Transition-metal-free arylations via photogenerated triplet 4-alkyl- and 4-trimethylsilyl- phenyl cations

Hisham Qrareya, Carlotta Raviola, Stefano Protti,* Maurizio Fagnoni* and Angelo Albini

PhotoGreen Lab, Department of Chemistry,
University of Pavia, V.Le Taramelli 12, 27100 Pavia, Italy.

fagnoni@unipv.it

SUPPORTING INFORMATION

96 PAGES

Table of Contents:

1 Computational data and cartesian coordinates

All calculations were carried out by using the Gaussian 09[S1] program package. Optimization of all of the stationary points was carried out at the B3LYP level of theory adopting the 6-311+G(2d,p) basis set. An unrestricted approach was adopted when triplet states were considered. Frequency calculations were performed in vacuo at the same level of theory to certify structures as minima. Solvent effect was included at the same level of theory (methanol bulk) by performing single point calculations on the geometries previously optimized in vacuo and using the CPCM method[S2] (RADII=UAHF option was adopted).

Optimized geometry listed in cartesian format (coordinates are given in Å), minimum energies and thermochemical data (in Hartree; the default options were adopted in the latter case, *viz.* temperature: 298.150 K and pressure: 1.00000 atm) for structures **1-5**, ^{3}**1**-^{3}**5**, **Ph-Cl**, ^{3}**Ph-Cl**, ^{1}**1**$^{+}$-^{1}**5**$^{+}$ ^{3}**1**$^{+}$-^{3}**5**$^{+}$, **1a-5a** are reported below. The structures of singlet phenyl cation (^{1}**Ph**$^{+}$) and benzene (**PhH**; notice that the two latter structures have been used in the isodesmic reaction in eq 1) were likewise reported. The energies labeled "E(stretch)" refer to single point calculations upon stretching the C-Cl bond up to 4.00 Å. Further notice that we evaluated the possibility of different arrangements of the alkyl chain for ^{1,3}**2'**, ^{1,3}**3**, their corresponding singlet and triplet phenyl cations (^{1,3}**2'**$^{+}$, ^{1,3}**3**$^{+}$**)** and **2'a**, **3a**. In all cases, the most stable conformer was reported.

Triplet energies (E_T) reported in Table 1 have been evaluated by subtracting the Gibbs free energy calculated at the B3LYP/6-311+G(2d,p) of the singlet state to the corresponding value for the triplet state. These Gibbs free energies values (G(B3LYP)) have been determined according to eq S1.

$$G(B3LYP) = E_0(B3LYP,CPCM) + \Delta G_{CORR}(B3LYP,vacuo) \quad (S1)$$

Where: - E_0(B3LYP,CPCM) is the total electronic energy calculated at the CPCM-B3LYP/6-311+G(2d,p) level (MeOH bulk);

- ΔG_{CORR}(B3LYP,vacuo) is the unscaled thermal correction to Gibbs free energy as from the output of the frequency calculation at the B3LYP/6-311+G(2d,p) level (in vacuo), also including the zero-point vibrational energy (ZPVE).

The conversion of energy values between Hartree and kcal mol^{-1} has been carried out according to the following relationship: 1 Hartree = 627.5095 kcal mol^{-1}.

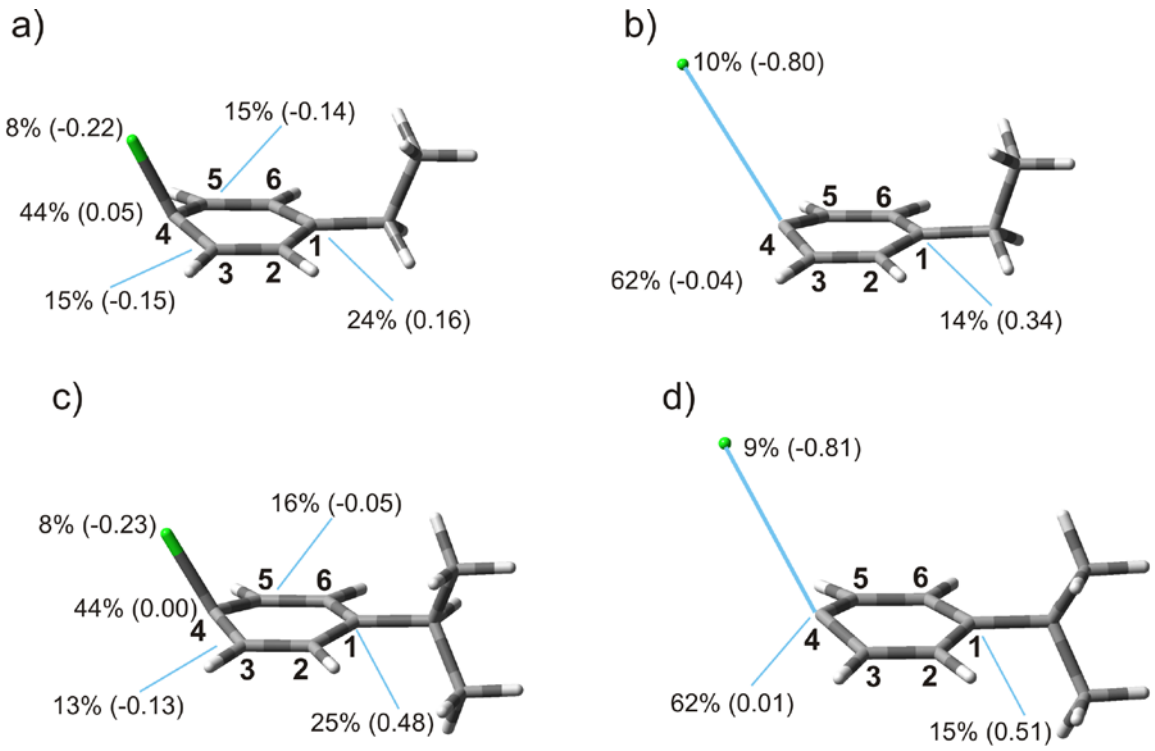


Figure S1. Geometries, spin densities, and ESP atomic charges (in parentheses) calculated in MeOH bulk at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level of theory for: (a) ^{3}**2'** (Ar−Cl bond length: 1.84 Å); (b) ^{3}**2'** upon stretching the Ar−Cl bond up to 4.00 Å; (c) ^{3}**3** (Ar−Cl bond length: 1.84 Å); (d) ^{3}**3** upon stretching the Ar−Cl bond up to 4.00 Å.

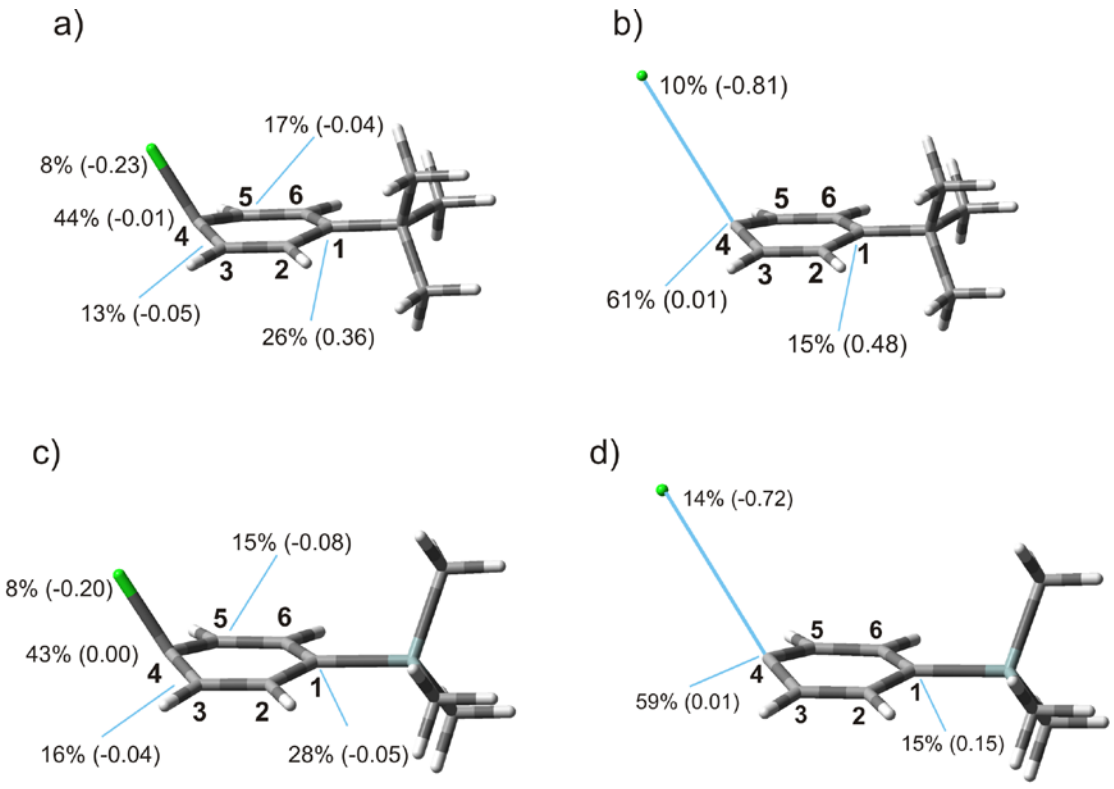


Figure S2. Geometries, spin densities, and ESP atomic charges (in parentheses) calculated in MeOH bulk at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level of theory for: (a) ^{3}**4** (Ar−Cl bond length: 1.84 Å); (b) ^{3}**4** upon stretching the Ar−Cl bond up to 4.00 Å; (c) ^{3}**5** (Ar−Cl bond length: 1.82 Å); (d) ^{3}**5** upon stretching the Ar−Cl bond up to 4.00 Å.

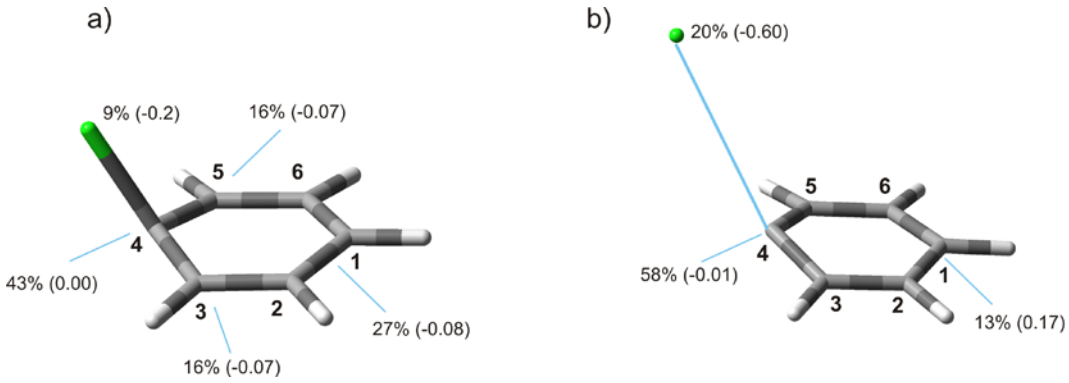


Figure S3. Geometries, spin densities, and ESP atomic charges (in parentheses) calculated in MeOH bulk at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level of theory for: (a) ^{3}**Ph-Cl** (Ar−Cl bond length: 1.83 Å); (b) ^{3}**Ph-Cl** upon stretching the Ar−Cl bond up to 4.00.

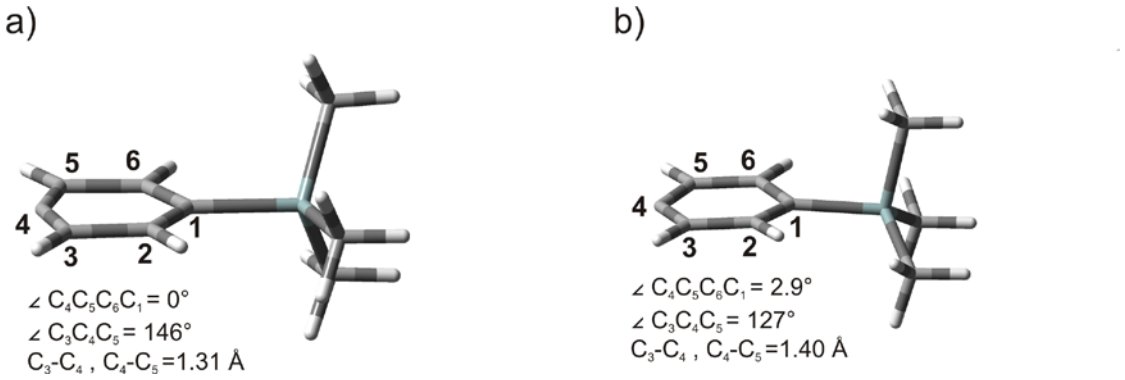
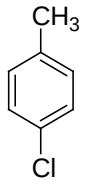


Figure S4. a) Bond lengths (Å), angles (∠, in degrees) and dihedral angles (∠, in degrees) for: (a) ^{1}**5**$^{+}$ and (b) ^{3}**5**$^{+}$.

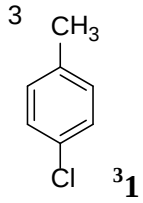


1

E(vacuo)	-731.2713928
Zero-point correction	0.117828
Thermal correction to Energy	0.125255
Thermal correction to Enthalpy	0.126199
Thermal correction to Gibbs Free Energy	0.084276

E(MeOH) -731.2802338

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.39035712
C	1.19034257	0.00000000	2.11956081
C	2.39167691	0.00622202	1.40865566
C	2.41294728	0.00627738	0.01845326
C	1.21171875	0.00179043	-0.67555103
H	-0.93007451	0.00223330	-0.55290786
H	-0.94923984	0.00237934	1.91489988
H	3.33275842	0.01351955	1.94765254
H	3.35135072	0.01337199	-0.52015358
Cl	1.22515864	0.00551389	-2.43482248
C	1.17888226	-0.03189857	3.62689946
H	1.17837010	-1.06157094	3.99813912
H	2.05793878	0.46385646	4.04258363
H	0.29132991	0.45985406	4.02906781

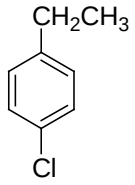


1

E(vacuo) -731.1482544
Zero-point correction 0.113677
Thermal correction to Energy 0.121752
Thermal correction to Enthalpy 0.122697
Thermal correction to Gibbs Free Energy 0.079248

E(MeOH) -731.158641
E(MeOH, Stretch) -731.1337495

C	-0.31269800	1.25063200	-0.65028200
C	0.97402500	1.22825600	-0.21238600
C	1.64432000	0.00000600	0.07691000
C	0.97403100	-1.22824800	-0.21238900
C	-0.31269100	-1.25063200	-0.65028200
C	-1.07412100	-0.00000300	-0.65012700
H	-0.80024000	2.17376900	-0.93953600
H	1.53330000	2.15549600	-0.13140500
H	1.53331000	-2.15548700	-0.13141300
H	-0.80022500	-2.17377300	-0.93953800
Cl	-2.43010900	-0.00000300	0.58911000
C	3.04242600	0.00000000	0.60663900
H	3.04693600	-0.00027900	1.70444700
H	3.59359000	-0.88740600	0.28681900
H	3.59343800	0.88765200	0.28725400

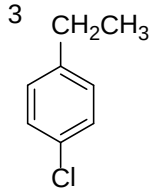


2’

E(vacuo)	-770.5962131
Zero-point correction	0.146626
Thermal correction to Energy	0.155155
Thermal correction to Enthalpy	0.156099
Thermal correction to Gibbs Free Energy	0.112223

E(MeOH) -770.6059976

C	0.75075300	1.20699800	-0.08922600
C	-0.62908700	1.19626700	-0.26017100
C	-1.34417800	0.00038200	-0.34768000
C	-0.62934500	-1.19571600	-0.26074200
C	0.75047700	-1.20682900	-0.08981000
C	1.42965600	-0.00000500	-0.00449100
H	1.29370200	2.14089300	-0.02737300
H	-1.15592300	2.14177100	-0.33207600
H	-1.15639000	-2.14106900	-0.33311000
H	1.29323600	-2.14086500	-0.02841900
Cl	3.17634300	-0.00026500	0.20672000
C	-2.84736200	0.00056300	-0.49836300
C	-3.58765100	-0.00083200	0.84829800
H	-3.15288900	-0.87491100	-1.07836900
H	-3.15283800	0.87726600	-1.07652700
H	-4.66980900	-0.00061300	0.69720600
H	-3.32830800	-0.88318600	1.43783400
H	-3.32819900	0.88024000	1.43970000

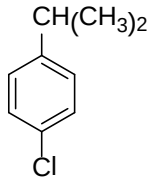


^{3}2’

E(vacuo)	-770.4730239
Zero-point correction	0.142529
Thermal correction to Energy	0.151790
Thermal correction to Enthalpy	0.152734
Thermal correction to Gibbs Free Energy	0.106101

E(MeOH)	-770.4843341
E(MeOH, Stretch)	-770.459698

C	-0.81620000	-1.24059800	-0.77203500
C	0.53244200	-1.21851200	-0.60042600
C	1.24644300	0.00829700	-0.43696900
C	0.52985900	1.23721600	-0.56809300
C	-0.81889600	1.26070300	-0.73964100
C	-1.56323500	0.00725100	-0.60310600
H	-1.35081900	-2.16174100	-0.97011200
H	1.09782100	-2.14472500	-0.64633200
H	1.09312600	2.16560100	-0.58930300
H	-1.35552800	2.18547100	-0.91392100
Cl	-2.64110400	-0.01307300	0.88530300
C	2.72500400	0.00630200	-0.19363300
C	3.08645700	-0.02189400	1.30576600
H	3.17217500	0.89565200	-0.64859500
H	3.17522600	-0.86362400	-0.68210500
H	4.17107800	-0.02192200	1.43690100
H	2.68013700	0.84953100	1.82313600
H	2.68431400	-0.91459600	1.78901100

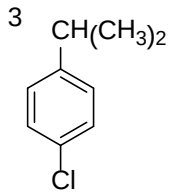


3

E(vacuo) -809.9204996
Zero-point correction 0.174470
Thermal correction to Energy 0.184386
Thermal correction to Enthalpy 0.185330
Thermal correction to Gibbs Free Energy 0.138371

E(MeOH) -809.9310942

C	-1.19352200	1.24978800	-0.00011800
C	-1.77489300	-0.00831900	0.00000500
C	-0.99061100	-1.15397600	0.00011200
C	0.39287400	-1.02866000	0.00009100
C	1.01349300	0.22395200	-0.00003700
C	0.19428500	1.35303400	-0.00013800
H	-1.81423800	2.13603500	-0.00019800
H	-1.45710900	-2.13028900	0.00020900
H	0.99319900	-1.93115300	0.00017600
H	0.64529400	2.33944200	-0.00023600
Cl	-3.52796500	-0.15727700	0.00003000
C	2.52684200	0.36203000	-0.00005600
C	3.15913900	-0.23586200	-1.26772600
C	3.15913300	-0.23552300	1.26777700
H	2.74624100	1.43482900	-0.00020000
H	2.73779100	0.21243500	-2.16988100
H	4.23867200	-0.06501200	-1.27484700
H	2.99434100	-1.31503100	-1.32314100
H	2.73777400	0.21301000	2.16981000
H	2.99434000	-1.31467800	1.32347500
H	4.23866500	-0.06466300	1.27486400

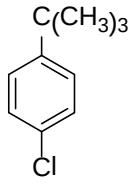


^{3}3

E(vacuo)	-809.7967396
Zero-point correction	0.170540
Thermal correction to Energy	0.181153
Thermal correction to Enthalpy	0.182097
Thermal correction to Gibbs Free Energy	0.132850

E(MeOH)	-809.8090117
E(MeOH, Stretch)	-809.7850925

C	-1.22561500	1.46751300	-0.07163800
C	-1.86053800	0.26471400	-0.61348700
C	-0.98299200	-0.75243000	-1.19301900
C	0.32654500	-0.76613600	-0.83391000
C	0.90008500	0.27939500	-0.03916500
C	0.08922600	1.40660900	0.27984900
H	-1.82016300	2.35691000	0.09848200
H	-1.40236100	-1.51236700	-1.84142600
H	0.96760200	-1.56189000	-1.19818500
H	0.55627100	2.25917300	0.76392000
Cl	-3.10097100	-0.45537300	0.54086800
C	2.35026500	0.23535300	0.37671000
C	3.30503100	0.15718300	-0.82967800
C	2.61853000	-0.91760800	1.36413200
H	2.56178300	1.17210700	0.90205600
H	3.14208900	0.98805500	-1.51897800
H	4.34335100	0.19404400	-0.49109200
H	3.17327400	-0.77307800	-1.38710500
H	1.97468600	-0.84500100	2.24272500
H	2.43822900	-1.88861100	0.89630800
H	3.65852500	-0.89556800	1.69977400

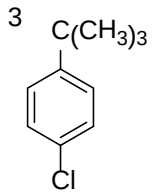


4

E(vacuo)	-849.2419438
Zero-point correction	0.202318
Thermal correction to Energy	0.213397
Thermal correction to Enthalpy	0.214341
Thermal correction to Gibbs Free Energy	0.165486

E(MeOH) -849.2522652

C	1.35609200	-1.19275200	-0.00001400
C	-0.03163300	-1.16949400	-0.00003000
C	-0.75514000	0.03002800	-0.00004800
C	-0.01738900	1.21511100	-0.00001700
C	1.37579400	1.21412800	-0.00000700
C	2.05362200	0.00744100	-0.00001100
H	1.89179500	-2.13299100	-0.00000600
H	-0.55476900	-2.11796400	-0.00002100
H	-0.52054500	2.17204000	-0.00001200
H	1.92477200	2.14667500	0.00000400
Cl	3.81253500	-0.00808800	0.00000800
C	-2.29192900	0.00240500	0.00000000
C	-2.90116100	1.41434400	0.00024500
C	-2.79334000	-0.73641700	-1.26042600
C	-2.79320500	-0.73680900	1.26025000
H	-2.61043100	1.98421300	0.88585100
H	-2.61029400	1.98457100	-0.88508700
H	-3.99084000	1.34070400	0.00015400
H	-2.43242700	-1.76566600	-1.29919500
H	-3.88614500	-0.76682900	-1.27213000
H	-2.45822100	-0.23059800	-2.16889100
H	-3.88600700	-0.76731800	1.27201600
H	-2.43218600	-1.76603500	1.29870100
H	-2.45806700	-0.23121500	2.16883400

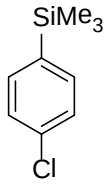


^{3}4

E(vacuo)	-849.1180243
Zero-point correction	0.198291
Thermal correction to Energy	0.210114
Thermal correction to Enthalpy	0.211058
Thermal correction to Gibbs Free Energy	0.159460

E(MeOH)	-849.129987
E(MeOH, Stretch)	-849.1058044

C	-1.36305800	-1.23334200	-0.73450600
C	-0.04104500	-1.19432000	-0.43623700
C	0.65771100	0.04148600	-0.20033900
C	-0.06026300	1.25308700	-0.41278000
C	-1.38693000	1.25808500	-0.73128900
C	-2.13707900	0.00391500	-0.65961700
H	-1.86569100	-2.16656900	-0.95903700
H	0.51724100	-2.12338300	-0.41994100
H	0.46772300	2.19724300	-0.38060100
H	-1.90483300	2.17787500	-0.97510500
Cl	-3.35874100	-0.01067300	0.71588600
C	2.13705700	0.00581600	0.17132100
C	2.72847900	1.41020500	0.37824000
C	2.30708000	-0.78707300	1.48996100
C	2.93953700	-0.69648300	-0.95080200
H	2.69496300	2.00701000	-0.53590900
H	2.20678500	1.95851300	1.16584100
H	3.77619000	1.32445000	0.67434800
H	1.94334100	-1.81183100	1.39944600
H	3.36407000	-0.83038500	1.76628600
H	1.76149600	-0.30895600	2.30648800
H	3.99961600	-0.73034500	-0.68612000
H	2.60661700	-1.72280800	-1.11359100
H	2.84215100	-0.15762700	-1.89589800

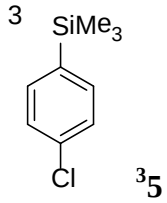


5

E(vacuo)	-1100.6861955
Zero-point correction	0.191414
Thermal correction to Energy	0.204883
Thermal correction to Enthalpy	0.205827
Thermal correction to Gibbs Free Energy	0.150733

E(MeOH) -1100.6956907

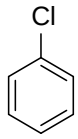
C	-1.73500000	1.21374800	-0.00016800
C	-0.34290400	1.20944500	-0.00014200
C	0.39555000	0.02013400	0.00001000
C	-0.33070200	-1.17934800	0.00014200
C	-1.72032900	-1.20077300	0.00011800
C	-2.41108600	0.00346300	-0.00003900
H	-2.28703700	2.14460500	-0.00028800
H	0.16727500	2.16598800	-0.00024600
H	0.18953600	-2.13194600	0.00026800
H	-2.26214100	-2.13759300	0.00022200
Cl	-4.16947900	-0.00793600	-0.00006600
C	2.89841800	-0.89980300	1.53905800
C	2.89846400	-0.90004700	-1.53882000
C	2.94449900	1.76688400	-0.00011500
H	2.56965100	-0.39175500	2.44908900
H	2.52318200	-1.92560900	1.57916000
H	3.99096600	-0.94680500	1.55623400
H	2.56971700	-0.39214000	-2.44893600
H	3.99101200	-0.94704800	-1.55596000
H	2.52323000	-1.92586000	-1.57877400
H	4.03791600	1.75832900	-0.00012600
H	2.62130100	2.32178700	-0.88458500
H	2.62131400	2.32196500	0.88424700
Si	2.28883900	0.00134100	0.00004000



E(vacuo)	-1100.5618924
Zero-point correction	0.187489
Thermal correction to Energy	0.201672
Thermal correction to Enthalpy	0.202617
Thermal correction to Gibbs Free Energy	0.144730

E(MeOH)	-1100.5722736
E(MeOH, Stretch)	-1100.54400

C	1.75017800	1.26286600	-0.70240800
C	0.41717600	1.24938200	-0.42890400
C	-0.31375700	0.03038100	-0.24852300
C	0.39899800	-1.20363200	-0.45304900
C	1.72955600	-1.23988000	-0.71792400
C	2.49912100	0.00400900	-0.63385200
H	2.27866300	2.18530600	-0.91206300
H	-0.11874400	2.19253500	-0.40558600
H	-0.15498200	-2.13787600	-0.44893900
H	2.24335300	-2.17025100	-0.92927500
Cl	3.71441700	-0.01435300	0.72439500
C	-3.05026800	-1.04772500	-1.14979700
C	-2.41354300	-0.75863500	1.84537300
C	-2.84979300	1.75558200	0.11416200
H	-2.93353700	-0.62944600	-2.15246000
H	-2.67335700	-2.07317300	-1.17084600
H	-4.12034000	-1.09586600	-0.92859600
H	-1.91661700	-0.17026600	2.62036200
H	-3.47847000	-0.80807000	2.09033200
H	-2.01344000	-1.77450700	1.89207500
H	-3.92072300	1.73697600	0.33442900
H	-2.37353200	2.39351800	0.86293500
H	-2.72432200	2.22885000	-0.86297300
Si	-2.16036100	0.00372600	0.13895800

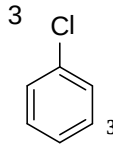


Ph-Cl

E(vacuo)	-691.9427128
Zero-point correction	0.090701
Thermal correction to Energy	0.096197
Thermal correction to Enthalpy	0.097141
Thermal correction to Gibbs Free Energy	0.060923

E(MeOH) -691.951203

C	0.00000000	-1.57003000	1.20308000
C	0.00000000	-0.17889500	1.21074000
C	0.00000000	0.50070100	0.00000000
C	0.00000000	-0.17889500	-1.21074000
C	0.00000000	-1.57003000	-1.20308000
C	0.00000000	-2.26843800	0.00000000
H	0.00000000	-2.10615100	2.14452000
H	0.00000000	0.37226600	2.14169600
H	0.00000000	0.37226600	-2.14169600
H	0.00000000	-2.10615100	-2.14452000
H	0.00000000	-3.35143900	0.00000000
Cl	0.00000000	2.25957200	0.00000000

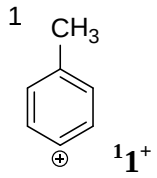


^{3}Ph-Cl

E(vacuo)	-691.8166689
Zero-point correction	0.086363
Thermal correction to Energy	0.092610
Thermal correction to Enthalpy	0.093555
Thermal correction to Gibbs Free Energy	0.054787

E(MeOH)	-691.8261642
E(MeOH, Stretch)	-691.7963053

C	-1.41593300	-1.23427700	-0.11031200
C	-0.21460800	-1.25619500	0.53048000
C	0.53365500	-0.00007000	0.65284600
C	-0.21451800	1.25614700	0.53051700
C	-1.41584300	1.23434000	-0.11026300
C	-2.01368400	0.00006000	-0.48499900
H	-1.95571700	-2.15838800	-0.28635900
H	0.22540000	-2.17762400	0.89179500
H	0.22563500	2.17751100	0.89181100
H	-1.95555300	2.15849800	-0.28628800
H	-2.97730000	0.00010200	-0.97789200
Cl	2.05194800	-0.00000700	-0.36956900

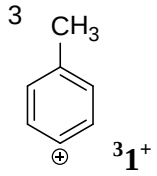


1^{+}

E(vacuo)	-270.6565086
Zero-point correction	0.111550
Thermal correction to Energy	0.118383
Thermal correction to Enthalpy	0.119327
Thermal correction to Gibbs Free Energy	0.079857

E(MeOH) -270.7527802

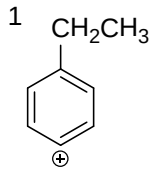
C	1.31394400	-1.26389800	0.00063500
C	-0.11387800	-1.20388400	-0.00707200
C	-0.82372000	0.00000600	-0.00971300
C	-0.11386800	1.20388600	-0.00707100
C	1.31395900	1.26388800	0.00063500
C	1.68963700	-0.00000500	0.01178900
H	1.88770000	-2.17987400	-0.00141600
H	-0.61458000	-2.16684300	-0.01117200
H	-0.61455800	2.16685200	-0.01117200
H	1.88772100	2.17986200	-0.00141600
C	-2.33061700	0.00000600	0.00574300
H	-2.69631900	-0.00032600	1.03590500
H	-2.73135500	0.88338300	-0.48992600
H	-2.73135300	-0.88305900	-0.49048900



E(vacuo)	-270.6382465
Zero-point correction	0.112828
Thermal correction to Energy	0.119341
Thermal correction to Enthalpy	0.120285
Thermal correction to Gibbs Free Energy	0.080207

E(MeOH) -270.7308358

C	1.24968500	-1.25399700	0.00329000
C	-0.12047100	-1.24464800	-0.00783800
C	-0.84142300	0.00001800	-0.01664600
C	-0.12045000	1.24466300	-0.00783800
C	1.24970700	1.25398100	0.00329100
C	1.87109600	-0.00001600	0.00663000
H	1.82290600	-2.17333900	0.00692700
H	-0.67932400	-2.17328100	-0.01359000
H	-0.67928300	2.17330800	-0.01359100
H	1.82294800	2.17330900	0.00692800
C	-2.31552400	0.00001300	-0.00226500
H	-2.64855900	-0.00035500	1.05154300
H	-2.73722300	0.89841600	-0.45470400
H	-2.73718900	-0.89814000	-0.45525200

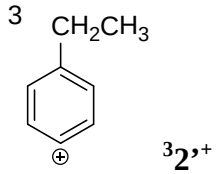


^{1}2'$^{+}$

E(vacuo)	-309.9828955
Zero-point correction	0.140449
Thermal correction to Energy	0.148364
Thermal correction to Enthalpy	0.149309
Thermal correction to Gibbs Free Energy	0.108079

E(MeOH) -310.0790445

C	-1.74178300	1.26374000	0.13673200
C	-0.34576300	1.20334200	-0.16588200
C	0.34784000	-0.00003500	-0.31782300
C	-0.34582500	-1.20336600	-0.16582400
C	-1.74185900	-1.26368100	0.13675800
C	-2.10666400	0.00004000	0.23038300
H	-2.30370400	2.17979500	0.25094700
H	0.14244700	2.16676400	-0.27416400
H	0.14233600	-2.16682000	-0.27404400
H	-2.30382200	-2.17970400	0.25101700
C	1.83121000	-0.00008000	-0.60990000
C	2.68089500	0.00004500	0.67226200
H	2.07452400	0.87500600	-1.21553800
H	2.07450700	-0.87529800	-1.21535500
H	3.73988000	0.00000300	0.41313200
H	2.48277400	0.88376900	1.28179400
H	2.48274700	-0.88354500	1.28198100

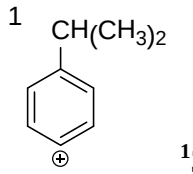


^{3}2'$^{+}$

E(vacuo)	-309.9657695
Zero-point correction	0.142118
Thermal correction to Energy	0.149729
Thermal correction to Enthalpy	0.150673
Thermal correction to Gibbs Free Energy	0.108840

