

Supplementary Material

The synthesis of symmetrical peripheral and non-peripheral octa-substituted metal-free phthalocyanines: simpler, better, faster, cheaper

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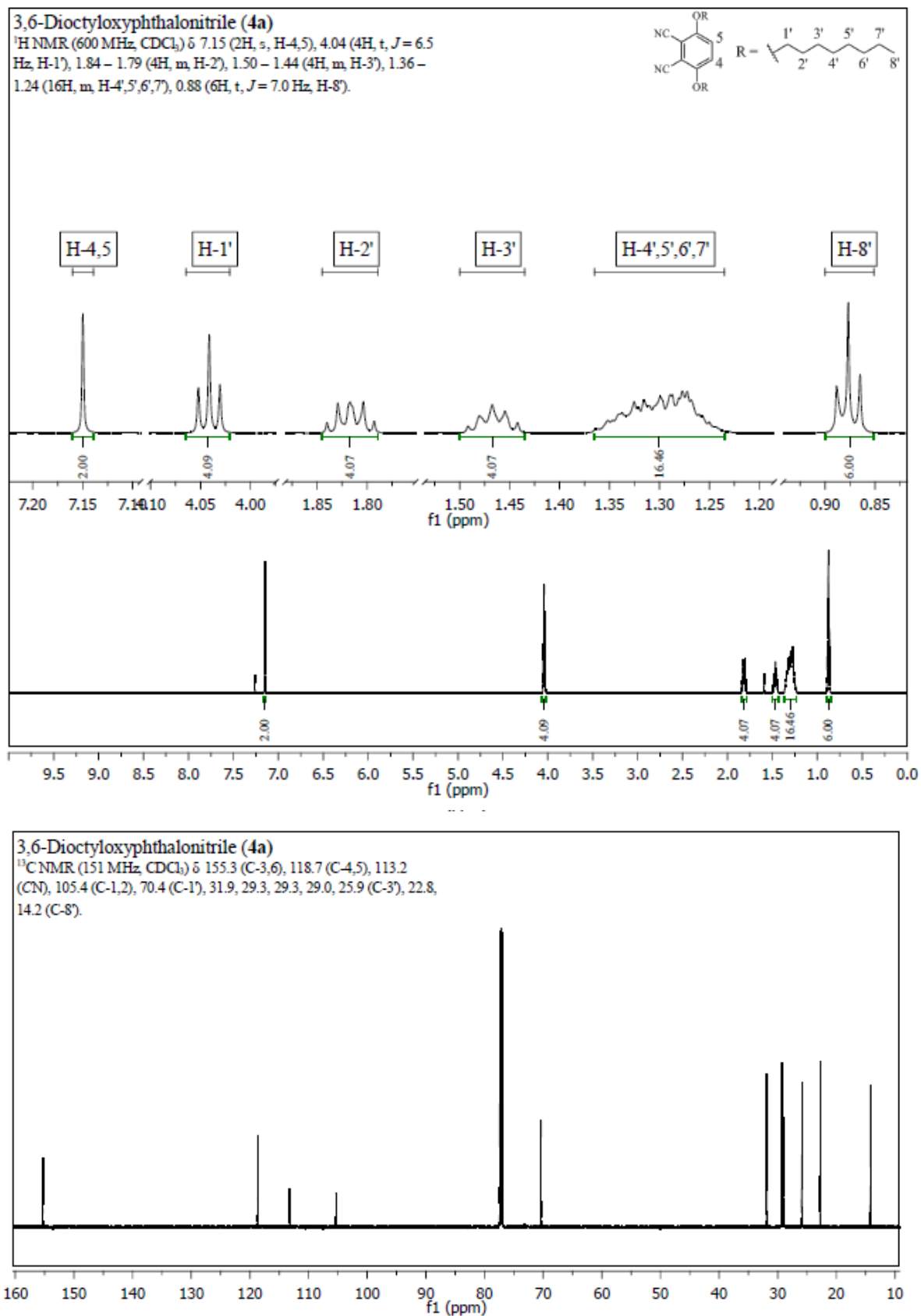
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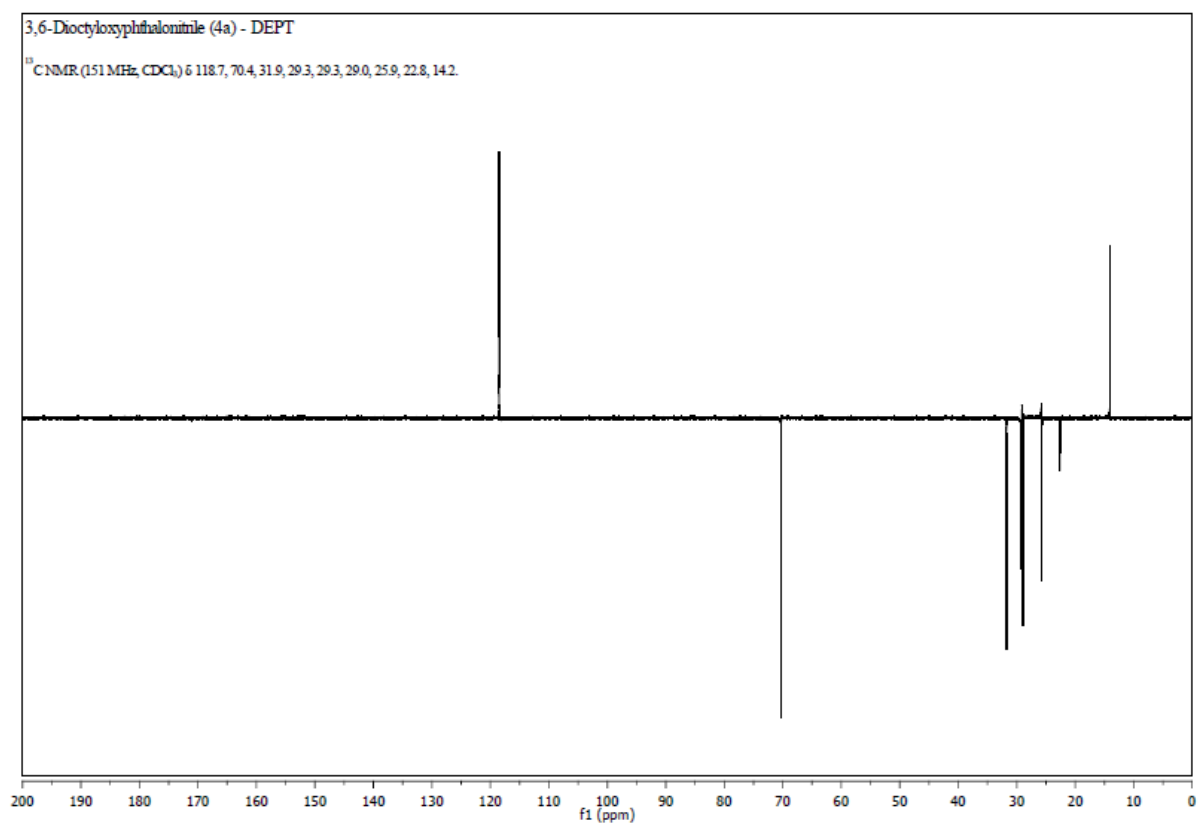
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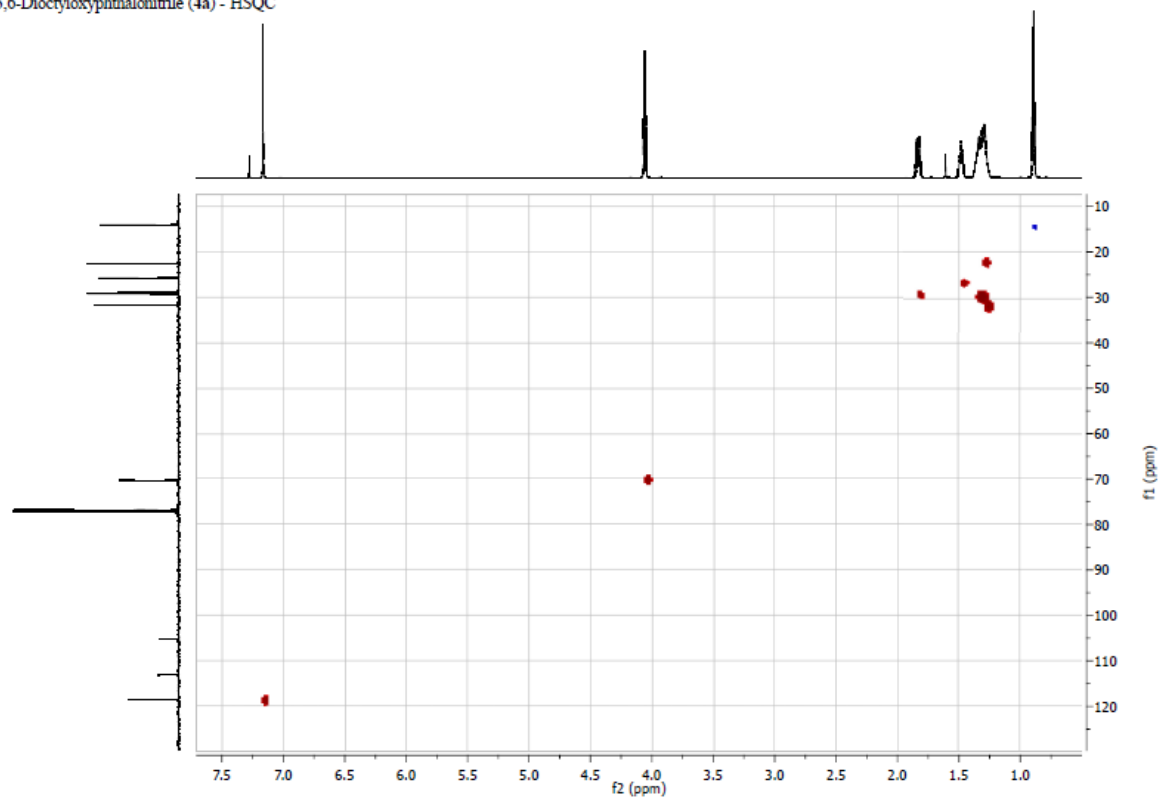
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3,6-Dioctyloxyphthalonitrile (4a)

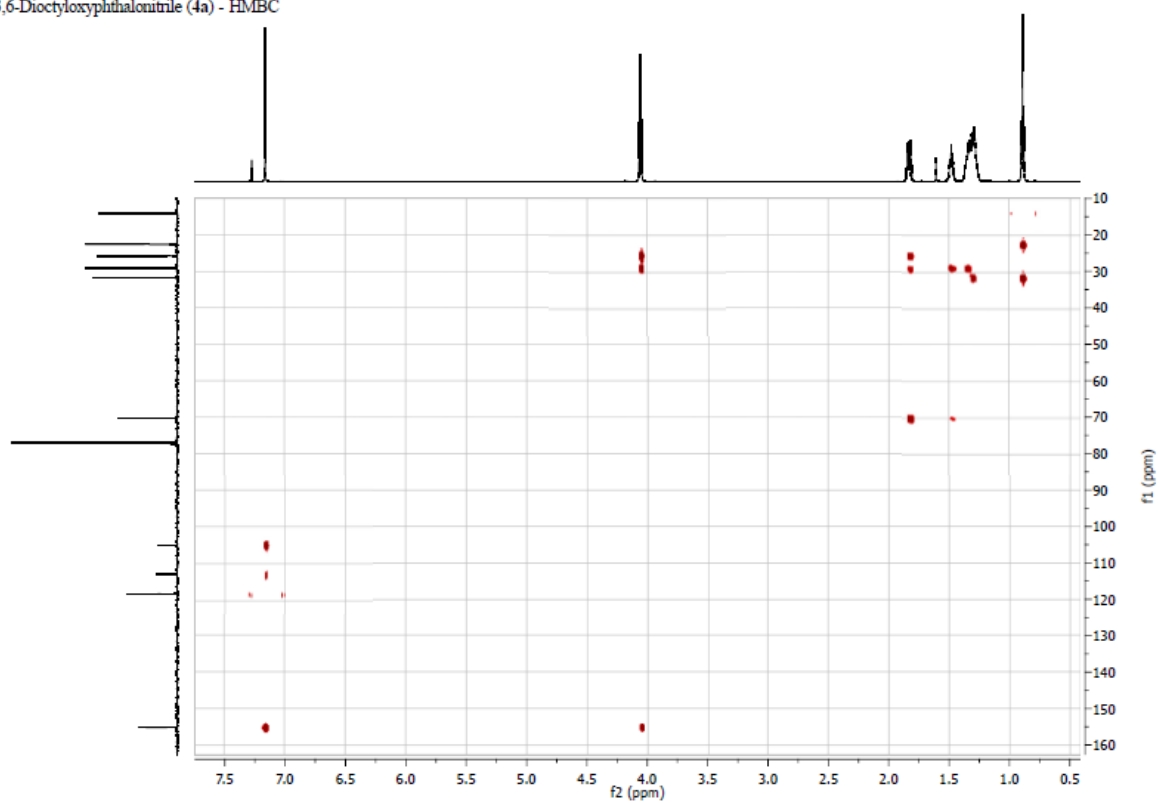




3,6-Dioctyloxyphthalonitrile (4a) - HSQC

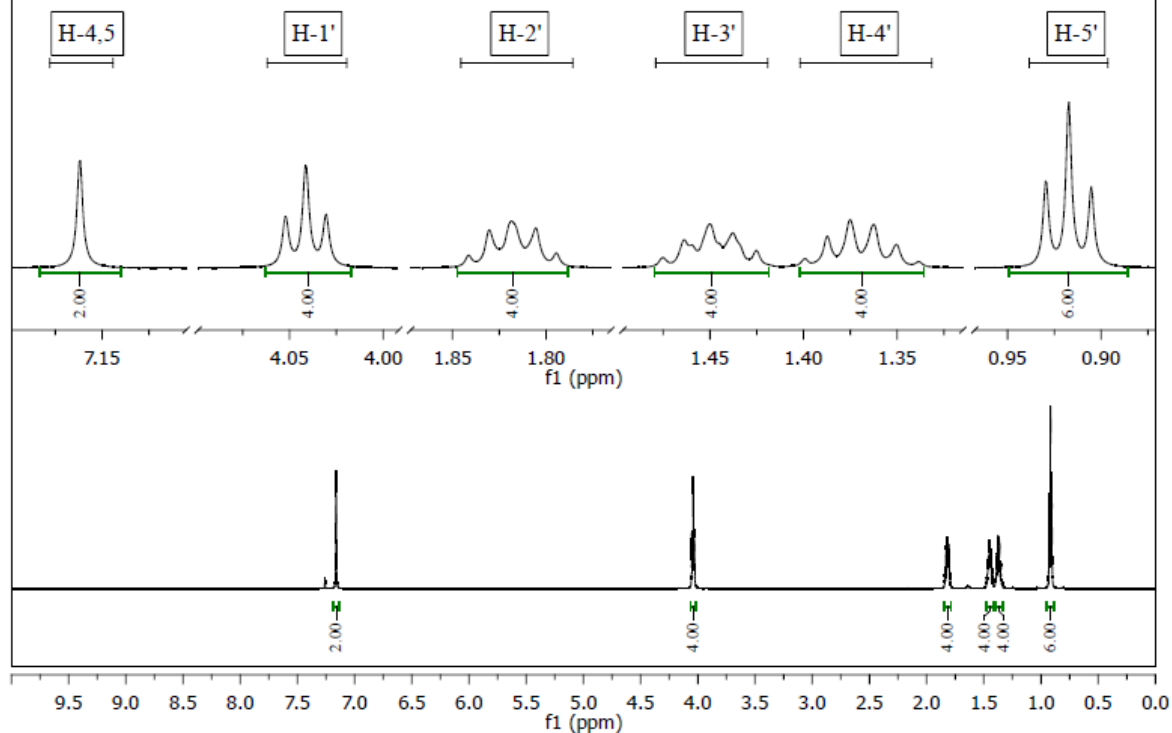
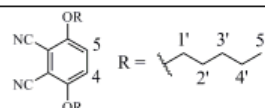


3,6-Dioctyloxyphthalonitrile (4a) - HMBC

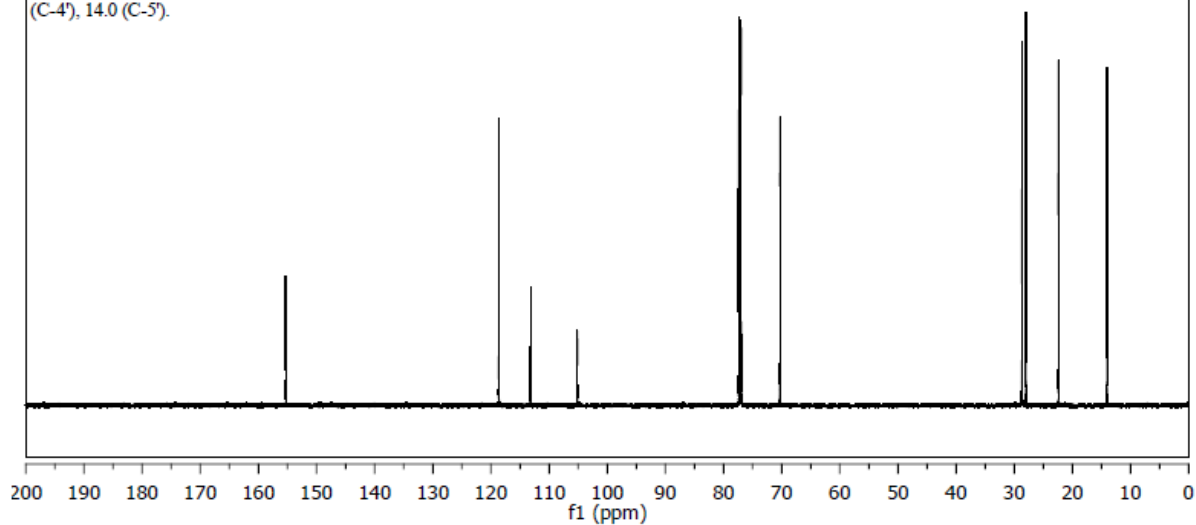


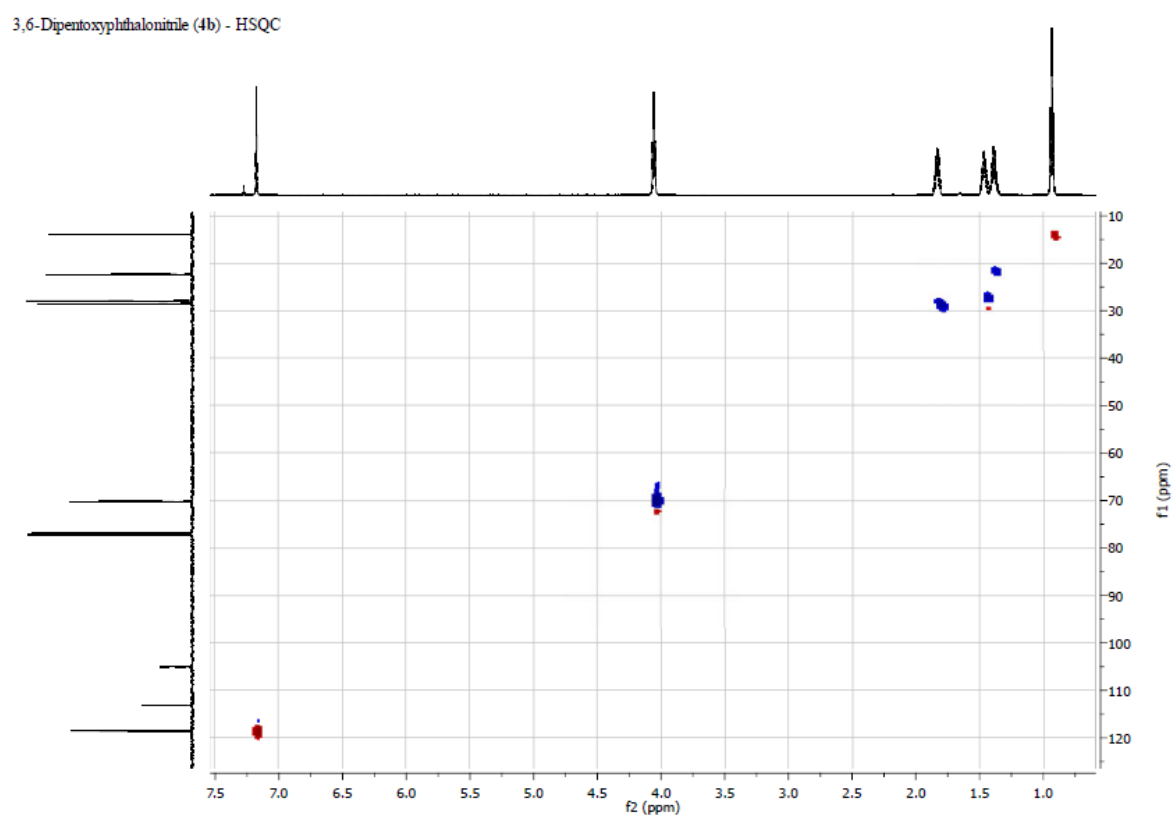
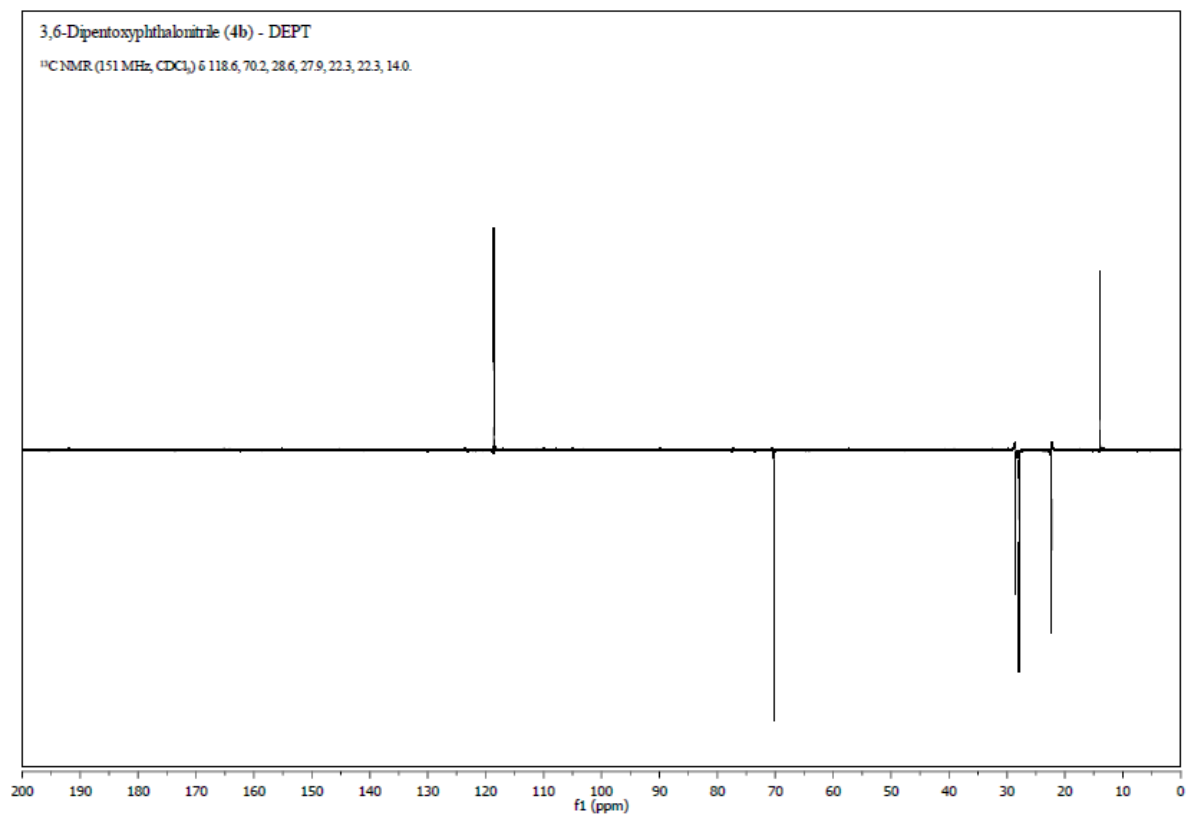
3,6-Dipentoxyphthalonitrile (**4b**)3,6-Dipentoxyphthalonitrile (**4b**)

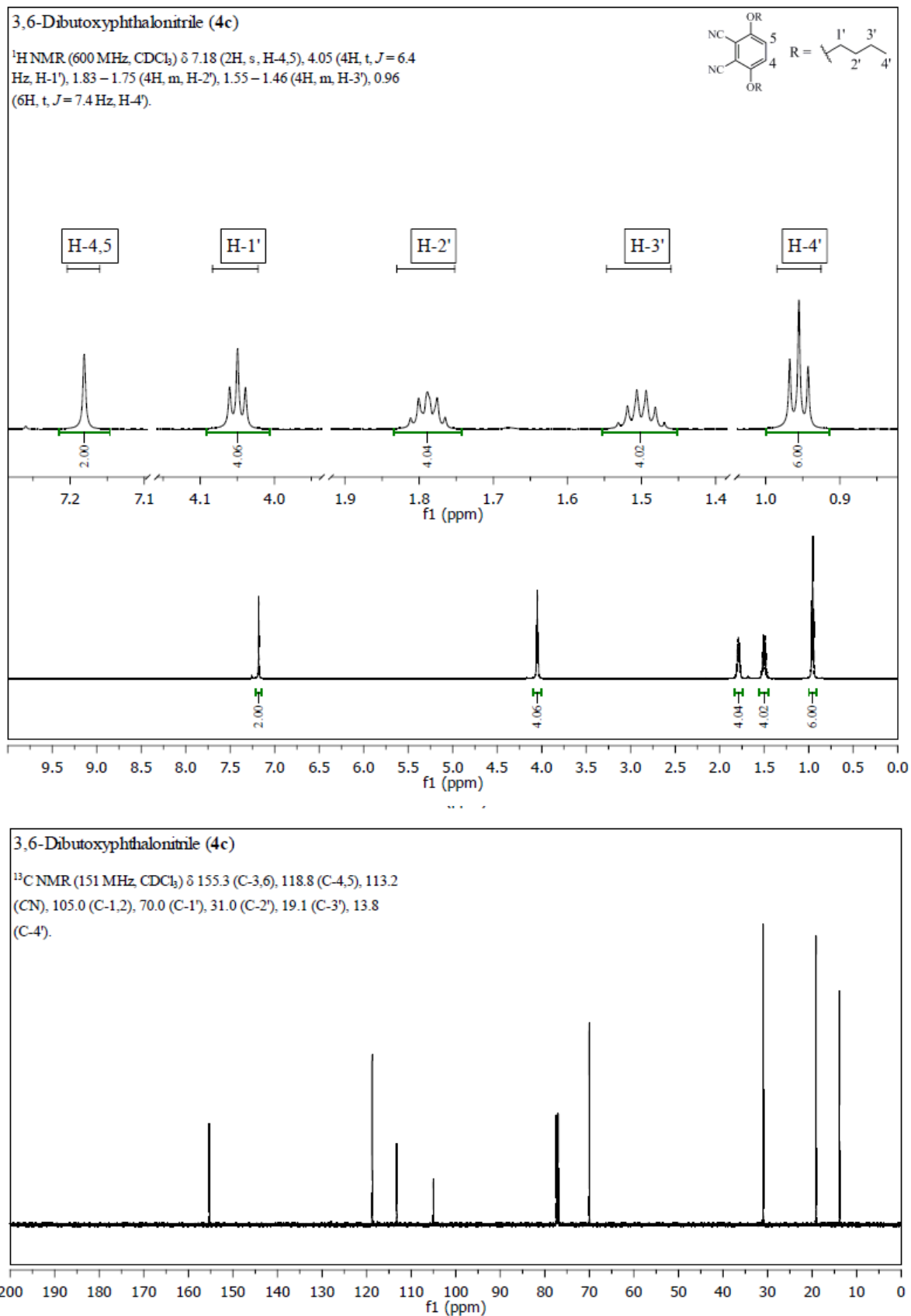
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.16 (2H, s, H-4,5), 4.04 (4H, t, $J = 6.5$ Hz, H-1'), 1.85 – 1.79 (4H, m, H-2'), 1.45 (4H, dt, $J = 14.9, 7.2$ Hz, H-3'), 1.40 – 1.33 (4H, m, H-4'), 0.92 (6H, t, $J = 7.3$ Hz, H-5').

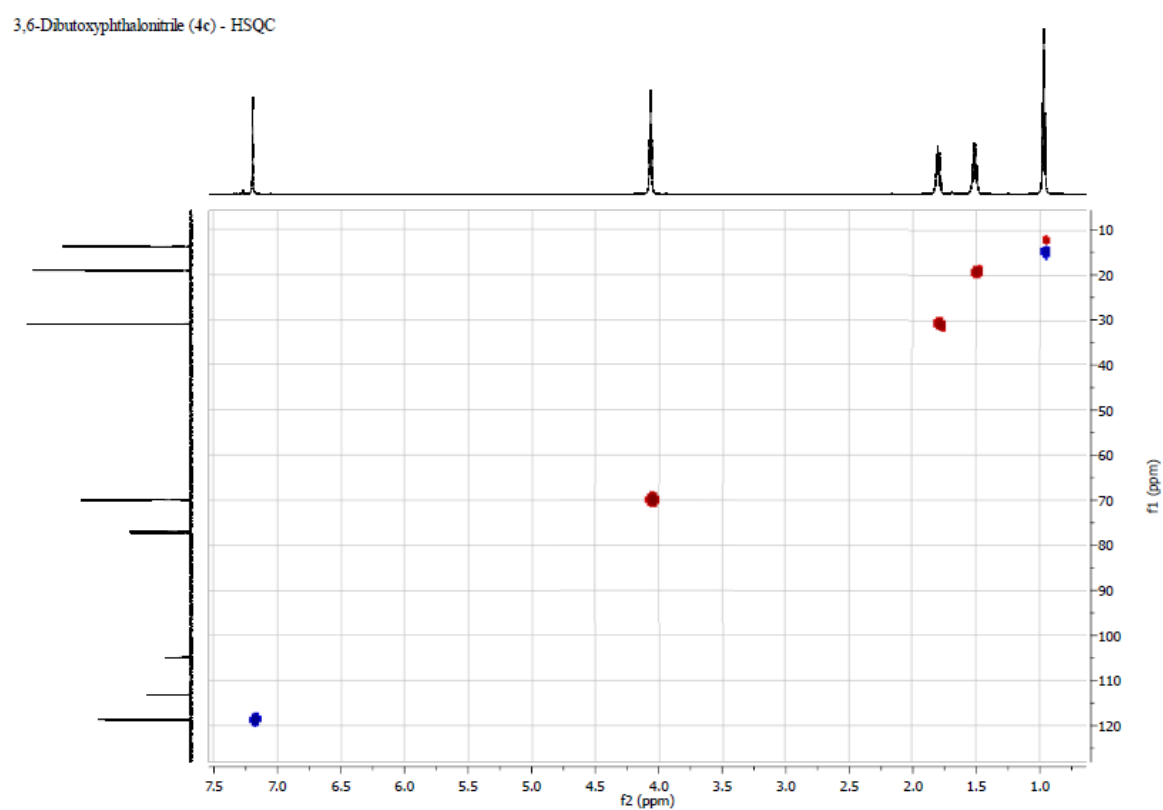
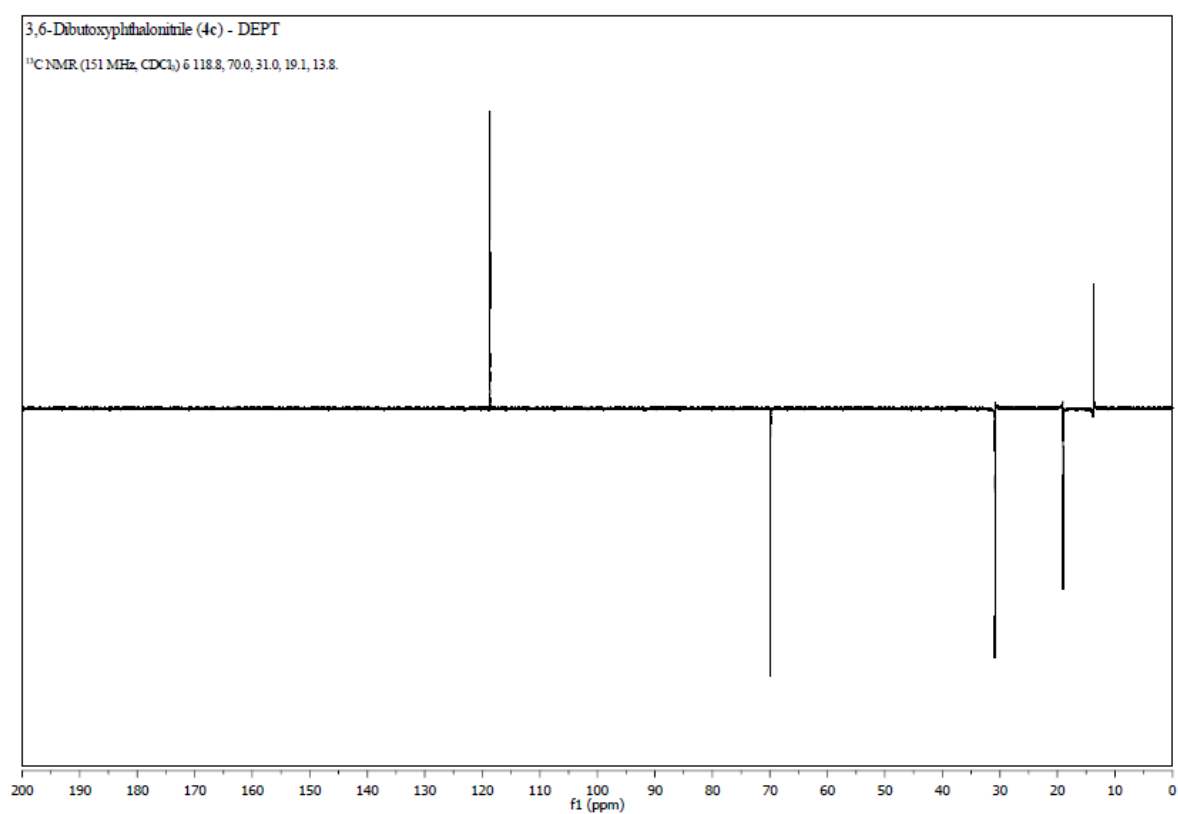
3,6-Dipentoxyphthalonitrile (**4b**)

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 155.3 (C-3,6), 118.7 (C-4,5), 113.2 (CN), 105.1 (C-1,2), 70.3 (C-1'), 28.7 (C-2'), 28.0 (C-3'), 22.4 (C-4'), 14.0 (C-5').

