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

Columnar self-assembly of novel benzylidenehydrazones and their difluoroboron complexes: structure-property correlations

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Supporting information

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1. Materials and methods

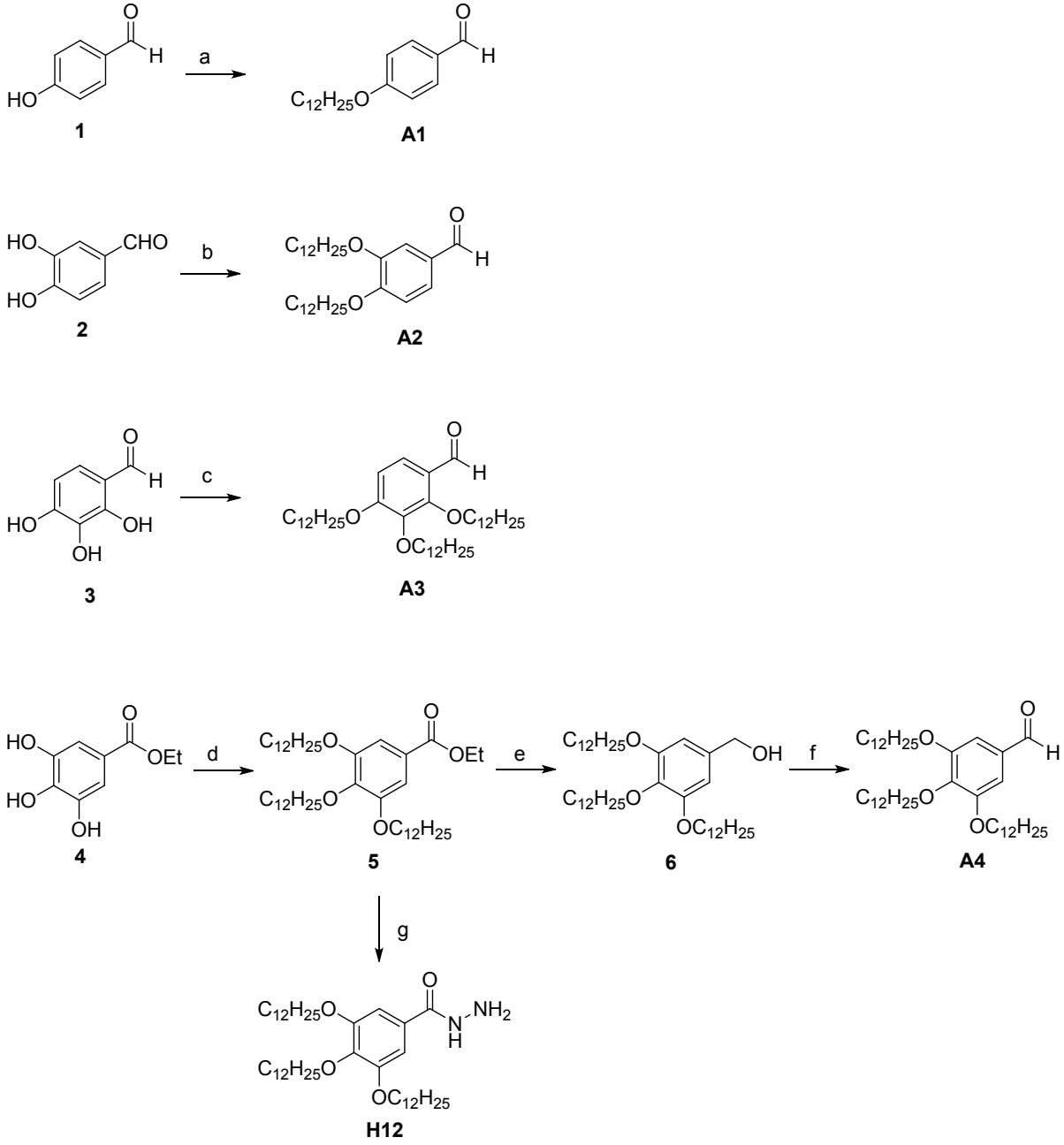
All the required reagents and solvents were purchased from Sigma Aldrich, Merck, Spectrochem and SD's Fine Chem. Ltd. and used without any further purifications. The solvents were dried using standard protocols. The reactions were performed under inert atmosphere and completion of the reaction was monitored by TLC technique. Chromatographic separations were carried out using silica gel of mesh size 100-200 and 230-400. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AMX 500 MHz, in $CDCl_3$ and TMS was used as an internal standard. FT-IR spectra were obtained by Bruker alpha Fourier transform IR spectrometer using ATR method. Elemental analysis was performed on a Carlo-Erba Flash 1112 analyser.

The LC properties of all the target molecules were established by recording Differential Scanning Calorimetry (DSC) thermograms using Parkin-Elmer Pyris-1 DSC. Optical textures of mesophases were captured using Olympus BX51 Polarized Optical Microscope (POM) in conjunction with a Mettler FP82HT hot stage and FP90 central processor. Variable temperature powder X-ray diffraction (XRD) measurements of unoriented samples filled in a Lindemann capillary of diameter of 1 mm (Hampton Research) were carried out on DY 1042-Empyrean XRD with Pixel 3D detector at Cu-Kα radiation.

The photophysical properties of all the liquid crystalline materials were studied using UV-visible spectra and they were recorded at room temperature using SPECORD S 600 spectrophotometer. Further, the Fluorescence spectra were acquired on a Perkin Elmer LS55 Fluorescence spectrophotometer at RT.

Theoretical calculations were made using the Gaussian 09 program. Geometry optimizations were performed using the Becke three-parameter exchange functional and the Lee-Yang-Parr B3LYP exchange correlation functionals with the 6-31G(d,p) basis set for C, H, N, B, and O. Calculations were performed under vacuum.

2. Synthesis scheme



Scheme S1. Synthesis of key-precursors. Reagents and conditions: (a) *n*-$C_{12}H_{25}Br$, anhydrous K_2CO_3, dry DMF, 80 ℃, overnight, 90 %; (b) *n*-$C_{12}H_{25}Br$, anhydrous K_2CO_3, Cat. KI, dry DMF, 80 ℃, overnight, 83 %; (c) *n*-$C_{12}H_{25}Br$, anhydrous K_2CO_3, Cat. KI, dry DMF, 80 ℃, 12 hrs, 80 %; (d) *n*-$C_{12}H_{25}Br$, anhydrous K_2CO_3, Cat. KI, dry DMF, 80 ℃, 12 hrs, 85 %; (e) LAH, dry THF, -5 ℃ to 25 ℃ , 20 hrs, 90 %; (f) PCC, dry DCM, RT, 4 hrs, 78 %; (g) NH_2-$NH_2.H_2O$, EtOH, reflux, 12 hrs, 75 %

