An Efficient Method to Prepare Aryl Acetates by the Carbonylation of Aryl Methyl Ethers or Phenols

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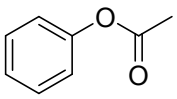
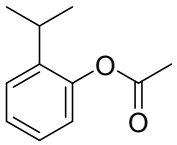
1. General remarks

All the chemicals were commercially available and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Mass spectroscopy (MS) measurements were performed on a GC-MS 2030 from Shimadzu. A Shimadzu 2014C GC system was used to monitor the reaction conversion.

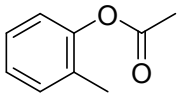
2. NMR and MS characterizations of the products



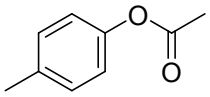
Phenyl acetate: ^{1}H NMR (400 MHZ, DMSO) δ 7.42 (t, 2H), 7.23 (t, 1H), 7.14 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 169.16, 150.35, 129.43, 125.72, 121.80, 20.9. MS: calculated for $C_8H_8O_2$ (M^+) 136.0; found 136.0.



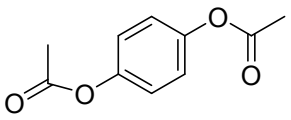
2-isopropylphenyl acetate： ^{1}H NMR (400 MHZ, DMSO) δ 7.37 (m, 1H), 7.23 (m, 1H), 7.21 (m, 1H), 7.03 (m, 1H), 2.98 (m, 1H), 2.30 (s, 3H), 1.15 (m, 6H). ^{13}C NMR (100 MHZ, DMSO) δ 169.42, 147.79, 139.82, 126.62, 126.58, 126.18, 122.32, 26.72, 22.82, 20.62. MS: calculated for $C_{11}H_{14}O_2$ (M^+) 178.0; found 178.0.



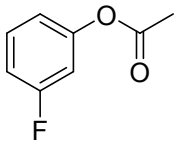
o-tolyl acetate: ^{1}H NMR (400 MHZ, DMSO) δ 7.27 (m, 1H), 7.23 (m, 1H), 7.16 (m, 1H), 7.06 (m, 1H), 2.29 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 168.82, 149.14, 130.86, 129.77, 126.88, 125.78, 122.04, 20.44, 15.61. MS: calculated for $C_{11}H_{14}O_2$ (M^+) 150.0; found 150.0.



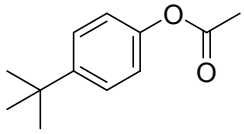
p-tolyl acetate: ^{1}H NMR (400 MHZ, DMSO) δ 7.21 (d, 2H), 6.99 (d, 2H), 2.29 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 169.24, 148.24, 134.84, 129.76, 121.45, 20.77, 20.32. MS: calculated for $C_{11}H_{14}O_2$ (M^+) 150.0; found 150.0.



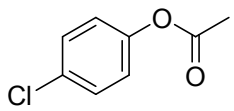
1,4-phenylene diacetate: ^{1}H NMR (400 MHZ, DMSO) δ 7.17 (s, 4H), 2.27 (s, 6H). ^{13}C NMR (100 MHZ, DMSO) δ 168.95, 147.83, 122.71, 20.75. MS: calculated for $C_{10}H_{10}O_4$ (M^+) 194.0; found 194.0.



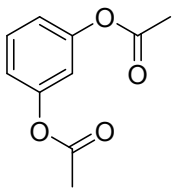
3-fluorophenyl acetate: ^{1}H NMR (400 MHZ, DMSO) δ 7.45 (m, 1H), 7.14 (m, 1H), 7.09 (m, 1H), 7.02 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 168.86, 163.41, 160.98, 151.54, 151.43, 130.71, 130.62, 118.13, 118.10, 112.79, 112.58, 109.94, 109.69, 20.52. MS: calculated for $C_8H_7FO_2$ (M^+) 154.0; found 154.0.



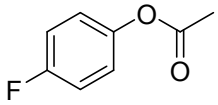
4-(tert-butyl)phenyl acetate: ^{1}H NMR (400 MHz, DMSO) δ 7.39 (d, 2H), 7.02 (d, 2H), 2.24 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (100 MHZ, DMSO) δ 169.65, 148.70, 148.42, 126.54, 121.60, 34.59, 31.60, 21.22. MS: calculated for $C_{12}H_{16}O_2$ (M^+) 192.1; found 192.1.



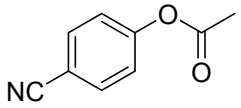
4-chlorophenyl acetate: ^{1}H NMR (400 MHz, DMSO) δ 7.46 (m, 2H), 7.18 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 169.02, 149.25, 129.88, 129.34, 123.75, 20.76. MS: calculated for $C_8H_7ClO_2$ (M^+) 170.0; found 170.0.



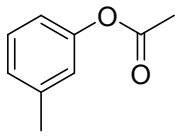
1,3-phenylene diacetate: ^{1}H NMR (400 MHz, DMSO) δ 7.44 (t, 1H), 7.05 (M, 2H), 7.01 (t, 1H), 2.25 (s, 6H). ^{13}C NMR (100 MHZ, DMSO) δ 169.15, 154.44, 134.48, 123.78, 118.84, 109.48, 21.33. MS: calculated for $C_{10}H_{10}O_4$ (M^+) 194.0; found 194.0.



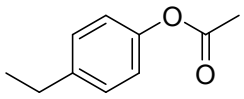
4-fluorophenyl acetate: ^{1}H NMR (400 MHz, DMSO) δ 7.24 (m, 2H), 7.20 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 169.73, 161.33, 158.93, 147.16, 124.09, 124.01, 116.58, 116.35, 21.08. MS: calculated for $C_8H_7FO_2$ (M^+) 154.0; found 154.0.



4-cyanophenyl acetate: ^{1}H NMR (400 MHz, DMSO) δ 7.94 (m, 2H), 7.38 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 169.15, 154.44, 134.48, 123.78, 118.84, 109.20, 21.01. MS: calculated for $C_9H_7NO_2$ (M^+) 161.0; found 161.1.



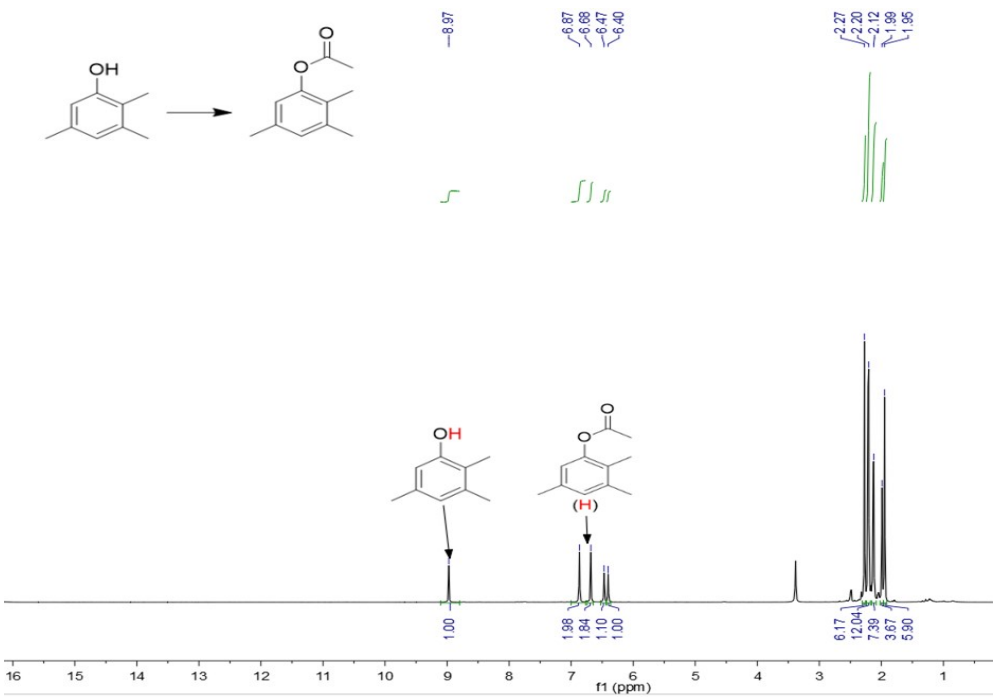
m-tolyl acetate: ^{1}H NMR (400 MHz, DMSO) δ 7.27 (t, 1H), 7.06 (d, 1H), 6.93 (m, 1H), 6.90 (m, 1H), 2.29 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 169.60, 151.00, 139.63, 129.59, 126.82, 122.71, 119.24, 21.18. MS: calculated for $C_{11}H_{14}O_2$ (M^+) 150.0; found 150.0.



4-ethylphenyl acetate: ^{1}H NMR (400 MHz, DMSO) δ 7.24 (d, 2H), 7.03 (d, 2H), 2.61(m, 2H), 2.25 (s, 3H), 1.17 (t, 3H). ^{13}C NMR (100 MHZ, DMSO) δ 169.75, 148.94, 141.64, 129.08, 122.00, 28.02, 21.27, 16.09. MS: calculated for $C_{10}H_{12}O_2$ (M^+) 164.0; found 164.0.

3. Quantity determination of the yield by 1H NMR

（1）



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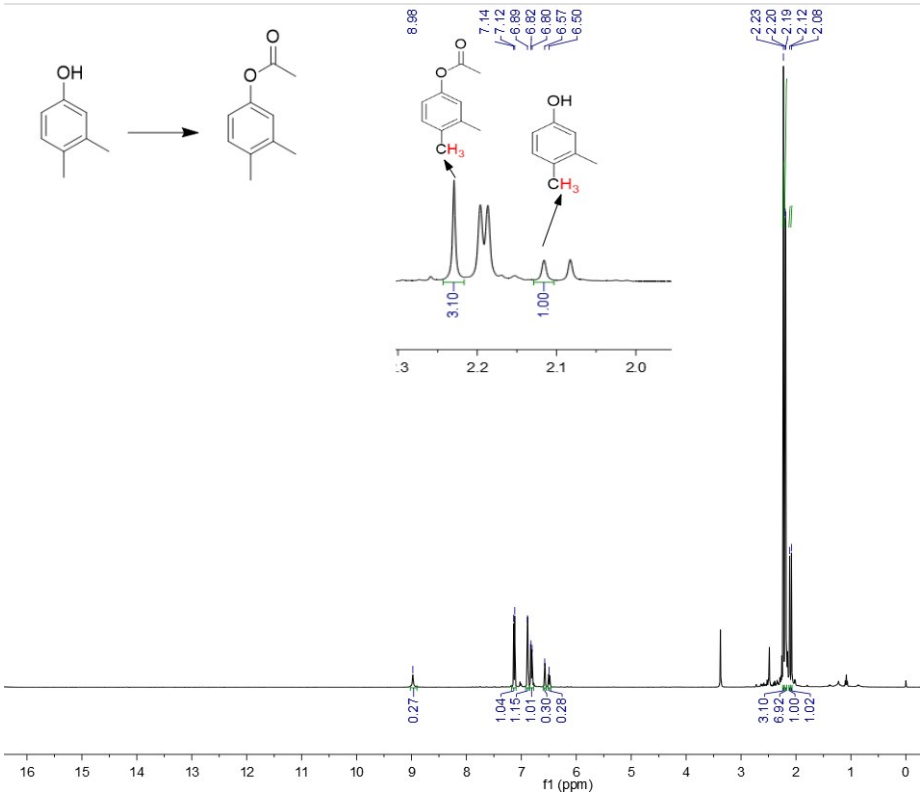

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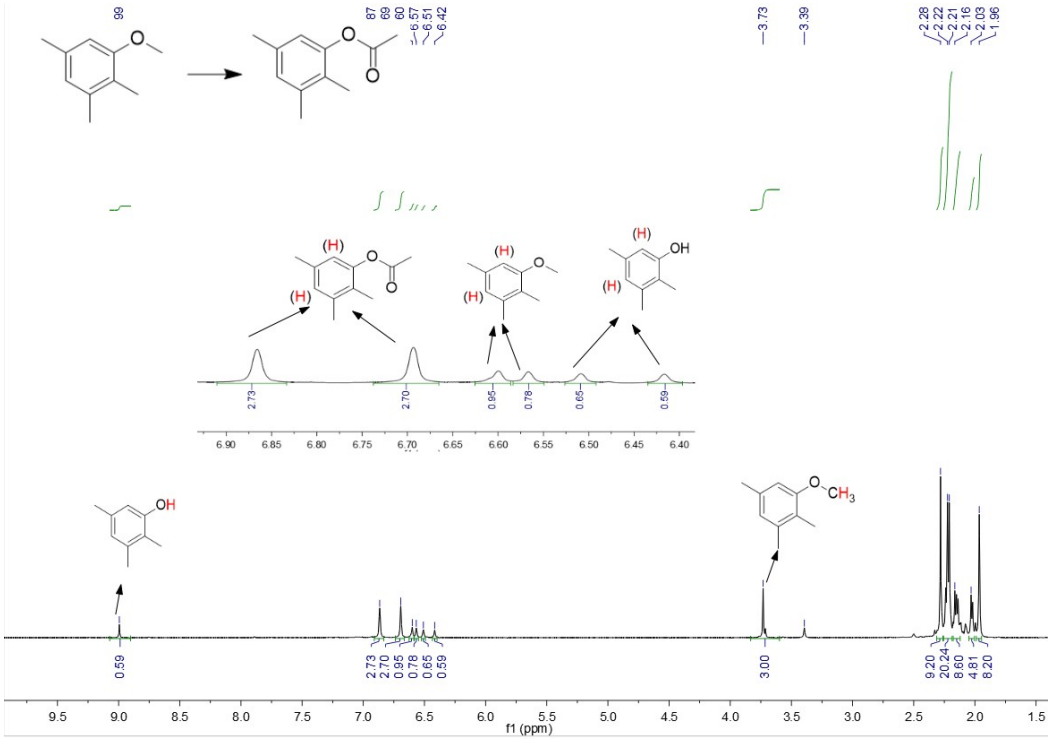

