Electronic Supplementary Material (ESI) for Chemical Communications

Tandem regio- and diastereo-selective synthesis of halogenated *C*-vinyl glycosides from unactivated arylacetylenes

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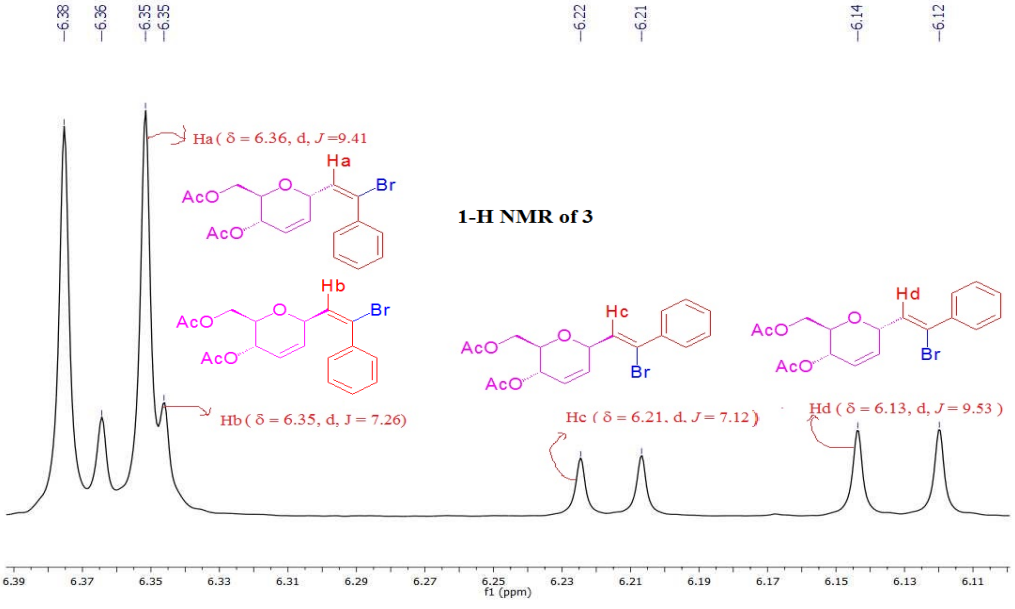
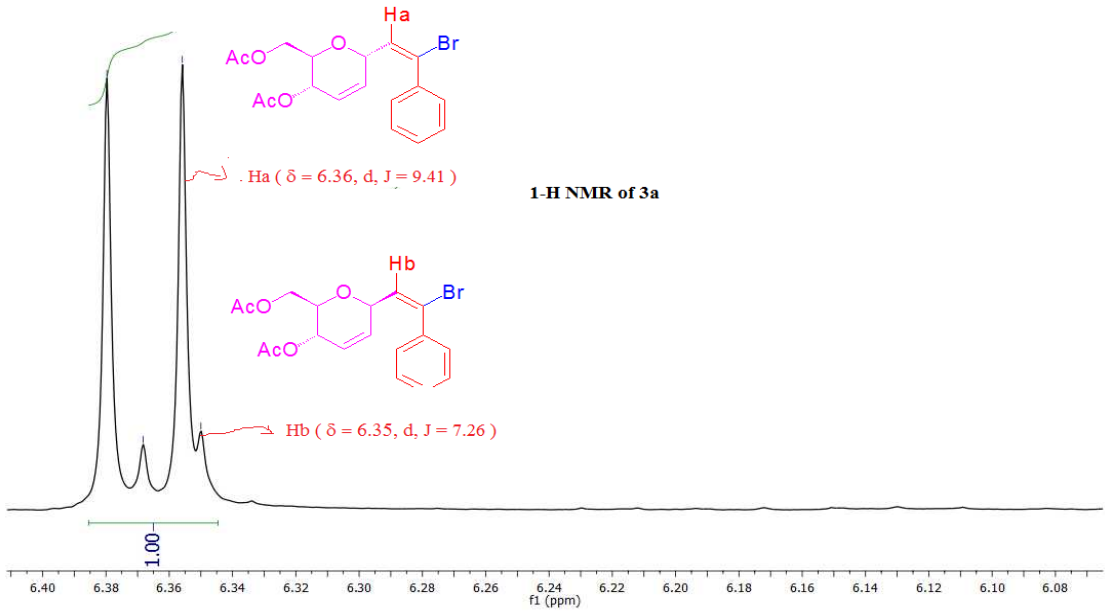
General information: ^{1}H and ^{13}C NMR spectra were recorded on 400 and 500 MHz spectrometers with TMS as the internal standard. Chemical shifts are expressed in parts per million (δ ppm). Silica gel coated aluminium plates were used for TLC. The products were

purified by column chromatography on silica gel (60-120/100-200 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. Exact Mass of all products were analysed by using HRMS having QTOF analyser. Reagents used were mostly purchased from Sigma Aldrich.

Representative procedure for glycosylation/halogenation with aryl acetylenes (1): Triacetyl-*O*-acetyl-D-glucal (272 mg, 1 mmol) in dichloroethane (10 mL) were placed in a dry, nitrogen -flushed, 100 mL round-bottom flask equipped with a magnetic stirring bar. The solution was cooled to -25 °C and Phenylacetylene (120 µL, 1.1 mmol) was added via syringe, followed by iron (III) bromide (0.33 mmol, 96 mg). The reaction solution gradually turned dark purple and was allowed to stir for another 1hour. The completion of the reaction was monitored through TLC. The reaction mixture was quenched with water, extracted with dichloromethane (3 × 15 mL). The organic layer was separated and dried over anhydrous $MgSO_4$. Product **3a** (334mg, *E*α:*E*β = 11.47:1, 85% yield) was isolated by flash column chromatography using petroleum ether/EtOAc as eluent.



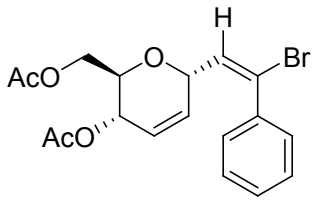
A



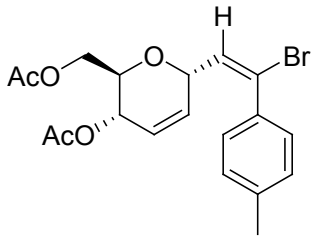
B

Fig 1: Product distribution obtained during the reaction of phenyl acetylene and glucal triacetate in presence of $FeBr_3$ at different temperatures. **A**. Reaction operated at rt. **B**. Reaction operated at -25 ^{o}C.

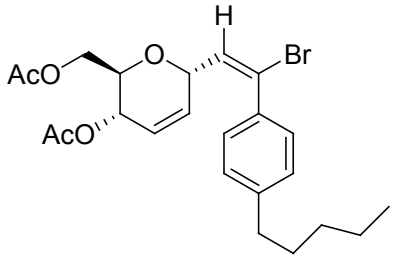
Spectral analysis



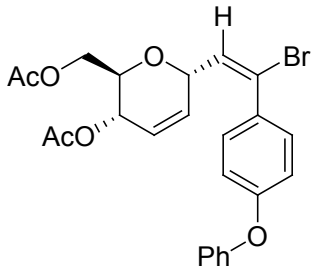
Prepared by the representative procedure **1** using tri-*O*-acetyl-D-glucal (1 mmol, 272 mg) and phenyl acetylene (1.1 mmol, 0.120 mL) to yield **3a** in 85% (334 mg) yield. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.47-7.32 (m, 5H), 6.37 (d, J = 9.5 Hz,1H), 5.81 (ddd, J = 10.6, 6.4, 5.1 Hz, 2H), 5.17 (dd, J = 7.3, 1.1, 1H), 4.64 (dd, J = 9.6, 1.6 Hz, 1H), 4.18 (ddd, J = 15.3, 12.0, 4.5 Hz, 3H), 4.0 (ddd, J = 7.3, 5.8, 3.2 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.86, 170.38, 137.63, 130.67, 129.89, 129.36, 128.81 (2C), 128.42 (2C), 127.10, 124.77, 70.23, 70.00, 64.45, 62.89, 21.09, 20.87. HRMS (ESI^{+}) m/z calcd. for $C_{18}H_{19}BrNaO_5$ $(M+Na)^{+}$ 417.0314, found 417.0305



Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-ethynyl-4-methylbenzene (0.55 mmol, 64 μL) to yield **3b** (74%,150 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 17.9 Hz, 2H), 6.33 (d, *J* = 9.5 Hz, 1H), 5.80 (ddd, *J* = 10.7, 6.2, 5.2 , 2H), 5.16 (dd, *J* = 7.2, 3.1 Hz, 1H), 4.64 (d, *J* = 9.6, 1H), 4.18 (ddd, *J* = 15.3,12.0, 4.5 Hz, 2H), 4.0 (ddd, *J* = 7.3, 5.8, 3.3 Hz, 1H) 2.36 (s, 3H) 2.10 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.91, 170.43, 139.50, 134.78, 130.80, 129.49, 129.07 (2C), 128.74 (2C), 127.45, 124.63, 70.27, 69.99, 64.50, 62.93, 21.33, 21.09, 20.87. HRMS (ESI^+) m/z calcd for $C_{19}H_{21}BrO_5$ $(M+H)^+$ 409.0645, found 409.0647.

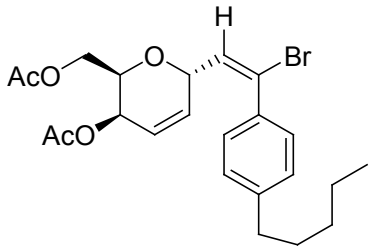


Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-ethynyl-4-pentylbenzene (0.55 mmol, 94μL) to yield **3c** (68%,157 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.34 (d, *J* = 9.5 Hz, 1H), 5.88 – 5.76 (m, 2H), 5.24 – 5.14 (m, 1H), 4.66 (d, *J* = 9.6 Hz, 1H), 4.23 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.14 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.00 (ddd, *J* = 7.3, 5.7, 3.2 Hz, 1H), 2.60 (t, *J* = 7.53), 2.10 (s, 3H), 2.09(s, 3H), 1.69–1.54 (m, 2H), 1.37–1.26 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.89, 170.41, 144.51, 134.90, 130.79, 129.40, 128.76(2C), 128.40 (2C), 127.59, 124.69, 70.33, 69.92, 64.51, 62.96, 35.71, 31.48, 30.96, 22.53, 21.08, 20.87, 14.04. HRMS (ESI^+) m/z calcd for $C_{23}H_{28}BrNaO_5$ $(M+Na)^+$ 487.1091, found 487.1080.

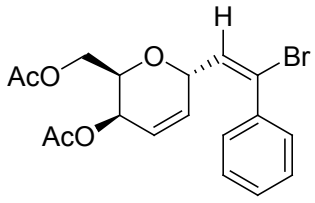


Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-(4-ethynylphenoxy)benzene(0.55 mmol, 98 μL) to yield **3d** (75%,182 mg).**^{1}H NMR**

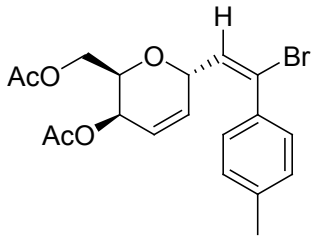
(400 MHz, Chloroform-d) δ 7.42–7.35 (m, 4H), 7.19–7.12 (m, 1H), 7.06–7.04 (m, 2H), 6.97–6.95 (m, 2H), 6.34 (d, *J* = 9.6 Hz, 1H), 5.82 (dt, *J* = 16.9, 7.4 Hz, 1H), 5.18 (d, *J* = 7.3 Hz, 1H), 4.66 (dd, *J* = 9.6, 1.2 Hz, 1H), 4.22 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.14 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.00 (ddd, *J* = 8.9, 5.8, 3.2 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.89, 170.41, 158.53, 156.06, 132.02, 130.70, 130.56 (2 X C), 129.98 (2 X C), 129.63, 127.09, 124.81, 124.17, 119.79(2 X C), 117.76(2C), 70.23, 70.01, 64.48, 62.90, 21.10, 20.88.HRMS (ESI^+) m/z calcd for $C_{24}H_{23}BrNaO_6$ $(M+Na)^+$ 509.0570 , found 509.0559.



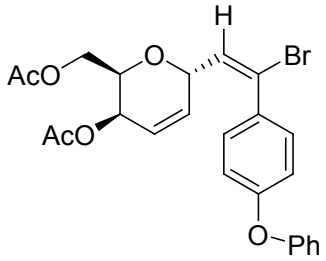
Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-galactal (0.5 mmol, 136 mg) and 1-ethynyl-4-pentylbenzene (0.55 mmol, 94 μL) to yield **3e** (65%,150 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.33 (d, *J* = 9.6 Hz, 1H), 6.03 (ddd, *J* = 10.1, 5.3, 2.0 Hz, 1H), 5.94 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.09 (d, *J* = 5.1 Hz, 1H), 4.72 (ddd, *J* = 9.6, 3.0, 2.2 Hz, 1H), 4.23–4.15 (m, 3H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.09 (s, 3H), 2.06 (s, 3H), 1.64–1.56 (m, 2H), 1.37–1.28 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.75, 170.46, 144.55, 134.90, 133.26, 128.80 (2 X C), 128.68, 128.40 (2 X C), 128.13, 122.42, 70.73, 68.87, 63.28, 62.77, 35.70, 31.45, 30.94, 22.51, 20.86, 20.84, 14.00. HRMS (ESI^+) m/z calcd for $C_{23}H_{29}BrO_5$ $(M+H)^+$ 465.1271, found 465.1264.



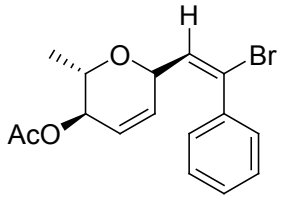
Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-galactal (0.5 mmol, 136 mg) and phenyl acetylene (0.55 mmol, 62 μL) to yield **3f** (82%,160 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.45 (dd, *J* = 7.8, 1.7 Hz 2H), 7.36 (dd, *J* = 7.1 Hz, 5.4, 3H), 6.37 (d, *J* = 9.5 Hz, 1H), 6.03 (ddd, *J* = 10.1, 5.3, 2.0, 1H), 5.93 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.09 (dd, *J* = 5.23, 1.5 Hz, 1H), 4.76-4.62 (m, 1H), 4.31-4.12 (m, 3H), 2.09 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 170.78, 170.48, 137.59, 133.08, 129.38, 129.15, 128.86 (2 X C), 128.42 (2 X C), 127.64, 122.53, 70.64, 68.87, 63.23, 62.75, 20.88, 20.86. HRMS (ESI^+) m/z calcd for $C_{18}H_{20}BrO_5$ $(M+H)^+$ 395.0489, found 395.0478.



Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-galactal (0.5 mmol, 136 mg) and 1-ethynyl-4-methylbenzene (0.55 mmol, 65 µL) to yield **3g** (72%,146 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.35 (d, *J* = 8.1 Hz 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.33 (d, *J* = 9.5 Hz, 1H), 6.02 (ddd, *J* = 10.1, 5.3, 2.0, 1H), 5.92 (dd, *J* = 10.3, 3.3 Hz, 1H), 5.09 (d, *J* = 5.2 Hz, 1H), 4.71(ddd, *J* = 9.5, 3.0, 2.2 Hz, 1H), 4.28-4.13(m, 3H), 2.36 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.78, 170.48, 137.59, 133.08, 129.38, 129.15, 128.86 (2 X C), 128.42 (2 X C), 127.64, 122.53, 70.64, 68.87, 63.23, 62.75, 20.88, 20.86. HRMS (ESI^+) m/z calcd for $C_{19}H_{21}BrO_5$ $(M+H)^+$ 409.0645, found 409.0639.

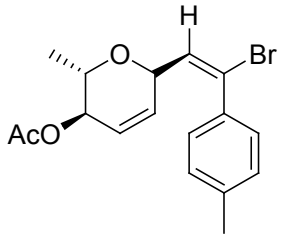


Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-galactal (0.5 mmol, 136 mg) and 1-(4-ethynylphenoxy)benzene (0.55 mmol, 98 µL) to yield **3h (**70%,170 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.46–7.41 (m, 2H), 7.40–7.33 (m, 2H), 7.18–7.13 (m, 1H), 7.04 (dt, *J* = 9.0, 1.8 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.34 (d, *J* = 9.6 Hz, 1H), 6.04 (ddd, *J* = 10.1, 5.3, 2.0 Hz, 1H), 5.94 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.09 (dd, *J* = 5.3, 1.4 Hz, 1H), 4.72 (ddd, *J* = 9.6, 3.0, 2.2 Hz, 1H), 4.25 – 4.16 (m, 2H), 4.14 (dd, *J* = 12.0, 3.2 Hz, 1H), 2.08 (s, 3H), 2.07 (s,3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.93, 169.64, 157.68, 155.24, 132.28, 131.14, 129.77 (2 X C), 129.11 (2 X C), 128.03, 126.82, 123.29, 121.71, 118.87 (2 X C), 116.96 (2 X C), 69.80, 68.05, 62.39, 61.90, 20.05, 20.02. HRMS (ESI^+) m/z calcd for $C_{24}H_{24}BrO_6$ $(M+H)^+$ 487.0751 , found 487.0742.

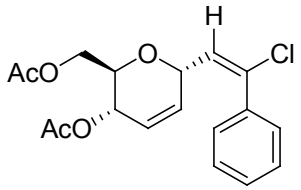


Prepared by the representative procedure **1** using 3,4 Di-*O*-acetyl-L-rhamnal (0.5 mmol, 107 mg) and phenyl acetylene (0.55 mmol, 62 µL) to yield **3i (**78%,131 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.46–7.41 (m, 2H), 7.40–7.33 (m, 3H), 6.36 (d, *J* = 9.6 Hz, 1H), 5.79 (d, *J* = 1.1 Hz, 2H), 4.93 – 4.86 (m, 1H), 4.56 (d, *J* = 9.6 Hz, 1H), 4.00 – 3.88 (m, 1H), 2.10

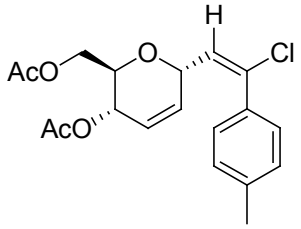
(s, 3H, 1.21 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.66, 137.72, 130.99, 130.69, 129.21, 128.82 (2 X C), 128.33 (2 X C), 126.52, 124.45, 69.35, 69.27, 68.55, 21.18, 17.52. HRMS (ESI^+) m/z calcd for $C_{16}H_{18}BrO_3$ $(M+H)^+$ 337.0434 , found 337.0421.



Prepared by the representative procedure **1** using of 3,4 Di-*O*-acetyl-L-rhamnal (0.5 mmol, 131 mg) and 1-ethynyl-4-methylbenzene (0.55 mmol, 64 µL) to yield **3j (**72%,126 mg); **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.33 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 6.33 (d, *J* = 9.6 Hz, 1H), 5.79 (bs, 2H), 4.90 (dd, *J* = 6.0, 2.1 Hz, 1H), 4.57 (d, *J* = 9.6 Hz, 1H), 3.93 (dq, *J* = 12.6, 6.3 Hz, 1H), 2.36 (s, 2H), 2.10 (s, 2H), 1.21 (d, *J* = 6.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.71, 139.35, 134.92, 131.17, 130.34, 129.01 (2 X C), 128.77 (2 X C), 126.87, 124.35, 69.40, 69.33, 68.60, 21.32, 21.22, 17.55. HRMS (ESI^+) m/z calcd for $C_{17}H_{19}BrO_3$ $(M+H)^+$ 350.0518 , found 350.0523.

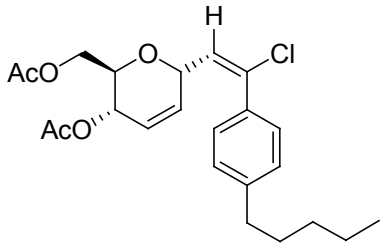


Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-glucal (1 mmol, 272 mg) and phenyl acetylene (1.1 mmol, 120 µL) to yield **4a** 87% (304 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.47 (dd, *J* = 6.6, 3.2 Hz, 1H), 7.39 (dd, *J* = 5.0, 1.9 Hz, 2H), 6.13 (d, *J* = 9.7 Hz, 1H), 5.81 (dt, *J* = 11.5,1.7 Hz, 1H), 5.18 (dd, *J* = 7.2, 1.2 Hz, 1H), 4.70 (d, *J* = 9.8 Hz, 1H), 4.23 (dd, *J* = 12.0, 5.8 Hz, 1H), 4.15 (dd, *J* = 12.0, 3.3 Hz, 1H), 4.01 (ddd, *J* = 7.2, 5.9, 3.2 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.90, 170.43, 137.30, 136.08, 130.99, 129.51, 128.69 (2 X C), 128.44 (2 X C), 125.66, 124.73, 69.99, 69.58, 64.50, 62.93, 21.10, 20.89. HRMS (ESI^+) m/z calcd for $C_{18}H_{19}ClNaO_5$ $(M+Na)^+$ 373.0813, found 373.0814

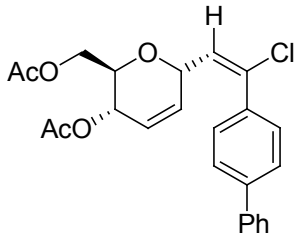


Prepared by the representative procedure 1 using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-ethynyl-4-methylbenzene (0.55 mmol, 62 µL) to yield **4b** (75%,136 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.36 (d, *J* = 8.1, Hz 2H), 7.19 (d, *J*= 7.9 Hz, 2H), 6.09 (d, *J* =

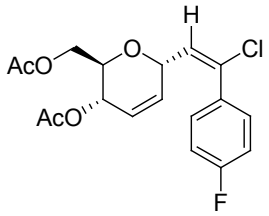
9.7 Hz, 1H), 5.92-5.75 (m, 1H), 5.18 (d, *J* = 7.3 Hz, 1H), 4.71 (d, *J* = 9.9 Hz, 1H), 4.23 (dd, *J* = 12.0, 5.8, Hz 1H), 4.15 (dd, *J* =12.0, 3.3 Hz, 1H), 4.01 (ddd, *J* = 6.9, 6.0, 3.3 Hz, 1H), 2.37 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.93, 170.45, 139.65, 137.53, 133.24, 131.13, 129.10 (2 X C), 128.65 (2 X C), 125.20, 124.59, 69.99, 69.63, 64.54, 62.97, 21.35, 21.11, 20.89. HRMS (ESI$^+$) m/z calcd for $C_{19}H_{21}ClNaO_5$ $(M+Na)^+$ 387.0975, found 387.0970



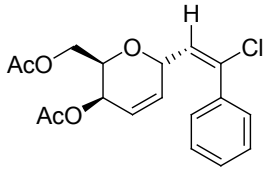
Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-ethynyl-4-pentylbenzene (0.55 mmol, 94 μL) to yield **4C (**72%,151 mg**). ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.09 (d, *J* = 9.8 Hz, 1H), 5.83 (bs, 1H), 5.19 (d, *J* = 7.2, Hz, 1H), 4.72 (d, *J* = 9.8 Hz, 1H), 4.19 (ddd, *J* = 15.2, 12.0, 4.5 Hz, 3H), 4.01 (dd, *J* = 6.4, 3.3 Hz, 1H), 2.61 (t, *J* = 7.58 Hz, 2H), 2.10 (s, 3H), 2.09(s,3H), 1.62 (m, 2H), 1.32 (m, 4H), 0.90 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.87, 170.40, 144.65, 137.61, 133.39, 131.14, 128.61, 128.41, 125.17, 125.12,124.74, 124.65, 70.00, 69.90, 64.61, 63.00, 35.72, 31.47, 30.95, 22.51, 20.89, 20.82, 14.05. HRMS (ESI$^+$) m/z calcd for $C_{23}H_{30}ClO_5$ $(M+H)^+$ 421.1776, found 421.1764.



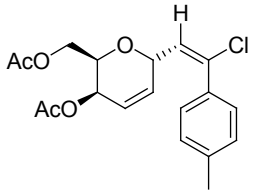
Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-ehynyl-4-phenyl-benzene (0.55 mmol, 90 μL) to yield **4d (**79%,168 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.70–7.51 (m, 6H), 7.49–7.43 (m, 2H), 7.39 (d, *J* = 7.3 Hz, 1H), 6.16 (d, *J* = 9.8 Hz, 1H), 5.93 – 5.78 (m, 2H), 5.24 – 5.14 (m, 1H) , 4.77 (dd, *J* = 9.8, 1.4 Hz, 1H), 4.22 (ddd, *J* = 15.3, 12.0, 4.5 Hz, 2H), 4.03 (ddd, *J* = 7.2, 5.8, 3.3 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.93, 170.45, 142.38, 140.14, 137.23, 134.92, 131.00, 129.21 (2 X C), 128.94 (2 X C), 127.86, 127.16 (2 X C), 127.12 (2 X C), 125.78, 124.80, 70.02, 69.63, 64.55, 62.99, 21.12, 20.19. HRMS (ESI$^+$) m/z calcd for $C_{24}H_{23}ClNaO_5$ $(M+Na)^+$ 449.1126, found 449.1127



Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-glucal (0.5 mmol, 136 mg) and 1-ethynyl-4-Fluorobenzene (0.55 mmol, 66 µL) to yield **4e (**80%,147 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.56–7.40 (m, 2H), 7.17–6.98 (m, 2H), 6.13 (d, *J* = 9.7 Hz, 1H), 5.91–5.77 (m, 2H), 5.19 (ddd, *J* = 7.3, 3.5, 2.1 Hz, 1H), 4.69–4.59 (m, 1H), 4.23 (dd, *J* = 12.0, 5.8 Hz, 1H), 4.16 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.01 (ddd, *J* = 7.3, 5.8, 3.3 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H).). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.87, 170.40, 163.14 (d, C-F Coupling), 136.51, 132.12, 130.81, 130.79, 130.74, 125.96, 124.92, 115.61, 115.44, 70.04, 69.47, 64.49, 62.91, 21.09, 20.88. HRMS (ESI^+) m/z calcd for $C_{18}H_{19}ClFO_5$ $(M+H)^+$ 369.0900, found 369.0890

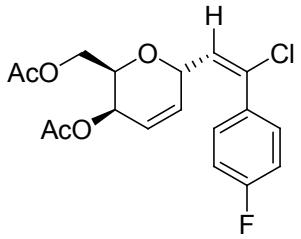


Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-galactal (0.5 mmol, 136 mg) and phenylacetylene (0.55 mmol, 56 µL) to yield **4f** 80% (140 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.53-7.48 (m, 2H), 7.41-7.35 (m, 3H), 6.13 (d, *J* = 9.8 Hz, 1H), 6.07-6.00 (m, 1H), 5.95 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.11 (d, *J* = 5.2 Hz, 1H), 4.83-4.70 (m, 1H), 4.29-4.15 (m, 2H), 2.09 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.38, 168.08, 135.41, 133.60, 130.95, 127.11, 126.32 (2 X C), 126.03 (2 X C), 122.48, 120.09, 67.57, 66.42, 60.86, 60.36, 18.48, 18.44. HRMS (ESI^+) m/z calcd for $C_{24}H_{23}ClNaO_5$ $(M+Na)^+$ 449.1126, found 449.1123

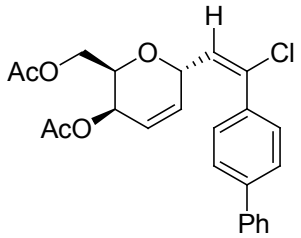


Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-galactal (0.5 mmol, 136 mg) and 1-ethynyl-4-methylbenzene (0.55 mmol,64 µL) to yield **4g (**74%,134 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.40 (d, *J* = 8.1, Hz 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.09 (d, *J* = 9.8 Hz, 1H), 6.03 (ddd, *J* =10.1, 5.2, 2.0 Hz, 1H), 5.94 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.10 (d, *J* = 5.2 Hz, 1H), 4.77 (ddd, *J* = 9.8, 3.2, 2.1 Hz, 1H), 4.29-4.17 (m, 1H), 2.37 (s, 3H), 2.37 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.80, 170.50, 139.67, 138.04, 133.49, 133.18, 129.07 (2 X C), 128.66 (2 X C), 124.44, 122.41, 70.05, 68.83, 63.31,

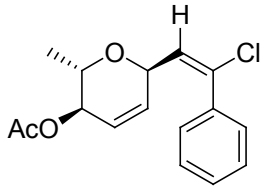
62.79, 21.34, 20.91, 20.86. HRMS (ESI$^+$) m/z calcd for $C_{19}H_{22}ClO_5$ $(M+H)^+$ 365.1150, found 365.1143.



Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-galactal (0.5 mmol, 136 mg) and 1-ethynyl-4-Fluorobenzene (0.55 mmol, 66 µL) to yield **4h (**78%,143 mg).**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.55–7.50 (m, 1H), 7.12–7.05 (m, 1H), 6.12 (d, *J* = 9.8 Hz, 1H), 6.05 (ddd, *J* = 10.1, 5.3, 2.0 Hz, 1H), 5.95 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.11 (d, *J* = 5.1 Hz, 1H), 4.71 (ddd, *J* = 9.8, 3.1, 2.1 Hz, 1H), 4.31 – 4.16 (m, 2H), 2.08(s, 3H), 2.077 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.77, 170.48, 163.16 (d, C-F coupling), 137.07, 133.19, 132.09, 132.06, 130.88, 130.81, 125.21, 122.68, 115.59, 115.42, 69.87, 68.92, 63.23, 62.75, 20.90, 20.85. HRMS (ESI$^+$) m/z calcd for $C_{18}H_{19}ClO_5$ $(M+H)^+$ 369.0900, found 369.0908

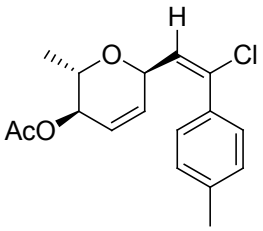


Prepared by the representative procedure **1** using of tri-*O*-acetyl-D-galactal (0.5 mmol, 136 mg) and 1-ehynyl-4-phenyl-benzene (0.55 mmol, 98 µL) to yield **4i (**75%,159 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.64–7.56 (m, 6H), 7.50–7.42 (m, 2H), 7.38 (ddd, *J* = 7.3, 3.8, 1.2 Hz, 1H), 6.15 (d, *J* = 9.8 Hz, 1H), 6.06 (ddd, *J* = 10.1, 5.2, 1.9 Hz, 1H), 5.98 (dd, *J* = 10.2, 3.3 Hz, 1H), 5.12 (d, *J* = 5.2 Hz, 1H), 4.83 (ddd, *J* = 9.8, 3.0, 2.0 Hz, 1H), 4.33–4.18 (m, 3H), 2.09 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.84, 170.54, 142.40, 140.14, 137.78, 134.87, 133.42, 129.27 (2 X C), 128.94 (2 X C), 127.86, 127.15 (2 X C), 127.11 (2 X C), 125.03, 122.56, 70.03, 68.90, 63.31, 62.83, 20.93, 20.90. HRMS (ESI$^+$) m/z calcd for $C_{24}H_{24}ClO_5$ $(M+H)^+$ 427.1307, found 427.1309.



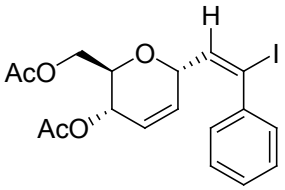
Prepared by the representative procedure **1** using 3,4 Di-*O*-acetyl-L-rhamnal (0.5 mmol, 107 mg) and phenyl acetylene (0.55 mmol, 56 µL) to yield **4j (**80%,116 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.51–7.47 (m, 2H), 7.41–7.37 (m, 2H), 6.12 (d, *J* = 9.8 Hz, 1H),

5.84–5.77 (m, 1H), 4.95–4.86 (m, 1H), 4.63 (dd, *J* = 9.7, 1.7 Hz, 1H), 3.95 (d, *J* = 6.3 Hz, 1H), 2.10 (s, 3H), 1.22 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.71, 136.72, 136.24, 131.37, 129.39, 128.71(2 X C), 128.37 (2 X C), 126.52, 124.40, 69.39, 68.63, 68.59, 21.22, 17.54. HRMS (ESI^+) m/z calcd for $C_{16}H_{18}ClO_3$ $(M+H)^+$ 293.0939, found 293.0934.

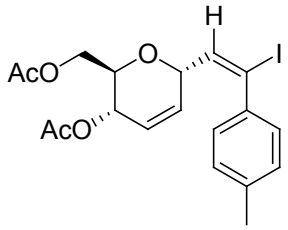


Prepared by the representative procedure **1** using 3,4 Di-*O*-acetyl-L-rhamnal (0.5 mmol, 107 mg) and 1-ethynyl-4-methylbenzene (0.55 mmol, 64 µL) to yield **4k (**72%,110 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.08 (d, *J* = 9.8 Hz, 2H), 4.91 (dd, *J* = 5.9, 1.7 Hz, 1H), 4.64 (dd, *J* = 9.7, 1.6 Hz, 1H), 3.95 (d, *J* = 6.3 Hz, 1H), 3.95 (p, *J* = 6.3 Hz, 1H), 2.37 (s, 2H), 2.11 (s, 3H), 1.22 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.77, 139.51, 136.95, 133.38, 131.53, 129.03, 128.62, 126.04, 124.23, 69.39, 68.67, 68.60, 21.36, 21.24, 17.53. HRMS (ESI^+) m/z calcd for $C_{17}H_{20}ClO_3$ $(M+H)^+$ 307.1095, found 307.1099.

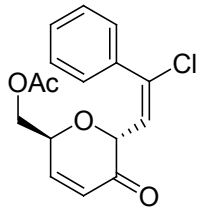
Typical procedure for preparation of iodo substituted vinyl glycosides (2): Tri-O-acetyl D-glucal (0.3 mmol, 82 mg) and dichloromethane (4 mL) were placed in a dry 50 mL round-bottomed flask equipped with a magnetic stirring bar. The solution was cooled to -30 °C and phenylacetylene (36 µL, 0.33 mmol) was added via syringe, followed by addition of Iodine (0.16 mmol, 45 mg). The reaction solution was stirred for 1hr. The reaction was quenched with hypo and extracted with dichloromethane (3 × 15 mL). The organic layer was separated and dried over anhydrous MgSO4. Product **5a** was obtained in 62% (82 mg).



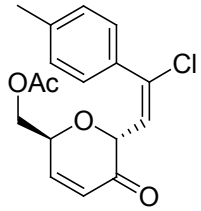
^{1}H NMR (400 MHz, Chloroform-d) δ 7.32–7.22 (m, 1H), 6.55 (dd, *J* = 9.2, 2.8 Hz, 1H), 5.72 (dd, *J* = 10.26, 9.05 Hz, 2H), 5.10 – 5.04 (m, 1H), 4.52 (d, *J* = 9.1 Hz, 1H), 4.23 – 4.02 (m, 2H), 3.96–3.86 (m, 1H), 2.03 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.38, 170.22, 140.72, 138.35, 130.45, 128.39, 128.37 (2 X C), 128.21 (2 X C), 124.45, 70.57, 69.94, 64.42, 62.86, 21.07, 20.82. HRMS (ESI^+) m/z calcd for $C_{18}H_{20}IO_5$ $(M+H)^+$ 443.0350, found 443.0342.



Prepared by general procedure **2** using Tri-*O*-acetyl-D-glucal (0.3 mmol, 82 mg) and *P*-methyl 1-ethynyl-4-methylbenzene (0.33 mmol, 38 µL) to yield **5b (5**7%, 78 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.19–7.16 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.52 (d, *J* = 9.1 Hz, 1H), 5.76–5.65 (m, 2H), 5.09–5.04 (m, 1H), 4.52 (dd, *J* = 9.2, 1.8 Hz, 1H), 4.09 (ddd, *J* = 15.4, 12.0, 4.6 Hz, 3H), 3.91 (dt, *J* = 6.5, 3.5 Hz, 1H), 2.27 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.80, 170.35, 138.93, 138.13, 138.08, 130.58, 129.02 (2 X C), 128.30 (2 X C), 124.52, 102.21, 70.69, 70.08, 64.49, 62.91, 21.25, 21.03, 20.81. HRMS (ESI^+) m/z calcd for $C_{19}H_{22}IO_5$ $(M+H)^+$457.0506, found 457. 0513

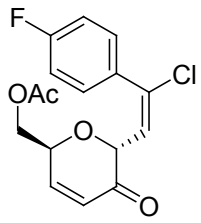


Prepared by the representative procedure **1** using of 2-acetoxy-tri-*O*-acetyl-D-galucal (0.5 mmol, 165 mg) and phenylacetylene (0.55 mmol, 56 µL) to yield **6a (**51%, 78 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.57–7.48 (m, 2H), 7.37–7.28 (m, 3H), 6.89 (dd, *J* = 10.5, 2.5 Hz, 1H), 6.15 (dd, *J* = 10.5, 2.3 Hz, 1H), 6.02 (d, *J* = 9.9 Hz, 1H), 4.72 (dd, *J* = 9.7, 4.3 Hz, 2H), 4.26 (dd, *J* = 11.8, 5.6 Hz, 1H), 4.17 (dd, *J* = 11.8, 4.1 Hz, 1H), 1.96 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.06 170.51, 146.36, 141.12, 135.81, 129.71, 128.94 (2C), 128.29 (2C), 127.40, 121.31, 75.44, 69.21, 64.29, 20.69. HRMS (ESI^+) m/z calcd for $C_{16}H_{15}ClNaO_4$ $(M+Na)^+$ 329.0551, found 329.0556

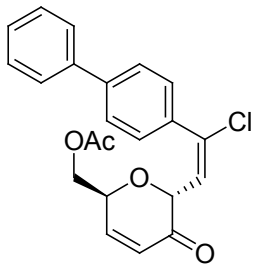


Prepared by the representative procedure **1** using of 2-Acetoxy-tri-*O*-acetyl-D-galucal (0.5 mmol, 165 mg) and 1-ethynyl-4-methylbenzene (0.55 mmol, 64 µL) to yield **6b (**46%, 73 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.96 (dd, *J* = 10.5, 2.4 Hz, 1H), 6.21 (d, *J* = 10.5 Hz, 1H), 6.05 (d, *J* = 9.9 Hz, 1H), 4.79 (d, *J* = 9.9 Hz, 2H), 4.32 (dd, *J* = 11.8, 5.6 Hz, 1H), 4.24 (dd, *J* = 11.8, 4.1 Hz, 1H), 2.37 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.24, 170.61, 146.38, 141.45, 139.91, 132.88,

128.94 (2C), 128.84 (2C), 127.39, 120.65, 75.45, 69.12, 64.29, 21.34, 20.73. HRMS (ESI^+) m/z calcd for $C_{17}H_{17}ClNaO_4$ $(M+Na)^+$ 343.0708, found 343.0702.



Prepared by the representative procedure **1** using of 2-Acetoxy-tri-*O*-acetyl-D-galucal (0.5 mmol, 165 mg) and 1-ethynyl-4-Fluorobenzene (0.55 mmol, 66 µL) to yield **6c (**52%, 84 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.60 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.98 (dd, *J* = 10.6, 2.3 Hz, 1H), 6.24 (dd, *J* = 10.5, 2.0 Hz, 1H), 6.09 (d, *J* = 9.9 Hz, 1H), 4.34 (dd, *J* = 11.9, 5.7 Hz, 1H), 4.24 (dd, *J* = 11.8, 4.0 Hz, 1H), 2.05 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.03, 170.58, 163.35 (d, C-F coupling), 146.54, 140.03, 131.13, 131.06, 128.33, 127.39, 121.45, 115.50, 115.33, 75.41, 69.15, 64.24, 20.76. HRMS (ESI^+) m/z calcd for $C_{16}H_{14}ClFNaO_4$ $(M+Na)^+$ 347.0462, found 347.0454.

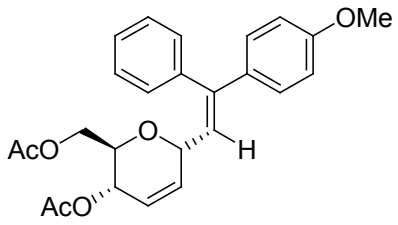


Prepared by the representative procedure 1 using of 2-Acetoxy-tri-*O*-acetyl-D-galucal (0.5 mmol, 165 mg) and 1-ehynyl-4-phenyl-benzene (0.55 mmol, 98 µL) to yield **6d (**52%, 99 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.63 (dt, *J* = 7.2, 6.2 Hz, 7H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.97 (dd, *J* = 10.5, 2.4 Hz, 1H), 6.30 – 6.20 (m, 1H), 6.24 (dd, *J* = 10.5, 2.2 Hz, 1H), 6.12 (d, *J* = 9.9 Hz, 1H), 4.86 (d, *J* = 9.9 Hz, 1H), 4.80 (dt, *J* = 6.5, 3.3 Hz, 1H), 4.35 (dd, *J* = 11.8, 5.6 Hz, 1H), 4.27 (dd, *J* = 11.8, 4.1 Hz, 1H), 2.02 (s, 3H)). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.21, 170.65, 146.51, 142.61, 141.02, 140.12, 134.60, 129.46 (2C), 128.95 (2 x C), 127.87, 127.43, 126.15(2 x C), 126.99 (2C), 121.31, 75.49, 69.21, 64.40, 20.77. HRMS (ESI^+) m/z calcd for $C_{22}H_{20}ClO_4$ $(M+H)^+$ 383.1045, found 383.1052.

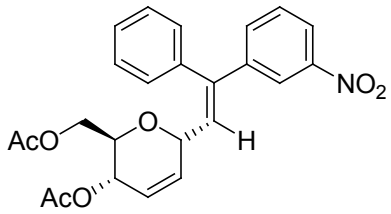
General procedure for Pd-catalyzed coupling between bromo substituted alkenyl glycoside 3a and Arylboronic Acids (3):

To a solution of Compound **3a** (0.3 mmol) in mixed solvent (PEG-400 0.5 mL and H_2O 1.5 mL) were added arylboronic acid (0.7 mmol), palladium acetate (0.012 mmol) and potassium phosphate (0.6 mmol). The reaction mixture was stirred at 40 °C for 24 h. After cooling to room temperature, the mixture was diluted with water and the combined aqueous phases were extracted three times with ethyl acetate. The organic layers were combined, dried with Na_2SO_4 and concentrated to yield the crude product, which was further purified by silica gel chromatography using petroleum ether and ethyl acetate as eluent to provide the

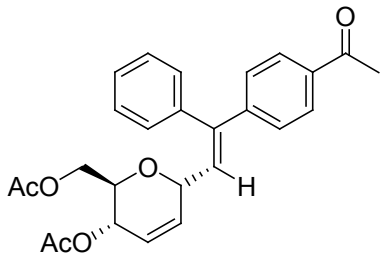
desired product.



Prepared by the general procedure **3** using compound **3a** (0.3 mmol, 118 mg), and *p*-methoxy phenylboronic acid (0.7 mmol, 106 mg), to yield **7a (**64%, 80 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.43–7.31 (m, 2H), 7.29–7.20 (m, 3H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.08 (d, *J* = 9.3 Hz, 1H), 5.83 (m, 2H), 5.20–5.13 (m, 1H), 4.73 (d, *J* = 9.3 Hz, 1H), 4.26–4.06 (m, 3H), 3.80 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.92, 170.76, 159.48, 145.48, 138.95, 134.16, 132.88, 129.70 (2 x C), 120.85 (2 x C), 128.30 (2 x C), 127.74, 123.47, 122.67, 115.26, 113.55 (2 x C), 70.07, 64.74, 63.09, 55.30, 21.13, 20.87. HRMS (ESI$^+$) m/z calcd for $C_{25}H_{26}NaO_6$ $(M+Na)^+$ 445.1622, found 445.1625.



