Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Electrochemical Epoxidation of Alkene with High Faradaic Efficiencies Using Water as an Oxygen Source

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1. General Information

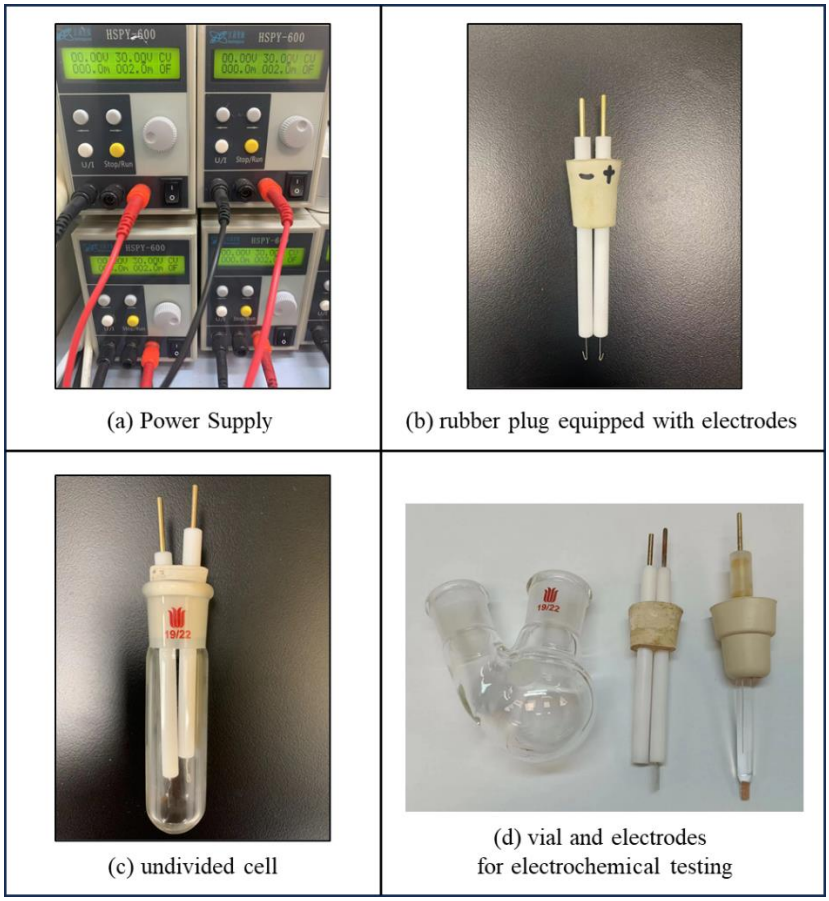
a. Materials

All manipulations were carried out in an inert atmosphere glovebox or using standard Schlenk techniques unless stated otherwise. All reagents were purchased from commercial suppliers (TCI, J&K, Bidepharm, Macklin, Sinopharm or Accela) or synthesized via known literature procedures. Chloroform ($CHCl_3$) (Sinopharm Chemical Reagent) was distilled from calcium hydride prior to use. Pyrrole (Macklin Chemical Reagent) and trimethylbenzaldehyde (Macklin Chemical Reagent) were distilled under reduced pressure prior to use.

b. Analytical Methods

NMR characterization was performed on 400 and 500 MHz spectrometers (101 and 126 MHz for ^{13}C NMR). ^{1}H NMR with TMS (δ = 0.0 ppm) or $CDCl_3$ (δ = 7.26 ppm) as the internal standard, ^{13}C NMR chemical shifts were referenced to the solvent resonance and ^{19}F NMR with trifluoroacetic acid as the external standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). The GC measurements were conducted on Shimadzu Nexis GC-2030 with an FID detector. GC-MS measurements were conducted on Shimadzu GCMS-QP2020 NX; HRMS (ESI) measurements were conducted on Thermo Scientific Exactive Plus; The UV-Vis spectra were recorded on Agilent Cary 60 UV-Vis spectrophotometer; Electrochemical experiments were conducted on Gamery 1010E potentiostat; The thermometer has not been calibrated.

Graphic guide for experimental Set-up



(a) Power Supply

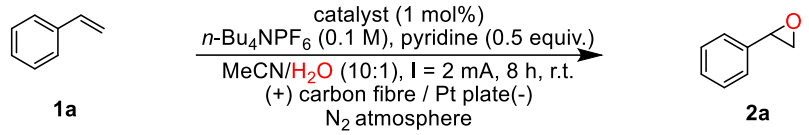
(b) rubber plug equipped with electrodes

(c) undivided cell

(d) vial and electrodes for electrochemical testing

2. Reaction Optimization

Table S1. Screening of the electrochemical catalysts.



Entry	catalysts	Yield of **2a** (%)
1	(TMP)MnCl	89
2	$MnBr_2$	n.d.
3	(salen)Mn	9
4	(TPP)MnCl	12

Reaction conditions: **1a** (0.3 mmol), catalysts (1 mol%), *n*-Bu_4NPF_6 (0.1 M) and pyridine (0.5 equiv.) in MeCN/H_2O (6.0 mL, 10:1) at ambient temperature. The yield was determined by GC analysis using mesitylene as an internal standard. n.d. = not detected.

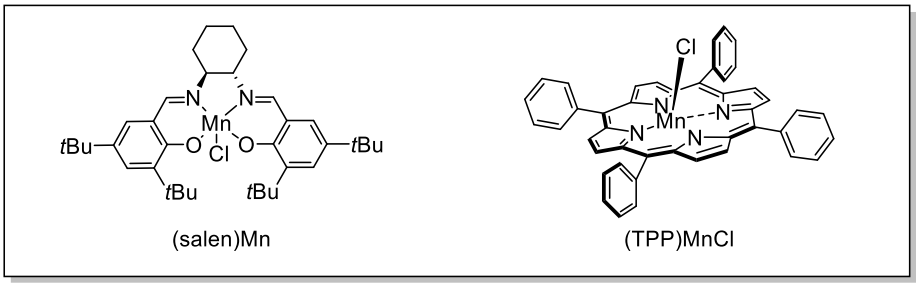
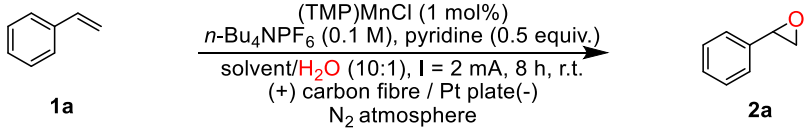


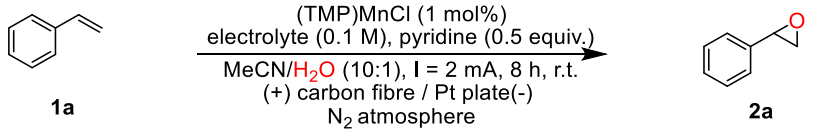
Table S2. Screening of the solvents.



Entry	solvents	Yield of **2a** (%)
1	DMA	n.d.
2	DMF	n.d.
3	DCM	50
4	DMSO	n.d.
5	THF	n.d.

Reaction conditions: **1a** (0.3 mmol), (TMP)MnCl (1 mol%), *n*-Bu_4NPF_6 (0.1 M) and pyridine (0.5 equiv.) in solvent/H_2O (6.0 mL, 10:1) at ambient temperature. The yield was determined by GC analysis using mesitylene as an internal standard. n.d. = not detected.

Table S3. Screening of the electrolyte.

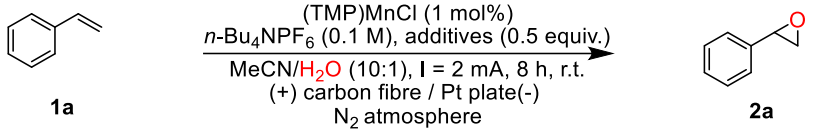


1a **2a**

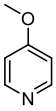
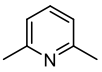
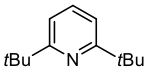
Entry	electrolyte	Yield of **2a** (%)
1	*n*-Bu_4NBF_4	85
2	$LiClO_4$	22
3	$LiBF_4$	24
4	$LiPF_6$	n.d.

Reaction conditions: **1a** (0.3 mmol), (TMP)MnCl (1 mol%), electrolyte (0.1 M), and pyridine (0.5 equiv.) in MeCN/H_2O (6.0 mL, 10:1) at ambient temperature. The yield was determined by GC analysis using mesitylene as an internal standard. n.d. = not detected.

Table S4. Screening of the additives.

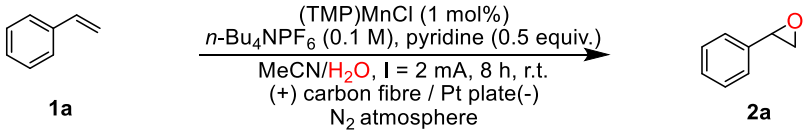


1a **2a**

Entry	additives	Yield of **2a** (%)
1		n.d.
2		n.d.
3		76
4		54
5		30

Reaction conditions: **1a** (0.3 mmol), (TMP)MnCl (1 mol%), *n*-Bu_4NPF_6 (0.1 M) and additives (0.5 equiv.) in MeCN/H_2O (6.0 mL, 10:1) at ambient temperature. The yield was determined by GC analysis using mesitylene as an internal standard. n.d. = not detected.

Table S5. Screening of the ratio of MeCN/H_2O .

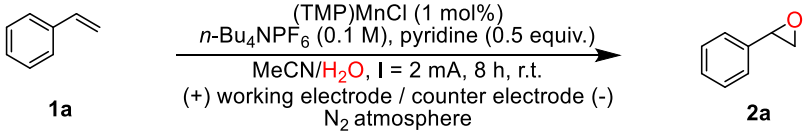


1a **2a**

Entry	the ratio of the mixed solvents	Yield of **2a** (%)
1	MeCN:H_2O = 20:1 (6 mL:0.3 mL)	72
2	MeCN:H_2O = 5:1 (5 mL:1 mL)	78
3	MeCN:H_2O = 2:1 (4 mL:2 mL)	79
4	MeCN:H_2O = 1:1 (3 mL:3 mL)	73
5	MeCN:H_2O = 1:2 (2 mL:4 mL)	73
6	MeCN:H_2O = 1:5 (1 mL:5 mL)	n.d.
7	MeCN:H_2O = 1:10 (0.6 mL:6 mL)	n.d.
8	MeCN:H_2O = 1:20 (0.3 mL:6 mL)	n.d.

Reaction conditions: **1a** (0.3 mmol), (TMP)MnCl (1 mol%), *n*-Bu_4NPF_6 (0.1 M) and pyridine (0.5 equiv.) in a mixture of MeCN/H_2O at ambient temperature. The yield was determined by GC analysis using mesitylene as an internal standard. n.d. = not detected.

Table S6. Screening of the electrodes.

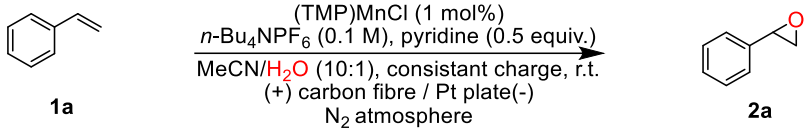


1a **2a**

Entry	electrode	Yield of **2a** (%)
1	(+) Pt plate / Pt plate (-)	n.d.
2	(+) graphite sheet / Pt plate (-)	52
3	(+) carbon fibre / Ni plate (-)	22
4	(+) carbon fibre / Ni foam (-)	26

Reaction conditions: **1a** (0.3 mmol), (TMP)MnCl (1 mol%), *n*-Bu_4NPF_6 (0.1 M) and pyridine (0.5 equiv.) in solvent/H_2O (6.0 mL, 10:1) at ambient temperature. The yield was determined by GC analysis using mesitylene as an internal standard. n.d. = not detected.

Table S7. Screening of the current.

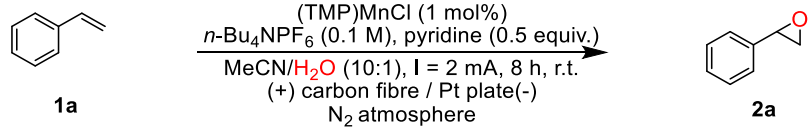


1a **2a**

Entry	current / time	Yield of **2a** (%)
1	1 mA / 16 h	73
2	3 mA / 5.36 h	75
3	4 mA / 4 h	78
4	5 mA / 3.2 h	74
5	10 mA / 1.6 h	70

Reaction conditions: **1a** (0.3 mmol), (TMP)MnCl (1 mol%), *n*-Bu_4NPF_6 (0.1 M) and pyridine (0.5 equiv.) in MeCN/H_2O (6.0 mL, 10:1) at ambient temperature. Input a consistent charge into the reaction. The yield was determined by GC analysis using mesitylene as an internal standard. n.d. = not detected.

Table S8. Other control experiments.

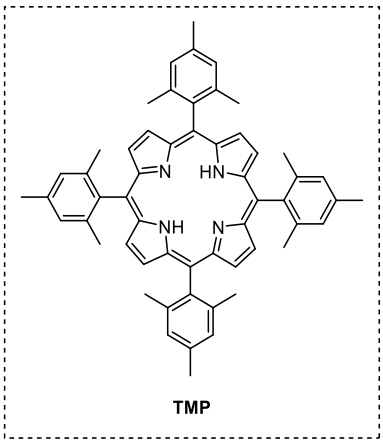


1a **2a**

Entry	Control experiments	Yield of **2a** (%)
1	no catalyst	n.d.
2	no pyridine	2
3	without electrolysis	n.d.
4	under air	66

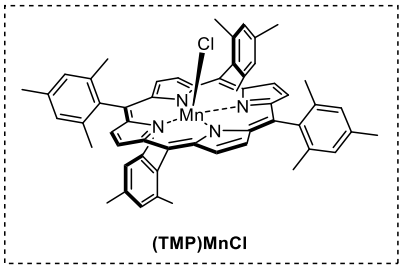
Reaction conditions: **1a** (0.3 mmol), (TMP)MnCl (1 mol%), *n*-Bu_4NPF_6 (0.1 M) and pyridine (0.5 equiv.) in MeCN/H_2O (6.0 mL, 10:1) at ambient temperature. The yield was determined by GC analysis using mesitylene as an internal standard. n.d. = not detected.

3. Preparation of porphyrin ligand and manganese porphyrin catalysts



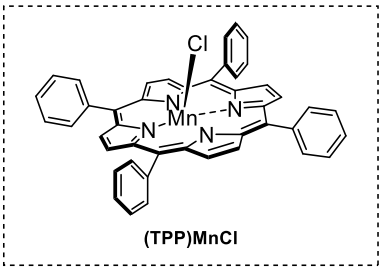
TMP

Tetramesitylporphyrin (TMP): This compound was synthesised according to the previous literature.[1] Under air atmosphere, pyrrole (536 mg, 8 mmol), trimethylbenzaldehyde (1.19 g, 8 mmol), MeOH (200 mL) and water (100 mL) were added to a three-necked flask equipped with a magnetic stir bar. Then HCl (20 mL, 12 M) was added to the mixture dropwise. The resulting solution was stirred at room temperature for 2 h. After that, the precipitate was collected by filtration and dissolved in 200 mL of DMF solution. This DMF solution was refluxed for an additional 1.5 h and stirred at room temperature overnight. After the reaction was completed, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography, eluting with PE/DCM (4:1). The product was further recrystallized with DCM and MeOH to afford a purple solid in 8% yield (130 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.62 (s, 8H), 7.27 (s, 8H), 2.62 (s, 12H), 1.85 (s, 24H), -2.50 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.6, 138.4, 137.7, 127.8, 117.7, 21.8, 21.6. HRMS-ESI (m/z): Calcd for $[C_{56}H_{54}N_4+H]^+$, 783.4426; found: 783.4423. These spectroscopic data correspond to the reported data[1].



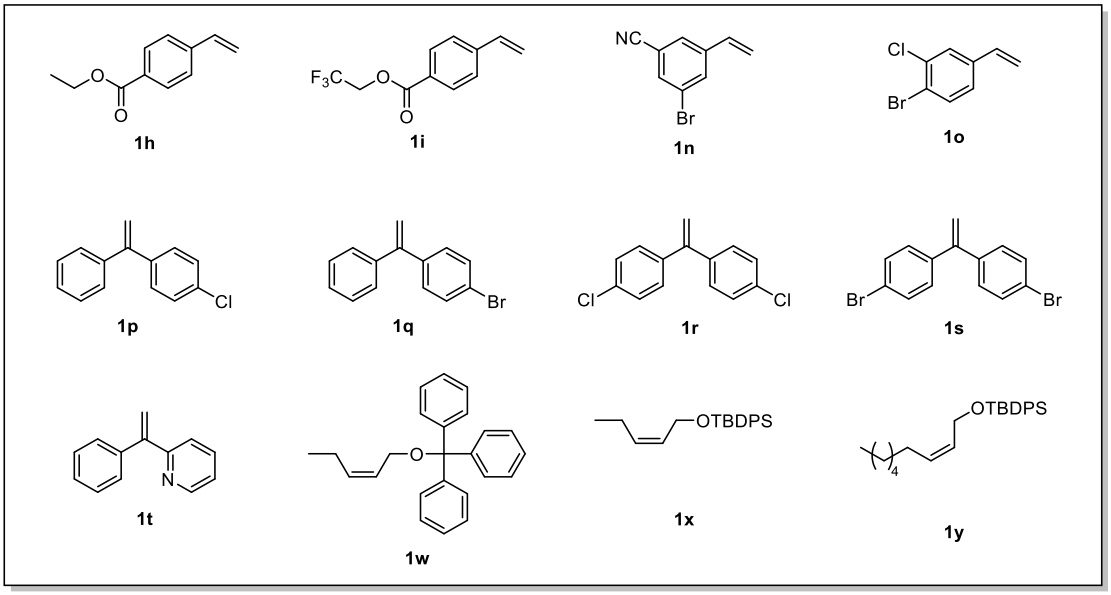
(TMP)MnCl

(Tetramesitylporphyrinato) manganese (III) chloride ((TMP)MnCl): Under nitrogen atmosphere, TMP (184 mg, 0.235 mmol) and manganese acetate (813 mg, 4.7 mmol were added to a 100 mL three-necked flask equipped with a magnetic stir bar. To this mixture were added approximately 30 mL DMF as a solvent. The reaction mixture was refluxed at 165 ℃ for 8 h. After the reaction was completed, the solvent was removed under reduced pressure. The resulting mixture was dissolved in DCM (100 mL) and treated with 10% aqueous HCl (70 mL) at room temperature for 4 h. The organic layer was separated, dried over $MgSO_4$, filtered and concentrated to dryness using a rotary evaporator. The residue was purified by flash column chromatography (eluting with DCM/MeOH=10:1) to afford pure (TMP)MnCl as a dark green solid (201 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03, 2.97, 2.89, 2.58, -20.27. UV-Vis: λ_{max} = 479 nm. HRMS-ESI (m/z): Calcd for $[C_{56}H_{52}ClMnN_4]$, 870.3261; found: 870.3253. These spectroscopic data correspond to the reported data[2].

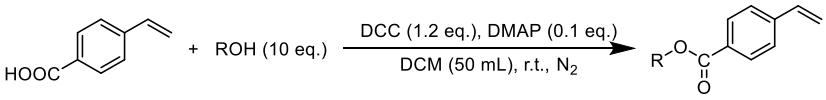


(*meso*-Tetraphenylporphyrinato) manganese(III) chloride ((TPP)MnCl): Under nitrogen atmosphere, TPP (*meso*-Tetraphenylporphyrine, 923 mg, 1.5 mmol) and manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 2.97 g, 15 mmol) were added to a 100 mL three-necked flask equipped with a magnetic stir bar. To this mixture were added approximately 40 mL DMF as a solvent. The reaction mixture was refluxed at 165 ℃ for 12 h. After cooling, the solvent was removed under reduced pressure. The resulting mixture was dissolved in DCM, washed with water and saturated NaCl solution over 3 times, dried over $MgSO_4$, filtered and concentrated to dryness using a rotary evaporator. The residue was purified by flash column chromatography (eluting with DCM/MeOH=50:1) to afford pure (TPP)MnCl as a dark green solid (931 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32, 8.03, 2.98, 2.90, -22.93. UV-Vis: λ_{max} = 477 nm. These spectroscopic data correspond to the reported data[3].

4. Starting material synthesis

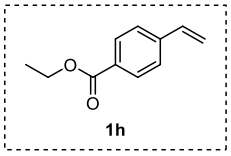


Synthesis procedure 1 (SP1): Preparation of esters.



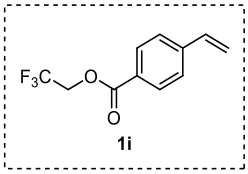
Under nitrogen atmosphere, 4-vinyl benzoic acid (1.48 g, 10 mmol), 1,3-dicyclohexyl-carbodiimide (2.48 g, 12 mmol), and DMAP (122 mg, 1 mmol) were added to a 100 mL three-necked flask equipped with a magnetic stir bar. To this mixture were added alcohol (100 mmol) and approximately 50 mL DCM as a solvent. The resulting solution was stirred under nitrogen for 12 h at room temperature. The mixture then was transferred to a separatory funnel, washed with brine and extracted with DCM. The organic layer was collected, dried over sodium sulfate and followed by filtration through celite. The volatiles were removed under reduced pressure and the residue was further purified by column

chromatography . The following compounds were prepared according to **SP1**.



1h

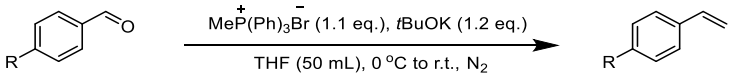
ethyl 4-vinylbenzoate (1h). The compound was obtained by silica gel chromatography (eluting with PE/EA=10:1) as a pale yellow oil (1.32 g, 75 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3, 1.7 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (d, *J* = 17.59 Hz, 1H), 5.37 (d, *J* = 10.90 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 141.8, 136.1, 129.9, 129.6, 126.1, 116.4, 60.9, 14.3. These spectroscopic data correspond to the reported data[4].



1i

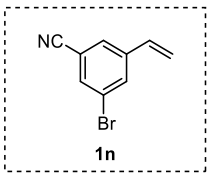
2,2,2-trifluoroethyl 4-vinylbenzoate (1i). The compound was obtained by silica gel chromatography (eluting with PE/EA=20:1) as a pale yellow oil (1 g, 43 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.89 (d, *J* = 17.5 Hz, 1H), 5.42 (d, *J* = 10.9 Hz, 1H), 4.70 (q, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7, 142.9, 135.8, 130.4, 127.4, 126.3, 124.5 (q, *J* = 272.7 Hz, 1C), 117.1, 60.9 (q, *J* = 30.3 Hz, 1C). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.67. These spectroscopic data correspond to the reported data[5].

Synthesis procedure 2 (SP2): Wittig Reaction.



Under a nitrogen atmosphere, ketone or aldehyde (1.0 equiv.) and methyltriphenylphosphine bromide (1.1 equiv.) were dissolved in 10 mL of THF. The THF solution of methyltriphenylphosphine bromide was placed in an ice water bath and cooled to 0 ℃. Then a solution of *t*BuOK (1.2 equiv.) in THF (10 mL) was added dropwise. The resulting yellow suspension was stirred at 0 ℃ for 20 min and warmed to room temperature. To this suspension, a solution of ketone or aldehyde was added in one portion. The mixture was further stirred at room temperature overnight. Then the insoluble solids were filtered out and the volatiles were removed under reduced pressure. The reaction mixture was purified by column chromatography over silica gel.

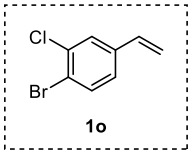
The following compounds were prepared according to **SP2**.



1n

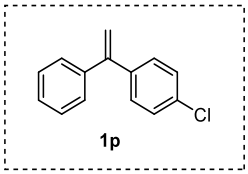
3-bromo-5-vinylbenzonitrile (1n). The compound was obtained by silica gel chromatography (eluting with PE/DCM=10:1) as a pale yellow oil (276 mg, 15 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.64 (s, 1H),

7.58 (s, 1H), 6.62 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.82 (d, *J* = 17.5 Hz, 1H), 5.44 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.5, 133.6, 133.5, 133.4, 128.4, 123.1, 118.2, 117.3, 114.4. These spectroscopic data correspond to the reported data[6].



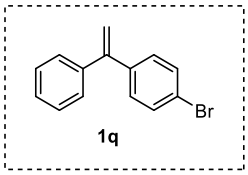
1o

1-bromo-2-chloro-4-vinylbenzene (1o). The compound was obtained by silica gel chromatography (eluting with PE/DCM=10:1) as a colorless oil (3.3 g, 64 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.2 Hz, 1H), 7.35 (s, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.48 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.65 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.3, 134.7, 134.6, 133.7, 127.9, 125.6, 121.3, 116.0. These spectroscopic data correspond to the reported data[7].



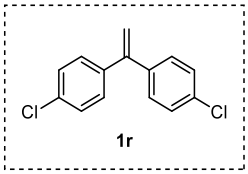
1p

1-chloro-4-(1-phenylvinyl)benzene (1p). The compound was obtained by silica gel chromatography (eluting with PE) as a colorless oil (693 mg, 33 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29–7.21 (m, 5H), 7.23–7.13 (m, 4H), 5.37 (d, *J* = 8.2, 1.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 141.1, 140.0, 133.7, 129.6, 128.4, 128.3, 128.3, 128.0, 114.8. These spectroscopic data correspond to the reported data[8].



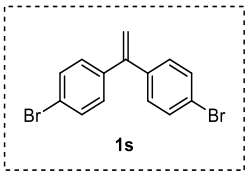
1q

1-bromo-4-(1-phenylvinyl)benzene (1q). The compound was obtained by silica gel chromatography (eluting with PE) as a colorless oil (968 mg, 37 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.28–7.16 (m, 5H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.35 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.1, 141.0, 140.5, 131.4, 130.0, 128.3, 128.3, 128.0, 121.9, 114.8. These spectroscopic data correspond to the reported data[9].

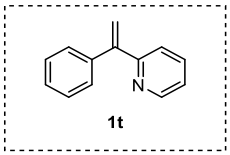


1r

4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (1r). The compound was obtained by silica gel chromatography (eluting with PE) as a white solid (930 mg, 38 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 –7.27 (m, 4H), 7.26–7.19 (m, 4H), 5.45 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.9, 139.5, 133.9, 129.5, 128.5, 115.2. These spectroscopic data correspond to the reported data[10].

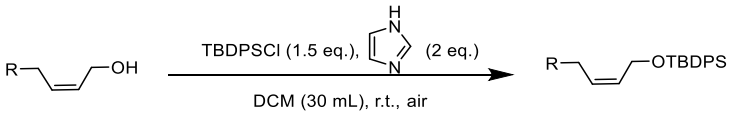


4,4'-(ethene-1,1-diyl)bis(bromobenzene) (1s). The compound was obtained by silica gel chromatography (eluting with PE) as a white solid (1.03 g, 30 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57–7.41 (m, 4H), 7.24–7.11 (m, 4H), 5.46 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.9, 139.5, 133.9, 129.5, 128.5, 115.2. These spectroscopic data correspond to the reported data[11].

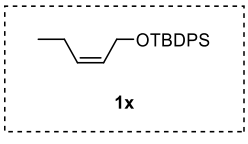


2-(1-phenylvinyl)pyridine (1t). The compound was obtained by silica gel chromatography (eluting with PE/EA=10:1, 5:1) as yellow oil (538 mg, 30 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 4.7 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 1H), 7.26 (brs, 5H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.13–7.06 (m, 1H), 5.91 (s, 1H), 5.51 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.6, 149.4, 149.2, 140.4, 136.3, 128.5, 128.3, 127.9, 122.9, 122.5, 117.7. These spectroscopic data correspond to the reported data[12].

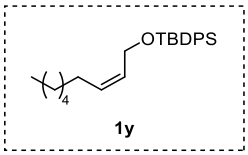
Synthesis procedure 3 (SP3): Protection of the hydroxyl group.



Under air conditions, alcohol (1.0 equiv.), imidazole (1.0 equiv) and DCM (30 mL) were added to a 100 mL three-necked flask equipped with a magnetic stir bar. Then TBDPSCl (1.5 equiv.) was added dropwise to the above mixed system. The reaction mixture was stirred at room temperature overnight. Water and DCM were added to the reaction mixture, and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layer was washed with saturated NaCl solution, dried over $MgSO_4$ and followed by filtration through celite. The volatiles were removed under reduced pressure and the residue was further purified by column chromatography The following compounds were prepared according to **SP3**.

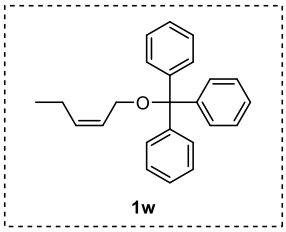


(Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (1x). The compound was obtained by silica gel chromatography (eluting with PE) as a colorless oil (1.754 g, 27 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 6.12 Hz, 4H), 7.39–7.24 (m, 6H), 5.49–5.25 (m, 2H), 4.18 (d, *J* = 6.2 Hz, 2H), 1.88–1.72 (m, 2H), 0.97 (s, 9H), 0.79 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.6, 134.0, 132.8, 129.6, 128.5, 127.7, 60.2, 26.9, 20.9, 19.2, 14.2. HRMS-ESI (m/z): Calcd for $[C_{21}H_{28}OSi+H]^+$, 325.1982; found: 325.1981.



1y

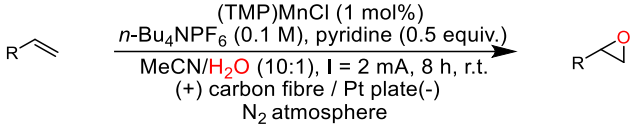
(Z)-tert-butyl(non-2-en-1-yloxy)diphenylsilane (1y). The compound was obtained by silica gel chromatography (eluting with PE) as a colorless oil (2.6 g, 69 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.69 Hz, 4H), 7.37–7.22 (m, 6H), 5.60–5.24 (m, 2H), 4.17 (d, *J* = 6.16, 1.68 Hz, 2H), 1.82–1.72 (m, 2H), 1.19–1.08 (m, 8H), 0.96 (s, 9H), 0.77 (t, *J* = 7.45, 6.30 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.6, 134.0, 131.3, 129.6, 129.0, 127.7, 60.3, 31.8, 29.6, 28.9, 27.6, 26.9, 22.7, 19.2, 14.1. HRMS-ESI (m/z): Calcd for $[C_{25}H_{36}OSi+H]^+$, 381.2608; found: 381.2608.



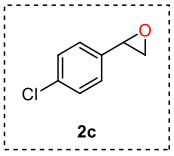
1w

(Z)-((pent-2-en-1-yloxy)methanetriyl)tribenzene (1w). The compound was prepared according to the SP3 with a small modification. Under air conditions, (Z)-pent-2-en-1-ol (20 mmol, 1.72 g, 2.02 mL, 1.0 equiv.) and triethylamine (40 mmol, 5.5 mL, 2.0 equiv.) and DCM (30 mL) were added to a 100 mL three-necked flask equipped with a magnetic stir bar. Then TrCl (1.5 equiv.) was added dropwise to the above mixed system. The reaction mixture was stirred at room temperature overnight. Water and DCM were added to the reaction mixture, and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layer was washed with saturated NaCl solution, dried over $MgSO_4$ and followed by filtration through celite. The volatiles were removed under reduced pressure and the residue was further purified by column chromatography (eluting with PE) as colorless oil (6.5 g, 94 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.40 Hz, 6H), 7.33–7.12 (m, 9H), 5.64–5.37 (m, 2H), 3.59 (d, *J* = 6.3 Hz, 2H), 2.01–1.75 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.3, 134.2, 128.7, 127.8, 126.9, 125.8, 86.8, 60.4, 21.1, 14.2. HRMS-ESI (m/z): Calcd for $[C_{24}H_{24}O+H]^+$, 329.1900; found: 329.1894.