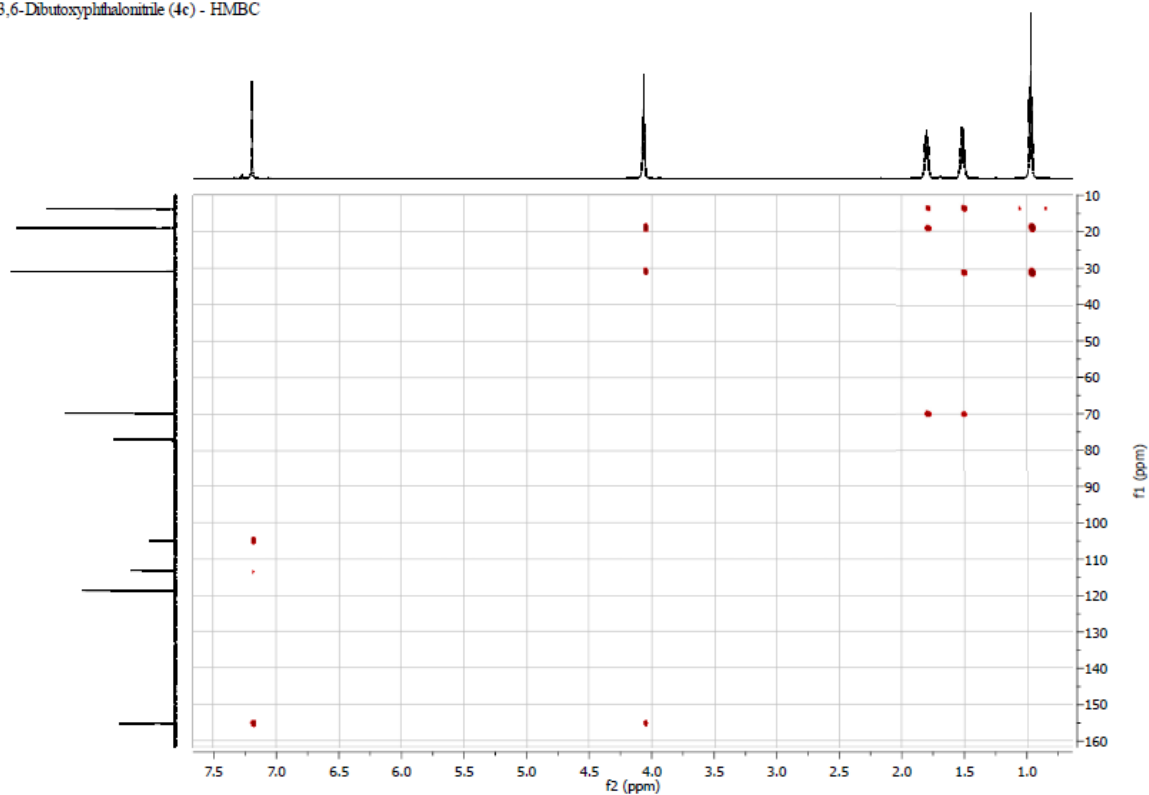




3,6-Dibutoxyphthalonitrile (**4c**)

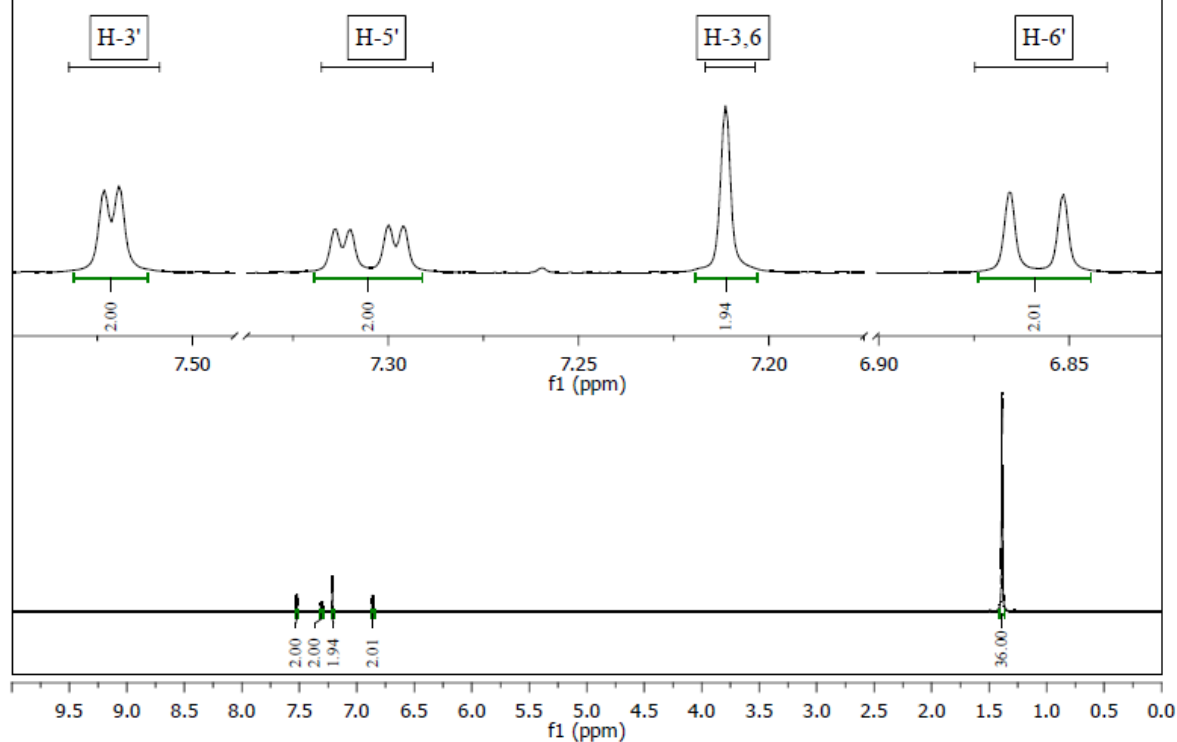
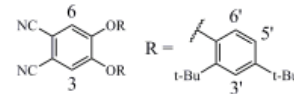


3,6-Dibutoxyphthalonitrile (4c) - HMBC

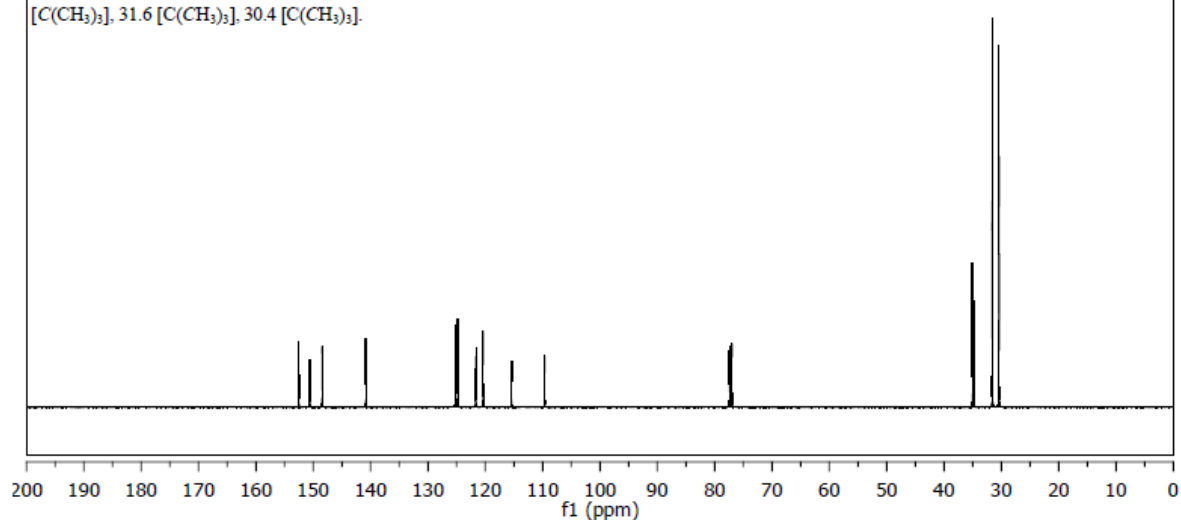


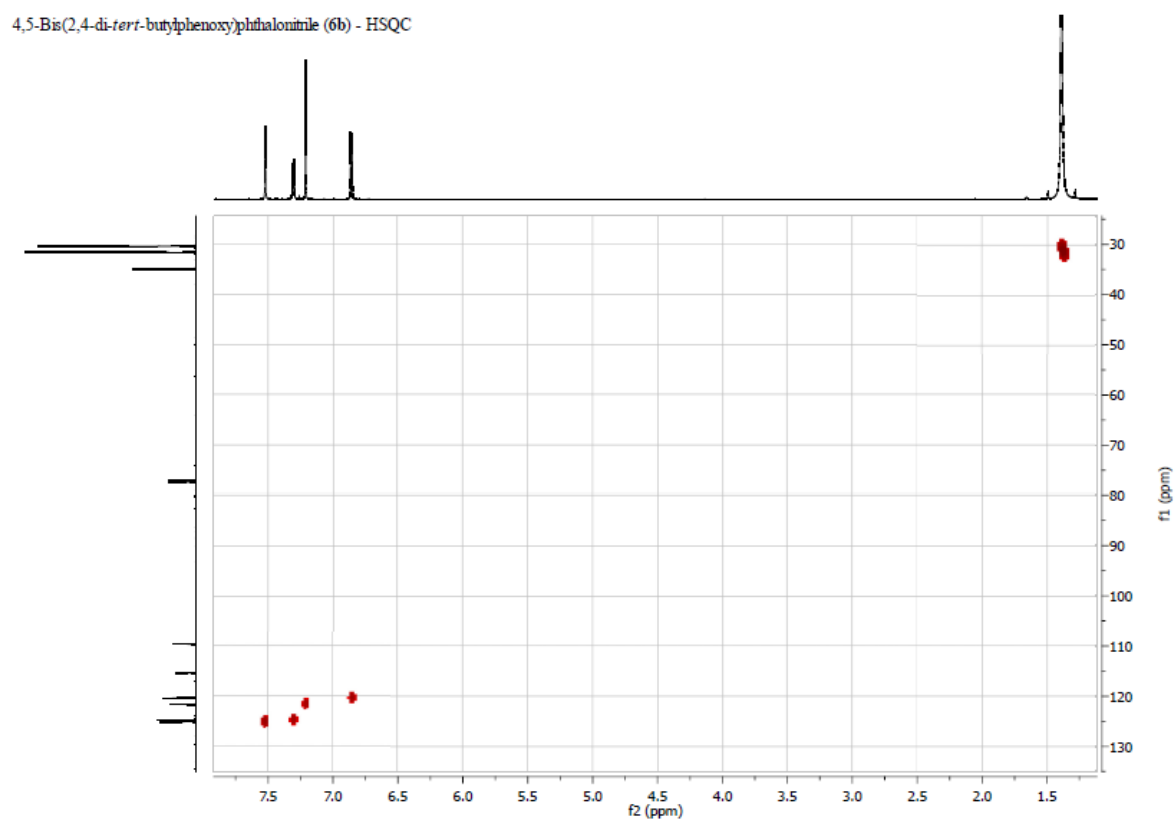
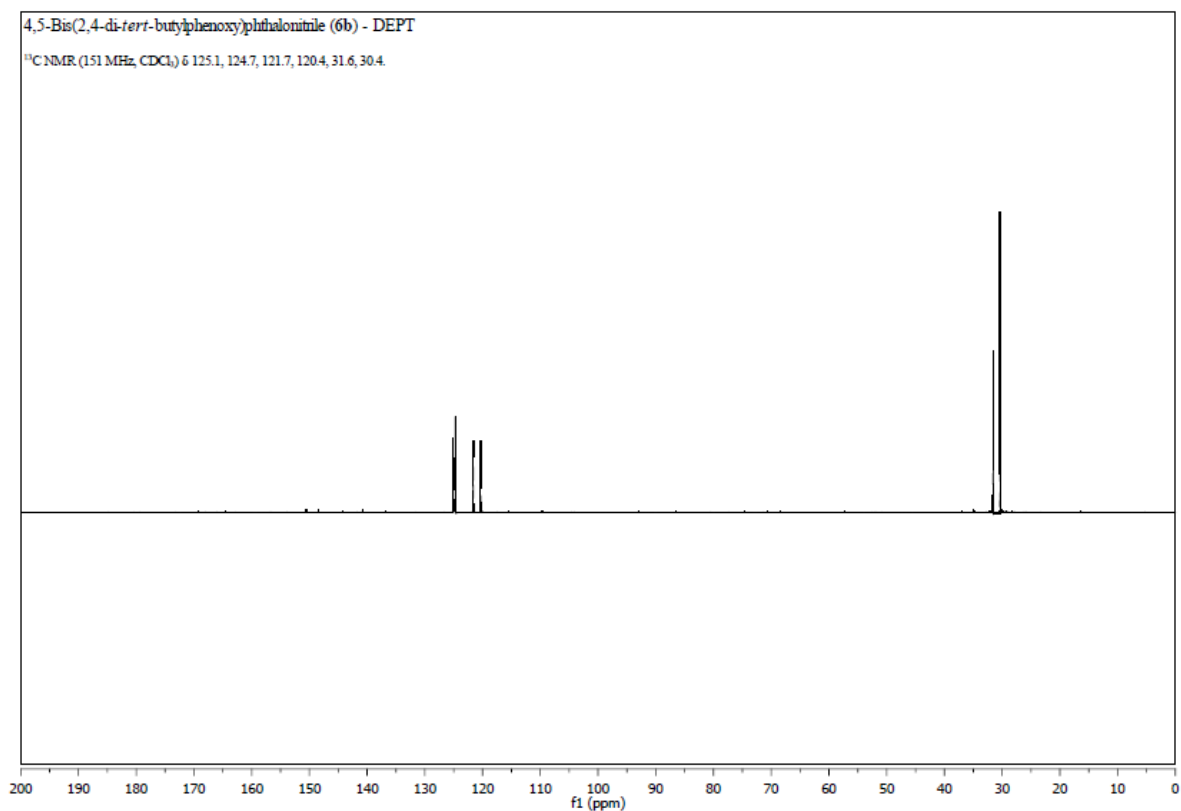
4,5-Bis(2,4-di-*tert*-butylphenoxy)phthalonitrile (**6b**)4,5-Bis(2,4-di-*tert*-butylphenoxy)phthalonitrile (**6b**)

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.52 (2H, d, $J = 2.3$ Hz, H-3'), 7.31 (2H, dd, $J = 8.4$, 2.3 Hz, H-5'), 7.21 (2H, s, H-3,6), 6.86 (2H, d, $J = 8.4$ Hz, H-6'), 1.39 (36H, s, $\text{C}(\text{CH}_3)_3$).

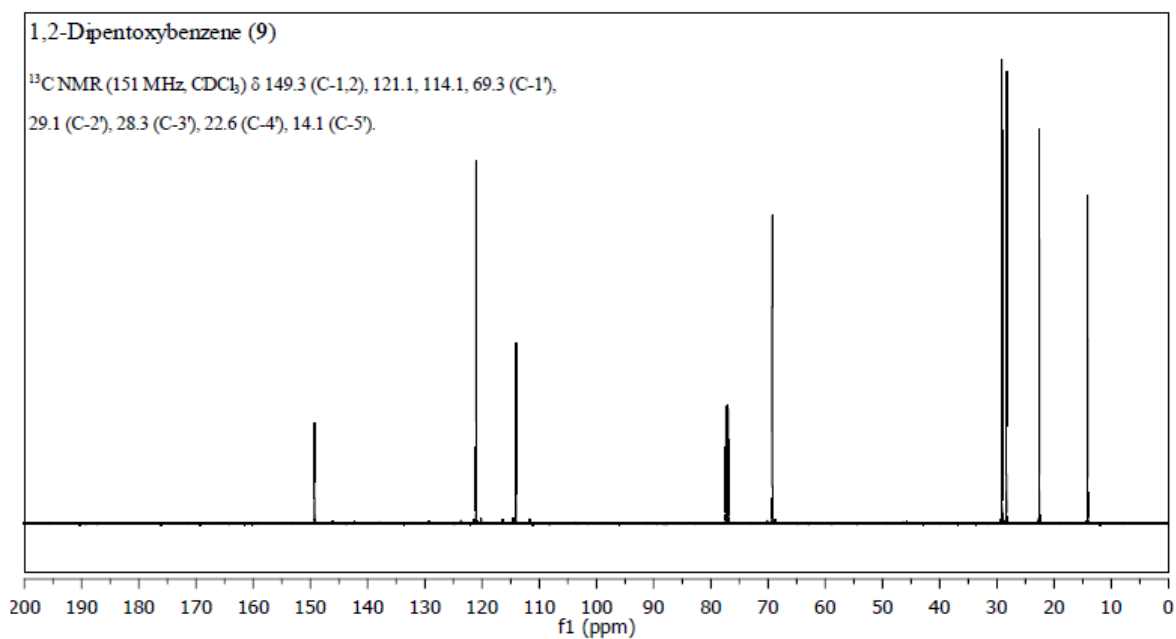
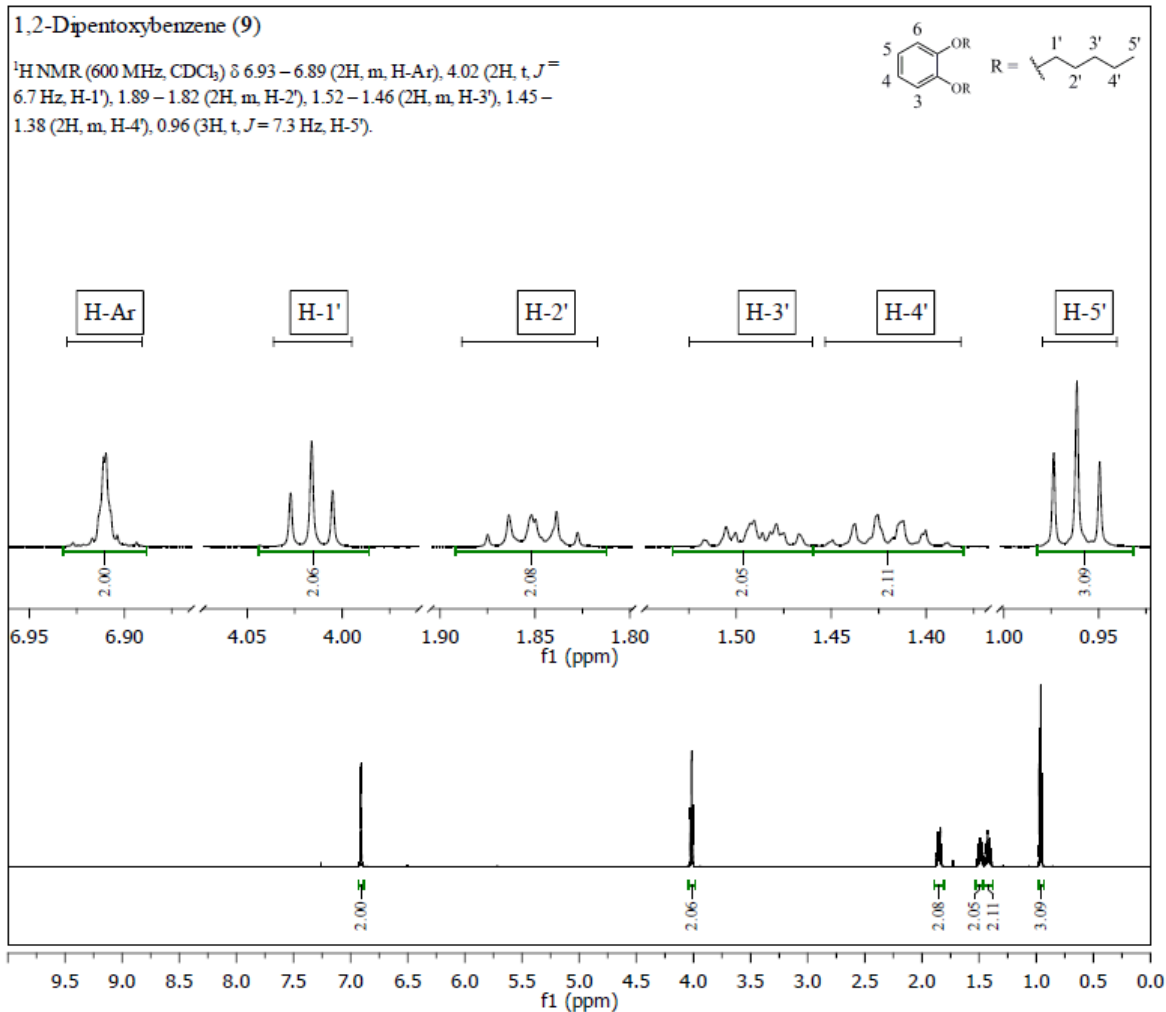
4,5-Bis(2,4-di-*tert*-butylphenoxy)phthalonitrile (**6b**)

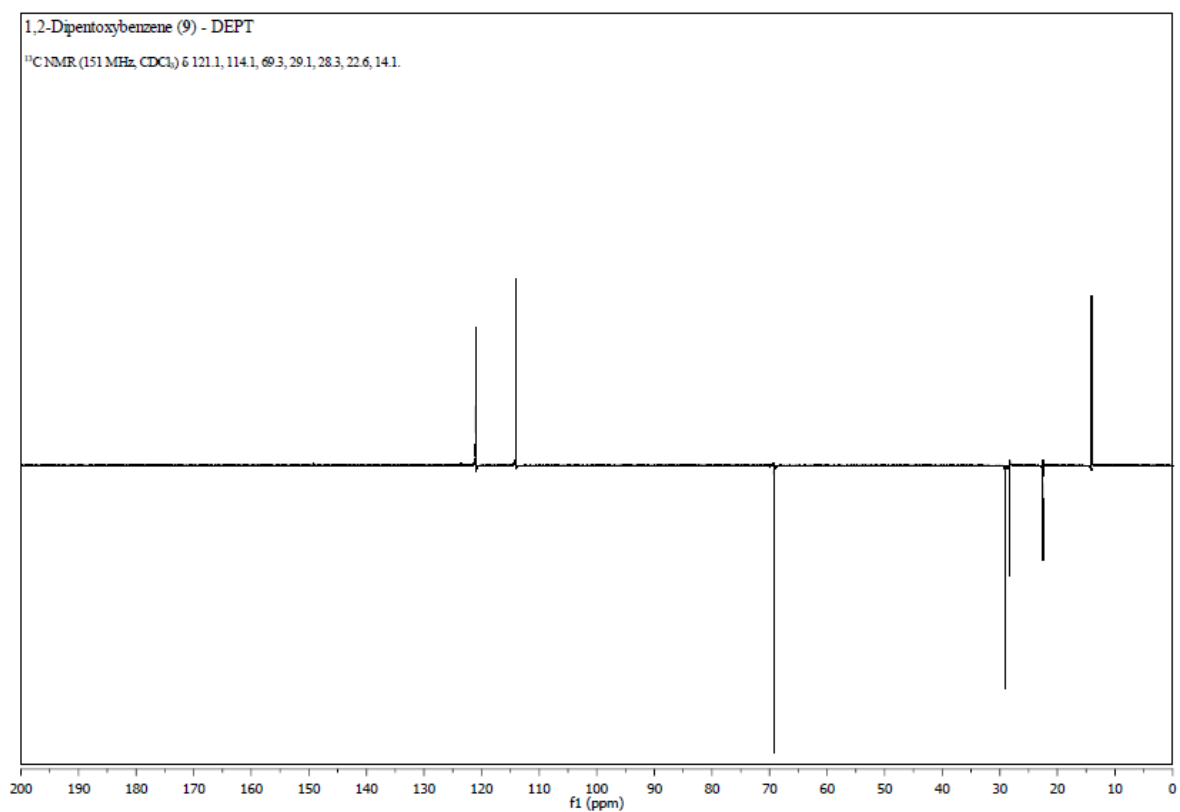
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 152.5, 150.6, 148.5, 140.8, 125.1 (C-3'), 124.7 (C-5'), 121.7 (C-3,6), 120.4 (C-6'), 115.4 (CN), 109.6 (C-1,2), 35.0 [$\text{C}(\text{CH}_3)_3$], 34.8 [$\text{C}(\text{CH}_3)_3$], 31.6 [$\text{C}(\text{CH}_3)_3$], 30.4 [$\text{C}(\text{CH}_3)_3$].



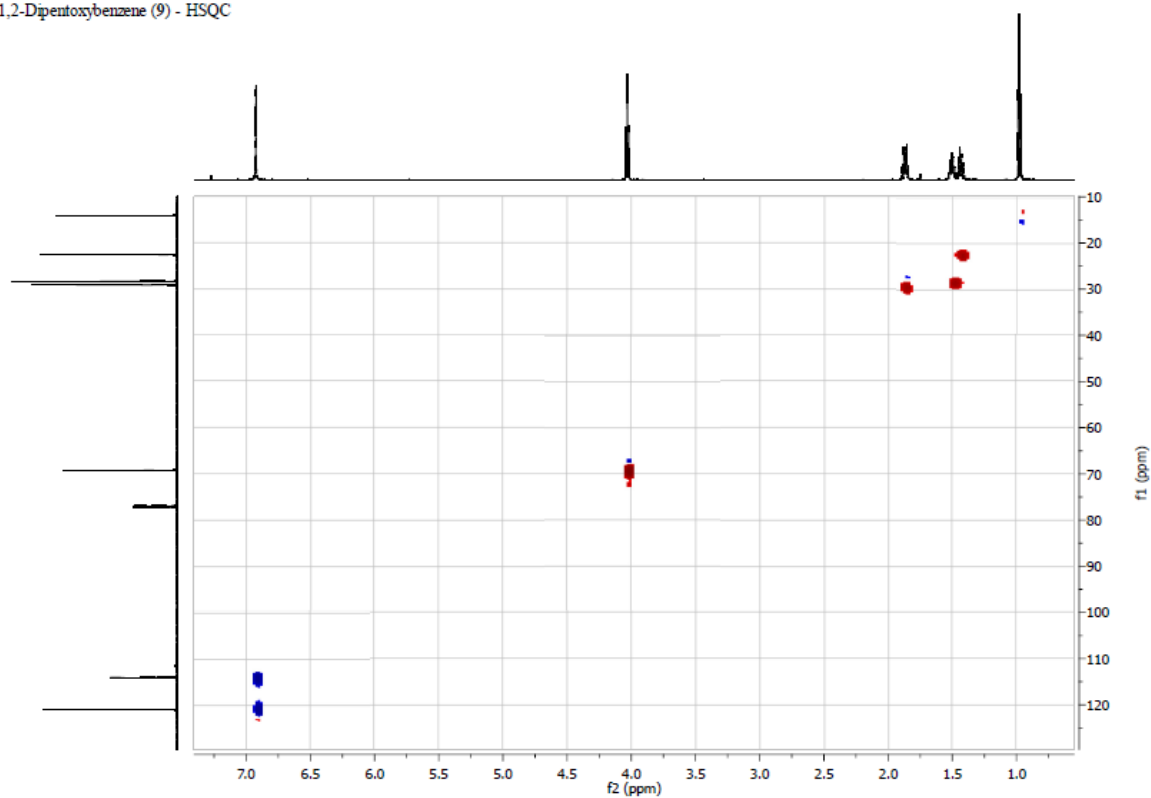


1,2-Dipentoxybenzene (9)

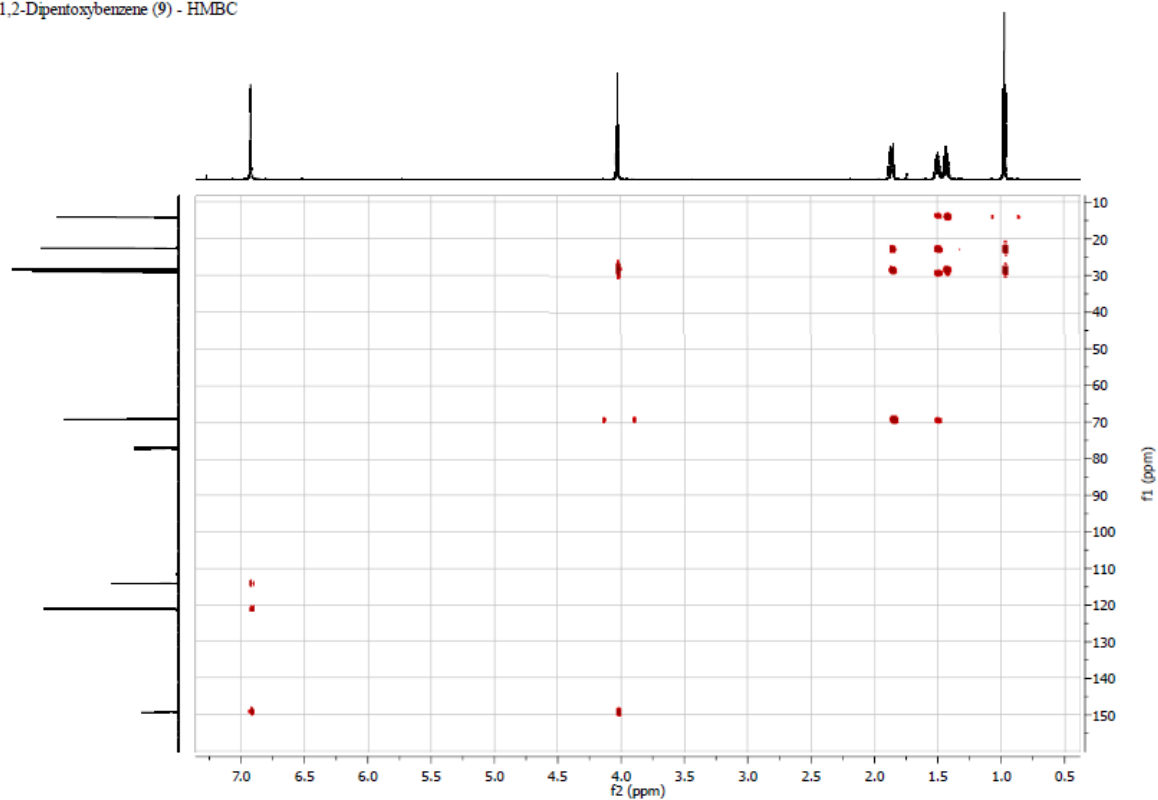


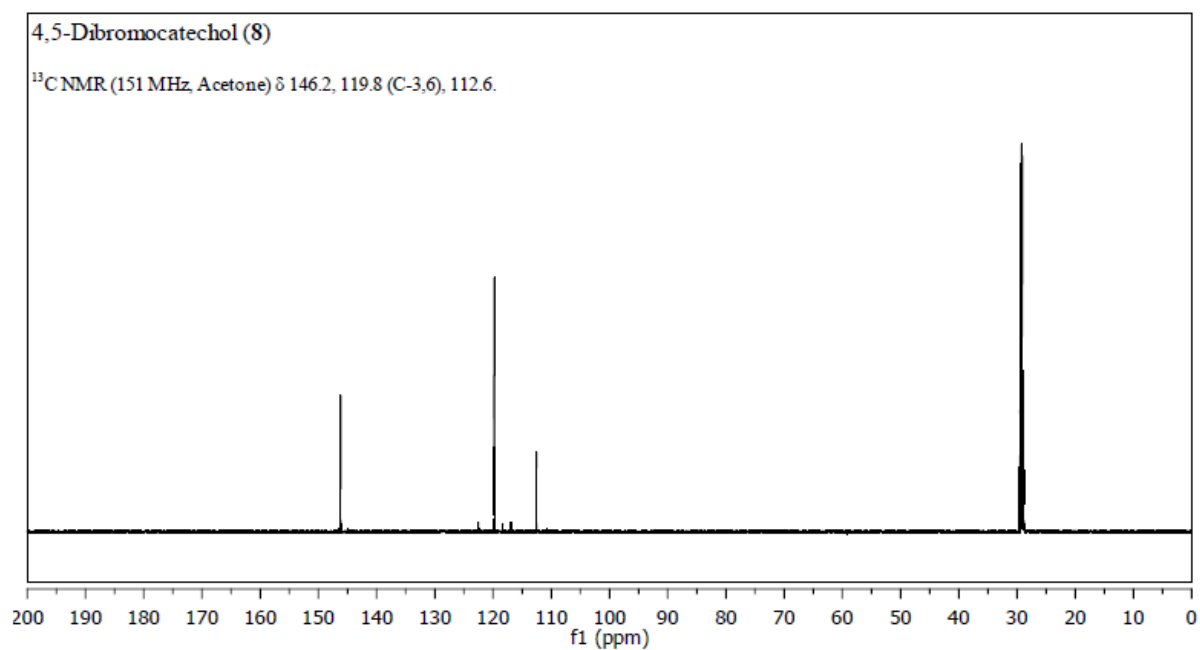
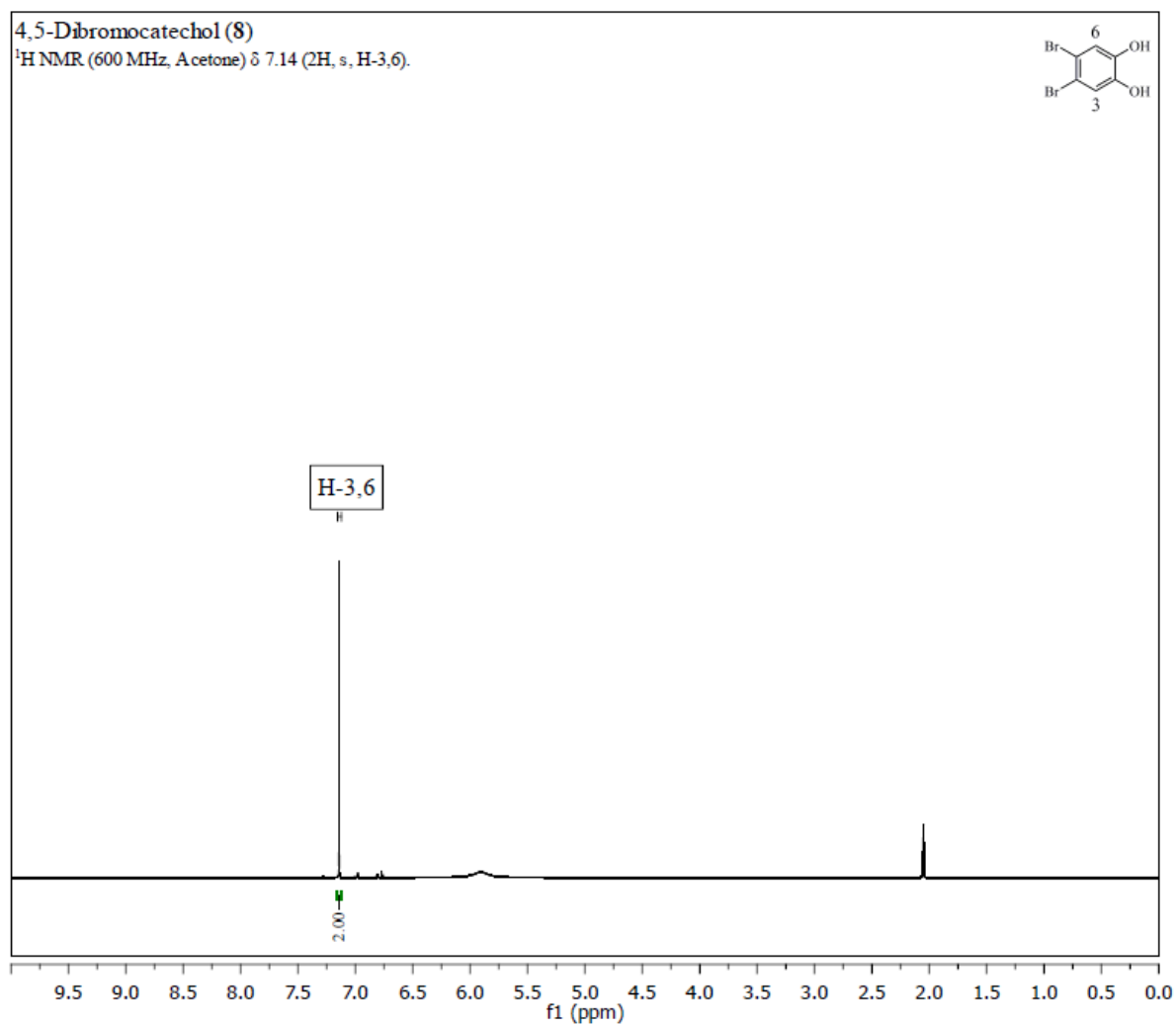


