Supporting Information

Asymmetric Synthesis of 1-Deoxyazasugars from Chiral Aziridines

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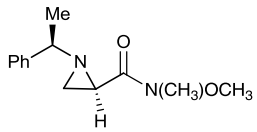
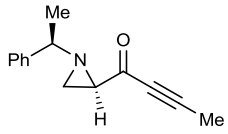
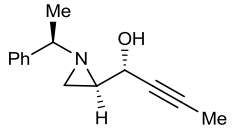
Spetral data for D-deoxyazasugars:



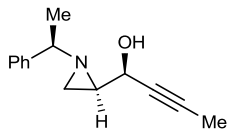
(*R*)-N-methoxy-N-methyl-1-[(*R*)-1-phenylethyl]aziridine-2-carboxamide (3'). mp = 55 °C; $[\alpha]_D^{20}$ = +87.69 (c = 0.472, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.46 – 7.24 (m, 5H), 3.82 (s, 3H), 3.26 (s, 3H), 2.69 (dd, *J* = 6.3, 3.2 Hz, 1H), 2.62 (q, *J* = 6.6 Hz, 1H), 2.18 (dd, *J* = 3.2, 1.2 Hz, 1H), 1.59 (dd, *J* = 6.4, 1.2 Hz, 1H), 1.49 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ 22.71, 31.91, 32.86, 35.13, 61.14, 69.21, 126.29, 126.49, 127.61, 143.17, 179.60; HRMS (ESI) calculated for $[C_{13}H_{18}N_2O_2+Na]^+$: 257.1266, Found 257.1262.



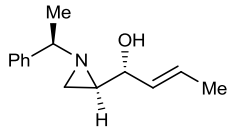
1-{(*R*)-1-[(*R*)-1-phenylethyl]aziridin-2-yl}but-2-yn-1-one (4'). $[\alpha]_D^{20}$ = +68.23 (c = 0.687, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.47 – 7.16 (m, 5H), 2.59 (q, *J* = 6.6 Hz, 1H), 2.39 (dd, *J* = 6.6, 3.0 Hz, 1H), 2.27 (dd, *J* = 3.0, 1.0 Hz, 1H), 2.05 (s, 3H), 1.71 (dd, *J* = 6.4, 1.0 Hz, 1H), 1.45 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ 4.46, 23.34, 35.54, 46.37, 69.82, 78.52, 92.29, 126.95, 127.42, 128.49, 143.68, 185.97; HRMS (ESI) calculated for $[C_{14}H_{15}NO+Na]^+$: 236.1052, Found 236.1053.



(*R*)-1-{(*R*)-1-[(*R*)-1-phenylethyl]aziridin-2-yl}but-2-yn-1-ol (5a'). $[\alpha]_D^{20}$ = +37.58 (c = 1.011, $CHCl_3$); ^1H NMR (200 MHz; $CDCl_3$) δ 7.42 – 7.22 (m, 5H), 4.24 – 4.10 (m, 1H), 2.88 (d, *J* = 6.7 Hz, 1H), 2.60 (q, *J* = 6.6 Hz, 1H), 1.95 (ddd, *J* = 7.2, 6.4, 3.4 Hz, 1H), 1.89 (d, *J* = 2.2 Hz, 3H), 1.77 (d, *J* = 3.5 Hz, 1H), 1.48 (d, *J* = 6.6 Hz, 3H), 1.38 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (50 MHz; $CDCl_3$) δ 3.32, 23.03, 30.41, 45.04, 62.00, 69.89, 78.68, 80.91, 126.60, 126.87, 128.13, 143.68; HRMS (ESI) calculated for $[C_{14}H_{17}NO+H]^+$: 216.1388, Found 216.1386.

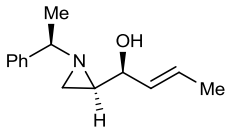


(*S*)-1-{(*R*)-1-[(*R*)-1-phenylethyl]aziridin-2-yl}but-2-yn-1-ol (5b'). $[\alpha]_D^{20}$ = +115.26 (c = 0.144, $CHCl_3$); ^1H NMR (200 MHz; $CDCl_3$) δ 7.40 – 7.22 (m, 5H), 4.54 – 4.44 (m, 1H), 2.95 (d, *J* = 3.2 Hz, 1H), 2.62 (q, *J* = 6.6 Hz, 1H), 1.96 (td, *J* = 7.8, 3.5 Hz, 1H), 1.89 (d, *J* = 3.5 Hz, 1H), 1.87 (d, *J* = 2.2 Hz, 3H), 1.44 (d, *J* = 6.6 Hz, 3H), 1.39 (d, *J* = 6.2 Hz, 1H); ^{13}C NMR (50 MHz; $CDCl_3$) δ 3.22, 22.79, 30.82, 44.35, 61.72, 68.91, 78.56, 81.14, 126.50, 126.79, 128.02, 143.51; HRMS (ESI) calculated for $[C_{14}H_{17}NO+H]^+$: 216.1388, Found 216.1383.

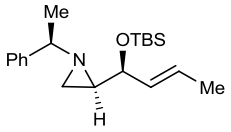


(*R*,*E*)-1-{(*R*)-1-[(*R*)-1-phenylethyl]aziridin-2-yl}but-2-en-1-ol (6a'). $[\alpha]_D^{20}$ = +50.74 (c = 0.335, $CHCl_3$); ^1H NMR (200 MHz; $CDCl_3$) δ 7.39 – 7.21 (m, 5H), 5.79 (dq, *J* = 15.4, 6.5 Hz, 1H), 5.61 (ddq, *J* = 15.3, 7.6, 1.4 Hz, 1H), 3.83 (q, *J* = 5.3 Hz, 1H), 2.69 (d, *J* = 5.8 Hz, 1H), 2.54 (q, *J* = 6.6 Hz, 1H), 1.74 (d, *J* = 6.6 Hz, 3H), 1.73 – 1.67 (m, 2H), 1.43 (d, *J* = 6.6 Hz, 3H), 1.36 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (50 MHz; $CDCl_3$) δ 17.57, 23.11, 30.75, 44.93, 69.00, 72.25, 126.57,

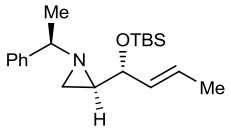
126.62, 126.80, 128.10, 131.31, 143.90; HRMS (ESI) calculated for $[C_{14}H_{19}NO+Na]^+$: 240.1365, Found 240.1364.



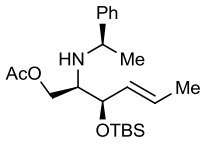
(*S*,*E*)-1-{(*R*)-1-[(*R*)-1-phenylethyl]aziridin-2-yl}but-2-en-1-ol (6b'). $[\alpha]_D^{20}$ = +130.90 (c = 1.009, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.40 – 7.19 (m, 5H), 5.82 (dq, *J* = 15.3, 6.4 Hz, 1H), 5.45 (ddq, *J* = 15.3, 7.2, 1.6 Hz, 1H), 4.25 (dd, *J* = 7.1, 2.3 Hz, 1H), 2.88 (bs, 1H), 2.63 (q, *J* = 6.5 Hz, 1H), 1.77 (dd, *J* = 7.1, 2.6 Hz, 1H), 1.73 (d, *J* = 6.6 Hz, 3H), 1.71 (d, *J* = 6.4 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 3H), 1.29 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR (50 MHz; $CDCl_3$) δ 17.74, 22.29, 29.31, 43.30, 68.73, 70.16, 126.64, 126.99, 128.02, 128.25, 130.92, 144.15; HRMS (ESI) calculated for $[C_{14}H_{19}NO+Na]^+$: 240.1364, Found 240.1362.



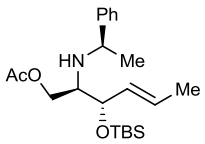
(*R*)-2-[(*R*,*E*)-1-(*t*-butyldimethylsilyloxy)but-2-enyl]-1-[(*R*)-1-phenylethyl)]aziridine (7a'). $[\alpha]_D^{20}$ = +78.46 (c = 1.231, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.40 – 7.21 (m, 5H), 5.73 – 5.42 (m, 2H), 3.63 (t, *J* = 6.4 Hz, 1H), 2.38 (q, *J* = 6.6 Hz, 1H), 1.71 (d, *J* = 9.4 Hz, 1H), 1.69 (d, *J* = 6.2 Hz, 3H), 1.61 (ddd, *J* = 10.5, 7.5, 3.5 Hz, 1H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.24 (d, *J* = 6.6 Hz, 1H), 0.94 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ –4.23, –4.17, 17.83, 18.50, 23.85, 26.11, 31.02, 45.75, 70.07, 76.77, 125.56, 125.98, 127.01, 128.38, 131.94, 145.10; HRMS (ESI) calculated for $[C_{20}H_{33}NOSi+Na]^+$: 354.2229, Found 354.2231.



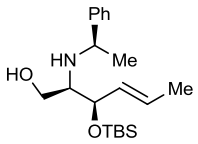
(*R*)-2-[(*S*,*E*)-1-(*t*-butyldimethylsilyloxy)but-2-enyl]-1-[(*R*)-1-phenylethyl)aziridine] (7b'). $[\alpha]_D^{20}$ = +17.41 (c = 0.54, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.38 – 7.21 (m, 5H), 5.73 – 5.66 (m, 2H), 3.73 (t, *J* = 6.4 Hz, 1H), 2.43 (q, *J* = 6.6 Hz, 1H), 1.73 (d, *J* = 5.7 Hz, 3H), 1.63 (d, *J* = 3.4 Hz, 1H), 1.56 (dd, *J* = 6.6, 3.4 Hz, 1H), 1.38 (d, *J* = 6.6 Hz, 3H), 1.31 (d, *J* = 6.1 Hz, 1H), 0.90 (s, 9H), 0.04 (s, 3H), –0.03 (s, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ –4.45, 17.65, 18.27, 23.45, 25.95, 32.19, 45.42, 69.73, 75.03, 125.30, 126.76, 126.85, 128.22, 132.61, 144.78; HRMS (ESI) calculated for $[C_{20}H_{33}NOSi+Na]^+$: 354.2229, Found 354.2233.



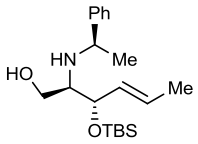
(2*R*,3*R*,*E*)-3-(*t*-butyldimethylsilyloxy)-2-[(*R*)-1-phenylethylamino]hex-4-enyl acetate (8a'). $[\alpha]_D^{20}$= +39.03 (c = 0.661, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.28 – 7.13 (m, 5H), 5.59 (dq, *J* = 15.4, 6.5 Hz, 1H), 5.43 (ddq, *J* = 15.2, 7.6, 1.6 Hz, 1H), 4.14 (t, *J* = 5.7 Hz, 1H), 3.91 (d, *J* = 5.7 Hz, 1H), 3.85 (d, *J* = 6.2 Hz, 1H), 3.76 (dd, *J* = 10.9, 6.4 Hz, 1H), 2.58 (ddd, *J* = 10.6, 6.3, 4.2 Hz, 1H), 1.90 (s, 3H), 1.67 (bs, 1H), 1.65 (d, *J* = 5.9 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H) , 0.81 (s, 9H), –0.07 (s, 3H), –0.09 (s, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ –4.95, –4.12, 17.82, 18.19, 21.04, 25.02, 25.95, 56.86, 59.08, 64.83, 72.94, 126.84, 126.90, 126.95, 128.36, 131.57, 146.12, 170.92; HRMS (ESI) calculated for $[C_{22}H_{37}NO_3Si+H]^+$: 392.2621, Found 392.2625.



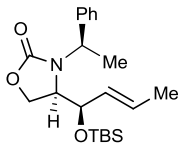
(2*R*,3*S*,*E*)-3-(*t*-butyldimethylsilyloxy)-2-[(*R*)-1-phenylethylamino]hex-4-enyl acetate (8b'). $[\alpha]_D^{20}$ = +34.48 (c = 0.872, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.40 – 7.19 (m, 5H), 5.59 (dq, *J* = 15.4, 6.5 Hz, 1H), 5.43 (ddq, *J* = 15.2, 7.6, 1.6 Hz, 1H), 4.25 (t, *J* = 5.7 Hz, 1H), 4.03 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.93 (dd, *J* = 6.6, 2.6 Hz, 1H), 3.87 (d, *J* = 7.1 Hz, 1H), 2.60 (td, *J* = 8.8, 4.2 Hz, 1H), 1.99 (s, 3H), 1.67 (d, *J* = 6.1 Hz, 3H), 1.61 (bs, 1H), 1.31 (d, *J* = 6.6, 3H), 0.90 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ –5.19, –4.31, 17.44, 17.90, 20.61, 24.85, 25.66, 55.94, 59.34, 64.18, 72.96, 126.57, 126.79, 126.85, 128.01, 131.41, 145.79, 170.29; HRMS (ESI) calculated for $[C_{22}H_{37}NO_3Si+H]^+$: 392.2621, Found 392.2615.



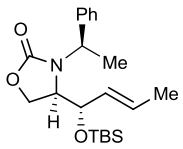
(2*R*,3*R*,*E*)-3-(*t*-butyldimethylsilyloxy)-2-[(*R*)-1-phenylethylamino]hex-4-en-1-ol (9a'). $[\alpha]_D^{20}$ = +61.81 (c = 0.11, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.35 – 7.21 (m, 5H), 5.66 (dq, *J* = 15.6, 6.3 Hz, 1H), 5.43 (ddq, *J* = 15.3, 7.2, 1.3 Hz, 1H), 4.13 (t, *J* = 6.6 Hz, 1H), 3.89 (q, *J* = 6.6 Hz, 1H), 3.28 (ddd, *J* = 18.7, 13.4, 5.3 Hz, 1H), 3.27 (dd, *J* = 5.2, 2.8 Hz, 1H), 2.55 (q, *J* = 5.4 Hz, 1H), 1.72 (d, *J* = 6.4 Hz, 3H), 1.34 (d, *J* = 6.6 Hz, 3H) , 0.89 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ –4.88, –4.00, 17.80, 18.14, 24.79, 25.93, 56.78, 60.97, 61.51, 73.91, 126.72, 127.14, 127.94, 128.57, 131.65, 145.93; HRMS (ESI) calculated for $[C_{20}H_{35}NO_2Si+H]^+$: 350.2515, Found 350.2513.



(2*R*,3*S*,*E*)-3-(*t*-butyldimethylsilyloxy)-2-[(*R*)-1-phenylethylamino]hex-4-en-1-ol (9b'). $[\alpha]_D^{20}$ = –65.52 (c = 1.172, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.36 – 7.20 (m, 5H), 5.57 (dq, *J* = 15.4, 6.5 Hz, 1H), 5.36 (ddq, *J* = 15.4, 6.8, 1.4 Hz, 1H), 4.31 (dd, *J* = 6.8, 3.9 Hz, 1H), 3.96 (q, *J* = 6.5 Hz, 1H), 3.49 (dd, *J* = 10.6, 6.6 Hz, 1H), 3.40 (dd, *J* = 10.7, 4.6 Hz, 1H), 2.39 (td, *J* = 8.4, 4.2 Hz, 1H), 1.67 (d, *J* = 6.2 Hz, 3H), 1.34 (d, *J* = 6.5 Hz, 3H) , 0.90 (s, 9H), 0.10 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ –5.01, –4.03, 17.60, 18.07, 24.94, 25.86, 55.27, 60.58, 60.69, 73.26, 126.81, 127.06, 127.15, 128.48, 131.74, 145.43; HRMS (ESI) calculated for $[C_{20}H_{35}NO_2Si + H]^+$: 350.2515, Found 350.2518.

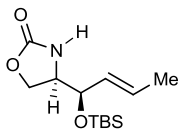


(*R*)-4-[(*R*,*E*)-1-(*t*-butyldimethylsilyloxy)but-2-enyl]-3-[(*R*)-1-phenylethyl]oxazolidin-2-one (10a'). $[\alpha]_D^{20}$ = +103.63 (c = 0.482, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.49 – 7.26 (m, 5H), 5.32 – 5.02 (m, 3H), 4.27 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.10 (t, *J* = 8.8 Hz, 1H), 3.75 (td, *J* = 8.1, 3.8 Hz, 1H), 3.55 (t, *J* = 4.9 Hz, 1H), 1.69 (d, *J* = 7.2 Hz, 3H), 1.58 (d, *J* = 7.2 Hz, 3H) , 0.81 (s, 9H), –0.11 (s, 3H), –0.13 (s, 3H); ^{13}C NMR (50 MHz; $CDCl_3$) δ –5.11, –4.69, 16.90, 17.84, 17.88, 25.63, 52.34, 57.38, 63.35, 71.01, 126.27, 127.68, 128.09, 128.55, 129.77, 140.71, 158.49; HRMS (ESI) calculated for $[C_{21}H_{33}NO_3Si + Na]^+$: 398.2127, Found 398.2124.

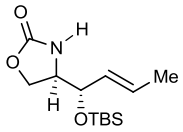


(*R*)-4-[(*S*,*E*)-1-(*t*-butyldimethylsilyloxy)but-2-enyl]-3-[(R)-1-phenylethyl]oxazolidin-2-one (10b'). $[\alpha]_D^{20}$ = +19.27 (c = 0.358, $CHCl_3$); ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.46 – 7.28 (m, 5H),

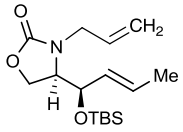
5.54 (dq, *J* = 15.3, 6.4 Hz, 1H), 5.23 (ddq, *J* = 15.0, 7.4, 1.6 Hz, 1H), 4.83 (q, *J* = 7.2 Hz, 1H), 4.26 (dd, *J* = 8.4, 4.5 Hz, 1H), 4.11 (t, *J* = 8.6 Hz, 1H), 3.83 (d, *J* = 8.7 Hz, 1H), 3.67 (ddq, *J* = 8.9, 4.5, 2.3 Hz, 1H), 1.77 (d, *J* = 7.2 Hz, 3H), 1.67 (d, *J* = 6.5 Hz, 3H) , 0.87 (s, 9H), –0.06 (s, 6H); ^{13}C NMR (50 MHz; $CDCl_3$) δ –5.17, –3.94, 17.56, 17.82, 18.29, 25.62, 53.83, 59.89, 62.74, 72.85, 127.22, 127.68, 128.53, 129.23, 129.37, 141.07, 158.28; HRMS (ESI) calculated for $[C_{21}H_{33}NO_3Si+Na]^+$: 398.2127, Found 398.2131.



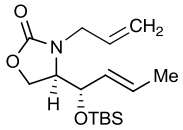
(*R*)-4-[(*R*,*E*)-1-(*t*-butyldimethylsilyloxy)but-2-enyl]oxazolidin-2-one (ent-11a). mp = 55 °C; $[\alpha]_D^{20}$ = –23.47 (c = 0.582, $CHCl_3$); HRMS (ESI) calculated for $[C_{13}H_{25}NO_3Si+Na]^+$: 294.1501, Found 294.1506.



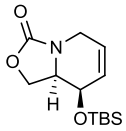
(*R*)-4-[(*S*,*E*)-1-(*t*-butyldimethylsilyloxy)but-2-enyl]oxazolidin-2-one (ent-11b). mp = 145 °C; $[\alpha]_D^{20}$ = +56.54 (c = 0.368, $CHCl_3$); HRMS (ESI) calculated for $[C_{13}H_{25}NO_3Si+Na]^+$: 294.1501, Found 294.1503.



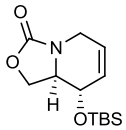
(*R*)-3-allyl-4-[(*R*,*E*)-1-(*t*-butyldimethylsilyloxy)but-2-enyl]oxazolidin-2-one (ent-12a). $[\alpha]_D^{20}$ = +104.70 (c = 0.296, $CHCl_3$); HRMS (ESI) calculated for $[C_{16}H_{29}NO_3Si+Na]^+$: 334.1814, Found 334.1819.



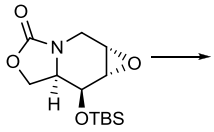
(*R*)-3-allyl-4-[(*S*,*E*)-1-(*t*-butyldimethylsilyloxy)but-2-enyl]oxazolidin-2-one (ent-12b). $[\alpha]_D^{20}$ = –3.98 (c = 0.828, $CHCl_3$); HRMS (ESI) calculated for $[C_{16}H_{29}NO_3Si+Na]^+$: 334.1814, Found 334.1813.



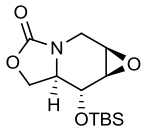
(8*R*,8a*R*)-8-(*t*-butyldimethylsilyloxy)-8,8a-dihydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (ent-13a). mp = 50 °C; $[\alpha]_D^{20}$ = –223.52 (c = 0.623, $CHCl_3$); HRMS (ESI) calculated for $[C_{13}H_{23}NO_3Si+Na]^+$: 292.1345, Found 292.1339.



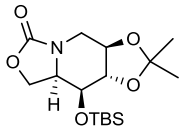
(8*S*,8a*R*)-8-(*t*-butyldimethylsilyloxy)-8,8a-dihydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (ent-13b). mp = 92 °C; $[\alpha]_D^{20}$ = +26.10 (c = 0.448, $CHCl_3$); HRMS (ESI) calculated for $[C_{13}H_{23}NO_3Si+Na]$: 292.1345, Found 292.1341.



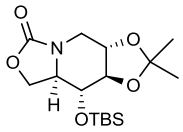
(1a*S*,6a*R*,7*S*,7a*S*)-7-(*t*-butyldimethylsilyloxy)tetrahydro-1a*H*-oxazolo[3,4-*a*]oxireno[2,3-*d*]pyridin-4(2*H*)-one (ent-14a). mp = 165 °C; $[\alpha]_D^{20}$ = –36.44 (c = 0.532, MeOH); HRMS (ESI) calculated for $[C_{13}H_{23}NO_4Si+H]^+$: 286.1475, Found 286.1475.



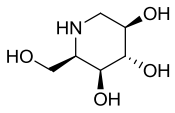
(1a*R*,6a*R*,7*R*,7a*R*)-7-(*t*-butyldimethylsilyloxy)tetrahydro-1a*H*-oxazolo[3,4-*a*]oxireno[2,3-*d*]pyridin-4(2*H*)-one (ent-14d). mp = 111 °C; $[\alpha]_D^{20}$ = –15.14 (c = 0.822, MeOH); HRMS (ESI) calculated for $[C_{13}H_{23}NO_4Si+H]^+$: 286.1475, Found 286.1471.



(3a*R*,8a*R*,9*S*,9a*S*)-9-(*t*-butyldimethylsilyloxy)-2,2-dimethyltetrahydro-3a*H*-[1,3]dioxolo[4,5-*d*]oxazolo[3,4-*a*]pyridin-6(4*H*)-one (ent-15a). mp = 86 °C; $[\alpha]_D^{20}$ = –42.2 (c = 0.676, $CHCl_3$); HRMS (ESI) calculated for $[C_{16}H_{29}NO_5Si+H]^+$: 344.1893, Found 344.1898

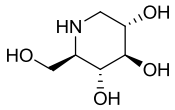


(3a*S*,8a*R*,9*R*,9a*R*)-9-(*t*-butyldimethylsilyloxy)-2,2-dimethyltetrahydro-3a*H*-[1,3]dioxolo[4,5-*d*]oxazolo[3,4-*a*]pyridin-6(4*H*)-one (ent-15d). mp = 72 °C; $[\alpha]_D^{20}$ = –21.10 (c = 0.457, $CHCl_3$); HRMS (ESI) calculated for $[C_{16}H_{29}NO_5Si+H]^+$: 344.1893, Found 344.1891



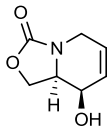
D-Ido-DNJ
1a

D-1-deoxyidonojirimycin (D-Ido-DNJ, (2*S*,3*R*,4*R*,5*S*)-2-(hydroxymethyl)piperidine-3,4,5-triol, ent-1a). mp = 136 °C , $[\alpha]_D^{20}$ = –10.3 (c = 0.683, H_2O); HRMS (ESI) calculated for $[C_6H_{13}NO_4+H]^+$: 164.0923, Found 164.0921

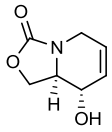


D-DNJ
1d

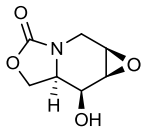
D-1-deoxynojirimycin (D-DJN, (2*R*,3*R*,4*R*,5*S*)-2-(hydroxymethyl)piperidine-3,4,5-triol, ent-1d). mp = 193 °C , $[\alpha]_D^{20}$ = +40.68 (c = 0.427, H_2O); HRMS (ESI) calculated for $[C_6H_{13}NO_4+H]^+$: 164.0923, Found 164.0925



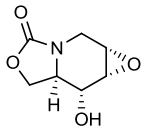
(8*S*,8a*S*)-8-hydroxy-8,8a-dihydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (ent-16b). mp = 105 °C; $[\alpha]_D^{20}$ = –295.84 (c = 0.545, MeOH); HRMS (ESI) calculated for $[C_7H_9NO_3+H]^+$: 156.0661, Found 156.0654



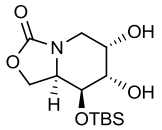
(8*R*,8a*S*)-8-hydroxy-8,8a-dihydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (ent-16e). mp = 98 °C; $[\alpha]_D^{20}$ = –26.72 (c = 0.432, MeOH); HRMS (ESI) calculated for $[C_7H_9NO_3+H]^+$: 156.0660, Found 156.0661.



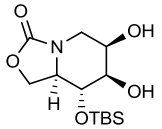
(1a*R*,6a*R*,7*S*,7a*S*)-7-hydroxytetrahydro-1a*H*-oxazolo[3,4-*a*]oxireno[2,3-*d*]pyridin-4(2*H*)-one (ent-17b). white solid : mp = 98 °C; $[\alpha]_D^{20}$ = –53.12 (c = 0.283, MeOH); HRMS (ESI) calculated for $C_7H_9NO_4$ [M + H]: 172.0610, Found 172.0617.



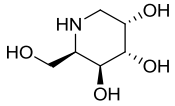
(1a*R*,6a*S*,7*S*,7a*R*)-7-hydroxytetrahydro-1a*H*-oxazolo[3,4-*a*]oxireno[2,3-*d*]pyridin-4(2*H*)-one (ent-17e). mp = 120 °C; $[\alpha]_D^{20}$= +47.13 (c = 0.233, MeOH); HRMS (ESI) calculated for $C_7H_9NO_4$ [M + H]: 172.0610, Found 172.0611.



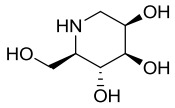
(6*S*,7*S*,8*S*,8a*R*)-8-(*t*-butyldimethylsilyloxy)-6,7-dihydroxy-tetrahydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (ent-18c). mp = 177 °C; $[\alpha]_D^{20}$ = –42.93 (c = 0.461, MeOH); HRMS (ESI) calculated for $[C_{13}H_{25}NO_5Si+H]^+$: 304.1580, Found 304.1584



(6*R*,7*R*,8*R*,8a*R*)-8-(*t*-butyldimethylsilyloxy)-6,7-dihydroxy-tetrahydro-1*H*-oxazolo[3,4-*a*]pyridin-3(5*H*)-one (ent-18f). mp = 120 °C; $[\alpha]_D^{20}$ = –28.13 (c = 0.386, MeOH); HRMS (ESI) calculated for $[C_{13}H_{25}NO_5Si+H]^+$: 304.1580, Found 304.1575



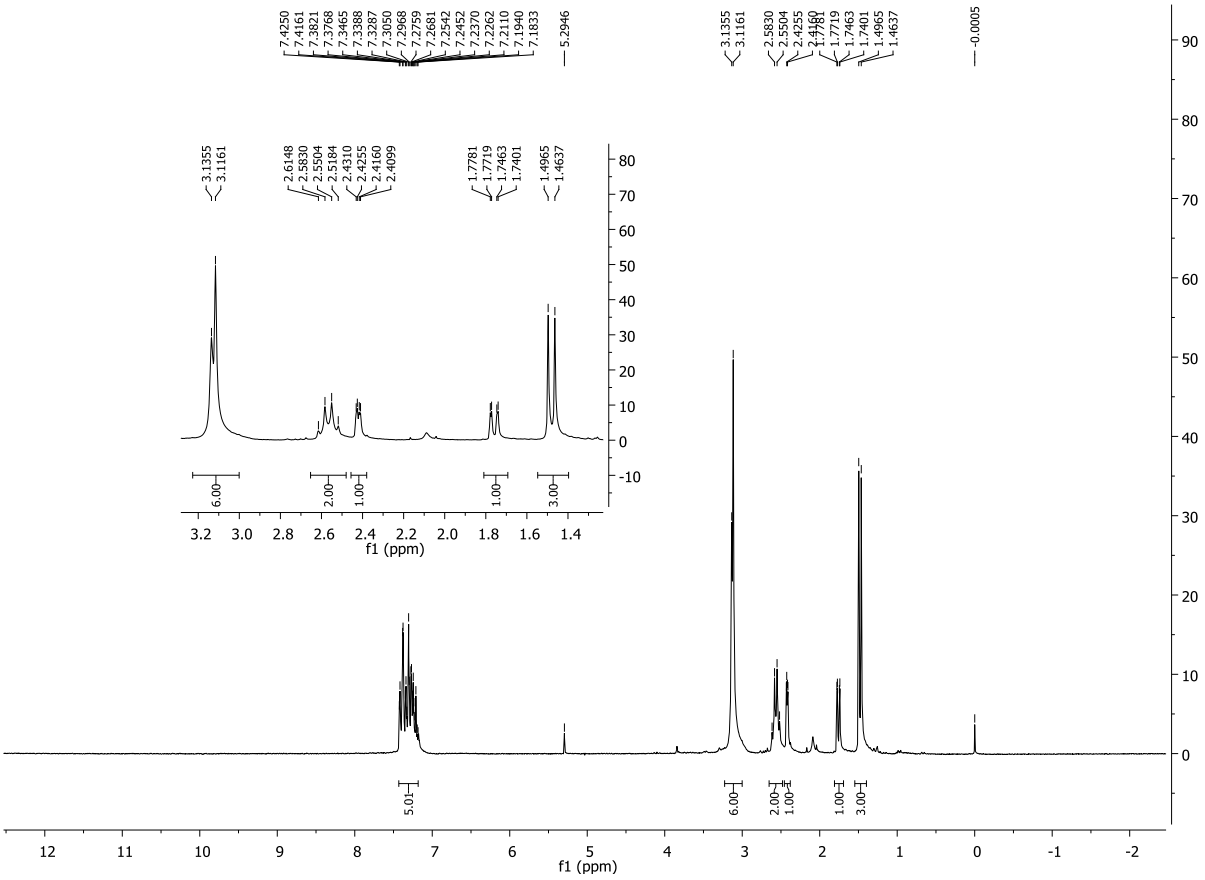
D-1-deoxygulonojirimycin (D-Gulo-DNJ, (2*R*,3*S*,4*S*,5*S*)-2-(hydroxymethyl)piperidine-3,4,5-triol, ent-1c). $[\alpha]_D^{20}$ = –15.21 (c = 0.672, H_2O); HRMS (ESI) calculated for $[C_6H_{13}NO_4+H]^+$: 164.0923, Found 164.0921



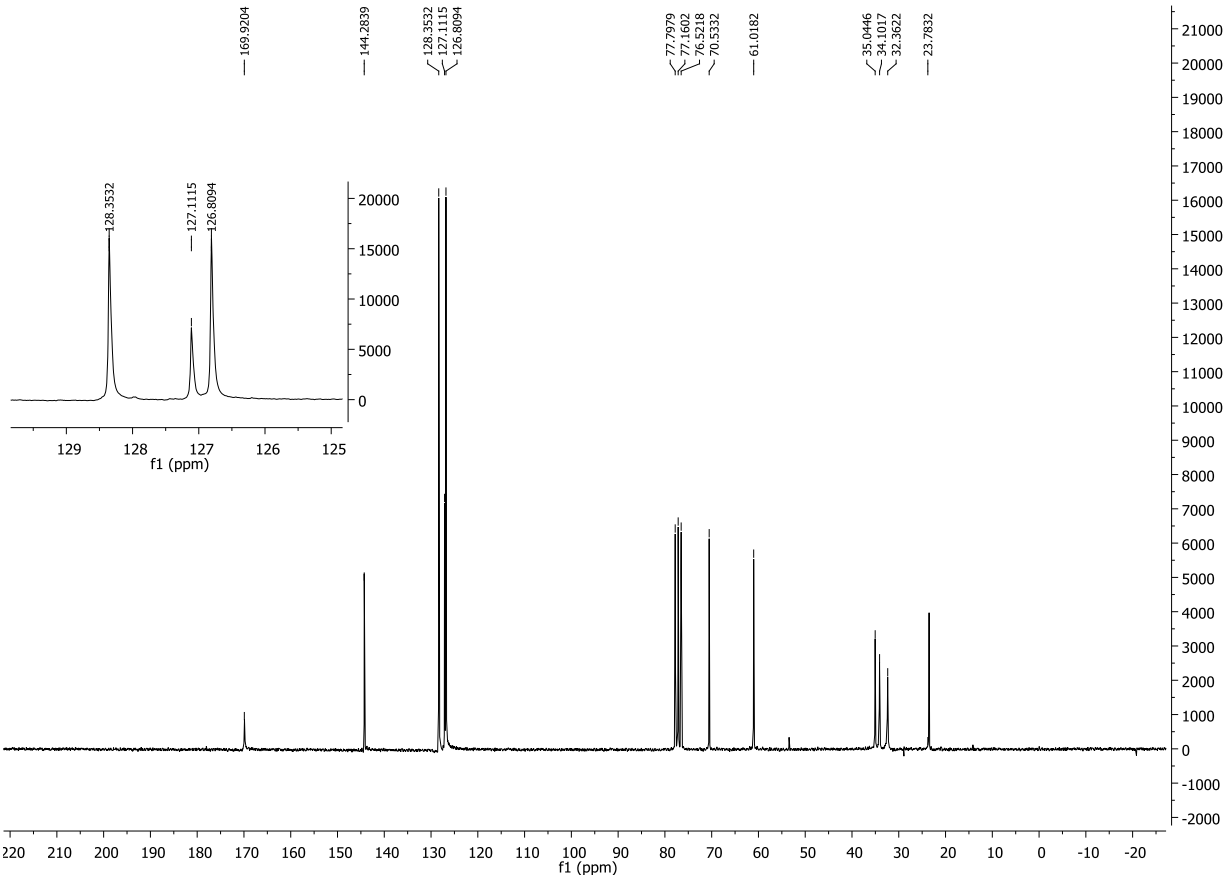
D-1-deoxymannojirimycin (D-Manno-DNJ, (2*R*,3*R*,4*R*,5*R*)-2-(hydroxymethyl)piperidine-3,4,5-triol, ent-1f). mp = 185 °C, $[\alpha]_D^{20}$ = –39.18 (c = 0.864, H_2O); HRMS (ESI) calculated for $[C_6H_{13}NO_4+H]^+$: 164.0923, Found 164.0927