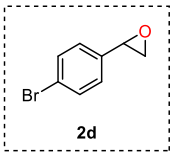
5. General procedure for electrochemical epoxidation of alkenes.



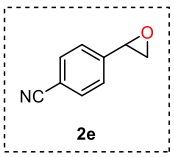
To an oven-dried 10 mL tube equipped with a stir bar was added (TMP)MnCl (0.003 mmol, 1 mol%), *n*-Bu_4NPF_6 (256 mg, 0.1 M). The tube was transferred into a nitrogen-filled glovebox and followed by the addition of acetonitrile (6 mL), pyridine (12 μL, 0.5 equiv.) and alkene (0.3 mmol, 1 equiv.). After that, the tube was sealed with a rubber plug equipped with carbon fibre (1.0×1.0 cm^2) and Pt electrodes (1.0×1.0 cm^2) and removed from the glovebox. Then bubbled water (600 μL) was added to the tube and the reaction mixture was electrolyzed under a constant current of 2 mA for 8 h. After the reaction was completed, the mixture was quenched with 4 mL of saturated sodium sulfite aqueous solution and extracted with EtOAc (3×10 mL). The organic phase was washed with brine (20 mL), dried over $MgSO_4$ and followed by filtration through celite. The volatiles were removed under reduced pressure and the residue was further purified by column chromatography or preparative thin-layer chromatography on silica gel.



2-(4-chlorophenyl)oxirane (2c). Following the above general procedure starting from 1-chloro-4-vinylbenzene (0.3 mmol). The crude mixture was purified with PE to afford the product as a yellow oil (33.4 mg, 72 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.84 (brs, 1H), 3.14 (brs, 1H), 2.76 (brs, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.2, 133.9, 128.7, 126.9, 51.8, 51.3. These spectroscopic data correspond to the reported data[13].

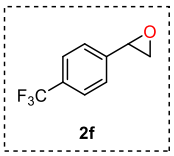


2-(4-bromophenyl)oxirane (2d). Following the above general procedure starting from 1-bromo-4-vinylbenzene (0.3 mmol). The crude mixture was purified with PE to afford the product as a yellow oil (40.6 mg, 68 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.82 (brs, 1H), 3.14 (brs, 1H), 2.75 (brs, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.7, 131.7, 127.2, 122.0, 51.9, 51.3. These spectroscopic data correspond to the reported data[13].



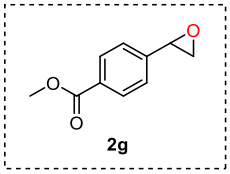
4-(oxiran-2-yl)benzonitrile (2e). Following the above general procedure starting from 4-vinylbenzonitrile (0.3 mmol). The crude mixture was purified with PE/EA=30:1 to afford the product as a yellow oil (33.4 mg, 77 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 3.90 (dd, *J* = 3.80, 2.61 Hz, 1H),

3.20 (dd, *J* = 5.4, 4.2 Hz, 1H), 2.75 (dd, *J* = 5.5, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.3, 132.4, 126.1, 118.7, 111.9, 51.6. These spectroscopic data correspond to the reported data[14].



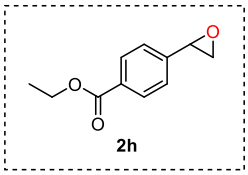
2f

4-(oxiran-2-yl)benzonitrile (2f). Following the above general procedure starting from 1-(trifluoromethyl)-4-vinylbenzene (0.3 mmol). The crude mixture was purified with PE to afford the product as a yellow oil (28 mg, 50 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.14 Hz, 2H), 7.39 (d, *J* = 8.17 Hz, 2H), 3.91 (dd, *J* = 4.11, 2.50 Hz, 1H), 3.18 (dd, *J* = 5.53, 4.09 Hz, 1H), 2.76 (dd, *J* = 5.51, 2.49 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 130.5 (q, *J* = 32.3 Hz, 1C), 125.8, 125.5 (q, *J* = 4.0 Hz, 1C), 122.71, 51.7, 51.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.61. These spectroscopic data correspond to the reported data[13].



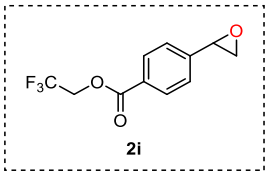
2g

methyl 4-(oxiran-2-yl)benzoate (2g). Following the above general procedure starting from methyl 4-vinylbenzoate (0.3 mmol). The crude mixture was purified with PE/EA=10:1 to afford the product as a yellow oil (32.6 mg, 61 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.98–3.85 (brs, 4H), 3.18 (brs, 1H), 2.79 (brs, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 142.9, 130.0, 129.8, 125.4, 52.2, 52.0, 51.5. These spectroscopic data correspond to the reported data[13].



2h

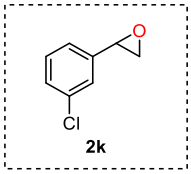
ethyl 4-(oxiran-2-yl)benzoate (2h). Following the above general procedure starting from methyl ethyl 4-vinylbenzoate (0.3 mmol). The crude mixture was purified with PE/EA=10:1 to afford the product as a yellow oil (31 mg, 54 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.90 (dd, *J* = 3.89, 2.6 Hz, 1H), 3.18 (dd, *J* = 5.5 Hz, 4.2 Hz, 1H), 2.78 (dd, *J* = 5.6, 2.5 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.3, 142.8, 130.4, 129.8, 125.4, 61.0, 52.0, 51.5, 14.3. These spectroscopic data correspond to the reported data[15].



2i

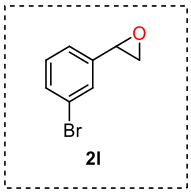
2,2,2-trifluoroethyl 4-(oxiran-2-yl)benzoate (2j). Following the above general procedure starting from methyl 2,2,2-trifluoroethyl 4-vinylbenzoate (0.3 mmol). The crude mixture was purified with PE/EA=10:1 to afford the product as a yellow oil (36.2 mg, 49 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* =

8.3 Hz, 2H), 4.70 (q, *J* = 8.4 Hz, 2H), 3.93 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.20 (dd, *J* = 5.5, 4.2 Hz, 1H), 2.78 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.6, 144.1, 130.3, 128.1, 125.6, 124.5 (q, *J* = 277.8 Hz, 1C) 61.0 (q, *J* = 36.4 Hz, 1C), 51.9, 51.6. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.65. HRMS-ESI (m/z): Calcd for [($C_{11}H_9F_3O_3$+H)+], 247.0577; found: 247.0576.



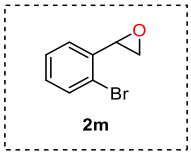
2k

2-(3-chlorophenyl)oxirane (2k). Following the above general procedure starting from methyl 1-chloro-3-vinylbenzene (0.3 mmol). The crude mixture was purified with PE/EA=50:1 to afford the product as a yellow oil (39.9 mg, 86 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32–7.21 (m, 3H), 7.21–7.12 (m, 1H), 3.83 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.14 (dd, *J* = 5.5, 4.1 Hz, 1H), 2.76 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.9, 134.6, 129.8, 128.3, 125.5, 123.8, 51.7, 51.2. These spectroscopic data correspond to the reported data[13].



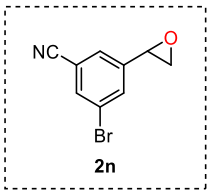
2l

2-(3-bromophenyl)oxirane (2l). Following the above general procedure starting from methyl 1-bromo-3-vinylbenzene (0.3 mmol). The crude mixture was purified with PE to afford the product as a yellow oil (50.1 mg, 84 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50–7.17 (m, 4H), 3.82 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.14 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.75 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.1, 131.3, 130.1, 128.4, 124.2, 122.7, 51.6, 51.3. These spectroscopic data correspond to the reported data[16].



2m

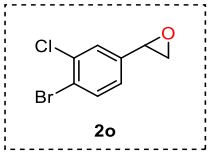
2-(2-bromophenyl)oxirane (2m). Following the above general procedure starting from methyl 1-bromo-2-vinylbenzene (0.3 mmol). The crude mixture was purified with PE/EA=50:1 to afford the product as a yellow oil (44.2 mg, 74 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50–7.07 (m, 4H), 3.82 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.14 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.75 (dd, *J* = 5.5, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.2, 132.3, 129.3, 127.7, 126.0, 122.6, 52.3, 50.8. These spectroscopic data correspond to the reported data[16].



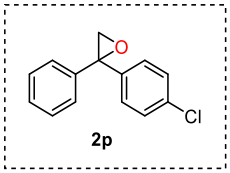
2n

3-bromo-5-(oxiran-2-yl)benzonitrile (2n). Following the above general procedure starting from methyl 3-bromo-5-vinylbenzonitrile (0.3 mmol). The crude mixture was purified with PE/DCM=1:1 to afford the product as a white solid

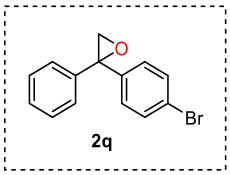
(42.8 mg, 64 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 –7.48 (m, 3H), 3.87 (dd, *J* = 4.1, 2.4 Hz, 1H), 3.19 (dd, *J* = 5.4, 4.0 Hz, 1H), 2.73 (dd, *J* = 5.4, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 134.3, 133.0, 127.8, 123.2, 117.0, 114.4, 51.5, 50.8. HRMS-ESI (m/z): Calcd for $[C_9H_6BrNO+H]^+$, 223.9706; found: 223.9703.



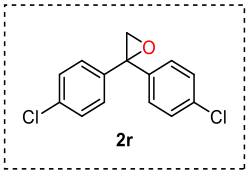
2-(4-bromo-3-chlorophenyl)oxirane (2o). Following the above general procedure starting from 1-bromo-2-chloro-4-vinylbenzene (0.3 mmol). The crude mixture was purified with PE/EA=10:1 to afford the product as a yellow oil (40 mg, 57 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 1H), 7.36 (s, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 3.81 (brs, 1H), 3.19–3.05 (m, 1H), 2.78–2.70 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 134.8, 133.8, 127.3, 125.0, 121.9, 51.3, 51.3. These spectroscopic data correspond to the reported data[17].



2-(4-chlorophenyl)-2-phenyloxirane (2p). Following the above general procedure starting from 1-chloro-4-(1-phenylvinyl)benzene (0.3 mmol). The crude mixture was purified with PE/EA=10:1 to afford the product as a yellow oil (44.2 mg, 64 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69–7.52 (m, 4H), 7.45–7.21 (m, 5H), 3.22 (d, *J* = 5.46 Hz, 1H), 3.15 (d, *J* = 5.46 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.0, 138.3, 133.9, 128.9, 128.5, 128.5, 128.3, 127.6, 61.4, 56.9. These spectroscopic data correspond to the reported data[18].

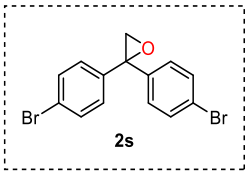


2-(4-bromophenyl)-2-phenyloxirane (2q). Following the above general procedure starting from 1-bromo-4-(1-phenylvinyl)benzene (0.3 mmol). The crude mixture was purified with PE/EA=10:1 to afford the product as a yellow oil (65.8 mg, 80 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.35–7.18 (m, 5H), 7.14 (d, J = 8.5 Hz, 2H), 3.22 (d, *J* = 5.5 Hz, 1H), 3.14 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 138.8, 131.5, 129.2, 128.4, 128.2, 127.5, 122.1, 61.4, 56.8. These spectroscopic data correspond to the reported data[19].



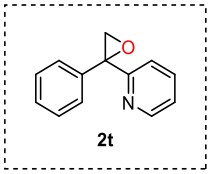
2,2-bis(4-chlorophenyl)oxirane (2r). Following the above general procedure starting from 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (0.3 mmol). The crude mixture was purified with PE/EA=10:1 to afford the product as a yellow oil (70.3 mg, 88 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.5 Hz, 4H), 7.26 (d, *J* = 8.6 Hz, 4H), 3.25 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.6, 134.2, 128.8, 128.6, 60.9, 56.8. These spectroscopic data

correspond to the reported data[10].



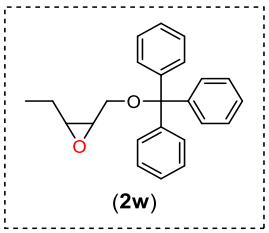
2s

2,2-bis(4-bromophenyl)oxirane (2s). Following the above general procedure starting from 4,4'-(ethene-1,1-diyl)bis(bromobenzene) (0.3 mmol). The crude mixture was purified with PE/EA=10:1 to afford the product as a yellow oil (75.4 mg, 71 % isolated yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.5 Hz, 4H), 7.20 (d, *J* = 8.5 Hz, 4H), 3.24 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.1, 131.6, 129.2, 122.4, 61.0, 56.7. These spectroscopic data correspond to the reported data[20].



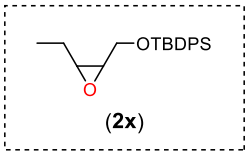
2t

2-(2-phenyloxiran-2-yl)pyridine (2t). Following the above general procedure starting from 4,4'-(ethene-1,1-diyl)bis(bromobenzene) (0.3 mmol). The crude mixture was purified with PE/EA=30:1 to afford the product as yellow oil (48.7 mg, 82 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60–8.50 (m, 1H), 7.65–7.52 (m, 1H), 7.42–7.35 (m, 2H), 7.34–7.10 (m, 5H), 3.48 (d, *J* = 5.9 Hz, 1H), 3.17 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.5, 149.3, 138.3, 136.7, 128.3, 128.1, 127.4, 122.9, 122.5, 62.0, 56.2. These spectroscopic data correspond to the reported data[21].



(**2w**)

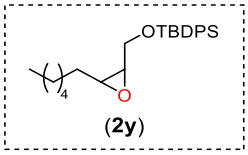
2-ethyl-3-((trityloxy)methyl)oxirane (2w). Following the above general procedure starting from (Z)-((pent-2-en-1-yloxy)methanetriyl)tribenzene (0.3 mmol). The crude mixture was purified with PE/EA=15:1 to afford the product as a yellow oil (82 mg, 76 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.7 Hz, 6H), 7.22 (t, *J* = 7.5 Hz, 6H), 7.15 (t, *J* = 7.3 Hz, 3H), 3.25 (dd, *J* = 10.1, 5.8 Hz, 1H), 3.12 (dd, *J* = 5.0 Hz, 1H), 3.03–2.84 (m, 2H), 1.38–1.18 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.9, 128.7, 127.9, 127.1, 86.8, 62.1, 57.8, 55.5, 21.3, 10.7. HRMS-ESI (m/z): Calcd for $[C_{24}H_{24}O_2+Na]^+$, 367.1669; found: 367.1664.



(**2x**)

tert-butyl((3-ethyloxiran-2-yl)methoxy)diphenylsilane (2x). Following the above general procedure starting from (Z)-tert-butyl(pent-2-en-1-yloxy)diphenylsilane (0.3 mmol). The crude mixture was purified with PE to afford the product as a yellow oil (78.5 mg, 77 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75–7.65 (m, 4H), 7.48–7.35 (m,

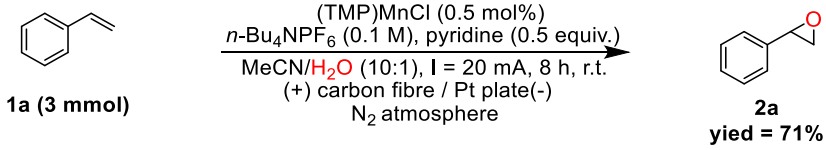
6H), 3.84–3.70 (m, 2H), 3.18 (td, *J* = 5.5, 4.3 Hz, 1H), 2.93 (td, *J* = 6.5, 4.3 Hz, 1H), 1.52–1.32 (m, 2H), 1.07 (s, 9H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.6, 135.59, 133.4, 133.23, 129.8, 127.8, 62.2, 58.0, 56.9, 26.8, 21.2, 19.2, 10.7. HRMS-ESI (m/z): Calcd for $[C_{21}H_{28}O_2Si+H]^+$, 341.1931; found: 341.1929.



(**2y**)

tert-butyl((3-hexyloxiran-2-yl)methoxy)diphenylsilane (2y). Following the above general procedure starting from (Z)-tert-butyl(non-2-en-1-yloxy)diphenylsilane (0.3 mmol). The crude mixture was purified with PE to afford the product as a yellow oil (64.2 mg, 54 % isolated yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72–7.66 (m, 4H), 7.49–7.33 (m, 6H), 3.85–3.70 (m, 2H), 3.16 (td, *J* = 5.5, 4.3 Hz, 1H), 2.95 (td, *J* = 5.9, 4.2 Hz, 1H), 1.41– 1.21 (m, 10H), 1.07 (s, 9H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.7, 135.6, 133.5, 133.2, 129.8, 127.7, 62.2, 56.9, 56.8, 31.7, 29.1, 27.9, 26.8, 26.6, 22.6, 19.2, 14.1. HRMS-ESI (m/z): Calcd for $[C_{25}H_{36}O_2Si+H]^+$, 397.2557; found: 397.2556.

Scale-up experiment.



1a (3 mmol) **2a**
yied = 71%

To an oven-dried 100 mL flask equipped with a stir bar was added (TMP)MnCl (0.015 mmol, 0.5 mol%), *n*-Bu_4NPF_6 (2.56 g, 0.1 M). The flask was transferred into a nitrogen-filled glovebox and followed by the addition of acetonitrile (60 mL), pyridine (120 μL, 0.5 equiv.) and styrene (3 mmol, 345 μL, 1 equiv.). The reaction bottle was removed from the glovebox and sealed with a rubber plug equipped with carbon fibre (2.0×2.0 cm^2) and Pt electrodes (1.0×1.0 cm^2). Then bubbled H_2O (6 mL) was added to the bottle and the reaction mixture was electrolyzed under a constant current of 20 mA for 8 h. After the reaction was completed, the mixture was quenched with 10 mL of saturated sodium sulfite aqueous solution and diluted with EtOAc. The yield was analyzed by gas chromatography (GC) using mesitylene as an internal standard.

6. Mechanistic investigation

Isotope labelling experiments

To an oven-dried 10 mL tube equipped with a stir bar was added (TMP)MnCl (0.003 mmol, 1 mol%), *n*-Bu_4NPF_6 (256 mg, 0.1 M). The tube was transferred into a nitrogen-filled glovebox and followed the addition of acetonitrile (6 mL), pyridine (12 μL, 0.5 equiv.) and styrene (0.3 mmol, 34.5 μL, 1 equiv.). The tube was removed from the glovebox and sealed with a rubber plug equipped with carbon fibre (1.0×1.0 cm^2) and Pt electrodes (1.0×1.0 cm^2). Then H_2O^{18} (600 μL) was added to the tube and the reaction mixture was electrolyzed under a constant current of 2 mA for 8 h. After the reaction was completed, the mixture was quenched with 4 mL of saturated sodium sulfite aqueous solution and diluted with EtOAc. The products were analyzed by gas chromatograph−mass spectrometry (GCMS). The results are shown in Figure S1.

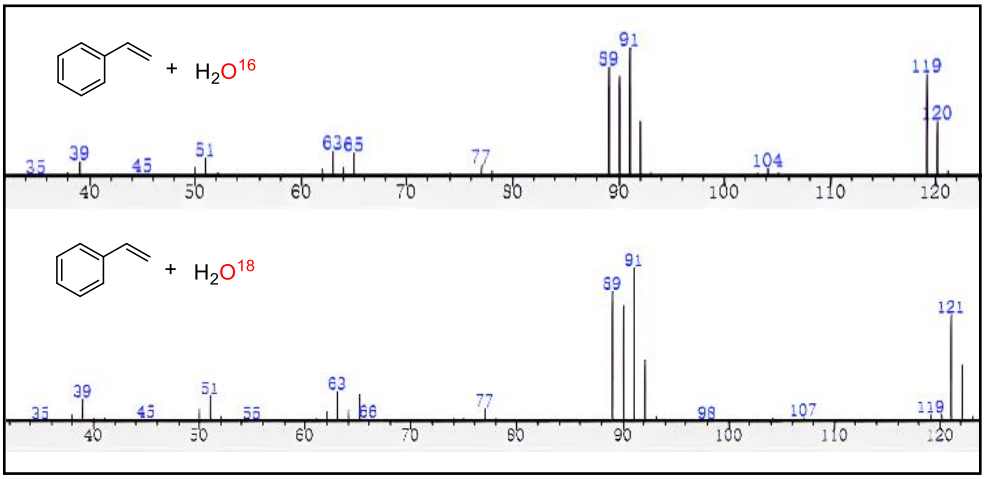
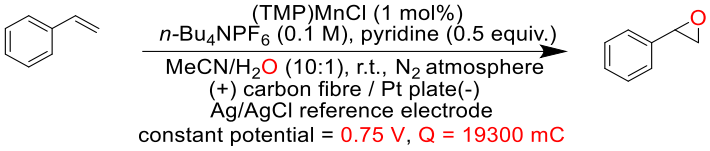


Figure S1. Isotopic distribution patterns obtained from epoxidation when using H_2O^{16} and H_2O^{18} as the oxygen source.

Constant potential electrolysis experiment.



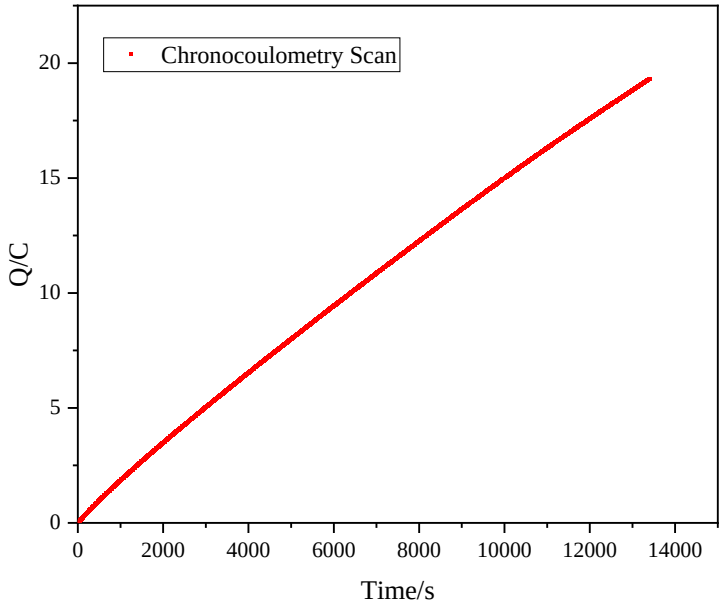


Figure S2. Reaction conditions: **1a** (0.3 mmol), (TMP)MnCl (1 mol%), *n*-Bu_4NPF_6 (0.1 M) and pyridine (0.5 equiv.) in MeCN/H_2O (6.0 mL, 10:1) at ambient temperature. The consistent potential experiment was measured at room temperature using a carbon fibre electrode working electrode, a platinum counter electrode, and a saturated Ag/AgCl reference electrode. Consistent potential = 0.75 V vs Fc/Fc^+, electricity = 19300 mC. The yield was determined by GC analysis using mesitylene as an internal standard.

7. References

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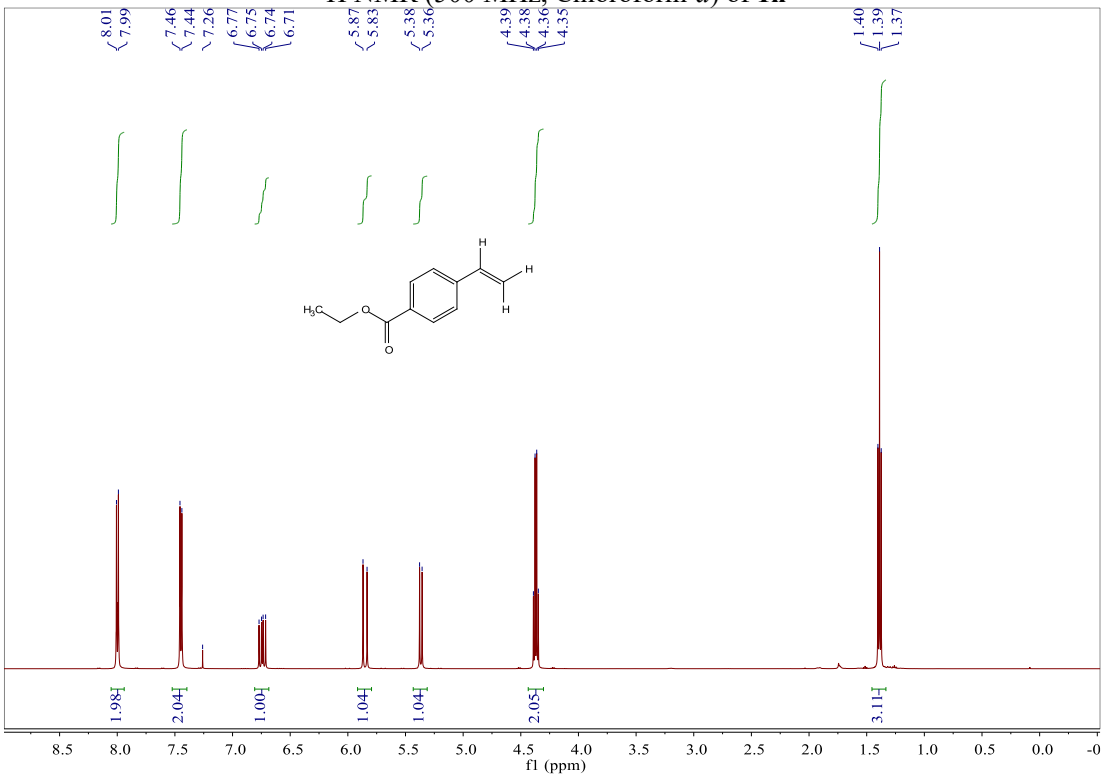
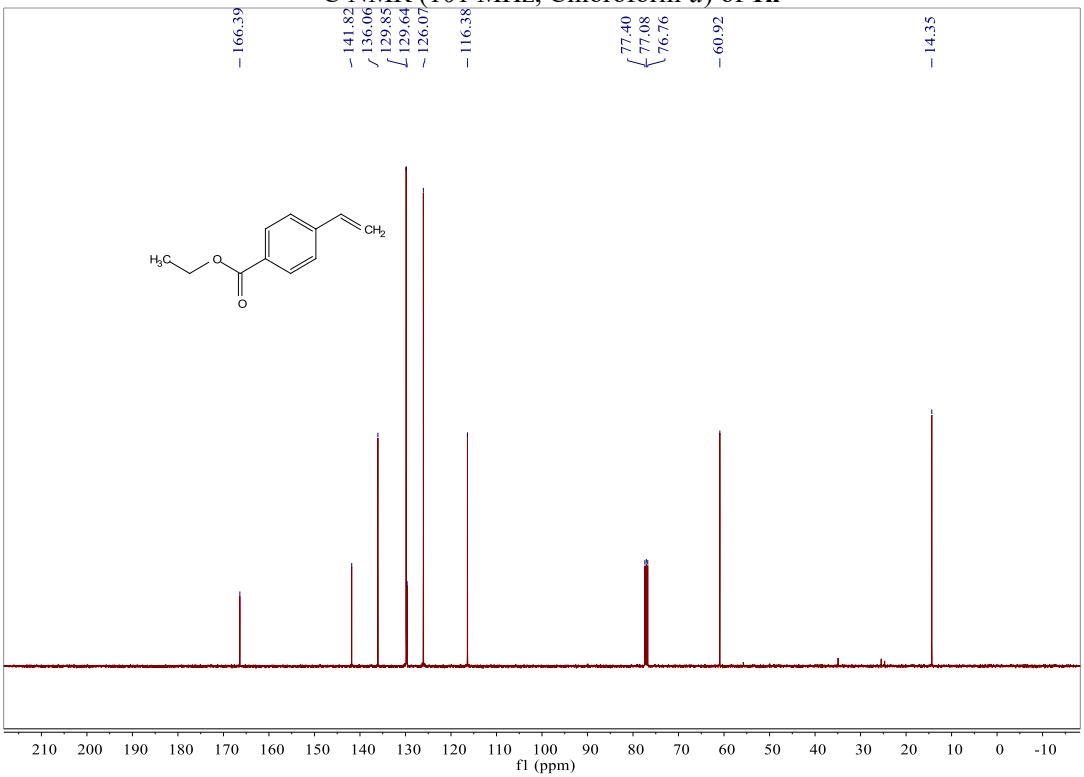
8. NMR Spectra

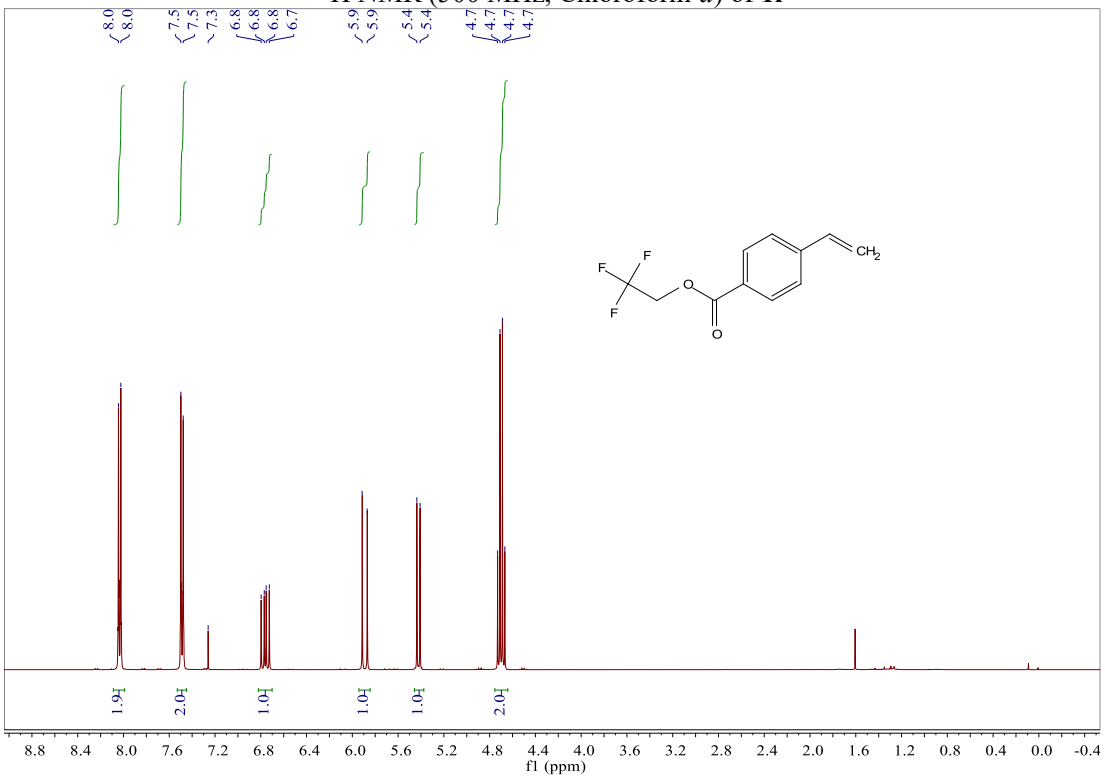
^{1}H NMR (500 MHz, Chloroform-*d*) of **1h**



