Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPLEMENTARY MATERIAL

Hexaphenylbenzene-Based Fluorescent Probes for Detection of Fluoride Ions

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1. General Experimental Methods

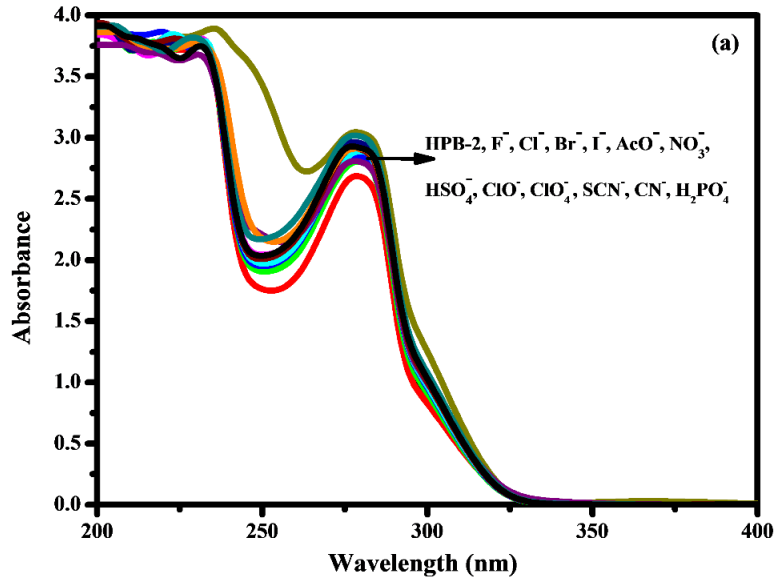
The UV-Vis absorption and fluorescence spectra of the samples were recorded using Shimadzu UV-3600 Plus UV-VIS-NIR Spectrophotometer and Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer, respectively. For the fluorescence measurements, sample solutions were excited at 300 nm and fluorescence intensities were recorded between 310-600 nm. Fourier Transform Infrared (FTIR) measurements of the samples were recorded with Bruker VERTEX 70v FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 (100) MHz Bruker spectrometer and were reported in δ units with $SiMe_4$ as the internal standard. The data for ^{1}H NMR are recorded as follows: chemical shift (d, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quarted, p = pentet, m = multiplet, bs = broad singlet, bd = broad doublet) and coupling constant(s) in Hz, integration. High-resolution mass spectrometry measurements were recorded on a Q-TOF mass spectrometer.

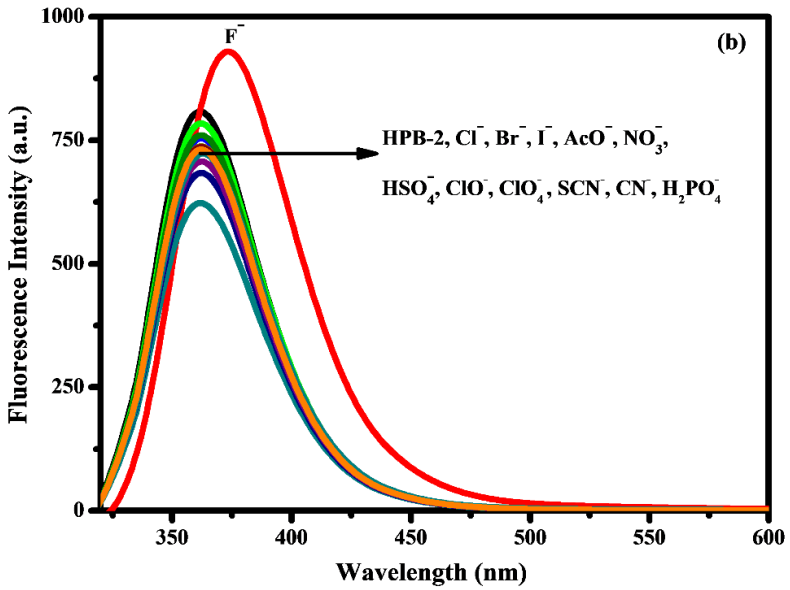
Fluorescence quantum yields of samples were calculated by using Parker-Rees equation (Equation 1).

$$\emptyset_s = \emptyset_r \left(\frac{D_S}{D_r}\right)\left(\frac{\eta_s^2}{\eta_r^2}\right)\left(\frac{1-10^{-OD_r}}{1-10^{-OD_s}}\right) \quad (1)$$

where *D* is the integrated area under the corrected fluorescence spectrum, *n* is the refractive index of the solution, and *OD* is the optical density at the excitation wavelength (λ_{ex}= 300 nm). The subscripts *s* and *r* refer to the sample and reference solutions, respectively. Quinine sulphate in 0.5 M H_2SO_4 solution was used as the reference. The fluorescence quantum yield of quinine sulphate is 0.54 in 0.5 M H_2SO_4 solution [1].

2. Photophysical Properties





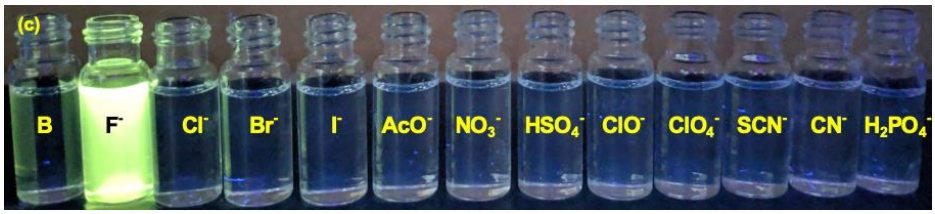


Fig. S1. (a) Absorption spectra of **HPB-2** in the absence and presence of 40 μM anions in THF. (b) Fluorescence spectra of **HPB-2** in the absence and presence of 40 μM anions in THF. (λ_{exc}=300 nm) (c) Photographs of **HPB-2** in the presence of anions under UV light. B; includes only **HPB-2** while the others contain **HPB-2** and an anion.

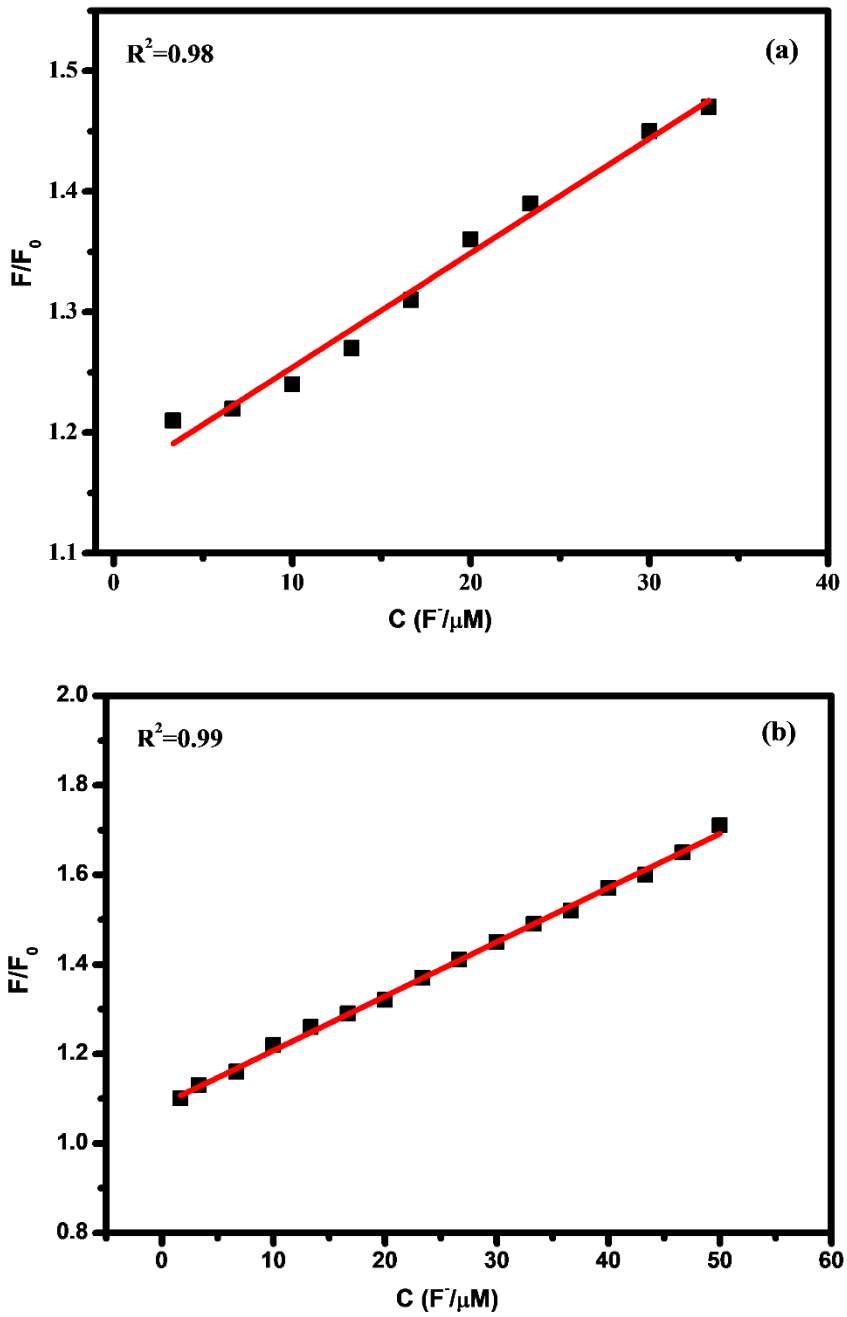


Fig. S2. Change fluorescence intensity of (a) **HPB-1** and (b) **HPB-2** with the increasing concentration of F^- ions.

