

Supplementary Material

The total synthesis of chrysophanol and aloesaponarin II, anthraquinone natural products from bio-renewable cashew nut shell liquid-derived phenolics

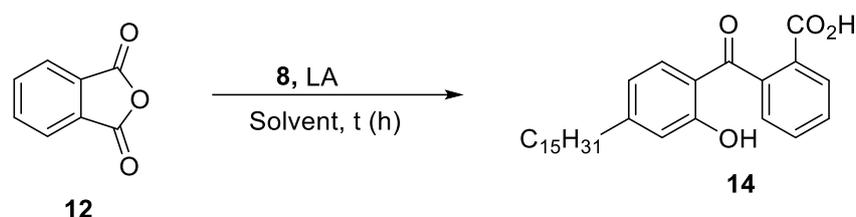
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**Scheme 1:** Attempted synthesis of **14****Table 1:** Explored conditions for the Friedel-Crafts acylation reaction

Entry	Lewis Acid (LA)	Equivalents	Acid/ Solvent	Duration	Temperature (°C)	Yield of 14
1	BF ₃ .OEt ₂	2.5 - 4	Neat	25 min – 3 h	0 – rt – reflux	N.R
2	BBr ₃	2	DCM	48 h	0 – rt	traces
3	BBr ₃	2.5 - 3	DCE	24 h	0 – rt – reflux	traces
4	AlCl ₃	1.5 - 4	DCM	24 h	0 – rt	12%
5	AlCl ₃	3	DCE	8 – 24 h	rt – reflux	30% – 58%
6	AlCl ₃	1.5 – 3.5	Methanesulfonic acid	2 – 48 h	rt – reflux	N.R
7	AlCl ₃	1.5 – 3.5	Polyphosphoric acid	2 – 48 h	rt – reflux	N.R
8	AlCl ₃	1.5 – 3.5	H ² SO ₄	2 – 48 h	rt – reflux	N.R
9	SnCl ₄	1.5 – 3.5	Methanesulfonic acid	2 – 48 h	rt – reflux	N.R
7	ZrCl ₄	2 – 3.8	Methanesulfonic acid	2 – 48 h	rt – reflux	N.R

N.R = No Reaction

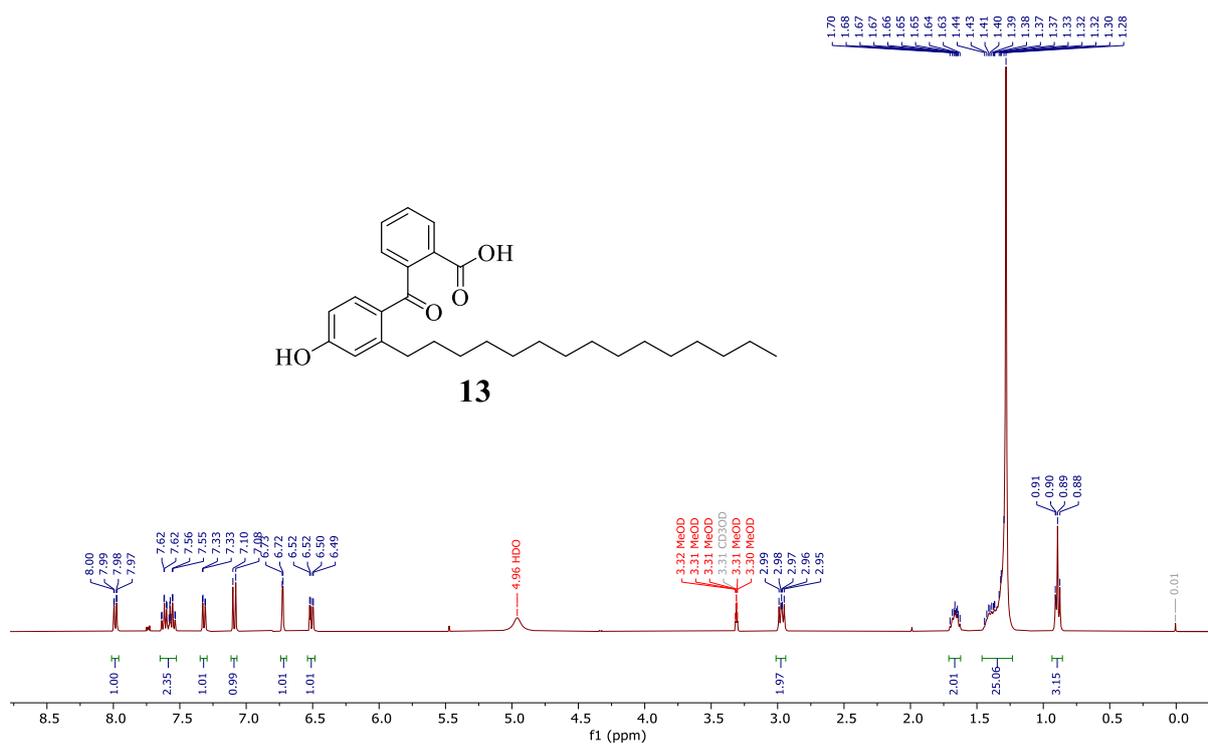


Figure 1: ¹H-NMR spectrum of 2-(4-hydroxy-2-pentadecylbenzoyl)benzoic acid (**13**).

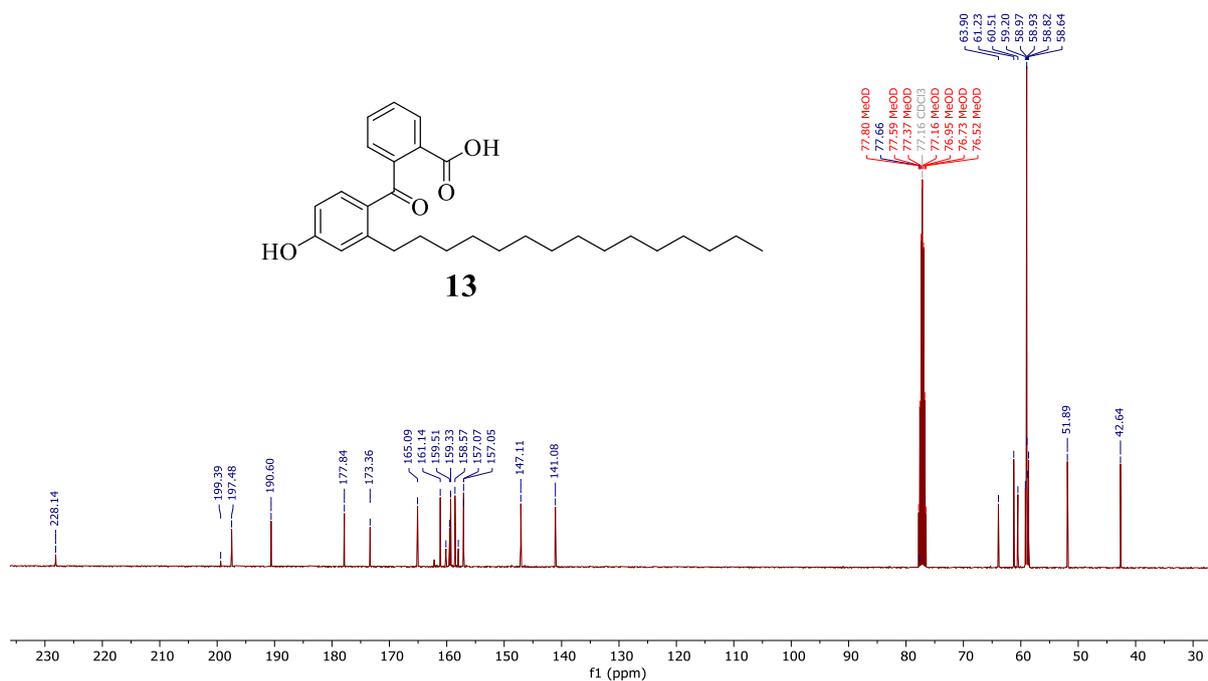


Figure 2: ¹³C-NMR spectrum of 2-(4-hydroxy-2-pentadecylbenzoyl)benzoic acid (**13**).

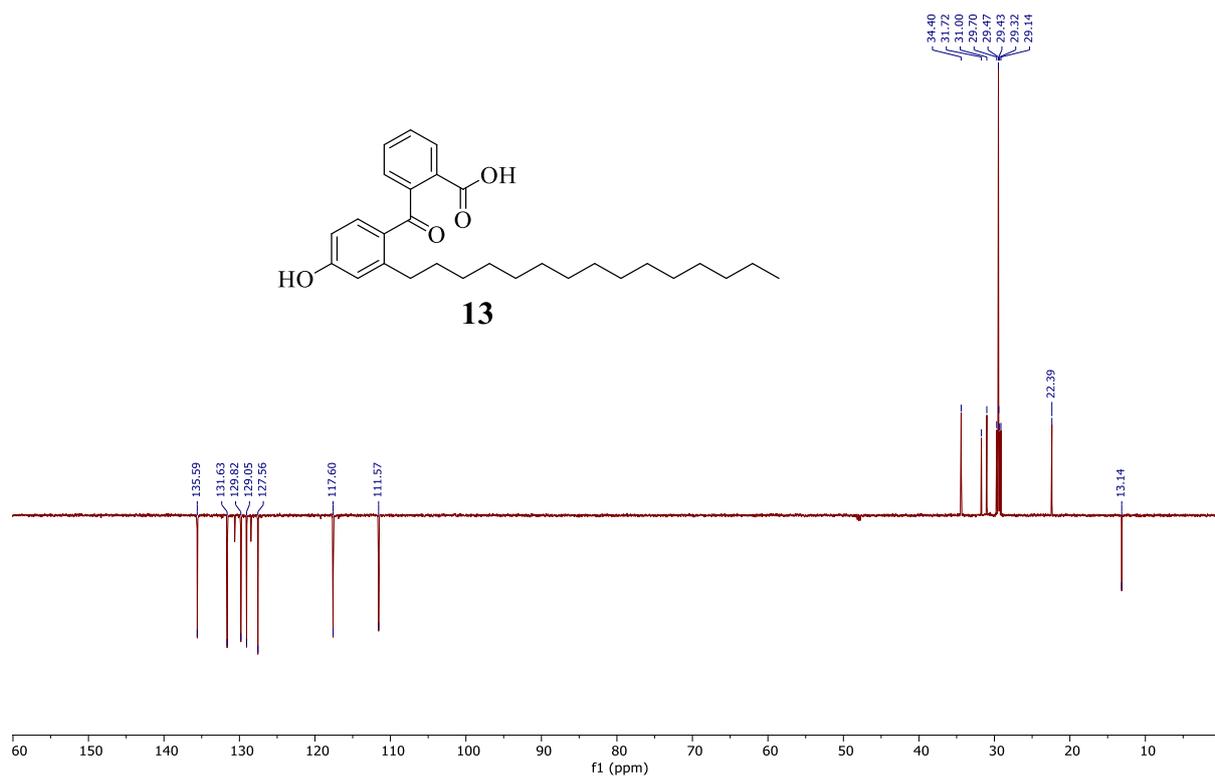


Figure 3: DEPT-135 NMR spectrum of 2-(4-hydroxy-2-pentadecylbenzoyl)benzoic acid (**13**).

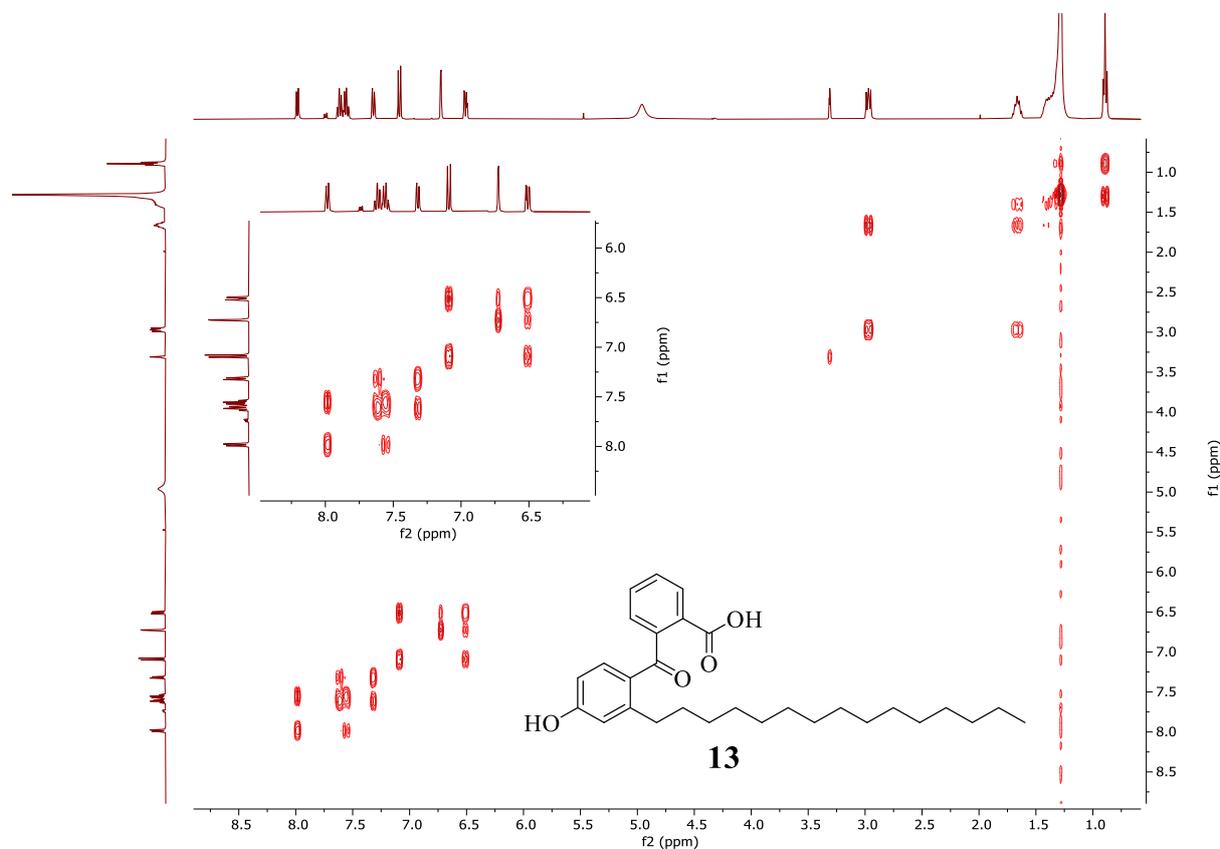


Figure 4: COSY NMR spectrum of 2-(4-hydroxy-2-pentadecylbenzoyl)benzoic acid (**13**).

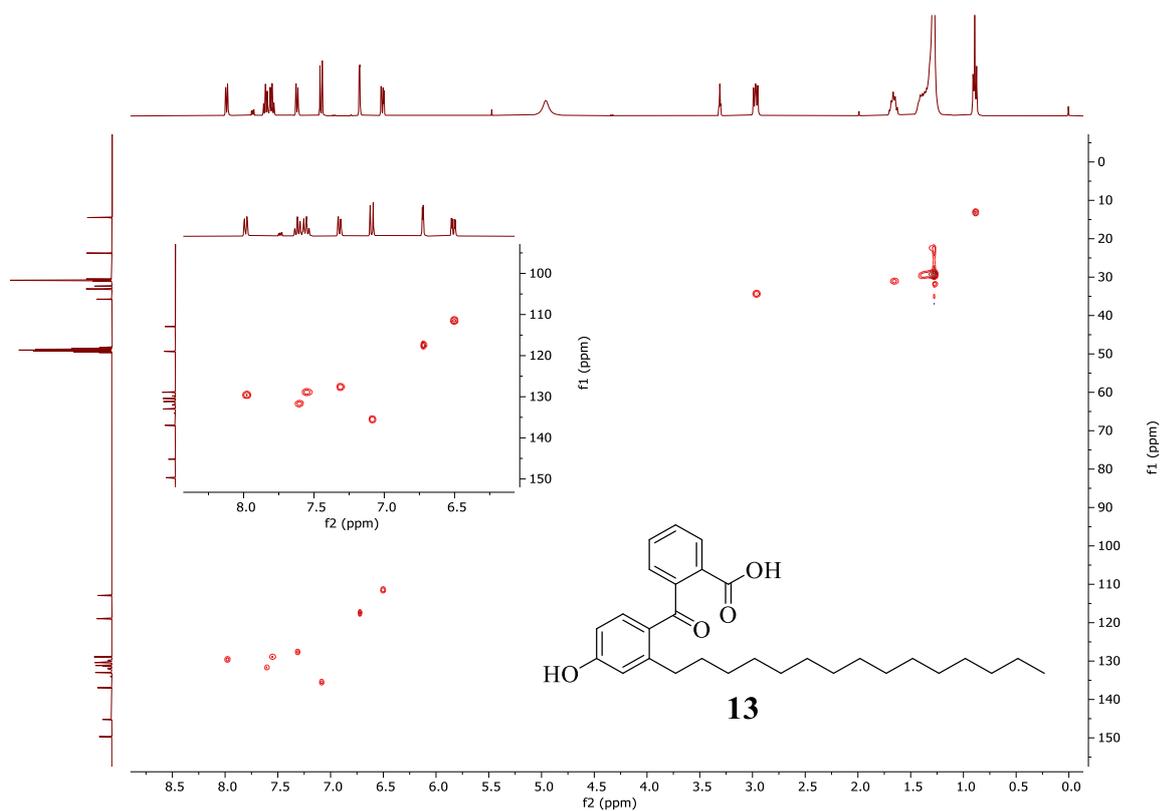


Figure 5: HSQC NMR spectrum of 2-(4-hydroxy-2-pentadecylbenzoyl)benzoic acid (**13**).