E(MeOH) -310.056927

C	-1.67005600	1.25317200	0.12292100
C	-0.32985200	1.24347300	-0.16459300
C	0.37289800	-0.00012200	-0.33130200
C	-0.33007200	-1.24357000	-0.16444700
C	-1.67027600	-1.25299300	0.12307300
C	-2.27816600	0.00015300	0.25048100
H	-2.23067800	2.17261800	0.24117600
H	0.21536600	2.17268900	-0.28413200
H	0.21498400	-2.17289600	-0.28387200
H	-2.23106600	-2.17232300	0.24144300
C	1.81574300	-0.00025300	-0.63233100
C	2.63999400	0.00014700	0.70525300
H	2.09005000	0.88915200	-1.20261500
H	2.09001800	-0.88998300	-1.20210800
H	3.69639400	0.00004000	0.43637700
H	2.42685300	0.88807600	1.29942700
H	2.42680400	-0.88740600	1.29996700

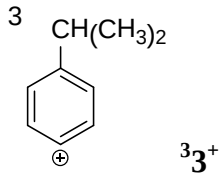


1 3$^+$

E(vacuo)	-349.3087689
Zero-point correction	0.168152
Thermal correction to Energy	0.177476
Thermal correction to Enthalpy	0.178420
Thermal correction to Gibbs Free Energy	0.133990

E(MeOH) -349.4045883

C	2.25962900	-1.08601900	-0.00003800
C	2.42481300	0.21984100	0.00004500
C	1.84511400	1.40675200	0.00001800
C	0.44858800	1.11669300	-0.00001700
C	-0.05938500	-0.18741900	-0.00001200
C	0.83618700	-1.25639000	0.00001200
H	2.97052400	-1.89977600	-0.00026200
H	2.26505800	2.40244200	0.00019200
H	-0.19791000	1.98789600	0.00008600
H	0.50039100	-2.28874200	-0.00007300
C	-1.55827600	-0.44643200	-0.00002800
C	-2.21986400	0.10521800	-1.27389800
C	-2.21984800	0.10508100	1.27392300
H	-1.68872400	-1.53212100	-0.00007700
H	-1.76464600	-0.30406400	-2.17754500
H	-3.27836100	-0.15775300	-1.28136600
H	-2.15256700	1.19525200	-1.32147200
H	-1.76460500	-0.30429500	2.17751300
H	-2.15256400	1.19511000	1.32160400
H	-3.27834000	-0.15790800	1.28137700



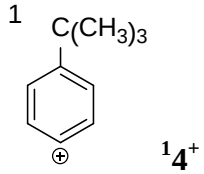
$^{3}\mathbf{3}^{+}$

E(vacuo) -349.2920697

Zero-point correction	0.169817
Thermal correction to Energy	0.178880
Thermal correction to Enthalpy	0.179824
Thermal correction to Gibbs Free Energy	0.134249

E(MeOH) -349.3824389

C	2.16401900	-1.06259800	-0.27965700
C	2.60422200	0.20784500	0.09595500
C	1.81234300	1.32746100	0.37092900
C	0.45714800	1.15852200	0.24460100
C	-0.08553400	-0.10826900	-0.16021200
C	0.80656600	-1.21465200	-0.39647000
H	2.85572500	-1.87425900	-0.47013900
H	2.25011600	2.27374900	0.66527900
H	-0.21352400	1.98515700	0.43911800
H	0.38400500	-2.16967500	-0.68746500
C	-1.54427900	-0.32217800	-0.29967100
C	-2.35939200	0.88781300	-0.76953000
C	-2.05945500	-0.83357200	1.10191800
H	-1.69514000	-1.15555300	-0.99297400
H	-1.97821900	1.28784500	-1.71045200
H	-3.39182600	0.57683800	-0.93221200
H	-2.37934200	1.69077300	-0.03048200
H	-1.53948400	-1.73383300	1.42776400
H	-1.94671100	-0.05938200	1.86103600
H	-3.11942900	-1.06389500	0.98334900

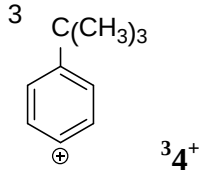


$^{1}4^{+}$

E(vacuo)	-388.6317075
Zero-point correction	0.195854
Thermal correction to Energy	0.206373
Thermal correction to Enthalpy	0.207317
Thermal correction to Gibbs Free Energy	0.160634

E(MeOH) -388.7255928

C	-2.27874000	-1.26124900	-0.00017400
C	-0.85542900	-1.18695100	-0.00002200
C	-0.14713300	0.02297800	-0.00001700
C	-0.87510700	1.21324100	-0.00003300
C	-2.30990000	1.26353500	-0.00016000
C	-2.67145900	-0.00022800	0.00037800
H	-2.84381900	-2.18222500	-0.00038400
H	-0.35539000	-2.14879100	0.00006100
H	-0.40000000	2.18649000	-0.00001600
H	-2.88513300	2.17794900	-0.00051800
C	1.39067400	0.00605400	-0.00001100
C	1.97654300	1.42775200	-0.00109100
C	1.88009600	-0.73178300	1.26649400
C	1.88027500	-0.73373600	-1.26528900
H	1.68875000	1.99330600	-0.89091800
H	1.68899800	1.99458600	0.88800200
H	3.06490400	1.36467600	-0.00116700
H	1.54214000	-1.76955000	1.29843200
H	2.97092400	-0.74453000	1.28130100
H	1.53794700	-0.23407700	2.17627600
H	2.97110300	-0.74640800	-1.27997200
H	1.54248400	-1.77160700	-1.29564200
H	1.53817000	-0.23750800	-2.17589500



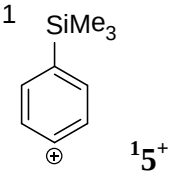
$^{3}\mathbf{4}^{+}$

E(vacuo) -388.615085
Zero-point correction 0.197484
Thermal correction to Energy 0.207796
Thermal correction to Enthalpy 0.208741
Thermal correction to Gibbs Free Energy 0.160854

E(MeOH) -388.7030593

C	-2.21513000	-1.24450800	-0.00000500
C	-0.84459500	-1.20982600	-0.00000600
C	-0.12193600	0.04450000	-0.00002400
C	-0.87262500	1.26663100	-0.00000600
C	-2.24486500	1.25139200	-0.00000600
C	-2.85547100	-0.00809900	-0.00000800
H	-2.76750300	-2.17628600	0.00000300
H	-0.28872600	-2.13753100	0.00000800
H	-0.34866400	2.21171500	-0.00000200
H	-2.82867200	2.16418300	-0.00000200
C	1.37455500	0.02589000	-0.00000700
C	2.01324300	1.42209300	-0.00001100
C	1.85596600	-0.75374900	1.26935600
C	1.85604000	-0.75379200	-1.26930900
H	1.74580700	1.99818300	-0.88819700
H	1.74584700	1.99817600	0.88819200
H	3.09811800	1.31709900	-0.00003300
H	1.50021100	-1.78332100	1.29724800
H	2.94659000	-0.77772500	1.24695800
H	1.53941500	-0.24823900	2.18238300
H	2.94666400	-0.77772700	-1.24687600
H	1.50033000	-1.78338000	-1.29716800
H	1.53950100	-0.24833800	-2.18237100

1

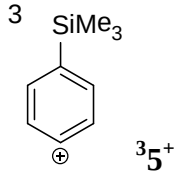


$^{1}5^{+}$

E(vacuo)	-640.0793126
Zero-point correction	0.184855
Thermal correction to Energy	0.197731
Thermal correction to Enthalpy	0.198675
Thermal correction to Gibbs Free Energy	0.145855

E(MeOH) -640.1702071

C	2.65370500	1.26040100	0.00000000
C	1.21145900	1.19846900	0.00000000
C	0.49287500	0.00856400	0.00000000
C	1.20573800	-1.18835100	0.00000000
C	2.64237400	-1.25459300	0.00000000
C	3.03788700	0.00279700	0.00000000
H	3.21073500	2.18581300	-0.00000100
H	0.73915500	2.17573300	0.00000000
H	0.72866500	-2.16390100	0.00000000
H	3.19933800	-2.18021400	0.00000100
C	-1.97782000	-0.90139800	-1.55575400
C	-1.97782000	-0.90139700	1.55575500
C	-2.02065000	1.78445700	0.00000000
H	-1.61580900	-0.40055200	-2.45645700
H	-1.62280900	-1.93462400	-1.57606300
H	-3.06921800	-0.93398700	-1.61343000
H	-1.61581200	-0.40054900	2.45645800
H	-3.06921800	-0.93398900	1.61342800
H	-1.62280600	-1.93462300	1.57606500
H	-3.11355600	1.81255800	0.00000000
H	-1.68957200	2.32853700	0.88824800
H	-1.68957300	2.32853600	-0.88825000
Si	-1.45542900	-0.00017400	0.00000000

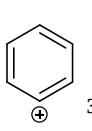


E(vacuo)	-640.0561927
Zero-point correction	0.186326
Thermal correction to Energy	0.199062
Thermal correction to Enthalpy	0.200007
Thermal correction to Gibbs Free Energy	0.145992

E(MeOH) -640.1396762

C	-2.57495800	-1.24751500	-0.04775900
C	-1.20203900	-1.23442600	0.04721100
C	-0.47253900	0.00004600	0.01815400
C	-1.20208200	1.23448300	0.04724400
C	-2.57500200	1.24751500	-0.04772600
C	-3.19312300	-0.00001300	-0.10709500
H	-3.14297600	-2.16962600	-0.07705300
H	-0.66375400	-2.17345500	0.10054100
H	-0.66383600	2.17353300	0.10058400
H	-3.14305900	2.16960200	-0.07700400
C	2.06910500	1.56057700	-0.85337900
C	1.81681000	-0.00057700	1.83460800
C	2.06902300	-1.56010400	-0.85426400
H	1.75910600	1.62490800	-1.89889500
H	1.74844000	2.46919100	-0.34043100
H	3.16214800	1.54899100	-0.83687700
H	1.43493300	-0.89283600	2.32884300
H	2.91157900	-0.00061000	1.88174600
H	1.43495700	0.89136300	2.32943500
H	3.16206600	-1.54858100	-0.83775000
H	1.74830500	-2.46898700	-0.34182600
H	1.75901300	-1.62382600	-1.89981400
Si	1.43442200	0.00003000	-0.04667700

3

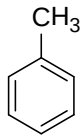


$^3Ph^+$

E(vacuo)	-231.2919396
Zero-point correction	0.085525
Thermal correction to Energy	0.090284
Thermal correction to Enthalpy	0.091228
Thermal correction to Gibbs Free Energy	0.056816

E(MeOH) -231.3884504

C	-1.26265100	0.75527300	0.00000000
C	0.00000100	1.37371800	0.00000100
C	1.26265200	0.75527300	0.00000000
C	1.25182400	-0.61592300	-0.00000100
C	-0.00000100	-1.30456200	0.00000000
C	-1.25182500	-0.61592200	-0.00000100
H	-2.17811500	1.33490300	0.00000000
H	2.17811700	1.33490100	0.00000000
H	2.17436300	-1.18392000	-0.00000100
H	-0.00000100	-2.38910400	0.00000700
H	-2.17436300	-1.18391900	-0.00000100

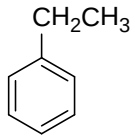


1a

E(vacuo)	-271.6460634
Zero-point correction	0.127262
Thermal correction to Energy	0.133523
Thermal correction to Enthalpy	0.134467
Thermal correction to Gibbs Free Energy	0.096123

E(MeOH) -271.6531118

C	-1.19747800	1.20099300	0.00201100
C	0.19349100	1.19805400	-0.00891100
C	0.91109100	0.00003500	-0.01119900
C	0.19353200	-1.19803200	-0.00891100
C	-1.19741700	-1.20102500	0.00201100
C	-1.89917400	-0.00002300	0.00857200
H	-1.73359700	2.14302700	0.00151100
H	0.73087400	2.14053700	-0.01820000
H	0.73095300	-2.14049500	-0.01819900
H	-1.73350400	-2.14307700	0.00151000
C	2.41926800	0.00001600	0.00930700
H	2.79827800	-0.00215700	1.03628900
H	2.82489500	-0.88253700	-0.48902000
H	2.82485800	0.88464900	-0.48532300
H	-2.98264400	-0.00005100	0.01414800

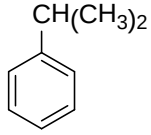


2'a

E(vacuo)	-310.970861
Zero-point correction	0.156126
Thermal correction to Energy	0.163458
Thermal correction to Enthalpy	0.164403
Thermal correction to Gibbs Free Energy	0.124086

E(MeOH) -310.9788072

C	-1.63346600	1.20144200	0.09548600
C	-0.27061400	1.19815800	-0.18321500
C	0.43297600	-0.00006500	-0.32510600
C	-0.27070900	-1.19821500	-0.18313400
C	-1.63356800	-1.20136900	0.09557100
C	-2.32038100	0.00006700	0.23717700
H	-2.16026800	2.14324300	0.19741400
H	0.25451100	2.14092600	-0.29765500
H	0.25433400	-2.14103700	-0.29750700
H	-2.16043900	-2.14312500	0.19756500
H	-3.38254200	0.00012200	0.45124100
C	1.92063700	-0.00012600	-0.59058800
C	2.76047400	0.00009200	0.69646000
H	2.18193900	0.87620000	-1.19082200
H	2.18191900	-0.87667000	-1.19051200
H	3.82866000	0.00003300	0.46561600
H	2.54490900	0.88184100	1.30422000
H	2.54487700	-0.88143200	1.30453500

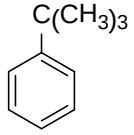


3a

E(vacuo)	-350.2950659
Zero-point correction	0.183956
Thermal correction to Energy	0.192669
Thermal correction to Enthalpy	0.193613
Thermal correction to Gibbs Free Energy	0.150229

E(MeOH) -350.3037965

C	-2.12739100	-1.07547400	-0.00004100
C	-2.64796900	0.21304900	0.00001400
C	-1.77862200	1.30015900	0.00005000
C	-0.40349300	1.09739900	0.00003400
C	0.13615100	-0.19266900	-0.00001800
C	-0.74911100	-1.27173100	-0.00005800
H	-2.79304000	-1.93097300	-0.00007200
H	-2.17318600	2.30978400	0.00009100
H	0.25592900	1.95812000	0.00006300
H	-0.35363900	-2.28216000	-0.00010200
C	1.63859900	-0.42553000	-0.00003000
C	2.30799200	0.13088900	1.26740400
C	2.30801100	0.13107300	-1.26736900
H	1.78971600	-1.51011100	-0.00010700
H	1.86063000	-0.29220000	2.16927900
H	3.37540400	-0.10505700	1.27351000
H	2.20854800	1.21790800	1.32457000
H	1.86064900	-0.29186500	-2.16931500
H	2.20859200	1.21810300	-1.32436800
H	3.37541900	-0.10489300	-1.27350500
H	-3.72002000	0.37034100	0.00002700



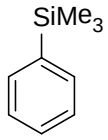
4a

E(vacuo) -389.6163956

Zero-point correction	0.211835
Thermal correction to Energy	0.221697
Thermal correction to Enthalpy	0.222641
Thermal correction to Gibbs Free Energy	0.177223

E(MeOH) -389.6248862

C	-2.18450700	-1.19592300	0.00000800
C	-0.79604900	-1.17562200	0.00002800
C	-0.07879500	0.02829400	0.00003500
C	-0.81851000	1.21293000	0.00000100
C	-2.21222400	1.19925800	-0.00000900
C	-2.90338400	-0.00417000	-0.00000100
H	-2.70685300	-2.14580300	0.00000300
H	-0.26486500	-2.12001600	0.00002100
H	-0.31401700	2.16943700	0.00000100
H	-2.75465600	2.13782200	-0.00002000
C	1.45896800	0.00554300	0.00000100
C	2.06629400	1.41837500	-0.00062500
C	1.96324200	-0.73140800	1.26032900
C	1.96312800	-0.73248200	-1.25974300
H	1.77419600	1.98750100	-0.88621200
H	1.77369300	1.98849000	0.88416200
H	3.15629600	1.34653000	-0.00028600
H	1.60449000	-1.76132200	1.29949500
H	3.05634300	-0.75876100	1.27230300
H	1.62641400	-0.22601200	2.16847700
H	3.05622400	-0.76001300	-1.27170300
H	1.60420400	-1.76236900	-1.29808400
H	1.62636900	-0.22775800	-2.16829100
H	-3.98682100	-0.01650000	-0.00000800



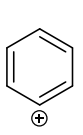
5a

E(vacuo)	-641.0604158
Zero-point correction	0.200908
Thermal correction to Energy	0.213172
Thermal correction to Enthalpy	0.214116
Thermal correction to Gibbs Free Energy	0.162501

E(MeOH) -641.0682757

C	2.55933400	1.19997100	0.00000100
C	1.16674500	1.20803100	-0.00000500
C	0.42738900	0.01836800	-0.00001200
C	1.14722400	-1.18581500	-0.00001100
C	2.53746000	-1.20350600	-0.00000500
C	3.24861100	-0.00705100	0.00000200
H	3.10498900	2.13679400	0.00000500
H	0.65385900	2.16350600	-0.00000700
H	0.61833700	-2.13410200	-0.00001700
H	3.06692500	-2.14954400	-0.00000500
C	-2.08096400	-0.89628400	-1.53794100
C	-2.08093600	-0.89595900	1.53814600
C	-2.12341700	1.76913000	-0.00018600
H	-1.75318400	-0.38853300	-2.44855700
H	-1.70653800	-1.92235200	-1.57891600
H	-3.17367000	-0.94179900	-1.55272700
H	-1.75315800	-0.38799900	2.44864700
H	-3.17364100	-0.94149600	1.55295200
H	-1.70648300	-1.92200800	1.57934300
H	-3.21689000	1.75971500	-0.00018400
H	-1.79991000	2.32442900	0.88392300
H	-1.79991100	2.32422700	-0.88442300
Si	-1.46441400	0.00391300	0.00000100
H	4.33239700	-0.01693100	0.00000800

1



$^{1}Ph^{+}$

E(vacuo)	-231.3231006
Zero-point correction	0.084422
Thermal correction to Energy	0.089312
Thermal correction to Enthalpy	0.090256
Thermal correction to Gibbs Free Energy	0.056797

E(MeOH) -231.4229974

C	-0.00001200	-1.18705300	-0.00000100
C	1.26622400	-0.81827500	-0.00000100
C	1.21032000	0.61262800	-0.00000100
C	0.00001200	1.29434400	0.00000000
C	-1.21030500	0.61264700	0.00000100
C	-1.26624000	-0.81825900	0.00000200
H	2.17998700	-1.39633100	0.00000600
H	2.16966200	1.11981100	0.00000200
H	0.00001900	2.37677700	0.00000000
H	-2.16964100	1.11984300	-0.00000200
H	-2.18001800	-1.39629000	-0.00000200

PhH

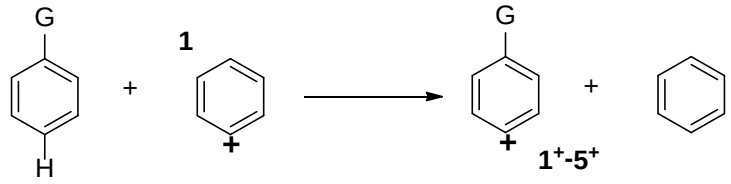
E(vacuo) -232.3174262
Zero-point correction 0.100081
Thermal correction to Energy 0.104485
Thermal correction to Enthalpy 0.105430
Thermal correction to Gibbs Free Energy 0.072621

E(MeOH) -232.3242389

C	-1.38839100	0.10076400	-0.00000100
C	-0.60679400	1.25253800	-0.00000900
C	0.78140300	1.15177600	-0.00000100
C	1.38838700	-0.10082500	-0.00000200
C	0.60684800	-1.25251100	-0.00000100
C	-0.78145300	-1.15174200	0.00000500
H	-2.46922700	0.17938100	0.00000900
H	-1.07924800	2.22784800	0.00001400
H	1.38978700	2.04860000	0.00002700
H	2.46923300	-0.17930200	0.00000900
H	1.07918100	-2.22788000	-0.00000600
H	-1.38972200	-2.04864400	-0.00000100

For all the structures reported in the isodesmic reaction in eq 1 G(B3LYP) values have been adopted, according to the definition given above in eq S2.

1a, G = Me
2'a, G = Et
3a, G = *i*Pr
4a, G = tBu
5a, G = $SiMe_3$



1^+-5^+

(S2)

Table S1. G(B3LYP) values for the isodesmic reaction reported in Figure 2

STRUCTURE	G(B3LYP) [HARTREE]
^{1}**1**$^+$	-270.6729232
^{3}**1**$^+$	-270.6506288
^{1}**2'**$^+$	-309.9709655
^{3}**2'**$^+$	-309.948087
^{1}**3**$^+$	-349.2705983
^{3}**3**$^+$	-349.2481899
^{1}**4**$^+$	-388.5649588
^{3}**4**$^+$	-388.5422053
^{1}**5**$^+$	-640.0243521
^{3}**5**$^+$	-639.9936842
^{3}**Ph**$^+$	-231.3316344
1a	-271.5569888
2'a	-310.854721
3a	-350.1535675
4a	-389.4476632
5a	-640.905775
^{1}**Ph**$^+$	-231.366200
PhH	-232.2516179

Table S2. Relative stability of phenyl cations according to the isodesmic reaction in eq 1

STRUCTURE	ΔG [kcal mol^{-1}]
$^{1}\mathbf{1}^{+}$	-0.85
$^{3}\mathbf{1}^{+}$	13.14
$^{1}\mathbf{2'}^{+}$	-1.04
$^{3}\mathbf{2'}^{+}$	13.31
$^{1}\mathbf{3}^{+}$	-1.54
$^{3}\mathbf{3}^{+}$	12.53
$^{1}\mathbf{4}^{+}$	-1.70
$^{3}\mathbf{4}^{+}$	12.58
$^{1}\mathbf{5}^{+}$	-2.51
$^{3}\mathbf{5}^{+}$	16.74
$^{3}\mathbf{Ph}^{+}$	21.69

2 Photophysical parameters for compounds 1 and 5.

Table S3

Ar-Cl	Solvent	λ_{abs} (nm), ε ($M^{-1}cm^{-1}$)	$\lambda_{em,}$ (nm)	Φ_F ($\times 10^2$)[a]
1	C_6H_{12}	270, 425	292	1.63
	MeOH	264, 440	295	1.34
5	C_6H_{12}	265, 215	289	1.18
	MeOH	264, 220	300	0.94

[a] Calculated by comparison with biphenyl (Φ_F = 0.18 in C_6H_{12}) see ref. S3

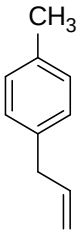
References.

S1 *Gaussian 09*, Revision A.02, Frisch, M. J; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P. ; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

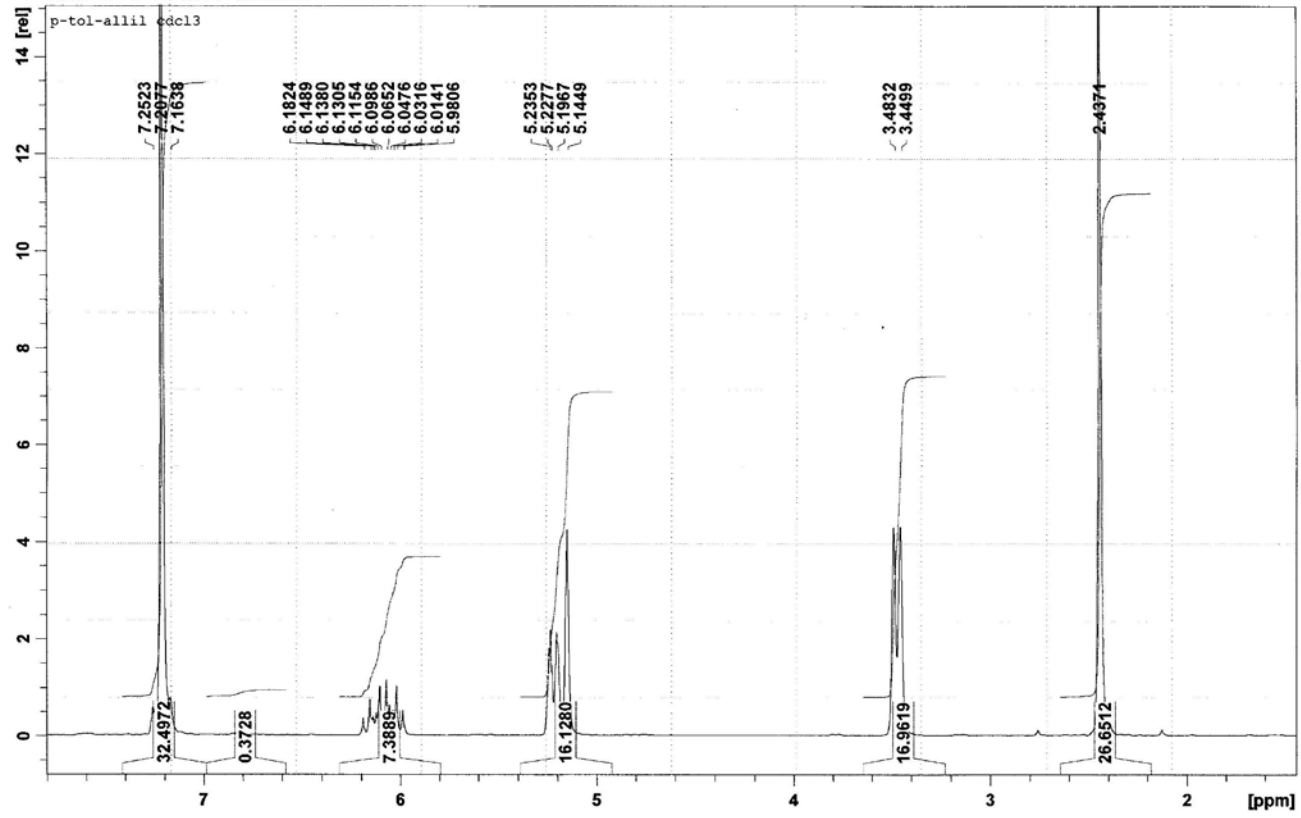
S2 (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995-2001. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comp. Chem.* **2003**, *24*, 669-681.

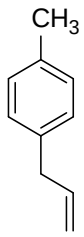
S3 Shimizu, M.; Kawaguchi, T.; Oda, K.; Tamejiro Hiyama, T. *Chem. Lett.* **2007**, *36*, 412-413.

3 ^{1}H and ^{13}C NMR of compounds 6-11, 13-16, 18-35

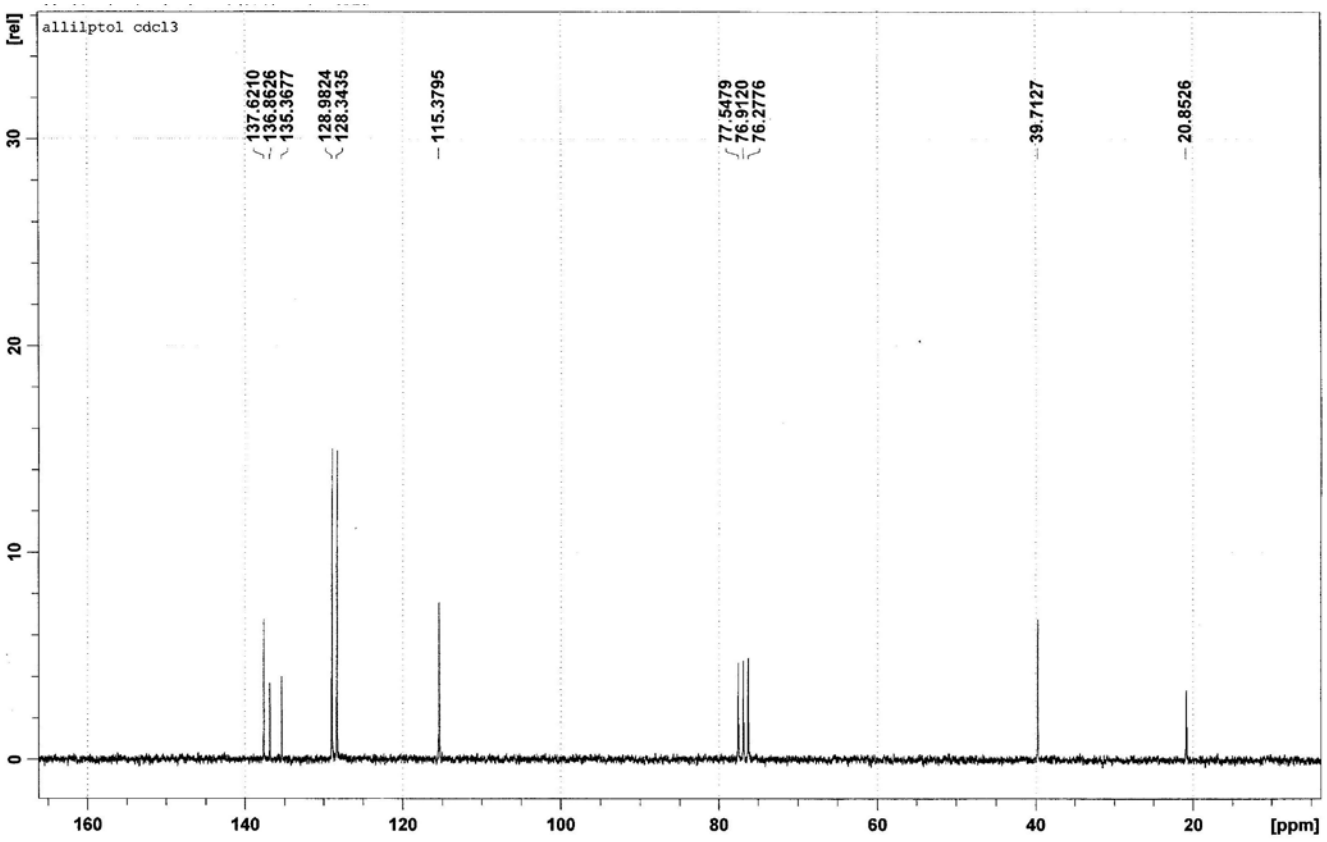


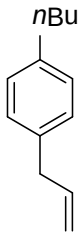
6 (^{1}H NMR , $CDCl_3$)



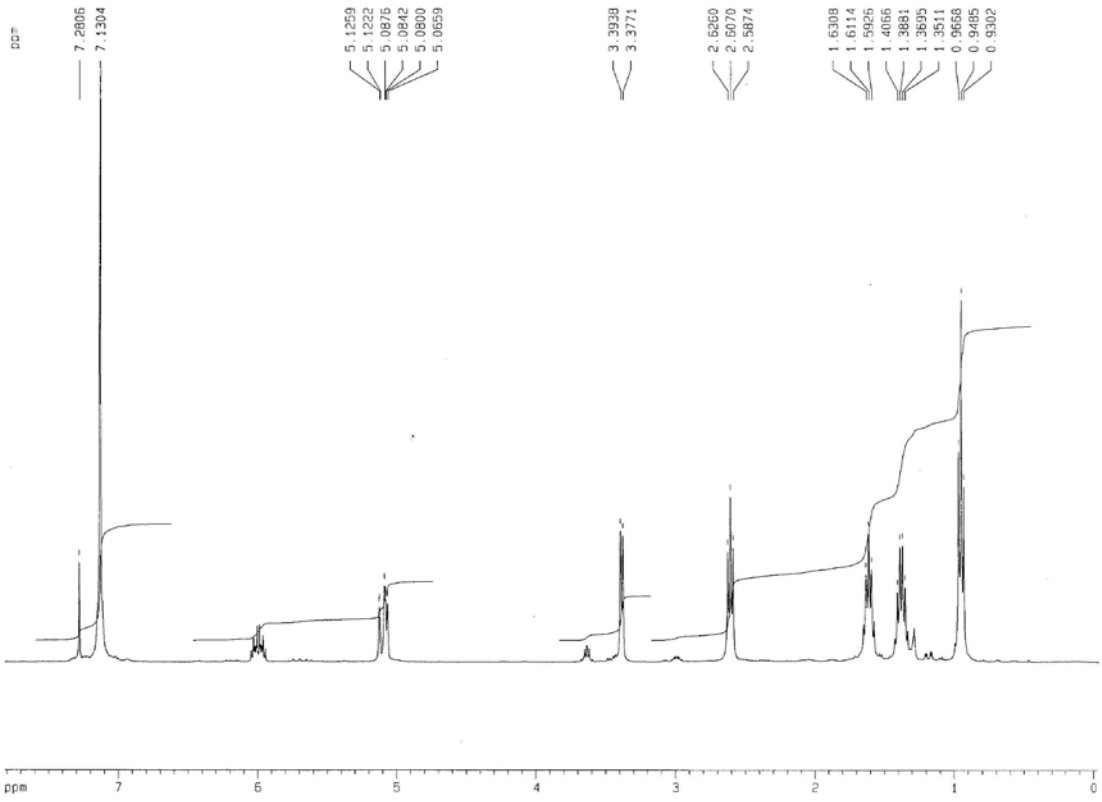


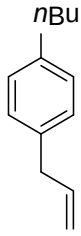
6 (^{13}C NMR , $CDCl_3$)



