

Supporting Information

Ester Functionalized *N*-Heterocyclic Carbene Complexes of Iridium(I): Efficient Catalysts for Transfer Hydrogenation Reactions

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Characterization Data of the Resulting Alcohols from the Catalytic Reactions:

1-Phenylethanol: Colorless liquid, ¹H NMR (400 MHz, CDCl₃, TMS, 25°C, ppm): δ = 1.47 (3H, d, J = 6.8 Hz, CHCH₃), 2.98 (1H, br, OH), 4.83 (1H, t, J = 6.4 Hz, OCHCH₃), 7.26-7.32 (1H, m, ArH), 7.36 (4H, d, J = 8.4 Hz, ArH). ¹³C NMR (100.6 MHz, CDCl₃, TMS, 25°C, ppm): δ = 25.1 (CHCH₃), 70.2 (OCHCH₃), 125.5, 127.4, 128.4, 145.9 (ArC).

1-(4-Bromophenyl)ethanol: Colorless liquid, ¹H NMR (400 MHz, CDCl₃, TMS, 25°C, ppm): δ = 1.37 (3H, d, J = 6.8 Hz, CHCH₃), 3.44 (1H, br, OH), 4.72 (1H, t, J = 6.4 Hz, OCHCH₃), 7.15 (2H, d, J = 8.4 Hz, ArH), 7.40 (2H, d, J = 8.4 Hz, ArH). ¹³C NMR (100.6 MHz, CDCl₃, TMS, 25°C, ppm): δ = 25.2 (CHCH₃), 69.5 (OCHCH₃), 121.0, 127.2, 131.4, 144.8 (ArC).

1-(4-Methoxyphenyl)ethanol: Colorless liquid, ¹H NMR (400 MHz, CDCl₃, TMS, 25°C, ppm): δ = 1.46 (3H, d, J = 6.8 Hz, CHCH₃), 2.05 (1H, br, OH), 3.79 (3H, s, OCH₃), 4.83 (1H, q, J = 6.4 Hz, OCHCH₃), 6.87 (2H, d, J = 4.0 Hz, ArH), 7.28 (2H, d, J = 4.0 Hz, ArH). ¹³C NMR (100.6 MHz, CDCl₃, TMS, 25°C, ppm): δ = 25.0 (CHCH₃), 55.3 (OCH₃), 69.9 (OCHCH₃), 113.8, 126.6, 138.0, 158.9 (ArC).

1-Phenylpropanol: Colorless liquid, ¹H NMR (400 MHz, CDCl₃, TMS, 25°C, ppm): δ = 0.92 (3H, t, J = 7.6 Hz, CHCH₂CH₃), 1.71-1.86 (2H, m, CHCH₂CH₃), 2.14 (1H, br, OH), 4.58 (1H, t, J = 6.8 Hz, OCHCH₂CH₃), 7.26-7.35 (5H, m, ArH). ¹³C NMR (100.6 MHz, CDCl₃, TMS, 25°C, ppm): δ = 10.1 (CHCH₂CH₃), 31.8 (CHCH₂CH₃), 75.9 (OCHCH₂CH₃), 125.9, 127.4, 128.3, 144.5 (ArC).

1-(3,4-Dimethylphenyl)ethanol: Colorless liquid, ¹H NMR (400 MHz, CDCl₃, TMS, 25°C, ppm): δ = 1.49 (3H, d, J = 6.8 Hz, CHCH₃), 2.06 (1H, br, OH), 2.28 (1H, s, ArCH₃), 2.29 (1H, s, ArCH₃), 4.82 (1H, q, J = 6.4 Hz, CHCH₃), 7.10-7.16 (3H, m, ArH). ¹³C NMR (100.6 MHz, CDCl₃, TMS, 25°C, ppm): δ = 19.4 (ArCH₃), 19.8 (ArCH₃), 25.1 (CHCH₃), 70.2 (OCHCH₃), 122.8, 126.7, 129.7, 135.7, 136.6, 143.4 (ArC).

1-(2-Chlorophenyl)ethanol: Colorless liquid, ¹H NMR (400 MHz, CDCl₃, TMS, 25°C, ppm): δ = 1.42 (3H, d, J = 6.8 Hz, CHCH₃), 3.43 (1H, br, OH), 5.22 (1H, q, J = 6.4 Hz, OCHCH₃), 7.16 (1H, t, J = 8.0 Hz, ArH), 7.23-7.30 (2H, m, ArH), 7.53 (1H, d, J = 8.4 Hz, ArH). ¹³C NMR (100.6 MHz, CDCl₃, TMS, 25°C, ppm): δ = 23.5 (CHCH₃), 66.7 (OCHCH₃), 126.4, 127.2, 128.3, 131.5, 143.2 (ArC).

Diphenyl carbinol: White solid, ^1H NMR (400 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 2.56 (1H, br, OH), 5.81 (1H, t, J = 6.4 Hz, OCHAr), 7.29-7.39 (10H, m, ArH). ^{13}C NMR (100.6 MHz, CDCl_3 , TMS, 25°C , ppm): 76.2 (OCHAr), 126.6, 127.6, 128.5, 143.8 (ArC).

Cyclohexanol: Colorless liquid, ^1H NMR (400 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 1.10-1.24, 1.45-1.49, 1.64-1.67, 1.80-1.83 (10H, 5m, $5\times\text{CH}_2$), 2.64 (1H, br, OH), 3.47-3.54 (1H, m, OCH). ^{13}C NMR (100.6 MHz, CDCl_3 , TMS, 25°C , ppm): 25.1, 25.4, 35.4 ($3\times\text{CH}_2$), 70.1 (OCH).

2-Heptanol: Colorless liquid, ^1H NMR (400 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 0.83 (3H, d, J = 7.2 Hz, CH_3), 1.10 (3H, d, J = 6.8 Hz, CHCH_3), 1.74-1.41 (8H, m, CH_2), 2.50 (1H, br, OH), 3.66-3.74 (1H, q, J = 6.4 Hz, OCH CH_3). ^{13}C NMR (100.6 MHz, CDCl_3 , TMS, 25°C , ppm): 13.9, 22.5, 23.2, 25.4 ($4\times\text{CH}_2$), 31.8, 39.2 ($2\times\text{CH}_3$), 67.8 (OCH CH_3).

Benzyl alcohol: Colorless liquid, ^1H NMR (400 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 3.58 (1H, br, OH), 4.59 (2H, d, J = 8.0 Hz, OCH_2), 7.33-7.41 (5H, m, ArH). ^{13}C NMR (100.6 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 66.2 (OCH_2), 127.0, 127.6, 128.5, 140.9 (ArC).

4-Methoxybenzyl alcohol: Colorless liquid, ^1H NMR (400 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 1.99 (1H, br, OH), 3.80 (3H, s, OCH_3), 4.58 (2H, s, OCH_2), 6.88 (2H, d, J = 8.4 Hz, ArH), 7.27 (2H, d, J = 8.4 Hz, ArH). ^{13}C NMR (100.6 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 55.3 (OCH_3), 64.9 (OCH_2), 113.9, 128.6, 133.1, 159.1 (ArC).

2-Methoxybenzyl alcohol: Colorless liquid, ^1H NMR (400 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 2.47 (1H, br, OH), 3.86 (3H, s, OCH_3), 4.69 (2H, d, J = 6.0 Hz, OCH_2), 6.88-6.97 (2H, m, ArH), 7.26-7.30 (2H, m, ArH). ^{13}C NMR (100.6 MHz, CDCl_3 , TMS, 25°C , ppm): δ = 55.2 (OCH_3), 62.0 (OCH_2), 110.2, 120.6, 128.7, 128.9, 129.1, 157.4 (ArC).

Table S1. Crystallographic data and structure refinement summary for **3a**, **3c** and **3d**.

Complex	3a	3c	3d
Formula	$\text{C}_{33}\text{H}_{44}\text{Cl Ir N}_2\text{O}$	$\text{C}_{37}\text{H}_{50}\text{Cl Ir N}_2\text{O}_2$	$\text{C}_{38}\text{H}_{52}\text{Cl Ir N}_2\text{O}_2$
Formula weight	712.35	782.44	796.47
Crystal system	Monoclinic		
Space group	P 1 21/c 1		
a (Å)	17.1507(5)	15.8455(5)	15.8134(6)
b (Å)	7.7780(2)	12.8111(4)	13.3320(4)
c (Å)	24.0381(8)	18.1170(5)	18.0822(6)
α (°)	106.298(3)	110.400(3)	111.855(4)
V (Å ³)	3077.8(2)	3447.1(2)	3538.2(2)
Z	4		
D_x (g cm ⁻³)	1.537	1.508	1.495
$F(000)$	1432	1584	1616
θ (°)	2.90 - 26.37	2.88 - 26.37	2.93 - 26.37
R_{int}	0.0323	0.0325	0.0288
Data/restrain/parameter	6286 / 0 / 337	7045 / 24 / 395	7221 / 0 / 405
GOF (F^2)	1.023	0.979	1.014
R_1, wR_2 [$I > 2\sigma(I)$]	0.0425, 0.0803	0.0356, 0.0729	0.0259, 0.0504
R_1, wR_2 (all data)	0.0700, 0.0925	0.0577, 0.0801	0.0388, 0.0549

Table S2. Intra- and intermolecular interaction geometry (Å, °)*.

Complex	D—H···A	D—H	H···A	D···A	D—H···A
3a	O1-H1···Cl1	0.82	2.45	3.255(5)	167
	C22-H22B···O1 ⁱ	0.97	2.51	3.448(8)	163
3c	C4-H4···Cg1	0.93	2.78	3.574(5)	144
	C12-H12···O1	0.98	2.48	3.425(6)	162
3d	C4-H4···Cg1	0.93	2.78	3.647(3)	140

* Cg1 refers the centroid of the C25–C30 ring in 3a, 3c and 3d.

Symmetry code: (i) 1-x, -1/2+y, 1/2-z.

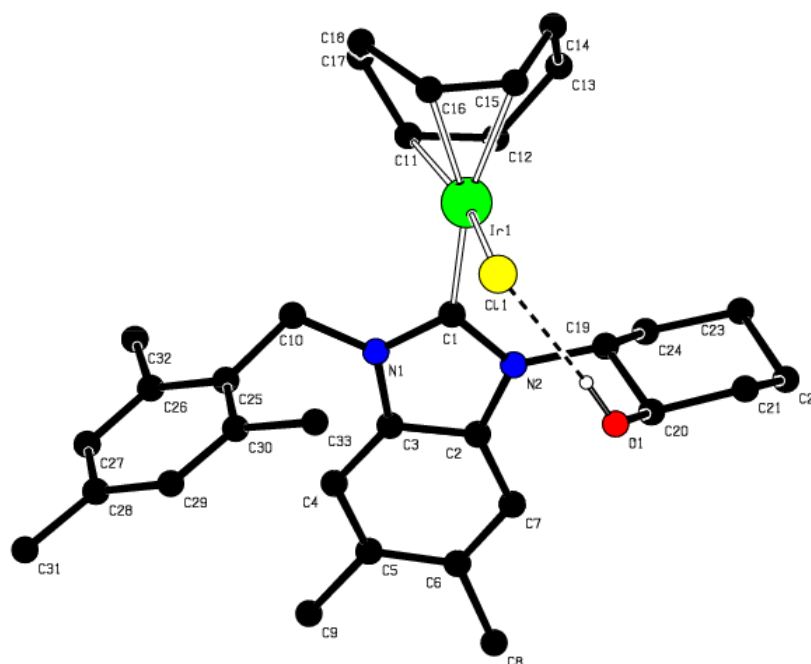


Figure S1. The molecular structure of **3a** showing intramolecular O-H···Cl type interaction as dashed lines. H atoms not involved in interactions have been omitted for clarity.

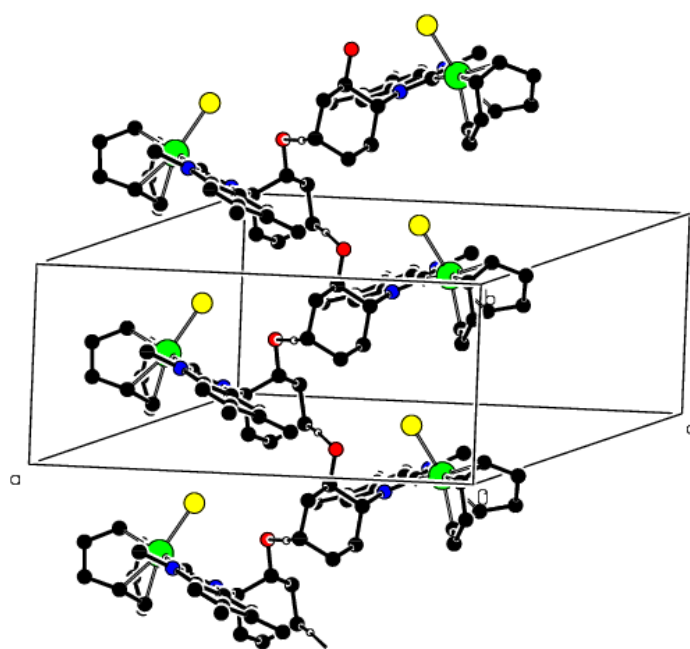


Figure S2. The crystal packing of **3a** showing the formation of zigzag chain along the *b* axis. C-H...O interactions are shown as dashed lines. H atoms not involved in interactions and trimethylphenyl groups have been omitted for clarity.

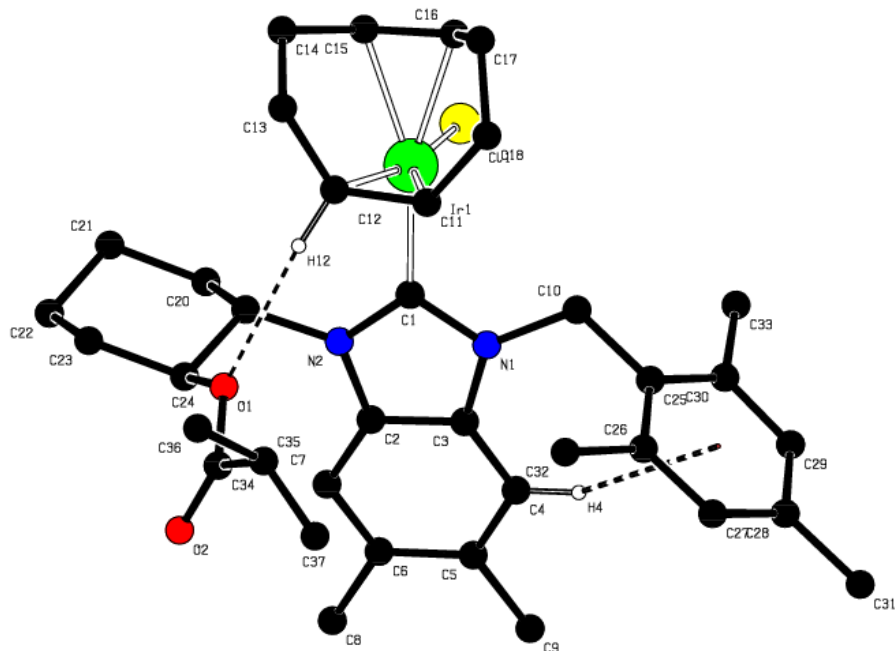


Figure S3. The molecular structure of **3c** showing intramolecular C-H...O and C-H... π type interactions as dashed lines. H atoms not involved in interactions have been omitted for clarity.

