Supporting Information

Palladium-Catalyzed Desilylative Acyloxylation of Silicon-Carbon Bonds on Trimethylsilylarenes: Synthesis of Phenol Derivatives from Trimethylsilylarenes

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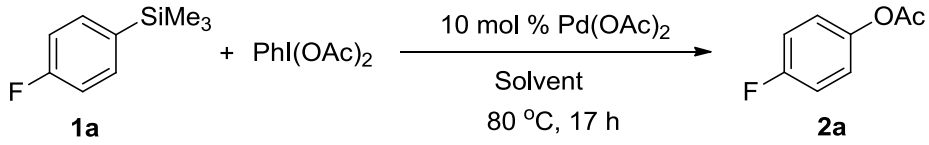
Contents

1. Solvent Effect on Pd-catalyzed Acetoxylation of 1a

Solvent effect on the Pd-catalyzed acetoxylation of 1-fluoro-4-(trimethylsilyl)benzene (**1a**)[a]



entry	solvent	yield (%)[b]
1	AcOH	32
2	DMF	0
3	MeCN	0
4	DCE	0
5	THF	0
6	DME	0
7	AcOH[c]	16

[a] Conditions: **1a** (0.2 mmol), $PhI(OAc)_2$ (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), solvent (1 mL), 80 °C, and 17 h. [b] Yield was determined by ^{19}F NMR using hexafluorobenzene as an internal standard. [c] Ac_2O (0.2 mL) was added.

2. General Procedure for Reaction of Trimethylsilylarenes 1 with $PhI(OCOCF_3)_2$ in the Presence of $Pd(OAc)_2$ in AcOH

A mixture of a trimethylsilylarene (**1**) (0.4 mmol), $PhI(OCOCF_3)_2$ (0.6 mmol), and $Pd(OAc)_2$ (0.02 mmol) in AcOH (1 mL) was stirred at 80 °C for 17 h. The reaction mixture was poured into aqueous $NaHCO_3$ solution and extract with CH_2Cl_2 (20 mL × 3). The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under a reduced pressure. The pruduct was separated by column chromatography on silica gel with hexane/AcOEt eluent.

3. One-pot Synthesis of Phenols by Desilylative Acetoxylation Followed by Hydrolysis

A mixture of **1** (0.4 mmol), $PhI(OAc)_2$ (0.6 mmol), and $Pd(OAc)_2$ (0.02 mmol) in AcOH (1 mL) was stirred at 80 °C for 17 h. To the reaction mixture, then, was added water (1 mL) and the mixture was stirred at 100 °C for 3 h. The reaction mixture was poured into aqueous $NaHCO_3$ solution and extract with CH_2Cl_2 (20 mL × 3). The combined organic extract was dried over anhydrous Na_2SO_4, and concentrated under a reduced pressure. The product was separated by column chromatography on silica gel with hexane/AcOEt eluent.

4. Spectral Data of Products

4-Fluorophenyl acetate (2a):[1] The product was obtained as a colorless oil. Yield, 0.055 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.04-7.05 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 115.8 (d, *J* = 23 Hz), 122.8 (d, *J* = 9 Hz), 146.4, 158.8, 160.0 (d, *J* = 242 Hz), 169.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.3.

Phenyl acetate (2b):[2] The product was obtained as a colorless oil. Yield, 0.048 g (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 7.09 (d, *J* = 8 Hz, 2H), 7.26 (t, *J* = 8 Hz 1H), 7.38 (t, *J* =8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 121.5, 125.8, 129.4, 150.1, 169.4.

4-Mehylphenyl acetate (2c):[3] The product was obtained as a colorless oil. Yield, 0.056 g (93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.34 (s, 3H), 6.96 (d, *J* = 8 Hz 2H), 7.17 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.0, 121.2, 129.9, 135.4, 148.4, 169.7.

4-Chlorophenyl acetate (2d):[4] The product was obtained as a colorless oil. Yield, 0.066 g (97%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.03 (d, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 122.9, 129.4, 131.1, 149.1, 169.1.

4-Bromophenyl acetate (2e):[5] The product was obtained as a colorless oil. Yield, 0.077 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.98 (d, *J* =8 Hz, 2H), 7.49 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 118.8, 123.3, 132.4, 149.6, 169.0.

4-Iodophenyl acetate (2f):[6] The product was obtained as a colorless oil. Yield, 0.098 g (94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.86 (d, *J* = 8 Hz, 2H), 7.68 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 89.8, 123.7, 138.4, 150.4, 169.0.

4-*tert*-Butylphenyl acetate (2g):[1] The product was obtained as a colorless oil. Yield, 0.075 g(98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 9H), 2.29 (s, 3H), 7.00 (d, *J* = 8 Hz, 2H), 7.38 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 31.3, 34.4, 120.8, 126.3, 148.3, 148.5, 169.6.

Ethyl 4-acetoxybenzoate (2h):[7] The product was obtained as a colorless oil. Yield, 0.076 g (91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, *J* = 7 Hz, 3H), 2.32 (s, 3H), 4.37 (q, *J* = 7 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 8.08 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 21.1, 61.0, 121.5, 128.0, 131.1, 154.1, 165.8, 168.8.

2-Acetylnaphthalene (2i):[1] The product was obtained as a white solid; mp 62–64 °C. Yield, 0.068 g (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 7.21-7.86 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 118.4, 121.0, 125.6, 126.5, 127.5, 127.7, 129.3, 131.4, 133.7, 148.3, 169.5.

4-(4'-Mehtylphenyl)phenyl acetate (2j):[8] The product was obtained as a yellow solid, mp 98–100 °C. Yield, 0.085 g (94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.39 (s, 3H), 7.14 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 7.46 (d, *J* = 8 Hz, 2H), 7.57 (d, *J* = 8 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.1, 121.7, 126.9, 127.9, 129.5, 137.1, 137.4, 138.9, 149.8, 169.5.

3-Methylphenyl acetate (2k):[9] The product was obtained as a colorless oil. Yield 0.052 g (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.35 (s, 3H), 6.87-6.90 (m, 2H), 7.04 (d, *J* = 8 Hz, 1H), 7.25 (t, *J* = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.2, 118.4, 122.1, 126.6, 129.1, 139.5, 150.6, 169.5.

3-Chlorophenyl acetate (2l):[10] The product was obtained as a colorless oil. Yield 0.060 g (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.00 (d, *J* = 8Hz, 1H), 7.13 (s, 1H), 7.20-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 119.9, 122.2, 126.0, 130.0, 134.5, 151.1, 168.8.

3-Bromophenyl acetate (2m):[11] The product was obtained as a colorless oil. Yield 0.077 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 7.05 (d, *J* = 8 Hz, 1H), 7.23-7.29 (m, 2H), 7.37 (d, *J* = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 120.4, 122.3, 125.0, 128.9, 130.4, 151.1, 168.9.

4-Trimethylsilylphenyl acetate (2n):[12] The product was obtained as a colorless oil. Yield 0.056 g (67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 9H), 2.30 (s, 3H), 7.07 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.1, 21.1, 120.8, 134.5, 137.9, 151.3, 169.4.

4-Fluoro-3-trimethysilylphenyl acetate (2o): The product was obtained as a colorless oil. Yield 0.077 g (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.31 (s, 9H), 2.29 (s, 3H), 6.96-7.04 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.3, 21.0, 115.5 (d, *J* = 28 Hz), 124.1 (d, *J* = 9 Hz), 127.4, 127.5, 146.4, 164.6 (d, *J* = 238 Hz), 169.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.3. HRMS (EI^+) calcd for $C_{11}H_{15}FO_2Si$ 226.0825, found 226.0825. Applying the principle of substituent additivity, the observed chemical shifts of aromatic carbons are in fair agreement with the values estimated by applying the principle of substituent additivity to **2o**, not for 2-fluoro-5-trimethylsilylphenyl acetate.

2-Naphthol (3a):[13] The product was obtained as a white solid, mp 118–120 °C. Yield 0.052 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 (s, 1H), 7.09-7.76 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.5, 117.7, 123.6, 126.3, 126.5, 127.7, 128.9, 129.8, 134.5, 153.2.

4-(4'-Methylphenyl)phenol (3b):[14]The product was obtained as a white solid, mp 151–153 °C. Yield 0.068 g (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 4.78 (s, 1H), 6.89 (d, *J* = 8 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H), 7.43-7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 115.6, 126.5, 128.2, 129.4, 133.9, 136.4, 137.8, 154.7.

2-Naphthyl propanoate (4a):[15] The product was obtained as a white solid, mp 42–44 °C. Yield 0.071g (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7 Hz, 3H), 2.65 (q, *J* = 7 Hz 2H), 7.22-7.84 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.1, 27.7, 118.4, 121.1, 125.6, 126.5, 127.6, 127.7, 129.3, 131.3, 133.7, 148.4, 173.1.

2-Naphthyl pentanoate (4b): The product was obtained as a colorless oil. Yield 0.079 g (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, *J* = 8 Hz, 3H), 1.48 (sext, *J* = 8 Hz, 2H), 1.79 (quint, *J* = 8 Hz, 2H), 2.62 (t, *J* = 8 Hz, 2H), 7.21-7.86 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 22.2, 27.0, 34.1, 118.5, 121.2, 125.6, 126.5, 127.6, 127.7, 129.3, 131.4, 133.7, 148.4, 172.5. HRMS (EI^+) calcd for $C_{15}H_{16}O_2$ 228.1150, found 228.1150.

2-Naphthyl 2-methylpropanoate (4c):[7] The product was obtained as a white solid; mp 30–32 °C. Yield 0.063 g (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (d, *J* = 8 Hz, 6H), 2.86 (q, *J* = 8 Hz, 1H), 7.21 (d, *J* = 8 Hz, 1H), 7.45-7.85 (m, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 34.2, 118.4, 121.1, 125.5, 126.4, 127.5, 127.7, 129.3, 131.3, 133.7, 148.5, 175.7.

2-Naphthyl cyclohexanecarboxylate (4d): The product was obtained as a white solid, mp 60–62 °C. Yield 0.046g (45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-2.13 (m, 10H), 2.58-2.64 (m, 1H), 7.19-7.85 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.3, 25.6, 28.9, 43.1, 118.3, 121.1, 125.4, 126.3, 127.4, 127.6, 129.2, 131.3, 133.7, 148.5, 174.5. HRMS (EI^+) calcd for $C_{17}H_{18}O_2$ 254.1307, found 254.1308.

2-Naphthyl cyclopropanecarboxylate (4e): The product was obtained as a white solid, mp 60–61 °C. Yield 0.048 g (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03-1.08 (m, 2H), 1.20-1.23 (m, 2H), 1.87-1.93 (m, 1H), 7.23-7.86 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.3, 13.0, 118.4, 121.2, 125.5, 126.4, 127.6, 127.7, 129.2, 131.3, 133.7, 148.4, 173.6. HRMS (EI^+) calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0837.

2-Naphthyl benzoate (4f):[16] The product was obtained as a white solid, mp 102–104 °C. Yield, 0.054 g (54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-8.27 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.7, 121.2, 125.7, 126.5, 127.6, 127.8, 128.6, 129.4, 129.5, 130.2, 131.5, 133.6, 133.8, 148.5, 165.3.

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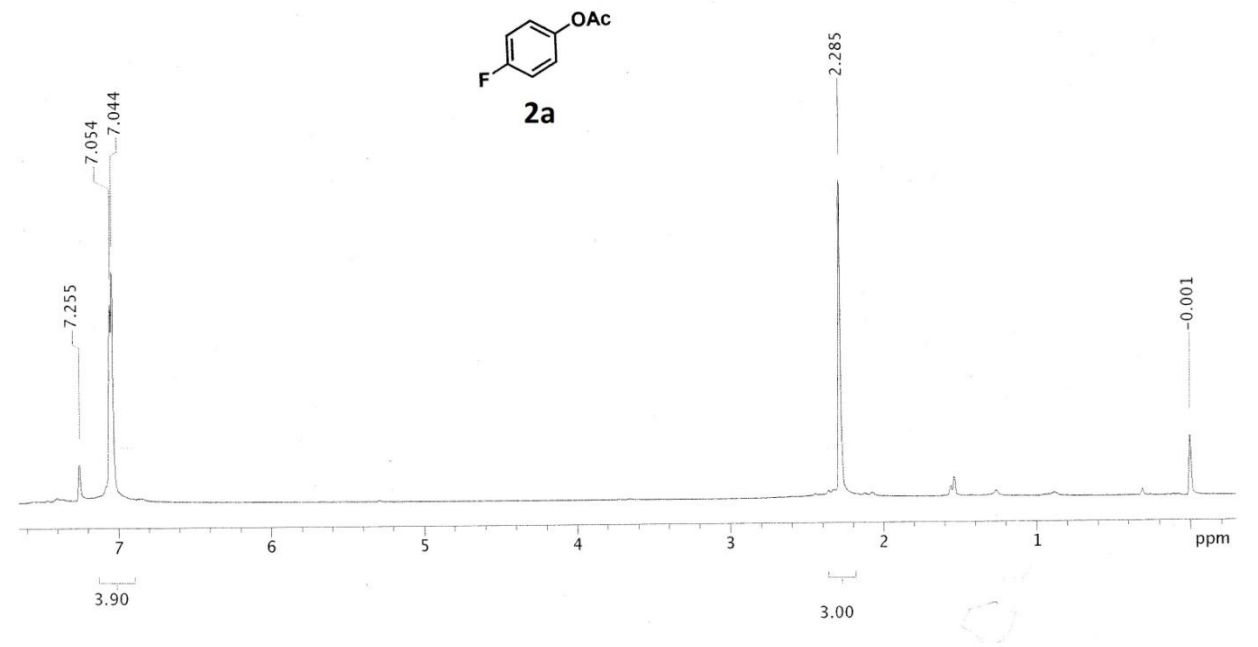
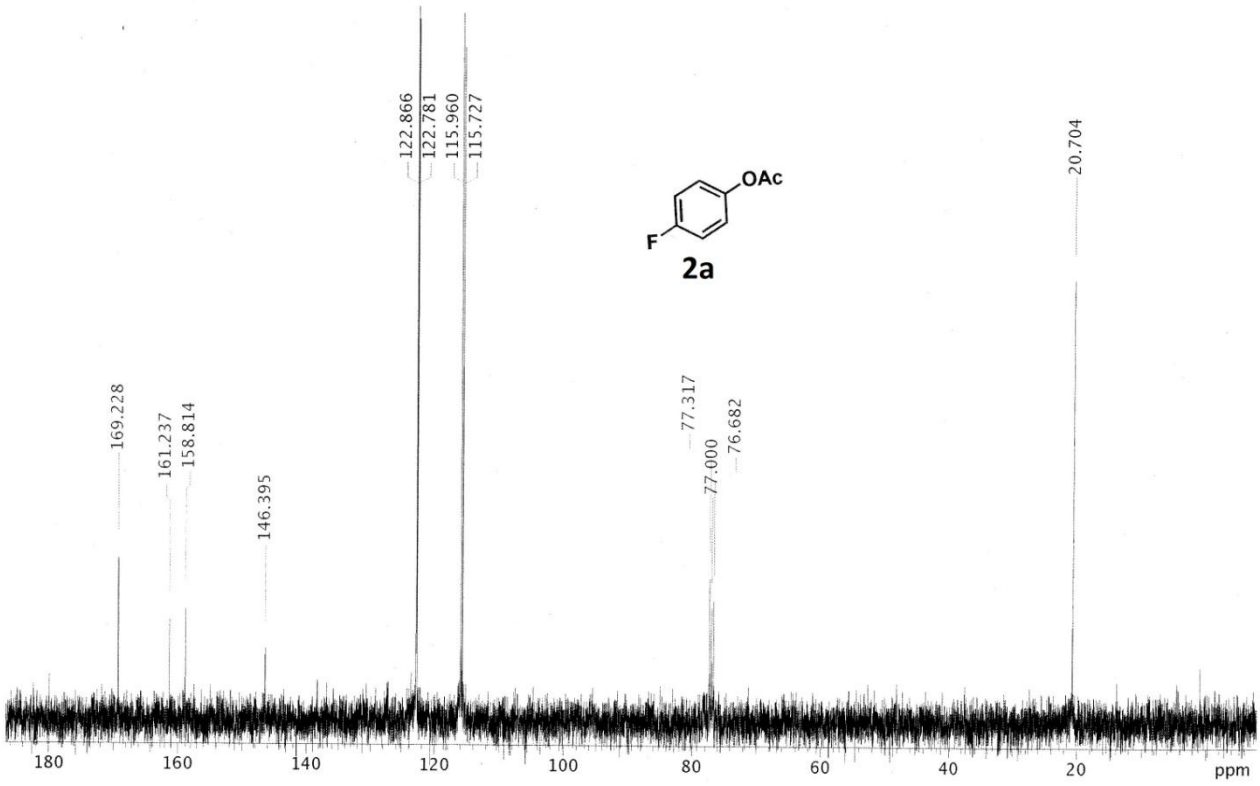
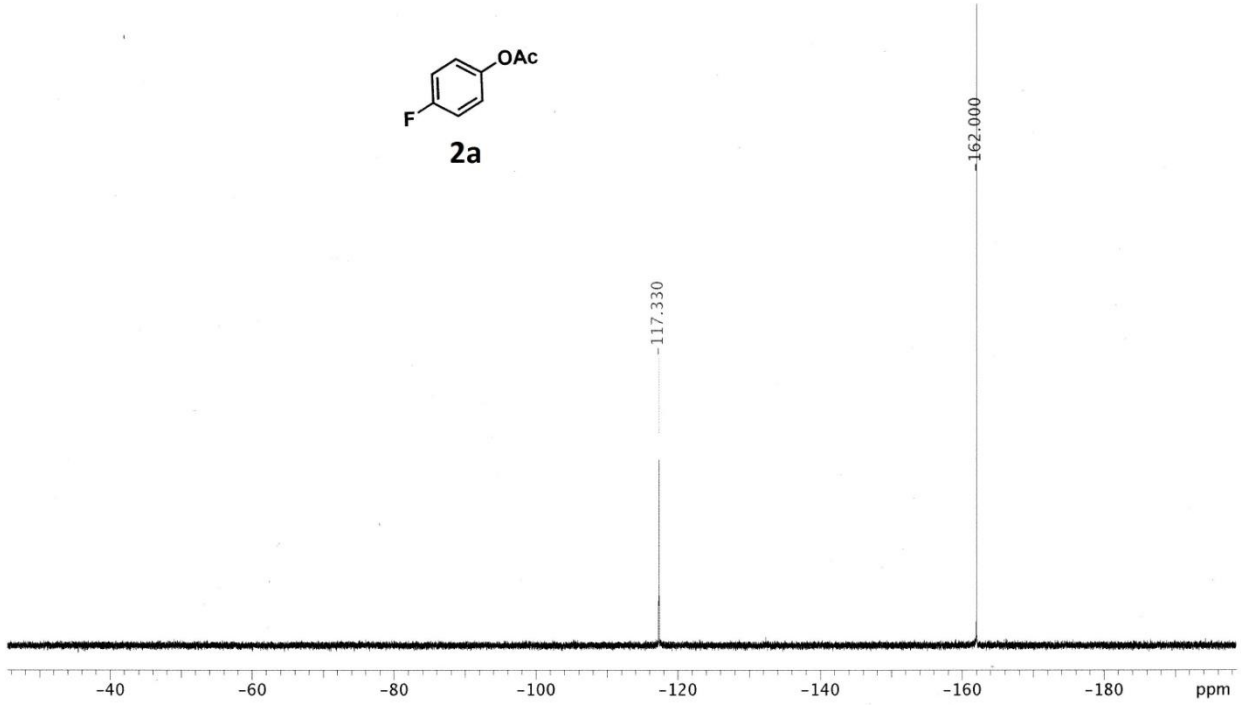
5. NMR Spectra of Products