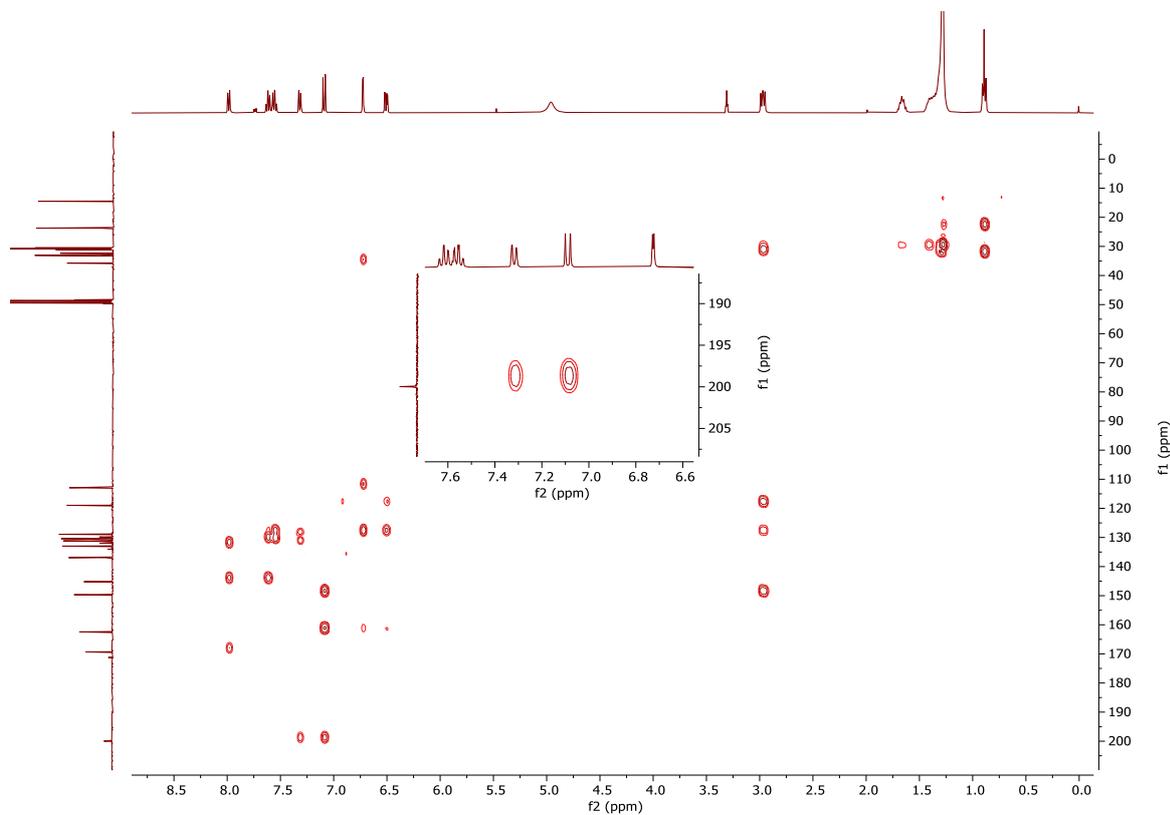


Figure 6: HMBC spectrum of 2-(4-hydroxy-2-pentadecylbenzoyl)benzoic acid (**13**).

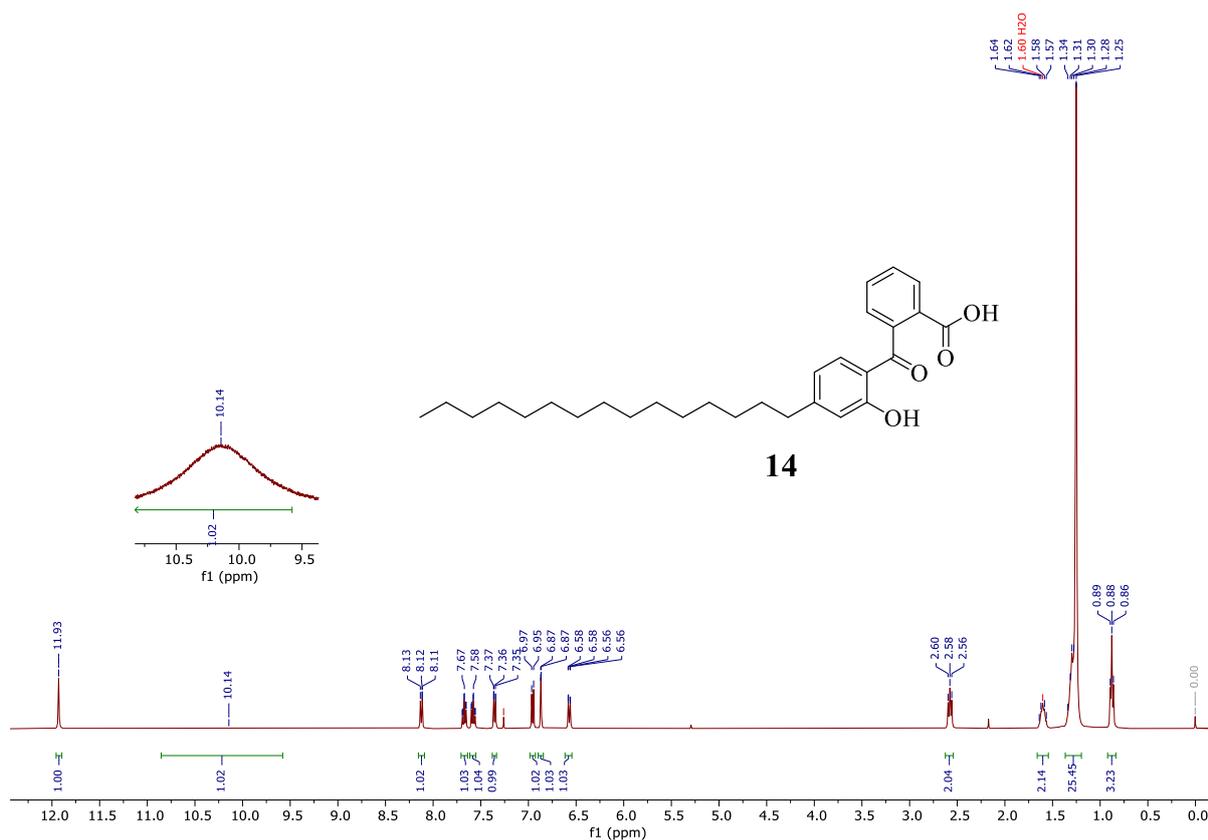


Figure 7: ¹H-NMR spectrum of 2-(2-hydroxy-4-pentadecylbenzoyl)benzoic acid (**14**).

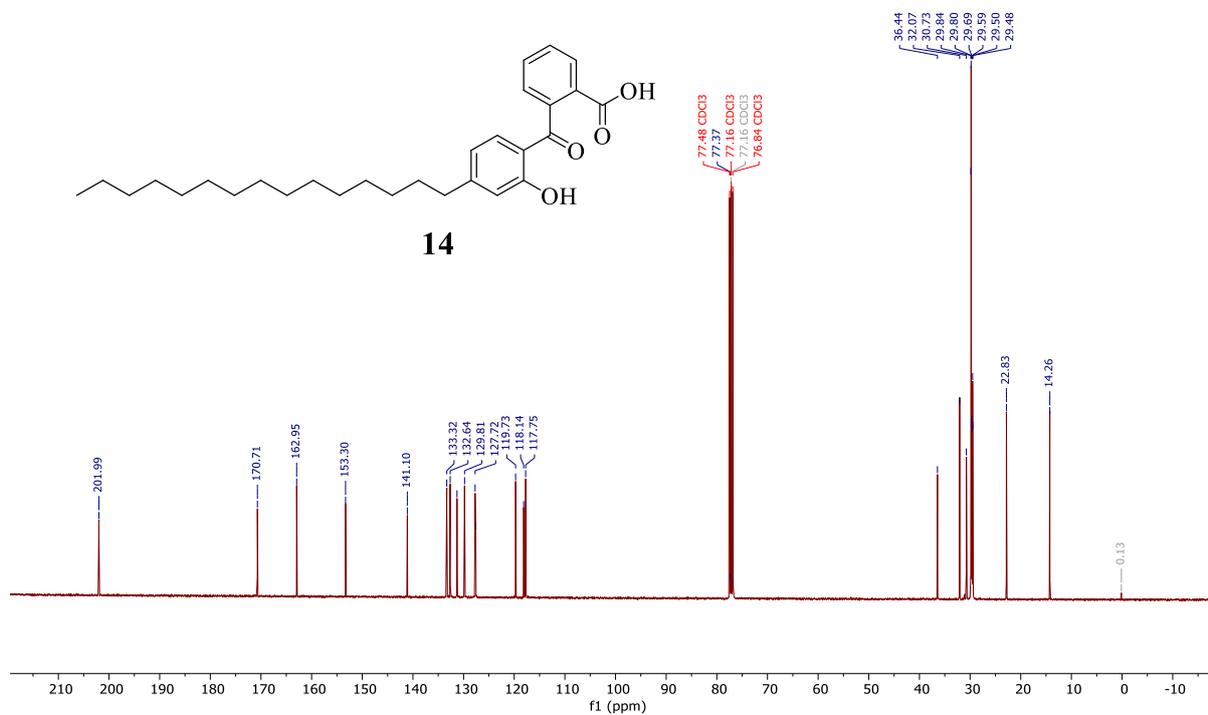


Figure 8: ¹³C-NMR spectrum of 2-(2-hydroxy-4-pentadecylbenzoyl)benzoic acid (**14**).

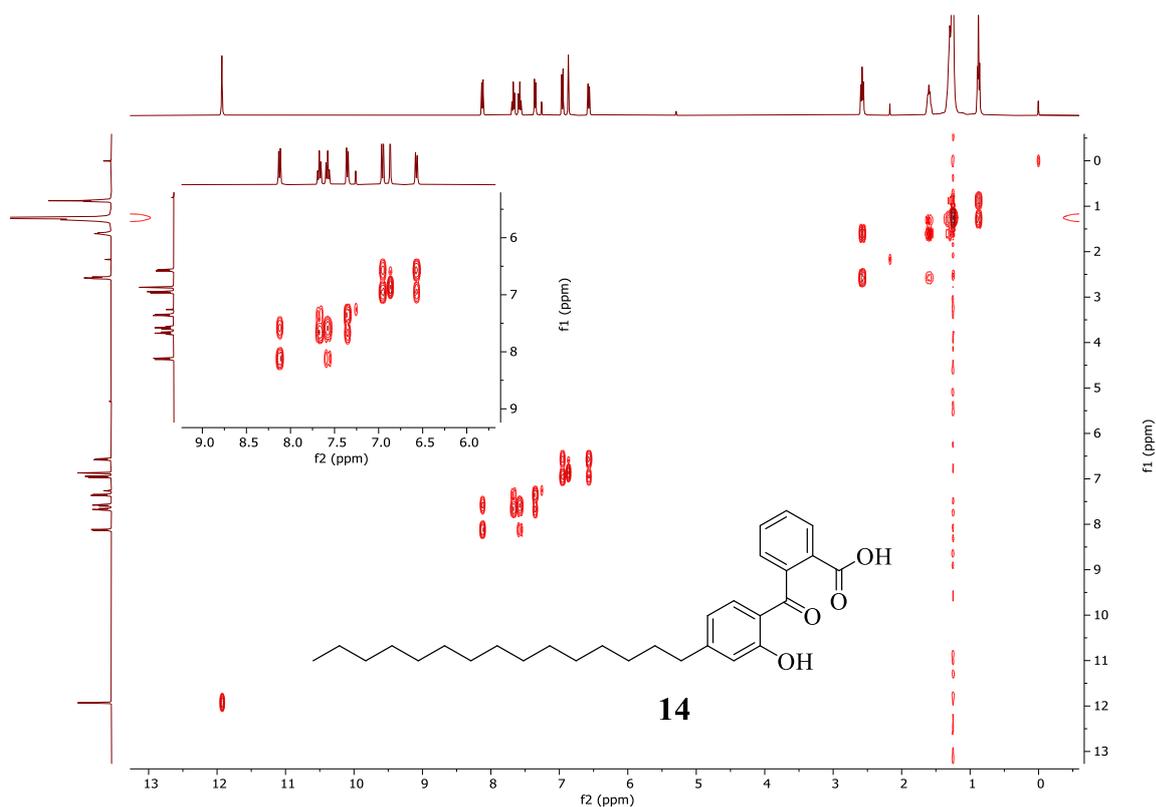


Figure 9: COSY NMR spectrum of 2-(2-hydroxy-4-pentadecylbenzoyl)benzoic acid (**14**).

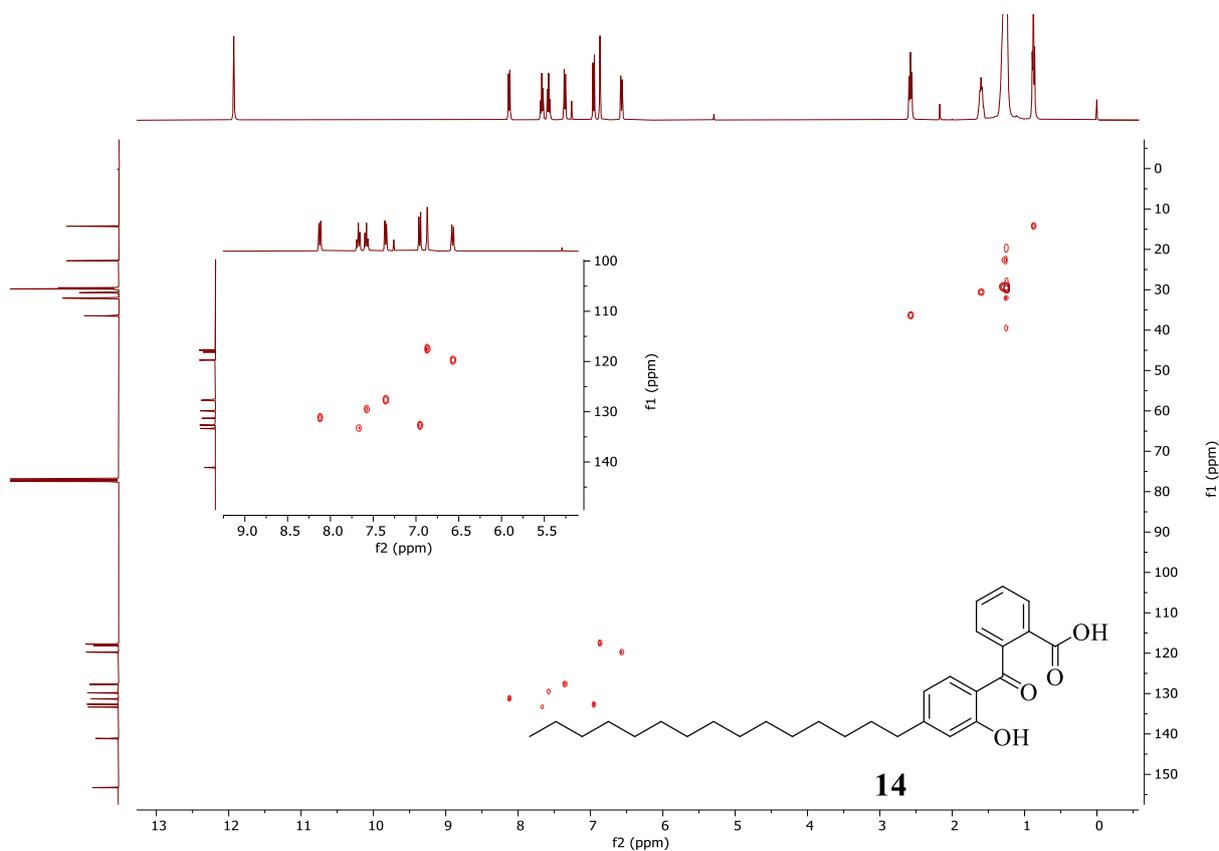


Figure 10: HSQC NMR spectrum of 2-(2-hydroxy-4-pentadecylbenzoyl)benzoic acid (**14**).