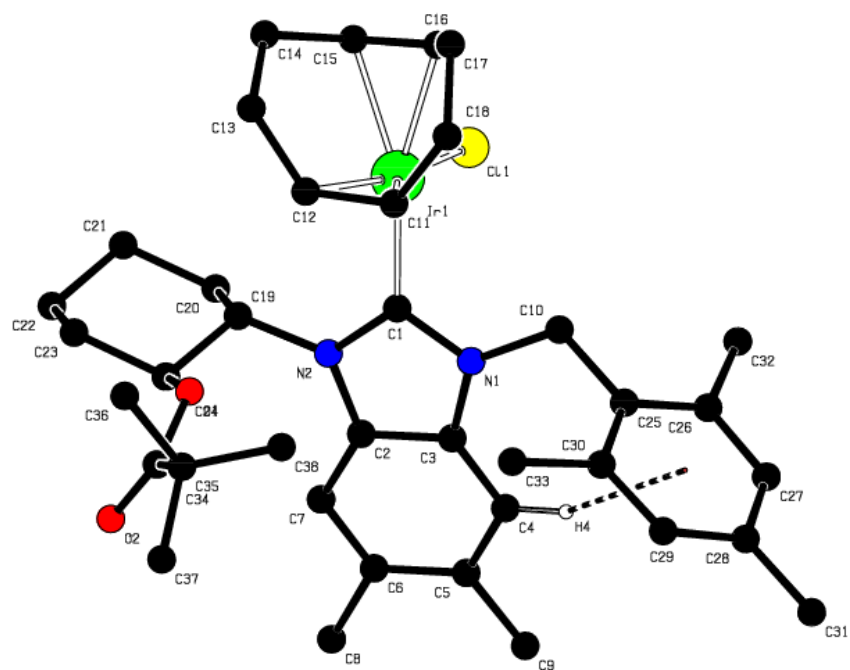
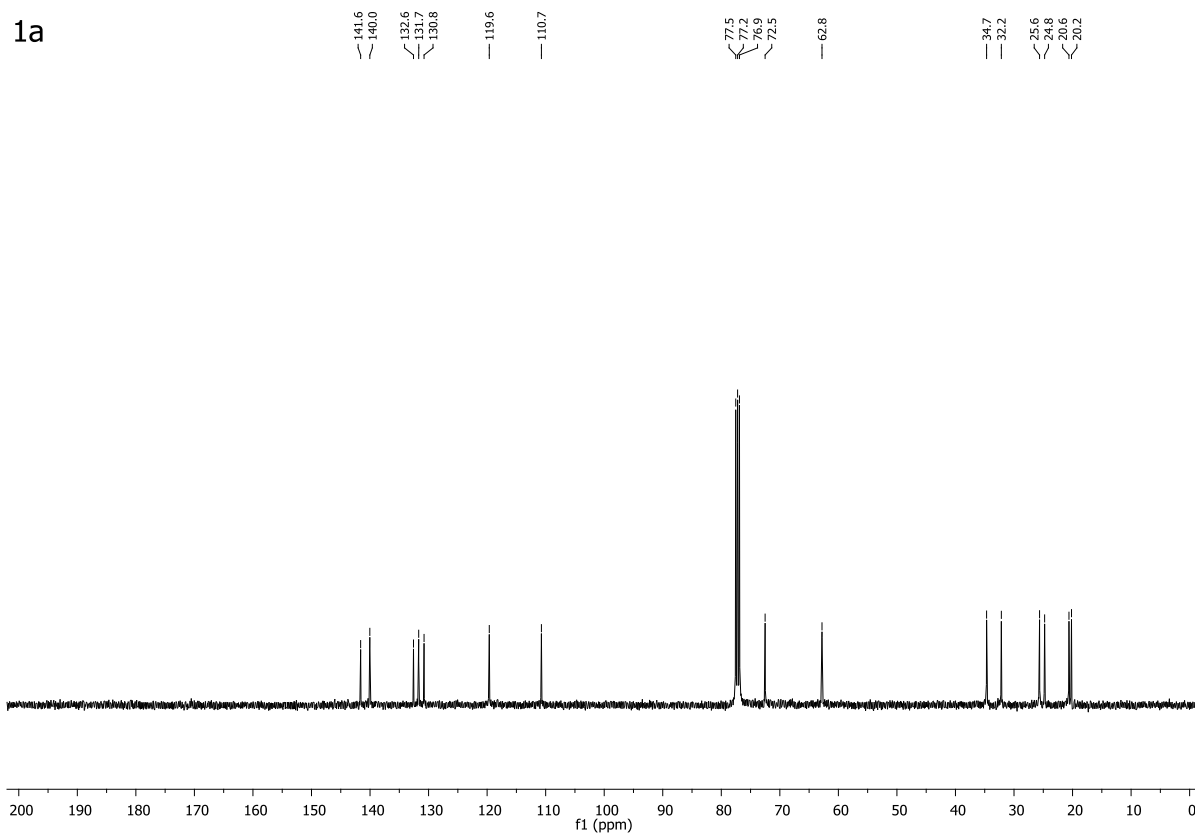
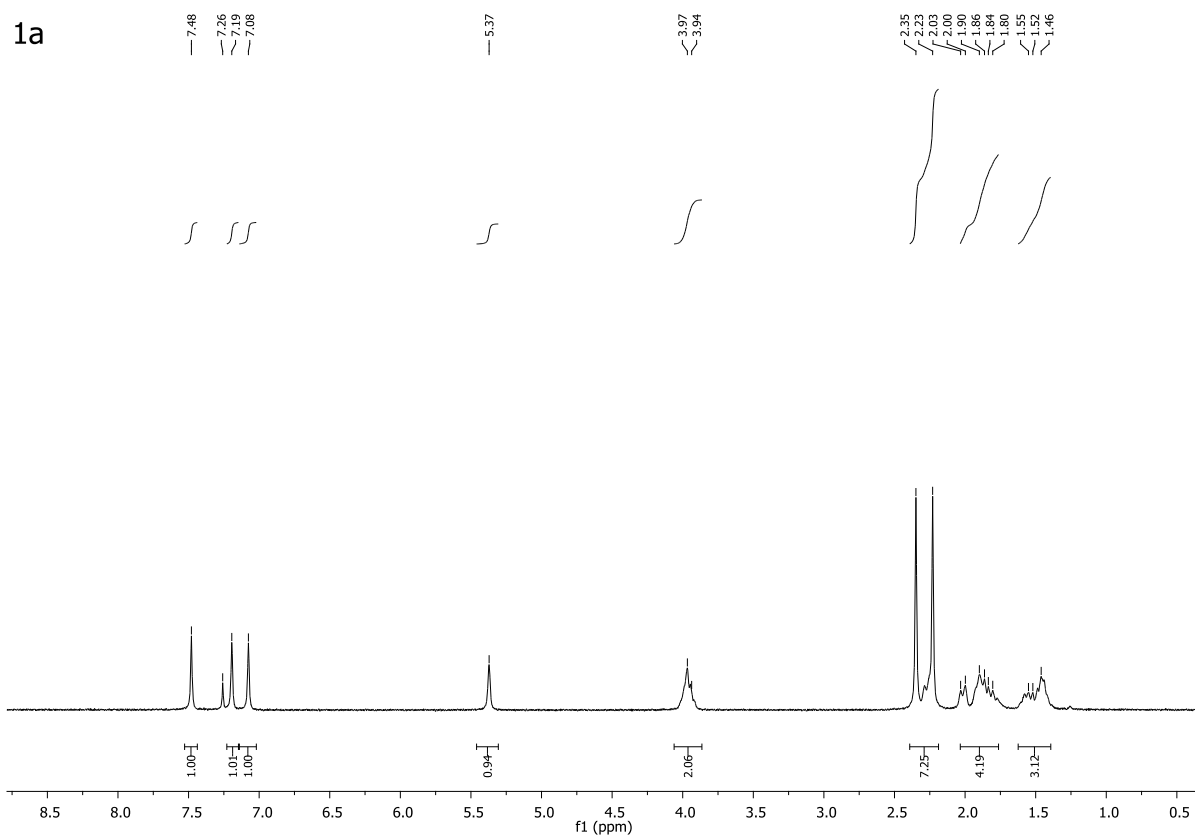
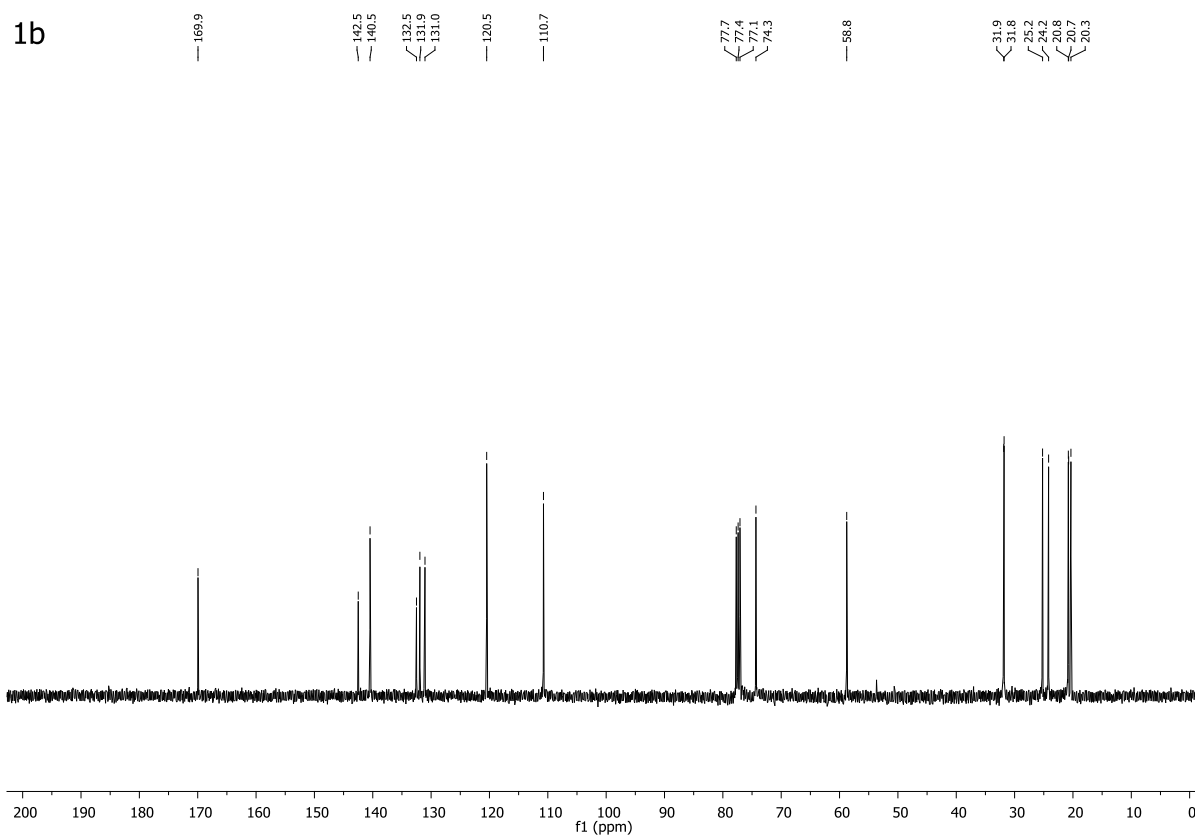
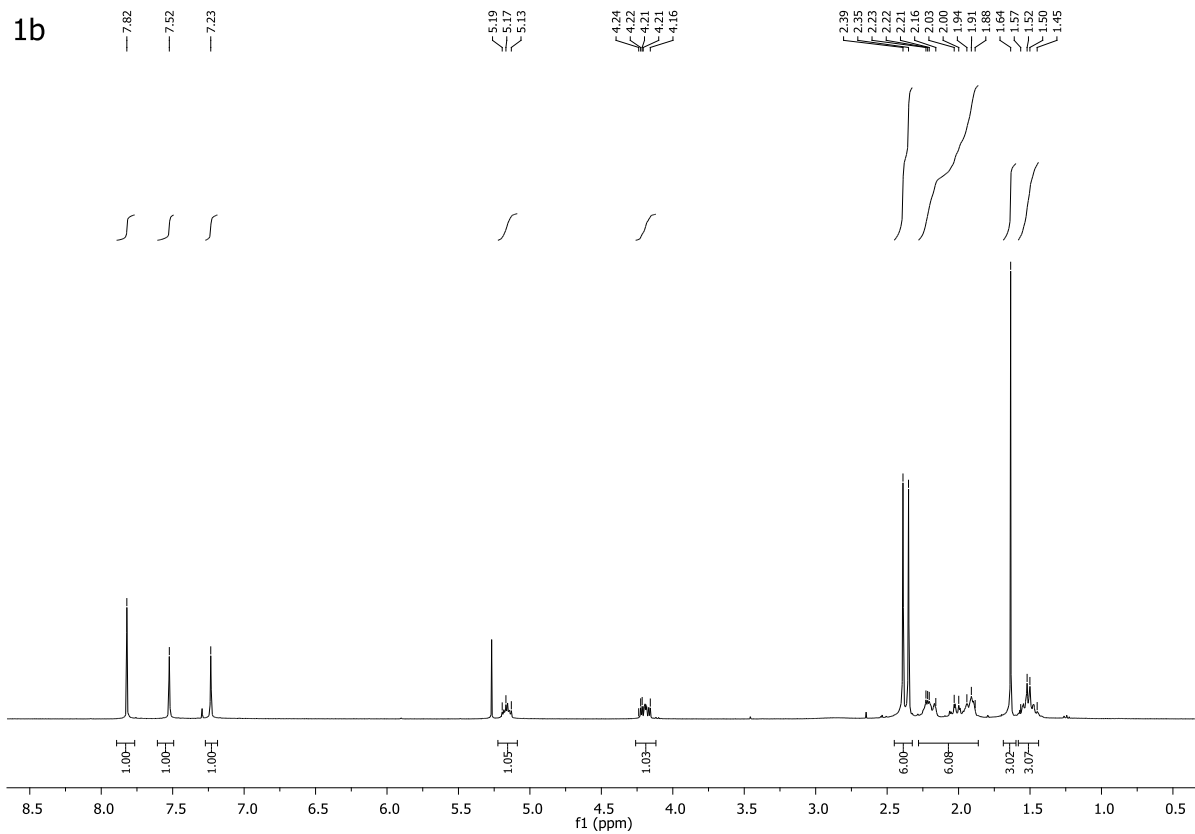
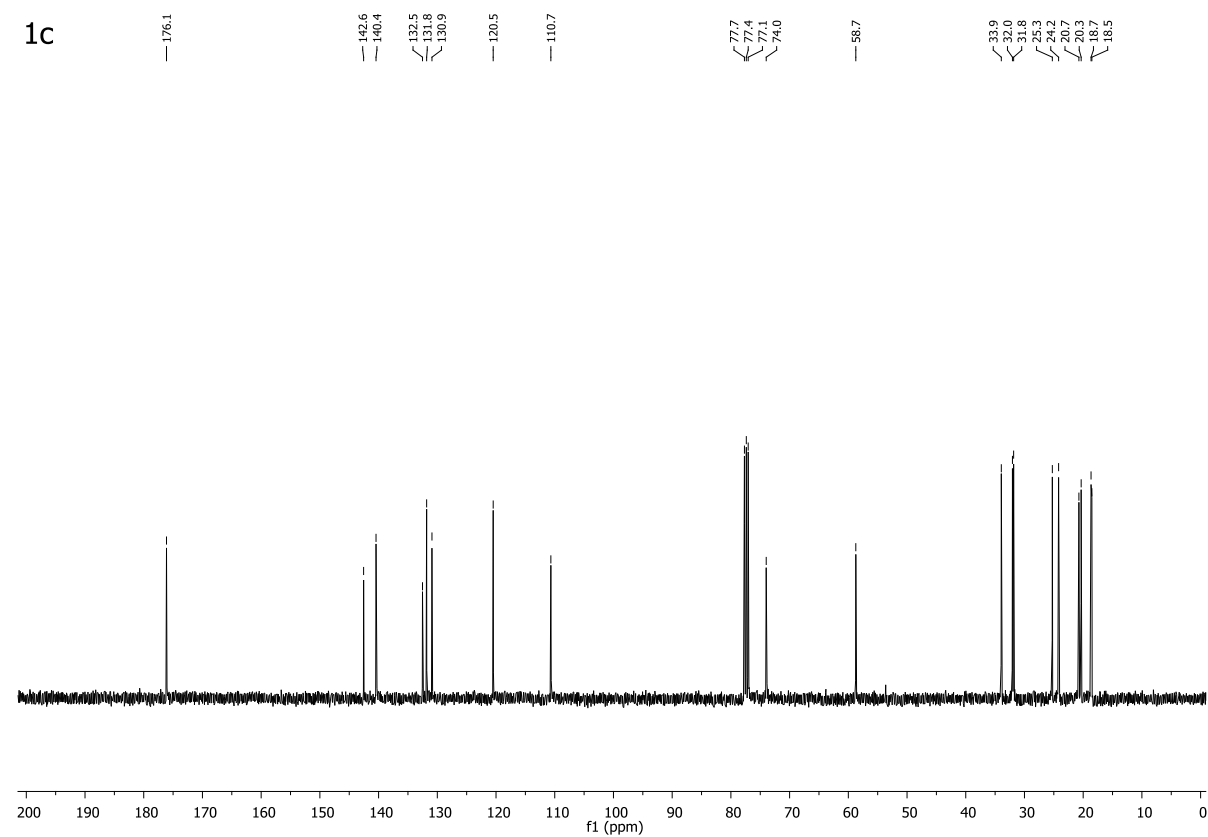
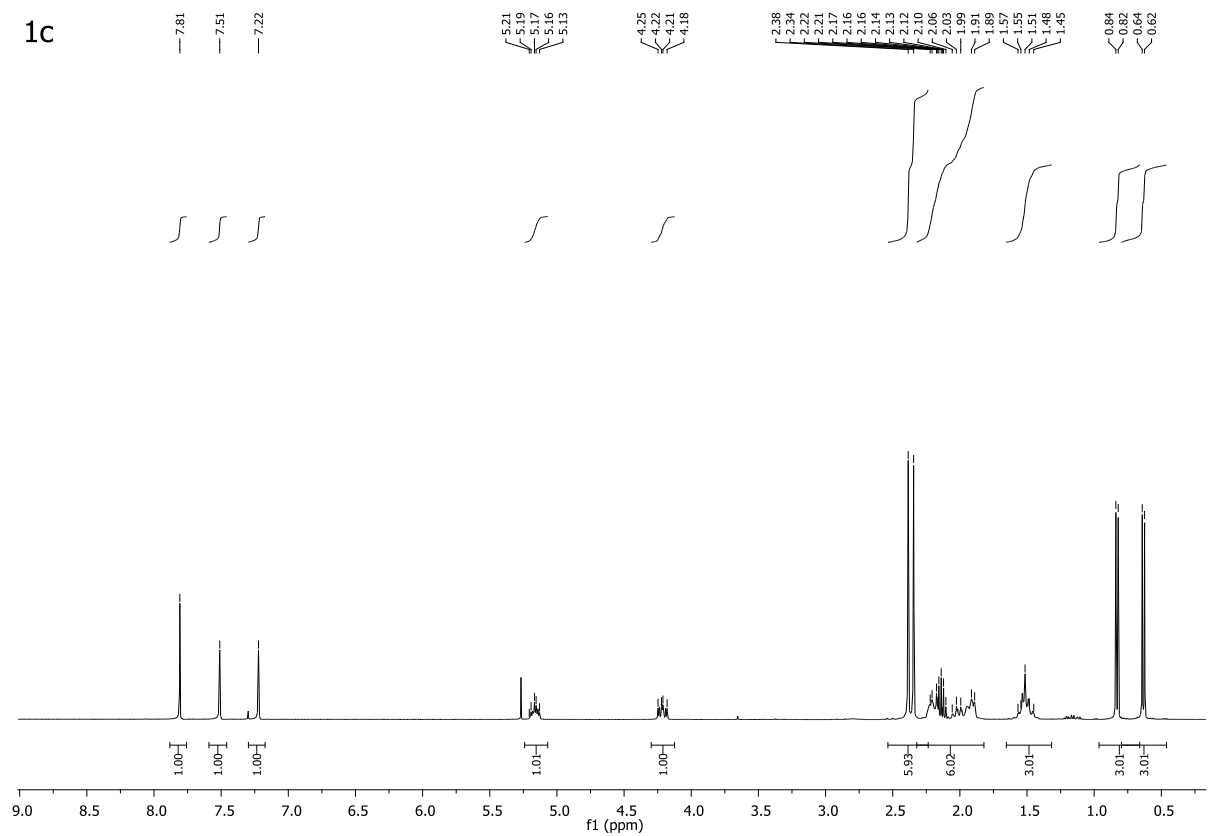


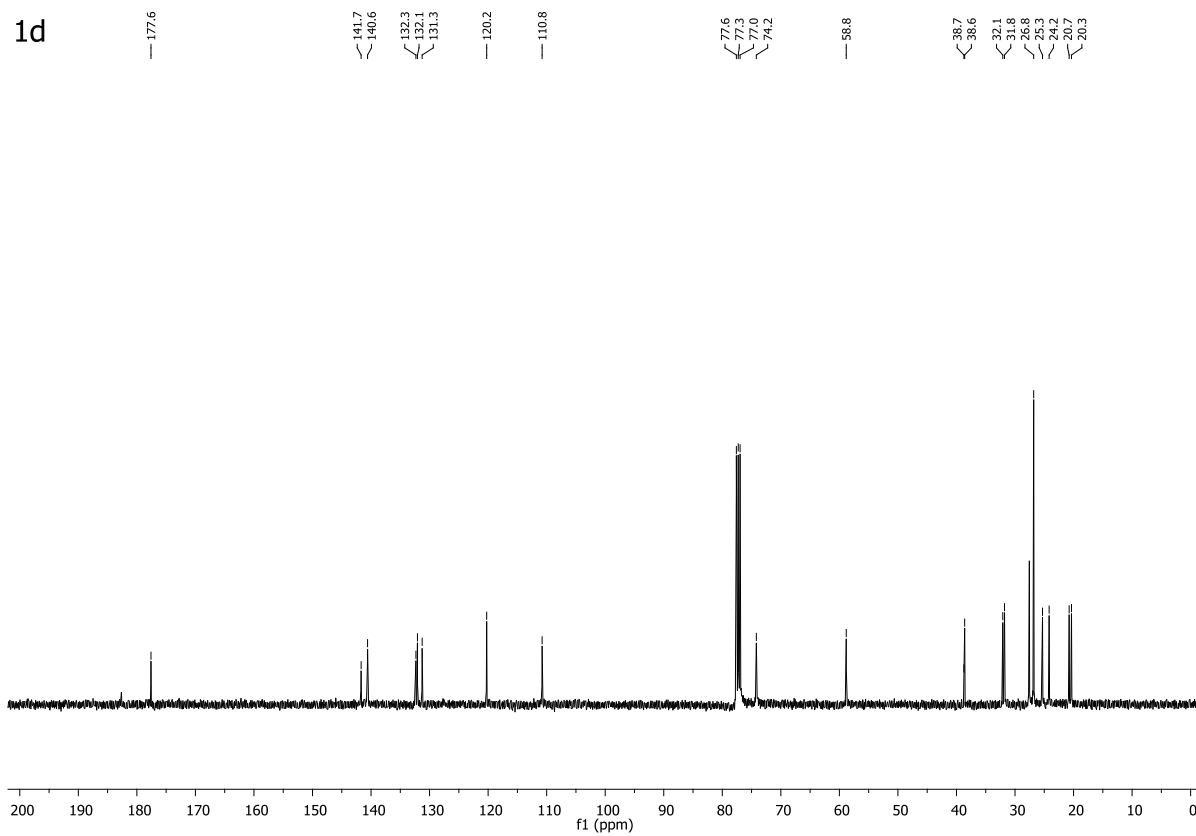
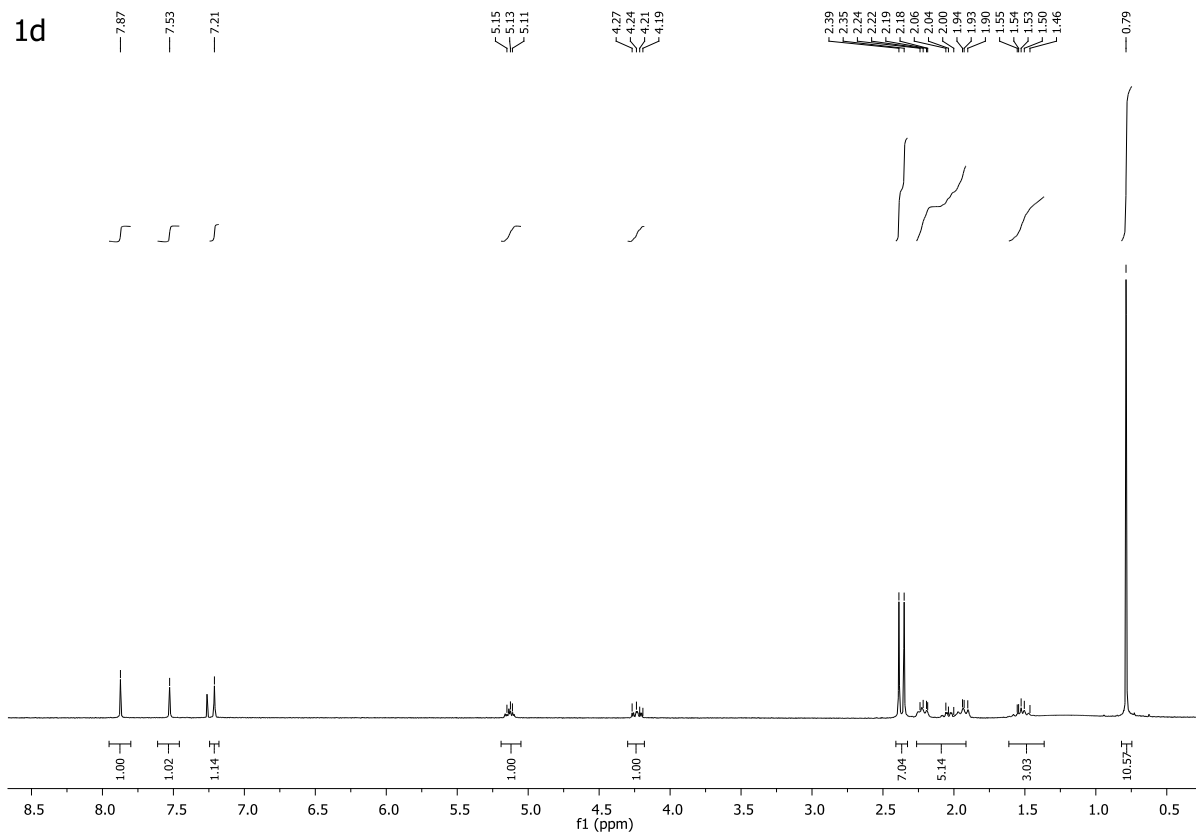
Figure S4. The molecular structure of **3d** showing intramolecular C-H... π type interaction as dashed lines. H atoms not involved in interactions have been omitted for clarity.

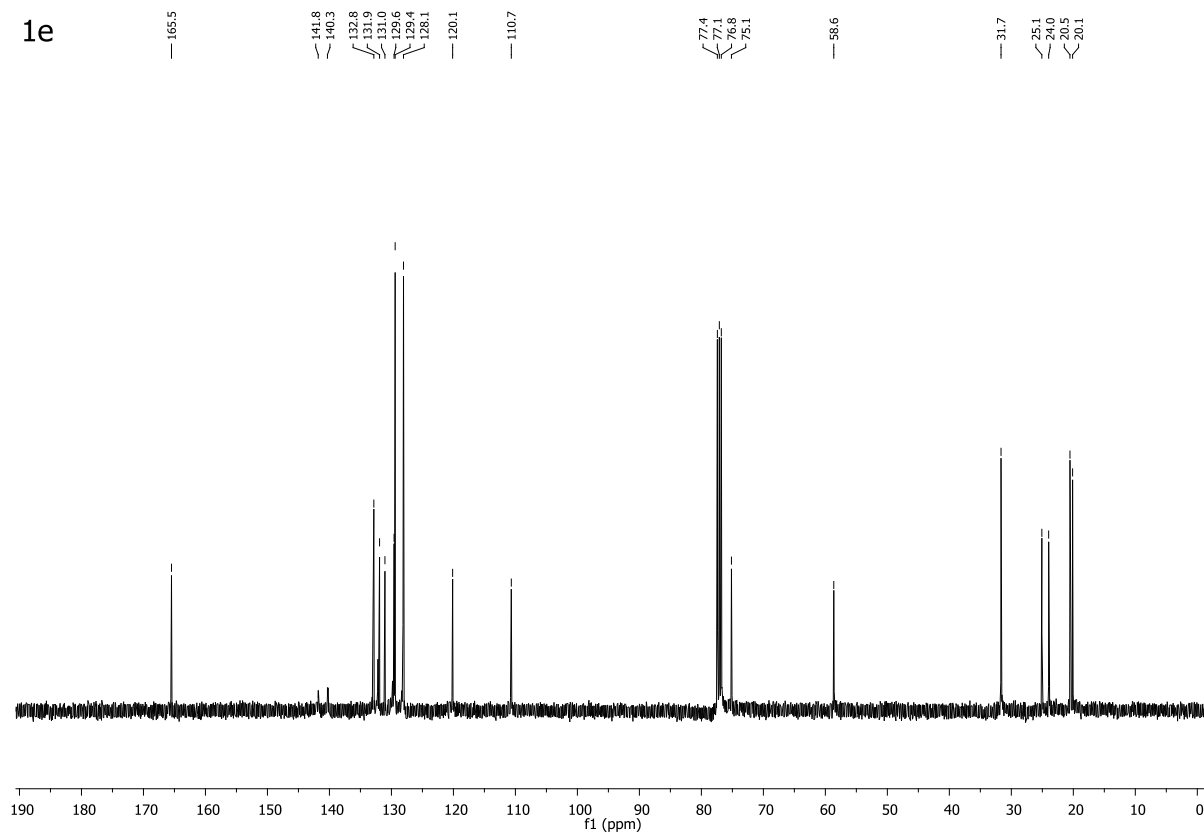
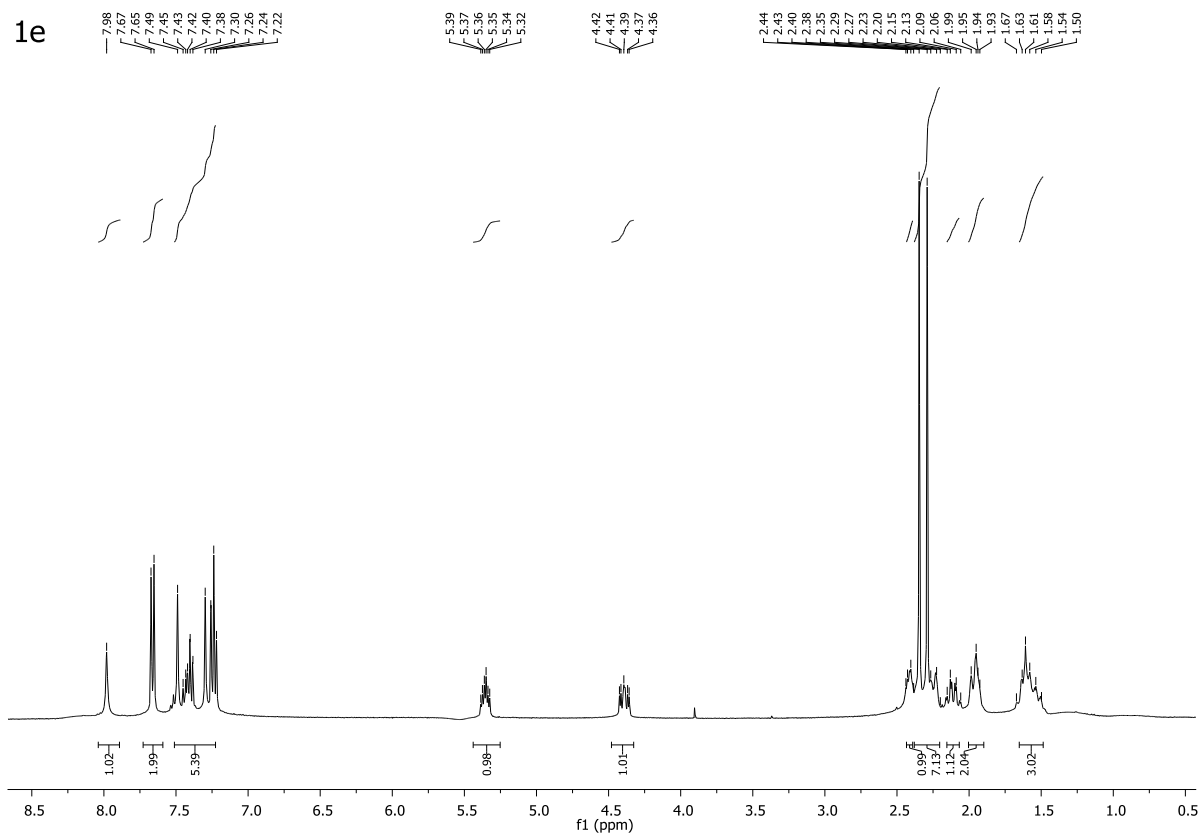
¹H and ¹³C NMR Spectra of Compounds 1a-e, 2a-e and 3a-e:

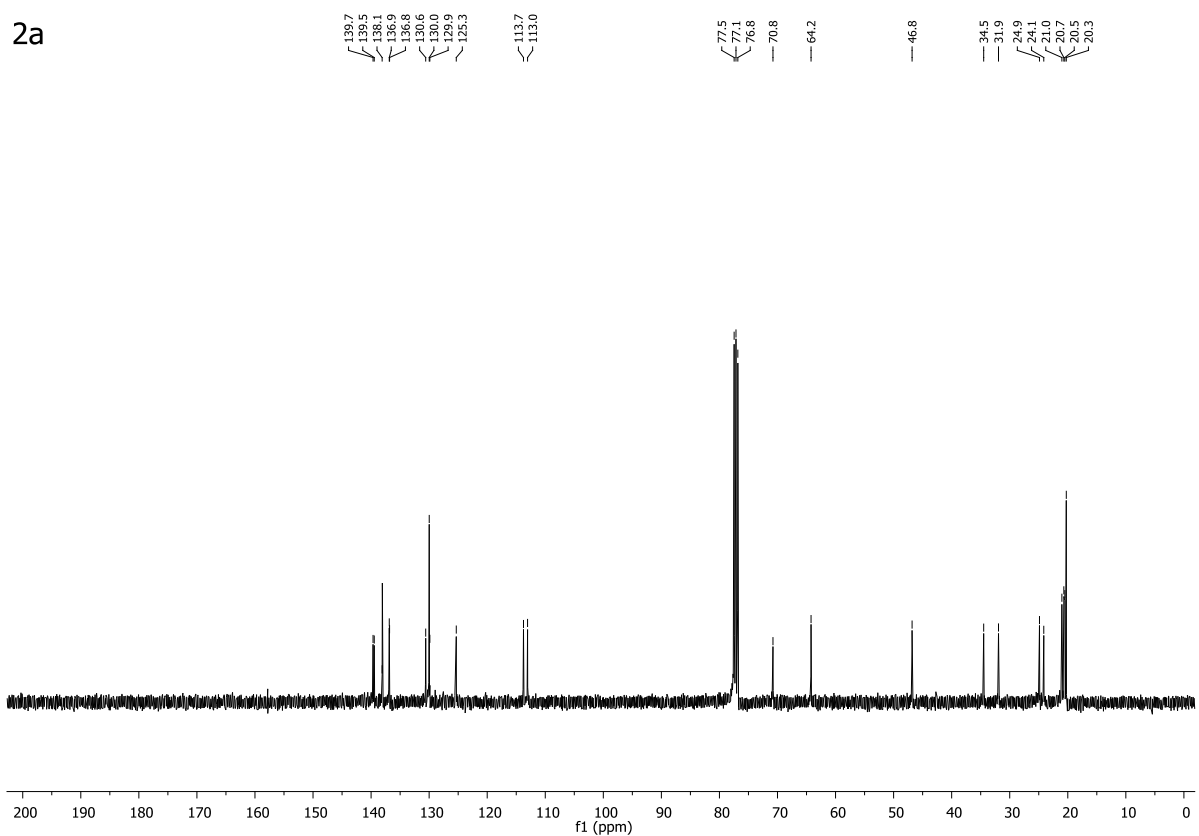
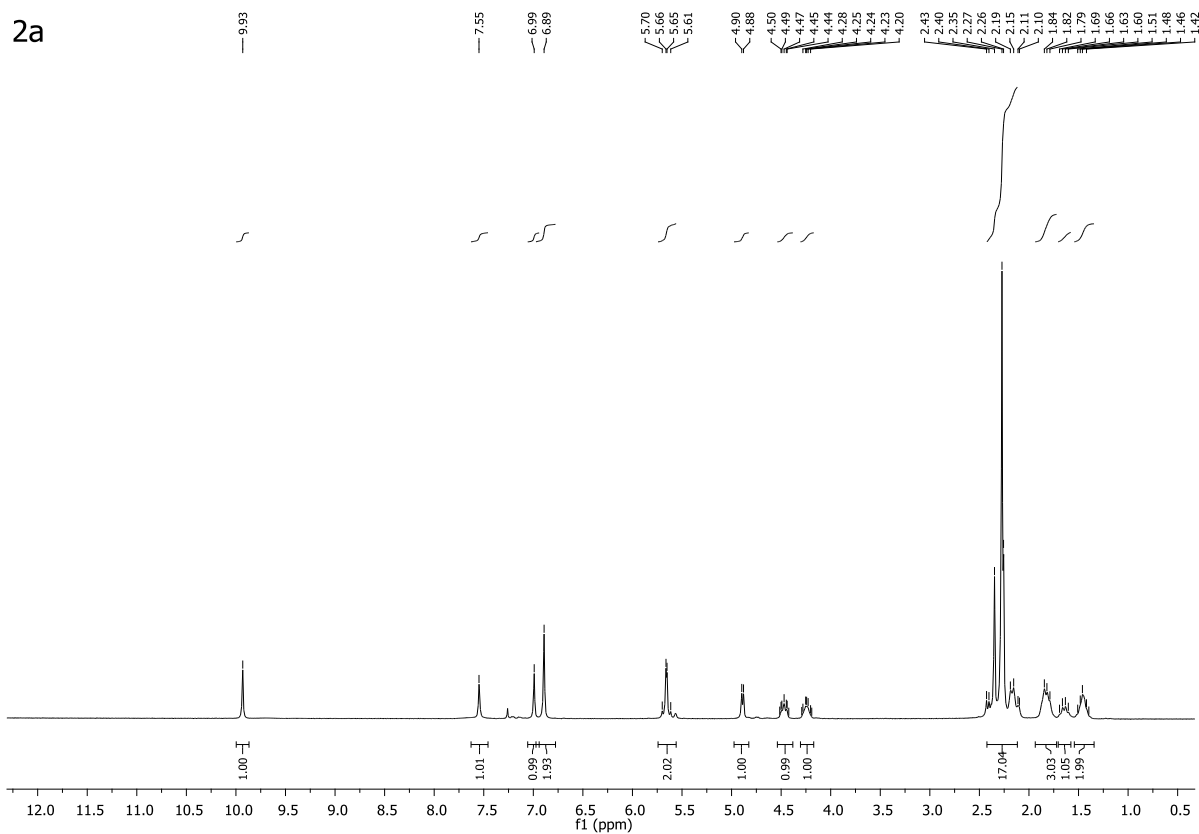


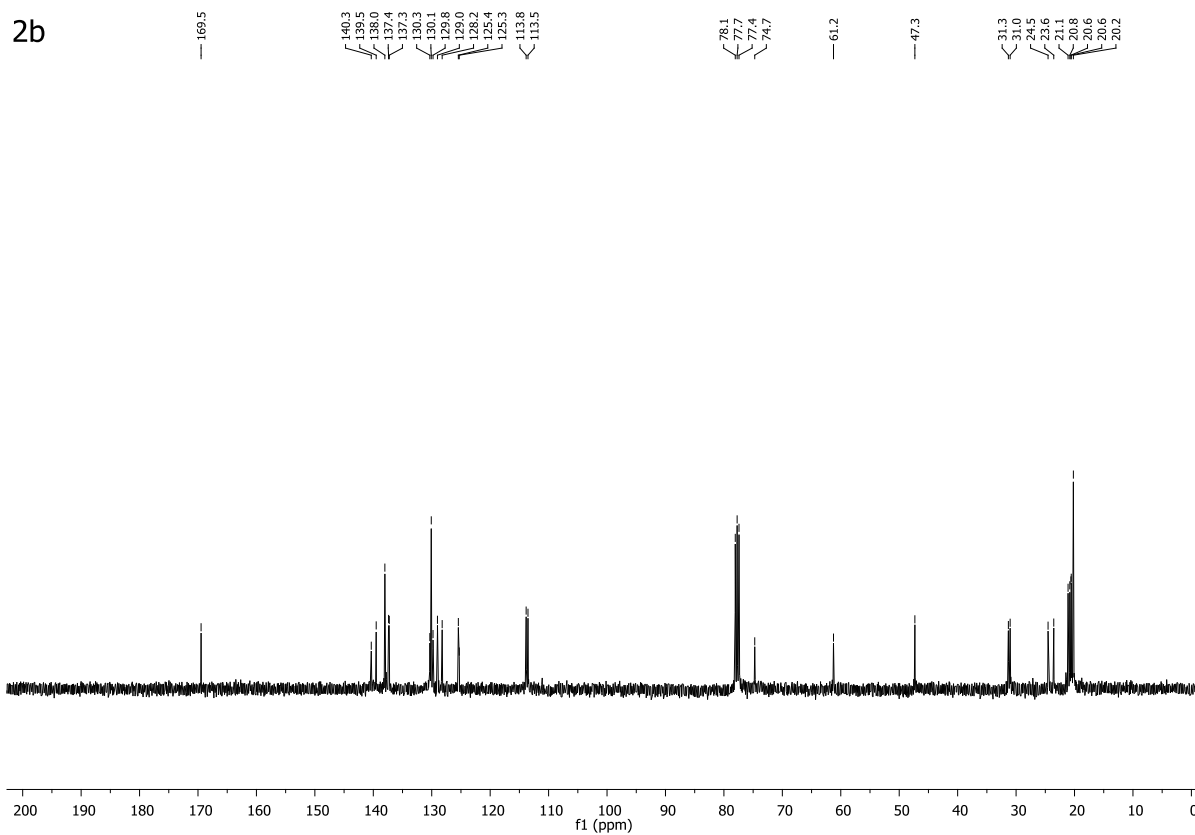
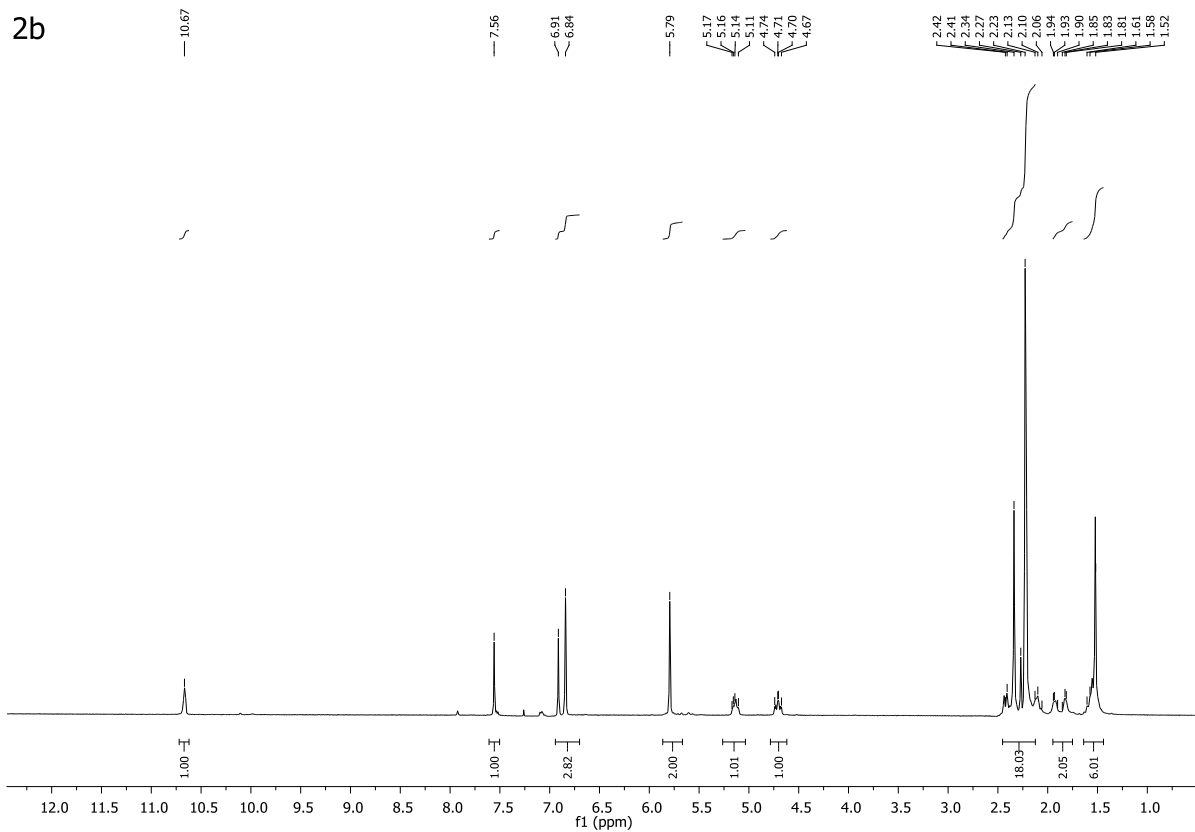


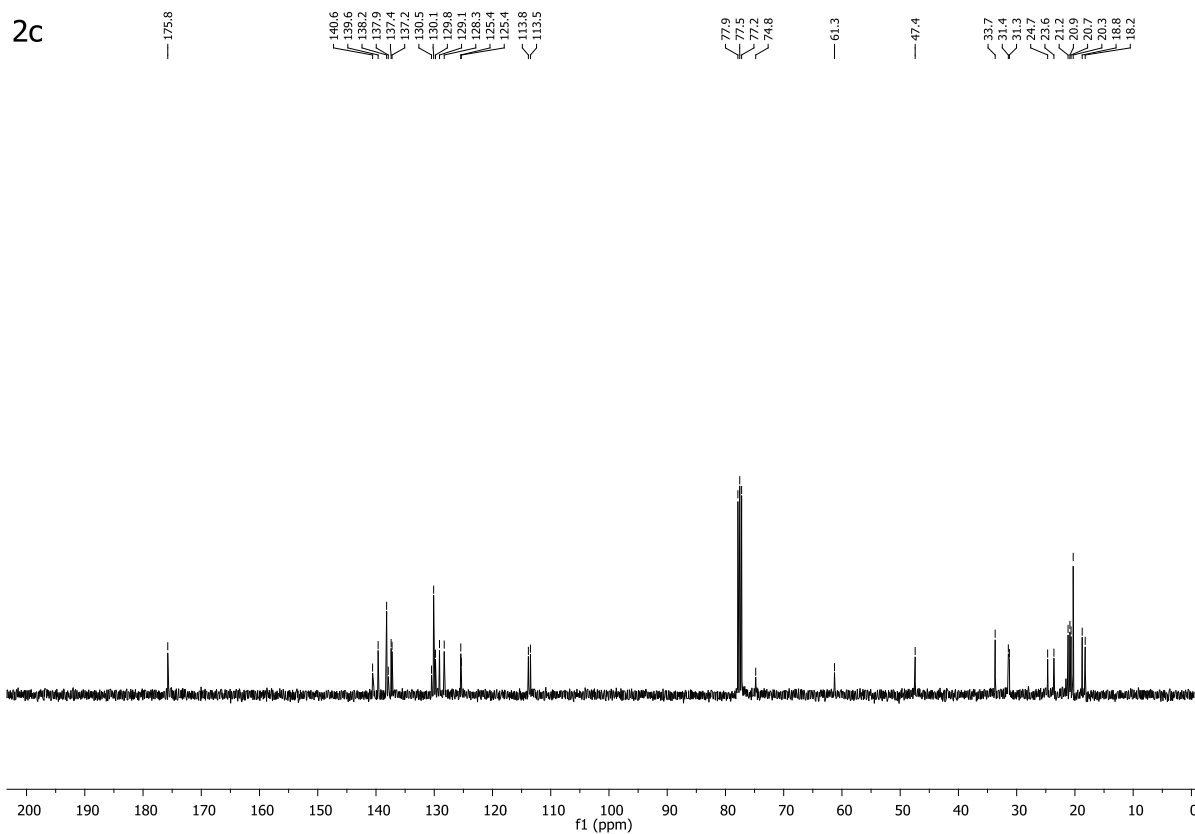
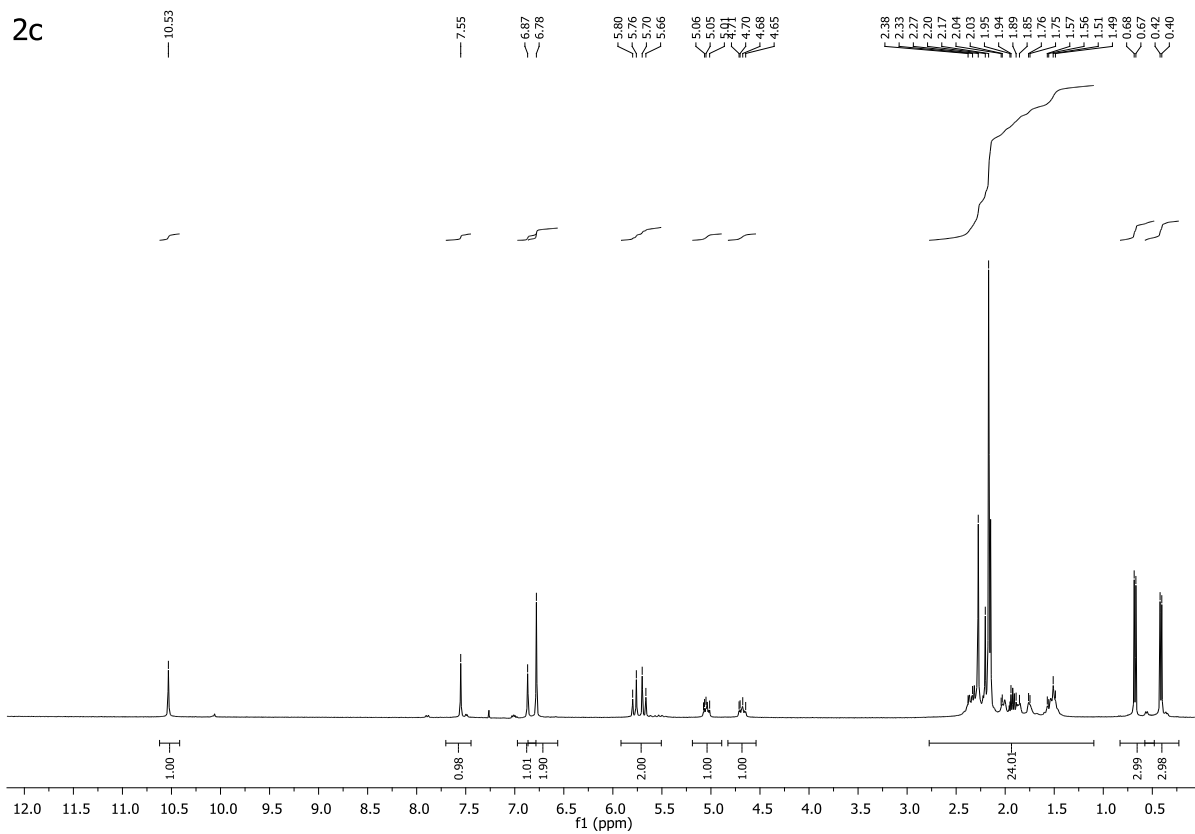


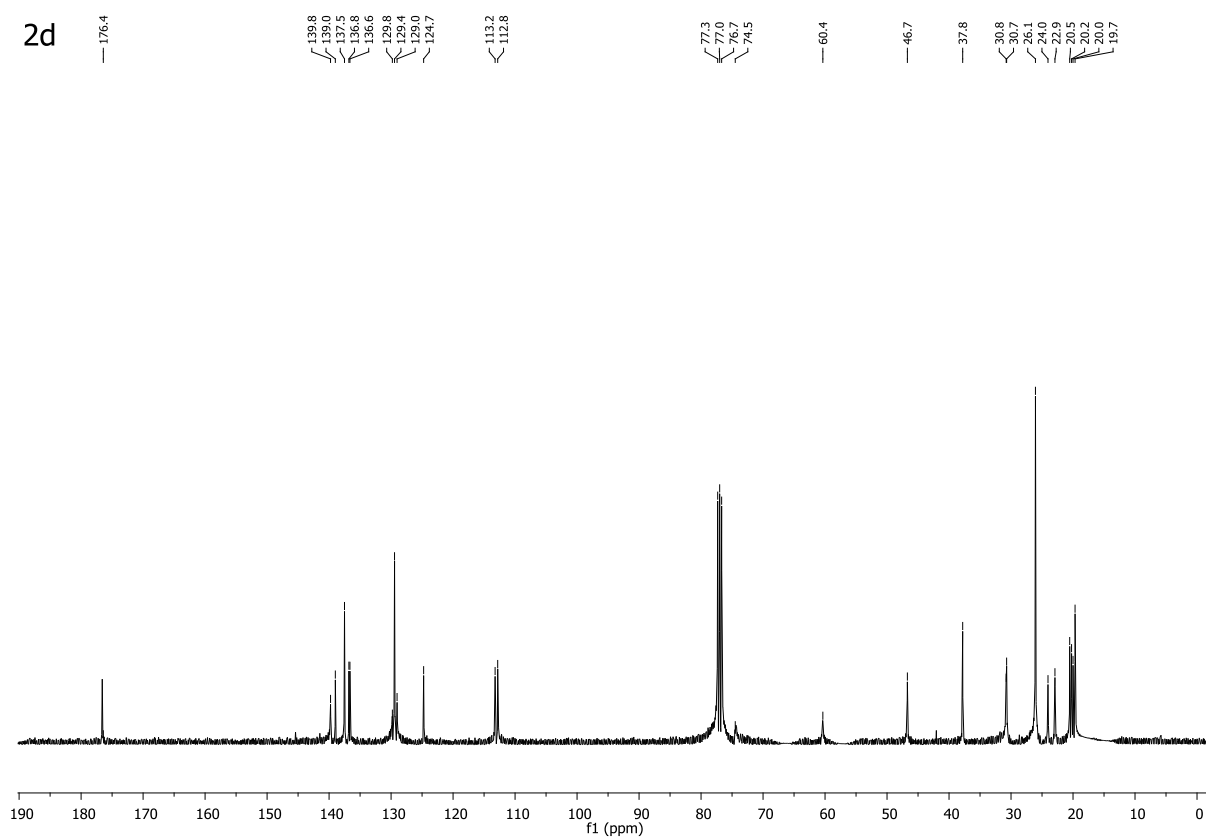
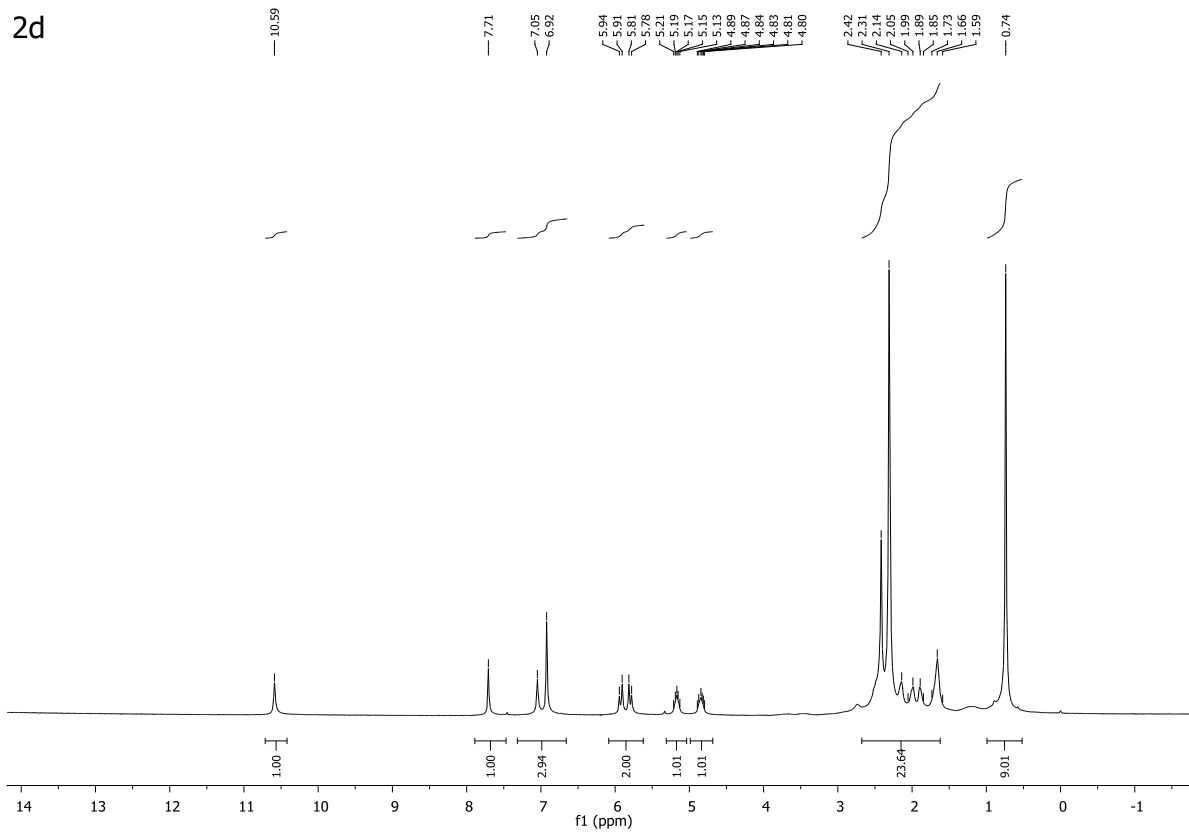


