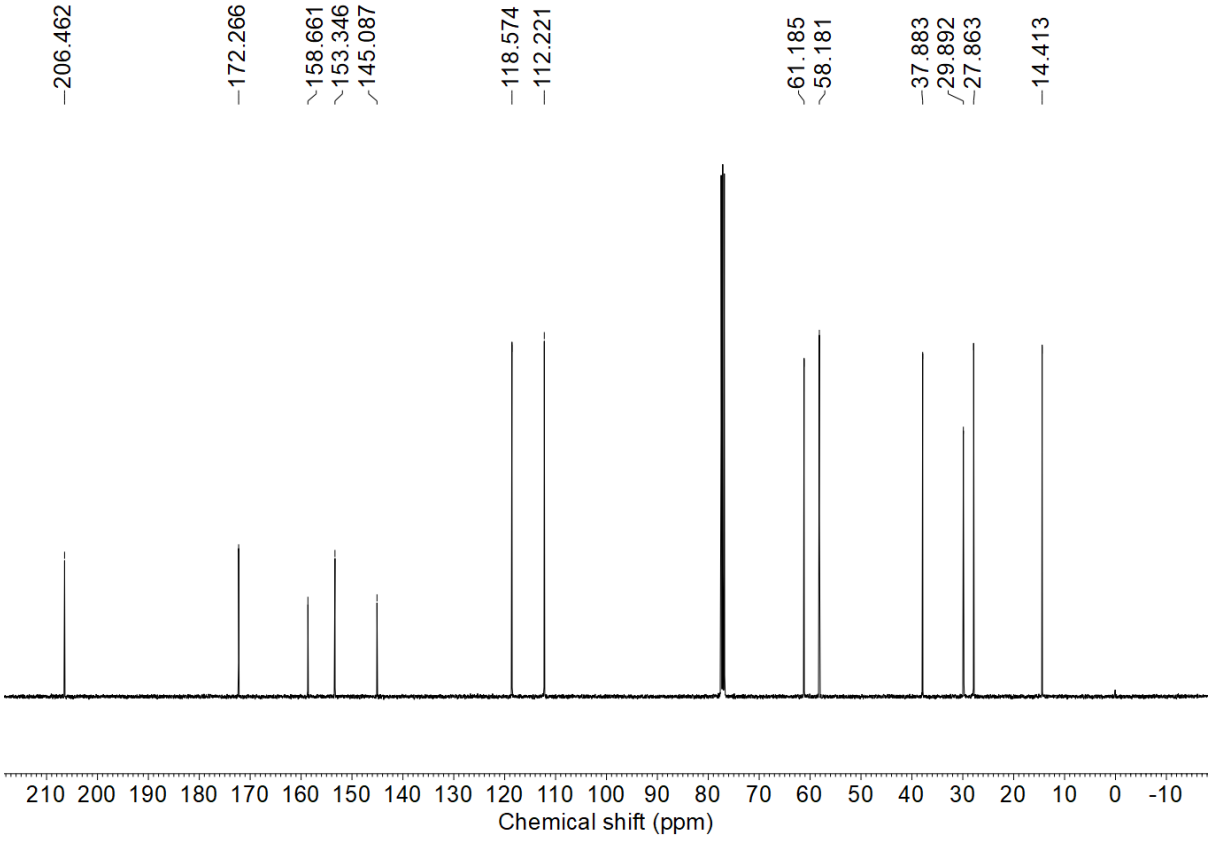


Figure S12. The ^{13}C-NMR spectrum of **1c**.

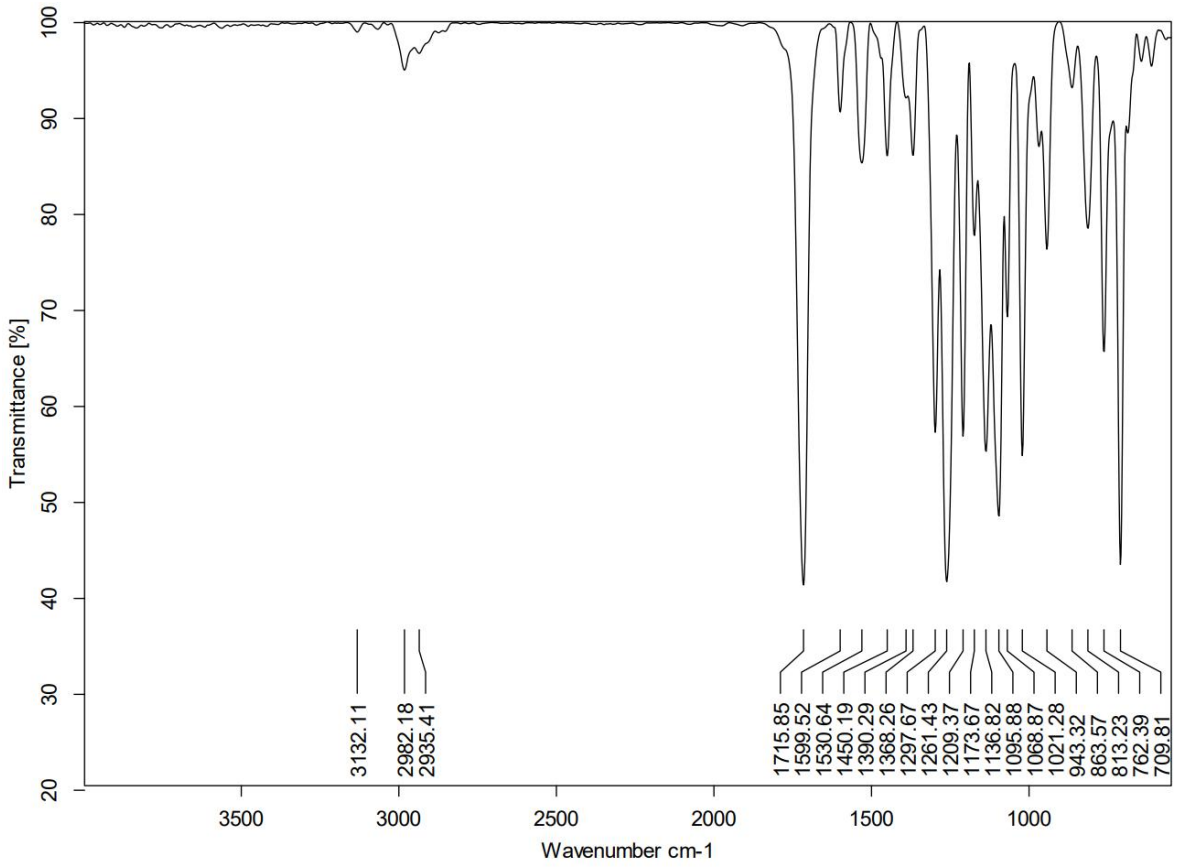


Figure S13. The FTIR spectrum of **1d**.

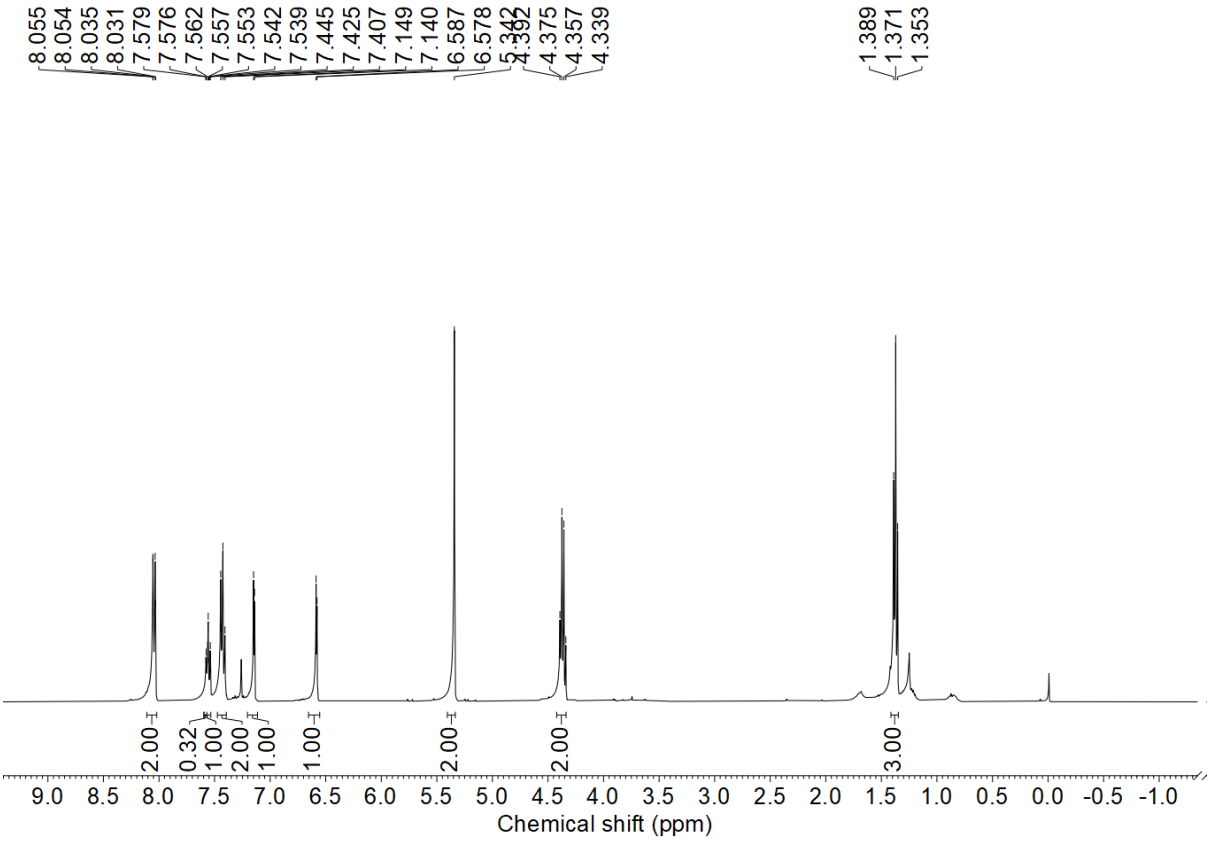


Figure S14. The ^{1}H-NMR spectrum of **1d**.

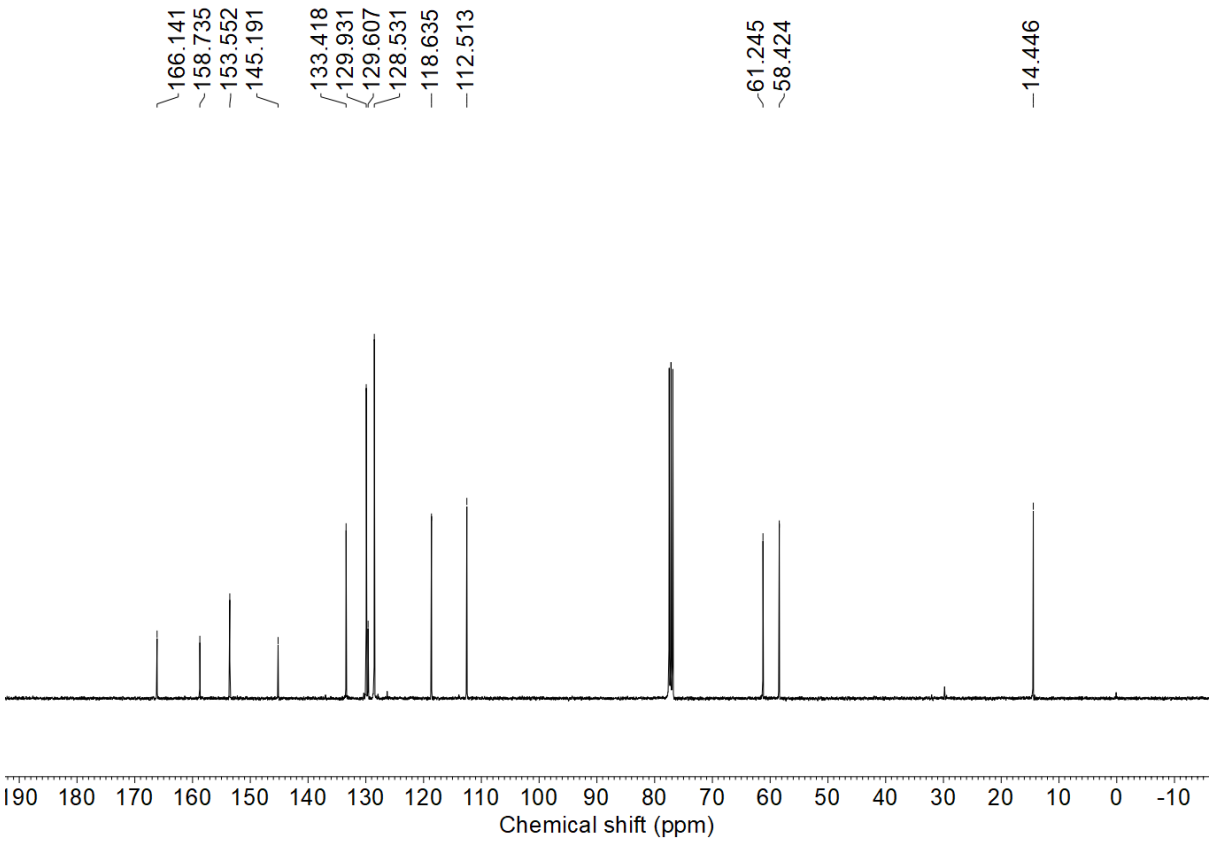


Figure S15. The ^{13}C-NMR spectrum of **1d**.

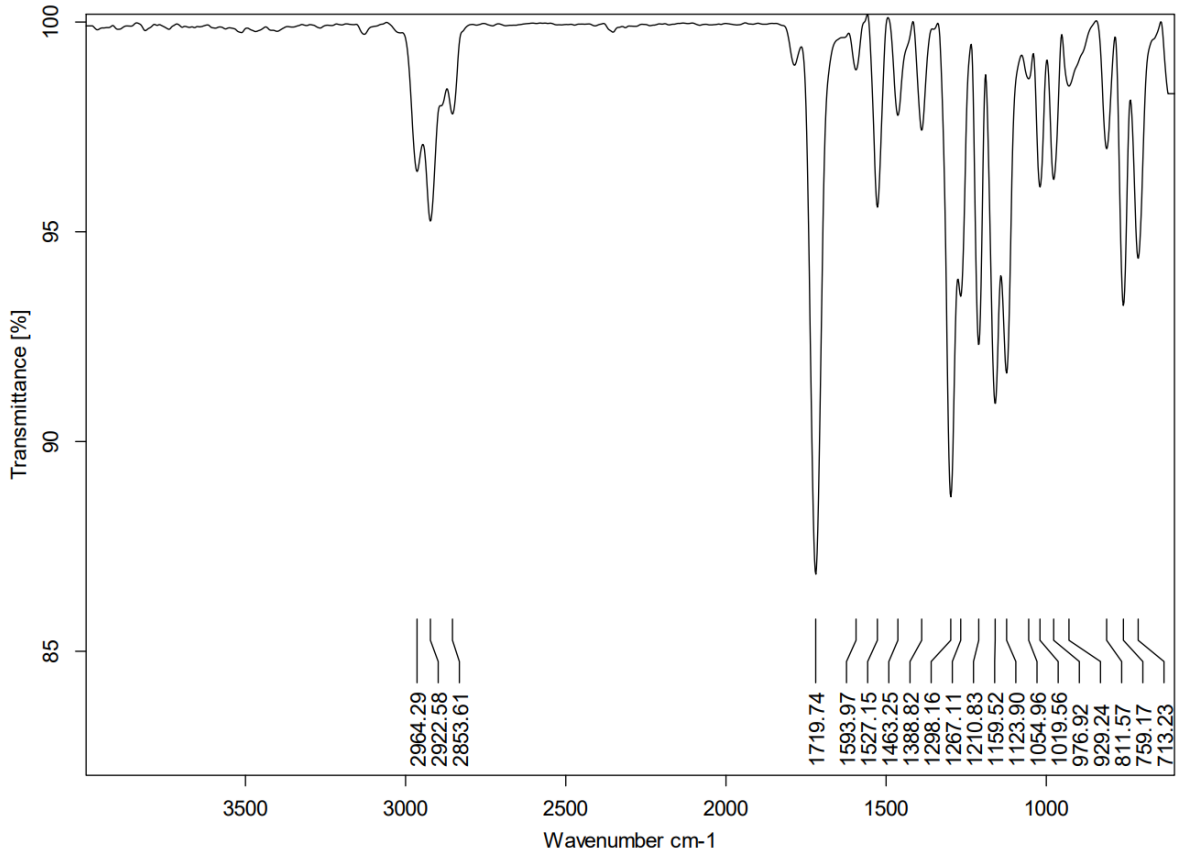


Figure S16. The FTIR spectrum of **2**.

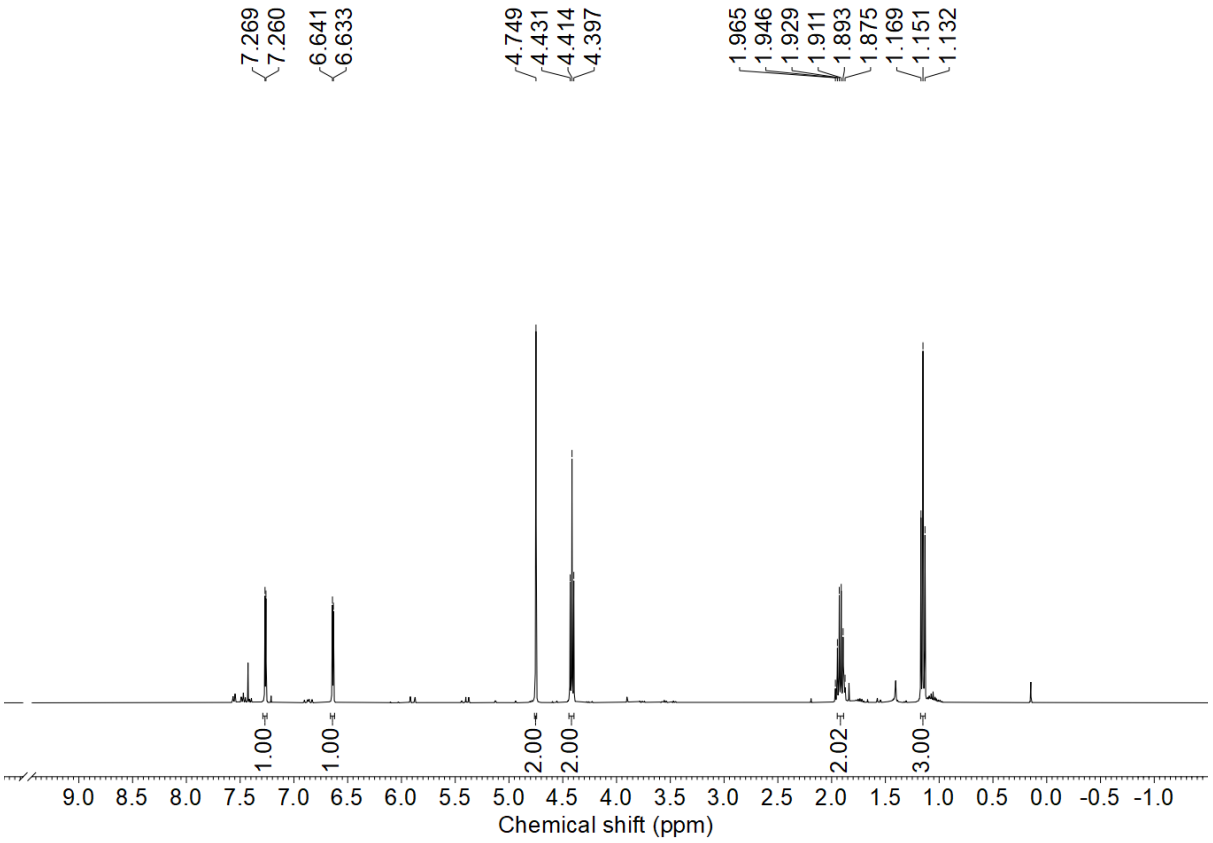


Figure S17. The ^{1}H-NMR spectrum of **2**.

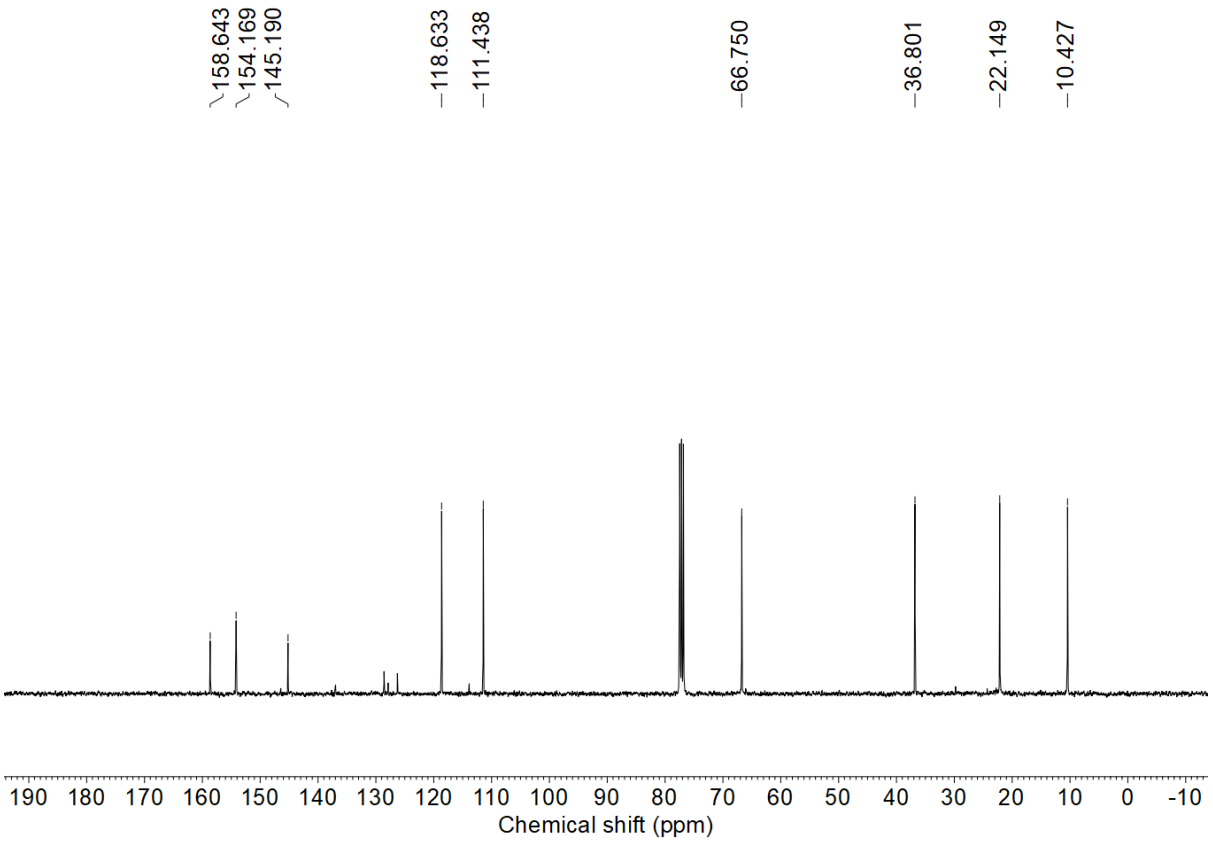


Figure S18. The ^{13}C-NMR spectrum of **2**.

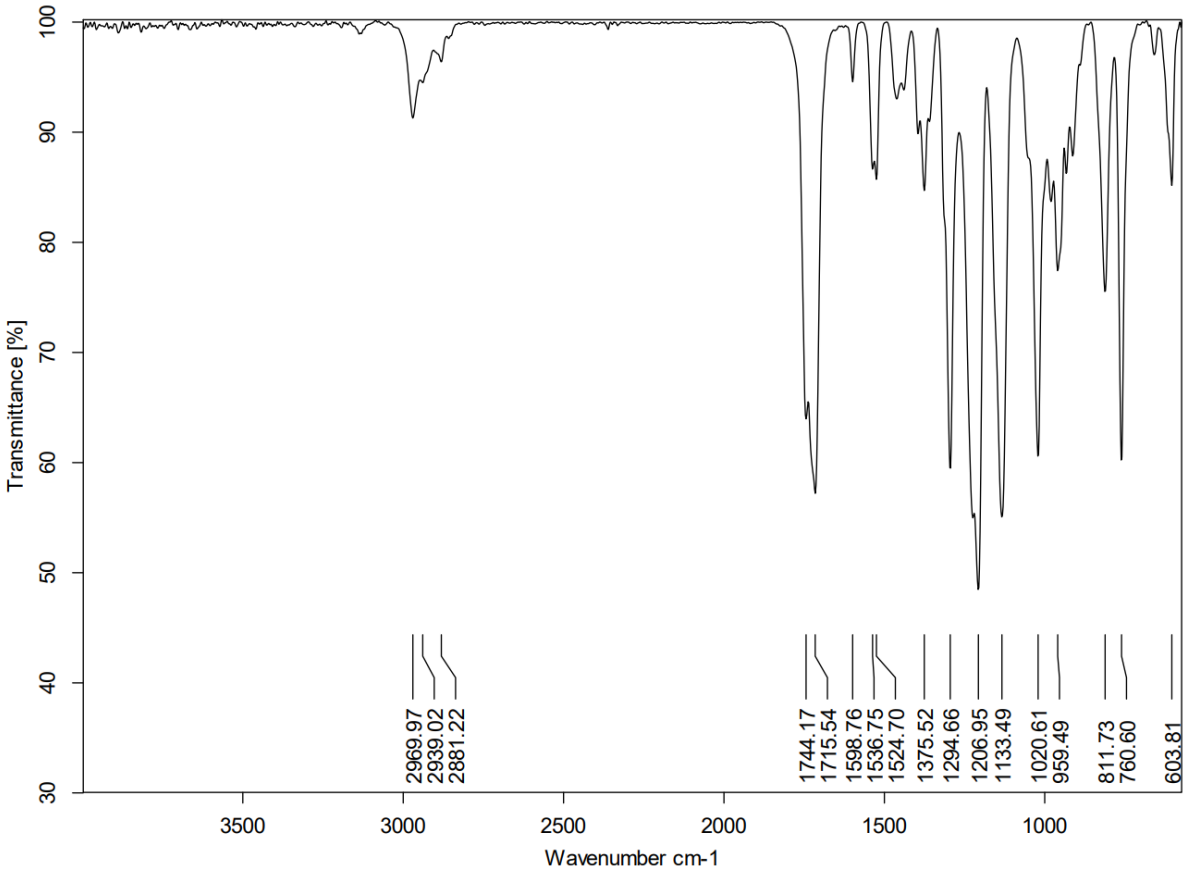


Figure S19. The FTIR spectrum of **2a**.

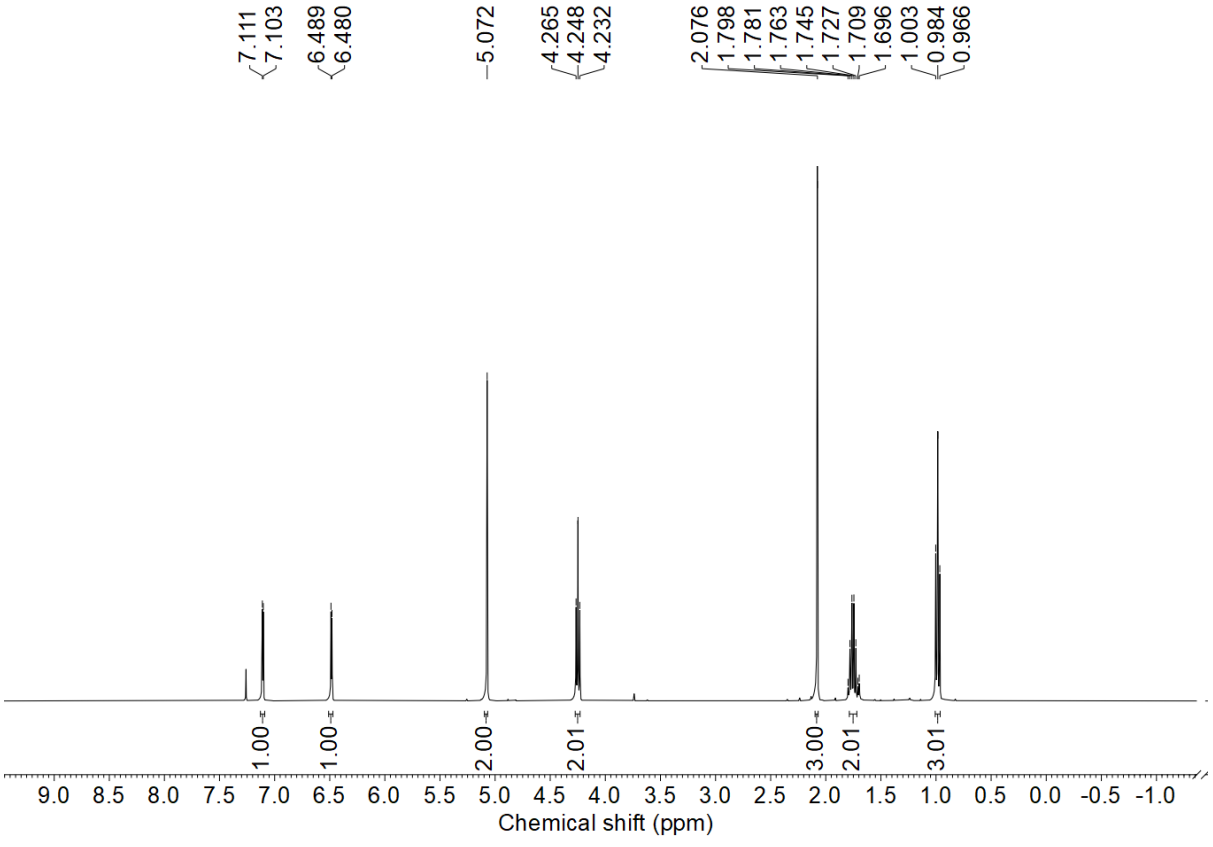


Figure S20. The ^{1}H-NMR spectrum of **2a**.

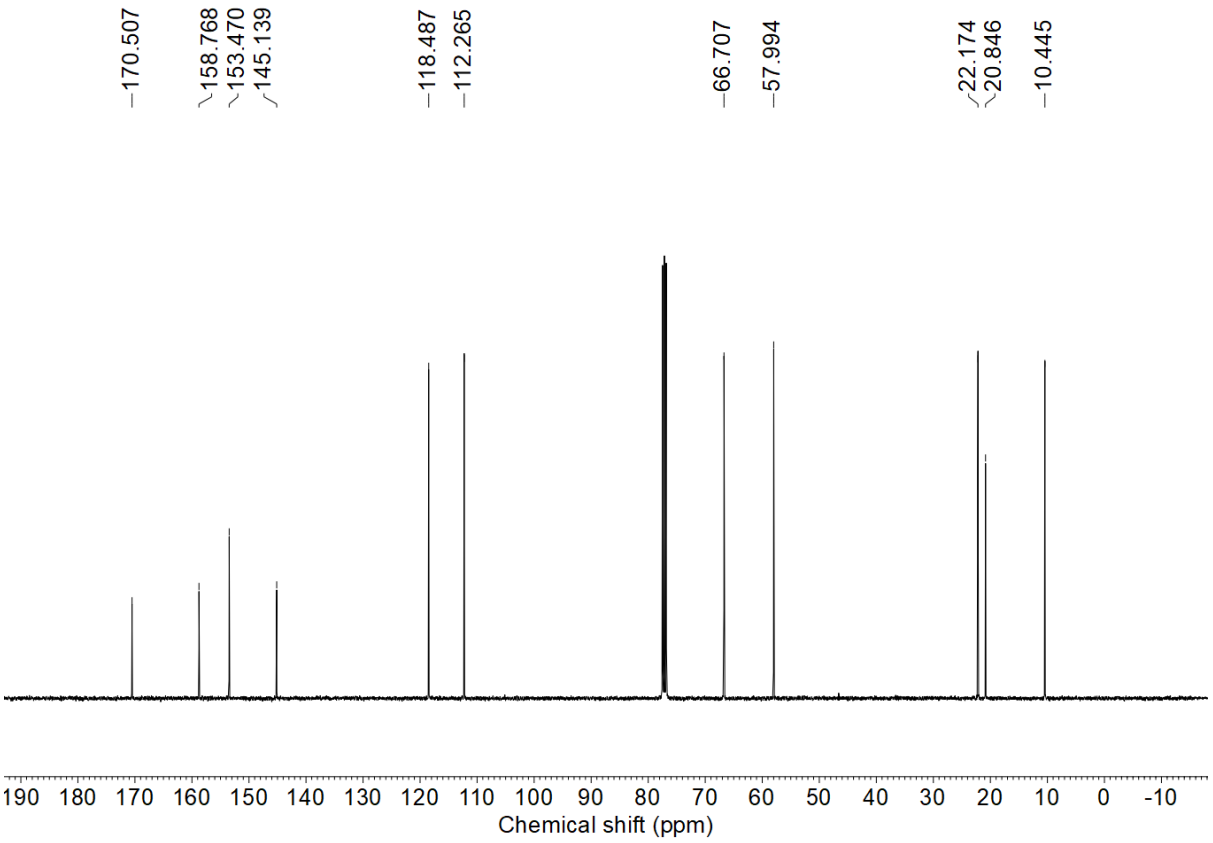


Figure S21. The ^{13}C-NMR spectrum of **2a**.

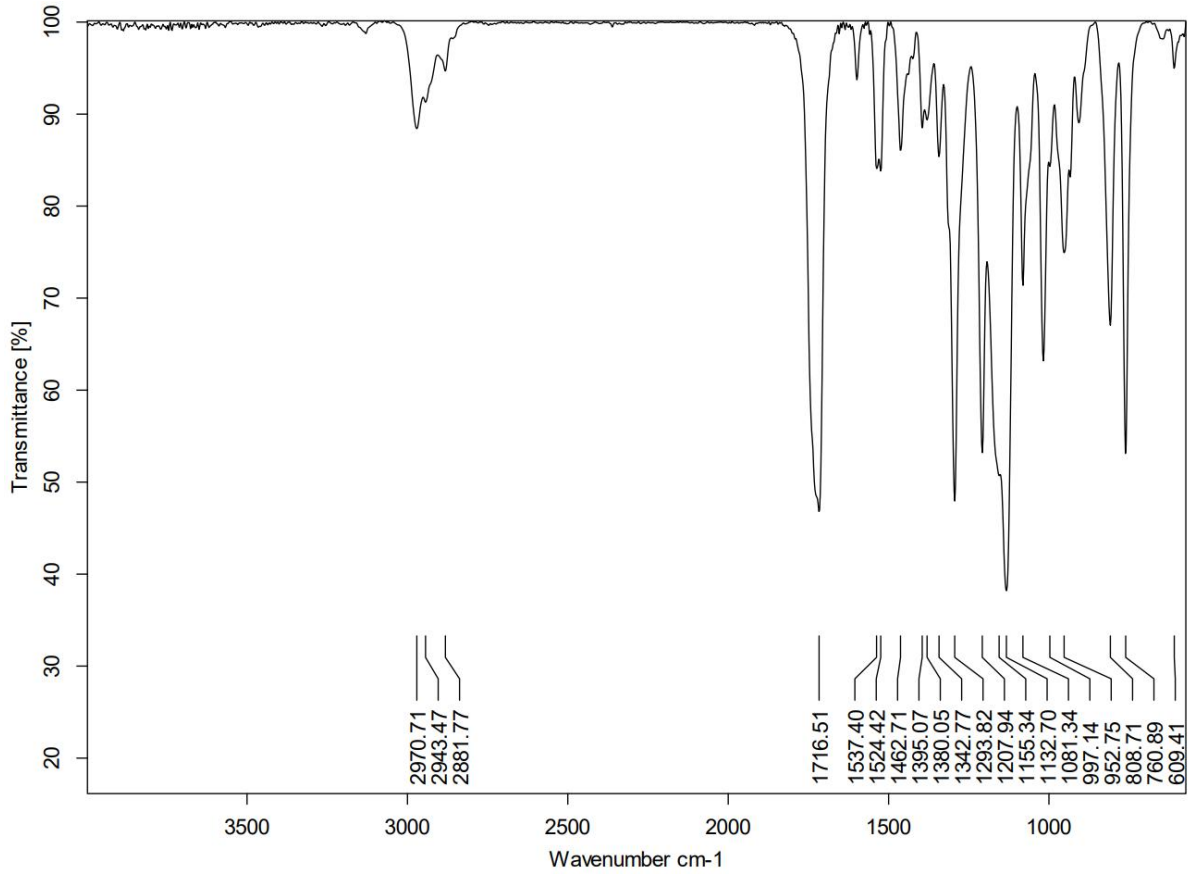


Figure S22. The FTIR spectrum of **2b**.

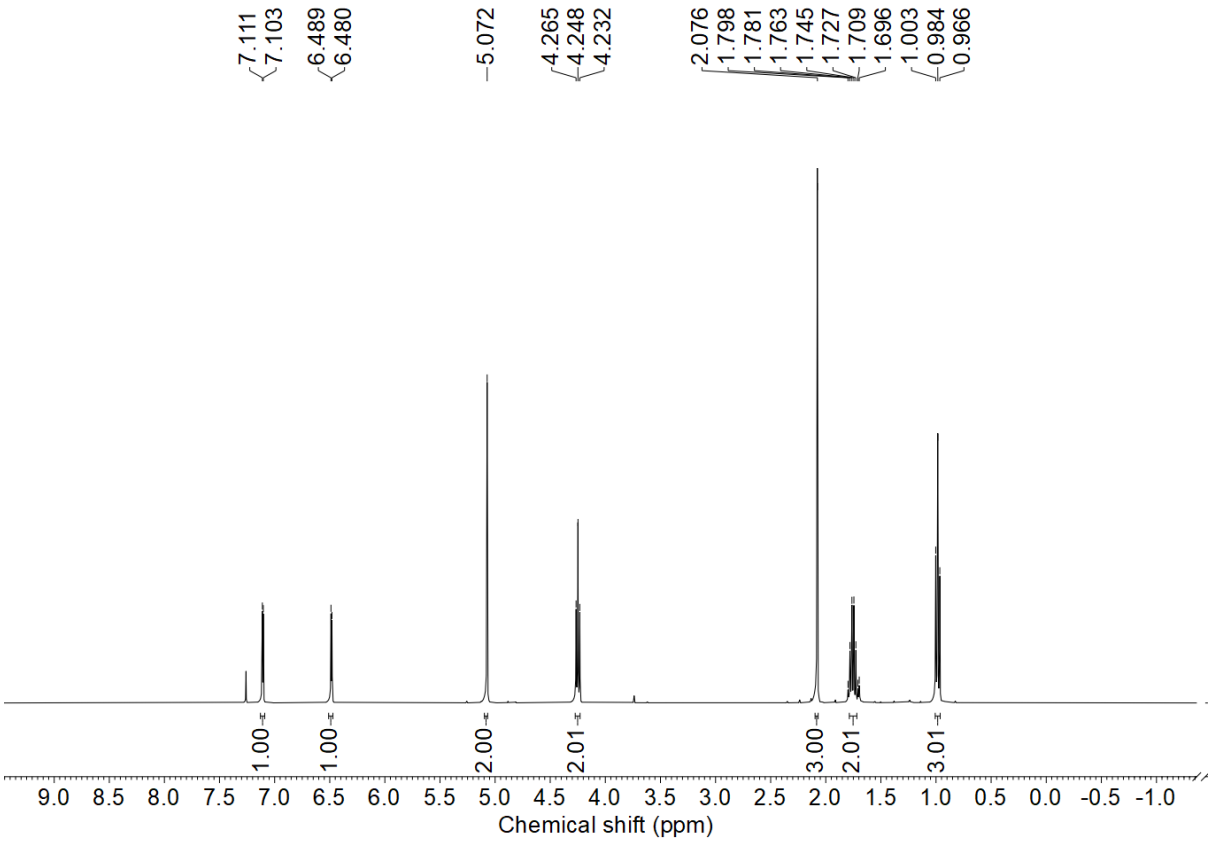


Figure S23. The ^{1}H-NMR spectrum of **2b**.

