Nano-$NiCo_2O_4$ -Catalyzed Dehydrogenative Direct Esterification and Amidation of Primary Alcohols under Microwave Conditions

Kumari Anchal,[a] Keya Roy,[b] Laksmikanta Adak,[b,]* and Subhash Banerjee[a,]*

[a.] *Department of Chemistry, Guru Ghasidas Vishwavidyalaya, Koni, Bilaspur-495009 (Chhattisgarh), India.*
[b.] *Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Botanic Garden, Howrah 711103, India*

SUPPORTING INFORMATION

ESI 1. General Information:

All chemicals and solvents were purchased from CDH, Merck, Sigma-Aldrich, TCI Chemicals, Sd-Fine, and HIMEDIA (India). Solvents were distilled before use, and all chemicals were used as received without further purification. Double-distilled water was employed to prepare $NiCo_2O_4$ nanoparticles and in organic reactions where required. Organic reactions were performed under ambient air, without an inert atmosphere, and oven-dried glassware was used for all the reactions. Thin-layer chromatography (TLC) was conducted on Merck 60F254 silica gel plates (0.25 mm thick), using ethyl acetate and petroleum ether as the eluting solvents. The powder X-ray diffraction (XRD) analysis of nano-$NiCo_2O_4$ was carried out using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (λ = 1.540806 Å), operating at 40 kV and 40 mA, with a step size of 0.02° and a scanning rate of 0.24°/min. High-resolution transmission electron microscopy (HR-TEM) of nano-$NiCo_2O_4$ was performed using a JEOL 4000 EX/II operating at 400 kV (point-to-point resolution of 0.165 nm) and a JEOL 2010 FEG operating at 200 kV (information limit of 0.11 nm). Fourier-transform infrared (FT-IR) spectroscopy was Thermo Scientific Nicolet Summit X spectrometer equipped with a diamond ATR crystal, a DTGS–KBr detector, and a KBr beamsplitter. The ^1H and ^{13}C NMR spectra of the synthesized compounds were recorded using a Bruker spectrometer operating at 400 MHz and 101 MHz, respectively, with $CDCl_3$ as the solvent.

ESI 2. Method for the preparation of nano-$NiCo_2O_4$ (By co-precipitation method):

At first, double-distilled water (500 mL) was heated in a 1000 mL beaker, and then, $NiCl_2$ (10.0 mmol) and $CoCl_2{\cdot}6H_2O$ (20.0 mmol) were dissolved. The colour of the solution turned to wine red. Next, NaOH solution (5 M) was prepared in double-distilled water separately in beakers (50 ml) and added dropwise to the resulting solution with continuous stirring till the pH was 10. After that, the grey precipitate was formed and washed with distilled water by the decantation process to make it alkali-free (pH 6-7). Furthermore, the precipitate was filtered and dried in an oven overnight. Finally, the dried material was ground and annealed at 400 ^oC in a muffle furnace. The obtained black material was nano-$NiCo_2O_4$.

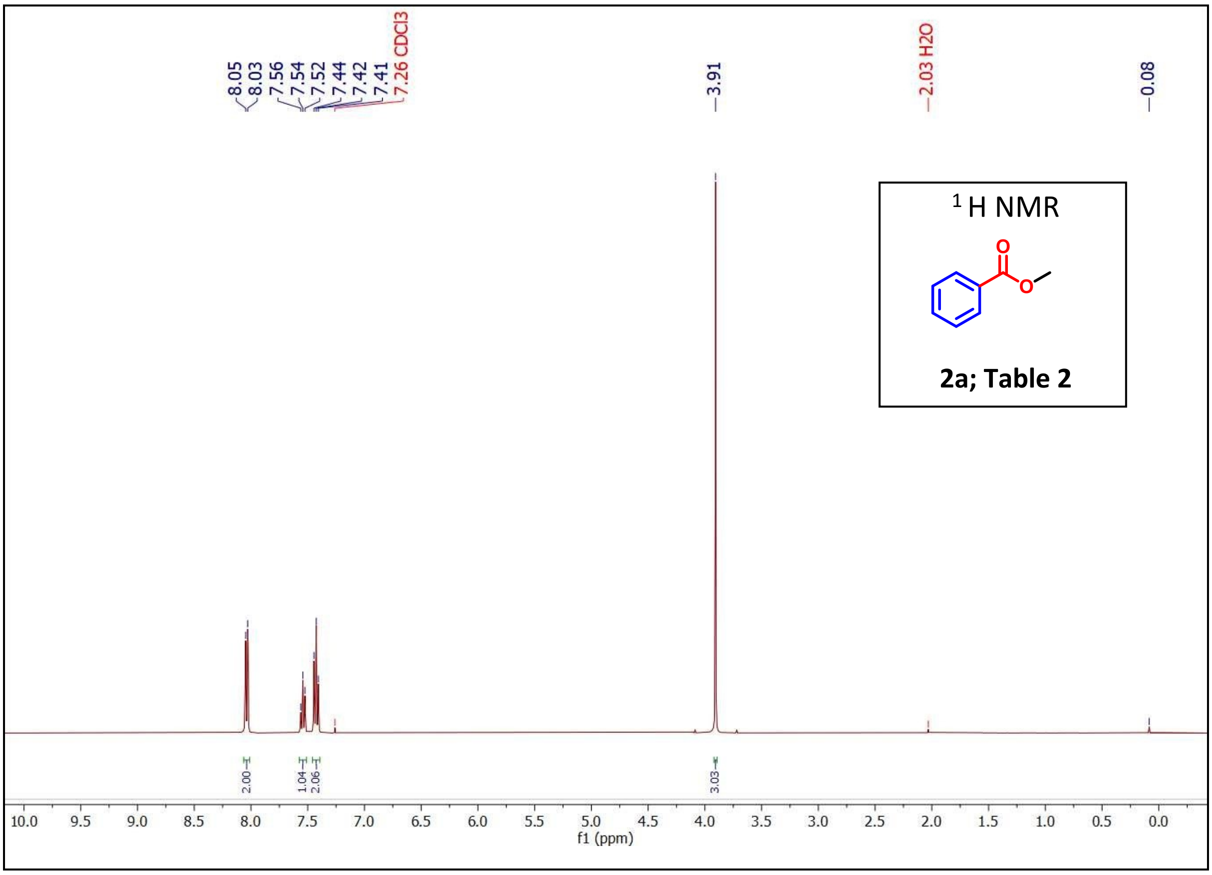
ESI 3. General experimental procedure for nano-$NiCo_2O_4$ catalyzed direct synthesis of ester from alcohol:

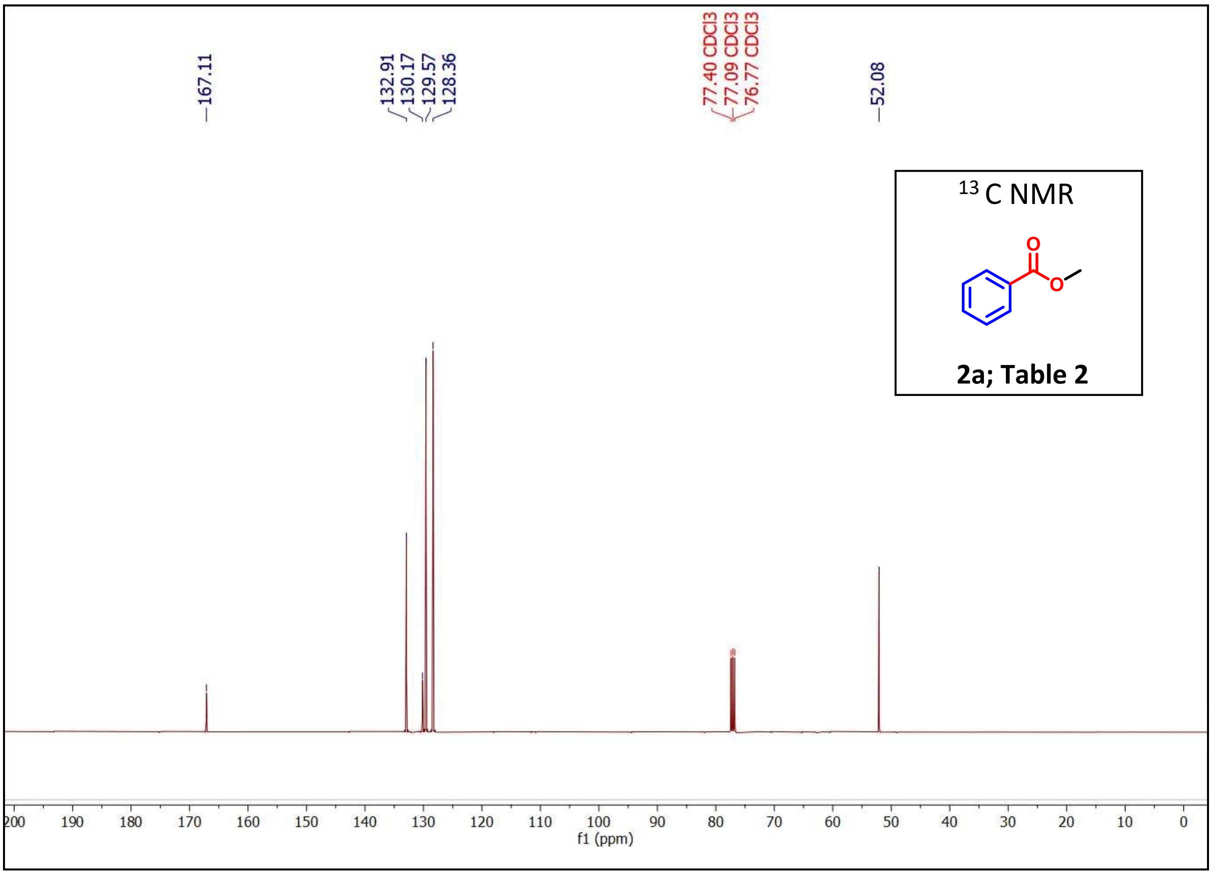
A microwave tube (10 mL) was charged with a mixture of benzyl alcohol (1.0 mmol), potassium hydroxide (2.0 equiv.), catalyst (30 mg), and methanol (2.0 mL). The reaction mixture was irradiated under microwave conditions using a CEM Discover System 908010 (700 W) for 10 minutes at 120 °C. The formation of the product was checked by TLC. Next, the catalyst was separated by simple filtration using filter paper (Whatman No. 40). Then, the product was extracted with ethyl acetate (5 ml), washed with brine solution and then distilled water, and further purified by column chromatography over silica gel (60–120 mesh) using ethyl acetate and petroleum ether (1:9) as an eluting solvent to obtain the pure product methyl benzoate. The formation of the product was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopic studies.

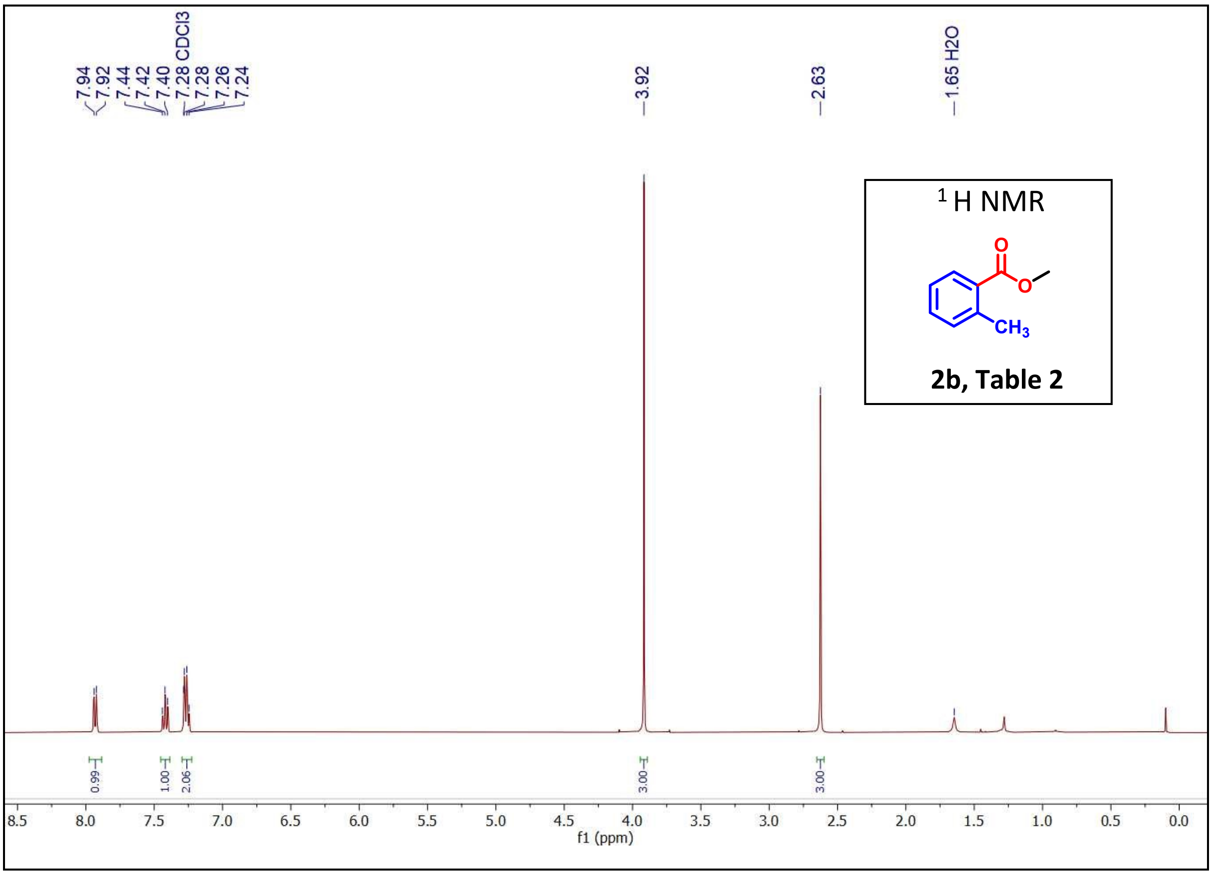
ESI 4. General experimental procedure for nano-$NiCo_2O_4$ catalyzed direct synthesis of amide from alcohol:

A microwave tube (10 mL) was charged with a mixture of benzyl alcohol (1.0 mmol), potassium hydroxide (2.0 equiv.), catalyst (30 mg), and benzylamine (1.5 mmol). The reaction mixture was irradiated under microwave conditions using a CEM Discover System 908010 (700 W) for 10 minutes at 120 °C. The formation of the product was checked by TLC. Next, the catalyst was separated by simple filtration using filter paper (Whatman No. 40). Then, the product was extracted with ethyl acetate (5 ml), washed with brine solution and then distilled water, and further purified by column chromatography over silica gel (60–120 mesh) using ethyl acetate and petroleum ether (1:9) as an eluting solvent to obtain the pure product methyl benzoate. The formation of the product was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopic studies.

ESI 5. Copies of ^{1}H NMR and ^{13}C NMR spectra of products listed in Table 2:



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7.26
7.24
3.92
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1.65 H2O
^{1}H NMR
O
O
CH$_3$
2b, Table 2
0.99
1.00
2.06
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
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2.5
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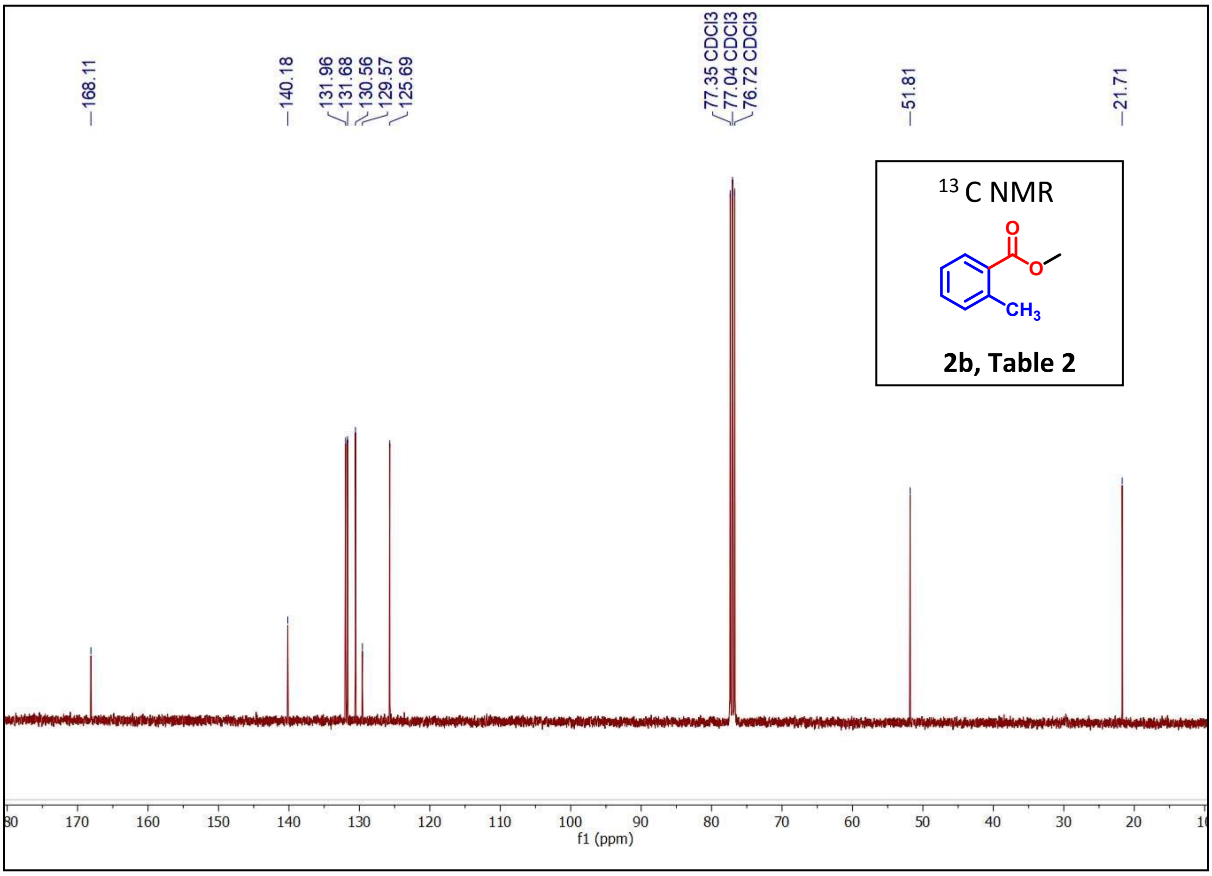
f1 (ppm)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129.57
125.69
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
51.81
21.71
^{13}C NMR
O
O
CH$_3$
2b, Table 2
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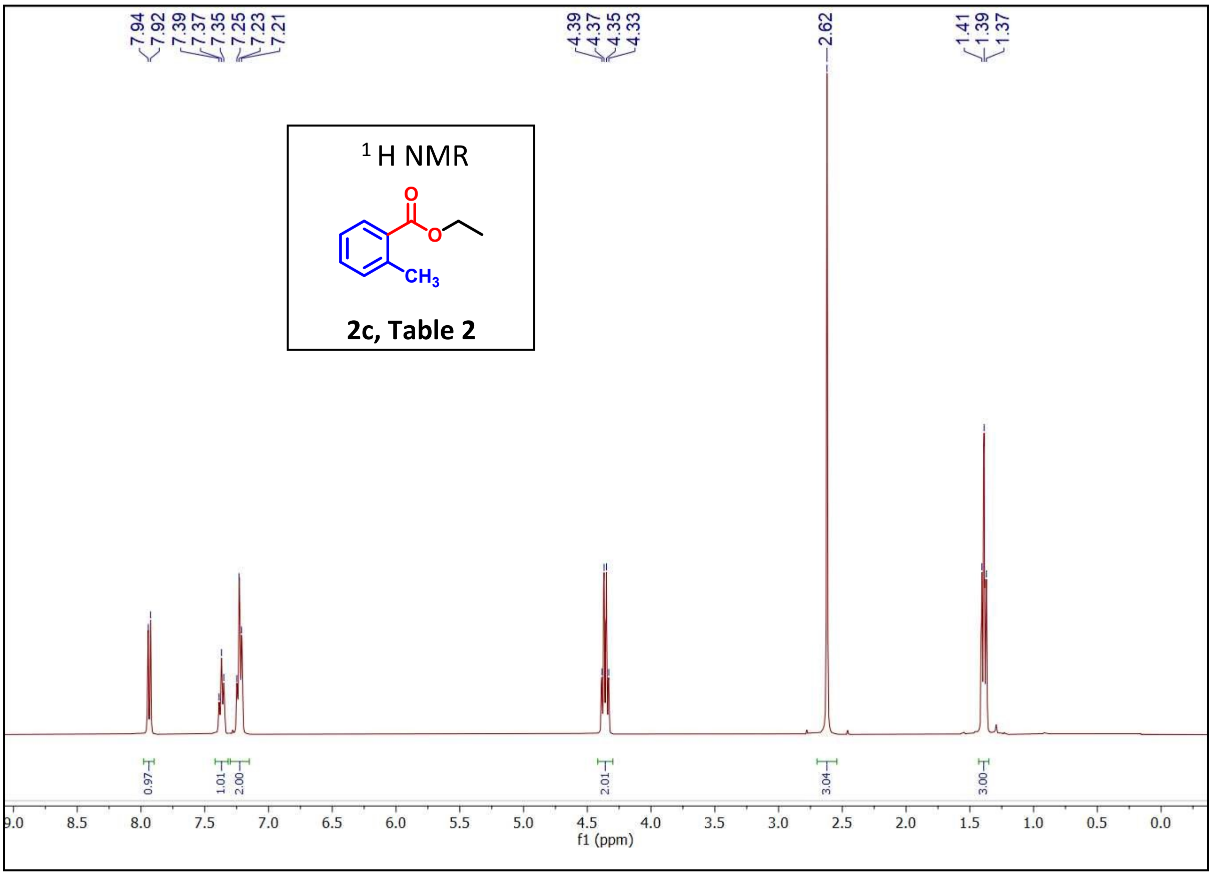
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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4.37
4.35
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2.62
1.41
1.39
1.37
1 H NMR
O
O
CH3
2c, Table 2
0.97
1.01
2.00
2.01
3.04
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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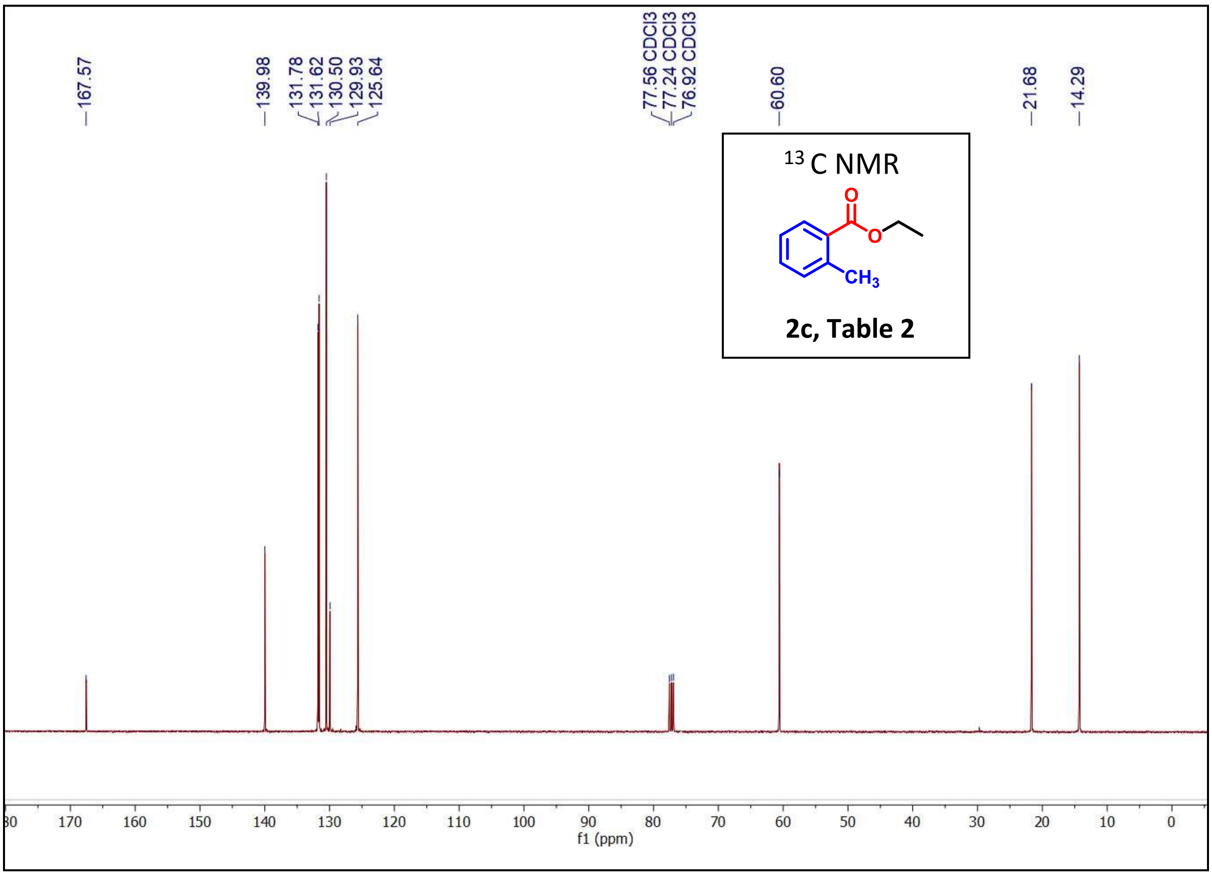
f1 (ppm)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77.24 CDCl3
76.92 CDCl3
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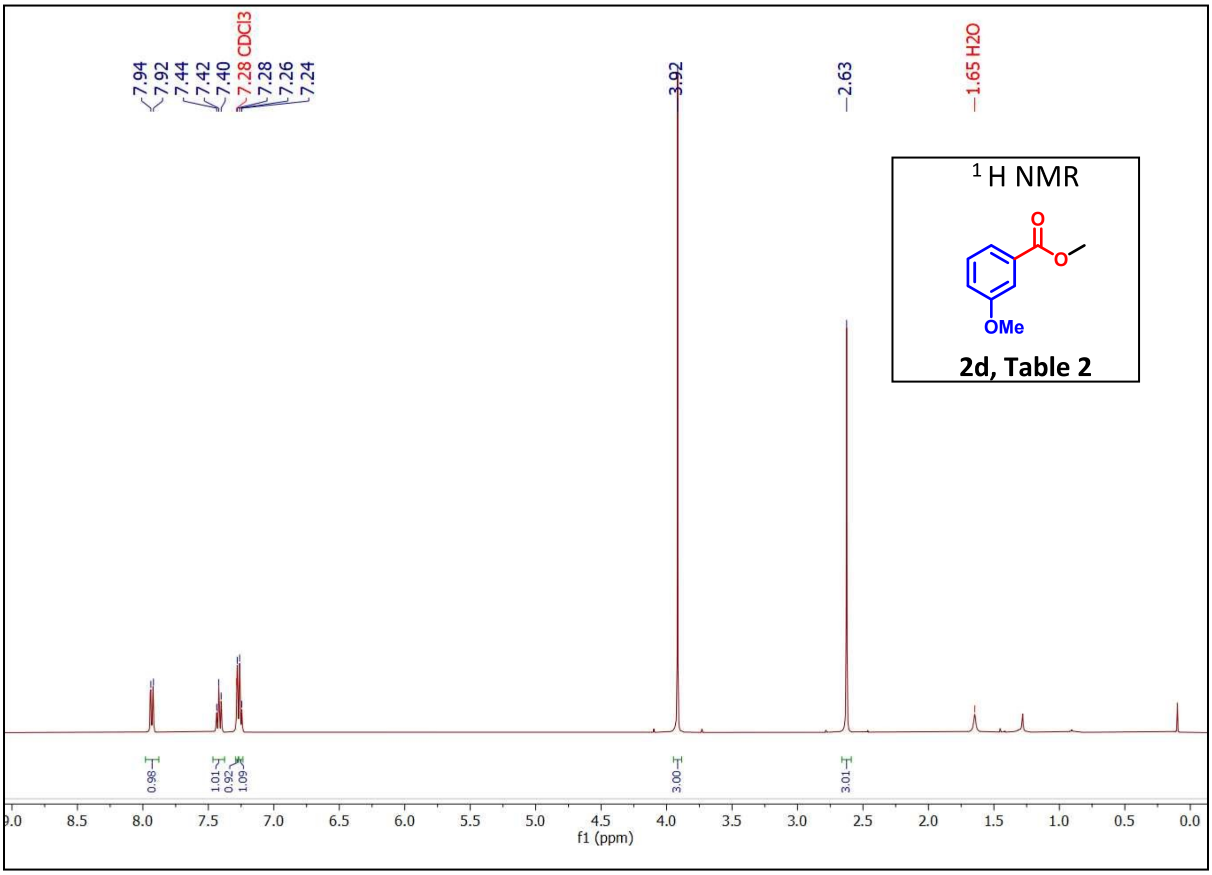
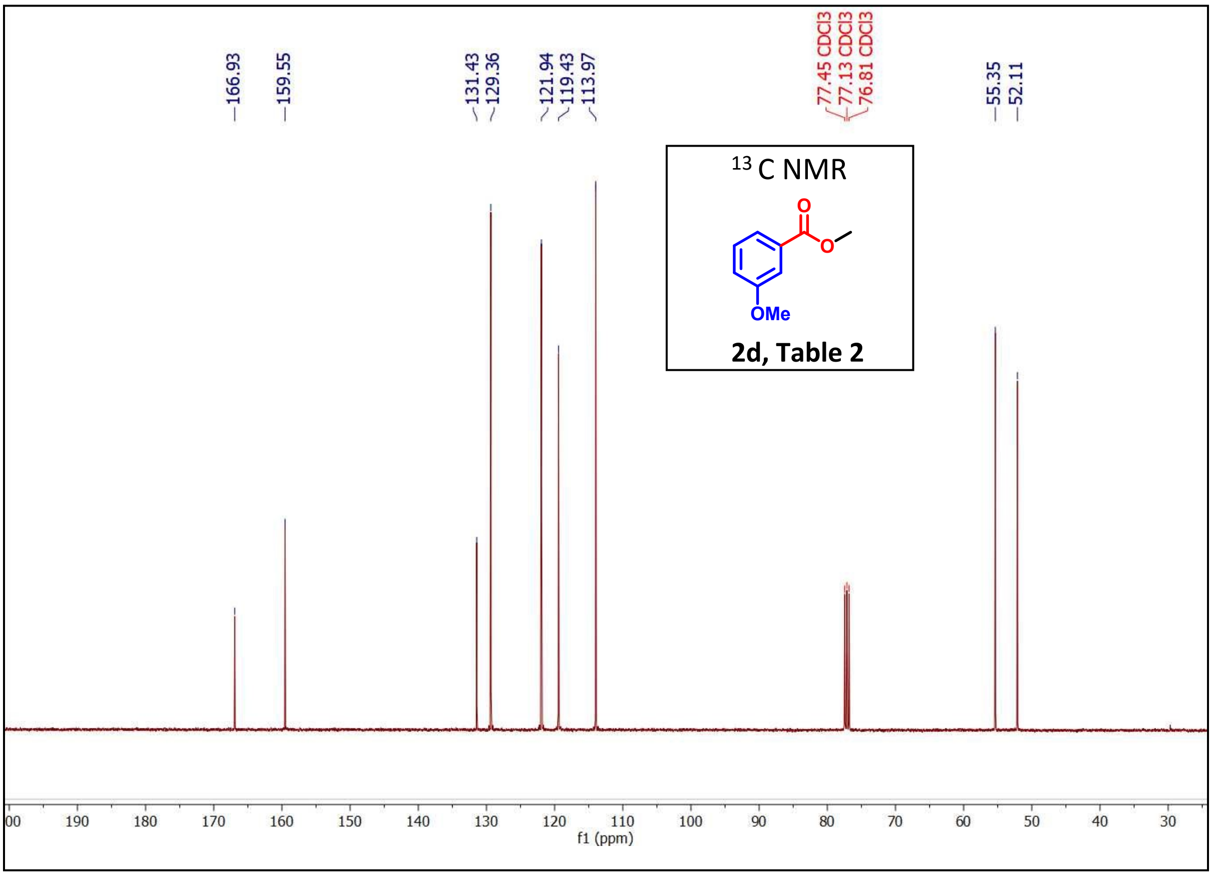
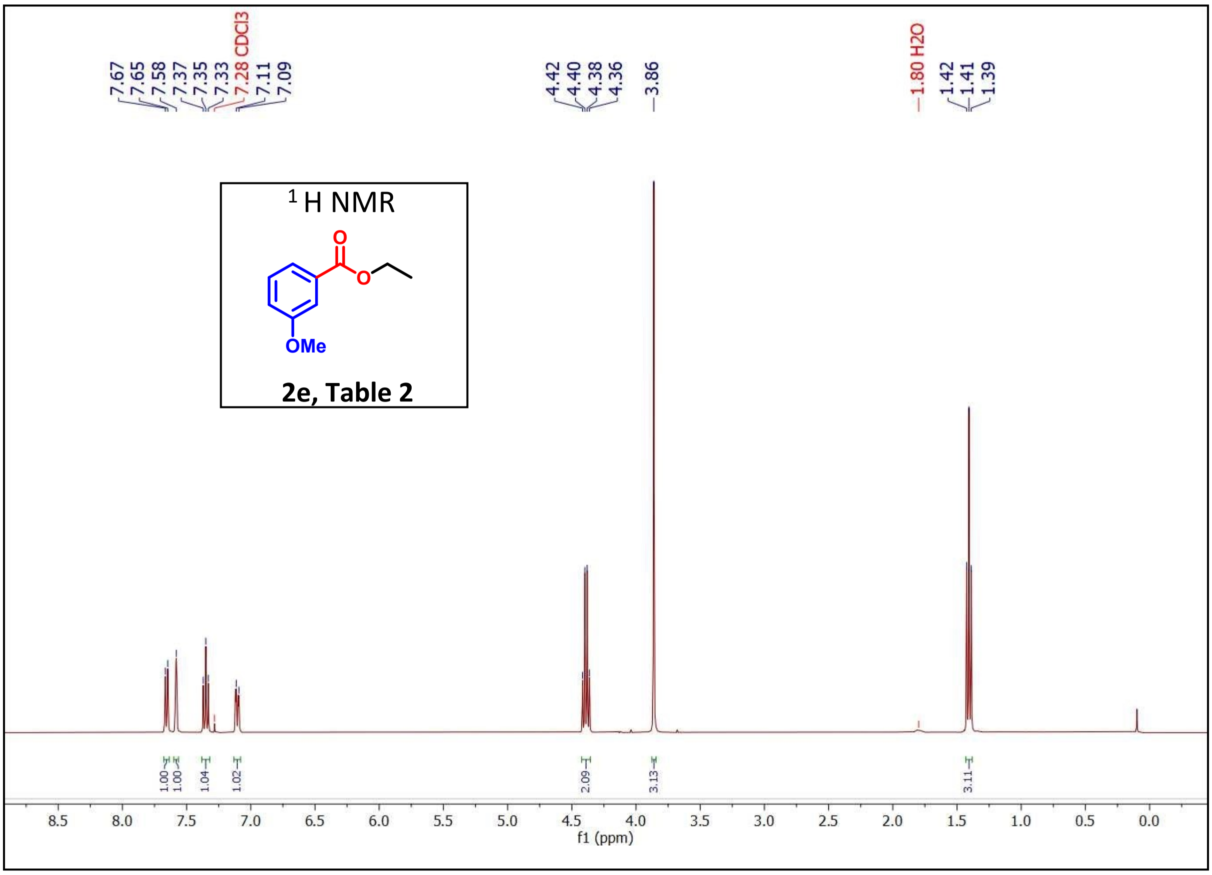
21.68
14.29
13 C NMR
O
O
CH3
2c, Table 2
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