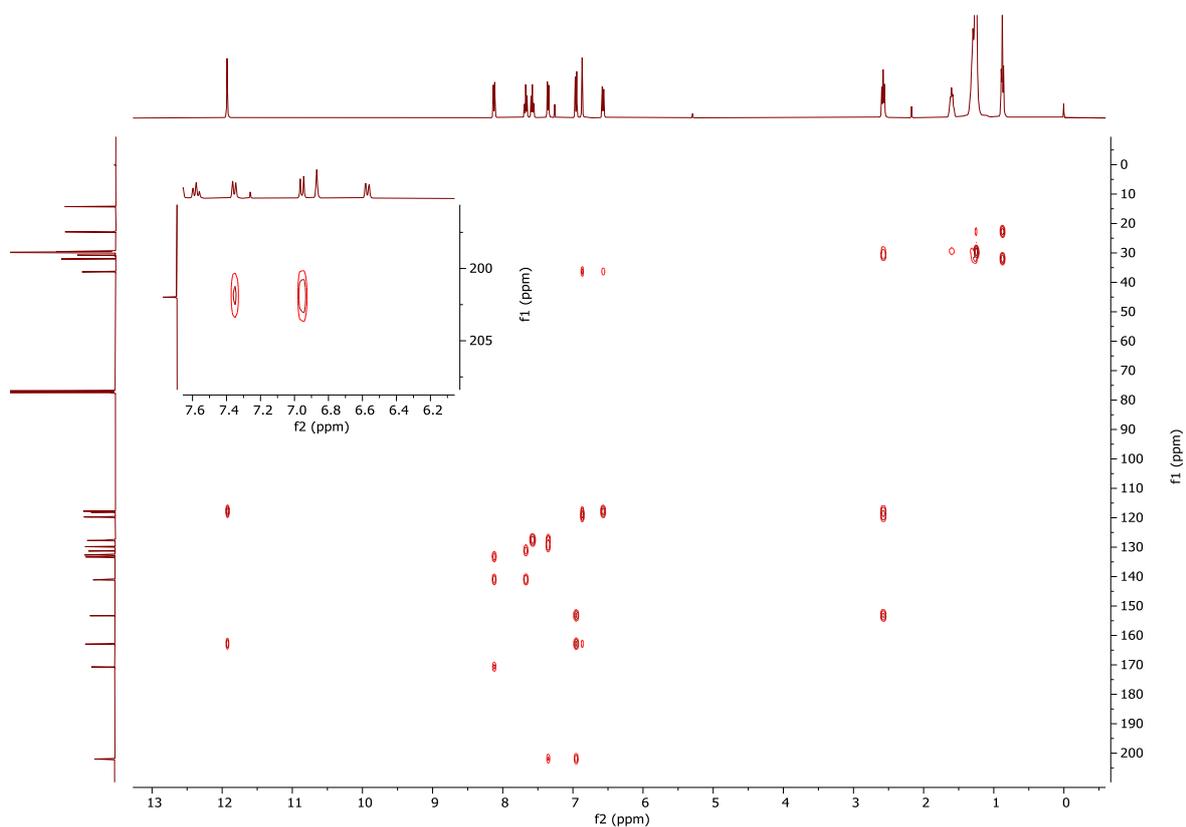


Figure 11: HMBC spectrum of 2-(2-hydroxy-4-pentadecylbenzoyl)benzoic acid (**14**).

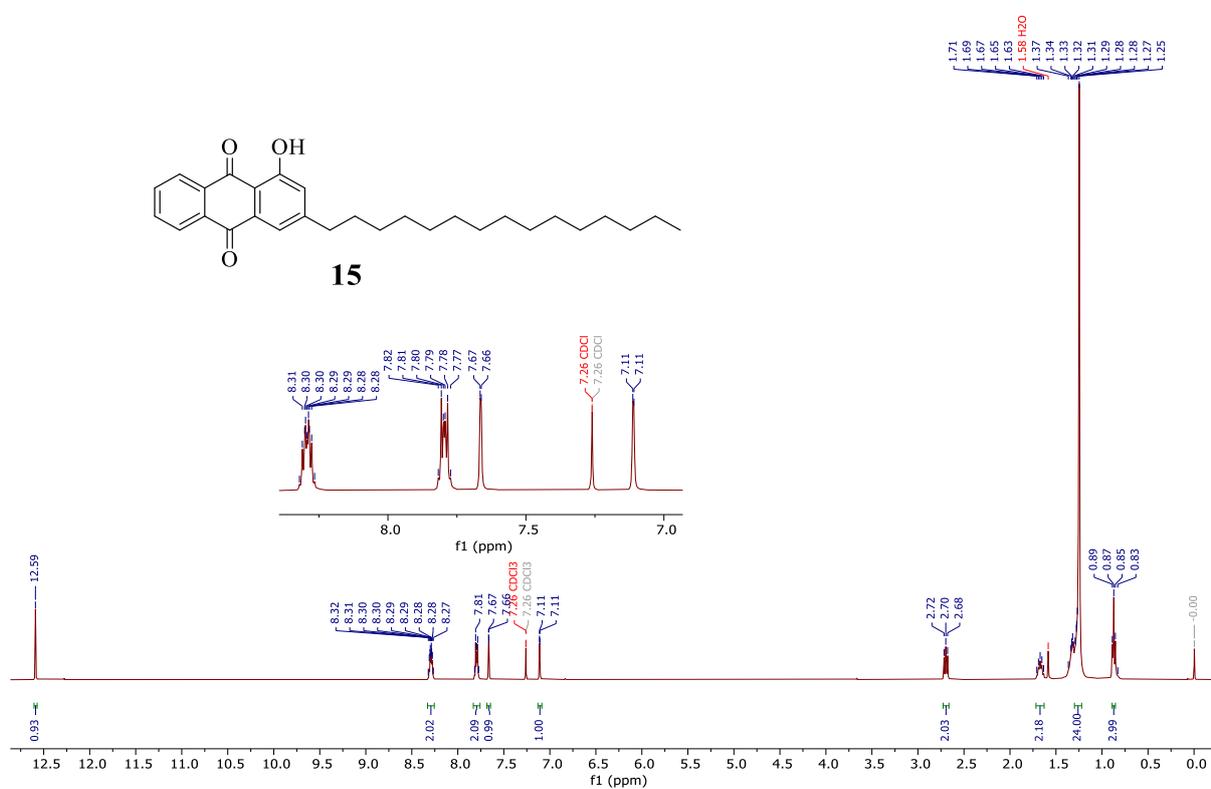


Figure 12: ¹H-NMR spectrum of 1-hydroxy-3-pentadecylanthracene-9,10-dione (**15**).

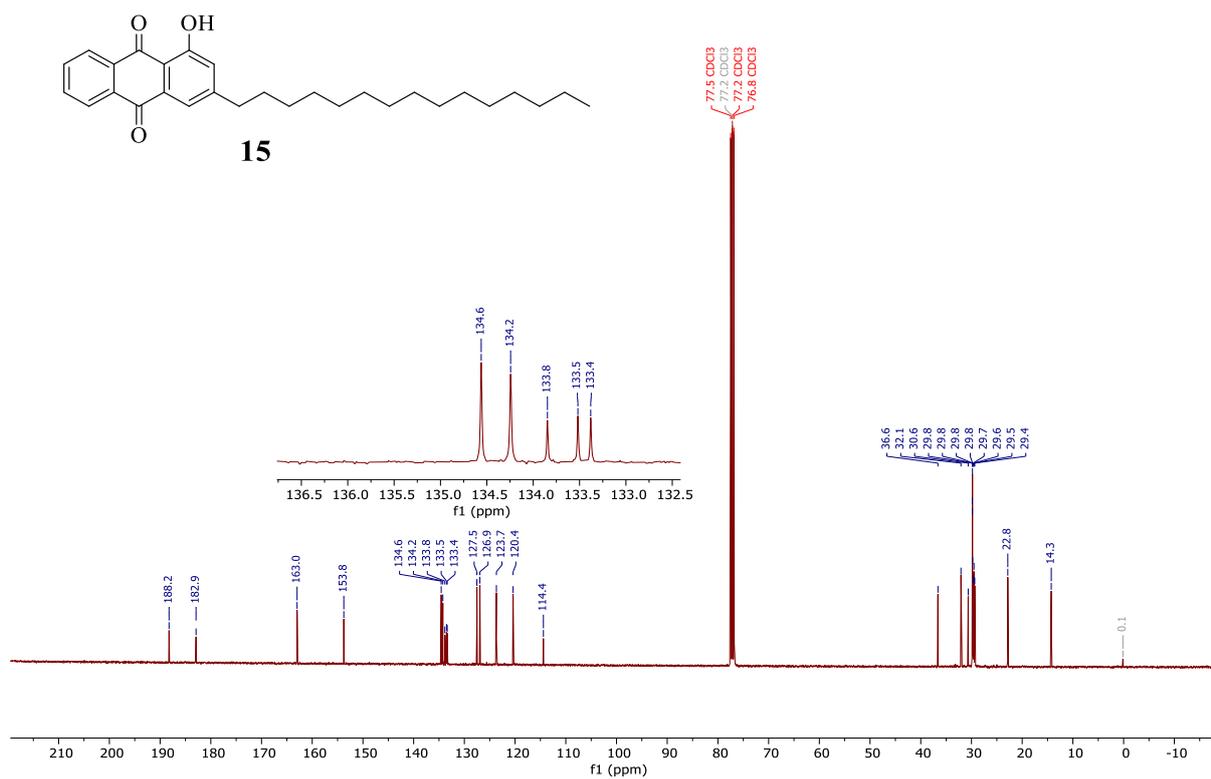


Figure 13: ¹³C-NMR spectrum of 1-hydroxy-3-pentadecylanthracene-9,10-dione (**15**).

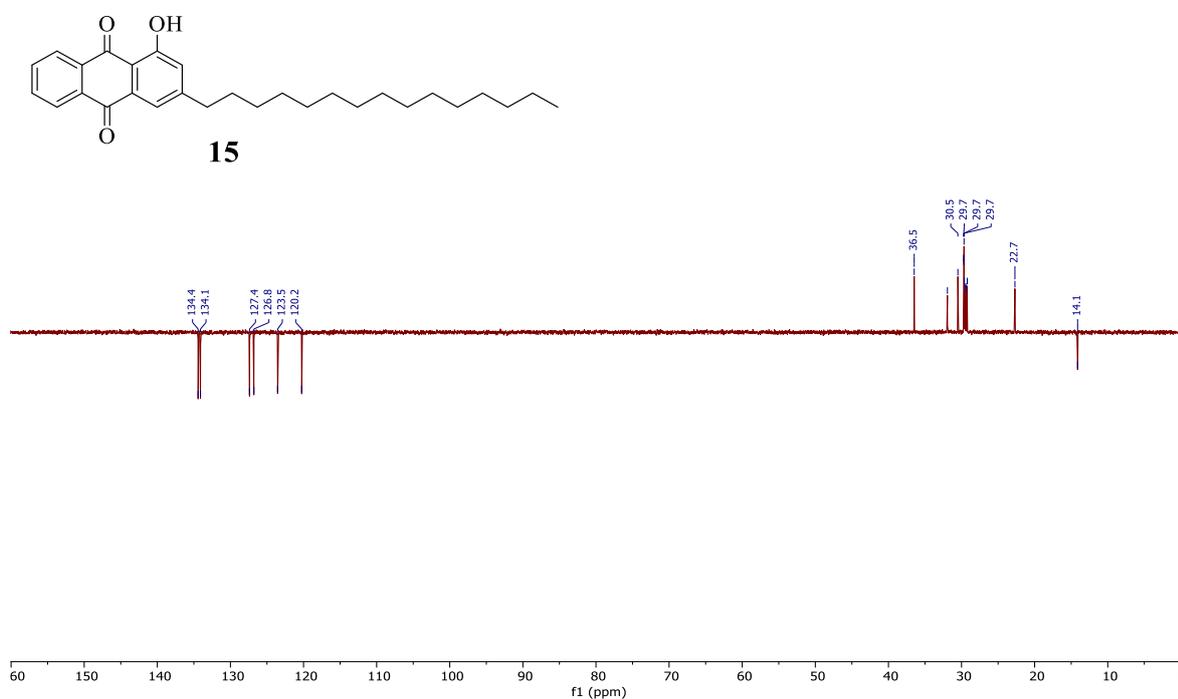


Figure 14: DEPT-135 NMR spectrum of 1-hydroxy-3-pentadecylanthracene-9,10-dione (**15**).

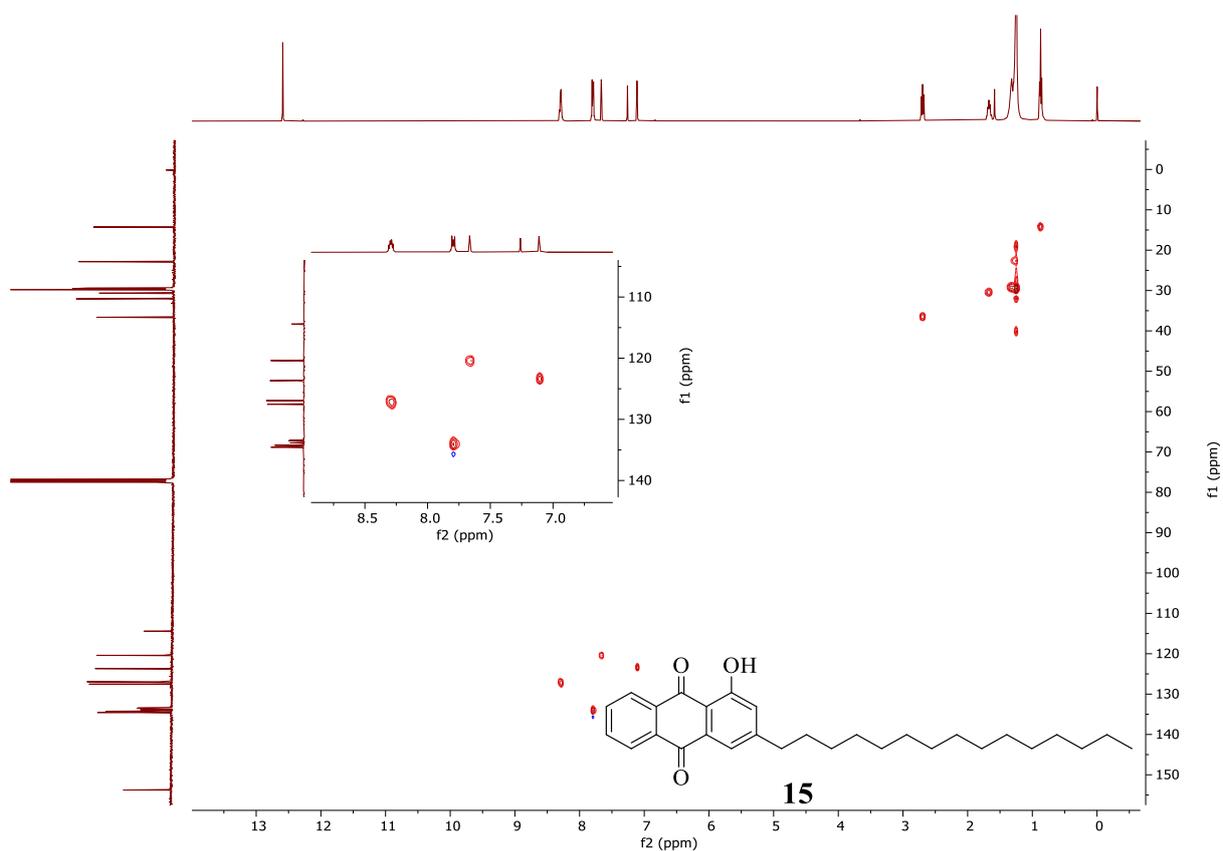


Figure 15: HSQC NMR spectrum of 1-hydroxy-3-pentadecylantracene-9,10-dione (**15**).

