

Supplementary Information

Aqueous solution of biogenic carboxylic acids as sustainable catalysts and green reaction media for the high-yielding synthesis of Biginelli adducts, Hantzsch esters, and substituted pyridines

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Characterization data of synthesized 3,4-Dihydropyrimidin-2(1H)-ones

Ethyl-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4a**):¹⁻³ Light yellow solid (1.171 g, 96%); Melting Point (°C): 202-204; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.19 (s, 1H), 7.73 (s, 1H), 7.27 (m, 5H), 5.14 (s, 1H), 3.98 (q, 2H, *J* = 7.2 Hz), 2.25 (s, 3H), 1.09 (t, 3H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 165.8, 152.6, 148.8, 145.3, 128.9, 127.7, 126.7, 99.7, 59.6, 54.4, 18.2, 14.5; FTIR (ATR, cm⁻¹): 3244, 3117, 2978, 1727, 1701, 1646.

Ethyl-4-(4-Methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4b**):¹⁻³ Light yellow solid (0.940 g, 88%), Melting Point (°C): 202-204; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.16 (s, 1H), 7.67 (s, 1H), 7.15 (d, 2H, *J* = 8.4 Hz), 6.88 (d, 2H, *J* = 8.4 Hz), 5.10 (s, 1H), 3.98 (q, 2H, *J* = 7.2 Hz), 3.72 (s, 3H), 2.25 (s, 3H), 1.11 (t, 3H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 170.6, 163.7, 157.4, 153.2, 142.3, 132.6, 118.9, 104.8, 64.4, 60.3, 58.6, 23.0, 19.3; FTIR (ATR, cm⁻¹): 3239, 3109, 2930, 1702, 1646.

Ethyl-6-methyl-4(4-nitrophenyl)-2oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4c**):^{2,3} Light yellow solid (0.940 g, 92%), Melting Point (°C): 209-211; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.35 (s, 1H), 8.21 (d, 2H, *J* = 8.8 Hz), 7.89 (s, 1H), 7.50 (d, 2H, *J* = 8.8 Hz), 5.28 (s, 1H), 3.99 (q, 2H, *J* = 7.2 Hz), 1.09 (t, 3H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 170.3, 157.2, 157.0, 154.6, 151.9, 132.9, 129.1, 103.4, 64.6, 58.9, 23.1, 19.3; FTIR (ATR, cm⁻¹): 3254, 3109, 2955, 1699, 1643.

Ethyl-4-(4-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4d**):^{1,2} Light yellow solid (0.780 g, 85%), Melting Point (°C): 196-198; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.30 (s, 1H), 7.82 (s, 1H), 7.43 (d, 2H, *J* = 12.0 Hz), 7.27 (d, 2H, *J* = 12.0 Hz), 5.18 (s, 1H), 4.00 (q, 2H, *J* = 6.8 Hz), 2.27 (s, 3H), 1.09 (t, 3H, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 165.6, 152.5, 149.4, 148.0, 131.2, 130.6, 129.7, 125.7, 122.0, 99.1, 59.8, 54.1, 18.3, 14.5; FTIR (ATR, cm⁻¹): 3235, 3101, 2924, 1699, 1644.

Ethyl-6-methyl-2-oxo-4(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4e**):^{2,3} Light yellow solid (1.050 g, 92%), Melting Point (°C): 212-214; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.14 (s, 1H), 7.68 (s, 1H), 7.11 (s, 4H), 5.10 (s, 1H), 3.98 (q, 2H, *J* = 6.8 Hz), 2.26 (s, 3H), 2.23 (s, 3H), 1.10 (s, 3H, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 165.4, 152.2, 148.1, 142.0, 136.3, 128.9, 126.1, 99.4, 59.1, 53.6, 20.6, 17.7, 14.1; FTIR (ATR, cm⁻¹): 3243, 3113, 2922, 1704, 1647.

Ethyl-4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4f**):^{1,2} Light yellow solid (0.952 g, 85%), Melting Point (°C): 175-177; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.22 (s, 1H), 7.74 (s, 1H), 7.27 (d, 1H, *J* = 5.6 Hz), 7.25 (d, 1H, *J* = 5.6 Hz), 7.16 (d, 1H, *J* = 8.8 Hz), 7.13 (d, 1H, *J* = 8.8 Hz), 5.15 (s, 1H), 3.98 (q, 2H, *J* = 6.8 Hz), 2.25 (s, 3H), 1.09 (t, 3H, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 165.2, 162.5, 160.1, 152.0, 148.5, 128.3, 128.2, 115.2, 115.0, 99.1, 59.2, 53.3, 17.8, 14.1; FTIR (ATR, cm⁻¹): 3238, 3110, 2927, 1695, 1642.

Ethyl-6-methyl-2-oxo-4(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4g**):¹ Light yellow solid (0.767 g, 86%), Melting Point (°C): 216-218; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.18 (s, 1H), 7.70 (s, 1H), 6.53 (s, 2H), 5.12 (s, 1H), 4.02 (q, 2H, *J* = 7.2 Hz), 3.72 (s, 6H), 3.63 (s, 3H), 2.25 (s, 3H), 1.13 (t, 3H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 165.4, 152.7, 152.2, 148.4, 140.5, 136.8, 103.4, 99.0, 60.0, 59.2, 55.8, 53.8, 17.8, 14.2; FTIR (ATR, cm⁻¹): 3229, 3096, 2953, 1704, 1651.

Ethyl-4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4h**):^{1,2} Light yellow solid (0.985 g, 94%), Melting Point (°C): 212-214; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.24 (s, 1H), 7.77 (s, 1H), 7.39 (d, 2H, *J* = 8.0 Hz), 7.25 (d, 2H, *J* = 8.0 Hz), 5.15 (s, 1H), 3.98 (q, 2H, *J* = 7.2 Hz), 2.25 (s, 3H), 1.09 (t, 3H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 165.2, 151.9, 148.7, 143.8, 131.8, 128.4, 128.2, 98.8, 59.2, 53.4, 17.8, 14.1; FTIR (ATR, cm⁻¹): 3339, 2980, 2931, 1724, 1695.

Ethyl-4-(4-ethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4i**):² Light yellow solid (0.930 g, 92%), Melting Point (°C): 187-188; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.14 (s, 1H), 7.66 (s, 1H), 7.13 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.8 Hz), 5.09 (s, 1H), 3.98 (q, 4H, *J* = 6.8 Hz), 2.24 (s, 3H), 1.30 (t, 3H, *J* = 6.8 Hz), 1.10 (t, 3H, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 165.4, 157.7, 152.1, 148.0, 136.9, 127.4, 114.1, 99.6, 62.9, 59.1, 53.3, 17.7, 14.6, 14.1; FTIR (ATR, cm⁻¹): 3237, 3108, 2978, 1702, 1646.

Ethyl-4-([1,1'-biphenyl]-4-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4j**):³ Light yellow solid (0.785 g, 85%), Melting Point (°C): 232-235; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 9.23 (s, 1H), 7.78 (s, 1H), 7.64 (d, 2H, *J* = 7.2 Hz), 7.62 (d, 2H, *J* = 8.2 Hz), 7.46 (d, 1H, *J* = 7.2 Hz), 7.44 (d, 1H, *J* = 7.2 Hz), 7.35 (t, 1H, *J* = 8.2 Hz), 7.33 (d, 2H, *J* = 8.2 Hz), 5.20 (s, 1H), 4.01 (q, 2H, *J* = 6.8 Hz), 2.27 (s, 3H), 1.30 (t, 3H, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 165.3, 152.2, 148.5, 144.0, 139.7, 139.2, 128.9, 127.4,

126.8, 126.8, 126.6, 99.2, 59.2, 53.6, 17.8, 14.1; FTIR (ATR, cm^{-1}): 3246, 3117, 2954, 1701, 1646.

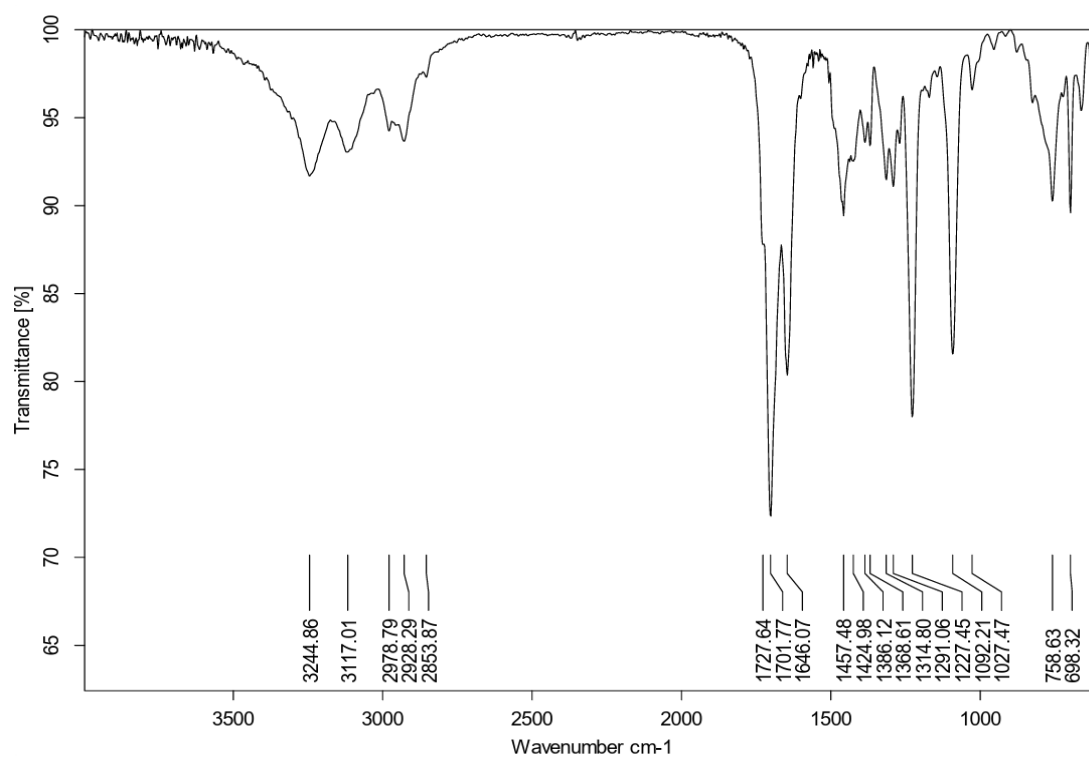


Figure S1. The FTIR spectrum of **4a**.

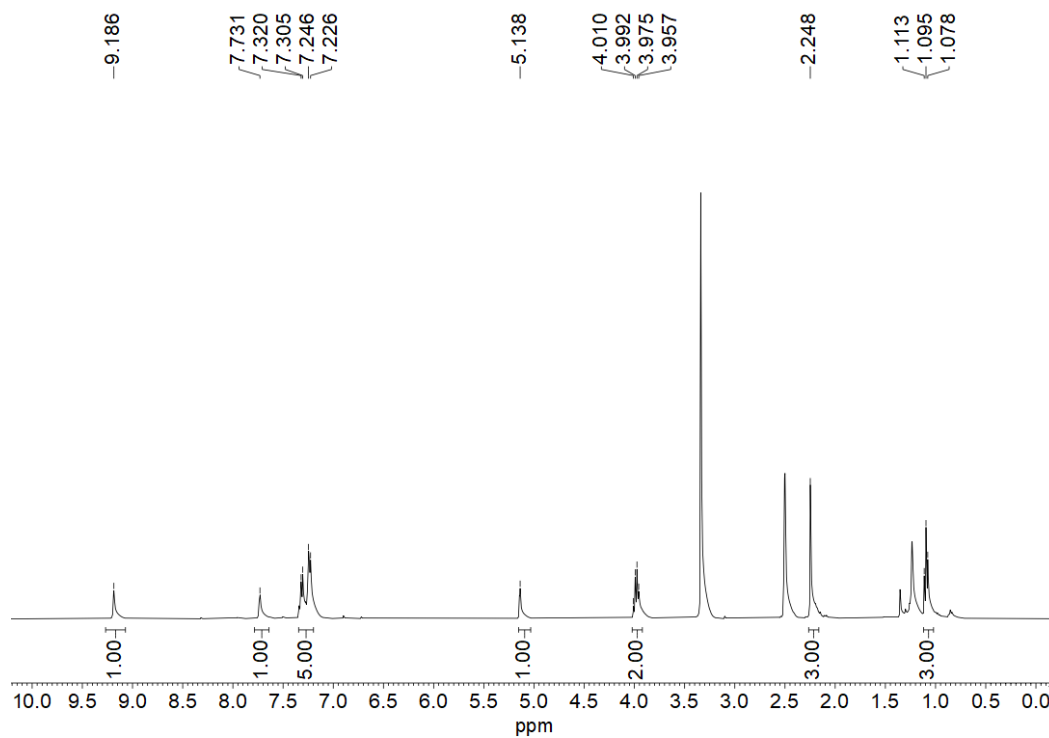


Figure S2. The $^1\text{H-NMR}$ spectrum of **4a**.

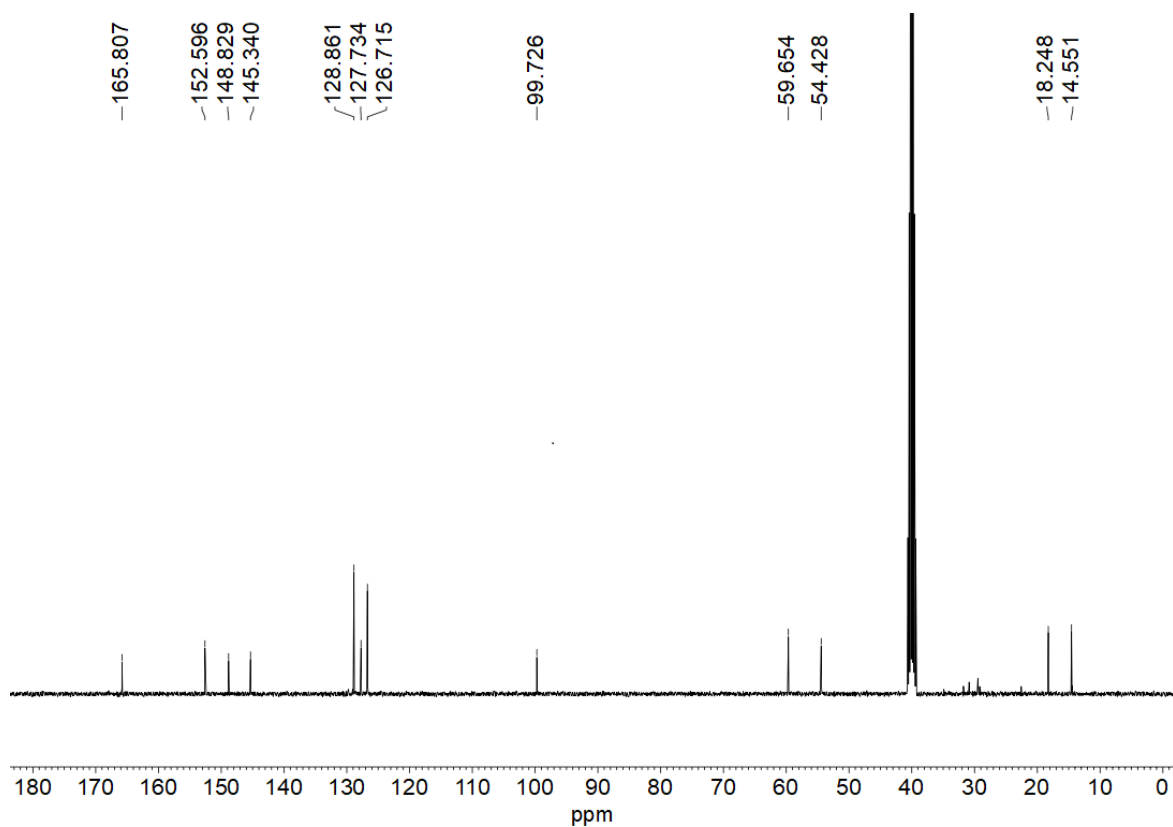


Figure S3. The ^{13}C -NMR spectrum of **4a**.

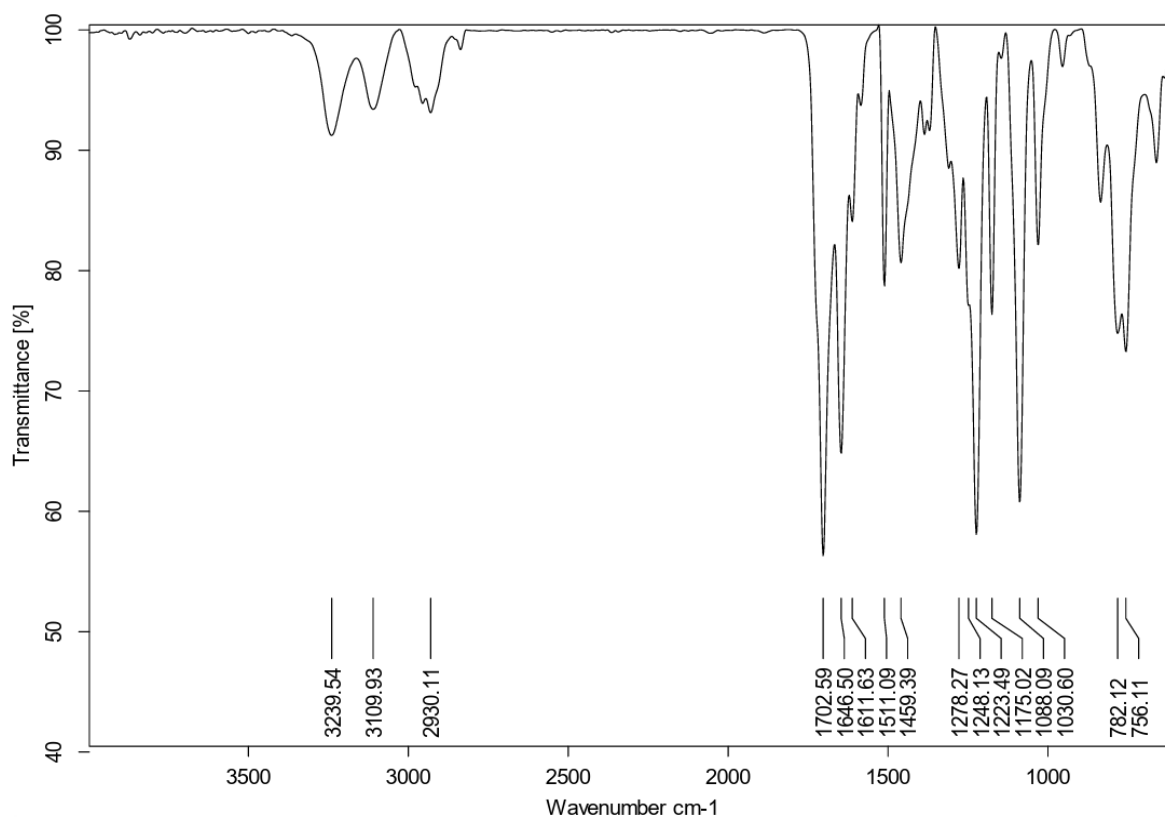


Figure S4. The FTIR spectrum of **4b**.

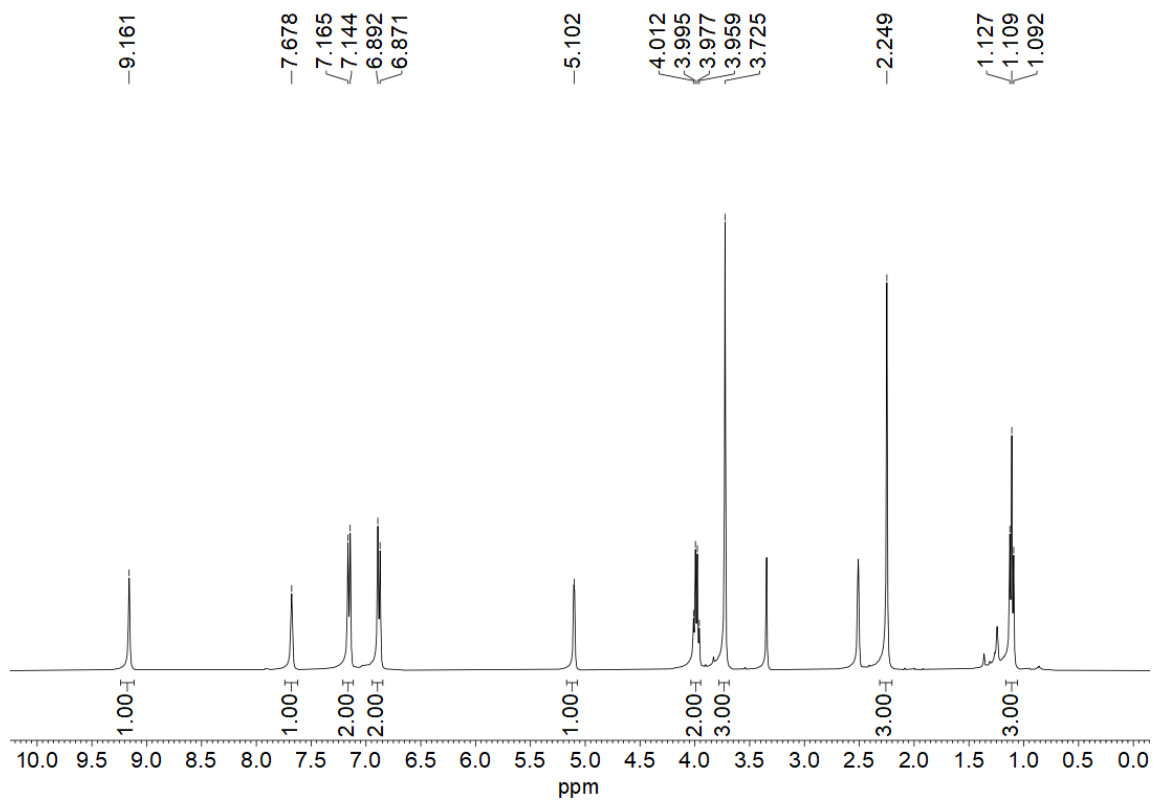


Figure S5. The ^1H -NMR spectrum of **4b**.

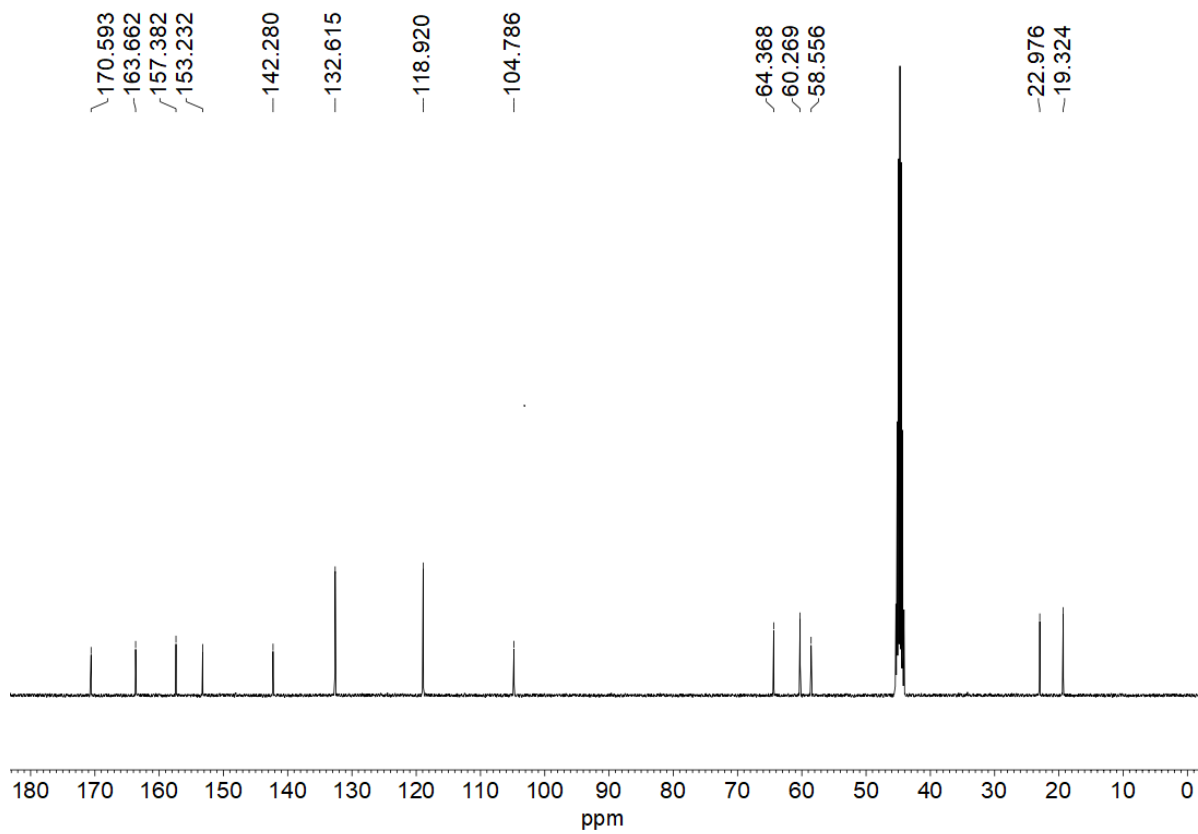


Figure S6. The ^{13}C -NMR spectrum of **4b**.

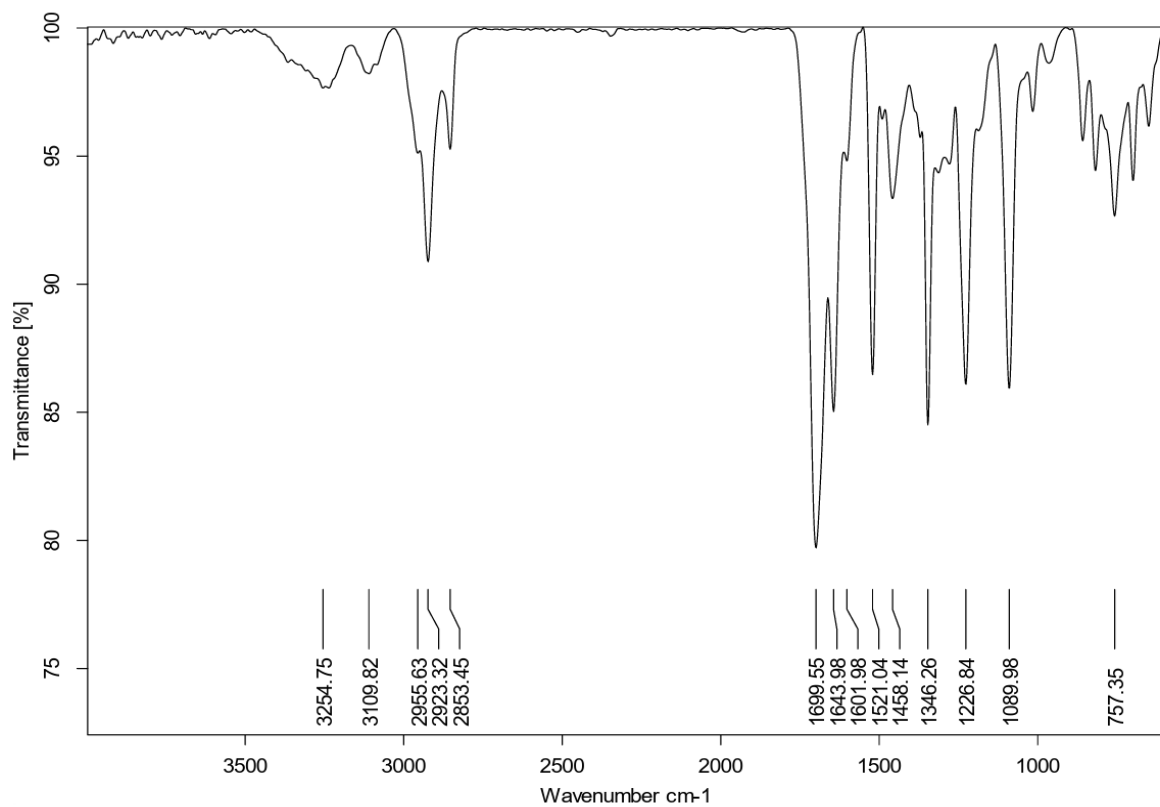


Figure S7. The FTIR spectrum of **4c**.

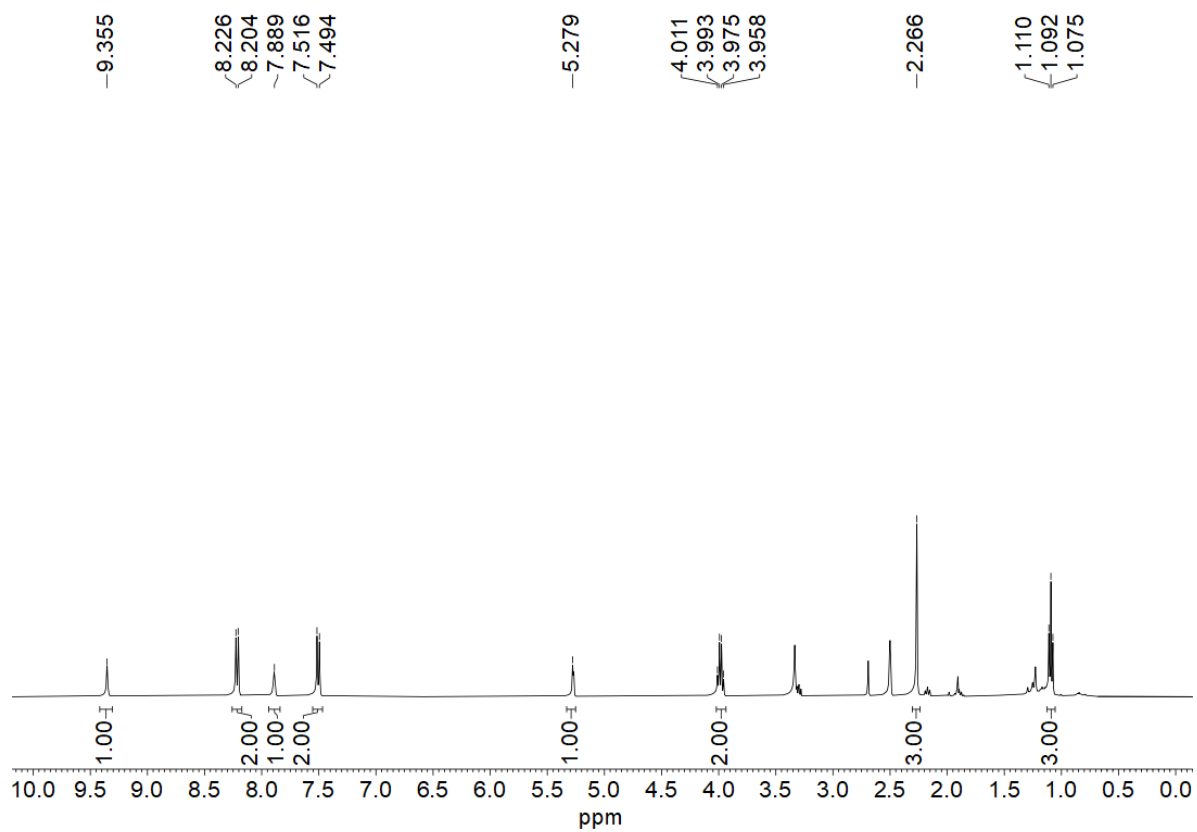


Figure S8. The $^1\text{H-NMR}$ spectrum of **4c**.

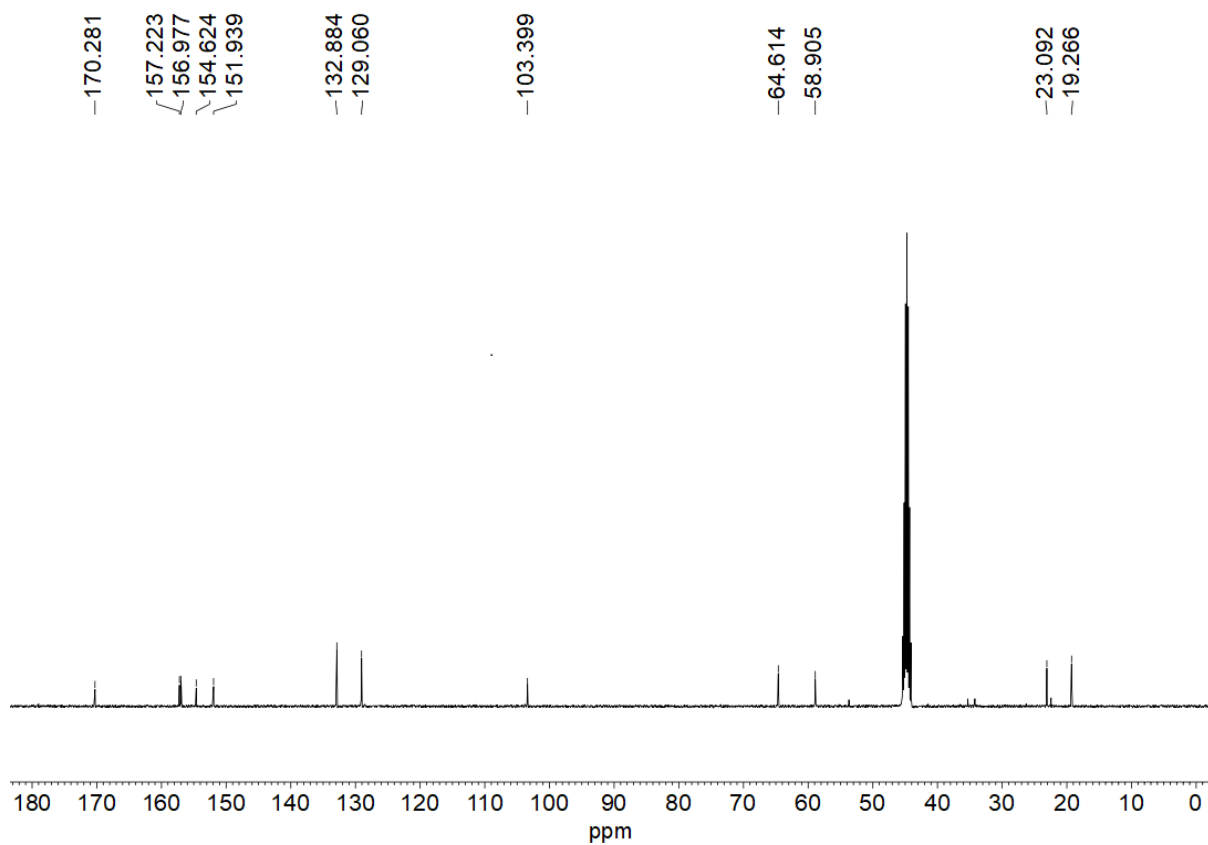


Figure S9. The ^{13}C -NMR spectrum of **4c**.