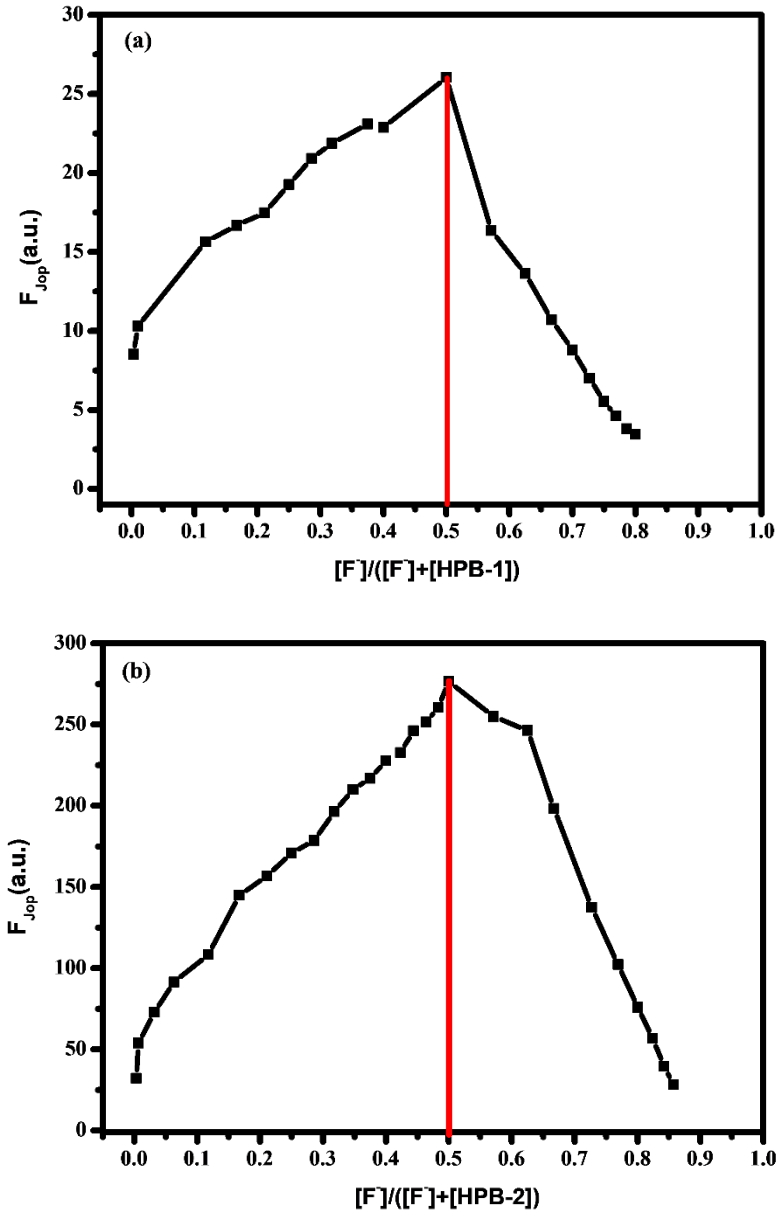


Fig. S3. Job's plot of (a) **HPB-1** and (b) **HPB-2** with F^- in THF.

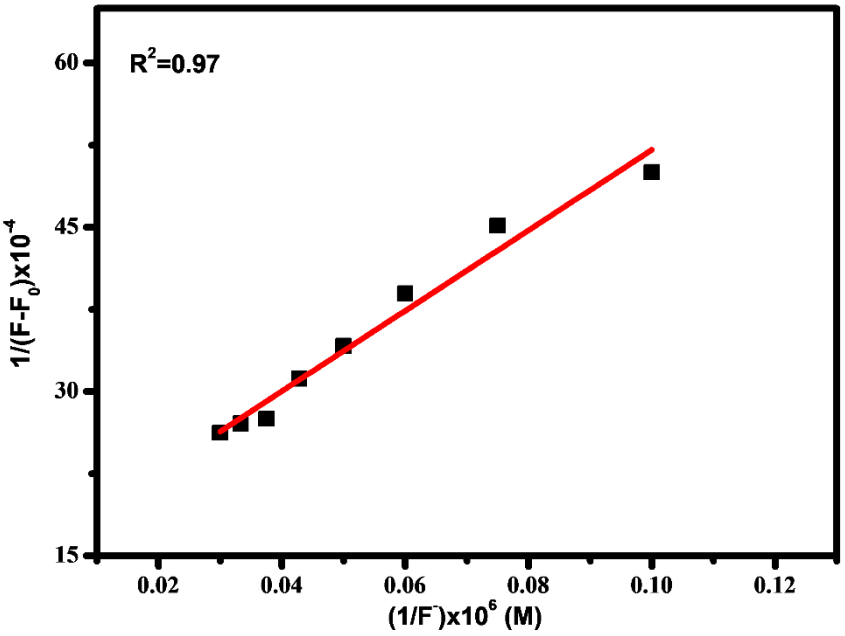


Fig. S4. Benesi-Hildebrand plot based on a 1:1 association stoichiometry between **HPB-1** and F^-.

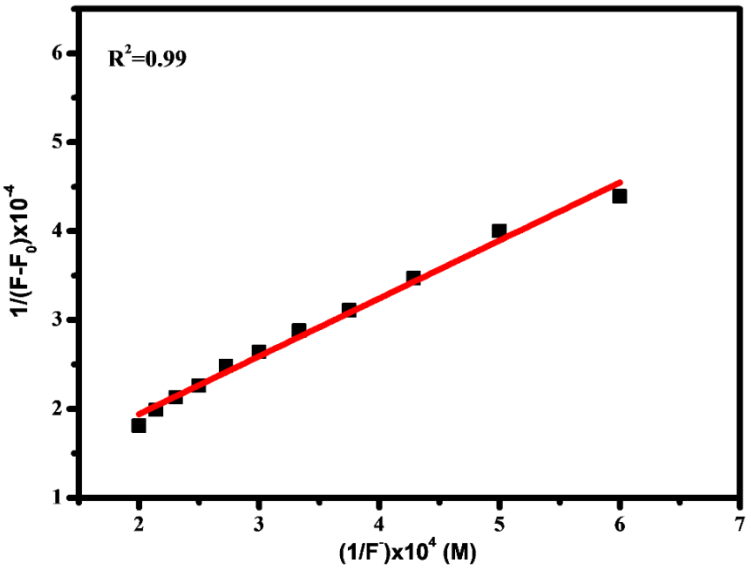
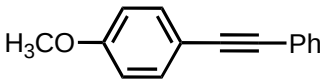


Fig. S5. Benesi-Hildebrand plot based on a 1:1 association stoichiometry between **HPB-2** and F^- ions.

3. Preparation of Starting Compounds for The Synthesis of HPB-1 and HPB-2

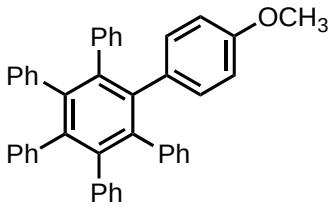
3.1. 1-Methoxy-4-(phenylethynyl)benzene (3) [2]



1-iodo-4-methoxybenzene (1 g, 4.45 mmol), $Pd(PPh_3)_2Cl_2$ (31 mg, 0.04 mmol), PPh_3 (23 mg, 0.08 mmol) was added and stirred at room temperature for 5 minutes. CuI (85 mg, 0.45 mmol) was added to the reaction mixture and stirred at 60 °C overnight. The reaction mixture, brought to room temperature, was extracted with diethyl ether (3×10 mL). The organic phase was washed sequentially with HCl (1N), NaOH (1N) and brine, then dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product obtained was purified by crystallization with ethanol. 1-Methoxy-4-(phenylethynyl)benzene (**3**) was obtained as yellow solid (909 mg, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.50 (m, 2H), 7.48–7.46 (m, AA' part of AA'BB' system, 2H), 7.37–7.29 (m, 3H), 6.88 – 6.86 (m, part BB' of system AA'BB', 2H), 3.81 (s, 3H). **APT ^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.9, 133.3, 131.7, 128.5, 128.2, 123.8, 115.6, 114.2, 89.6, 88.3, 55.5.

3.2. 4-Methoxy-3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl (5) [3]

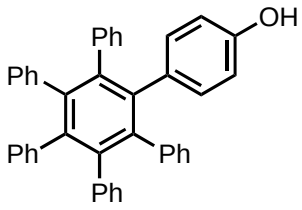


2,3,4,5-Tetraphenylcyclopenta-2,4-dien-1-one (738 mg, 1.92 mmol) and 1-methoxy-4-(phenylethynyl)benzene (400 mg, 1.92 mmol) were dissolved in 2.5 mL of Ph_2O. The reaction mixture was boiled at 258 °C for 6 hours. Then, the solid formed in the reaction mixture brought

to room temperature and was washed with ethanol and hexane. The crude product was purified by crystallization from ethanol. 4-Methoxy-3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl (**XX**) was obtained as white solid (760 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90–6.79 (m, 25H), 6.73–6.70 (m, AA' part of AA'BB' system, 2H), 6.41–6.38 (m, BB' of AA'BB' system) part, 2H), 3.60 (s, 3H). **APT ^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.0, 140.8, 140.73, 140.69, 140.6, 140.3, 140.2, 139.9, 133.0, 132.4, 131.4, 126.64, 126.55, 125.14, 125.11, 112.1, 54.9. (The resonances of the 4 carbon atoms overlap).

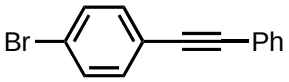
3.3. 3',4',5',6'-Tetraphenyl-[1,1':2',1''-terphenyl]-4-ol (6) [3]



Solution of 4-methoxy-3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl (350 mg, 0.62 mmol) in 5 mL of dichloromethane (DCM) cooled to -78 °C. Then, a solution of BBr_3 (0.06 mL, 0.62 mmol) in 3 mL of dichloromethane was added dropwise to the solution. After the reaction was brought to room temperature, it was stirred for 12 hours more. The reaction was stopped by adding water. It was extracted with DCM (3×20 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuo. The obtained crude product was purified by crystallization with acetone. 3',4',5',6'-Tetraphenyl-[1,1':2',1''-terphenyl]-4-ol (**6**) was obtained as white solid (273 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 – 6.79 (m, 25H), 6.68 – 6.66 (m, AA' part of AA'BB' system, 2H), 6.34 – 6.32 (m, BB' of AA'BB' system part, 2H), 4.35 (s, 1H).