2d, Table 2



2d, Table 2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4.38
4.36
3.86
1.80 H2O
1.42
1.41
1.39
1 H NMR
O
O
OMe
2e, Table 2
1.00
1.00
1.04
1.02
2.09
3.13
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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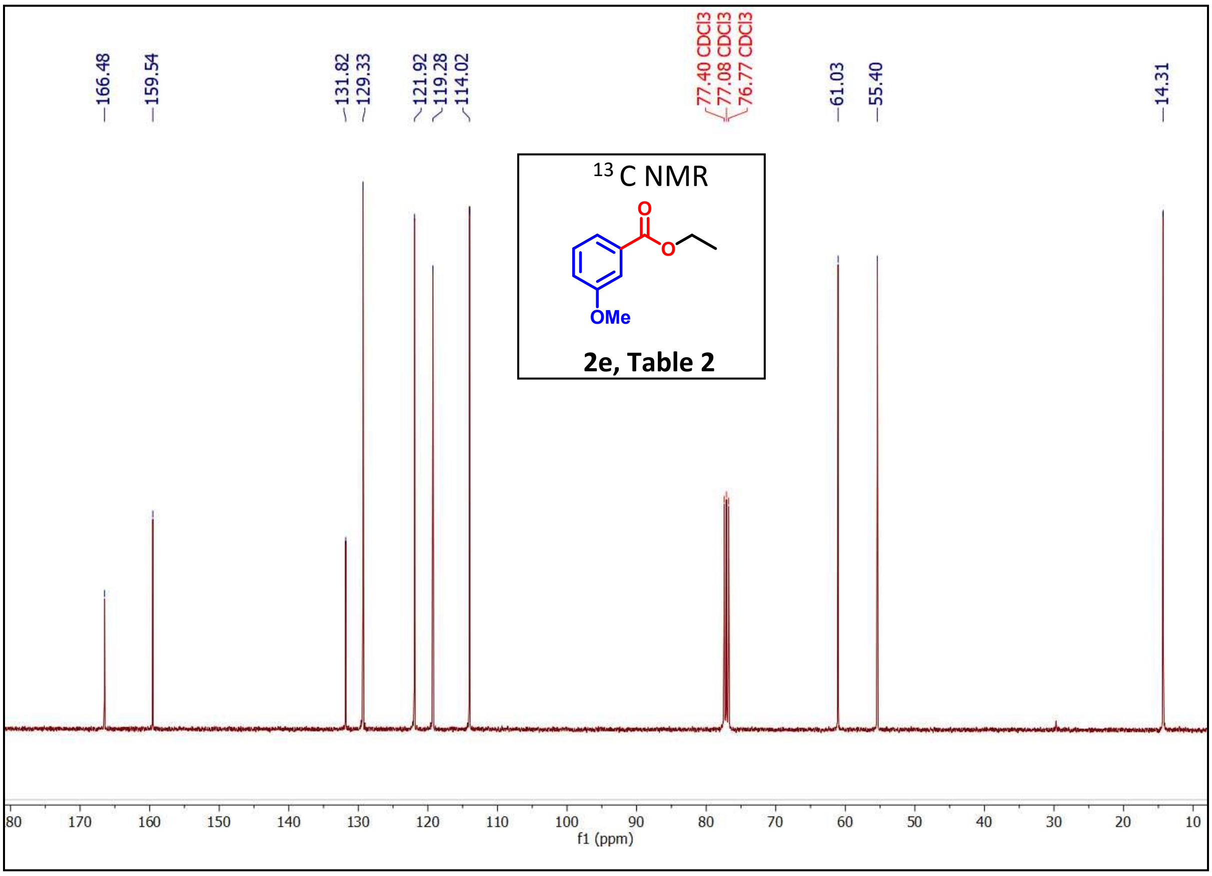
f1 (ppm)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76.77 CDCl3
61.03
55.40
14.31
13 C NMR
O
O
OMe
2e, Table 2
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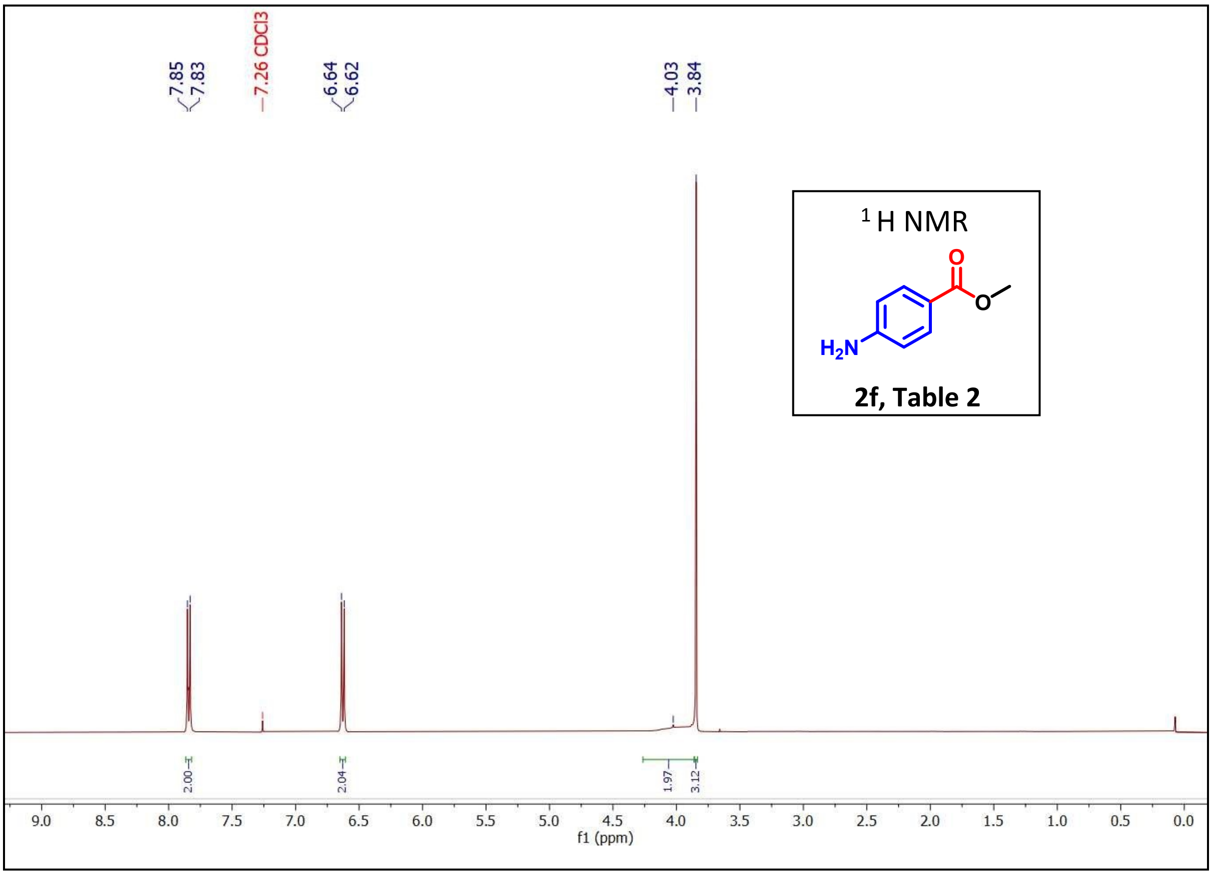
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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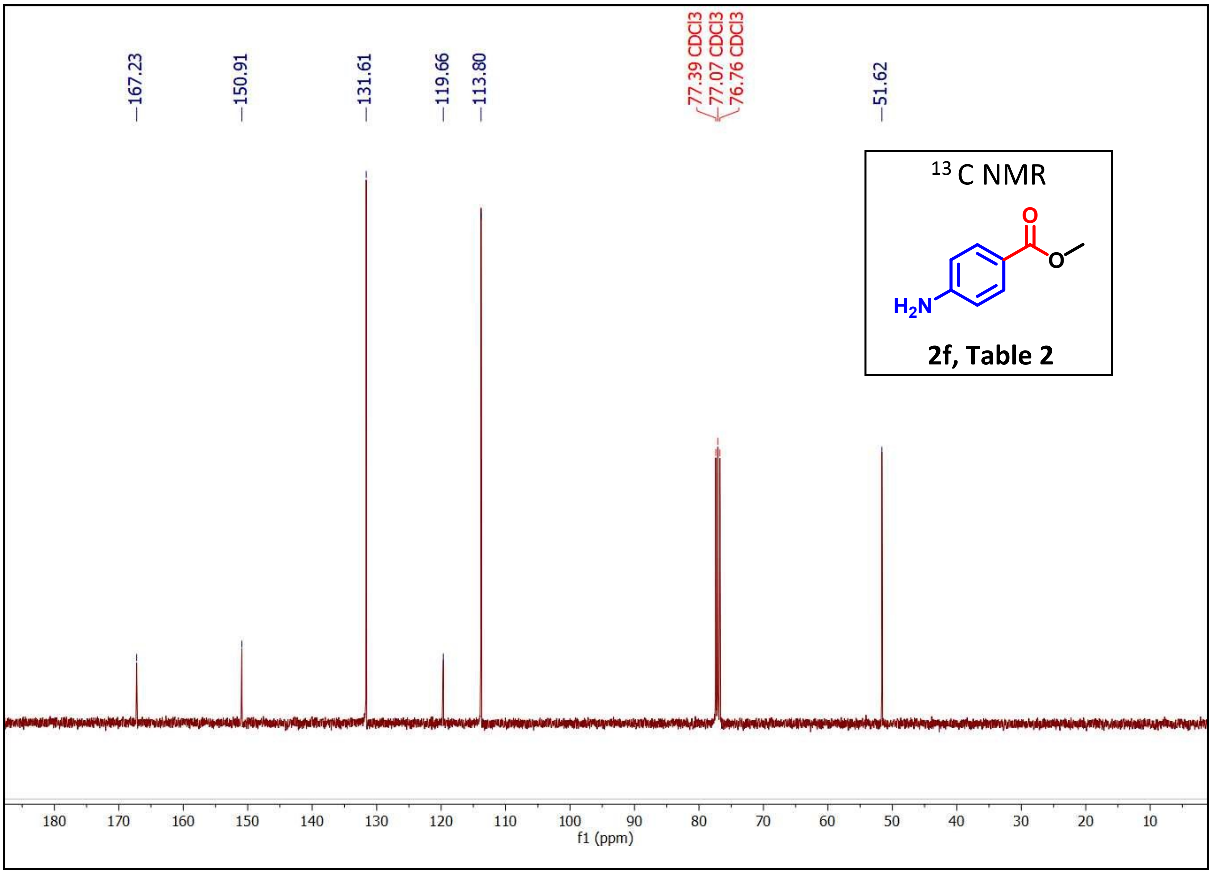
6.64
6.62
4.03
3.84
^{1}H NMR
O
O
H_2N
2f, Table 2
2.00
2.04
1.97
3.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.39 CDCl3
77.07 CDCl3
76.76 CDCl3
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O
O
H_2N
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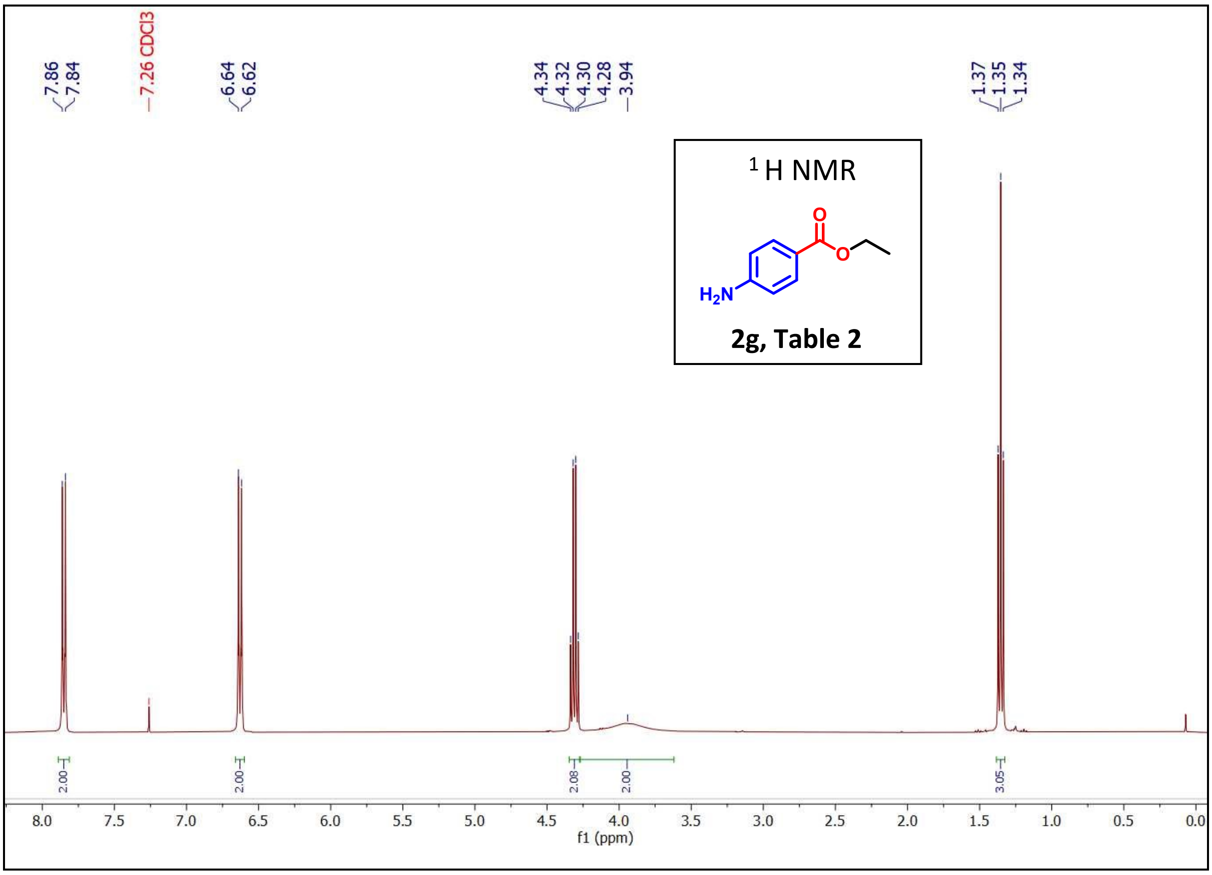
f1 (ppm)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1.34
^{1}H NMR
O
O
H_2N
2g, Table 2
2.00
2.00
2.08
2.00
3.05
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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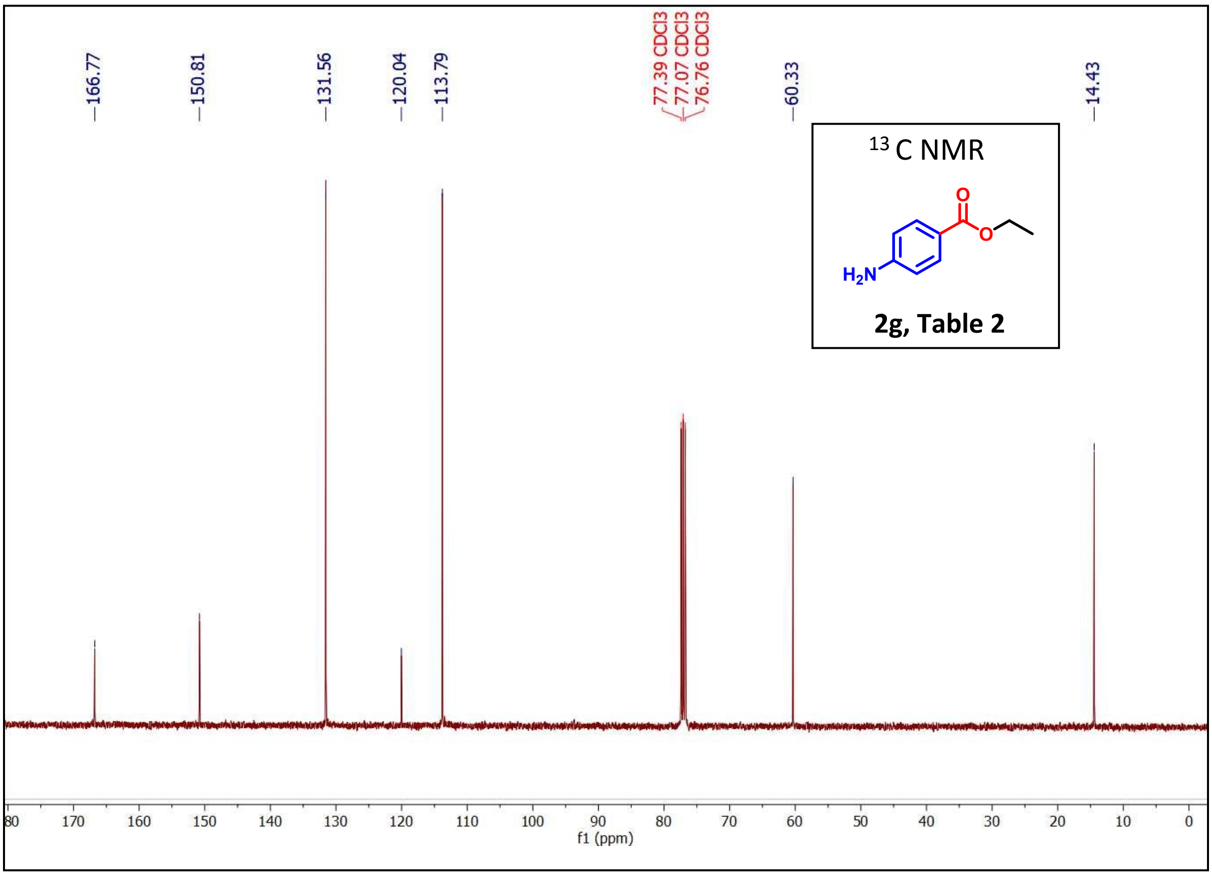
f1 (ppm)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77.07 CDCl3
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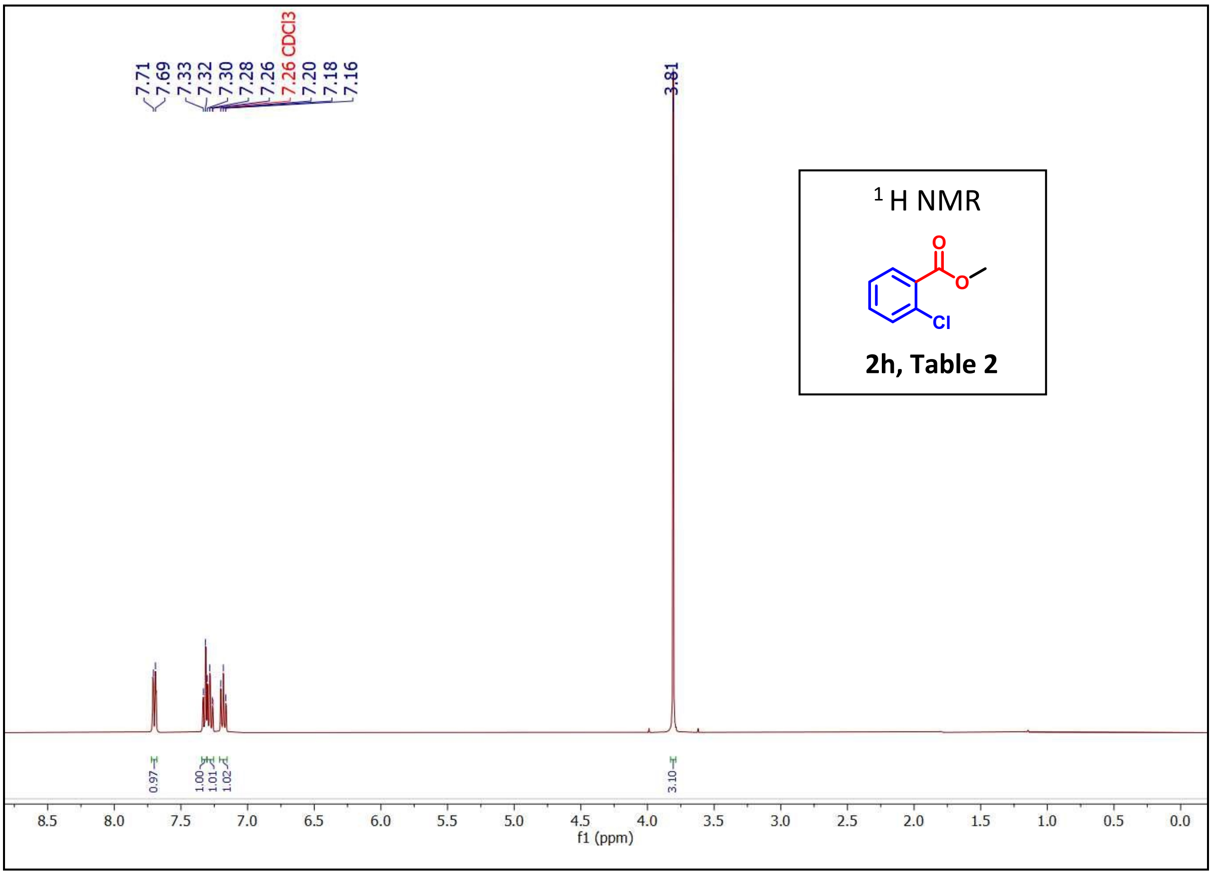
^{13}C NMR
O
O
H_2N
2g, Table 2
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.28
7.26
7.26 CDCl3
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0.97
1.00
1.01
1.02