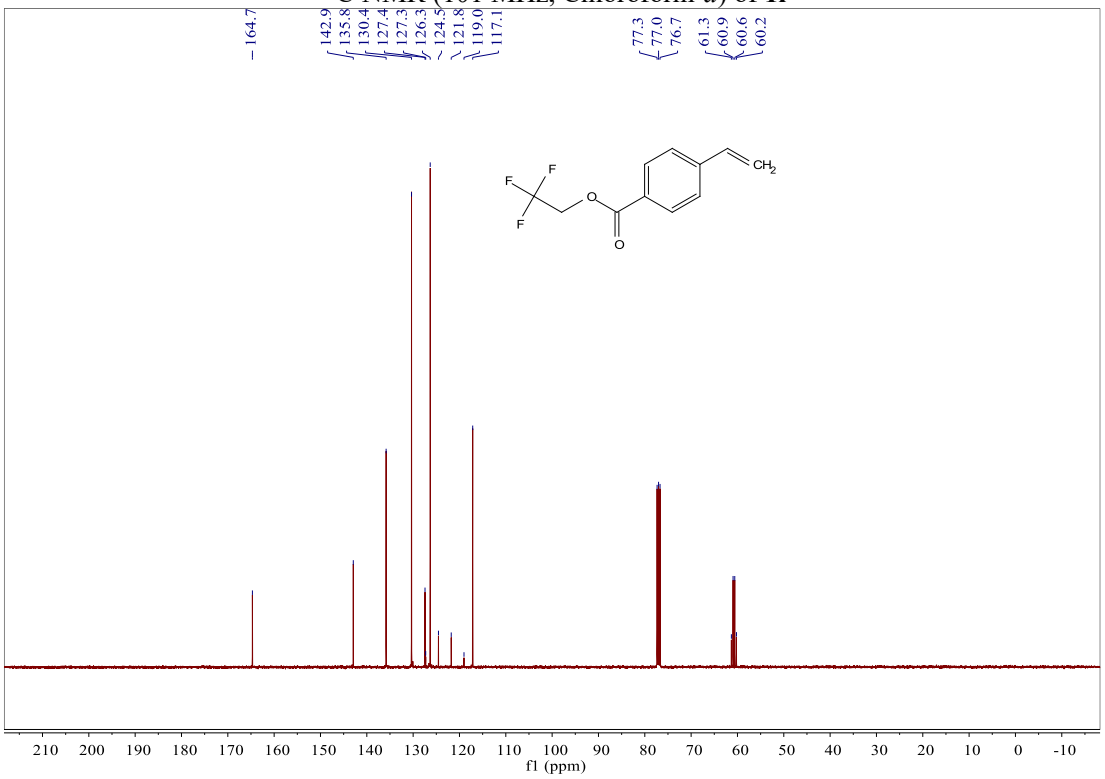
^{13}C NMR (101 MHz, Chloroform-*d*) of **1h**



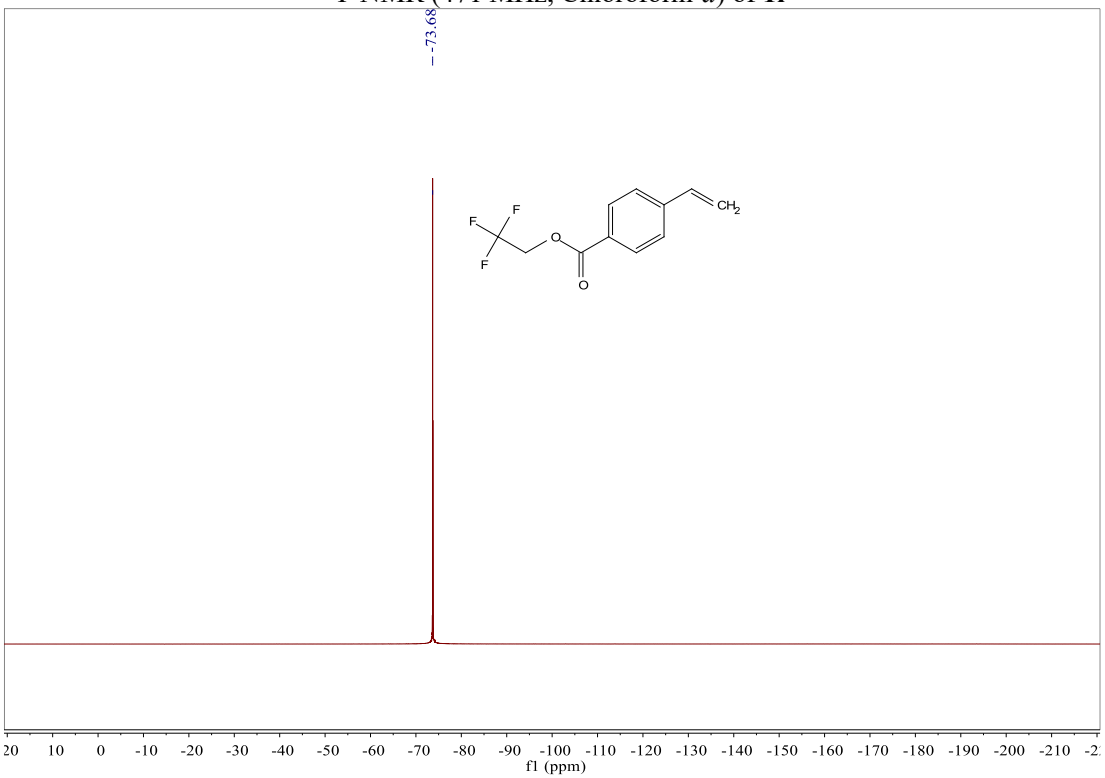
^{1}H NMR (500 MHz, Chloroform-*d*) of **1i**



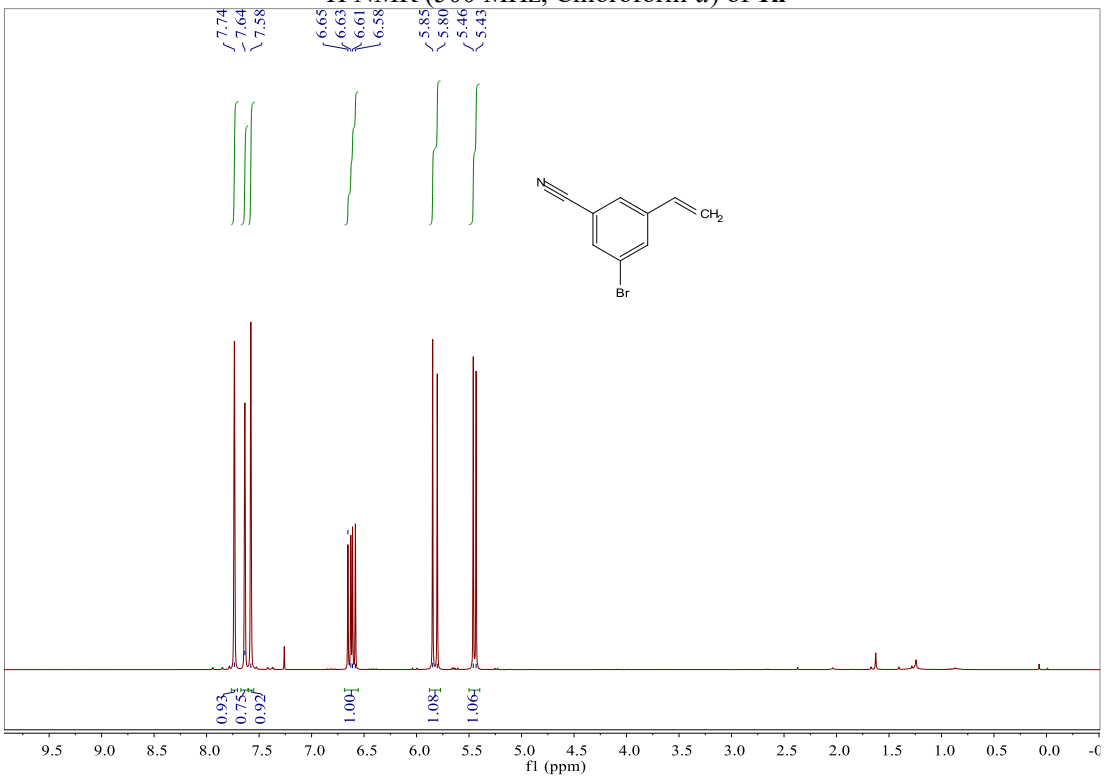
^{13}C NMR (101 MHz, Chloroform-*d*) of **1i**



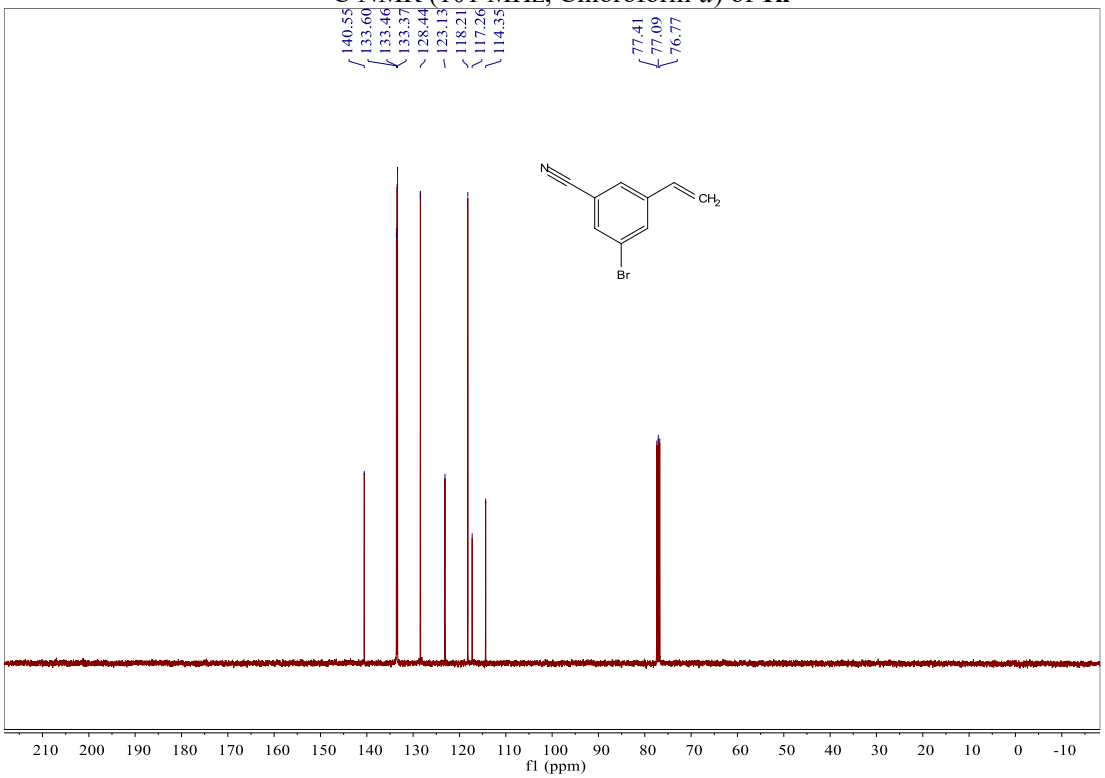
^{19}F NMR (471 MHz, Chloroform-*d*) of **1i**



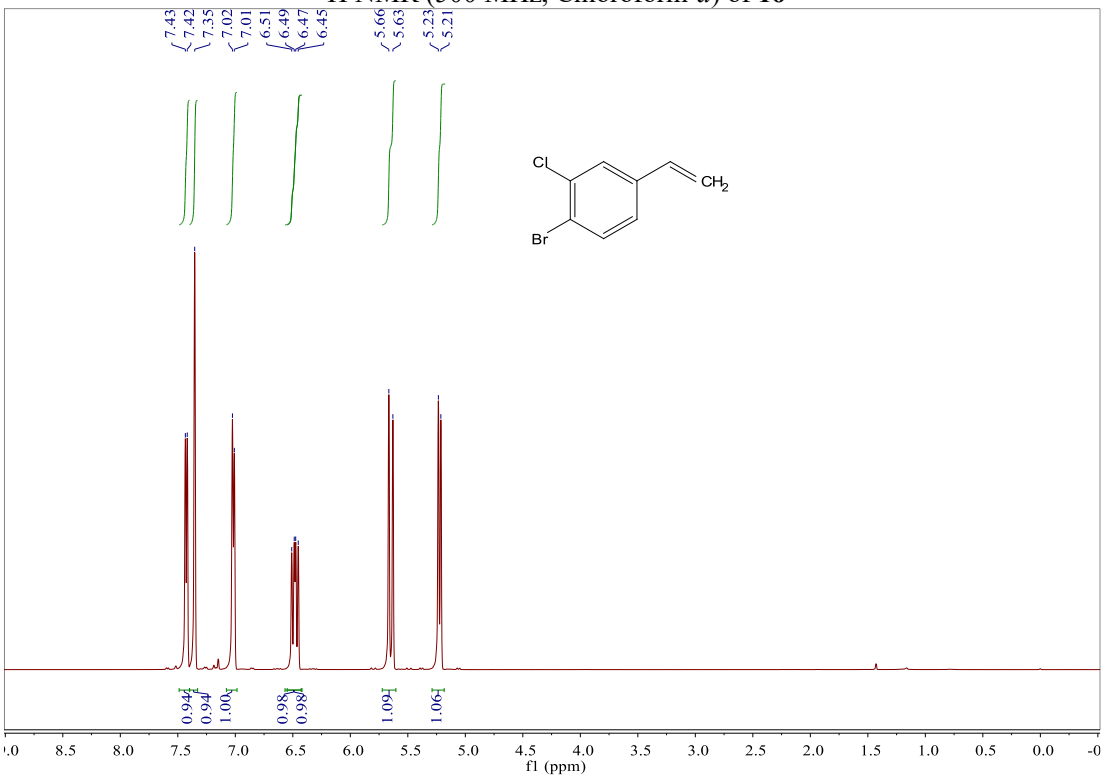
^{1}H NMR (500 MHz, Chloroform-*d*) of **1n**



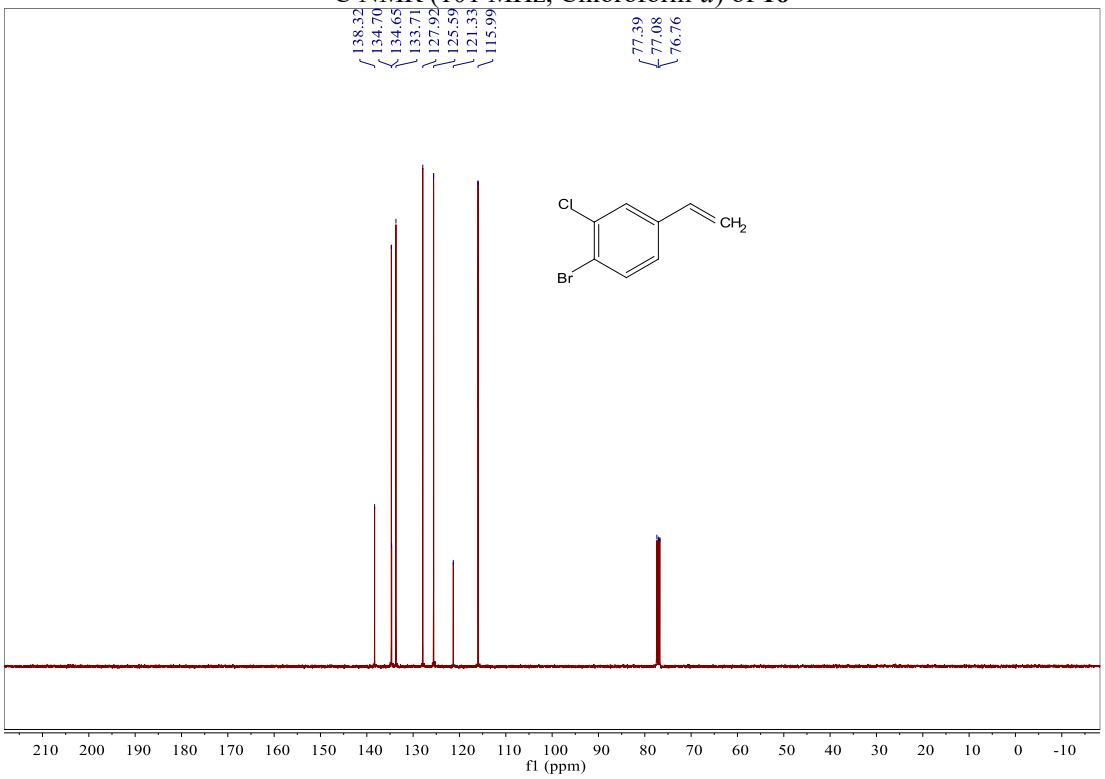
^{13}C NMR (101 MHz, Chloroform-*d*) of **1n**



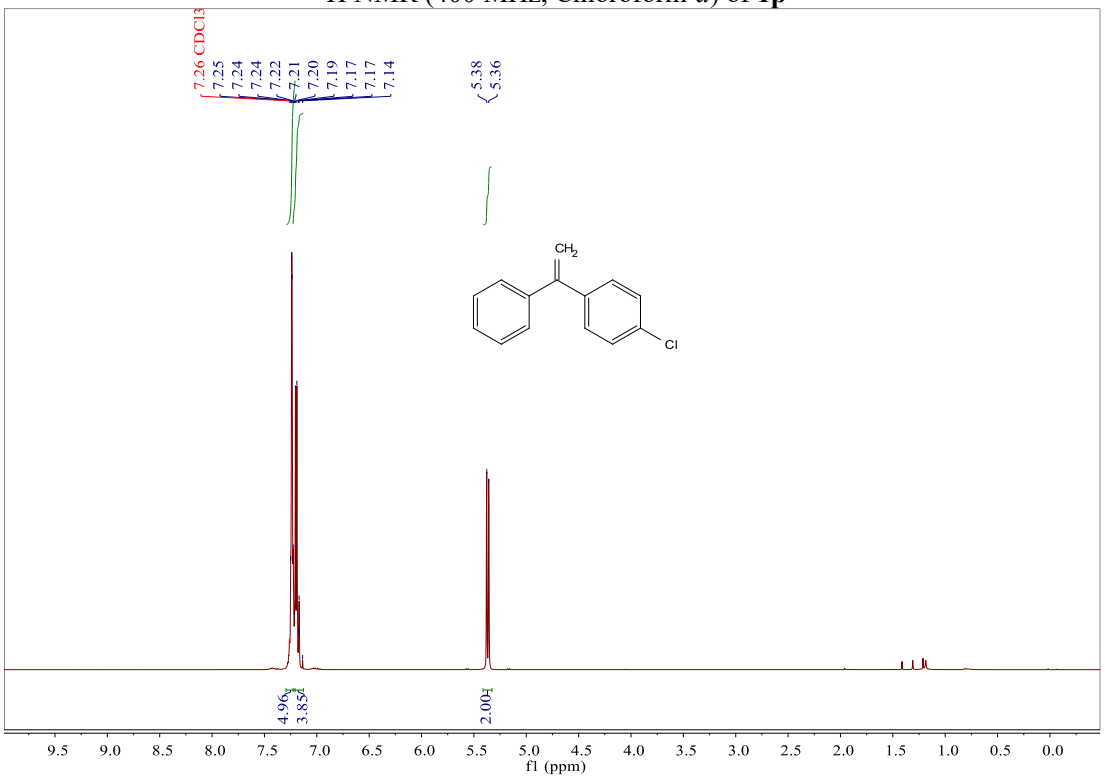
^{1}H NMR (500 MHz, Chloroform-*d*) of **1o**



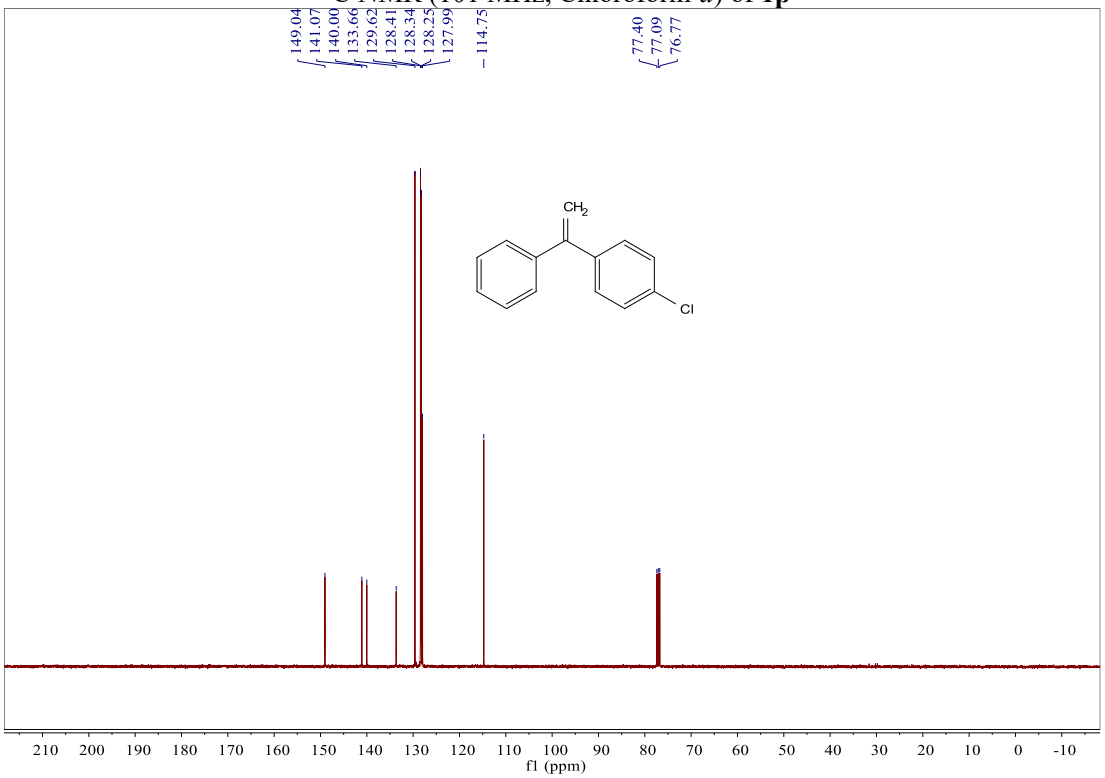
^{13}C NMR (101 MHz, Chloroform-*d*) of **1o**



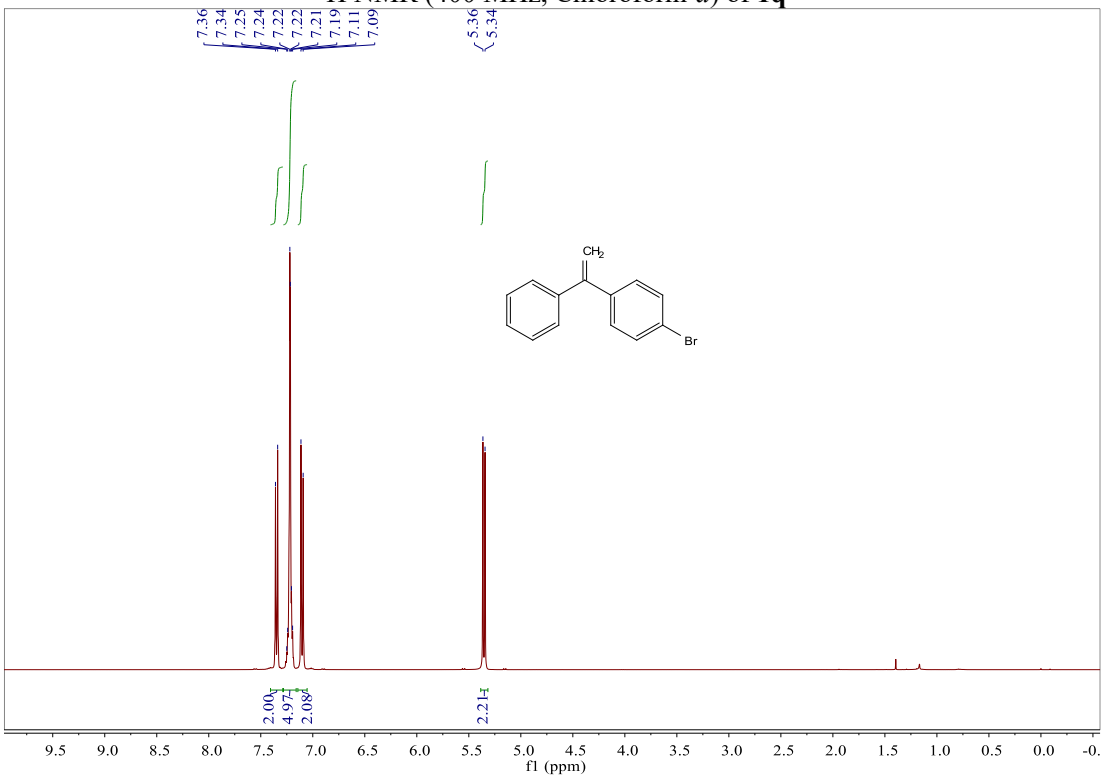
^{1}H NMR (400 MHz, Chloroform-*d*) of **1p**



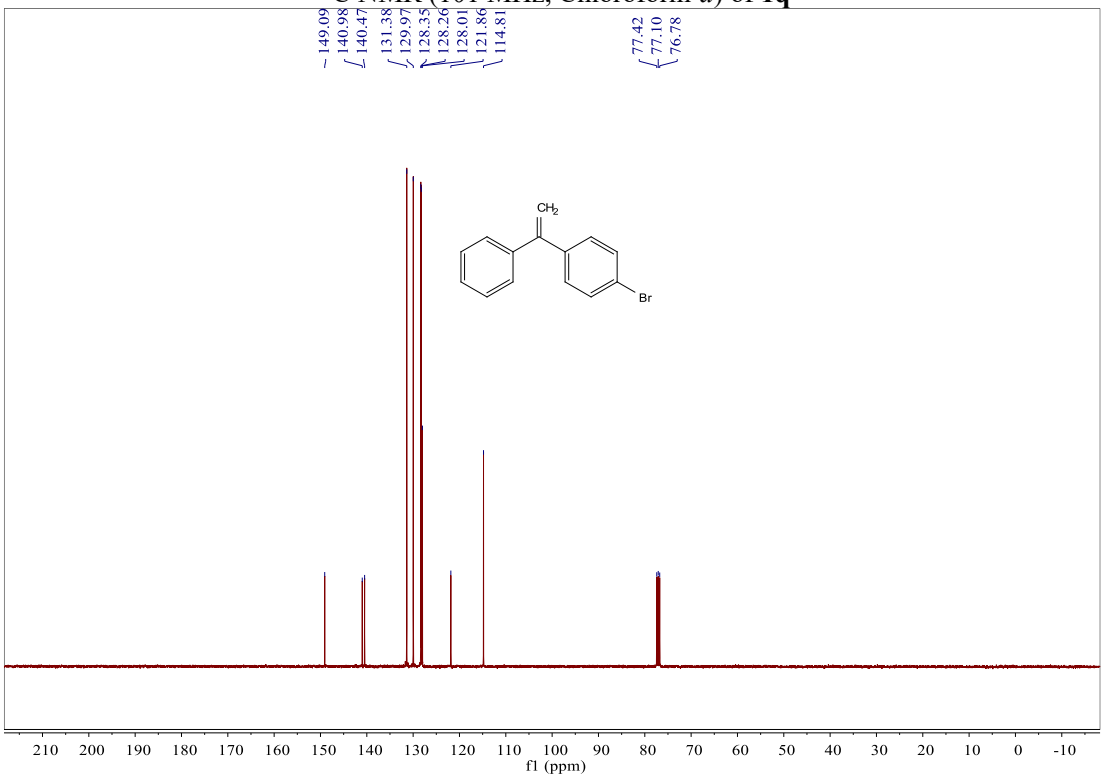
^{13}C NMR (101 MHz, Chloroform-*d*) of **1p**



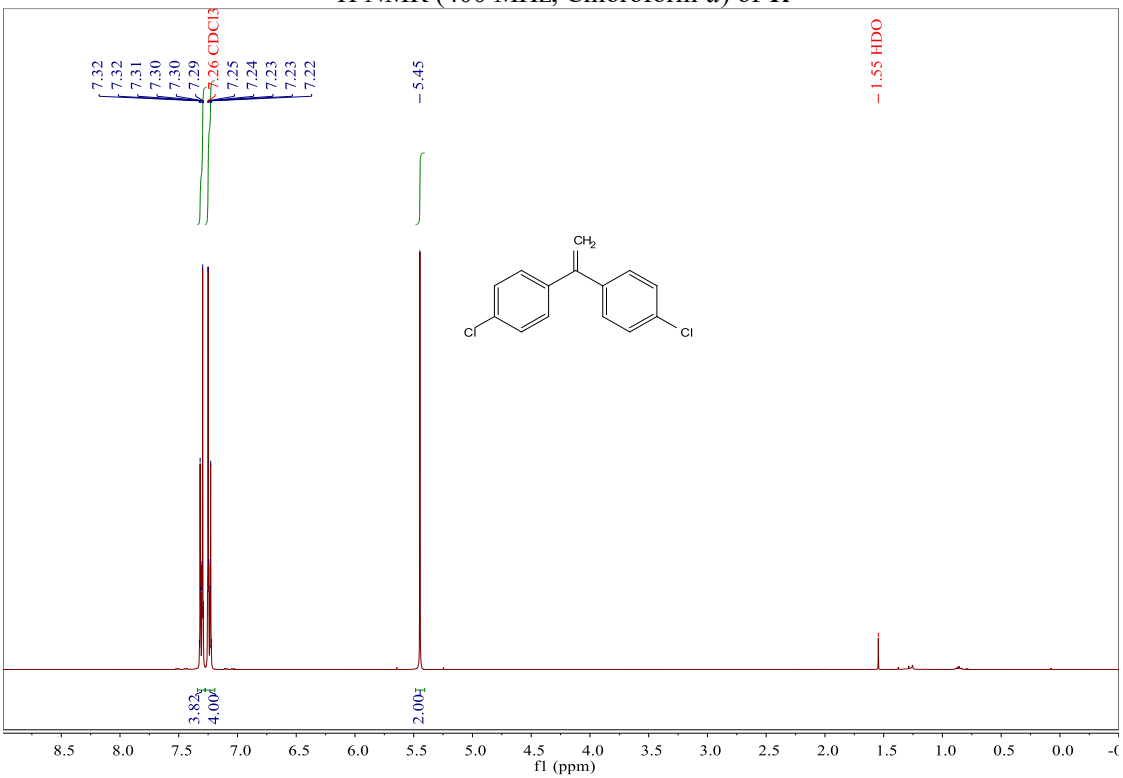
^{1}H NMR (400 MHz, Chloroform-*d*) of **1q**