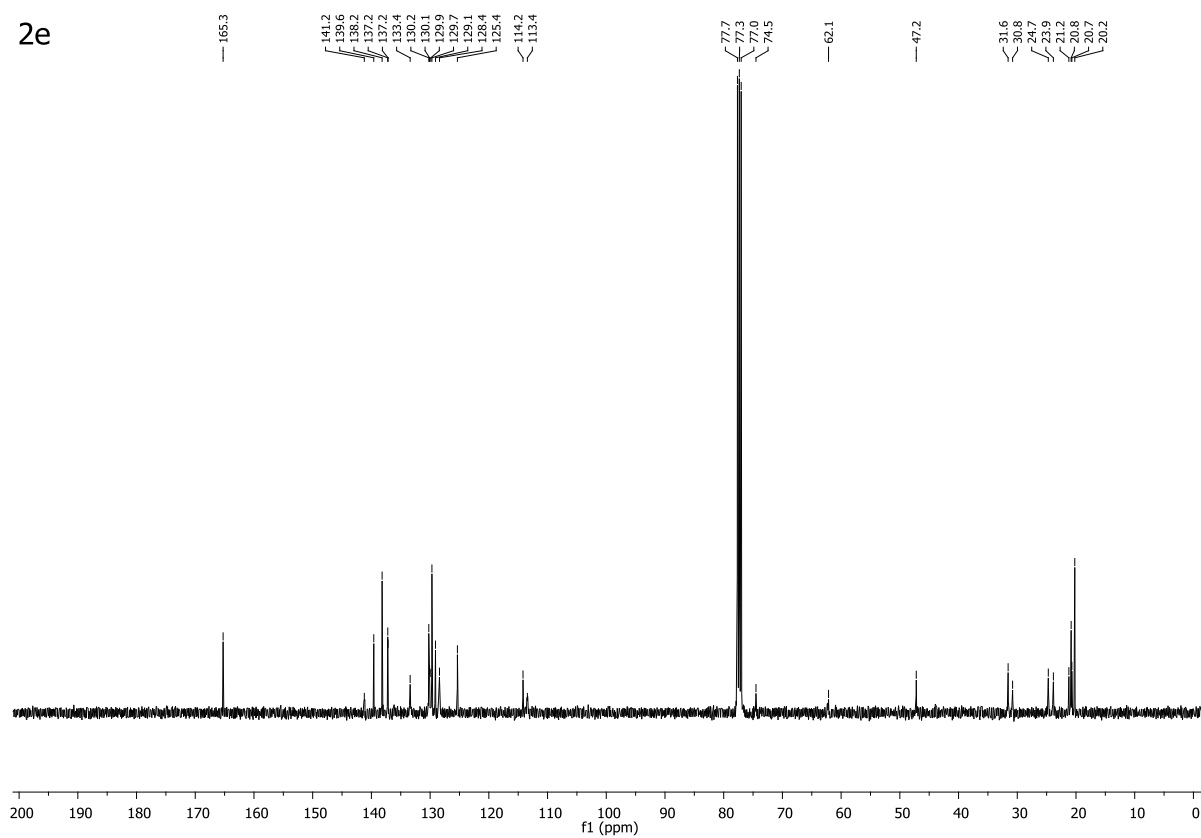
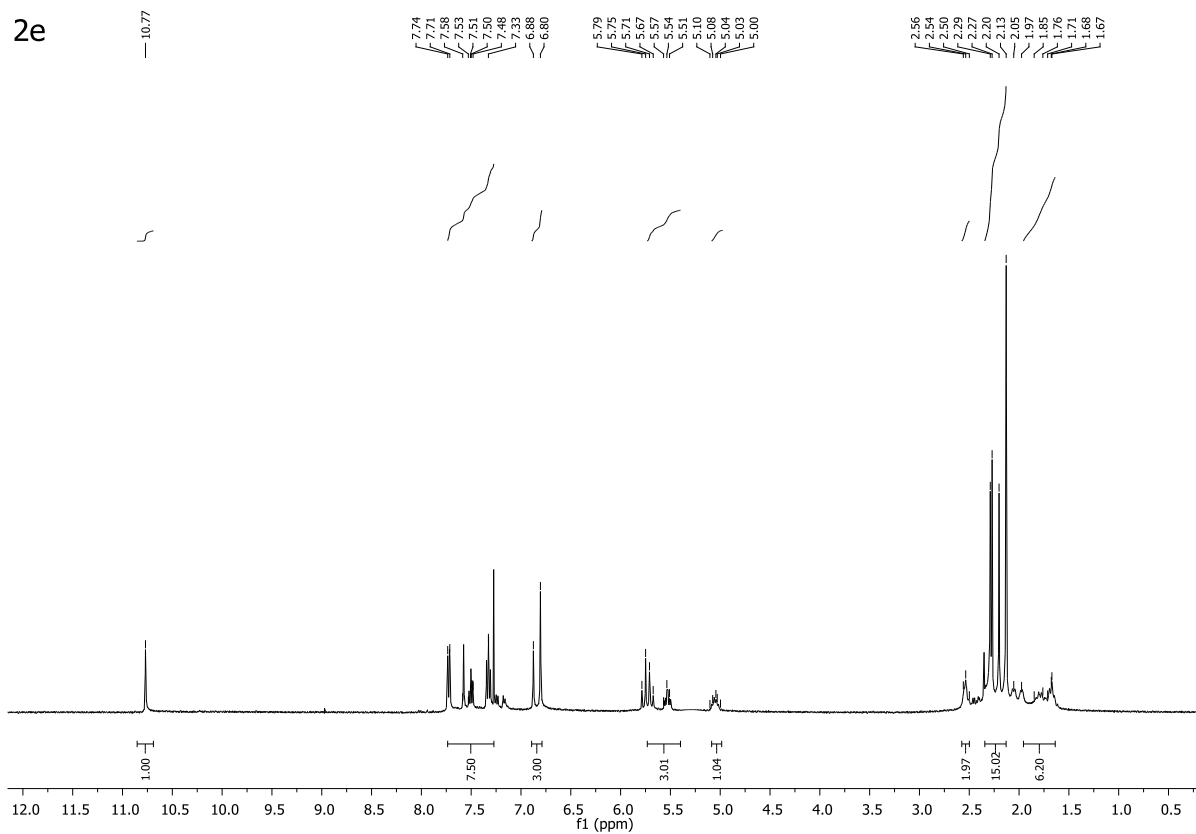


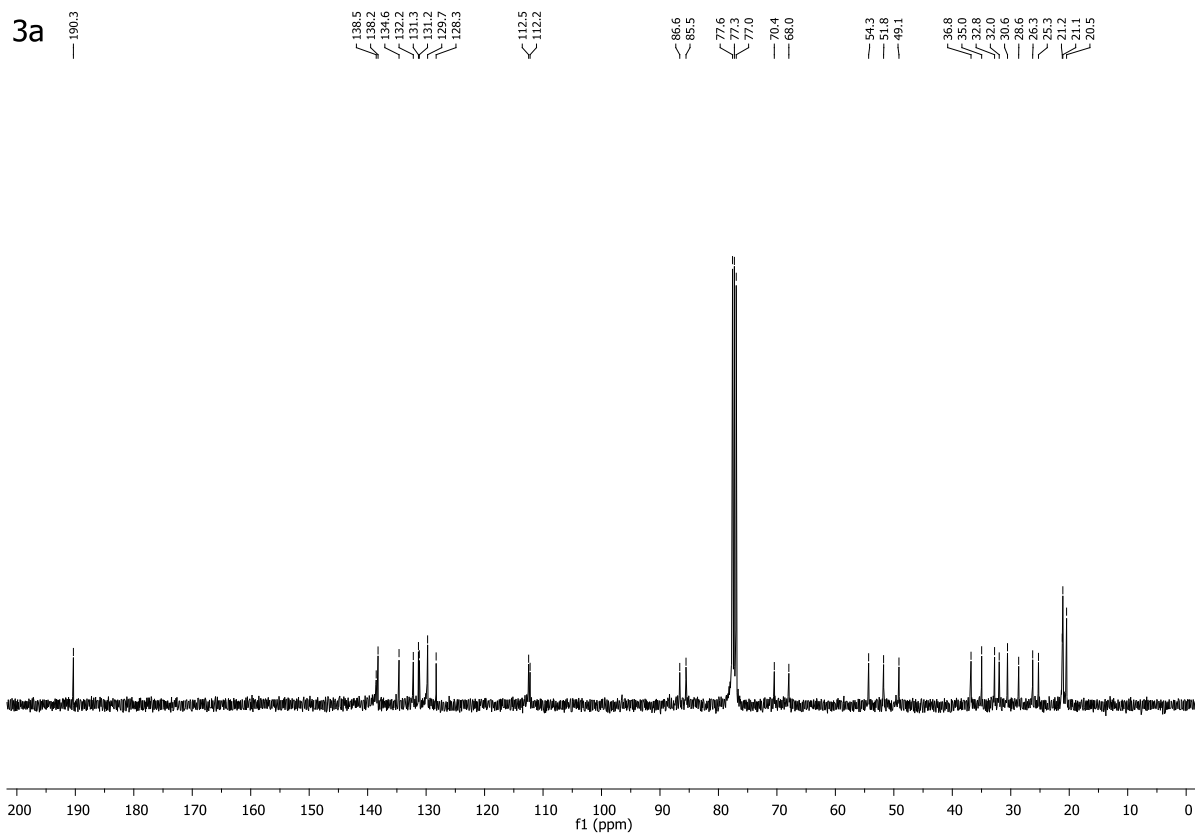
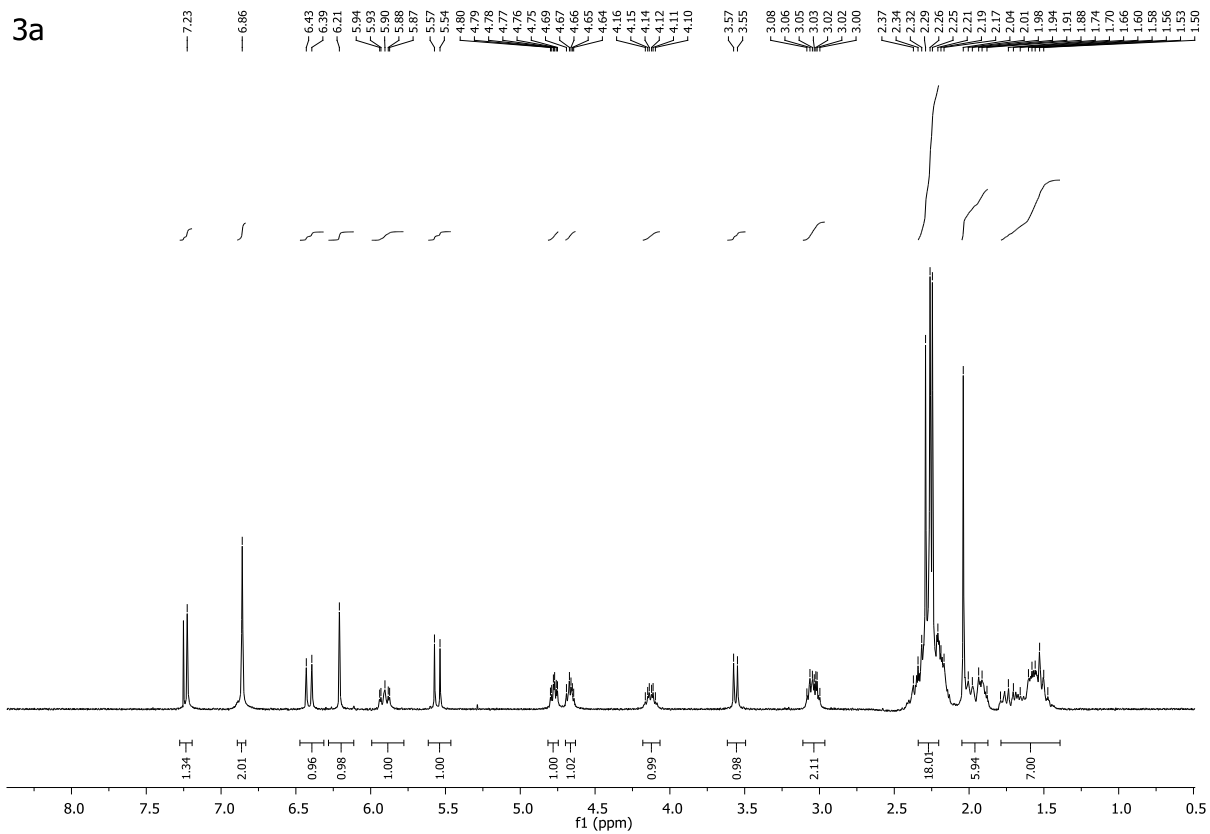


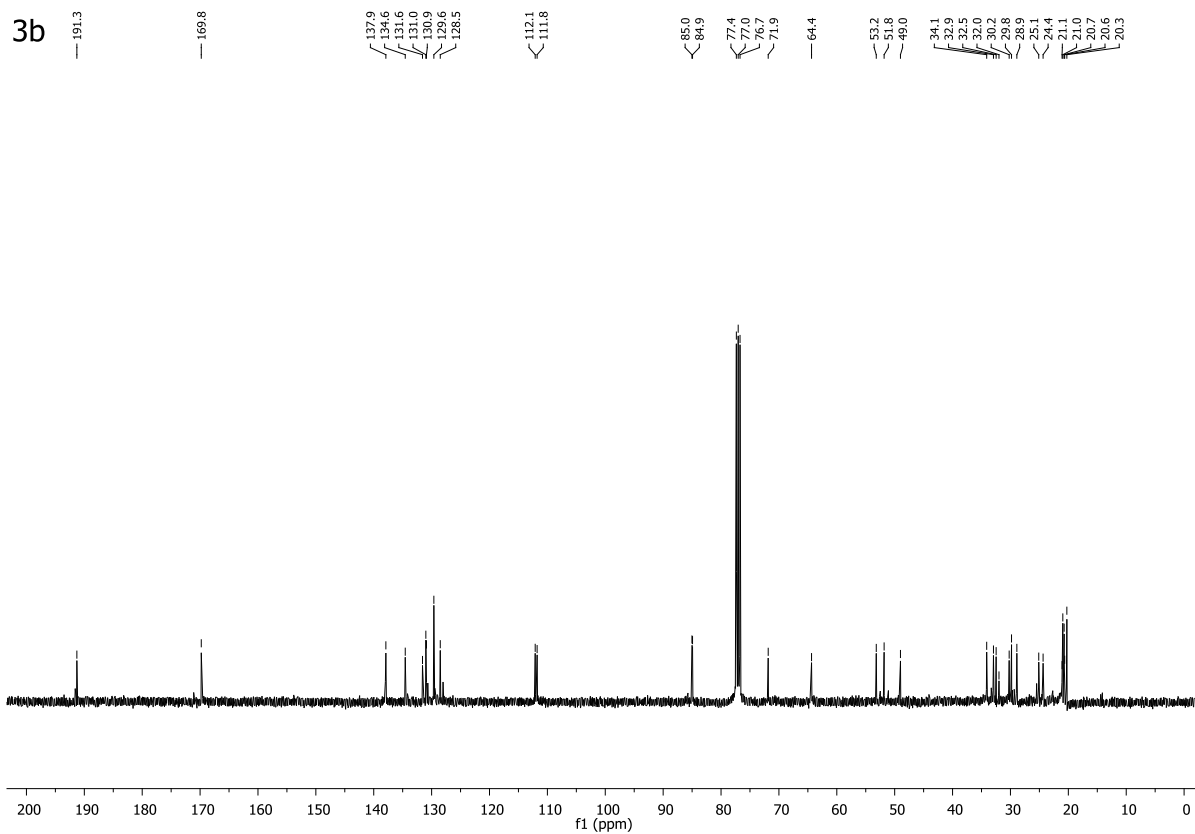
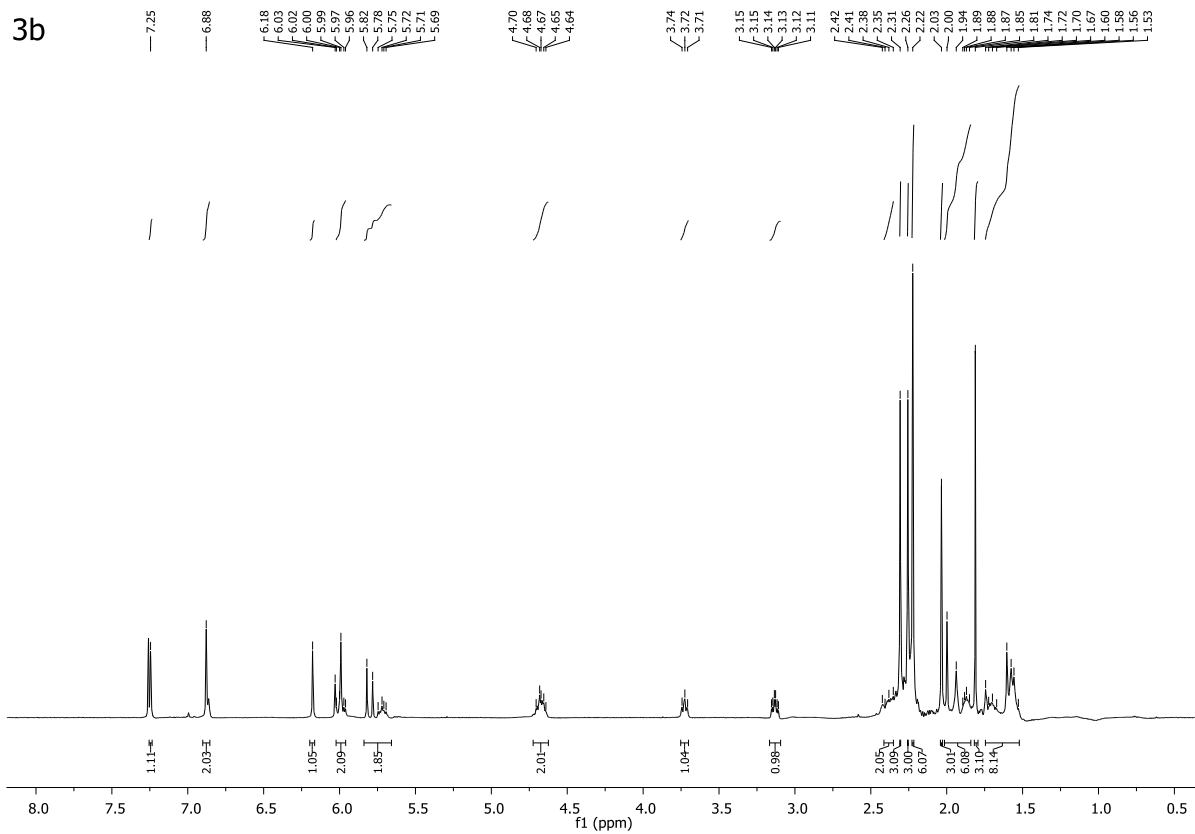


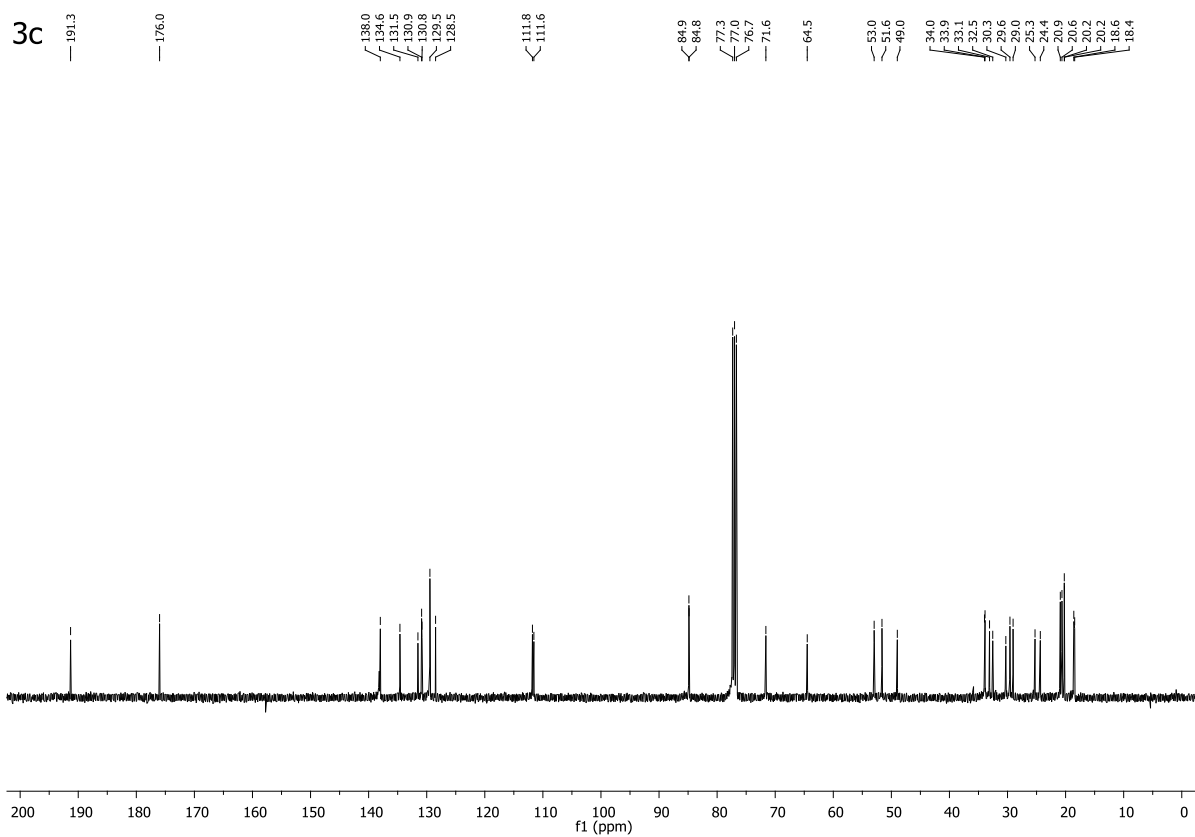
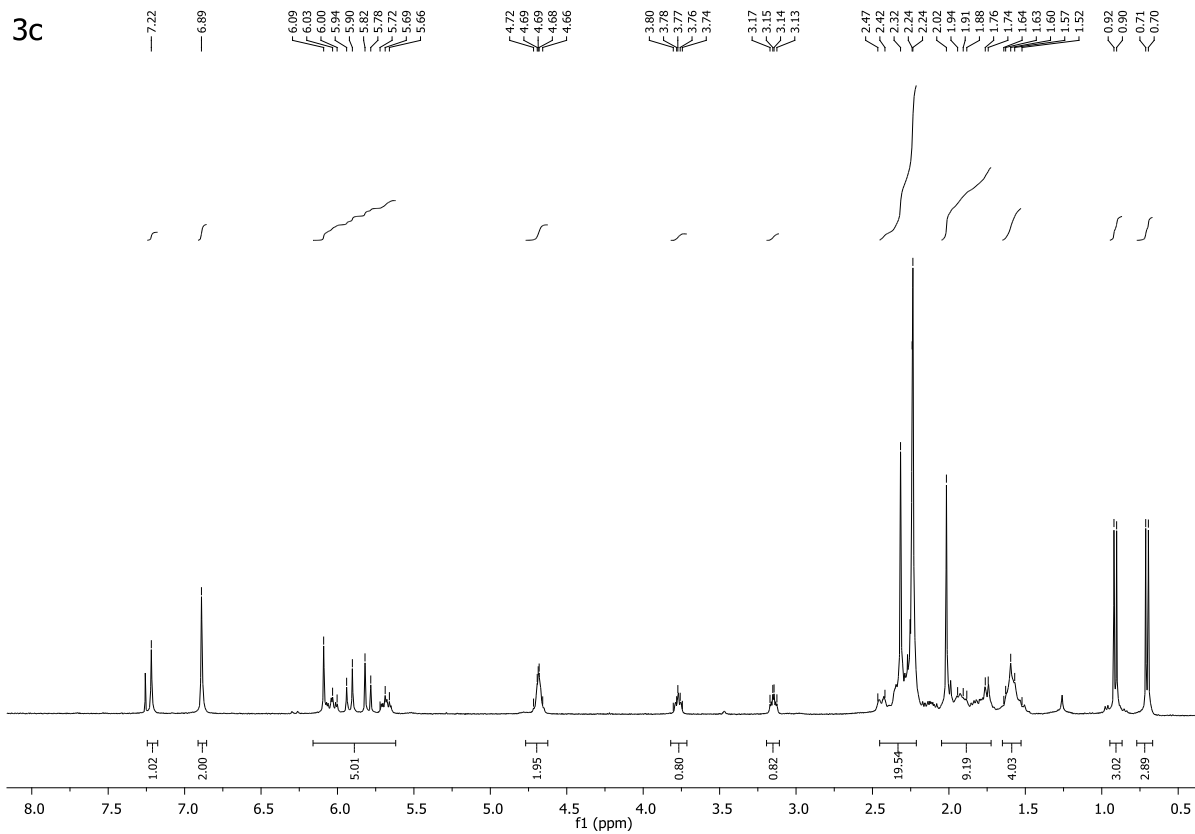




