

Supporting Information

A practical one-pot synthesis of dehydroalanine esters

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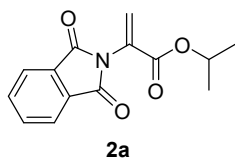
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1. General methods of synthesis

All commercially available solvents and reagents were used without further purification unless otherwise specified. Reactions were monitored by thin layer chromatography (TLC) on Silica Gel 60 F254 plates. Purification was performed by flash column chromatography separations using silica gel (200-300 mesh). Melting points (mp) were measured on a X4 micro melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZS 400MHz NMR spectrometer with Me_4Si as the internal standard in $\text{DMSO}-d_6$ or CDCl_3 . High resolution mass spectra (HRMS) were recorded on an Agilent 6500 Time-of-Flight (TOF) LC/MS system.

2. General procedure for preparation of 2, 3 and 4

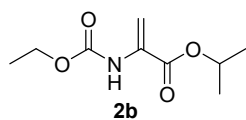
To a solution of serine derivatives (1.0 mmol) in DMF (5 mL) was added Cs_2CO_3 (489 mg, 1.5 mmol), 4 Å zeolite (90 mg) and haloalkanes (1.5 mmol). The reaction was stirred at 60 °C until completion (monitored by TLC). The resulting mixture was filtered, and the filtration cake was washed with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v/v = 60:1 to 40:1) to give the desired products **2**, **3** and **4**.



2a

Isopropyl 2-(1,3-dioxoisindolin-2-yl)acrylate (2a). White solid

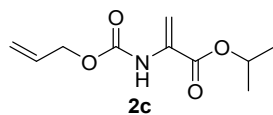
(181mg, 70% yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.96 – 7.91 (m, 2H), 7.91 – 7.86 (m, 2H), 6.58 (s, 1H), 6.12 (s, 1H), 4.95 (p, J = 6.1 Hz, 1H), 1.17 (d, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 166.65, 162.14, 135.68, 131.75, 129.70, 129.38, 124.29, 70.04, 21.88; HRMS calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 282.07368, found 282.07374.



2b

Isopropyl 2-((ethoxycarbonyl)amino)acrylate (2b). Colorless oil

(119mg, 59% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.15 (s, 1H), 6.15 (s, 1H), 5.72 (d, J = 1.4 Hz, 1H), 5.10 (p, J = 6.3 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 1.30 – 1.25 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.36, 153.53, 131.65, 105.23, 70.09, 61.31, 21.78, 14.55; HRMS calcd for $\text{C}_9\text{H}_{15}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 224.08933, found 224.08889.

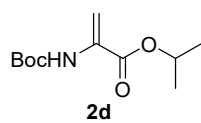


2c

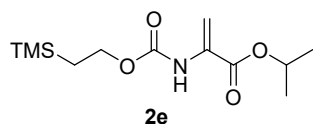
Isopropyl 2-(((allyloxy)carbonyl)amino)acrylate (2c).

Colorless oil (130mg, 61% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.22 (s, 1H), 6.17 (s, 1H), 5.98 – 5.86 (m, 1H), 5.75 (d, J = 1.4 Hz, 1H), 5.33 (dq, J = 17.4, 1.6 Hz, 1H), 5.27 – 5.21 (m, 1H), 5.11 (p, J = 6.4 Hz, 1H), 4.61 (dt, J = 5.5, 1.5 Hz, 2H), 1.30 (d, J = 6.2 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.30, 153.14, 132.36, 131.57, 118.37,

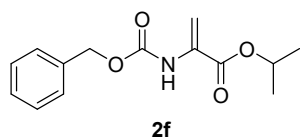
105.53, 70.16, 65.91, 21.78; HRMS calcd for $C_{10}H_{15}NO_4Na$ $[M + Na]^+$ m/z 236.08933, found 236.08922.



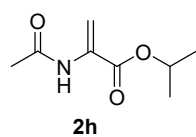
Isopropyl 2-((tert-butoxycarbonyl)amino)acrylate (2d). Colorless oil (158mg, 69% yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.09 (s, 1H), 5.68 (d, $J = 1.6$ Hz, 1H), 5.09 (p, $J = 6.3$ Hz, 1H), 1.46 (s, 9H), 1.28 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.56, 152.69, 131.87, 104.66, 80.66, 69.96, 28.33, 21.77; HRMS calcd for $C_{14}H_{13}NO_4Na$ $[M + Na]^+$ m/z 252.12118, found 252.11987.



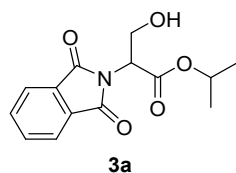
Isopropyl 2-(((2-(trimethylsilyl)ethoxy)carbonyl)amino)acrylate (2e). Colorless oil (139mg, 51% yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.15 (s, 1H), 5.72 (d, $J = 1.4$ Hz, 1H), 5.10 (p, $J = 6.3$ Hz, 1H), 4.30 – 4.07 (m, 2H), 1.29 (d, $J = 6.3$ Hz, 6H), 1.05 – 0.95 (m, 2H), 0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.39, 153.68, 131.68, 105.14, 70.07, 63.63, 21.78, 17.75, -1.43; HRMS calcd for $C_{12}H_{23}NO_4SiNa$ $[M + Na]^+$ m/z 296.12886, found 296.12814.



Isopropyl 2-(((benzyloxy)carbonyl)amino)acrylate (2f). Colorless oil (66mg, 25% yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 5H), 6.19 (s, 1H), 5.76 (d, $J = 1.4$ Hz, 1H), 5.15 (s, 2H), 5.10 (p, $J = 6.3$ Hz, 1H), 1.29 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.26, 153.26, 135.98, 131.58, 128.71, 128.47, 128.35, 105.61, 70.17, 67.10, 21.78; HRMS calcd for $C_{14}H_{17}NO_4Na$ $[M + Na]^+$ m/z 286.10498, found 286.10511.

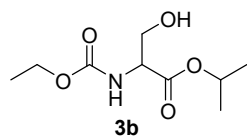


Isopropyl 2-acetamidoacrylate (2h). Colorless oil (89mg, 52% yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.60 (m, 1H), 6.53 (s, 1H), 5.83 (d, $J = 1.4$ Hz, 1H), 5.09 (p, $J = 6.3$ Hz, 1H), 2.10 (s, 3H), 1.29 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.89, 163.75, 131.43, 108.16, 70.20, 24.75, 21.76; HRMS calcd for $C_8H_{14}NO_3$ $[M + H]^+$ m/z 172.09682, found 172.09670.

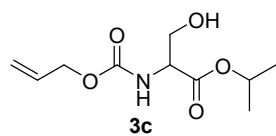


Isopropyl 2-(1,3-dioxoisindolin-2-yl)-3-hydroxypropanoate (3a). White solid (67mg, 24% yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, $J = 5.5$, 3.1 Hz, 2H), 7.74 (dd, $J = 5.5$, 3.1 Hz, 2H), 5.08 (p, $J = 6.3$ Hz, 1H), 4.96 (t, $J = 5.1$ Hz, 1H), 4.17 (t, $J = 4.2$ Hz, 2H), 3.50 (s, 1H), 1.23 (dd, $J = 10.1$, 6.3 Hz, 6H); ^{13}C NMR

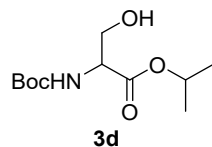
(101 MHz, CDCl₃) δ 168.24, 167.62, 134.55, 131.80, 123.82, 70.30, 61.22, 55.02, 21.75; HRMS calcd for C₁₄H₁₅NO₅Na [M + Na]⁺ m/z 300.08424, found 300.08334.



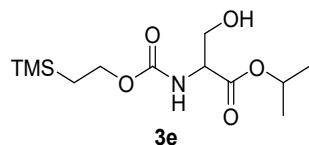
Isopropyl (ethoxycarbonyl)serinate (3b). Colorless oil (66mg, 30% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.68 (d, J = 7.7 Hz, 1H), 5.06 (p, J = 6.4 Hz, 1H), 4.35 (dt, J = 7.4, 3.8 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.92 (dd, J = 10.5, 6.1 Hz, 2H), 2.65 (s, 1H), 1.30 – 1.19 (m, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 170.20, 156.68, 69.81, 63.64, 61.46, 56.27, 21.82, 21.78, 14.60; HRMS calcd for C₉H₁₇NO₅Na [M + Na]⁺ m/z 242.09989, found 242.09886.



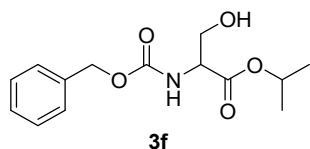
Isopropyl ((allyloxy)carbonyl)serinate (3c). Colorless oil (62mg, 27% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.89 (m, 1H), 5.77 (d, J = 7.6 Hz, 1H), 5.30 (d, J = 17.2 Hz, 1H), 5.20 (d, J = 10.4 Hz, 1H), 5.06 (p, J = 6.2 Hz, 1H), 4.56 (d, J = 5.4 Hz, 2H), 4.35 (dt, J = 7.8, 3.9 Hz, 1H), 3.93 (td, J = 9.5, 7.6, 3.7 Hz, 2H), 2.60 (s, 1H), 1.25 (dd, J = 6.4, 3.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 170.12, 156.28, 132.57, 118.07, 69.90, 66.09, 63.56, 56.30, 21.83, 21.79; HRMS calcd for C₁₀H₁₇NO₅Na [M + Na]⁺ m/z 254.09989, found 254.09886.



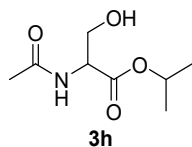
Isopropyl (tert-butoxycarbonyl)serinate (3d). Colorless oil (47mg, 19% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.55 – 5.37 (m, 1H), 5.05 (p, J = 6.1 Hz, 1H), 4.29 (s, 1H), 3.96 – 3.81 (m, 2H), 2.65 (s, 1H), 1.42 (s, 9H), 1.24 (dd, J = 6.2, 3.5 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 170.38, 155.94, 80.30, 69.68, 63.81, 56.03, 28.37, 21.84, 21.80; HRMS calcd for C₁₁H₂₁NO₅Na [M + Na]⁺ m/z 270.13119, found 270.13012.



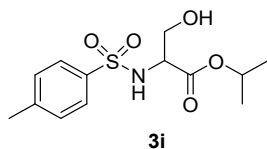
Isopropyl ((2,2,2-trichloroethoxy)carbonyl)serinate (3e). Colorless oil (102mg, 35% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.59 (d, J = 7.3 Hz, 1H), 5.07 (p, J = 6.2 Hz, 1H), 4.35 (d, J = 7.2 Hz, 1H), 4.23 – 4.09 (m, 2H), 3.98 – 3.84 (m, 2H), 2.49 (s, 1H), 1.25 (dd, J = 6.1, 3.1 Hz, 6H), 1.04 – 0.91 (m, 2H), 0.02 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 170.17, 156.78, 69.81, 63.75, 56.26, 21.82, 21.79, 17.78, -1.42; HRMS calcd for C₁₂H₂₅NO₅SiNa [M + Na]⁺ m/z 314.13942, found 314.13814.



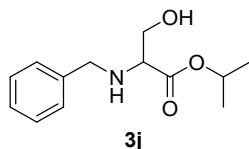
Isopropyl ((benzyloxy)carbonyl)serinate (3f). White solid (141mg, 50% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.26 (m, 5H), 5.72 (d, J = 7.5 Hz, 1H), 5.09 (d, J = 15.0 Hz, 3H), 4.38 (dt, J = 7.8, 3.7 Hz, 1H), 3.94 (d, J = 4.6 Hz, 2H), 2.31 (s, 1H), 1.25 (dd, J = 6.4, 3.2 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.99, 156.36, 136.19, 128.66, 128.31, 69.94, 67.27, 63.66, 56.35, 21.82, 21.79; HRMS calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_5\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 304.11554, found 304.11444.



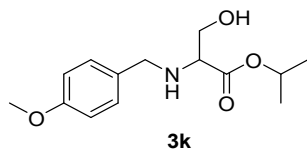
Isopropyl acetylserinate (3h). Colorless oil (62mg, 33% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.55 – 6.40 (m, 1H), 5.08 (td, J = 6.3, 3.6 Hz, 1H), 4.60 (dt, J = 7.2, 3.6 Hz, 1H), 3.92 (d, J = 3.8 Hz, 2H), 2.67 (s, 1H), 2.05 (s, 3H), 1.27 (dd, J = 6.4, 3.2 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.80, 170.04, 70.02, 63.96, 55.23, 23.25, 21.80; HRMS calcd for $\text{C}_8\text{H}_{15}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 212.08933, found 212.0884.



Isopropyl tosylserinate (3i). White solid (45mg, 15% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.26 (m, 5H), 5.72 (d, J = 7.5 Hz, 1H), 5.09 (d, J = 15.0 Hz, 3H), 4.38 (dt, J = 7.8, 3.7 Hz, 1H), 3.94 (d, J = 4.6 Hz, 2H), 2.31 (s, 1H), 1.25 (dd, J = 6.4, 3.2 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.99, 156.36, 136.19, 128.66, 128.36, 128.25, 69.94, 67.27, 63.66, 56.35, 21.82, 21.79; HRMS calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_5\text{SNa}$ $[\text{M} + \text{Na}]^+$ m/z 324.08761, found 324.08677.

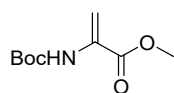


Isopropyl benzylserinate (3j). White solid (97mg, 41% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 4.4 Hz, 4H), 7.27 (d, J = 4.3 Hz, 1H), 5.05 (p, J = 6.2 Hz, 1H), 3.86 (d, J = 12.9 Hz, 1H), 3.80 – 3.68 (m, 2H), 3.57 (dd, J = 10.7, 6.6 Hz, 1H), 3.36 (dd, J = 6.6, 4.4 Hz, 1H), 1.30 – 1.20 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.60, 139.48, 128.63, 128.38, 127.42, 69.05, 62.58, 62.09, 52.23, 21.96, 21.90; HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_3\text{Na}$ $[\text{M} + \text{H}]^+$ m/z 238.14377, found 238.14277.



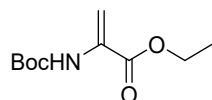
Isopropyl (4-methoxybenzyl)serinate (3k). White solid (120mg, 45% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 5.05 (p, J = 6.2 Hz, 1H), 3.78 (s, 4H), 3.73 (dd, J = 10.7, 4.5 Hz, 1H), 3.65 (d, J = 12.6 Hz, 1H), 3.55 (dd, J = 10.8, 6.7 Hz, 1H), 3.35 (dd, J = 6.6, 4.5 Hz, 1H), 2.24 (s, 2H), 1.24 (t, J = 5.7 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.65,

158.96, 131.59, 129.59, 113.99, 69.01, 62.53, 61.93, 55.37, 51.61, 21.97, 21.90; HRMS calcd for C₁₄H₂₂N₂O₄ [M + H]⁺ *m/z* 268.14176, found 268.14246.



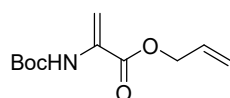
4a

Methyl 2-((tert-butoxycarbonyl)amino)acrylate (4a). Colorless oil (129mg, 64% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.00 (s, 1H), 6.13 (s, 1H), 5.69 (d, *J* = 1.5 Hz, 1H), 3.80 (s, 3H), 1.45 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 164.53, 152.64, 131.35, 105.23, 80.77, 52.96, 28.31; HRMS calcd for C₉H₁₅NO₄Na [M + Na]⁺ *m/z* 224.08933, found 224.08909.



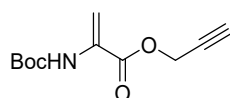
4b

Ethyl 2-((tert-butoxycarbonyl)amino)acrylate (4b). Colorless oil (146mg, 68% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.00 (s, 1H), 6.10 (s, 1H), 5.69 (d, *J* = 1.5 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.44 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.03, 152.64, 131.58, 104.88, 80.67, 62.12, 28.30, 14.16; HRMS calcd for C₁₀H₁₇NO₄Na [M + Na]⁺ *m/z* 238.10498, found 238.10496.



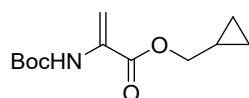
4c

Allyl 2-((tert-butoxycarbonyl)amino)acrylate (4c). Colorless oil (136mg, 60% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.99 (s, 1H), 6.15 (s, 1H), 5.98 – 5.86 (m, 1H), 5.75 (d, *J* = 1.5 Hz, 1H), 5.39 – 5.21 (m, 2H), 4.70 (d, *J* = 5.7 Hz, 2H), 1.46 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 163.76, 152.63, 131.50, 131.41, 118.95, 105.35, 80.76, 66.52, 28.32; HRMS calcd for C₁₁H₁₇NO₄Na [M + Na]⁺ *m/z* 250.10498, found 250.10510.



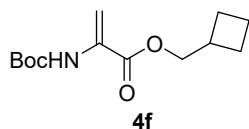
4d

Prop-2-yn-1-yl 2-((tert-butoxycarbonyl)amino)acrylate (4d). Colorless oil (133mg, 59% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.95 (s, 1H), 6.21 (s, 1H), 5.79 (d, *J* = 1.5 Hz, 1H), 4.80 (dd, *J* = 2.4, 0.8 Hz, 2H), 2.50 (d, *J* = 0.8 Hz, 1H), 1.47 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 163.39, 152.58, 130.96, 106.39, 80.93, 76.93, 75.69, 53.41, 28.32; HRMS calcd for C₁₁H₁₅NO₄Na [M + Na]⁺ *m/z* 248.08933, found 248.08919.



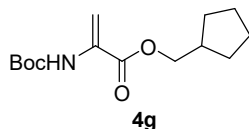
4e

Cyclopropylmethyl 2-((tert-butoxycarbonyl)amino)acrylate (4e). Colorless oil (121mg, 50% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, *J* = 0.9 Hz, 1H), 6.13 (s, 1H), 5.75 (s, 1H), 4.03 (d, *J* = 7.3 Hz, 2H), 1.47 (s, 9H), 1.22 – 1.11 (m, 1H), 0.58 (dd, *J* = 8.3, 1.6 Hz, 2H), 0.34 – 0.27 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 164.19, 152.68, 131.62, 105.02, 80.70, 70.87, 28.33, 9.76, 3.41; HRMS calcd for C₁₂H₁₉NO₄Na [M + Na]⁺ *m/z* 264.12063, found 264.12063.



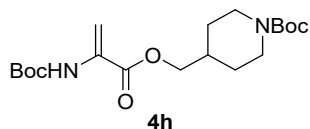
Cyclobutylmethyl 2-((tert-butoxycarbonyl)amino)acrylate (4f).

Colorless oil (130mg, 51% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.07 – 6.94 (m, 1H), 6.13 (s, 1H), 5.71 (d, J = 1.6 Hz, 1H), 4.17 (d, J = 6.4 Hz, 2H), 2.67 (p, J = 7.3 Hz, 1H), 2.12 – 2.03 (m, 2H), 1.99 – 1.85 (m, 2H), 1.84 – 1.72 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.26, 152.69, 131.56, 104.90, 80.72, 69.71, 34.05, 28.33, 24.74, 18.48; HRMS calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 278.13628, found 278.13597.



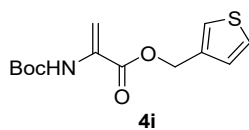
Cyclopentylmethyl 2-((tert-butoxycarbonyl)amino)acrylate (4g).

Colorless oil (119mg, 44% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.01 (s, 1H), 6.12 (s, 1H), 5.70 (d, J = 1.6 Hz, 1H), 4.09 (d, J = 7.2 Hz, 2H), 2.25 (p, J = 7.5 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.66 – 1.51 (m, 4H), 1.47 (s, 9H), 1.32 – 1.21 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.22, 152.69, 131.59, 104.83, 80.71, 69.95, 38.53, 29.35, 28.33, 25.38; HRMS calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 292.15193, found 292.15140.



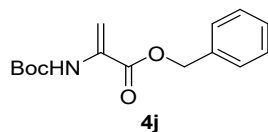
Tert-butyl 4-(((2-((tert-butoxycarbonyl)amino)acryloyl)oxy)methyl)piperidine-1-carboxylate (4h).

White solid (146mg, 38% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.97 (s, 1H), 6.12 (s, 1H), 5.68 (s, 1H), 4.08 (dd, J = 21.0, 9.6 Hz, 4H), 2.68 (t, J = 13.1 Hz, 2H), 1.83 (t, J = 5.7 Hz, 1H), 1.67 (d, J = 13.1 Hz, 2H), 1.45 (s, 9H), 1.42 (s, 9H), 1.23 – 1.13 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.07, 154.86, 152.65, 131.41, 105.12, 80.83, 79.60, 69.90, 35.68, 28.69, 28.52, 28.32; HRMS calcd for $\text{C}_{19}\text{H}_{32}\text{N}_2\text{O}_6\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 407.21526, found 407.21445.



Thiophen-3-ylmethyl 2-((tert-butoxycarbonyl)amino)acrylate (4i).

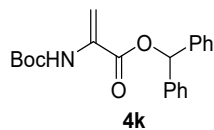
White solid (136mg, 48% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.32 (q, J = 1.7 Hz, 2H), 7.11 – 7.08 (m, 1H), 7.01 (s, 1H), 6.16 (s, 1H), 5.75 (d, J = 1.6 Hz, 1H), 5.24 (d, J = 1.4 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.93, 152.65, 136.05, 131.40, 127.63, 126.54, 124.90, 105.55, 80.82, 62.75, 28.33; HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_4\text{SNa}$ $[\text{M} + \text{Na}]^+$ m/z 306.07705, found 306.07657.



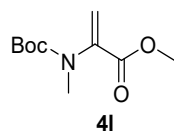
Benzyl 2-((tert-butoxycarbonyl)amino)acrylate (4j).

White solid (67mg, 24% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.32 (m, 5H), 7.03 (s, 1H), 6.17 (s, 1H), 5.78 (d, J = 1.4 Hz, 1H), 5.25 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (101

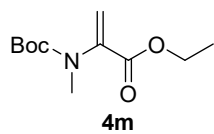
MHz, CDCl₃) δ 163.99, 152.66, 135.27, 131.42, 128.76, 128.64, 128.31, 105.55, 80.82, 67.73, 28.33; HRMS calcd for C₁₅H₁₉NO₄Na [M + Na]⁺ m/z 300.12063, found 300.12054.



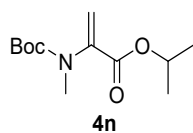
Bnzhydryl 2-((tert-butoxycarbonyl)amino)acrylate (4k). White solid (67mg, 19% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.52 (s, 1H), 7.41 (d, J = 7.2 Hz, 4H), 7.32 (t, J = 7.5 Hz, 4H), 7.25 (dd, J = 8.4, 6.1 Hz, 2H), 6.82 (s, 1H), 5.67 (d, J = 14.3 Hz, 2H), 1.33 (s, 9H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 163.32, 153.40, 140.78, 134.40, 129.09, 128.41, 127.03, 110.22, 80.14, 78.14, 28.41; HRMS calcd for C₂₁H₂₃NO₄Na [M + Na]⁺ m/z 376.15193, found 376.15085.



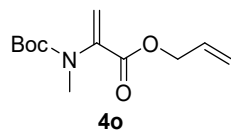
Methyl 2-((tert-butoxycarbonyl)(methyl)amino)acrylate (4l). Colorless oil (129mg, 60% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.79 (s, 1H), 5.31 (s, 1H), 3.77 (s, 3H), 3.11 (s, 3H), 1.41 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 165.50, 153.99, 141.60, 115.37, 81.25, 52.31, 36.74, 28.19; HRMS calcd for C₁₀H₁₇NO₄Na [M + Na]⁺ m/z 238.10498, found 238.10498.



Ethyl 2-((tert-butoxycarbonyl)(methyl)amino)acrylate (4m). Colorless oil (147mg, 64% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.80 (s, 1H), 5.32 (s, 1H), 4.22 (q, J = 7.0 Hz, 2H), 3.11 (s, 3H), 1.41 (s, 9H), 1.30 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.99, 154.08, 141.91, 115.53, 81.15, 61.39, 36.83, 28.21, 14.26; HRMS calcd for C₁₁H₁₉NO₄Na [M + Na]⁺ m/z 252.12120, found 252.11987.



Isopropyl 2-((tert-butoxycarbonyl)(methyl)amino)acrylate (4n). Colorless oil (173mg, 71% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.82 (s, 1H), 5.34 (s, 1H), 5.06 (p, J = 6.2 Hz, 1H), 3.09 (s, 3H), 1.42 (s, 9H), 1.28 (d, J = 6.3 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 164.29, 154.19, 142.23, 81.01, 68.96, 36.96, 28.24, 21.89; HRMS calcd for C₁₂H₂₁NO₄Na [M + Na]⁺ m/z 266.13628, found 266.13576.



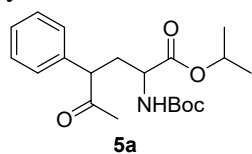
Allyl 2-((tert-butoxycarbonyl)(methyl)amino)acrylate (4o). Colorless oil (147mg, 61% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.83 (s, 1H), 5.38 – 5.31 (m, 2H), 5.24 (d, J = 10.5 Hz, 1H), 4.67 – 4.63 (m, 2H), 3.11 (s, 3H), 1.40 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 164.60, 154.03, 141.64, 131.82, 118.71, 115.99, 81.23, 66.01, 36.83, 28.20; HRMS calcd for C₁₂H₁₉NO₄K [M + K]⁺ m/z 280.09457, found

280.09449.

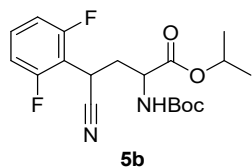
3. Synthesis of 5a and 5b

To a solution of 1-phenylacetone (20 g, 0.15 mol) in DMSO (80 mL) was added Cs_2CO_3 (24.3 g, 0.075 mol), and the mixture was stirred at room temperature for 15 minutes. A solution of isopropyl 2-((tert-butoxycarbonyl)amino)acrylate (**2d**) (34 g, 0.15 mol) in DMSO (40 mL) was added to the reaction mixture. The reaction was stirred at room temperature for 2 h until completion (monitored by TLC). The mixture was diluted with methyl tert-butyl ether (120 mL) and filtered to remove insoluble material. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (dichloromethane) to obtain the desired product **5a** (41 g, 77% yield) as a light yellow oil.

Following the preparation process of **5a**, the desired product **5b** was obtained as a yellow oil from **2d** and 2,6-difluorobenzyl cyanide in 75% yield.



Isopropyl 2-((tert-butoxycarbonyl)amino)-5-oxo-4-phenylhexanoate (5a). ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, $J = 7.4$ Hz, 2H), 7.26 (d, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 7.4$ Hz, 2H), 5.10 (d, $J = 8.2$ Hz, 1H), 4.95 (p, $J = 6.4$ Hz, 1H), 4.22 (q, $J = 7.5, 6.3$ Hz, 1H), 3.79 (dd, $J = 9.1, 5.2$ Hz, 1H), 2.68 (m, 1H), 2.05 (s, 3H), 1.72 (dd, $J = 16.2, 6.3$ Hz, 1H), 1.43 (s, 9H), 1.22 (dd, $J = 12.5, 6.2$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 207.05, 172.00, 155.55, 138.47, 129.18, 128.40, 127.66, 79.87, 69.34, 55.41, 52.21, 35.74, 29.15, 28.38, 21.81, 21.77; HRMS calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_5\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 386.19379, found 386.19329.



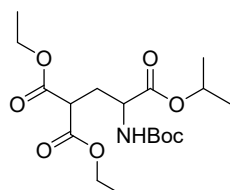
Isopropyl 2-((tert-butoxycarbonyl)amino)-4-cyano-4-(2,6-difluorophenyl)butanoate (5b). ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.28 (m, 1H), 6.94 (t, $J = 8.3$ Hz, 2H), 5.06 (dq, $J = 12.3, 5.8$ Hz, 1H), 4.42 – 4.14 (m, 1H), 3.51 (m, $J = 69.2, 18.6, 4.4$ Hz, 1H), 2.49 (dq, $J = 14.3, 6.7$ Hz, 1H), 1.45 (s, 1H), 1.43 (d, $J = 3.4$ Hz, 9H), 1.24 (m, $J = 14.8, 12.2, 5.7$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.31, 170.54, 159.48, 133.15, 130.86, 115.56, 112.28, 112.06, 80.04, 70.26, 69.60, 49.87, 34.50, 28.34, 21.77; HRMS calcd for $\text{C}_{19}\text{H}_{24}\text{F}_2\text{N}_2\text{O}_5\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 405.17041, found 405.16012.

4. Synthesis of 6a and 6b

Following the preparation process of **5a**, the desired product **6a** was obtained as a colorless oil from **2d** and diethyl malonate in 72% yield.

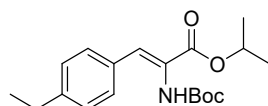
To a solution of **2d** (460 mg, 2 mmol) and 1-ethyl-4-iodobenzene (460 mg, 2 mmol) in DMF (8 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (115 mg, 0.1 mmol) and K_2CO_3 (280 mg, 2 mmol). The reaction was stirred at 100 °C under nitrogen for 5 h until completion (monitored by TLC). The mixture was quenched with H_2O , and then extracted with

ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v/v = 80:1 to 60:1) to afford the desired product **6b** (533 mg, 80% yield) as a light yellow oil.



6a

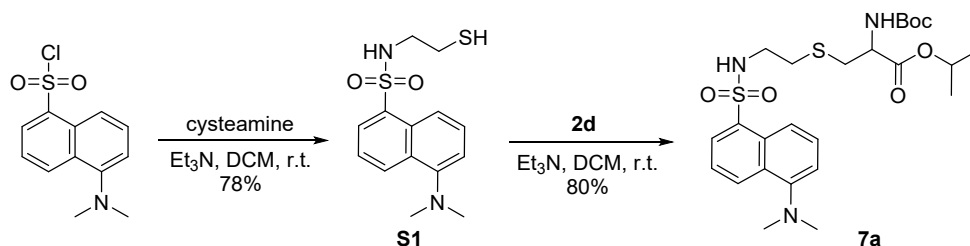
1,1-Diethyl 3-isopropyl 3-((tert-butoxycarbonyl)amino)propane-1,1,3-tricarboxylate (6a). ^1H NMR (400 MHz, CDCl_3) δ 5.03 – 4.97 (m, 2H), 4.29 (m, 1H), 4.21 – 4.13 (m, 4H), 3.43 (t, J = 8.0, 1H), 2.49 – 2.41 (m, 1H), 2.16 – 2.08 (m, 1H), 1.39 (s, 9H), 1.26 – 1.22 (m, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.47, 169.25, 168.78, 155.41, 80.04, 69.54, 61.81, 52.10, 48.77, 31.43, 28.33, 21.81, 21.76, 14.09; HRMS calcd for $\text{C}_{18}\text{H}_{31}\text{NO}_8\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 412.20497, found 412.19378.



6b

Isopropyl (Z)-2-((tert-butoxycarbonyl)amino)-3-(4-ethylphenyl)acrylate (6b). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (dd, J = 25.8, 7.6 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.18 (d, J = 7.0 Hz, 2H), 6.28 (s, 1H), 5.15 – 5.09 (m, 1H), 2.63 (q, J = 7.6 Hz, 2H), 1.47 – 1.35 (m, 9H), 1.31 (dd, J = 6.3, 2.6 Hz, 6H), 1.21 (t, J = 7.7 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.33, 152.89, 145.65, 134.42, 131.70, 129.94, 129.71, 129.08, 128.55, 128.11, 80.78, 69.32, 28.86, 28.22, 22.00, 15.43; HRMS calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$ m/z 356.19401, found 356.18406.

5. Synthesis of 7a and 7b

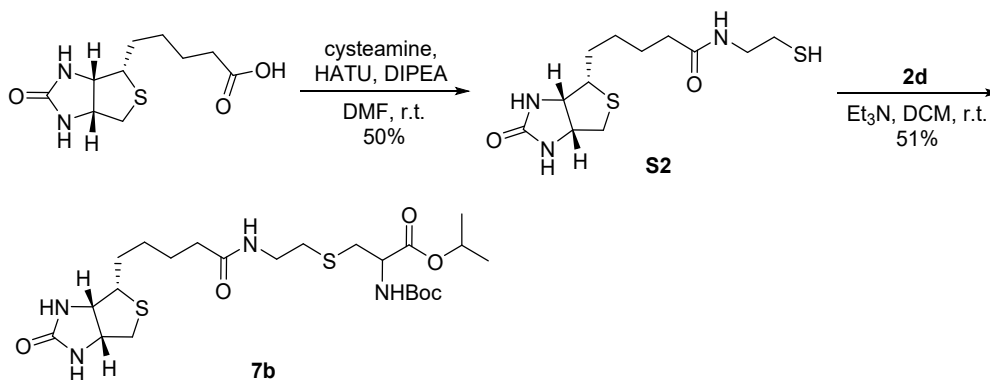


To a solution of dansyl chloride (1.1 g, 4 mmol) and cysteamine (300 mg, 4 mmol) in dichloromethane (15 mL) was added Et_3N (0.5 mL). The reaction was stirred at room temperature for 0.5 h until completion (monitored by TLC). The mixture was quenched with H_2O and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (dichloromethane/methanol, 20:1 to 10:1) to give intermediate **S1** (969 mg, 78% yield) as a yellow oil.

To a solution of **2d** (460 mg, 2 mmol) and intermediate **S1** (745 mg, 2.4 mmol) in dichloromethane (8 mL) was added Et_3N (0.3 mL). The reaction was stirred at room temperature for 12 h until completion (monitored by TLC). The mixture was quenched

with 2M HCl and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v/v = 80:1 to 60:1) to afford the desired product **7a** (864 mg, 80% yield) as a light yellow oil.

Isopropyl N-(tert-butoxycarbonyl)-S-(2-((5-(dimethylamino)naphthalene)-1-sulfonamido)ethyl)cysteinate (7a). ¹H NMR (400 MHz, CDCl₃) δ 8.56 – 8.50 (d, *J* = 8.5 Hz, 1H), 8.30 – 8.22 (dd, *J* = 18.2, 8.0 Hz, 2H), 7.57 – 7.48 (m, 2H), 7.20 – 7.15 (d, *J* = 7.7 Hz, 1H), 5.54 – 5.48 (t, *J* = 6.2 Hz, 1H), 5.27 – 5.21 (d, *J* = 7.9 Hz, 1H), 5.03 – 4.96 (p, *J* = 6.2 Hz, 1H), 4.35 – 4.29 (q, *J* = 6.0 Hz, 1H), 3.08 – 3.02 (q, *J* = 6.0 Hz, 2H), 2.87 (s, 6H), 2.75 – 2.62 (m, 2H), 2.58 – 2.51 (td, *J* = 6.2, 2.0 Hz, 2H), 1.41 (s, 9H), 1.23 – 1.18 (dd, *J* = 8.4, 6.3 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 170.26, 155.31, 152.10, 134.73, 130.67, 129.98, 129.71, 129.61, 128.56, 123.28, 118.82, 115.35, 80.35, 69.89, 53.60, 45.52, 41.99, 34.45, 33.06, 28.38, 21.83, 21.79; HRMS calcd for C₂₅H₃₈N₃O₆S₂ [M + H]⁺ *m/z* 540.21238, found 540.22032.



To a solution of D-biotin (2.0 g, 8 mmol) and cysteamine (620 mg, 8 mmol) in DMF (25 mL) was added DIPEA (1.0 g, 8 mmol) and HATU (3.08 g, 8 mmol). The reaction was stirred at room temperature for 12 h until completion (monitored by TLC). The mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (dichloromethane/methanol, 20:1 to 10:1) to afford intermediate **S2** (1.2 g, 50% yield) as a white solid.