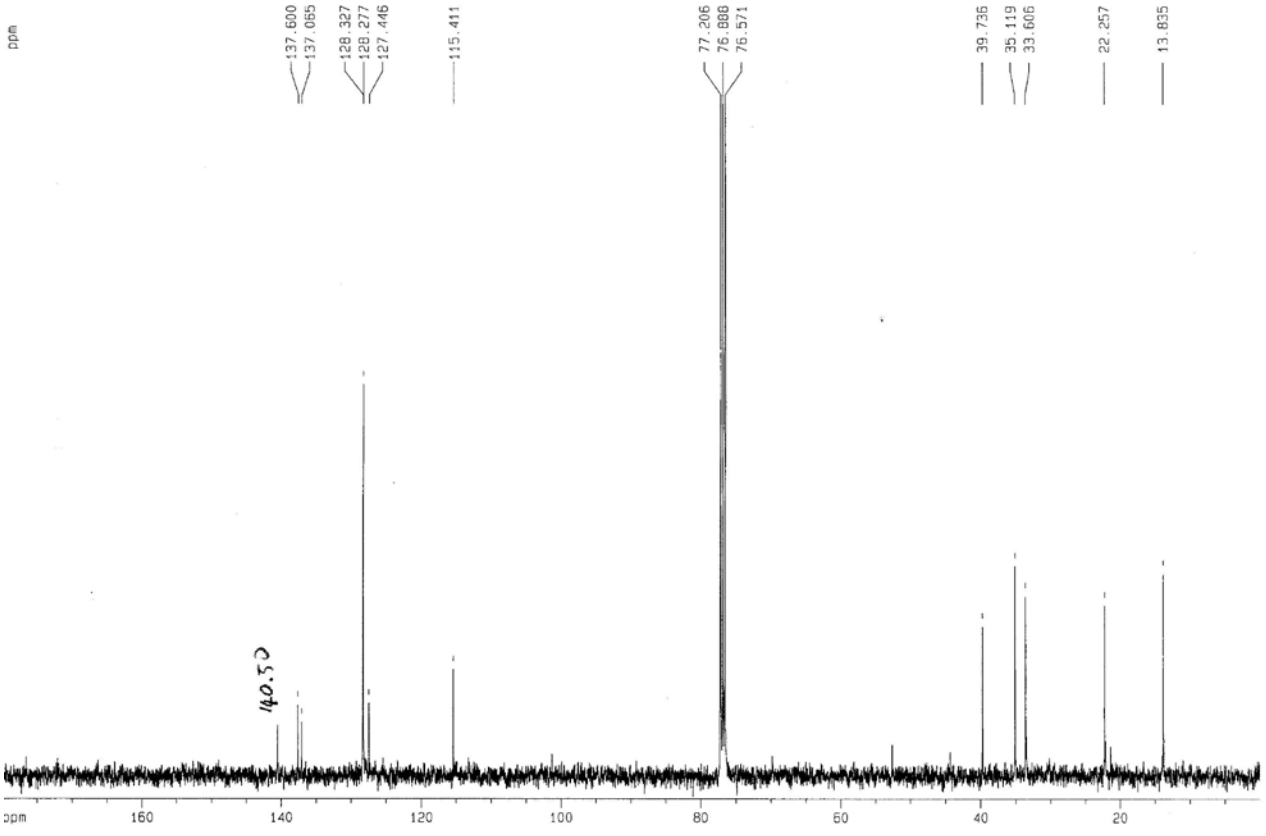


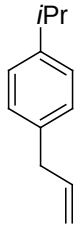
7 (^{1}H NMR , $CDCl_3$)



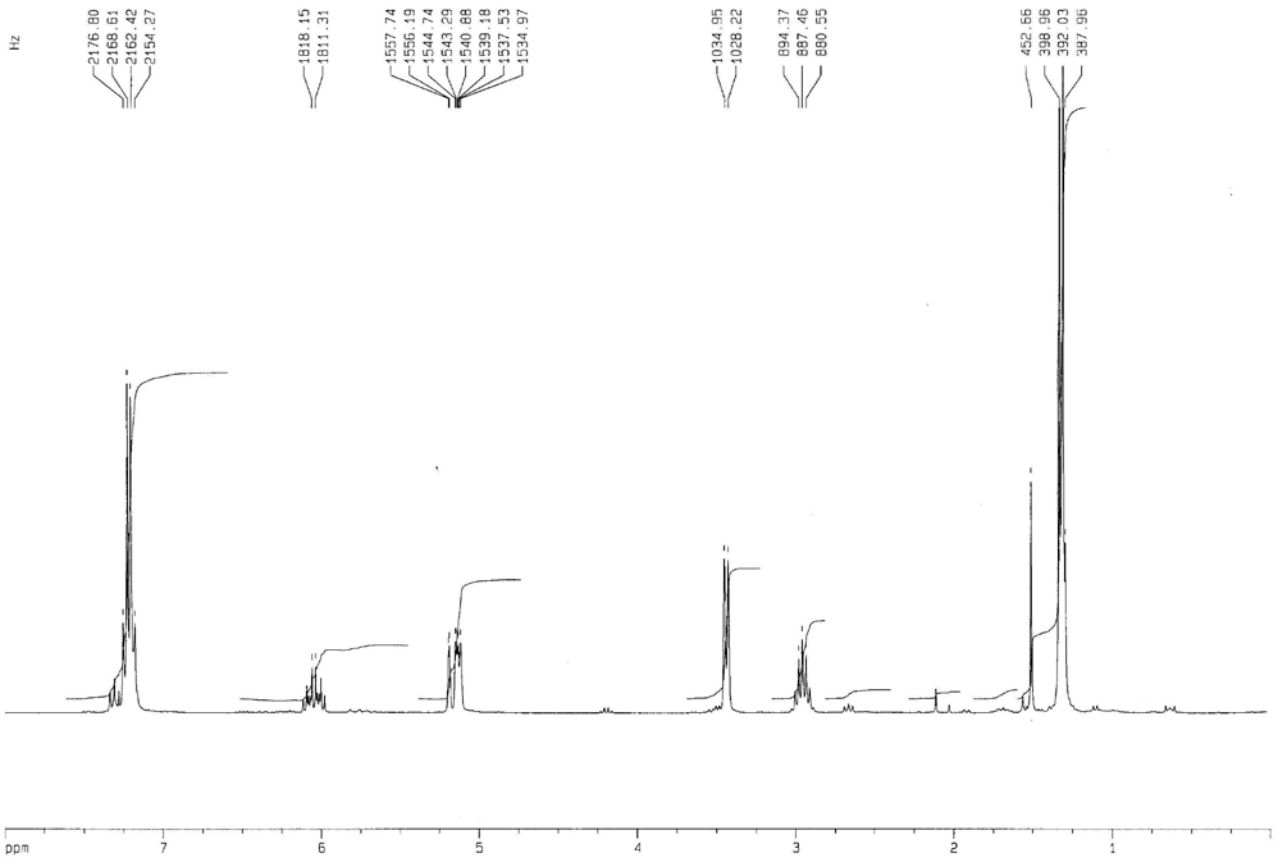


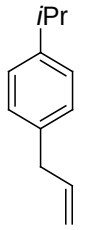
7 (^{13}C NMR , $CDCl_3$)



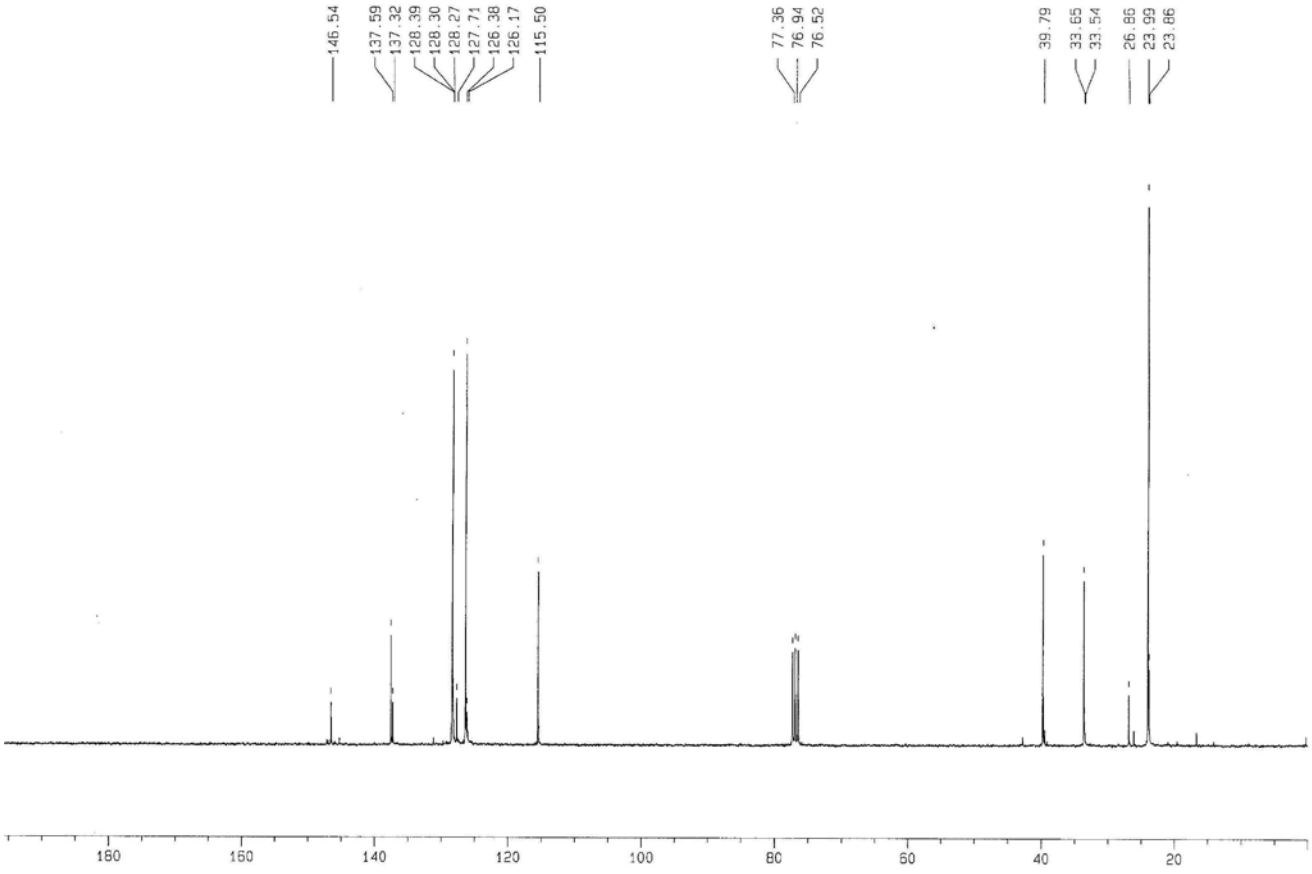


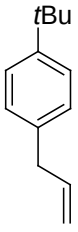
8 (^{1}H NMR , $CDCl_3$)



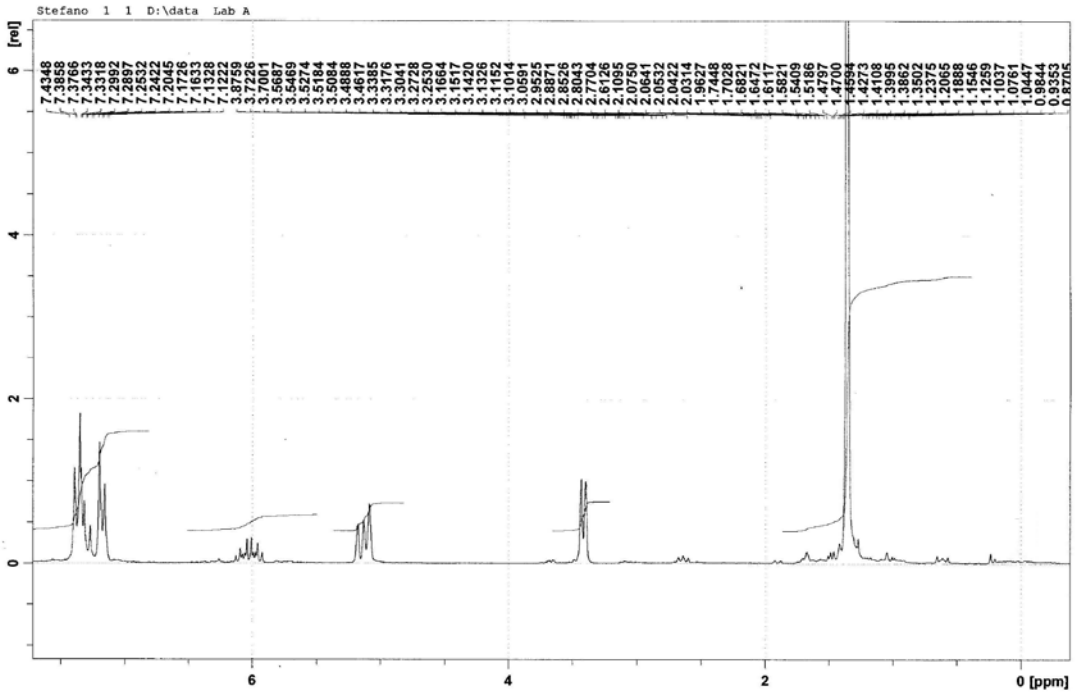


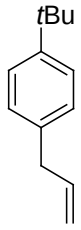
8 (^{13}C NMR , $CDCl_3$)



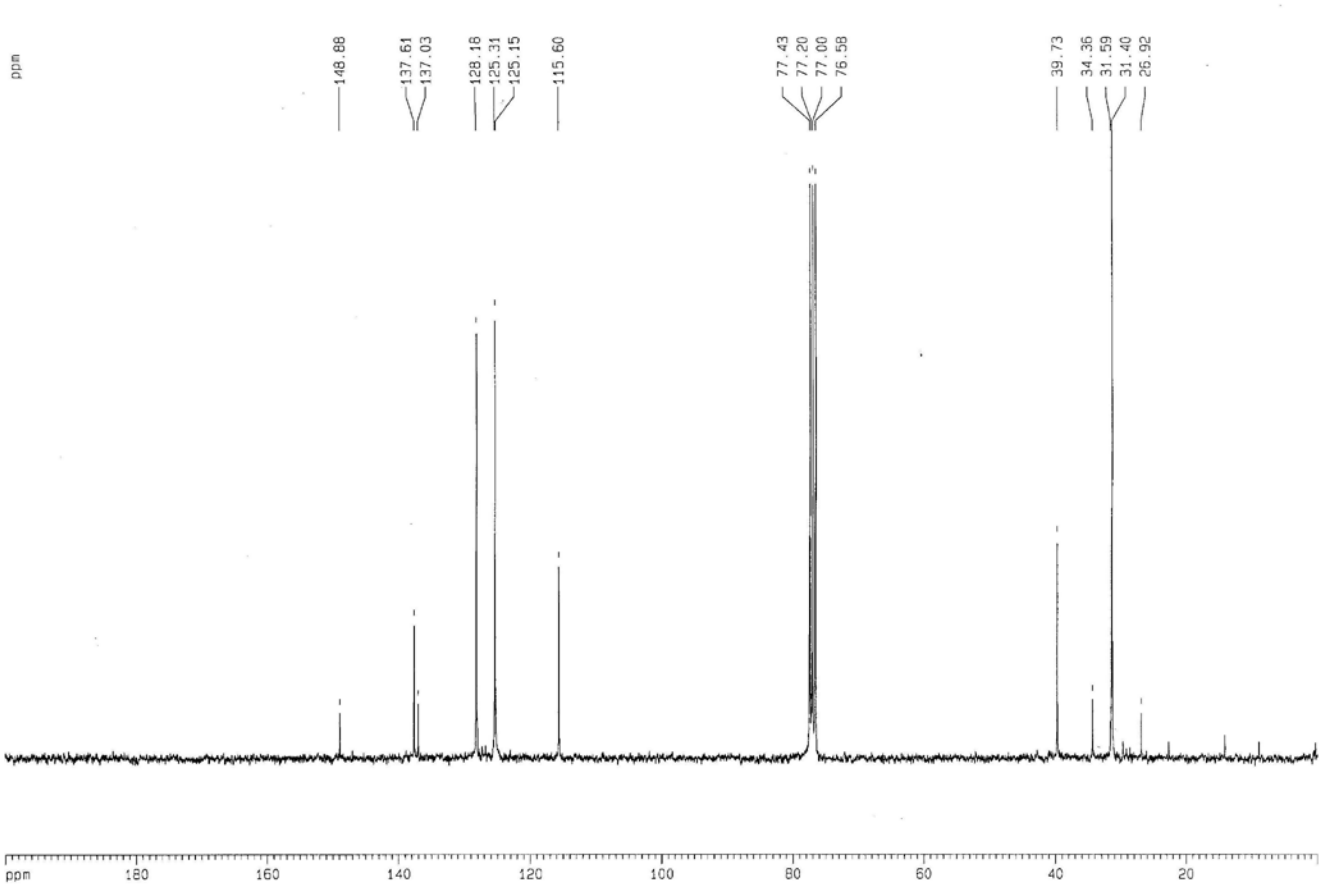


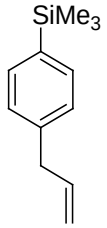
9 (^{1}H NMR , $CDCl_3$)



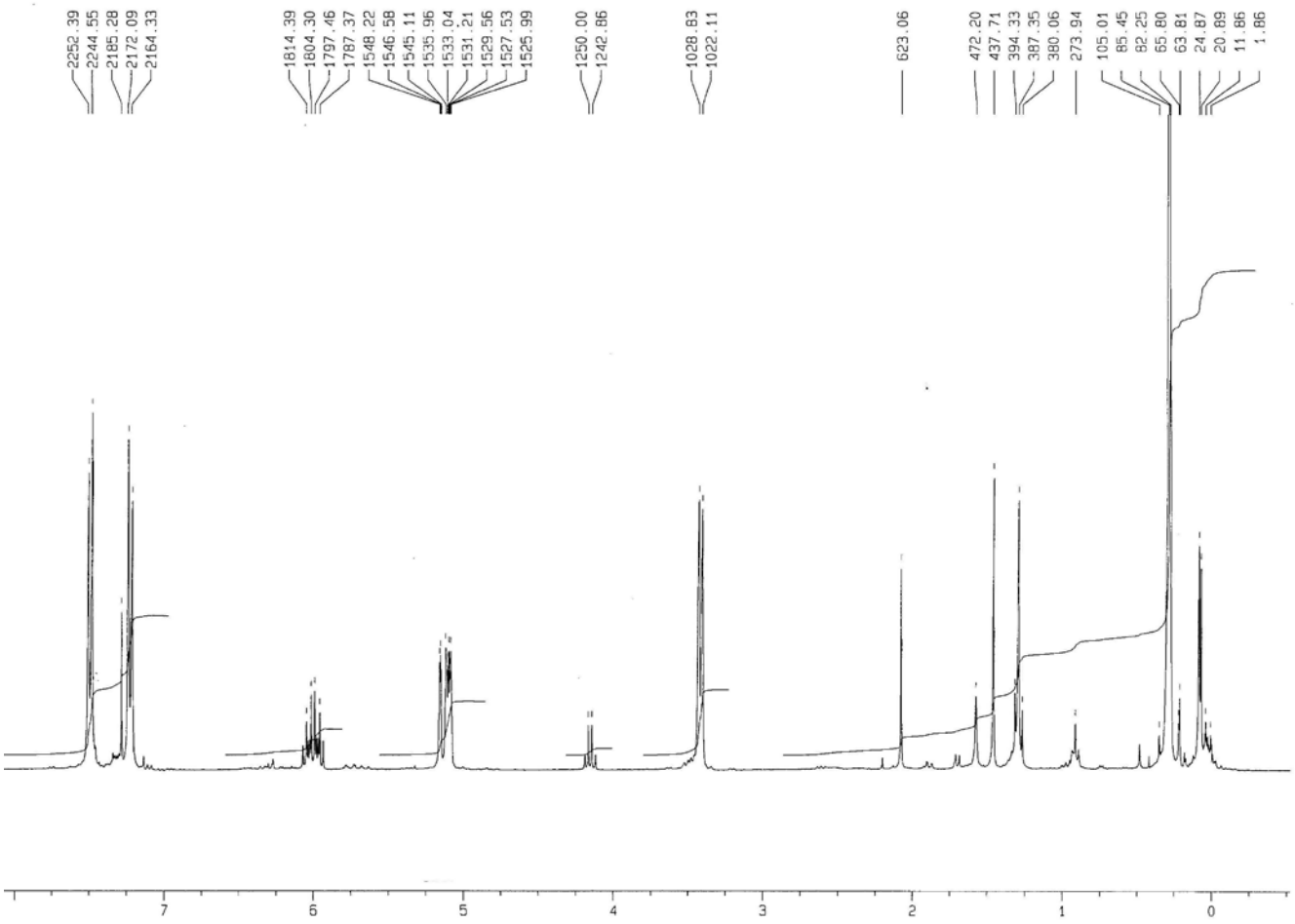


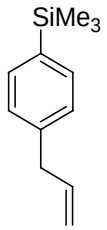
9 (^{13}C NMR , $CDCl_3$)



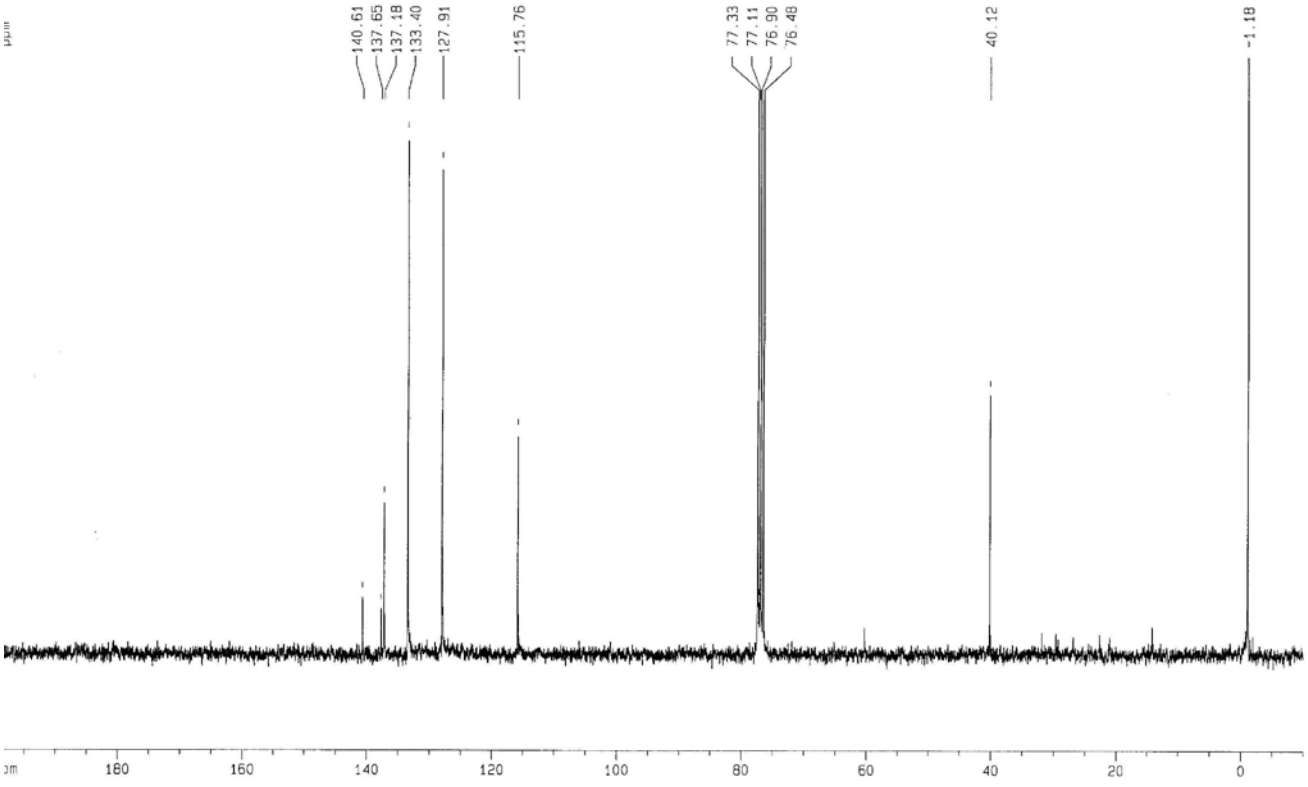


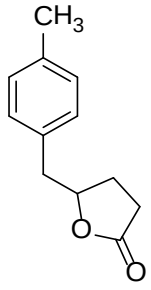
10 (^{1}H NMR , $CDCl_3$)



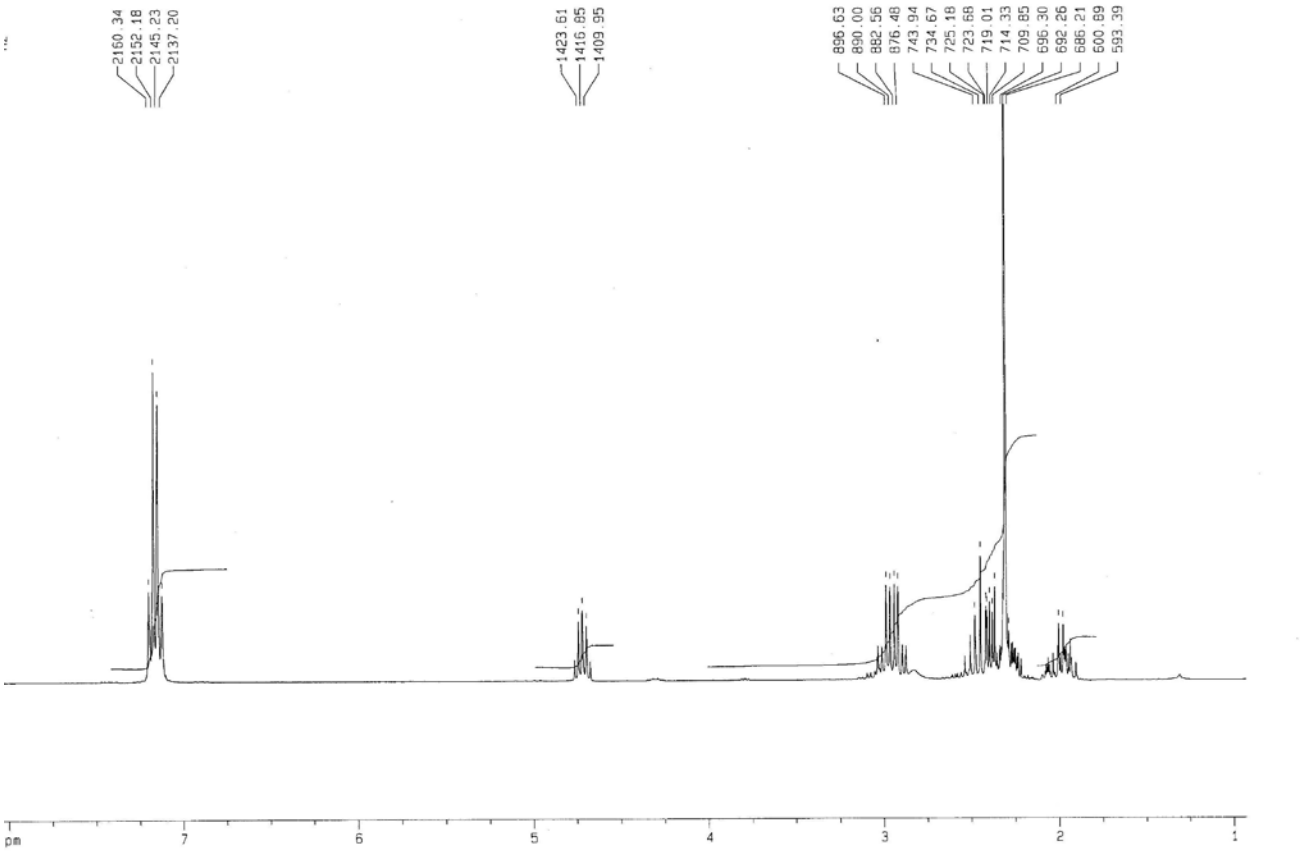


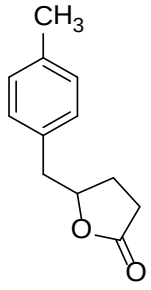
10 (^{13}C NMR , $CDCl_3$)



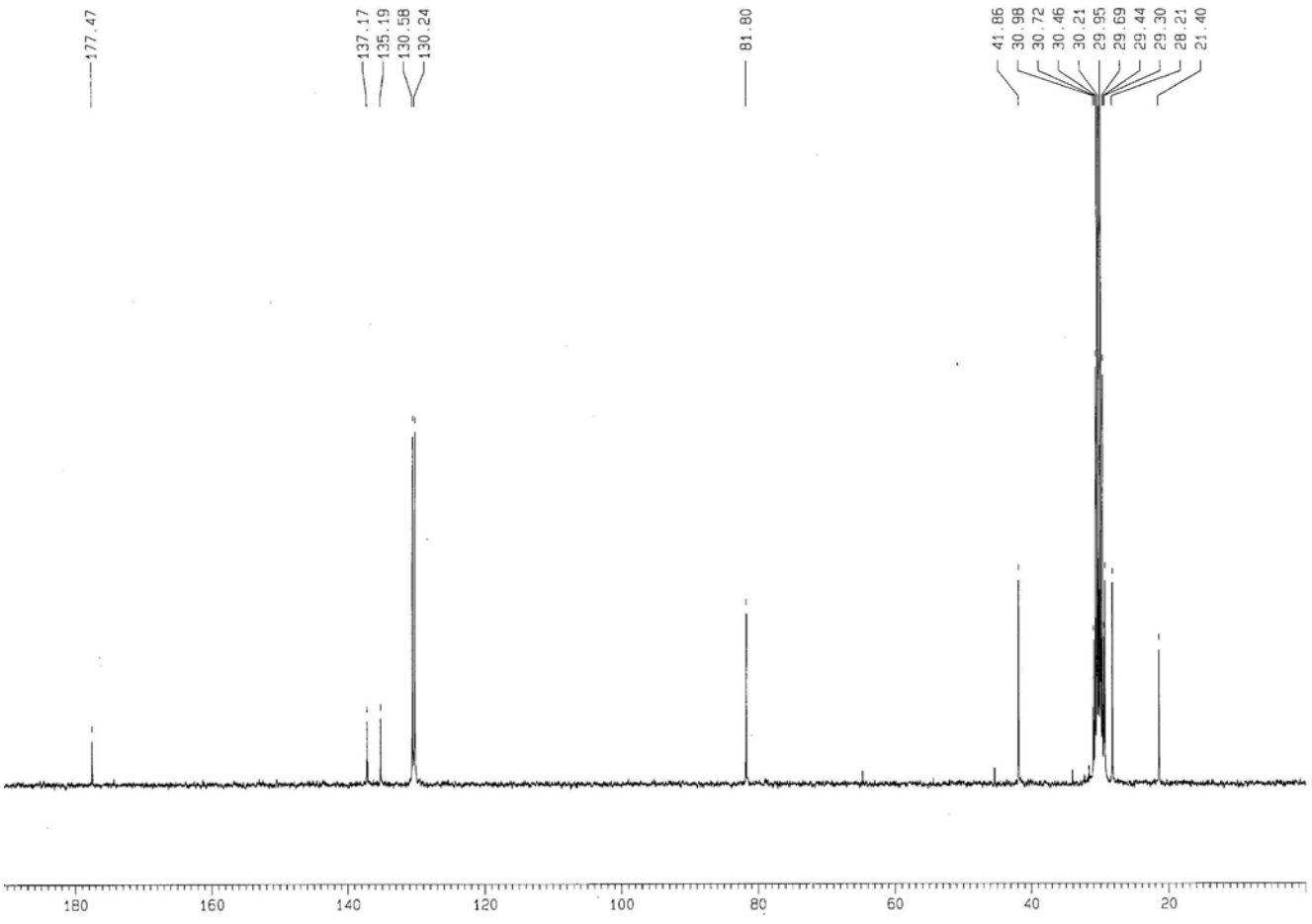


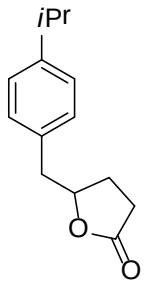
11 (^{1}H NMR , CD_3COCD_3)