^{1}H and ^{13}C NMR Spectra of all compounds

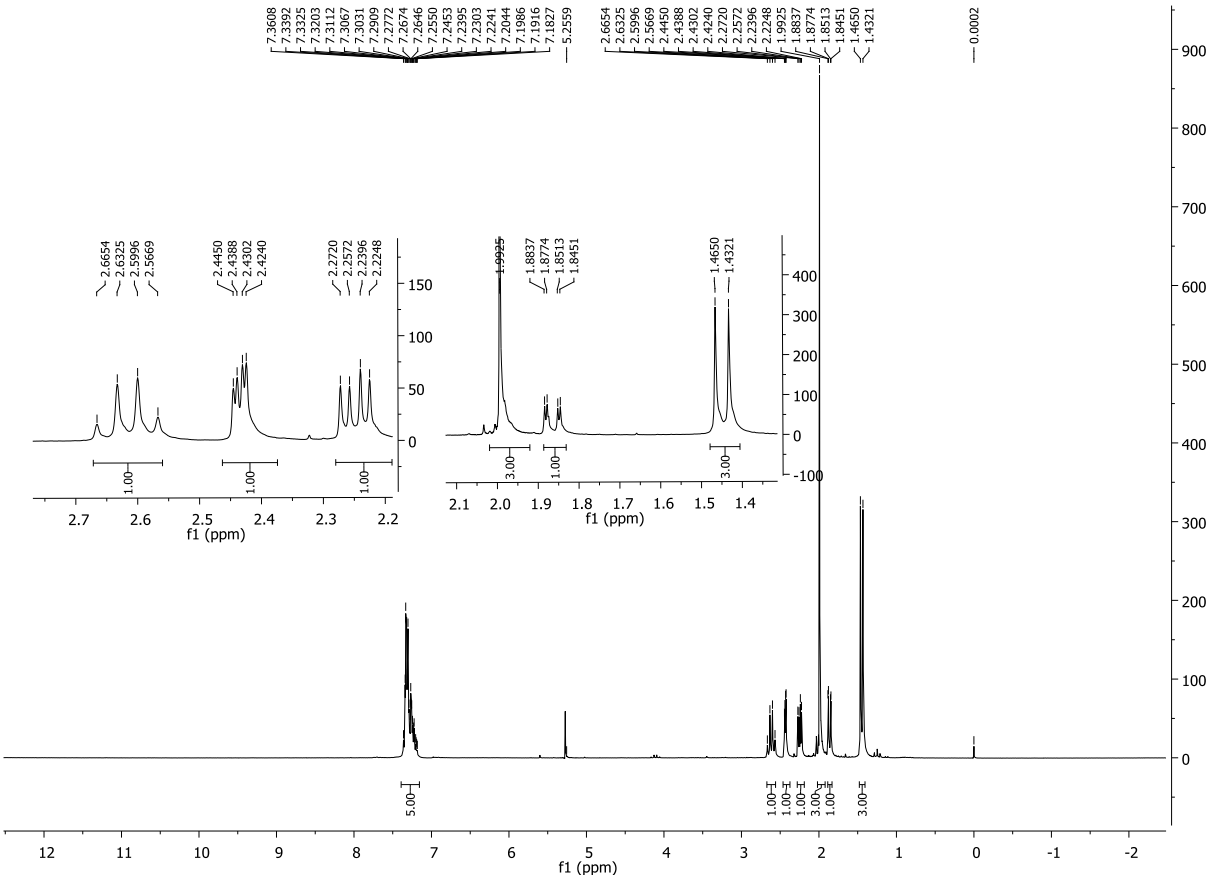
^{1}H NMR ($CDCl_3$, 200MHz) of **3**



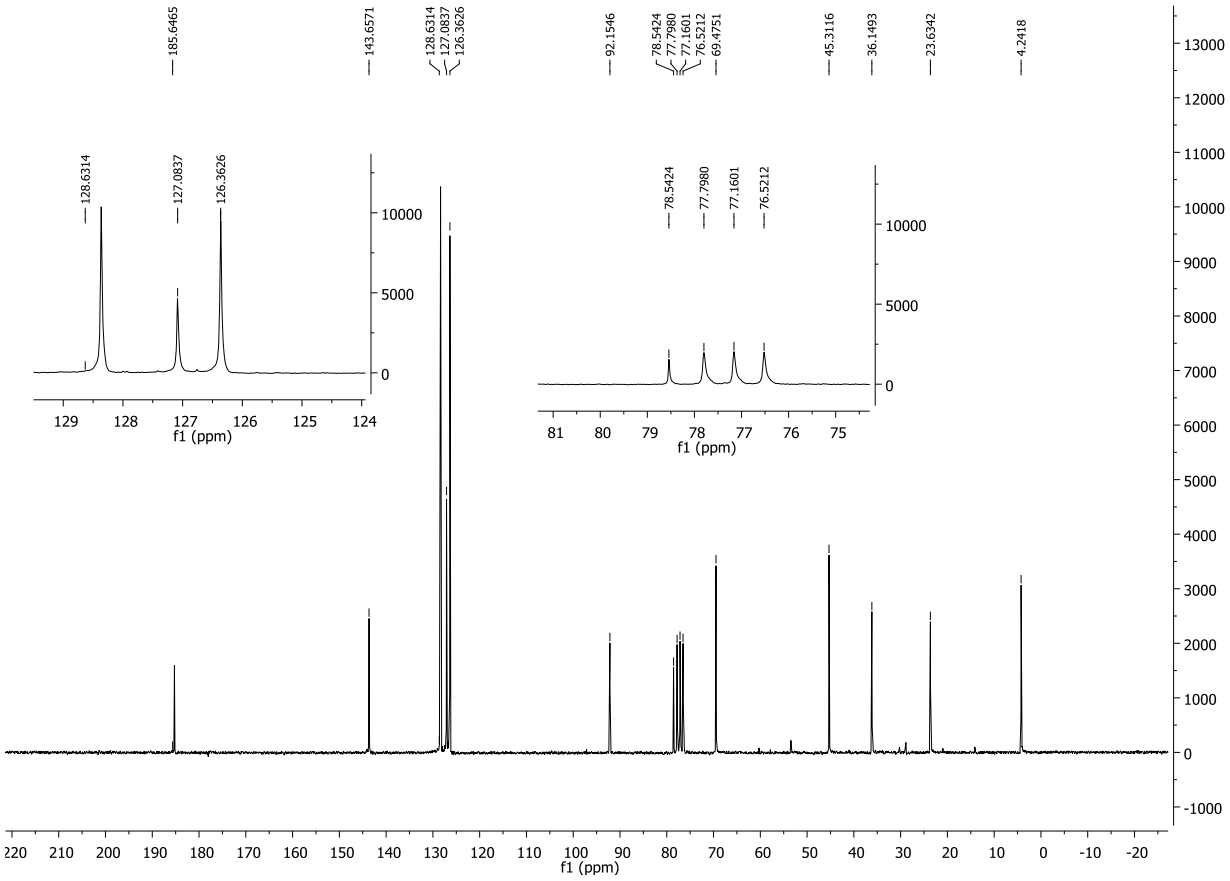
^{13}C NMR ($CDCl_3$, 50 MHz) of **3**



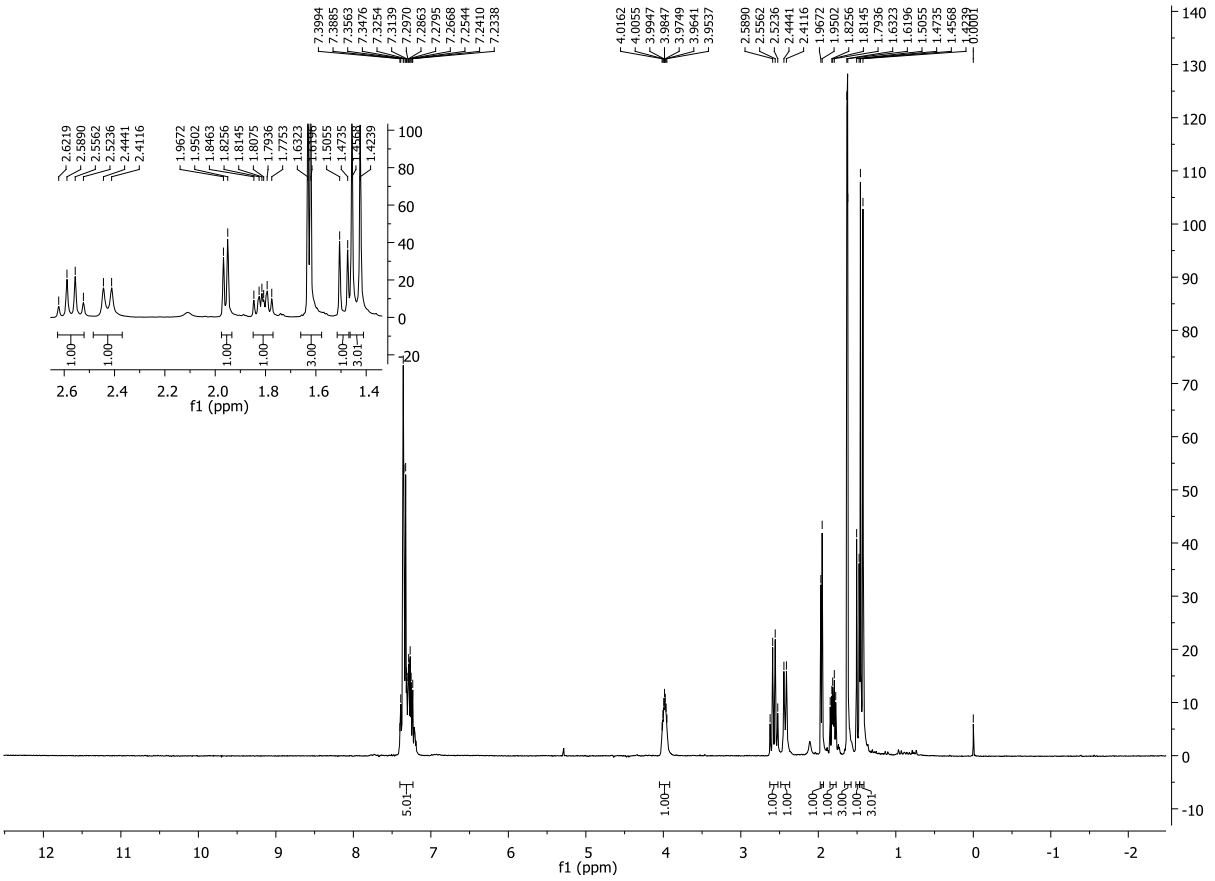
^{1}H NMR ($CDCl_3$, 200MHz) of **4**



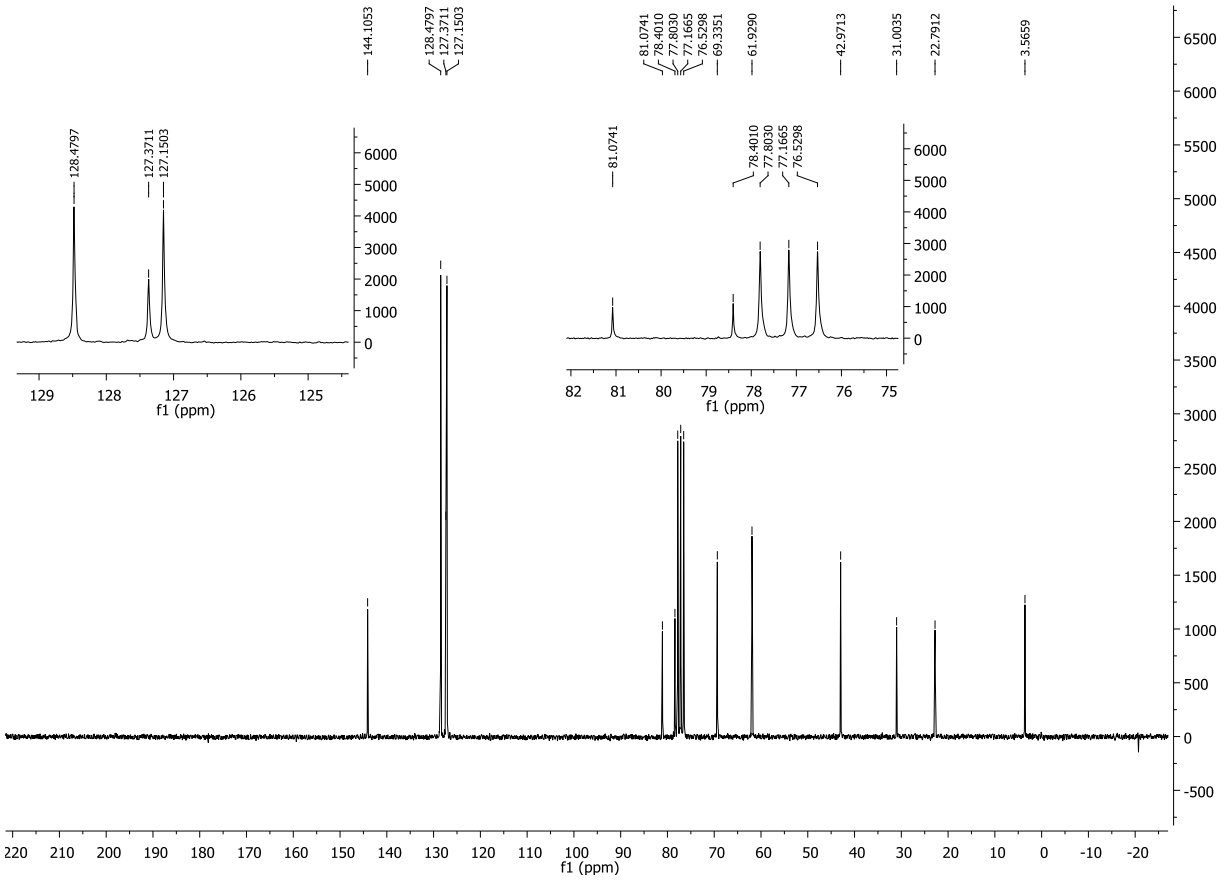
^{13}C NMR ($CDCl_3$, 50 MHz) of **4**



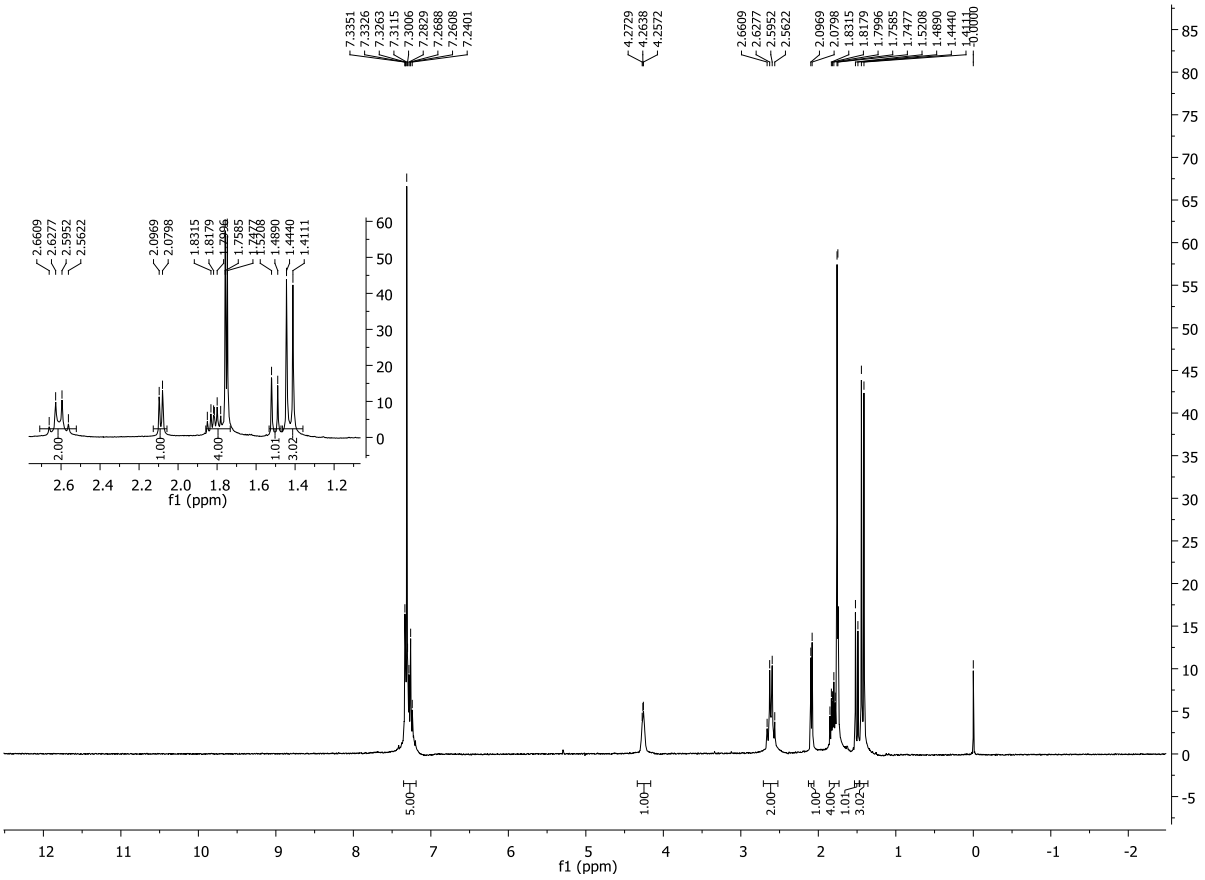
^{1}H NMR ($CDCl_3$, 200MHz) of **5a**



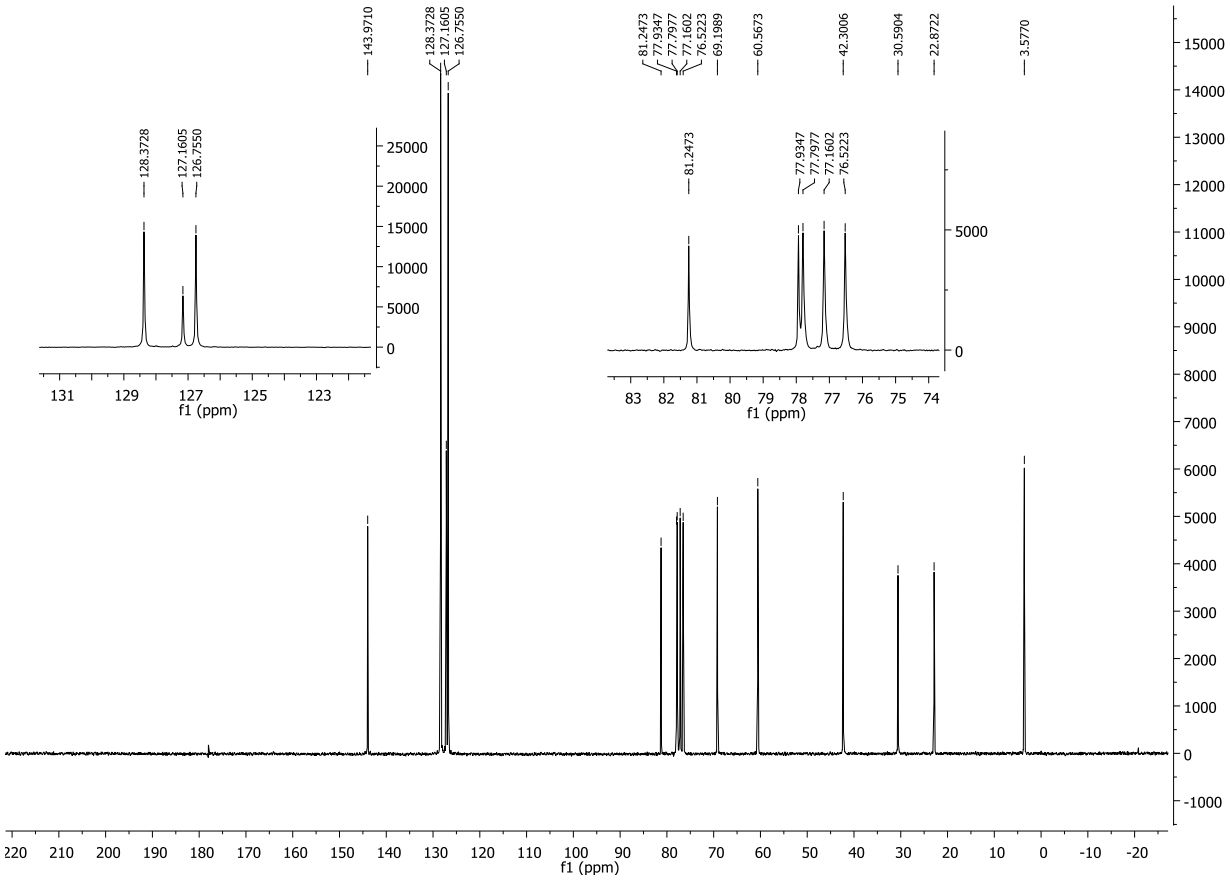
^{13}C NMR ($CDCl_3$, 50 MHz) of **5a**



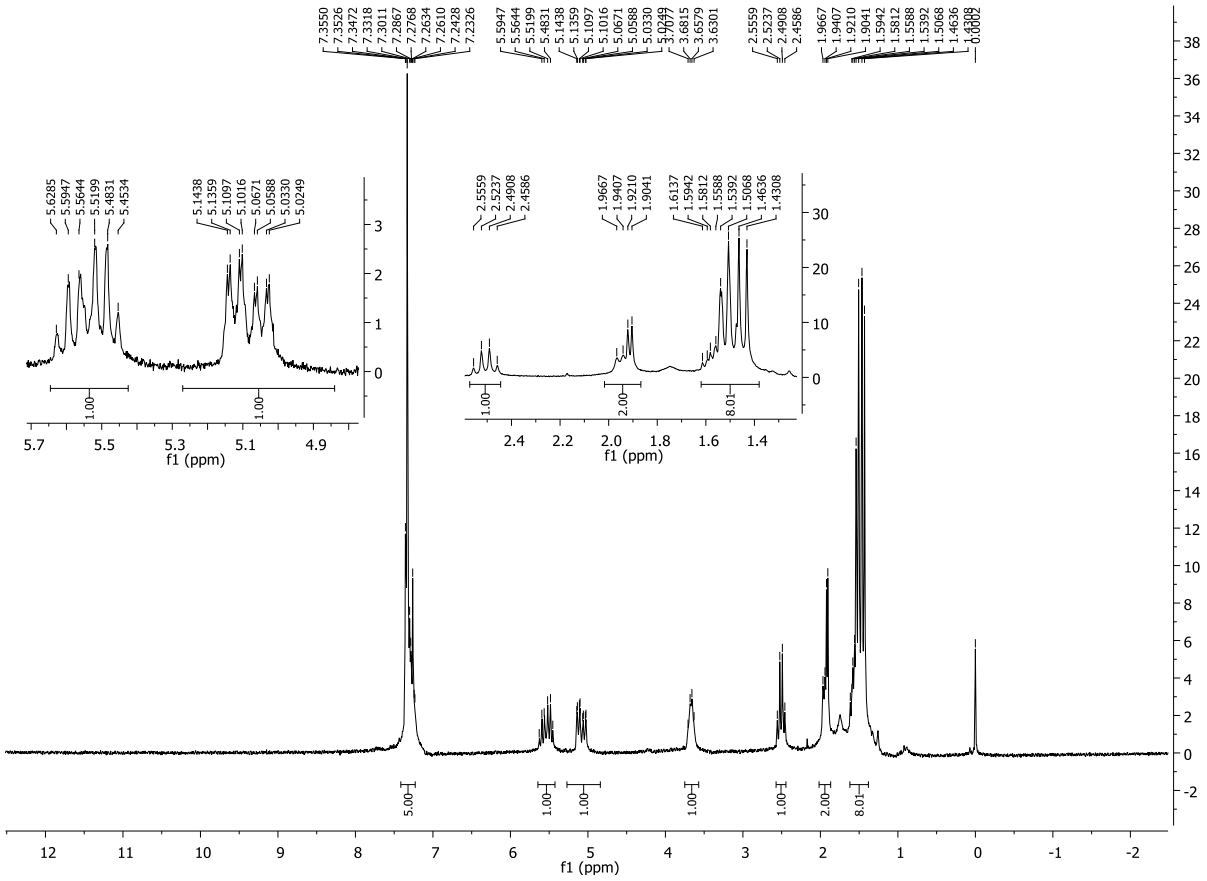
^{1}H NMR ($CDCl_3$, 200MHz) of **5b**



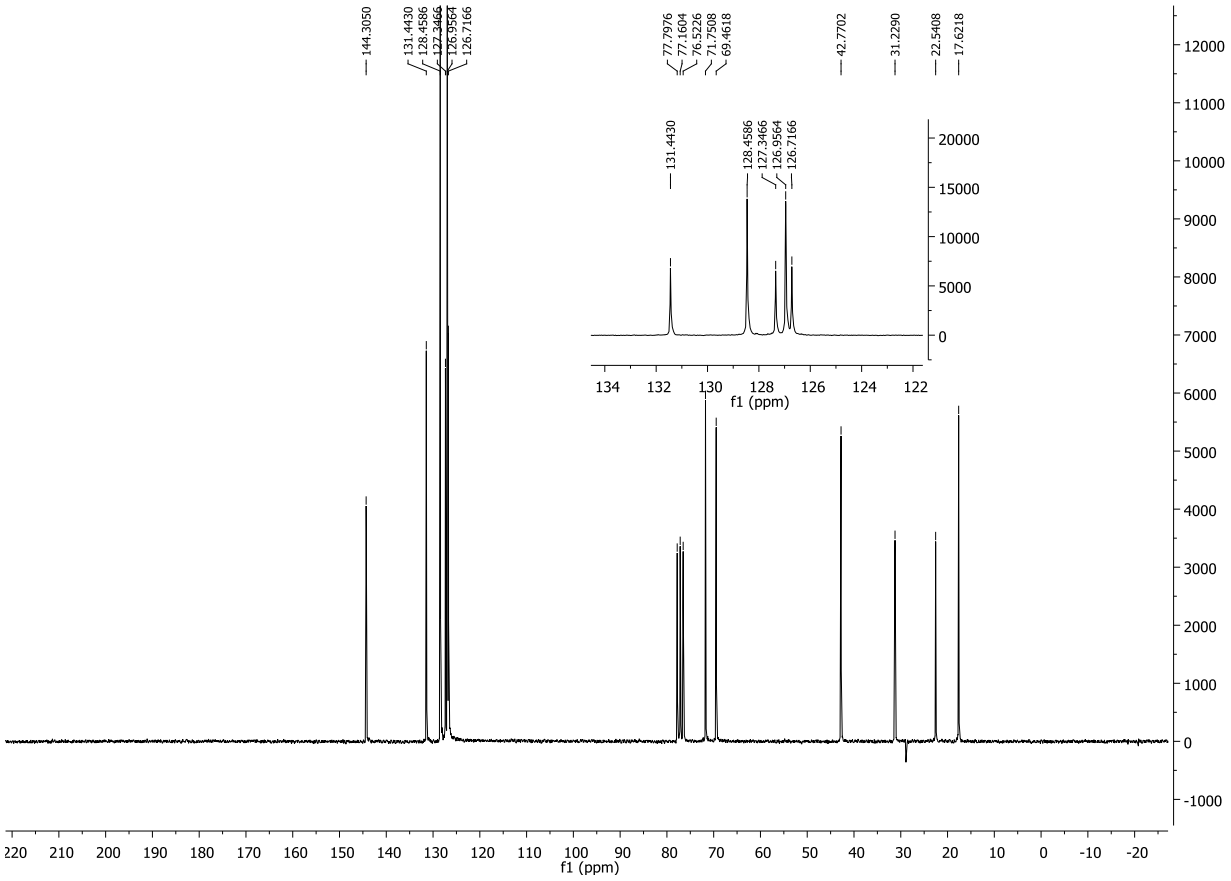
^{13}C NMR ($CDCl_3$, 50 MHz) of **5b**



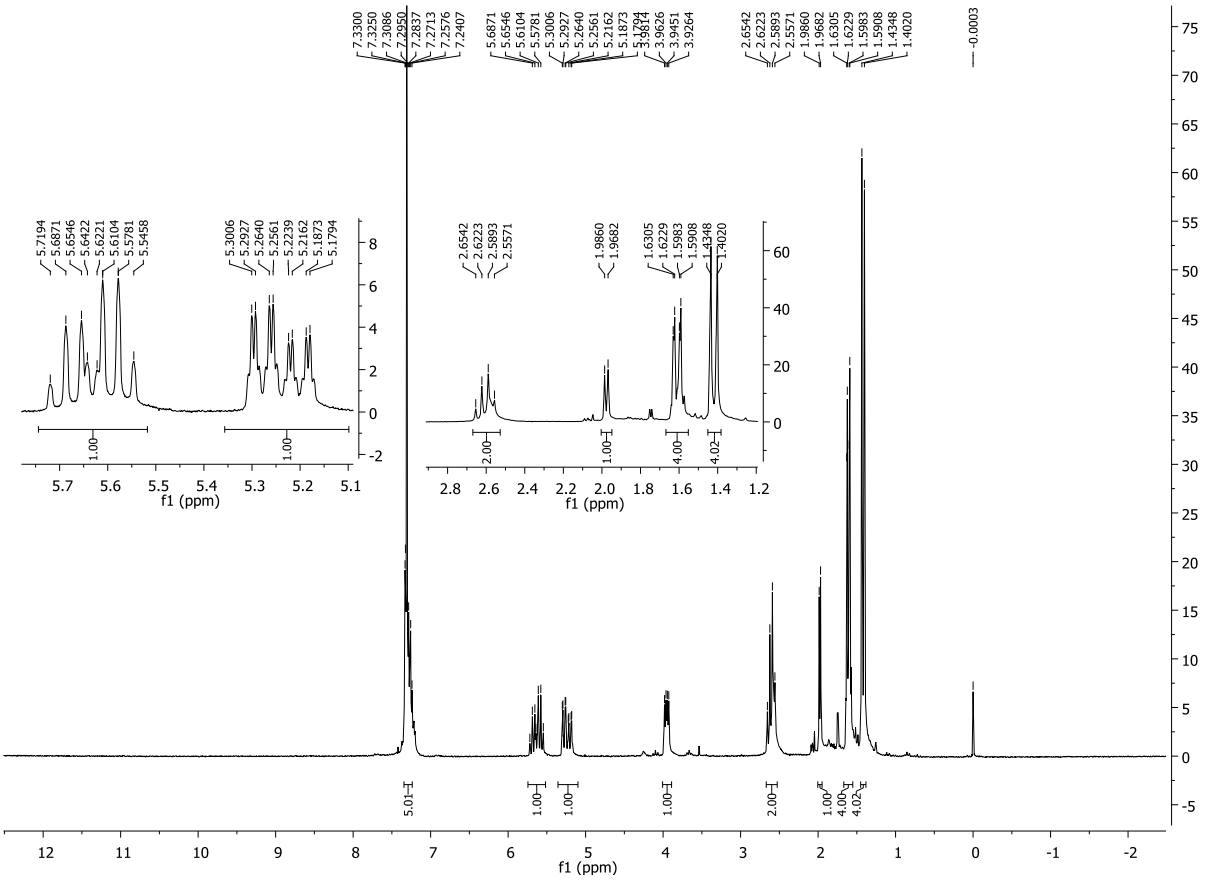
^{1}H NMR ($CDCl_3$, 200MHz) of **6a**



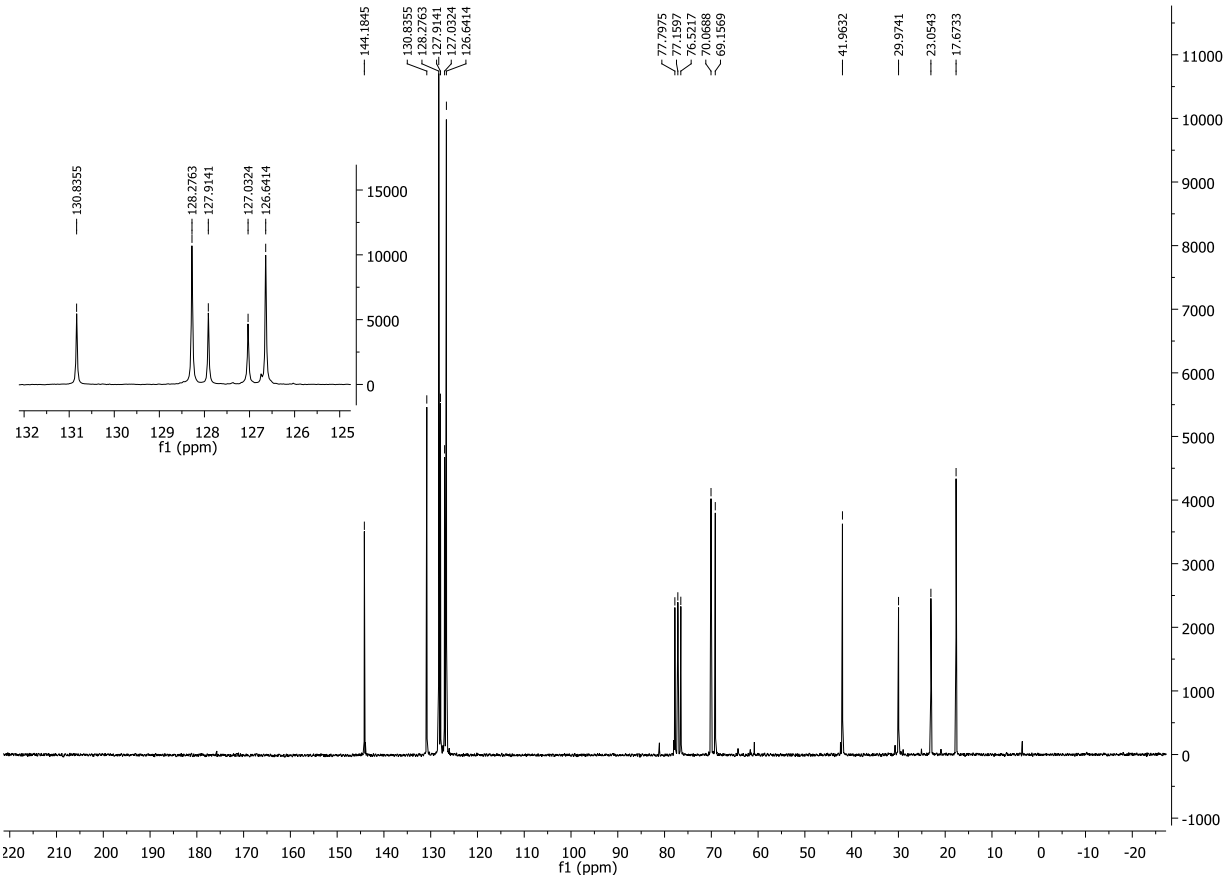
^{13}C NMR ($CDCl_3$, 50 MHz) of **6a**



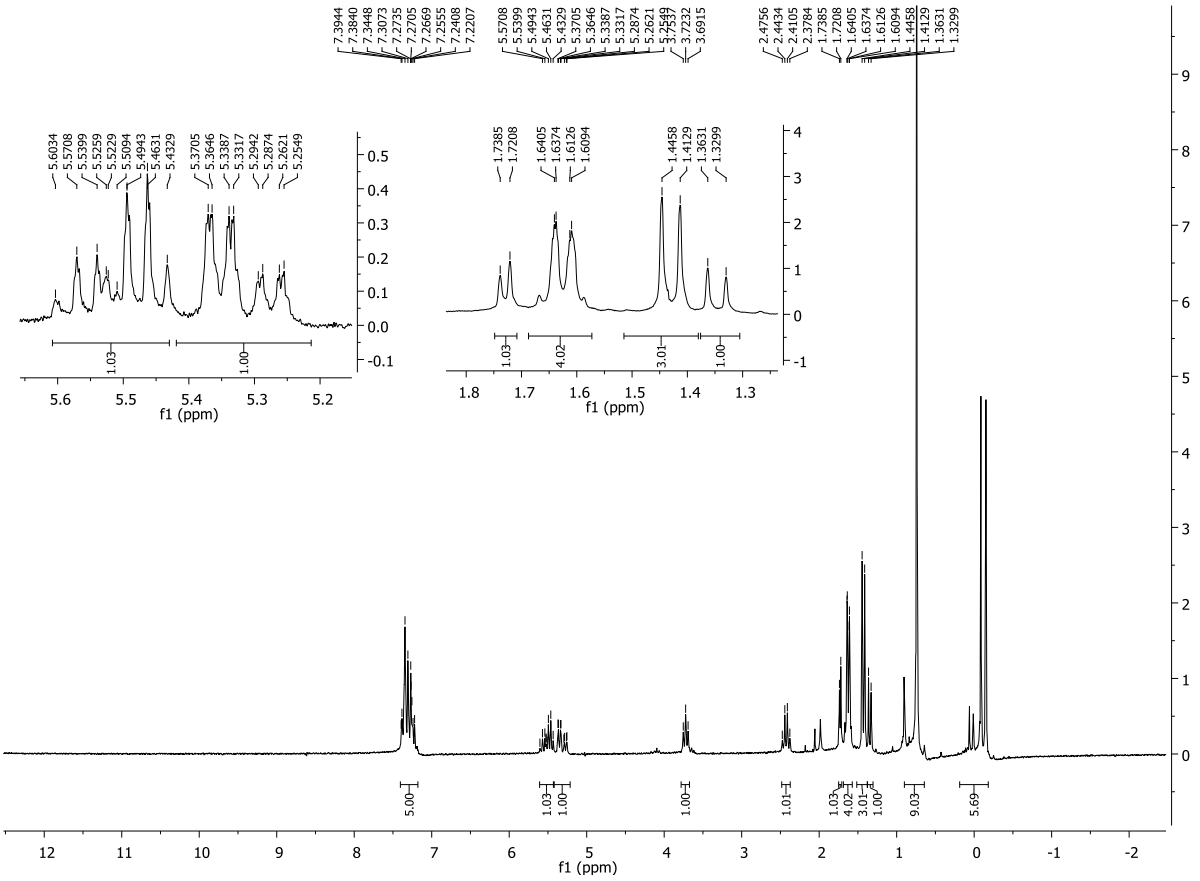
^{1}H NMR ($CDCl_3$, 200MHz) of **6b**



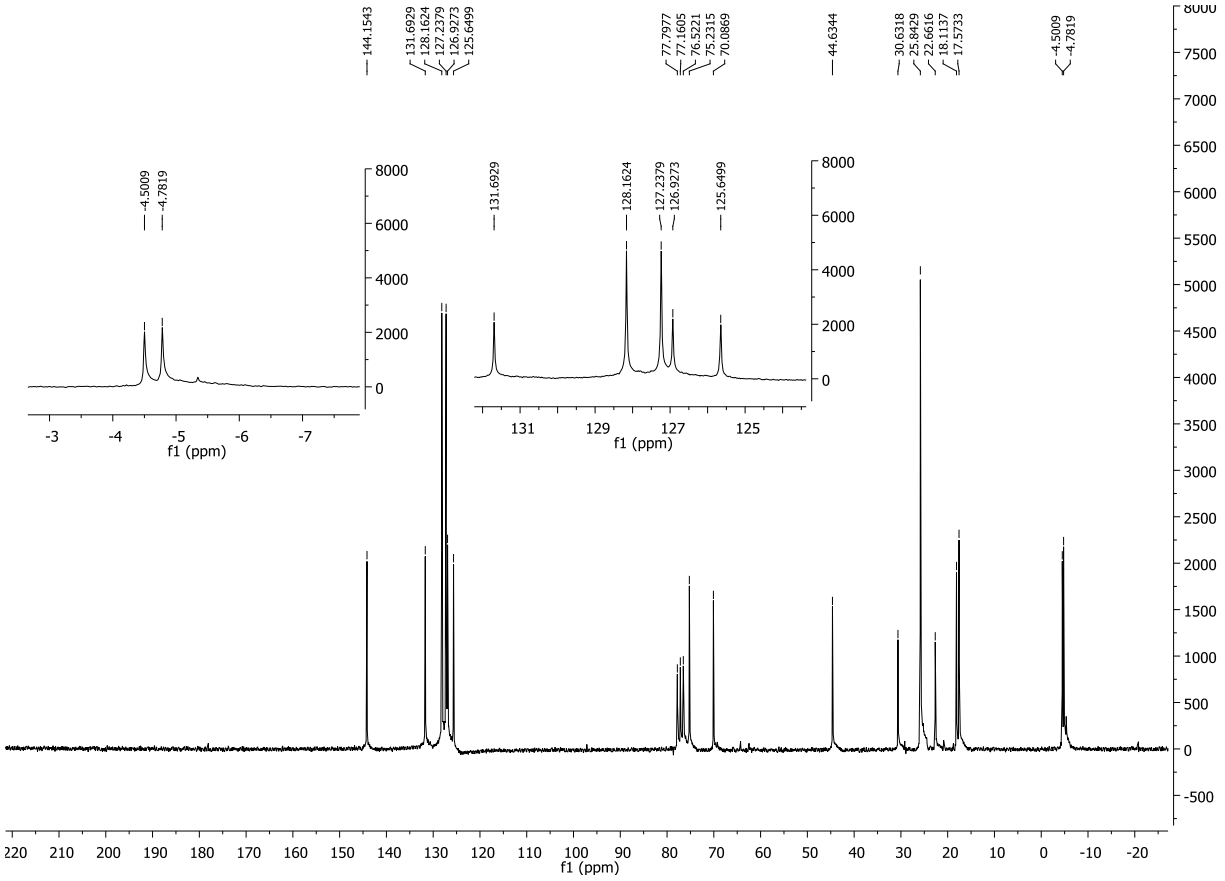
^{13}C NMR ($CDCl_3$, 50 MHz) of **6b**



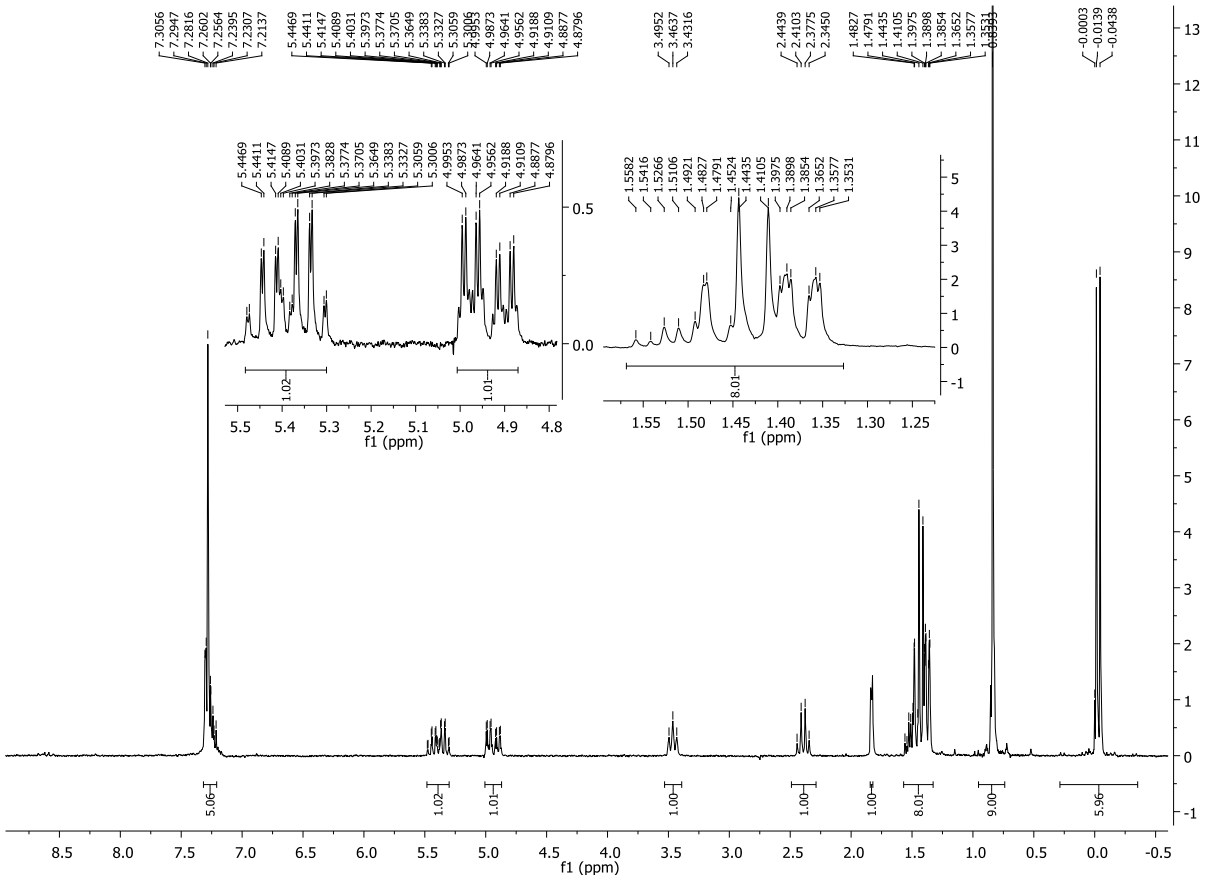
^{1}H NMR ($CDCl_3$, 200MHz) of **7a**



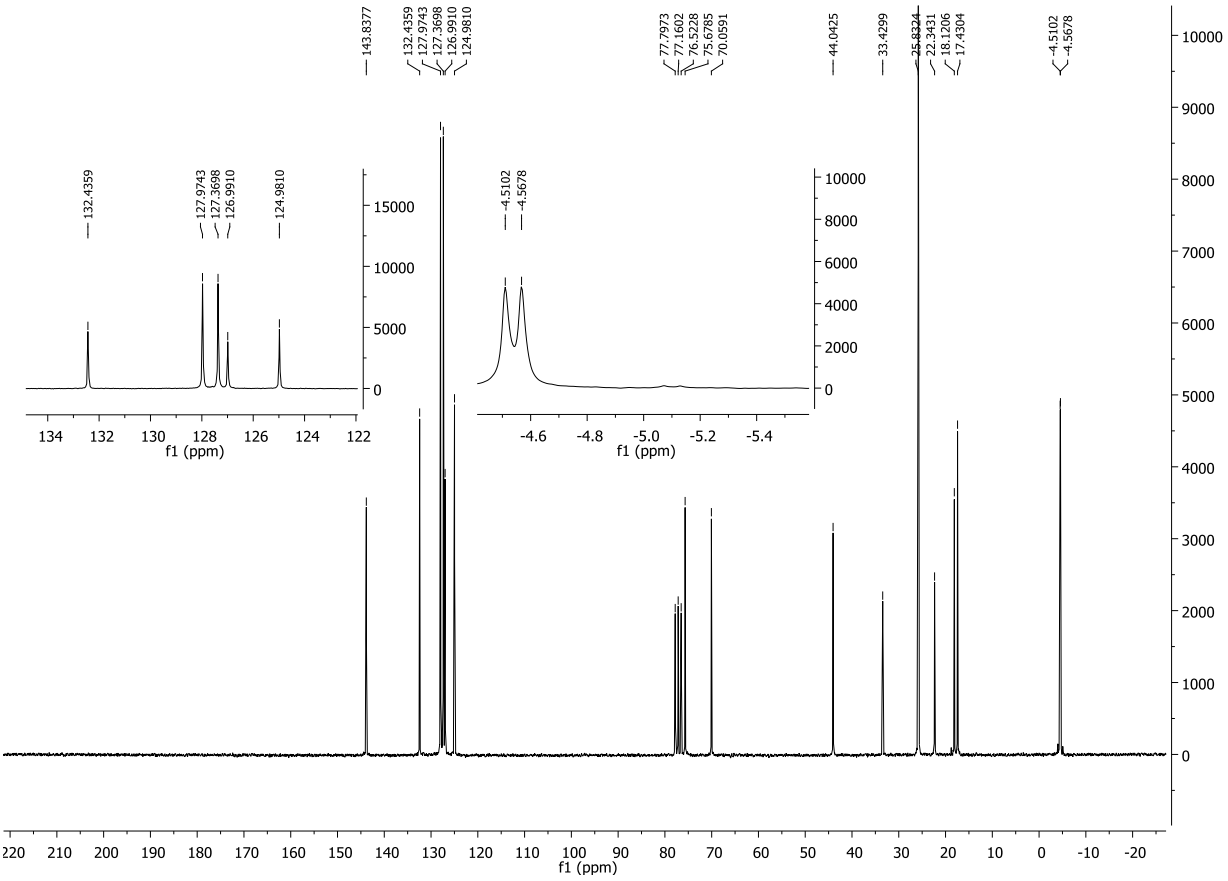
^{13}C NMR ($CDCl_3$, 50 MHz) of **7a**