3. Experimental methods

General procedure for the synthesis of hydrazones **HZ1-4**

The equimolar mixture of aldehyde **A1** (1 g, 3.44 mmol, 1 equiv.) and hydrazide **H12** (2.3 g, 3.44 mmol, 1 equiv.) was taken in 20 mL of absolute ethanol. To this mixture, catalytic amount of glacial acetic acid was added and reflexed for 2 hours. Then, the mixture was kept for cooling at ambient conditions; the obtained precipitate was filtered and washed with ethanol. The repeated recrystallization with DCM and methanol, **HZ1** was isolated in 75 % as white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 9.47 (s, 1H), 8.25 (s, 1H), 7.66 (s, 2H), 7.04 (d, 2H, *J* = 8.0 Hz), 6.89 (d, 2H, *J* = 8.0 Hz), 3.98 (m, 8H), 1.80 (m, 8H), 1.46 (m, 8H), 1.28 (m, 64H), 0.89 (t, 12H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 161.18, 153.19, 141.47, 129.32, 126.05, 114.77, 114.68, 105.94, 73.55, 69.37, 68.16, 31.93, 30.35, 29.51, 26.08, 22.69, 14.10; FTIR (ATR, ν_{max} in cm^{-1}): ν- 3210 (N-H), 2916 (Ar C-H), 2848 (Aliph C-H), 1646 (C=O), 1609 (Ar C=C); Elemental Anal. Calcd (%) for $C_{62}H_{108}N_2O_5$: C, 77.45; H, 11.32; N, 2.91; Found: C, 77.94; H, 11.12; N, 2.56

The compounds **HZ2-4** were synthesized by adopting similar procedure as described for the synthesis of **HZ1**.

For **HZ2** (Yield, 70 %). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 9.19 (s, 1H), 8.21 (s, 1H), 7.45 (m, 2H), 7.03 (m, 3H), 6.85 (d, 1H, *J* = 7.5 Hz), 3.98 (m, 10H), 1.83-1.69 (m, 10H), 1.48 (m, 10H), 1.28 (m, 80H), 0.89 (t, 15H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 153.25, 151.57, 149.51, 141.58, 126.41, 122.54, 112.54, 105.89, 73.57, 69.27, 31.93, 30.34, 29.55, 26.07, 22.69, 14.10; FTIR (ATR, ν_{max} in cm^{-1}): ν- 3208 (N-H), 2916 (Ar C-H), 2848 (Aliph C-H), 1637 (C=O), 1578 (Ar C=C); Elemental Anal. Calcd (%) for $C_{74}H_{132}N_2O_6$: C, 77.57; H, 11.61; N, 2.44; Found: C 77.31, H 11.78, N, 2.83;

For **HZ3** (Yield, 72 %). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 9.16 (s, 1H), 8.43 (s, 1H), 7.82 (s, 1H) 6.95 (m, 2H), 6.70 (s, 1H), 4.00 (m, 12H), 1.80-1.68 (m, 12H), 1.48 (m, 12H), 1.28 (m, 96H), 0.90 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 152.75, 144.34, 141.14, 108.72, 106.17, 73.60, 68.55, 31.93, 30.30, 29.38, 26.15, 22.69, 14.0 9; FTIR (ATR, ν_{max} in cm^{-1}): ν- 3252 (N-H), 2917 (Ar C-H), 2850 (Aliph C-H),

1643 (C=O), 1576 (Ar C=C); Elemental Anal. Calcd (%) for $C_{86}H_{156}N_2O_7$: C, 77.65; H, 11.82; N, 2.11; Found: C, 80.10; H, 11.53; N, 2.25.

For **HZ4** (Yield, 69 %). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 9.35 (s, 1H), 8.22 (s, 1H), 7.28-6.94 (m, 4H), 4.00 (m, 12H), 1.80-1.75(m, 12H), 1.47 (m, 12H), 1.28 (m, 96H), 0.91 (t, 15H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 153.31, 141.61, 140.60, 128.54, 106.18, 73.54, 69.35, 31.93, 30.36, 29.56, 26.12, 22.69, 14.19; FTIR (ATR, ν_{max} in cm^{-1}): ν- 3251 (N-H), 2917 (Ar C-H), 2849 (Aliph C-H), 1641 (C=O), 1576 (Ar C=C); Elemental Anal. Calcd (%) for $C_{86}H_{156}N_2O_7$: C, 77.65; H, 11.82; N, 2.11; Found: C, 77.99; H, 11.63; N, 2.49.

General procedure for the synthesis of BF_2 complexes **FB1-4**

A mixture of hydrazone **HZ1** (0.5g, 0.52 mmol, 1 equiv.) and *N*,*N*-Diisopropylethylamine (0.2g, 1.56 mmol, 3 equiv.) in dichloroethane was heated to 50 ℃ for 15 minutes. Boron trifluoride diethyl etherate (0.11g, 0.79 mmol, 1.5 equiv.) was then added to the mixture and continued the stirring at 70 ℃ for overnight. After completion of the reaction, the mixture mass was cooled and poured into ice cold water. Then, aqueous mixture was extracted twice with dichloromethane and dried the combined organic layers. Finally, the crude was purified by silica-gel column chromatography (100-200 mesh size) using mixture of pet-ether and ethyl acetate as eluents, yielded **FB1** (Yield, 42 %). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 8.32 (d, 2H, *J* = 8.0 Hz), 7.68 (s, 1H), 7.31 (s, 2H), 6.98 (d, 2H, *J* = 8.5 Hz), 4.00 (m, 8H), 1.77-1.67 (m, 8H), 1.41 (m, 8H), 1.19 (m, 64H), 0.91 (t, 12H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 164.32, 153.10, 149.17, 136.78, 121.69, 121.60, 115.25, 107.54, 73.65, 69.41, 68.68, 31.93, 30.35, 29.57, 26.09, 26.13, 26.06, 25.95, 22.69, 14.10; FTIR (ATR, ν_{max} in cm^{-1}): ν- 2918 (Ar C-H), 2849 (Aliph C-H), 1645 (Ar C=N), 1601(Ar C=C); Elemental Anal. Calcd (%) for $C_{62}H_{107}BF_2N_2O_5$; C, 73.78; H, 10.69; N, 2.78.; Found: C, 73.39; H, 10.59; N, 2.82.

The remaining members of the series, **FB2-4** were synthesized by following the similar procedure as described for the synthesis of **FB1**.

For **FB2** (Yield, 51 %). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 8.47 (s, 1H), 7.74 (s, 1H), 7.66 (d, 1H, *J* = 8.0 Hz), 7.39 (s, 1H), 7.00 (d, 2H, *J* = 8.5 Hz), 4.07 (m, 10H), 1.91-1.76 (m, 10H), 1.59-1.51 (m, 10H), 1.38-1.28 (m, 80H), 0.901 (t, 15H, *J* = 8.5 Hz); ^{13}C

NMR (125 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 153.09, 149.45, 130.71, 121.77, 112.04, 107.15, 73.66, 69.06, 31.93, 30.37, 29.43, 26.17, 25.94, 22.69, 14.10; FTIR (ATR, ν_{max} in cm^{-1}): ν- 2917 (Ar C-H), 2849 (Aliph C-H), 1643 (Ar C=N), 1593 (Ar C=C); Elemental Anal. Calcd (%) for $C_{74}H_{131}BF_2N_2O_6$: C, 74.46; H, 11.06; N, 2.35; Found: C, 74.85; H, 11.01; N, 2.23.