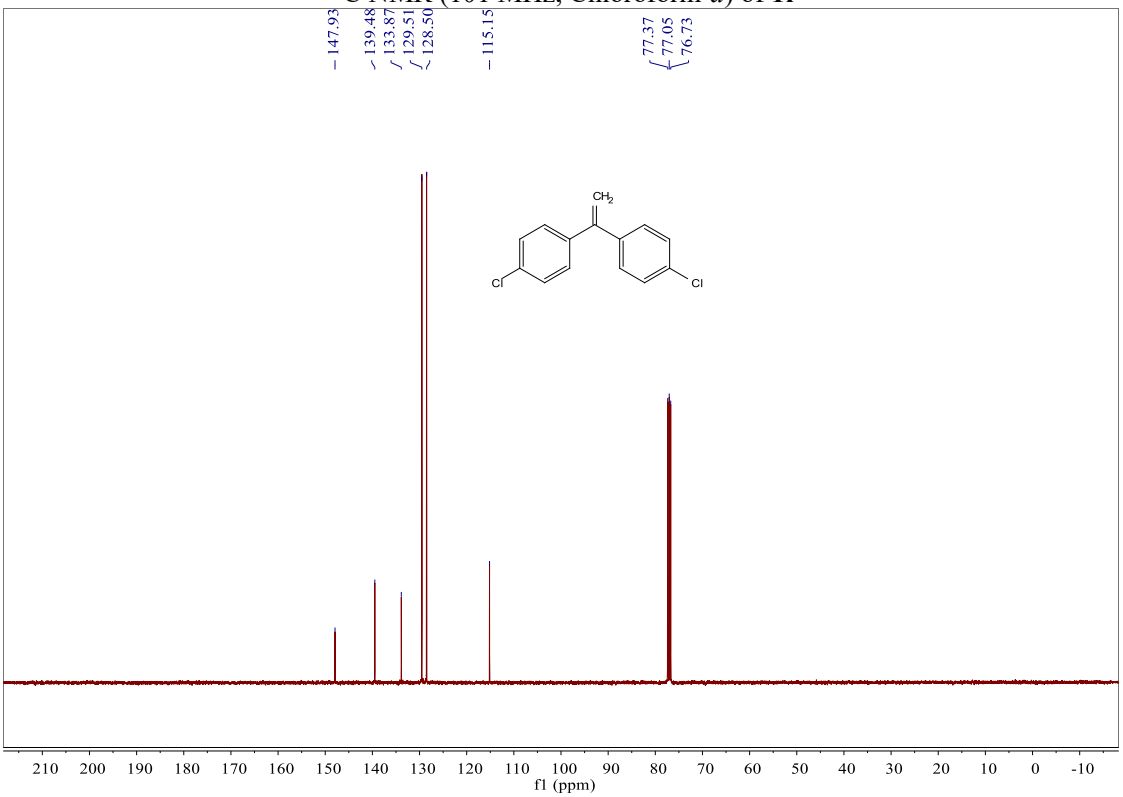
^{13}C NMR (101 MHz, Chloroform-*d*) of **1q**



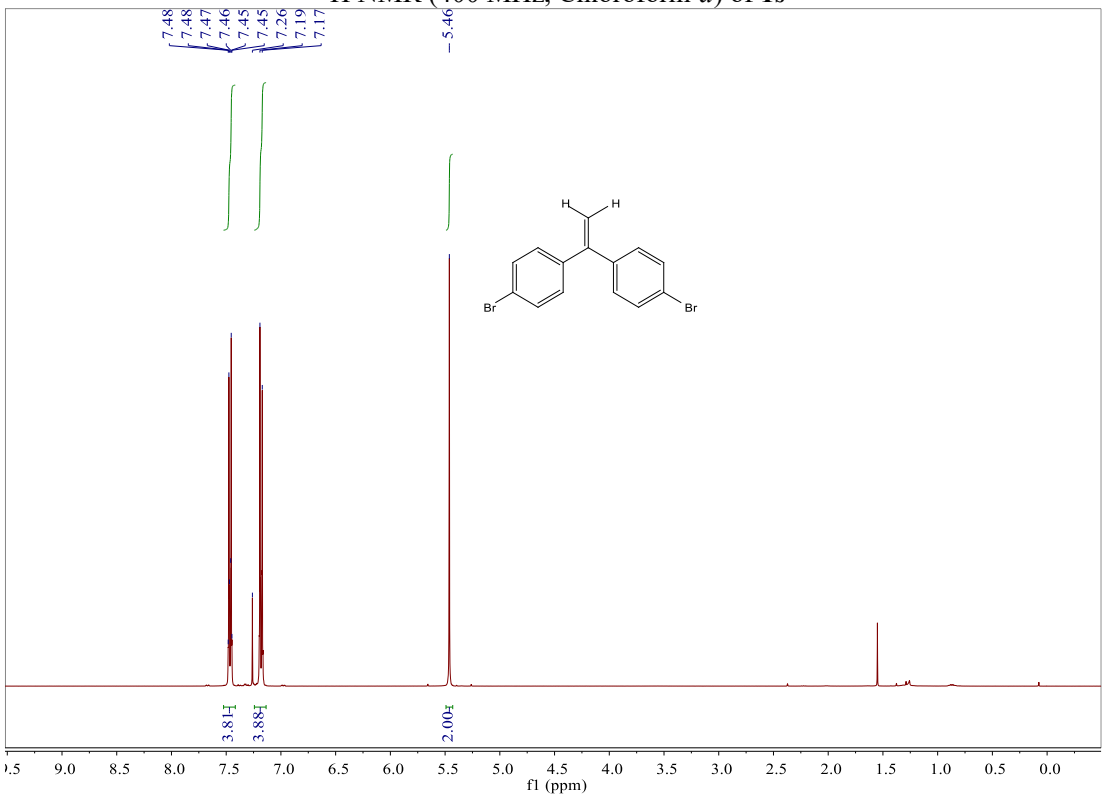
^{1}H NMR (400 MHz, Chloroform-*d*) of **1r**



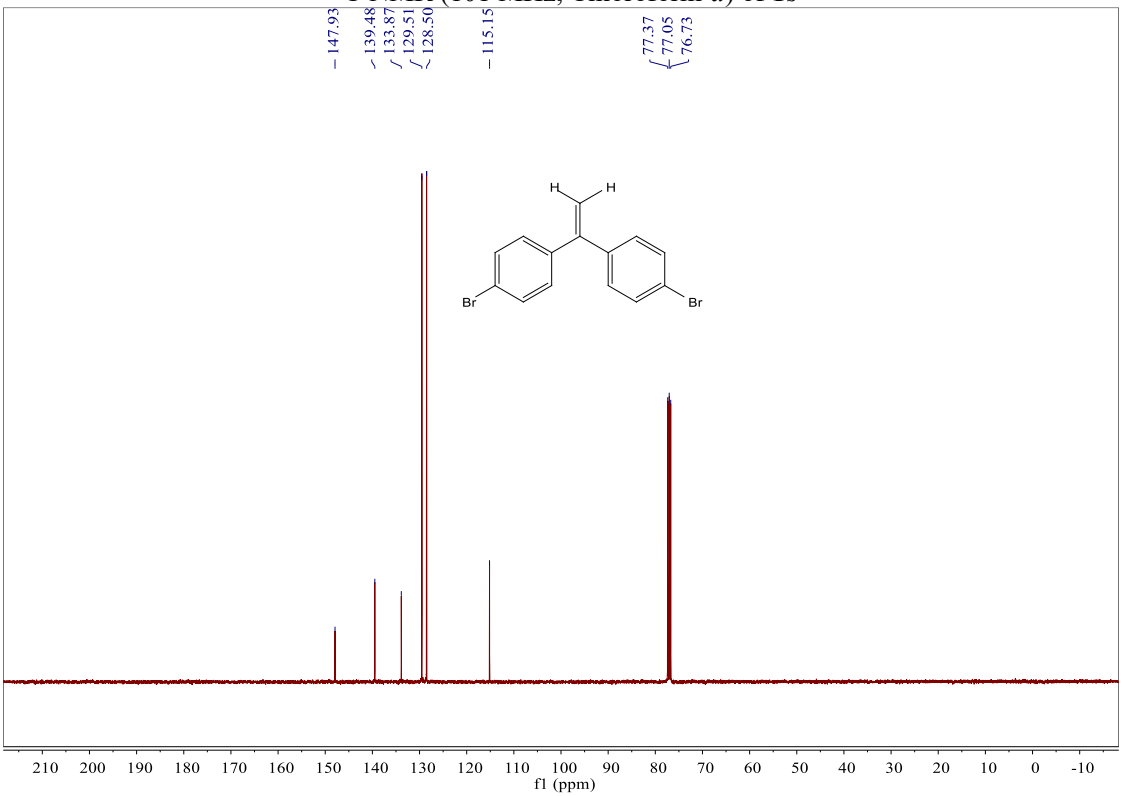
^{13}C NMR (101 MHz, Chloroform-*d*) of **1r**



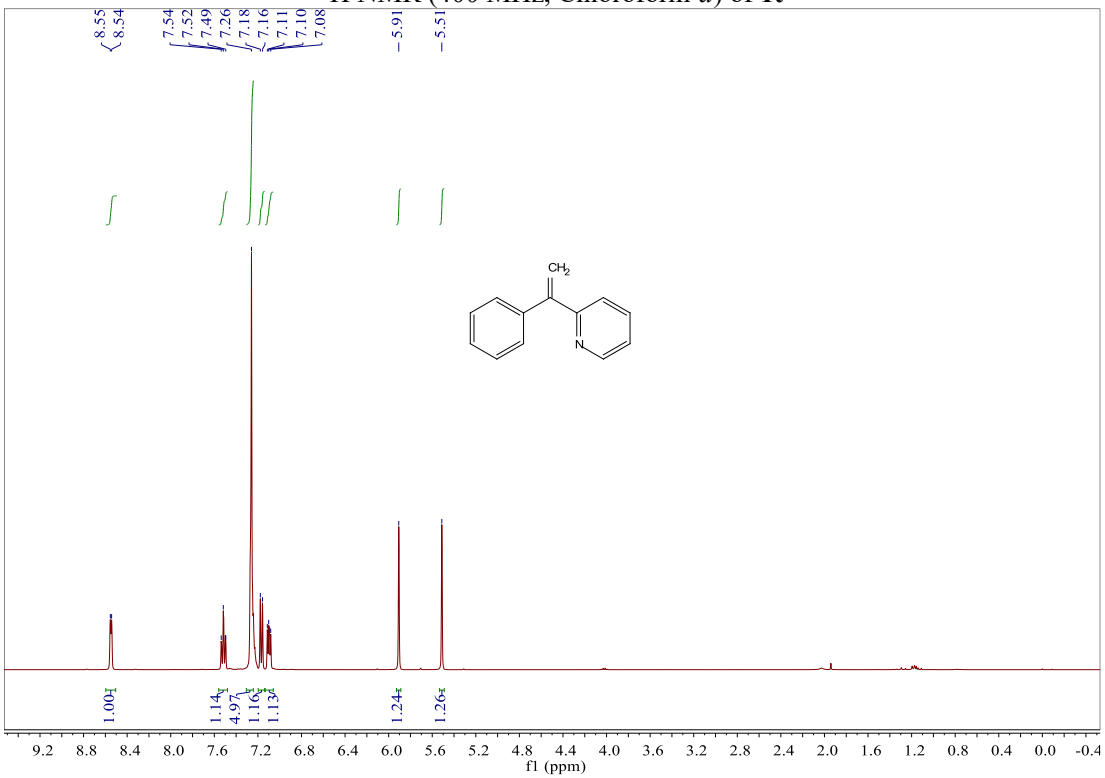
^{1}H NMR (400 MHz, Chloroform-*d*) of **1s**



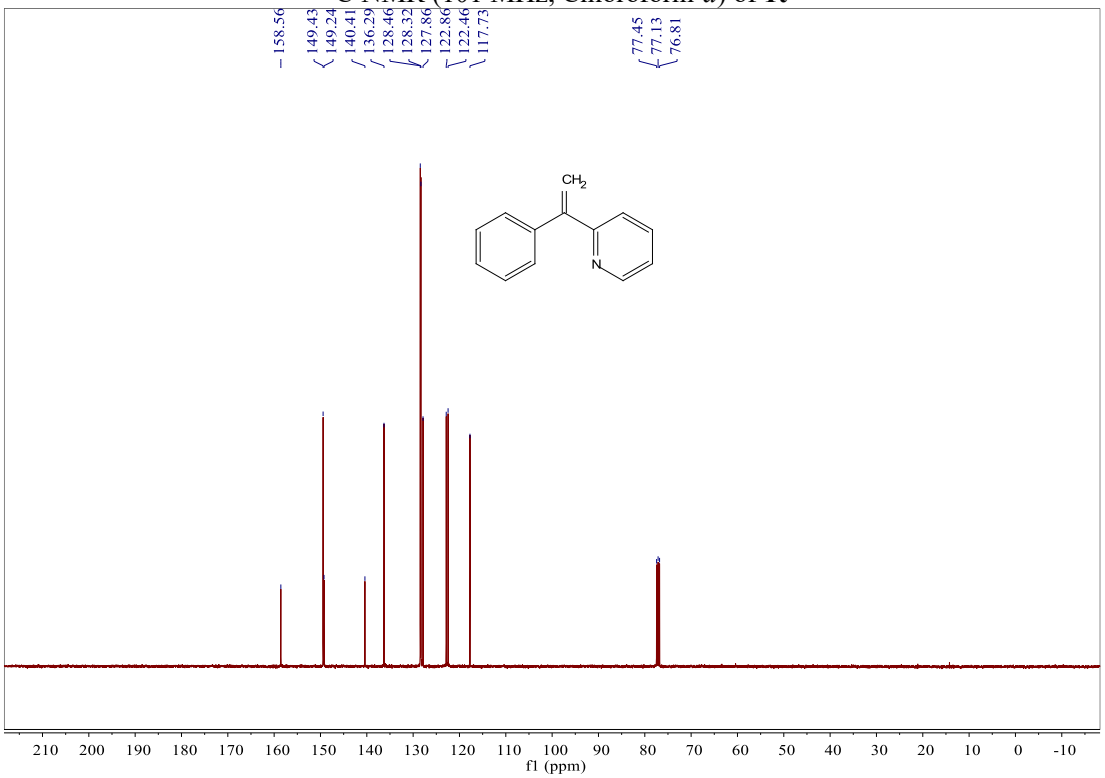
^{13}C NMR (101 MHz, Chloroform-*d*) of **1s**



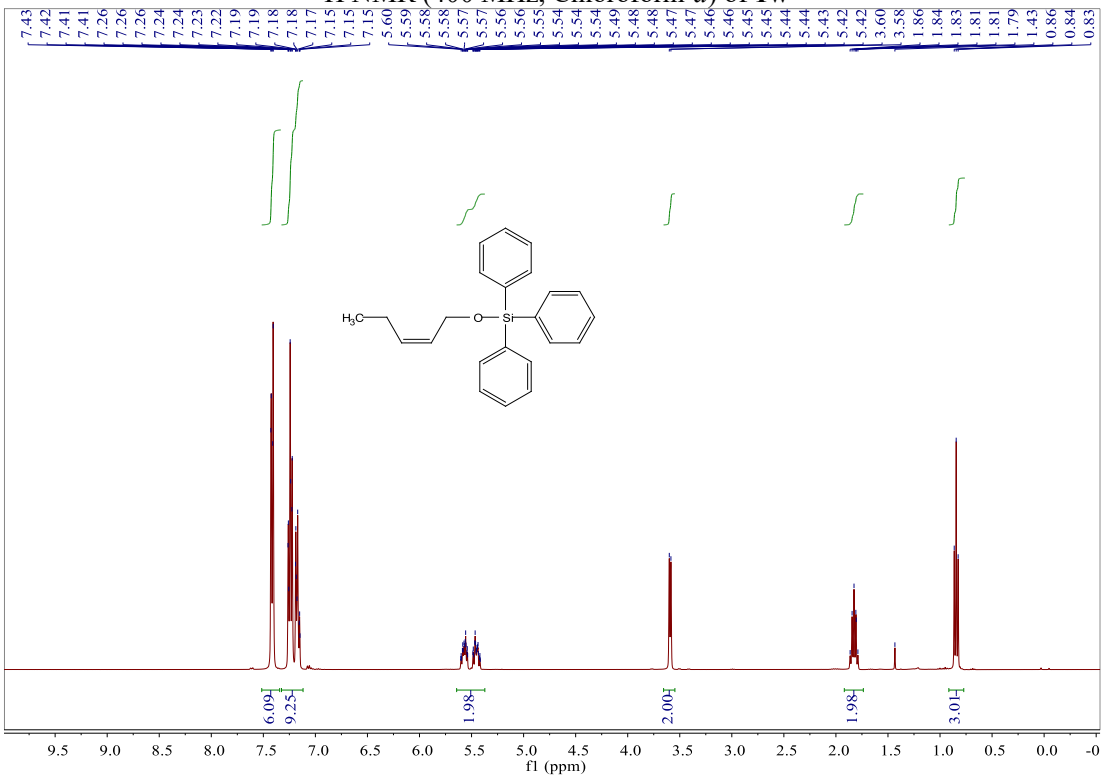
^{1}H NMR (400 MHz, Chloroform-*d*) of **1t**



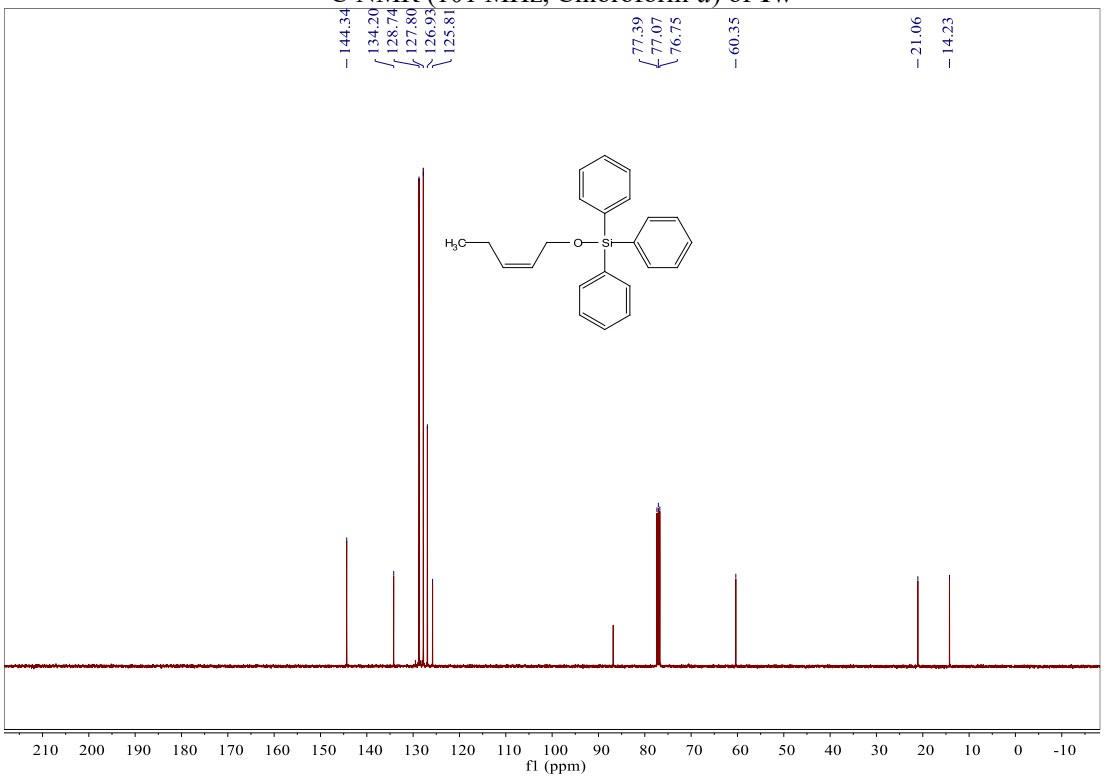
^{13}C NMR (101 MHz, Chloroform-*d*) of **1t**



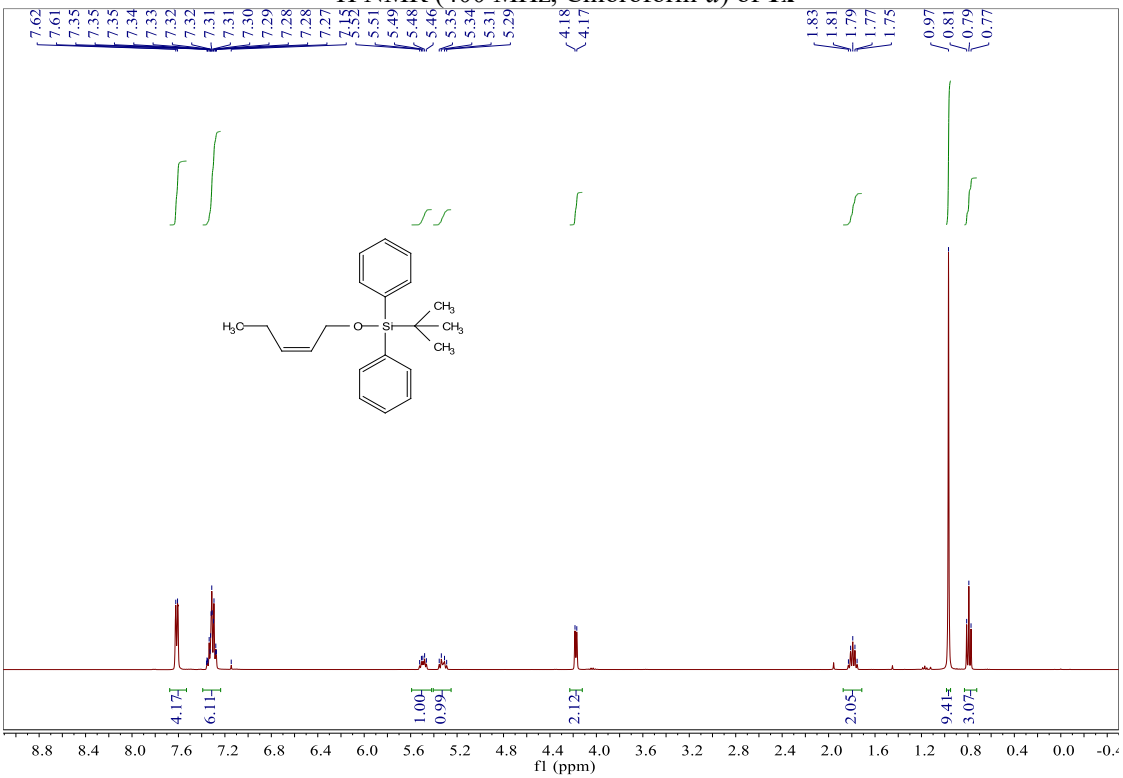
^{1}H NMR (400 MHz, Chloroform-*d*) of **1w**



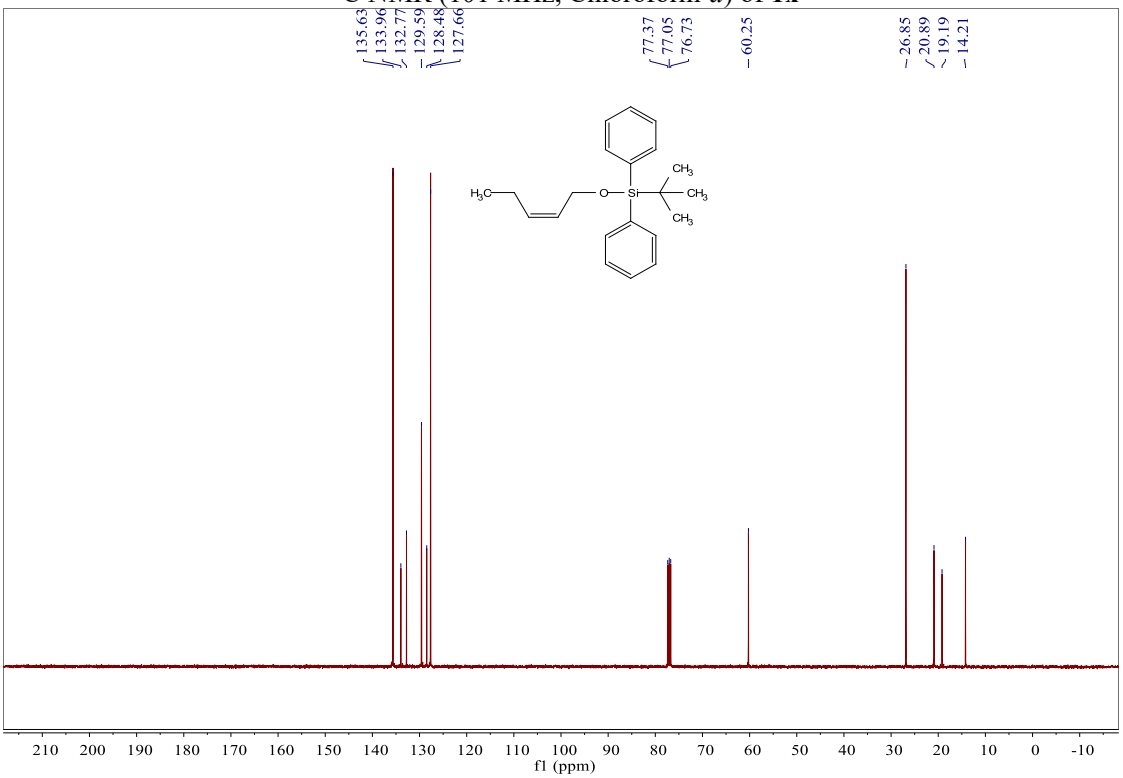
^{13}C NMR (101 MHz, Chloroform-*d*) of **1w**



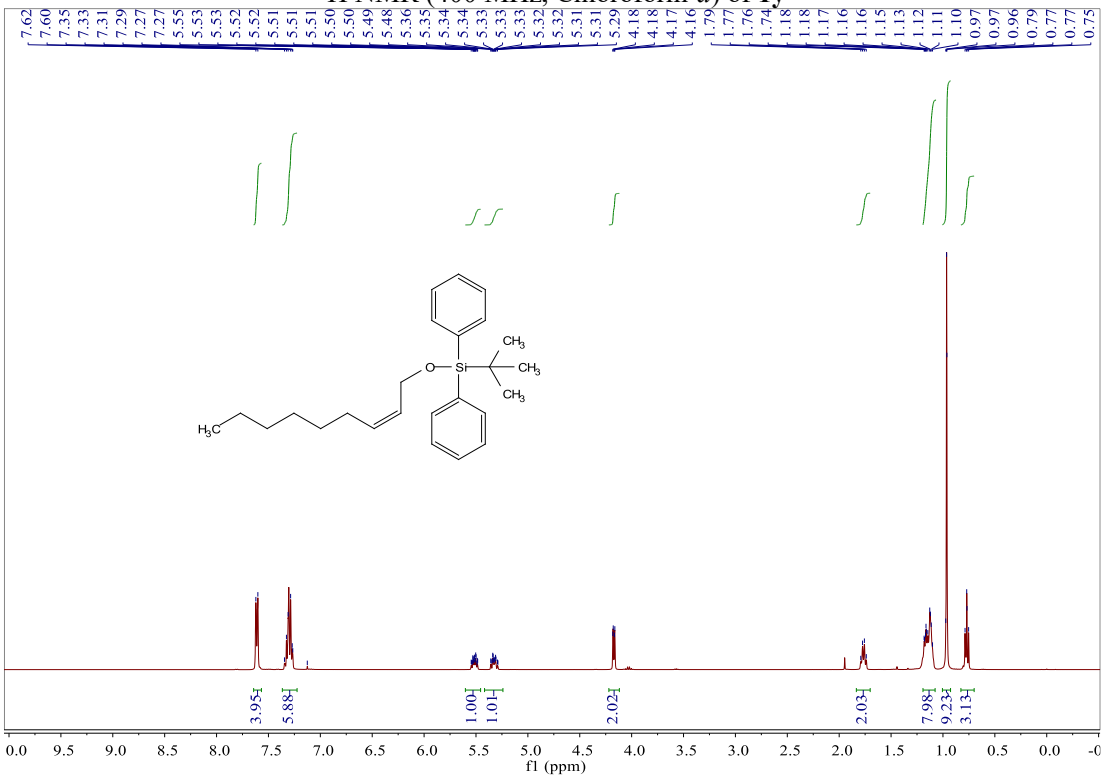
^{1}H NMR (400 MHz, Chloroform-*d*) of **1x**



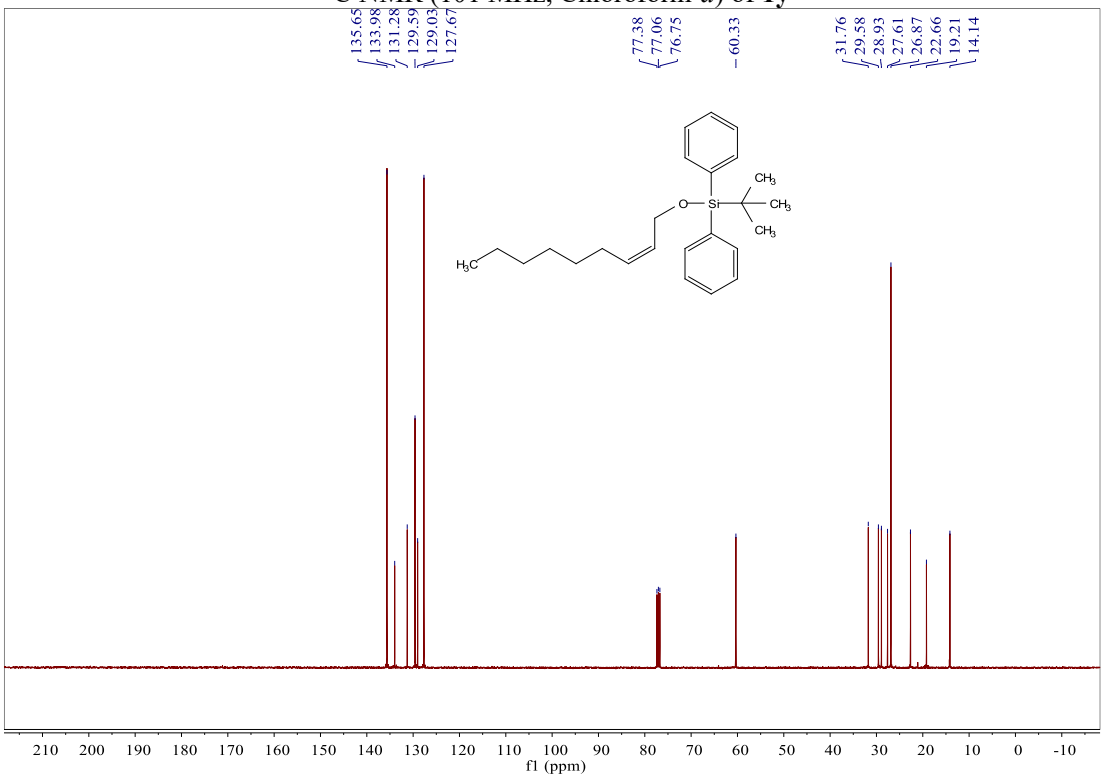
^{13}C NMR (101 MHz, Chloroform-*d*) of **1x**



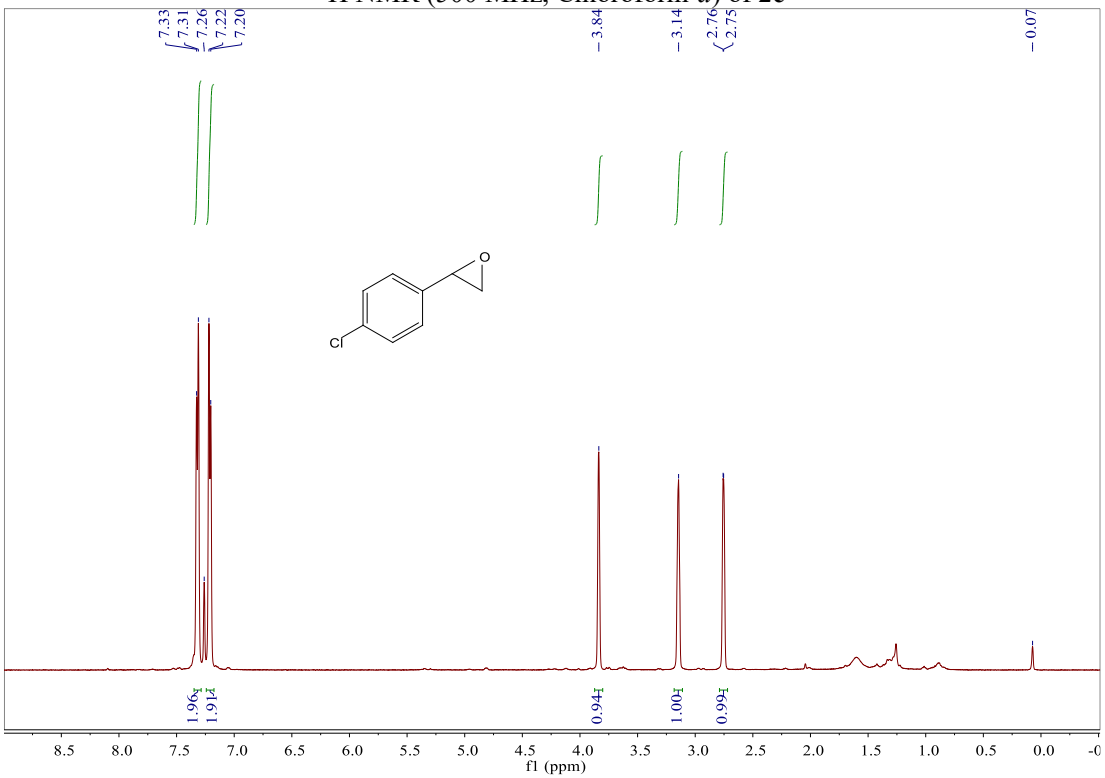
^{1}H NMR (400 MHz, Chloroform-*d*) of **1y**