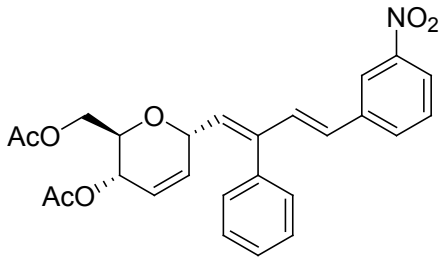
Prepared by the general procedure **3** using compound **3a** (0.3 mmol, 118 mg), and *m*-nitrophenylboronic acid (0.7 mmol, 117 mg), to yield **7b (**52%, 68 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.26–8.11 (m, 1H), 7.69–7.48 (m, 1H), 7.48–7.30 (m, 4H), 7.26–7.15 (m, 2H), 6.26 (d, *J* = 9.2 Hz, 1H), 5.86 (bs, 2H), 5.20 – 5.14 (m, 1H), 4.80 (d, *J* = 9.2 Hz, 1H), 4.27–4.07 (m, 2H), 2.11 (s, 1H), 2.09 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.86, 170.46, 148.38, 143.77, 143.36, 137.39, 133.72, 131.56, 129.55 (2 x C), 129.21, 128.81 (2 x C), 128.52, 127.26, 124.25, 122.67, 122.18, 70.30, 69.73, 64.51, 62.93, 21.10, 20.85. HRMS (ESI$^+$) m/z calcd for $C_{24}H_{27}N_2O_7$ $(M+ NH_4)^+$ 445.1813, found 445.1809.



Prepared by the general procedure **3** using compound **3a** (0.3 mmol, 118 mg), and *m*-nitrophenylboronic acid (0.7 mmol, 114 mg), to yield **7c** 54% (70 mg). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.37 (dd, *J* = 22.2, 7.8 Hz, 5H), 7.26 – 7.19 (m, 2H), 6.26 (d, *J* = 9.2 Hz, 1H), 5.86 (bs, 2H), 5.17 (d, *J* = 6.1 Hz, 1H), 4.79 (d, *J* = 9.0 Hz,

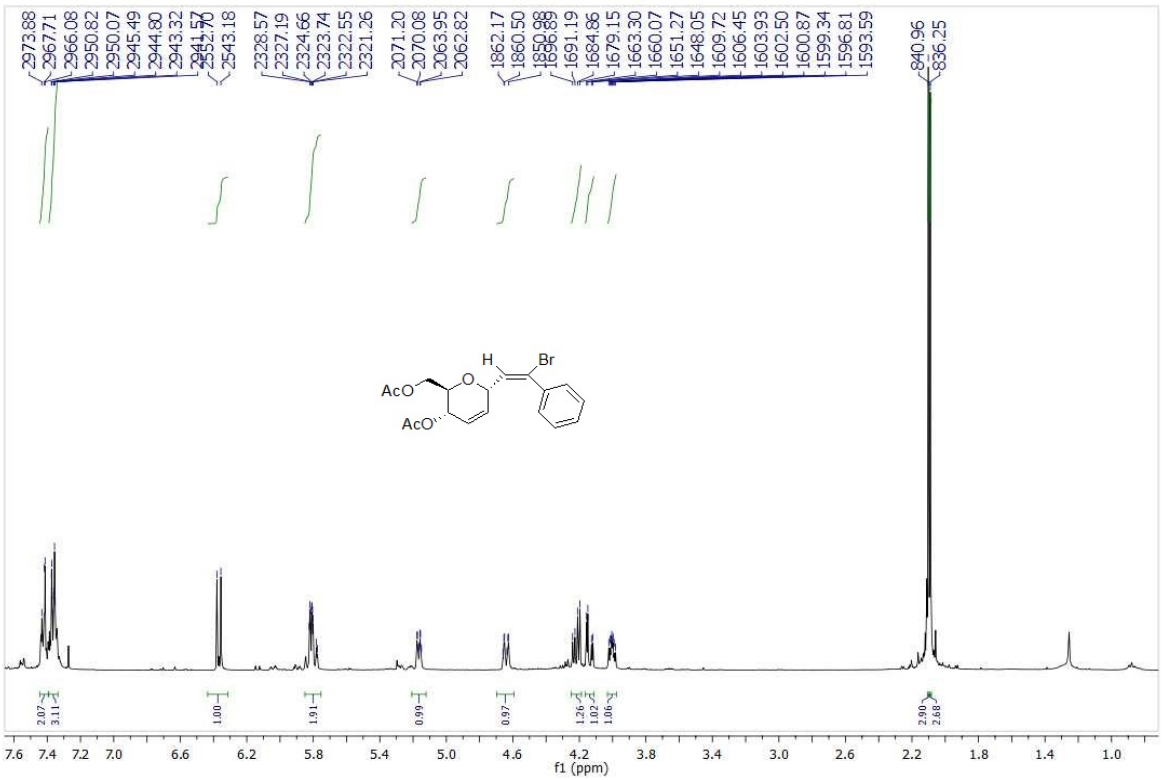
1H), 4.27 – 4.05 (m, 3H), 2.59 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.77, 170.90, 170.49, 146.14, 144.91, 137.99, 136.29, 131.84, 129.61 (2 x C), 128.58 (2 x C), 128.36 (2 x C), 127.80 (2 x C), 126.69, 124.00, 115.53, 70.23, 69.82, 64.60, 62.97, 26.65, 21.11, 20.85. HRMS (ESI^+) m/z calcd for $C_{26}H_{26}NaO_6$ $(M+Na)^+$ 457.1622, found 457.1618.

Typical procedure for Pd-Catalyzed Heck Coupling (4). A mixture of alkenylbromide **3a** (0.3 mmol, 118 mg), *p*-nitrostyrene (0.3mmol, 45 µL), PEG-2000 (1 g), TEA (0.3 mmol, 30 µL), and $Pd(OAc)_2$ (0.03 mmol, 6.7 mg) were placed in a 10-mL round-bottomed flask and heated at 80°C. After 8h the reaction mixture was cooled, extracted with cold diethyl ether (15 mL), and purified by column chromatography to yield **8a (**57%, 79 mg)

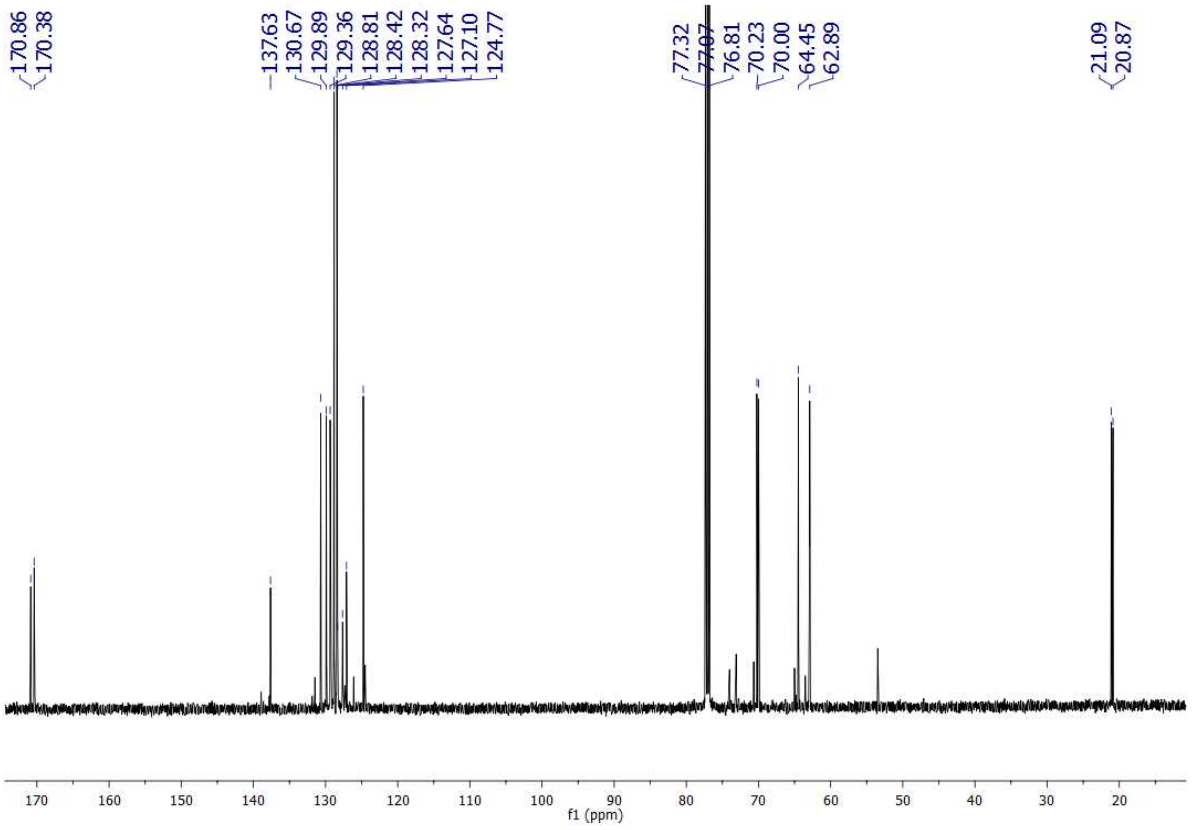


^{1}H NMR (400 MHz, Chloroform-d) δ 8.14 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.54–7.41 (m, 4H), 7.31–7.20 (m, 3H), 7.09 (d, *J* = 15.9 Hz, 1H), 5.81 (d, *J* = 9.1 Hz, 1H), 5.75 (bs, 2H) 4.61 (d, *J* = 8.9 Hz, 1H), 4.61 (d, *J* = 8.9 Hz, 1H), 4.24 – 4.12 (m, 2H), 3.69 – 3.58 (m, 1H), 3.49 (bs, 1H), 2.11 (s,3H), 2.06 (S, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.95, 170.32, 148.61, 143.61, 138.79, 136.13, 134.81, 132.16, 131.97, 131.34, 130.21, 129.45, 129.31 (2 x C), 128.53 (2 x C), 127.93, 125.56, 122.12, 121.24, 73.64, 72.72, 65.13, 62.89, 21.02, 20.65. HRMS (ESI^+) m/z calcd for $C_{26}H_{26}NaO_7$ $(M+H)^+$ 464.1704,found 464.1709.

