Supporting Information

Periodic acid-Promoted Methylenation of Imidazoheteroarenes: A Green Approach Using Ethylene Glycol as C1 Source

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I. EXPERIMENTAL PROCEDURES

Unless otherwise stated, all reagents and solvents were obtained from commercial sources and used without any further purification.

I.I Thin layer chromatography

Reaction monitoring and retention factor (*Rf*) determination were performed on pre-coated thin layer chromatography (TLC) sheets (ALUGRAM® Xtra SIL G/UV_{254}, MACHEREY-NAGEL, 0.20 mm thickness of layer) which were visualized either by quenching of ultraviolet or fluorescence light (λ_{max}= 254 and 366 nm, respectively) or by staining with iodine vapor and sprayed with vanillin–sulfuric acid solution, followed by heating the plate with a heat gun.[1]

I.II Column chromatography

Column chromatography was performed on silica gel (Silica gel 60, MACHEREY-NAGEL, 130 – 270 mesh particle size).

I.III Melting points

The melting points (MP) of the synthesized compounds were determined on a digital melting point instrument model MQAPF-301 (Microchemistry), using a heating rate of 2–3 °C min^{-1}. Data is expressed in degrees Celsius (°C).

I.IV Nuclear magnetic resonance spectroscopy

All proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 400 MHz or 100 MHz on a Bruker AVANCE DRX spectrometer. Spectra were recorded in $CDCl_3$. Chemical shifts (δ) were reported in part per million (ppm) in relation to tetramethylsilane (TMS, used as an internal standard for ^{1}H NMR spectra), and $CDCl_3$ (used as an internal standard for ^{13}C NMR spectra). For ^{1}H NMR spectra data are reported as follows: chemical shift (δ), multiplicity and coupling constant (*J*). Multiplicity of peaks are described as singlets (*s*), doublets (*d*), doublet of doublets (*dd*), doublet of doublets of doublets (*ddd*), triplets (*t*), doublet of triplets (*dt*), and multiplets (*m*).

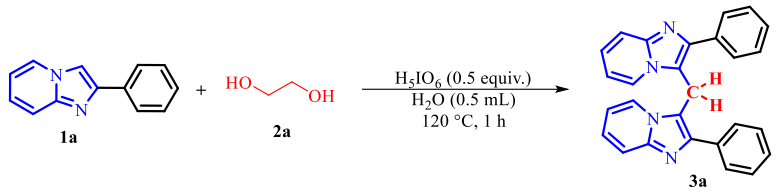
I.V High Resolution Mass Spectrometry

HRMS analyzes were performed on a microTOF-QII mass spectrometer (Bruker), located at the Center for Structural Molecular Biology (CEBIME – UFSC). The spectrometer was operated in positive (+) and negative (-) ion modes, using Atmospheric Pressure Photoionization (APPI) or Electrospray Ionization (ESI) as the ionization mode. Data were processed in Bruker Data Analysis software version 4.0 and reported as m/z.

II. SUBSTRATES

The starting materials, imidazo[1,2-*a*]pyridines [2-8] and imidazo[2,1-*b*]thiazoles[9-10] were prepared according to the literature reports.

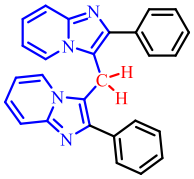
III. GENERAL PROCEDURE FOR THE PREPARATION OF COMPOUND 3/4:



2-Phenylimidazo[1,2-*a*]pyridine **1a** or its derivatives (0.3 mmol), ethylene glycol (**2a**) (0.15 mmol), and water (0.5 mL) were added to a 20 mL Schlenk tube equipped with a magnetic stir bar. Periodic acid (0.15 mmol) was then added, and the tube was sealed. The reaction mixture was stirred for 1 hour at 120 °C in an oil bath. After the reaction time had elapsed, the system was allowed to cool to room temperature. The reaction mixture was transferred to a separation funnel, and saturated sodium bicarbonate ($NaHCO_3$) solution (10 mL) was added. The mixture was subsequently extracted with ethyl acetate (10 mL × 3). The organic phase was dried with anhydrous magnesium sulfate ($MgSO_4$), filtered, and concentrated under vacuum using a rotary evaporator. The crude product was purified by silica gel column chromatography with a suitable ethyl acetate/hexane mixture to provide the desired product.

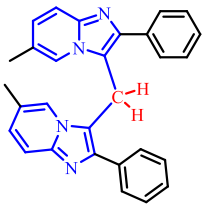
IV. CHARACTERIZATION DATA

Bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)methane (3a)



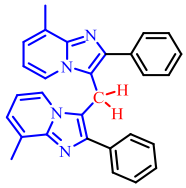
White solid, 57.1 mg, 95%; TLC (*Rf*): 0.23 (Ethyl Acetate, 100%); MP: 215-219 °C (216-218 °C)[14]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.80 – 7.76 (*m*, 4H), 7.54 – 7.48 (*m*, 6H), 7.45 – 7.40 (*m*, 2H), 7.33 (*dt*, *J* = 6.9, *J* = 1.1 Hz, 2H), 7.04 (*ddd*, *J* = 9.1, *J* = 6.8, *J* = 1.2 Hz, 2H), 6.46 (*td*, *J* = 6.8, *J* = 1.2 Hz, 2H), 4.98 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.0, 144.2, 134.4, 129.0, 128.9, 128.3, 124.4, 123.8, 117.5, 114.4, 112.3, 19.8.

Bis(6-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methane (3b)



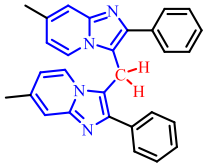
White solid, 62.6 mg, 94%; TLC (*Rf*): 0.36 (Hexane/Ethyl Acetate, 50:50); MP: 272-277 °C (273-275 °C)[14]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (*d*, *J* = 7.9 Hz, 4H), 7.59 – 7.54 (*m*, 4H), 7.48 – 7.43 (*m*, 2H), 7.37 (*d*, *J* = 9.1 Hz, 2H), 7.02 (*s*, 2H), 6.83 (*dt*, *J* = 9.1, *J* = 1.6 Hz, 2H), 4.92 (*s*, 2H), 1.87 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.9, 143.5, 134.9, 129.0, 128.1, 127.4, 122.0, 121.6, 116.4, 114.4, 19.0, 17.9.

Bis(8-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methane (3c)



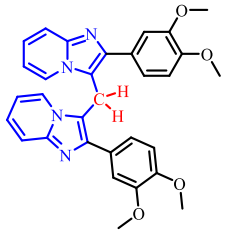
White solid, 107 mg, 76%; TLC (*Rf*): 0.26 (Hexane/Ethyl Acetate, 50:50); MP: 184-190 ºC (178-179ºC)[11]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.73 (*m*, 4H), 7.49 – 7.42 (*m*, 4H), 7.39 – 7.34 (*m*, 2H), 7.20 (*d*, *J* = 6.8 Hz, 2H), 6.78 – 6.73 (*m*, 2H), 6.36 – 6.30 (*m*, 2H), 4.83 (*s*, 2H), 2.52 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 143.4, 134.4, 128.9, 128.5, 127.8, 127.1, 122.9, 121.4, 114.7, 112.1, 19.8, 16.9.

Bis(7-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methane (3d)



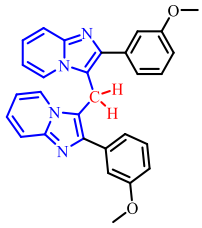
White solid, 60.6 mg, 97%; TLC (*Rf*): 0.32 (Hexane/Ethyl Acetate, 50:50); MP: 216-218 °C (215-217 ºC)[14]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.83 – 7.74 (*m*, 4H), 7.55 – 7.49 (*m*, 4H), 7.46 – 7.40 (*m*, 2H), 7.25 (*s*, 2H), 7.18 (*d*, *J* = 7.0 Hz, 2H), 6.27 (*dd*, *J* = 7.1, *J* = 1.6 Hz, 2H), 4.93 (*s*, 2H), 2.25 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* (ppm): 145.5, 143.7, 135.4, 134.6, 129.0, 128.9, 128.2, 123.1, 115.8, 115.0, 114.0, 21.2, 19.8.

Bis(2-(3,4-dimethoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)methane (3e)



White solid, 65.6 mg, 84%; TLC (*Rf*): 0.05 (Hexane/Ethyl acetate, 50:50); MP: 150-155 °C (192-193 ºC)[12]; ^{1}H NMR (200 MHz, $CDCl_3$) *δ* (ppm): 7.55 (*d*, *J* = 9.0 Hz, 2H), 7.43 – 7.36 (*m*, 4H), 7.28 (*dd*, *J* = 8.1, *J* = 1.7 Hz, 2H), 7.12 – 7.02 (*m*, 2H), 6.99 (*d*, *J* = 8.3 Hz, 2H), 6.49 (*t*, *J* = 6.7 Hz, 2H), 4.98 (*s*, 2H), 3.98 (*s*, 6H), 3.96 (*s,* 6H); ^{13}C NMR (50 MHz, $CDCl_3$) *δ* (ppm): 149.5, 149.3, 144.8, 143.9, 127.0, 124.5, 123.9, 121.3, 117.2, 114.1, 112.4, 112.2, 111.2, 56.2, 56.1, 19.8; HRMS (ESI+) m/z:$[M+H]^+$ calc. for $C_{31}H_{29}N_4O_4$, 521.2183; found: 521.2195.

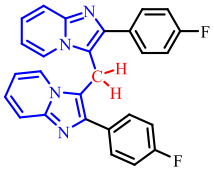
Bis(2-(3-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)methane (3f)



Beige solid, 60.1 mg, 87%; TLC (*Rf*): 0.16 (Hexane/Ethyl Acetate, 50:50); MP: 120-134 °C; ^{1}H NMR (200 MHz, $CDCl_3$) *δ* (ppm): 7.56 – 7.46 (*m*, 2H), 7.44 – 7.27 (*m*, 8H), 7.14 – 6.88 (*m*, 4H),

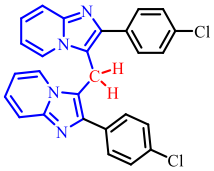
6.60 – 6.31 (*m*, 2H), 4.97 (*s*, 2H), 3.86 (*s*, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 160.0, 144.9, 144.0, 135.7, 129.8, 124.4, 123.9, 121.4, 117.4, 114.5, 114.3, 114.2, 112.3, 55.4, 19.7; HRMS (ESI+) m/z: $[M+H]^+$ calc. for $C_{29}H_{25}N_4O_2$, 461.1972; found: 461.1979.

Bis(2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methane (3g)



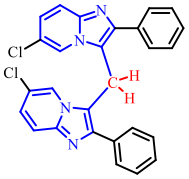
White solid, 60.4 mg, 92%; TLC (*Rf*): 0.23 (Hexane/Ethyl Acetate, 50:50); MP: 189-192 °C (190-192 ºC)[14]; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 – 7.63 (*m*, 4H), 7.53 (*dt*, *J* = 9.1, 1.0 Hz, 2H), 7.37 (*dt*, *J* = 6.9, 1.0 Hz, 2H), 7.18 – 7.11 (*m*, 4H), 7.09 (*ddd*, *J* = 9.0, 6.8, 1.2 Hz, 2H), 6.54 (*td*, *J* = 6.8, 1.2 Hz, 2H), 4.87 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.7 (*d*, J_{F-C} = 248.1 Hz), 144.9, 143.3, 130.5 (*d*, J_{F-C} = 8.2 Hz), 130.3 (*d*, J_{F-C} = 3.3 Hz), 124.5, 123.5, 117.5, 115.7 (*d*, J_{F-C} = 21.6 Hz), 113.9, 112.5, 19.9.

Bis(2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methane (3h)



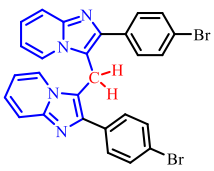
White solid, 57.8 mg, 82%; TLC (*Rf*): 0.34 (Hexane/Ethyl Acetate, 50:50); MP: 250-255 °C (250-252 ºC)[11]; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.63 (*d*, ^3J = 8.4 Hz, 4H), 7.53 (*d*, ^3J = 9.1 Hz, 2H), 7.46 – 7.32 (*m*, 6H), 7.09 (*ddd*, *J* = 9.0, *J* = 6.8, *J* = 0.9 Hz, 2H), 6.55 (*td*, *J* = 6.8, *J* = 1.1 Hz, 2H), 4.88 (*s*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 145.1, 143.2, 134.3, 132.7, 130.0, 129.0, 124.7, 123.5, 117.7, 114.1, 112.7, 20.1.

Bis(6-chloro-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methane (3i)



White solid, 37.3 mg, 53%; TLC (*Rf*): 0.64 (Hexane/Ethyl Acetate, 50:50); MP: 225-230 °C (234-236 ºC)[11]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 – 7.72 (*m*, 4H), 7.59 – 7.54 (*m*, 4H), 7.51 – 7.47 (*m*, 2H), 7.45 – 7.42 (*m*, 2H), 7.34 – 7.23 (*m*, 2H), 7.01 (*dd*, ^3J = 9.5, ^4J = 1.9 Hz, 2H), 4.90 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.4, 143.5, 133.7, 129.3, 129.1, 128.8, 126.0, 122.0, 120.7, 117.8, 114.8, 19.2.

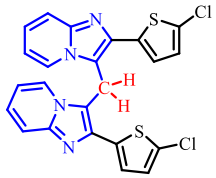
Bis(2-(4-bromophenyl)imidazo[1,2-*a*]pyridin-3-yl)methane (3j)



White solid, 63.6 mg, 76%; TLC (*Rf*): 0.64 (Hexane/Ethyl Acetate, 50:50); MP: 255-260 °C (254-255 ºC) [11]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 (*s*, 8H), 7.54 (*d*, *J* = 9.1 Hz, 2H), 7.36 (*d*, *J*

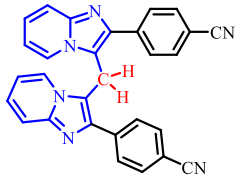
= 6.9 Hz, 2H), 7.10 (*ddd*, *J* = 8.8, *J* = 6.8, *J* = 0.9 Hz, 2H), 6.56 (*td*, *J* = 6.8, *J* = 0.8 Hz, 2H), 4.87 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.1, 143.2, 133.1, 131.9, 130.2, 124.7, 123.5, 122.6, 117.7, 114.1, 112.8, 20.1.

Bis(2-(5-chlorothiophen-2-yl)imidazo[1,2-*a*]pyridin-3-yl)methane (3k)



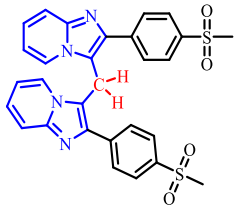
Pale brown solid, 53 mg, 73%; TLC (*Rf*): 0.60 (Hexane/Ethyl Acetate, 50:50); MP: 247-250 °C (253-254 ºC)[13]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, *J* = 9.0 Hz, 2H), 7.50 (s, 2H), 7.28 (d, *J* = 3.9 Hz, 2H), 7.13 – 7.08 (m, 2H), 6.99 (d, *J* = 3.9 Hz, 2H), 6.58 (t, *J* = 6.8 Hz, 2H), 5.01 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 145.4, 137.8, 135.8, 131.3, 127.2, 125.3, 125.0, 123.7, 117.6, 113.4, 113.3, 20.4; HRMS (ESI+) m/z:$[M+H]^+$ calc. for $C_{23}H_{15}Cl_2N_4S_2$, 481.0110; found: 481.0115.

4,4'-(Methylenebis(imidazo[1,2-*a*]pyridine-3,2-diyl))dibenzonitrile (3l)



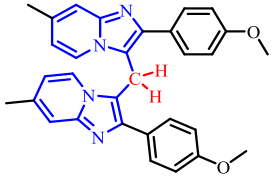
White solid, 57.8 mg, 86%; TLC (*Rf*): 0.31 (Hexane/Ethyl Acetate, 50:50); MP: 294-296 °C (295-297 ºC)[14]; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm): 7.63 (*d*, *J* = 8.5 Hz, 4H), 7.53 (*d*, *J* = 9.1 Hz, 2H), 7.44 – 7.33 (*m*, 6H), 7.09 (*ddd*, *J* = 8.9, *J* = 6.8, *J* = 1.0 Hz, 2H), 6.55 (*td*, *J* = 6.8, *J* = 0.9 Hz, 2H), 4.87 (*s*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 145.1, 143.2, 134.3, 132.7, 130.0, 129.0, 124.7, 123.5, 117.7, 114.1, 112.7, 20.1.

Bis(2-(4-(methylsulfonyl)phenyl)imidazo[1,2-*a*]pyridin-3-yl)methane (3m)



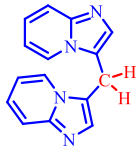
Pale red-brown solid, 56.3 mg, 67%; TLC (*Rf*): 0.083 (Hexane/Ethyl Acetate, 50:50); MP: 273-275 °C (274-275 ºC)[11]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 8.4 Hz, 4H), 7.79 (d, *J* = 8.6 Hz, 4H), 7.57 (d, *J* = 9.1 Hz, 2H), 7.50 (d, *J* = 6.9 Hz, 2H), 7.20 (d, *J* = 6.8 Hz, 2H), 6.71 (td, *J* = 6.8, 1.2 Hz, 2H), 4.93 (s, 2H), 3.09 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 145.0, 142.3, 139.6, 139.2, 129.0, 127.3, 125.1, 123.0, 117.8, 114.4, 113.1, 44.4, 29.5.

