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# Synthesis of N-(substituted phenyl) acetamides.

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# Synthesis of N-(substituted phenyl) acetamides

Thesis submitted in partial fulfillment of Honors

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## Background

N-phenylacetamide (**1**, Figure 2a) is a compound that is easily synthesized from a mixture of aniline and acetyl chloride. By utilizing substituted anilines instead of aniline, N-(substituted phenyl)acetamides are made. Phenylacetamides have been utilized successfully as chelating ligands in the synthesis of tetrakis-(N-phenylacetamide) dirhodium(II) (Figure 1). We propose to make substituted acetamides to serve as ligands for future tetrakis-(N-substituted phenylacetamide) dirhodium(II) complexes.

## Introduction

$Rh_2L_4$ (where L=OAc or $NHCOCH_3$) are effective catalysts for cyclopropanation reactions.[1] A high yield is provided with minimal interference from normally competitive carbenoid dimerization when undergoing cyclopropanation where L=OAc.[2] However, this causes the formation of two different stereoisomers with no specificity. This low stereoselectivity is due to there being no steric hindrance for either the *cis* or *trans* isomers.[3] Where L=$NHCOCH_3$, an increase in the *trans* (anti) stereoselectivities, in cyclopropanation reactions, is observed.[4]

Where L=NPhCOCH$_3$ an enhancement in *cis* stereoselectivity has been observed. Using the 2,2- *cis* and 2,2- *trans* isomers of Rh$_2$(N{C$_6$H$_5$}COCH$_3$)$_4$ (Figure 1) were effective for stereoselectivity of *cis* cyclopropanes at a *cis*/*trans* ratio of up to 1.8.[5] The phenyl group in the catalyst is considered a pendant group because it sticks out from the main structure of the compound. The pendant groups cause steric hindrance and will only allow the alkene to approach the rhodium stabilized carbene from one direction. The steric hindrance between the amide phenyl group with the R group of the alkene must be greater than the hindrance between the R group of the alkene and the carbene. The pendant amide phenyl group also restricts the orientation in which the carbene will be able to approach the rhodium catalyst.

It is believed that by increasing the size of the pendant amide phenyl group the steric hindrance exhibited on the R group of the alkene will be increased when it approaches the rhodium stabilized carbene. Additionally the larger pendant amide phenyl groups of the catalyst will further restrict the orientation of the carbene. To increase the steric hindrance it is necessary to add a substituent at the 2 and 6 positions of the pendant amide phenyl group. The following five analogues of **1** will be synthesized for use as ligands for dirhodium catalysts: N-(2,4,6-trimethylphenyl)-acetamide (**2**, Figure 2b), N-[2,6-bis(1-methylethyl)phenyl]-acetamide (**3**, Figure 2c), 2,2,2-trifluoro-N-phenyl-acetamide (**4**, Figure 2d), 2,2,2-trifluoro-N-(2,4,6-trimethylphenyl)-acetamide (**5**, Figure 2e), and 2,2,2-trifluoro-N-[2,6-bis(1-methylethyl)phenyl]-acetamide (**6**, Figure 2f). These compounds will then be utilized to form Rh$_2$L$_4$ catalysts in a future research project.

## Experimental

### Synthesis of N-phenylacetamide (**1**)

4.90 mL (0.0537 mol) of aniline was dissolved in 75 mL of toluene. 1.91 mL (0.0269 mol) of acetyl chloride was added to the aniline solution dropwise with stirring. The solution was then heated to reflux and maintained at reflux for 2 hours with stirring. The mixture was then allowed to cool resulting in the formation of a solid. The solid was separated from the filtrate by vacuum filtration.

The solid was recovered and washed with 100 mL of DI water. The product, N-phenylacetamide, was recovered by adding 25 mL of diethyl ether to the aqueous solution with stirring. This mixture was then placed in a separatory funnel and the aqueous layer was removed. The organic layer was saved to combine with the filtrate from the reaction mixture.

The filtrate from the reaction mixture was removed by rotary evaporation and the solid that was recovered was redissolved in 75 mL of diethyl ether. This was then combined with the diethyl ether from above in a separatory funnel. This solution was then washed with 5 mL of DI water, 12.5 mL of 5% HCl, 12.5 mL of 5% NaOH, and an additional 5 mL of DI water. The diethyl ether was then removed via rotary evaporation.

The product was purified by recrystallization in isopropanol. Approximately 18 mL of isopropanol was used to dissolve 2.51 g of the product with heating in a small Erlenmeyer flask. A pea-sized amount of charcoal was added to the flask and the mixture was heated to reflux and maintained at reflux for about 5 minutes. About 3-4 pea-sized equivalents of celite were used to extract the charcoal and assist in filtration. The mixture was then gravity-filtered hot and washed with hot isopropanol. The liquid that was recovered from the filtration was then put in an ice bath to recrystalize. Scratching was used to begin the recrystallization. The mixture was allowed to cool for approximately 2 hours then vacuum filtered and washed with cold isopropanol.

2.98 g of **1** was synthesized with a percent yield of 79.12%. The product was a white crystalline solid that had a melting point of 114-117 °C after it had dried. The IR spectrum showed peaks at 3290 $cm^{-1}$ for N-H stretch, 1662 $cm^{-1}$ for C=O stretch, 1597 $cm^{-1}$ for C=C aromatic stretch, and 750 $cm^{-1}$ for C-H aromatic out of plane bend as shown in Figure 3. The proton NMR spectrum ($CDCl_3$) showed peaks at $\delta$ 7.47 ppm (d, 2H, ortho), 7.29 ppm (t, 2H, meta), 7.08 ppm (t, 1H, para), 2.14 ppm (s, 3H, alkyl), and 1.71 ppm (s, 1H, N-H) and the carbon NMR spectrum showed peaks at $\delta$ 168 ppm, 137 ppm, 129 ppm, 124 ppm, 119 ppm, and 24 ppm as shown in Figure 4.

Literature values for **1** were 114-116 °C for the melting point, IR peaks at 3294 $cm^{-1}$ for N-H stretch, 3150 $cm^{-1}$ for C-H aromatic stretch, 1665 $cm^{-1}$ for C=O stretch, 1600 $cm^{-1}$ and 1557 $cm^{-1}$ for C=C aromatic stretch, and 755 $cm^{-1}$ for C-H aromatic out of plane bend, and proton NMR peaks at $\delta$ 8.6 ppm (s, 1H), 7.4 ppm (d, 2H), 7.2 ppm (t, 2H), 7.0 ppm (t, 1H) and 2.0 ppm (s, 3H).[6]

## Synthesis of N-(2,4,6-trimethylphenyl) acetamide (**2**)

7.5 mL (0.0537 mol) of 2,4,6-trimethylaniline was dissolved in 75 mL of toluene. 1.91 mL (0.0269 mol) of acetyl chloride was added to the 2,4,6-trimethylaniline solution drop wise with stirring. The solution was then heated to reflux and maintained at reflux for 2 hours with stirring. The mixture was then allowed to cool and the solid and the filtrate were separated by vacuum filtration.

The solid was recovered and washed with 100 mL of DI water. The product, N-(2,4,6-trimethyphenyl)-acetamide, was recovered by adding 25 mL of diethyl ether to the water solution with stirring. This mixture was then placed in a separatory funnel and the aqueous layer was removed. The organic layer was saved to combine with the filtrate from the reaction mixture.

The filtrate from the reaction mixture was removed by rotary evaporation and the solid that was recovered was redissolved in 75 mL of diethyl ether. This was then combined with the diethyl ether from above in a separatory funnel. This solution was then washed with 5 mL of DI water, 12.5 mL of 5% HCl, 12.5 mL of 5% NaOH, and an additional 5 mL of DI water. The diethyl ether was then removed via rotary evaporation. The final product was purified via sublimation.

An alternate synthesis of N-(2,4,6-trimethylphenyl) acetamide was also utilized. 1 mL of 2,4,6-trimethylaniline was dissolved in 10 mL of pyridine with stirring in a round bottom flask and 3 mL of acetic anhydride was added to this solution while stirring. This solution was then stirred at room temperature overnight.

40 mL of water was then used to quench the reaction mixture. The precipitate from the reaction mixture was then removed via vacuum filtration and washed with water. The sample was then dried under reduced pressure. The final product was purified via sublimation.

4.48 g of **2** was synthesized giving a percent yield of 94.12%. The product was a white crystalline solid that had a melting point of 219 °C. The IR spectrum showed peaks at 3230 $cm^{-1}$ for N-H stretch, 2916 $cm^{-1}$ for C-H aromatic stretch, 1643 $cm^{-1}$ for C=O stretch, 1533 $cm^{-1}$ for C=C aromatic stretch, 1290 $cm^{-1}$ for C-N stretch, and 717 $cm^{-1}$ for C-H aromatic out of plane bend as shown in Figure 5. The proton NMR ($CDCl_3$) showed peaks at $\delta$ 6.92 ppm (d, 2H), 6.75 ppm (s, 1H), 6.64 ppm (s, 1H), 2.25 ppm (m, 9H), and 1.70 ppm (d, 3H) and the carbon NMR showed peaks at $\delta$ 168 ppm, 137 ppm, 136 ppm, 135 ppm, 131 ppm, 129 ppm, 23 ppm, 21 ppm, and 18 ppm as shown in Figure 6.

Literature melting point for **2** was 218-219 °C.[7] The literature values for the proton NMR spectrum showed peaks at $\delta$ 6.86 ppm for *p*-hydrogen's, 6.70 ppm for N-H, and 2.05 ppm for alkyl hydrogen's. The carbon NMR spectrum showed peaks at $\delta$ 168 ppm, 137 ppm, 136 ppm, 128 ppm, 23 ppm, 21 ppm and 18 ppm. The IR spectrum showed peaks at 3236 $cm^{-1}$ for N-H stretch, 3042 $cm^{-1}$ for C-H aromatic stretch, 1646 $cm^{-1}$ for C=O stretch, 1541 $cm^{-1}$ for C=C aromatic stretch, 1291 $cm^{-1}$ for C-N stretch, and 717 $cm^{-1}$ for C-H aromatic out of plane bend. [8]

## Synthesis of N-[2,6-bis(1-ethylmethyl)phenyl]-acetamide (**3**)

1.5 mL of 2,6-diisopropylaniline was dissolved in10 mL of pyridine with stirring in a round bottom flask and 3 mL of acetic anhydride was added to this solution while stirring. This solution was then stirred at room temperature overnight.

40 mL of water was then used to quench the reaction mixture. The precipitate from the reaction mixture was then removed via vacuum filtration and washed with water. The sample was then dried under reduced pressure. The final product was purified via sublimation.