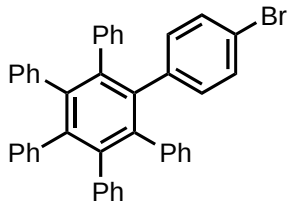
3.4. 1-Bromo-4-(phenylethynyl)benzene (8) [4]



1-bromo-4-iodobenzene (1 g, 3.56 mmol), $Pd(PPh_3)_2Cl_2$ (25 mg, 0.04 mmol), PPh_3 (19 mg, 0.08 mmol) was added and stirred at room temperature for 5 minutes. CuI (68 mg, 0.36 mmol) was added to the reaction mixture and stirred at 60 °C overnight. The reaction mixture, brought to room temperature, was extracted with diethyl ether (3×10 mL). The organic phase was washed sequentially with HCl (1N), NaOH (1N) and brine, dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product obtained was purified by crystallization with ethanol. 1-Bromo-4-(phenylethynyl)benzene (**8**) was obtained as yellow solid (872 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.50 (m, 2H), 7.48 – 7.46 (m, AA' part of AA'BB' system, 2H), 7.39 – 7.37 (m, AA'BB' system BB' part, 2H), 7.36 – 7.32 (m, 3H). **APT ^{13}C NMR (100 MHz, $CDCl_3$):** δ 133.1, 131.64, 131.62, 128.5, 128.4, 123.0, 122.5, 122.3, 90.6, 88.4.

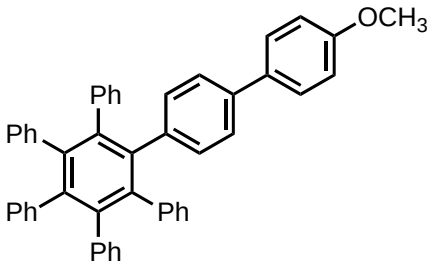
3.5. 4-Bromo-3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl (9) [5]



2,3,4,5-Tetraphenylcyclopenta-2,4-dien-1-one (598 mg, 1.56 mmol) and 1-bromo-4-(phenylethynyl)benzene (400 mg, 1.56 mmol) were dissolved in 2 mL Ph_2O. The reaction mixture was boiled at 258 °C for 24 hours. The solid formed in the reaction mixture, which was then brought to room temperature, was washed with acetone. The crude product was purified by crystallization with acetone. 4-Bromo-3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl (**9**) was obtained as white solid (735 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 – 6.96 (m, AA' part of AA'BB' system, 2H), 6.90 – 6.77 (m, 25H), 6.71 – 6.69 (m, BB' of AA'BB' system) part, 2H). **APT ^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.7, 140.52, 140.46, 140.4, 140.3, 140.2, 139.7, 139.0, 133.0, 131.4, 129.8, 126.8, 126.6, 125.5, 125.3, 119.5. (The resonances of the 4 carbon atoms overlap).

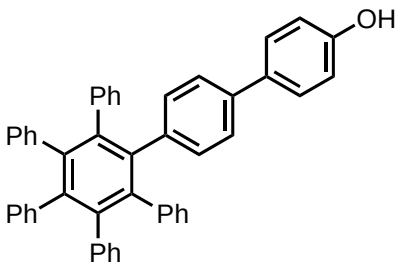
3.6. 4'''-Methoxy-3',4',5',6'-tetraphenyl-1,1':2',1'':4'',1'''-quaterphenyl (11) [5]



2,3,4,5-Tetraphenylcyclopenta-2,4-dien-1-one (598 mg, 1.56 mmol) and 1-bromo-4-(phenylethynyl)benzene (400 mg, 1.56 mmol) were dissolved in 2 mL Ph_2O. The reaction mixture was boiled at 258 °C for 24 hours. The solid formed in the reaction mixture, which was then brought to room temperature, was washed with acetone. The crude product was purified by crystallization with acetone. 4-Bromo-3',4',5',6'-tetraphenyl-1,1':2',1''-terphenyl (**11**) was obtained as white solid (735 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.36 (m, AA'BB' sisteminin AA' kısmı, 2H), 7.08 – 7.06 (m, AA'BB' sisteminin AA' kısmı, 2H), 7.02 – 6.65 (m, 29H), 3.79 (s, 3H).

3.7. 3',4',5',6'-Tetraphenyl-[1,1':2',1'':4'',1'''-quaterphenyl]-4'''-ol (12) [5]



4'''-Methoxy-3',4',5',6'-tetraphenyl-1,1':2',1'':4'',1'''-quaterphenyl (350 mg, 0.55 mmol) in 5 mL of DCM was cooled to -78°C. Then, BBr_3 (0.05 mL, 0.55 mmol) solution in 3 mL DCM was added dropwise to the solution. After the reaction was brought to room temperature, it was stirred for 12 hours. After the reaction was complete, it was stopped with water. It was extracted with DCM (3×20 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuo. The obtained crude product was purified by crystallization with acetone. 3',4',5',6'-Tetraphenyl-[1,1':2',1'':4'',1'''-quaterphenyl]-4'''-ol (**12**) was obtained as white solid (325 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.30 (m, AA' portion of AA'BB' system, 2H), 7.06 – 7.04 (m, AA' portion of AA'BB' system, 2H), 6.89 – 6.81 (m, 27H), 6.79 – 6.77 (m, BB' part of AA'BB' system, 2H), 4.65 (s, 1H). **APT ^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.7, 140.6, 140.4, 140.0, 139.2, 136.9, 133.6, 131.8, 131.4, 127.9, 126.6 (2C), 125.2 (2C), 124.6, 115.4. (The resonances of the 8 carbon atoms overlap).

References

[1] E. Bozkurt, H.I. Gul, *Inorg. Chim. Acta*, 2020, **502**, 119288.

[2] B. Agrahari, S. Layek, R. Ganguly, D.D. Pathak, *Inorg. Chim. Acta*, 2018, **471**, 345-354.

[3] S. Matsumura, A.R. Hlil, C. Lepiller, J. Gaudet, D. Guay, A.S. *Macromolecules*, 2008, **41**, 277-280.