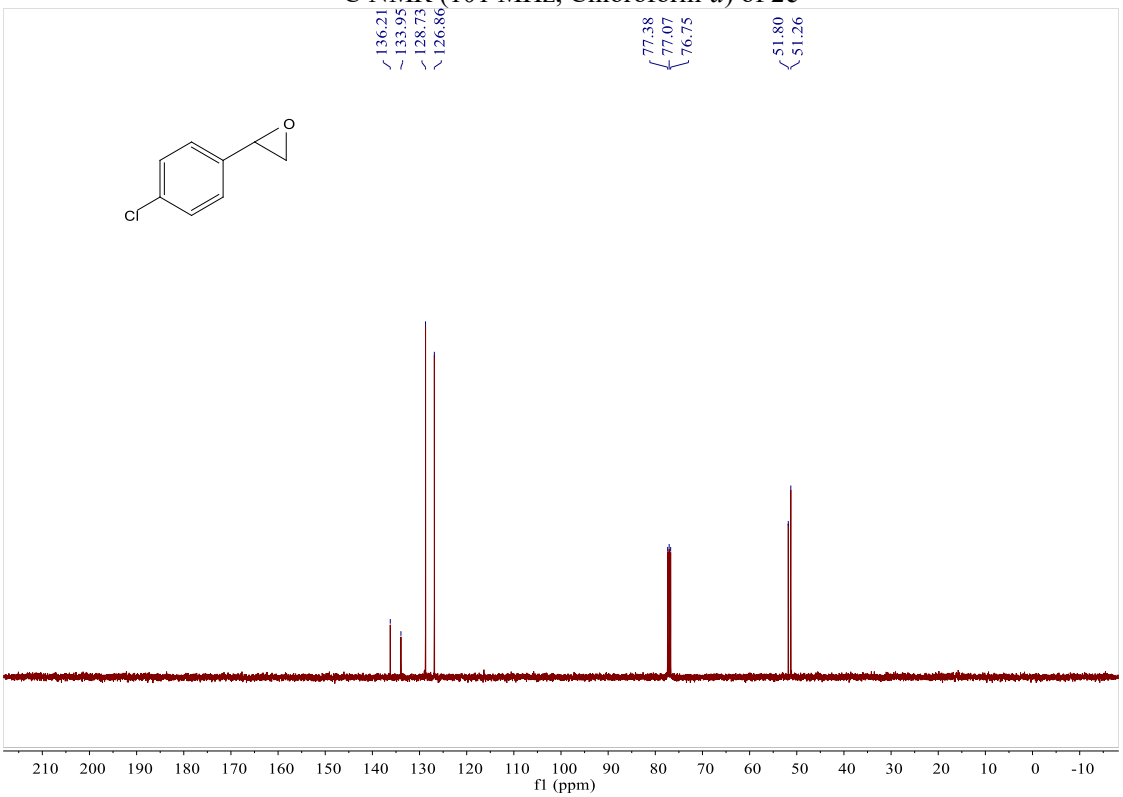
^{13}C NMR (101 MHz, Chloroform-*d*) of **1y**



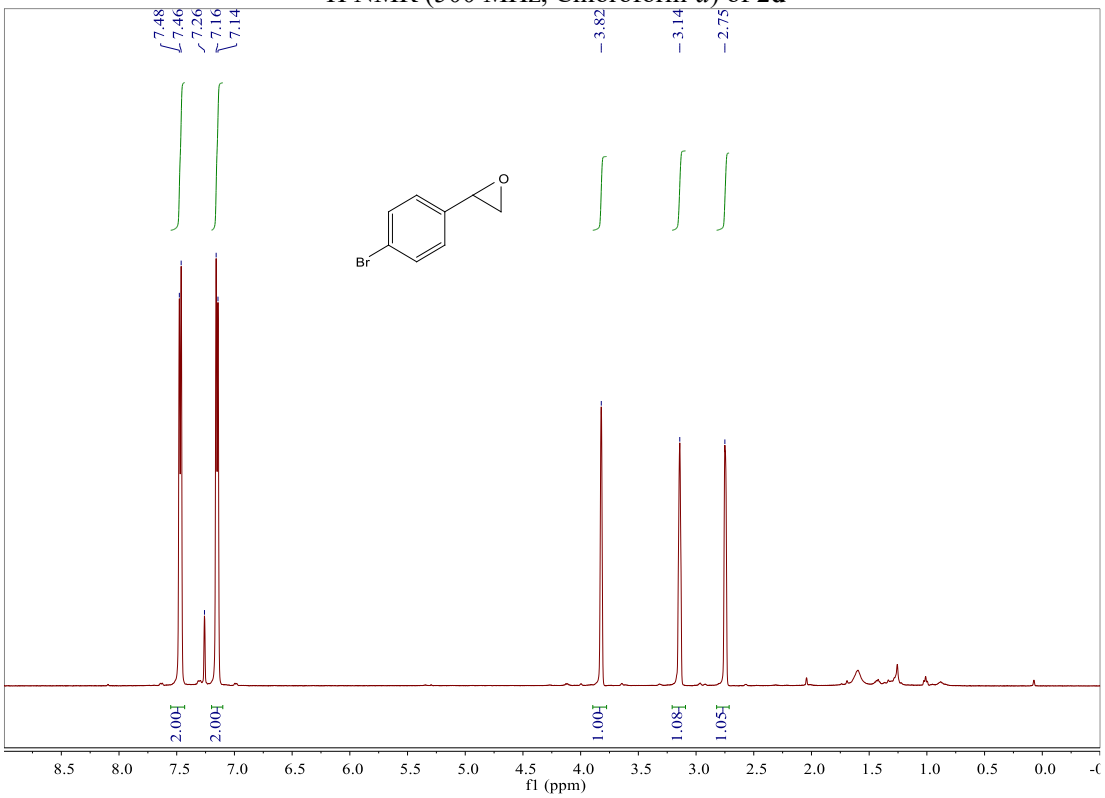
^{1}H NMR (500 MHz, Chloroform-*d*) of **2c**



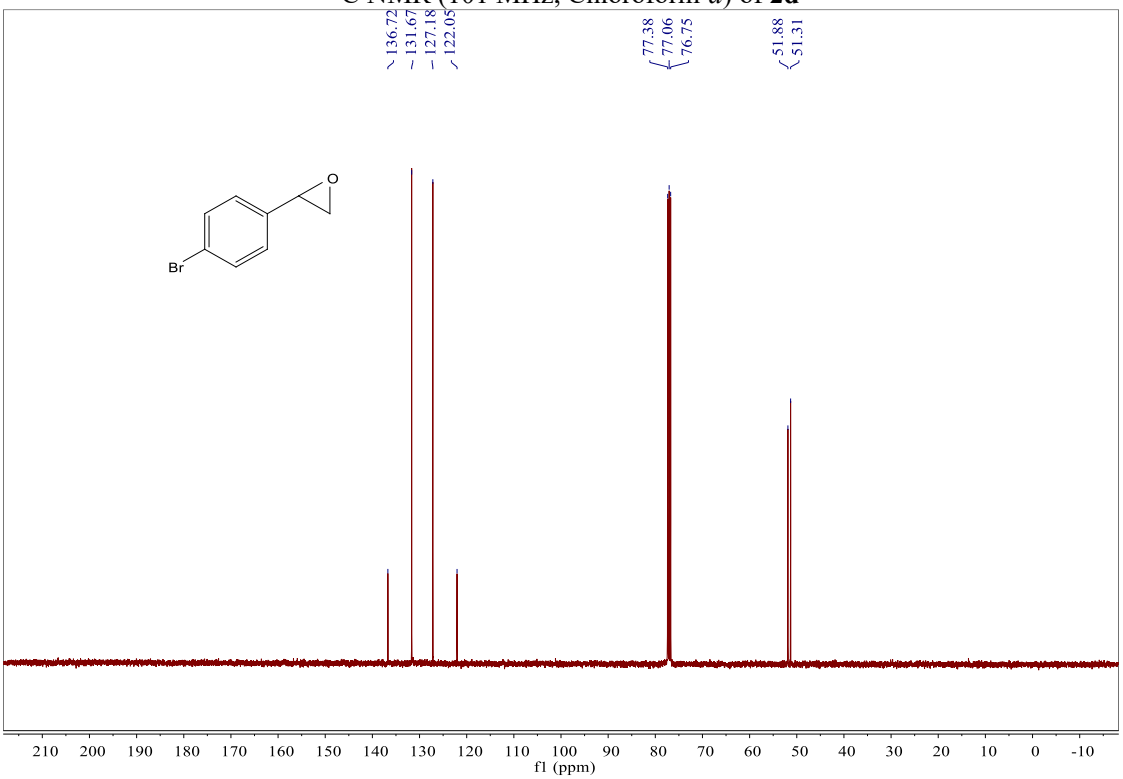
^{13}C NMR (101 MHz, Chloroform-*d*) of **2c**



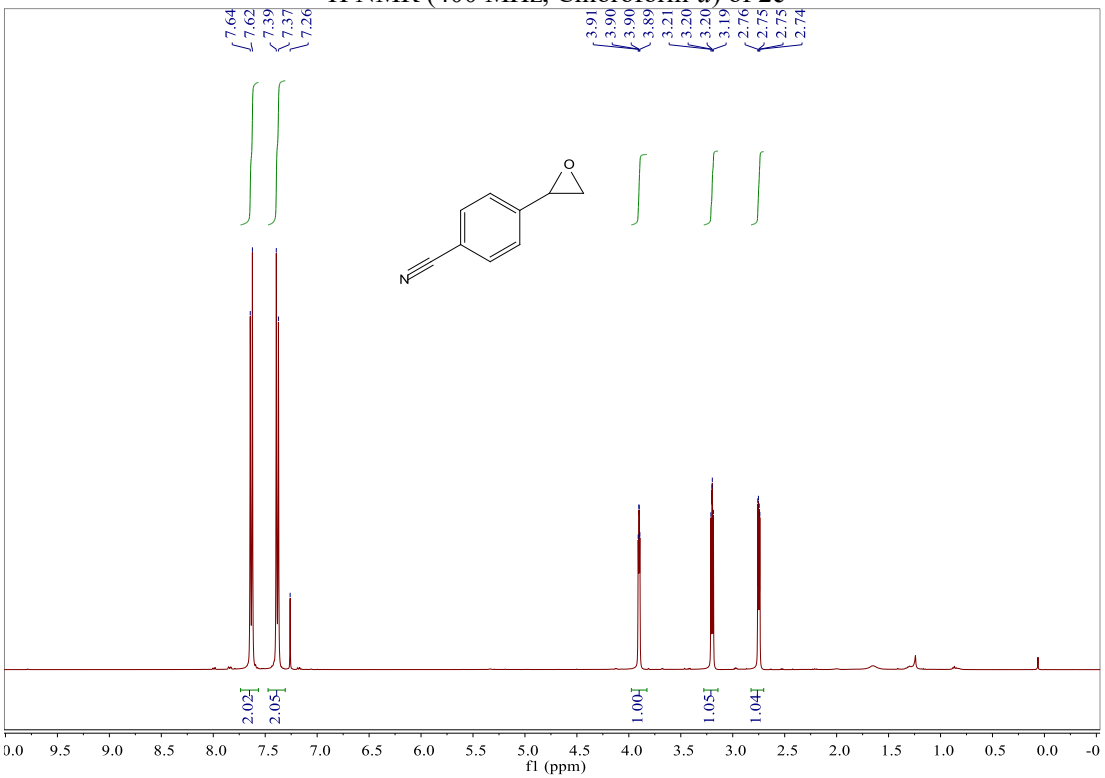
^{1}H NMR (500 MHz, Chloroform-*d*) of **2d**



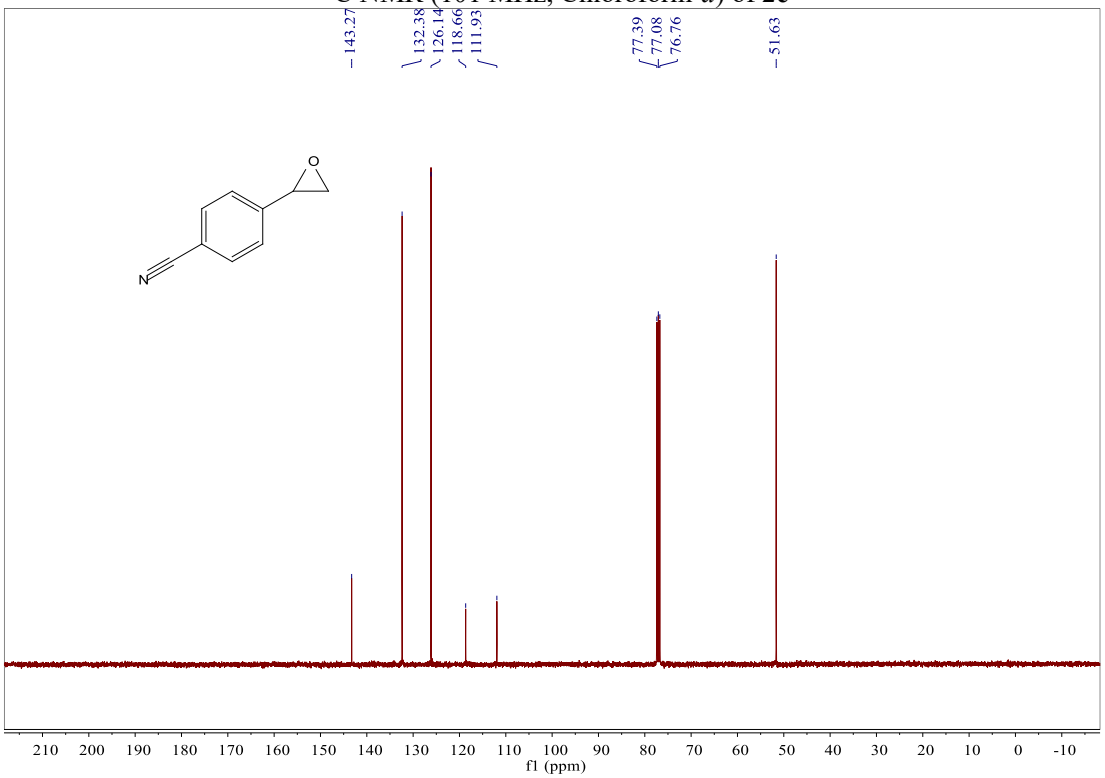
^{13}C NMR (101 MHz, Chloroform-*d*) of **2d**



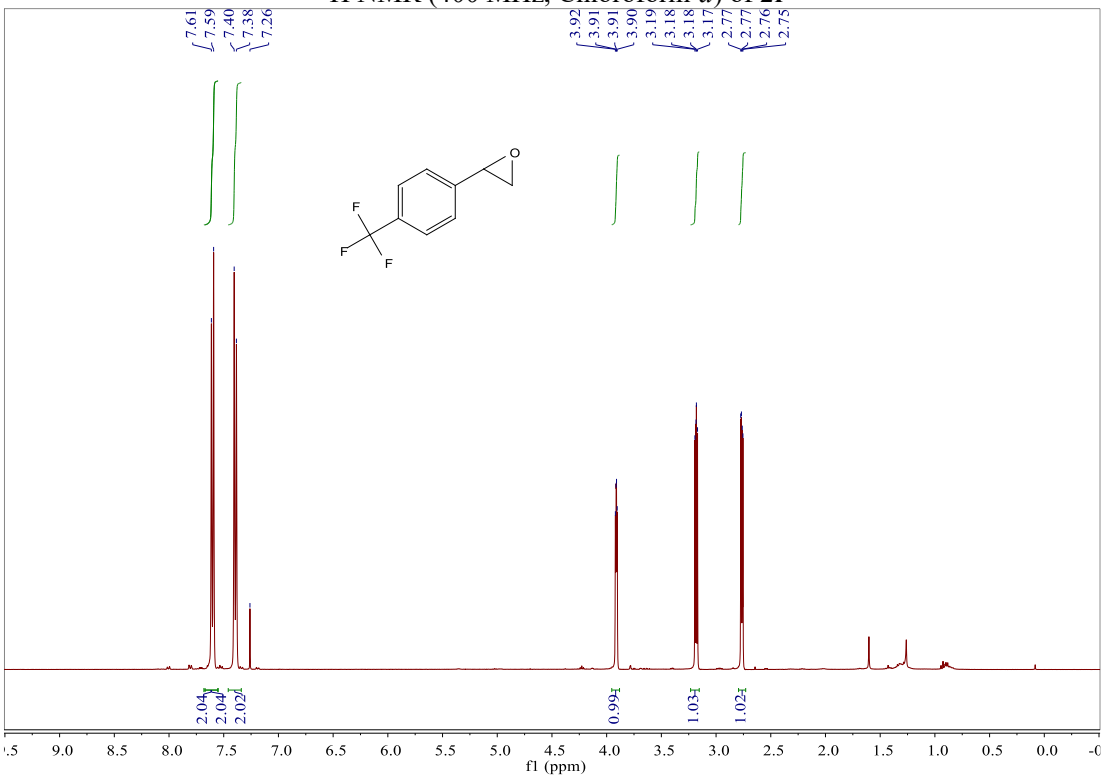
^{1}H NMR (400 MHz, Chloroform-*d*) of 2**e**



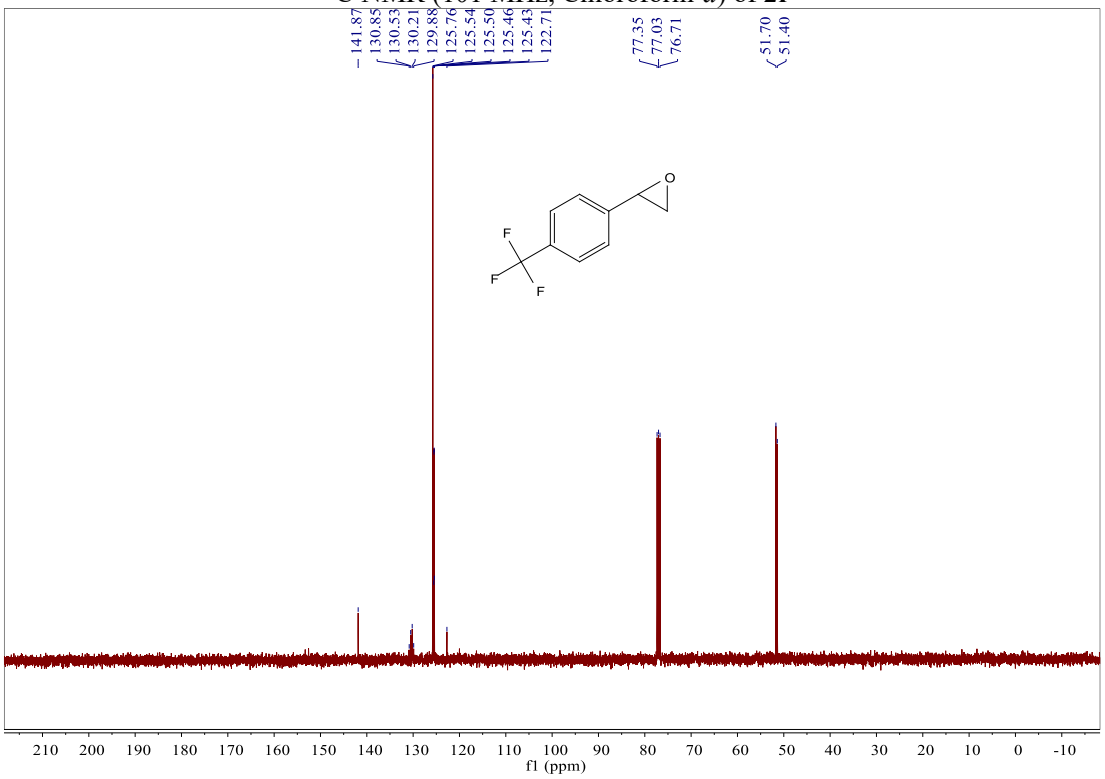
^{13}C NMR (101 MHz, Chloroform-*d*) of **2e**



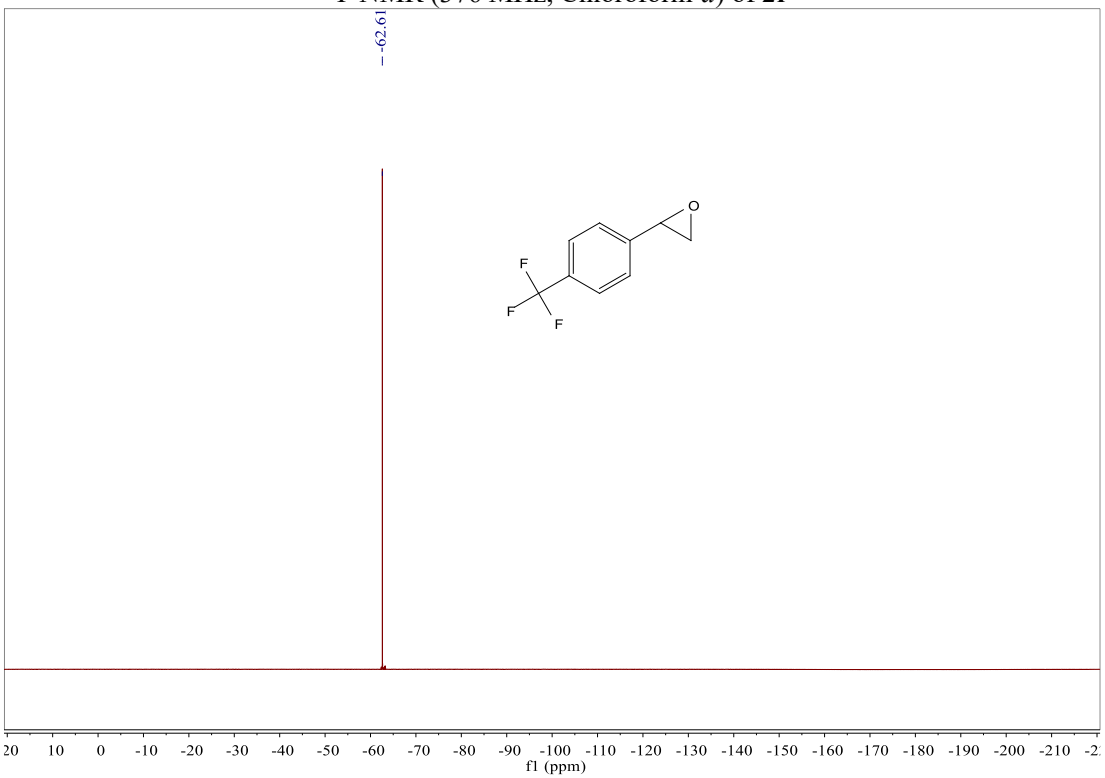
^{1}H NMR (400 MHz, Chloroform-*d*) of **2f**



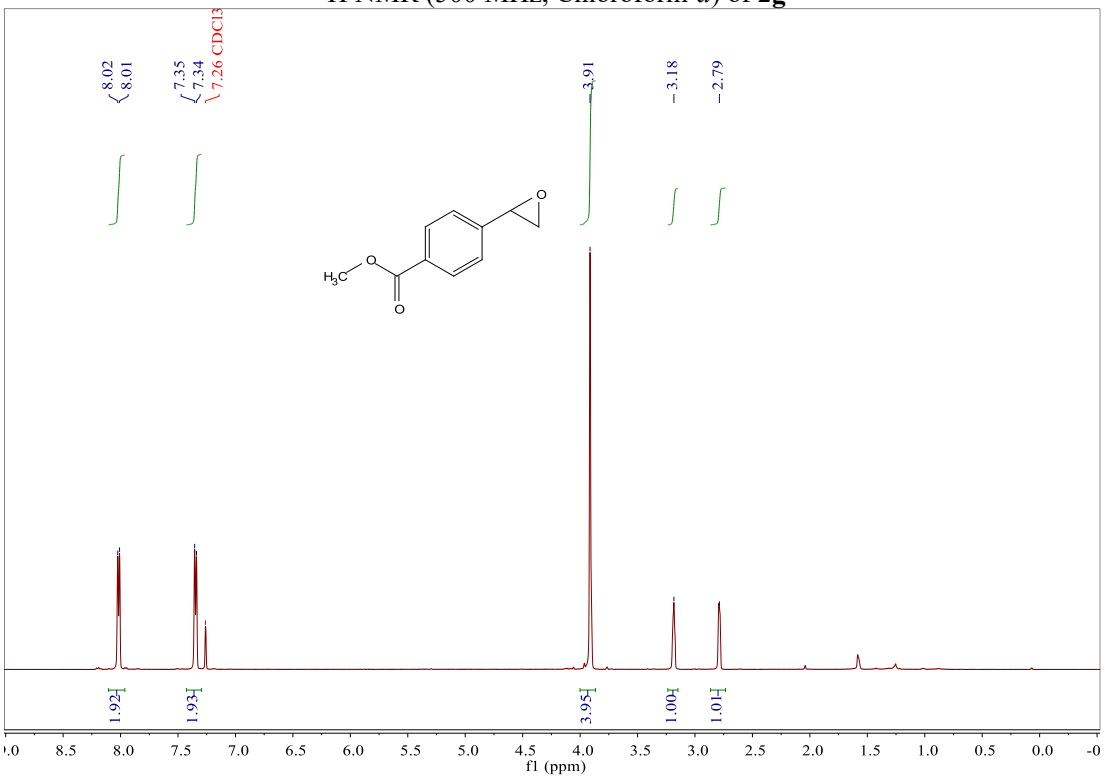
^{13}C NMR (101 MHz, Chloroform-*d*) of **2f**



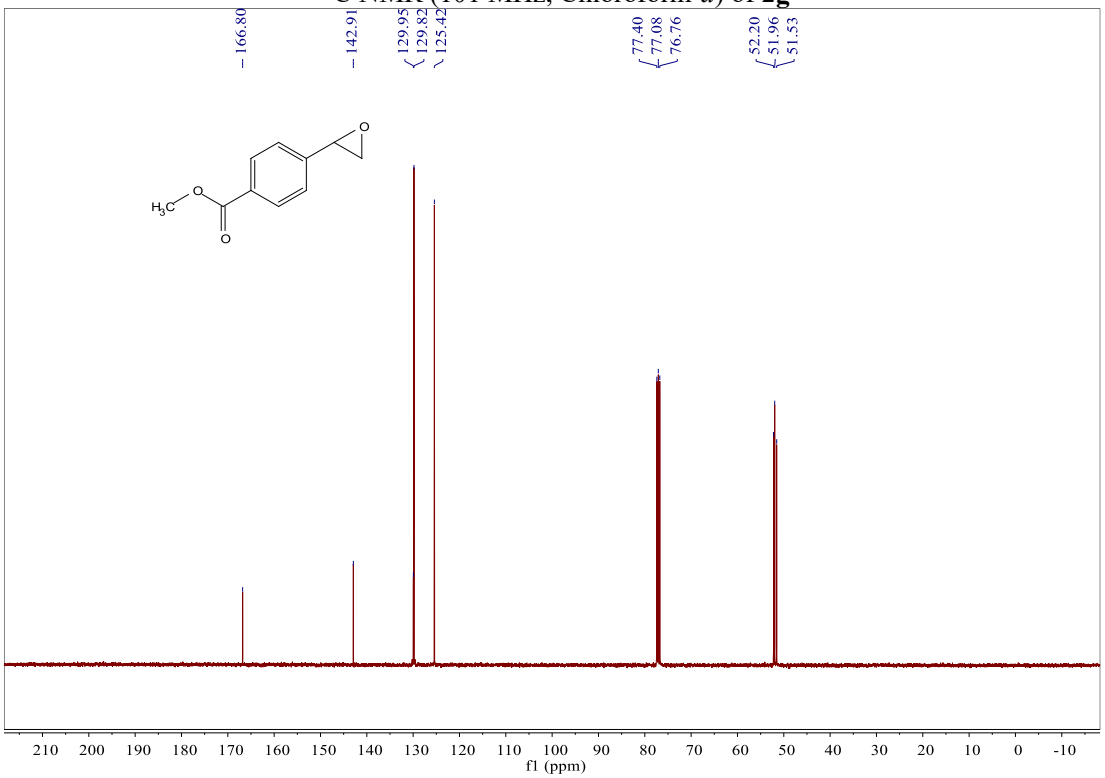
^{19}F NMR (376 MHz, Chloroform-*d*) of **2f**



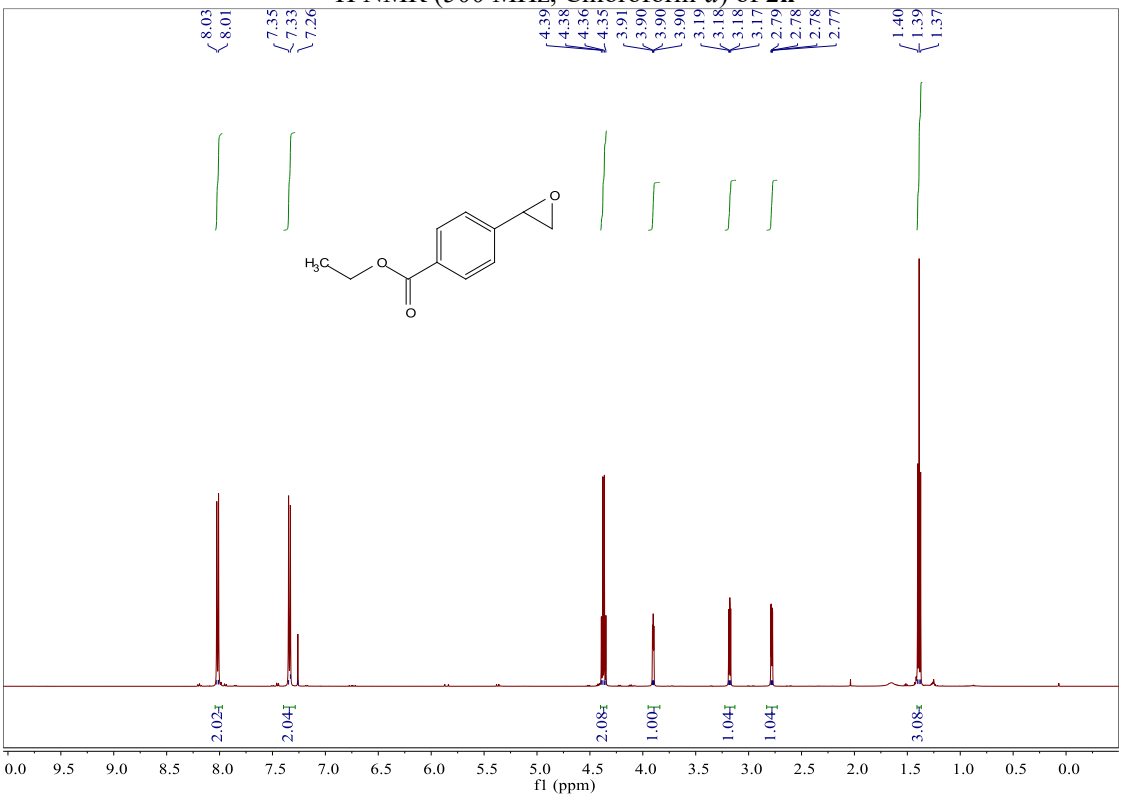
^{1}H NMR (500 MHz, Chloroform-*d*) of **2g**