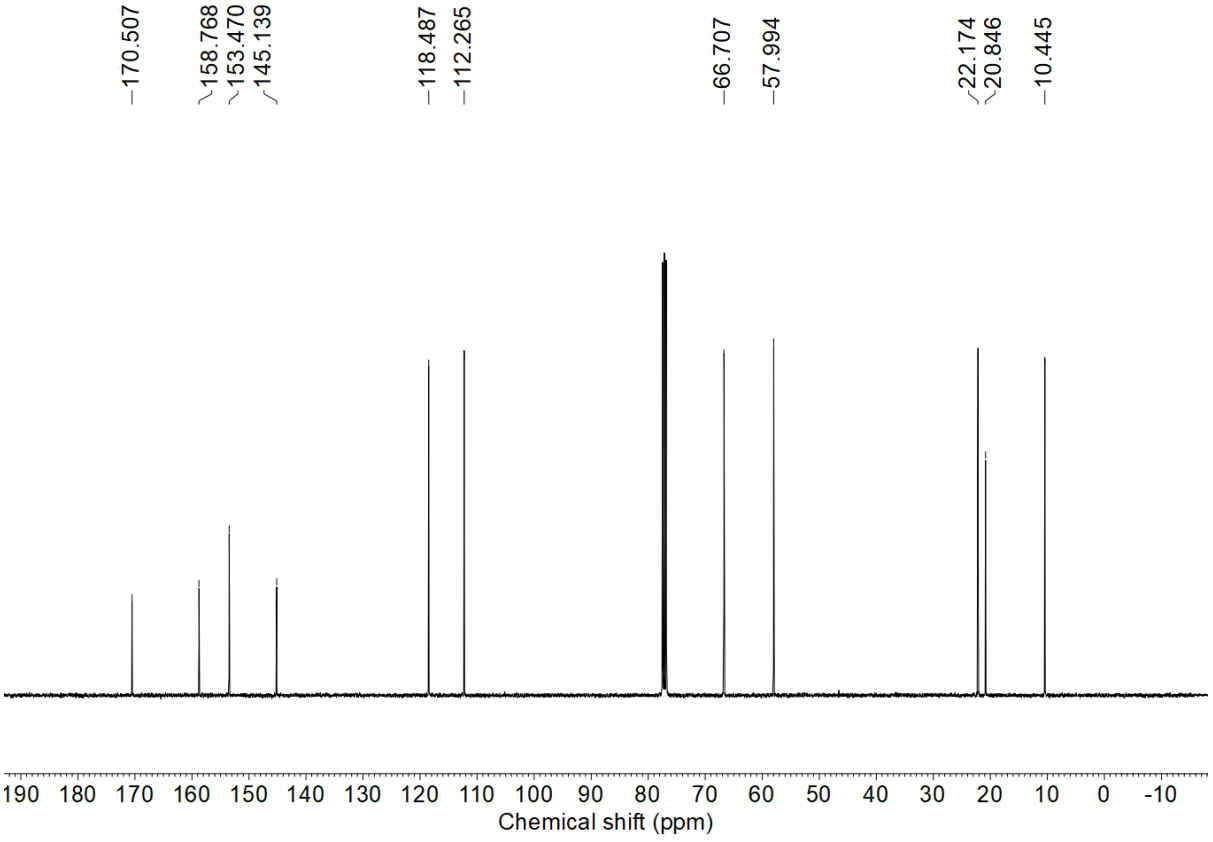


Figure S24. The ^{13}C-NMR spectrum of **2b**.

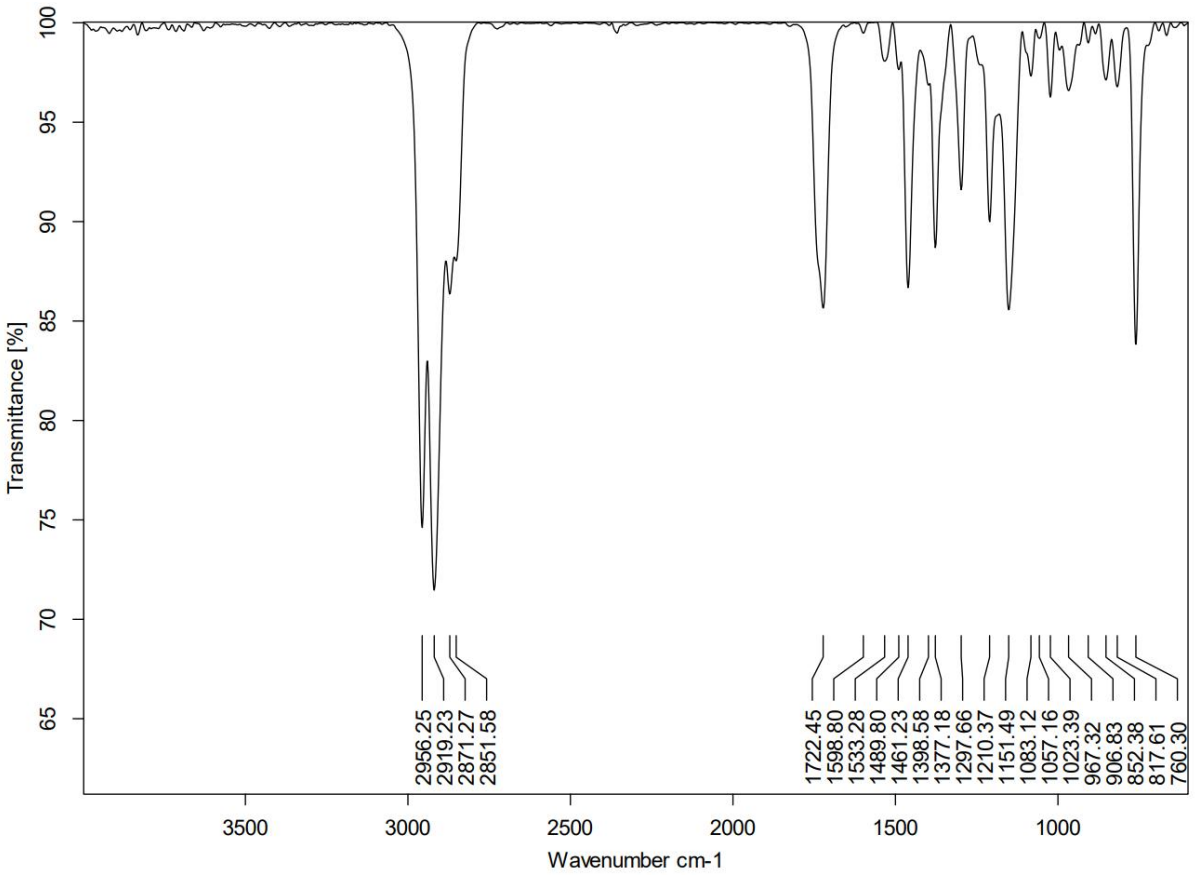


Figure S25. The FTIR spectrum of **2c**.

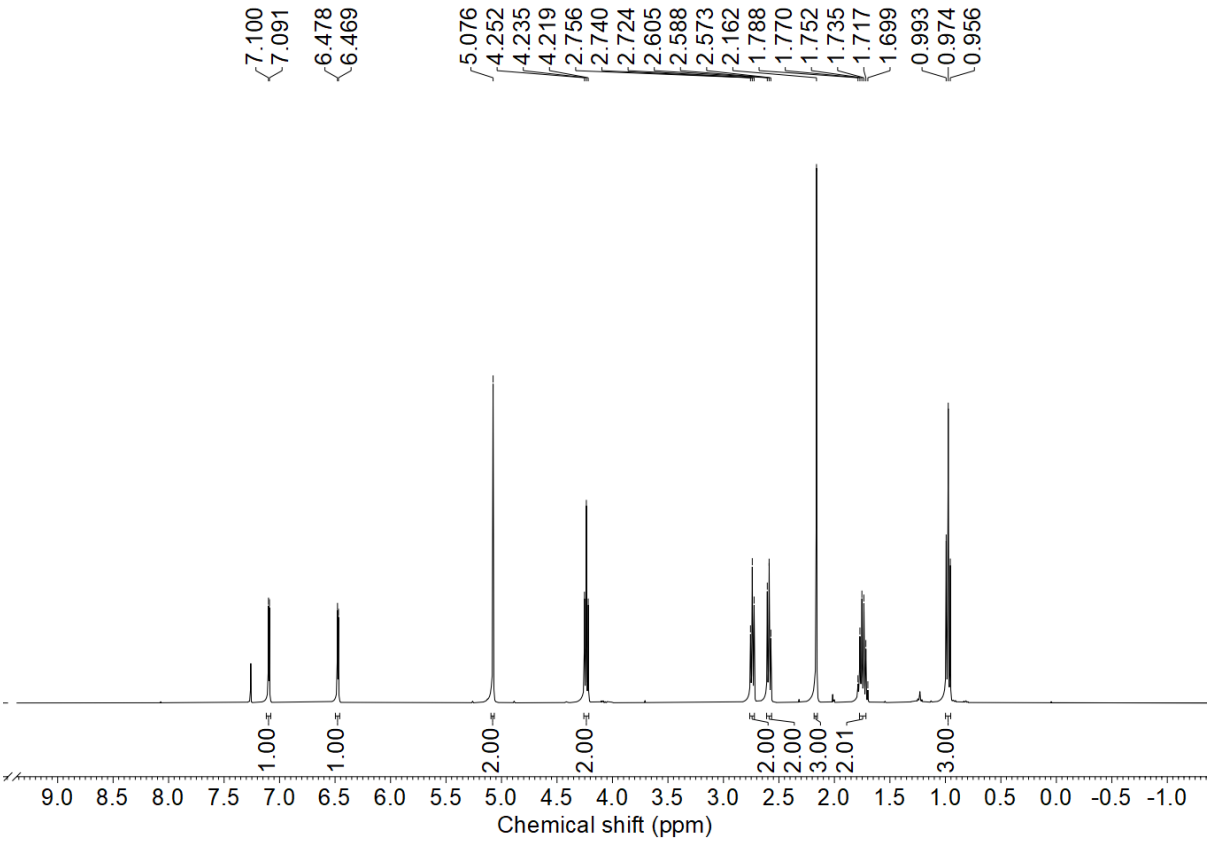


Figure S26. The ^{1}H-NMR spectrum of **2c**.

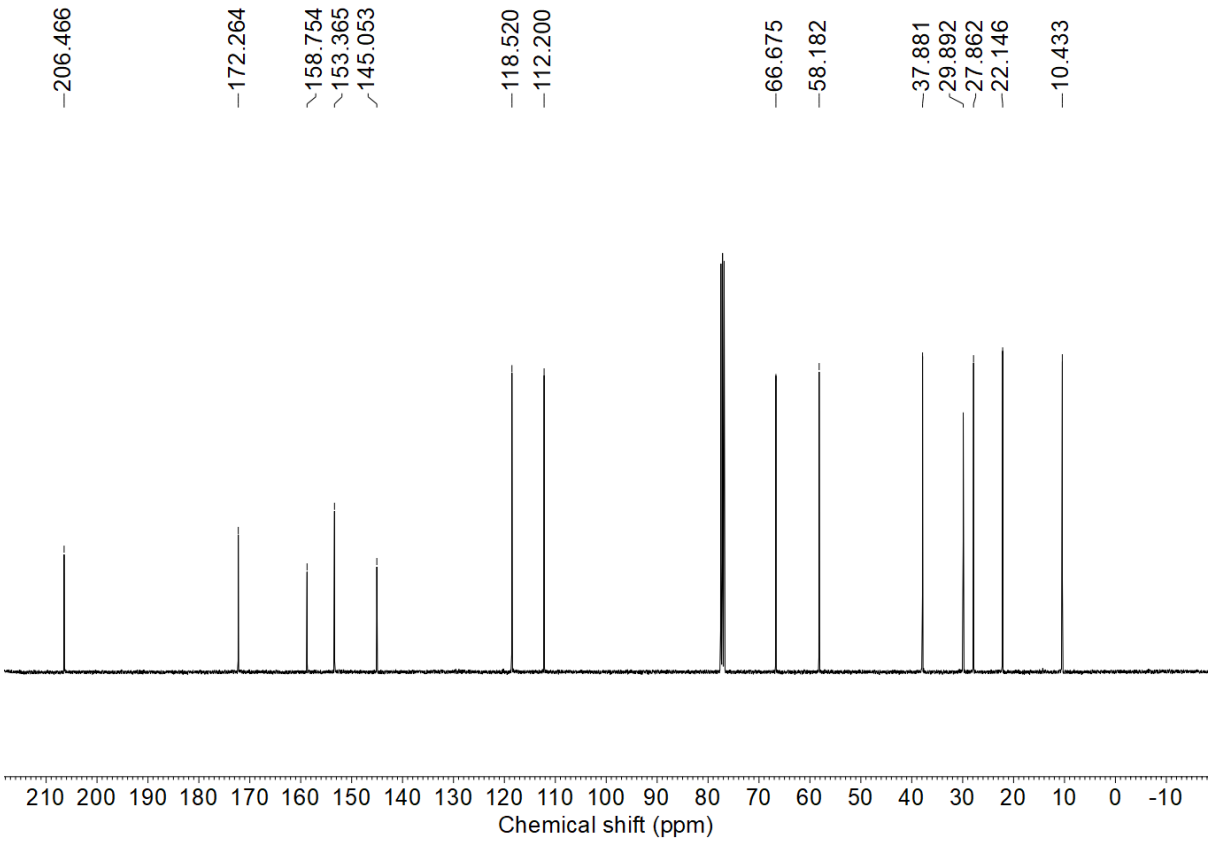


Figure S27. The ^{13}C-NMR spectrum of **2c**.

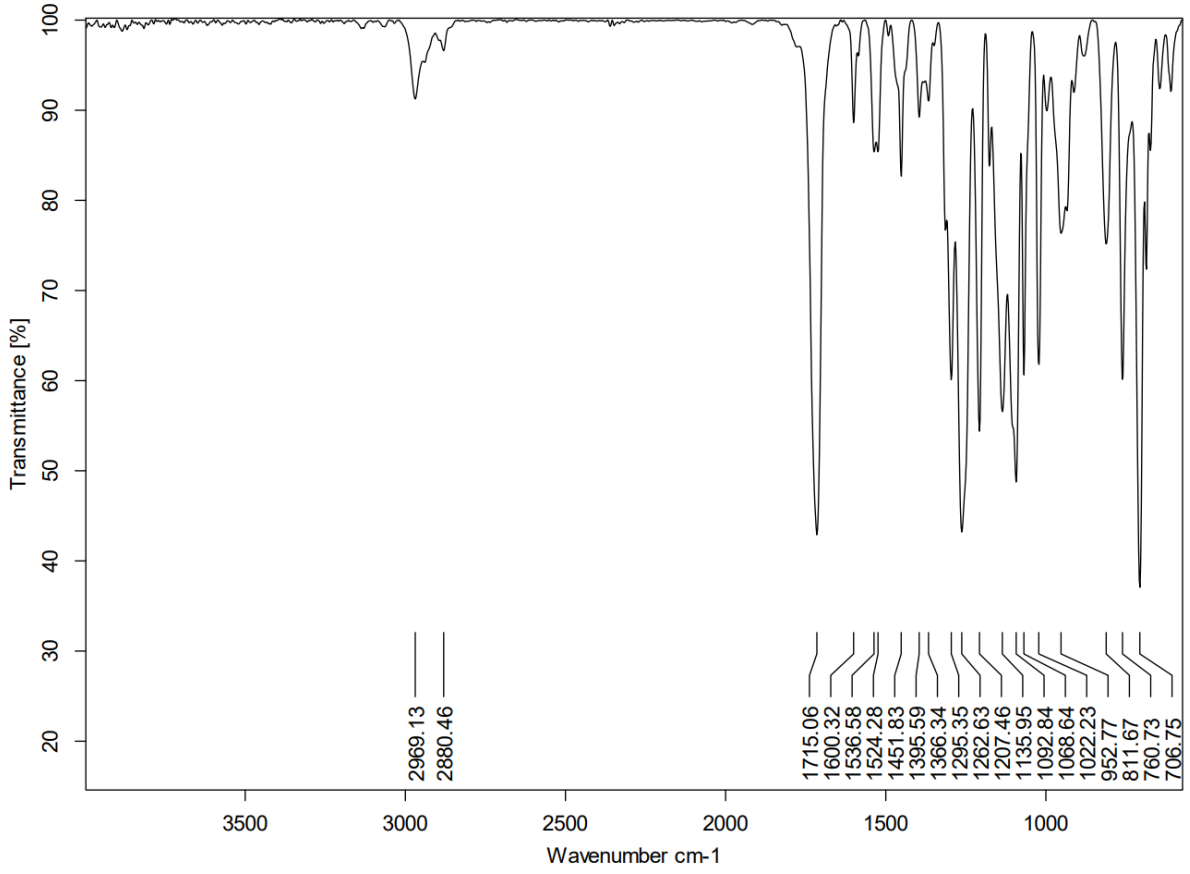


Figure S28. The FTIR spectrum of **2d**.

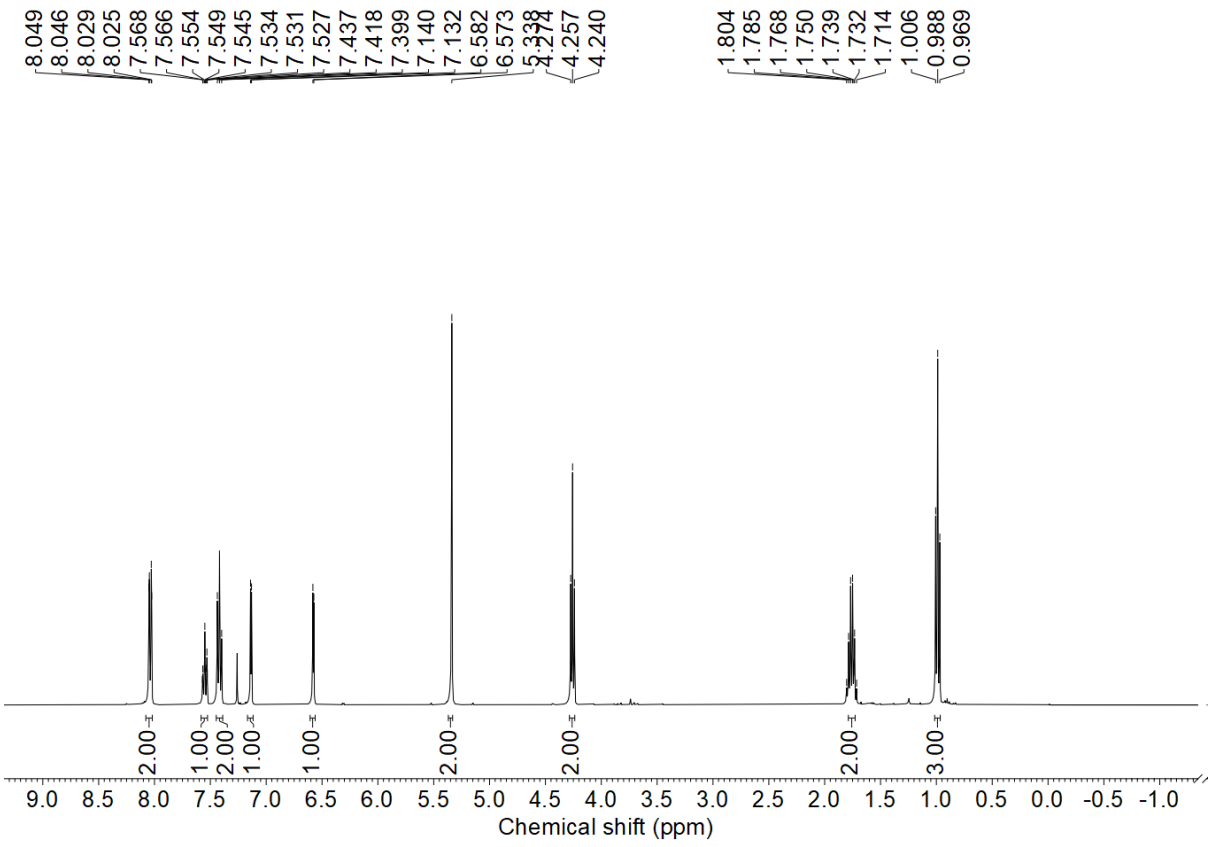


Figure S29. The ^{1}H-NMR spectrum of **2d**.

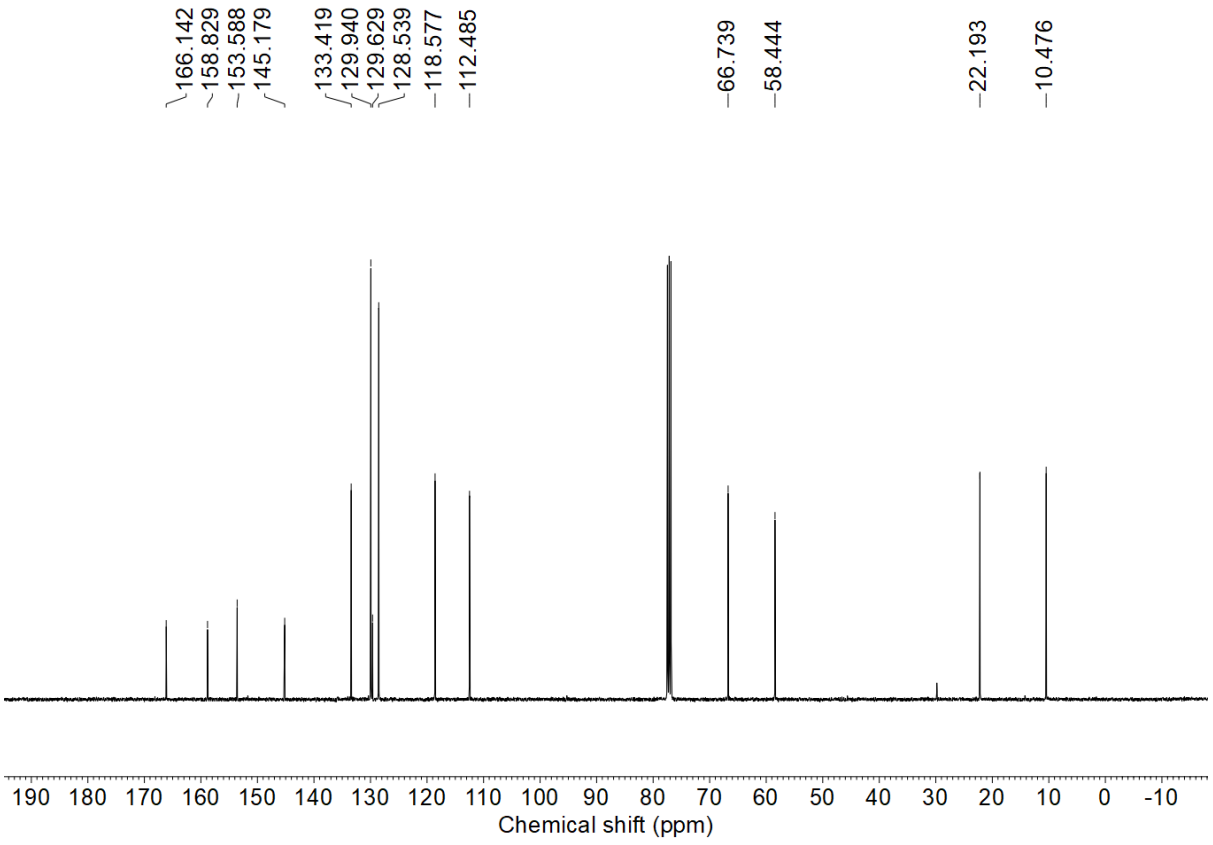


Figure S30. The ^{13}C-NMR spectrum of **2d**.

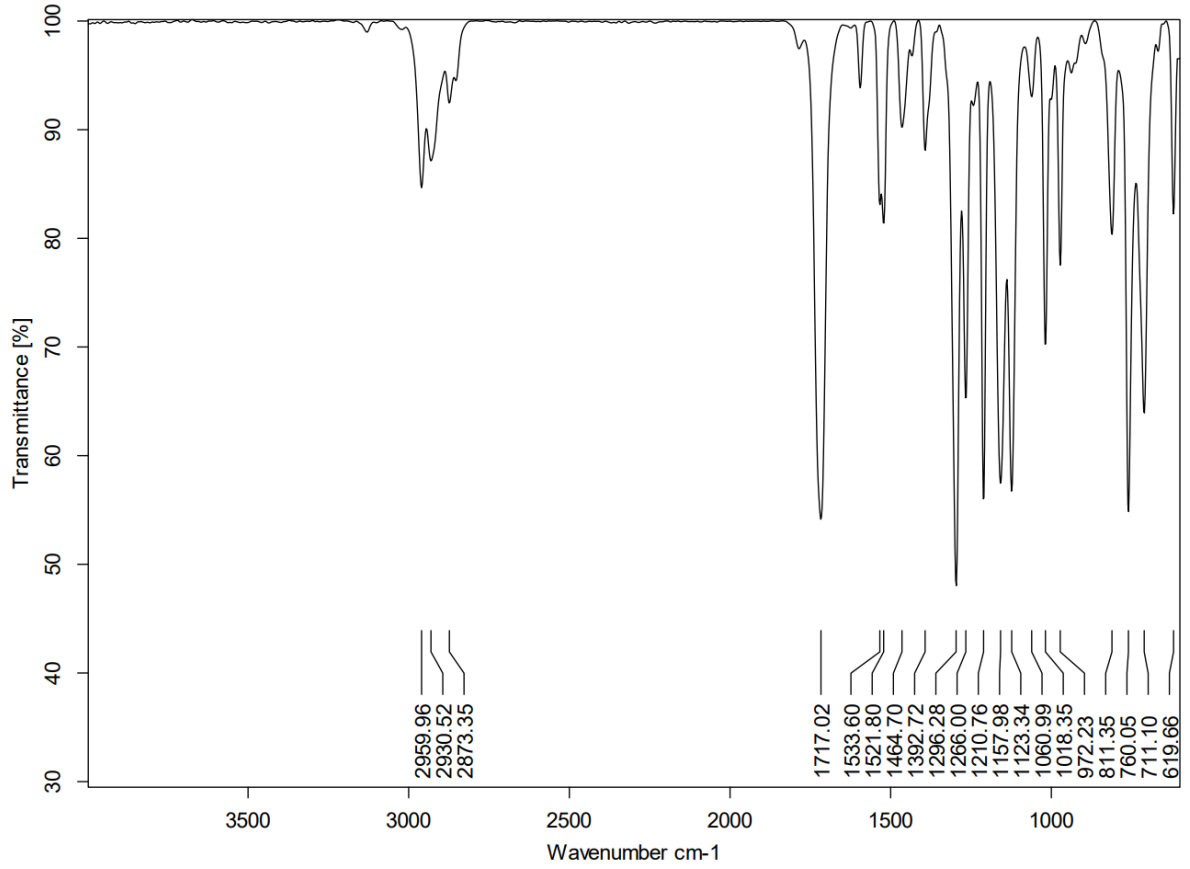


Figure S31. The FTIR spectrum of **3**.

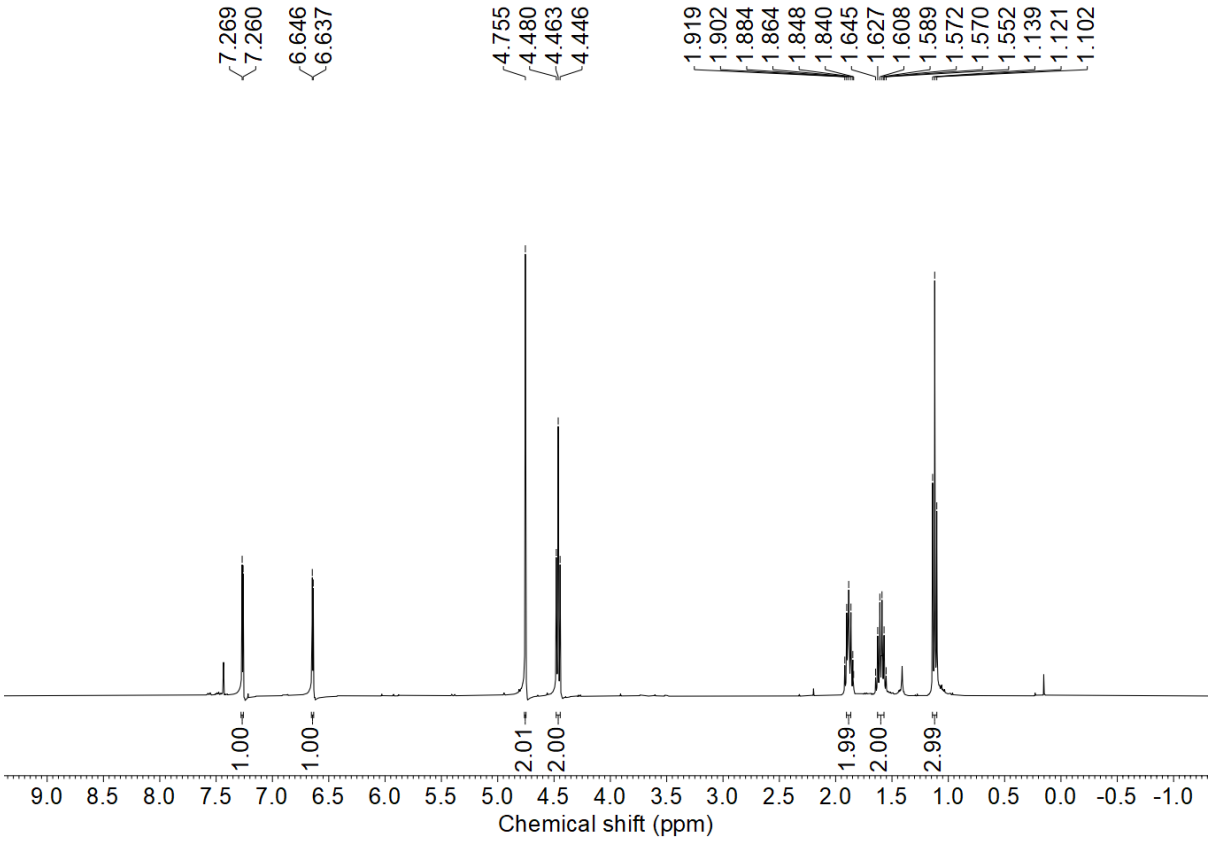


Figure S32. The ^{1}H-NMR spectrum of **3**.

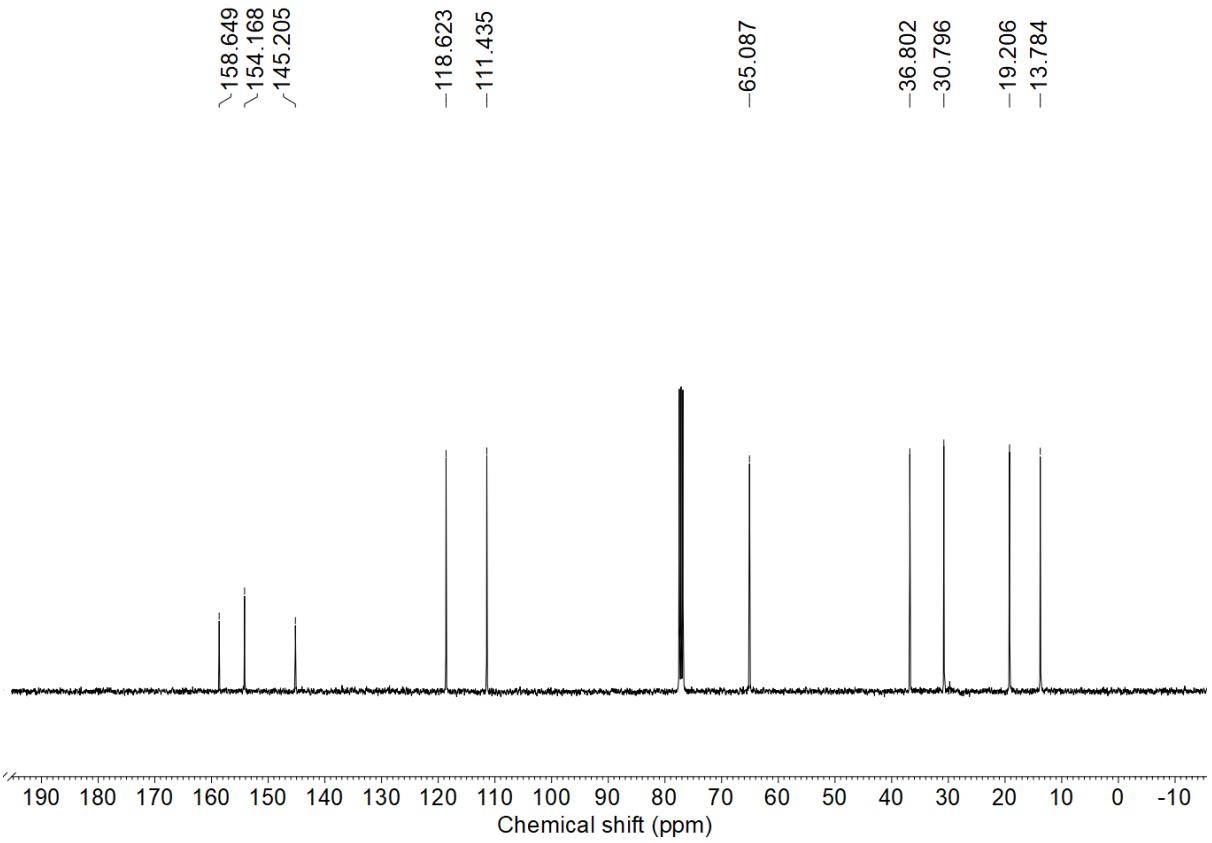


Figure S33. The ^{13}C-NMR spectrum of **3**.

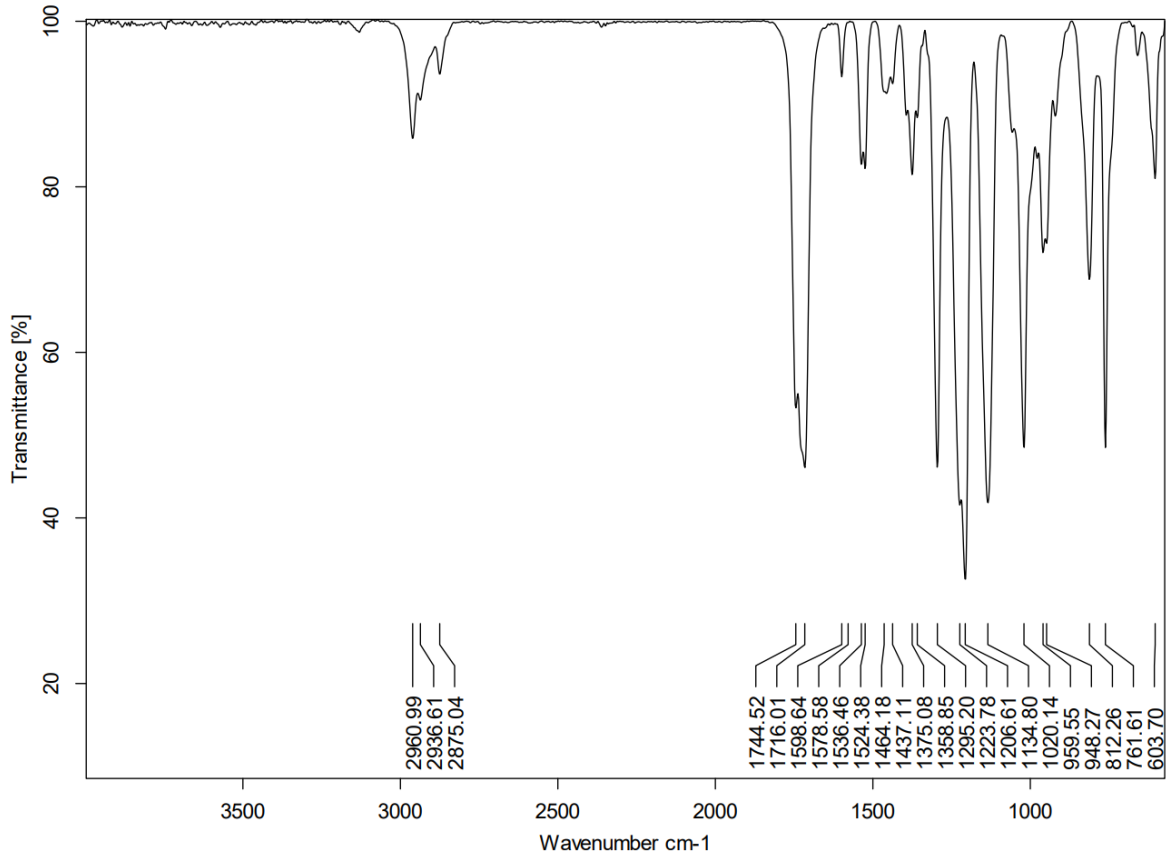


Figure S34. The FTIR spectrum of **3a**.

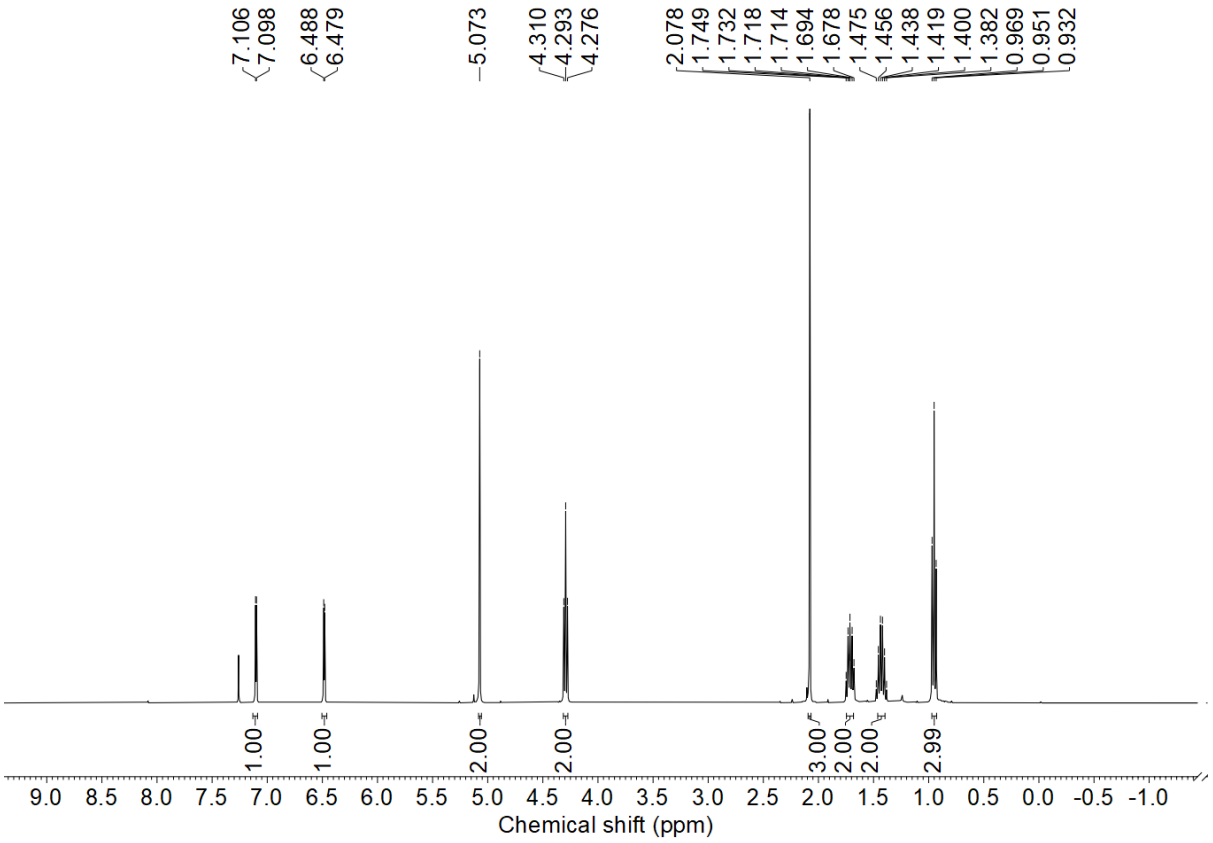


Figure S35. The ^{1}H-NMR spectrum of **3a**.