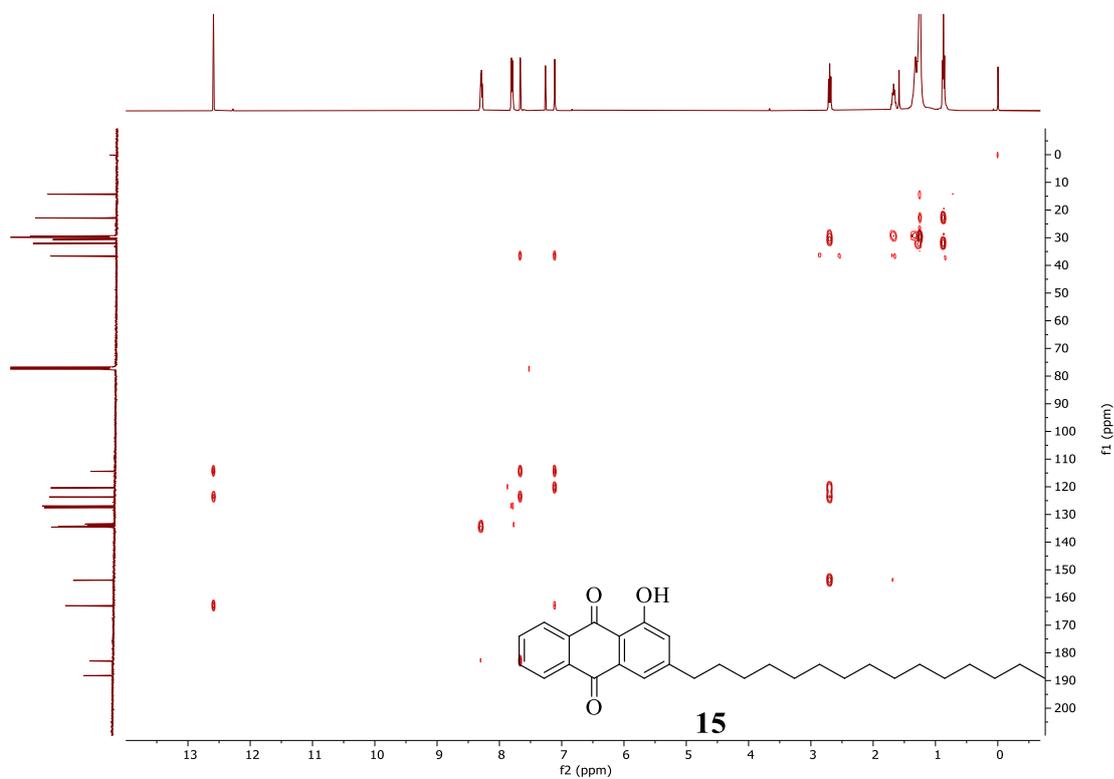


Figure 16: HMBC NMR spectrum of 1-hydroxy-3-pentadecylantracene-9,10-dione (**15**).

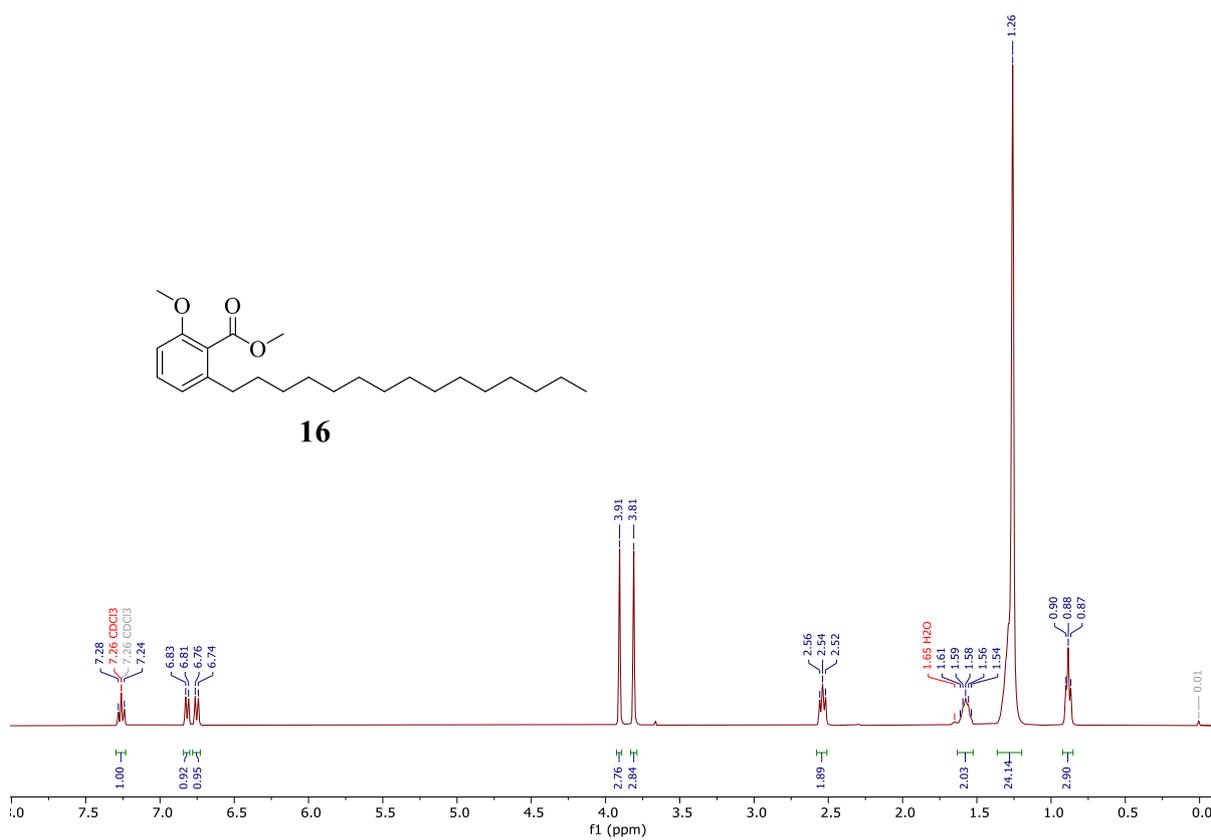


Figure 17: ¹H-NMR spectrum of methyl 2-methoxy-6-pentadecylbenzoate (16).

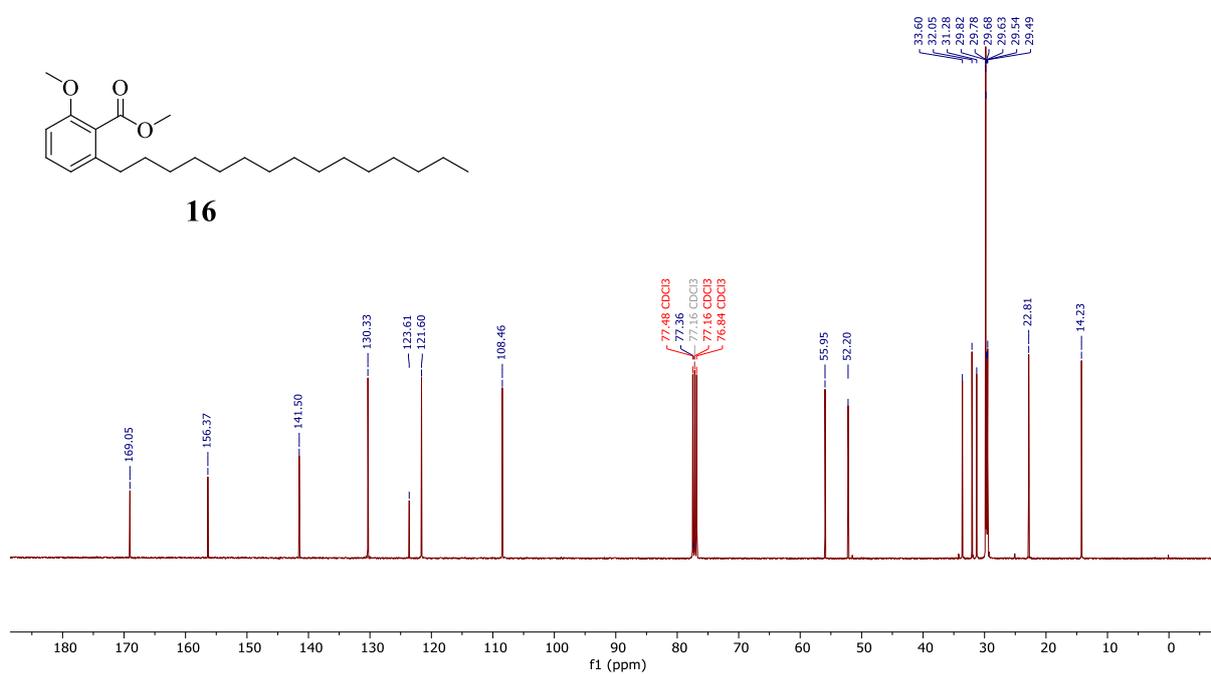


Figure 18: ¹³C-NMR spectrum of methyl 2-methoxy-6-pentadecylbenzoate (16).

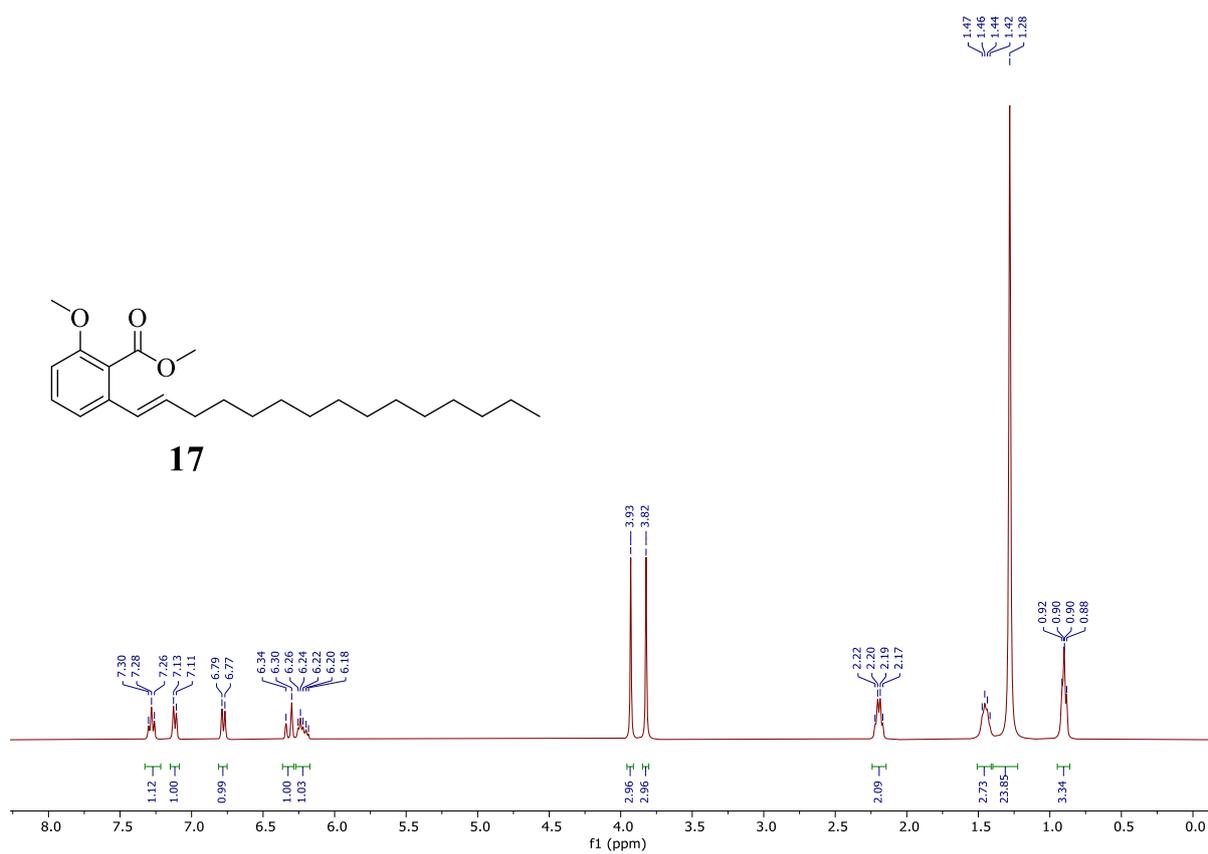


Figure 19: ¹H-NMR spectrum of methyl 2-methoxy-6-(pentadec-1-en-1-yl)benzoate (**17**).

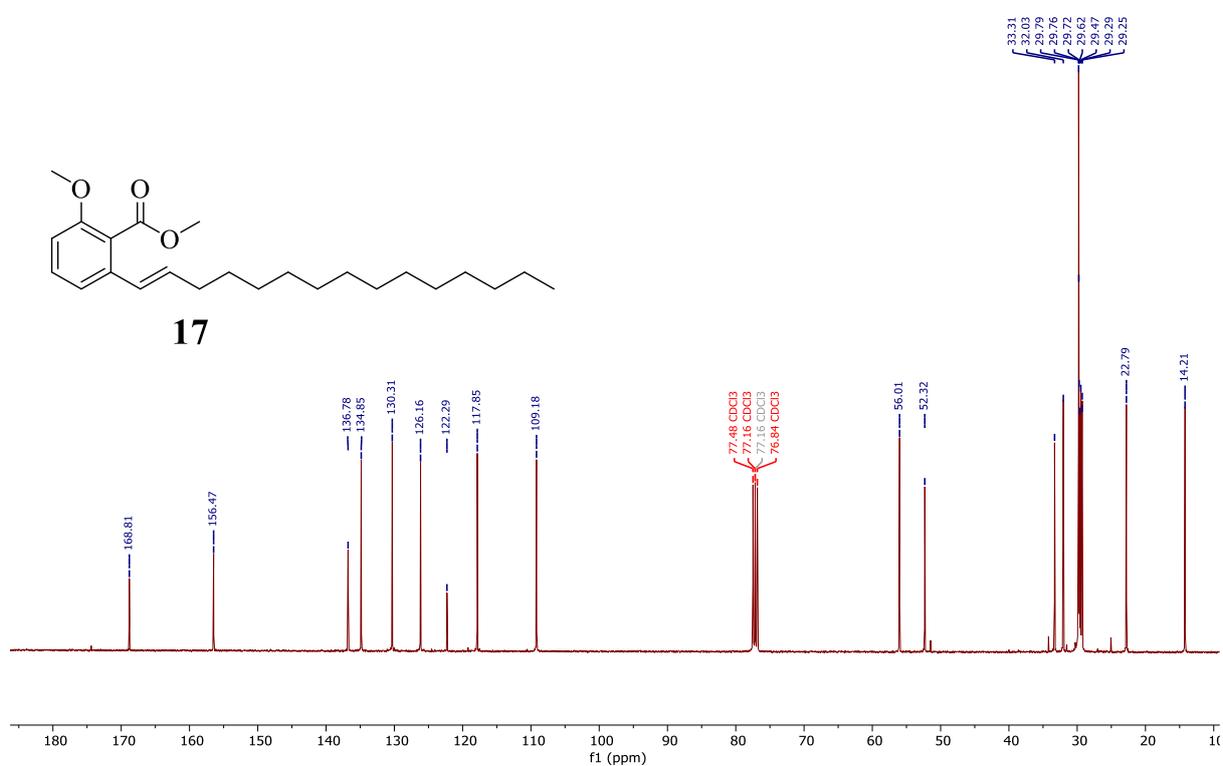


Figure 20: ¹³C-NMR spectrum of methyl 2-methoxy-6-(pentadec-1-en-1-yl)benzoate (**17**).

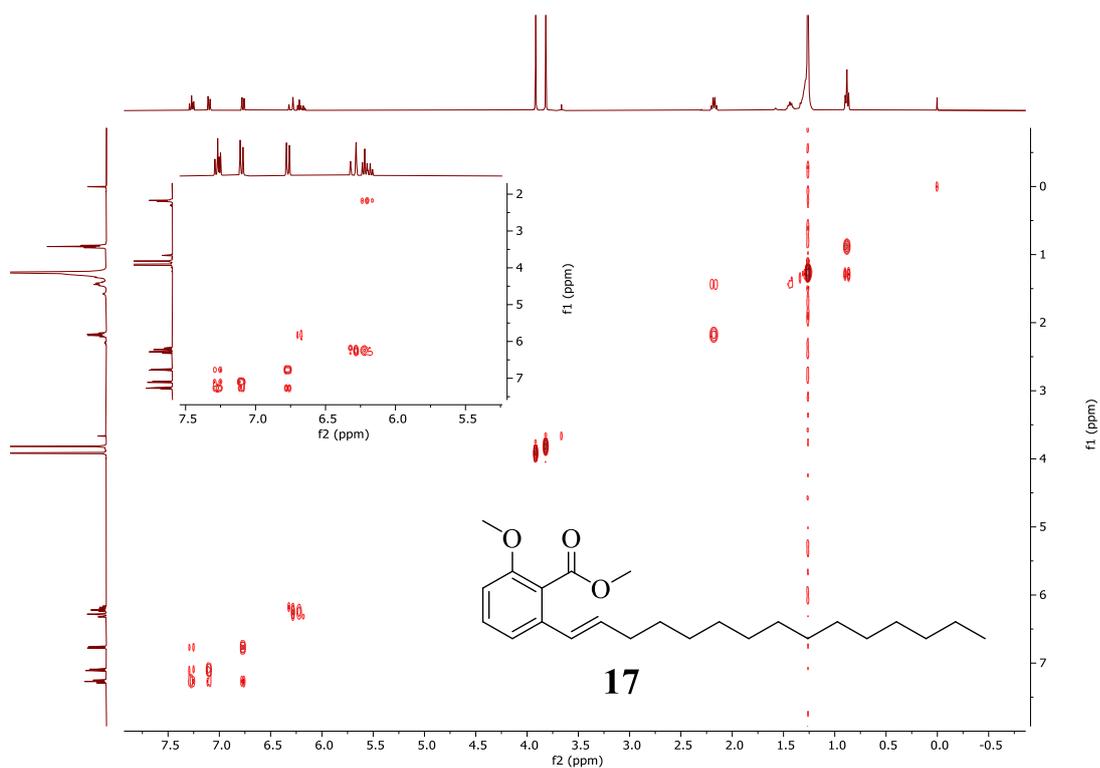


Figure 21: COSY NMR spectrum of methyl 2-methoxy-6-(pentadec-1-en-1-yl)benzoate (**17**).