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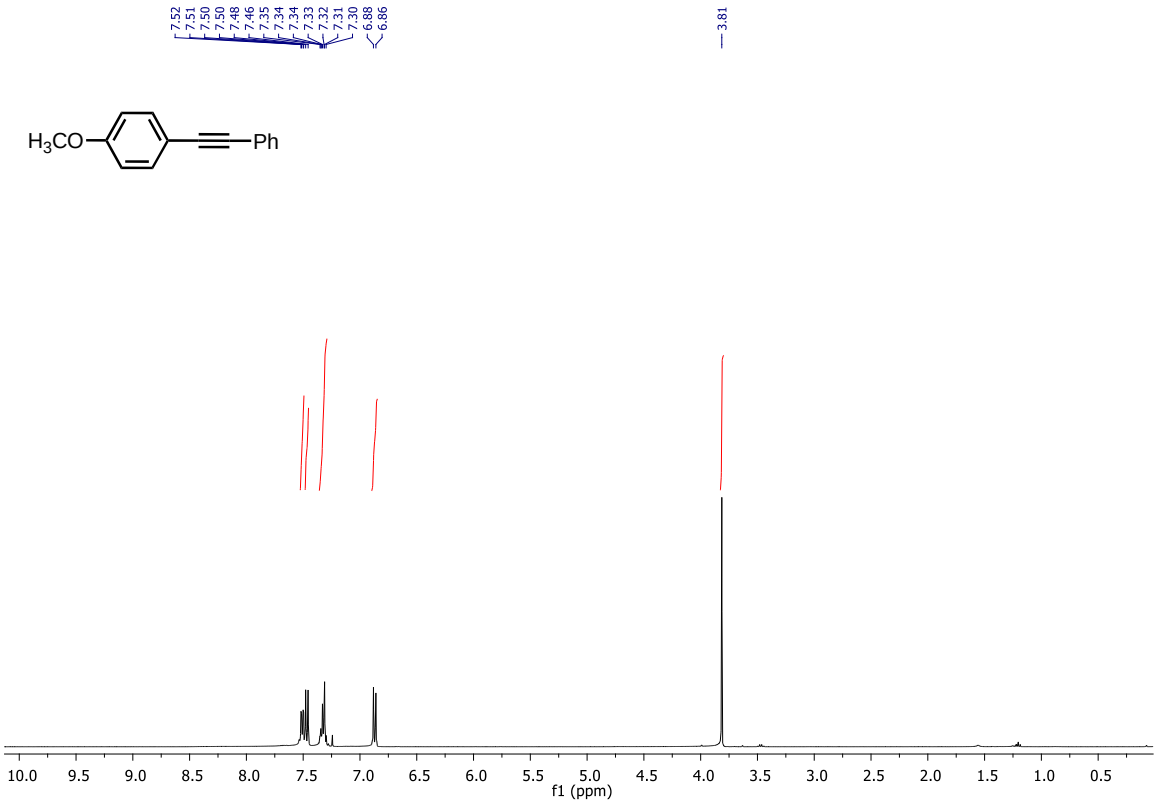
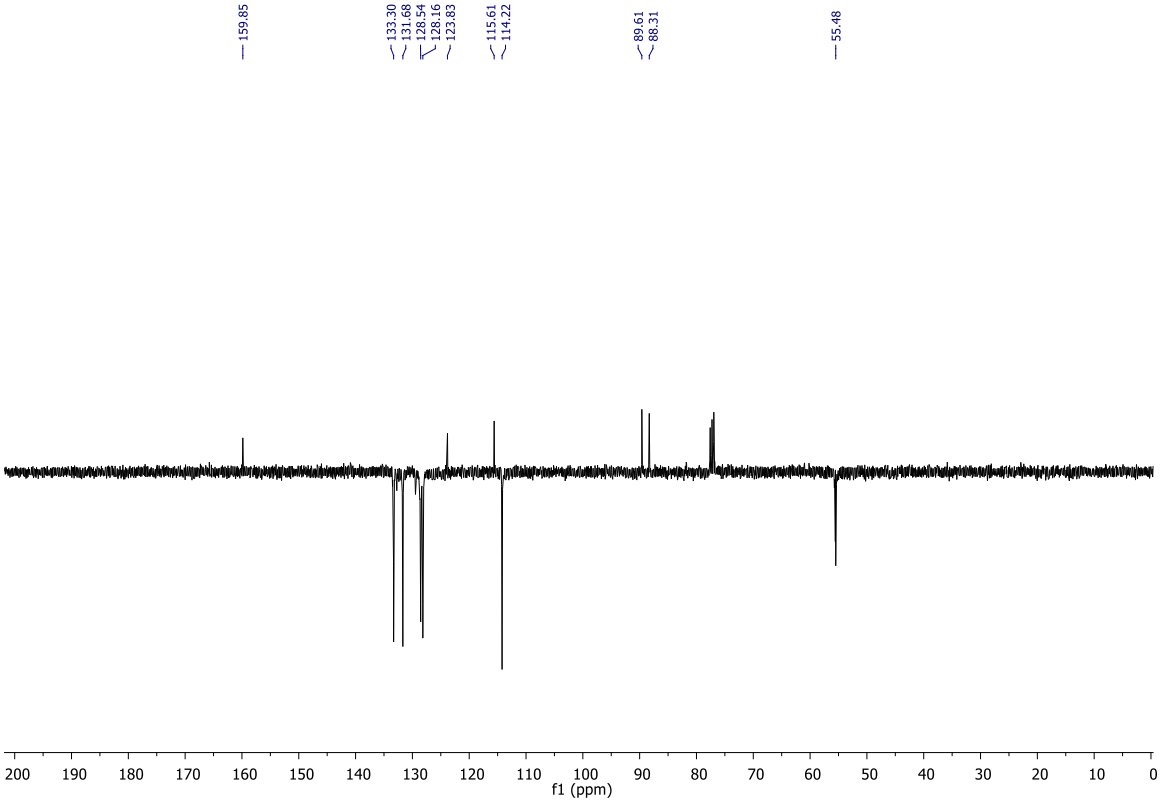
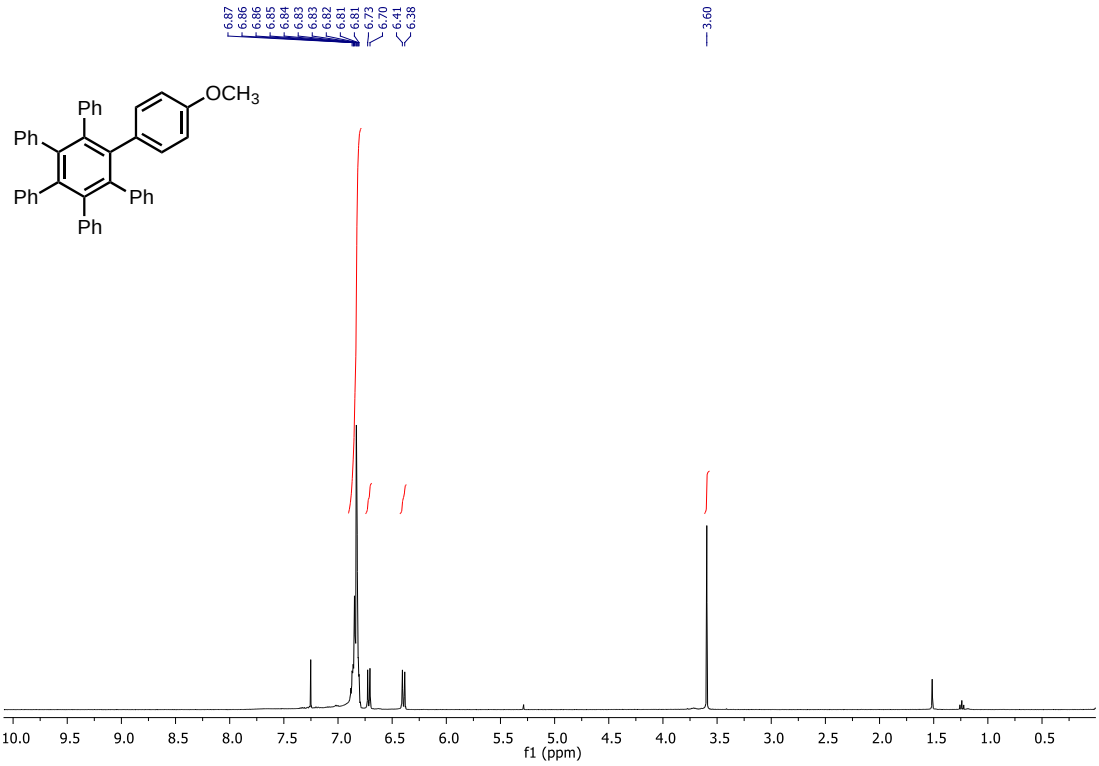
[5] K. Wunderlich, C. Grigoriadis, G. Zardalidis, M. Klapper, R. Graf, H.-J.r. Butt, K. Müllen, G. Floudas, *Macromolecules*, 2014, **47**, 5691-5702.