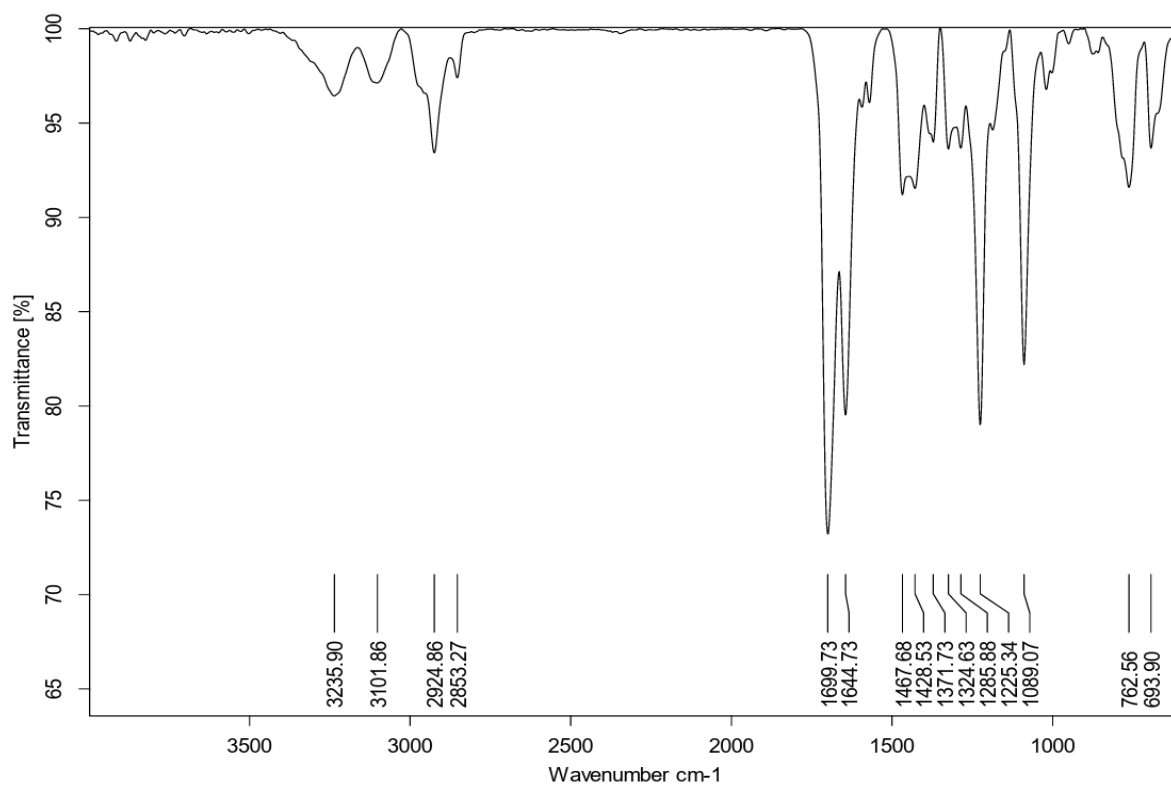


Figure S10. The FTIR spectrum of **4d**.

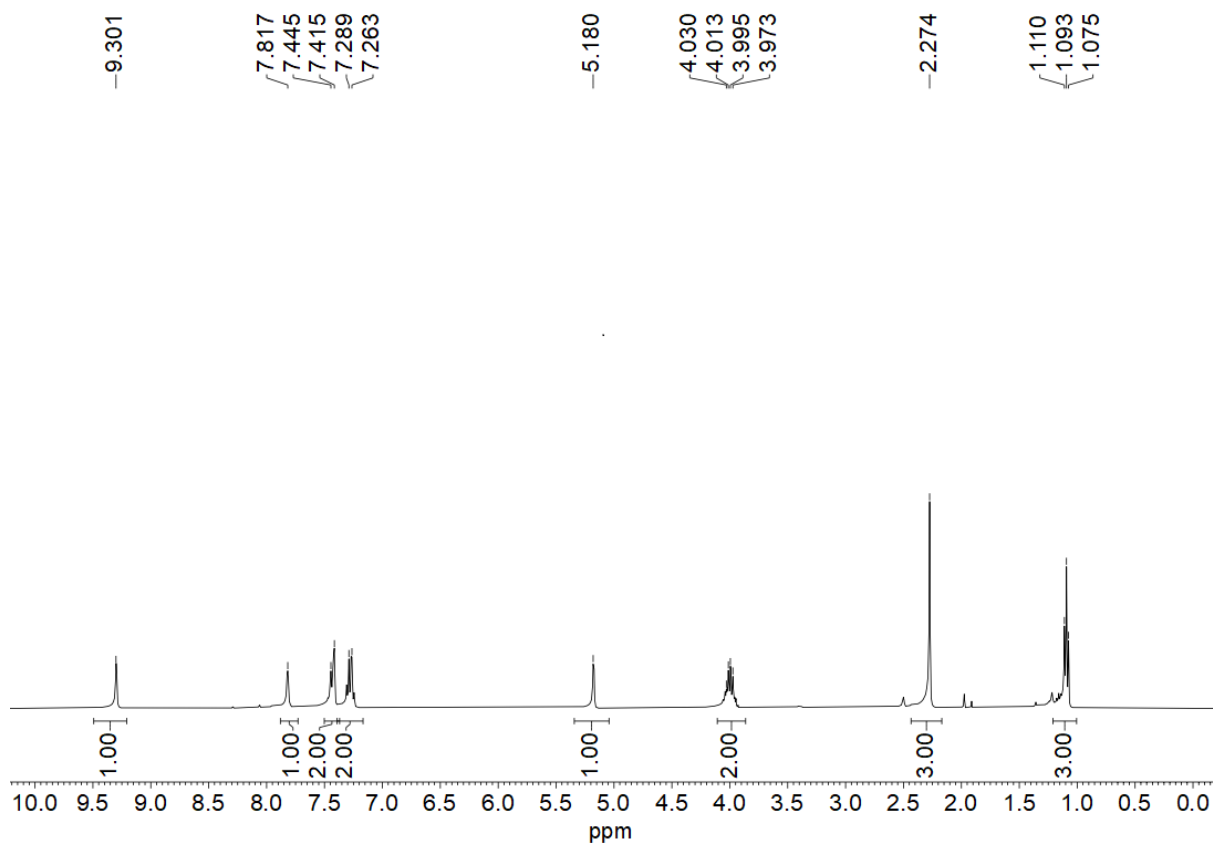


Figure S11. The ^1H -NMR spectrum of **4d**.

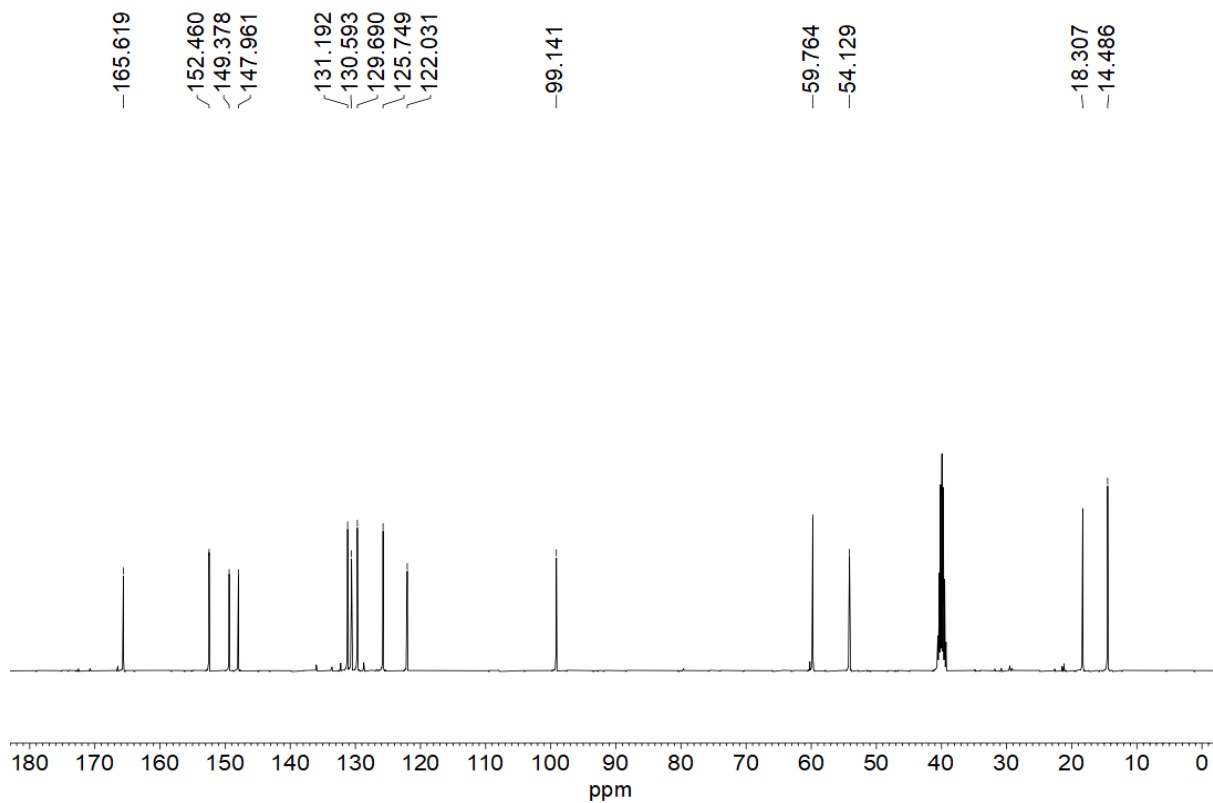


Figure S12. The ^{13}C -NMR spectrum of **4d**.

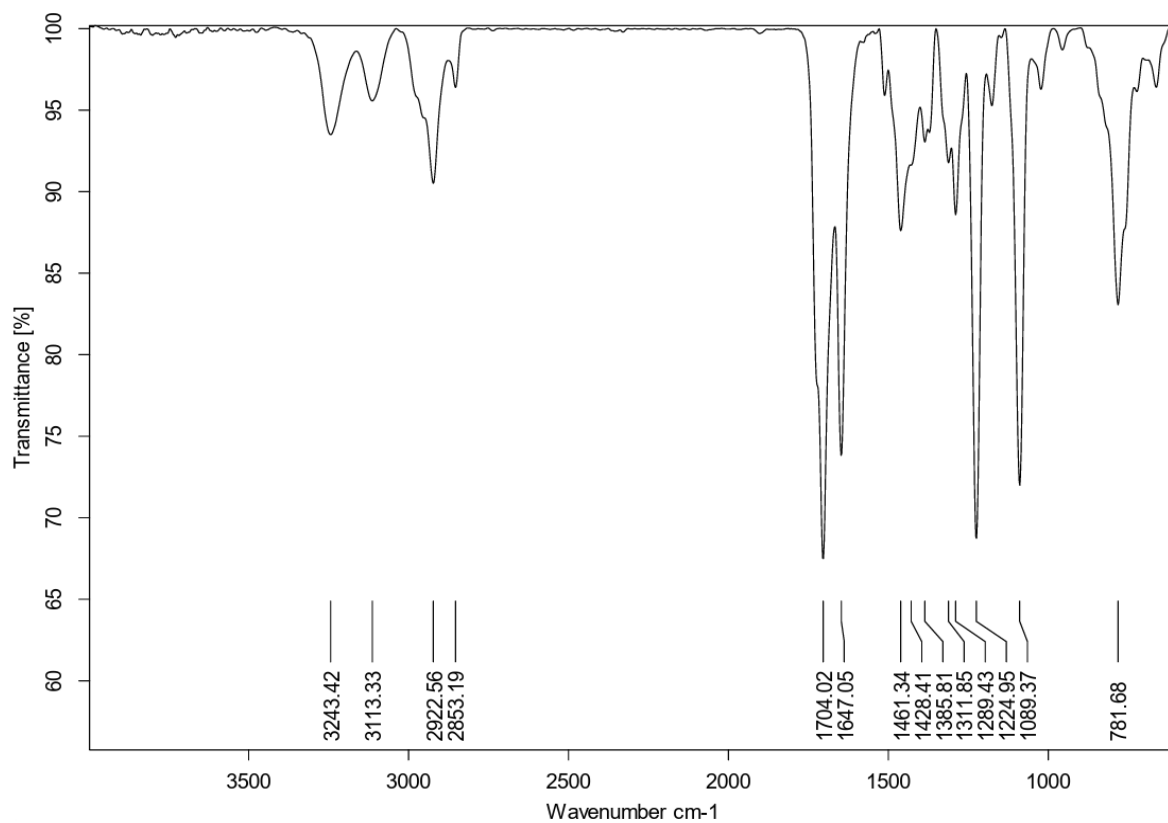


Figure S13. The FTIR spectrum of **4e**.

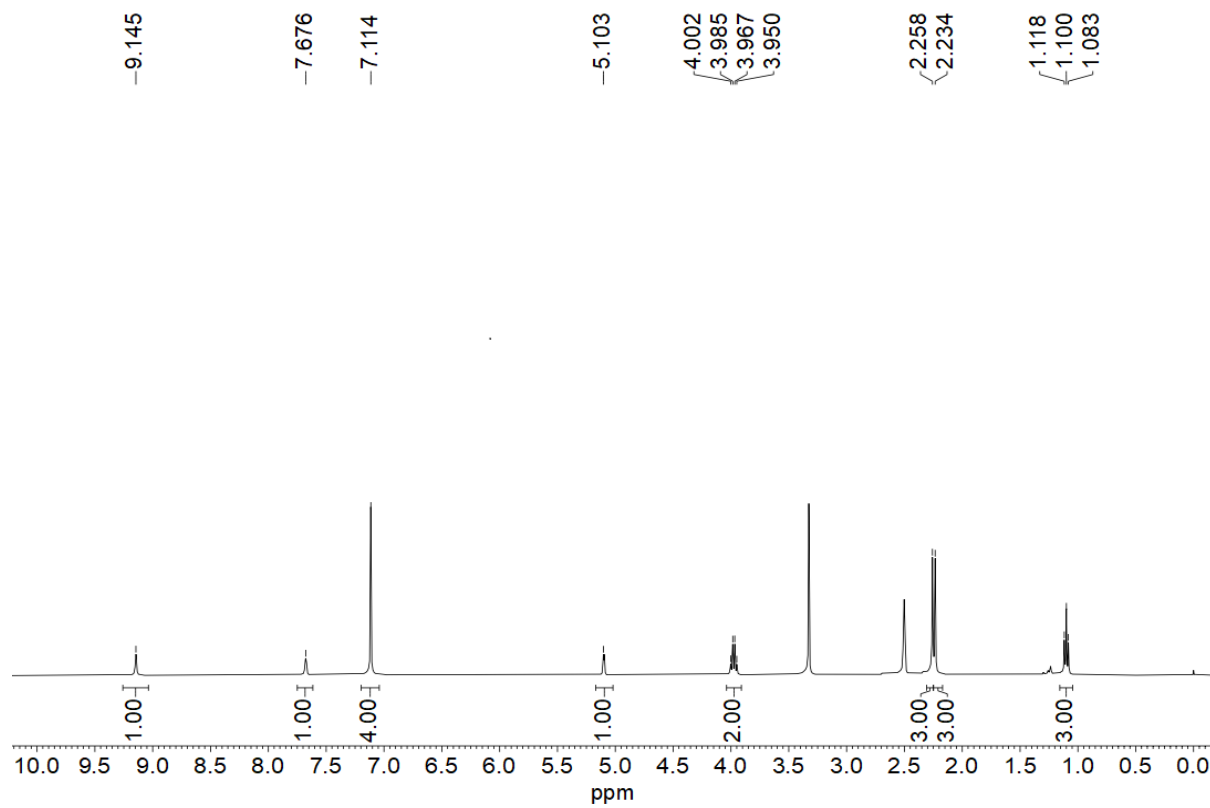


Figure S14. The ¹H-NMR spectrum of **4e**.

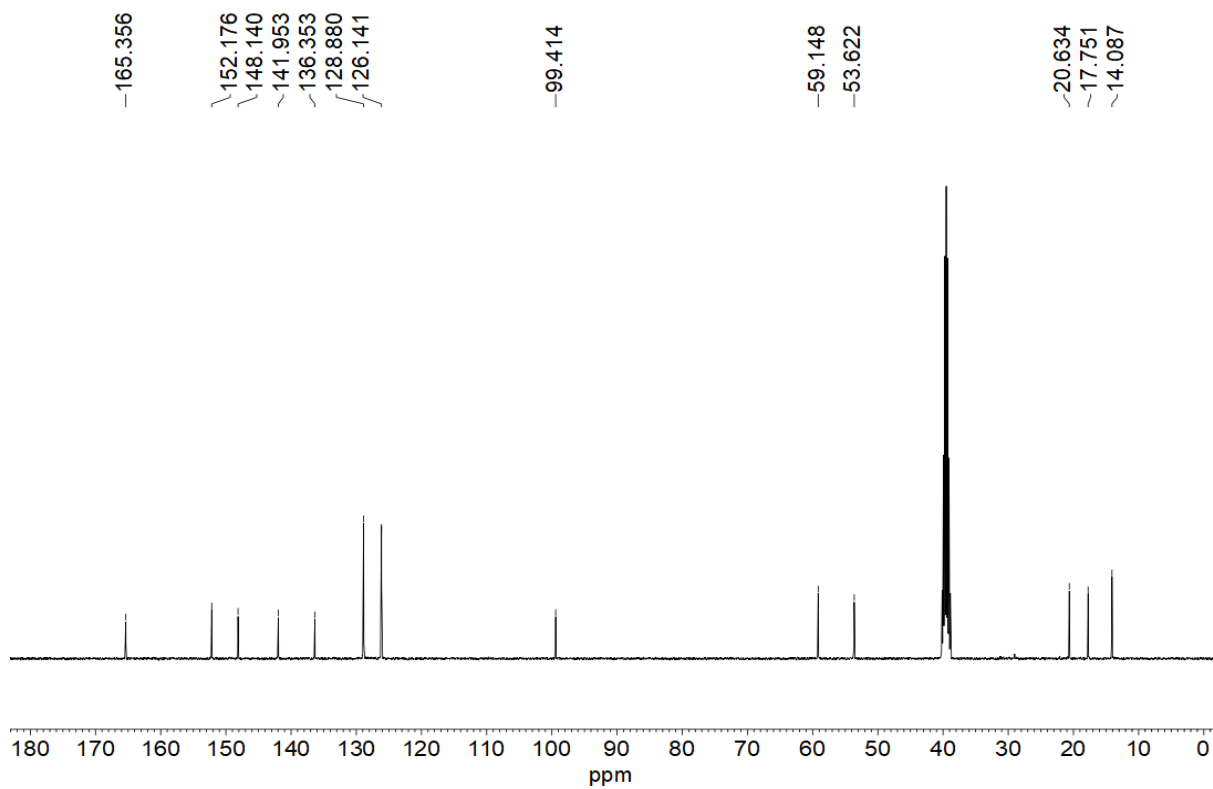


Figure S15. The ^{13}C -NMR spectrum of **4e**.

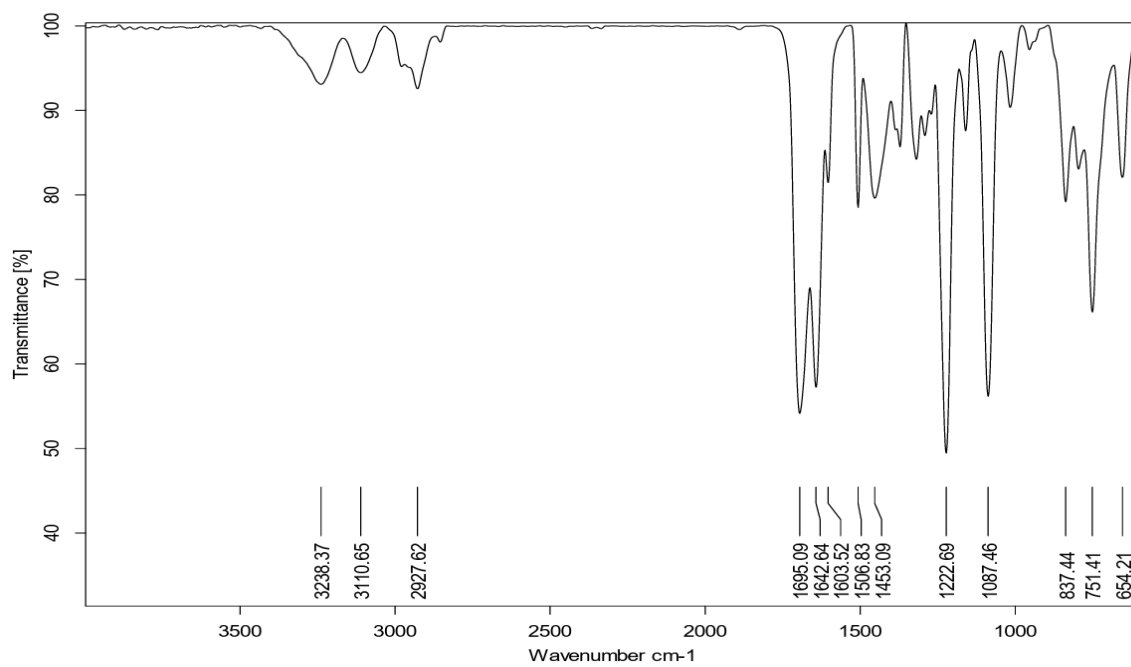


Figure S16. The FTIR spectrum of **4f**.

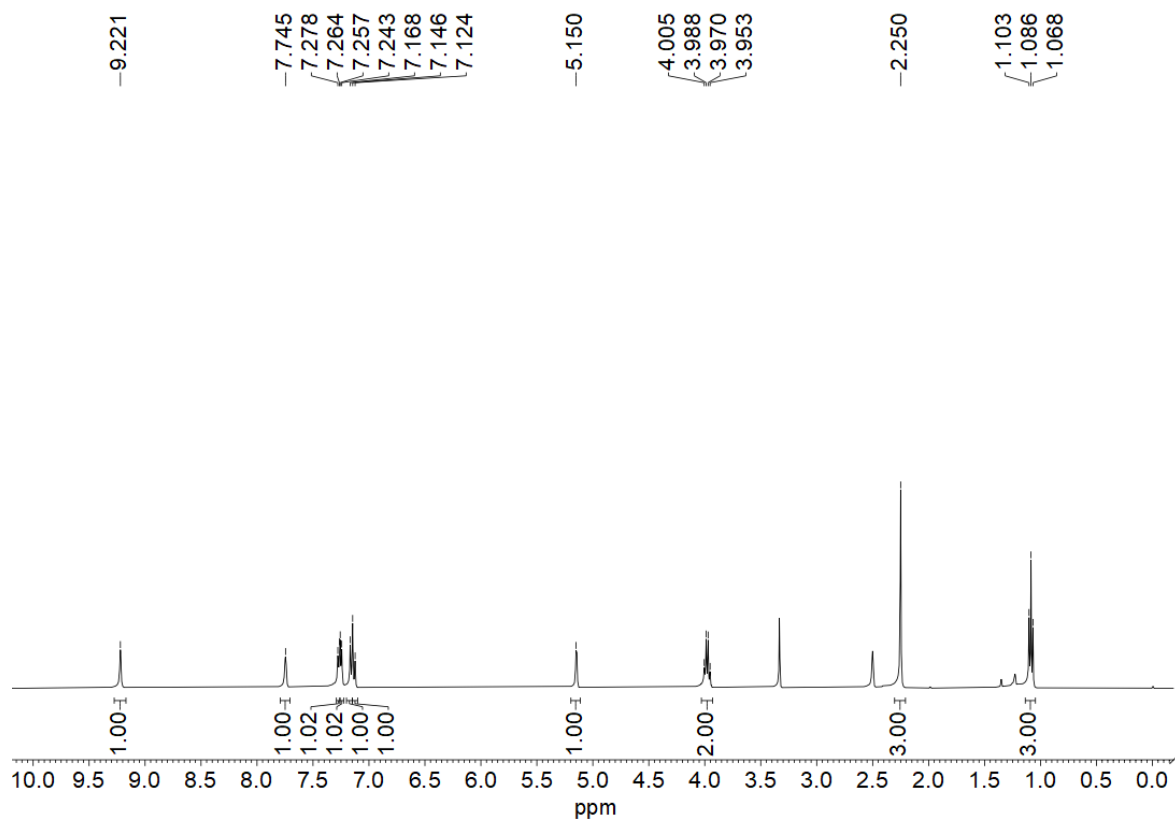


Figure S17. The ^1H -NMR spectrum of **4f**.

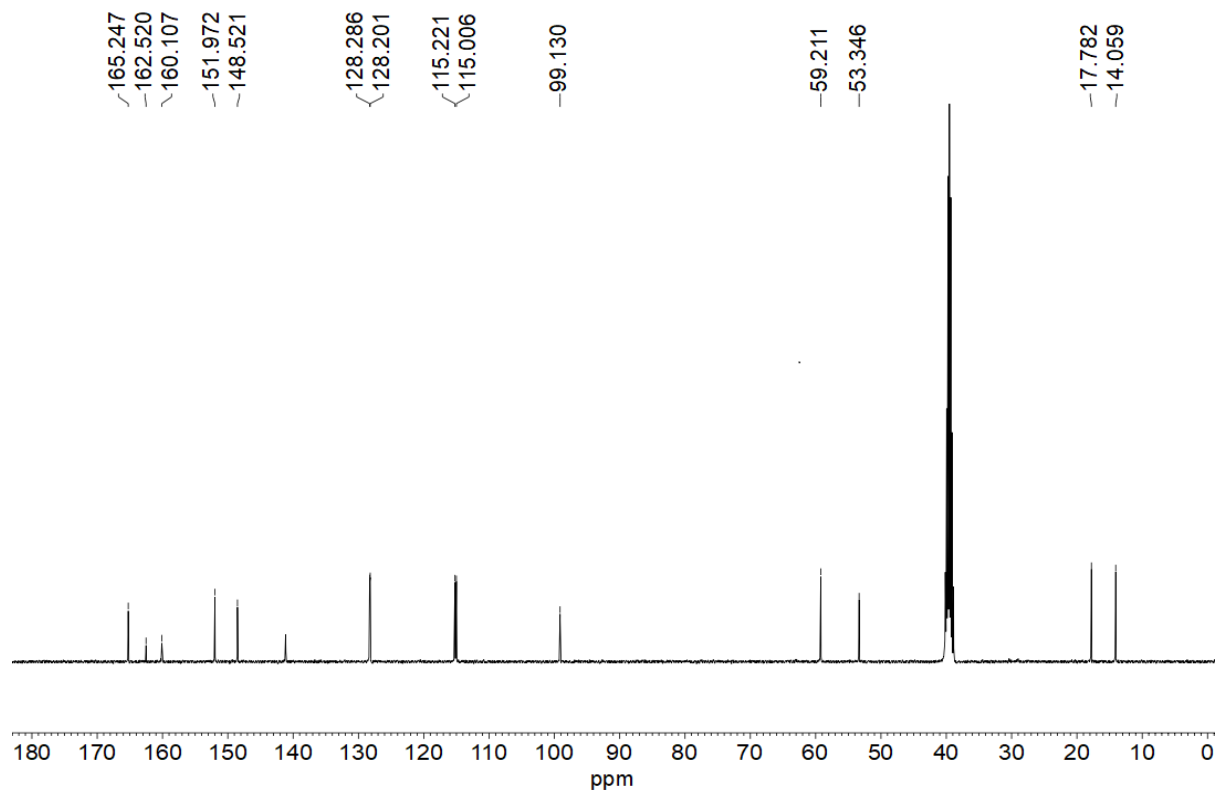


Figure S18. The ^{13}C -NMR spectrum of **4f**.

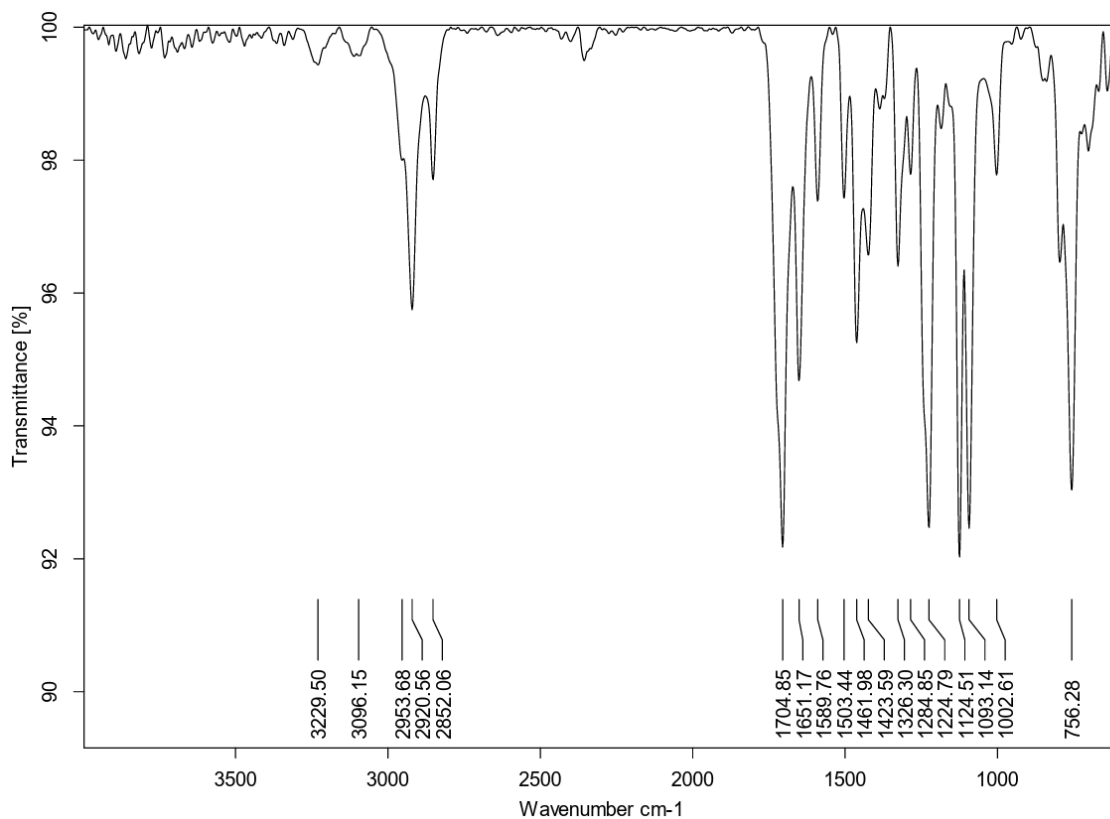


Figure S19. The FTIR spectrum of **4g**.

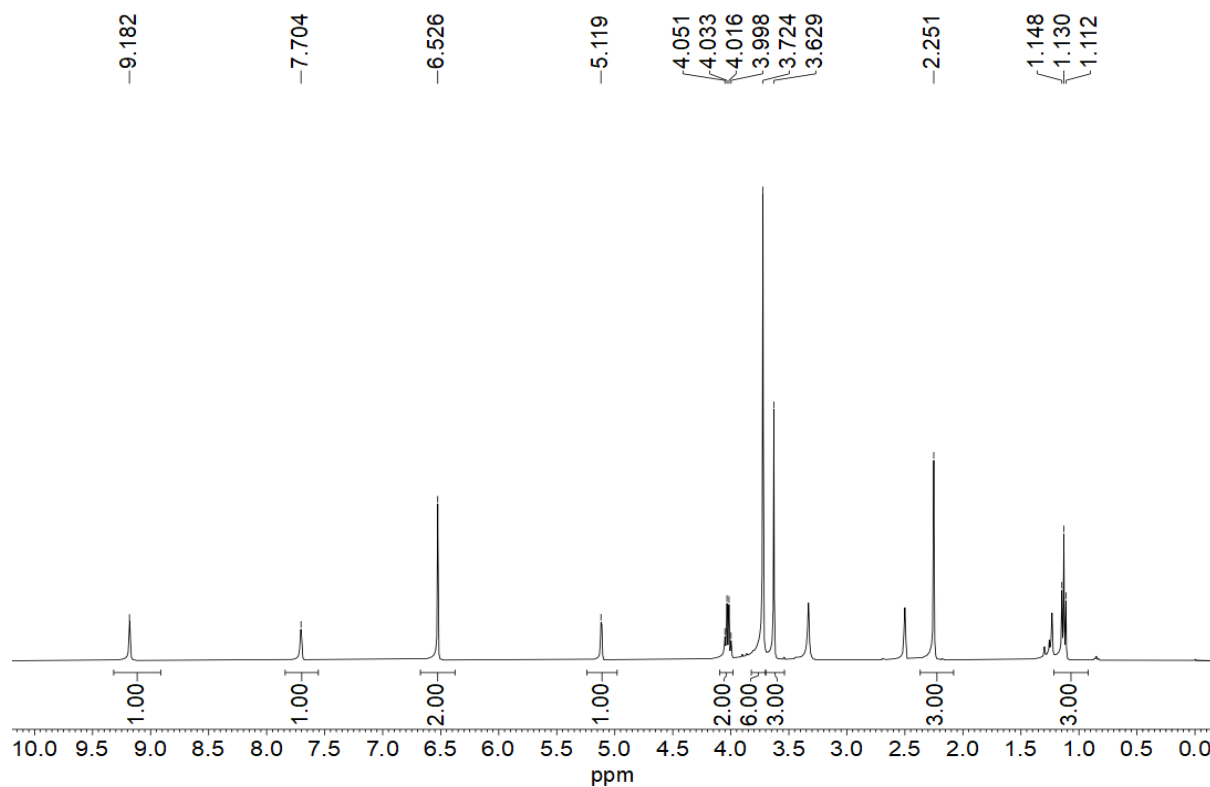


Figure S20. The ¹H-NMR spectrum of **4g**.

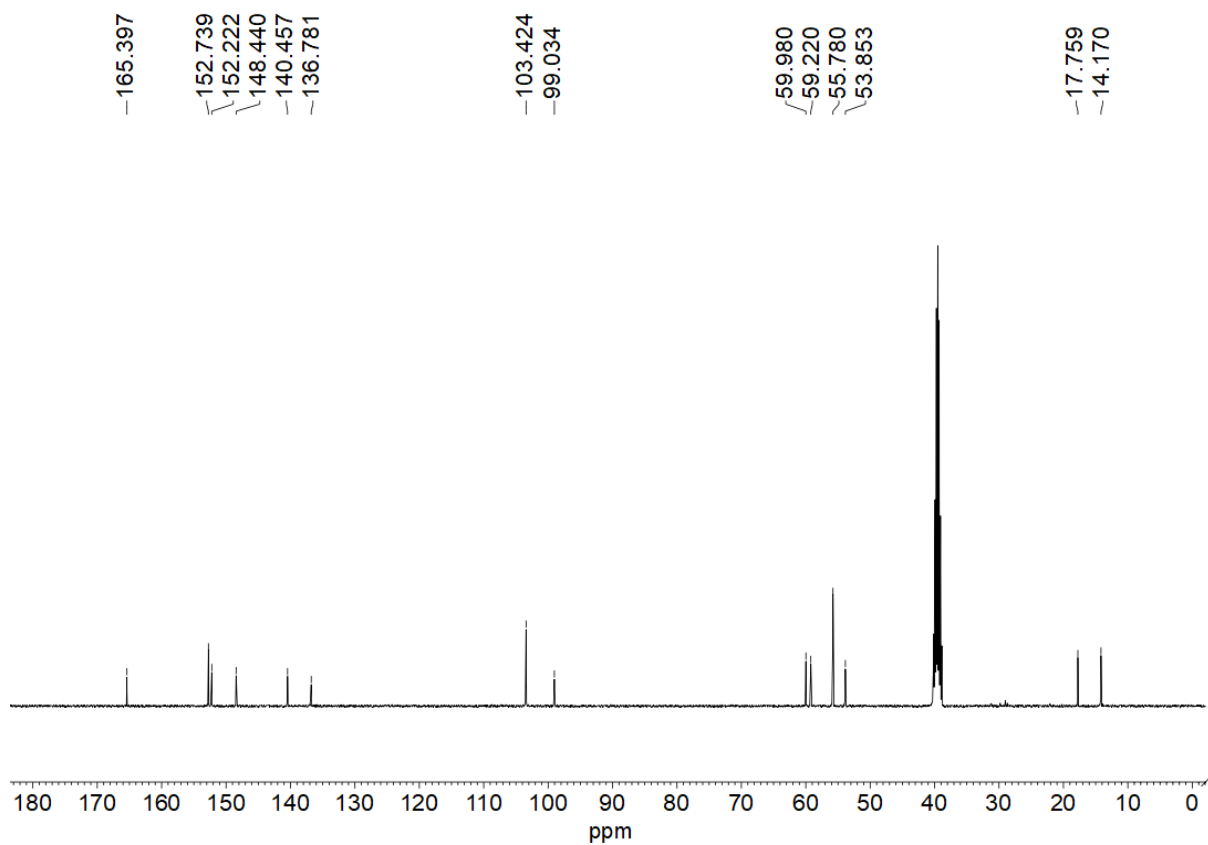


Figure S21. The ^{13}C -NMR spectrum of **4g**.