1.33 g of **3** was synthesized giving a percent yield of 76.44%. The product was a white crystalline solid that had a melting point of 188-190 °C. The IR spectrum showed peaks at 3265 cm$^{-1}$ for N-H stretch, 2960 cm$^{-1}$ for C-H aromatic stretch, 1647 cm$^{-1}$ for C=O stretch, 1516 cm$^{-1}$ for C=C aromatic stretch, 1284 cm$^{-1}$ for C-N stretch, and 705 cm$^{-1}$ for C-H aromatic out of plane bend as shown in Figure 7. The proton NMR spectrum ($CDCl_3$) showed peaks at δ 1.17 ppm (m, triplet of doublets, 12H), 2.18 ppm (s, 3H), 3.06 ppm (sept, 1H), 3.18 ppm (sept, 1H), 6.92 ppm (s, 1H), and 7.17 ppm (m, 3H) and the carbon NMR showed peaks at δ 173 ppm, 169 ppm, 146 ppm, 132 ppm, 131 ppm, 129 ppm, 128 ppm, 124 ppm, 123 ppm, 28 ppm, 24 ppm, 23 ppm, and 22 ppm as shown in Figure 8.

Multiple melting points were found for **3** in literature with 198-200 °C[10] being the highest. This was slightly higher than the measured melting point that could be due to solvents. The measured melting point was very sharp which indicates that impurities were most likely all removed. Literature proton NMR showed δ 9.20 ppm (s, 1H), 7.50 ppm (t, 1H), 7.30 ppm (d, 2H), 3.05 ppm (sept, 2H), and 1.10 ppm (d, 6H). Carbon NMR showed δ 169 ppm, 146 ppm, 133 ppm, 127 ppm, 123 ppm, 28 ppm, 24 ppm, 23 ppm, and 22 ppm.[9]

### Synthesis of 2,2,2-trifluoro-N-phenylacetamide (**4**)

4 mL of aniline was dissolved in 25 mL of pyridine with stirring. 10 mL of trifluoroacetic anhydride was added drop wise to this solution and it was stirred at room temperature for 4 hours. 100 mL of deionized water was added to the mixture to remove salts and precipitate the product. The product was placed in an ice bath for 30 minutes to chill and then was recovered by vacuum filtration. The filtrate was chilled over night in the freezer and then filtered again in the morning. The product was purified by sublimation.

4.36 g of **4** was synthesized giving a percent yield of 52.63%. The product was a white crystalline solid that had a melting point of 86-89 °C. The IR spectrum showed peaks at 3315 $cm^{-1}$ for N-H stretch, 1701 $cm^{-1}$ for C=O stretch, 1544 $cm^{-1}$ for C=C aromatic stretch, 1284 $cm^{-1}$ for C-N stretch, 1143 $cm^{-1}$ for C-H aromatic in plane bend, and 729 $cm^{-1}$ for C-H aromatic out of plane bend as shown in Figure 9. The proton NMR spectrum ($CDCl_3$) showed peaks at δ 7.25 ppm (t, 1H, para), 7.38 ppm (t, 2H, meta), 7.55 ppm (d, 2H, ortho), and 8.09 ppm (s, 1H, N-H) and the carbon NMR showed peaks at δ 155 ppm, 154 ppm, 135 ppm, 129 ppm, 126 ppm, 120 ppm, 117 ppm, and 114 ppm as shown in Figure 10.

**4** had a literature melting point of 88-89 °C.[10] IR data showed peaks at 3317 $cm^{-1}$ for N-H stretch, 1700 $cm^{-1}$ for C=O stretch, 1548 $cm^{-1}$ for C=C aromatic stretch, 1283 $cm^{-1}$ for C-N stretch, and 1141 $cm^{-1}$ for C-H aromatic in plane bend. Proton NMR showed peaks at δ 7.20-7.36 (m, 3H), 7.55 (m, 2H), and 8.77 (s, 1H). Carbon NMR showed peaks at δ 154 ppm, 136 ppm, 129 ppm, 128 ppm, 125 ppm, 121 ppm, 118 ppm, and 113 ppm.[11]

### Synthesis of 2,2,2-trifluoro-N-(2,4,6-trimethylphenyl)-acetamide (**5**)

5 mL of 2,4,6-trimethylaniline was dissolved in 25 mL of pyridine with stirring. 10 mL of trifluoroacetic anhydride was added drop wise to this solution while in an ice bath and it was stirred at room temperature for 4 hours. Approximately 250 mL of deionized water was added to the mixture to remove salts and precipitate the product. The mixture was chilled for 2 hours to increase the yield. The product was recovered by vacuum filtration. The filtrate was chilled over night in the freezer and then filtered again in the morning. The product was purified by sublimation.

4.29 g of **5** was synthesized giving a percent yield of 55%. The product was a light yellow crystalline solid. This compound had a melting point of 130-134 °C. The IR spectrum showed peaks at 3265 $cm^{-1}$ for N-H stretch, 1701 $cm^{-1}$ for C=O stretch, 1558 $cm^{-1}$ for C=C aromatic stretch, 1157 $cm^{-1}$ for C-H aromatic in plane bend, and 705 $cm^{-1}$ C-H aromatic out of plane bend as shown in Figure 11. The proton NMR spectrum ($CDCl_3$) showed peaks at δ 2.18 ppm (s, 6H), 2.31 ppm (s, 3H), 6.91 ppm (s, 1H), and 7.54 ppm (s, 2H) and the carbon NMR showed peaks at δ

156 ppm, 155 ppm, 138 ppm, 135 ppm, 129 ppm, 128 ppm, 124 ppm, 117 ppm, and 114 ppm as shown in Figure 12.

There was no published data available for **5** on melting point, IR or NMR; however, predicted NMR data showed peaks at δ 1.6 ppm, 2.1 ppm, 6.9 ppm, and 9.2 ppm for proton NMR and δ 18 ppm, 21 ppm, 117 ppm, 128 ppm, 133 ppm, and 155 ppm for carbon NMR.[12]

### Synthesis of 2,2,2-trifluoro-N-[2,6-bis(1-ethylmethyl)phenyl]-acetamide (**6**)

9 mL of 2,6-diisopropylaniline was dissolved in 25 mL of pyridine with stirring. 10 mL of trifluoroacetic anhydride was added drop wise to this solution while in an ice bath and it was stirred at room temperature for 4 hours. Approximately 250 mL of deionized water was added to the mixture to remove salts and precipitate the product. The mixture was chilled for 2 hours to increase the yield. The product was recovered by vacuum filtration. The filtrate was chilled over night in the freezer and then filtered again in the morning. The product was purified by recrystallization.

Recrystallization was performed by dissolving the raw product in hexanes after it had been determined that the product was slightly soluble in hexanes. The solid was dissolved in hexanes with heating and stirring. Just enough hexanes were added so that the solid was dissolved. The solution was then vacuum filtered hot and washed with hot hexanes. The solution was then placed in the freezer overnight to chill. This solid was then collected via vacuum filtration and the recrystalization process was repeated.

5.90 g of **6** was synthesized giving a percent yield of 47.73%. The product was a light pink color and had a melting point of 182-183 °C. The IR spectrum showed peaks at 3228 $cm^{-1}$ for N-H stretch, 2962 $cm^{-1}$ for C-H alkyl stretch, 1701 $cm^{-1}$ for C=O stretch, 1541 $cm^{-1}$ for C=C aromatic stretch, 1159 $cm^{-1}$ for C-H aromatic in plane bend, and 723 $cm^{-1}$ for C-H aromatic out of plane bend as shown in Figure 13. The proton NMR spectrum ($CDCl_3$) showed peaks at δ 1.16 ppm (d, 12H), 2.94 ppm (sept, 2H), 7.21 ppm (d, 2H), 7.37 ppm (t, 1H), and 7.69 ppm (s, 1H) and the carbon NMR showed peaks at δ 146 ppm, 129 ppm, 123 ppm, 28 ppm and 23 ppm as shown in Figure 14.

There was no published data available for **6** on melting point or IR. The published proton NMR showed peaks at δ 9.45 ppm (s, 1H), 7.25 ppm (t, 1H), 7.15 ppm (d, 2H), 3.02 ppm (sept, 2H), and 1.15 ppm (d, 6H). The carbon NMR showed peaks at δ 156 ppm, 145 ppm, 129 ppm, 123 ppm, 116 ppm, 28 ppm, and 23 ppm.[10]

## Discussion

Compounds **1** and **4** showed consistency with all literature data through out. Compounds **2**, **3**, **5**, and **6** all had some peculiarities in NMR spectra, although the IR data was consistent with literature data. Upon first analysis of the NMR spectra of compound **2** it was believed that a mixture of two compounds had been synthesized and that these compounds were in a 2:1 ratio. It was initially believed from the spectra that this mixture could be comprised of the imide and the amide (Figure 15). This is most notable in the multiplet that was observed from 2.3 to 2.1 ppm in Figure 6. However, Moriyasu et. al. showed that *E*- and *Z*-forms of acetanilides

(Figure 16) could separate at low temperatures due to the *o*-methyl restricting the carbonyl – nitrogen bond. The carbonyl – nitrogen bond is further restricted upon the addition of methyl's at both *o*-positions causing the *E*- and *Z*-forms to separate at a higher temperature.[13] The NMRs were all taken at -20 °C which is shown to be sufficiently low to cause splitting of the peaks.

This finding explains the splitting of not only compound **2**, but also compound **3**. Compound **3** has larger substituents at the *o*-position than compound **2** which also caused splitting of the peaks. Compound **5** is very similar to compound **2** in structure with a $CF_3$ group substituted for the alkyl $CH_3$. The splitting that was observed in the proton NMRs of compounds **2** and **3** was also observed in the carbon NMRs. In the NMRs of compounds **5** and **6** splitting was expected but did not occur. The electron density that occurred due to the $CF_3$ group may have caused a shift more towards the *Z*-form of these compounds, which would explain why the *E*-form was not observed in these NMRs.

The *Z*-form is the predominately observed form in the NMR. In Figure 6 the *E* and *Z*-forms are overlaid at the multiplet observed at 2.2 ppm. The larger peaks show the *Z*-form at the peaks observed at 6.6 ppm and 6.8 ppm. In Figure 8 the *Z*-form is shown by the peaks at 1.7 ppm, 3.0 ppm and 7.1 ppm and the *E*-form by peaks at 1.8 ppm, 3.1 ppm and the multiplet at 7.3 ppm.

Peaks for proton NMR of compound **2** are as follows: alkyl H at 1.70 (3H), aromatic methyls at 2.25 (9H), N-H at 6.64 and 6.75 (1H), and aromatic H at 6.92 (2H). The proton NMR of compound **3** shows isopropyl alkyl H at 1.17 (12H), alkyl

H at 1.72 and 2.18 (3H), isopropyl C-H at 3.06 and 3.18 (2H), N-H at 6.92 (1H) and aromatic H at 7.17 (3H). The proton NMR of compound **5** shows ortho methyl at 2.18 (6H), para methyl at 2.31 (3H), N-H at 6.91 (1H), and meta H at 7.54 (2H). The proton NMR of compound **6** shows isopropyl alkyl at 1.16 (12H), isopropyl C-H at 2.94 (2H), meta aromatic H at 7.21 (2H), para aromatic H at 7.37 (1H) and N-H at 7.69 (1H).