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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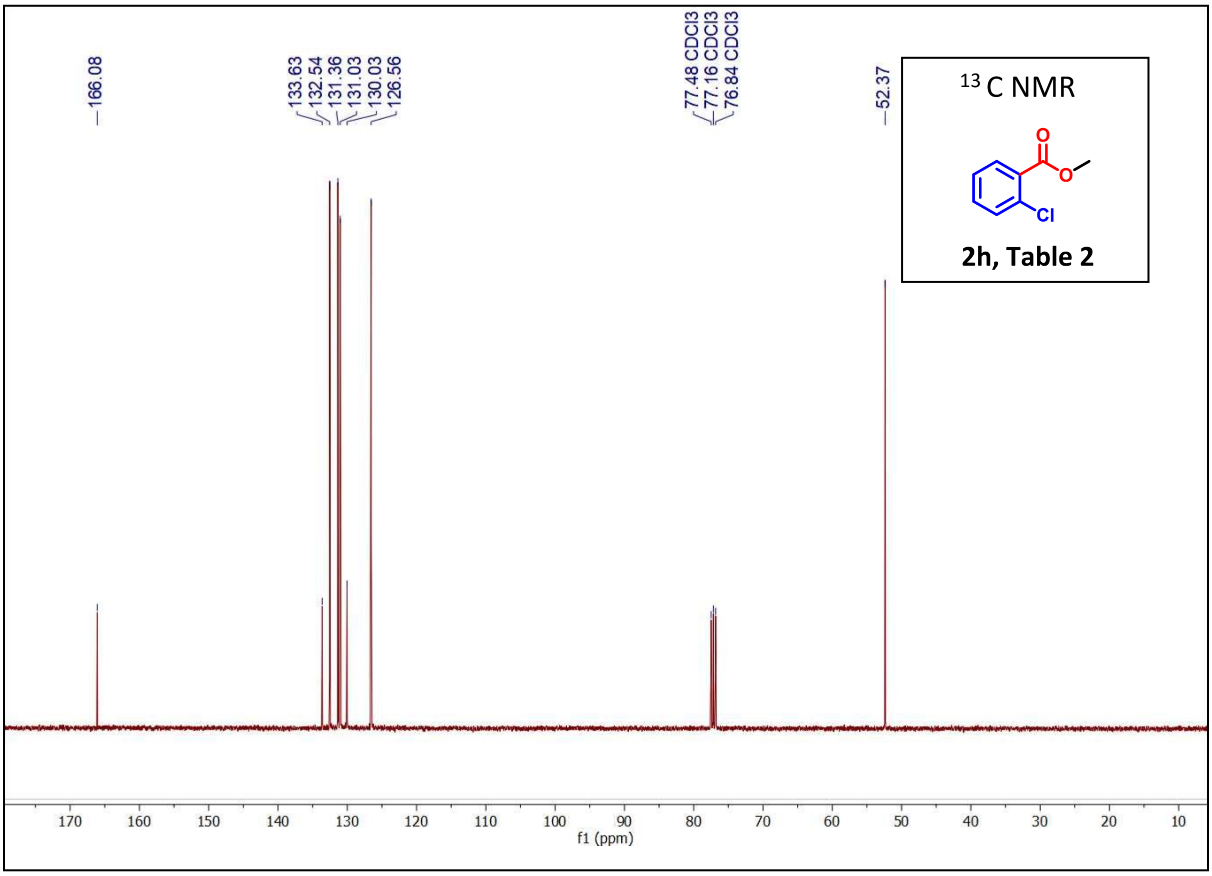
f1 (ppm)
1 H NMR
O
O
Cl
2h, Table 2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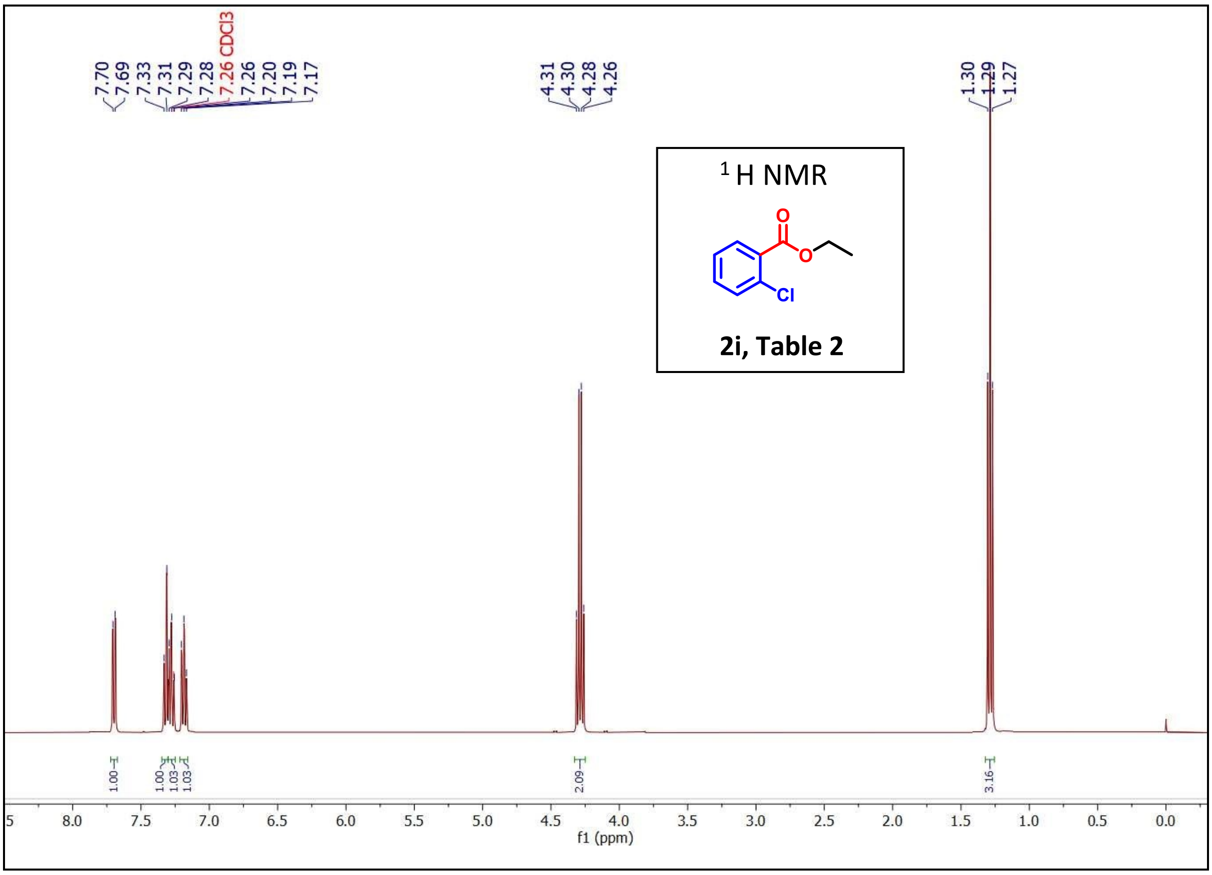
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
13 C NMR
O
O
Cl
2h, Table 2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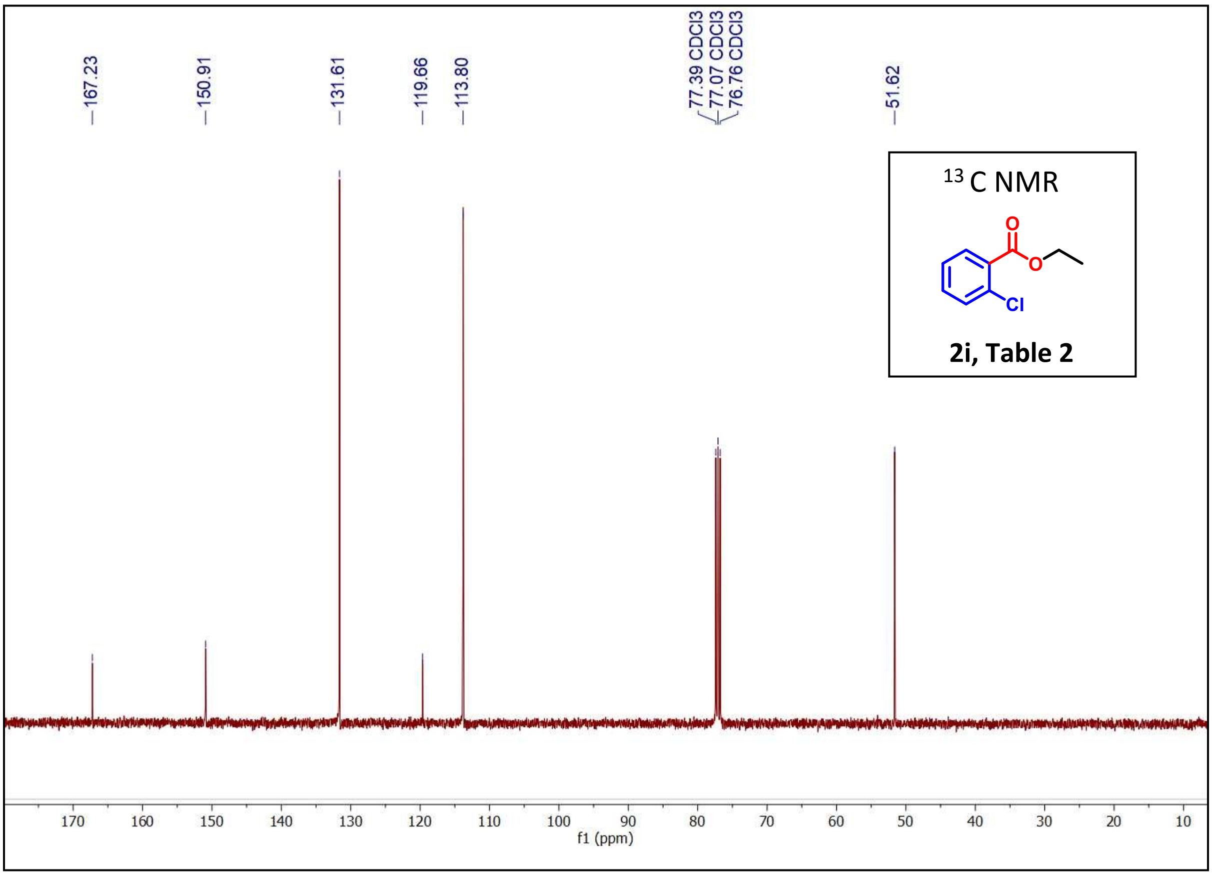
4.31
4.30
4.28
4.26
1.30
1.29
1.27
^{1}H NMR
O
O
Cl
2i, Table 2
1.00
1.00
1.03
1.03
2.09
3.16
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.61
119.66
113.80
77.39 CDCl3
77.07 CDCl3
76.76 CDCl3
51.62
^{13}C NMR
O
O
Cl
2i, Table 2
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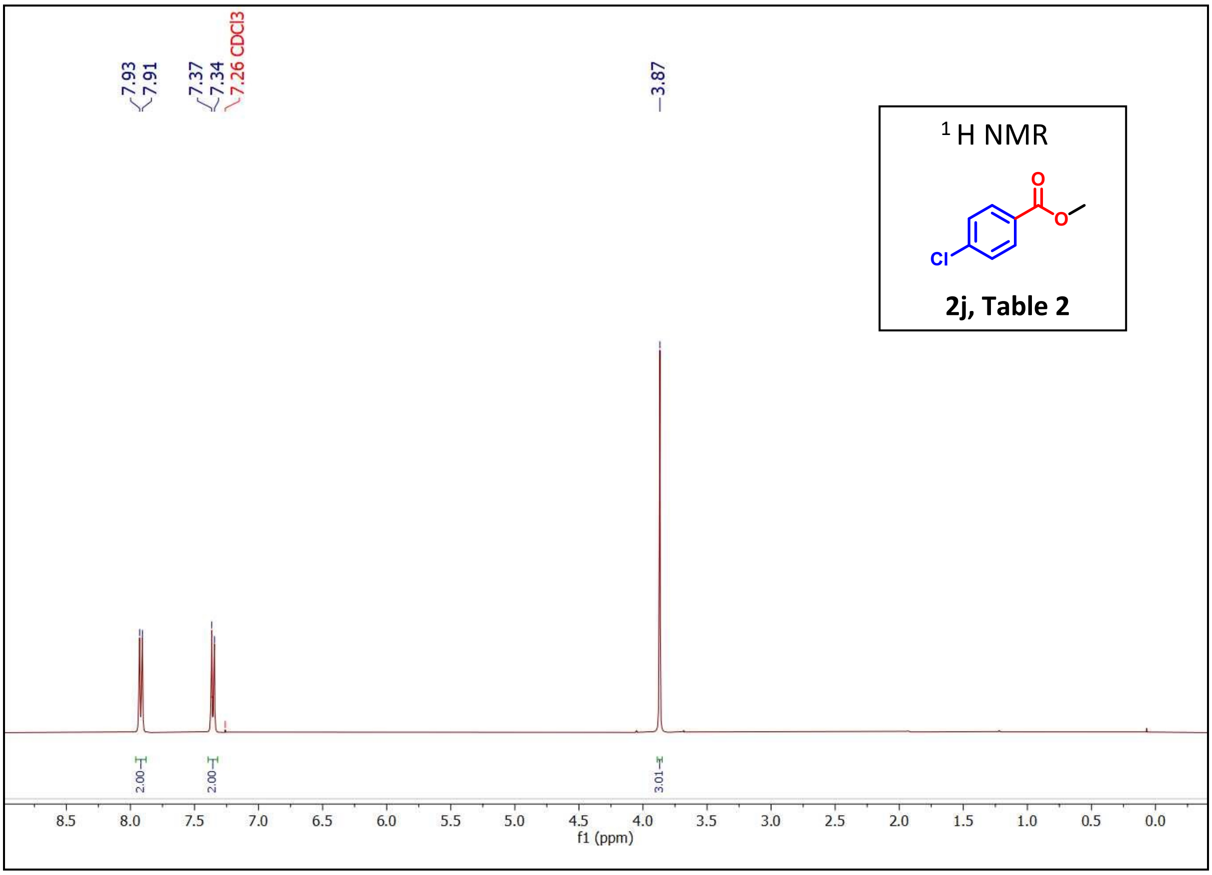
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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O
O
Cl
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2.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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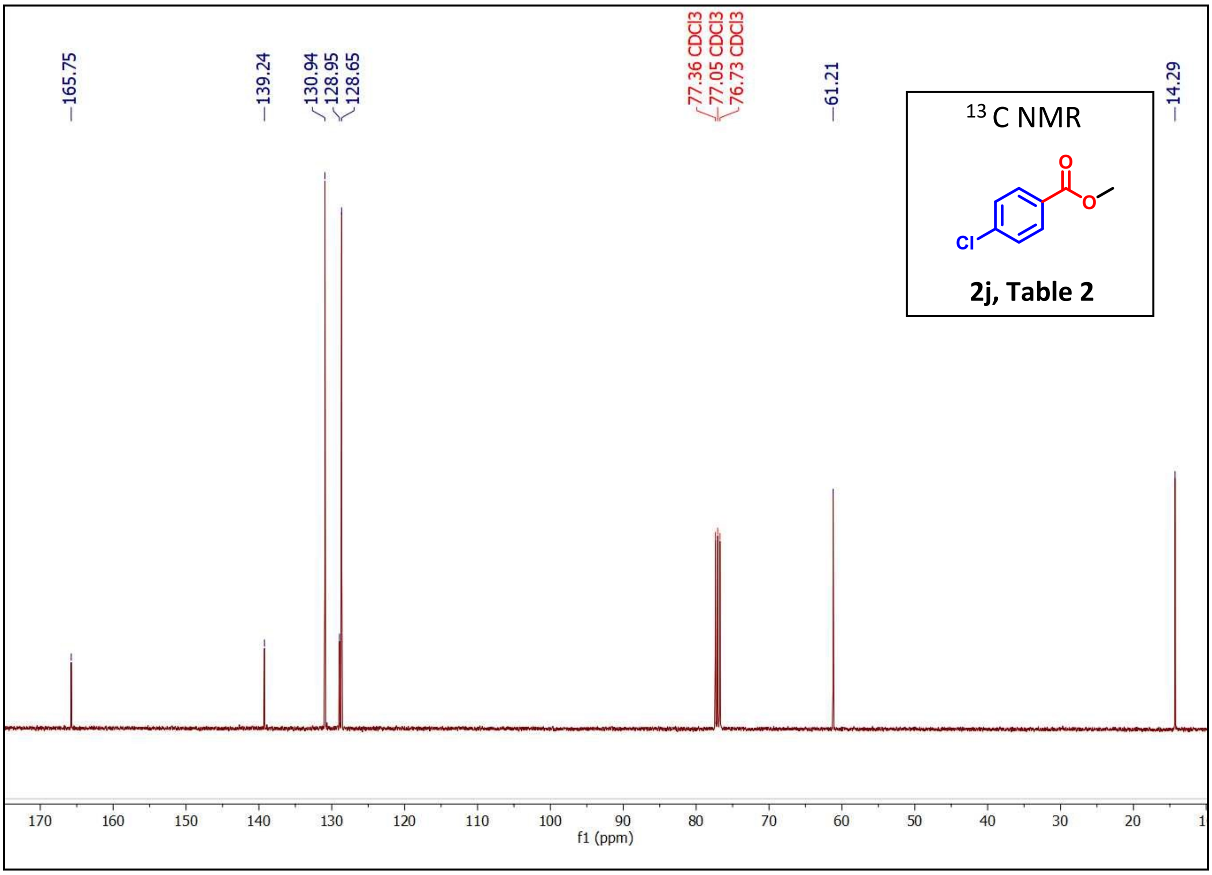
0.0
f1 (ppm)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77.05 CDCl3
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^{13}C NMR
O
O
Cl
2j, Table 2
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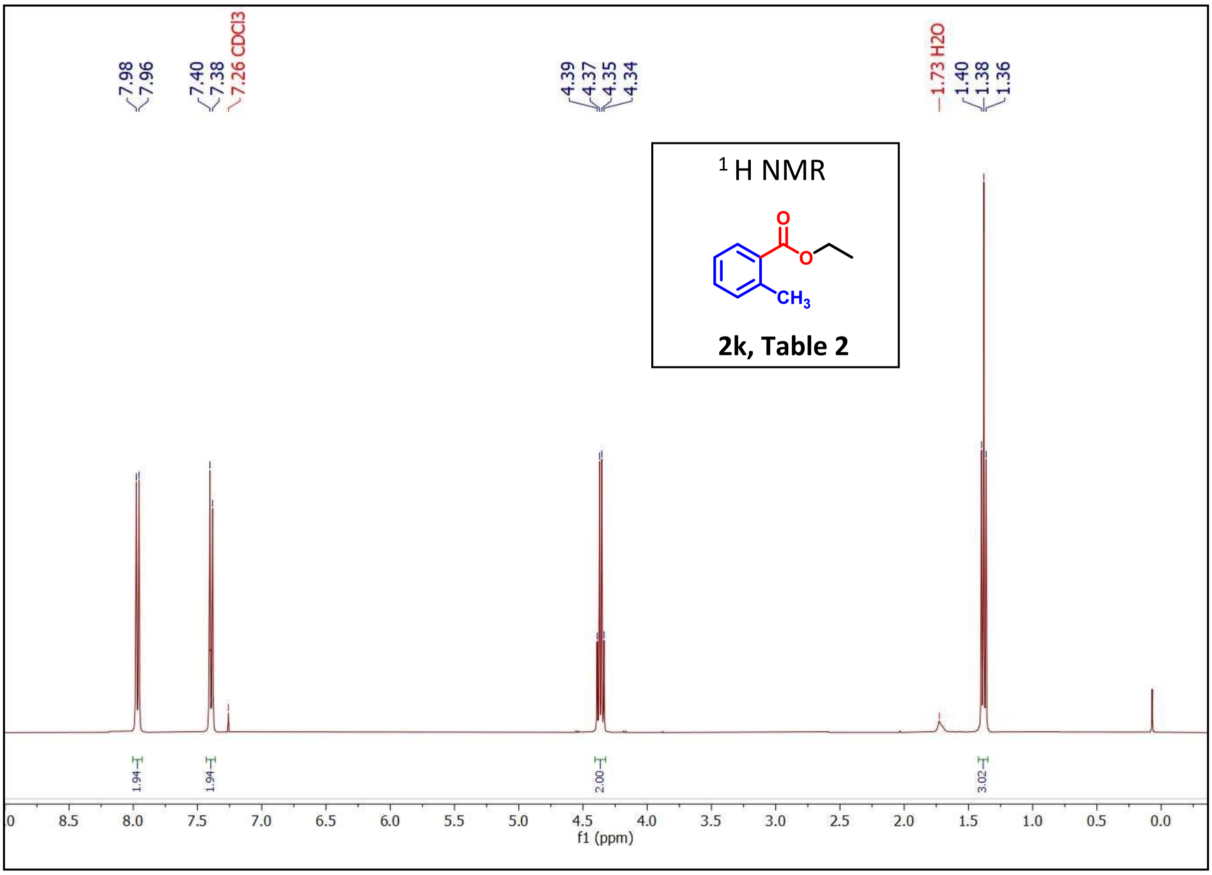
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)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4.37
4.35
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1.38
1.36
1H NMR
O
O
CH3
2k, Table 2
1.94
1.94
2.00
3.02
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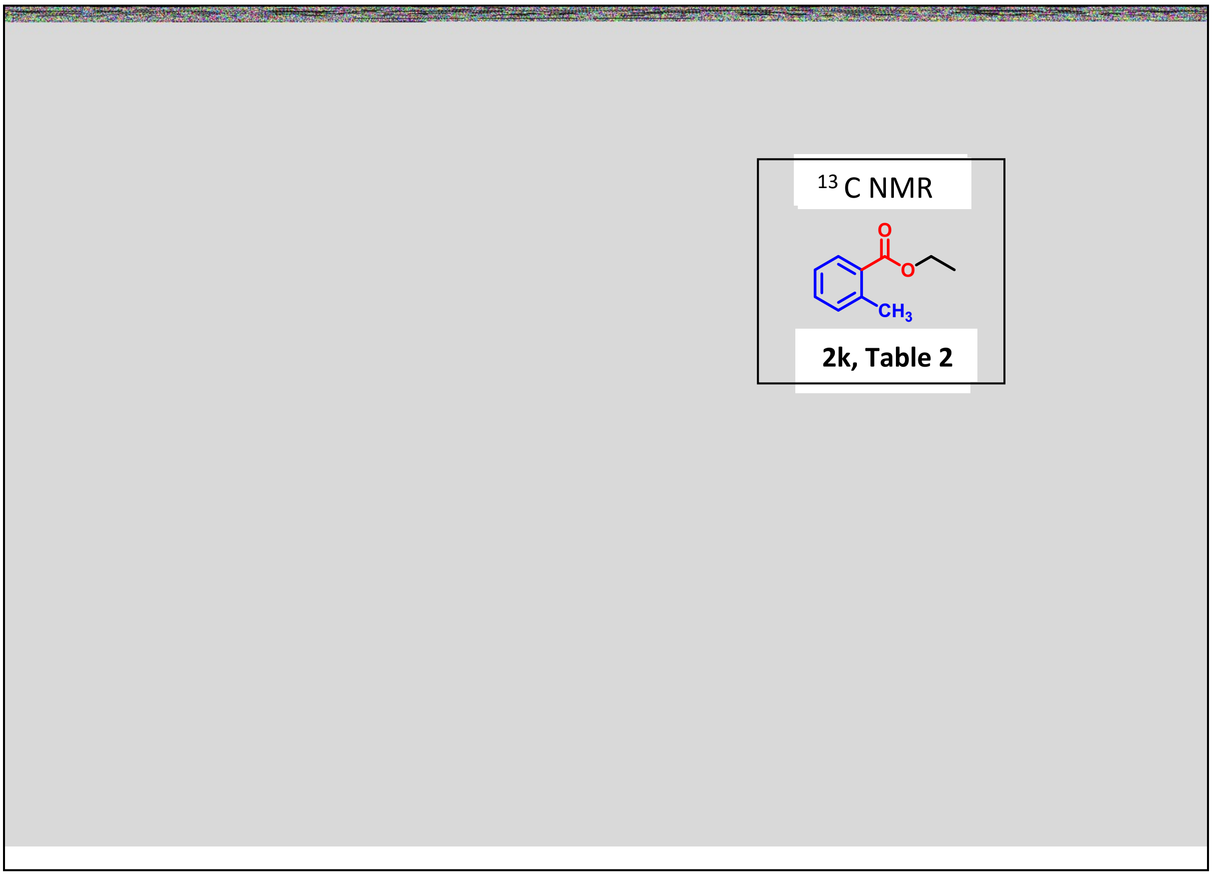
f1 (ppm)