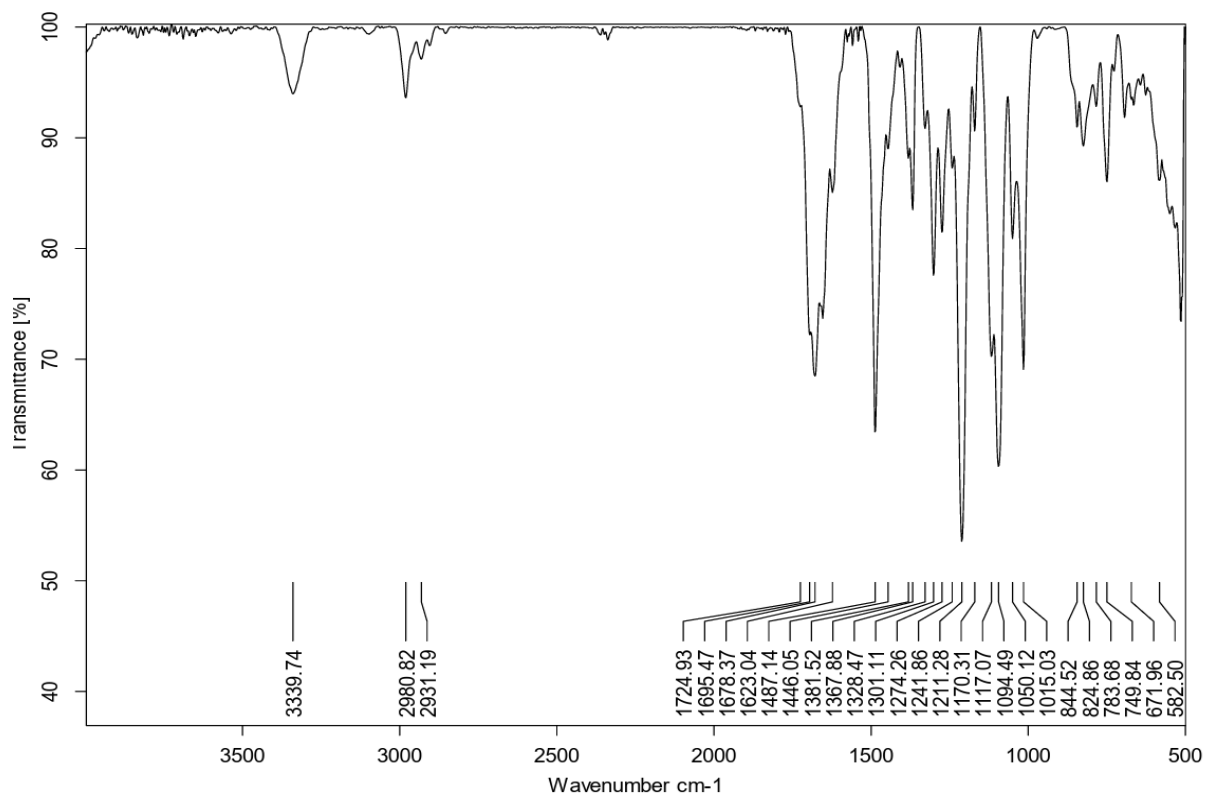


Figure S22. The FTIR spectrum of **4h**.

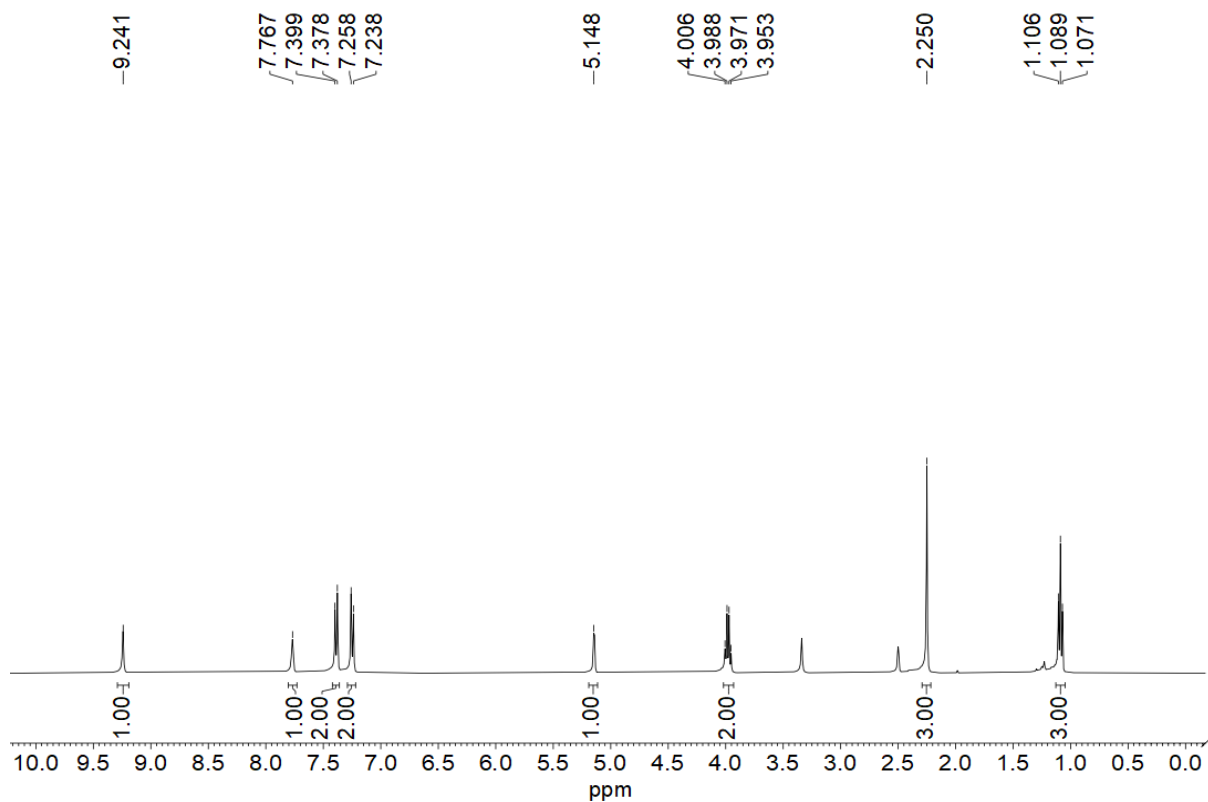


Figure S23. The ^1H -NMR spectrum of **4h**.

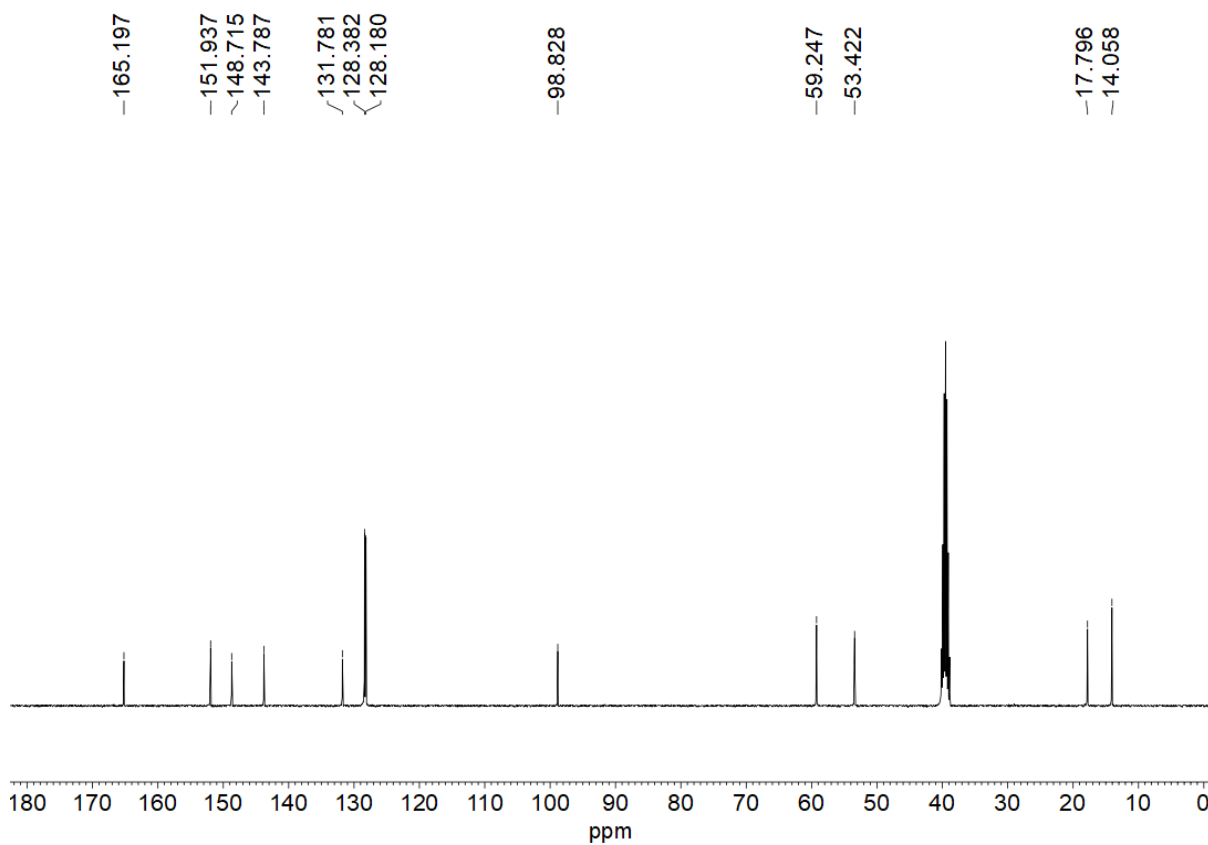


Figure S24. The ^{13}C -NMR spectrum of **4h**.

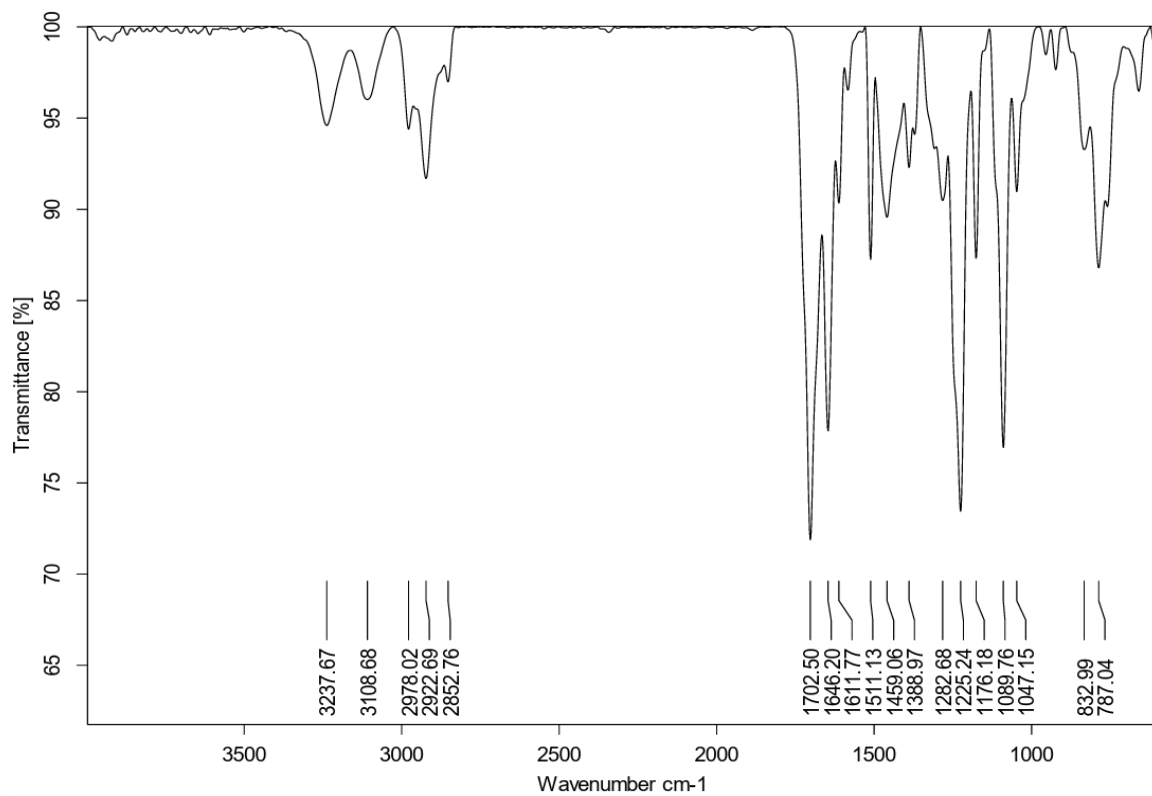


Figure S25. The FTIR spectrum of **4i**.

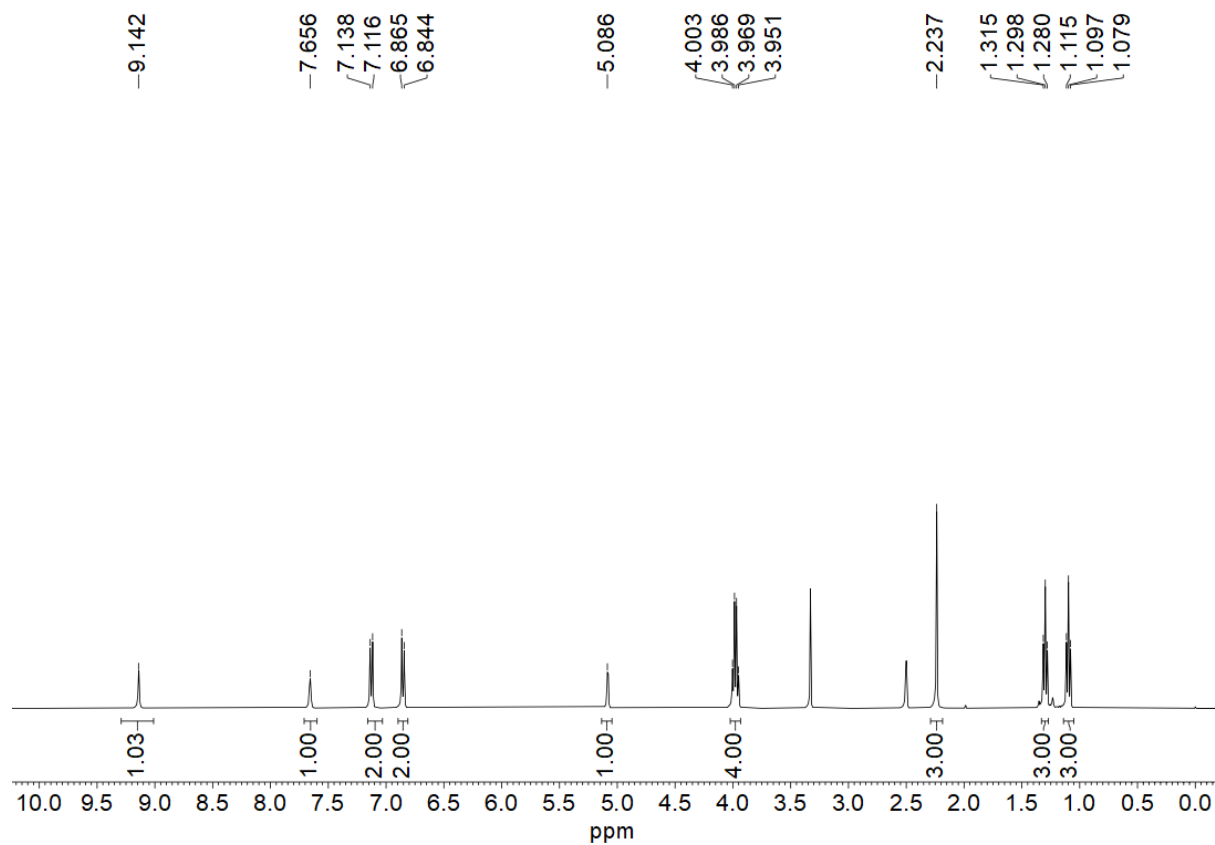


Figure S26. The ¹H-NMR spectrum of **4i**.

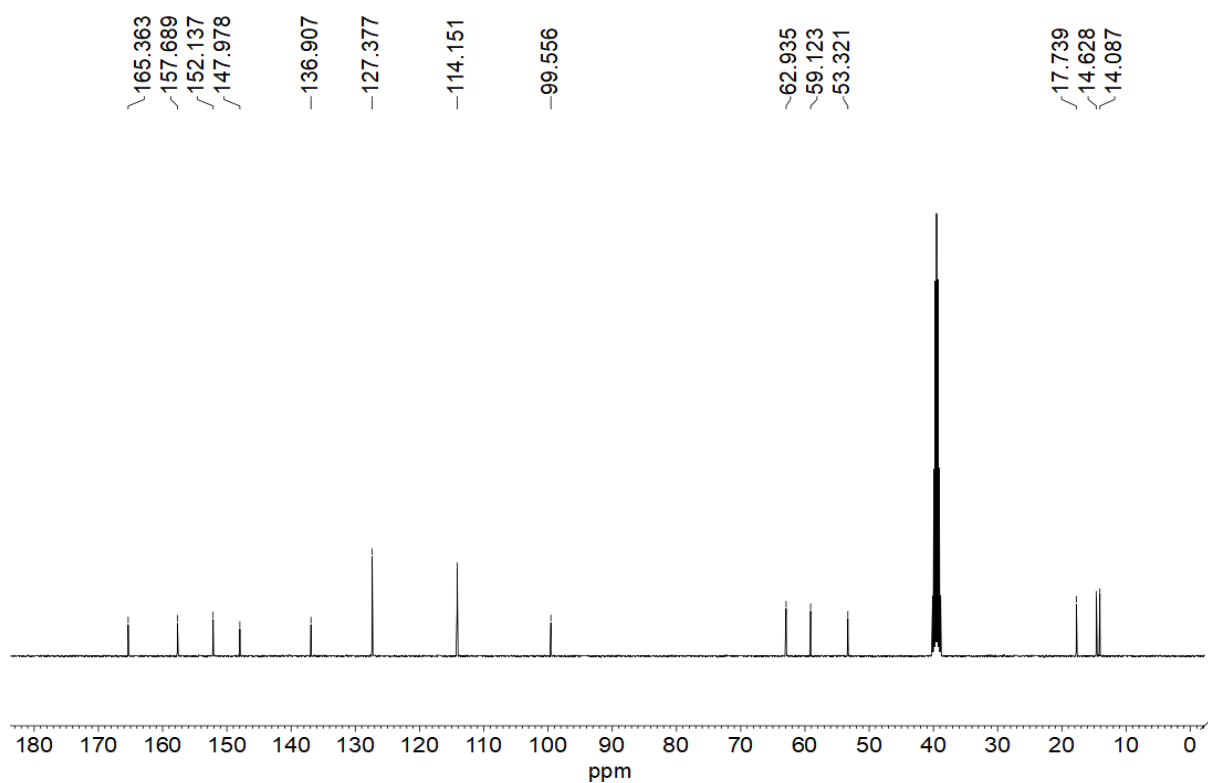


Figure S27. The ^{13}C -NMR spectrum of **4i**.

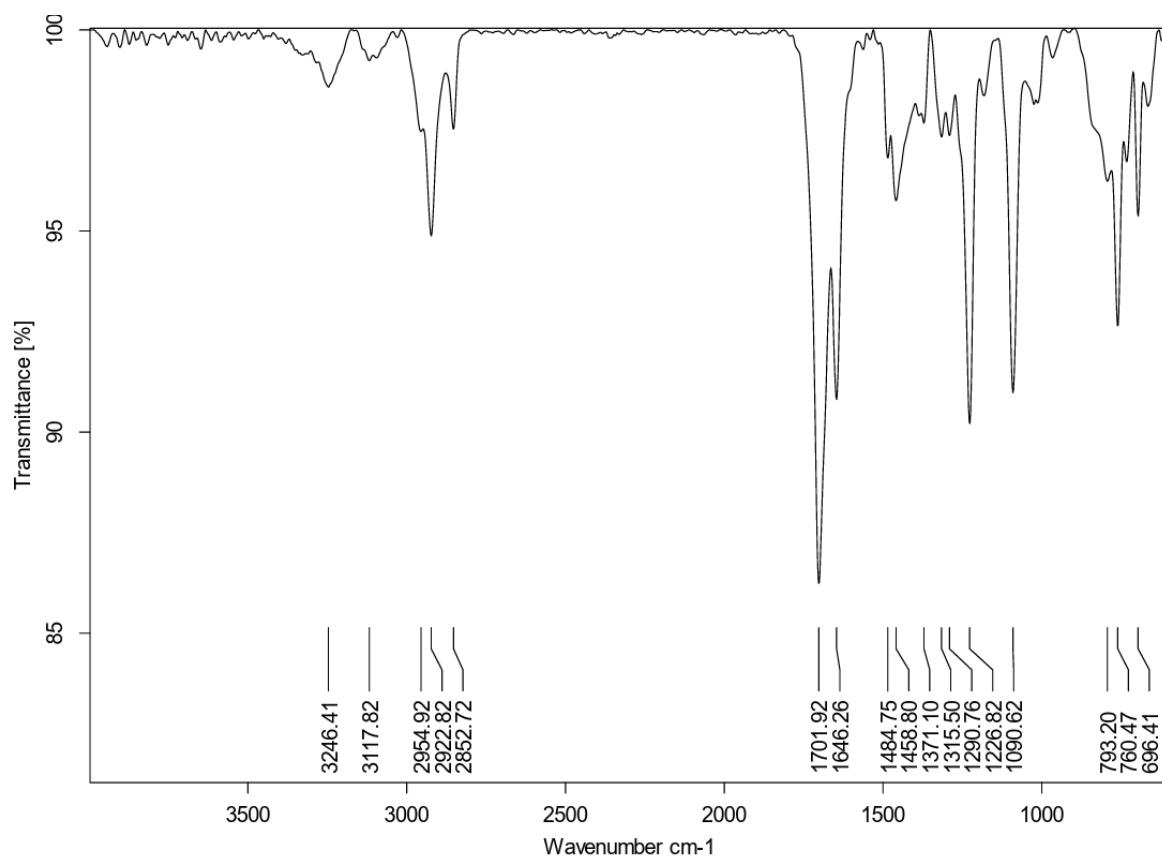


Figure S28. The FTIR spectrum of **4j**.

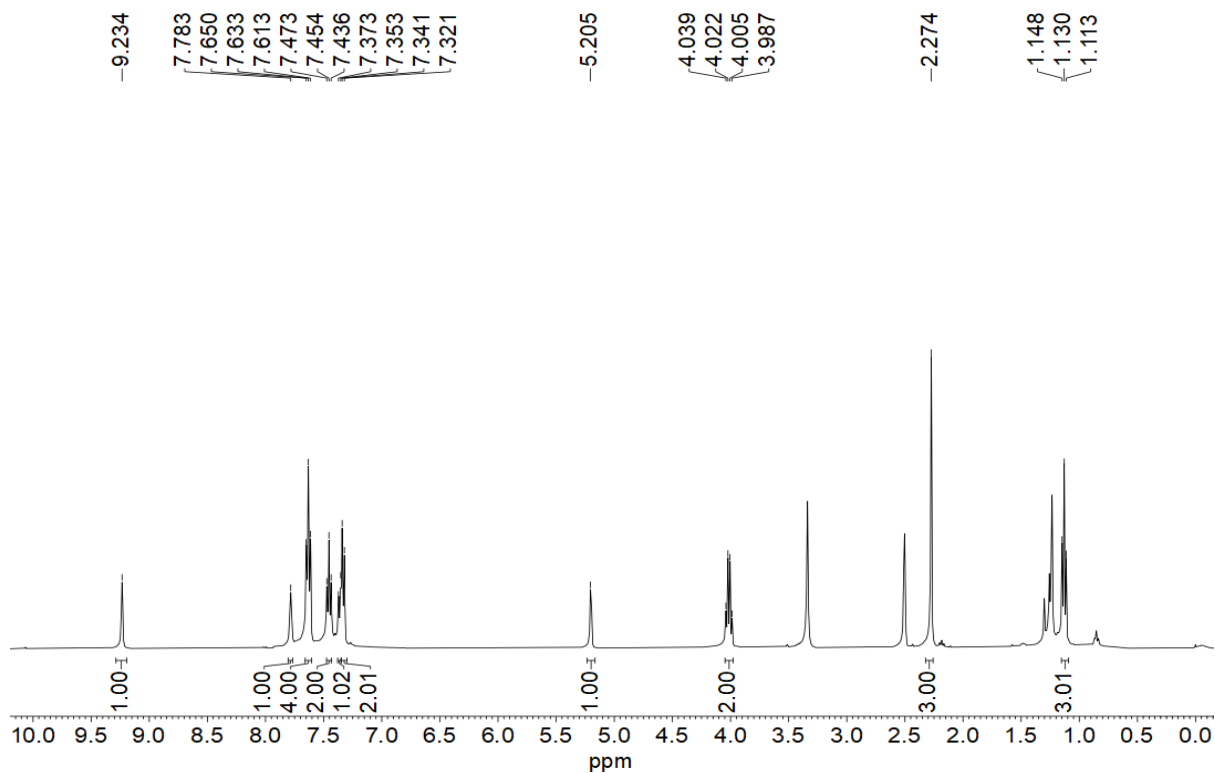


Figure S29. The ^1H -NMR spectrum of **4j**.

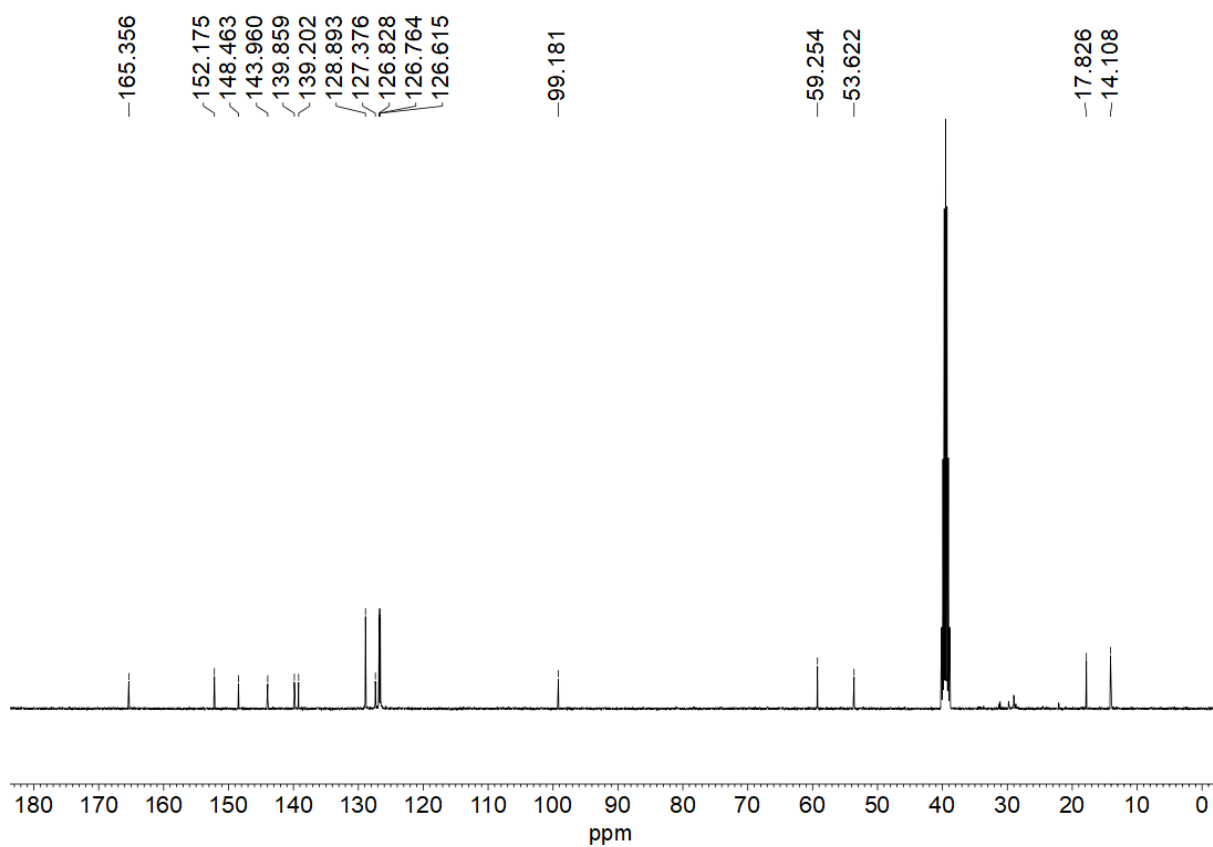


Figure S30. The ^{13}C -NMR spectrum of **4j**.

Characterization data of synthesized 1,4-Dihydropyridines (DHPs)

Diethyl-2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (**6a**):^{4,5} Light yellow solid (1.427 g, 92%), Melting Point (°C): 156-157; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 8.79 (s, 1H), 7.20 (d, 2H, *J* = 7.6 Hz), 7.16 (t, 2H, *J* = 7.6 Hz), 7.08 (t, 1H, *J* = 7.6 Hz), 4.87 (s, 1H), 3.99 (q, 4H, *J* = 7 Hz), 2.26 (s, 6H), 1.12 (t, 6H, *J* = 7 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 166.9, 148.2, 145.3, 127.8, 127.3, 125.8, 101.9, 59.0, 38.9, 18.2, 14.1; FTIR (ATR, cm⁻¹): 3339, 2954, 2920, 1735, 1682.

Diethyl-4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6b**):^{4,5} Light yellow solid (1.187 g, 90%), Melting Point (°C): 157-159; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 8.74 (s, 1H), 7.05 (d, 2H, *J* = 8 Hz), 6.76 (d, 2H, *J* = 8 Hz), 4.80 (s, 1H), 3.99 (q, 4H, *J* = 6.8 Hz), 3.67 (s, 3H), 2.25 (s, 6H), 1.13 (t, 6H, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 167.6, 158.0, 145.5, 141.1, 128.8, 113.7, 102.7, 59.5, 55.4, 38.5, 18.7, 14.7; FTIR (ATR, cm⁻¹): 3339, 2979, 2904, 1693, 1678.

Diethyl-2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (**6c**):^{4,5} Light yellow solid (1.090 g, 88%), Melting Point (°C): 131-132; ¹H-NMR (400 MHz, CDCl₃, δ ppm): 8.06 (d, 2H, *J* = 8.8 Hz), 7.44 (d, 2H, *J* = 8.8 Hz), 6.08 (s, 1H), 5.08 (s, 1H), 4.07 (q, 4H, *J* = 7.2 Hz), 2.32 (s, 6H), 1.20 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 167.3, 155.4, 146.4, 145.1, 129.0, 123.4, 103.2, 60.1, 40.3, 19.7, 14.4; FTIR (ATR, cm⁻¹): 3344, 2955, 2922, 1694, 1680.

Diethyl-4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6d**):⁴ Light yellow solid (0.970 g, 88%), Melting Point (°C): 163-165; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 8.84 (s, 1H), 7.39 (d, 2H, *J* = 8.2 Hz), 7.11 (d, 2H, *J* = 8.2 Hz), 4.85 (s, 1H), 3.98 (q, 4H, *J* = 7.2 Hz), 2.27 (s, 6H), 1.12 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 166.8, 147.5, 145.6, 130.7, 129.6, 118.9, 101.5, 59.1, 38.7, 18.2, 14.1; FTIR (ATR, cm⁻¹): 3336, 2956, 2924, 1695, 1679.

Diethyl-2,6-dimethyl-4-(p-tolyl)-1,4-dihydropyridine-3,5-dicarboxylate (**6e**):⁴ Light yellow solid (1.271 g, 89%), Melting Point (°C): 137-138; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 8.75 (s, 1H), 7.03 (d, 2H, *J* = 8.2 Hz), 6.99 (d, 2H, *J* = 8.2 Hz), 4.82 (s, 1H), 3.97 (q, 4H, *J* = 7.2 Hz), 2.25 (s, 6H), 2.20 (s, 3H), 1.13 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 167.0, 145.3, 145.1, 134.7, 128.4, 127.2, 102.0, 85.9, 38.4, 20.5, 18.2, 14.1; FTIR (ATR, cm⁻¹): 3332, 2955, 2923, 1694, 1623.

Diethyl-4-(4-fluorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6f**):⁴ Light yellow solid (1.275 g, 91%), Melting Point (°C): 138-139; ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.23 (d, 1H, *J* = 8.8 Hz), 7.21 (d, 1H, *J* = 8.8 Hz), 6.88 (d, 1H, *J* = 8.8 Hz), 6.86 (d, 1H, *J* = 8.8 Hz), 5.89 (s, 1H), 4.96 (s, 1H), 4.07 (q, 4H, *J* = 7.2 Hz), 2.30 (s, 6H), 1.21 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 167.8, 162.7, 160.3, 144.2, 143.9, 129.6, 129.5, 114.7, 114.5, 104.2, 59.9, 39.2, 19.6, 14.4; FTIR (ATR, cm⁻¹): 3336, 2955, 2924, 1697, 1683.

Diethyl-2,6-dimethyl-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyridine-3,5-dicarboxylate (**6g**):⁵ Light yellow solid (0.897 g, 84%), Melting Point (°C): 157-159; ¹H-NMR (400 MHz, CDCl₃, δ ppm): 6.48 (s, 2H), 5.86 (s, 1H), 4.94 (s, 1H), 4.09 (q, 4H, 7.2 Hz), 3.76 (s, 9H), 2.30 (s, 6H), 1.21 (t, 6H, 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 167.8, 152.8, 144.0, 143.6, 136.7, 105.3, 104.2, 104.1, 60.9, 60.0, 56.1, 39.9, 19.8, 19.7, 14.6; FTIR (ATR, cm⁻¹): 3338, 2955, 2923, 1692, 1654.

Diethyl-4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6h**):^{4,5} Light yellow solid (1.151 g, 89%), Melting Point (°C): 144-146; ¹H-NMR (400 MHz, DMSO-d₆, δ ppm): 8.85 (s, 1H), 7.24 (d, 2H, *J* = 8.0 Hz), 7.19 (d, 2H, *J* = 8.0 Hz), 4.89 (s, 1H), 3.99 (q, 4H, *J* = 8.0 Hz), 2.29 (s, 6H), 1.11 (t, 6H, *J* = 8.0 Hz); ¹³C-NMR (100 MHz, DMSO-d₆, δ ppm): 166.8, 147.2, 145.6, 130.5, 129.3, 127.7, 101.6, 59.0, 38.7, 18.2, 14.1; FTIR (ATR, cm⁻¹): 3328, 2980, 2931, 1728, 1675.

Diethyl-4-(4-ethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6i**):⁴ Light yellow solid (1.094 g, 88%), Melting Point (°C): 104-106; ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.16 (d, 2H, *J* = 8.8 Hz), 6.72 (d, 2H, *J* = 8.8 Hz), 6.21 (s, 1H), 4.92 (s, 1H), 4.08 (q, 4H, *J* = 7.2 Hz), 3.95 (q, 2H, *J* = 7.2 Hz), 2.27 (s, 6H), 1.35 (t, 3H, *J* = 7.2 Hz), 1.21 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 168.0, 157.3, 144.1, 140.4, 129.0, 113.8, 104.1, 104.1, 63.3, 59.8, 38.8, 19.4, 19.4, 15.0, 14.4; FTIR (ATR, cm⁻¹): 3335, 2956, 2921, 1693, 1662.

Diethyl-4-([1,1'-biphenyl]-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6j**):^{6,7} Light yellow solid (0.912 g, 82%), Melting Point (°C): 140-142; ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.46-7.19 (m, 9H), 6.05 (s, 1H), 4.96 (s, 1H), 4.02 (q, 4H, *J* = 7.2 Hz), 2.22 (s, 6H), 1.14 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 167.9, 147.1, 144.4, 141.3, 139.0, 128.8, 128.8, 128.5, 127.1, 127.0, 126.8, 104.0, 59.9, 39.5, 19.6, 14.4; FTIR (ATR, cm⁻¹): 3345, 2955, 2924, 1694, 1679.