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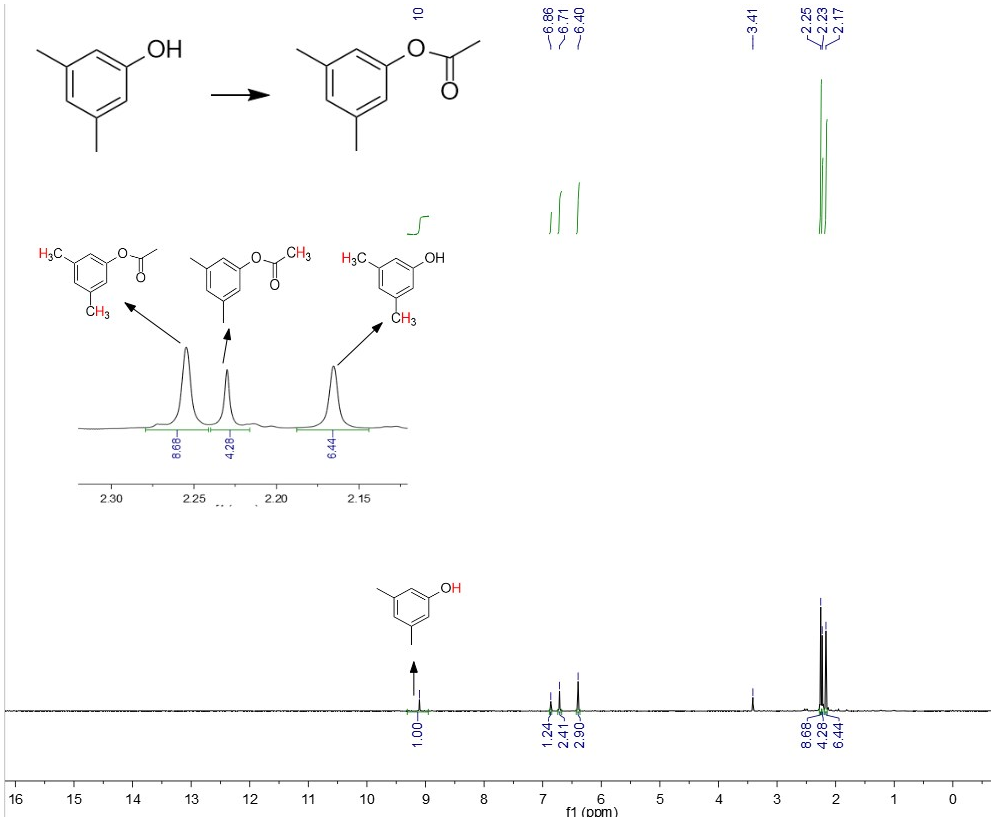

4. Original MS spectra

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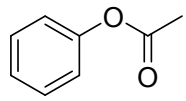

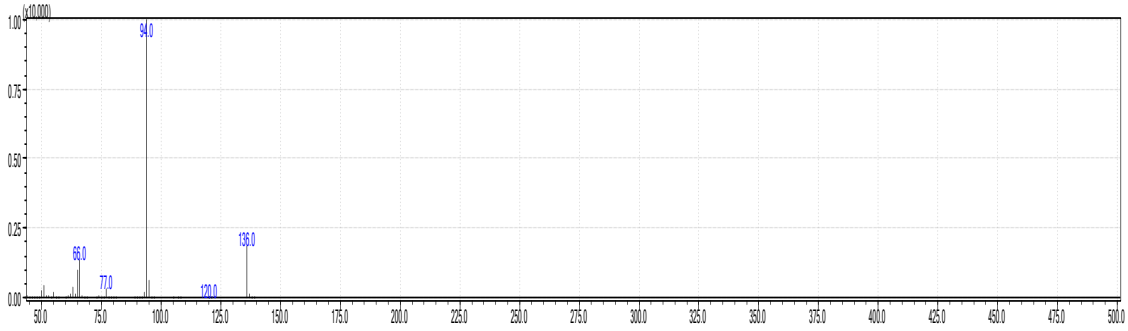

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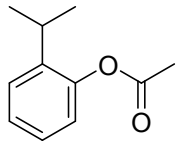

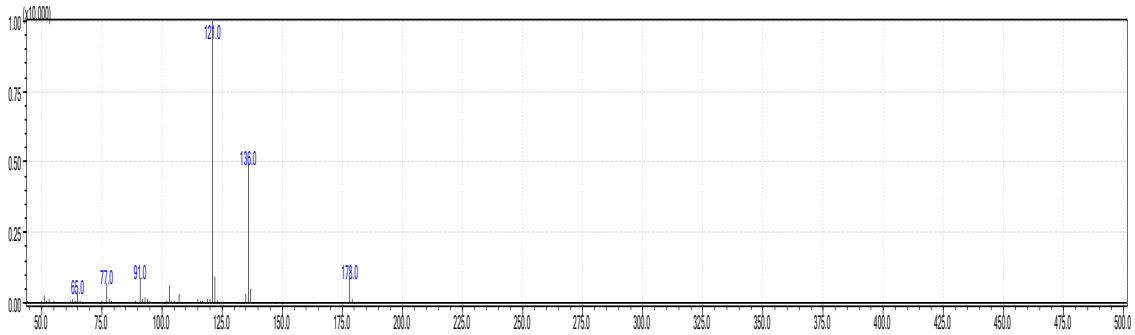

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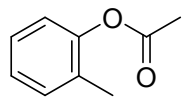

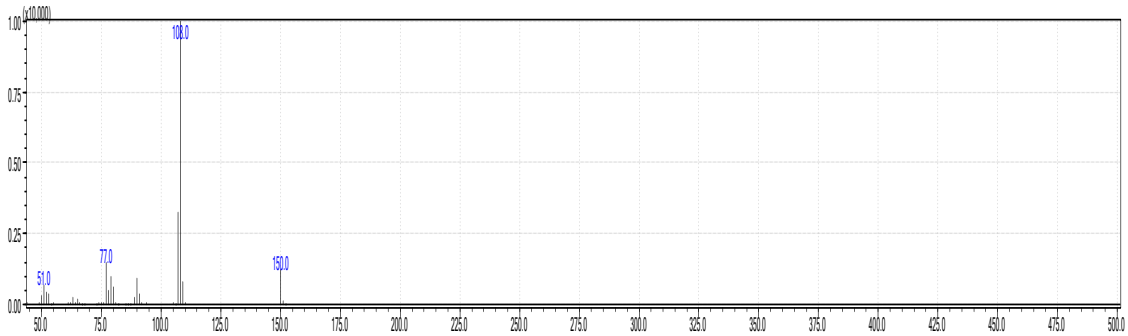

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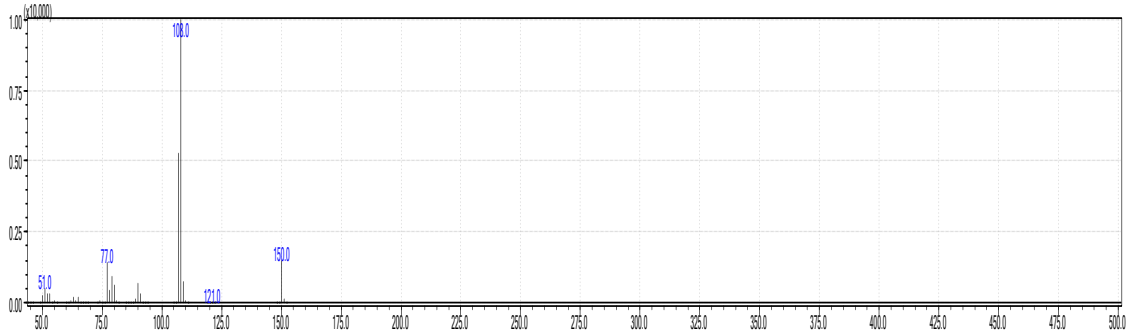
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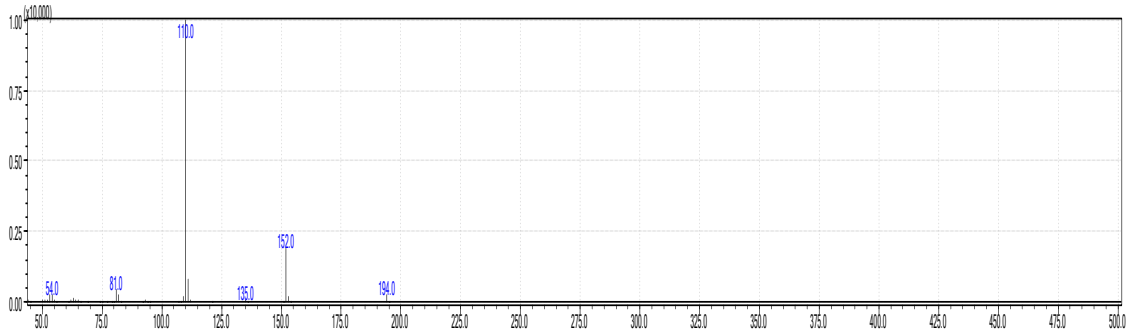
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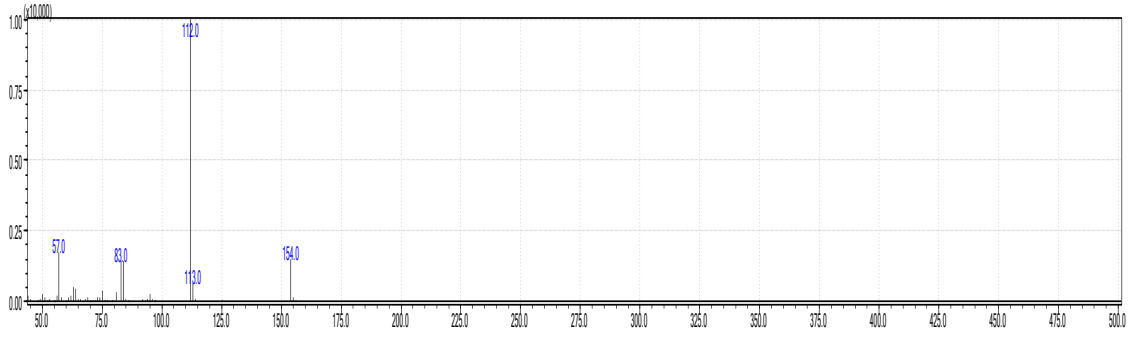
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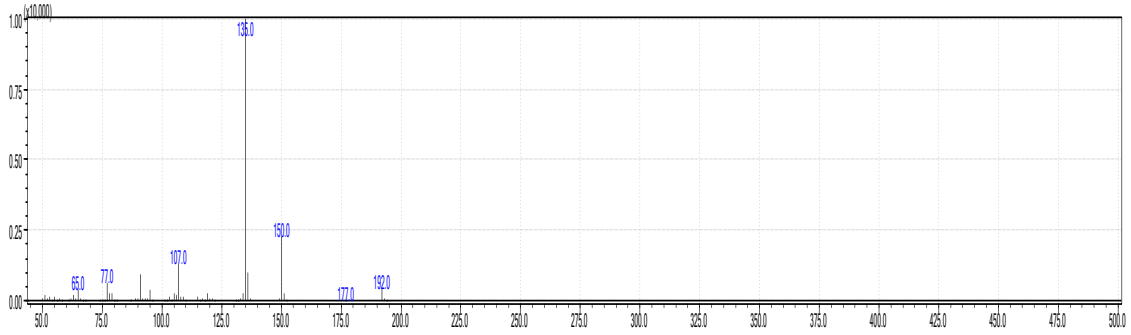
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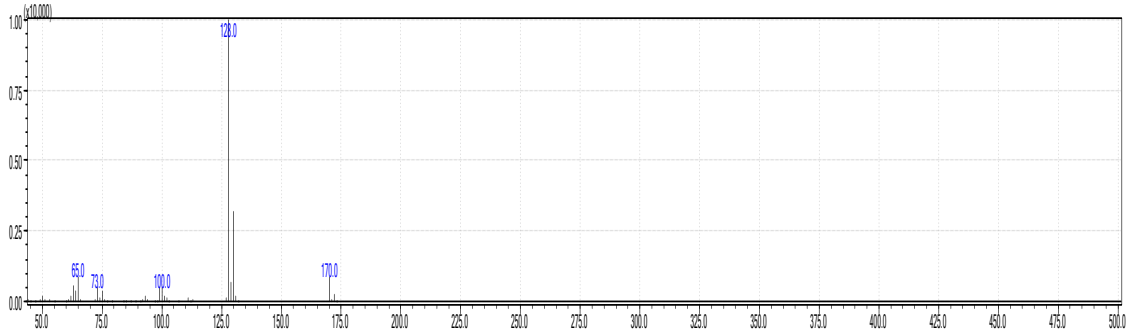
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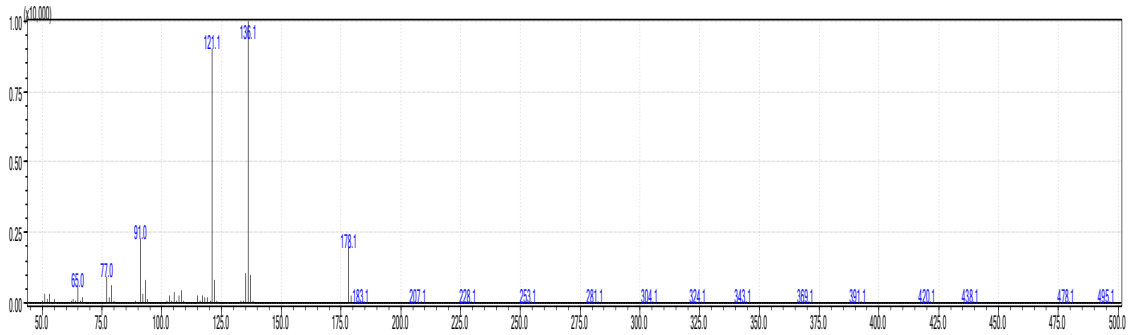
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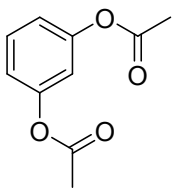