4. ^{1}H NMR, APT ^{13}C NMR and HRMS Spectra



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3.60
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Ph
Ph
Ph
Ph
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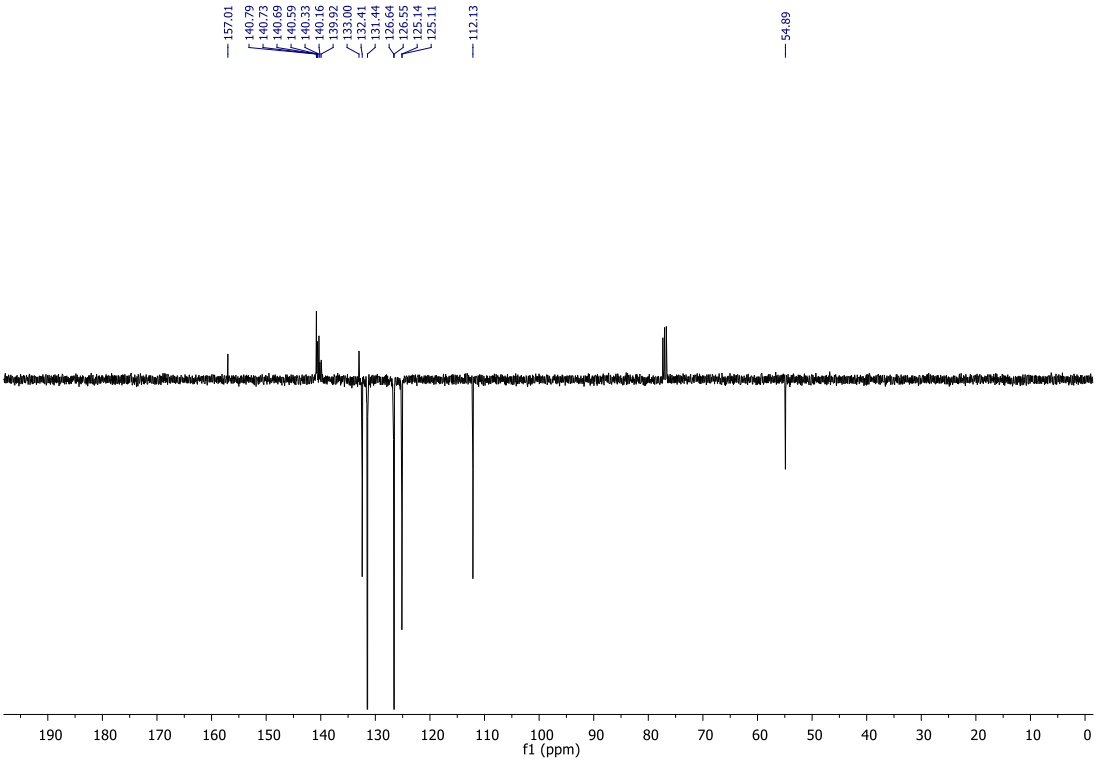
f1 (ppm)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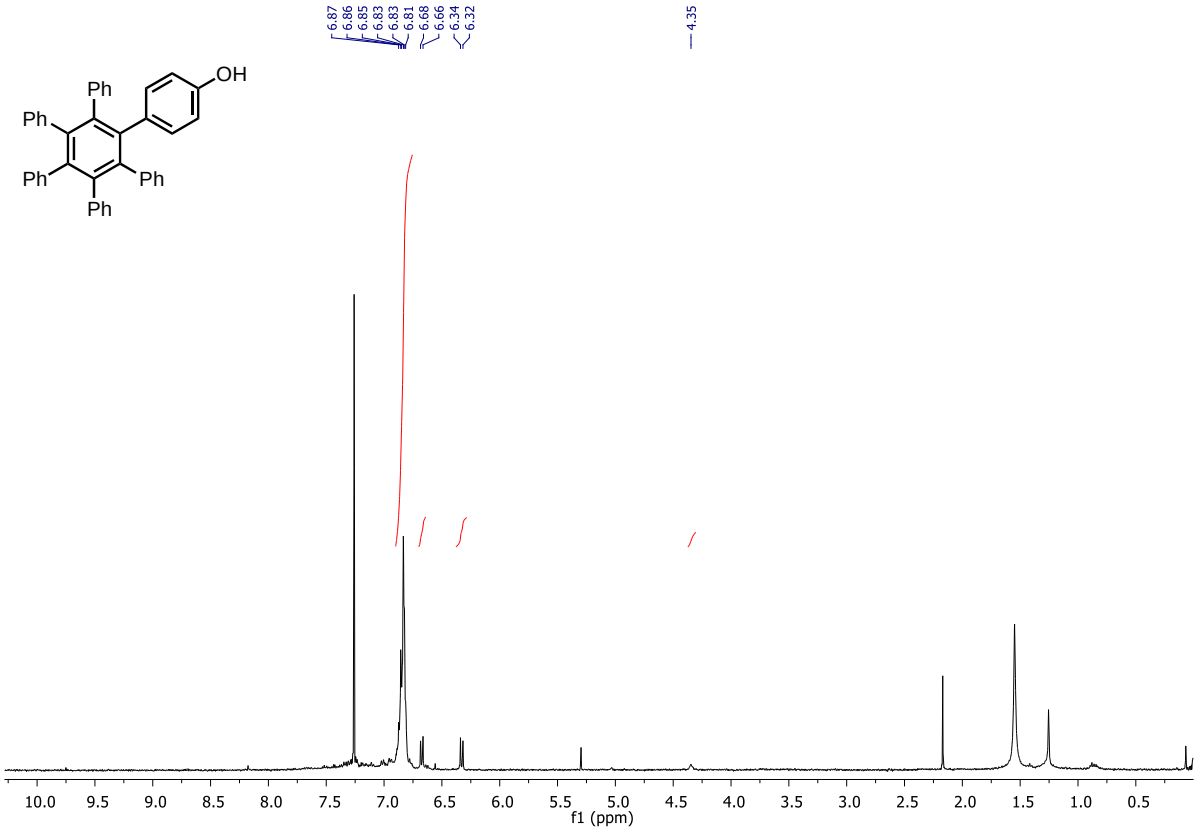
f1 (ppm)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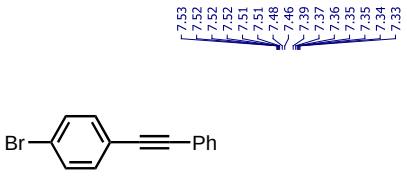
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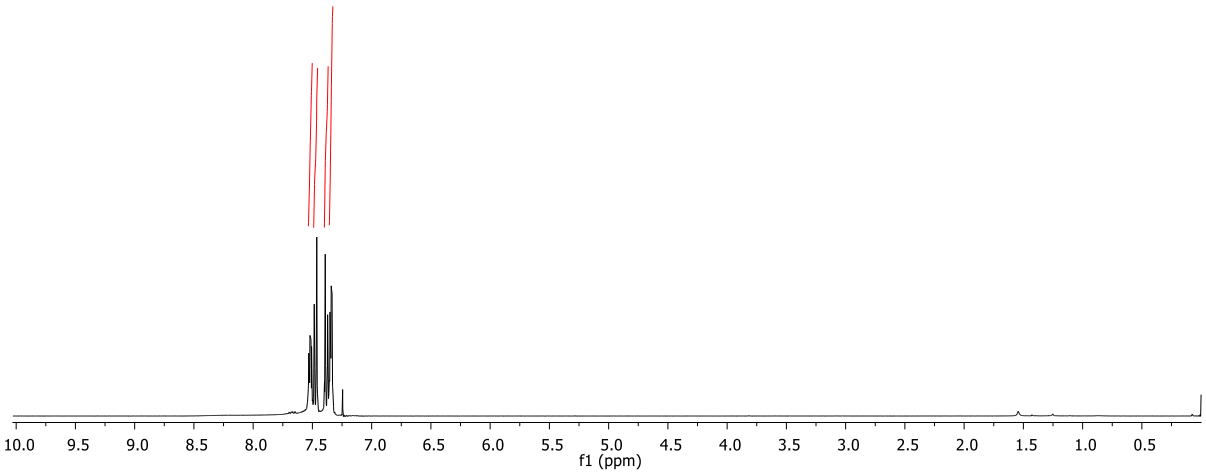
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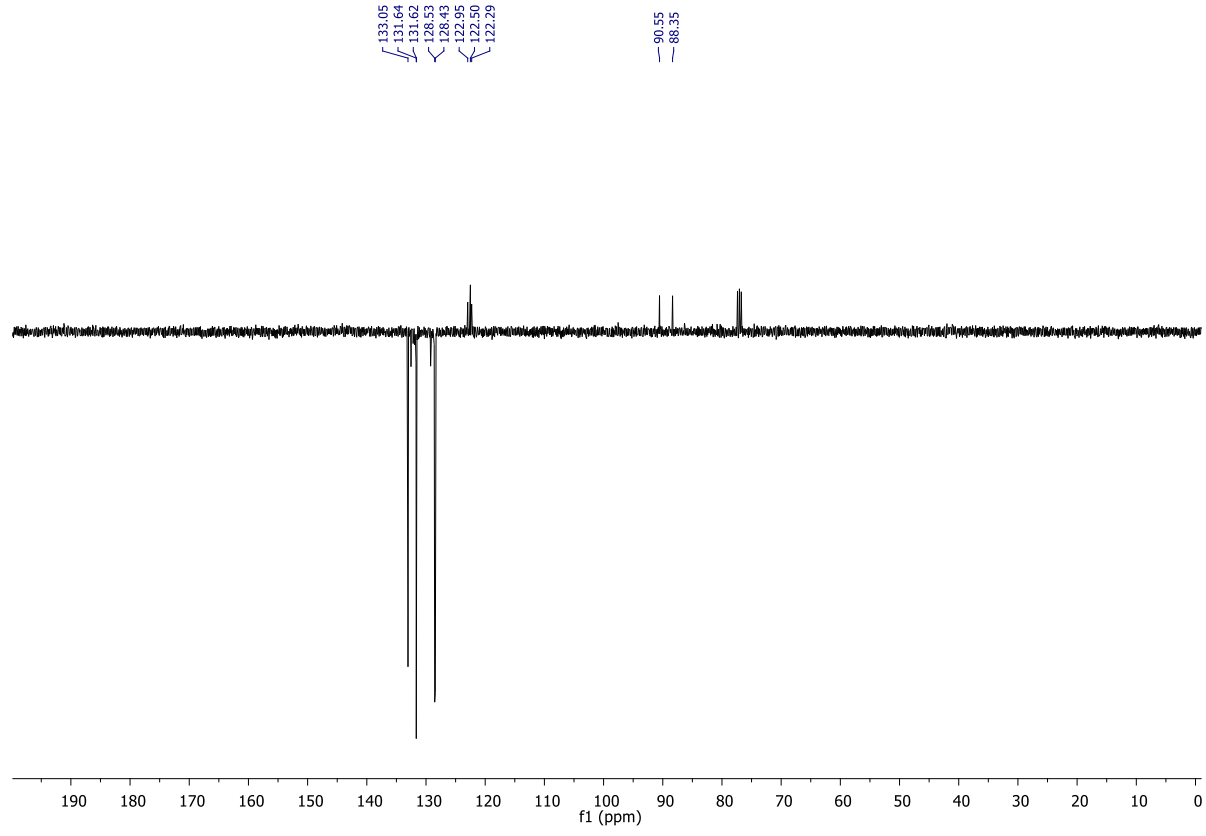
f1 (ppm)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90