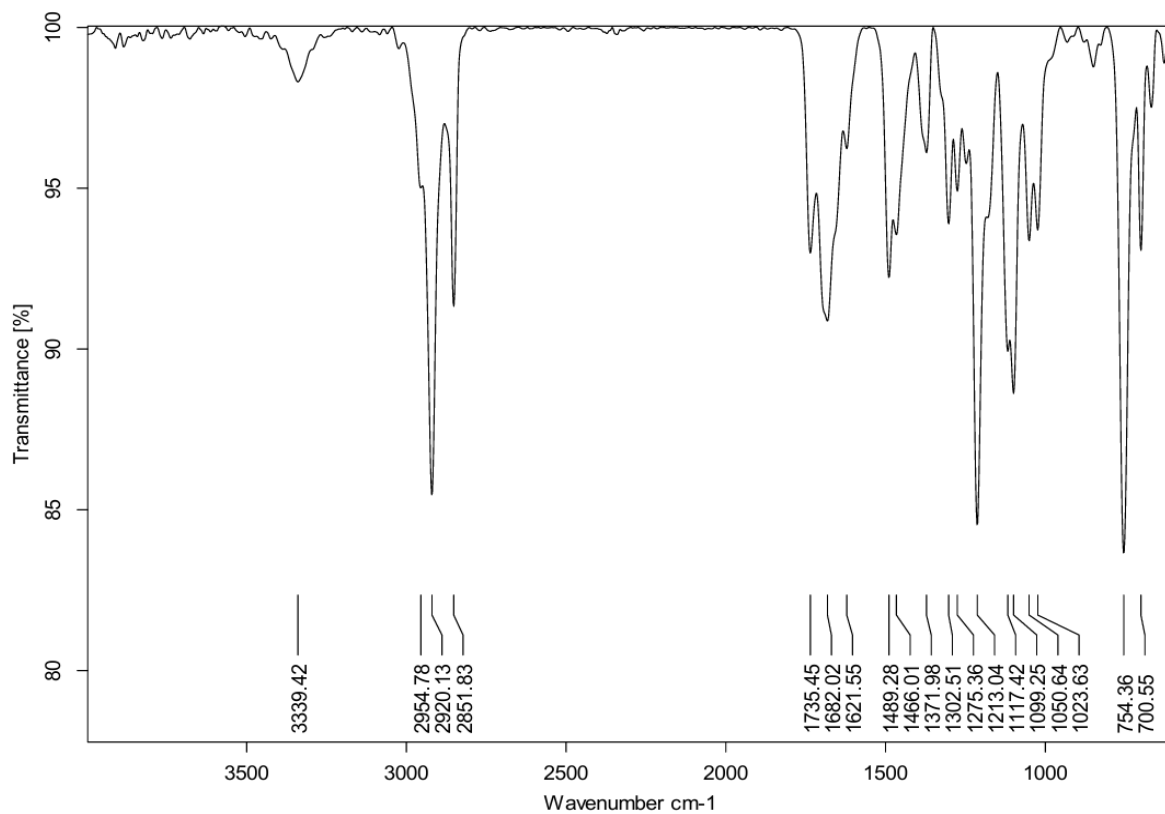


Figure S31. The FTIR spectrum of **6a**.

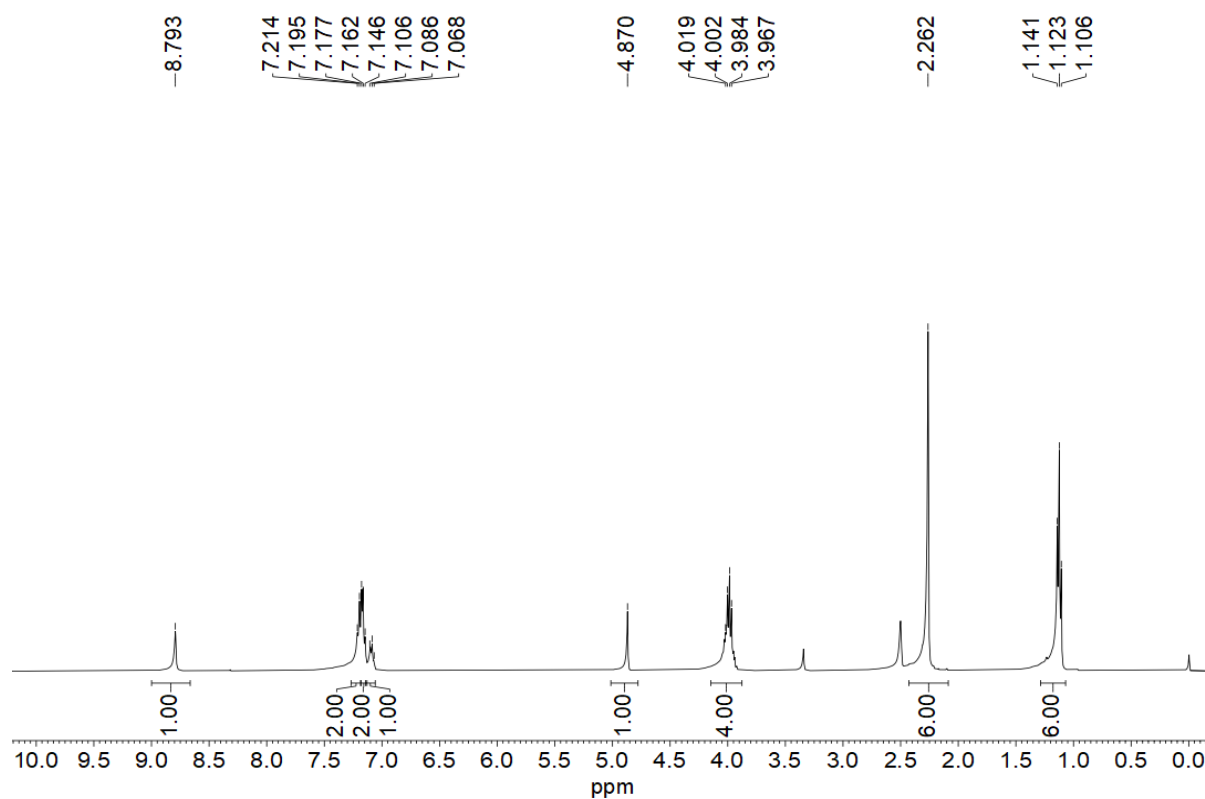


Figure S32. The ¹H-NMR spectrum of **6a**.

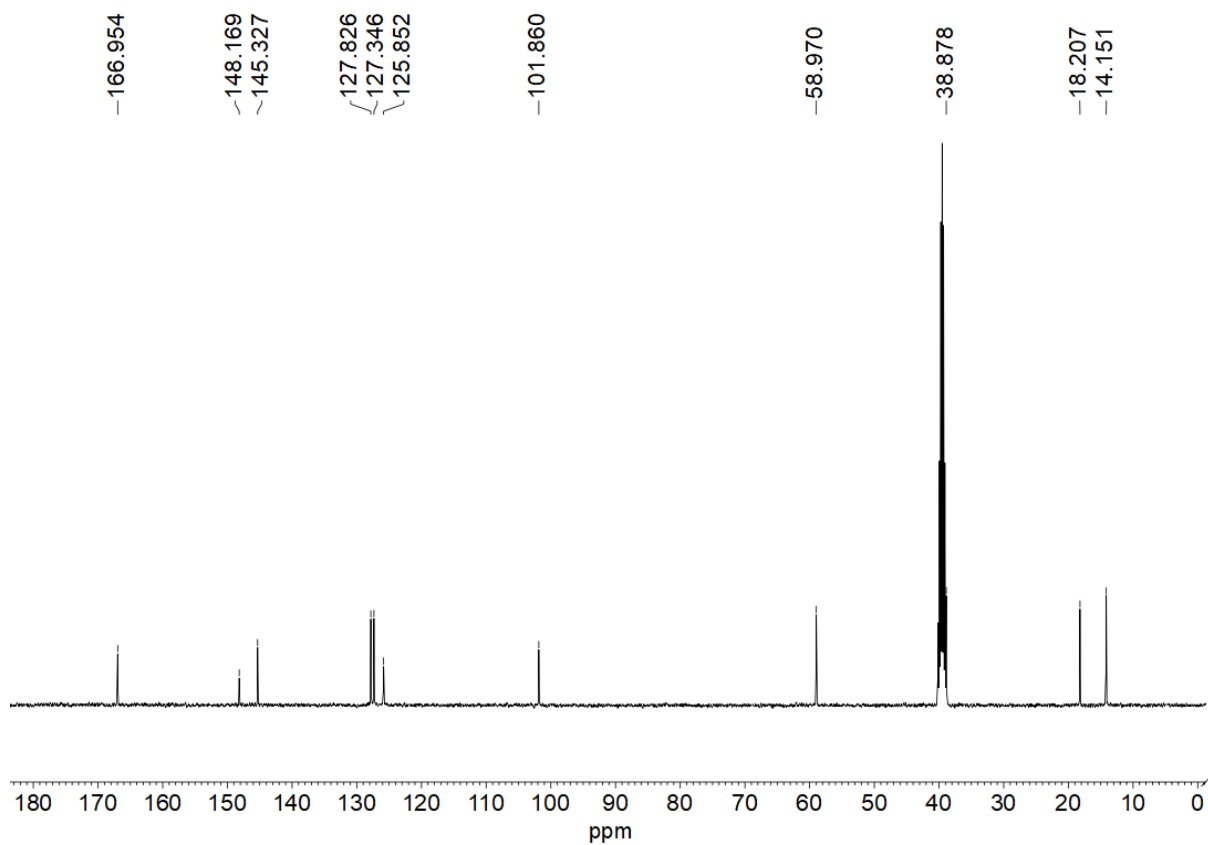


Figure S33. The ^{13}C -NMR spectrum of **6a**.

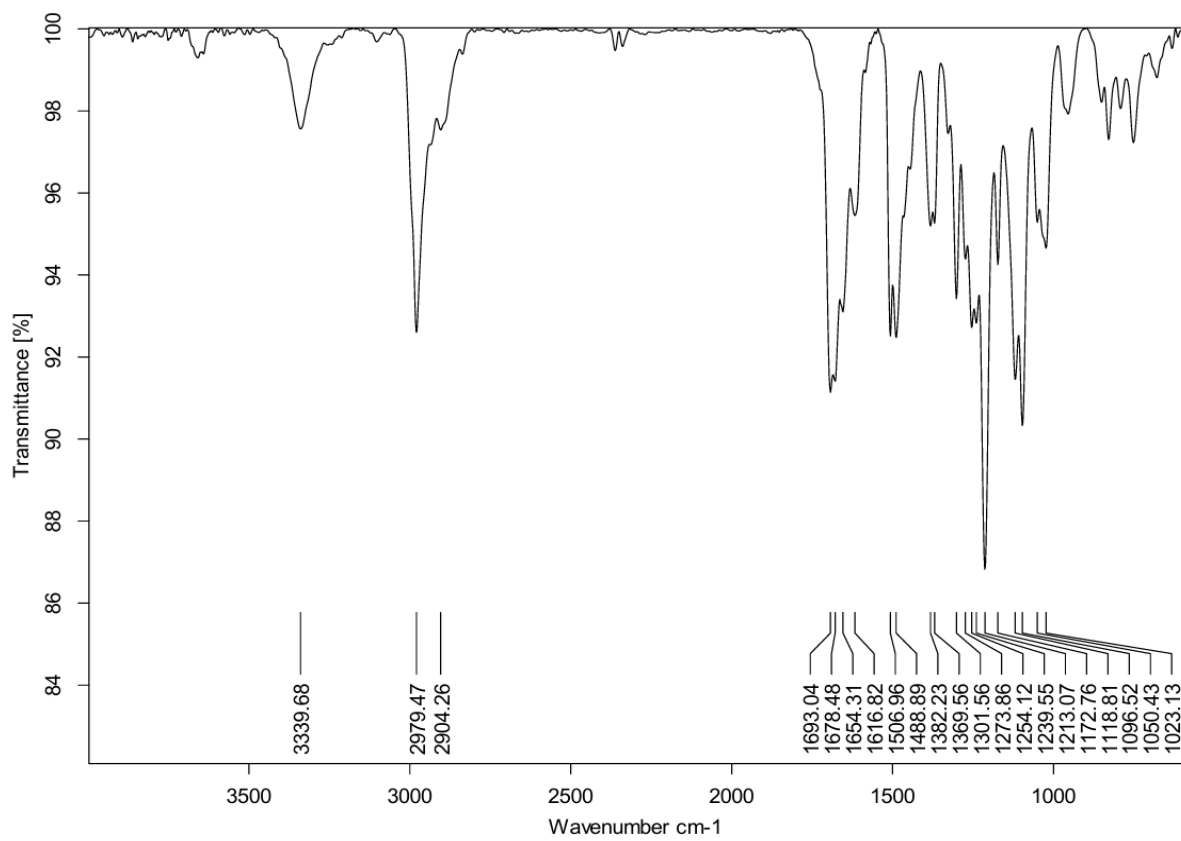


Figure S34. The FTIR spectrum of **6b**.

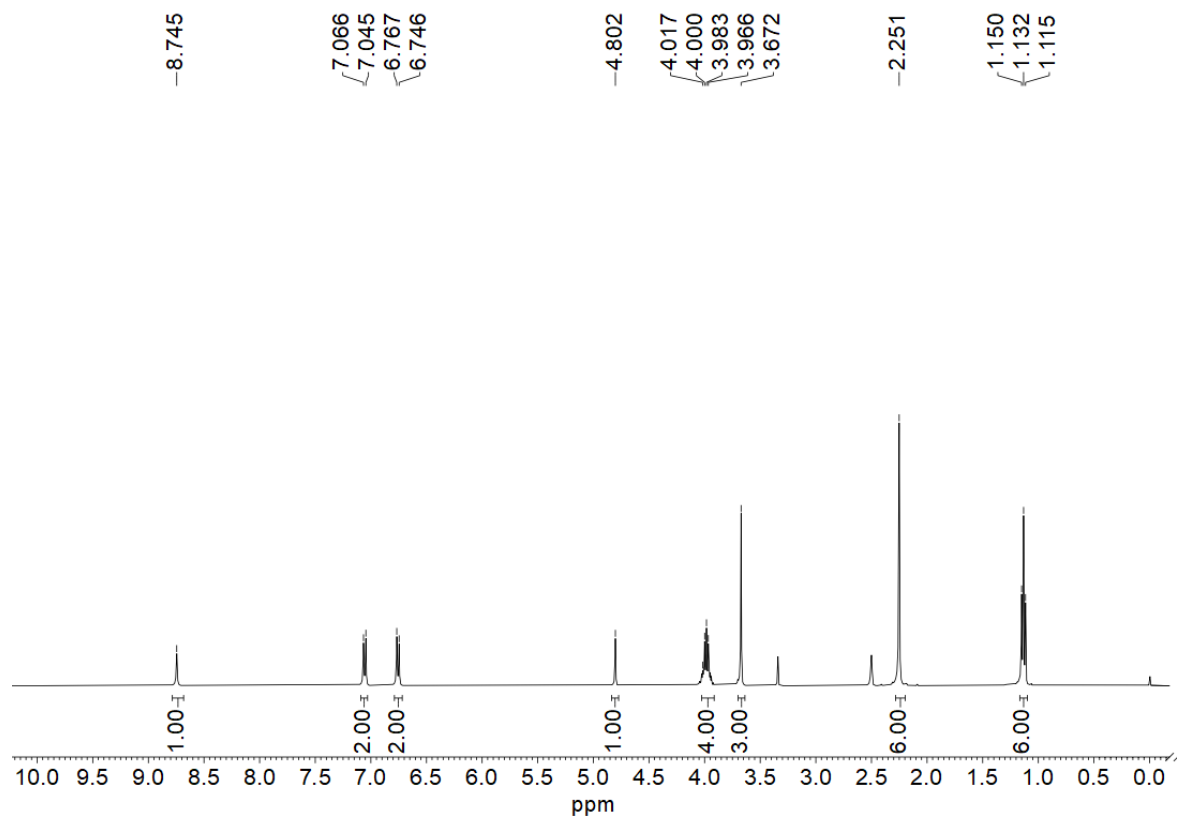


Figure S35. The ^1H -NMR spectrum of **6b**.

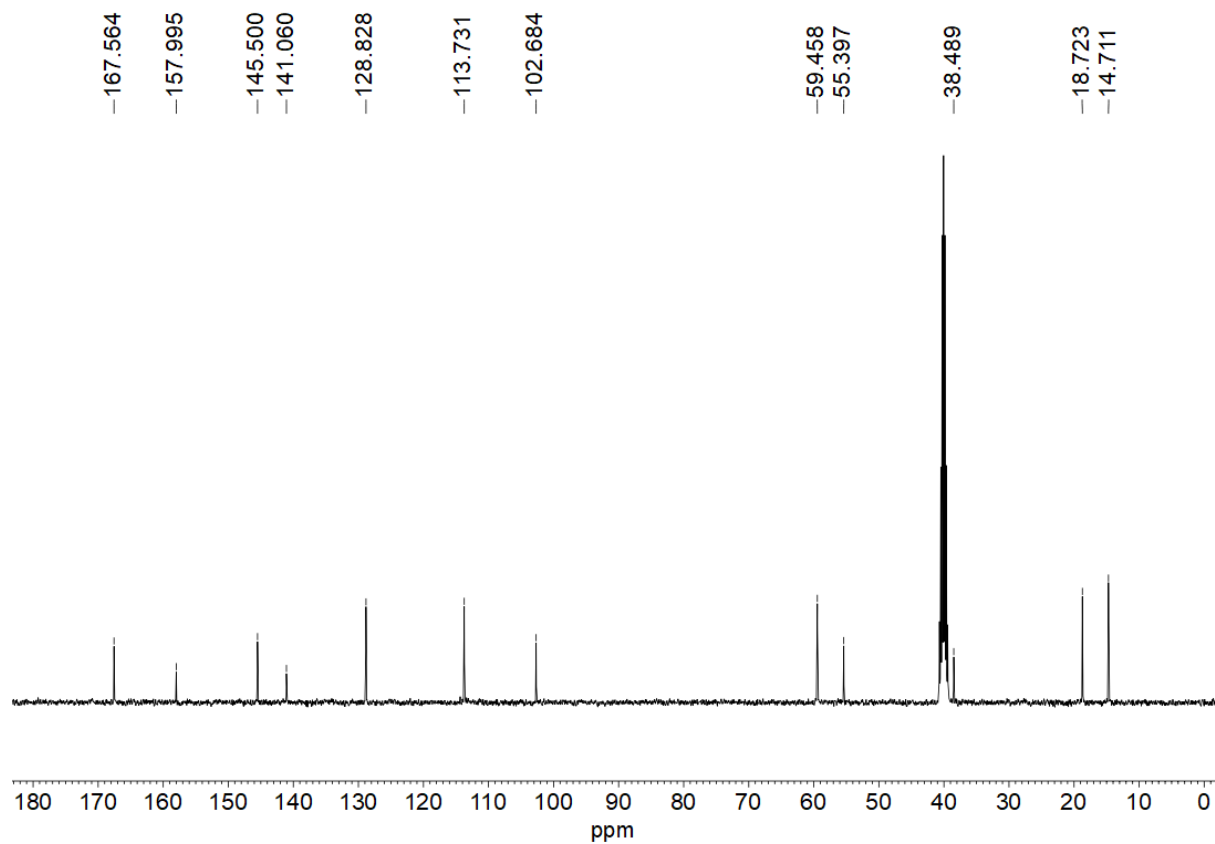


Figure S36. The ^{13}C -NMR spectrum of **6b**.

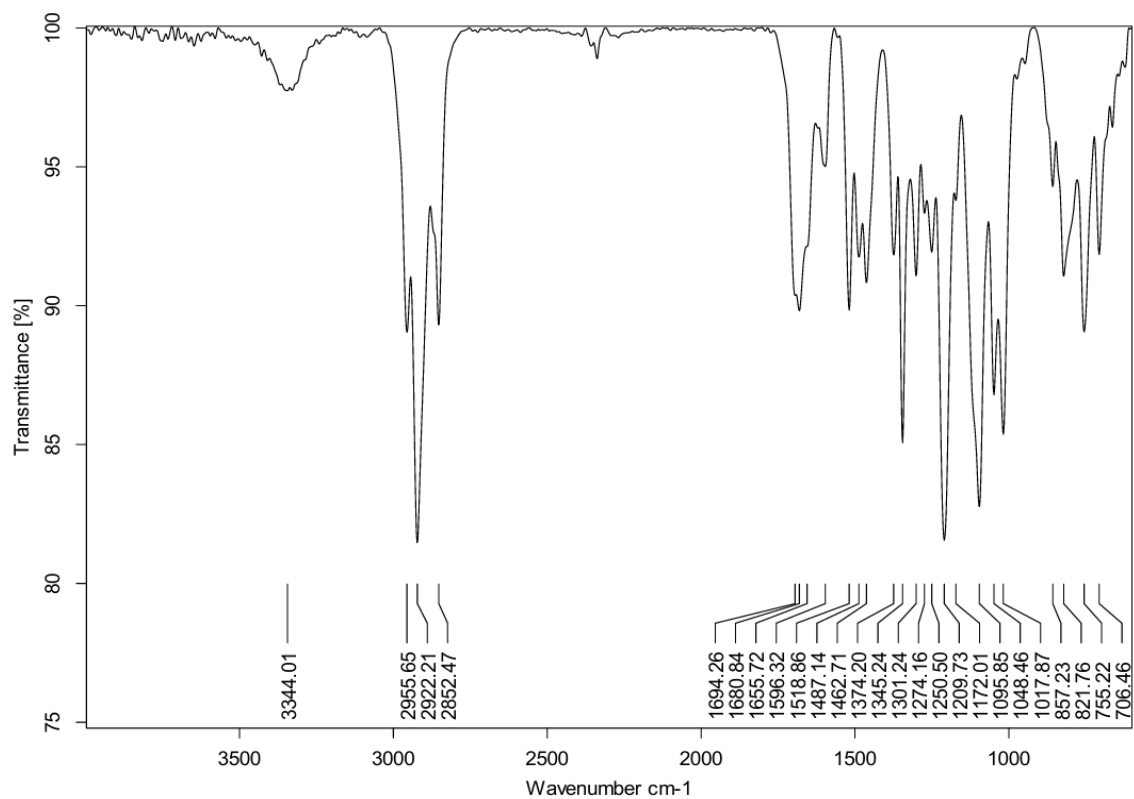


Figure S37. The FTIR spectrum of **6c**.

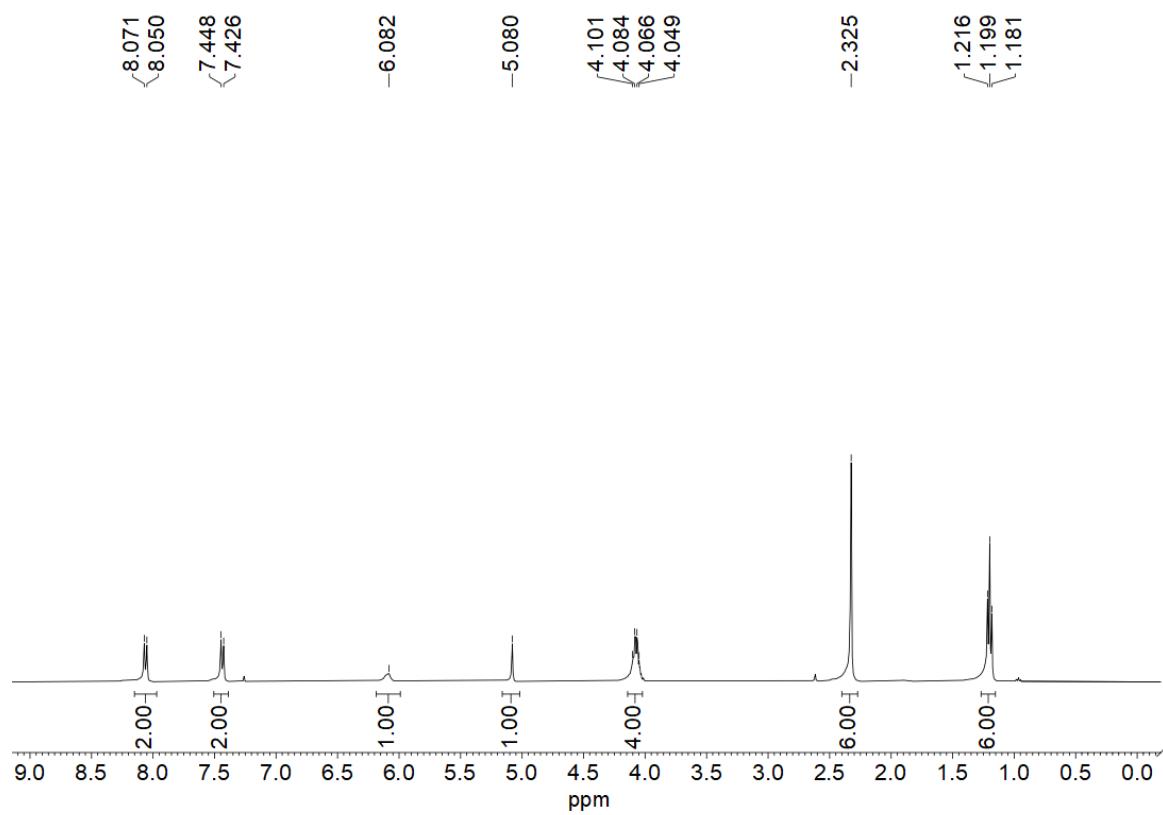


Figure S38. The ¹H-NMR spectrum of **6c**.

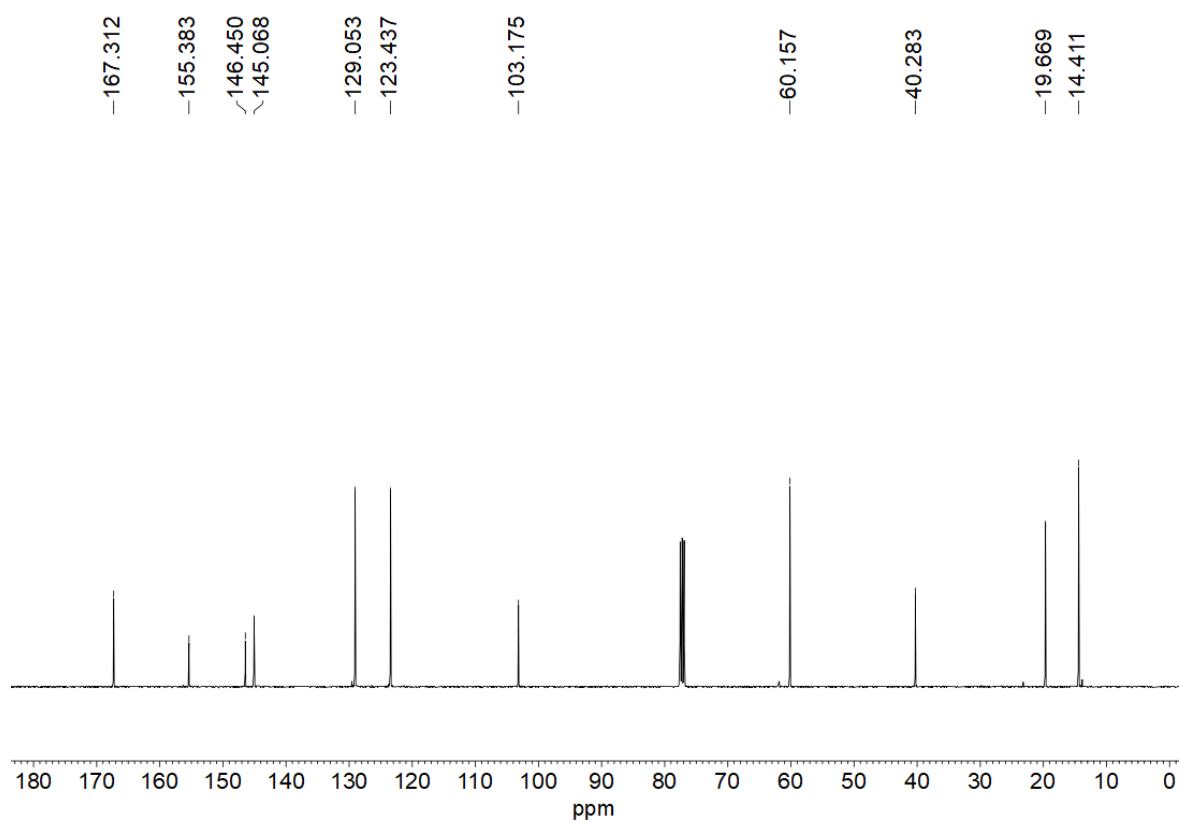


Figure S39. The ^{13}C -NMR spectrum of **6c**.

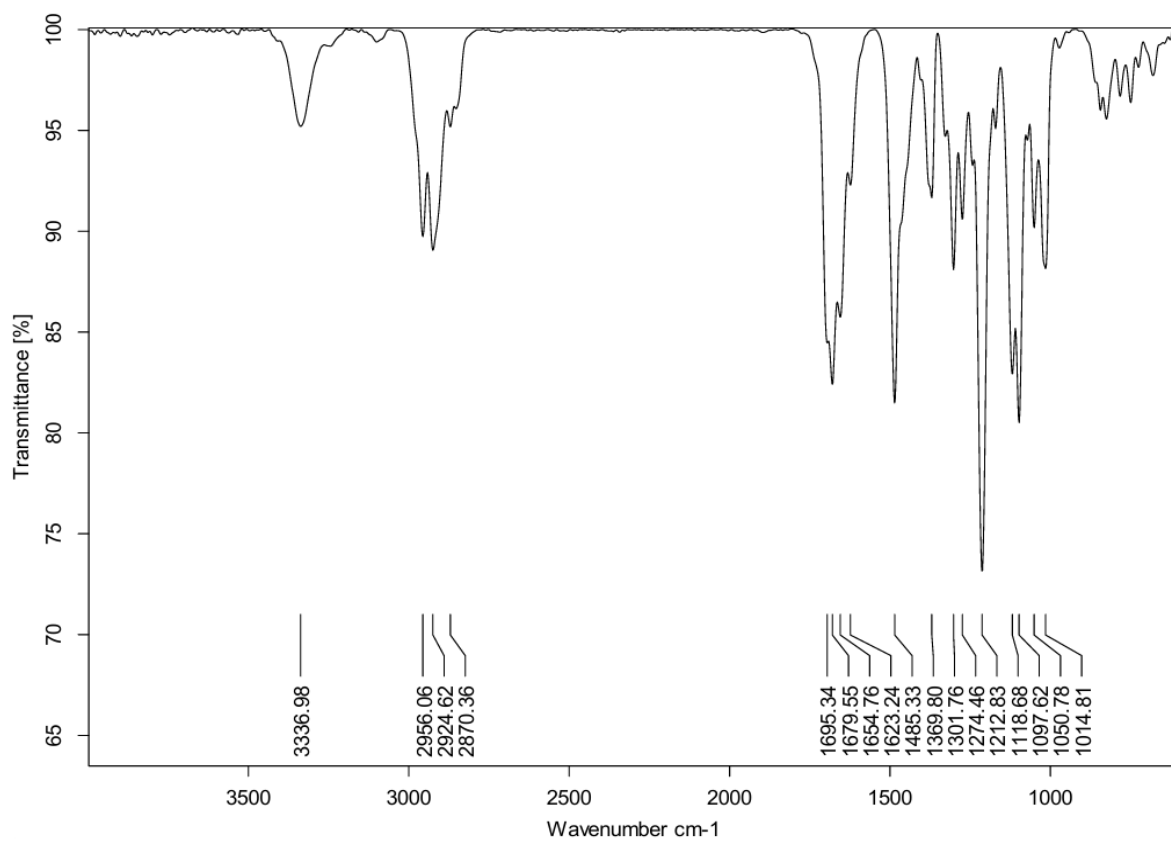


Figure S40. The FTIR spectrum of **6d**.

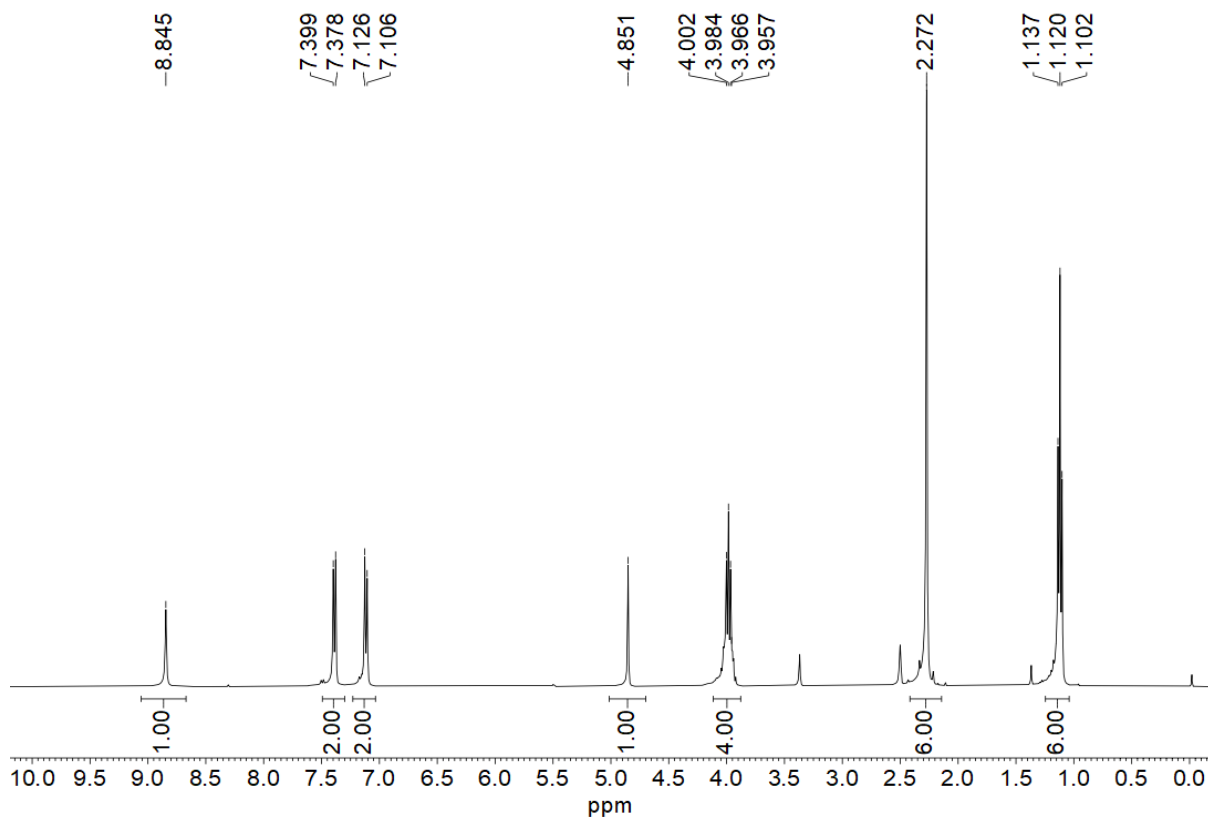


Figure S41. The ^1H -NMR spectrum of **6d**.