## Conclusion

Compounds **1** through **6** were all synthesized successfully. Compounds **1** and **2** were synthesized from substituted aniline and acetyl chloride in approximately a 1:2 ratio. Compounds **2** and **3** were synthesized from substituted aniline and acetic anhydride in approximately a 1:2 ratio. Compounds **4**, **5** and **6** were all synthesized from substituted aniline and trifluoroacetic anhydride in approximately a 1:2 ratio.

The melting points for all six compounds were sharp and accurate to previously established literature values. IR data was accurate to previously established data. NMR data was accurate to literature data save for where splitting of peaks occurred due to the presence of *E*- and *Z*-forms of the compound being present.

A reliable protocol for the synthesis of acetamides has been established so that different acetamides may be synthesized in the future for rhodium catalyst and x-ray crystallography studies. The acetamides that were synthesized in this project will all be utilized to study $Rh_2L_4$ complexes where L is an acetamide. Both x-ray crystallography and catalytic studies will be done in the future.

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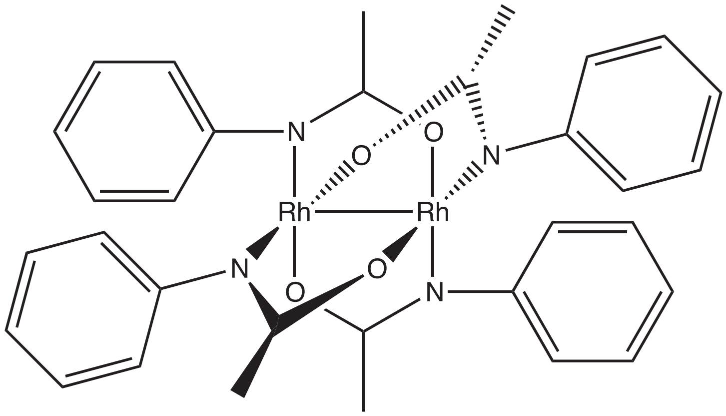
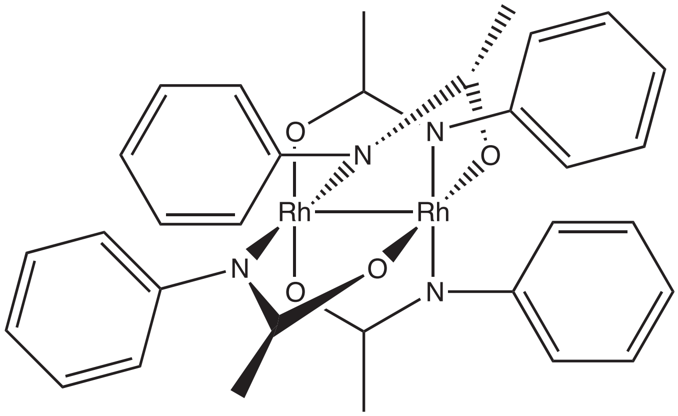
Figure 1

a)



b)

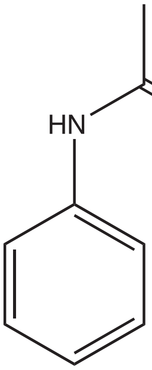


a) 2,2-*cis*-tetrakis-(N-phenylacetamide) dirodium(II)

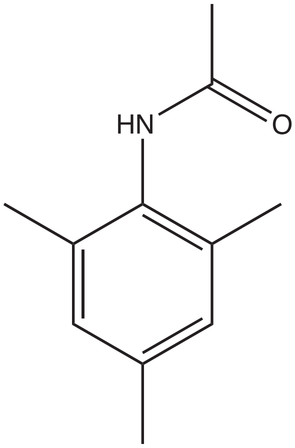
b) 2,2-*trans*-tetrakis-(N-phenylacetamide) dirhodium(II)

Figure 2

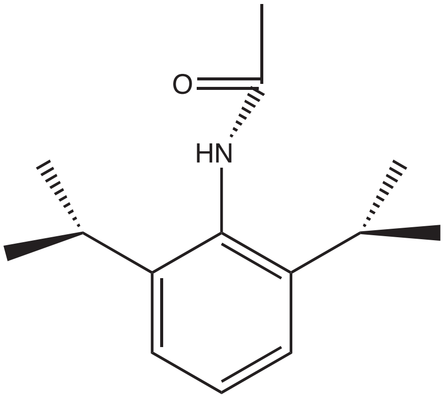
a) N-phenylacetamide



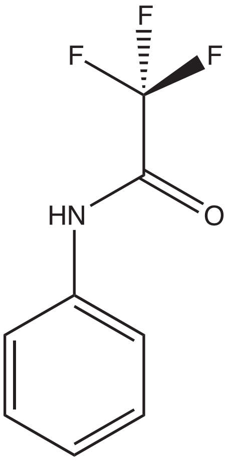
b) N-(2,4,6-trimethylphenyl)-acetamide



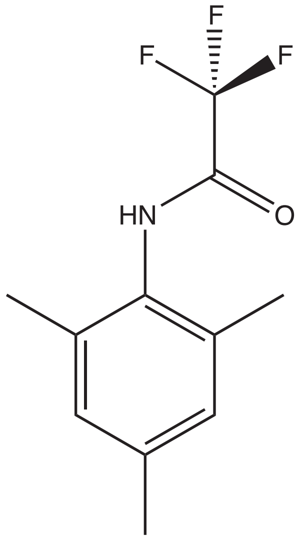
c) N-[2,6-bis(1-methylethyl)phenyl]-acetamide



d) 2,2,2-trifluoro-N-phenyl-acetamide



e) 2,2,2-trifluoro-N-(2,4,6-trimethylphenyl)-acetamide



f) 2,2,2-trifluoro-N-[2,6-bis(1-methylethyl)phenyl]-acetamide

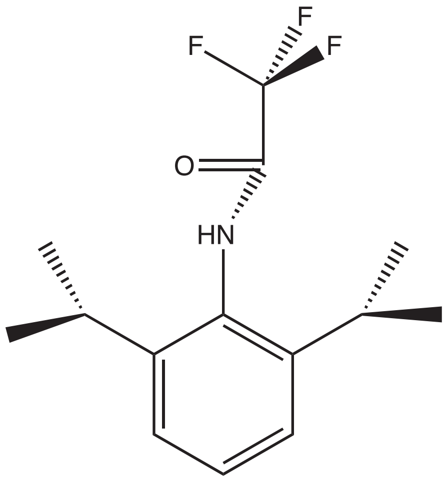
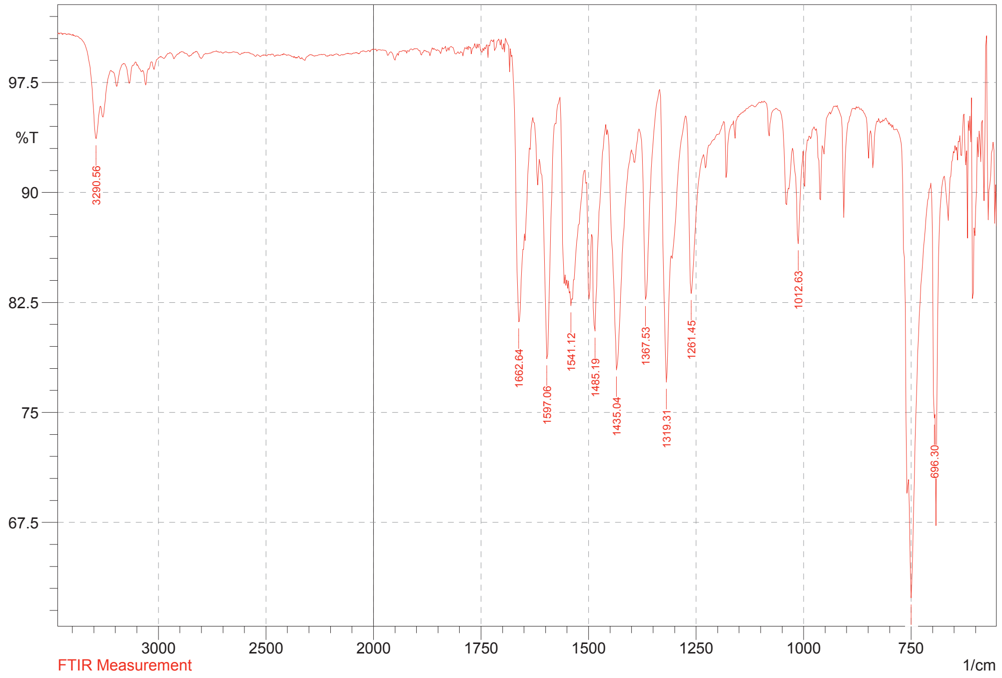