13C NMR
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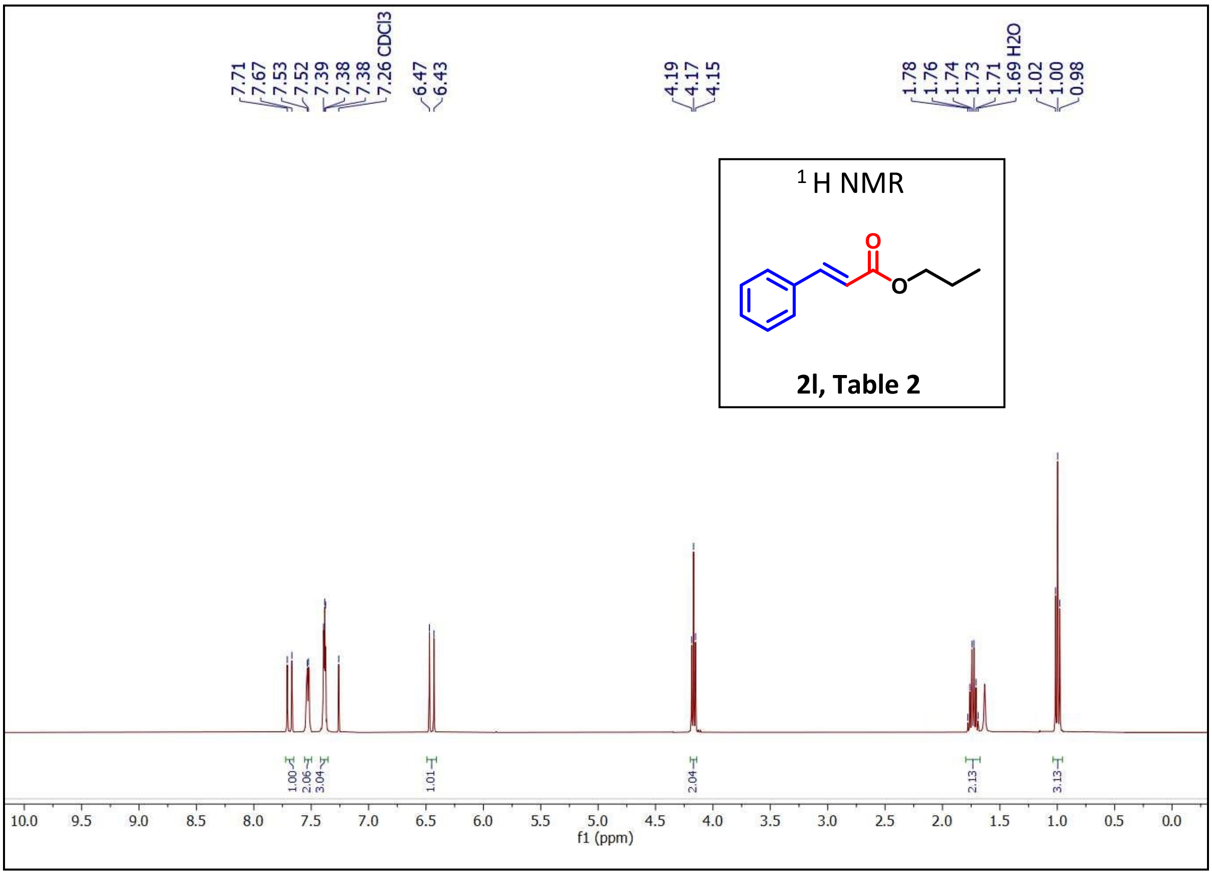
CH3
2k, Table 2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4.15
1.78
1.76
1.74
1.73
1.71
1.69 H2O
1.02
1.00
0.98
1 H NMR
O
O
2l, Table 2
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2.06
3.04
1.01
2.04
2.13
3.13
10.0
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7.5
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6.5
6.0
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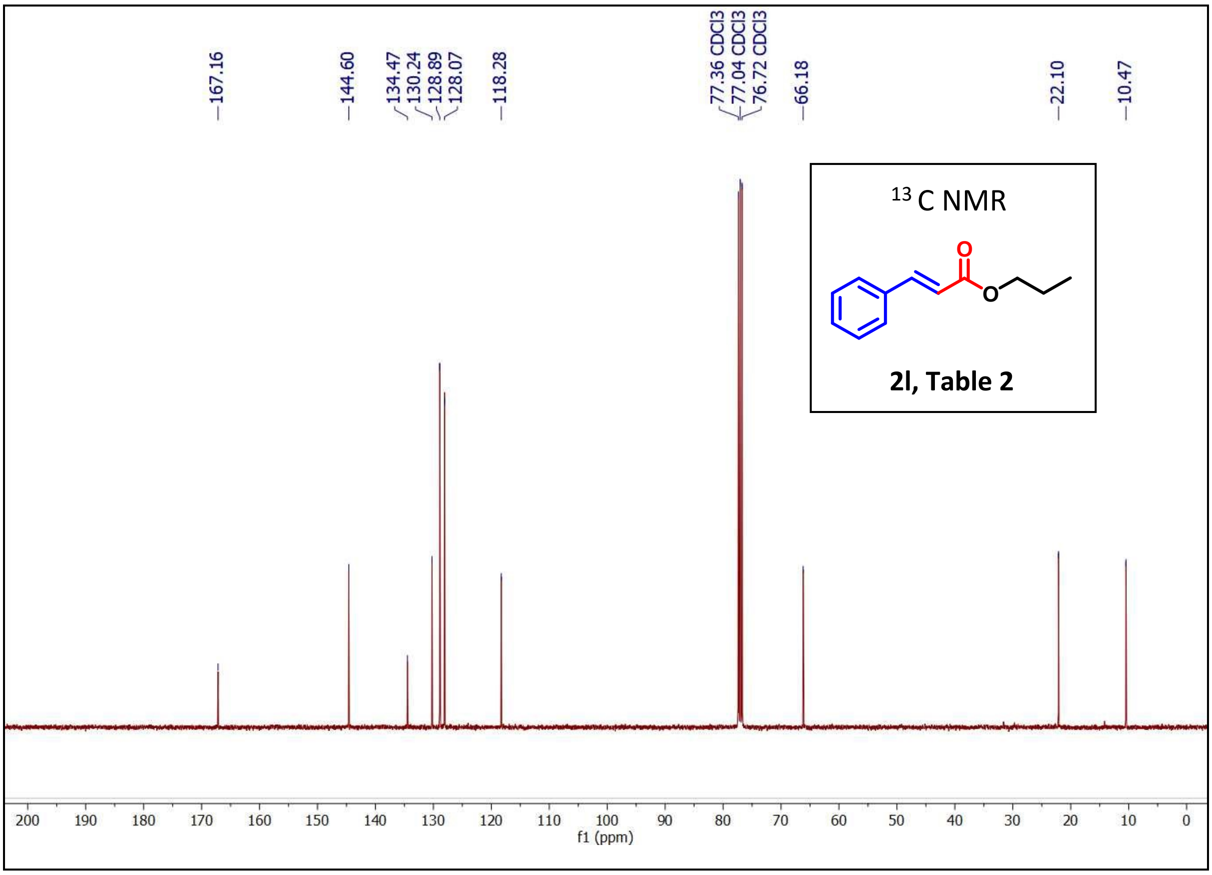
f1 (ppm)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118.28
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
66.18
22.10
10.47
13 C NMR
O
O
2l, Table 2
200
190
180
170
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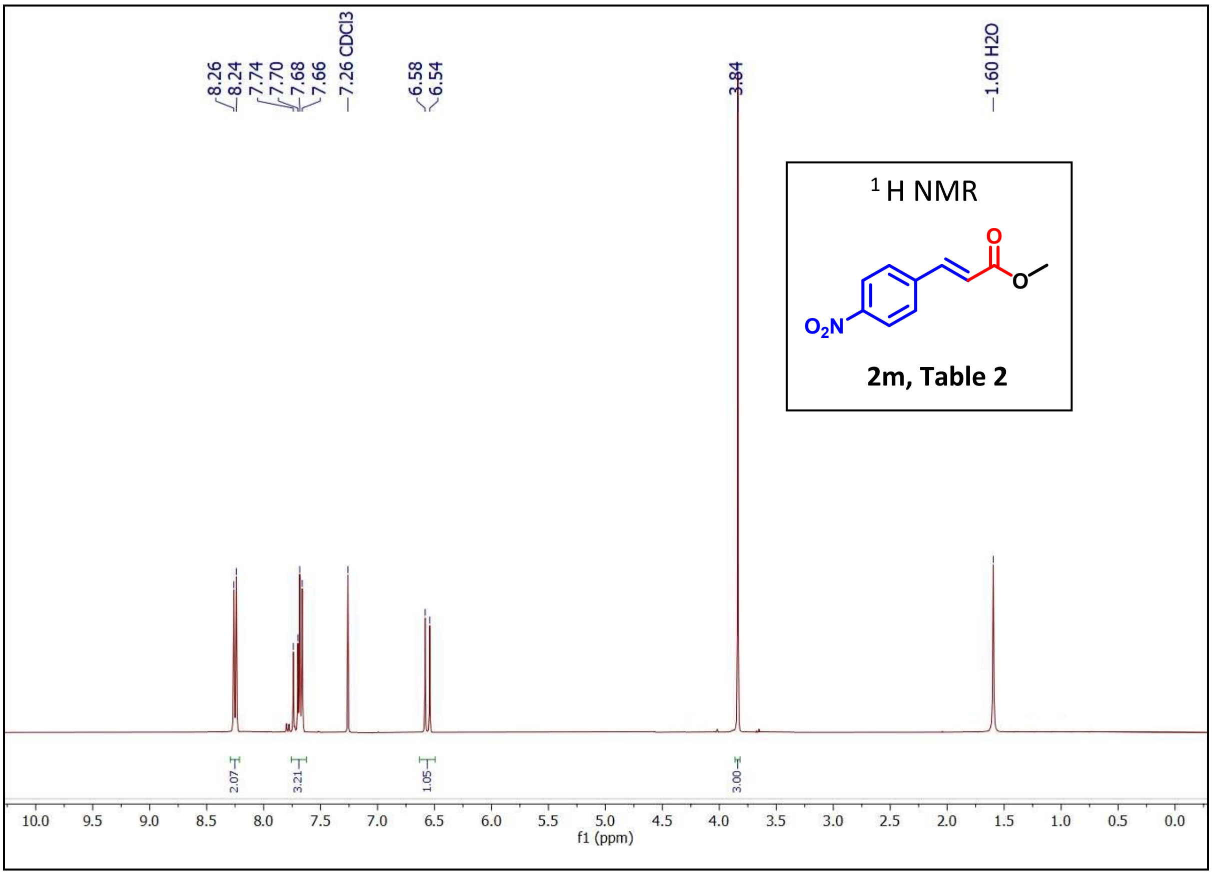
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26 CDCl3
6.58
6.54
3.84
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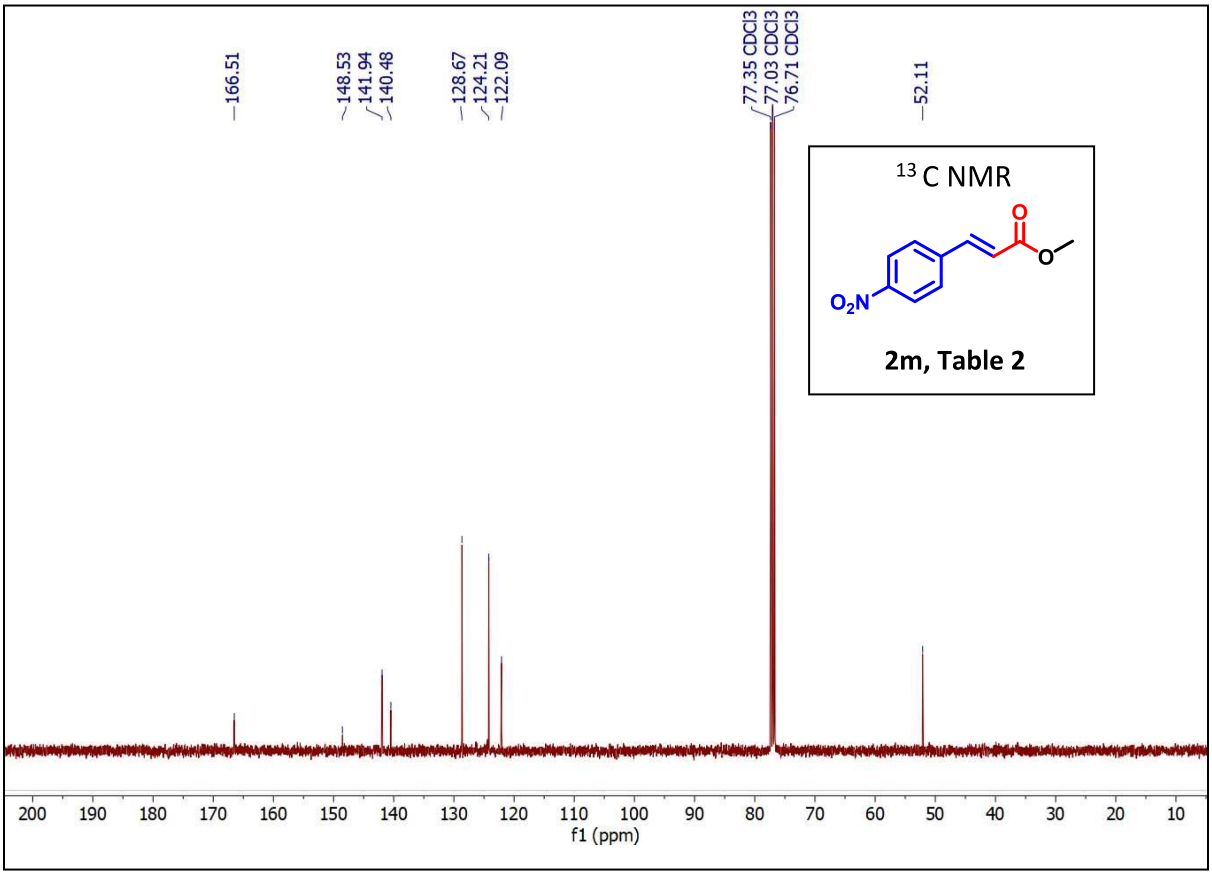
1 H NMR
O
O
O2N
2m, Table 2
2.07
3.21
1.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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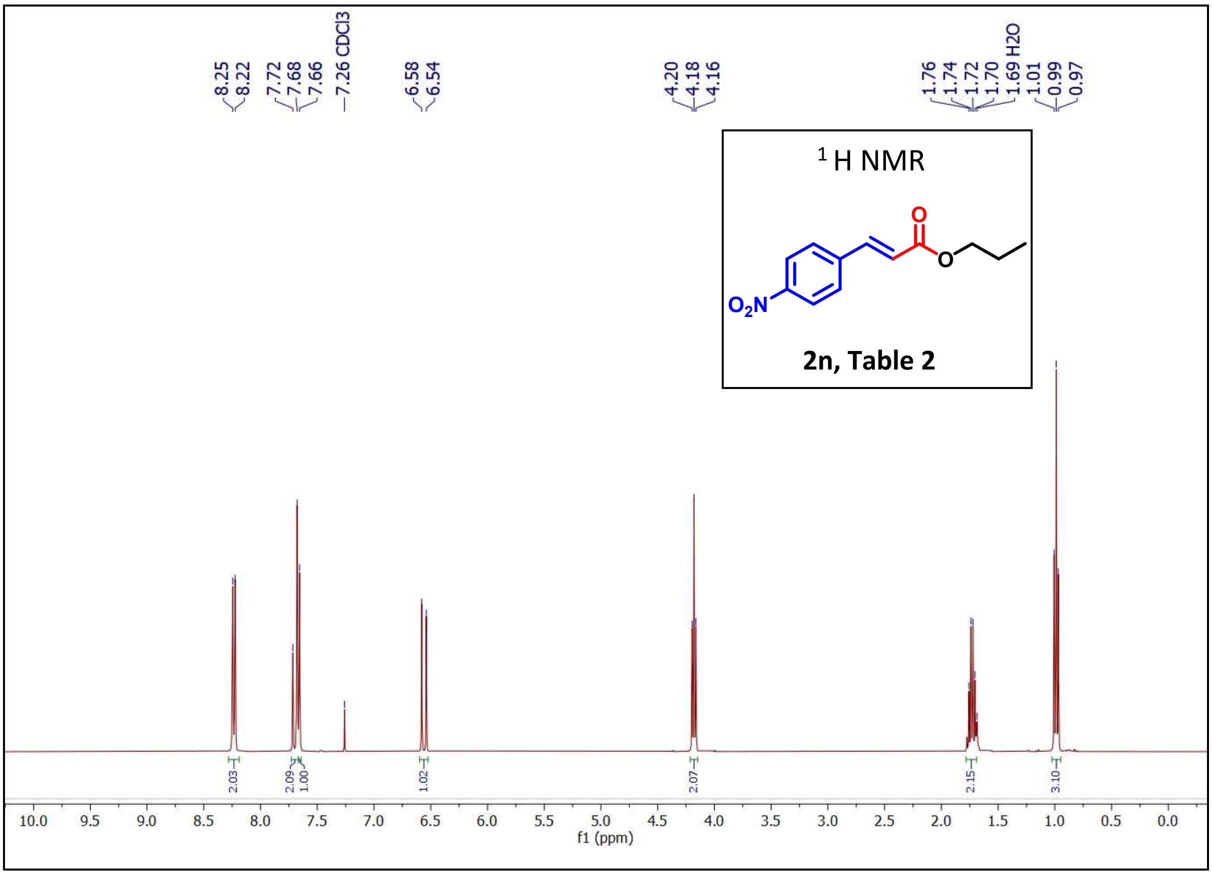
140.48
128.67
124.21
122.09
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
52.11
13 C NMR
O
O
O2N
2m, Table 2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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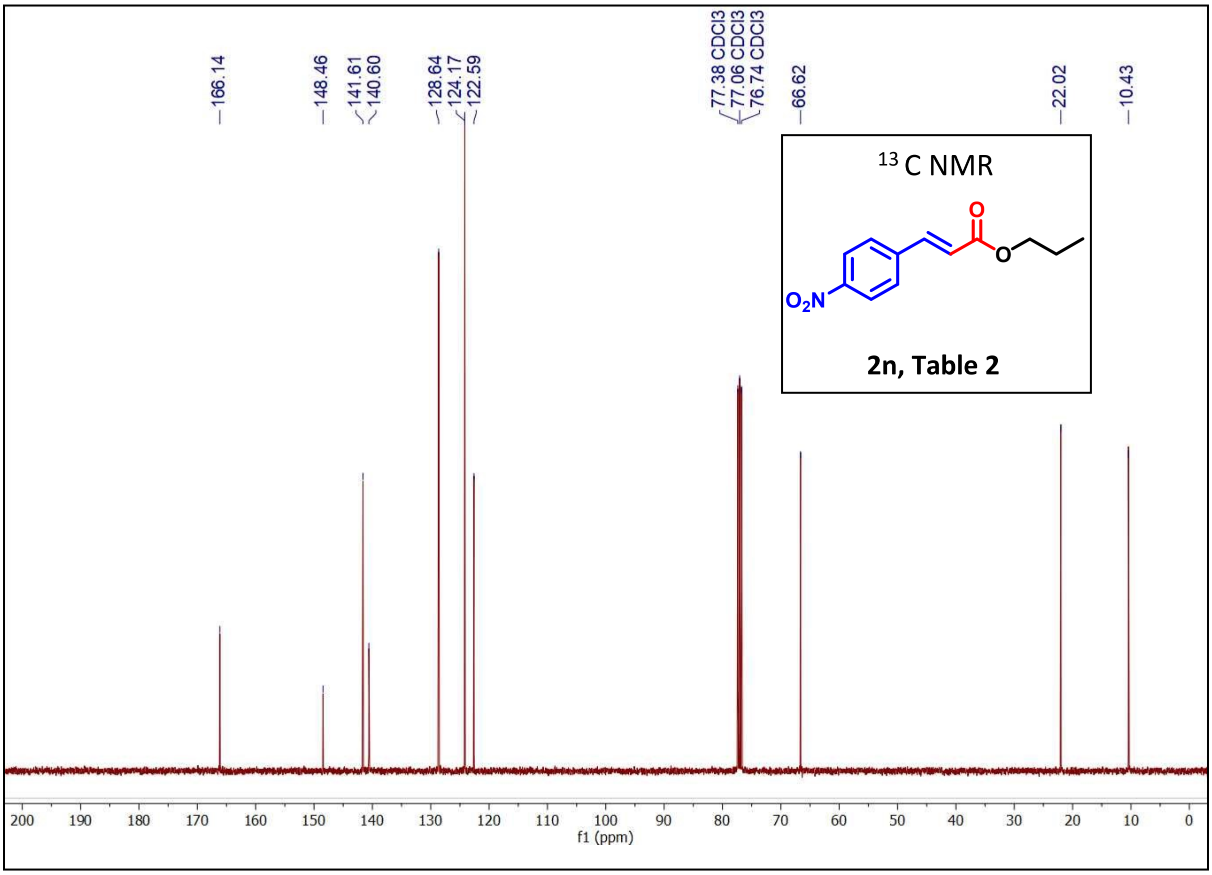
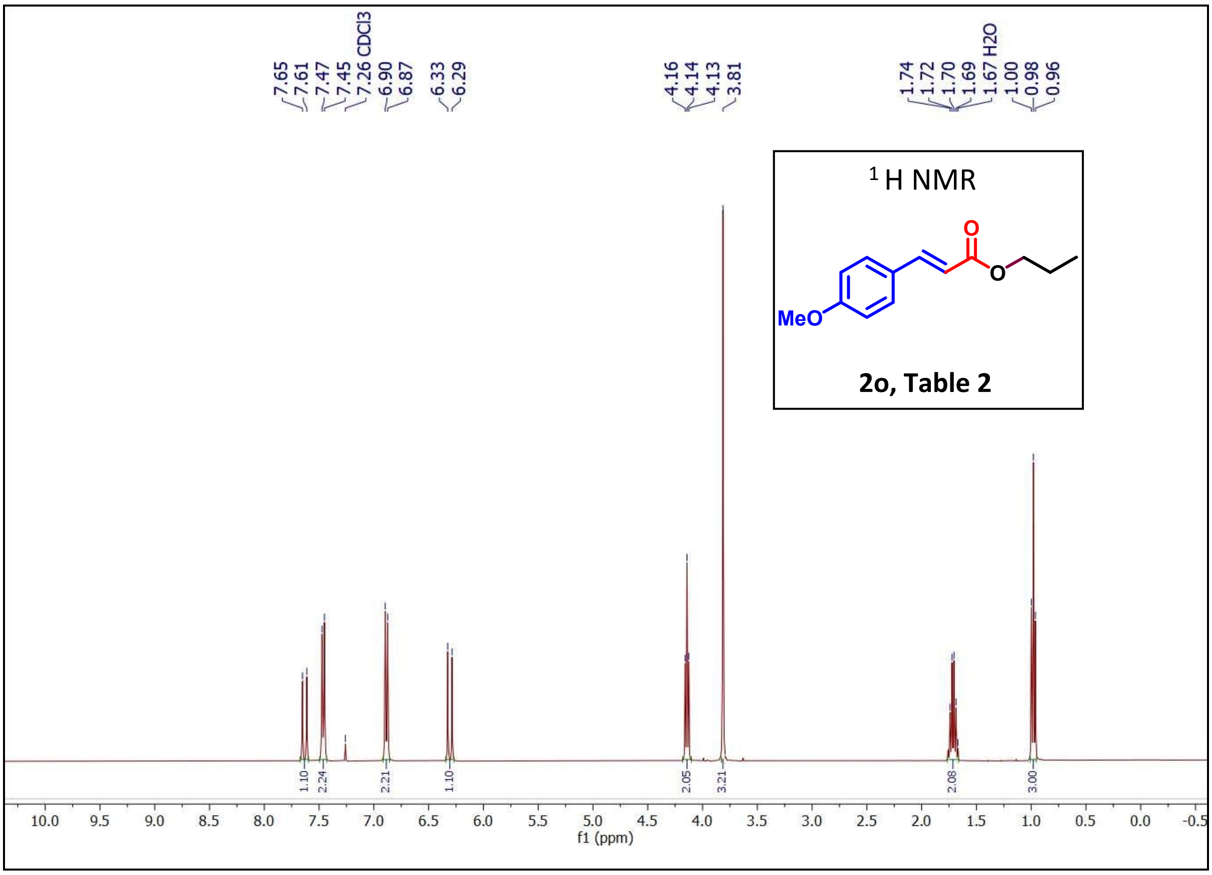
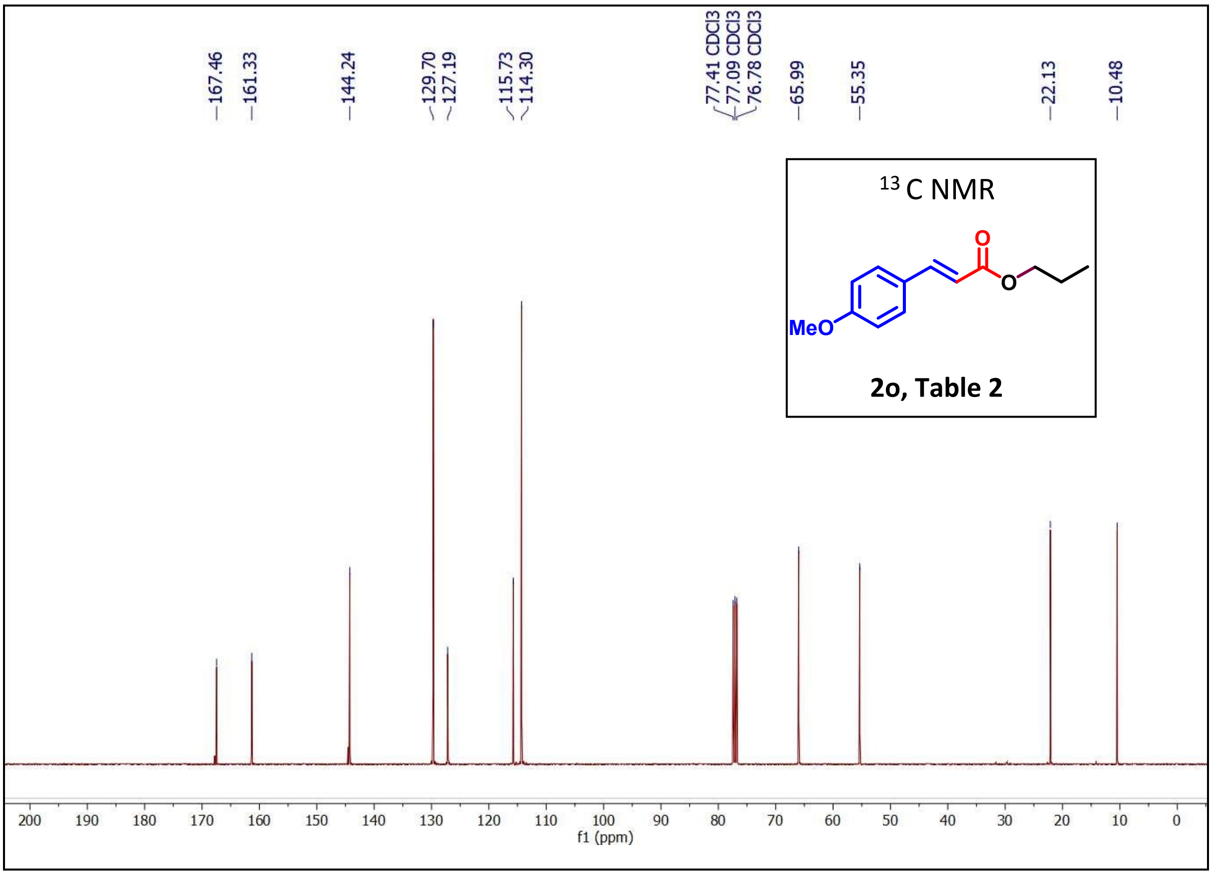
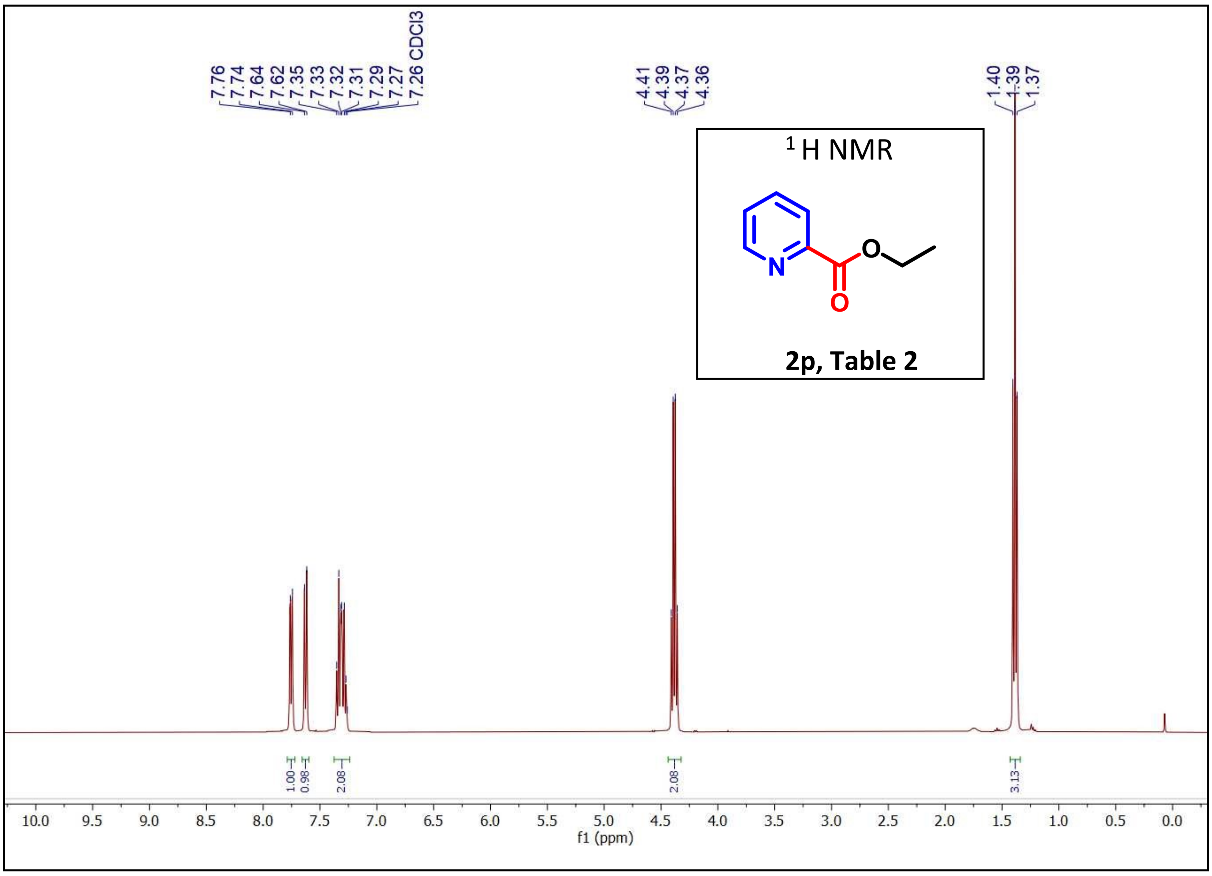
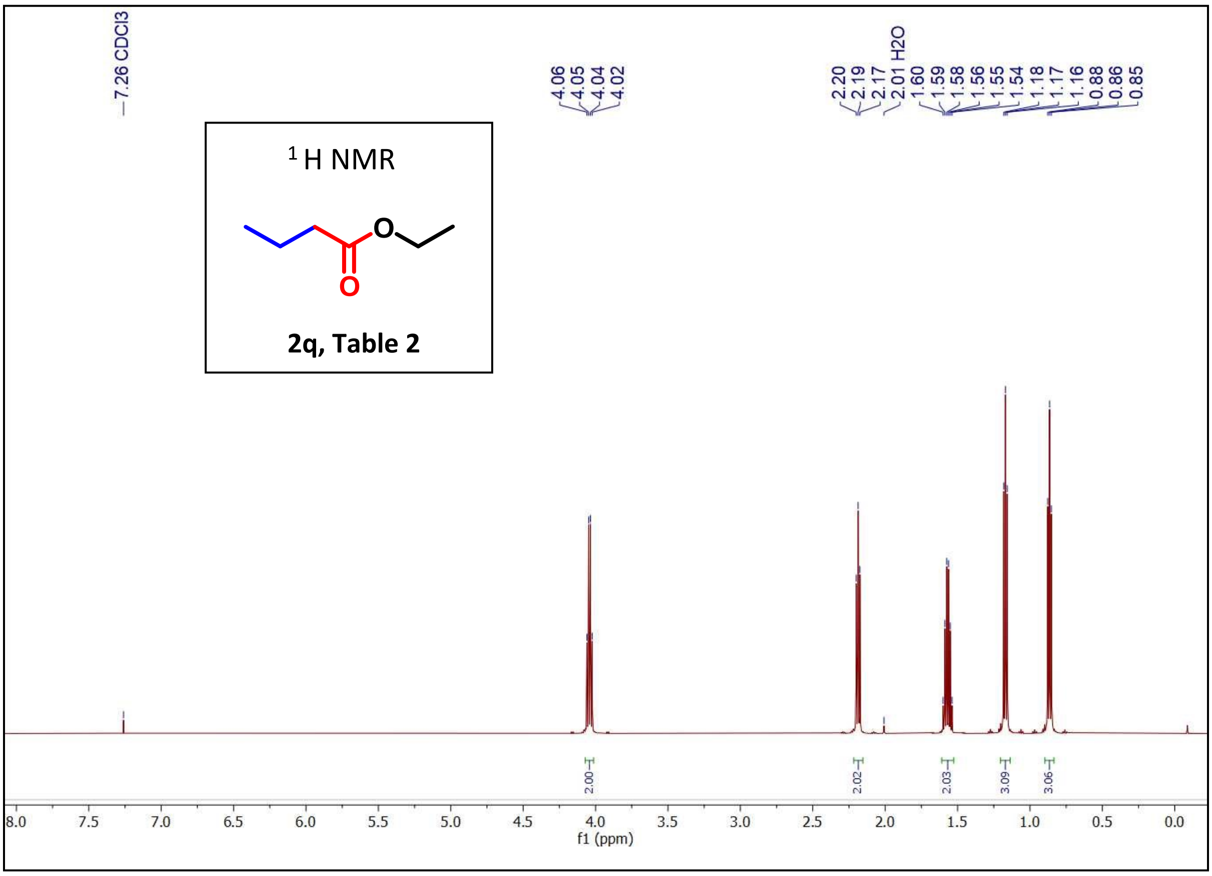
8.22
7.72
7.68
7.66
7.26 CDCl3
6.58
6.54
4.20
4.18
4.16
1.76
1.74
1.72
1.70
1.69 H2O
1.01
0.99
0.97
1 H NMR
O
O
O2N
2n, Table 2
2.03
2.09
1.00
1.02
2.07
2.15
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