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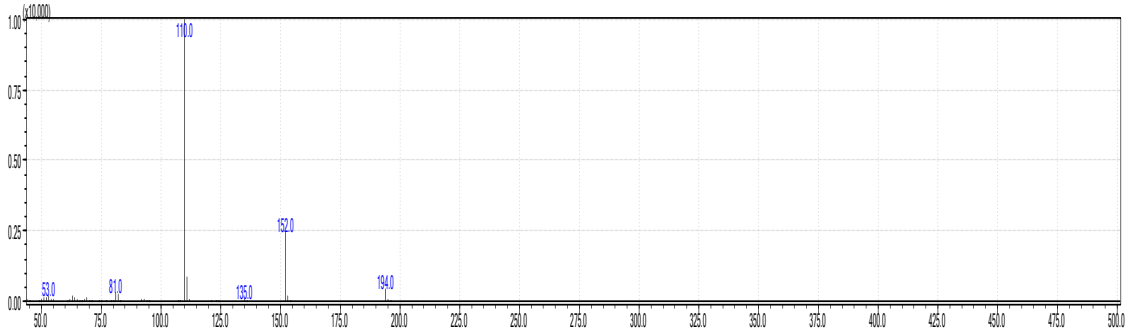
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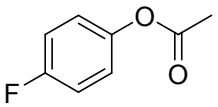

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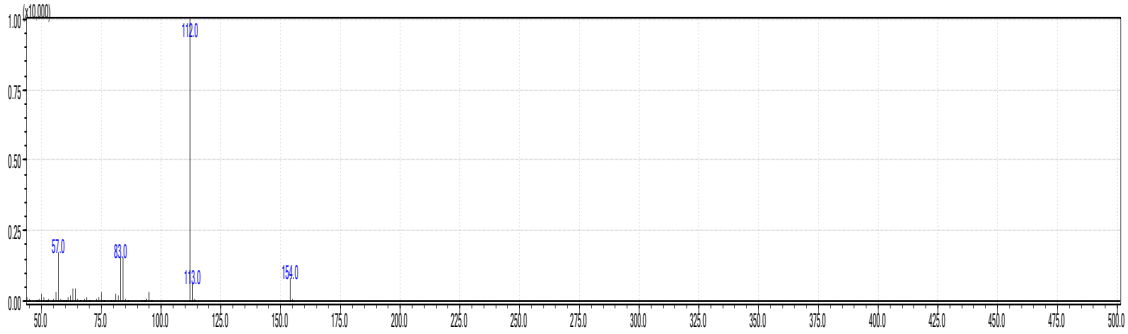
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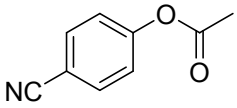

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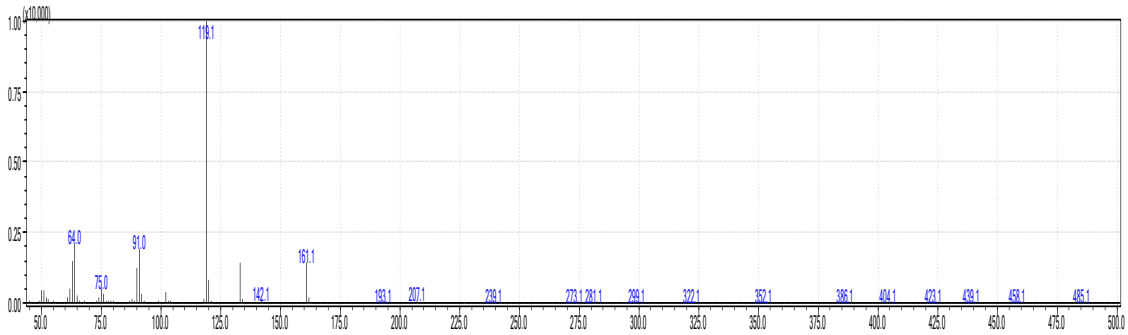
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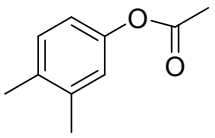

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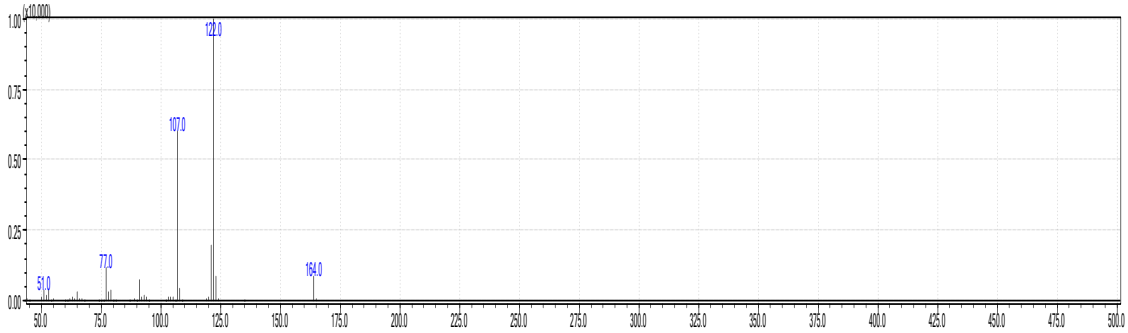
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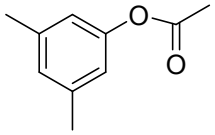

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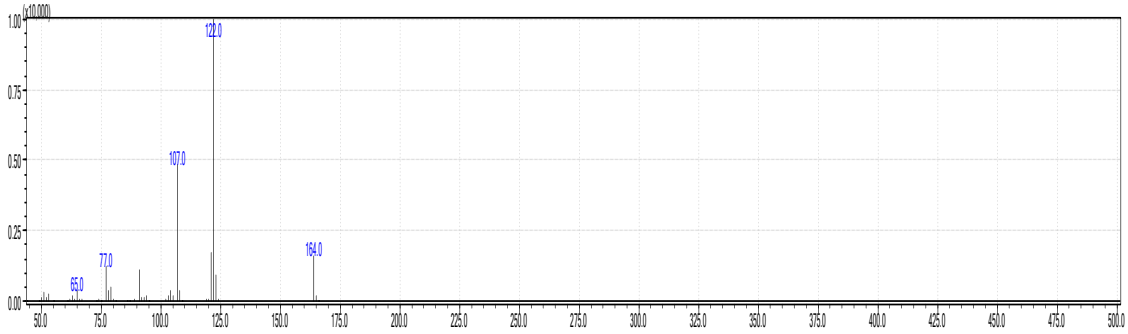
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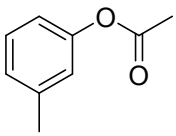

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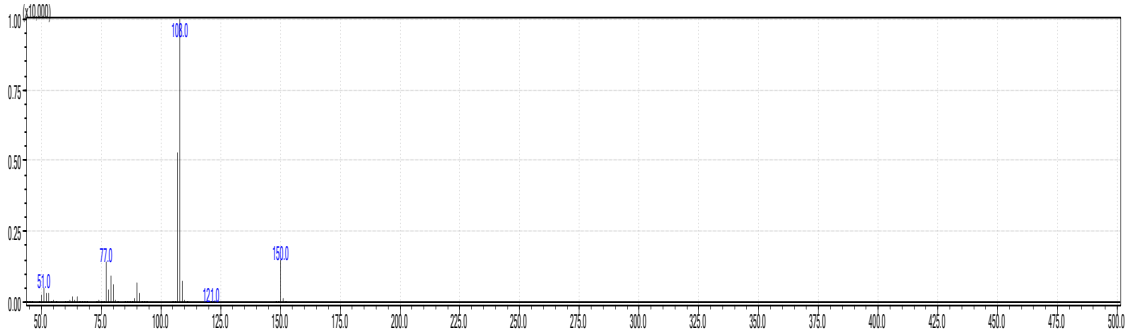
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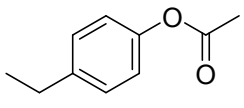
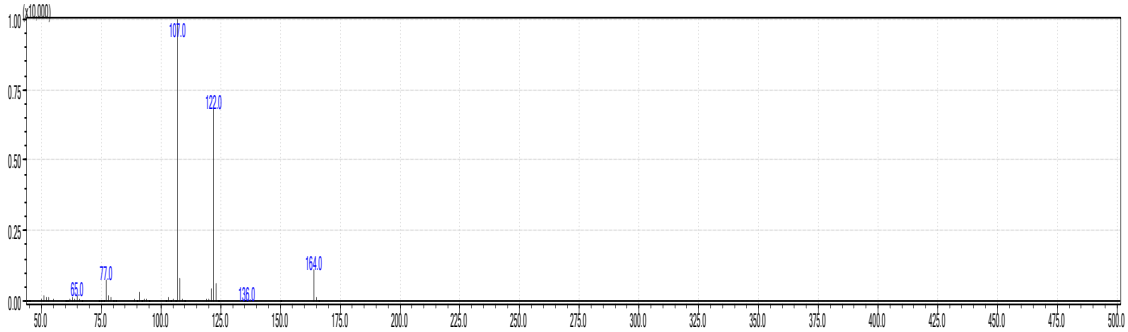
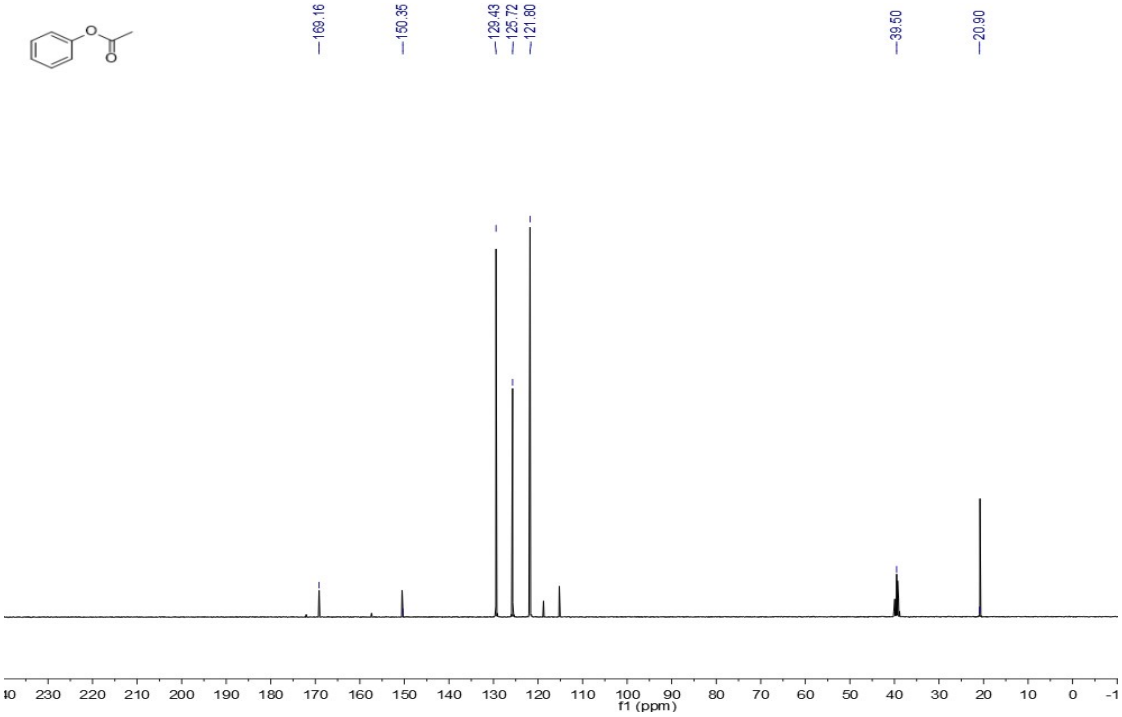
(16) 
O
O

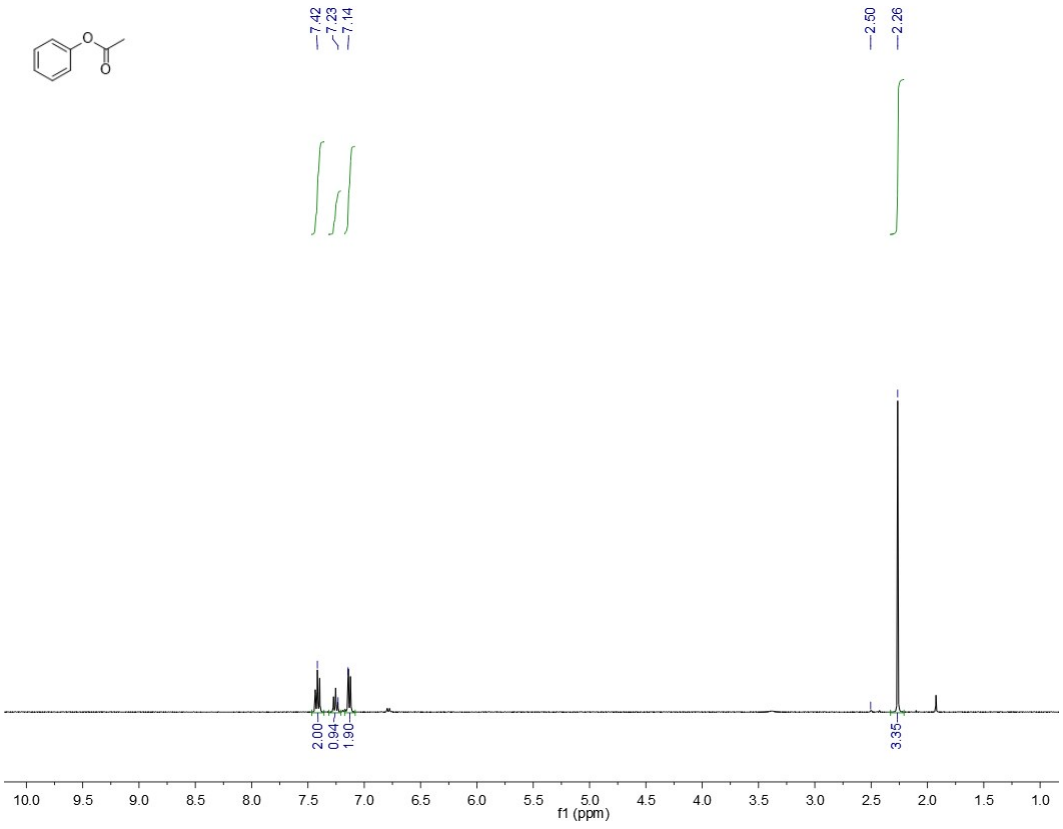

(x10,000)
1.00
0.75
0.50
0.25
0.00
107.0
122.0
164.0
77.0
65.0
136.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
325.0
350.0
375.0
400.0
425.0
450.0
475.0
500.0