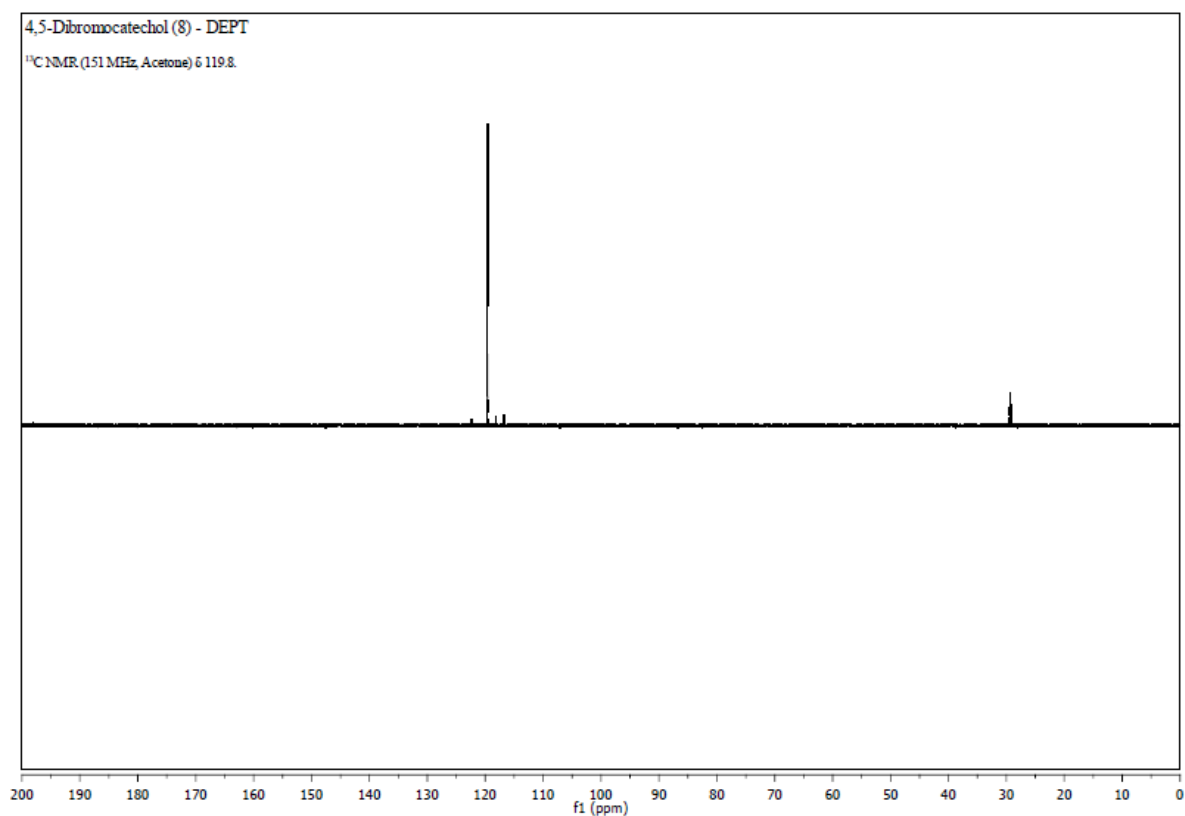
1,2-Dipentoxylbenzene (9) - HSQC



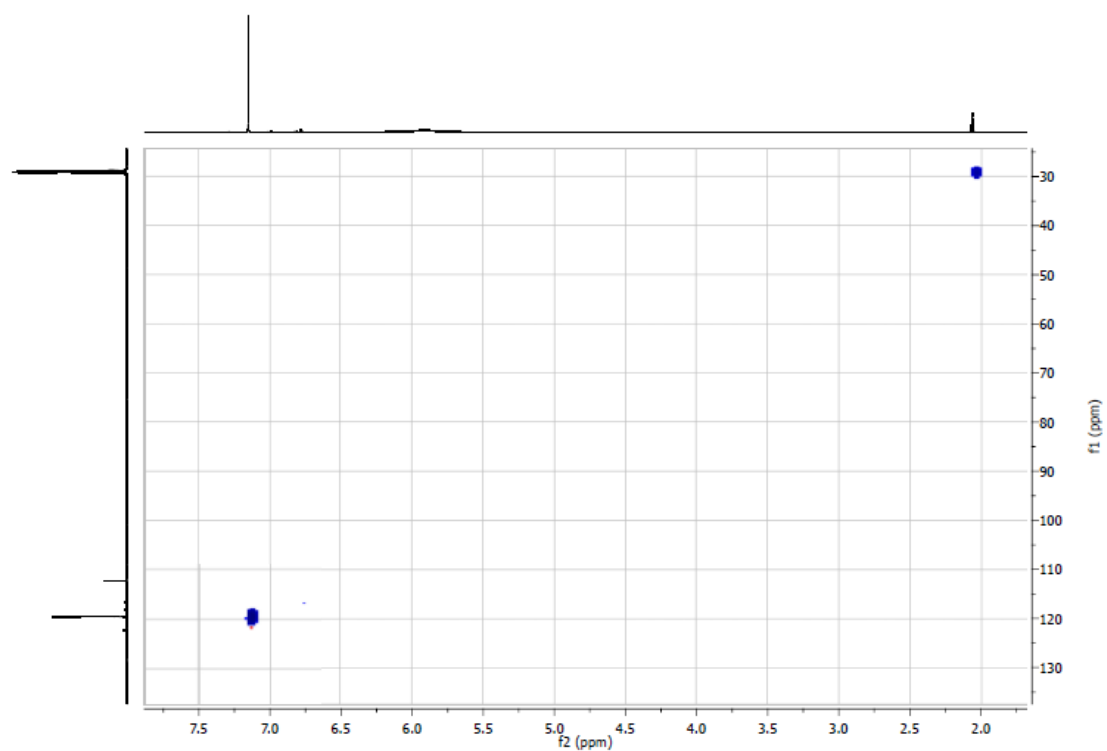
1,2-Dipentoxylbenzene (9) - HMBC



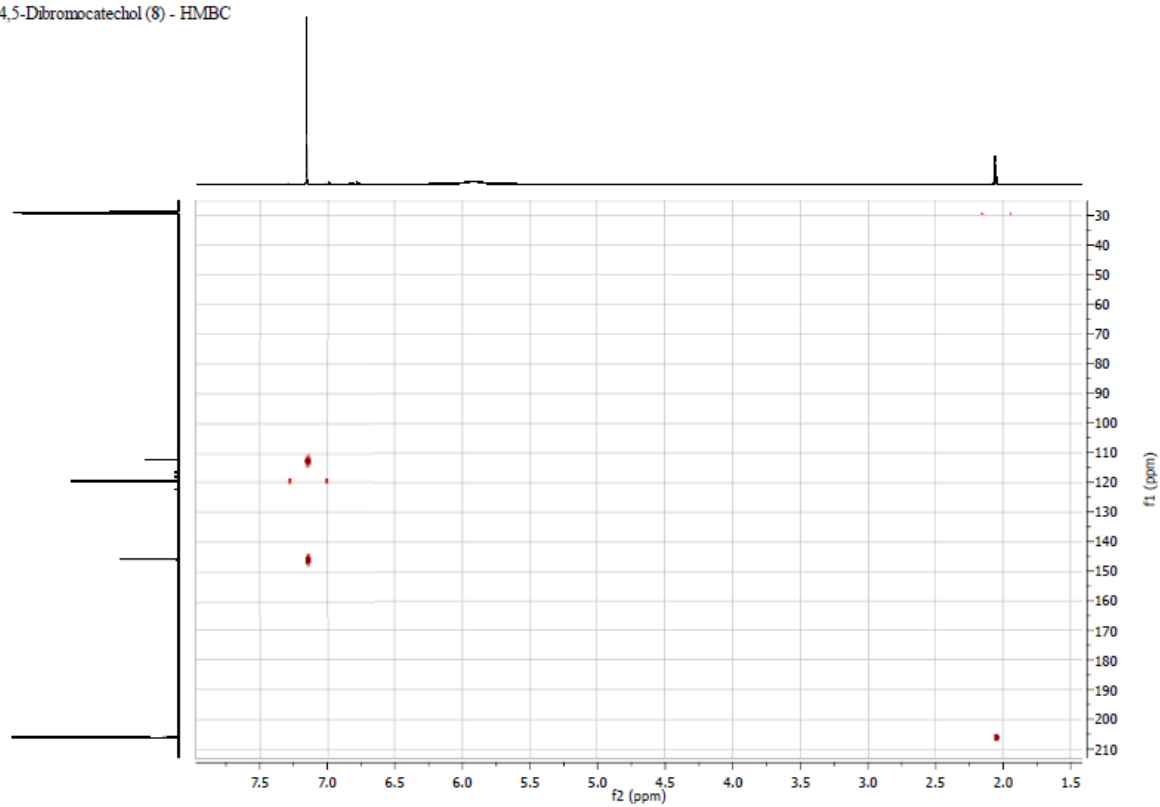
4,5-Dibromocatechol (**8**)

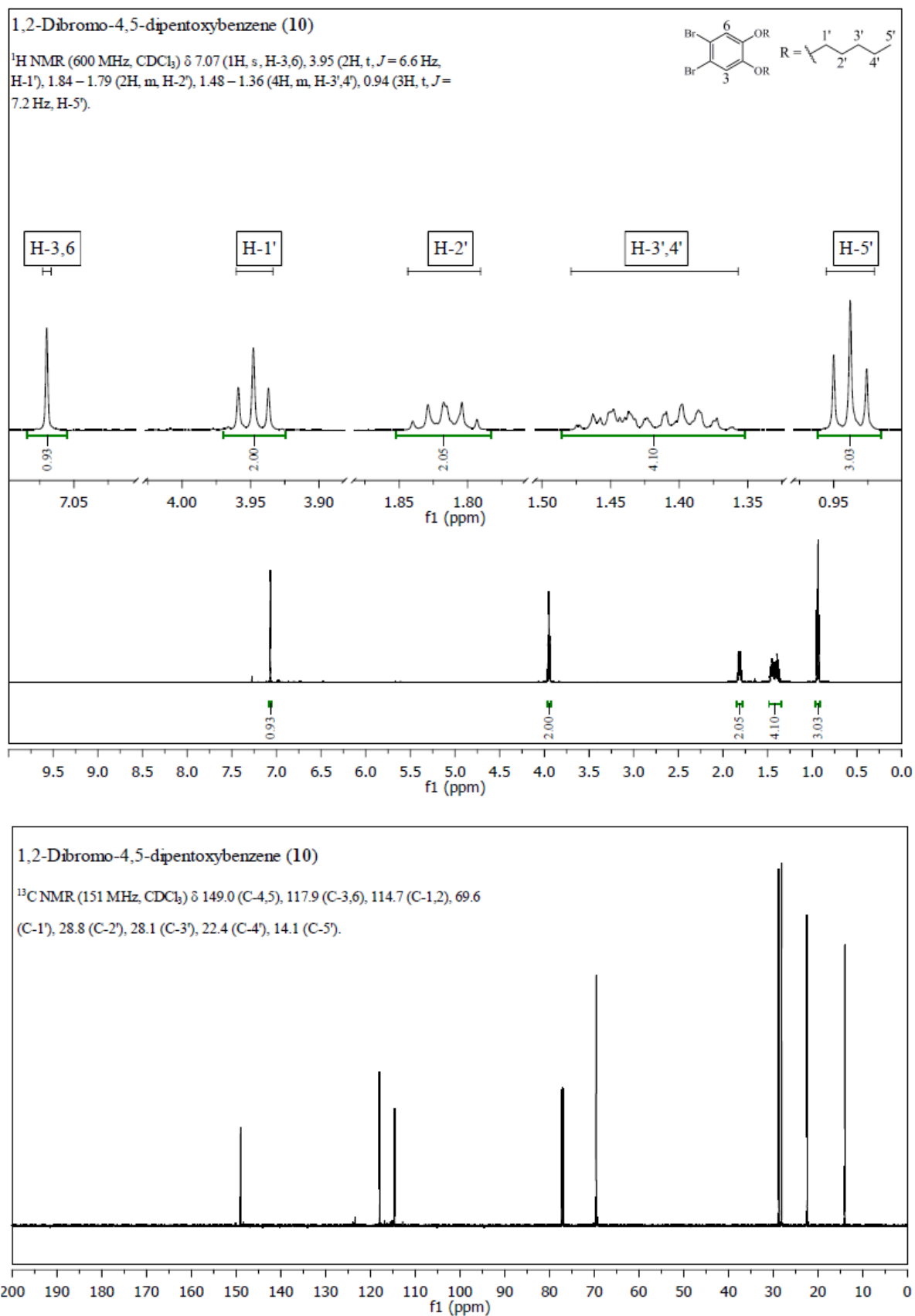


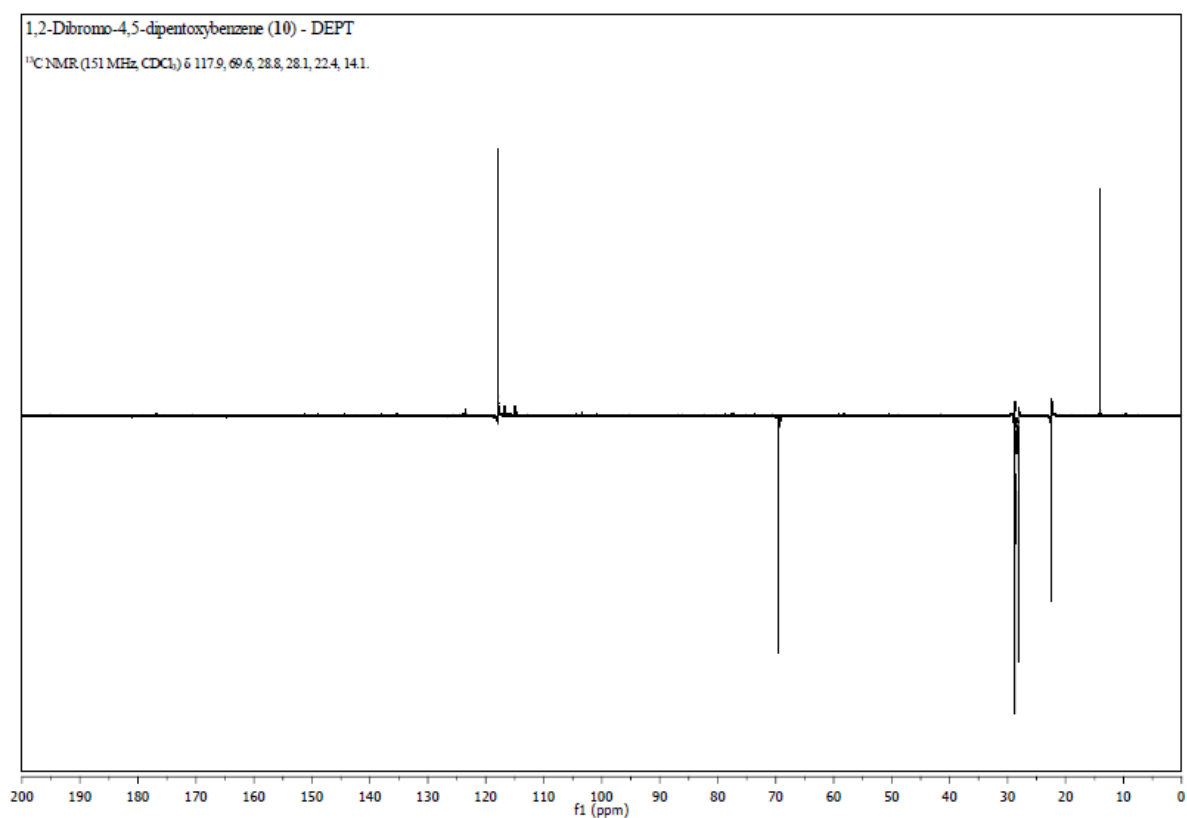
4,5-Dibromocatechol (8) - HSQC



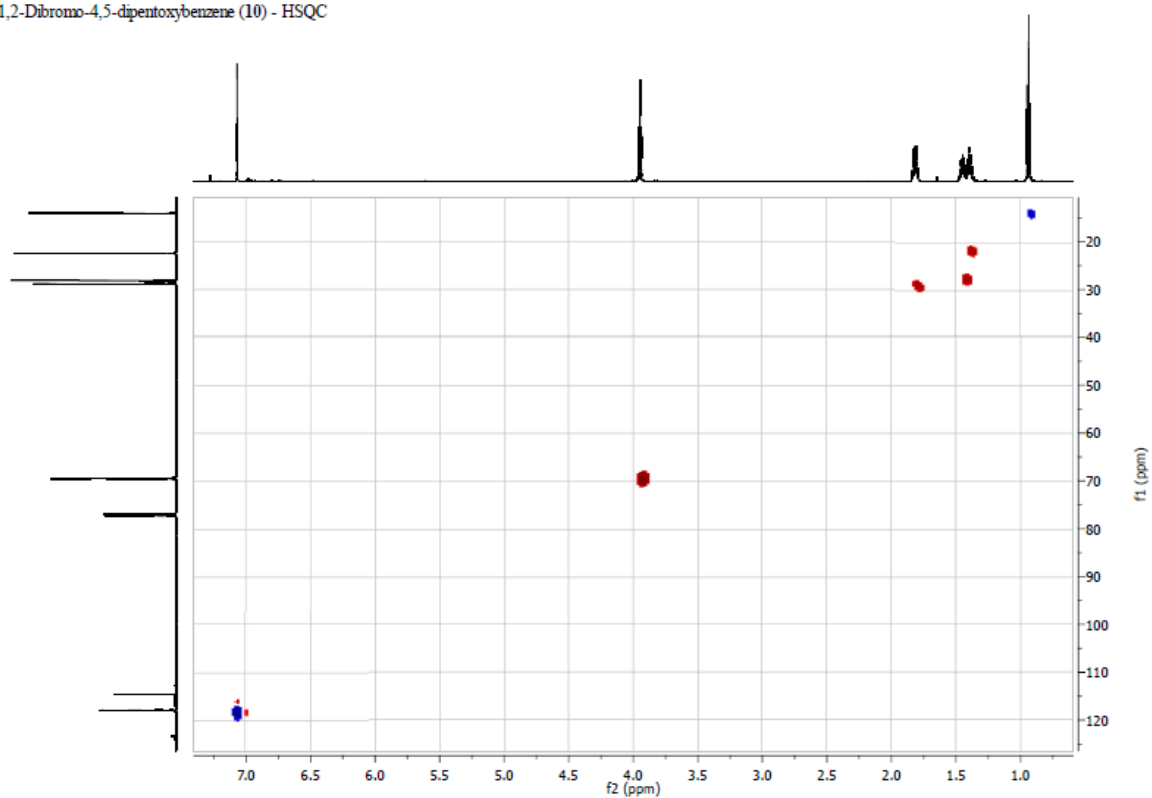
4,5-Dibromocatechol (8) - HMBC



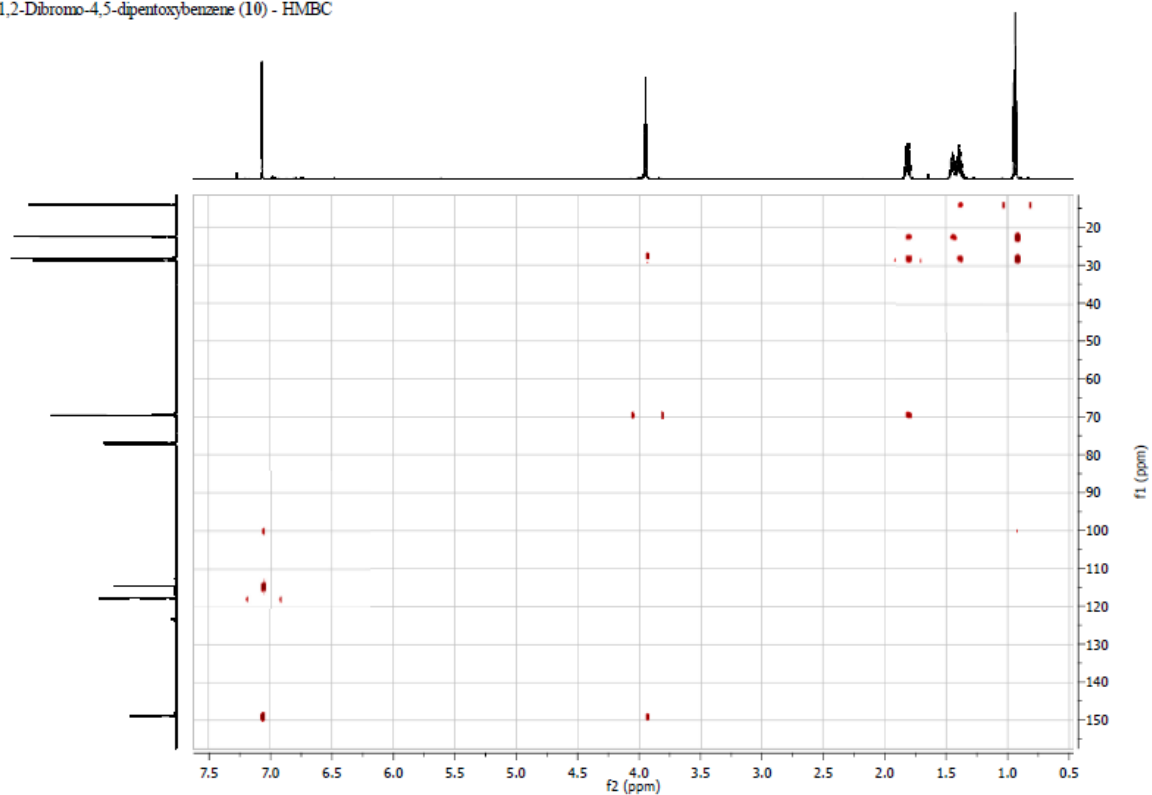
1,2-Dibromo-4,5-dipentoxybenzene (**10**)



1,2-Dibromo-4,5-dipentoxybenzene (10) - HSQC

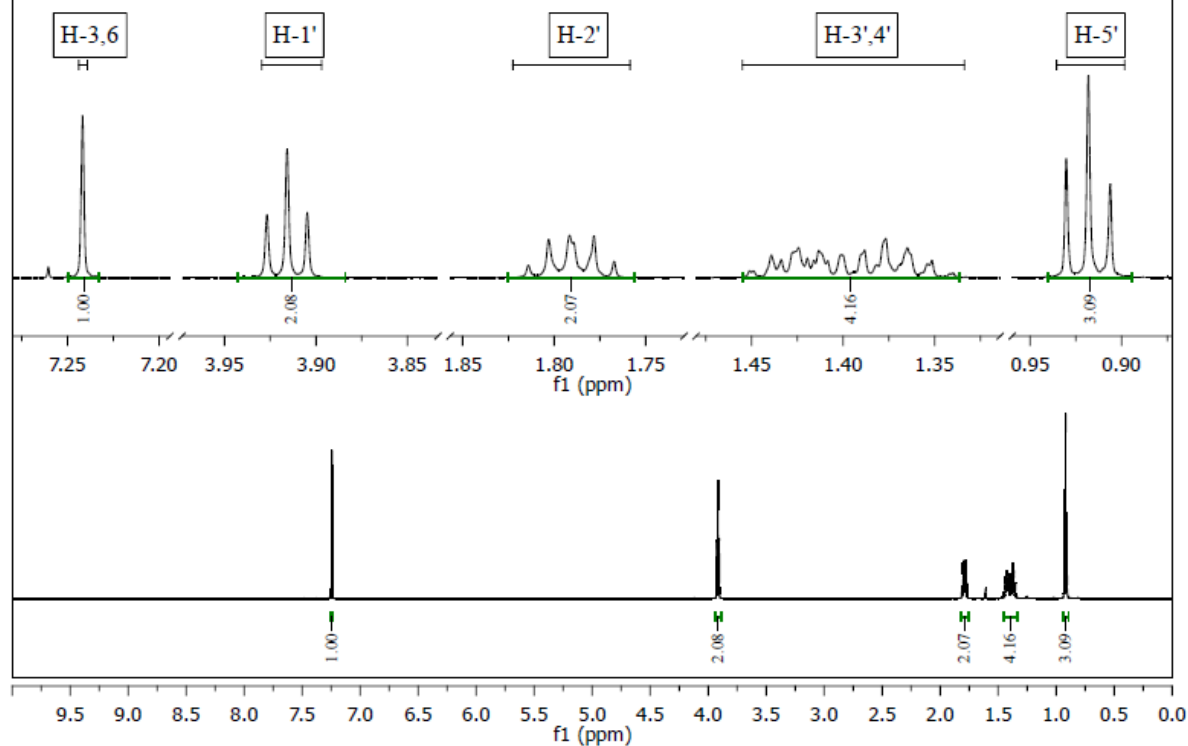
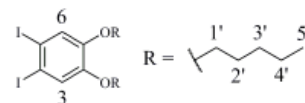


1,2-Dibromo-4,5-dipentoxybenzene (10) - HMBC

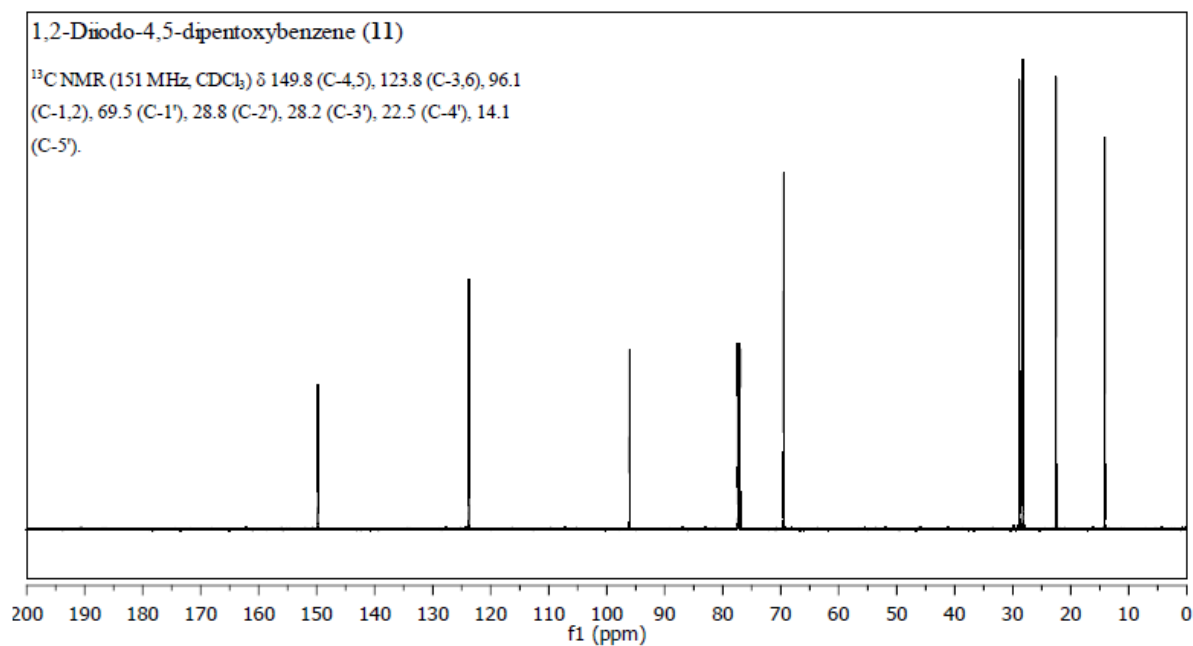


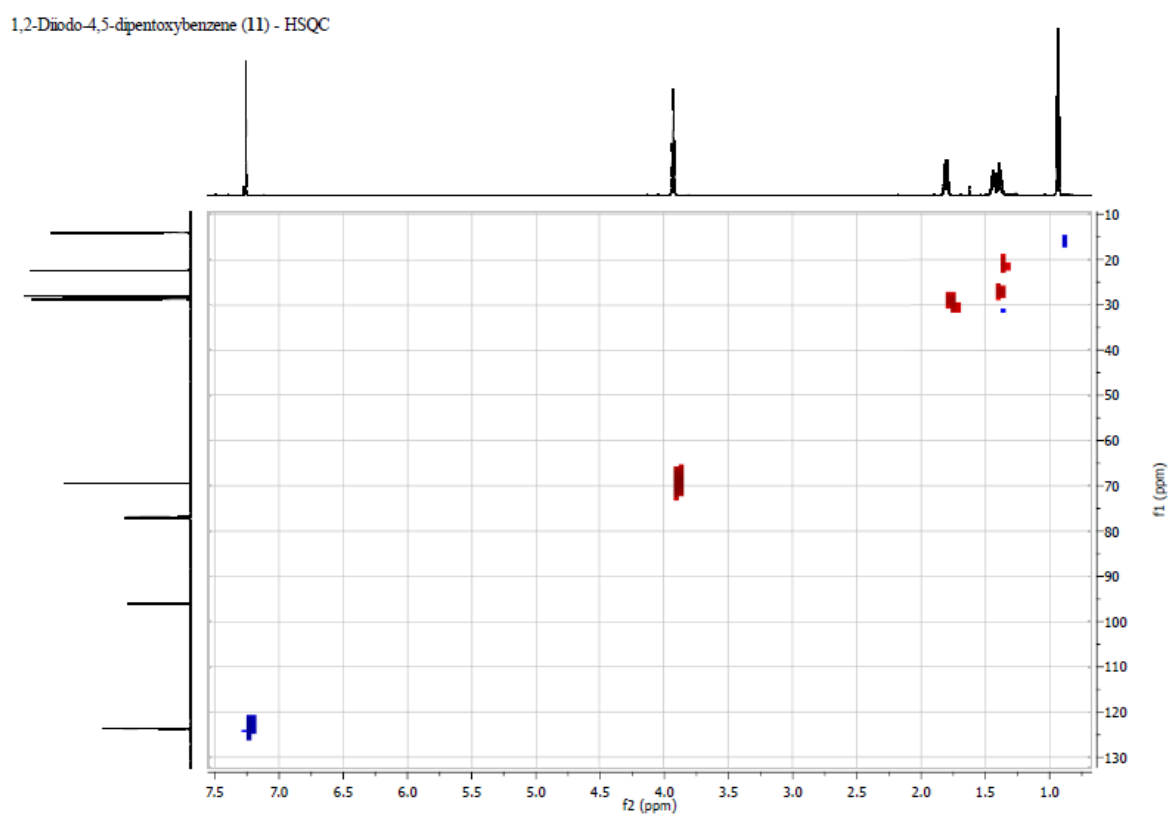
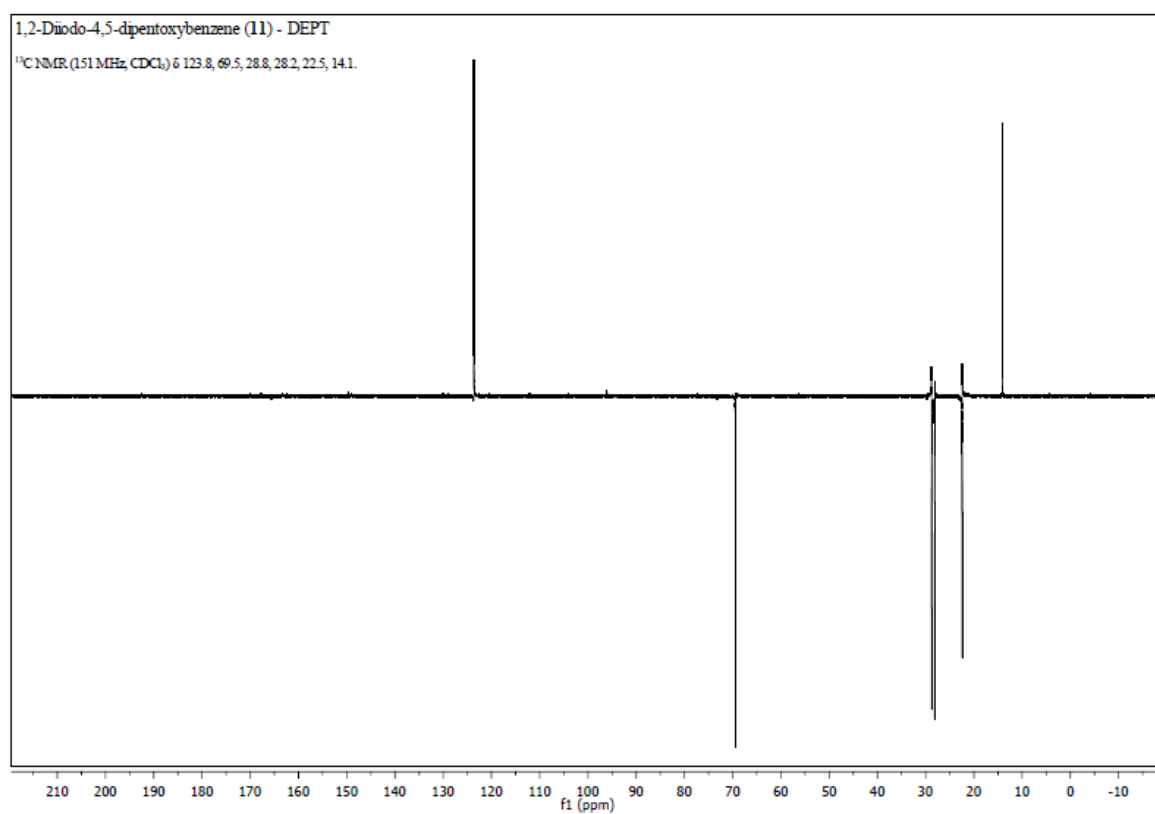
1,2-Diiodo-4,5-dipentoxybenzene (**11**)1,2-Diiodo-4,5-dipentoxybenzene (**11**)

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.24 (1H, s, H-3,6), 3.92 (2H, t, $J = 6.6$ Hz, H-1'), 1.82–1.76 (2H, m, H-2'), 1.46–1.33 (4H, m, H-3',4'), 0.92 (3H, t, $J = 7.2$ Hz, H-5').

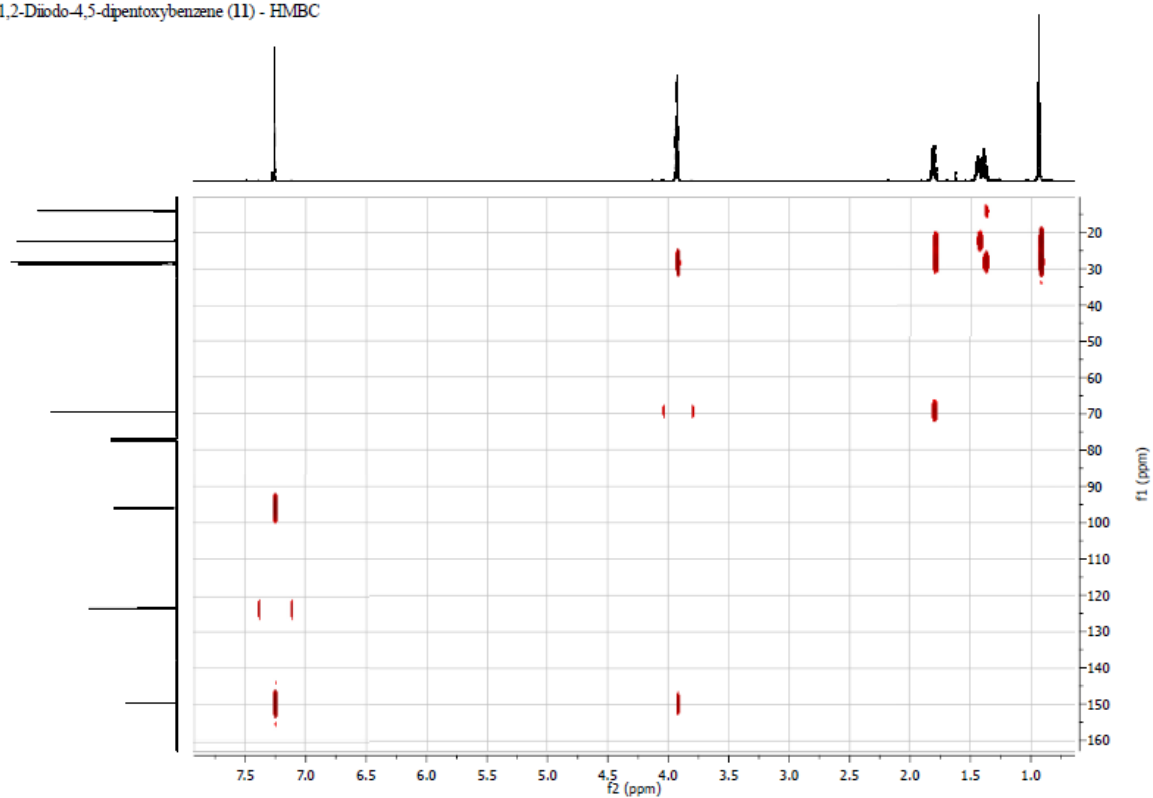
1,2-Diiodo-4,5-dipentoxybenzene (**11**)

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 149.8 (C-4,5), 123.8 (C-3,6), 96.1 (C-1,2), 69.5 (C-1'), 28.8 (C-2'), 28.2 (C-3'), 22.5 (C-4'), 14.1 (C-5').