For **FB3** (Yield, 55 %). ^1H NMR (500 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 8.92 (d, 1H, *J* = 9.0 Hz), 8.27 (s, 1H), 7.39 (s, 2H), 6.83 (d, 1H, *J* = 9.0 Hz), 4.21 (t, 2H, *J* = 6.0 Hz), 4.13 (t, 2H, *J* = 5.5 Hz), 4.07 (m, 6H), 3.98 (t, 2H, *J* = 5.5 Hz), 1.90-1.79 (m, 12H), 1.51 (m, 96H), 0.901 (t, 18H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 159.55, 156.45, 153.07, 145.13, 142.99, 140.95, 130.17, 121.80, 116.26, 108.21, 107.54, 75.57, 73.76, 69.29, 31.93, 30.24, 29.54, 26.13, 14.10; FTIR (ATR, ν_{max} in cm^{-1}): ν- 2916 (Ar C-H), 2849 (Aliph C-H), 1638 (Ar C=N), 1587 (Ar C=C); Elemental Anal. Calcd (%) for $C_{86}H_{155}BF_2N_2O_7$: C, 74.96; H, 11.34; N, 2.03; Found: C, 74.66; H, 11.49; N, 1.98.

For **FB4** (Yield, 60 %). ^1H NMR (500 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 7.65 (s, 1H), 7.64 (s, 1H), 7.30 (s, 2H), 4.06 (t, 2H, *J* = 6.0 Hz), 4.00-3.94 (s, 10H), 1.76-1.69 (m, 12H), 1.41 (m, 12H), 1.51 (m, 96H), 0.809 (t, 18H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ℃, TMS, δ in ppm): δ- 153.10, 153.02. 149.51, 144.25, 143.04, 123.49, 121.41, 112.76, 107.14, 112.76, 107.14, 73.79, 69.15, 31.93, 30.40, 29.54, 26.12, 14.10; FTIR (ATR, ν_{max} in cm^{-1}): ν- FTIR (ATR, ν_{max} in cm^{-1}): ν- 2918 (Ar C-H), 2849 (Aliph C-H), 1645 (Ar C=N), 1587 (Ar C=C); Elemental Anal. Calcd (%) for $C_{86}H_{155}BF_2N_2O_7$: C, 74.96; H, 11.34; N, 2.03; Found: C, 74.78; H, 11.31; N, 2.12.