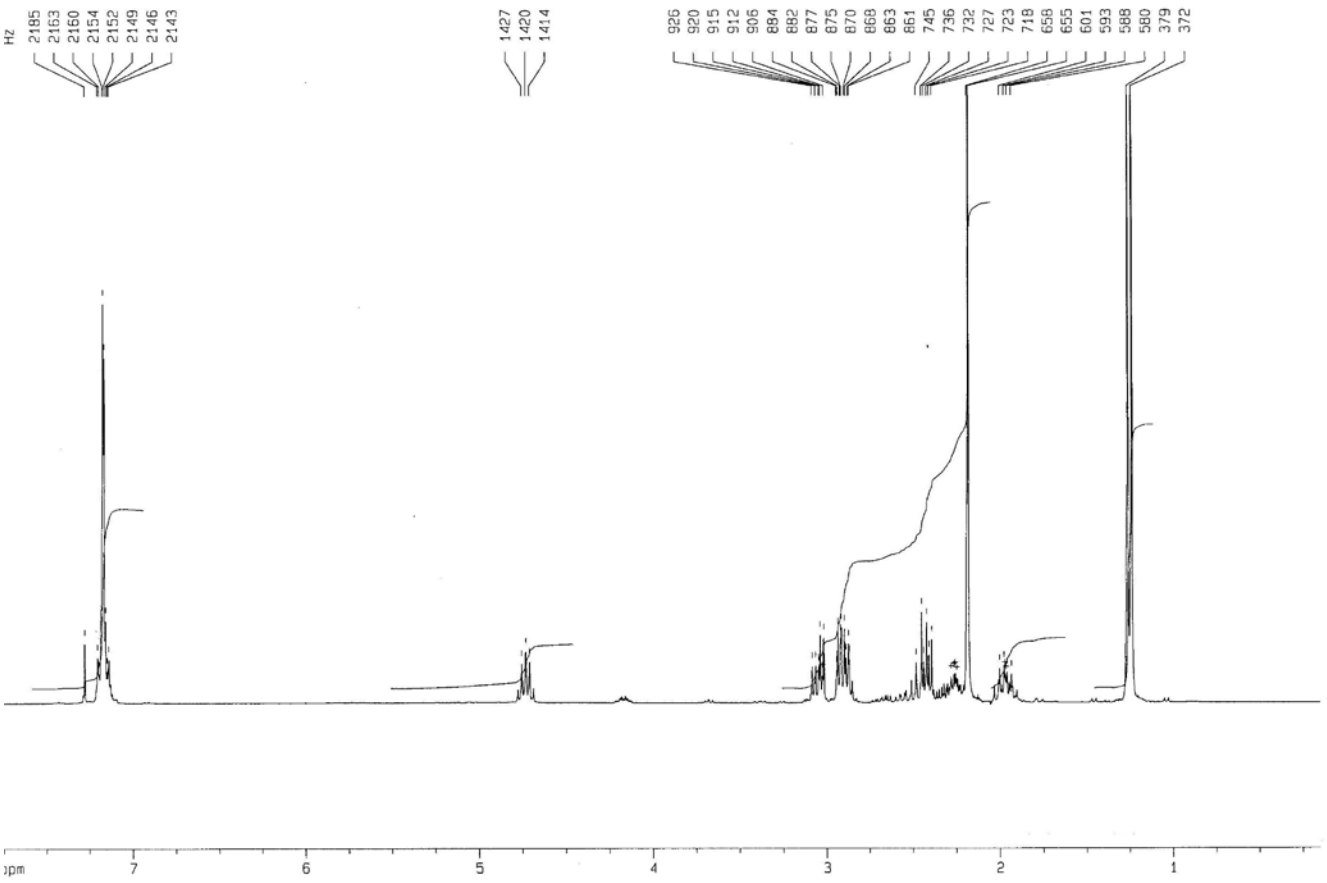


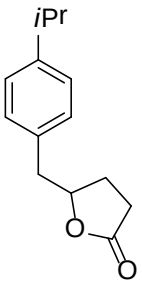
11 (^{13}C NMR , CD_3COCD_3)



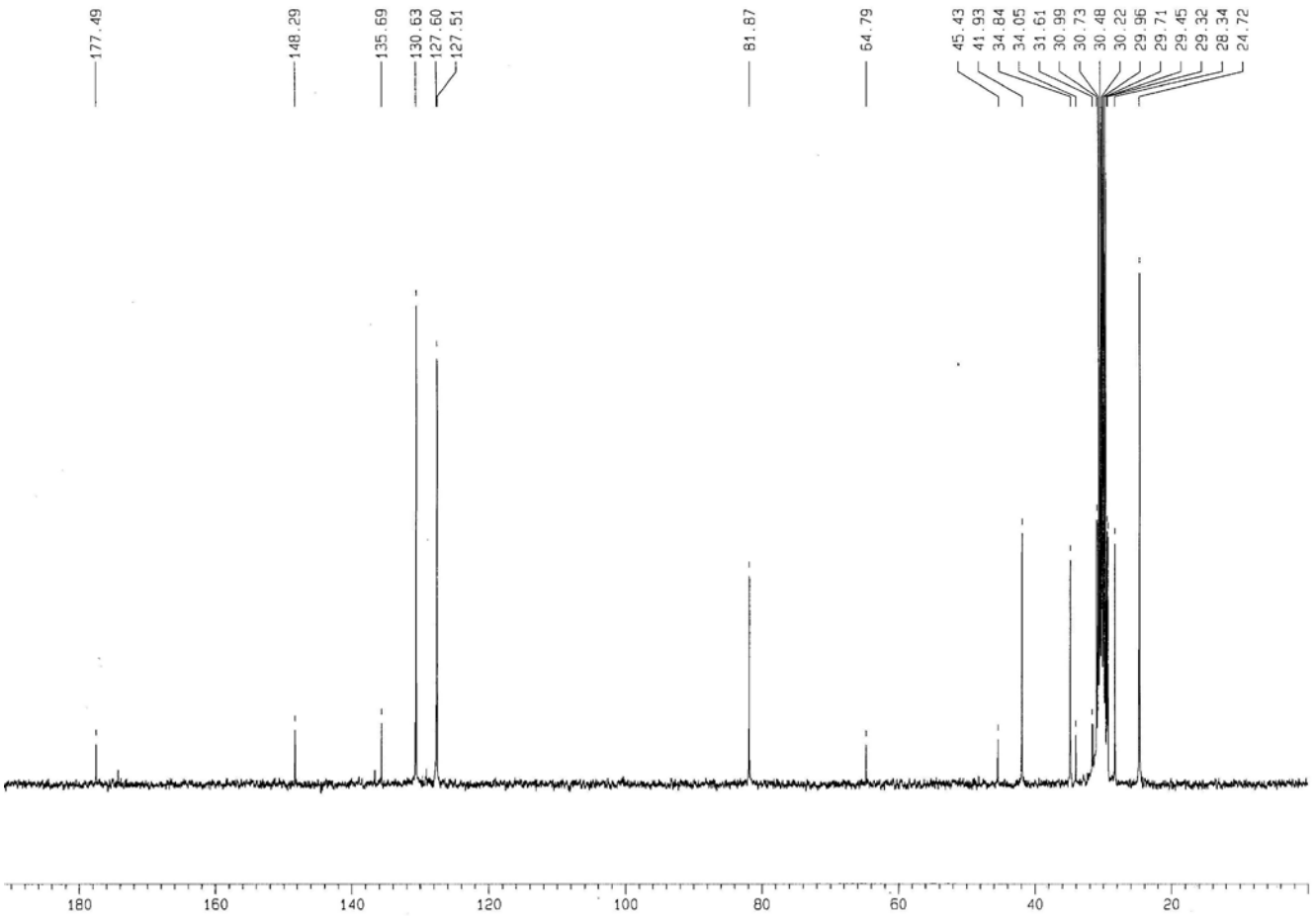


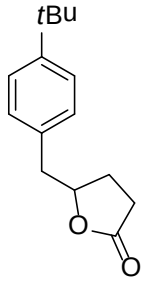
13 (^{1}H NMR , CD_3COCD_3)



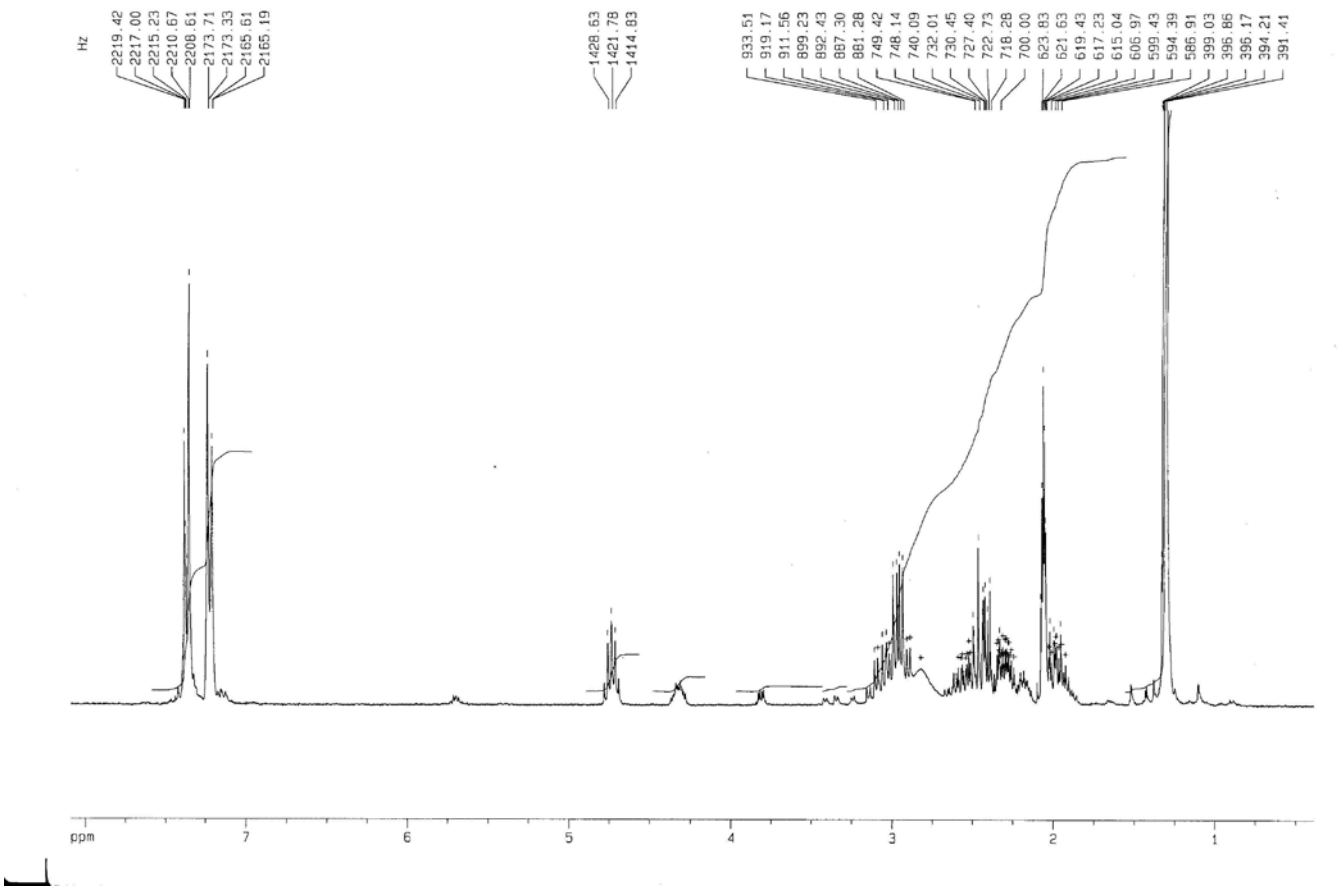


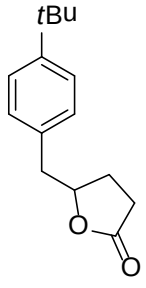
13 (^{13}C NMR , CD_3COCD_3)



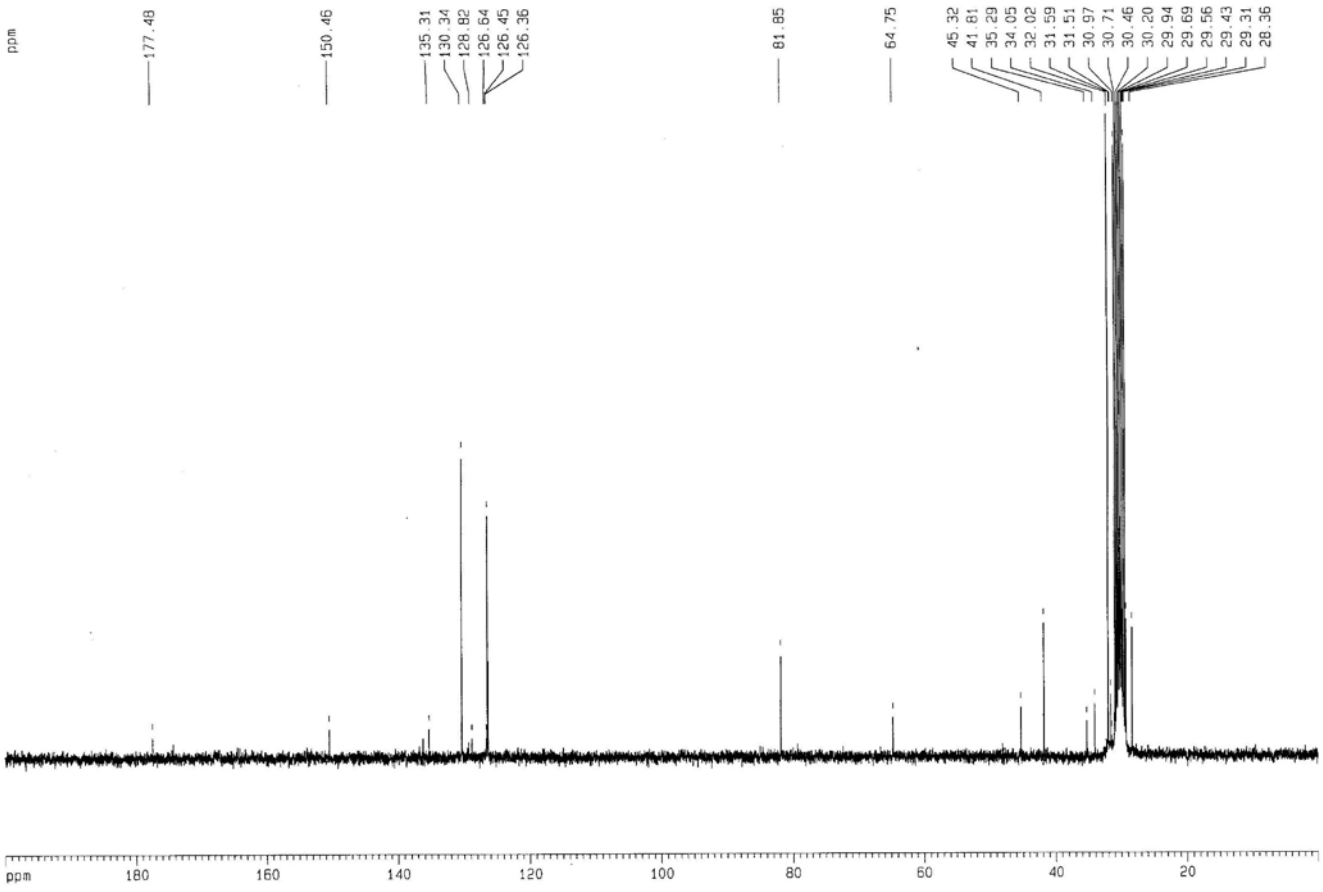


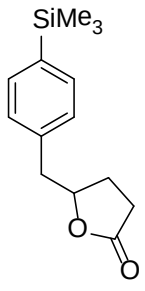
14 (^{1}H NMR , CD_3COCD_3)



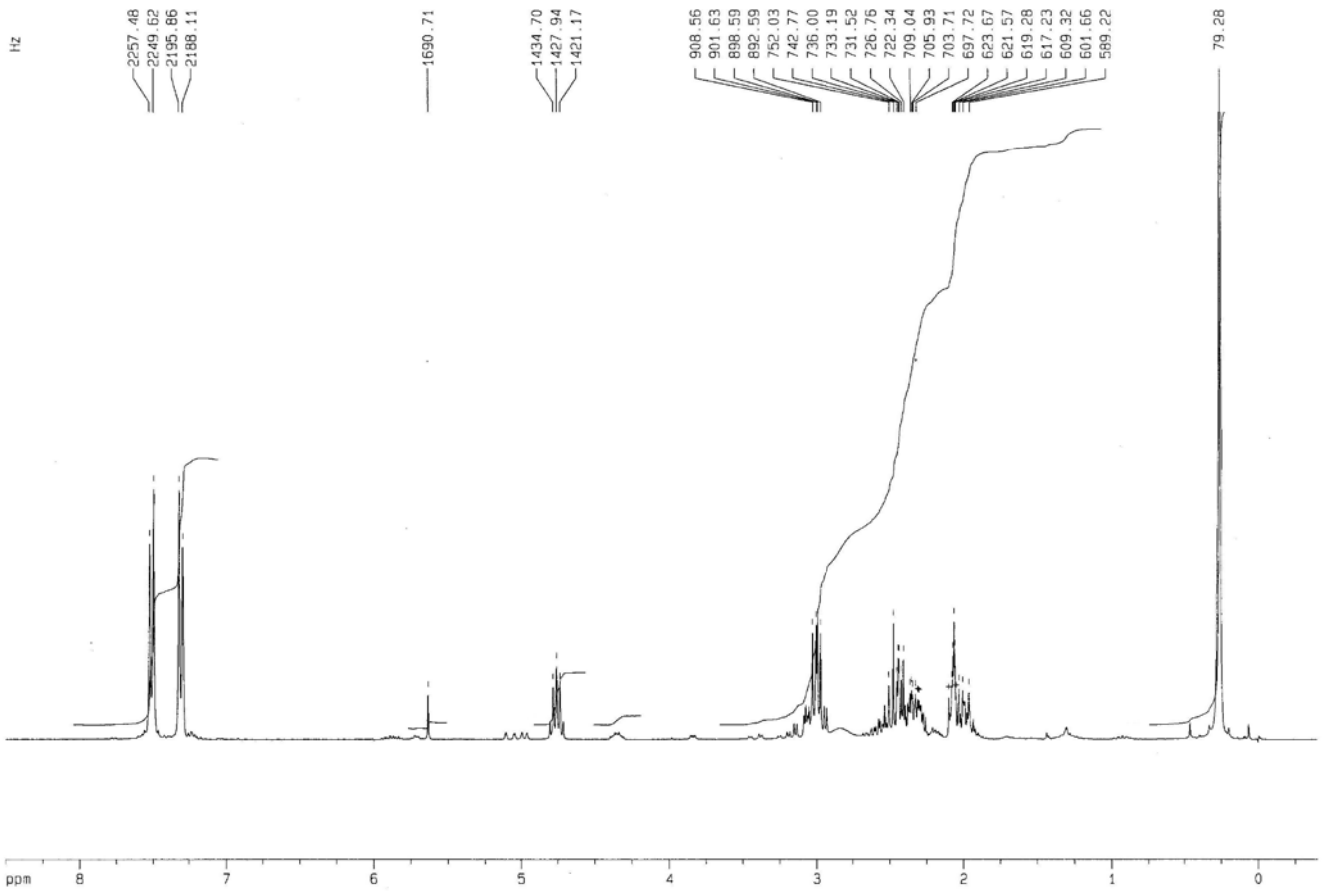


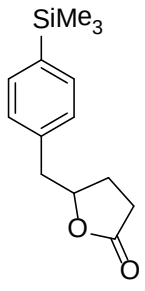
14 (^{13}C NMR , CD_3COCD_3)



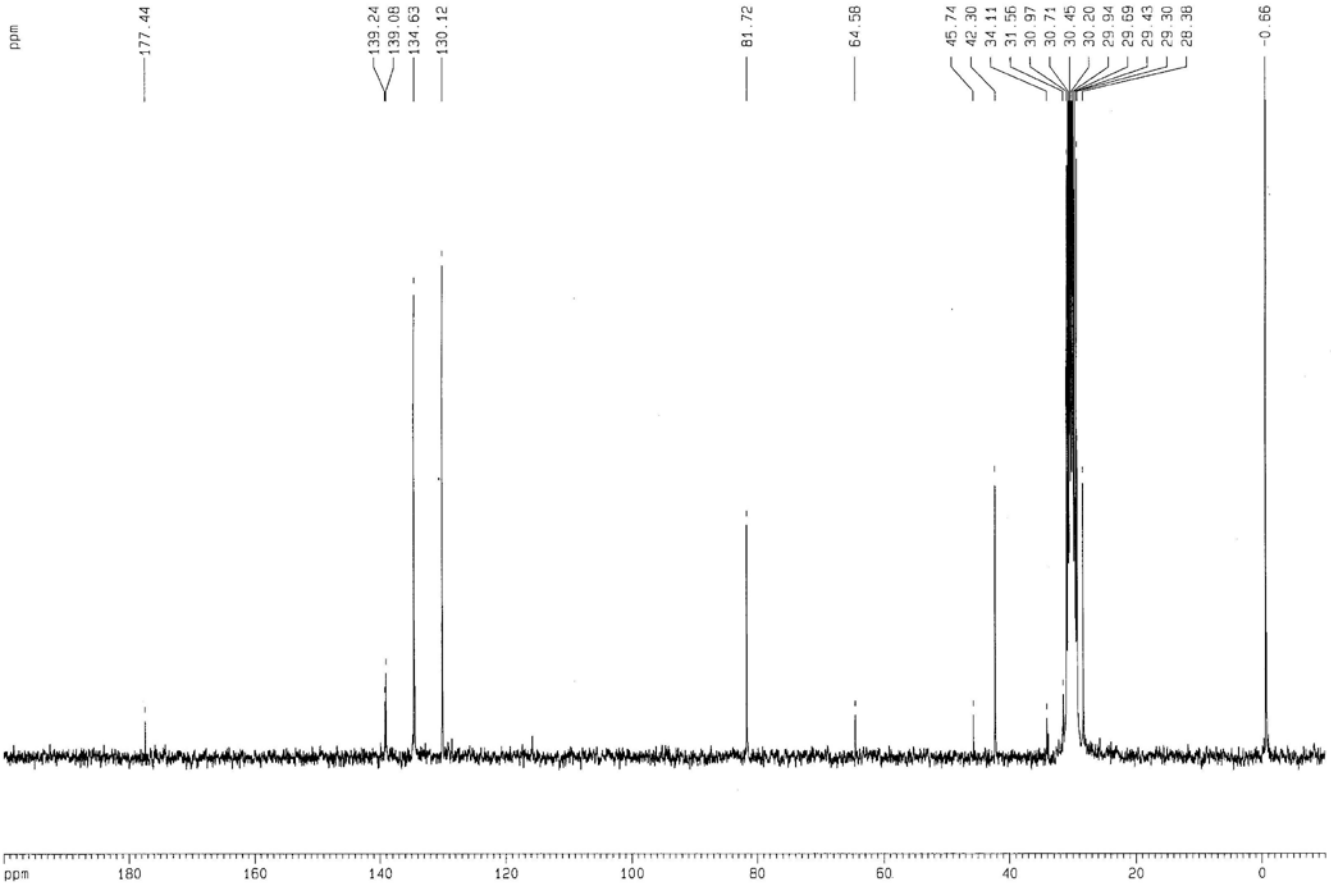


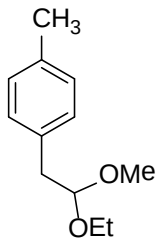
15 (^{1}H NMR , CD_3COCD_3)



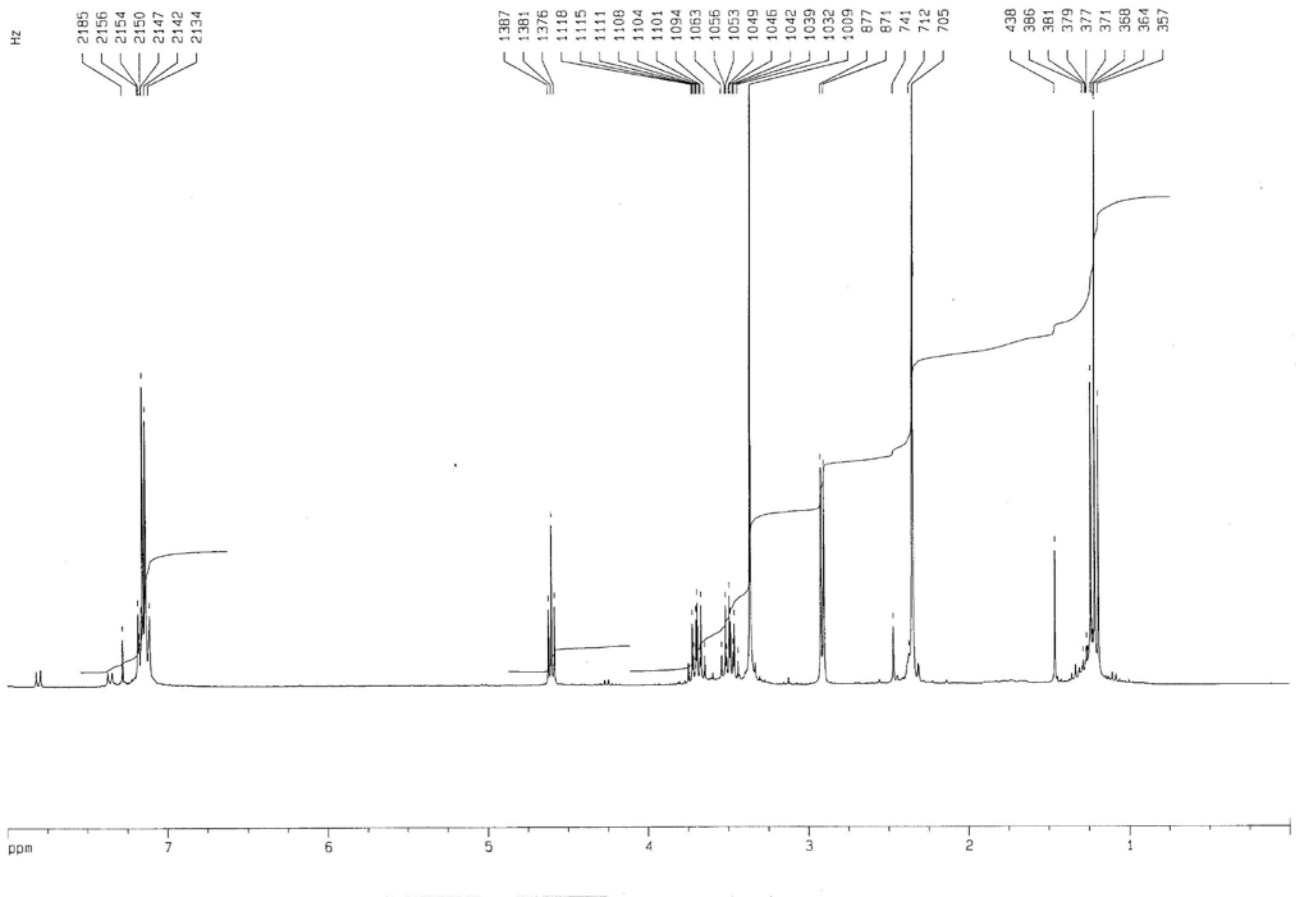


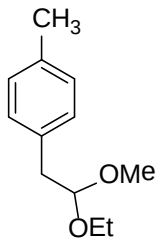
15 (^{13}C NMR, CD_3COCD_3)



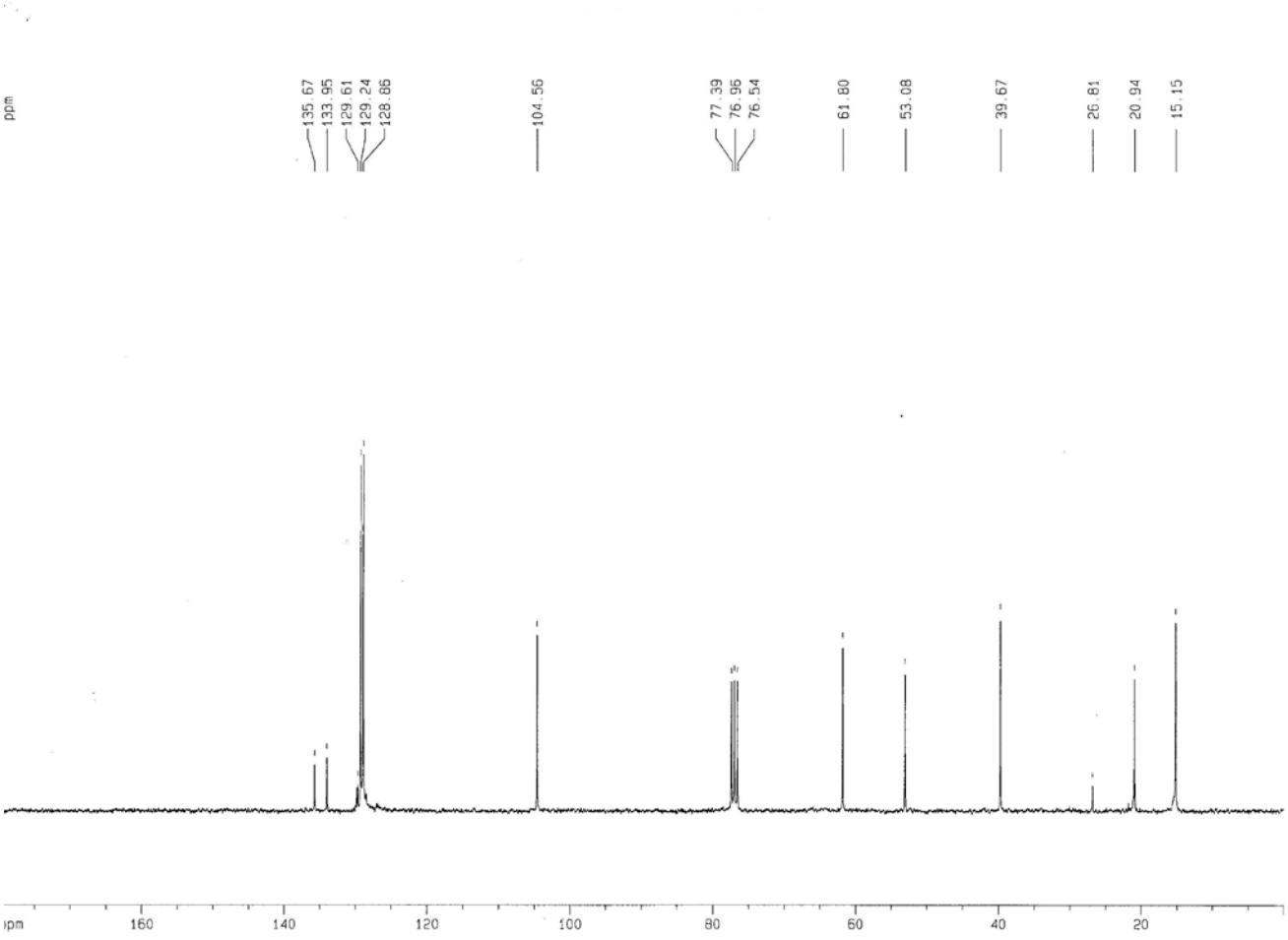


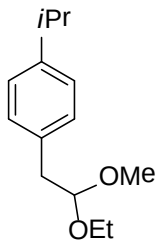
16 (^{1}H NMR , $CDCl_3$)



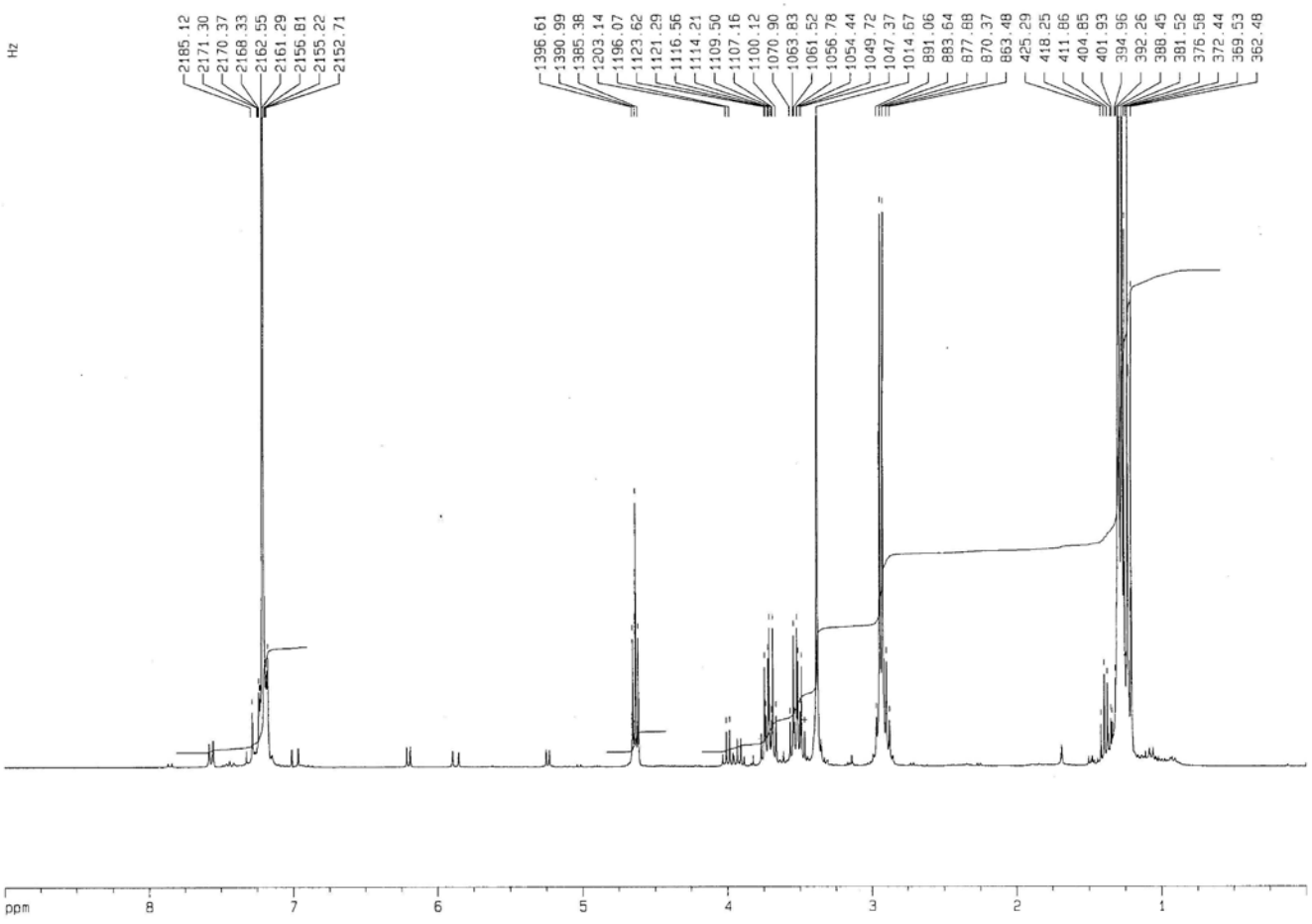


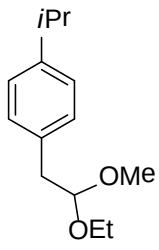
16 (^{13}C NMR , $CDCl_3$)