Bis(2-(4-methoxyphenyl)-7-methylimidazo[1,2-*a*]pyridin-3-yl)methane (3n)



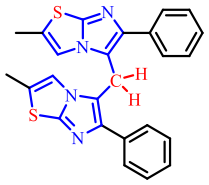
White solid, 63.3 mg, 87%; TLC (*Rf*): 0.60 (Hexane/Ethyl Acetate, 50:50); MP: 203-205 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 – 7.70 (*m*, 4H), 7.23 (*s*, 2H), 7.19 (*d*, *J* = 7.1 Hz, 2H), 7.06 – 7.02 (*m*, 4H), 6.26 (*dd*, *J* = 7.1, *J* = 1.5 Hz, 2H), 4.87 (*s*, 2H), 3.86 (*s*, 6H), 2.24 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.5, 145.2, 143.4, 135.0, 130.0, 127.0, 123.0, 115.5, 114.6, 114.2, 113.4, 55.3, 21.1, 19.7; HRMS (ESI+) m/z: $[M+H]^+$ calc. for $C_{31}H_{29}N_4O_2$, 489.2285; found: 489.2291.

Bis(imidazo[1,2-a]pyridin-3-yl)methane (3o)



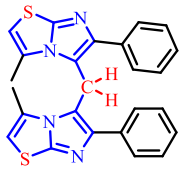
White solid, 36 mg, 36%; TLC (*Rf*): 0.30 (Hexane/Ethyl Acetate, 50:50); MP: 235-239 °C (219-221 ºC)[11]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): δ 7.93 (d, *J* = 6.9 Hz, 2H), 7.64 (d, *J* = 9.2 Hz, 2H), 7.49 (s, 2H), 7.24 – 7.15 (m, 2H), 6.80 (t, J = 6.9 Hz, 2H), 4.52 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 146.3, 132.7, 124.2, 123.3, 118.2, 112.7, 20.2.

Bis(2-methyl-6-phenylimidazo[2,1-*b*]thiazol-5-yl)methane (4a)



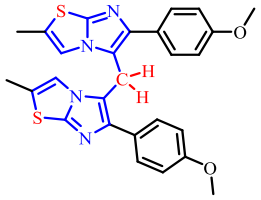
White solid, 53.9 mg, 84%; TLC (*Rf*): 0.53 (Hexane/Ethyl acetate, 50:50); MP: 235-239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 – 7.71 (m, 4H), 7.53 – 7.48 (m, 4H), 7.42 – 7.37 (m, 2H), 6.19 – 6.17 (m, 2H), 4.72 (s, 2H), 2.17 – 2.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.9, 143.3, 134.8, 129.0, 128.1, 127.7, 126.6, 117.4, 114.1, 21.2, 14.2; HRMS (ESI+) m/z:$[M+H]^+$ calc. for $C_{25}H_{21}N_4S_2$, 441.1202; found: 441.1208.

Bis(3-methyl-6-phenylimidazo[2,1-*b*]thiazol-5-yl)methane (4b)



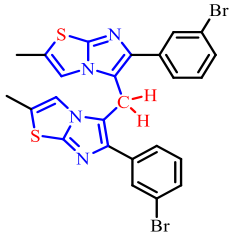
White solid, 56.5 mg, 85%; TLC (*Rf*): 0.35 (Hexane/Ethyl acetate, 50:50); MP: 198-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.27 – 7.23 (m, 4H), 7.20 – 7.15 (m, 6H), 6.18 (d, J = 1.2 Hz, 2H), 4.80 (s, 2H), 2.33 – 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.6, 145.6, 134.0, 129.0, 127.9, 127.6, 127.1, 119.0, 107.4, 22.0, 14.4; HRMS (ESI+) m/z:$[M+H]^+$ calc. for $C_{25}H_{21}N_4S_2$, 441.1202; found: 441.1208.

Bis(6-(4-methoxyphenyl)-2-methylimidazo[2,1-*b*]thiazol-5-yl)methane (4c)



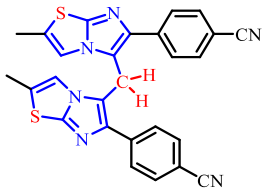
Pale brown solid, 67 mg, 89%; TLC (*Rf*): 0.65 (Hexane/Ethyl acetate, 50:50); MP: 210-215 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 – 7.62 (m, 4H), 7.07 – 6.99 (***m***, 4H), 6.24 – 6.22 (m, 2H), 4.64 (*s*, 2H), 3.87 (*s*, 6H), 2.18 – 2.17 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.2, 148.6, 143.0, 129.3, 127.3, 126.3, 116.7, 114.4, 114.1, 55.5, 21.2, 14.2; HRMS (ESI+) m/z:$[M+H]^+$ calc. for $C_{27}H_{25}N_4O_2S_2$, 501.1413; found: 501.1419.

Bis(6-(3-bromophenyl)-2-methylimidazo[2,1-*b*]thiazol-5-yl)methane (4d)



White solid, 52 mg, 58%; TLC (*Rf*): 0.61 (Hexane/Ethyl acetate, 50:50); MP: 180-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 (*t*, J = 1.7 Hz, 2H), 7.58 (*ddd*, J = 7.7, J = 1.5, J = 1.1 Hz, 2H), 7.50 (*ddd*, J = 8.0, J = 2.0, J = 1.0 Hz, 2H), 7.33 (*t*, J = 7.9 Hz, 2H), 6.23 – 6.22 (*m*, 2H), 4.65 (*s*, 2H), 2.21 – 2.21 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.1, 141.9, 136.6, 131.0, 130.6, 130.3, 127.4, 126.3, 123.1, 117.3, 113.7, 21.2, 14.2; HRMS (ESI+) m/z:$[M+H]^+$ calc. $C_{25}H_{19}Br_2N_4S_2$, 598.9392; found: 598.9398.

4,4'-(5,5'-methylenebis(2-methylimidazo[2,1-b]thiazole-6,5-diyl))dibenzonitrile (4e)



White solid, 46.4 mg, 63%; TLC (*Rf*): 0.36 (Hexane/Ethyl acetate, 50:50); MP: 200-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81 (m, 4H), 7.74 (m, 4H), 6.33 (d, J = 1.5 Hz, 2H), 4.74 (s, 2H), 2.26 – 2.26 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 149.7, 141.8, 138.9, 132.7, 128.5, 128.1, 118.9, 117.6, 113.3, 111.1, 22.1, 14.3; HRMS (ESI+) m/z:$[M+H]^+$ calc. for $C_{27}H_{19}N_6S_2$, 492.1141 found: 492.1140.

V. REFERENCES

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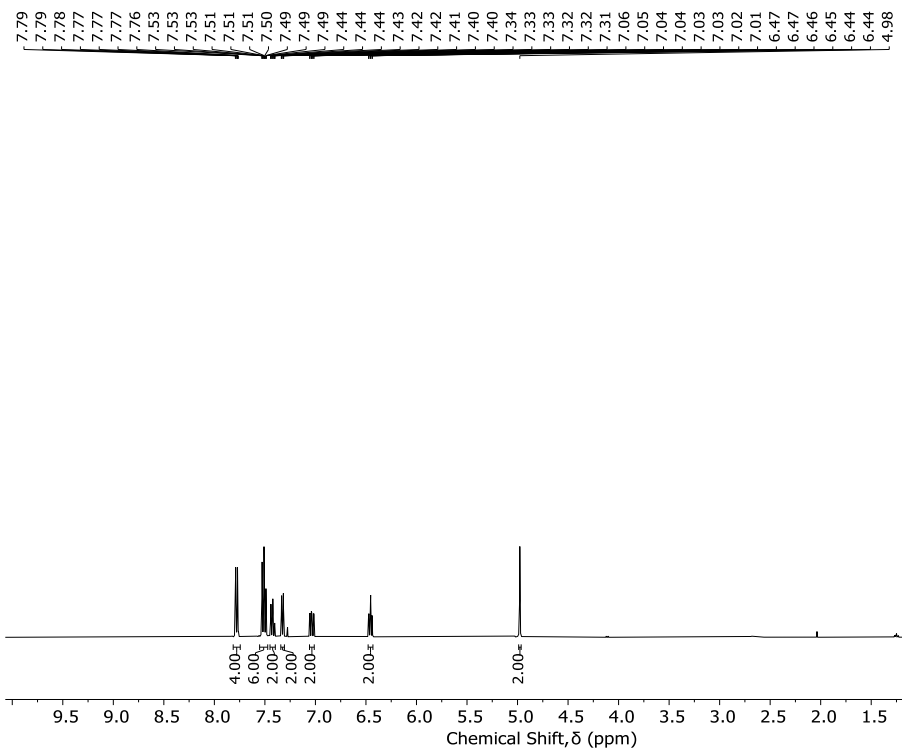
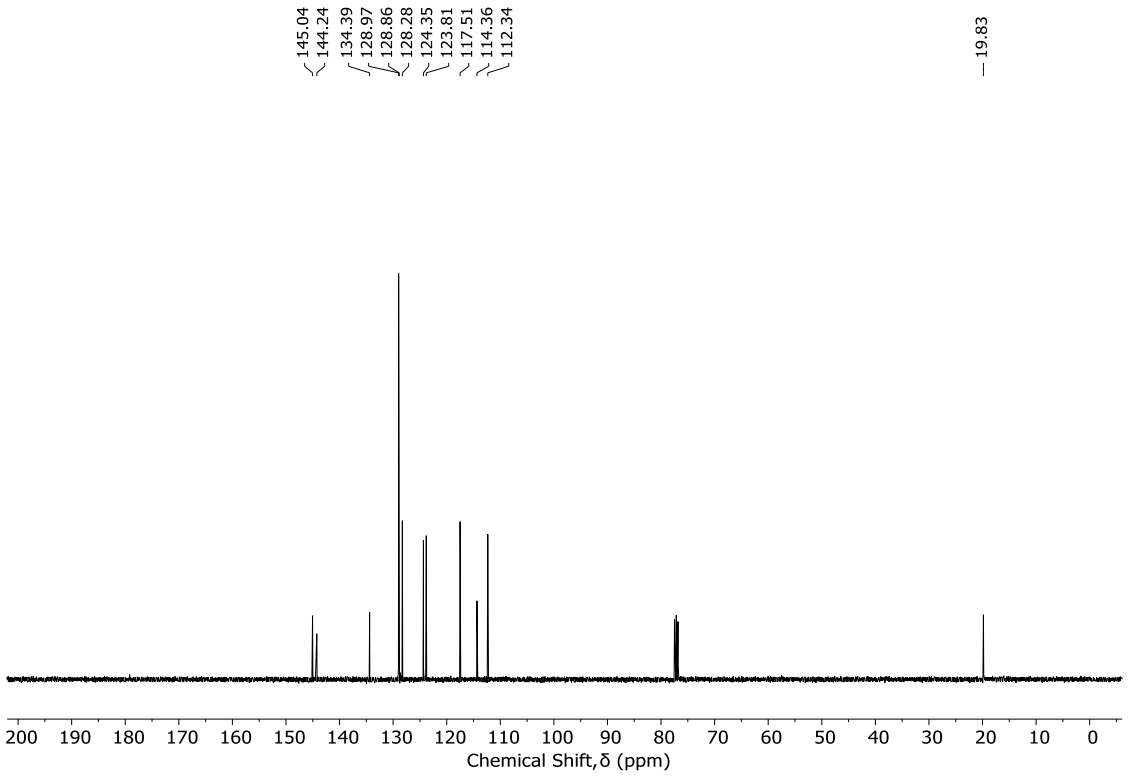
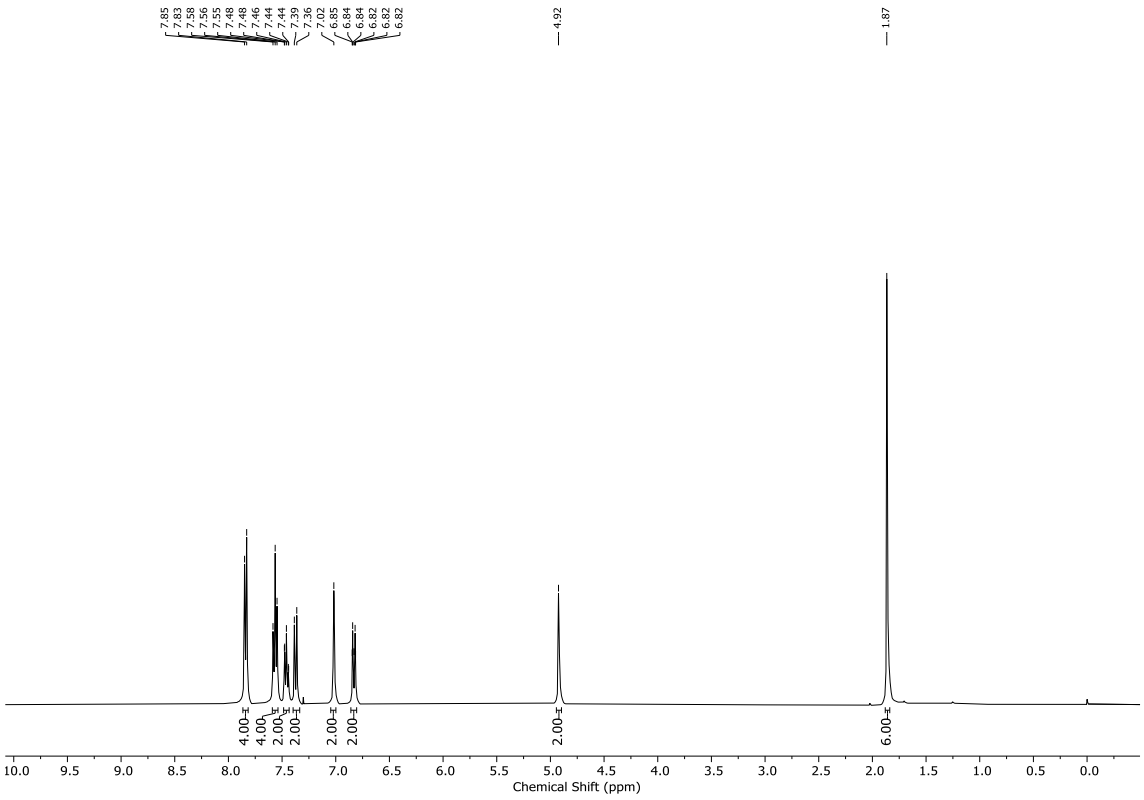
VI. ^{1}H NMR AND ^{13}C NMR SPECTRA OF COMPOUNDS



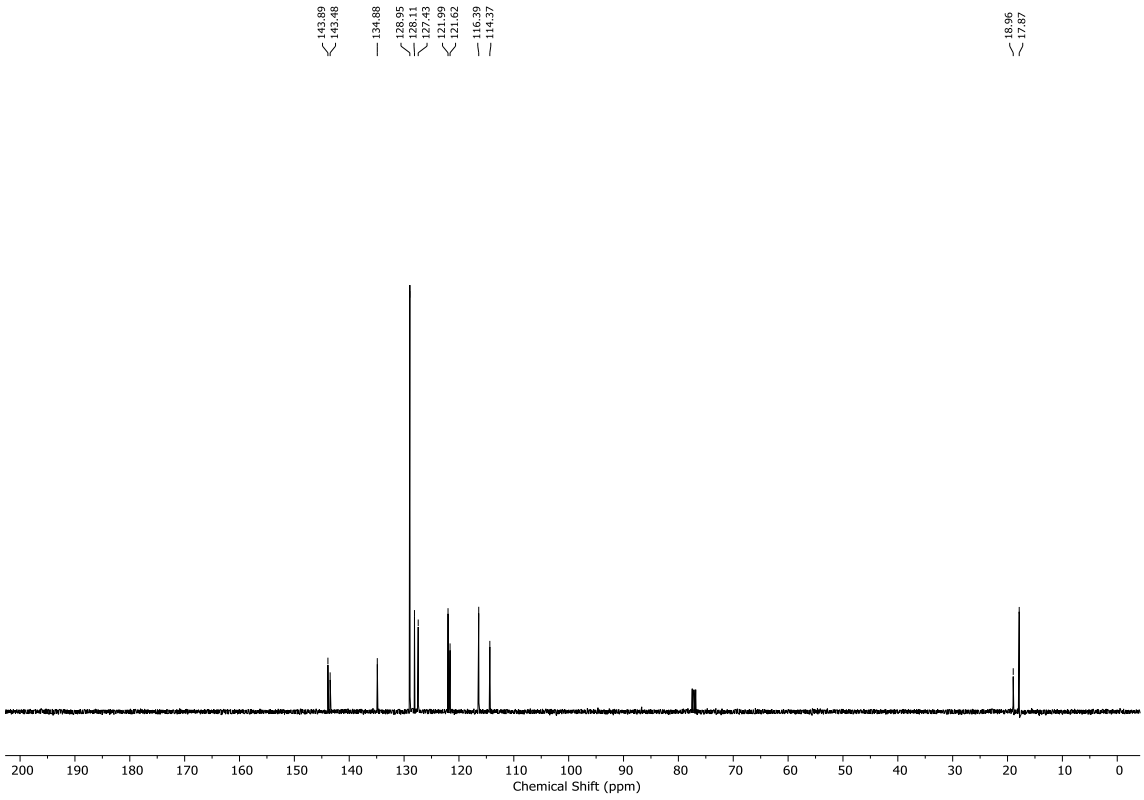
^{1}H NMR Spectra of **3a** in $CDCl_3$ at 400 MHz