4. FTIR spectra

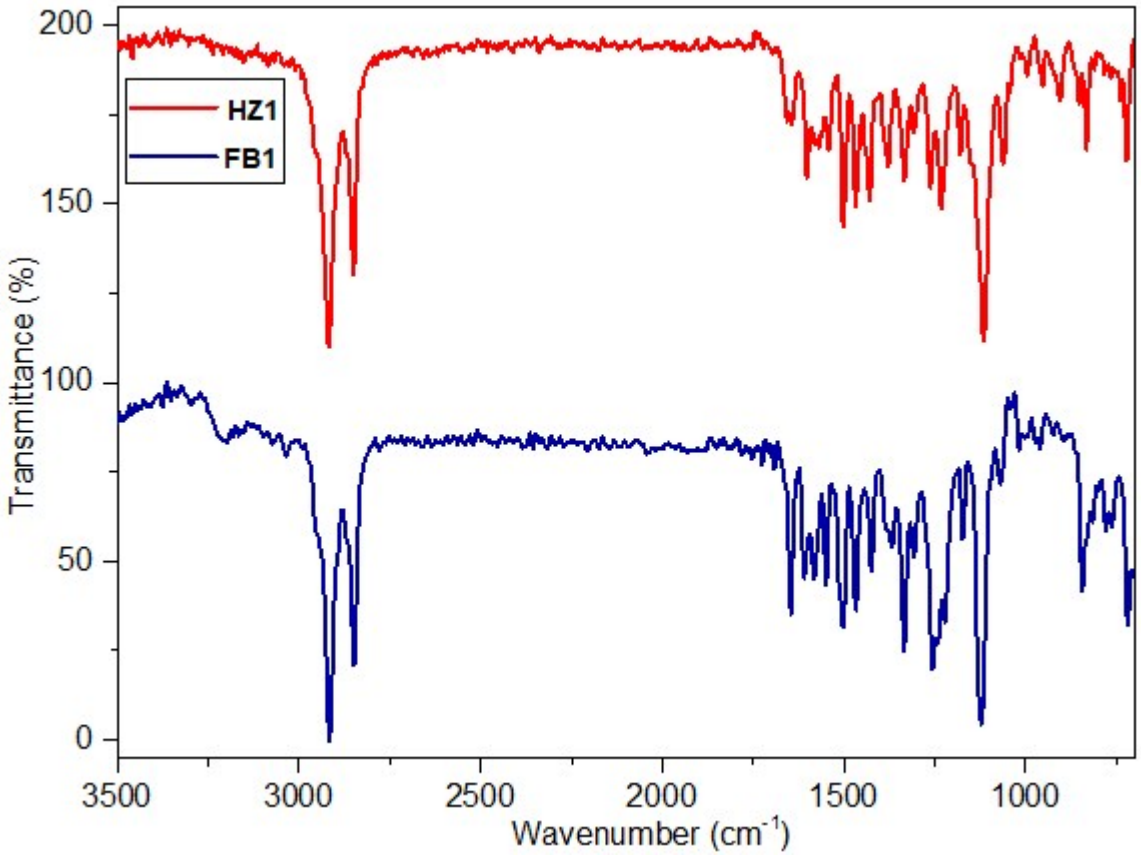


Figure S1. FTIR spectra of **HZ1** and **FB1**

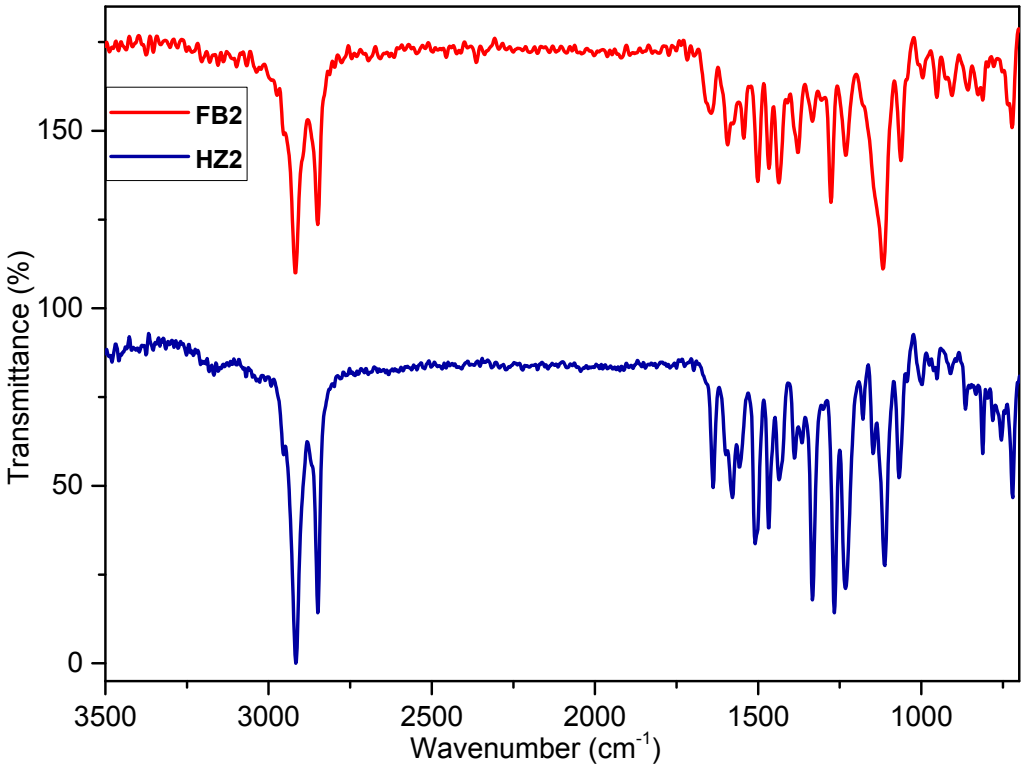


Figure S2. FTIR spectra of **HZ2** and **FB2**

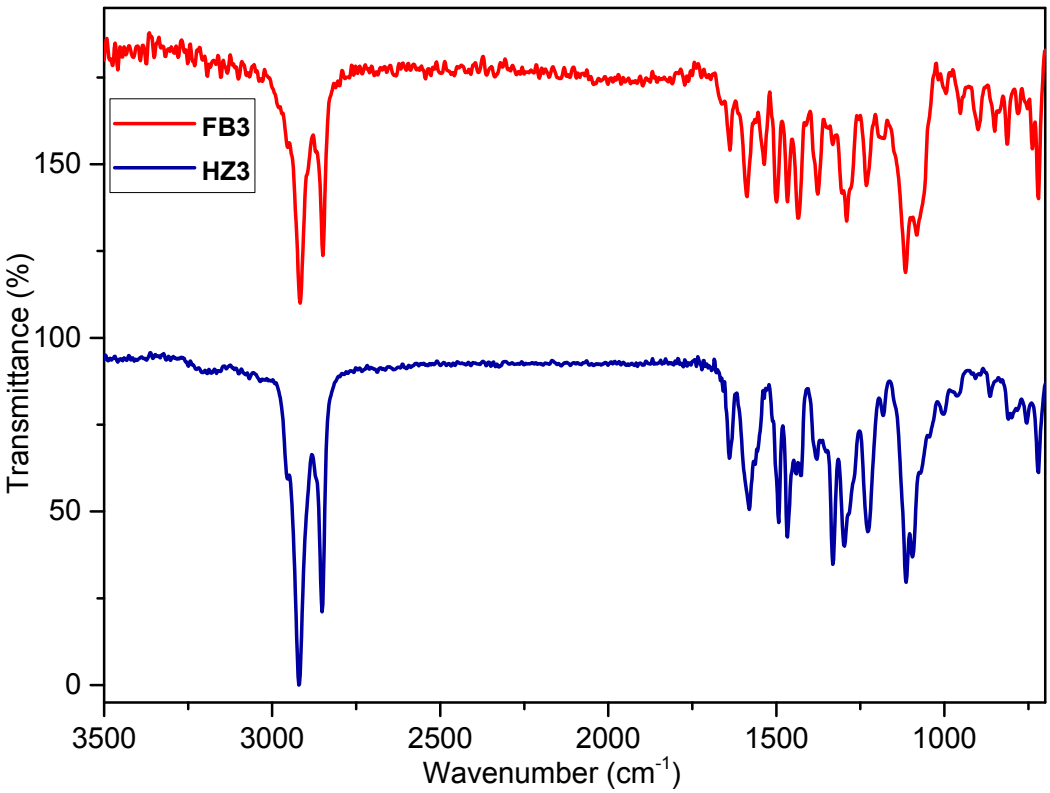


Figure S3. FTIR spectra of **HZ3** and **FB3**

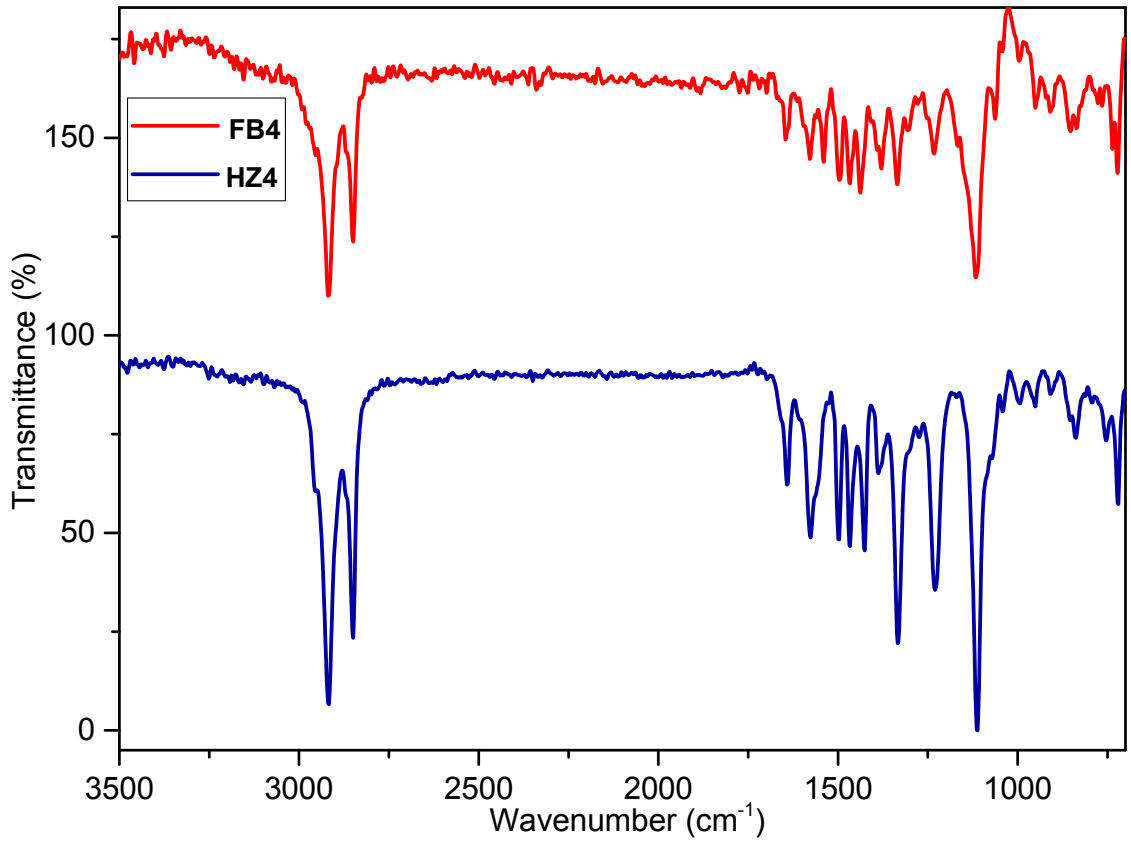