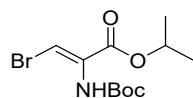
Following the preparation process of **7a**, the desired product **7b** was obtained as a white solid from **2d** and intermediate **S2** in 51% yield.

Isopropyl N-(tert-butoxycarbonyl)-S-(2-((5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanamido)ethyl)cysteinate (7b). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.90 (brs, 1H), 7.23 (brs, 1H), 6.40 (s, 1H), 6.33 (s, 1H), 4.85 (dt, *J* = 13.1, 6.5 Hz, 1H), 4.26 (t, *J* = 6.2 Hz, 1H), 4.08 (t, *J* = 5.9 Hz, 1H), 3.96 (q, *J* = 7.5 Hz, 1H), 3.17 – 3.10 (m, 2H), 3.05 (t, *J* = 7.1 Hz, 1H), 2.77 (dd, *J* = 12.0, 4.8 Hz, 2H), 2.71 – 2.64 (m, 1H), 2.53 (d, *J* = 12.9 Hz, 3H), 2.01 (t, *J* = 7.5 Hz, 2H), 1.53 (s, 2H), 1.44 (d, *J* = 7.8 Hz, 2H), 1.33 (d, *J* = 4.0 Hz, 9H), 1.25 (d, *J* = 7.3 Hz, 2H), 1.14 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 172.61, 171.06, 170.34, 163.28, 78.92, 68.73, 61.56, 59.73, 55.95, 54.47, 38.93, 38.77, 35.68, 32.77, 31.62, 28.72, 28.66, 28.57, 25.76, 22.04, 22.00, 21.96, 21.86; HRMS calcd for C₂₃H₄₀N₄O₆S₂Na [M + Na]⁺

m/z 555.23893, found 555.22923.

6. Synthesis of **8a**, **8b**, **8c** and **8d**

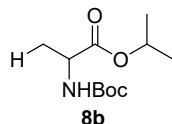
To a solution of **2d** (460 mg, 2 mmol) in dichloromethane (8 mL) was added NBS (350 mg, 2 mmol). The reaction was stirred at room temperature for 2 h until completion (monitored by TLC). The mixture was quenched with H₂O and extracted with dichloromethane. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 80:1 to 60:1) to afford **8a** (308 mg, 50% yield) as a white solid.



8a Isopropyl (Z)-3-bromo-2-((tert-butoxycarbonyl)amino)acrylate

(8a). ¹H NMR (400 MHz, CDCl₃) δ 6.82 (s, 1H), 6.13 (s, 1H), 5.13-5.07 (m, 1H), 1.46 (s, 9H), 1.28 (d, J = 6.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 161.88, 151.93, 133.25, 108.64, 81.67, 70.00, 28.18, 21.81; HRMS calcd for C₁₁H₁₈BrNO₄Na [M + Na]⁺ m/z 330.04192, found 330.03177.

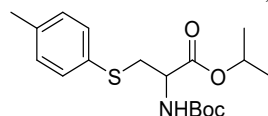
To a solution of **2d** (460 mg, 2 mmol) in methanol (8 mL) was added 10% Pd/C (30 mg). The reaction was stirred at room temperature under hydrogen atmosphere overnight until completion (monitored by TLC). The mixture was filtered and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 80:1 to 60:1) to afford **8b** (384 mg, 83% yield) as a yellow oil.



8b Isopropyl (tert-butoxycarbonyl)alaninate (**8b**). ¹H NMR (400 MHz,

CDCl₃) δ 5.06 (m, 1H), 5.03 – 4.95 (m, 1H), 4.24 – 4.17 (m, 1H), 1.40 (s, 9H), 1.32 (d, J = 7.2 Hz, 3H), 1.20 (t, J = 6.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 172.99, 155.20, 79.75, 68.91, 49.42, 28.39, 21.81, 21.74, 18.77; ¹³C NMR (101 MHz, CDCl₃) δ 172.99, 155.20, 79.75, 68.91, 49.42, 28.39, 21.81, 21.74, 18.77; HRMS calcd for C₁₁H₂₁NO₄Na [M + Na]⁺ m/z 254.14706, found 254.13663.

To a solution of **2d** (460 mg, 2 mmol) and 4-methylbenzenethiol (300 mg, 2.4 mmol) in dichloromethane (8 mL) was added Et₃N (0.3 ml). The reaction was stirred at room temperature for 12 h until completion (monitored by TLC). The mixture was quenched with 2M HCl and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 80:1 to 60:1) to afford **8c** (325 mg, 46% yield) as a light yellow solid.

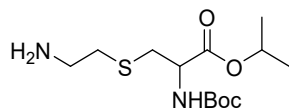


8c Isopropyl N-(tert-butoxycarbonyl)-S-(p-tolyl)cysteinate (**8c**).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 5.29

(d, $J = 8.0$ Hz, 1H), 4.95 – 4.88 (m, 1H), 4.48 – 4.44 (m, 1H), 3.35 (dd, $J = 13.9, 4.6$ Hz, 1H), 3.25 (dd, $J = 14.0, 5.2$ Hz, 1H), 2.29 (s, 3H), 1.38 (s, 9H), 1.20 (d, $J = 6.3$ Hz, 3H), 1.13 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.21, 155.02, 137.16, 132.48, 131.60, 129.89, 79.90, 69.62, 53.75, 37.90, 28.34, 21.80, 21.65, 21.11; HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_4\text{SNa}$ $[\text{M} + \text{Na}]^+$ m/z 376.16608, found 376.15614.

Following the preparation process of **8c**, the desired product **8d** was obtained as a light yellow oil from **2d** and cysteamine in 57% yield.



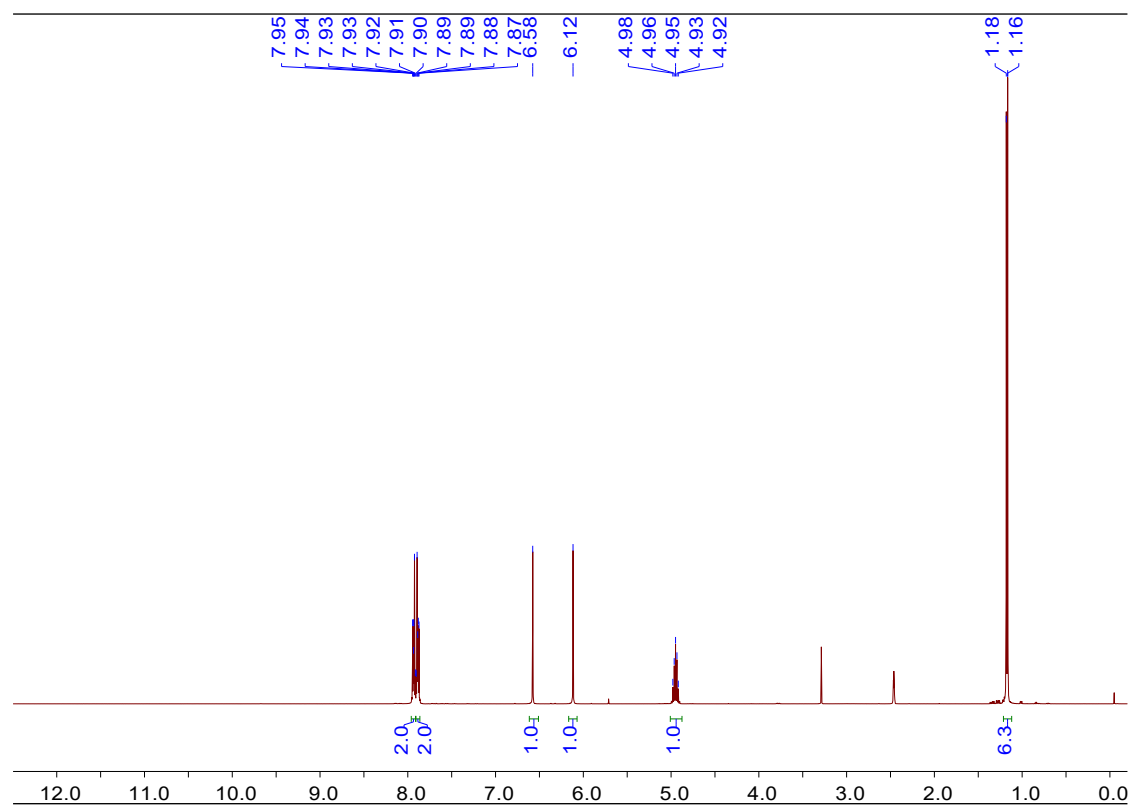
8d

Isopropyl

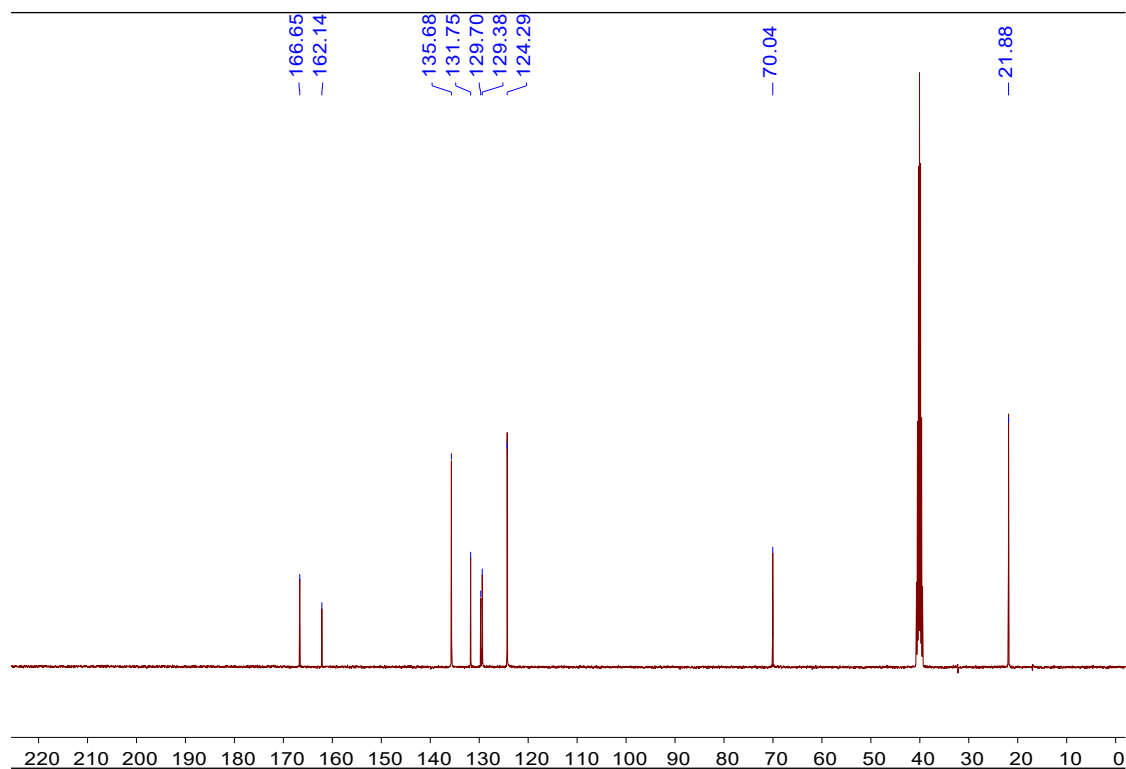
S-(2-aminoethyl)-N-(tert-

butoxycarbonyl)cysteinate (8d). ^1H NMR (400 MHz, CDCl_3) δ 5.61 (s, 1H), 5.02 – 4.96 (m, 1H), 4.40 – 4.36 (m, 1H), 2.88 (t, $J = 4.7$ Hz, 2H), 2.79 (t, $J = 6.2$ Hz, 2H), 2.57 (t, $J = 6.6$ Hz, 2H), 1.37 (s, 9H), 1.28 (s, 2H), 1.19 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.51, 155.28, 79.92, 69.52, 53.70, 41.12, 37.02, 34.34, 28.36, 21.82, 21.77; HRMS calcd for $\text{C}_{13}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ $[\text{M} + \text{H}]^+$ m/z 307.16133, found 307.16900.

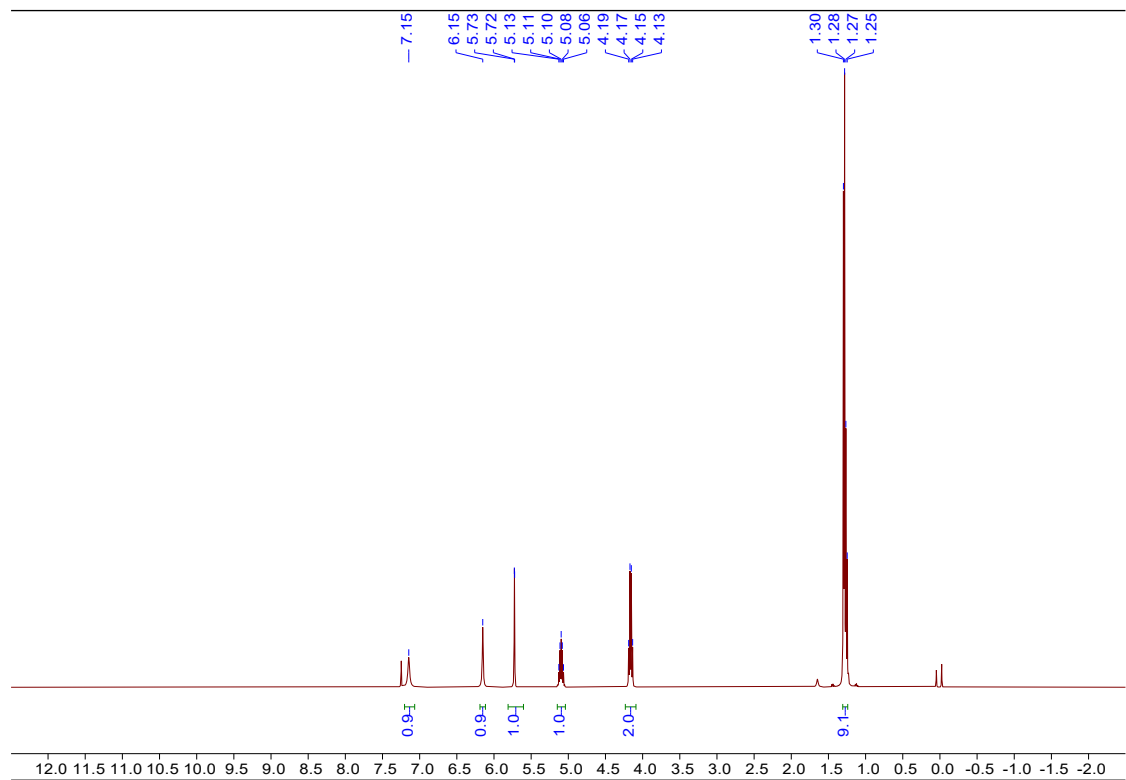
7. Copies of ^1H NMR and ^{13}C NMR spectra for 2-8



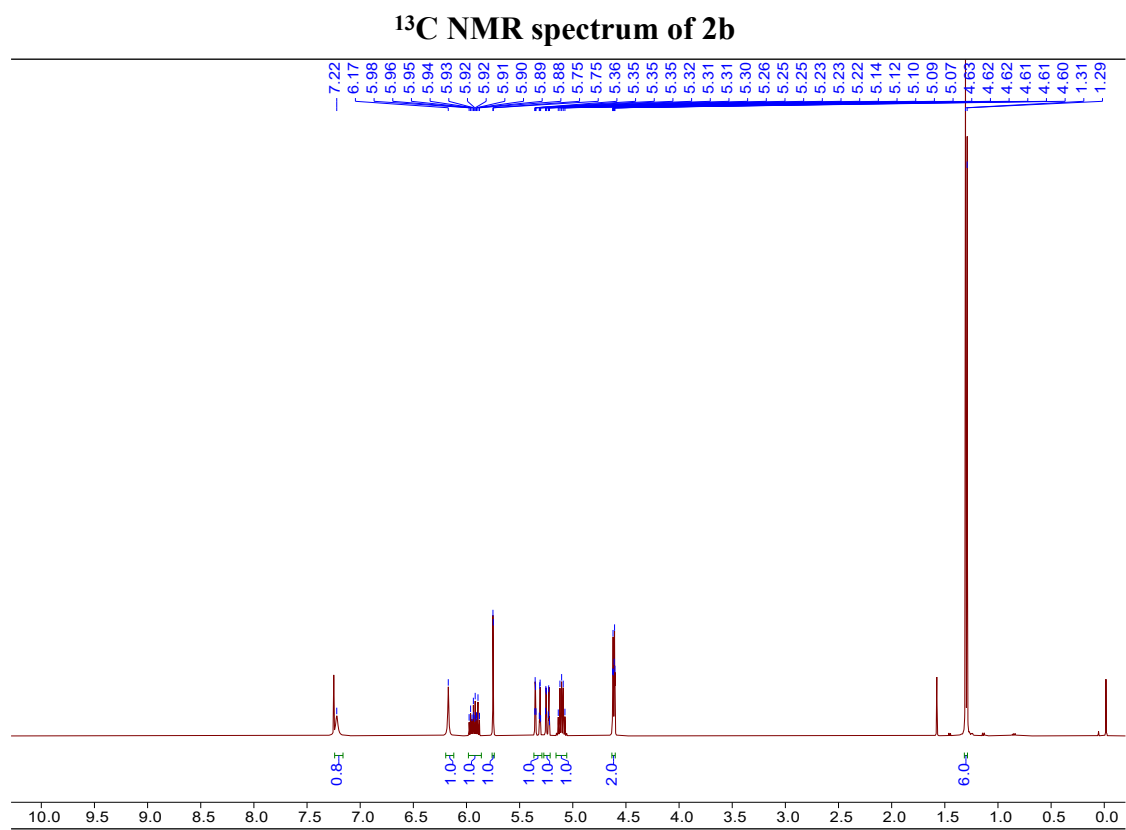
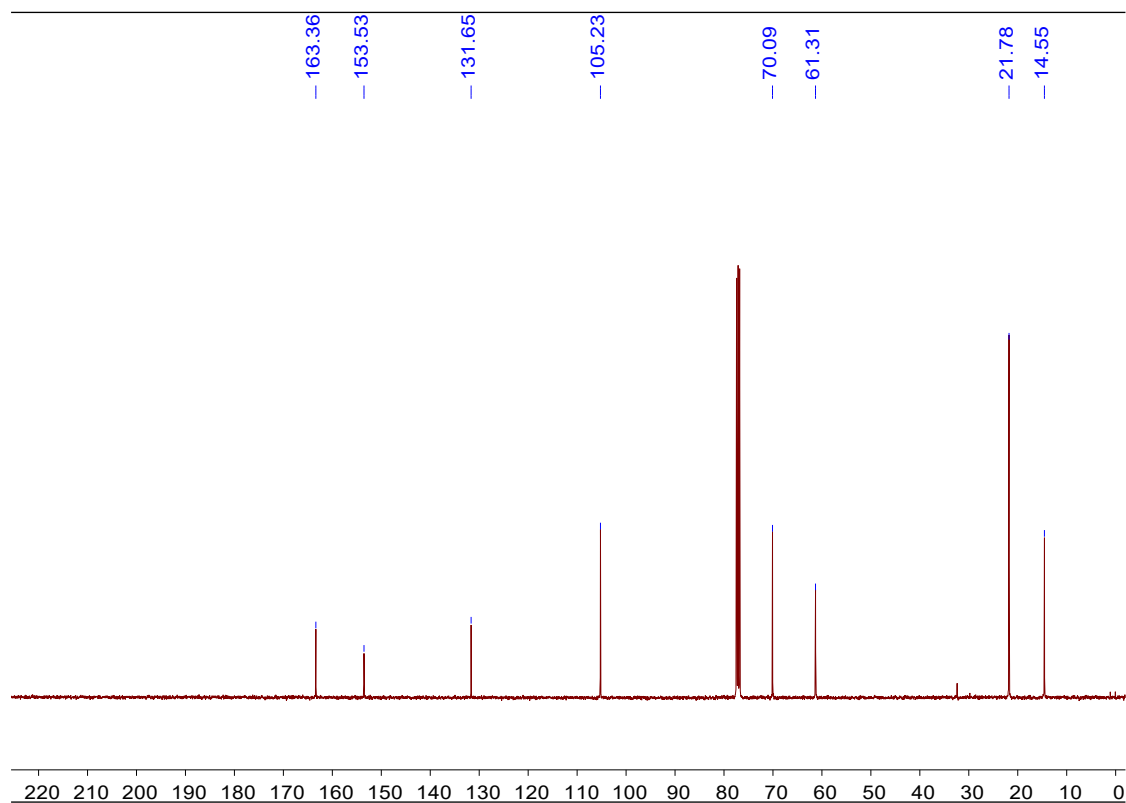
^1H NMR spectrum of 2a

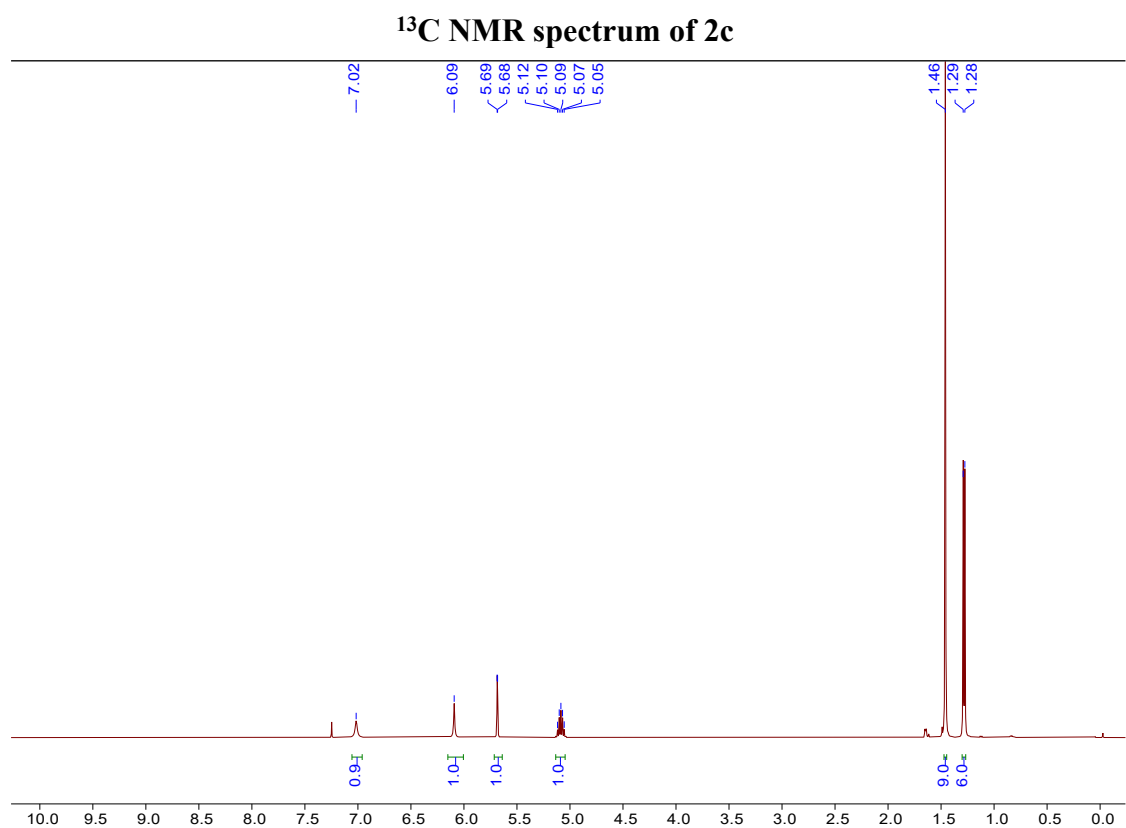
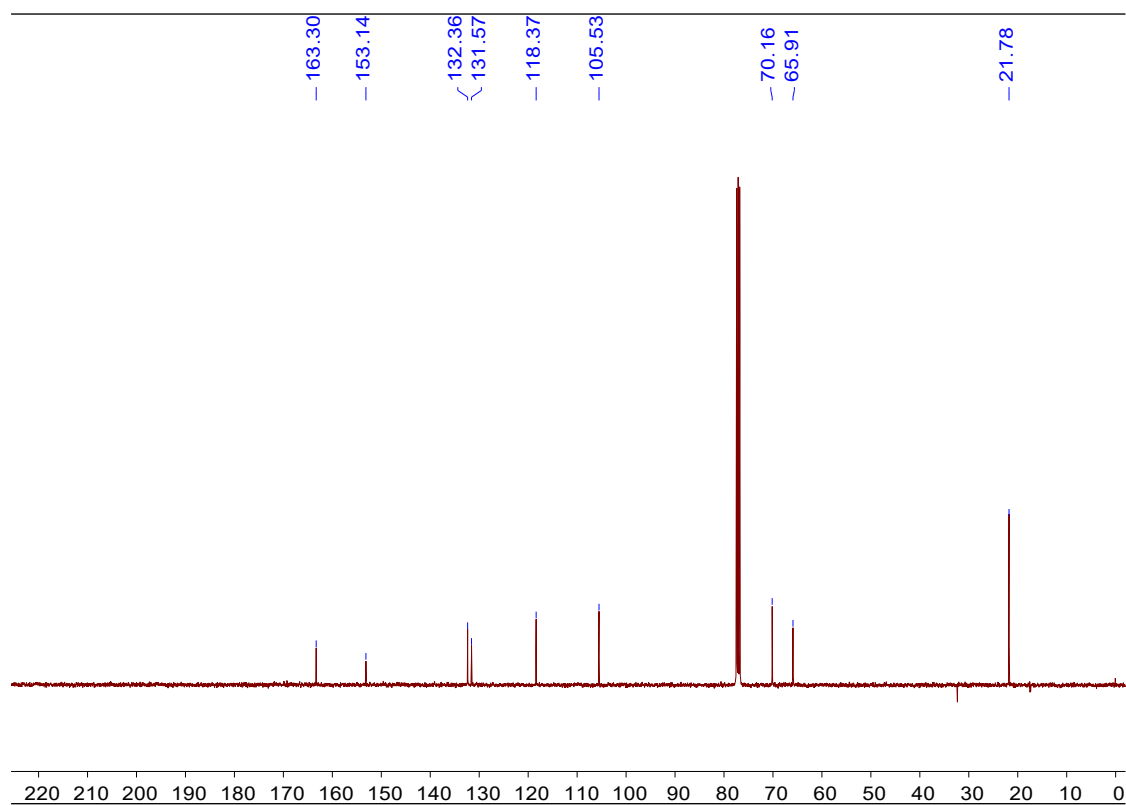