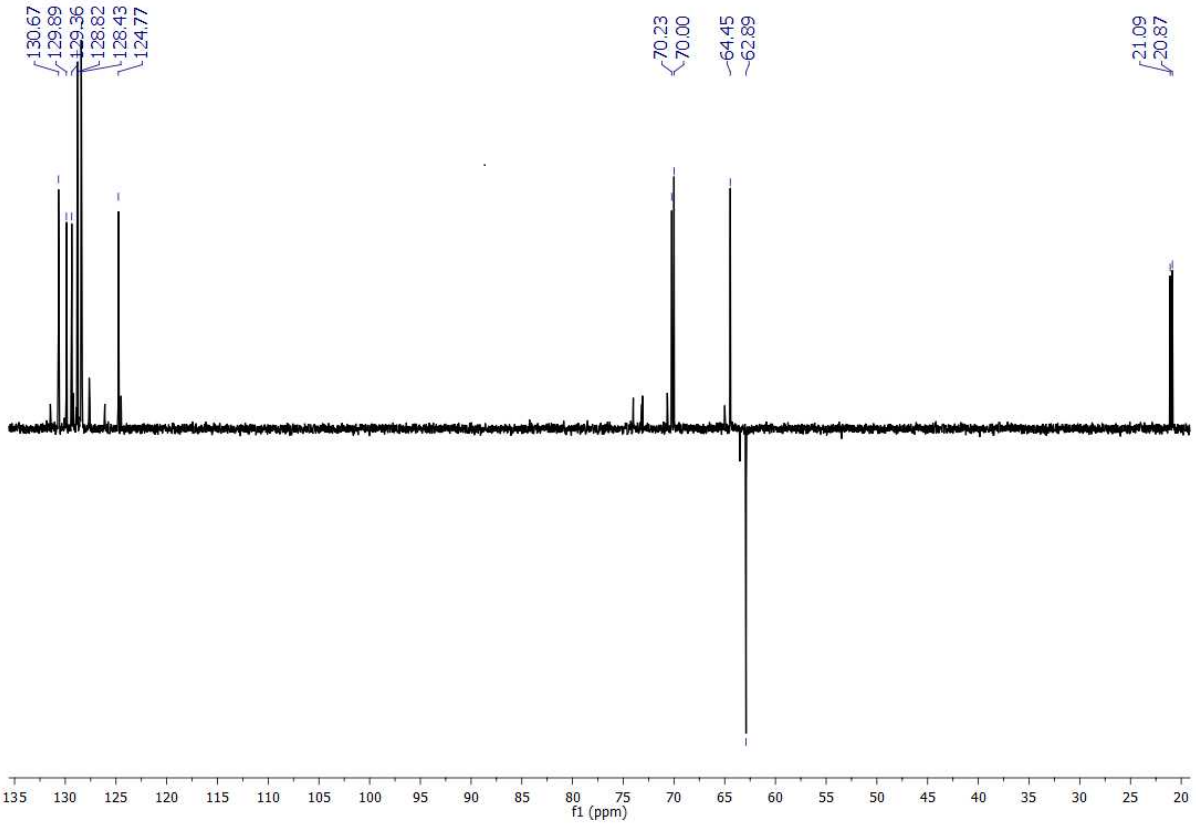
^{1}H NMR of compound **3a**



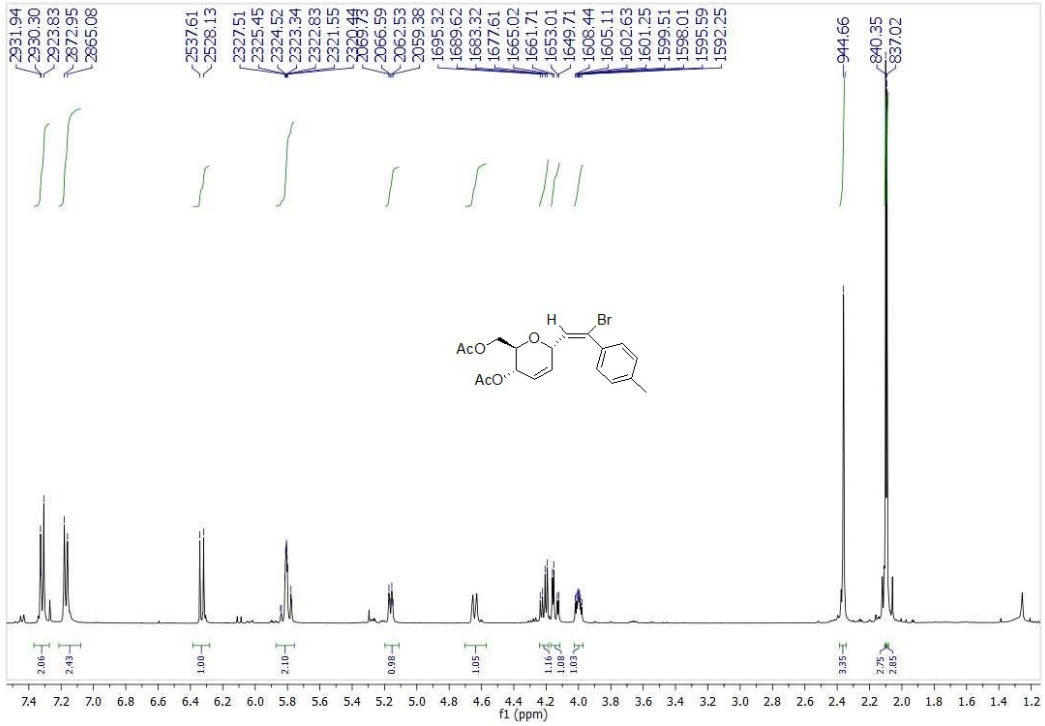
^{13}C NMR of compound **3a**



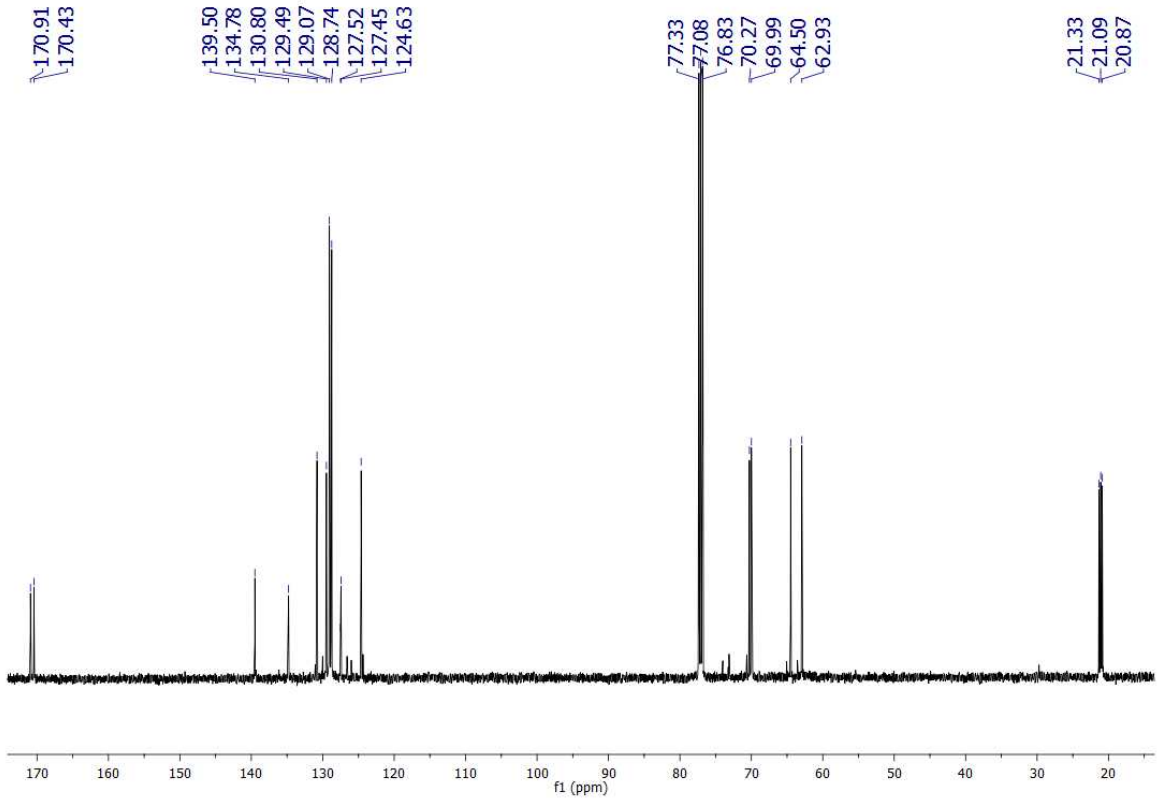
DEPT of compound **3a**



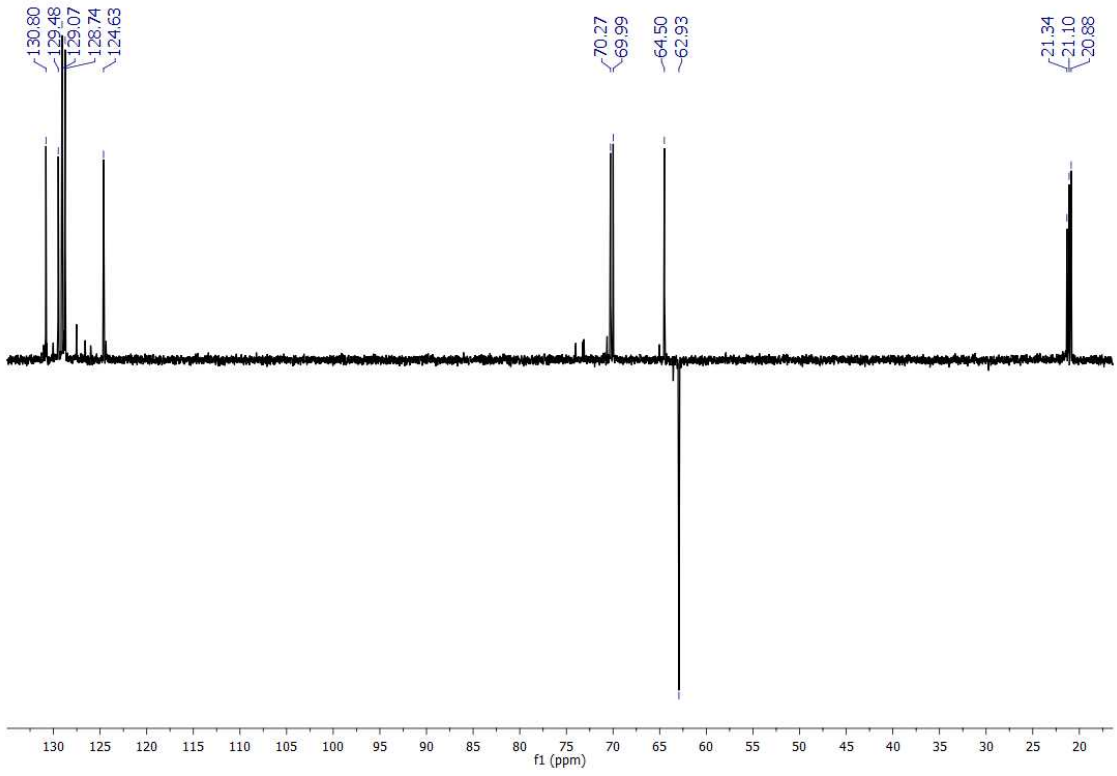
^{1}H NMR of compound **3b**



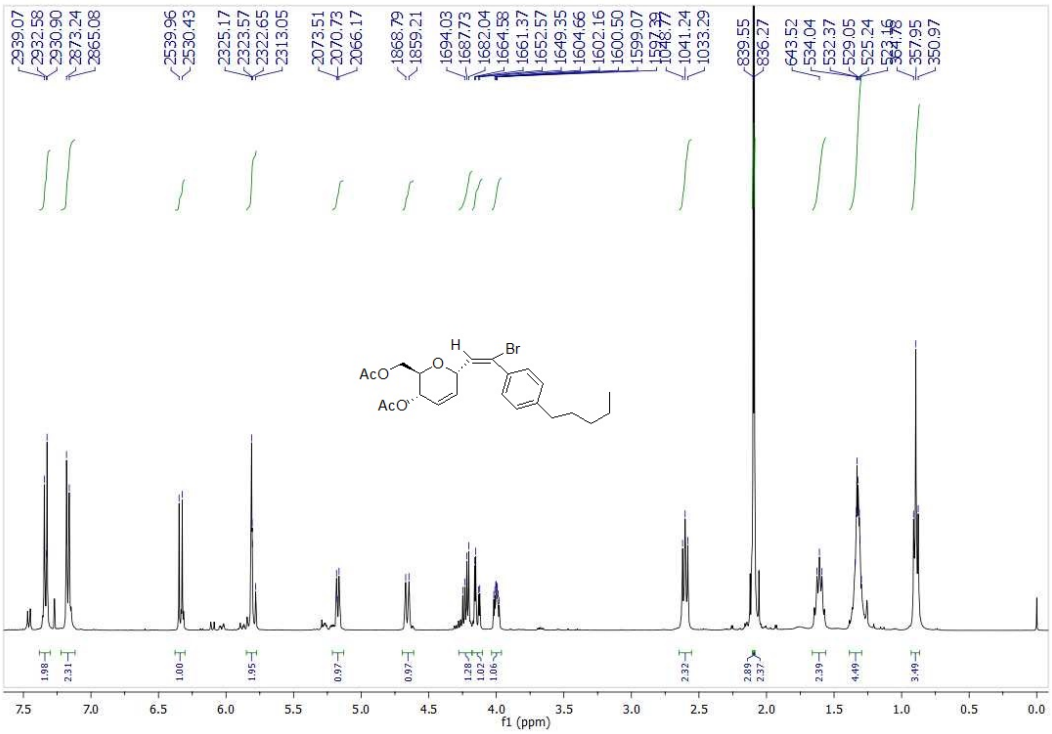
^{13}C NMR of compound **3b**



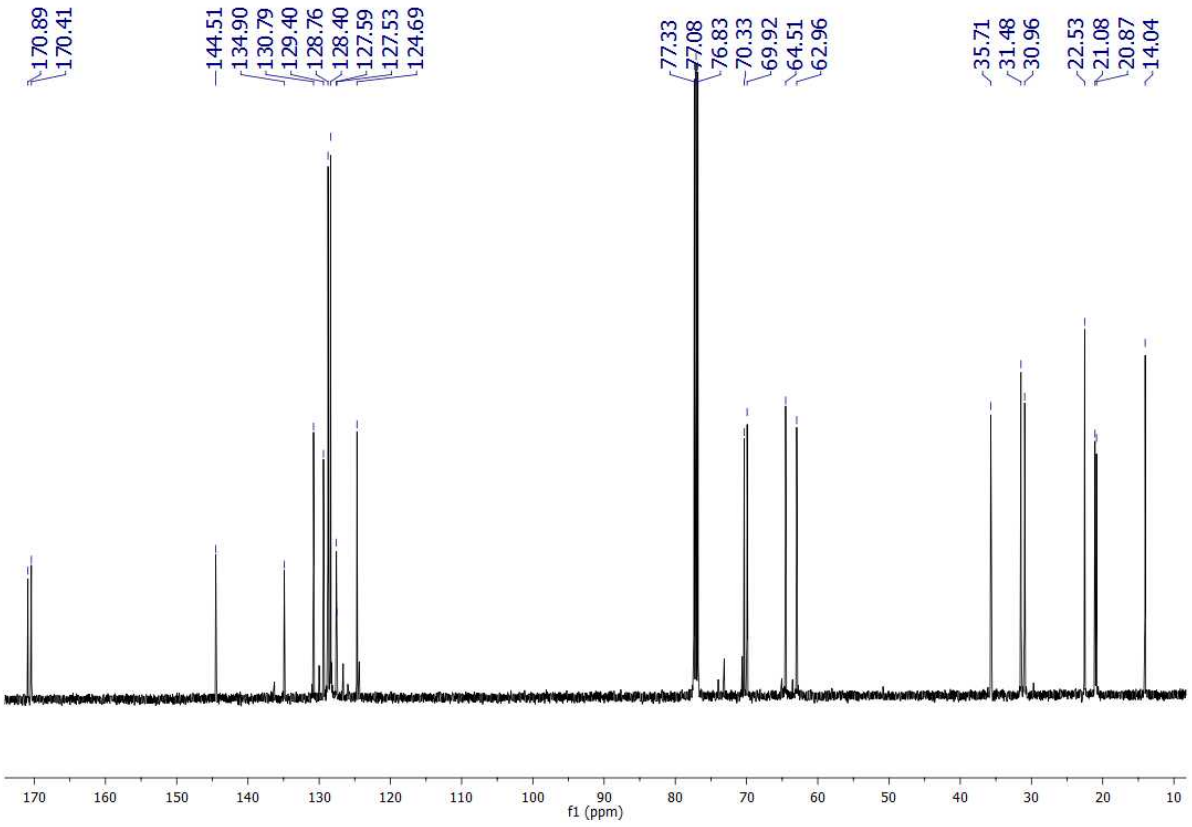
DEPT of compound **3b**



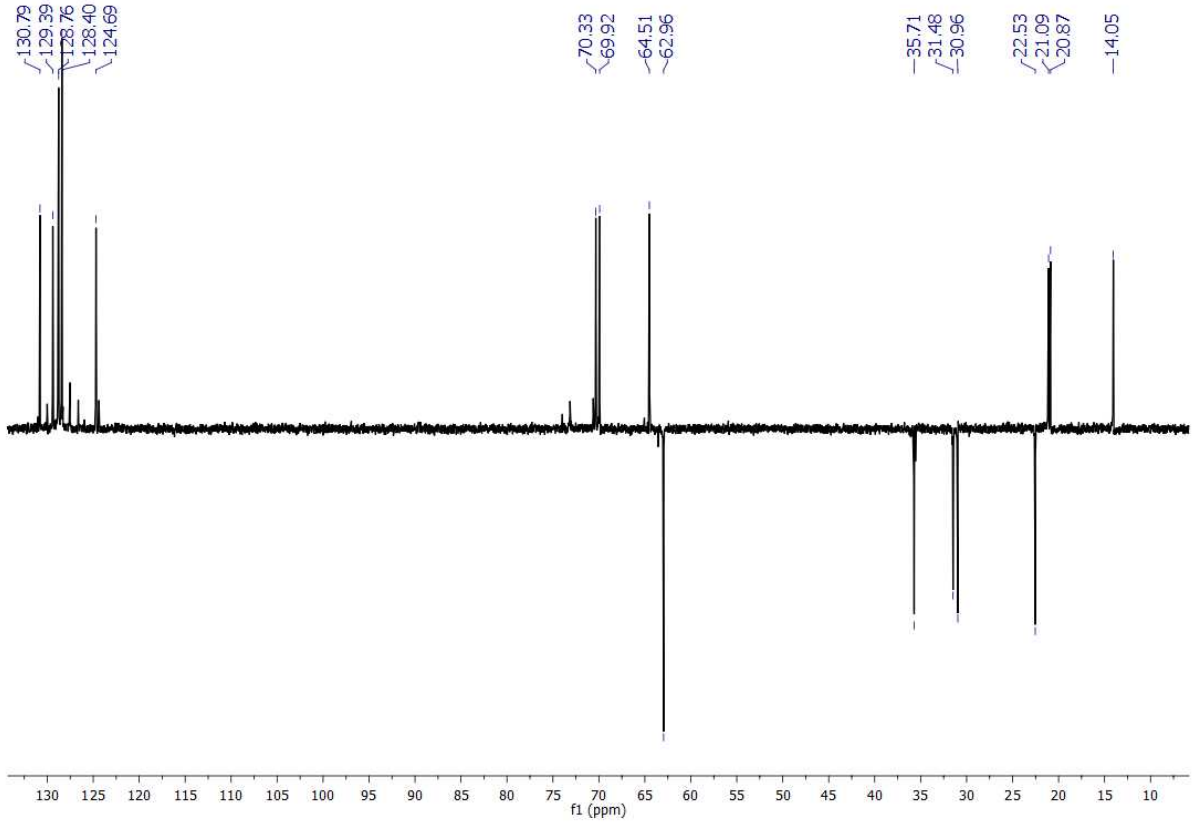
^{1}H NMR of compound **3C**



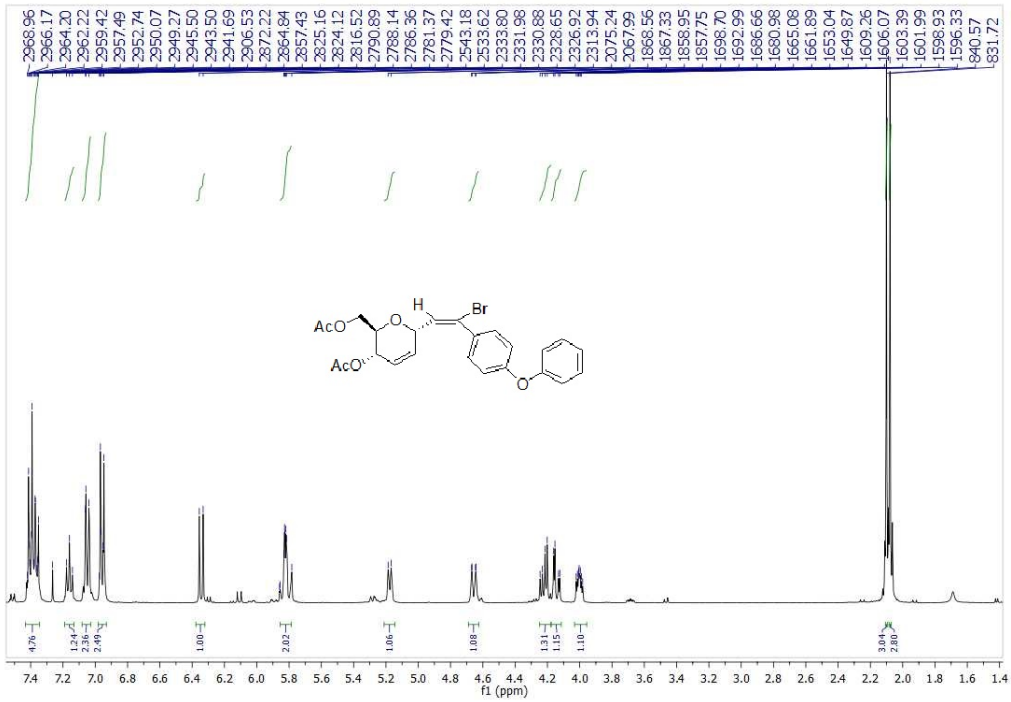
^{13}C NMR of compound **3C**



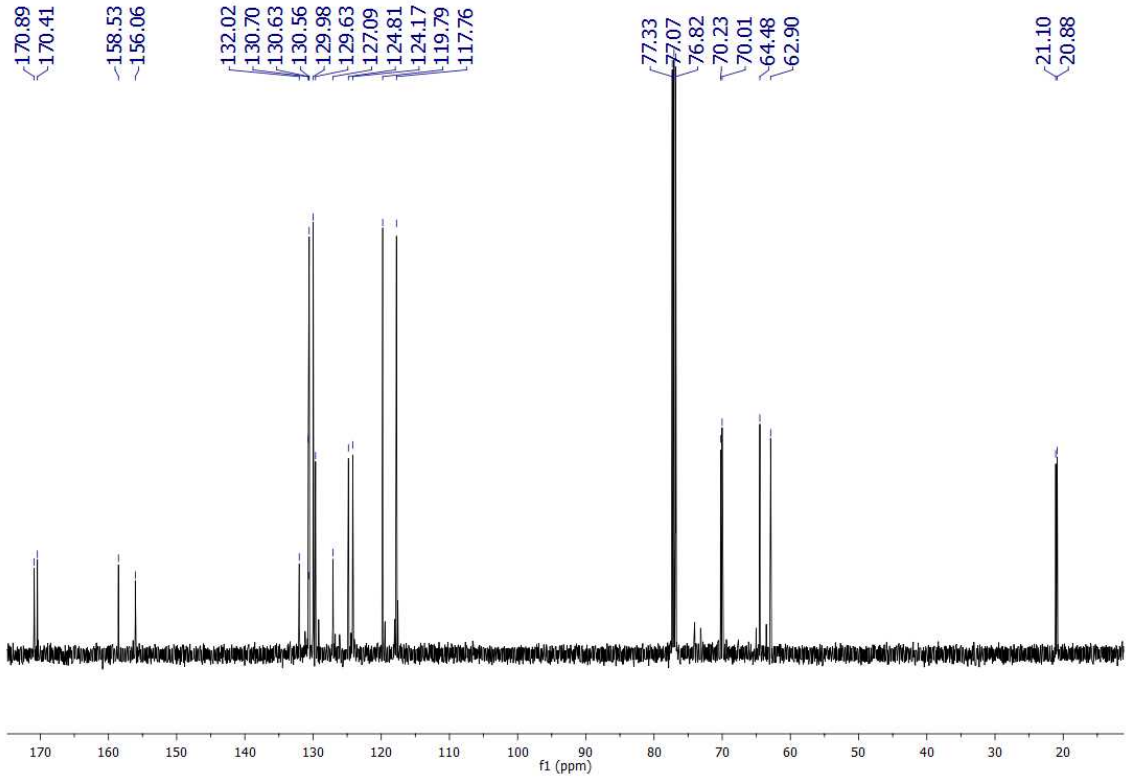
DEPT of compound **3C**



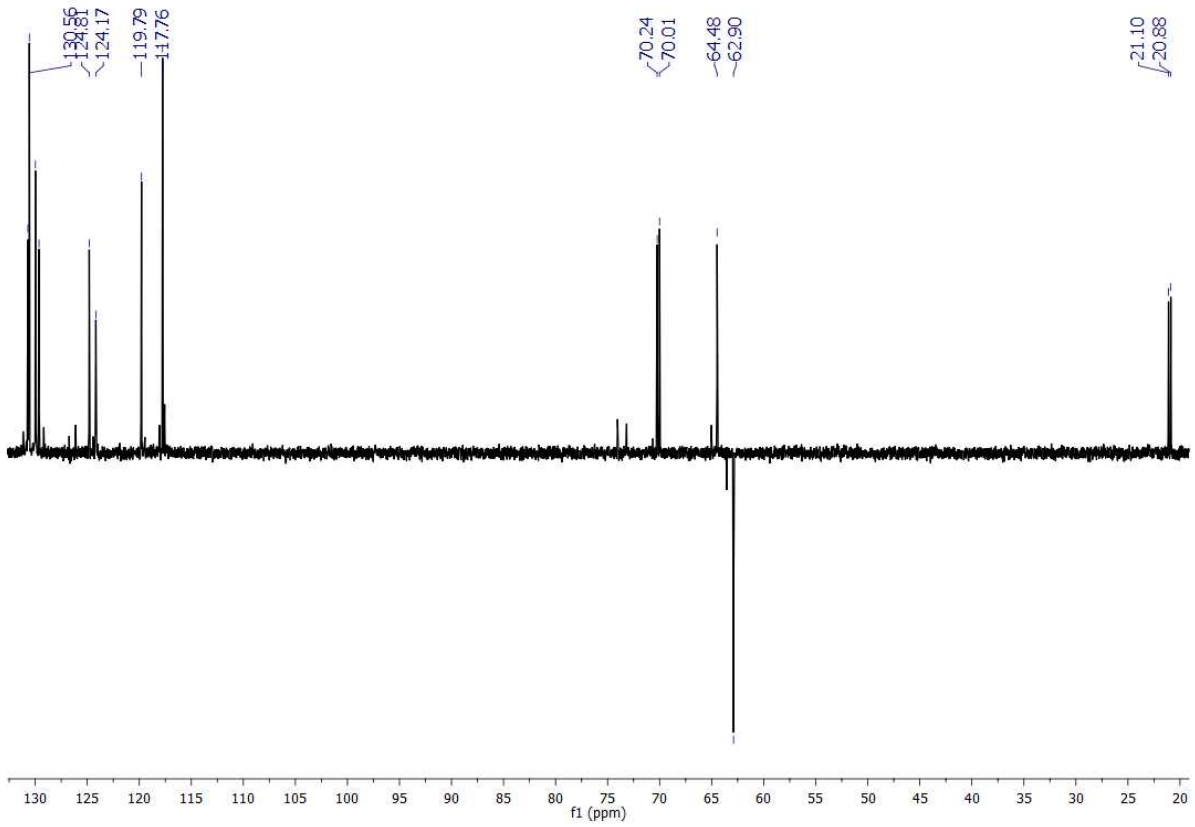
^{1}H NMR of compound **3d**



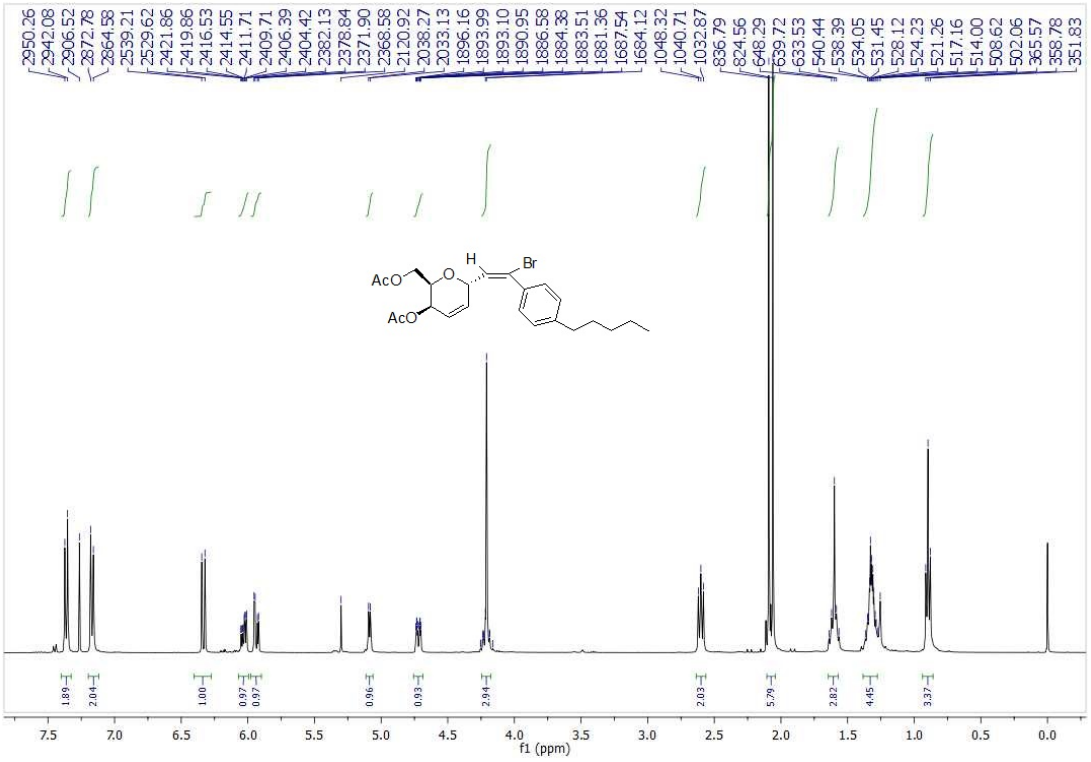
^{13}C NMR of compound **3d**



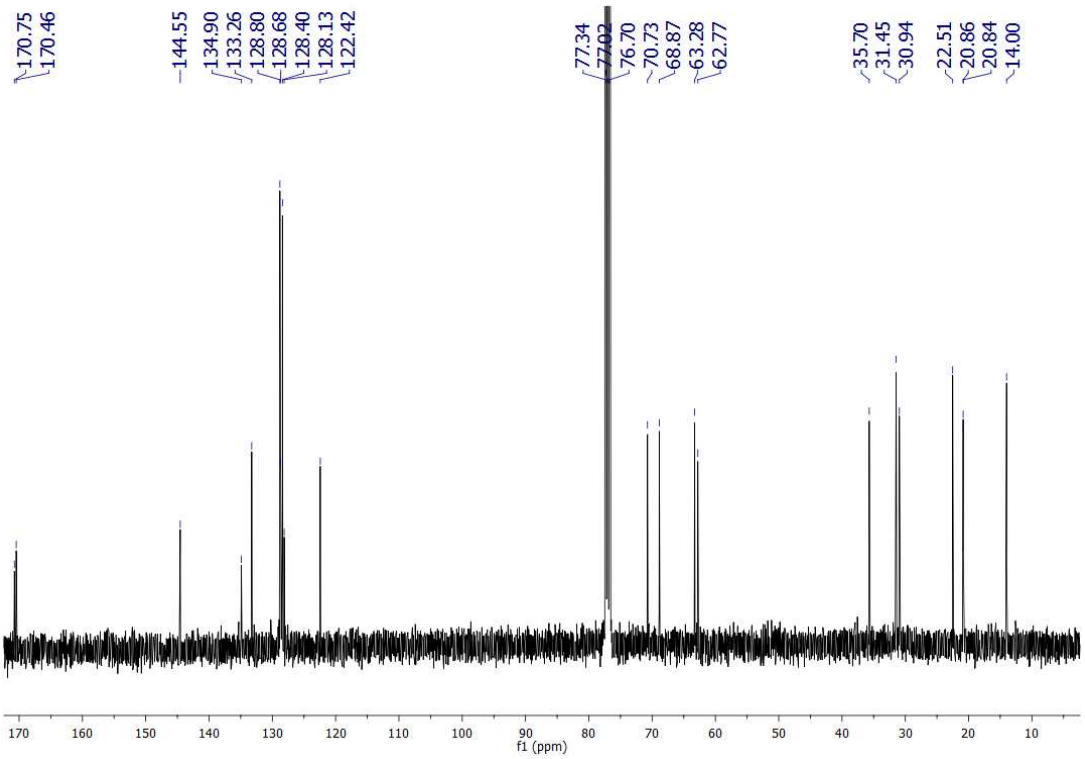
DEPT of compound **3d**



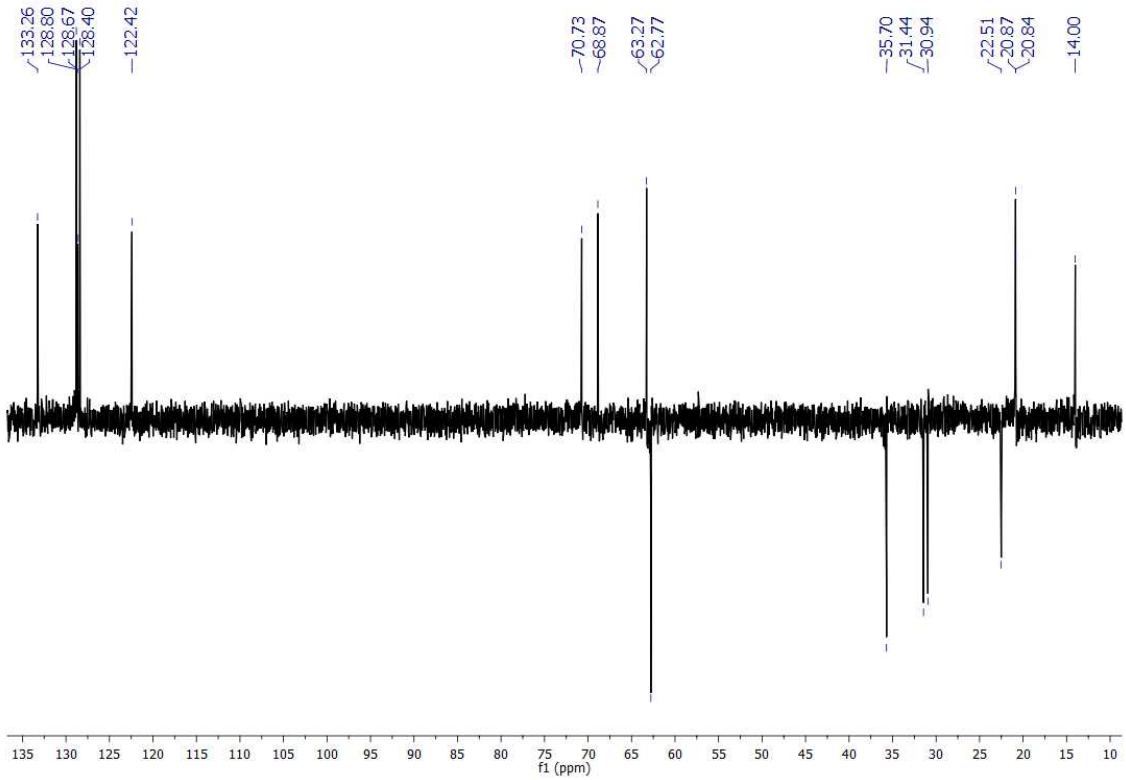
^{1}H NMR of compound **3e**



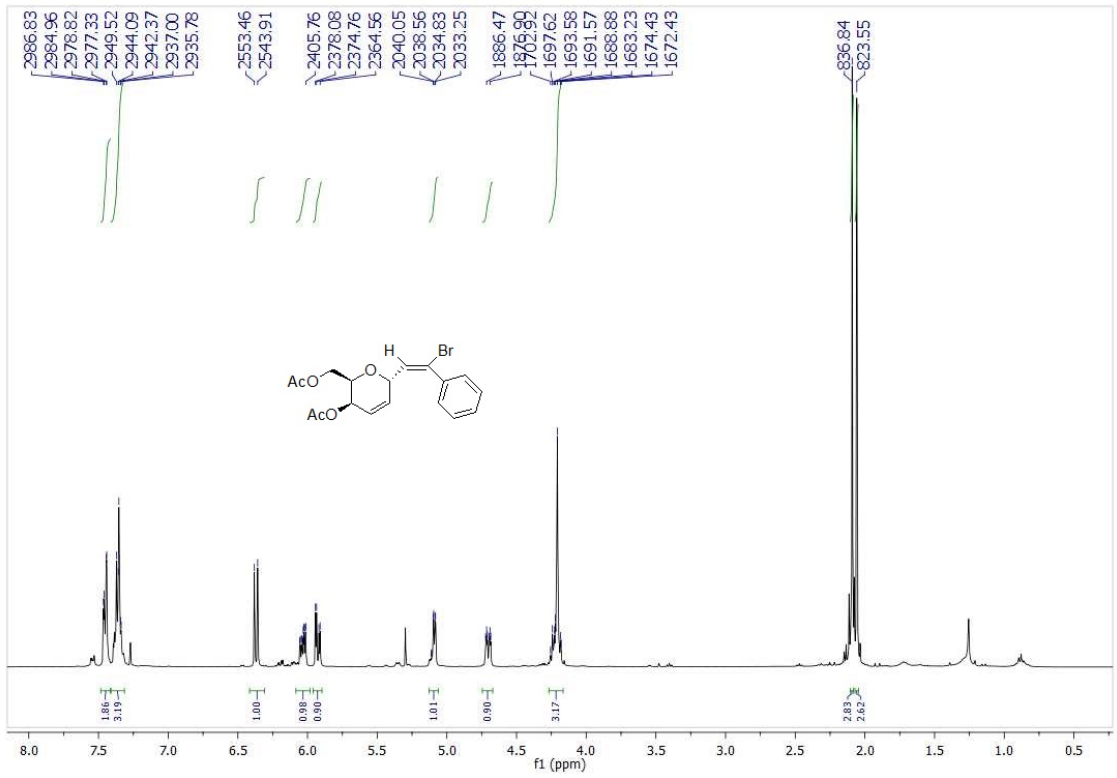
^{13}C NMR of compound **3e**



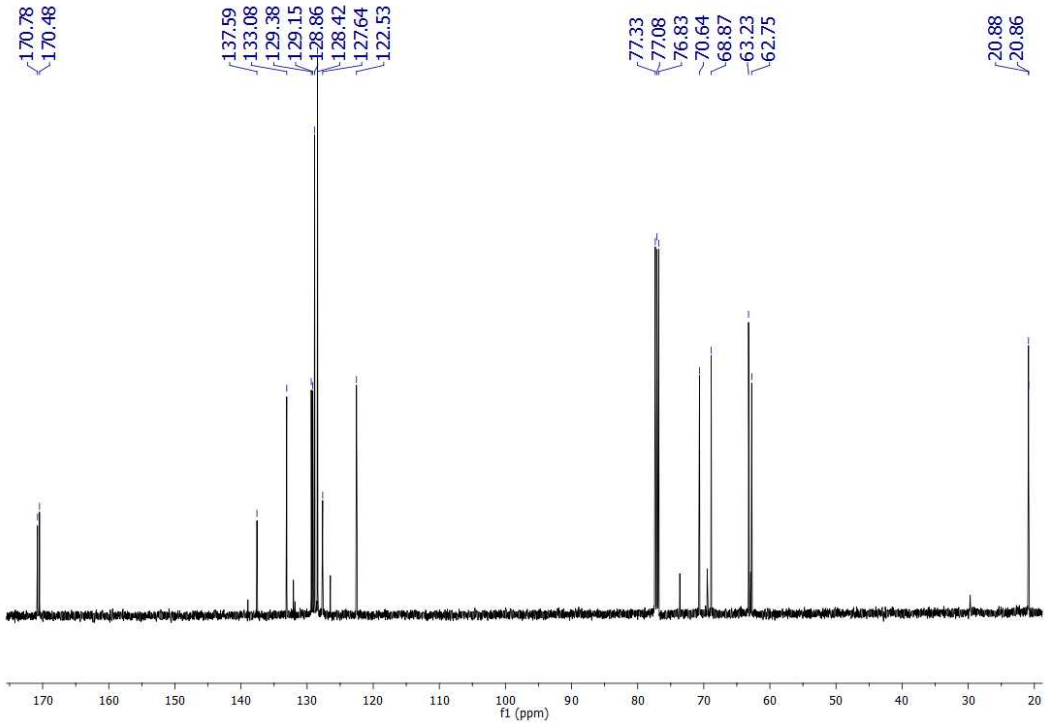
DEPT of compound **3e**



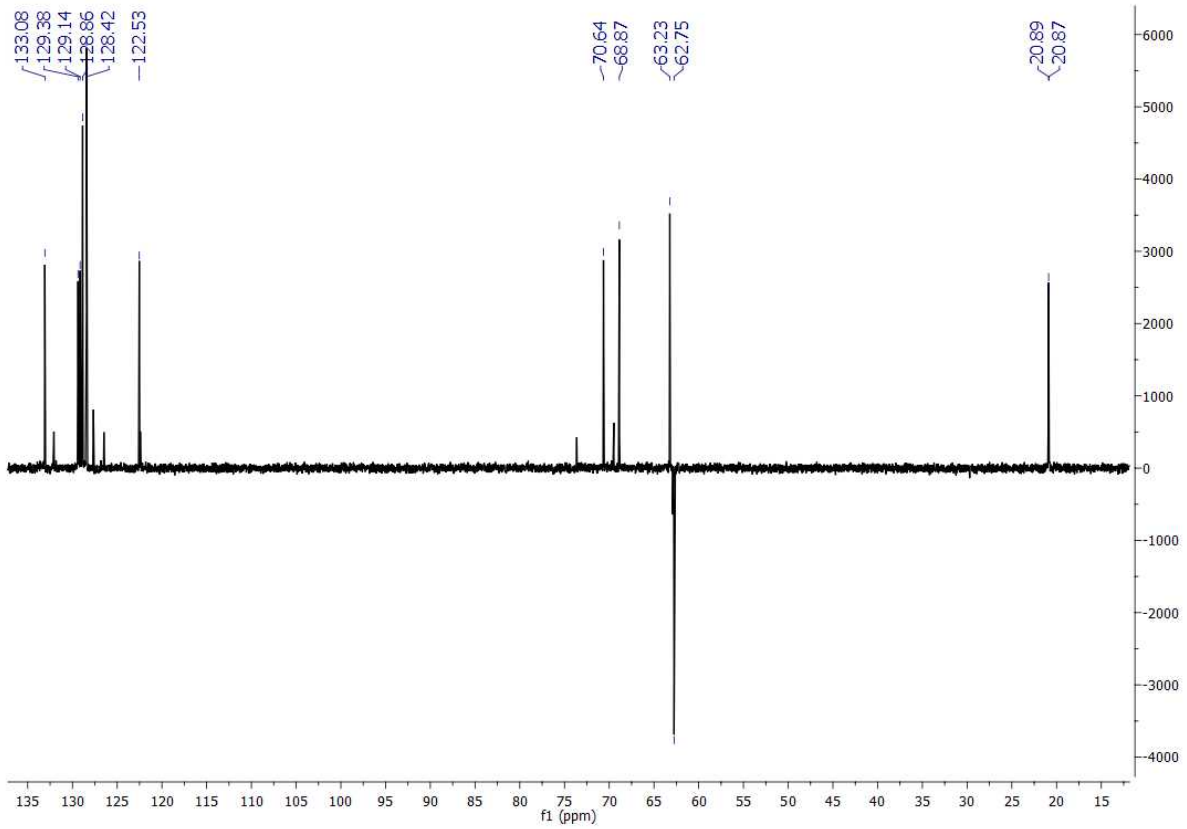
^{1}H NMR of compound **3f**



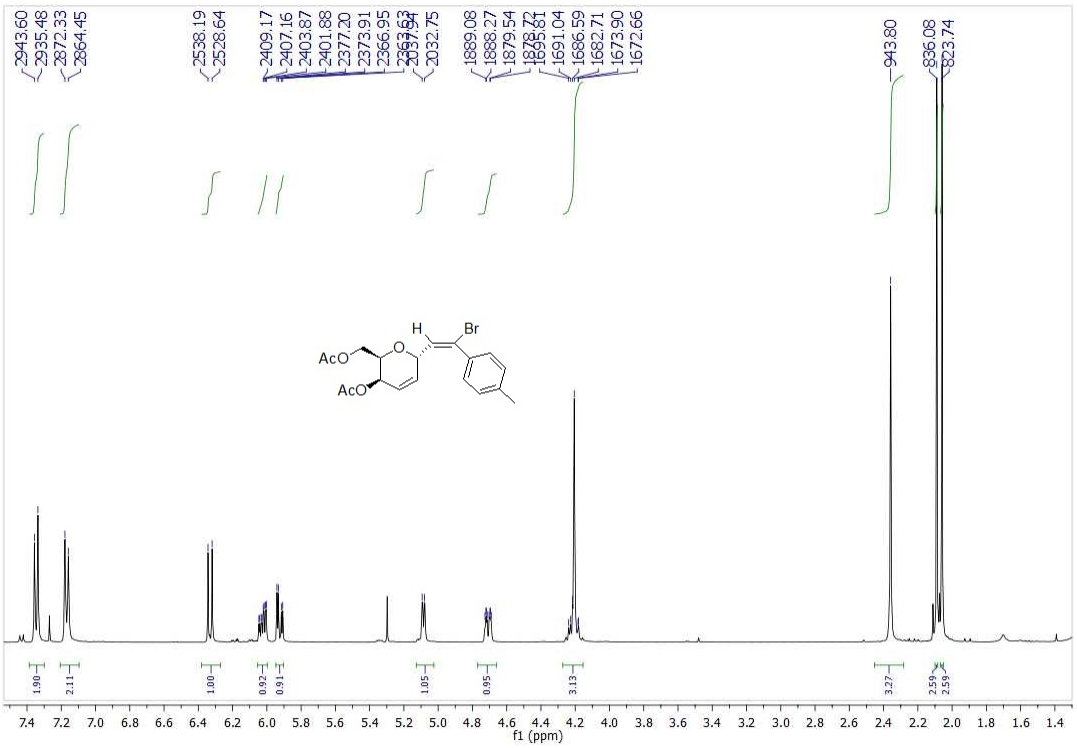
^{13}C NMR of compound **3f**



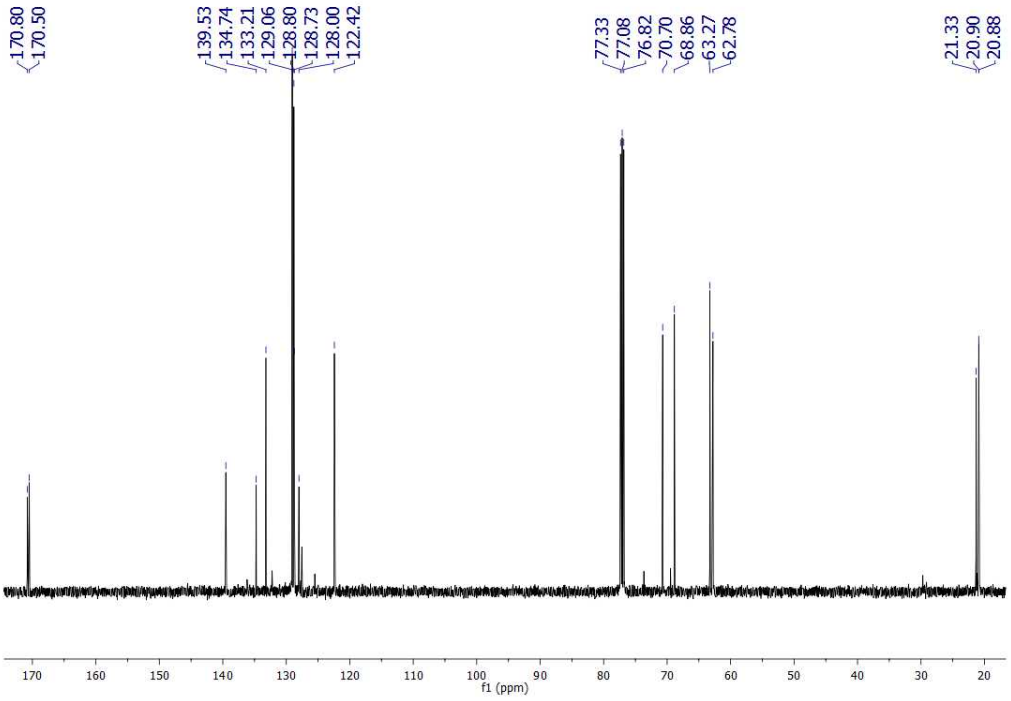