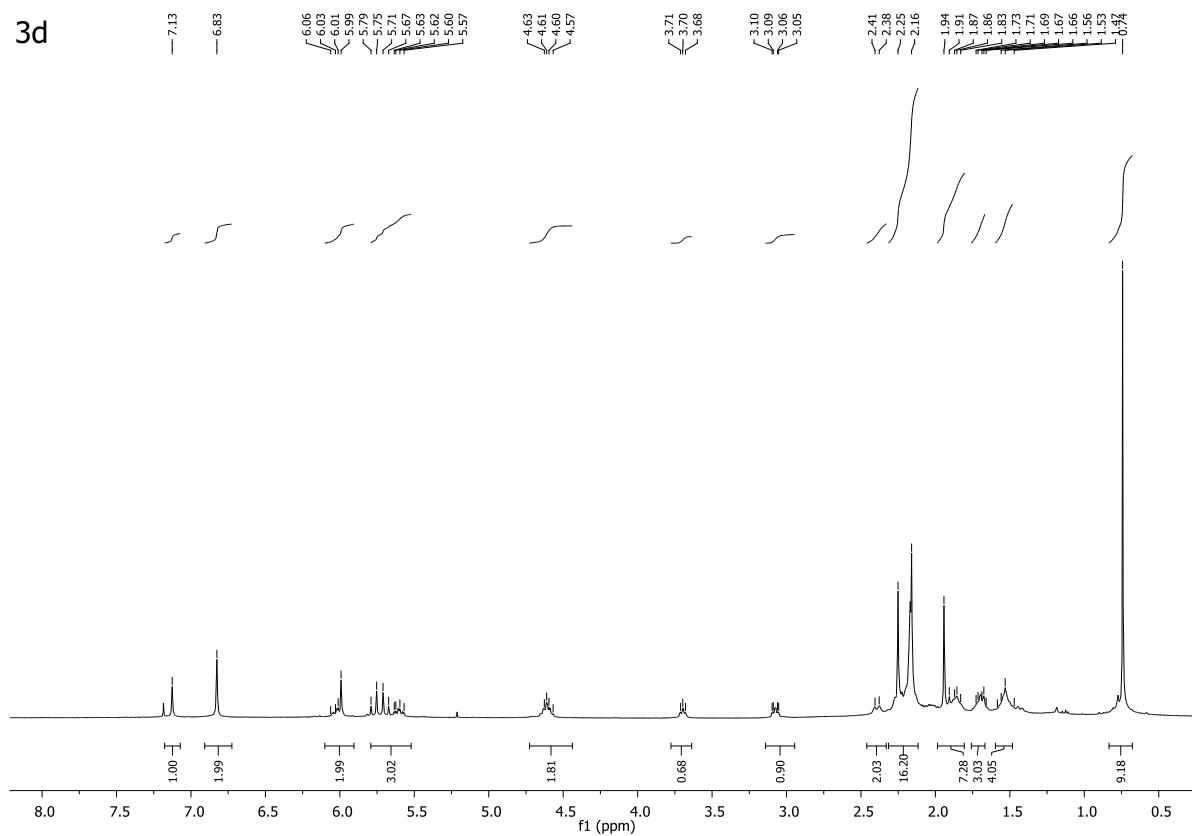




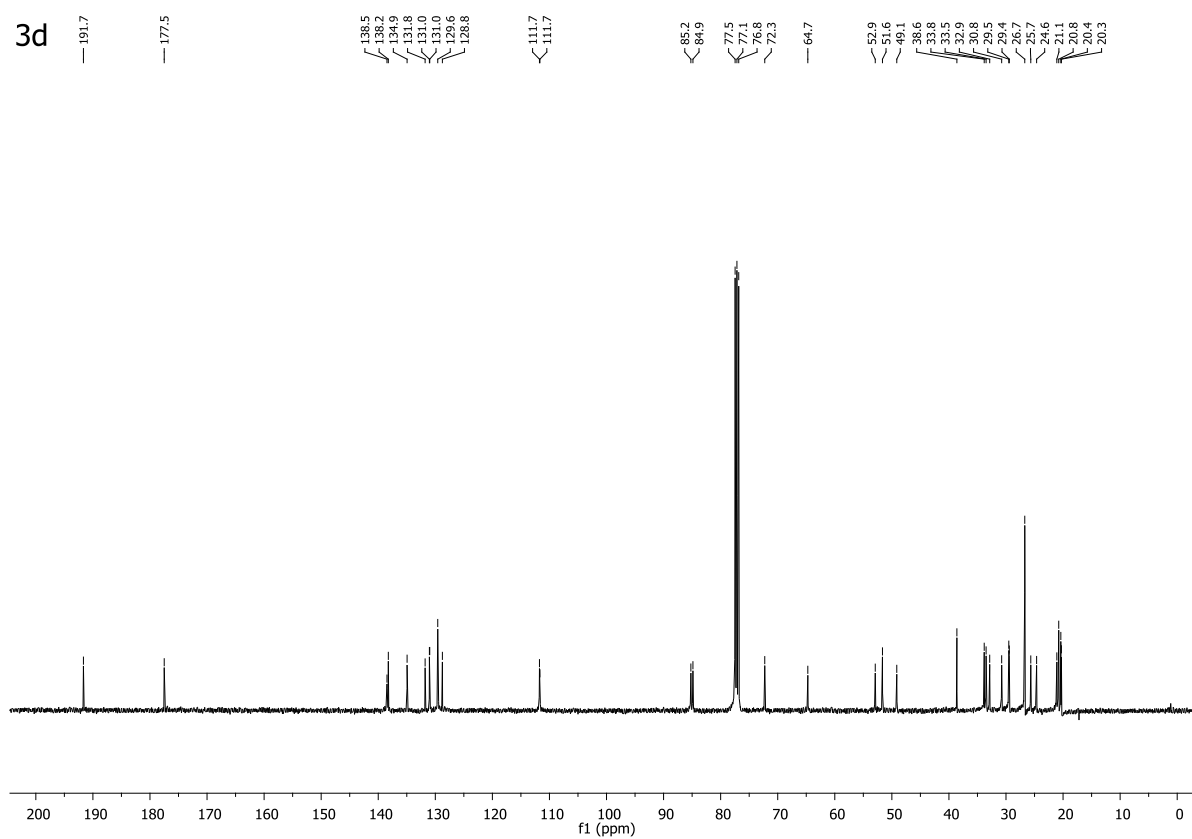


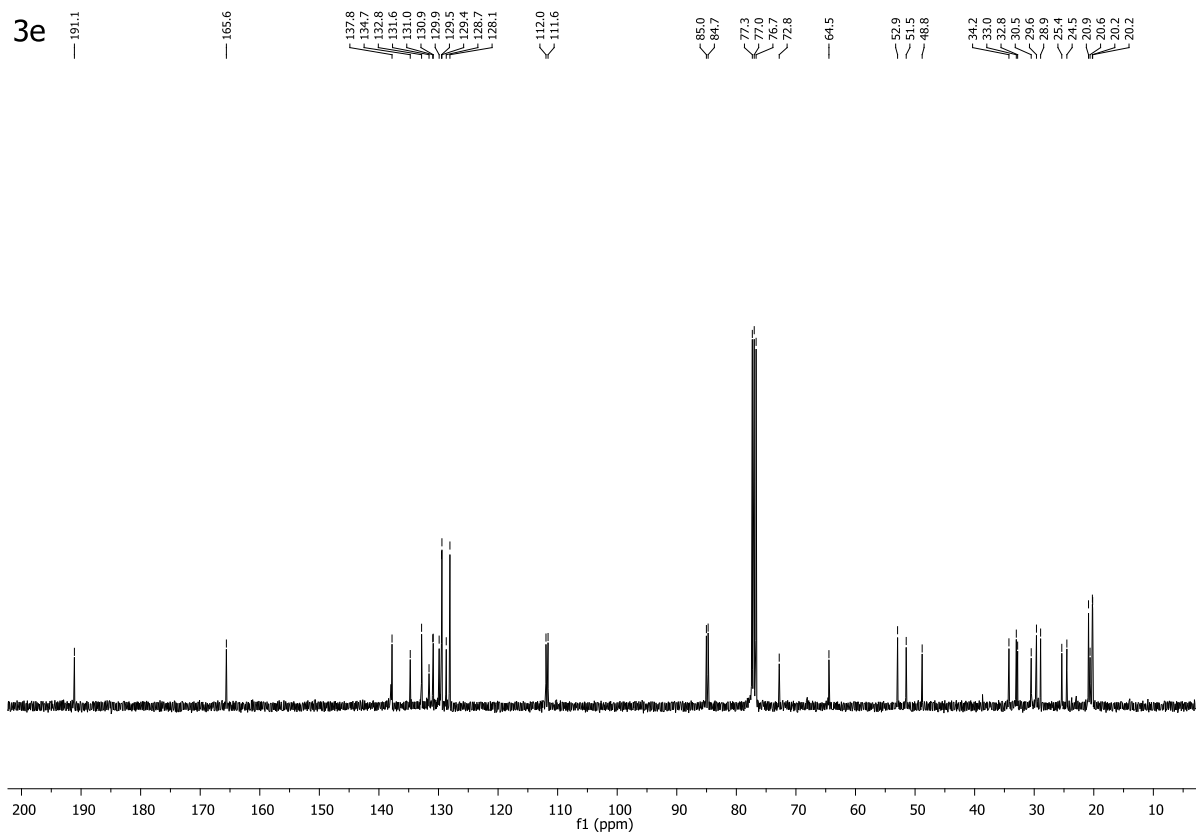
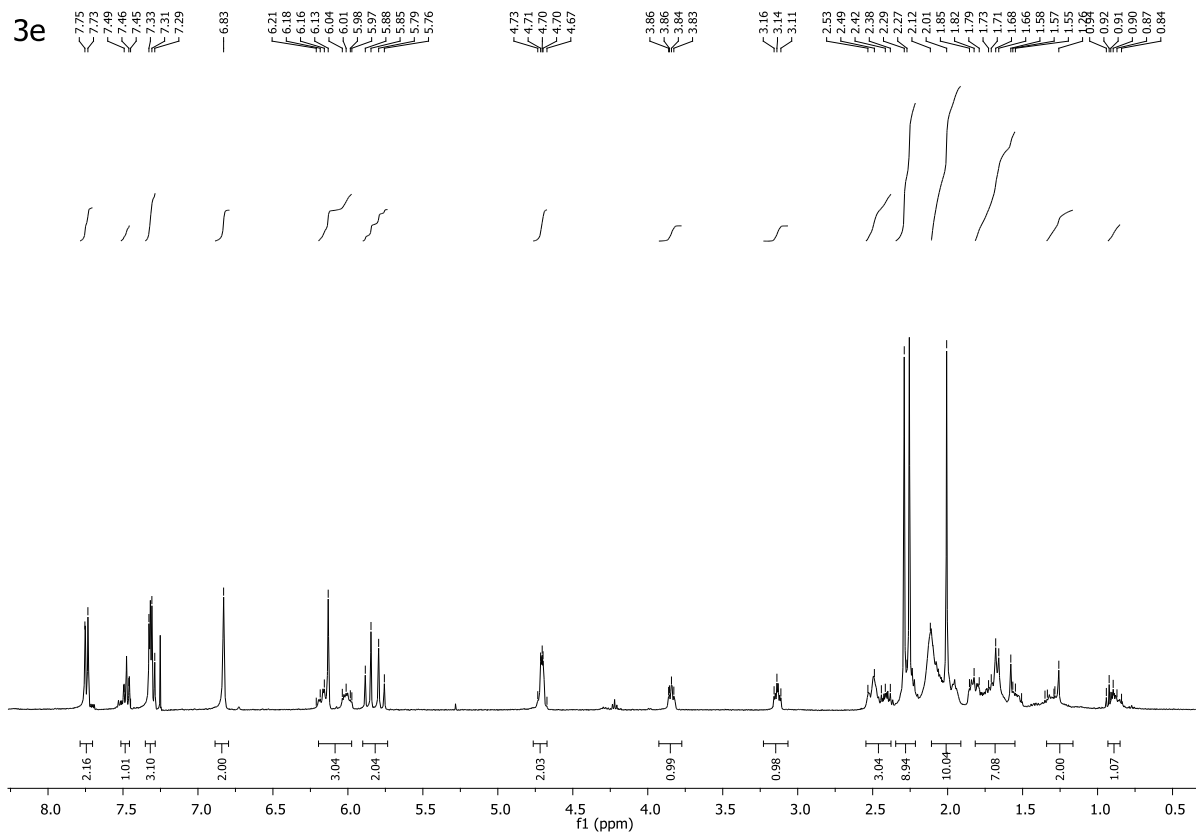


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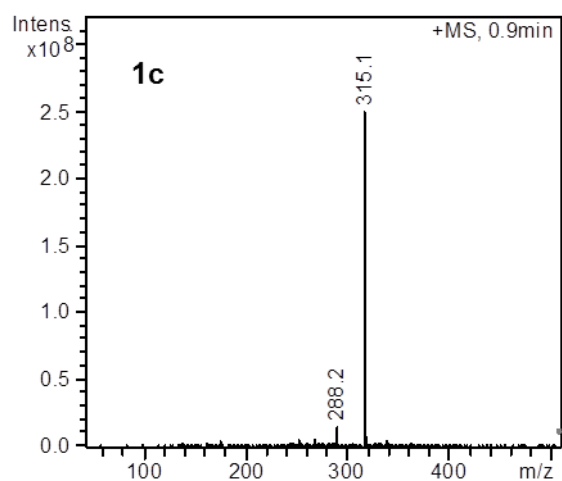
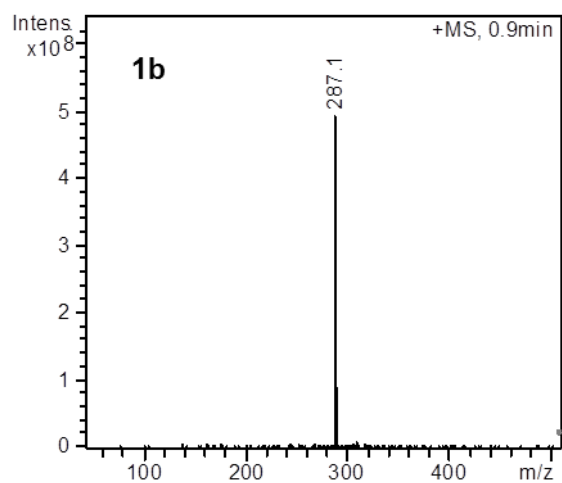
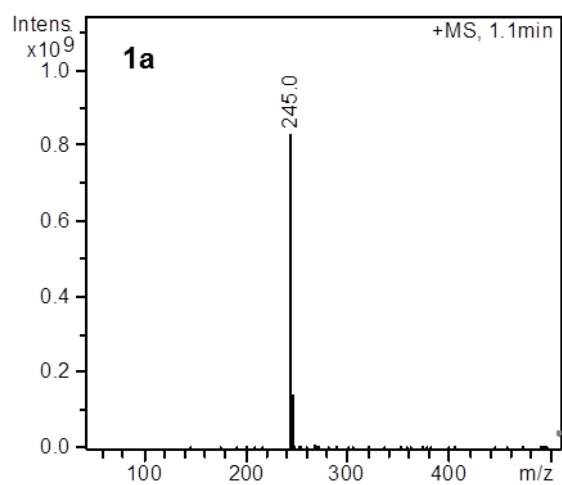


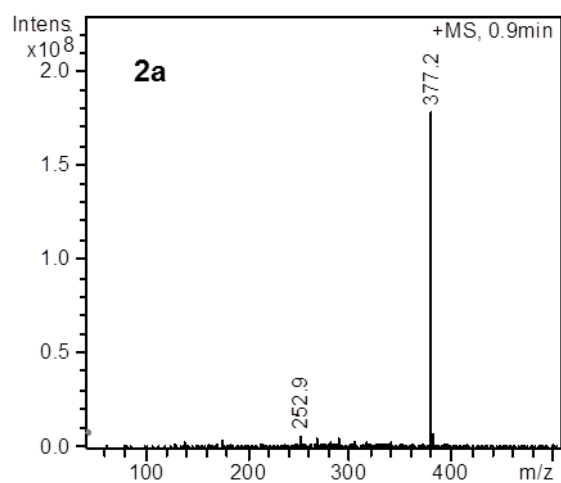
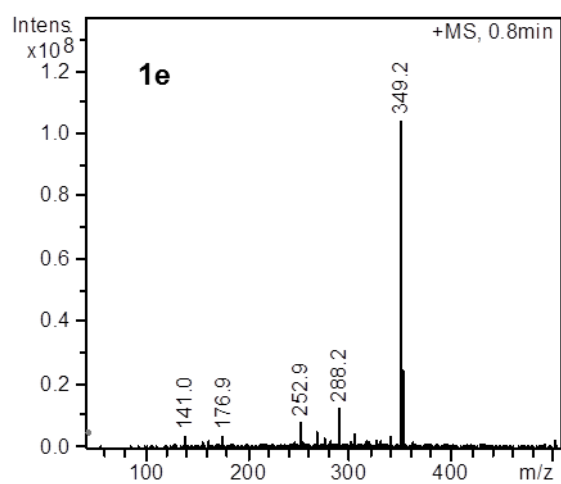
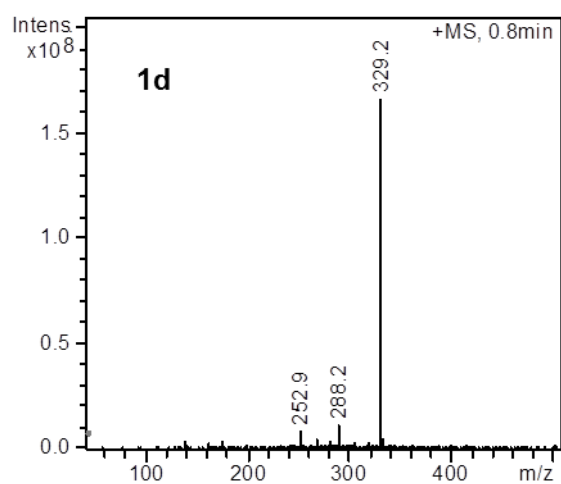
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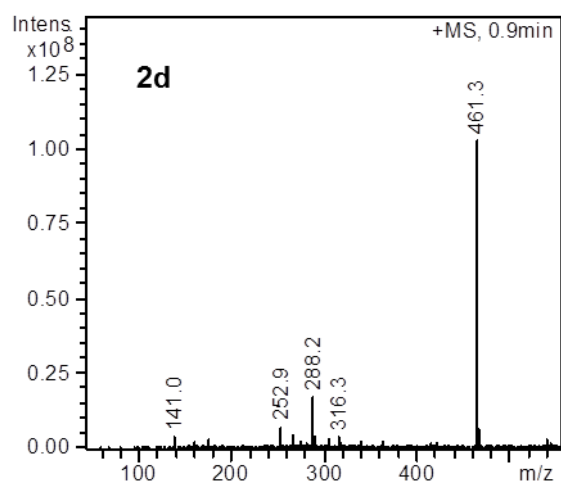
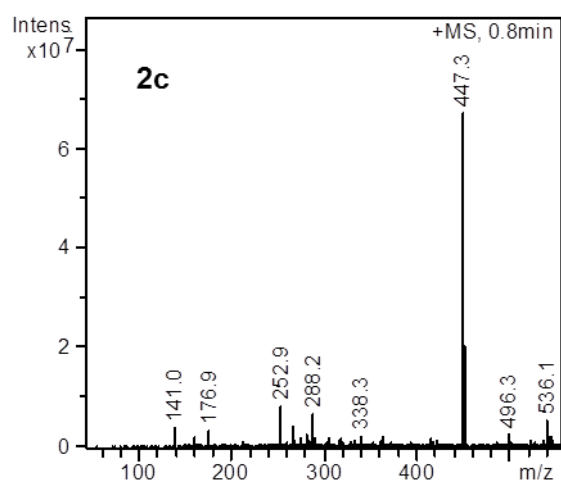
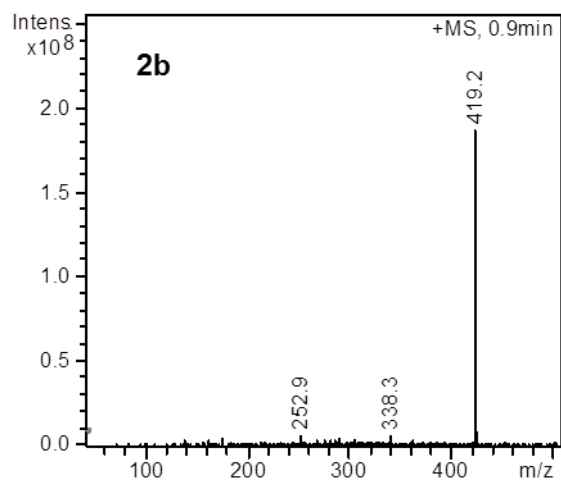


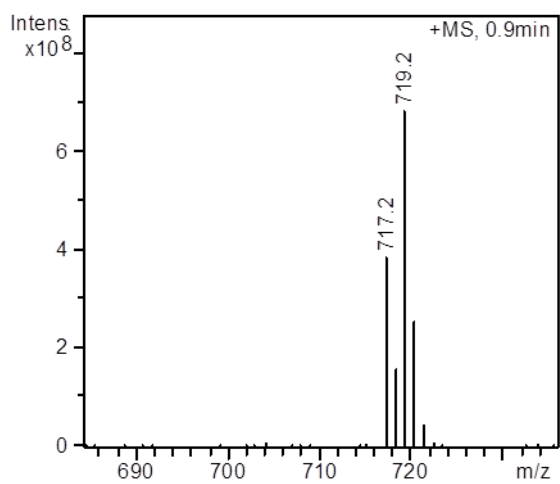
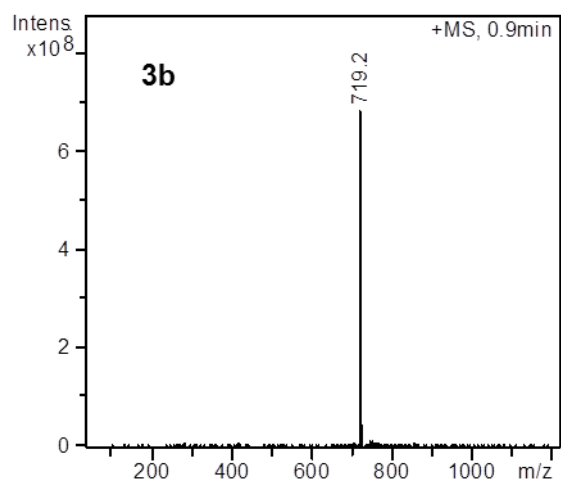
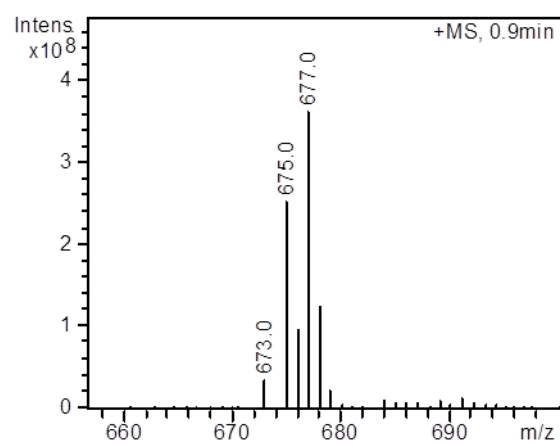
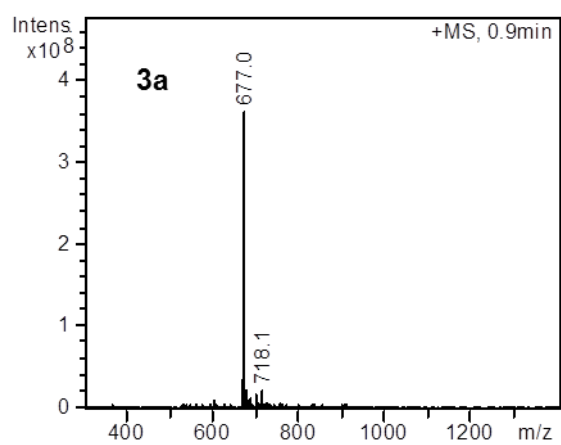
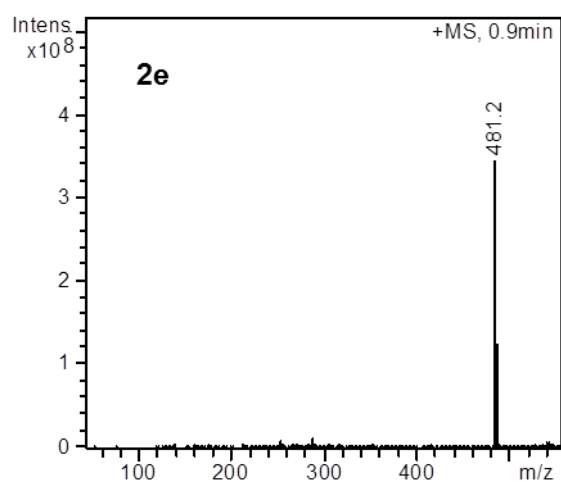


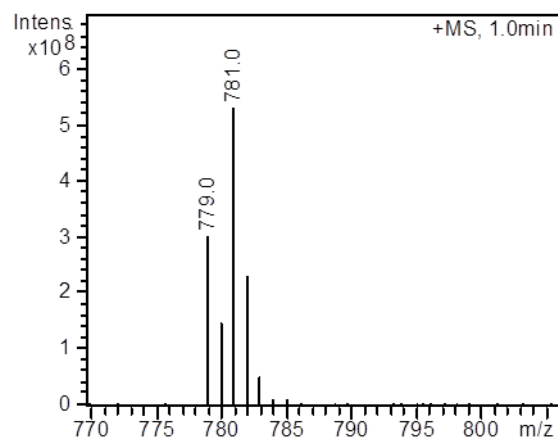
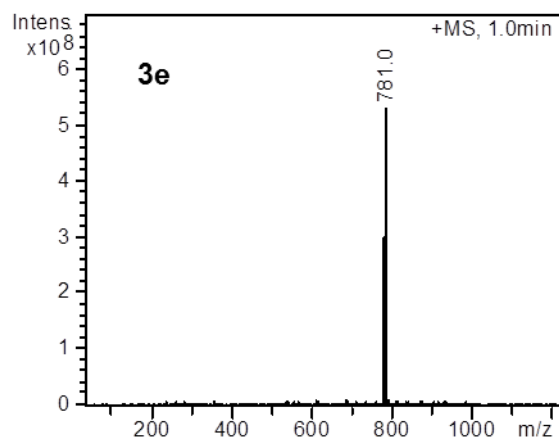
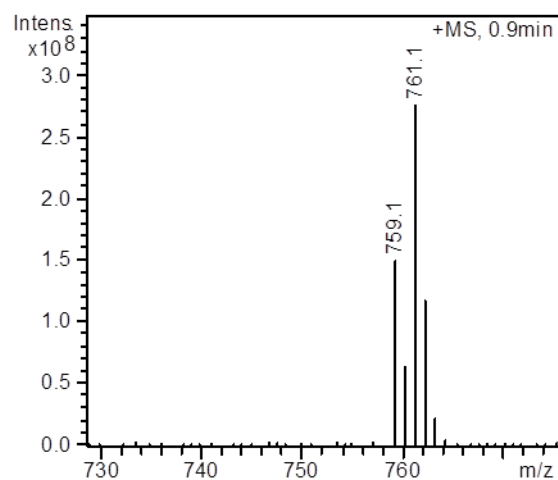
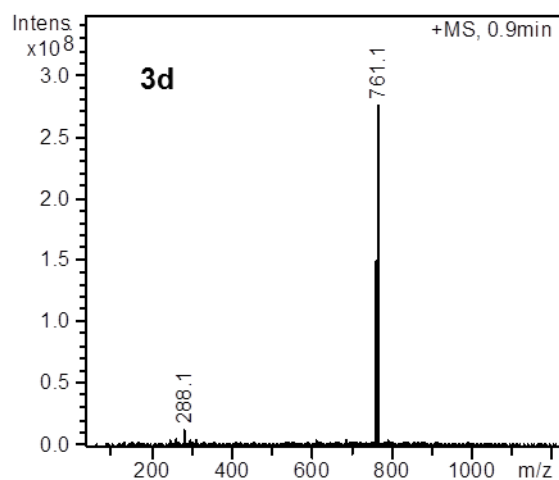
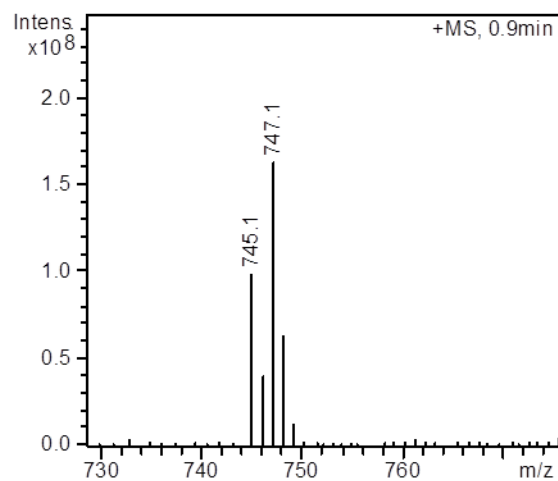
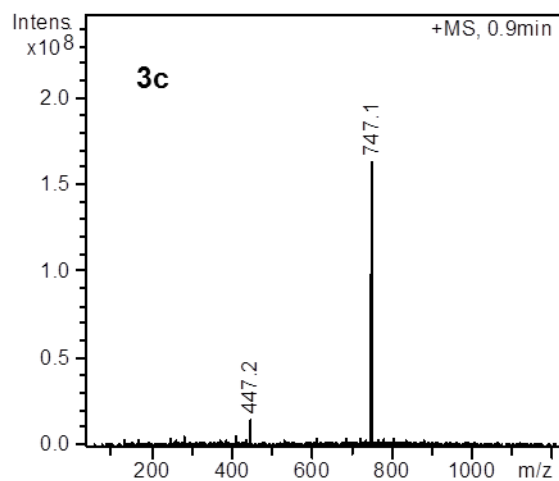
Mass Spectra of Compounds 1a-e, 2a-e and 3a-e:





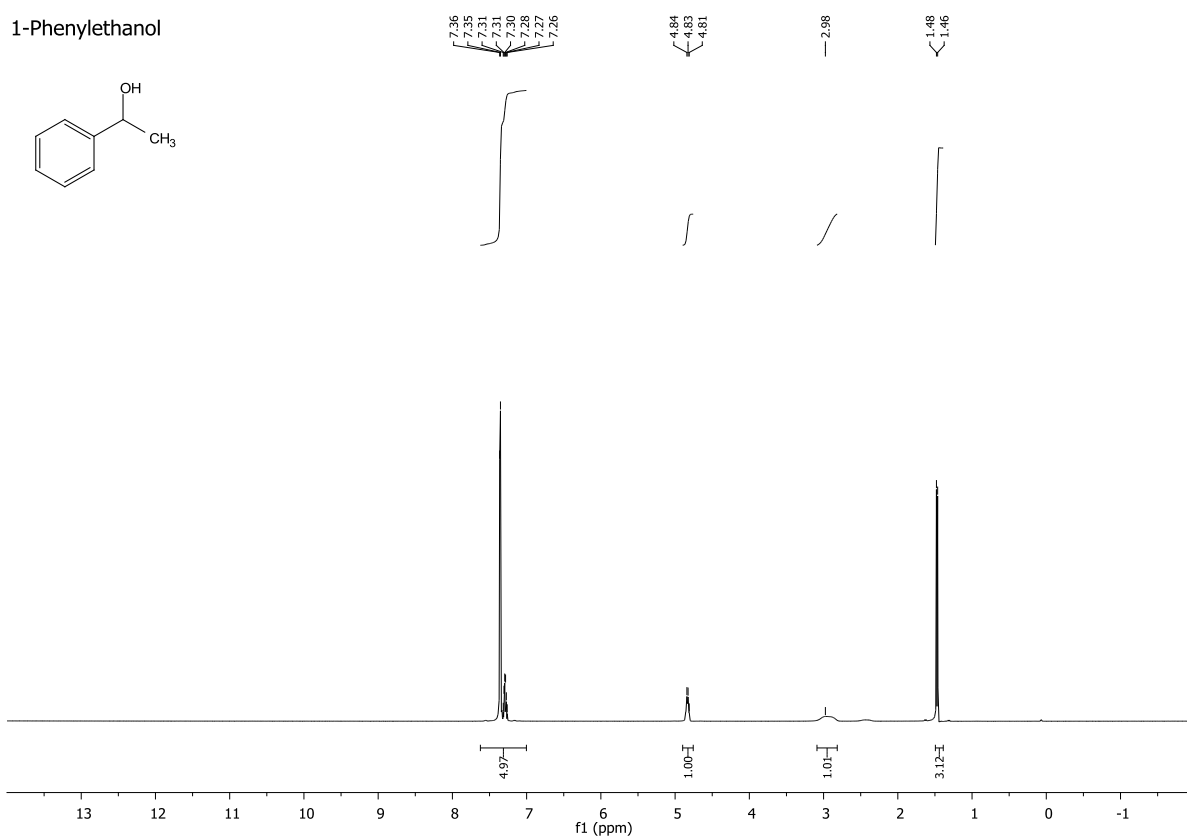




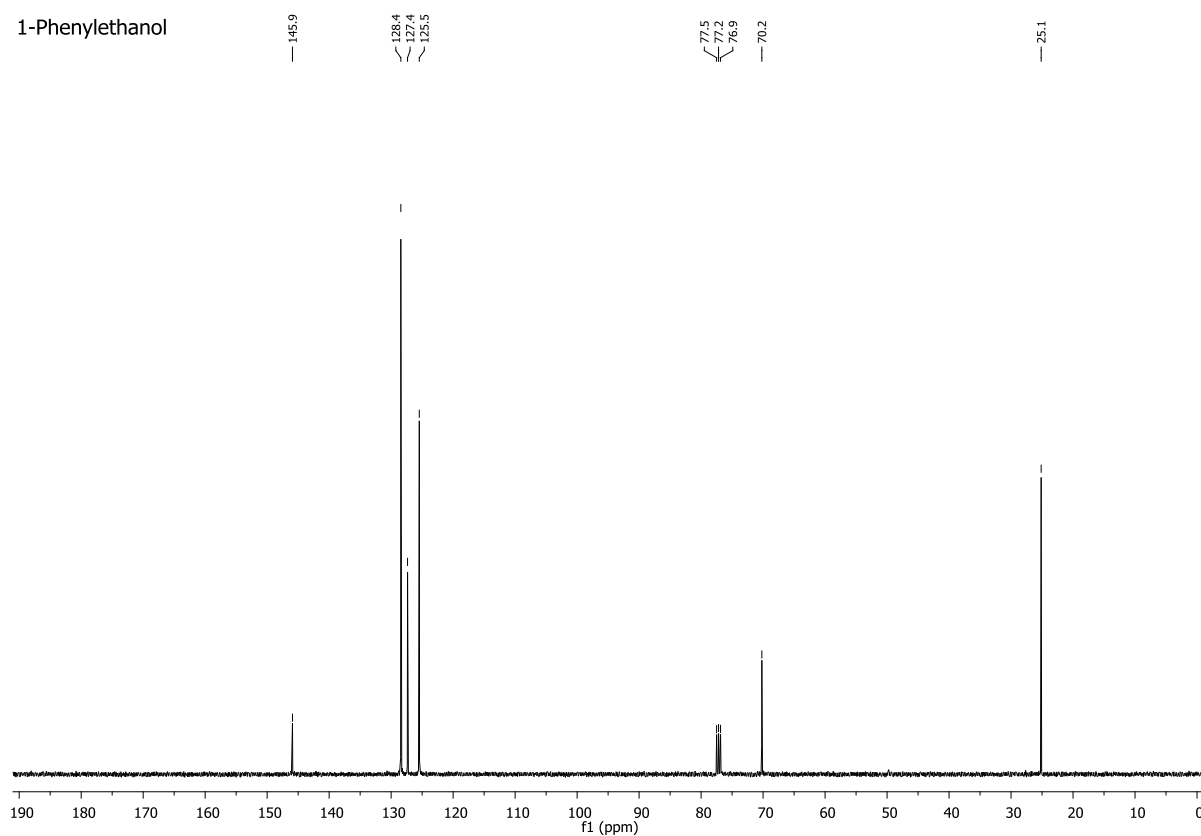


¹H and ¹³C NMR Spectra of the Resulting Alcohols from the Catalytic Reactions:

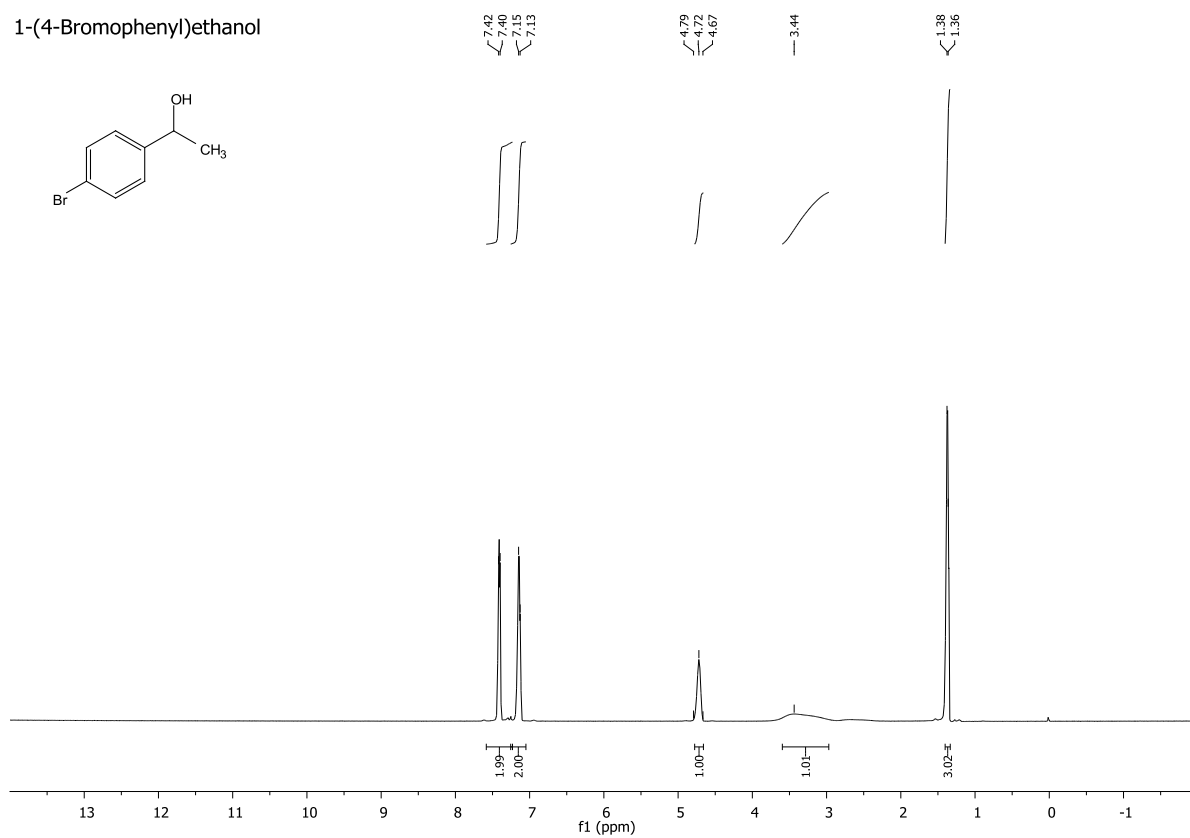
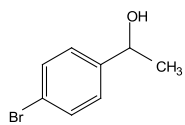
1-Phenylethanol



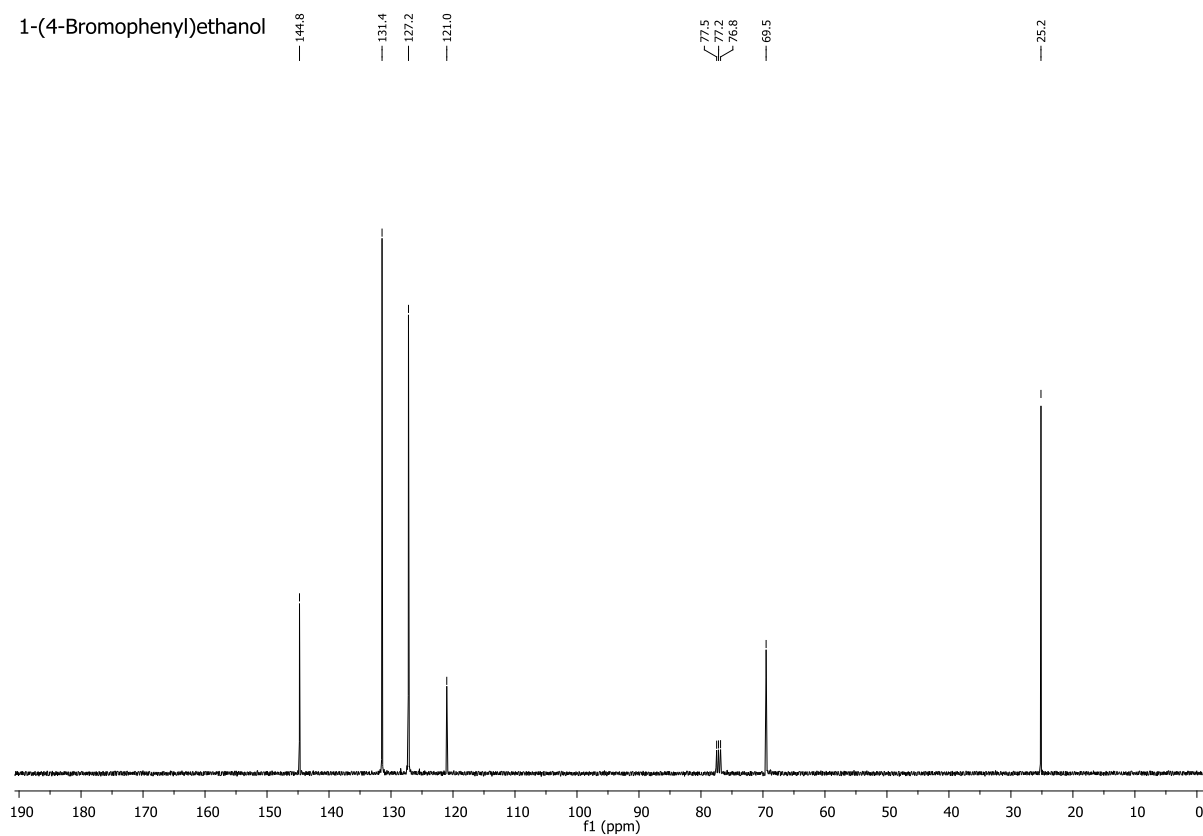
1-Phenylethanol



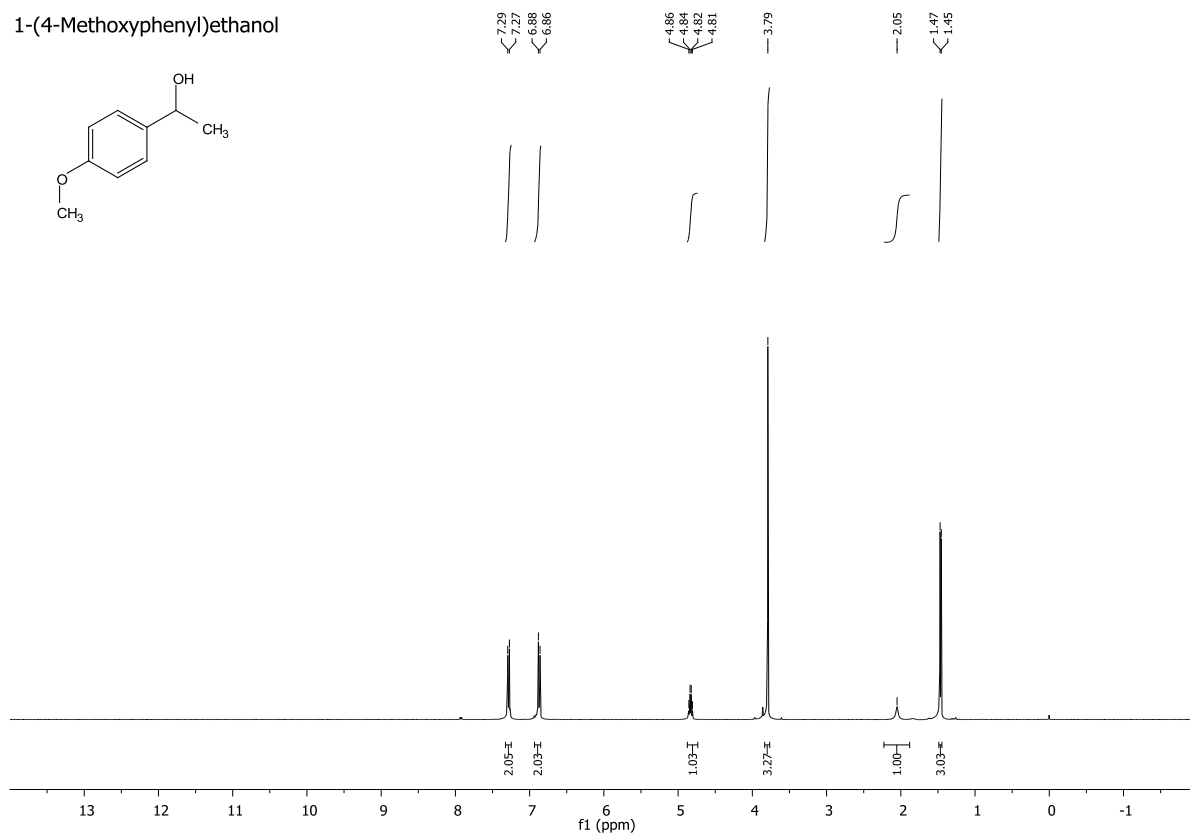
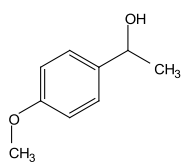
1-(4-Bromophenyl)ethanol