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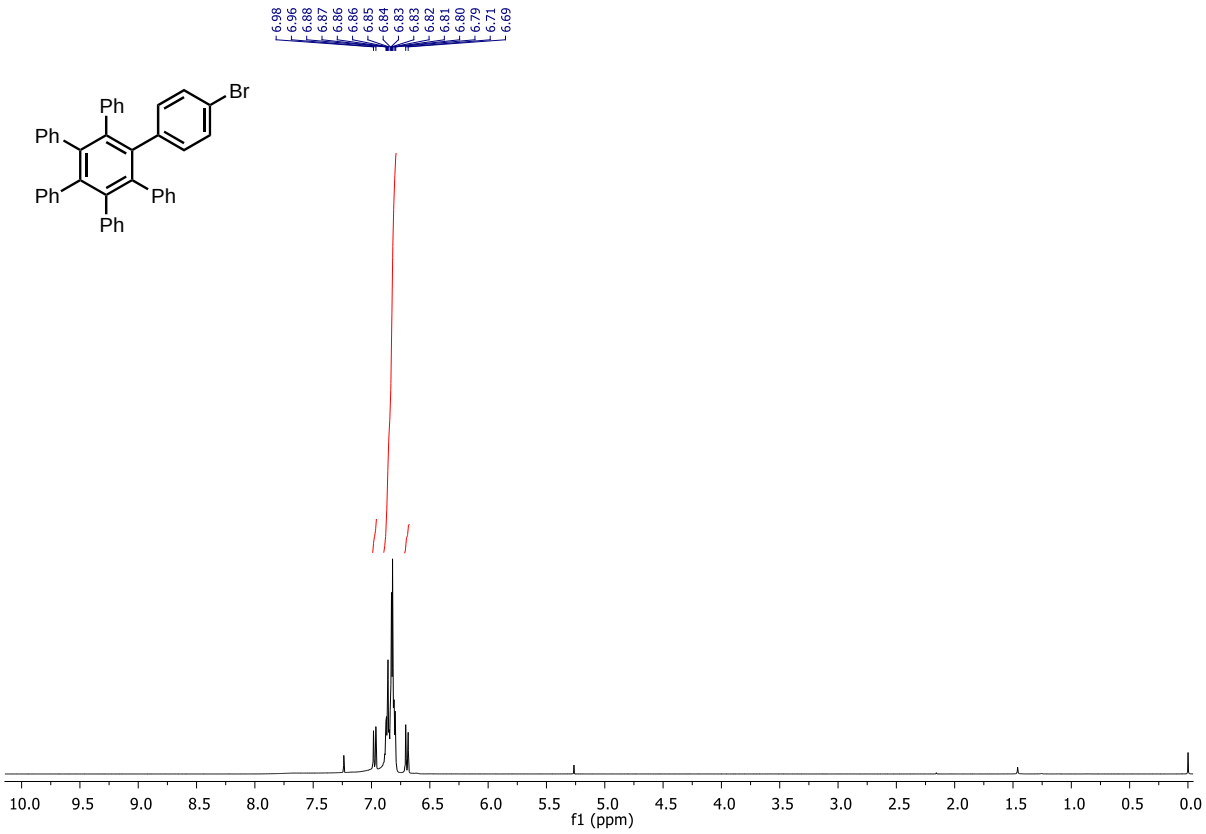
f1 (ppm)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6.71
6.69
Br
Ph
Ph
Ph
Ph
Ph
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9.0
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8.0
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6.5
6.0
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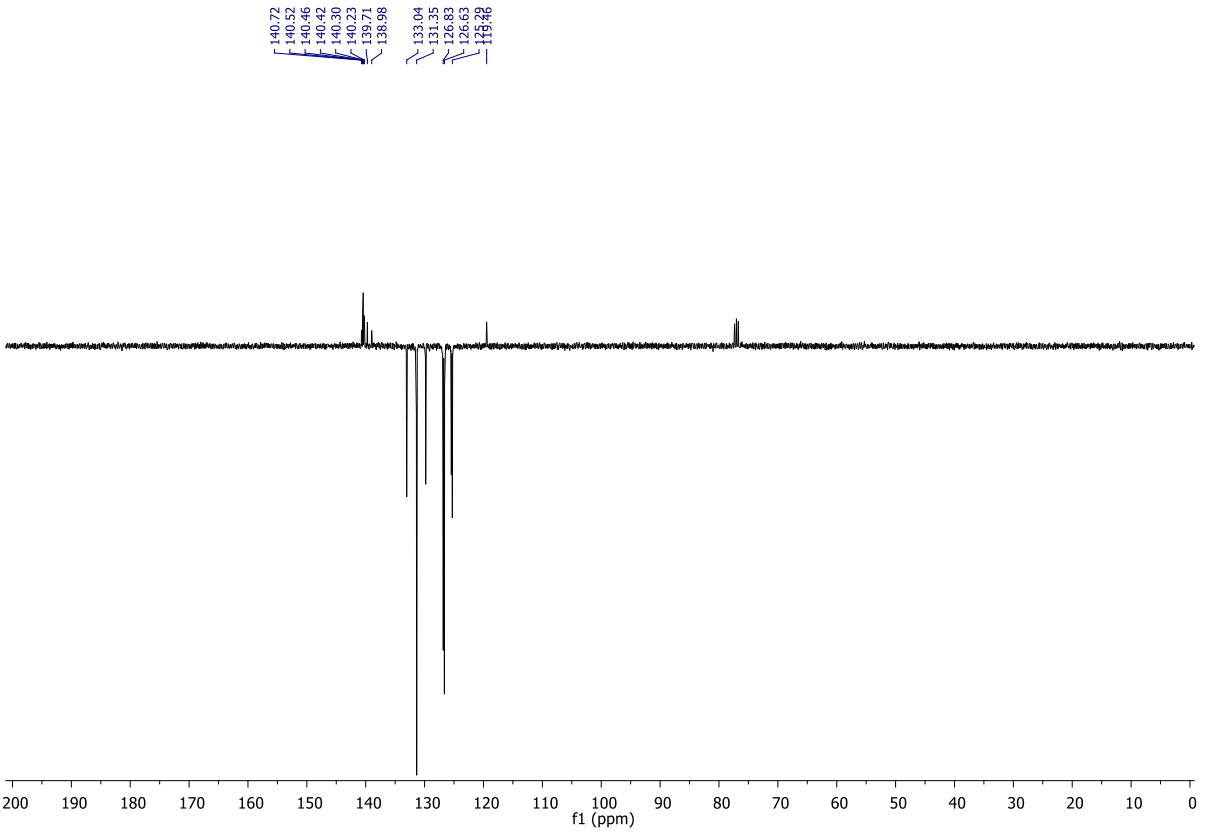
0.0
f1 (ppm)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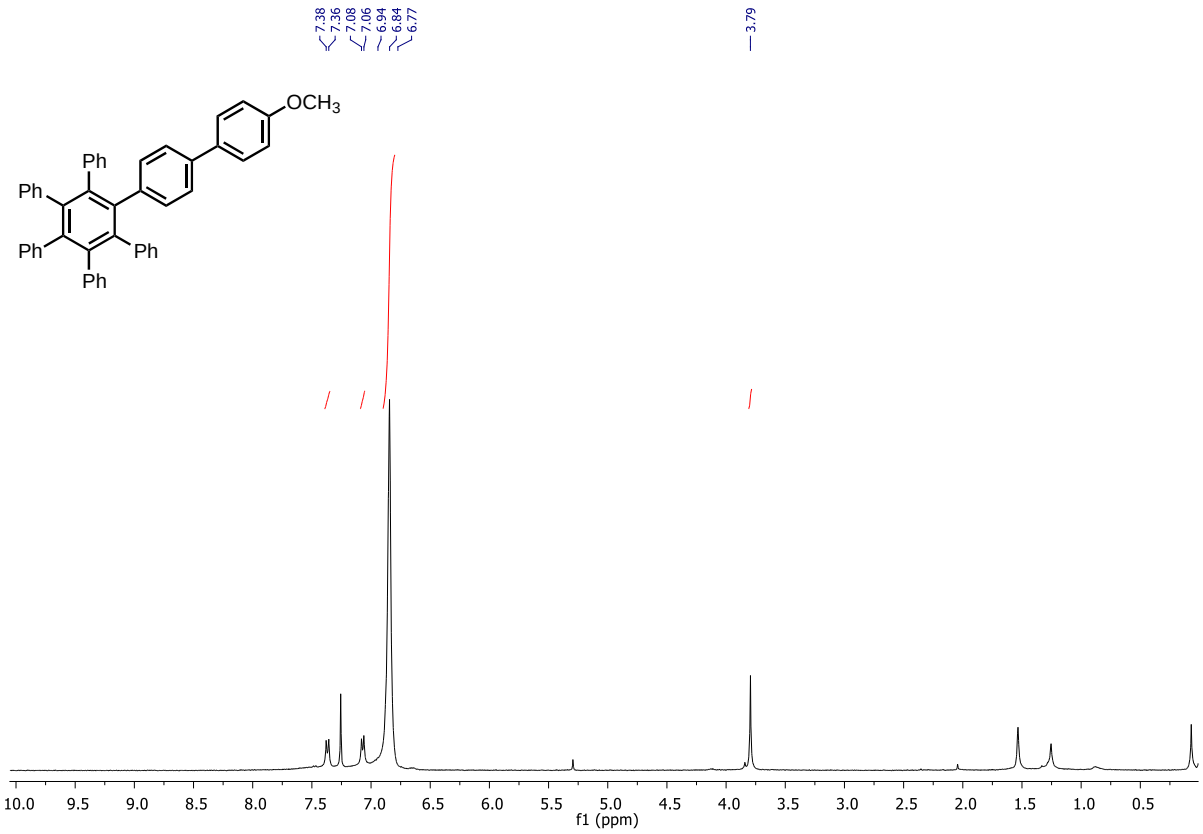
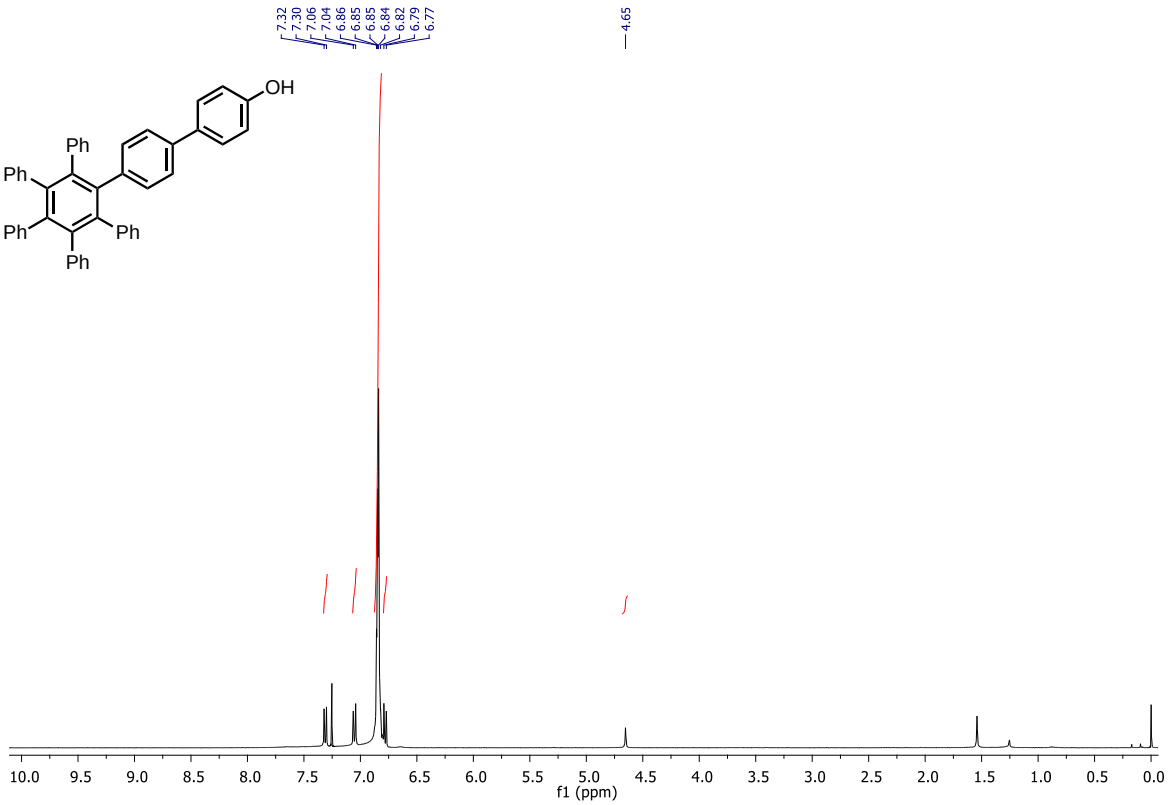
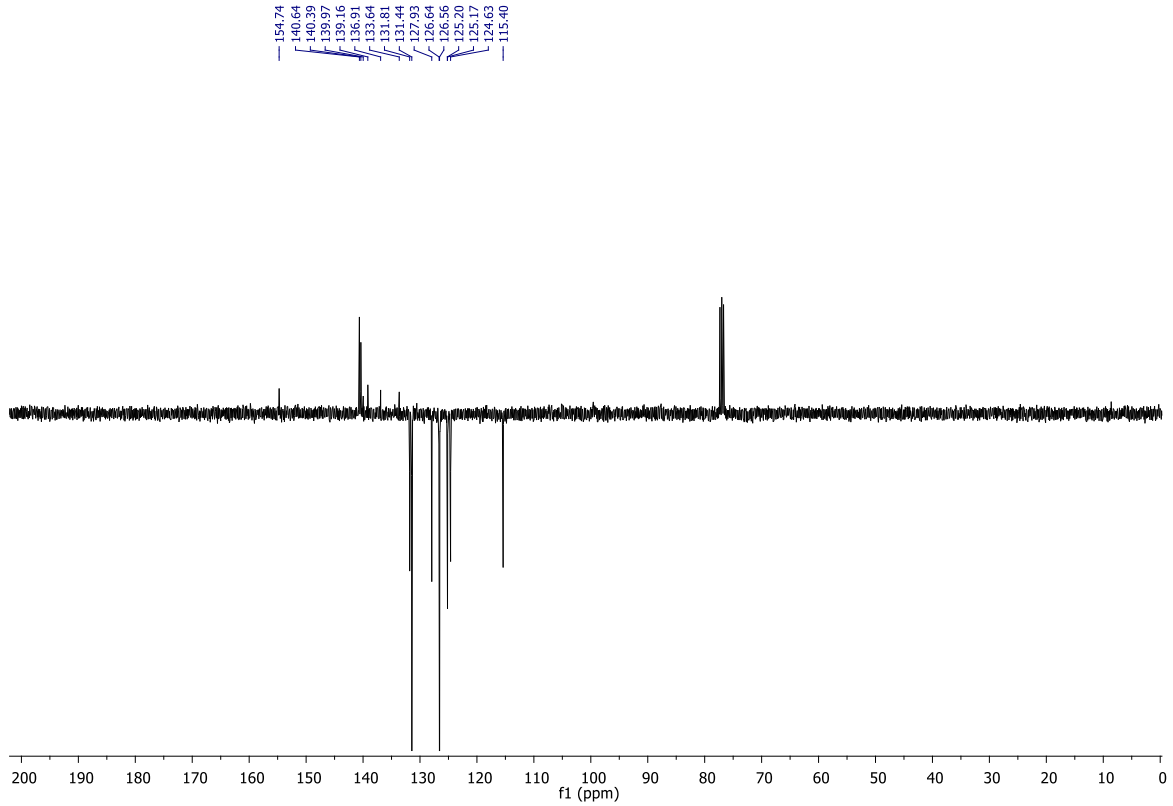
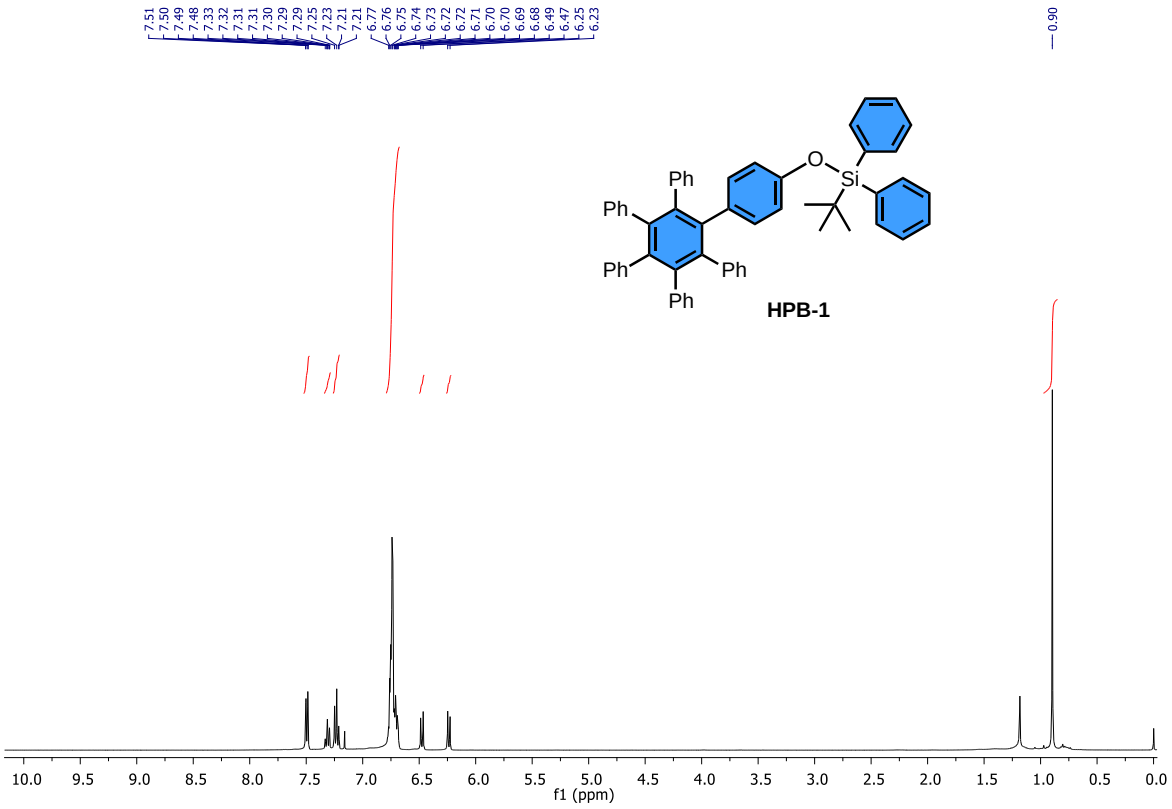
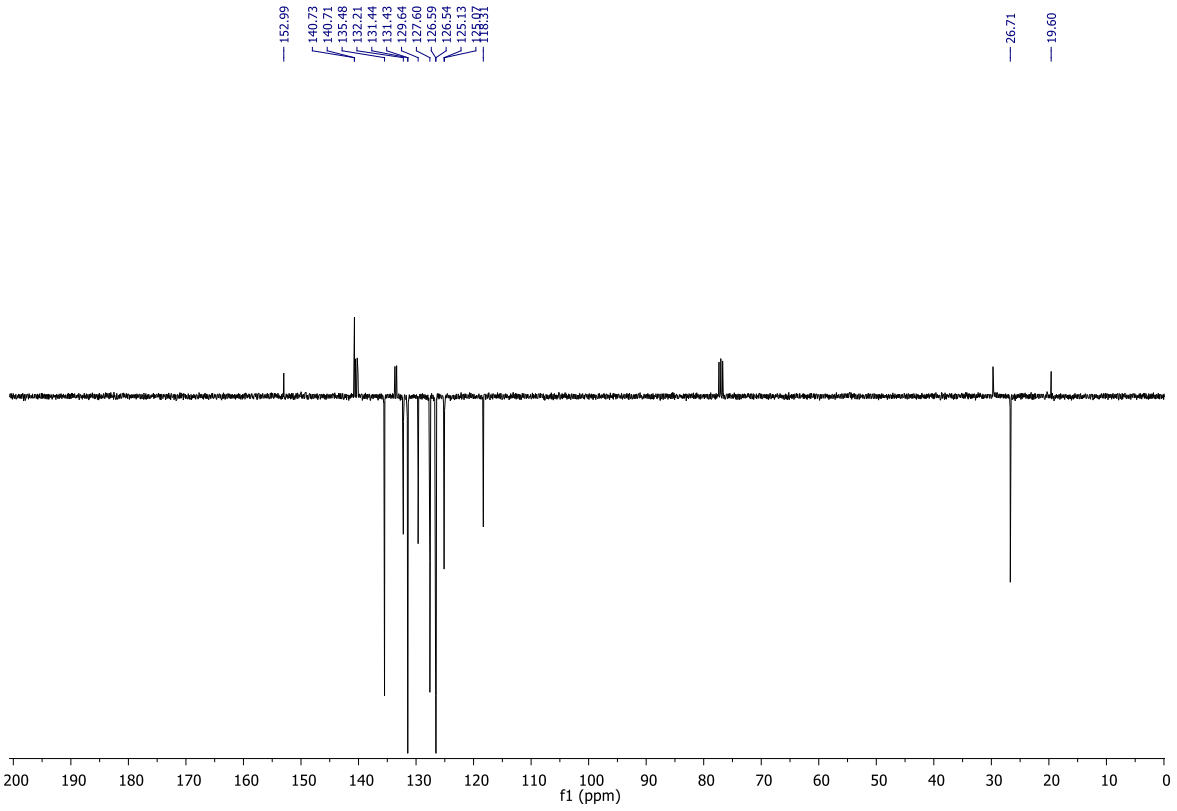
10
0
f1 (ppm)