Figure 3

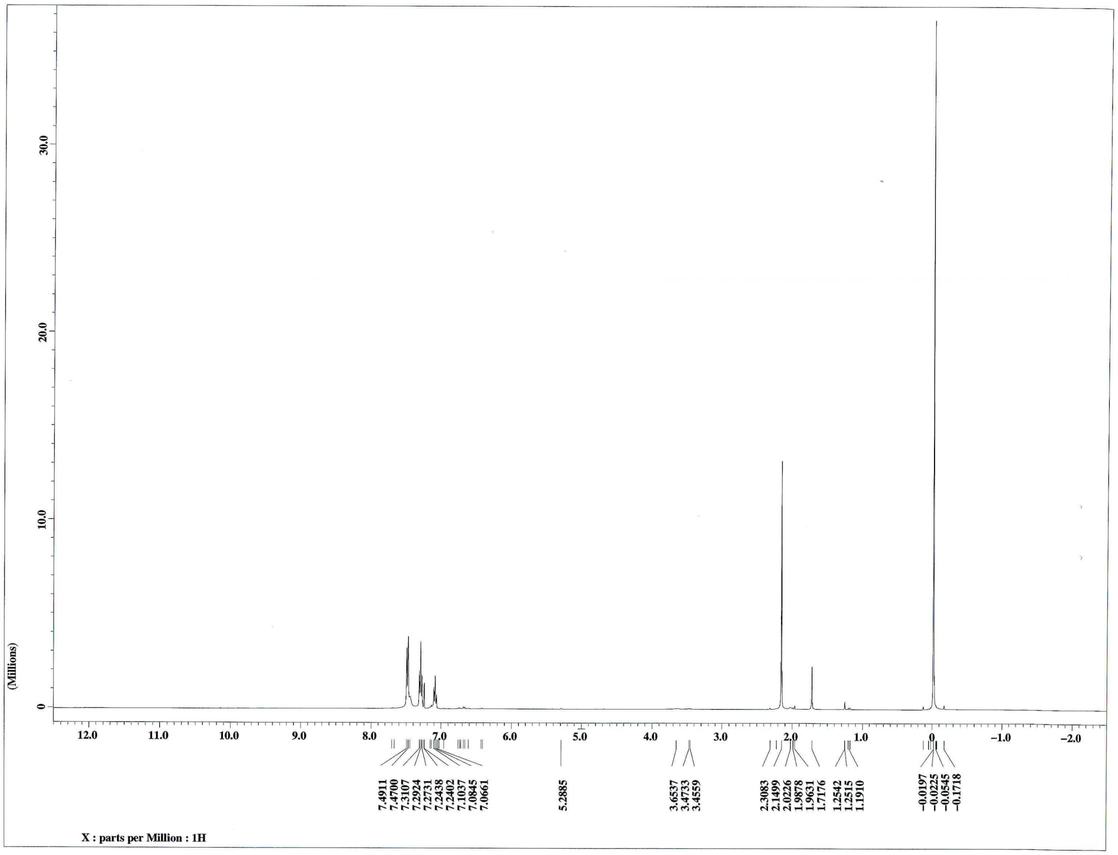


| | Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|---|---|---|---|---|---|---|---|
| 1 | 696.3 | 74.62 | 3.4 | 704.02 | 694.37 | 0.84 | 0.03 |
| 2 | 750.31 | 62.35 | 10.31 | 756.1 | 704.02 | 5.39 | 0.32 |
| 3 | 1012.63 | 86.49 | 6.42 | 1026.13 | 1001.06 | 1.11 | 0.31 |
| 4 | 1261.45 | 83.12 | 11.26 | 1274.95 | 1232.51 | 2.09 | 0.93 |
| 5 | 1319.31 | 77.06 | 13.48 | 1334.74 | 1307.74 | 1.94 | 0.86 |
| 6 | 1367.53 | 82.7 | 12.5 | 1382.96 | 1334.74 | 1.92 | 1 |
| 7 | 1435.04 | 77.89 | 15.87 | 1456.26 | 1400.32 | 3.51 | 1.9 |
| 8 | 1485.19 | 80.54 | 8.36 | 1492.9 | 1460.11 | 1.86 | 0.48 |
| 9 | 1541.12 | 82.27 | 0.72 | 1543.05 | 1539.2 | 0.32 | 0.01 |
| 10 | 1597.06 | 78.66 | 14.76 | 1614.42 | 1577.77 | 2.15 | 1.08 |
| 11 | 1662.64 | 81.18 | 10.03 | 1678.07 | 1653 | 1.39 | 0.55 |
| 12 | 3290.56 | 93.67 | 3.14 | 3379.29 | 3269.34 | 0.95 | 0.11 |

IR of N-phenylacetamide

Figure 4

a) Proton NMR of N-phenylacetamide



## b) Carbon NMR of N-phenylacetamide

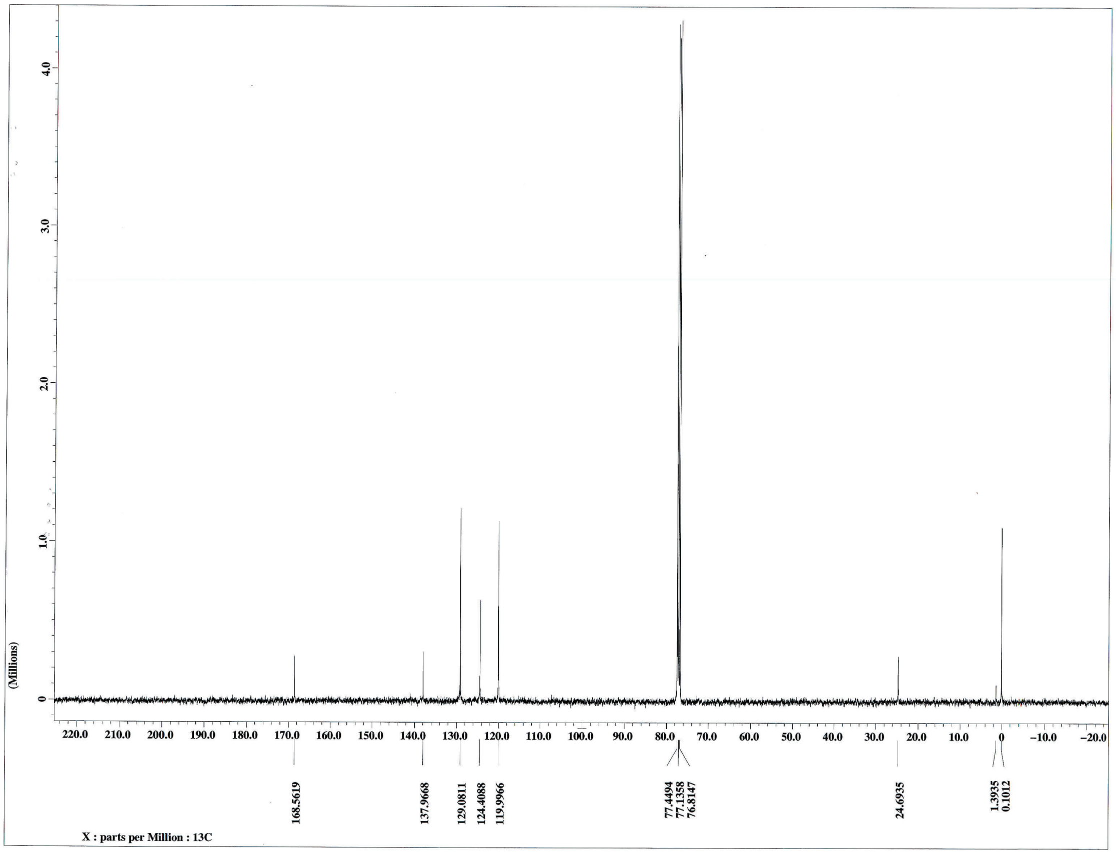
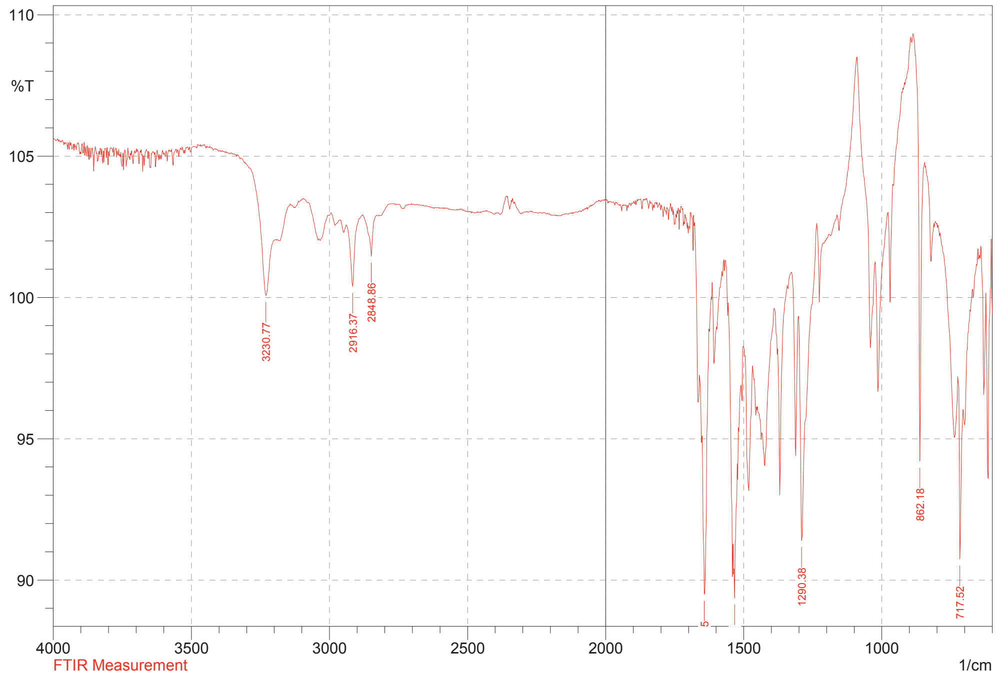


Figure 5

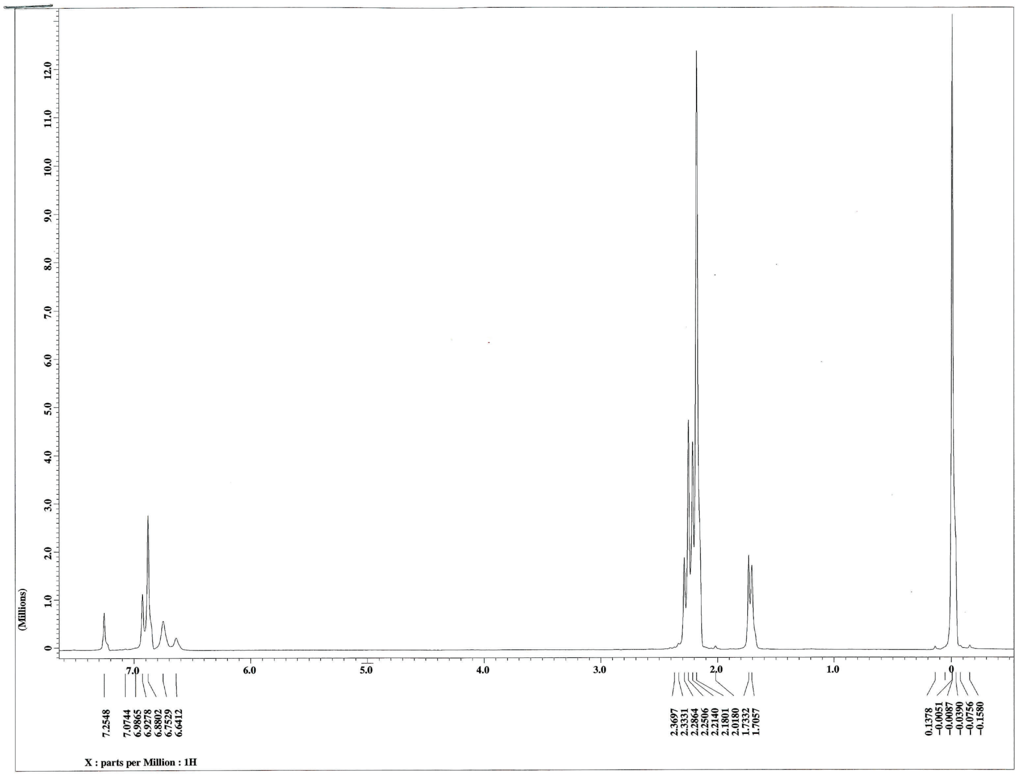


| No. | Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|---|---|---|---|---|---|---|---|
| 1 | 717.52 | 90.743 | 5.986 | 725.23 | 705.95 | 0.477 | 0.188 |
| 2 | 862.18 | 94.21 | 12.43 | 887.26 | 844.82 | -0.797 | 0.455 |
| 3 | 1290.38 | 91.403 | 8.511 | 1301.95 | 1236.37 | 0.738 | 1.01 |
| 4 | 1533.41 | 89.361 | 1.66 | 1535.34 | 1523.76 | 0.44 | 0.034 |
| 5 | 1643.35 | 89.496 | 6.772 | 1651.07 | 1625.99 | 0.761 | 0.427 |
| 6 | 2848.86 | 101.469 | 1.45 | 2879.72 | 2829.57 | -0.525 | 0.102 |
| 7 | 2916.37 | 100.393 | 2.313 | 2939.52 | 2879.72 | -0.538 | 0.165 |
| 8 | 3230.77 | 100.072 | 2.927 | 3288.63 | 3196.05 | -0.921 | 0.388 |