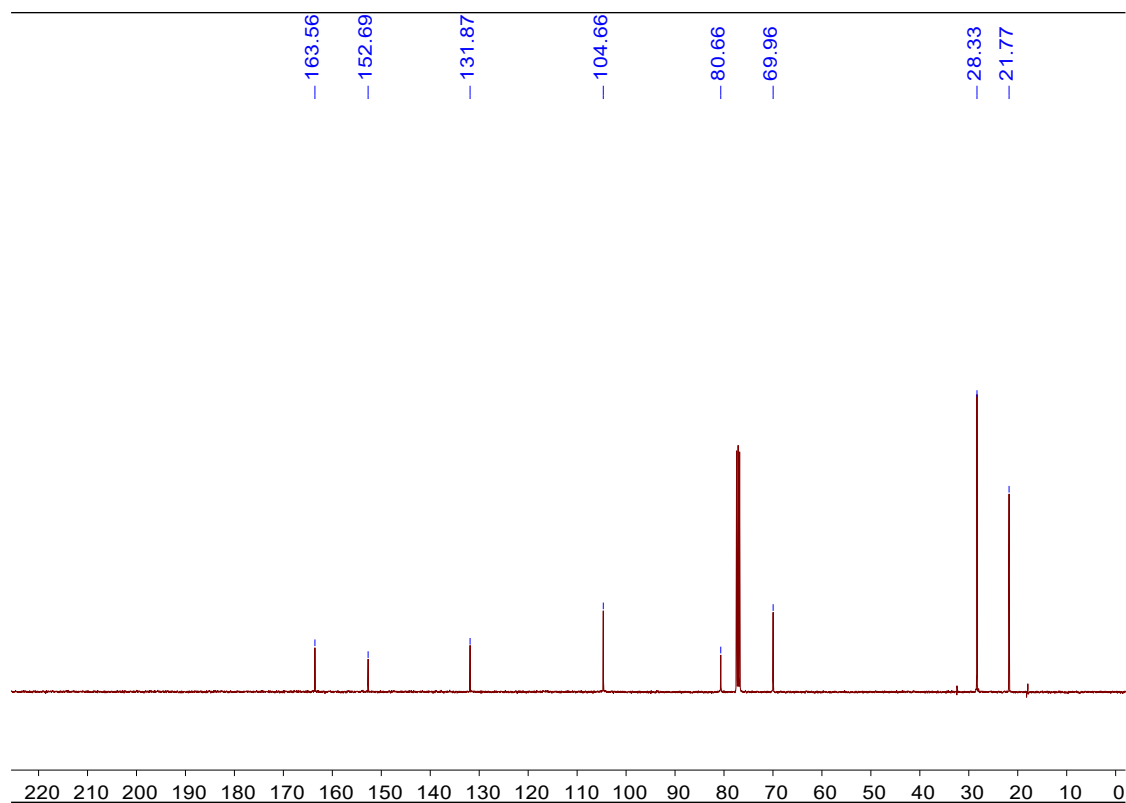
¹³C NMR spectrum of 2a



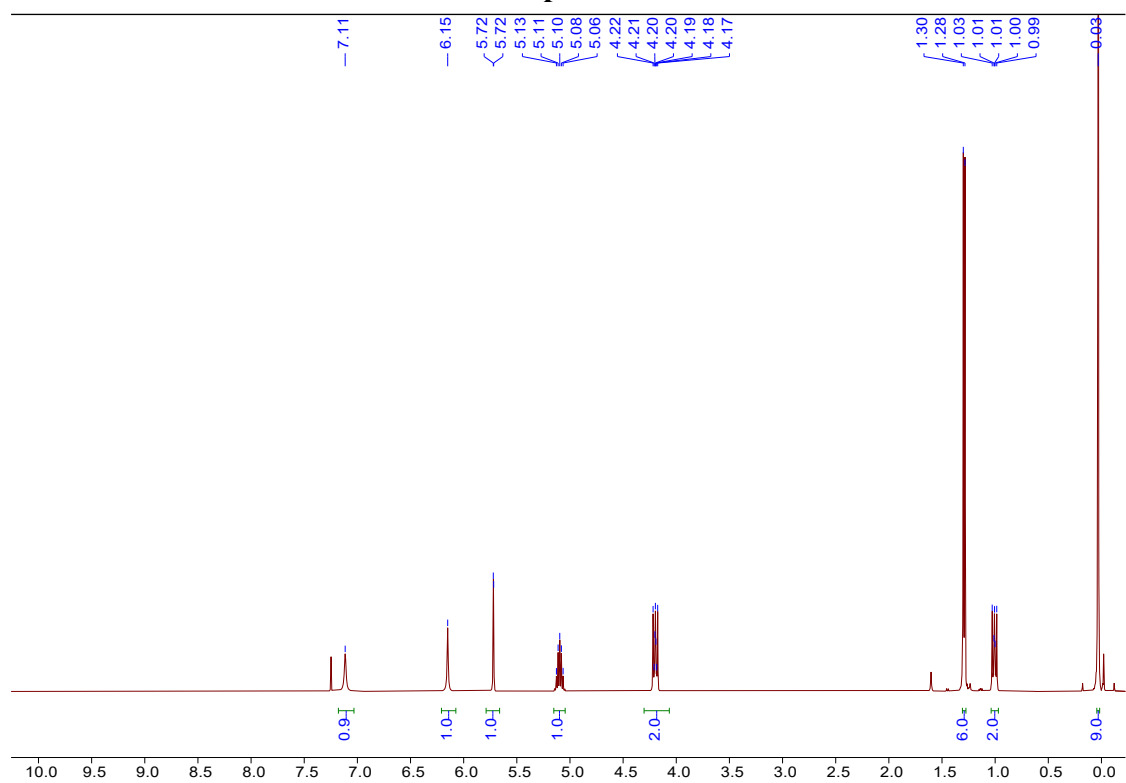
¹H NMR spectrum of 2b



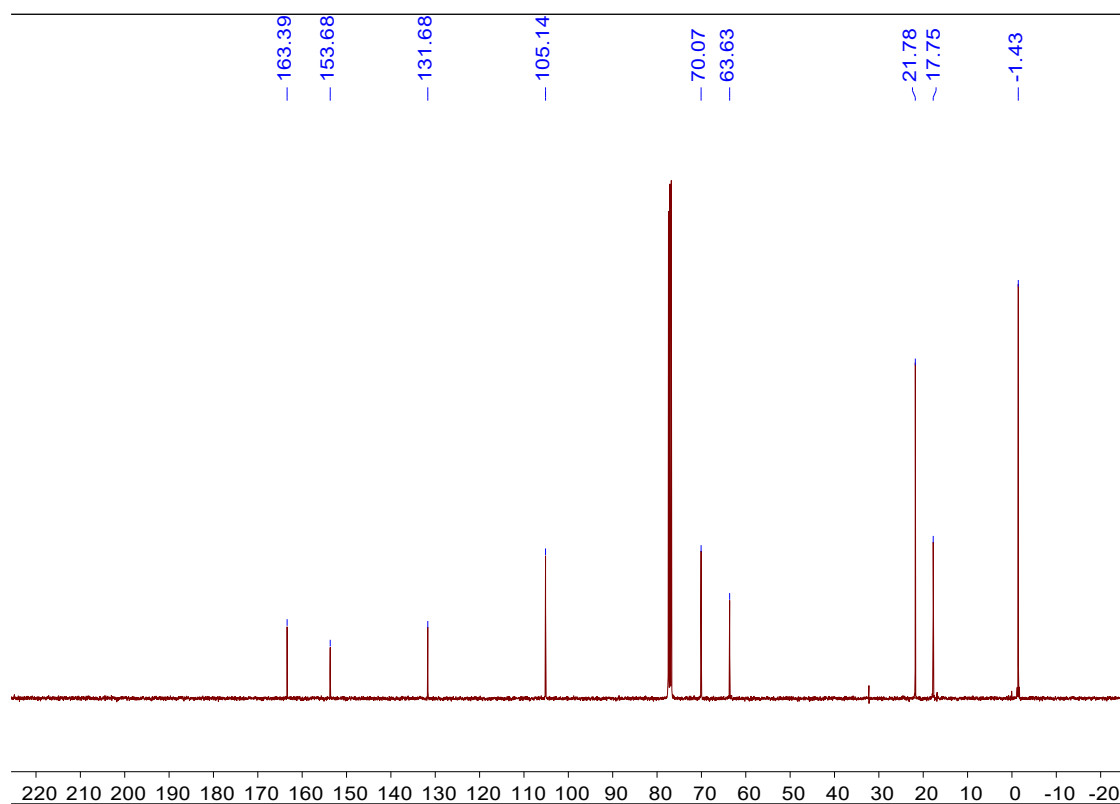




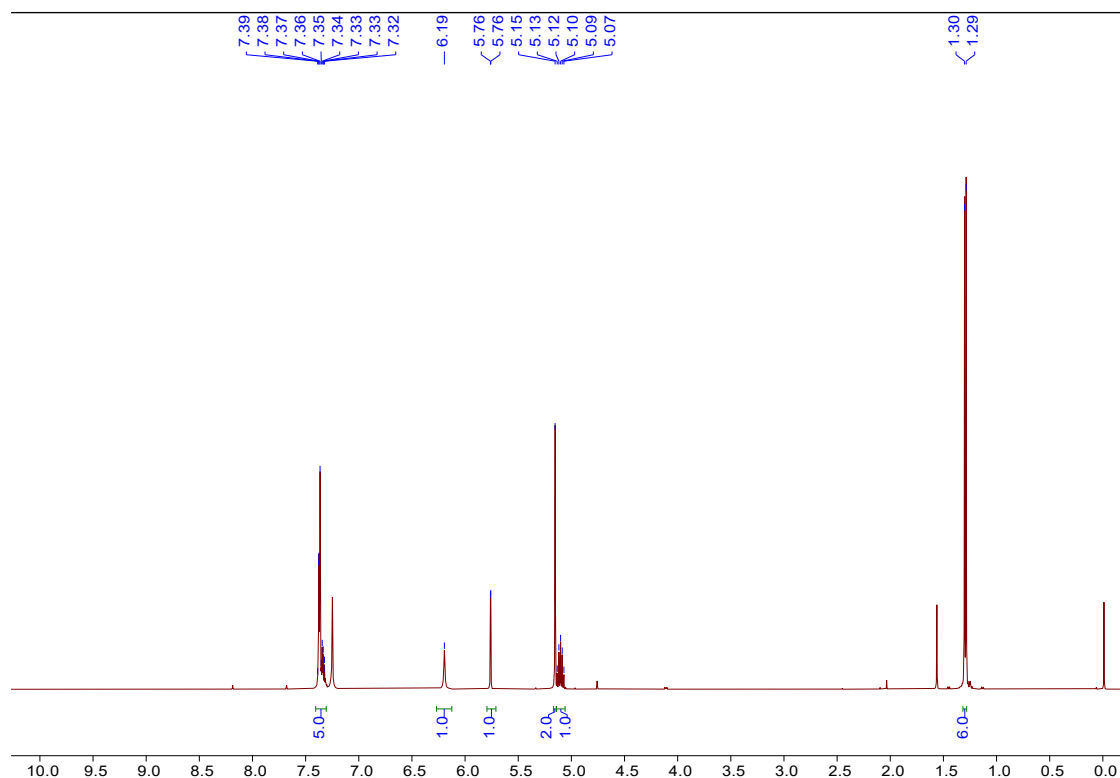
^{13}C NMR spectrum of 2d



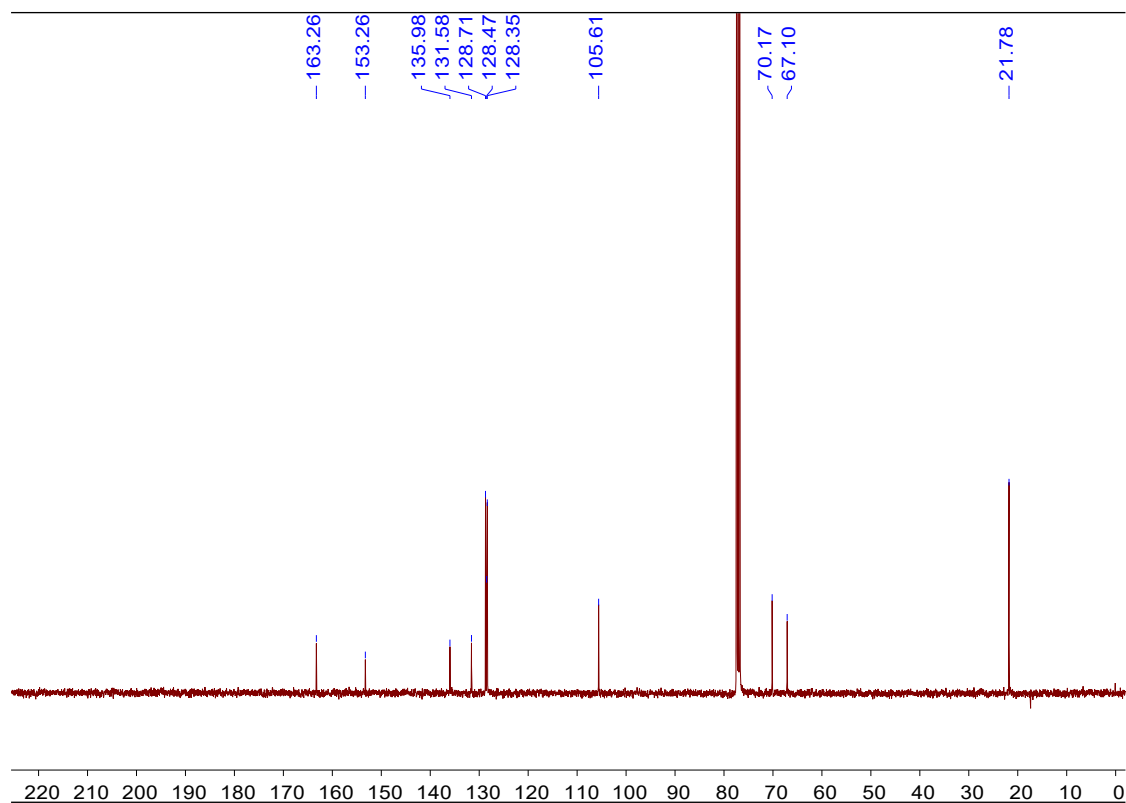
^1H NMR spectrum of 2e



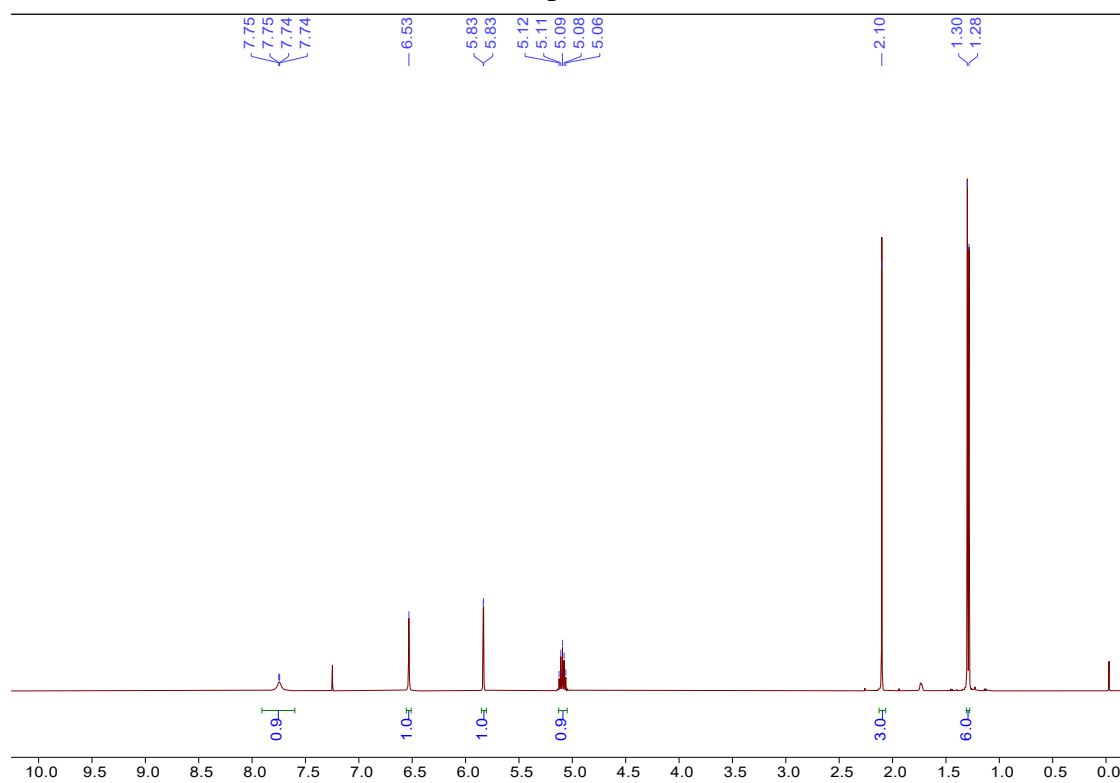
^{13}C NMR spectrum of 2e



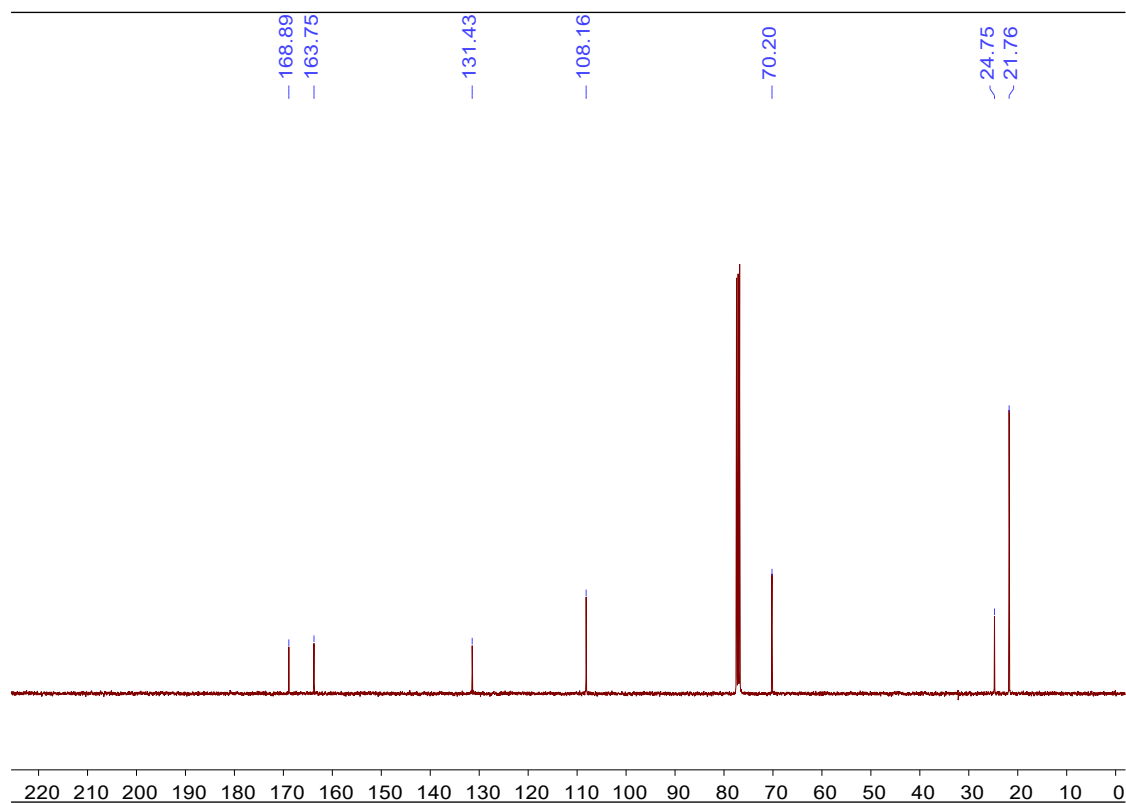
¹H NMR spectrum of 2f



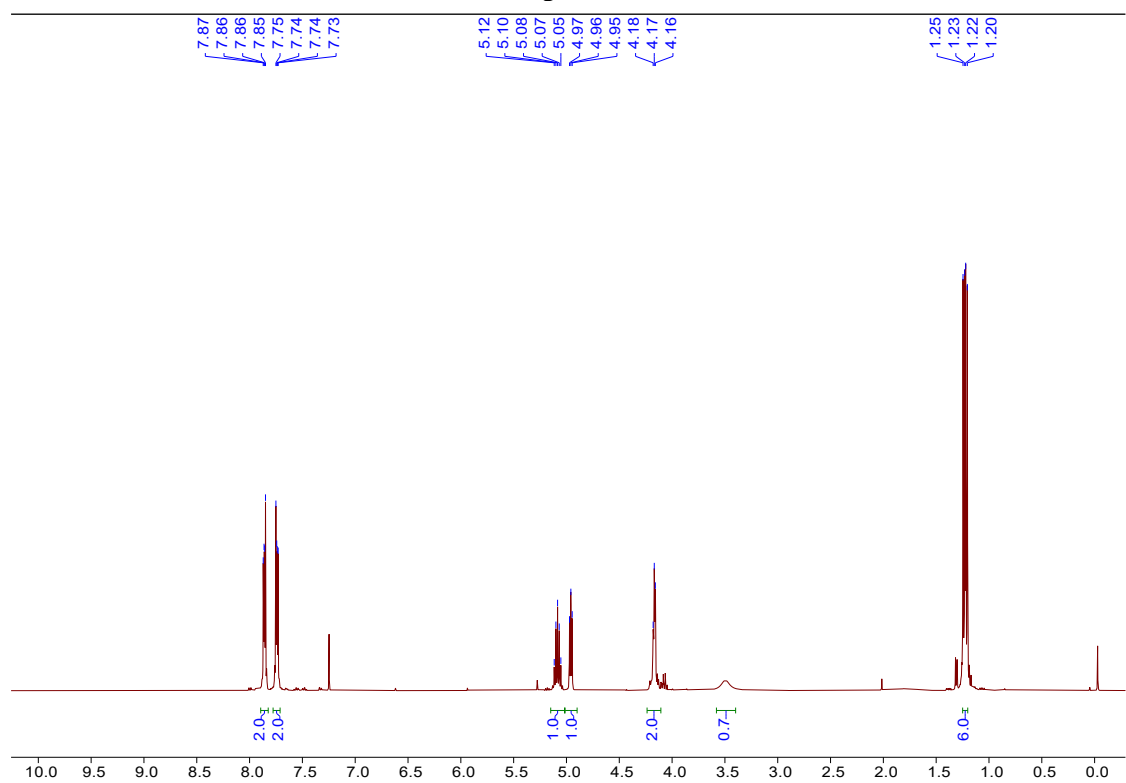
^{13}C NMR spectrum of 2f



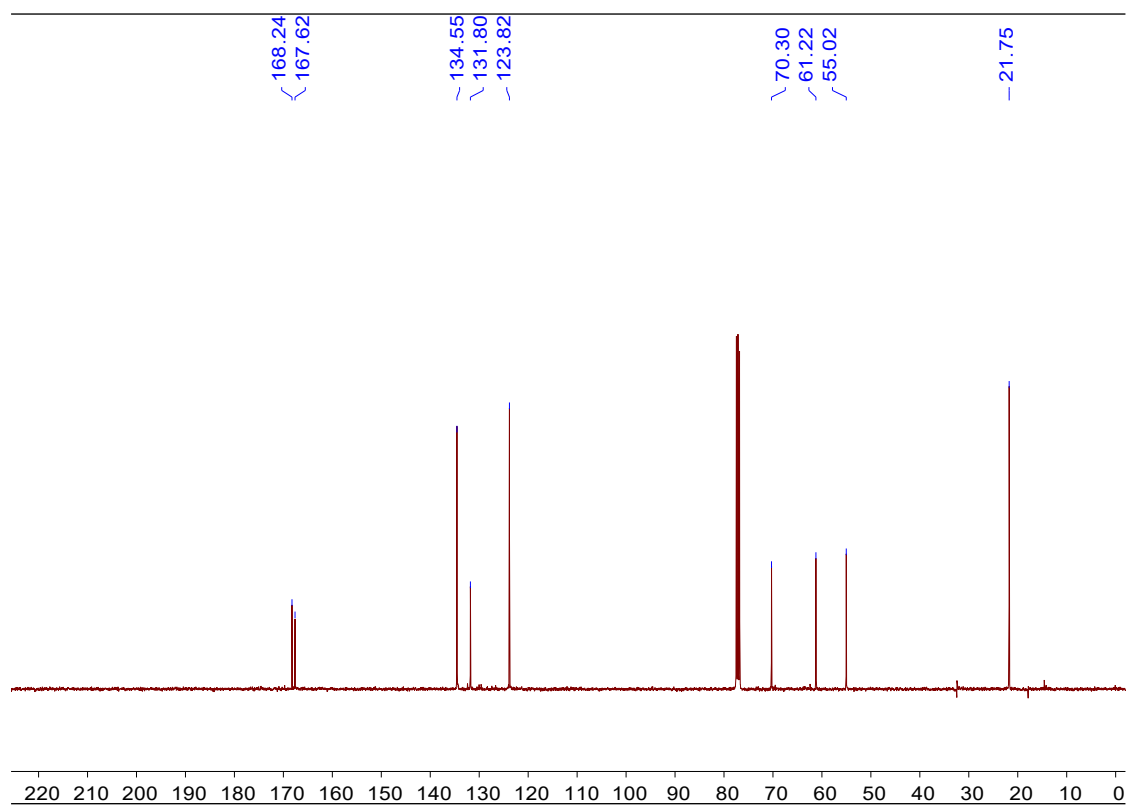
^1H NMR spectrum of 2h



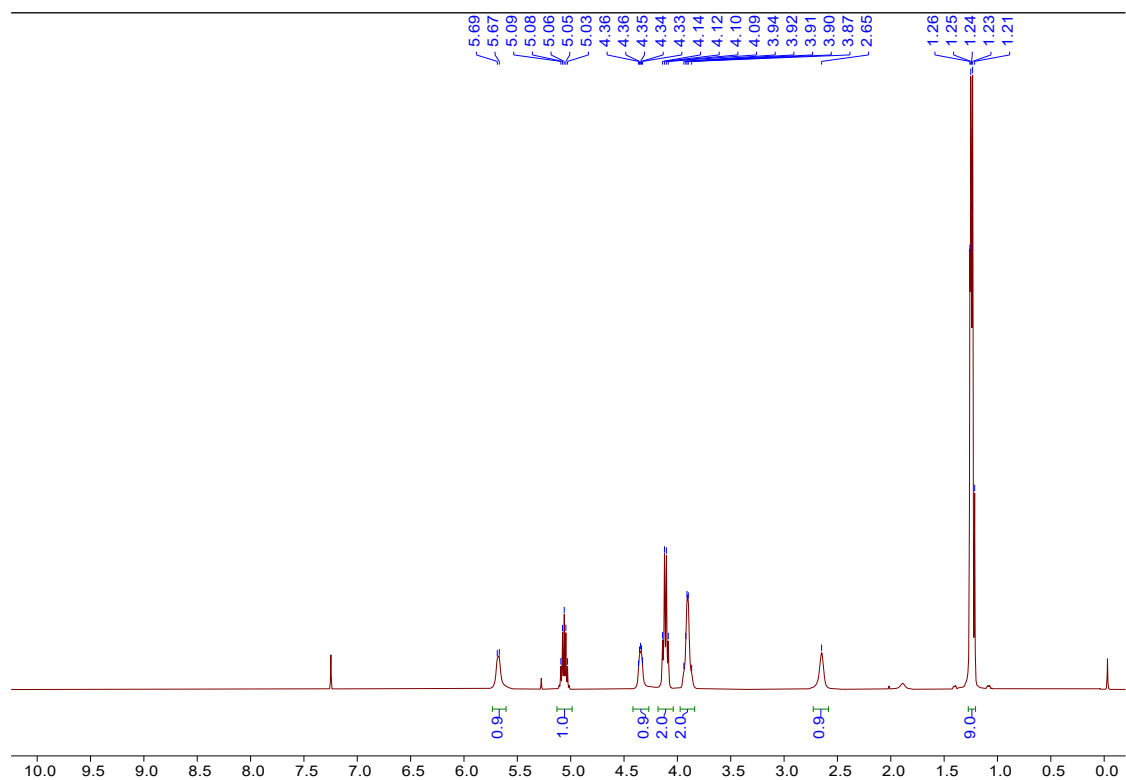
¹³C NMR spectrum of 2h



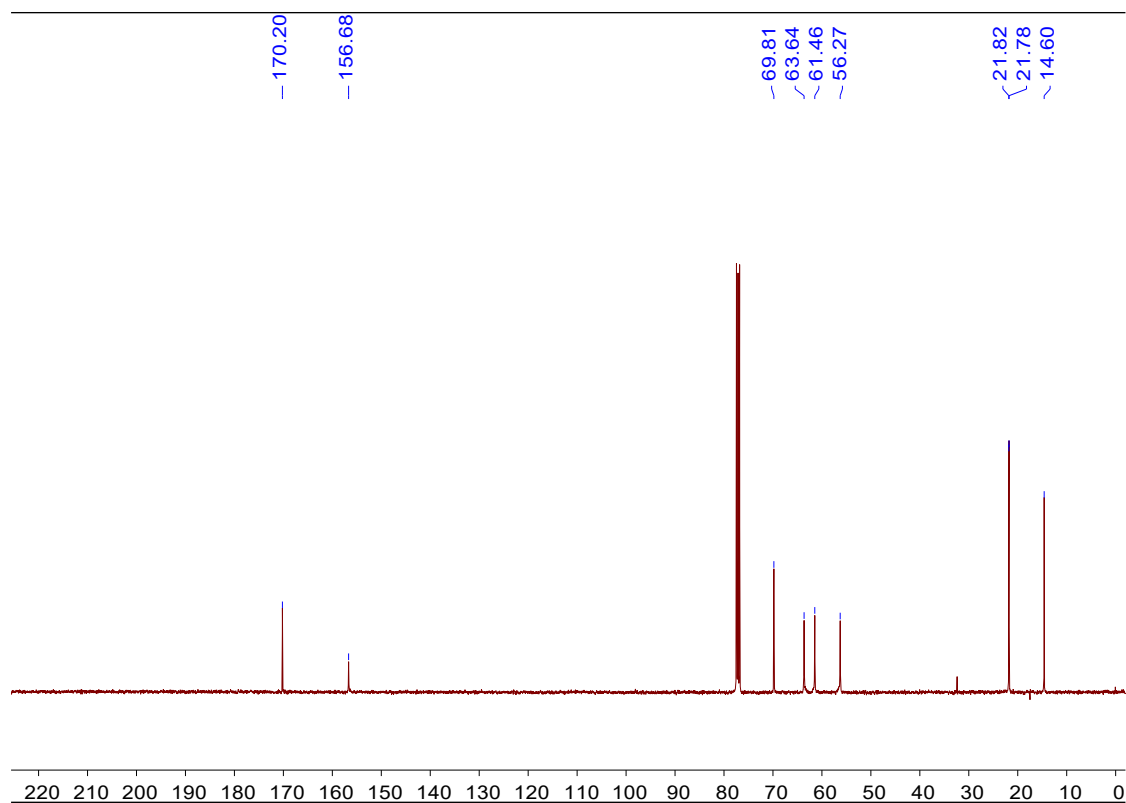
¹H NMR spectrum of 3a



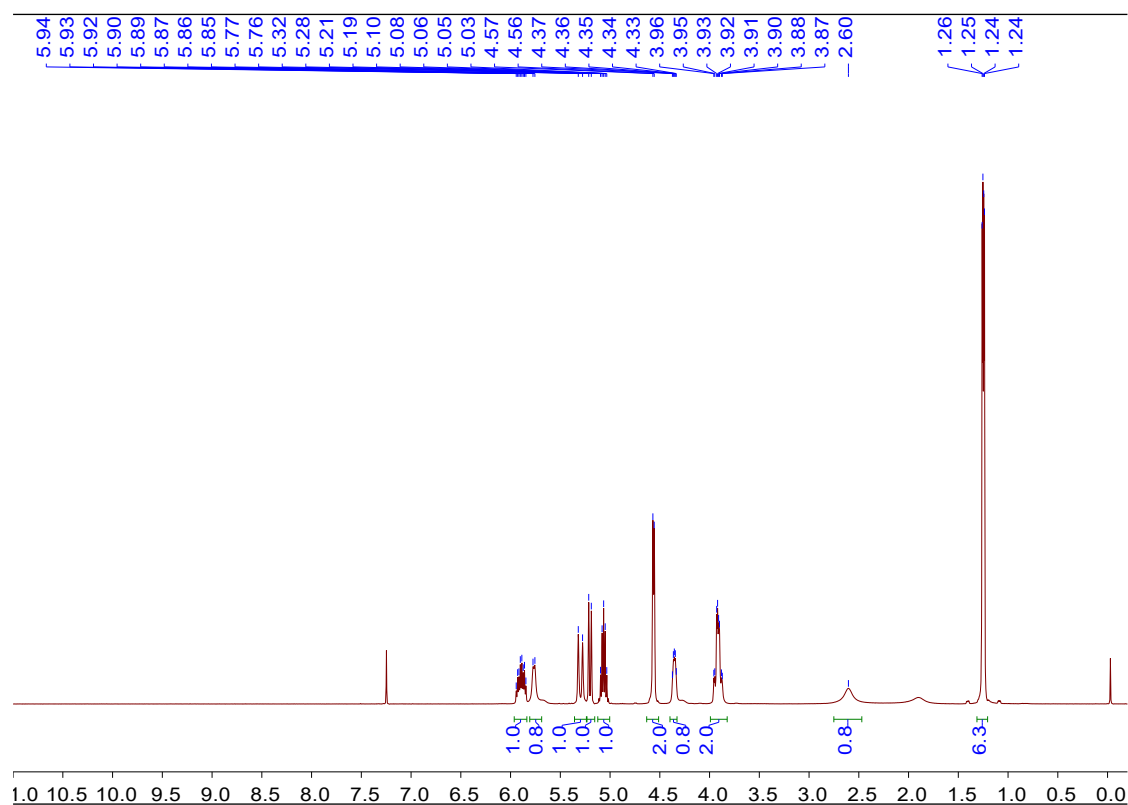
¹³C NMR spectrum of 3a



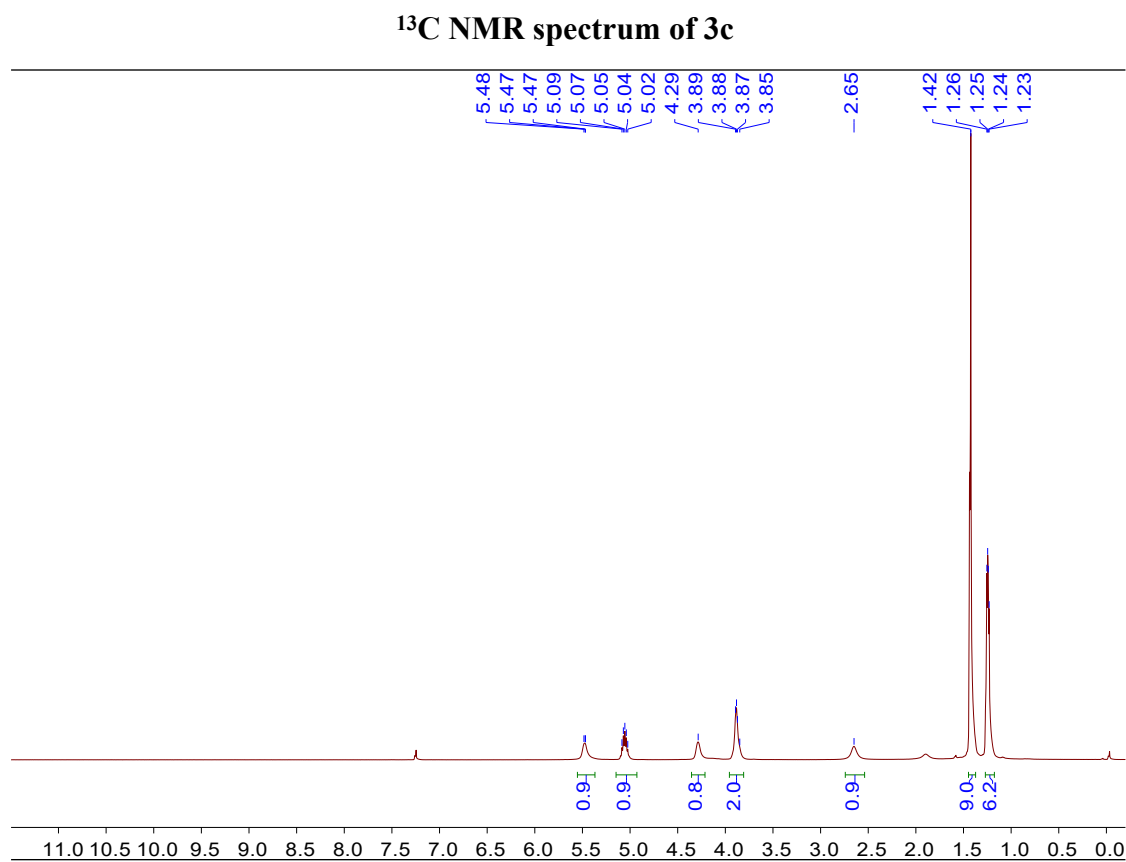
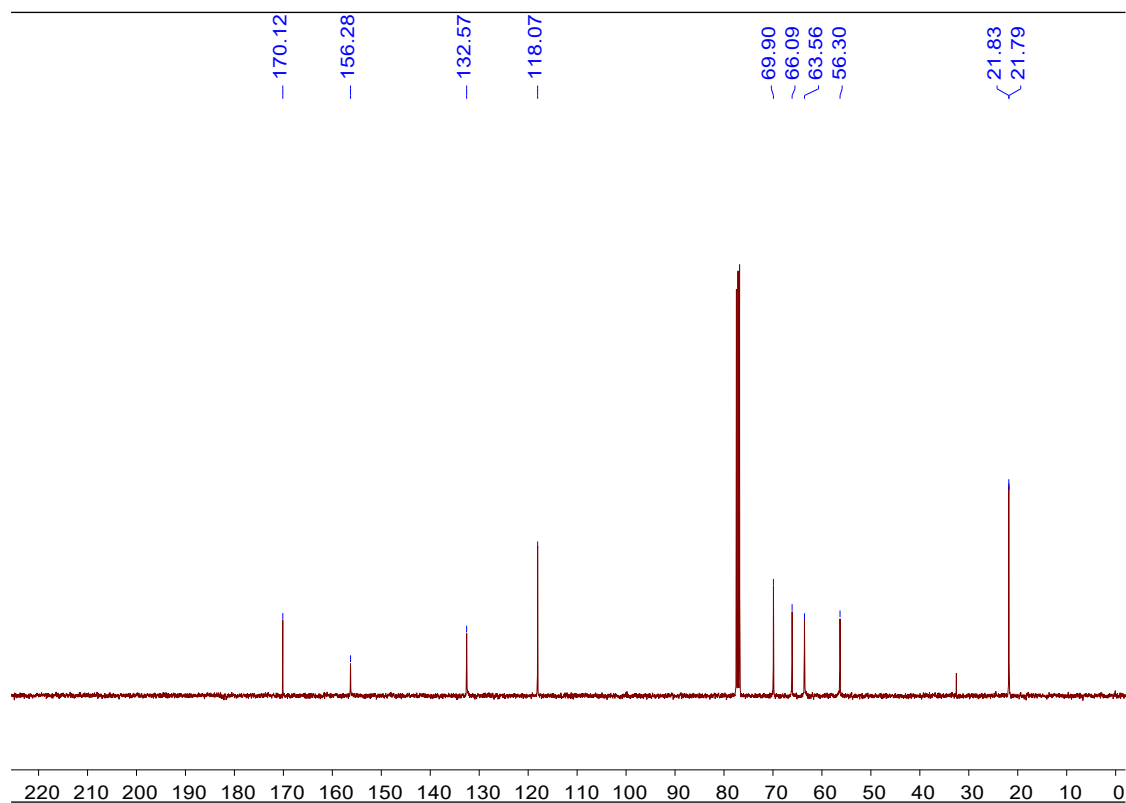
¹H NMR spectrum of 3b