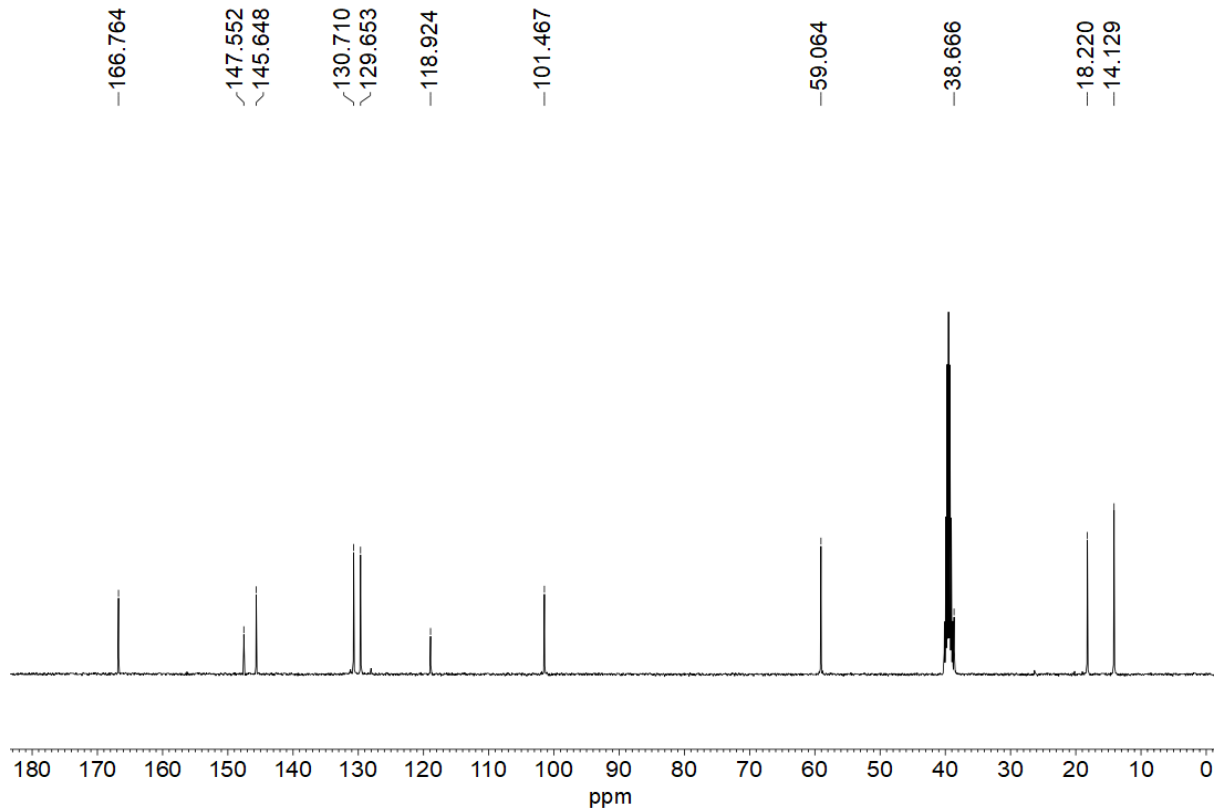


Figure S42. The ^{13}C -NMR spectrum of **6d**.

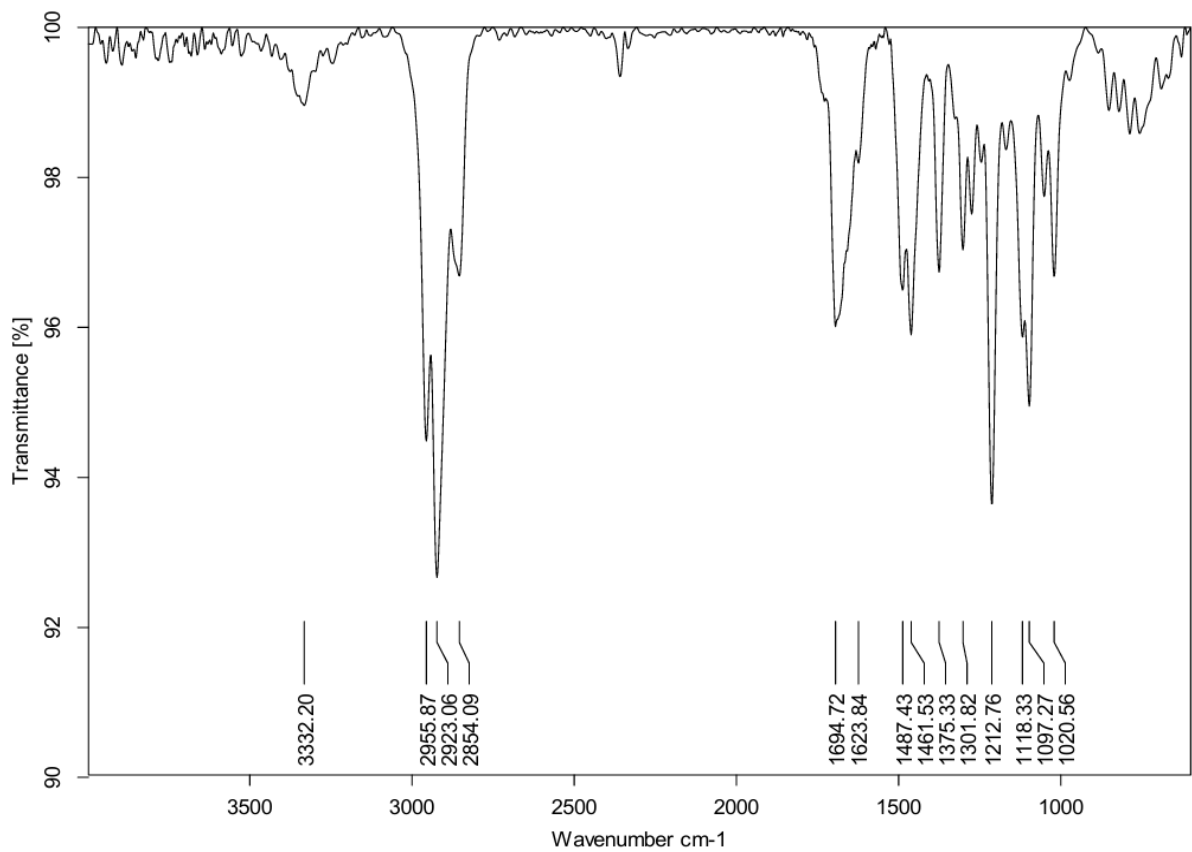


Figure S43. The FTIR spectrum of **6e**.

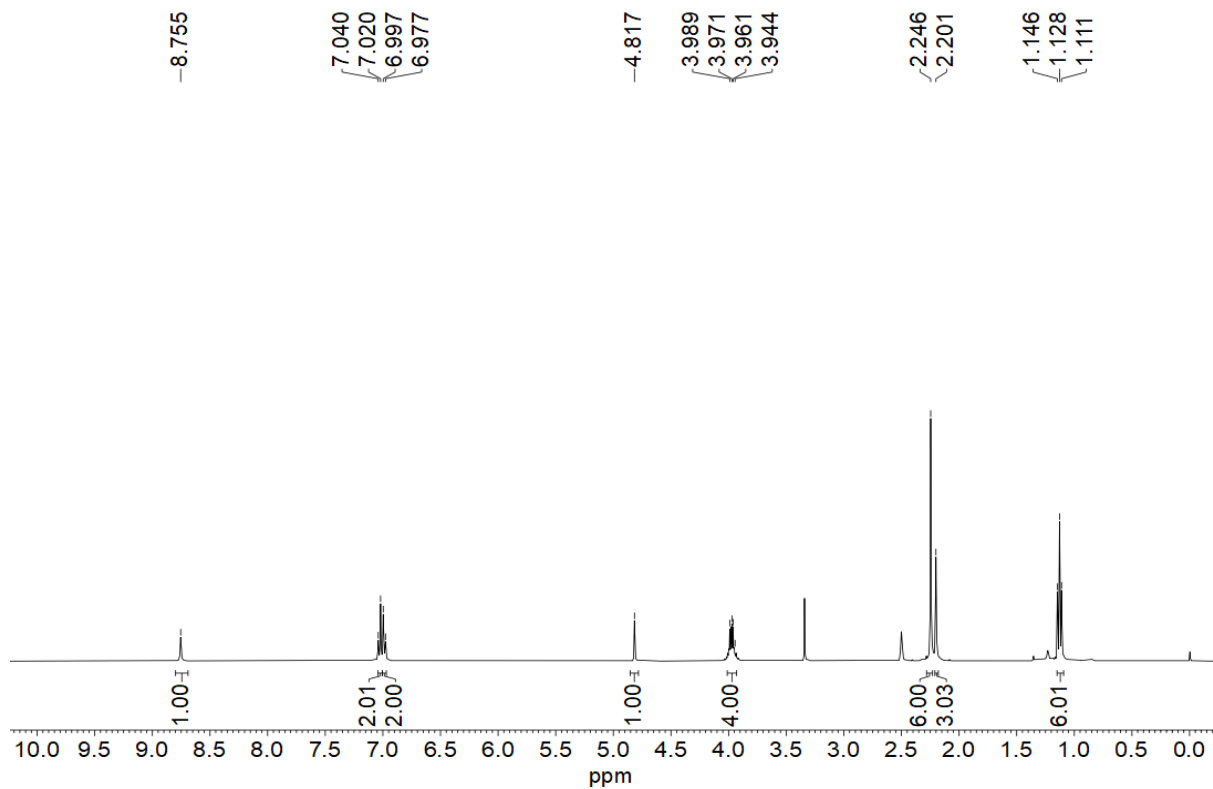


Figure S44. The ¹H-NMR spectrum of **6e**.

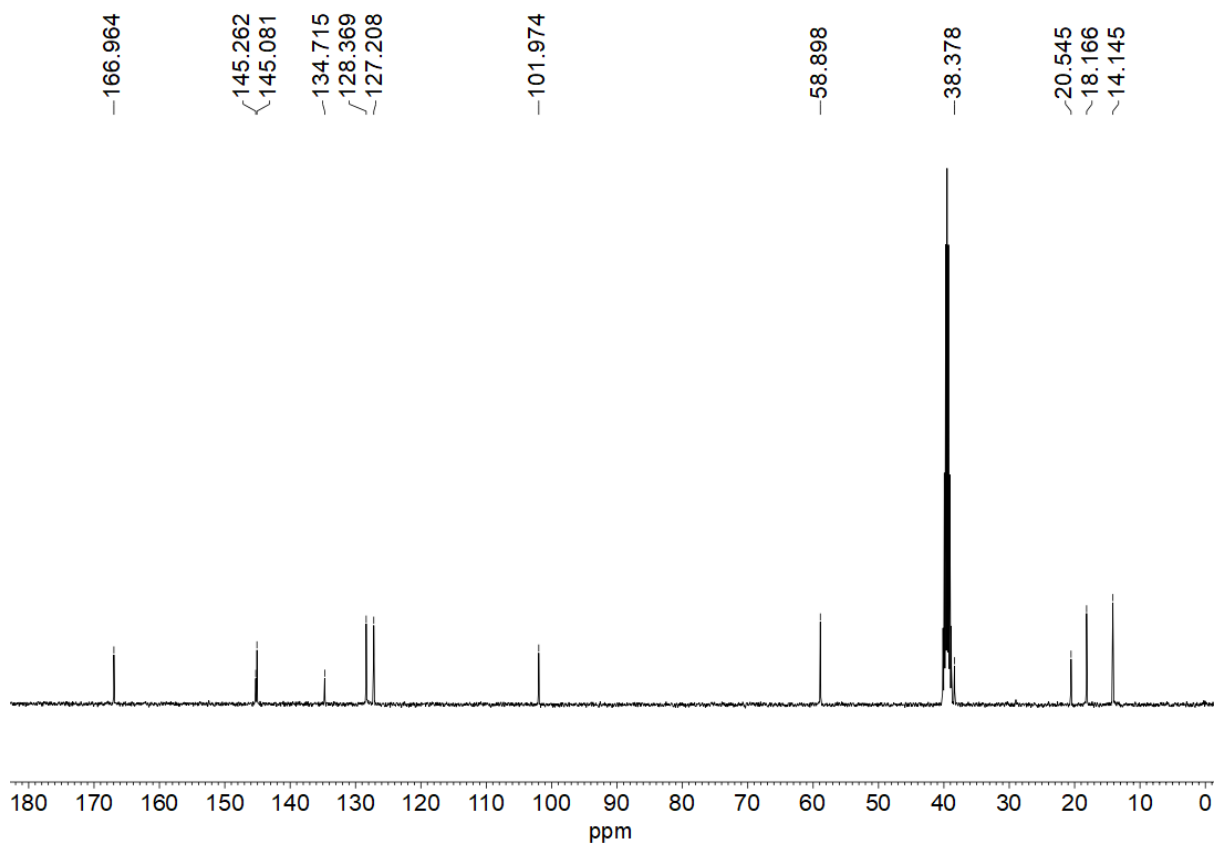


Figure S45. The ^{13}C -NMR spectrum of **6e**.

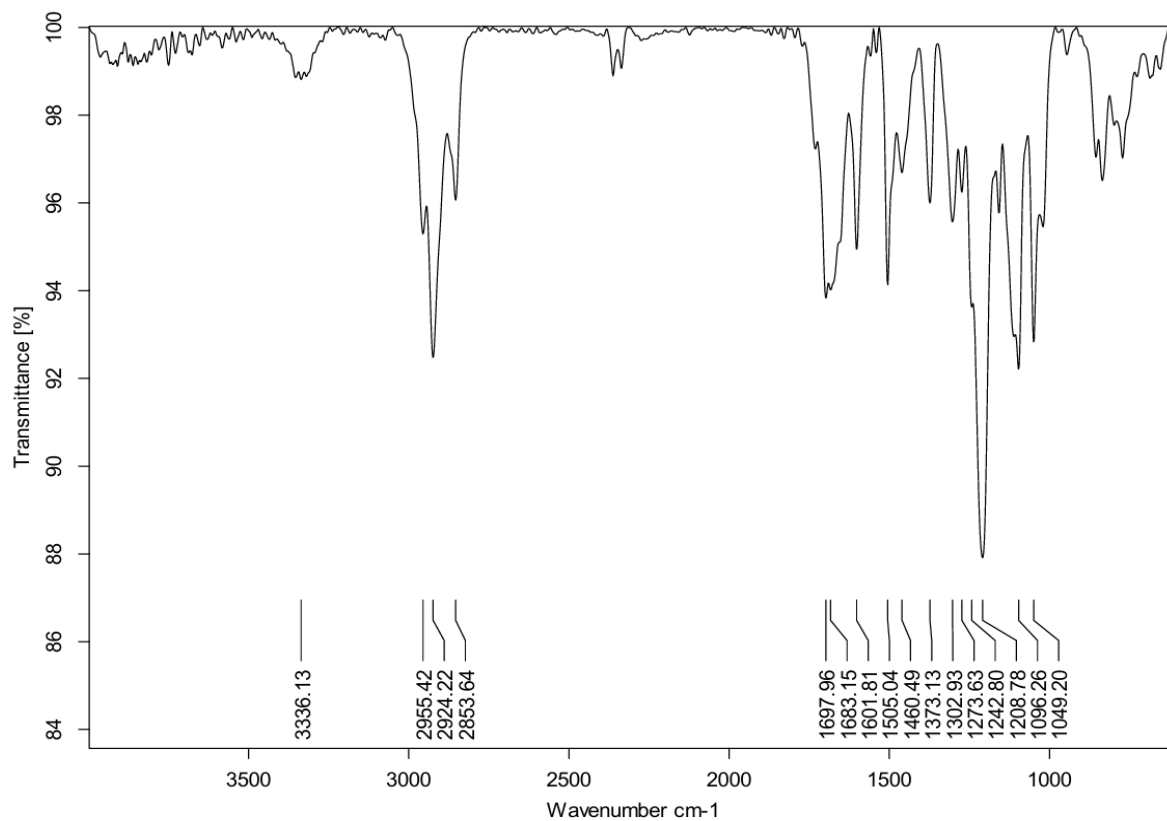


Figure S46. The FTIR spectrum of **6f**.

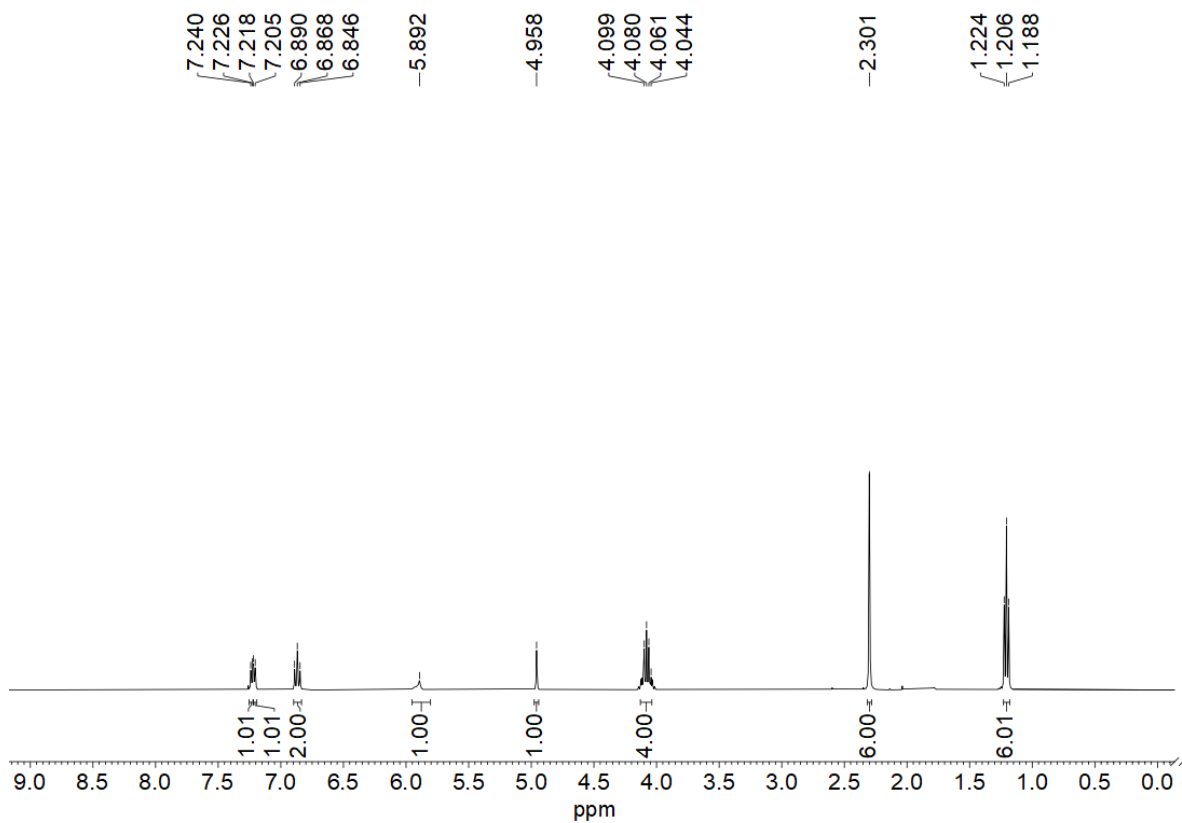


Figure S47. The ^1H -NMR spectrum of **6f**.

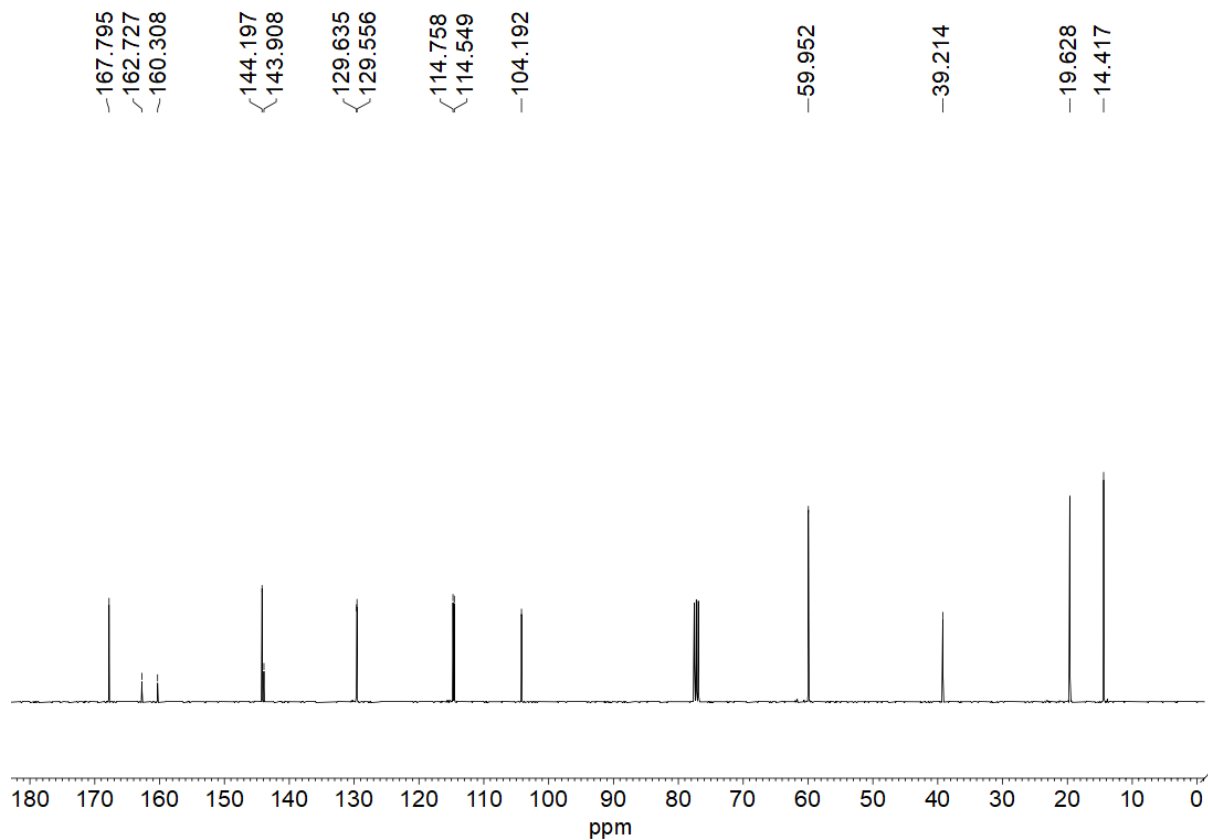


Figure S48. The ^{13}C -NMR spectrum of **6f**.

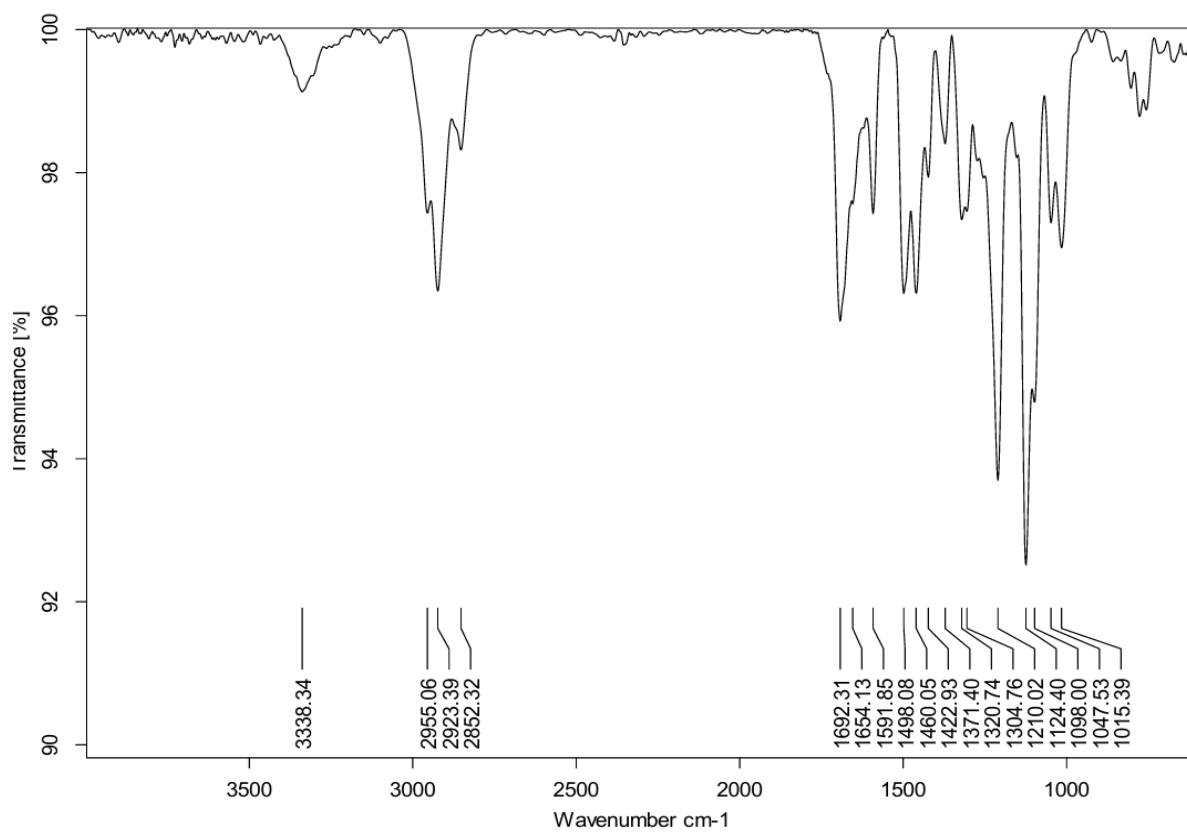


Figure S49. The FTIR spectrum of **6g**.

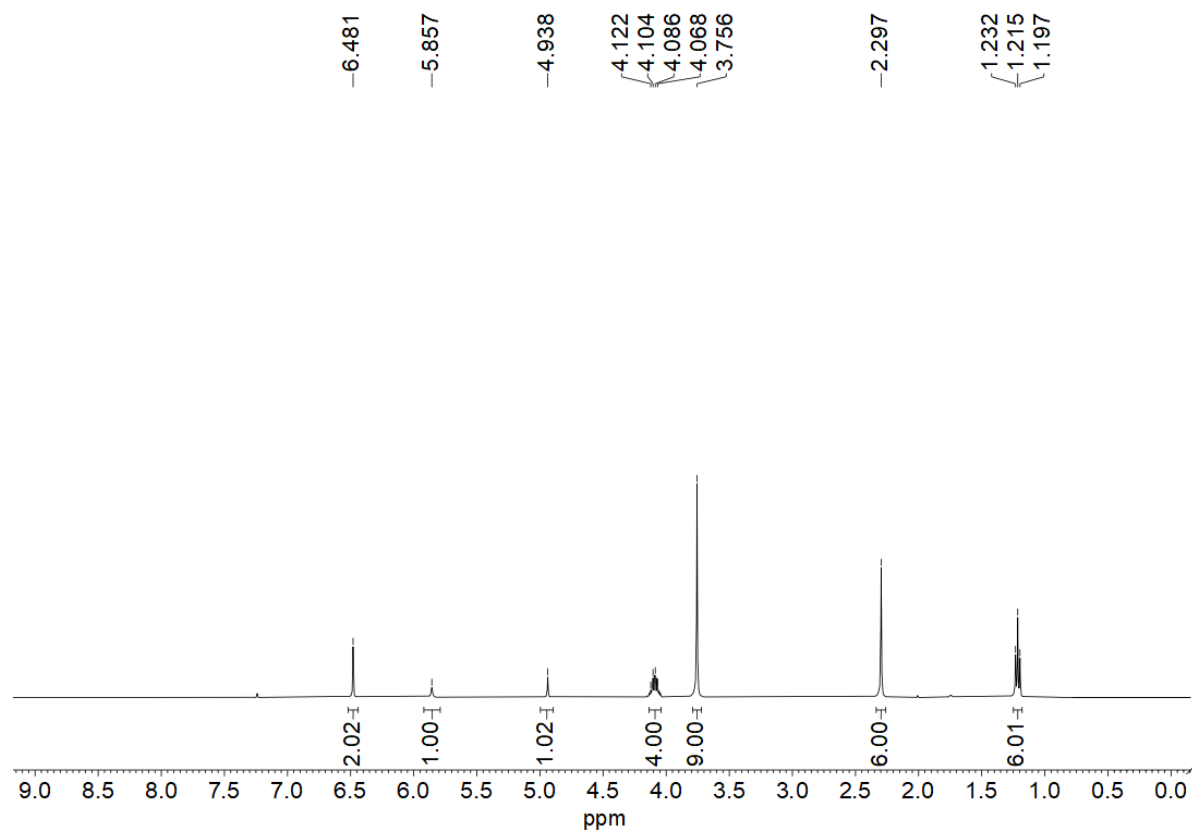


Figure S50. The ¹H-NMR spectrum of **6g**.

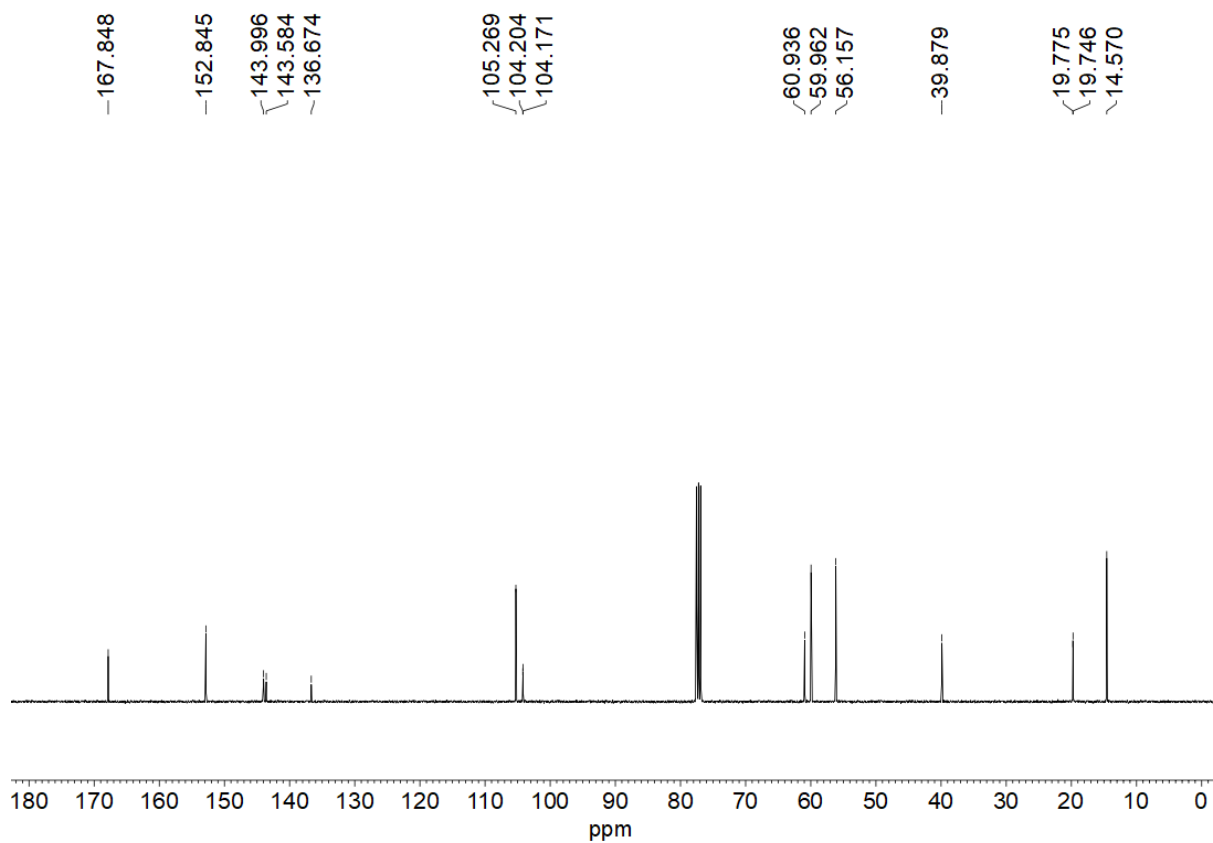


Figure S51. The ^{13}C -NMR spectrum of **6g**.

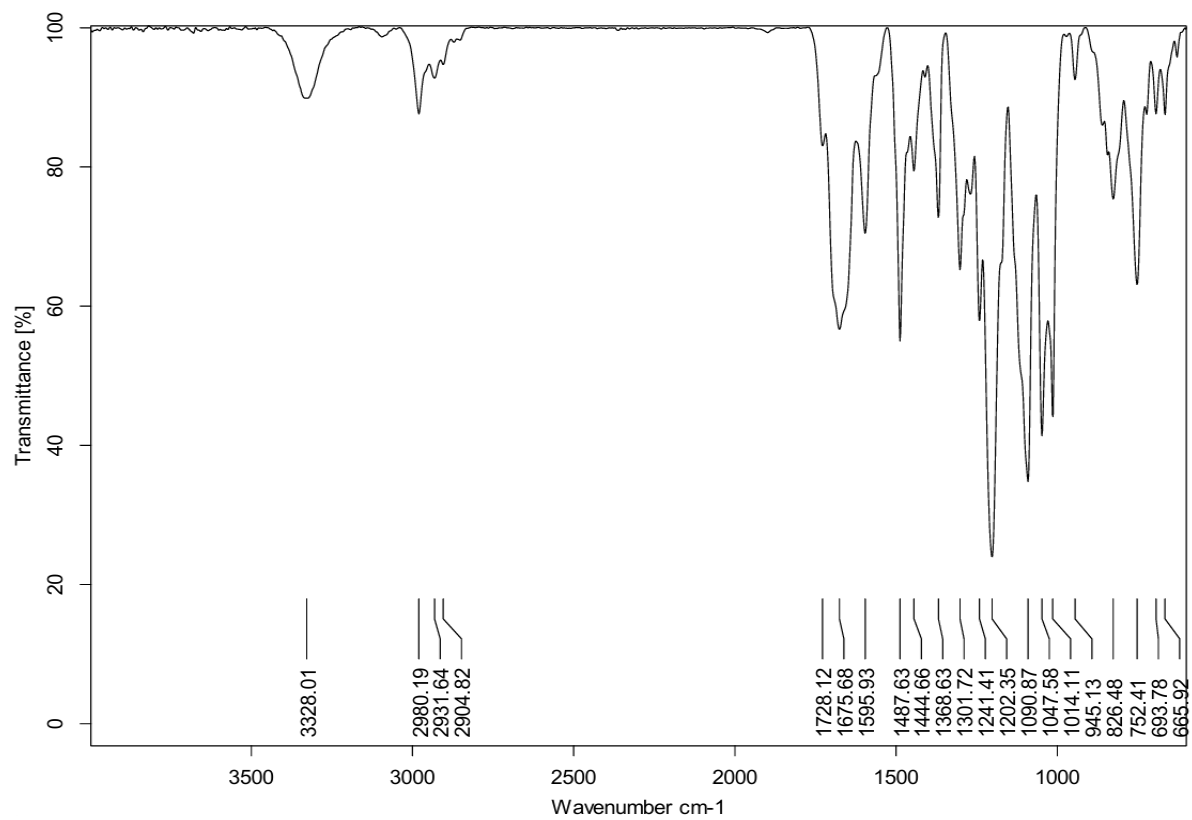


Figure S52. The FTIR spectrum of **6h**.

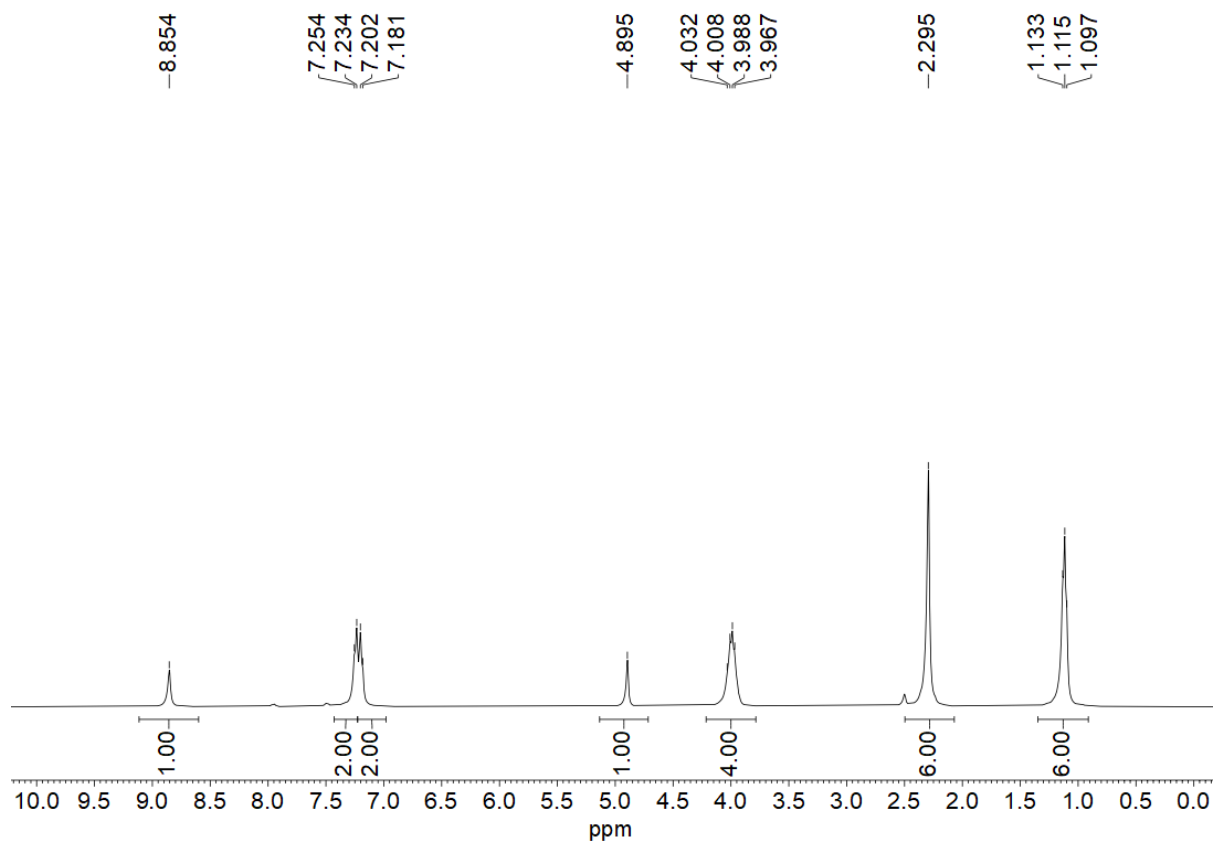


Figure S53. The ^1H -NMR spectrum of **6h**.