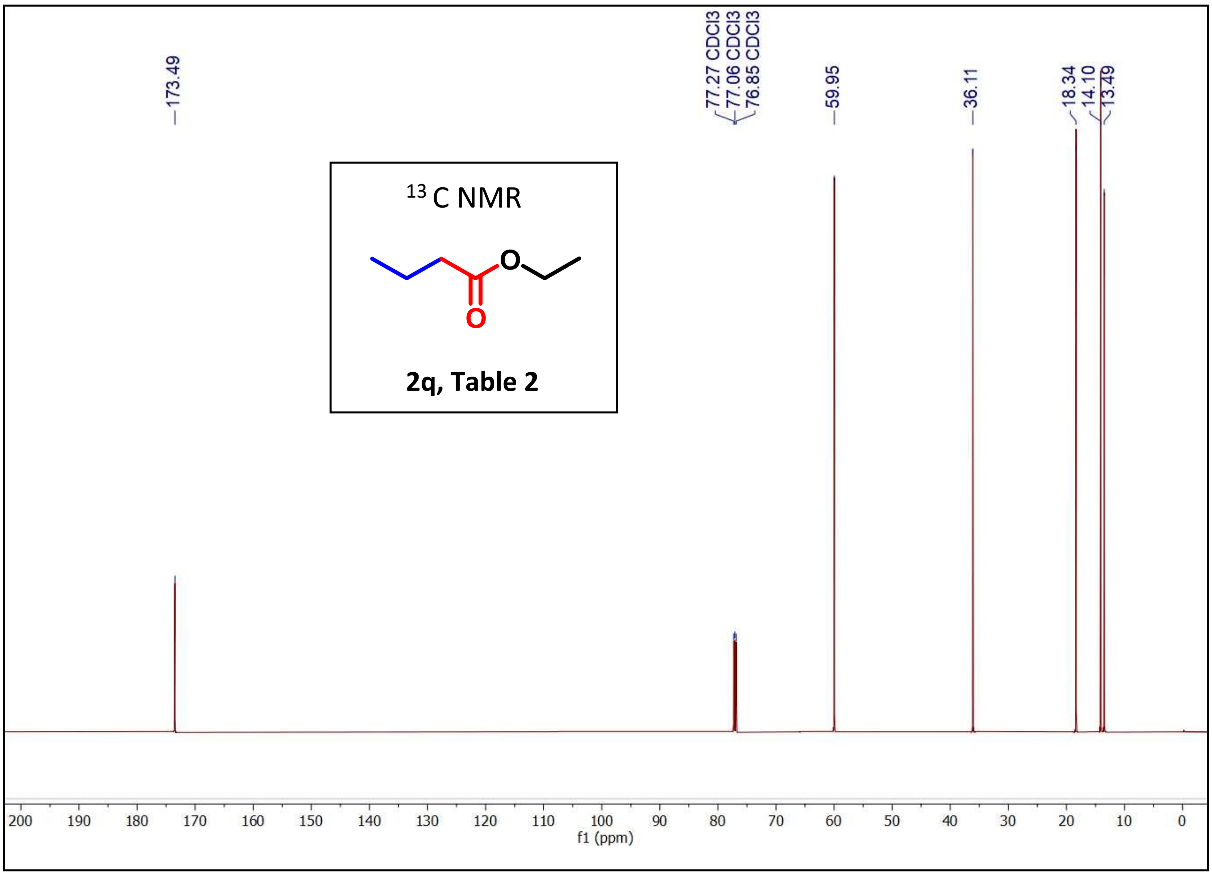

166.14
148.46
141.61
140.60
128.64
124.17
122.59
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
66.62
22.02
10.43
13 C NMR
O
O
O2N
2n, Table 2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