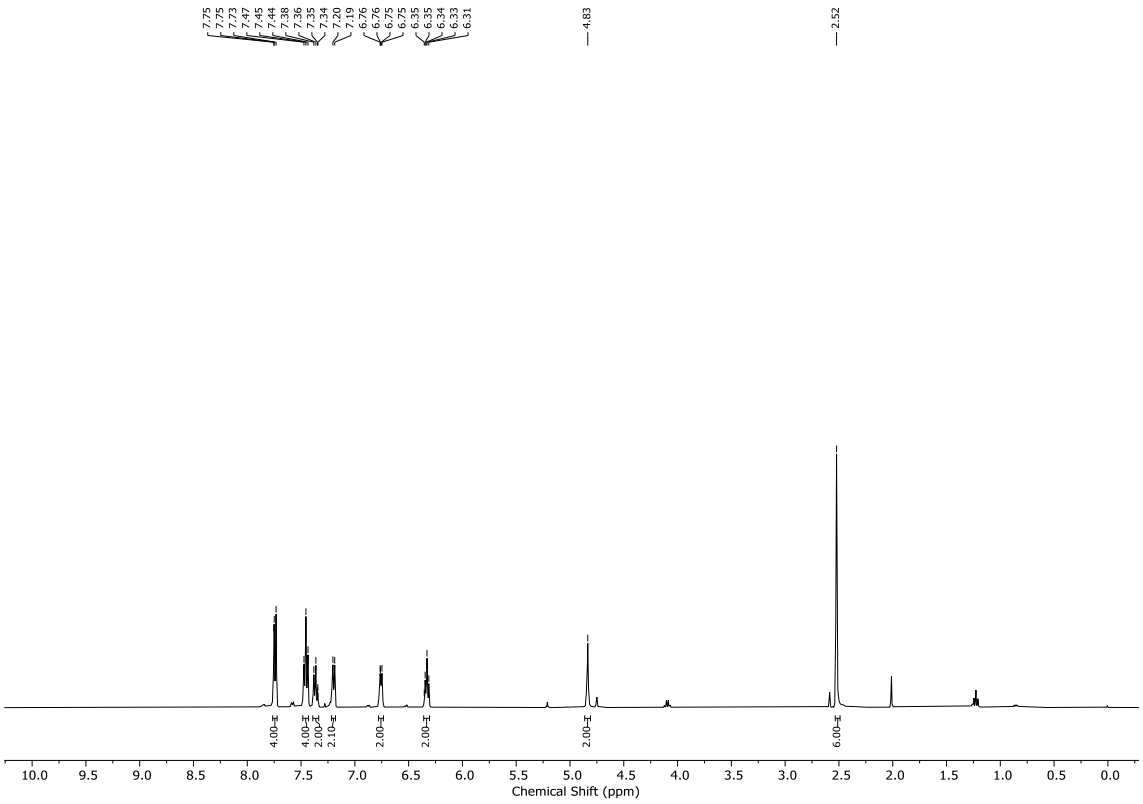
^{13}C NMR Spectra of **3a** in $CDCl_3$ at 100 MHz



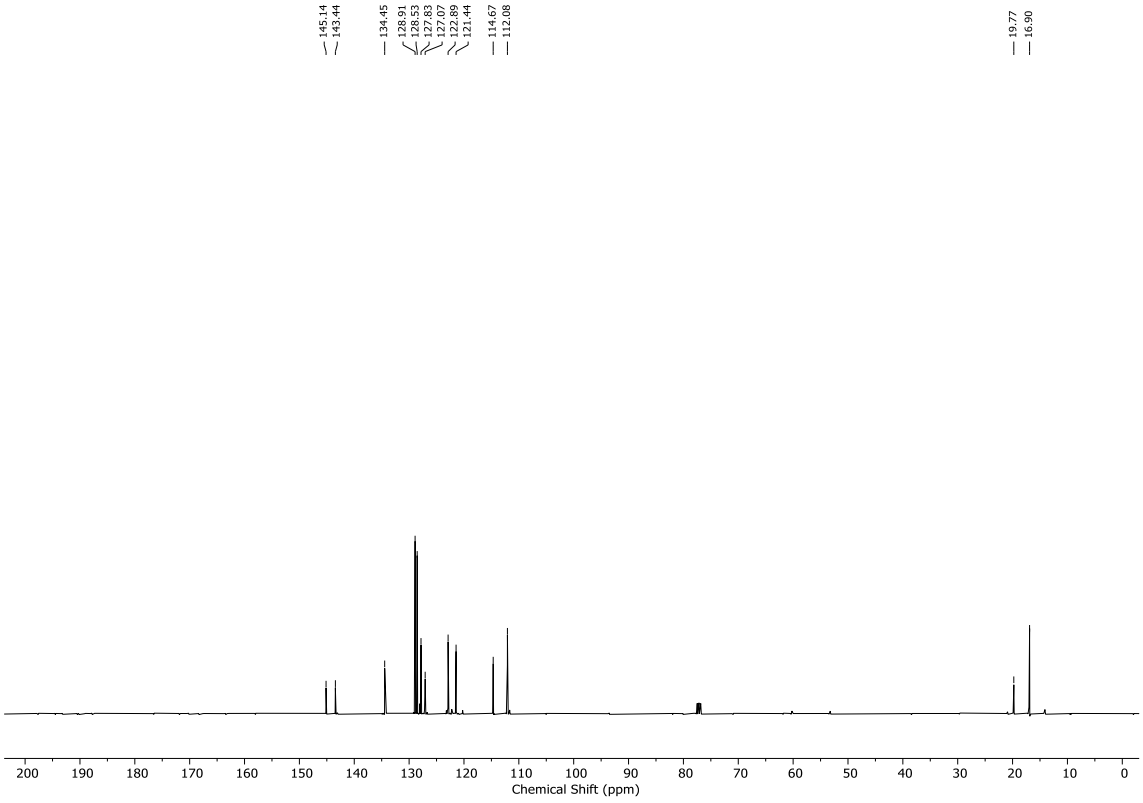
^{1}H NMR Spectra of **3b** in $CDCl_3$ at 400 MHz



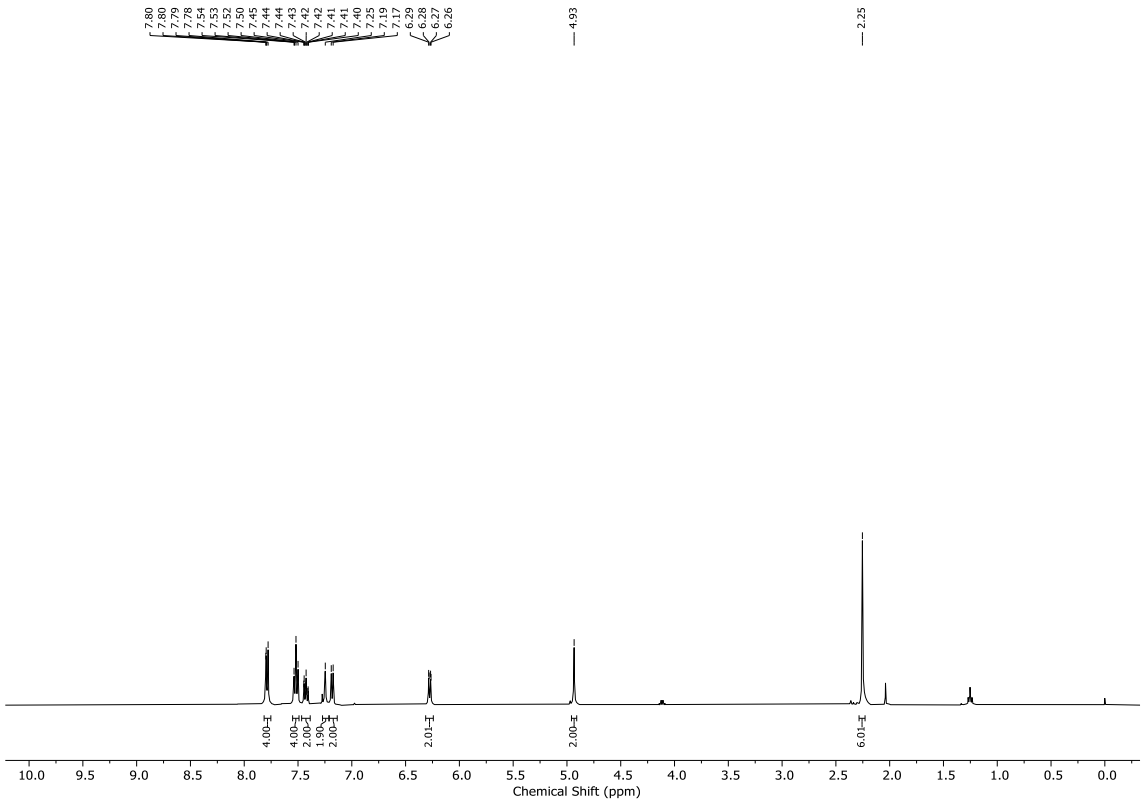
^{13}C NMR Spectra of **3b** in $CDCl_3$ at 100 MHz



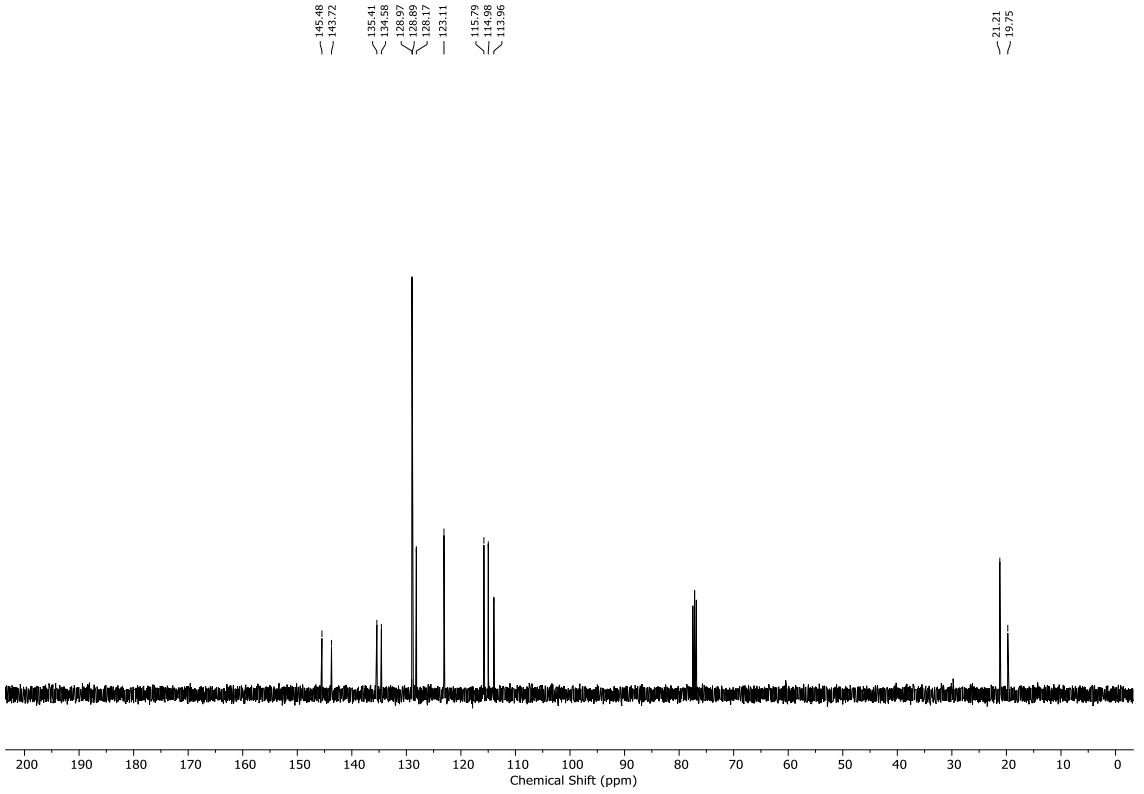
^{1}H NMR Spectra of **3c** in $CDCl_3$ at 400 MHz



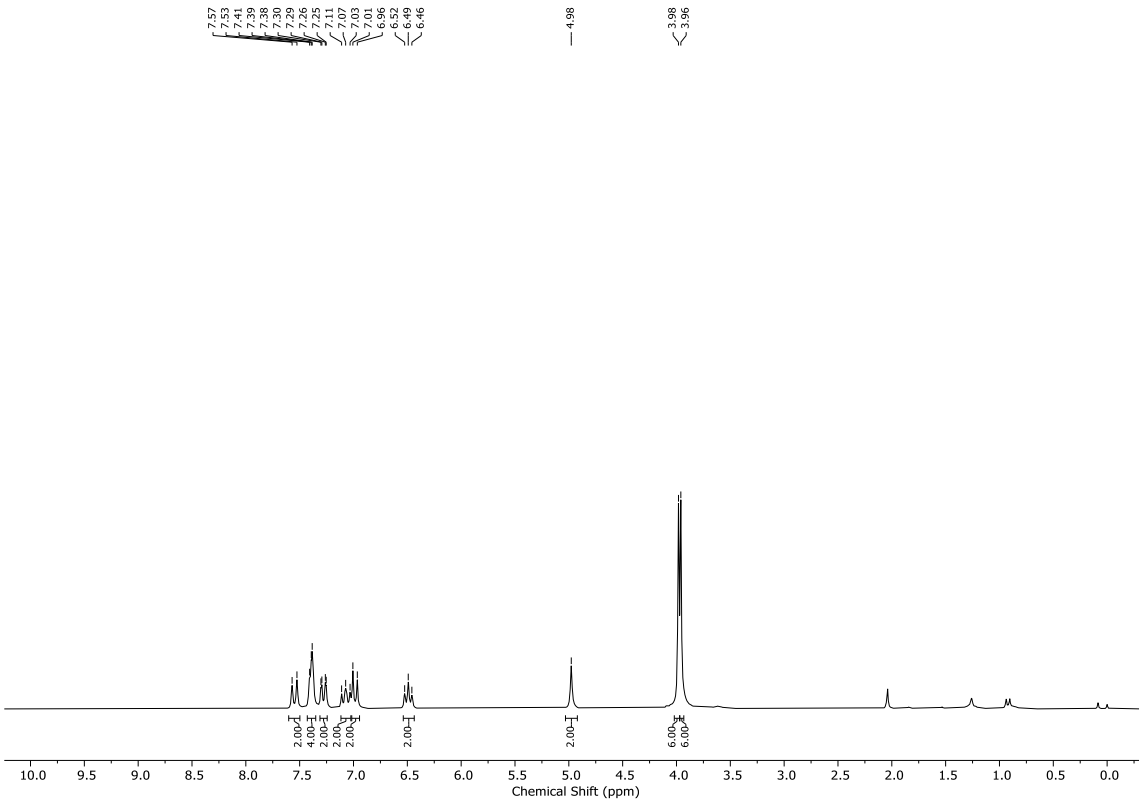
^{13}C NMR Spectra of **3c** in $CDCl_3$ at 100 MHz



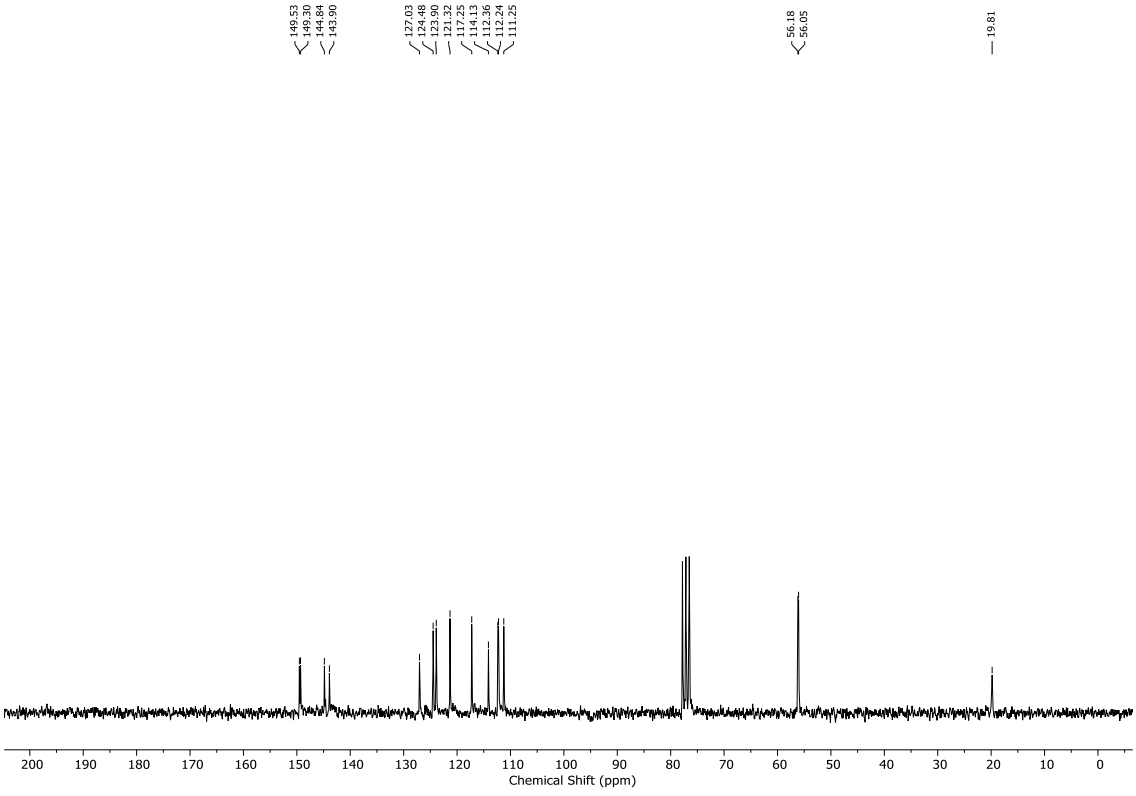
^{1}H NMR Spectra of **3d** in $CDCl_3$ at 400 MHz