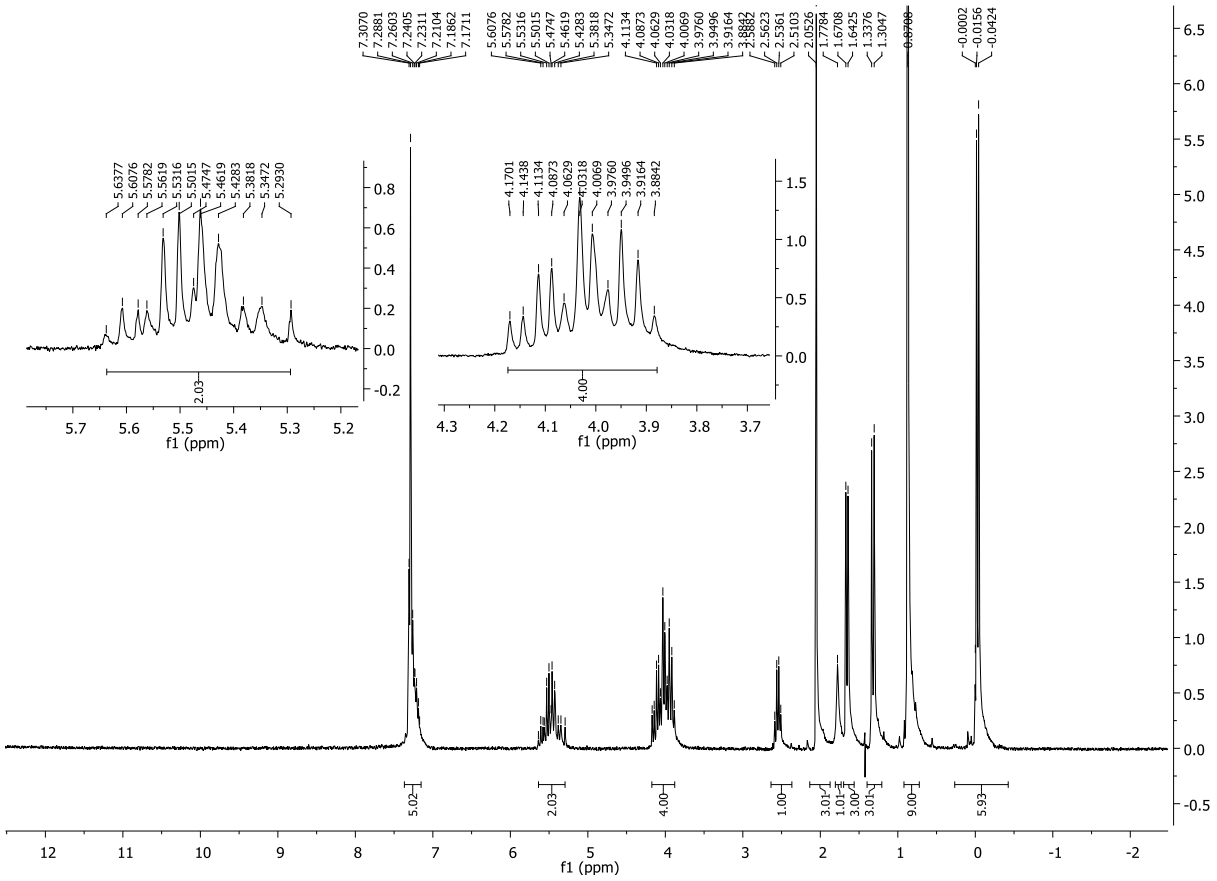
^{1}H NMR ($CDCl_3$, 200MHz) of **7b**



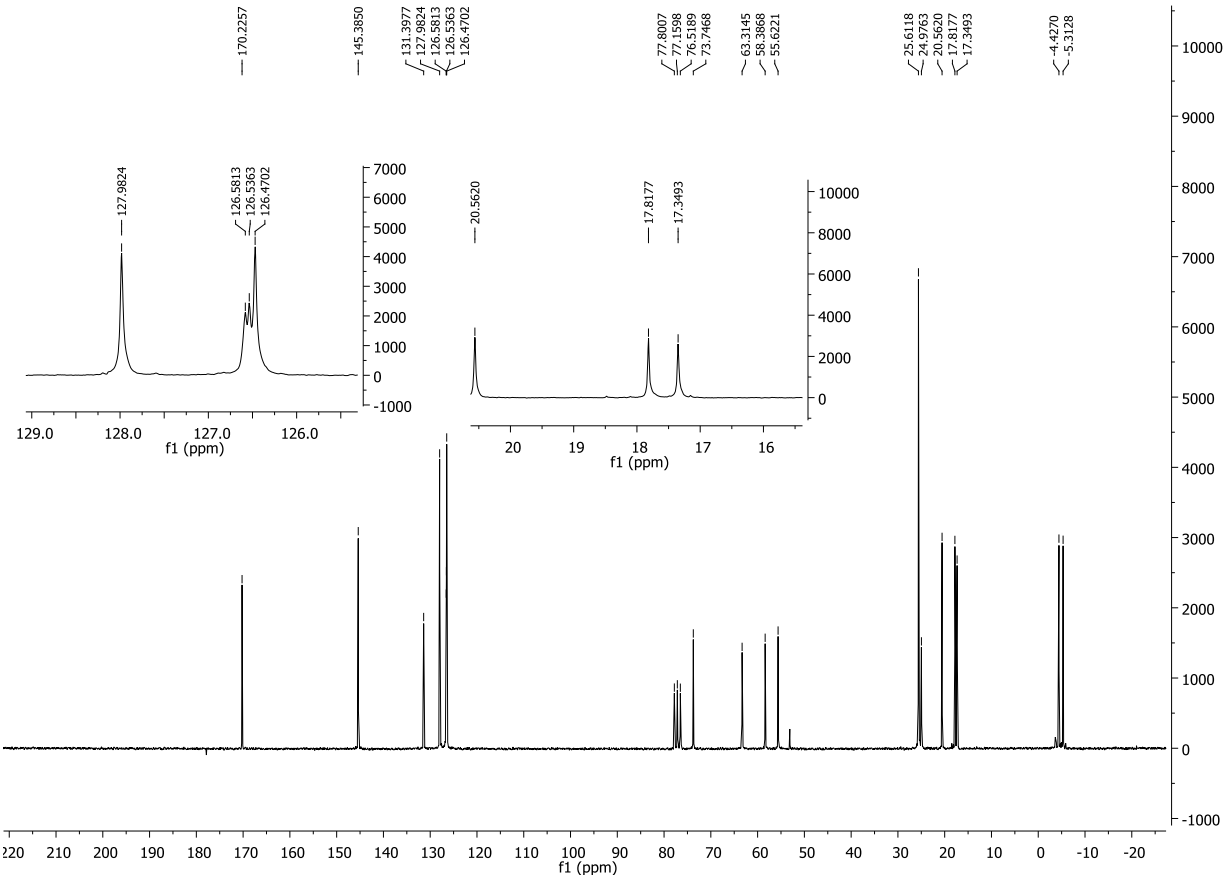
^{13}C NMR ($CDCl_3$, 50 MHz) of **7b**



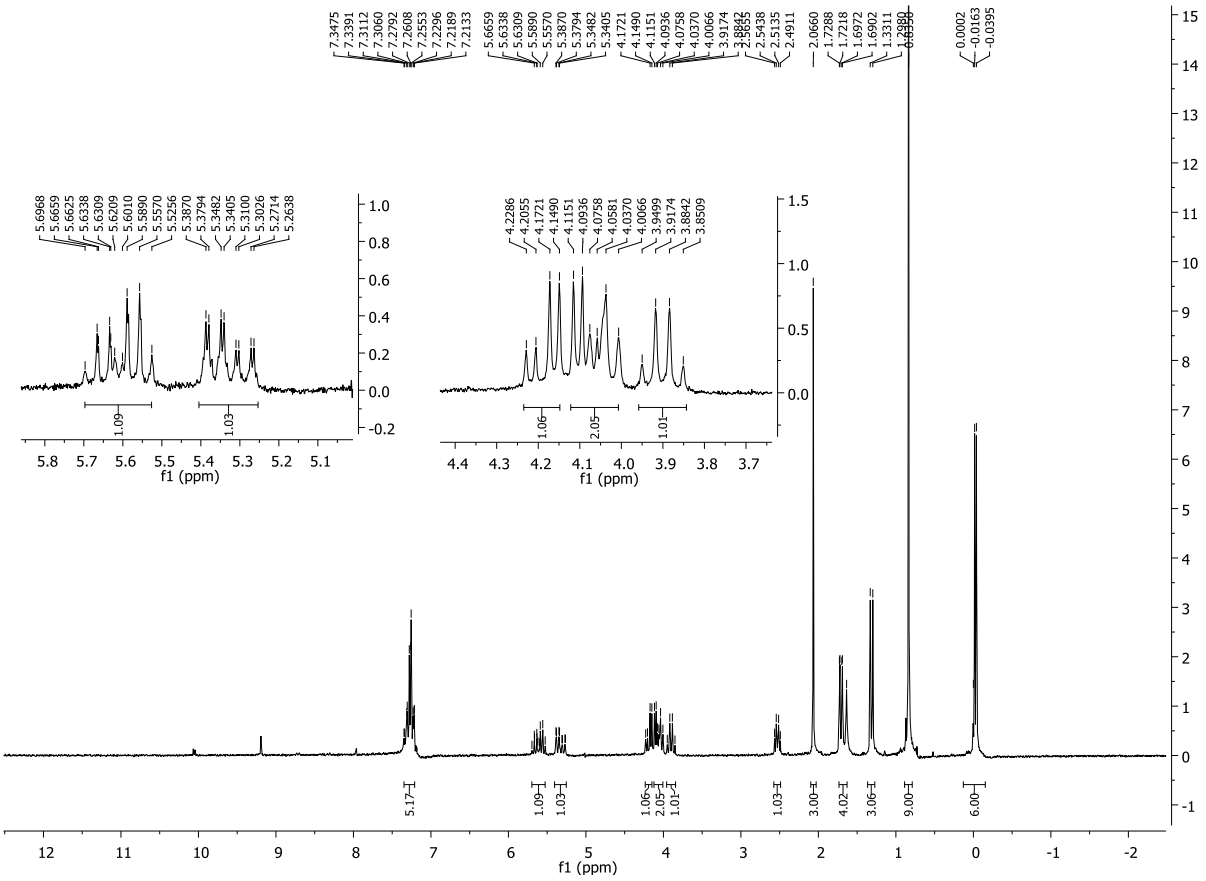
^{1}H NMR ($CDCl_3$, 200MHz) of **8a**



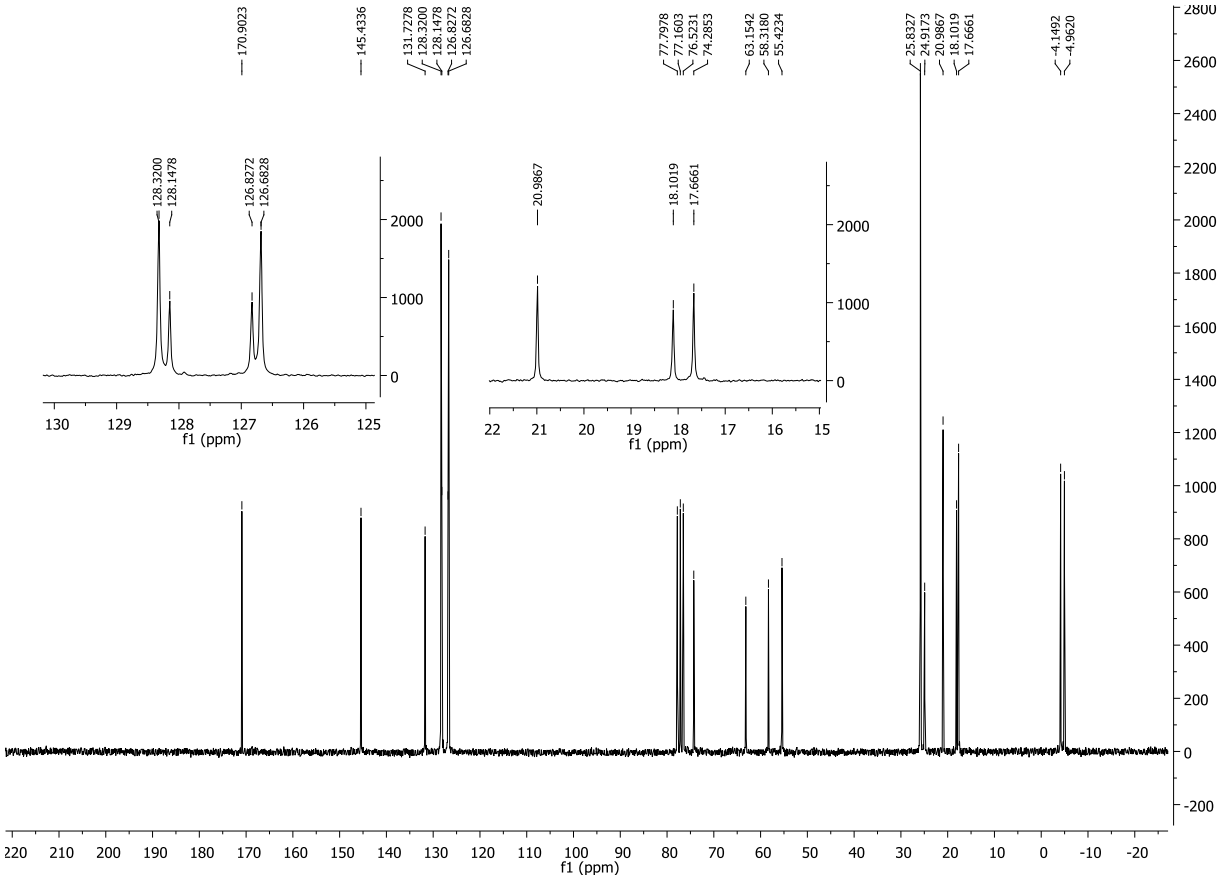
^{13}C NMR ($CDCl_3$, 50 MHz) of **8a**



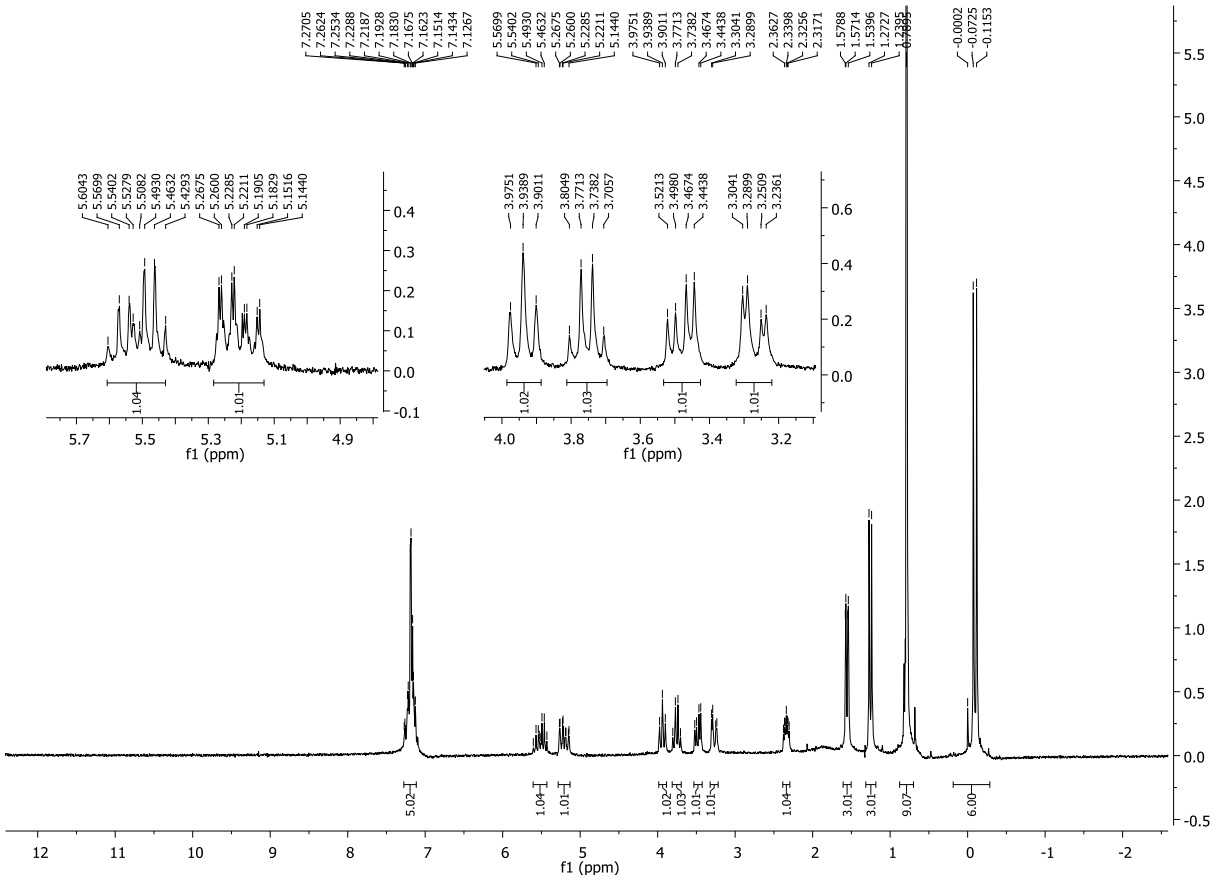
^{1}H NMR ($CDCl_3$, 200MHz) of **8b**



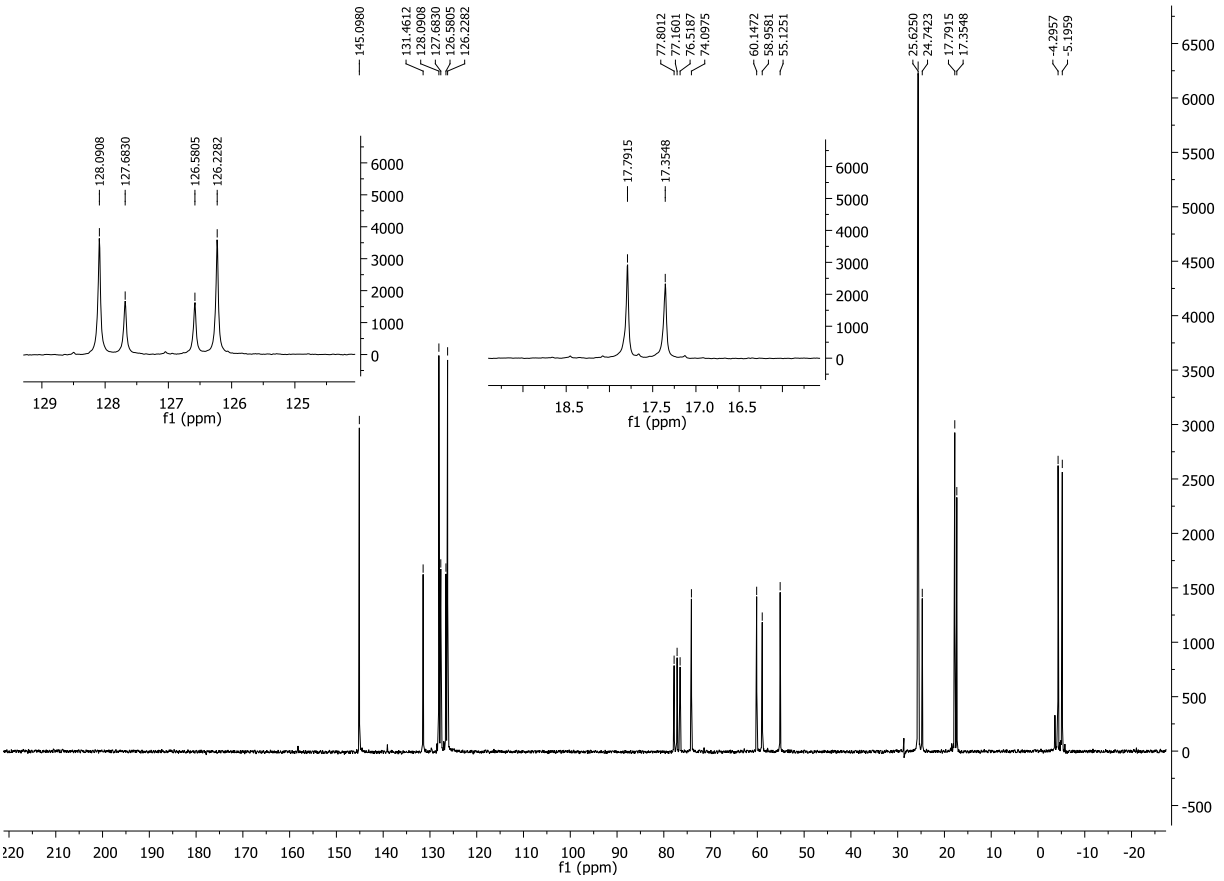
^{13}C NMR ($CDCl_3$, 50 MHz) of **8b**



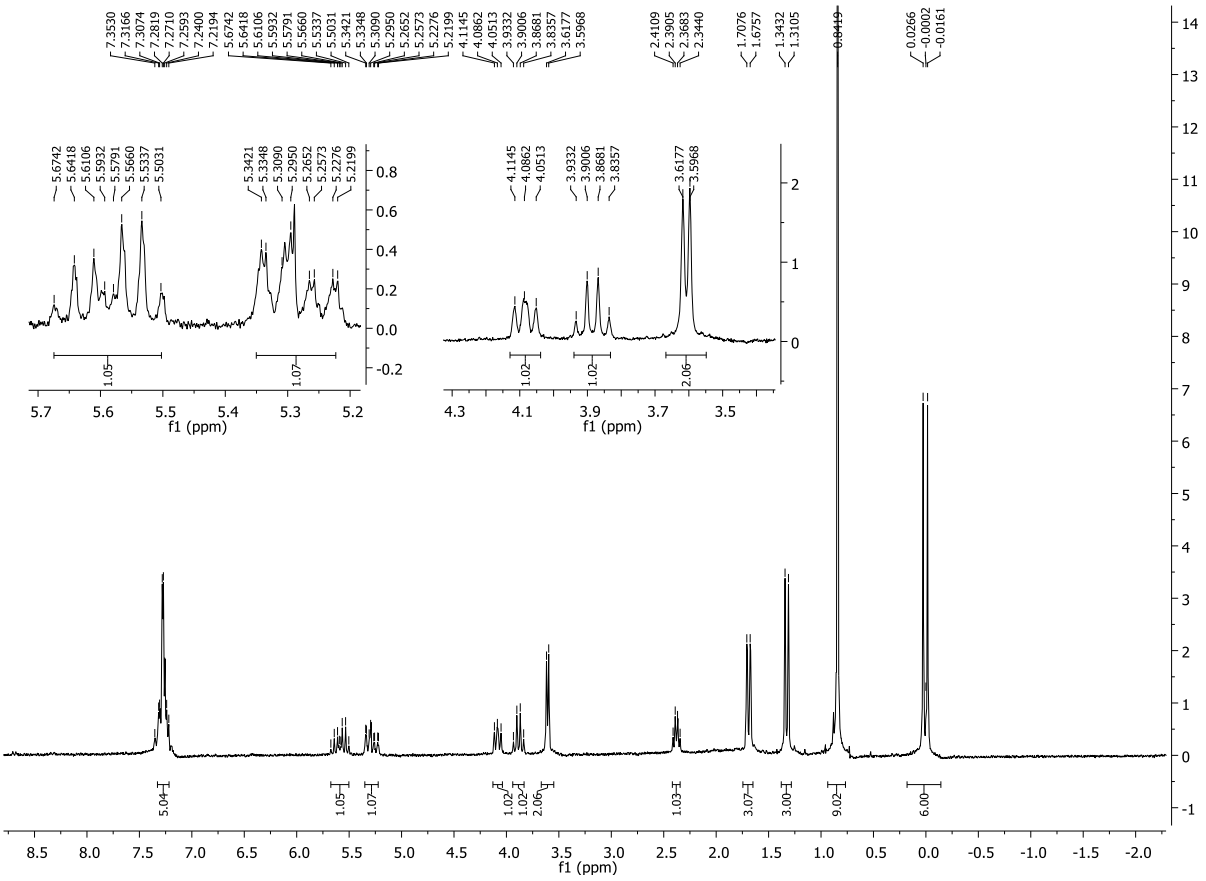
^{1}H NMR ($CDCl_3$, 200MHz) of **9a**



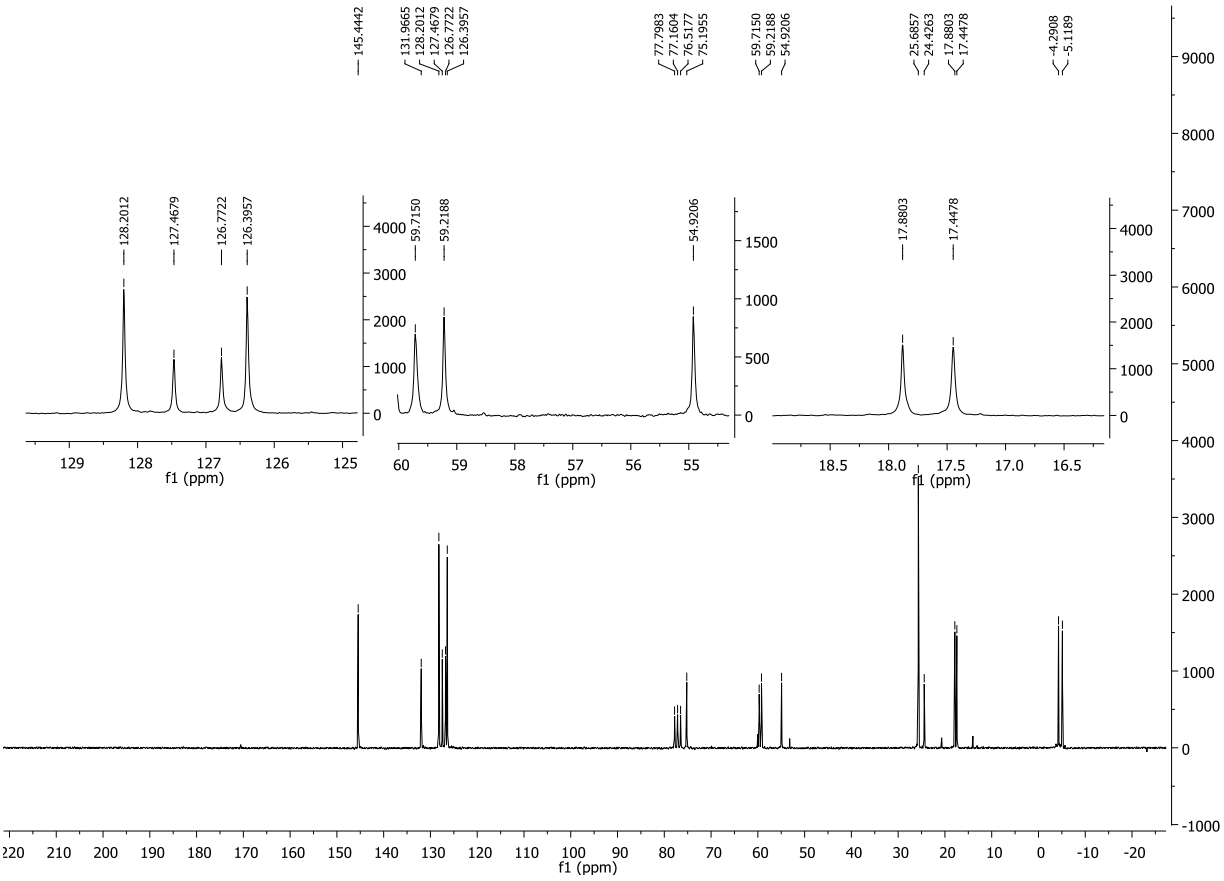
^{13}C NMR ($CDCl_3$, 50 MHz) of **9a**



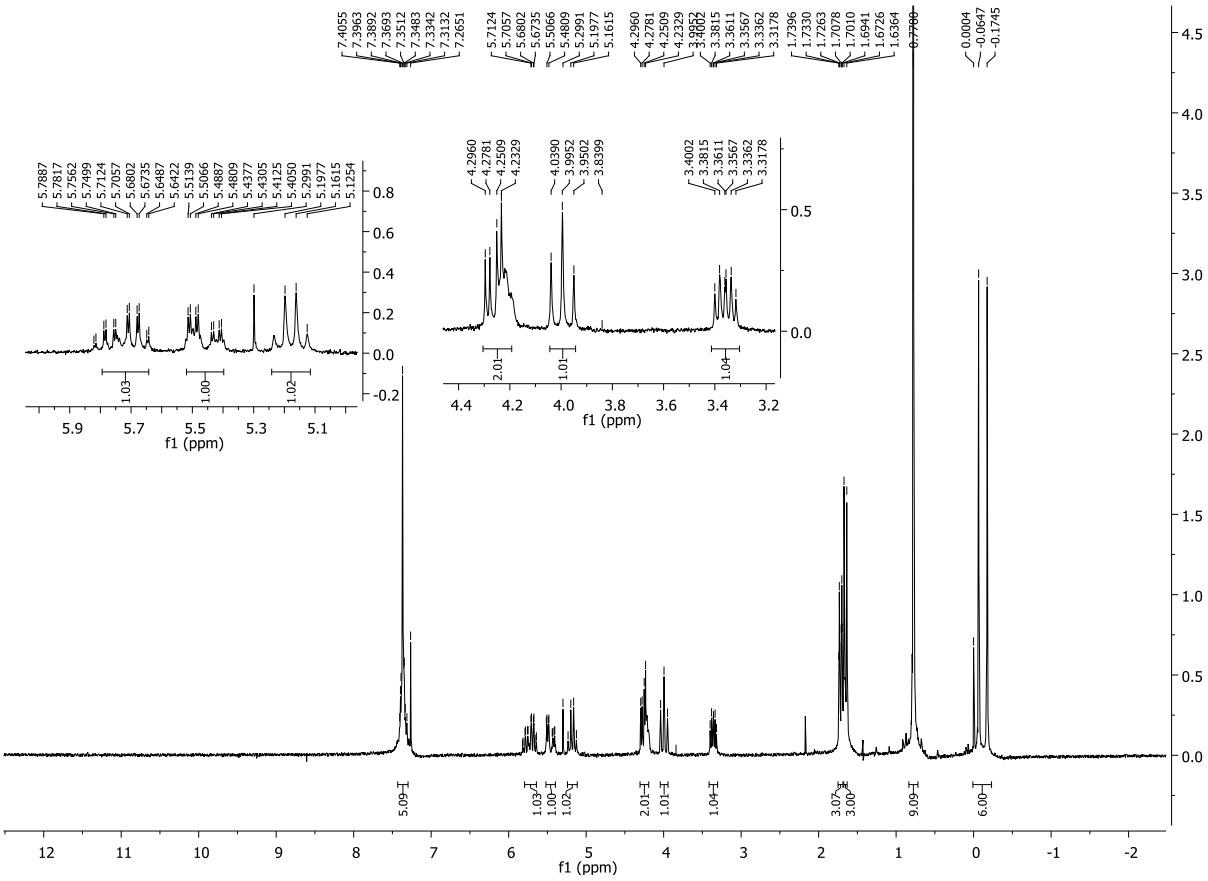
^{1}H NMR ($CDCl_3$, 200MHz) of **9b**



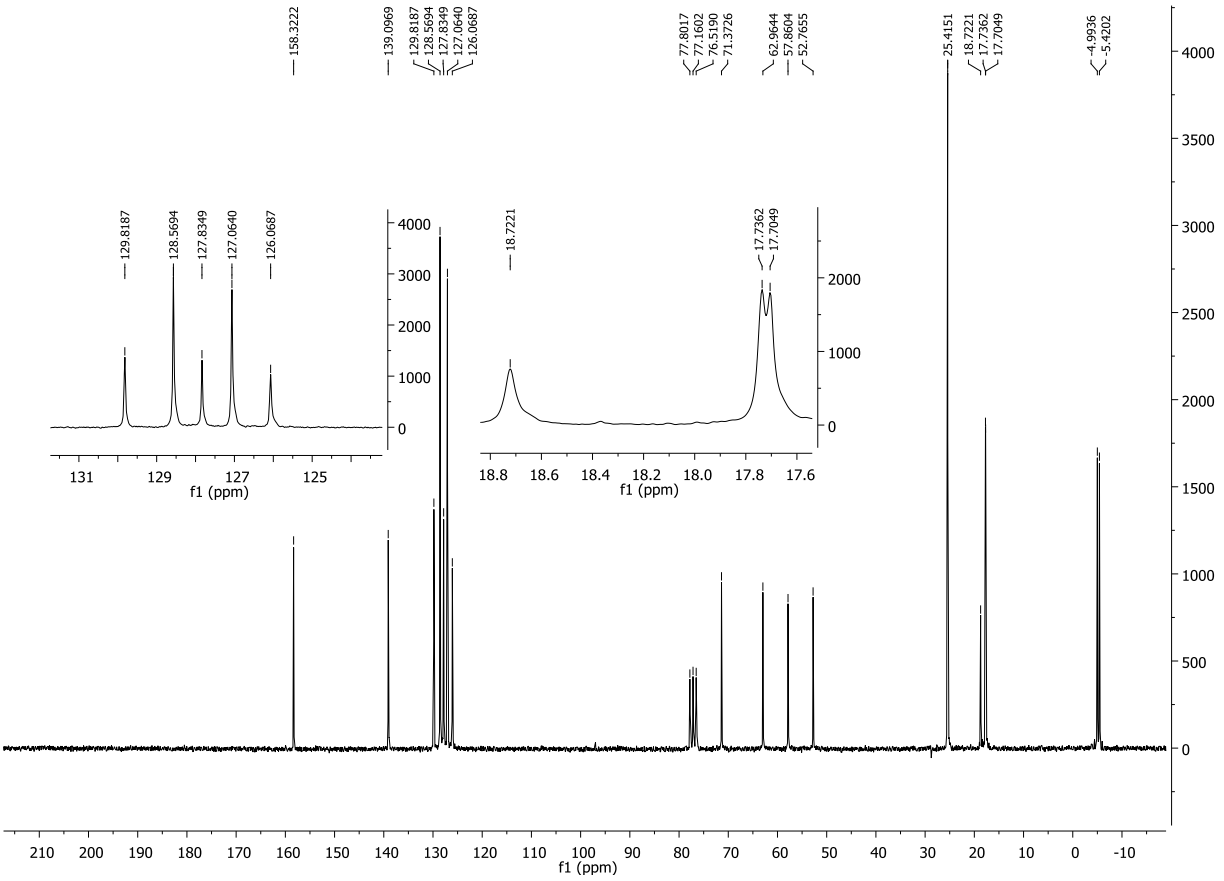
^{13}C NMR ($CDCl_3$, 50 MHz) of **9b**



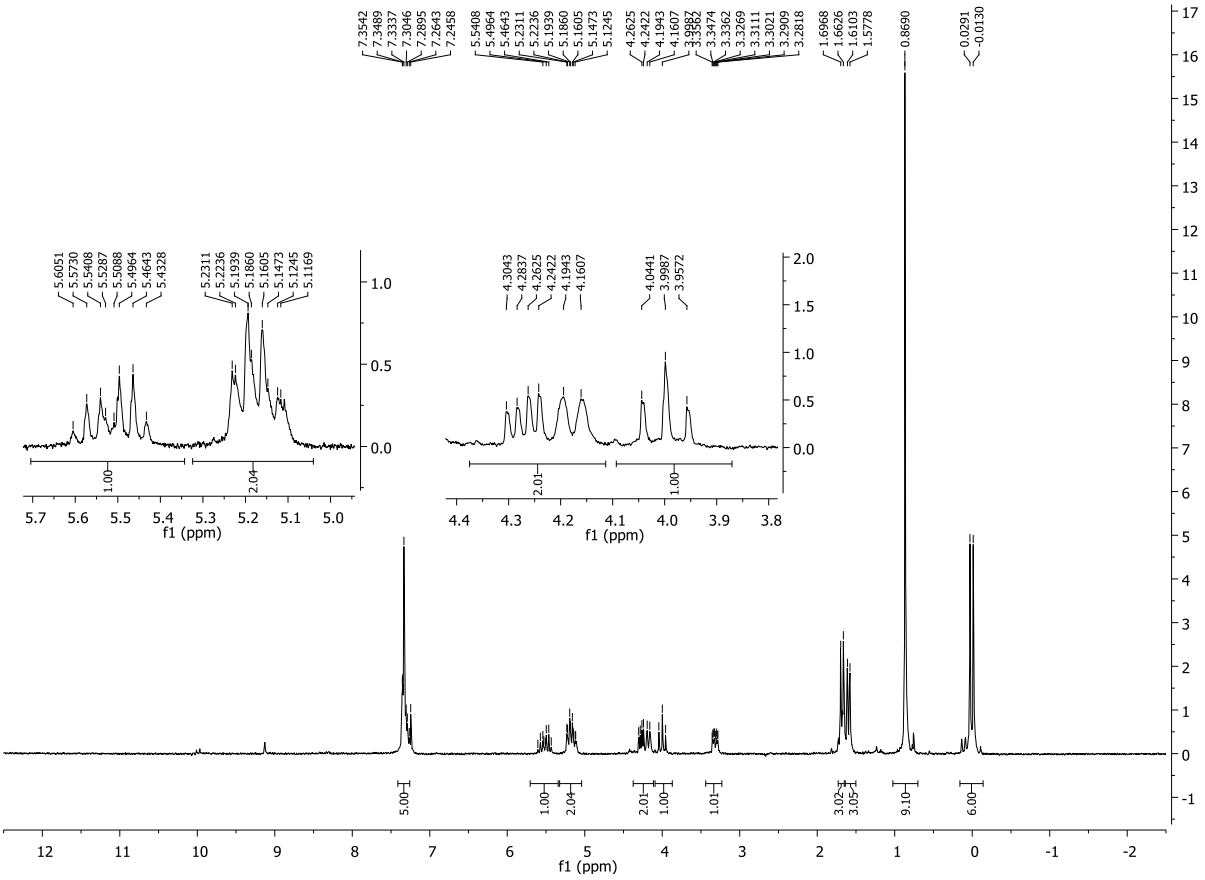
^{1}H NMR ($CDCl_3$, 200MHz) of **10a**



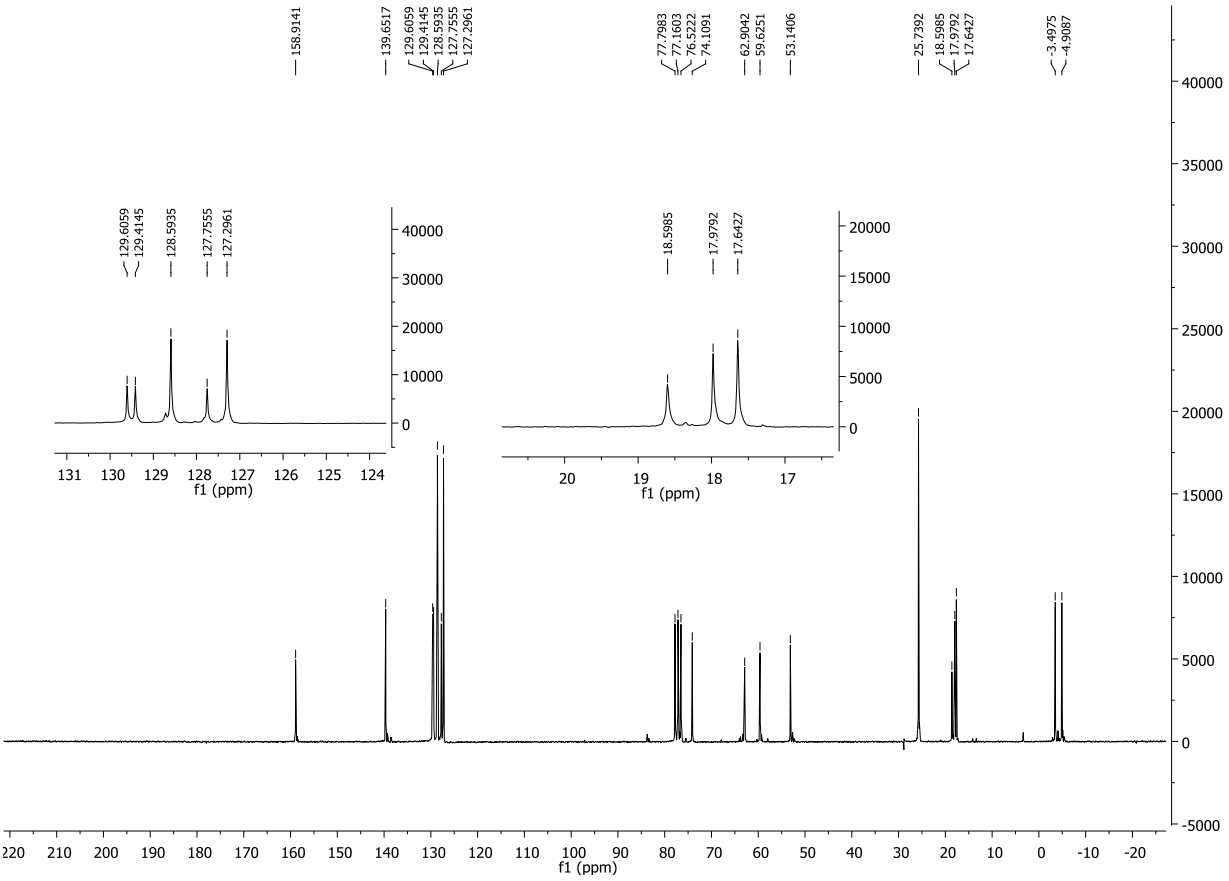
^{13}C NMR ($CDCl_3$, 50 MHz) of **10a**



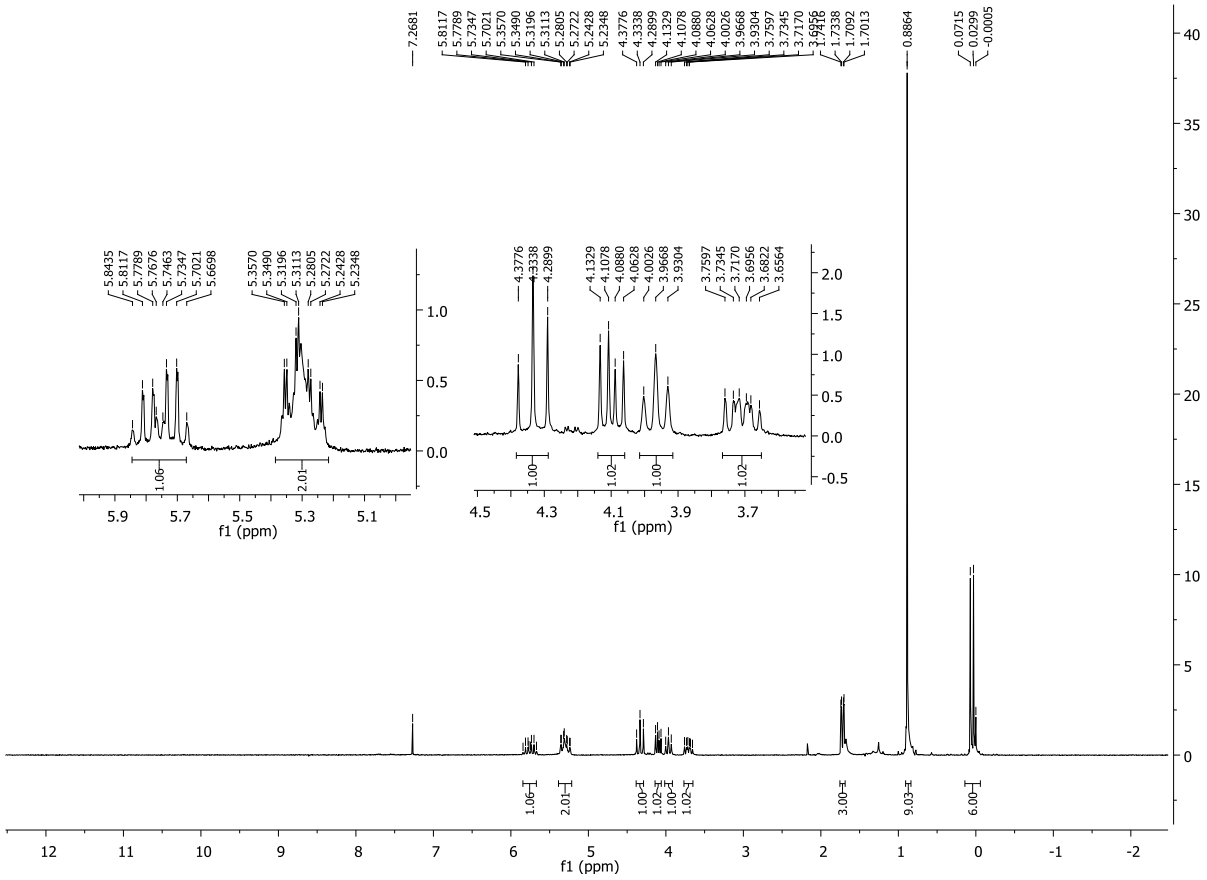
^{1}H NMR ($CDCl_3$, 200MHz) of **10b**



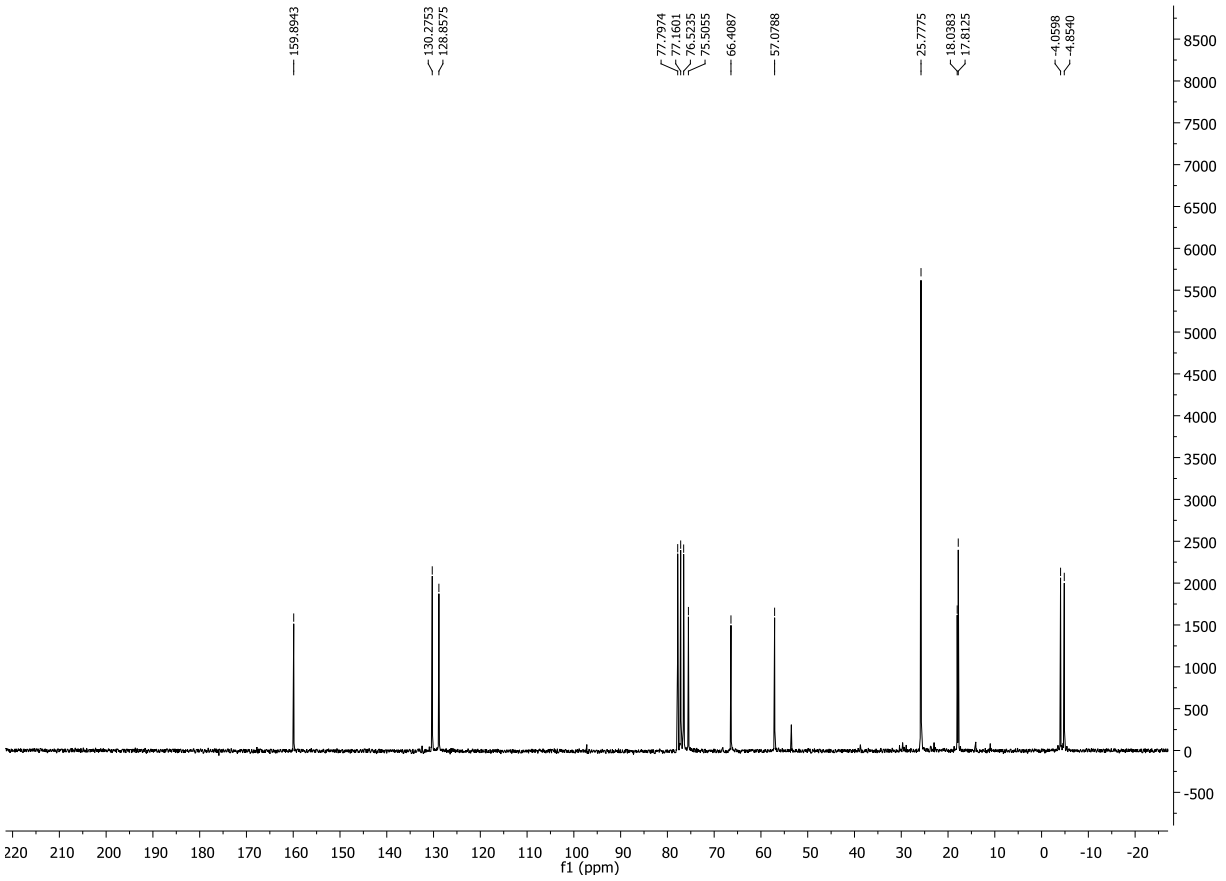
^{13}C NMR ($CDCl_3$, 50 MHz) of **10b**