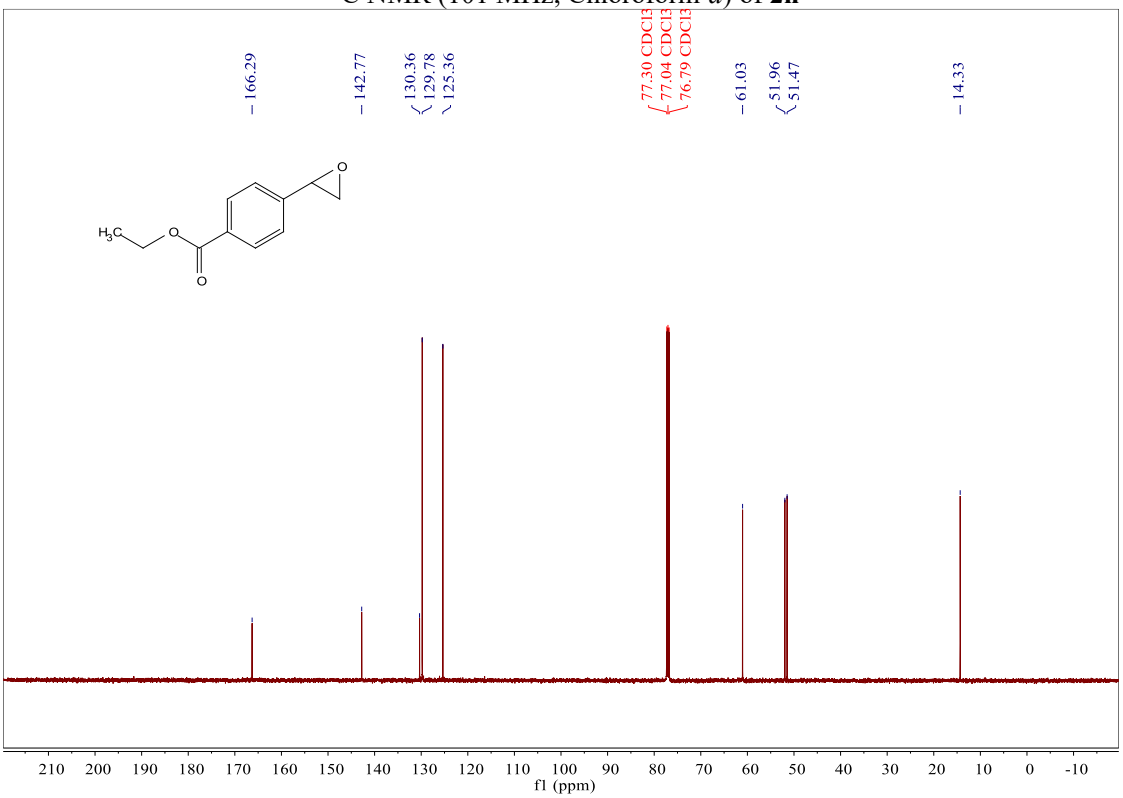
^{13}C NMR (101 MHz, Chloroform-*d*) of **2g**



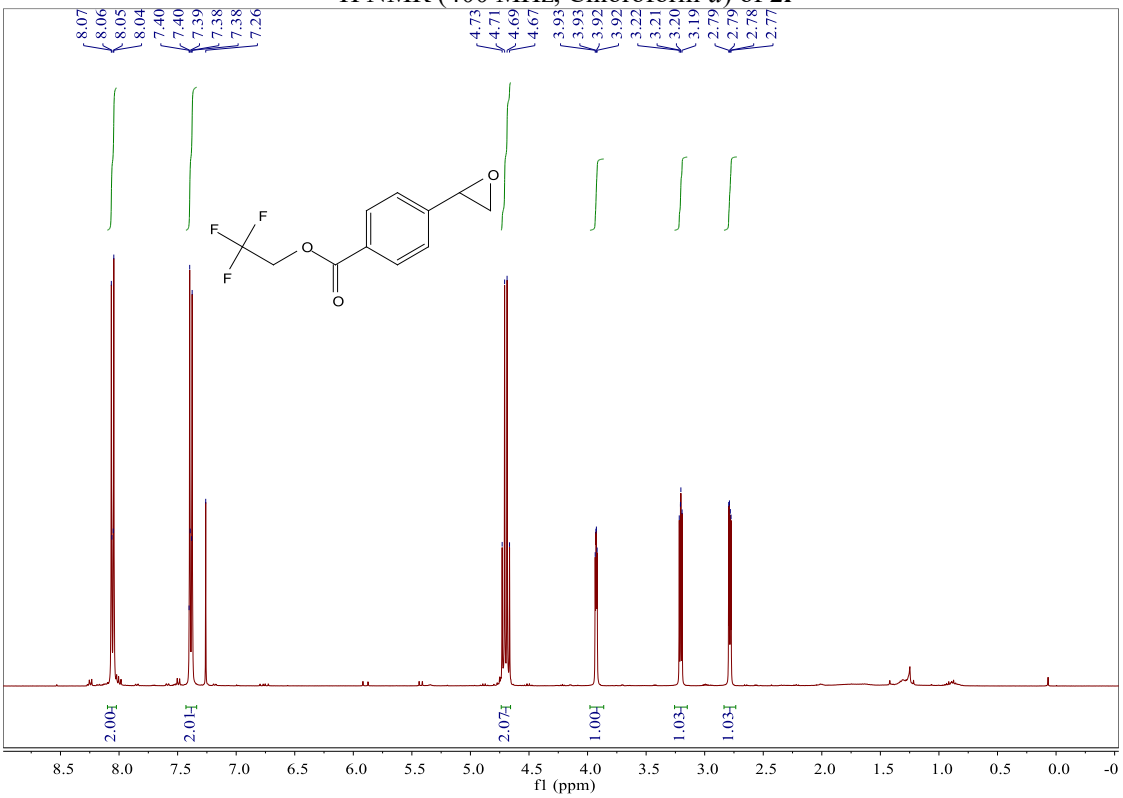
^{1}H NMR (500 MHz, Chloroform-*d*) of **2h**



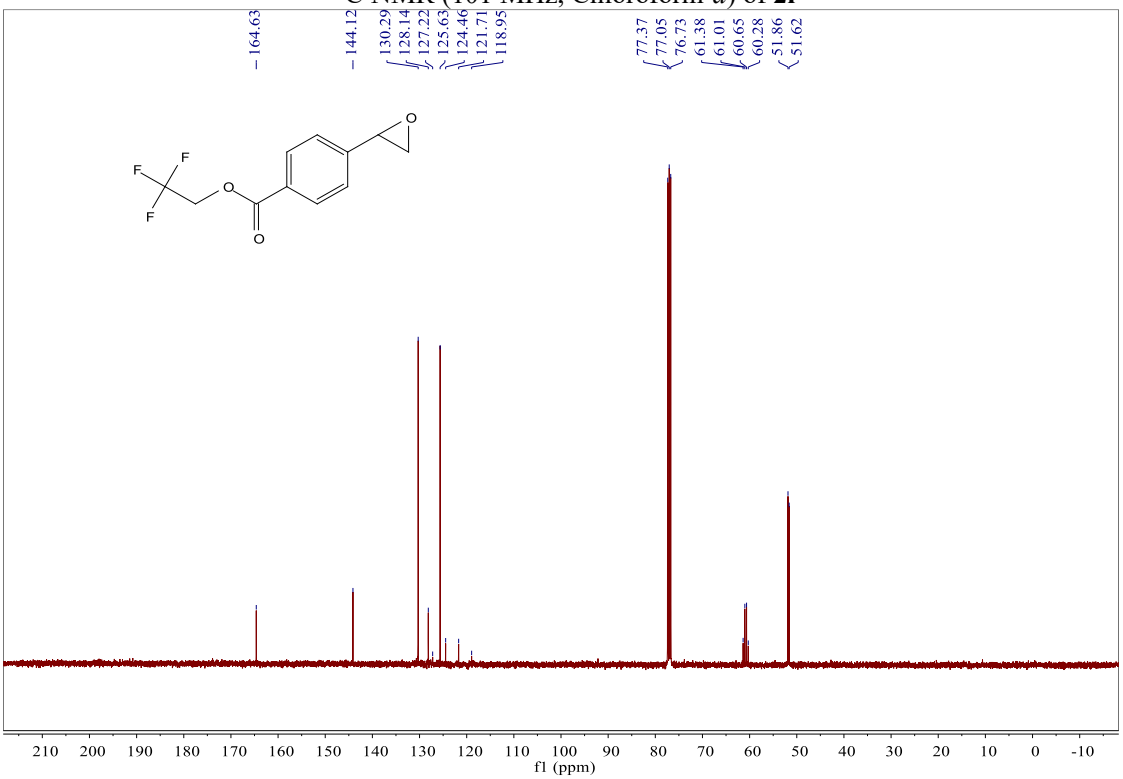
^{13}C NMR (101 MHz, Chloroform-*d*) of **2h**



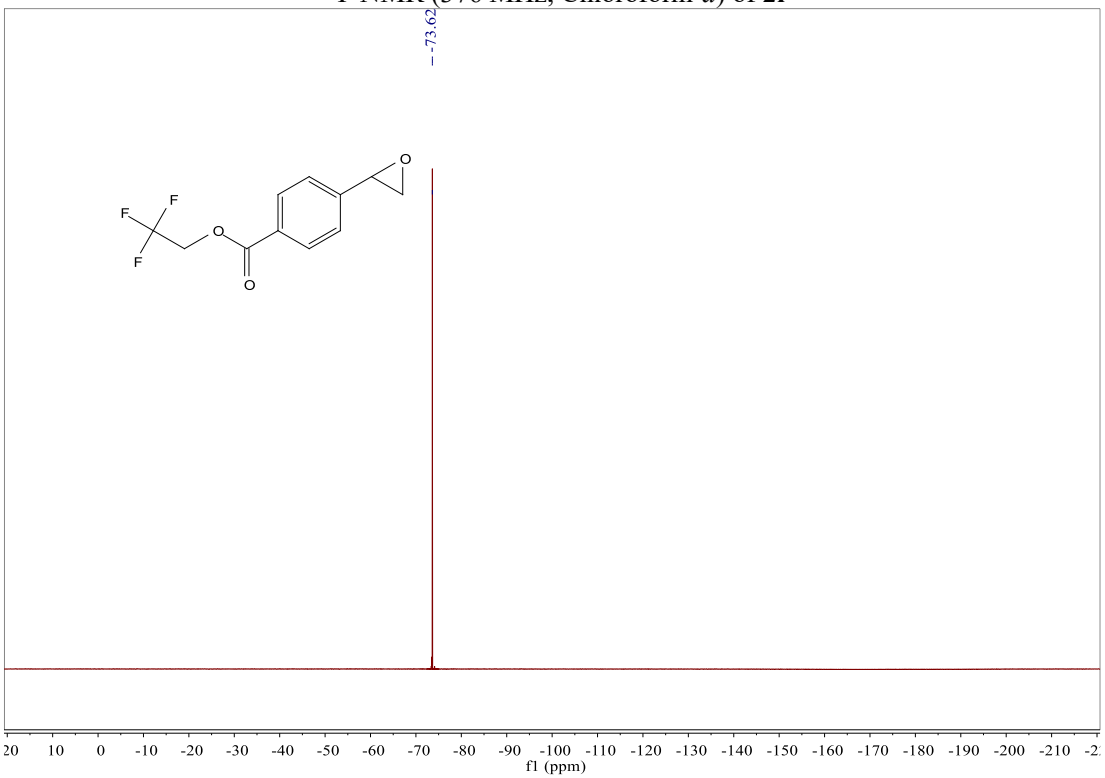
^{1}H NMR (400 MHz, Chloroform-*d*) of **2i**



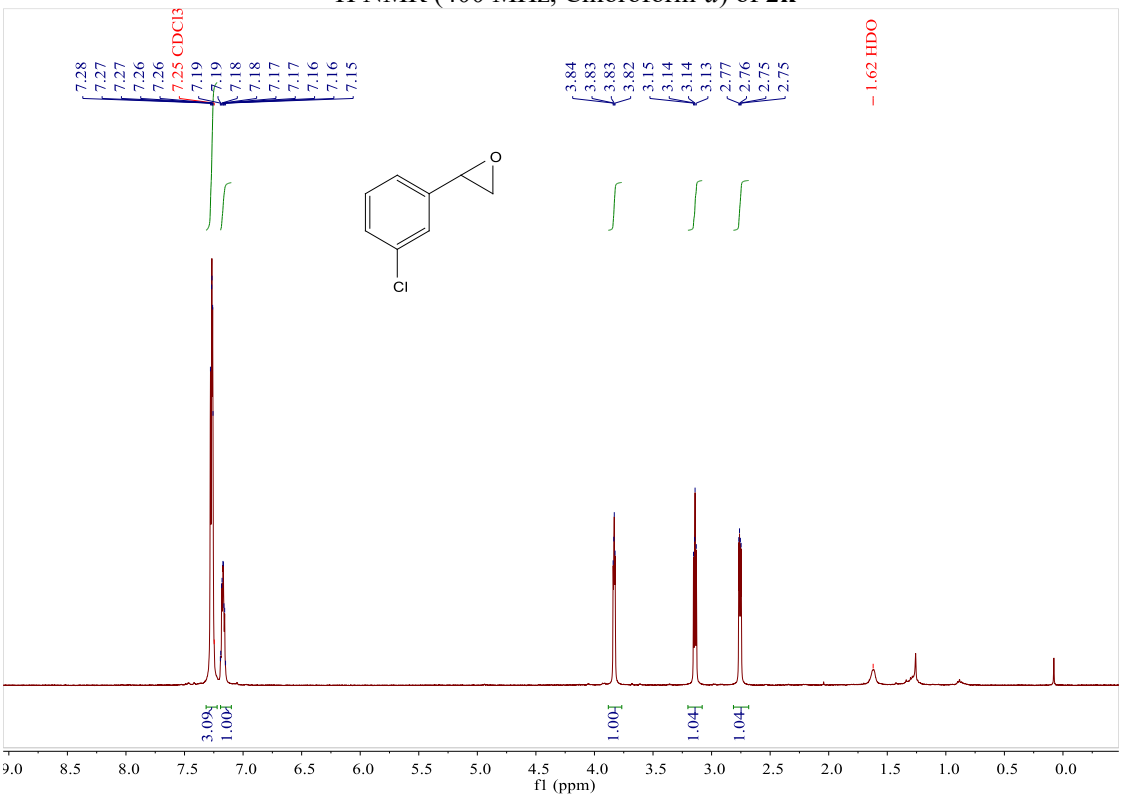
^{13}C NMR (101 MHz, Chloroform-*d*) of **2i**



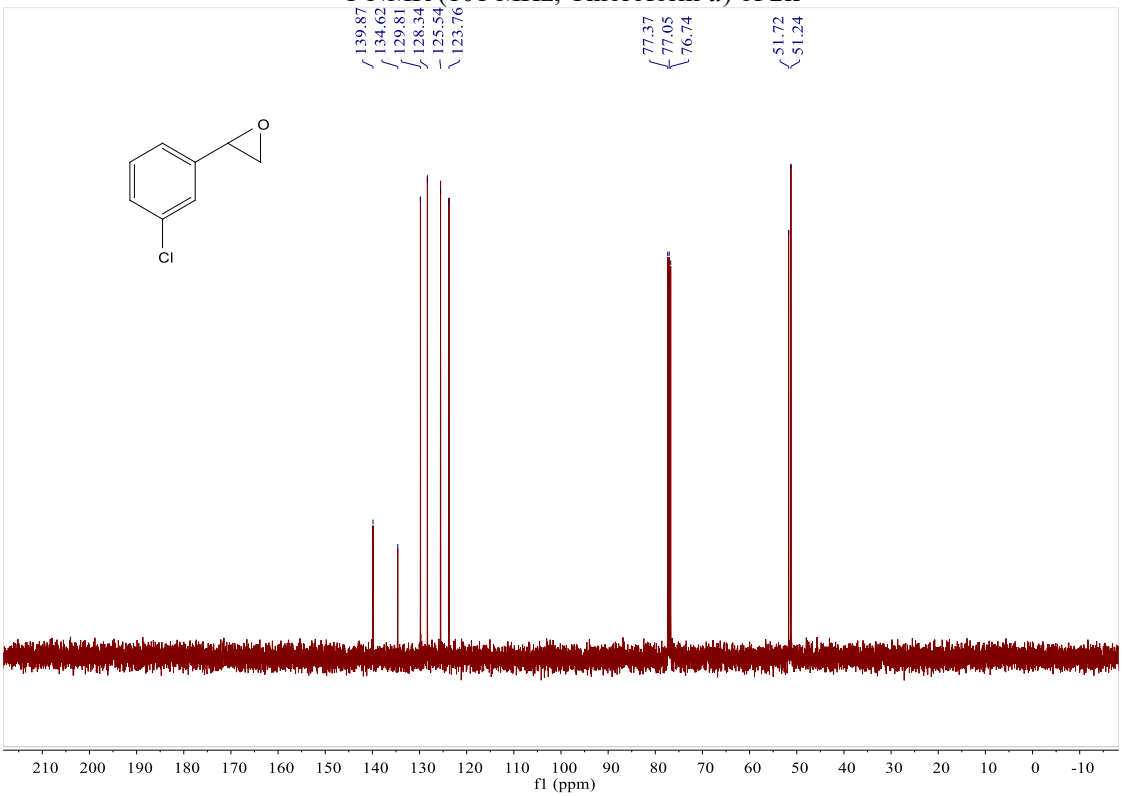
^{19}F NMR (376 MHz, Chloroform-*d*) of **2i**



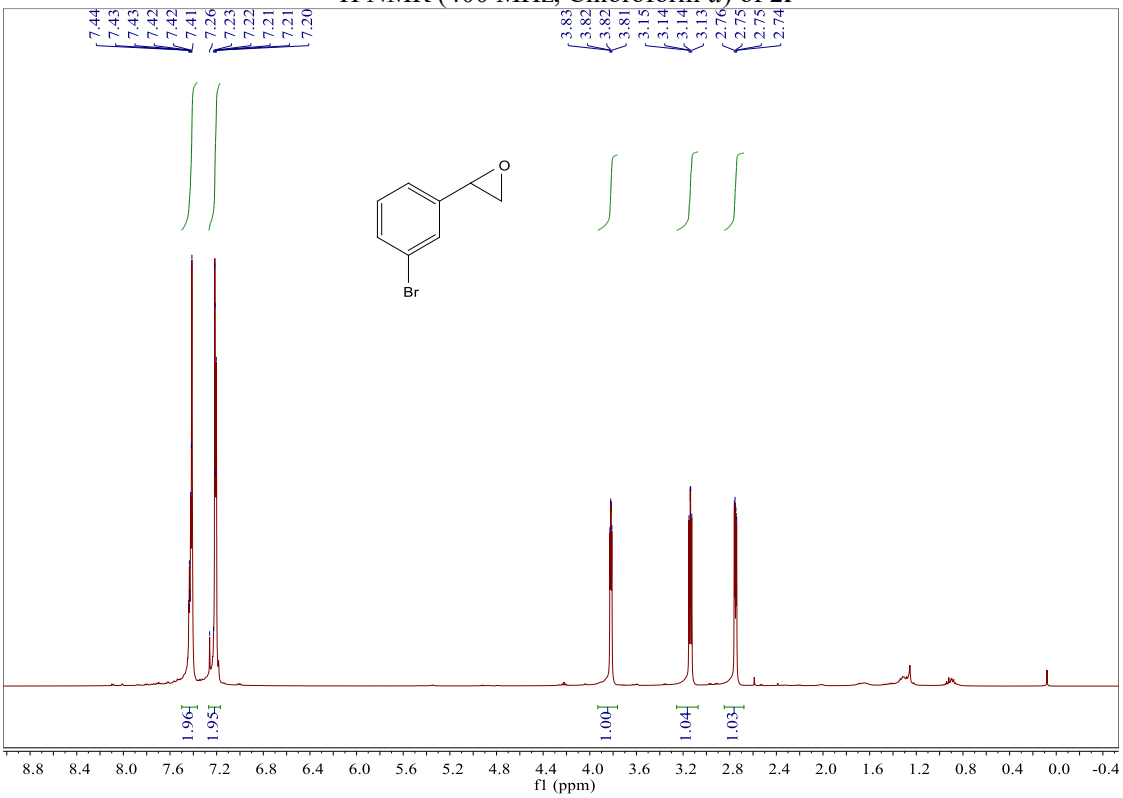
^{1}H NMR (400 MHz, Chloroform-*d*) of **2k**



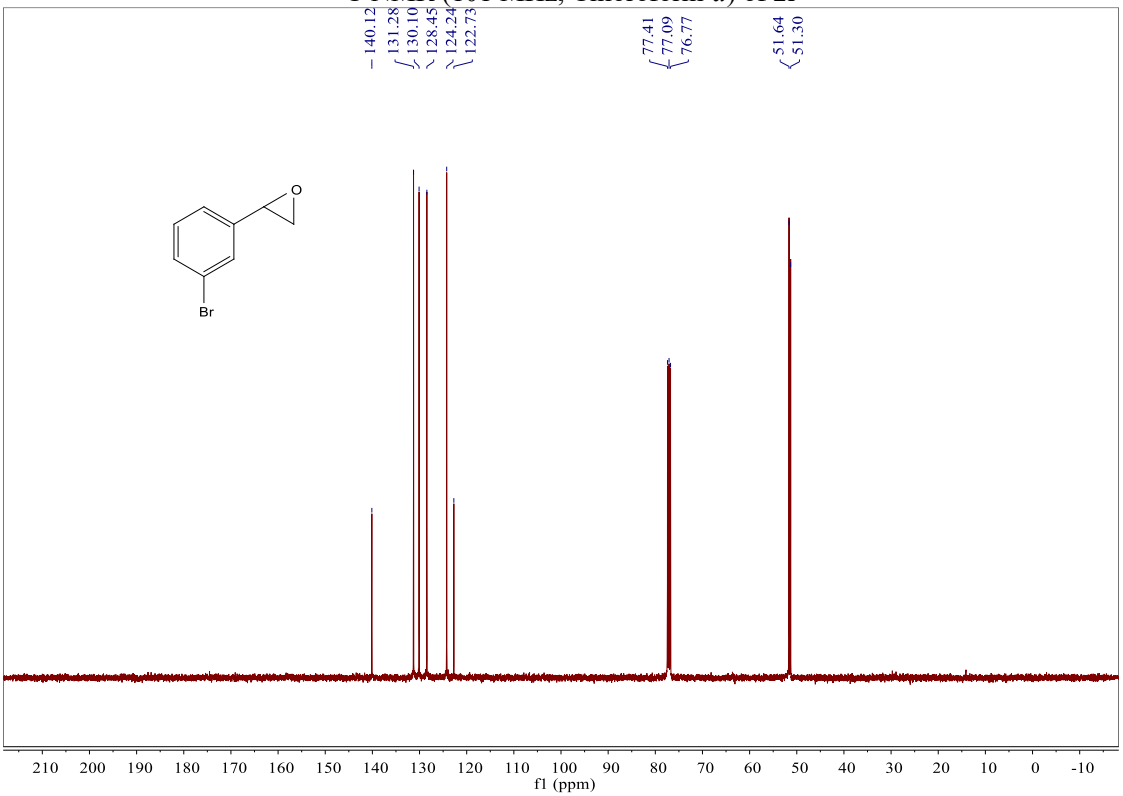
^{13}C NMR (101 MHz, Chloroform-*d*) of **2k**



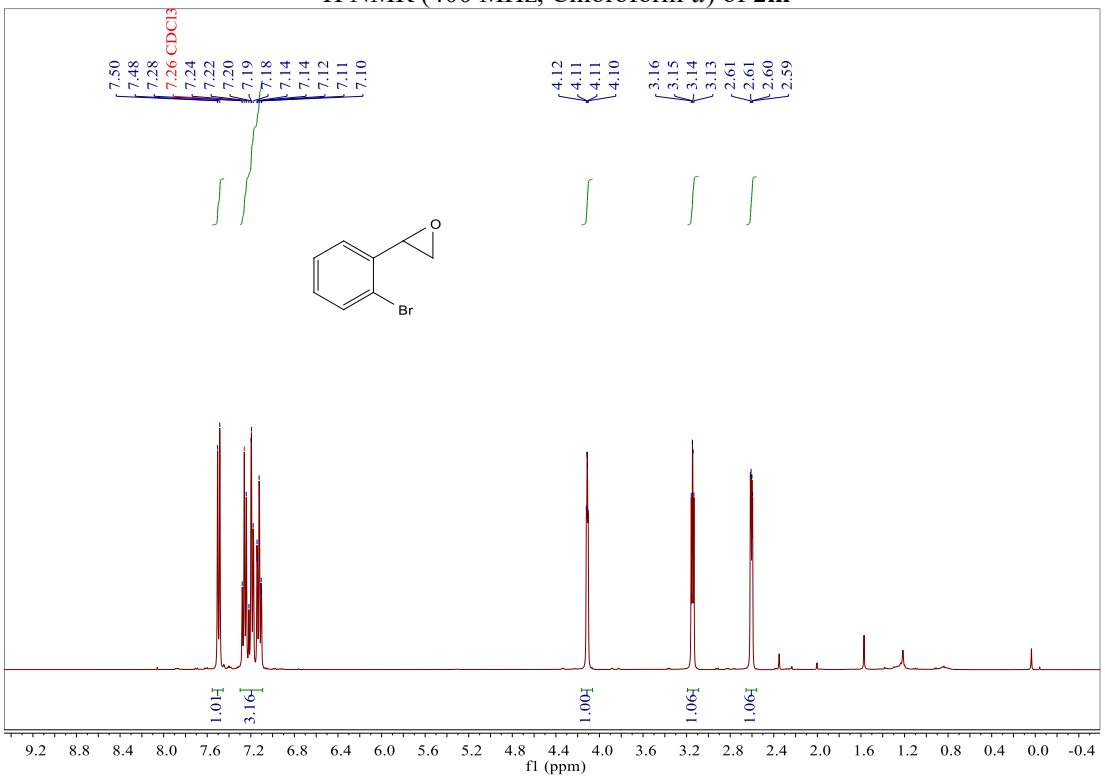
^{1}H NMR (400 MHz, Chloroform-*d*) of **2l**



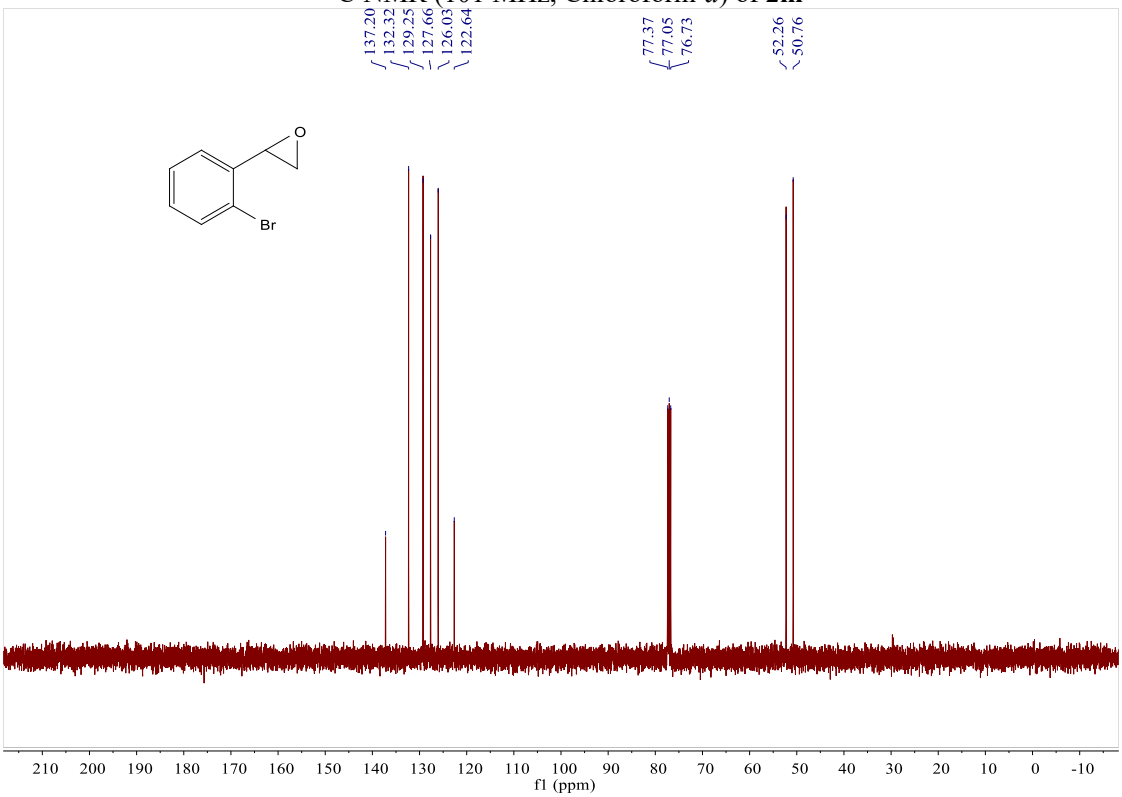
^{13}C NMR (101 MHz, Chloroform-*d*) of **2l**



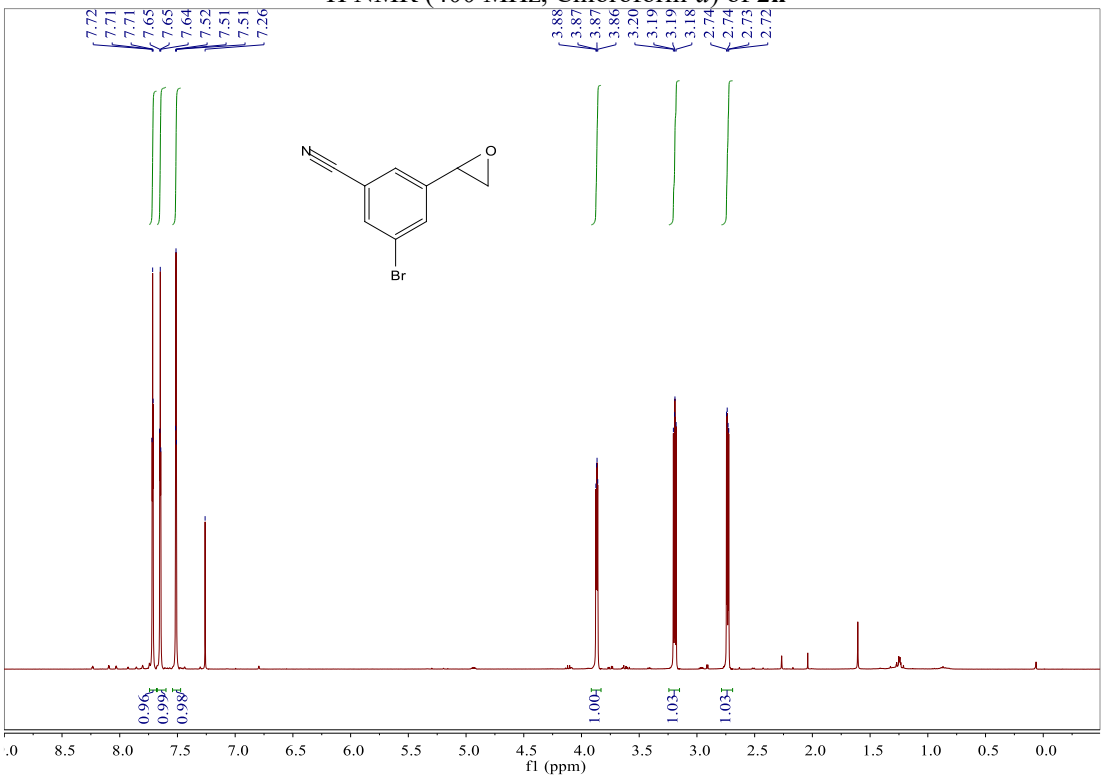
^{1}H NMR (400 MHz, Chloroform-*d*) of **2m**