4-Fluorophenyl acetate (2a)






OAc
F
2a
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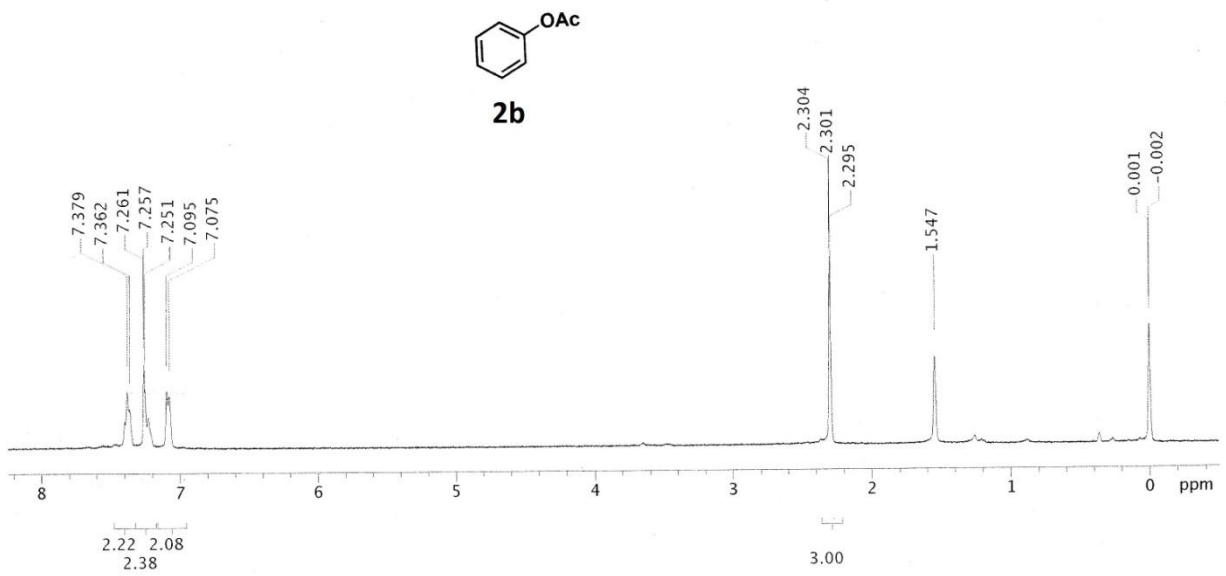
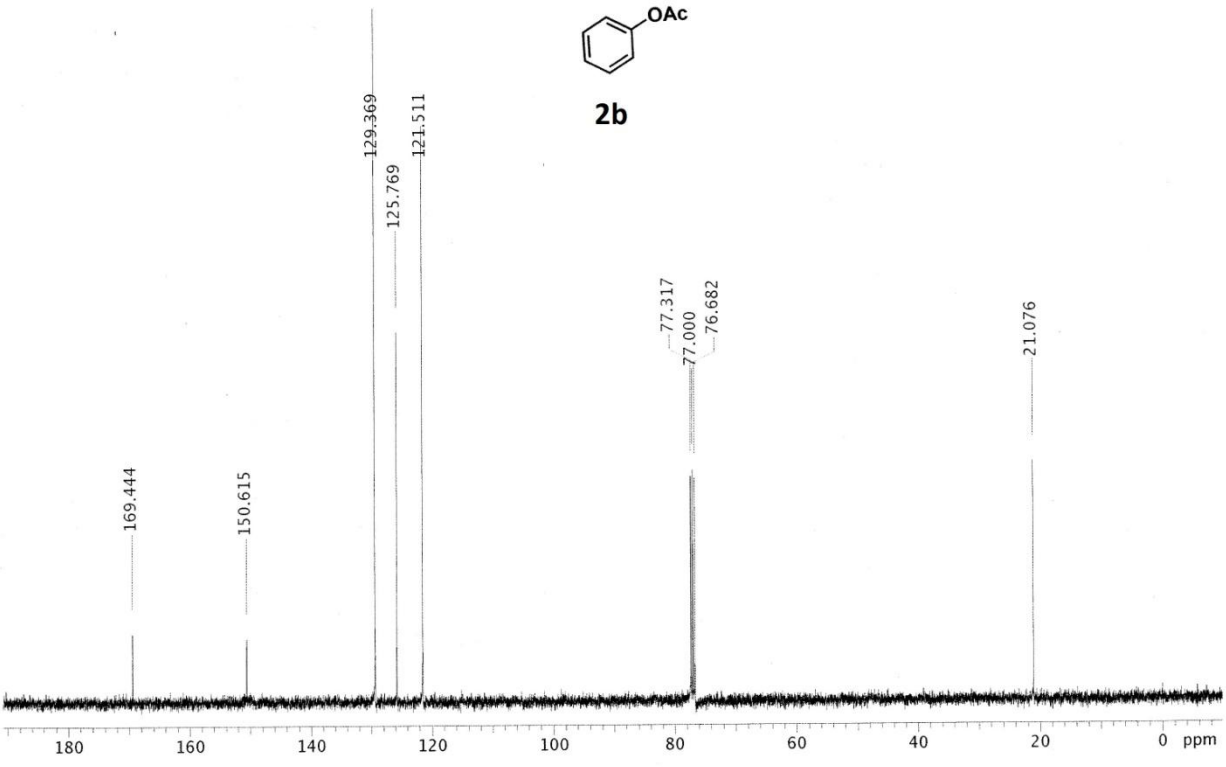
ppm

Phenyl acetate (2b)





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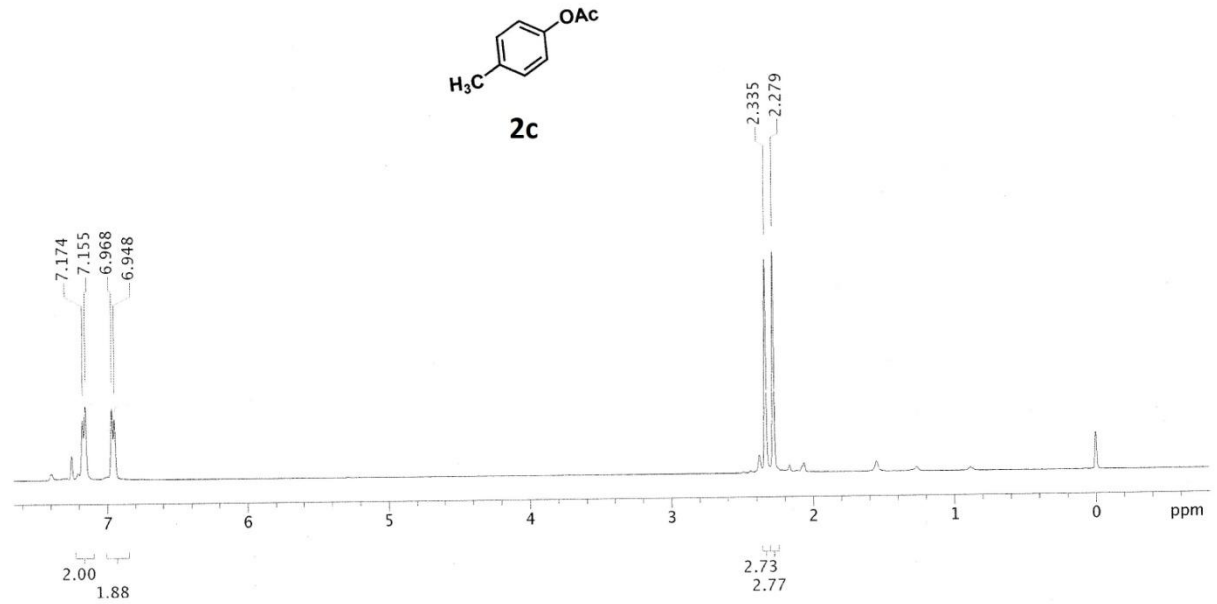

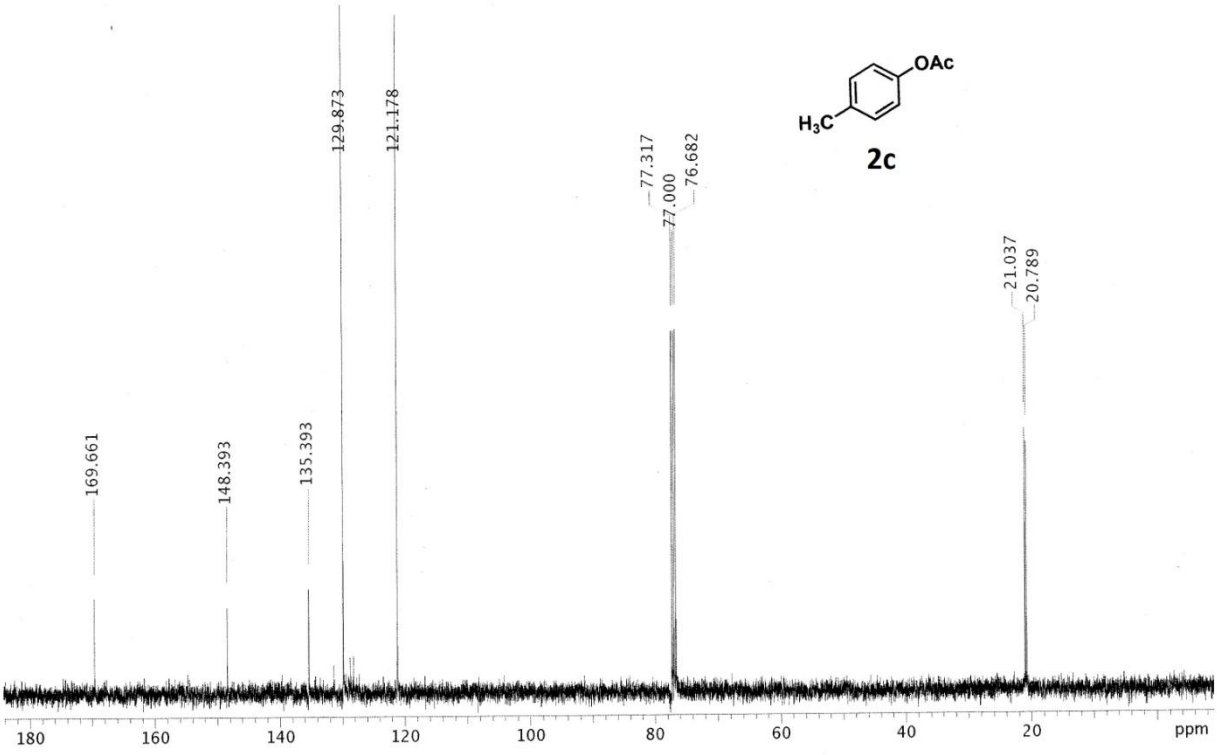

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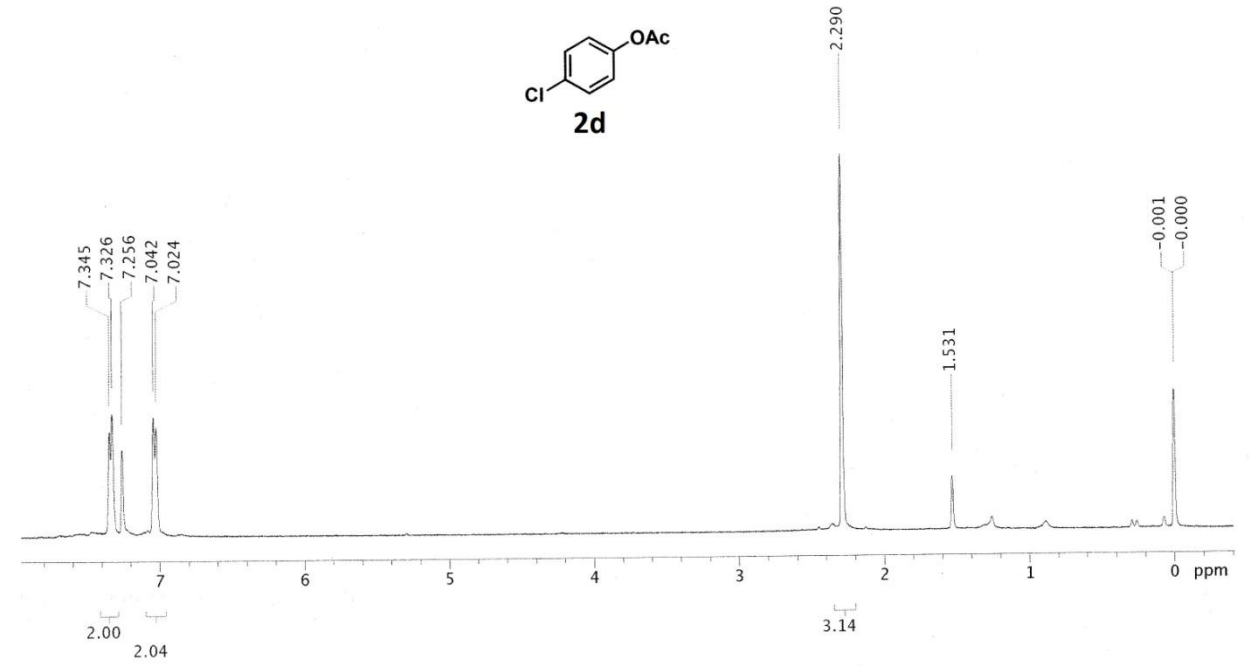