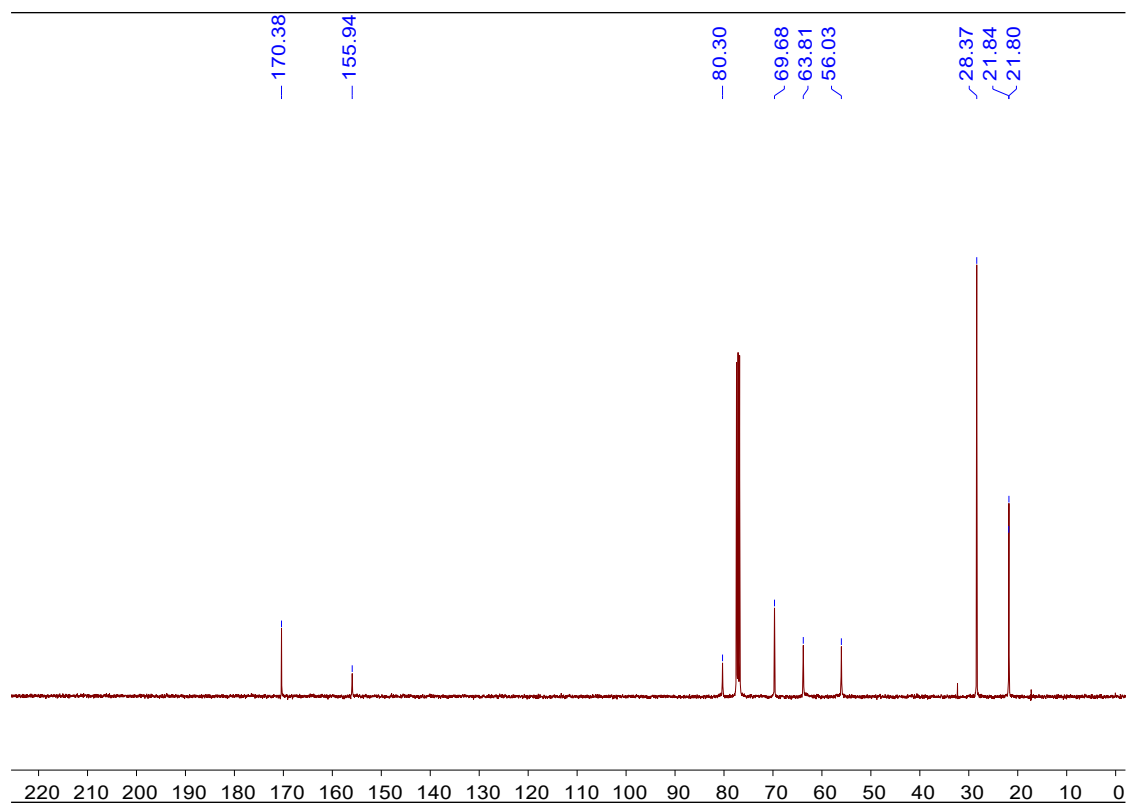


¹³C NMR spectrum of 3b

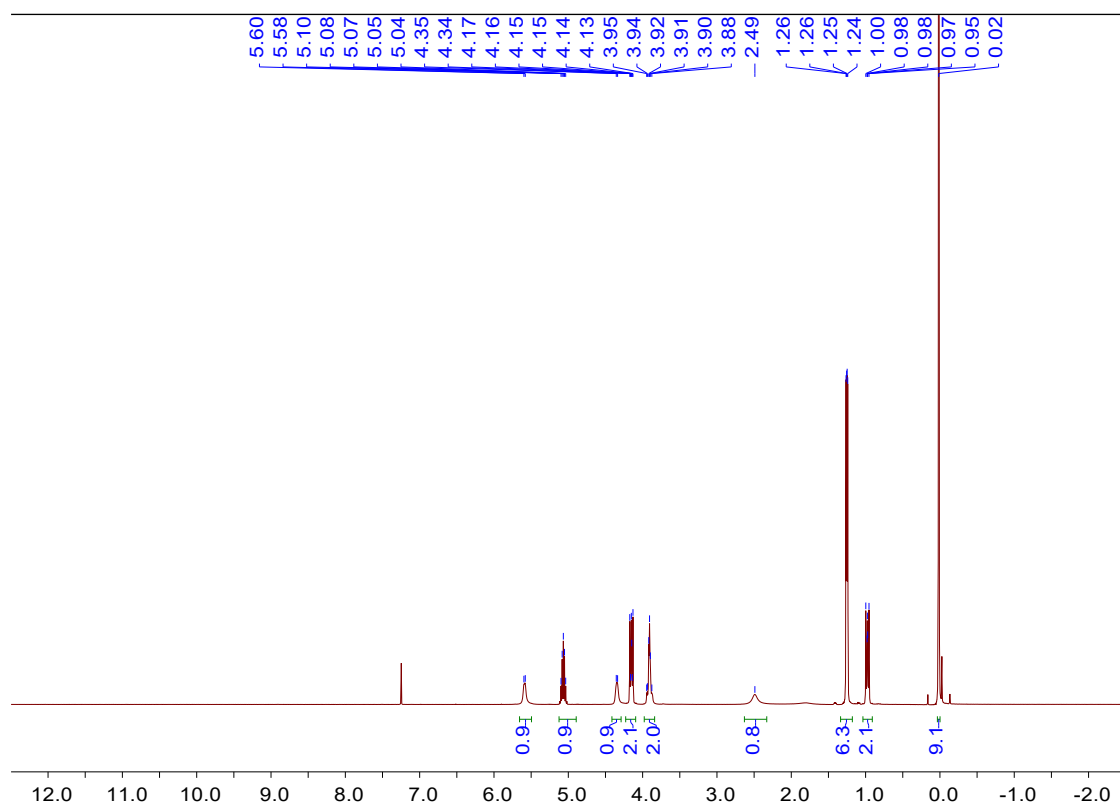


^1H NMR spectrum of 3c

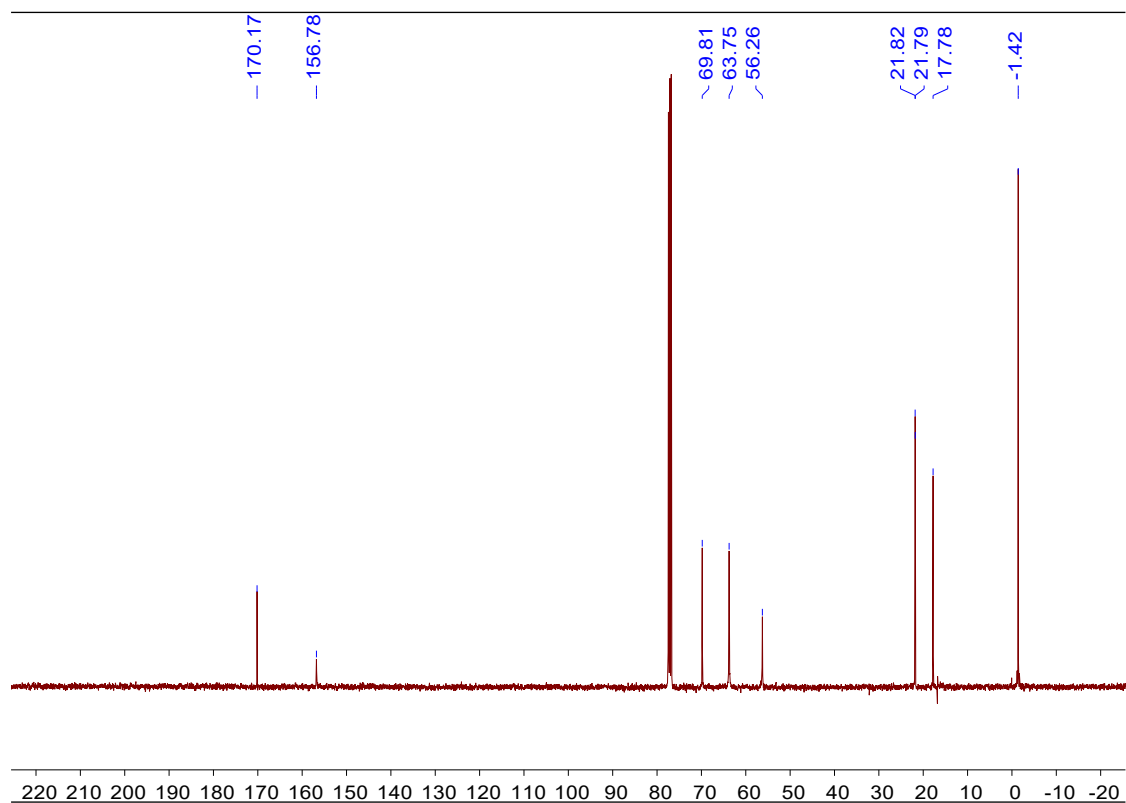




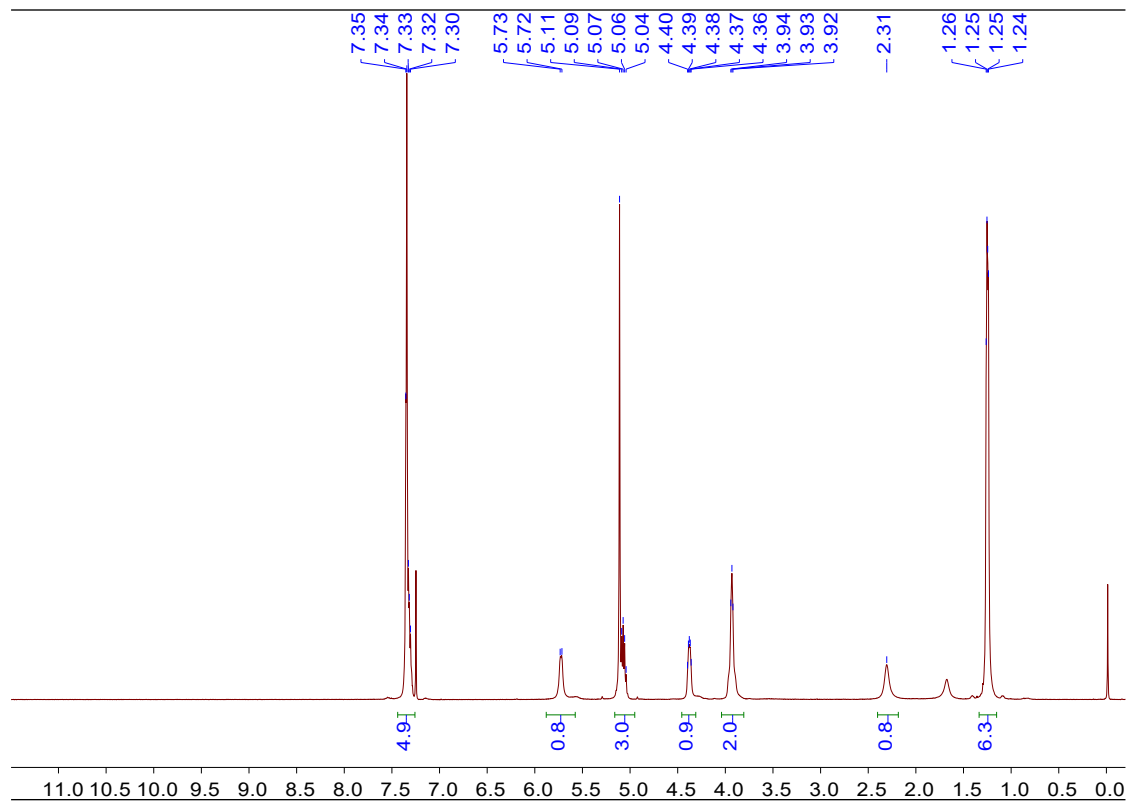
¹³C NMR spectrum of 3d



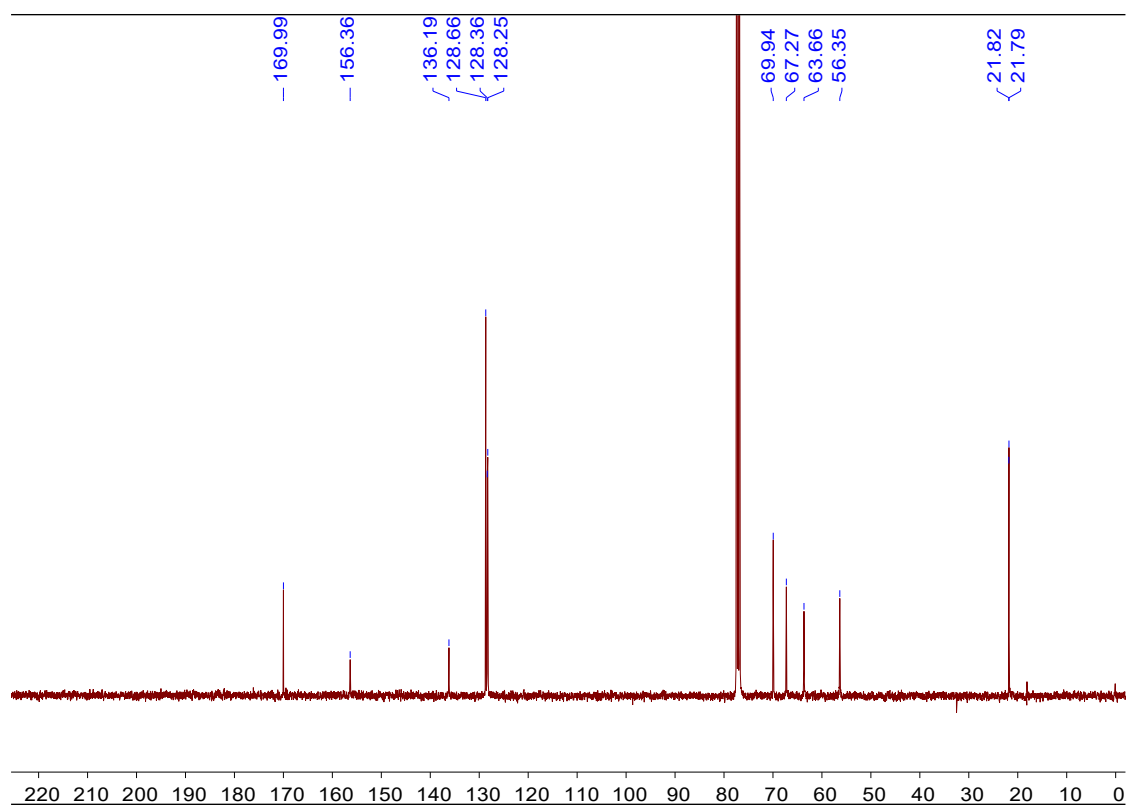
¹H NMR spectrum of 3e



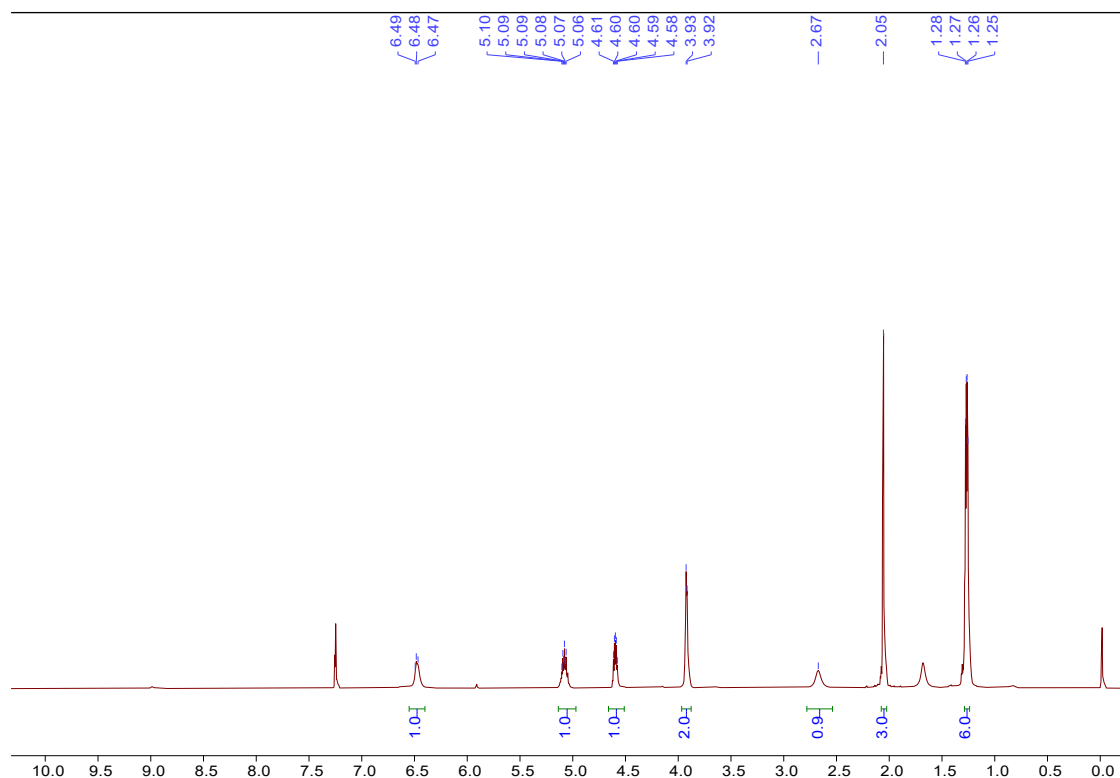
^{13}C NMR spectrum of **3e**



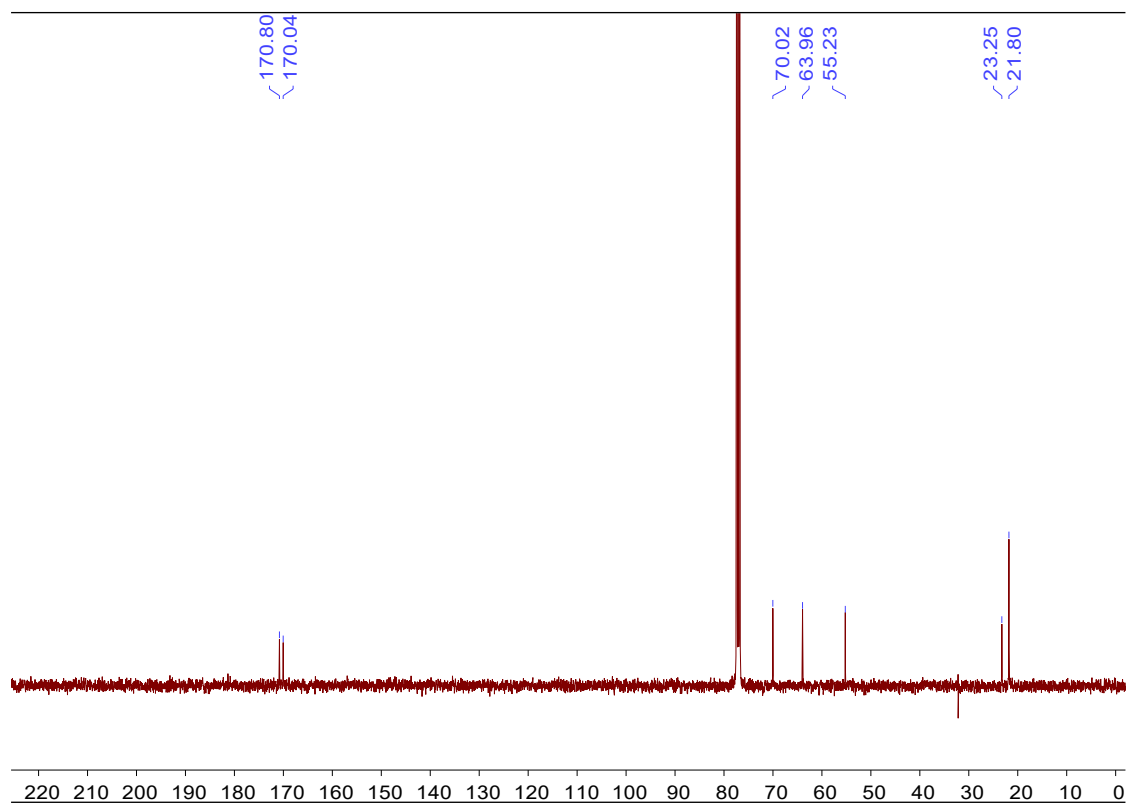
^1H NMR spectrum of **3f**



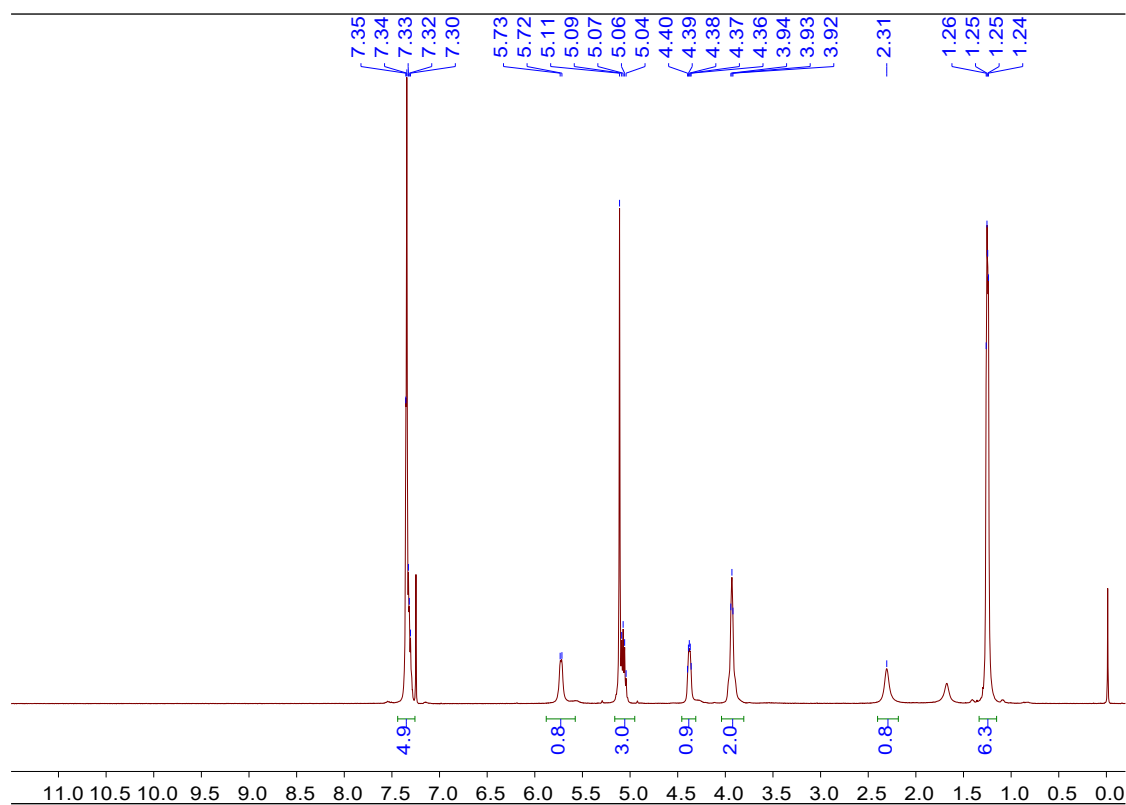
¹³C NMR spectrum of 3f



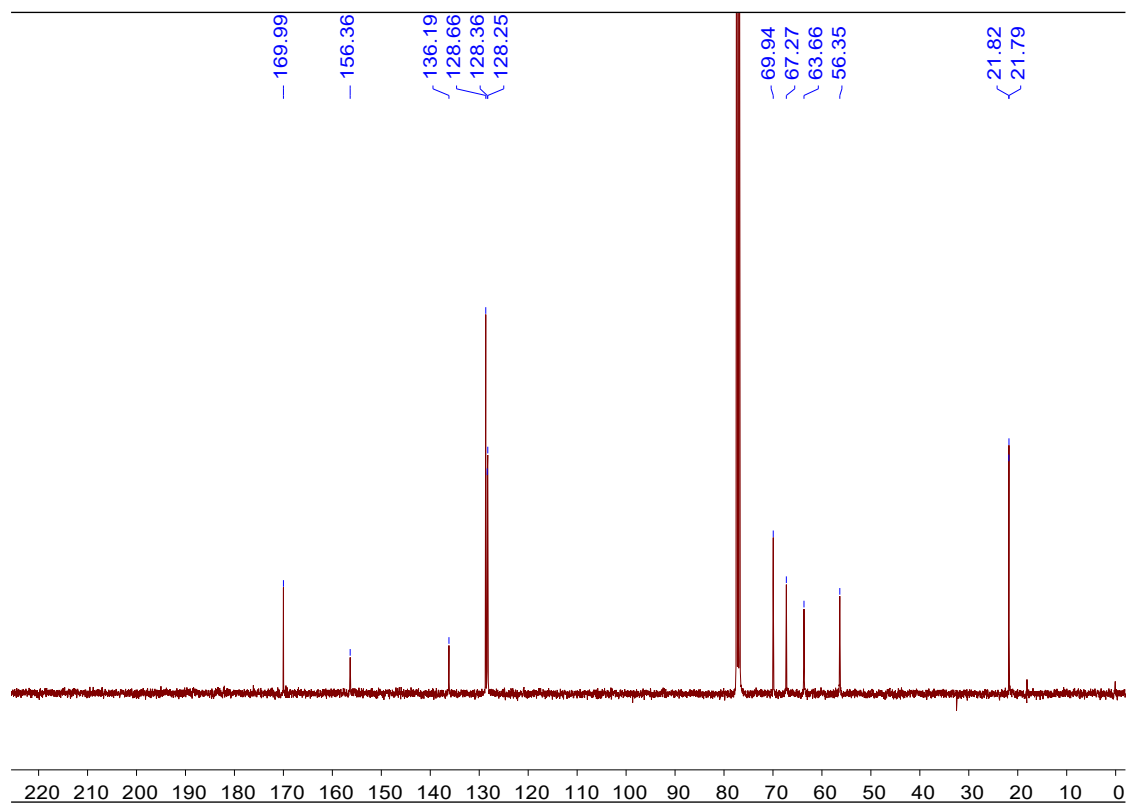
¹H NMR spectrum of 3h



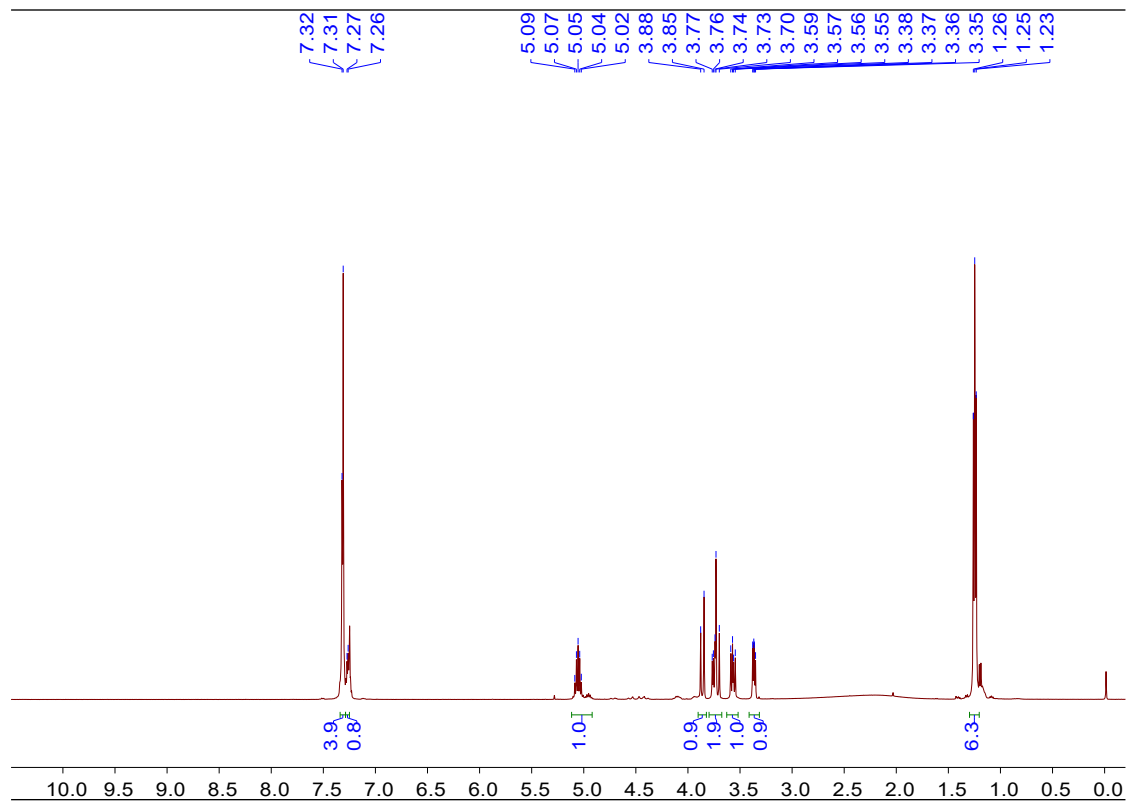
^{13}C NMR spectrum of 3h



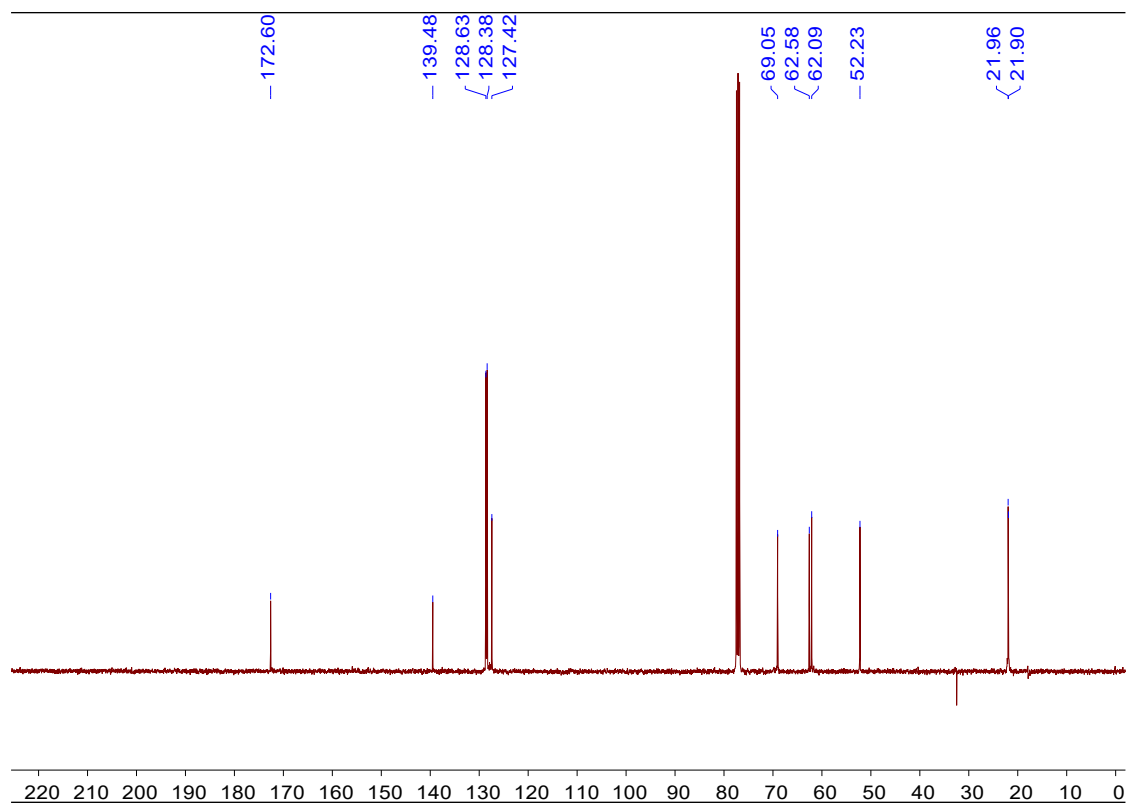
^1H NMR spectrum of 3i



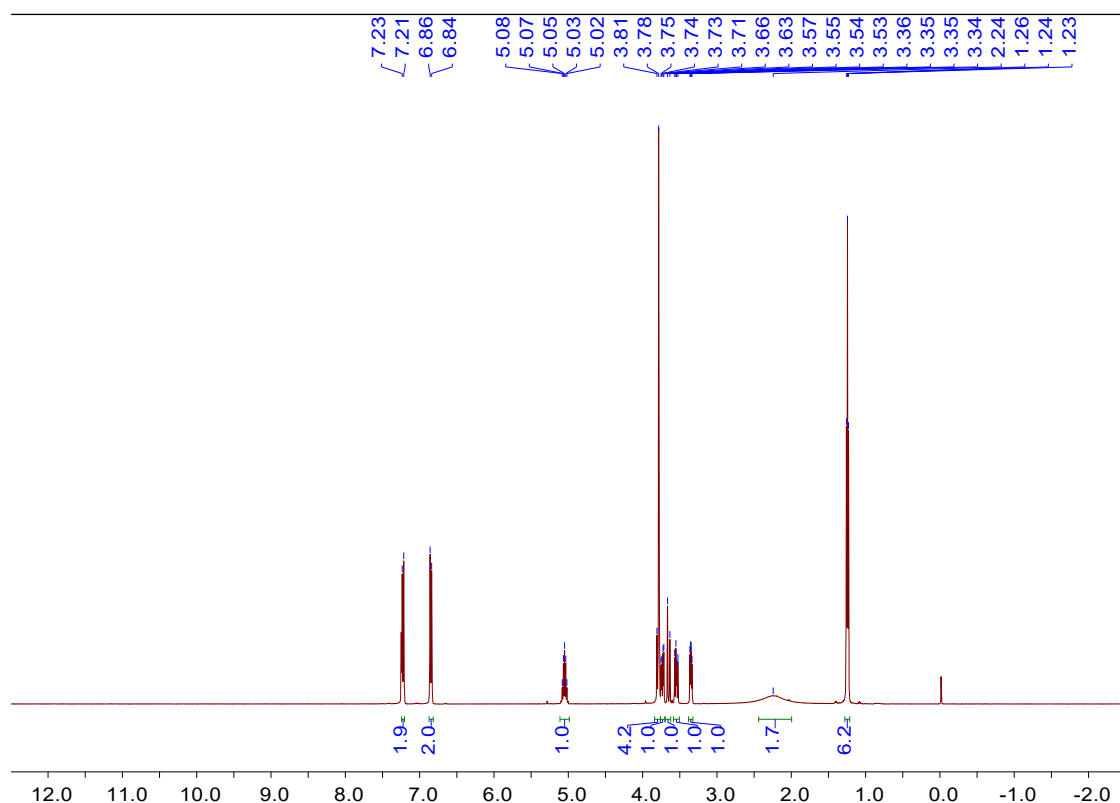