IR of N-(2,4,6-trimethylphenyl)-acetamide

Figure 6

a) $^1H$ NMR of N-(2,4,6-trimethylphenyl)-acetamide



b) $^{13}$C NMR of N-(2,4,6-trimethylphenyl)-acetamide

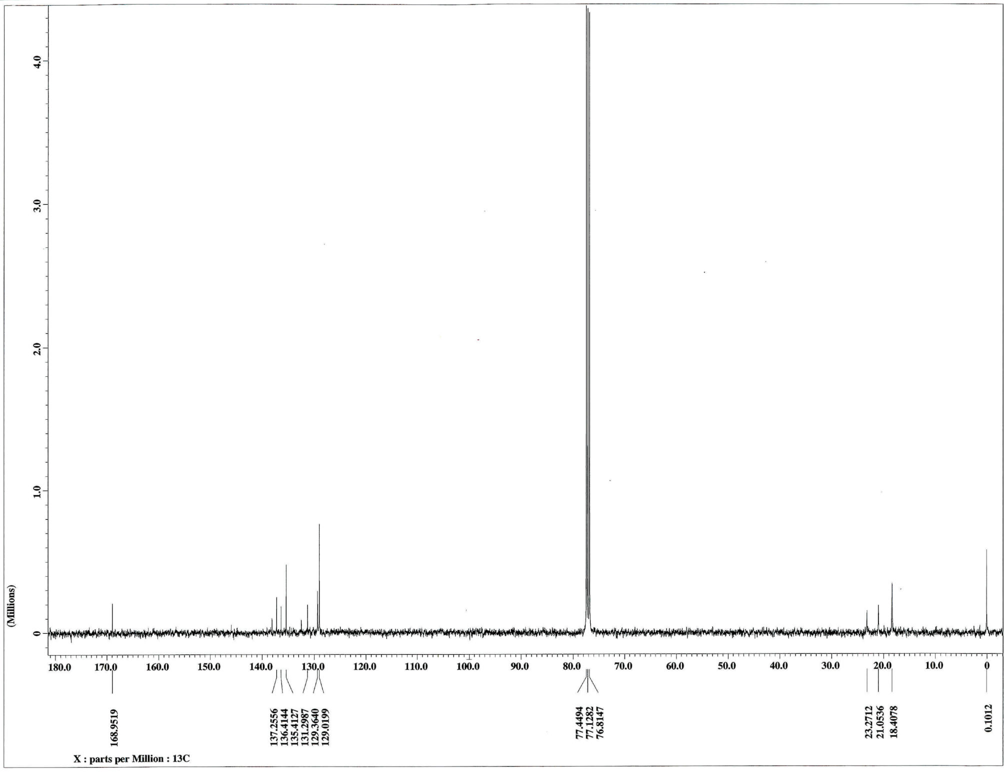
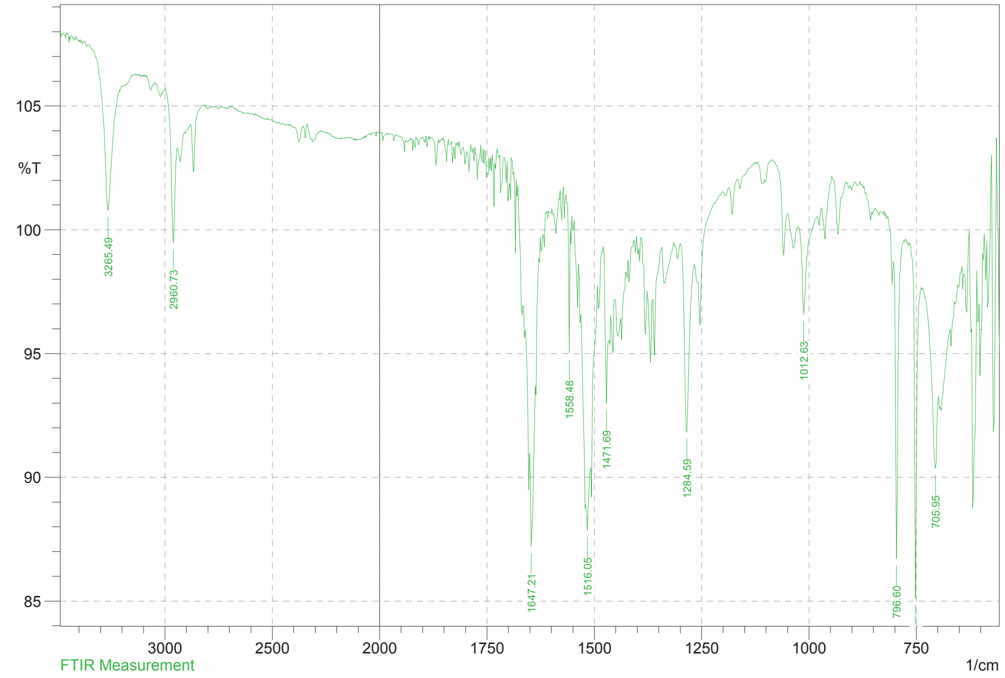


Figure 7

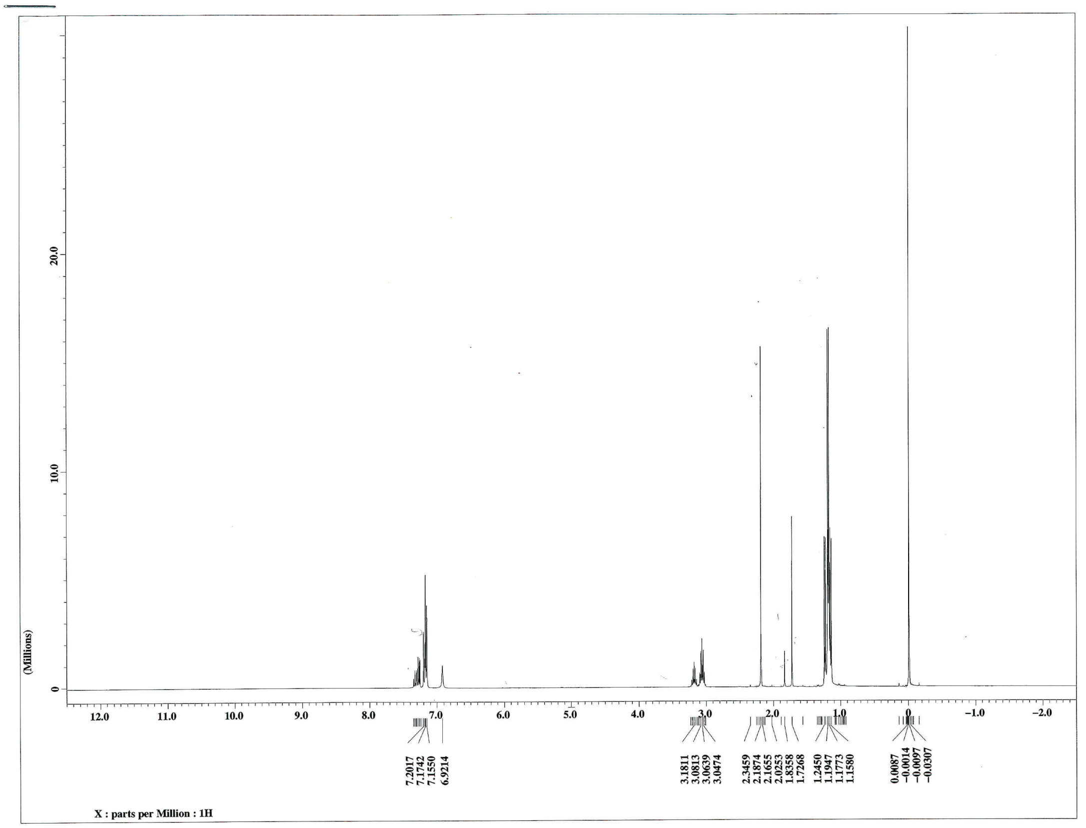


| | Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|---|---|---|---|---|---|---|---|
| 1 | 705.95 | 90.37 | 3.83 | 734.88 | 698.23 | 0.92 | 0.18 |
| 2 | 752.24 | 85.13 | 13.44 | 765.74 | 738.74 | 0.52 | 0.35 |
| 3 | 796.6 | 86.73 | 12.25 | 804.32 | 779.24 | 0.43 | 0.34 |
| 4 | 1012.63 | 96.58 | 3.67 | 1026.13 | 979.84 | 0.14 | 0.2 |
| 5 | 1284.59 | 91.83 | 7.23 | 1300.02 | 1267.23 | 0.55 | 0.41 |
| 6 | 1471.69 | 93 | 4.16 | 1479.4 | 1465.9 | 0.25 | 0.09 |
| 7 | 1516.05 | 87.86 | 1.54 | 1519.91 | 1508.33 | 0.58 | 0.03 |
| 8 | 1558.48 | 95.02 | 5.31 | 1566.2 | 1556.55 | 0.02 | 0.05 |
| 9 | 1647.21 | 87.2 | 4.53 | 1651.07 | 1637.56 | 0.63 | 0.16 |
| 10 | 2960.73 | 99.48 | 4.57 | 2999.31 | 2943.37 | -0.72 | 0.34 |
| 11 | 3265.49 | 100.79 | 5.55 | 3340.71 | 3211.48 | -2.53 | 0.99 |