Figure S4. FTIR spectra of **HZ4** and **FB4**

5. NMR Spectra

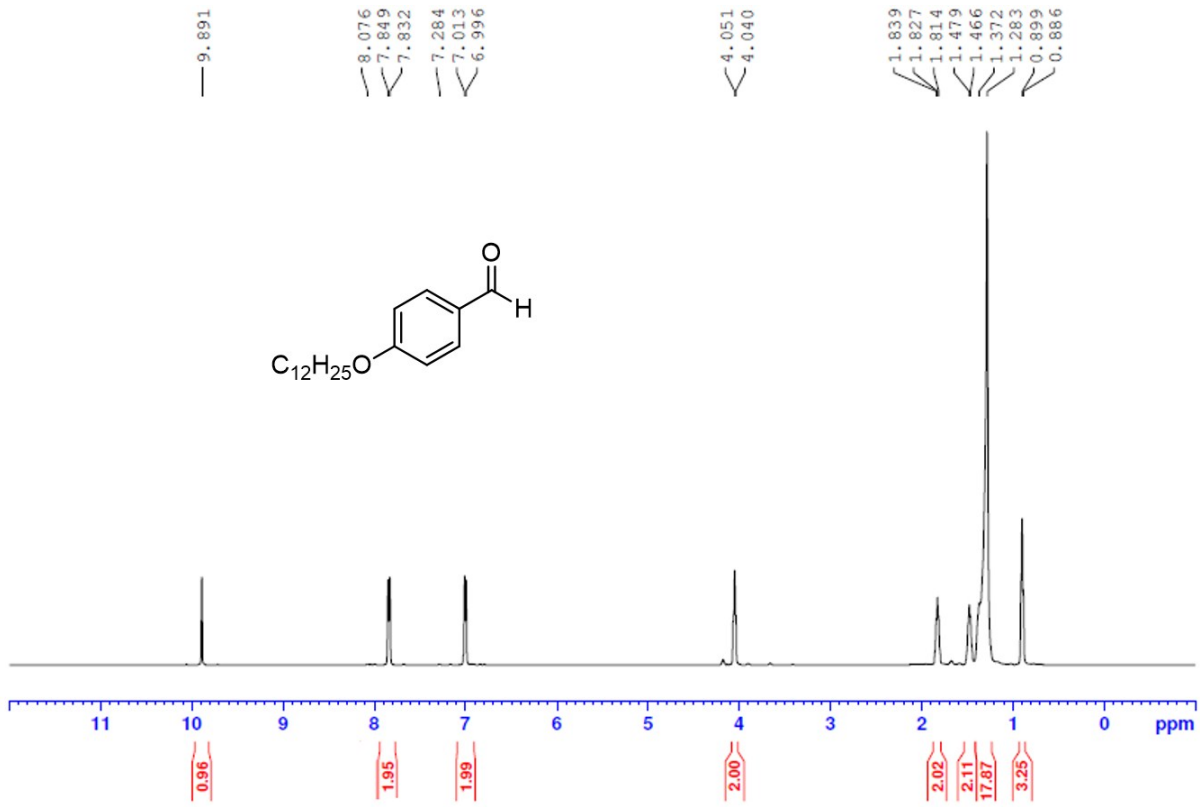


Figure S5. ^{1}H-NMR spectrum of **A1** recorded in $CDCl_3$ (500 MHz)

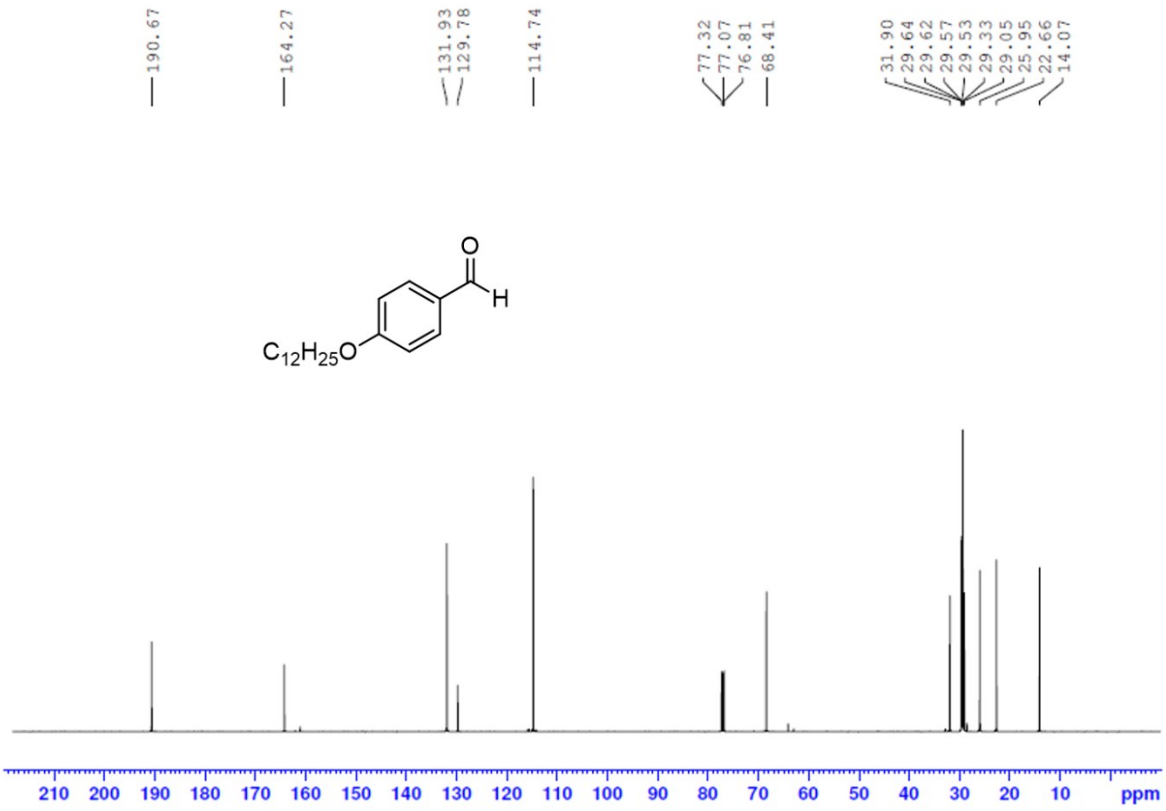


Figure S6. ^{13}C-NMR spectrum of **A1** recorded in $CDCl_3$ (125 MHz)