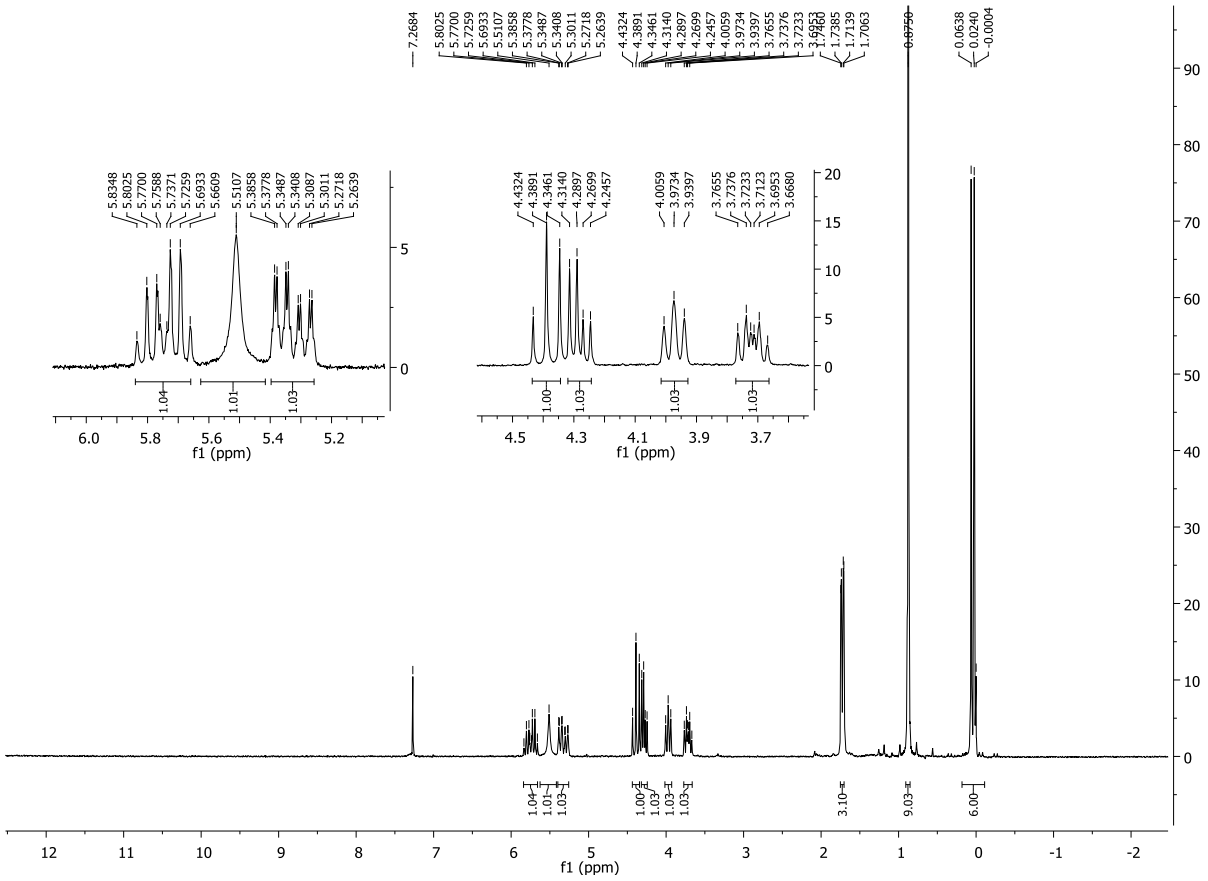
^{1}H NMR ($CDCl_3$, 200MHz) of **11a**



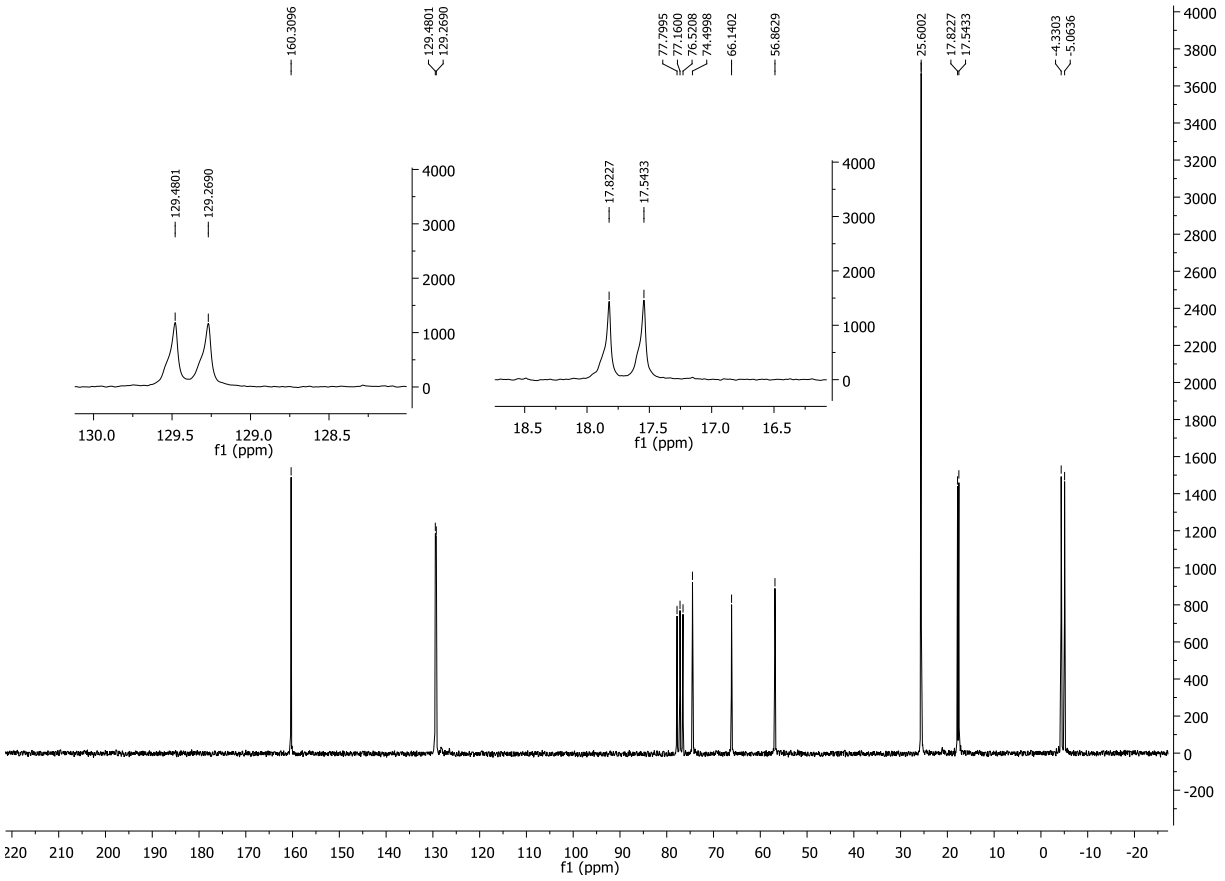
^{13}C NMR ($CDCl_3$, 50 MHz) of **11a**



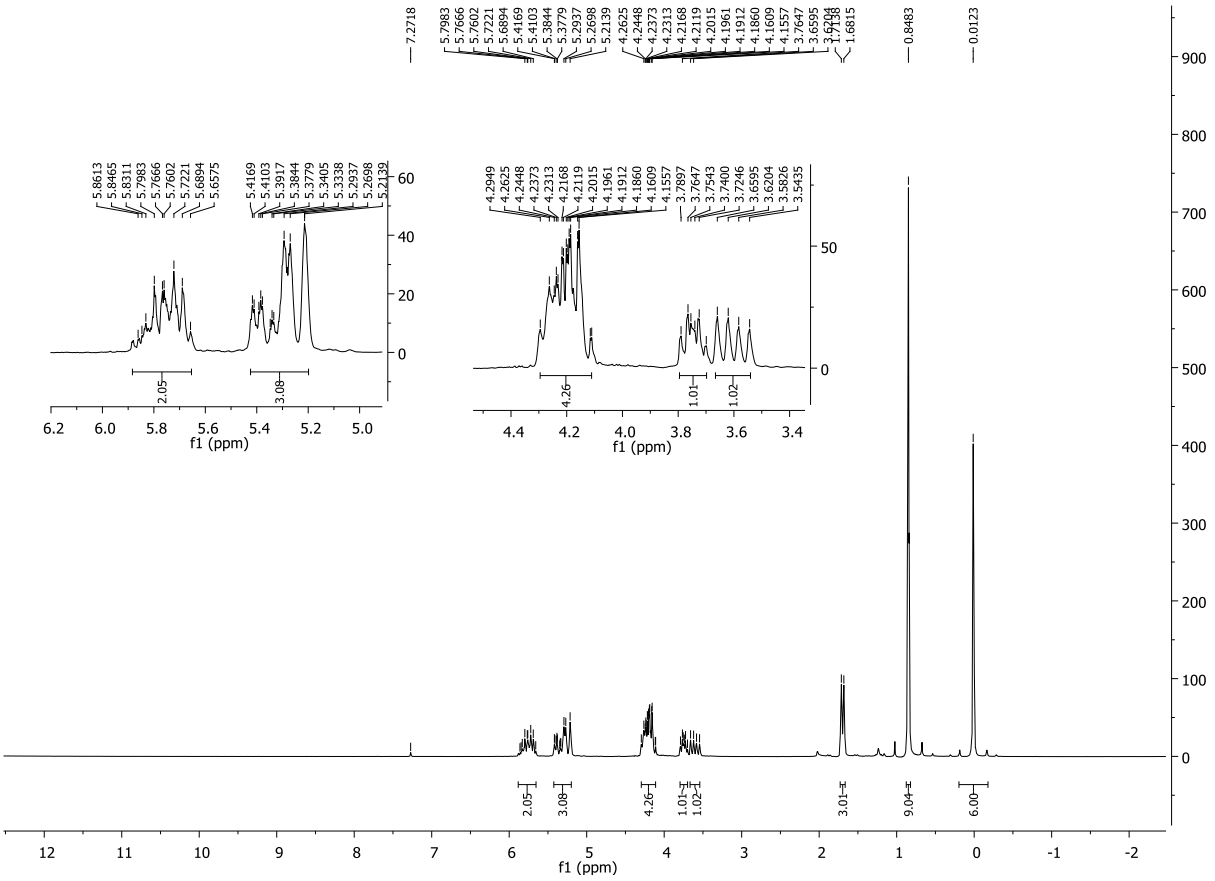
^{1}H NMR ($CDCl_3$, 200MHz) of **11b**



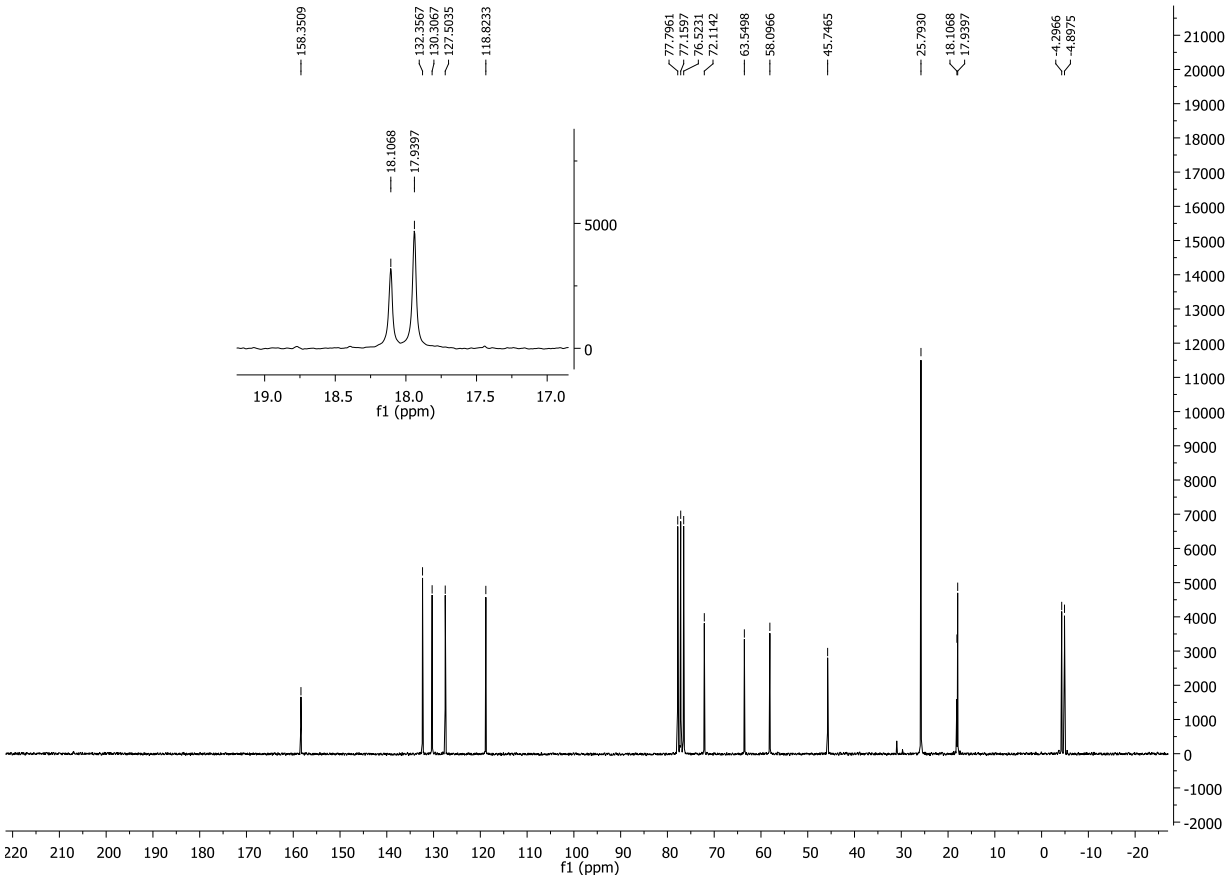
^{13}C NMR ($CDCl_3$, 50 MHz) of **11b**



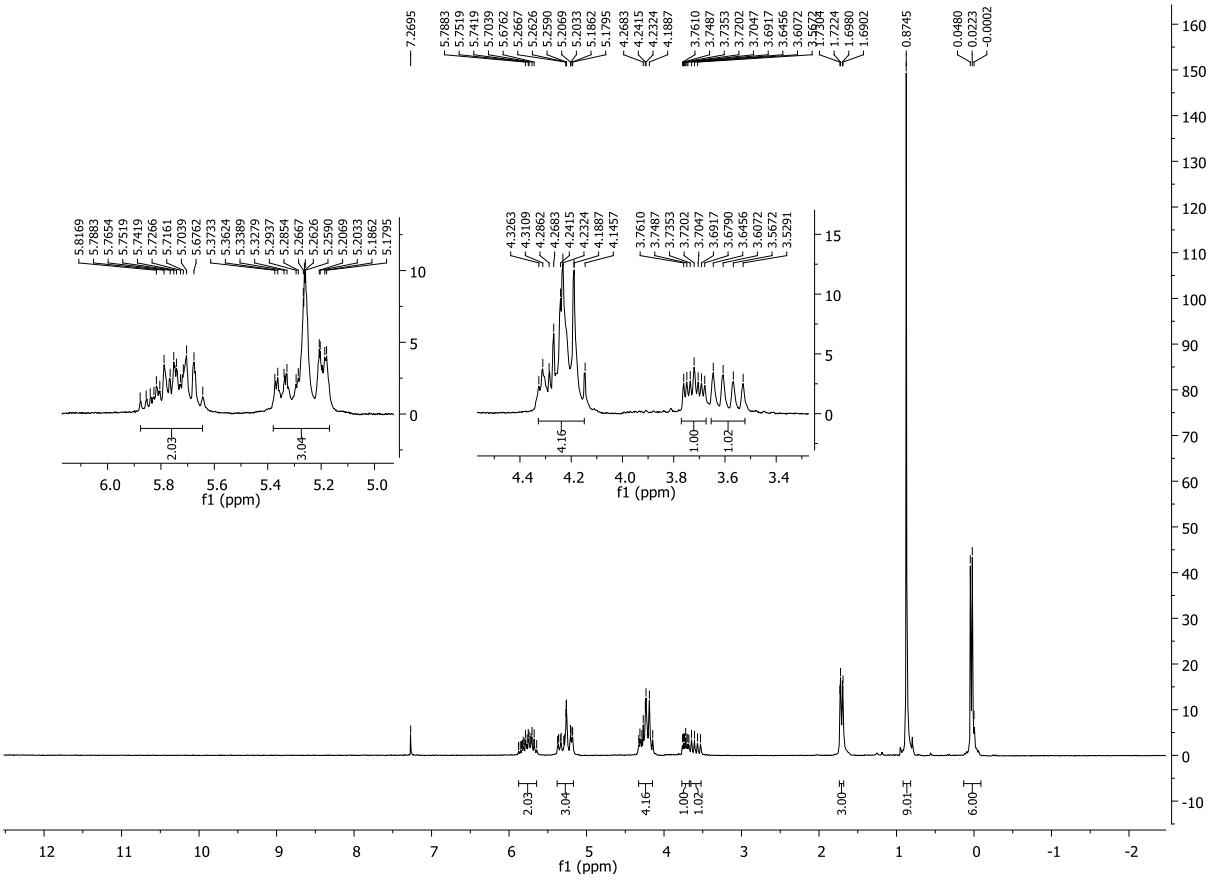
^{1}H NMR ($CDCl_3$, 200MHz) of **12a**



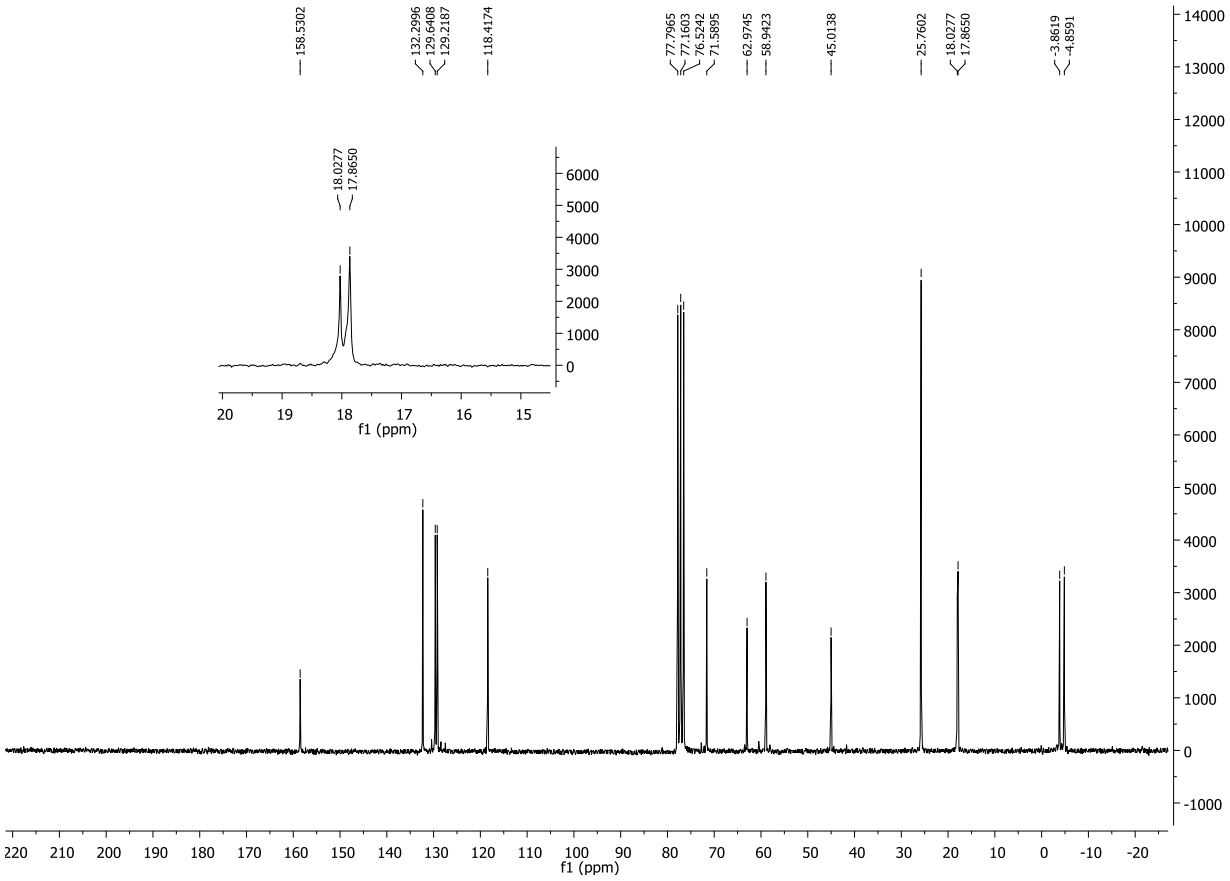
^{13}C NMR ($CDCl_3$, 50 MHz) of **12a**



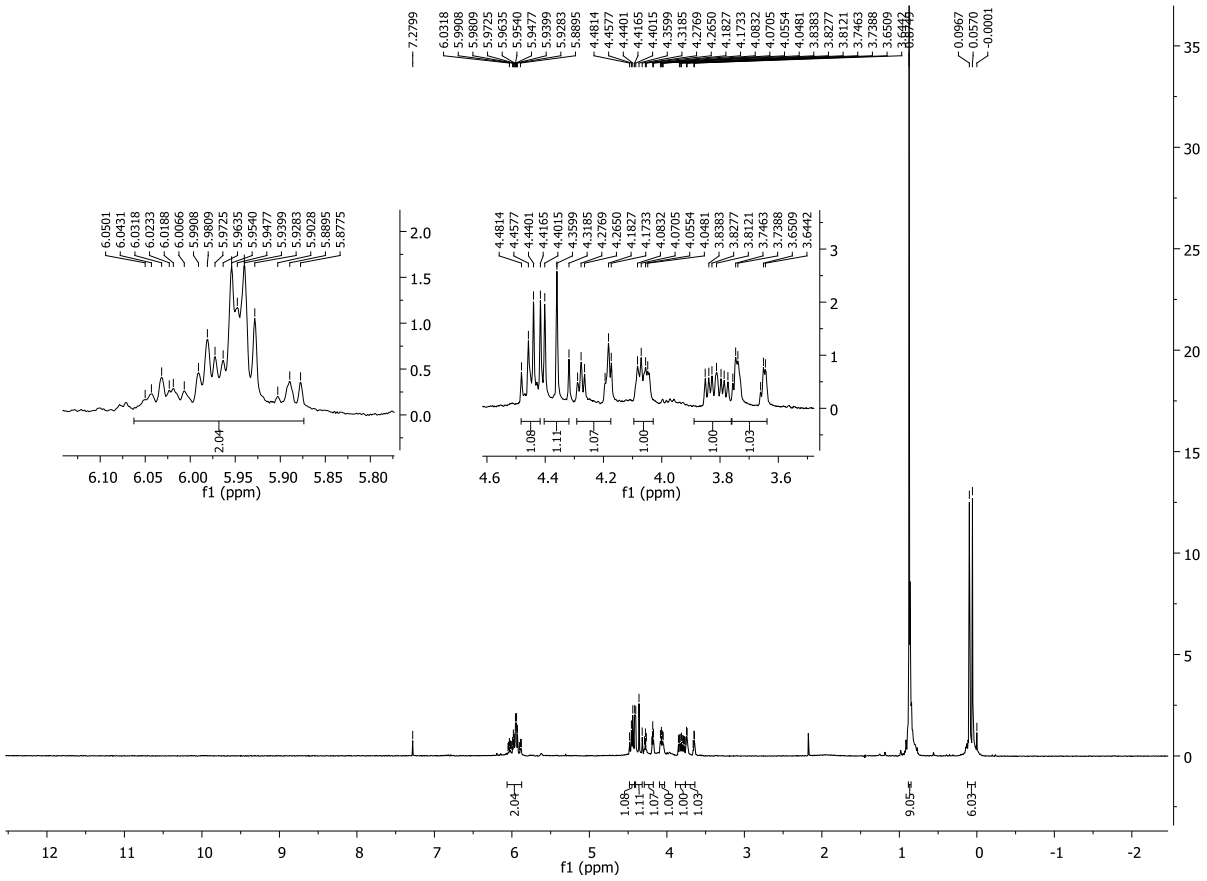
^{1}H NMR ($CDCl_3$, 200MHz) of **12b**



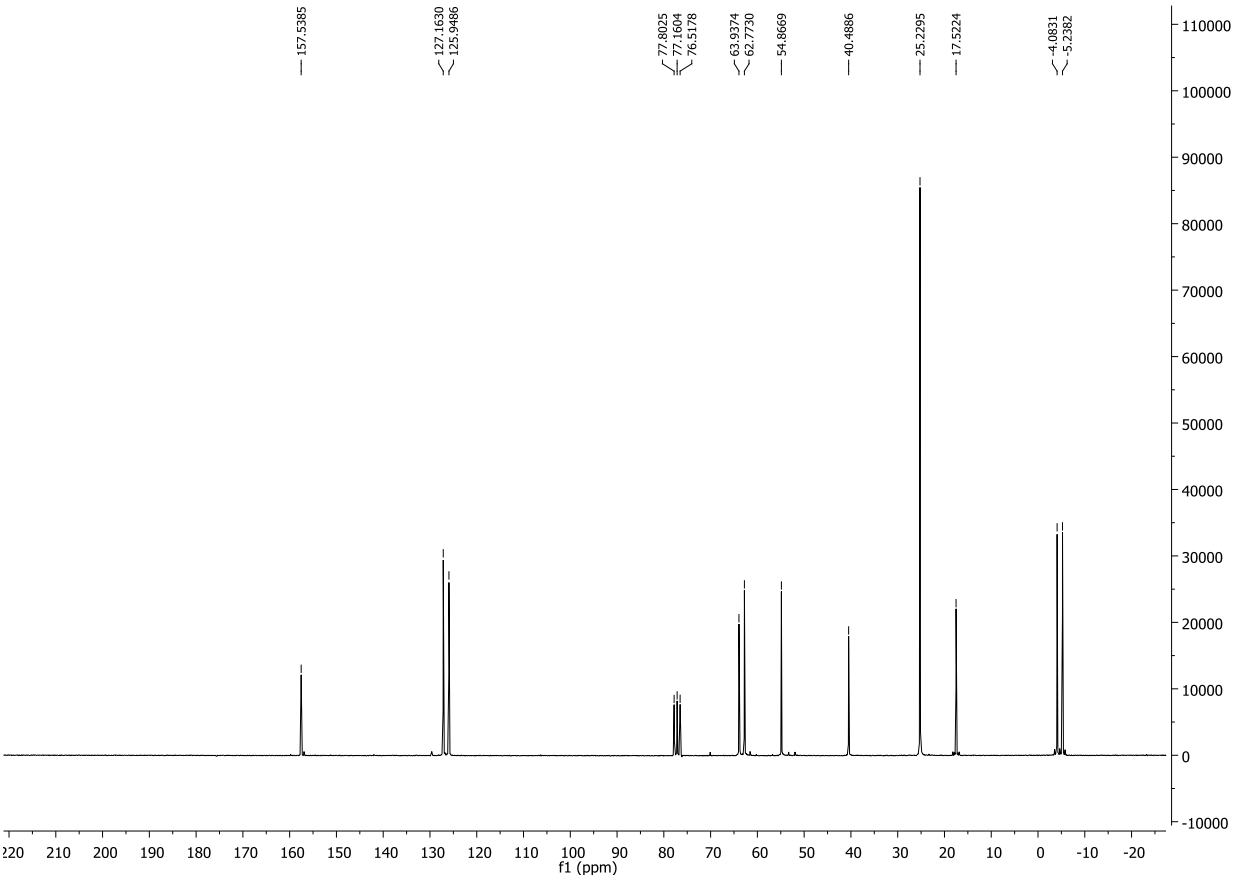
^{13}C NMR ($CDCl_3$, 50 MHz) of **12b**



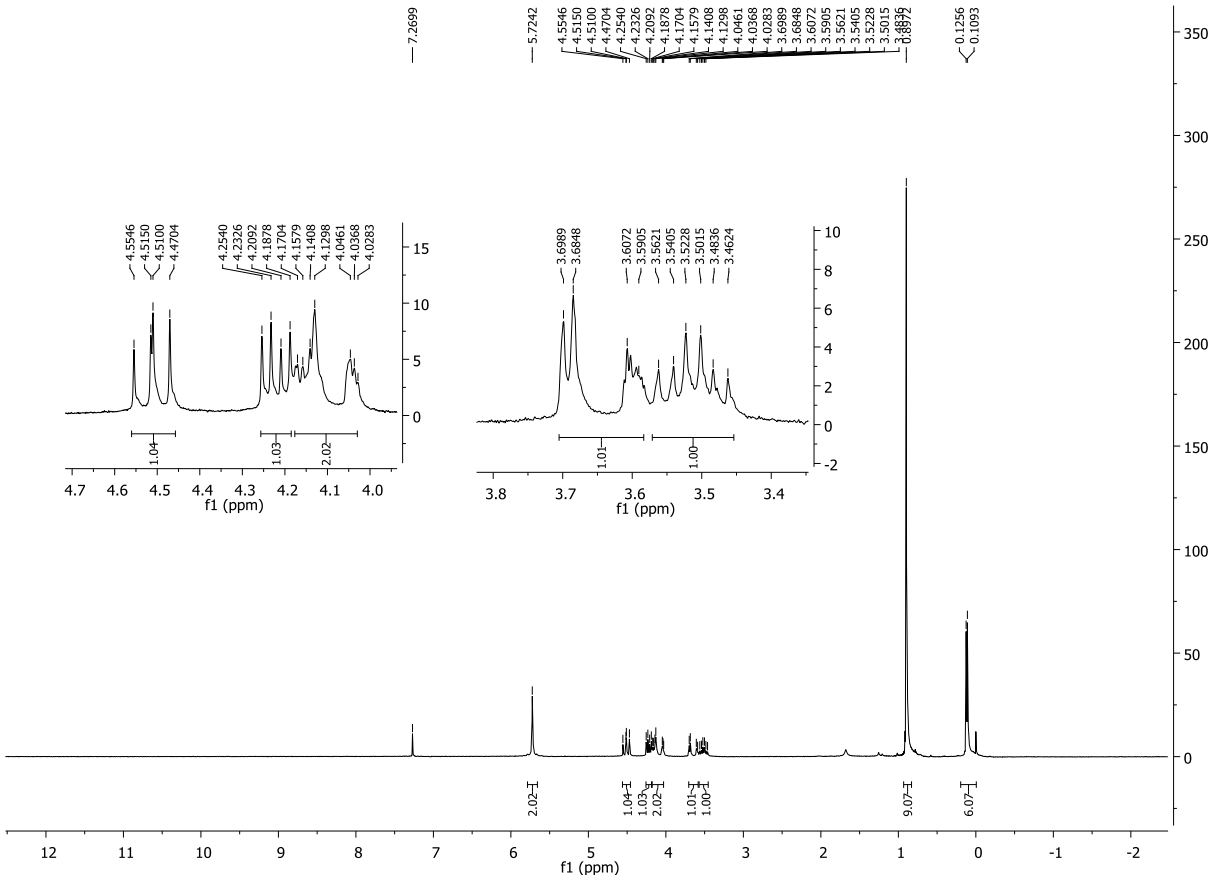
^{1}H NMR ($CDCl_3$, 200MHz) of **13a**



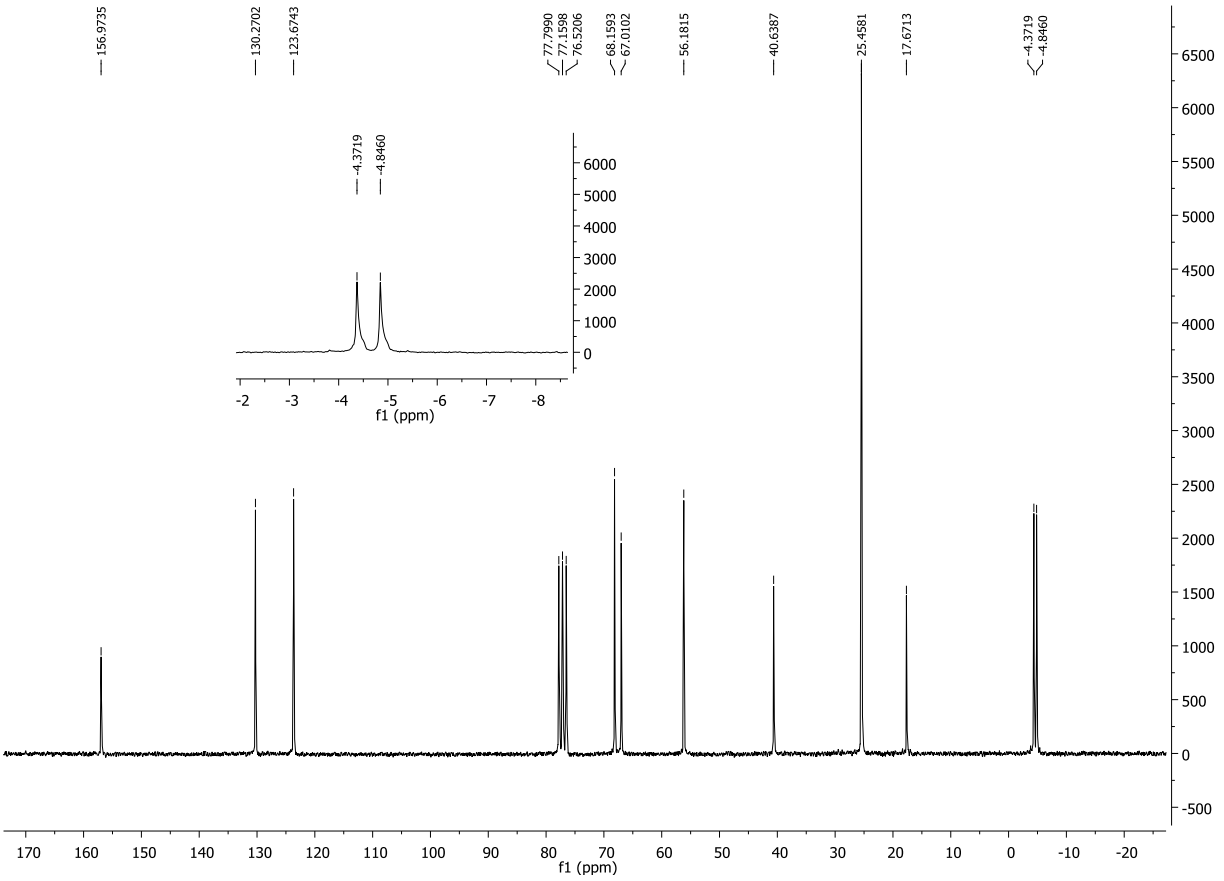
^{13}C NMR ($CDCl_3$, 50 MHz) of **13a**



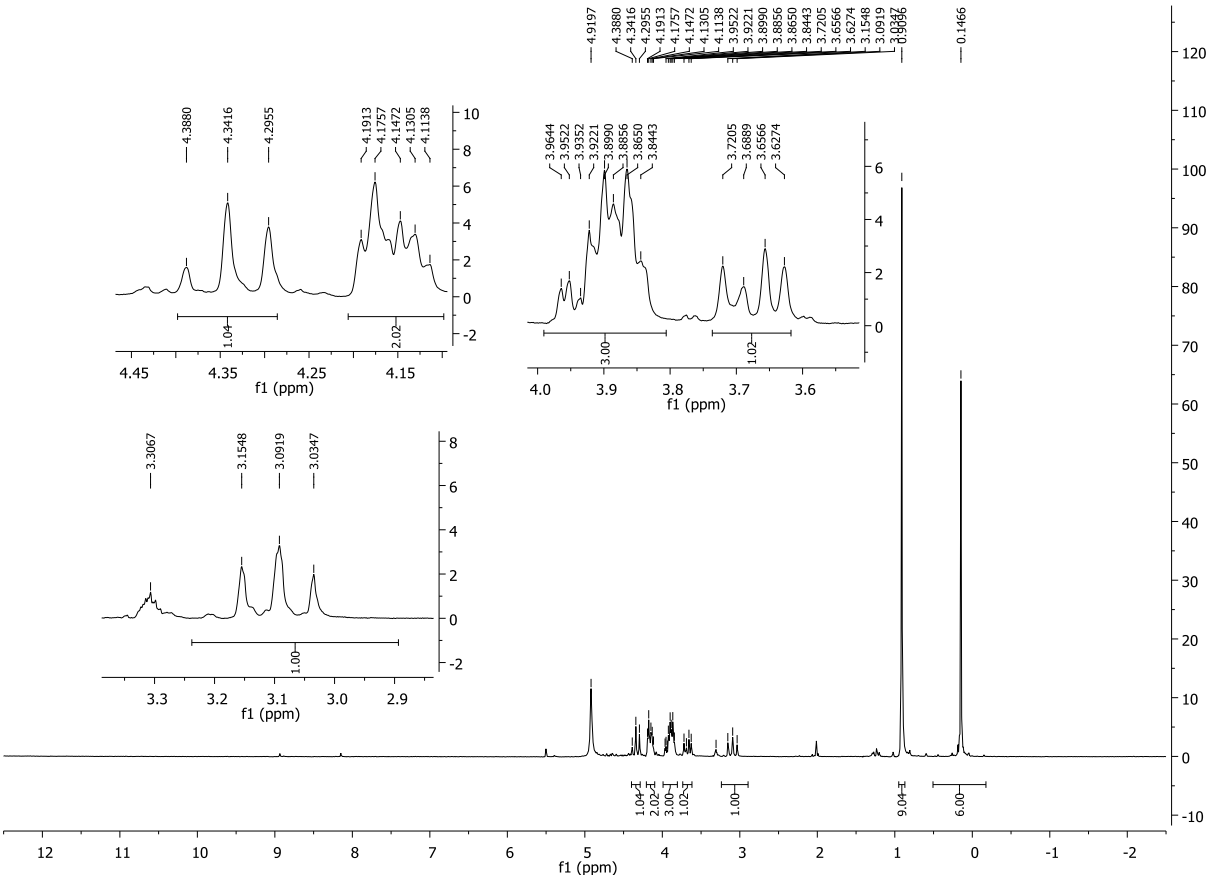
^{1}H NMR ($CDCl_3$, 200MHz) of **13b**



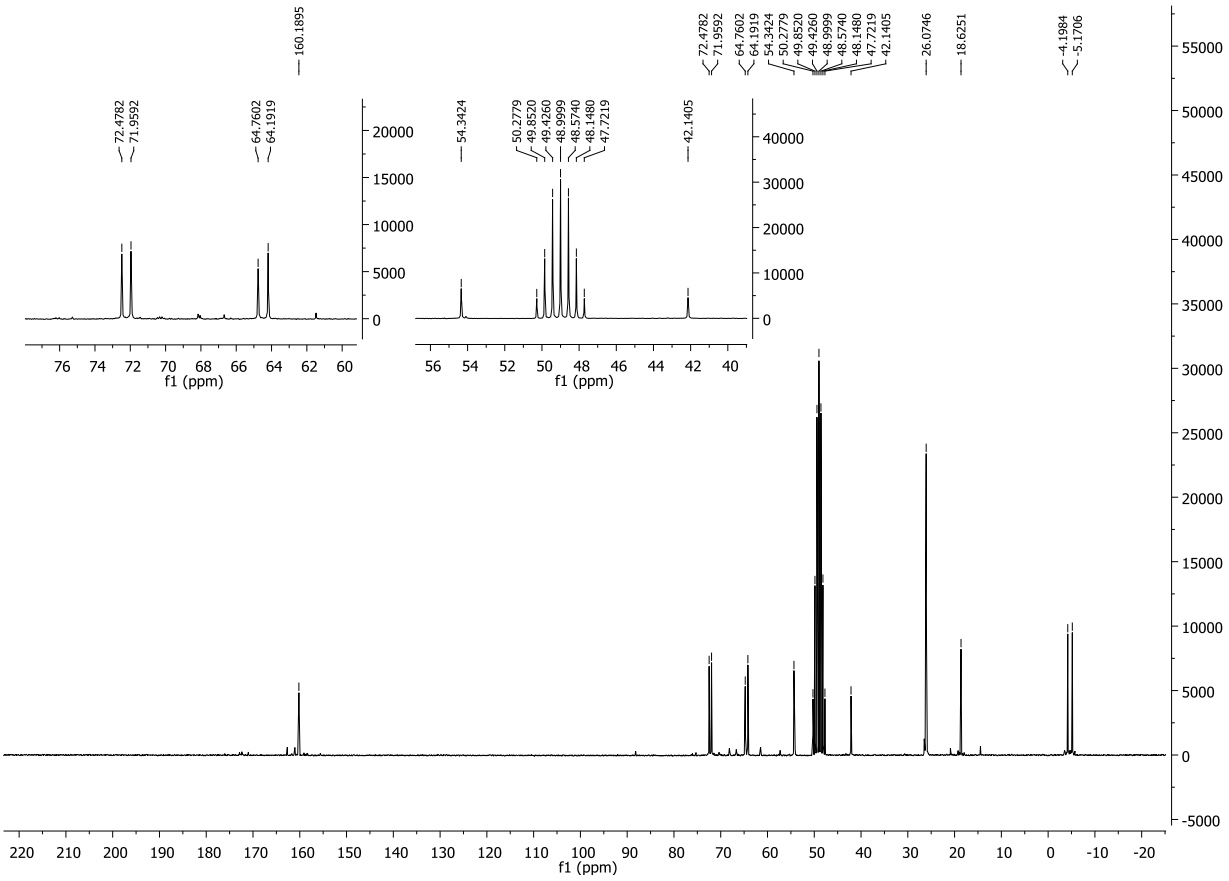
^{13}C NMR ($CDCl_3$, 50 MHz) of **13b**