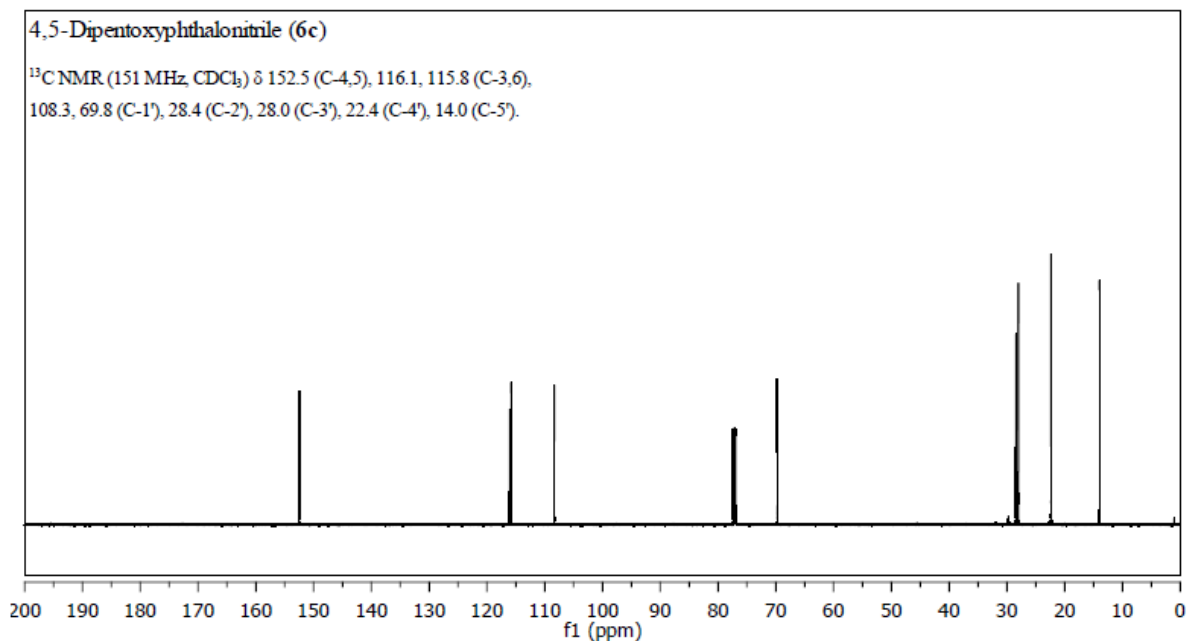
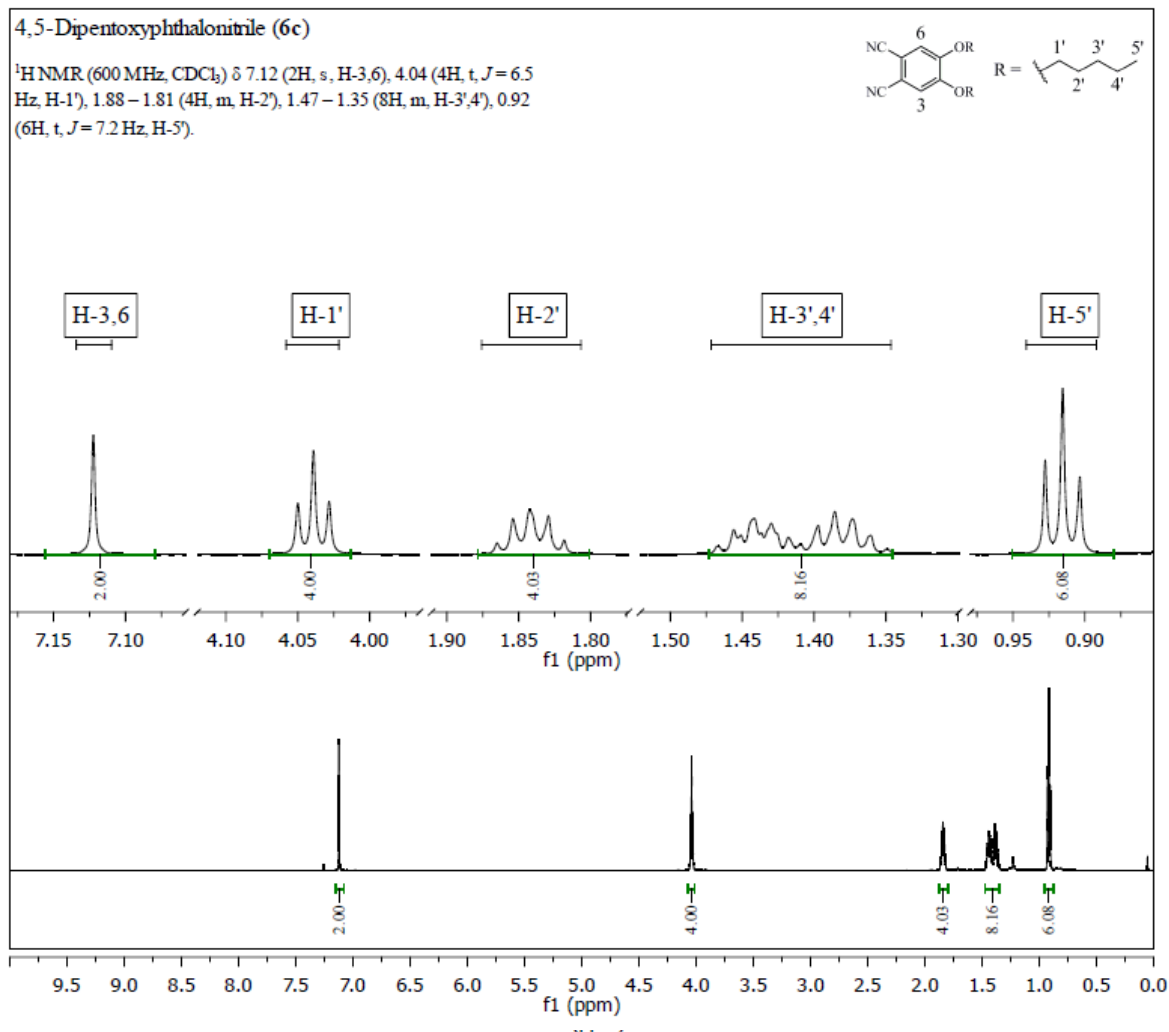


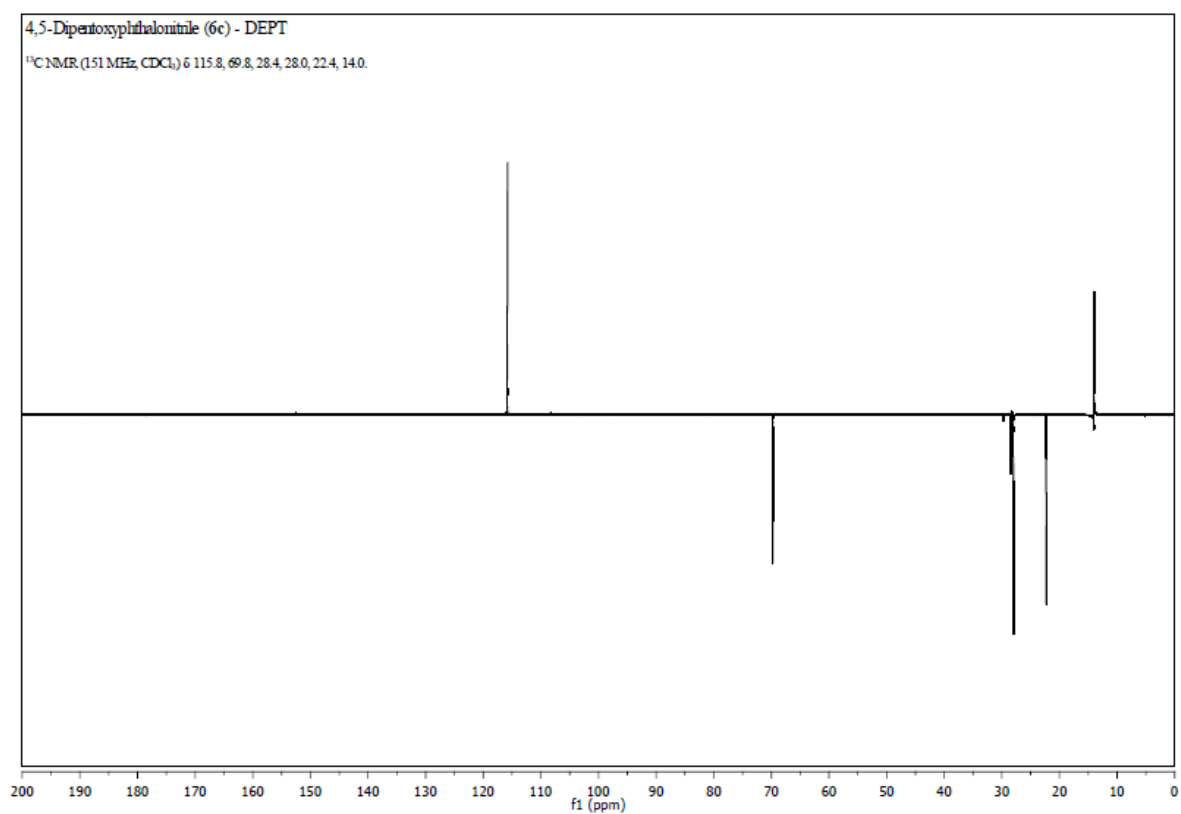


1,2-Diiodo-4,5-dipentoxybenzene (11) - HMBC

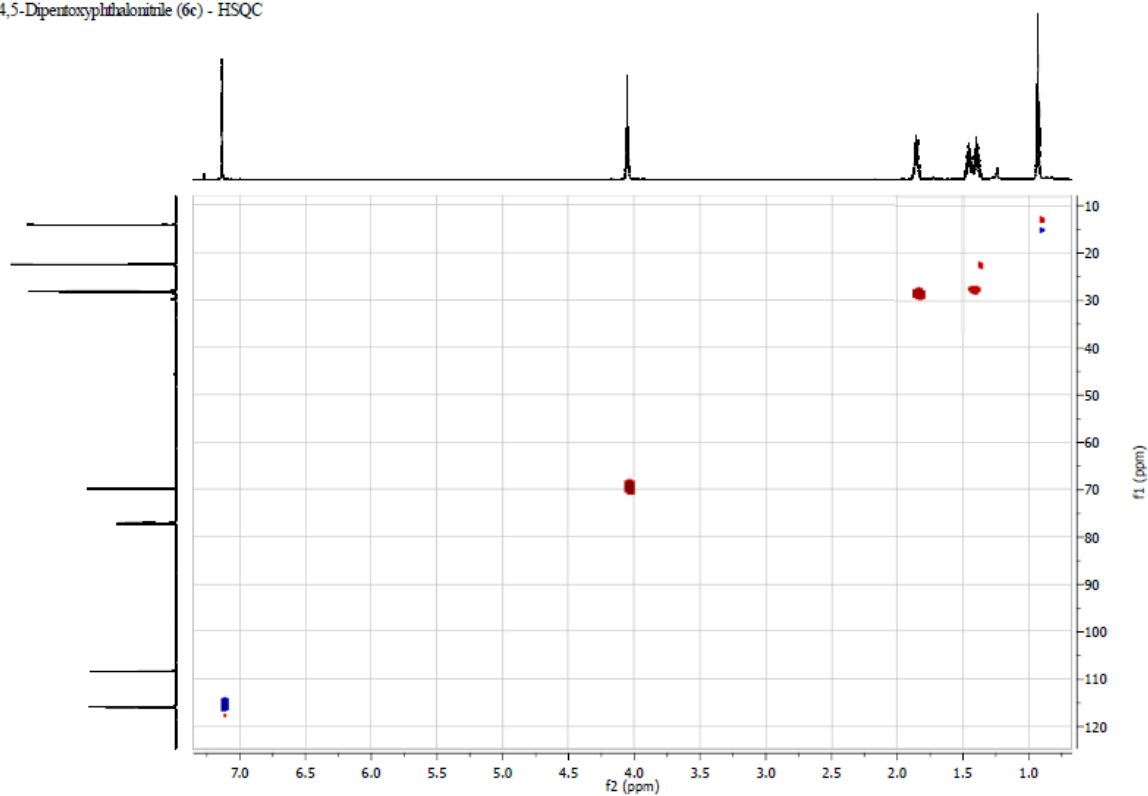


4,5-Dipentoxyphthalonitrile (6c)

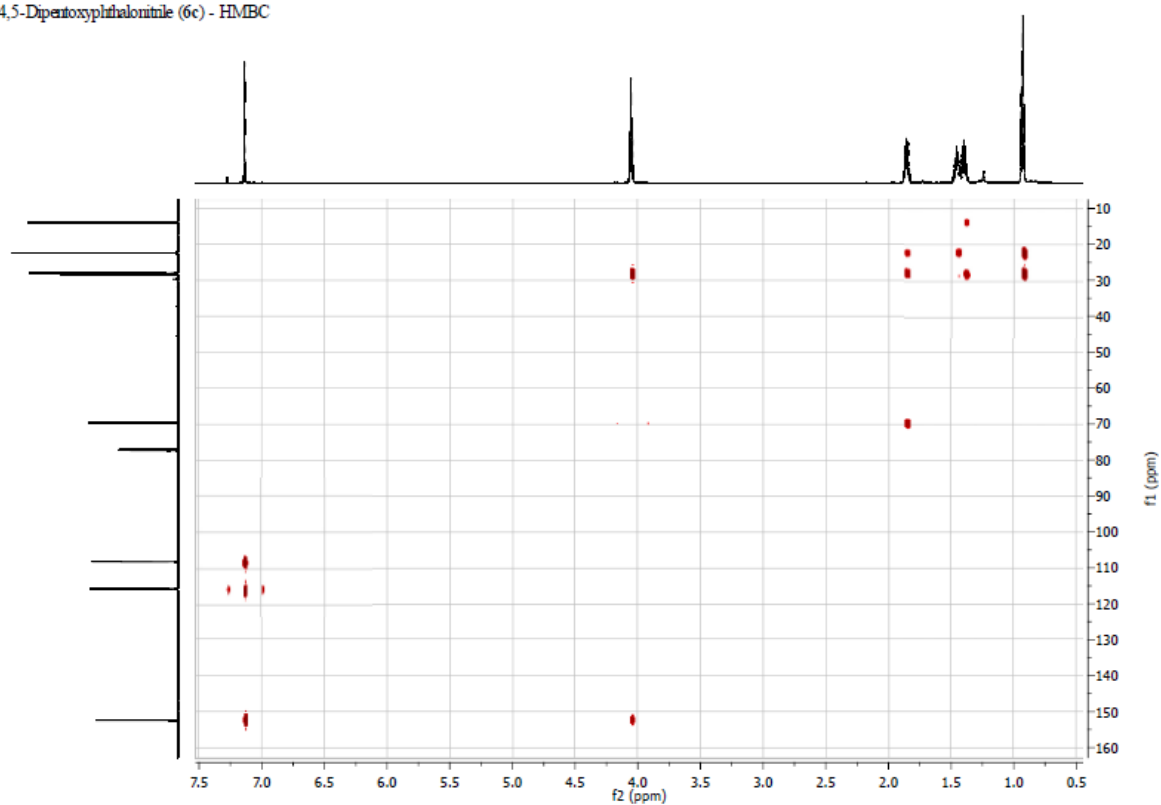




4,5-Dipentoxypthalonitrile (6c) - HSQC



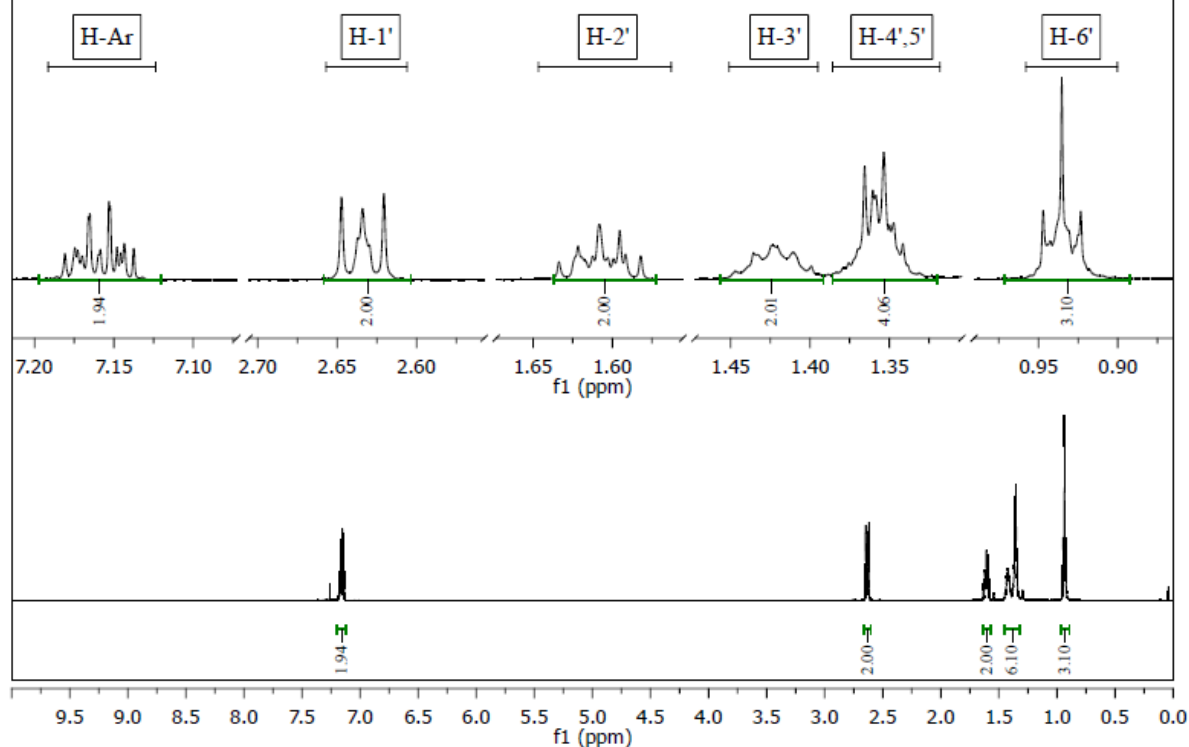
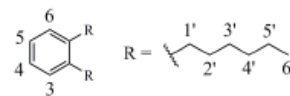
4,5-Dipentoxypthalonitrile (6c) - HMBC



1,2-Dihexylbenzene (13a)

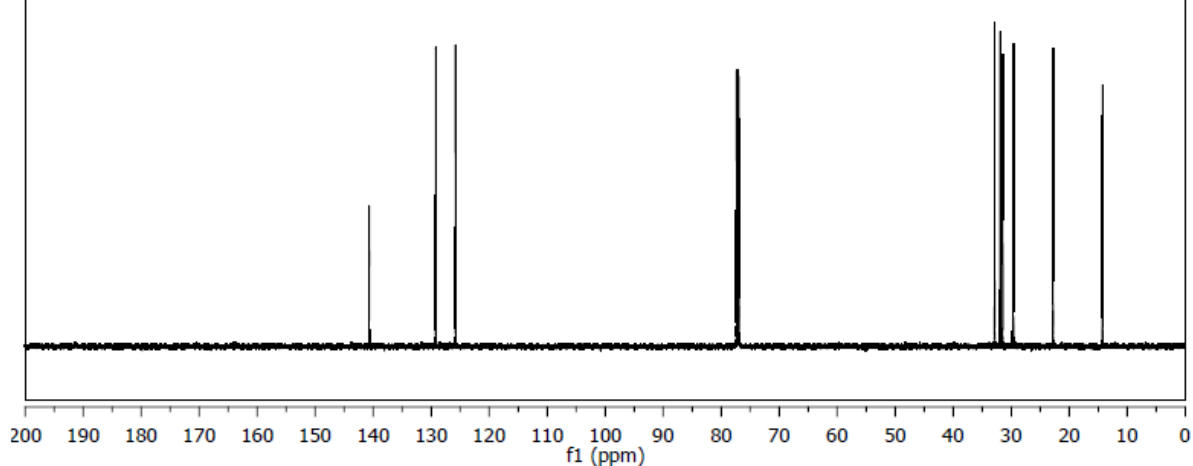
1,2-Dihexylbenzene (13a)

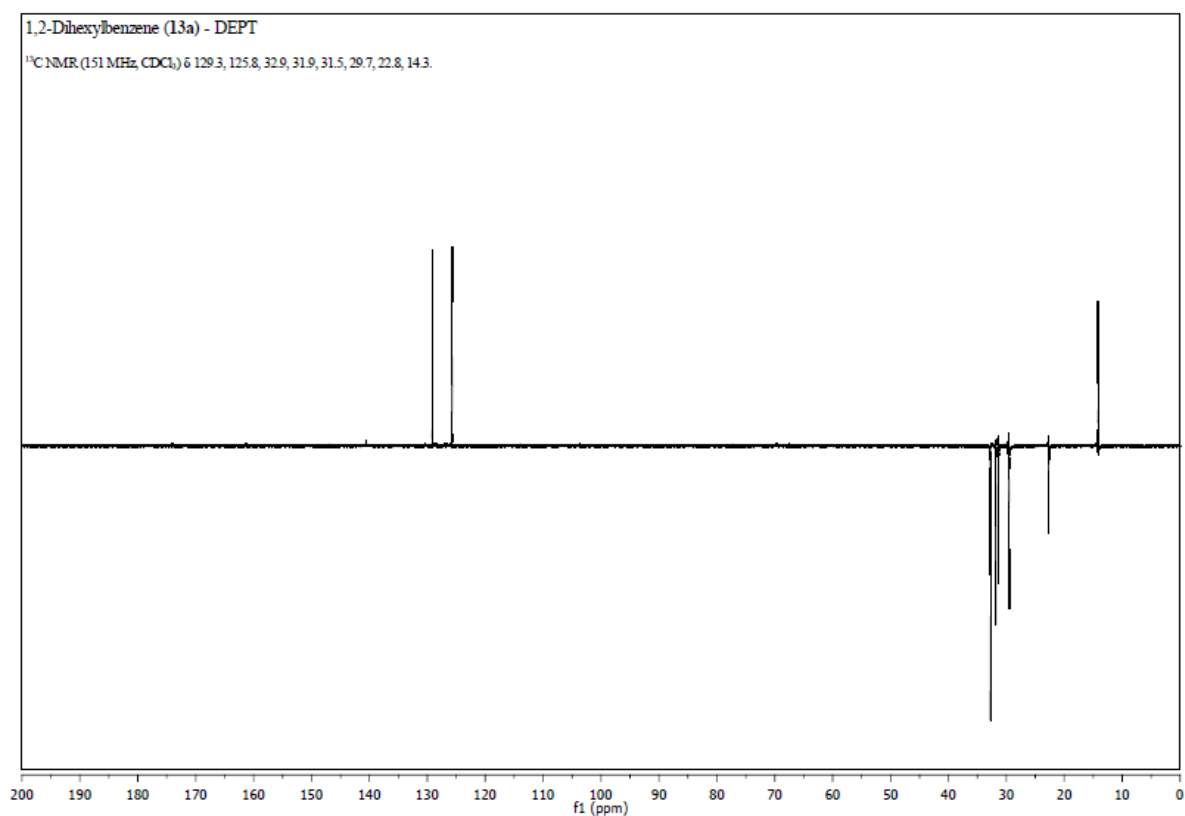
^1H NMR (600 MHz, CDCl_3) δ 7.19 – 7.12 (2H, m, H-Ar), 2.66 – 2.61 (2H, m, H-1'), 1.65 – 1.56 (2H, m, H-2'), 1.45 – 1.40 (2H, m, H-3'), 1.39 – 1.32 (4H, m, H-4',5'), 0.96 – 0.90 (3H, m, H-6').



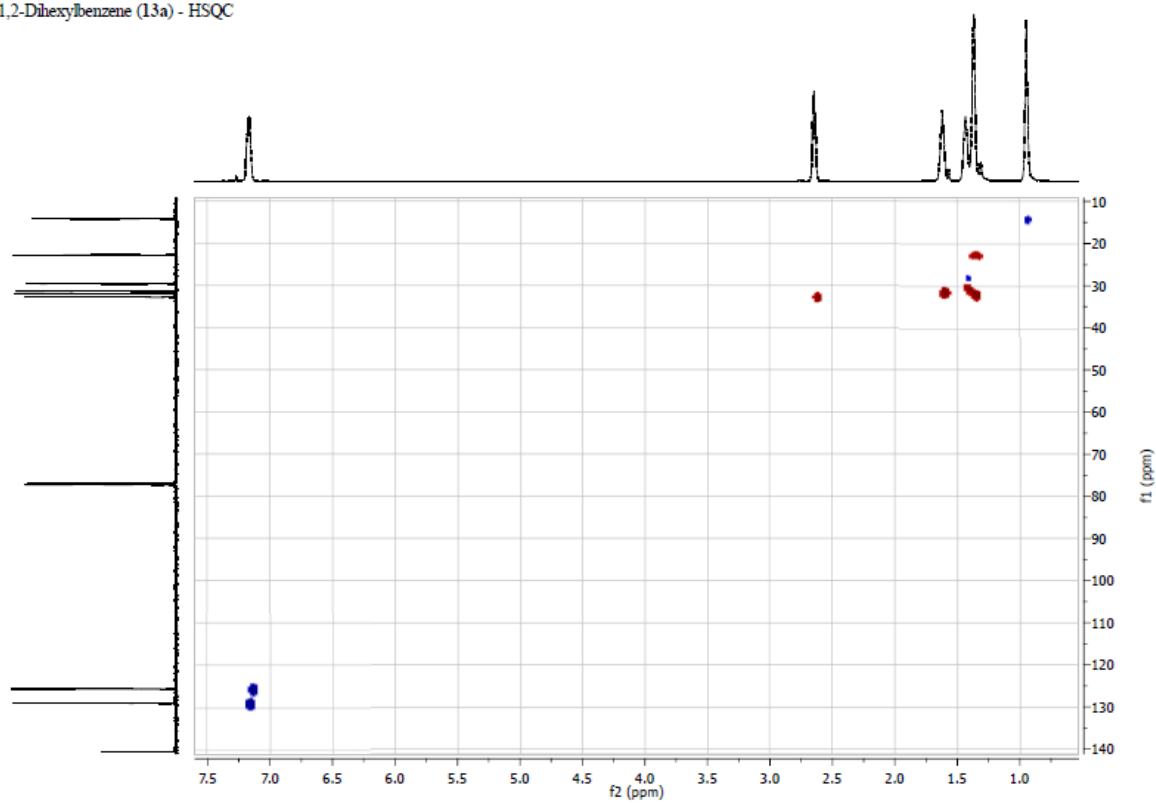
1,2-Dihexylbenzene (13a)

^{13}C NMR (151 MHz, CDCl_3) δ 140.7 (C-1,2), 129.2 (C-4,5), 125.8 (C-3,6), 32.9 (C-1'), 31.9 (C-2'), 31.5 (C-3'), 29.7 (C-4'), 22.8 (C-5'), 14.3 (C-6').

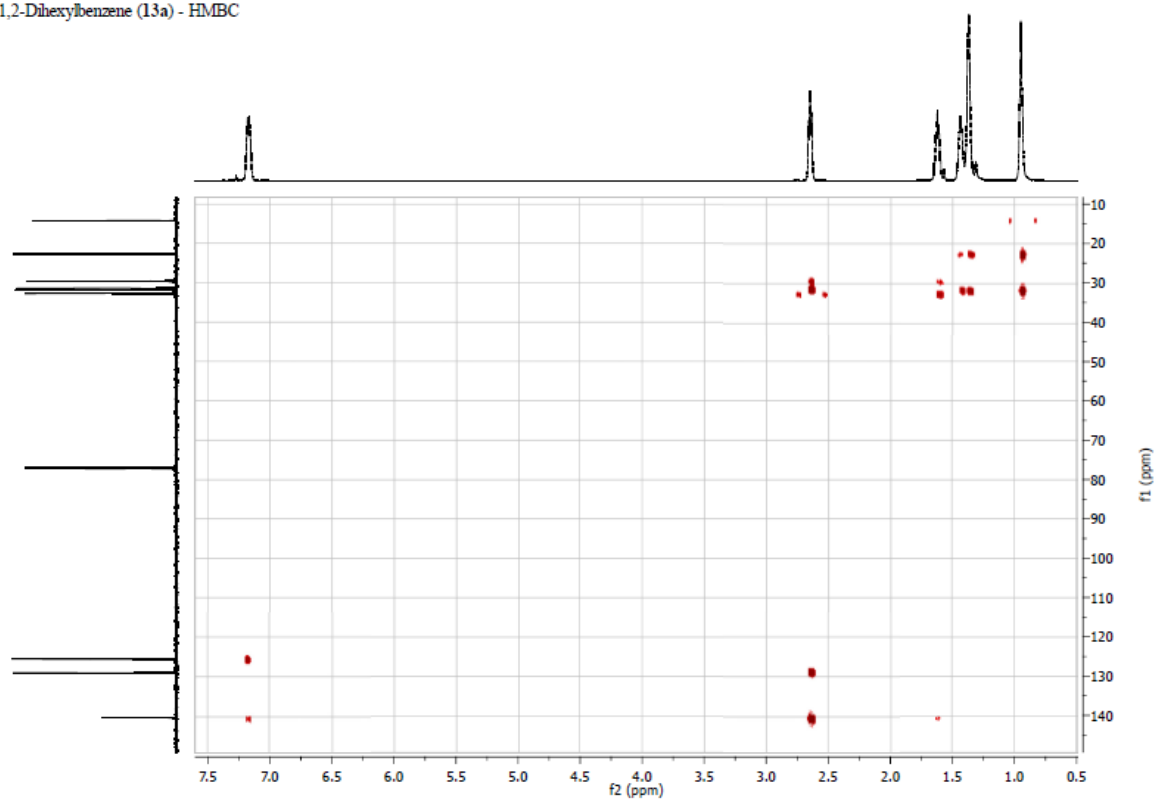




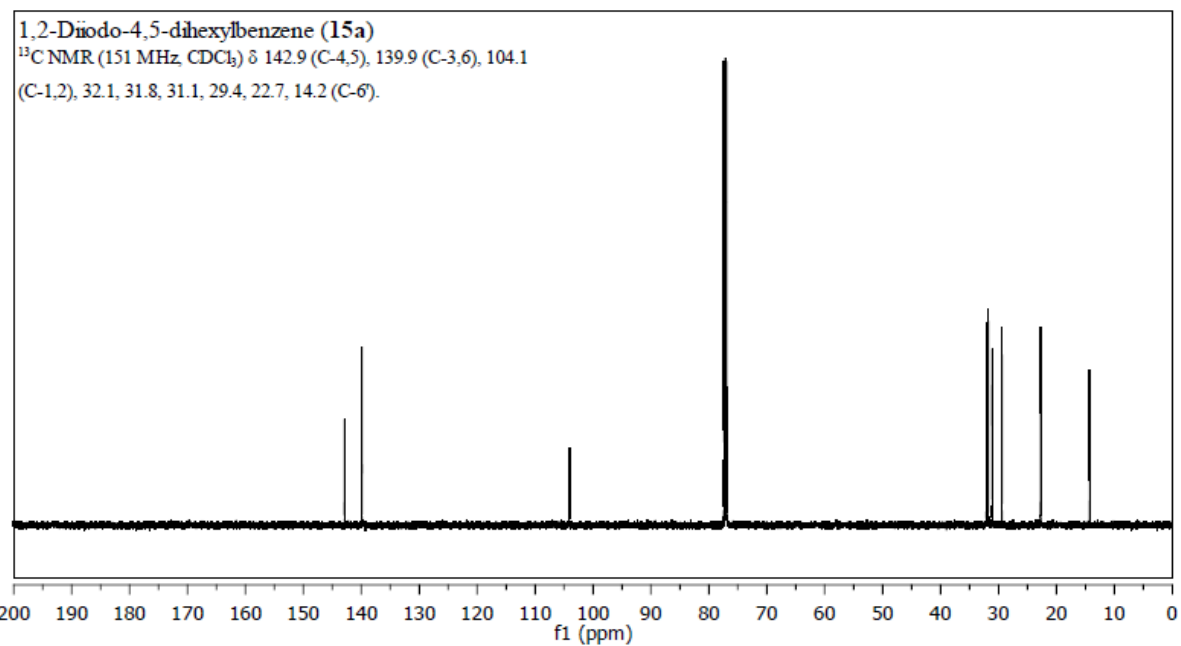
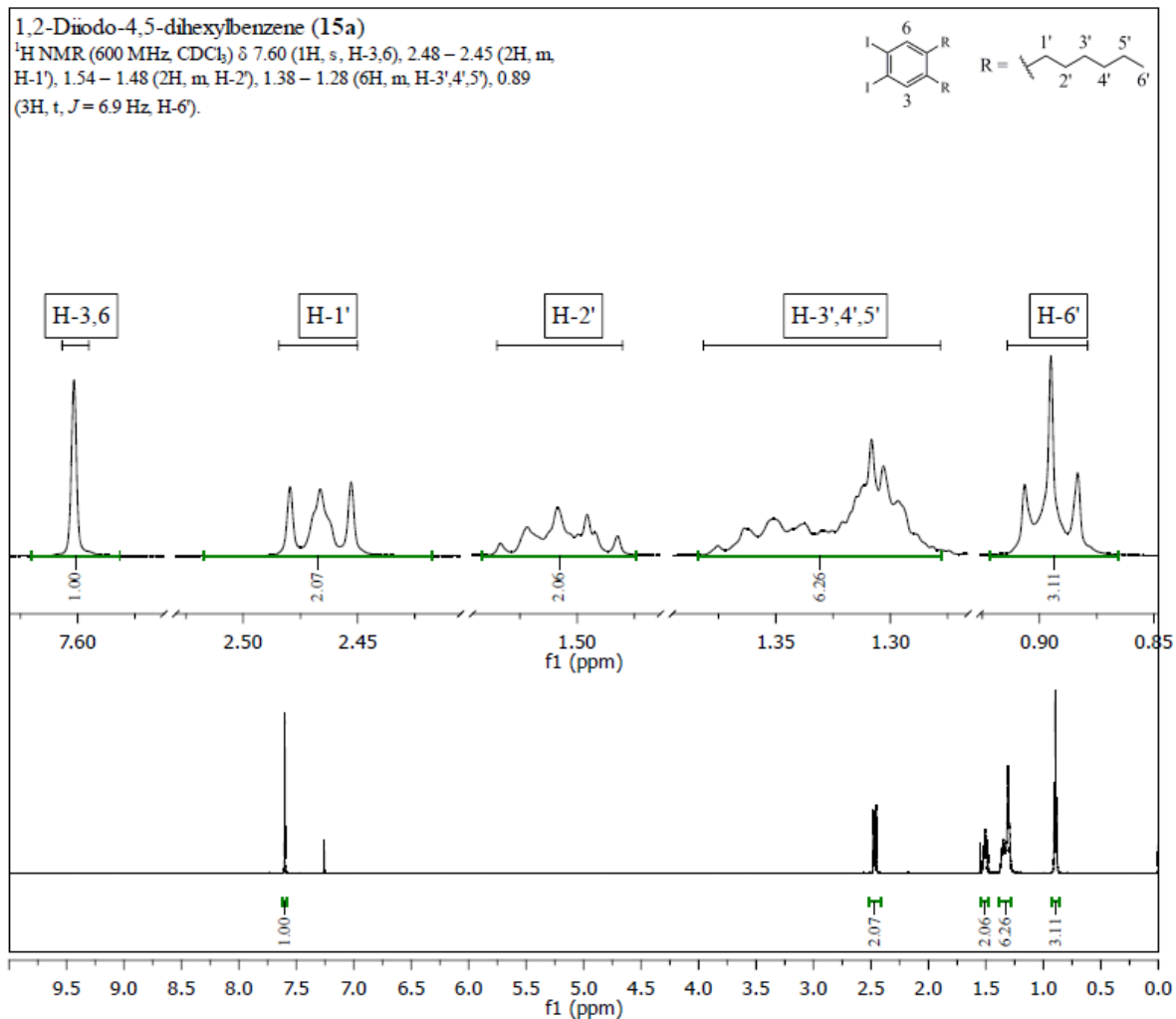
1,2-Dihexylbenzene (13a) - HSQC

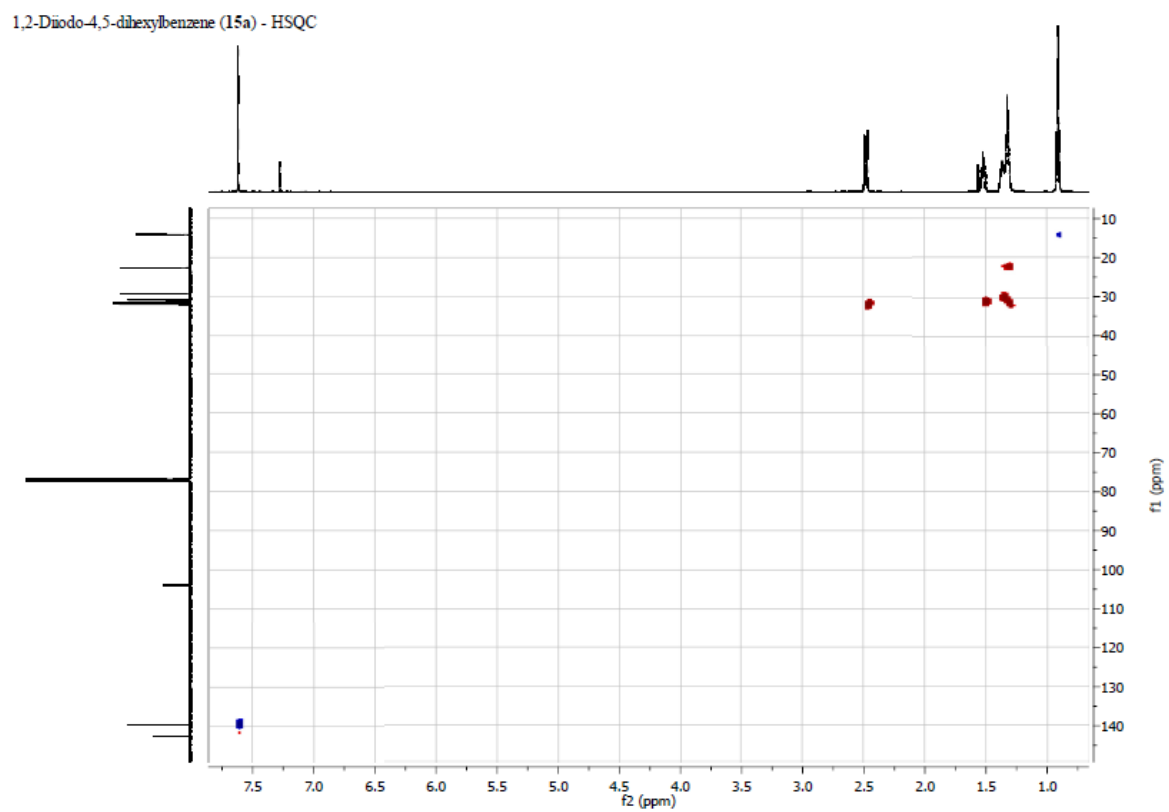
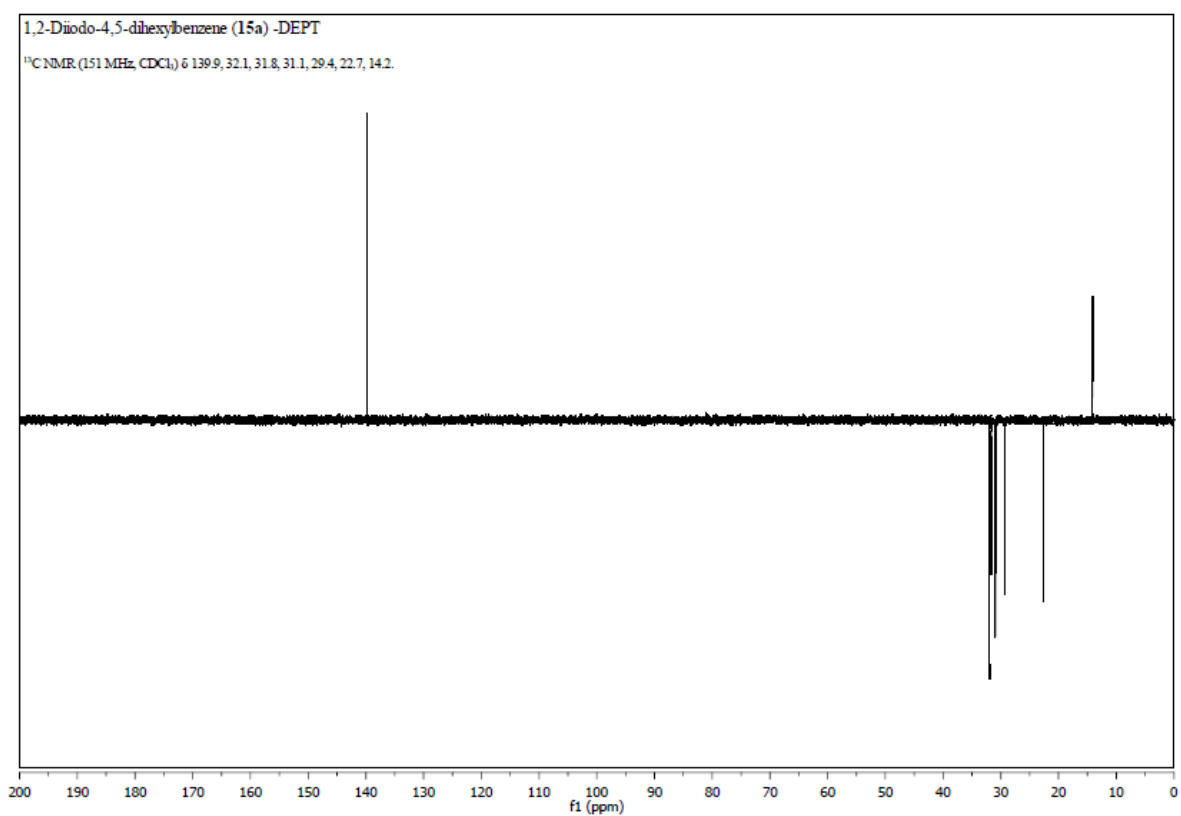