DEPT of compound **3f**



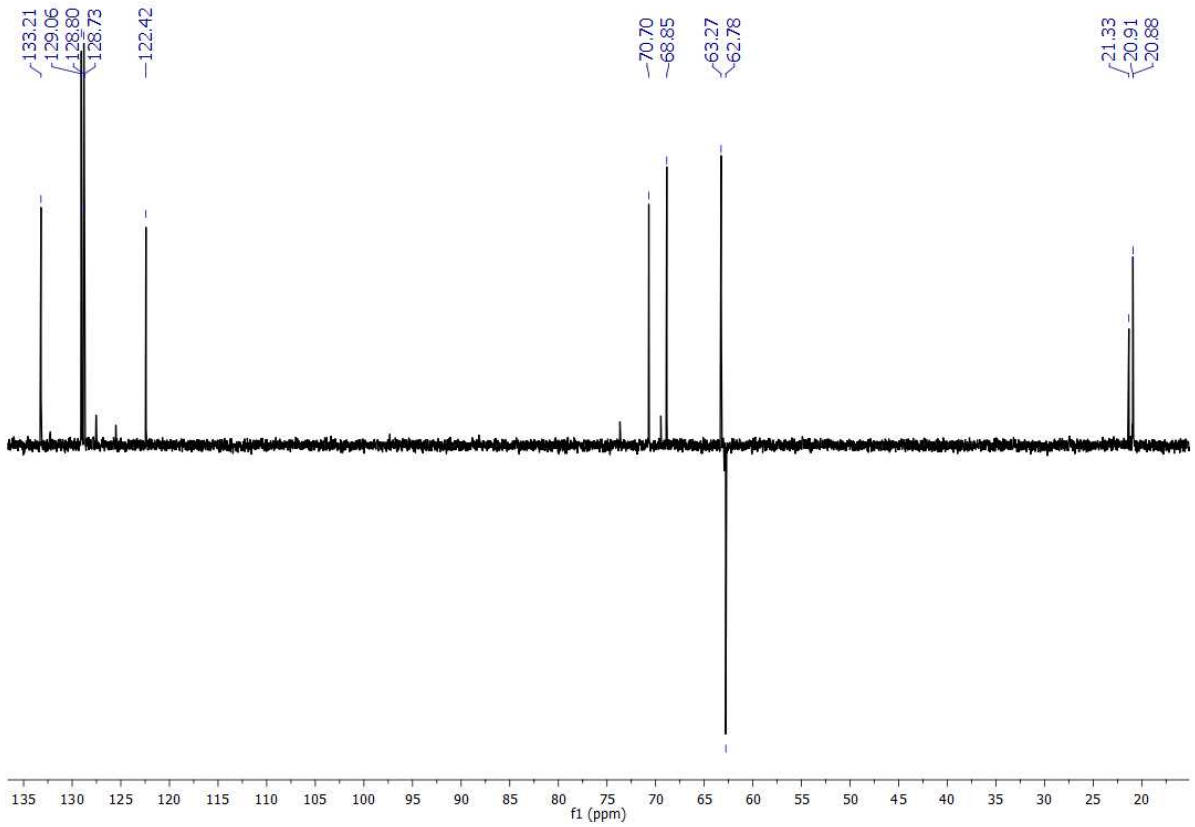
^{1}H NMR of compound **3g**



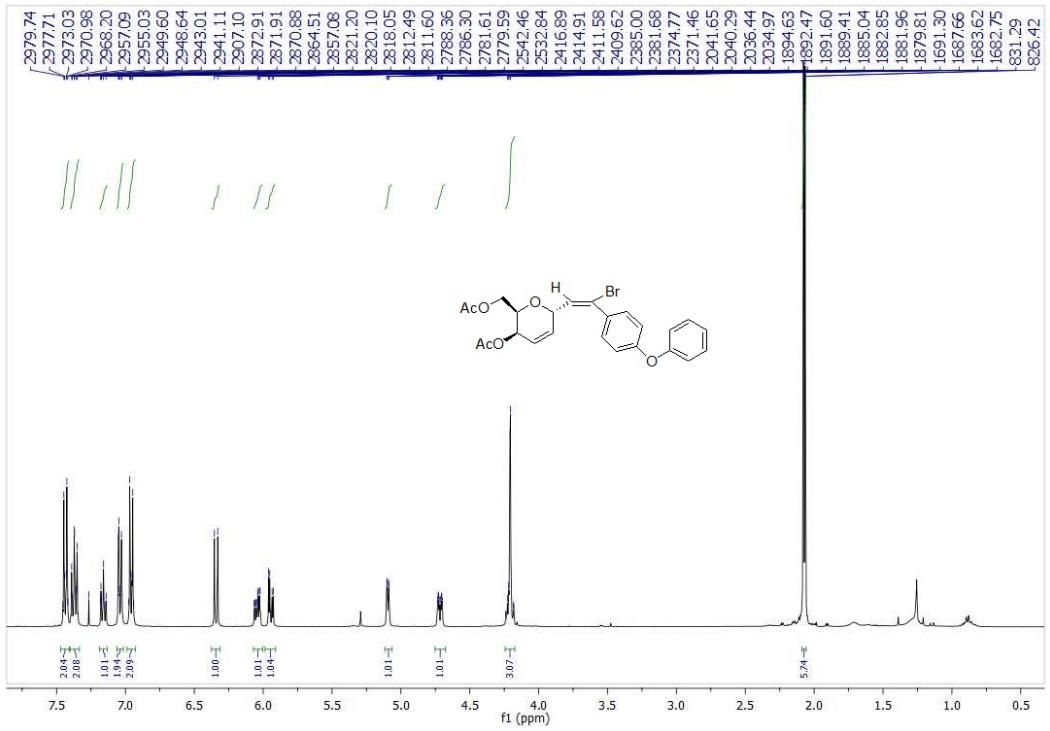
^{13}C NMR of compound **3g**



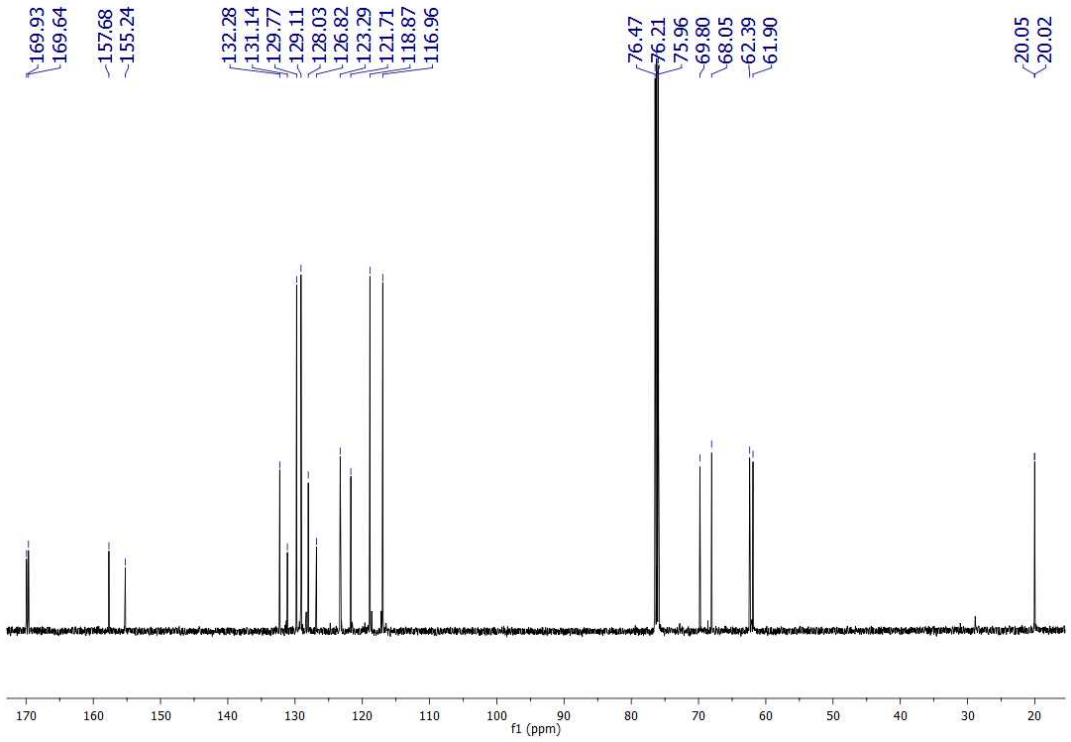
DEPT of compound **3g**



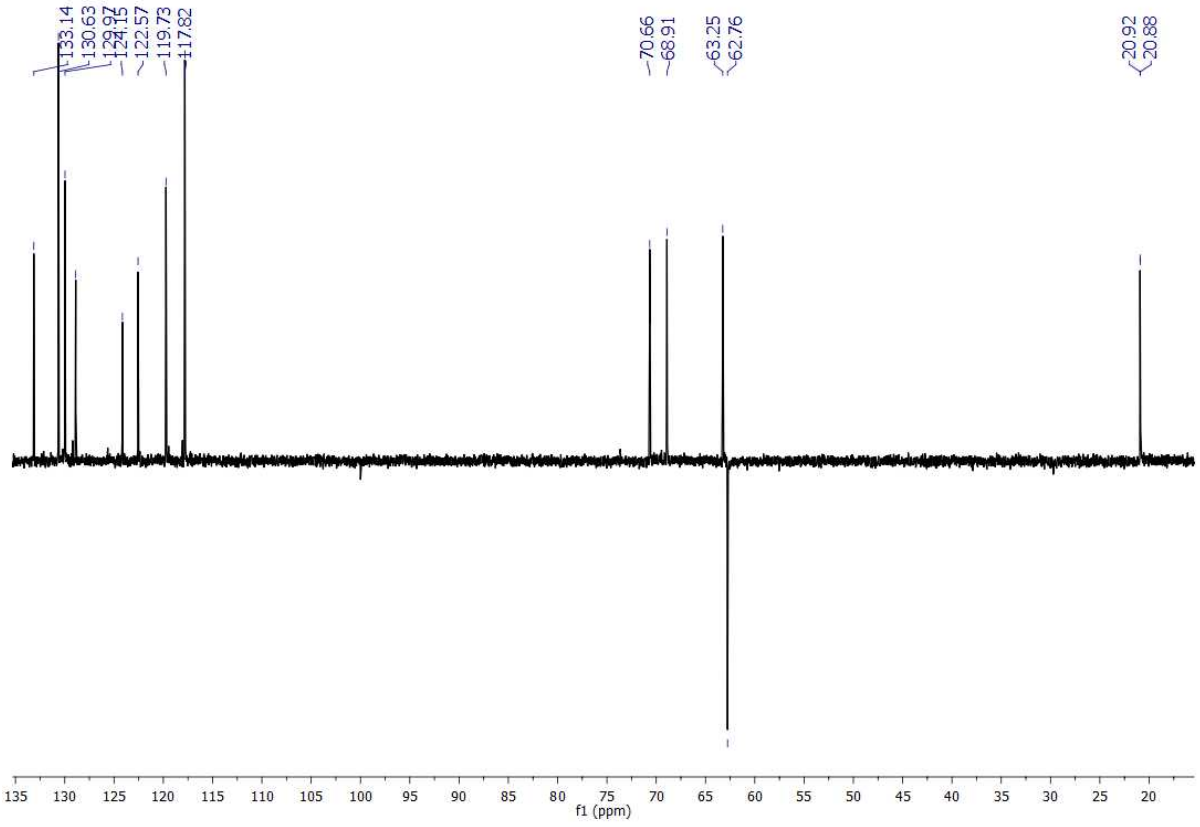
^{1}H NMR of compound **3h**



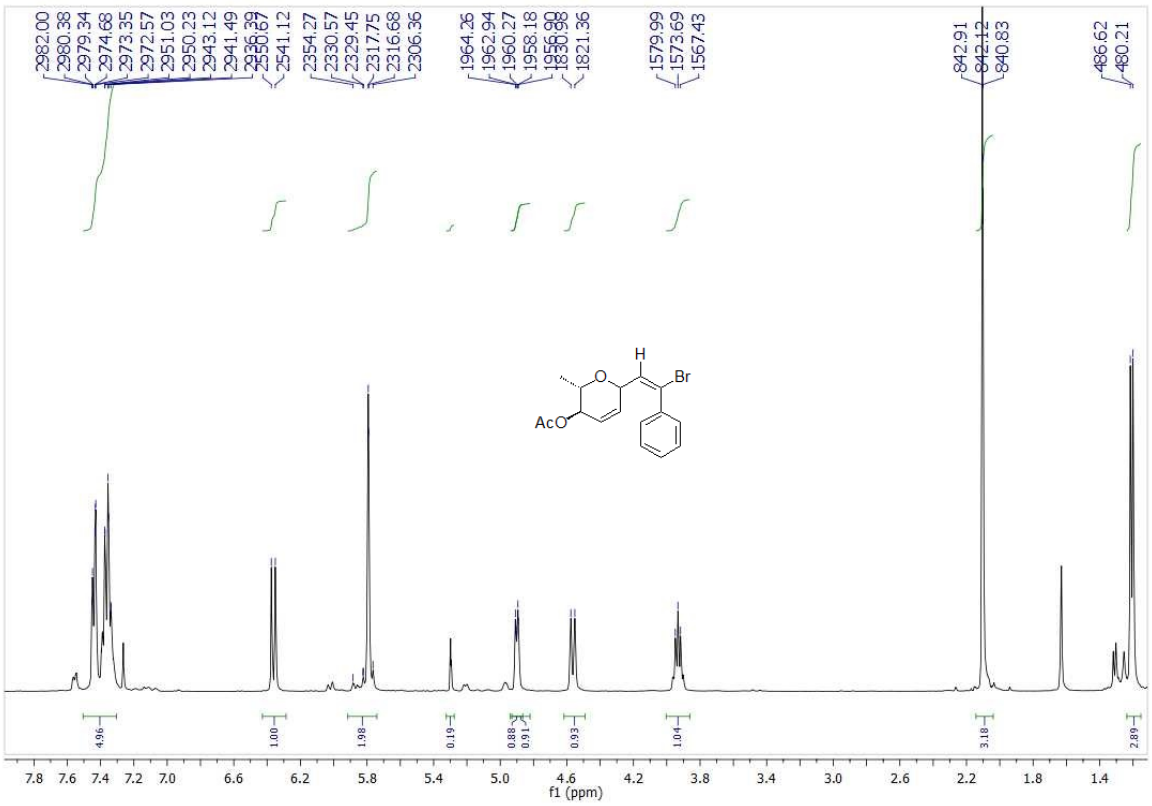
^{13}C NMR of compound **3h**



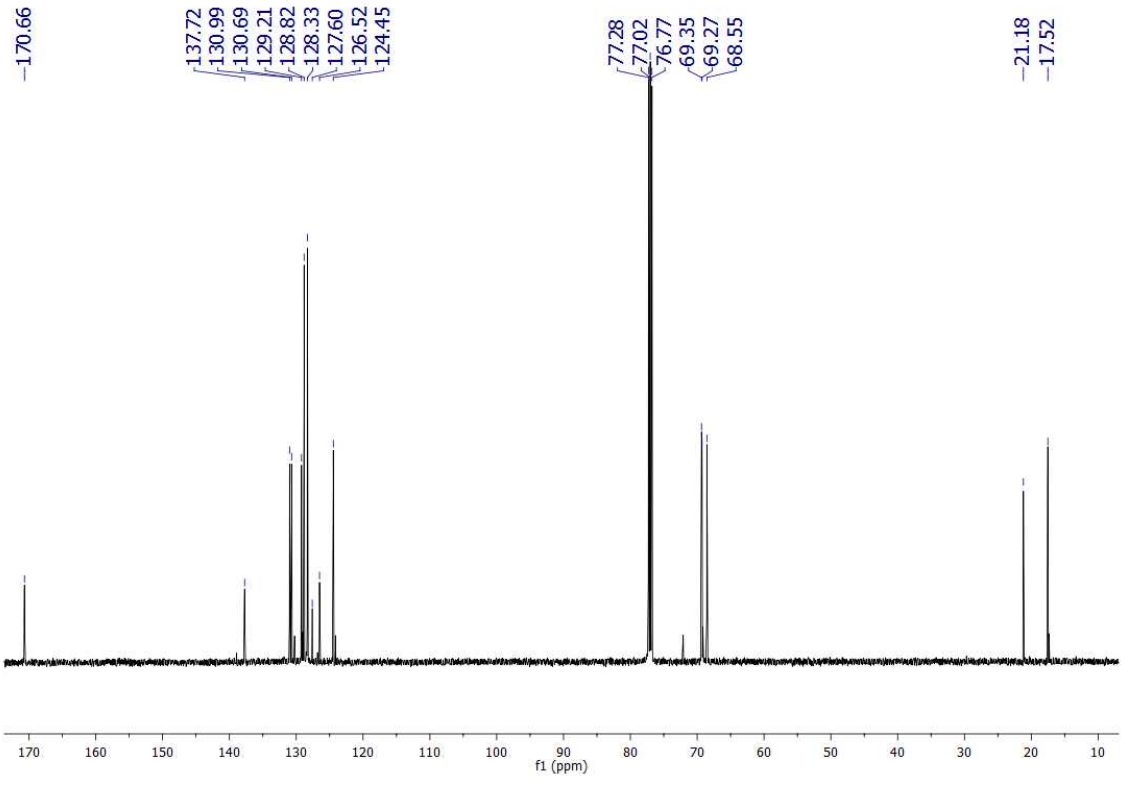
DEPT of compound **3h**



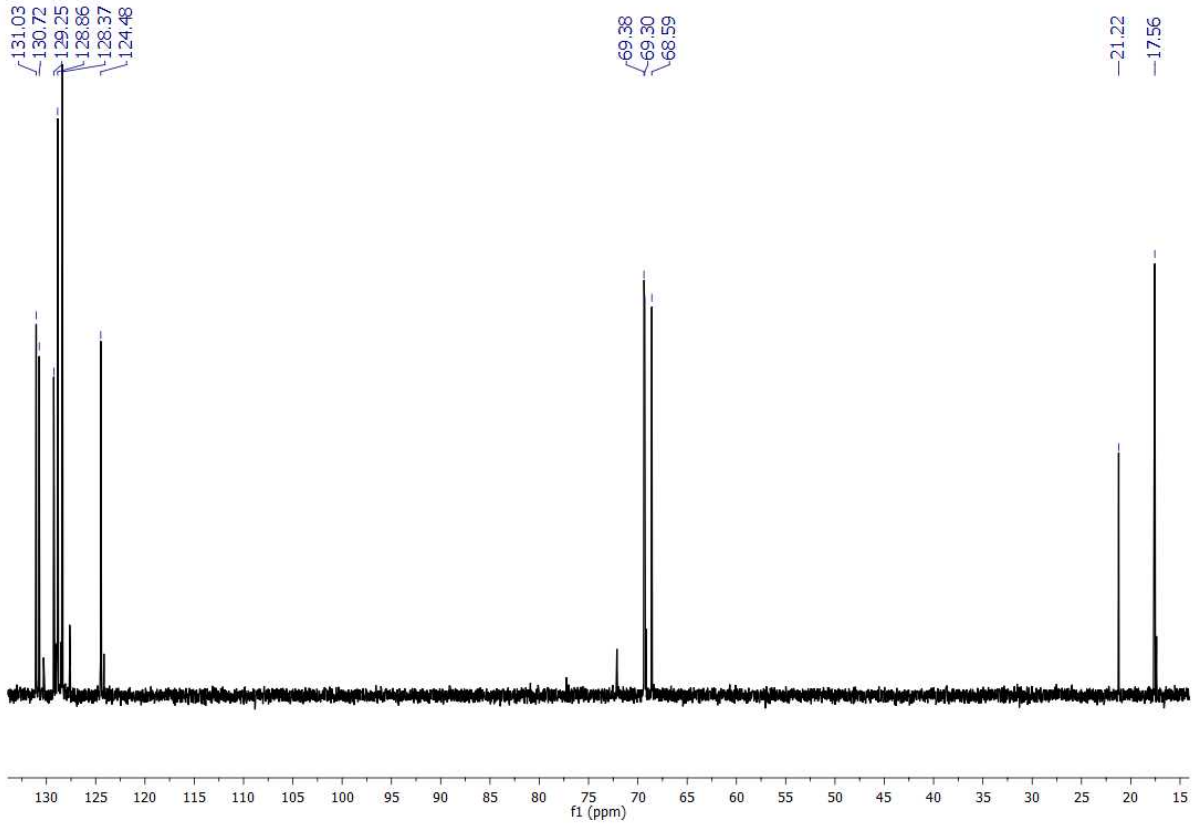
^{1}H NMR of compound **3i**



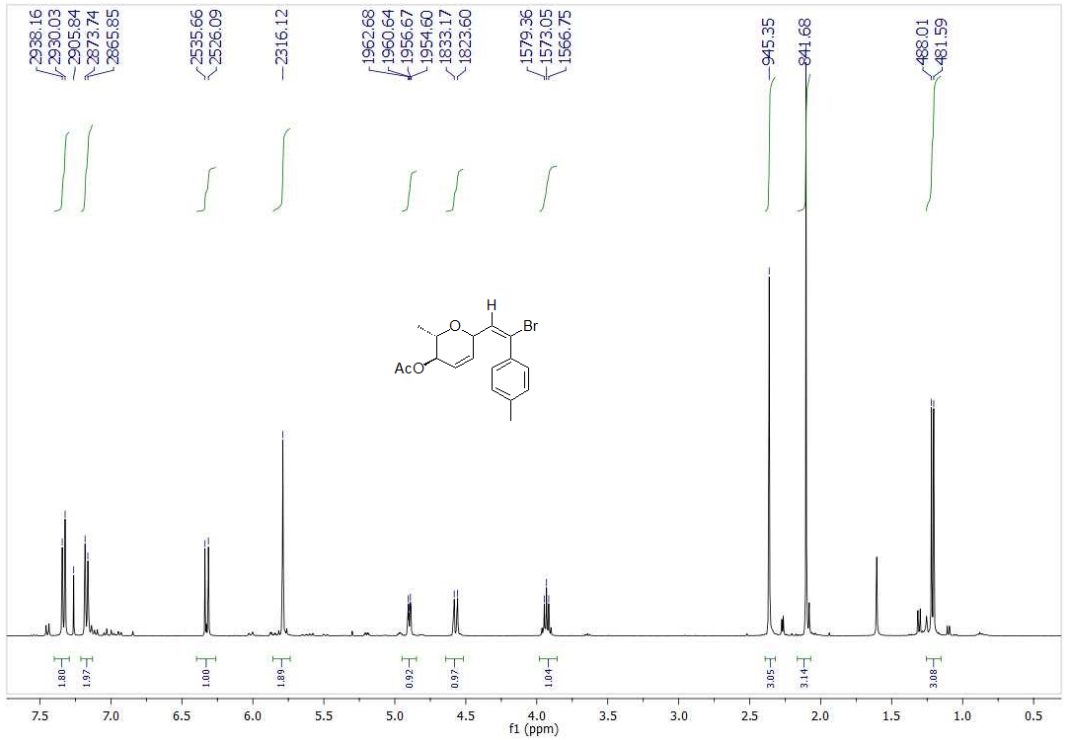
^{13}C NMR of compound **3i**



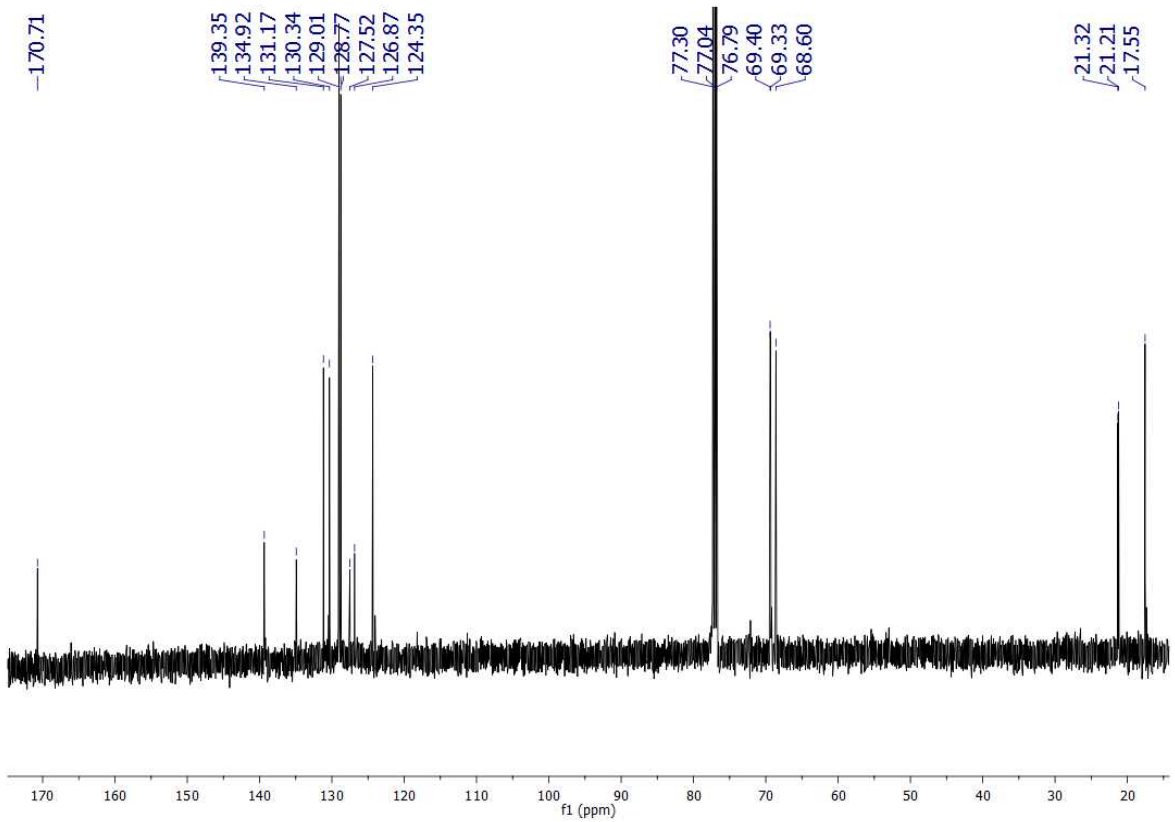
DEPT of compound **3i**



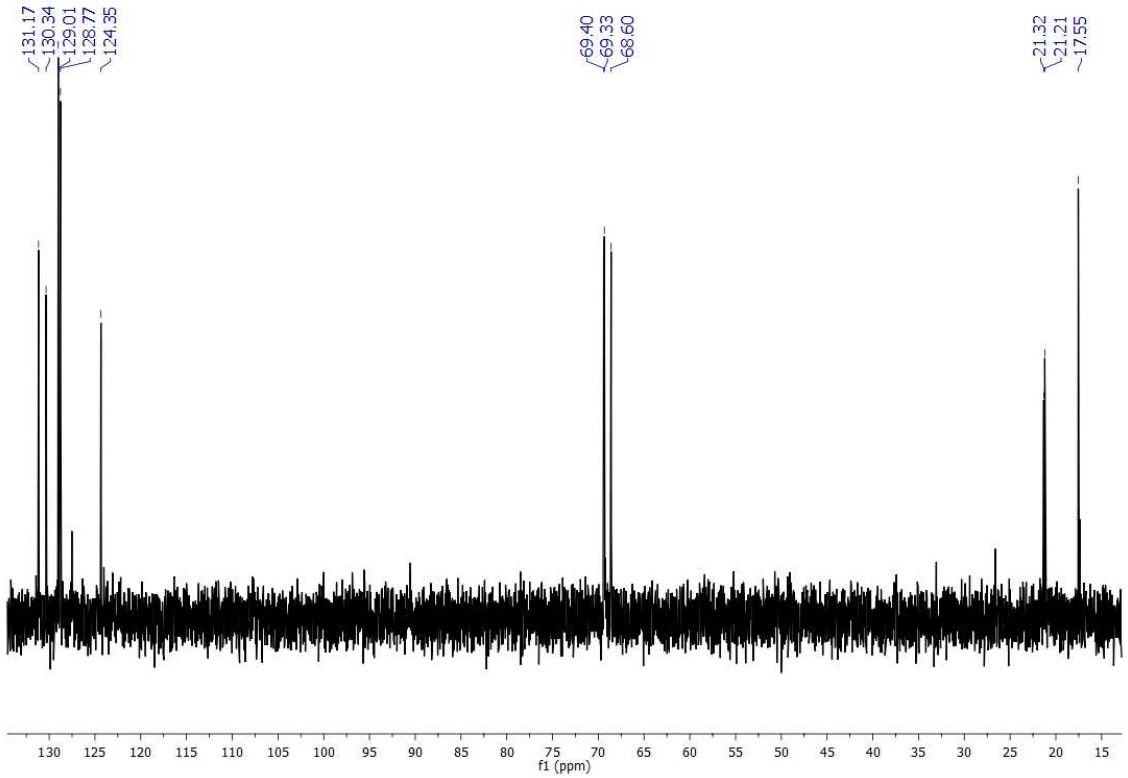
^{1}H NMR of compound **3j**



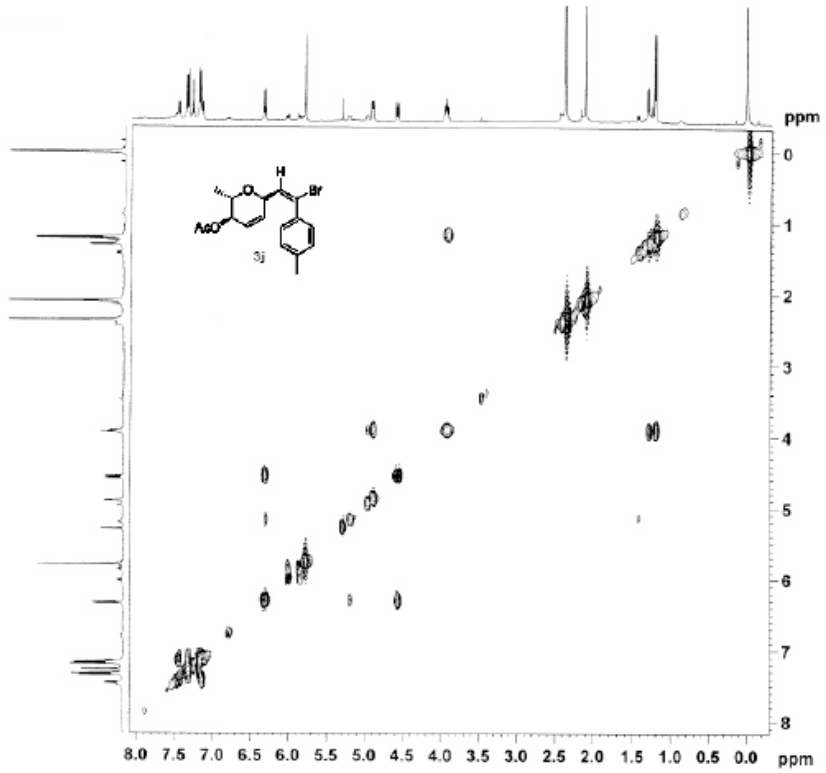
^{13}C NMR of compound **3j**



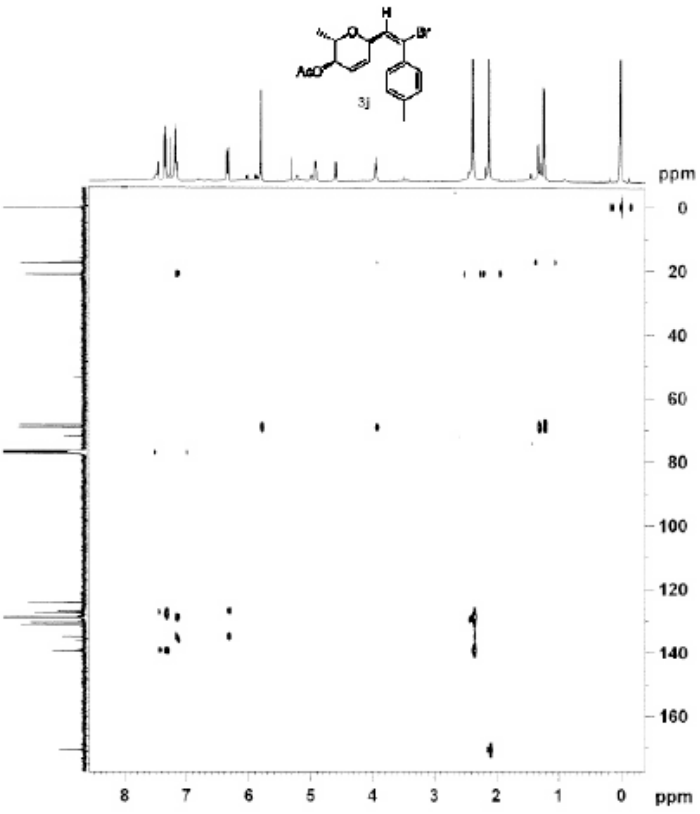
DEPT of compound **3j**



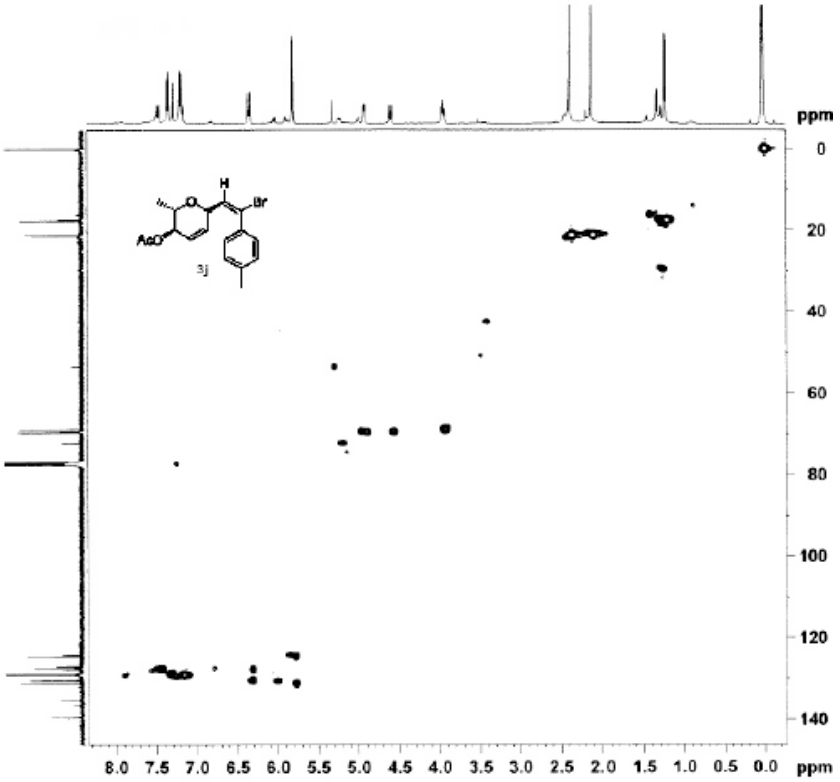
^{1}H-^{1}H COSY of compound 3j



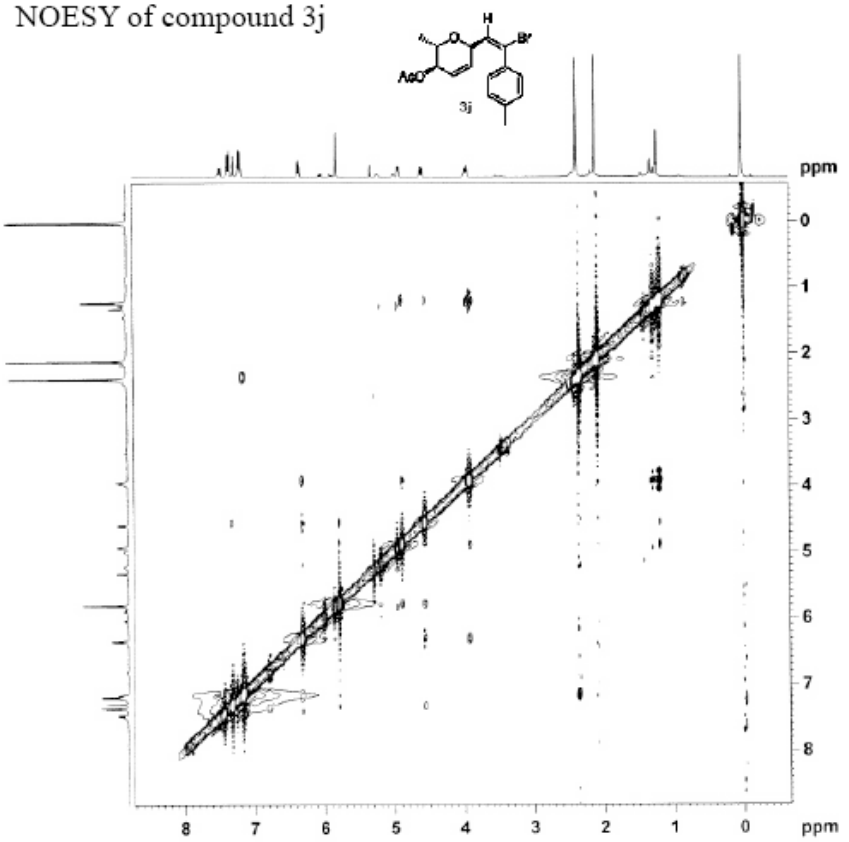
HMBC of compound 3j



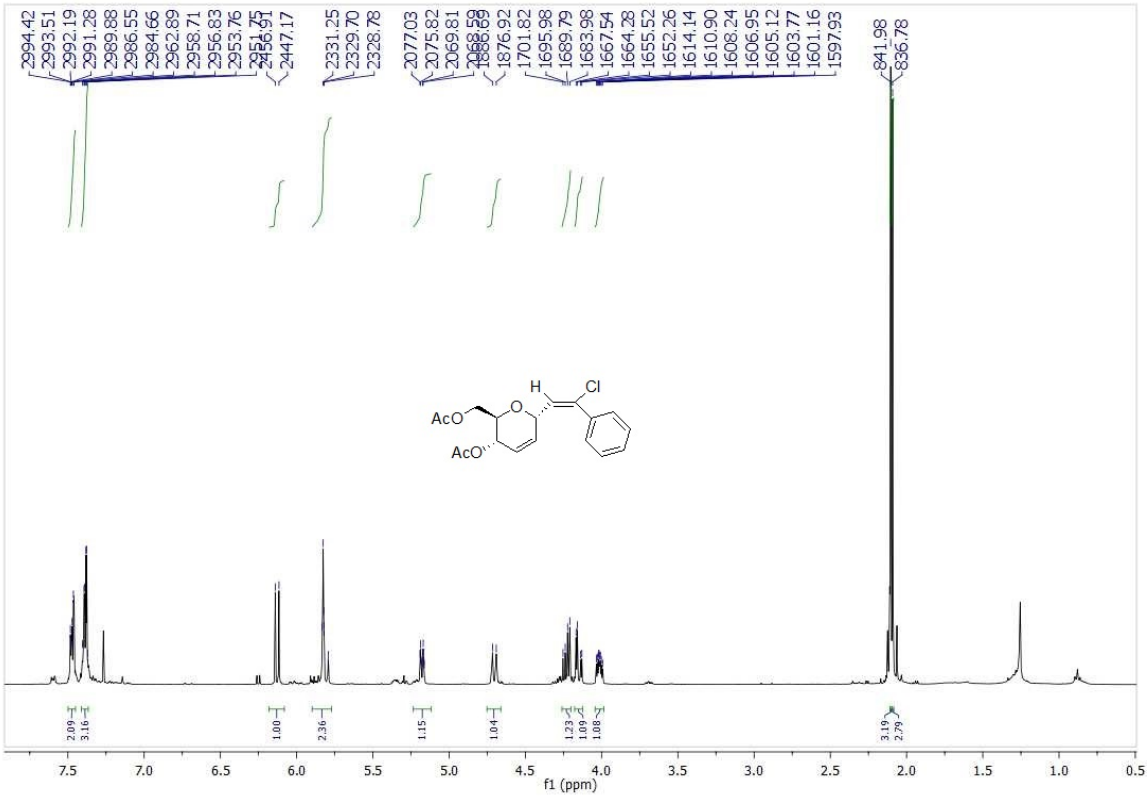
HSQC of compound 3j



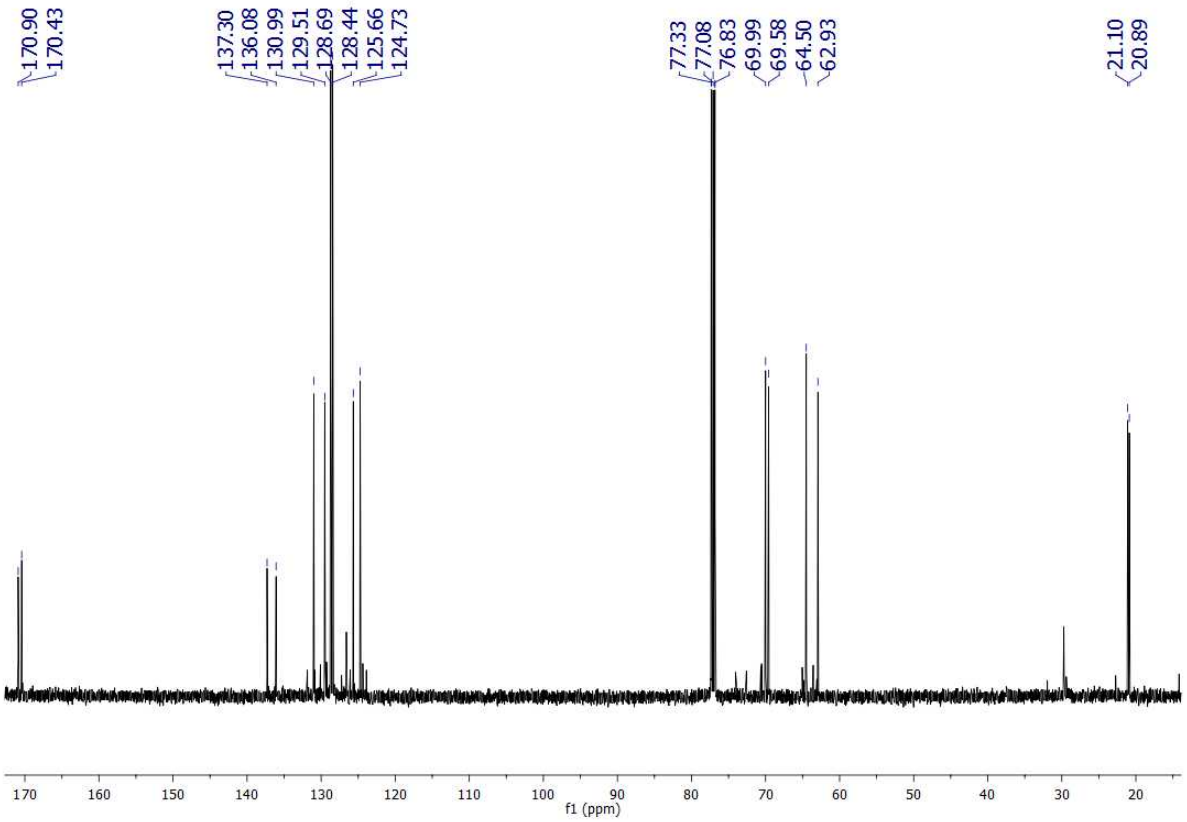
NOESY of compound 3j



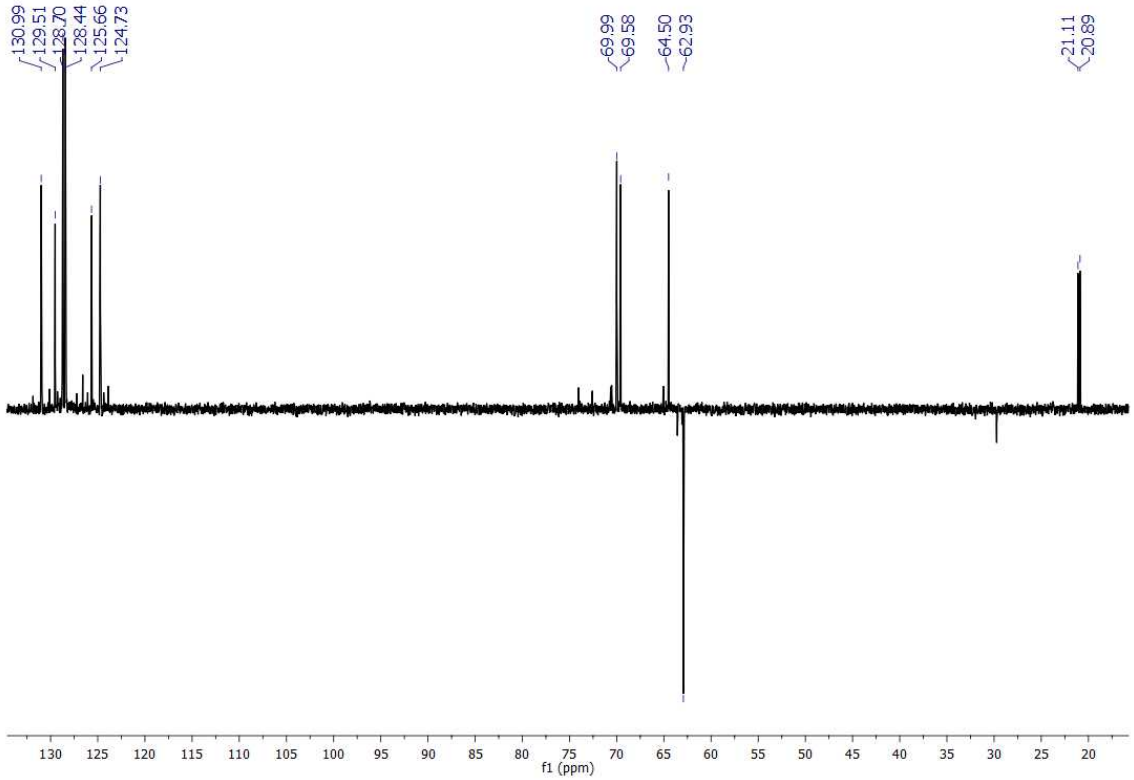
^{1}H NMR of compound 4a