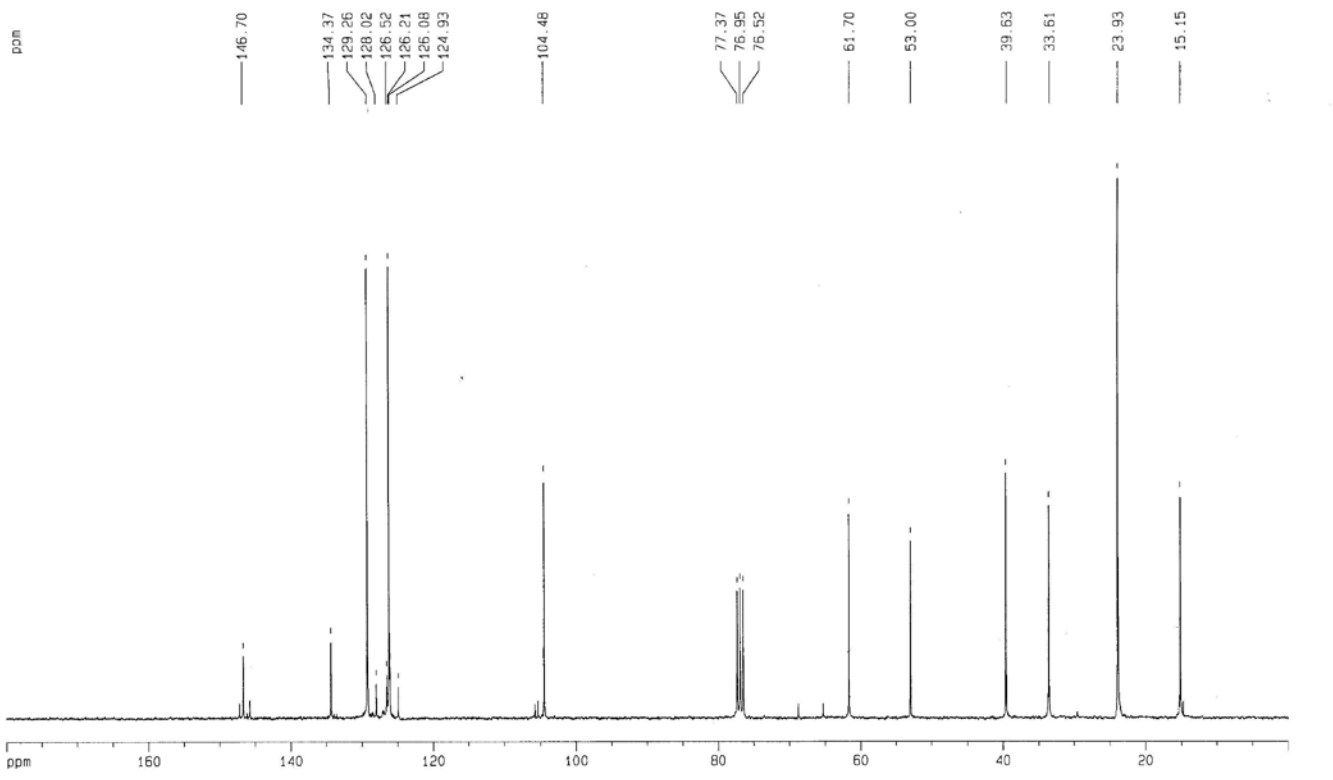


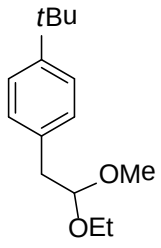
18 (^{1}H NMR , $CDCl_3$)



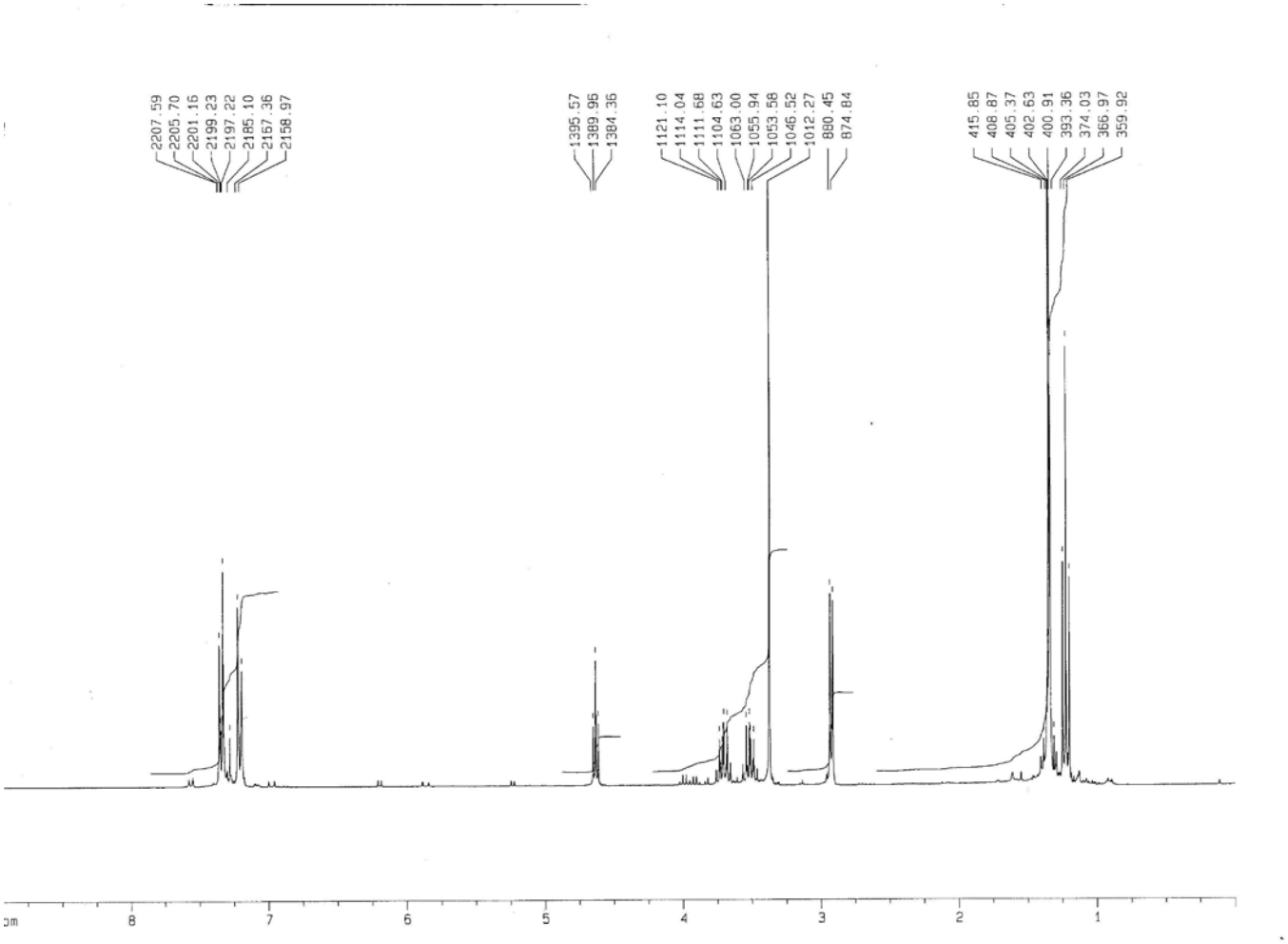


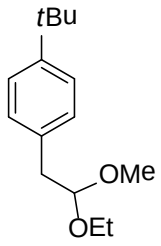
18 (^{13}C NMR , $CDCl_3$)



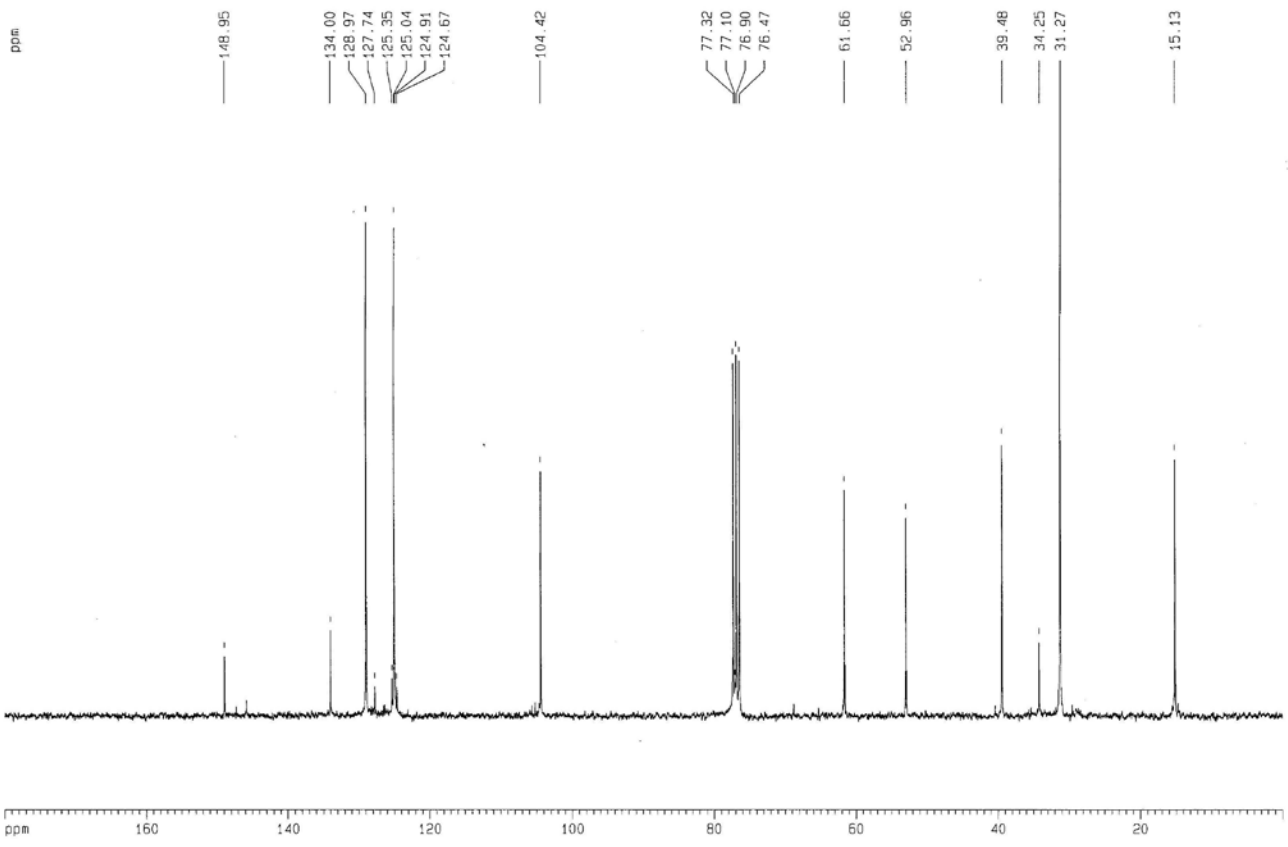


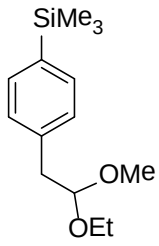
19 (^{1}H NMR , $CDCl_3$)



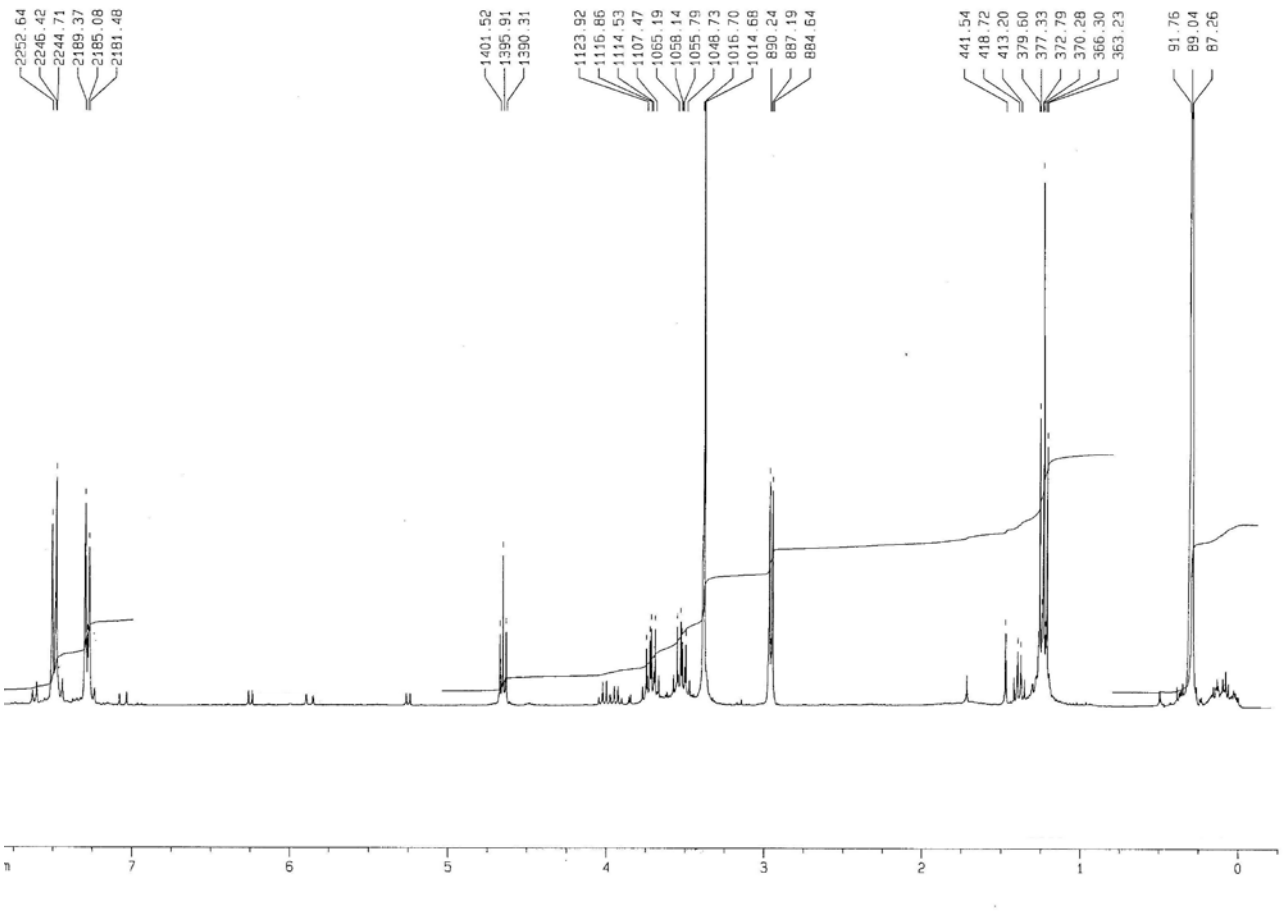


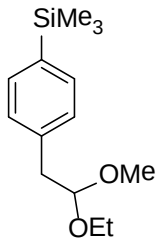
19 (^{13}C NMR , $CDCl_3$)



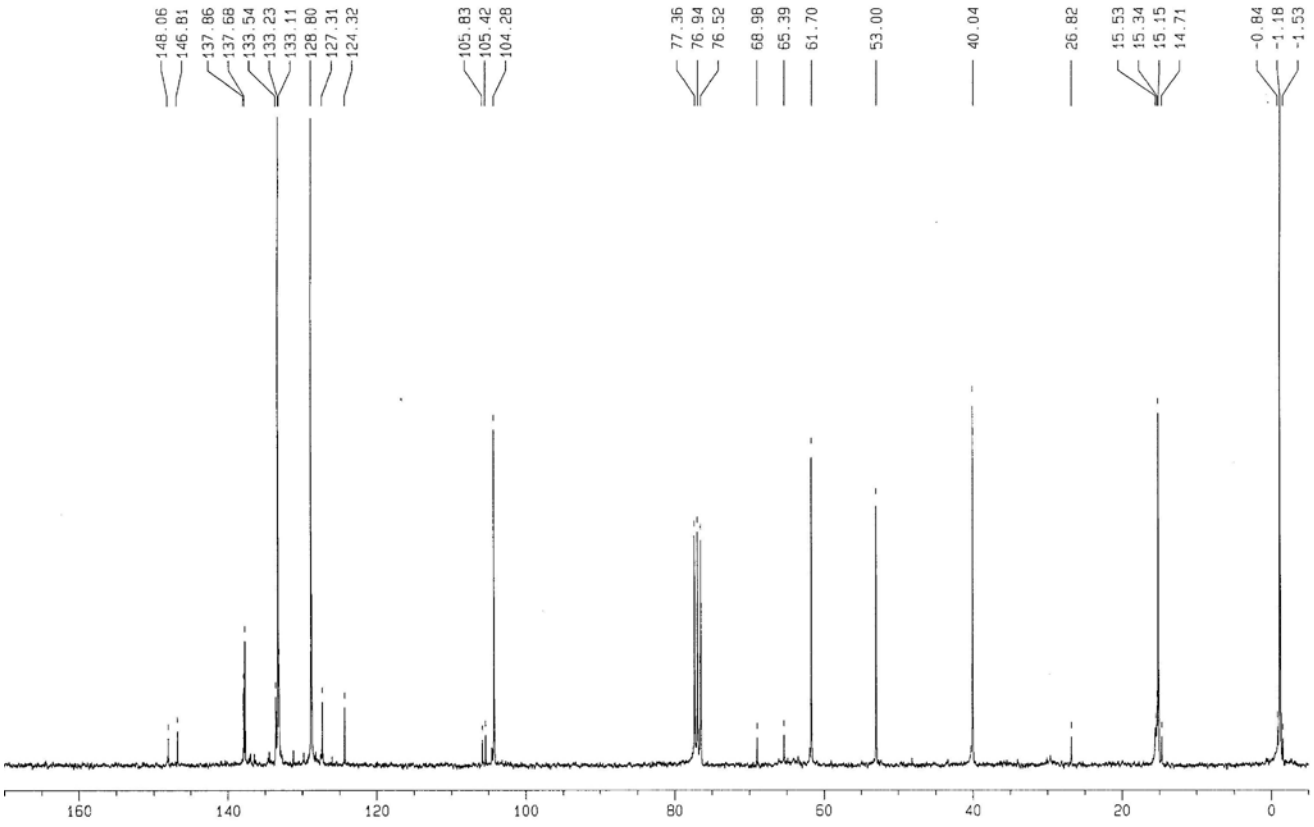


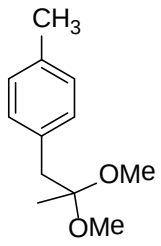
20 (^{1}H NMR , $CDCl_3$)



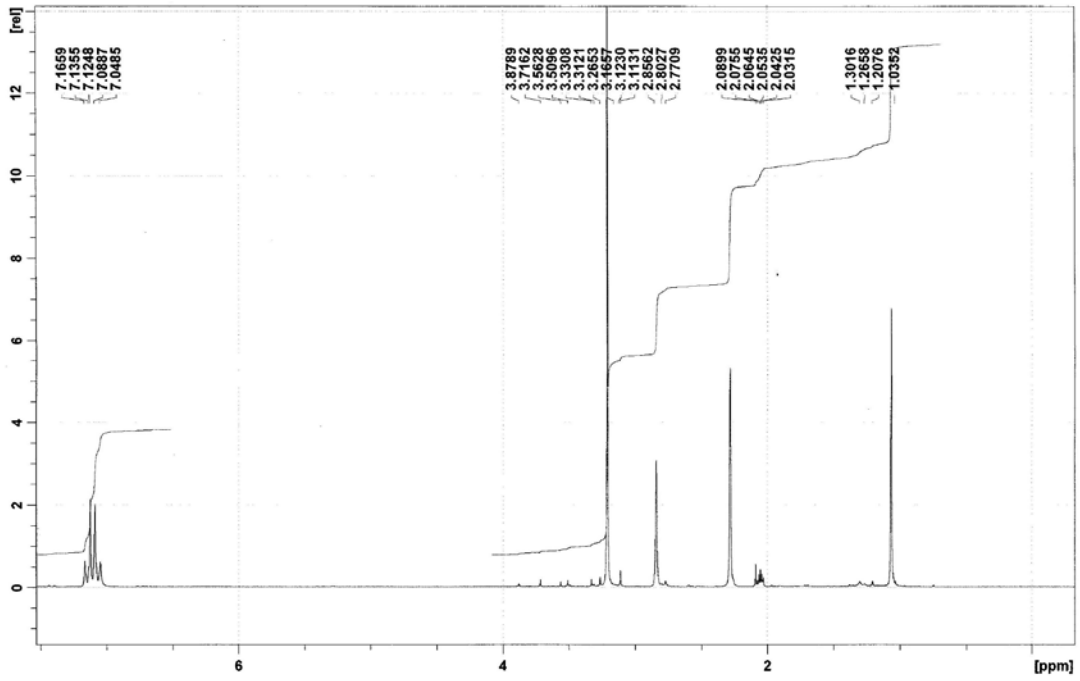


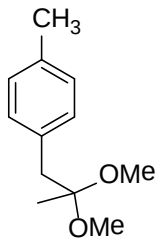
20 (^{13}C NMR , $CDCl_3$)



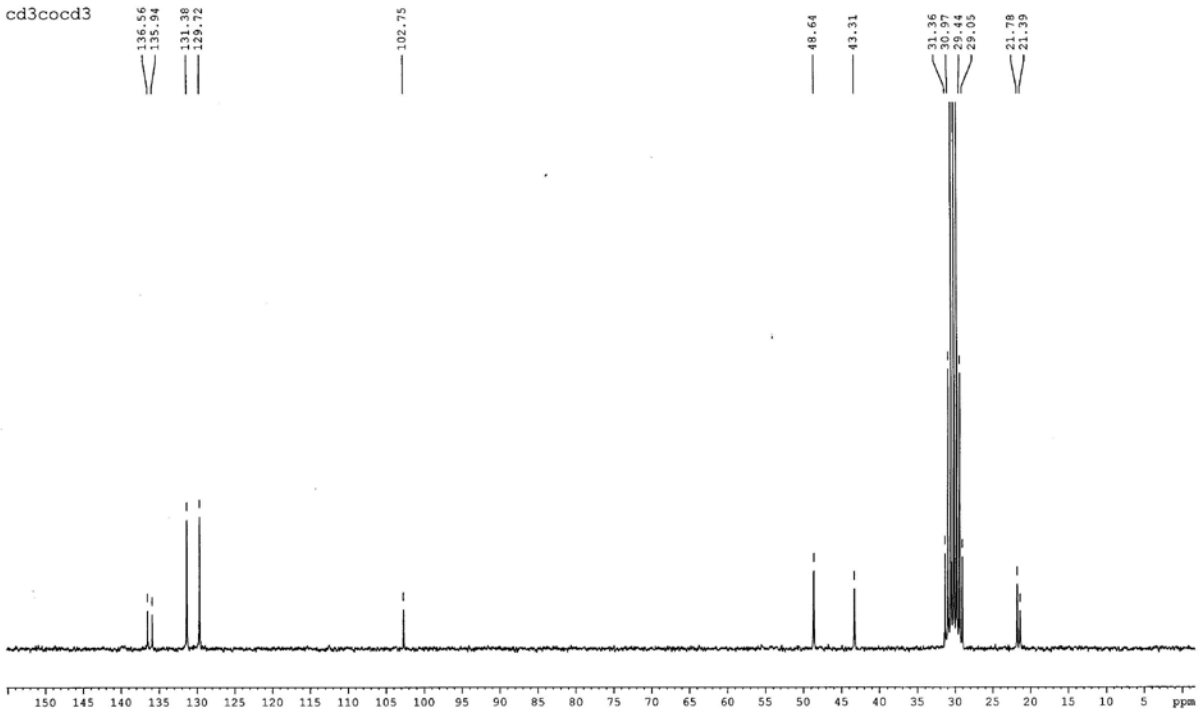


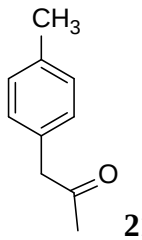
21 (^{1}H NMR , $CDCl_3$)



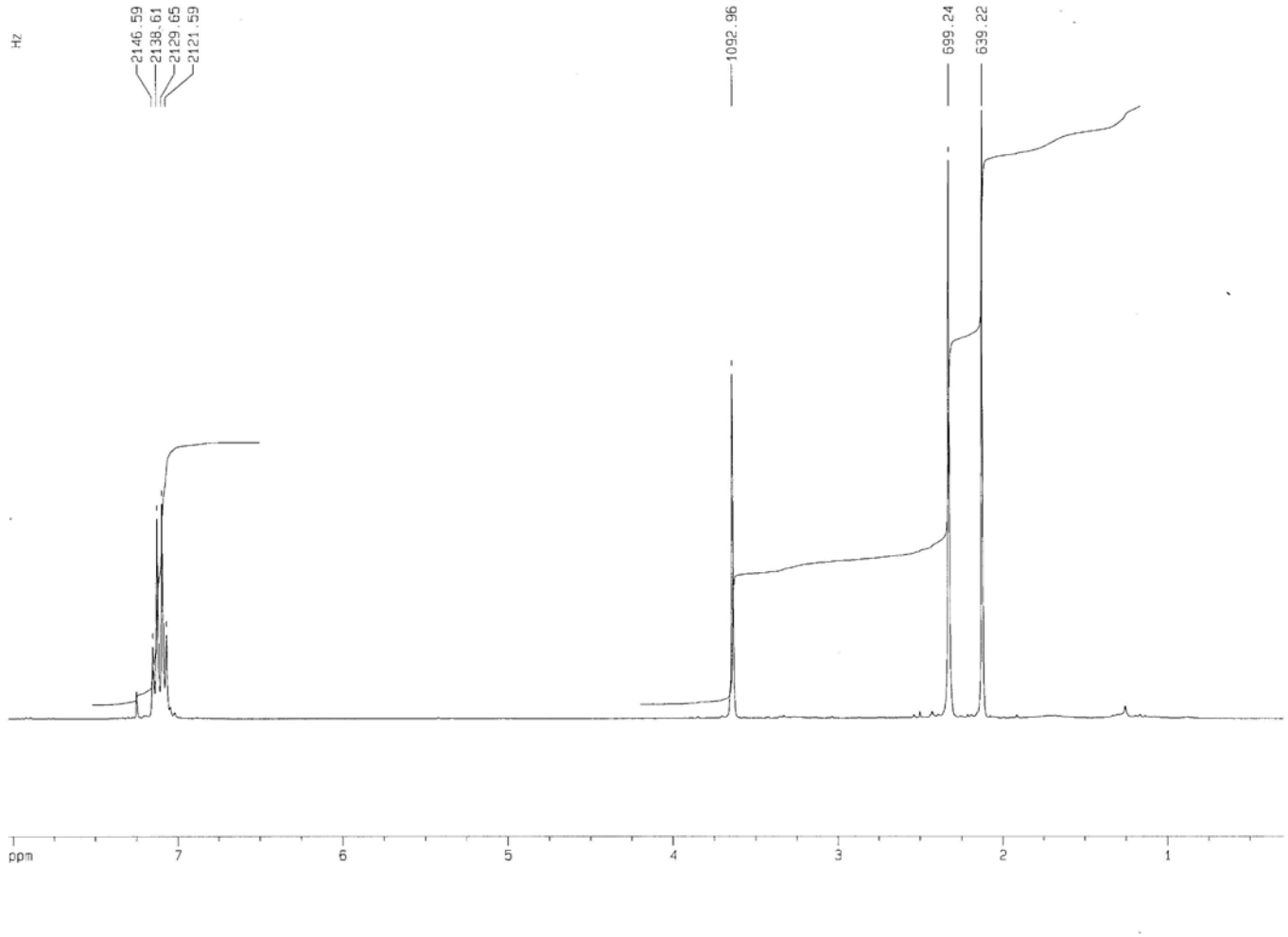


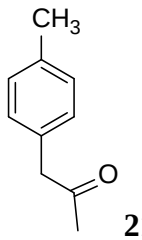
21 (^{13}C NMR , $CDCl_3$)



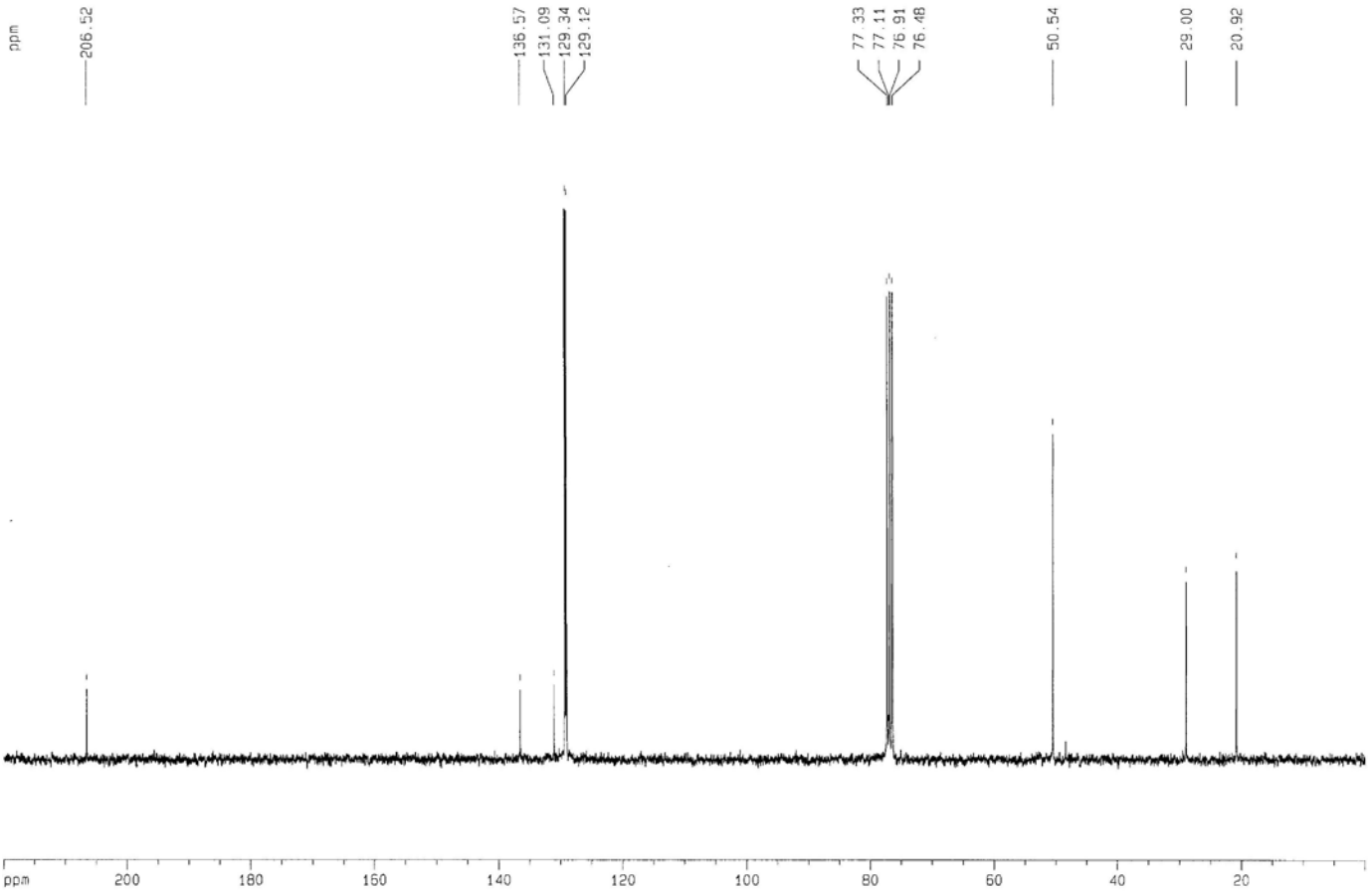


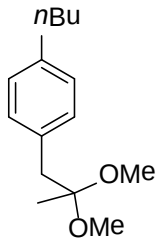
21' (^{1}H NMR , $CDCl_3$)