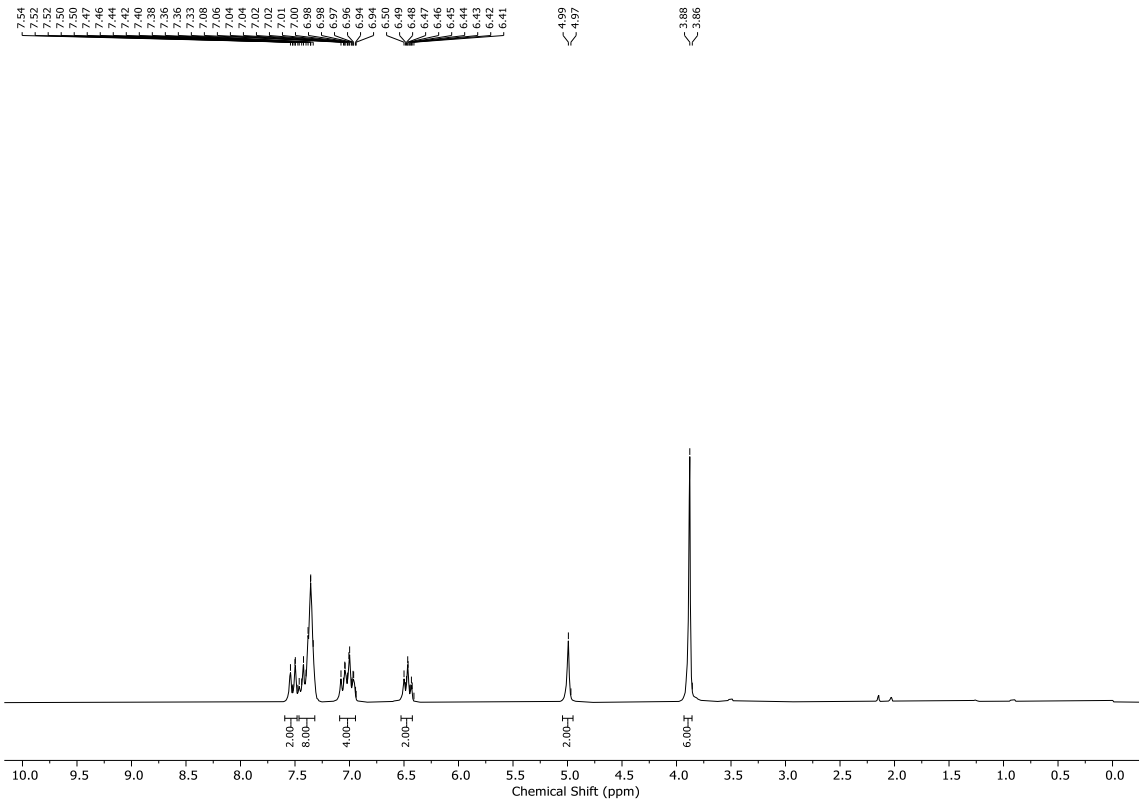
^{13}C NMR Spectra of **3d** in $CDCl_3$ at 100 MHz



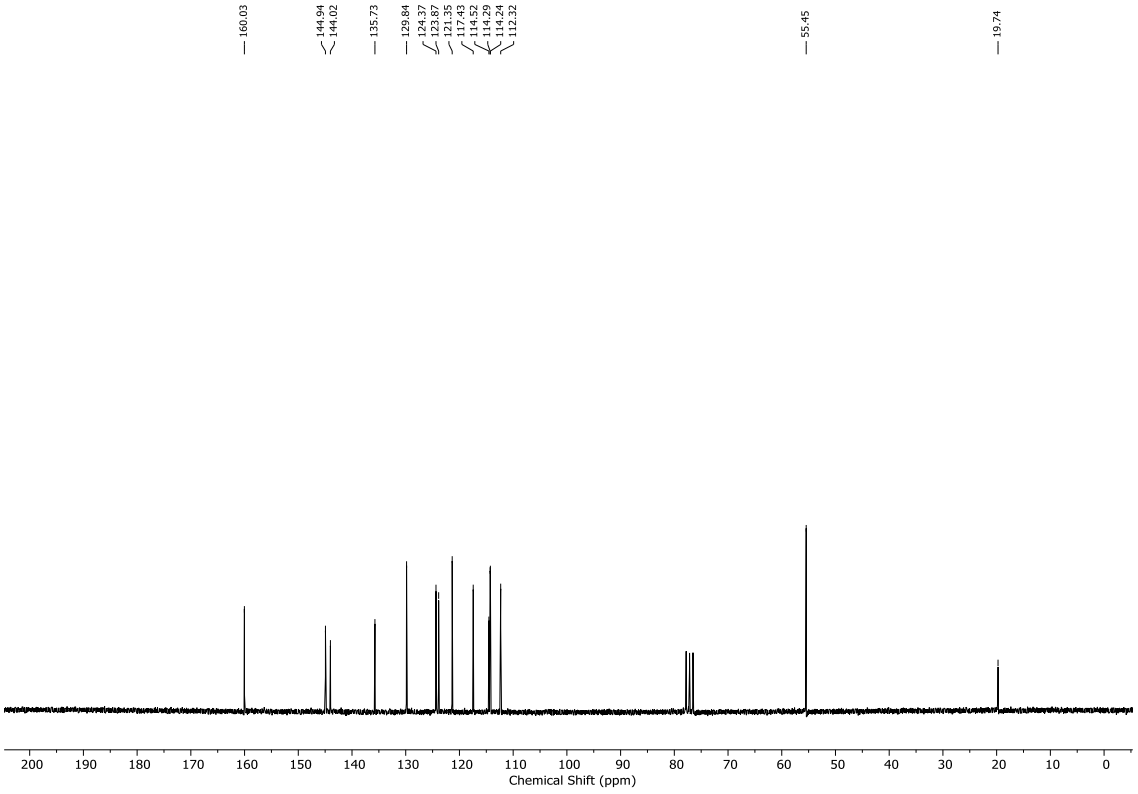
^{1}H NMR Spectra of **3e** in $CDCl_3$ at 200 MHz



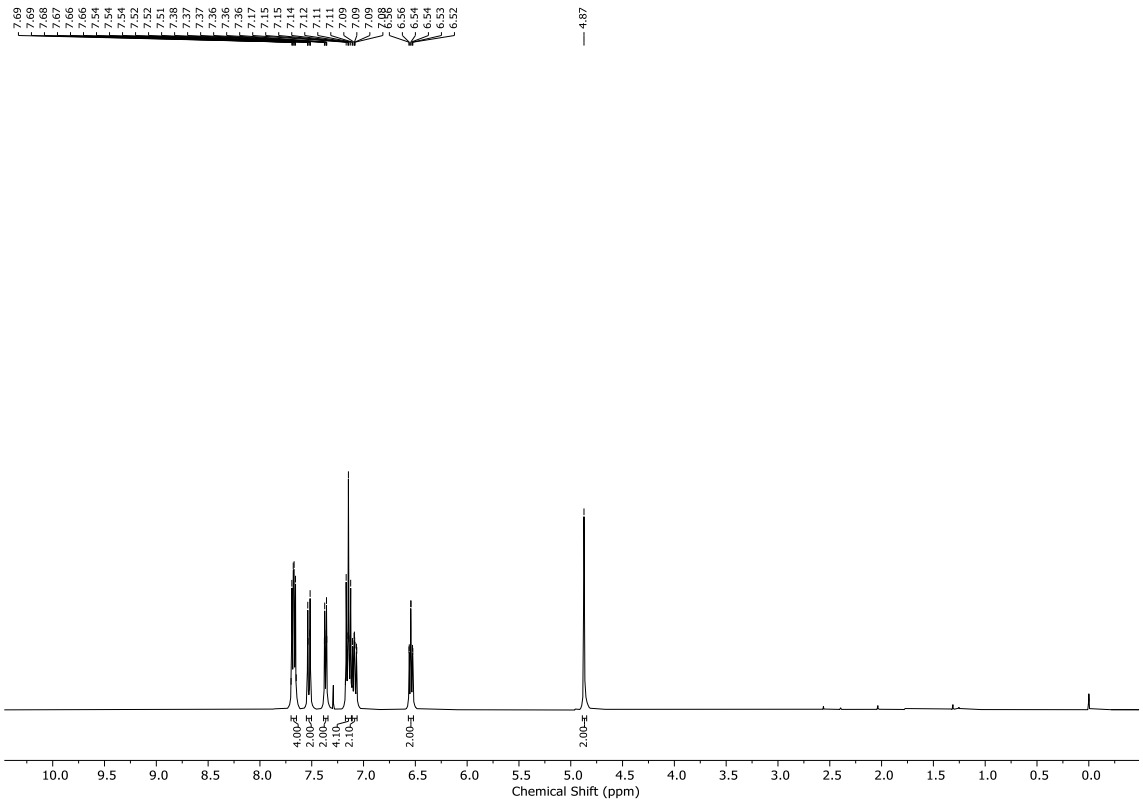
^{13}C NMR Spectra of **3e** in $CDCl_3$ at 50 MHz



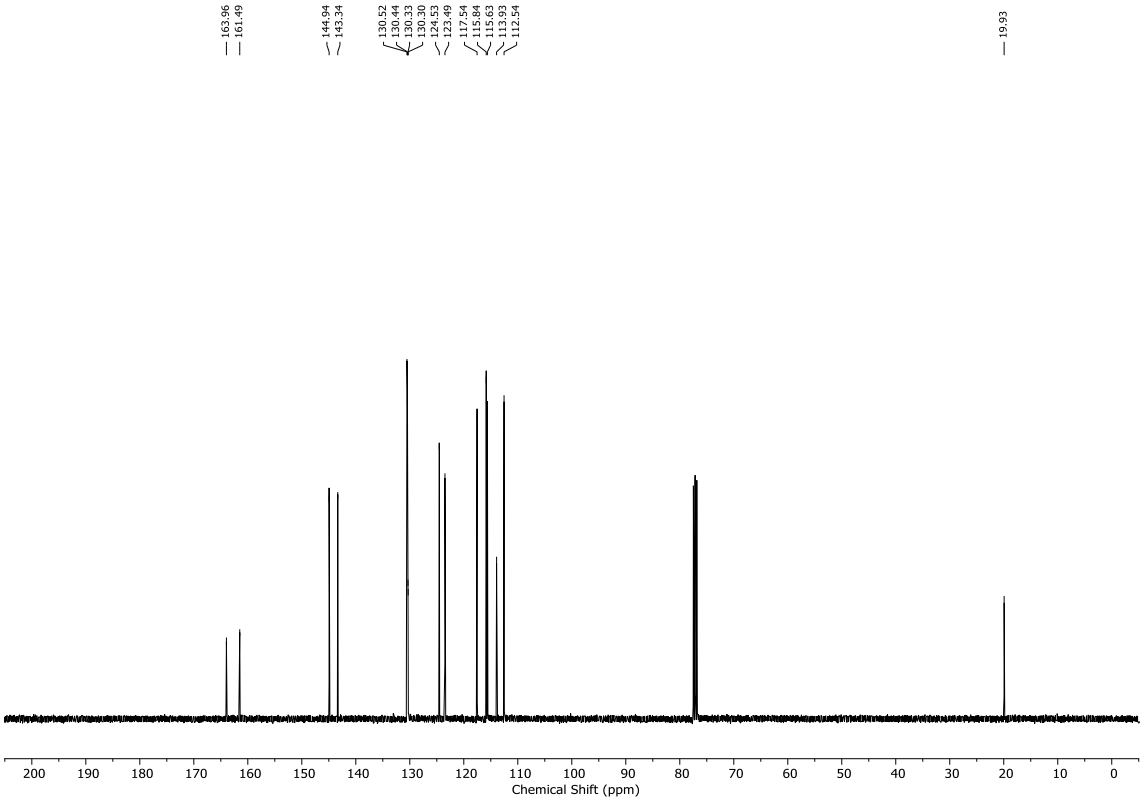
^{1}H NMR Spectra of **3f** in $CDCl_3$ at 200 MHz



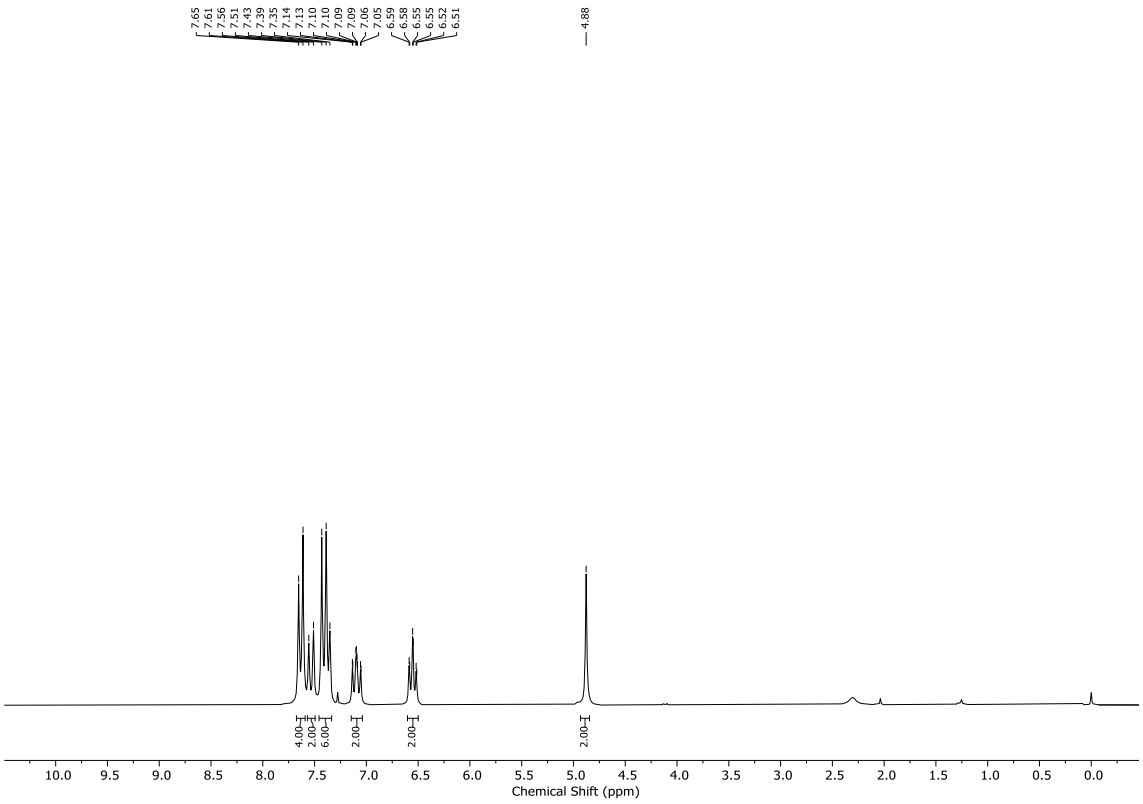
^{13}C NMR Spectra of **3f** in $CDCl_3$ at 50 MHz



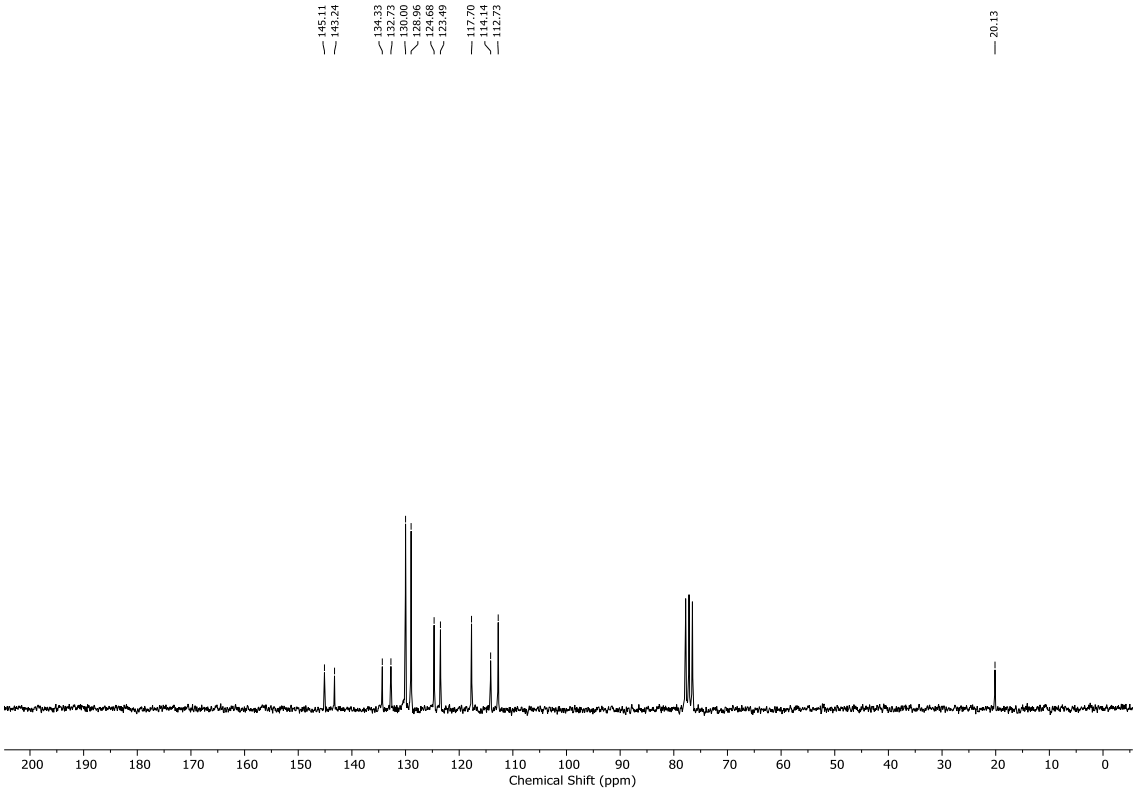
^{1}H NMR Spectra of **3g** in $CDCl_3$ at 400 MHz