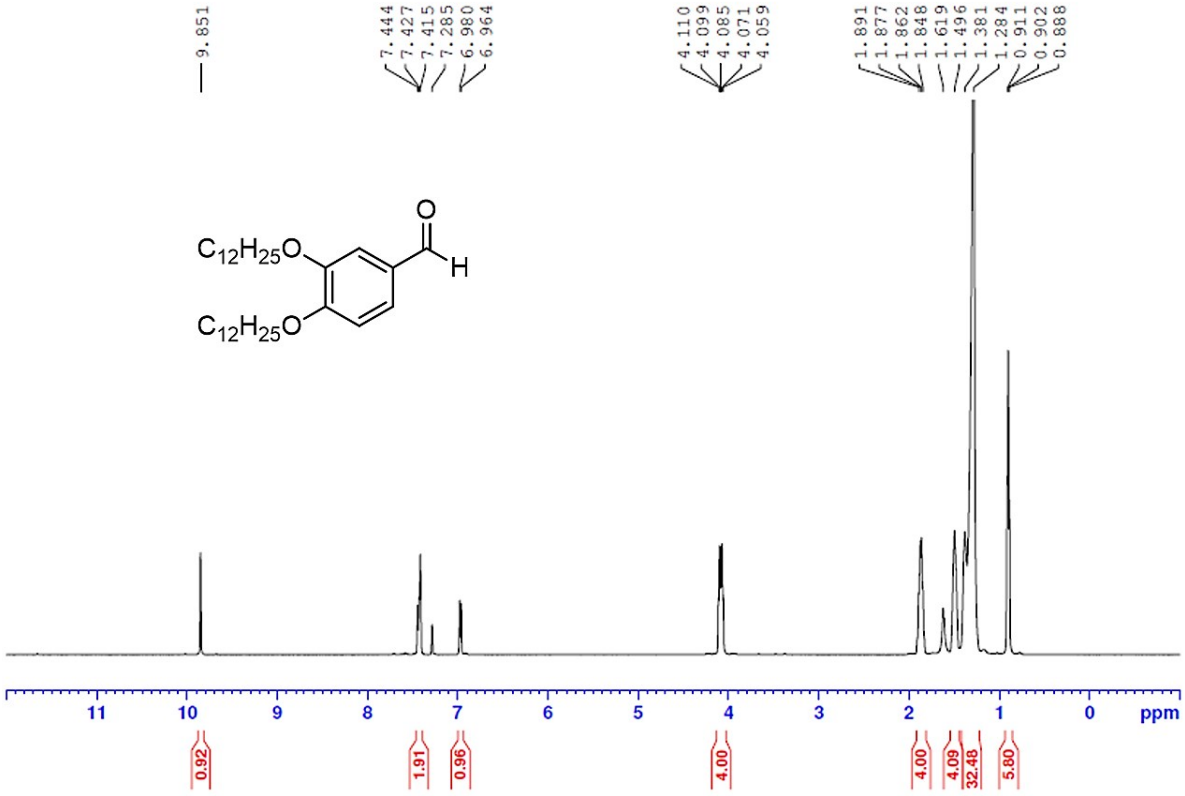


Figure S7. ^{1}H-NMR spectrum of **A2** recorded in $CDCl_3$ (500 MHz)

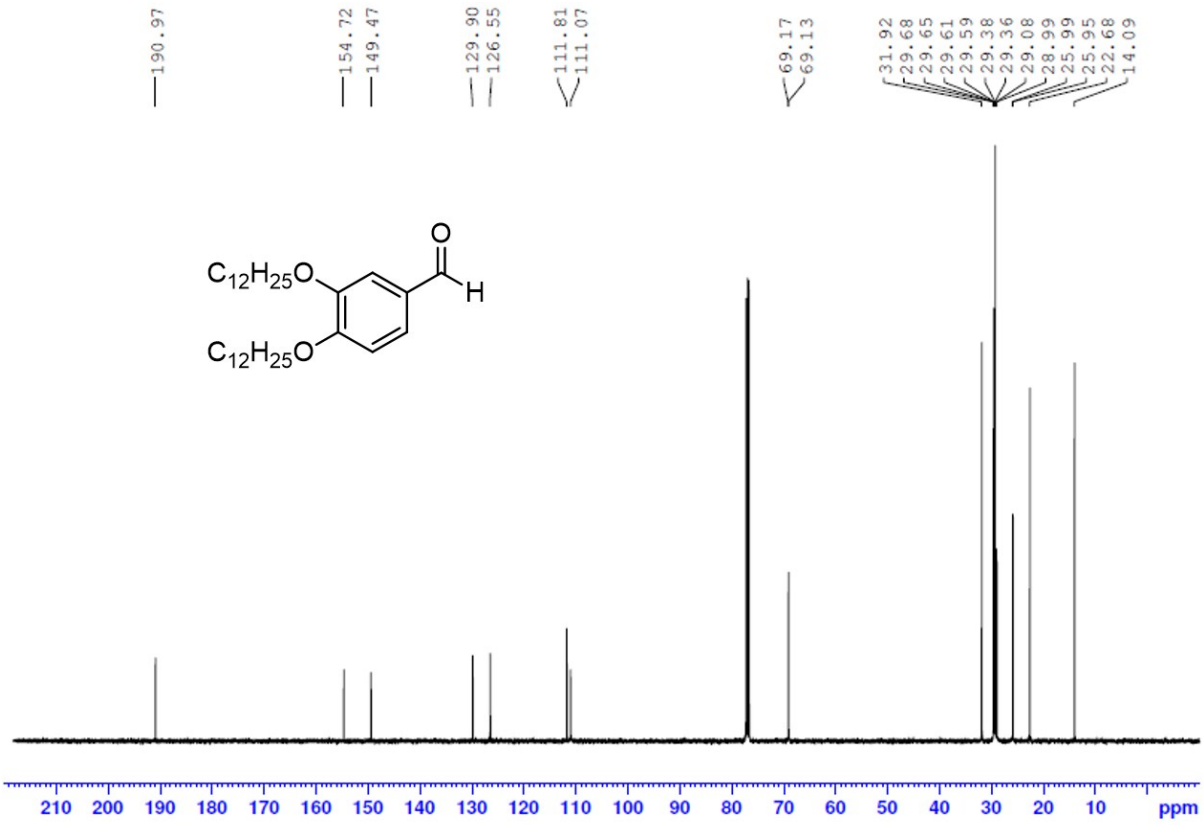


Figure S8. ^{13}C-NMR spectrum of **A2** recorded in $CDCl_3$ (125 MHz)