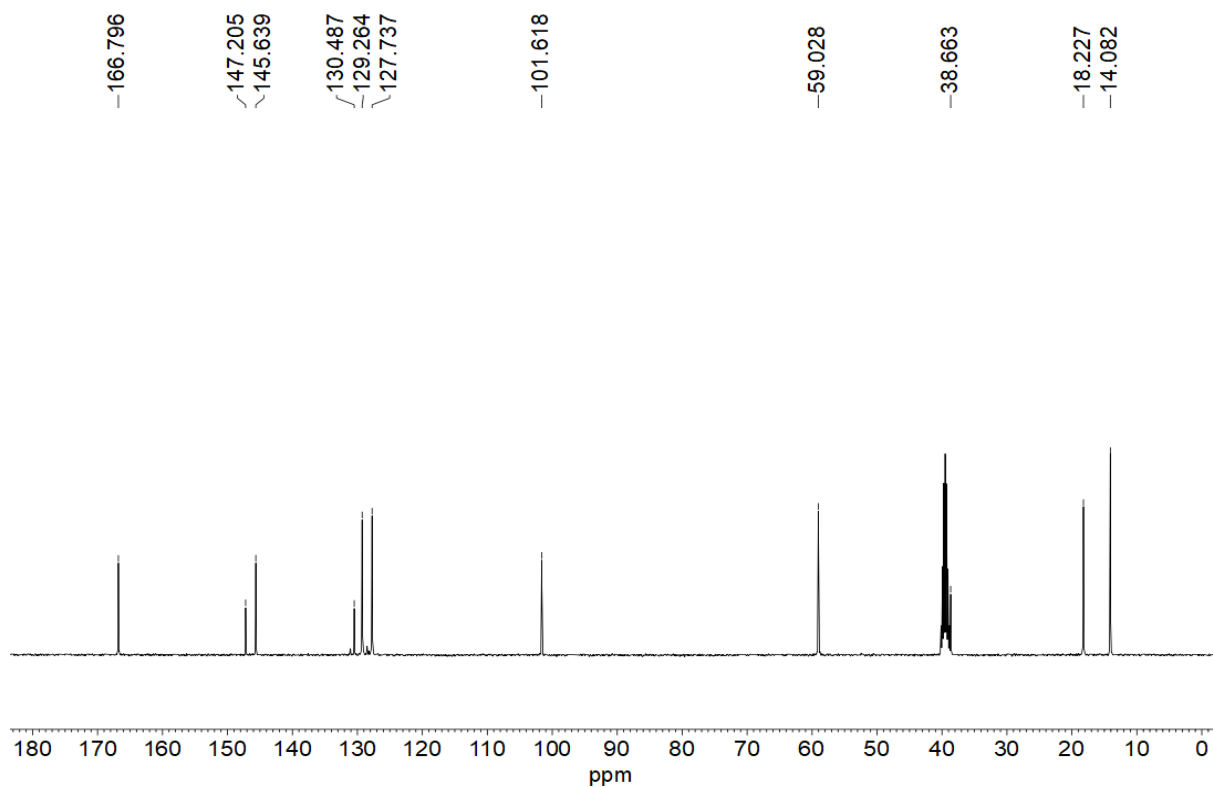


Figure S54. The ^{13}C -NMR spectrum of **6h**.

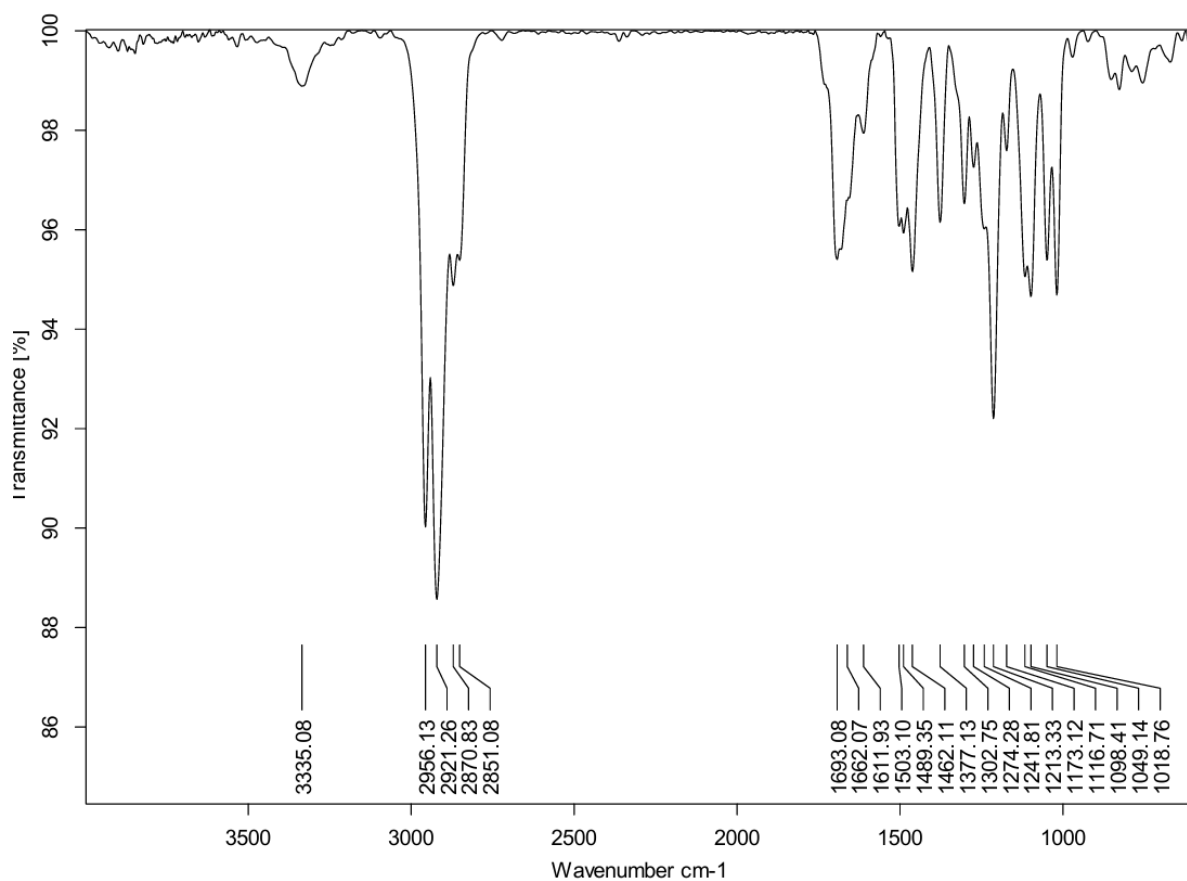


Figure S55. The FTIR spectrum of **6i**.

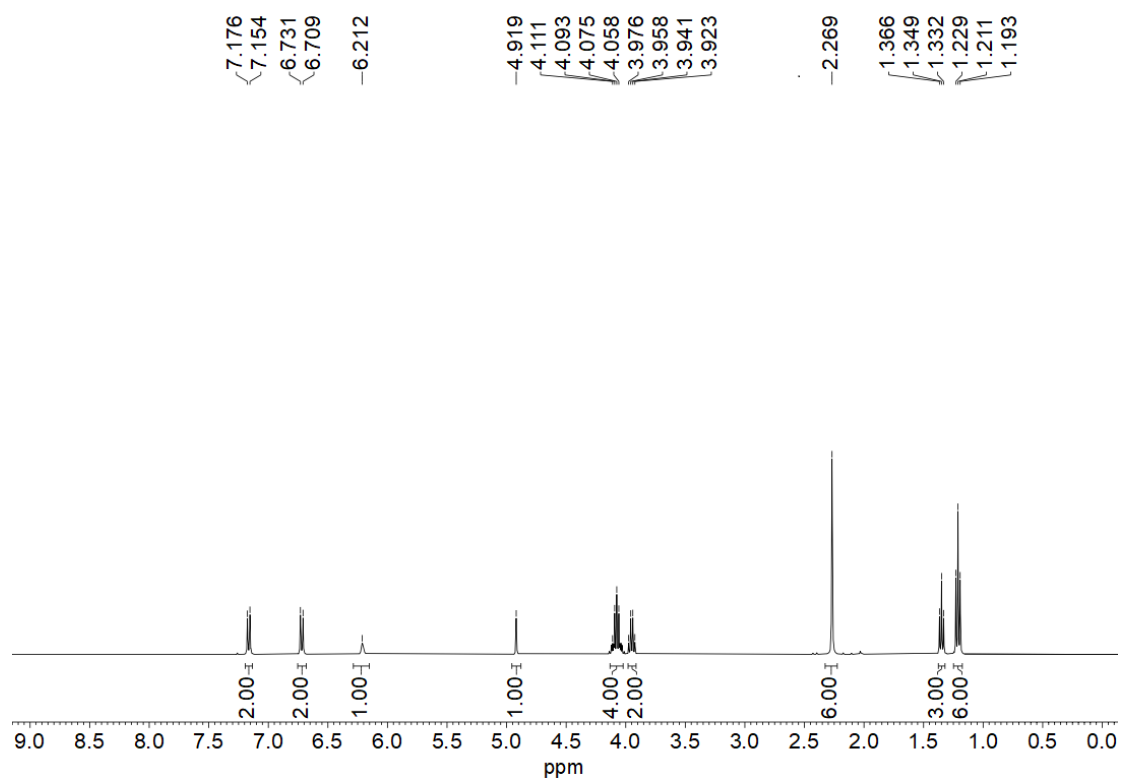


Figure S56. The ¹H-NMR spectrum of **6i**.

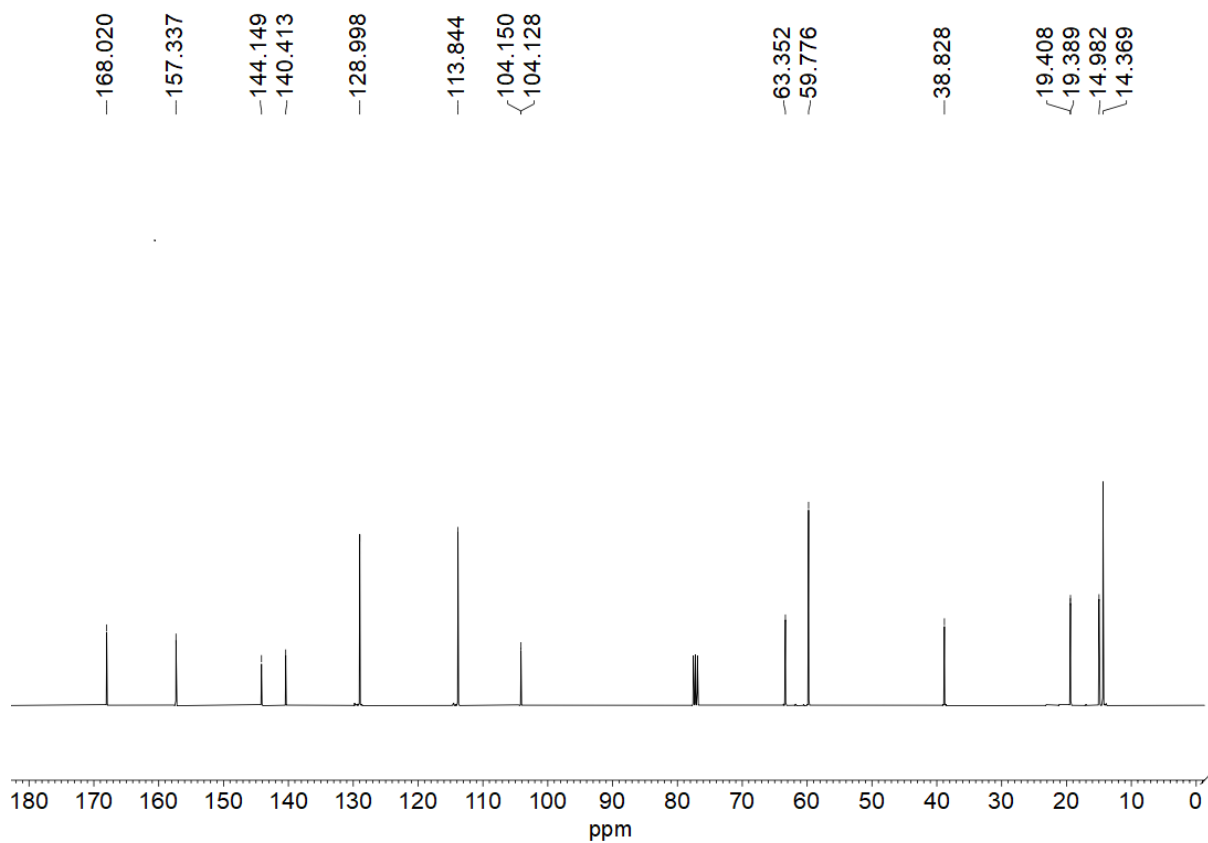


Figure S57. The ^{13}C -NMR spectrum of **6i**.

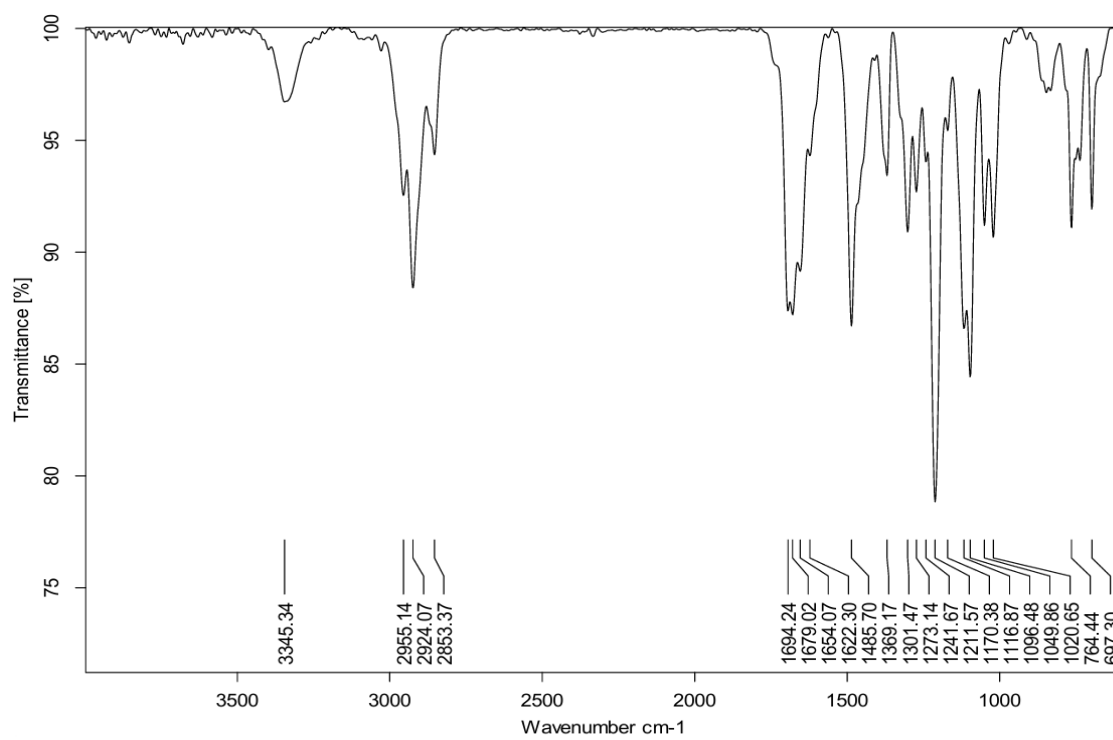


Figure S58. The FTIR spectrum of **6j**.

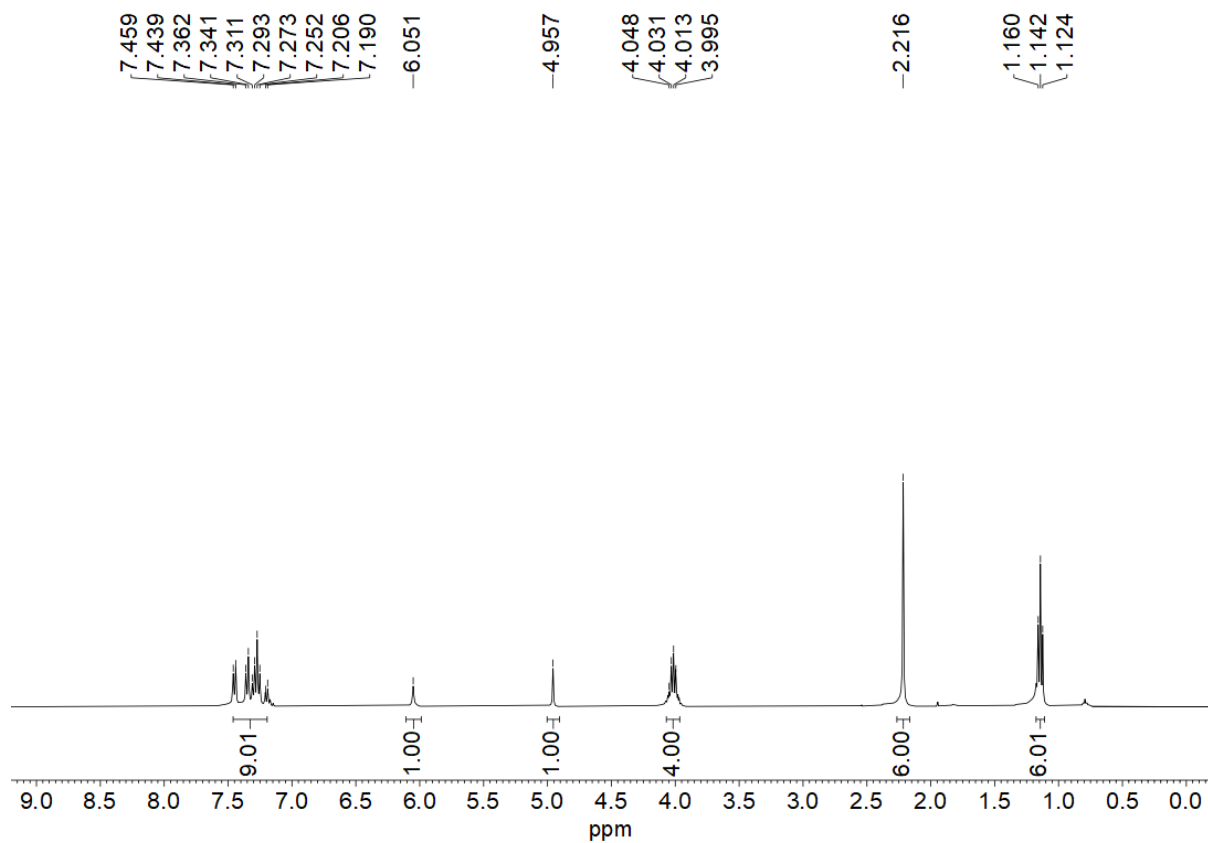


Figure S59. The ^1H -NMR spectrum of **6j**.

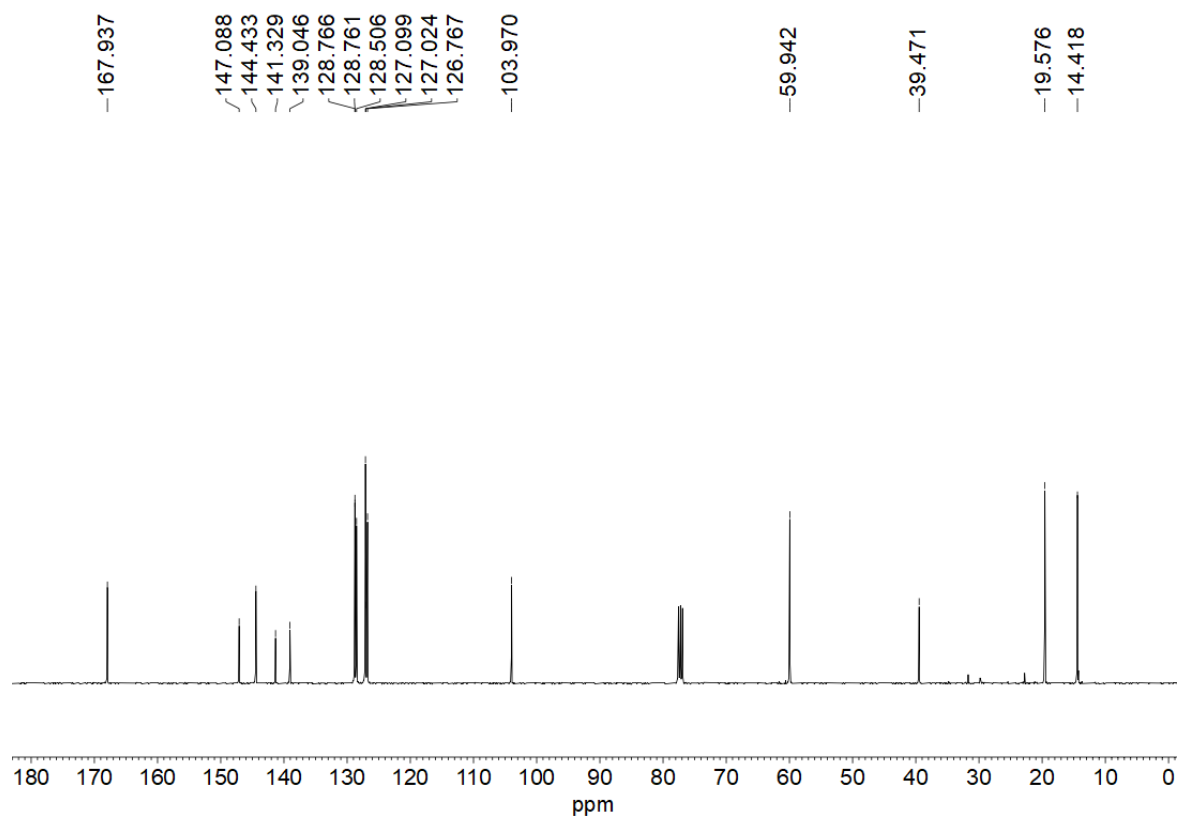


Figure S60. The ^{13}C -NMR spectrum of **6j**.

Characterization data of substituted pyridines by oxidizing 1,4-dihydropyridines (DHPs):

Diethyl 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (**7a**):^{8,9} Light yellow solid (0.486 g, 98%), Melting point: 61 °C, ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.35-7.21 (m, 5H), 3.97 (q, 4H, *J* = 7.2 Hz), 2.58 (s, 6H), 0.87 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 168.0, 155.6, 146.3, 136.7, 128.6, 128.2, 127.1, 61.5, 23.0, 13.7; FTIR (ATR, cm⁻¹): 2982, 1722, 1557, 1231, 1103, 1041.

Diethyl 4-(4-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (**7b**):^{8,9} Light yellow solid (0.482 g, 97%), Melting point: 57 °C, ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.11 (d, 2H, *J* = 8.8 Hz), 6.82 (d, 2H, *J* = 8.8 Hz), 3.97 (q, 4H, *J* = 7.2 Hz), 3.72 (s, 3H), 2.51 (s, 6H), 0.90 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 168.0, 159.9, 155.1, 145.9, 129.4, 128.6, 127.3, 113.6, 61.3, 55.2, 22.7, 13.7; FTIR (ATR, cm⁻¹): 2982, 1720, 1556, 1230, 1103, 1034.

Diethyl 2,6-dimethyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate (**7c**):⁸ Light yellow solid (0.482 g, 97%), Melting point: 114 °C, ¹H-NMR (400 MHz, CDCl₃, δ ppm): 8.19 (d, 2H, *J* = 8.4 Hz), 7.40 (d, 2H, *J* = 8.4 Hz), 3.97 (q, 4H, *J* = 7.2 Hz), 2.55 (s, 6H), 0.90 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 167.1, 156.1, 147.9, 144.0, 143.3, 129.5, 126.3, 123.2, 61.7, 23.1, 13.7; FTIR (ATR, cm⁻¹): 2982, 1720, 1556, 1227, 1102, 1038.

Diethyl 4-(4-bromophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (**7d**):⁹ Light yellow solid (0.487 g, 98%), Melting point: 51 °C, ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.49 (d, 2H, *J* = 8.4 Hz), 7.11 (d, 2H, *J* = 8.4 Hz), 4.01 (q, 4H, *J* = 7.2 Hz), 2.57 (s, 6H), 0.95 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 167.7, 155.8, 145.0, 135.6, 131.4, 130.0, 126.9, 123.0, 61.6, 23.1, 13.8; FTIR (ATR, cm⁻¹): 2981, 1720, 1555, 1228, 1101, 1039.

Diethyl 2,6-dimethyl-4-(p-tolyl)pyridine-3,5-dicarboxylate (**7e**):^{8,9} Light yellow solid (0.477 g, 96%), Melting point: 72 °C, ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.10 (d, 2H, *J* = 8.4 Hz), 7.07 (d, 2H, *J* = 8.4 Hz), 3.96 (q, 4H, *J* = 7.2 Hz), 2.53 (s, 6H), 2.29 (s, 3H), 0.88 (t, 6H, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 168.0, 155.2, 146.2, 138.3, 133.6, 128.8, 128.7, 128.0, 127.1, 61.3, 22.8, 21.2, 13.6; FTIR (ATR, cm⁻¹): 2981, 1720, 1555, 1229, 1102, 1039.

Diethyl 4-(4-fluorophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (**7f**):^{8,9} Light yellow oil (0.482 g, 97%), ¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.23 (d, 1H, *J* = 8.4 Hz), 7.20 (d, 1H, *J*

= 8.8 Hz), 7.05 (d, 1H, $J = 8.8$ Hz), 7.03 (d, 1H, $J = 8.4$), 4.01 (q, 4H, $J = 7.2$ Hz), 2.57 (s, 6H), 0.94 (t, 6H, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ ppm): 167.9, 164.2, 161.7, 155.6, 145.1, 132.5, 130.3, 130.2, 127.2, 115.4, 115.2, 61.6, 23.0, 13.8; FTIR (ATR, cm^{-1}): 2983, 1720, 1557, 1226, 1101, 1039.

Diethyl 2,6-dimethyl-4-(3,4,5-trimethoxyphenyl)pyridine-3,5-dicarboxylate (**7g**):⁸ Light yellow solid (0.467 g, 94%), Melting point: 105 °C., ^1H -NMR (400 MHz, CDCl_3 , δ ppm): 6.47 (s, 2H), 4.04 (q, 4H, $J = 7.2$ Hz), 3.82 (s, 3H), 3.79 (s, 6H), 2.56 (s, 6H), 0.96 (t, 6H, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ ppm): 168.2, 155.5, 153.1, 145.9, 138.3, 132.1, 127.0, 105.7, 61.1, 61.1, 56.3, 23.0, 13.9; FTIR (ATR, cm^{-1}): 2973, 1720, 1554, 1228, 1103, 1044.

Diethyl 4-(4-chlorophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (**7h**):⁹ Light yellow solid (0.472 g, 95%), Melting point: 70 °C, ^1H -NMR (400 MHz, CDCl_3 , δ ppm): 7.33 (d, 2H, $J = 8.4$ Hz), 7.17 (d, 2H, $J = 8.4$ Hz), 4.01 (q, 4H, $J = 7.2$ Hz), 2.57 (s, 6H), 0.95 (t, 6H, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ ppm): 167.7, 155.7, 145.0, 135.1, 134.8, 129.7, 128.5, 126.9, 61.6, 23.0, 13.8; FTIR (ATR, cm^{-1}): 2982, 1720, 1555, 1228, 1102, 1039.

Diethyl 4-(4-ethoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (**7i**):¹⁰ Light yellow oil (0.477 g, 96%), ^1H -NMR (400 MHz, CDCl_3 , δ ppm): 7.13 (d, 2H, $J = 8.8$ Hz), 6.84 (d, 2H, $J = 8.8$ Hz), 4.00 (q, 6H, $J = 7.2$ Hz), 2.54 (s, 6H), 1.37 (t, 3H, $J = 7.2$ Hz), 0.93 (t, 6H, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ ppm): 168.1, 159.2, 155.2, 145.9, 129.5, 128.6, 127.3, 114.2, 63.5, 61.4, 22.9, 14.8, 13.8; FTIR (ATR, cm^{-1}): 2981, 1720, 1556, 1229, 1102, 1038.

Diethyl 4-([1,1'-biphenyl]-4-yl)-2,6-dimethylpyridine-3,5-dicarboxylate (**7j**):⁷ Light yellow solid (0.472 g, 95%), Melting point: 142 °C, ^1H -NMR (400 MHz, CDCl_3 , δ ppm): 7.62-7.32 (m, 9H), 4.03 (q, 4H, $J = 7.2$ Hz), 2.62 (s, 6H), 0.92 (t, 6H, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ ppm): 168.0, 155.6, 146.0, 141.5, 140.4, 135.7, 129.0, 128.7, 127.8, 127.2, 127.1, 126.9, 61.5, 23.0, 13.7; FTIR (ATR, cm^{-1}): 2981, 1720, 1560, 1230, 1103, 1040.

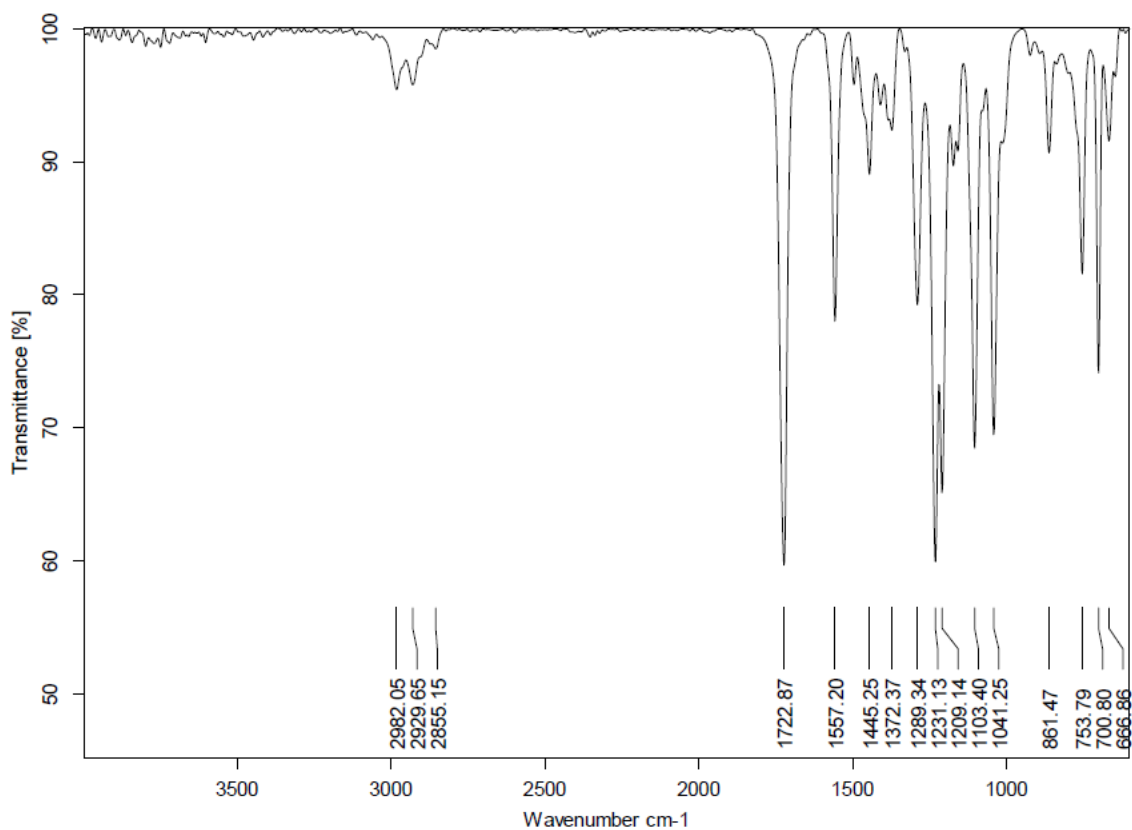


Figure S61. The FTIR spectrum of **7a**.

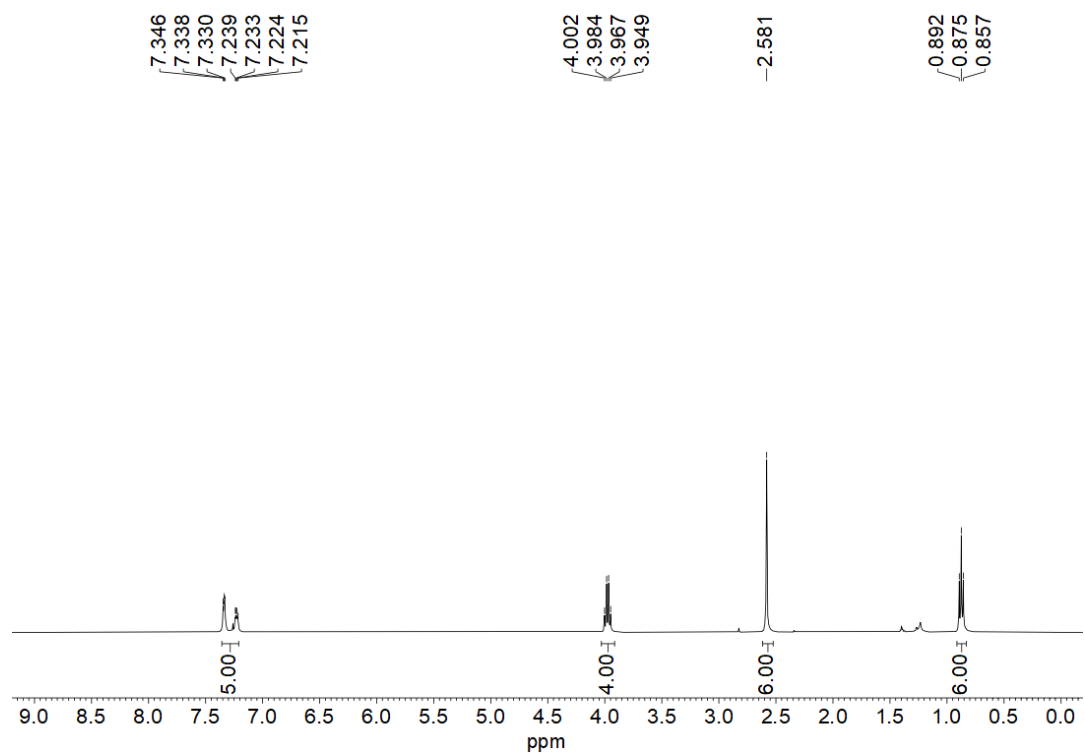


Figure S62. The ¹H-NMR spectrum of **7a**.