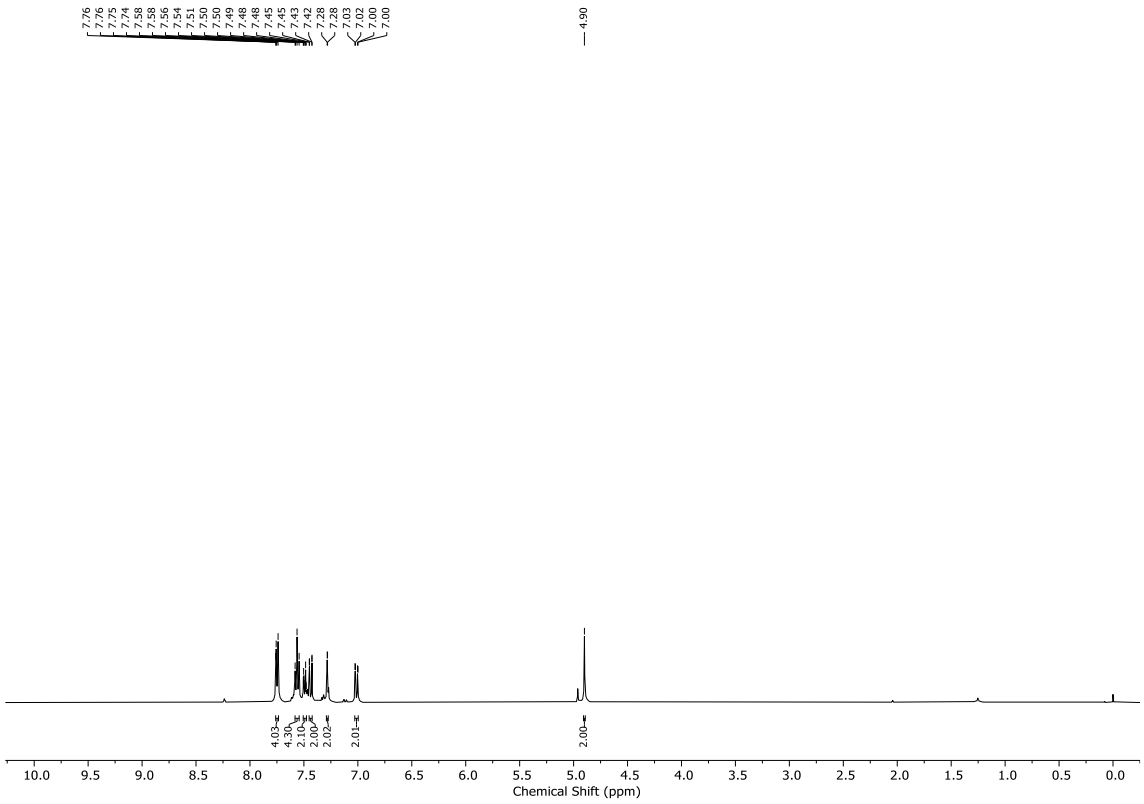
^{13}C NMR Spectra of **3g** in $CDCl_3$ at 100 MHz



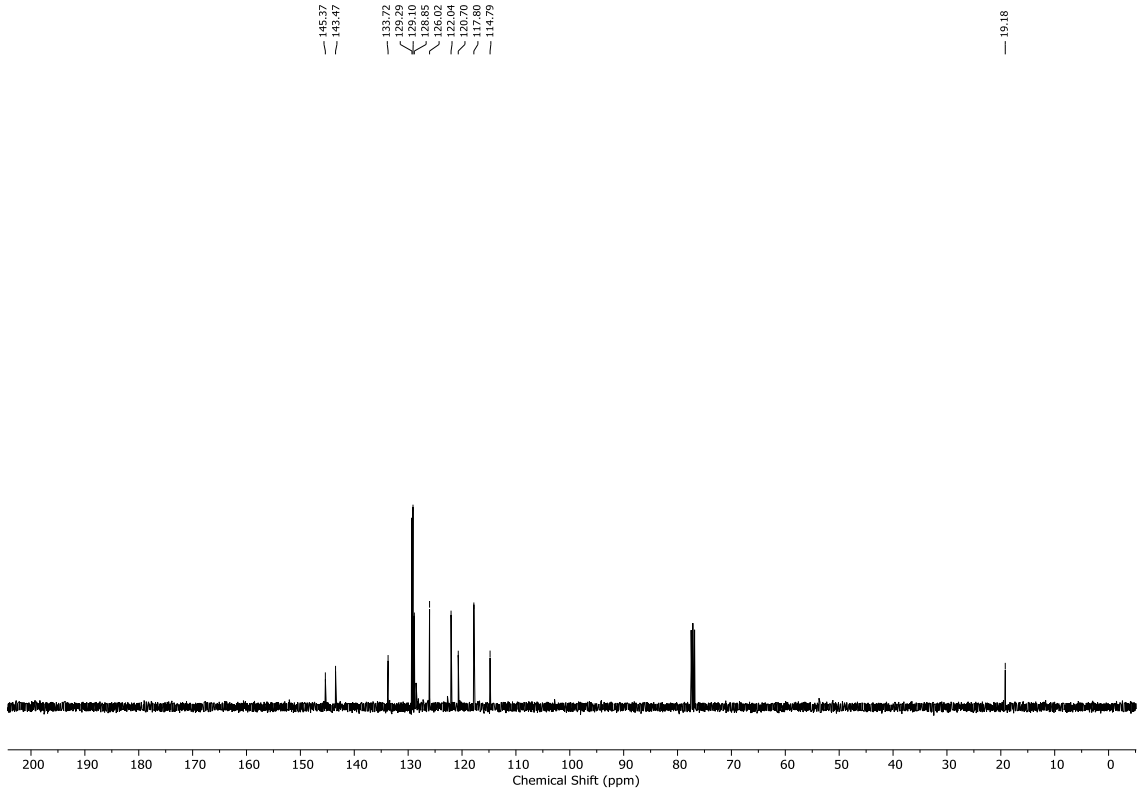
^{1}H NMR Spectra of **3h** in $CDCl_3$ at 200 MHz



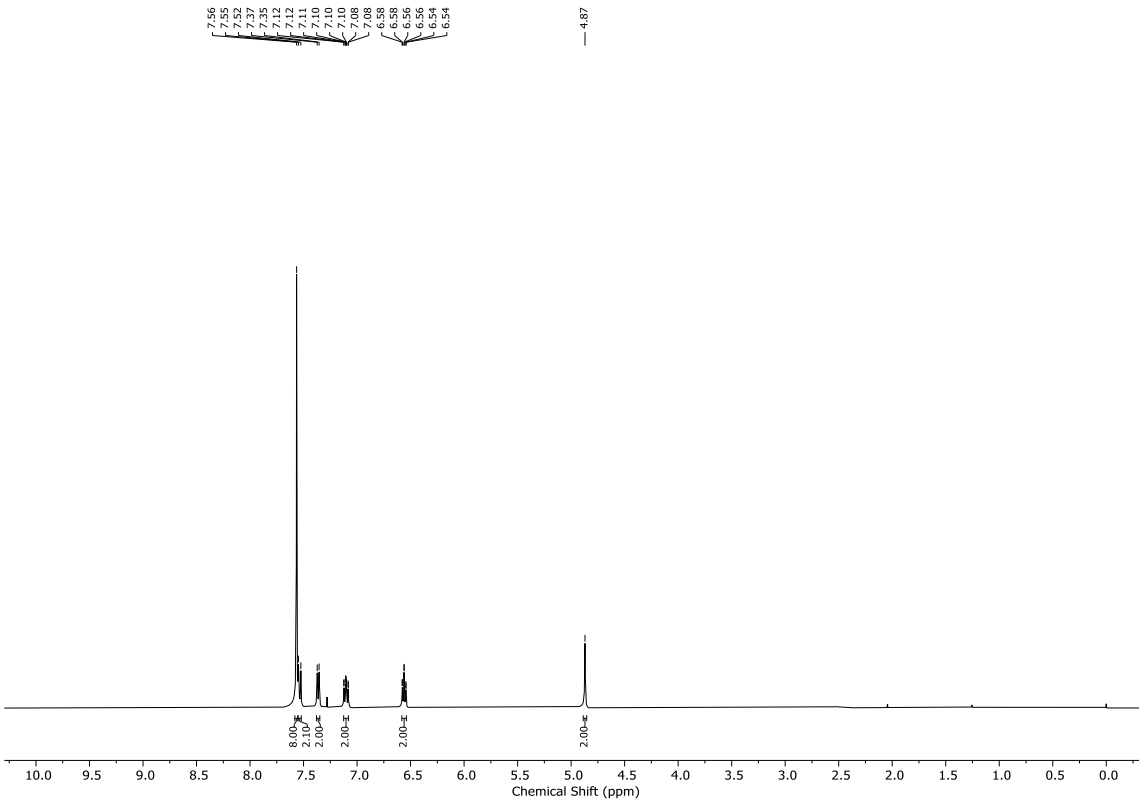
^{13}C NMR Spectra of **3h** in $CDCl_3$ at 50 MHz



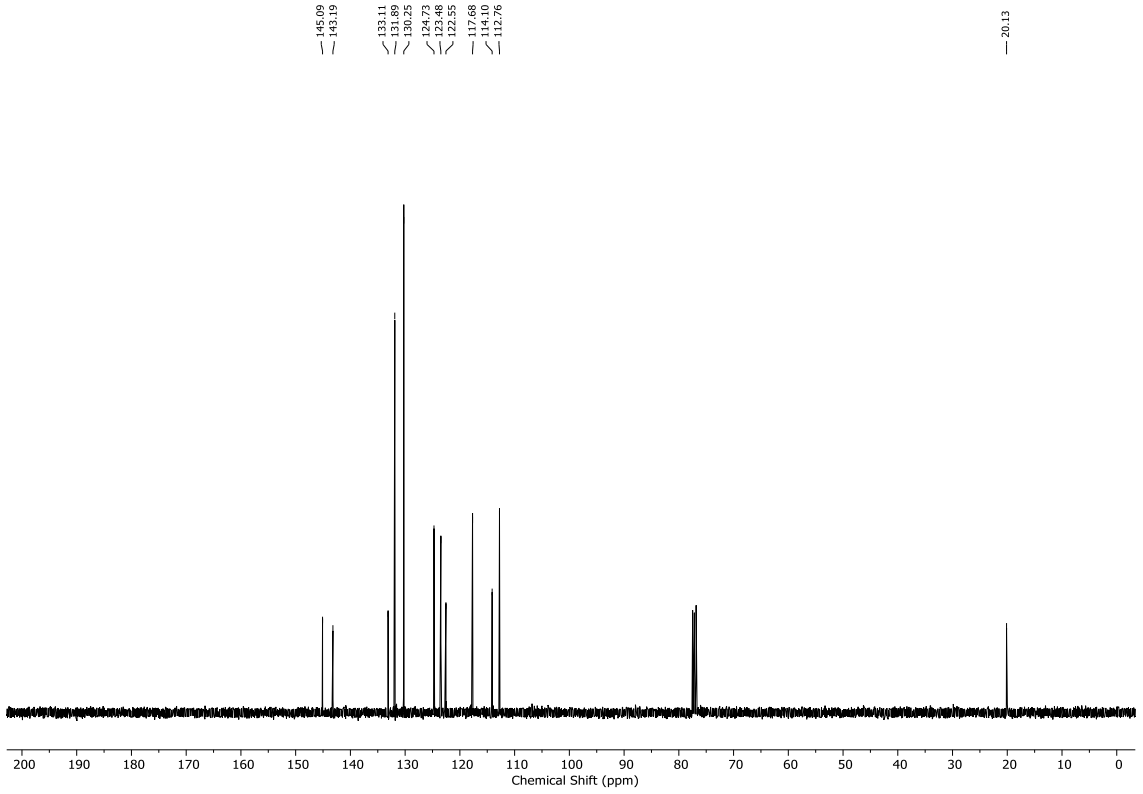
^{1}H NMR Spectra of **3i** in $CDCl_3$ at 400 MHz



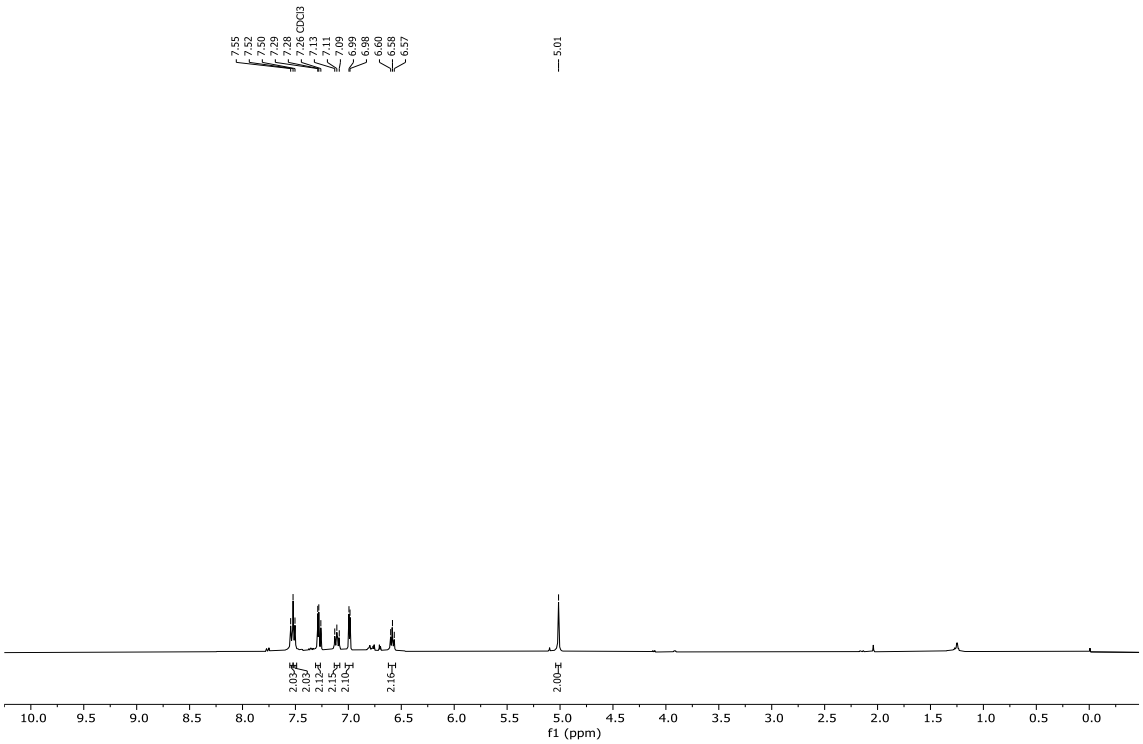
^{13}C NMR Spectra of **3i** in $CDCl_3$ at 100 MHz



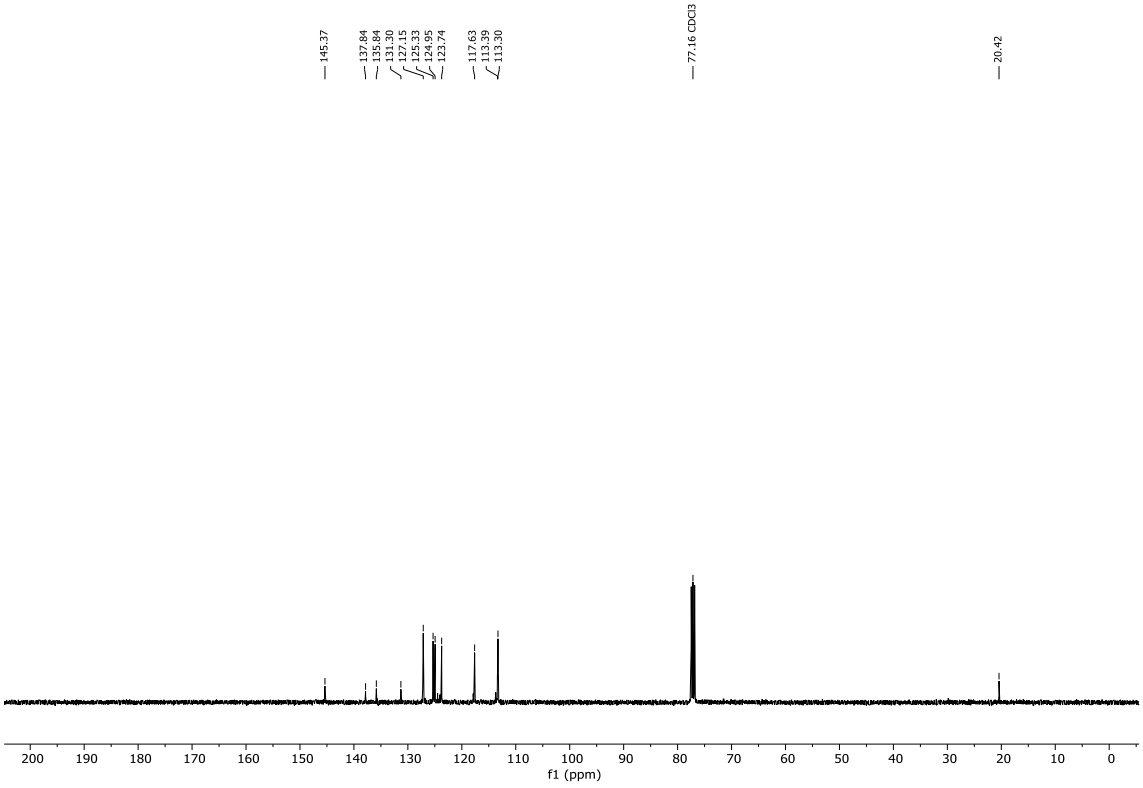
^{1}H NMR Spectra of **3j** in $CDCl_3$ at 400 MHz