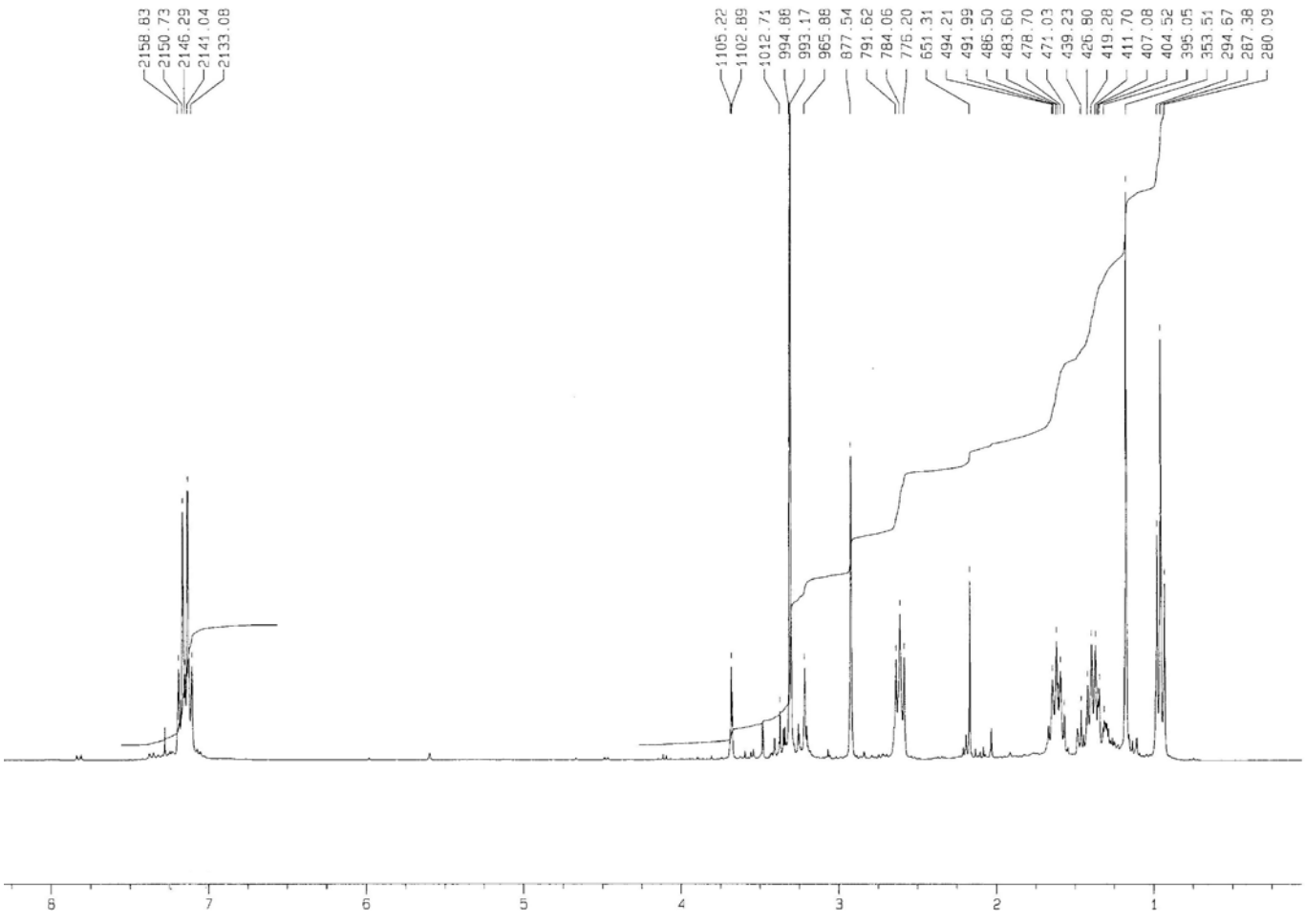


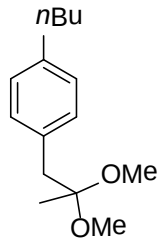
21' (^{13}C NMR , $CDCl_3$)



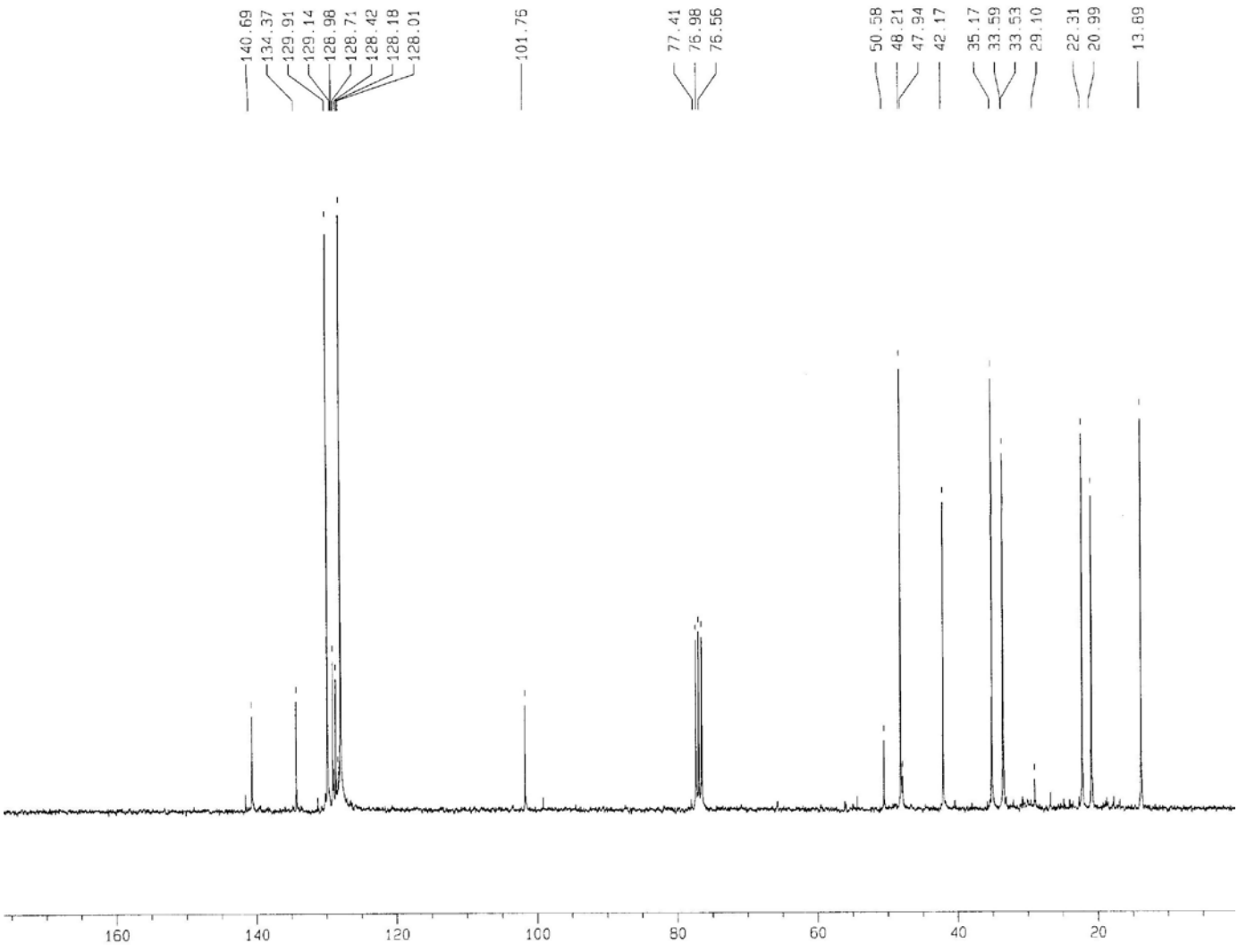


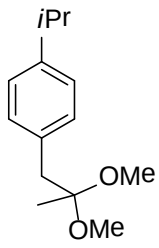
22 (^{1}H NMR , $CDCl_3$)



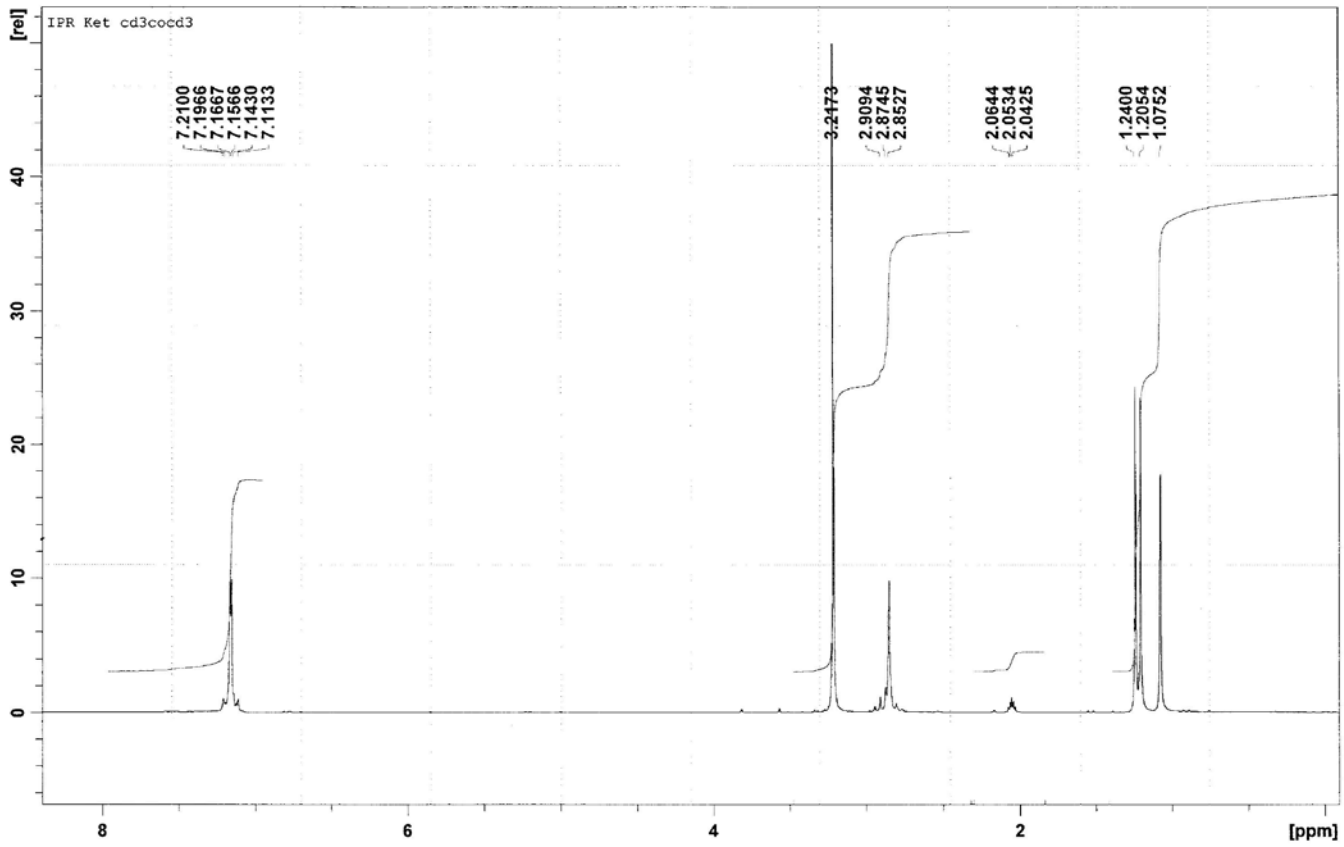


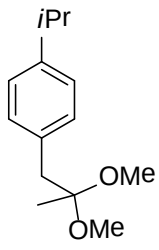
22 (^{13}C NMR , $CDCl_3$)



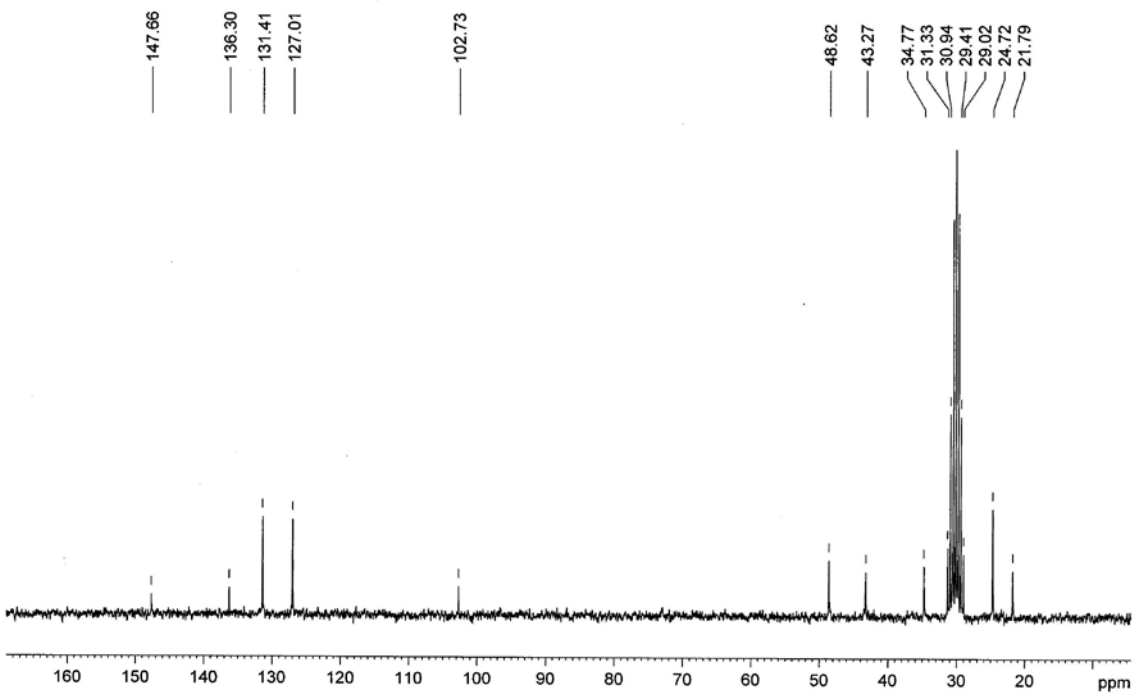


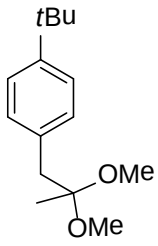
23 (^{1}H NMR , CD_3COCD_3)



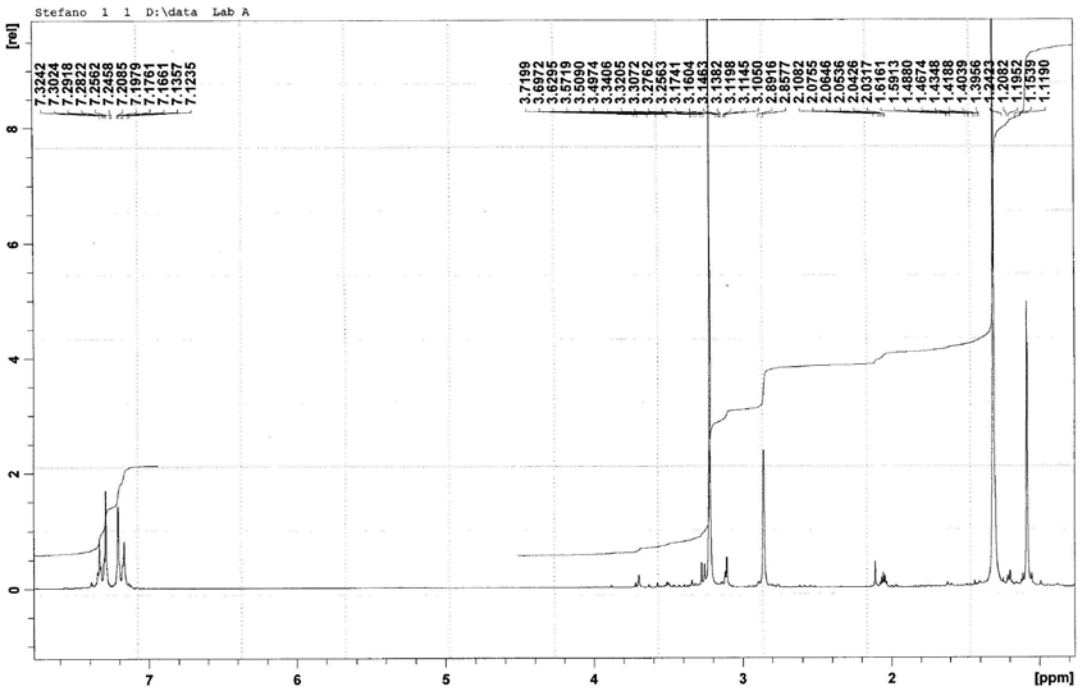


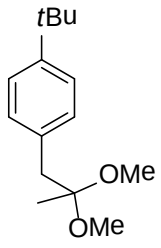
23 (^{13}C NMR , $CDCl_3$)



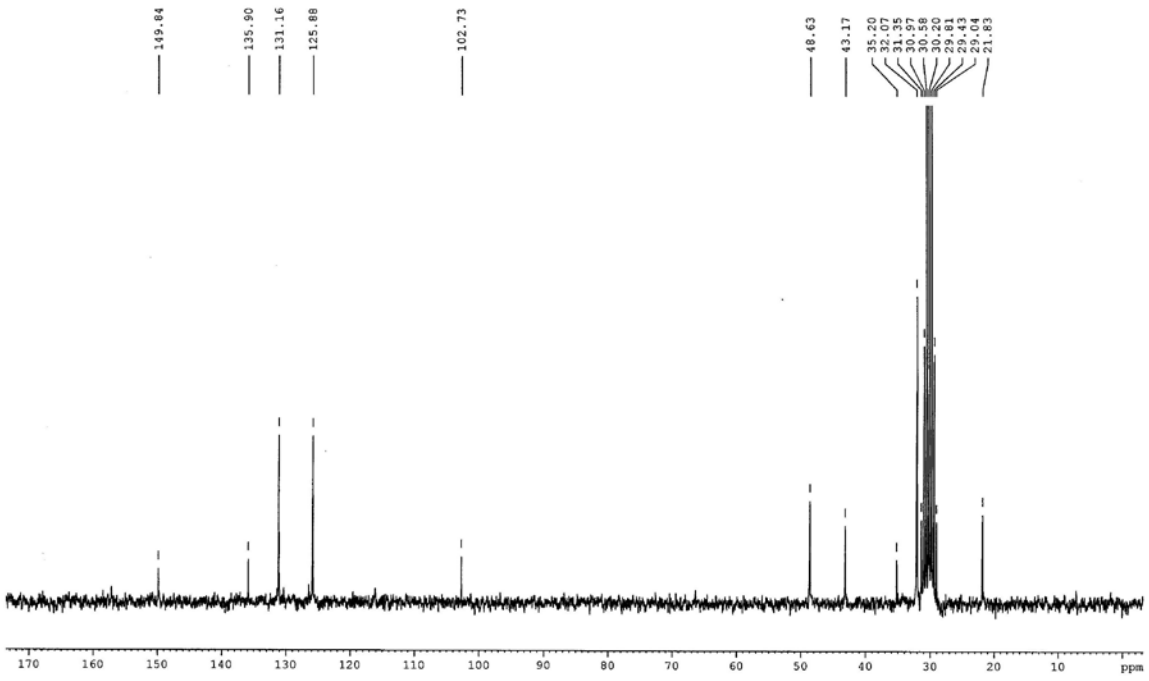


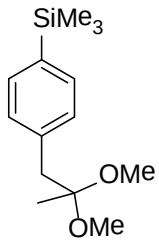
24 (^{1}H NMR , $CDCl_3$)



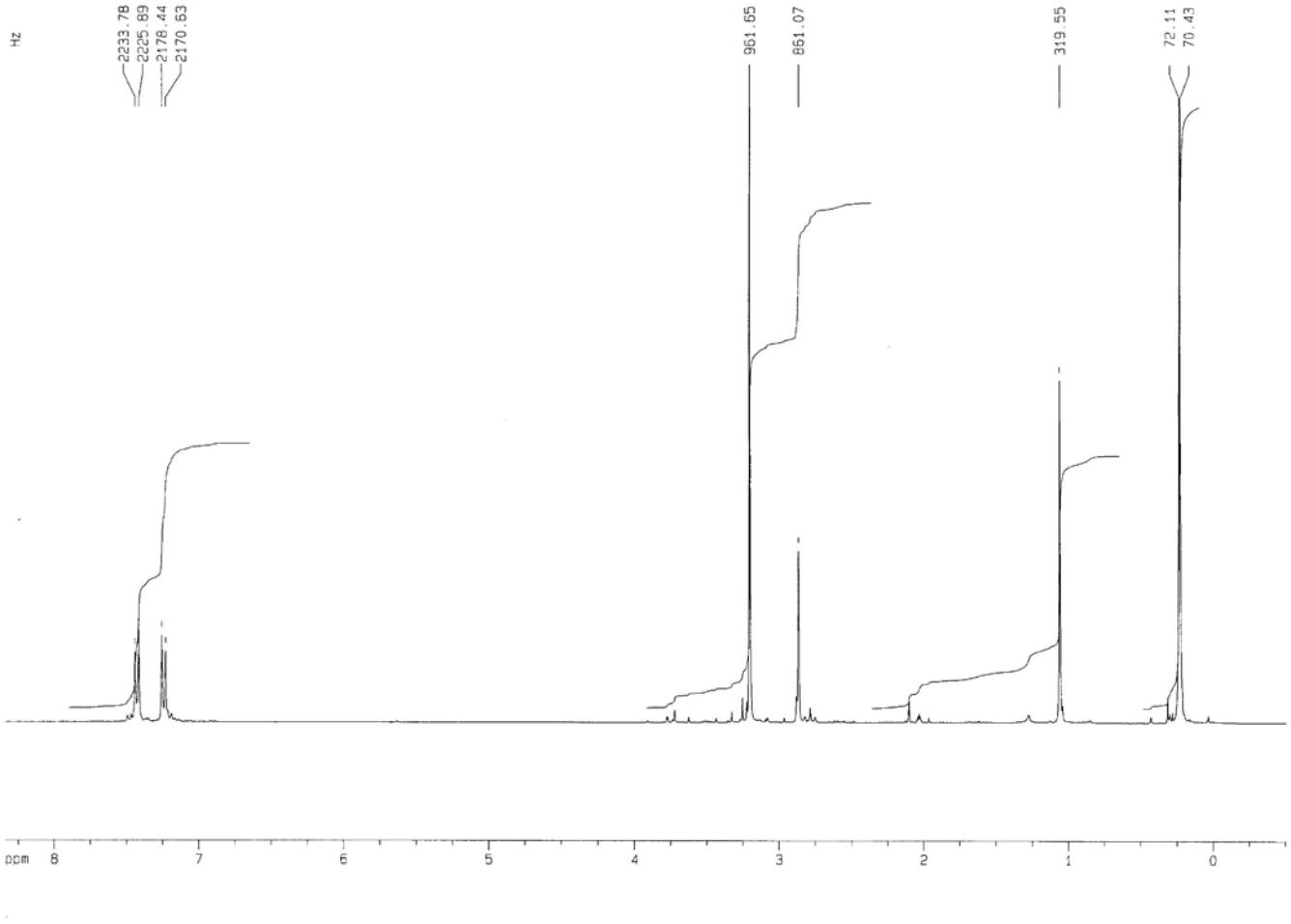


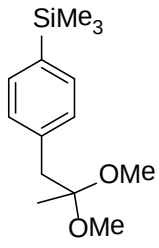
24 (^{13}C NMR , $CDCl_3$)



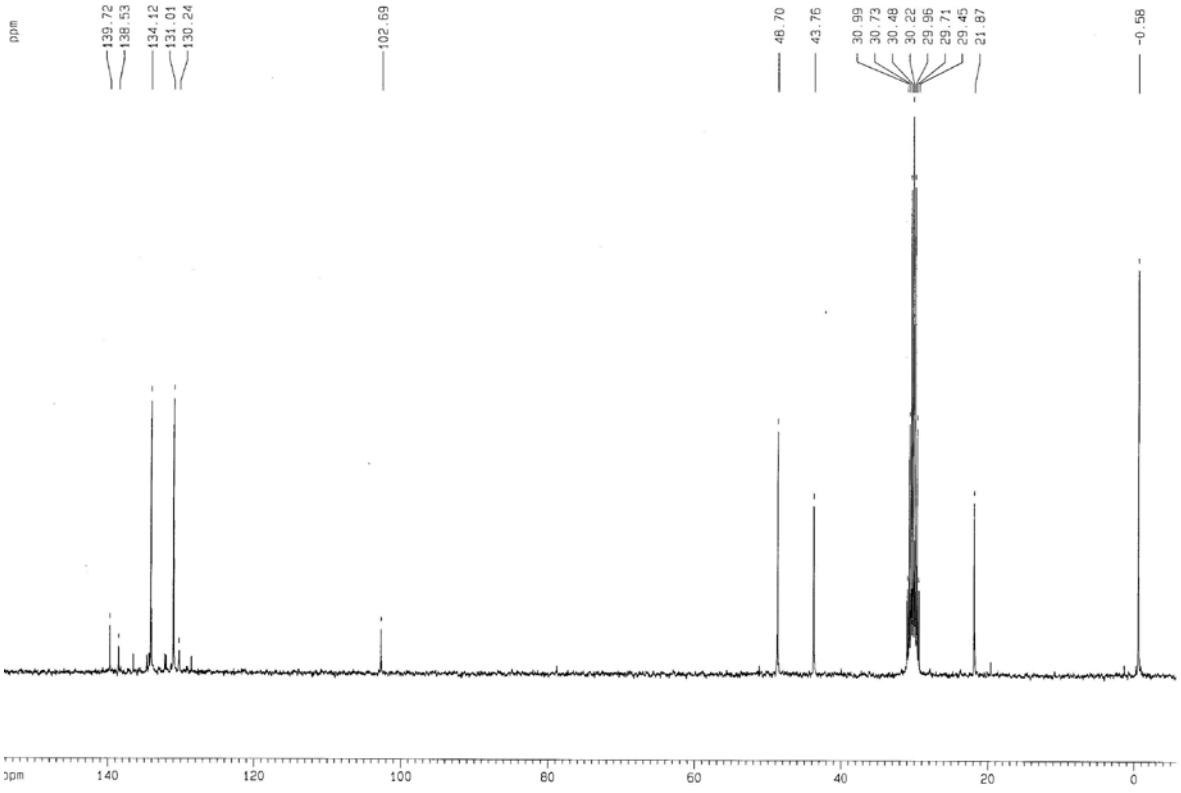


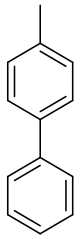
25 (^{1}H NMR , CD_3COCD_3)



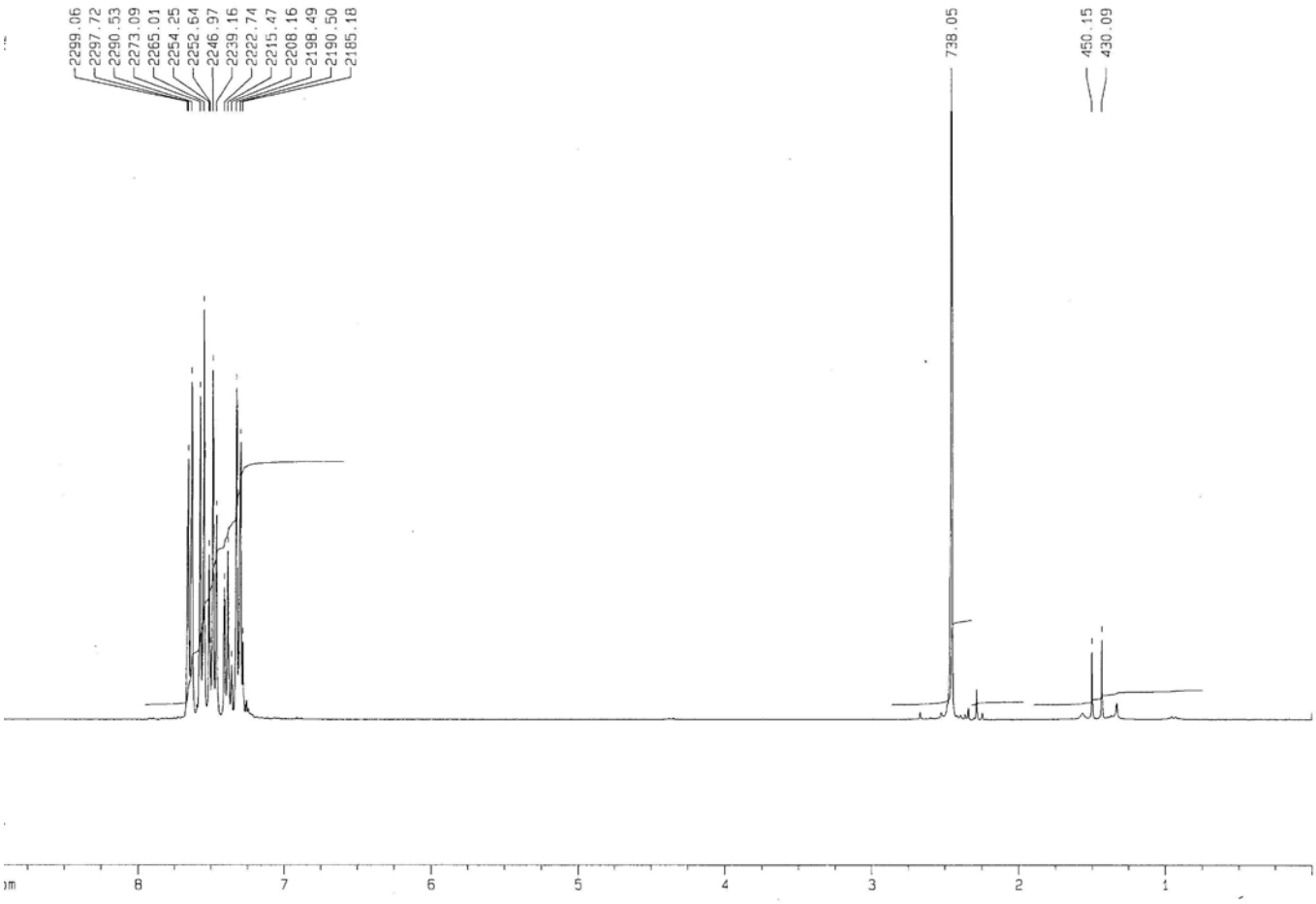


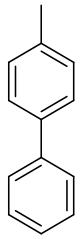
25 (^{13}C NMR , CD_3COCD_3)



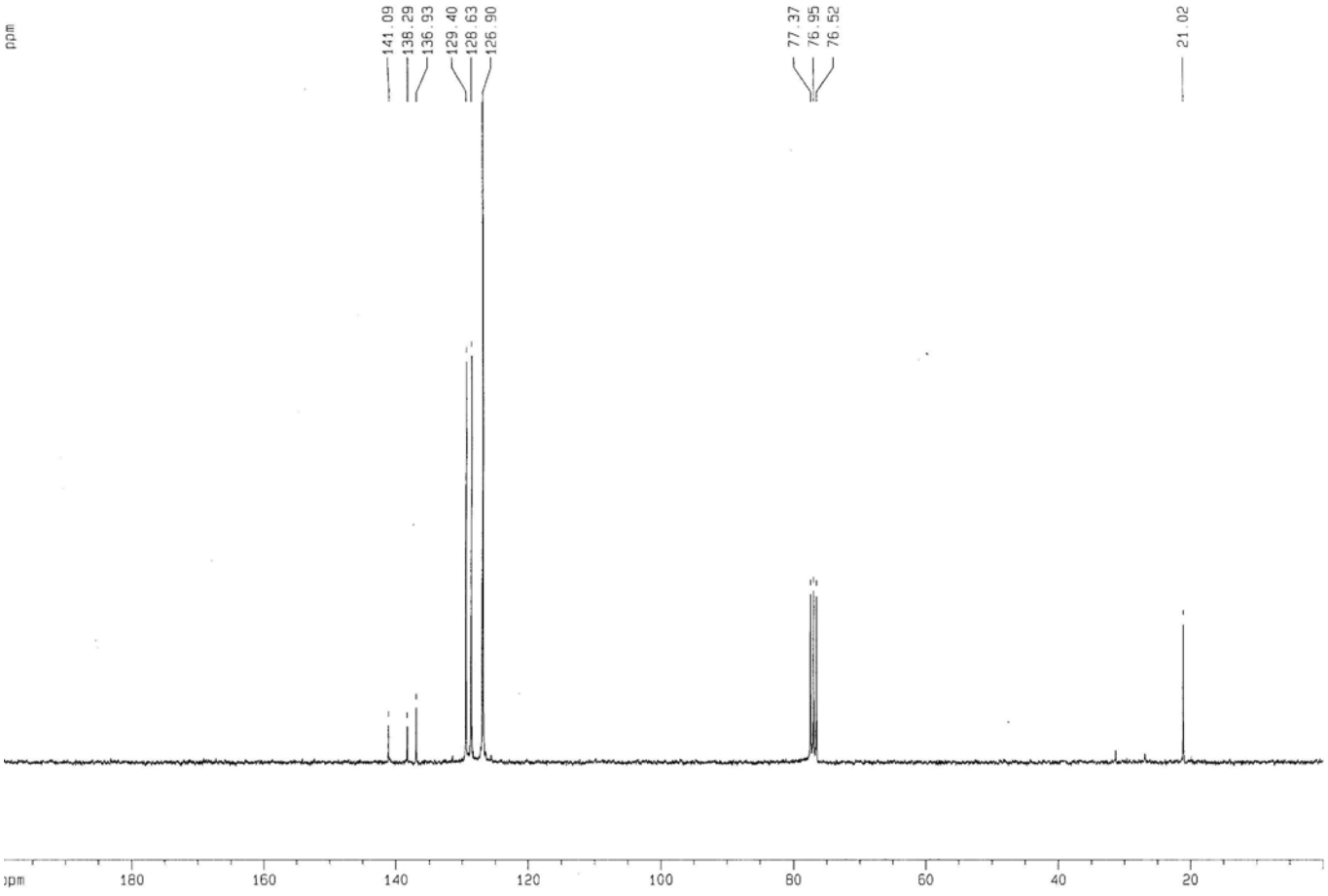


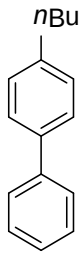
26 (^{1}H NMR , $CDCl_3$)