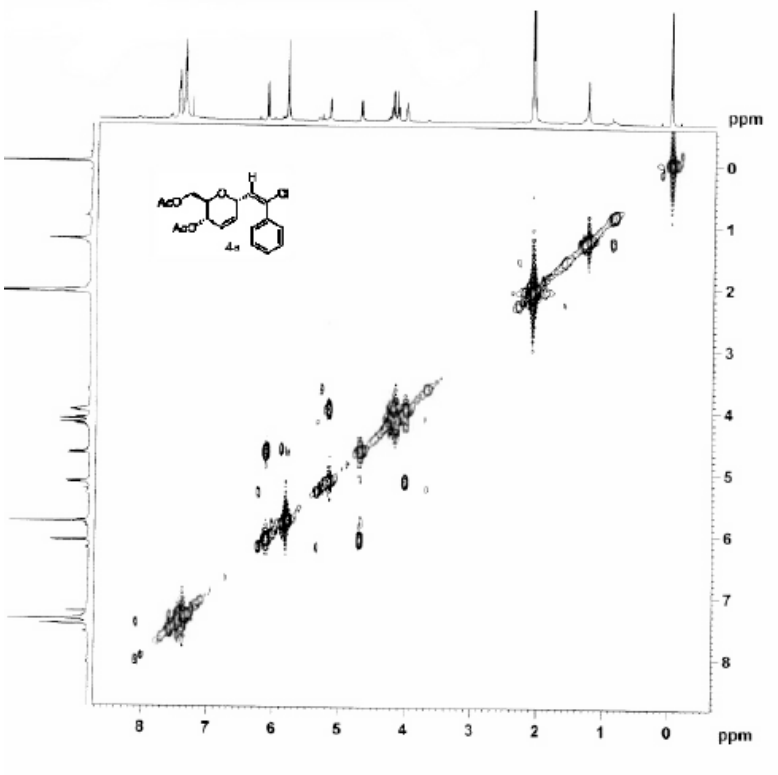
^{13}C NMR of compound 4a



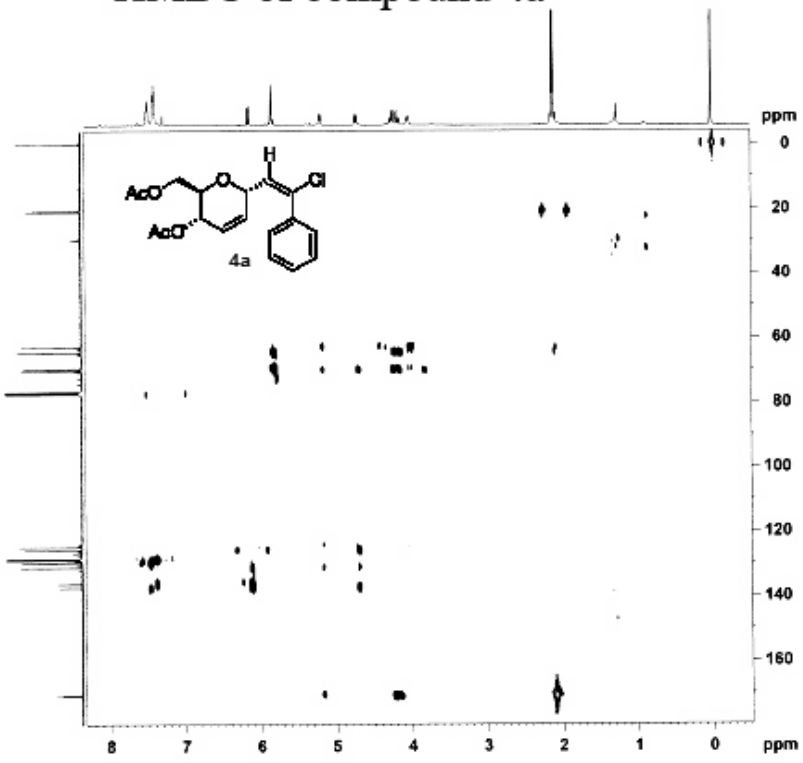
DEPT of compound 4a



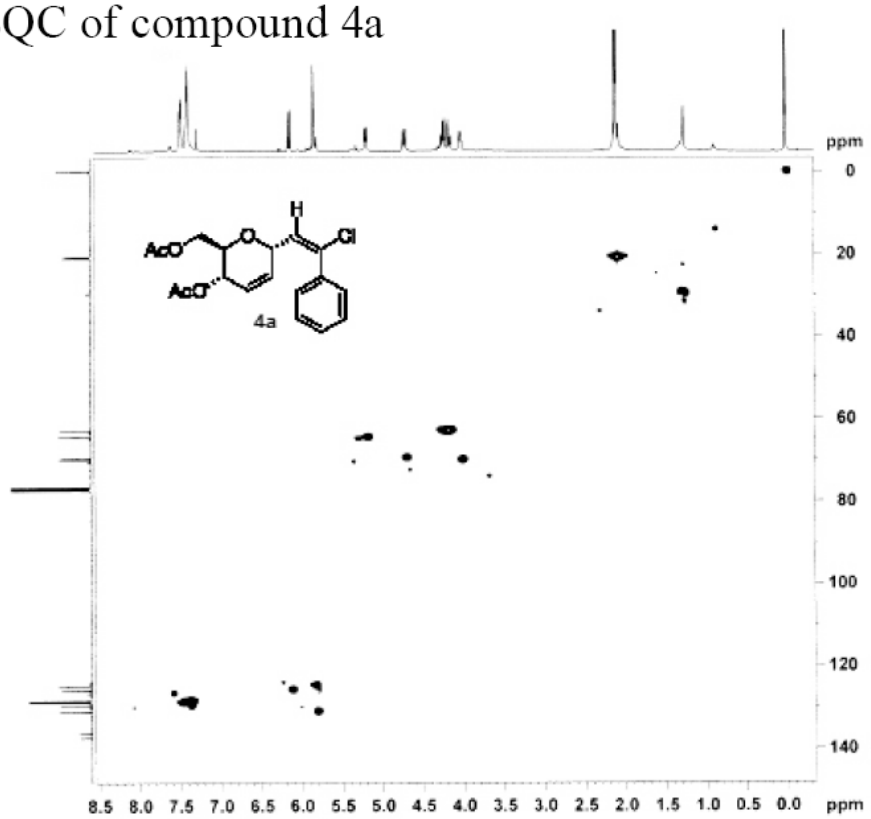
^{1}H-^{1}H COSY of compound 4a



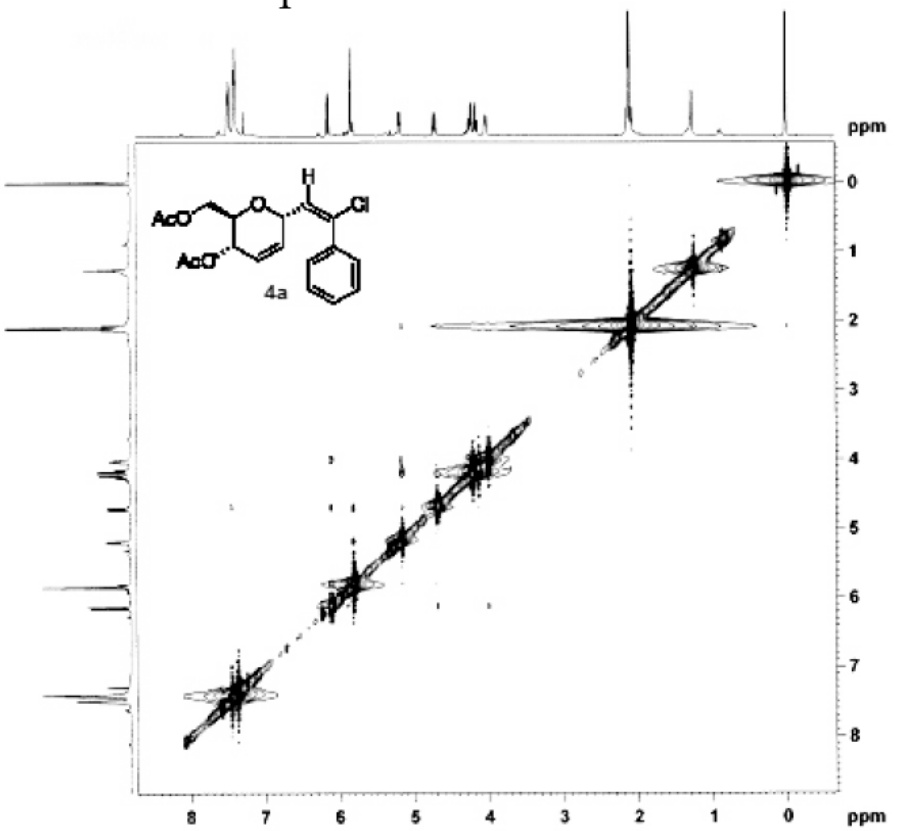
HMBC of compound 4a



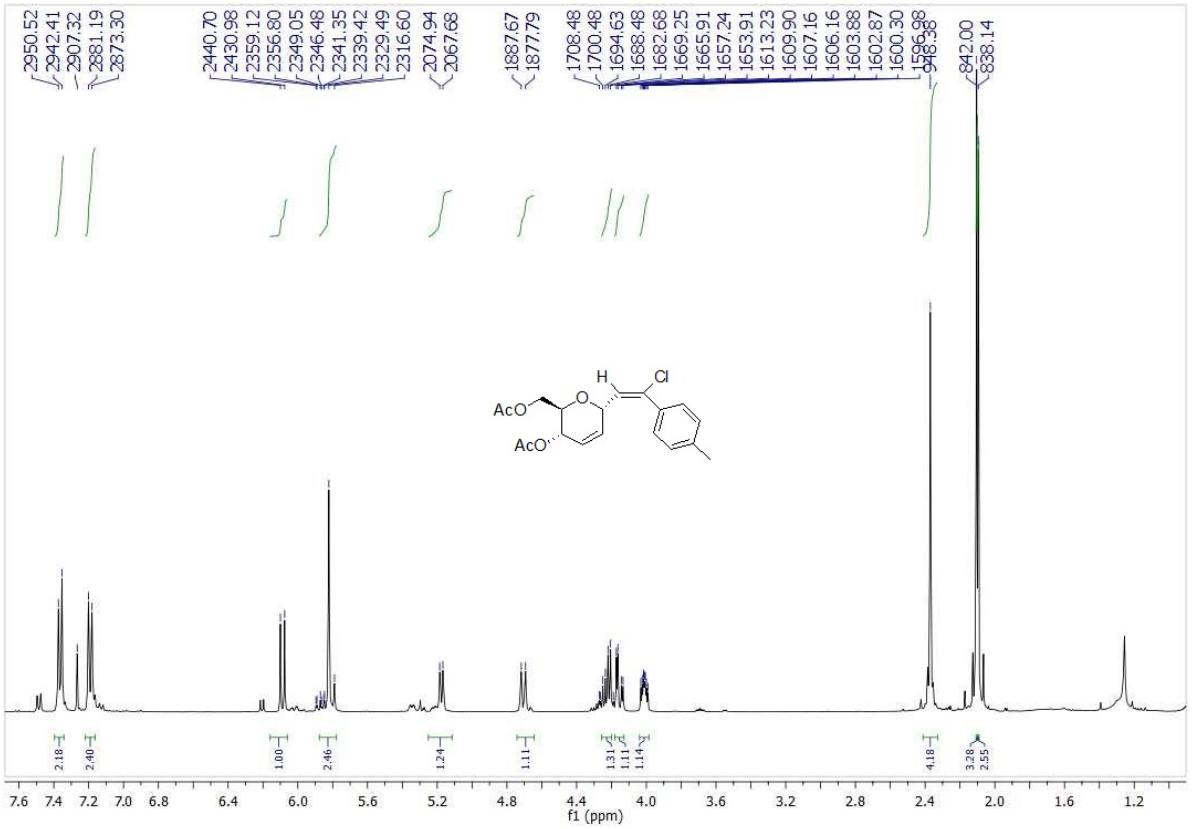
HSQC of compound 4a



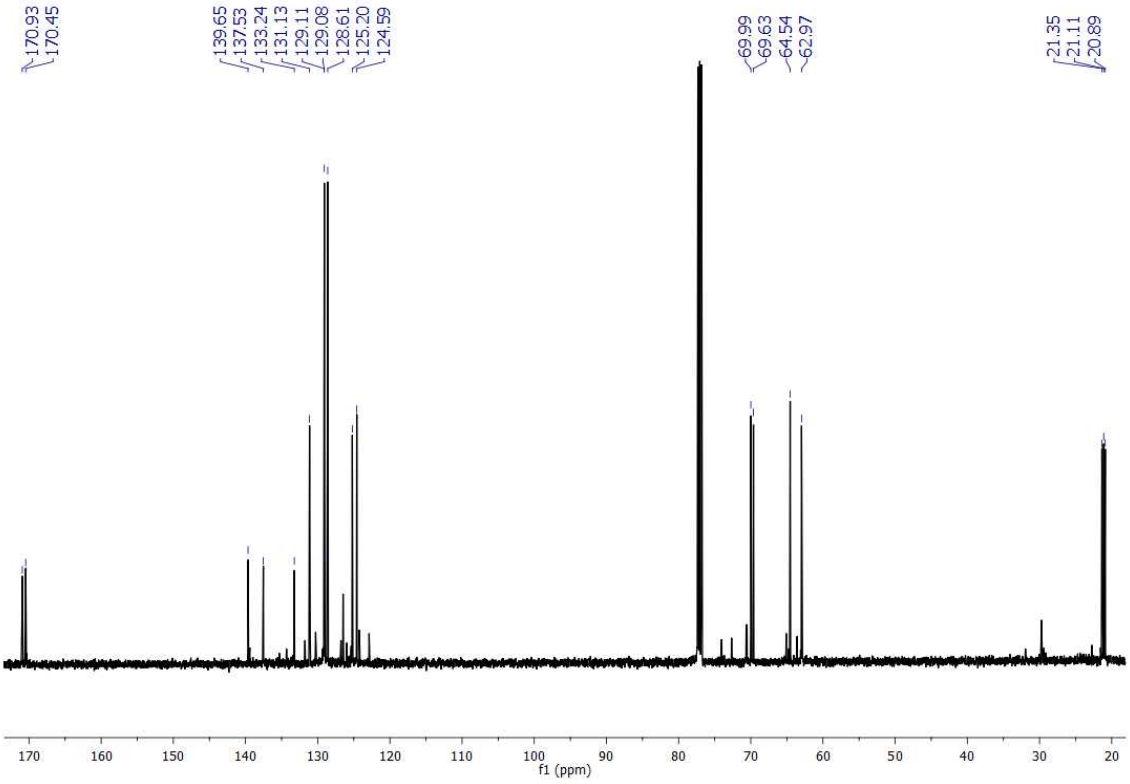
NOESY of compound 4a



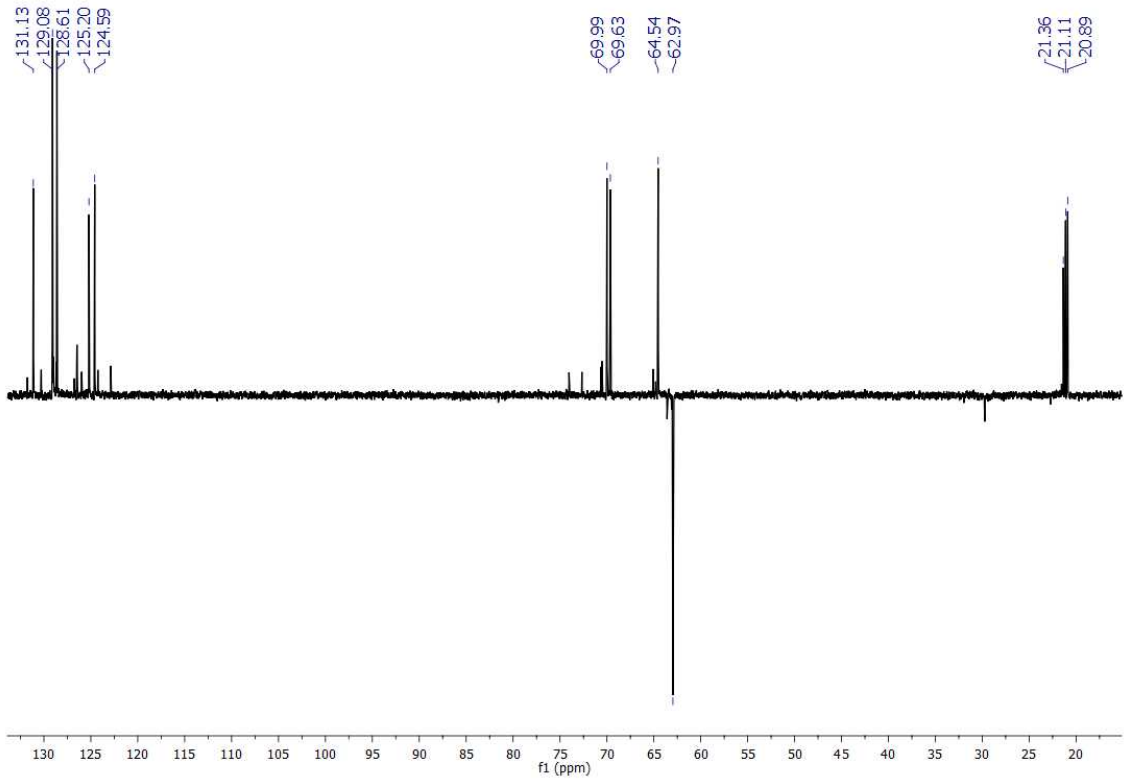
^{1}H NMR of compound 4b



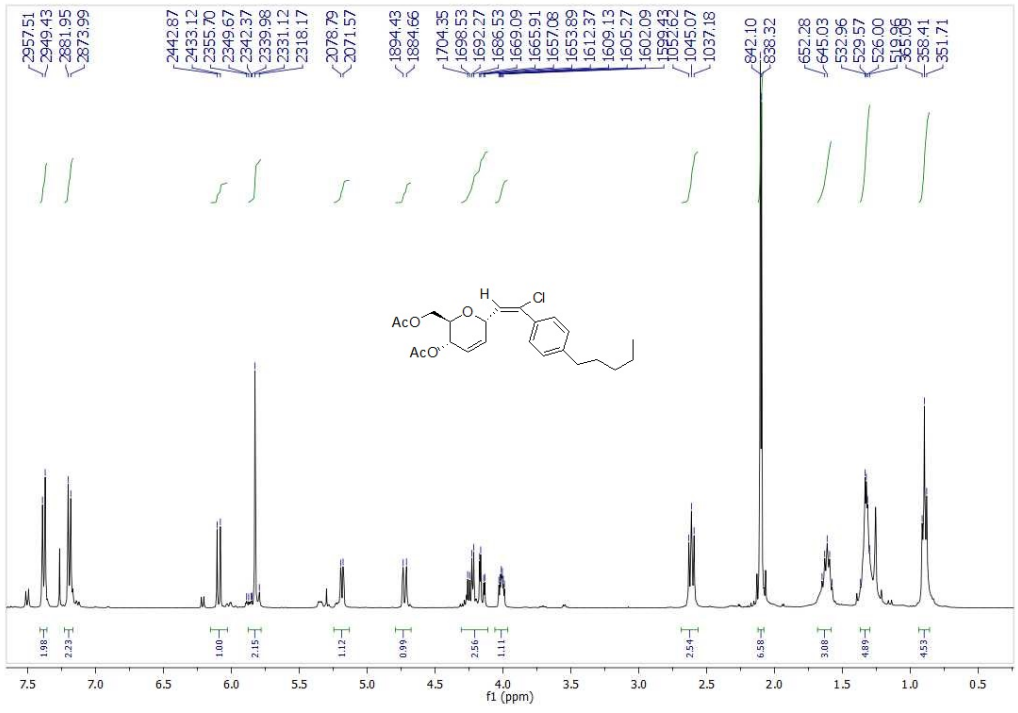
^{13}C NMR of compound 4b



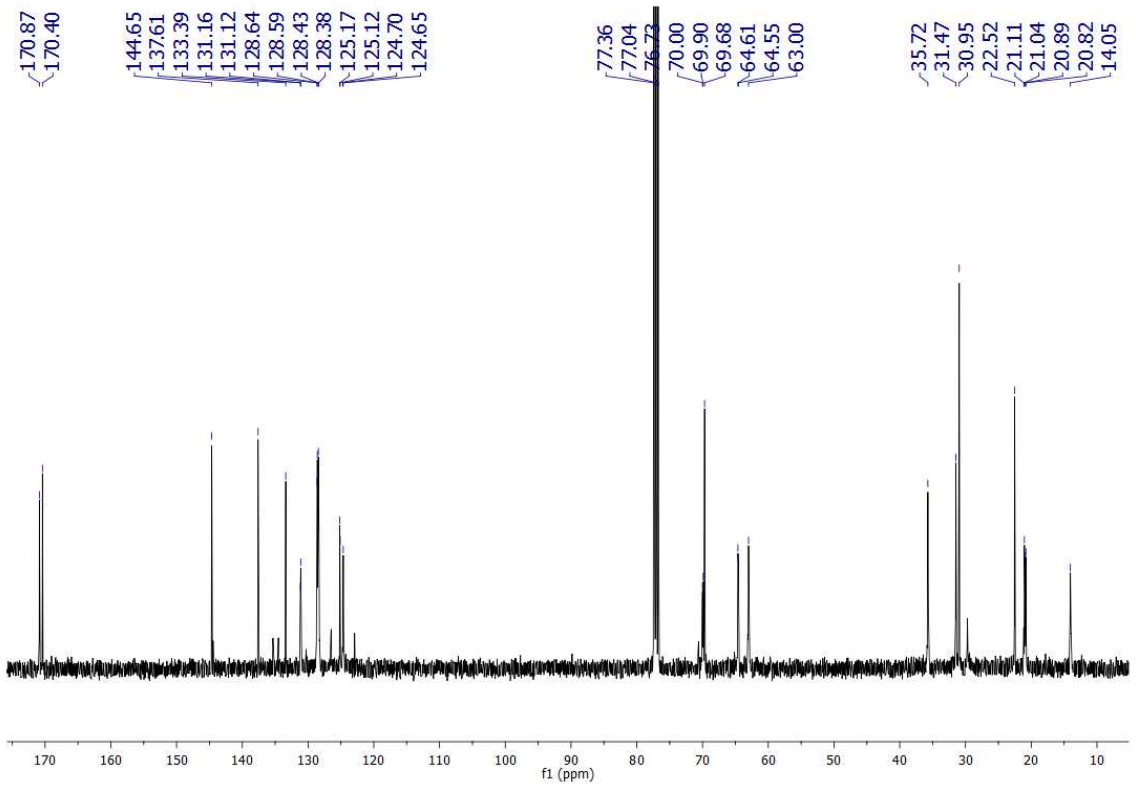
DEPT of compound 4b



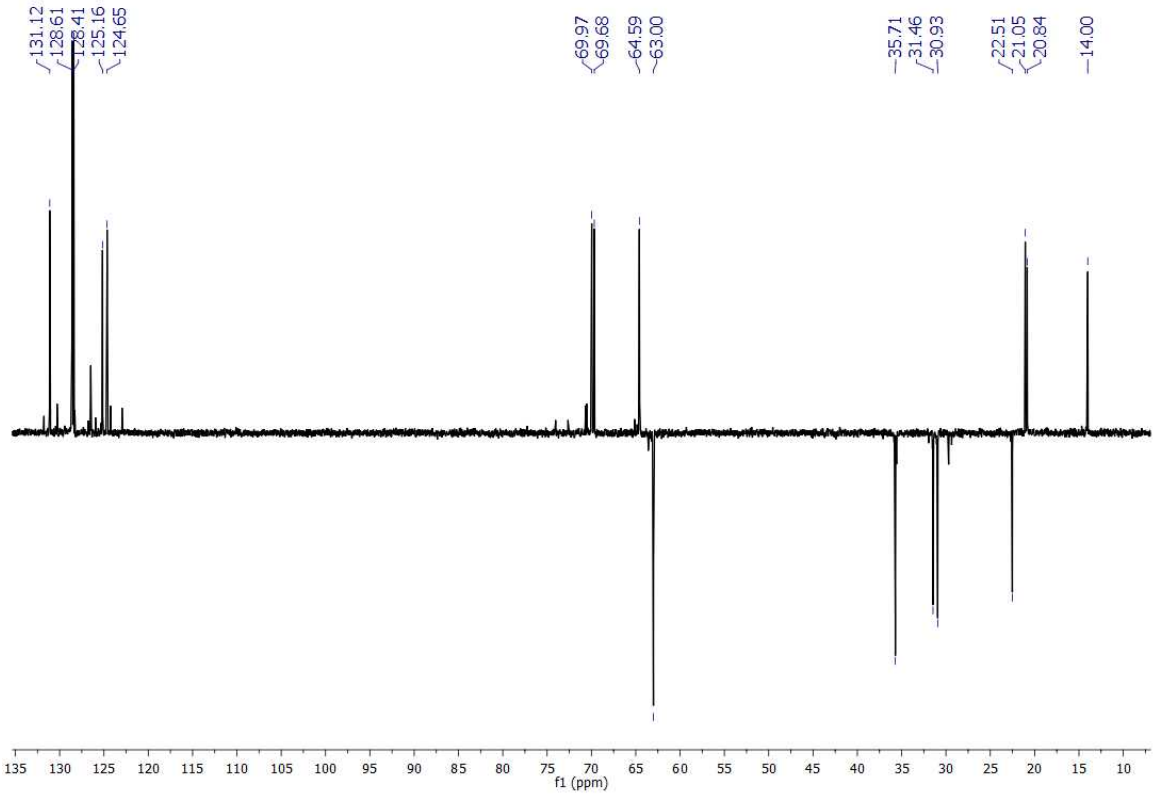
^{1}H NMR of compound 4c



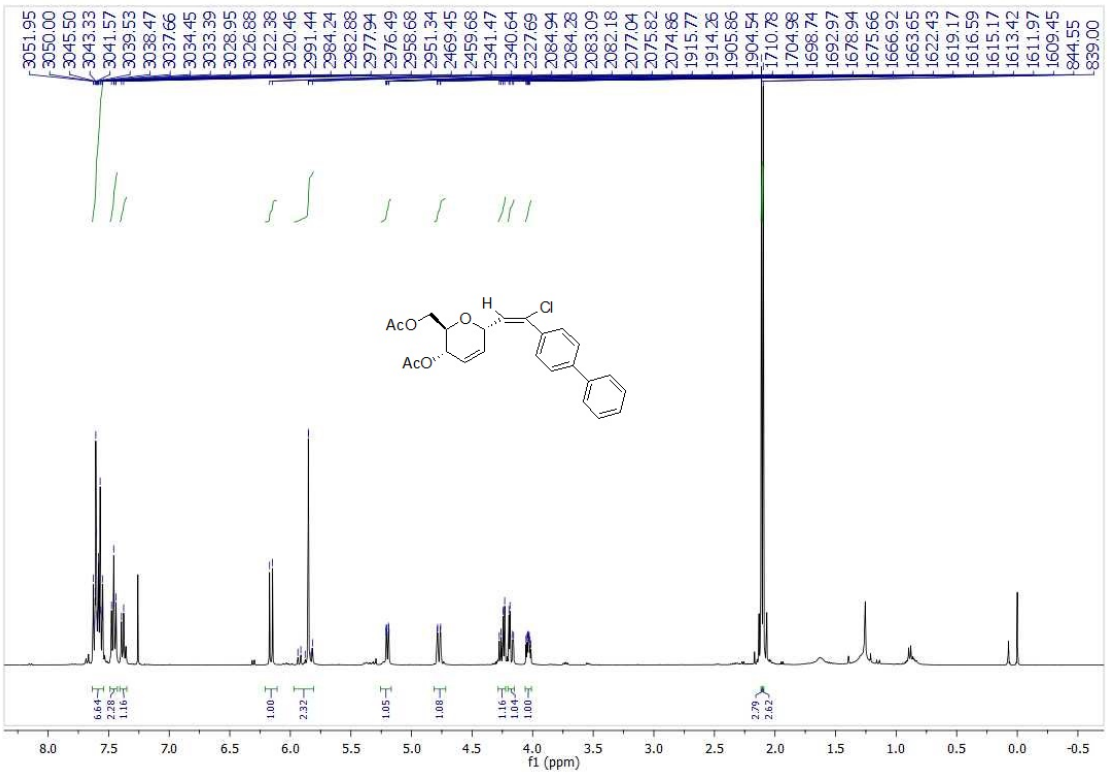
^{13}C NMR of compound 4c



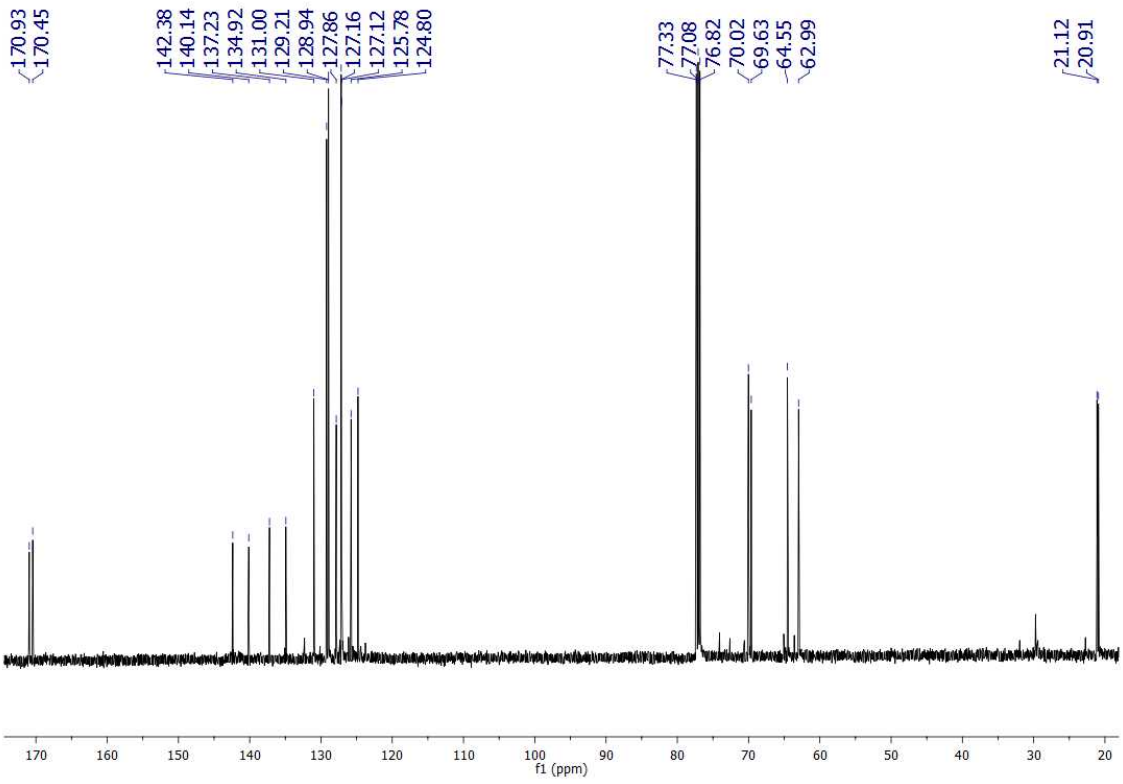
DEPT of compound 4c



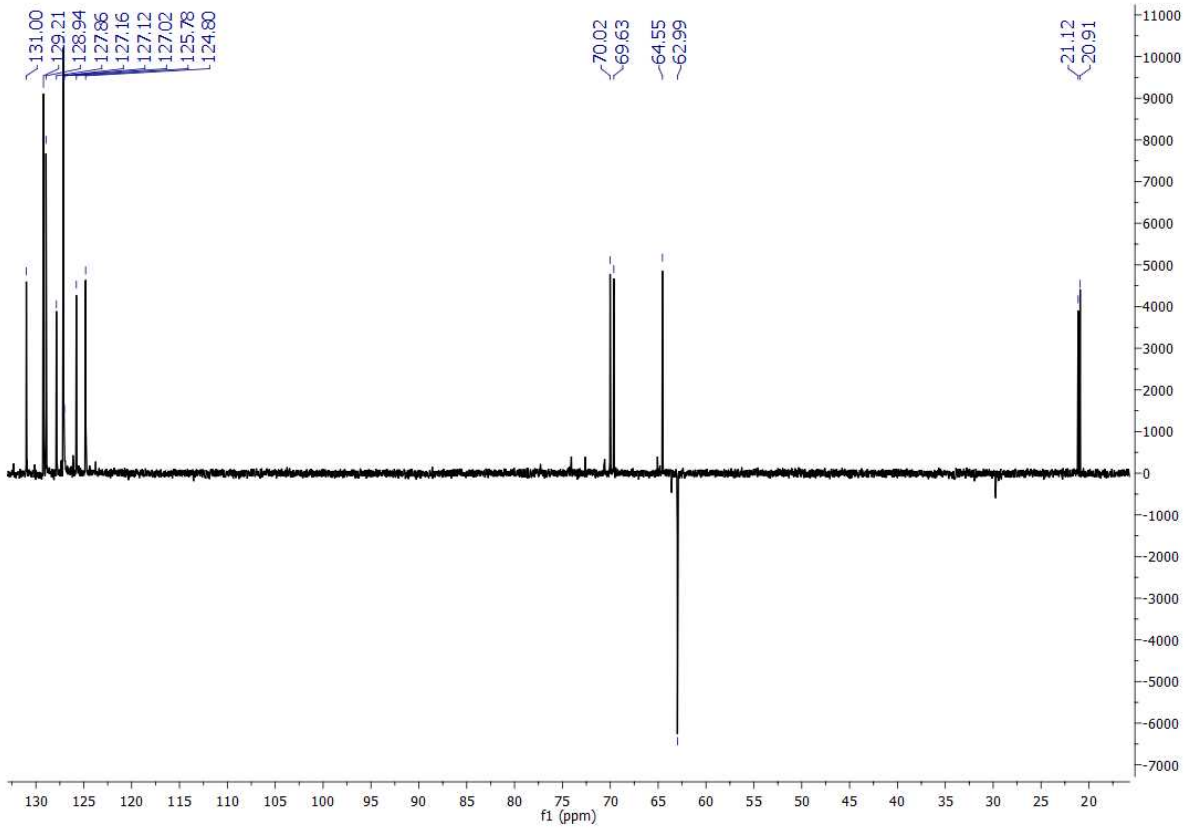
^{1}H NMR of compound 4d



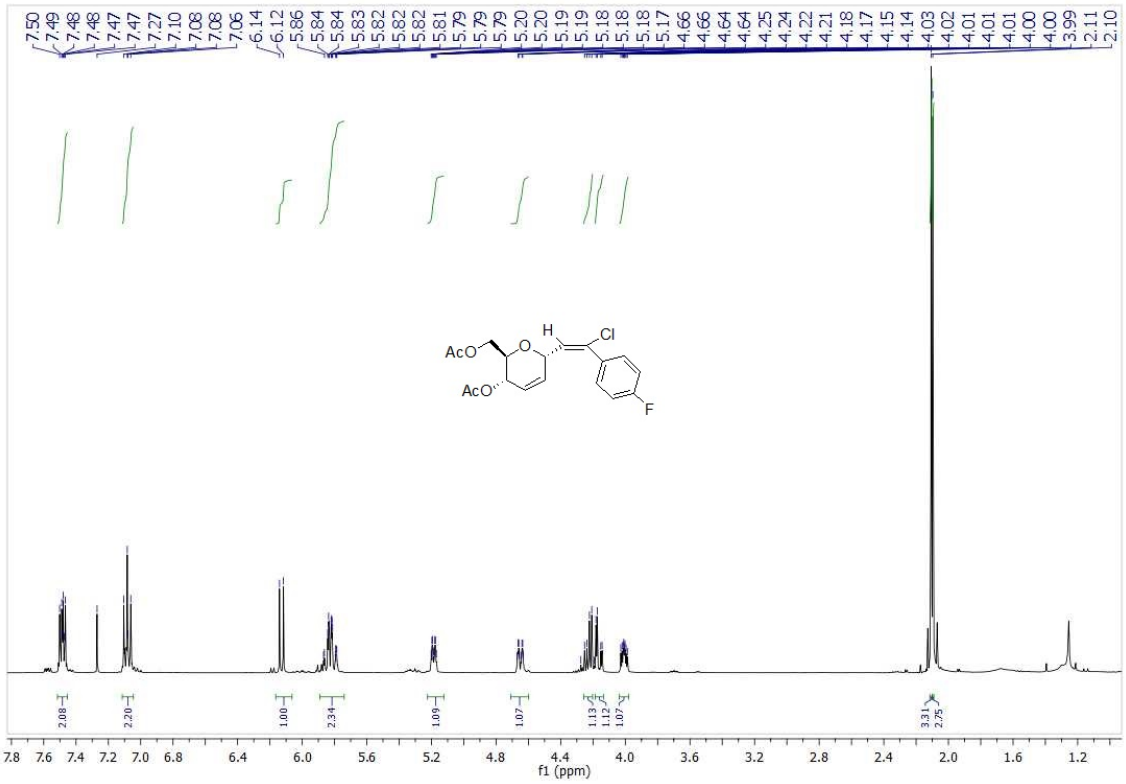
^{13}C NMR of compound 4d



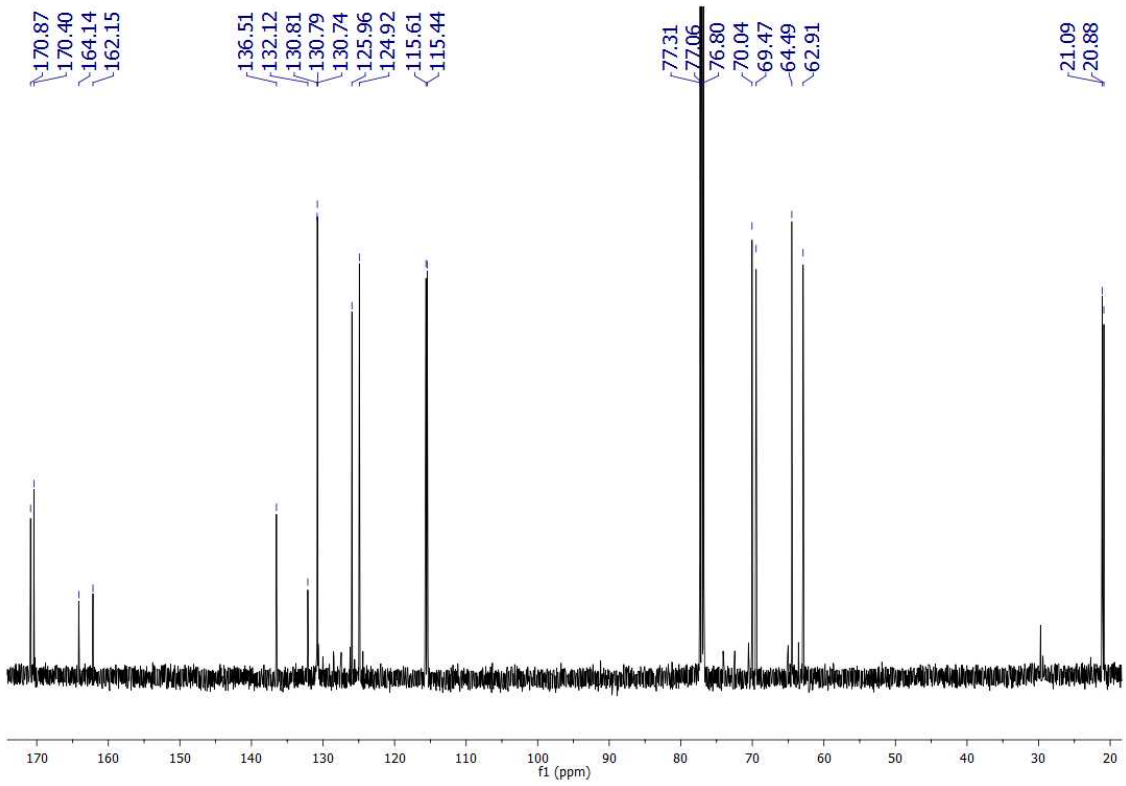
DEPT of compound 4d



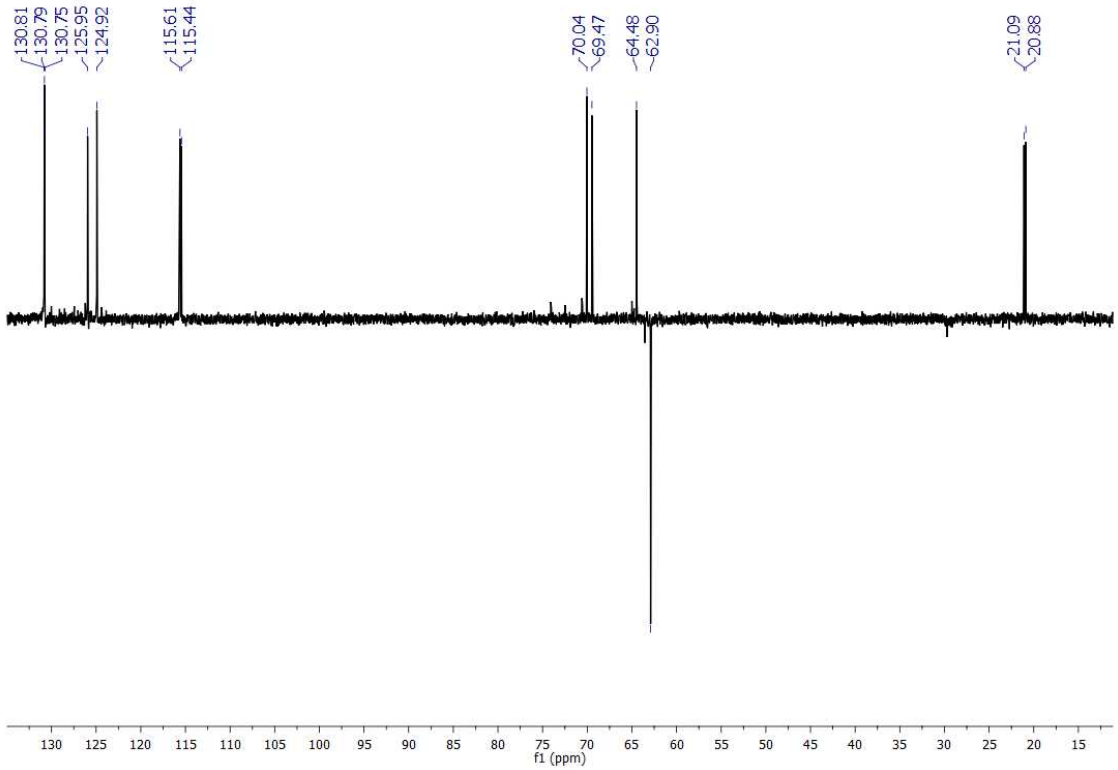
^{1}H NMR of compound 4e



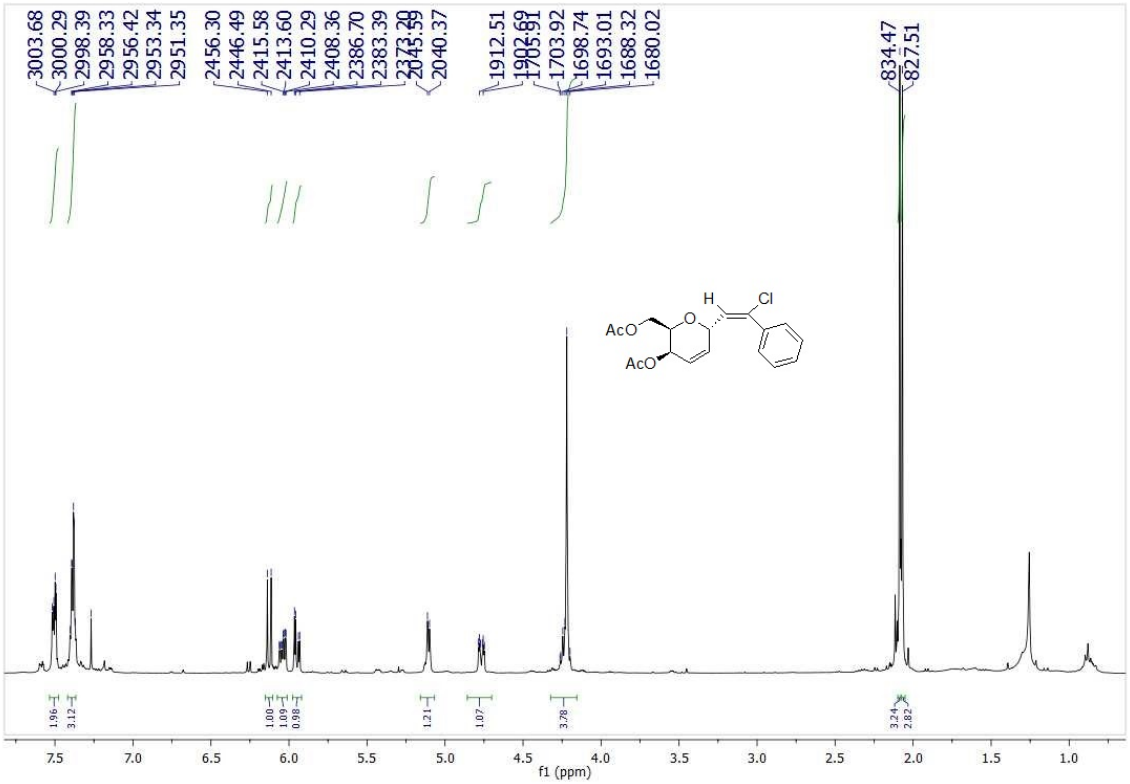
^{13}C NMR of compound 4e



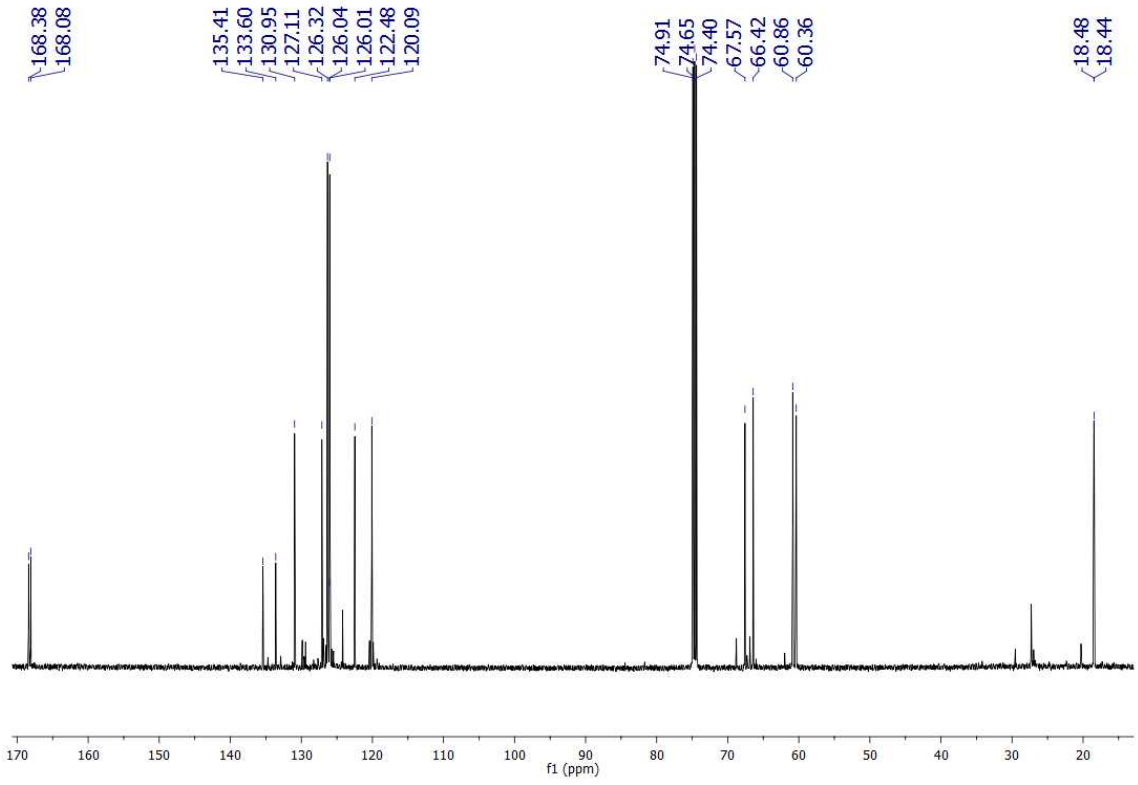
DEPT of compound 4e



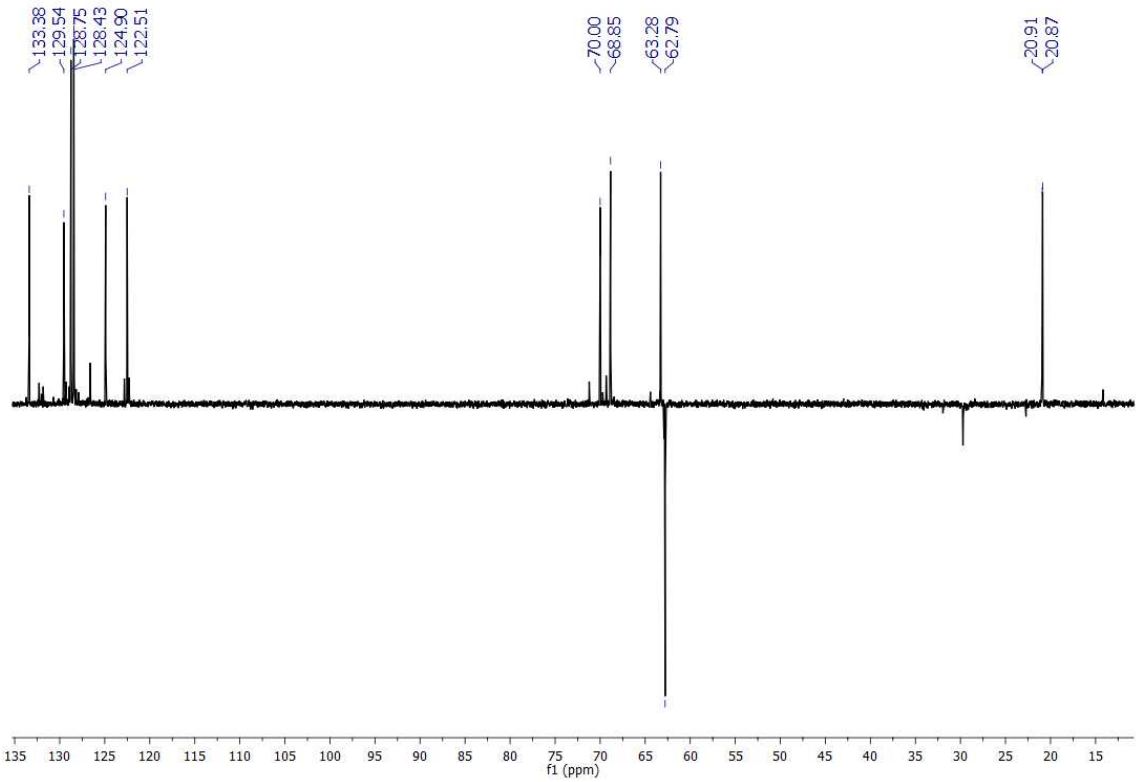