5. Original NMR spectra

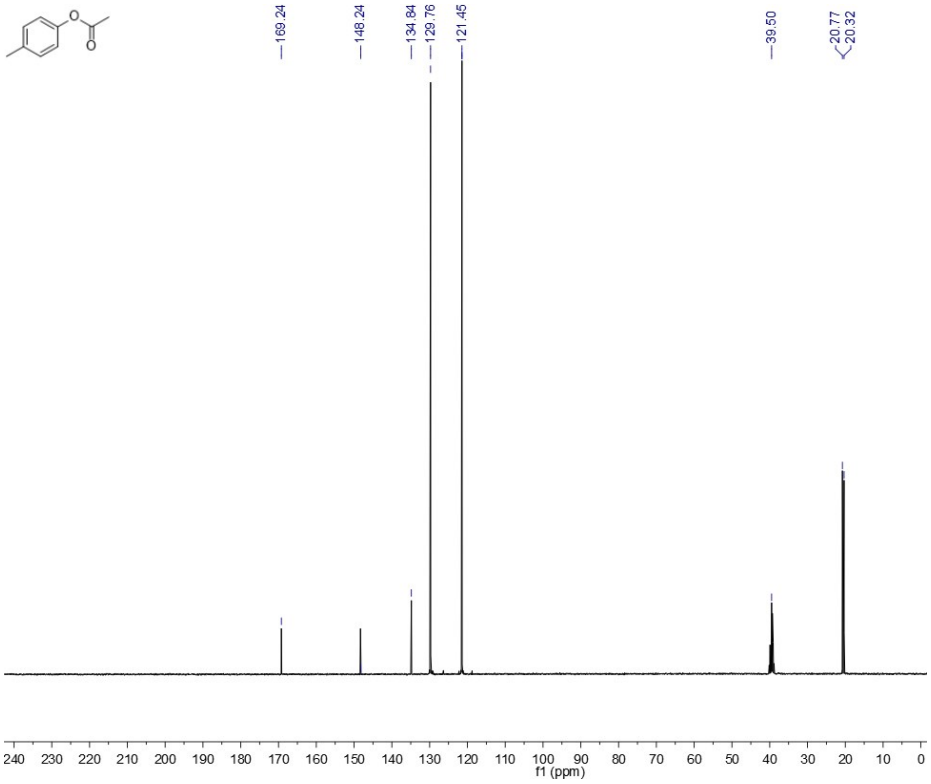
^{13}C NMR



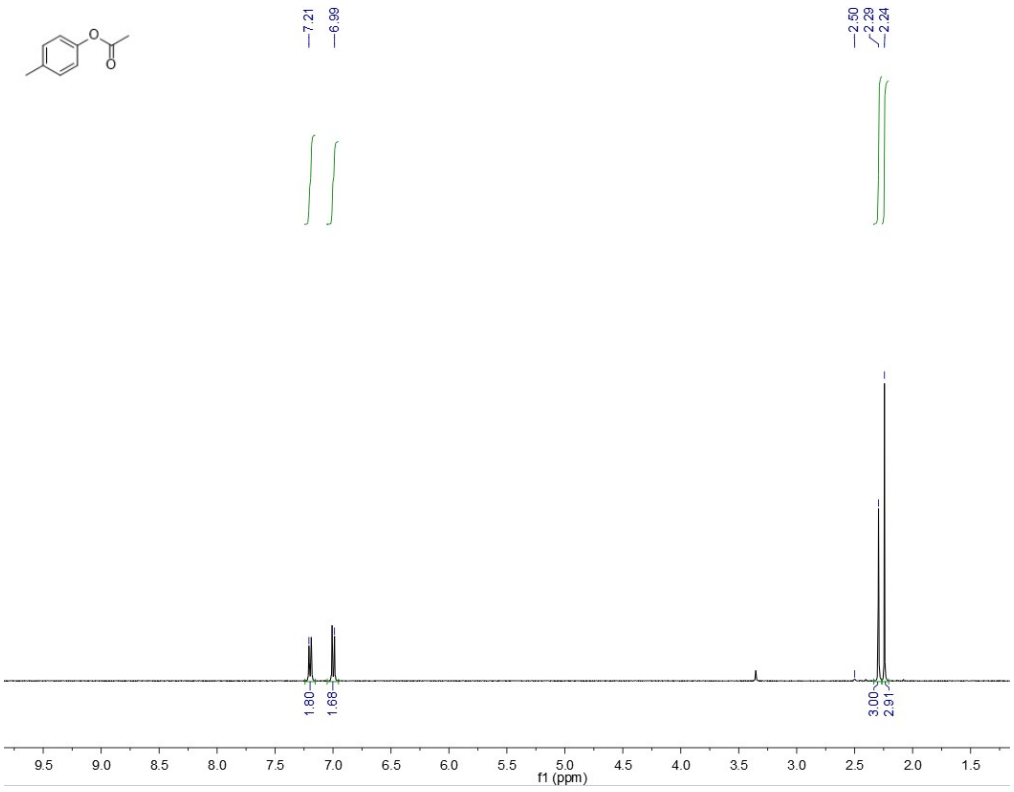
^{1}H NMR



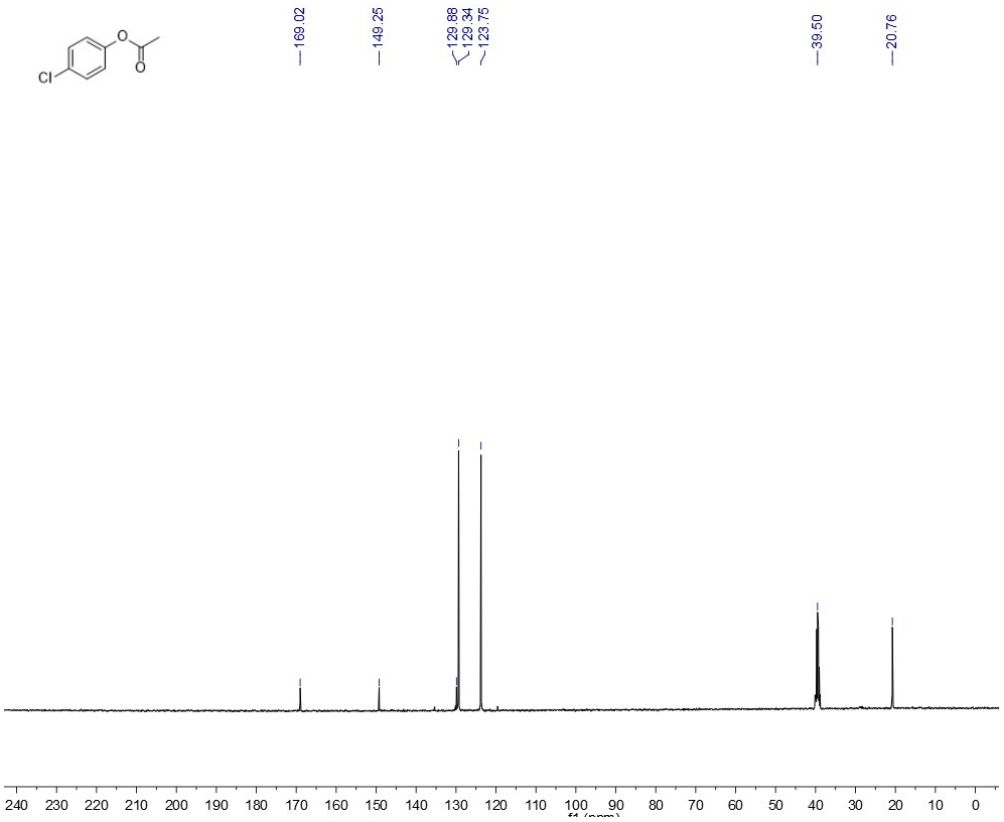
^{13}C NMR



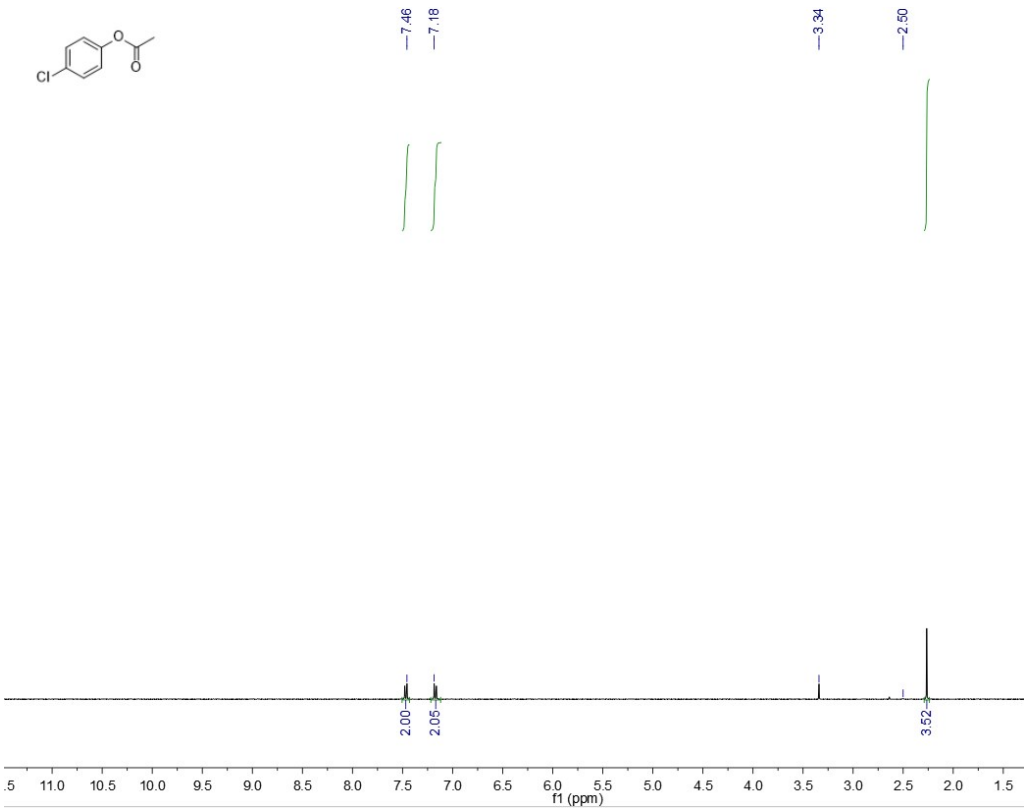
^{1}H NMR



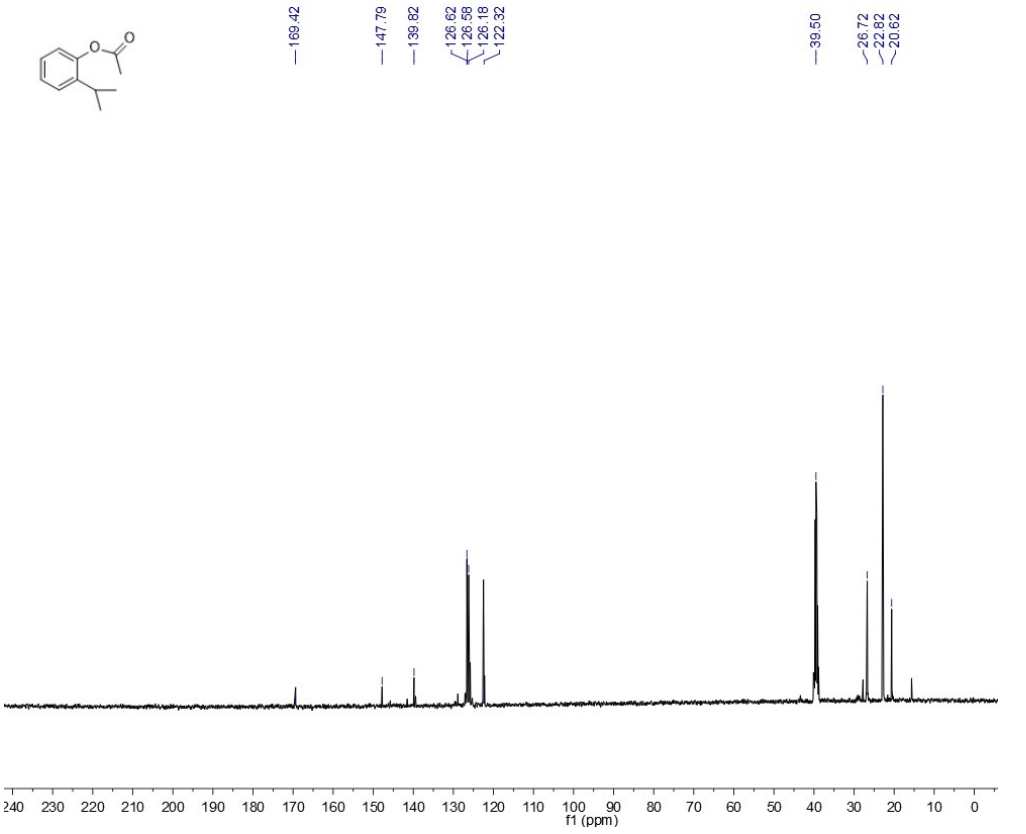
^{13}C NMR



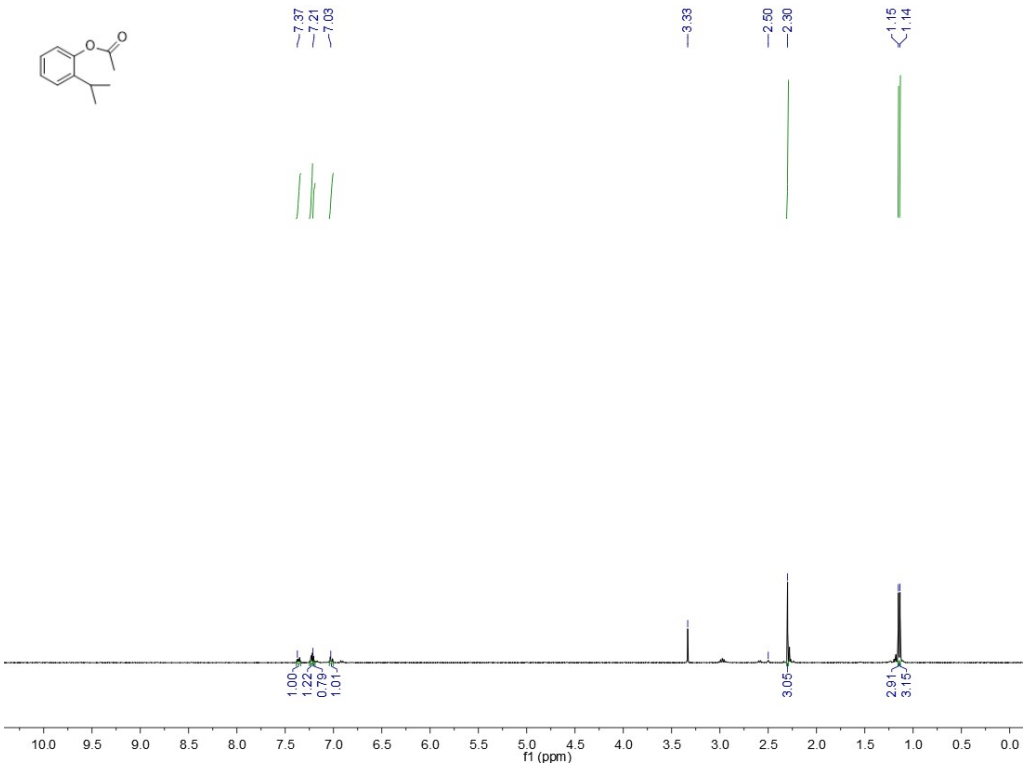
^{1}H NMR



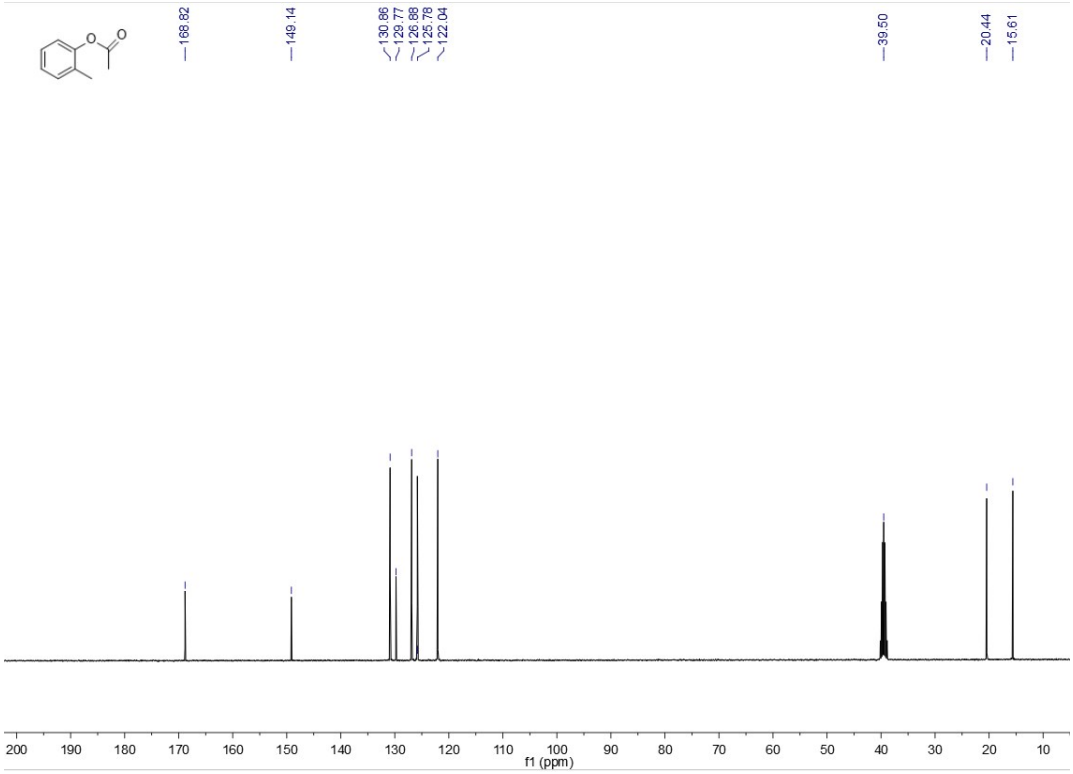