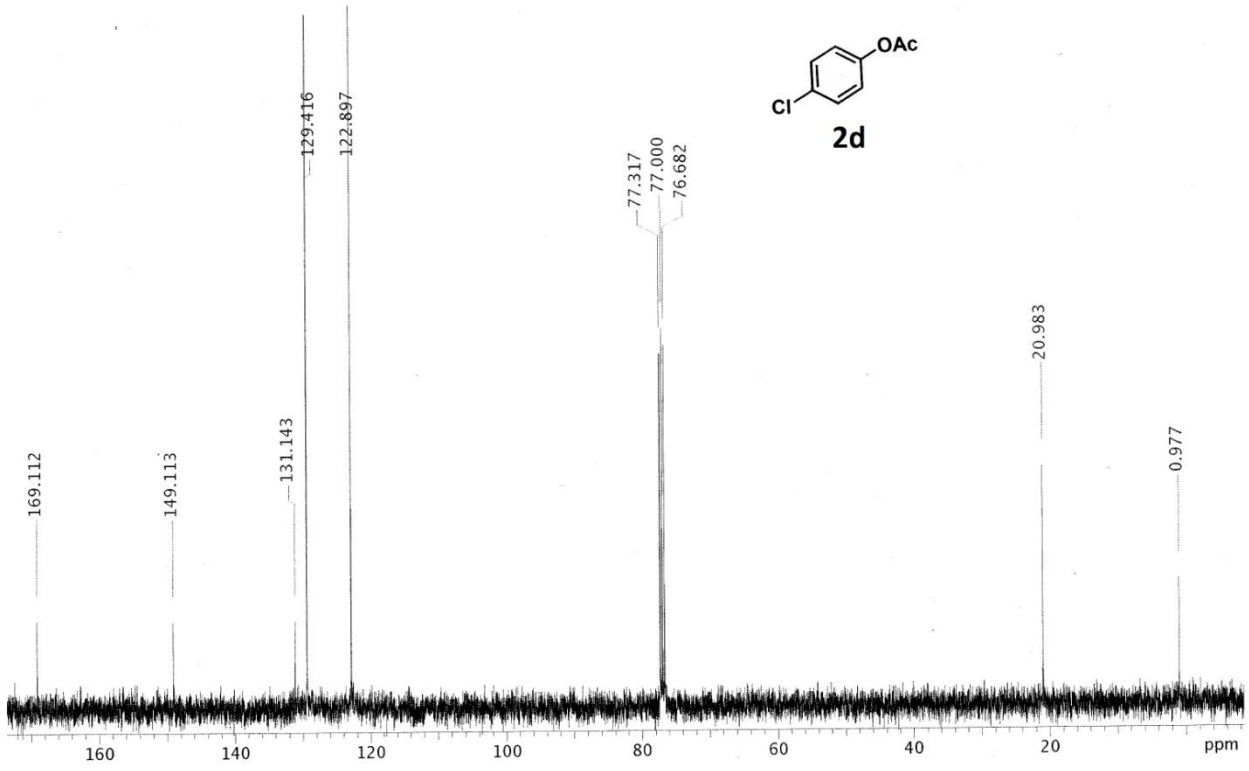

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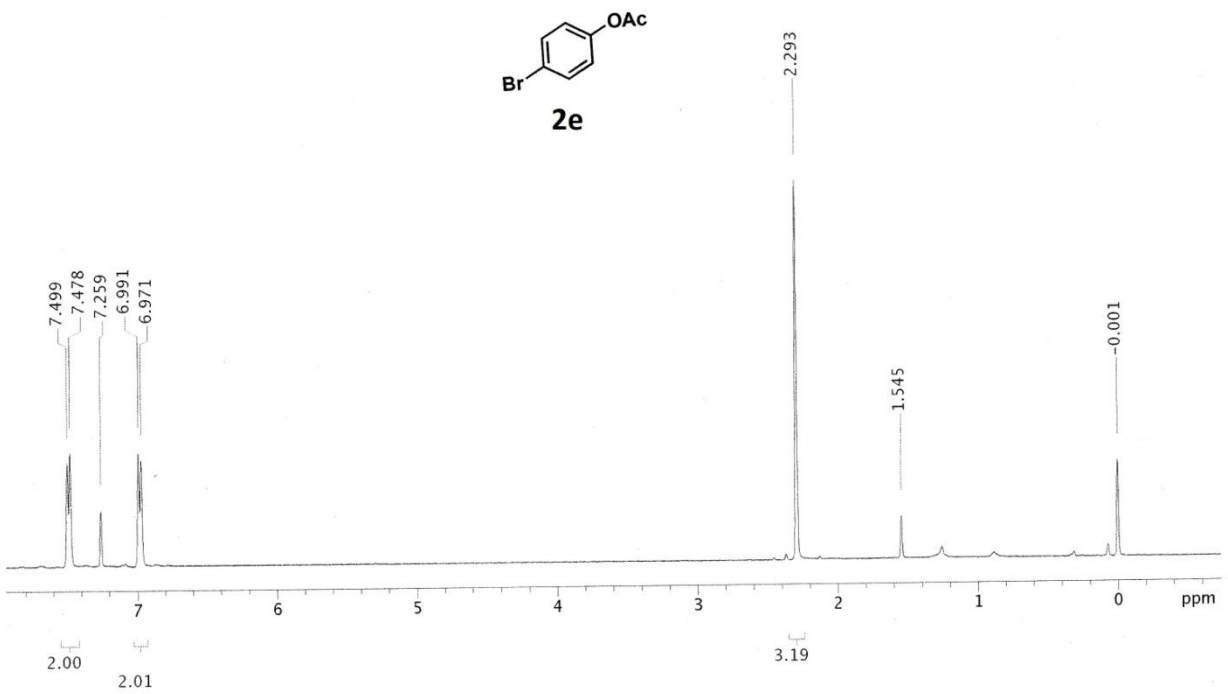

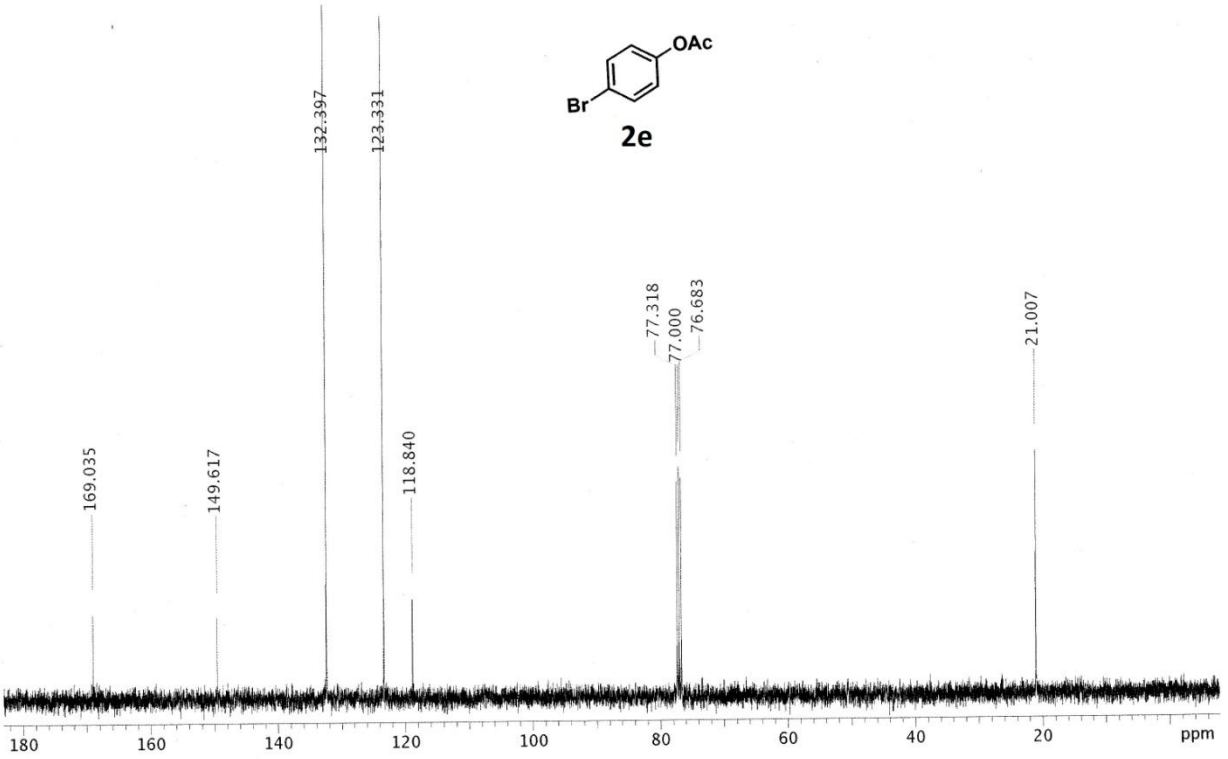

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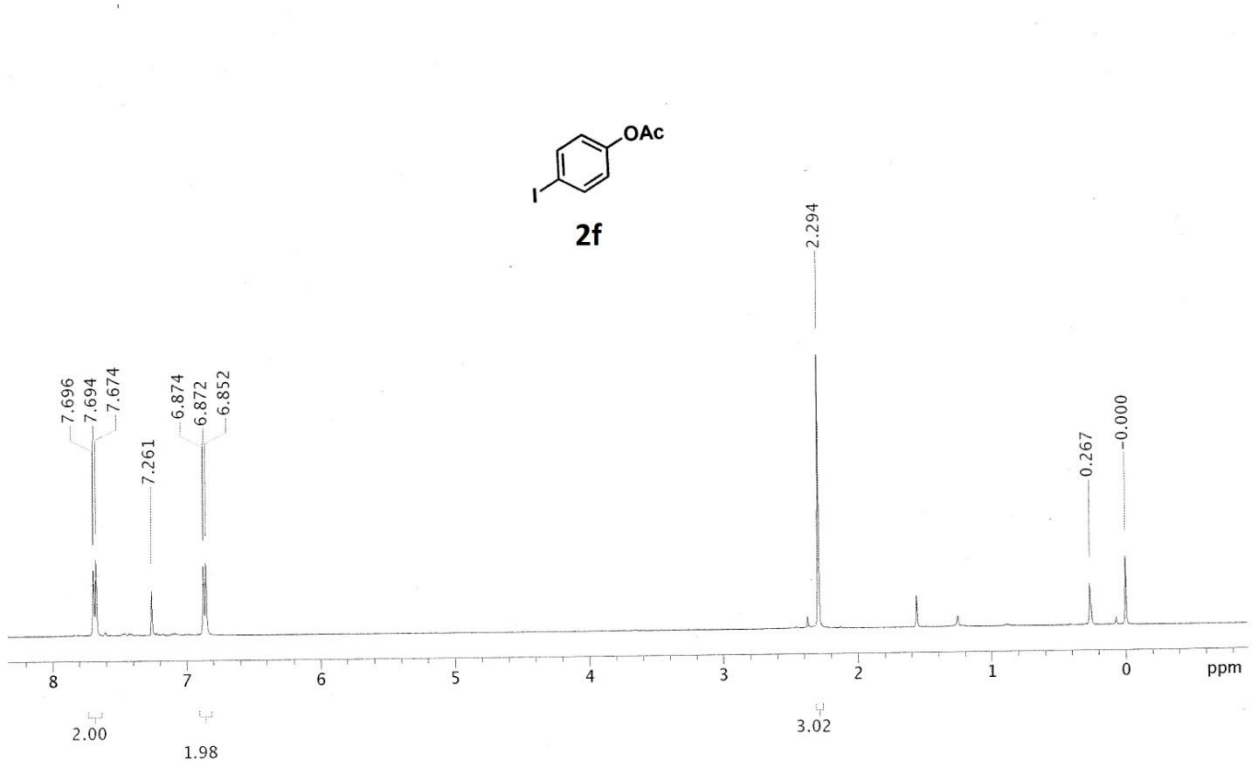

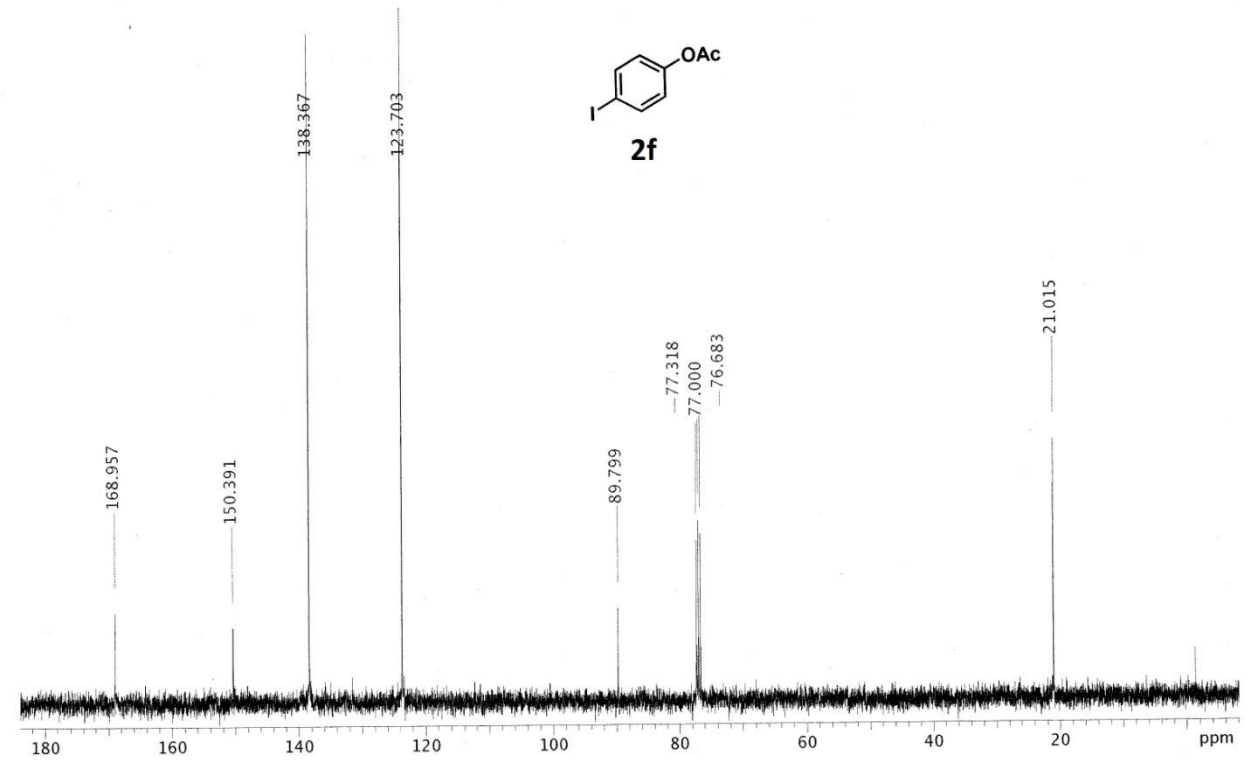

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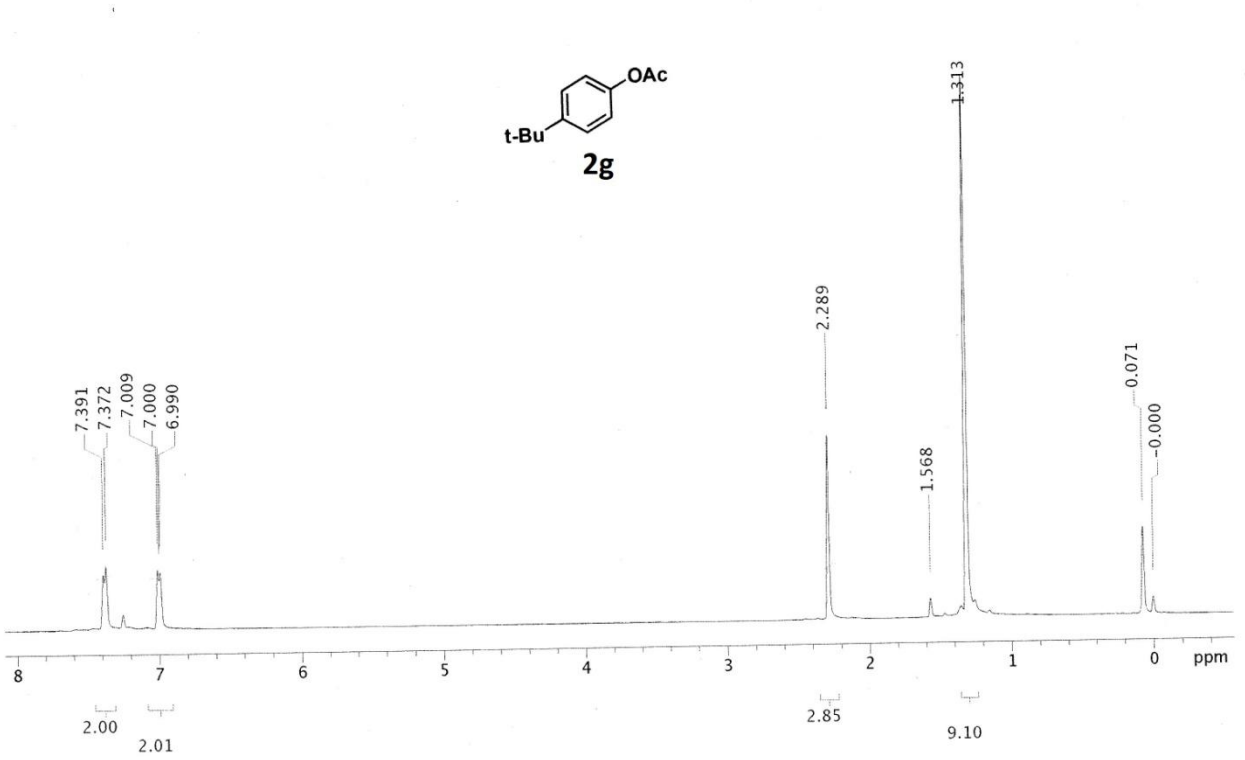