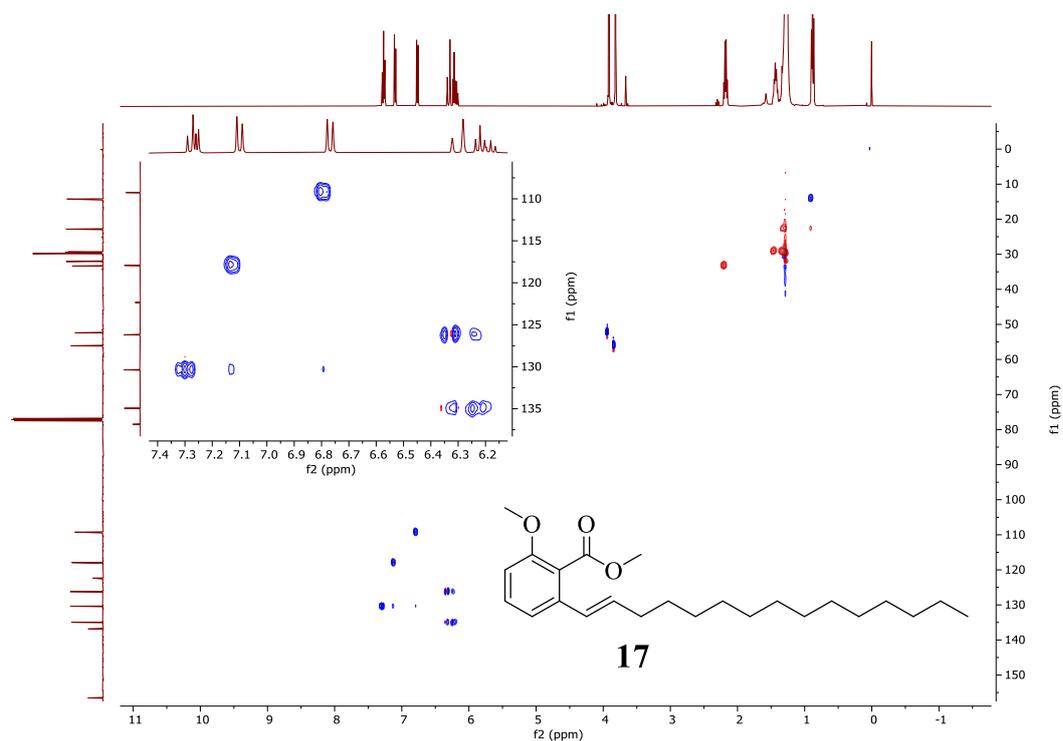


Figure 22: HSQC NMR spectrum of methyl 2-methoxy-6-(pentadec-1-en-1-yl)benzoate (**17**).

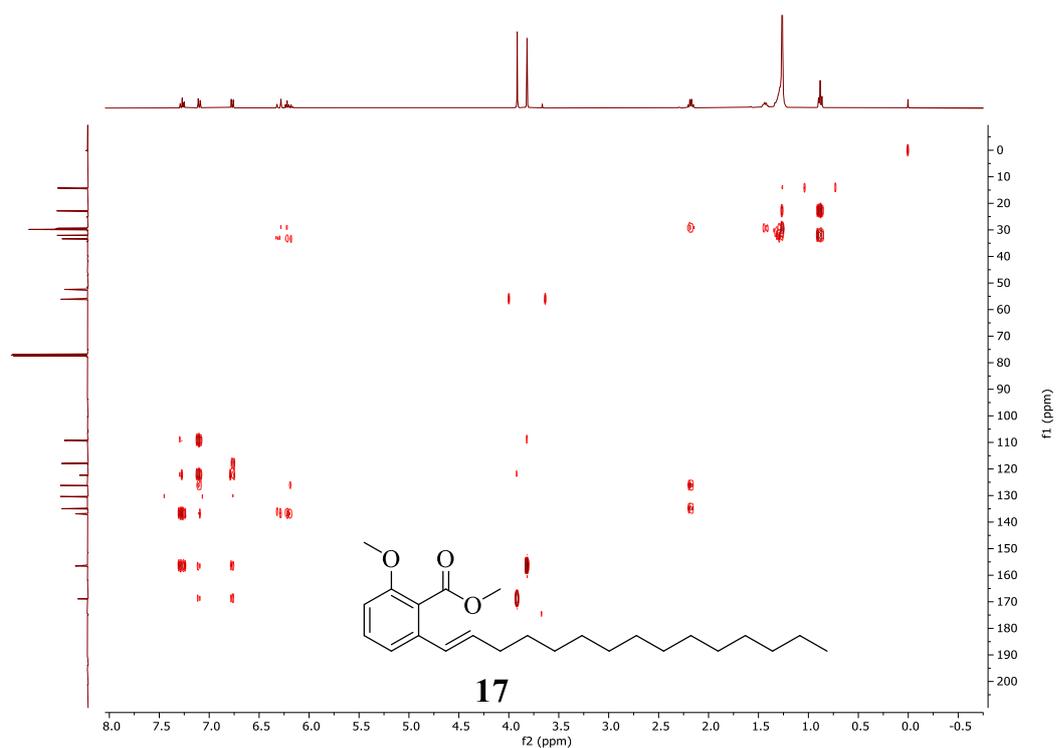


Figure 23: HMBC NMR spectrum of methyl 2-methoxy-6-(pentadec-1-en-1-yl)benzoate (**17**).

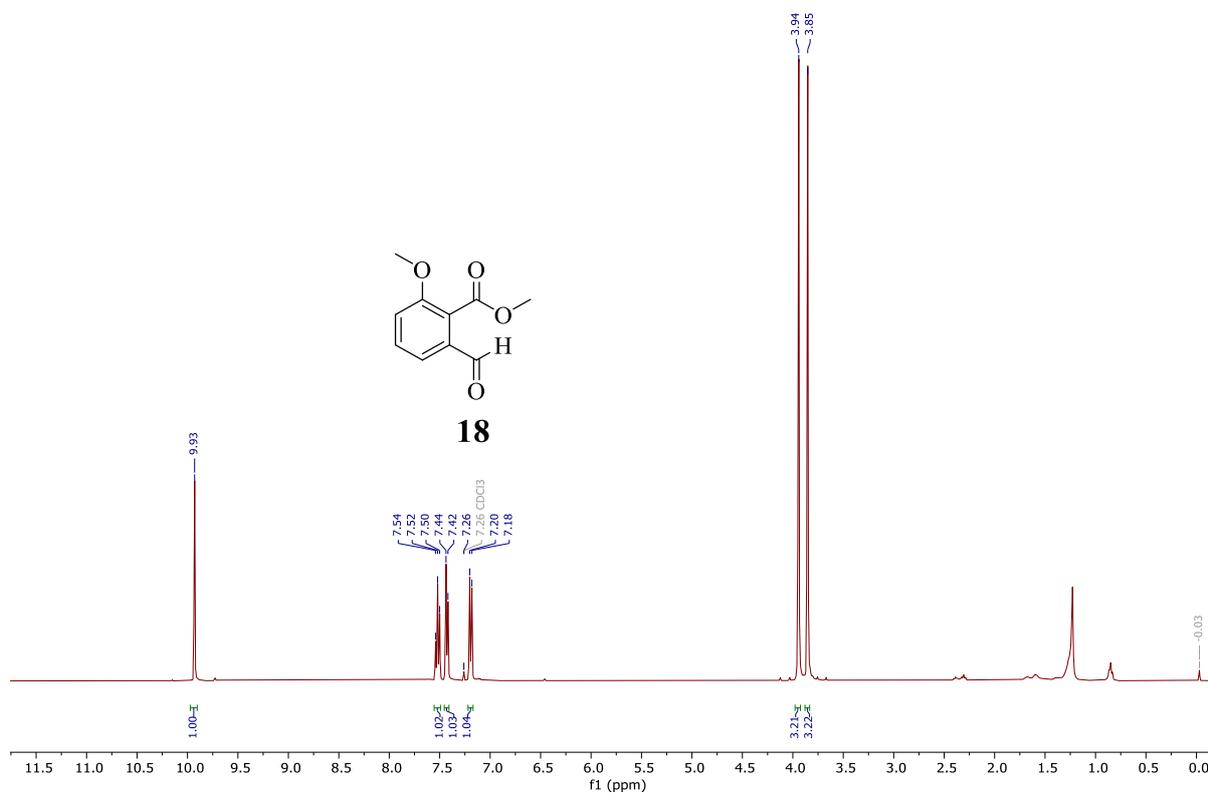


Figure 24: ¹H-NMR spectrum of methyl 2-formyl-6-methoxybenzoate (**18**).

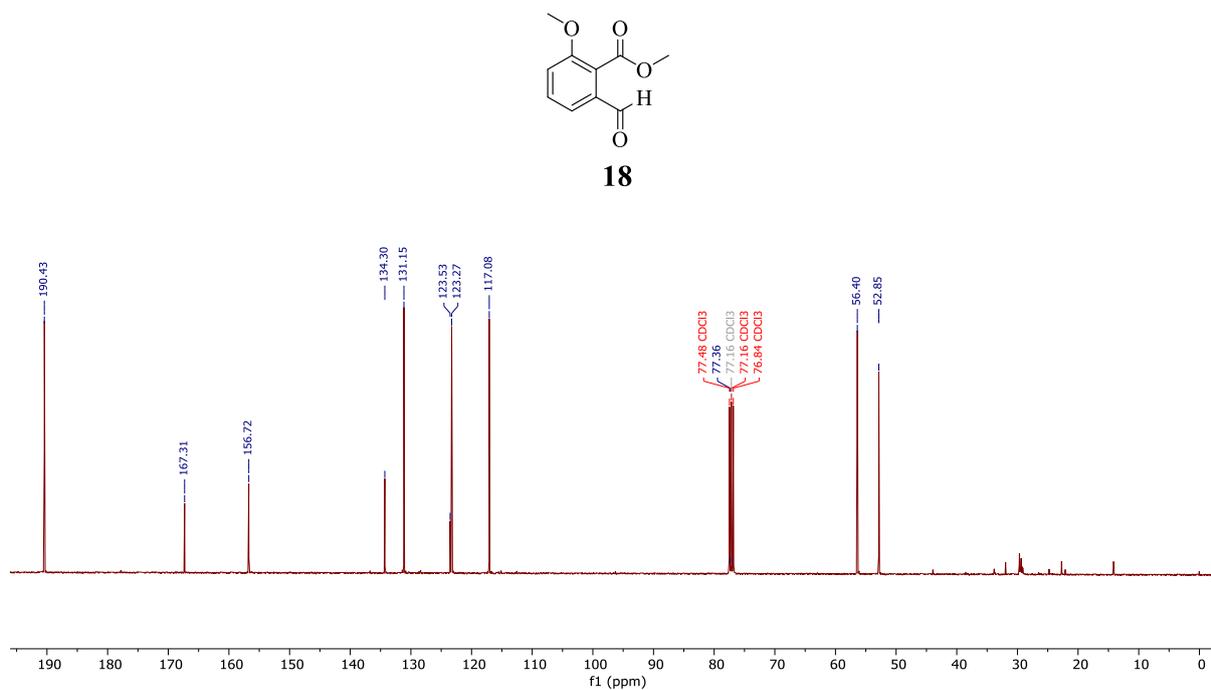


Figure 25: ¹³C-NMR spectrum of methyl 2-formyl-6-methoxybenzoate (18).

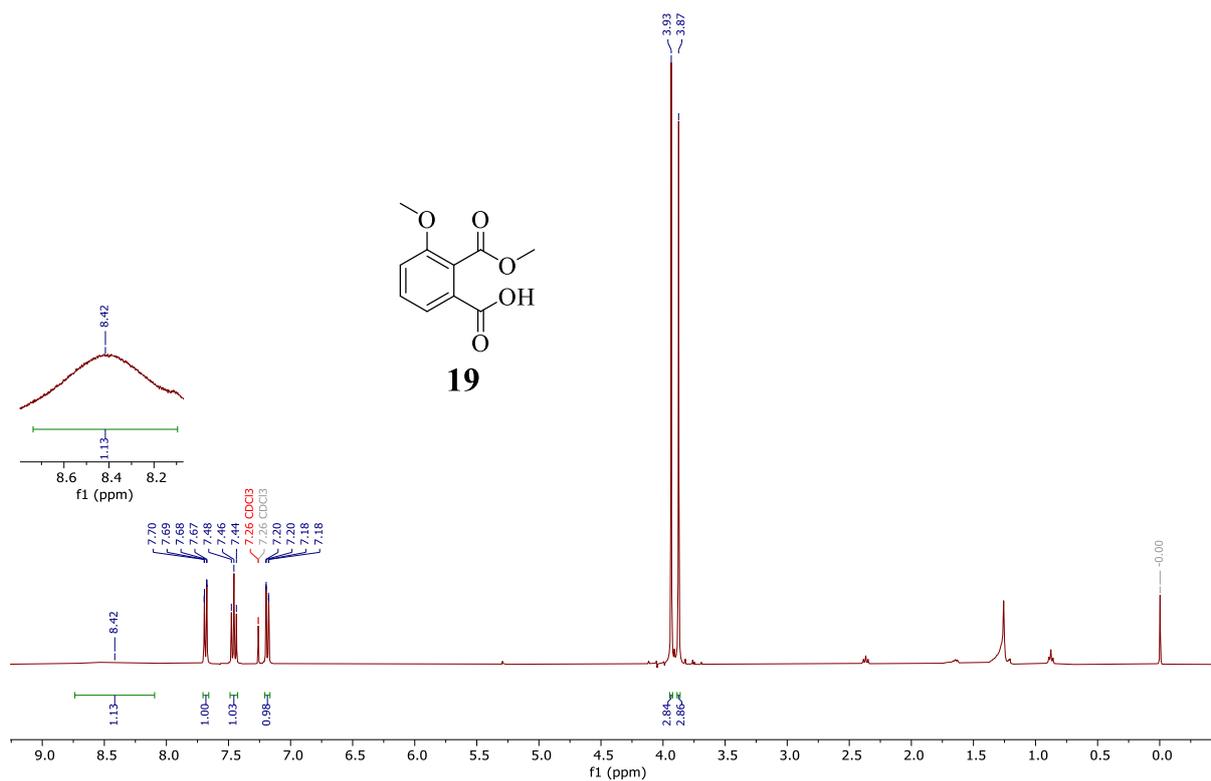


Figure 26: ¹H-NMR spectrum of 3-methoxy-2-(methoxycarbonyl)benzoic acid (19).

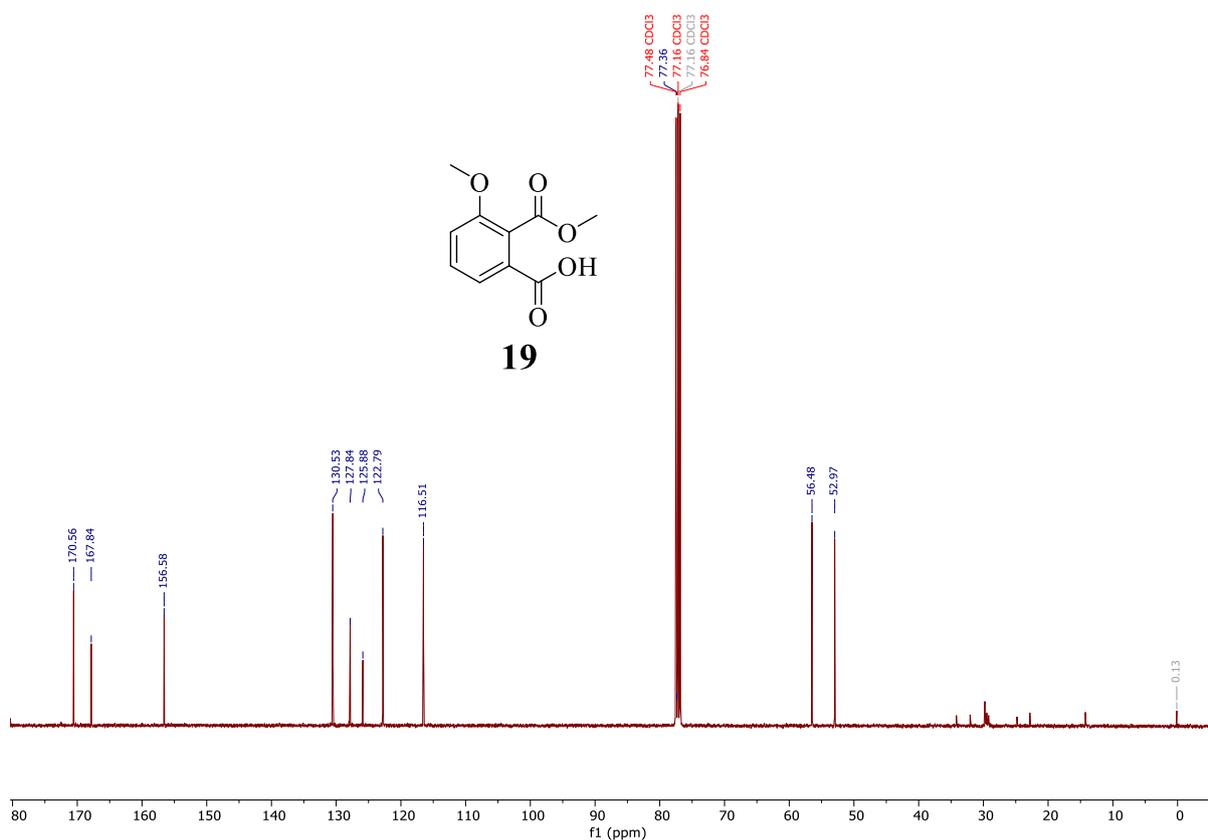


Figure 27: ¹³C-NMR spectrum of 3-methoxy-2-(methoxycarbonyl)benzoic acid (**19**).