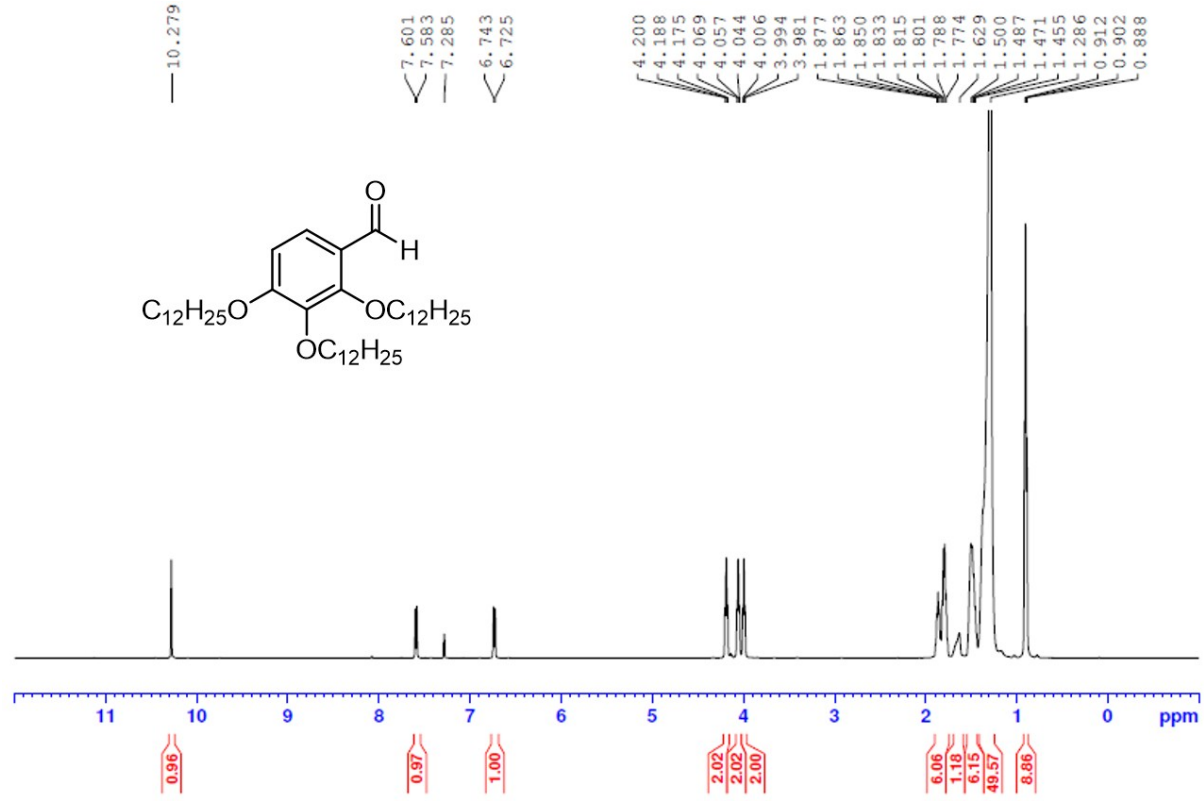


Figure S9. ^{1}H-NMR spectrum of **A3** recorded in $CDCl_3$ (500 MHz)

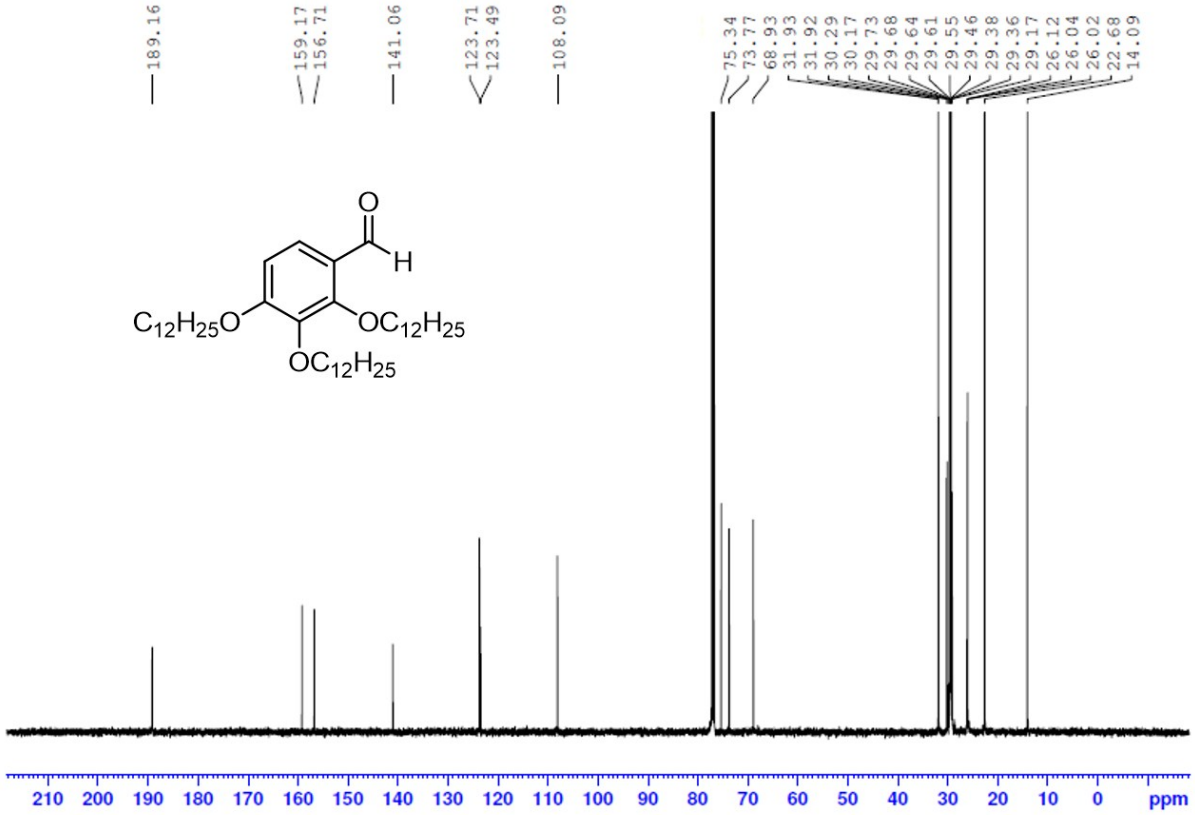


Figure S10. ^{13}C-NMR spectrum of **A3** recorded in $CDCl_3$ (125 MHz)

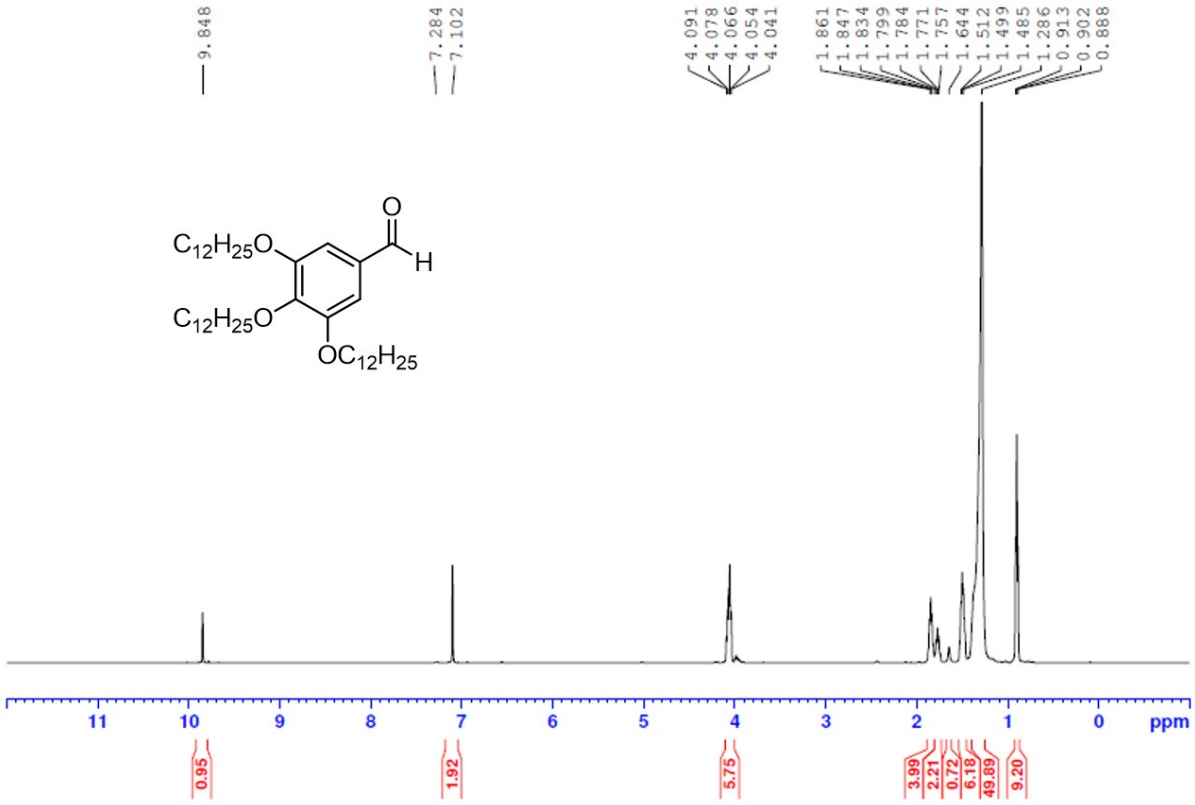


Figure S11. ^{1}H-NMR spectrum of **A4** recorded in $CDCl_3$ (500 MHz)