^{13}C NMR spectrum of **3i**



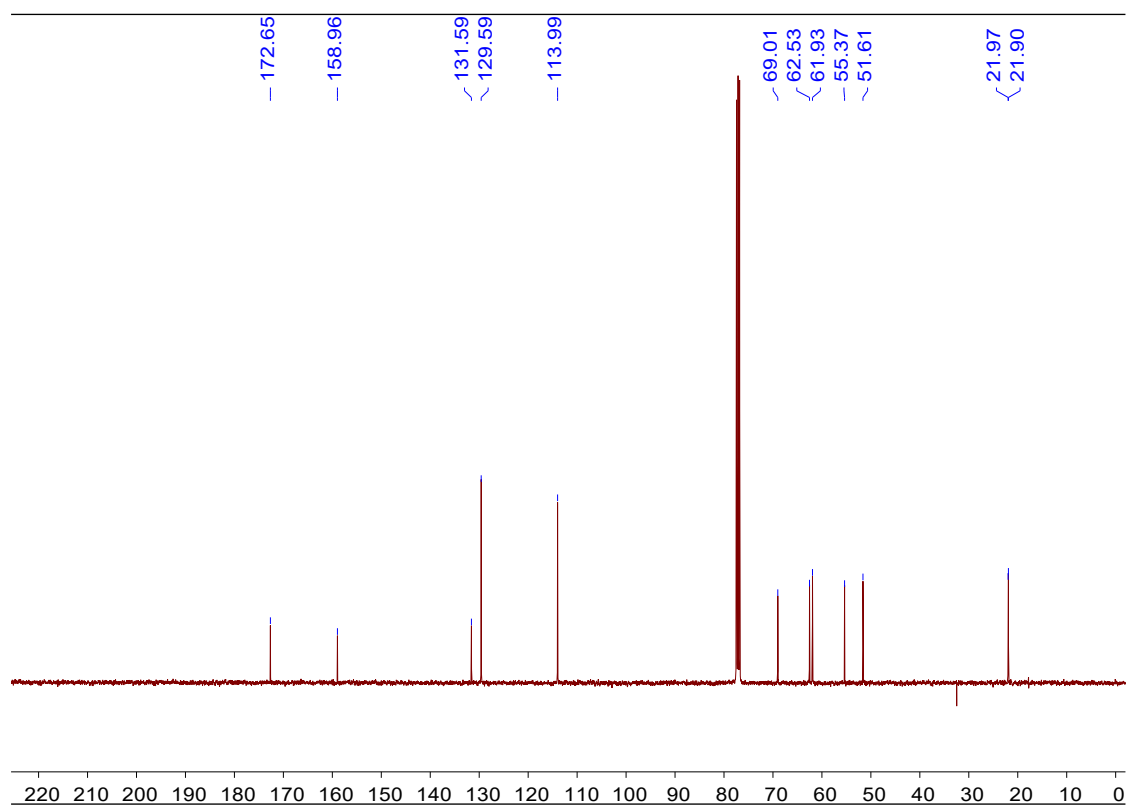
^1H NMR spectrum of **3j**



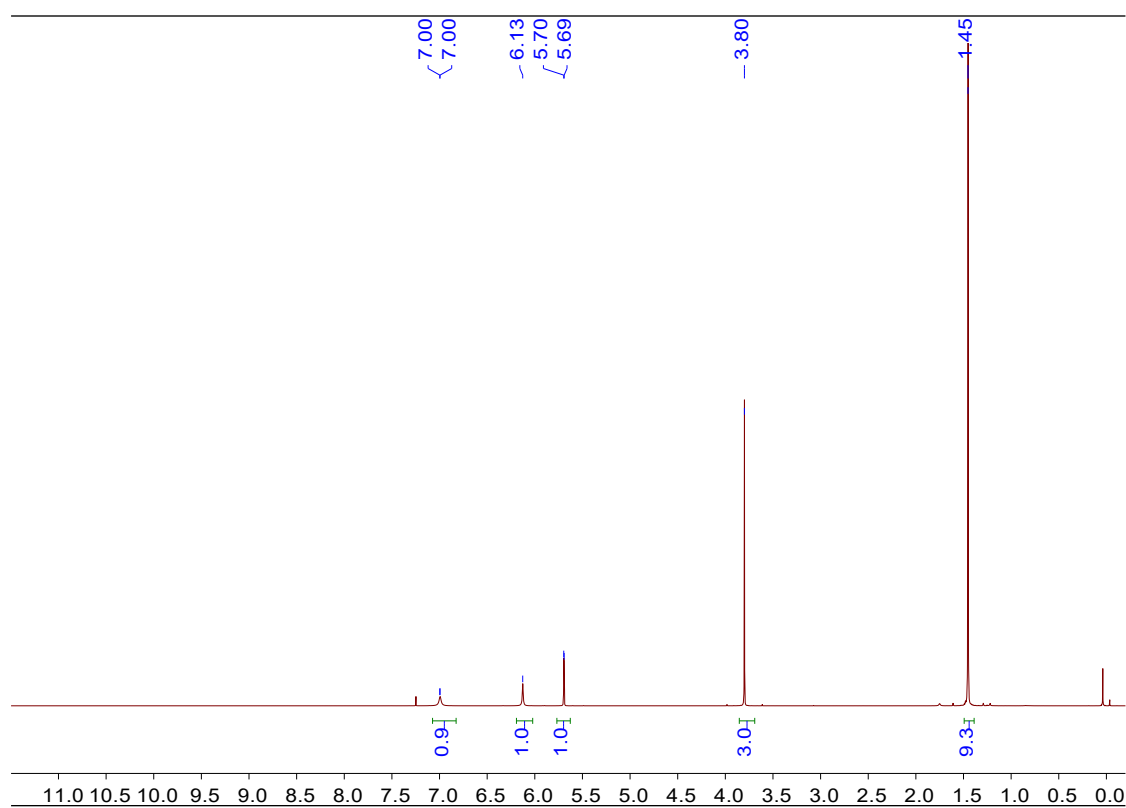
¹³C NMR spectrum of 3j



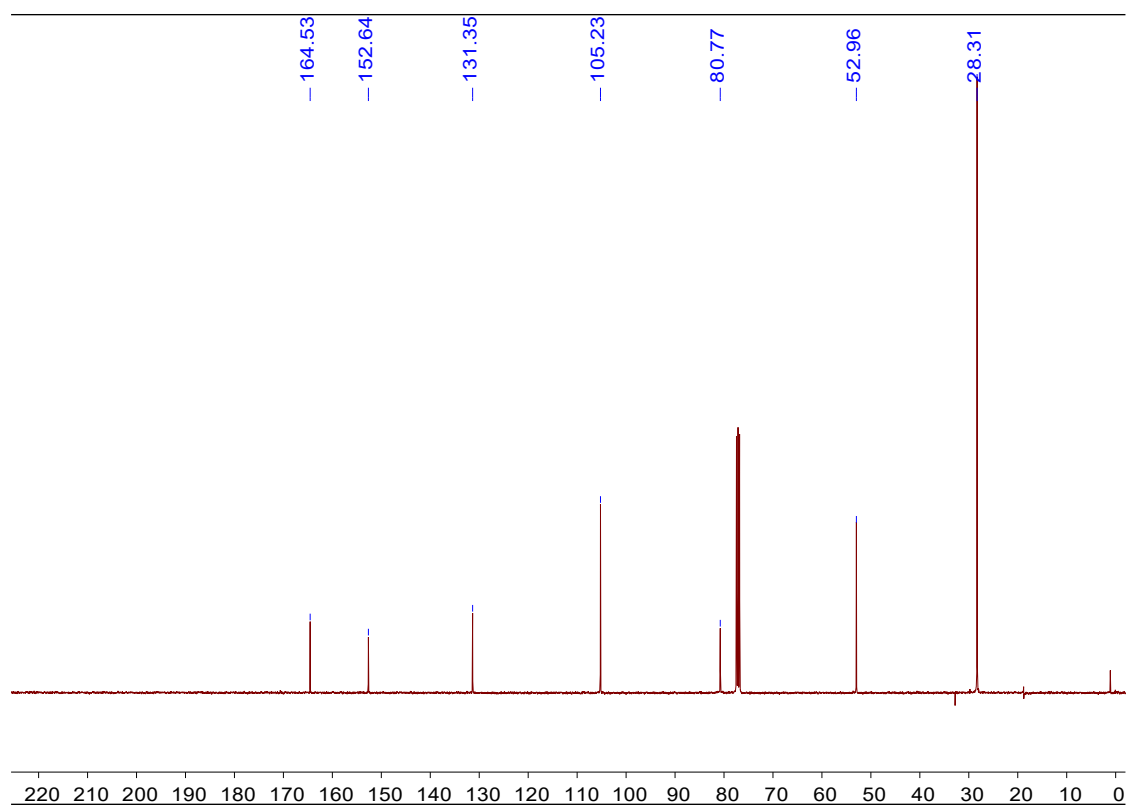
¹H NMR spectrum of 3k



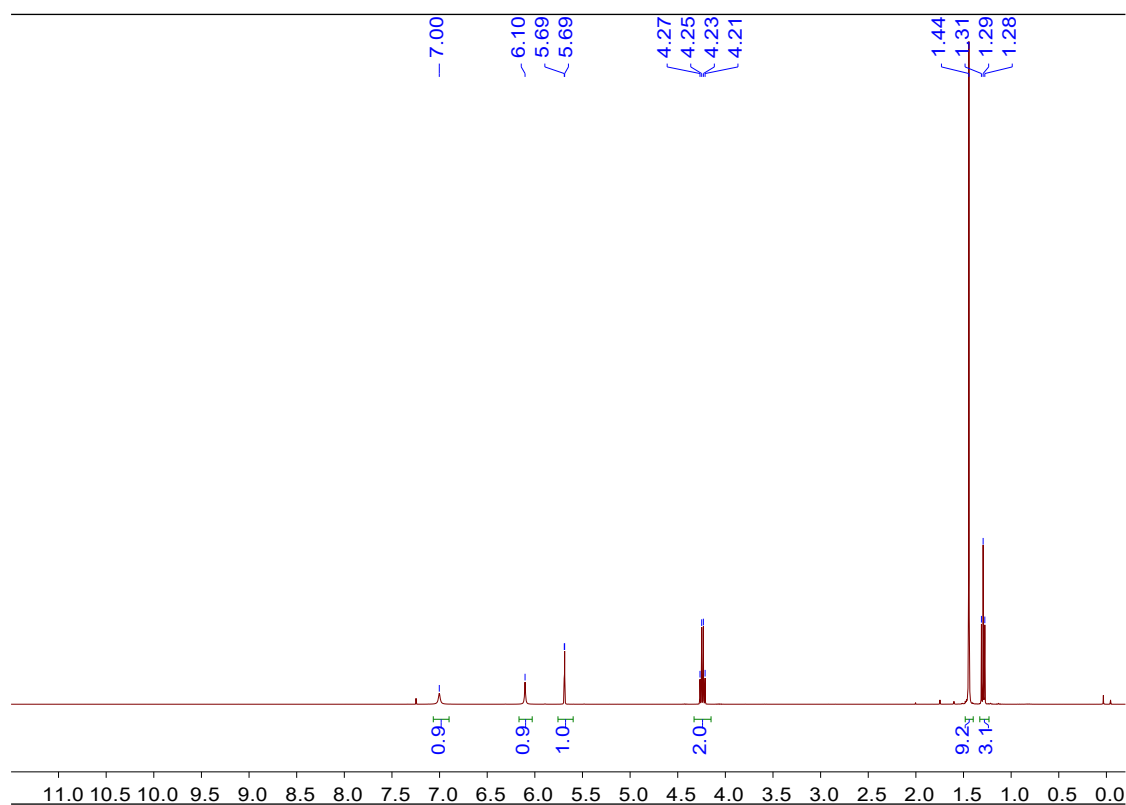
¹³C NMR spectrum of 3k



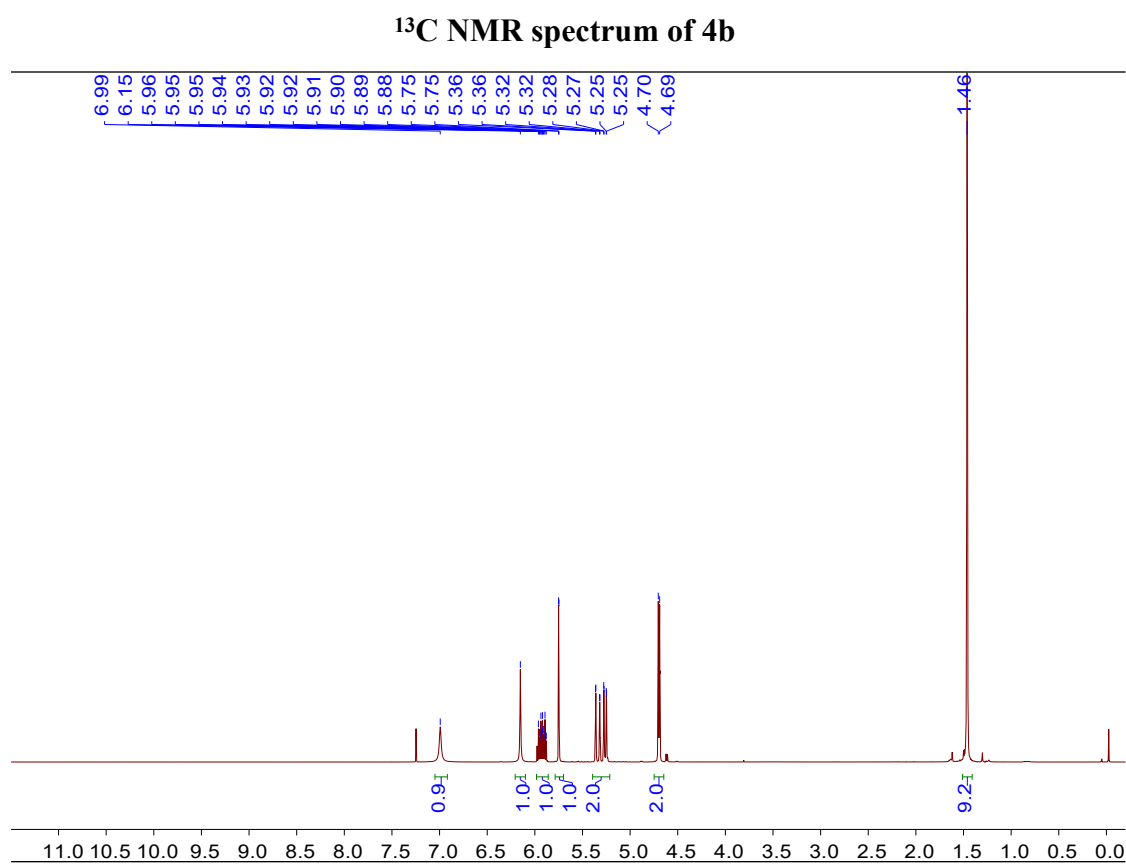
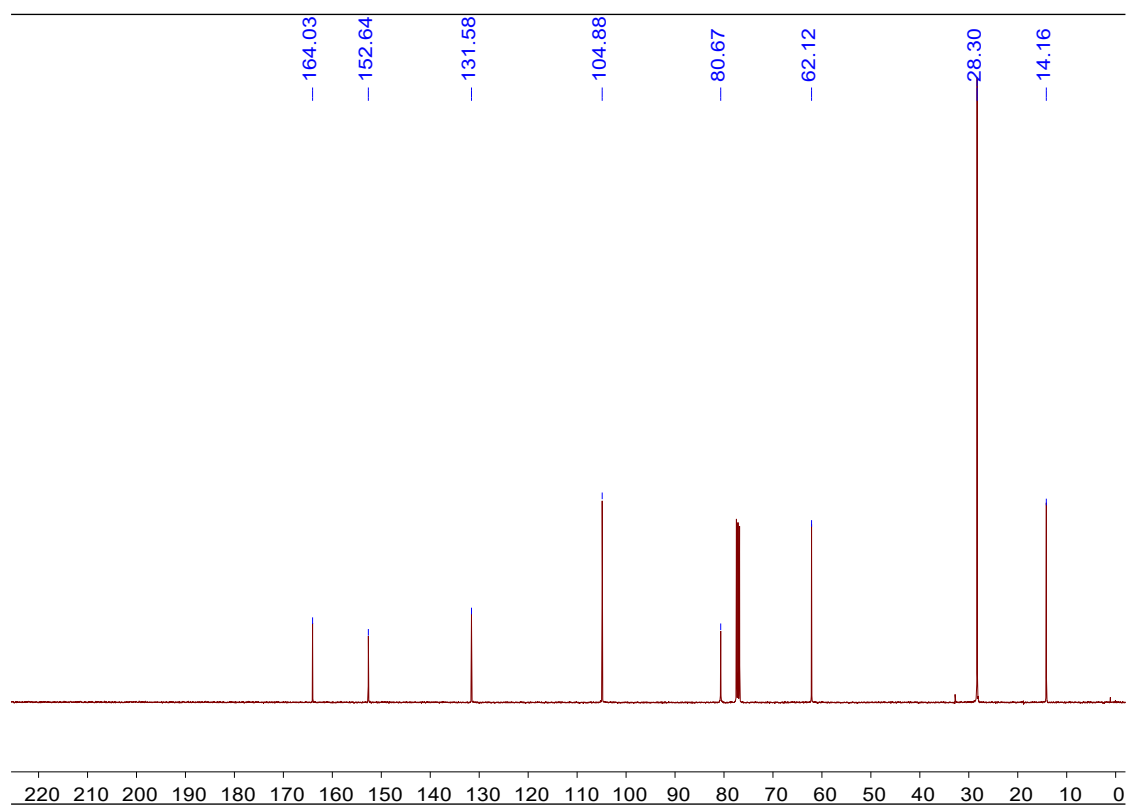
¹H NMR spectrum of 4a



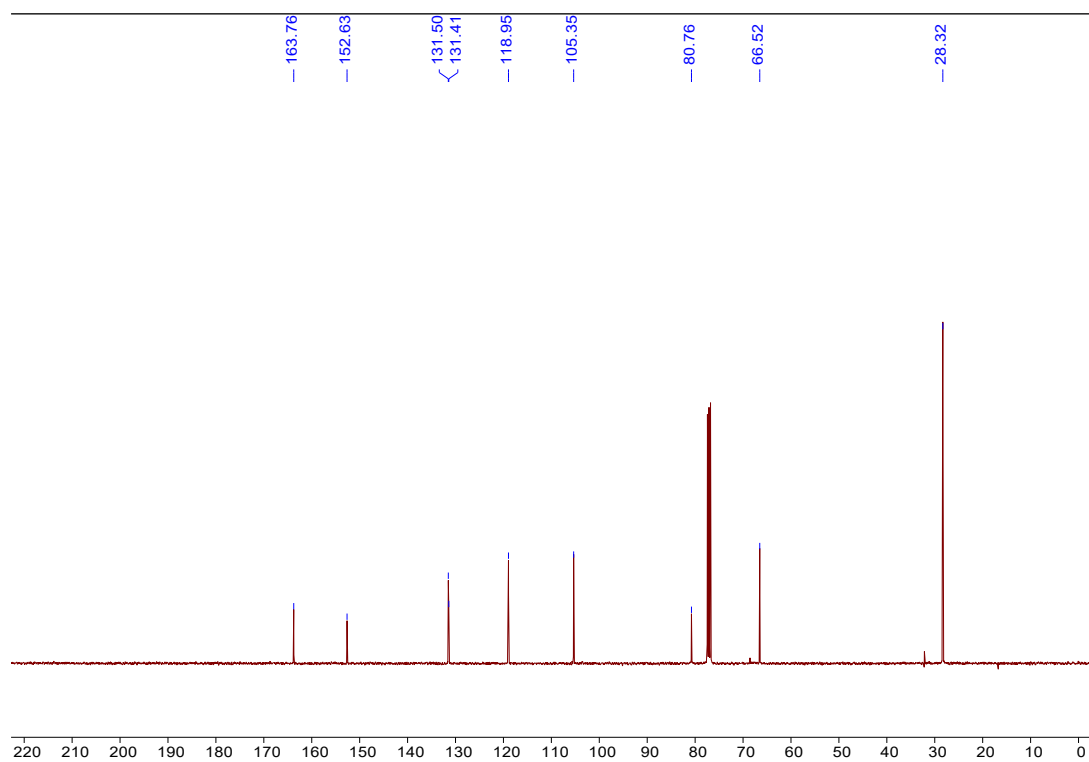
^{13}C NMR spectrum of 4a



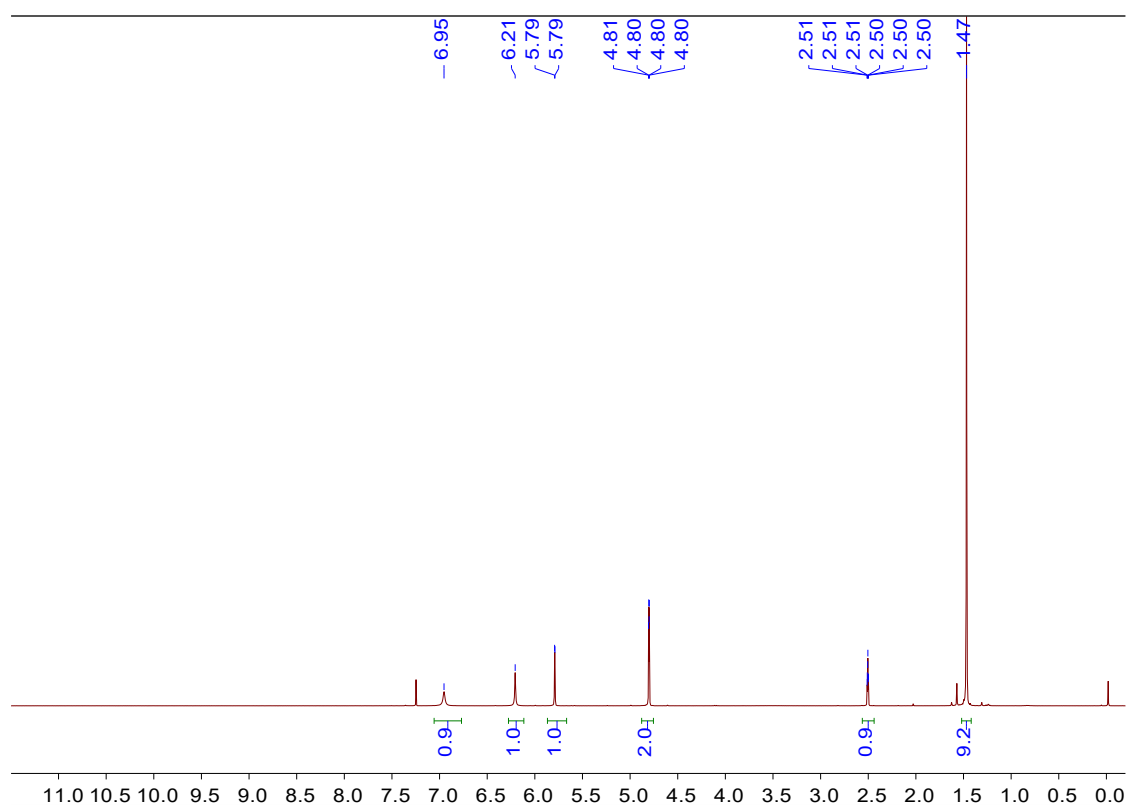
¹H NMR spectrum of 4b



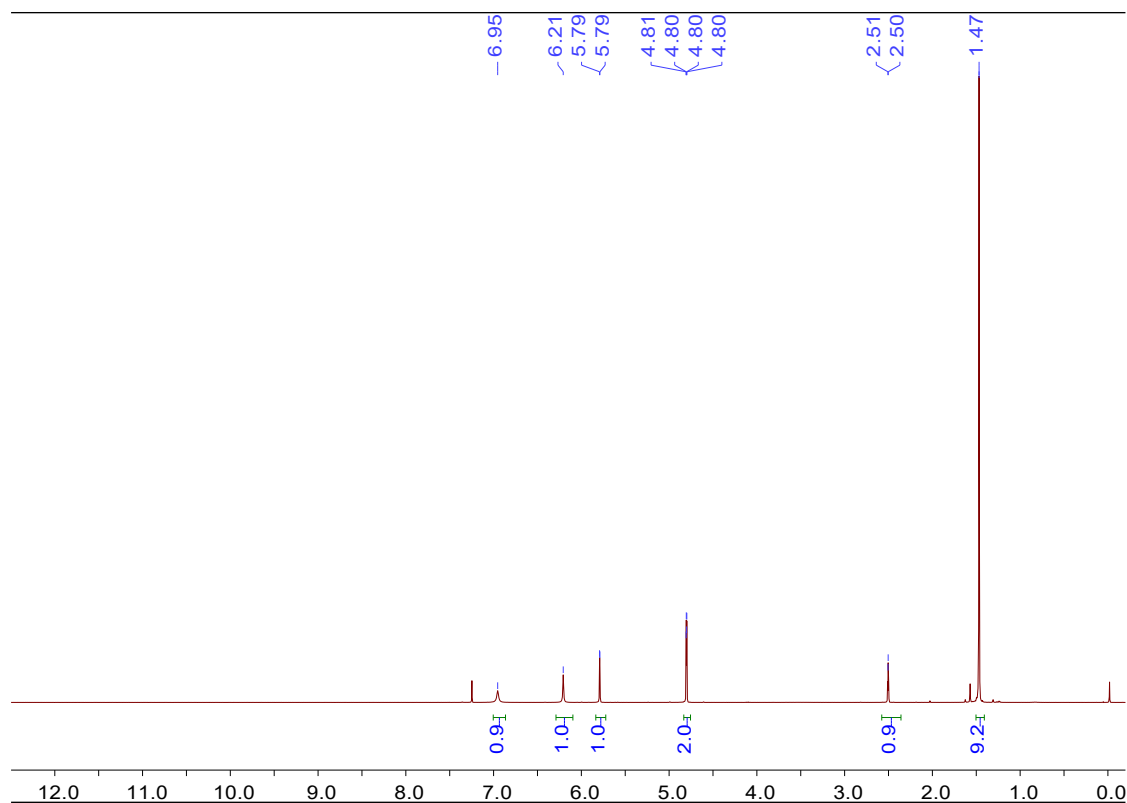
^1H NMR spectrum of 4c



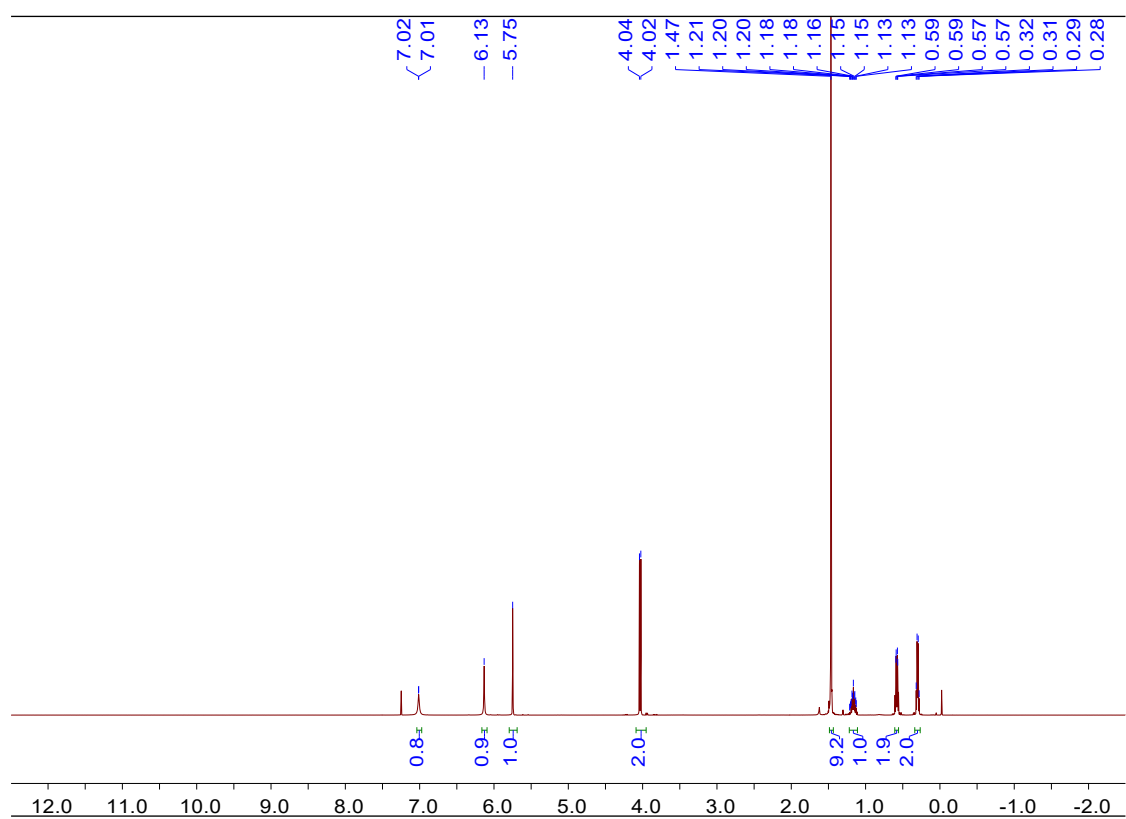
¹³C NMR spectrum of 4c



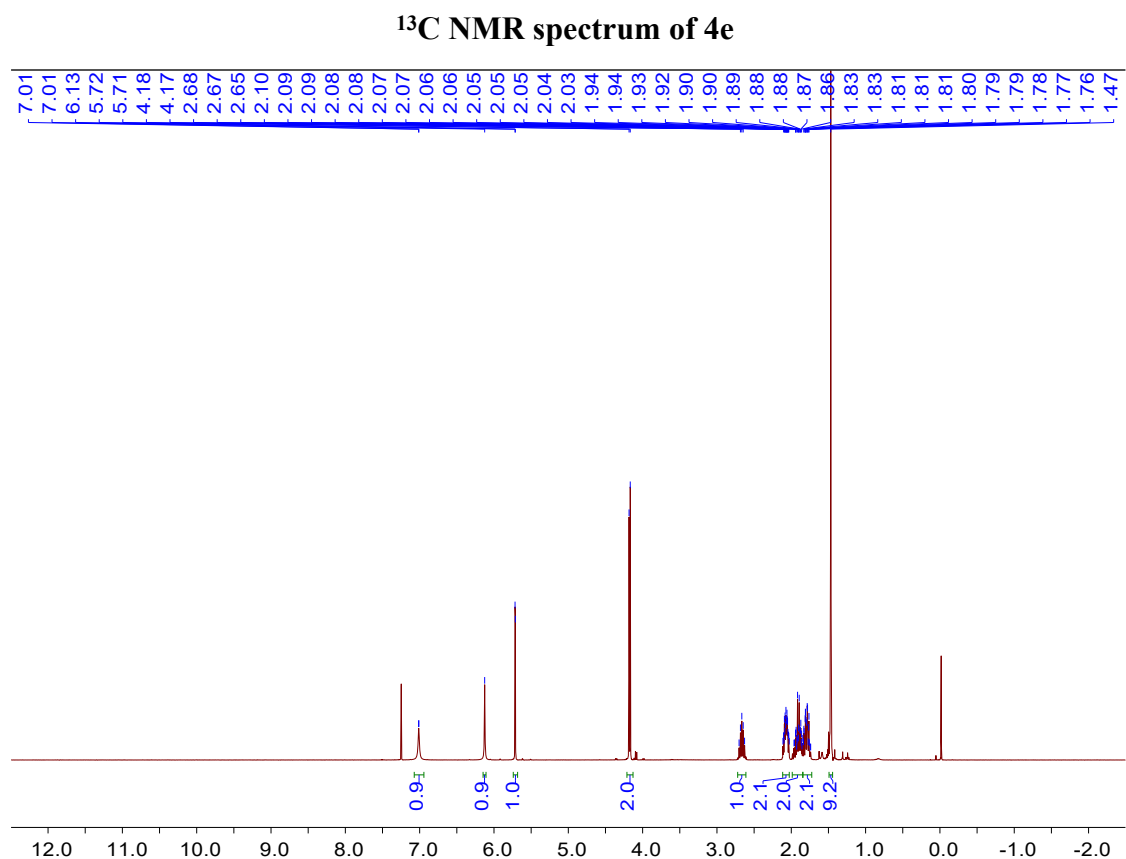
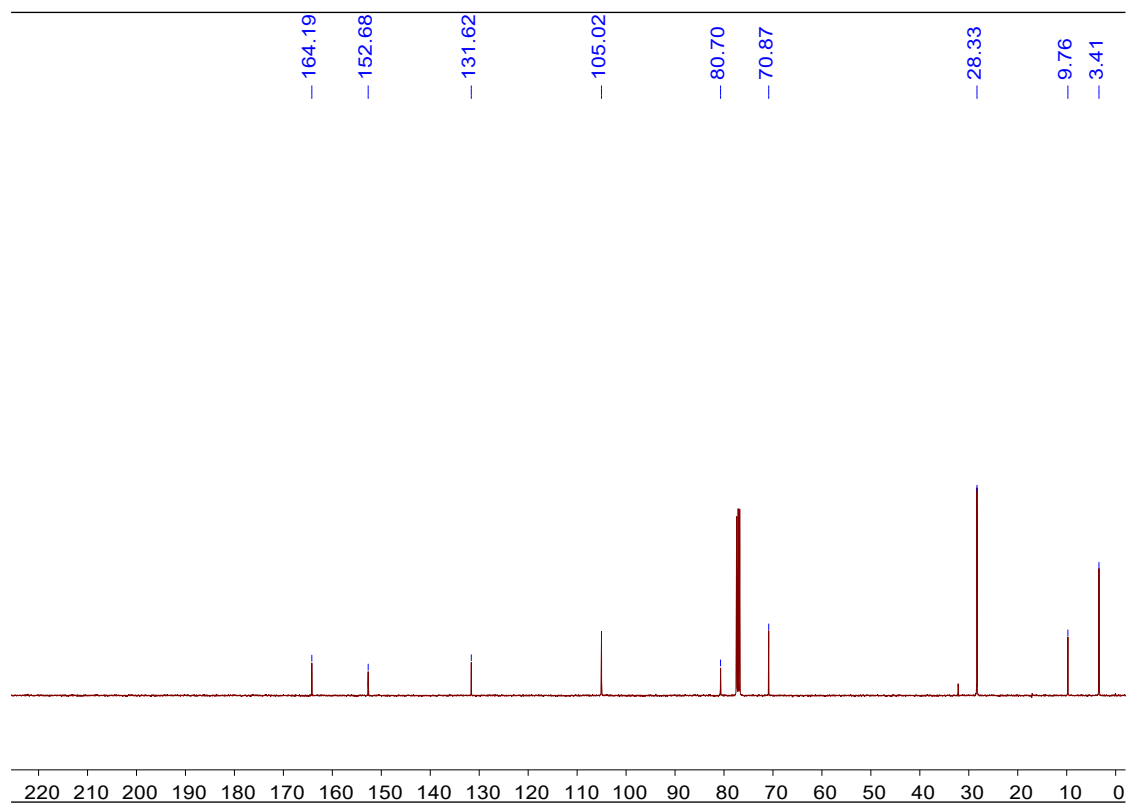
¹H NMR spectrum of 4d