IR of N-[2,6-bis(1-methylethyl)phenyl]-acetamide

Figure 8

a) $^1$H NMR of N-[2,6-bis(1-methylethyl)phenyl]-acetamide



b) $^{13}$C NMR of N-[2,6-bis(1-methylethyl)phenyl]-acetamide

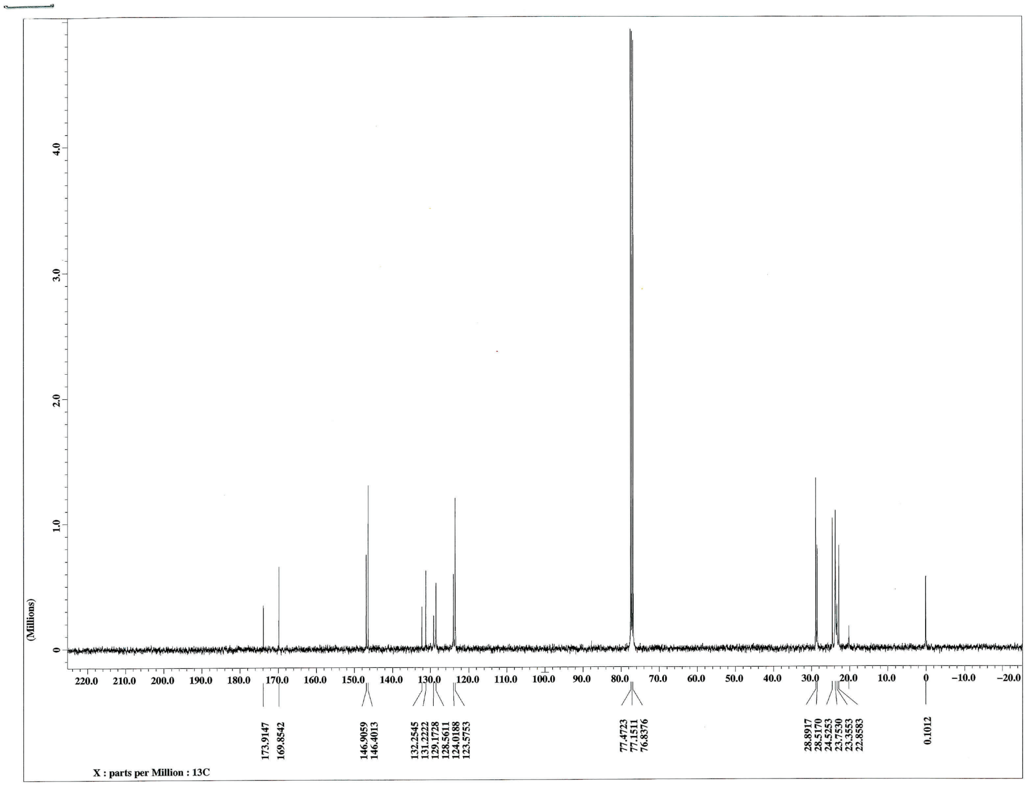
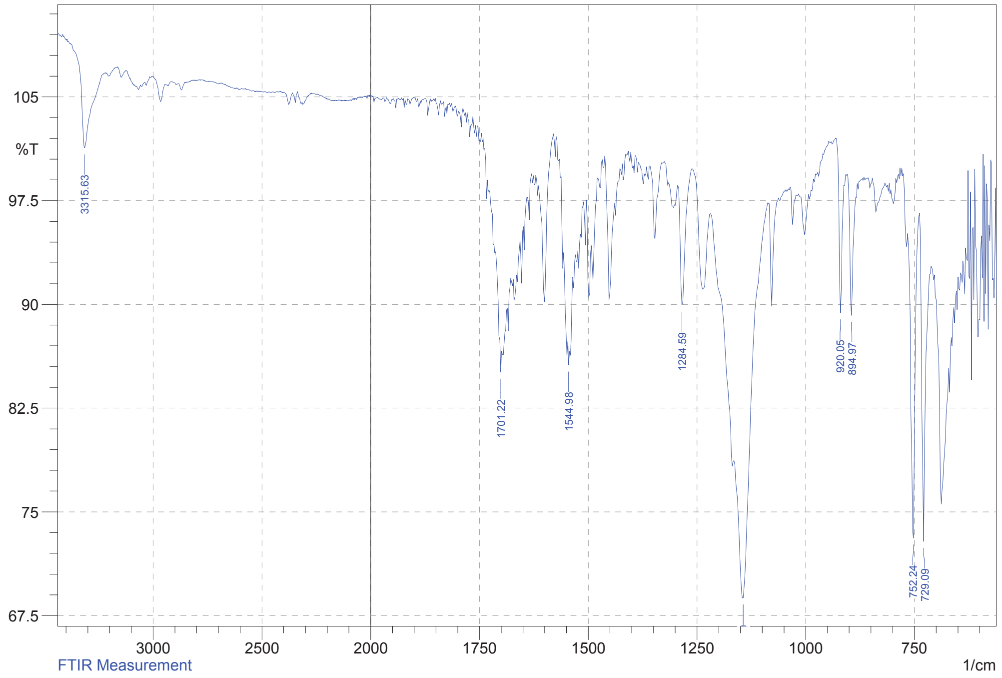


Figure 9

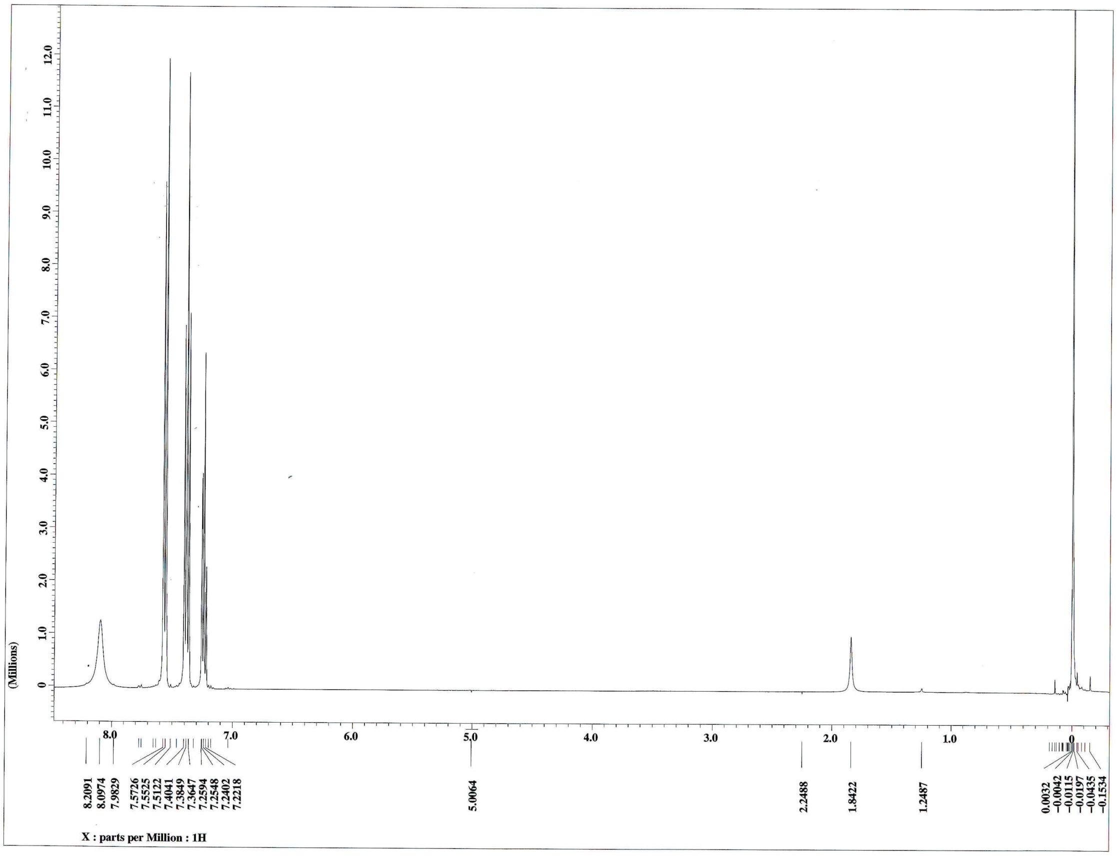


| | Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|---|---|---|---|---|---|---|---|
| 1 | 729.09 | 72.86 | 22.35 | 738.74 | 711.73 | 1.7 | 1.06 |
| 2 | 752.24 | 73.11 | 22.74 | 765.74 | 738.74 | 1.65 | 1.15 |
| 3 | 894.97 | 89.21 | 9.36 | 904.61 | 885.33 | 0.46 | 0.33 |
| 4 | 920.05 | 89.39 | 10.57 | 931.62 | 912.33 | 0.3 | 0.32 |
| 5 | 1143.79 | 68.77 | 15.06 | 1165 | 1087.85 | 6.48 | 2.01 |
| 6 | 1284.59 | 89.95 | 9.02 | 1294.24 | 1261.45 | 0.62 | 0.51 |
| 7 | 1544.98 | 85.61 | 1.34 | 1546.91 | 1543.05 | 0.25 | 0.01 |
| 8 | 1701.22 | 85.09 | 2.54 | 1712.79 | 1699.29 | 0.67 | 0.06 |
| 9 | 3315.63 | 101.33 | 6.02 | 3363.86 | 3248.13 | -2.4 | 1.07 |