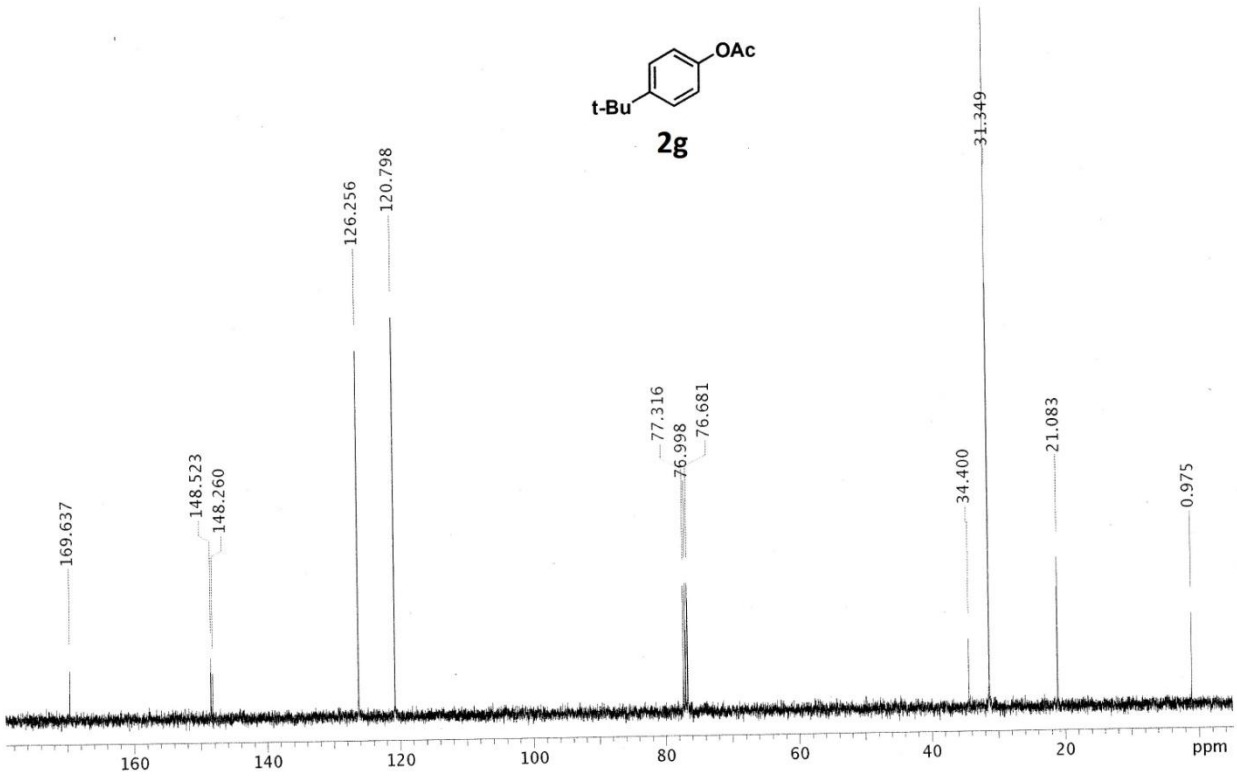

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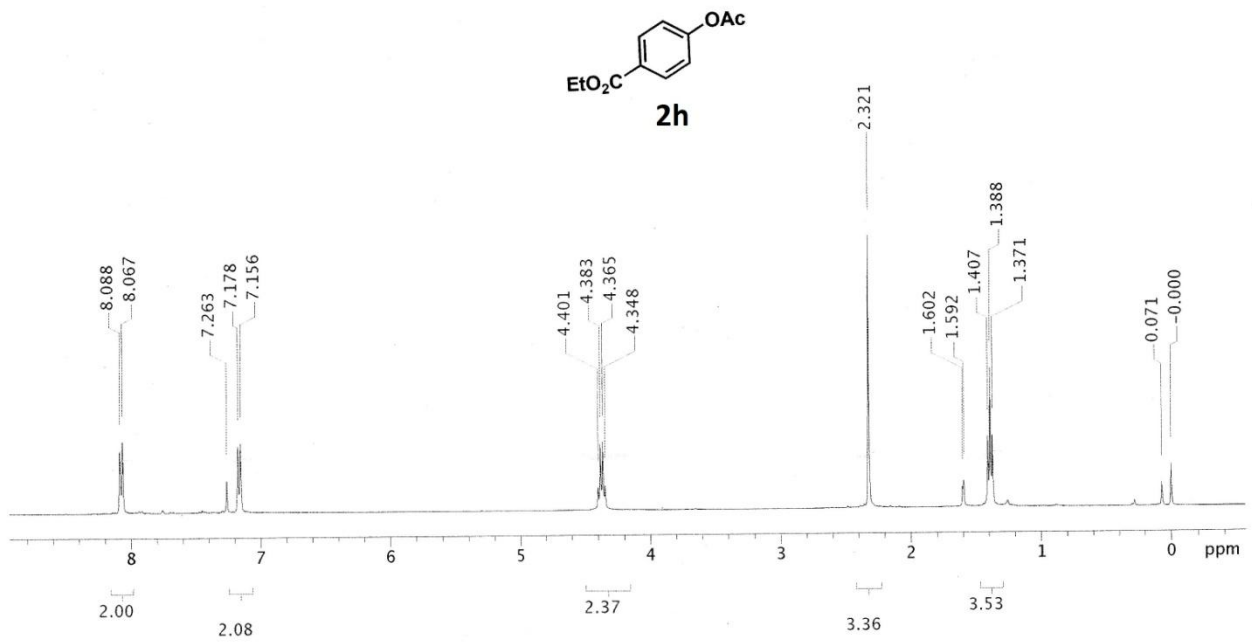
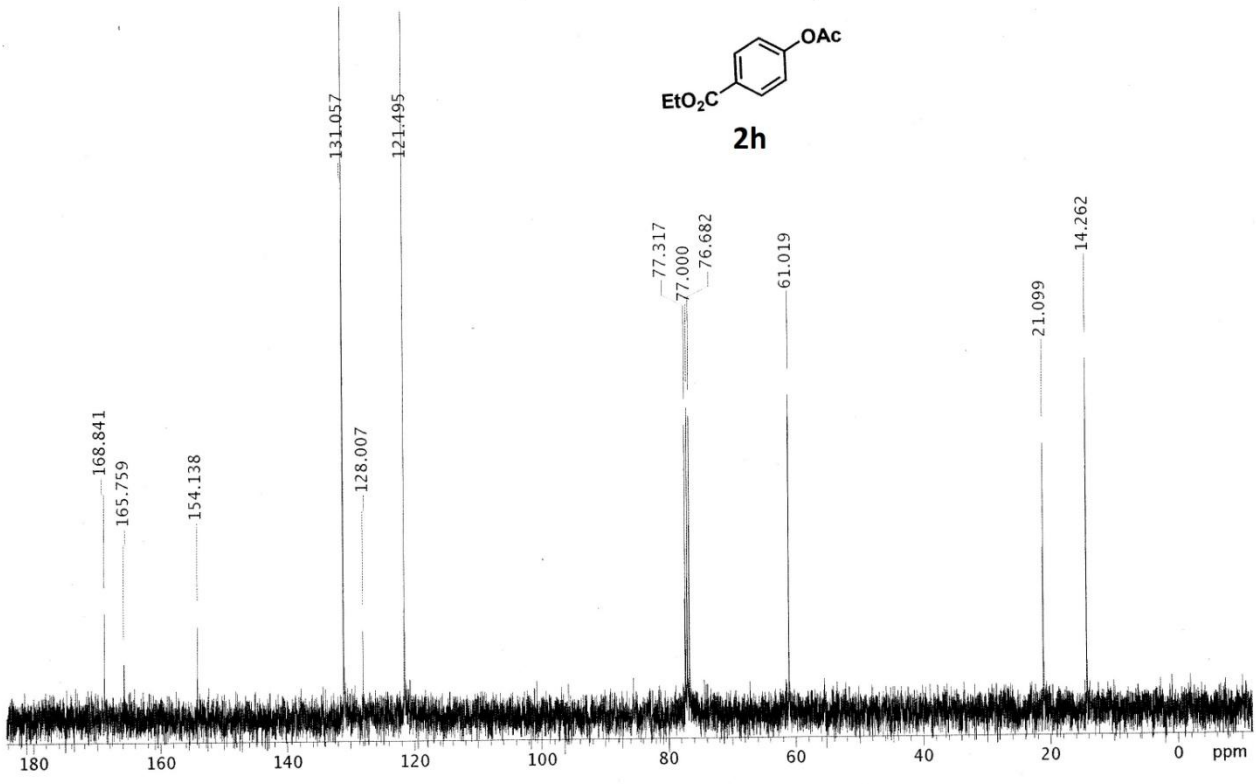
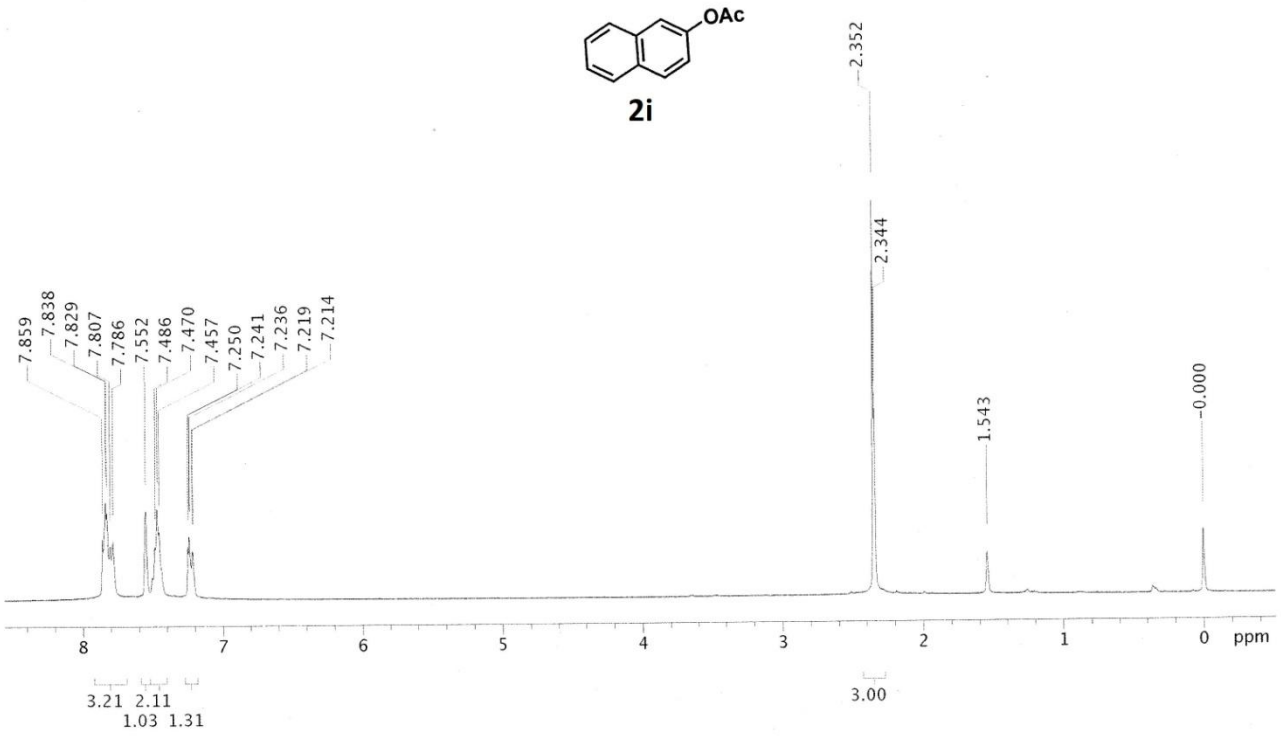
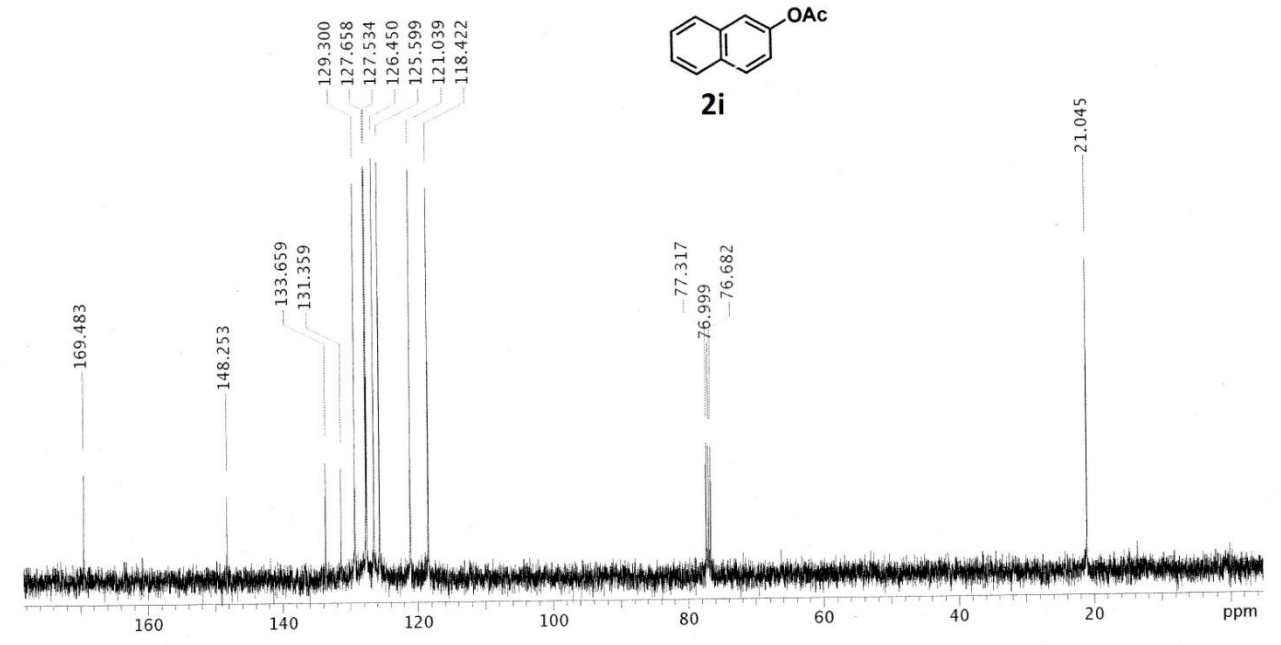


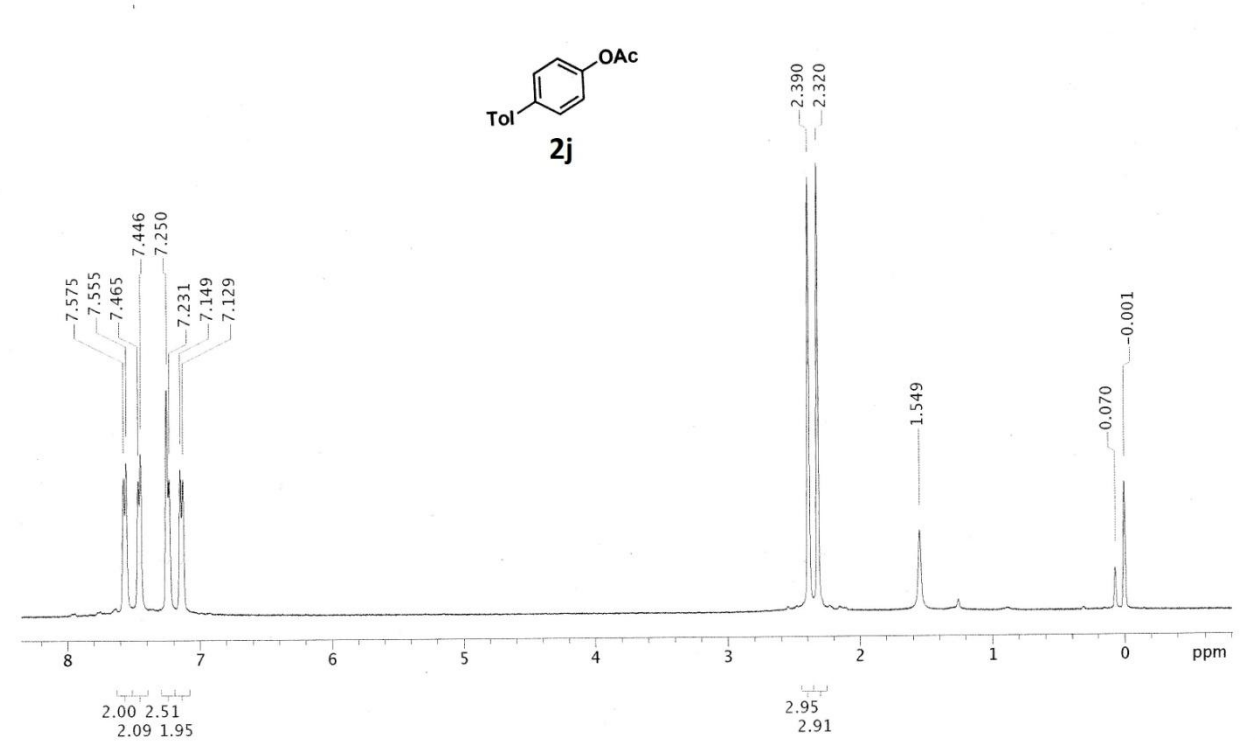


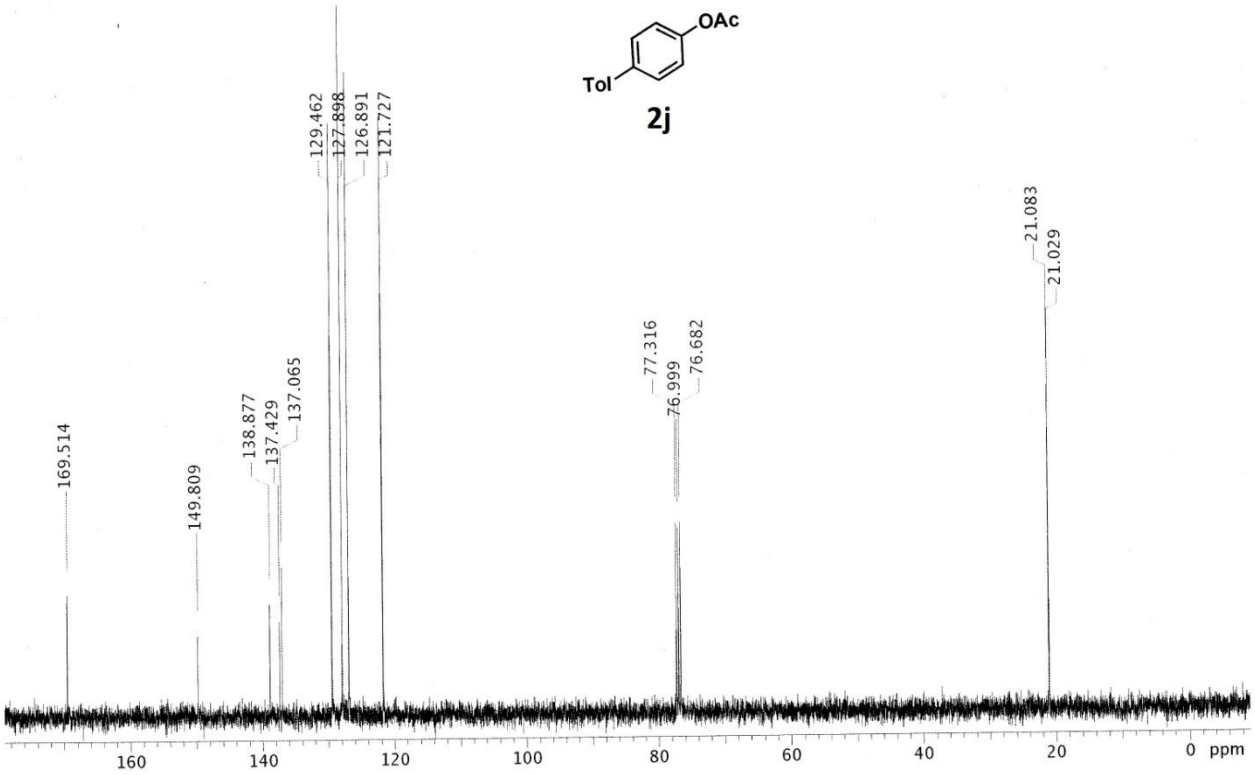
2-Acetylnaphthalene (2i)