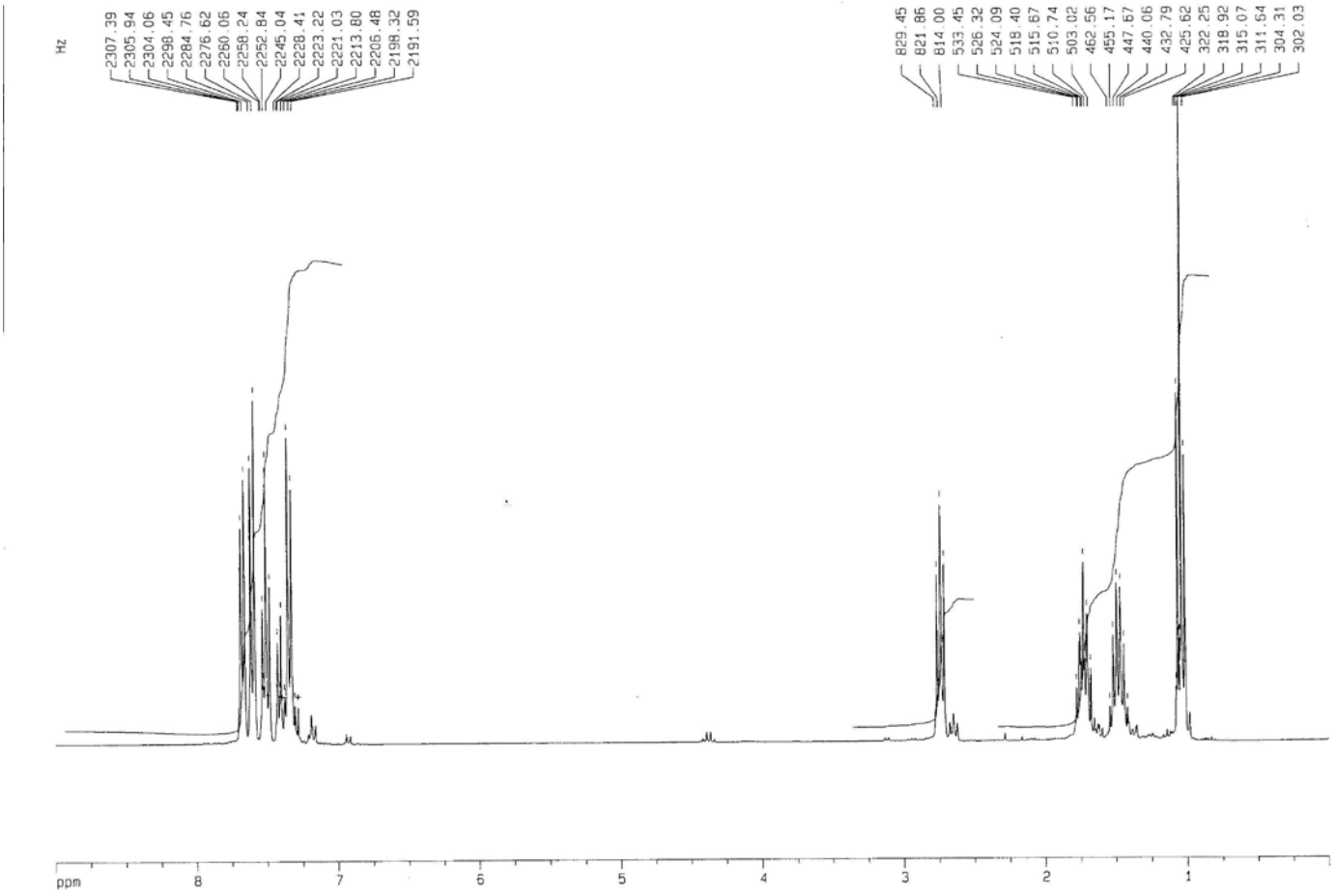


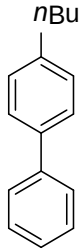
26 (^{13}C NMR , $CDCl_3$)



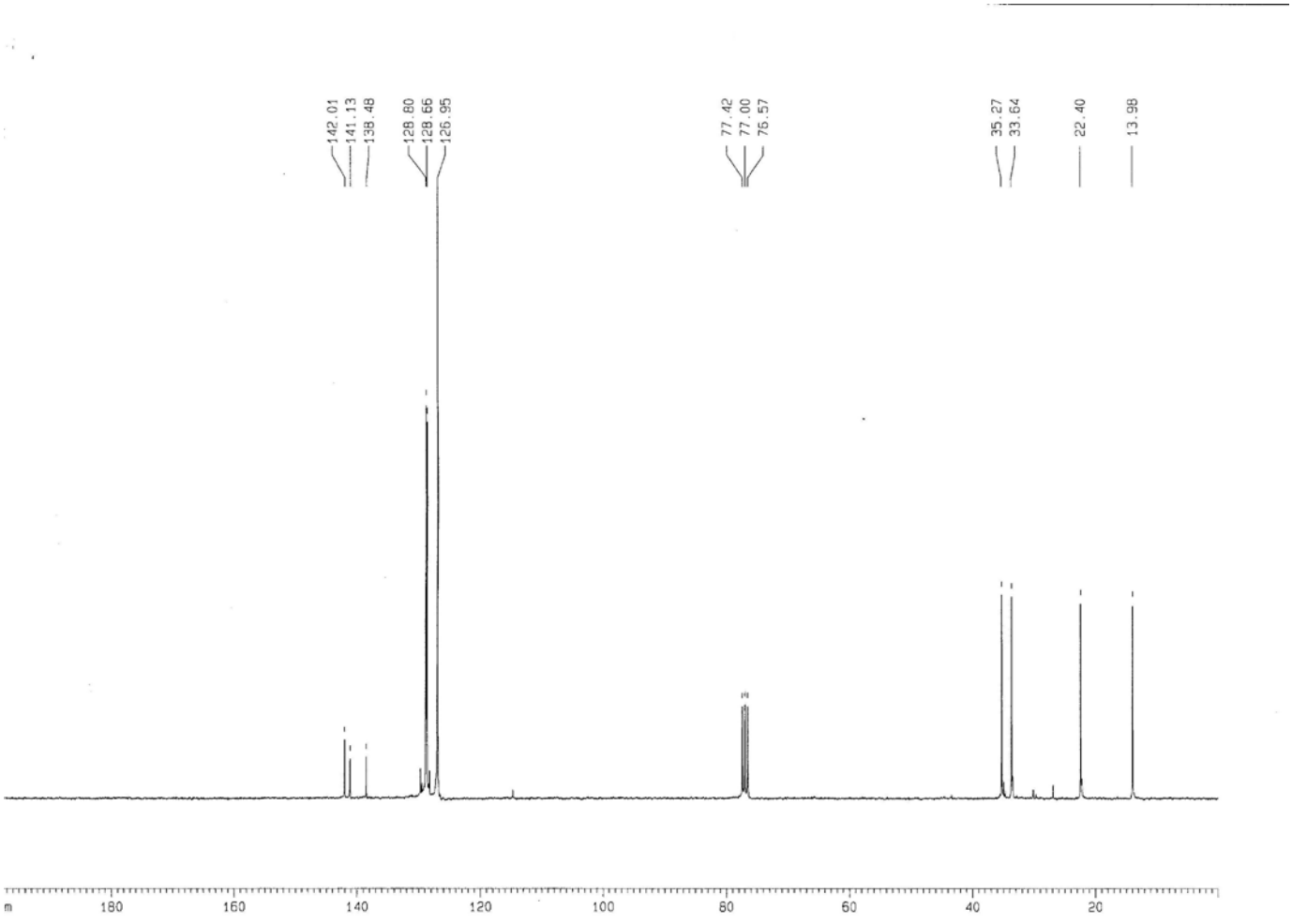


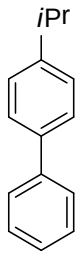
27 (^{1}H NMR , $CDCl_3$)



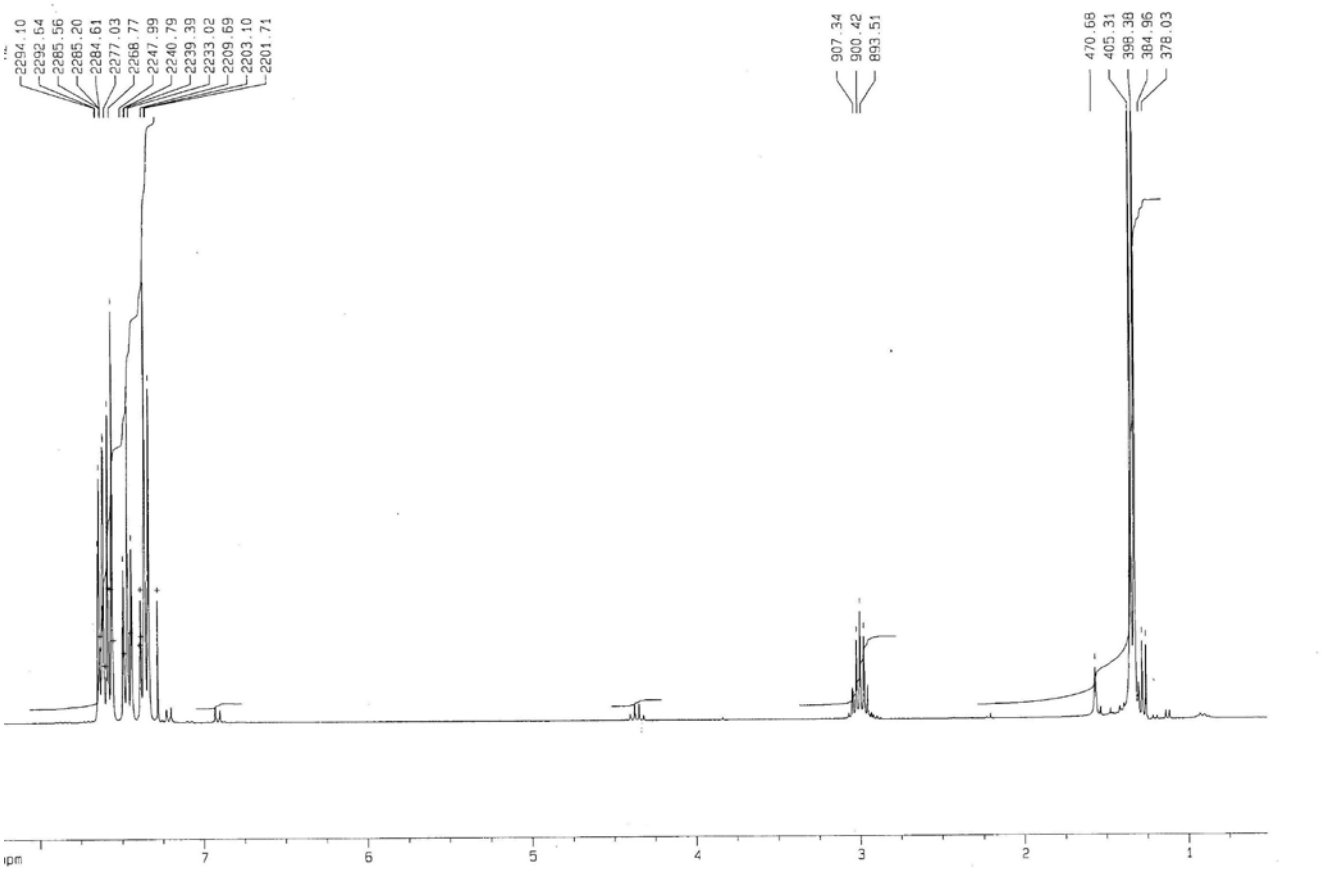


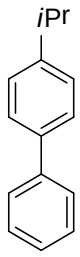
27 (^{13}C NMR , $CDCl_3$)



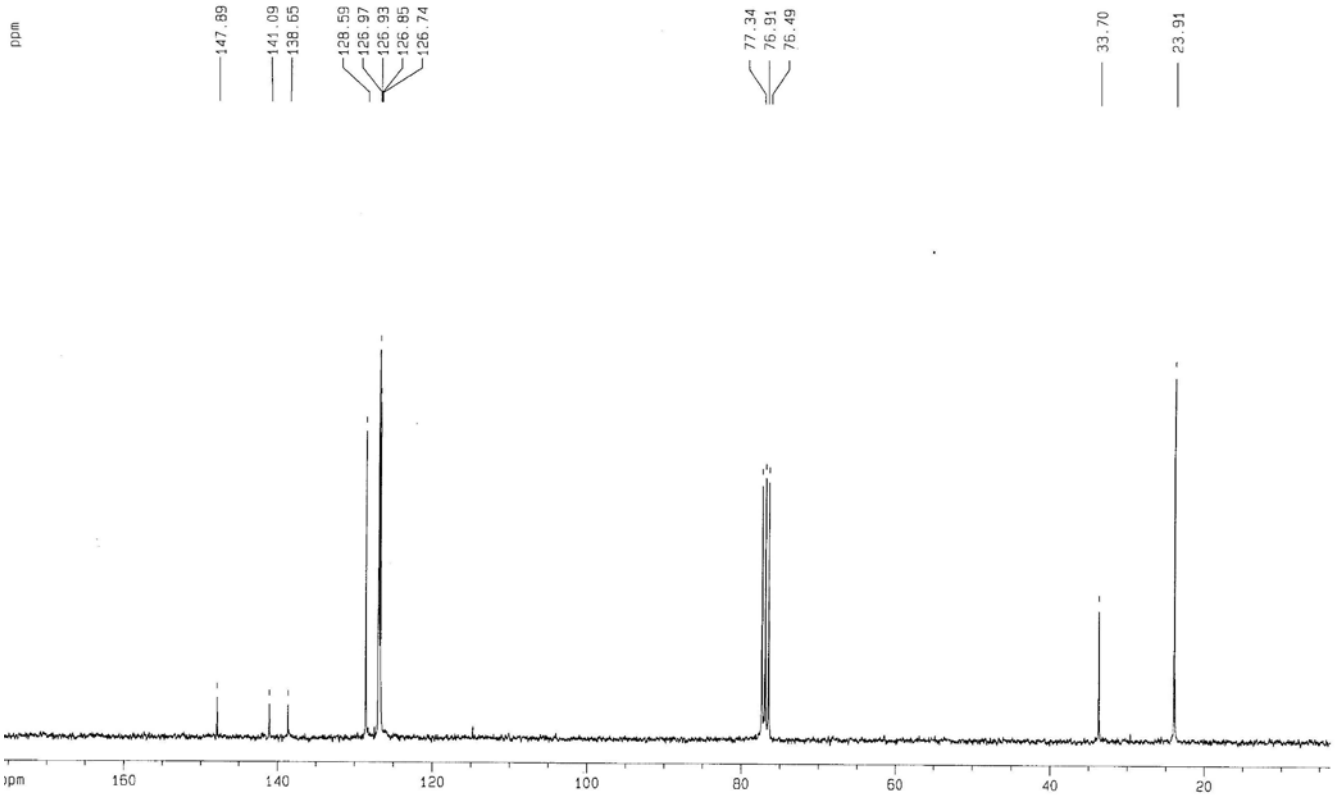


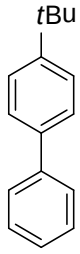
28 (^{1}H NMR , $CDCl_3$)



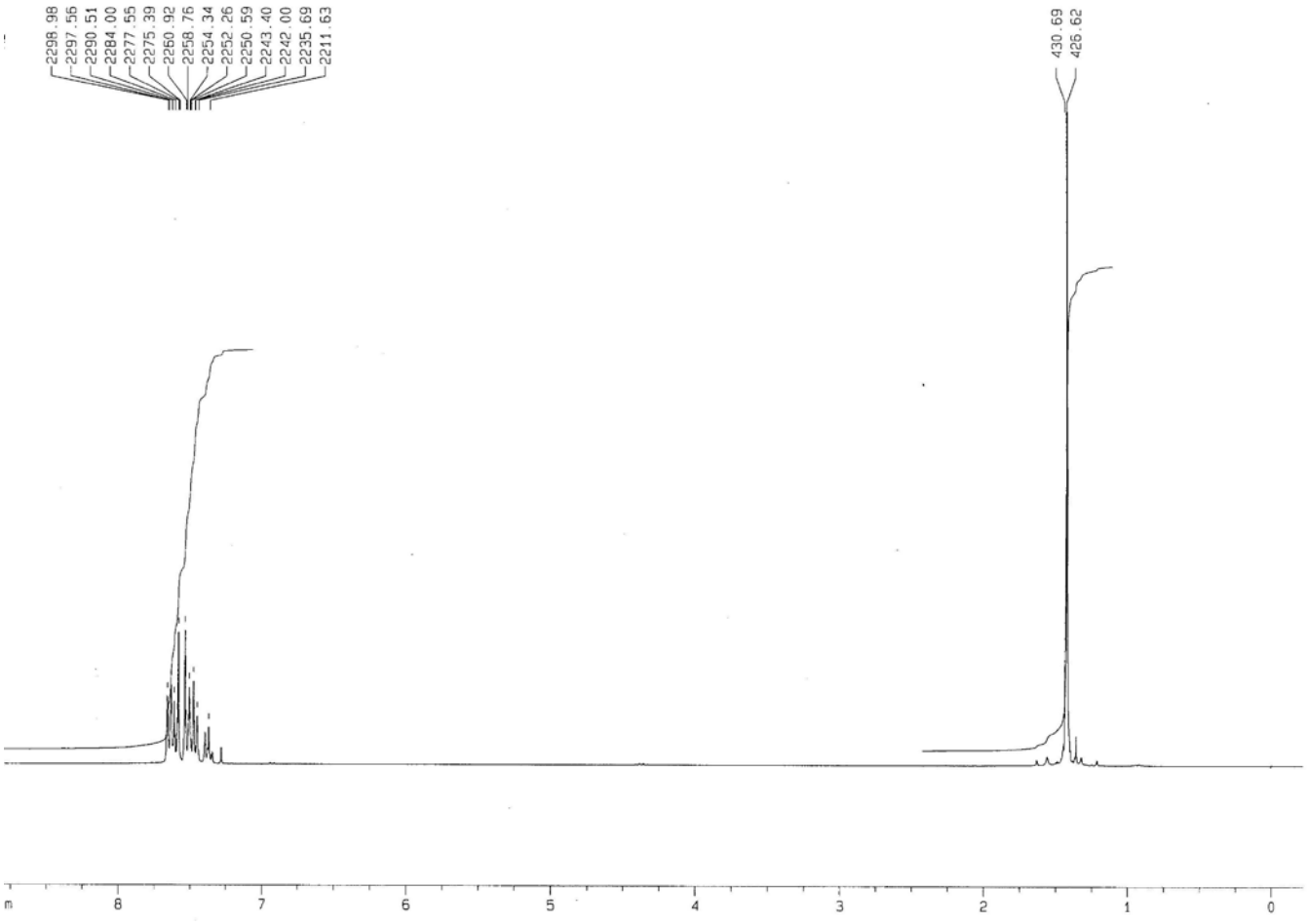


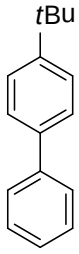
28 (^{13}C NMR , $CDCl_3$)



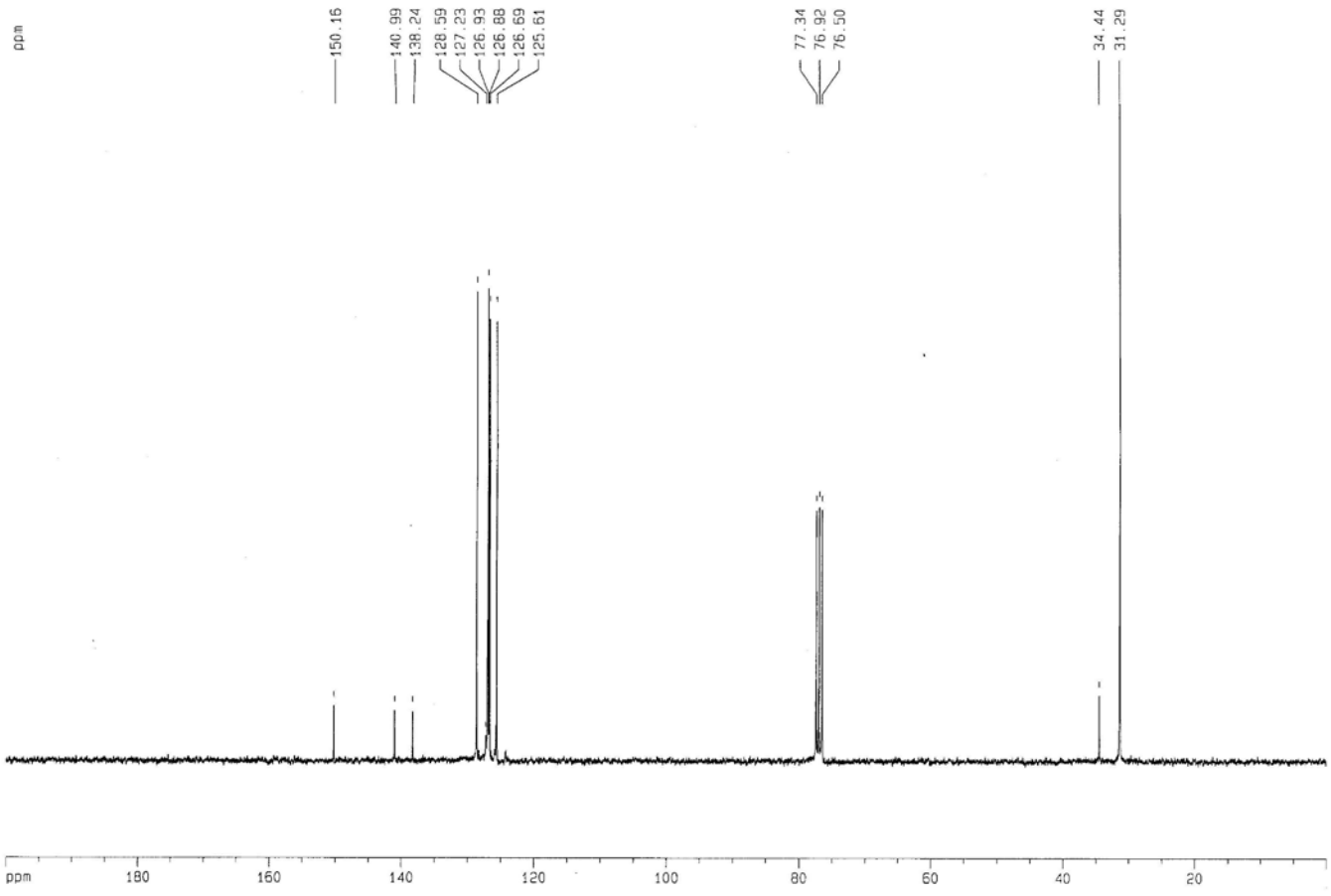


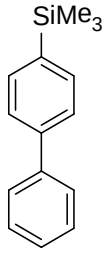
29 (^{1}H NMR , $CDCl_3$)



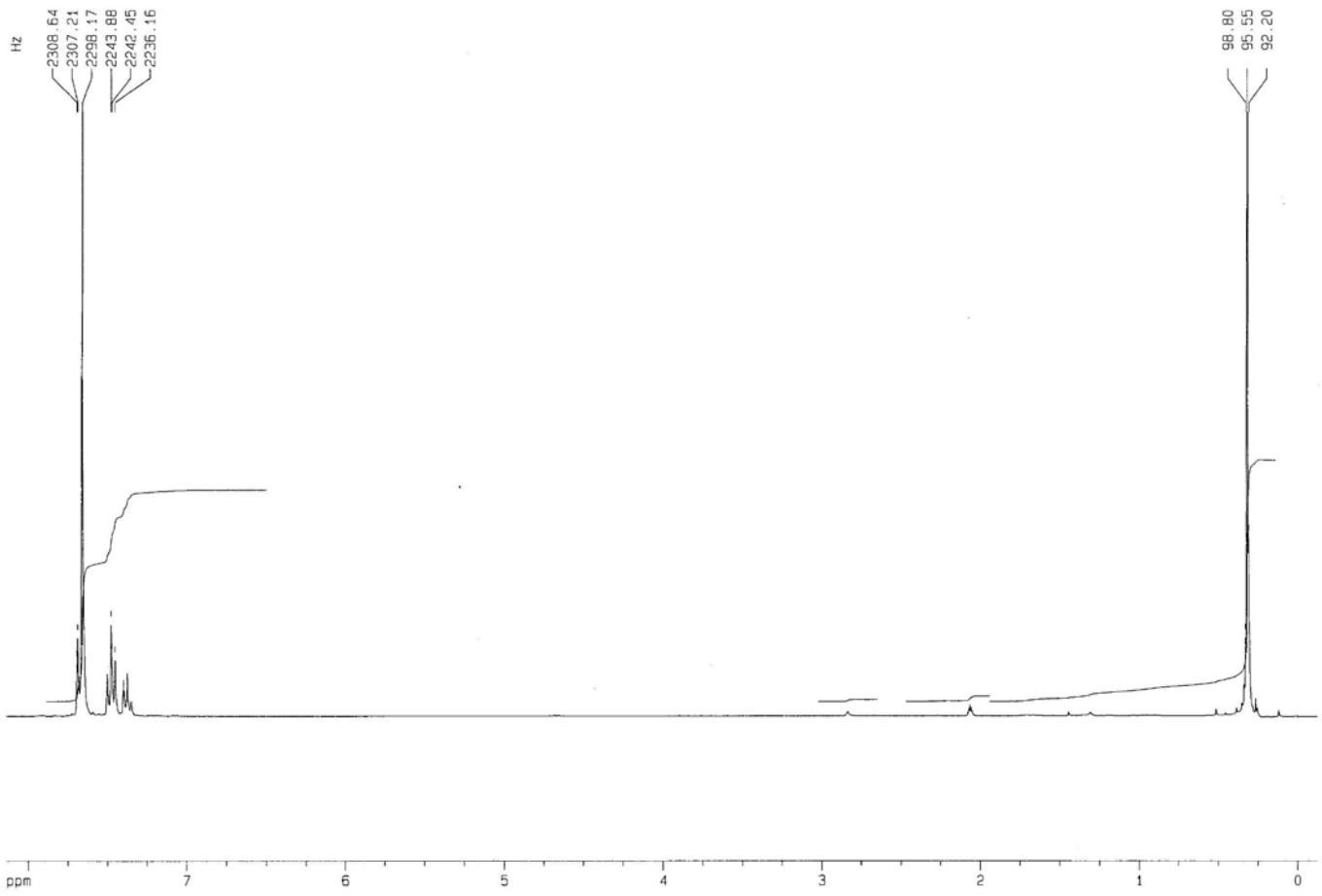


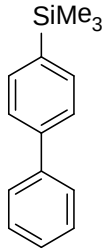
29 (^{13}C NMR , $CDCl_3$)



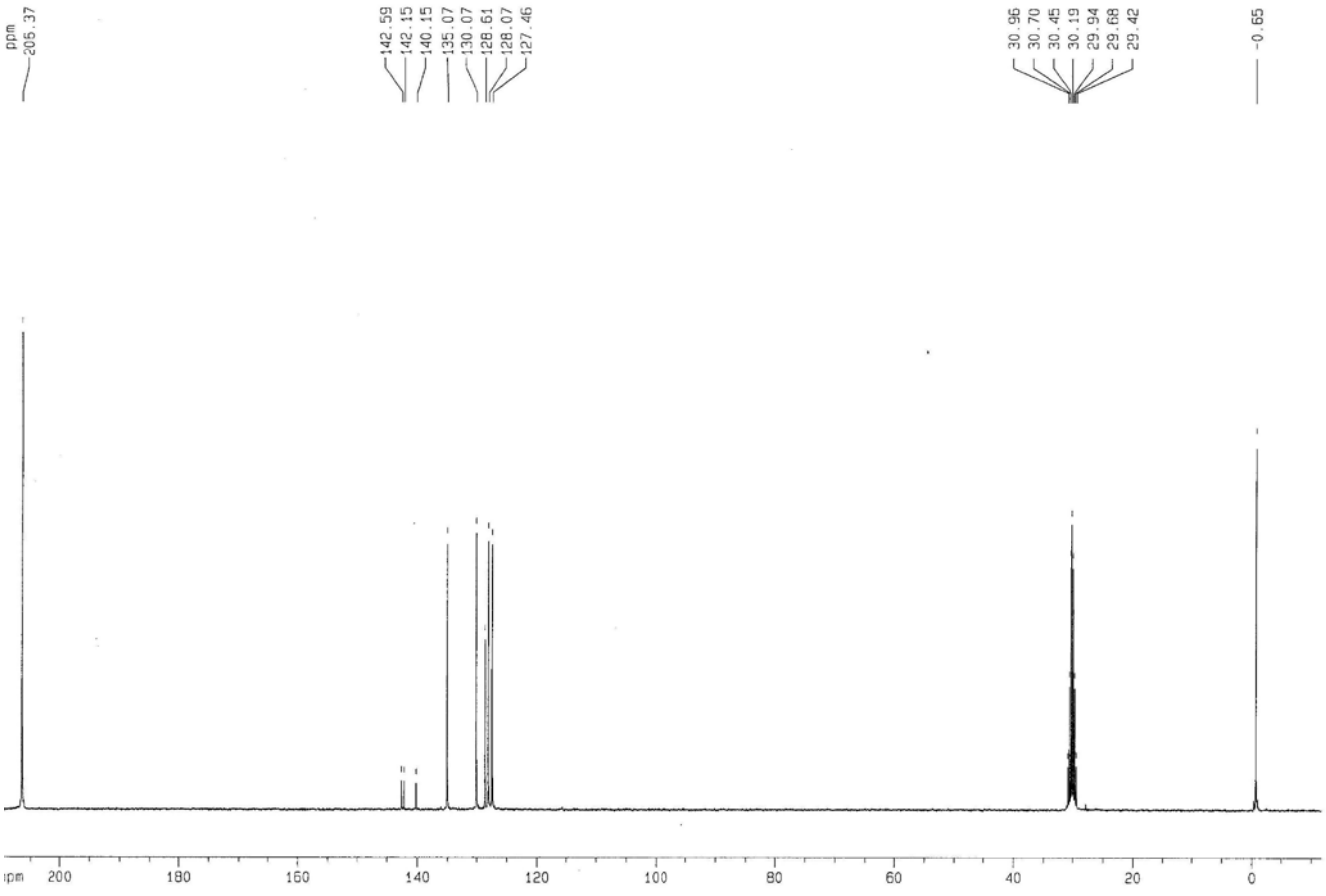


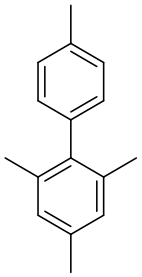
30 (^{1}H NMR , CD_3COCD_3)