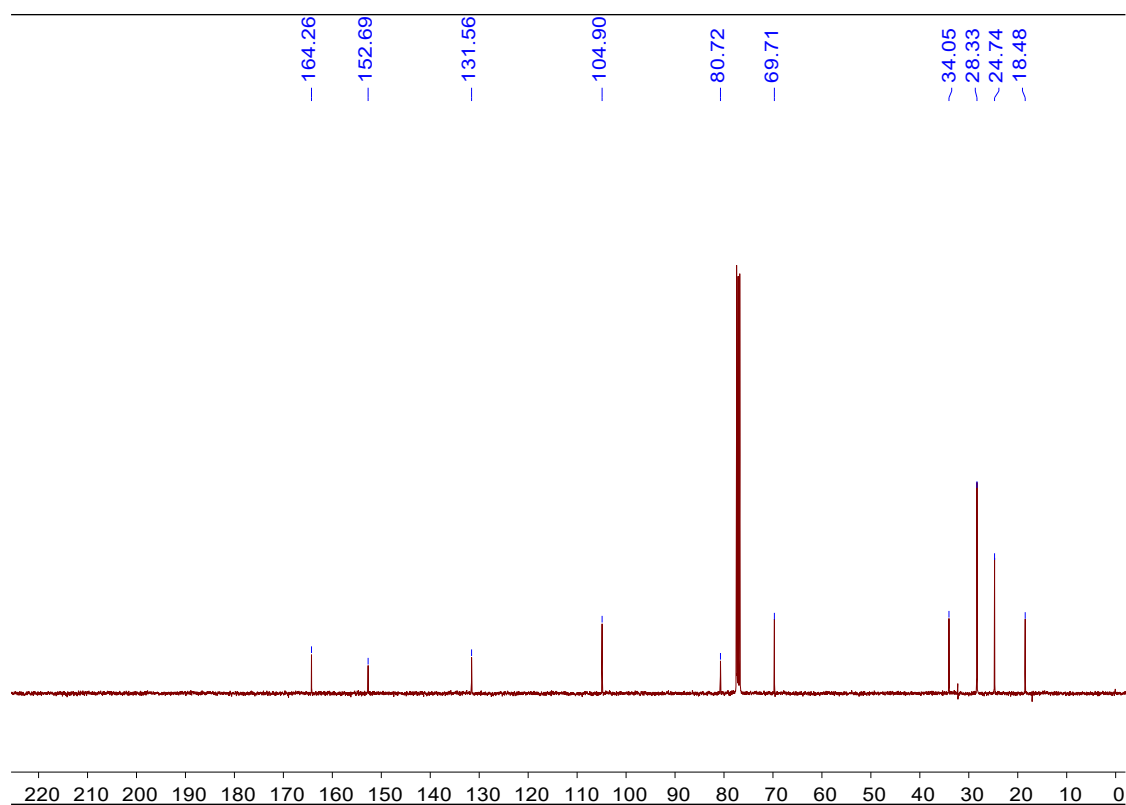
^{13}C NMR spectrum of 4d



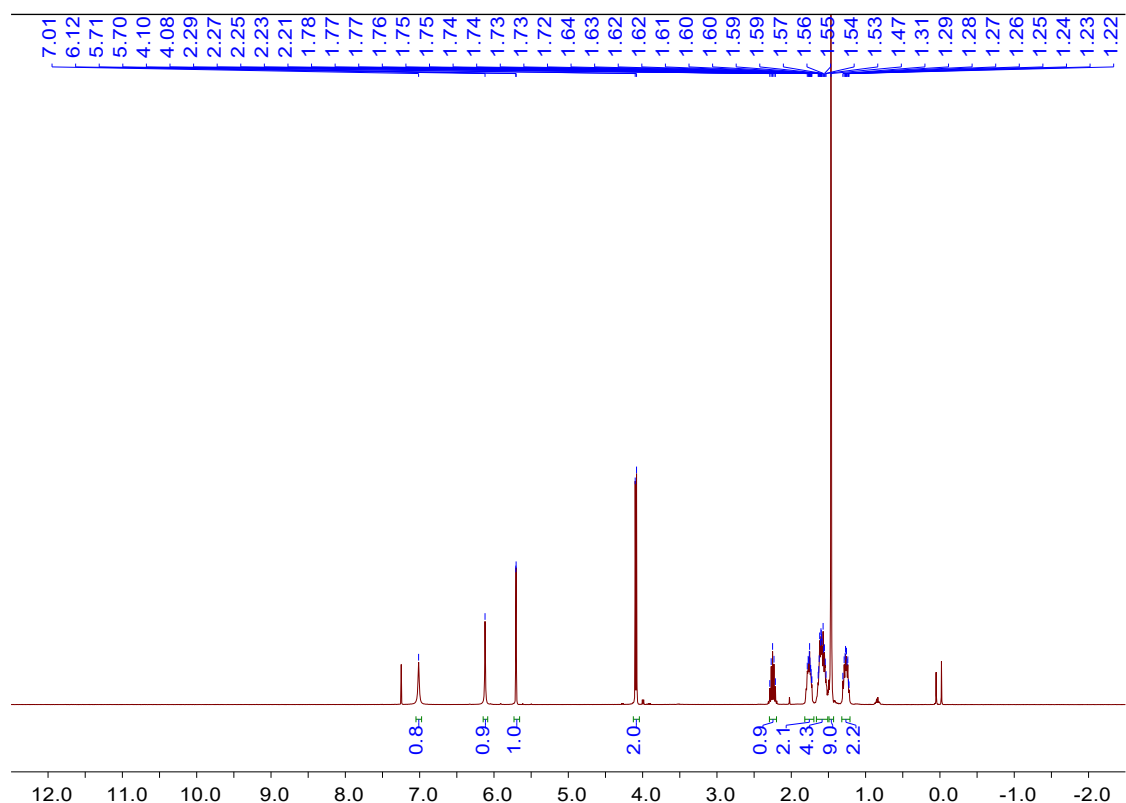
¹H NMR spectrum of 4e



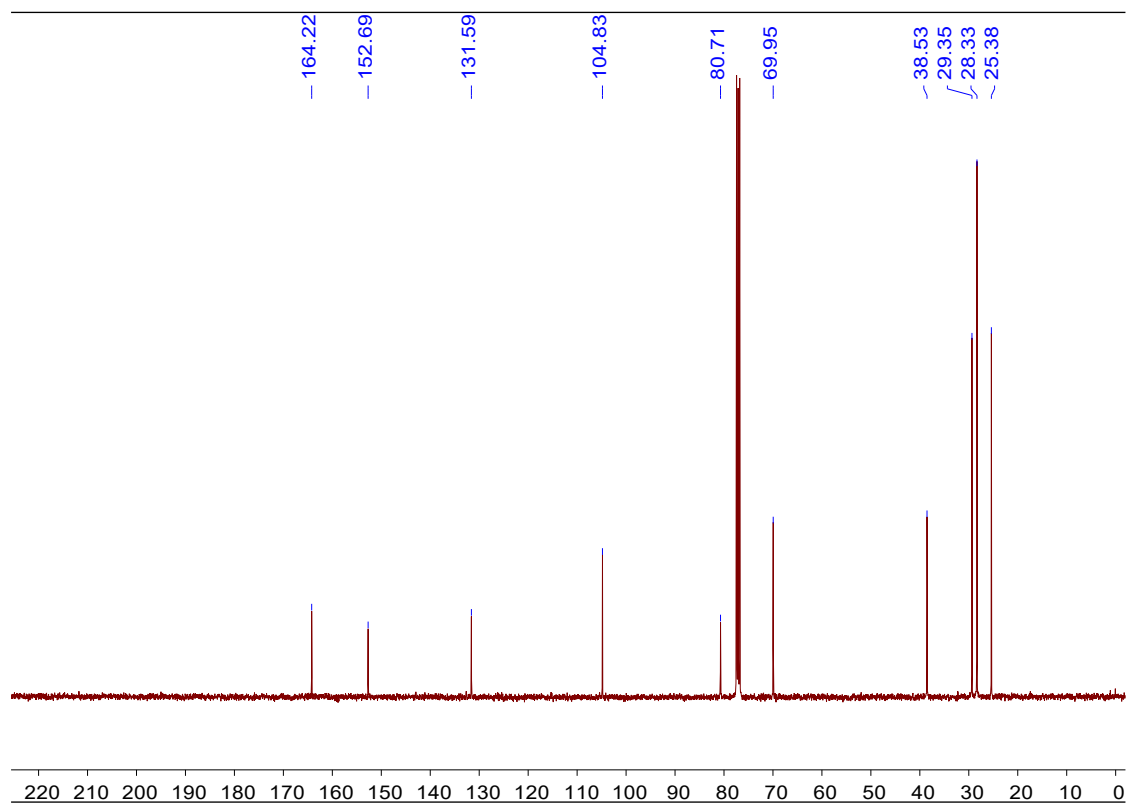
¹H NMR spectrum of 4f



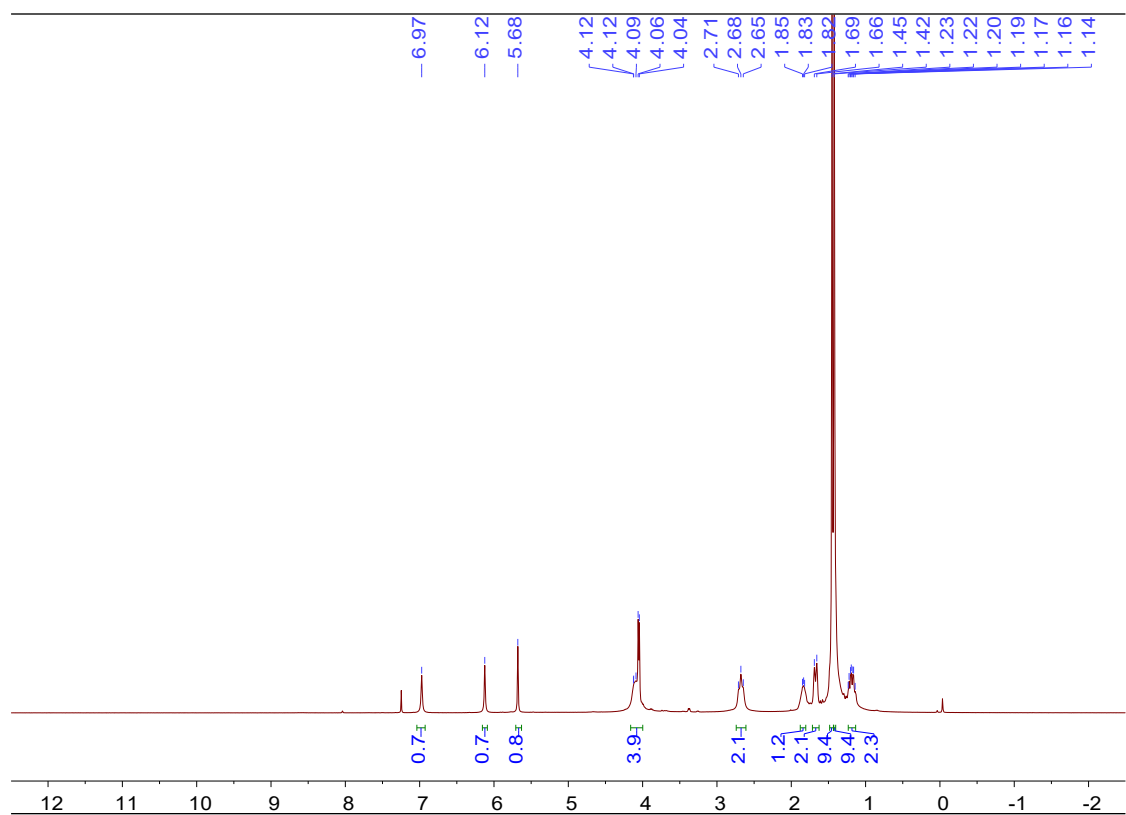
^{13}C NMR spectrum of 4f



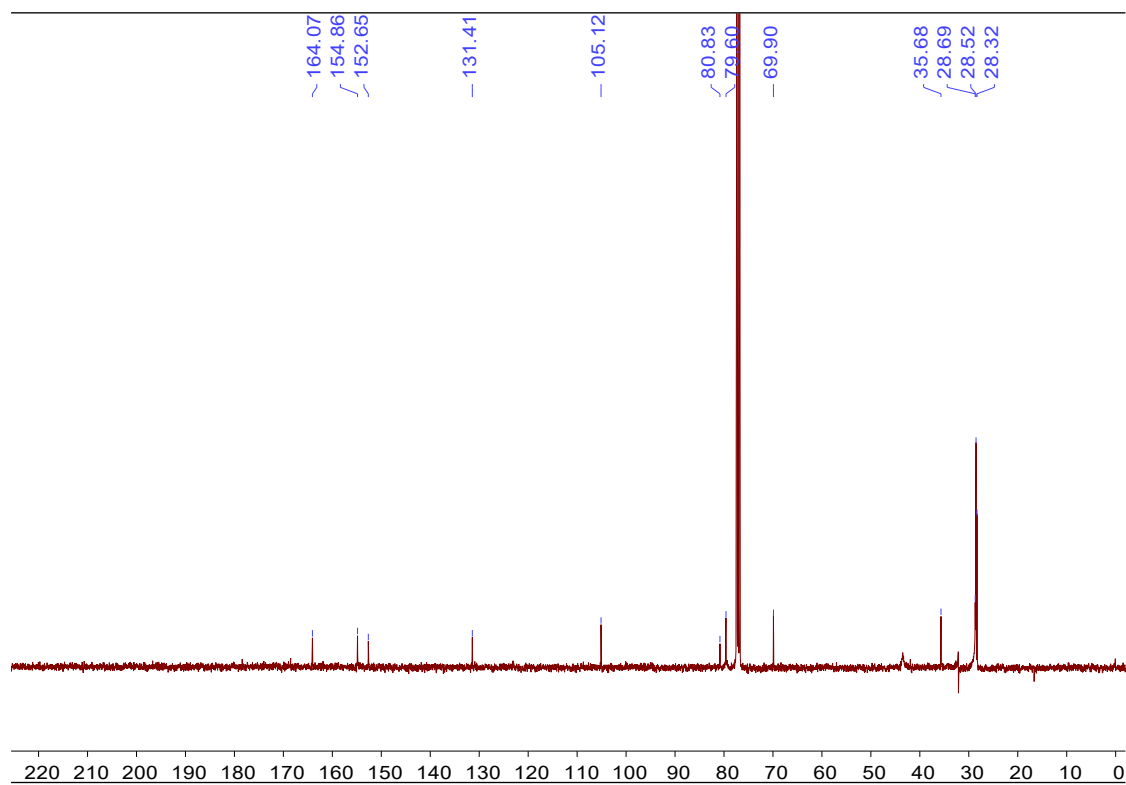
¹H NMR spectrum of 4g



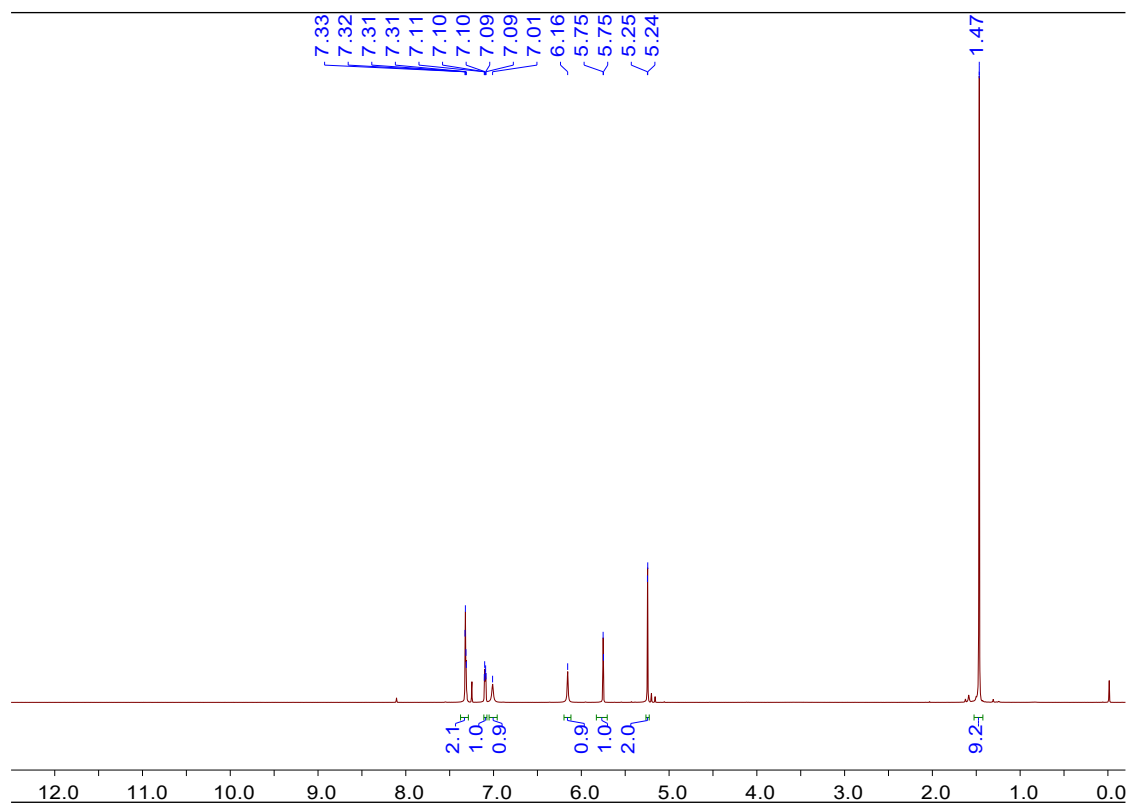
^{13}C NMR spectrum of 4g



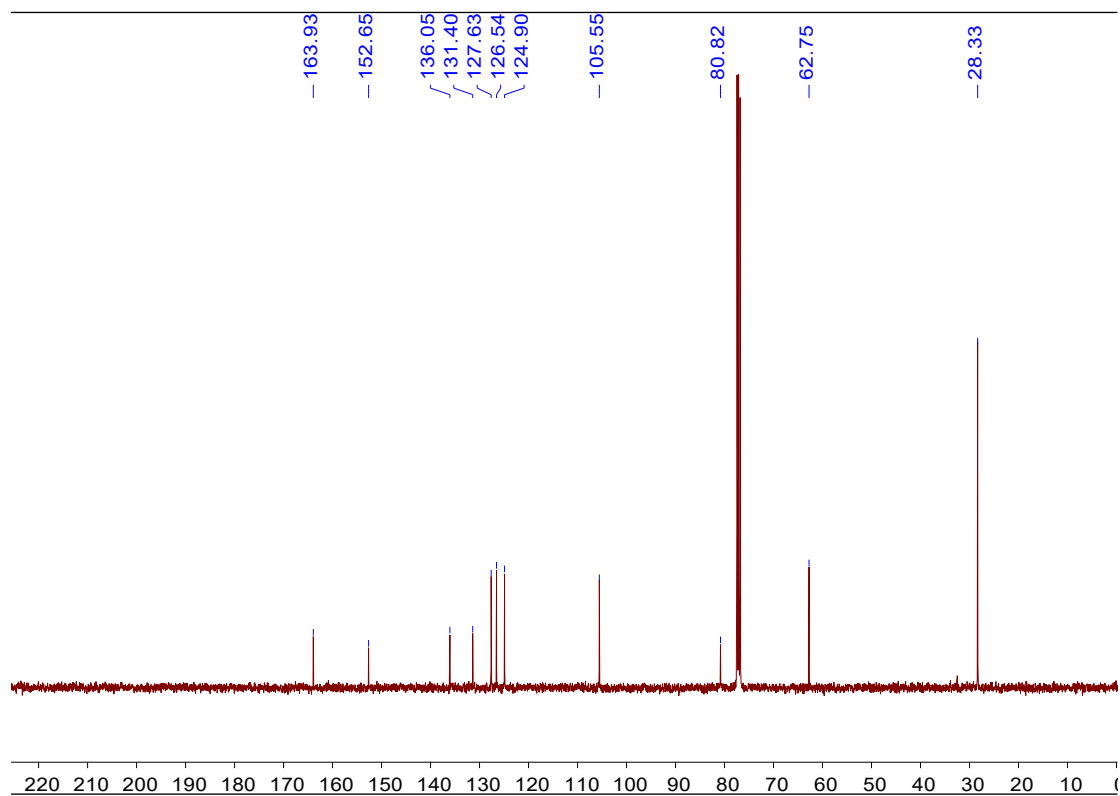
^1H NMR spectrum of 4h



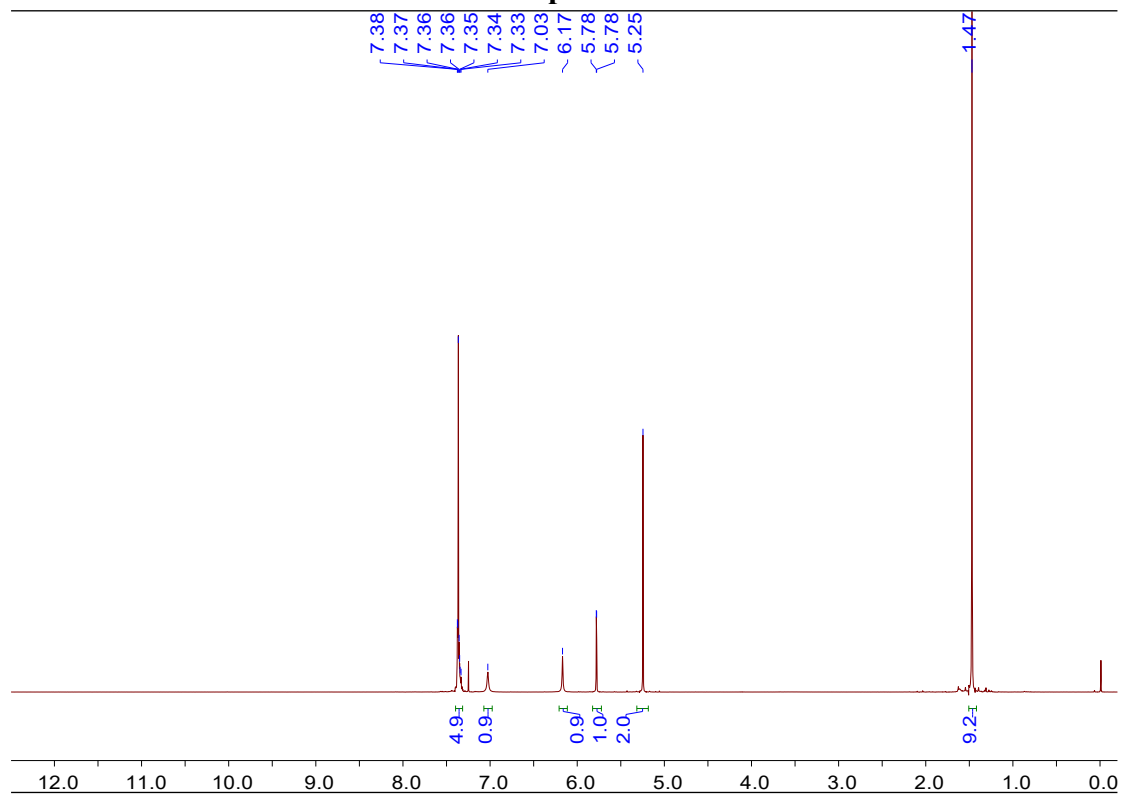
^{13}C NMR spectrum of 4h



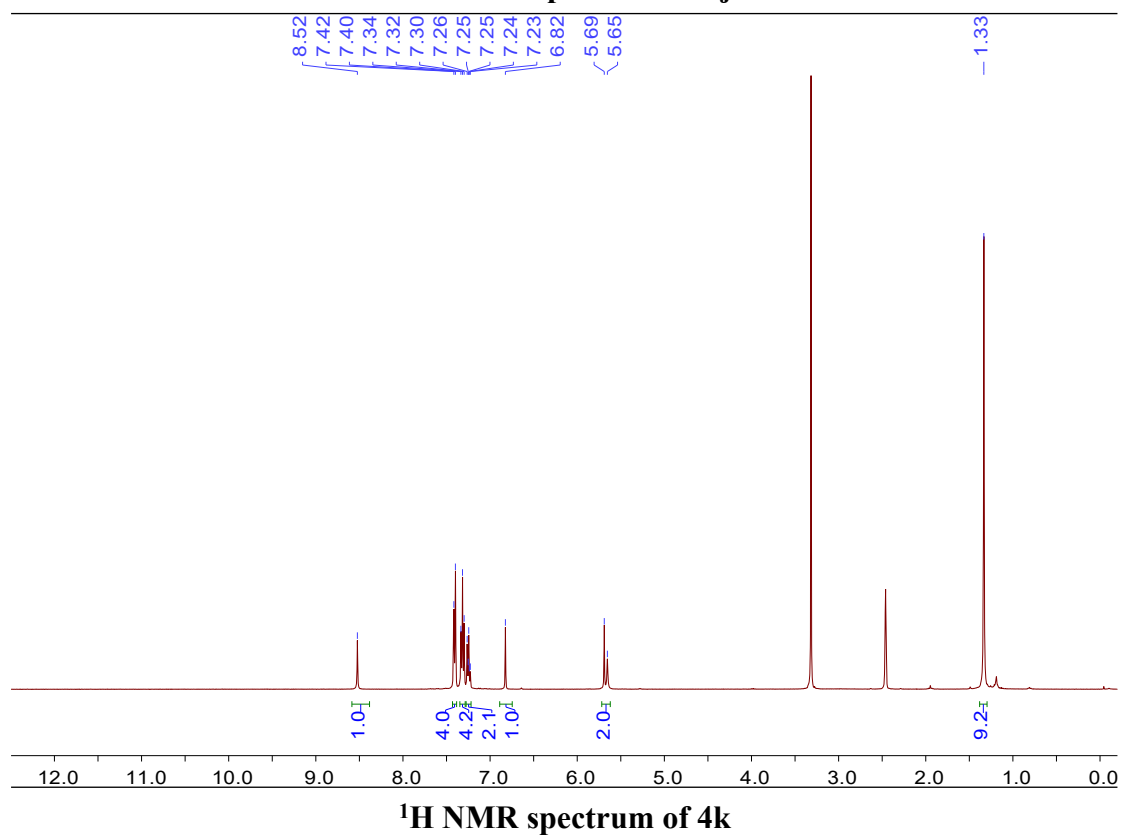
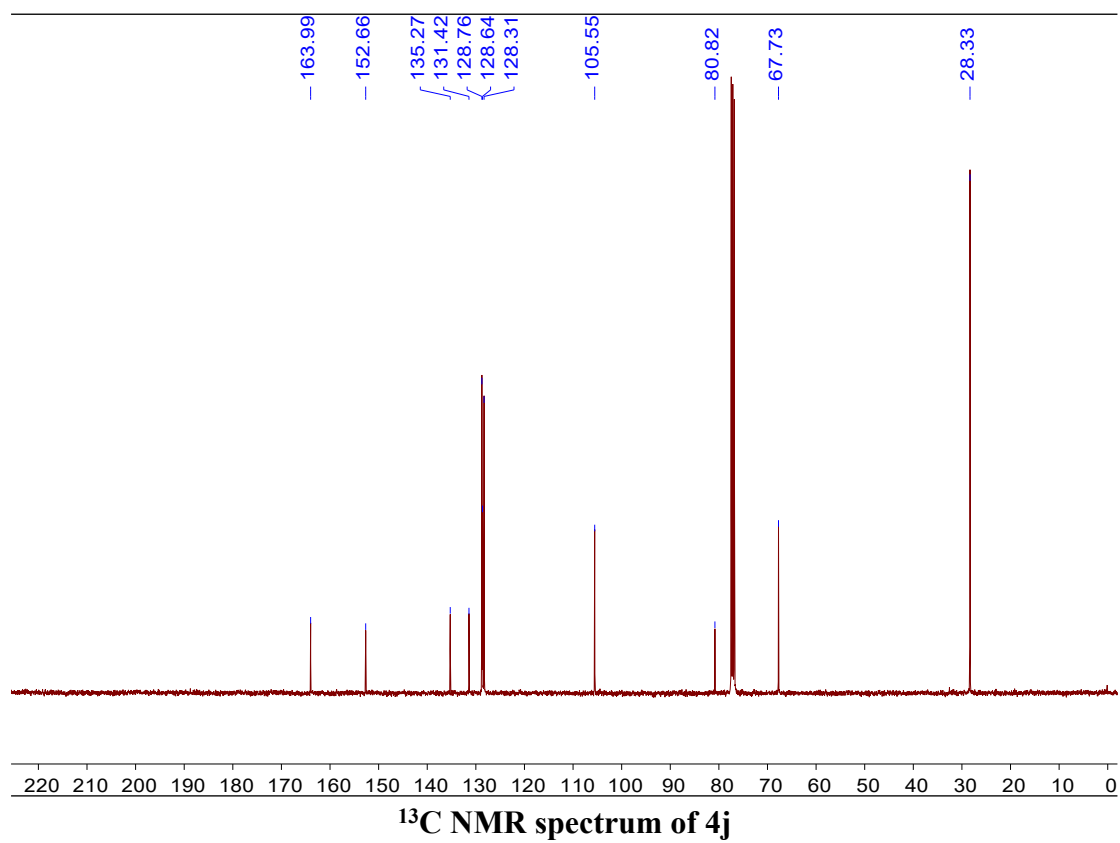
^1H NMR spectrum of 4i

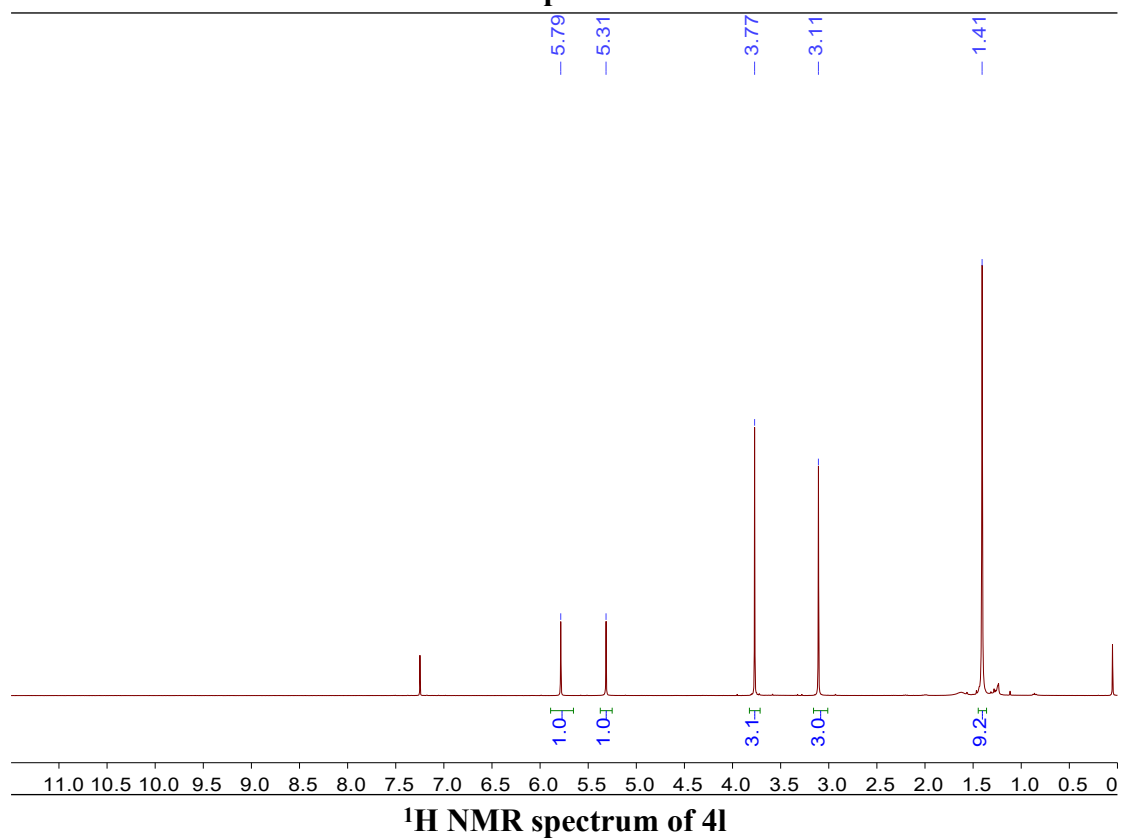
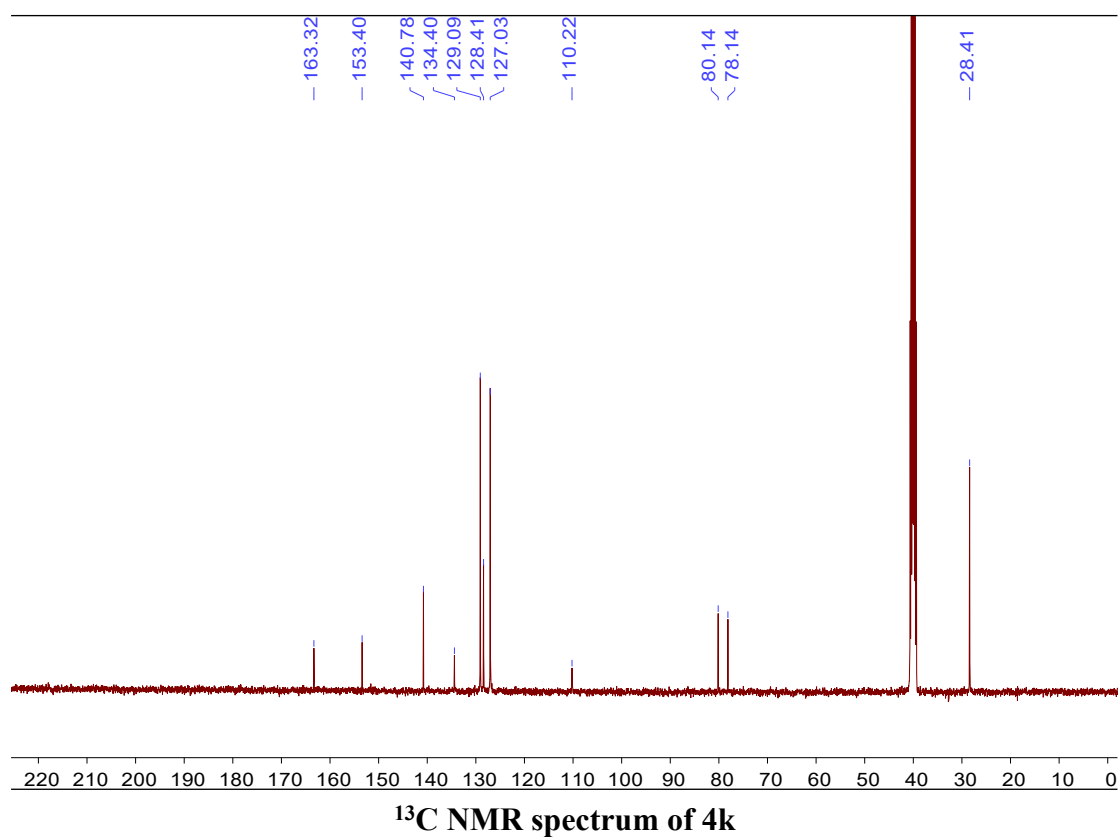


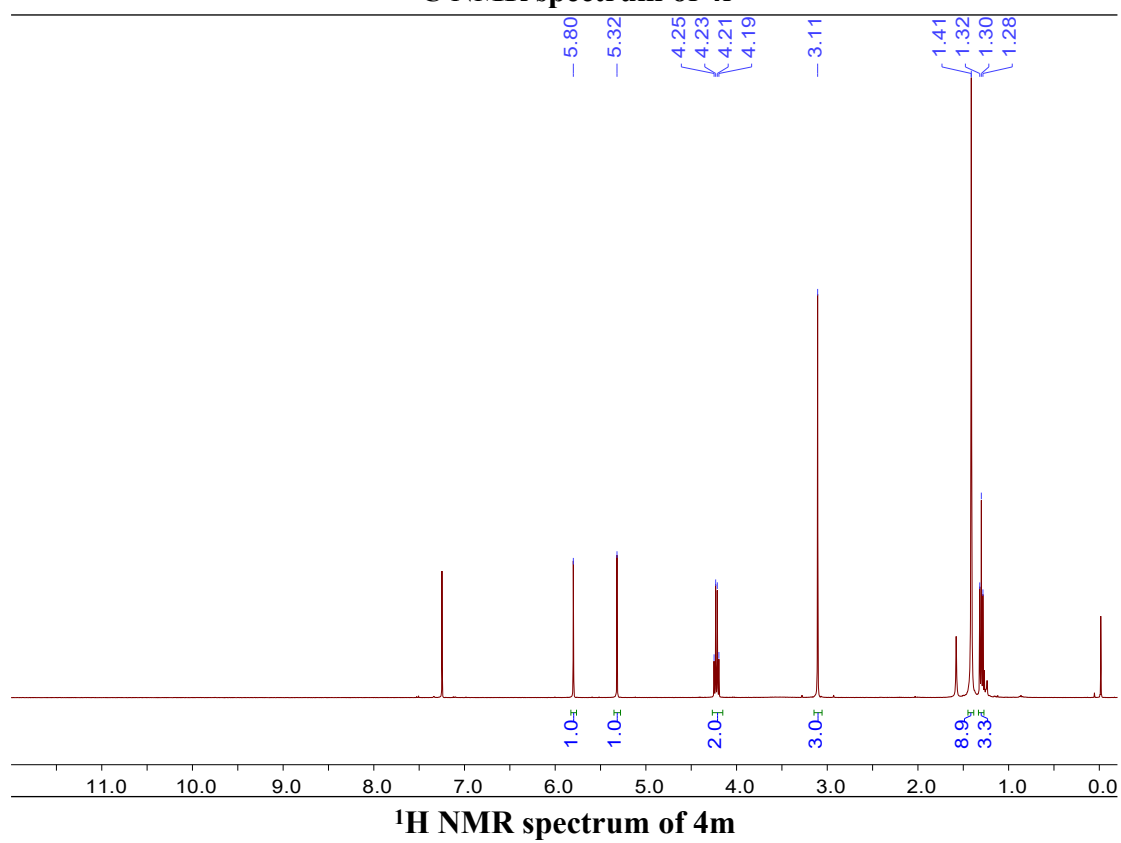
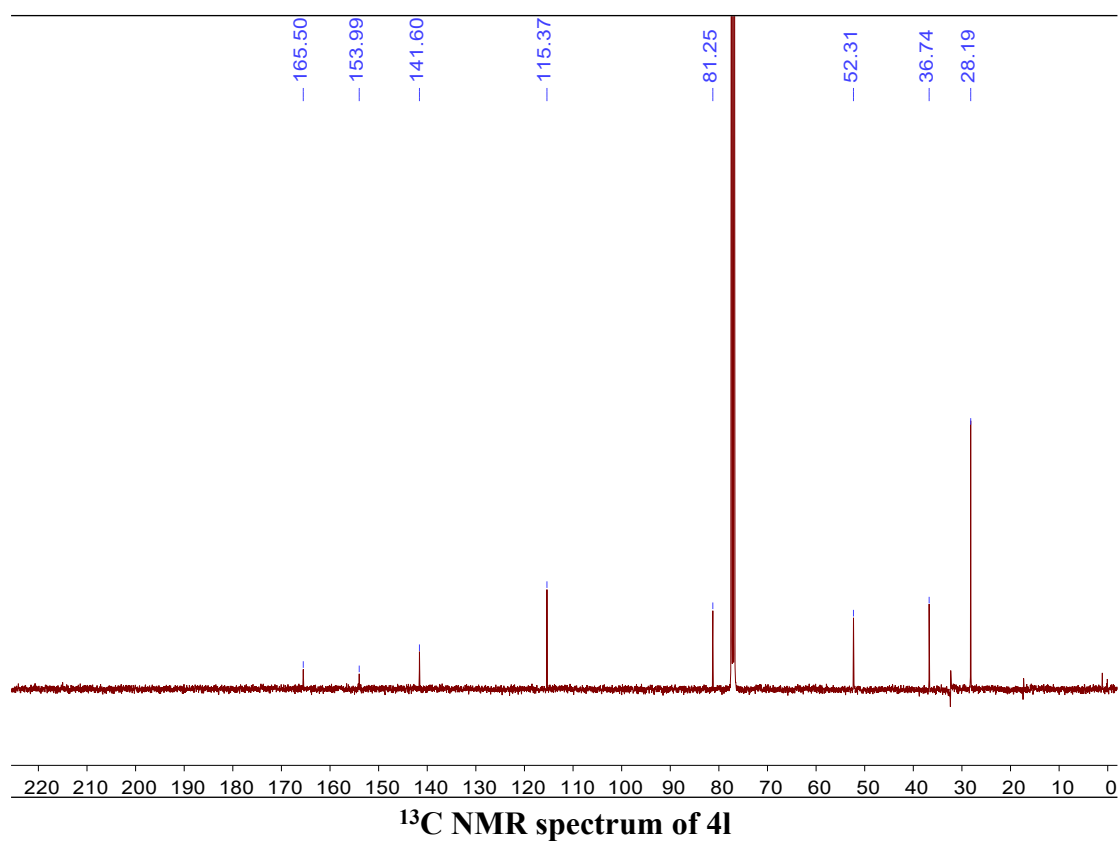
^{13}C NMR spectrum of 4i