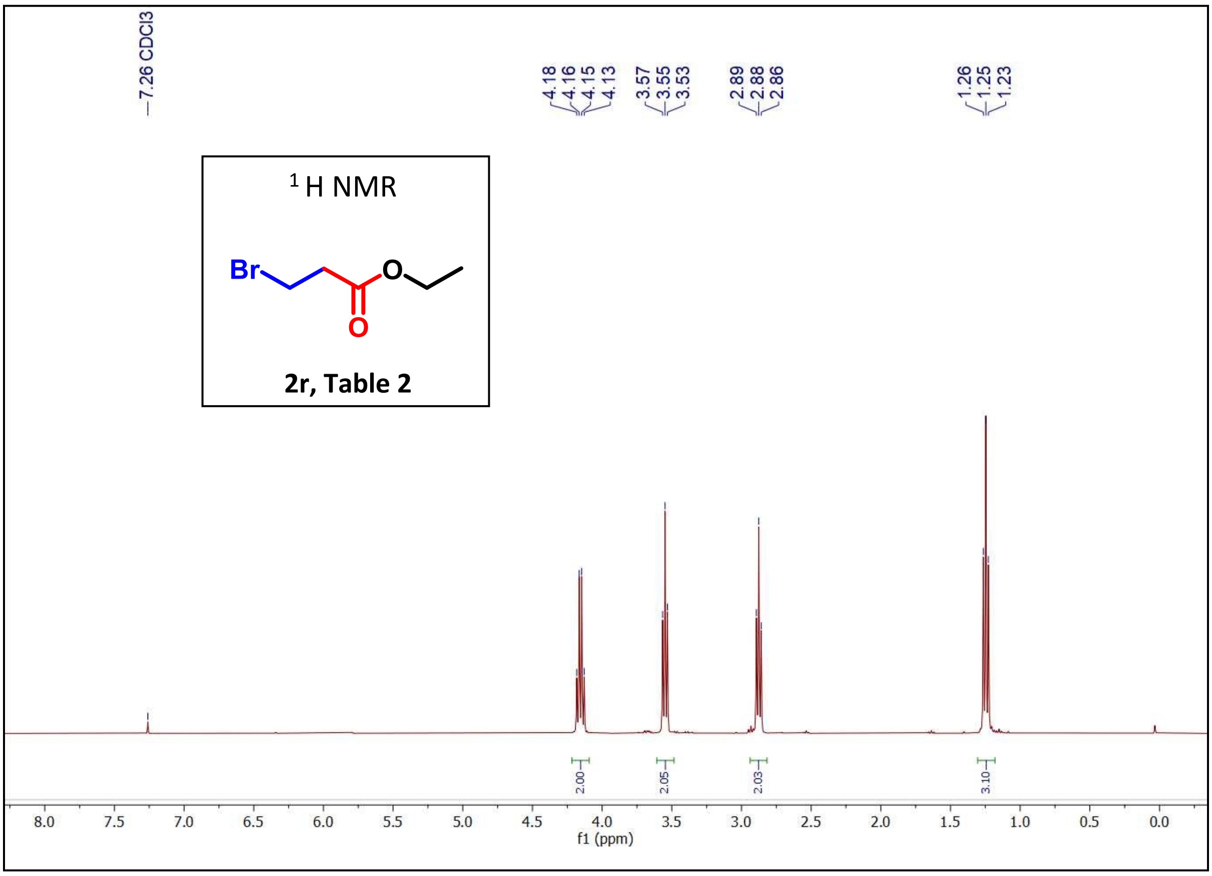

7.65
7.61
7.47
7.45
7.26 CDCl3
6.90
6.87
6.33
6.29
4.16
4.14
4.13
3.81
1.74
1.72
1.70
1.69
1.67 H2O
1.00
0.98
0.96
1 H NMR
O
O
MeO
2o, Table 2
1.10
2.24
2.21
1.10
2.05
3.21
2.08
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


167.46
161.33
144.24
129.70
127.19
115.73
114.30
77.41 CDCl3
77.09 CDCl3
76.78 CDCl3
65.99
55.35
22.13
10.48
13 C NMR
O
O
MeO
2o, Table 2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

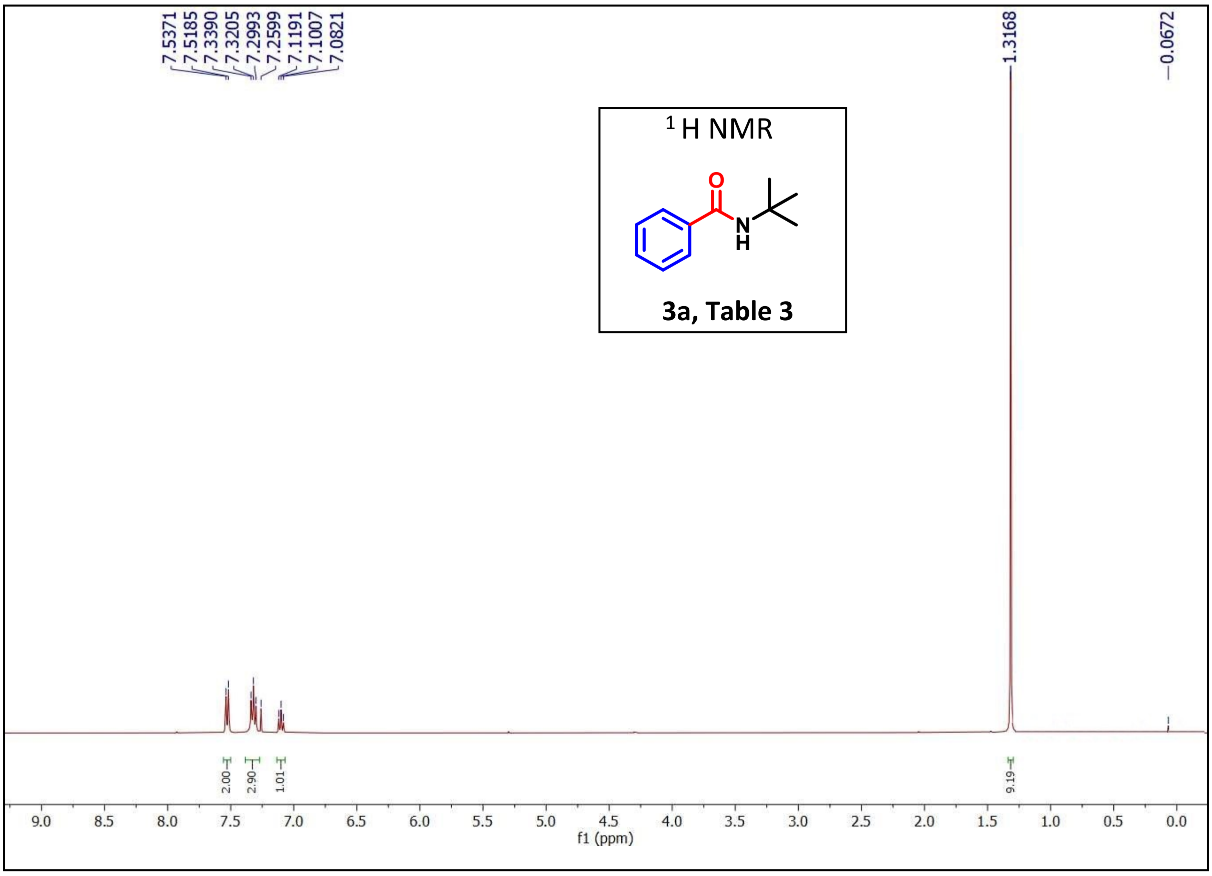

7.76
7.74
7.64
7.62
7.35
7.33
7.32
7.31
7.29
7.27
7.26 CDCl3
4.41
4.39
4.37
4.36
1.40
1.39
1.37
^{1}H NMR
N
O
O
2p, Table 2
1.00
0.98
2.08
2.08
3.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

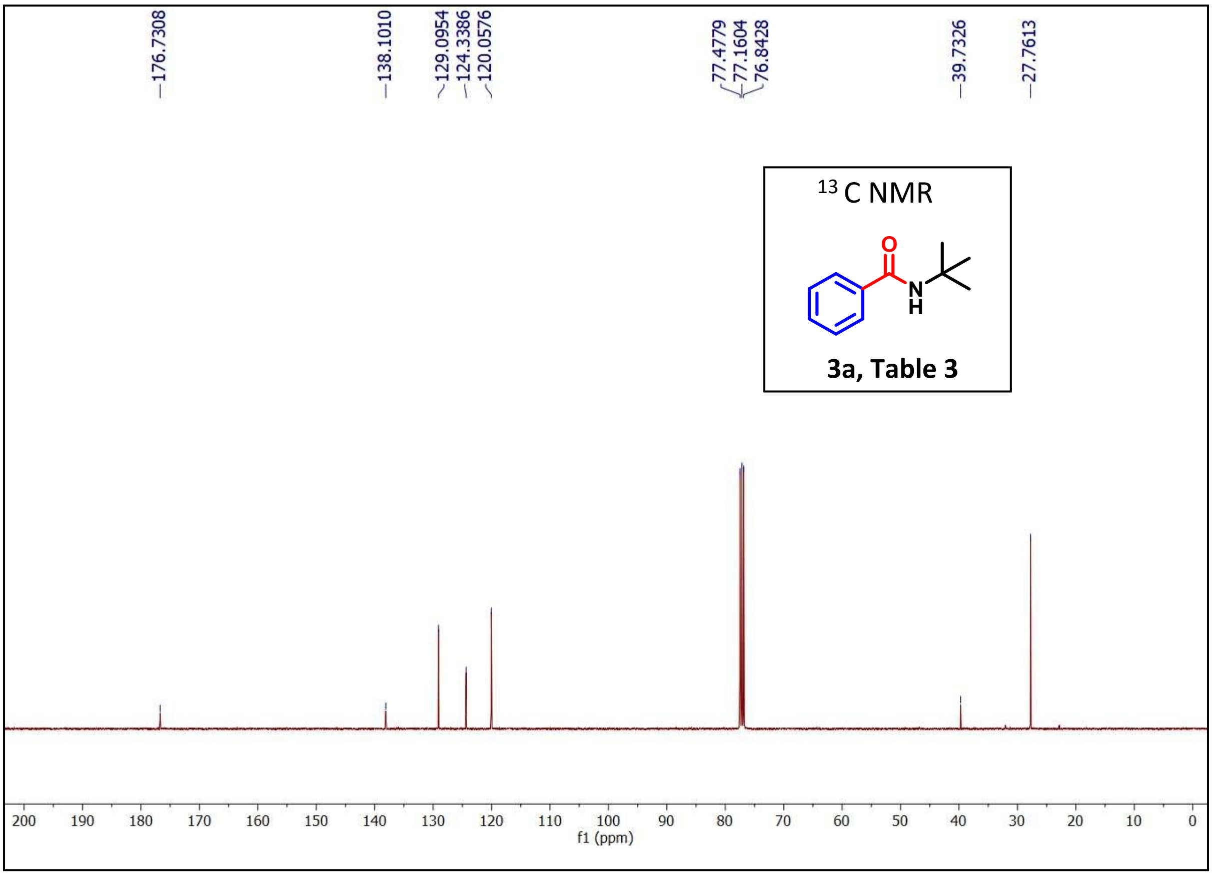

7.26 CDCl3
4.06
4.05
4.04
4.02
2.20
2.19
2.17
2.01 H2O
1.60
1.59
1.58
1.56
1.55
1.54
1.18
1.17
1.16
0.88
0.86
0.85
^{1}H NMR
O
O
2q, Table 2
2.00
2.02
2.03
3.09
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

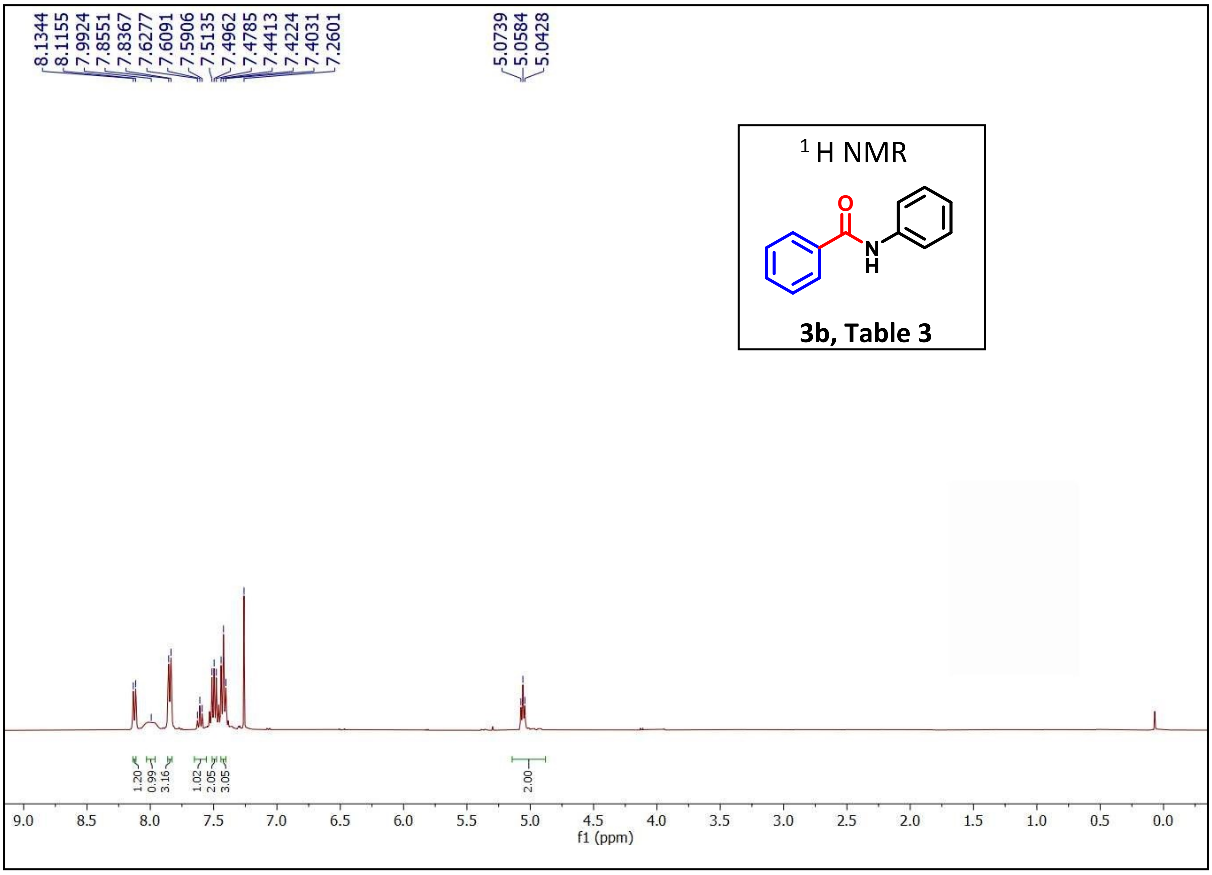

173.49
77.27 CDCl3
77.06 CDCl3
76.85 CDCl3
59.95
36.11
18.34
14.10
13.49
^{13}C NMR
O
O
2q, Table 2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

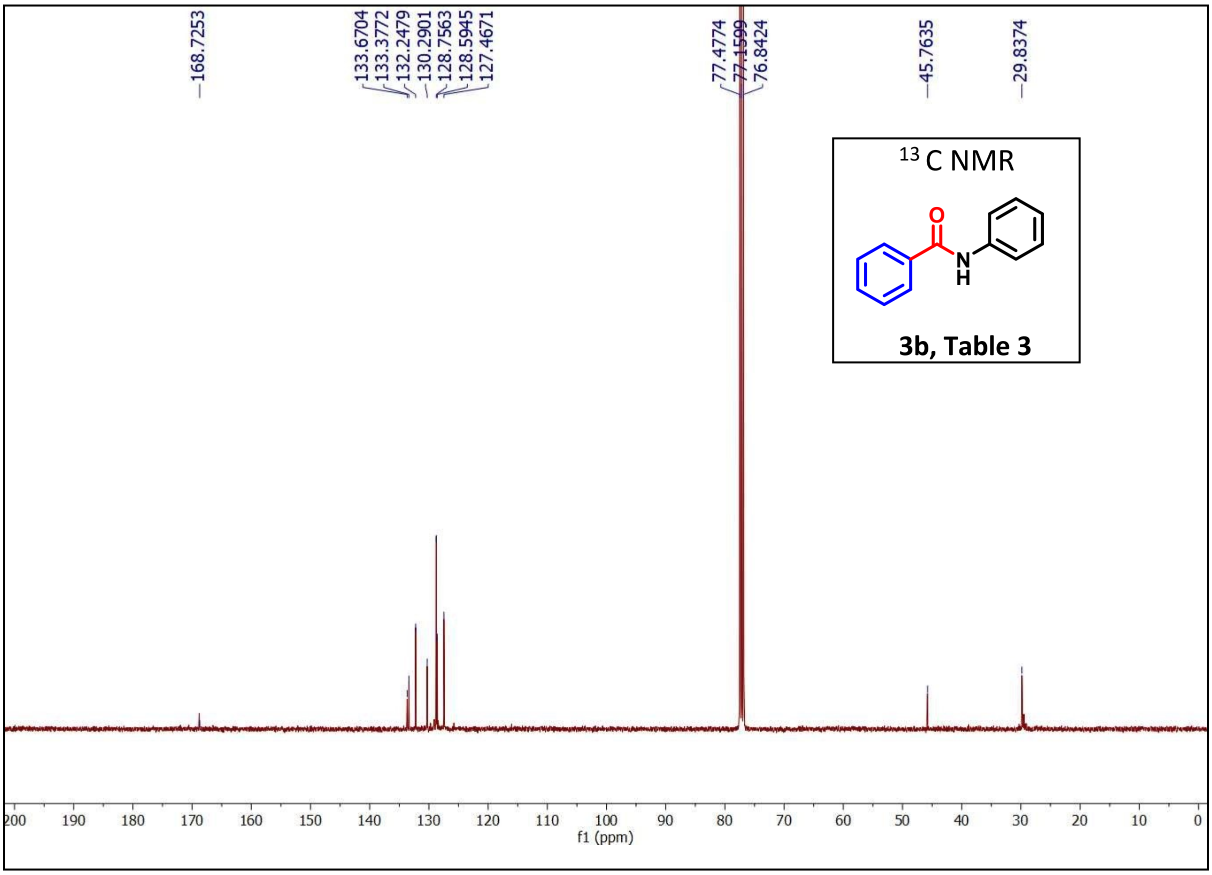

7.26 CDCl3
4.18
4.16
4.15
4.13
3.57
3.55
3.53
2.89
2.88
2.86
1.26
1.25
1.23
^{1}H NMR
Br
O
O
2r, Table 2
2.00
2.05
2.03
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

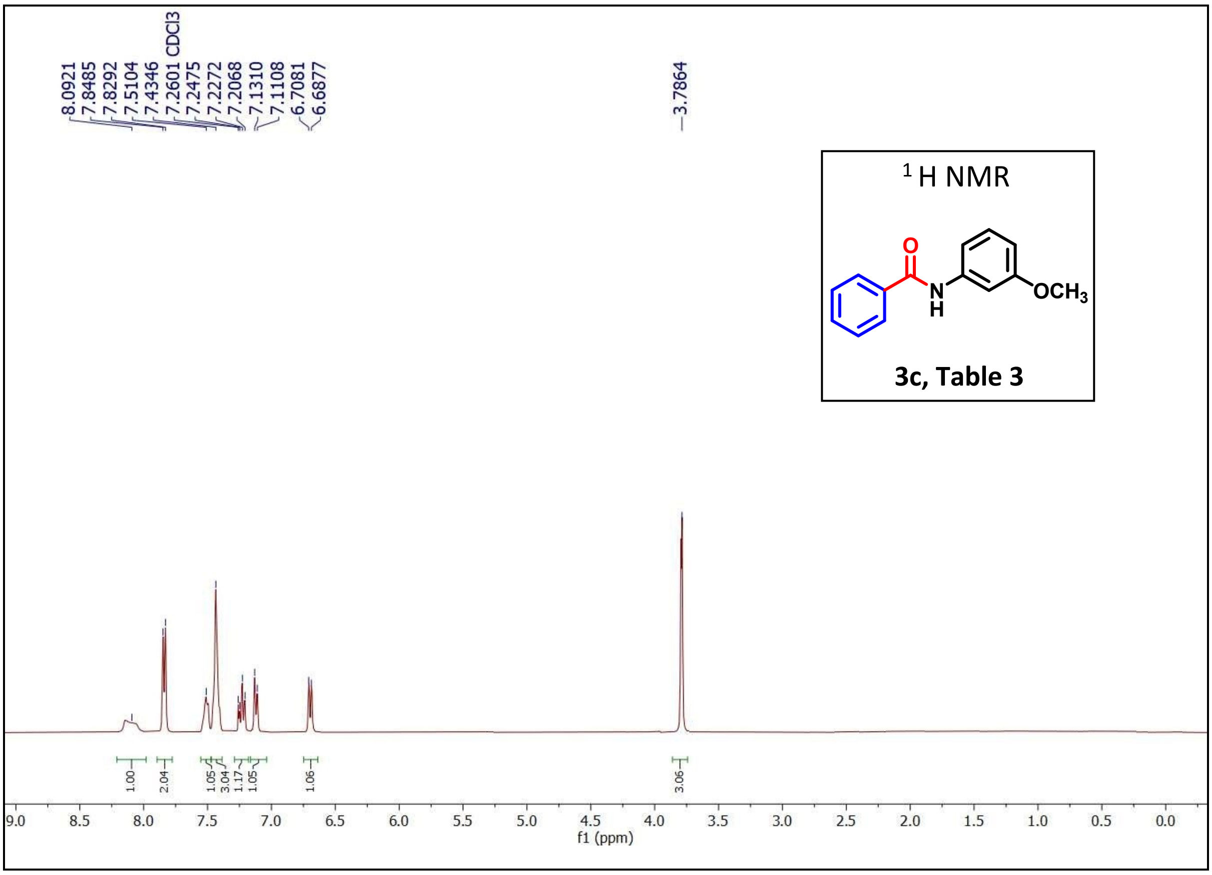
ESI 6. Copies of ^{1}H NMR and ^{13}C NMR spectra of products listed in Table 3:

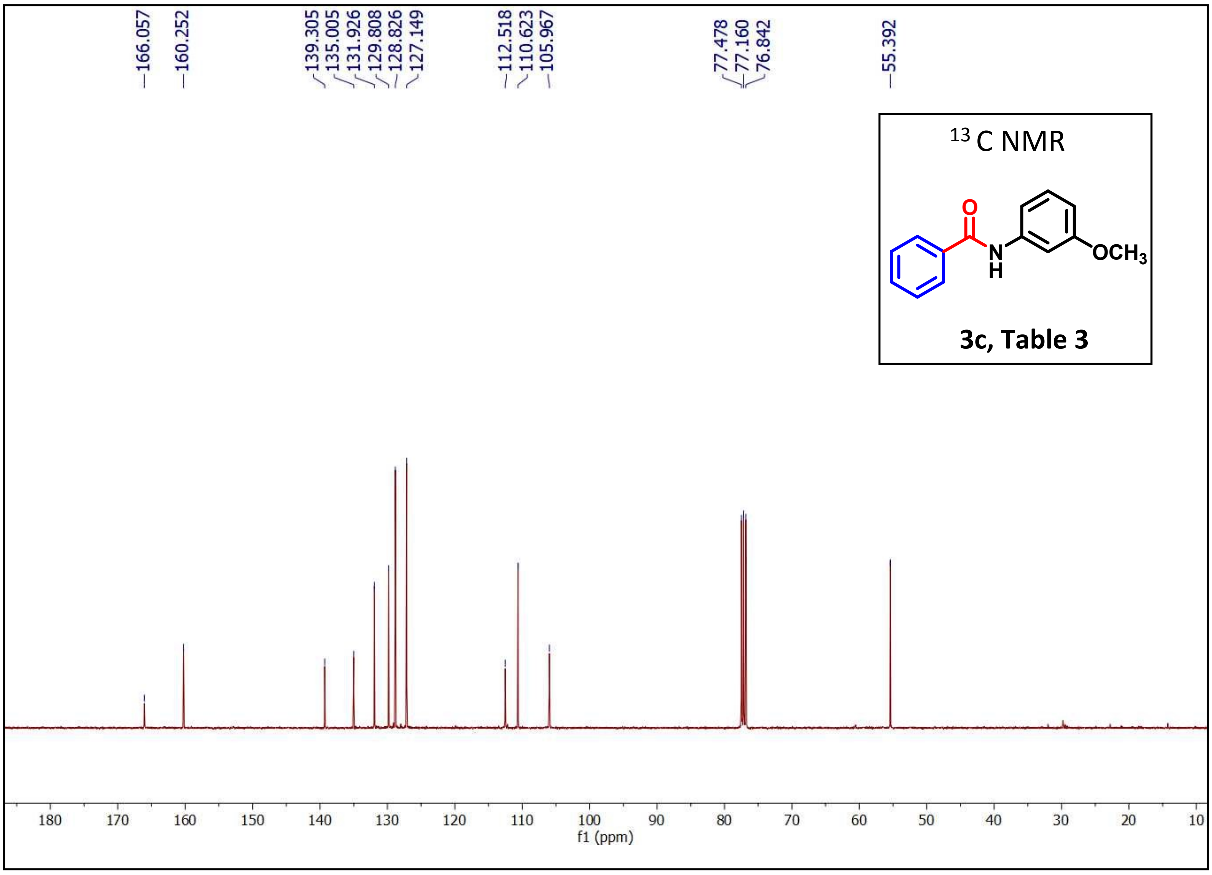


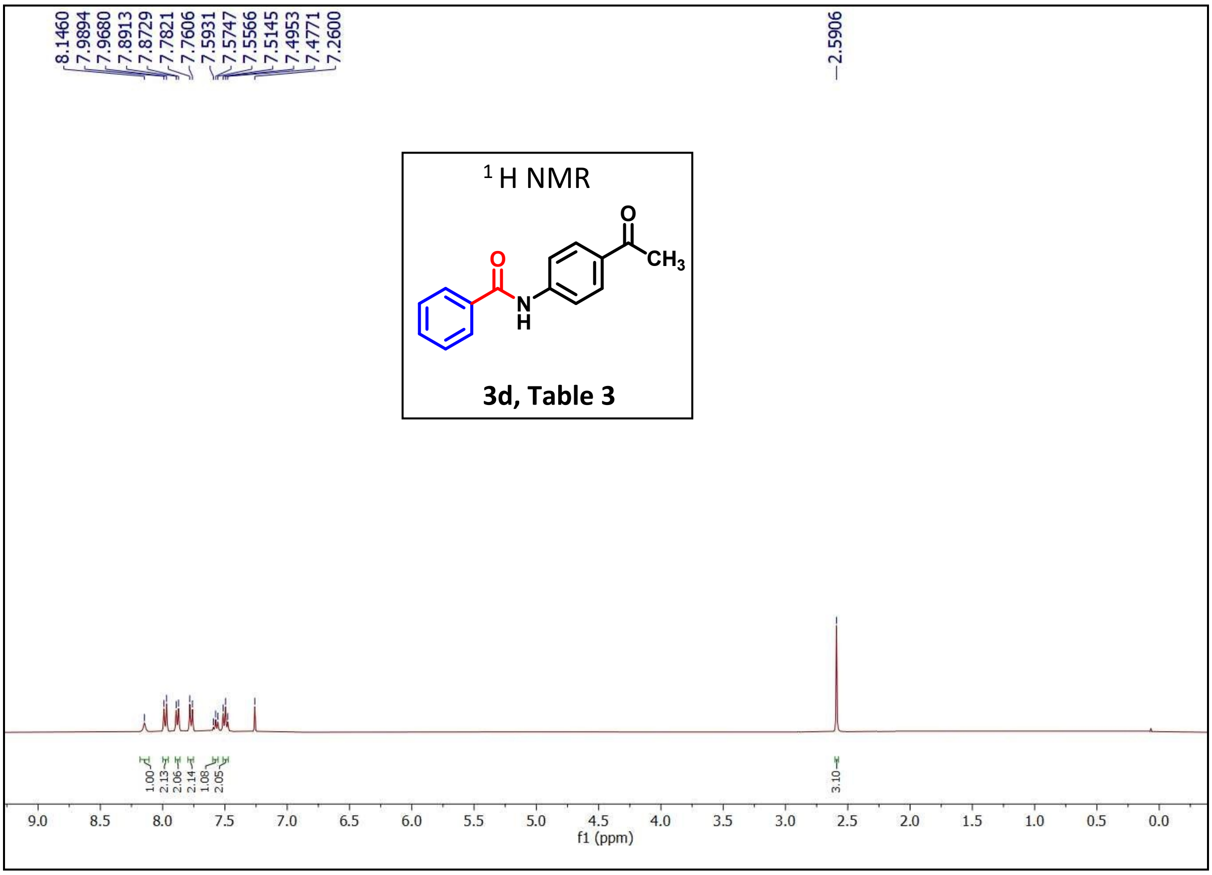


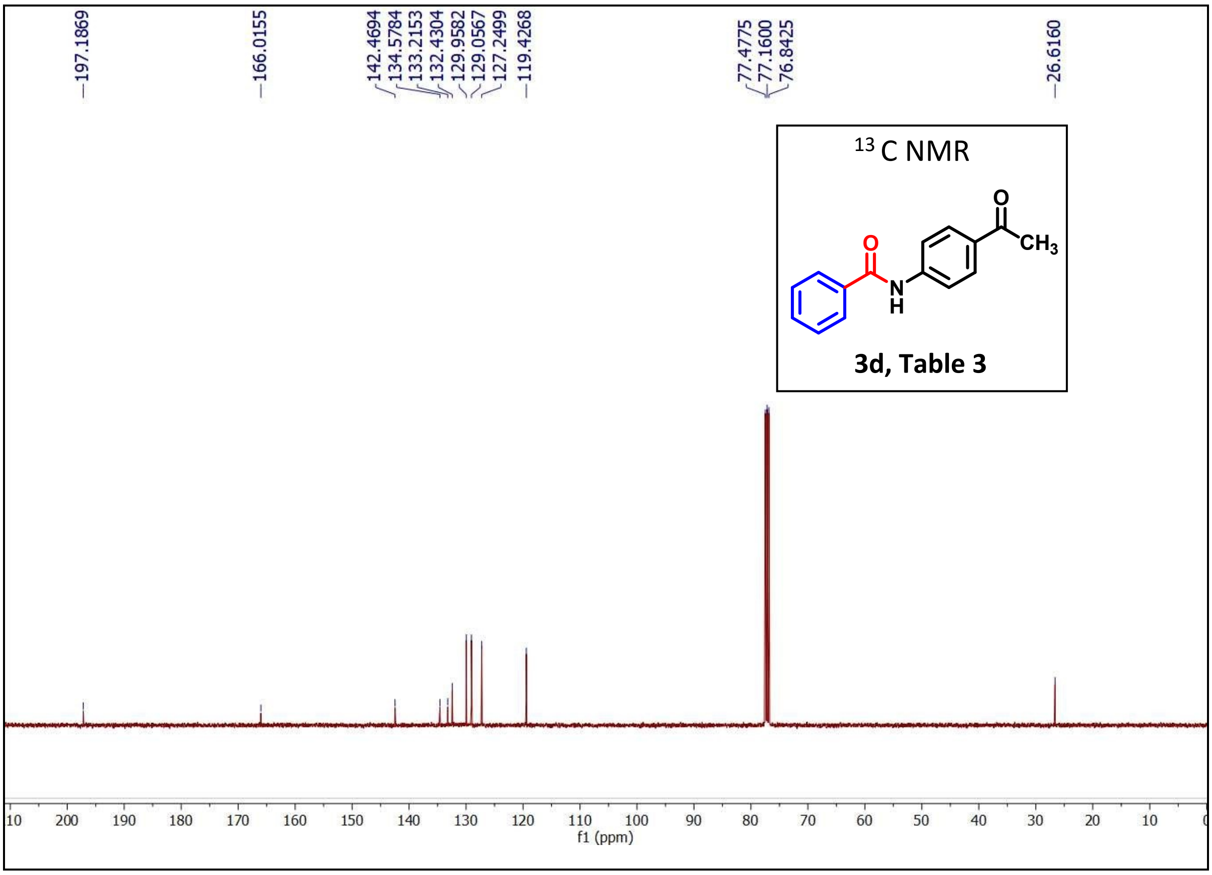

8.1344
8.1155
7.9924
7.8551
7.8367
7.6277
7.6091
7.5906
7.5135
7.4962
7.4785
7.4413
7.4224
7.4031
7.2601
5.0739
5.0584
5.0428
^{1}H NMR
O
N
H
3b, Table 3
1.20
0.99
3.16
1.02
2.05
3.05
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

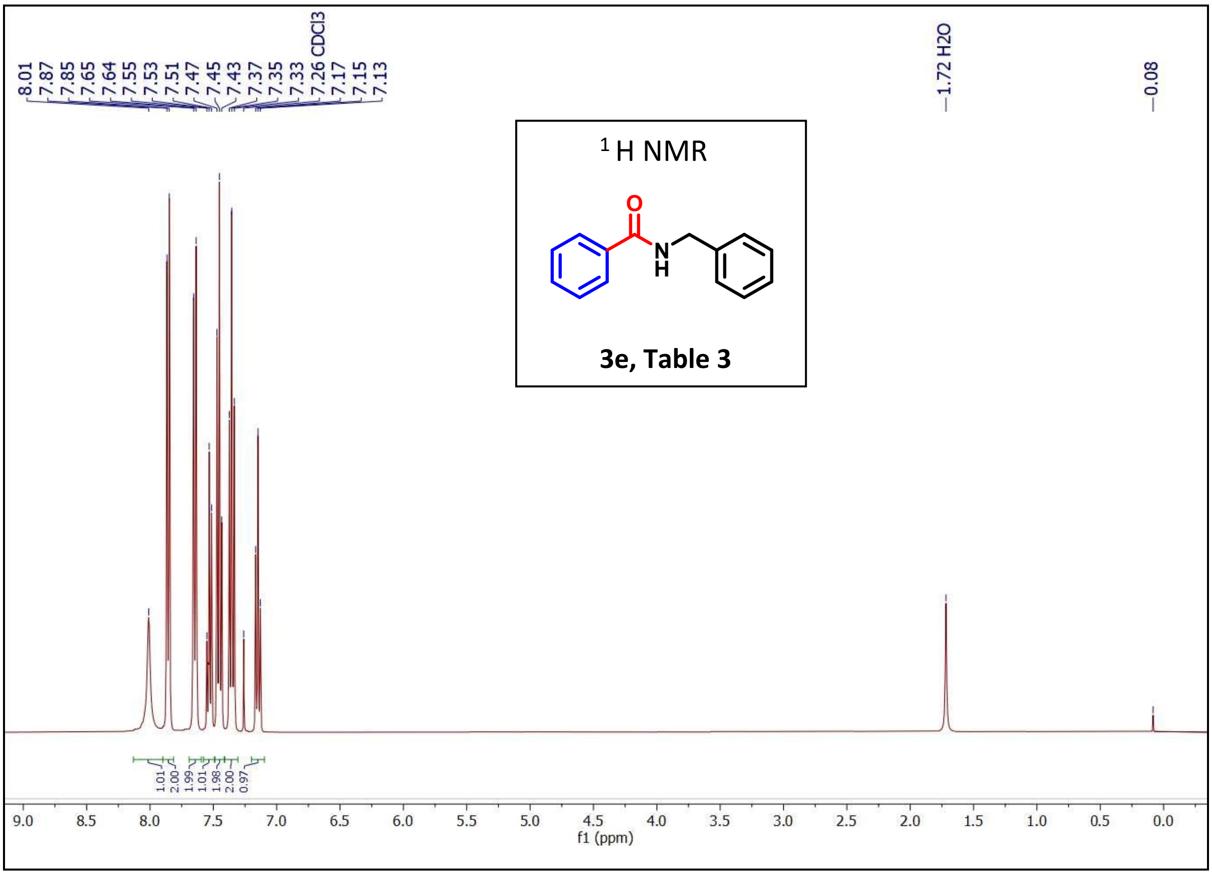

168.7253
133.6704
133.3772
132.2479
130.2901
128.7563
128.5945
127.4671
77.4774
77.1599
76.8424
45.7635
29.8374
^{13}C NMR
O
N
H
3b, Table 3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

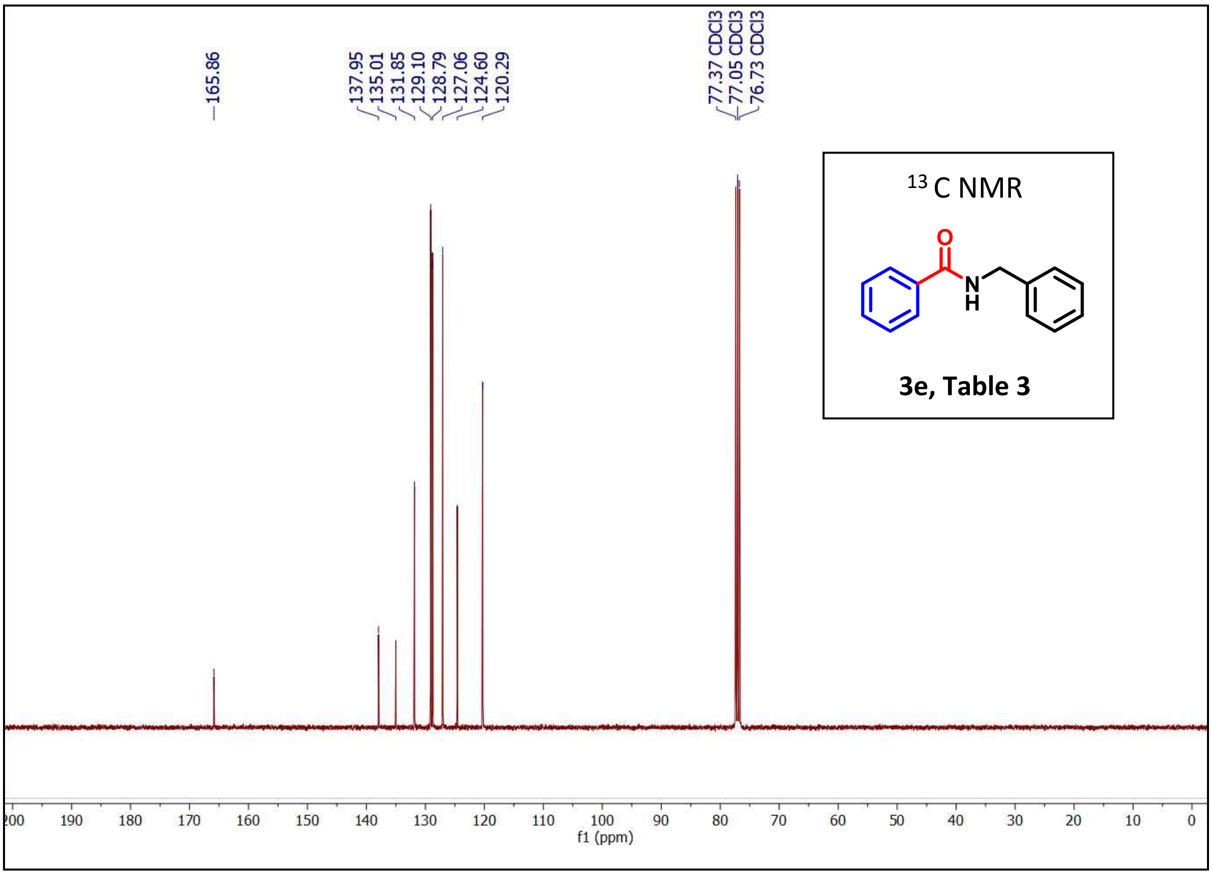

8.0921
7.8485
7.8292
7.5104
7.4346
7.2601 CDCl3
7.2475
7.2272
7.2068
7.1310
7.1108
6.7081
6.6877
3.7864
^{1}H NMR
O
N
H
OCH$_3$
3c, Table 3
1.00
2.04
1.05
3.04
1.17
1.05
1.06
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.057
160.252
139.305
135.005
131.926
129.808
128.826
127.149
112.518
110.623
105.967
77.478
77.160
76.842
55.392
^{13}C NMR
O
N
H
OCH$_3$
3c, Table 3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.1460
7.9894
7.9680
7.8913
7.8729
7.7821
7.7606
7.5931
7.5747
7.5566
7.5145
7.4953
7.4771
7.2600
2.5906
1 H NMR
O
CH3
O
N
H
3d, Table 3
1.00
2.13
2.06
2.14
1.08
2.05
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.1869
166.0155
142.4694
134.5784
133.2153
132.4304
129.9582
129.0567
127.2499
119.4268
77.4775
77.1600
76.8425
26.6160
13 C NMR
O
CH3
O
N
H
3d, Table 3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.01
7.87
7.85
7.65
7.64
7.55
7.53
7.51
7.47
7.45
7.43
7.37
7.35
7.33
7.26 CDCl3
7.17
7.15
7.13
1.72 H2O
0.08
1 H NMR
O
N
H
3e, Table 3
1.01
2.00
1.99
1.01
1.98
2.00
0.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.86
137.95
135.01
131.85
129.10
128.79
127.06
124.60
120.29
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
13 C NMR
O
N
H
3e, Table 3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)