^{1}H NMR of compound 4f



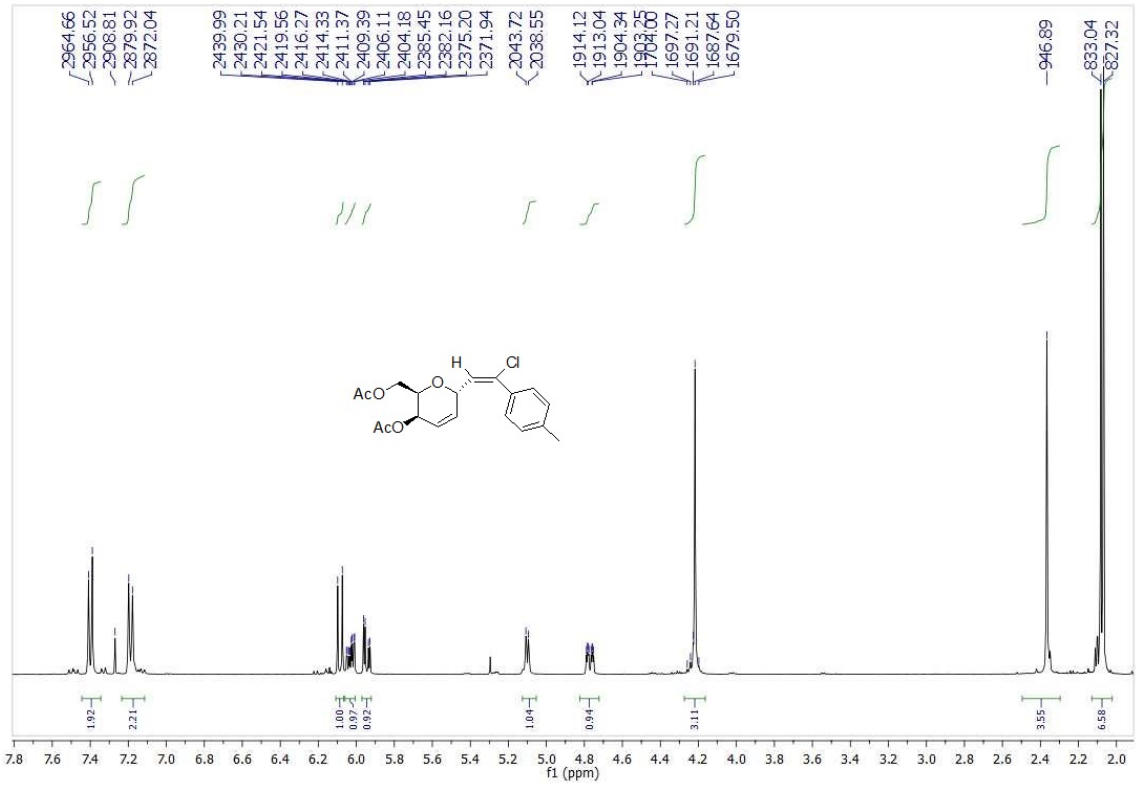
^{13}C NMR of compound 4f



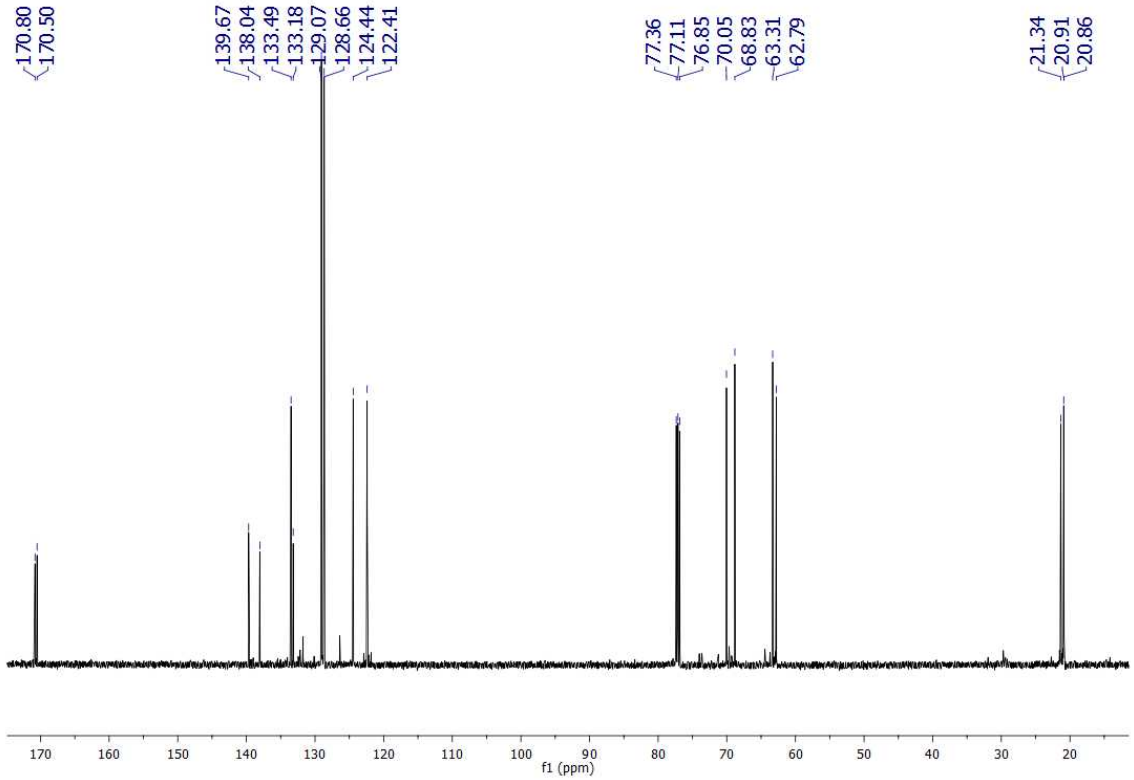
DEPT of compound 4f



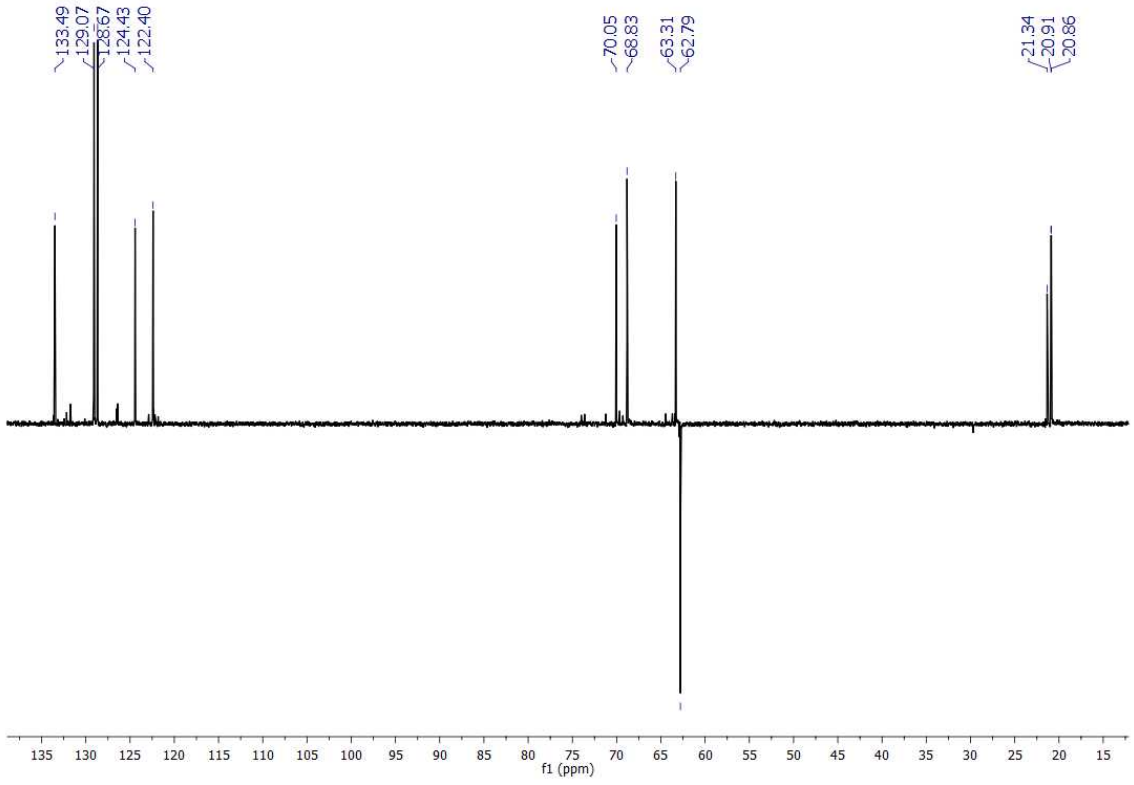
^{1}H NMR of compound 4g



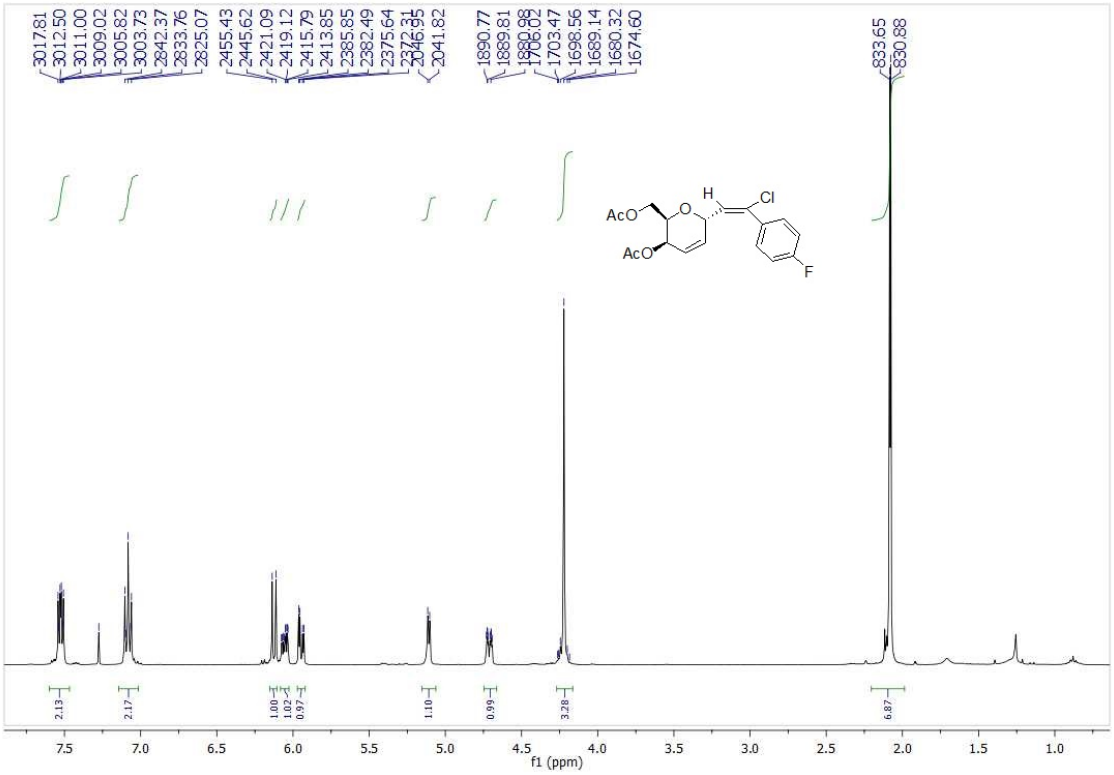
^{13}C NMR of compound 4g



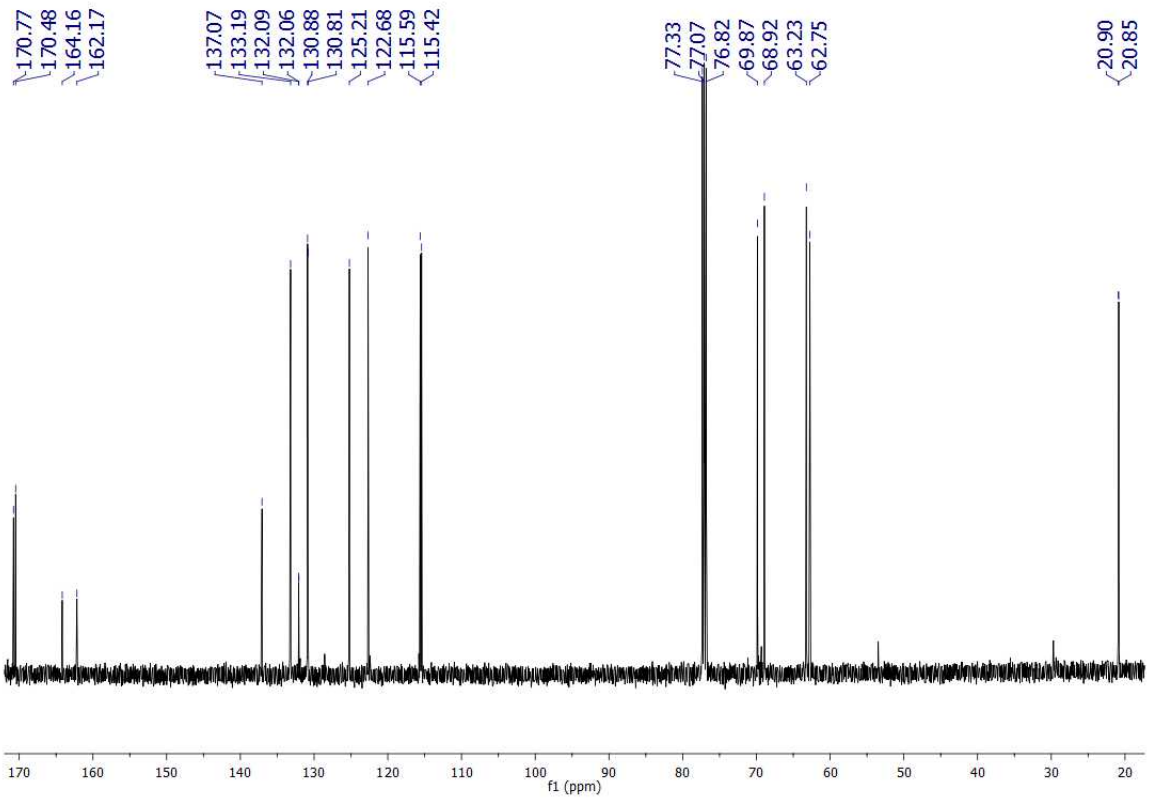
DEPT of compound 4g



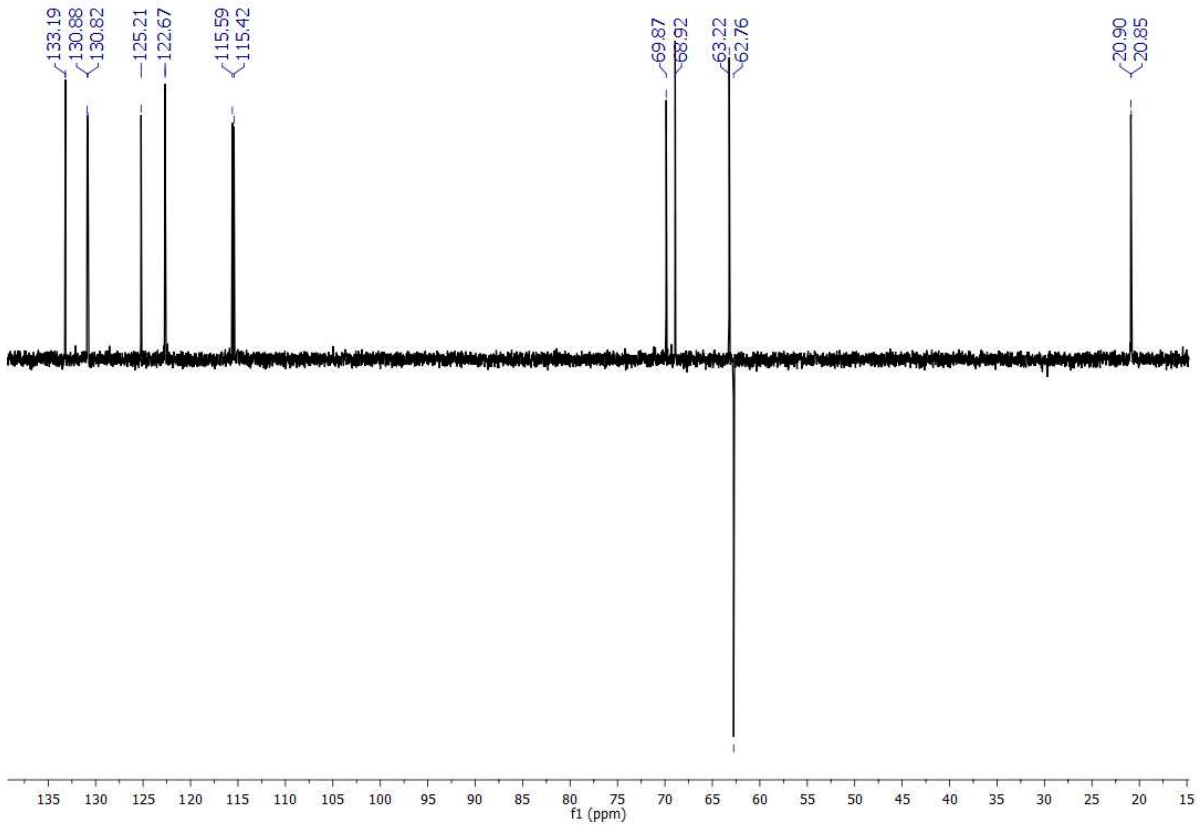
^{1}H NMR of compound 4h



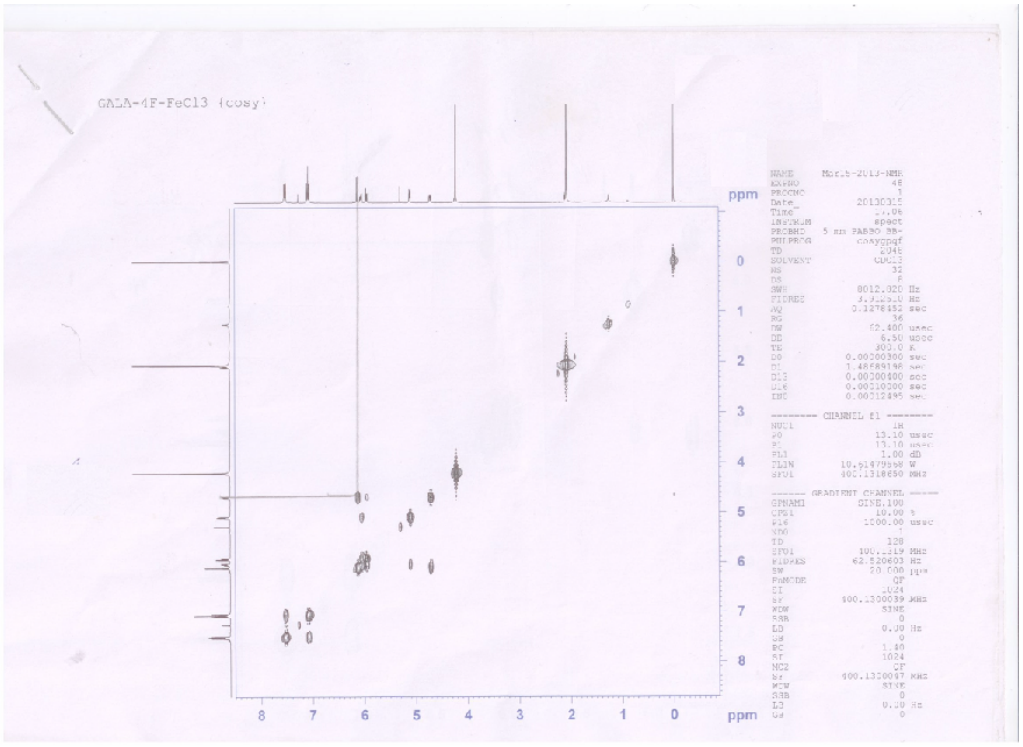
^{13}C NMR of compound 4h



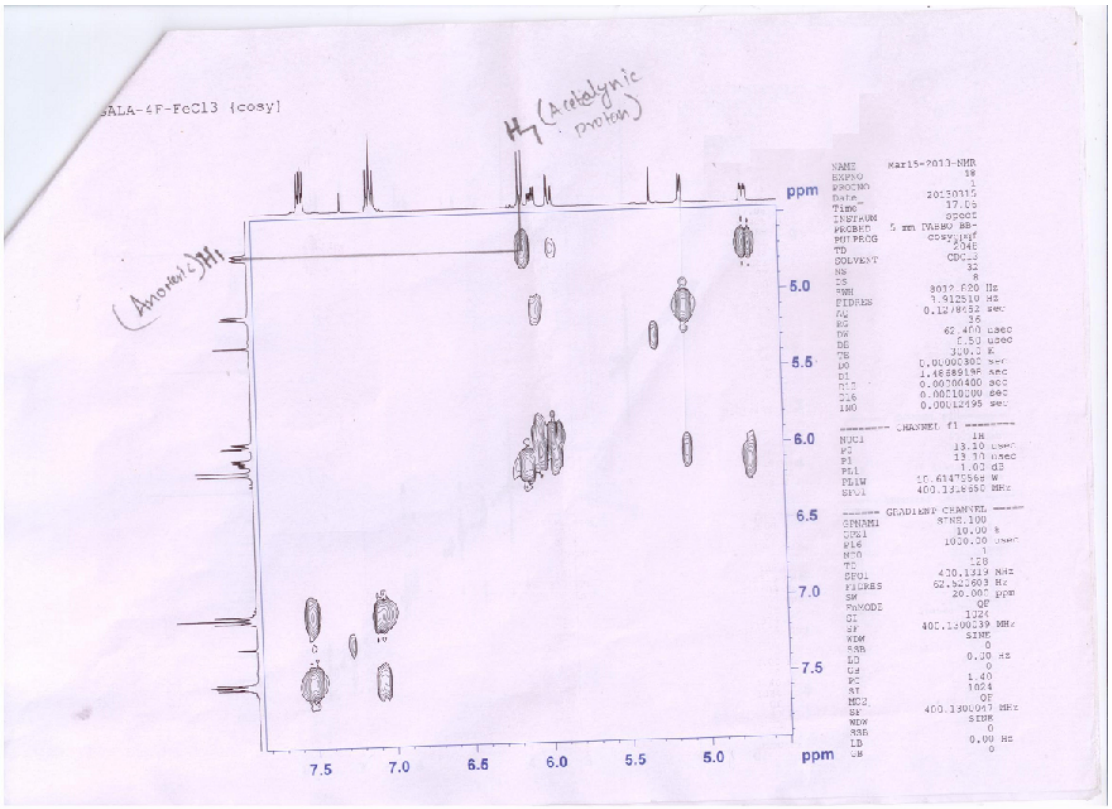
DEPT of compound 4h



COSY of compound 4h



COSY (exp) of compound 4h



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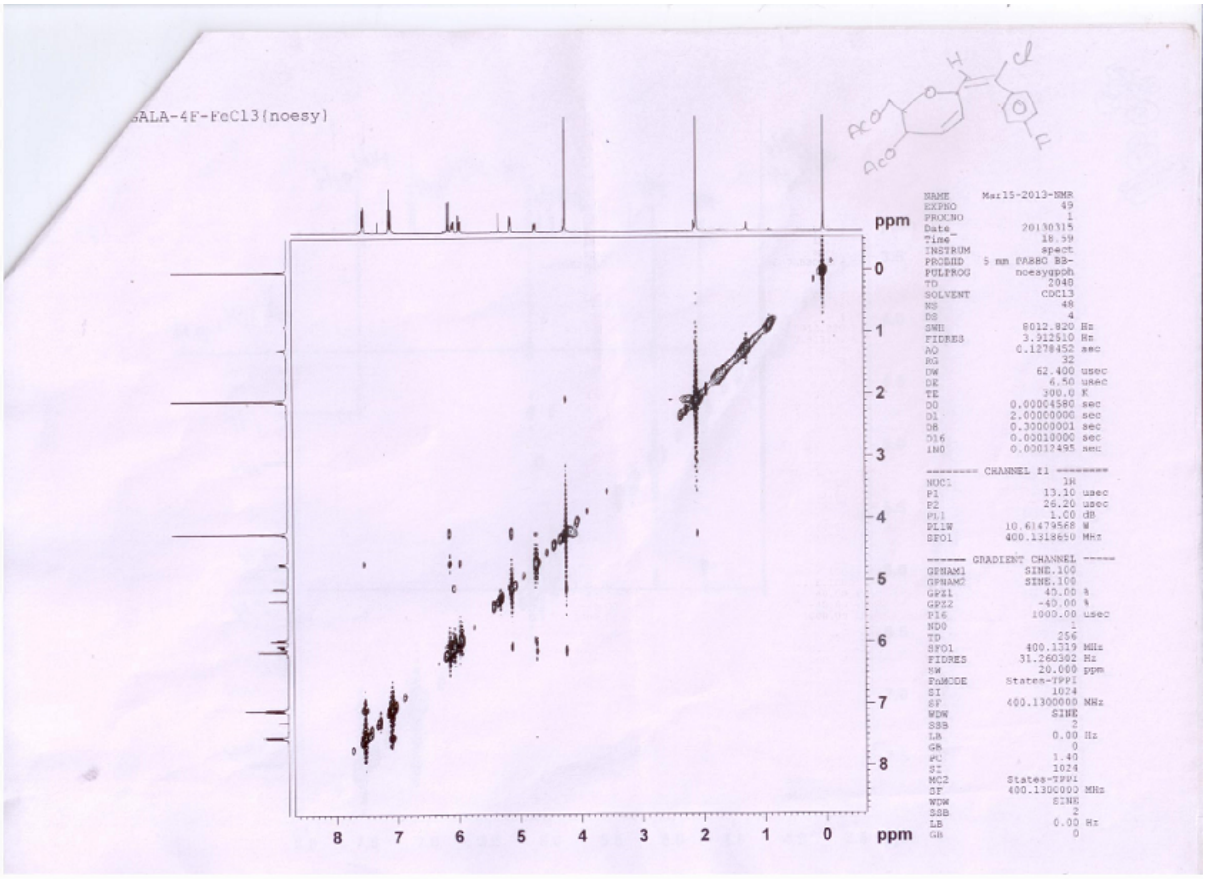
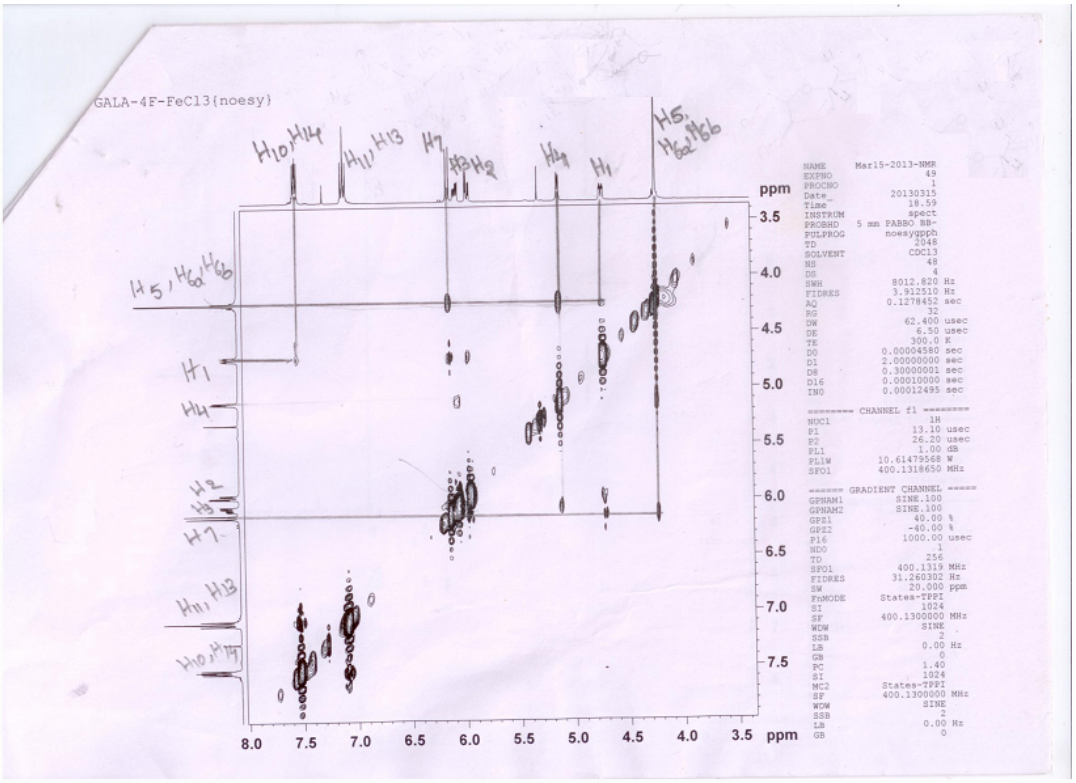
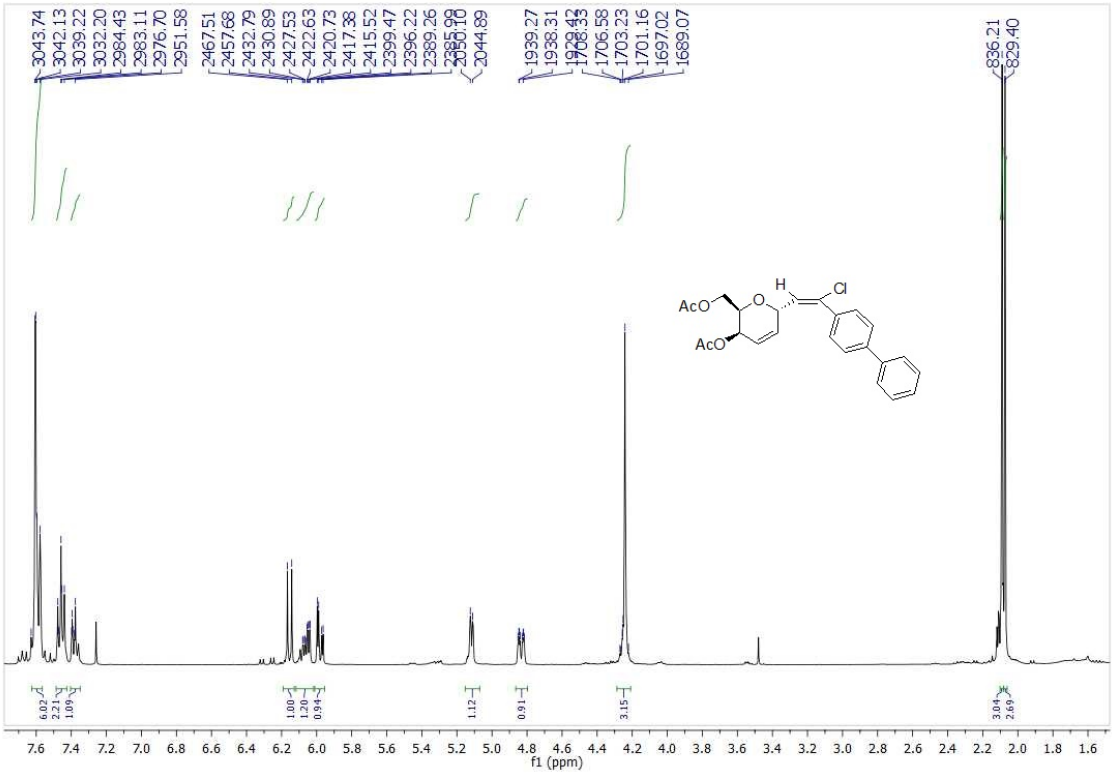


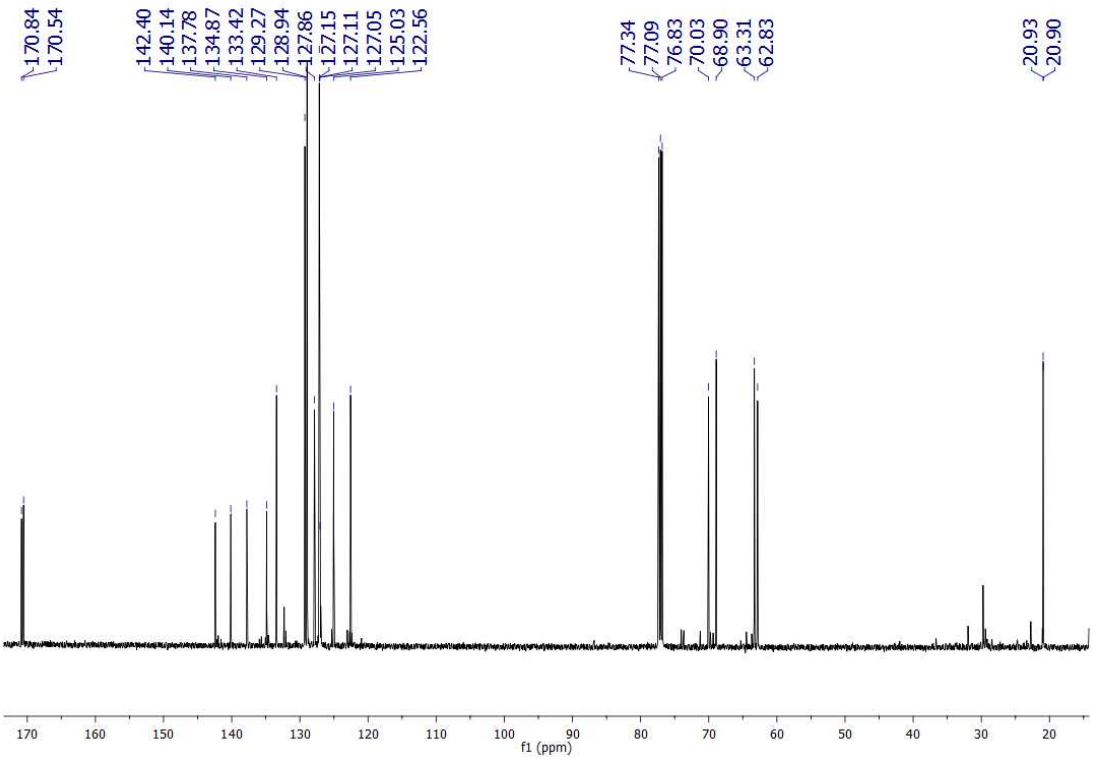
NOESY (exp) of compound 4h



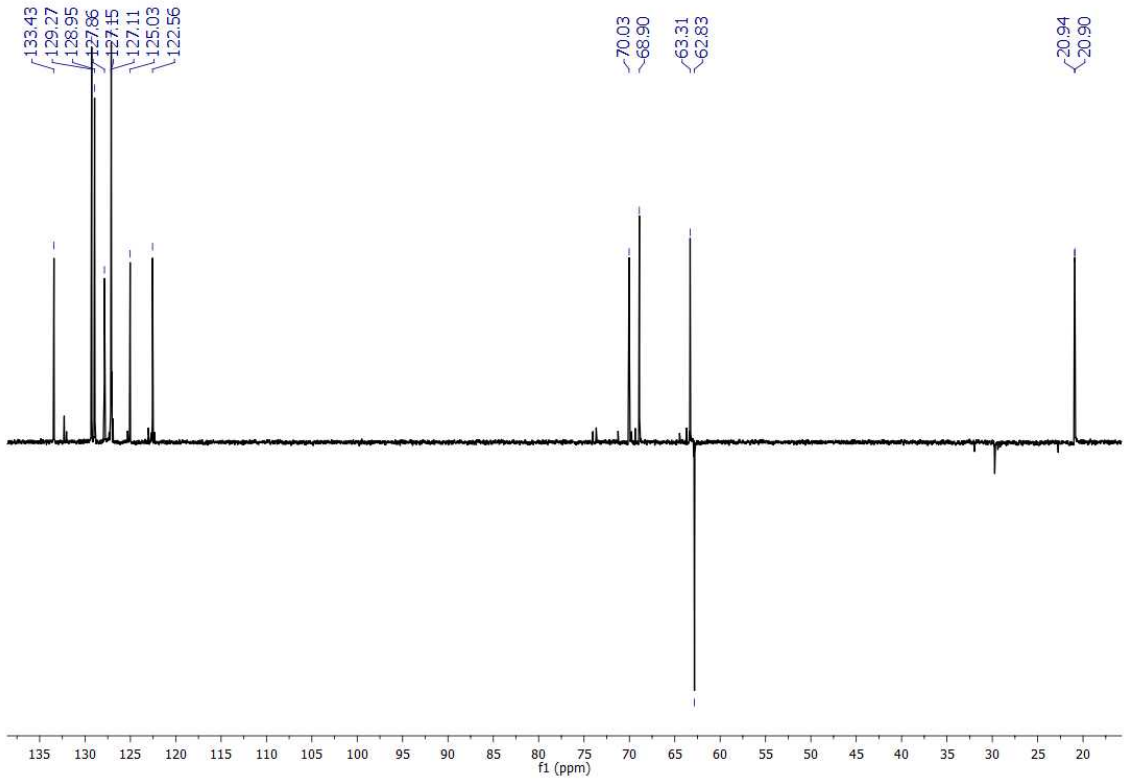
^{1}H NMR of compound 4i



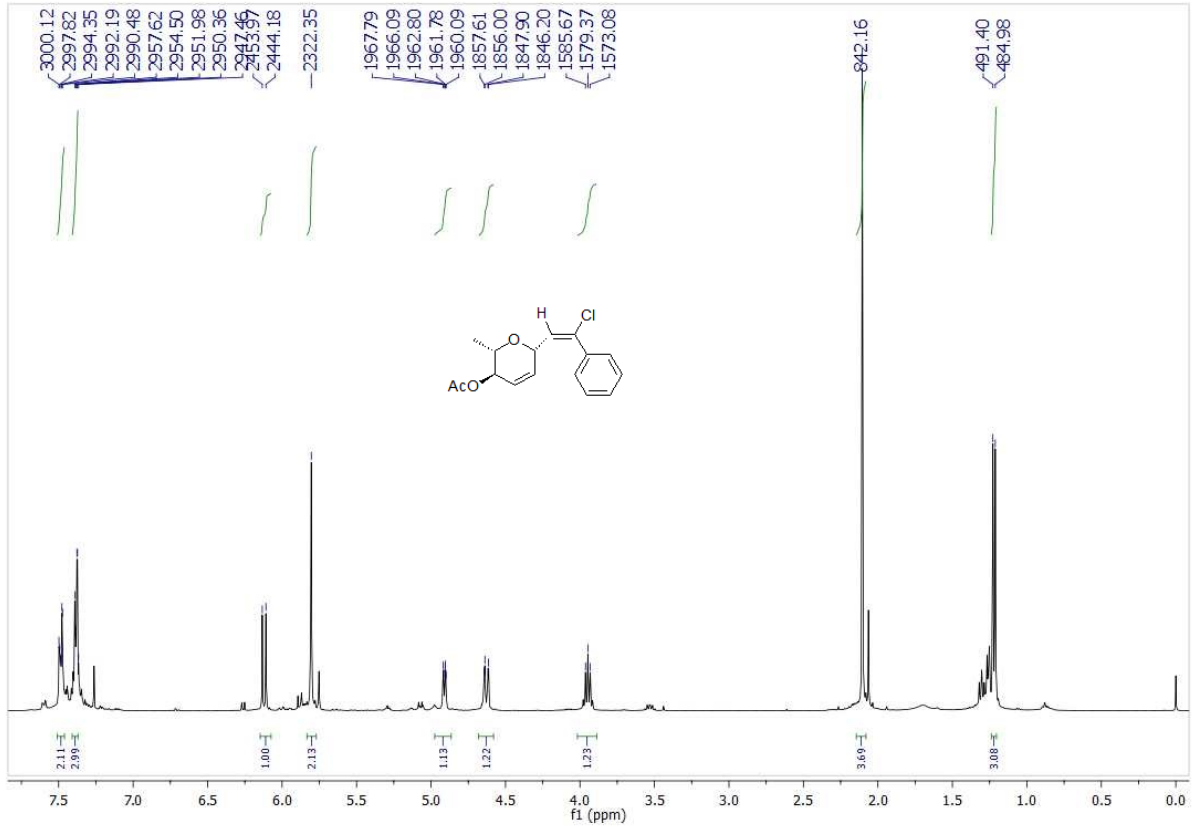
^{13}C NMR of compound 4i



DEPT of compound 4i



^{1}H NMR of compound 4j



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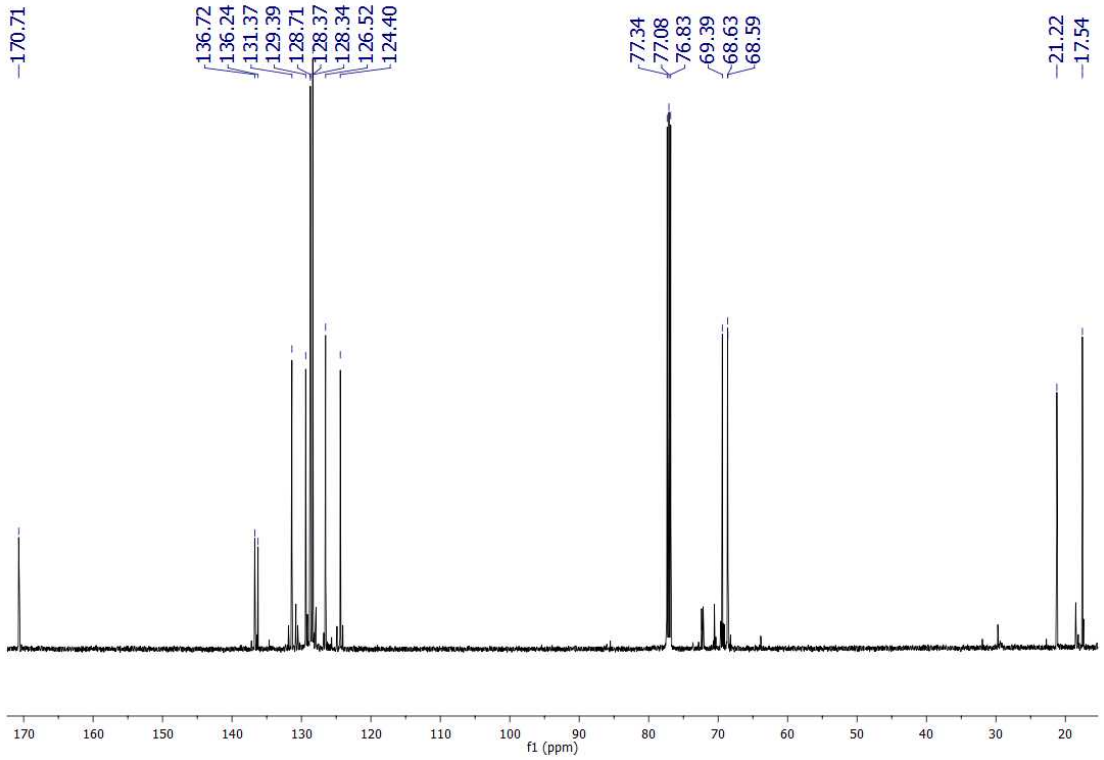
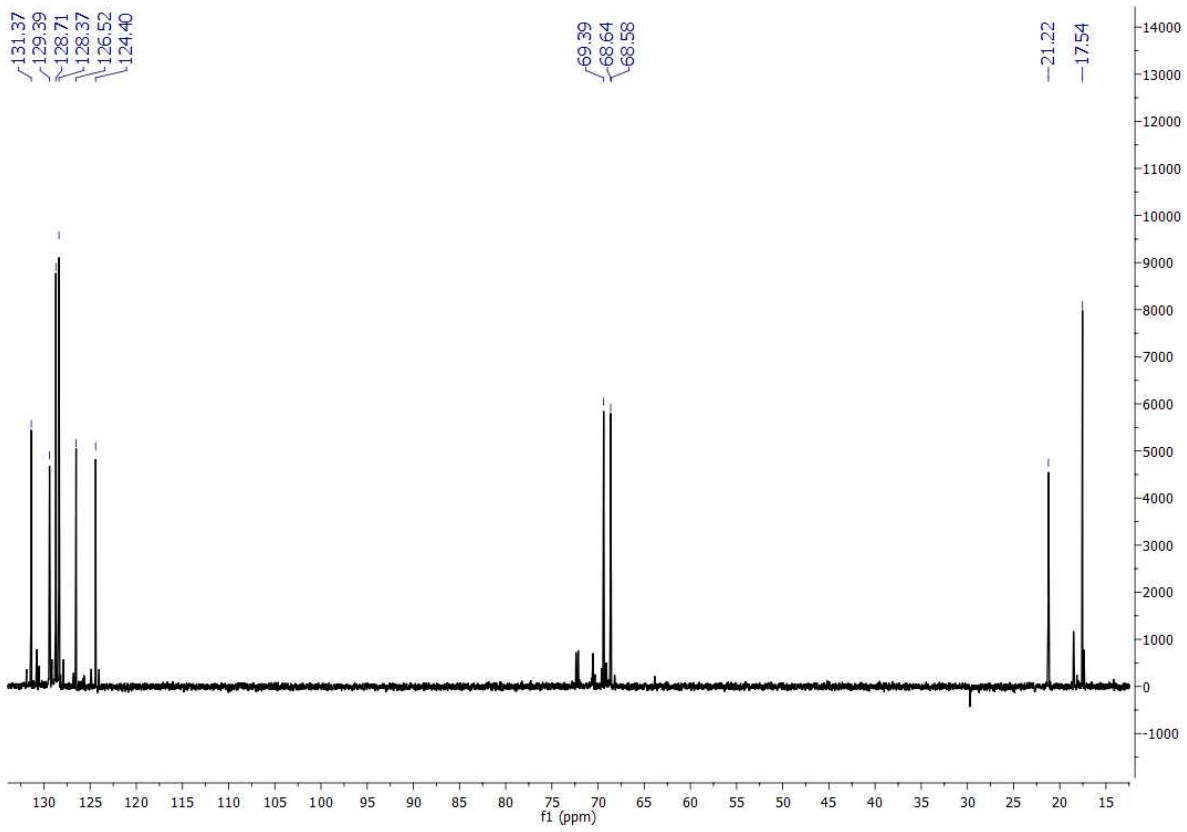
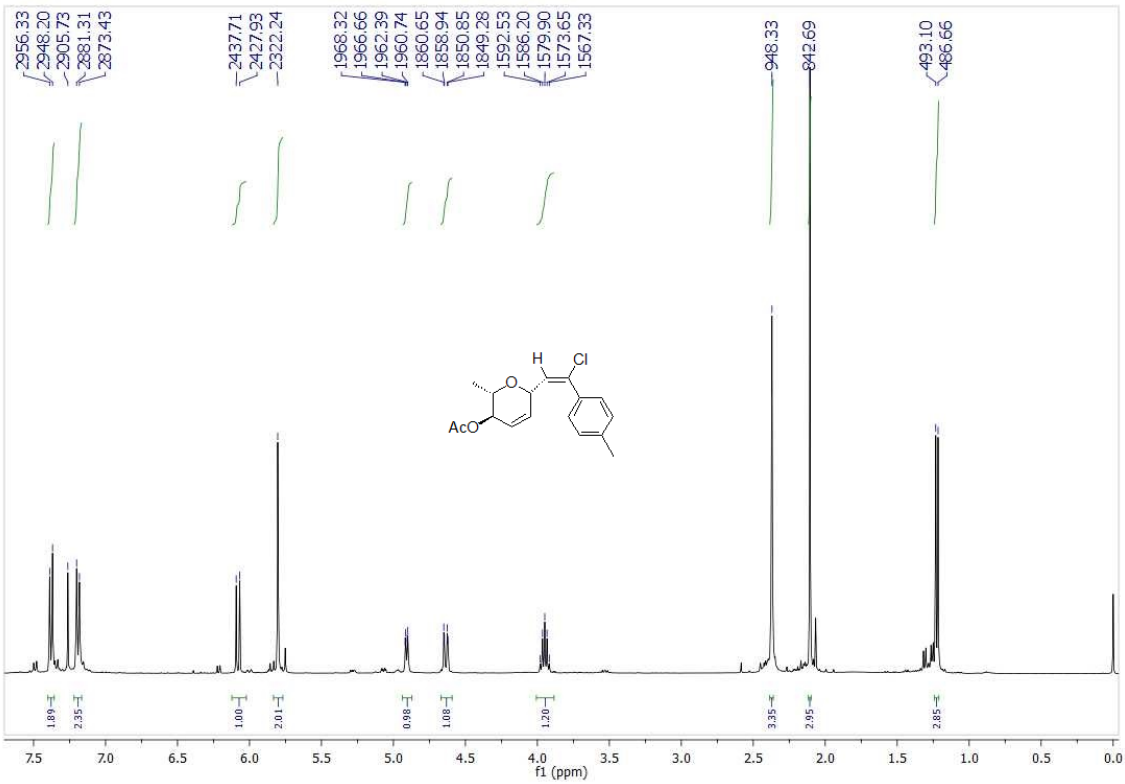