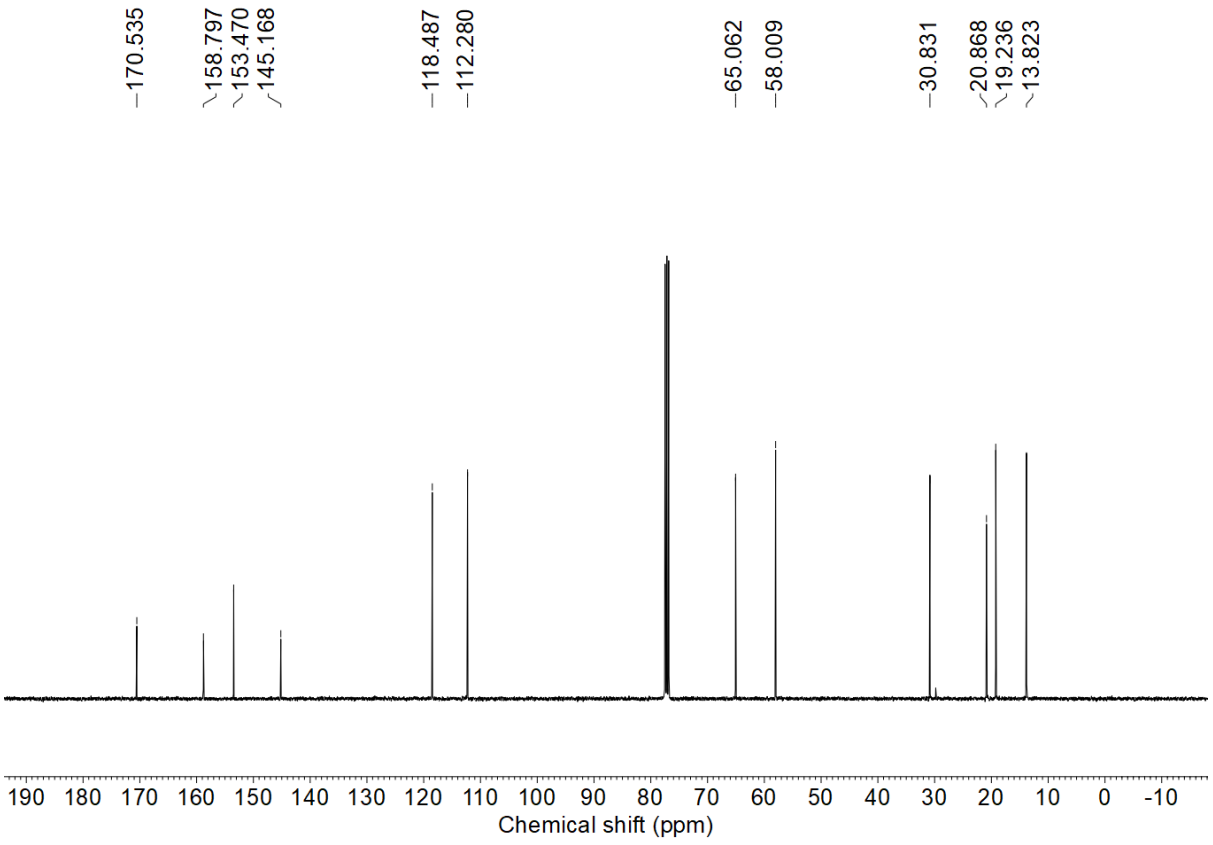


Figure S36. The ^{13}C-NMR spectrum of **3a**.

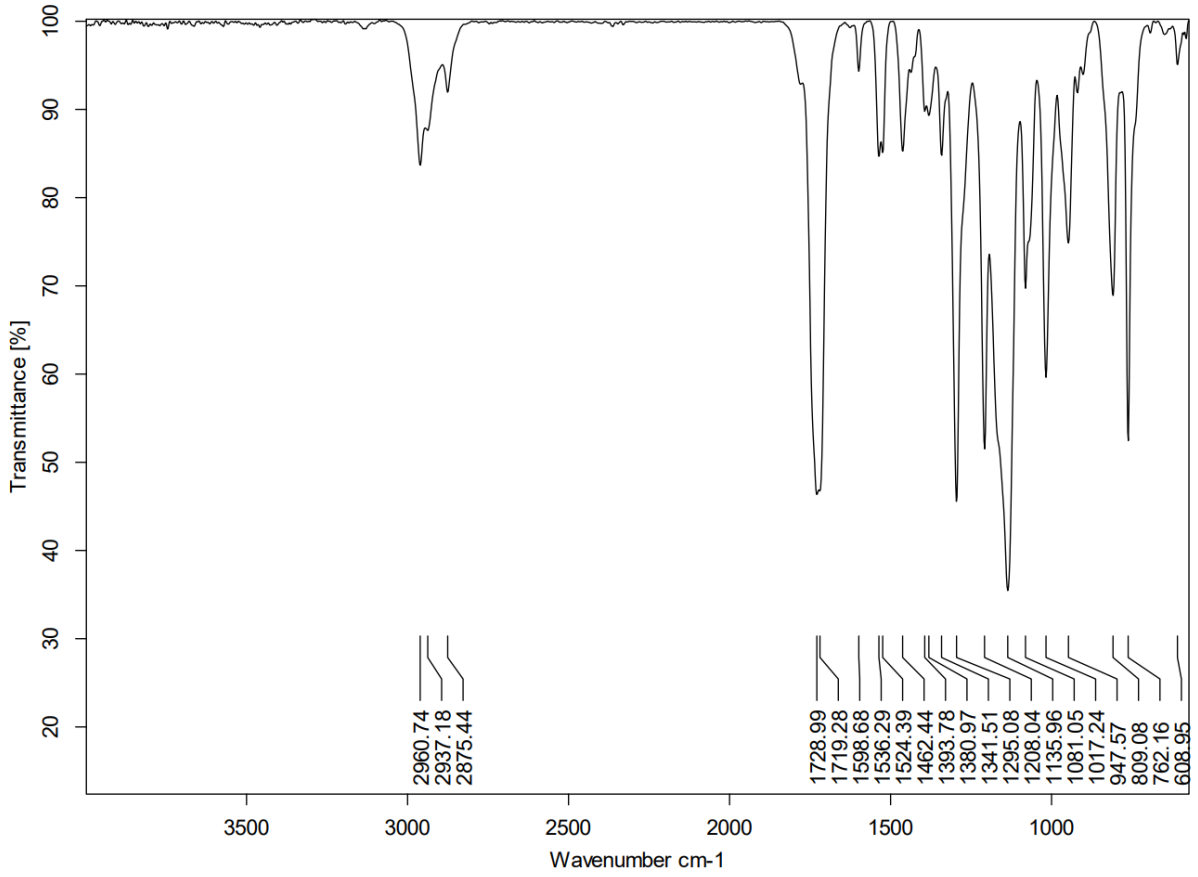


Figure S37. The FTIR spectrum of **3b**.

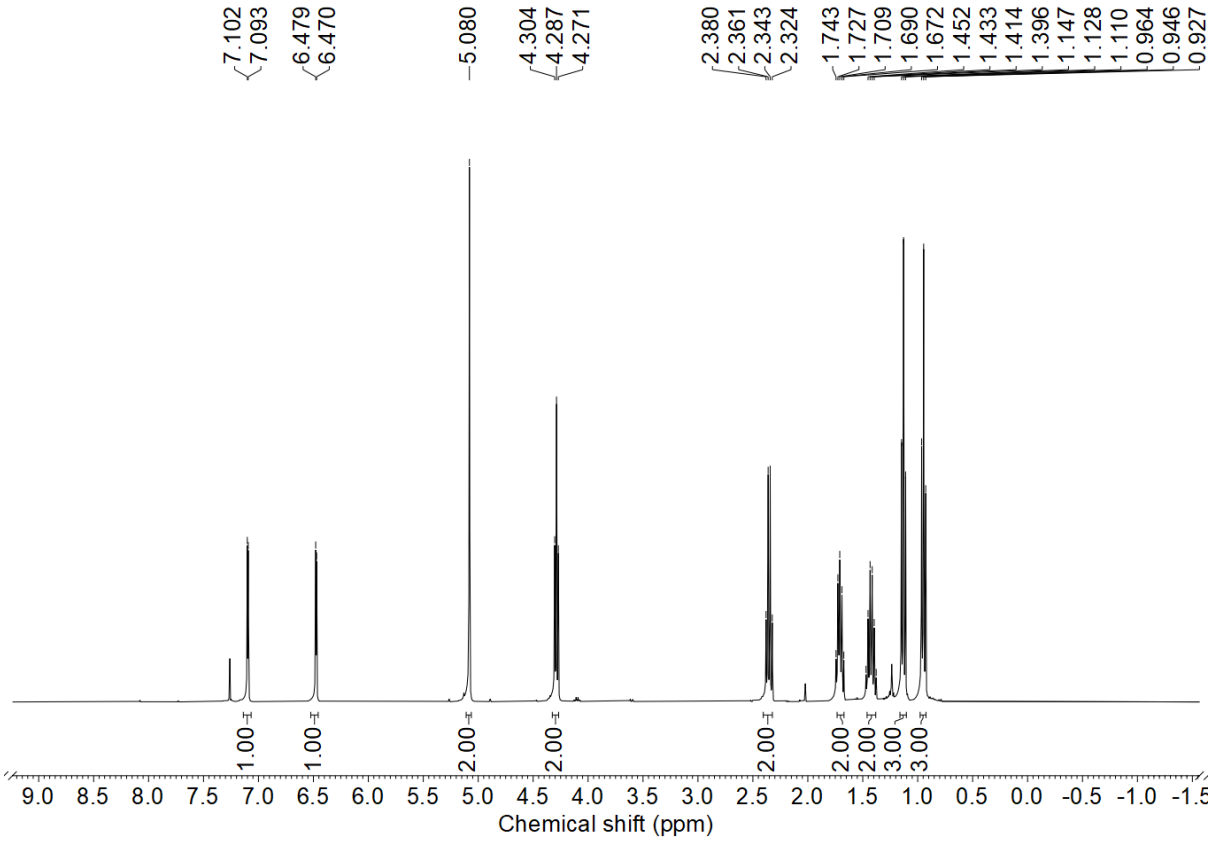


Figure S38. The ^{1}H-NMR spectrum of **3b**.

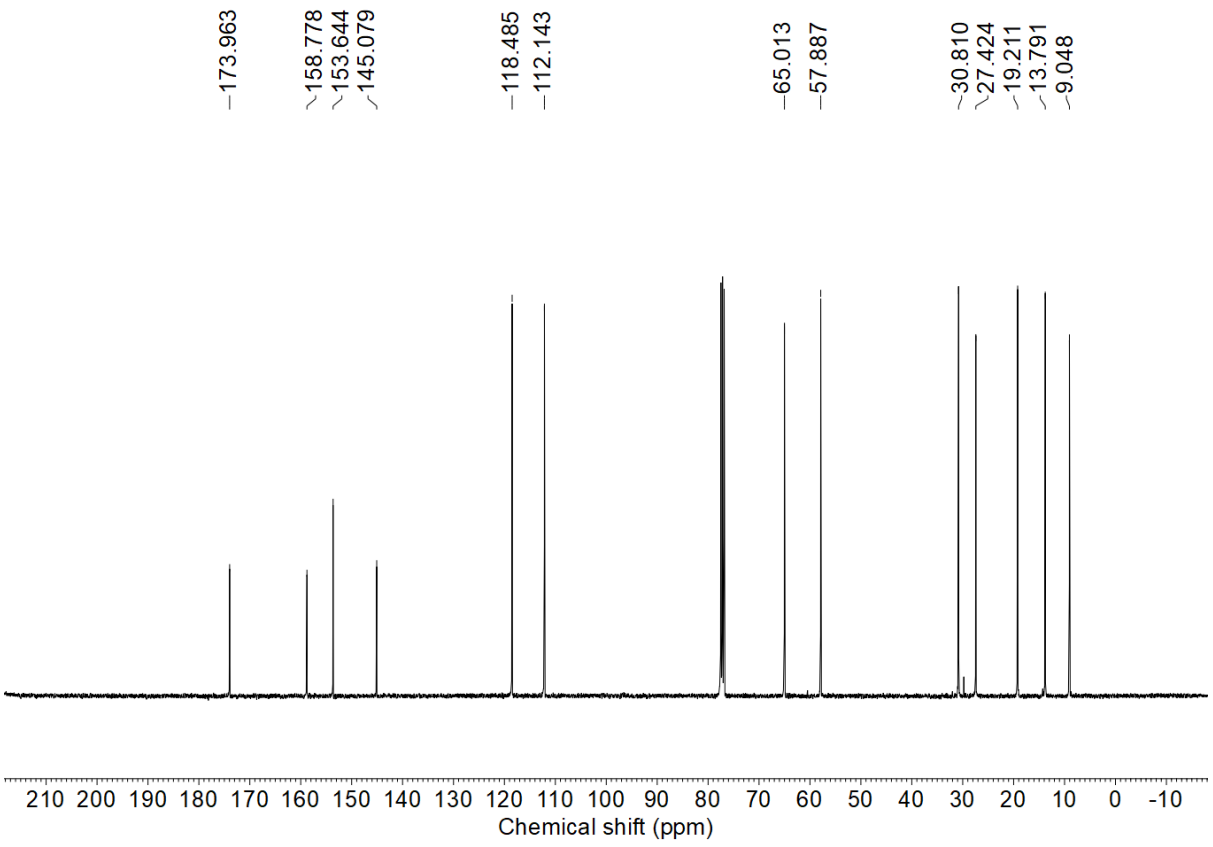


Figure S39. The ^{13}C-NMR spectrum of **3b**.

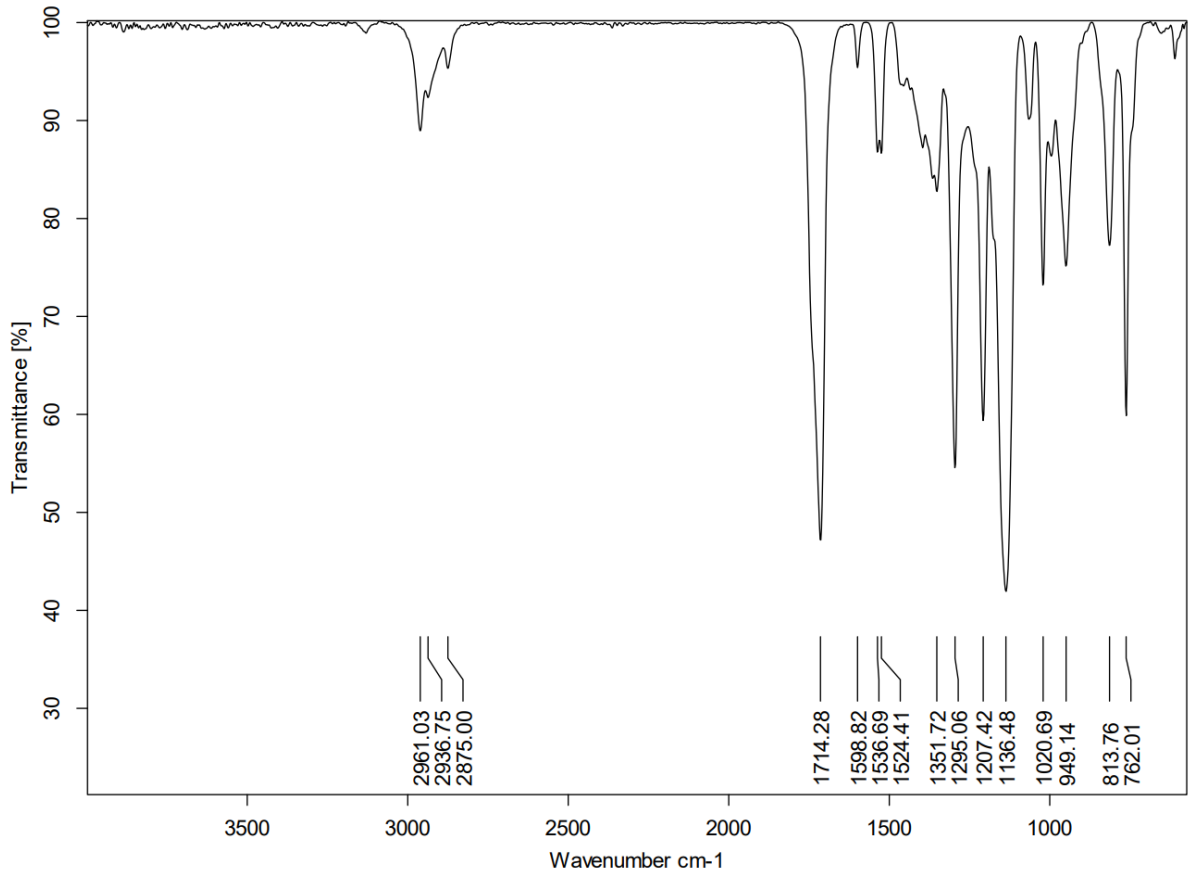


Figure S40. The FTIR spectrum of **3c**.

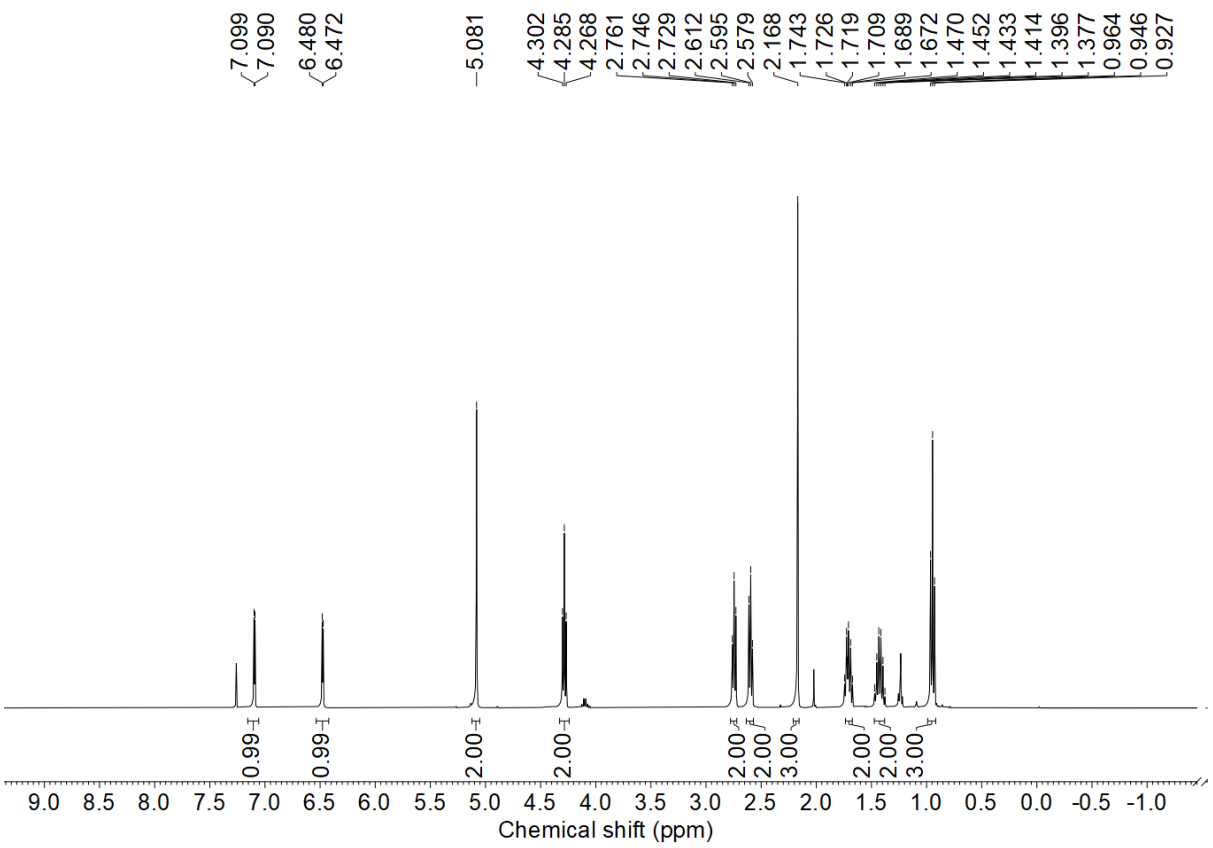


Figure S41. The ^{1}H-NMR spectrum of **3c**.

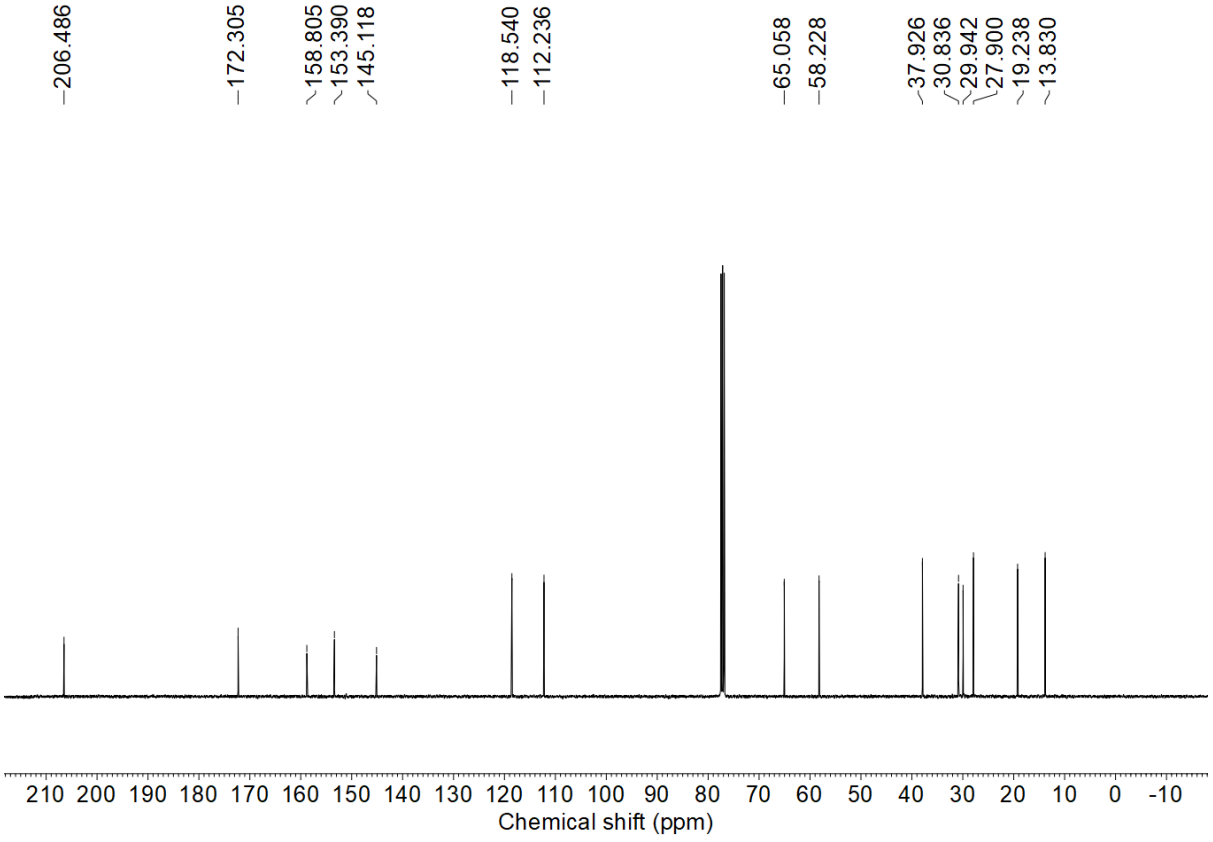


Figure S42. The ^{13}C-NMR spectrum of **3c**.

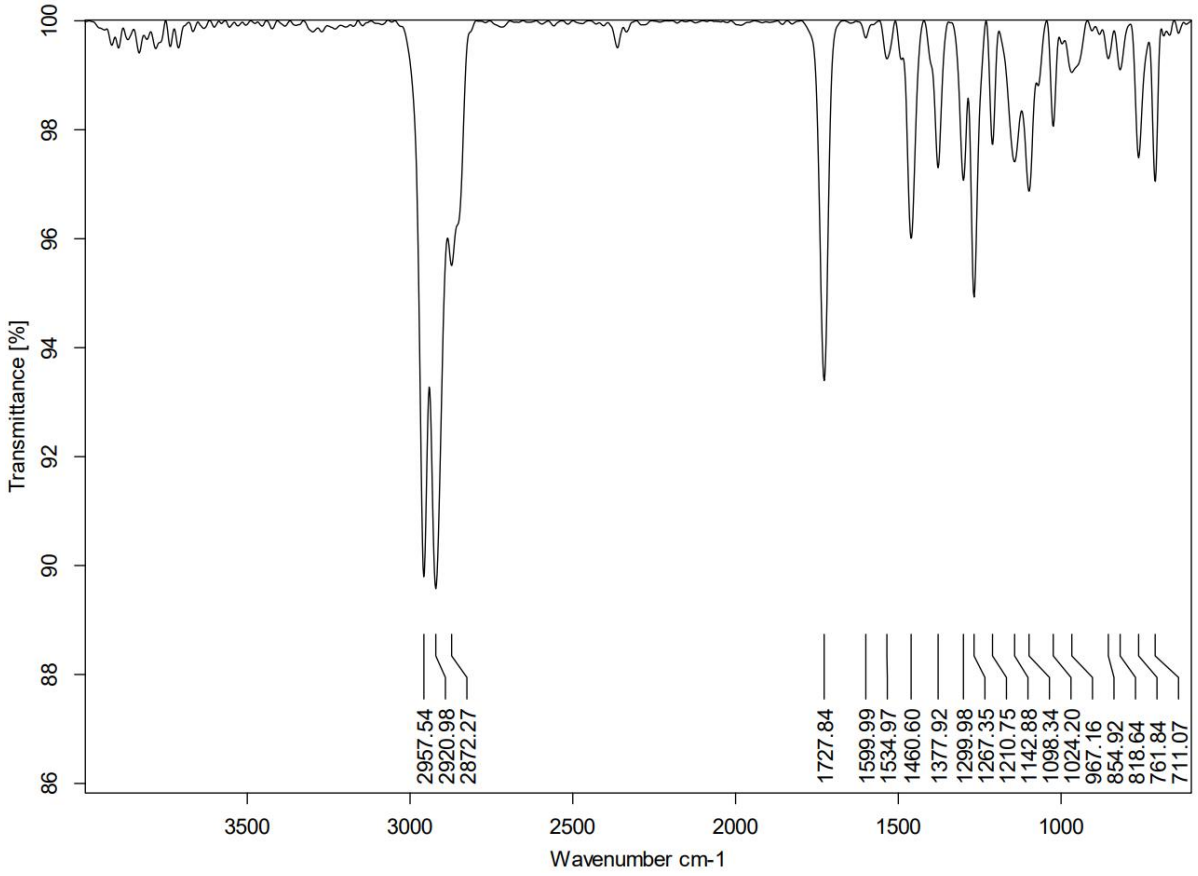


Figure S43. The FTIR spectrum of **3d**.

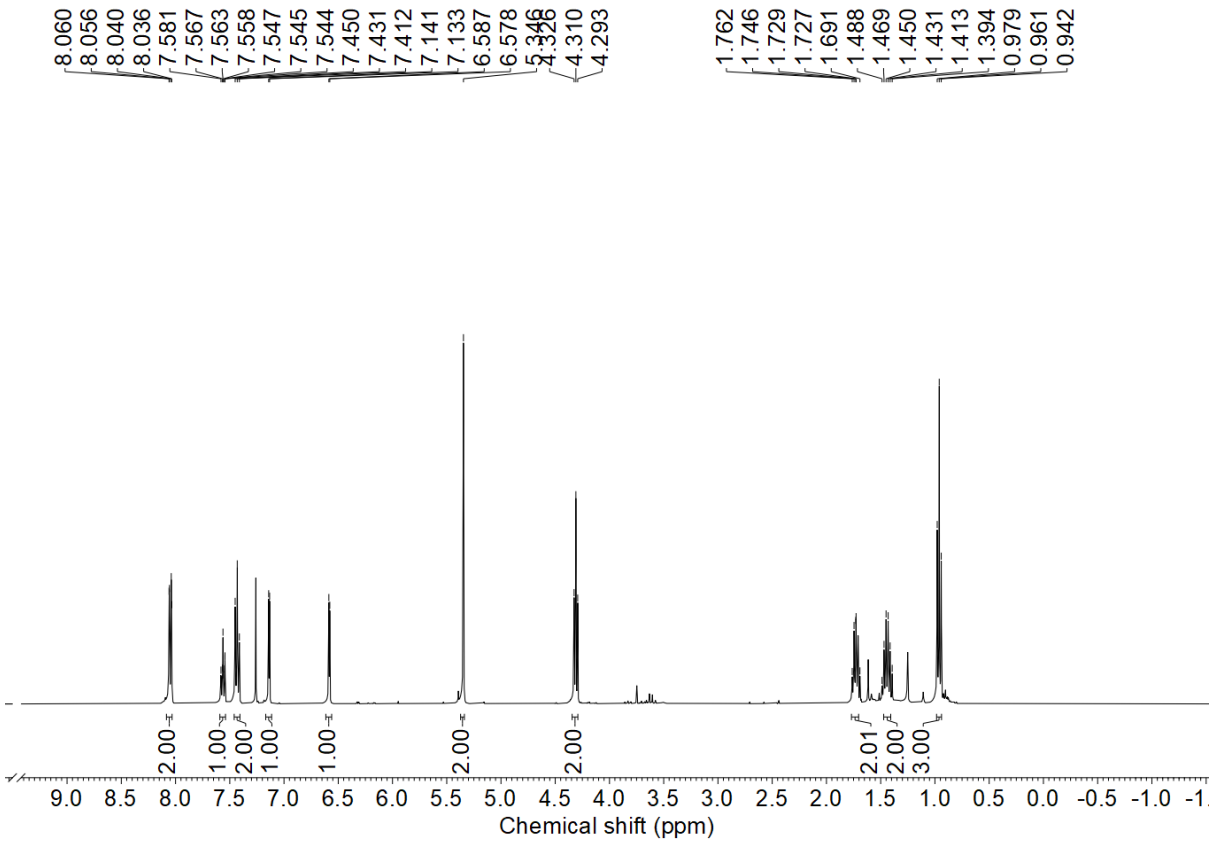


Figure S44. The ^{1}H-NMR spectrum of **3d**.

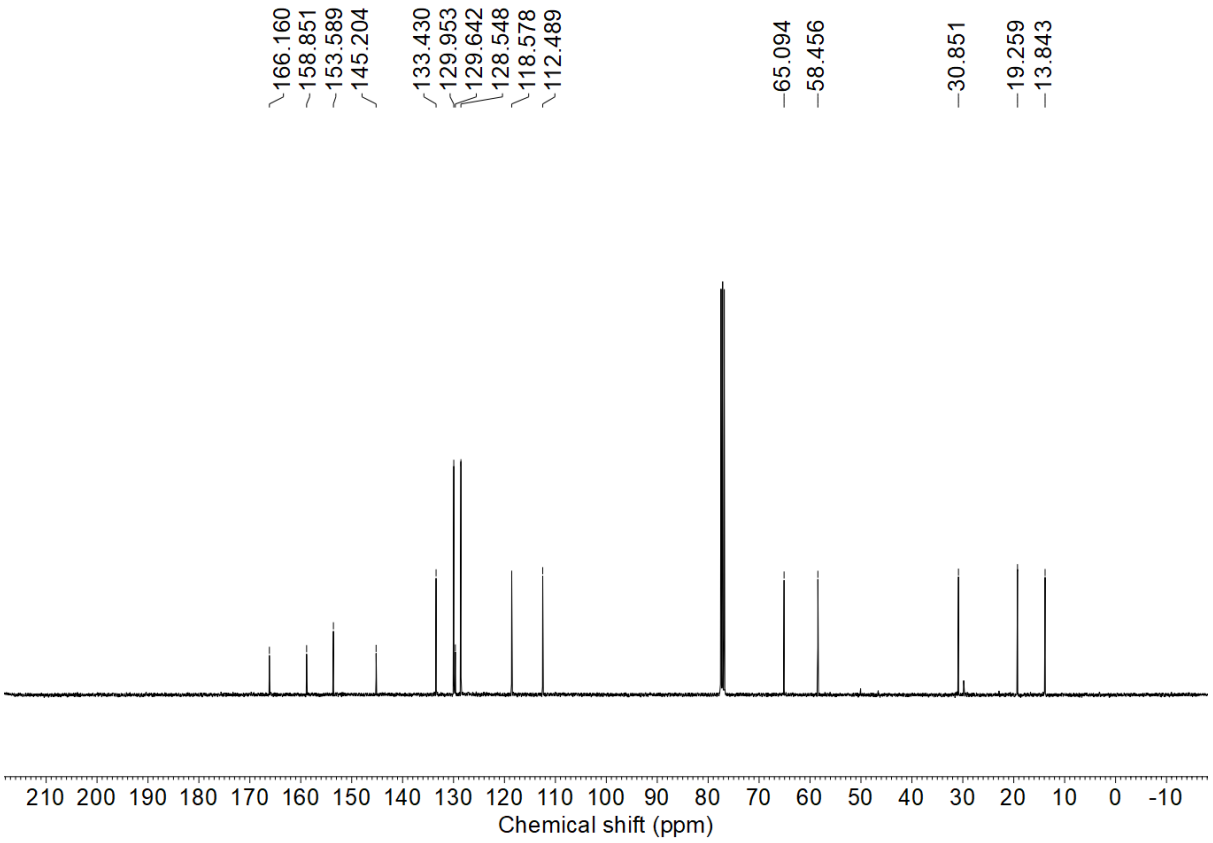


Figure S45. The ^{13}C-NMR spectrum of **3d**.

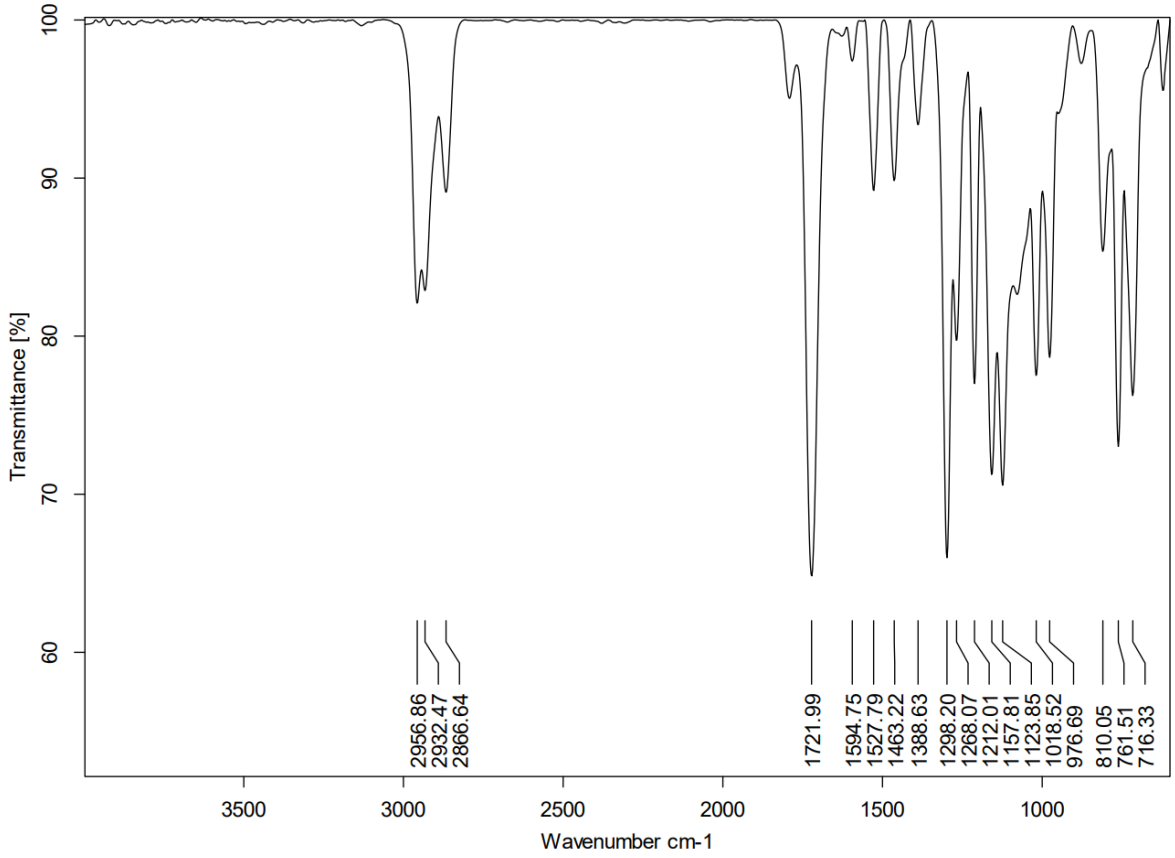


Figure S46. The FTIR spectrum of **4**.