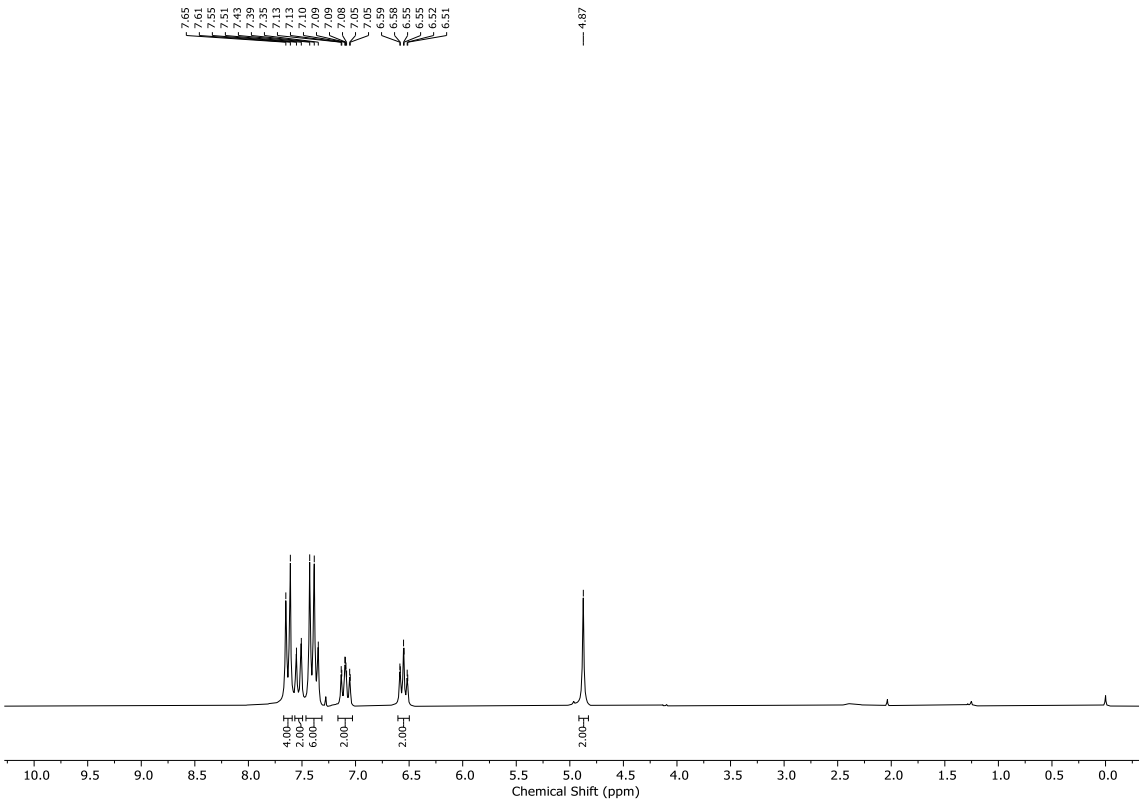
^{13}C NMR Spectra of **3j** in $CDCl_3$ at 100 MHz



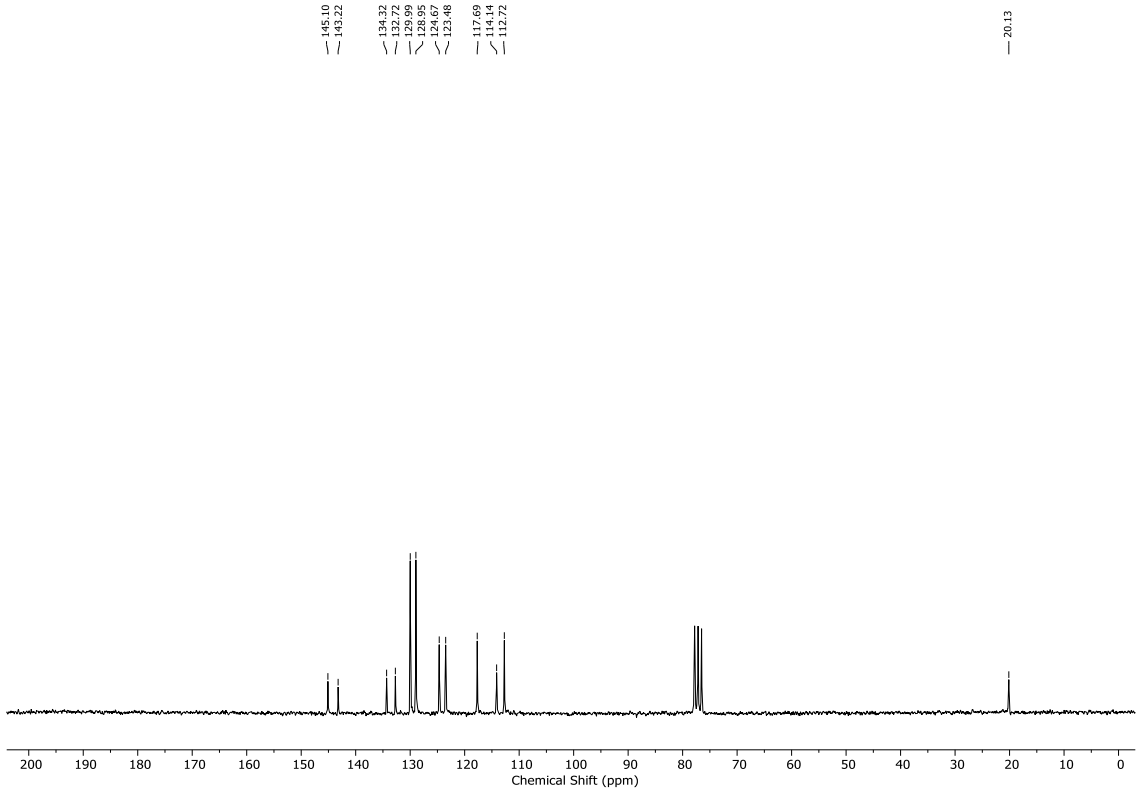
^{1}H NMR Spectra of **3k** in $CDCl_3$ at 400 MHz



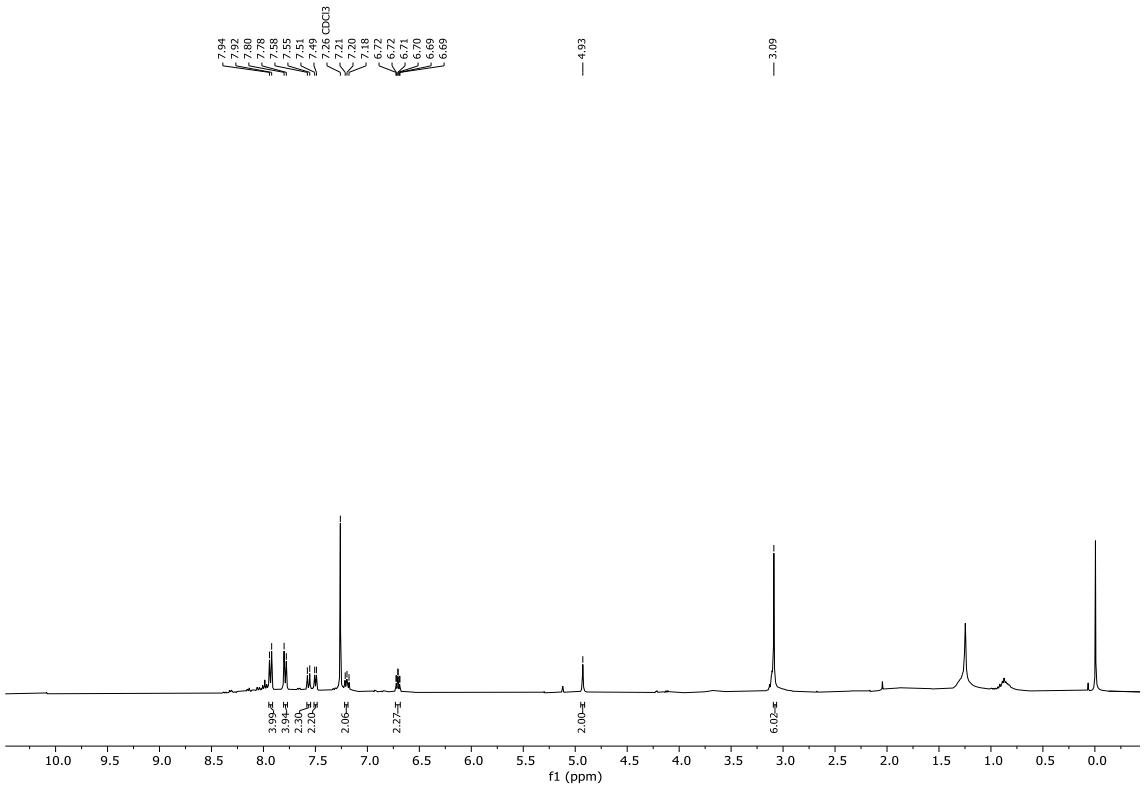
^{13}C NMR Spectra of **3k** in $CDCl_3$ at 100 MHz



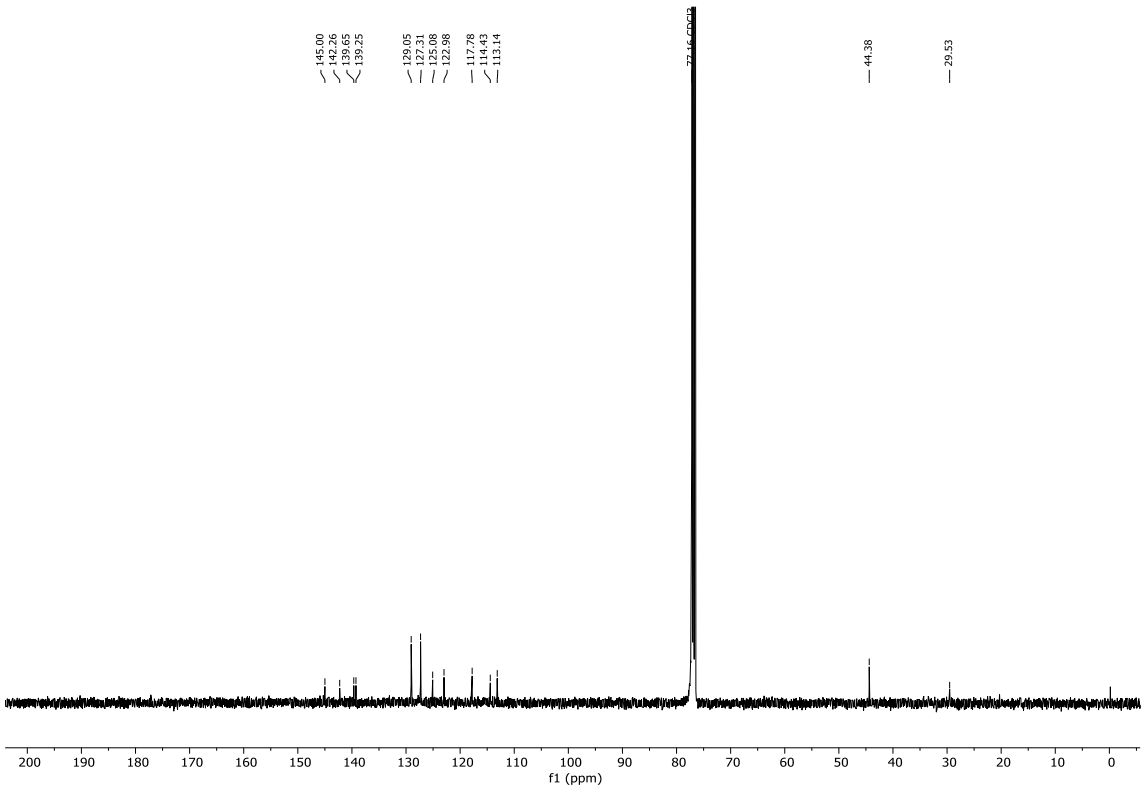
^{1}H NMR Spectra of **3l** in $CDCl_3$ at 200 MHz



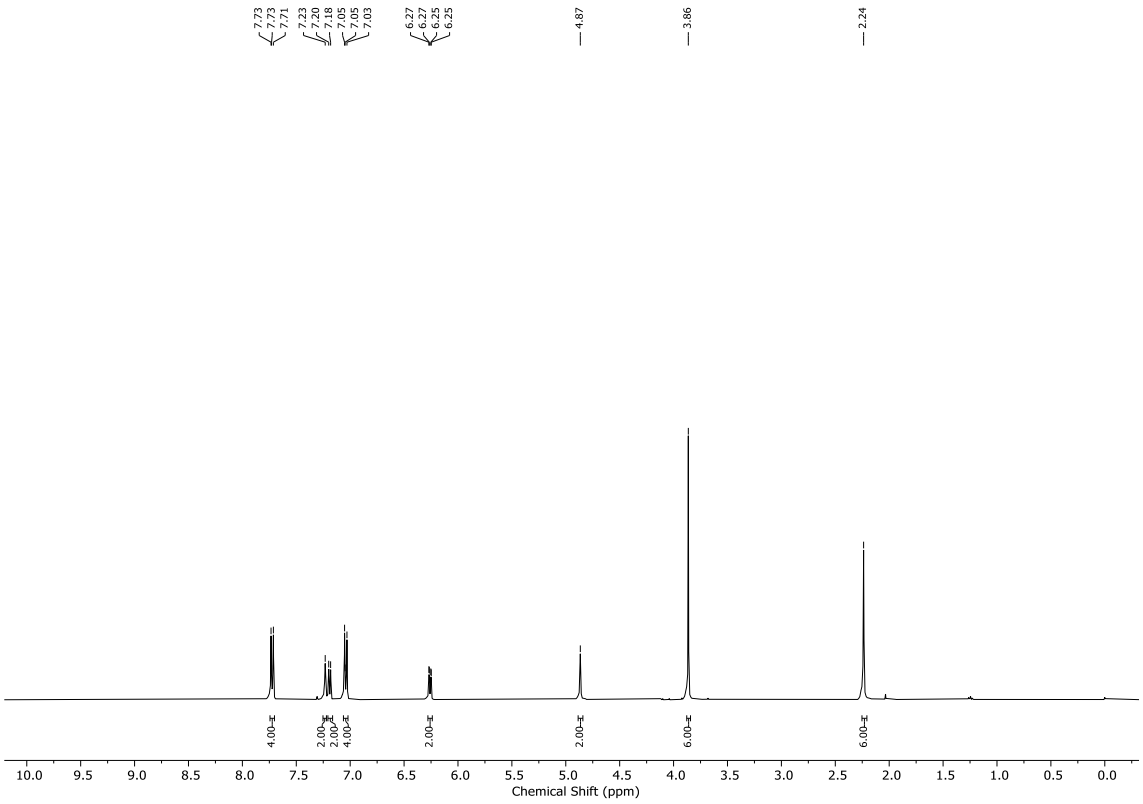
^{13}C NMR Spectra of **3l** in $CDCl_3$ at 50 MHz



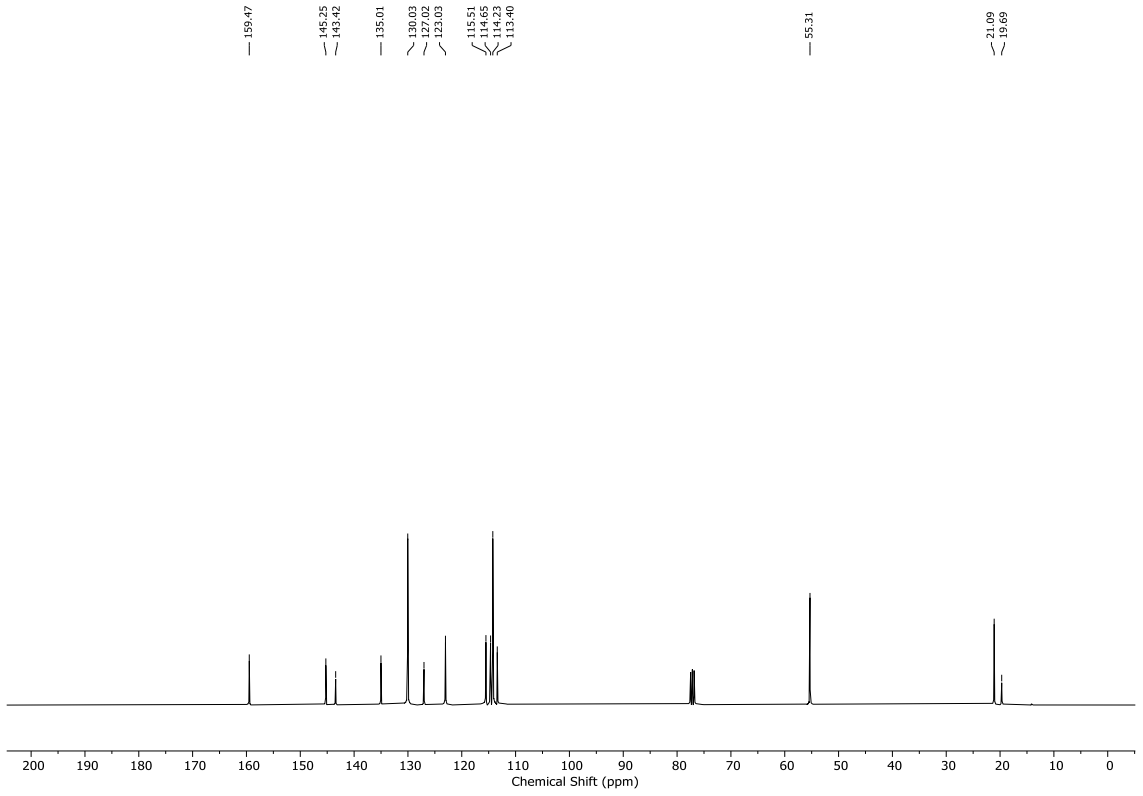
^{1}H NMR Spectra of **3m** in $CDCl_3$ at 400 MHz