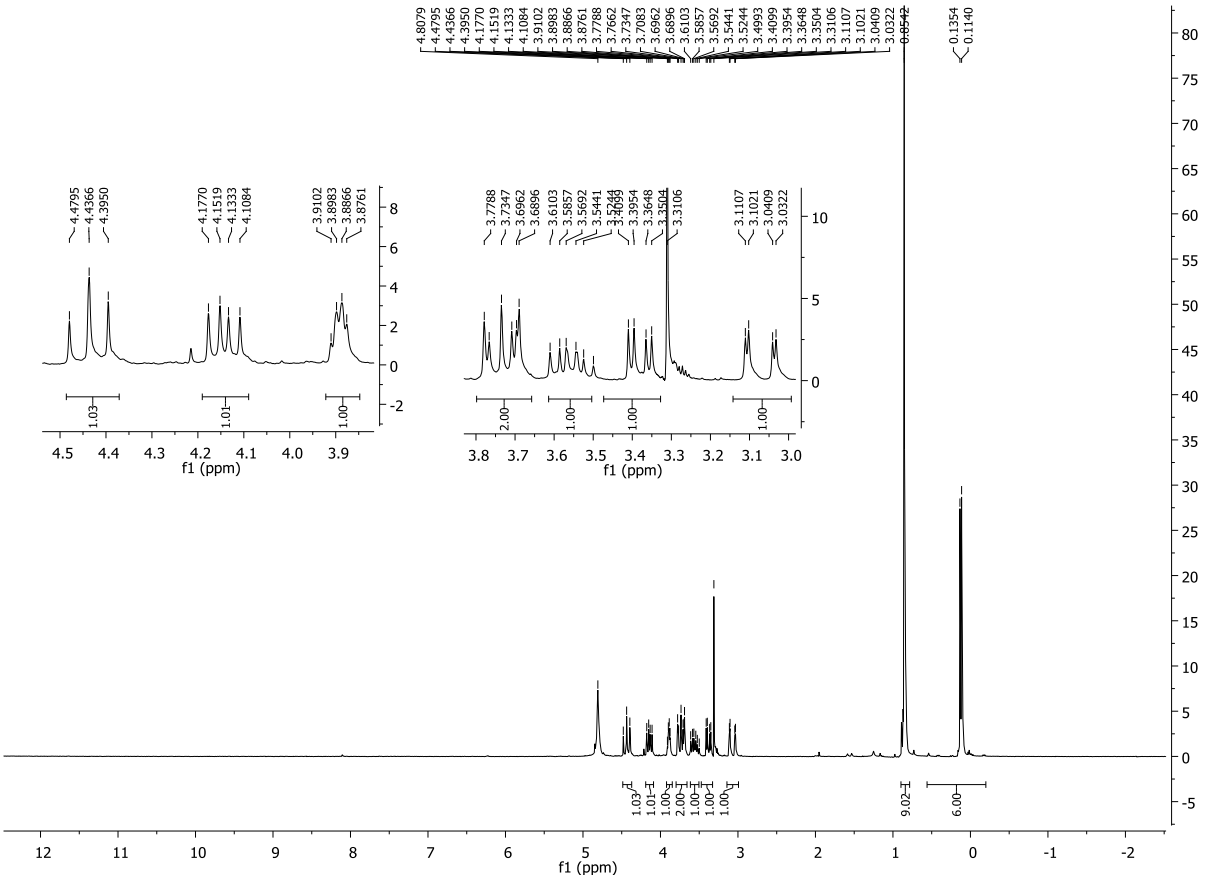
^{1}H NMR (CD_3OD, 200MHz) of **14a**



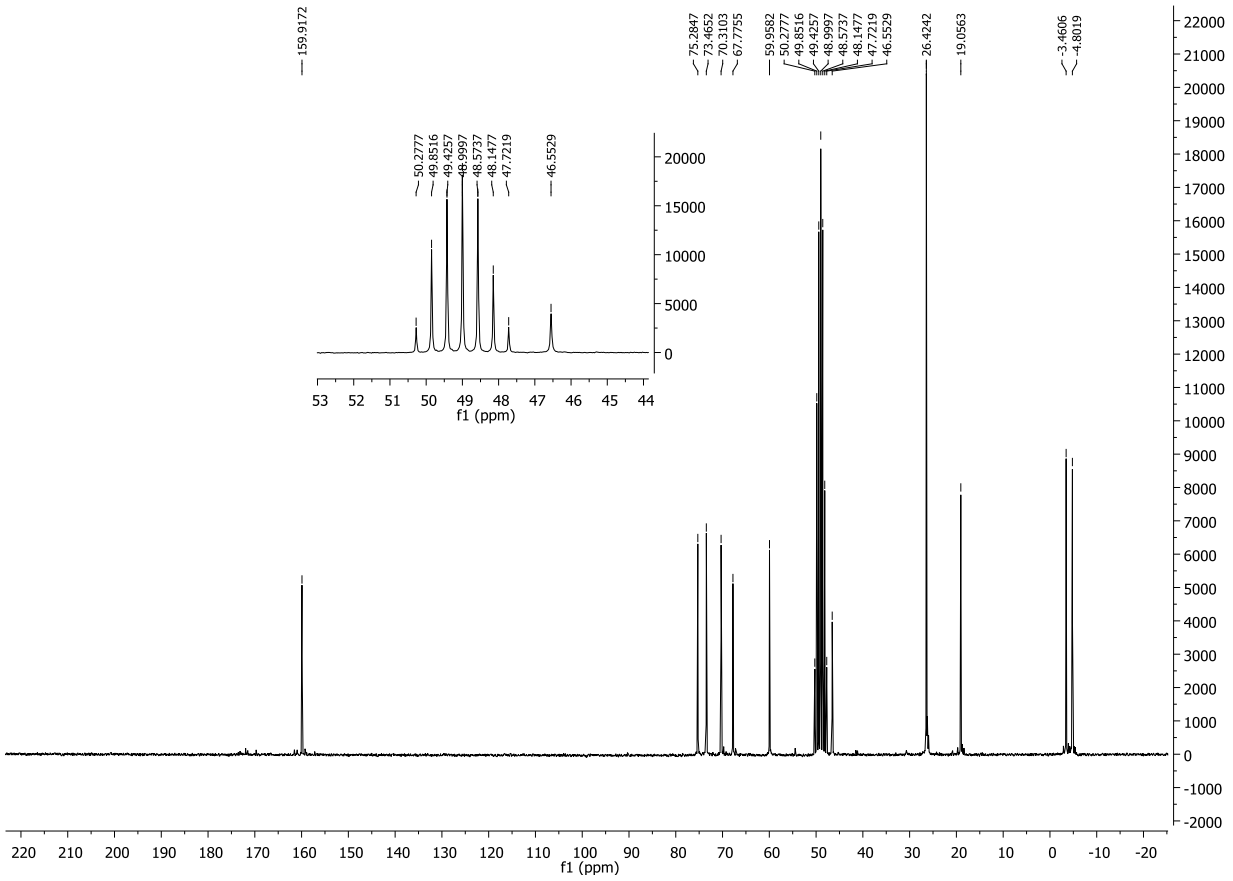
^{13}C NMR (CD_3OD, 50 MHz) of **14a**



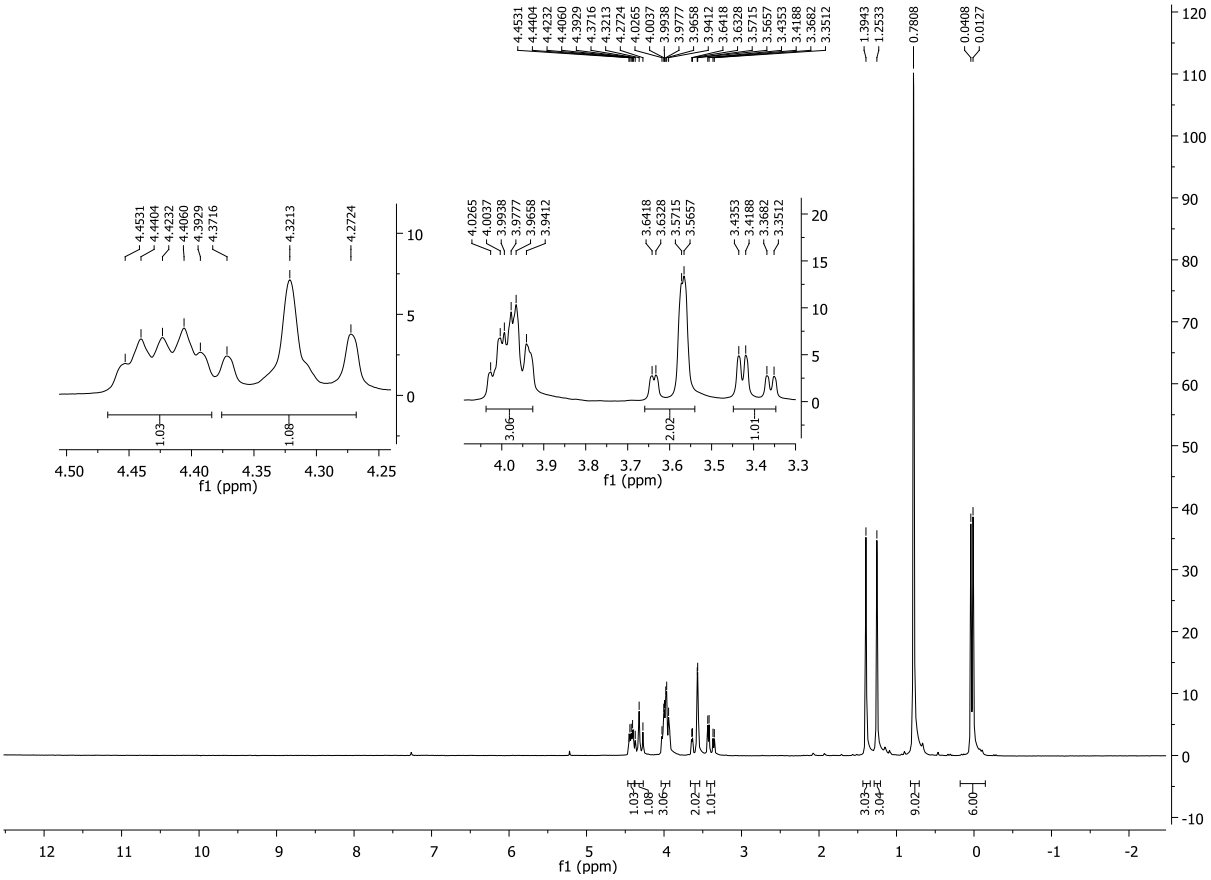
^{1}H NMR (CD_3OD, 200MHz) of **14d**



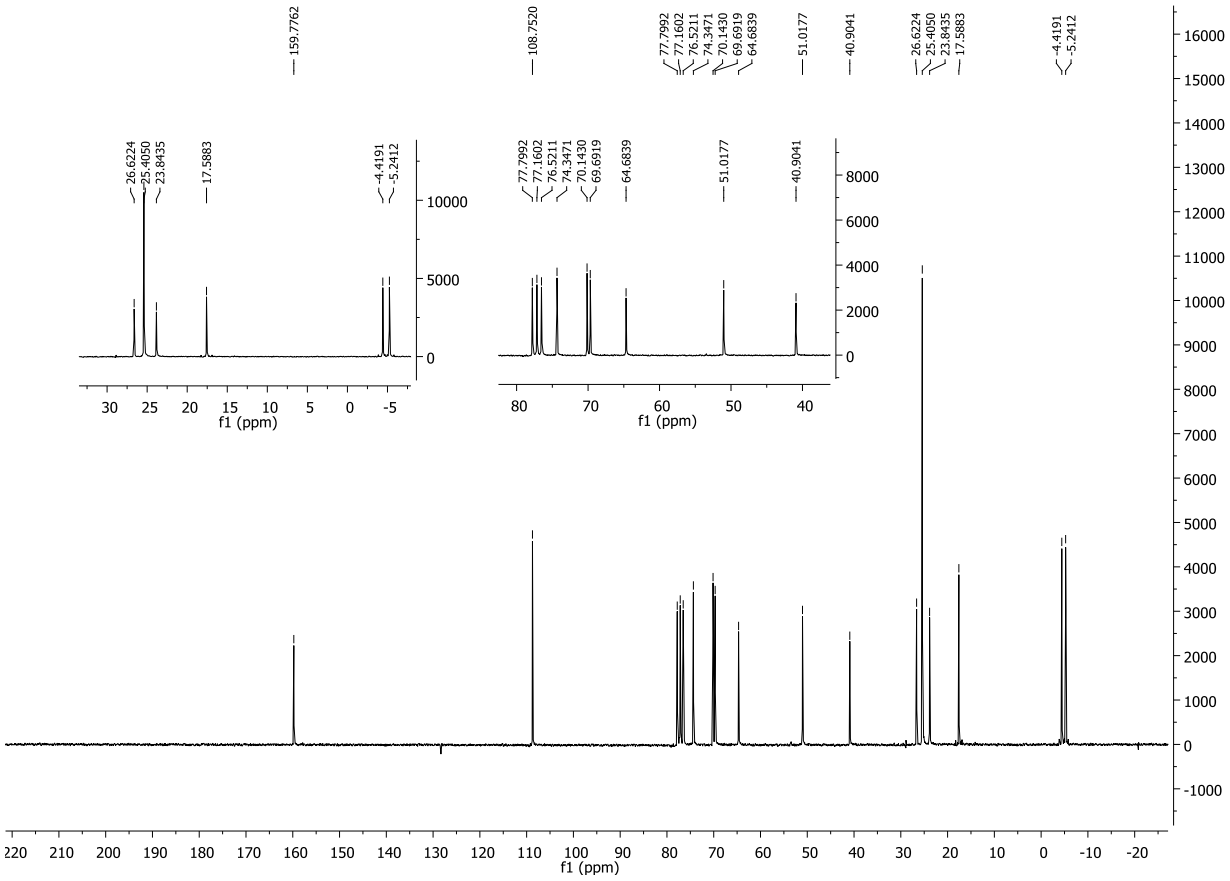
^{13}C NMR (CD_3OD, 50 MHz) of **14d**



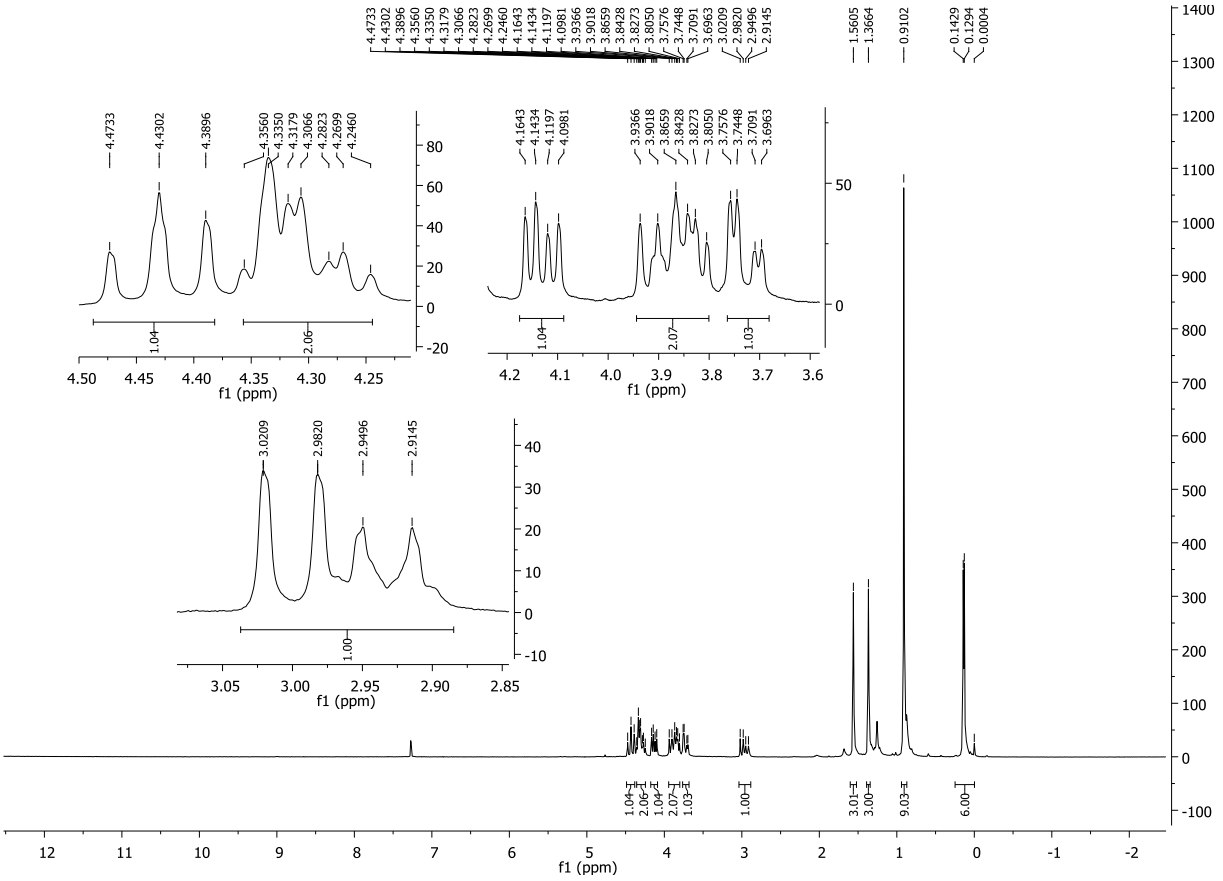
^{1}H NMR ($CDCl_3$, 200MHz) of **15a**



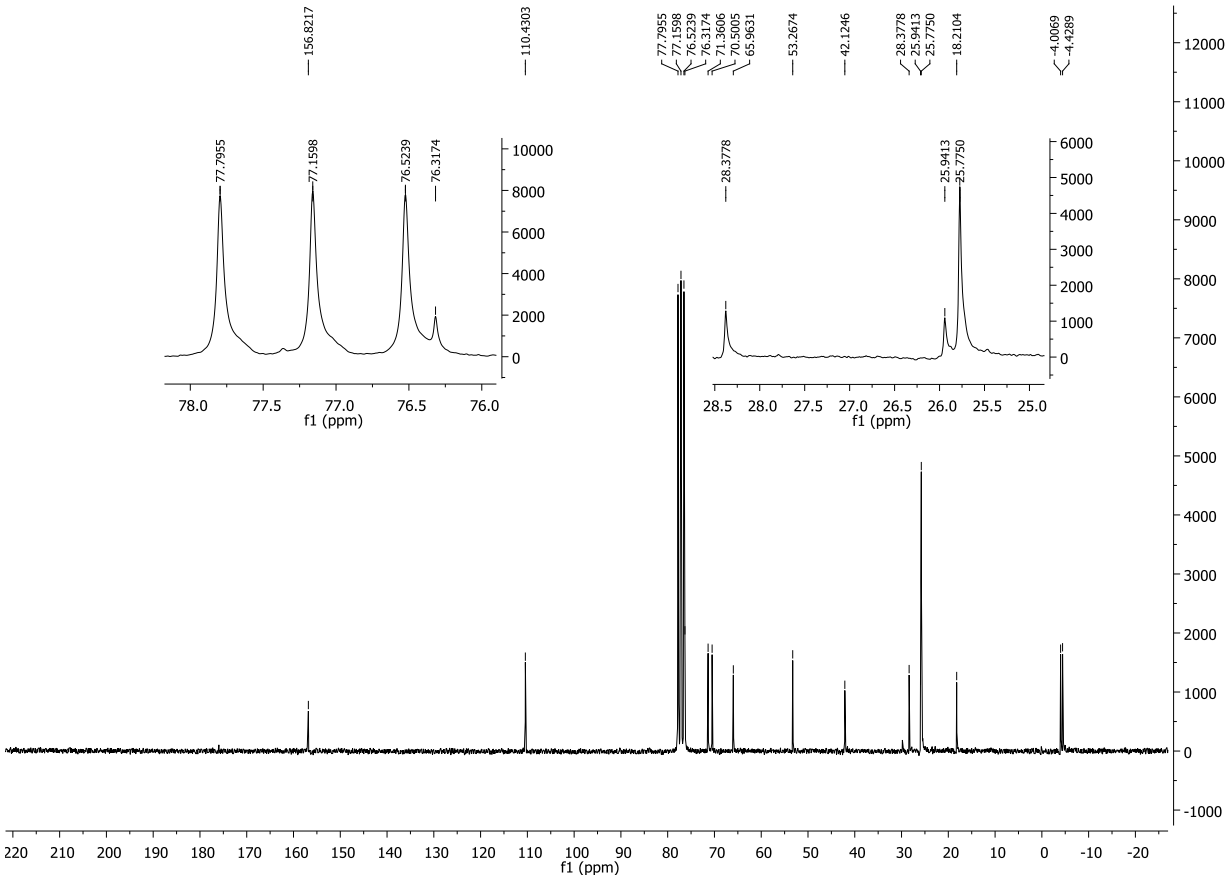
^{13}C NMR ($CDCl_3$, 50 MHz) of **15a**



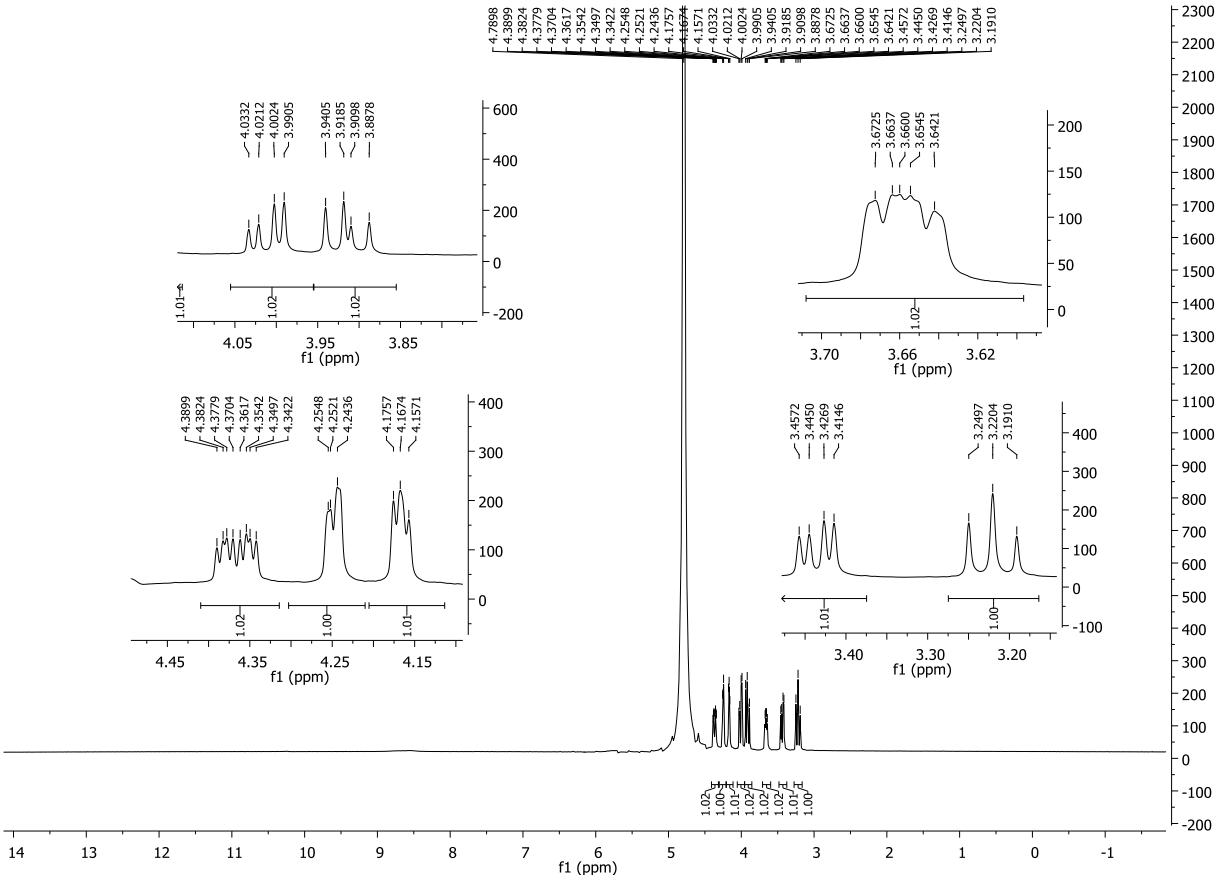
^{1}H NMR ($CDCl_3$, 200MHz) of **15d**



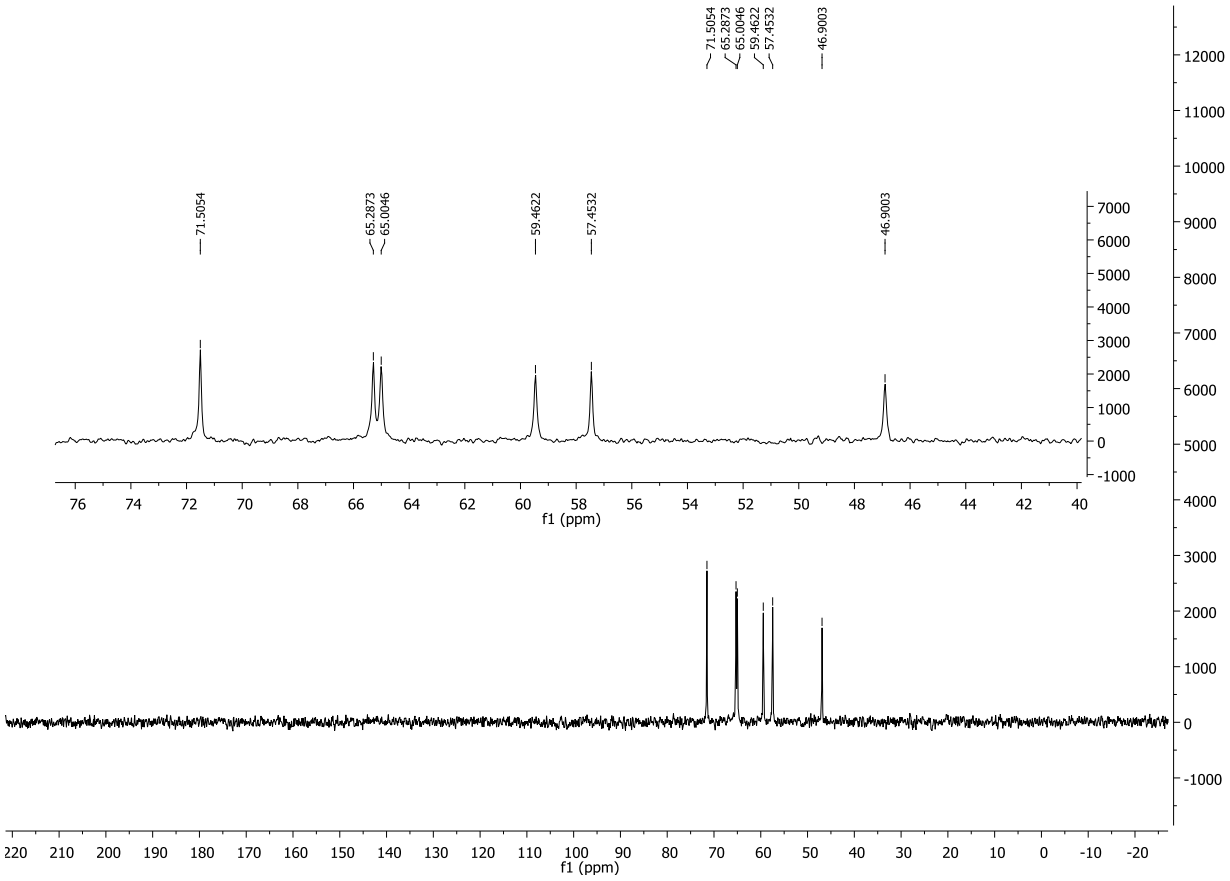
^{13}C NMR ($CDCl_3$, 50 MHz) of **15d**