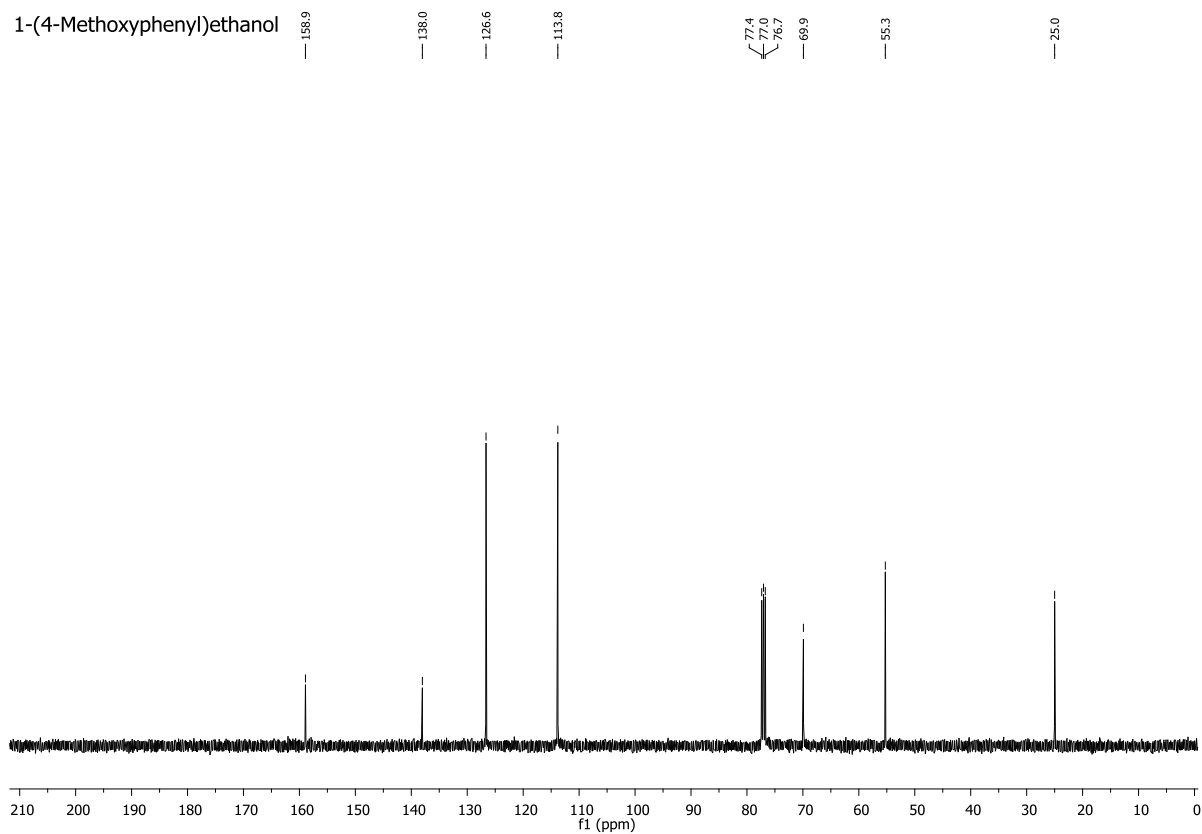
1-(4-Bromophenyl)ethanol



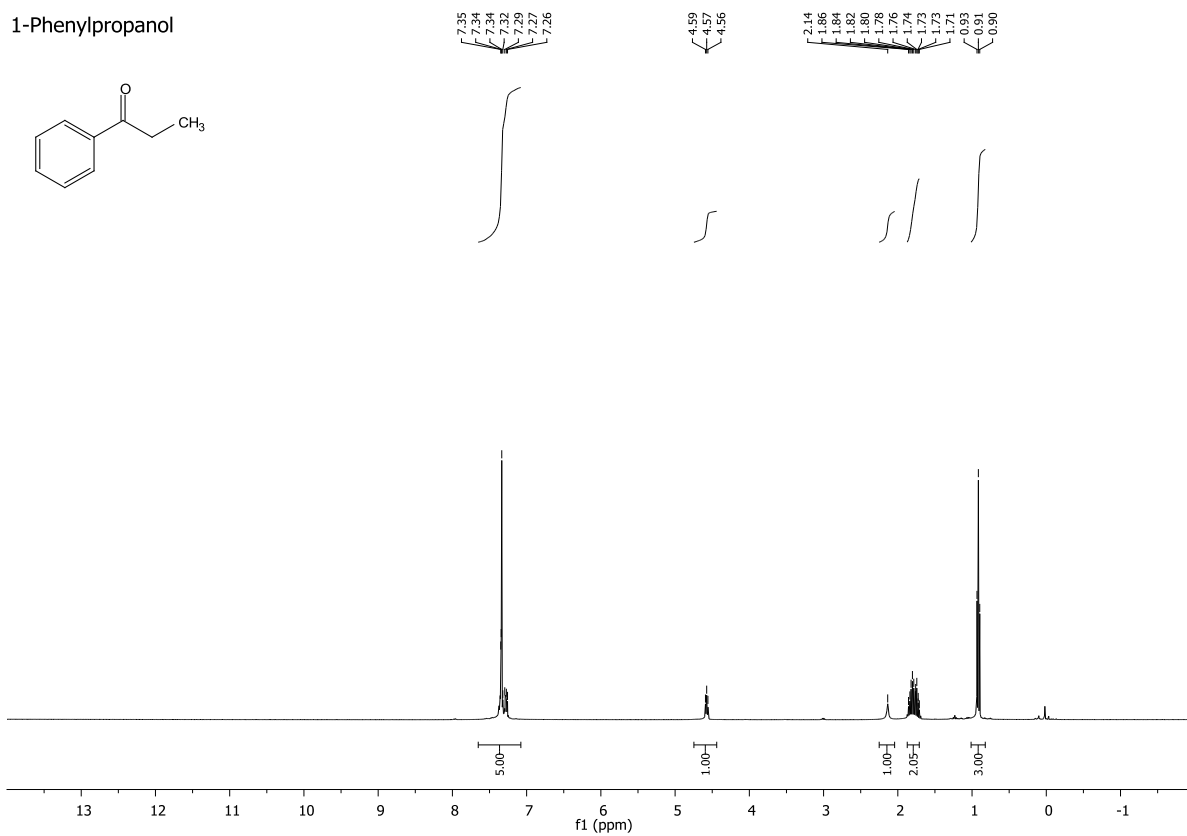
1-(4-Methoxyphenyl)ethanol



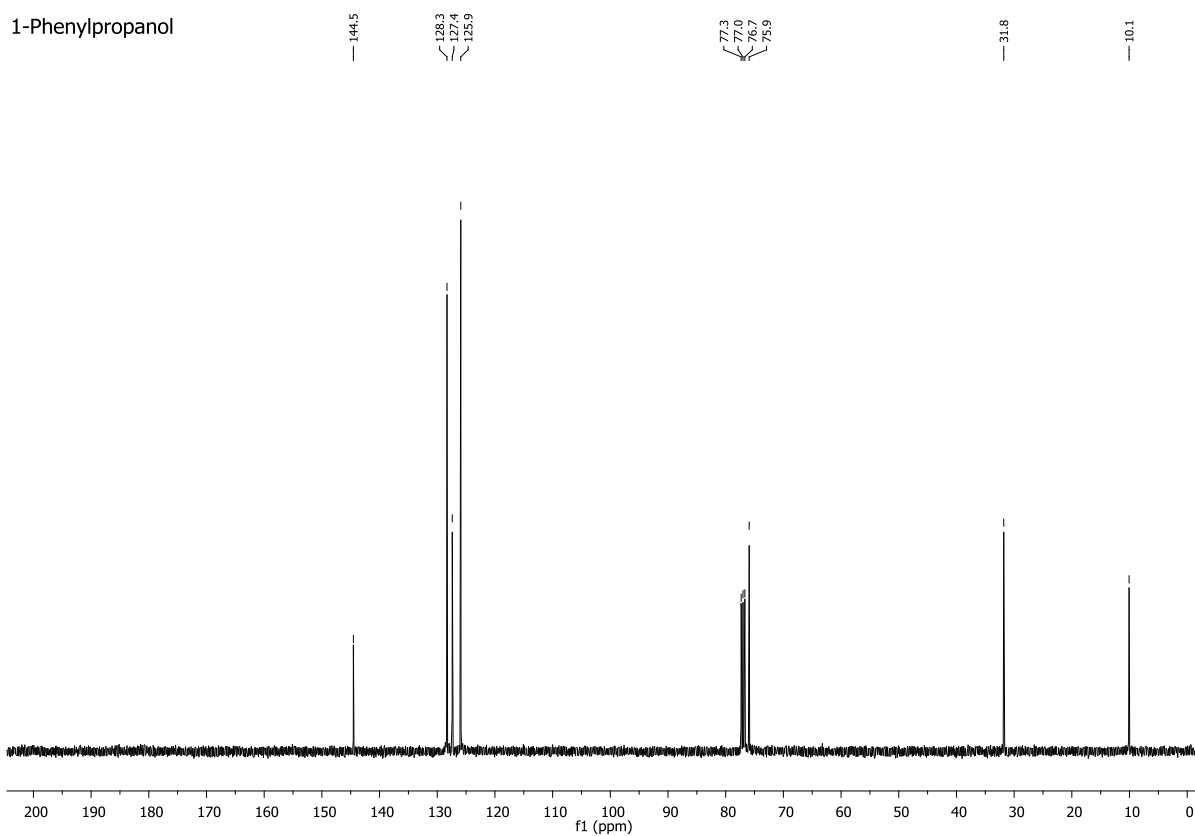
1-(4-Methoxyphenyl)ethanol



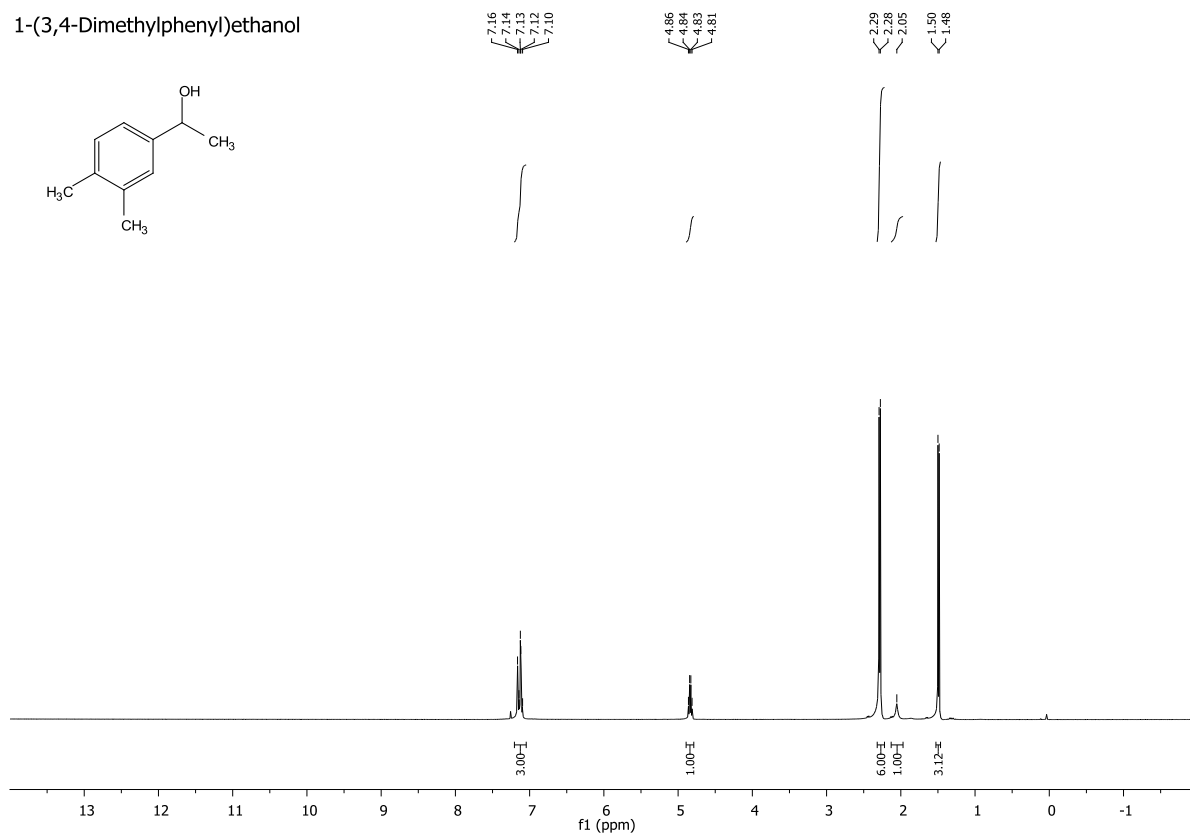
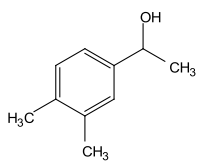
1-Phenylpropanol



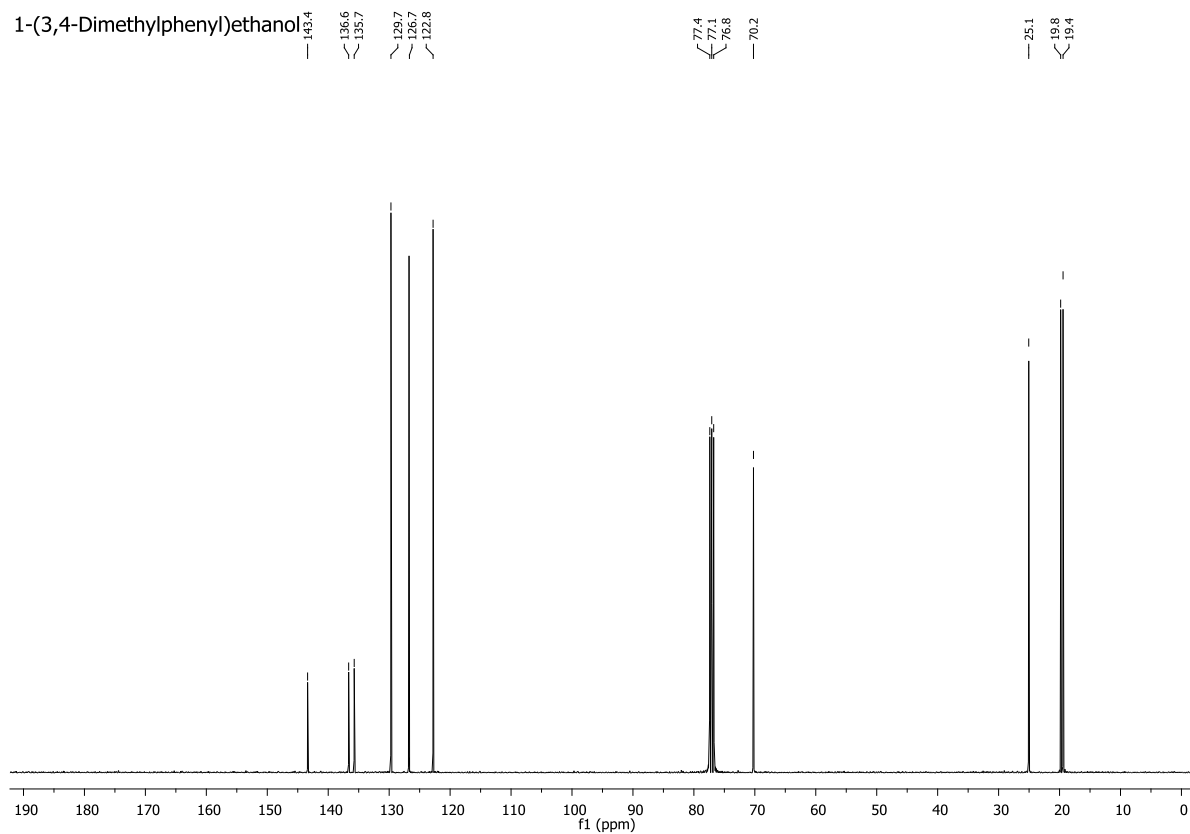
1-Phenylpropanol



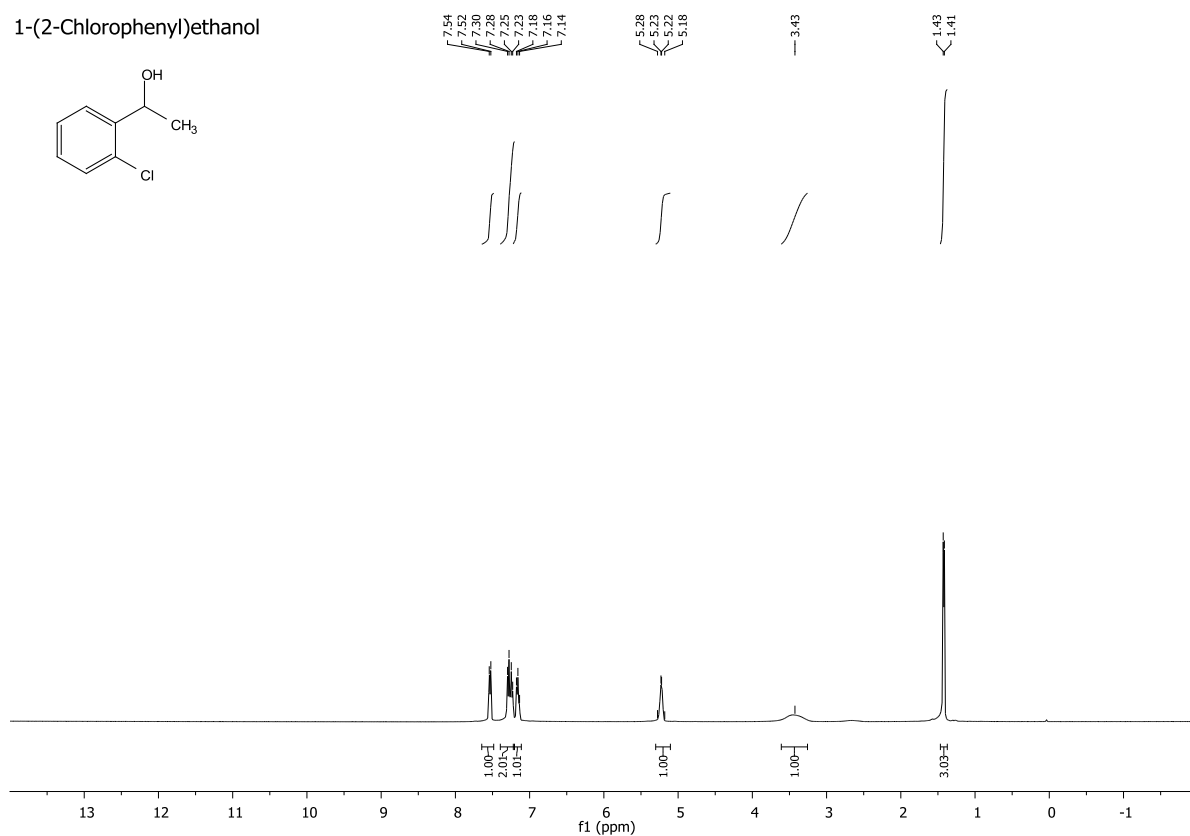
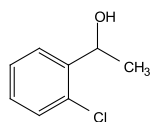
1-(3,4-Dimethylphenyl)ethanol



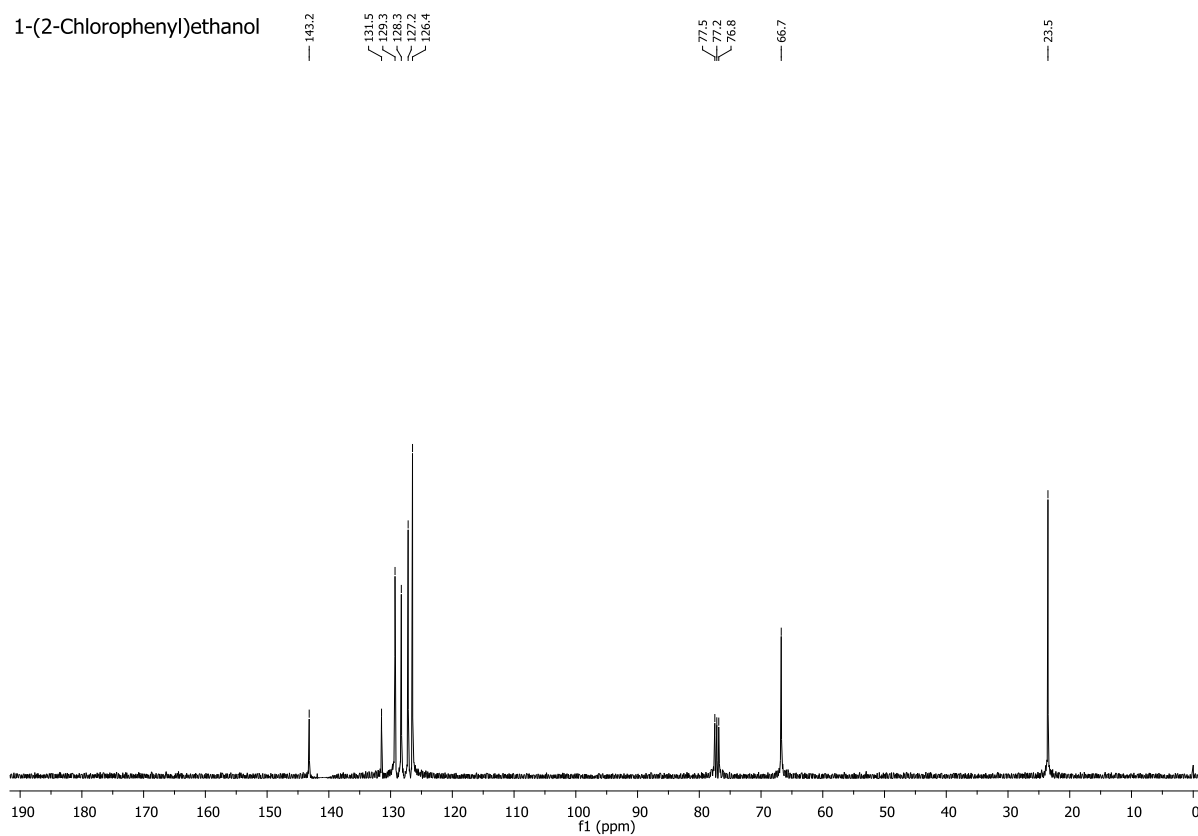
1-(3,4-Dimethylphenyl)ethanol



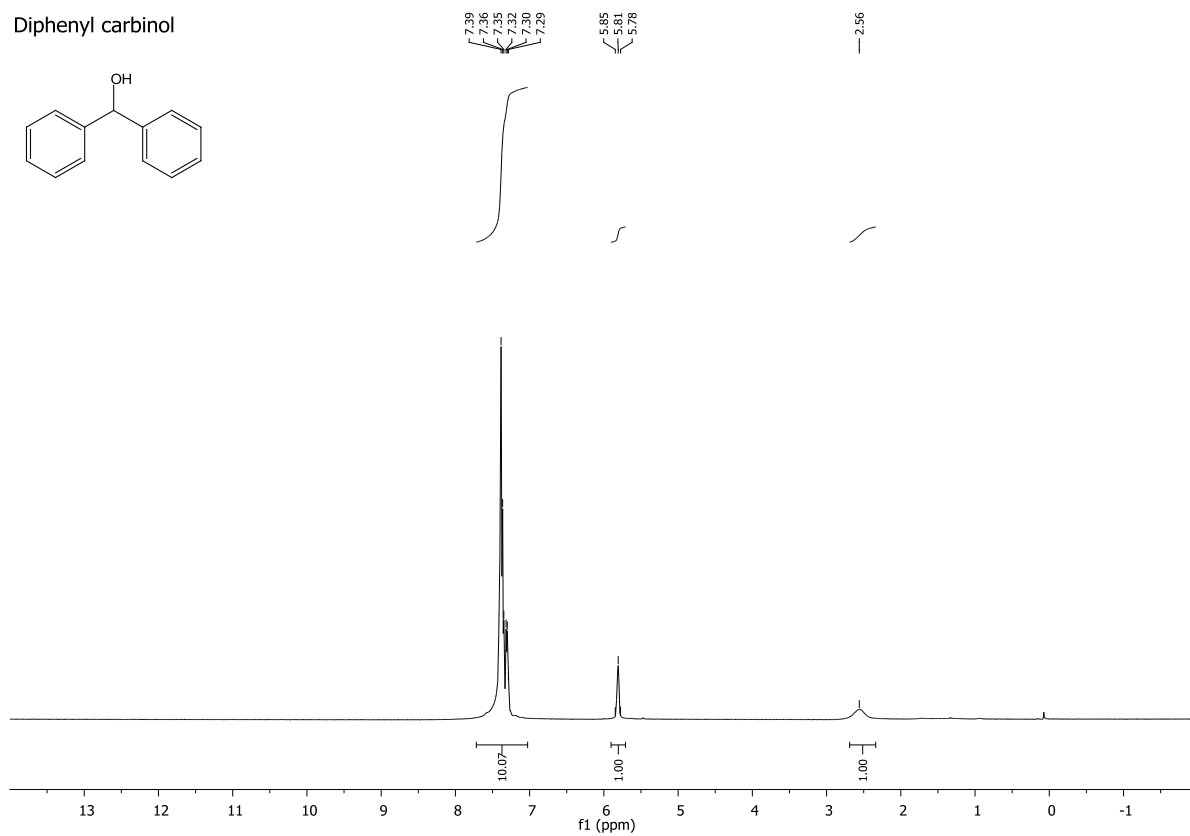
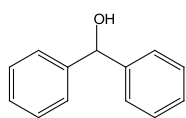
1-(2-Chlorophenyl)ethanol



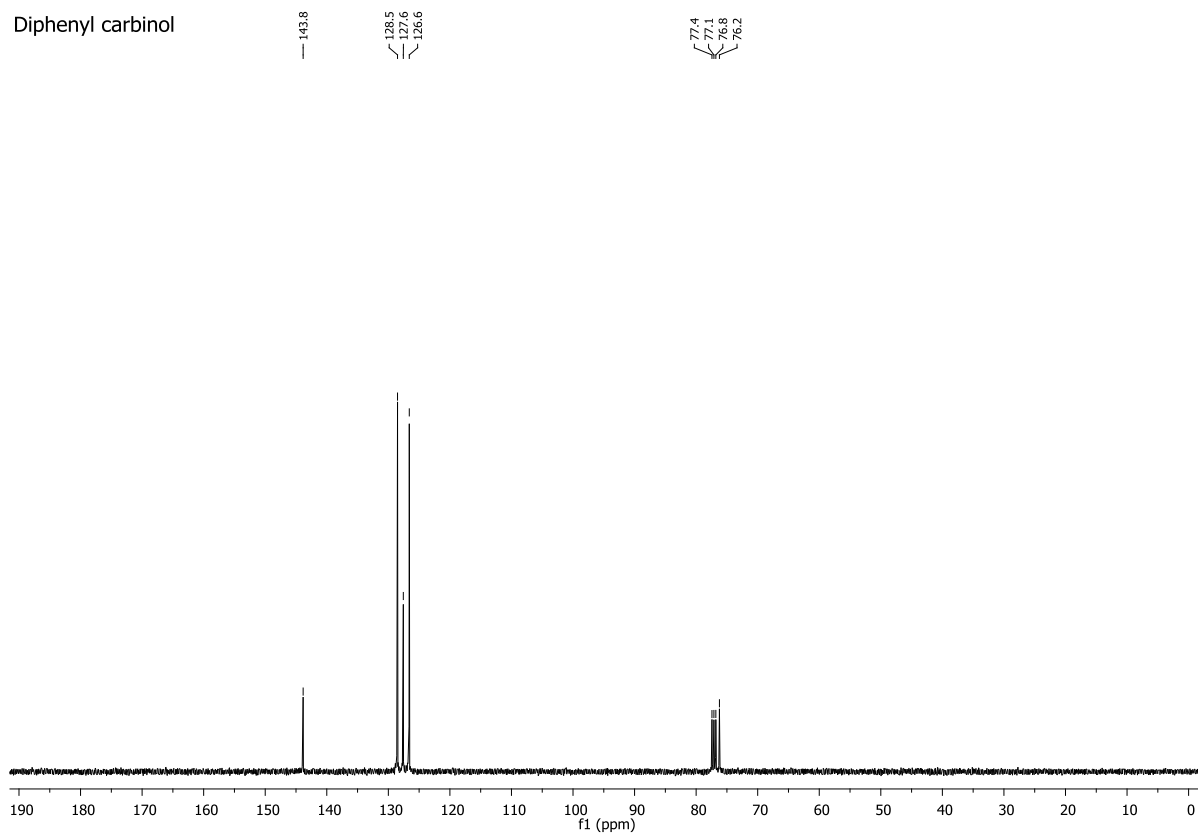
1-(2-Chlorophenyl)ethanol



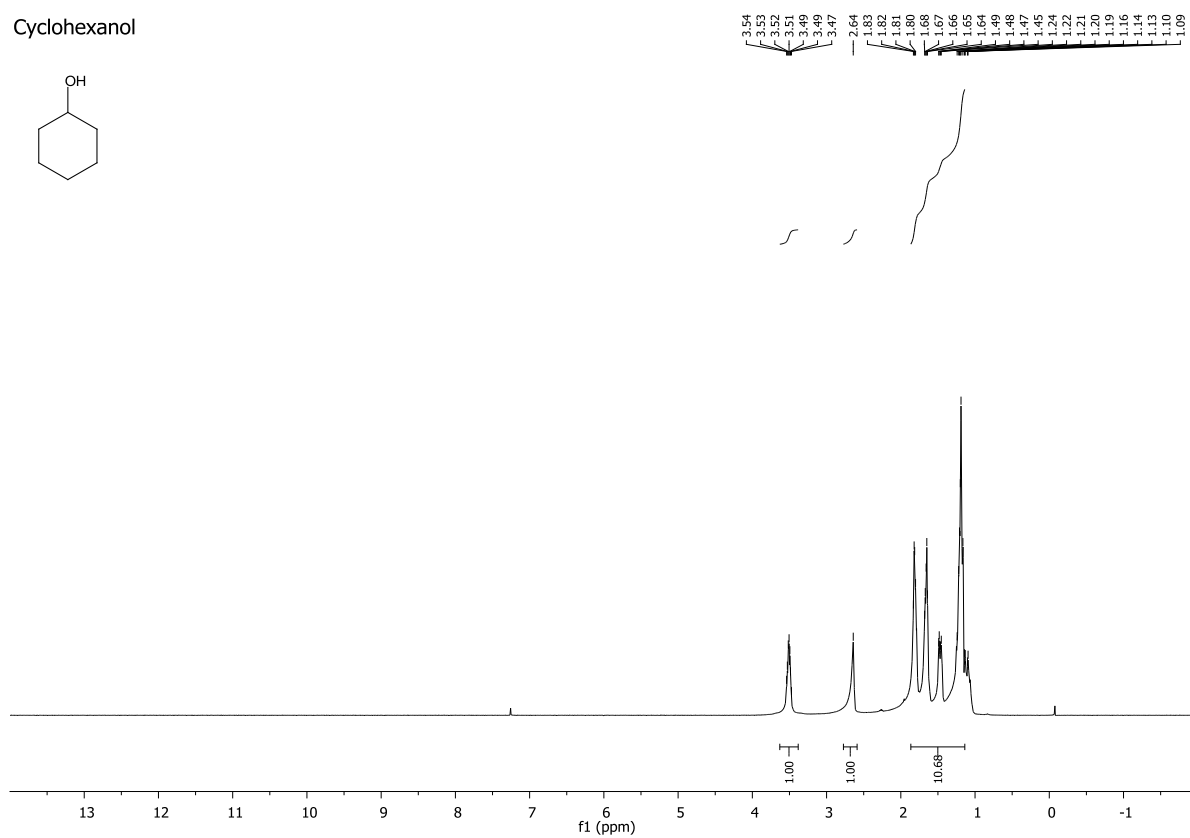
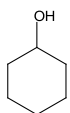
Diphenyl carbinol