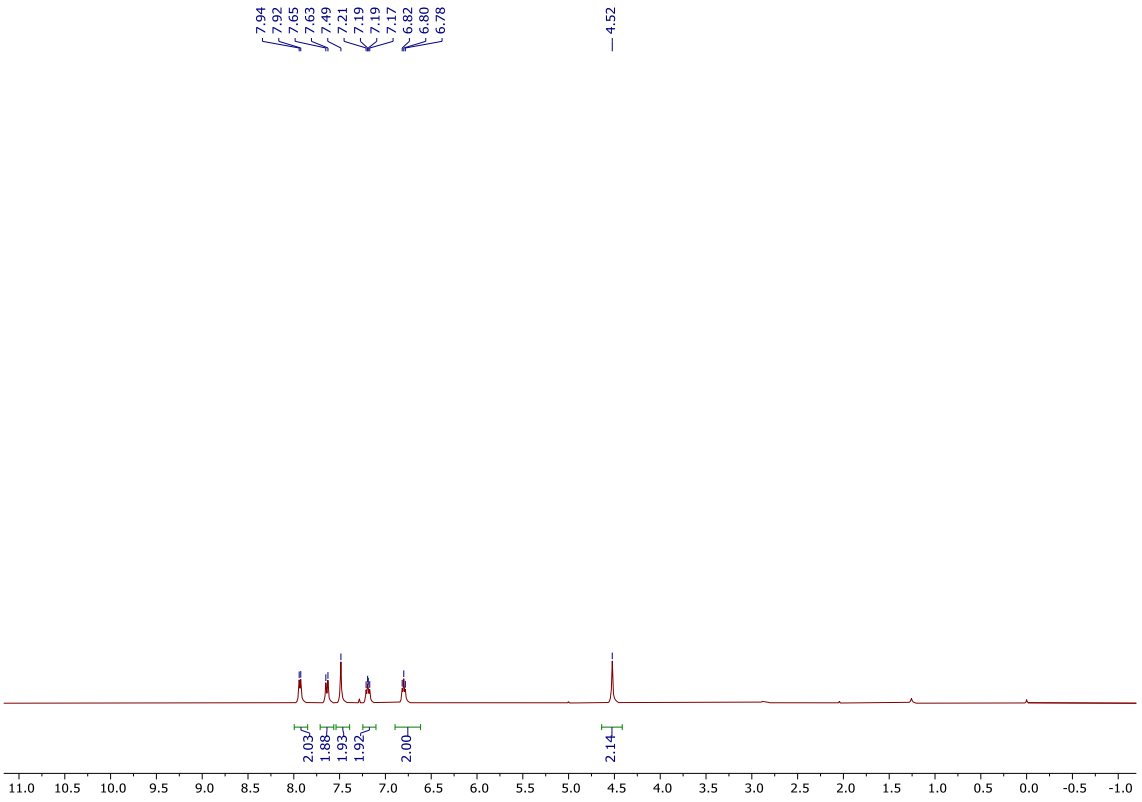
^{13}C NMR Spectra of **3m** in $CDCl_3$ at 100 MHz



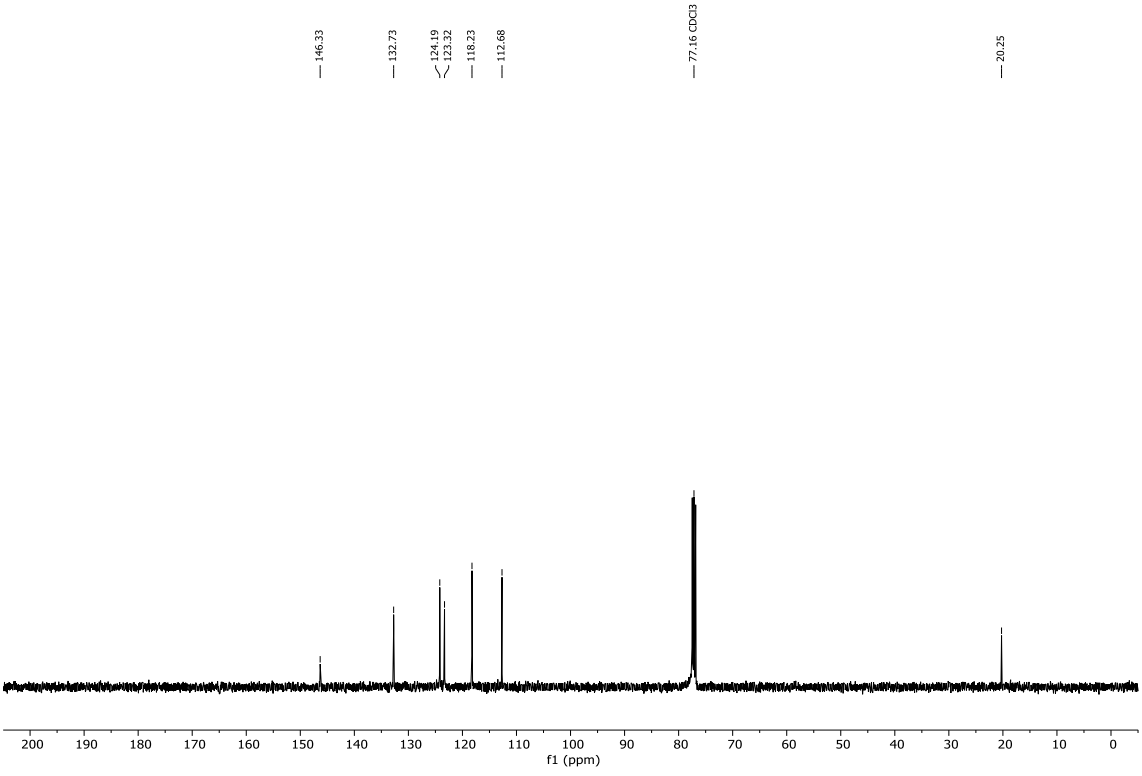
^{1}H NMR Spectra of **3n** in $CDCl_3$ at 400 MHz



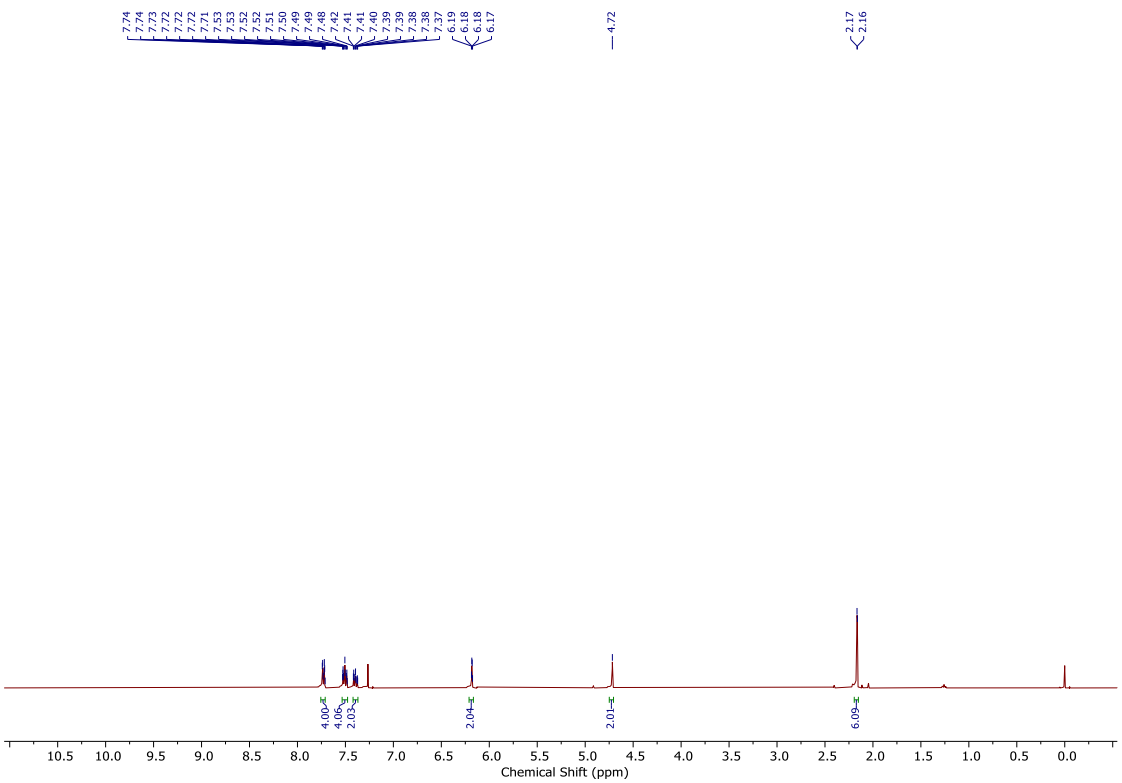
^{13}C NMR Spectra of **3n** in $CDCl_3$ at 100 MHz



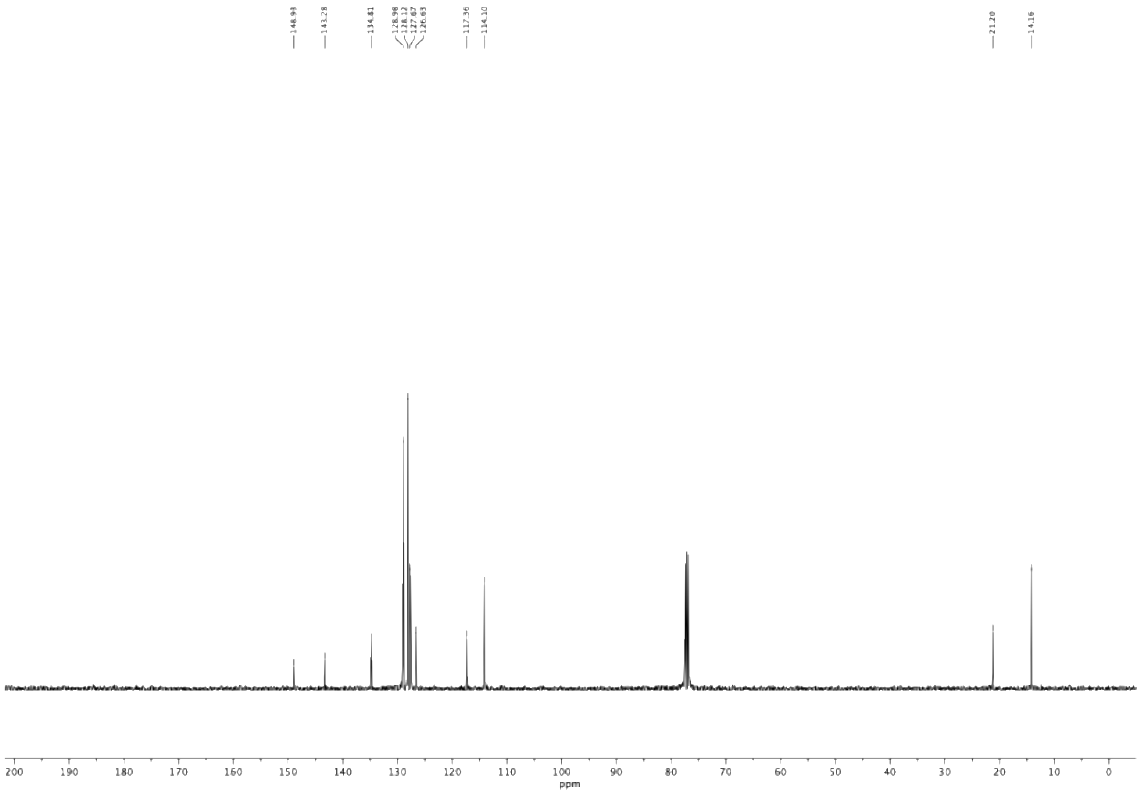
^{1}H NMR Spectra of **3o** in $CDCl_3$ at 400 MHz



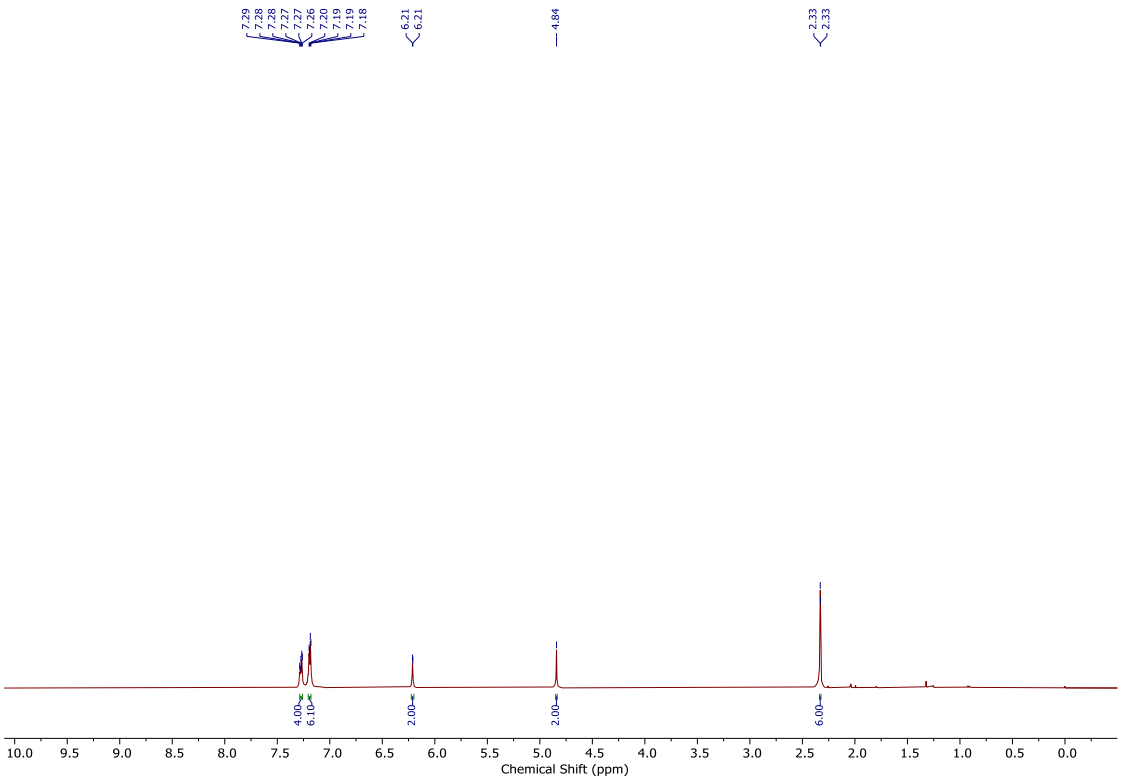
^{13}C NMR Spectra of **3o** in $CDCl_3$ at 100 MHz



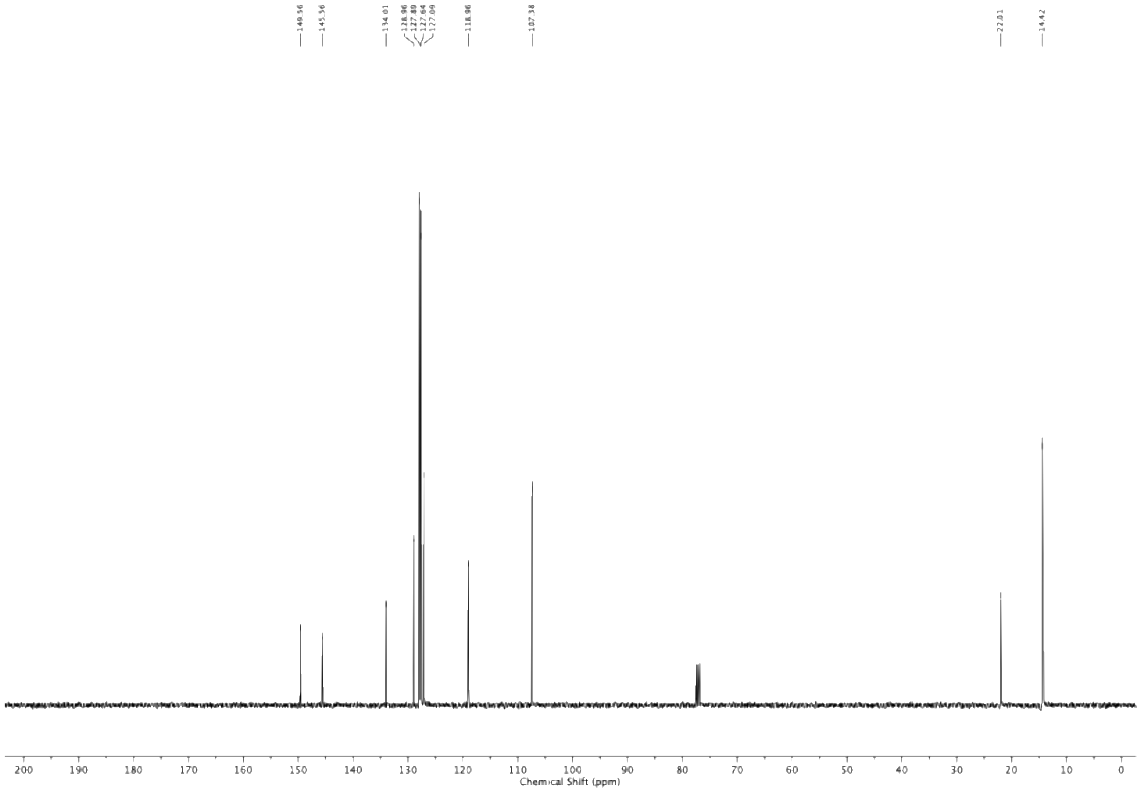
^{1}H NMR Spectra of **4a** in $CDCl_3$ at 400 MHz