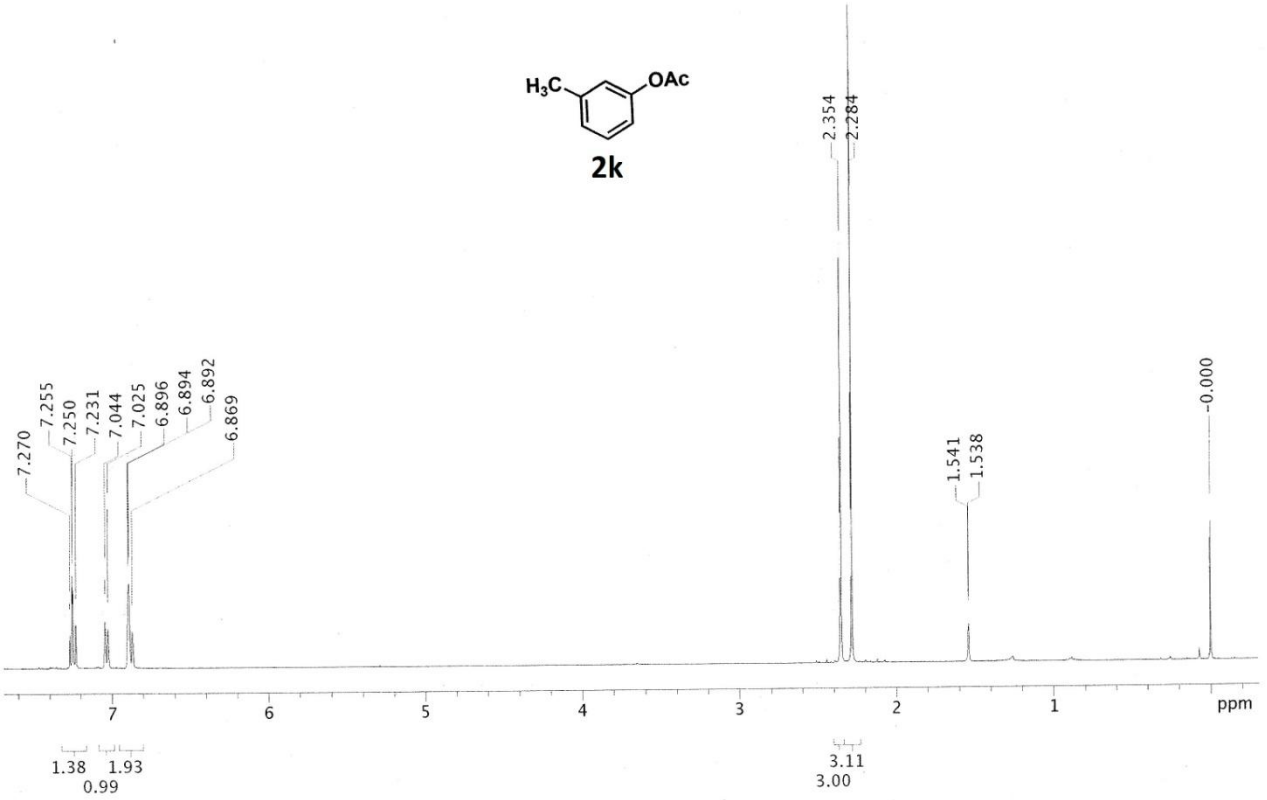


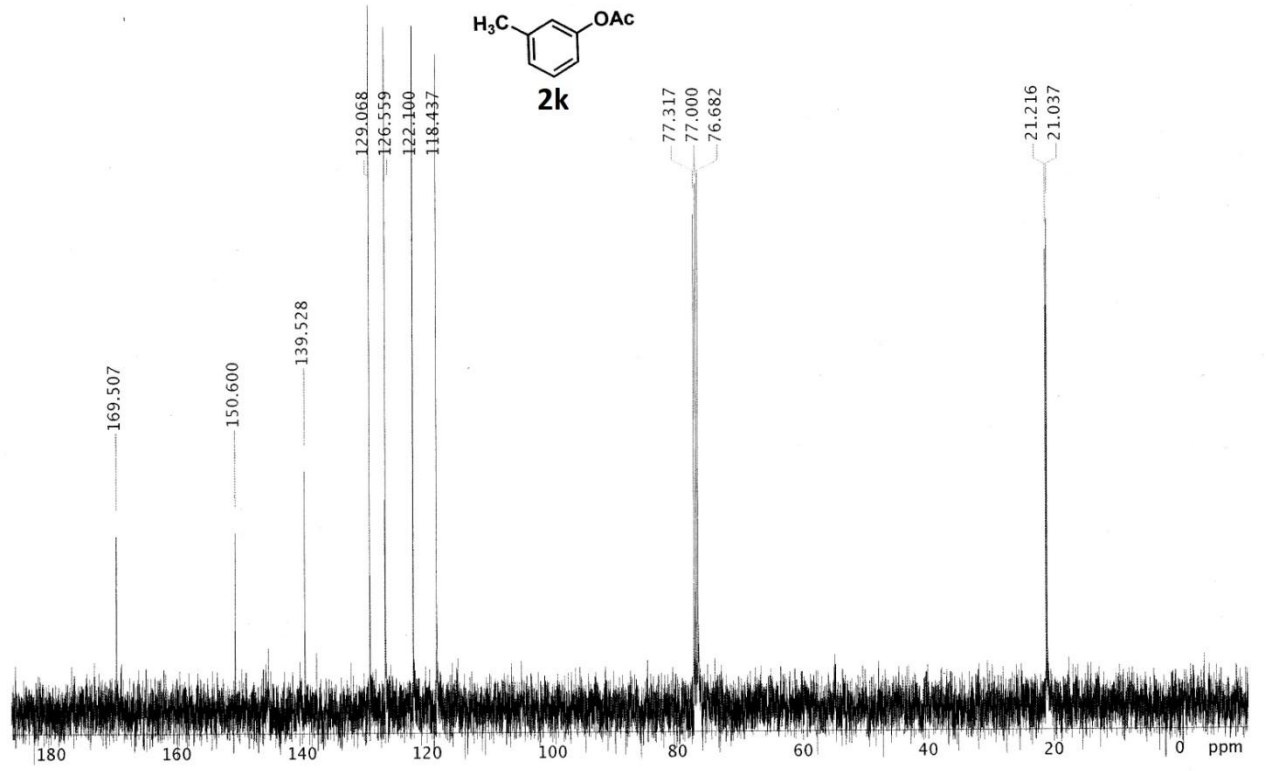
4-(4’-Mehtylphenyl)phenyl acetate (2j)



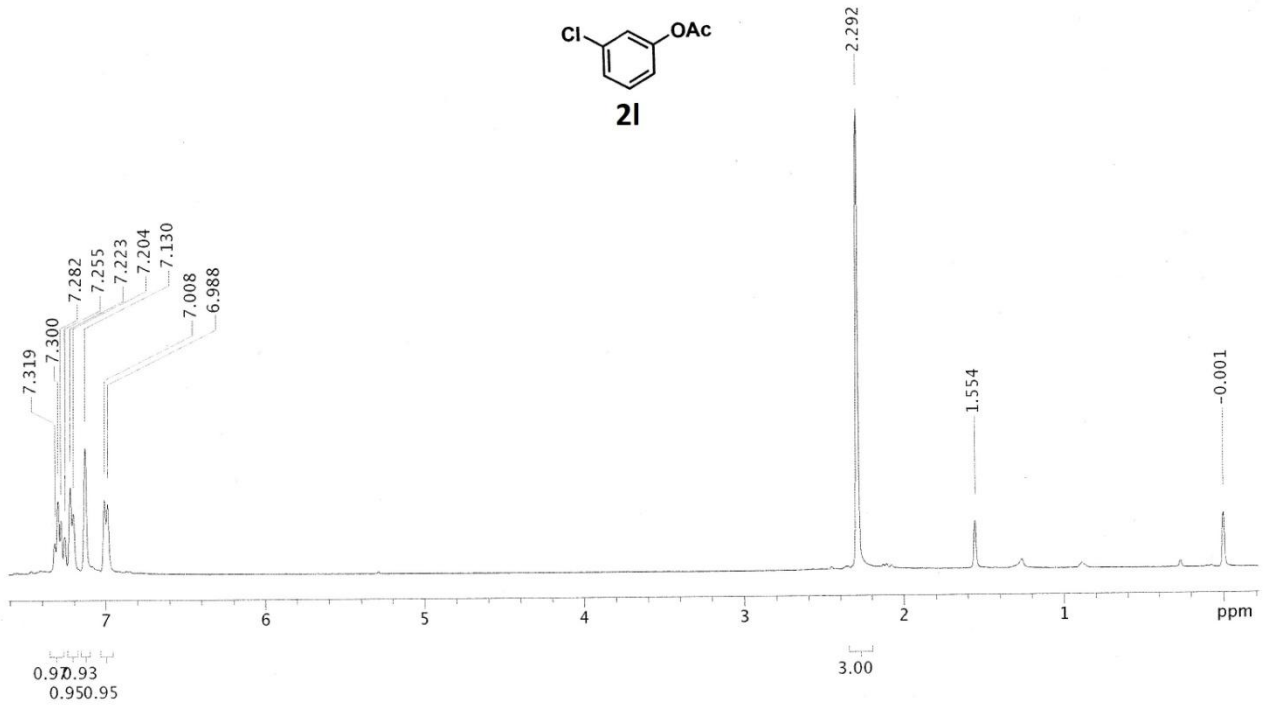


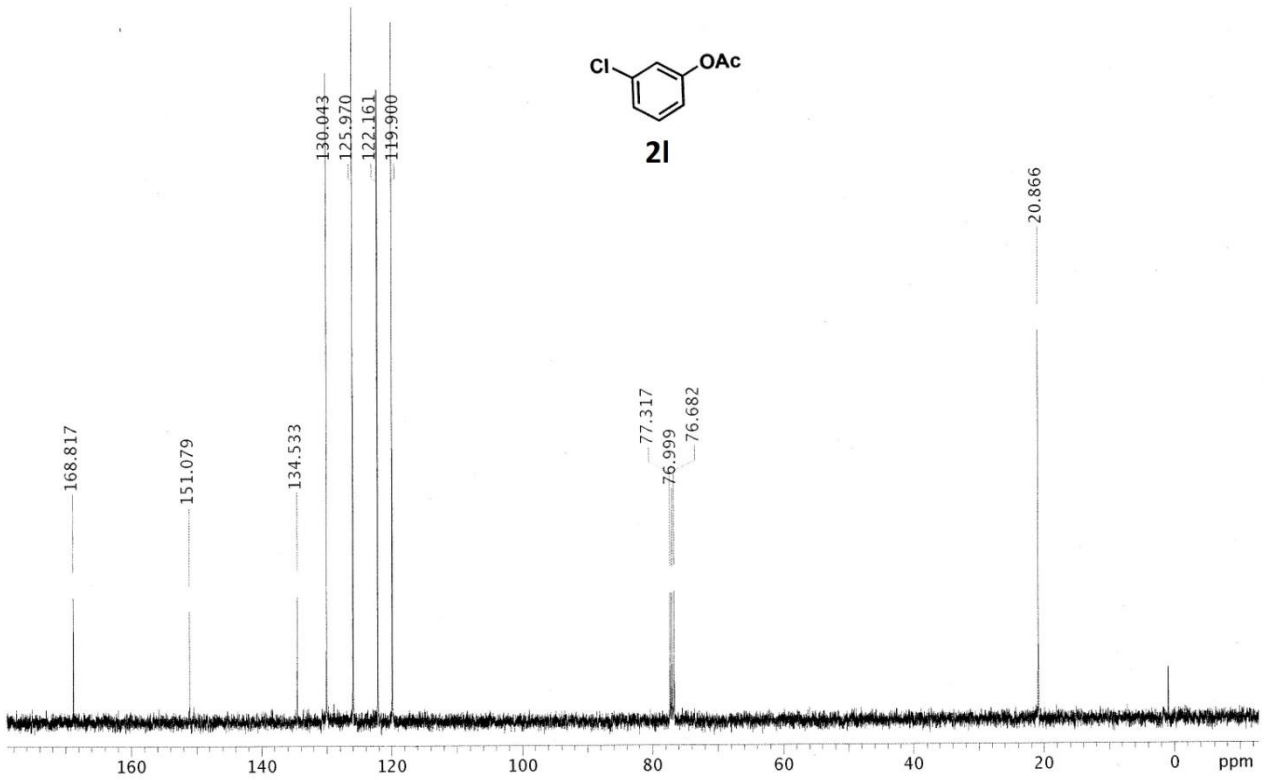
3-Methylphenyl acetate (2k)



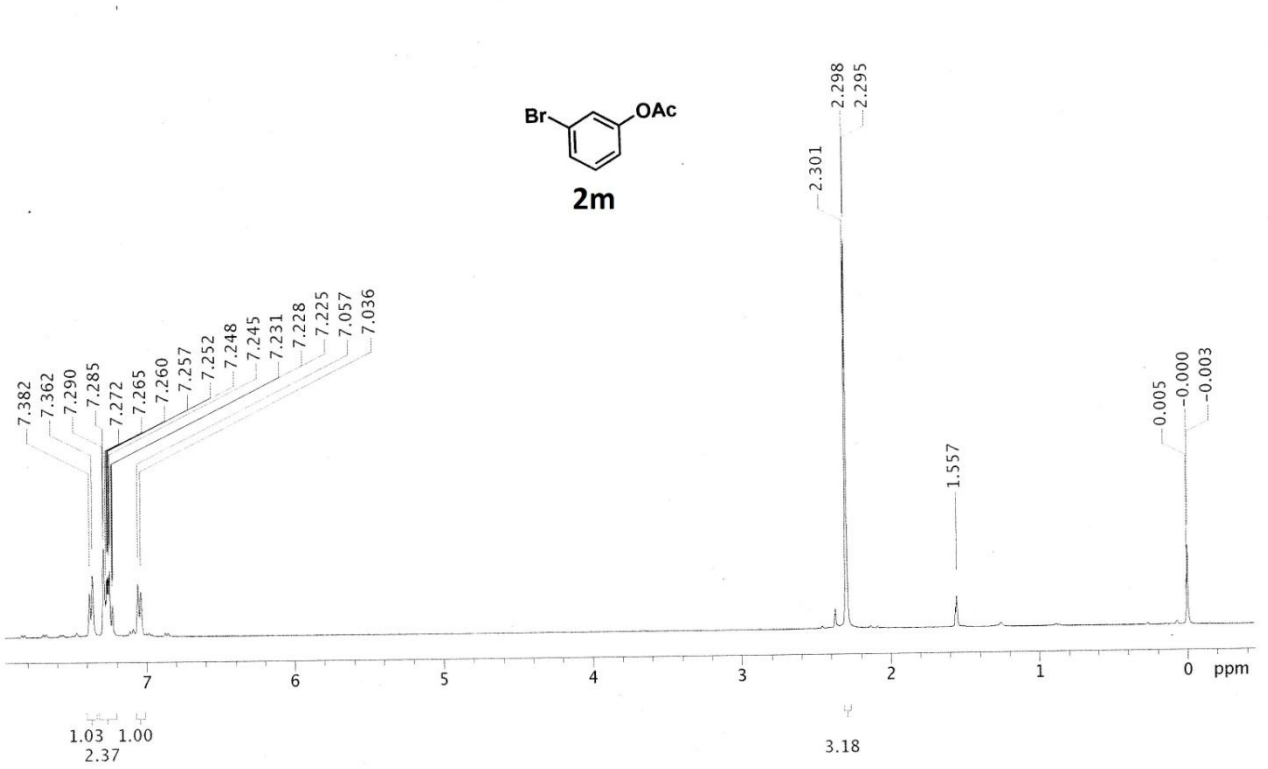


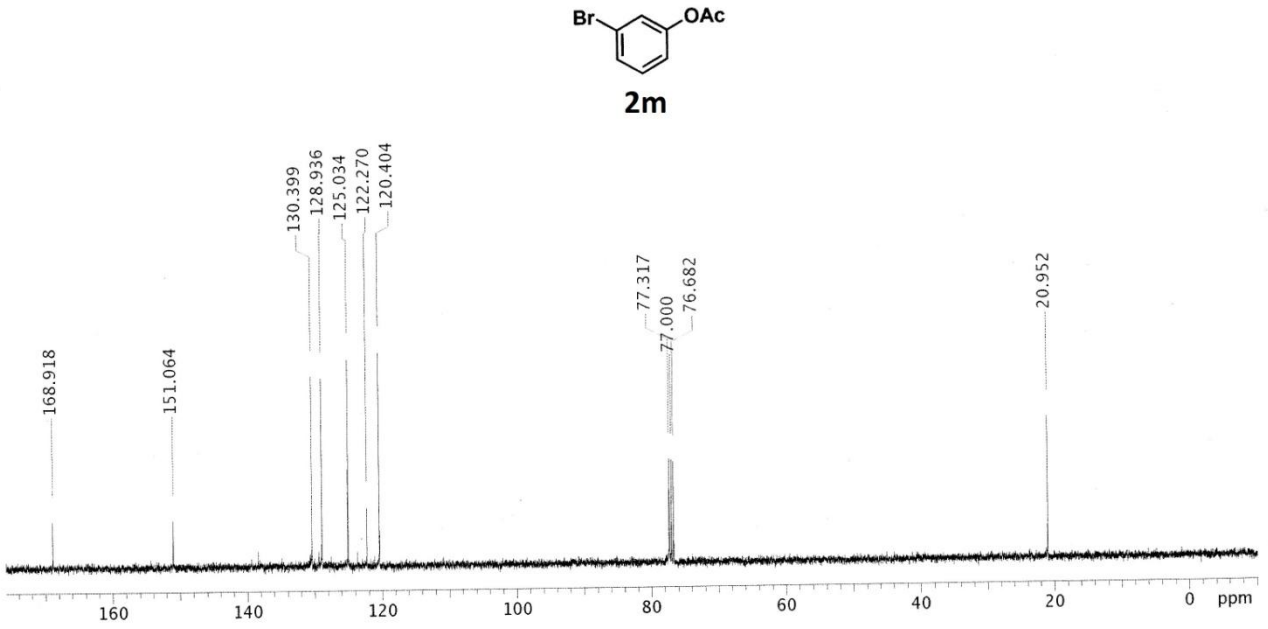
3-Chlorophenyl acetate (2l)