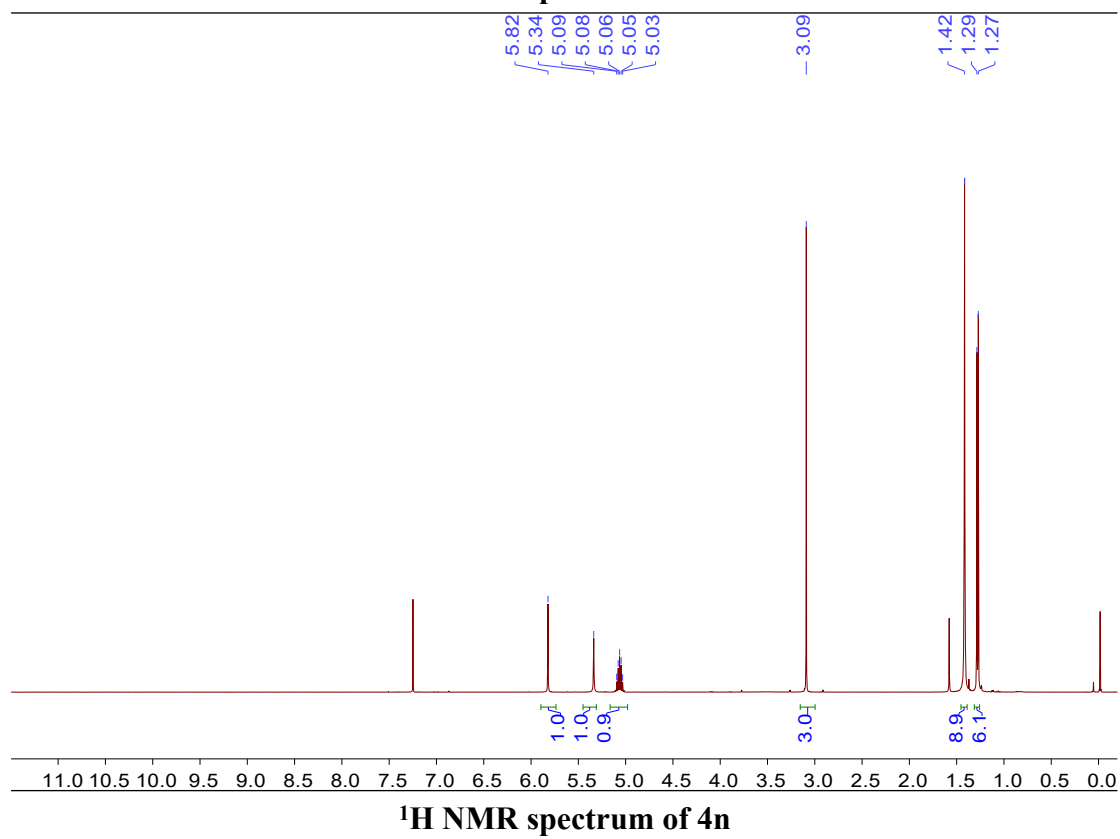
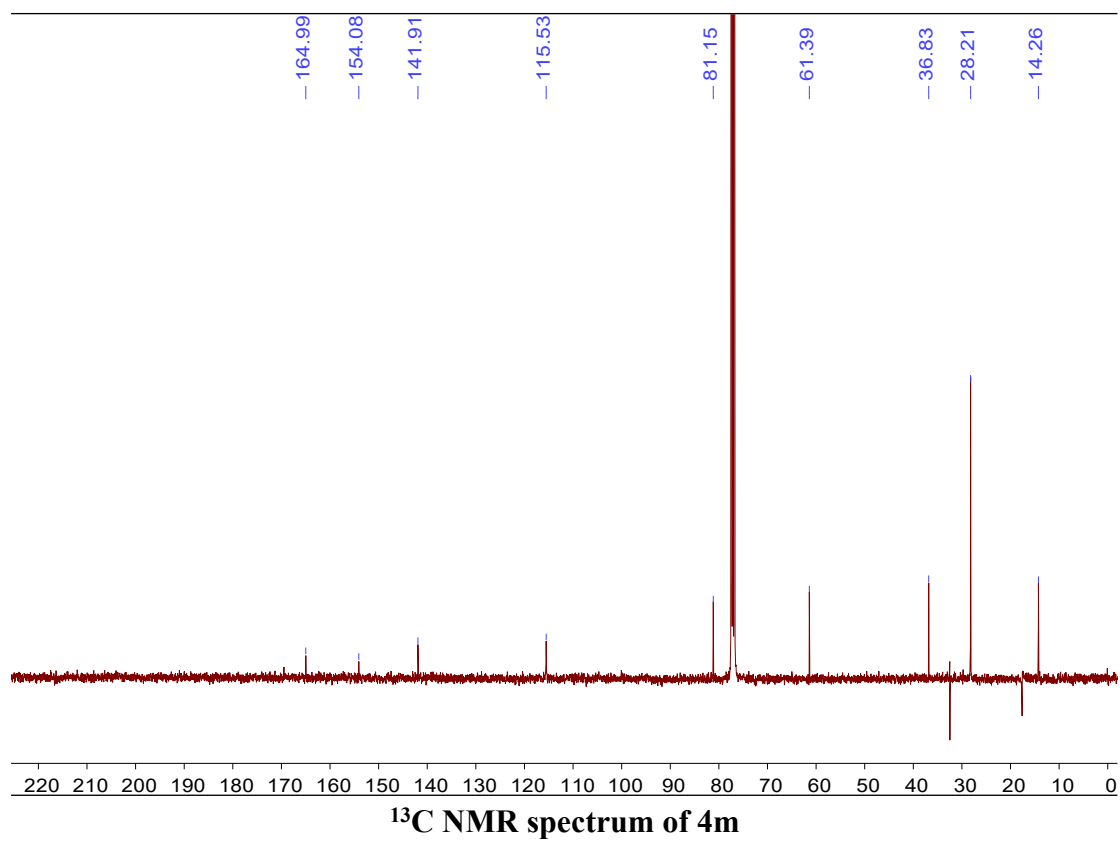


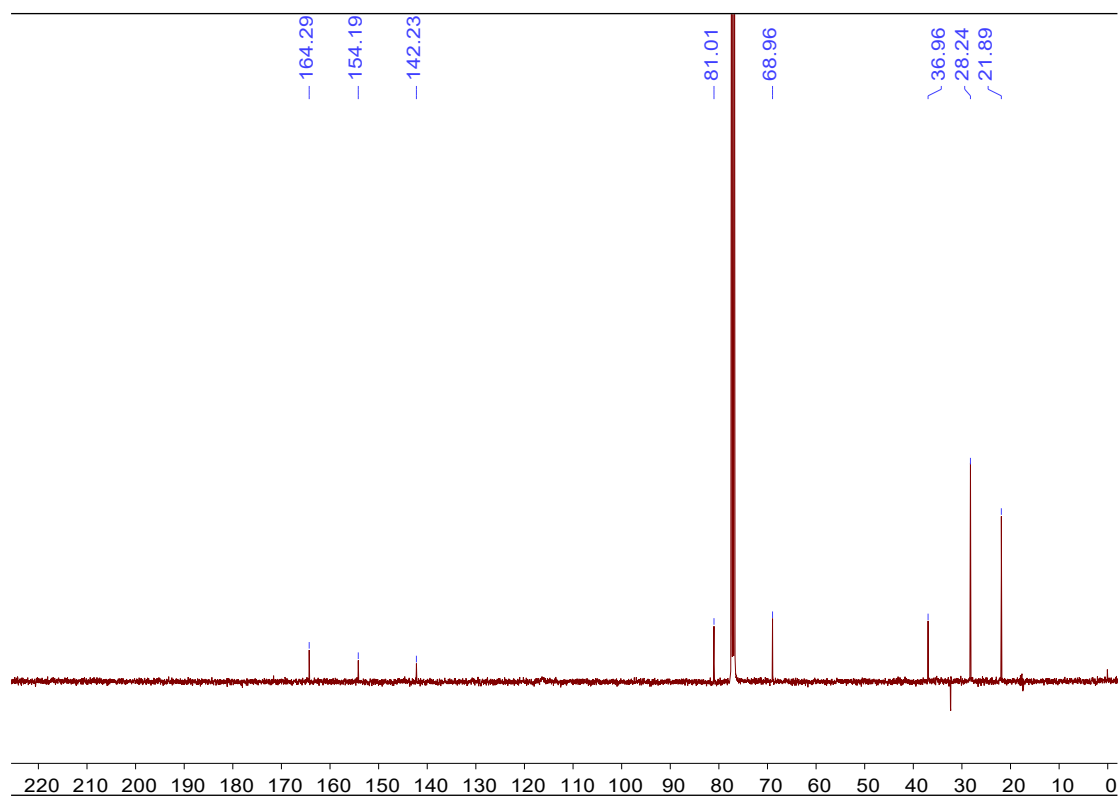
^1H NMR spectrum of 4j



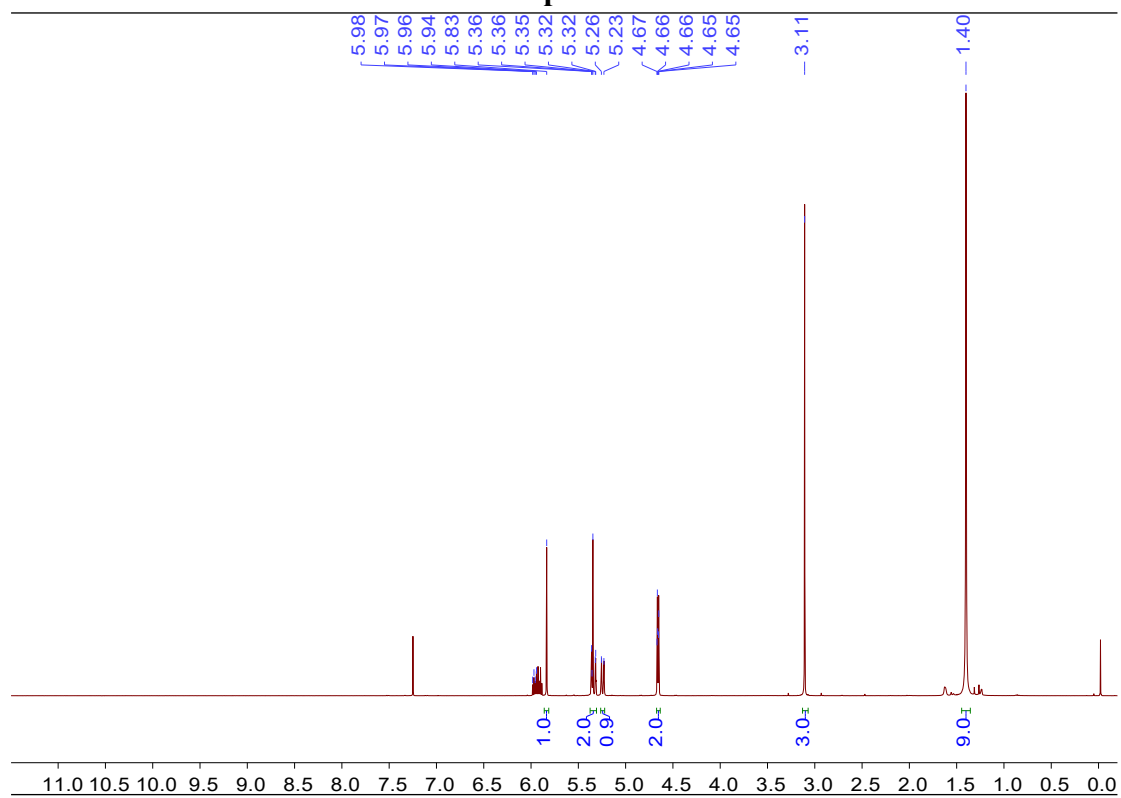




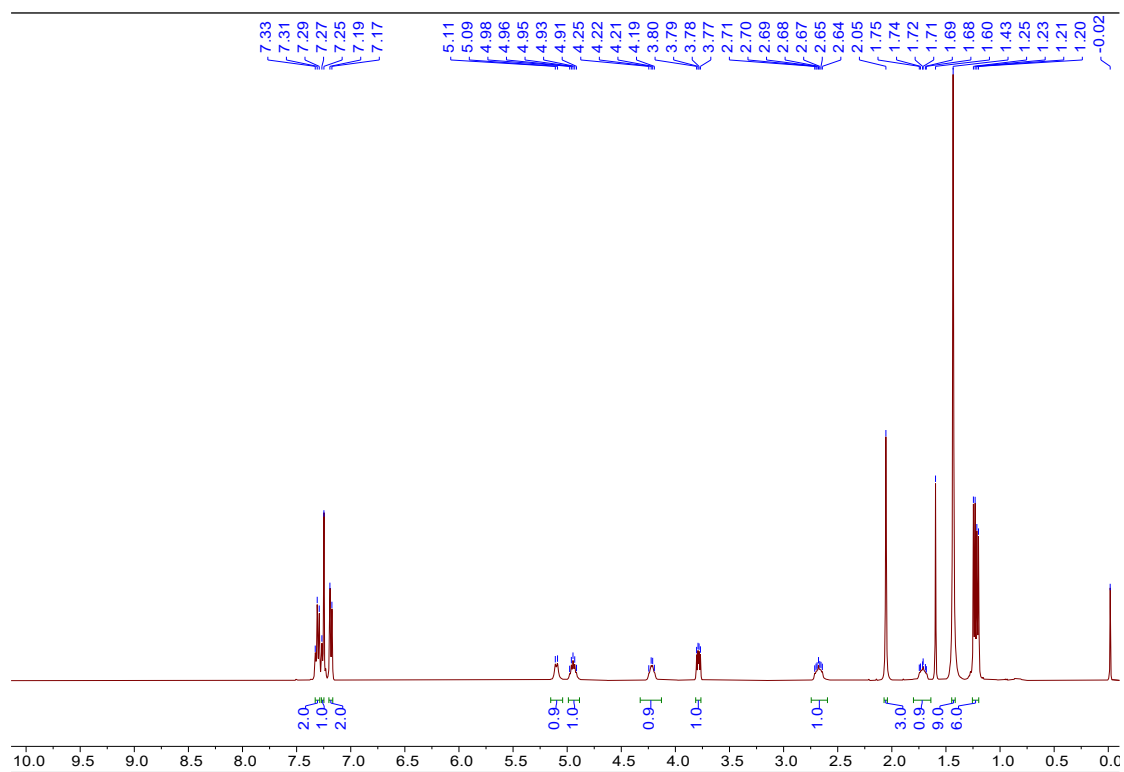
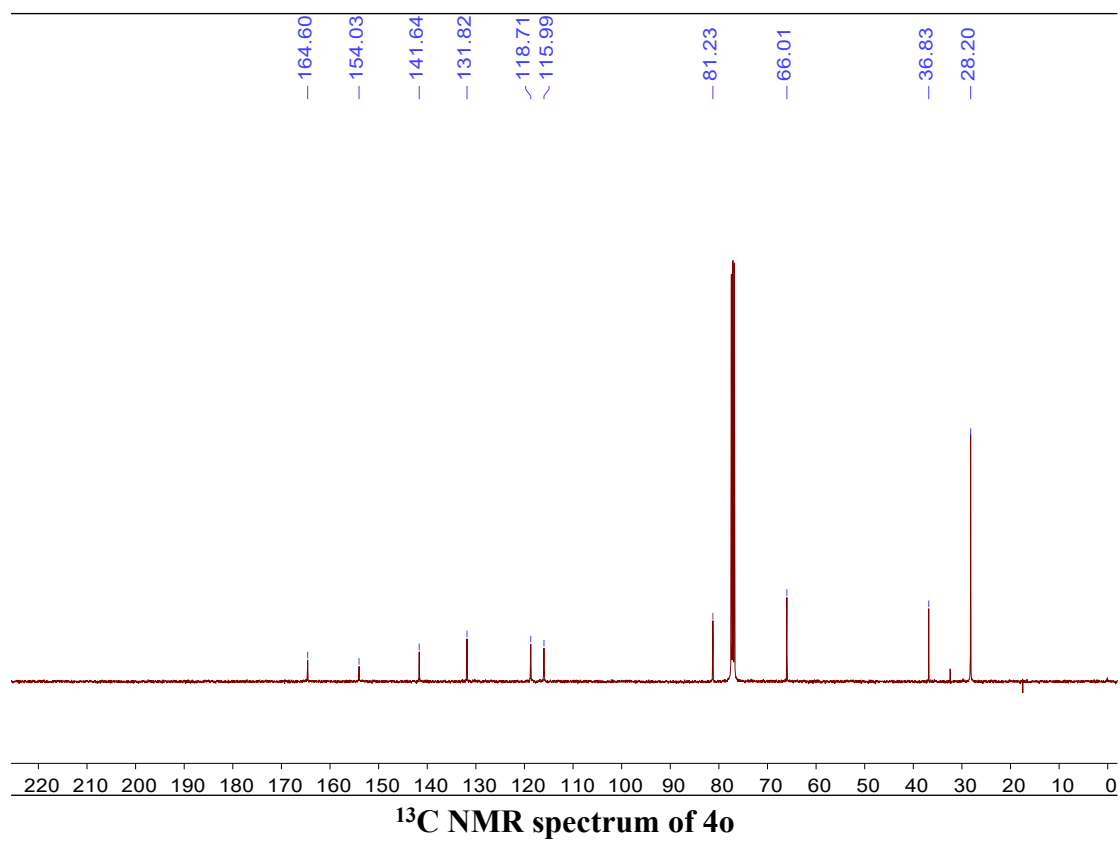


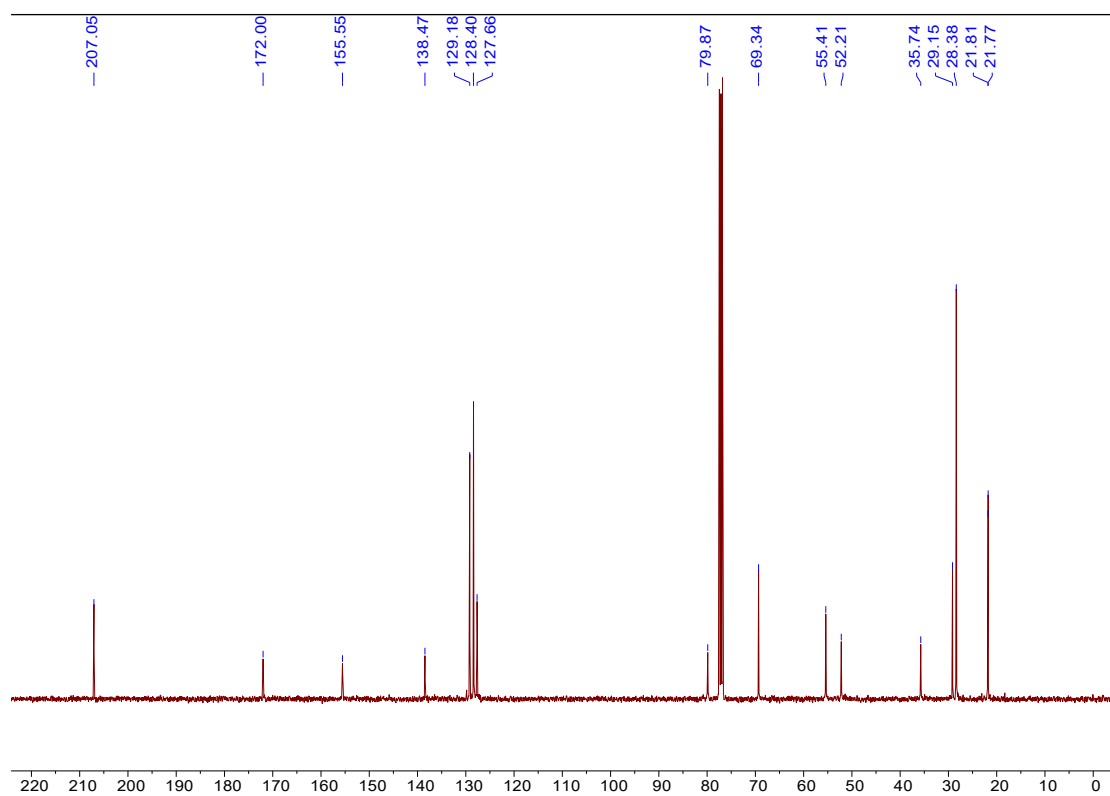


¹³C NMR spectrum of 4n

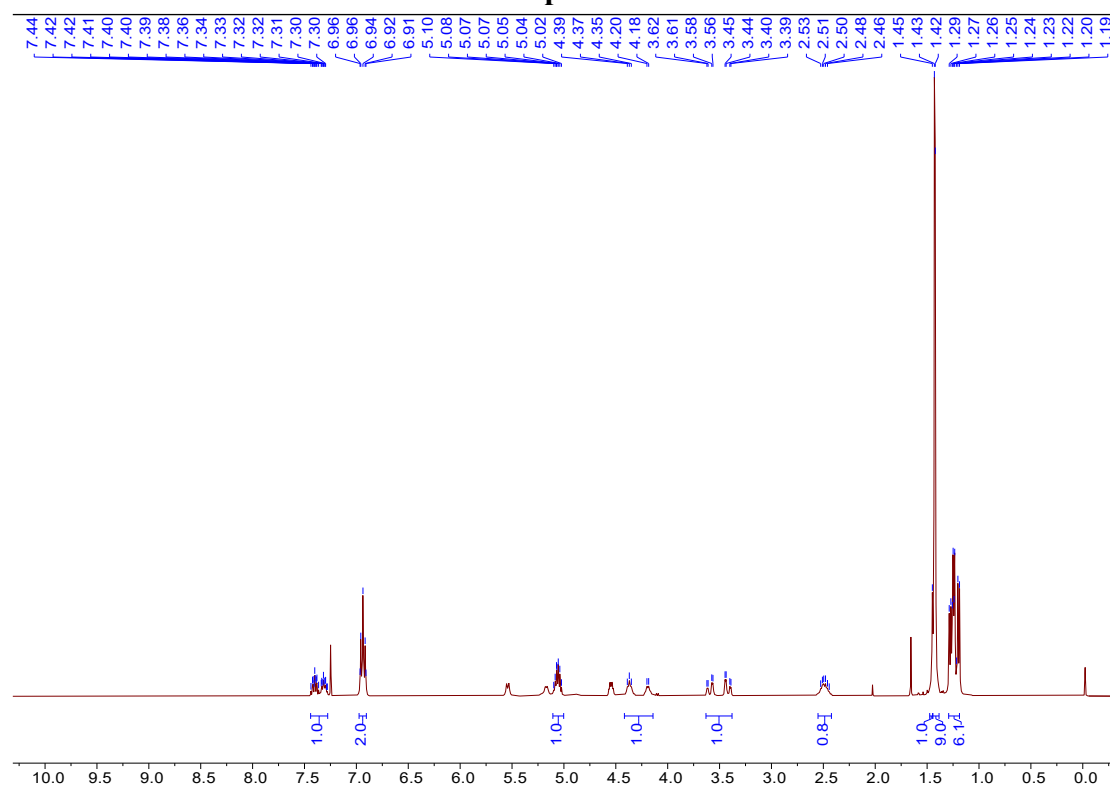


¹H NMR spectrum of 4o

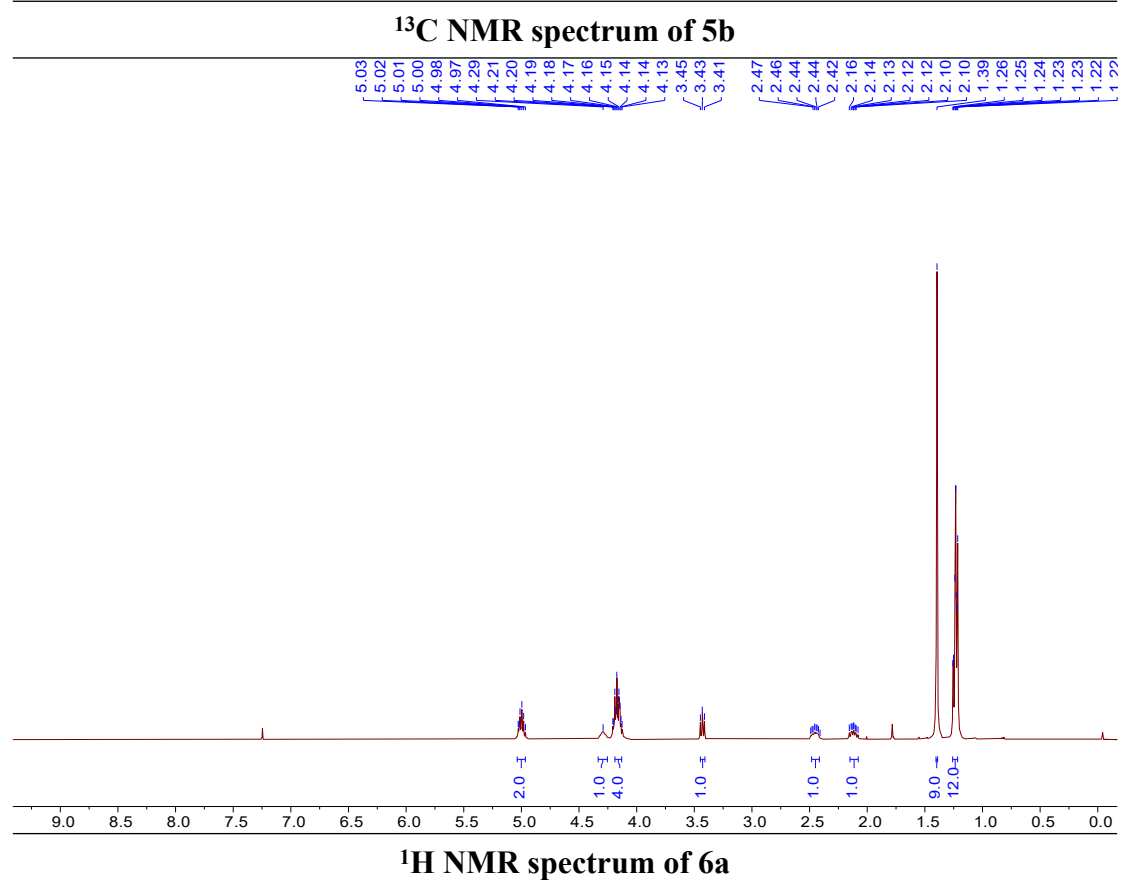
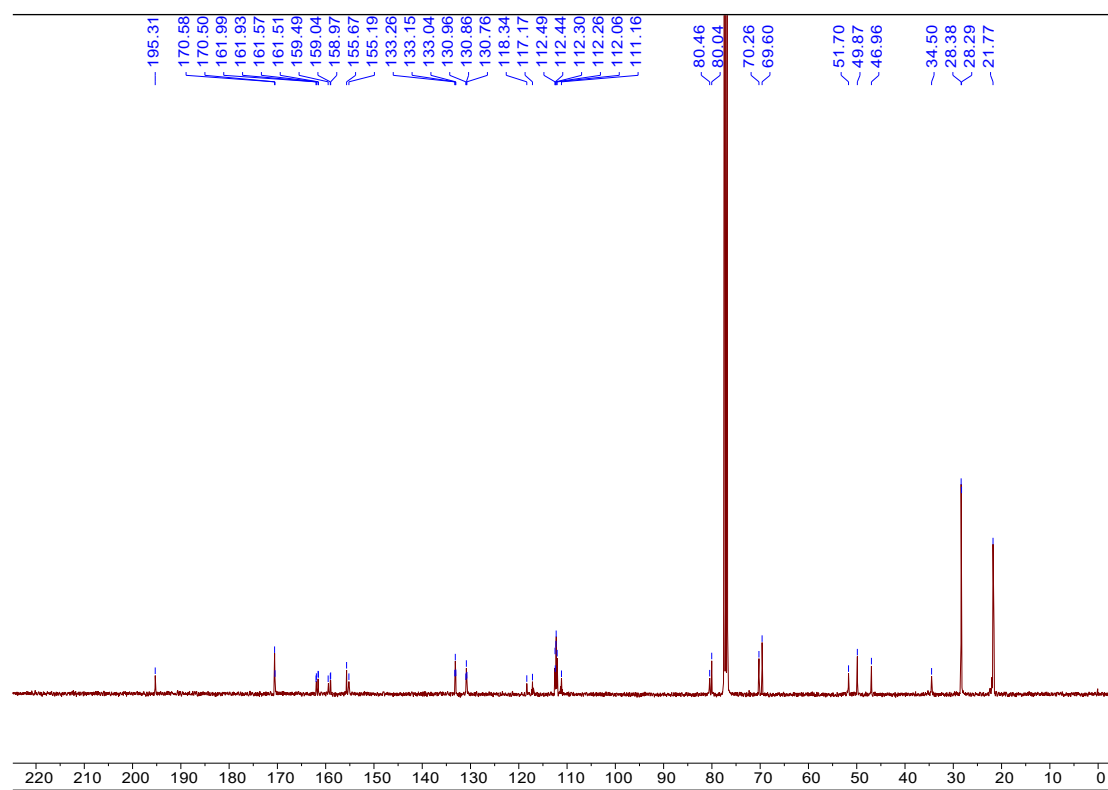


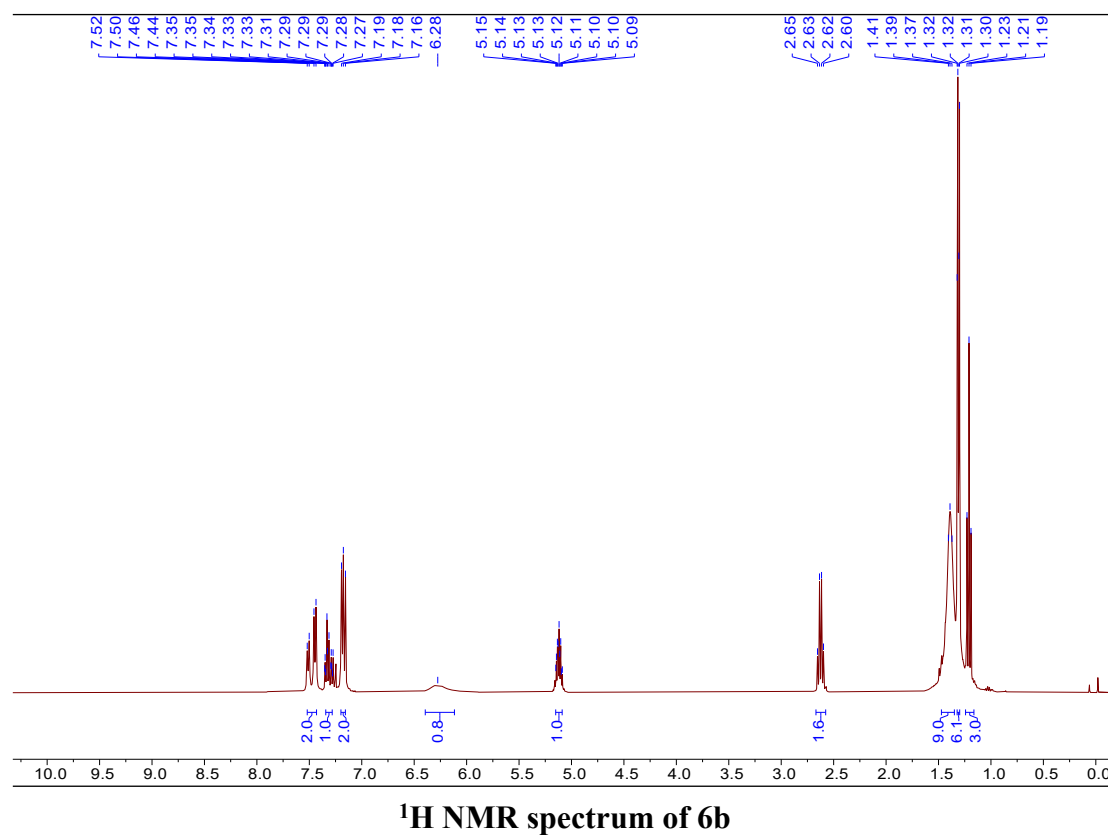
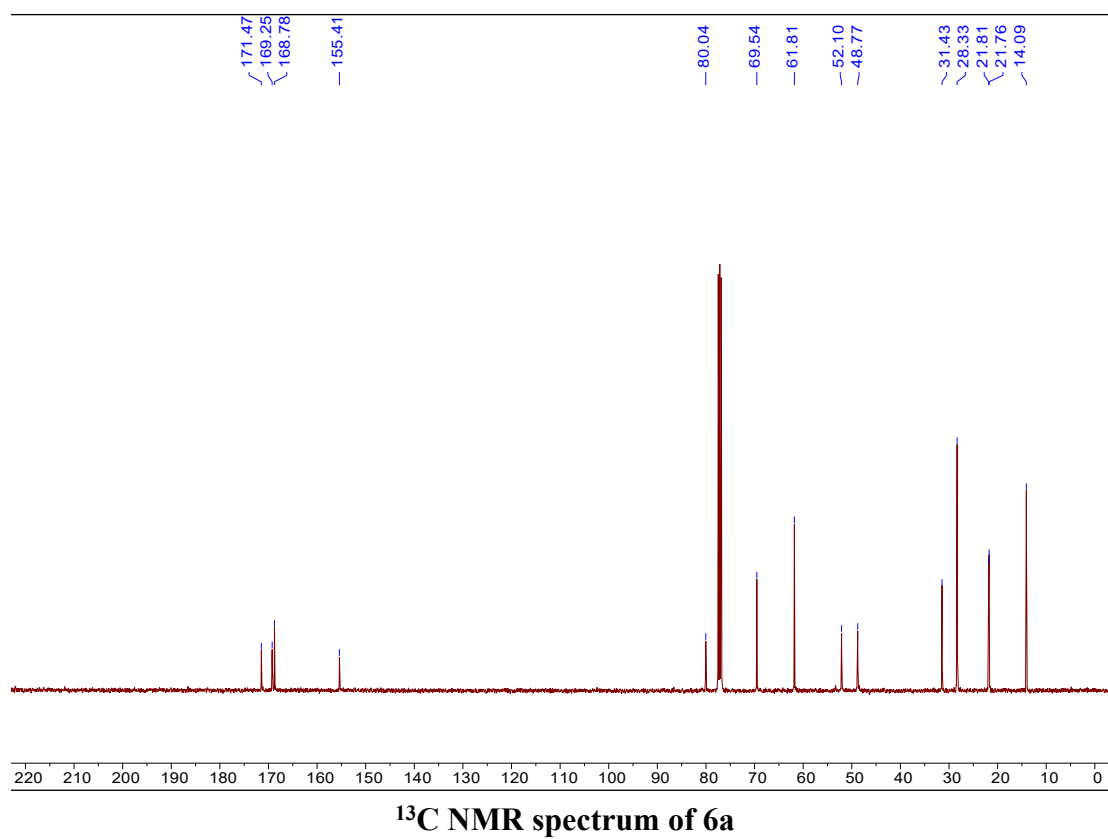