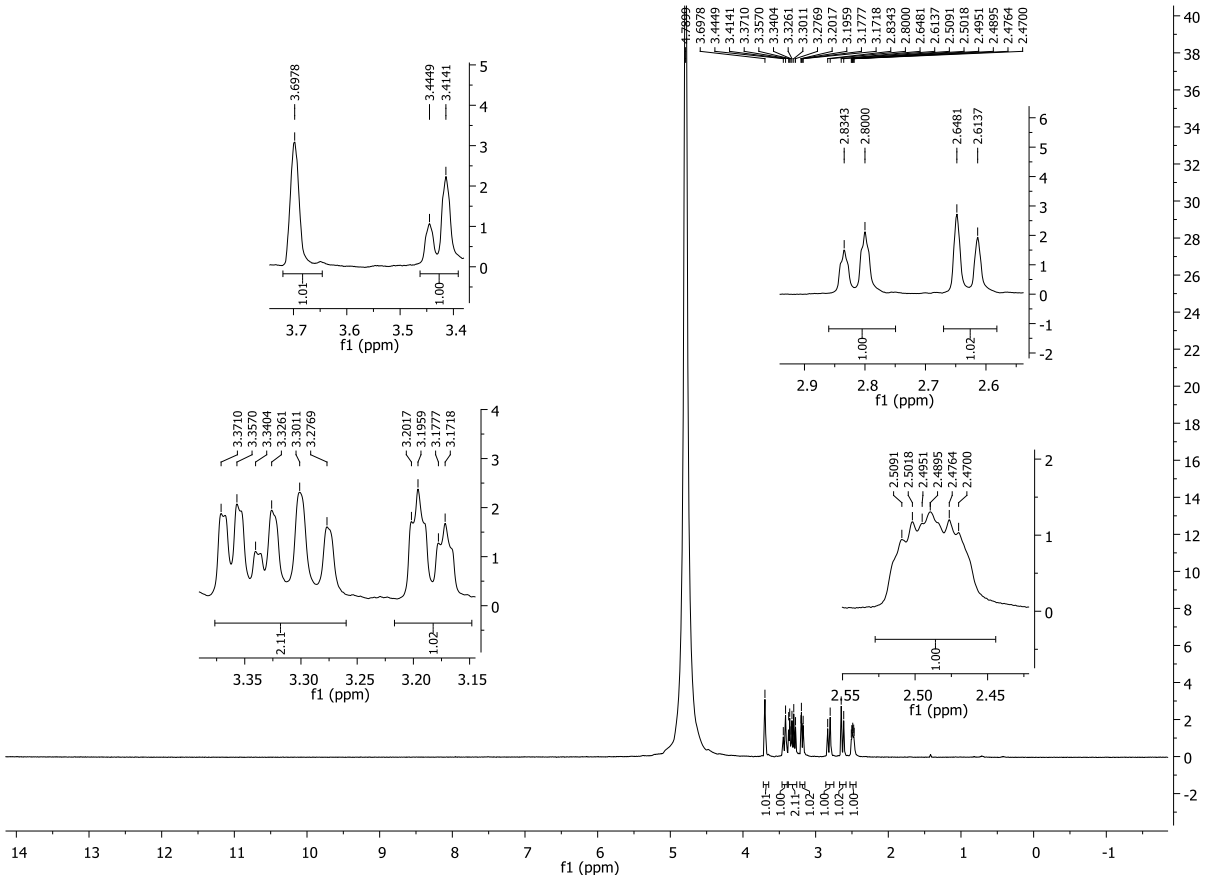
^{1}H NMR (D_2O, 400MHz) of **1a**



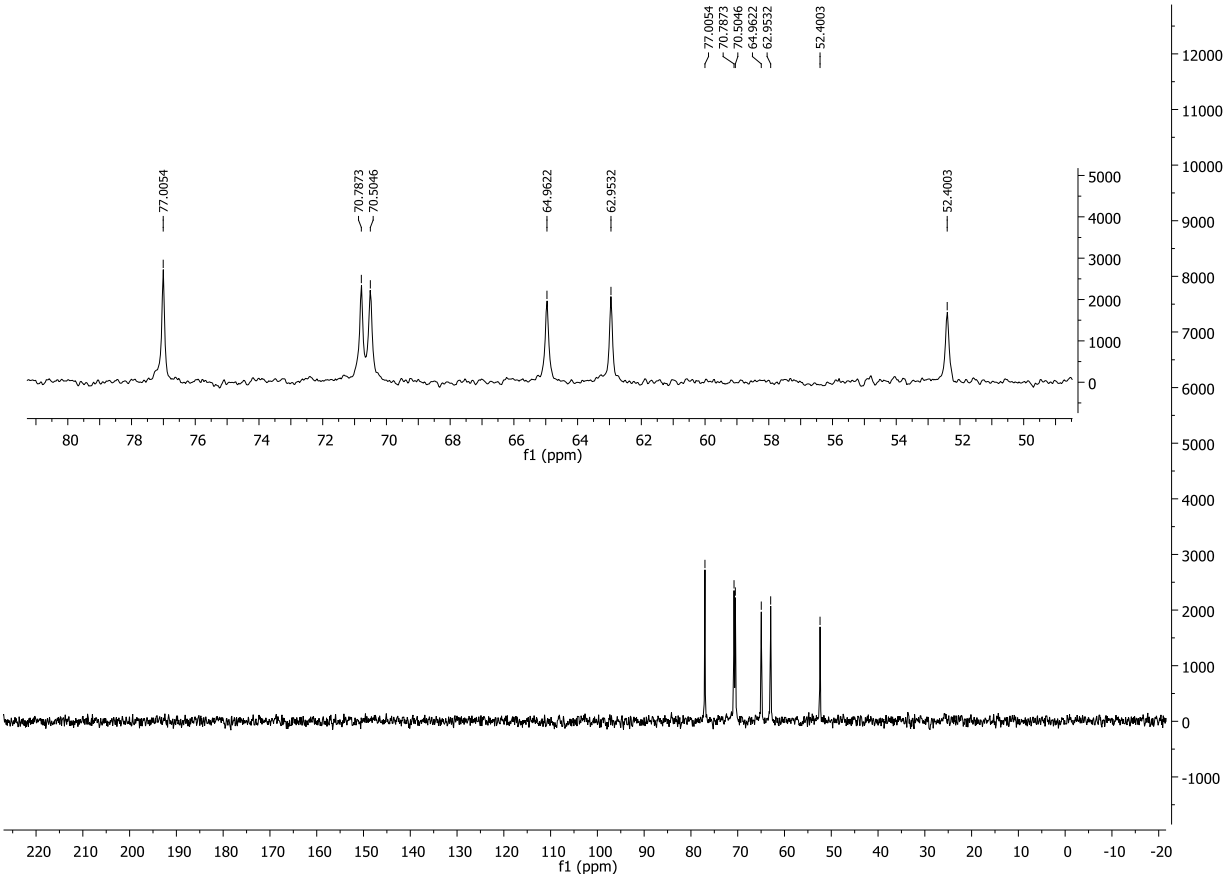
^{13}C NMR (D_2O, 50 MHz) of **1a**



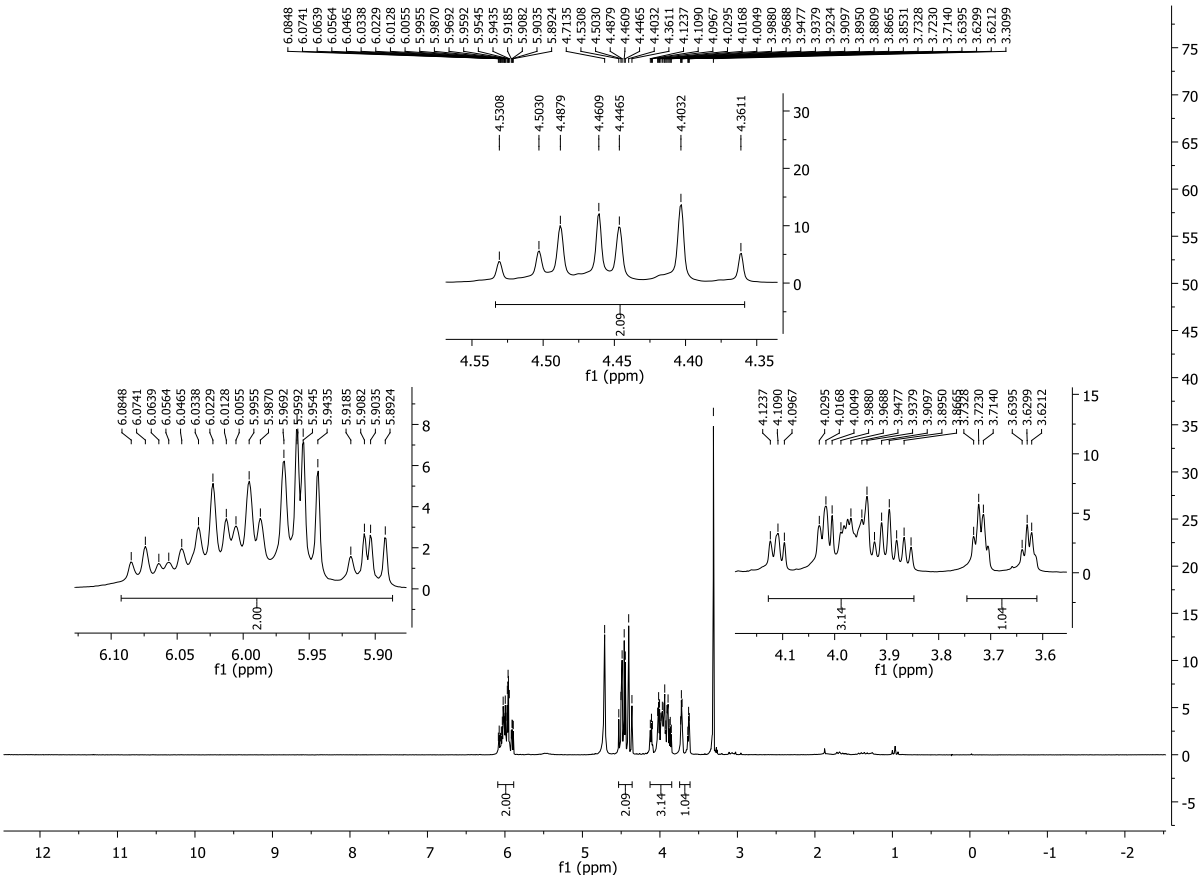
^{1}H NMR (D_2O, 400MHz) of **1d**



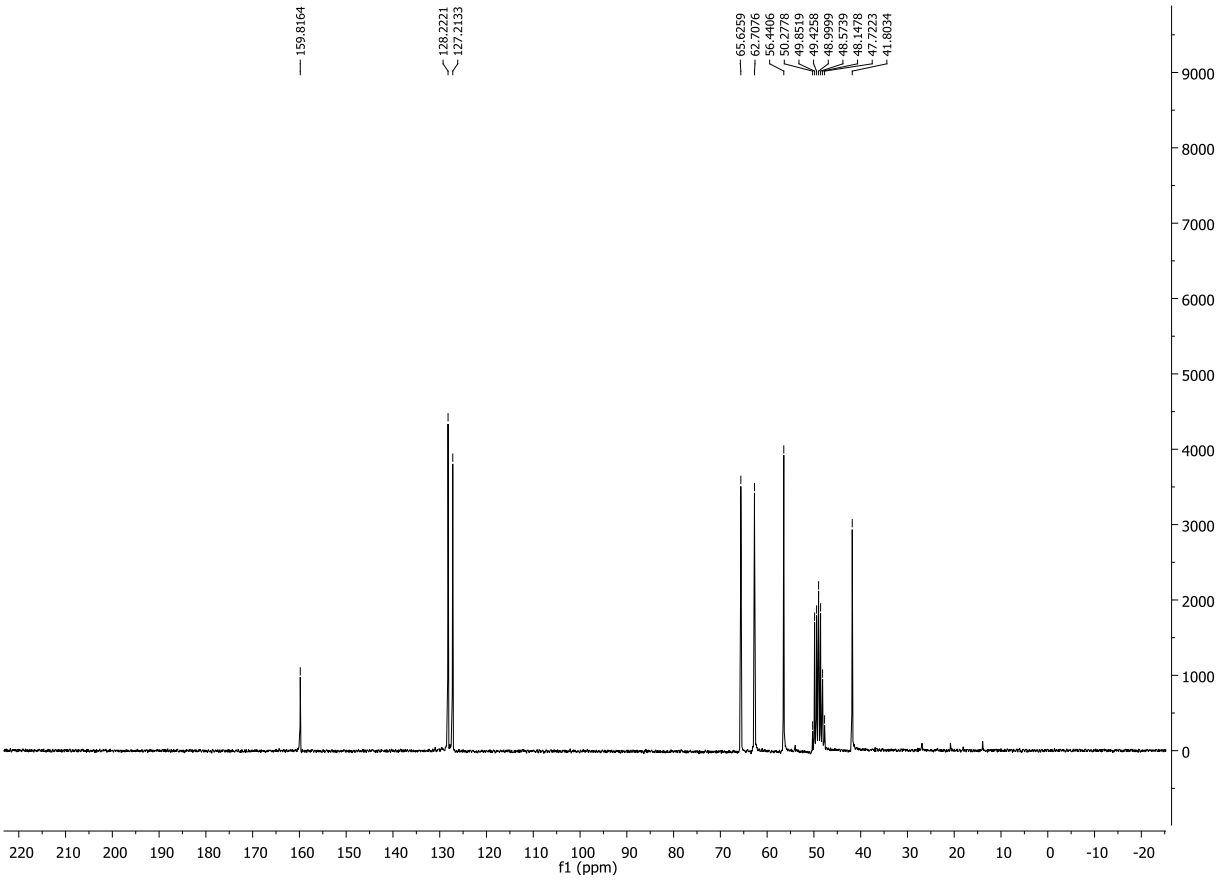
^{13}C NMR (D_2O, 50 MHz) of **1d**



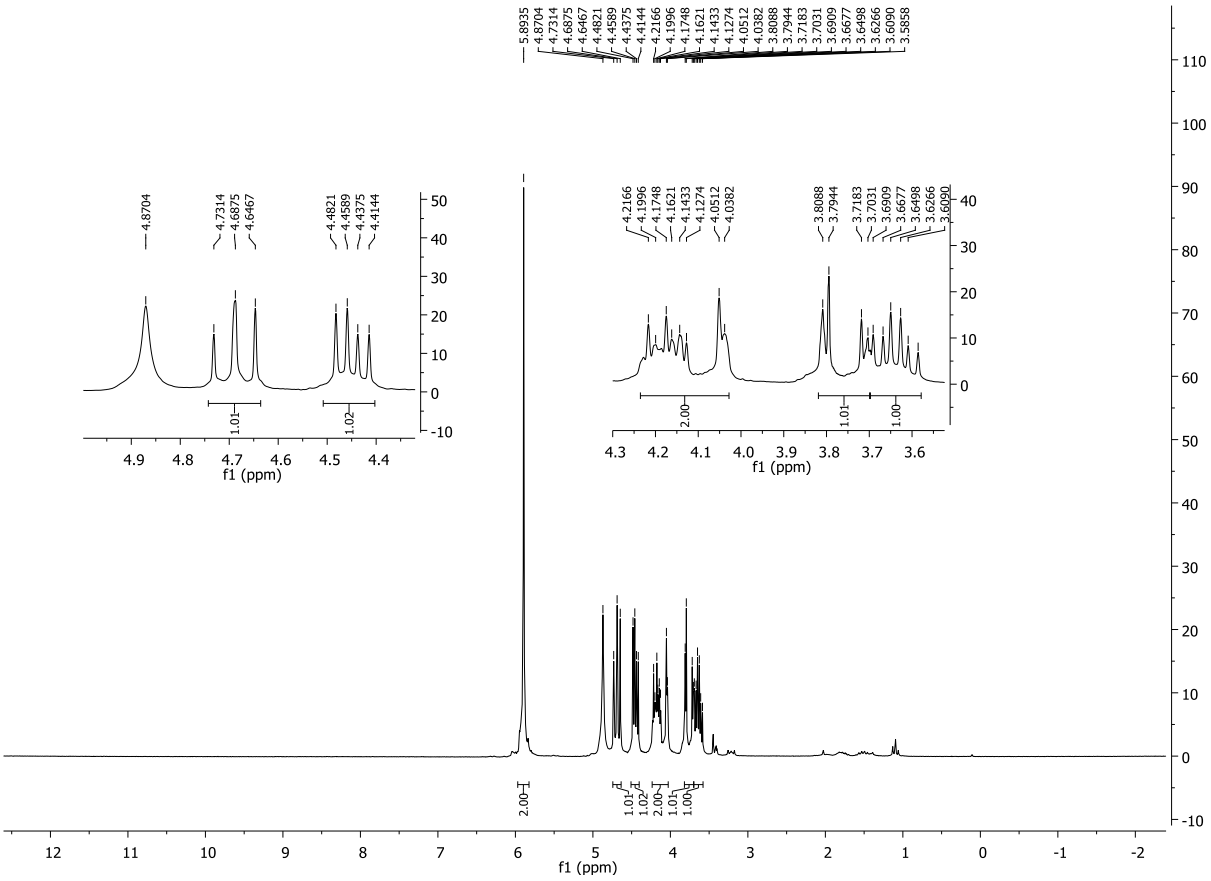
^{1}H NMR (CD_3OD, 200MHz) of **16b**



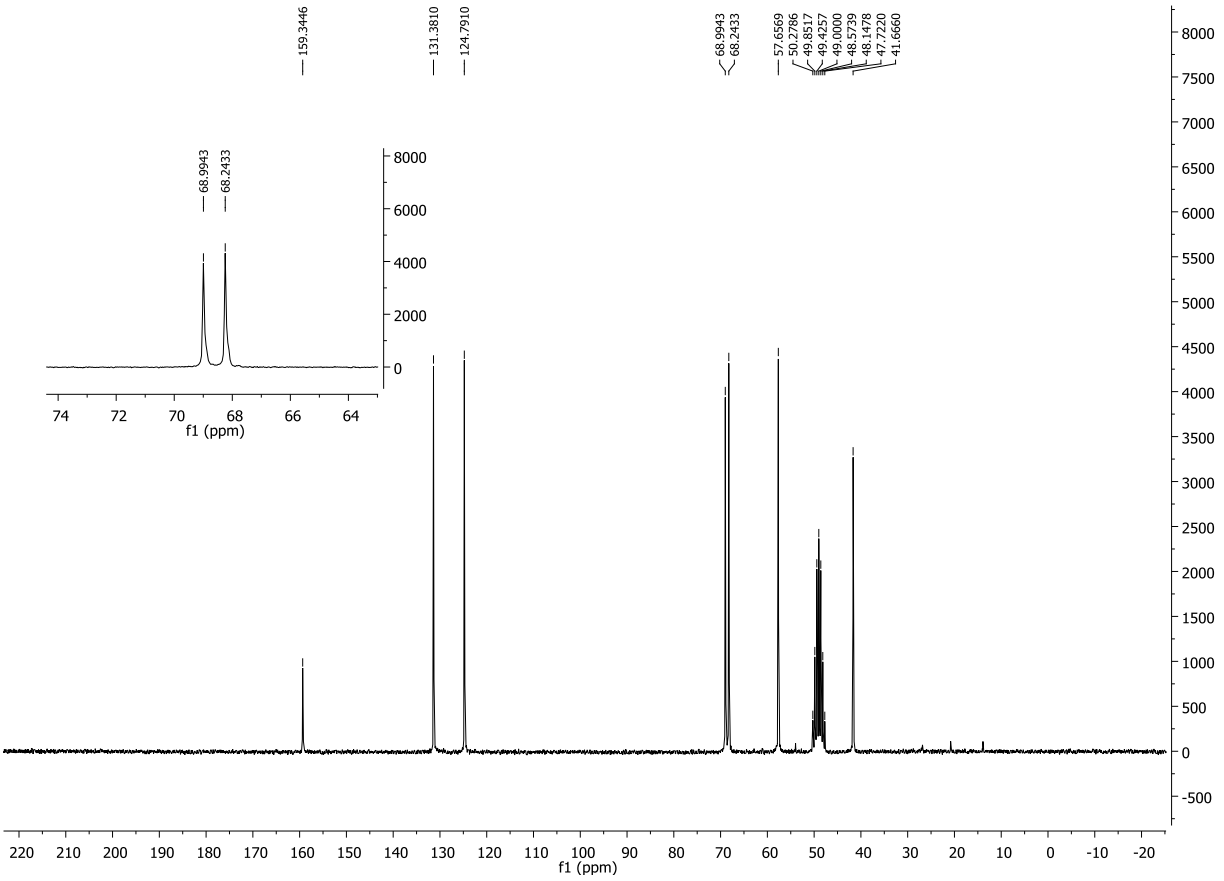
^{13}C NMR (CD_3OD, 50 MHz) of **16b**



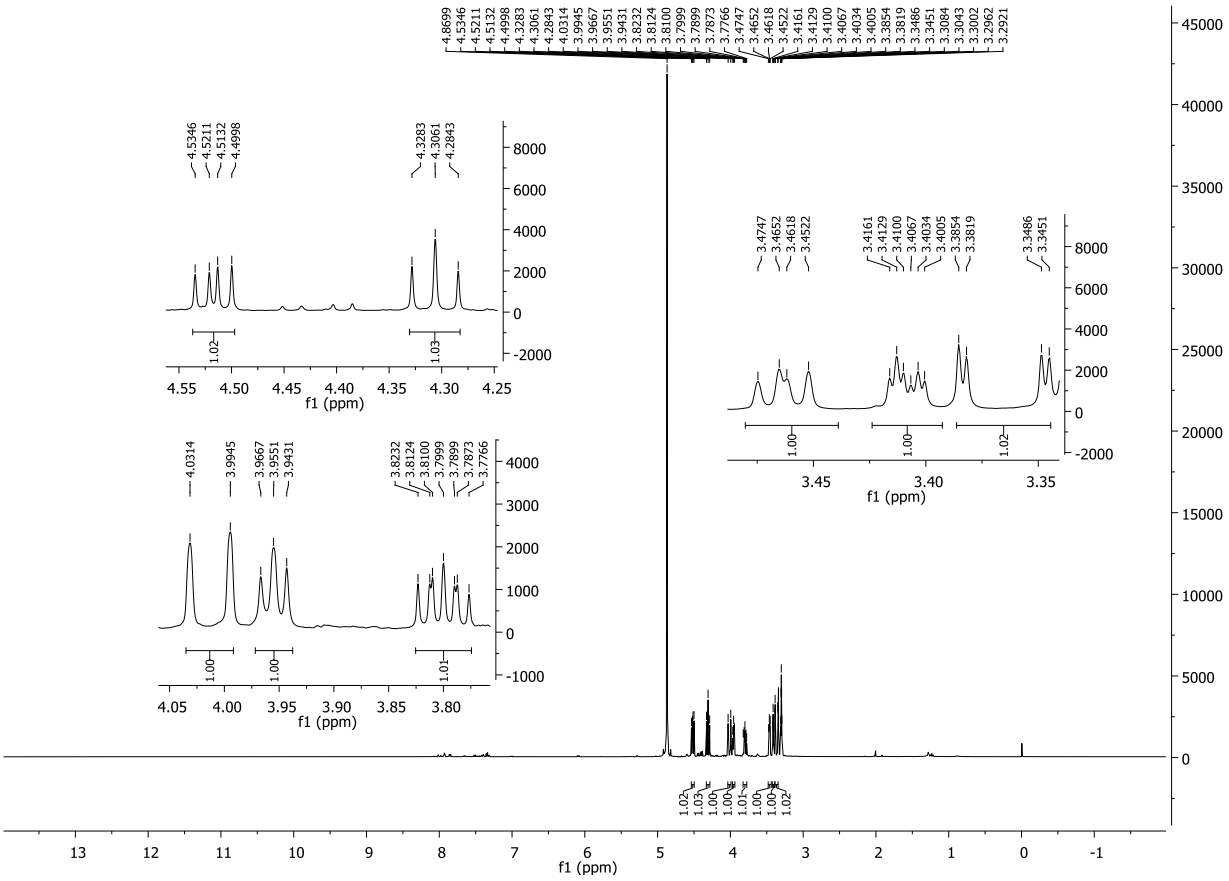
^{1}H NMR (CD_3OD, 200MHz) of **16e**



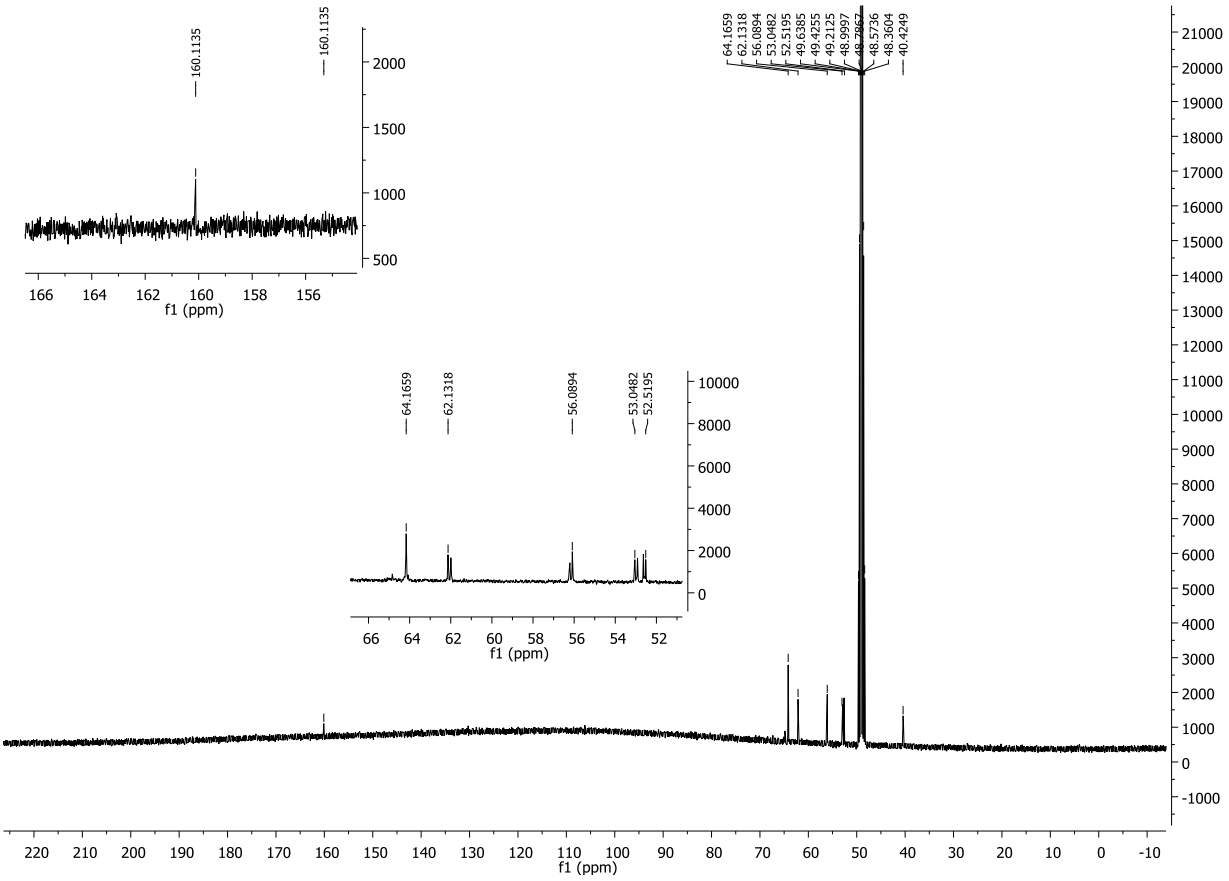
^{13}C NMR (CD_3OD, 50 MHz) of **16e**



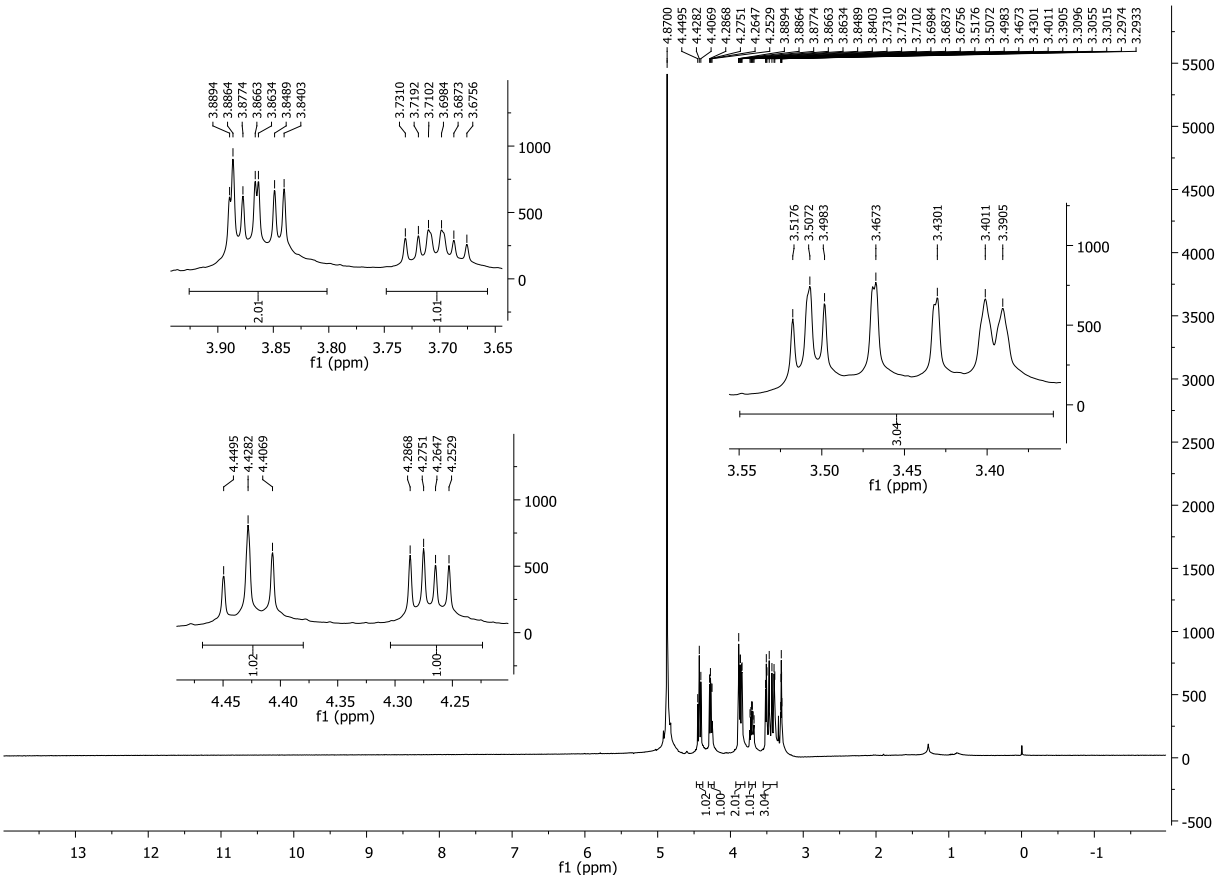
^{1}H NMR (CD_3OD, 400MHz) of **17b**



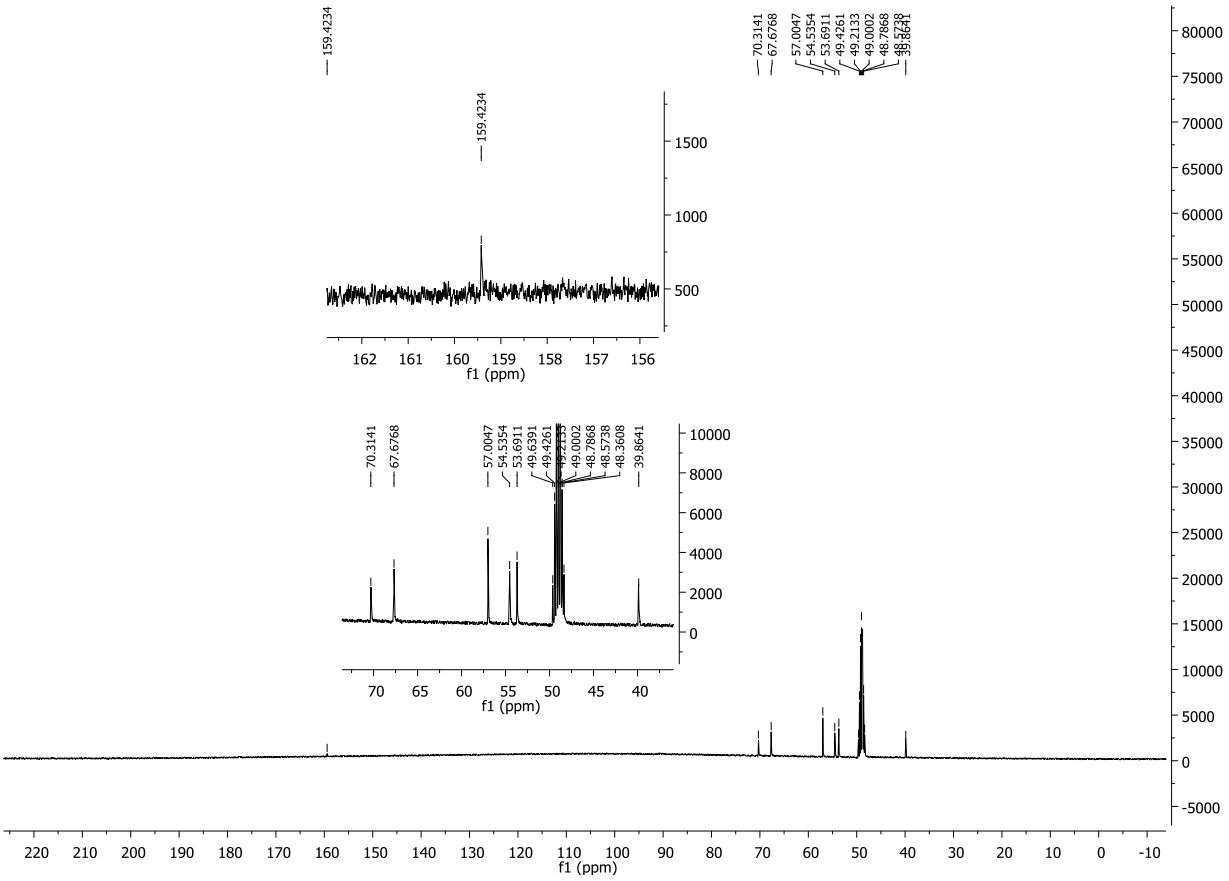
^{13}C NMR (CD_3OD, 100 MHz) of **17b**



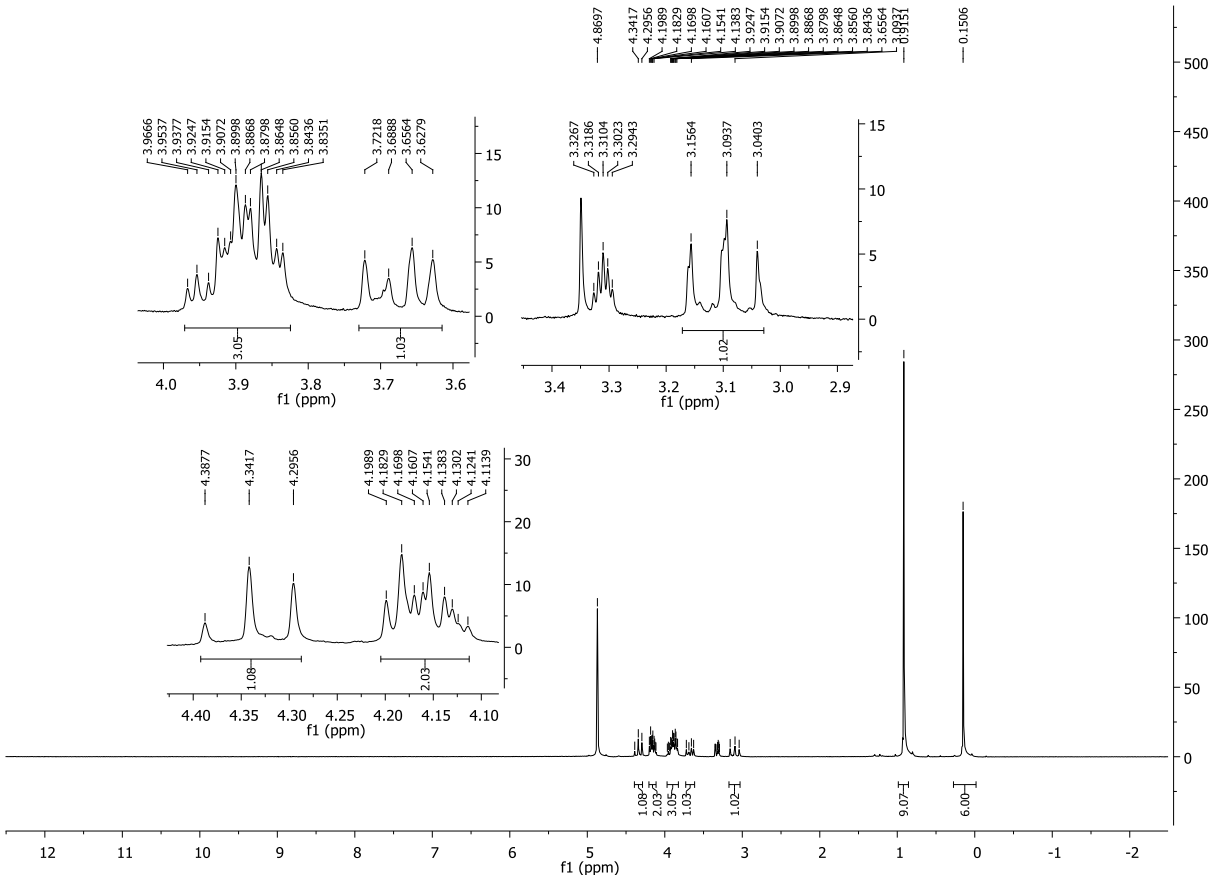
^{1}H NMR (CD_3OD, 400MHz) of **17e**



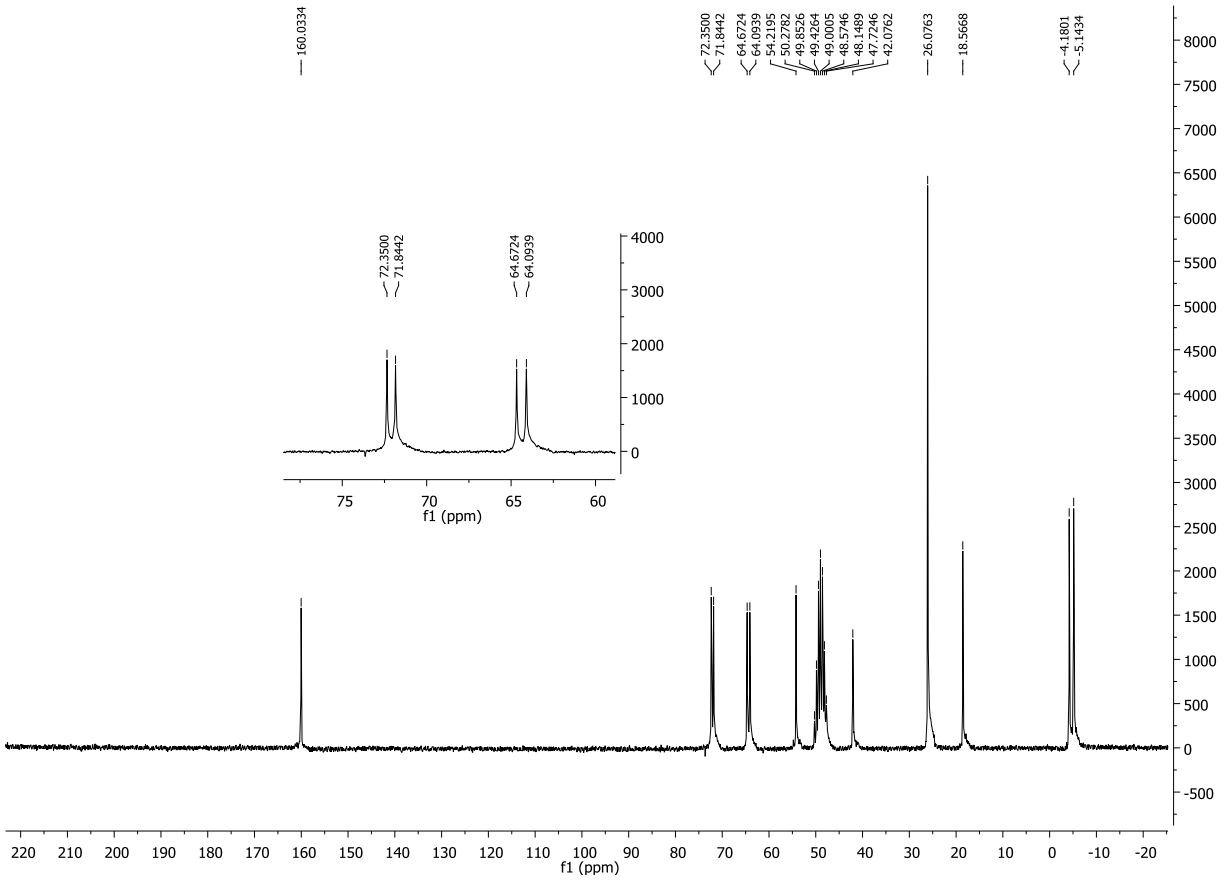
^{13}C NMR (CD_3OD, 100 MHz) of **17e**



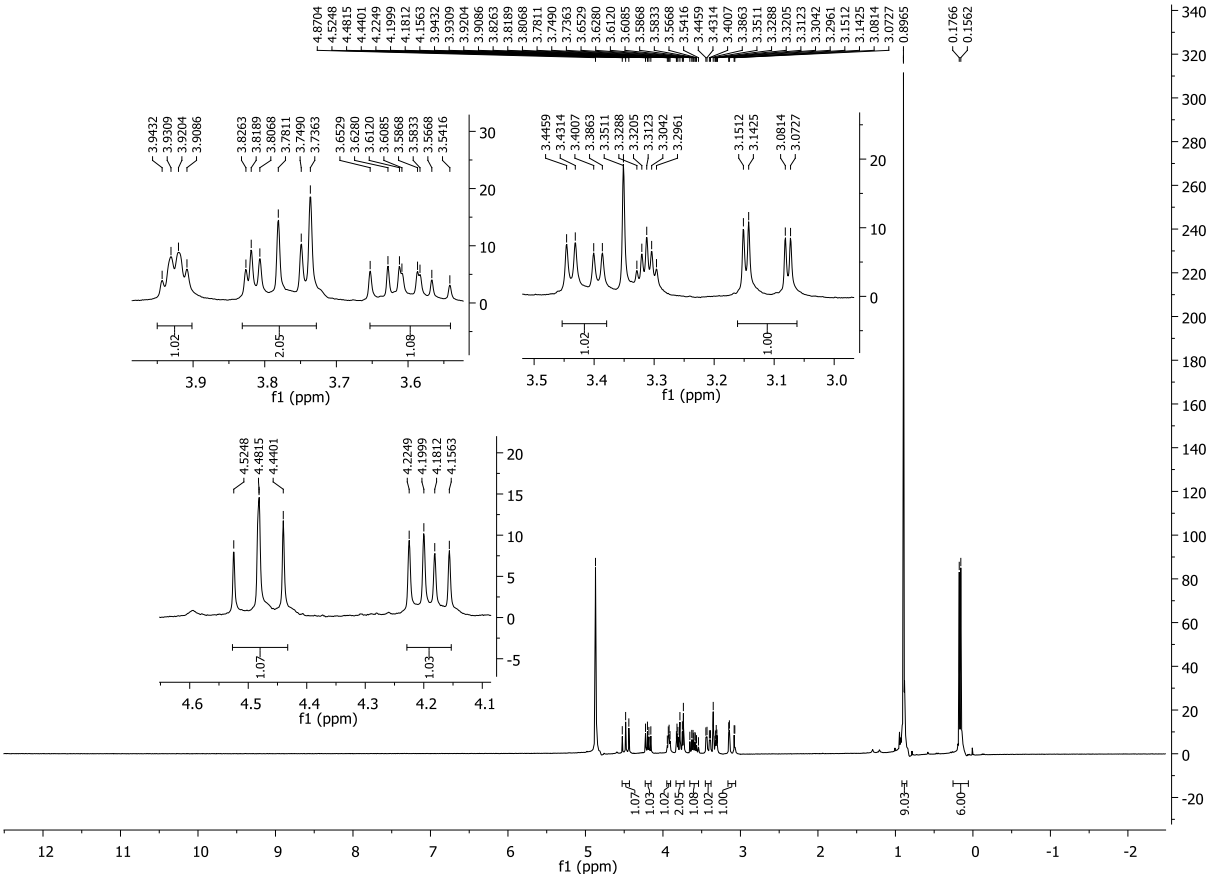
^{1}H NMR (CD_3OD, 200MHz) of **18c**



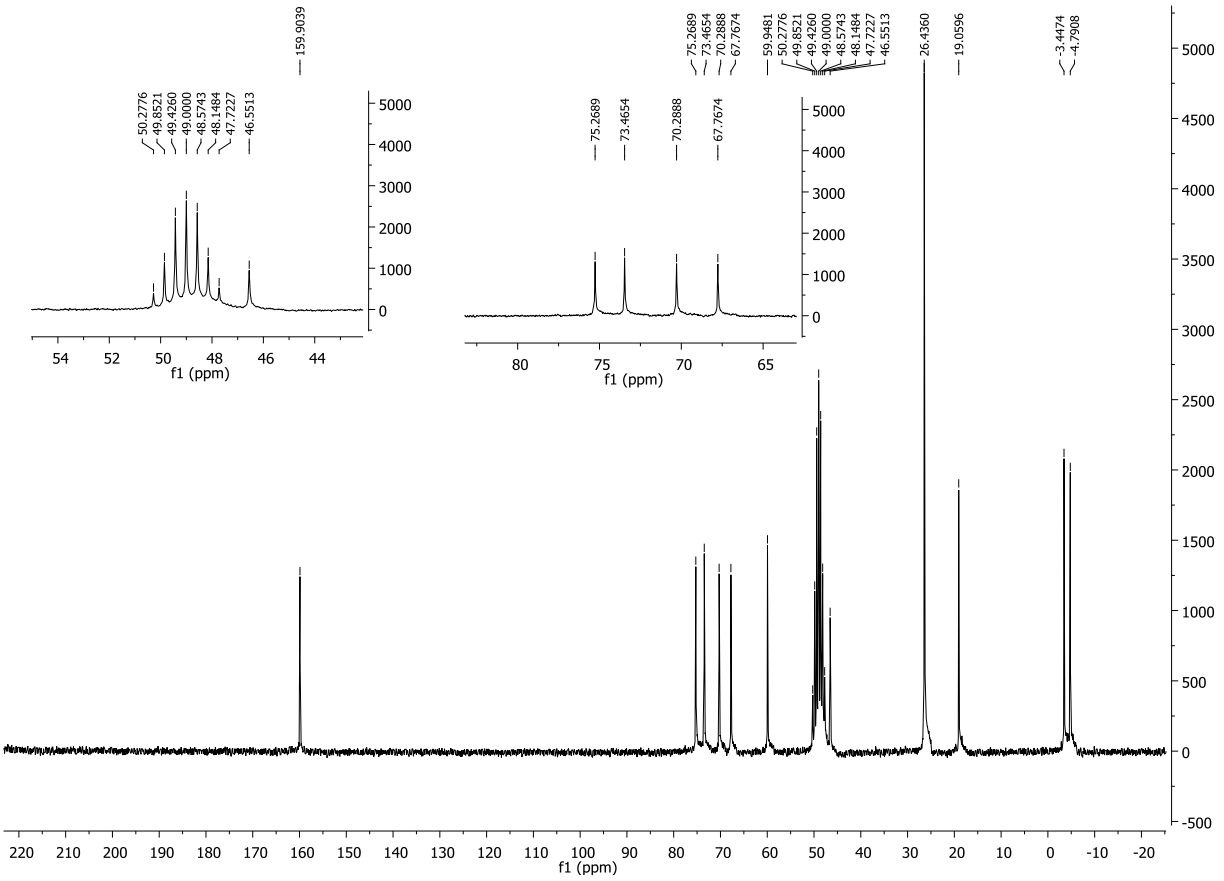
^{13}C NMR (CD_3OD, 50 MHz) of **18c**



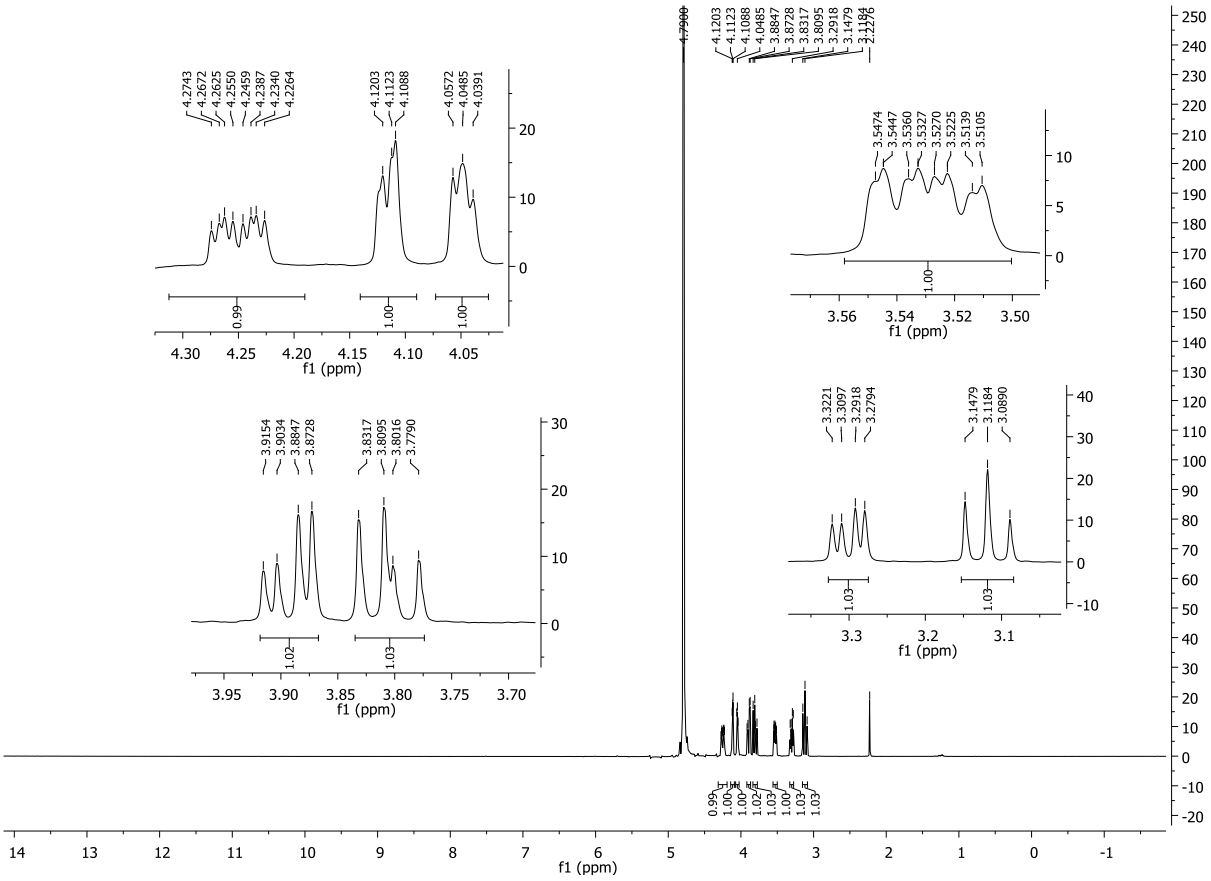
^{1}H NMR (CD_3OD, 200MHz) of **18f**



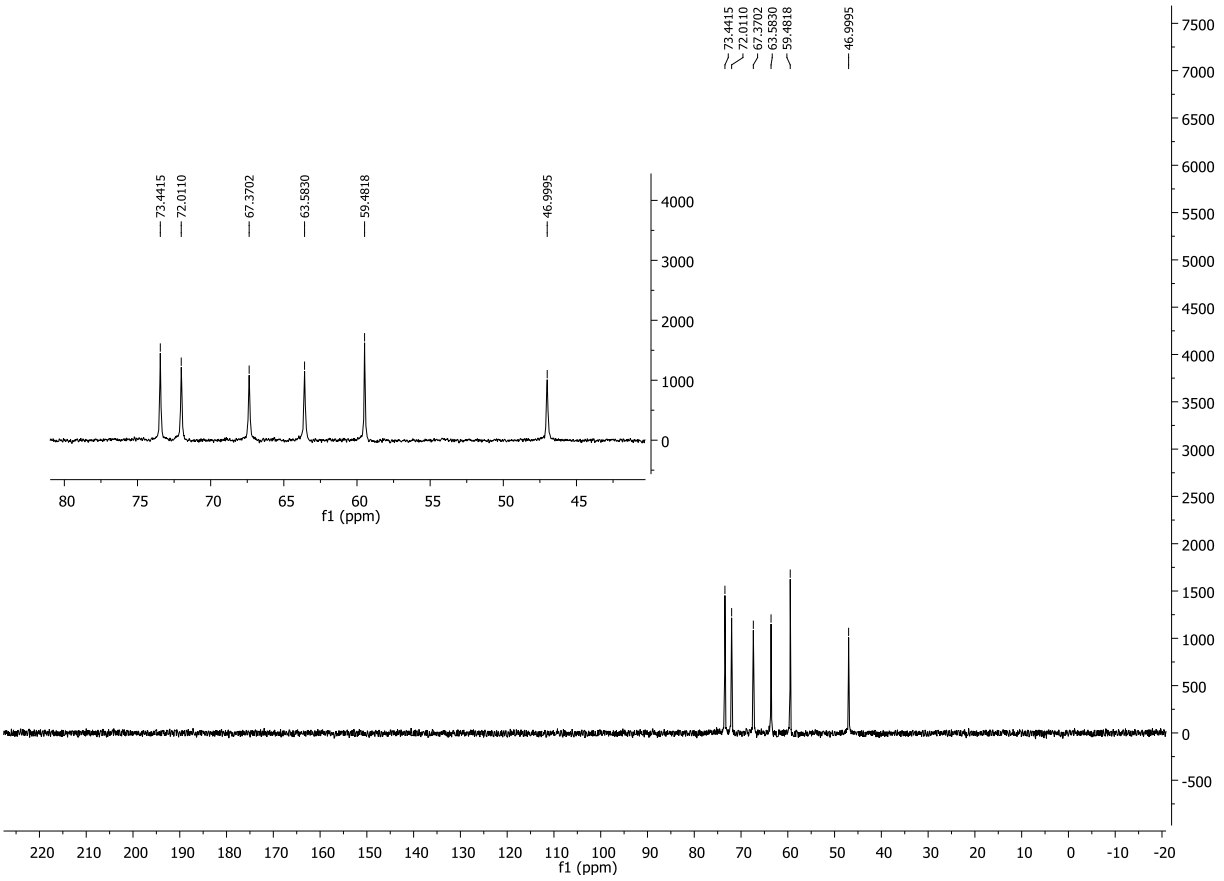
^{13}C NMR (CD_3OD, 50 MHz) of **18f**