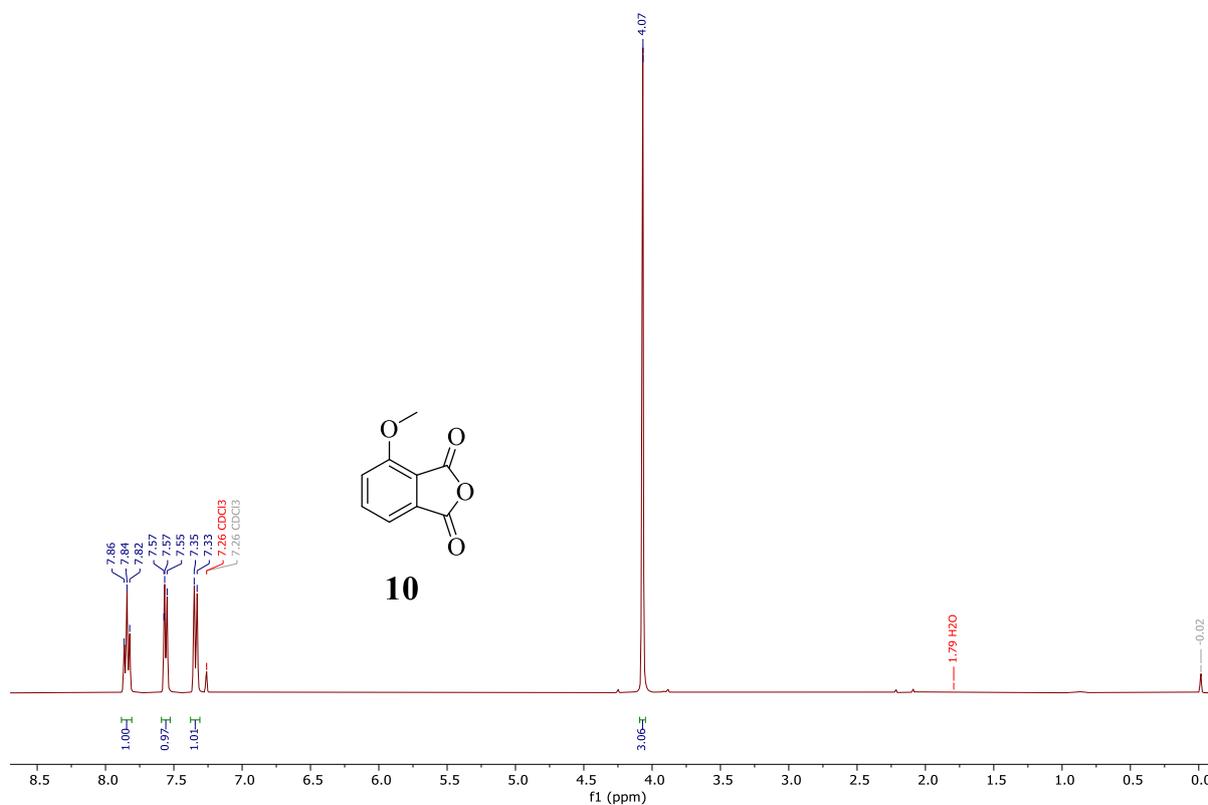


Figure 28: ¹H-NMR spectrum of 3-methoxyphthalic anhydride (**10**).

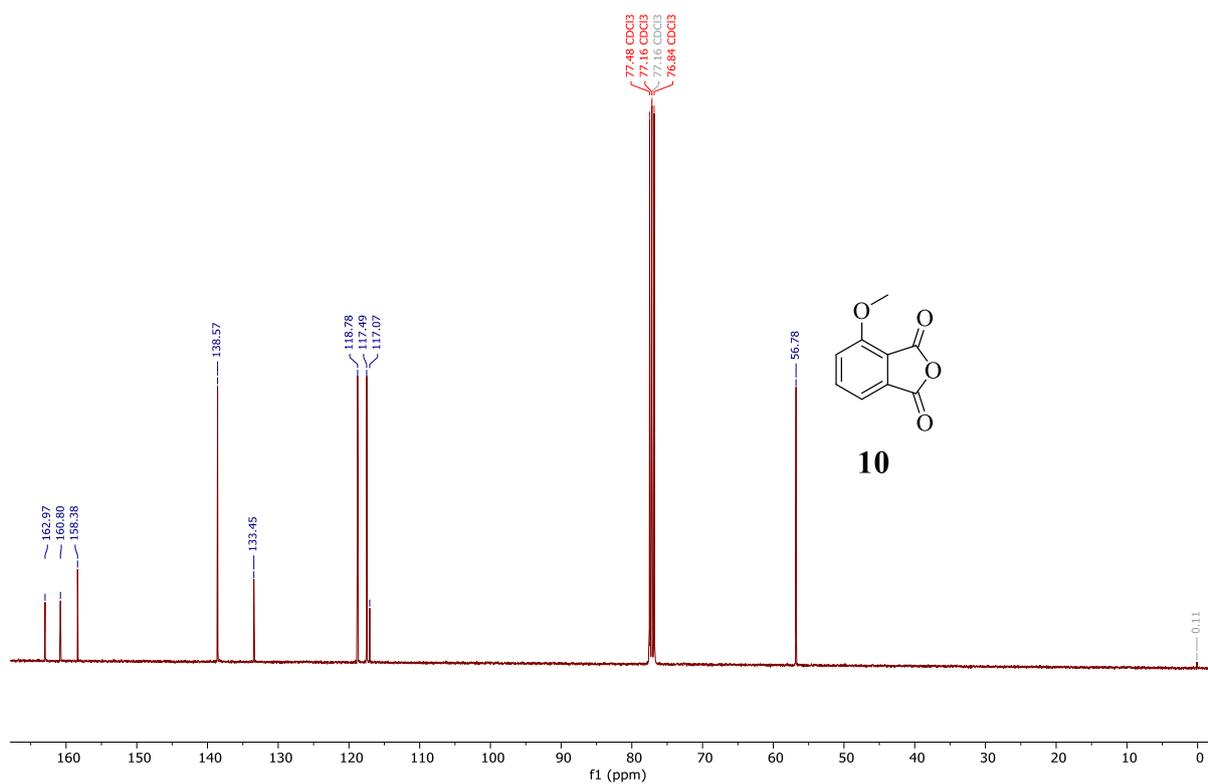


Figure 29: $^{13}\text{C-NMR}$ spectrum of 3-methoxy phthalic anhydride (10).

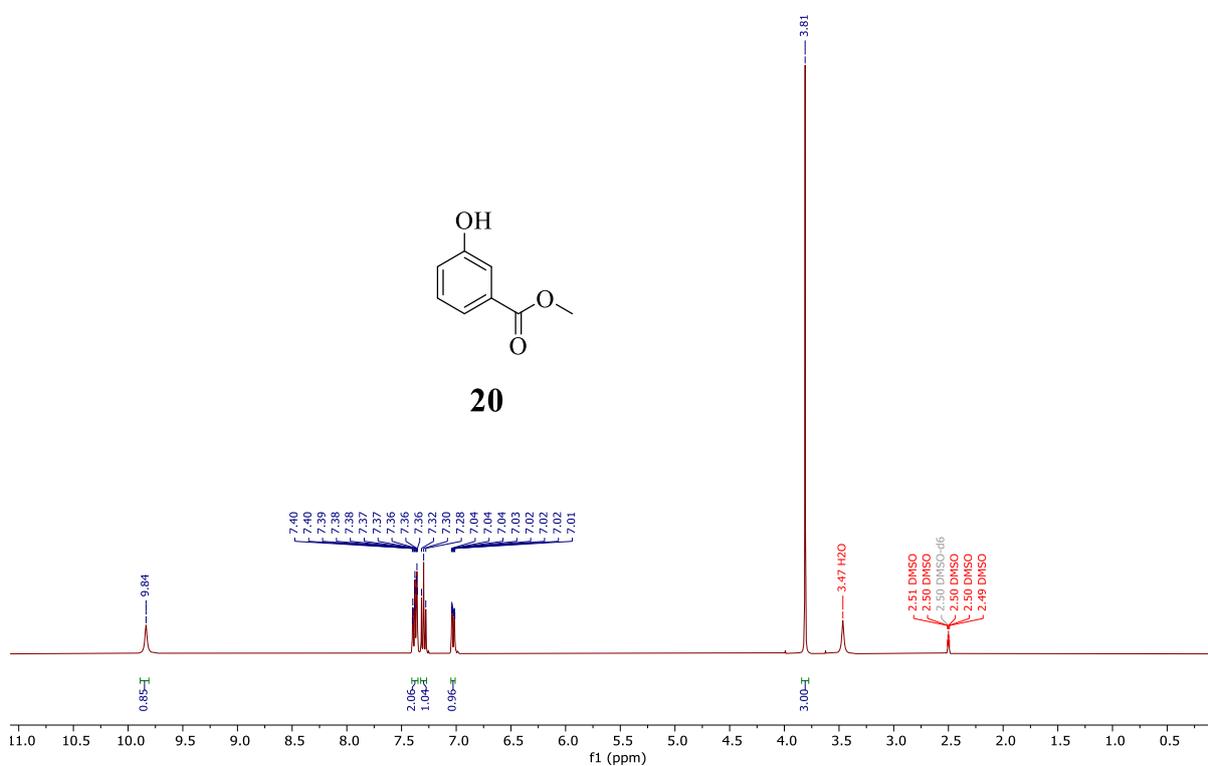


Figure 30: $^1\text{H-NMR}$ spectrum of methyl 3-hydroxybenzoate (20).

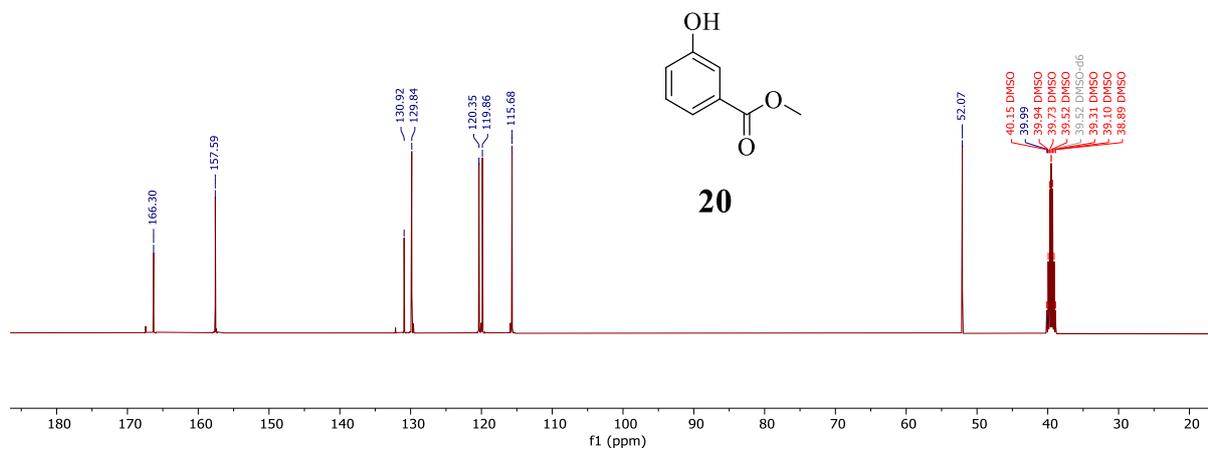


Figure 31: ¹³C-NMR spectrum of methyl 3-hydroxybenzoate (**20**).

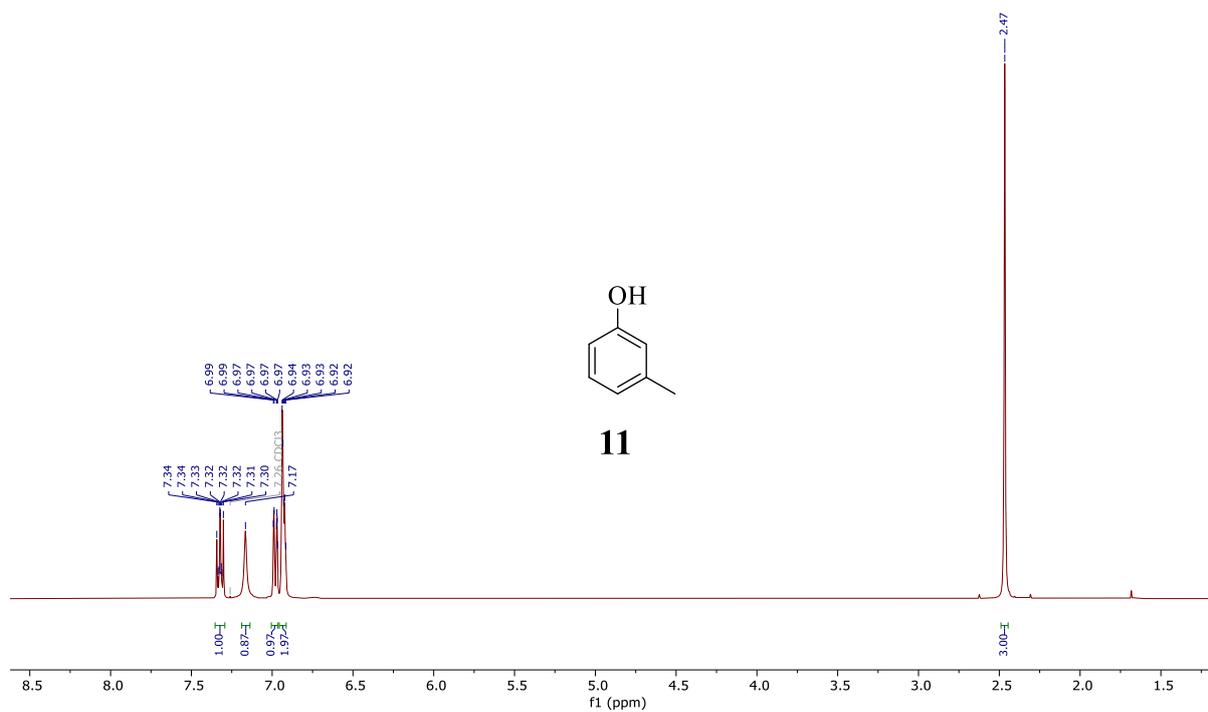


Figure 32: ¹H-NMR spectrum of 3-methylphenol (**11**).

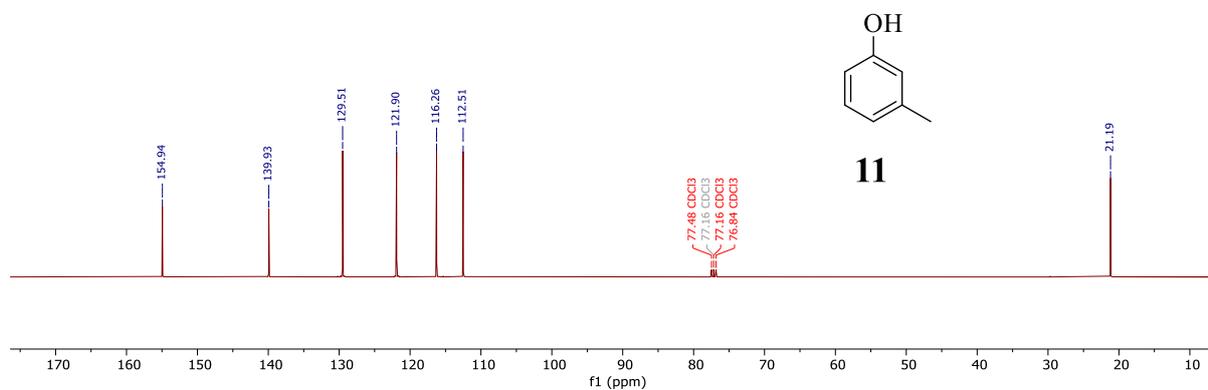


Figure 33: ¹³C-NMR spectrum of 3-methylphenol **11**.