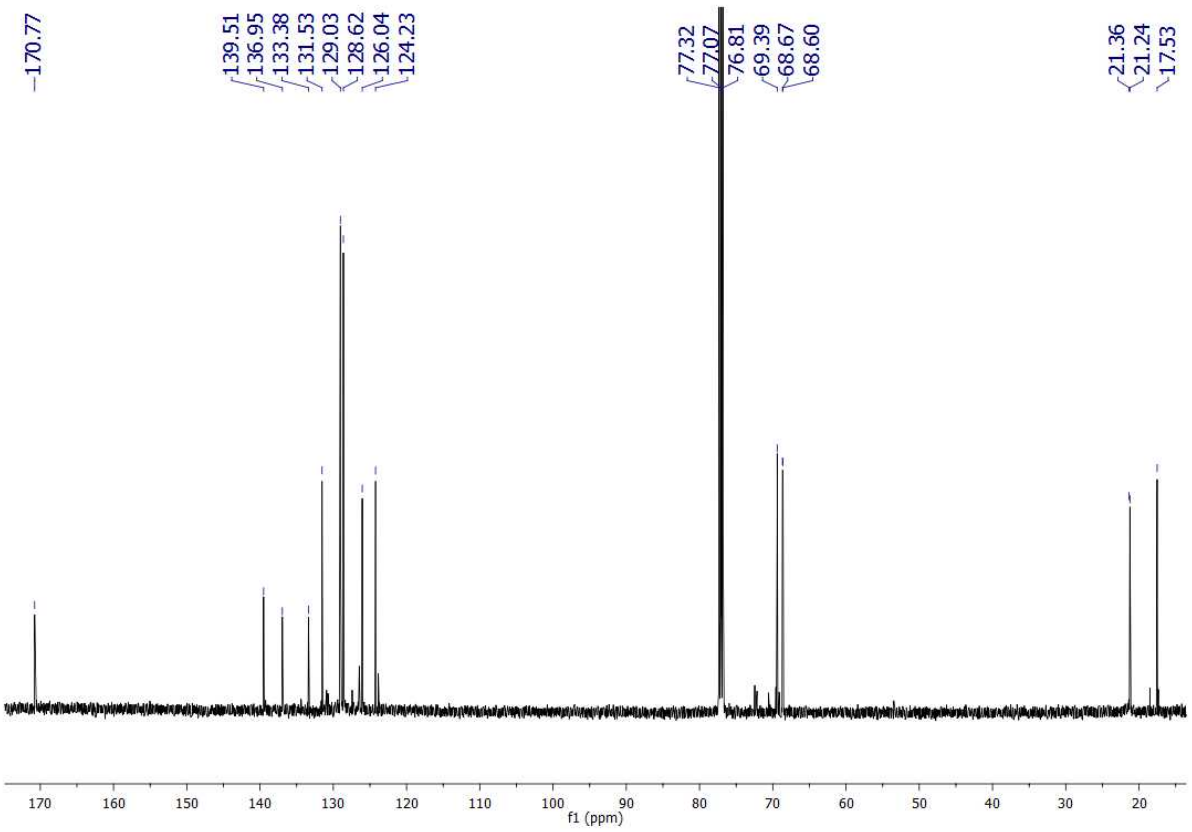
DEPT of compound 4j



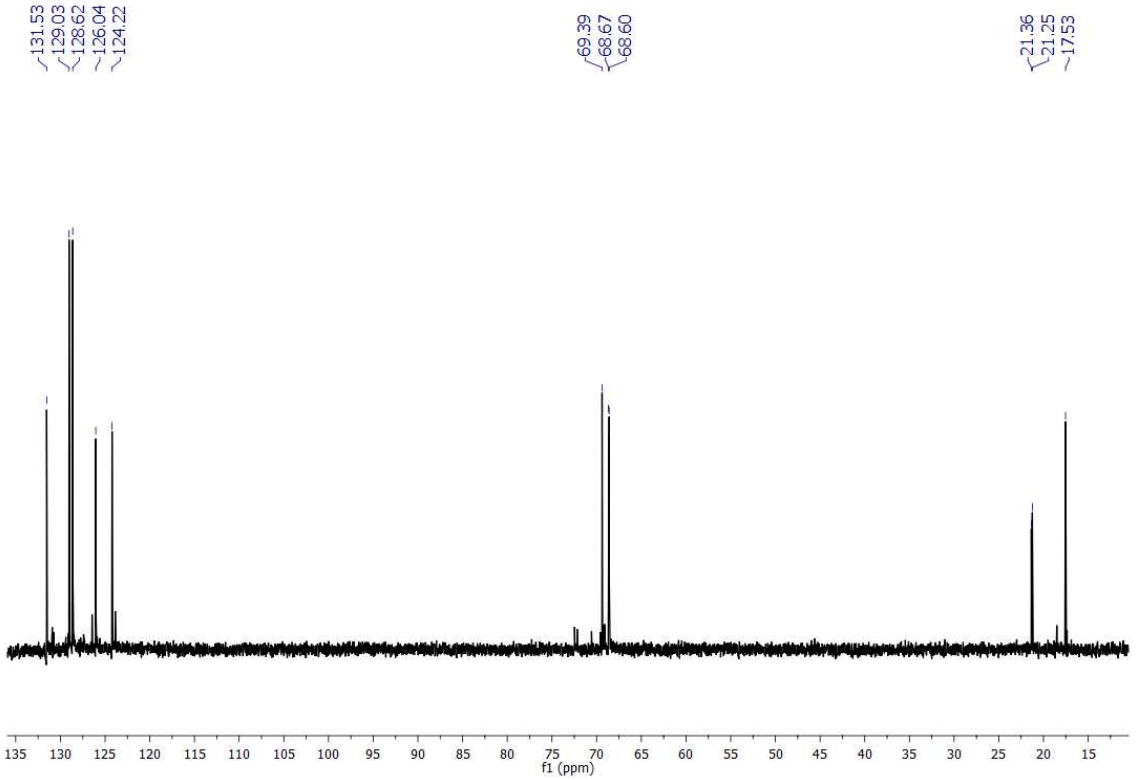
^{1}H NMR of compound 4k



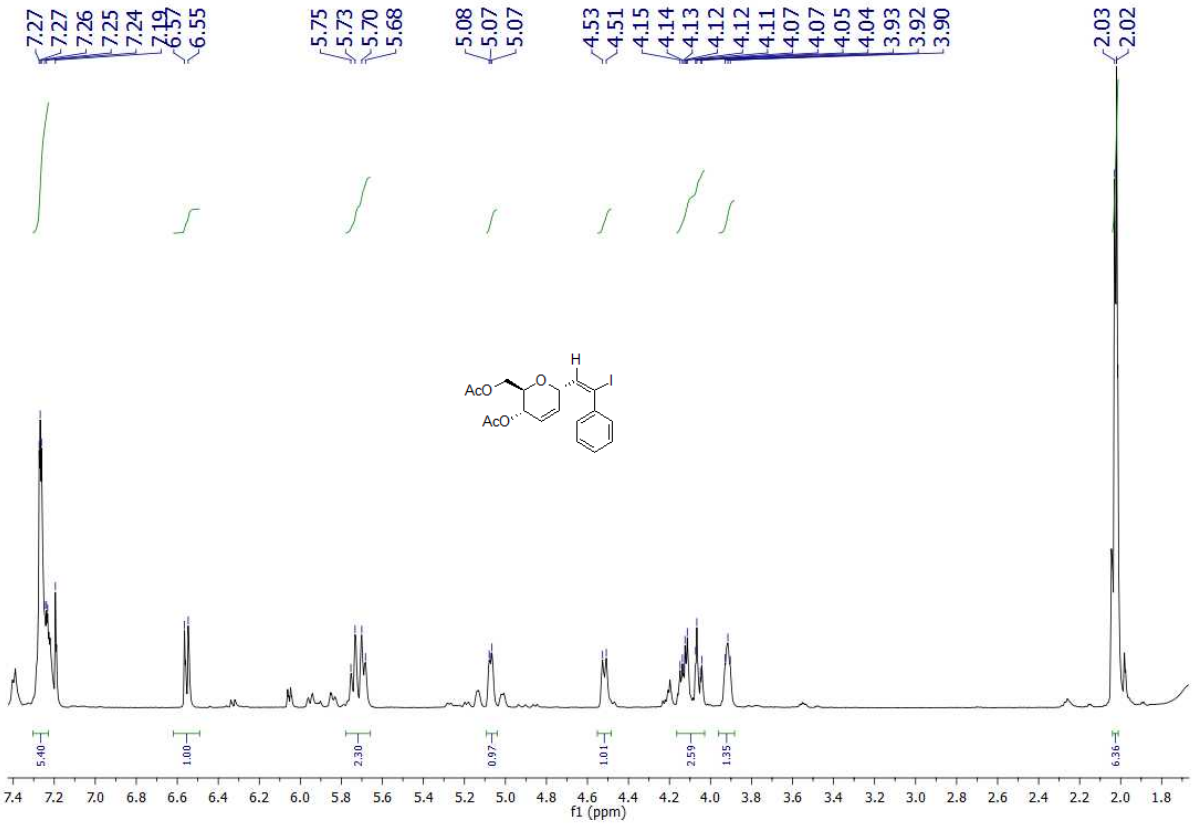
^{13}C NMR of compound 4k



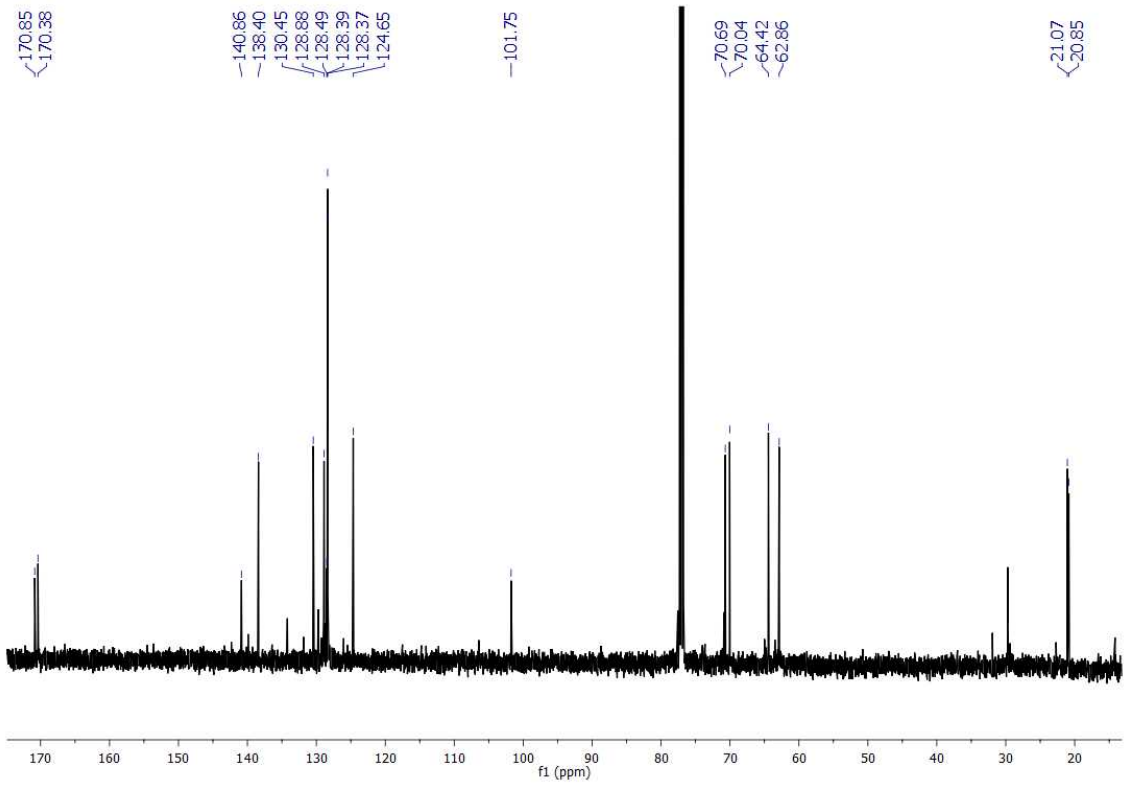
DEPT of compound 4k



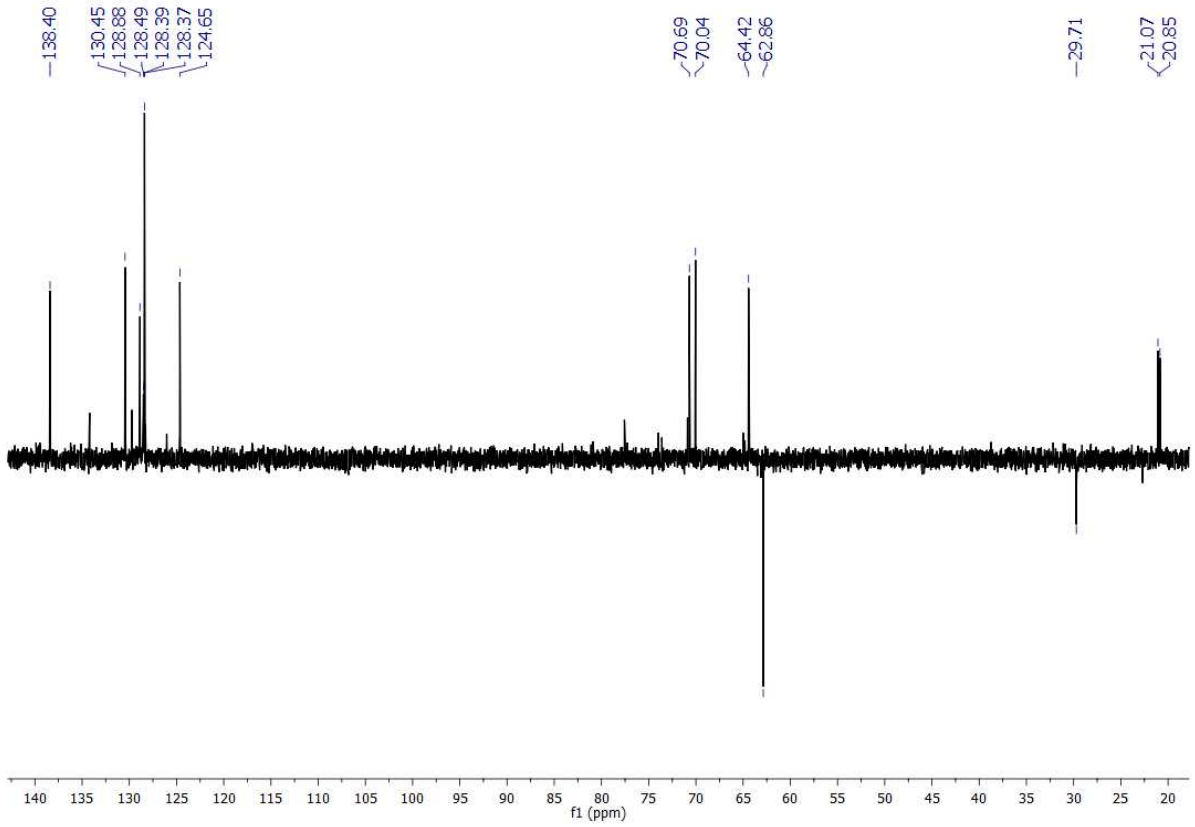
^{1}H NMR of compound 5a



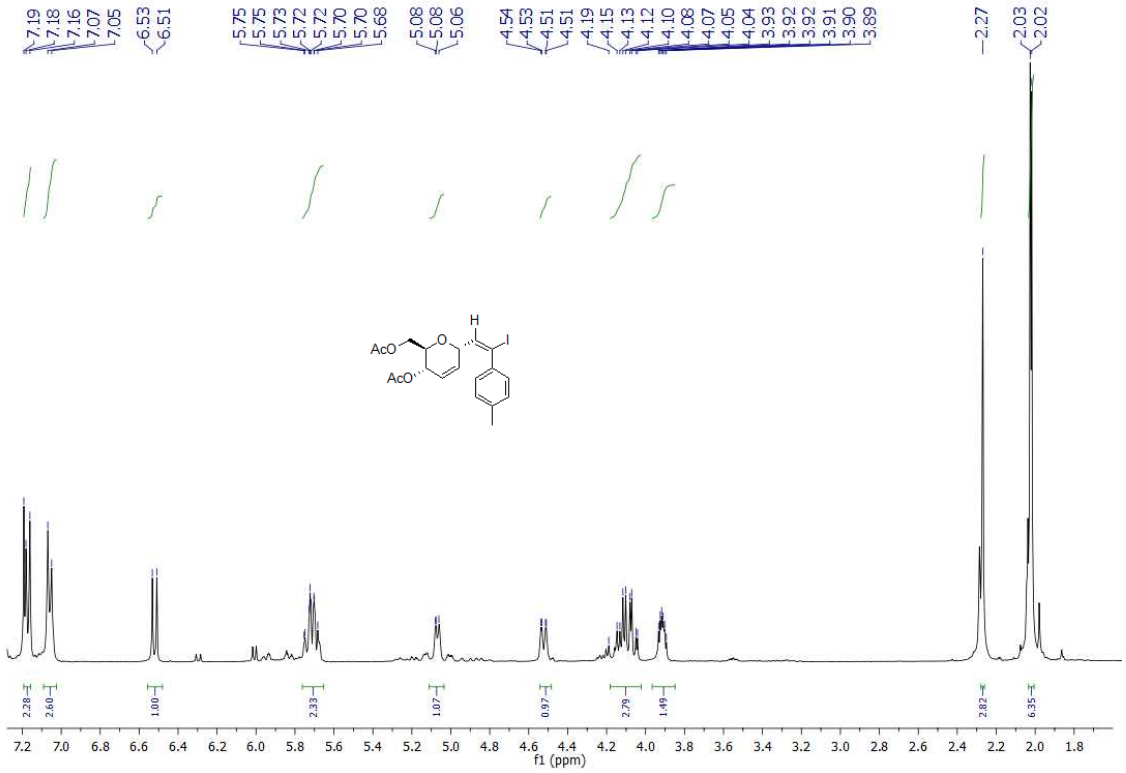
^{13}C NMR of compound 5a



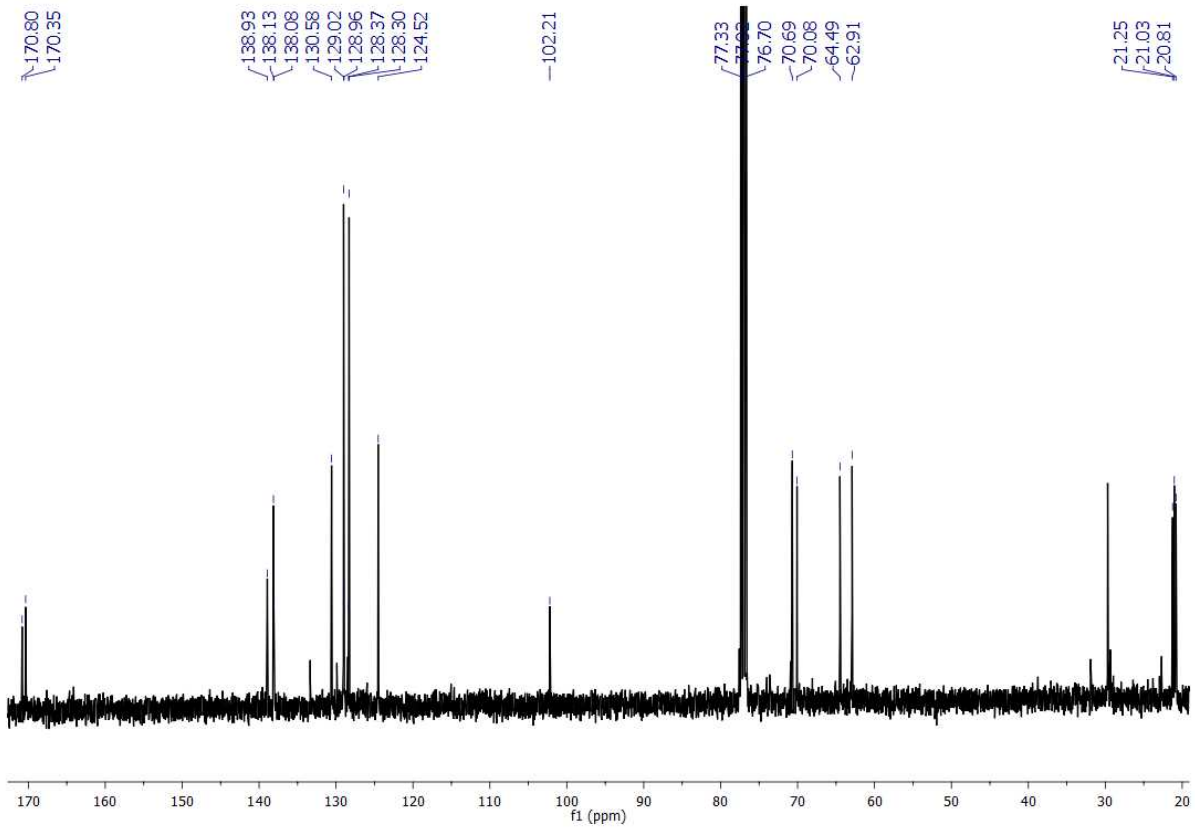
DEPT of compound 5a



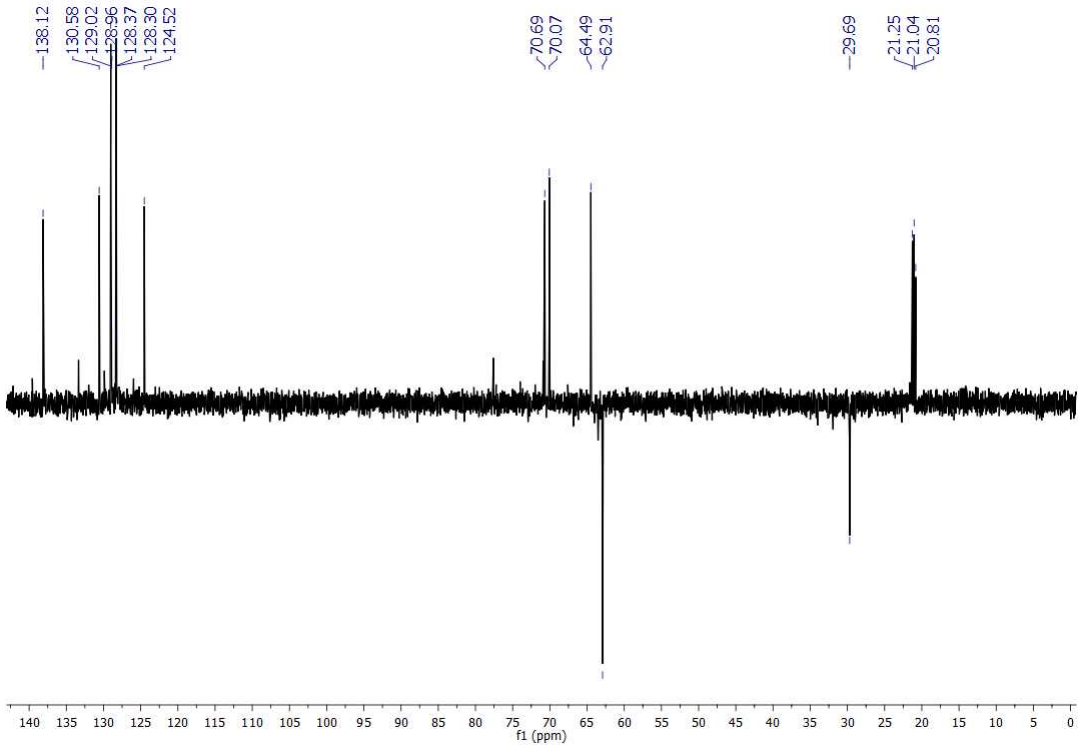
^{1}H NMR of compound 5b



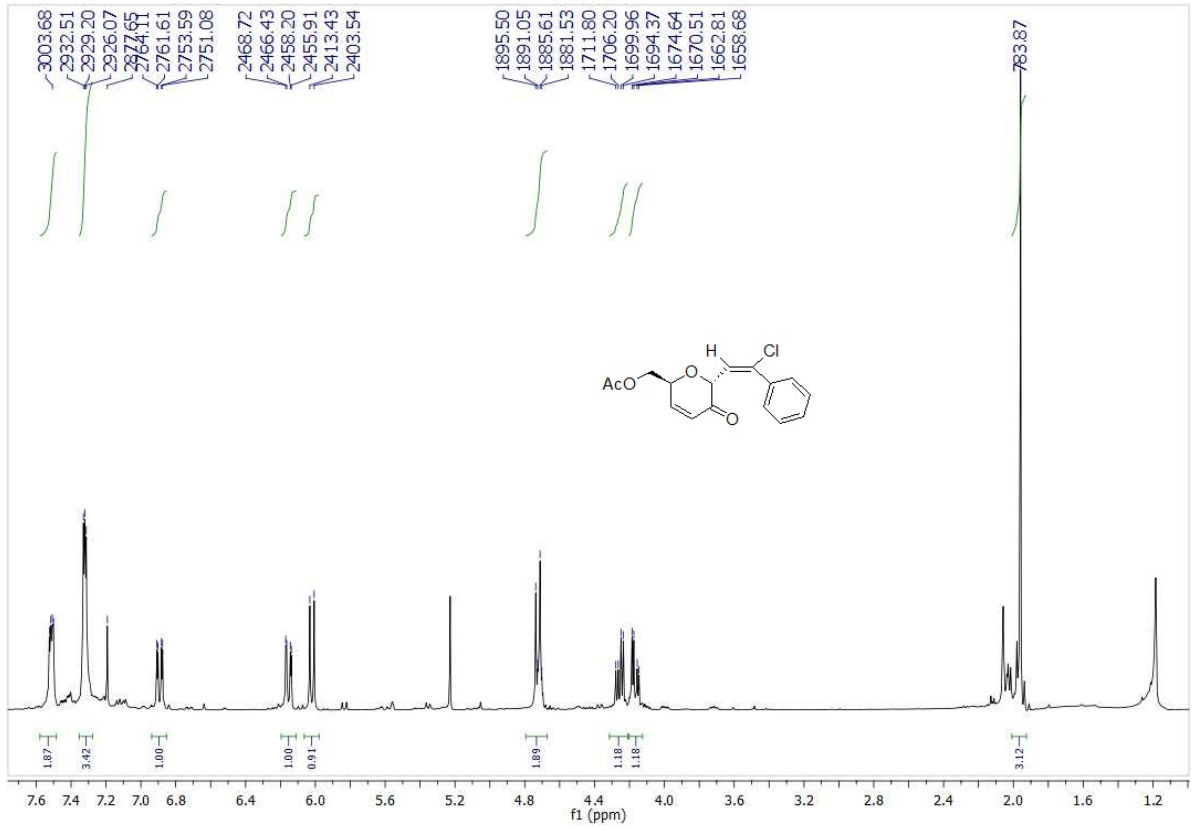
^{13}C NMR of compound 5b



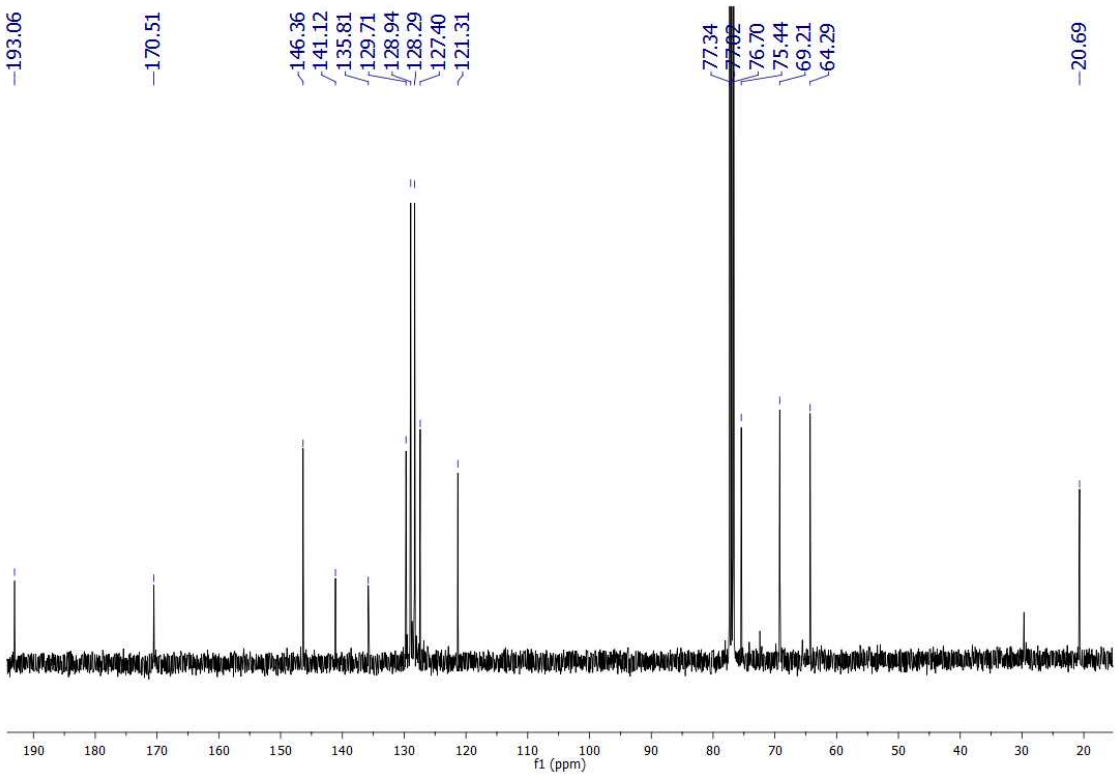
DEPT of compound 5b



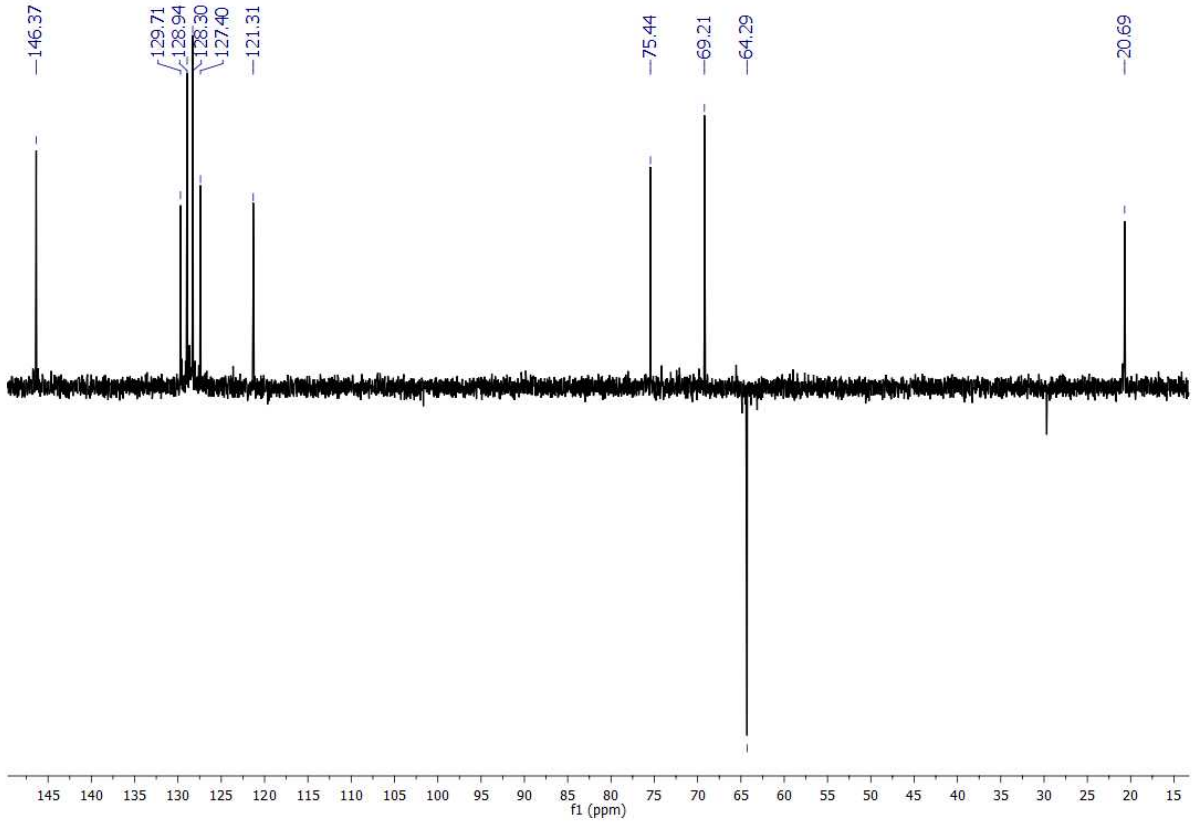
^{1}H NMR of compound 6a



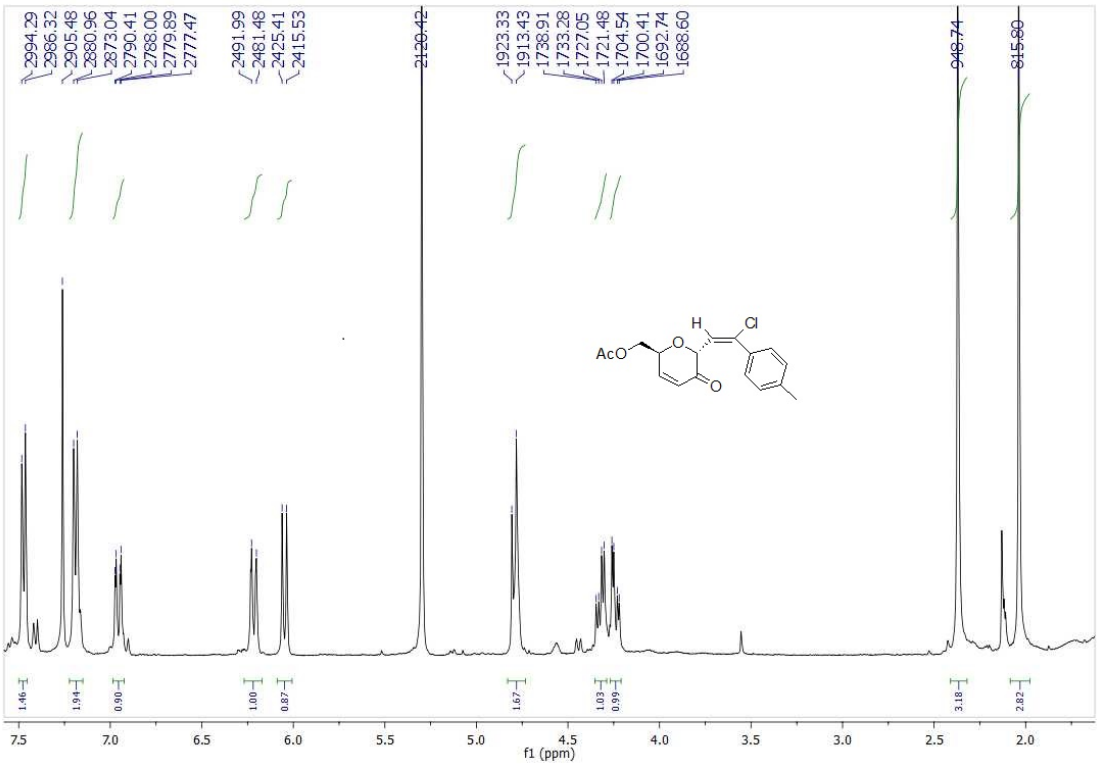
^{13}C NMR of compound 6a



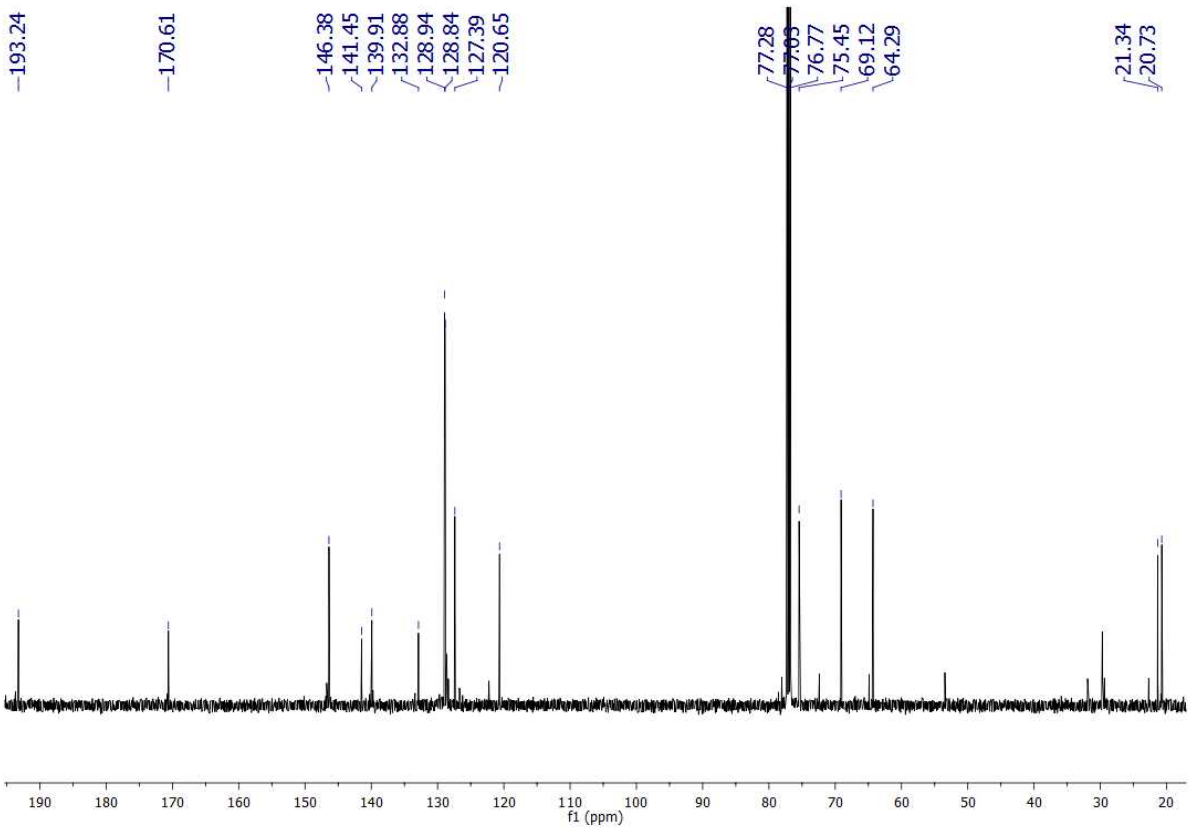
DEPT of compound 6a



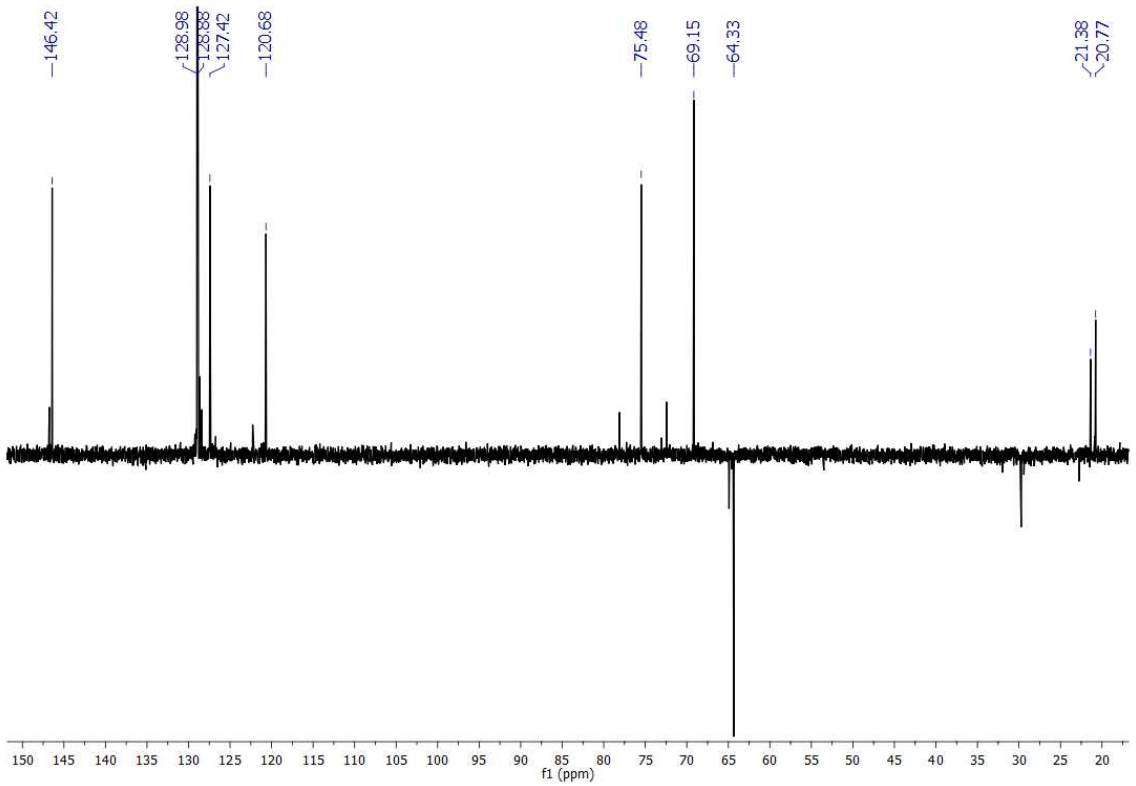
^{1}H NMR of compound 6b



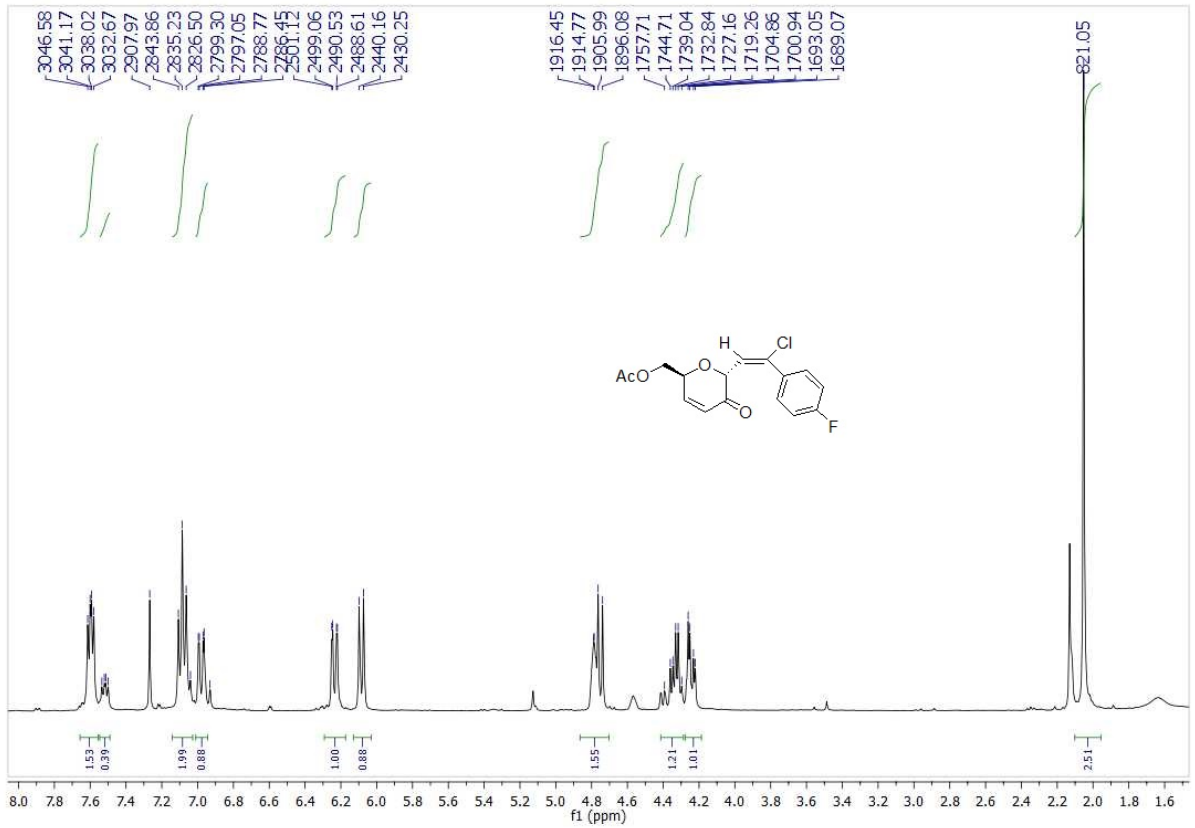
^{13}C NMR of compound 6b



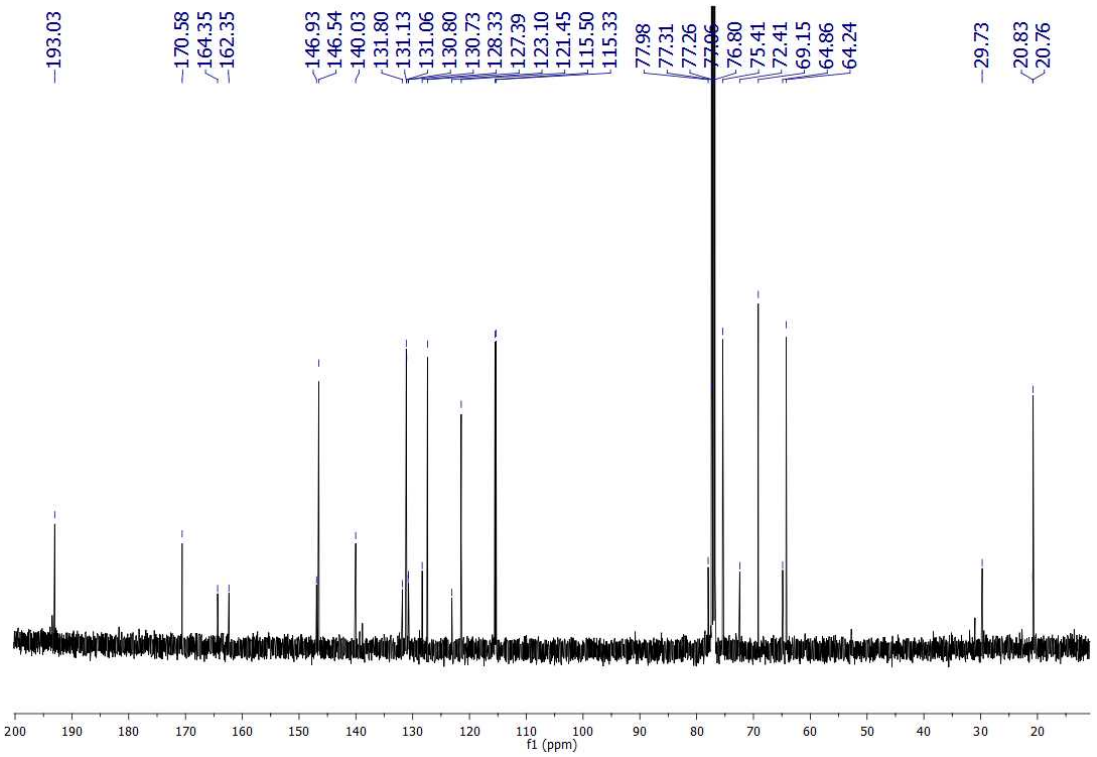
DEPT of compound 6b



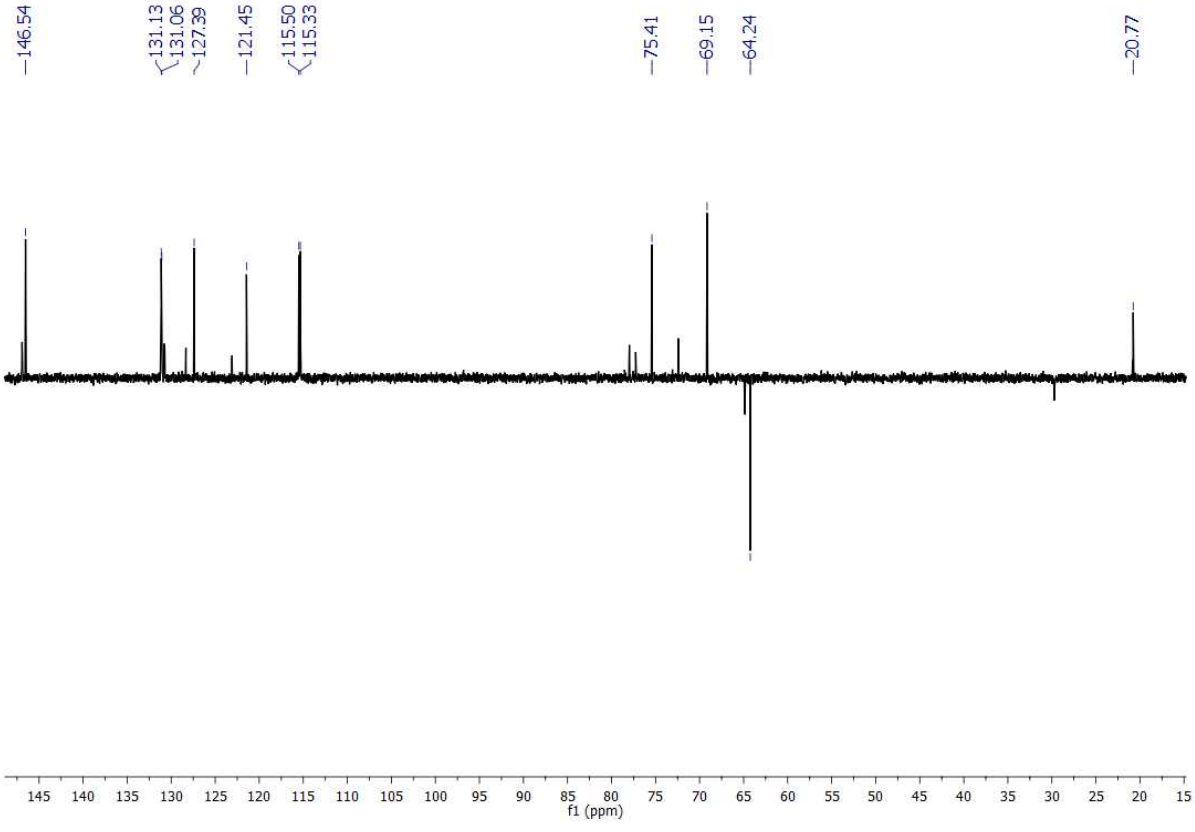
^{1}H NMR of compound 6c



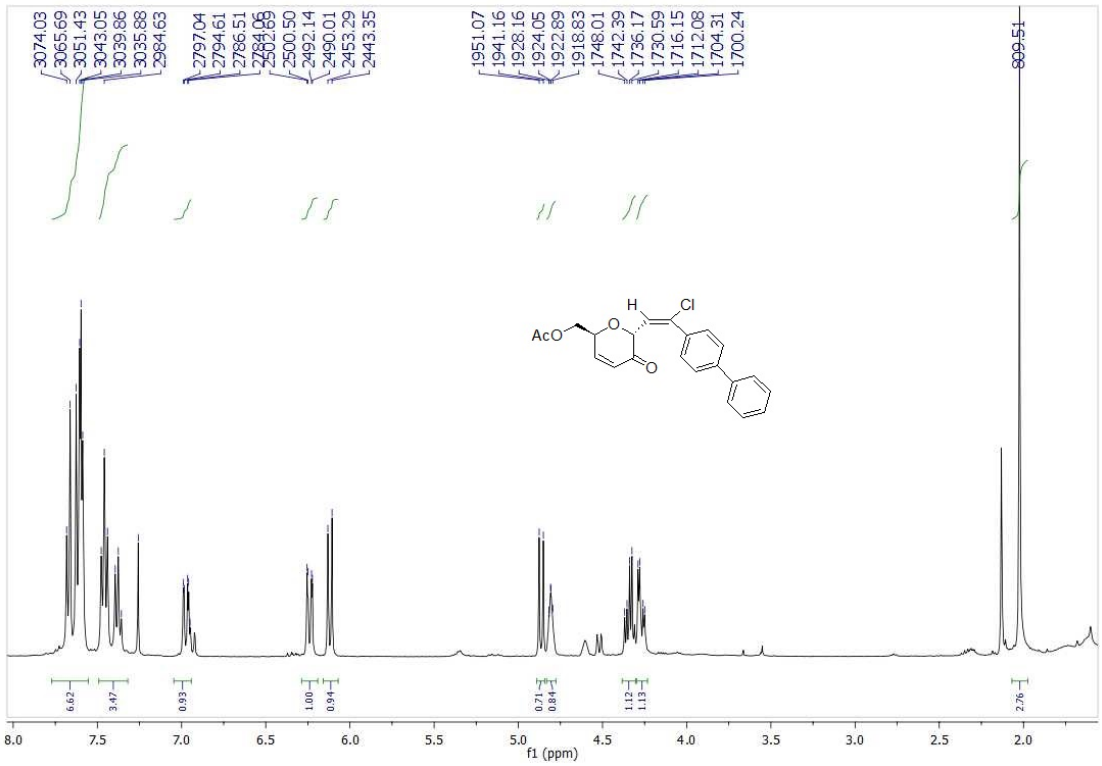
^{13}C NMR of compound 6c