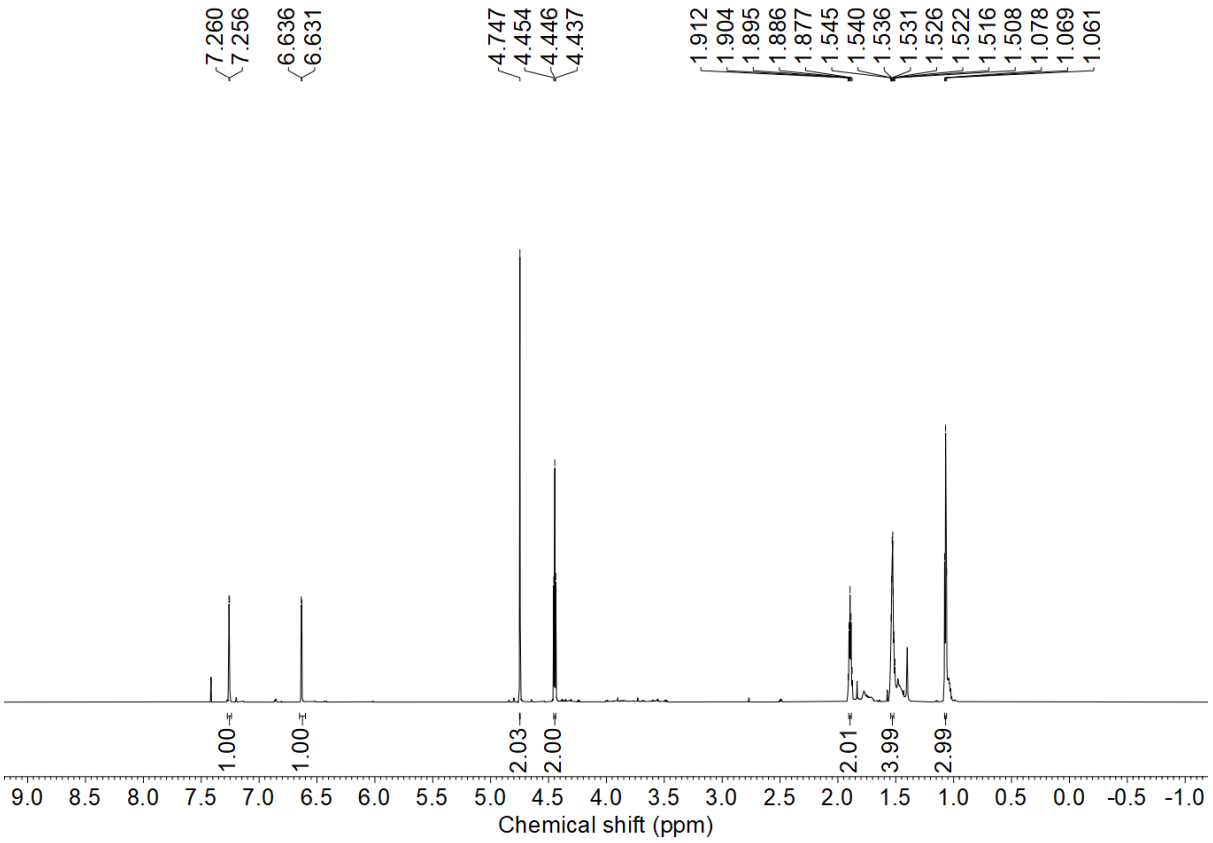


Figure S47. The ^{1}H-NMR spectrum of **4**.

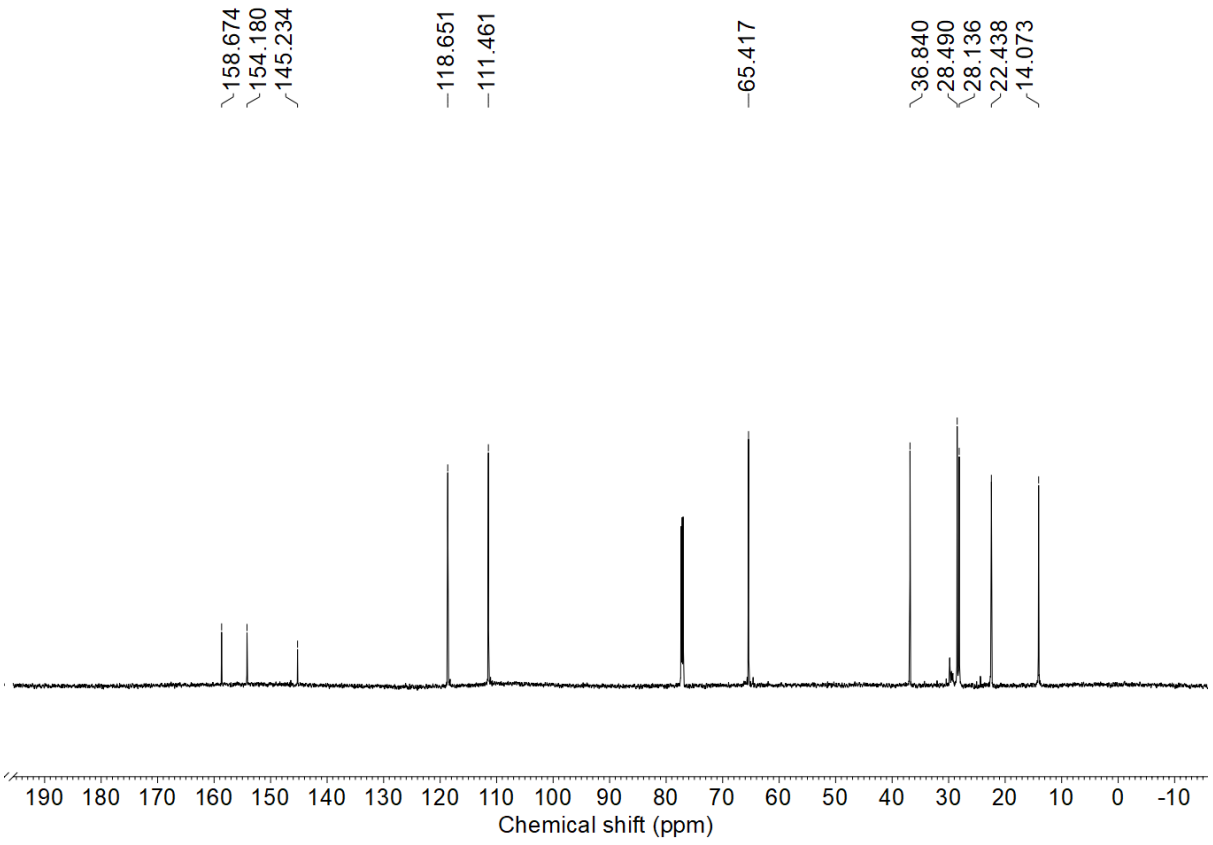


Figure S48. The ^{13}C-NMR spectrum of **4**.

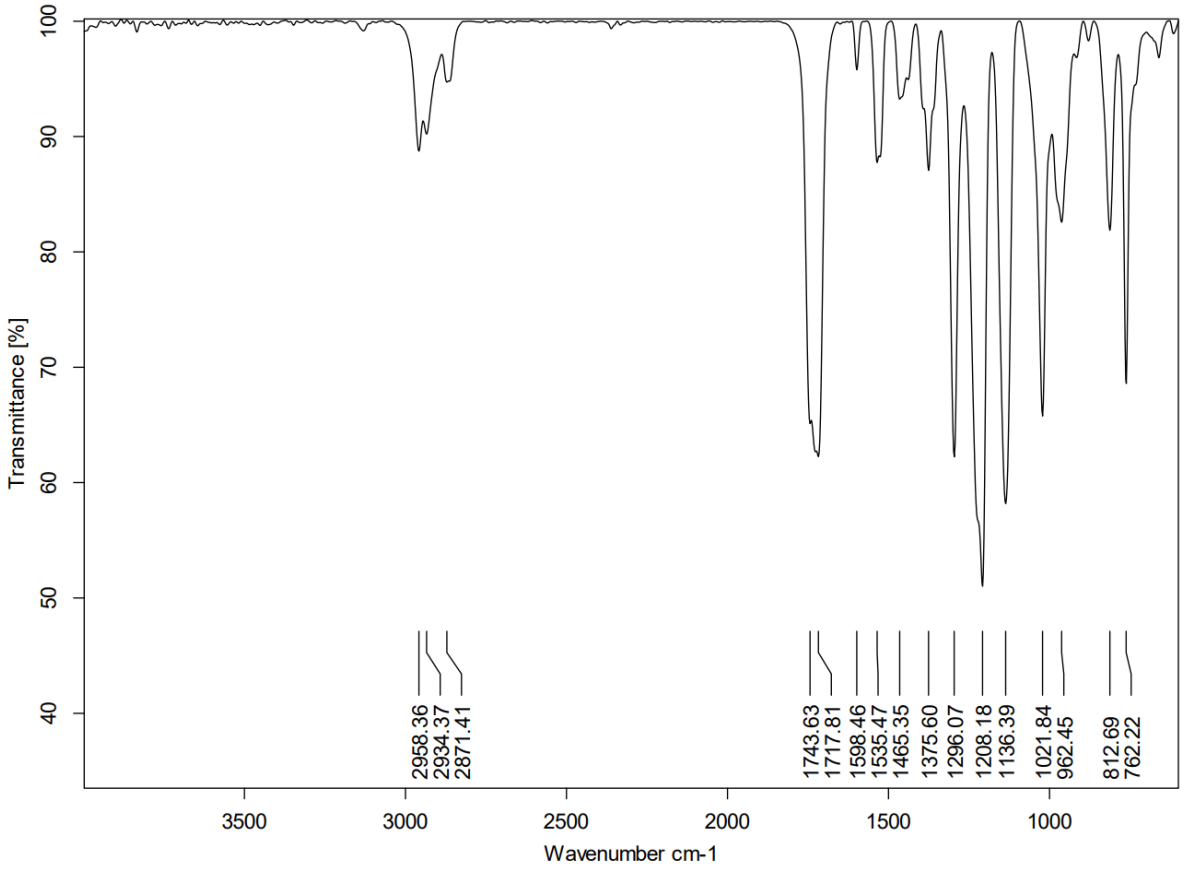


Figure S49. The FTIR spectrum of **4a**.

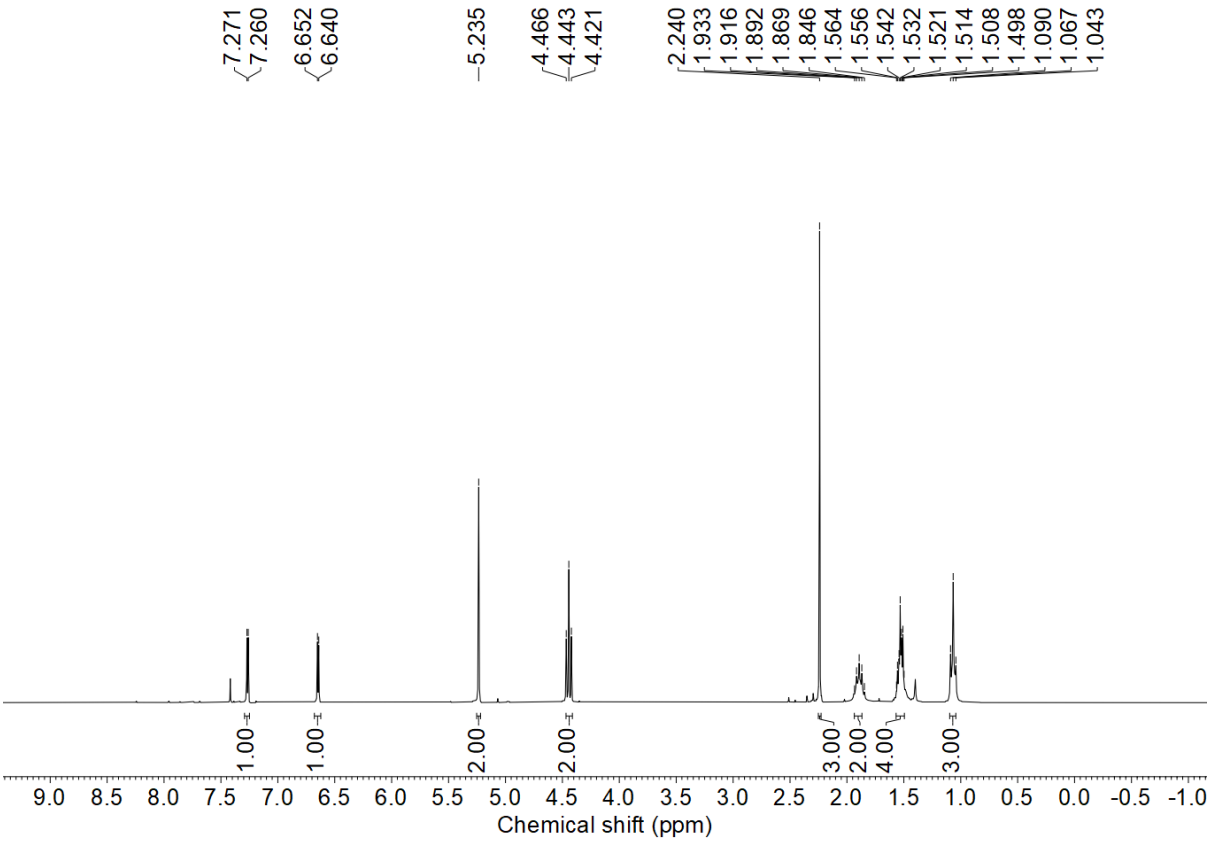


Figure S50. The ^{1}H-NMR spectrum of **4a**.

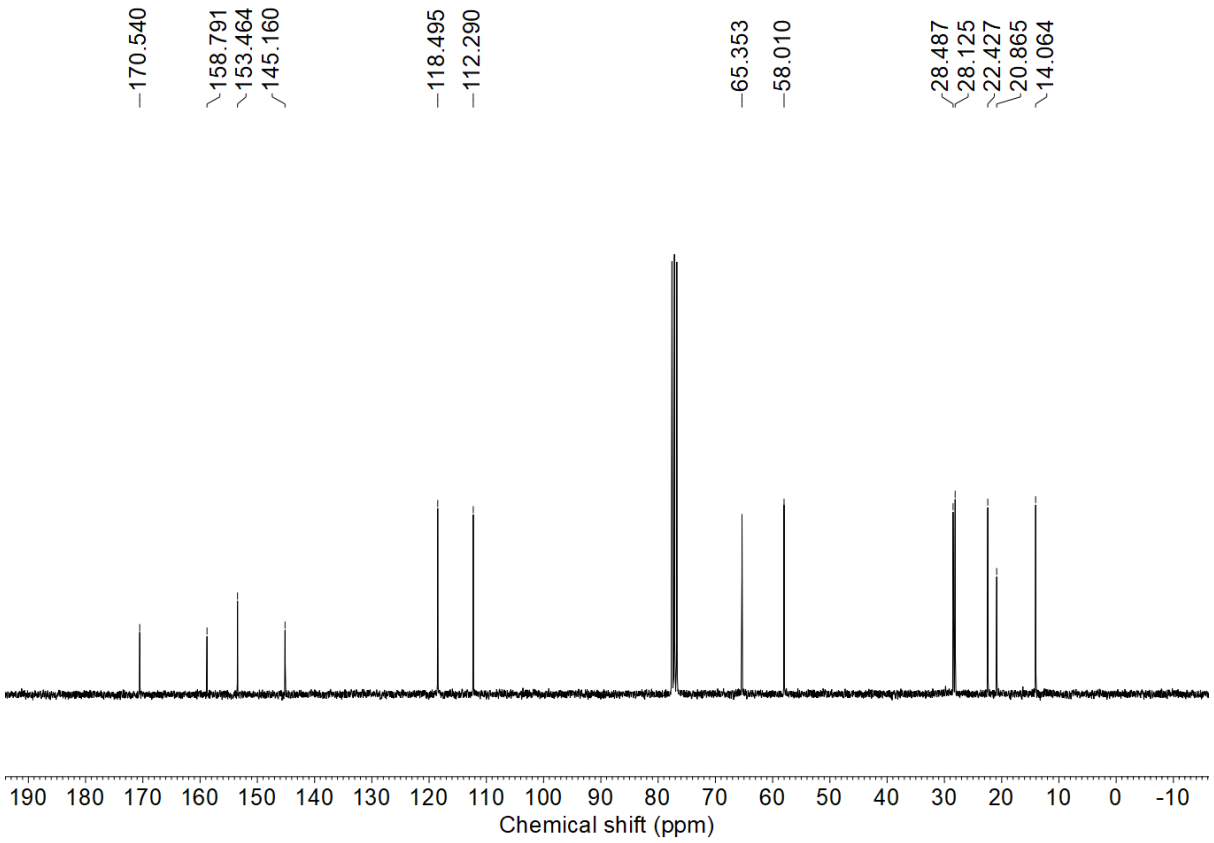


Figure S51. The ^{13}C-NMR spectrum of **4a**.

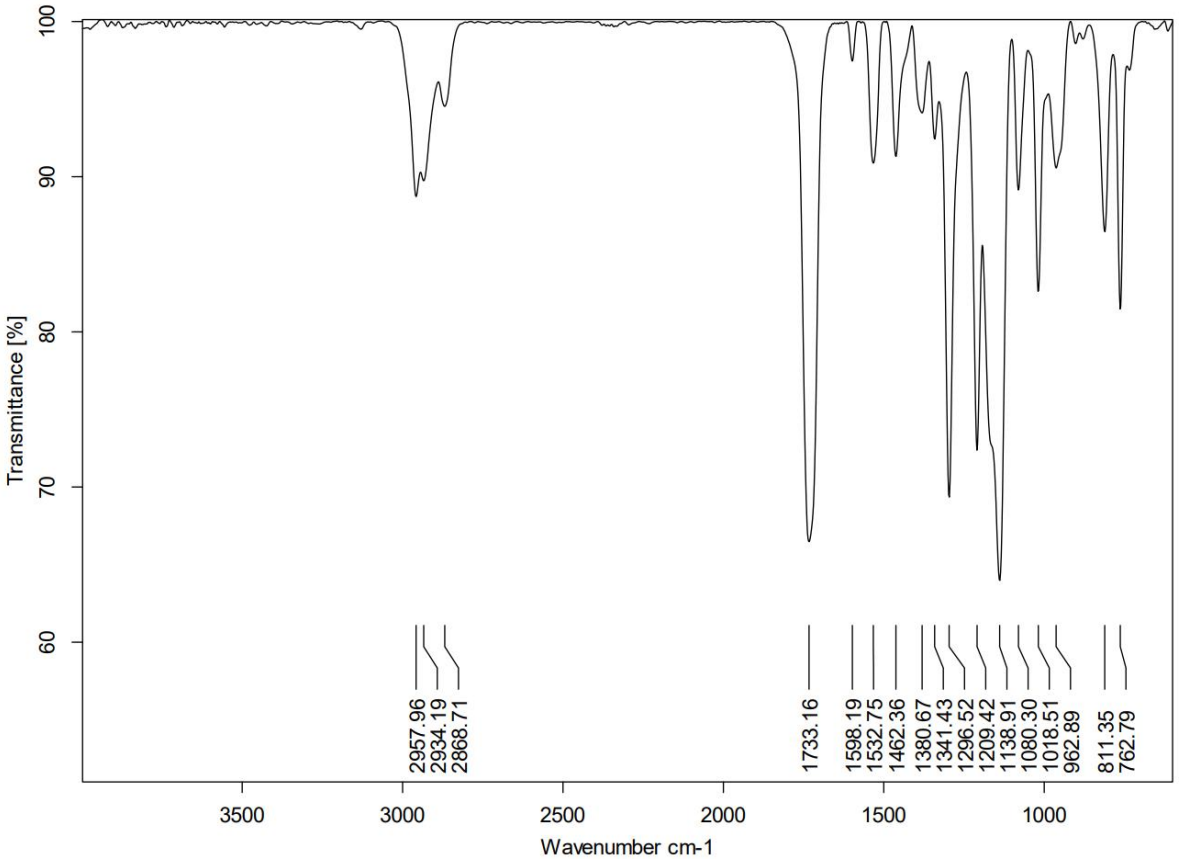


Figure S52. The FTIR spectrum of **4b**.

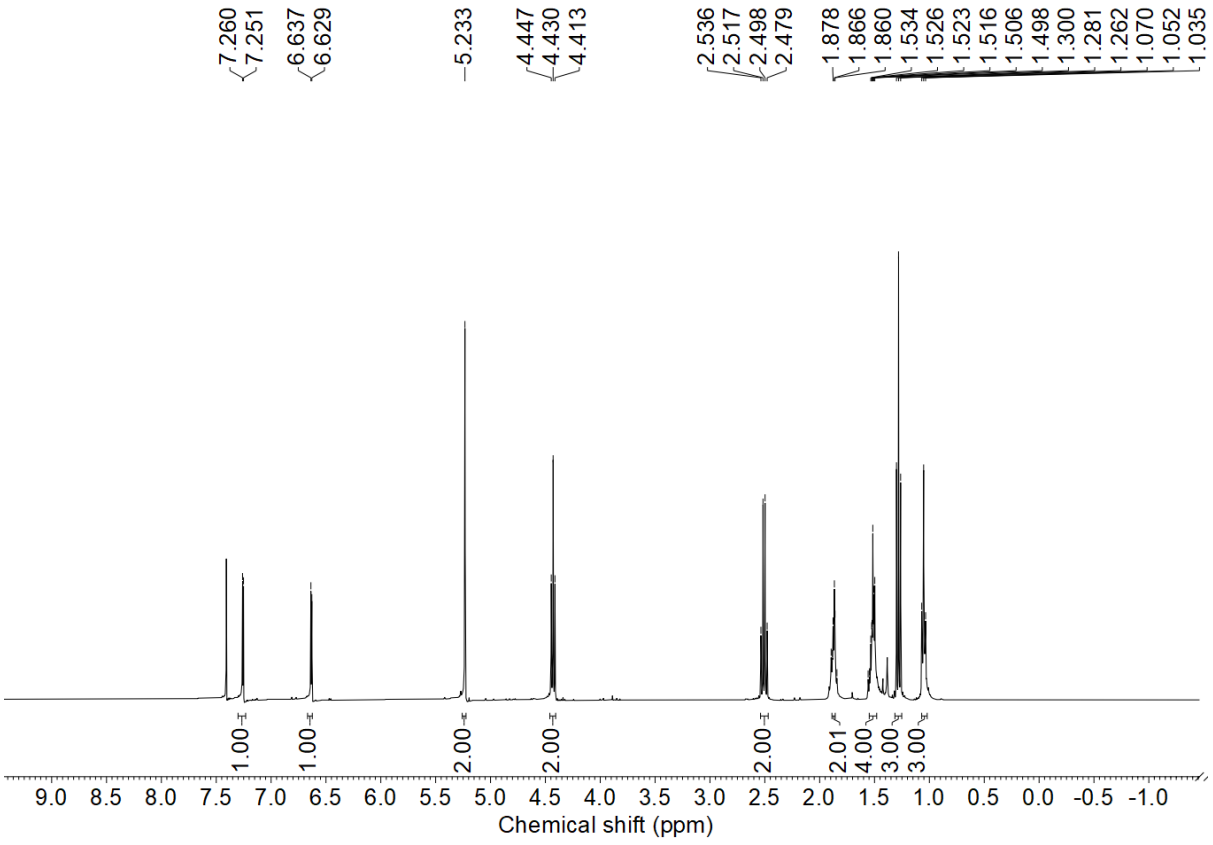


Figure S53. The ^{1}H-NMR spectrum of **4b**.

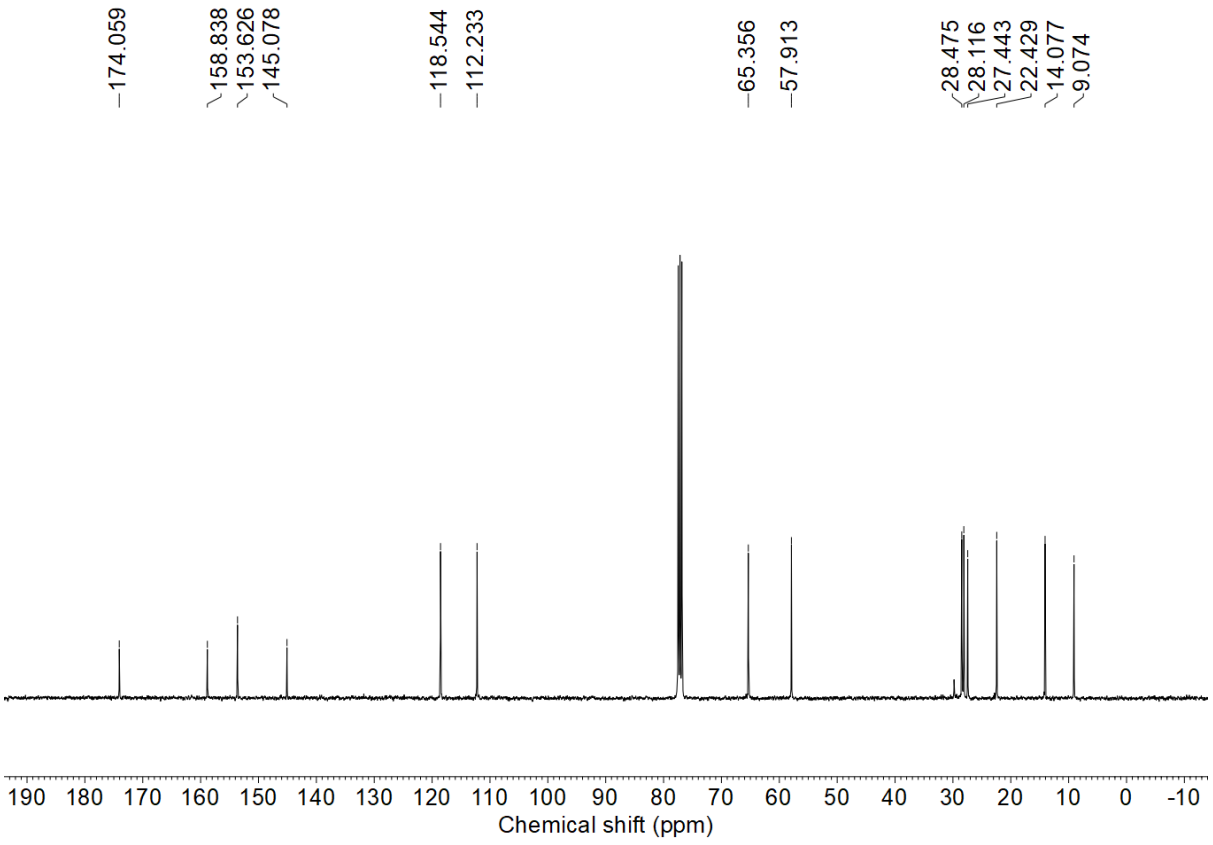


Figure S54. The ^{13}C-NMR spectrum of **4b**.

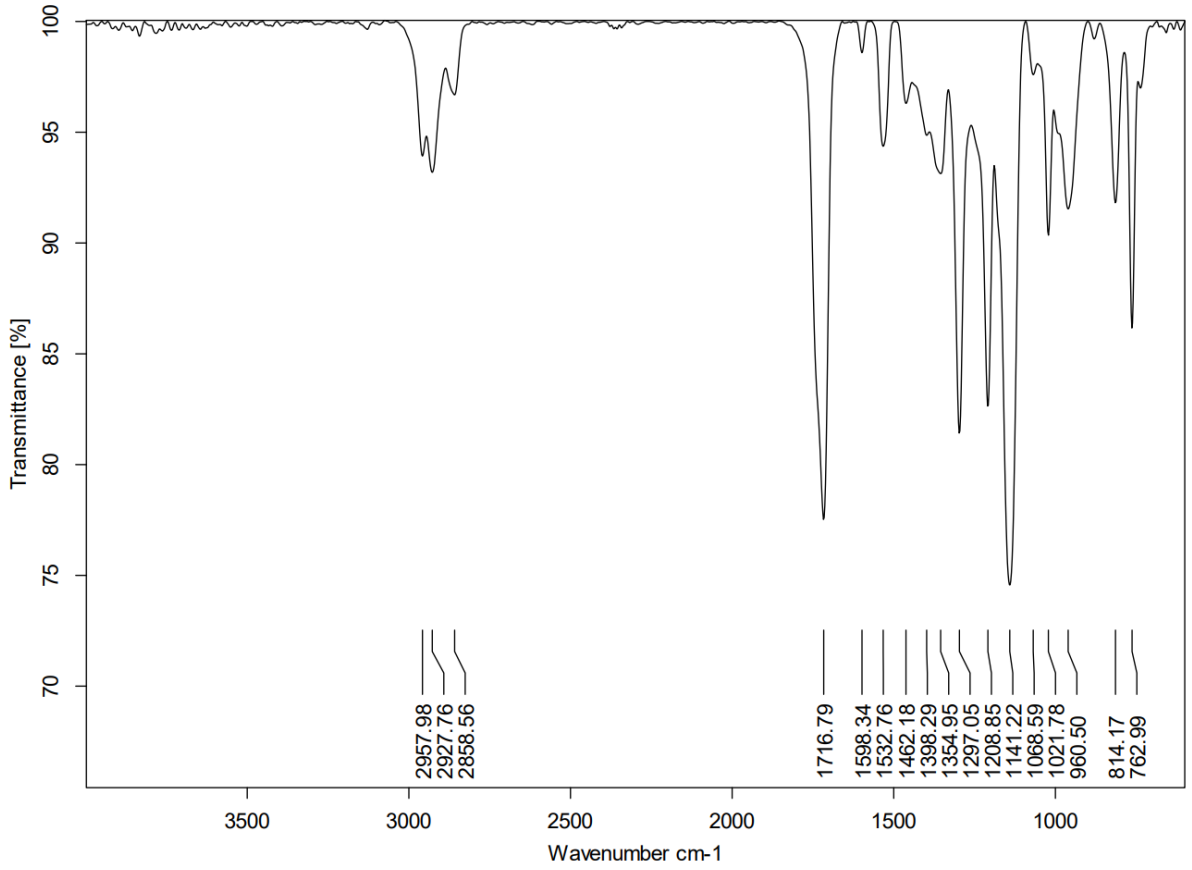


Figure S55. The FTIR spectrum of **4c**.

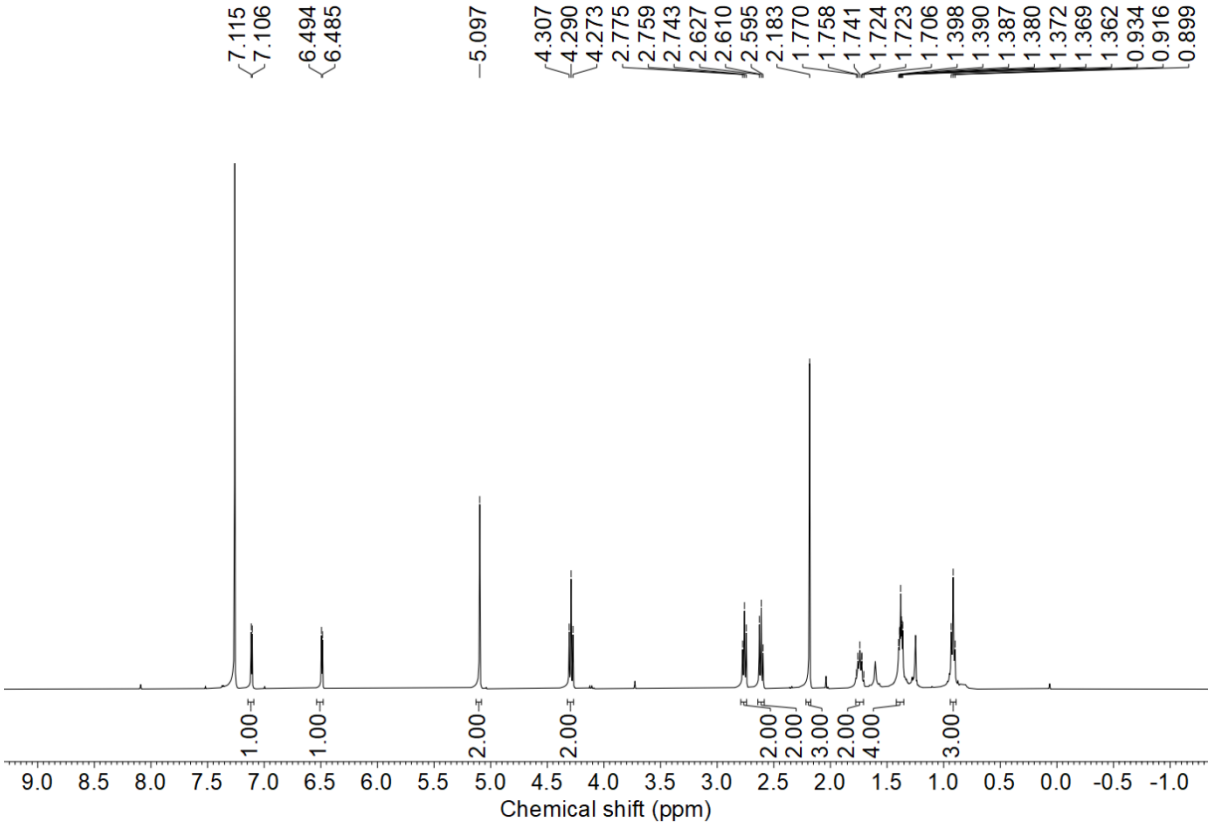


Figure S56. The ^{1}H-NMR spectrum of **4c**.

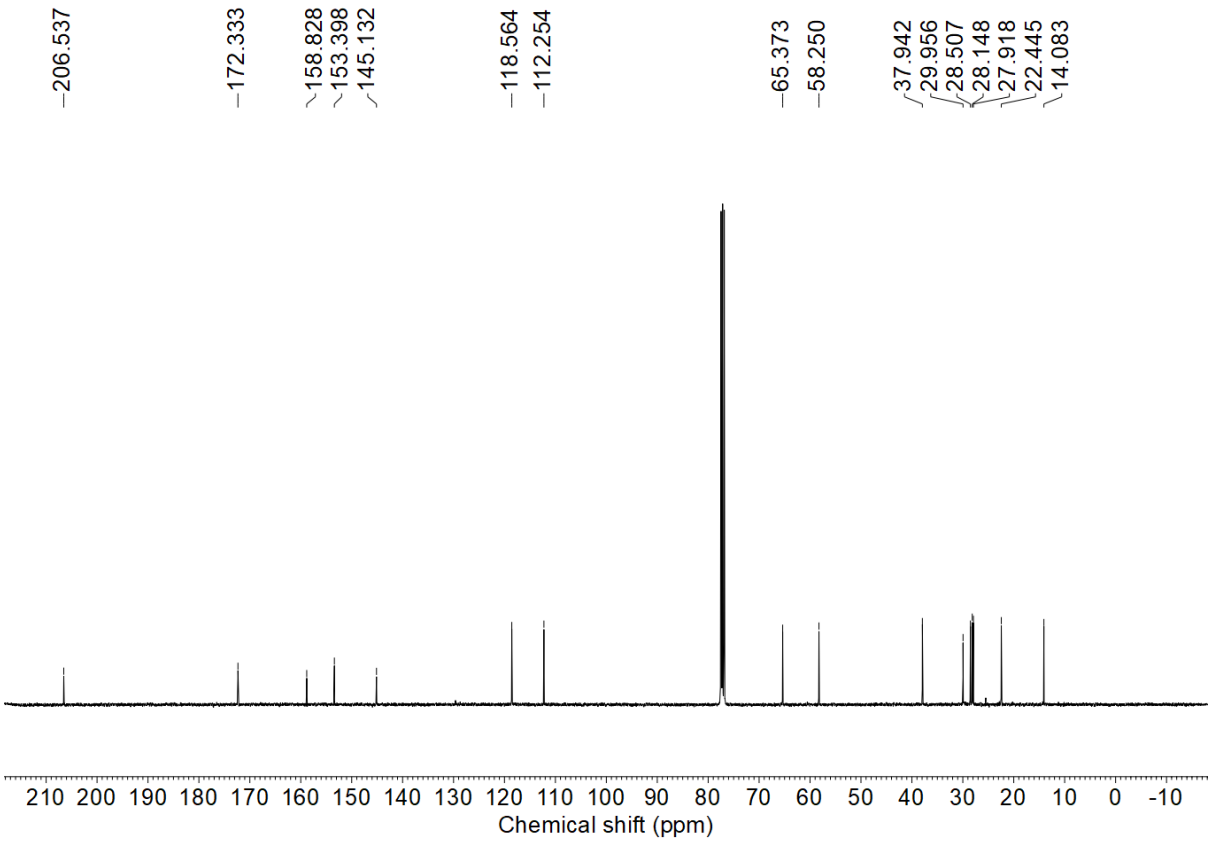


Figure S57. The ^{13}C-NMR spectrum of **4c**.

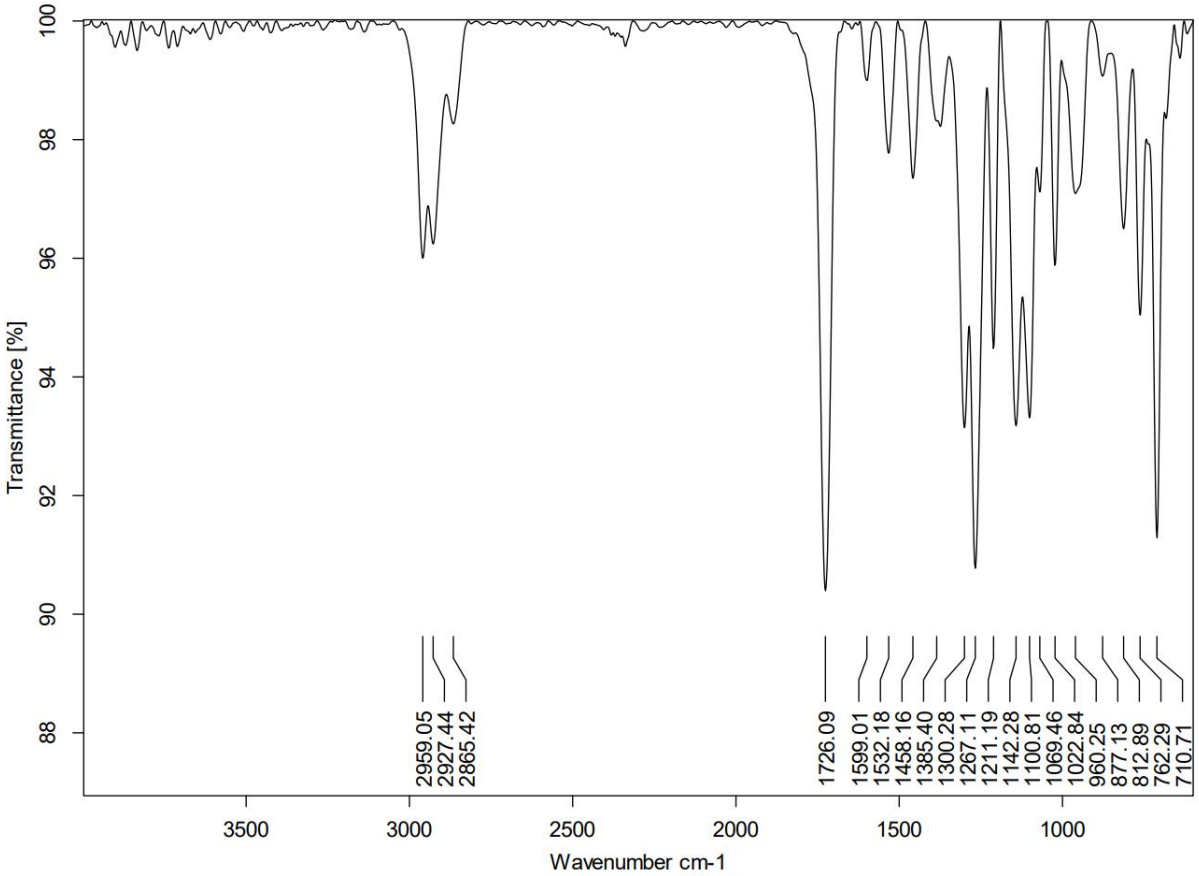


Figure S58. The FTIR spectrum of **4d**.