^{13}C NMR



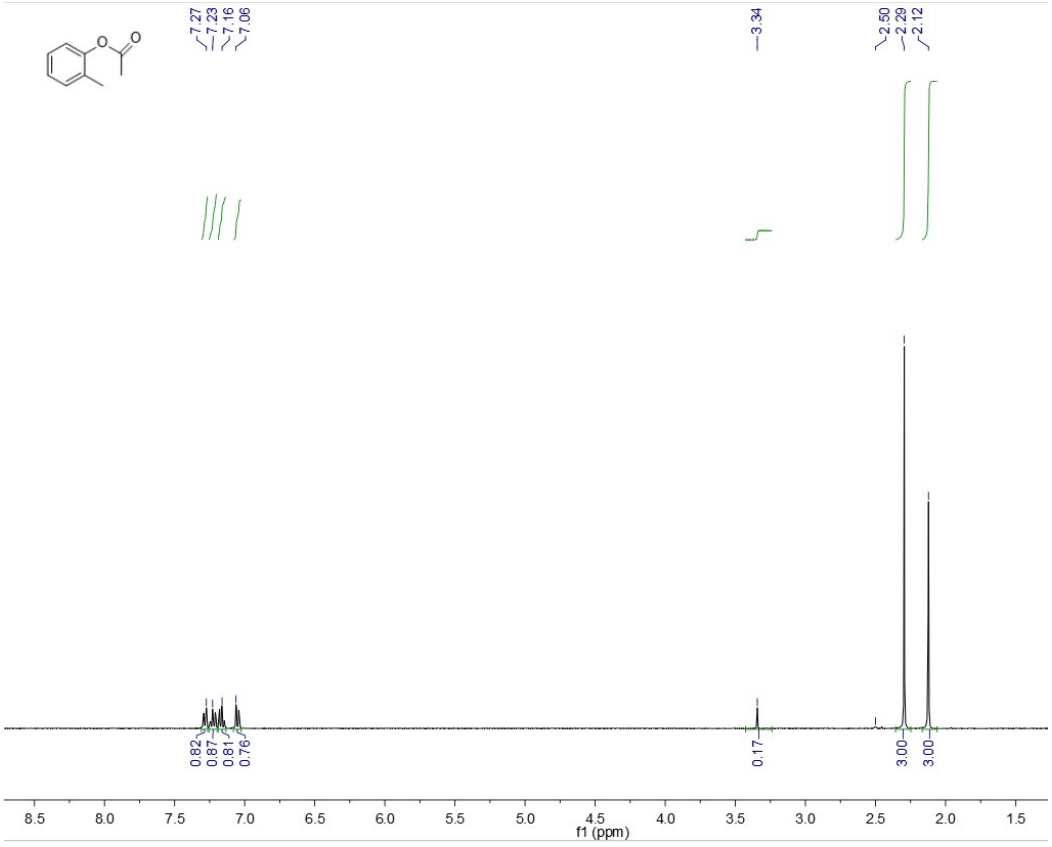
^{1}H NMR



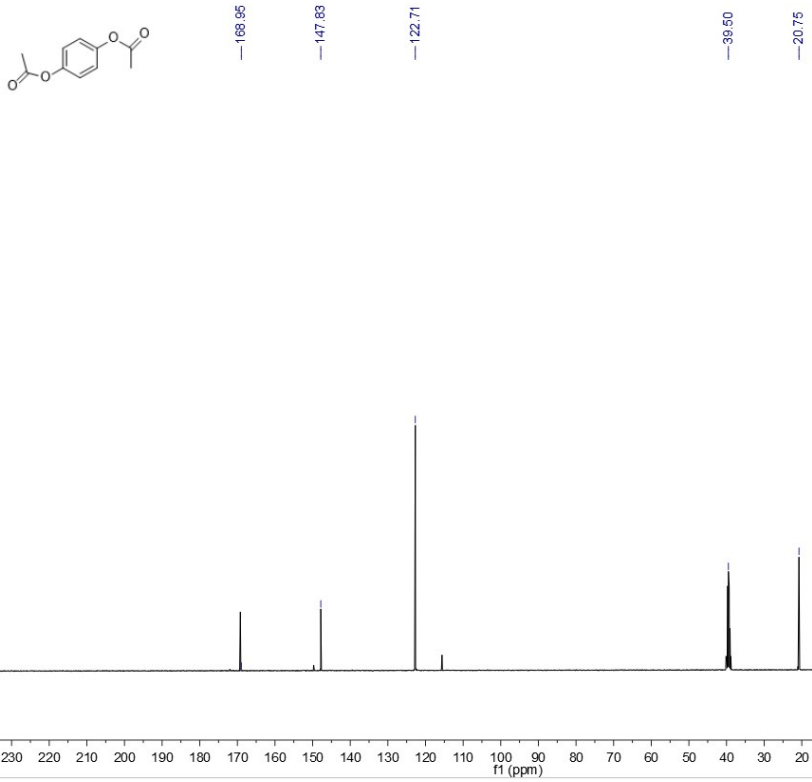
^{13}C NMR



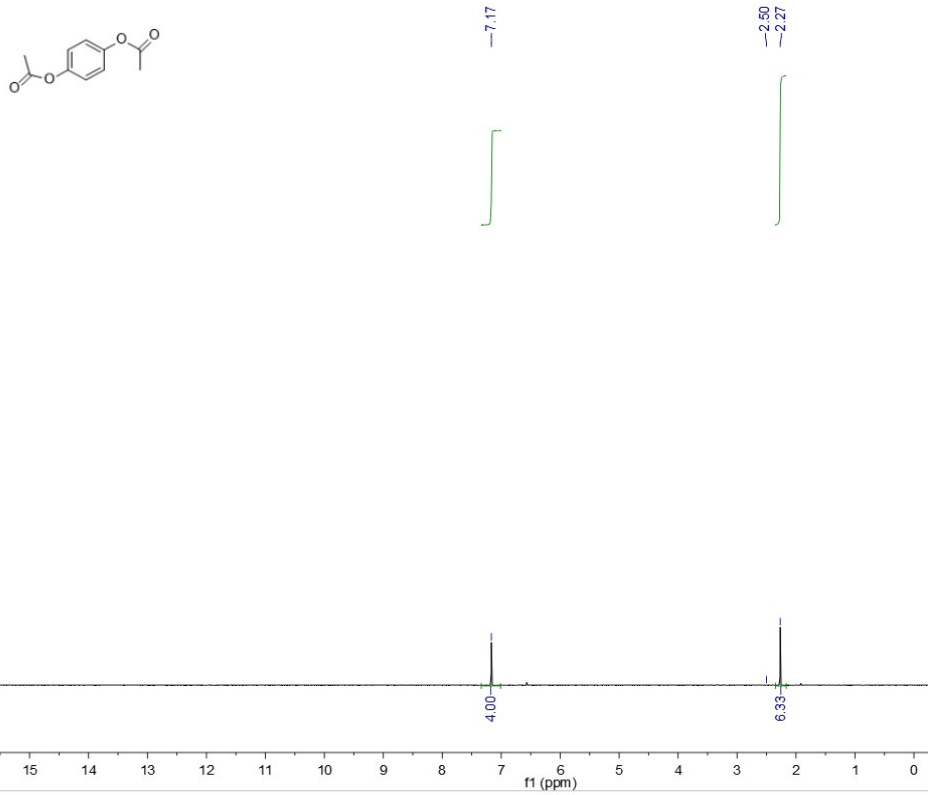
^{1}H NMR



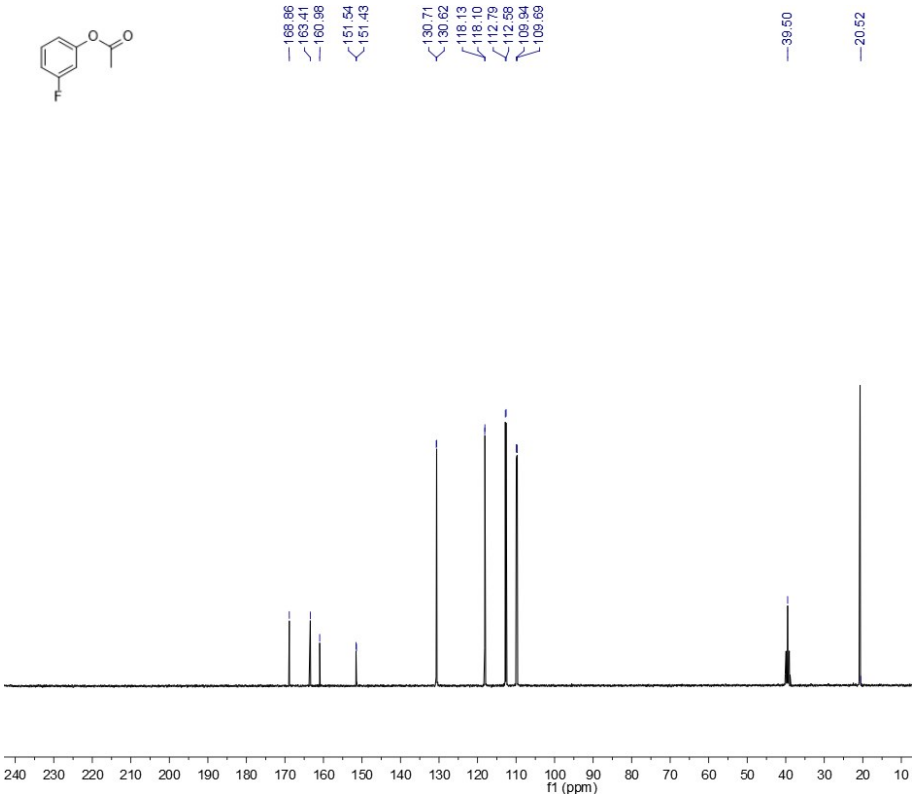
^{13}C NMR



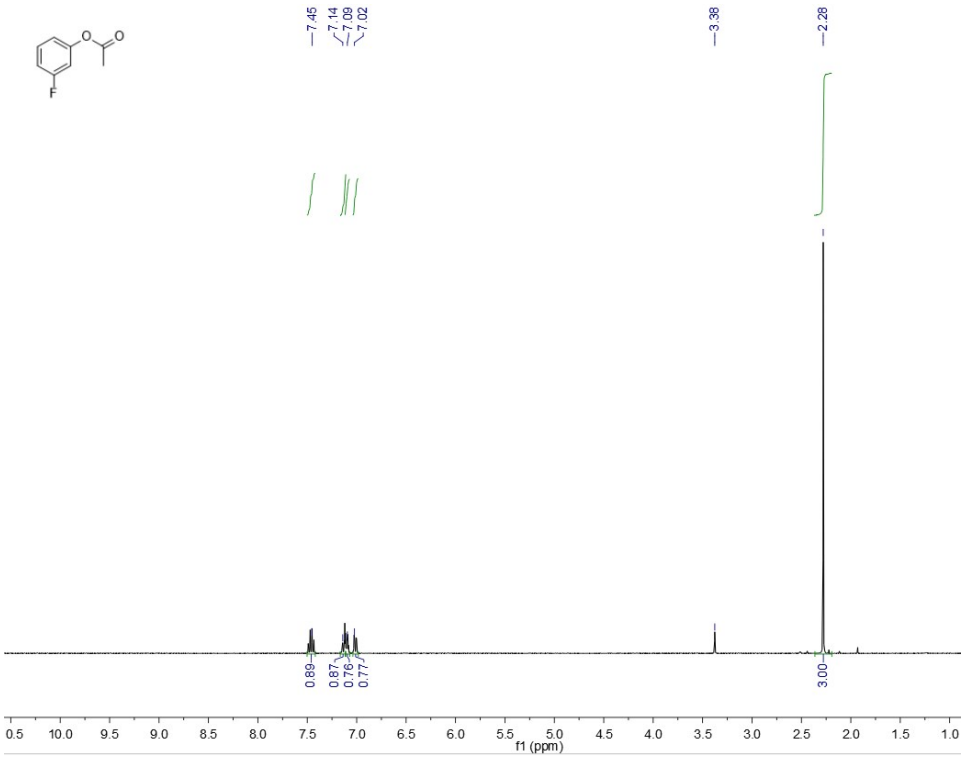
^{1}H NMR



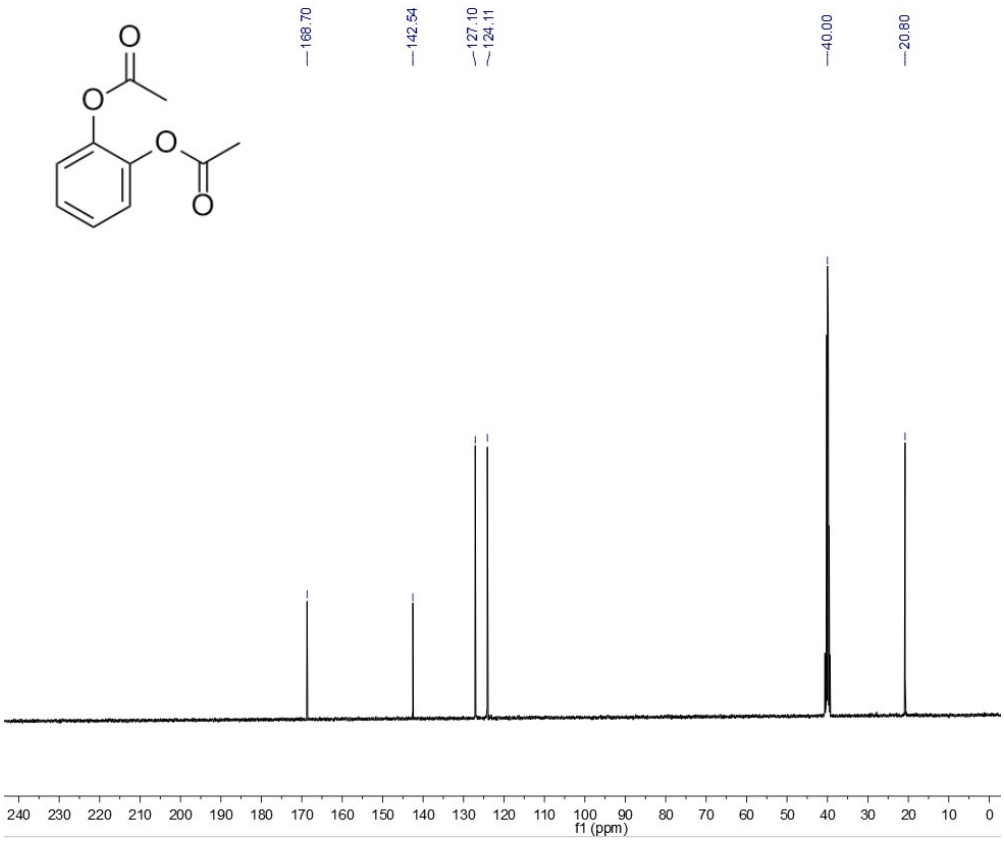
^{13}C NMR