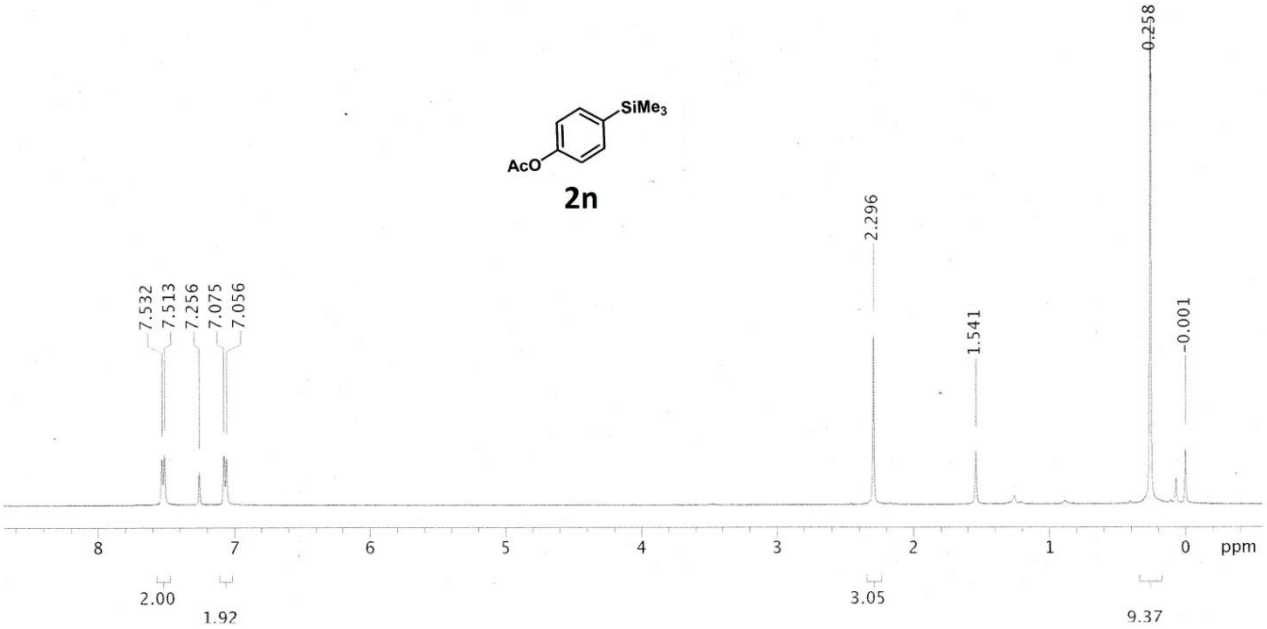


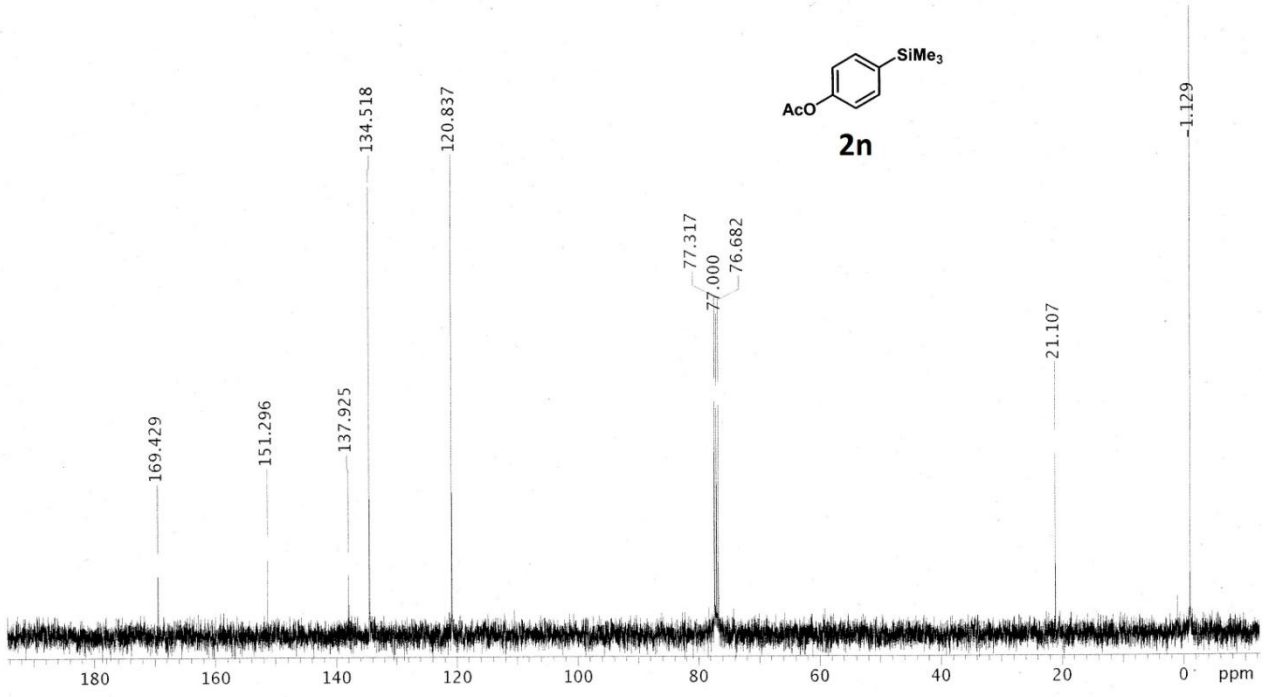
3-Bromophenyl acetate (2m)



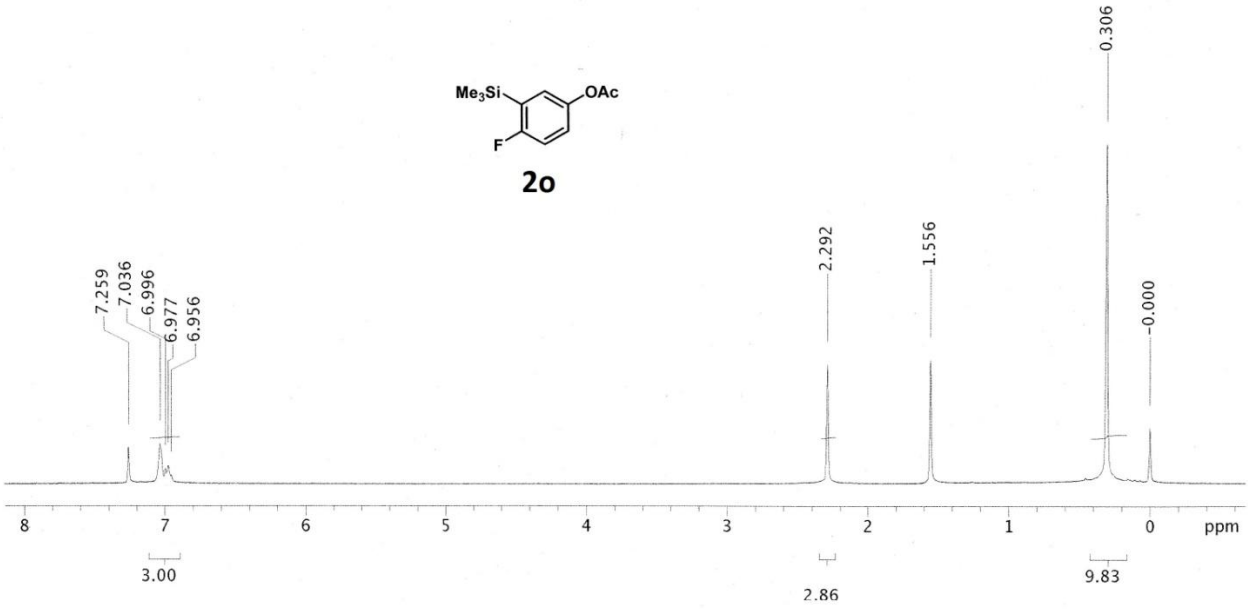


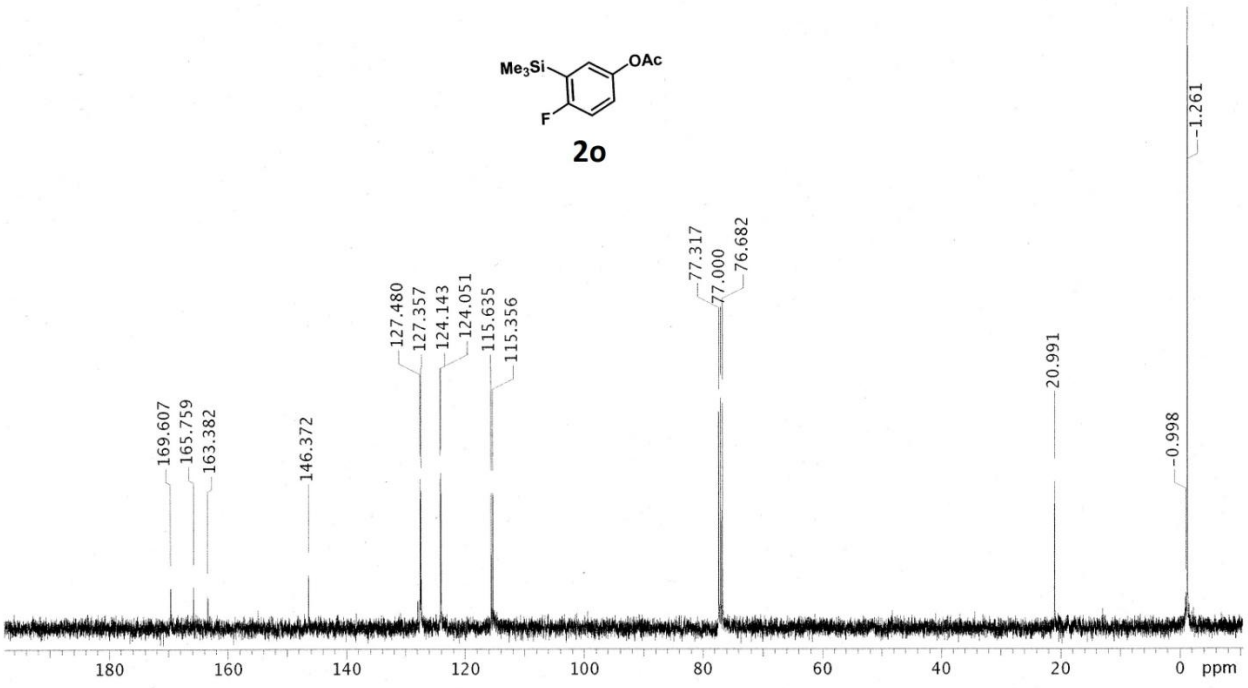
4-Trimethylsilylphenyl acetate (2n)

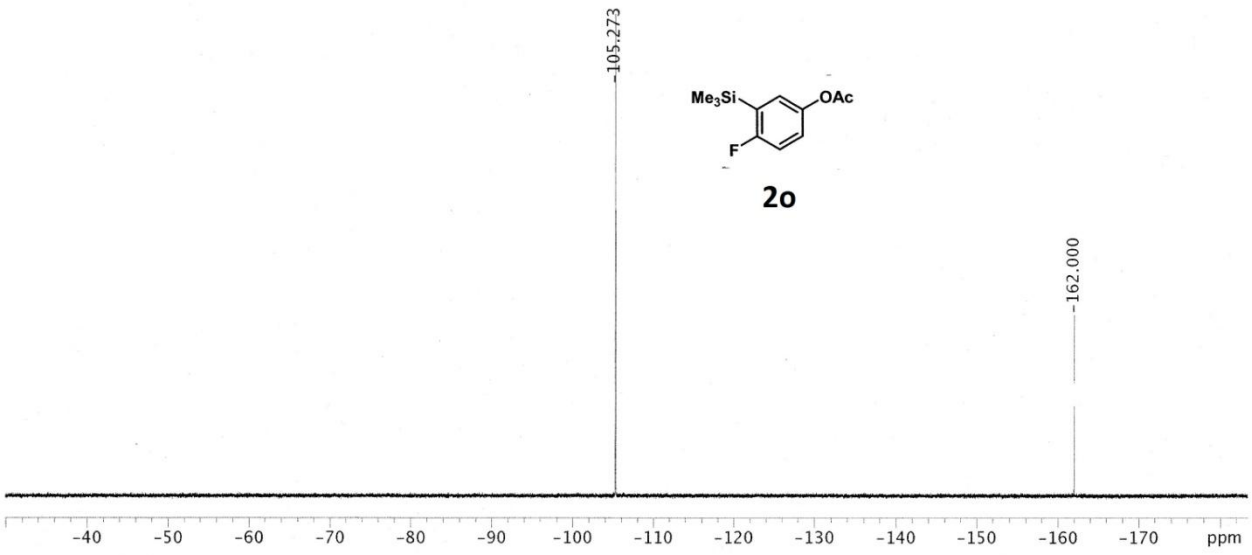




4-Fluoro-3-trimethysilylphenyl acetate (2o)



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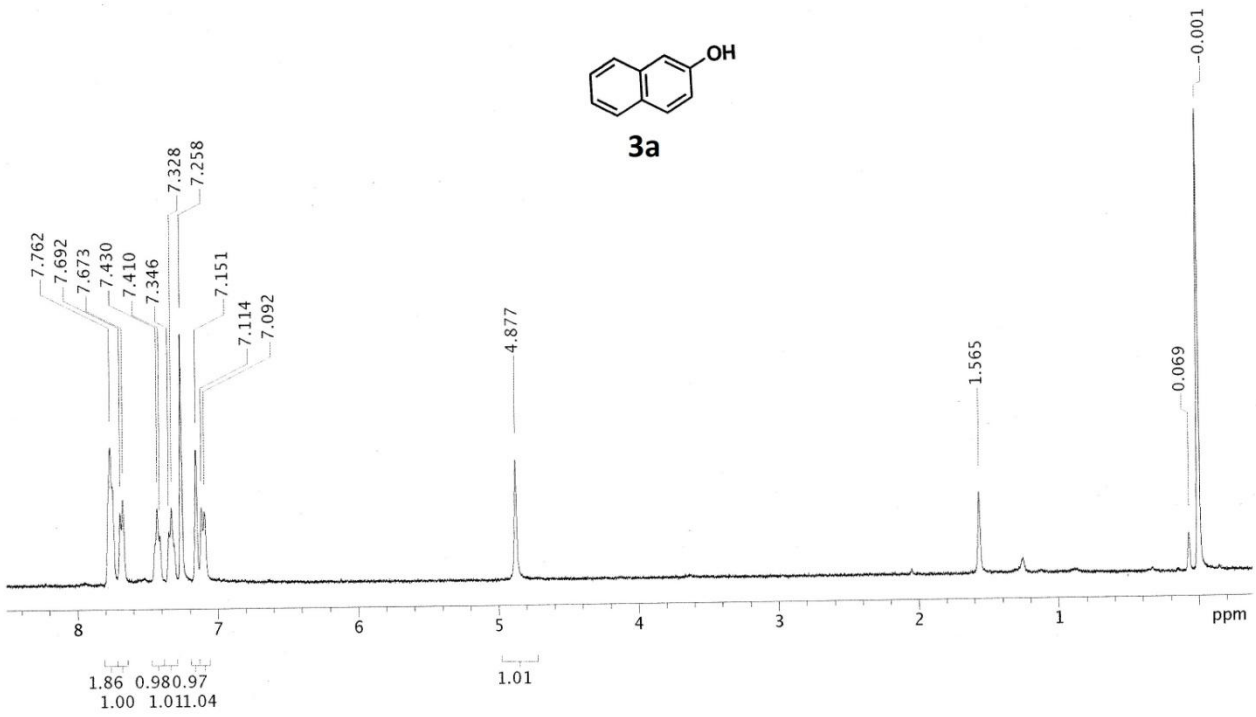
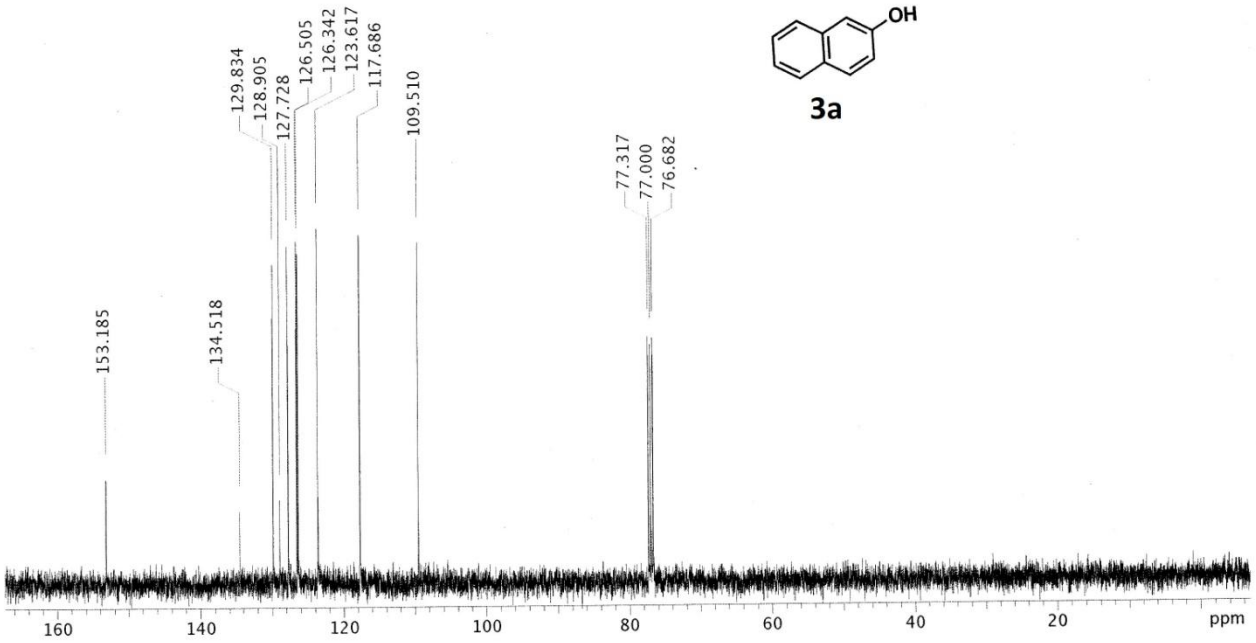
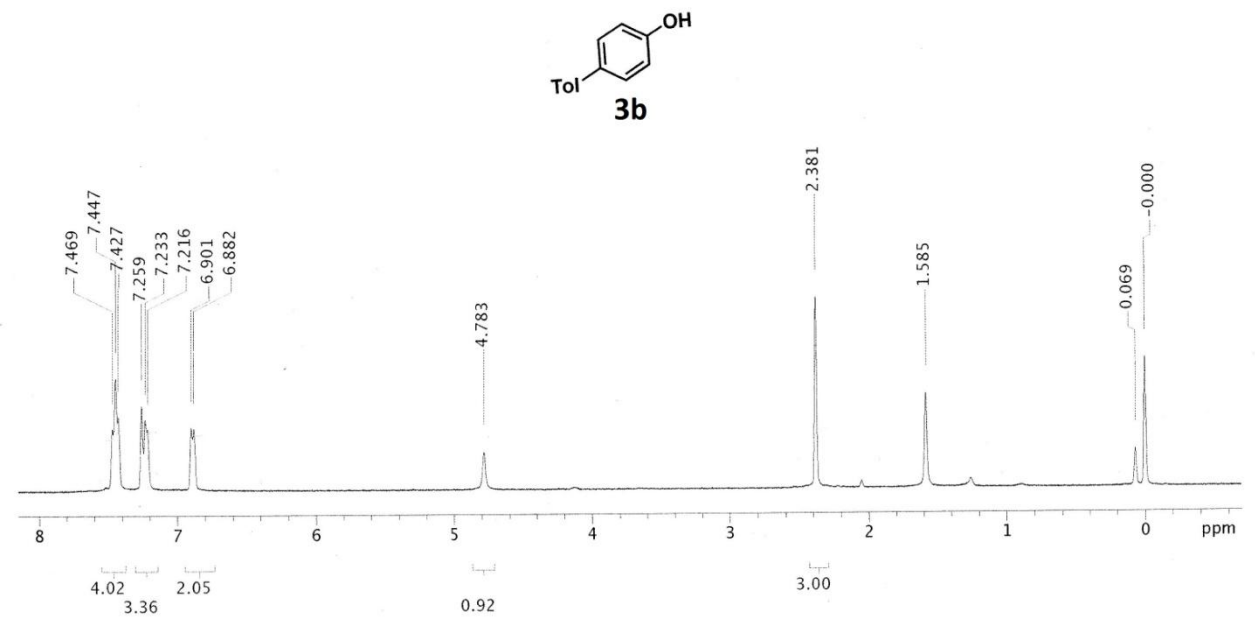
Me3Si
OAc
F
2o
-162.000
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
ppm