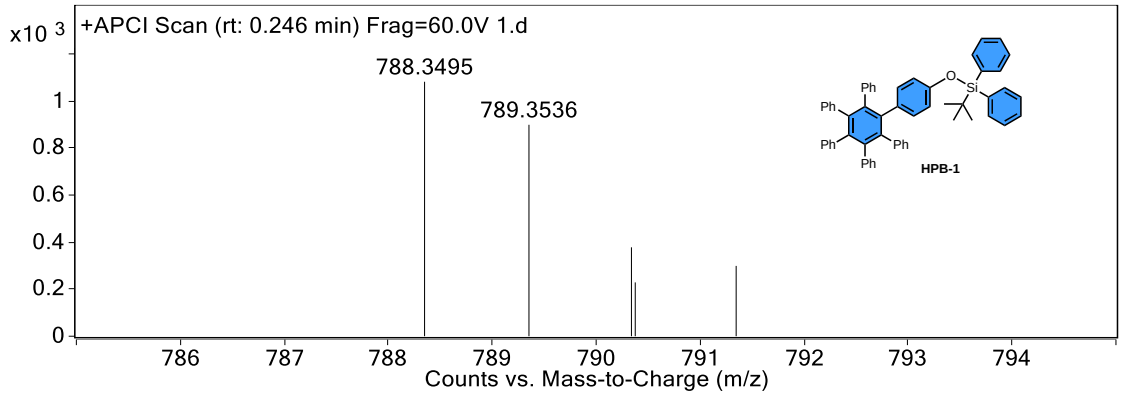

7.38
7.36
7.08
7.06
6.94
6.84
6.77
3.79
OCH3
Ph
Ph
Ph
Ph
Ph
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