1,2-Dihexylbenzene (13a) - HMBC

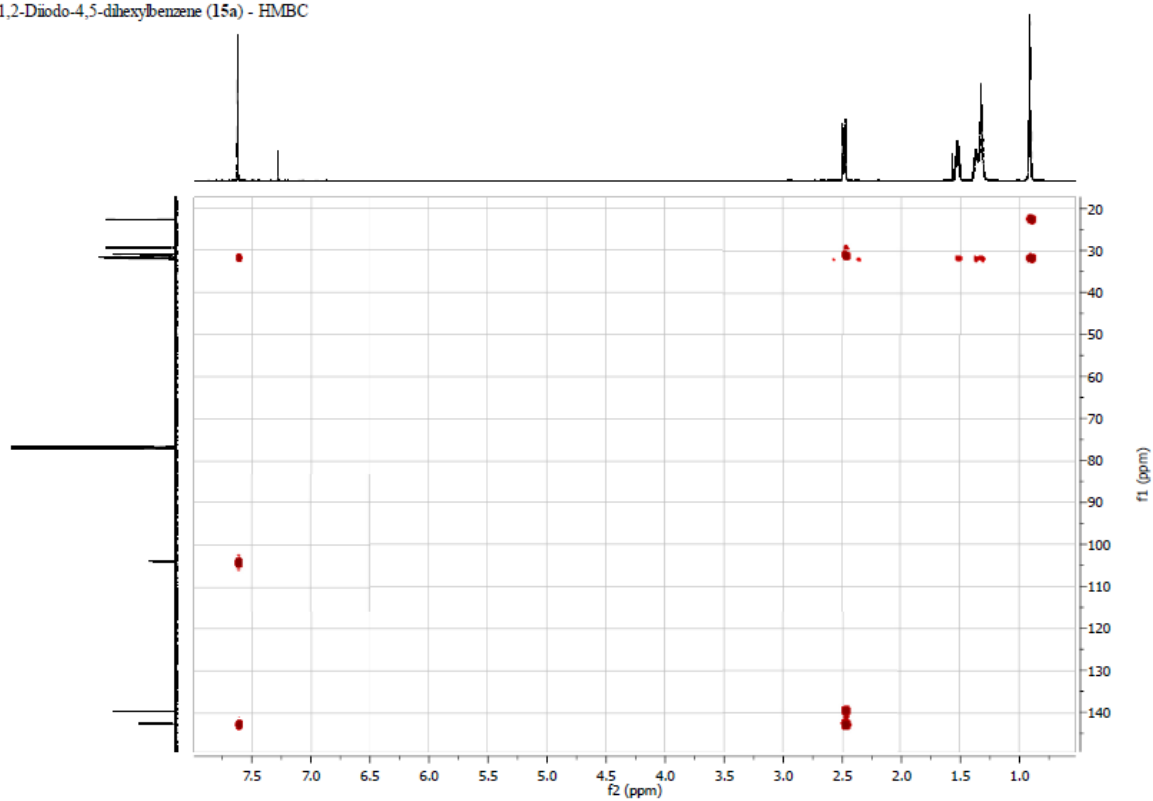


1,2-Diiodo-4,5-dihexylbenzene (15a)



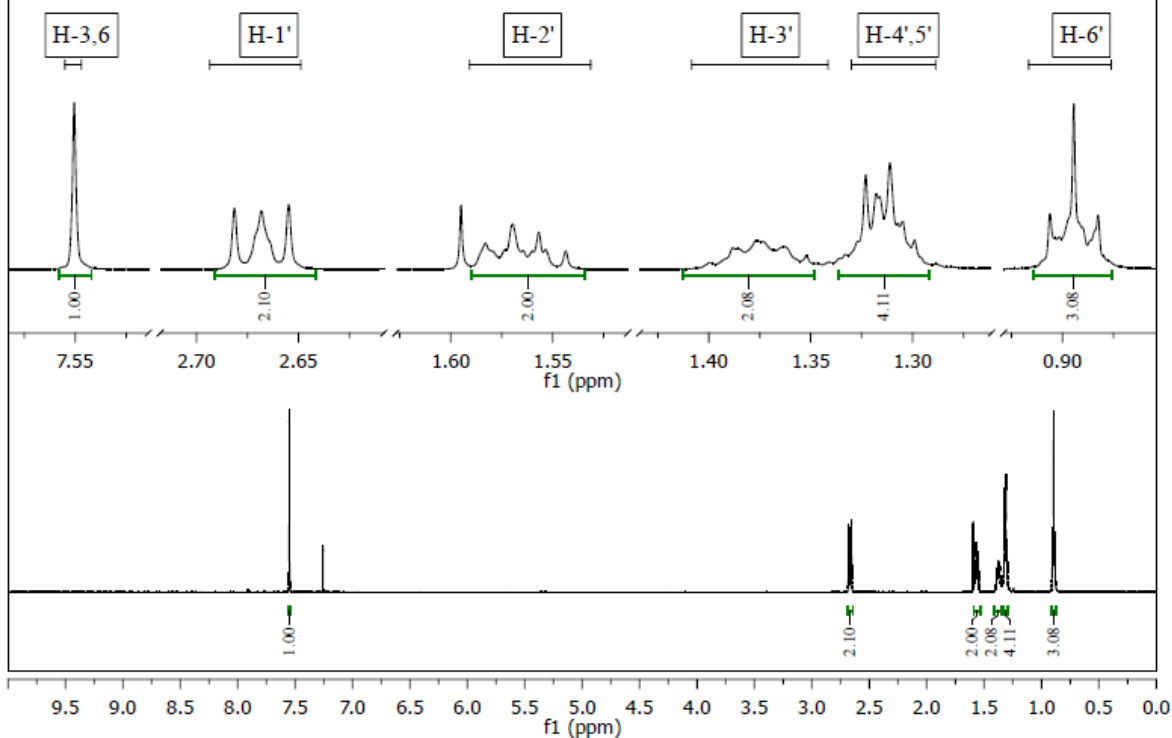
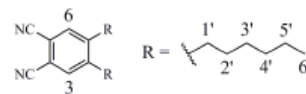


1,2-Diiodo-4,5-dihexylbenzene (15a) - HMBC

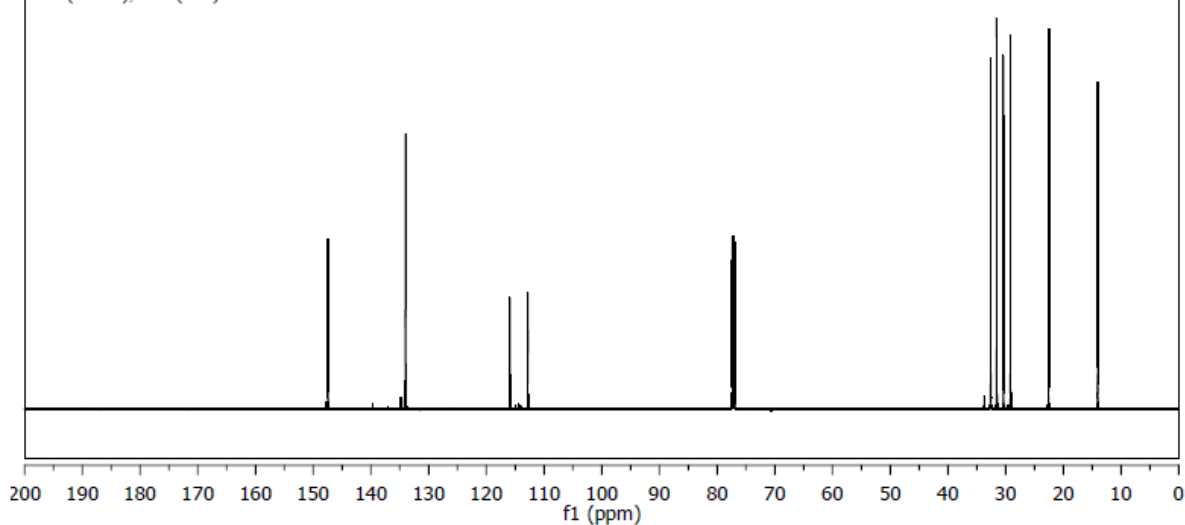


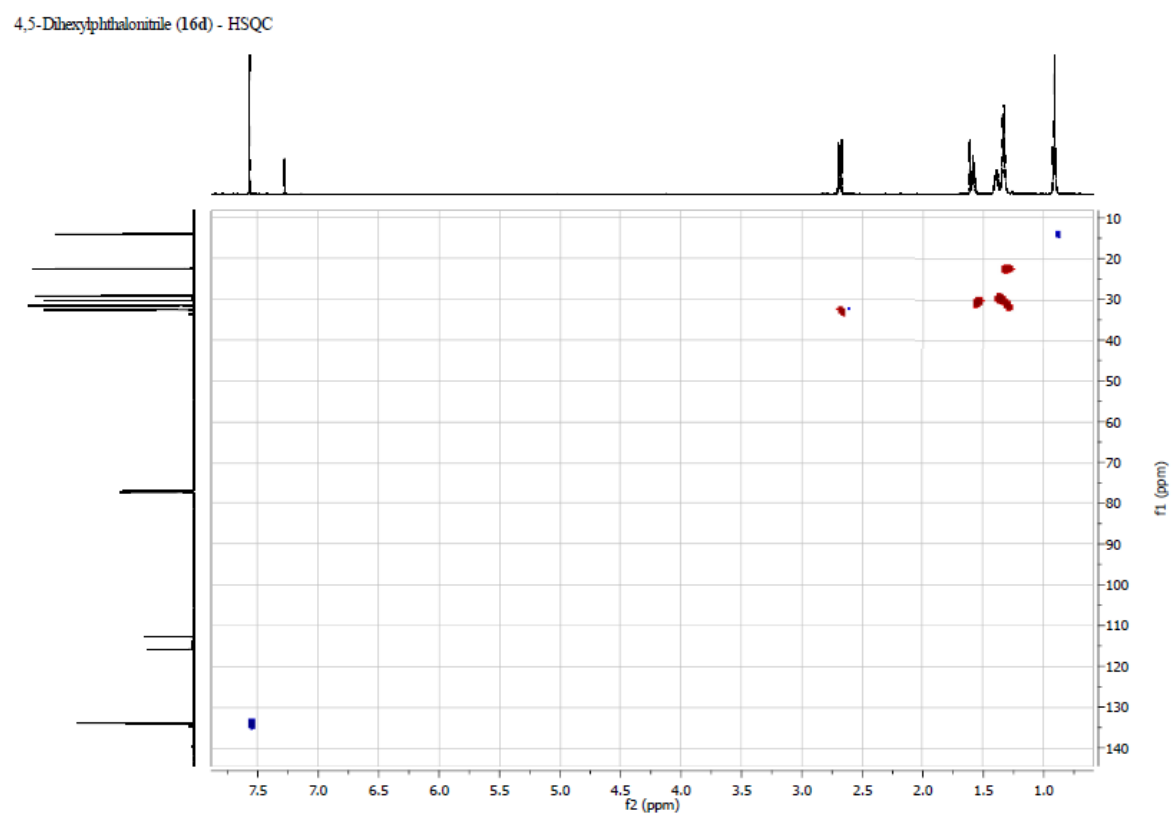
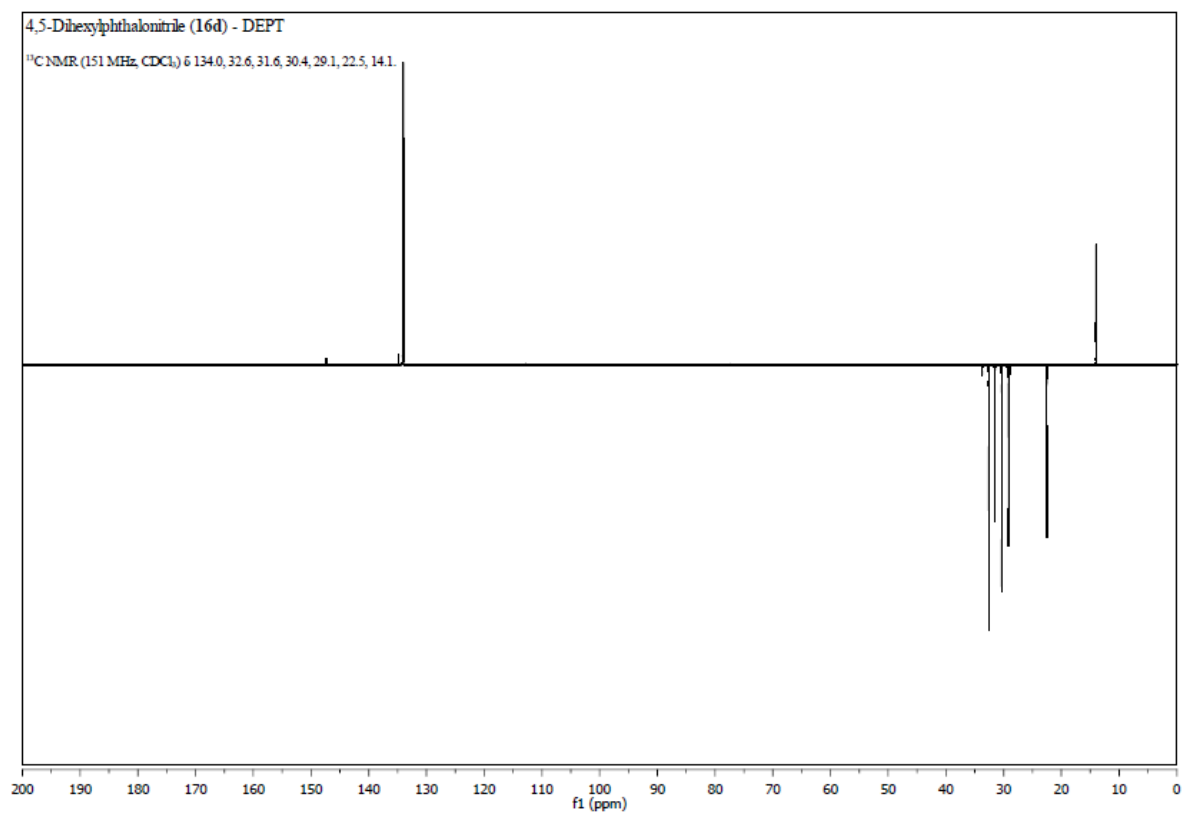
4,5-Dihexylphthalonitrile (**16d**)4,5-Dihexylphthalonitrile (**16d**)

^1H NMR (600 MHz, CDCl_3) δ 7.55 (s, 2H), 2.67 (t, $J = 8.0$ Hz, 4H), 1.59 – 1.53 (m, 4H), 1.41 – 1.34 (m, 4H), 1.33 – 1.29 (m, 8H), 0.89 (t, $J = 7.1$ Hz, 6H).

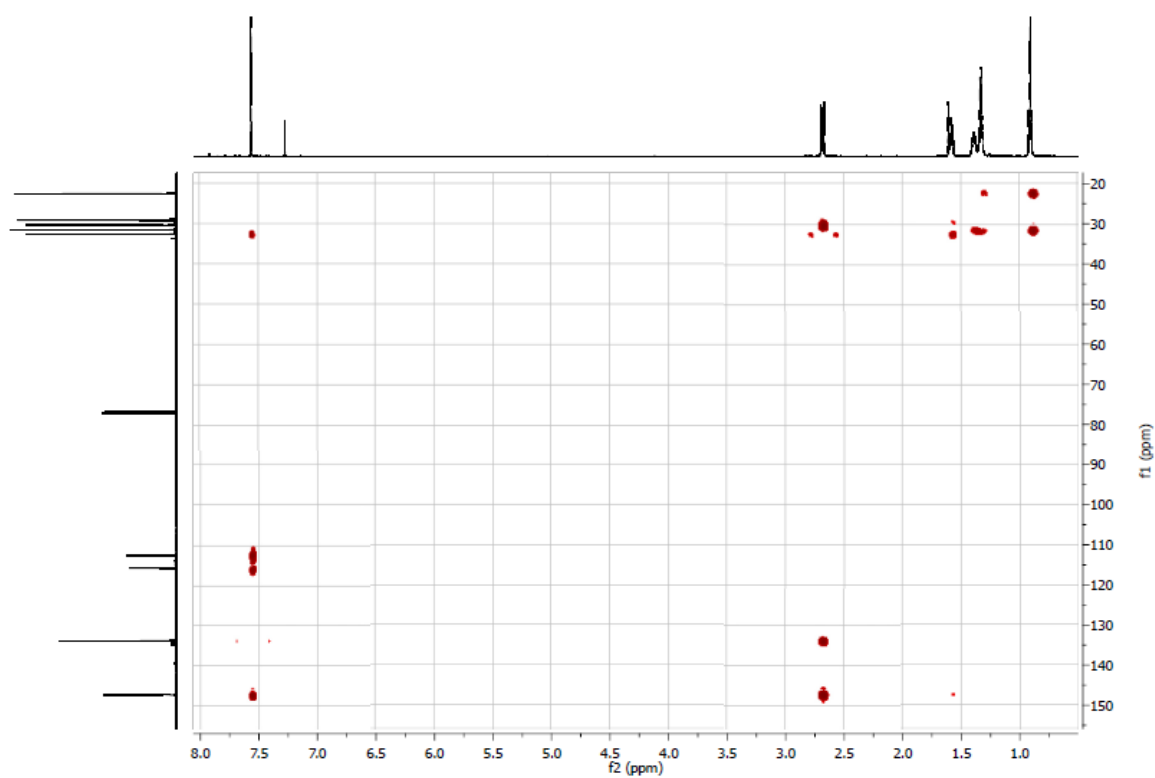
4,5-Dihexylphthalonitrile (**16d**)

^{13}C NMR (151 MHz, CDCl_3) δ 147.5 (C-4,5), 134.0 (C-3,6), 115.9 (CN), 112.8 (C-1,2), 32.6 (C-1'), 31.6 (C-4'/5'), 30.4 (C-2'), 29.2 (C-3'), 22.5 (C-4'/5'), 14.1 (C-6').





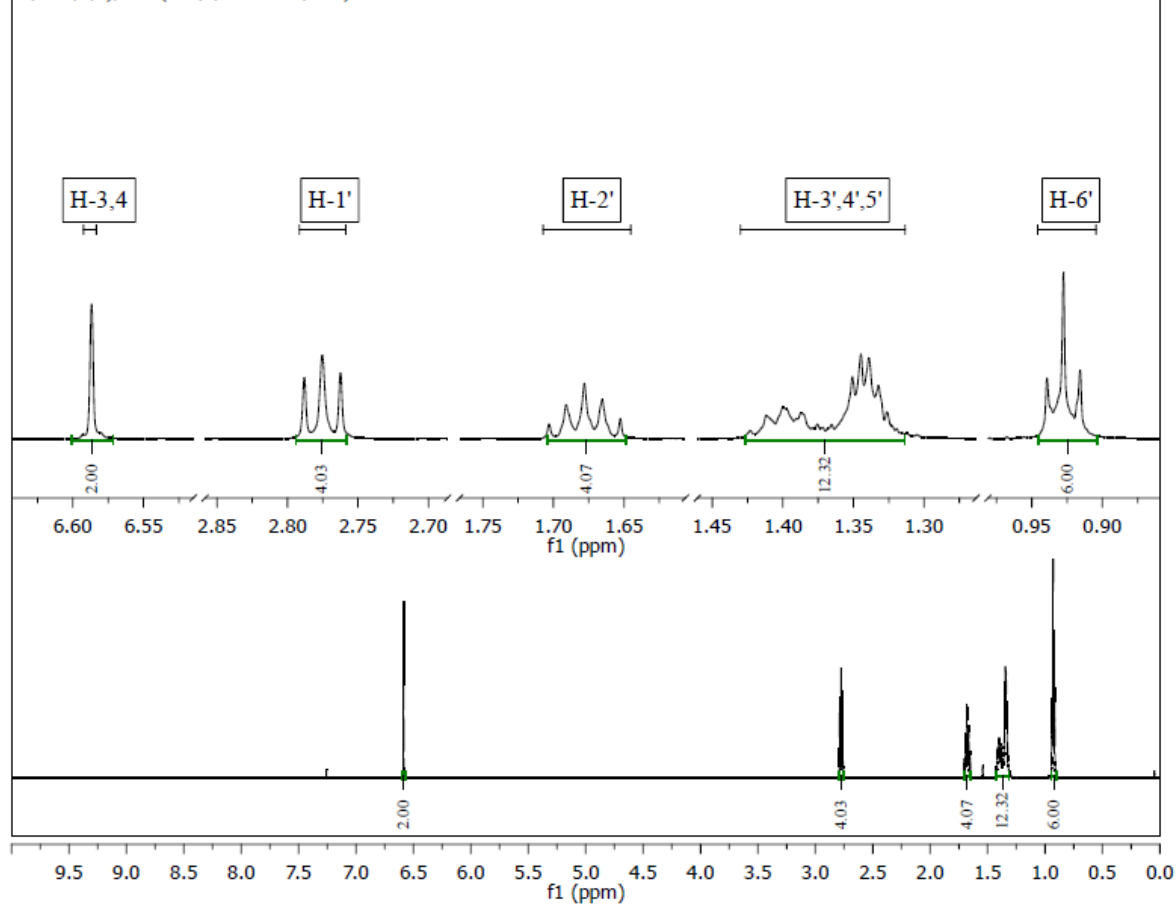
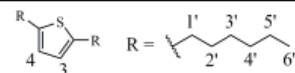
4,5-Dihexylphthalonitrile (16d) - HMBC



2,5-Dihexylthiophene (23a)

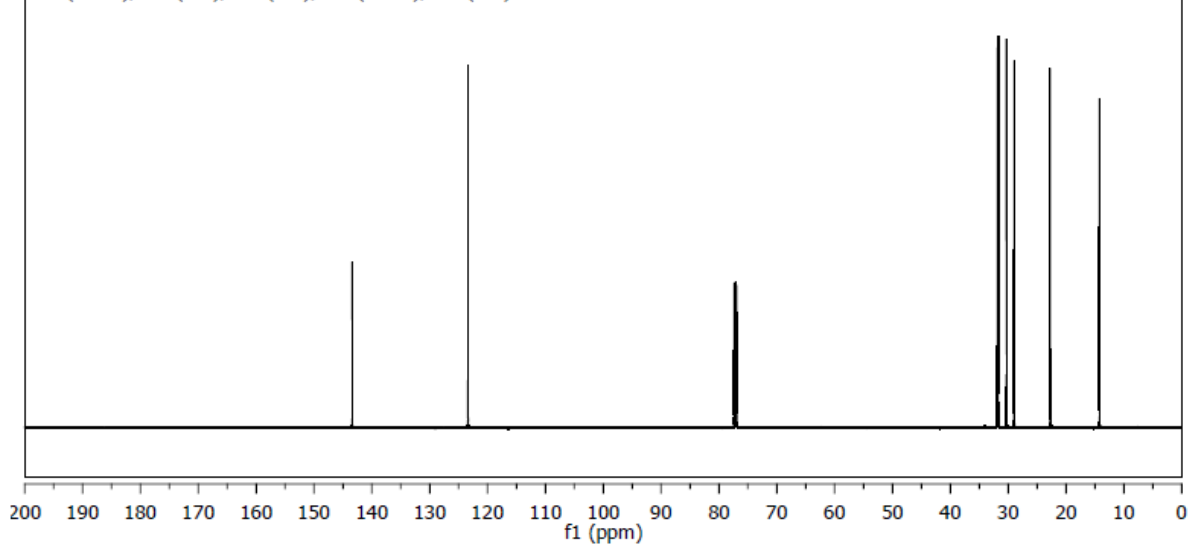
2,5-Dihexylthiophene (23a)

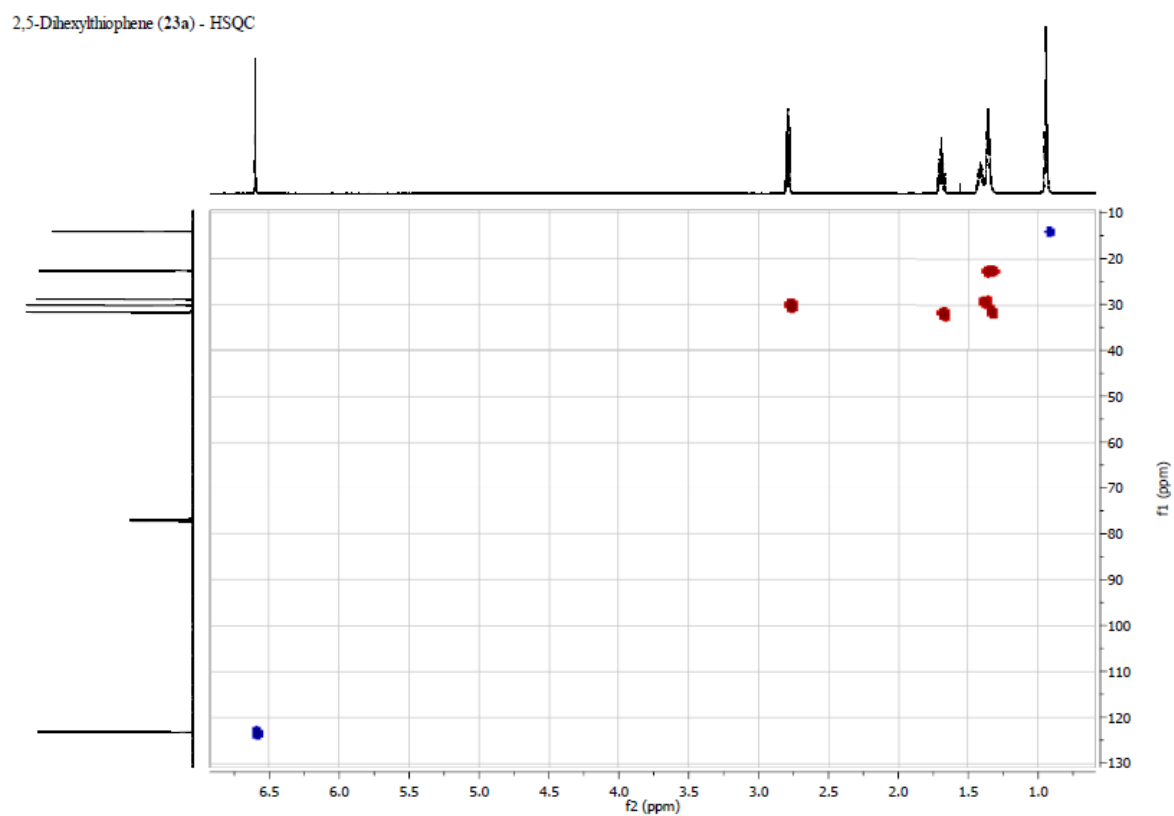
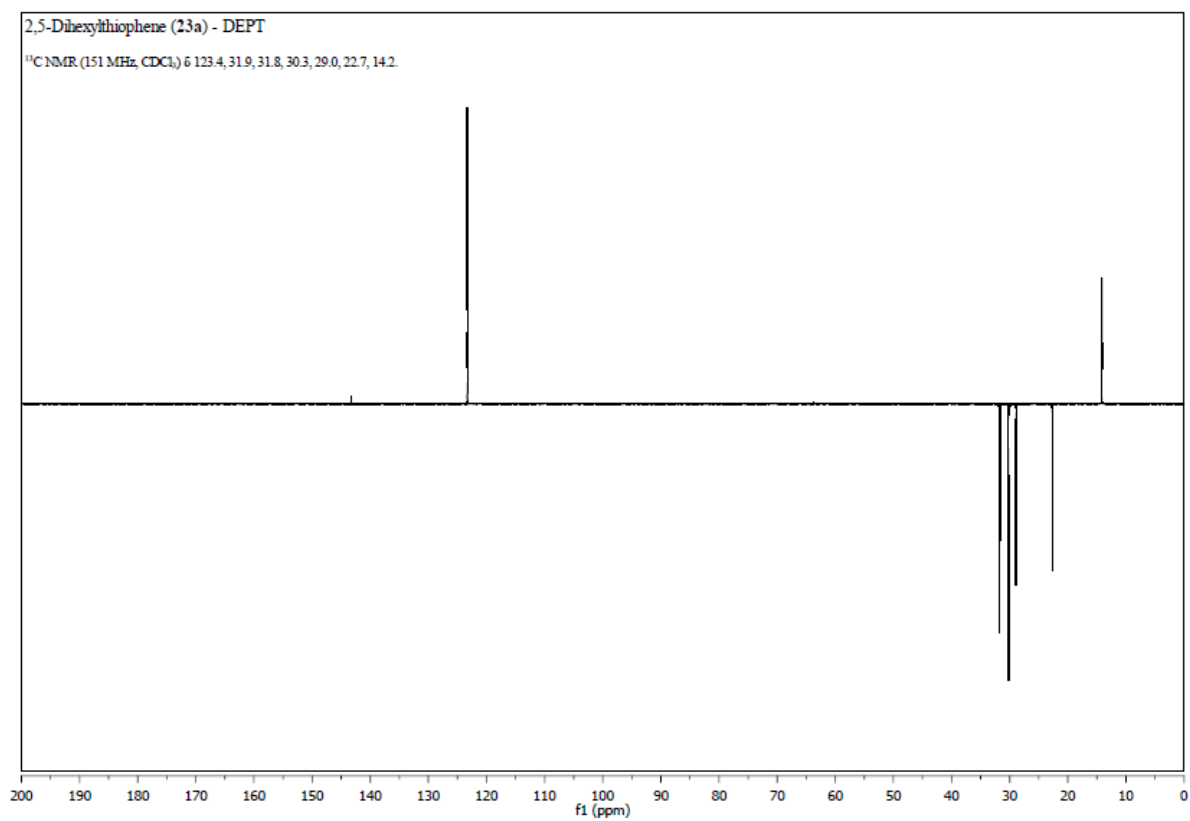
^1H NMR (600 MHz, CDCl_3) δ 6.59 (2H, s, H-3,4), 2.78 (4H, t, $J = 7.7$ Hz, H-1'), 1.71 – 1.65 (4H, m, $J = 15.3, 7.5$ Hz, H-2'), 1.43 – 1.31 (12H, m, H-3',4',5'), 0.93 (12H, t, $J = 7.0$ Hz, H-6').



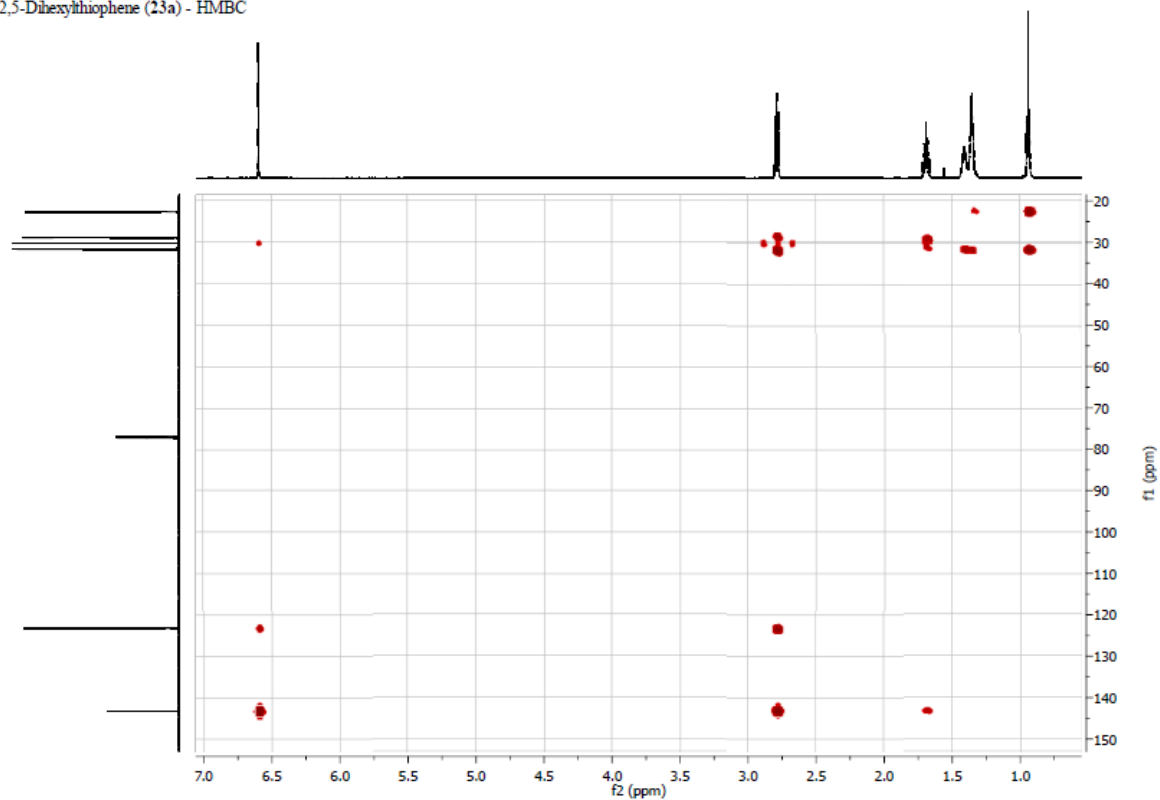
2,5-Dihexylthiophene (23a)

^{13}C NMR (151 MHz, CDCl_3) δ 143.4 (C-3,4), 123.4 (C-2,5), 31.9 (C-2), 31.8 (C-4'/5'), 30.3 (C-1'), 29.0 (C-3'), 22.7 (C-4'/5'), 14.2 (C-6').