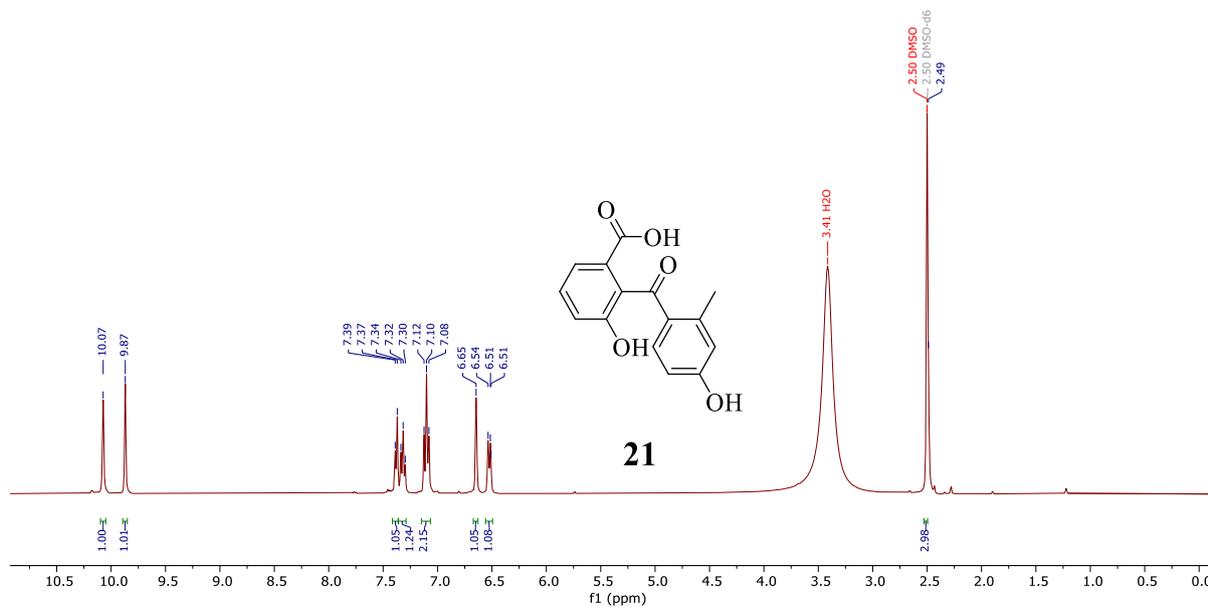


Figure 34: ¹H-NMR spectrum of 3-hydroxy-2-(4-hydroxy-2-methylbenzoyl)benzoic acid (**21**).

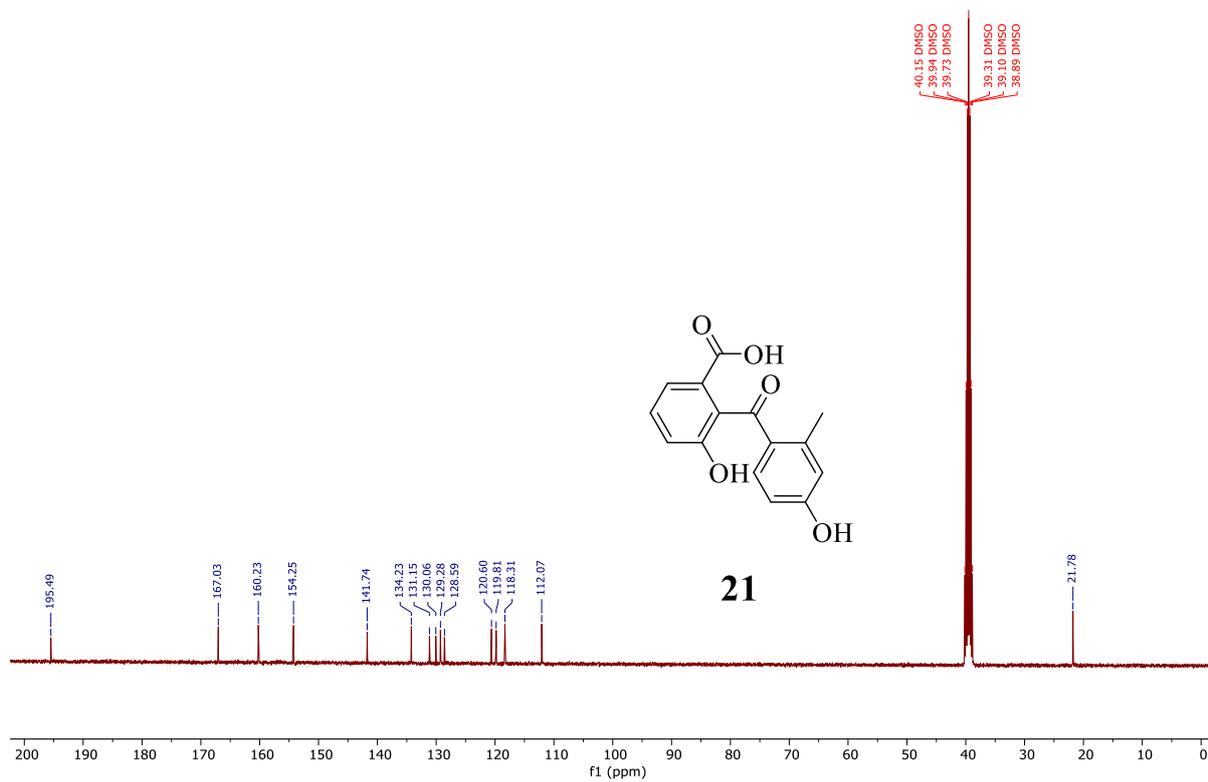


Figure 35: ^{13}C -NMR spectrum of 3-hydroxy-2-(4-hydroxy-2-methylbenzoyl)benzoic acid (**21**).

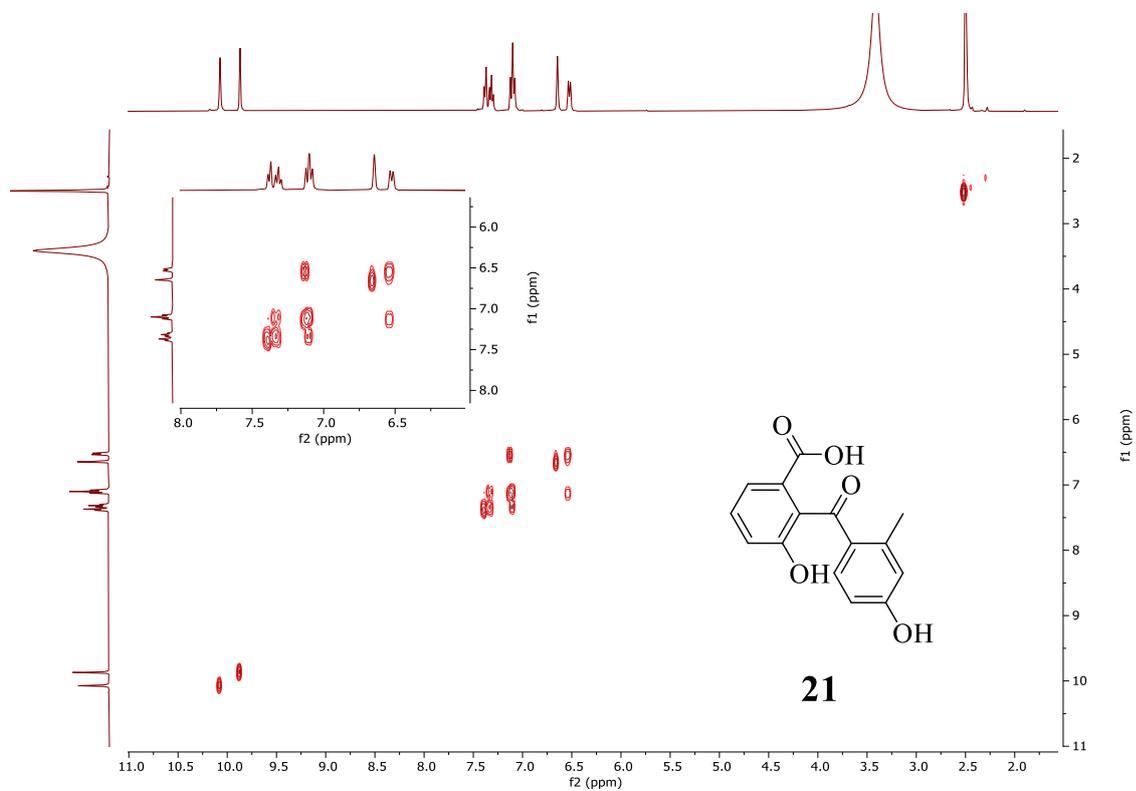


Figure 36: COSY NMR spectrum of 3-hydroxy-2-(4-hydroxy-2-methylbenzoyl)benzoic acid (**21**).

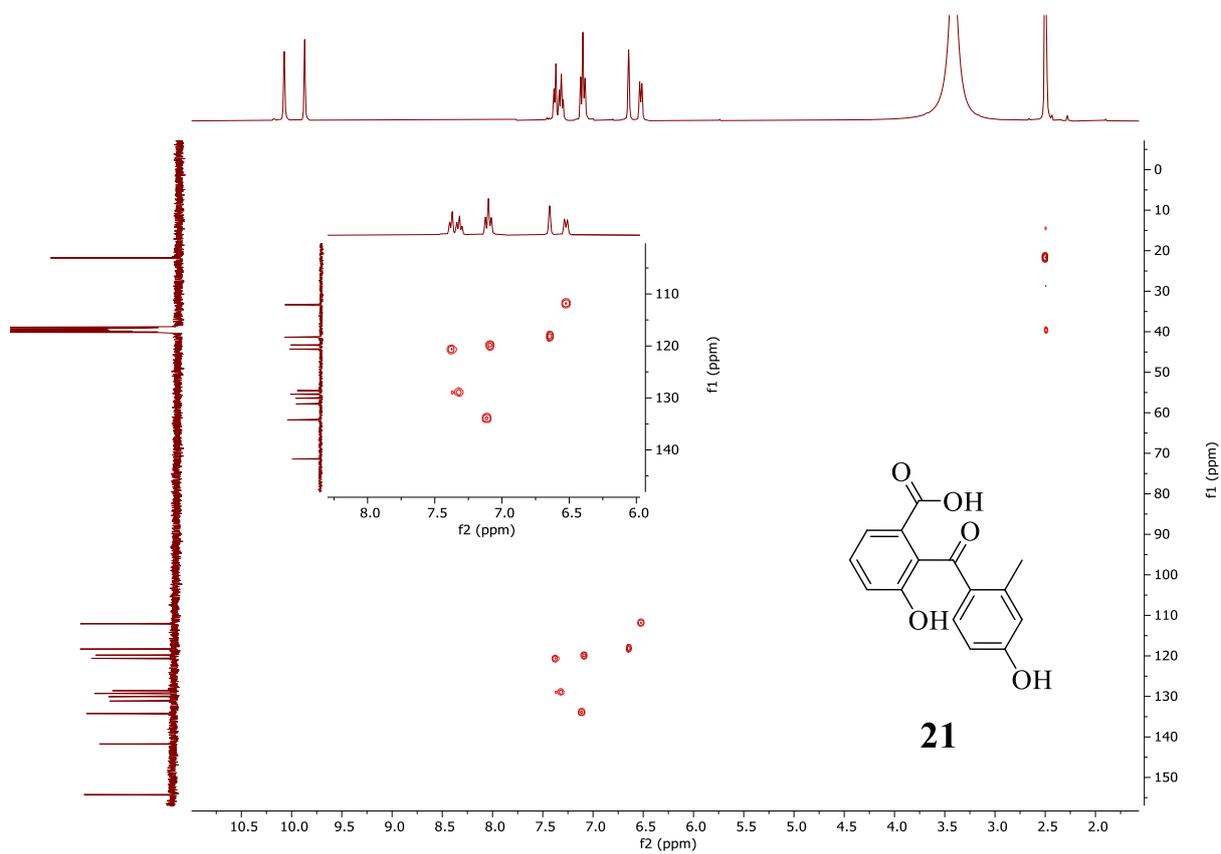


Figure 37: HSQC NMR spectrum of 3-hydroxy-2-(4-hydroxy-2-methylbenzoyl)benzoic acid (21).

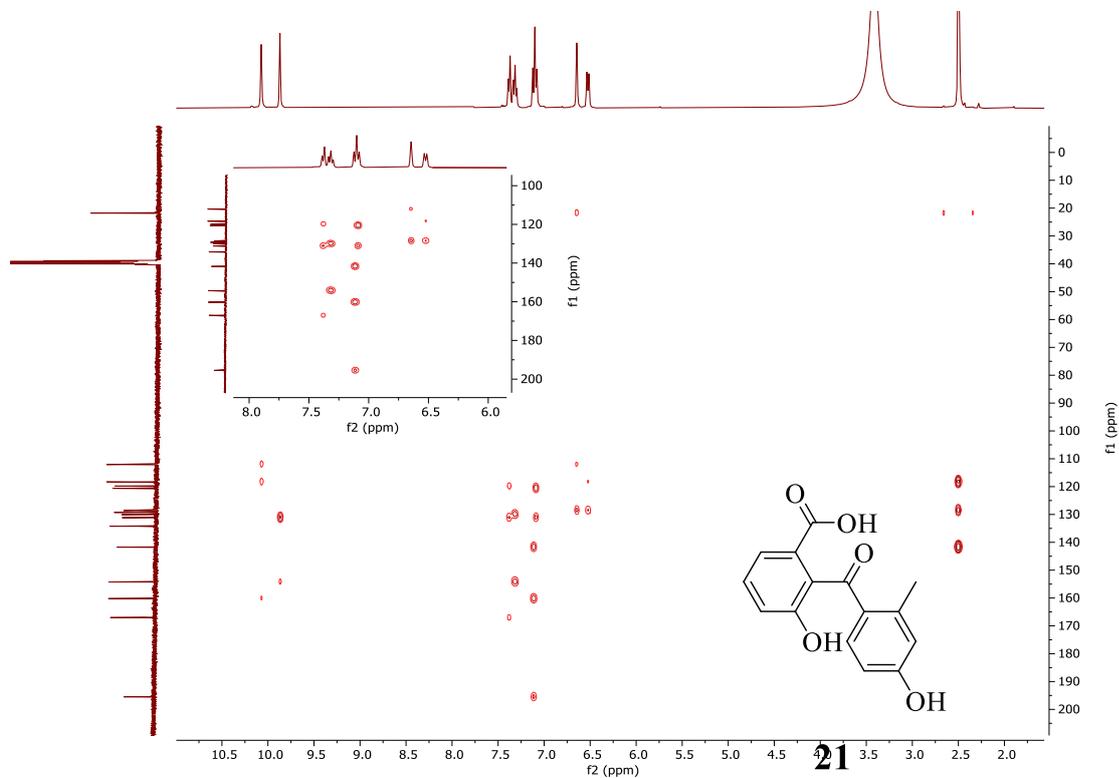


Figure 38: HMBC NMR spectrum of 3-hydroxy-2-(4-hydroxy-2-methylbenzoyl)benzoic acid (21).

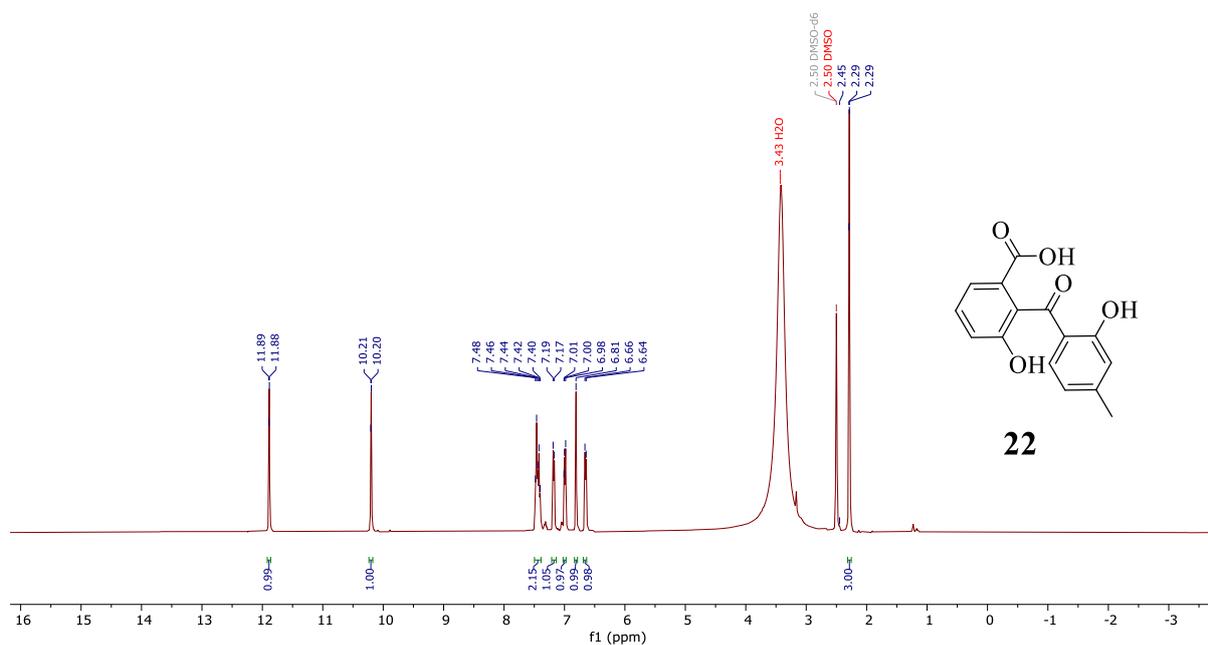


Figure 39: $^1\text{H-NMR}$ spectrum of 3-hydroxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (**22**).