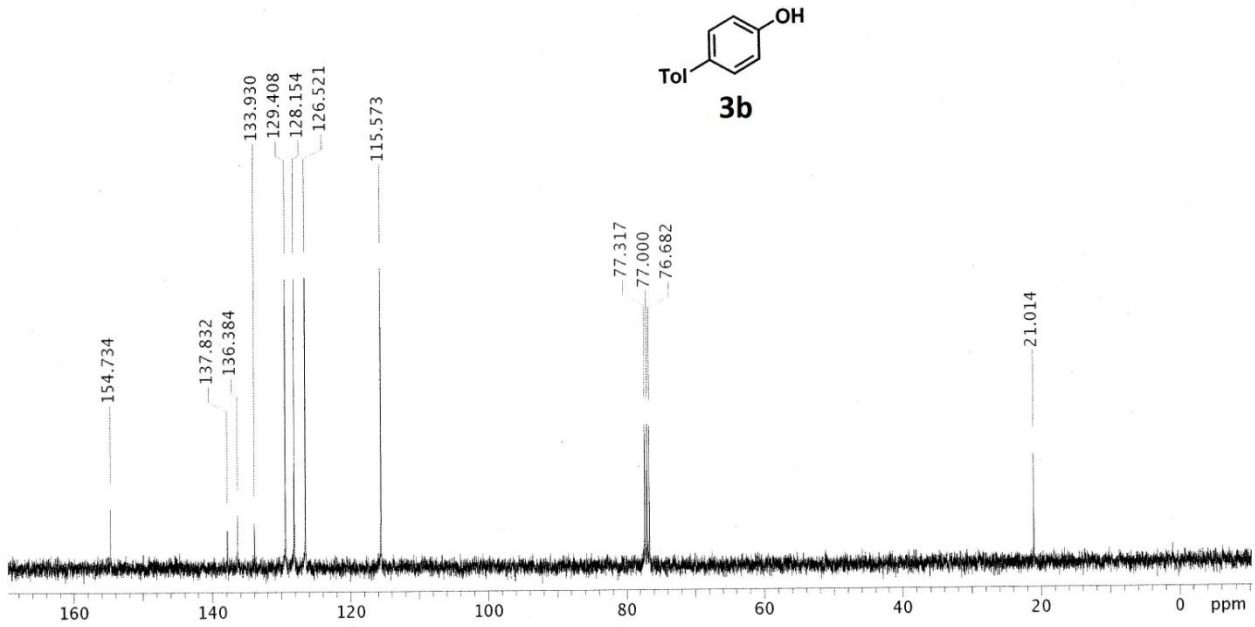
2-Naphthol (3a)



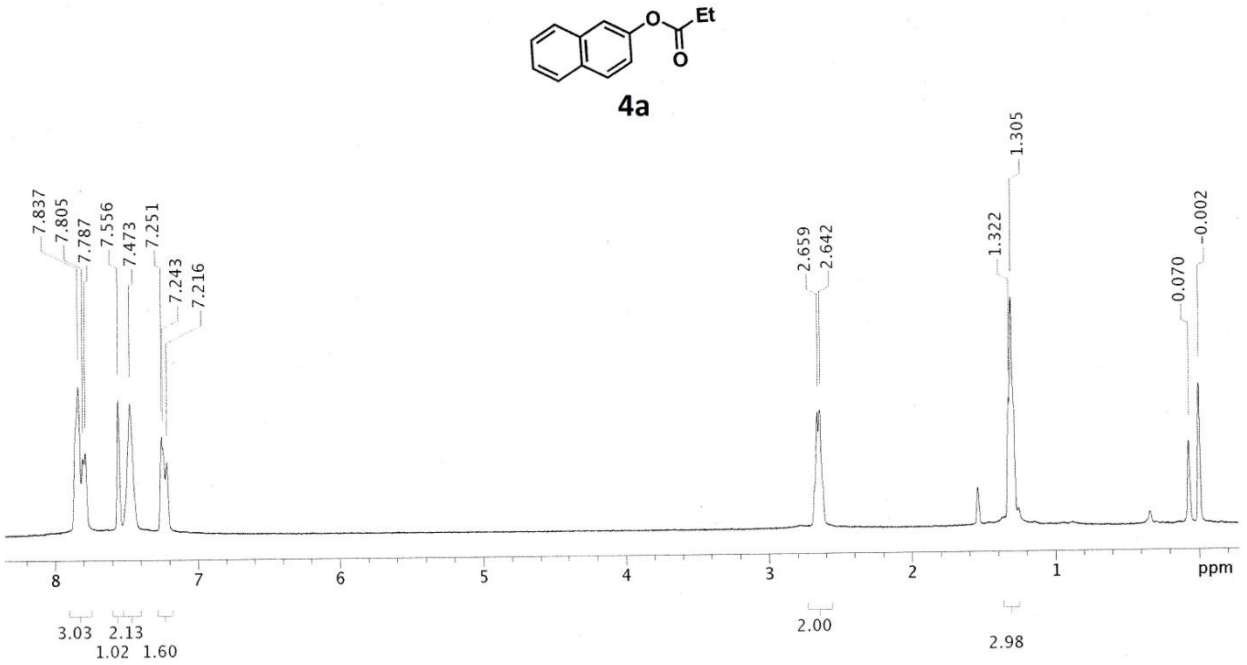


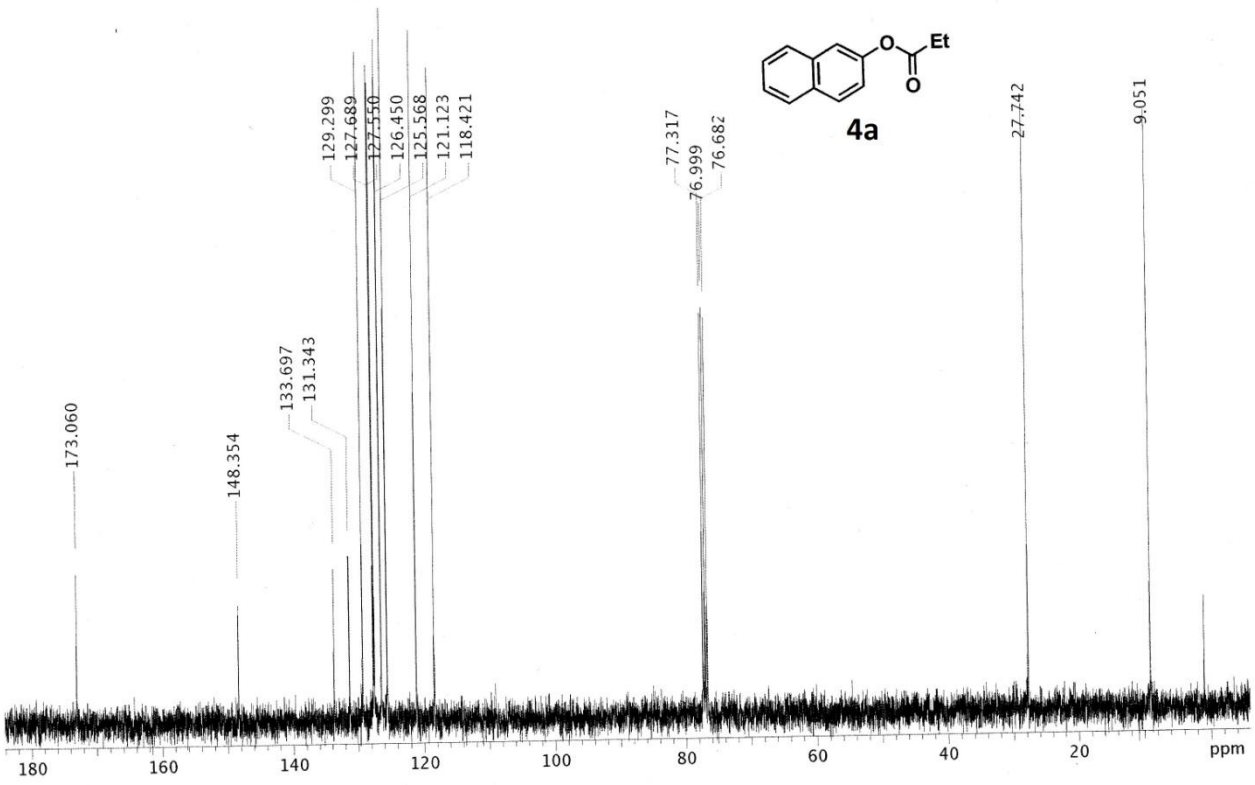
4-(4’-Methylphenyl)phenol (3b)



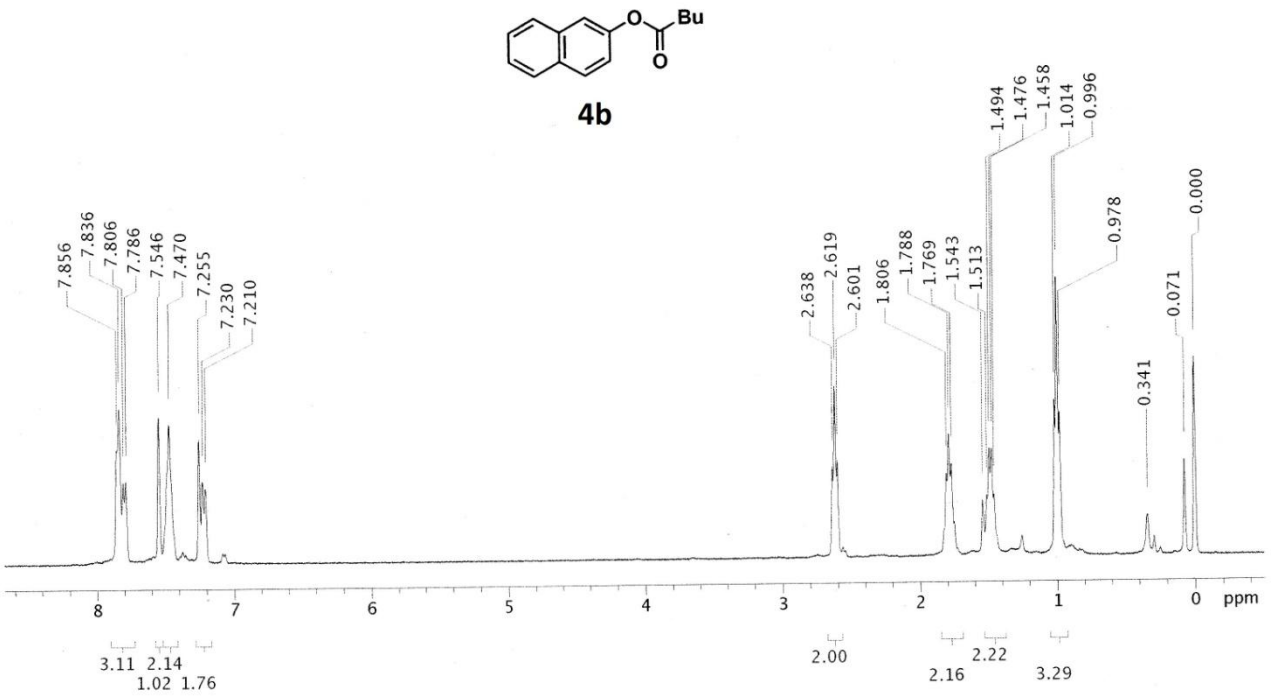


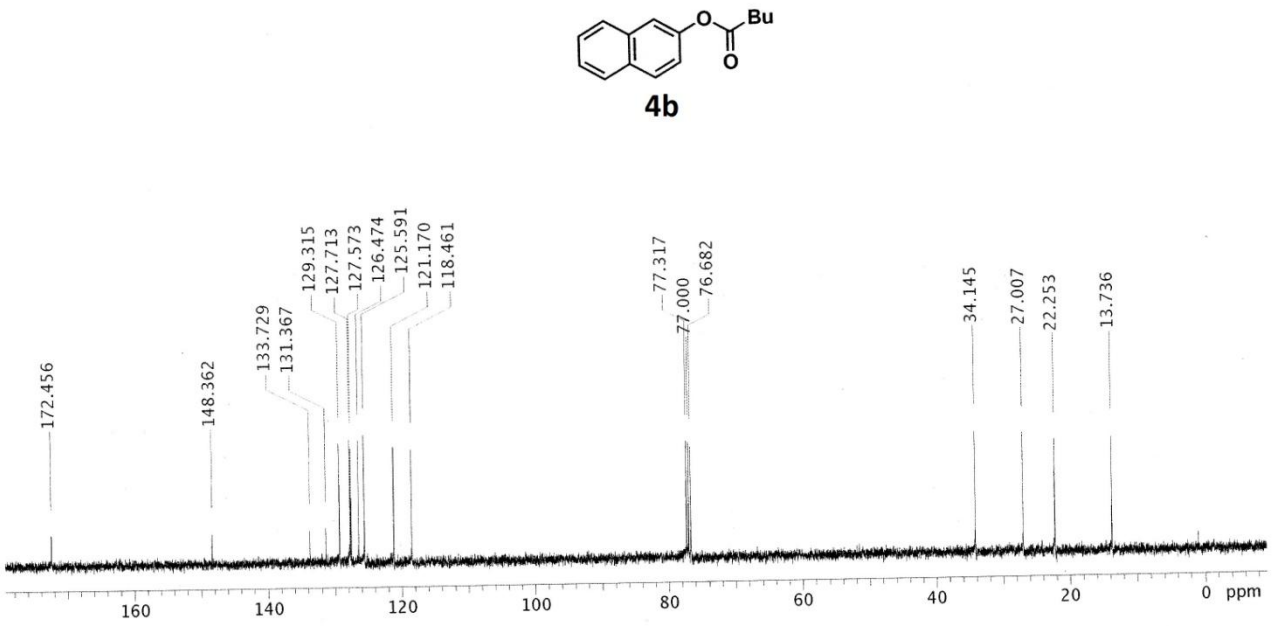
2-Naphthyl propanoate (4a)