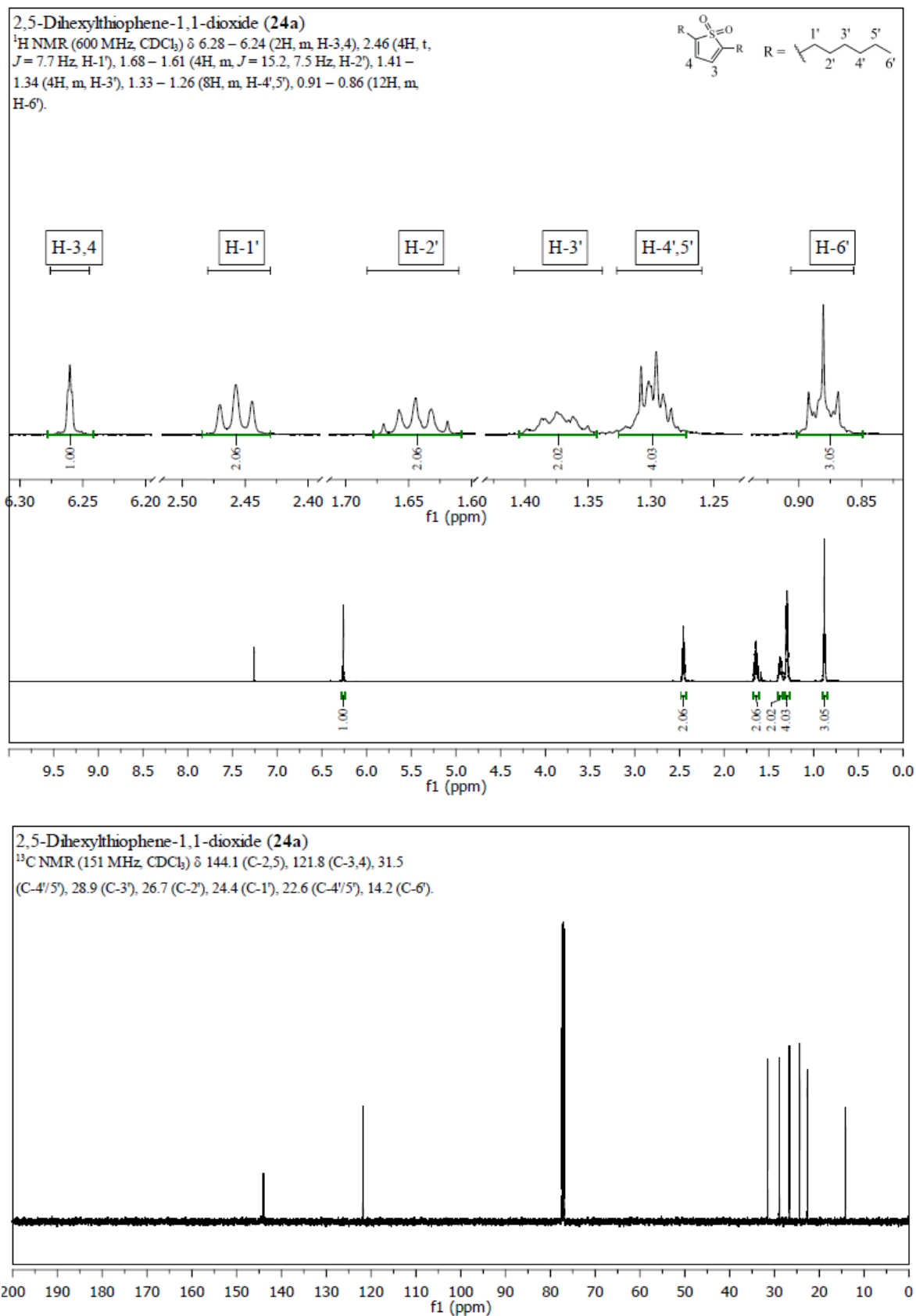




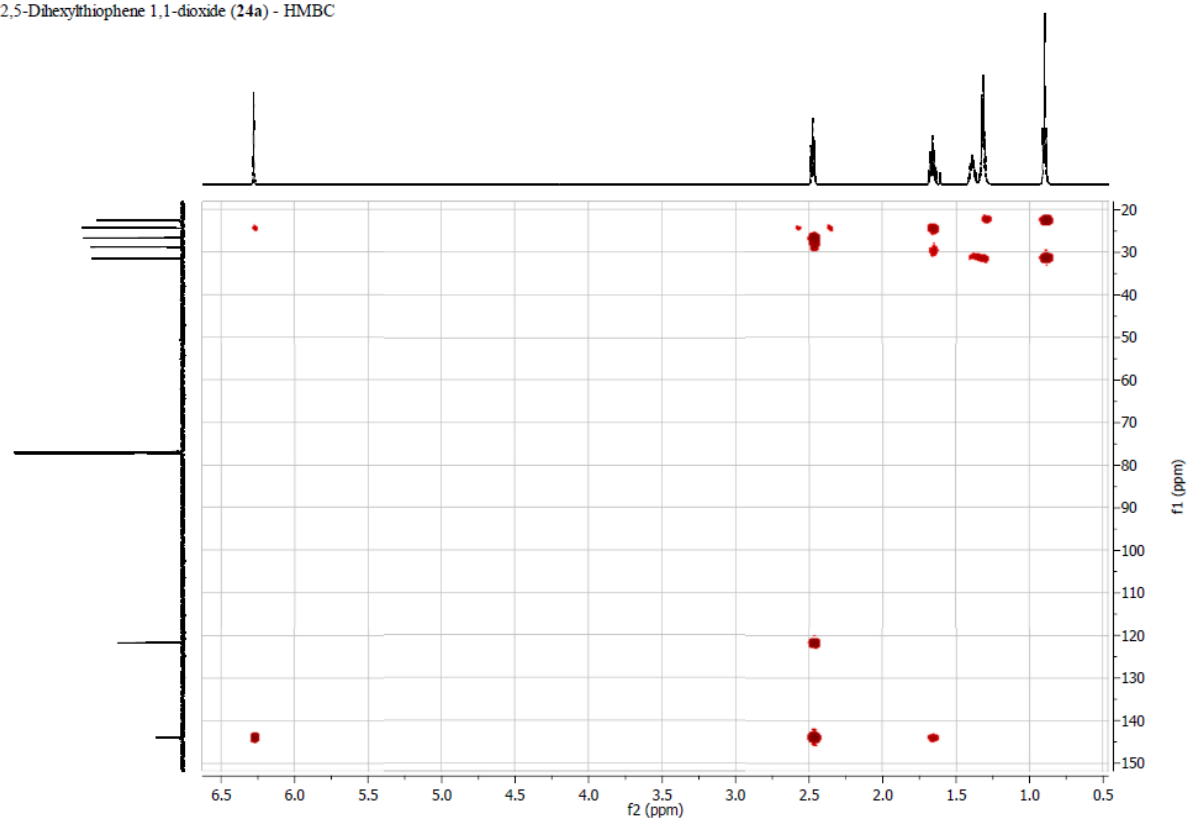
2,5-Dihexylthiophene (23a) - HMBC



2,5-Dihexylthiophene 1,1-dioxide (24a)

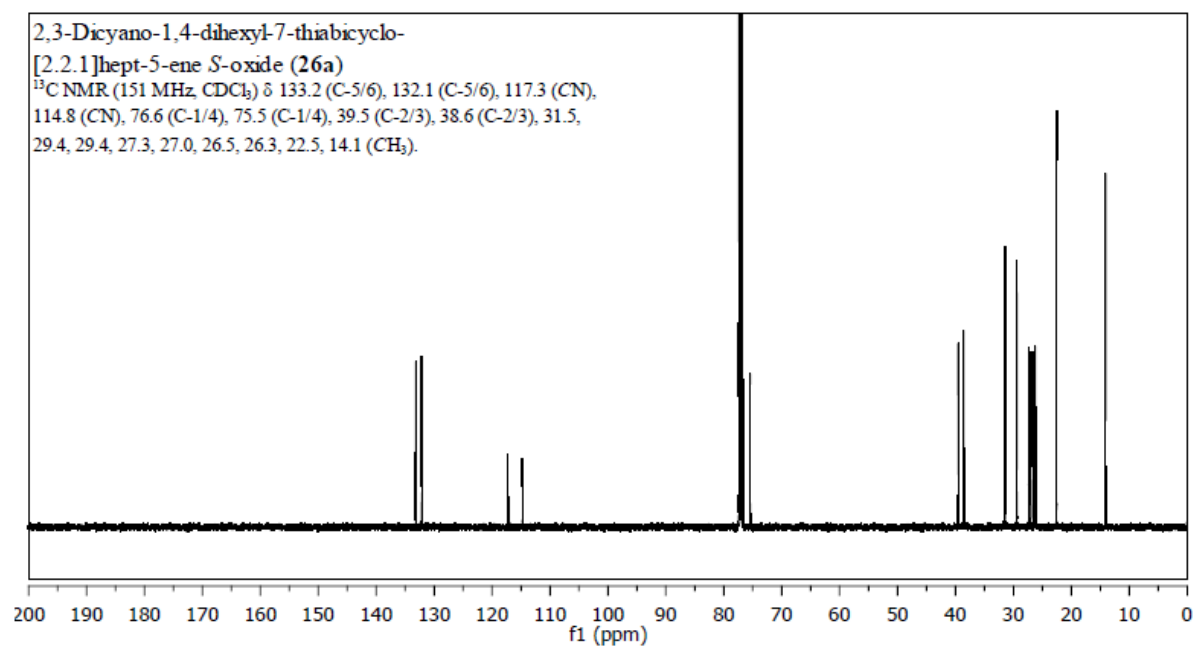
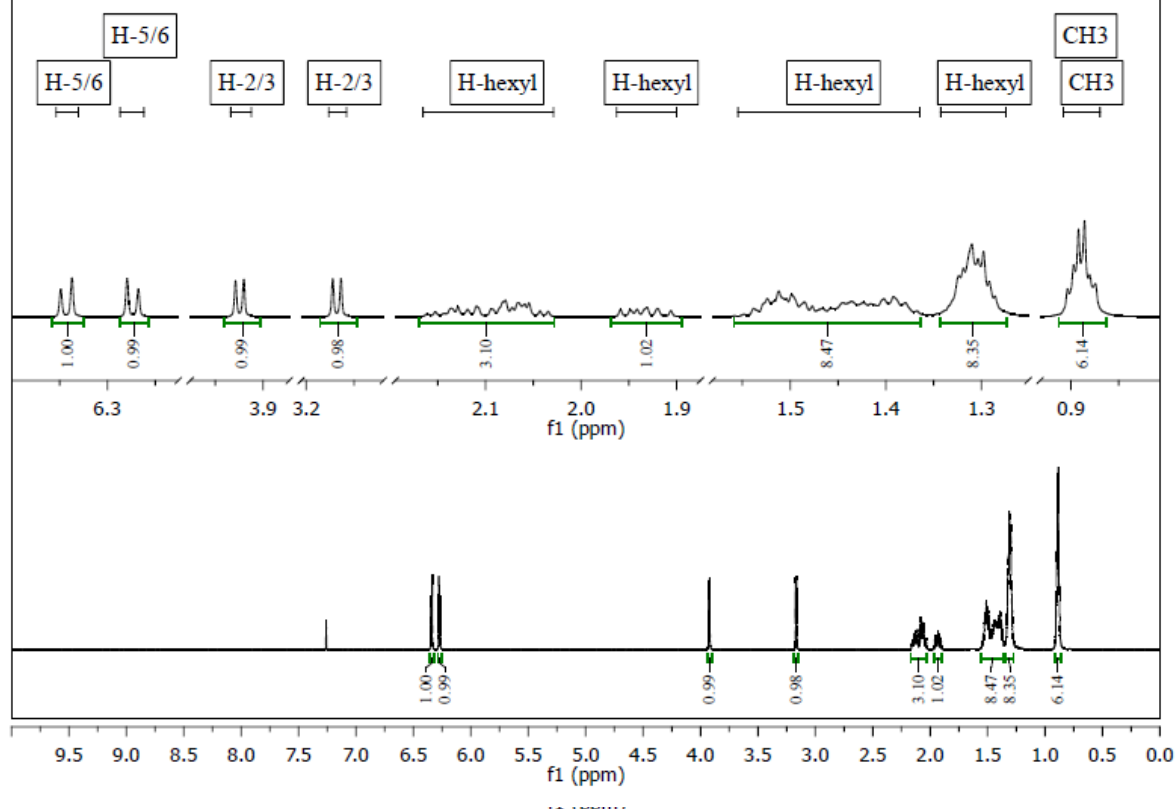
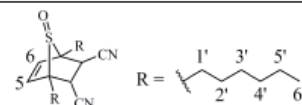


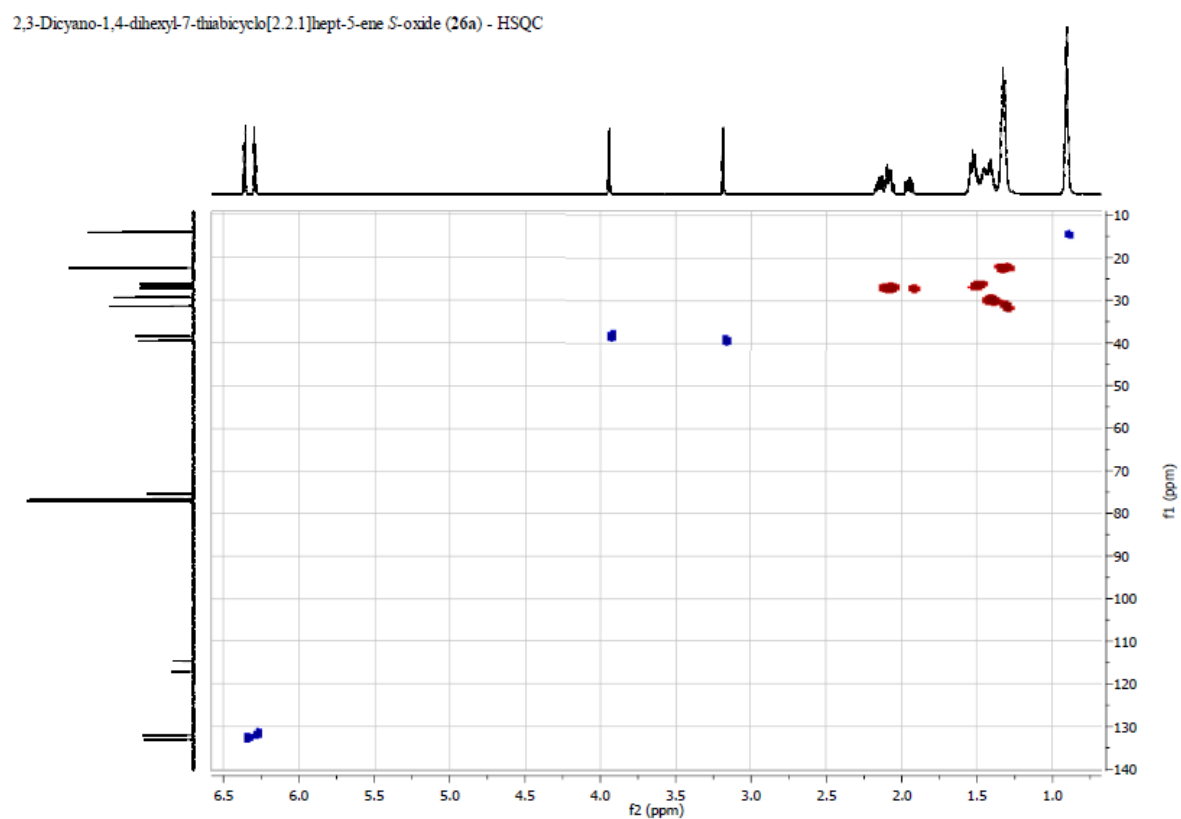
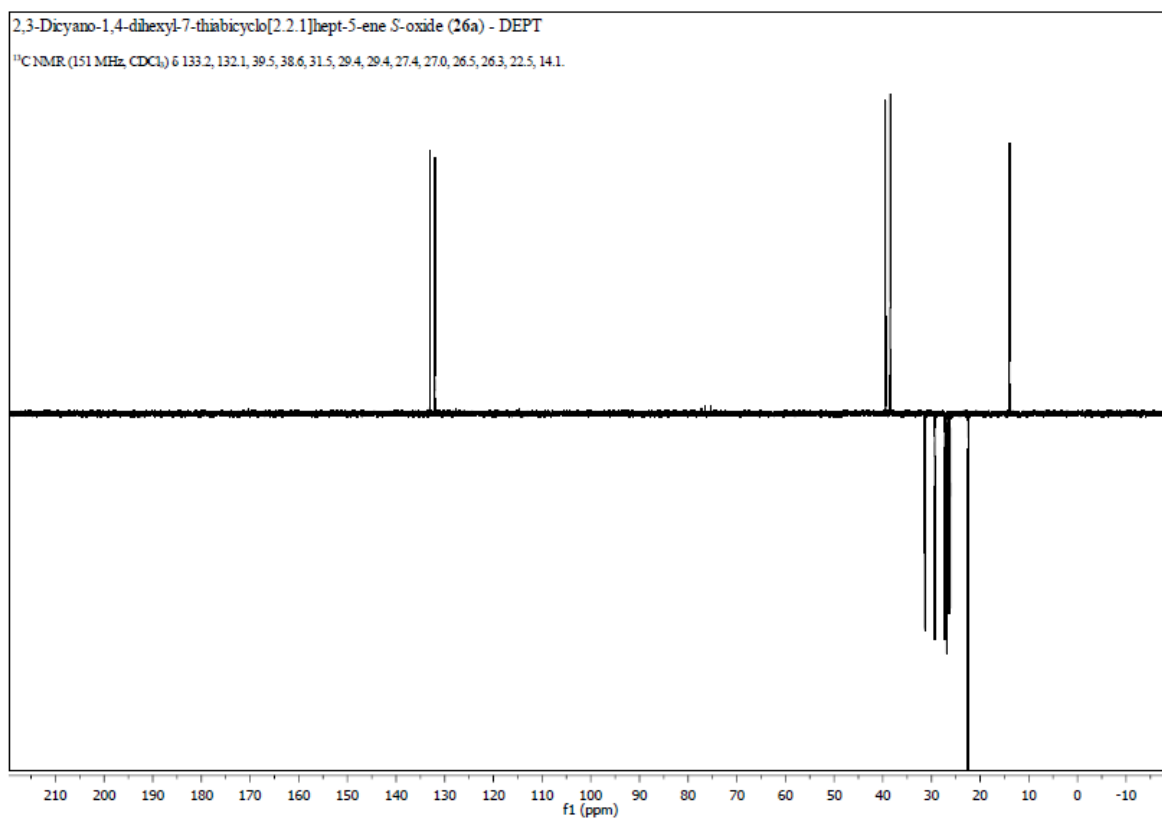
2,5-Dihexylthiophene 1,1-dioxide (24a) - HMBC

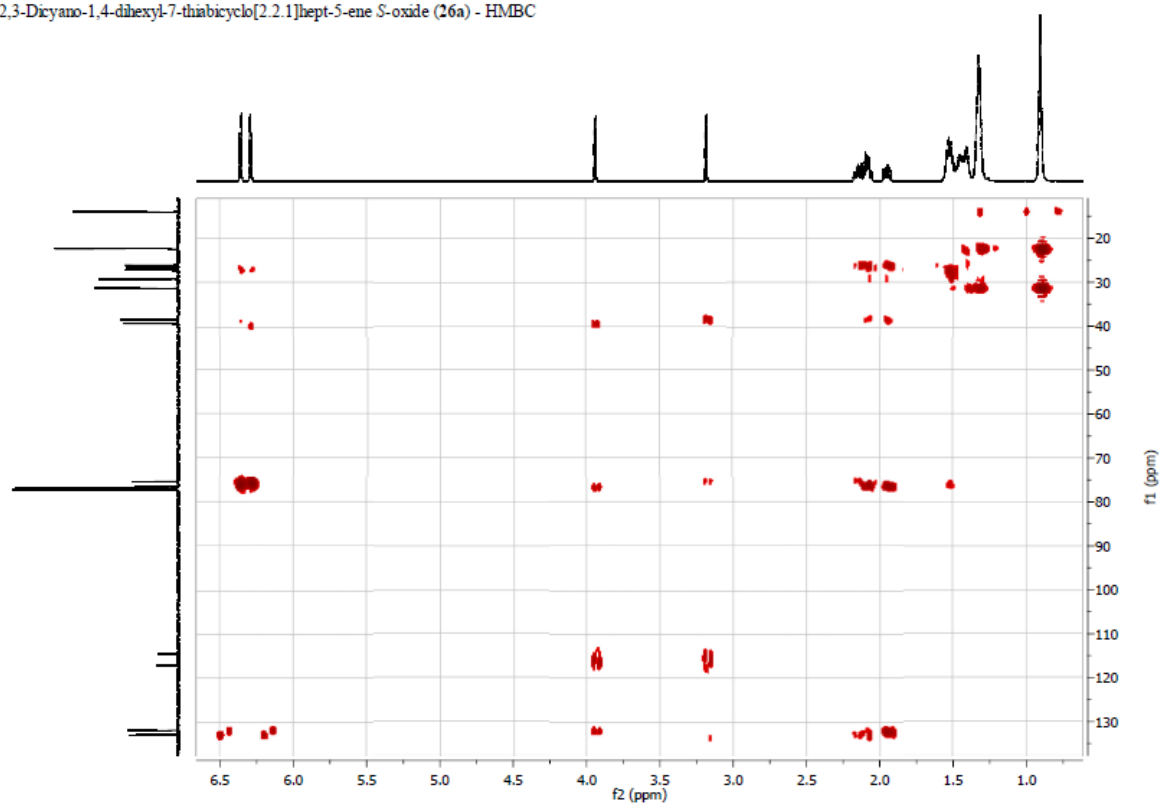


2,3-Dicyano-1,4-dihexyl-7-thiabicyclo[2.2.1]hept-5-ene *S*-oxide (26a)2,3-Dicyano-1,4-dihexyl-7-thiabicyclo-
[2.2.1]hept-5-ene *S*-oxide (26a)

¹H NMR (600 MHz, CDCl₃) δ 6.34 (1H, d, *J* = 7.0 Hz, H-5/6), 6.27 (1H, d, *J* = 7.0 Hz, H-5/6), 3.92 (1H, d, *J* = 5.2 Hz, H-2/3), 3.17 (1H, d, *J* = 5.2 Hz, H-2/3), 2.17–2.03 (3H, m, H-hexyl), 1.96–1.90 (1H, m, H-hexyl), 1.55–1.36 (8H, m, H-hexyl), 1.34–1.27 (8H, m, H-hexyl), 0.89 (3H, t, *J* = 7.0 Hz, CH₃), 0.89 (3H, t, *J* = 6.8 Hz, CH₃).



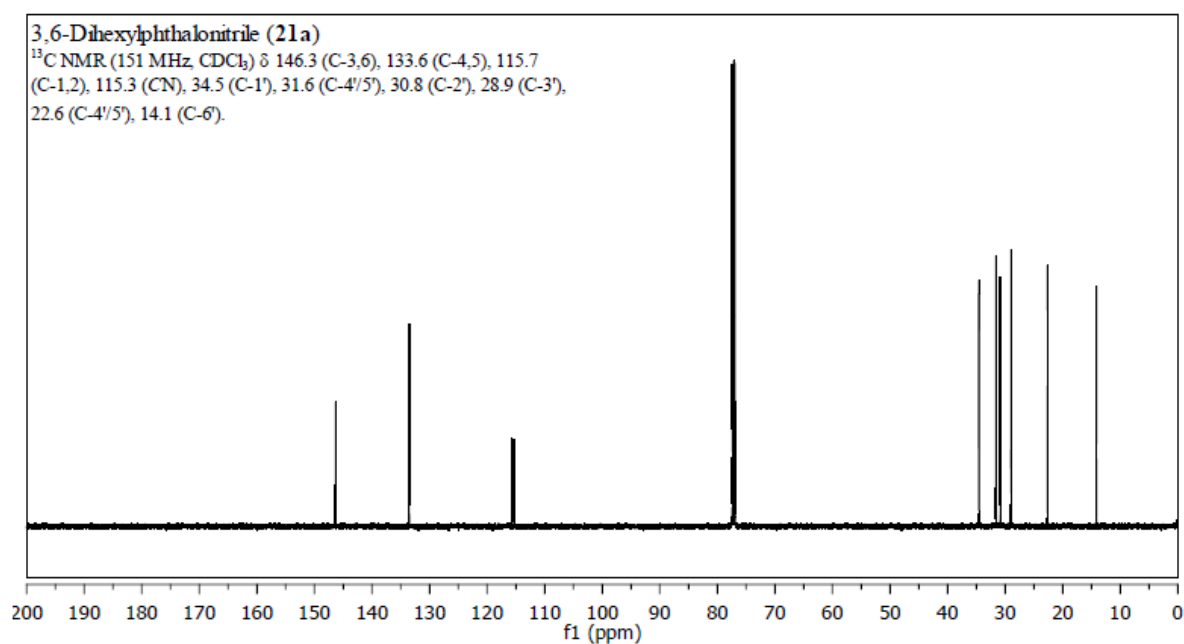
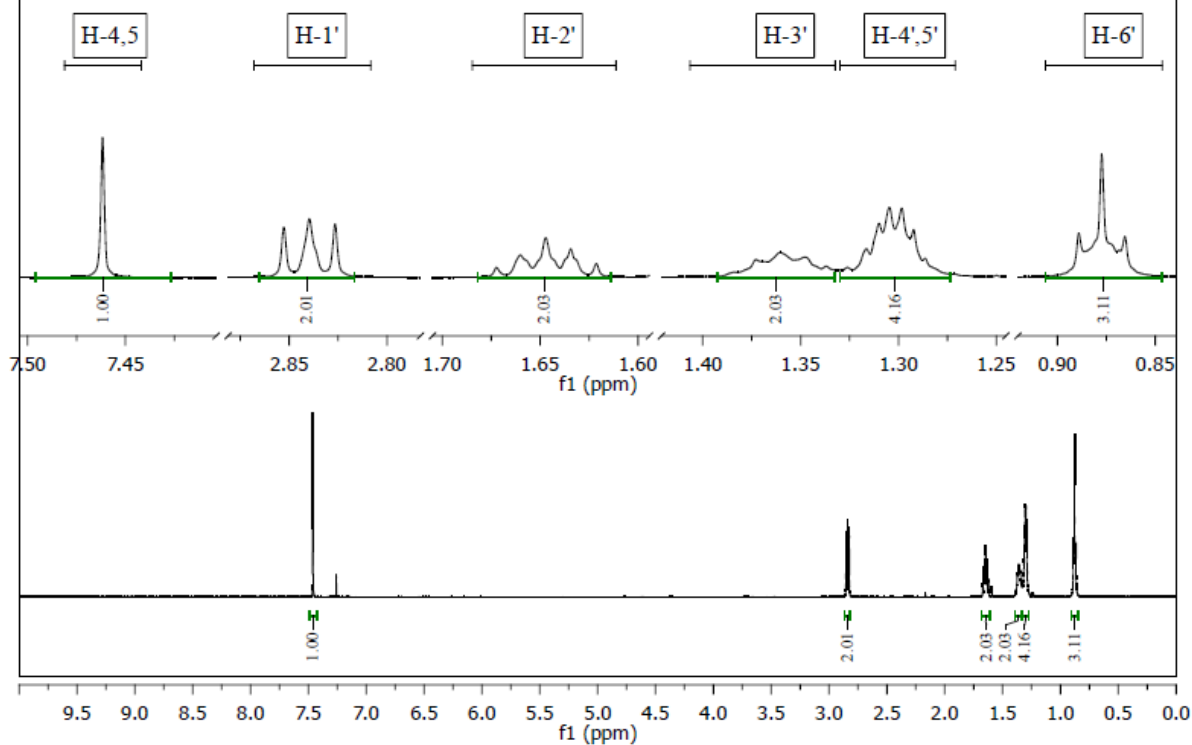
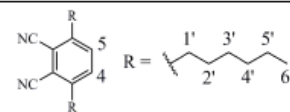


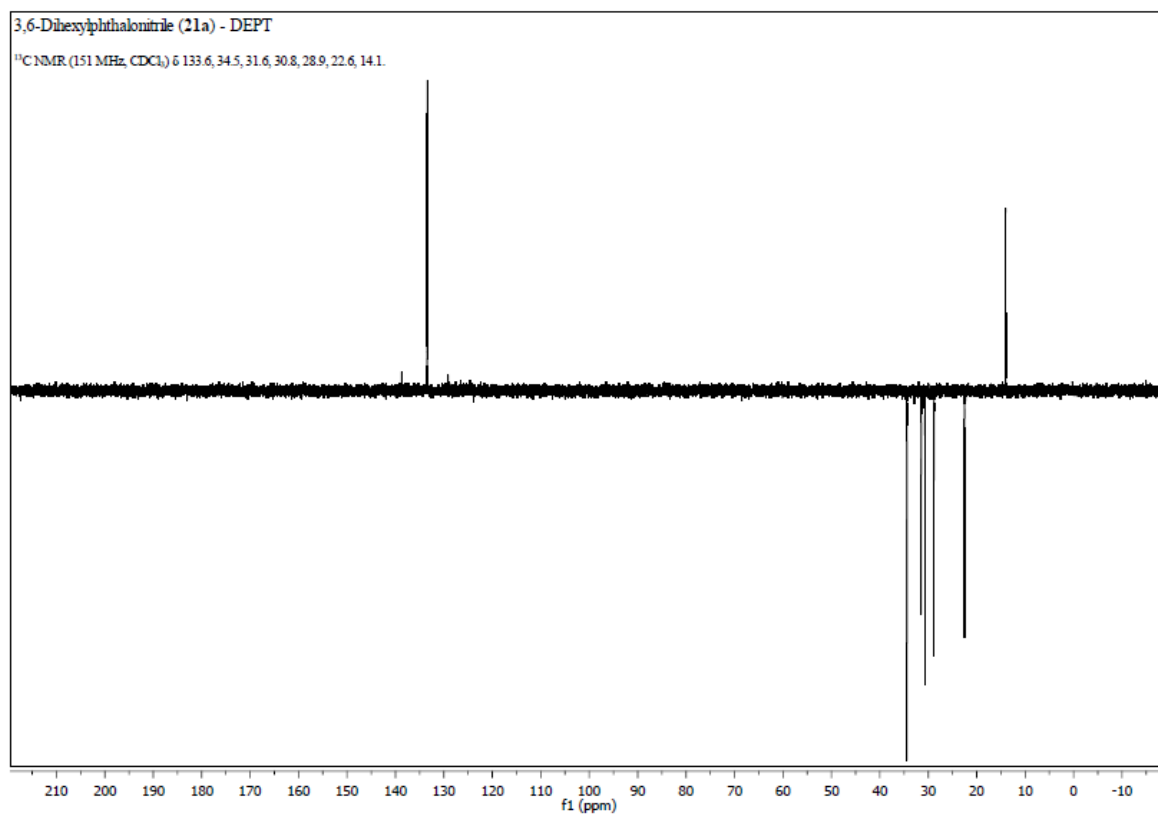
2,3-Dicyano-1,4-dihexyl-7-thiabicyclo[2.2.1]hept-5-ene *S*-oxide (26a) - HMBC

3,6-Dihexylphthalonitrile (21a)

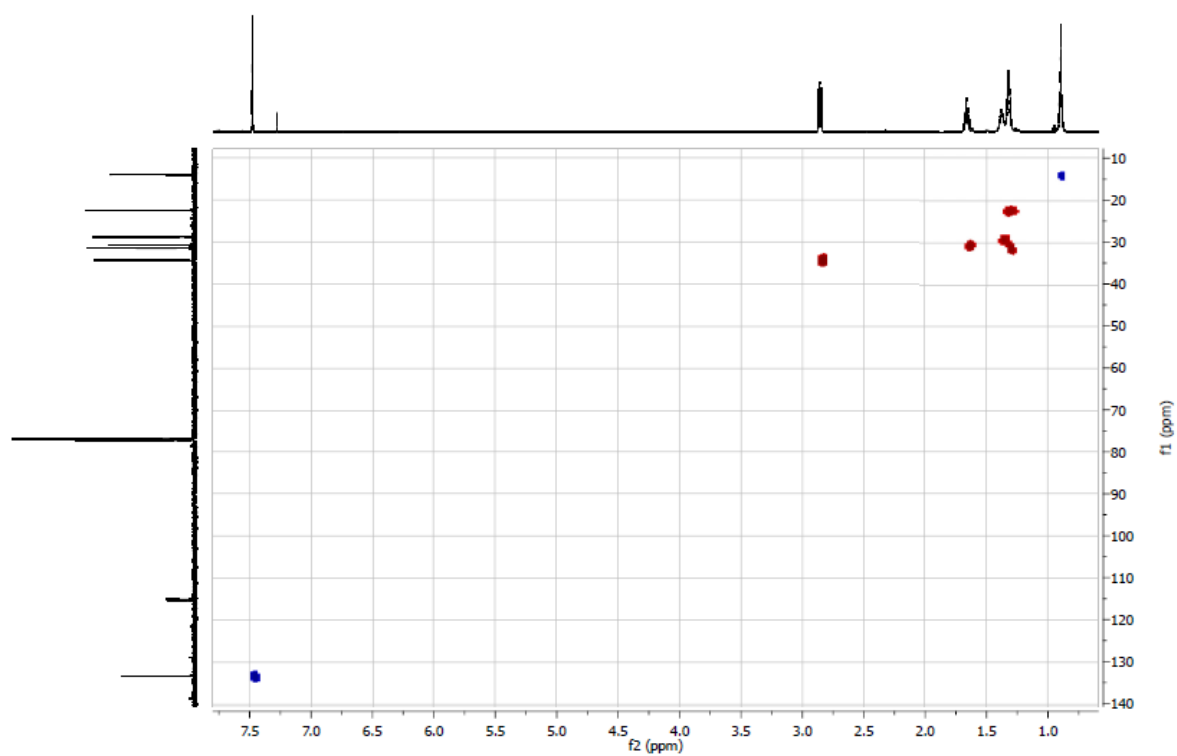
3,6-Dihexylphthalonitrile (21a)

^1H NMR (600 MHz, CDCl_3) δ 7.46 (2H, s, H-4,5), 2.84 (4H, t, $J = 7.9$ Hz, H-1'), 1.68 – 1.61 (4H, m, H-2'), 1.41 – 1.33 (4H, m, H-3'), 1.33 – 1.27 (8H, m, H-4',5'), 0.88 (12H, t, $J = 7.0$ Hz, H-6').

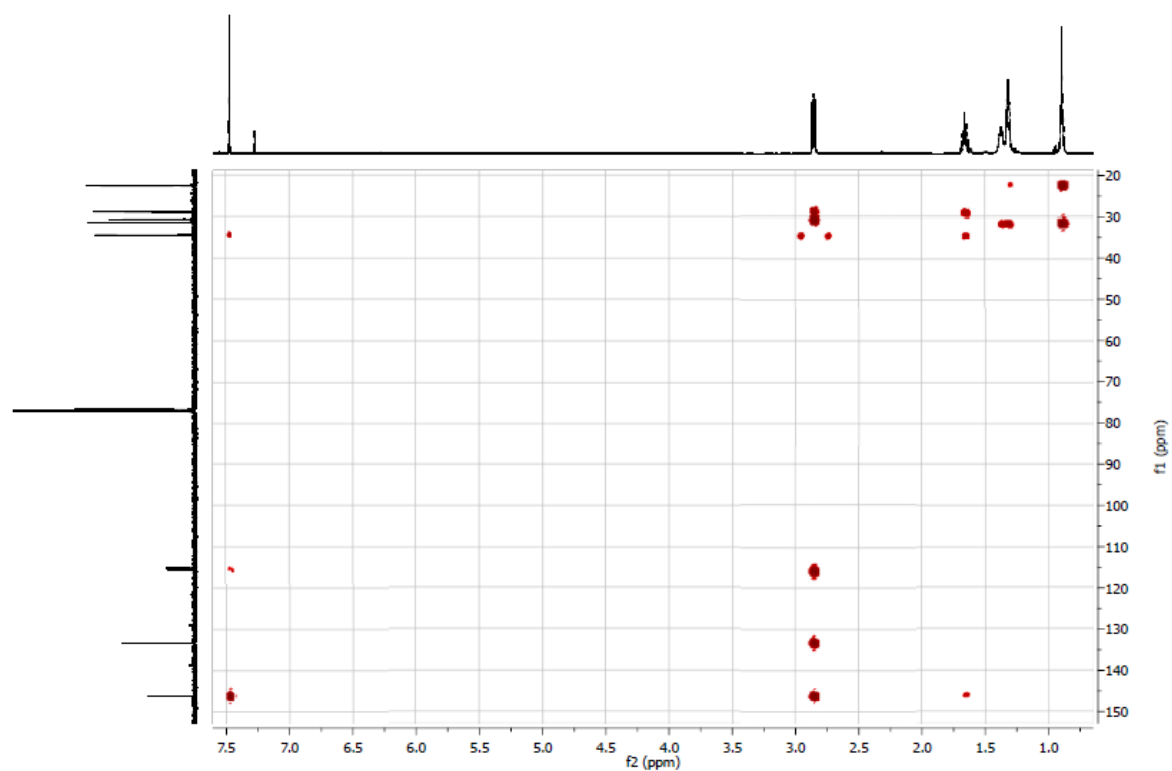




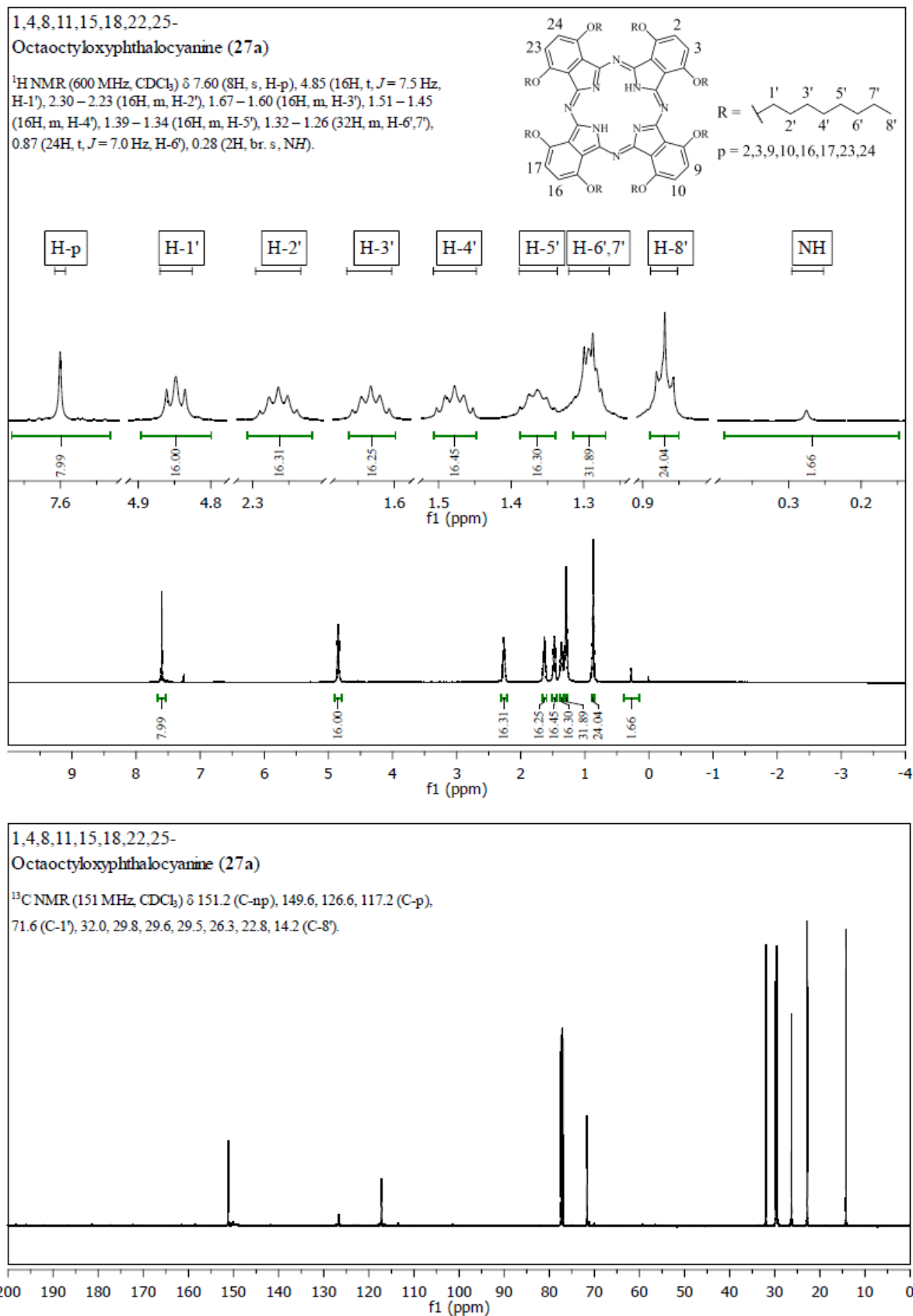
3,6-Dihexylphthalonitrile (21a) - HSQC

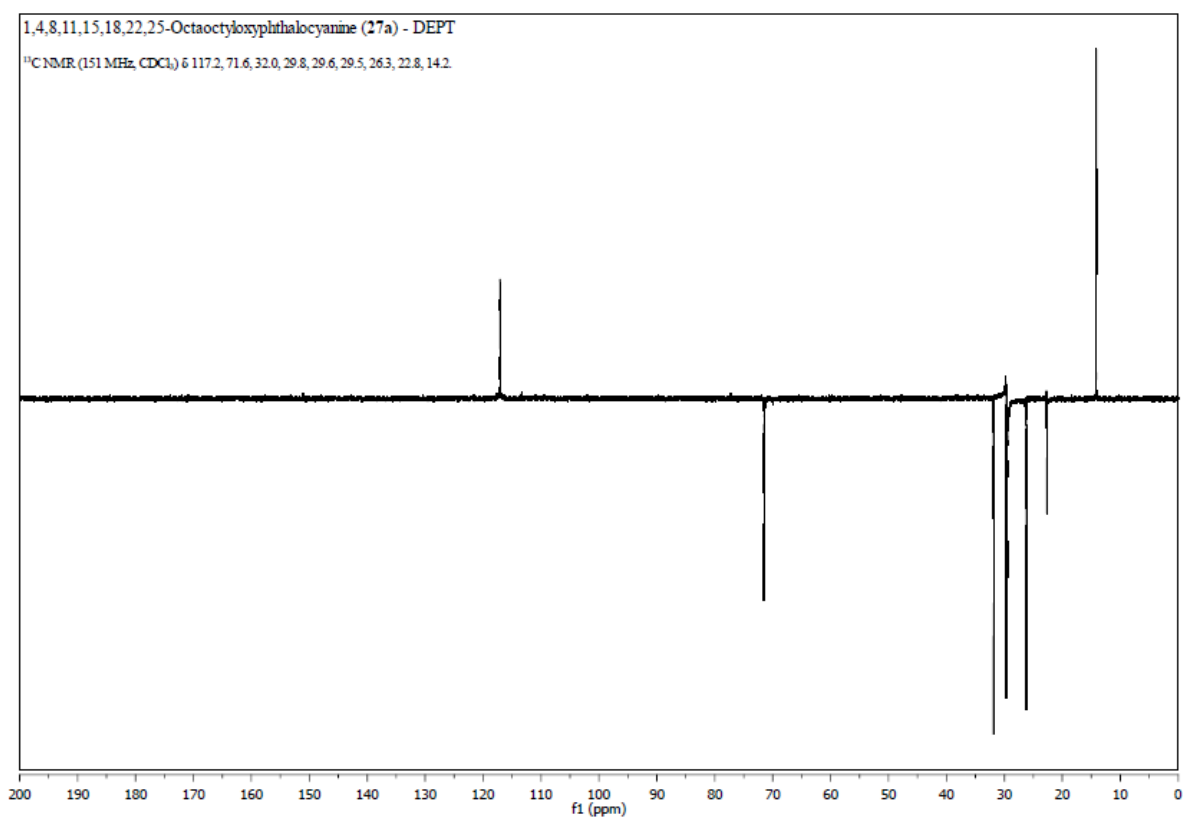


3,6-Dihexylphthalonitrile (21a) - HMBC

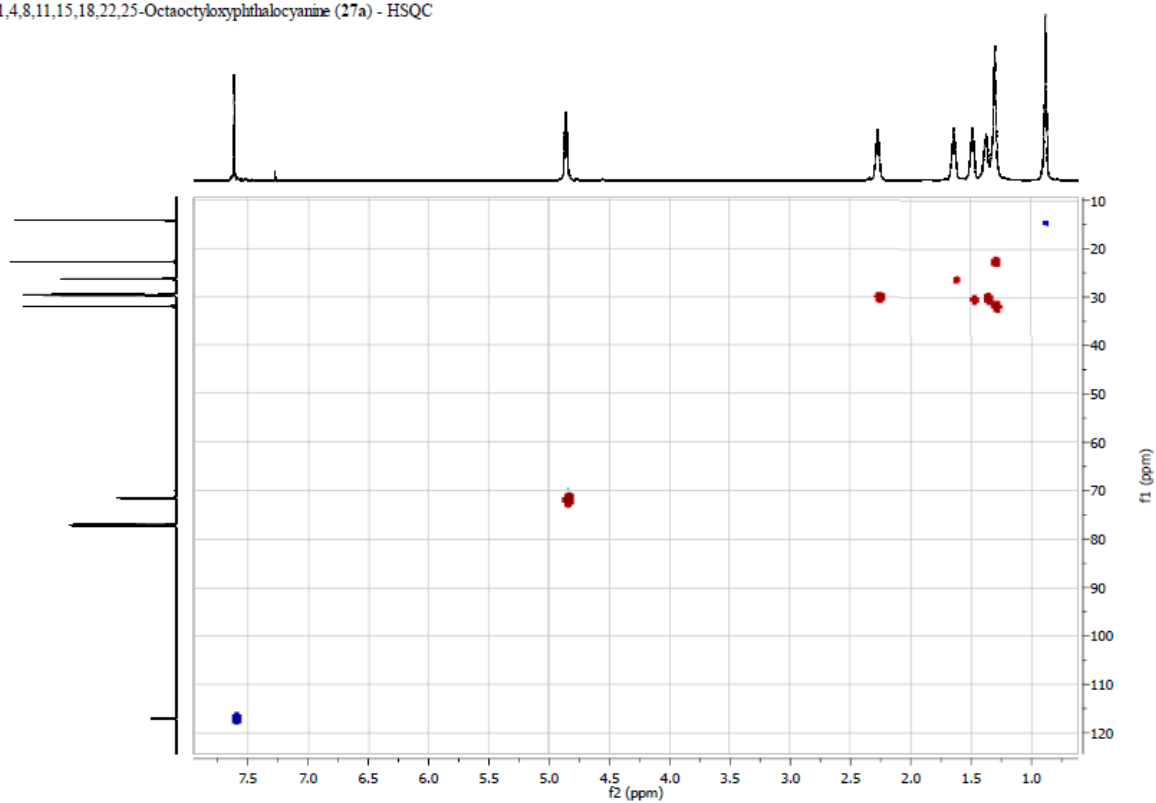


1,4,8,11,15,18,22,25-Octaoctyloxyphthalocyanine (27a)