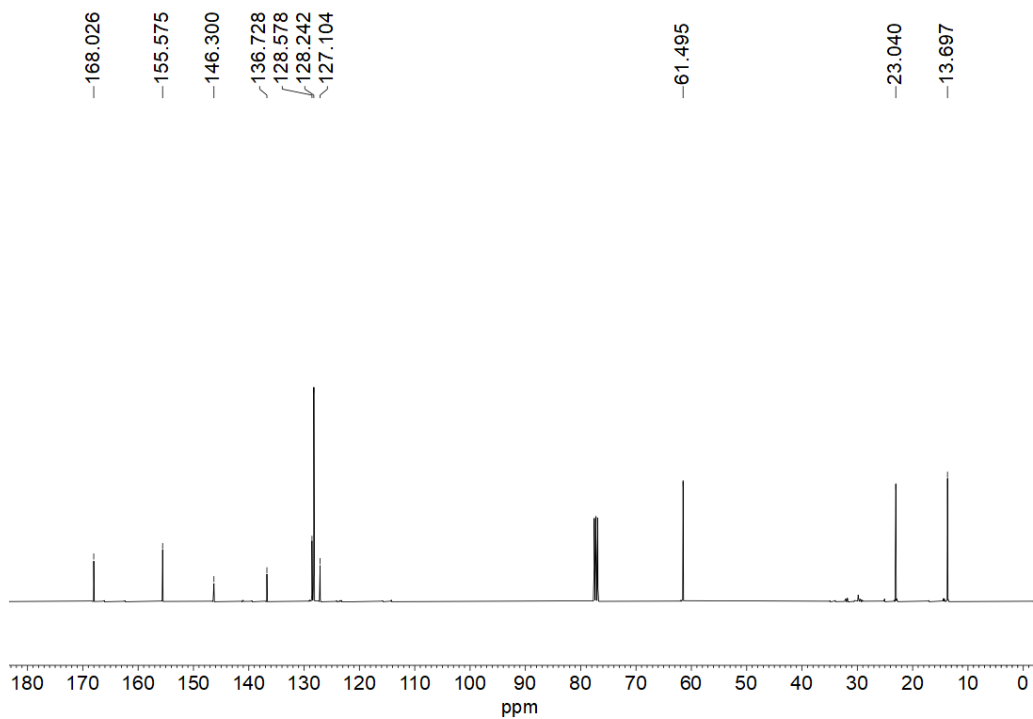


Figure S63. The ^{13}C -NMR spectrum of 7a.

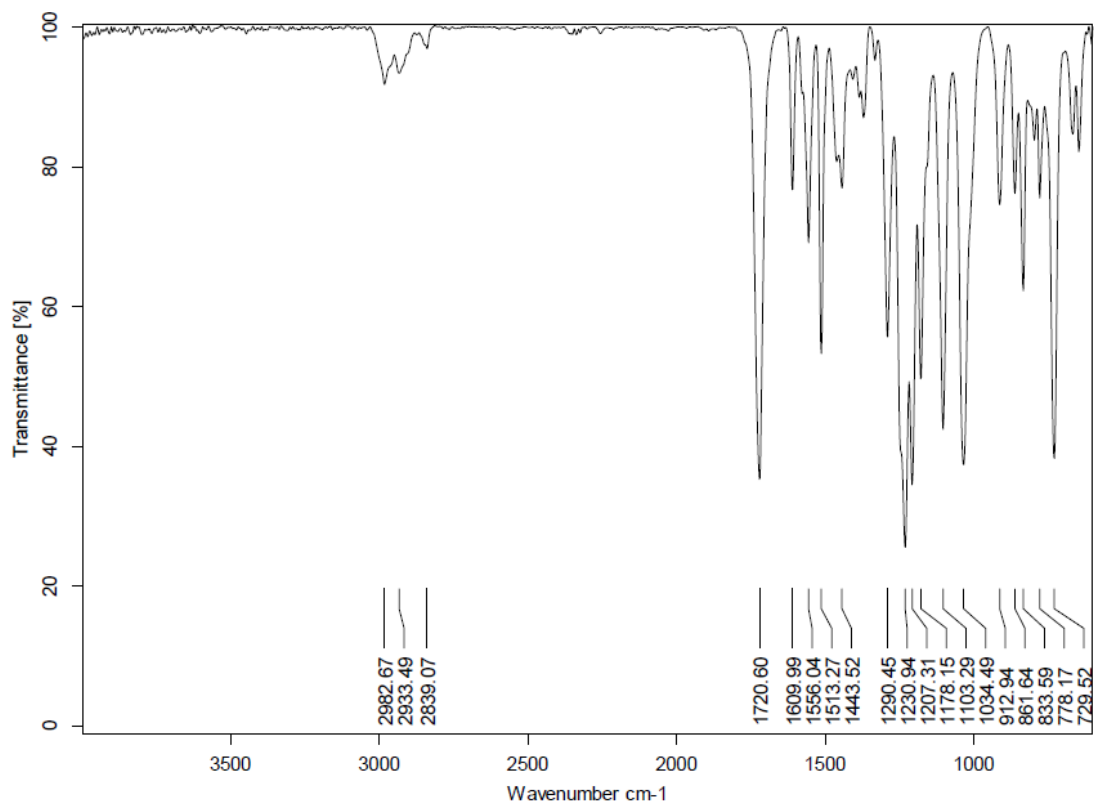


Figure S64. The FTIR spectrum of 7b.

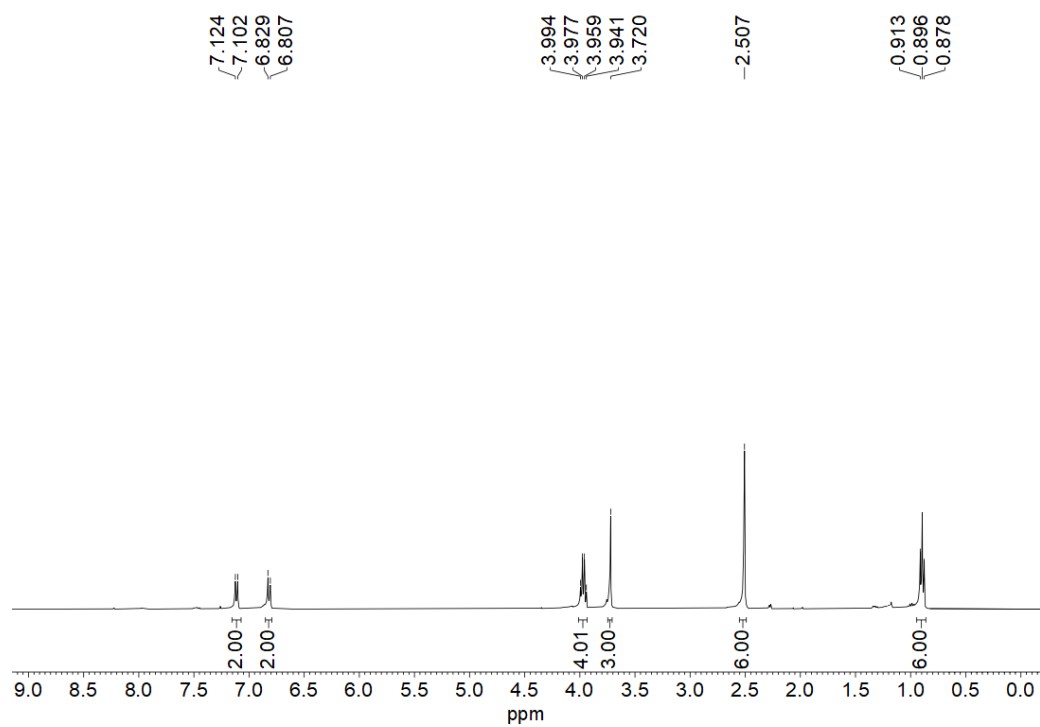


Figure S65. The ^1H -NMR spectrum of **7b**.

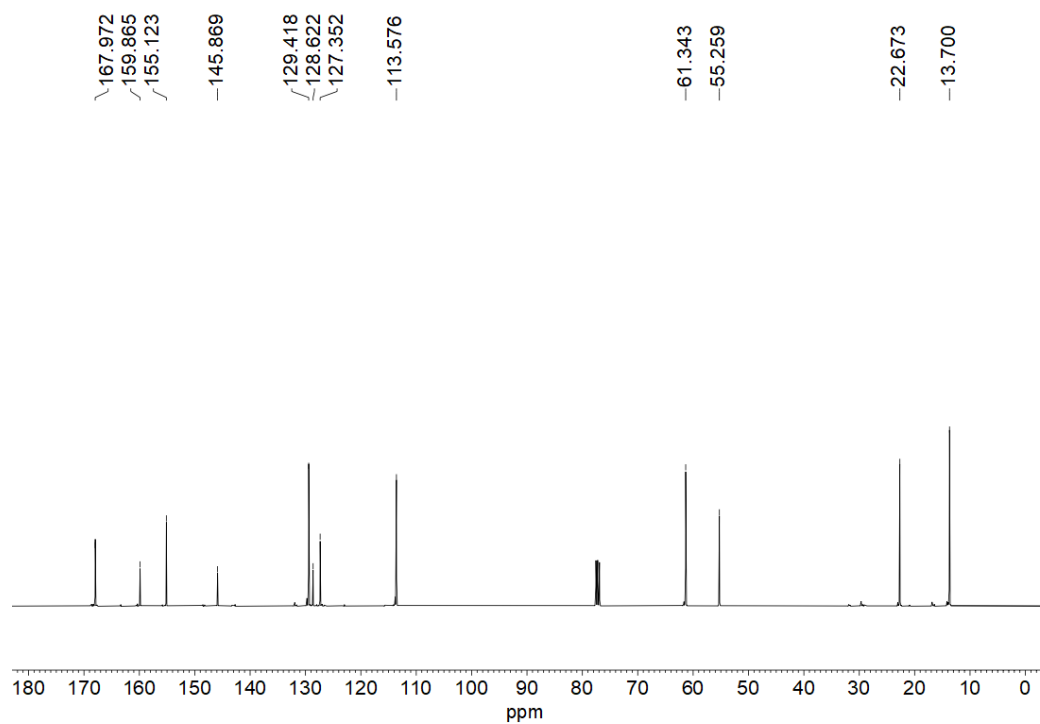


Figure S66. The ^{13}C -NMR spectrum of **7b**.

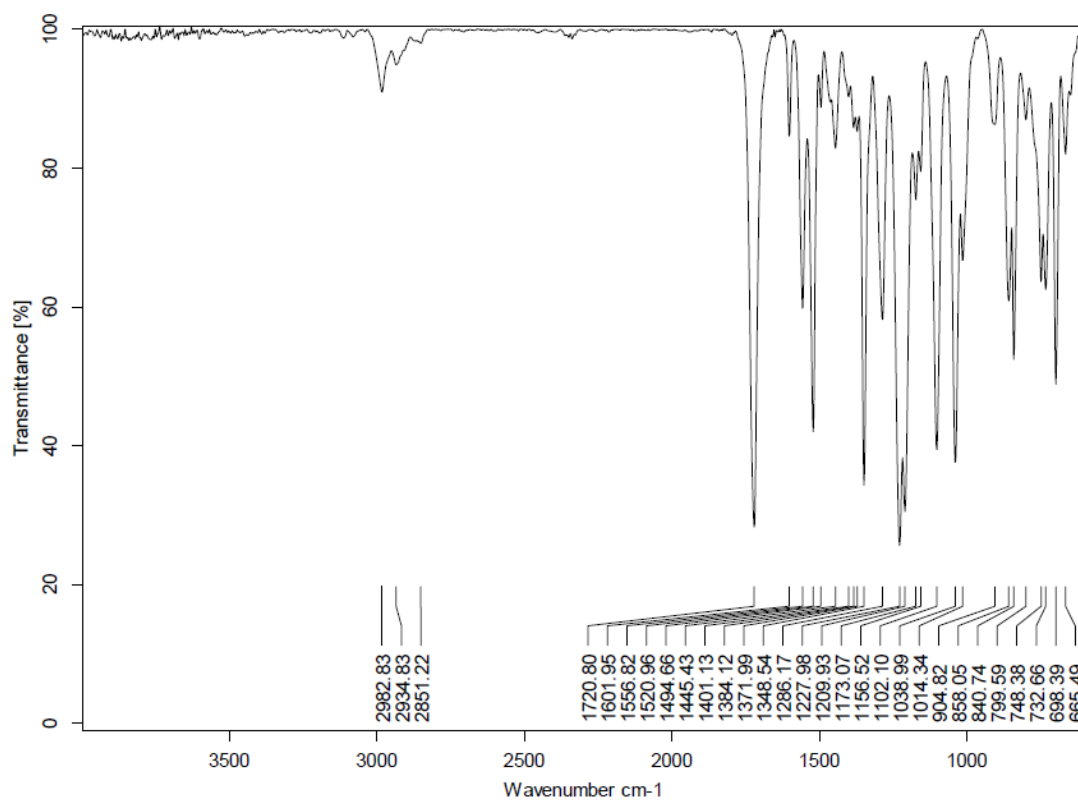


Figure S67. The FTIR spectrum of **7c**.

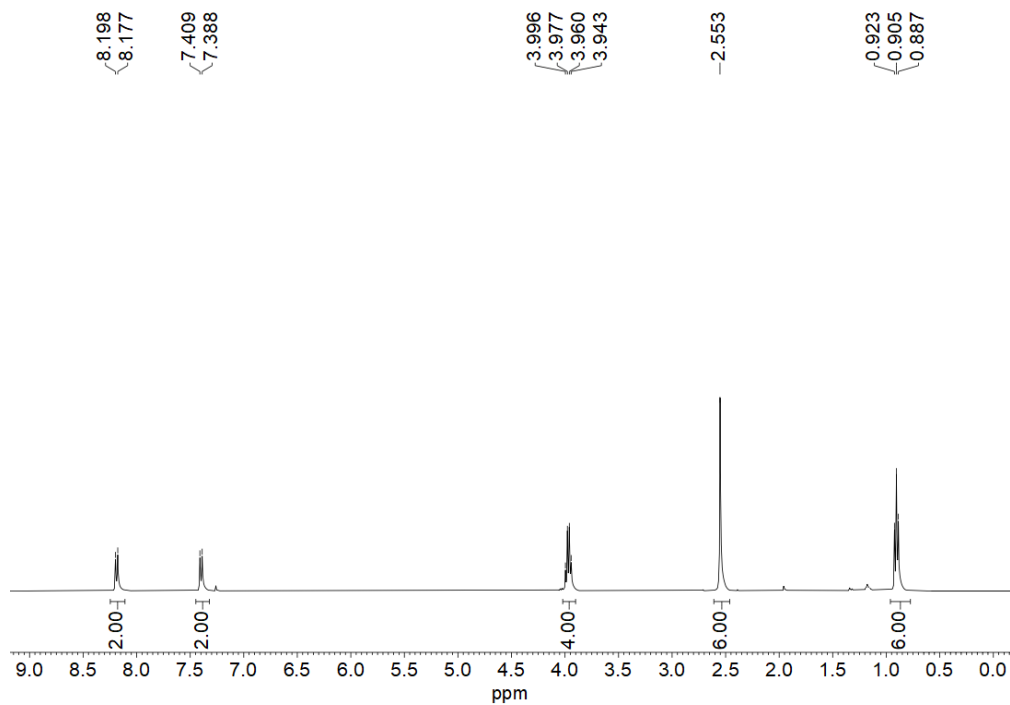


Figure S68. The ¹H-NMR spectrum of **7c**.

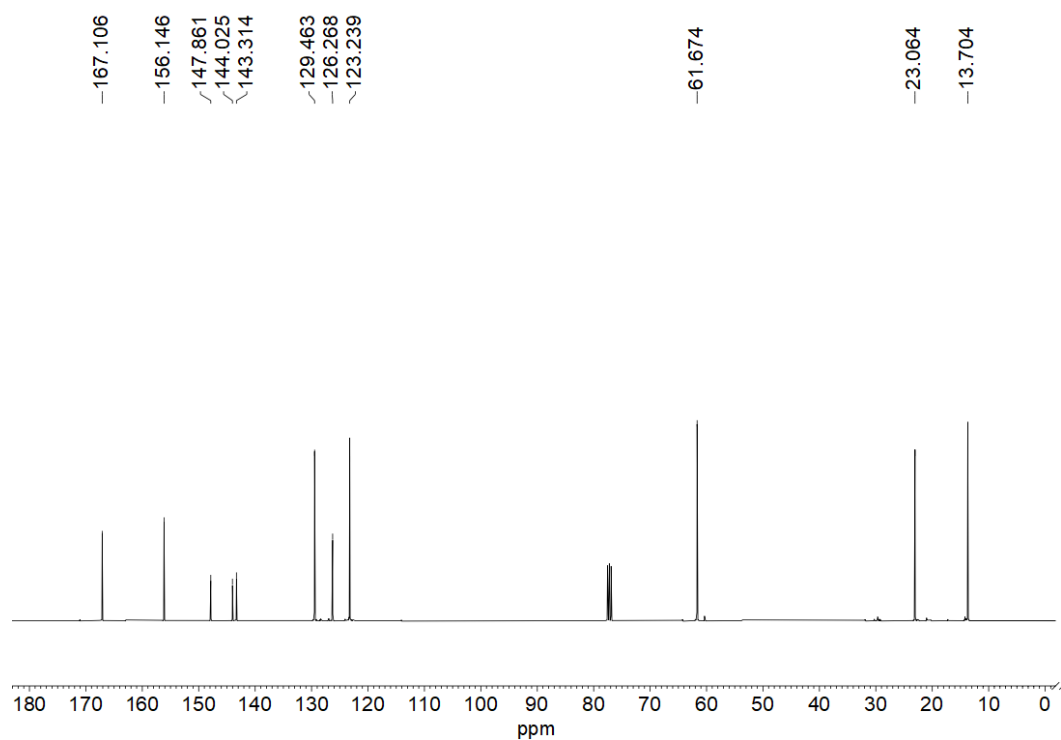


Figure S69. The ^{13}C -NMR spectrum of **7c**.

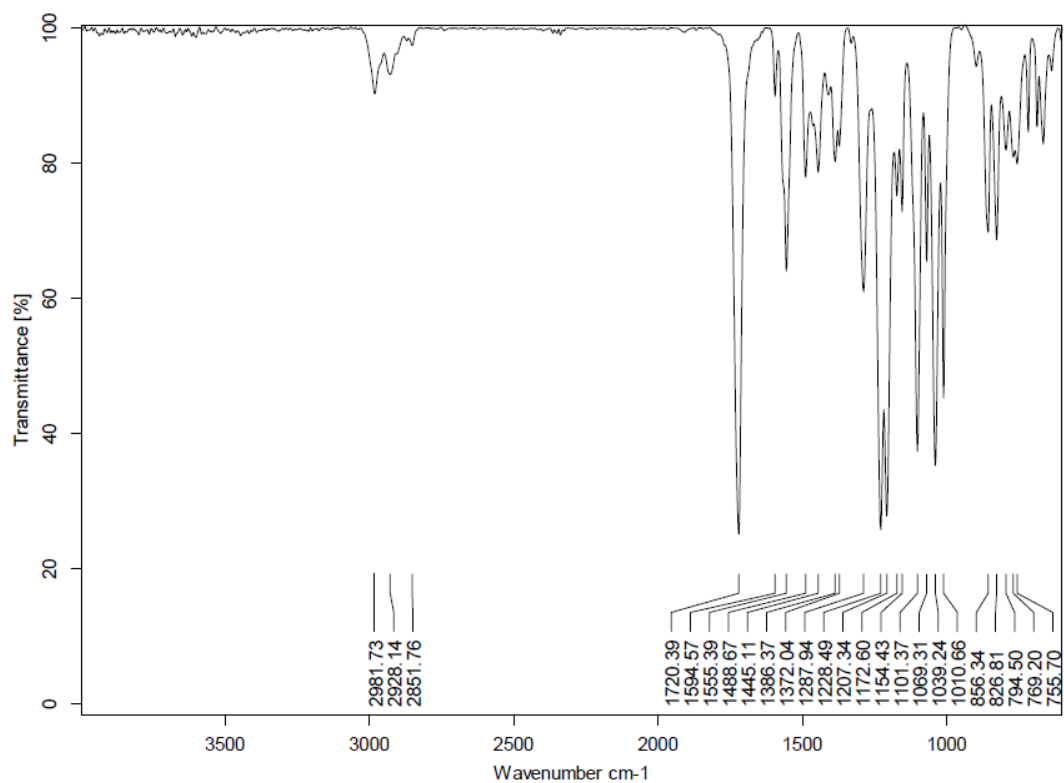


Figure S70. The FTIR spectrum of **7d**.

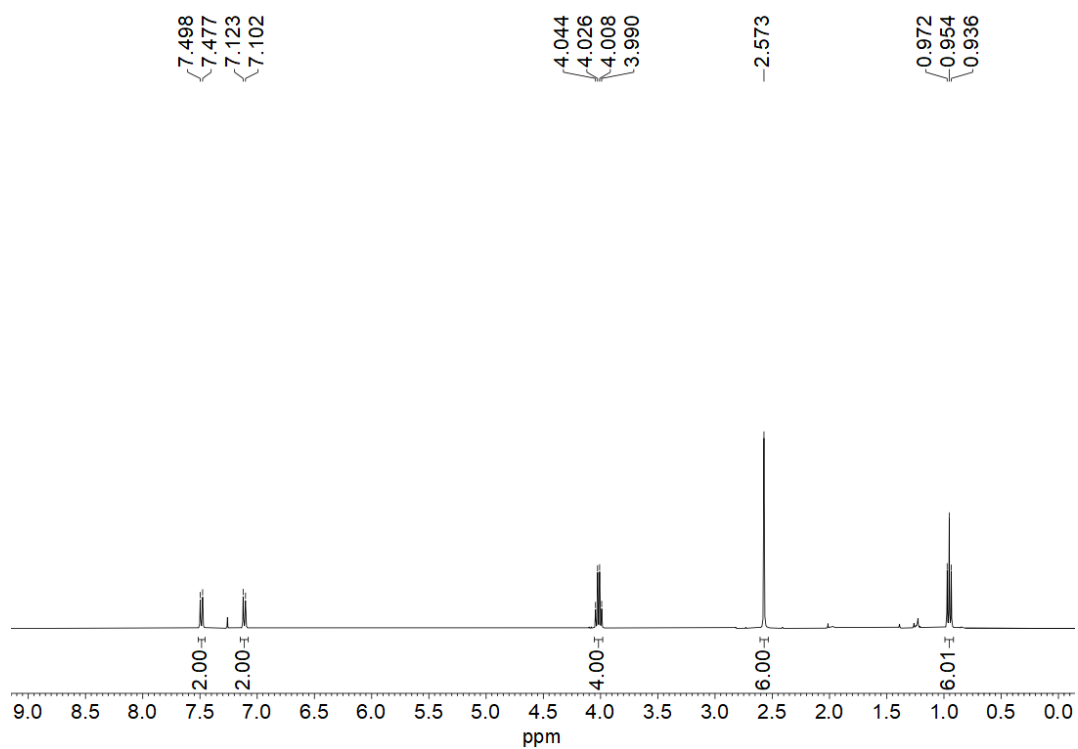


Figure S71. The ^1H -NMR spectrum of **7d**.

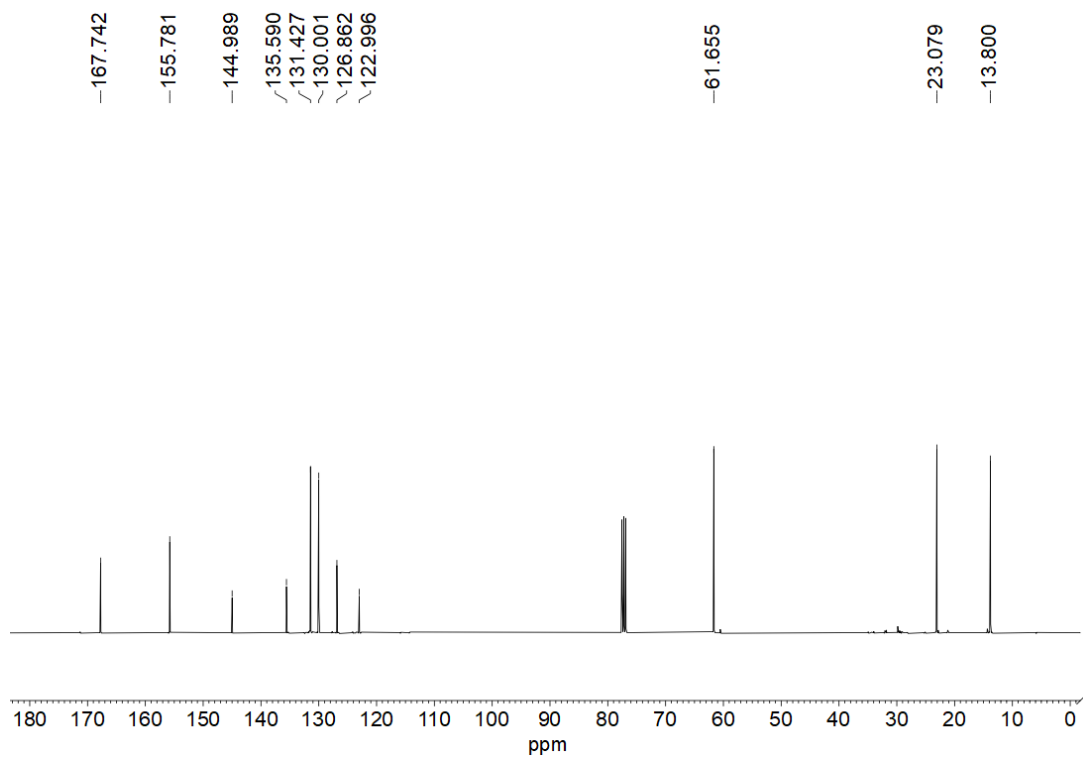


Figure S72. The ^{13}C -NMR spectrum of **7d**.

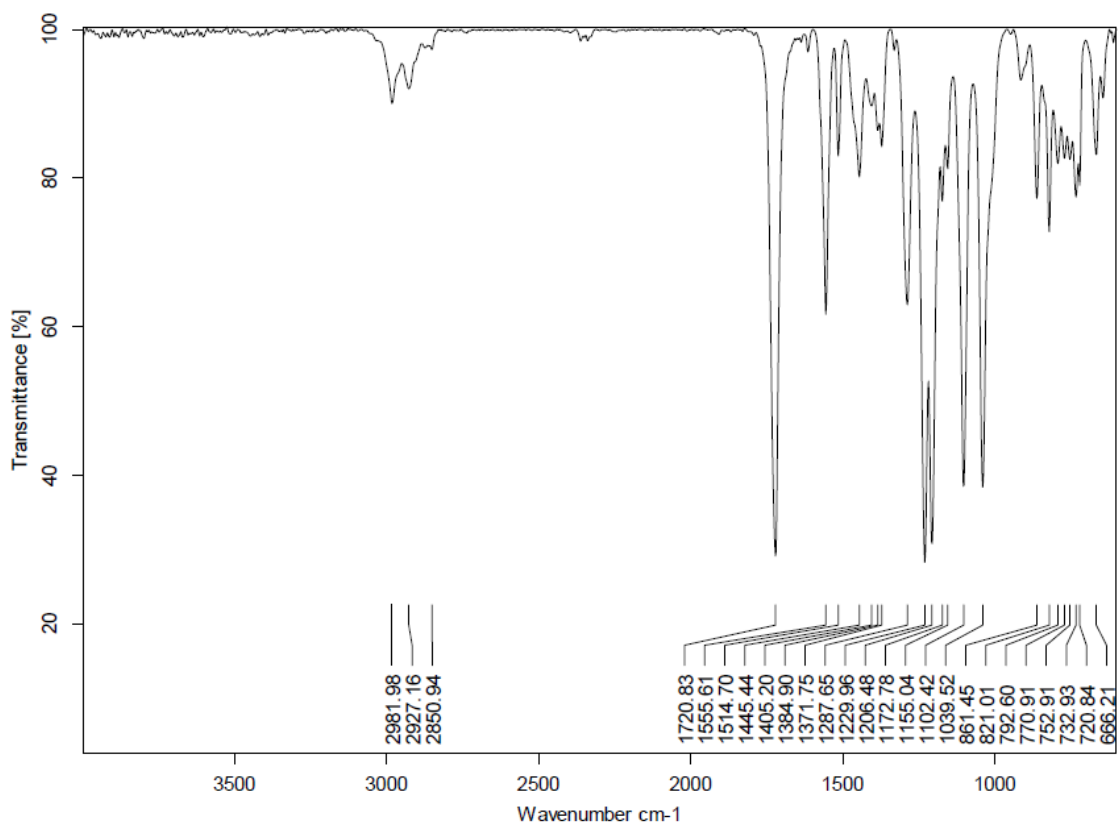


Figure S73. The FTIR spectrum of **7e**.

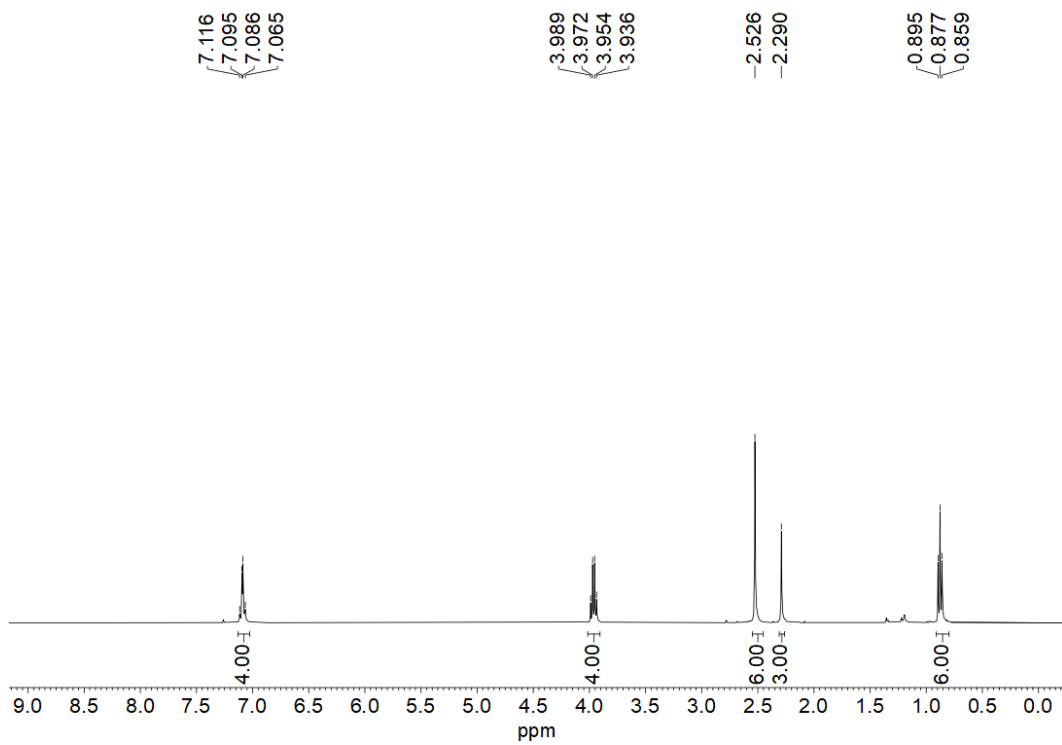


Figure S74. The ¹H-NMR spectrum of **7e**.

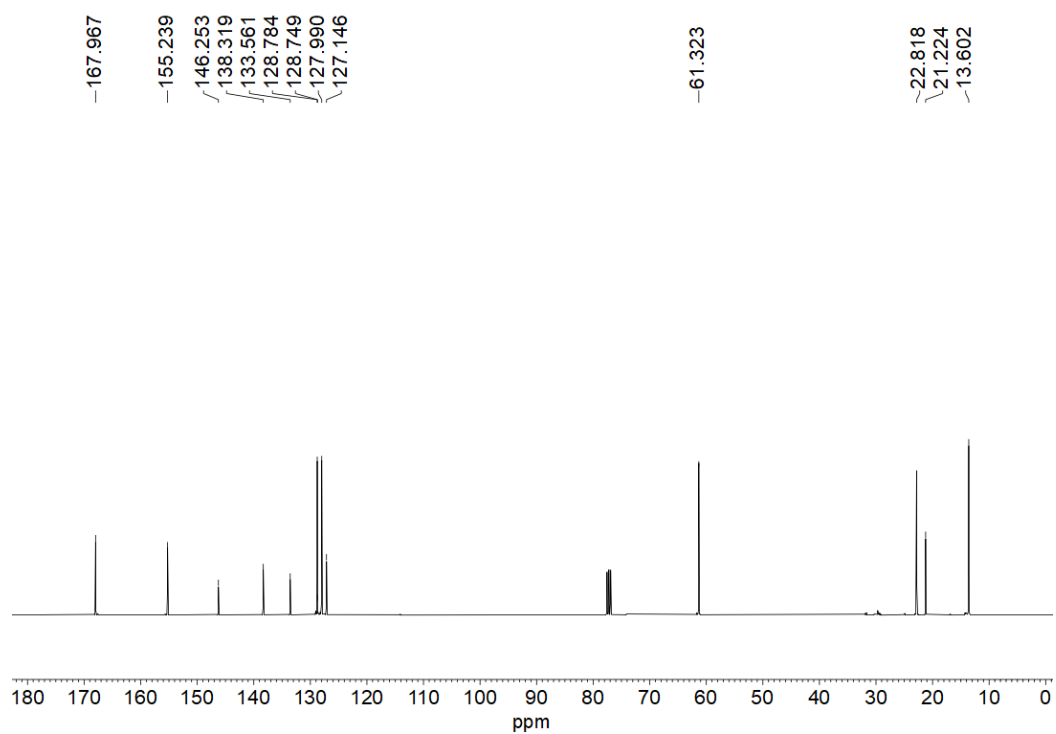


Figure S75. The ^{13}C -NMR spectrum of **7e**.

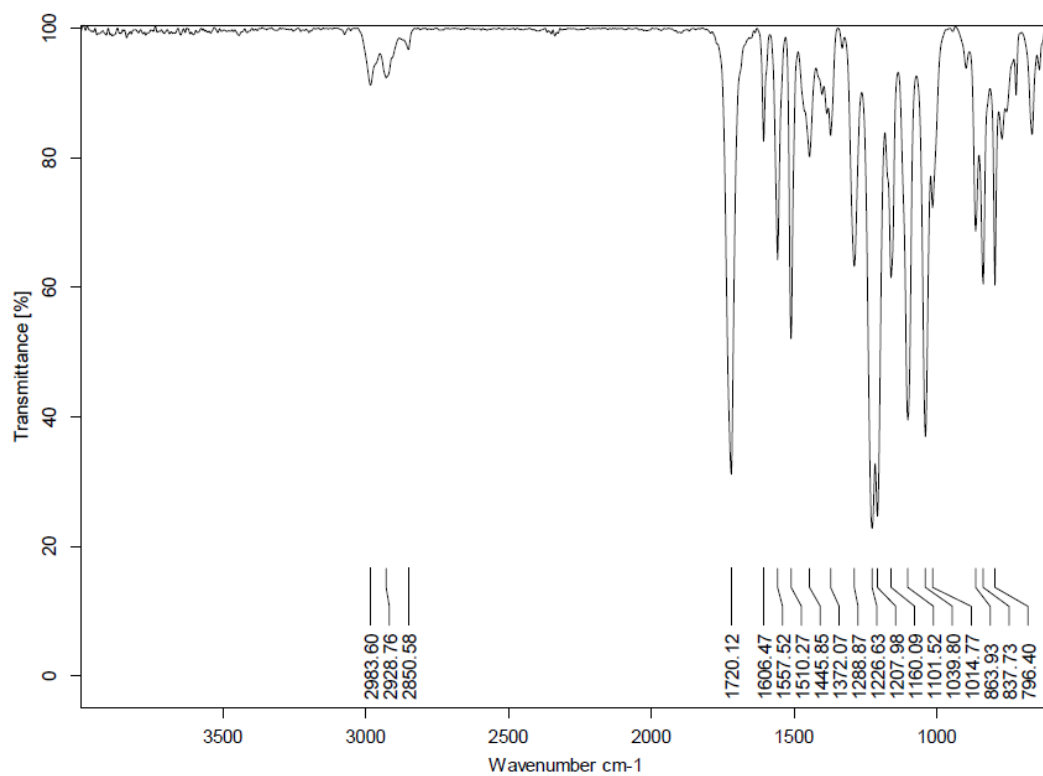


Figure S76. The FTIR spectrum of **7f**.