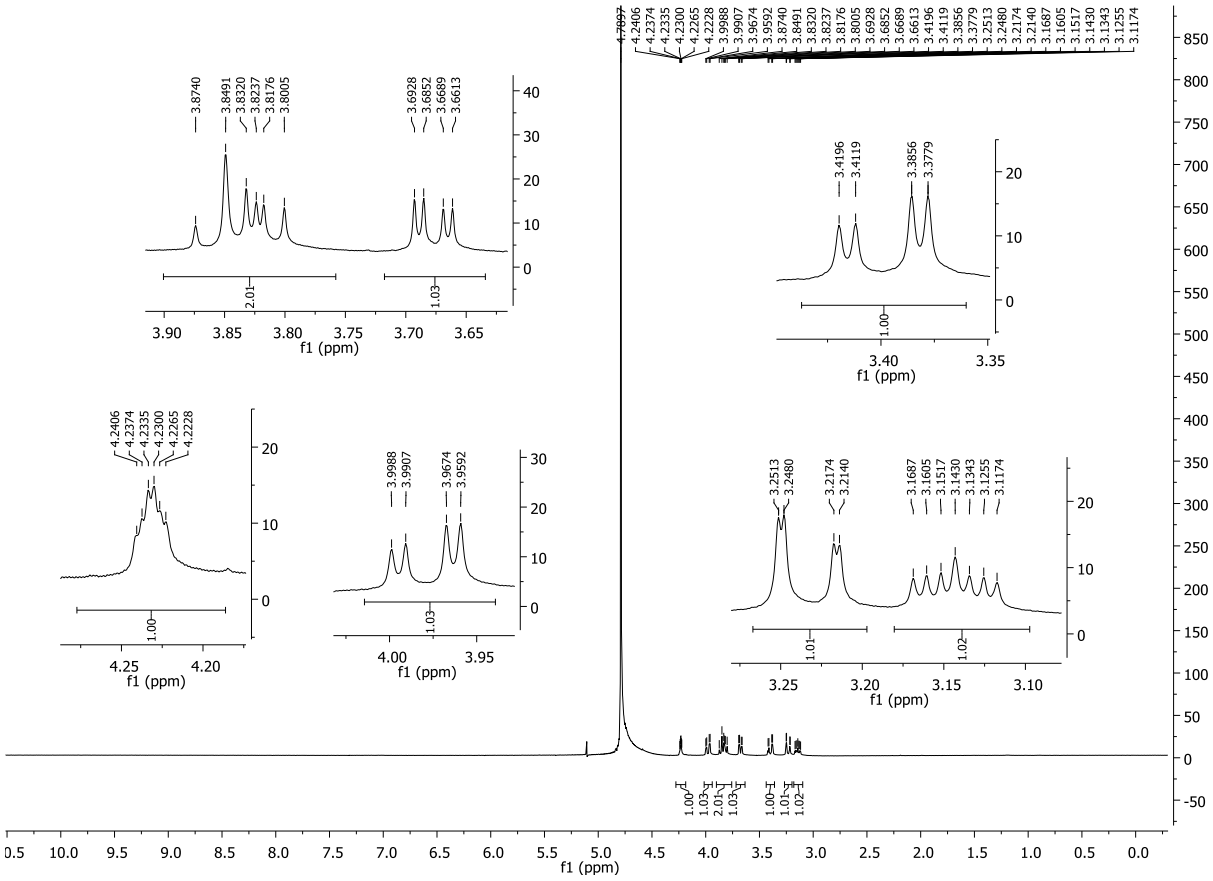
^{1}H NMR (D_2O, 400MHz) of **1c**



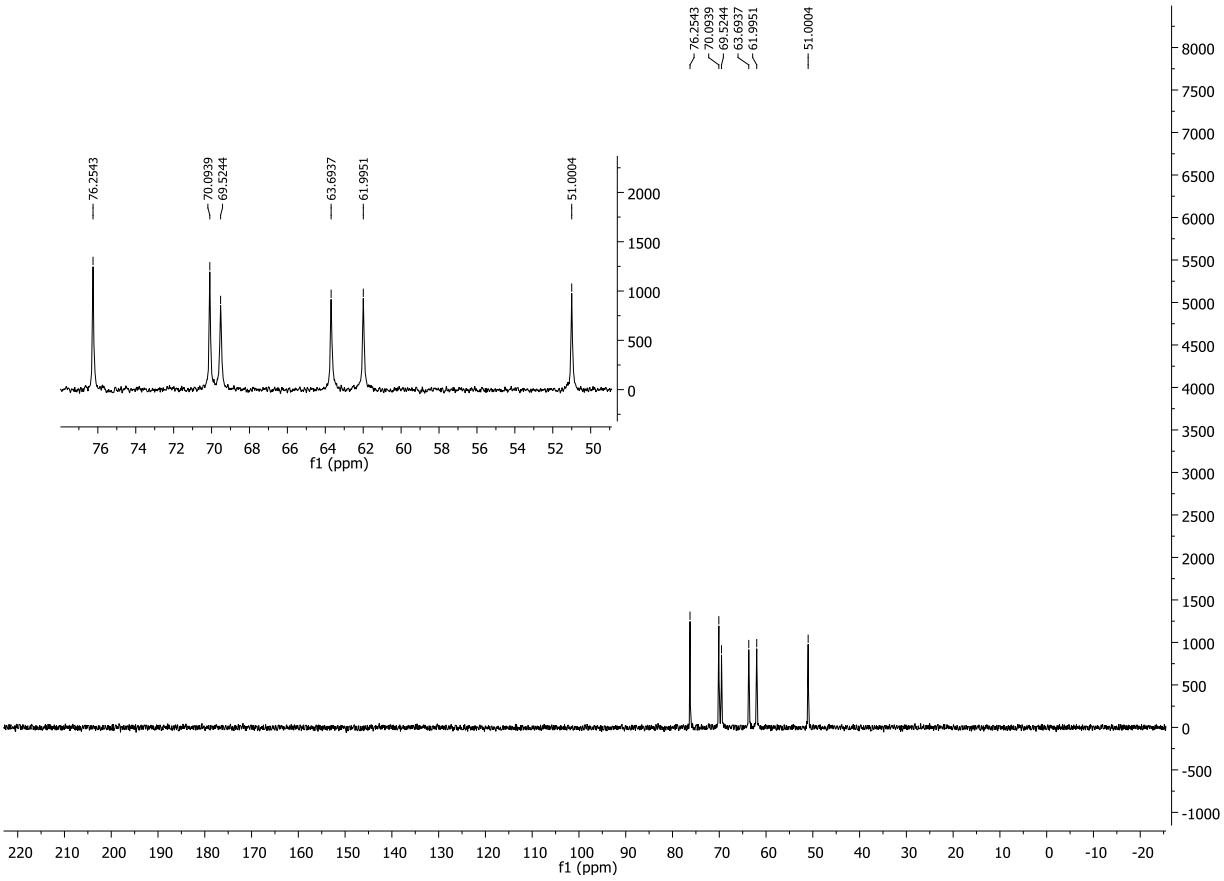
^{13}C NMR (D_2O, 50MHz) of **1c**



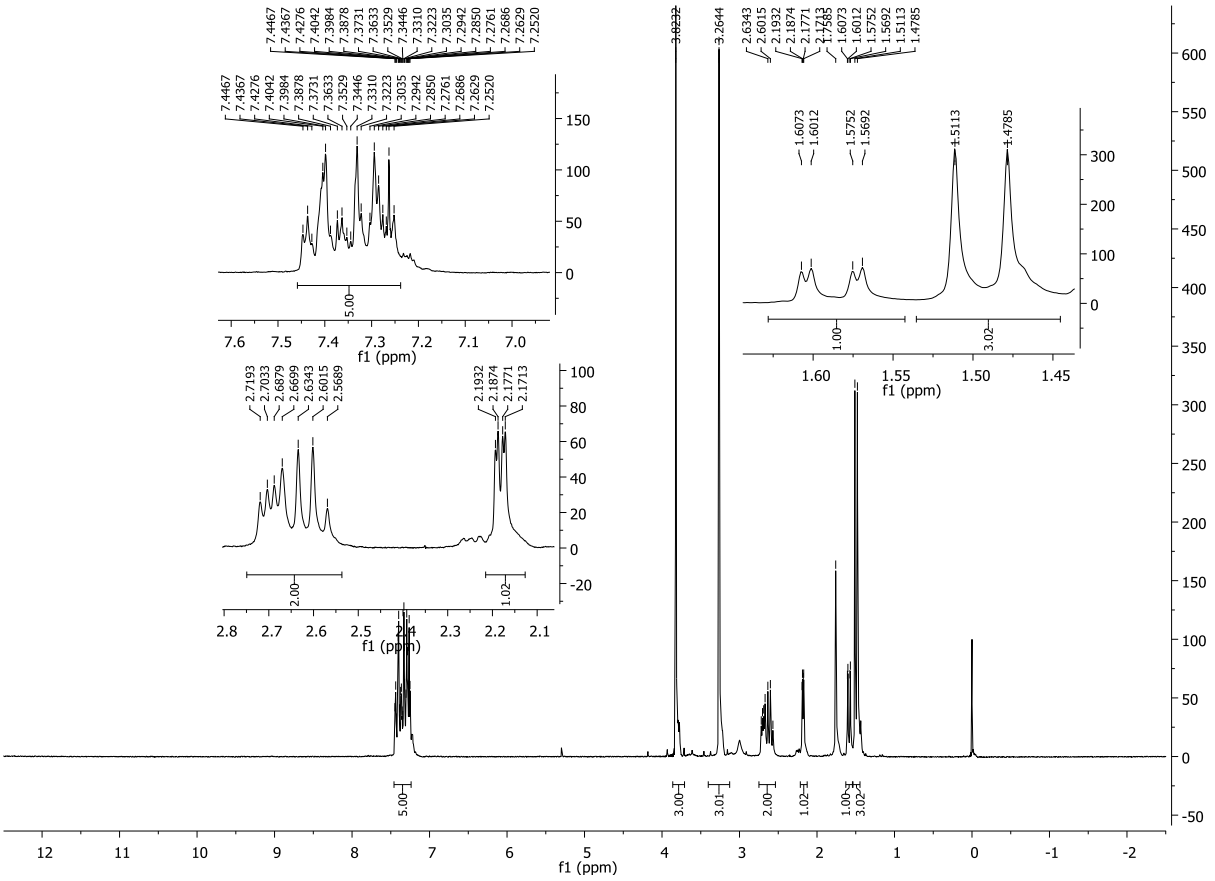
^{1}H NMR (D_2O, 400MHz) of **1f**



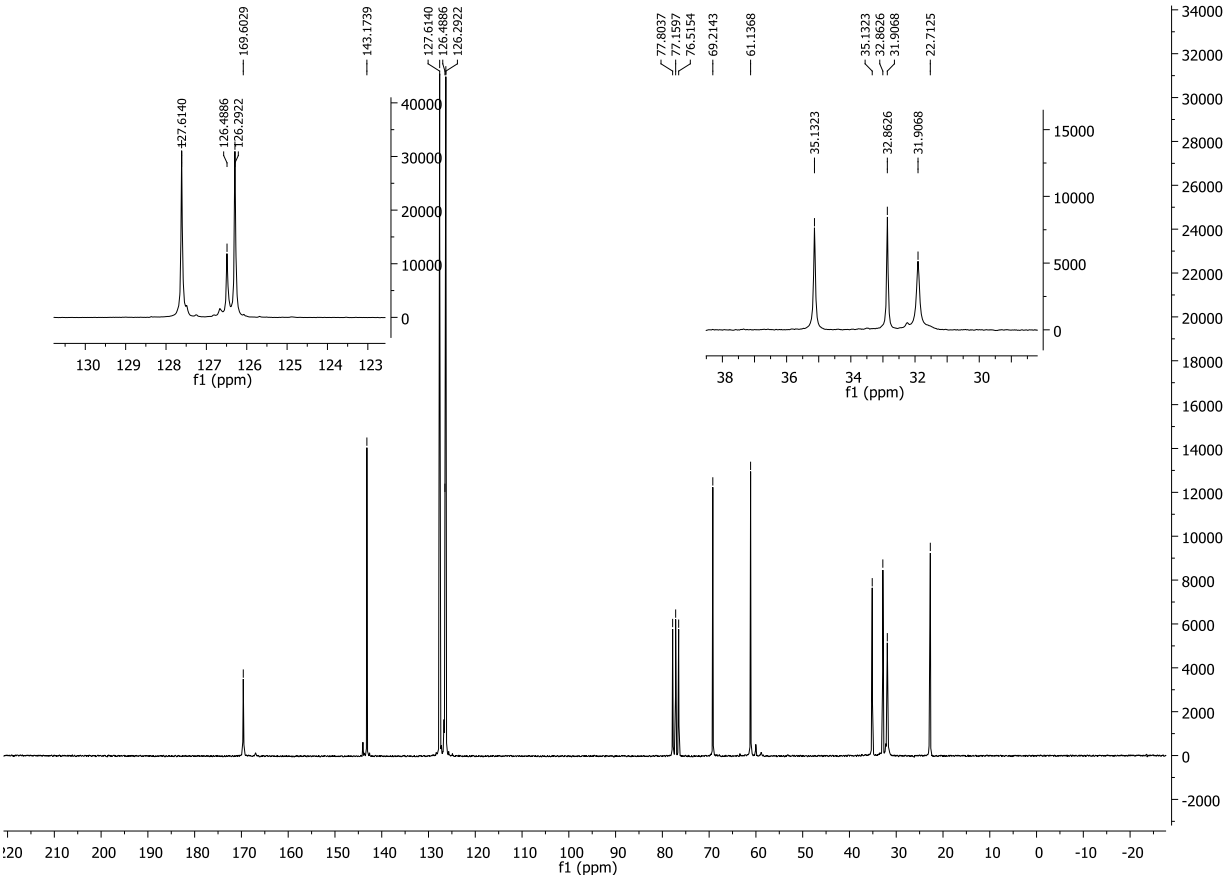
^{13}C NMR (D_2O, 50MHz) of **1f**



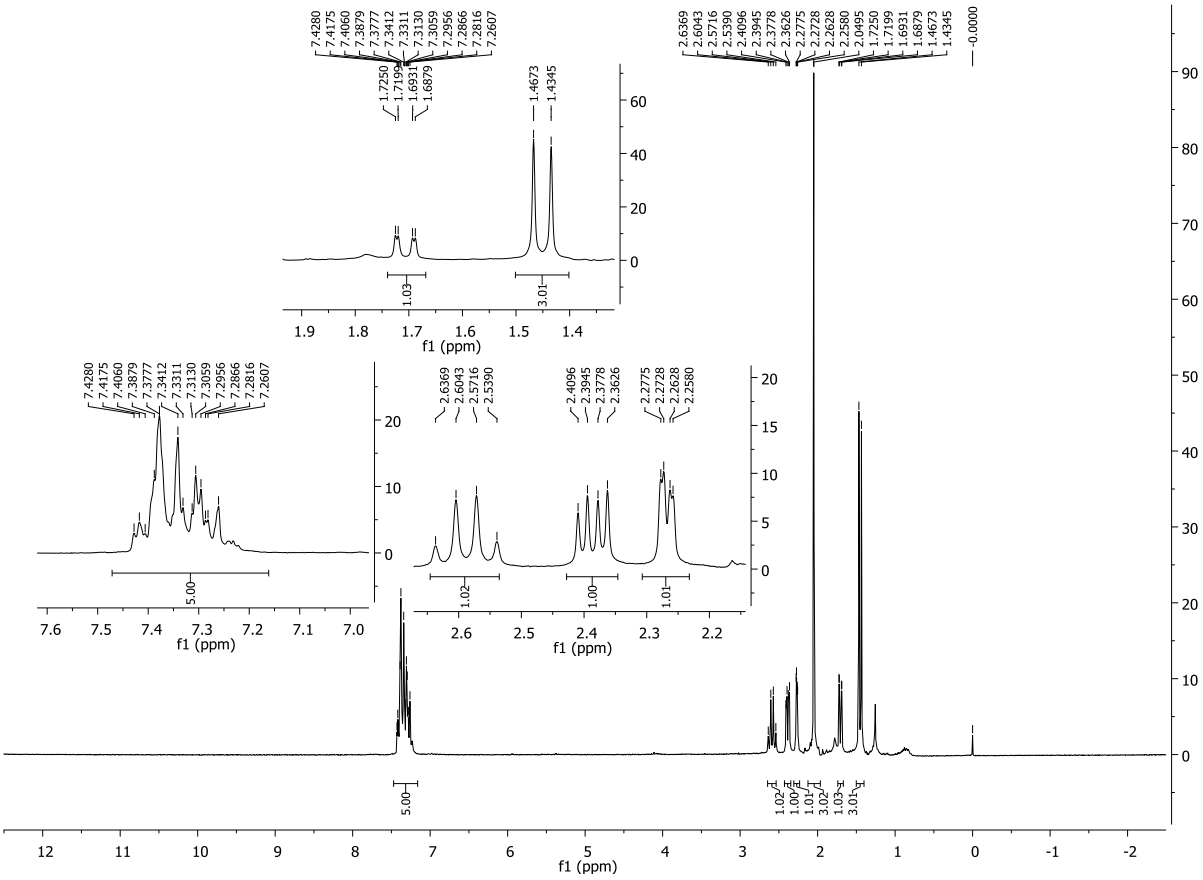
^{1}H NMR ($CDCl_3$, 200MHz) of **3'**



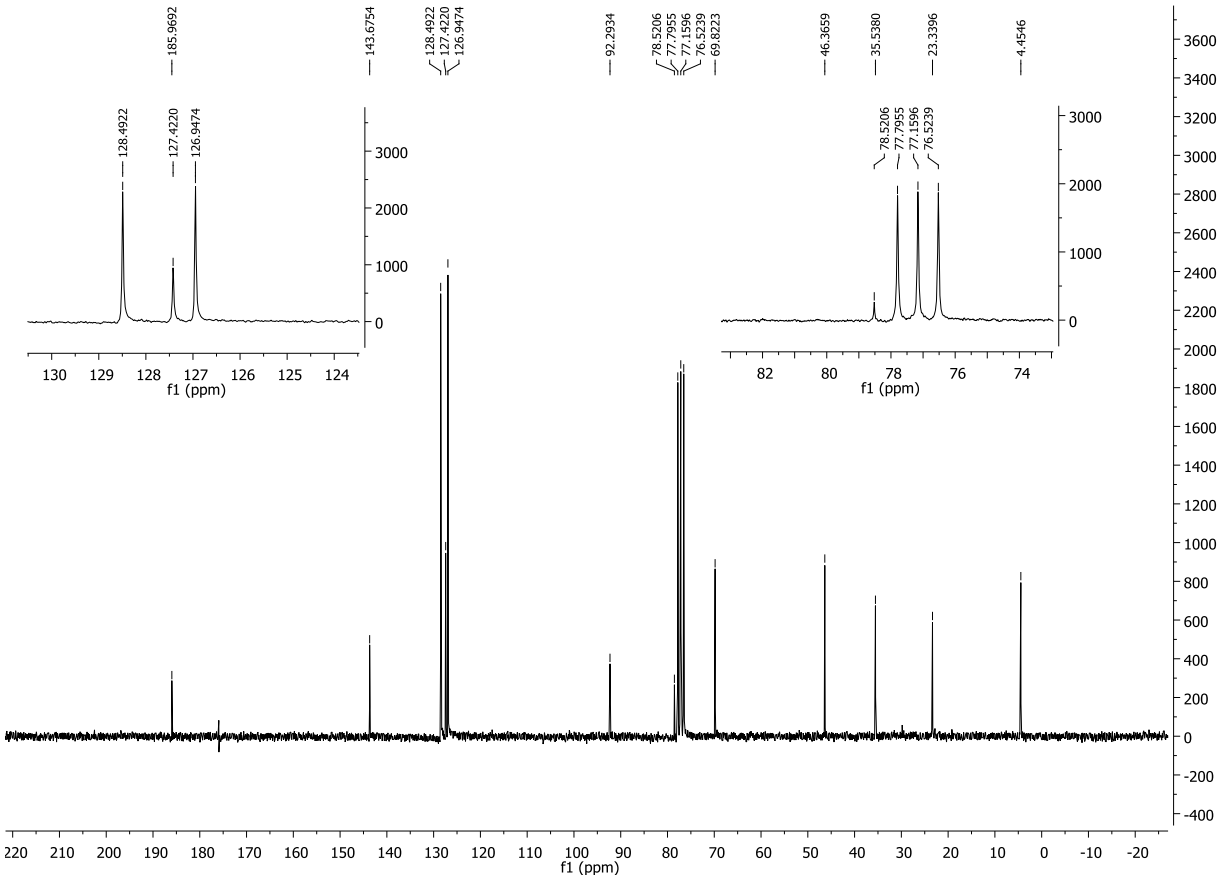
^{13}C NMR ($CDCl_3$, 50 MHz) of **3'**



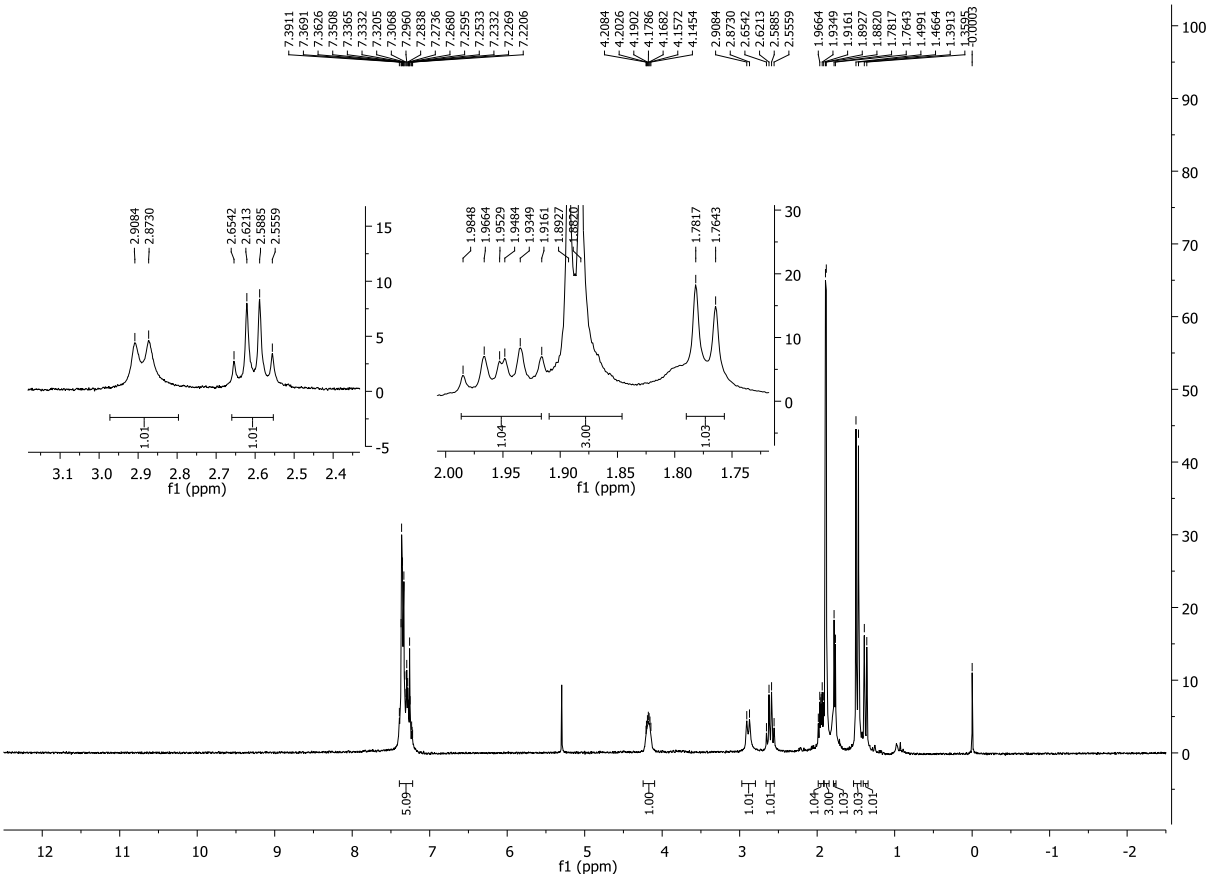
^{1}H NMR ($CDCl_3$, 200MHz) of **4'**



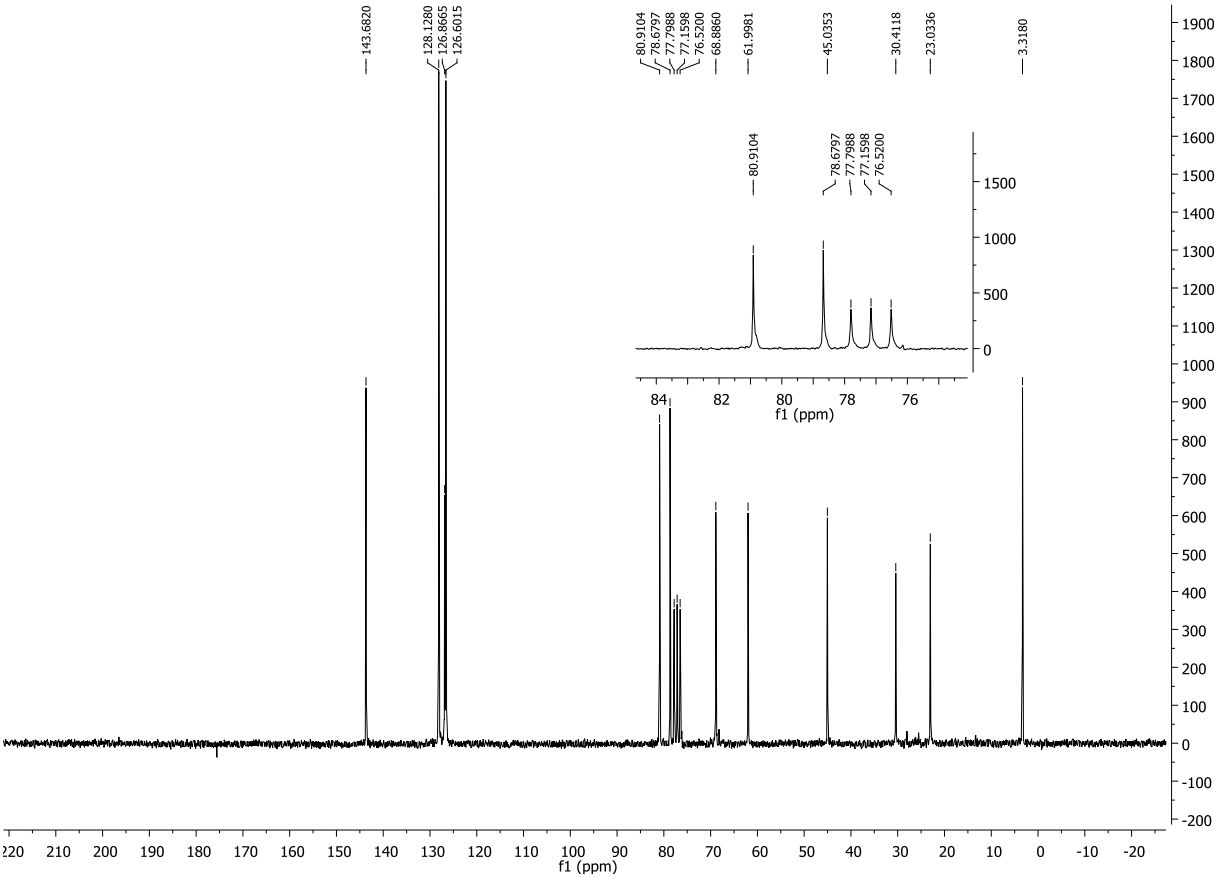
^{13}C NMR ($CDCl_3$, 50 MHz) of **4'**



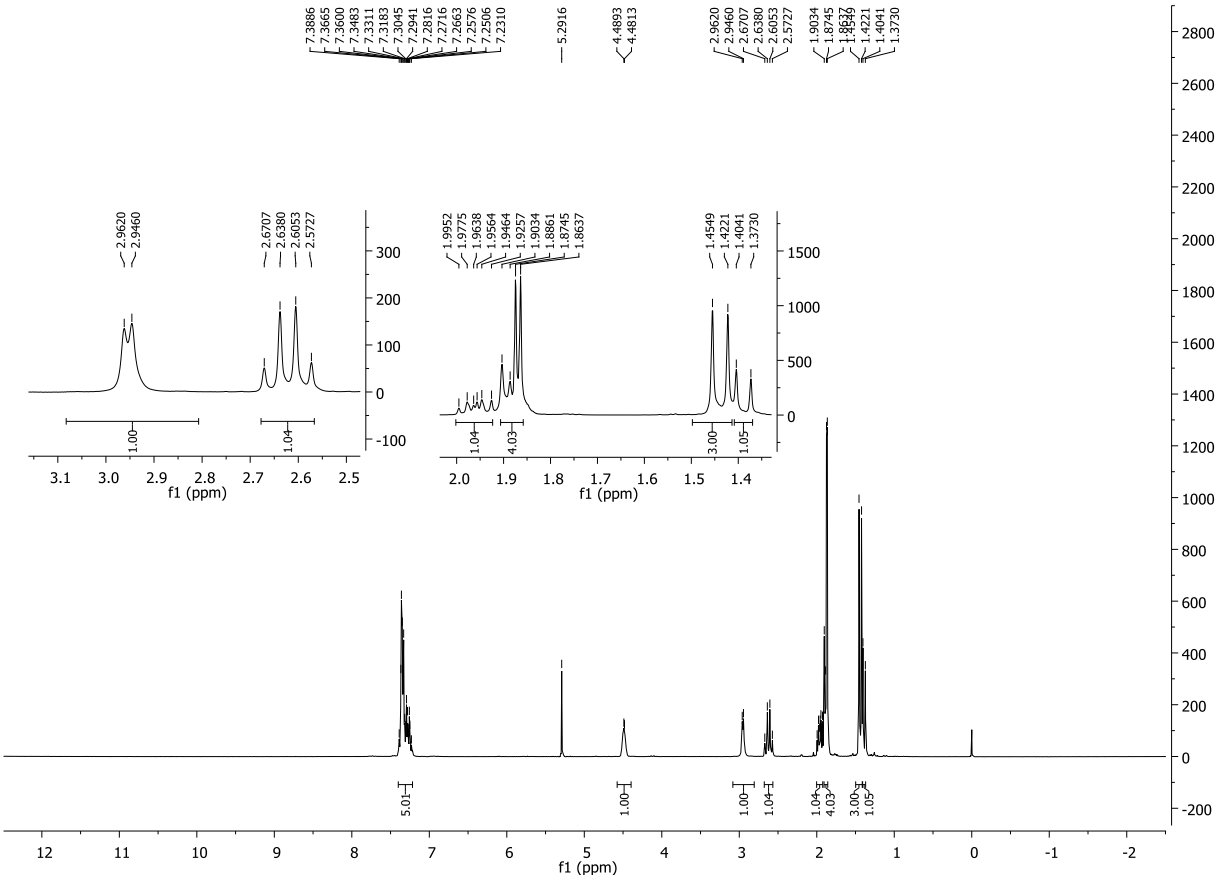
^{1}H NMR ($CDCl_3$, 200MHz) of **5a'**



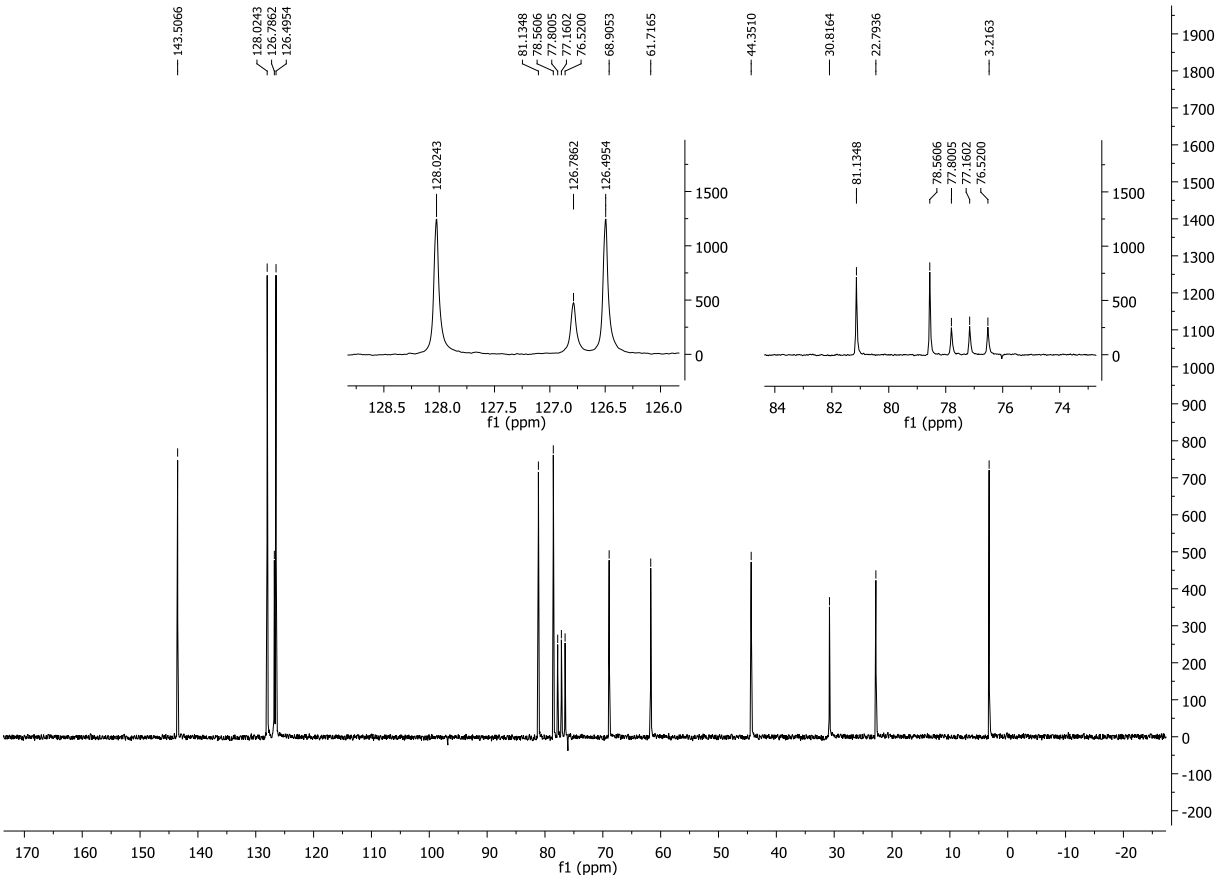
^{13}C NMR ($CDCl_3$, 50 MHz) of **5a'**



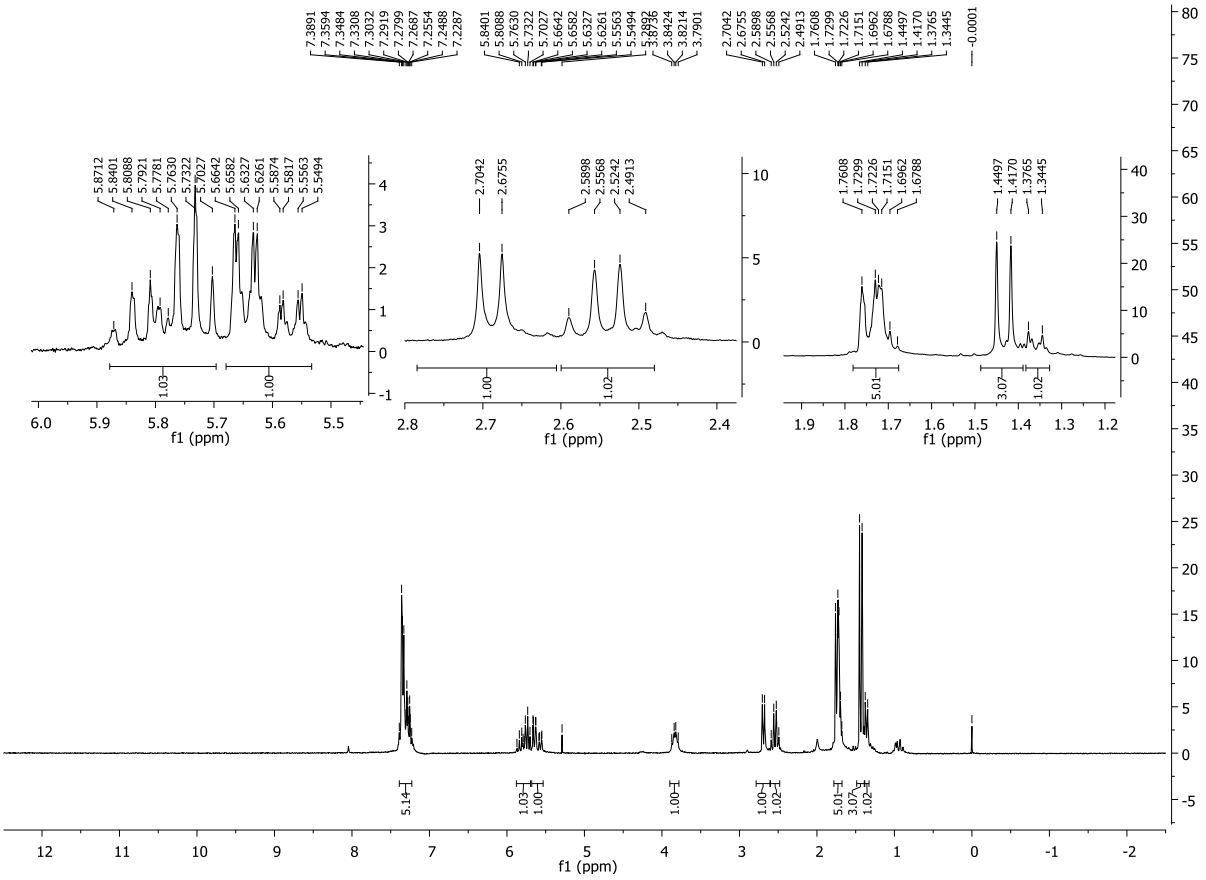
^{1}H NMR ($CDCl_3$, 200MHz) of **5b'**



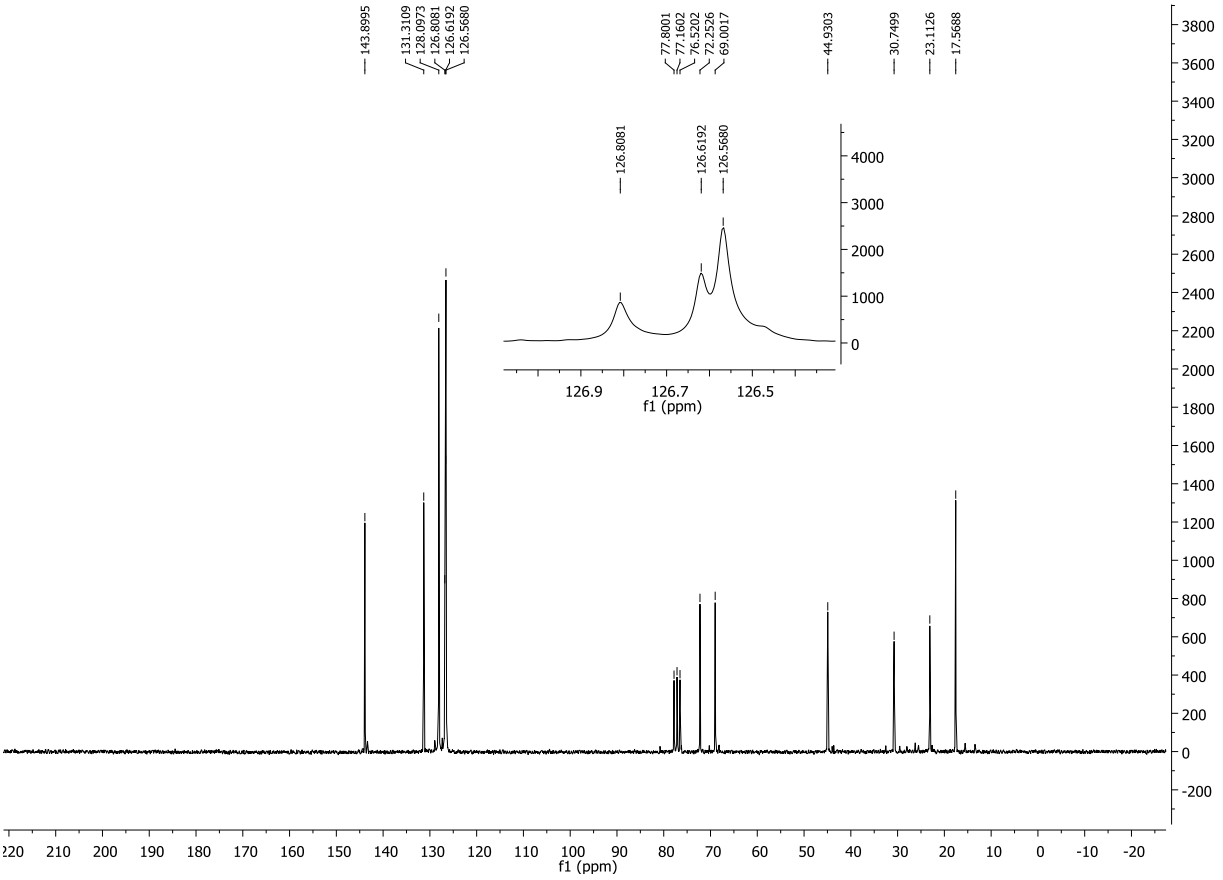
^{13}C NMR ($CDCl_3$, 50 MHz) of **5b'**



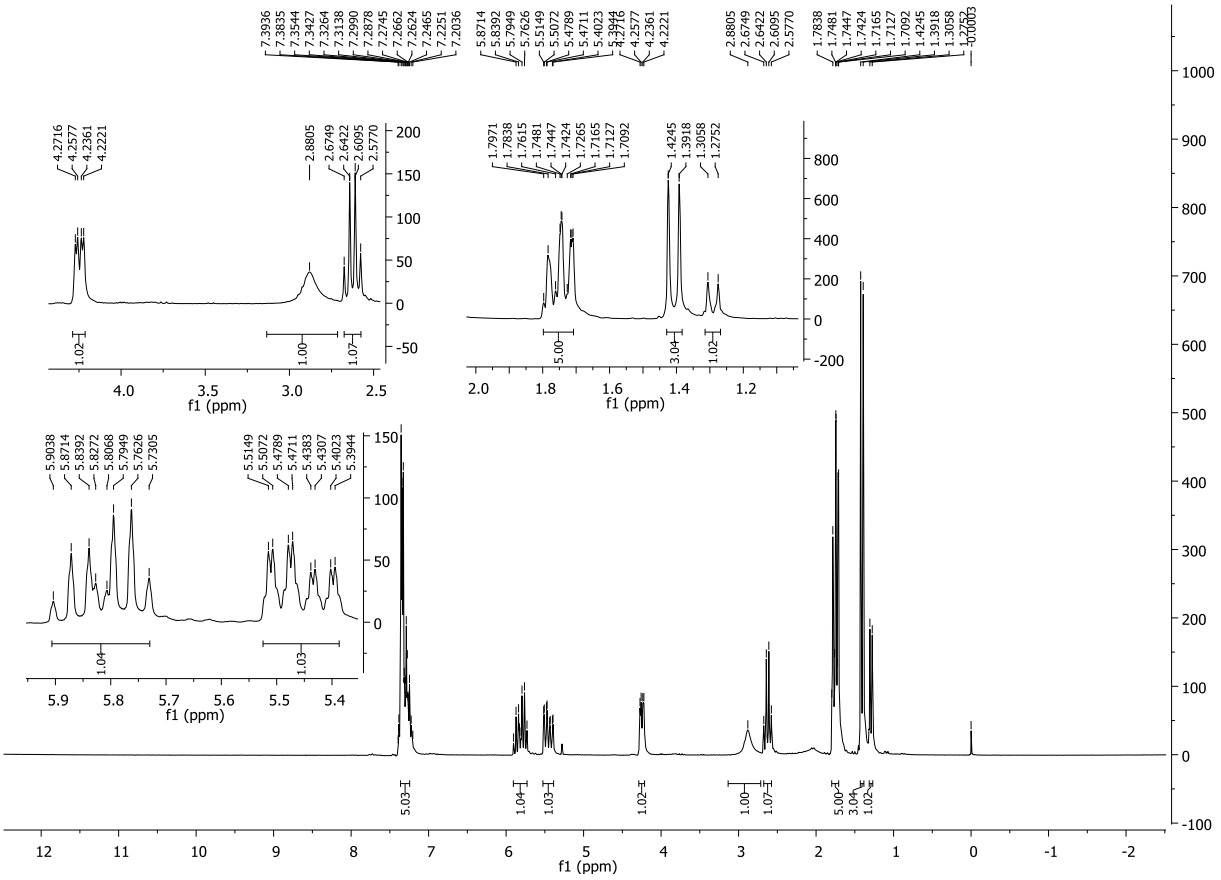
^{1}H NMR ($CDCl_3$, 200MHz) of **6a'**



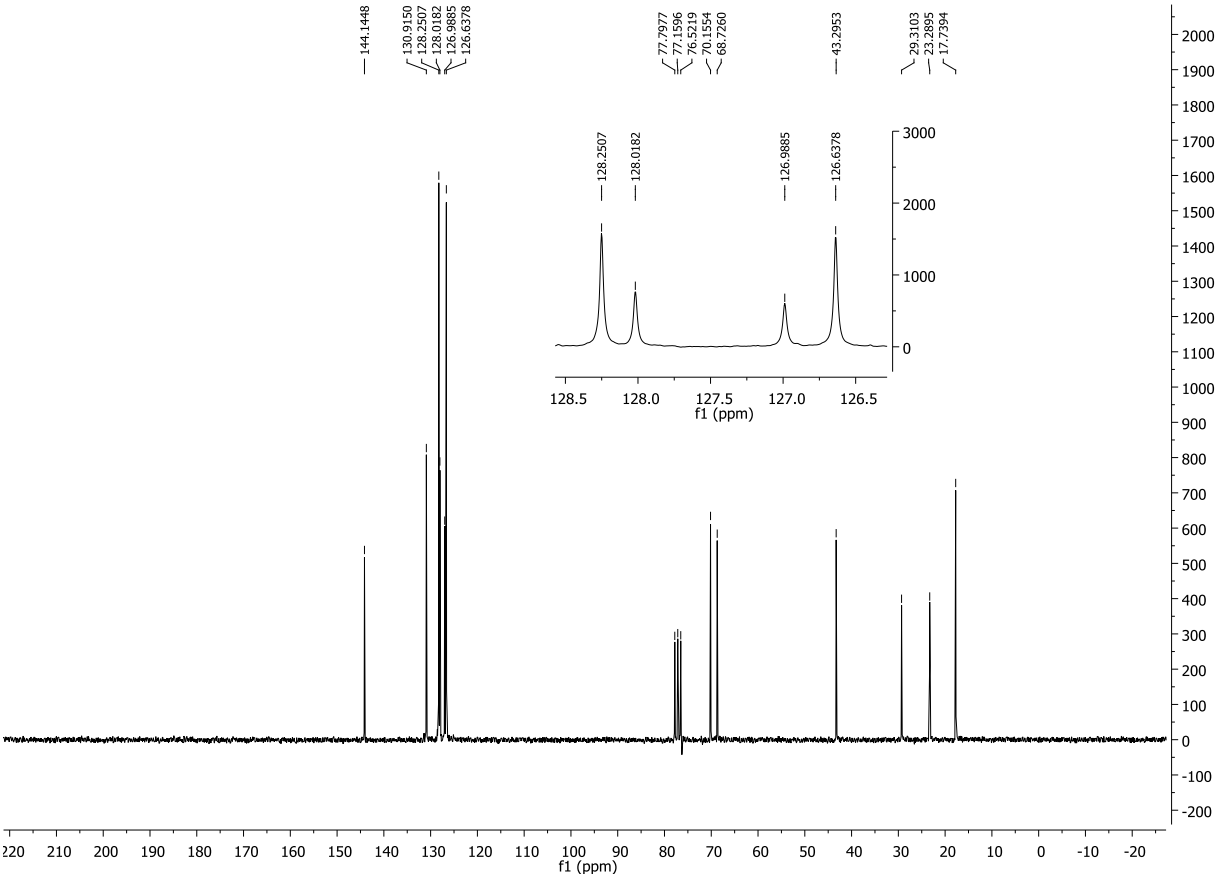
^{13}C NMR ($CDCl_3$, 50 MHz) of **6a'**



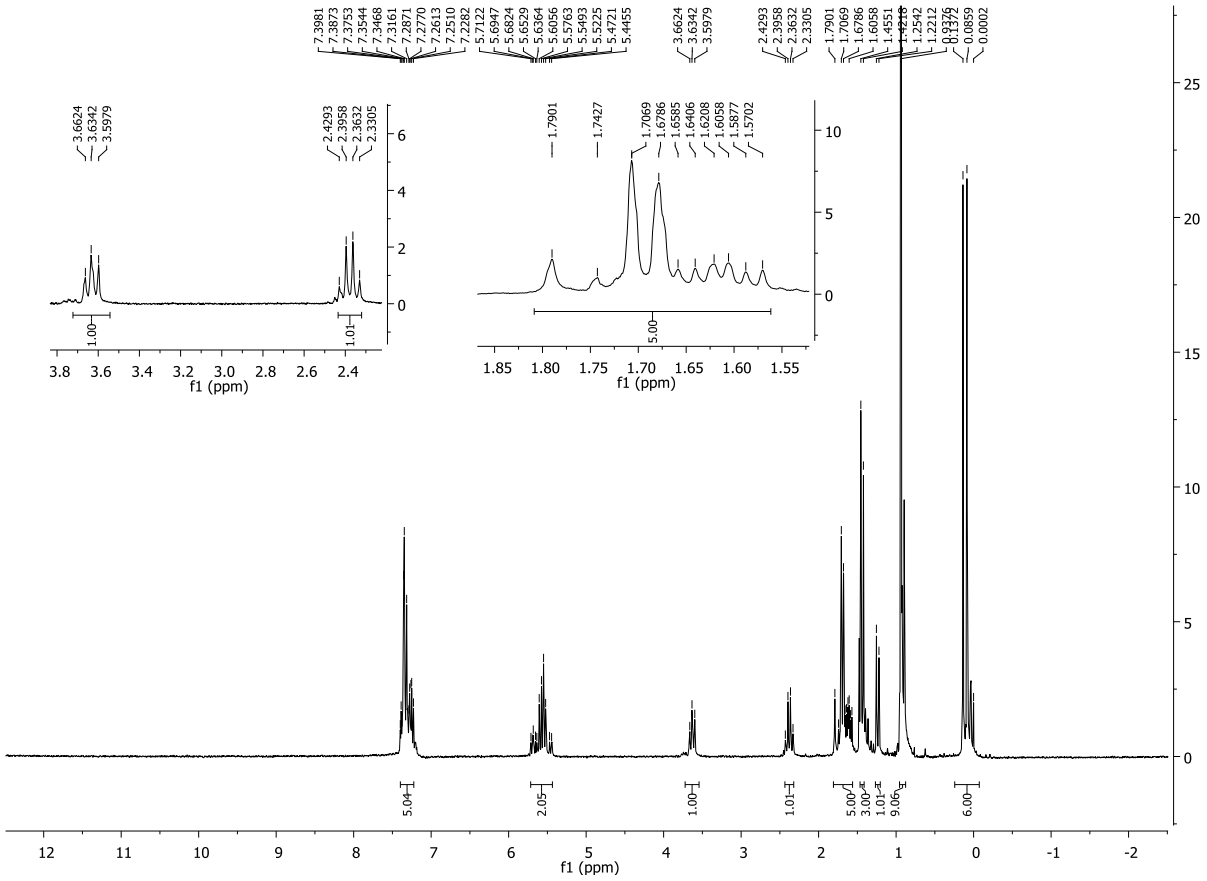
^{1}H NMR ($CDCl_3$, 200MHz) of **6b'**



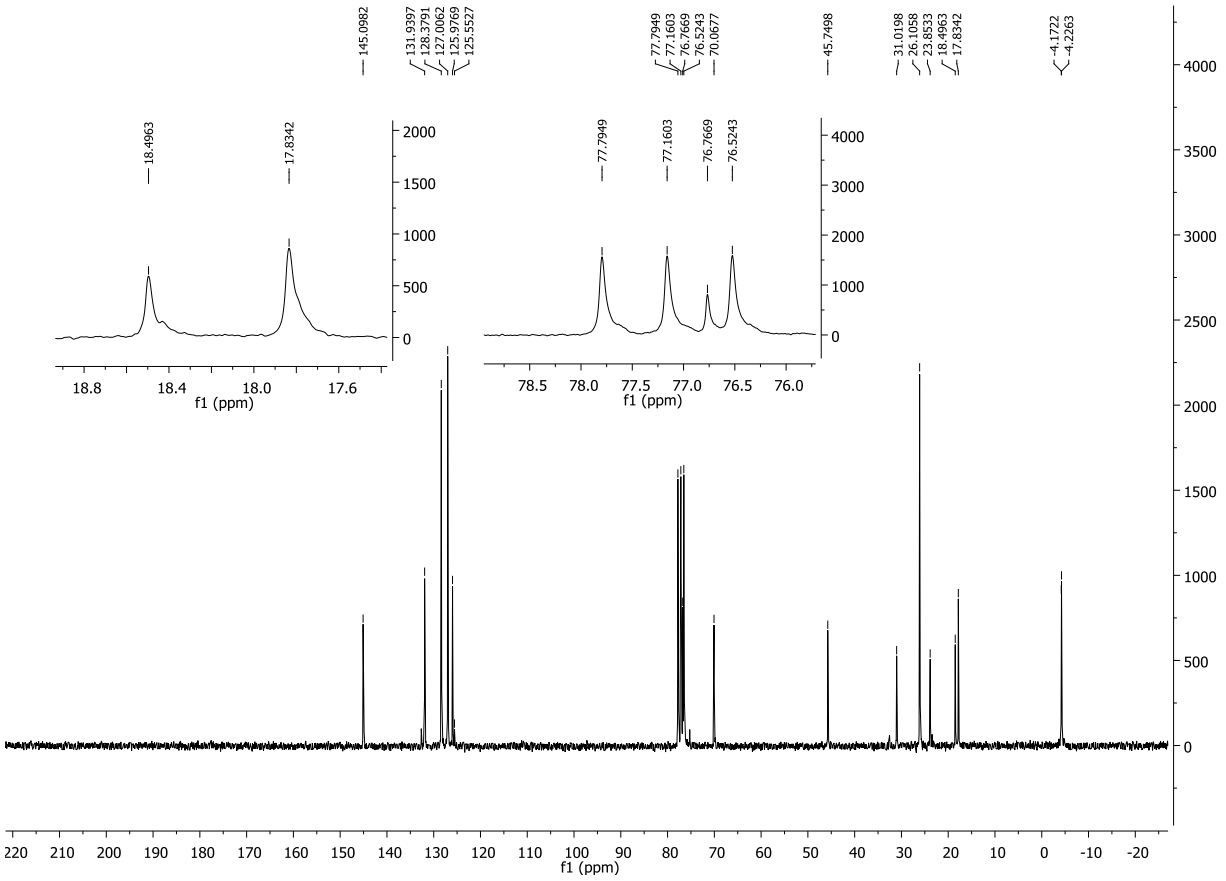
^{13}C NMR ($CDCl_3$, 50 MHz) of **6b'**