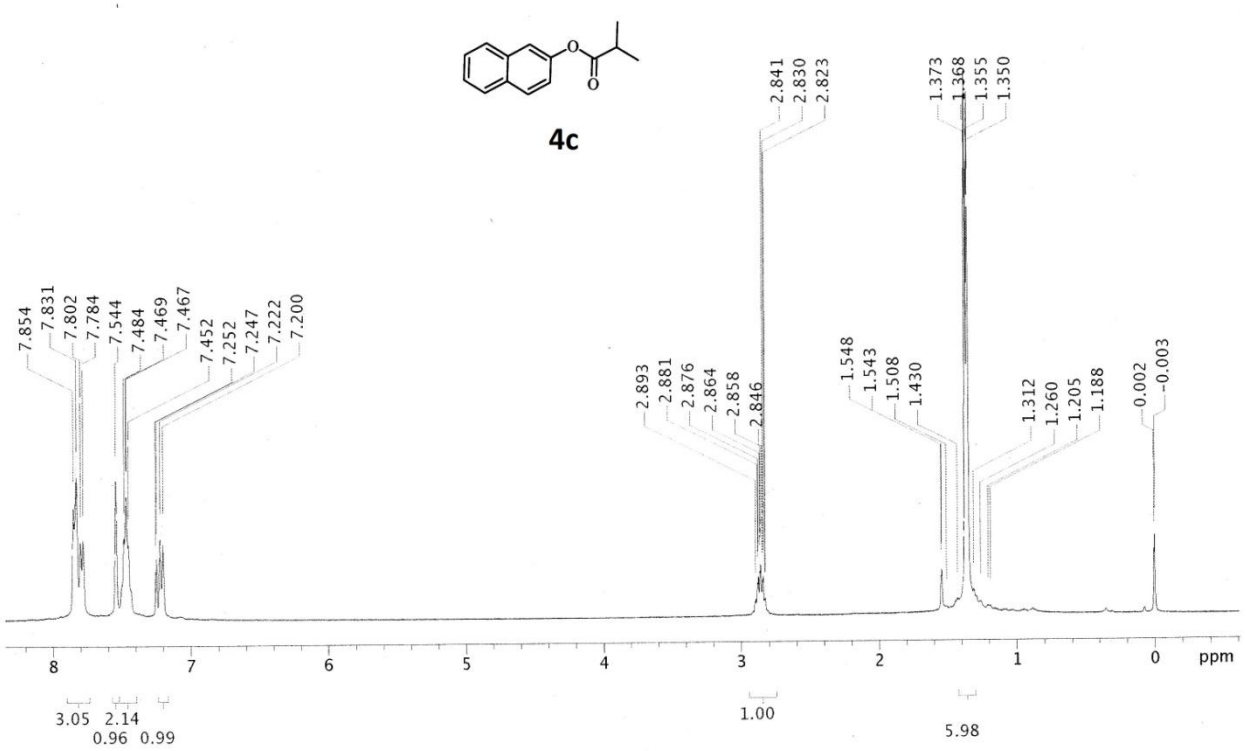


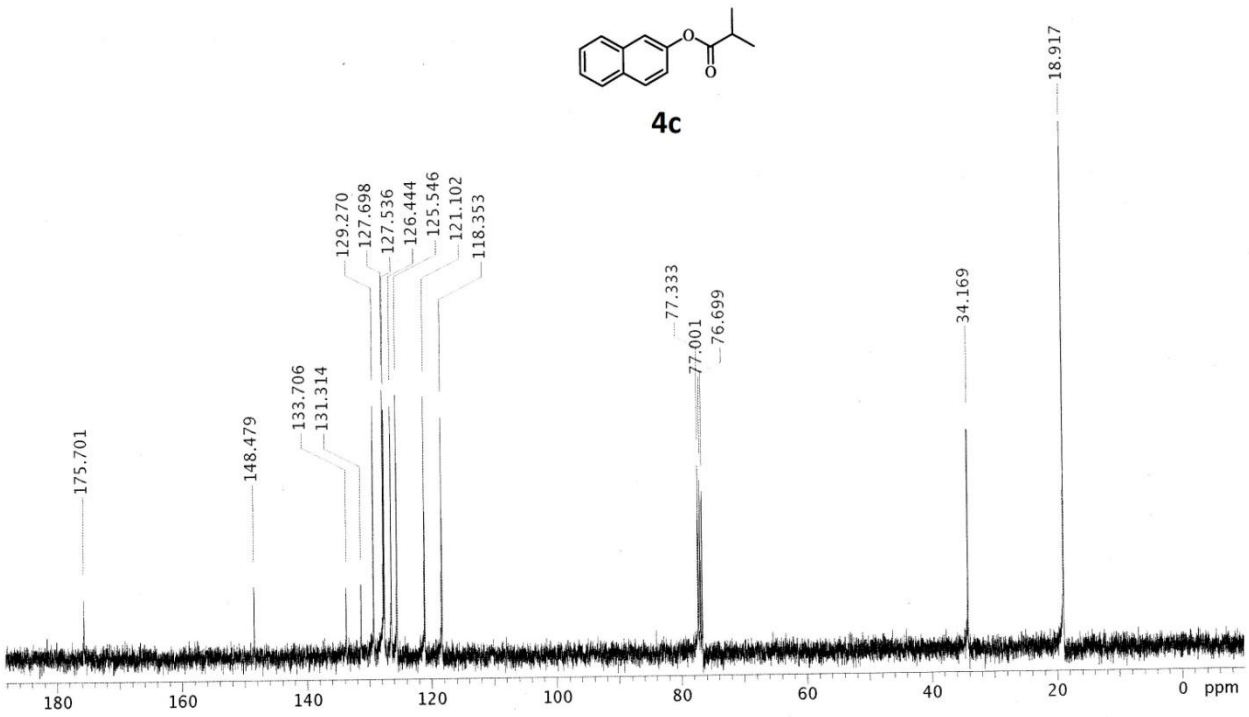
2-Naphthyl pentanoate (4b)



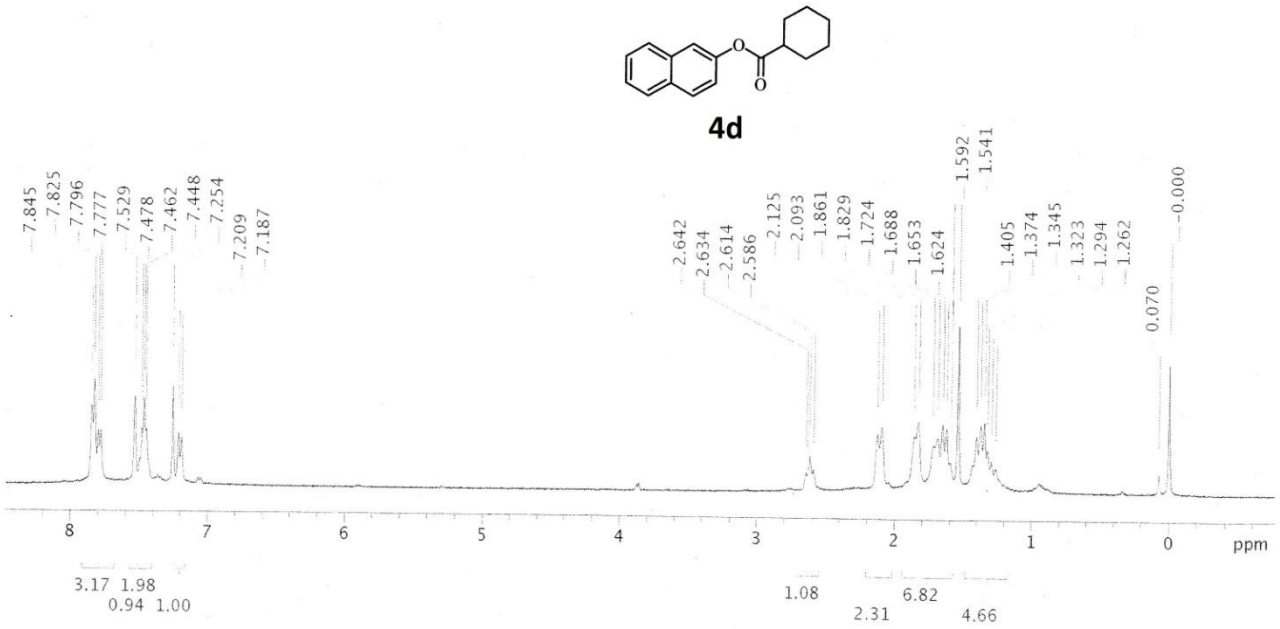


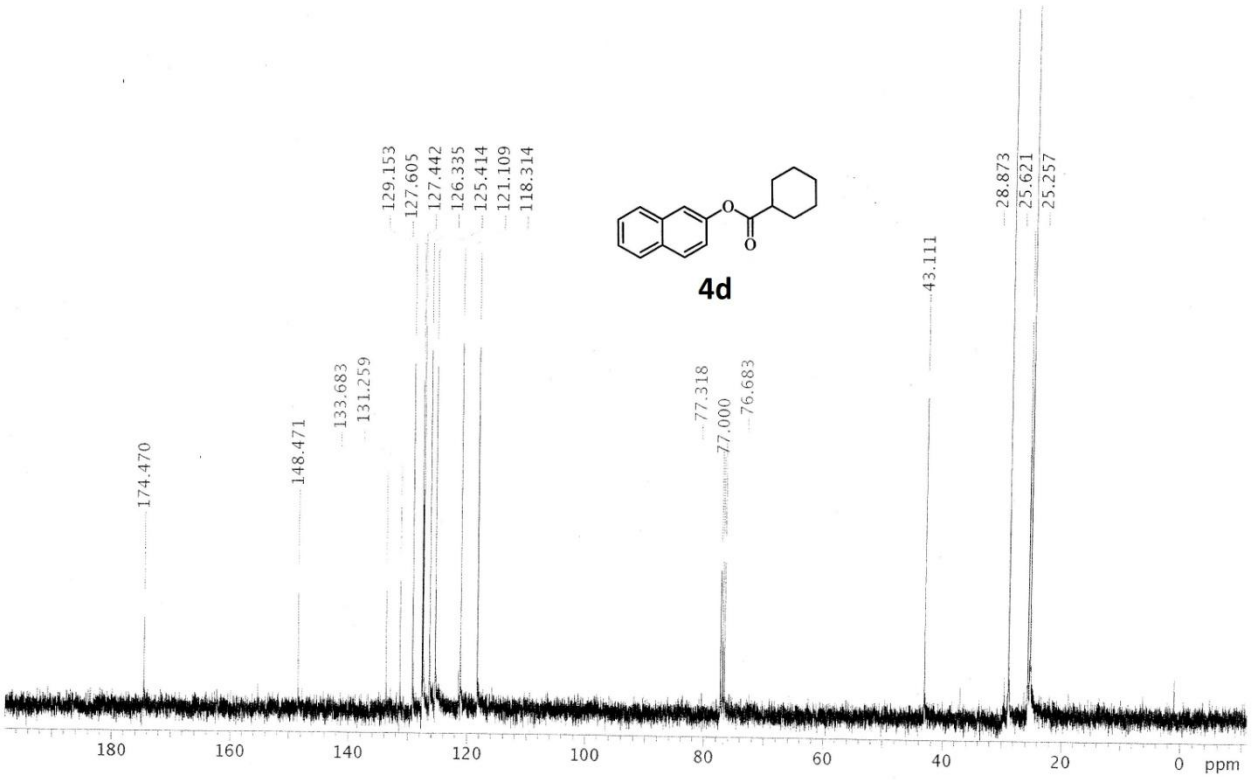
2-Naphthyl 2-methylpropanoate (4c)



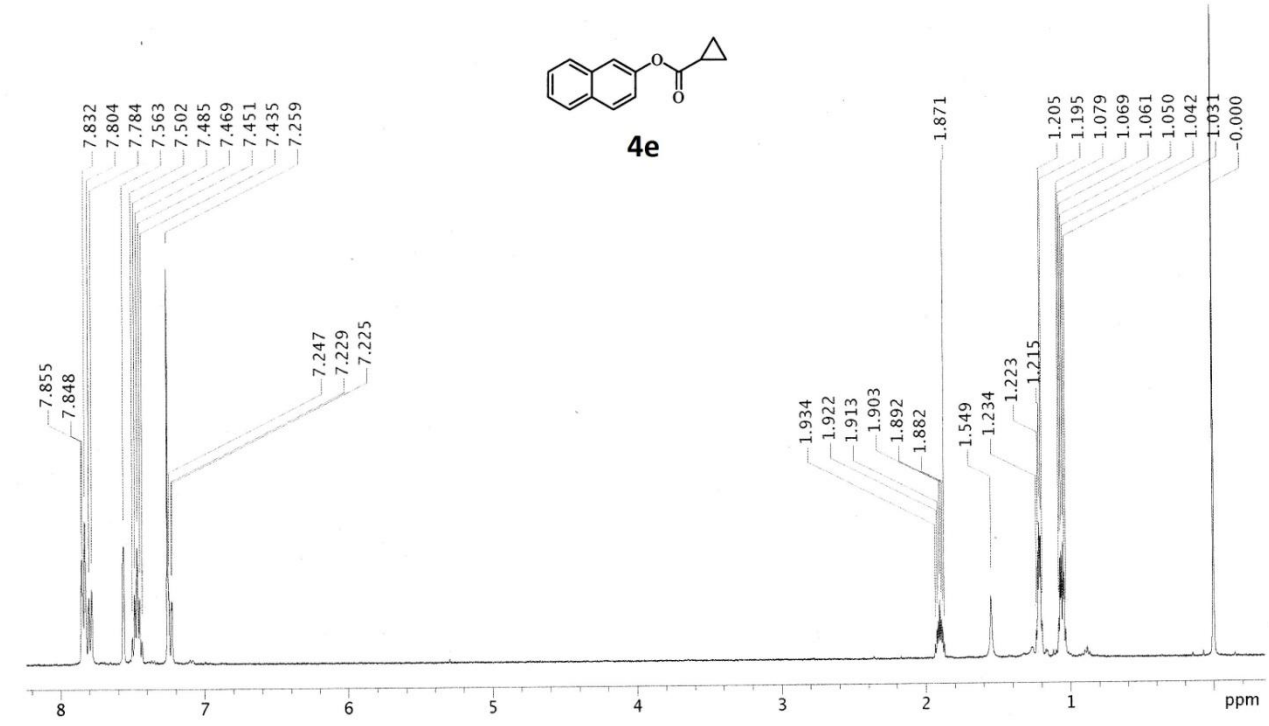


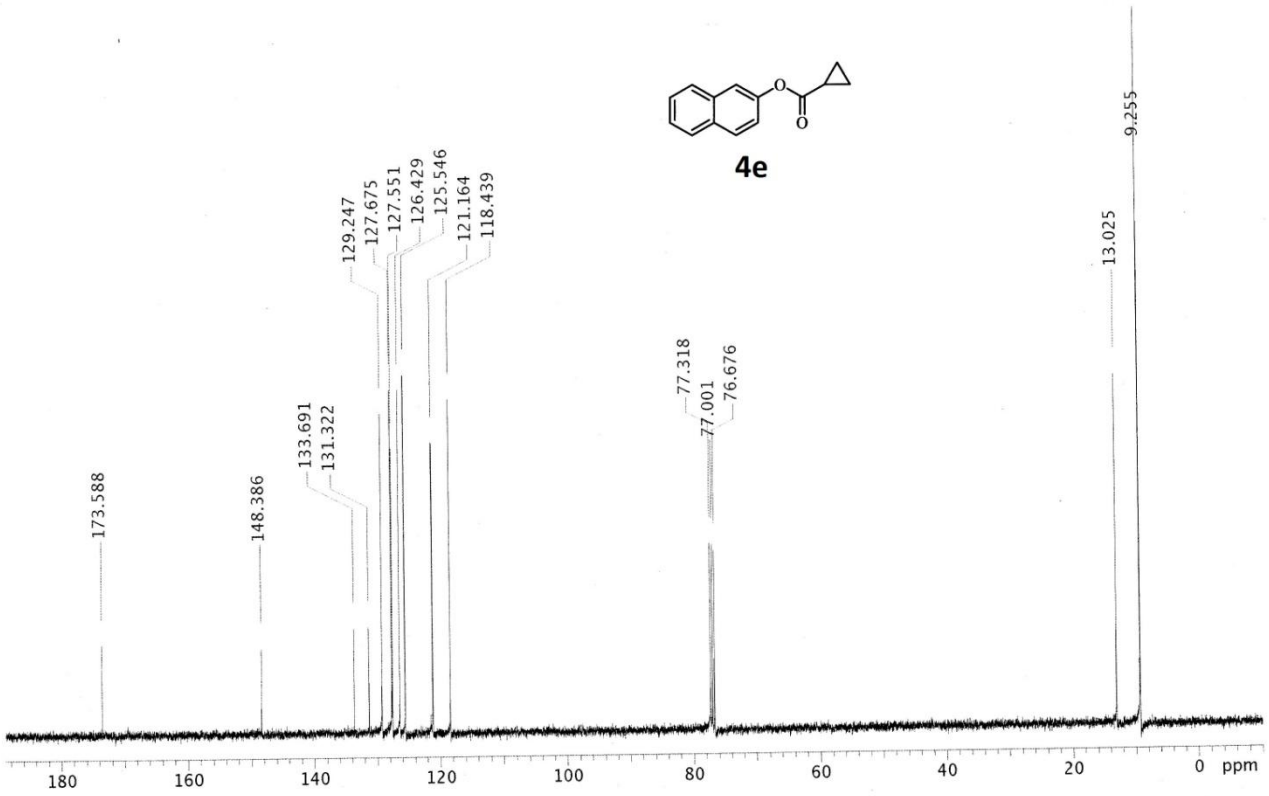
2-Naphthyl cyclohexanecarboxylate (4d)





2-Naphthyl cyclopropanecarboxylate (4e)





2-Naphthyl benzoate (4f)