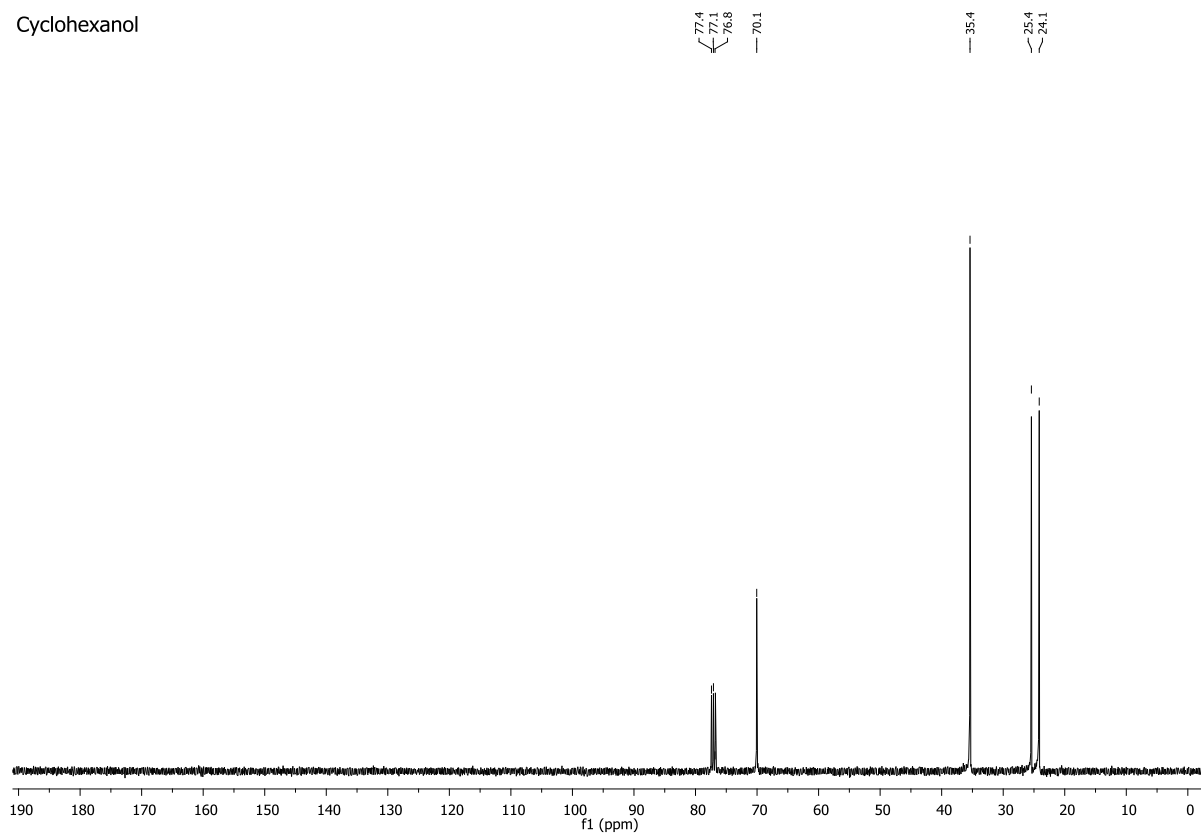
Diphenyl carbinol



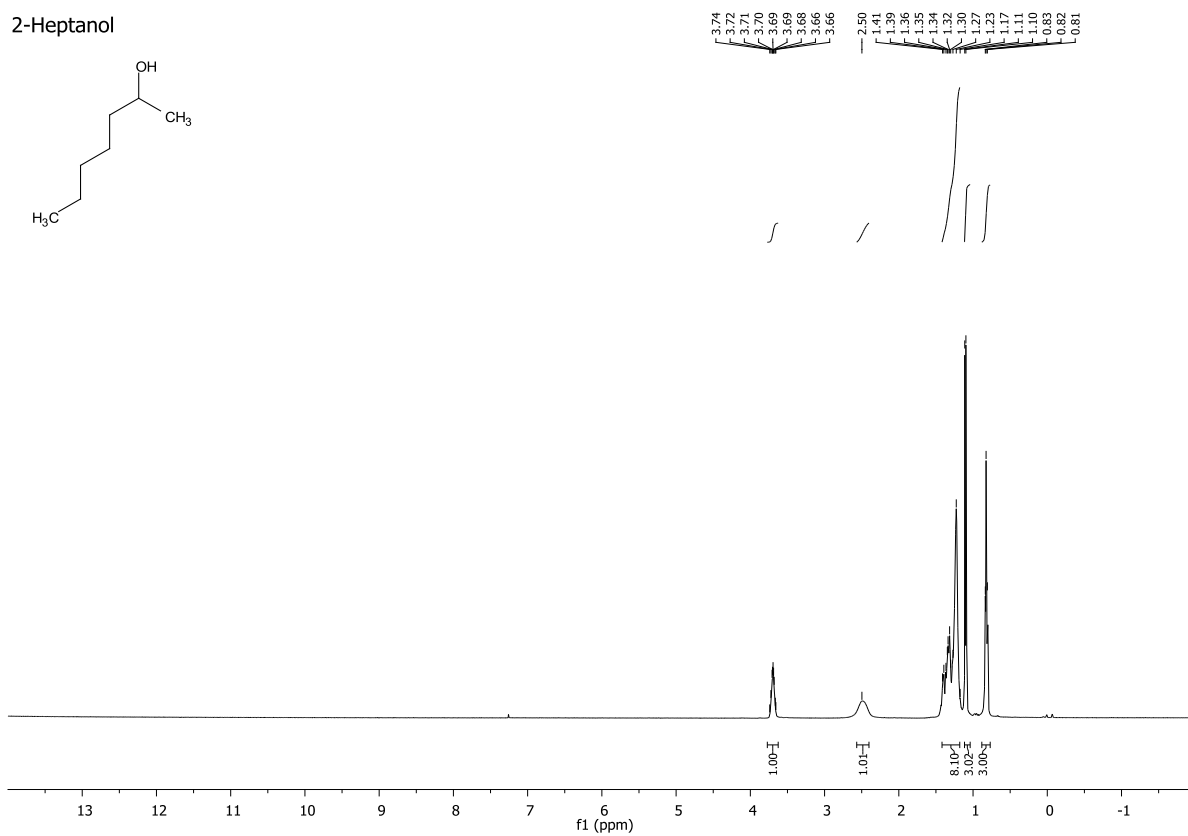
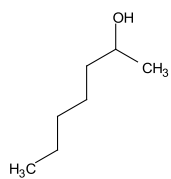
Cyclohexanol



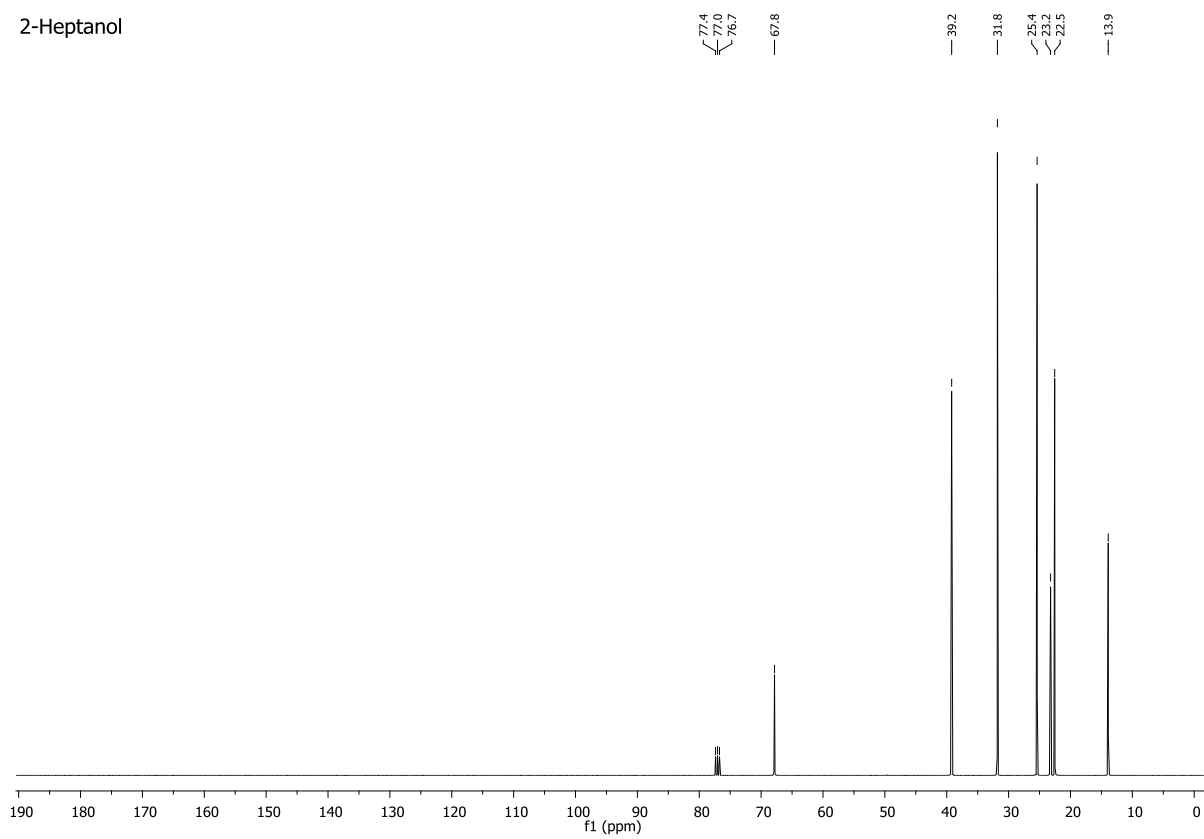
Cyclohexanol



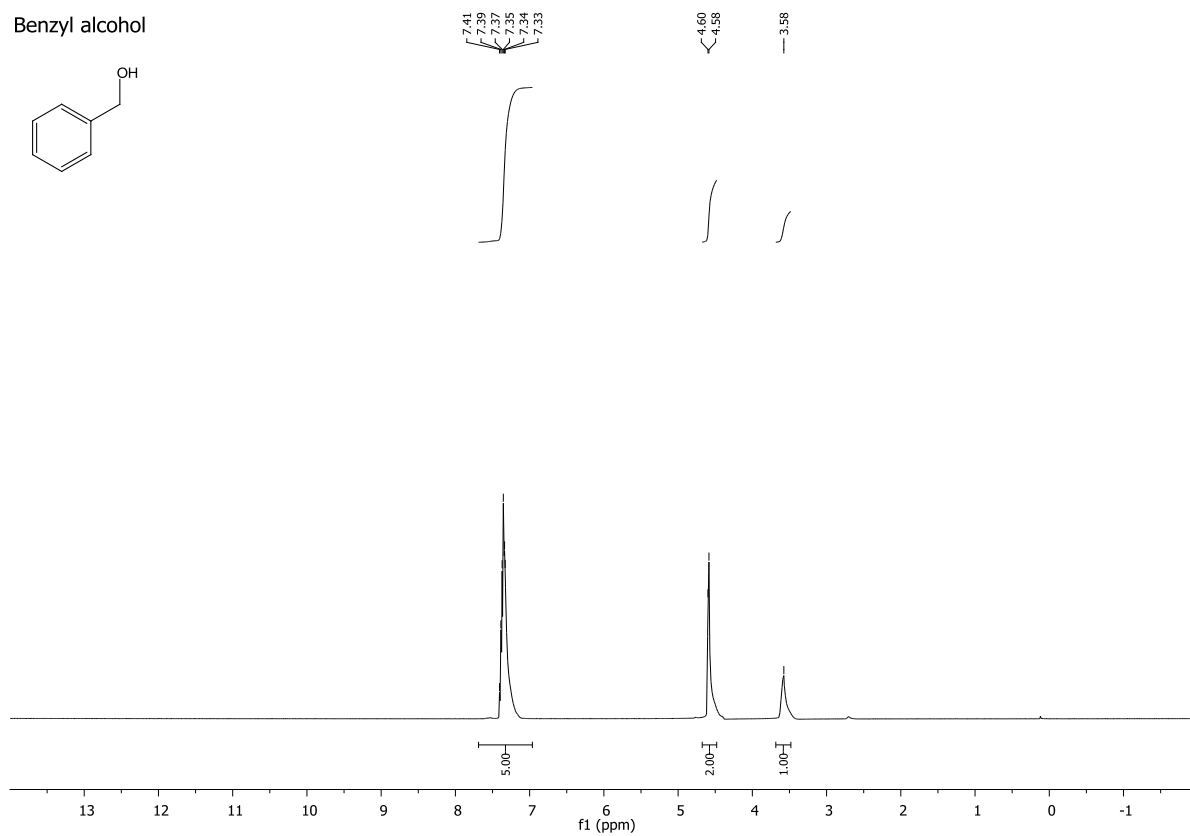
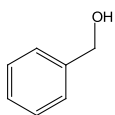
2-Heptanol



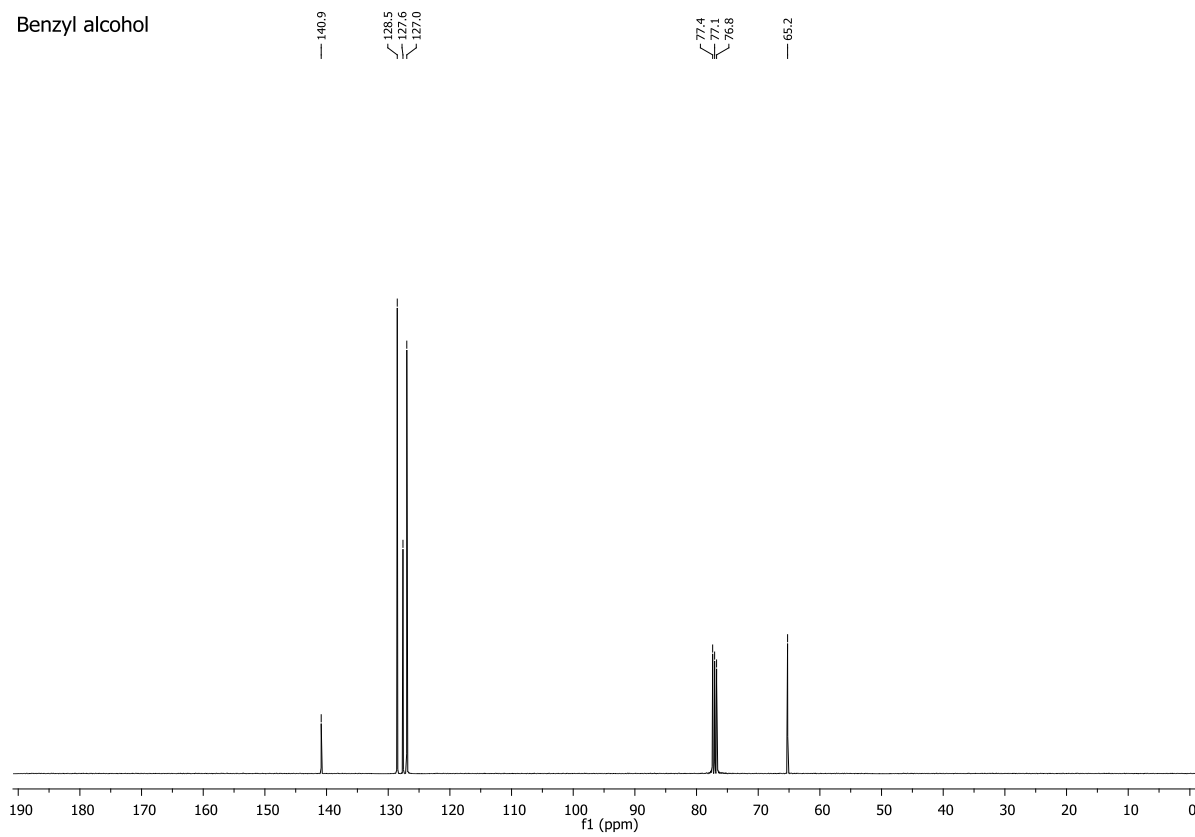
2-Heptanol



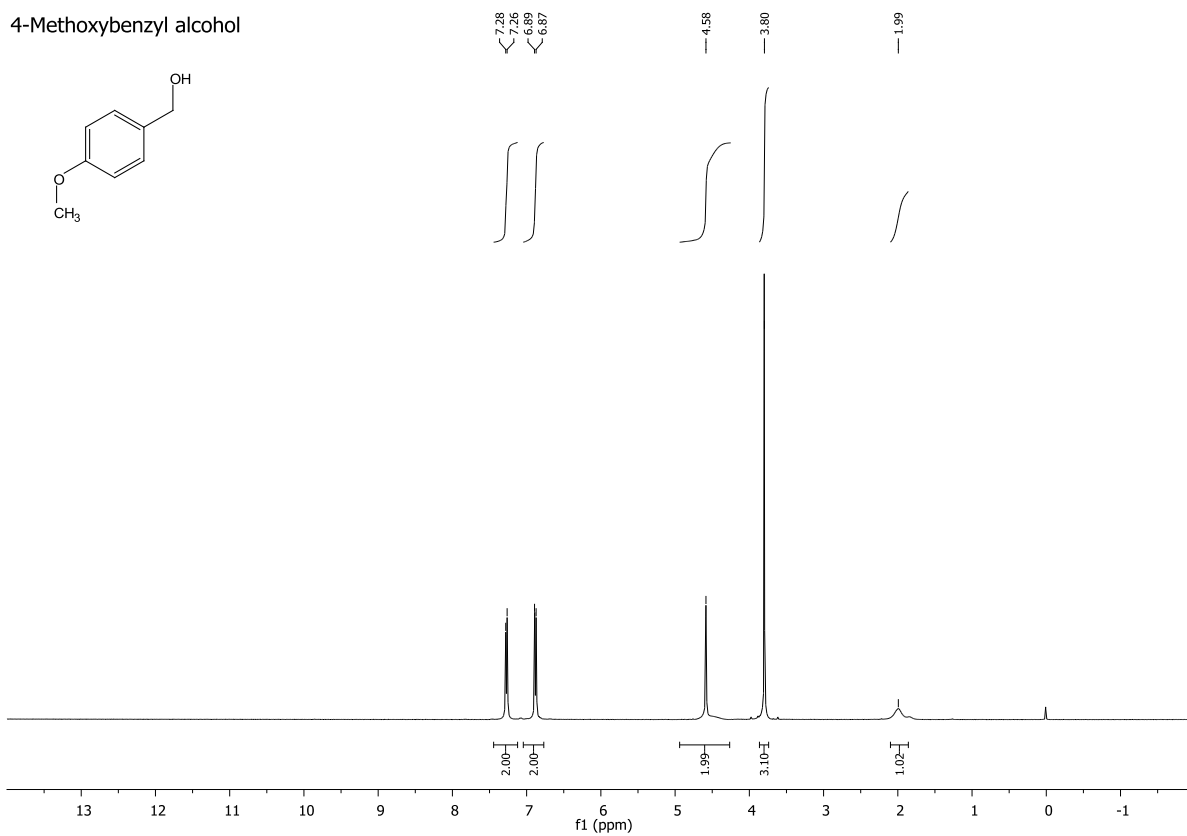
Benzyl alcohol



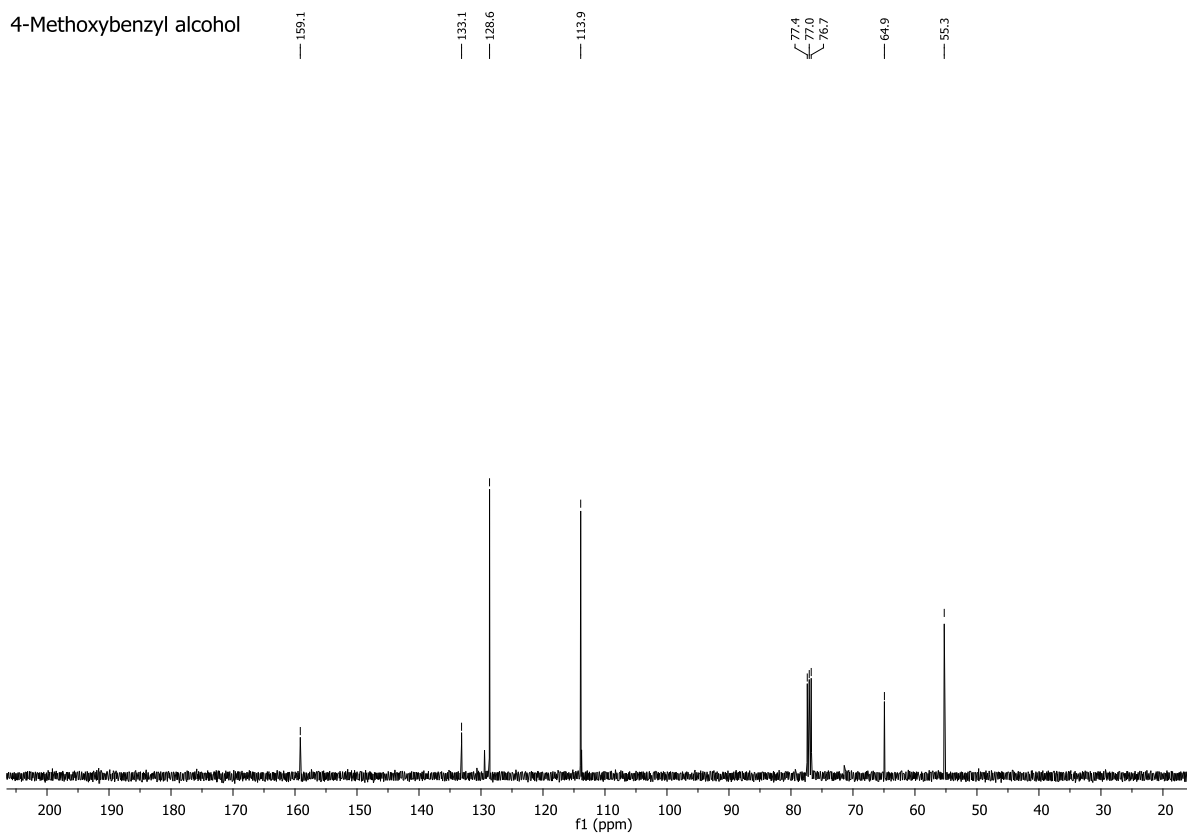
Benzyl alcohol



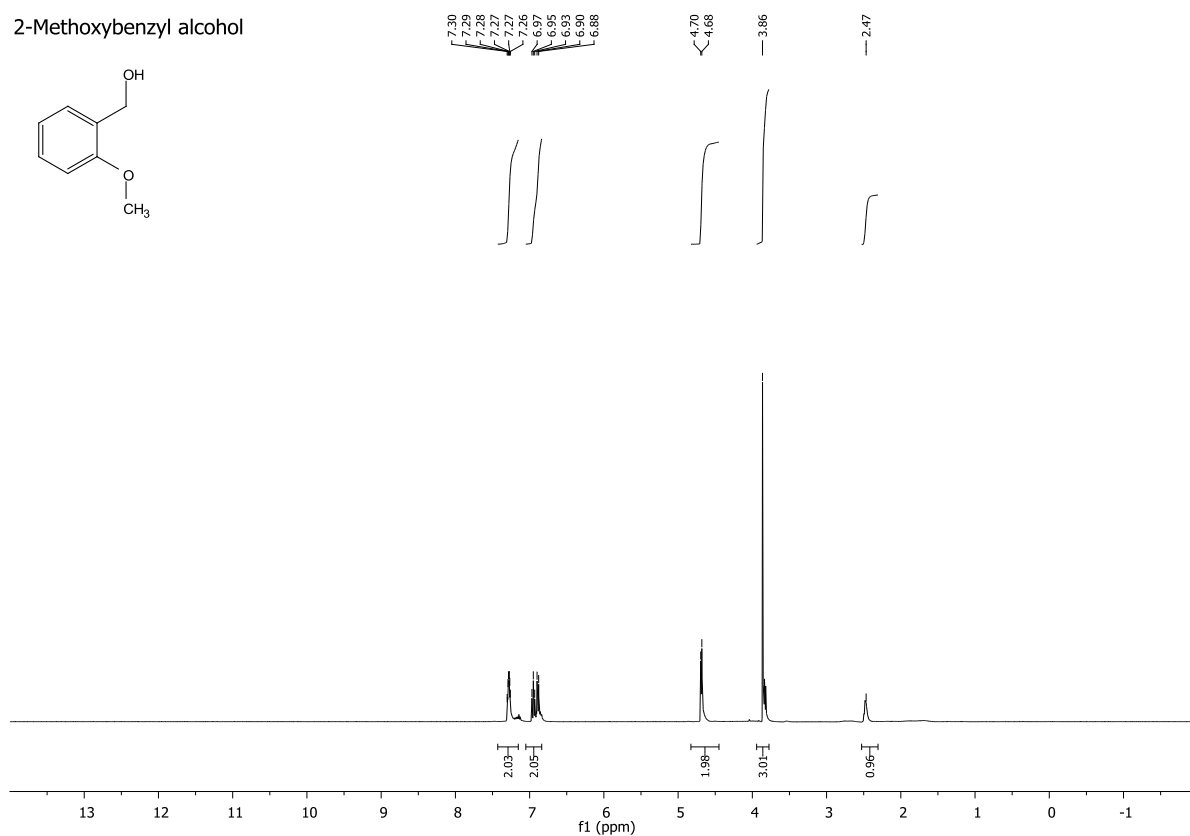
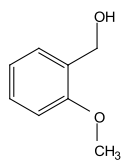
4-Methoxybenzyl alcohol



4-Methoxybenzyl alcohol



2-Methoxybenzyl alcohol



2-Methoxybenzyl alcohol