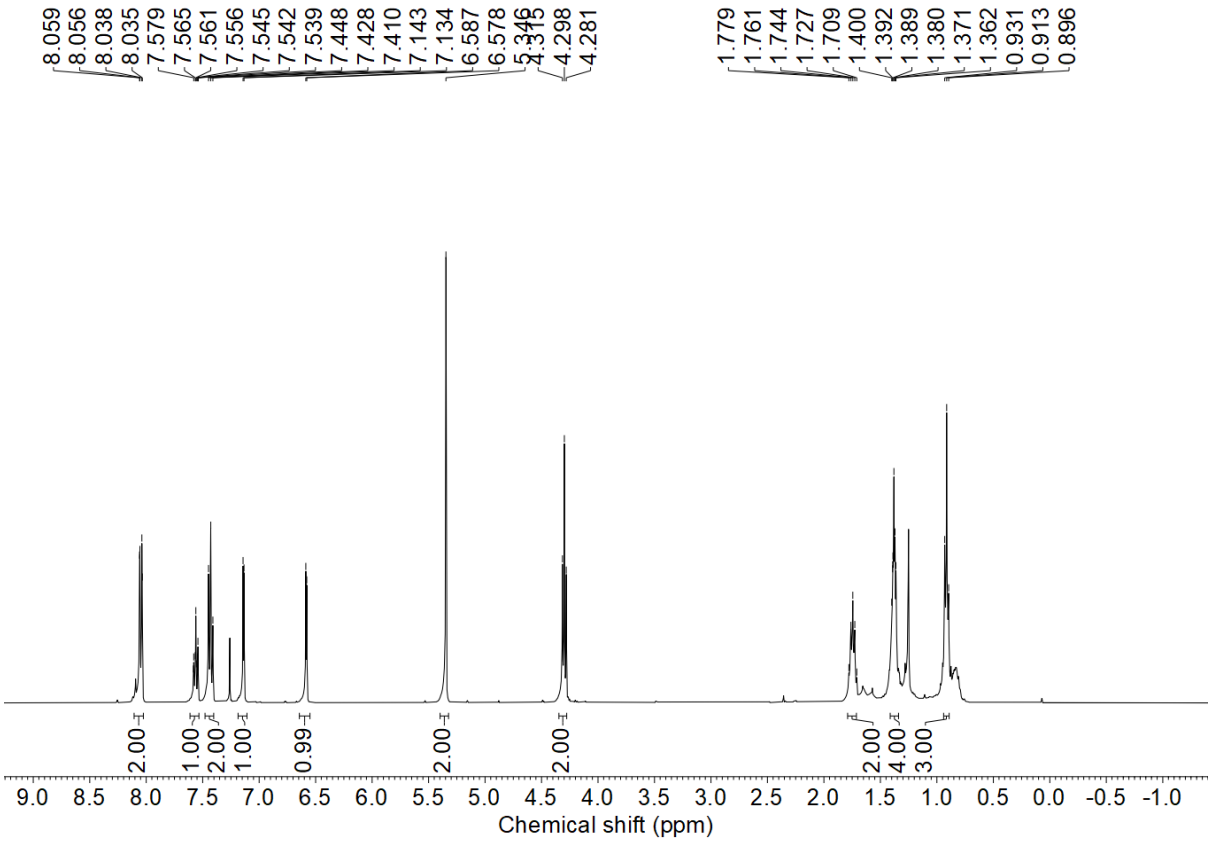


Figure S59. The ^{1}H-NMR spectrum of **4d**.

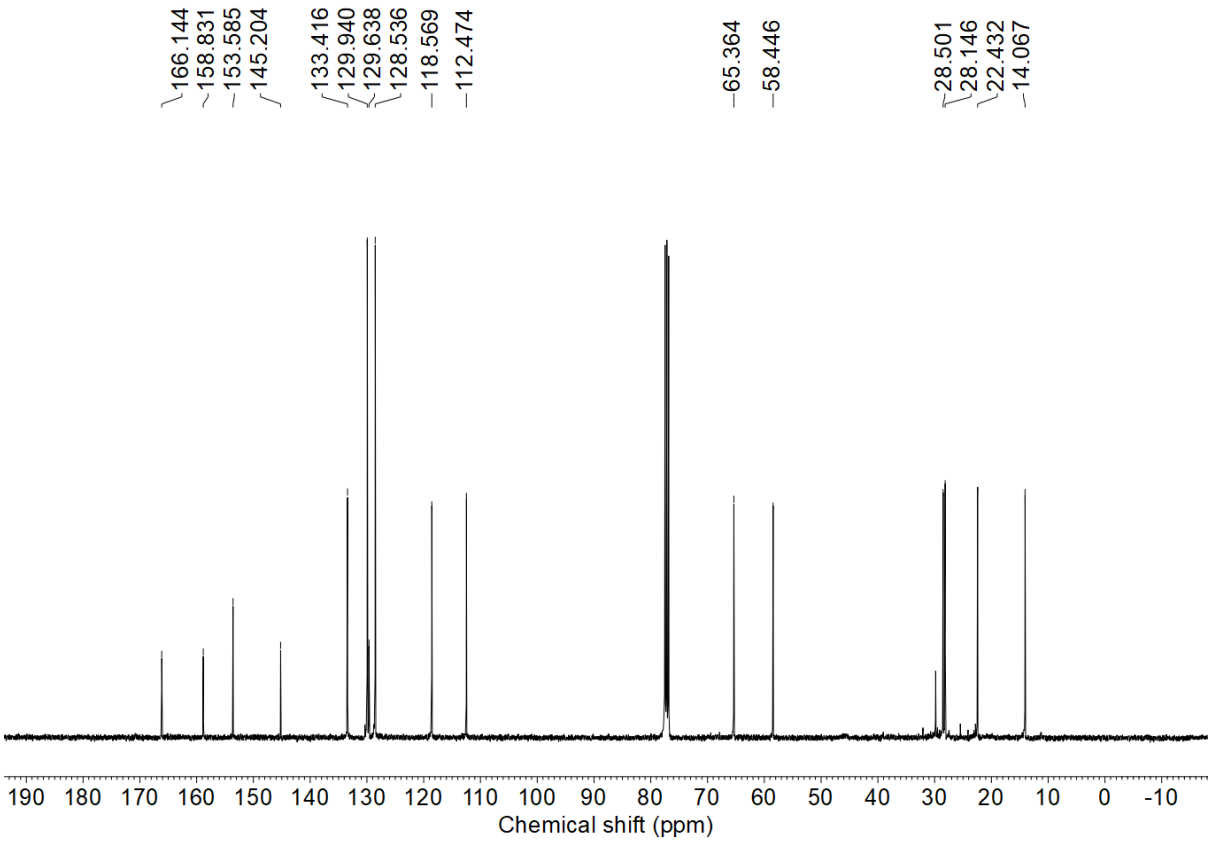


Figure S60. The ^{13}C-NMR spectrum of **4d**.

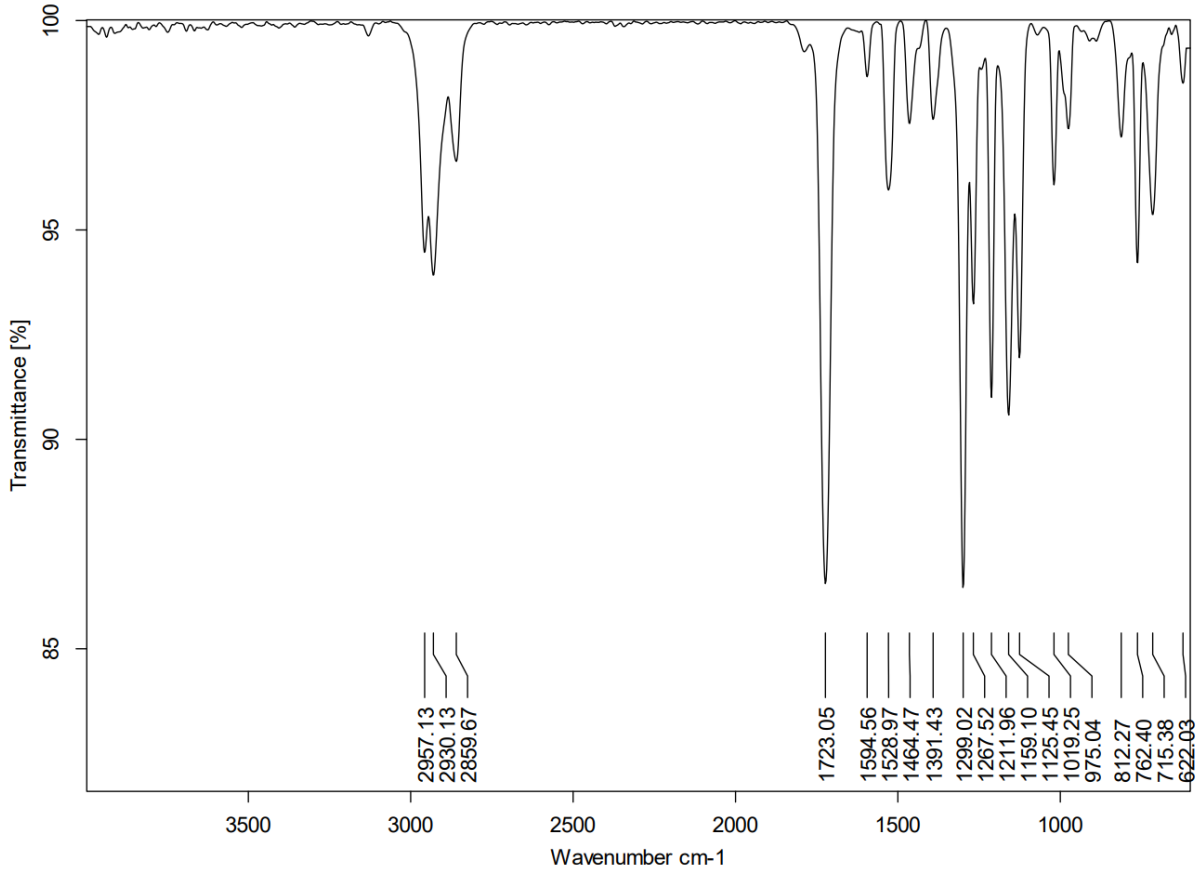


Figure S61. The FTIR spectrum of **5**.

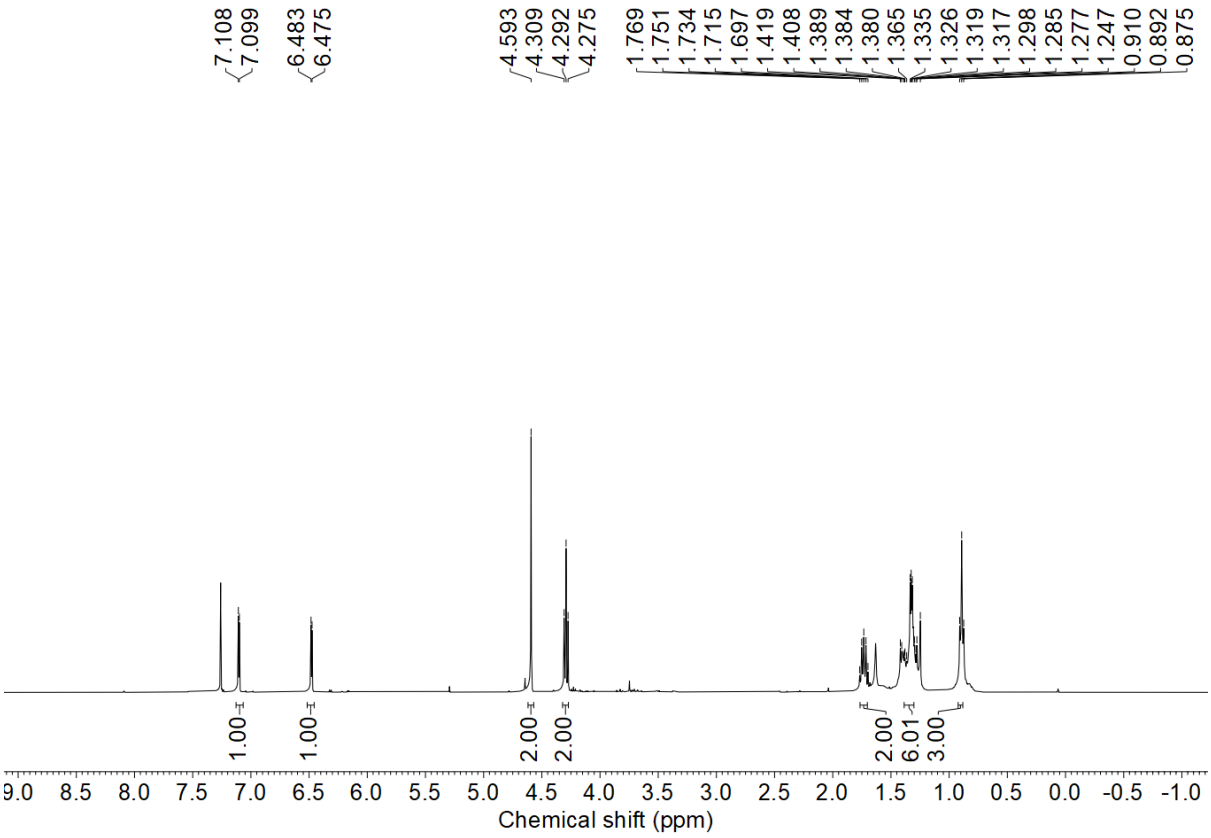


Figure S62. The ^{1}H-NMR spectrum of **5**.

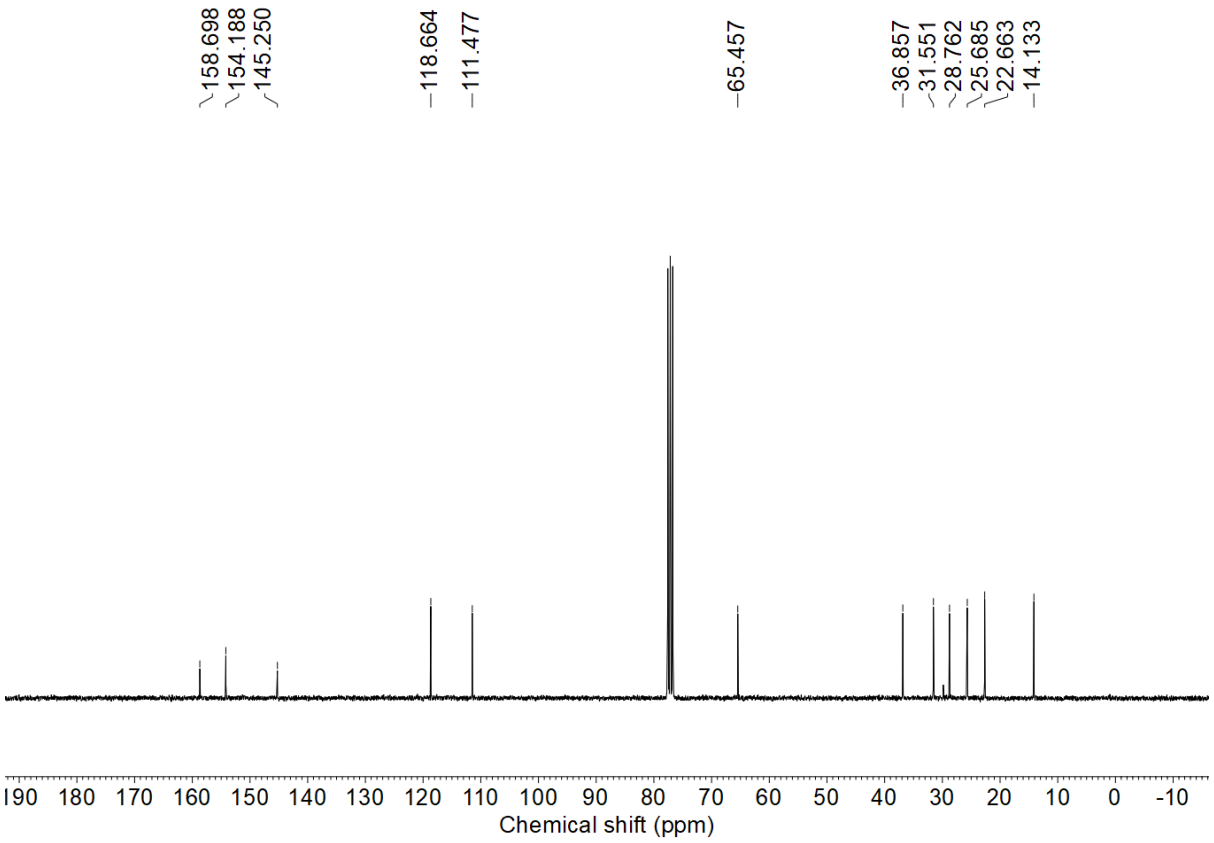


Figure S63. The ^{13}C-NMR spectrum of **5**.

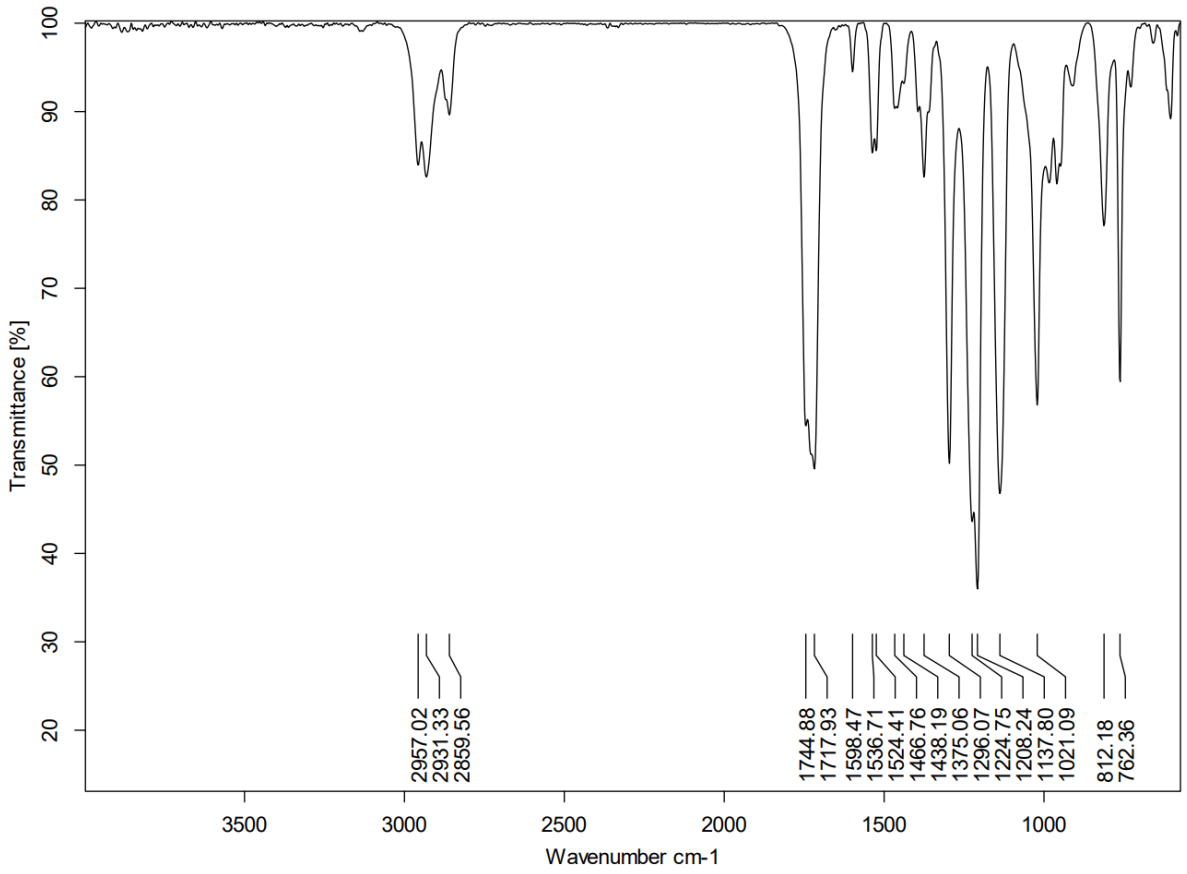


Figure S64. The FTIR spectrum of **5a**.

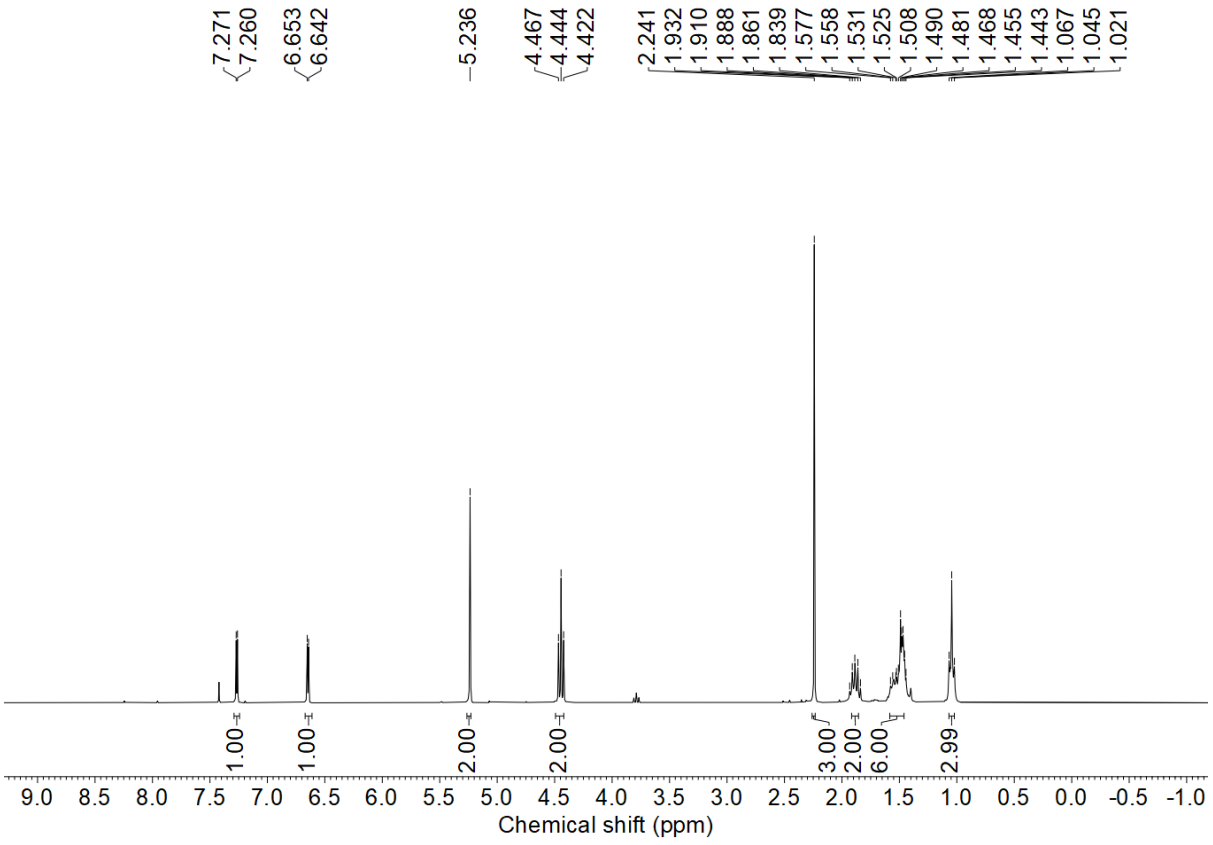


Figure S65. The ^{1}H-NMR spectrum of **5a**.

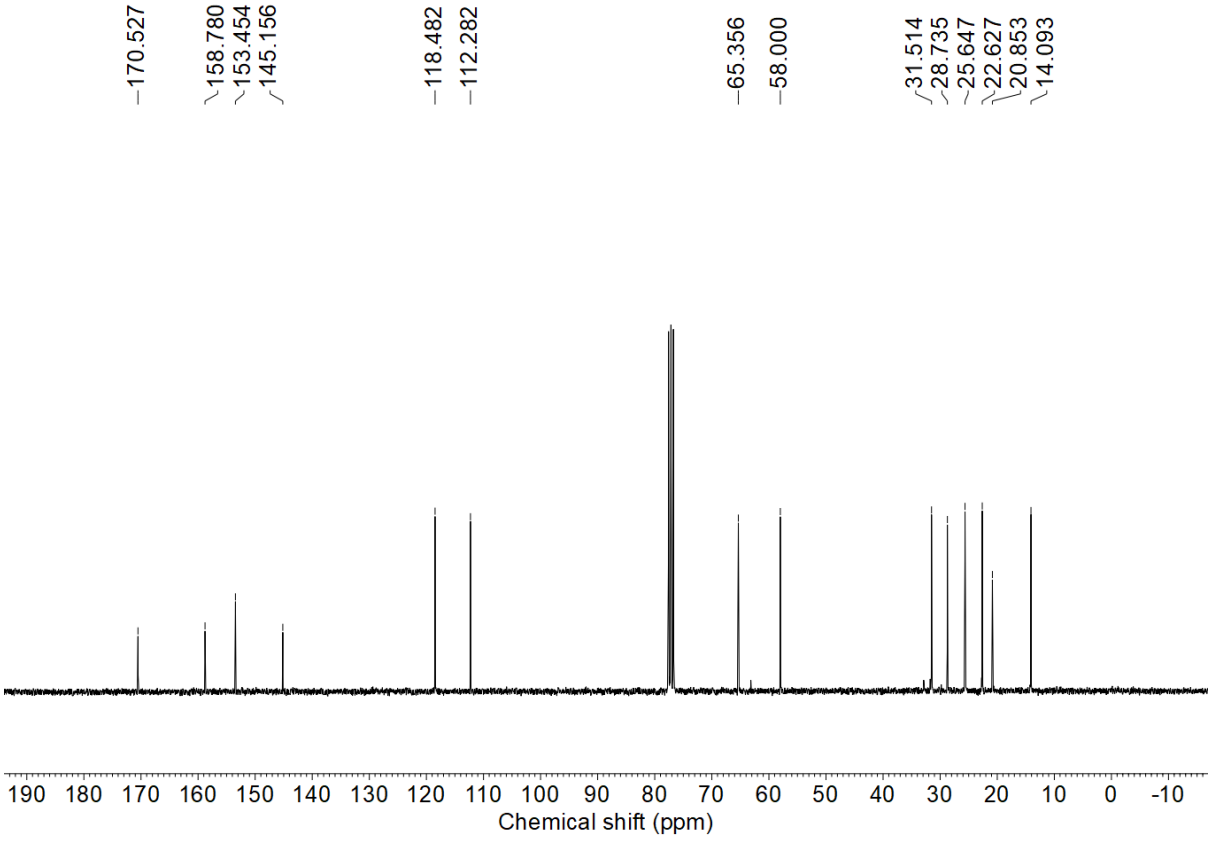


Figure S66. The ^{13}C-NMR spectrum of **5a**.

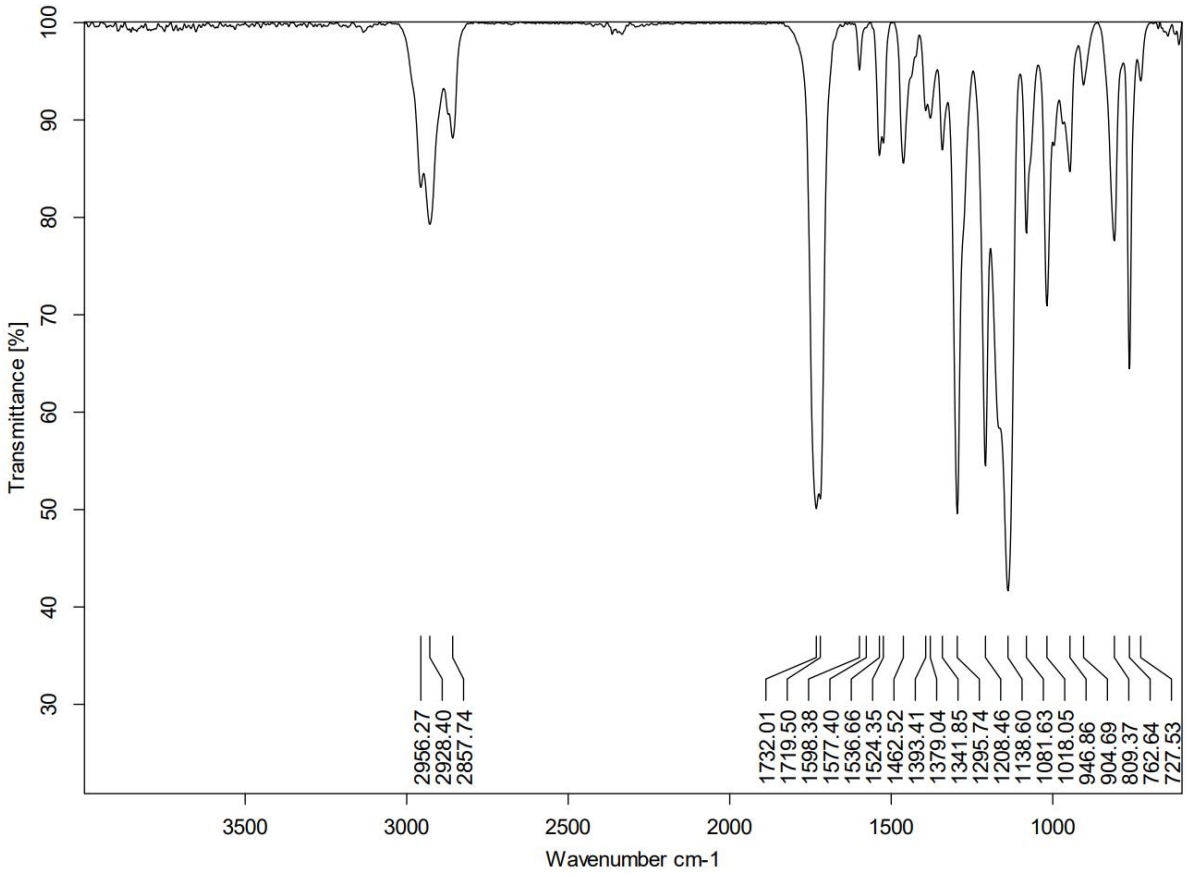


Figure S67. The FTIR spectrum of **5b**.

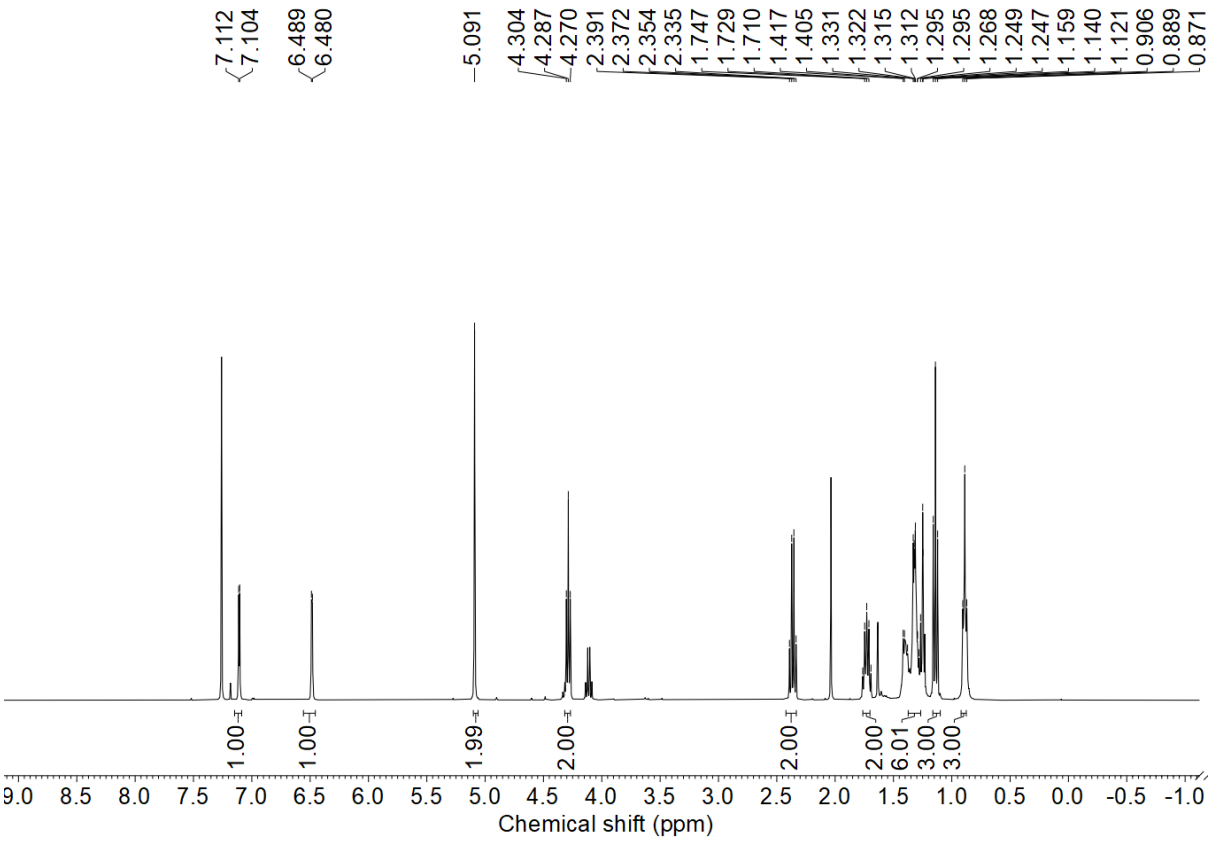


Figure S68. The ^{1}H-NMR spectrum of **5b**.

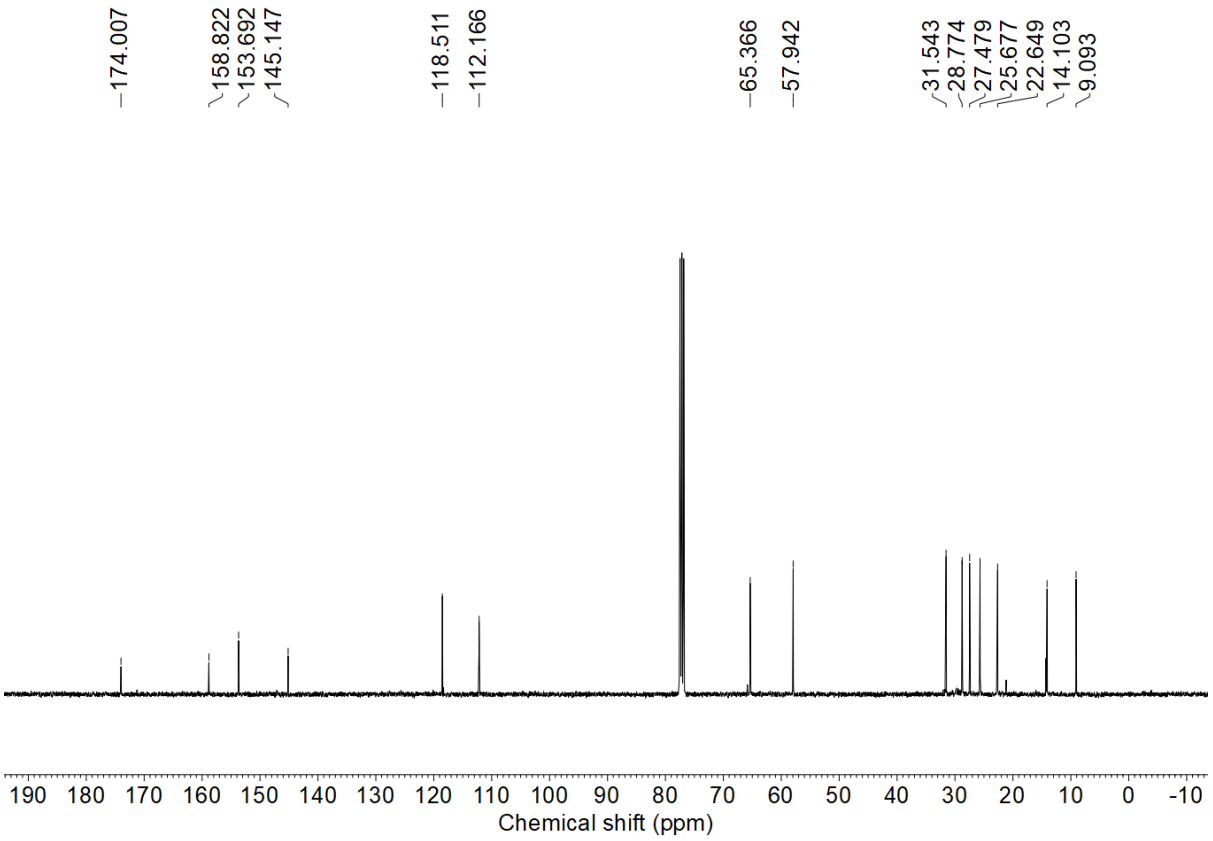


Figure S69. The ^{13}C-NMR spectrum of **5b**.

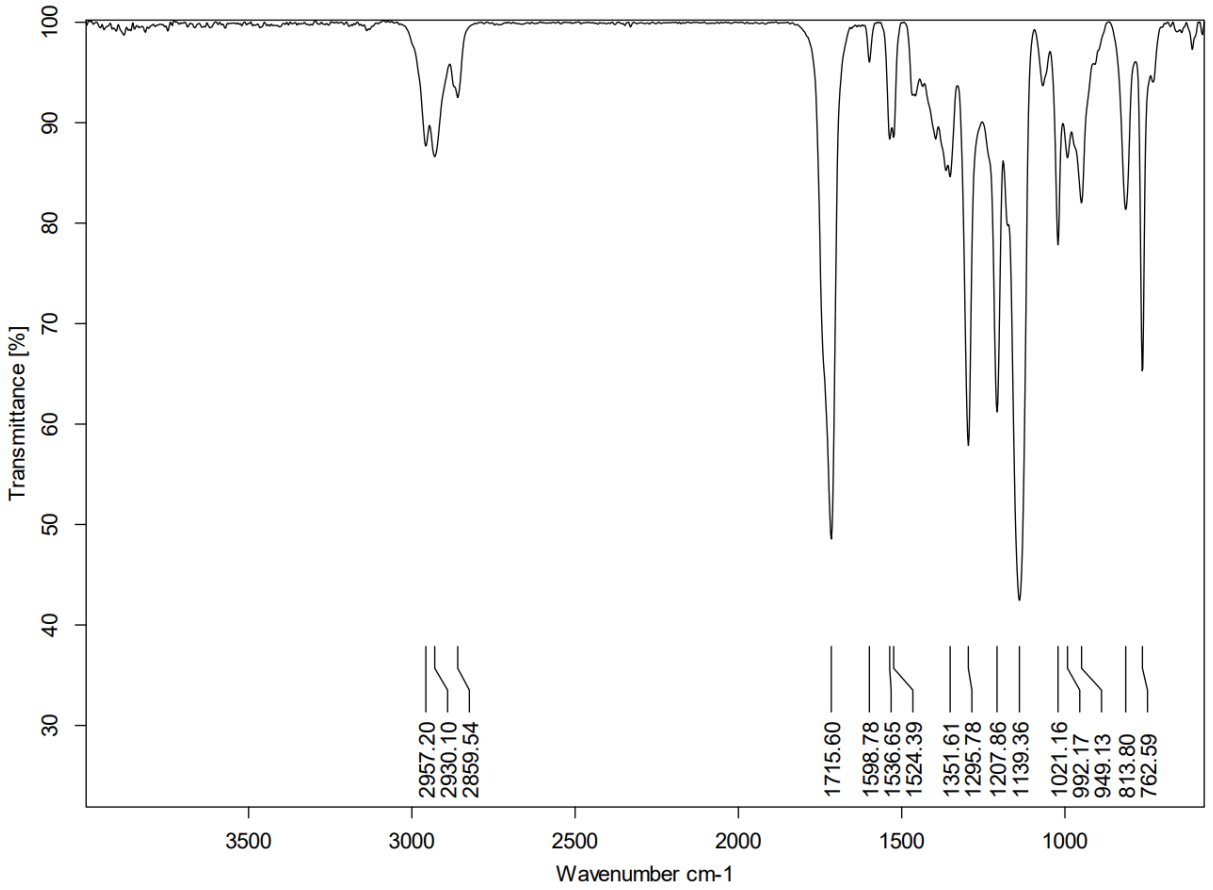


Figure S70. The FTIR spectrum of **5c**.