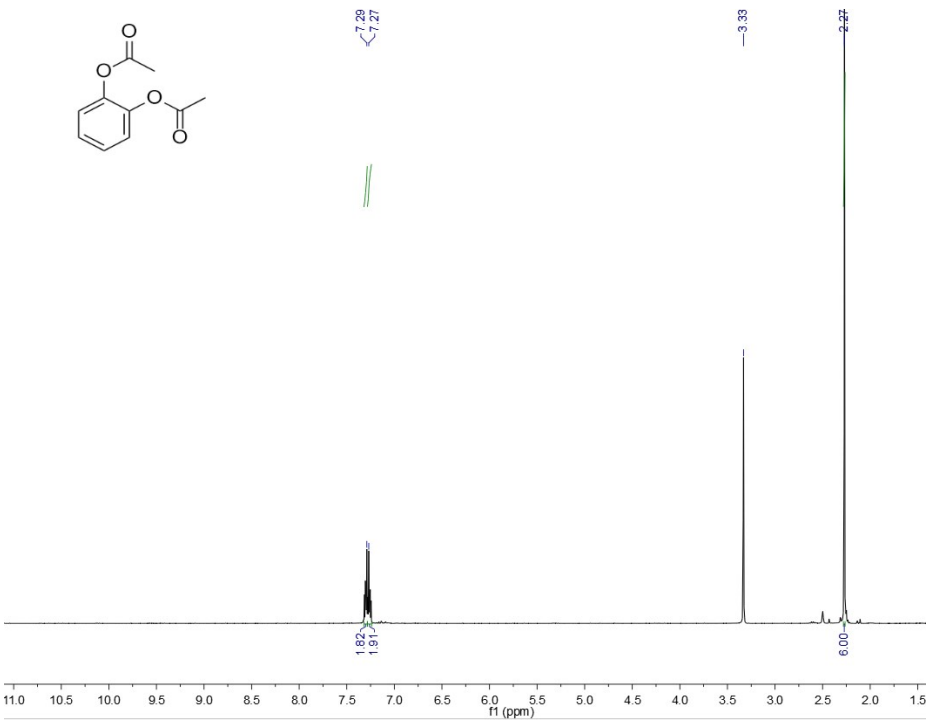
^{1}H NMR



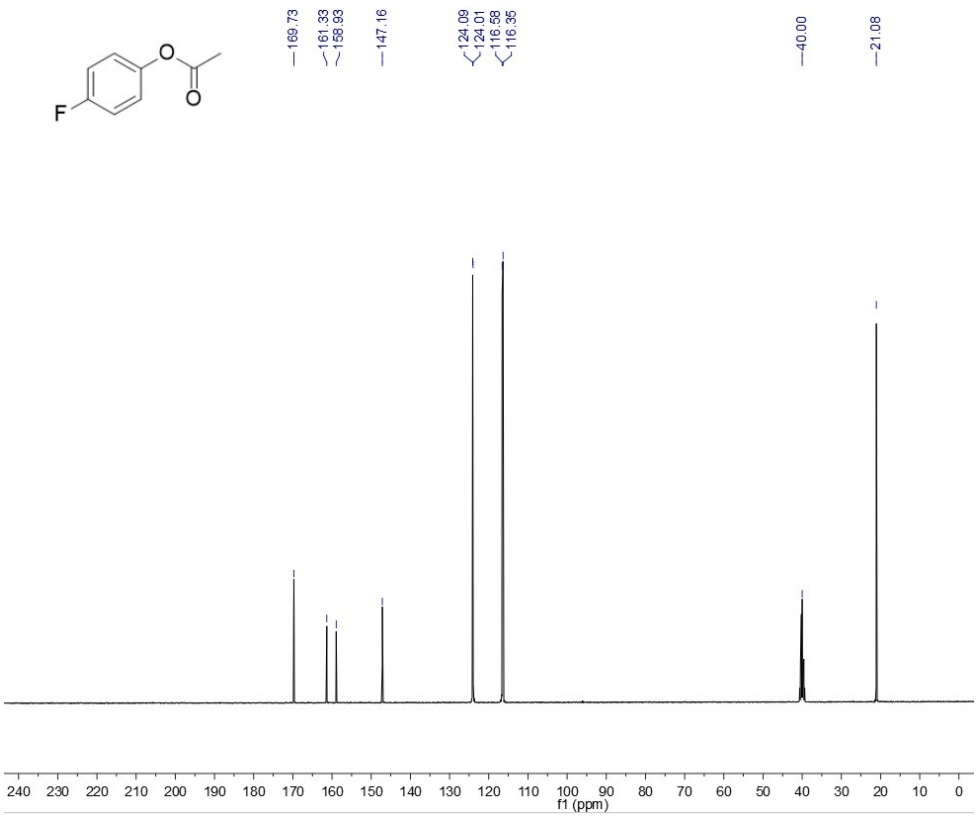
^{13}C NMR



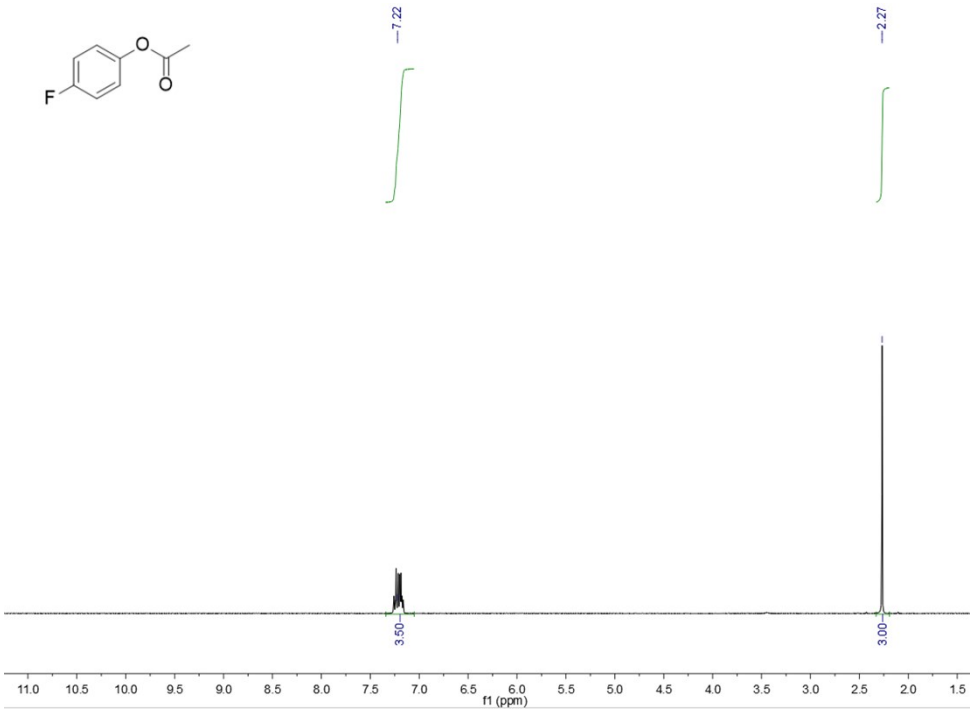
^{1}H NMR



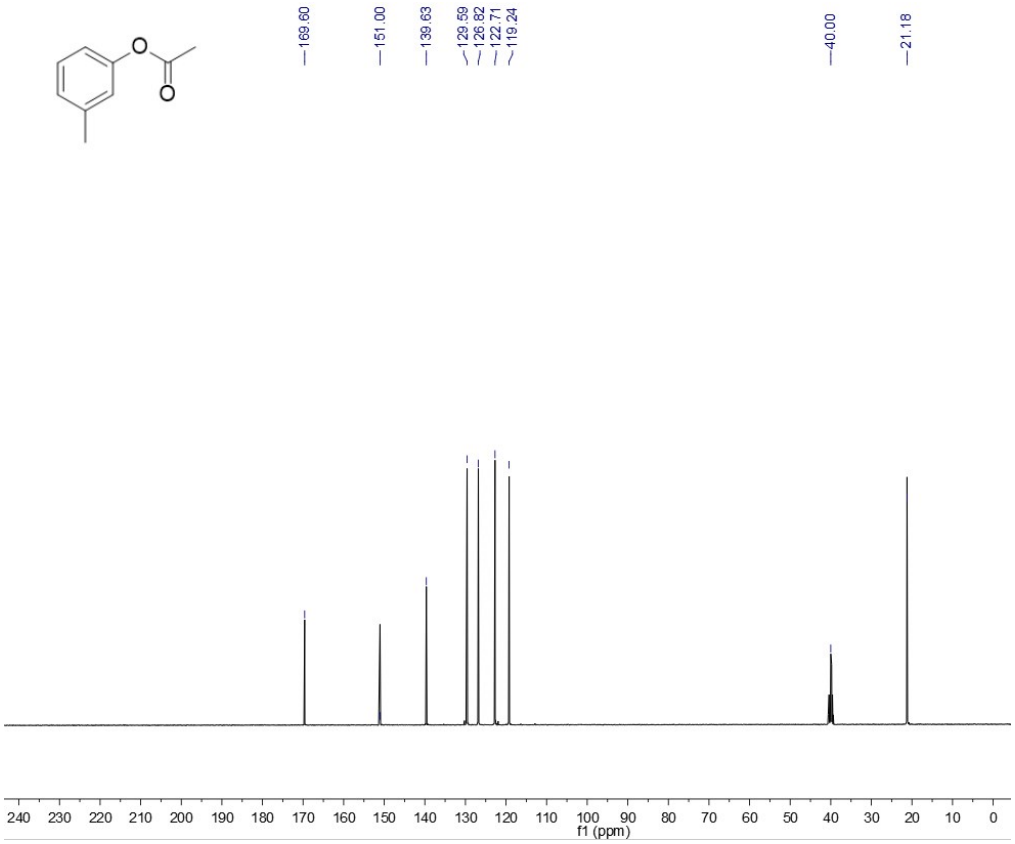
^{13}C NMR



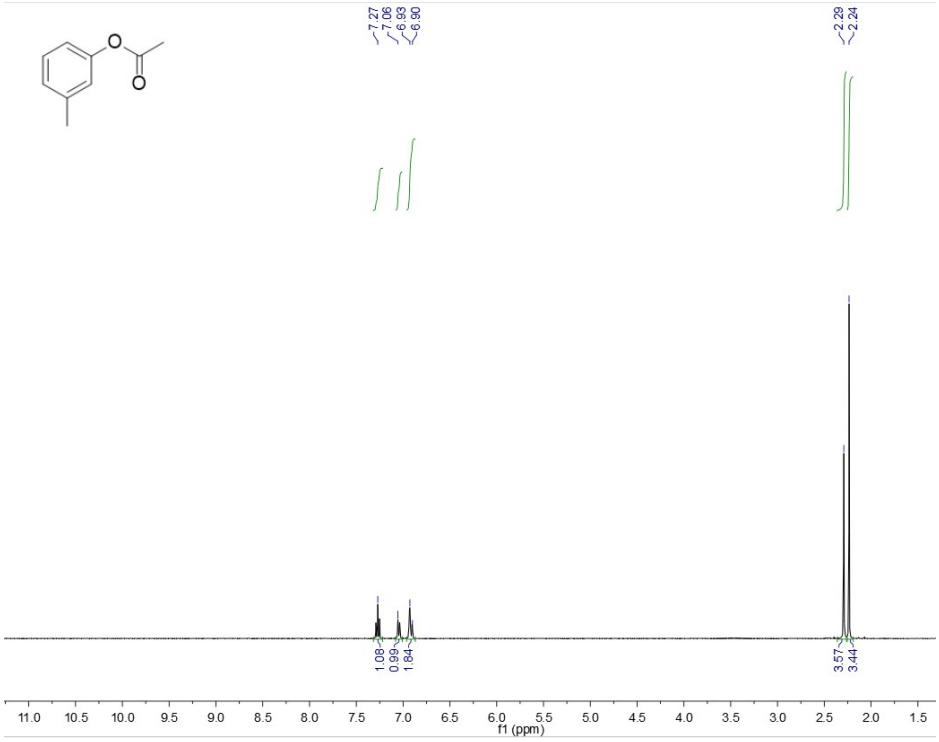
^{1}H NMR



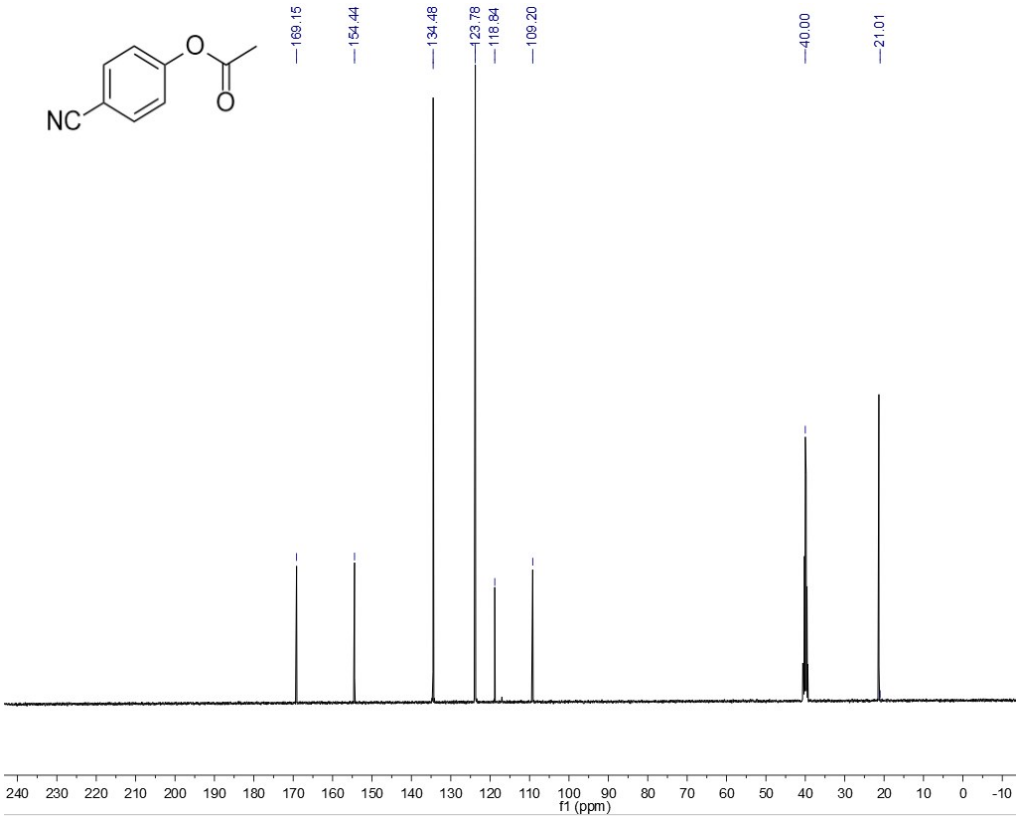
^{13}C NMR



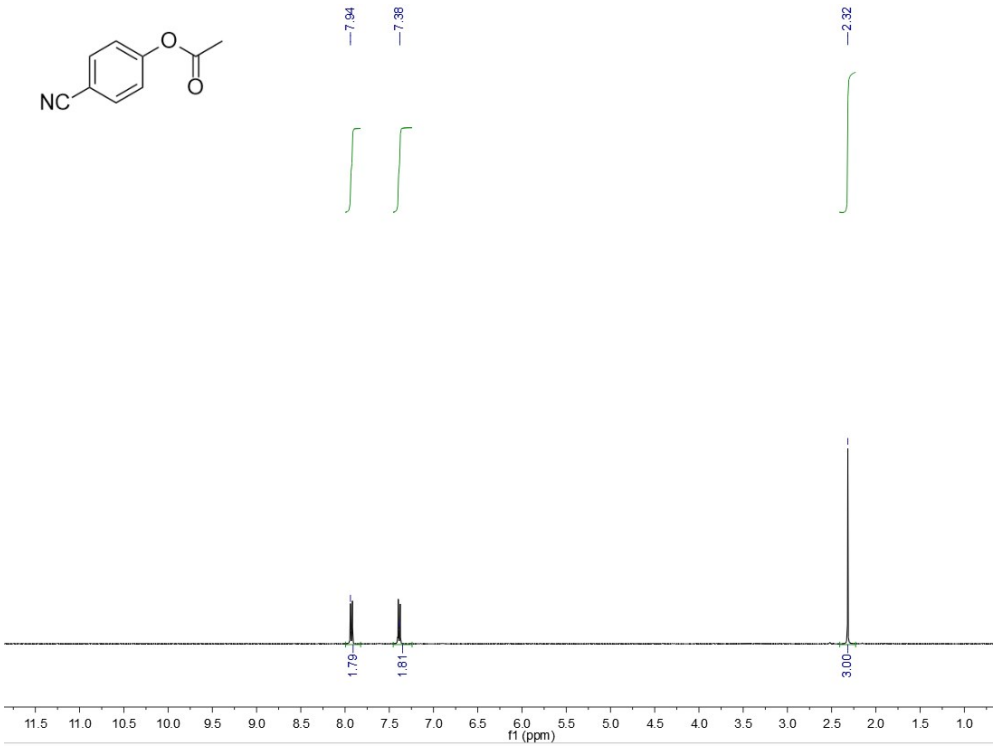
^{1}H NMR