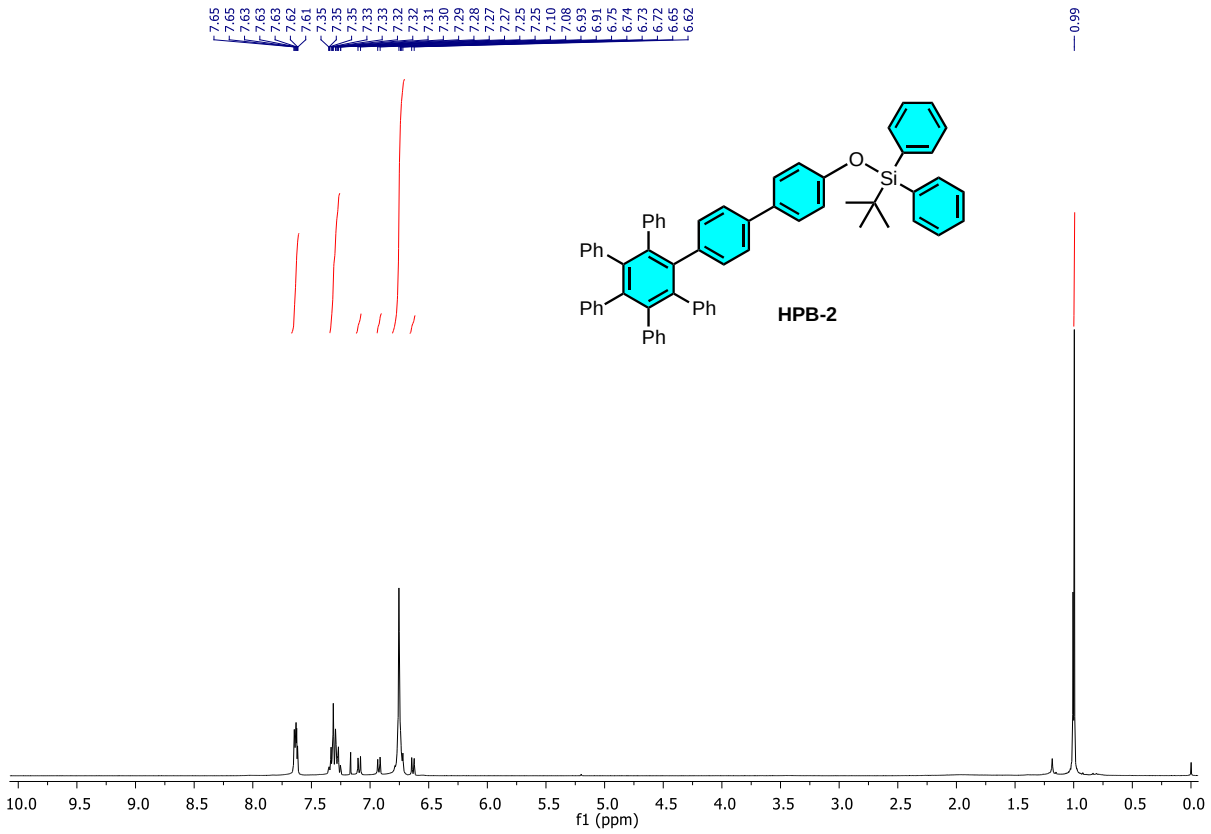

7.32
7.30
7.06
7.04
6.86
6.85
6.84
6.82
6.79
6.77
4.65
OH
Ph
Ph
Ph
Ph
Ph
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

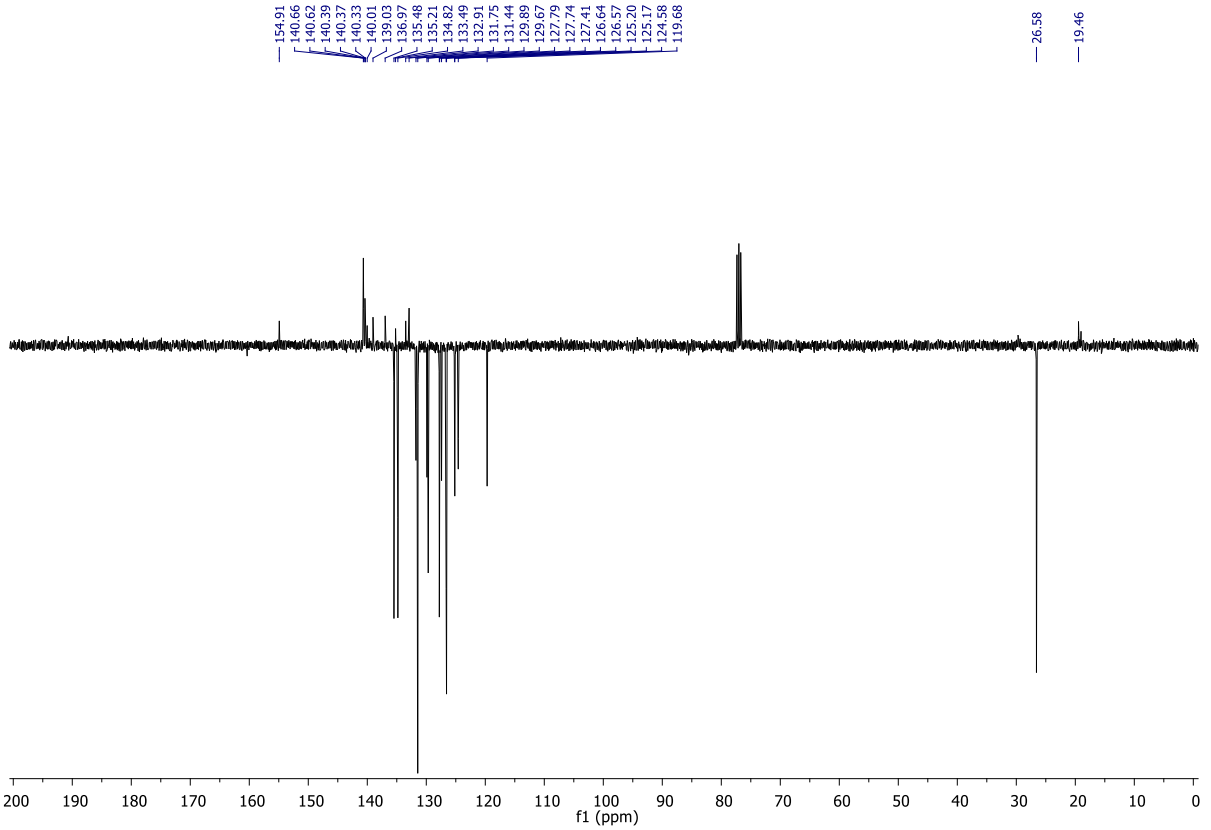

154.74
140.64
140.39
139.97
139.16
136.91
133.64
131.81
131.44
127.93
126.64
126.56
125.20
125.17
124.63
115.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

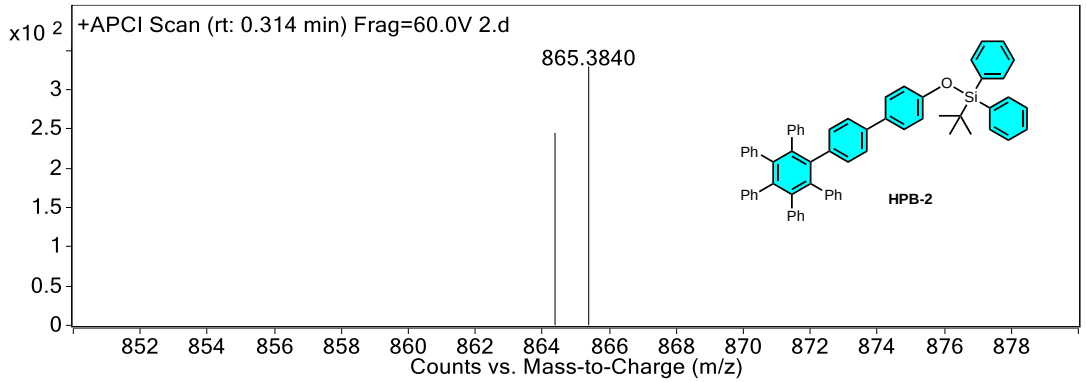

7.51
7.50
7.49
7.48
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.25
7.23
7.21
7.21
6.77
6.76
6.75
6.74
6.73
6.72
6.72
6.71
6.70
6.70
6.69
6.68
6.49
6.47
6.25
6.23
0.90
Ph
Ph
Ph
Ph
Ph
O
Si
HPB-1
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


152.99
140.73
140.71
135.48
132.21
131.44
131.43
129.64
127.60
126.59
126.54
125.13
125.07
118.31
26.71
19.60
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


x10 3
+APCI Scan (rt: 0.246 min) Frag=60.0V 1.d
788.3495
789.3536
1
0.8
0.6
0.4
0.2
0
786
787
788
789
790
791
792
793
794
Counts vs. Mass-to-Charge (m/z)
Ph
Ph
Ph
Ph
Ph
O
Si
HPB-1


7.65
7.65
7.63
7.63
7.63
7.62
7.61
7.35
7.35
7.35
7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.28
7.27
7.27
7.25
7.25
7.10
7.08
6.93
6.91
6.75
6.74
6.73
6.72
6.65
6.62
0.99
Ph
Ph
Ph
Ph
Ph
O
Si
HPB-2
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)


154.91
140.66
140.62
140.39
140.37
140.33
140.01
139.03
136.97
135.48
135.21
134.82
133.49
132.91
131.75
131.44
129.89
129.67
127.79
127.74
127.41
126.64
126.57
125.20
125.17
124.58
119.68
26.58
19.46
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


x10 2
+APCI Scan (rt: 0.314 min) Frag=60.0V 2.d
865.3840
3
2.5
2
1.5
1
0.5
0
852
854
856
858
860
862
864
866
868
870
872
874
876
878
Counts vs. Mass-to-Charge (m/z)
Ph
Ph
Ph
Ph
Ph
O
Si
HPB-2