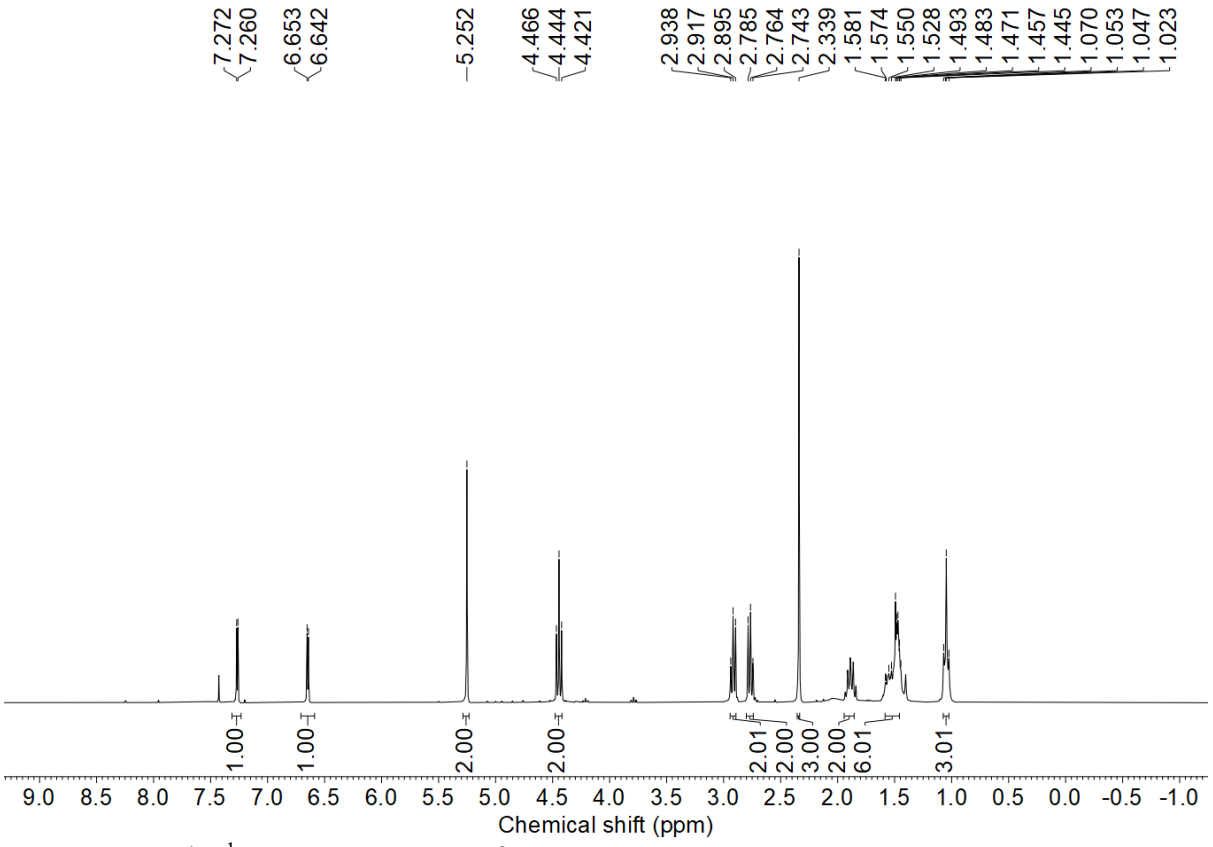


Figure S71. The ^{1}H-NMR spectrum of **5c**.

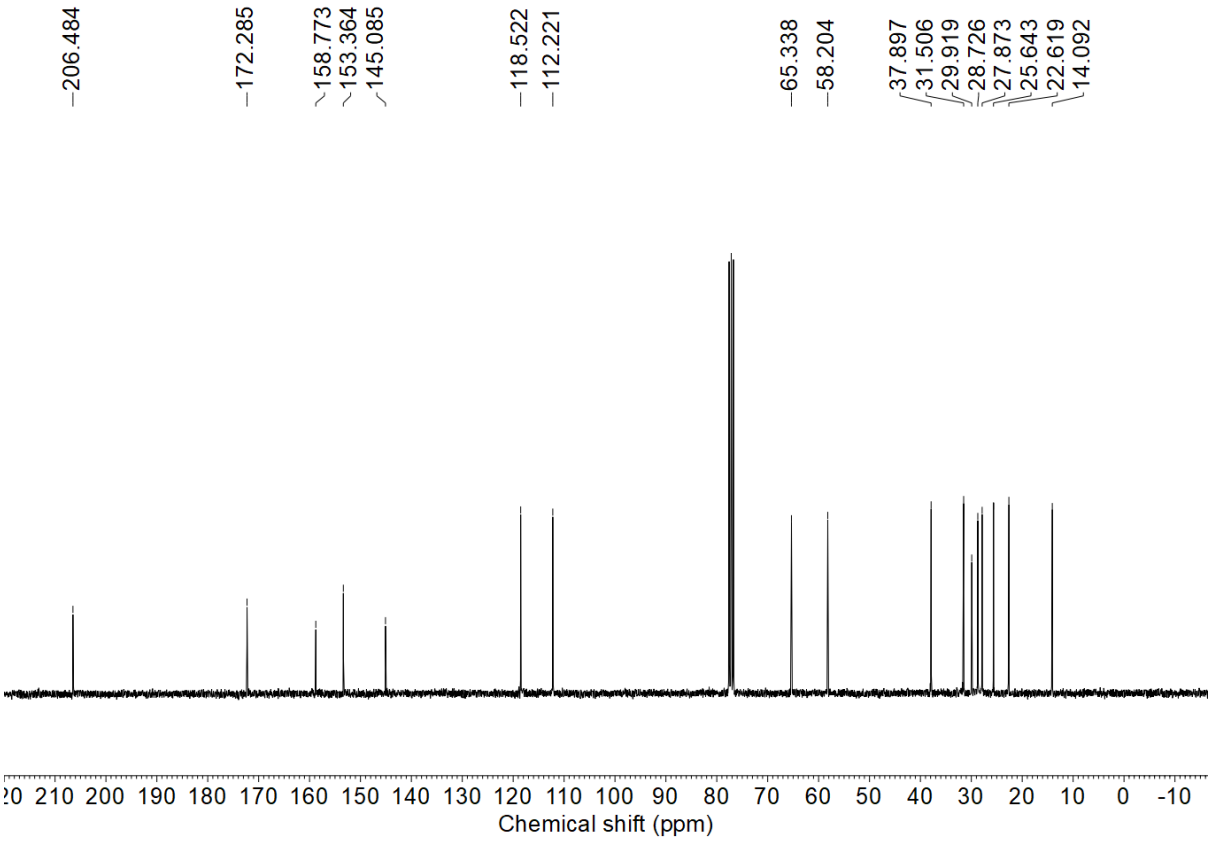


Figure S72. The ^{13}C-NMR spectrum of **5c**.

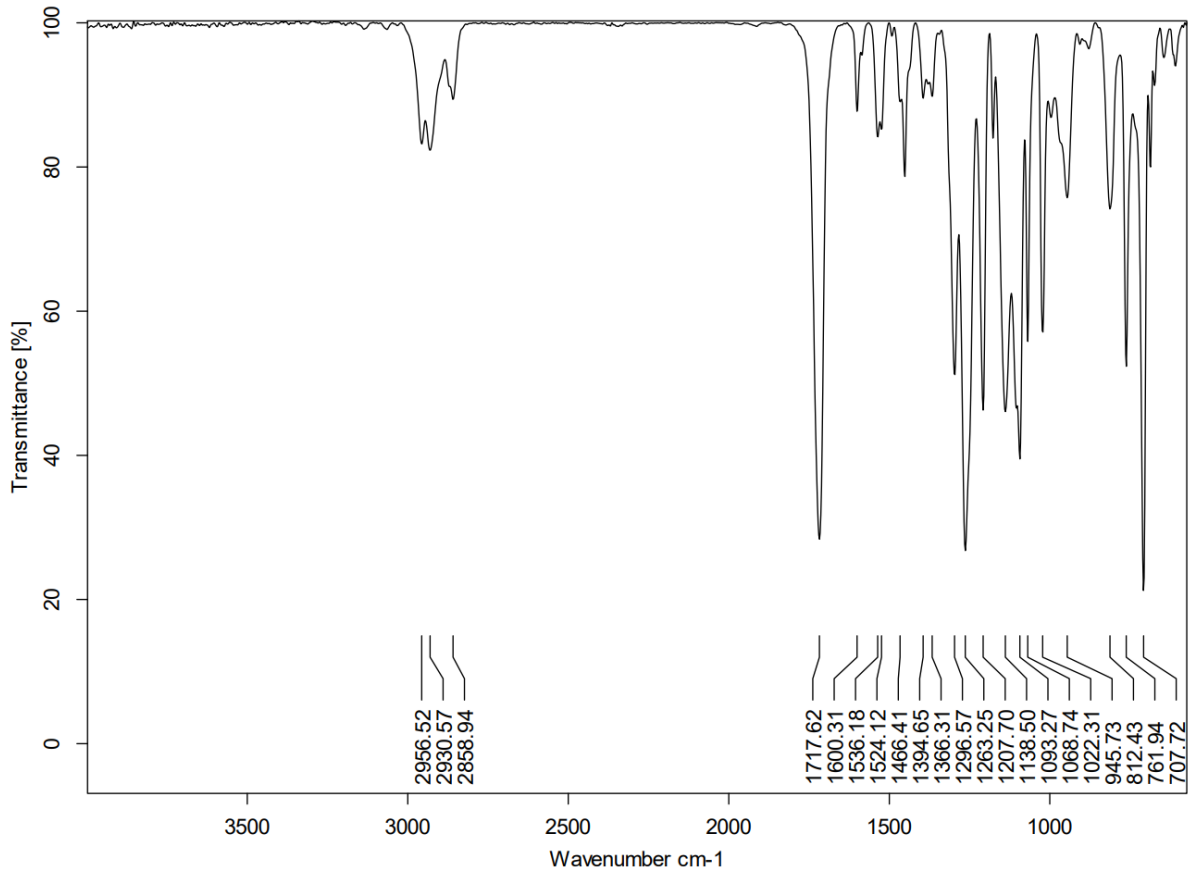


Figure S73. The FTIR spectrum of **5d**.

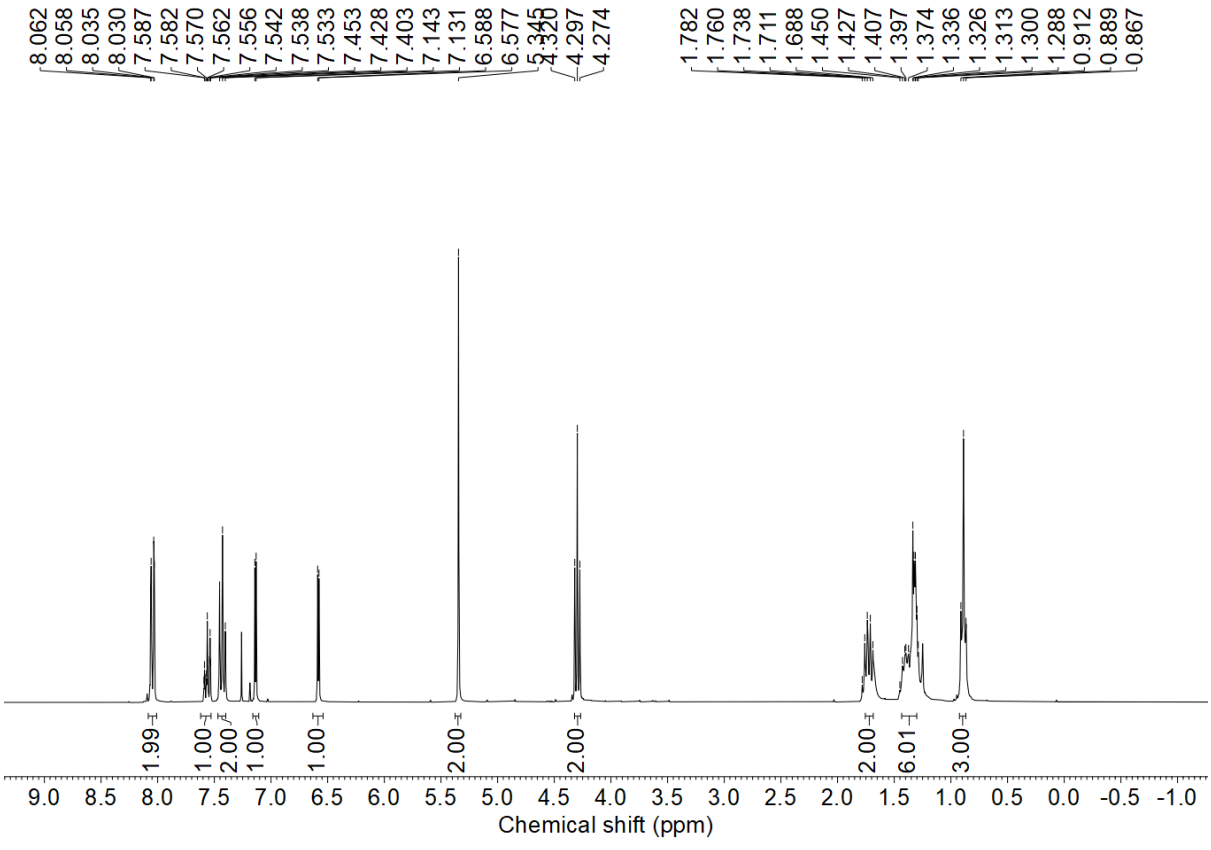


Figure S74. The ^{1}H-NMR spectrum of **5d**.

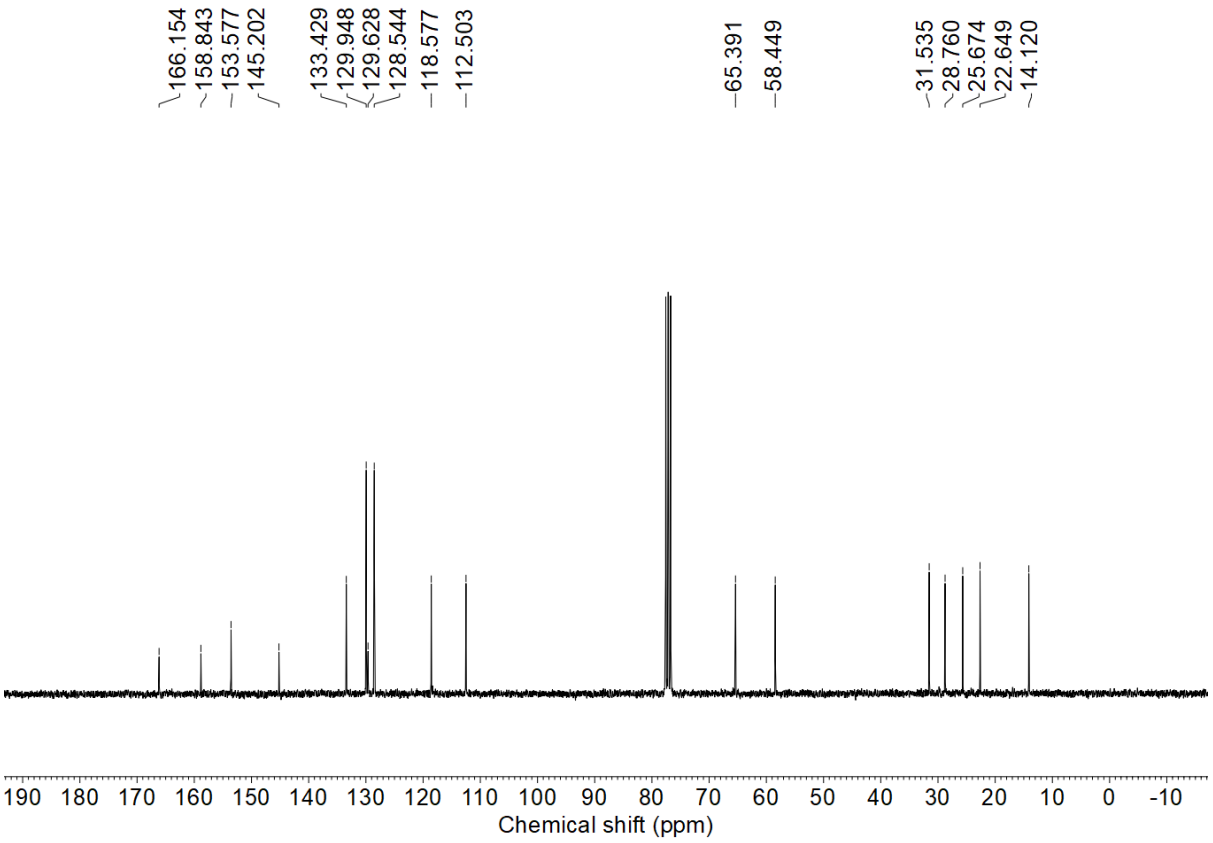


Figure S75. The ^{13}C-NMR spectrum of **5d**.

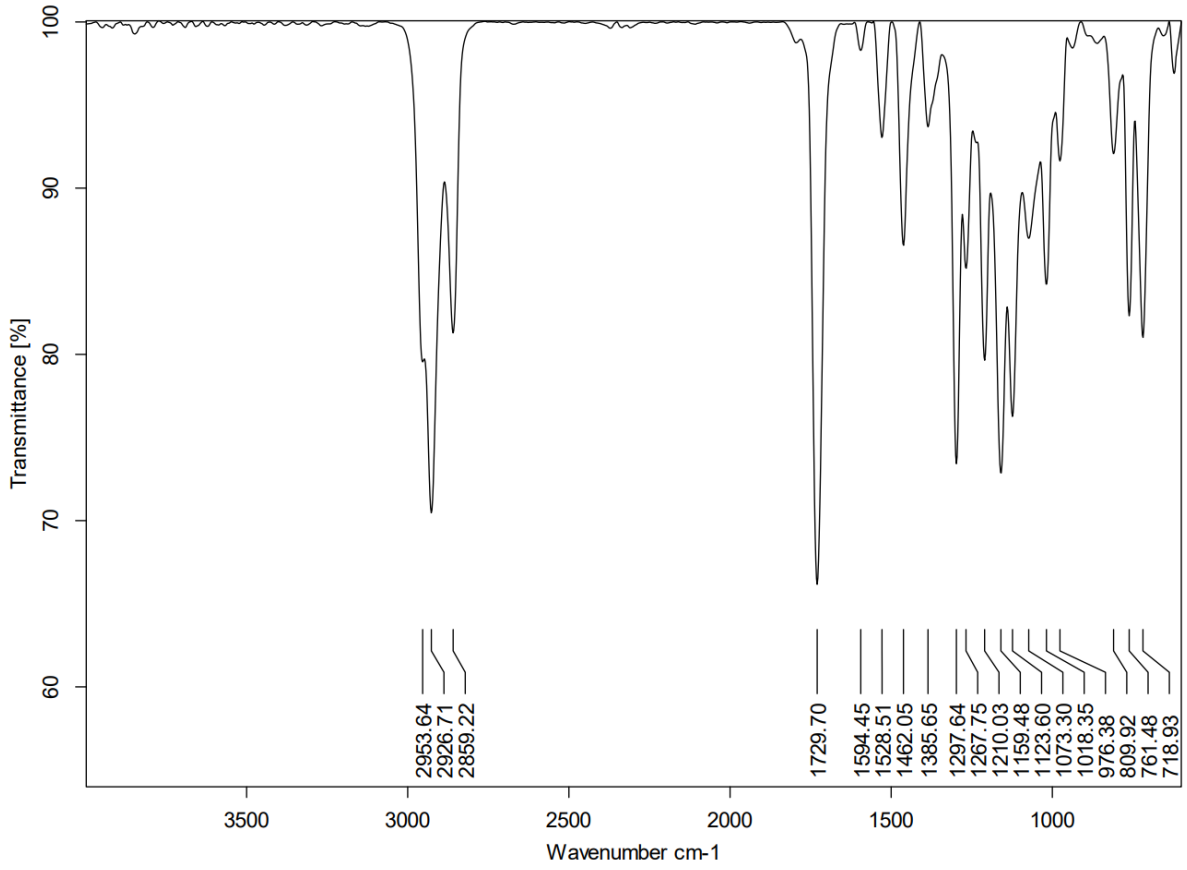


Figure S76. The FTIR spectrum of **6**.

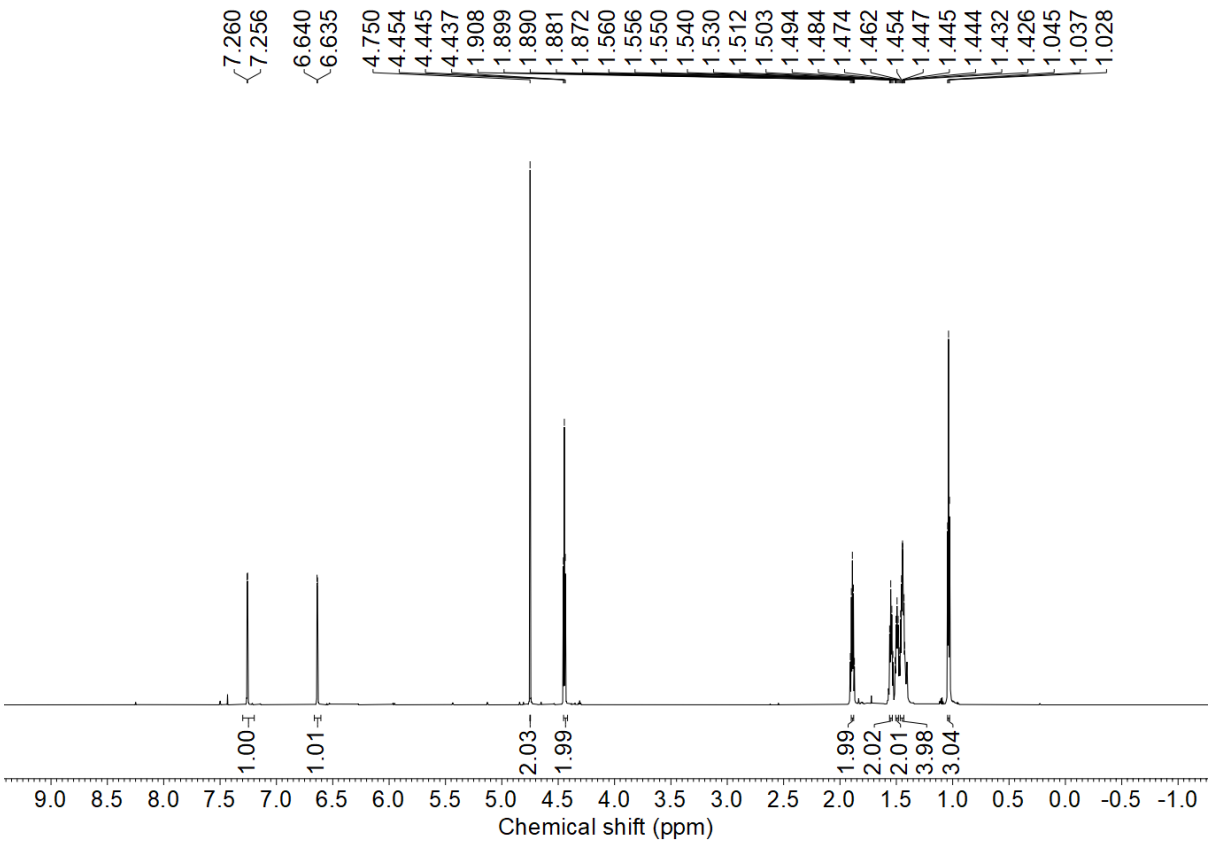


Figure S77. The ^{1}H-NMR spectrum of **6**.

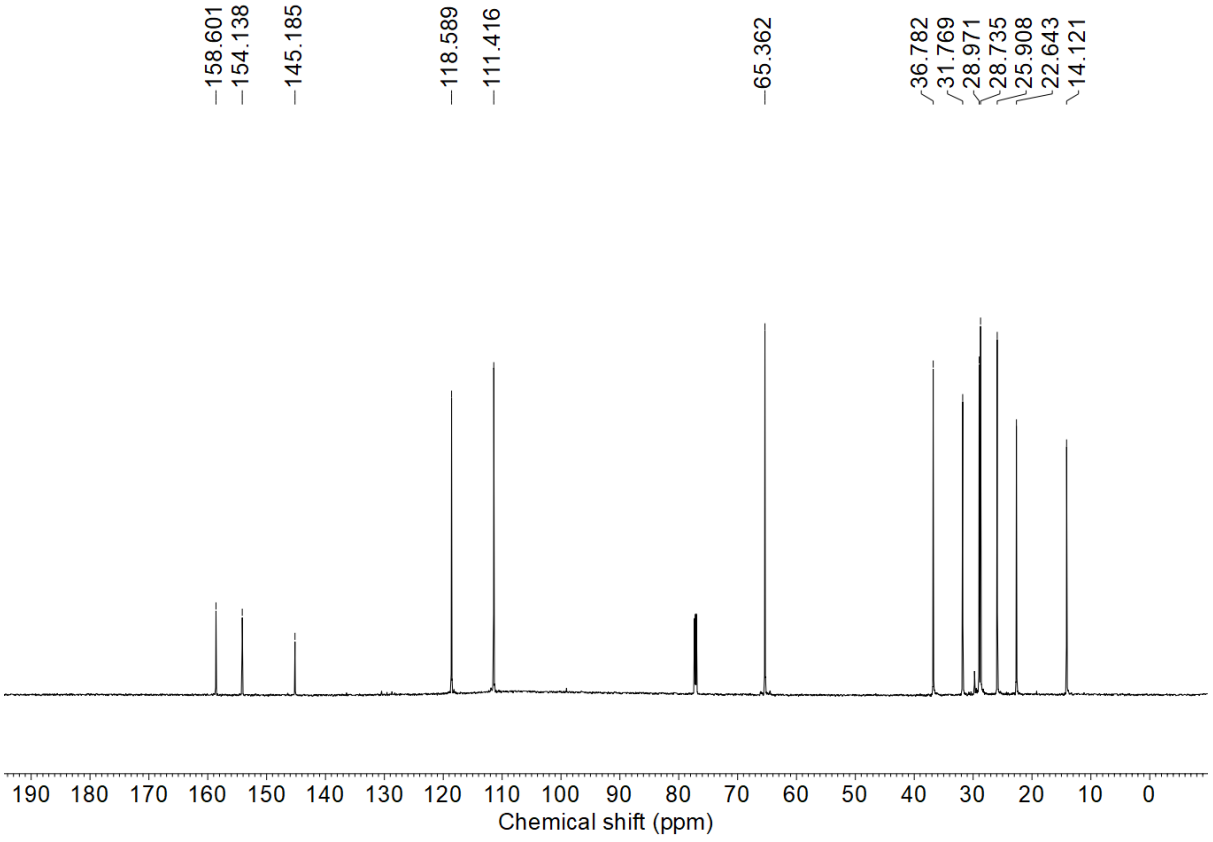


Figure S78. The ^{13}C-NMR spectrum of **6**.

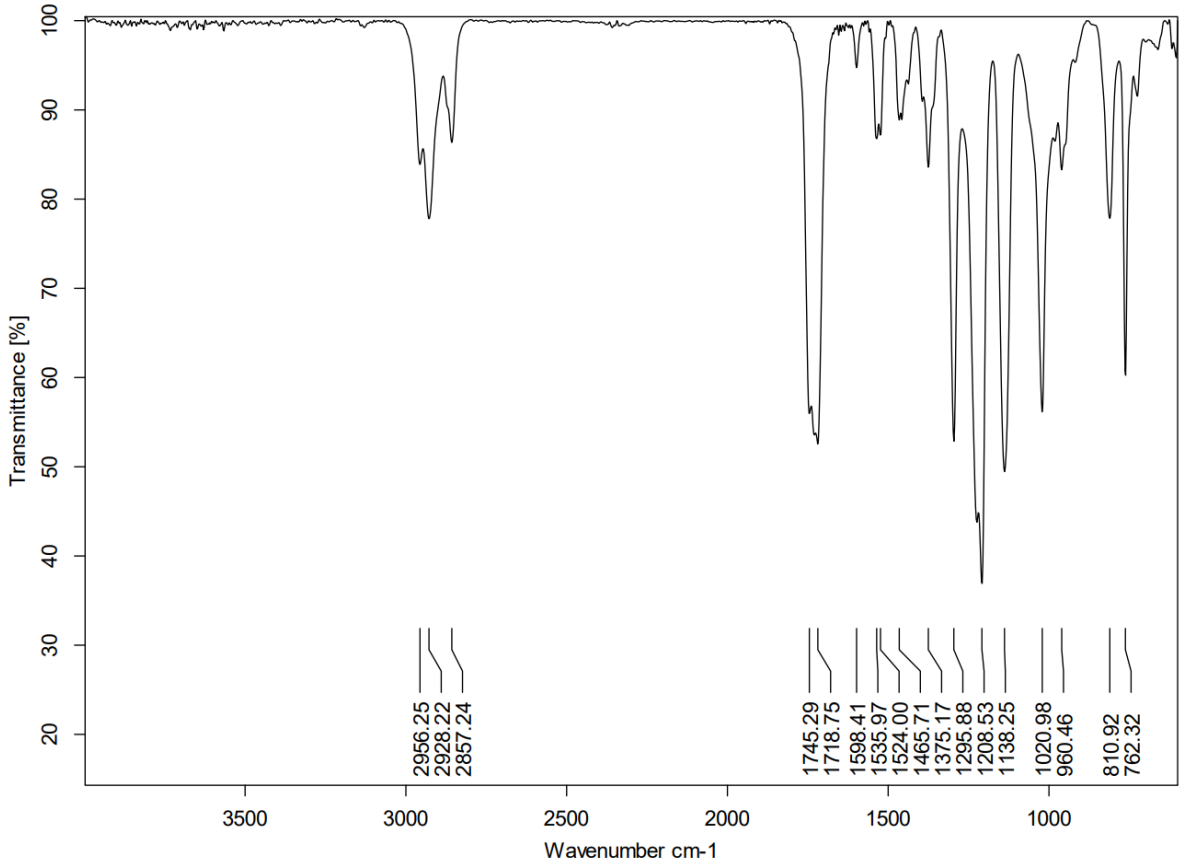


Figure S79. The FTIR spectrum of **6a**.

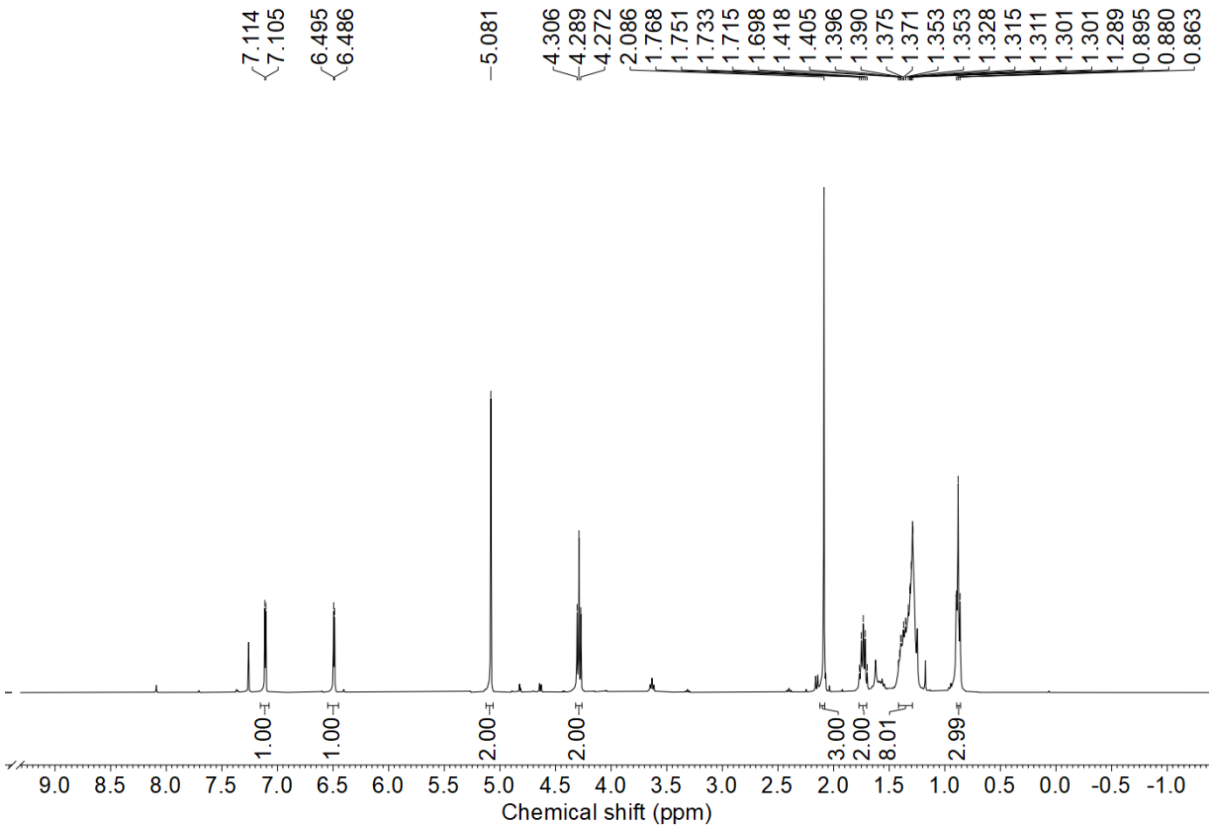


Figure S80. The ^{1}H-NMR spectrum of **6a**.

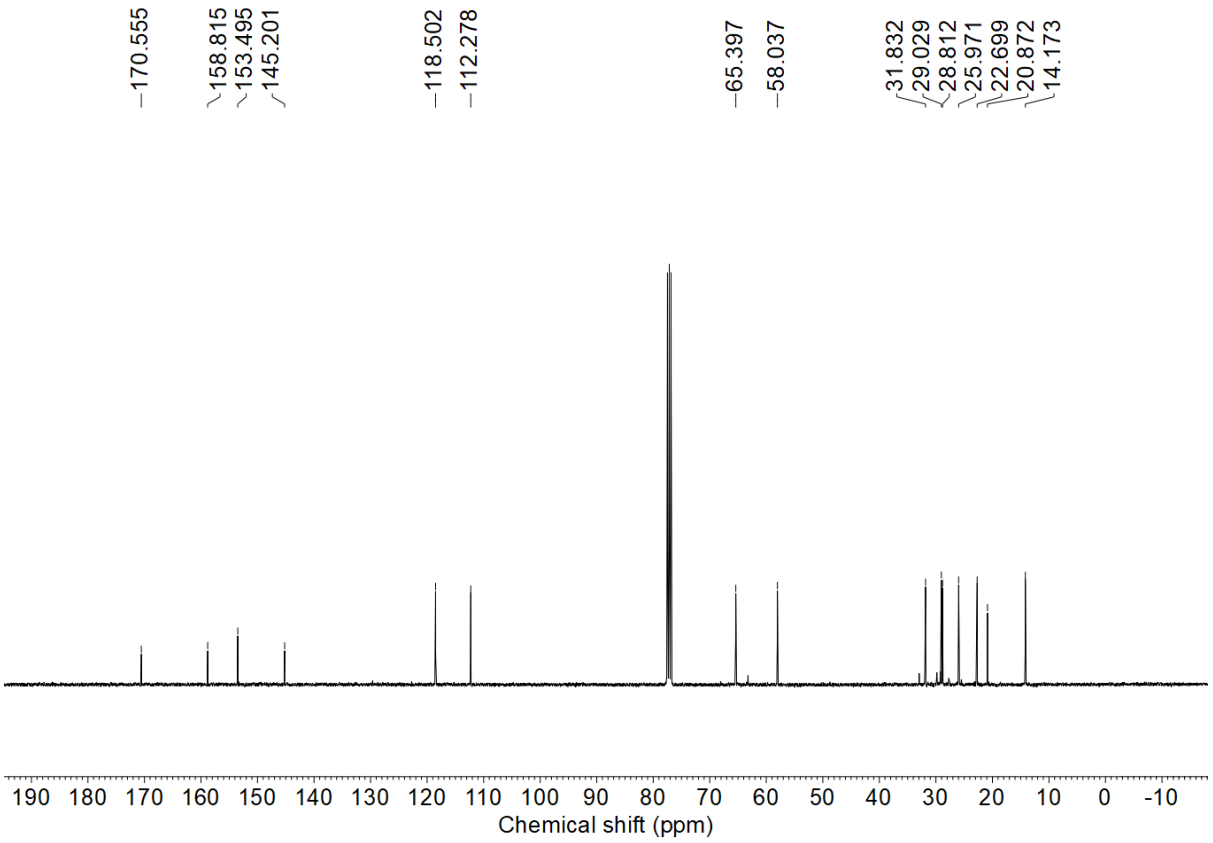


Figure S81. The ^{13}C-NMR spectrum of **6a**.