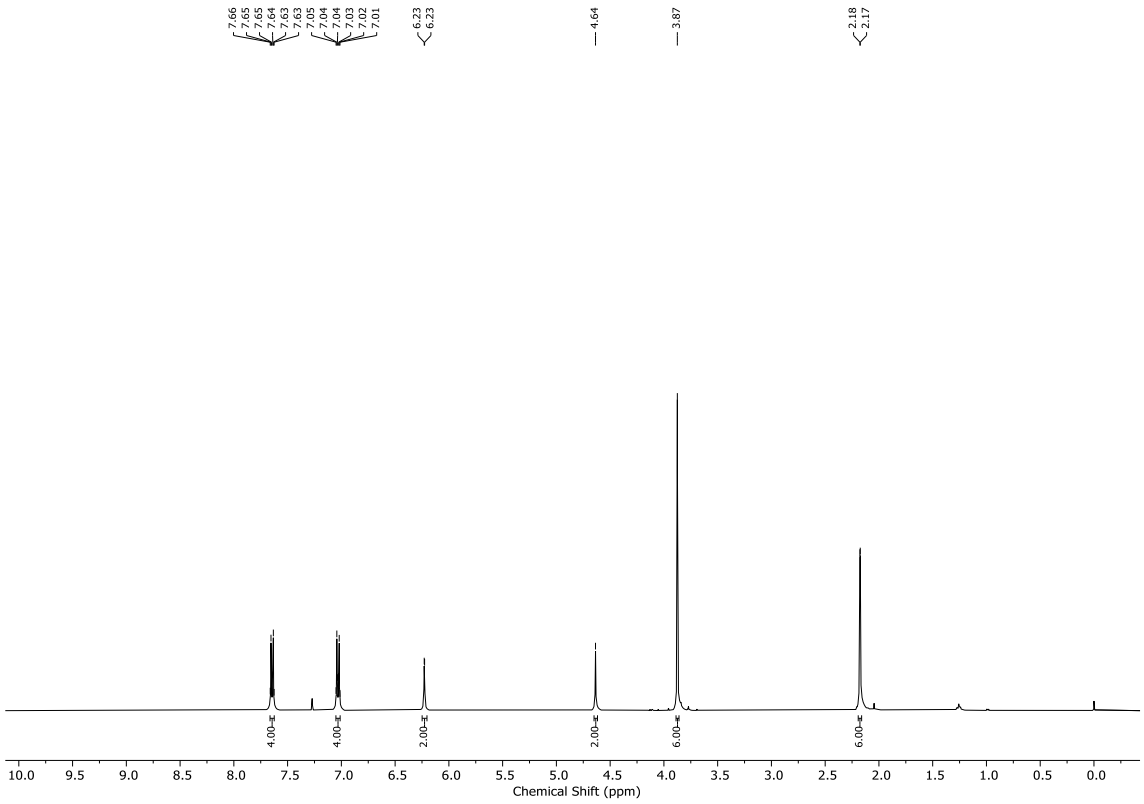
^{13}C NMR Spectra of **4a** in $CDCl_3$ at 100 MHz



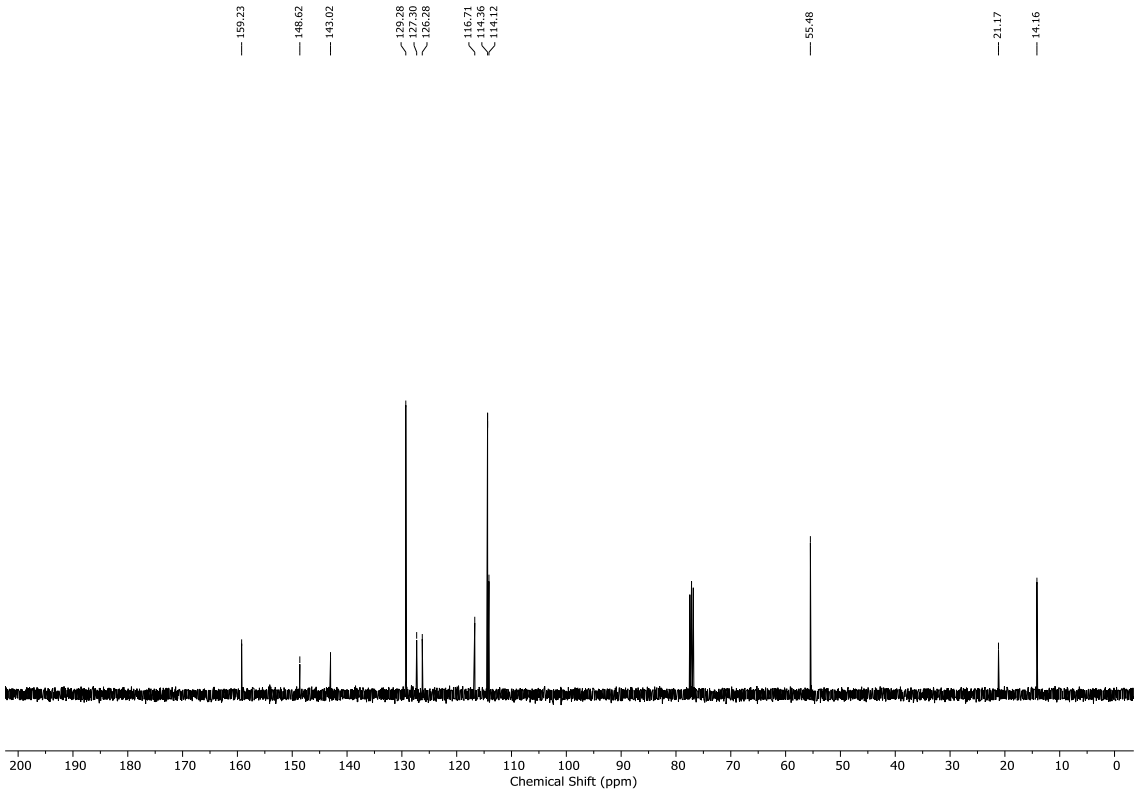
^{1}H NMR Spectra of **4b** in $CDCl_3$ at 400 MHz



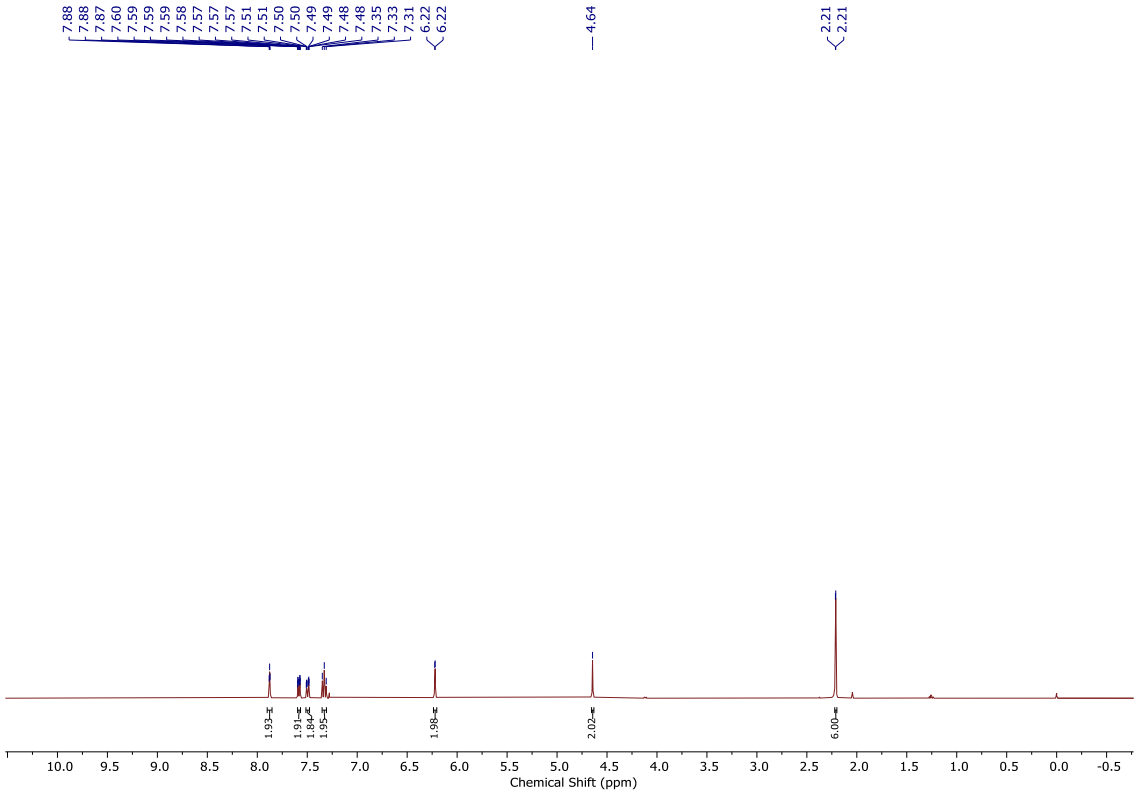
^{13}C NMR Spectra of **4b** in $CDCl_3$ at 100 MHz



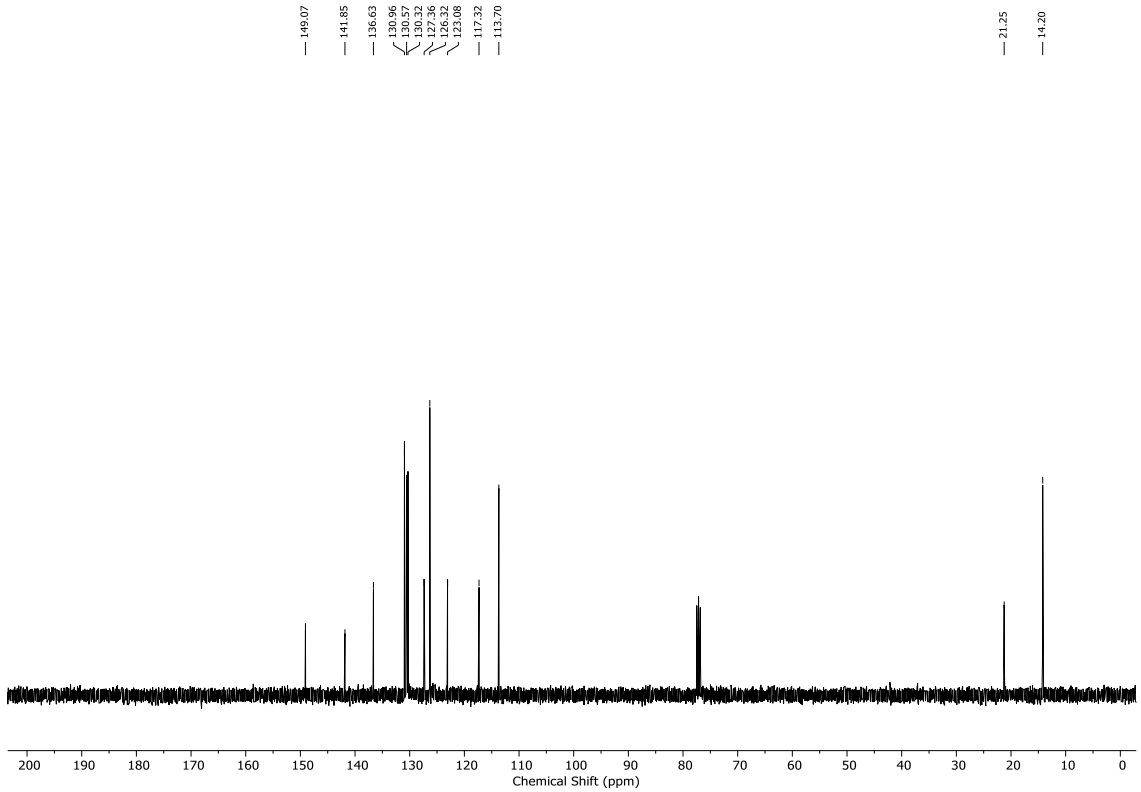
^{1}H NMR Spectra of **4c** in $CDCl_3$ at 400 MHz



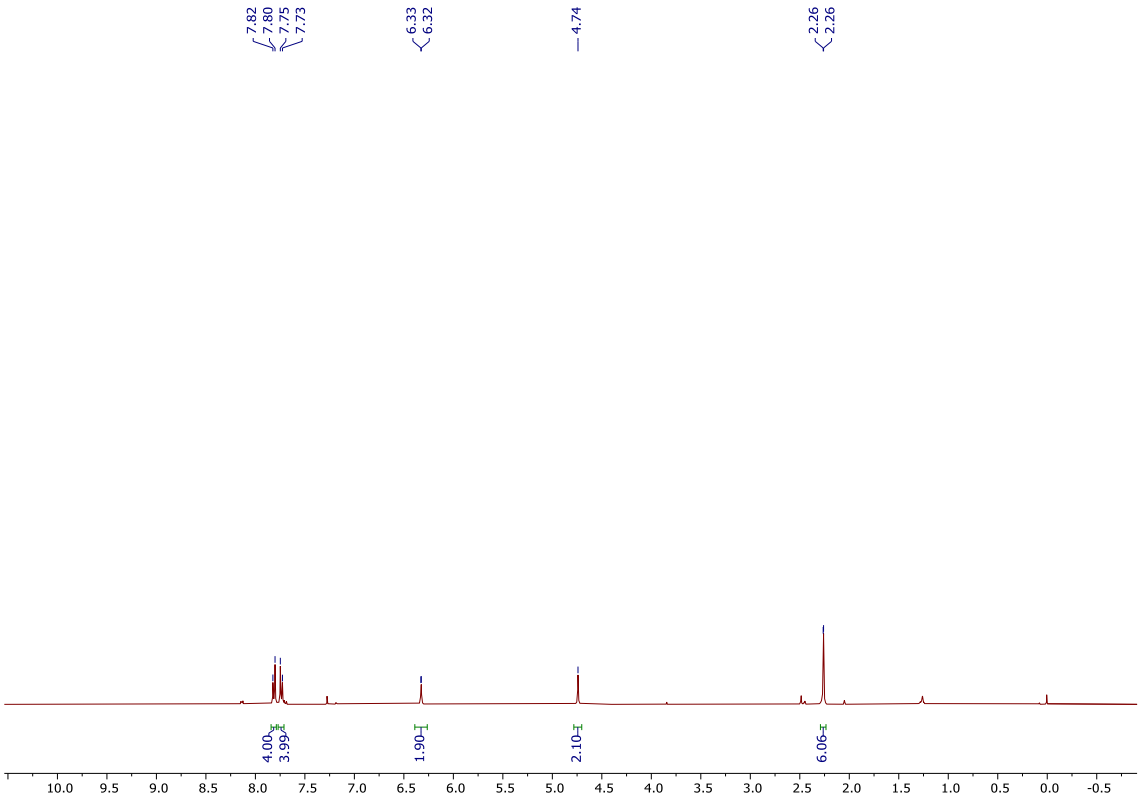
^{13}C NMR Spectra of **4c** in $CDCl_3$ at 100 MHz



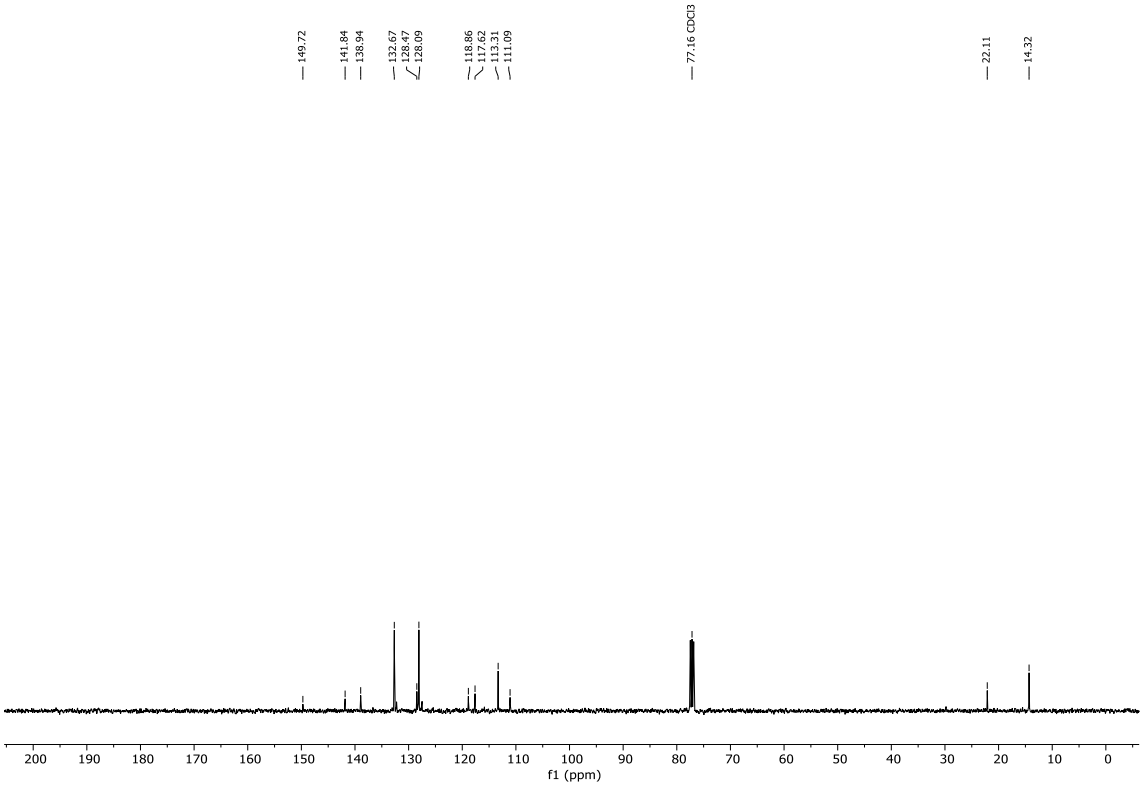
^{1}H NMR Spectra of **4d** in $CDCl_3$ at 400 MHz



^{13}C NMR Spectra of **4d** in $CDCl_3$ at 100 MHz



^{1}H NMR Spectra of **4e** in $CDCl_3$ at 400 MHz



^{13}C NMR Spectra of **4e** in $CDCl_3$ at 100 MHz