DEPT of compound 6c



^{1}H NMR of compound 6d



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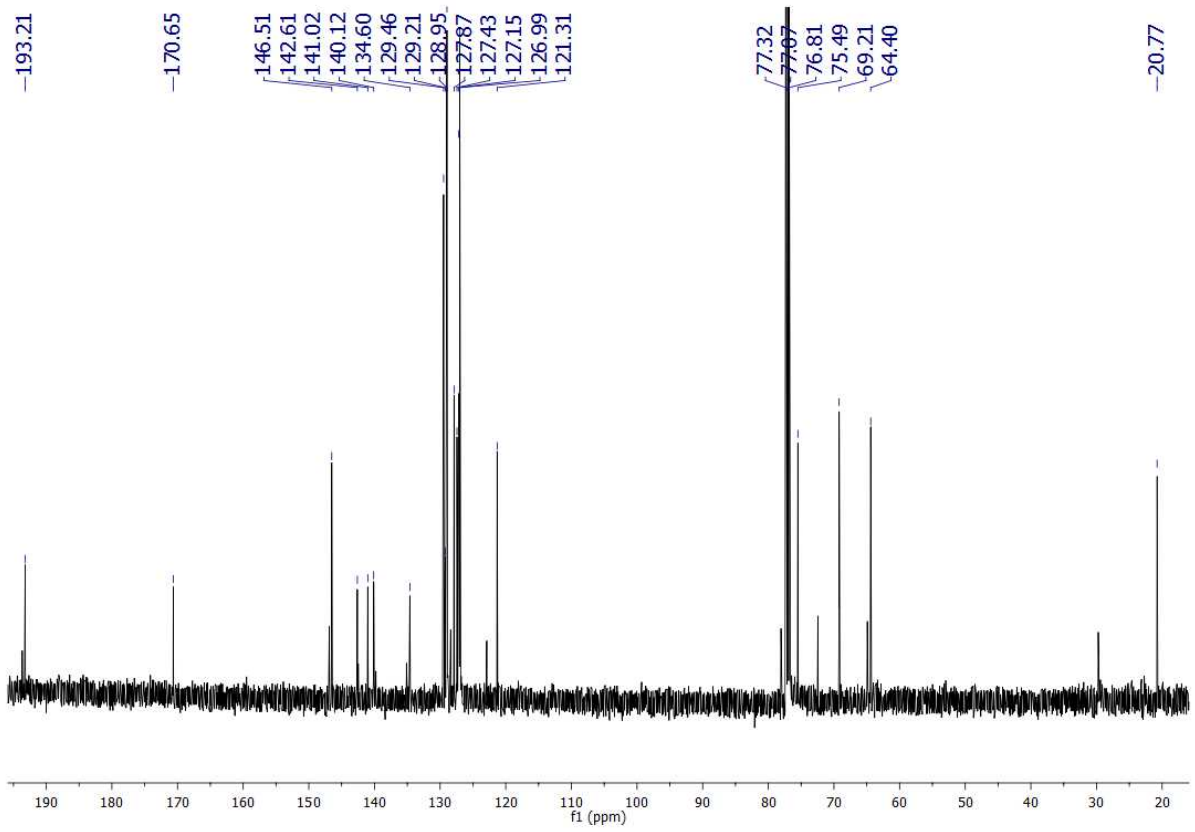
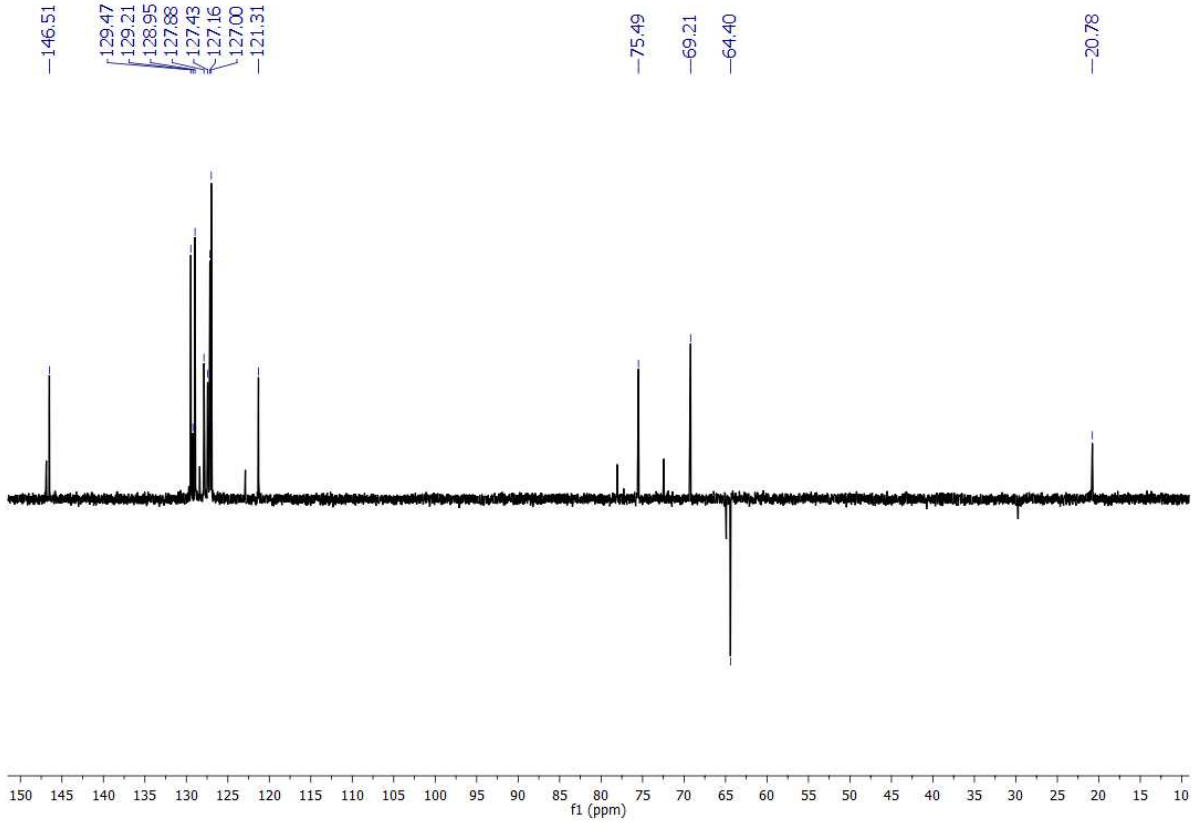
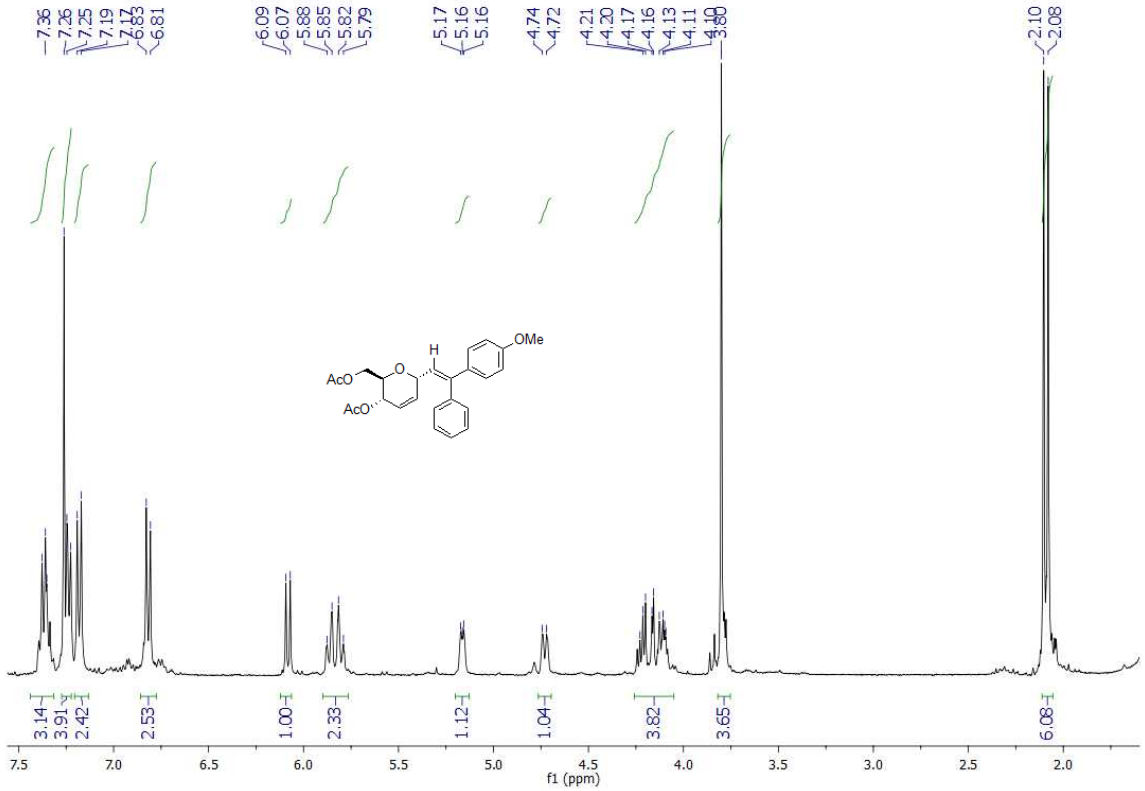


DEPT of compound 6d



^{1}H NMR of compound 7a



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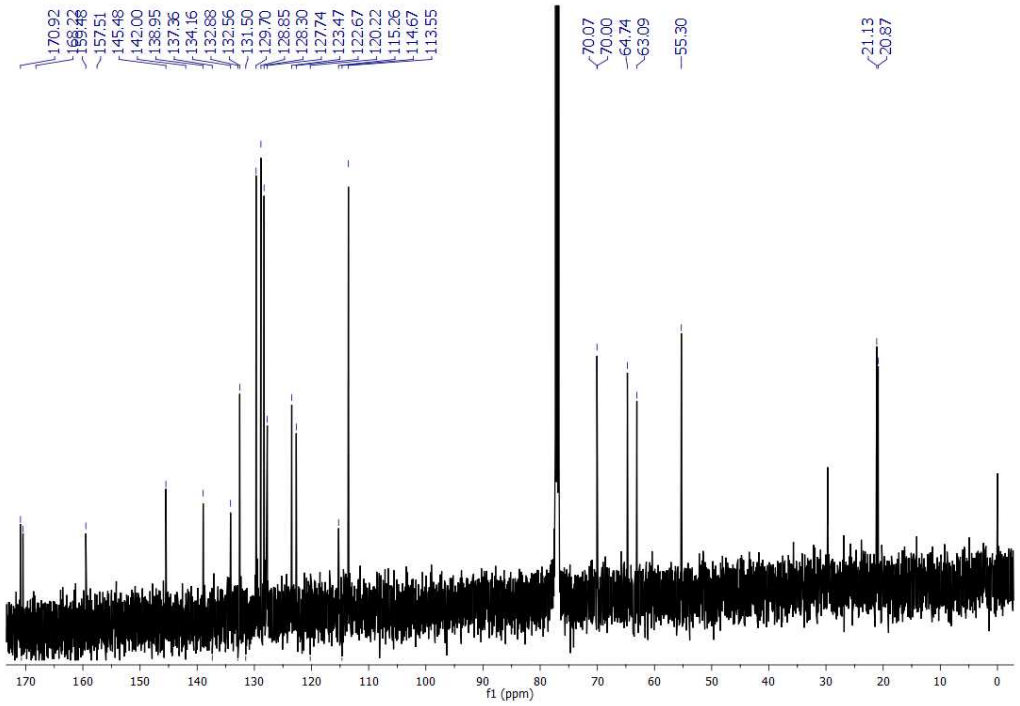
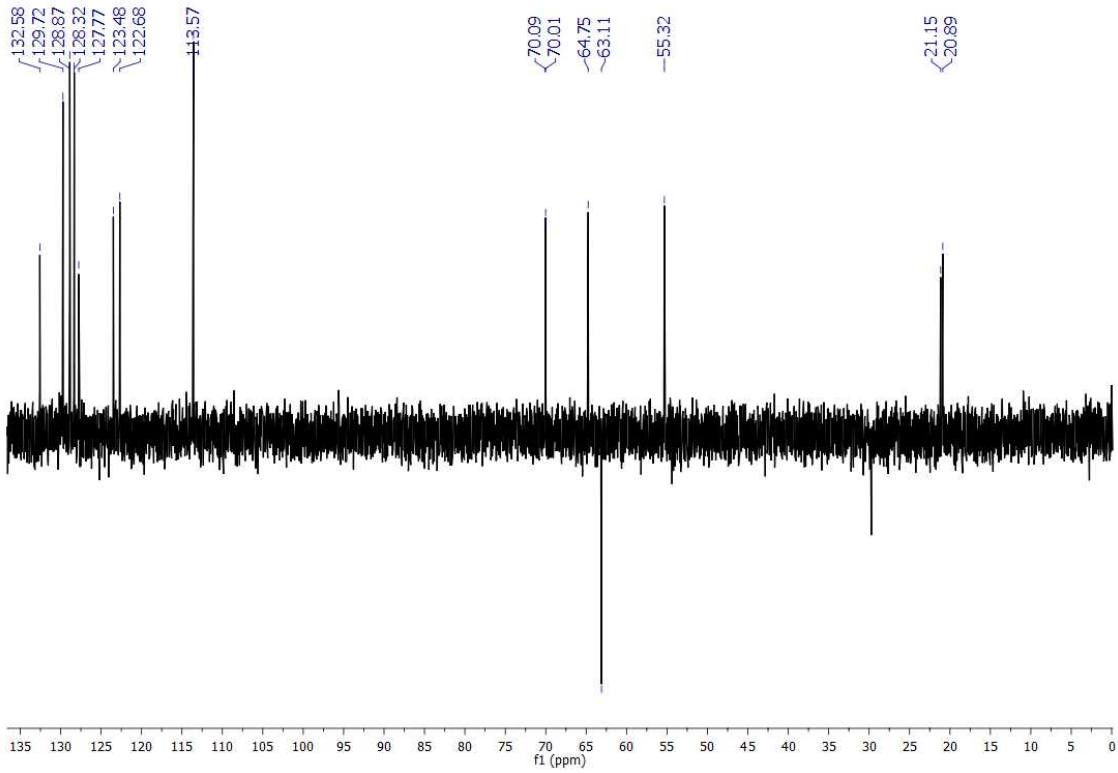
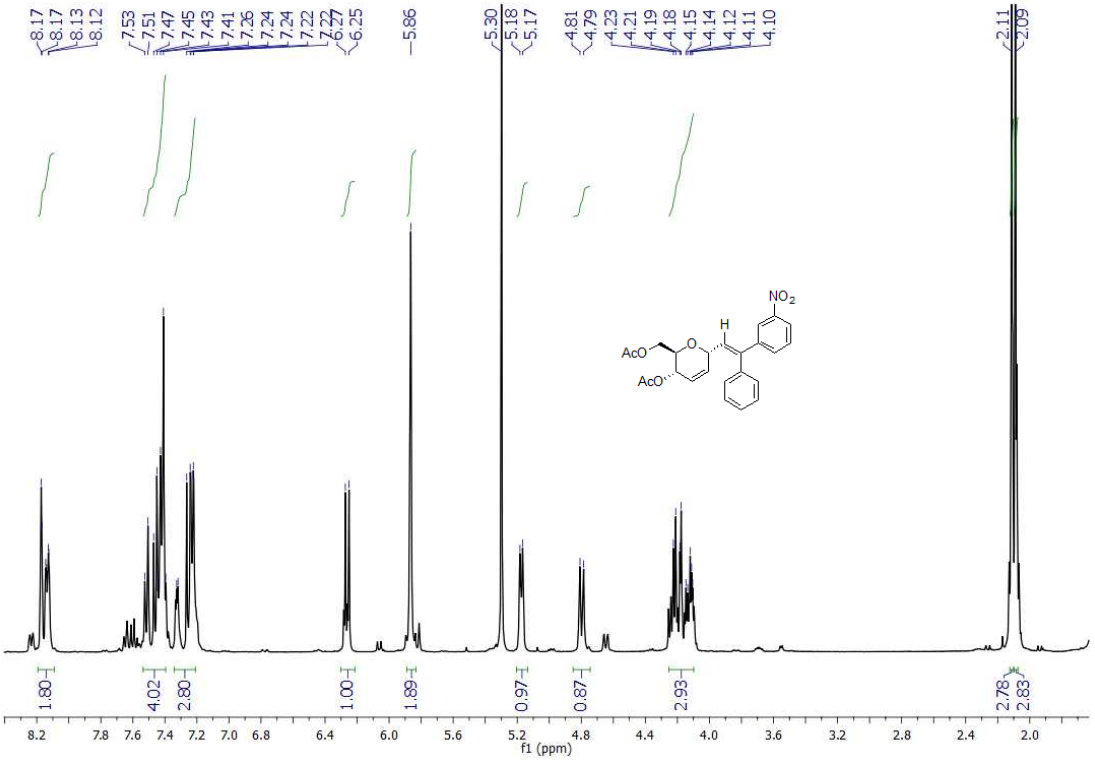


DEPT of compound 7a



^{1}H NMR of compound 7b



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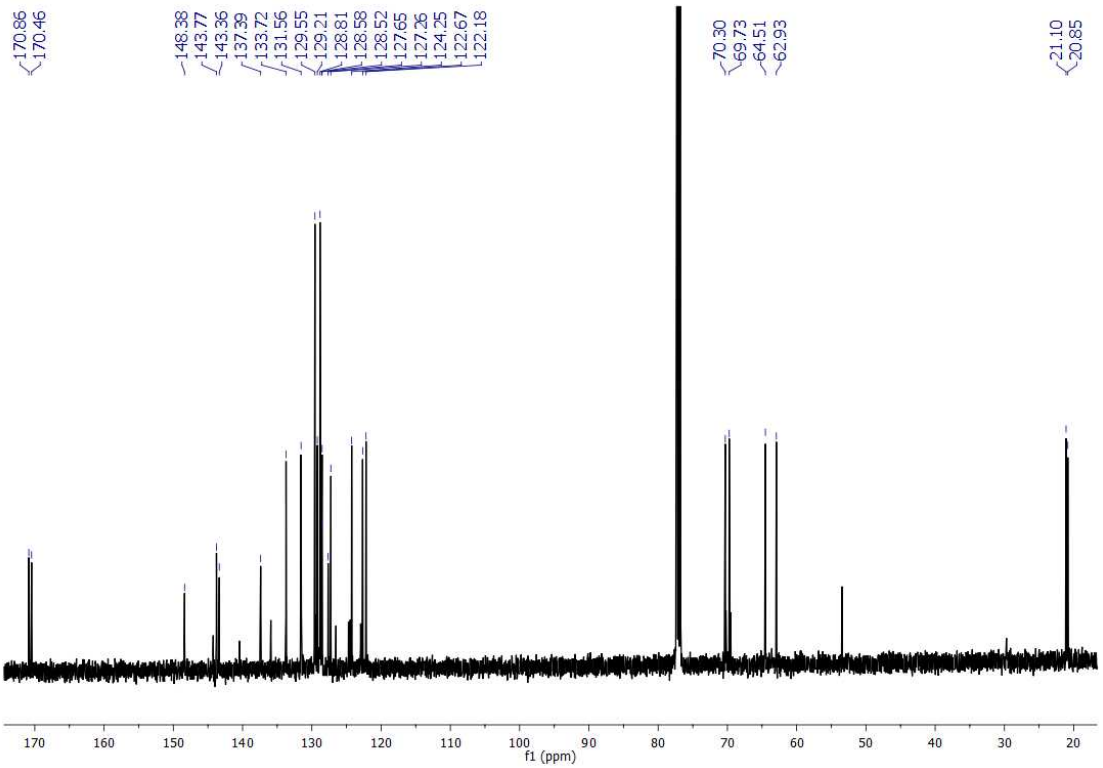
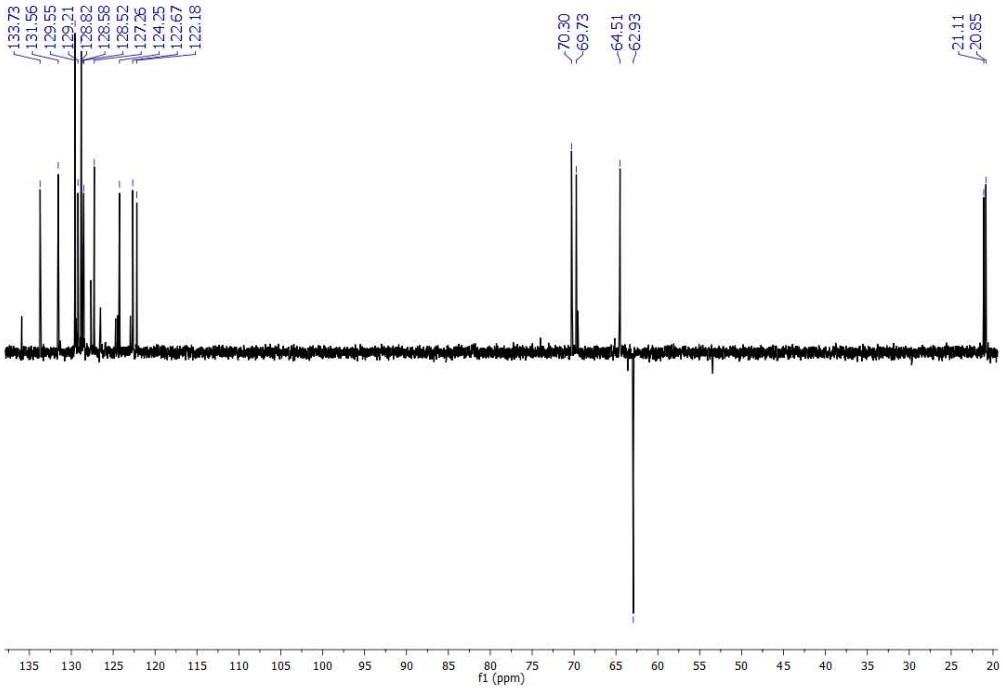
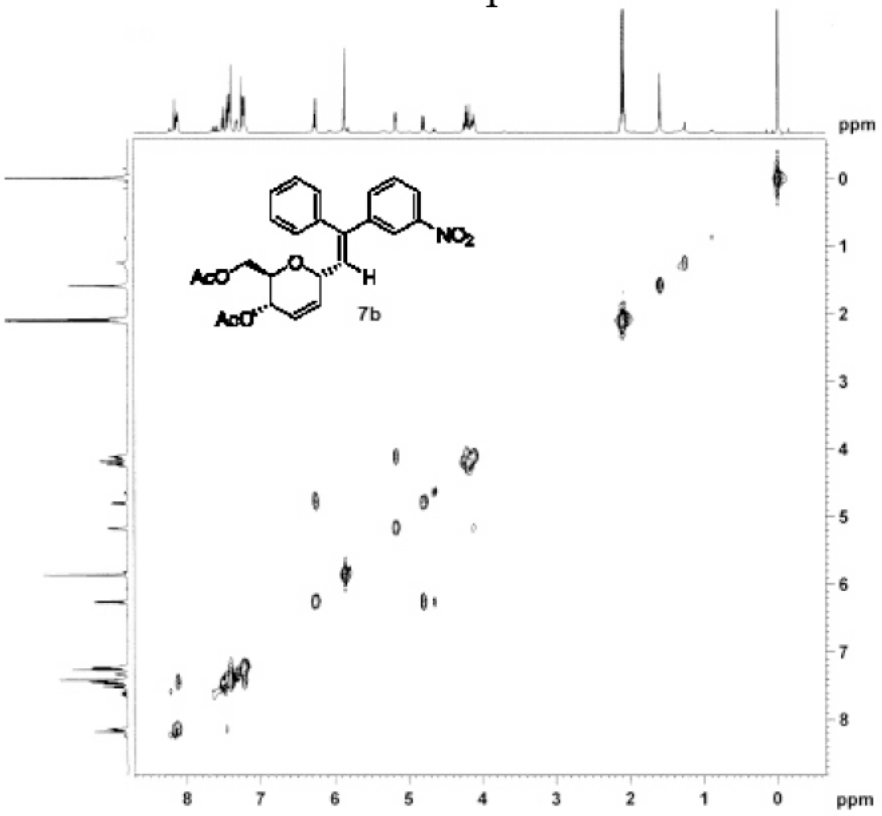


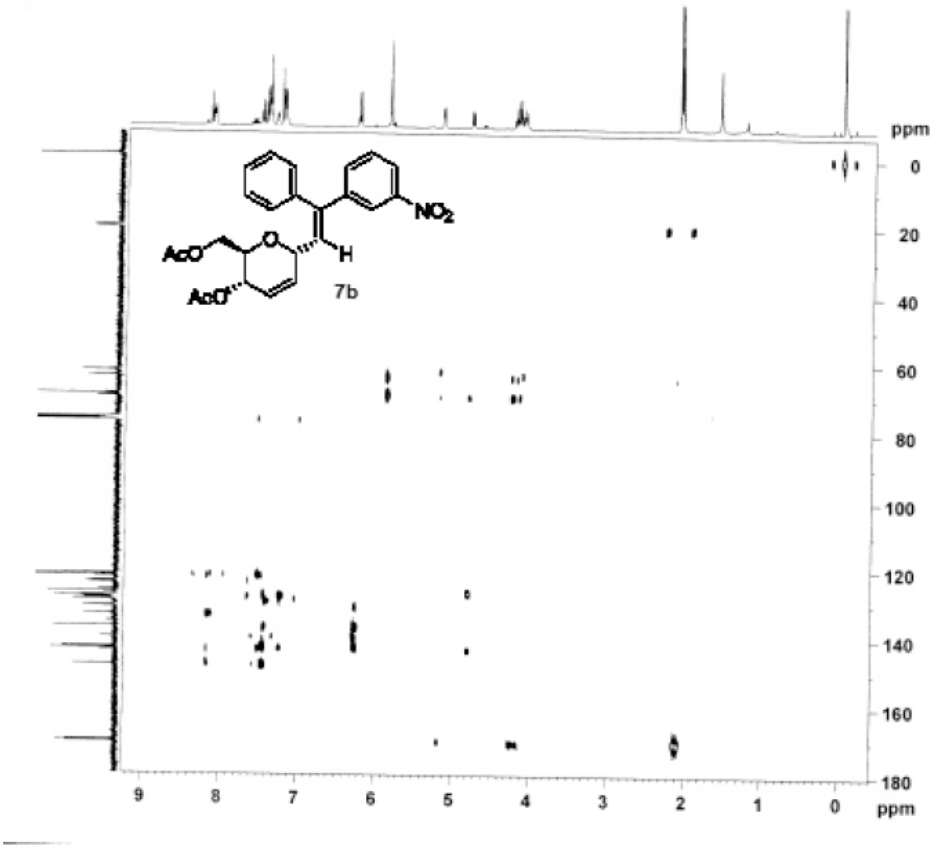
DEPT of compound 7b



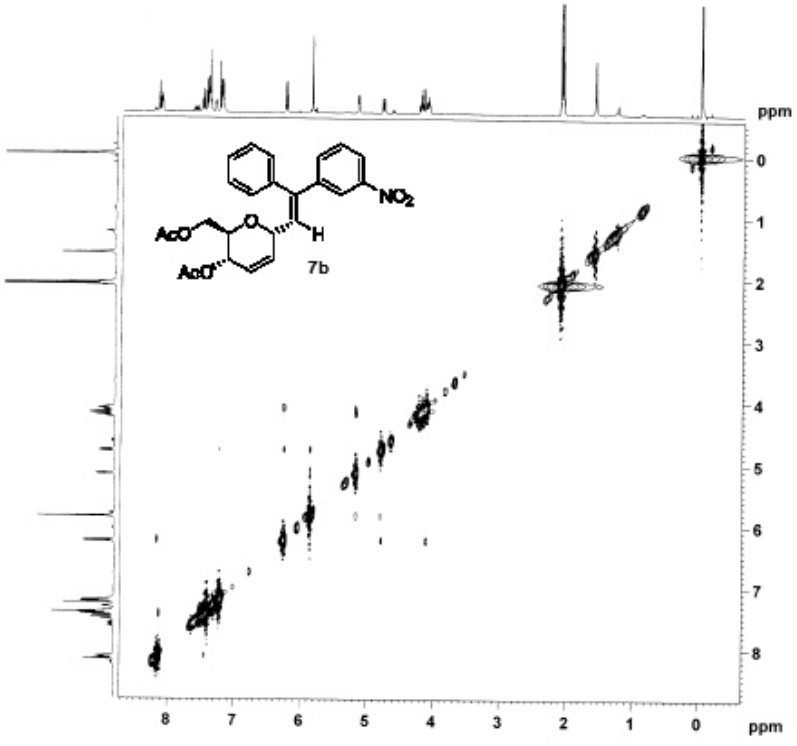
1H-1H COSY of compound 7b



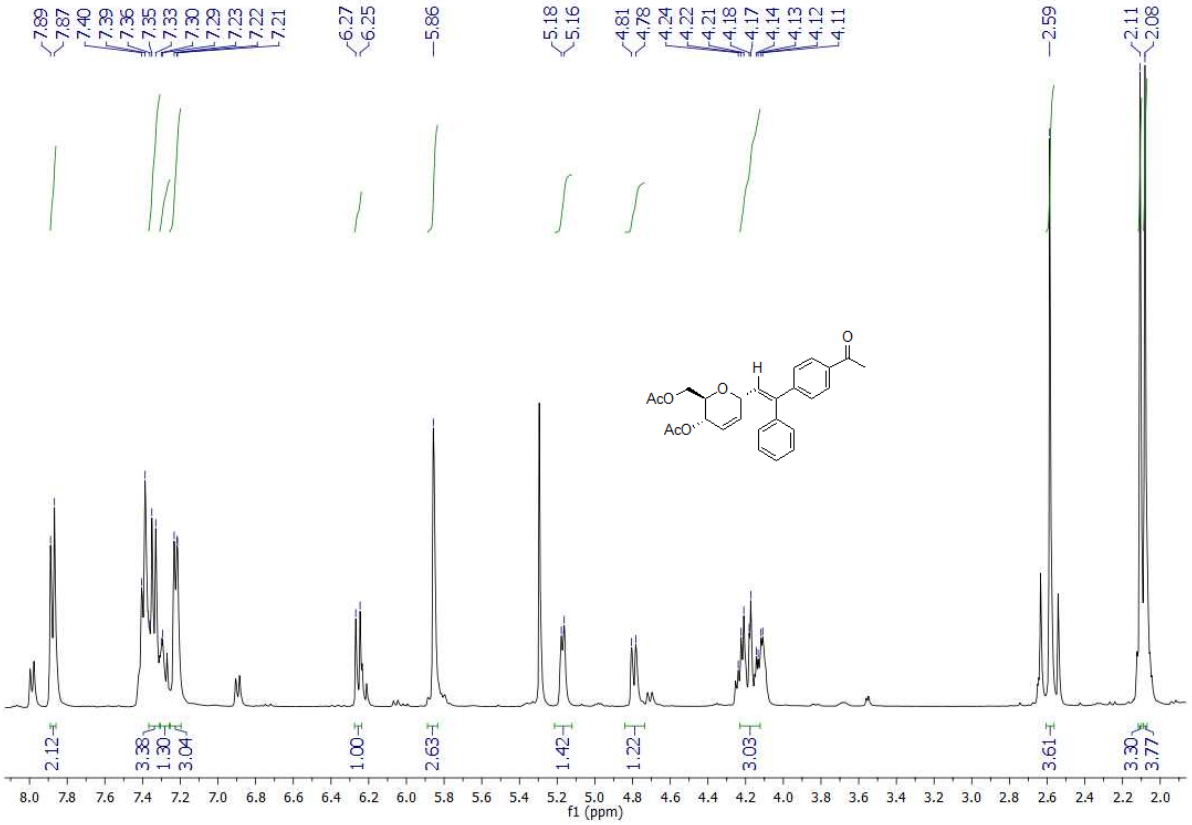
HMBC of compound 7b



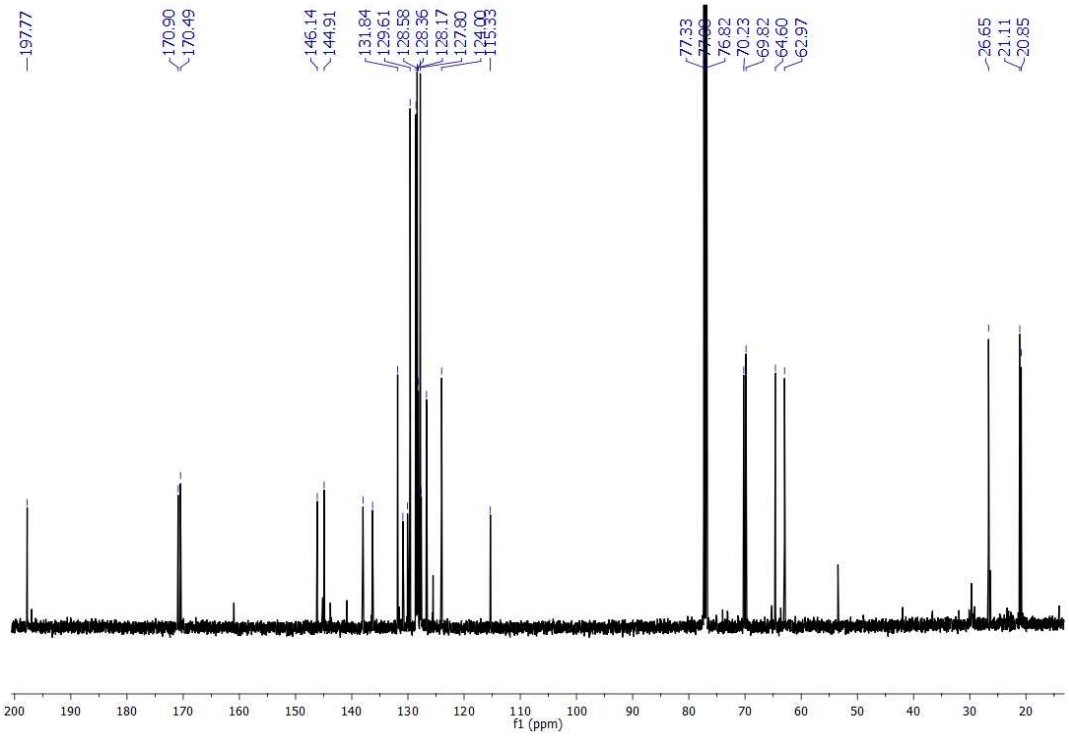
NOESY of compound 7b



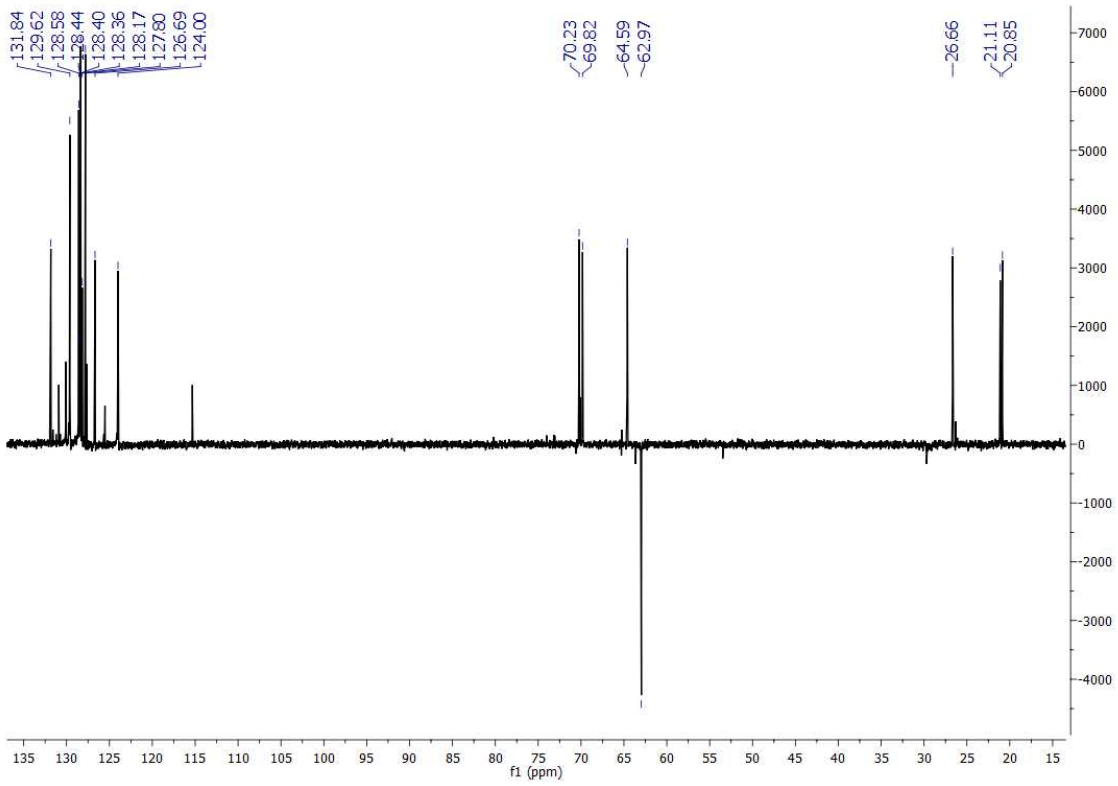
^{1}H NMR of compound 7c



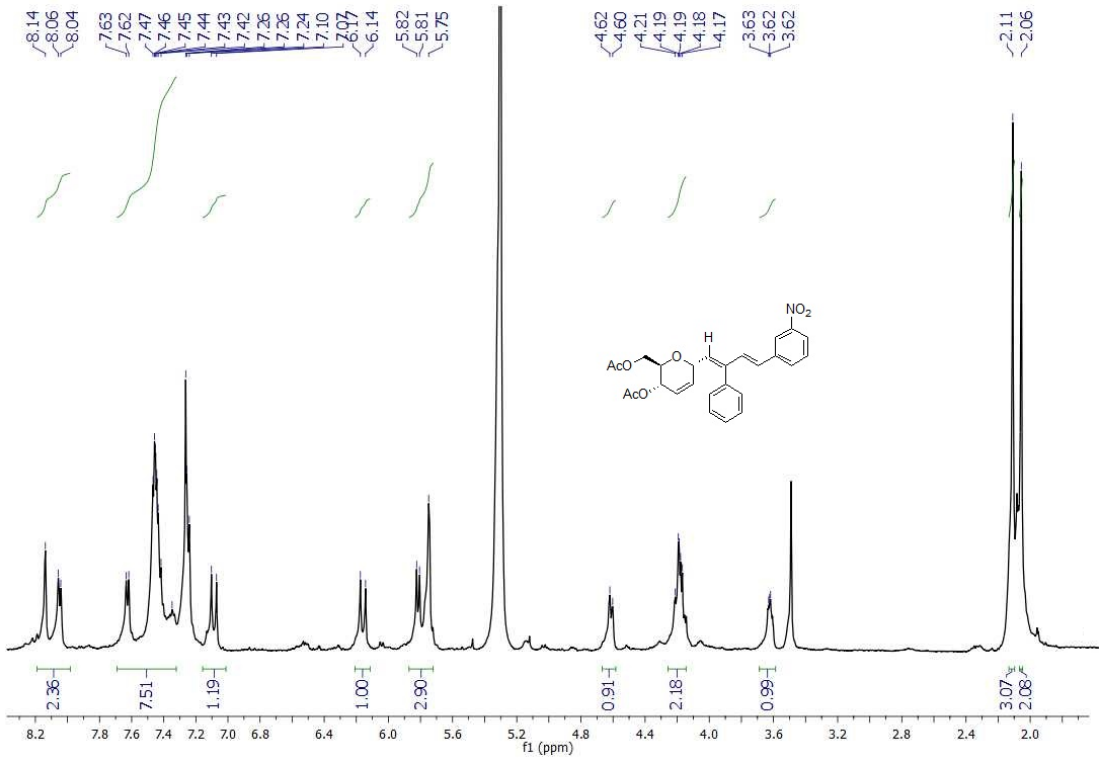
^{13}C NMR of compound 7c



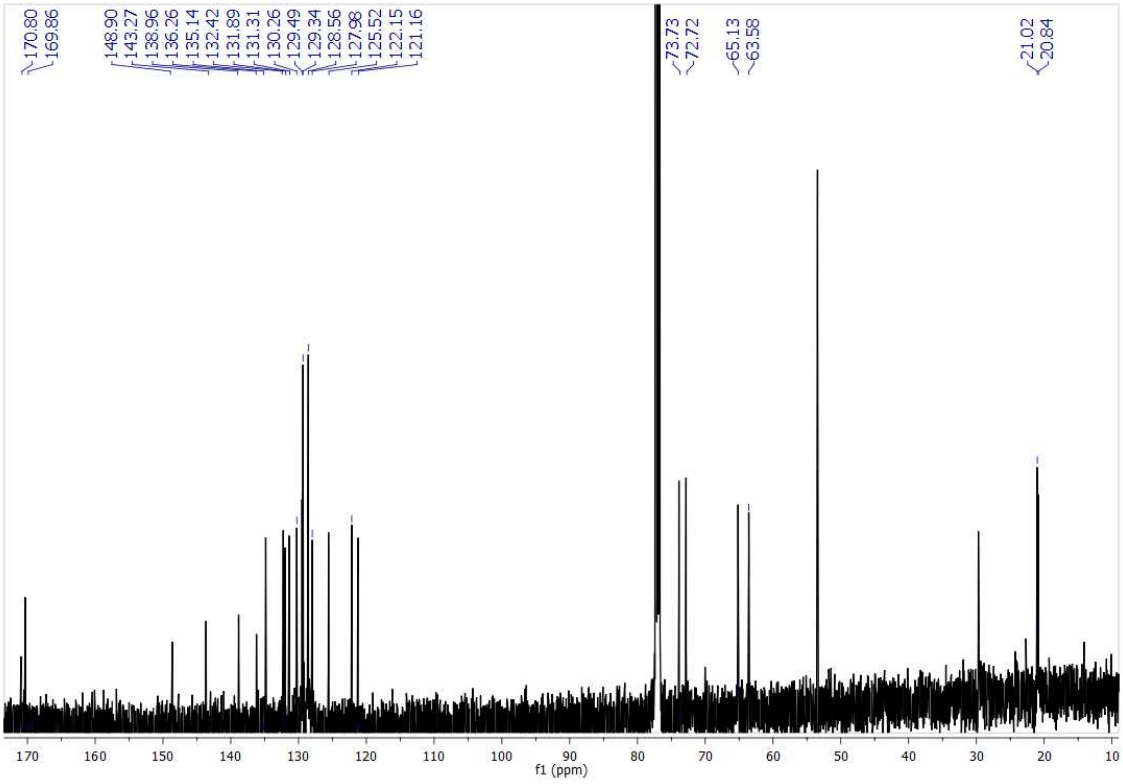
DEPT of compound 7c



^{1}H NMR of compound 8a



^{13}C NMR of compound 8a



DEPT of compound 8a