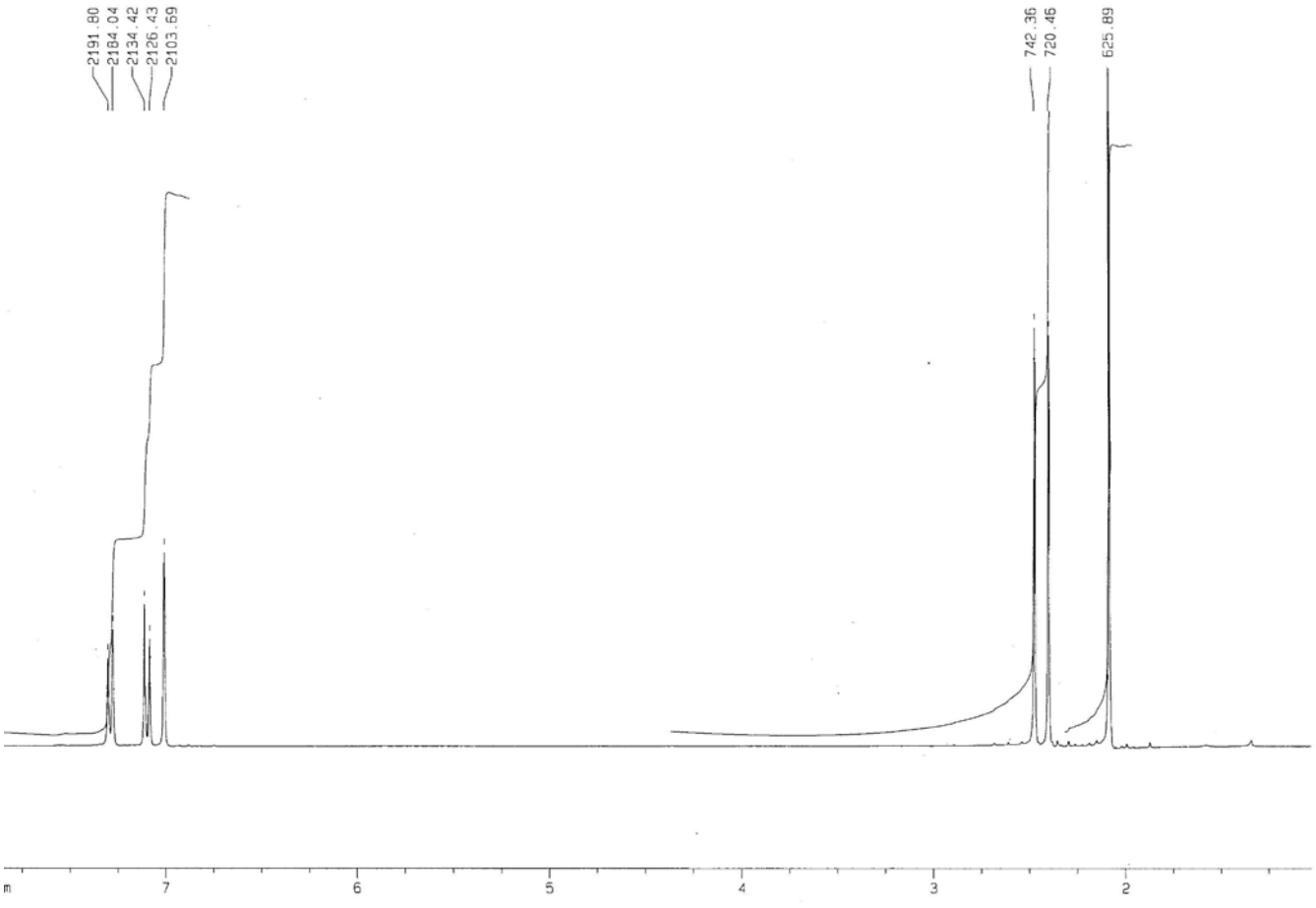


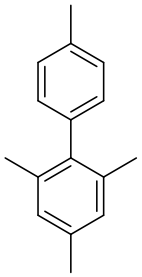
30 (^{13}C NMR , CD_3COCD_3)



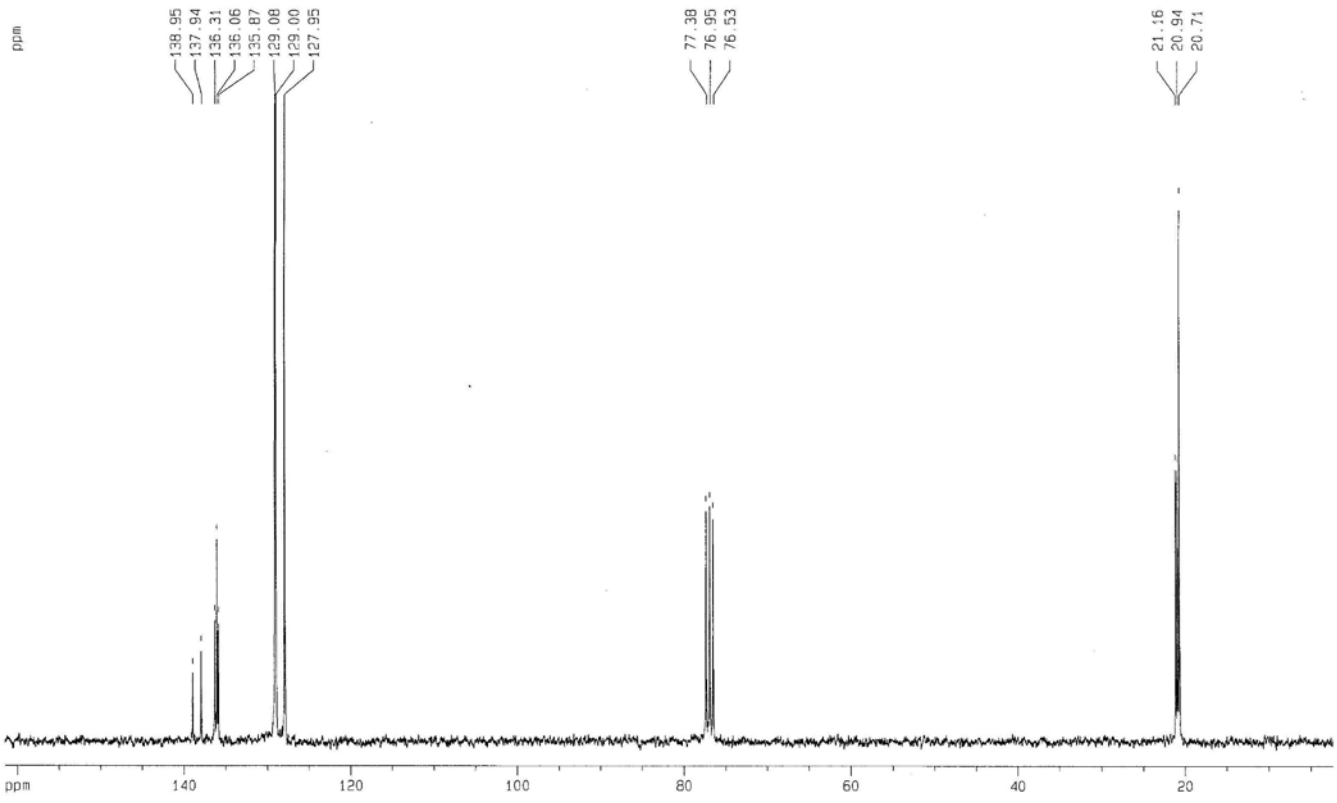


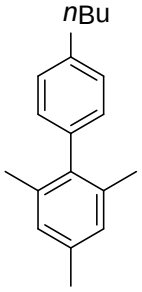
31 (^{1}H NMR , $CDCl_3$)



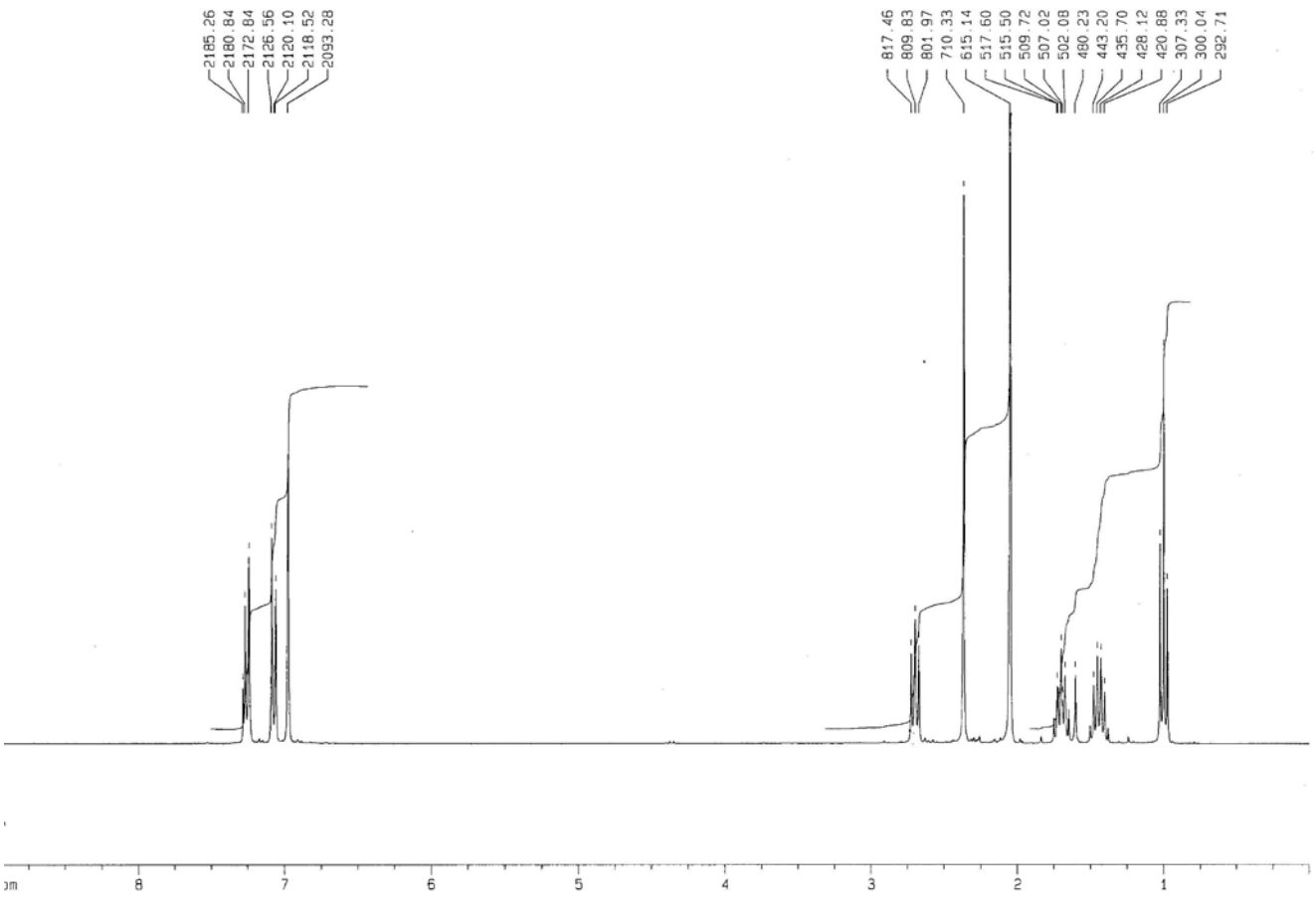


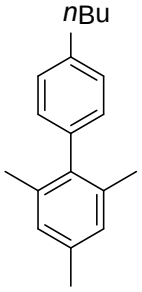
31 (^{13}C NMR , $CDCl_3$)



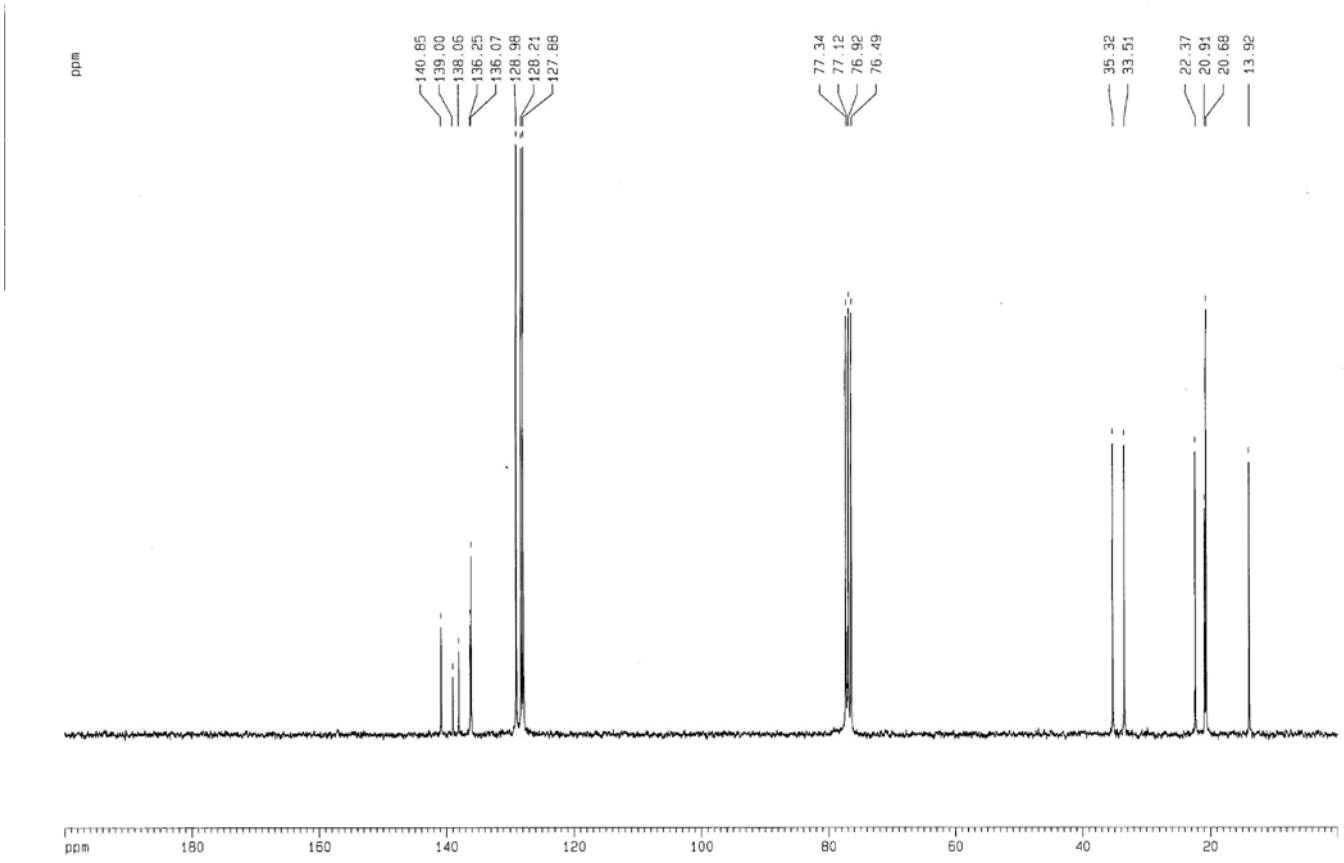


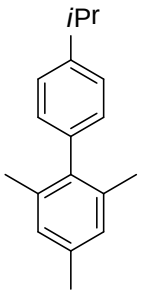
32 (^{1}H NMR , $CDCl_3$)



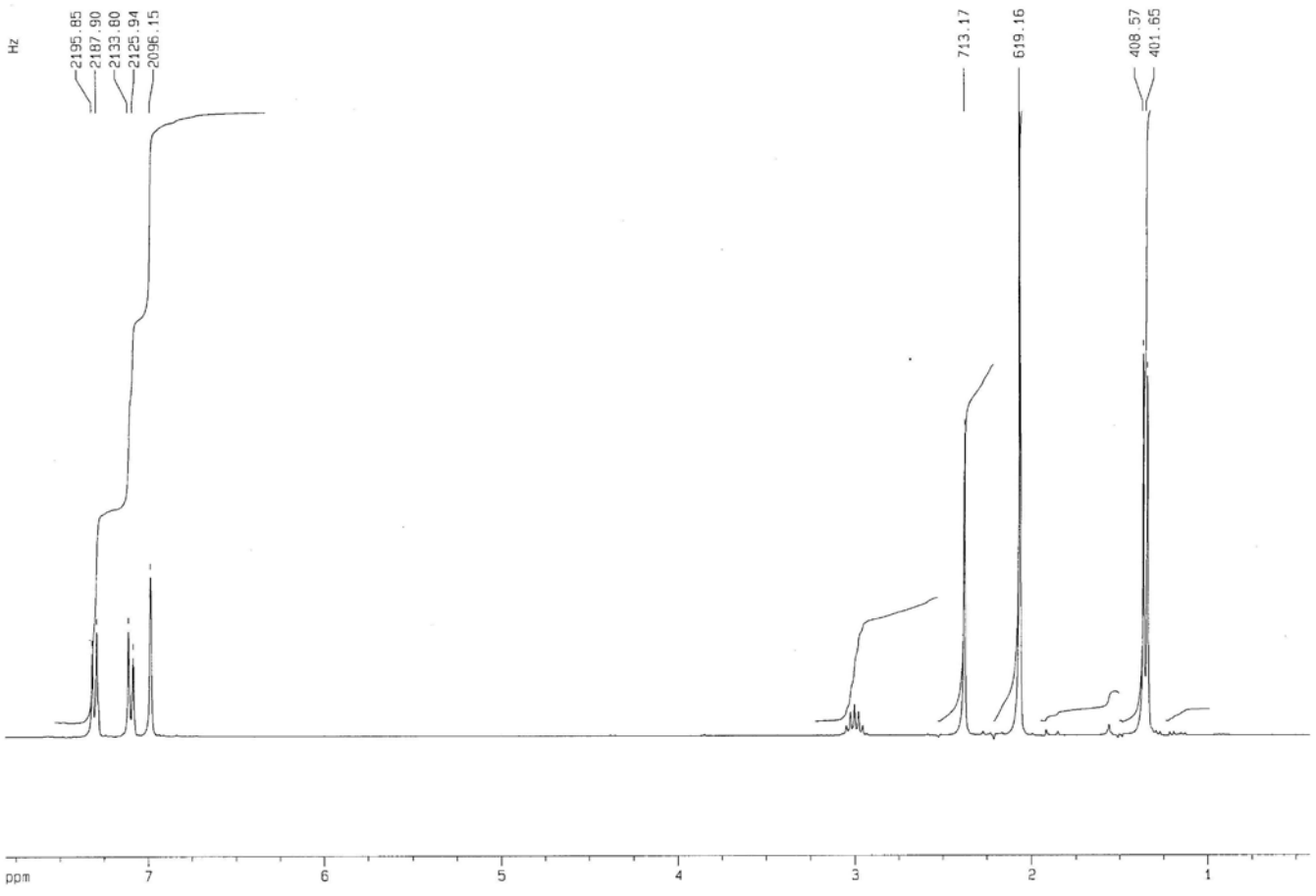


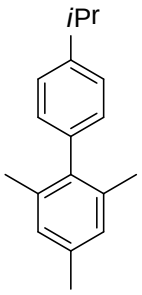
32 (^{13}C NMR , $CDCl_3$)



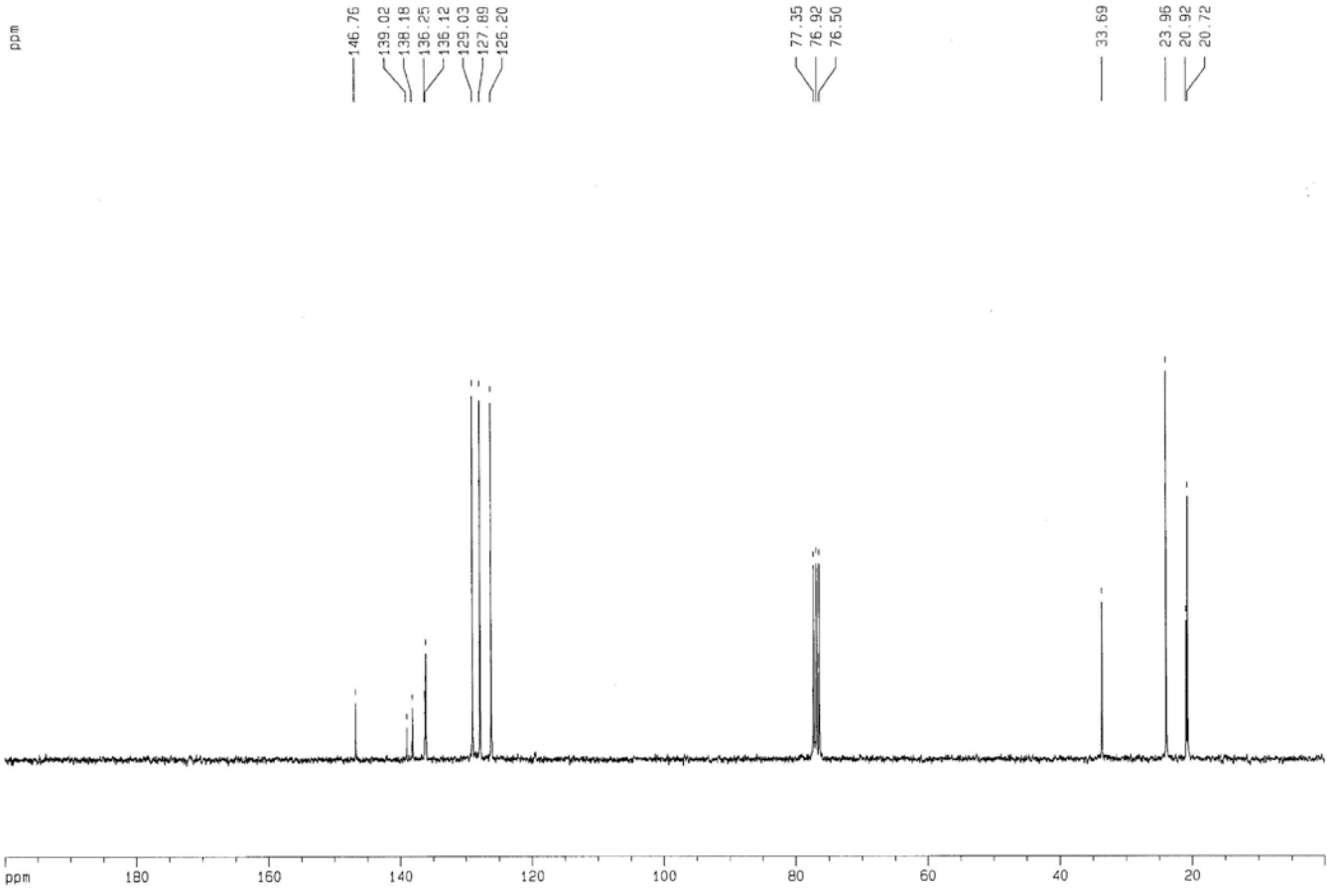


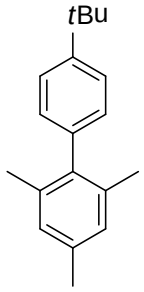
33 (^{1}H NMR , $CDCl_3$)



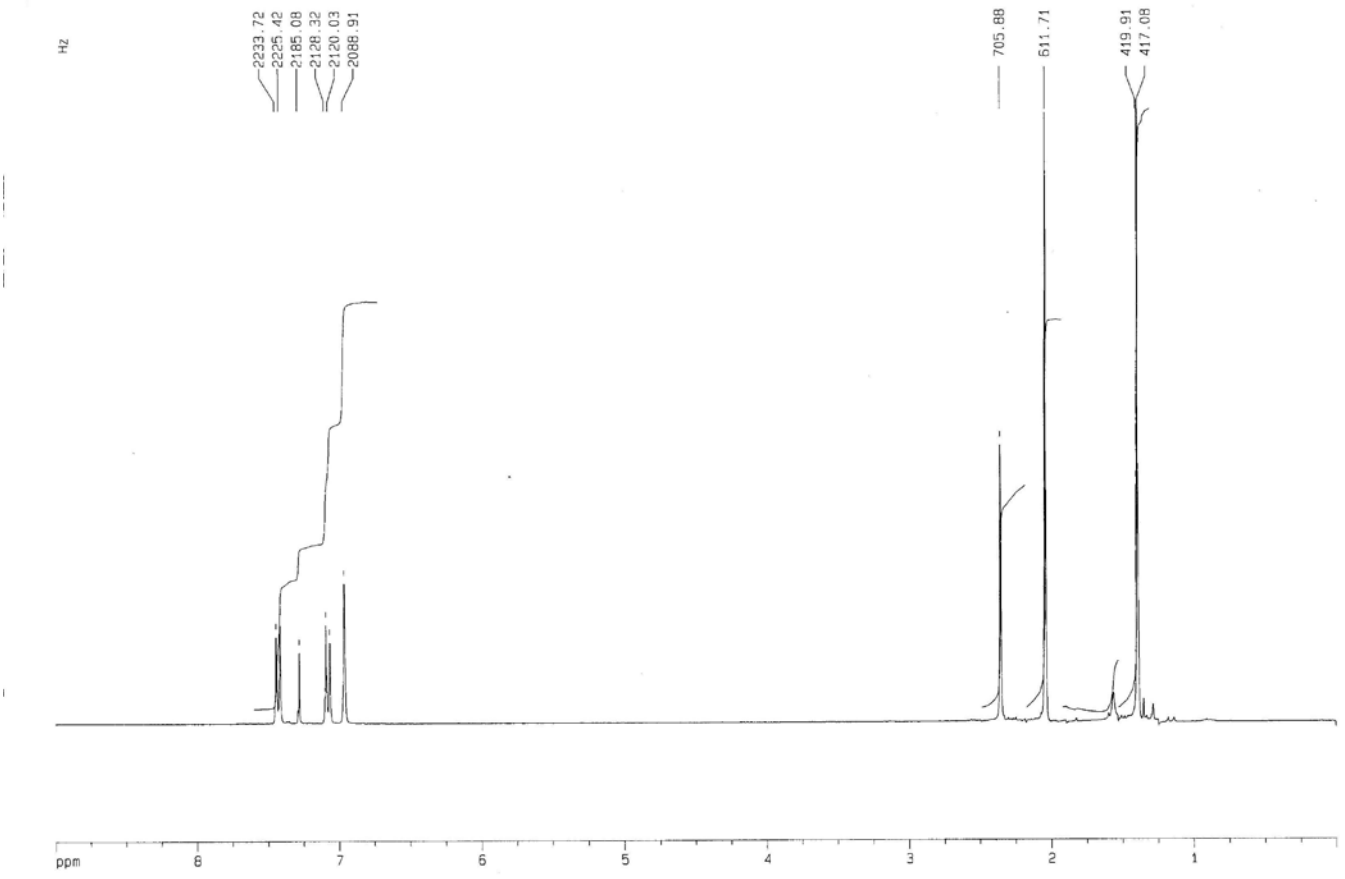


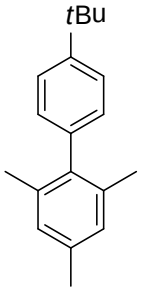
33 (^{13}C NMR , $CDCl_3$)



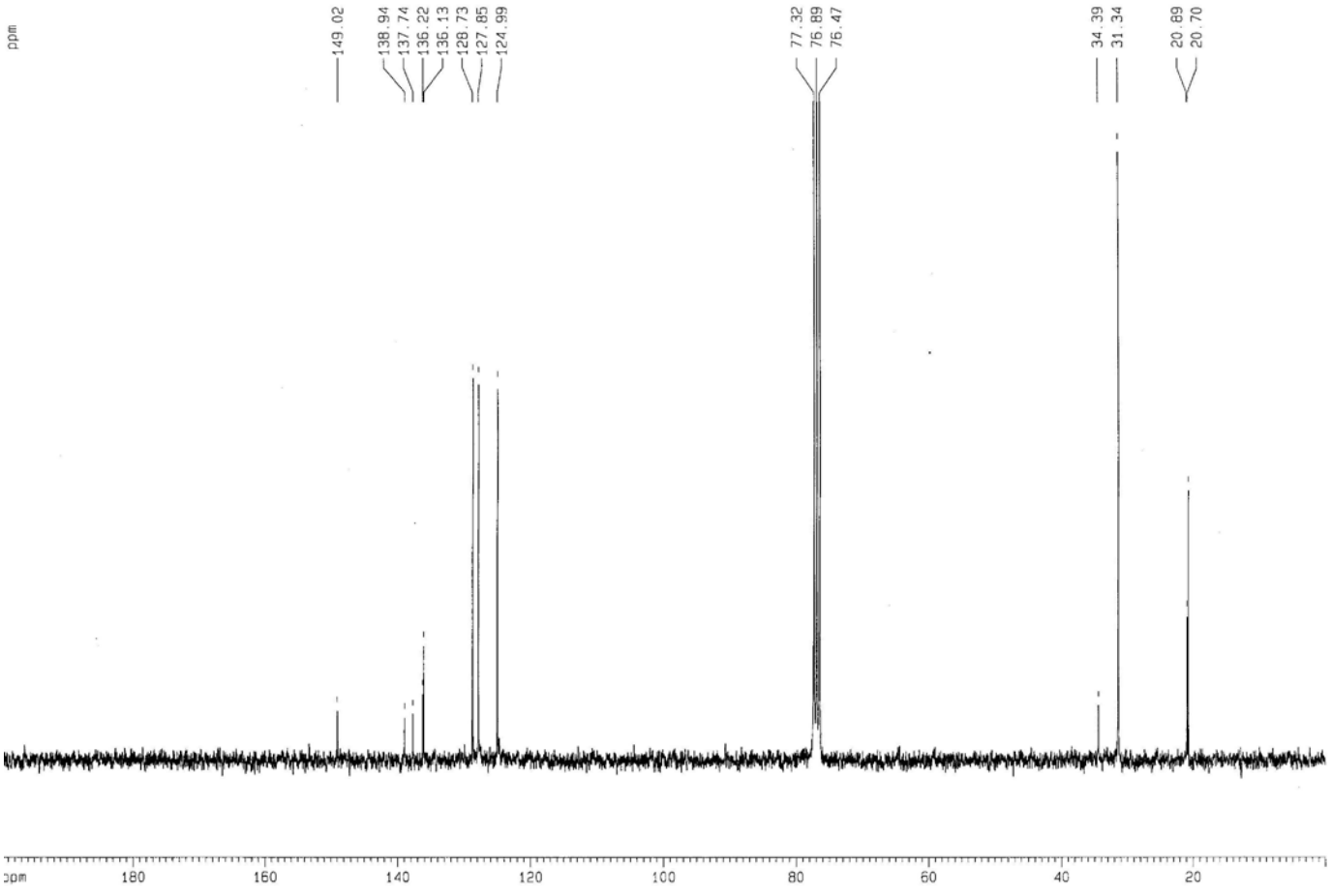


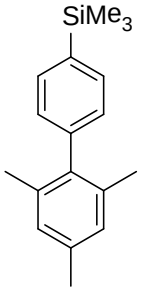
34 (^{1}H NMR , $CDCl_3$)



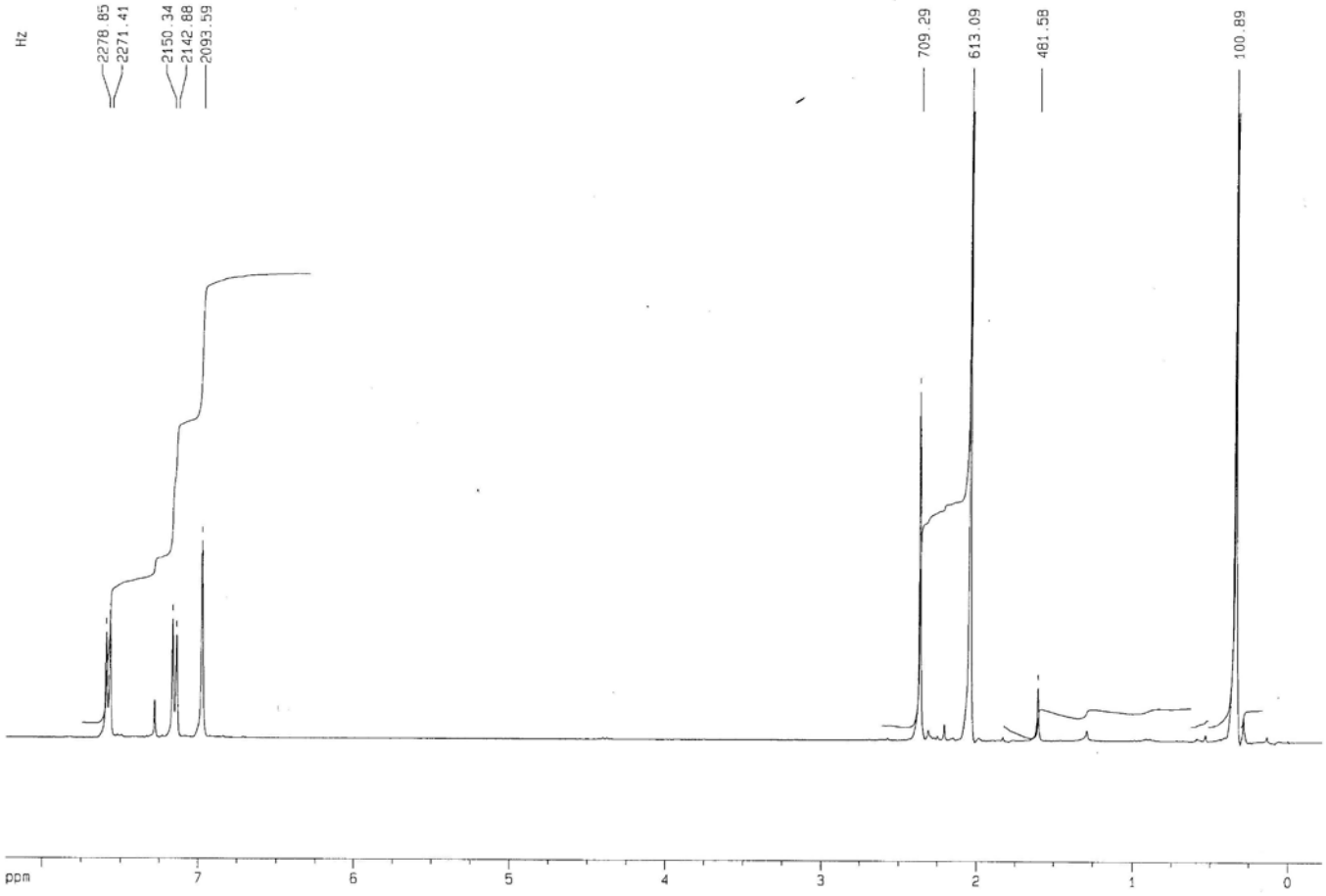


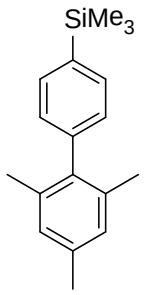
34 (^{13}C NMR , $CDCl_3$)





35 (^{1}H NMR , $CDCl_3$)





35 (^{13}C NMR , $CDCl_3$)