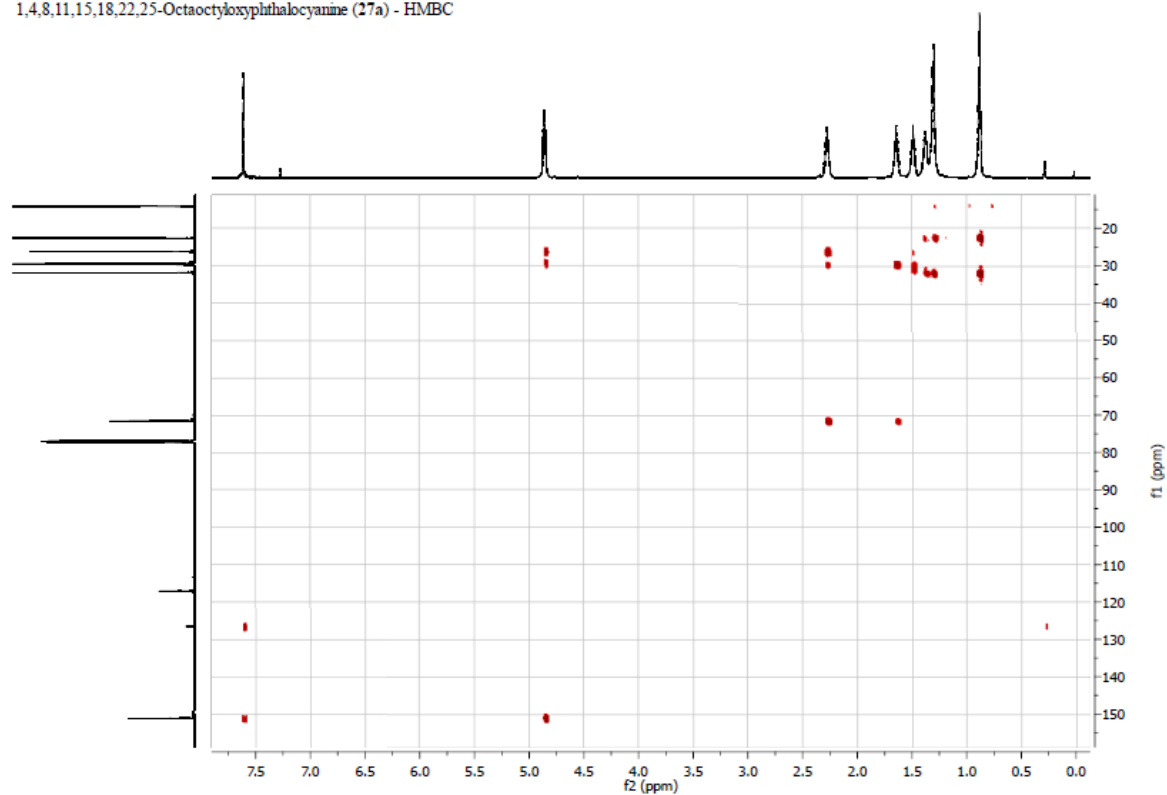




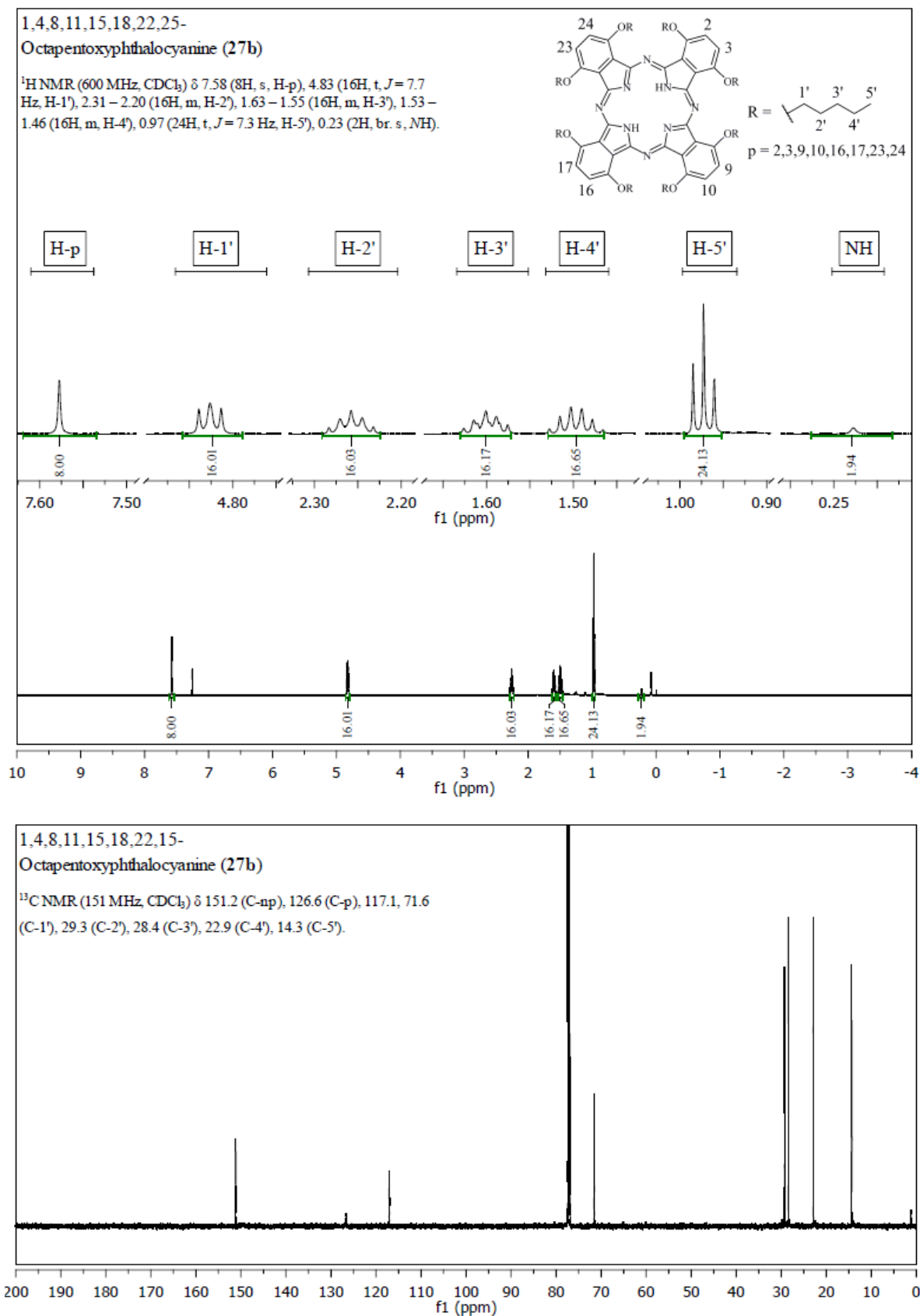
1,4,8,11,15,18,22,25-Octaoctyloxyphthalocyanine (27a) - HSQC

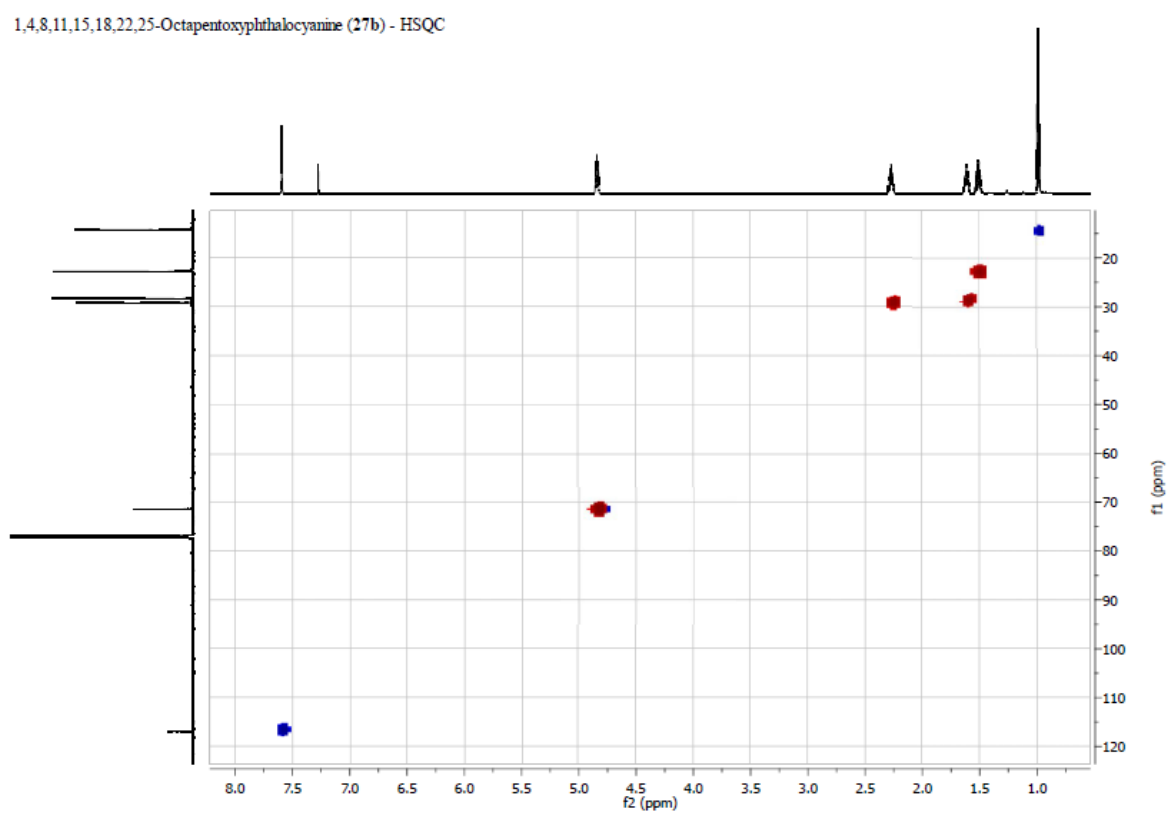
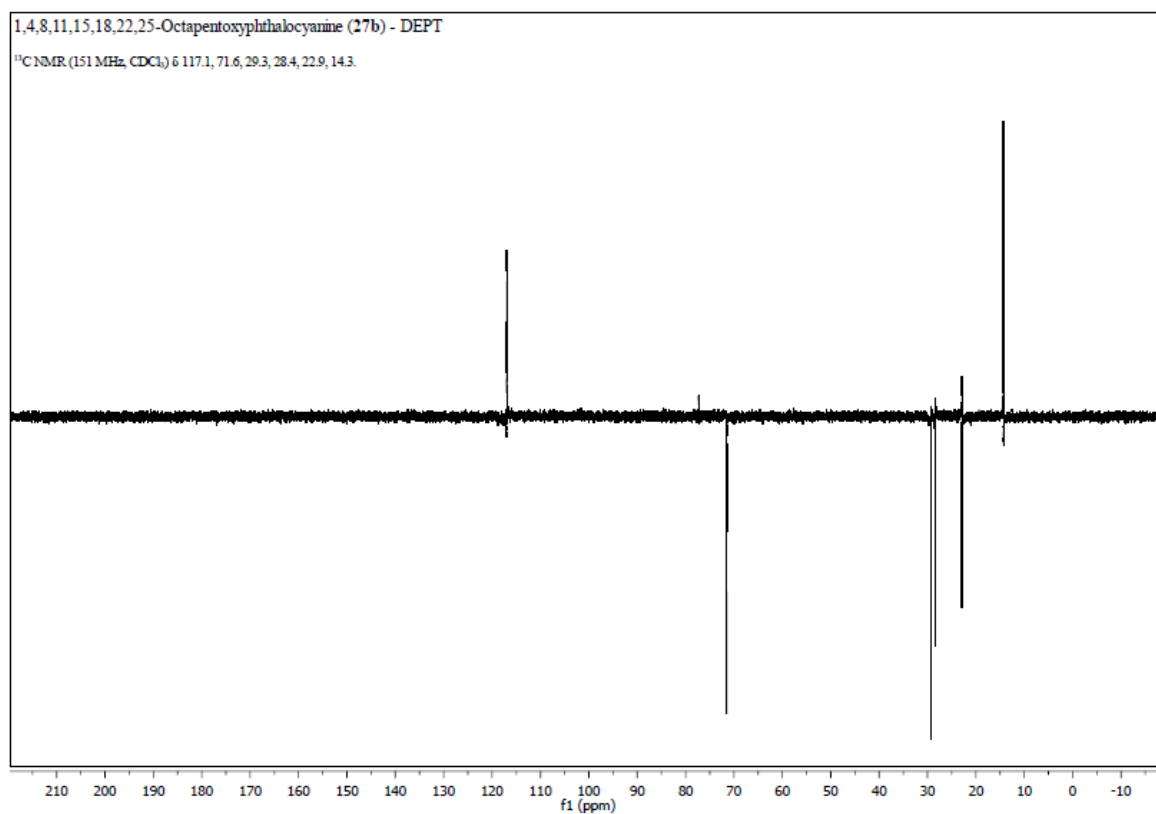


1,4,8,11,15,18,22,25-Octaoctyloxyphthalocyanine (27a) - HMBC

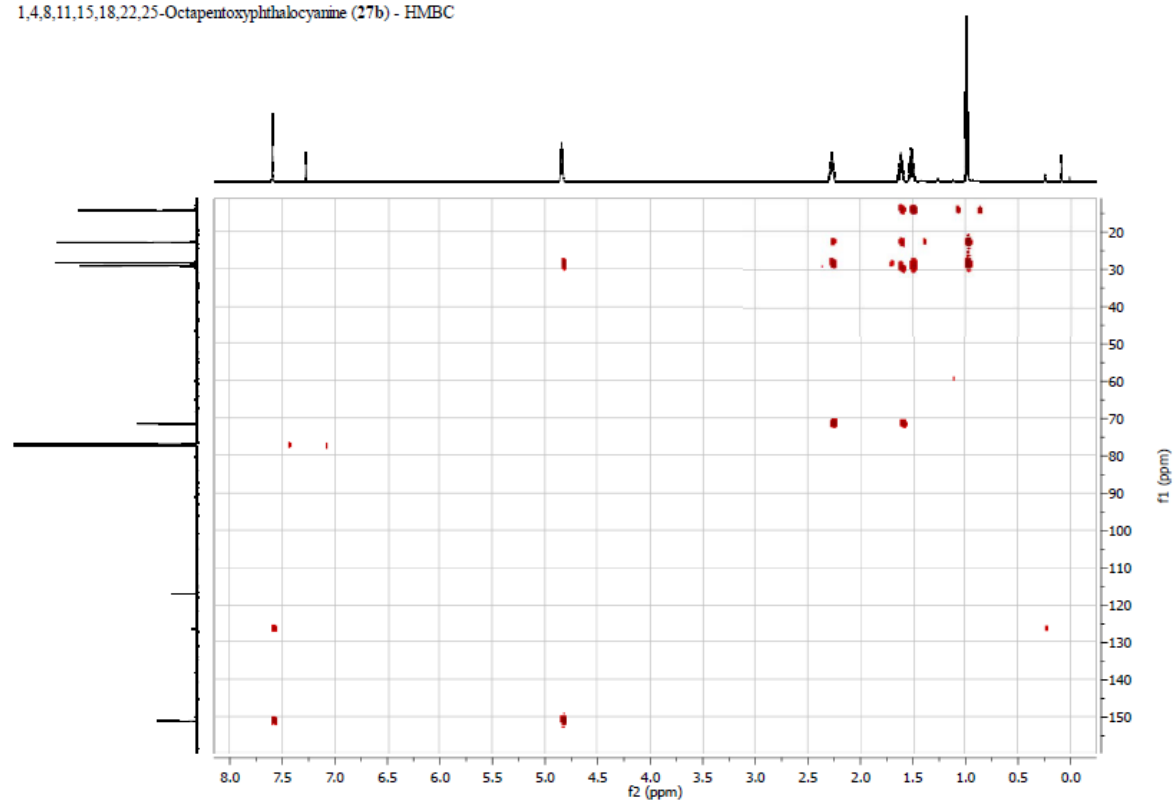


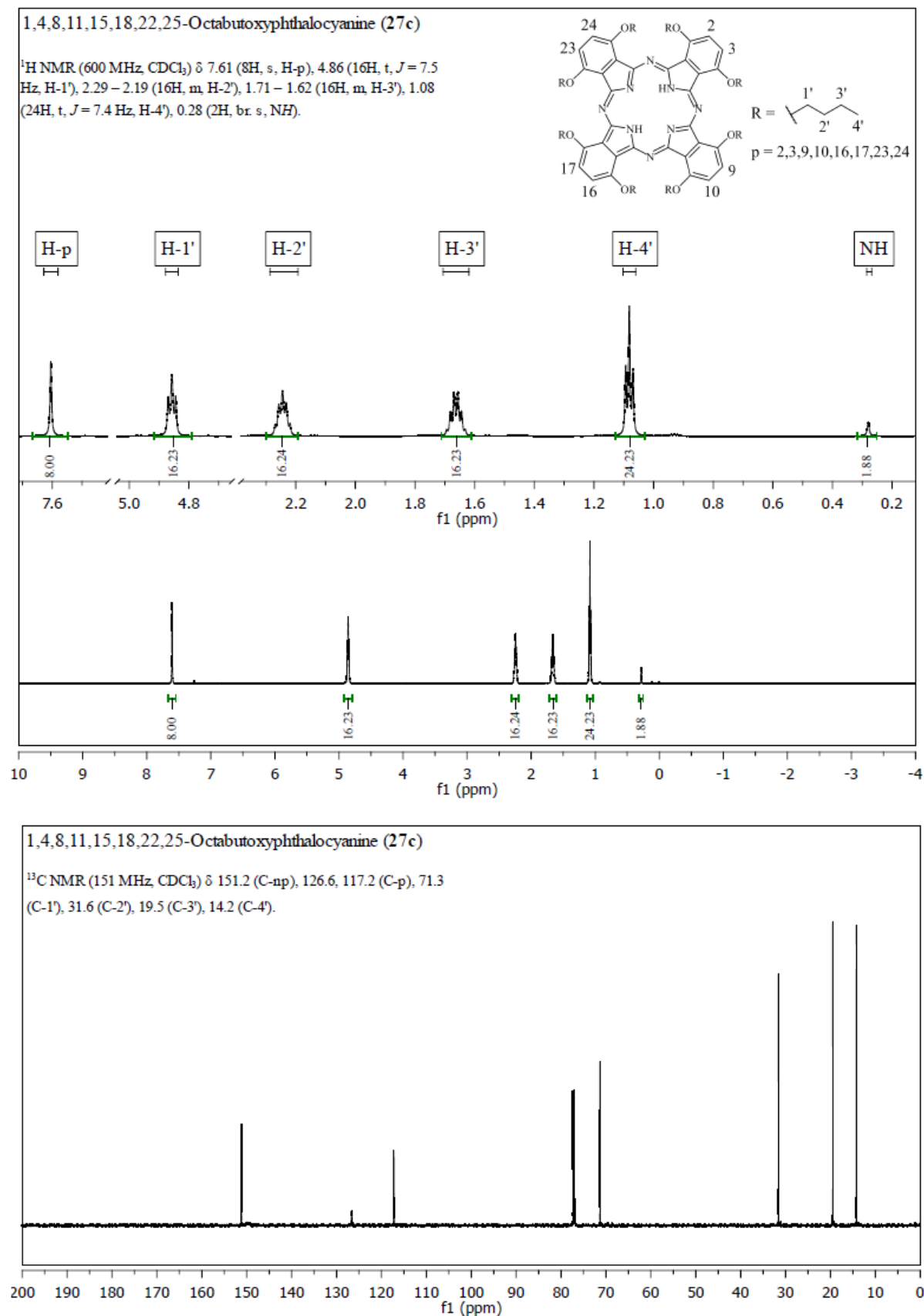
1,4,8,11,15,18,22,25-Octapentoxypthalocyanine (27b)

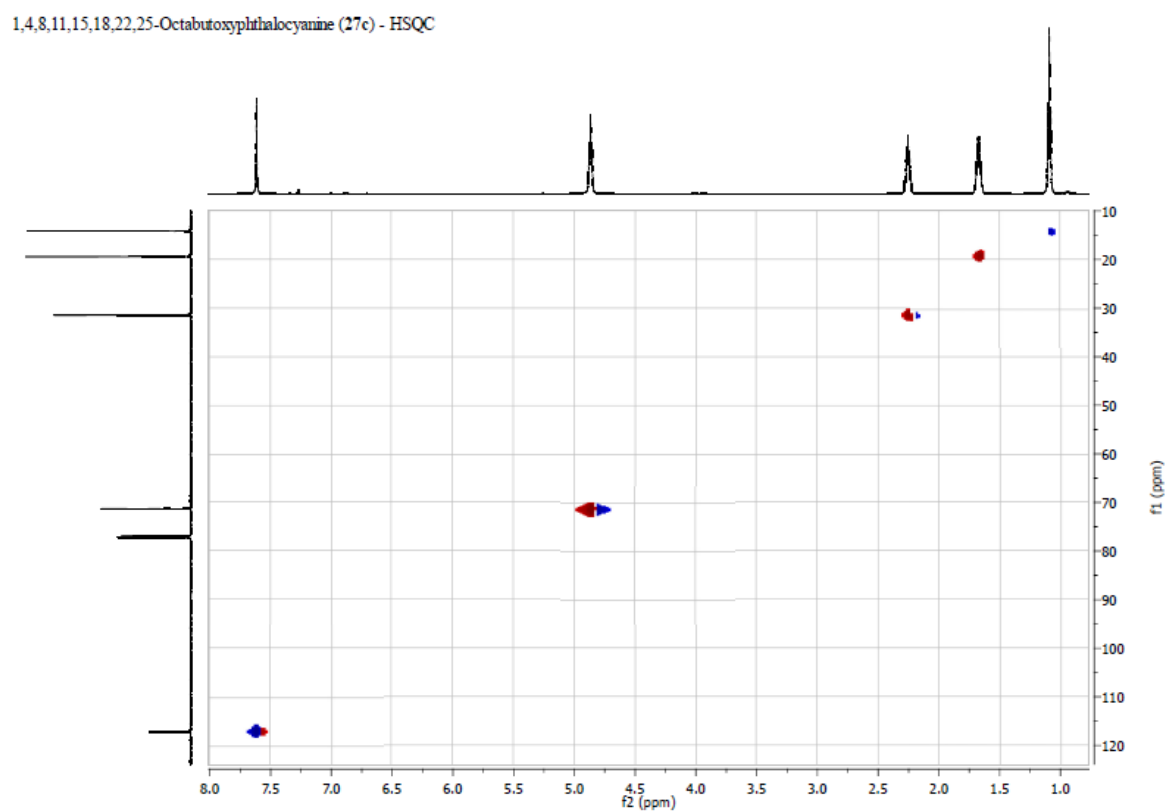
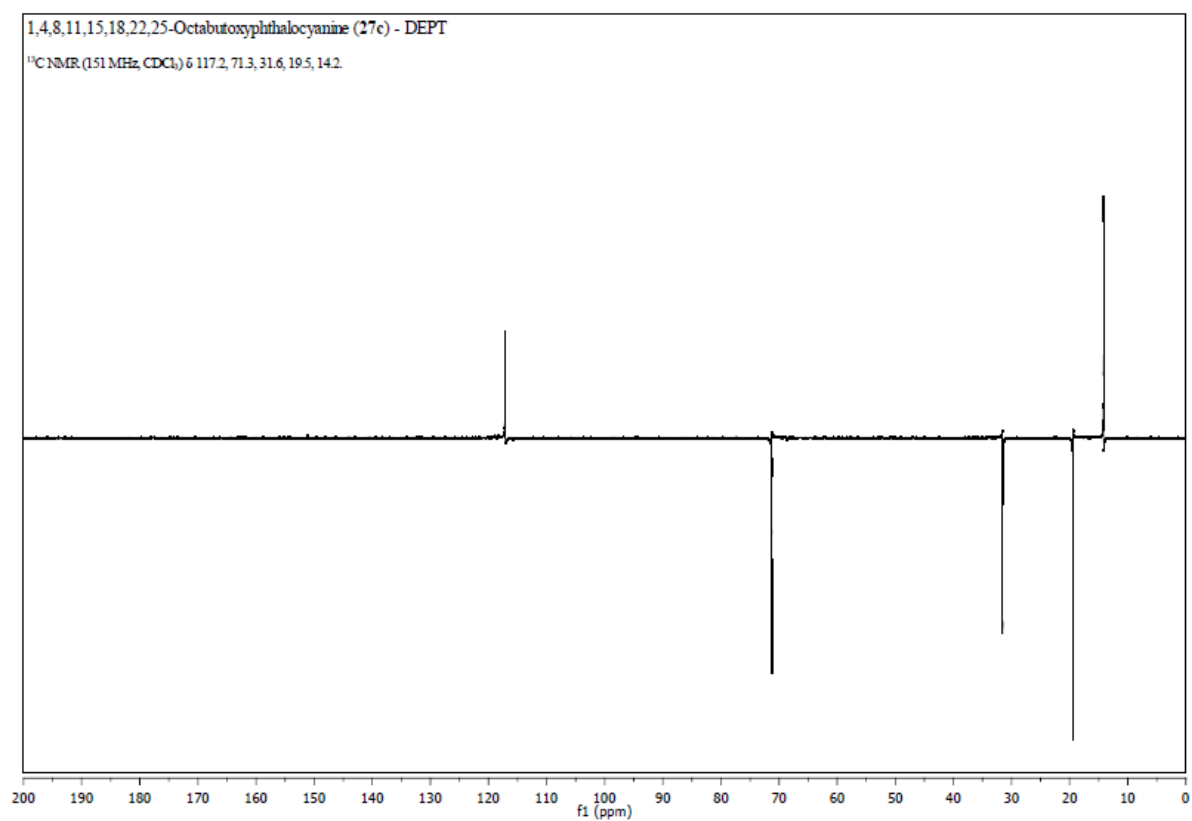




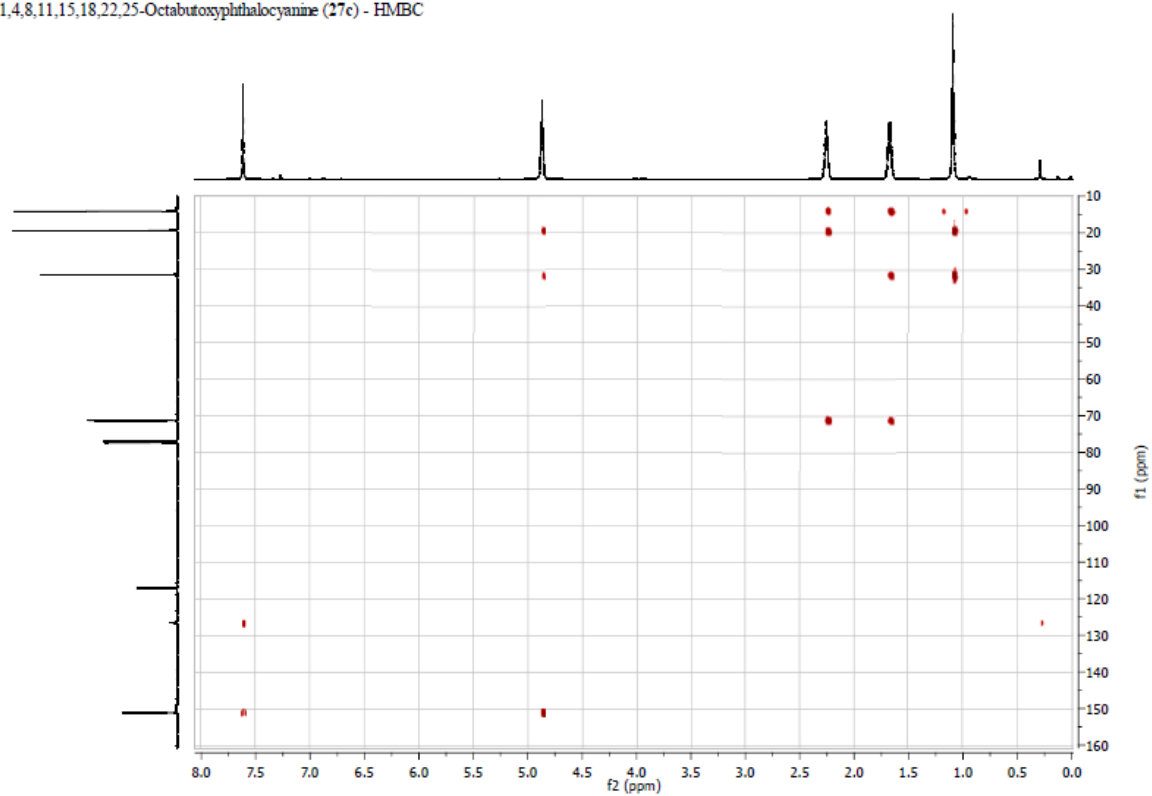
1,4,8,11,15,18,22,25-Octapentoxypthalocyanine (27b) - HMBC



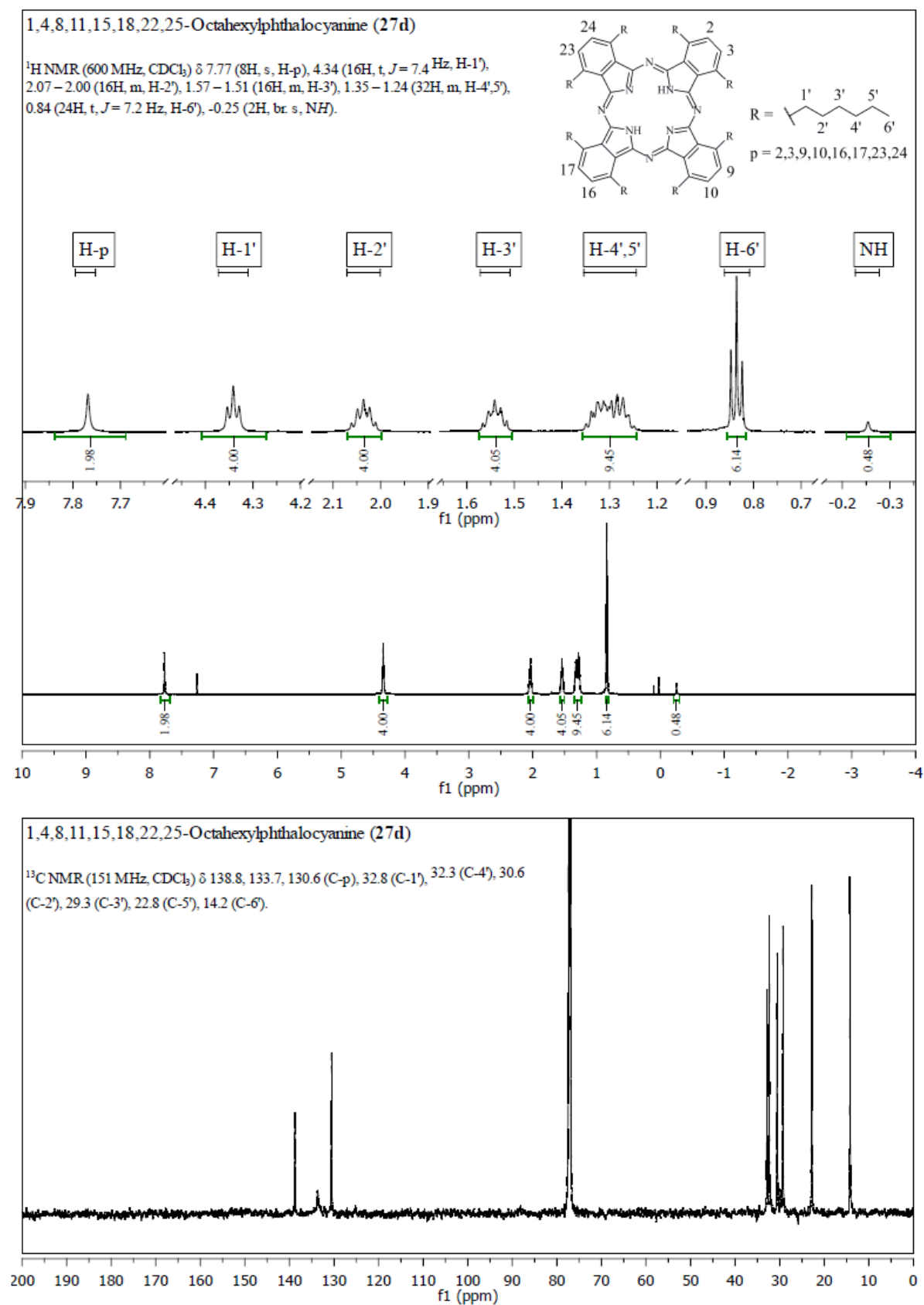
1,4,8,11,15,18,22,25-Octabutoxyphthalocyanine (**27c**)