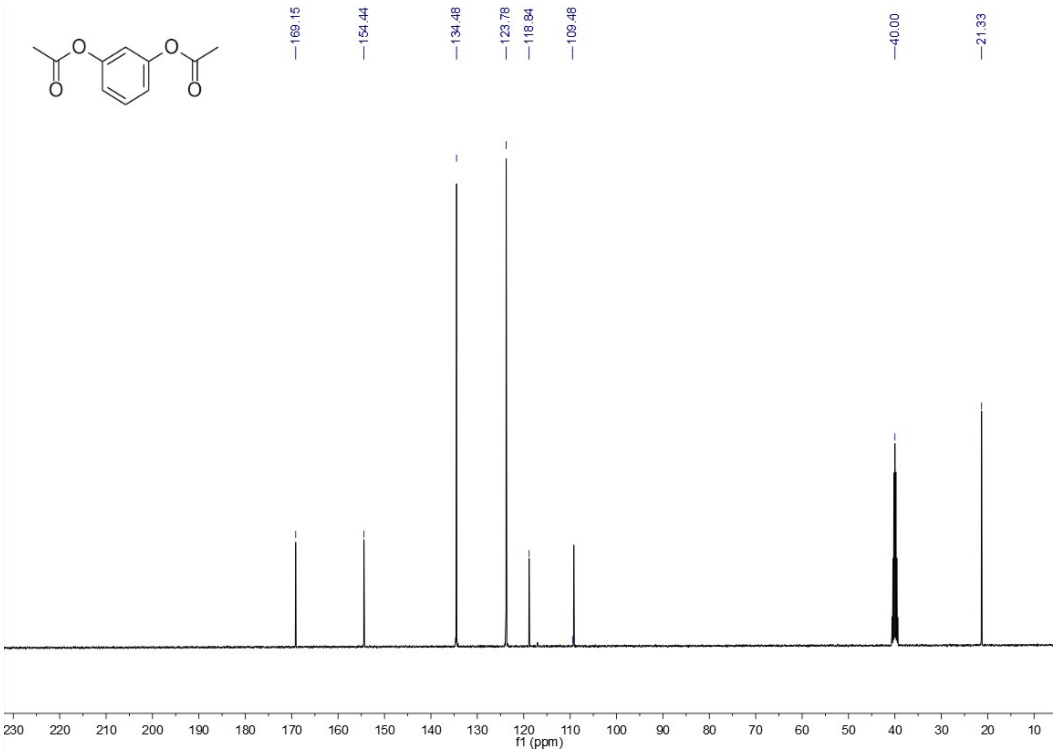
^{13}C NMR



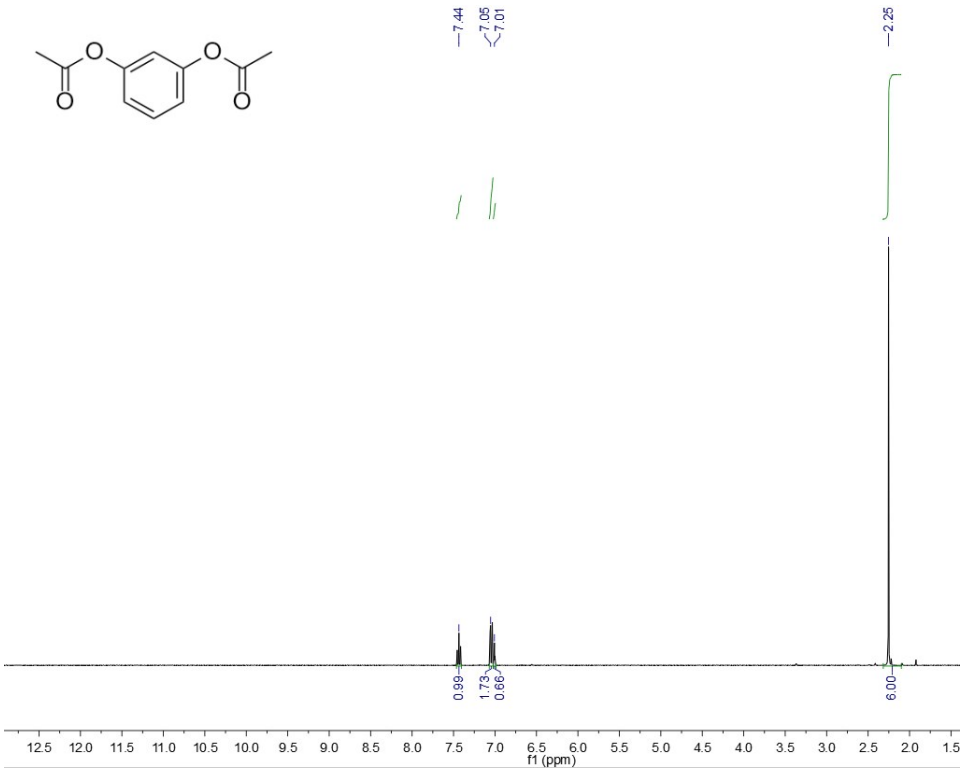
^{1}H NMR



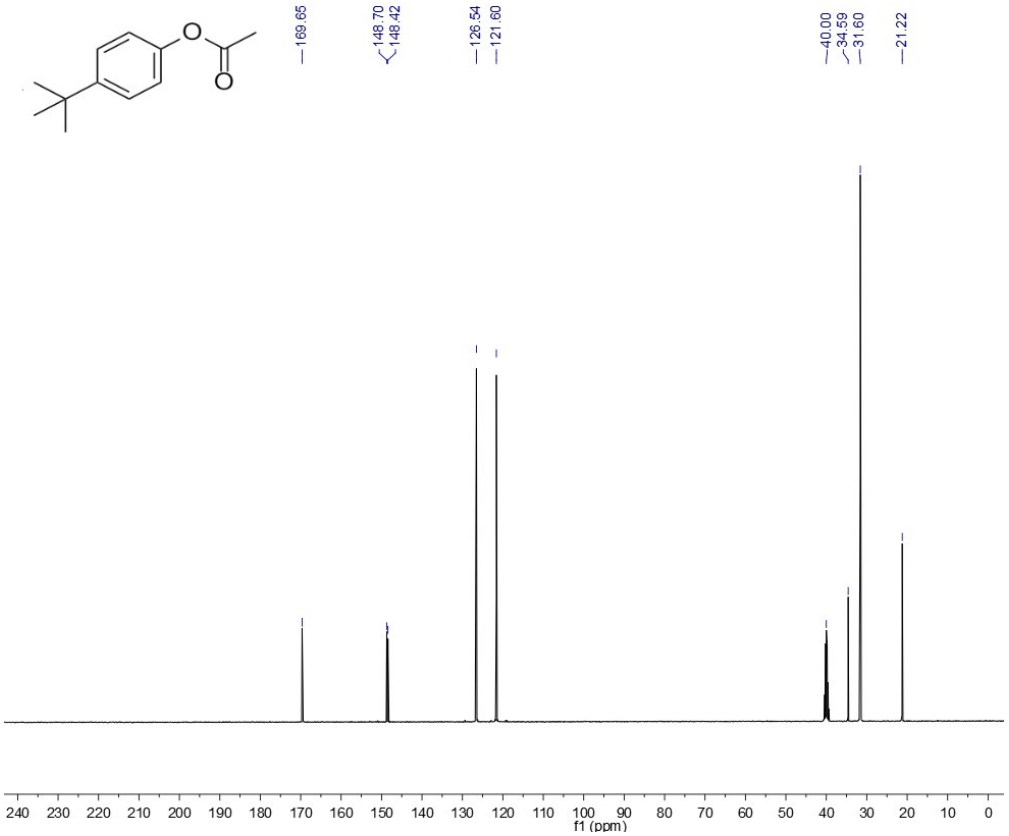
^{13}C NMR


169.15
154.44
134.48
123.78
118.84
109.48
40.00
21.33
f1 (ppm)

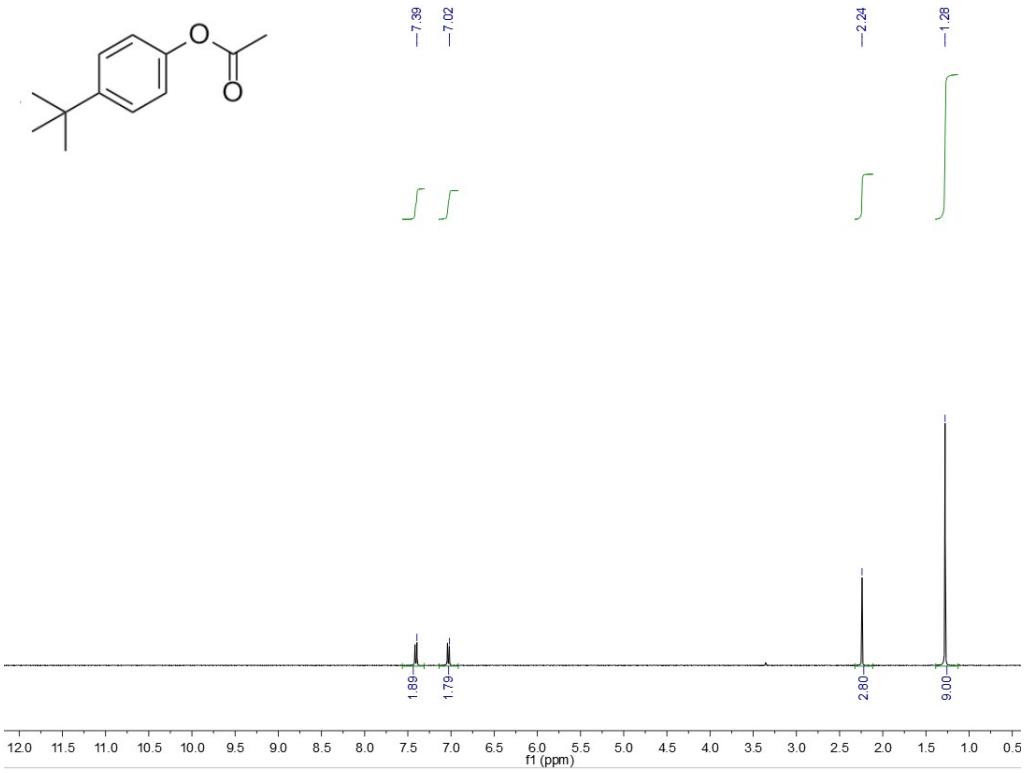
^{1}H NMR


7.44
7.05
7.01
2.25
0.99
1.73
0.66
6.00
f1 (ppm)

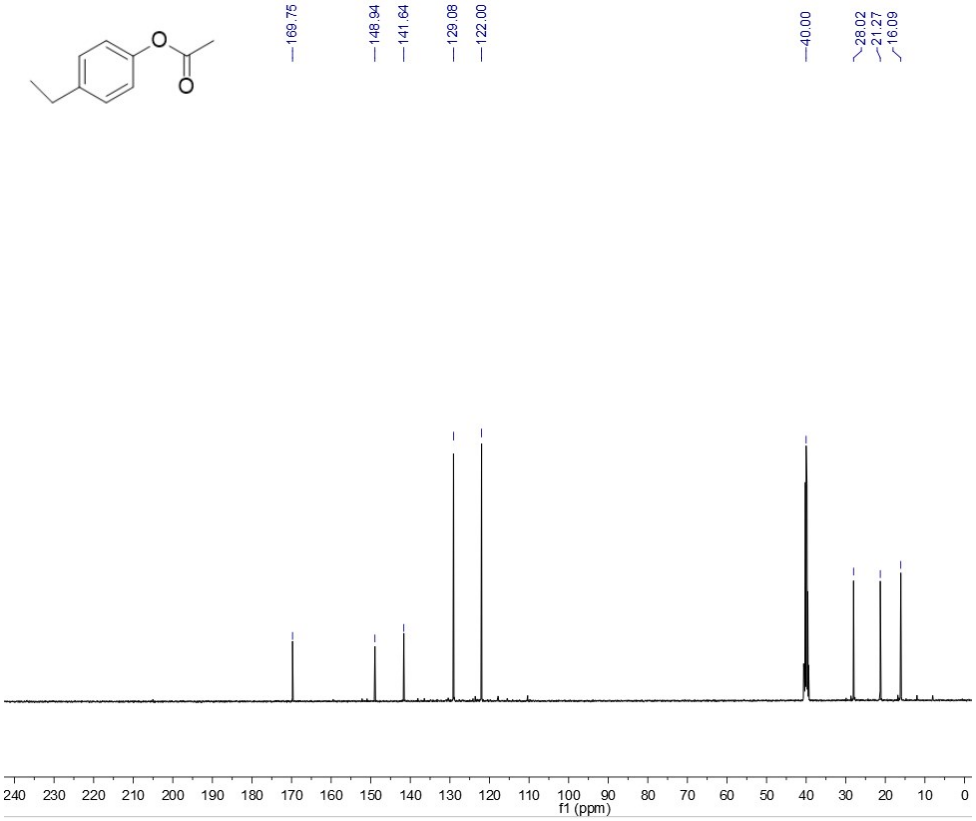
^{13}C NMR