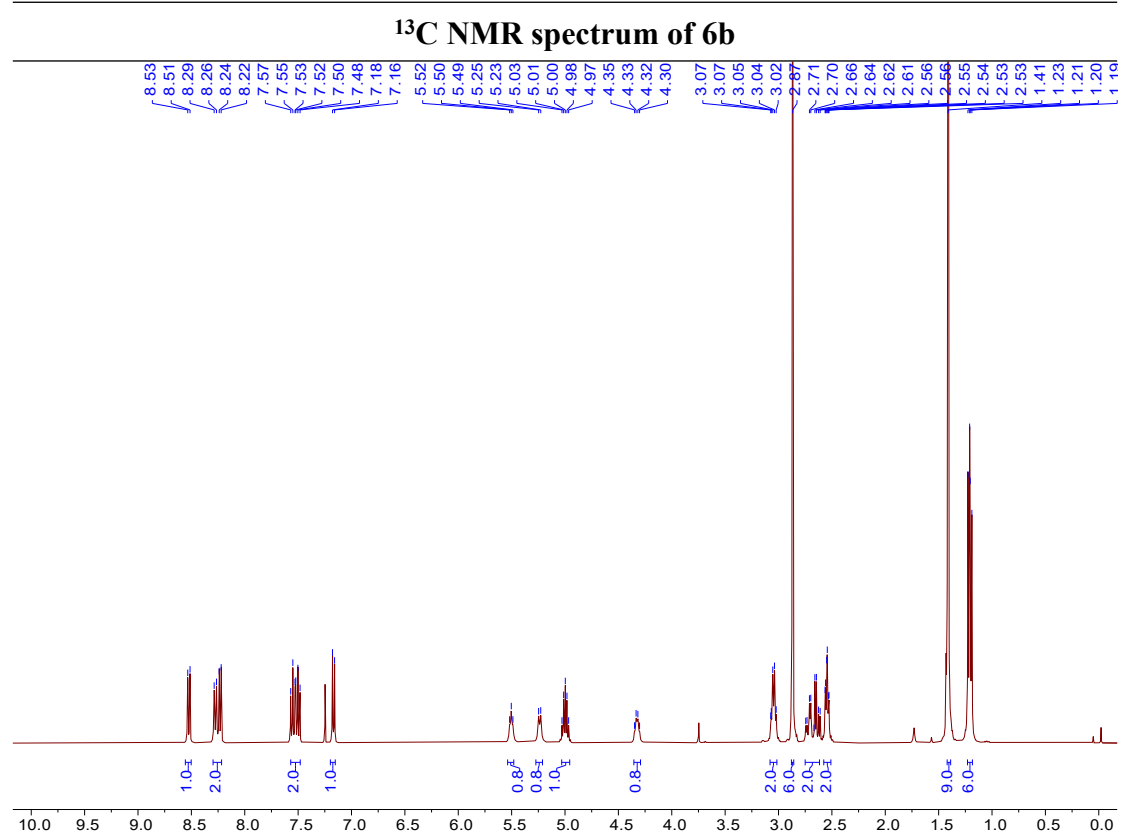
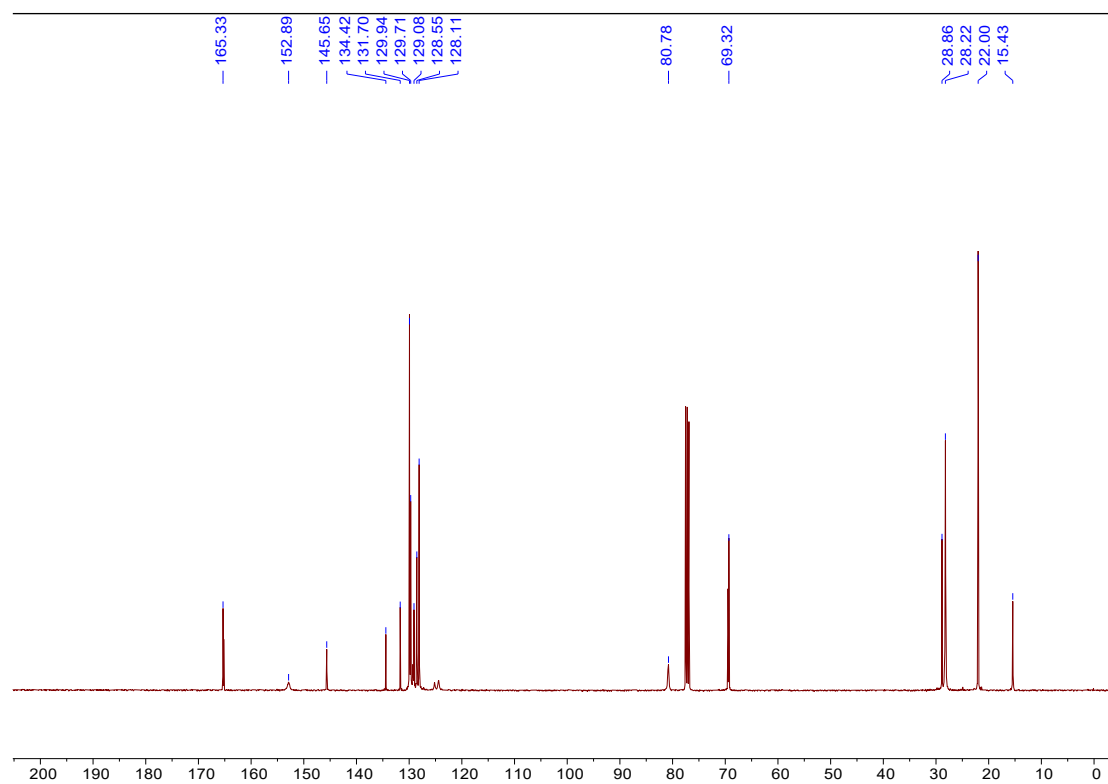
¹³C NMR spectrum of 5a

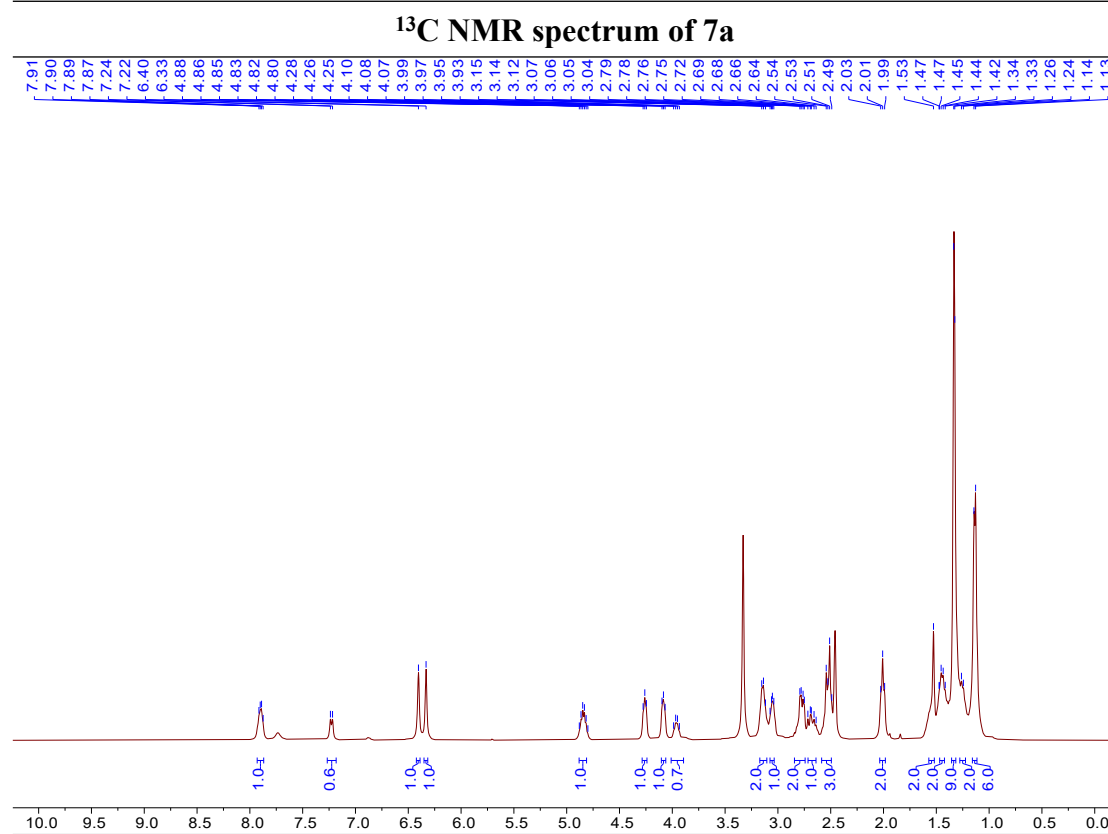
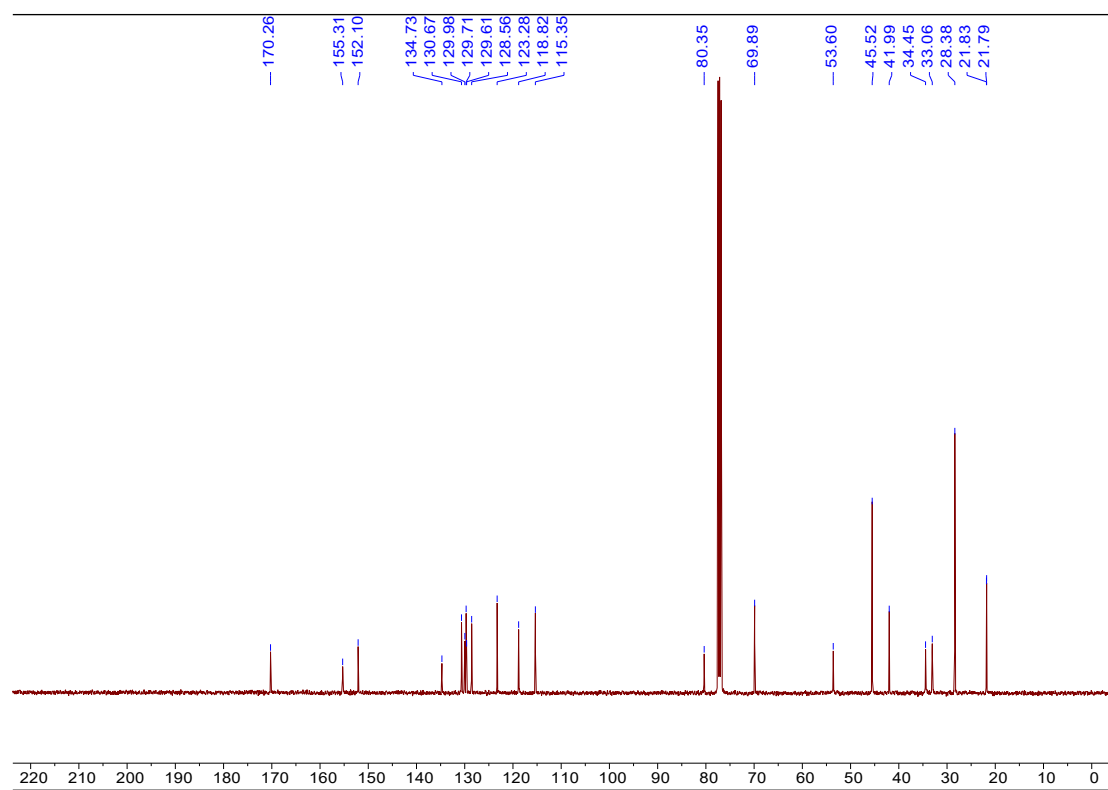


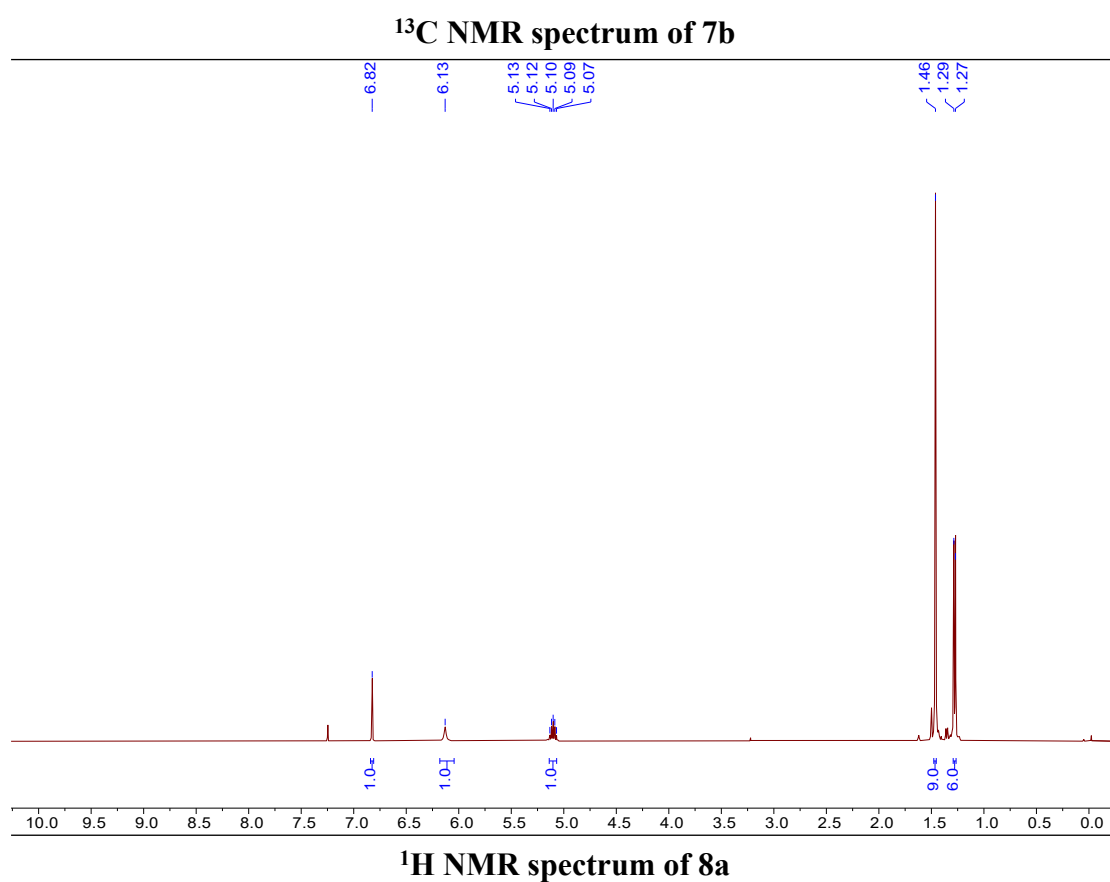
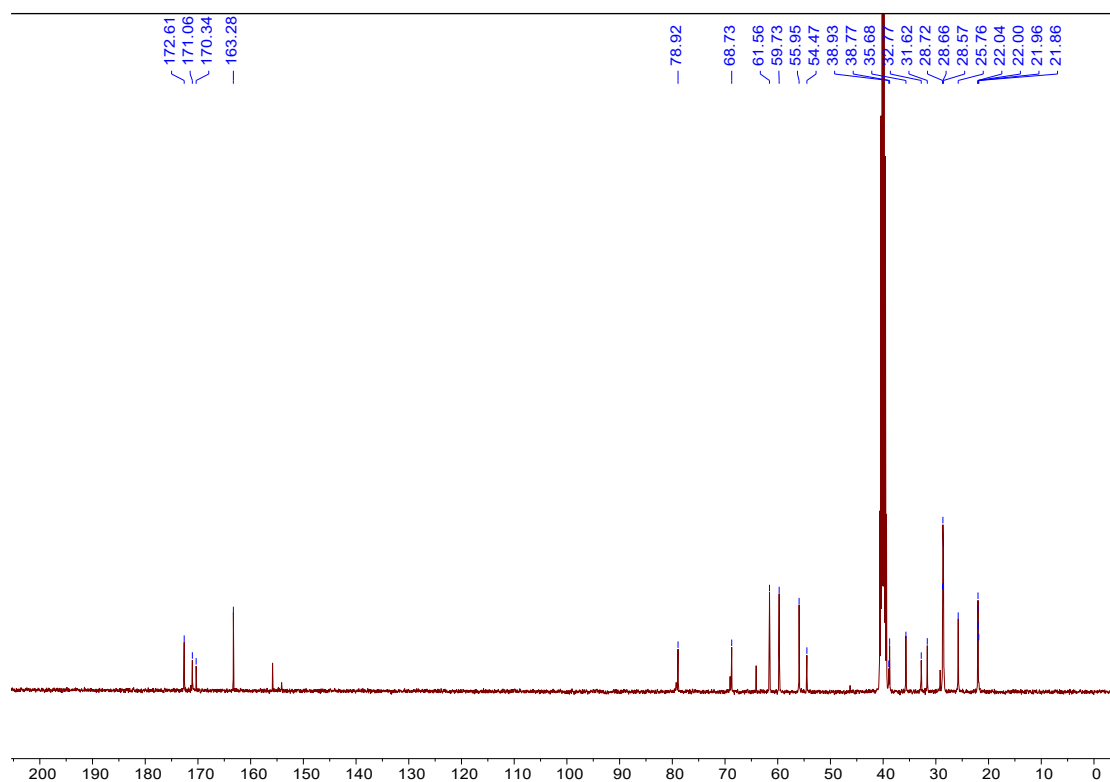
¹H NMR spectrum of 5b

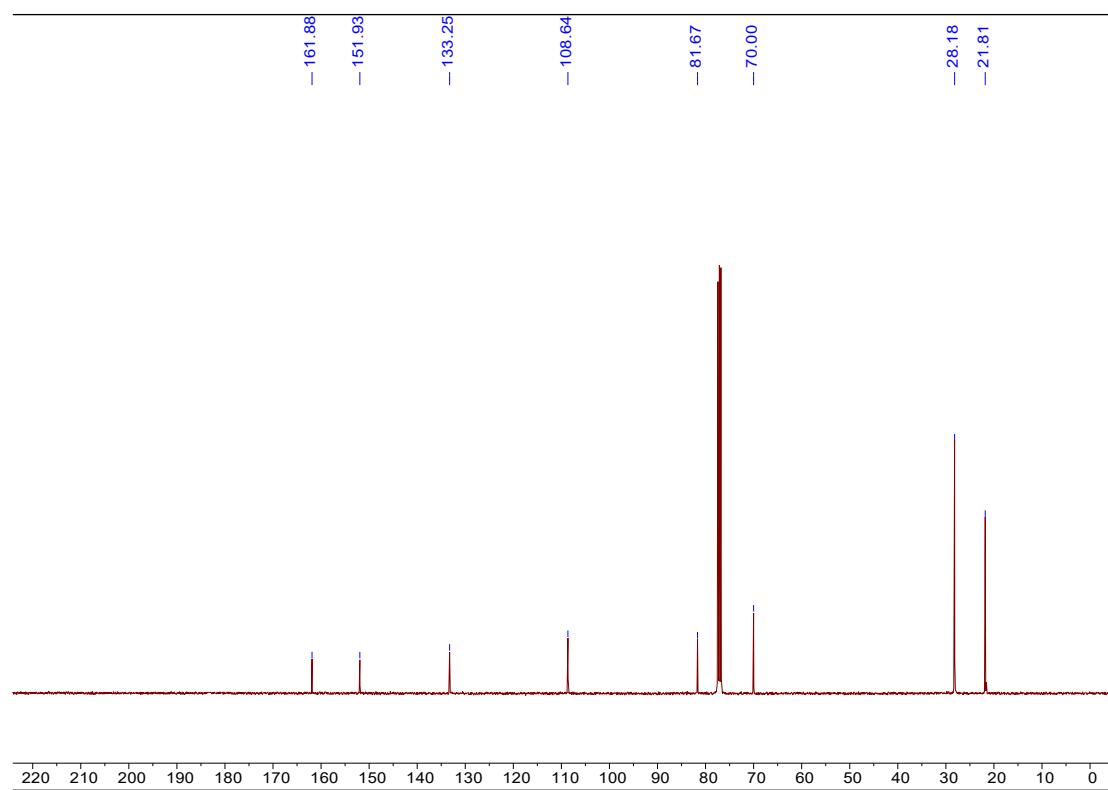




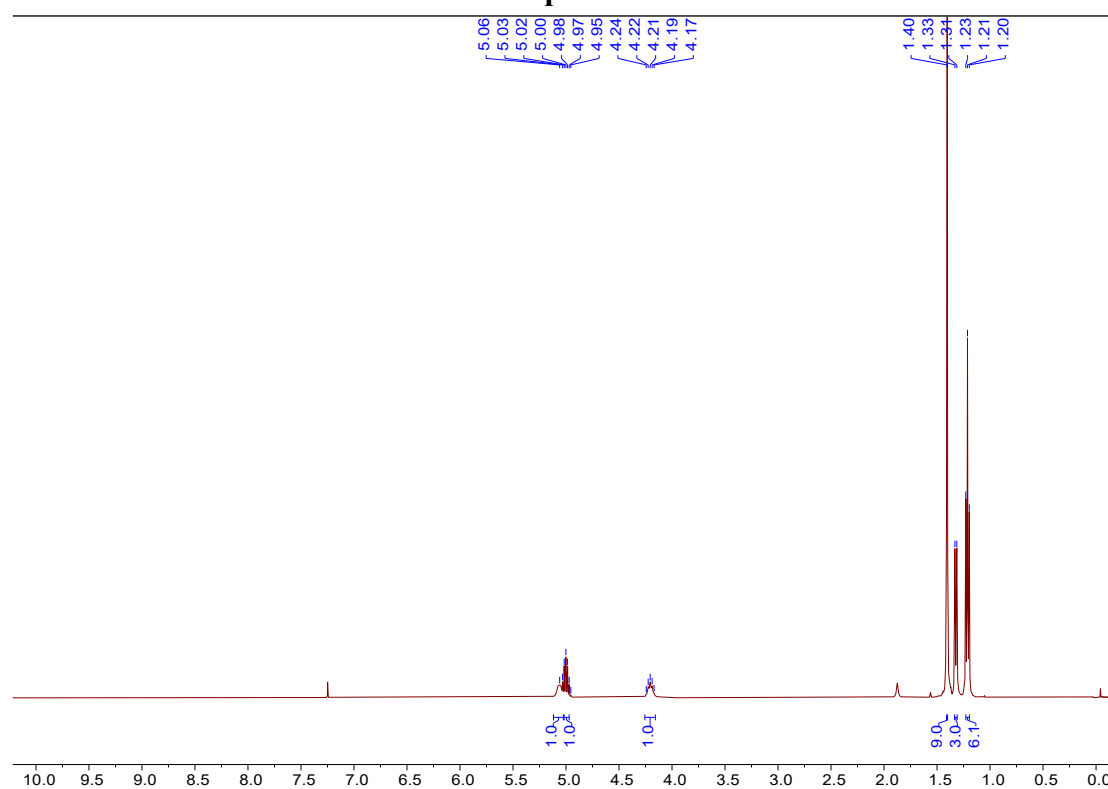




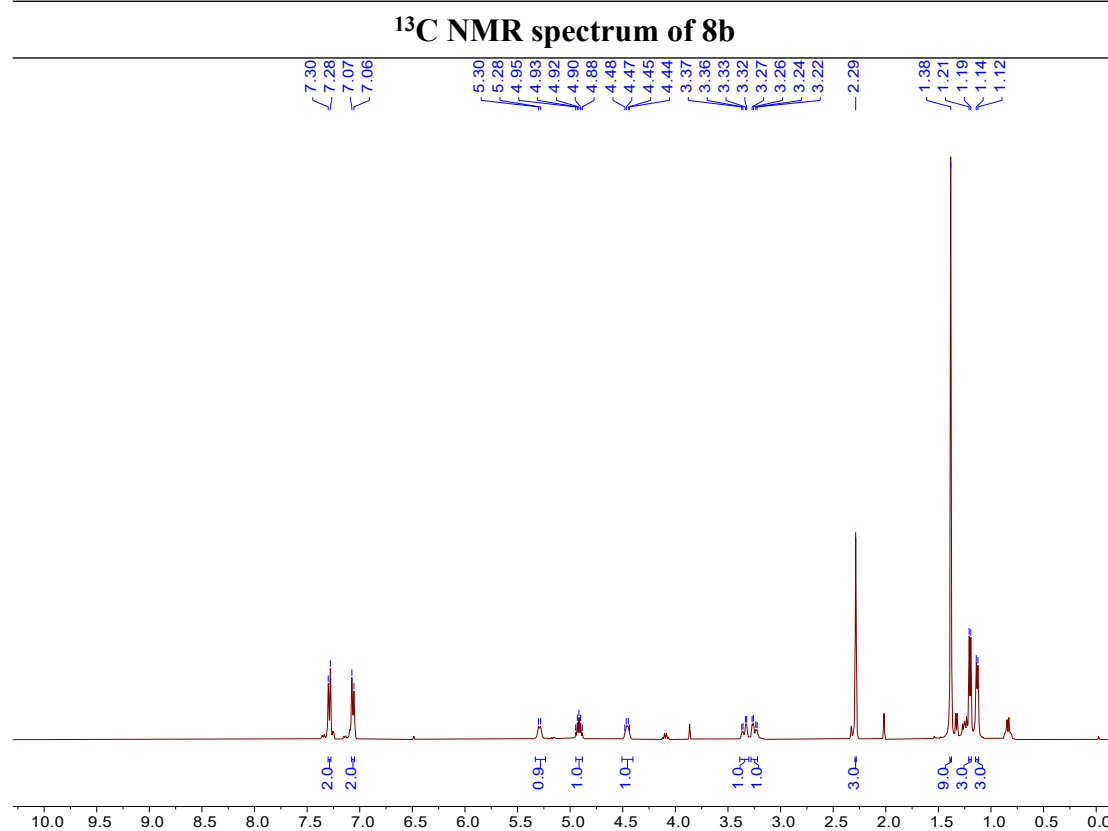
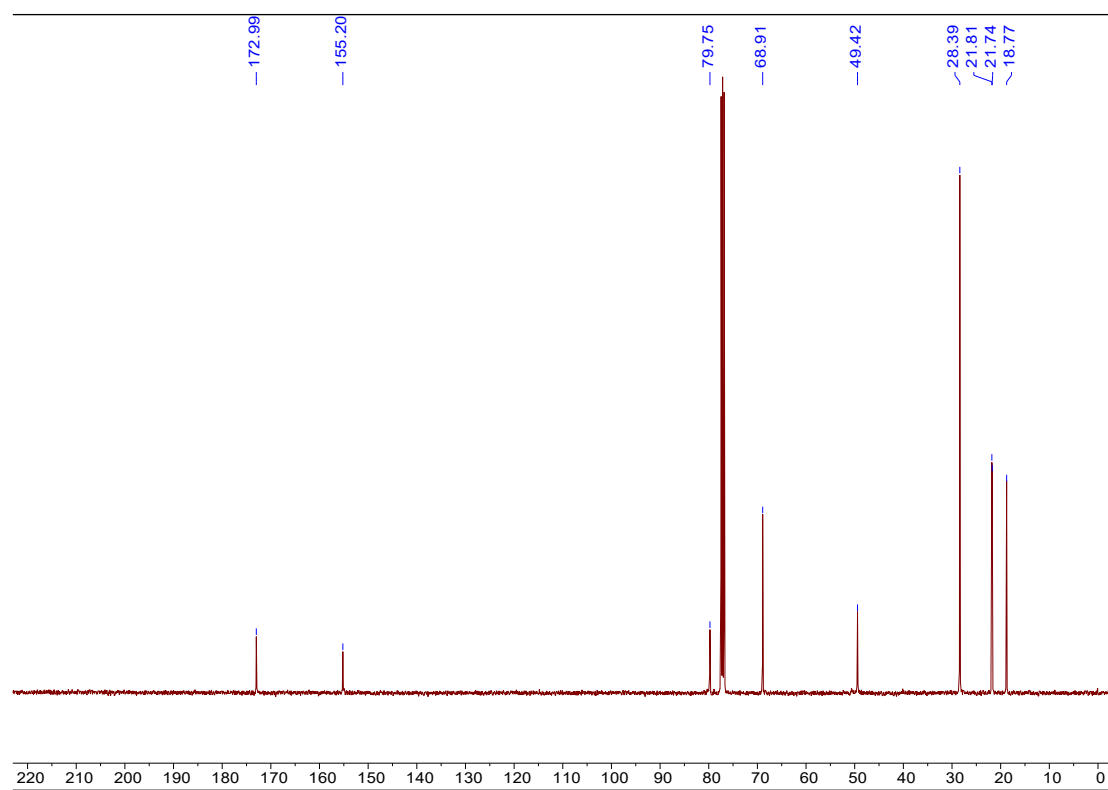


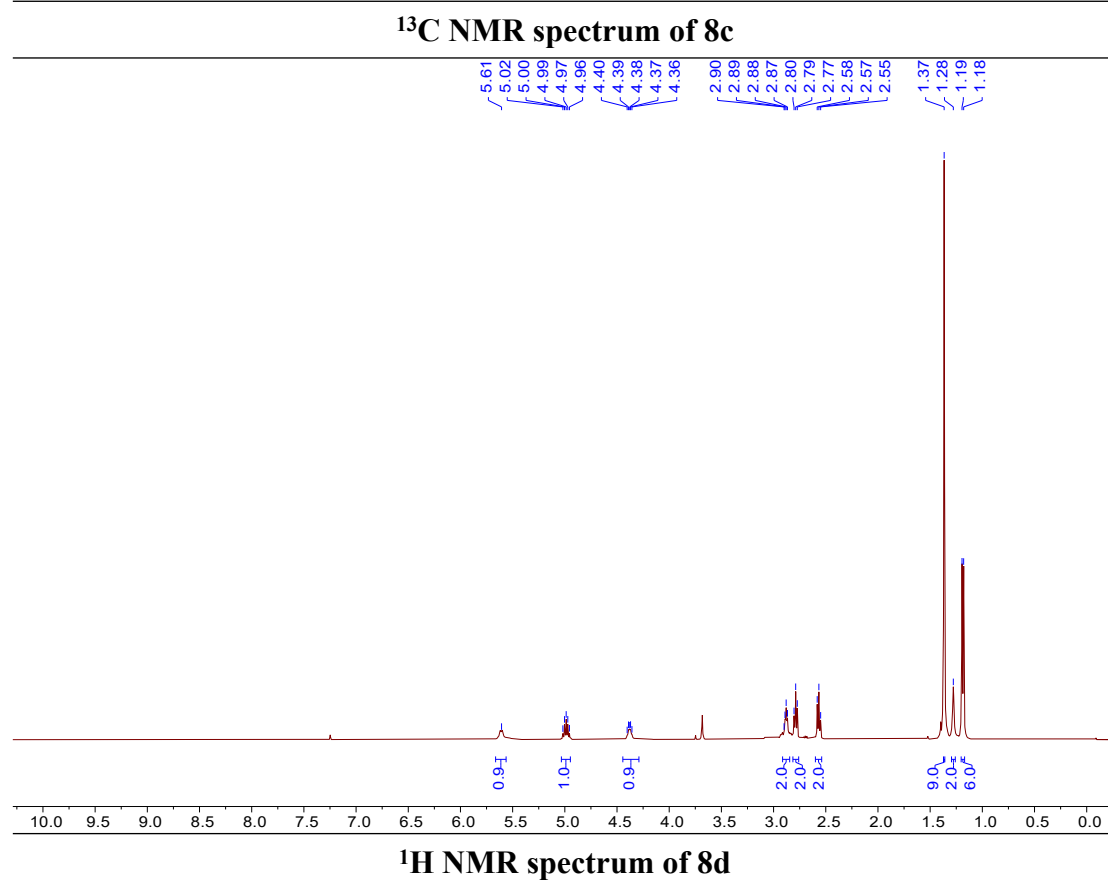
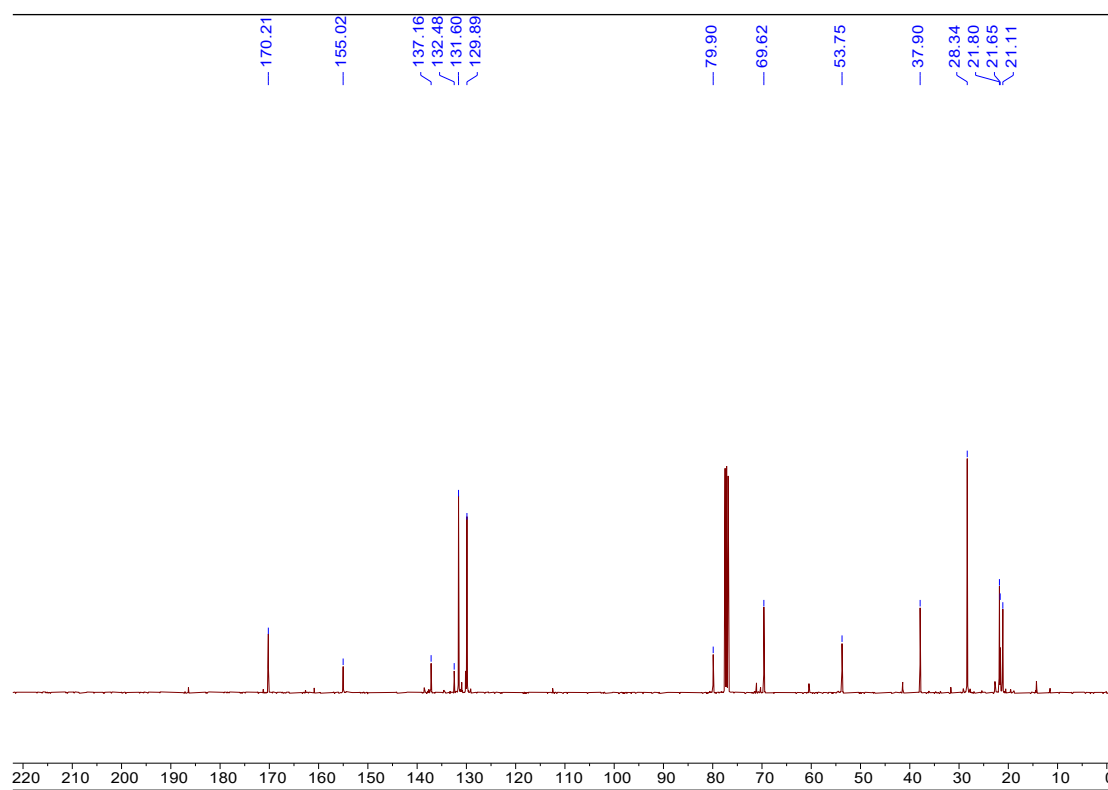


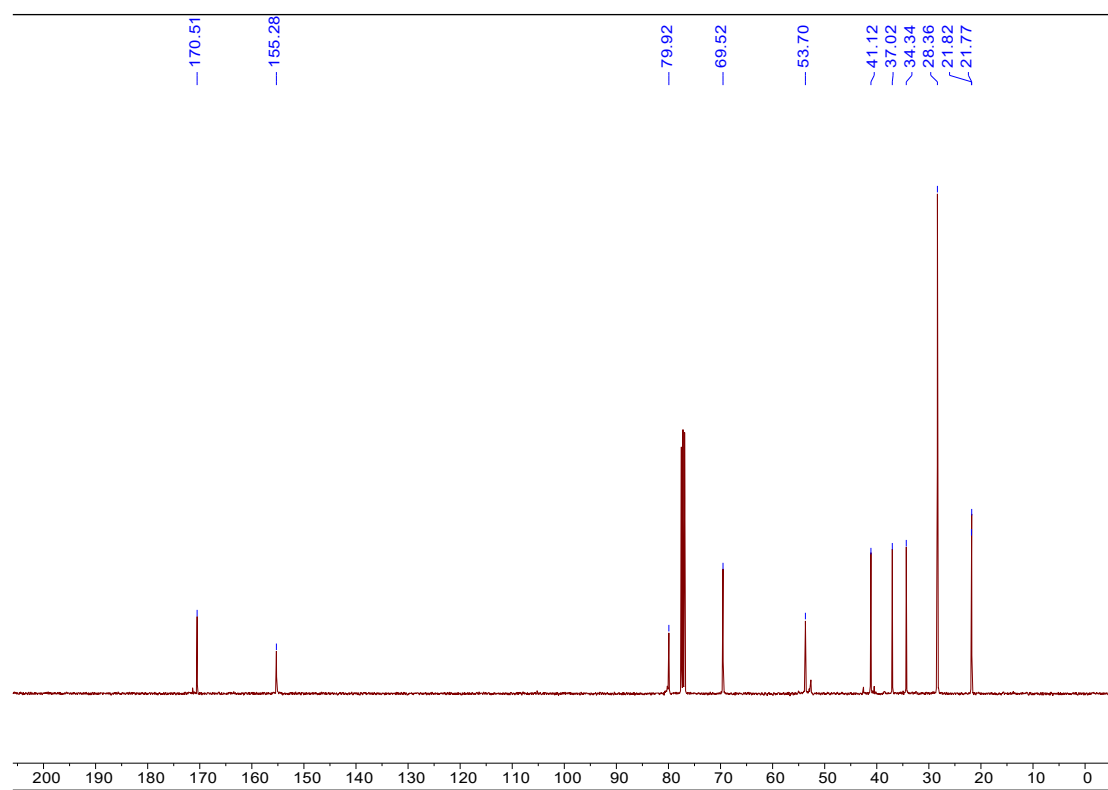
^{13}C NMR spectrum of 8a



^1H NMR spectrum of 8b







^{13}C NMR spectrum of 8d