IR of 2,2,2-trifluoro-N-phenyl-acetamide

Figure 10

a) $^1$H NMR of 2,2,2-trifluoro-N-phenyl-acetamide



b) $^{13}$C NMR of 2,2,2-trifluoro-N-phenyl-acetamide

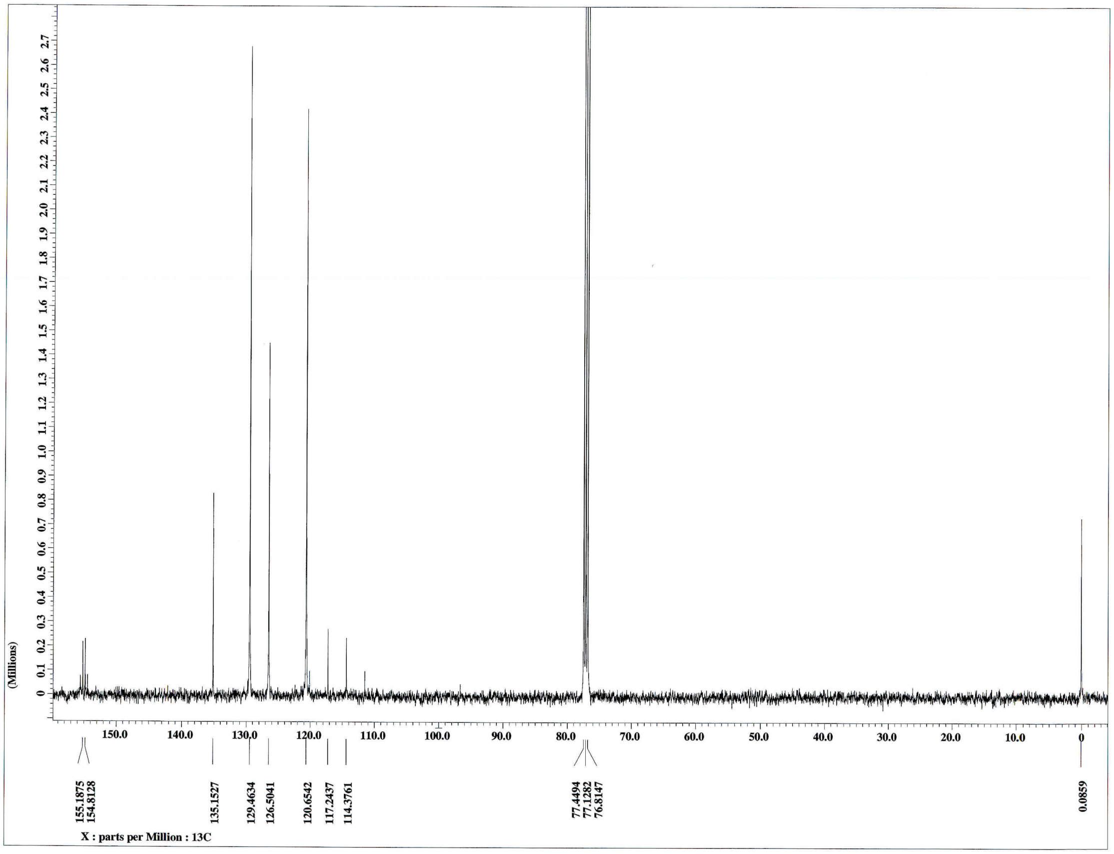
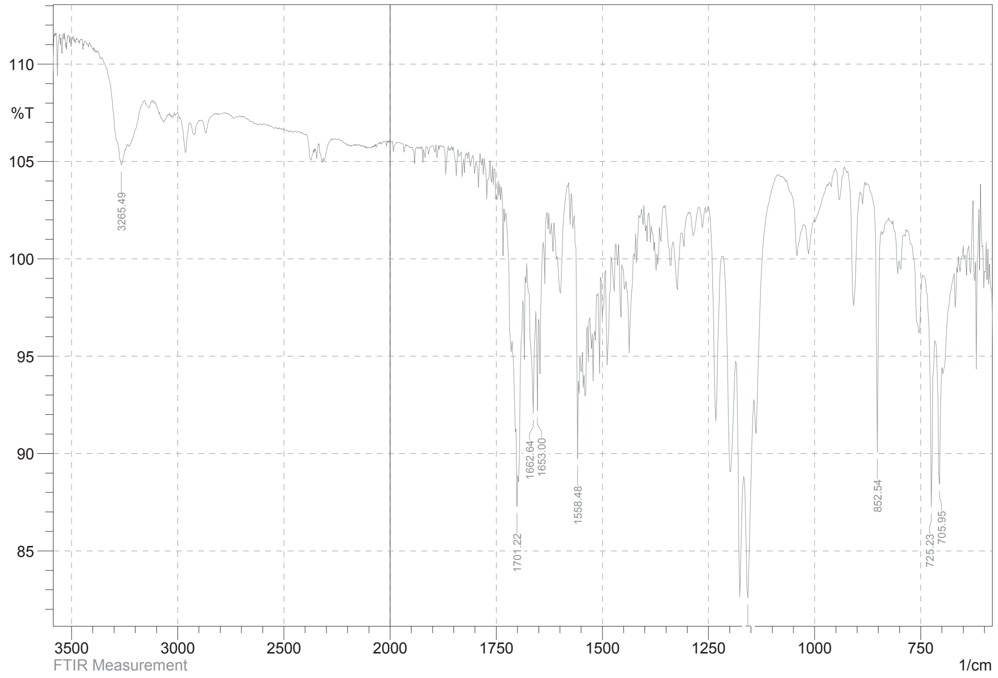


Figure 11

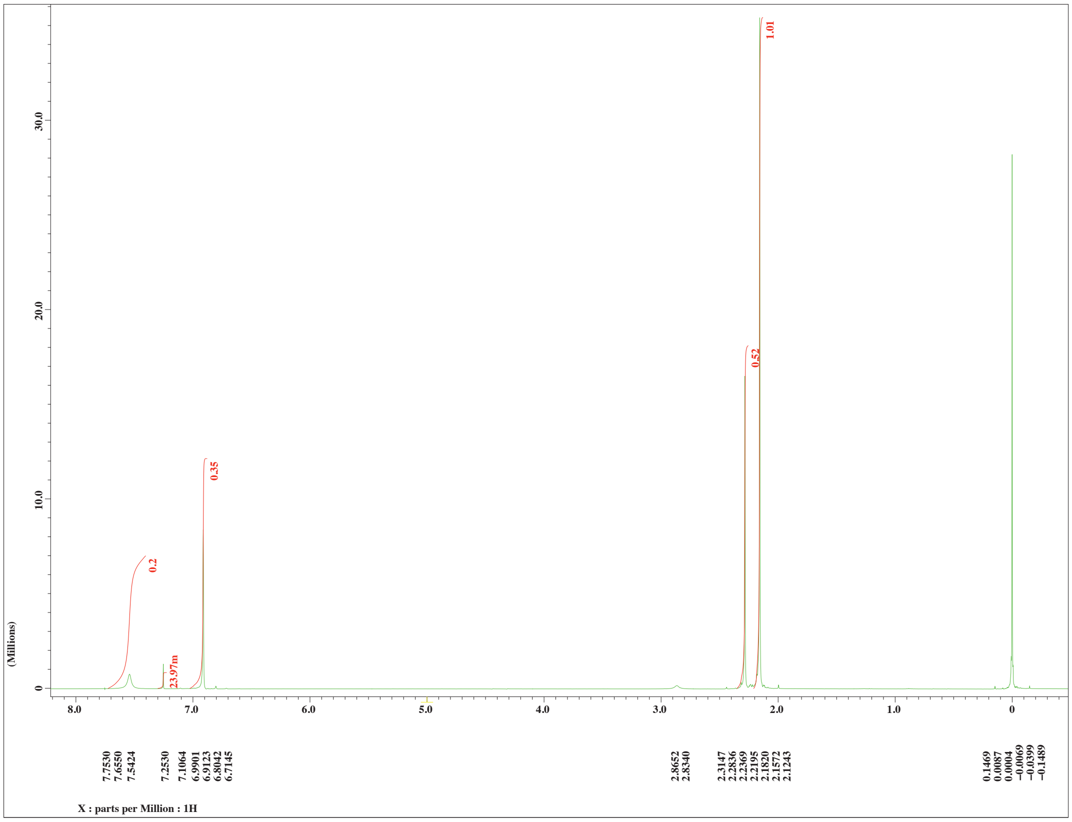


| | Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|---|---|---|---|---|---|---|---|
| 1 | 705.95 | 88.44 | 6.43 | 717.52 | 700.16 | 0.56 | 0.18 |
| 2 | 725.23 | 87.25 | 9.44 | 746.45 | 717.52 | 0.55 | 0.23 |
| 3 | 852.54 | 90.05 | 12.05 | 877.61 | 842.89 | -0.13 | 0.26 |
| 4 | 1157.29 | 82.58 | 7.89 | 1166.93 | 1143.79 | 1.4 | 0.43 |
| 5 | 1558.48 | 89.73 | 5.69 | 1566.2 | 1556.55 | 0.13 | 0.04 |
| 6 | 1653 | 92.2 | 4.84 | 1656.85 | 1651.07 | 0.13 | 0.06 |
| 7 | 1662.64 | 92.07 | 5.91 | 1678.07 | 1656.85 | 0.37 | 0.23 |
| 8 | 1701.22 | 87.29 | 2.78 | 1703.14 | 1699.29 | 0.2 | 0.03 |
| 9 | 3265.49 | 104.82 | 1 | 3286.7 | 3248.13 | -0.87 | 0.08 |

IR of 2,2,2-trifluoro-N-(2,4,6-trimethylphenyl)-acetamide

Figure 12

a) $^1$H NMR of 2,2,2-trifluoro-N-(2,4,6-trimethylphenyl)-acetamide



### b) $^{13}$C NMR of 2,2,2-trifluoro-N-(2,4,6-trimethylphenyl)-acetamide

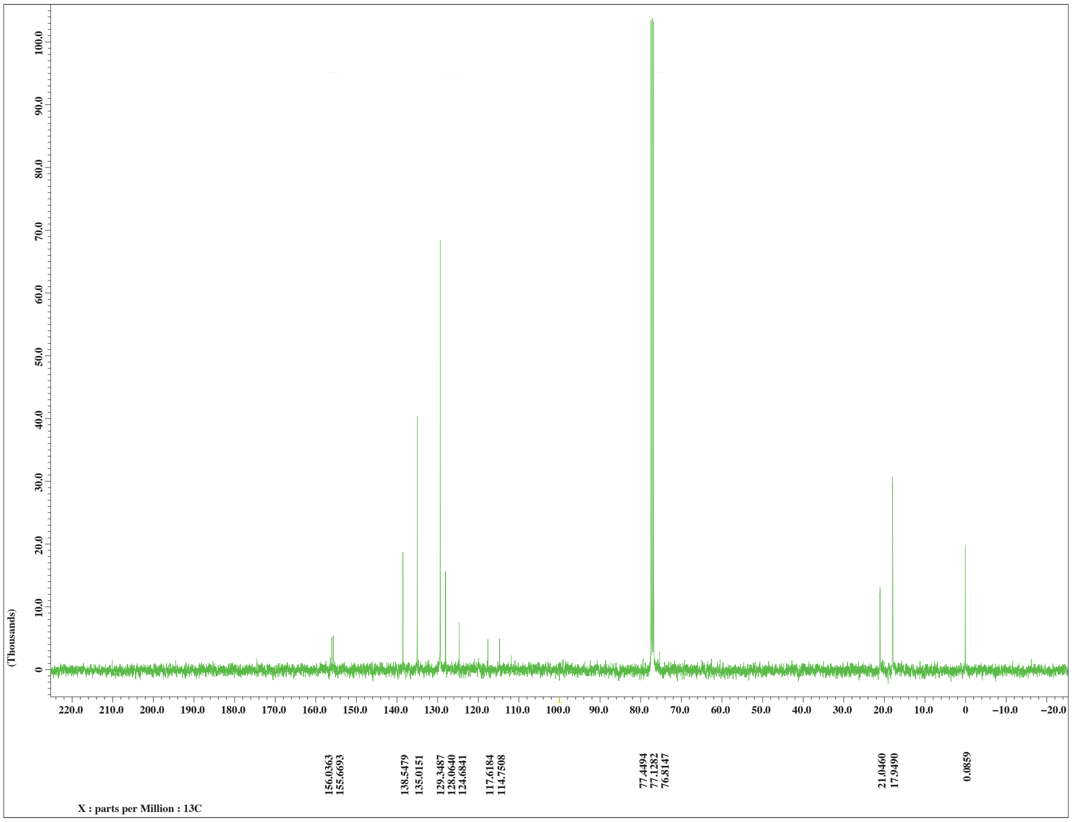
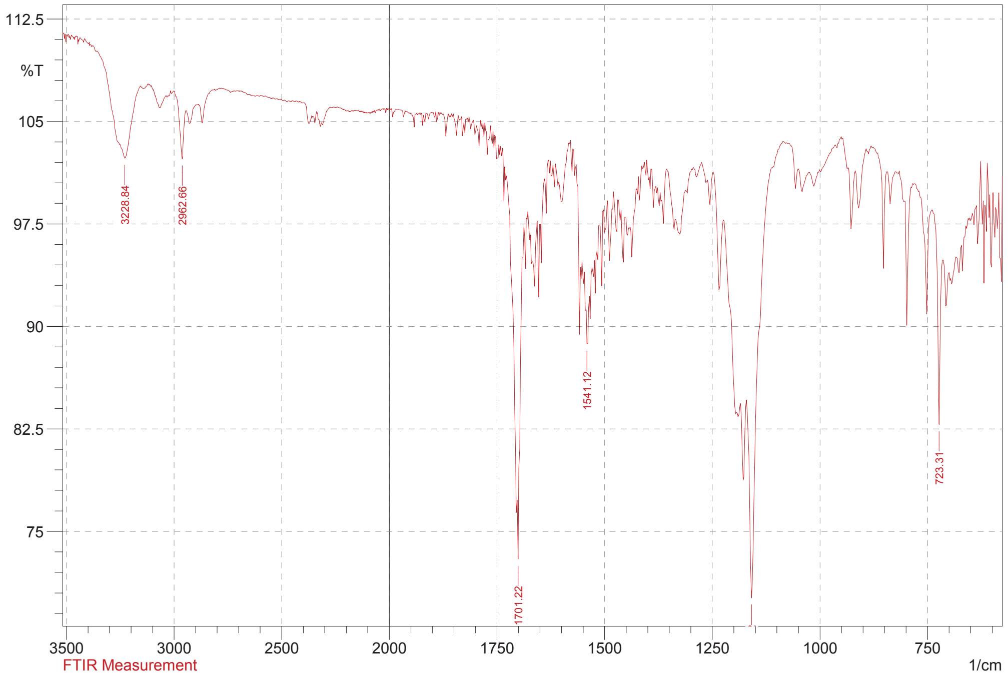