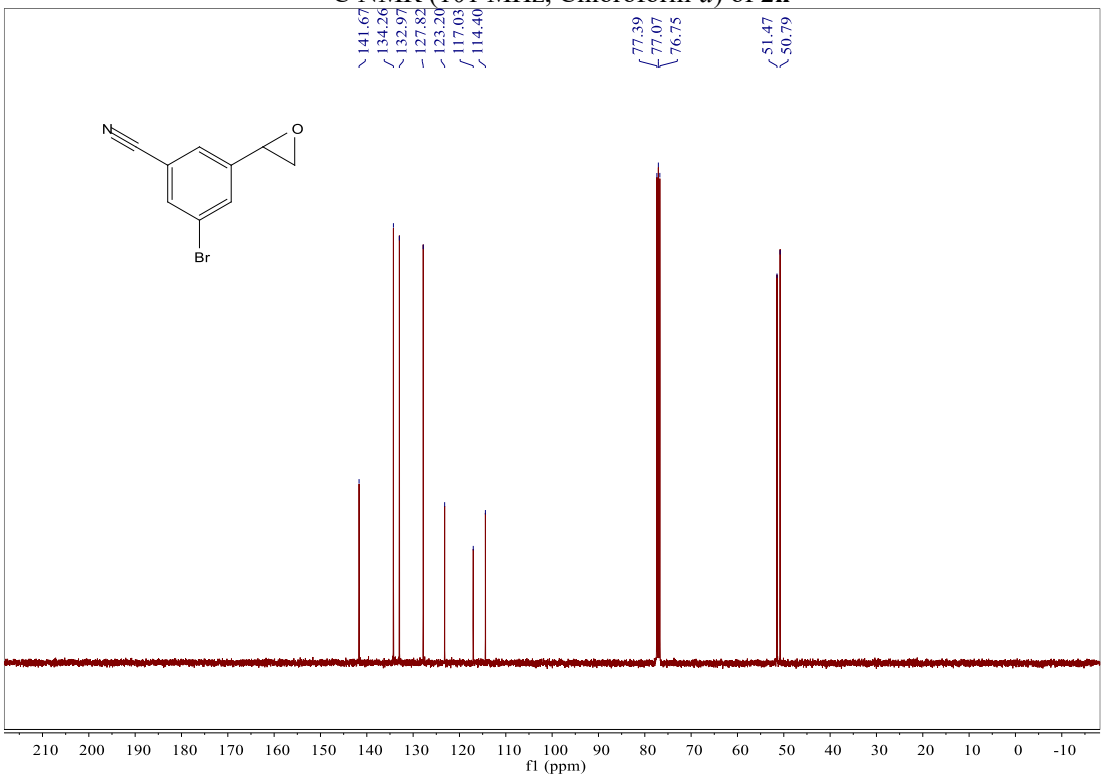
^{13}C NMR (101 MHz, Chloroform-*d*) of **2m**



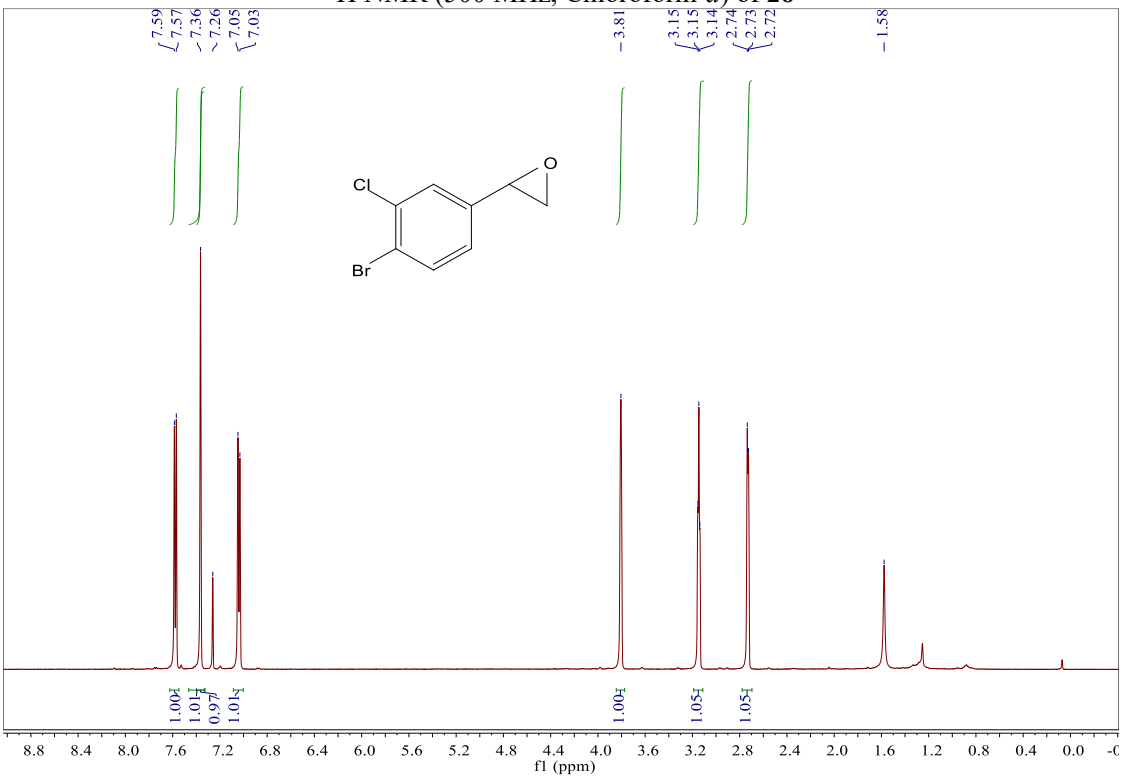
^{1}H NMR (400 MHz, Chloroform-*d*) of **2n**



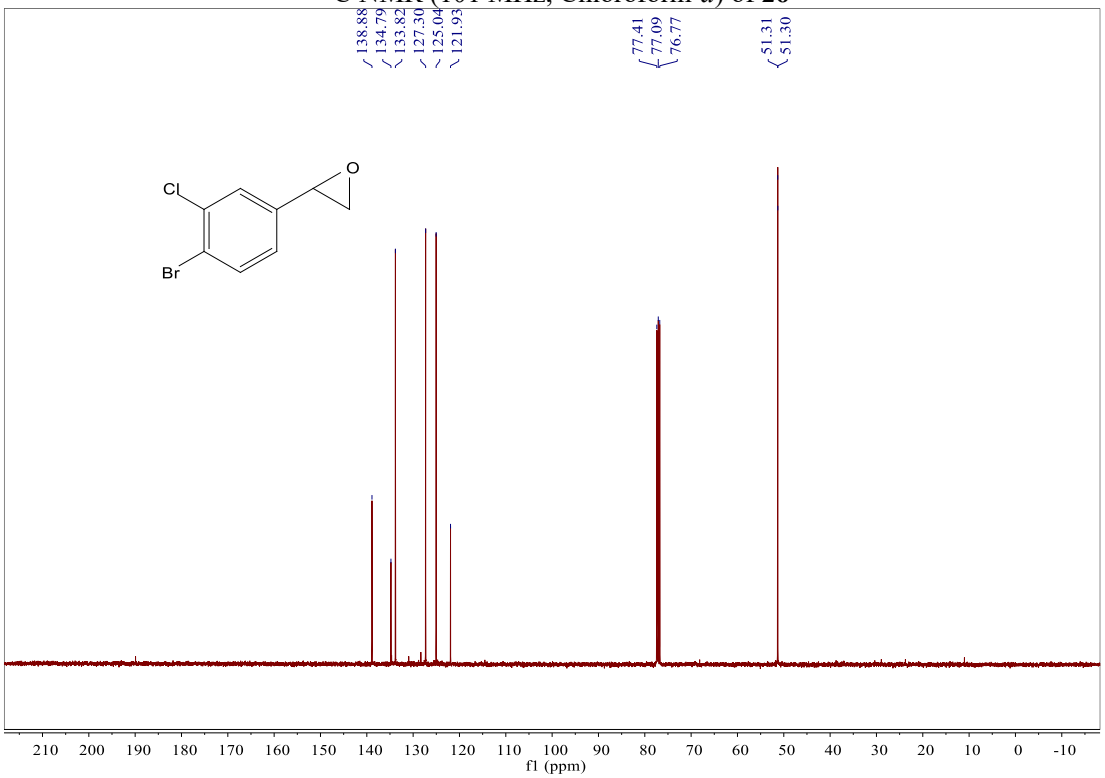
^{13}C NMR (101 MHz, Chloroform-*d*) of **2n**



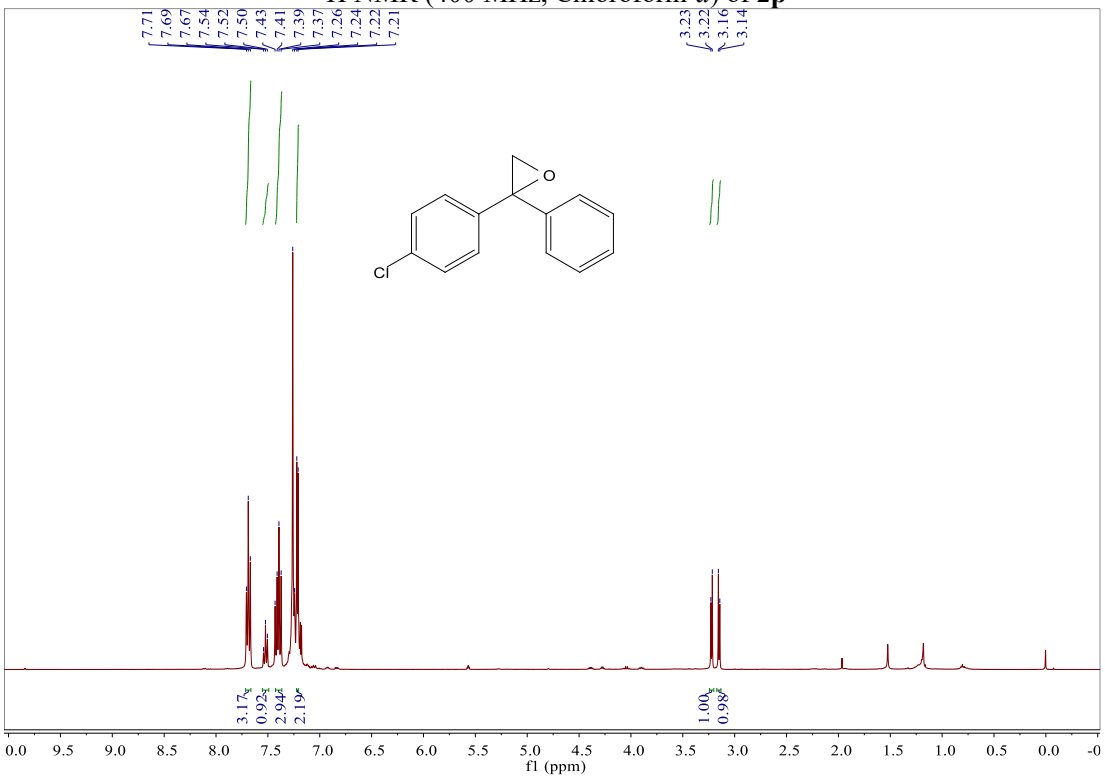
^{1}H NMR (500 MHz, Chloroform-*d*) of **2o**



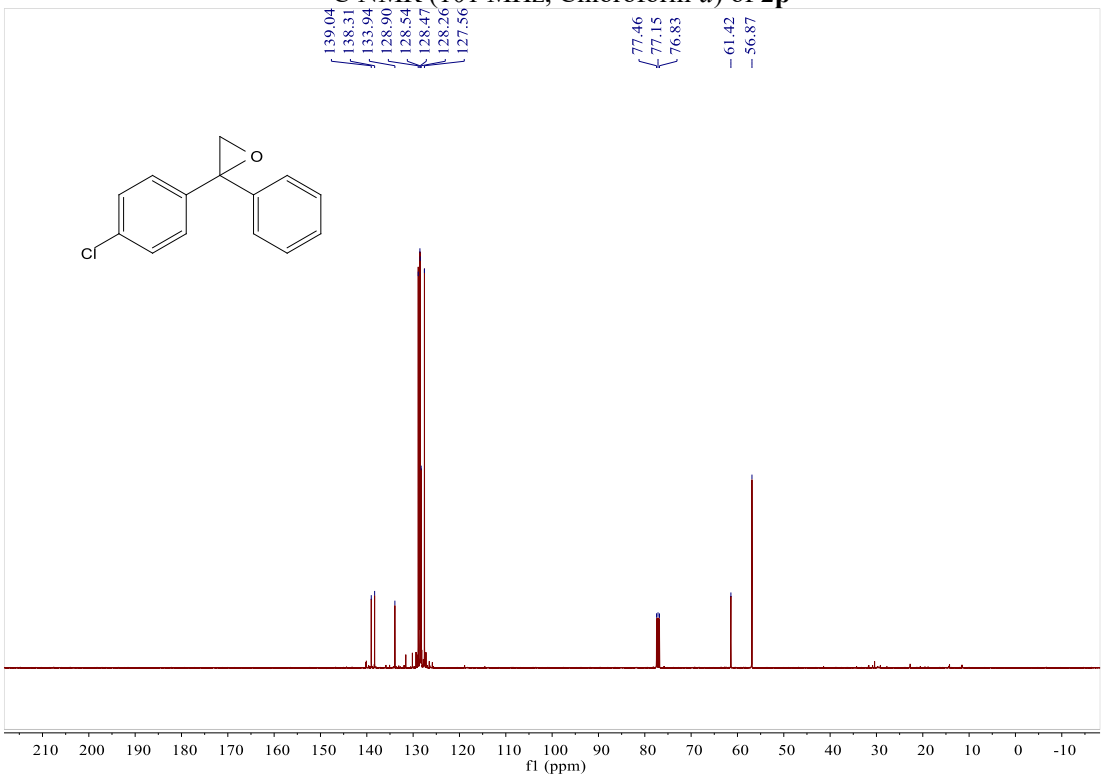
^{13}C NMR (101 MHz, Chloroform-*d*) of **2o**



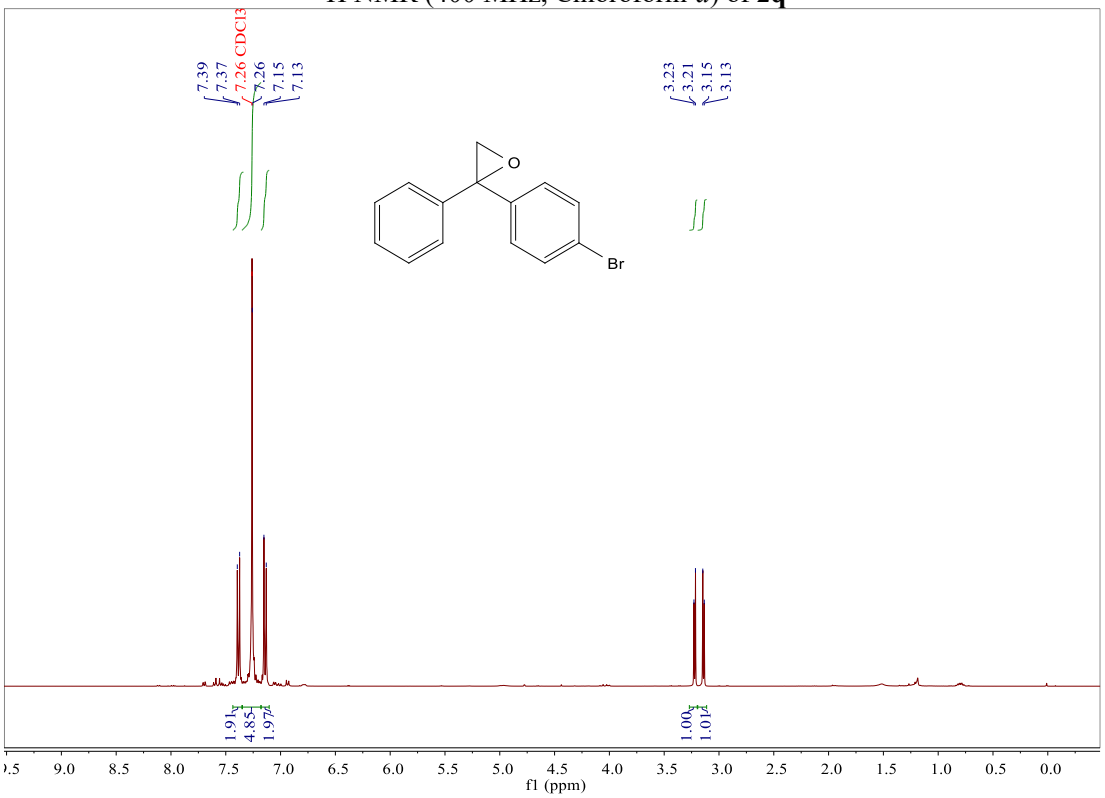
^{1}H NMR (400 MHz, Chloroform-*d*) of **2p**



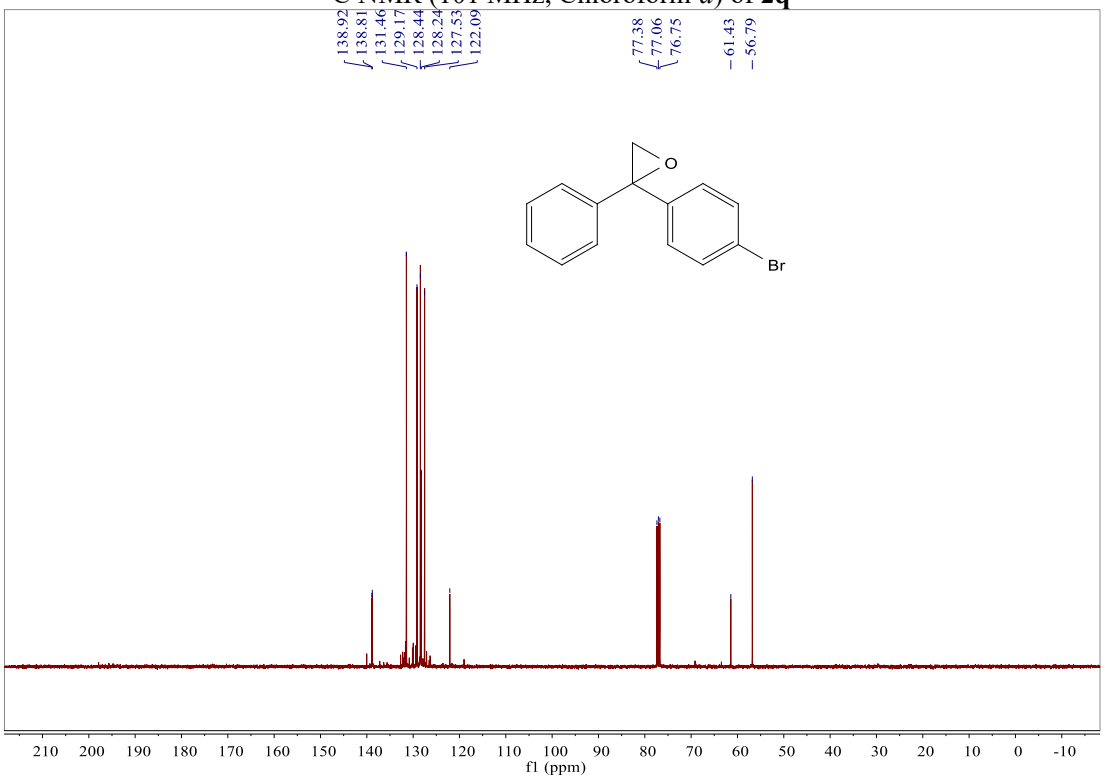
^{13}C NMR (101 MHz, Chloroform-*d*) of **2p**



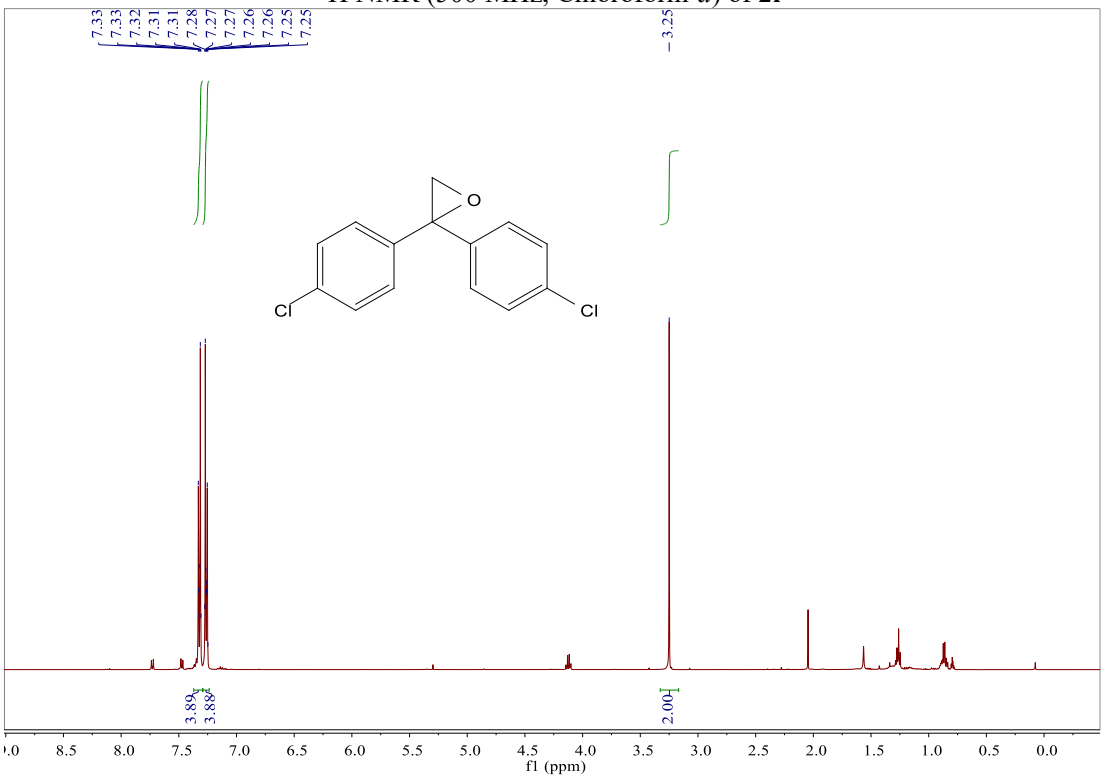
^{1}H NMR (400 MHz, Chloroform-*d*) of **2q**



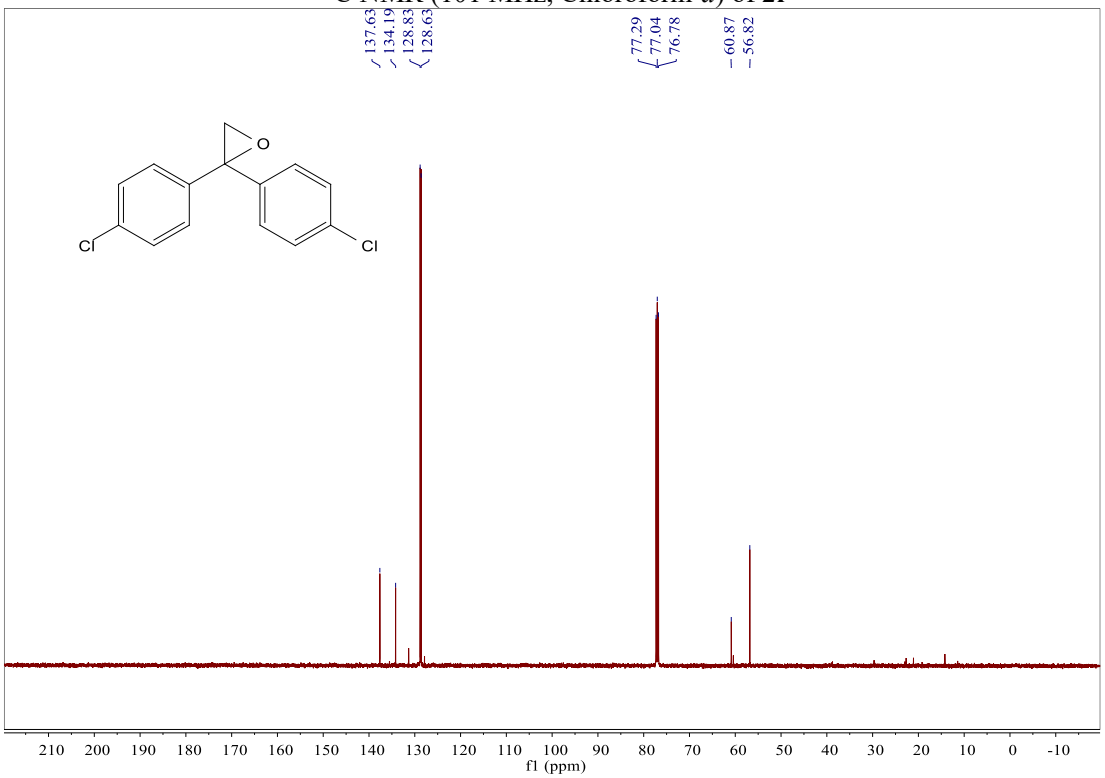
^{13}C NMR (101 MHz, Chloroform-*d*) of **2q**



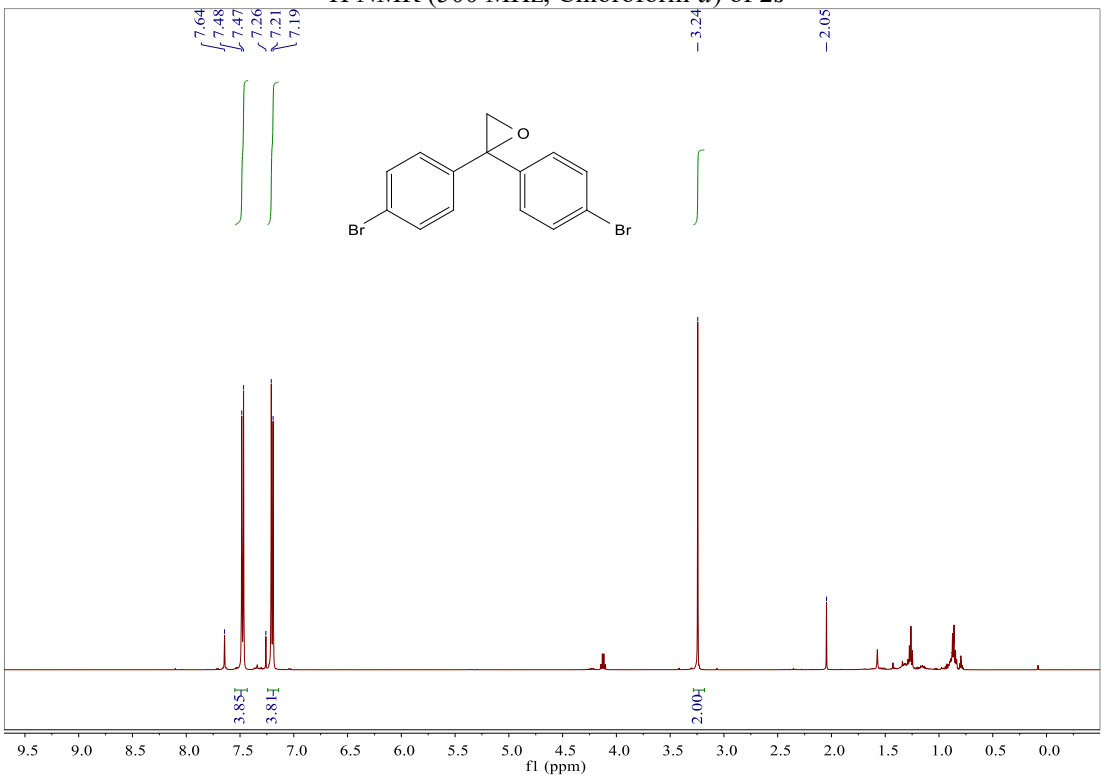
^{1}H NMR (500 MHz, Chloroform-*d*) of **2r**



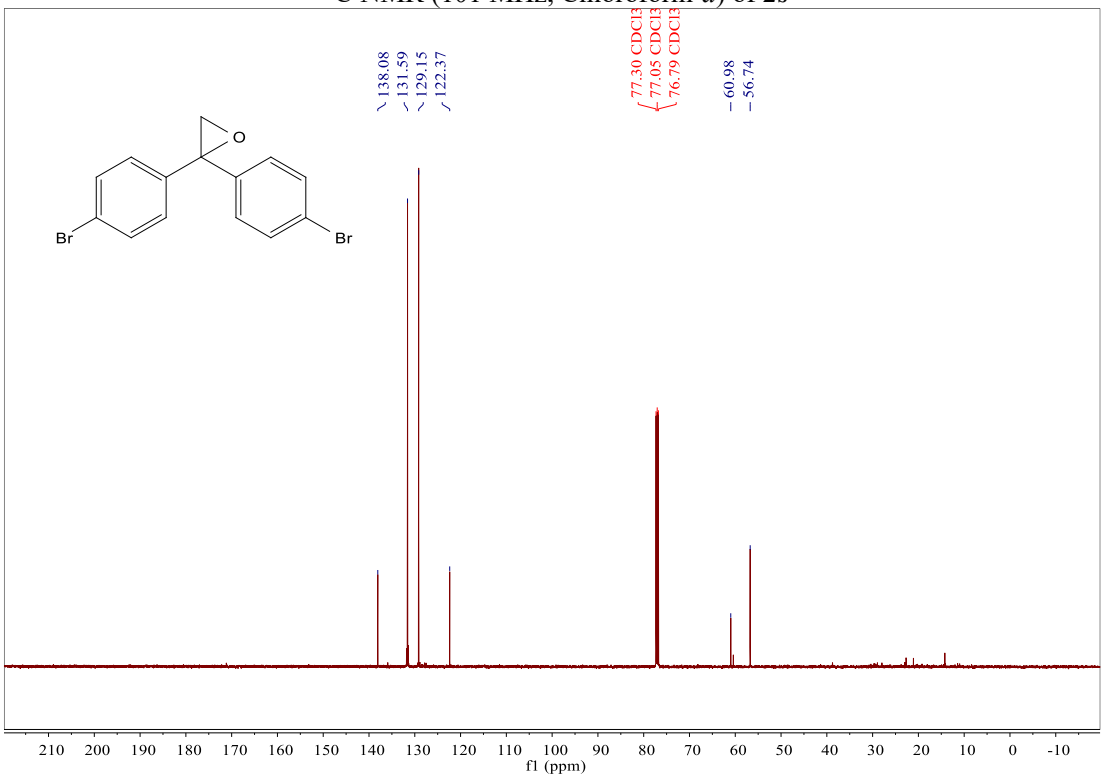
^{13}C NMR (101 MHz, Chloroform-*d*) of **2r**