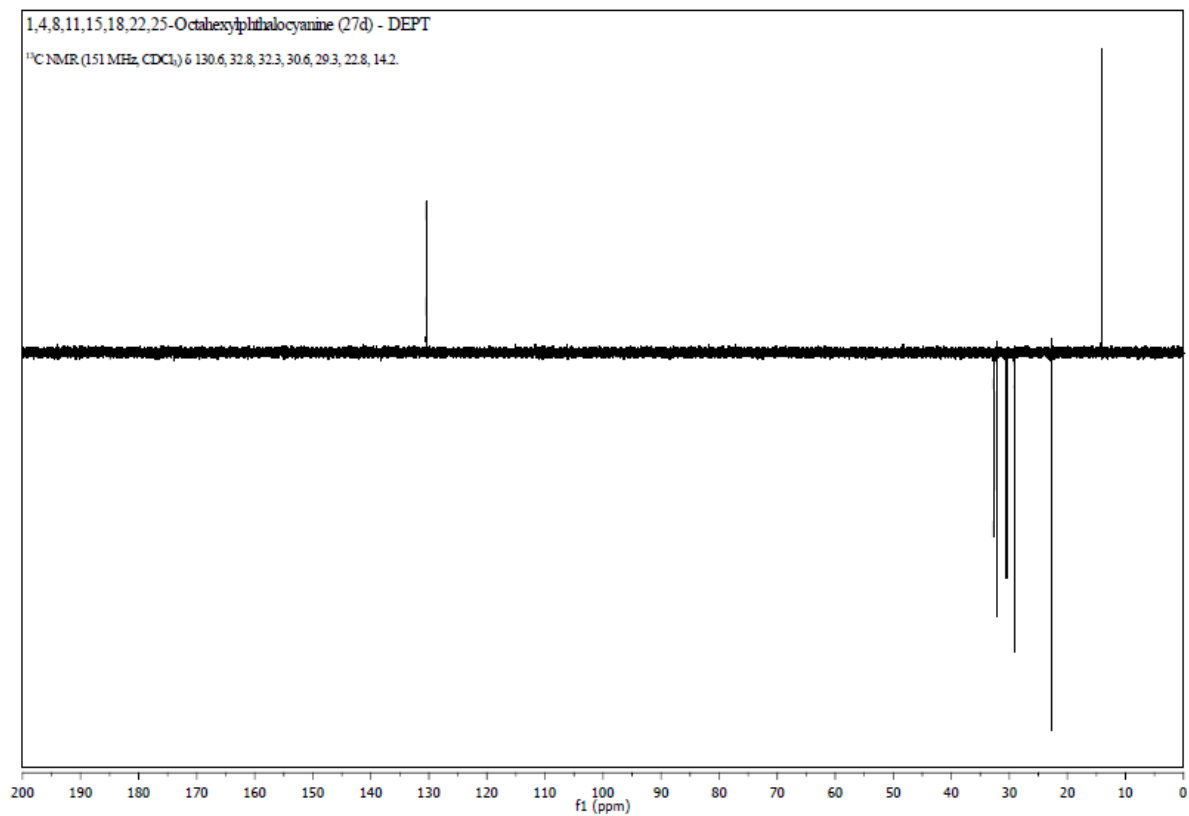


1,4,8,11,15,18,22,25-Octabutoxyphthalocyanine (27c) - HMBC

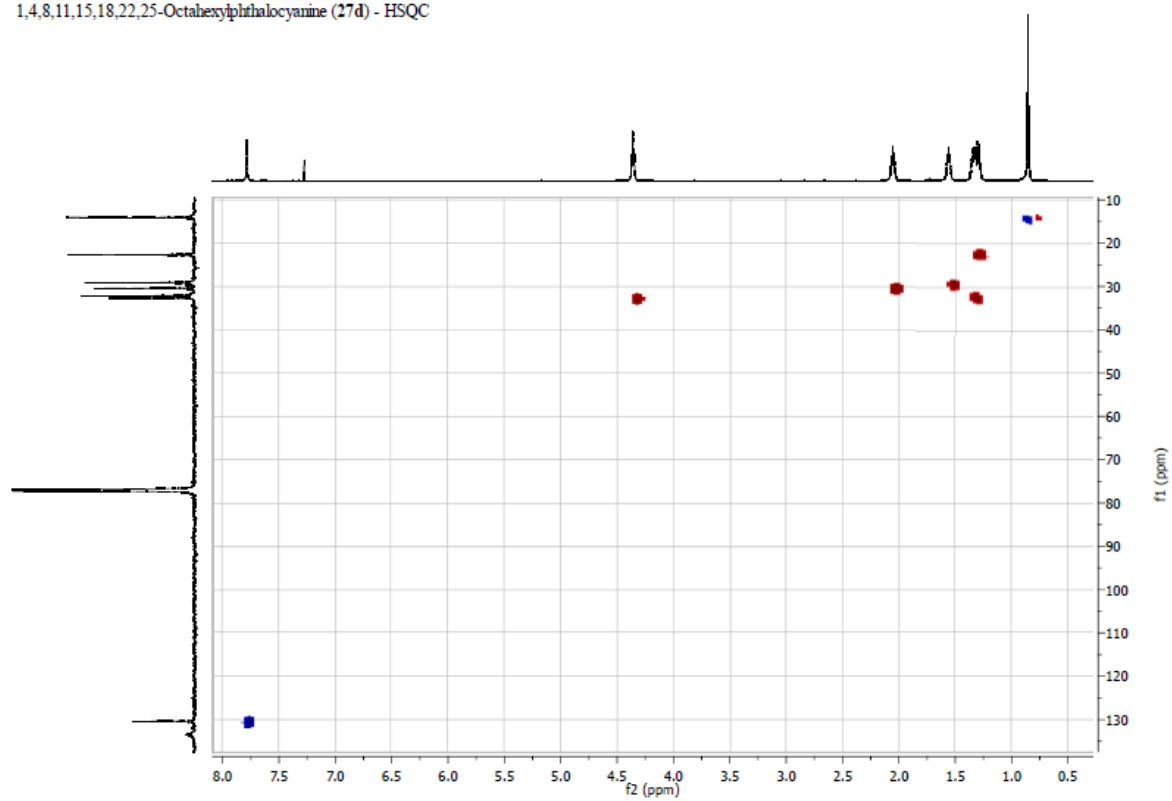


1,4,8,11,15,18,22,25-Octahexylphthalocyanine (27d)

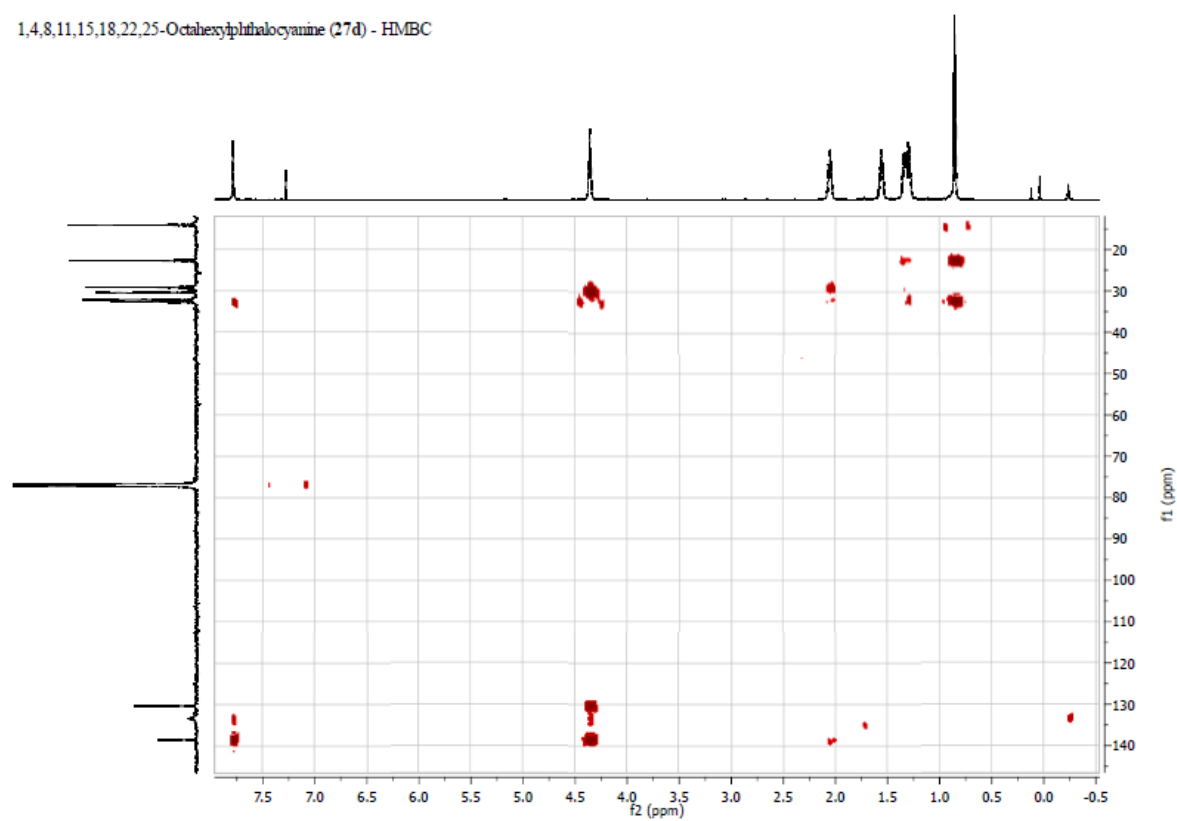




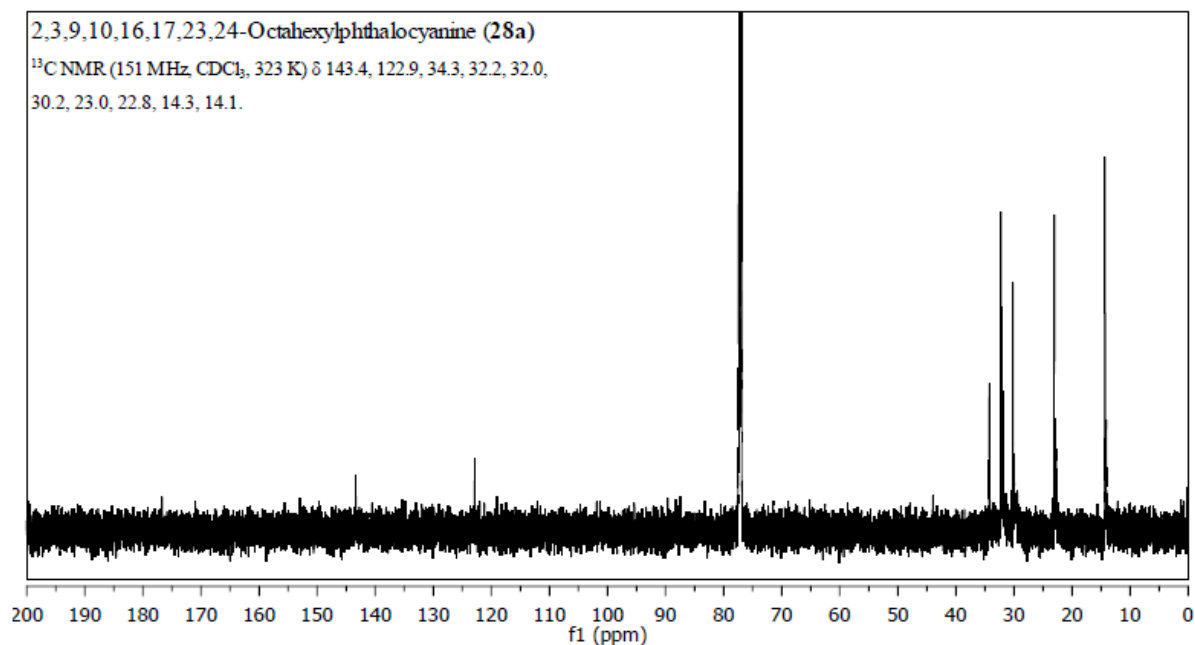
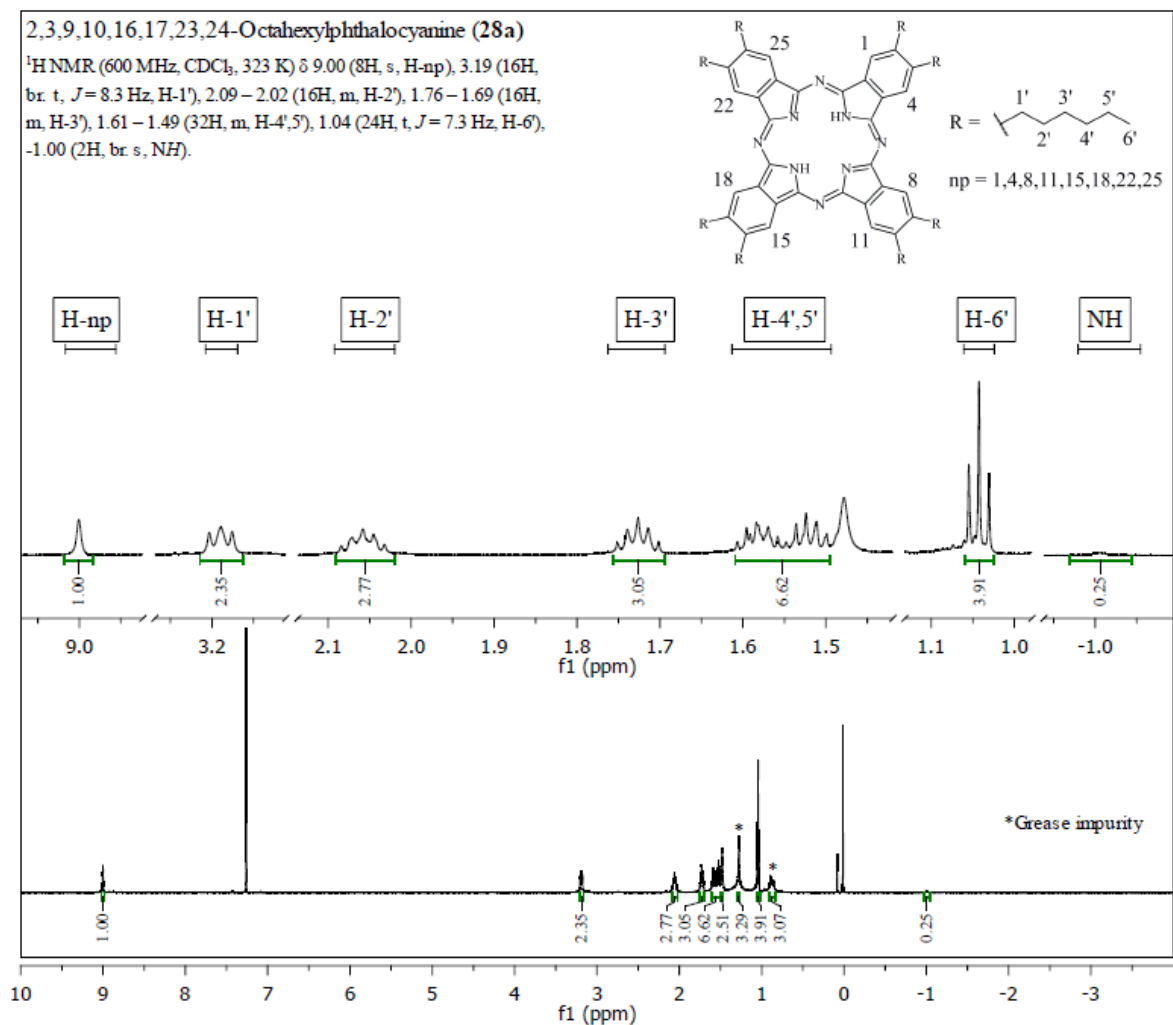
1,4,8,11,15,18,22,25-Octahexylphthalocyanine (27d) - HSQC

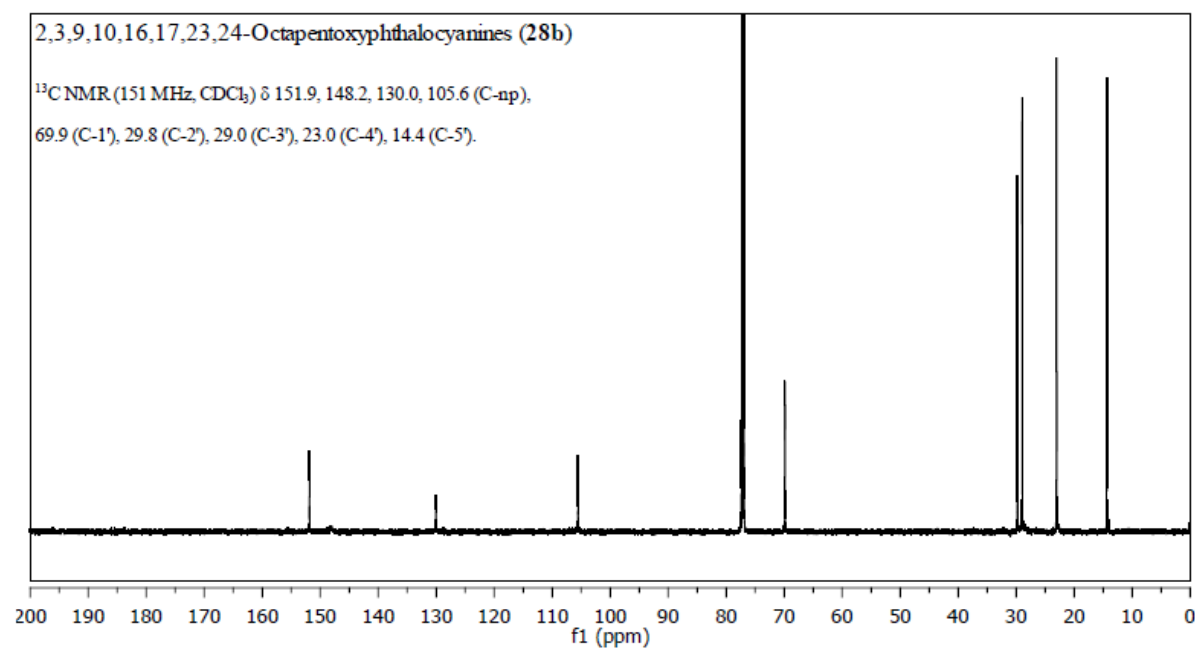
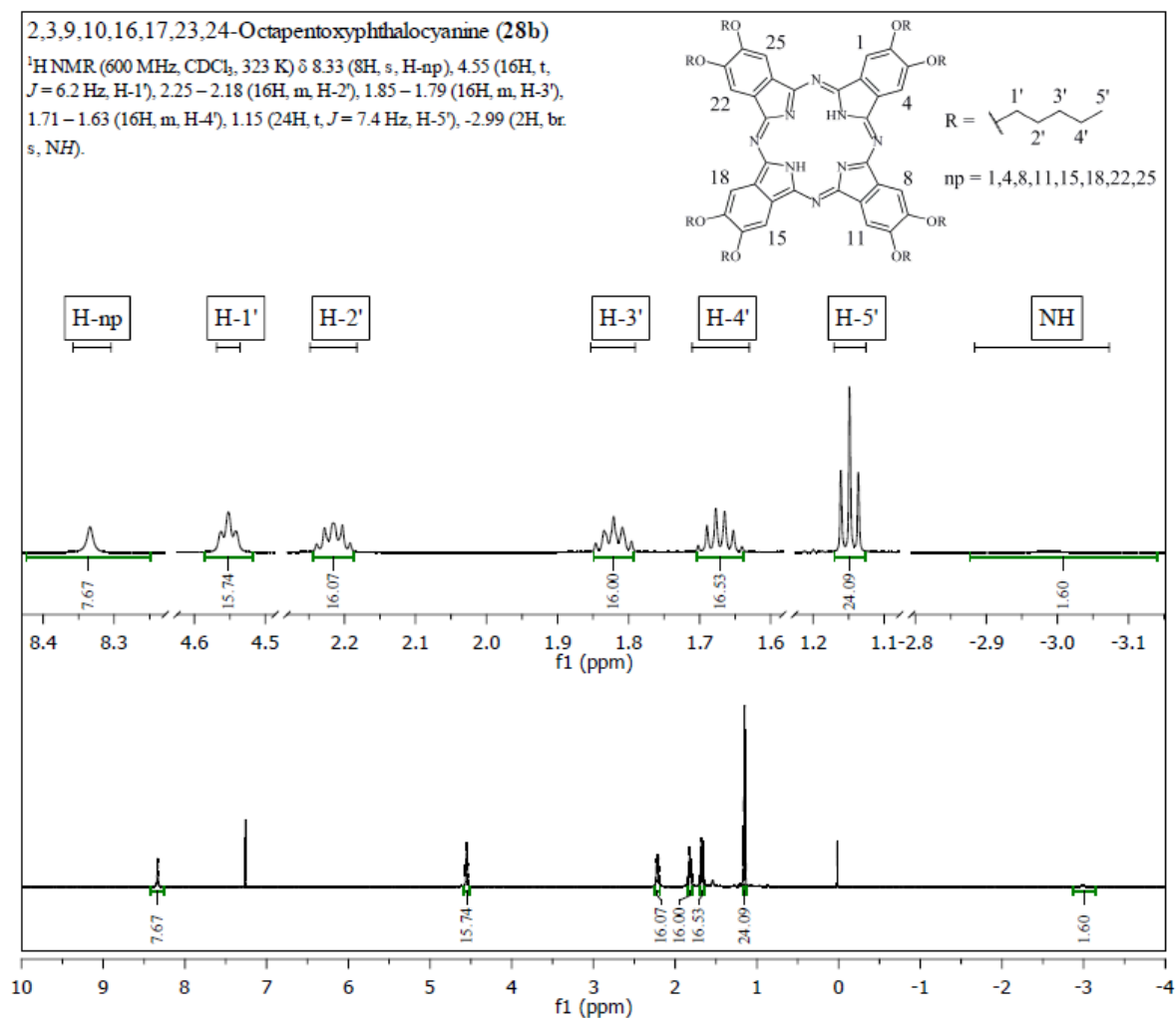


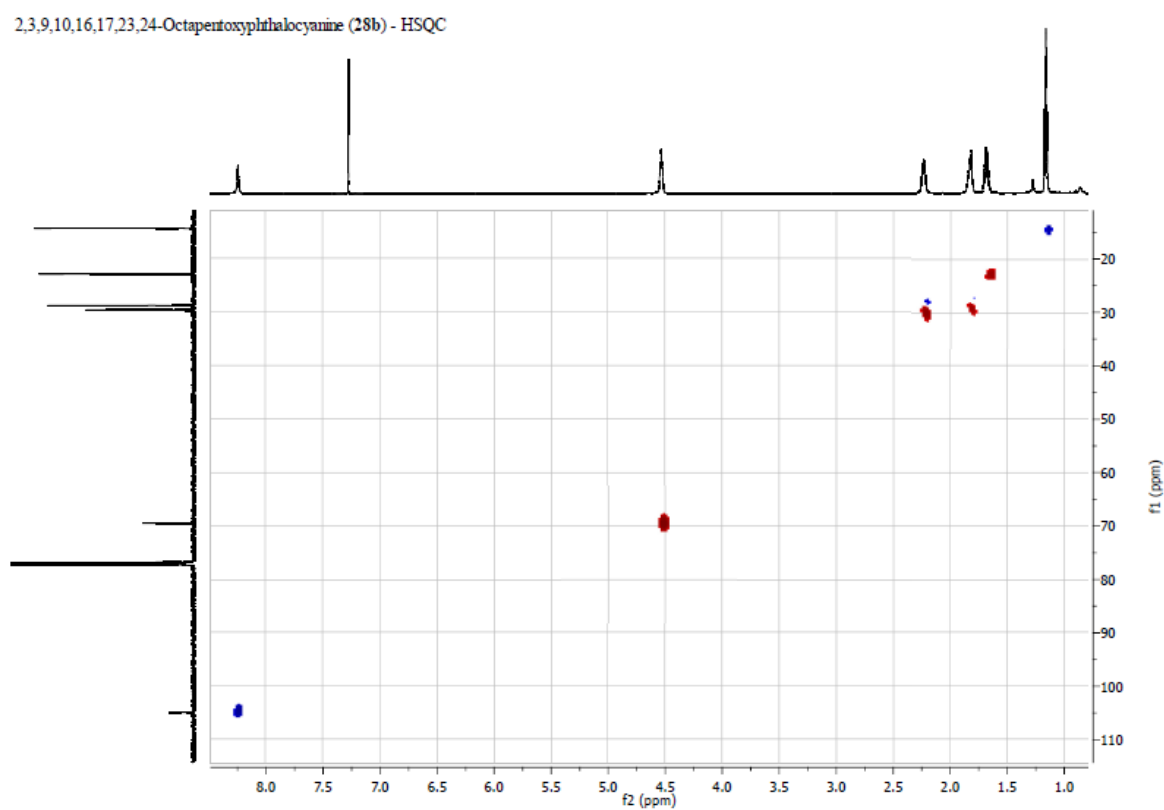
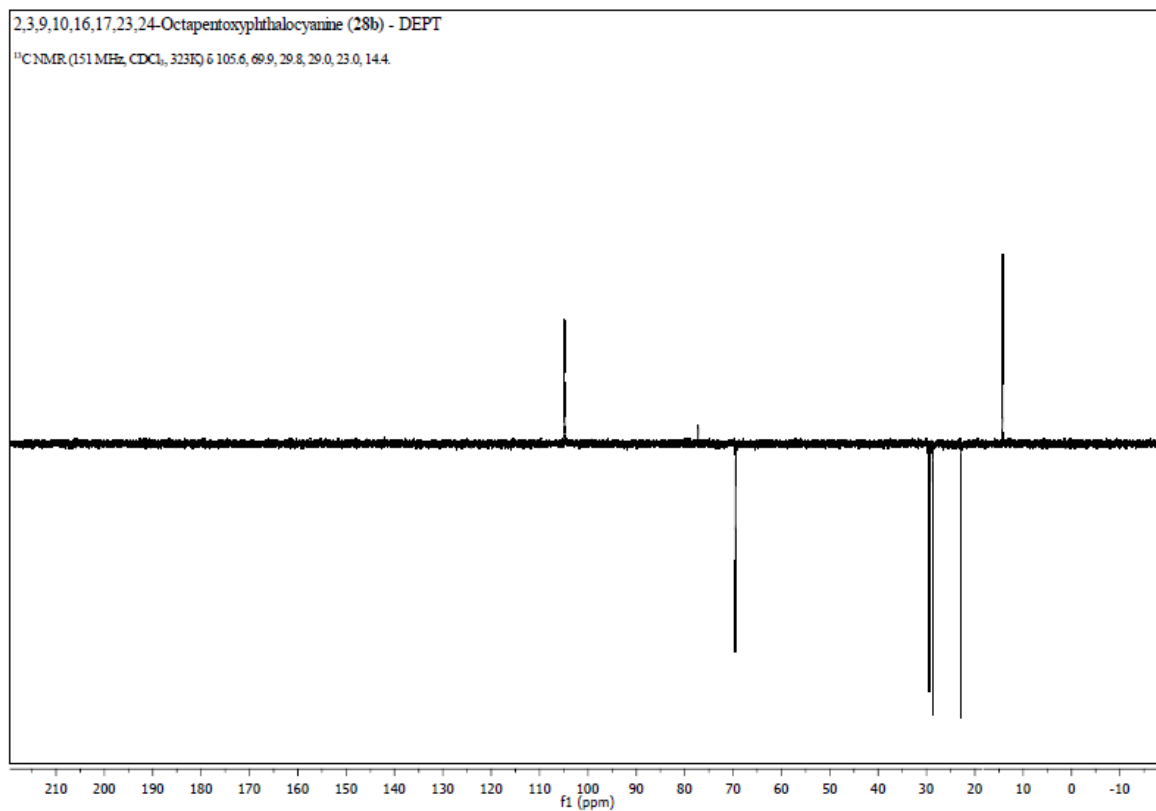
1,4,8,11,15,18,22,25-Octahexyphthalocyanine (27d) - HMBC



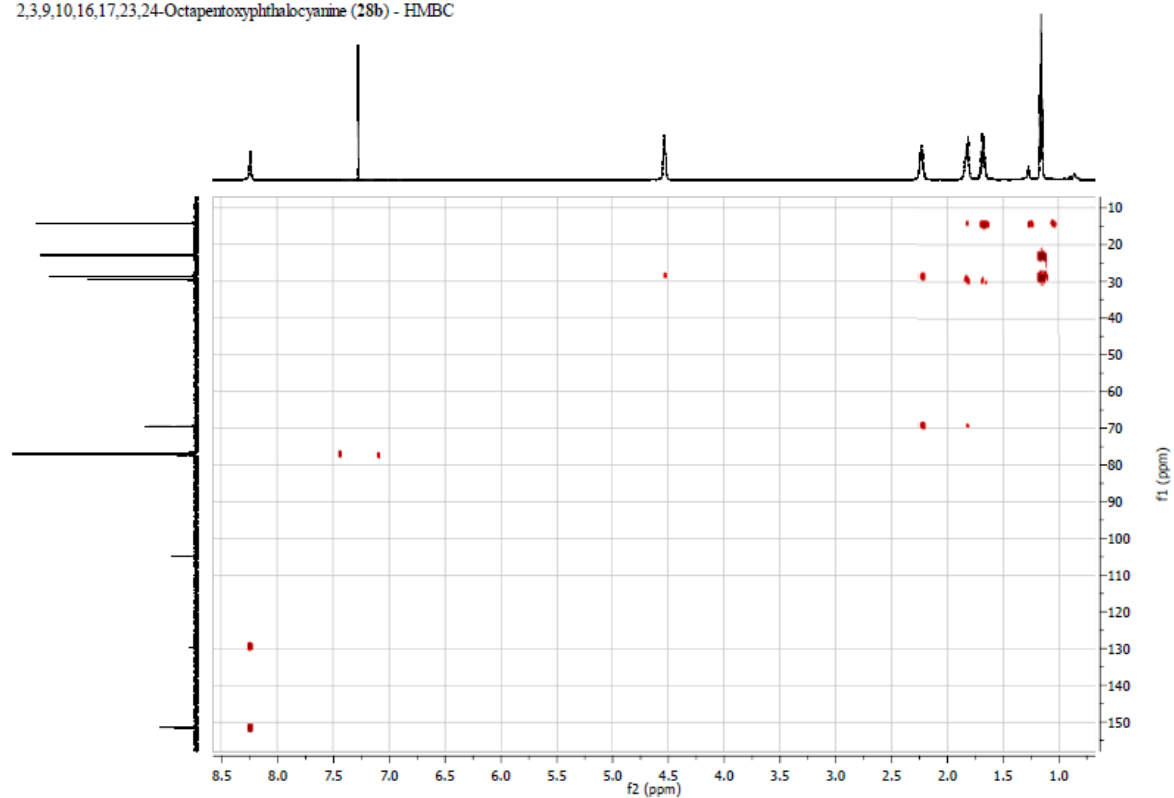
2,3,9,10,16,17,23,24-Octahexylphthalocyanine (28a)

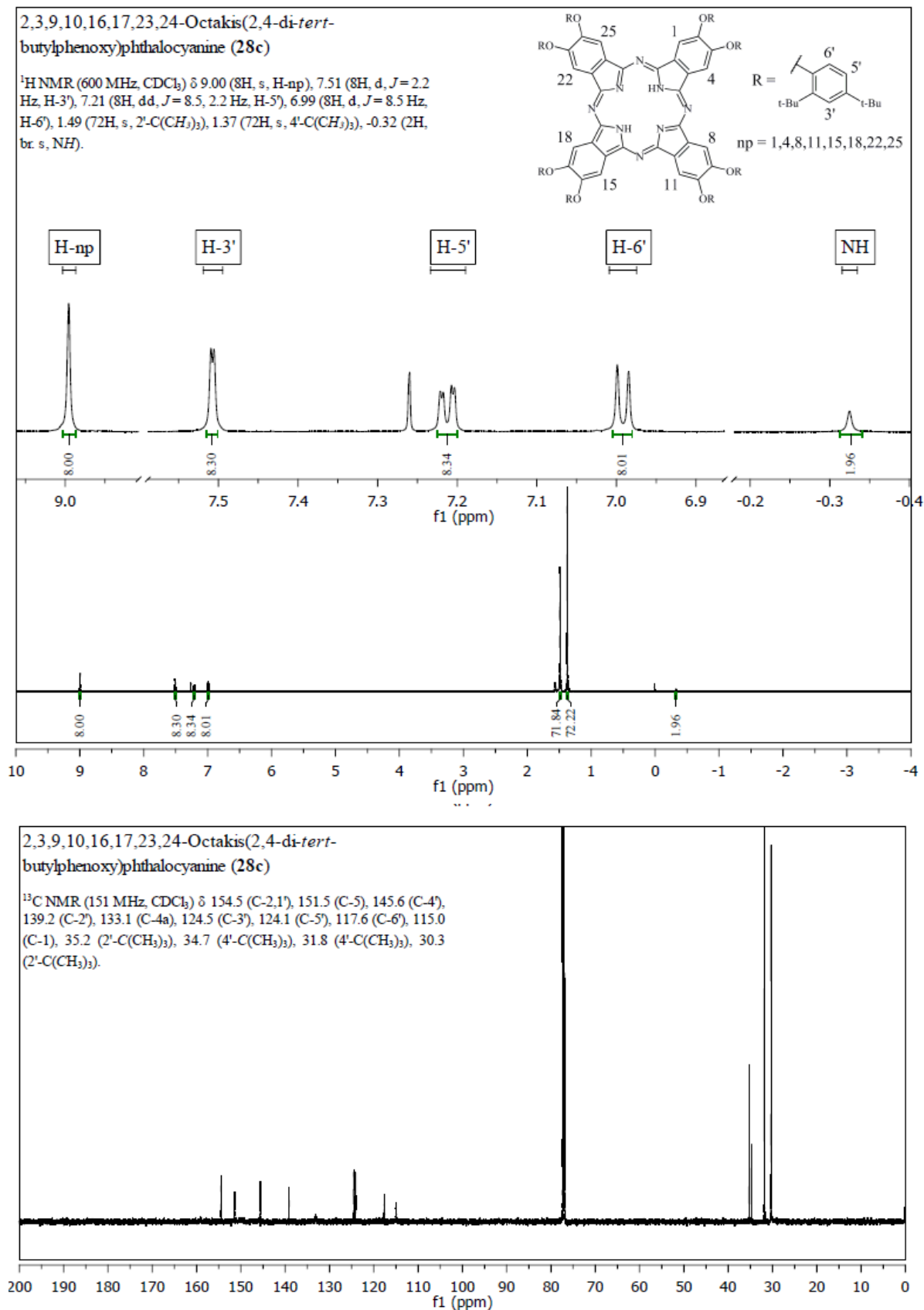


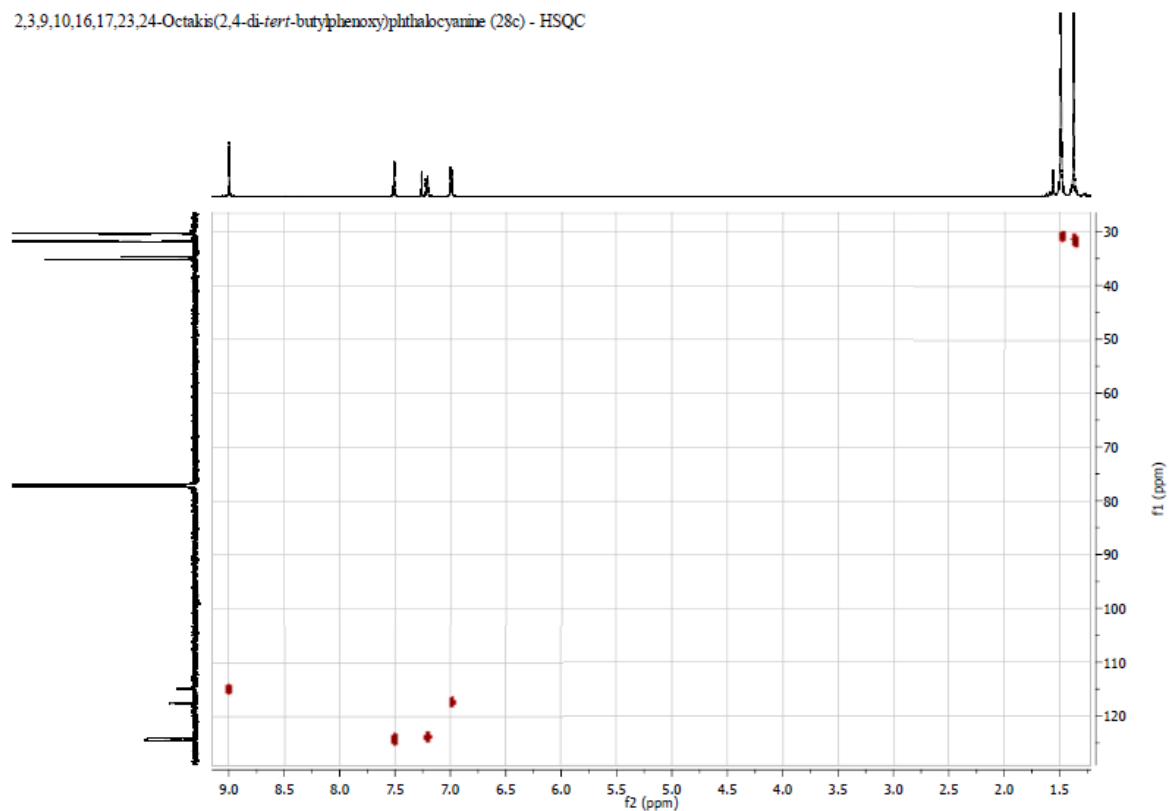
2,3,9,10,16,17,23,24-Octapentoxypthalocyanine (**28b**)



2,3,9,10,16,17,23,24-Octapentoxypthalocyanine (28b) - HMBC



2,3,9,10,16,17,23,24-Octakis(2,4-di-*tert*-butylphenoxy)phthalocyanine (28c)

2,3,9,10,16,17,23,24-Octakis(2,4-di-*tert*-butylphenoxy)phthalocyanine (28c) - HSQC2,3,9,10,16,17,23,24-Octakis(2,4-di-*tert*-butylphenoxy)phthalocyanine (28c) - HMBC