Figure 13

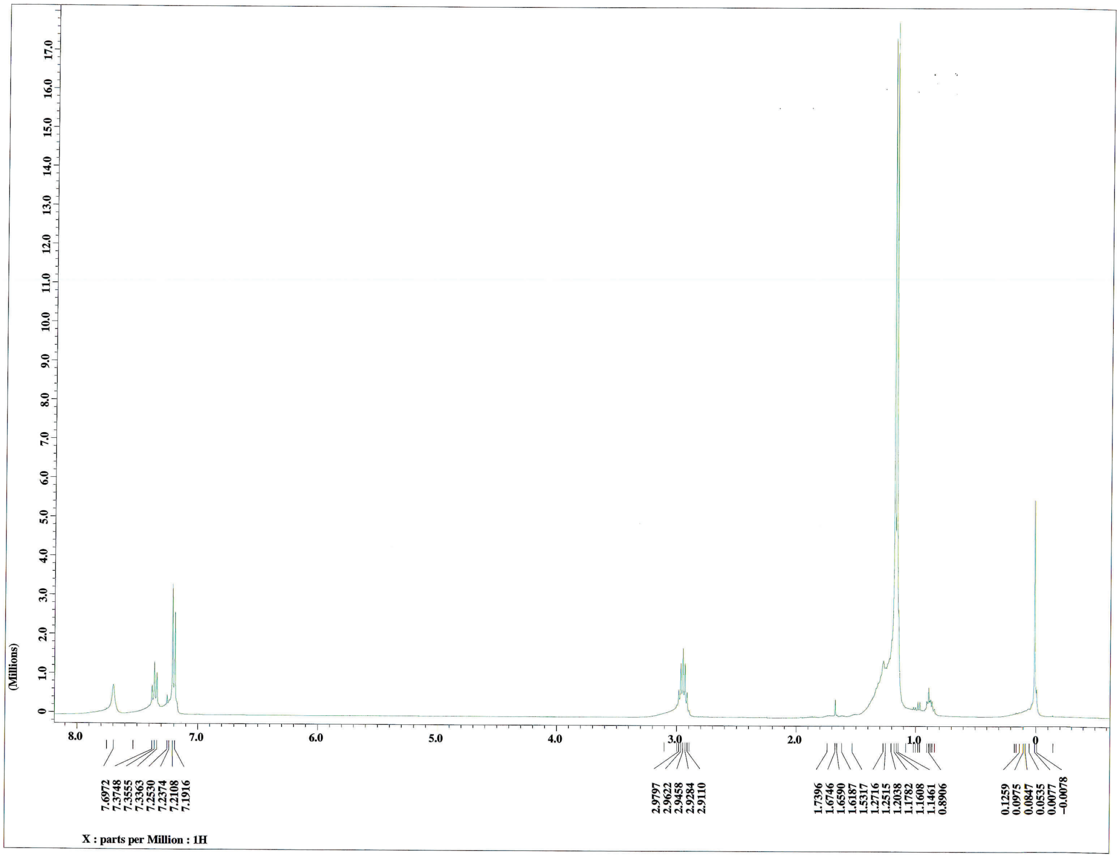


| | Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|---|---|---|---|---|---|---|---|
| 1 | 723.31 | 82.82 | 13.35 | 740.67 | 713.66 | 0.76 | 0.37 |
| 2 | 1159.22 | 70.13 | 17.9 | 1170.79 | 1112.93 | 3.24 | 1.35 |
| 3 | 1541.12 | 88.71 | 2.75 | 1543.05 | 1535.34 | 0.35 | 0.06 |
| 4 | 1701.22 | 72.98 | 6.81 | 1703.14 | 1687.71 | 1.02 | 0.07 |
| 5 | 2962.66 | 102.25 | 3.94 | 2989.66 | 2945.3 | -0.88 | 0.3 |
| 6 | 3228.84 | 102.31 | 2.06 | 3251.98 | 3157.47 | -1.85 | 0.33 |

IR of 2,2,2-trifluoro-N-[2,6-bis(1-methylethyl)phenyl]-acetamide

Figure 14

a) $^1H$ NMR of 2,2,2-trifluoro-N-[2,6-bis(1-methylethyl)phenyl]-acetamide



b) $^{13}$C NMR of 2,2,2-trifluoro-N-[2,6-bis(1-methylethyl)phenyl]-acetamide

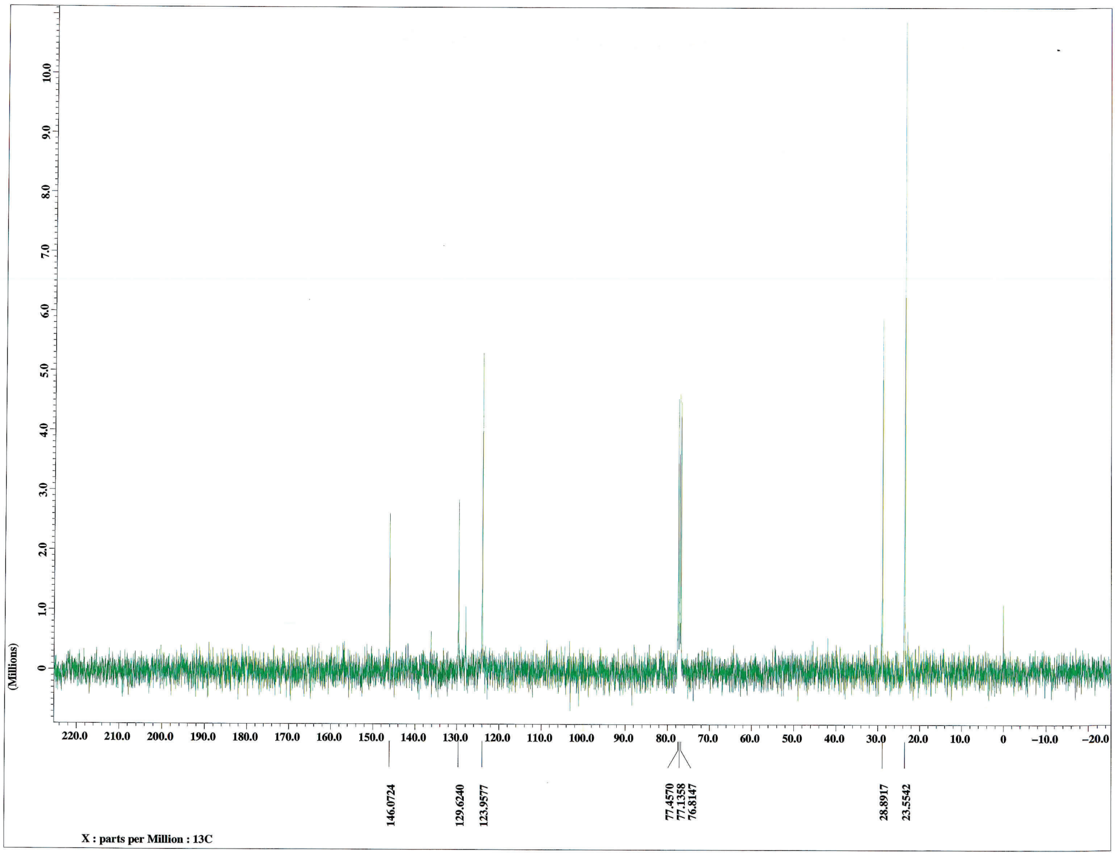
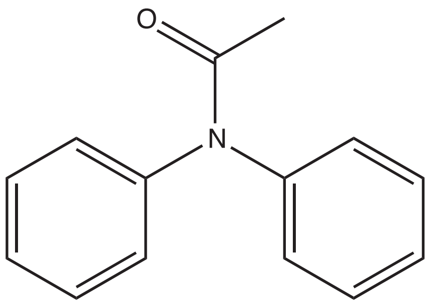
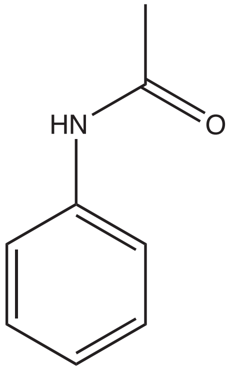


Figure 15

Imide vs. amide



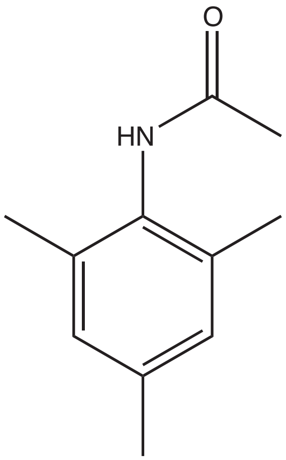
N,N-diphenyl-acetamide



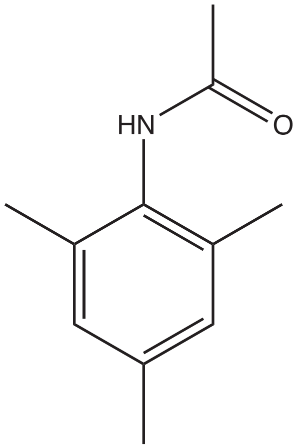
N-phenyl-acetamide

Figure 16

*E*- and *Z*-form of N-(2,4,6-trimethylphenyl)-acetamide



*E*-form



*Z*-form