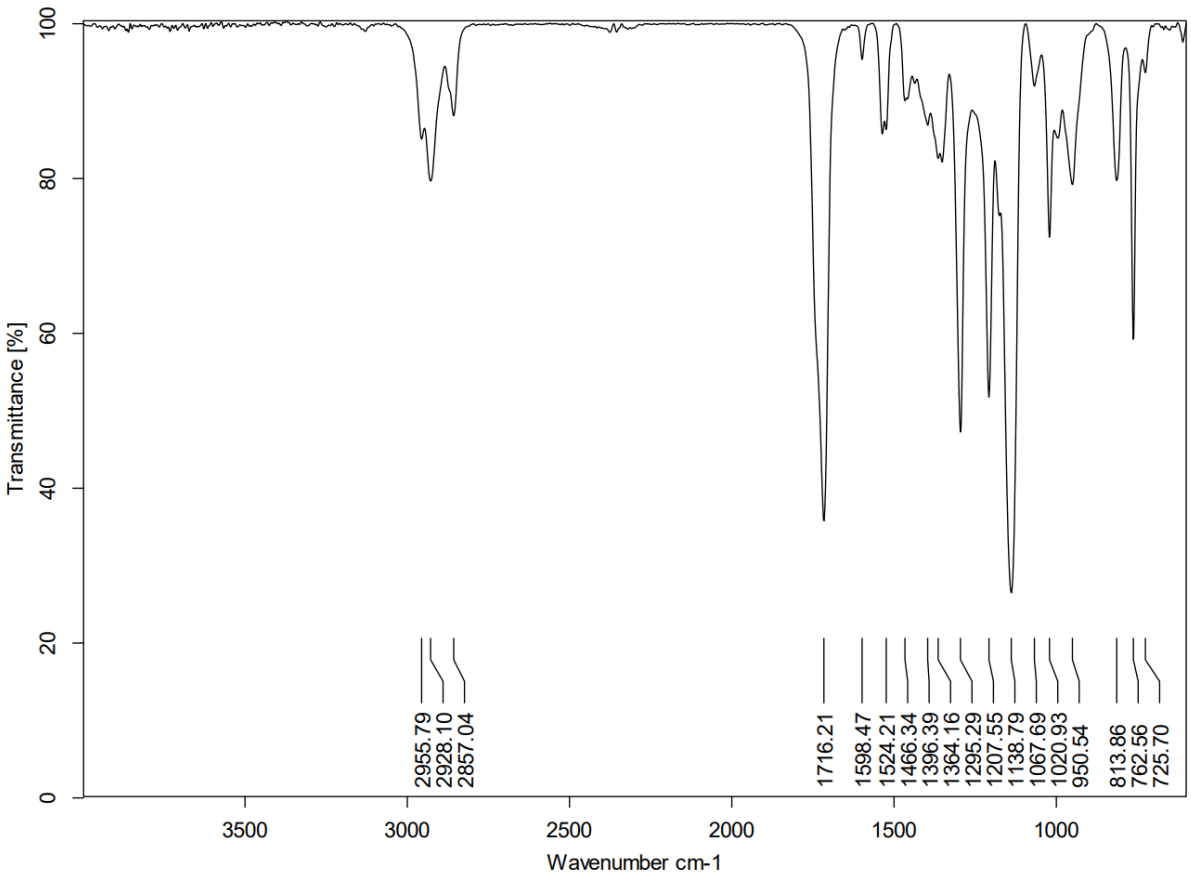


Figure S82. The FTIR spectrum of **6b**.

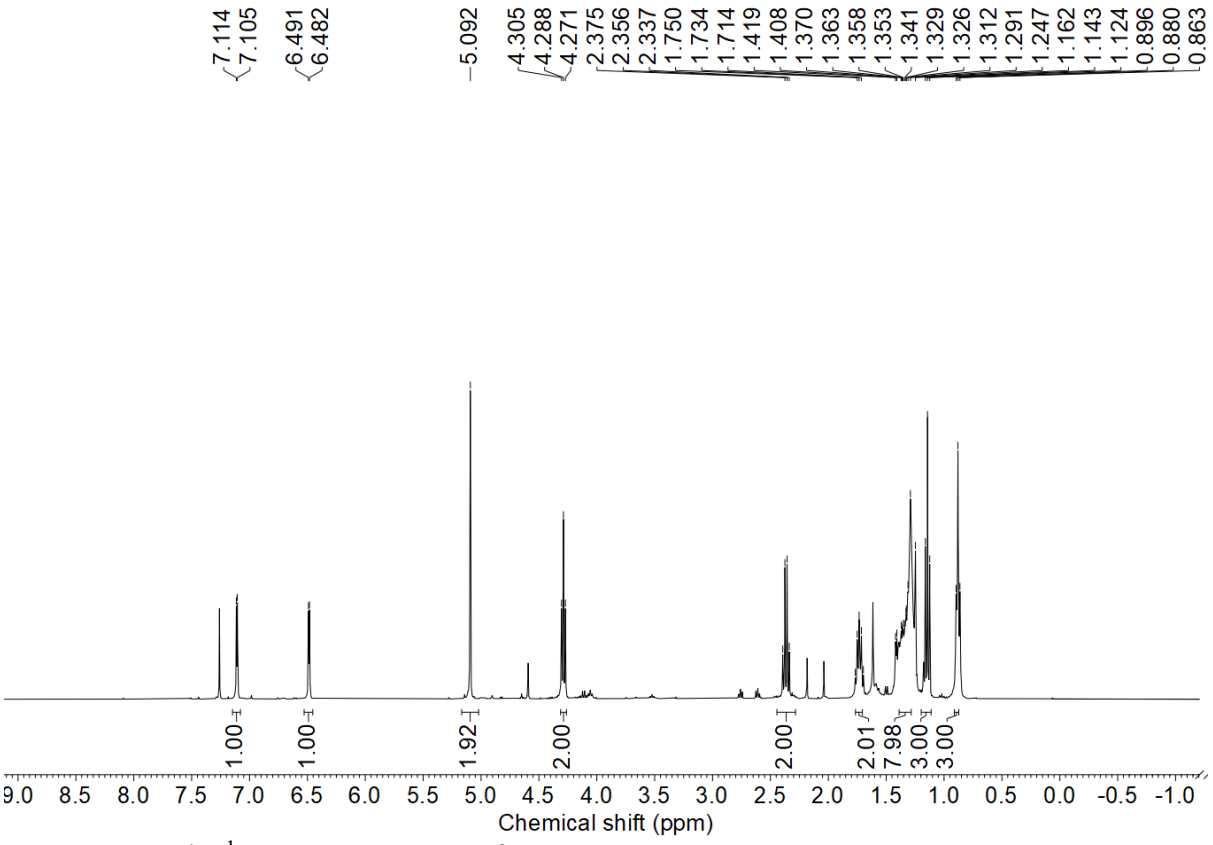


Figure S83. The ^{1}H-NMR spectrum of **6b**.

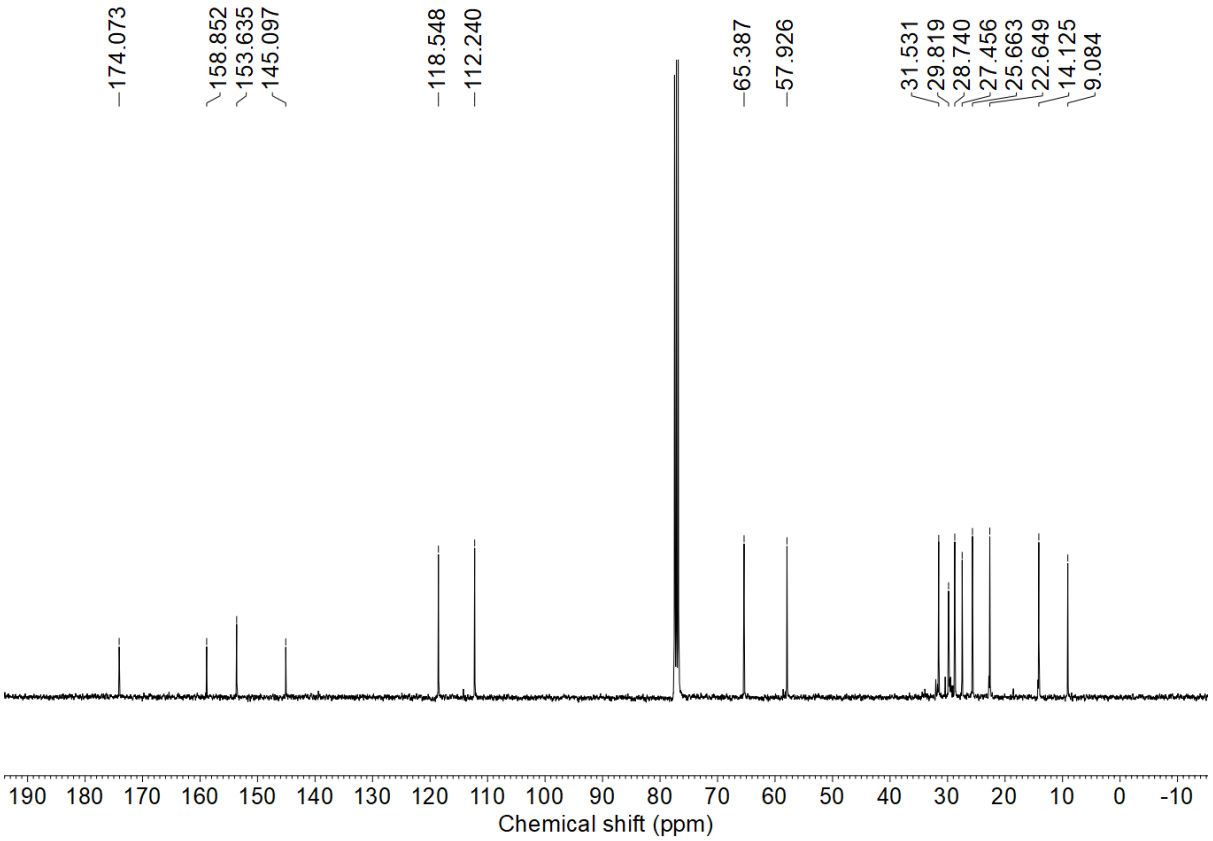


Figure S84. The ^{13}C-NMR spectrum of **6b**.

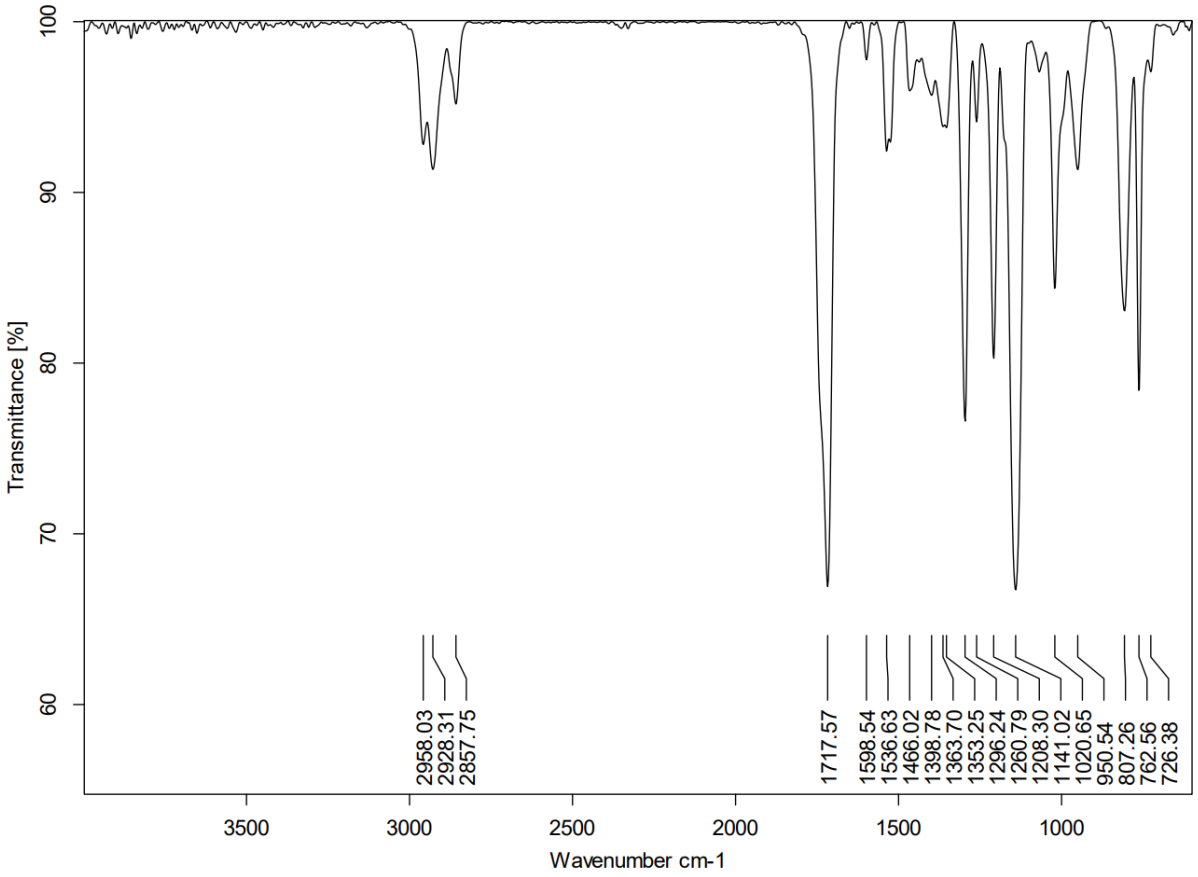


Figure S85. The FTIR spectrum of **6c**.

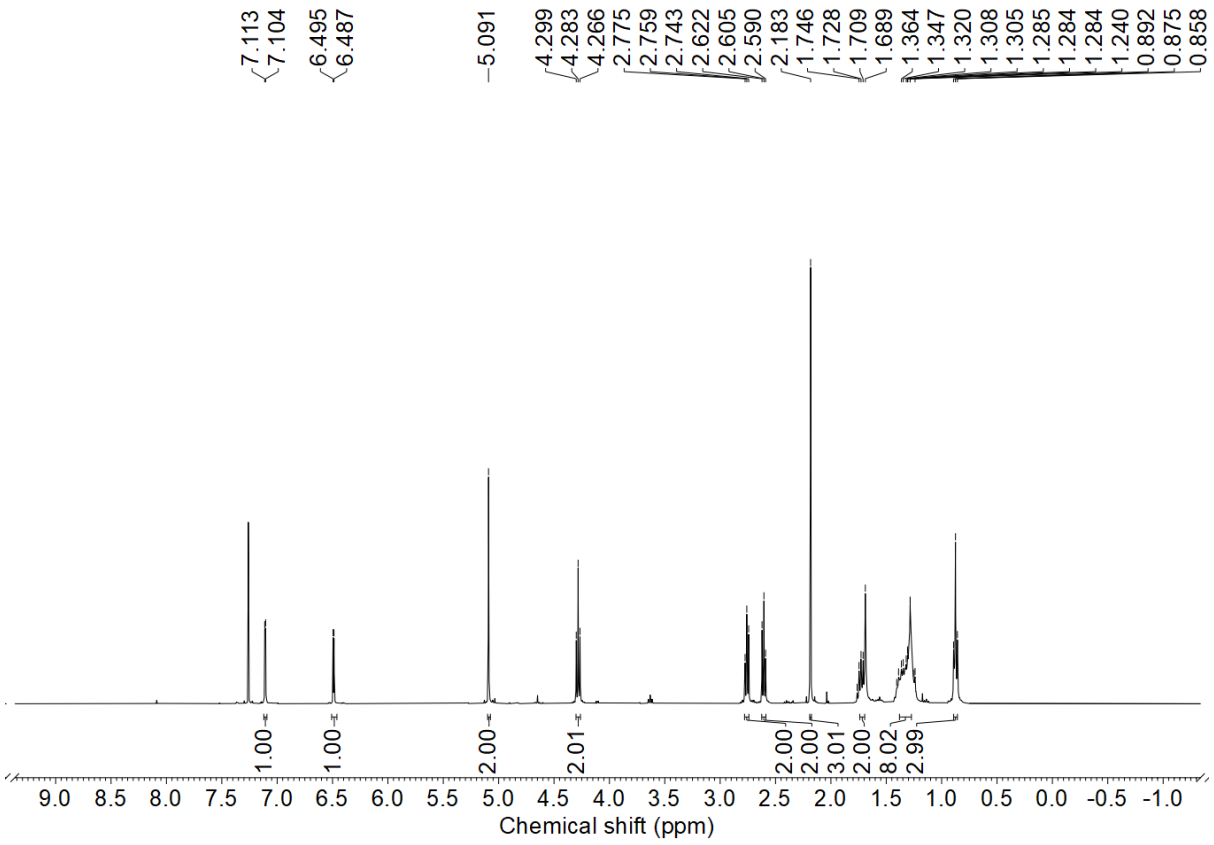


Figure S86. The ^{1}H-NMR spectrum of **6c**.

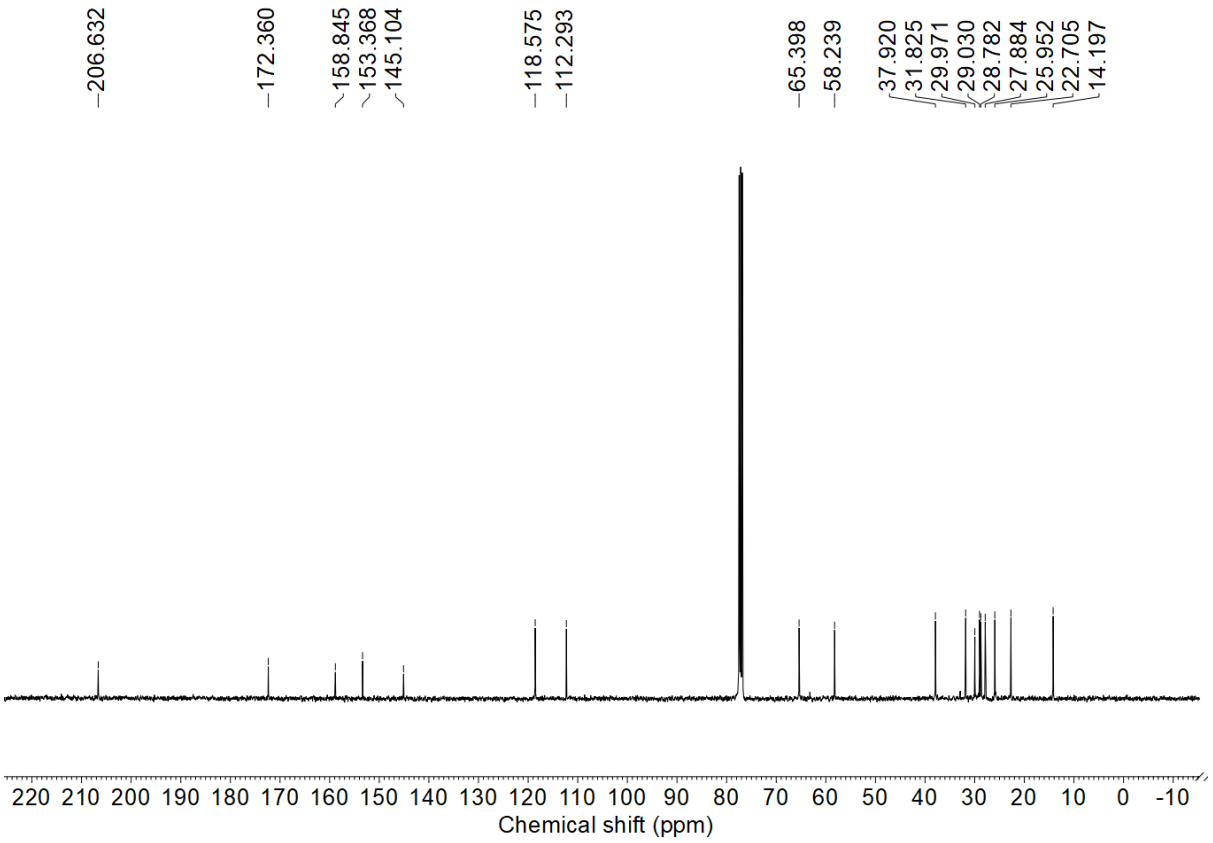


Figure S87. The ^{13}C-NMR spectrum of **6c**.

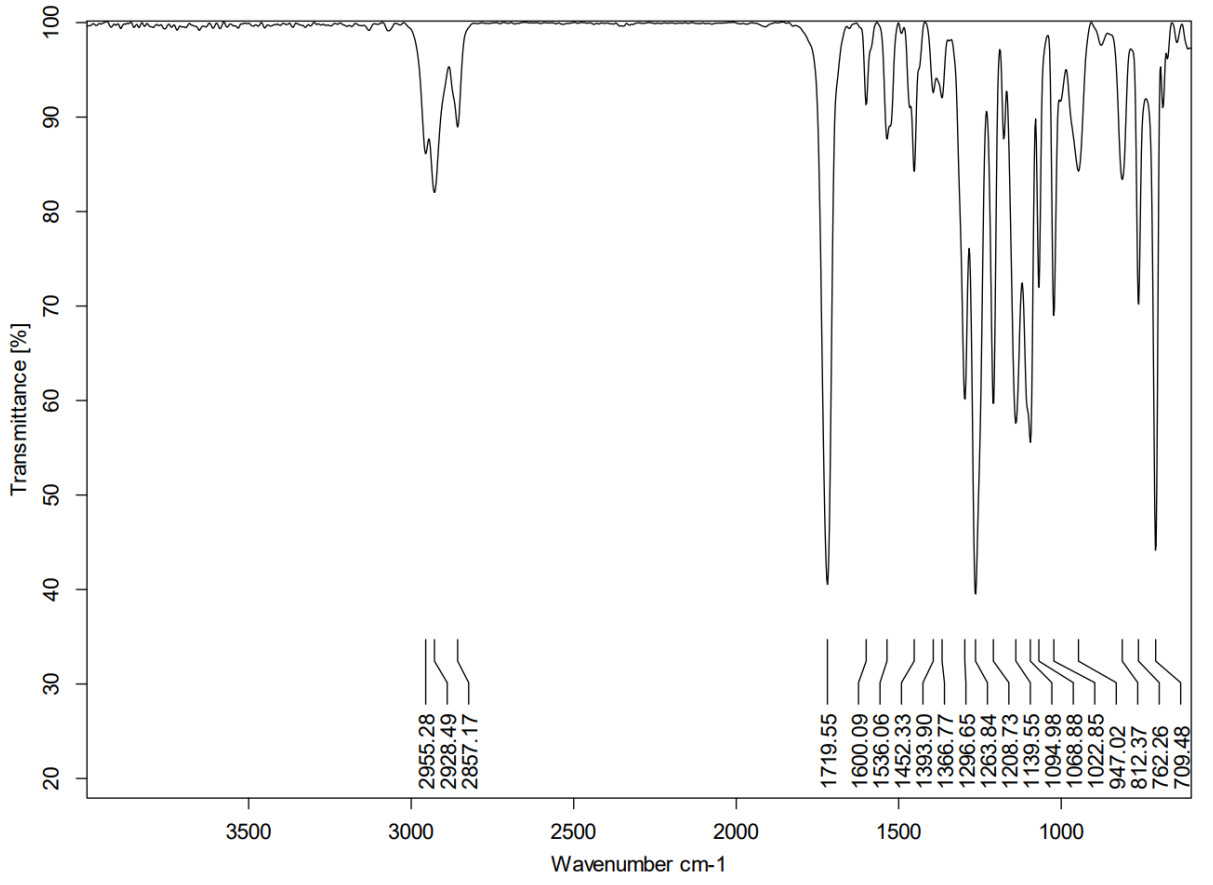


Figure S88. The FTIR spectrum of **6d**.

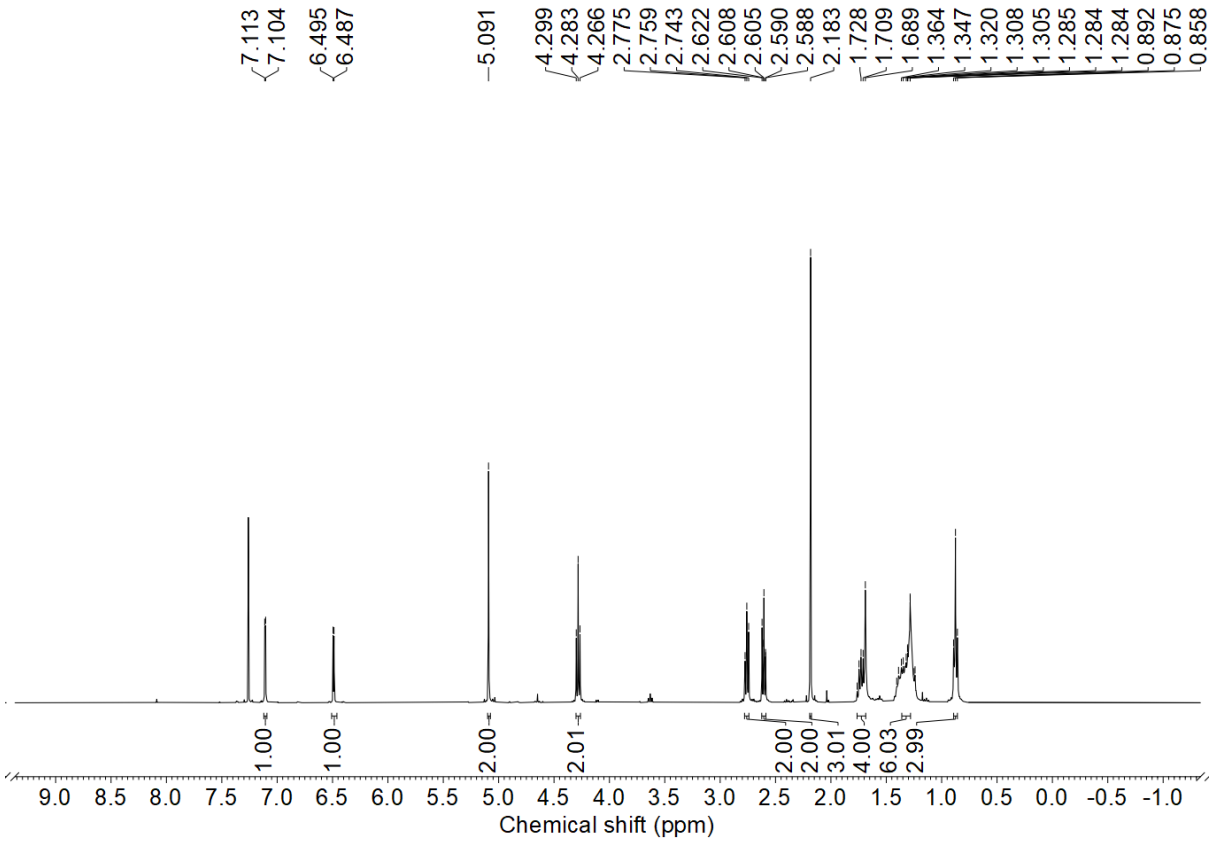


Figure S89. The ^{1}H-NMR spectrum of **6d**.

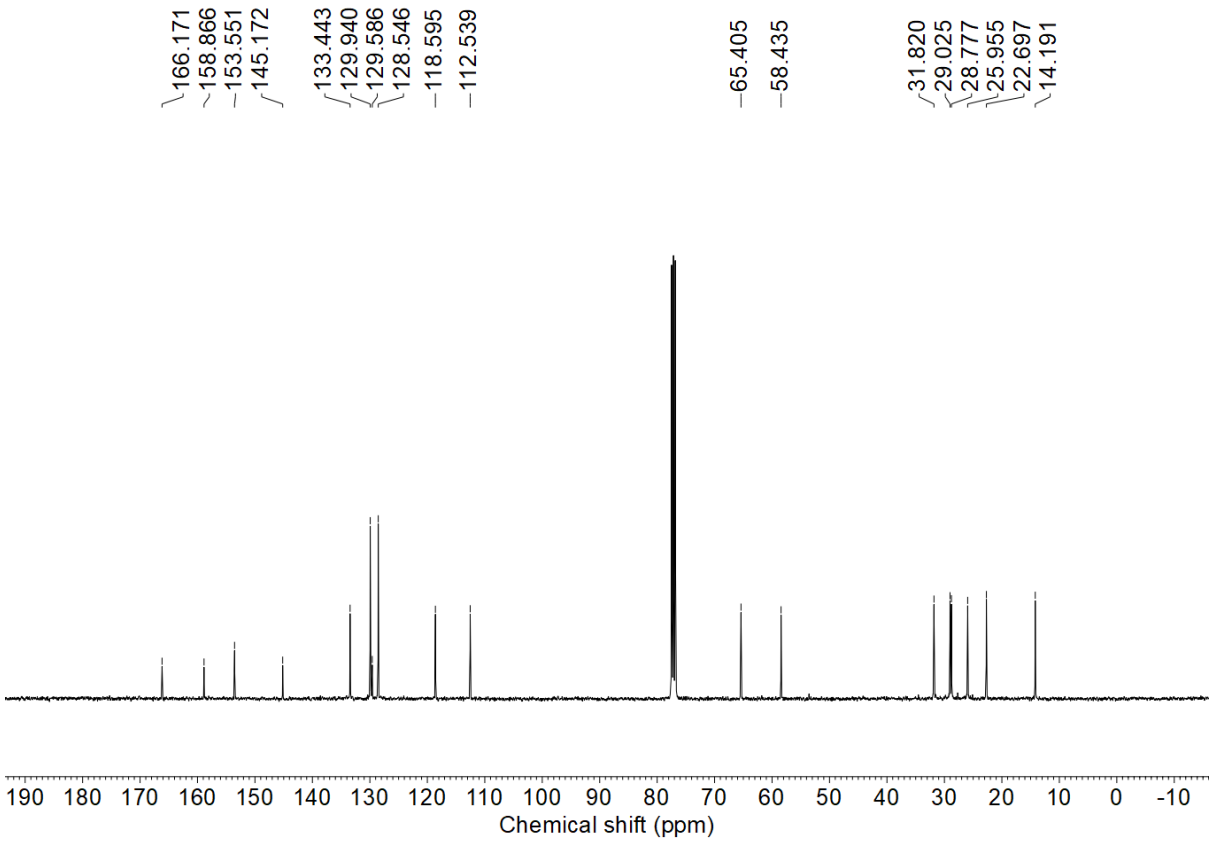


Figure S90. The ^{13}C-NMR spectrum of **6d**.

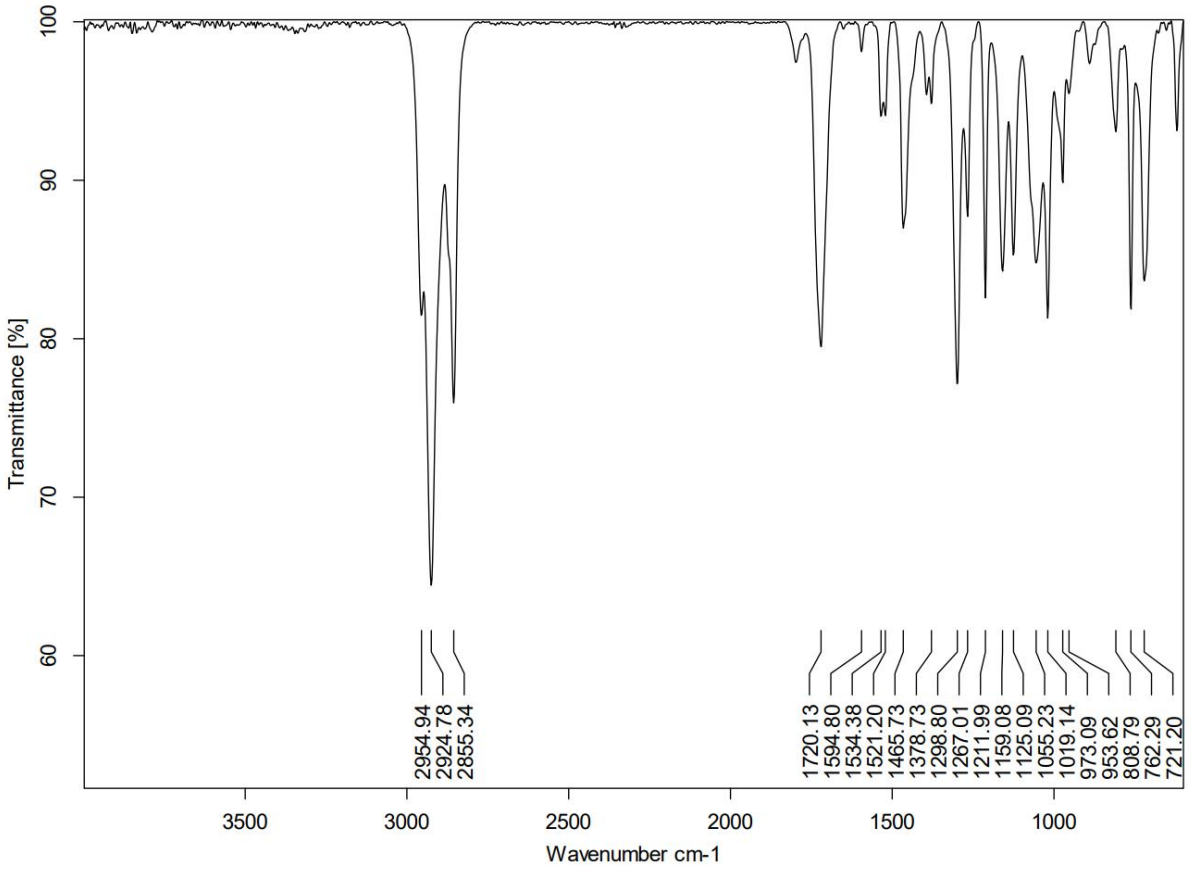


Figure S91. The FTIR spectrum of **7**.

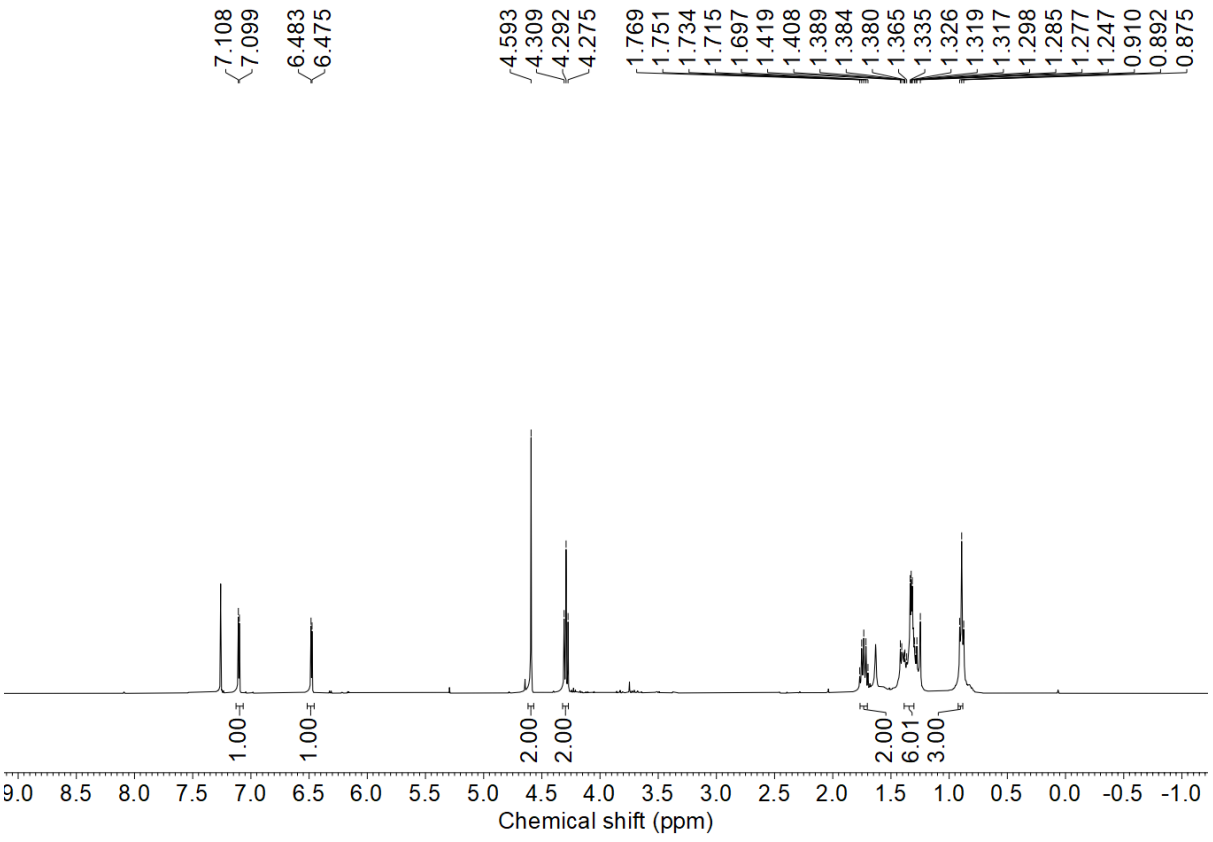


Figure S92. The ^{1}H-NMR spectrum of **7**.

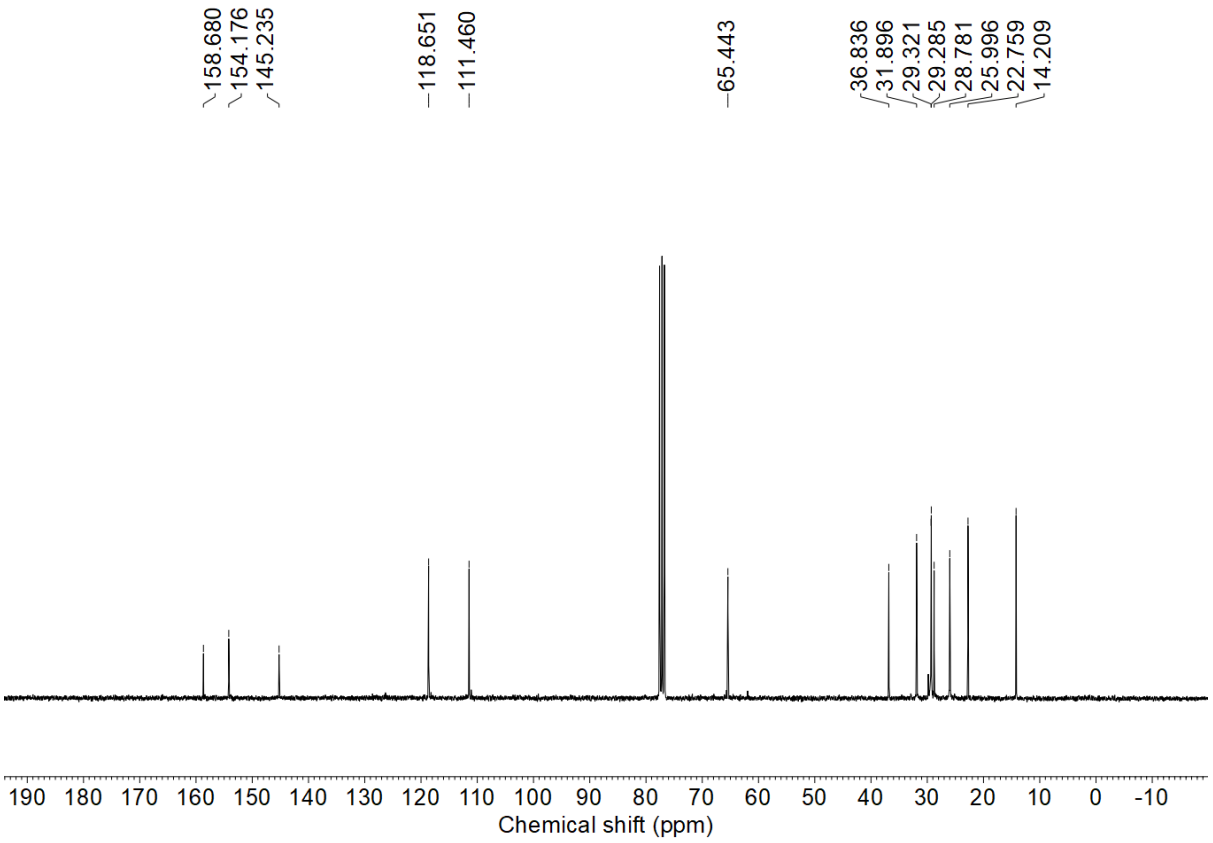


Figure S93. The ^{13}C-NMR spectrum of **7**.