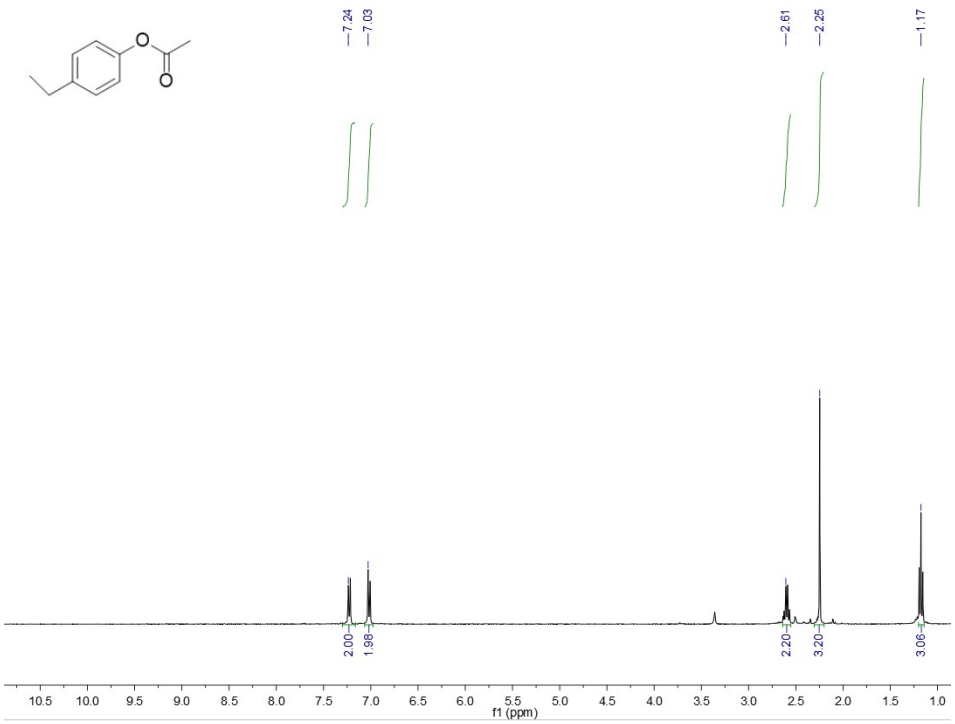
^{1}H NMR



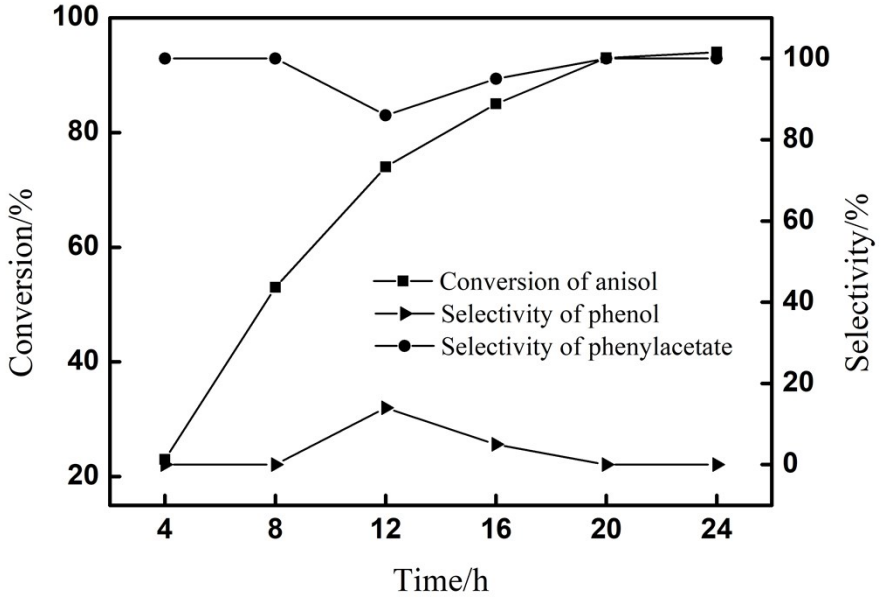
^{13}C NMR



^{1}H NMR



6. The conversion and selectivity of the reaction at different time



Condition: 2 mmol anisole, 2 mol% $IrCl_3$ as catalyst, 5 mL solvent, 5 mol% PPh_3, 3 mmol CH_3I, 5 bar CO, 180℃, 20 h.

7. ^{31}P NMR of PPh_3, PPh_3+MeI and the solution after the reaction