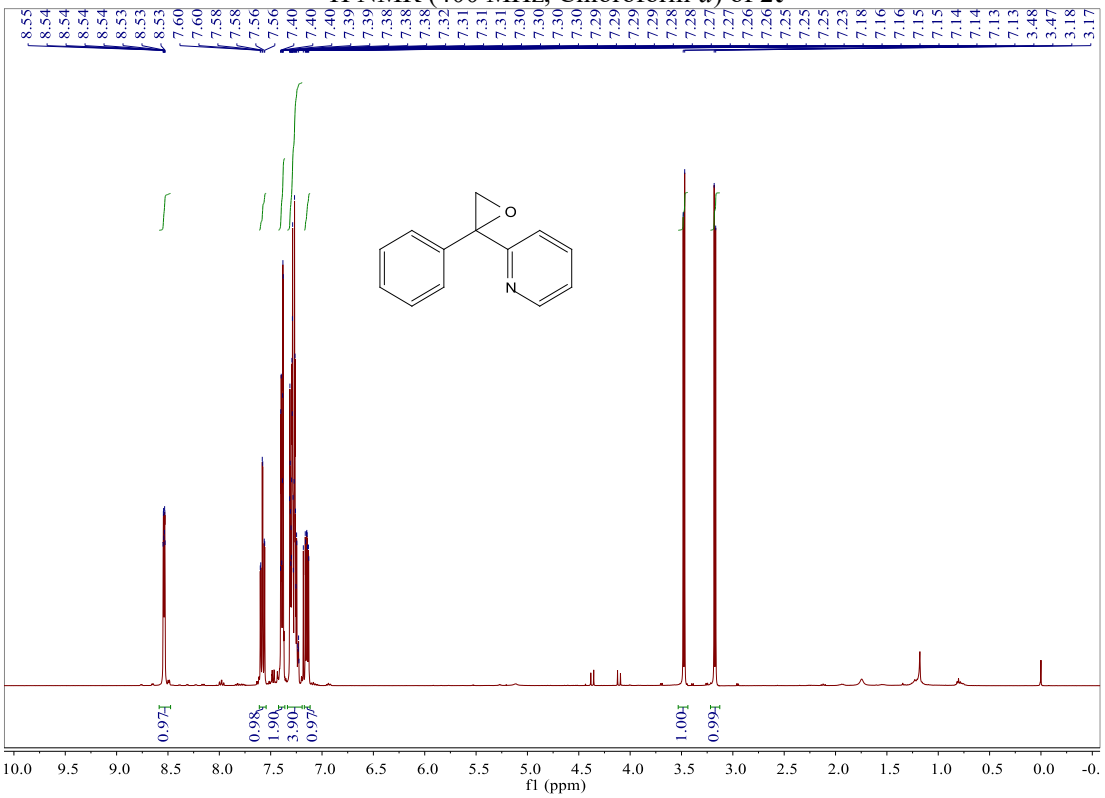
^{1}H NMR (500 MHz, Chloroform-*d*) of **2s**



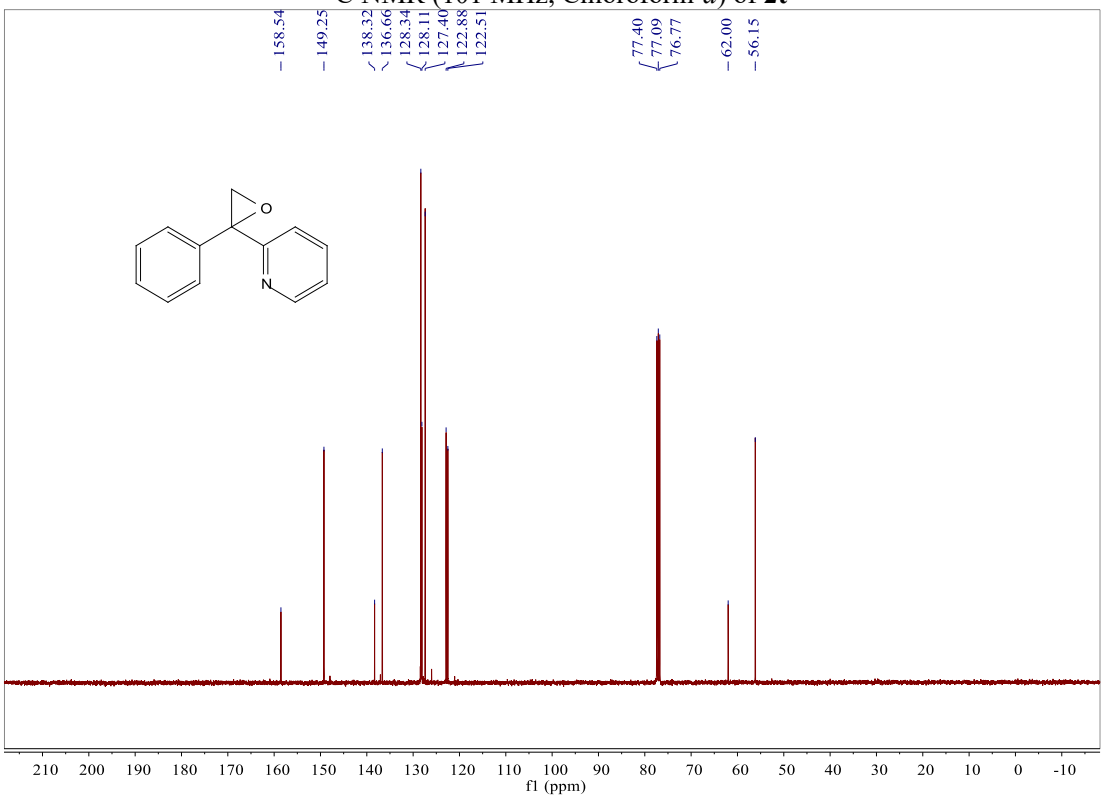
^{13}C NMR (101 MHz, Chloroform-*d*) of **2s**



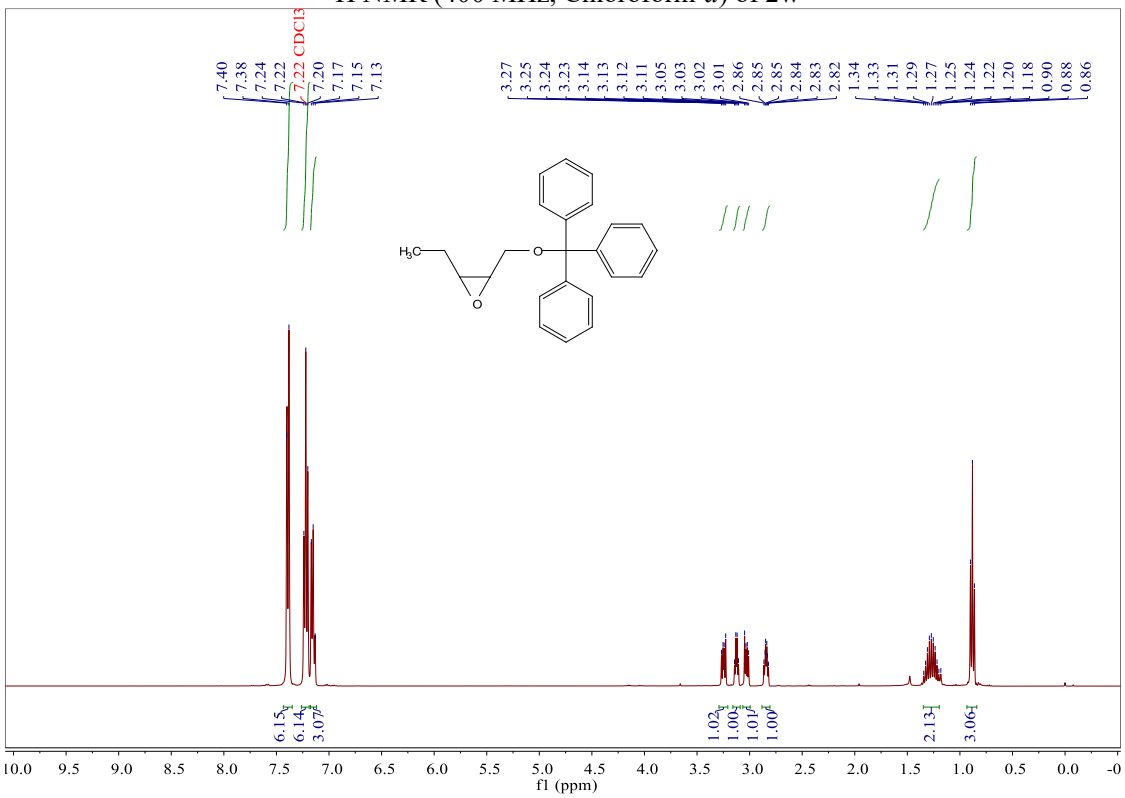
^{1}H NMR (400 MHz, Chloroform-*d*) of **2t**



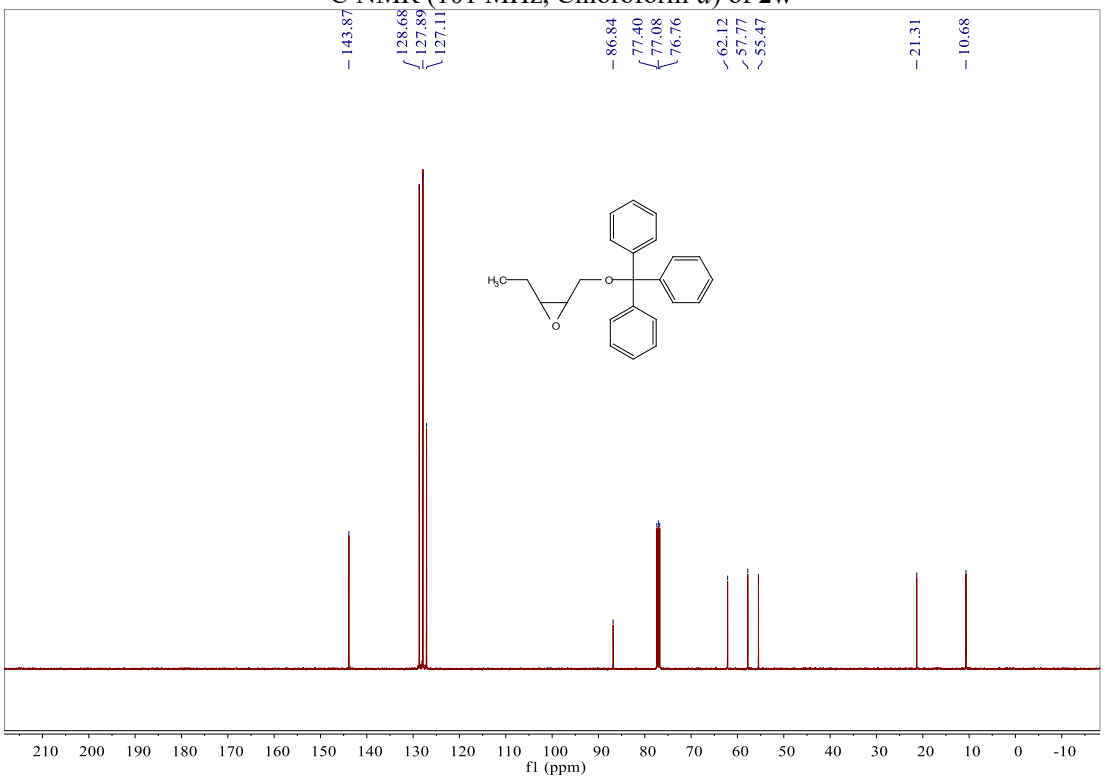
^{13}C NMR (101 MHz, Chloroform-*d*) of **2t**



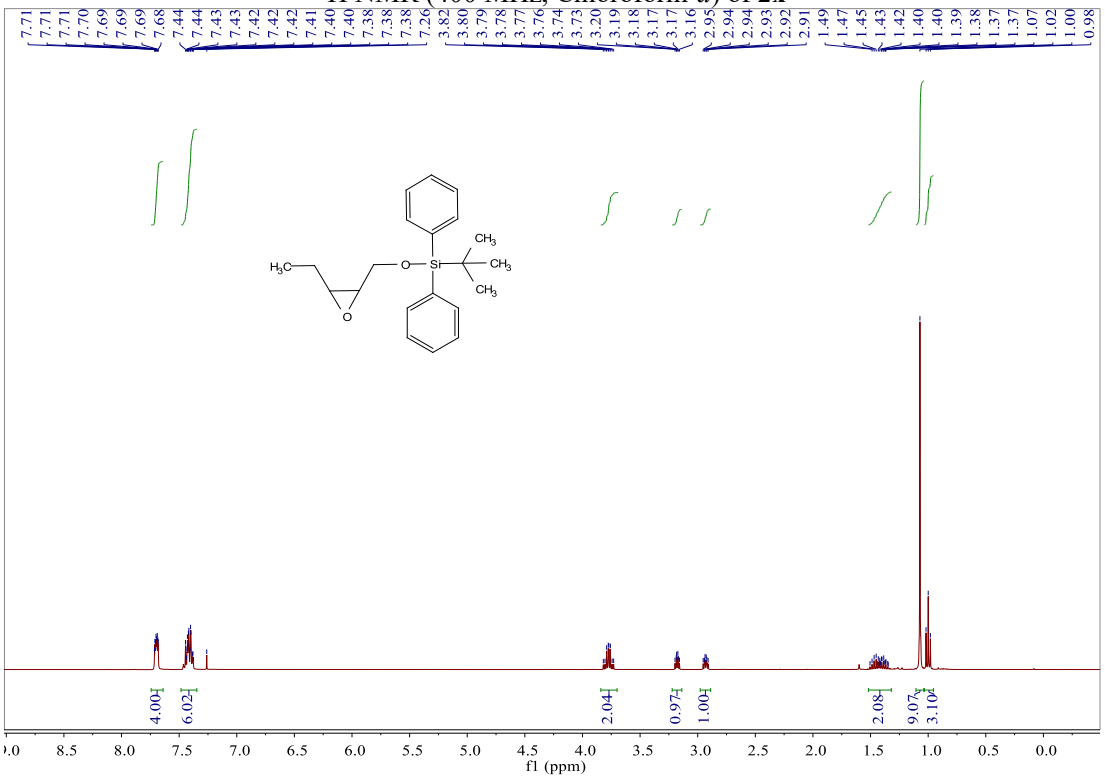
^{1}H NMR (400 MHz, Chloroform-*d*) of **2w**



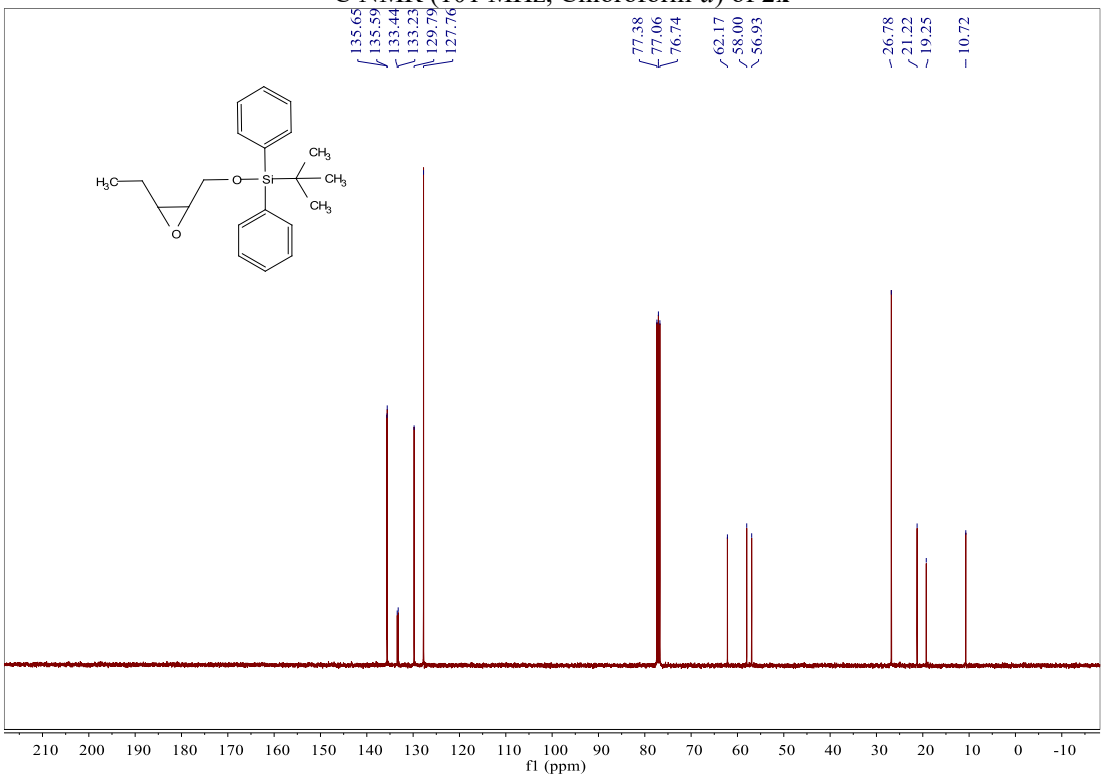
^{13}C NMR (101 MHz, Chloroform-*d*) of **2w**



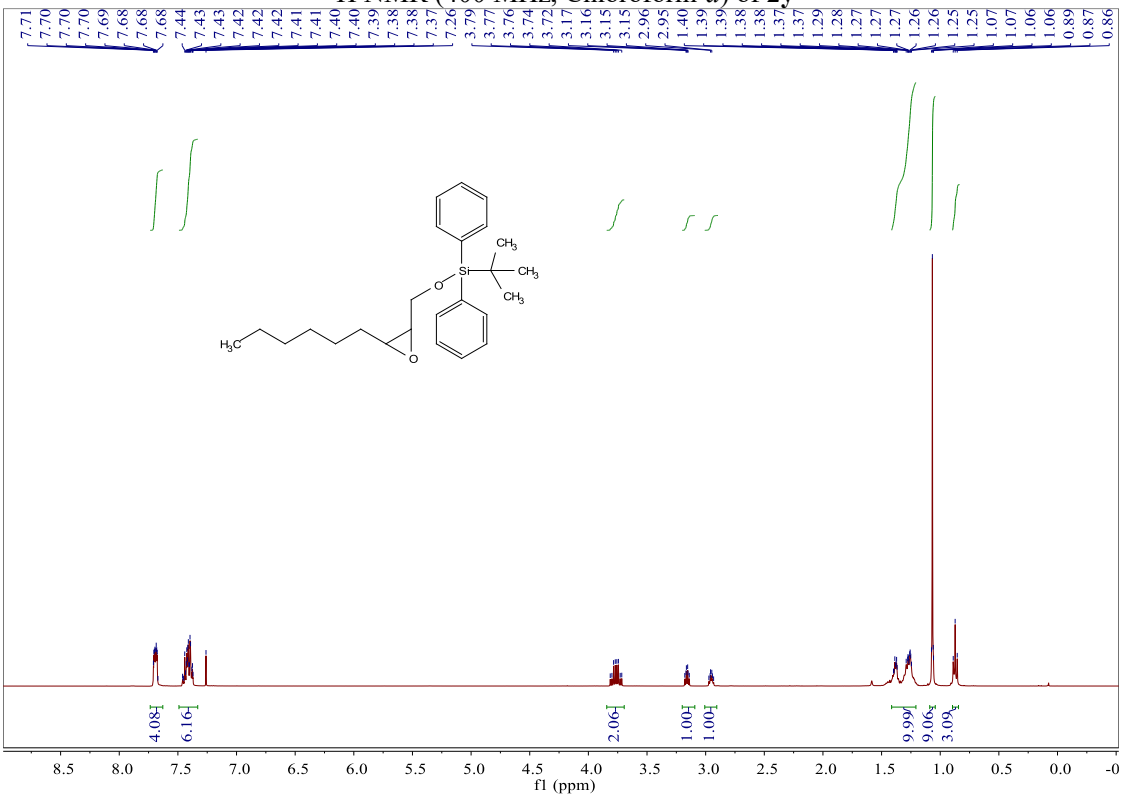
^{1}H NMR (400 MHz, Chloroform-*d*) of **2x**



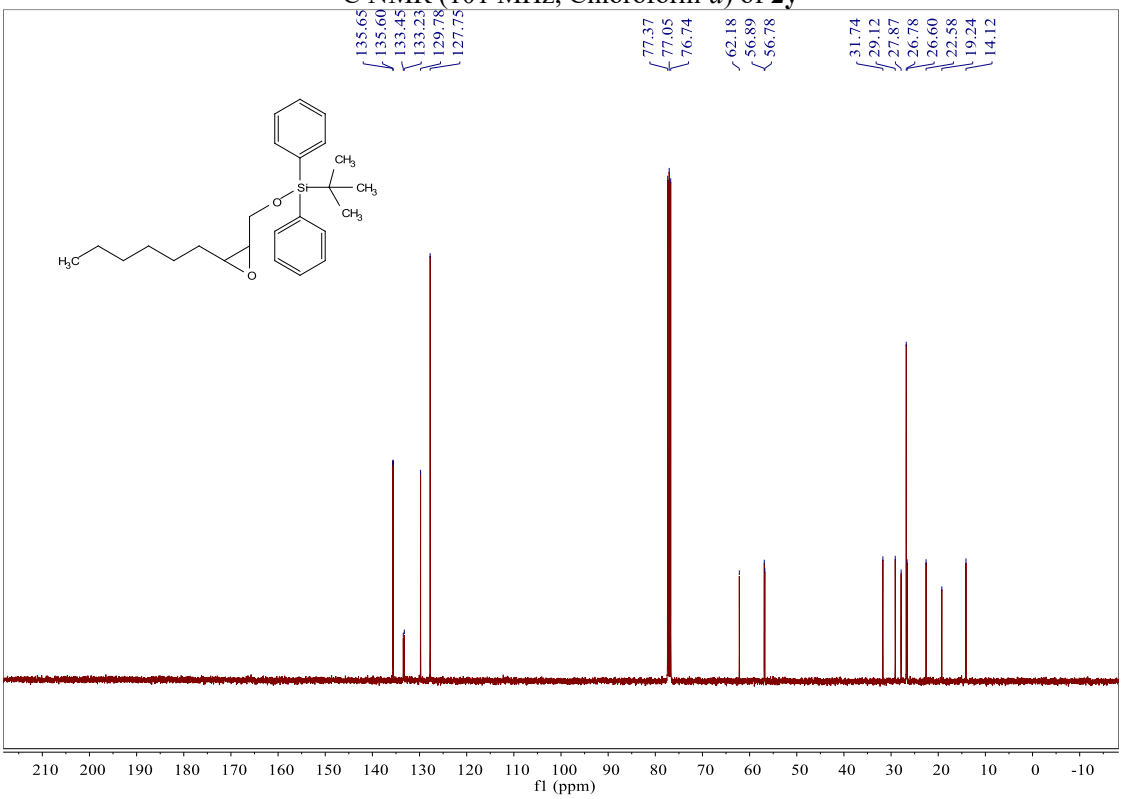
^{13}C NMR (101 MHz, Chloroform-*d*) of **2x**



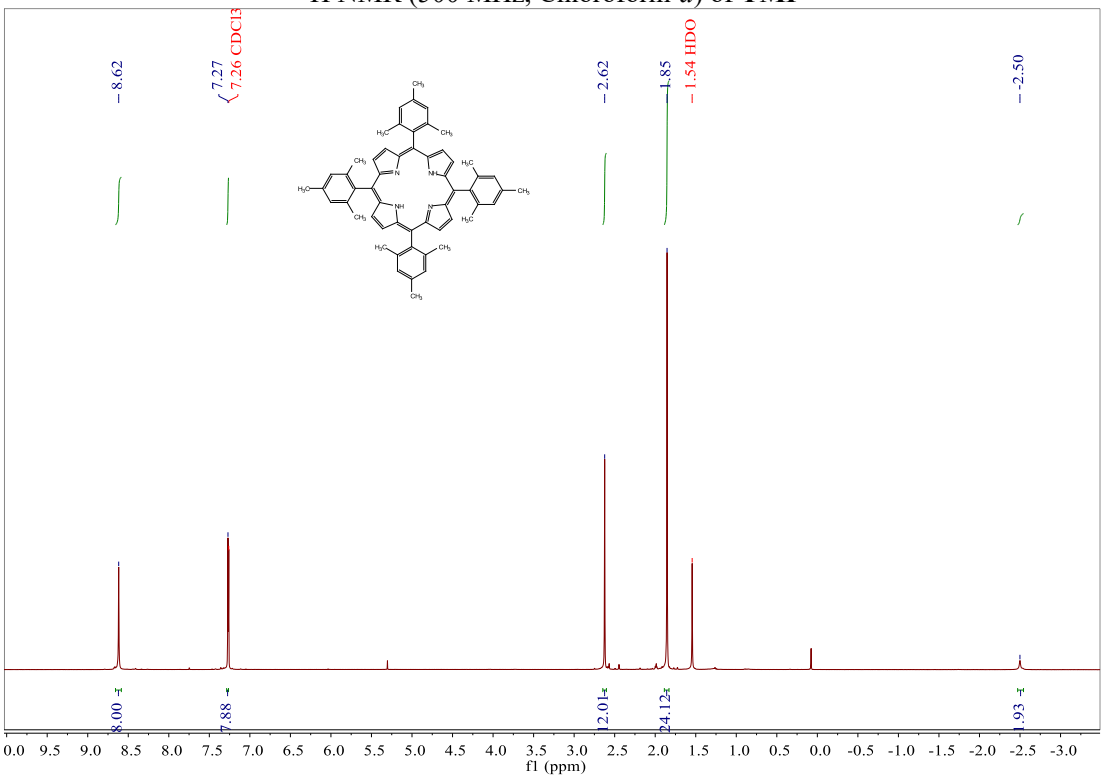
^{1}H NMR (400 MHz, Chloroform-*d*) of **2y**



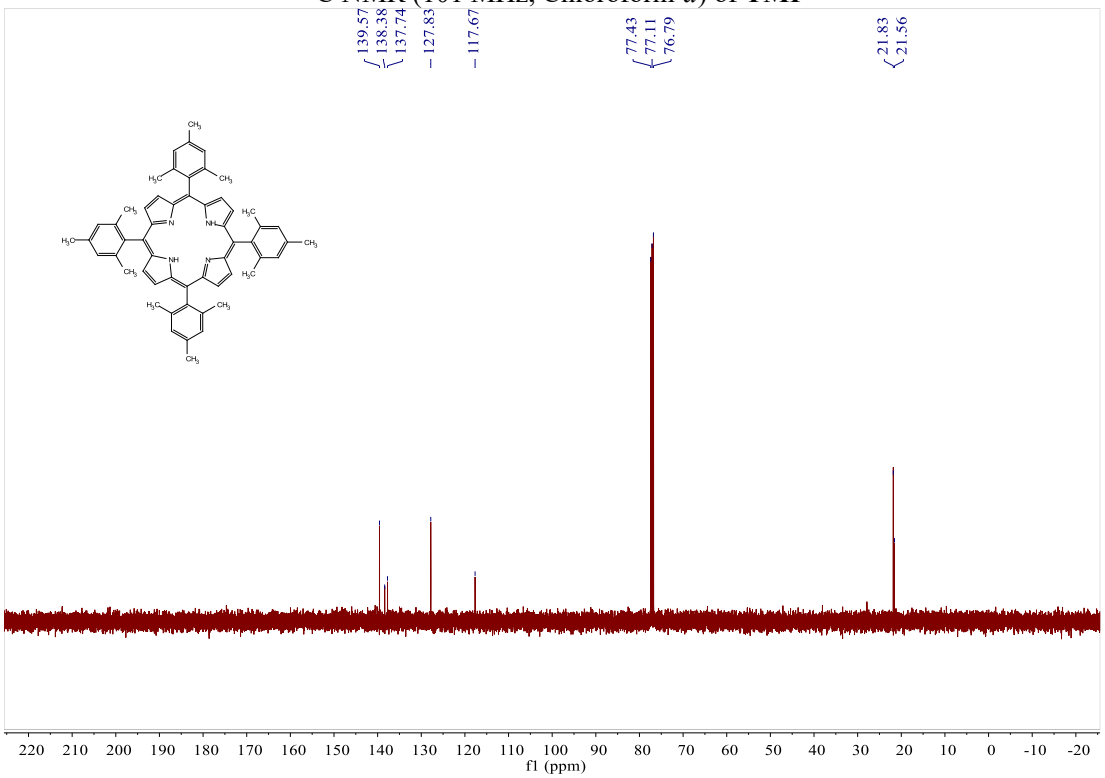
^{13}C NMR (101 MHz, Chloroform-*d*) of **2y**



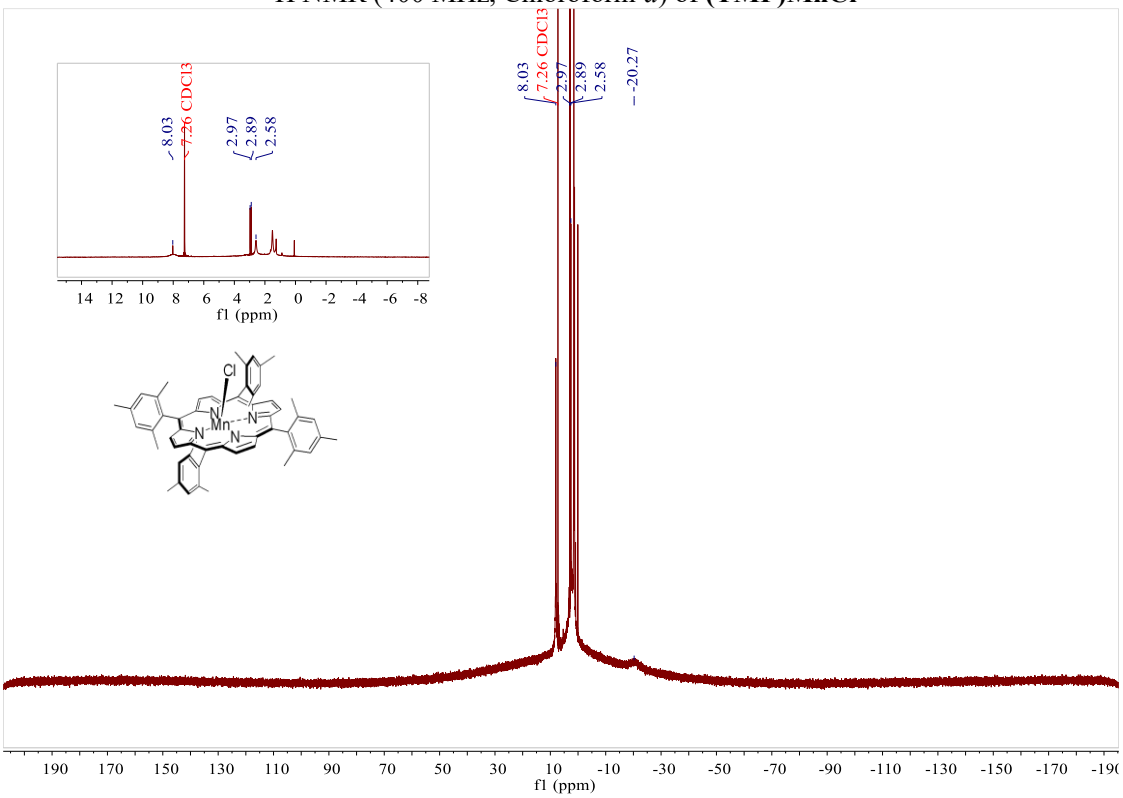
^{1}H NMR (500 MHz, Chloroform-*d*) of **TMP**



^{13}C NMR (101 MHz, Chloroform-*d*) of **TMP**



^{1}H NMR (400 MHz, Chloroform-*d*) of **(TMP)MnCl**



^{1}H NMR (400 MHz, Chloroform-*d*) of **(TPP)MnCl**