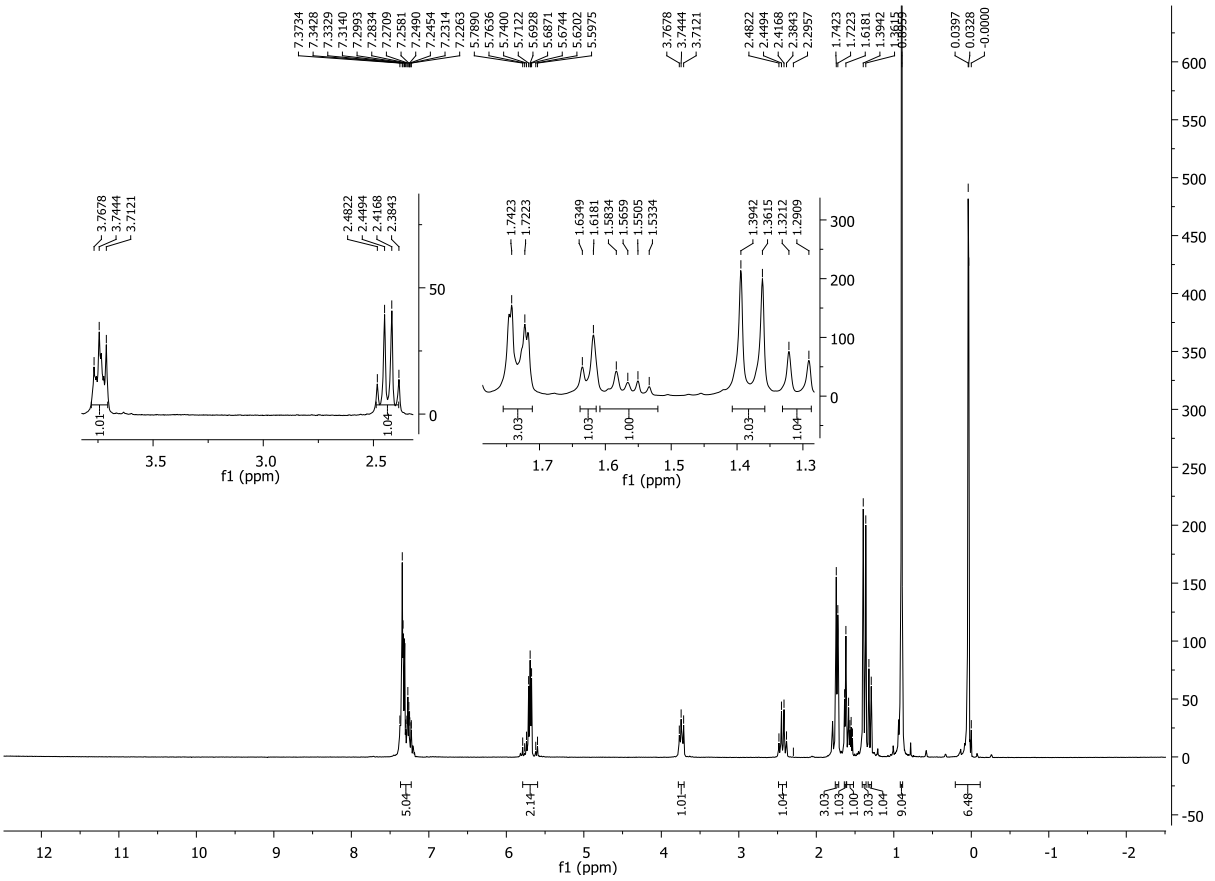
^{1}H NMR ($CDCl_3$, 200MHz) of **7a'**



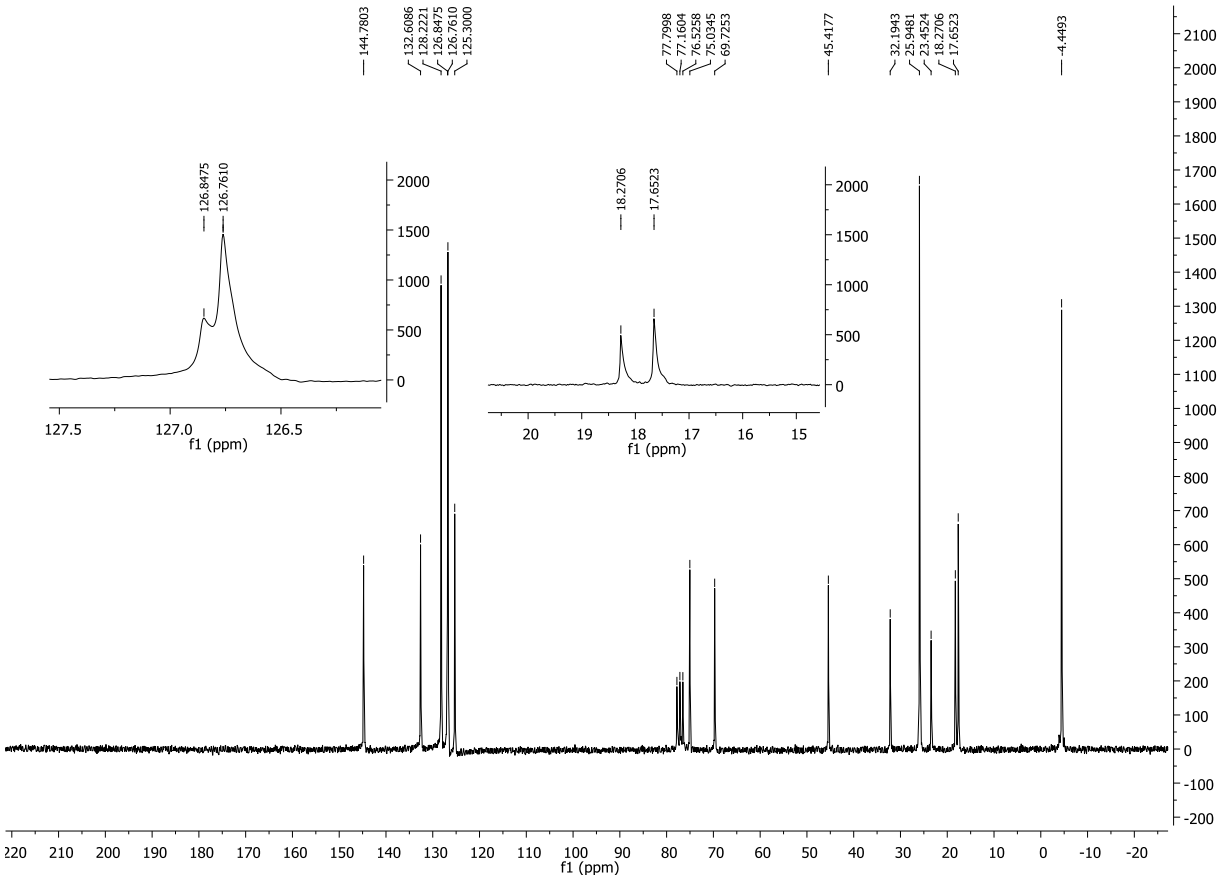
^{13}C NMR ($CDCl_3$, 50 MHz) of **7a'**



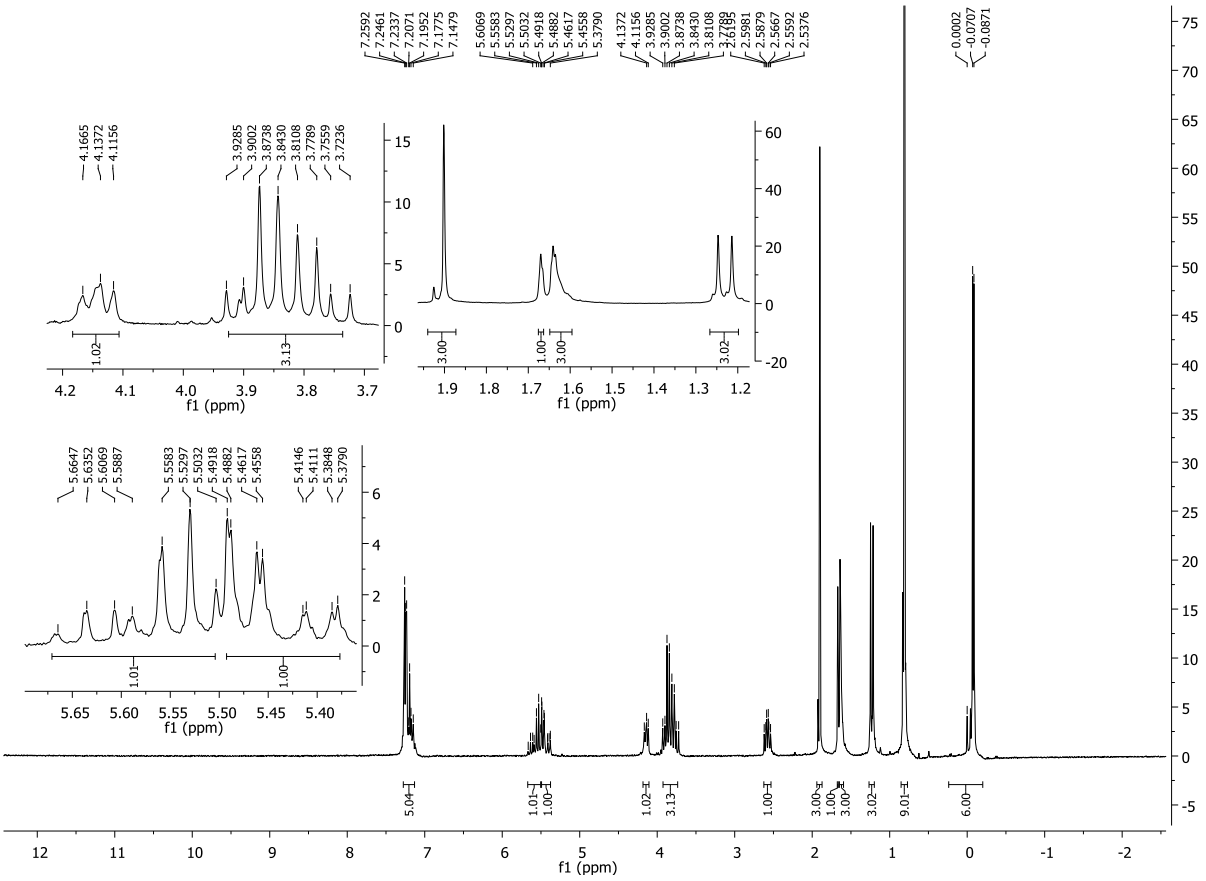
^{1}H NMR ($CDCl_3$, 200MHz) of **7b'**



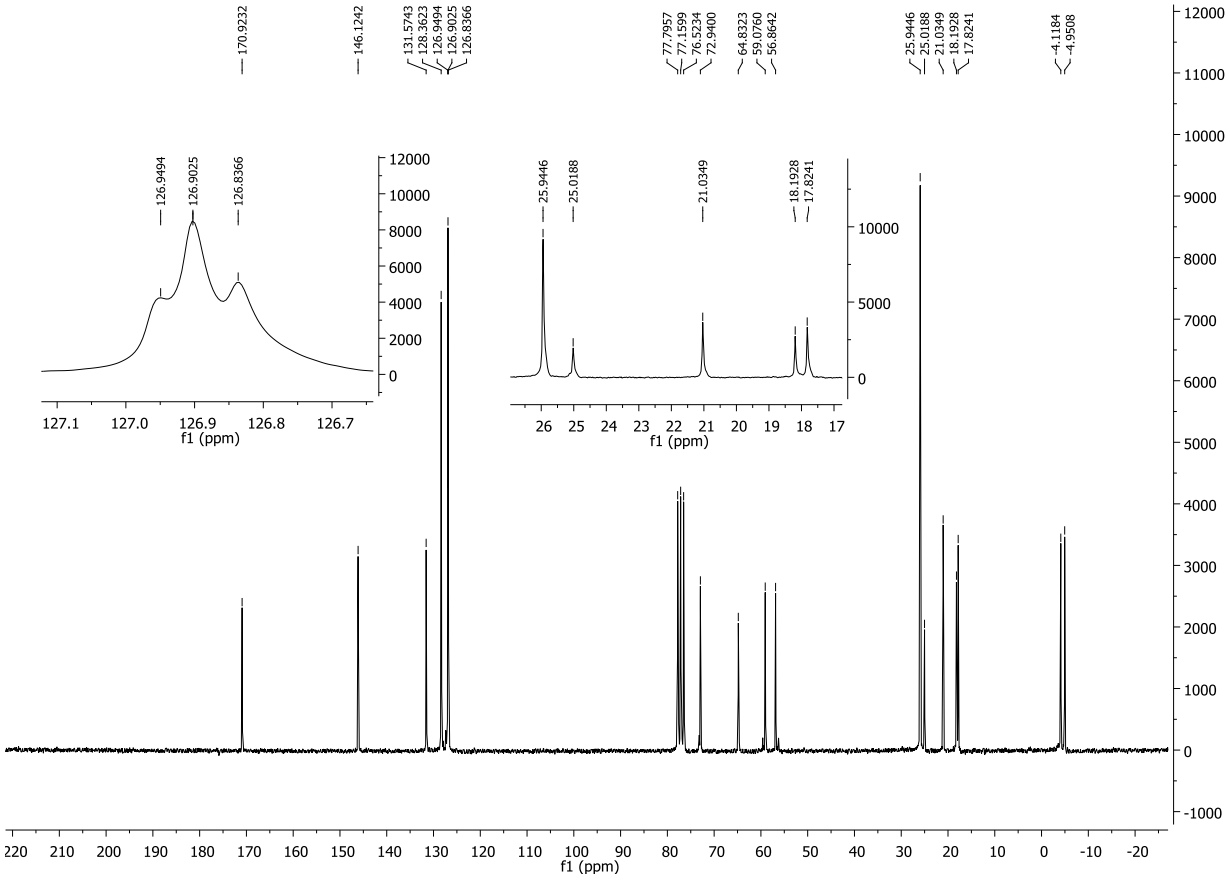
^{13}C NMR ($CDCl_3$, 50 MHz) of **7b'**



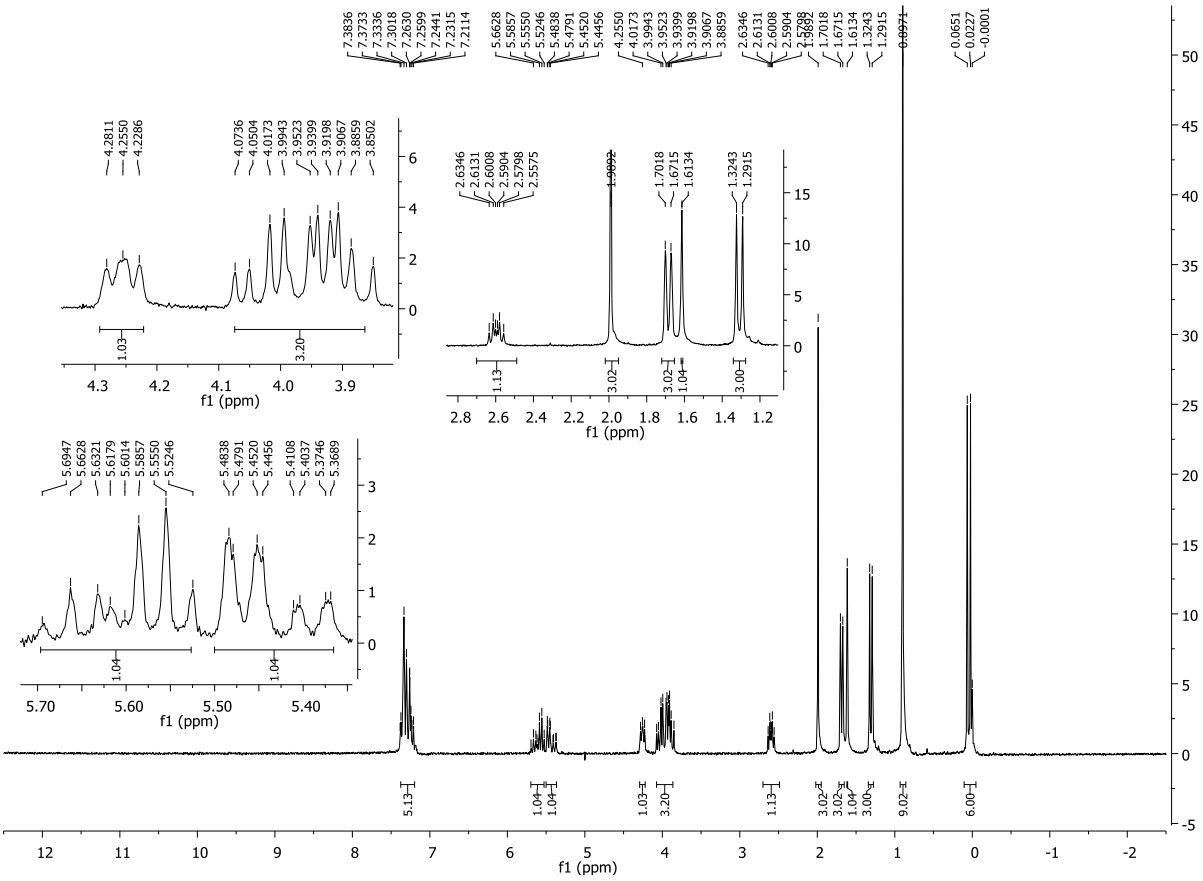
^{1}H NMR ($CDCl_3$, 200MHz) of **8a'**



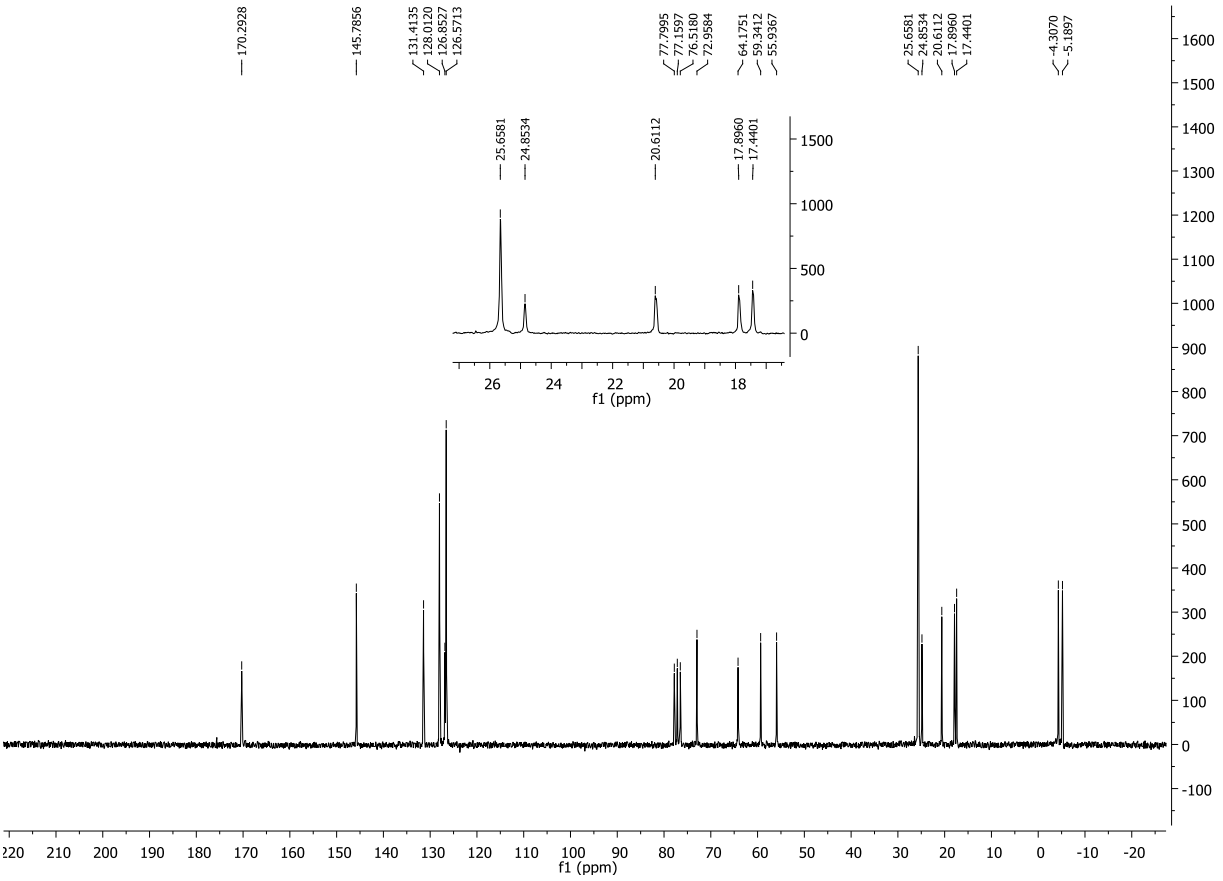
^{13}C NMR ($CDCl_3$, 50 MHz) of **8a'**



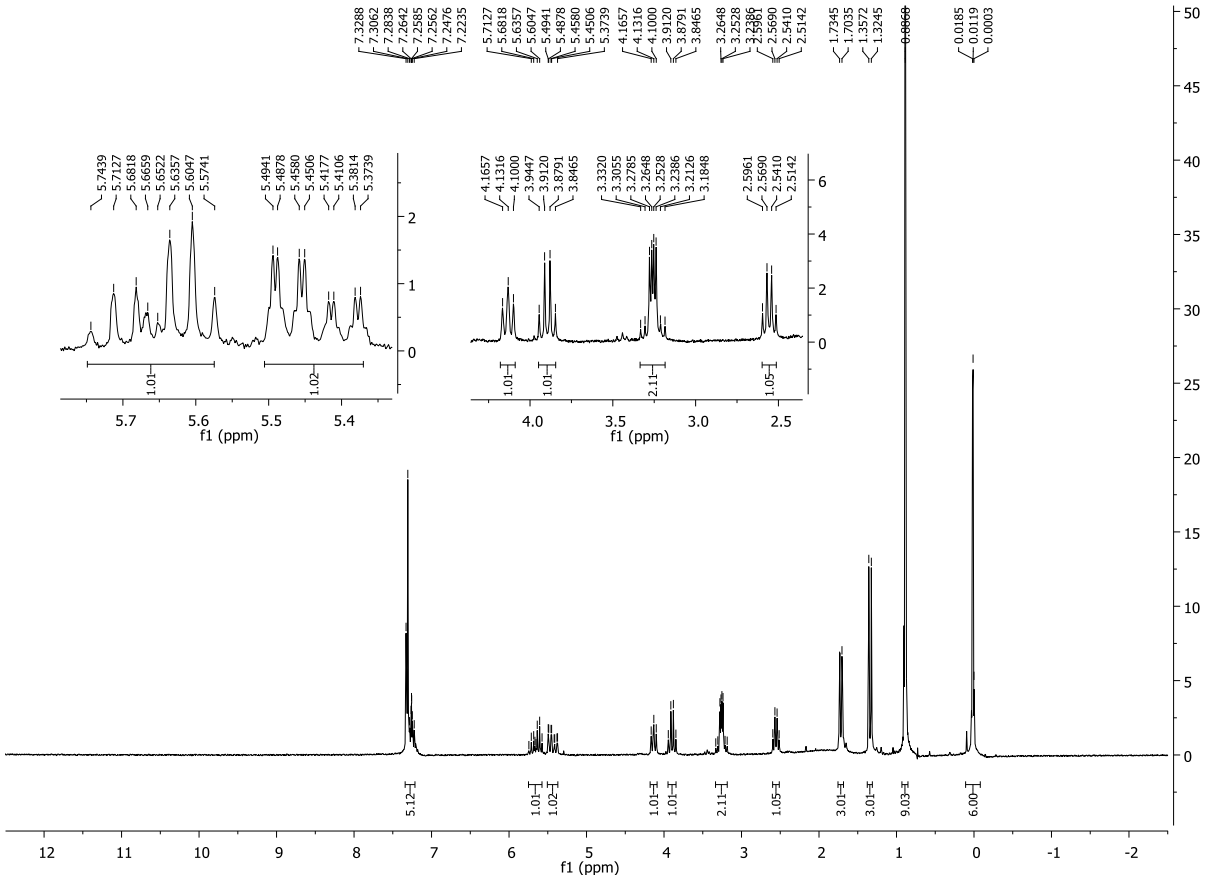
^{1}H NMR ($CDCl_3$, 200MHz) of **8b'**



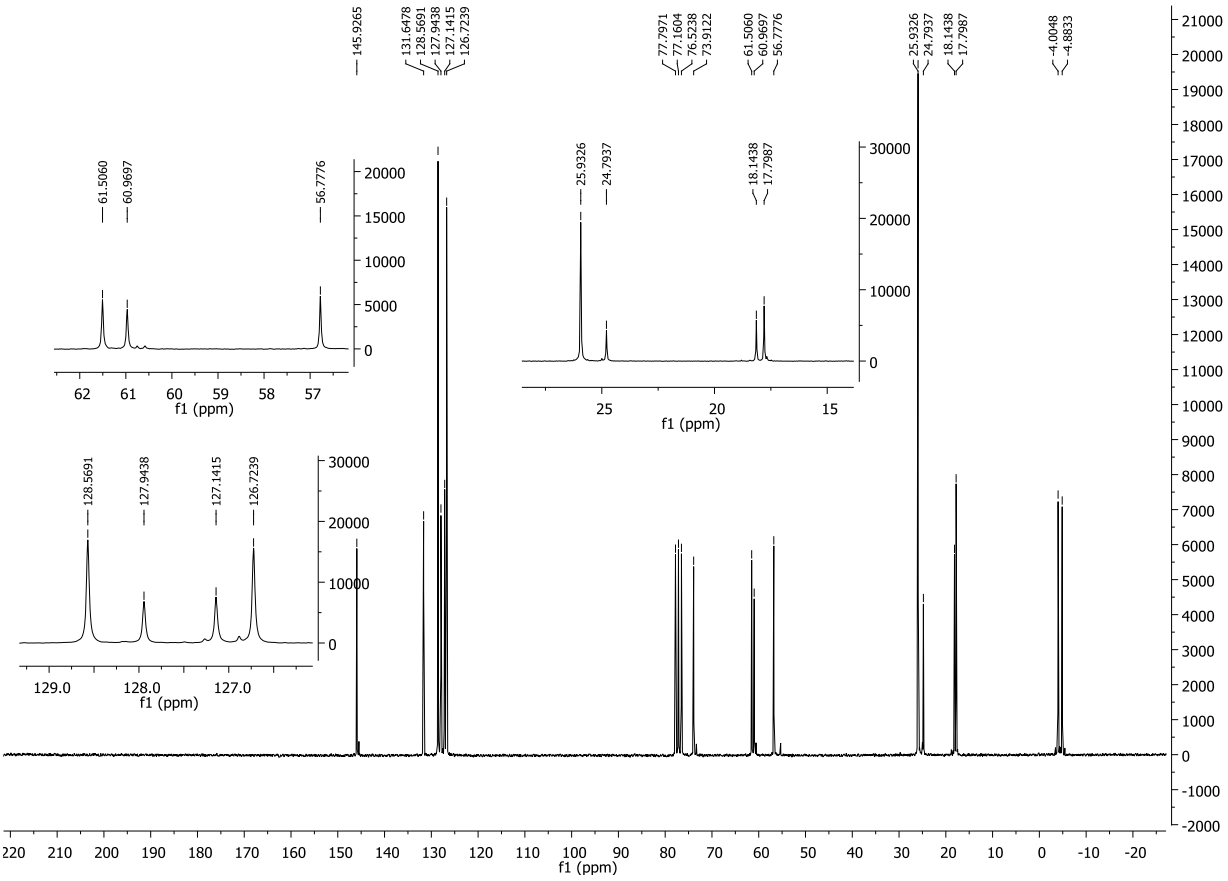
^{13}C NMR ($CDCl_3$, 50 MHz) of **8b'**



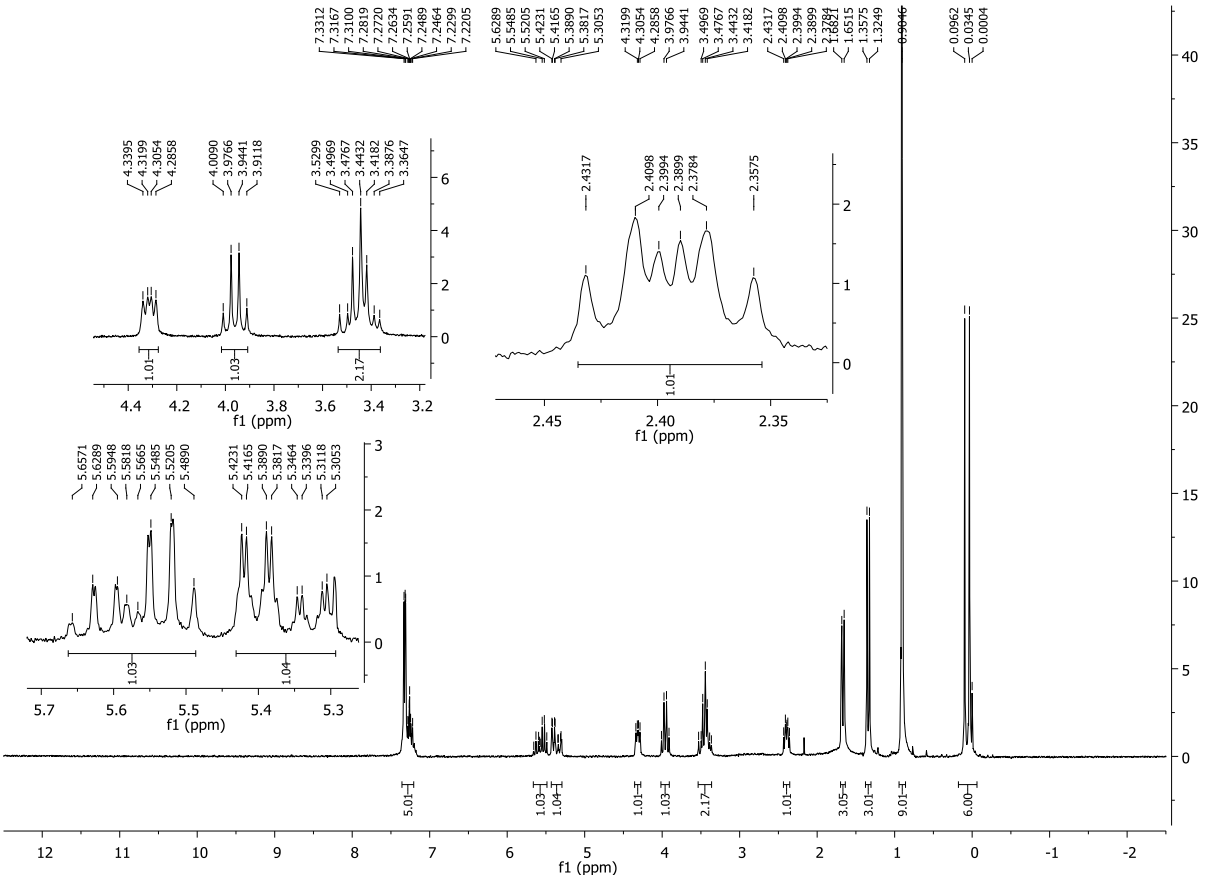
^{1}H NMR ($CDCl_3$, 200MHz) of **9a'**



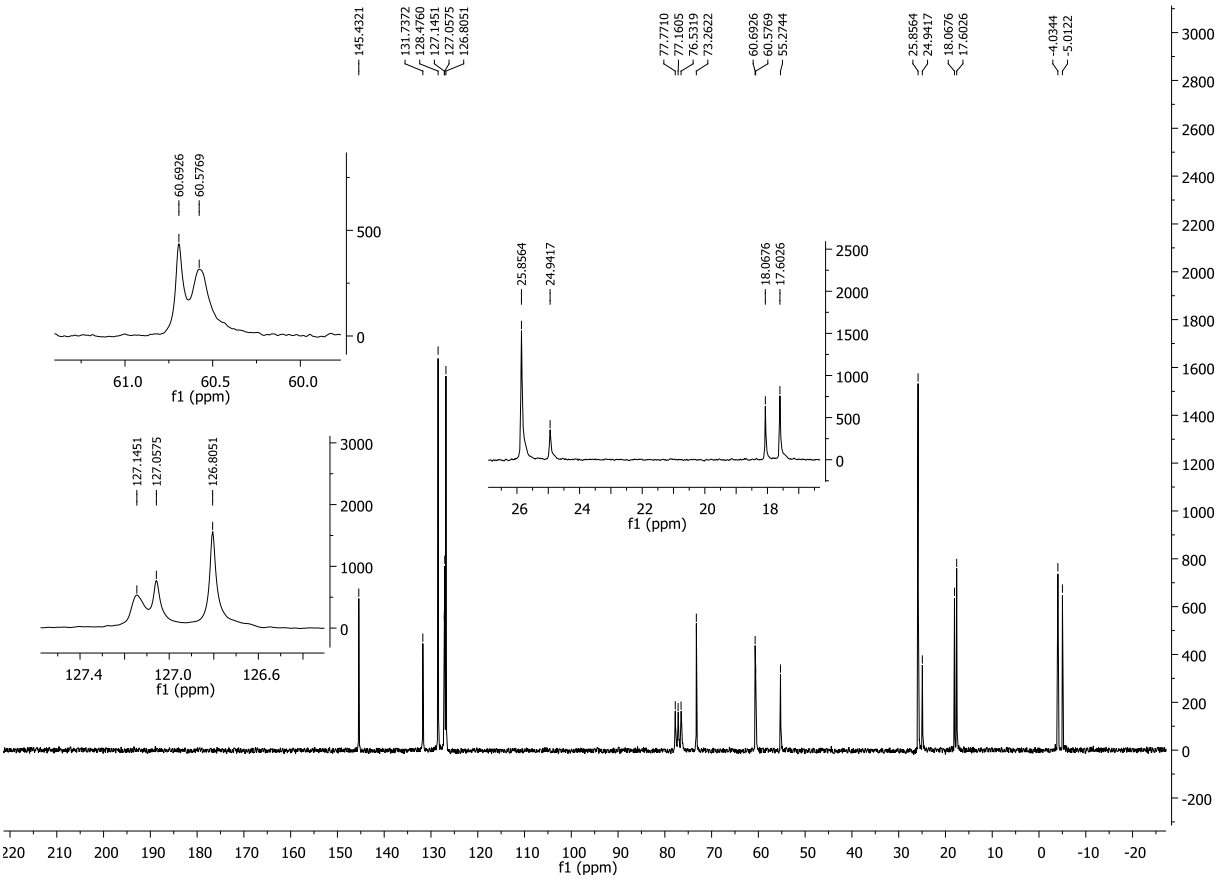
^{13}C NMR ($CDCl_3$, 50 MHz) of **9a'**



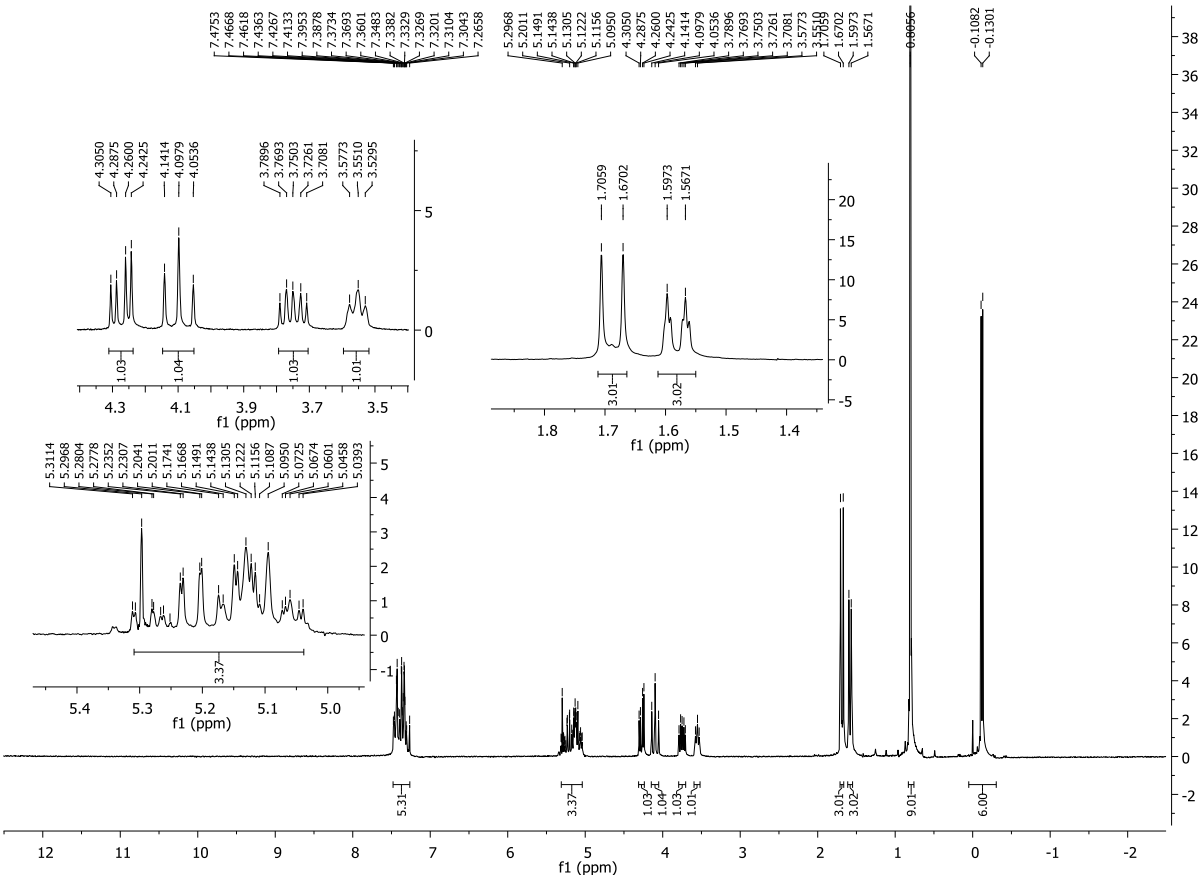
^{1}H NMR ($CDCl_3$, 200MHz) of **9b'**



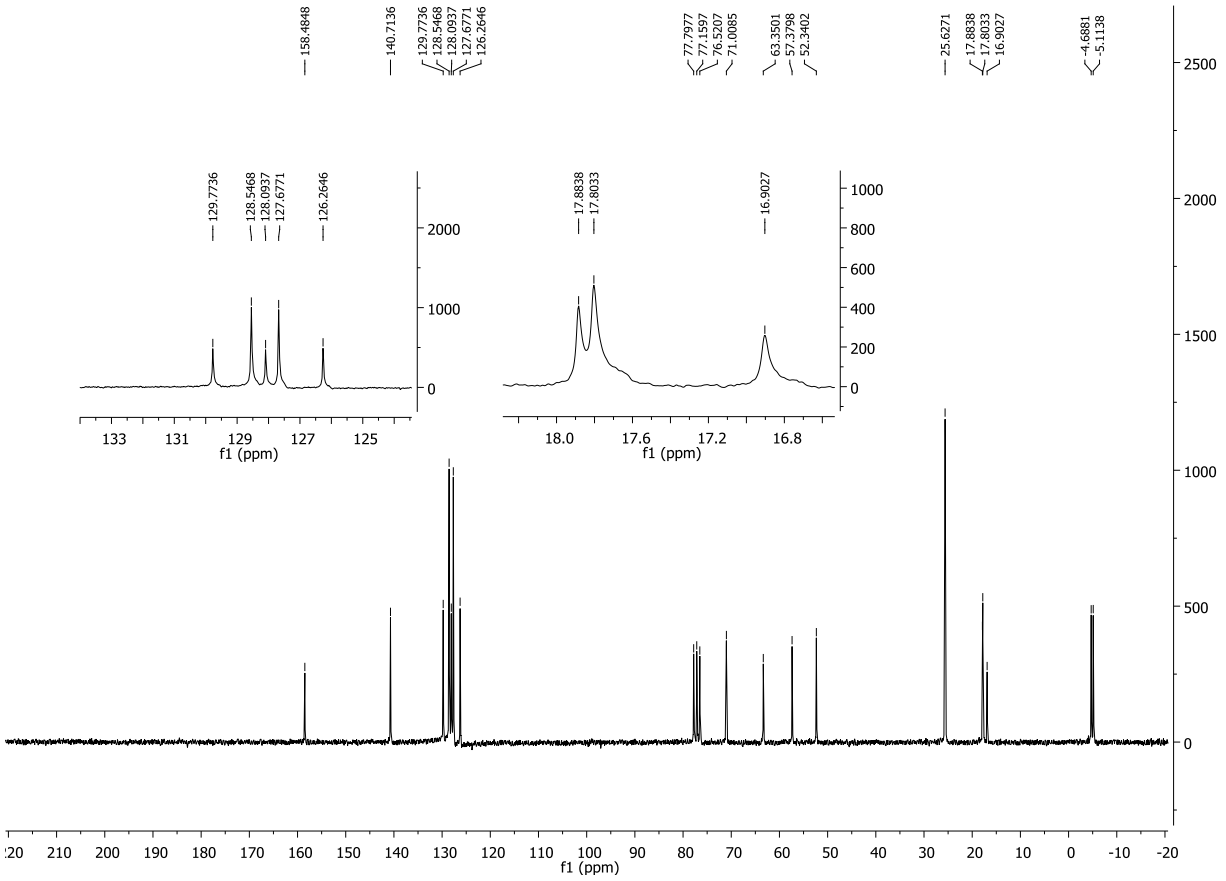
^{13}C NMR ($CDCl_3$, 50 MHz) of **9b'**



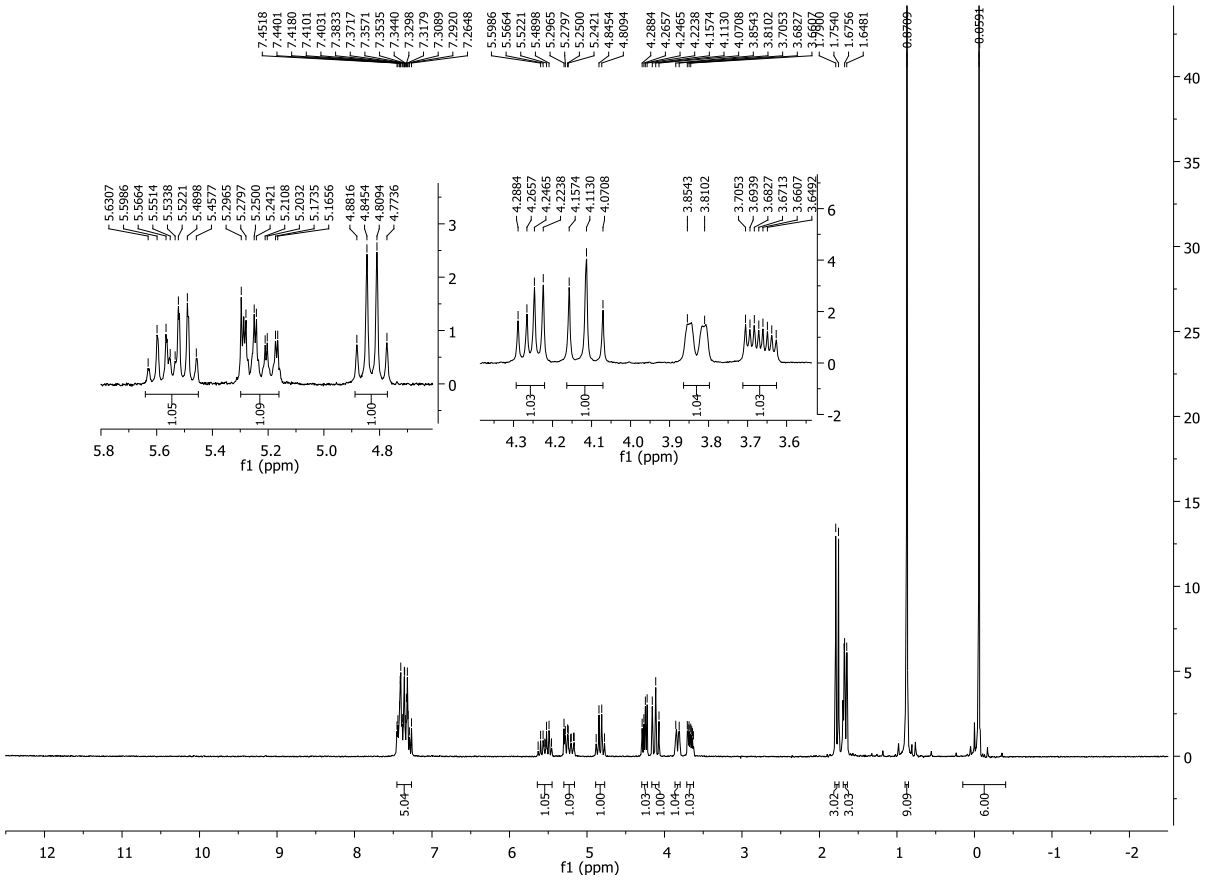
^{1}H NMR ($CDCl_3$, 200MHz) of **10a'**



^{13}C NMR ($CDCl_3$, 50 MHz) of **10a'**



^{1}H NMR ($CDCl_3$, 200MHz) of **10b'**



^{13}C NMR ($CDCl_3$, 50 MHz) of **10b'**