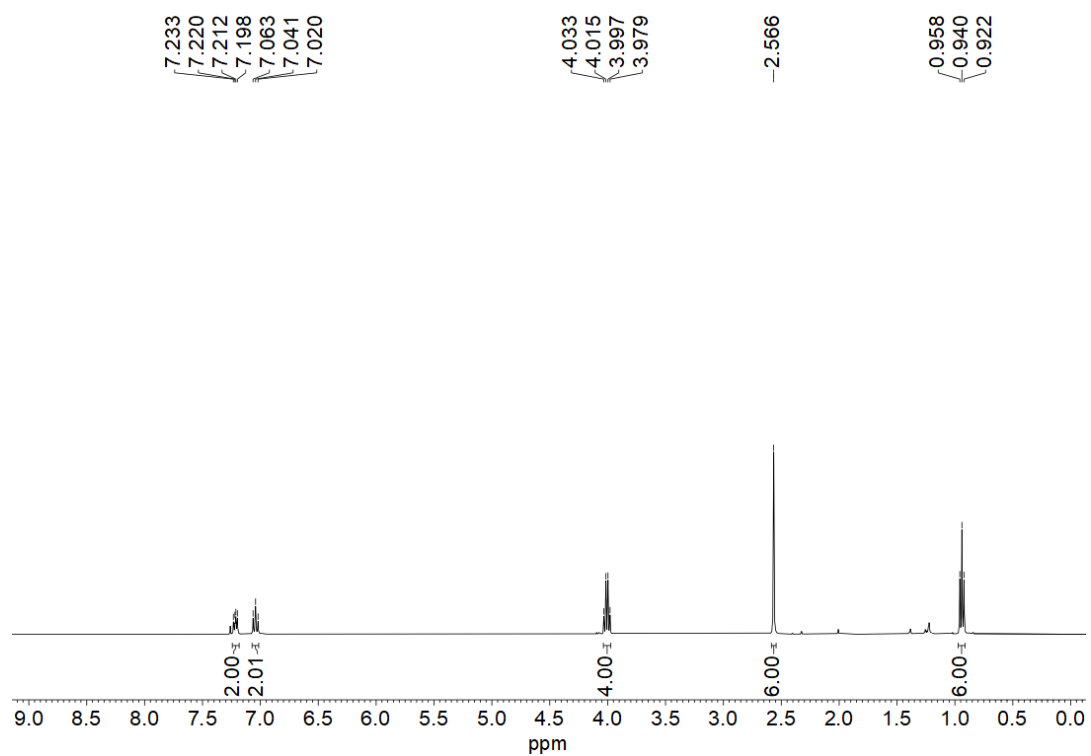


Figure S77. The ^1H -NMR spectrum of **7f**.

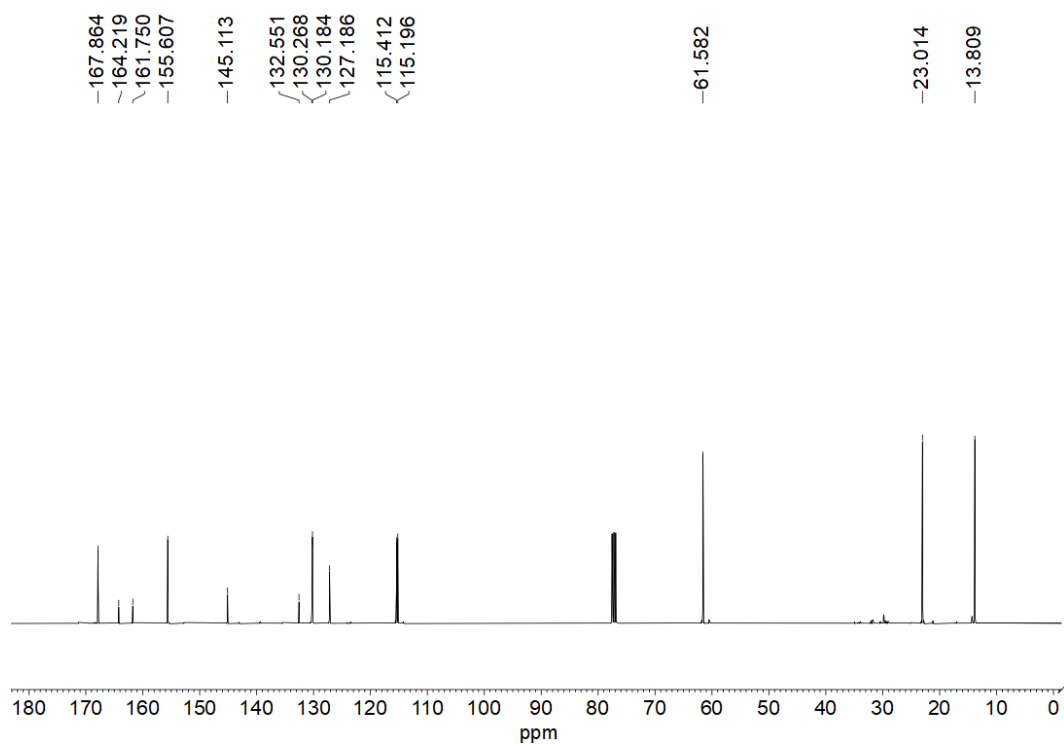


Figure S78. The ^{13}C -NMR spectrum of **7f**.

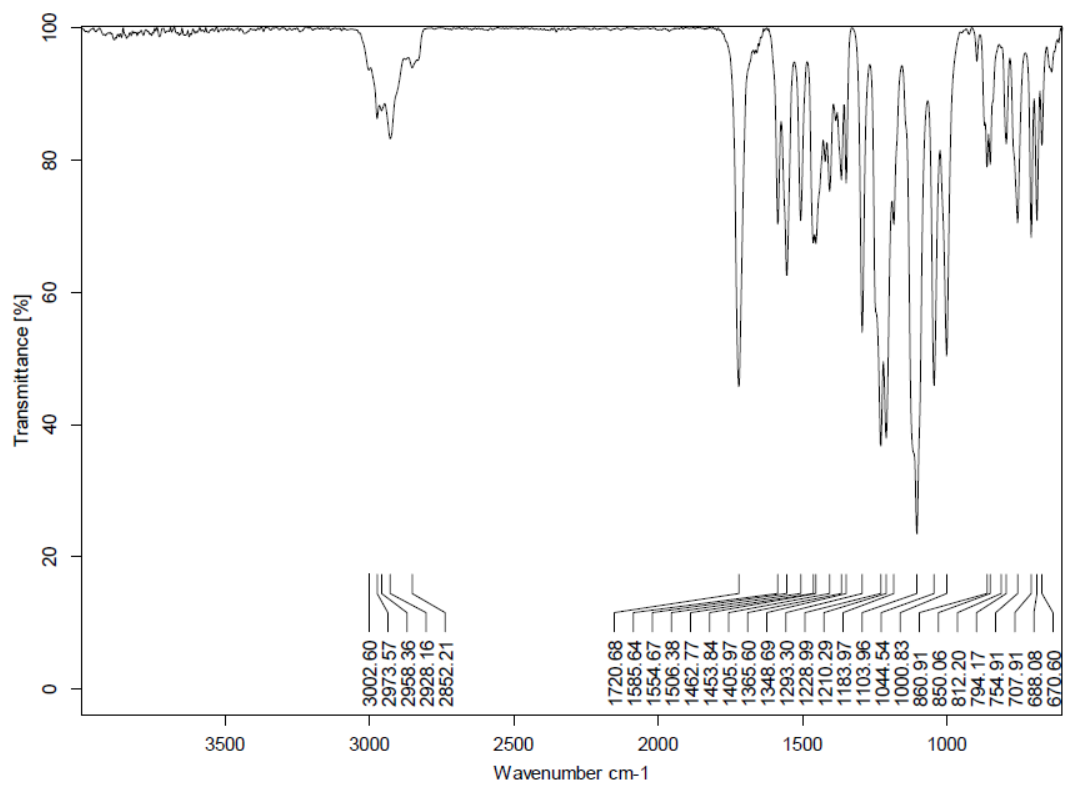


Figure S79. The FTIR spectrum of **7g**.

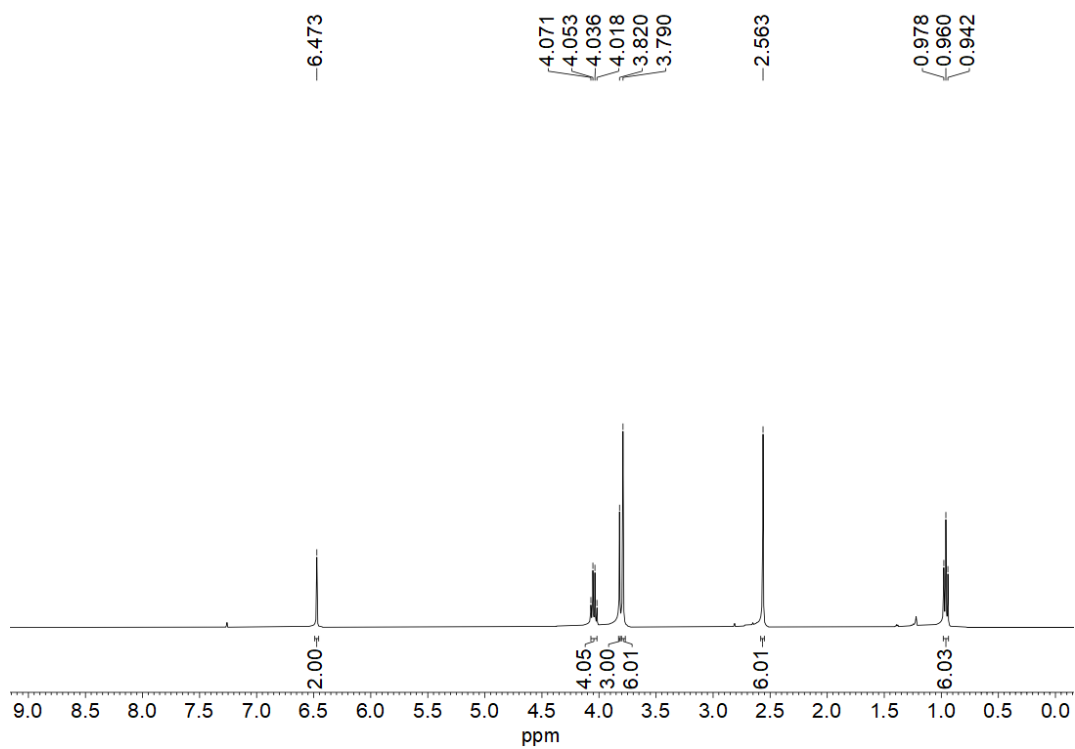


Figure S80. The ^1H -NMR spectrum of **7g**.

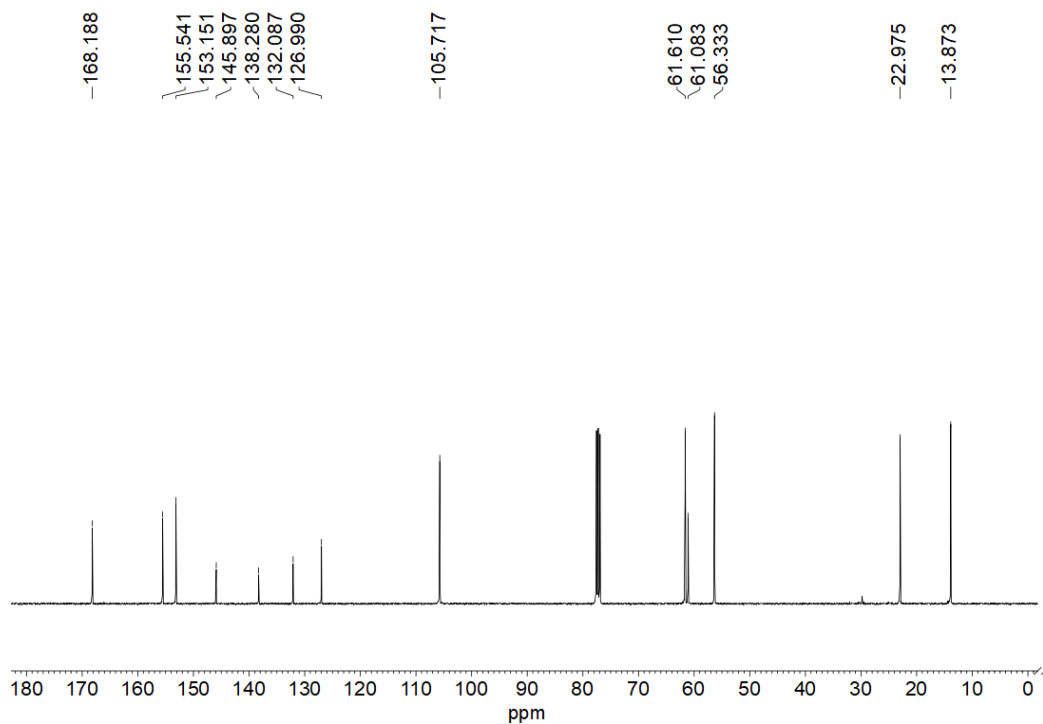


Figure S81. The ^{13}C -NMR spectrum of **7g**.

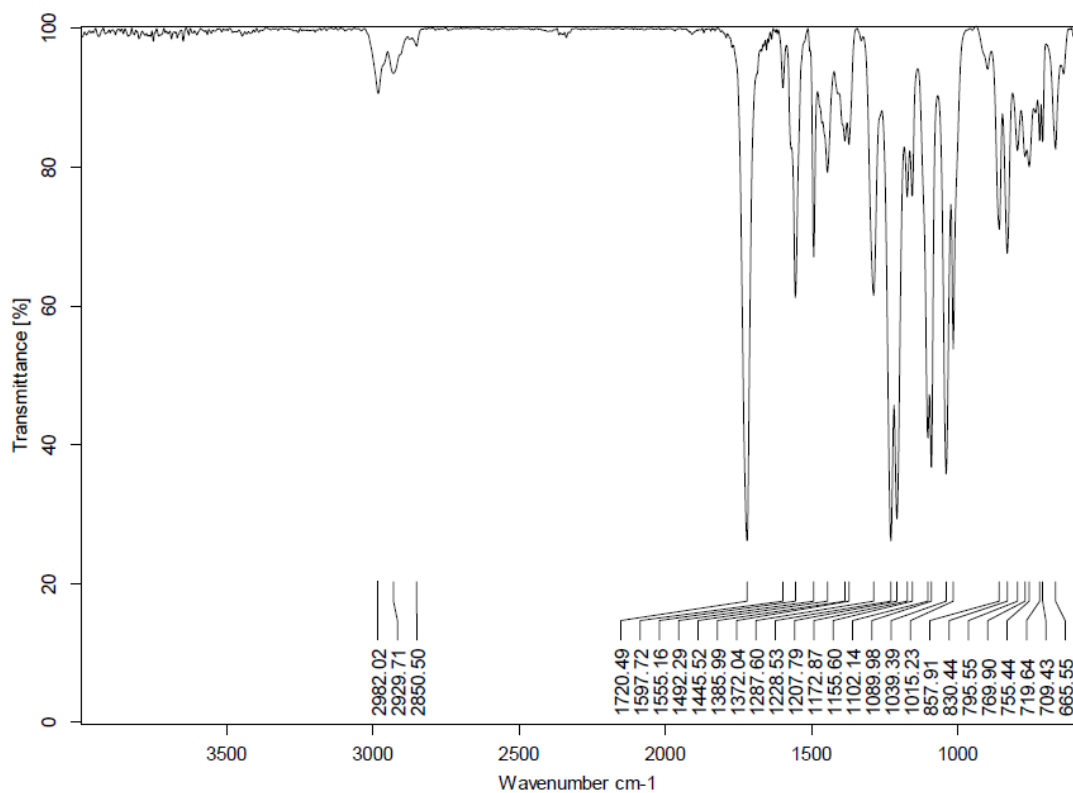


Figure S82. The FTIR spectrum of **7h**.

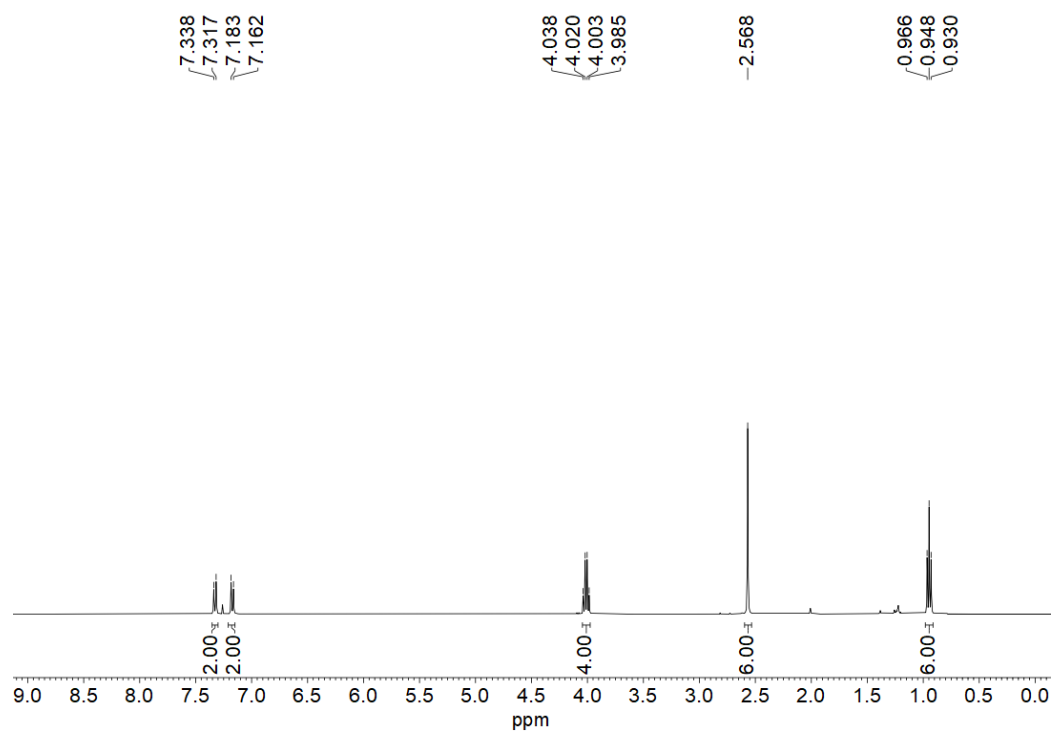


Figure S83. The ¹H-NMR spectrum of **7h**.

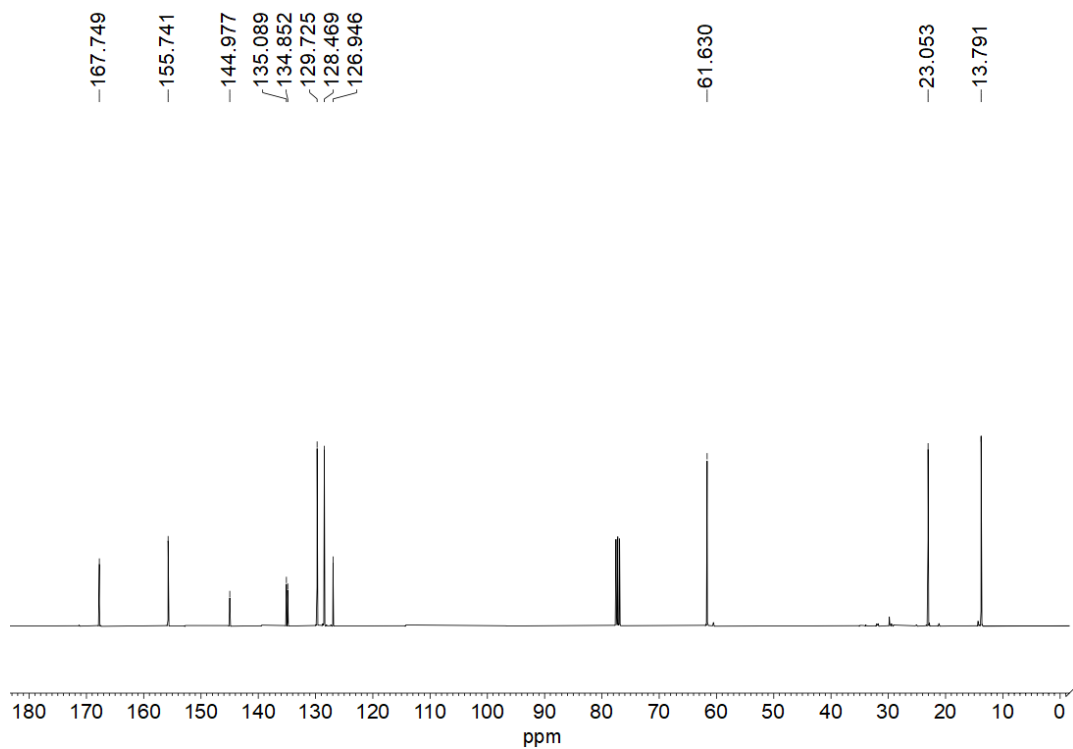


Figure S84. The ¹³C-NMR spectrum of **7h**.

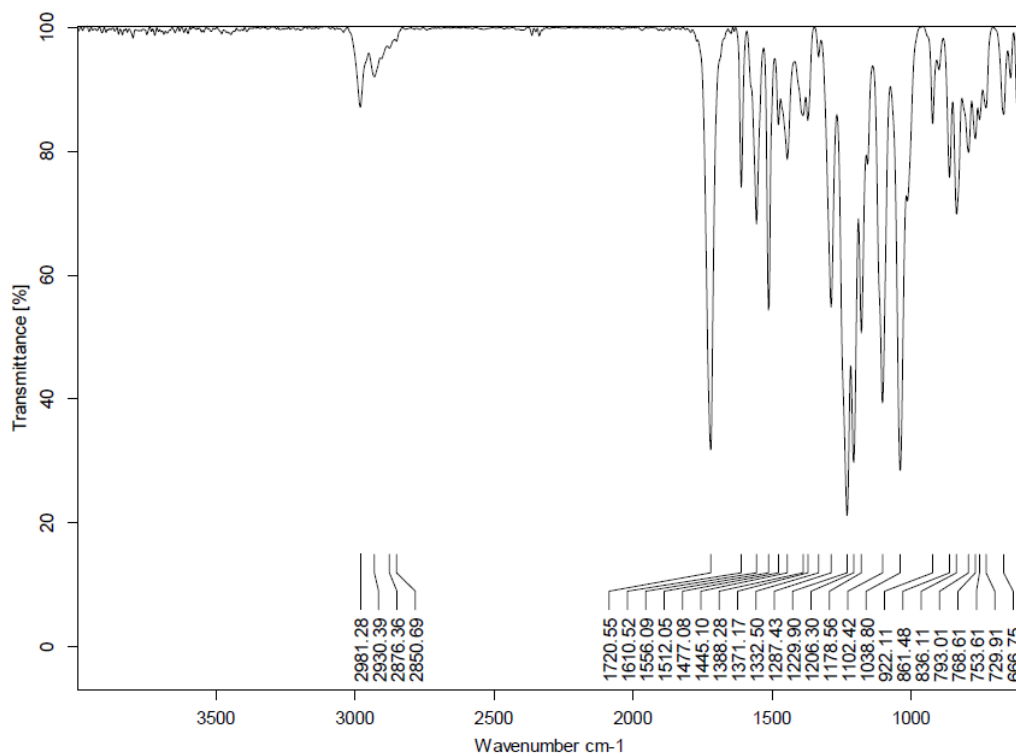


Figure 85. The FTIR spectrum of **7i**.

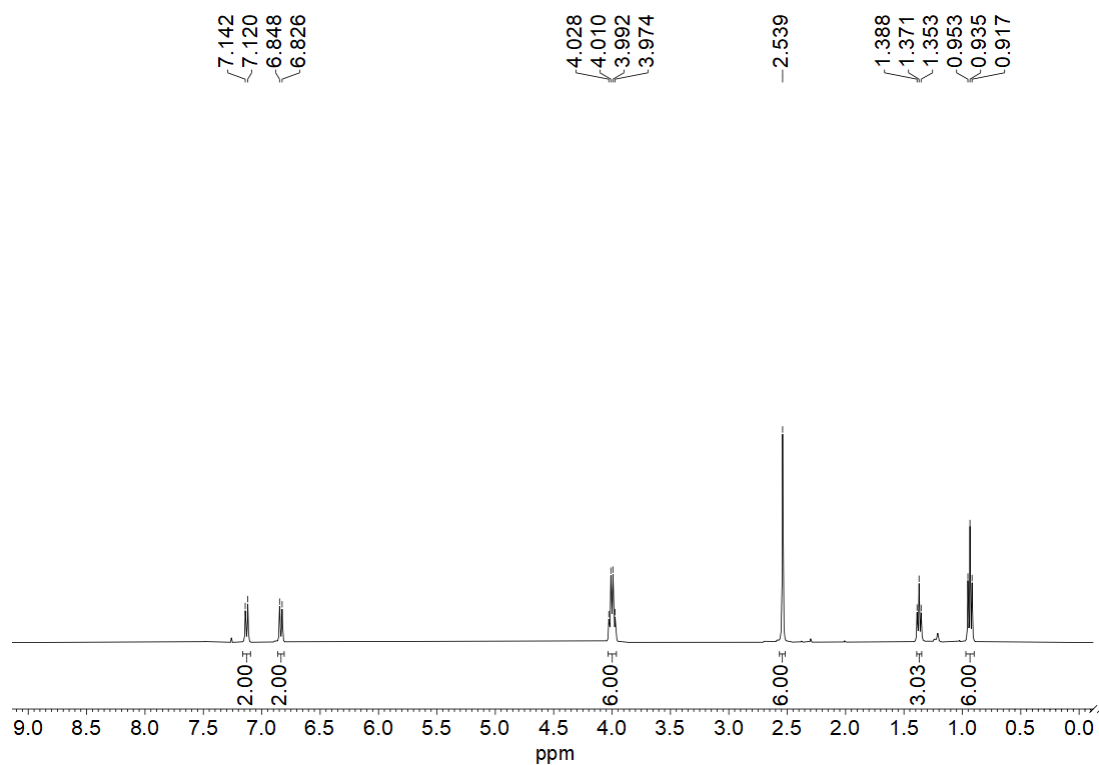


Figure 86. The ¹H-NMR spectrum of **7i**.

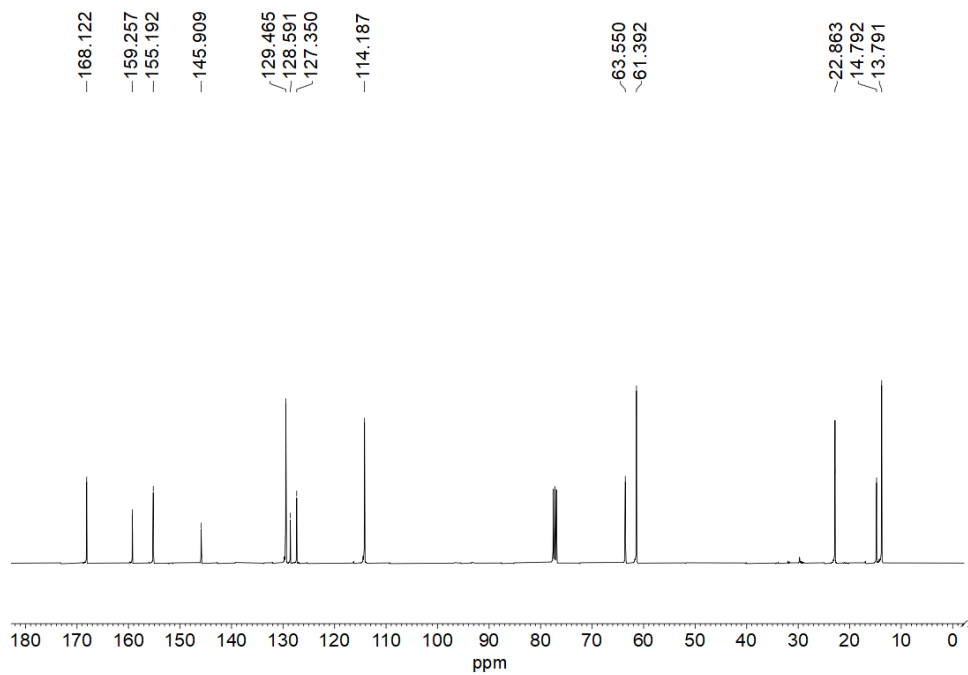


Figure 87. The ^{13}C -NMR spectrum of **7i**.

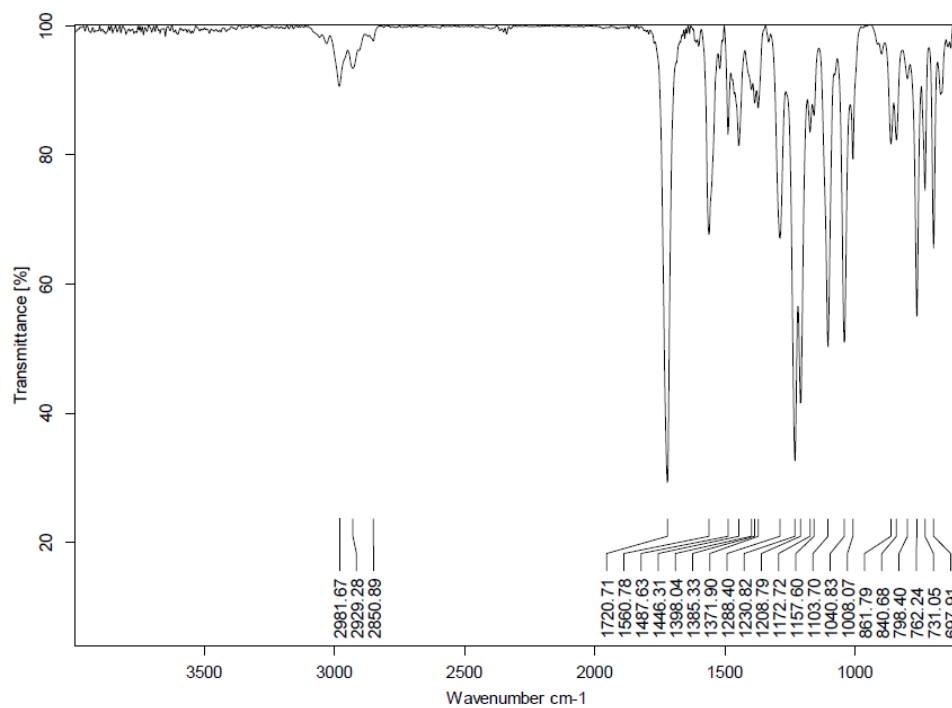


Figure 88. The FTIR spectrum of **7j**.

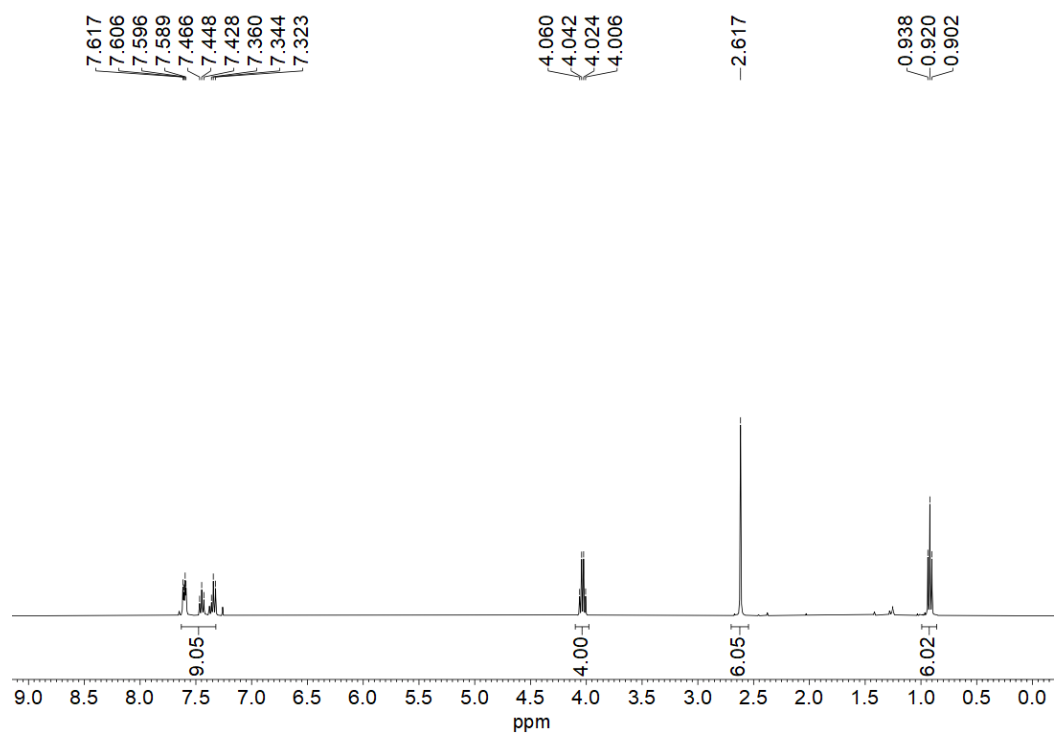


Figure 89. The ^1H -NMR spectrum of **7j**.

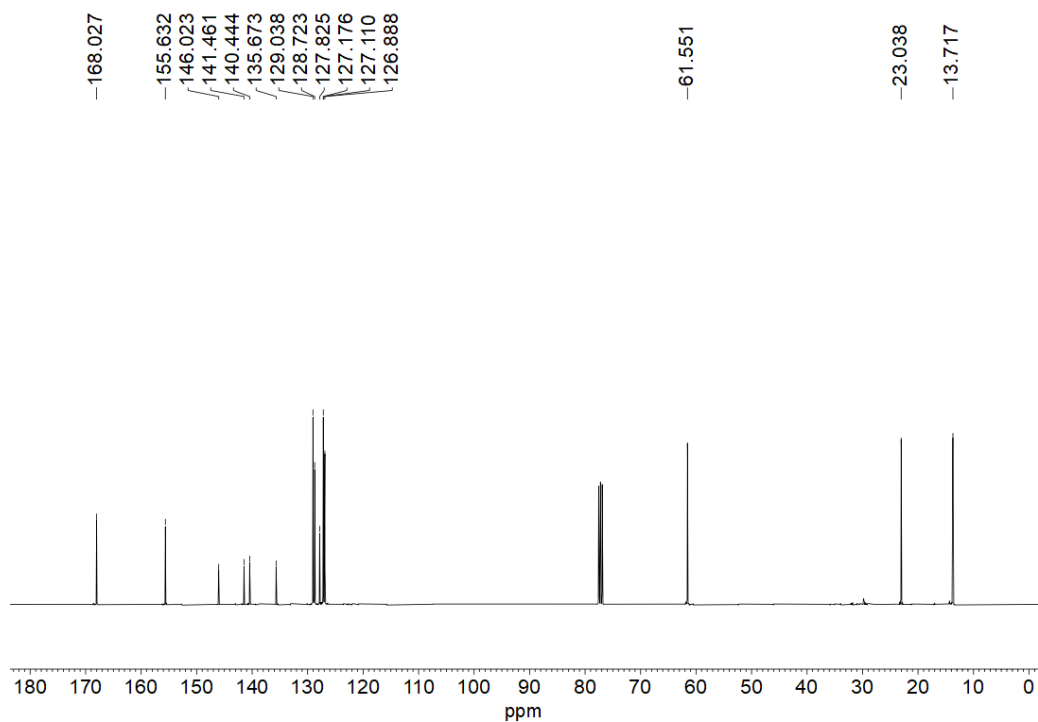


Figure 90. The ^{13}C -NMR spectrum of **7j**.

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