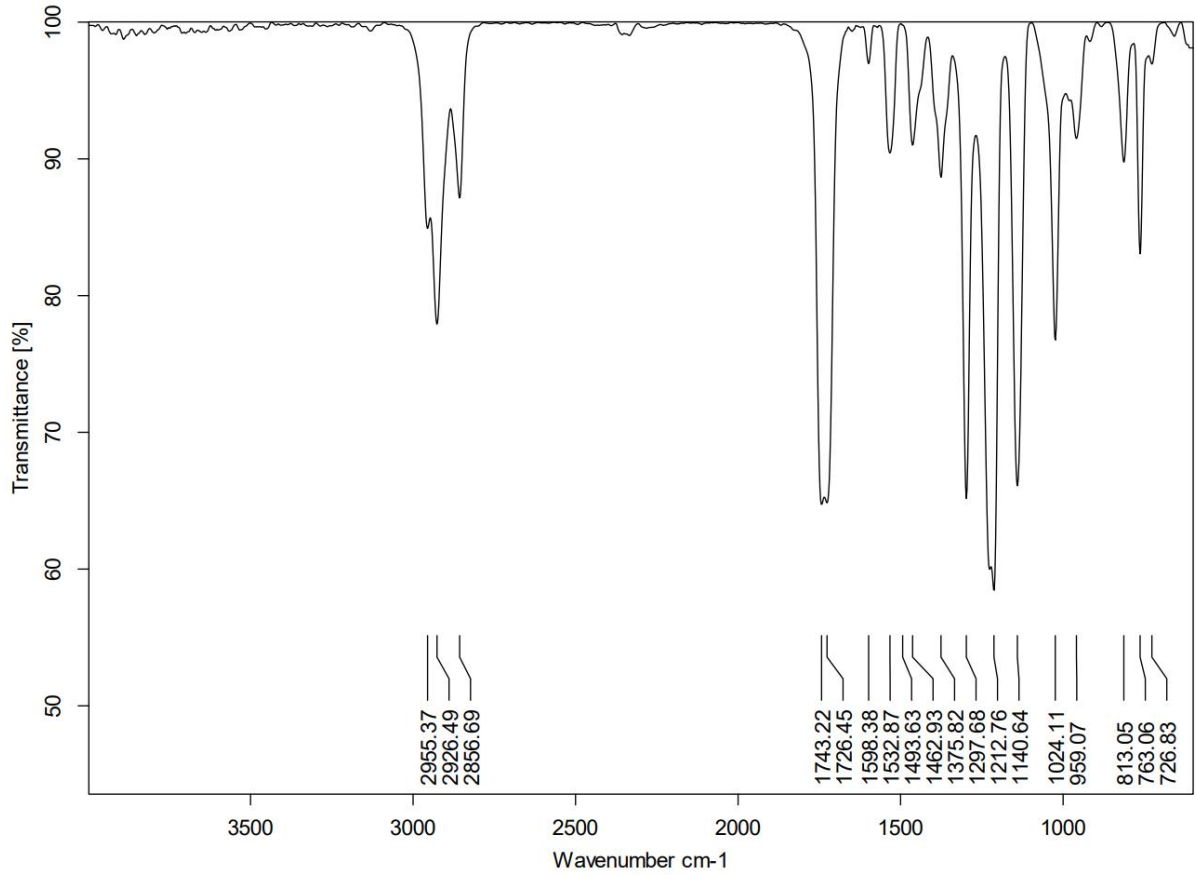


Figure S94. The FTIR spectrum of **7a**.

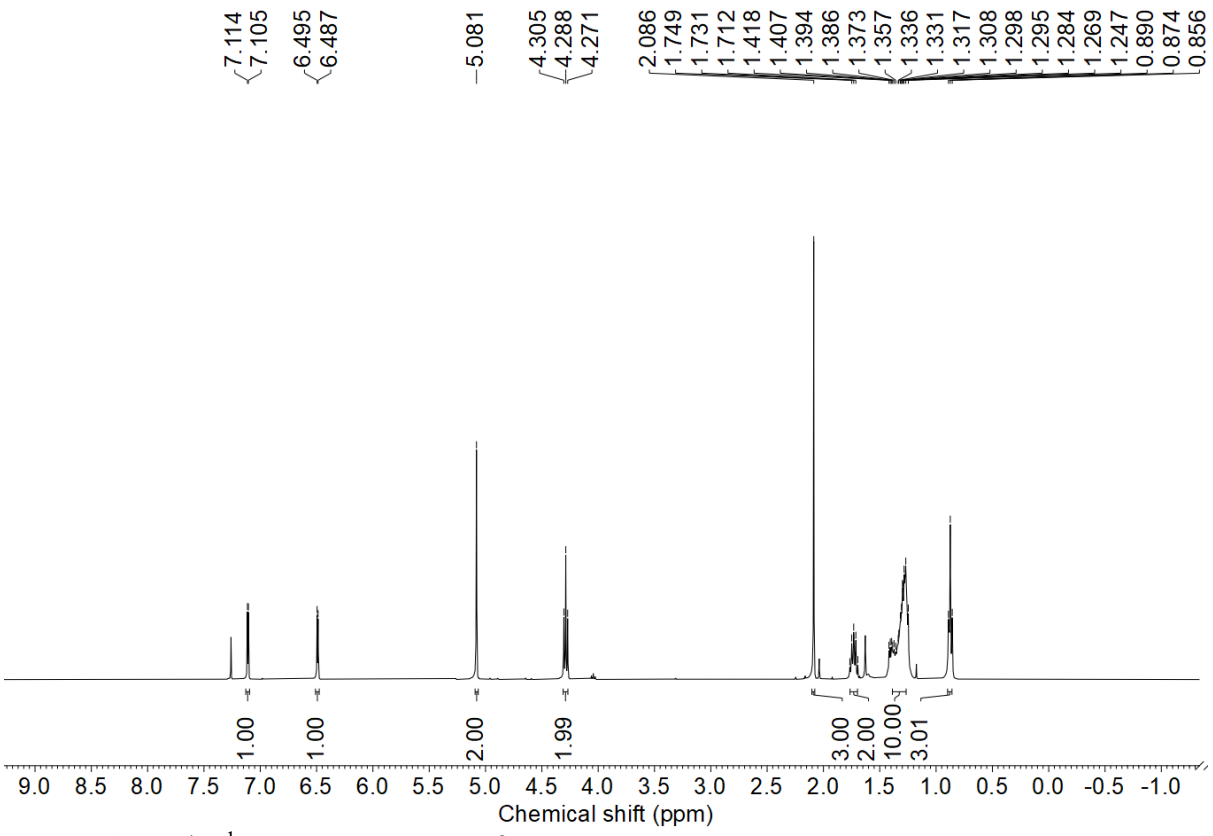


Figure S95. The ^{1}H-NMR spectrum of **7a**.

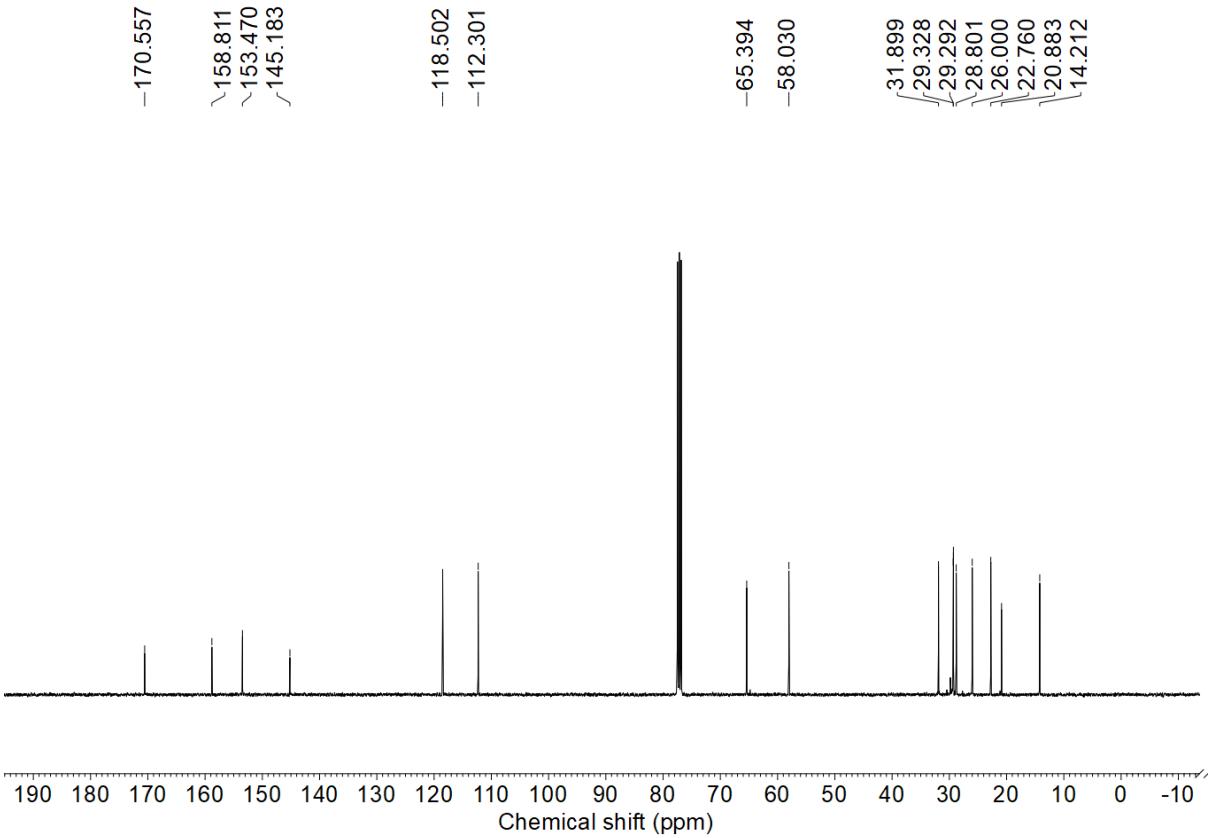


Figure S96. The ^{13}C-NMR spectrum of **7a**.

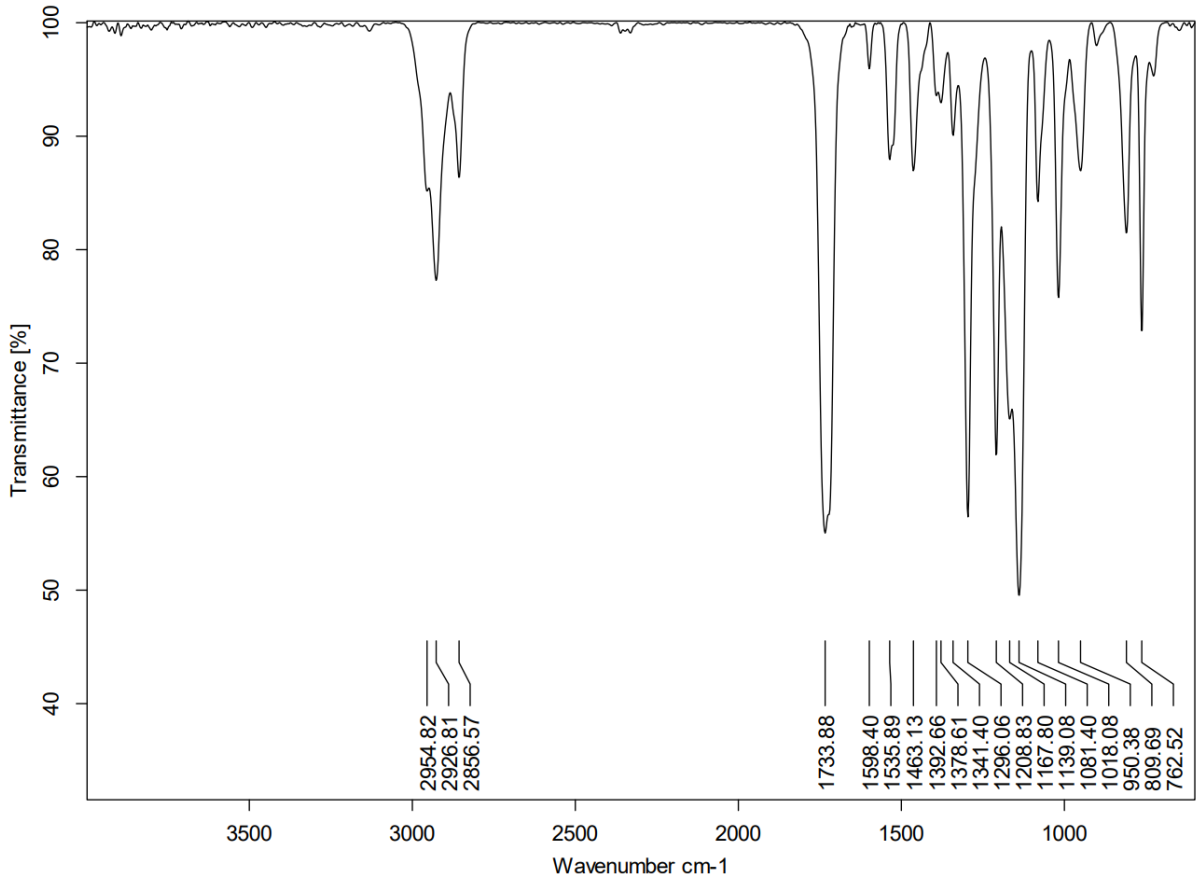


Figure S97. The FTIR spectrum of **7b**.

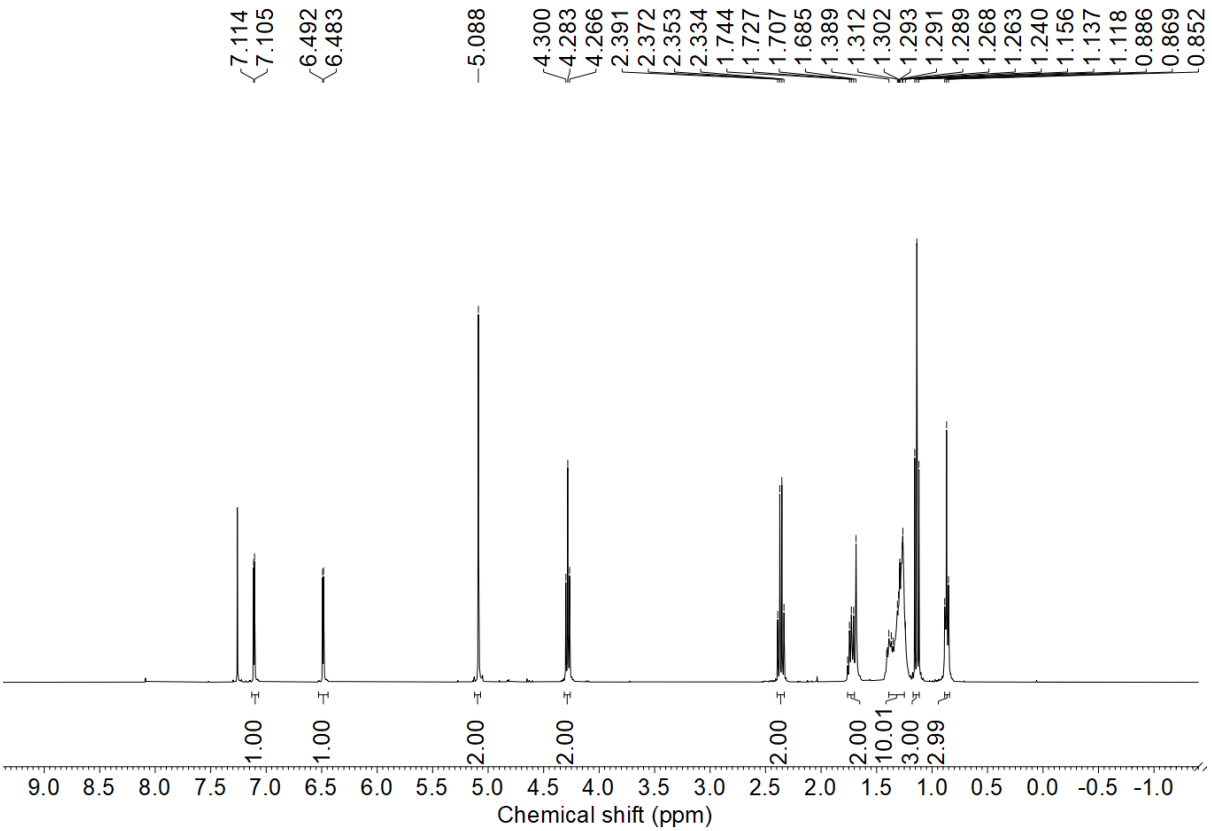


Figure S98. The ^{1}H-NMR spectrum of **7b**.

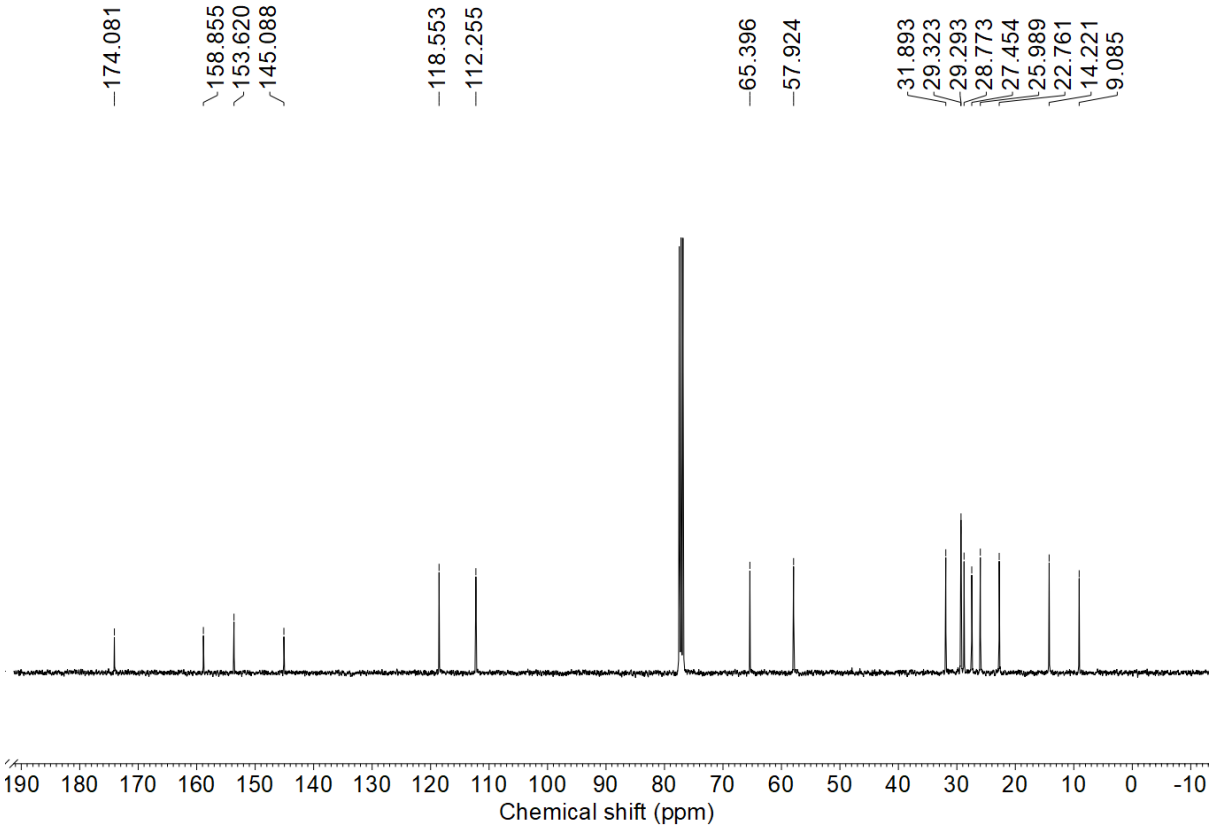


Figure S99. The ^{13}C-NMR spectrum of **7b**.

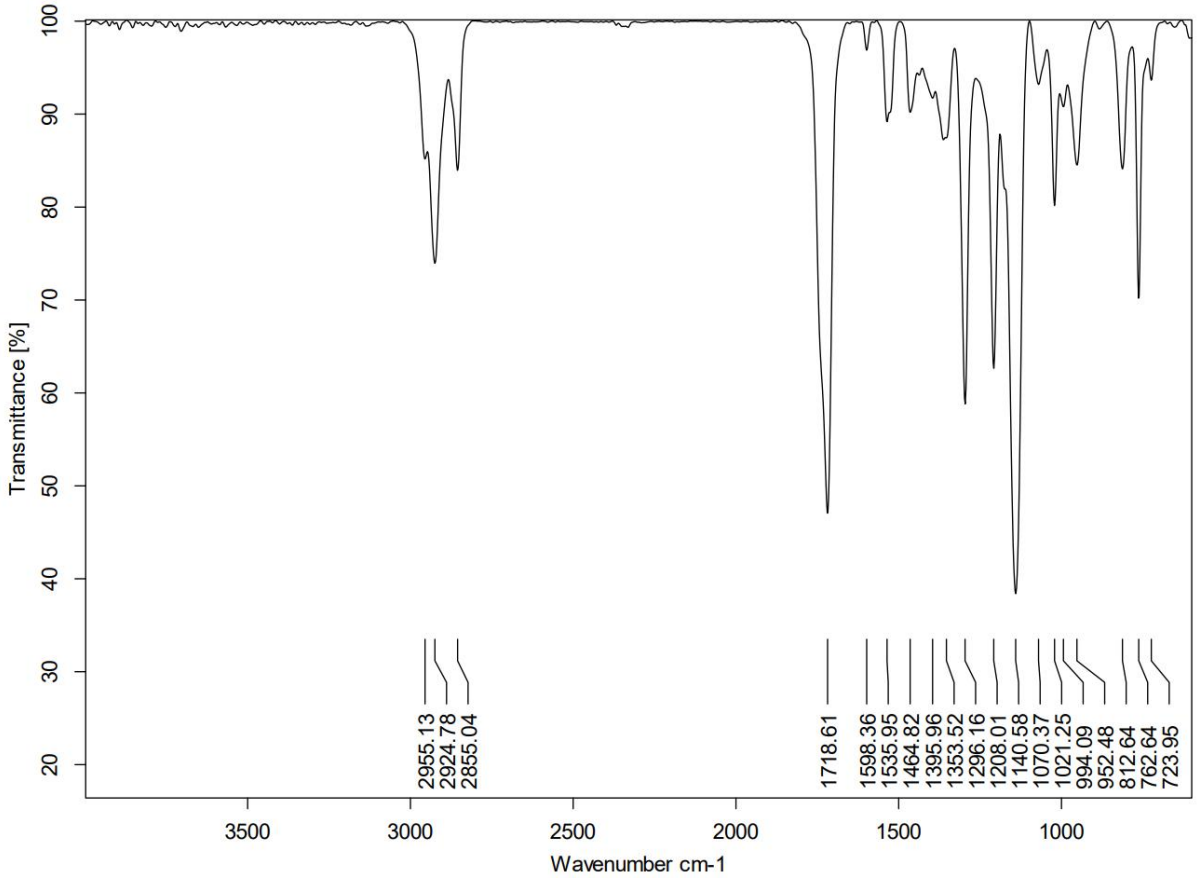


Figure S100. The FTIR spectrum of **7c**.

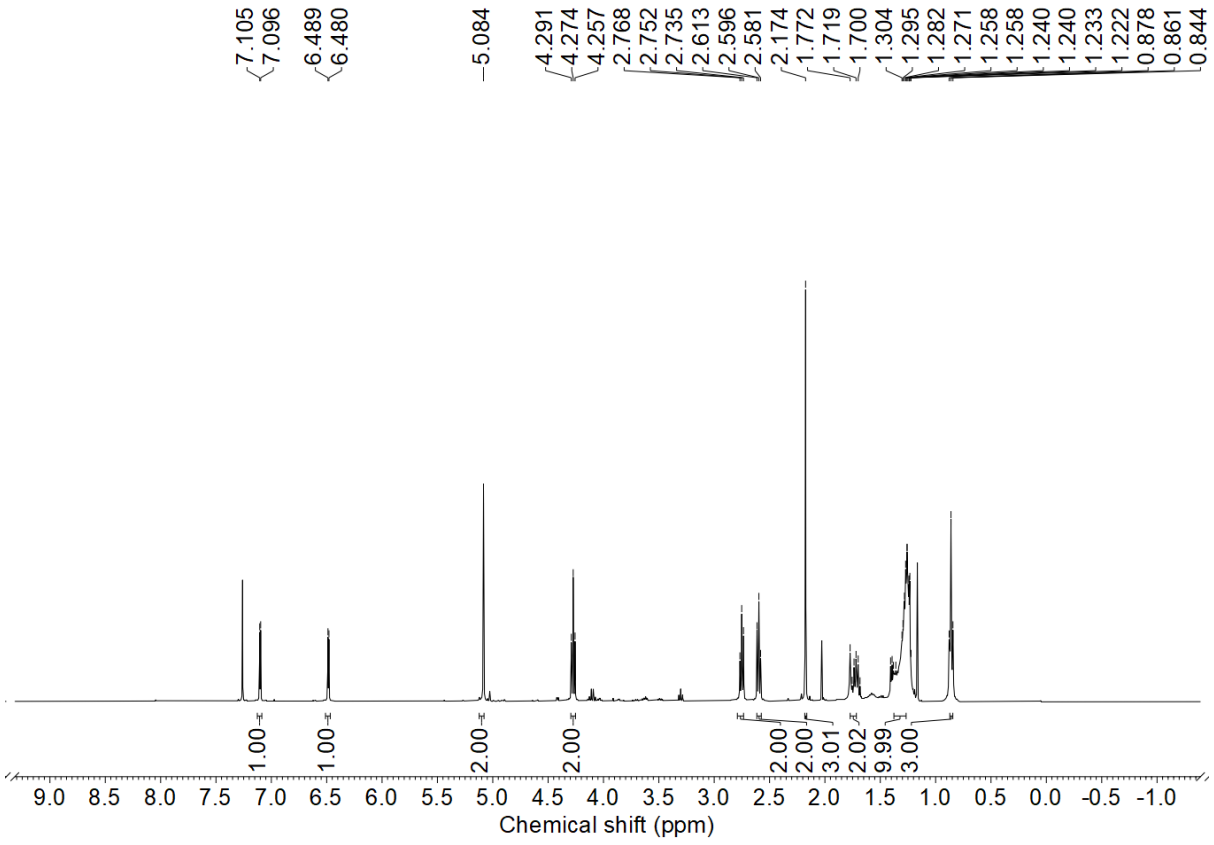


Figure S101. The ^{1}H-NMR spectrum of **7c**.

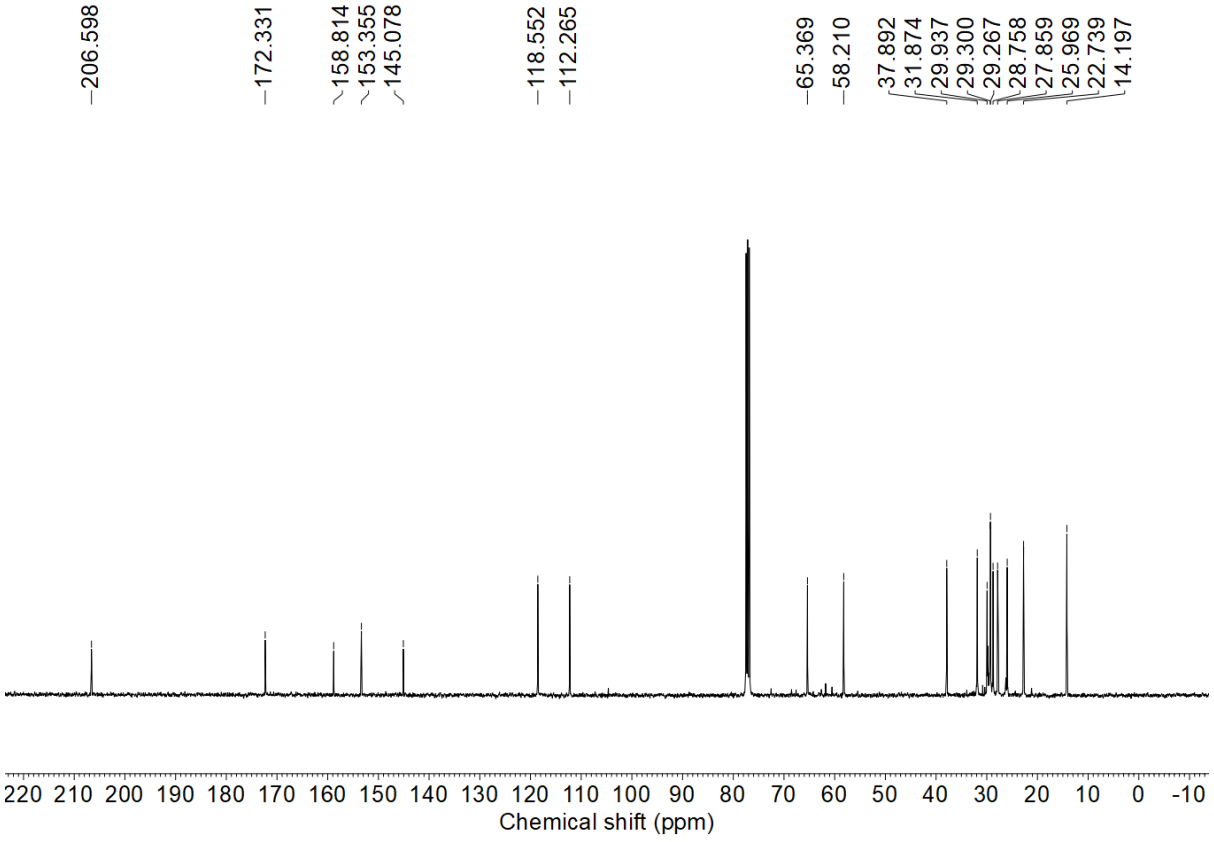


Figure S102. The ^{13}C-NMR spectrum of **7c**.

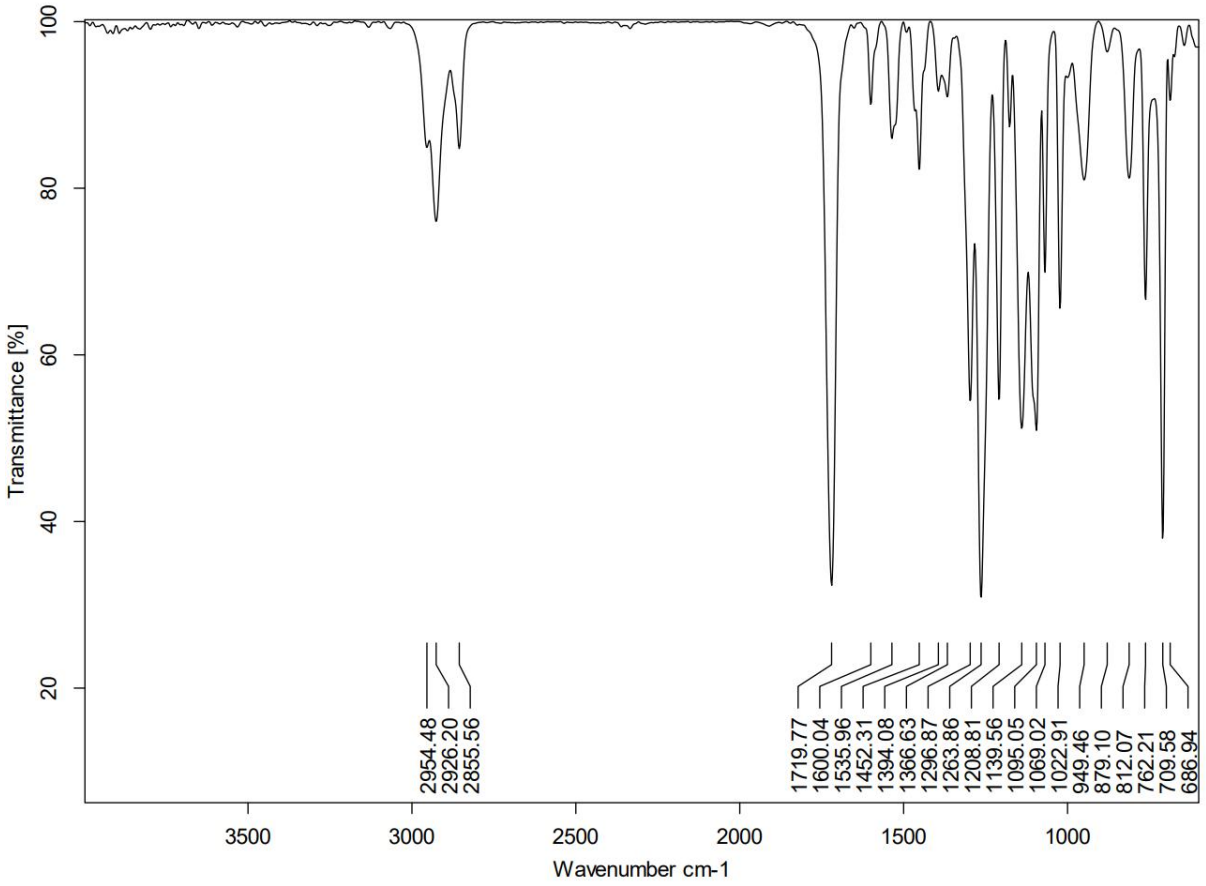


Figure S103. The FTIR spectrum of **7d**.

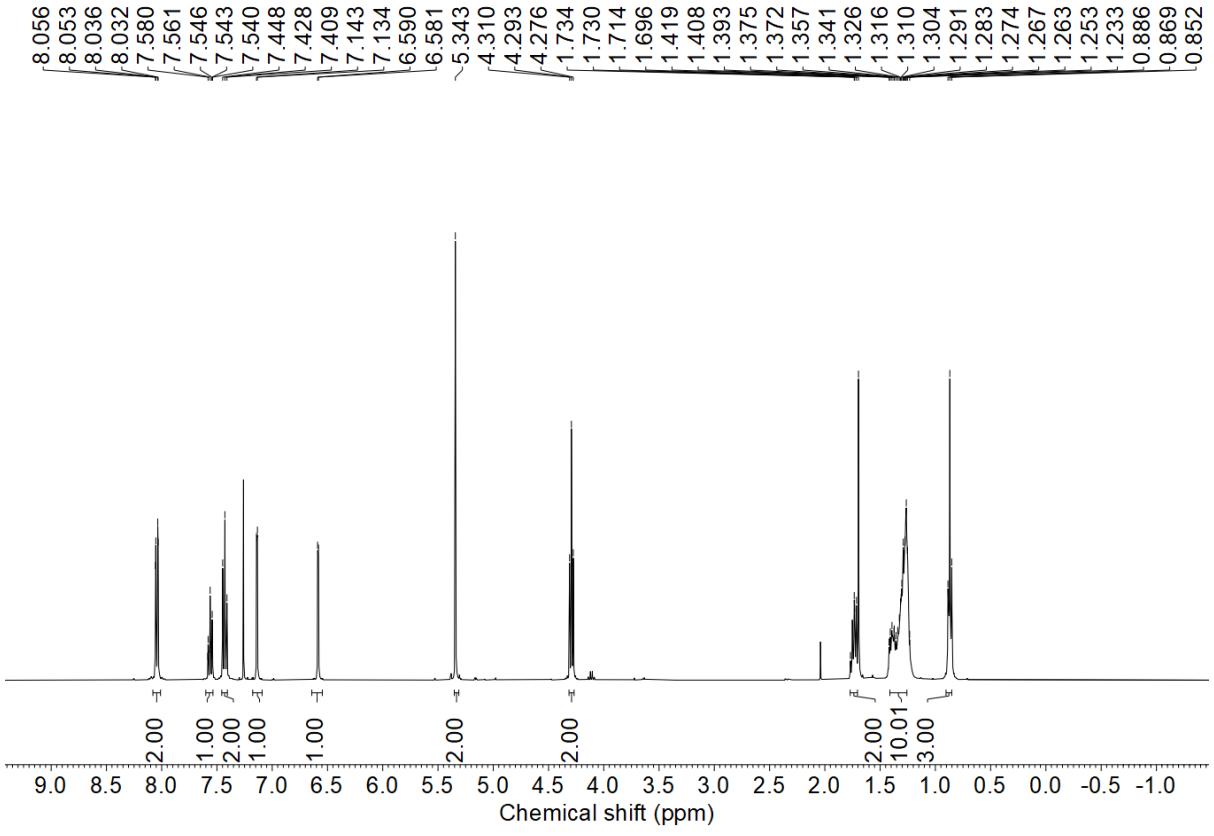


Figure S104. The ^{1}H-NMR spectrum of **7d**.

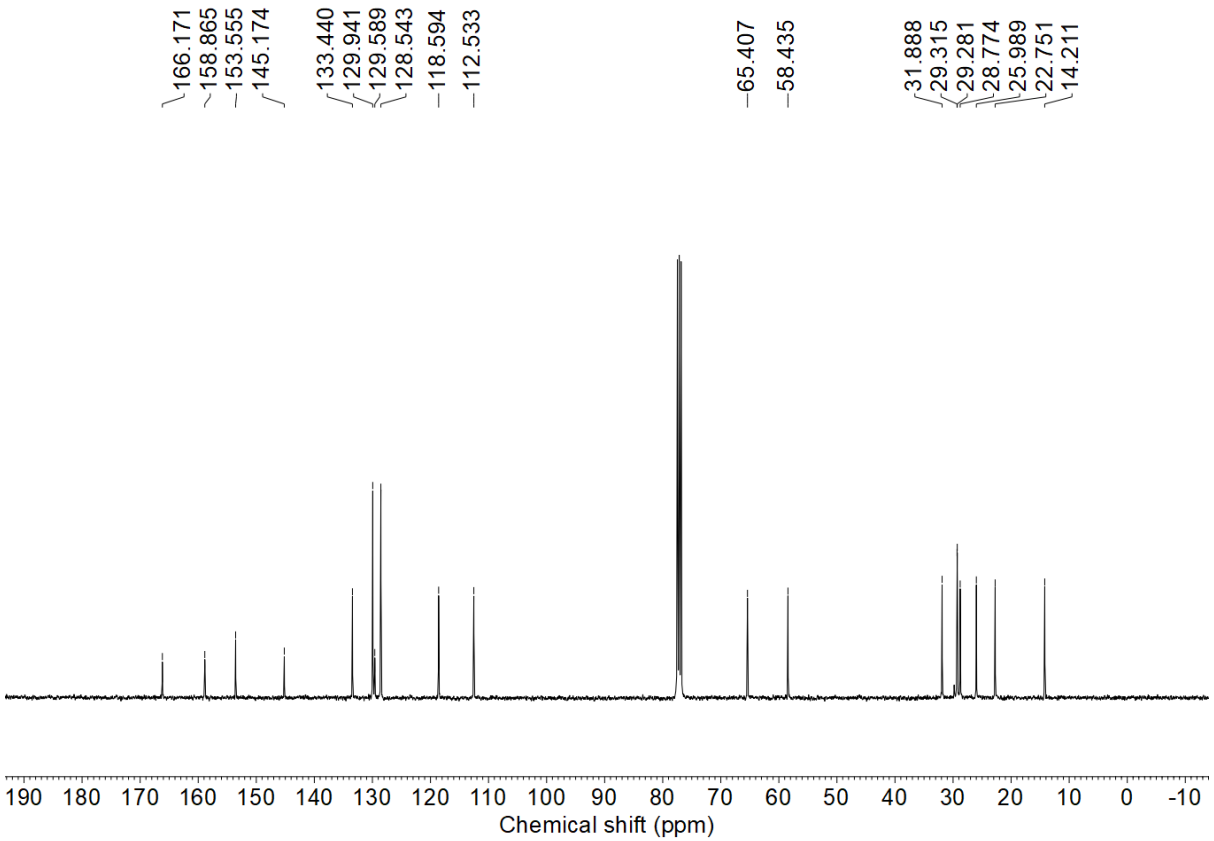


Figure S105. The ^{13}C-NMR spectrum of **7d**.