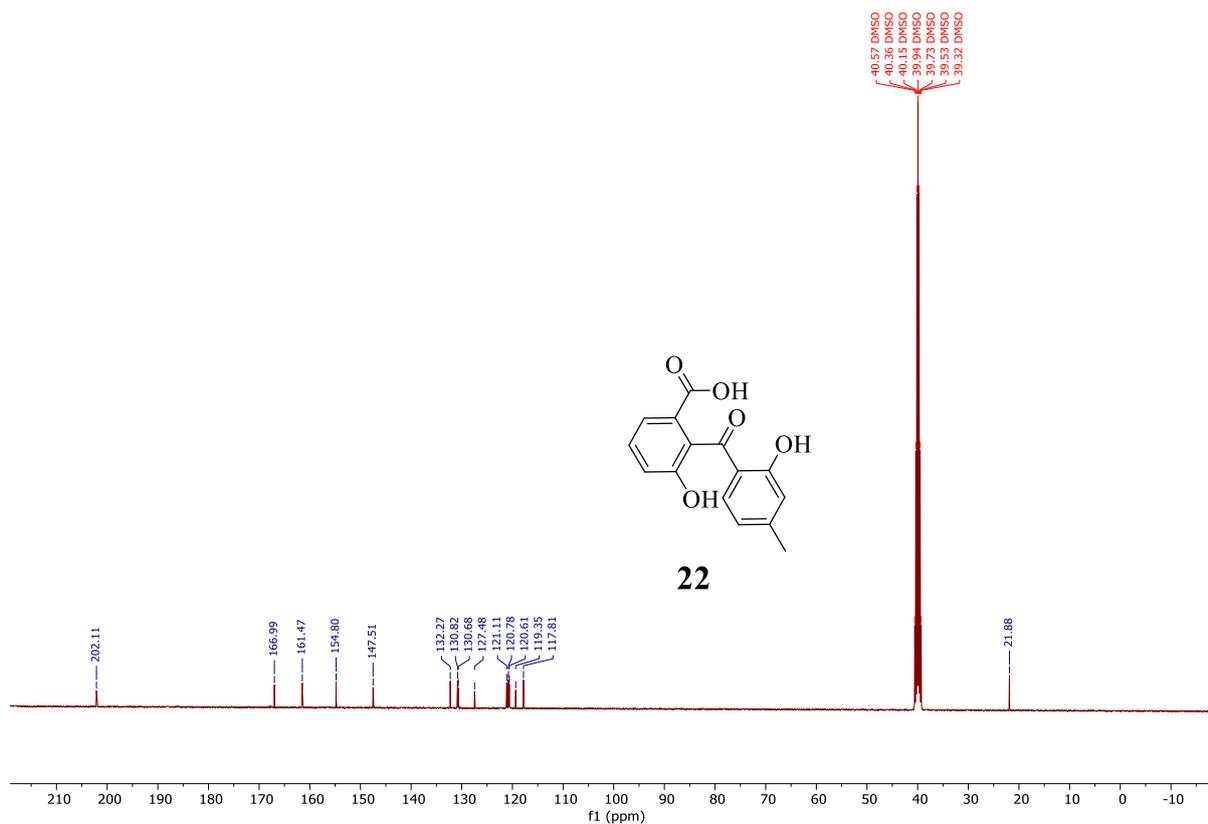


Figure 40: $^{13}\text{C-NMR}$ spectrum of 3-hydroxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (**22**).

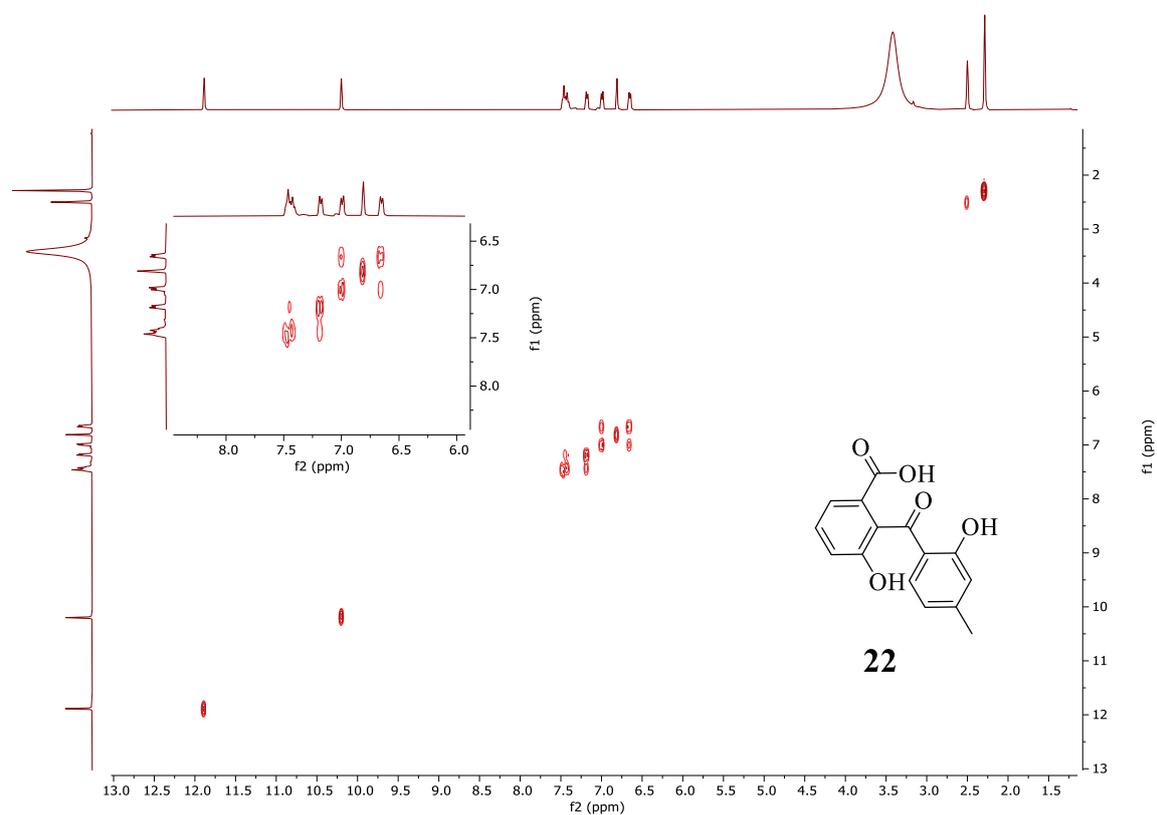


Figure 41: COSY NMR spectrum of 3-hydroxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (22).

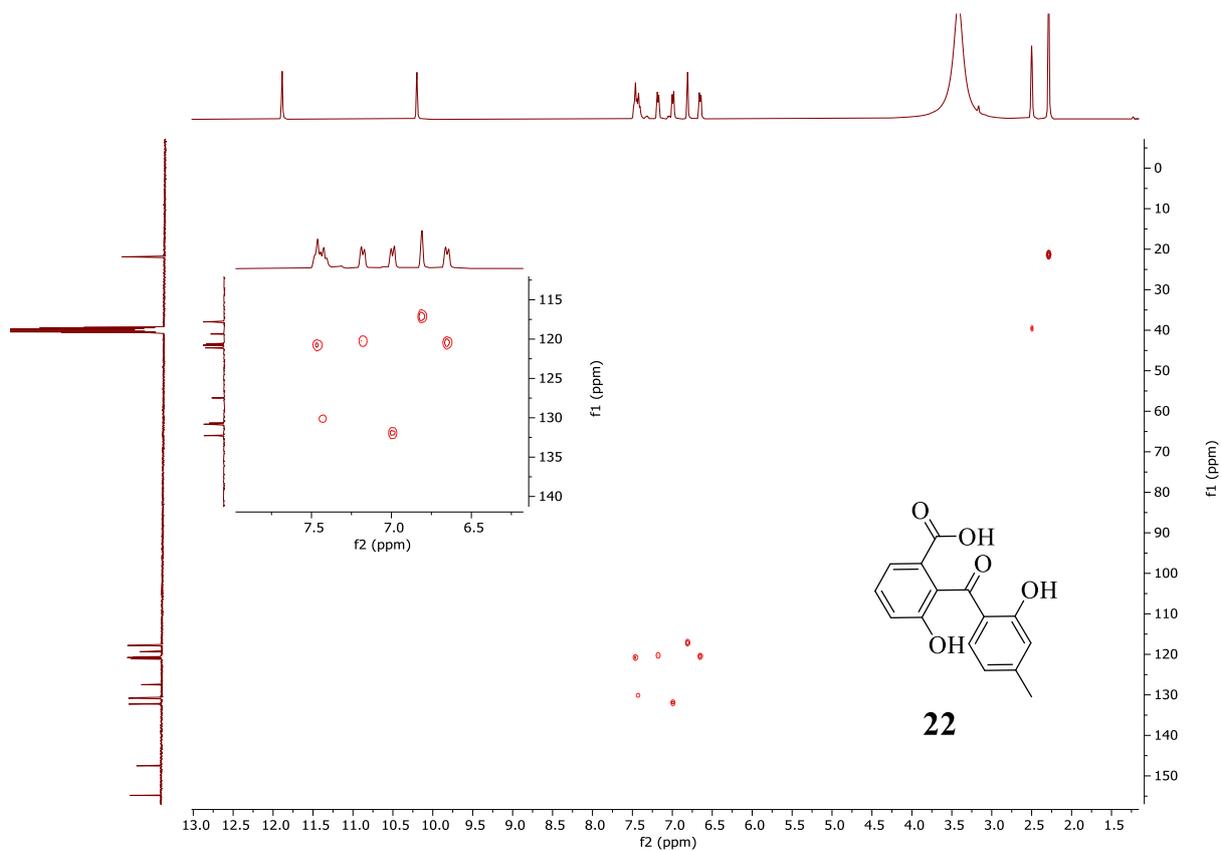


Figure 42: HSQC NMR spectrum of 3-hydroxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (22).

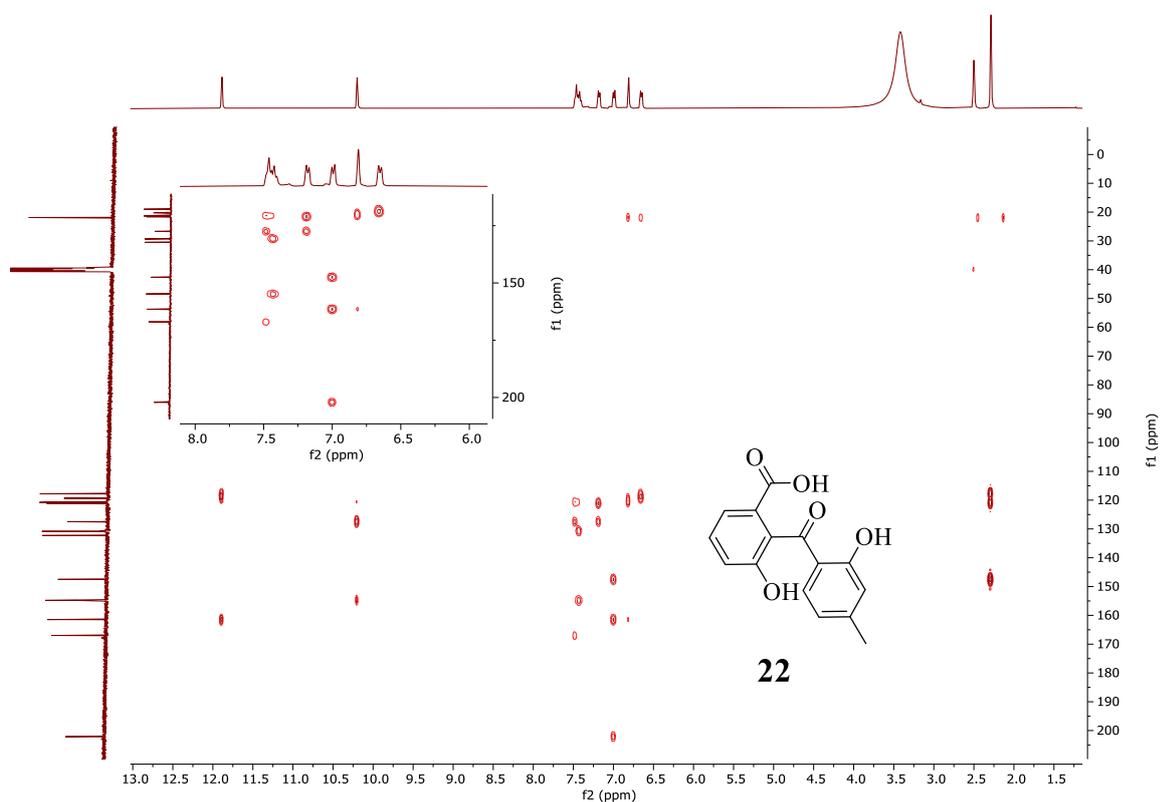


Figure 43: HMBC spectrum of 3-hydroxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (**22**).

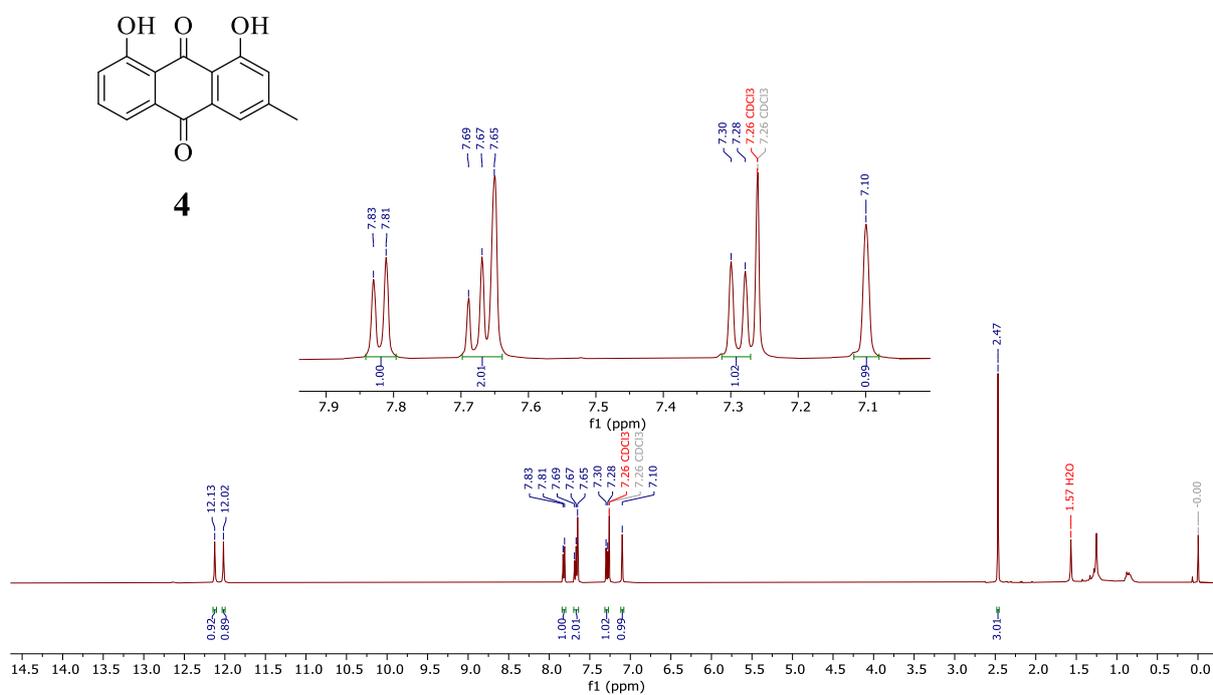


Figure 44: ¹H-NMR spectrum of 1,8-dihydroxy-3-methylantracene-9,10-dione (**4**).