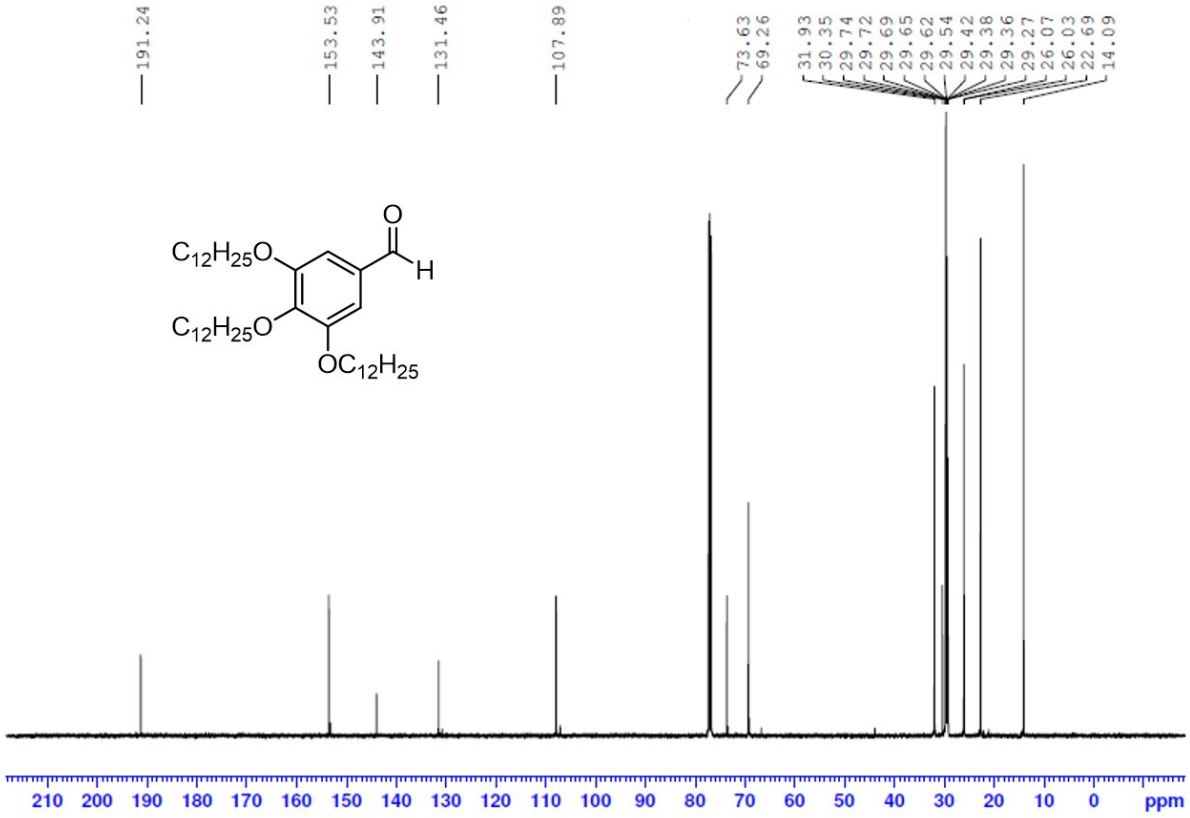


Figure S12. ^{13}C-NMR spectrum of **A4** recorded in $CDCl_3$ (125 MHz)

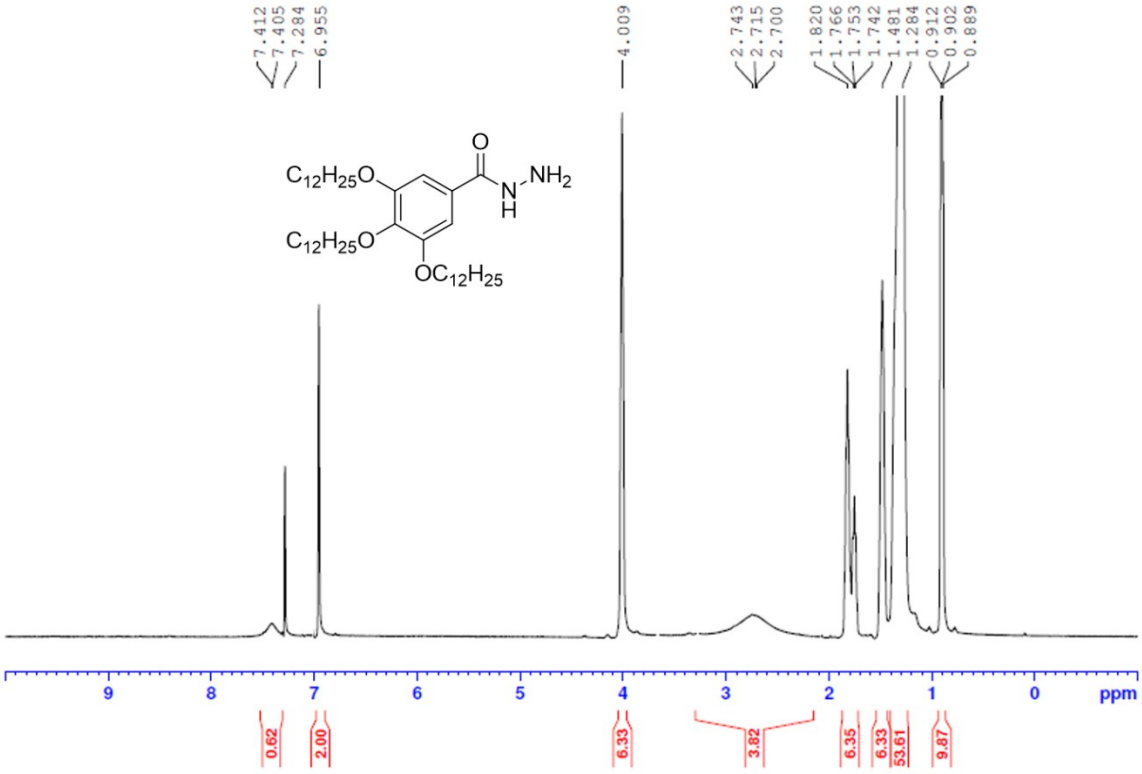


Figure S13. ^{1}H-NMR spectrum of **H12** recorded in $CDCl_3$ (500 MHz)

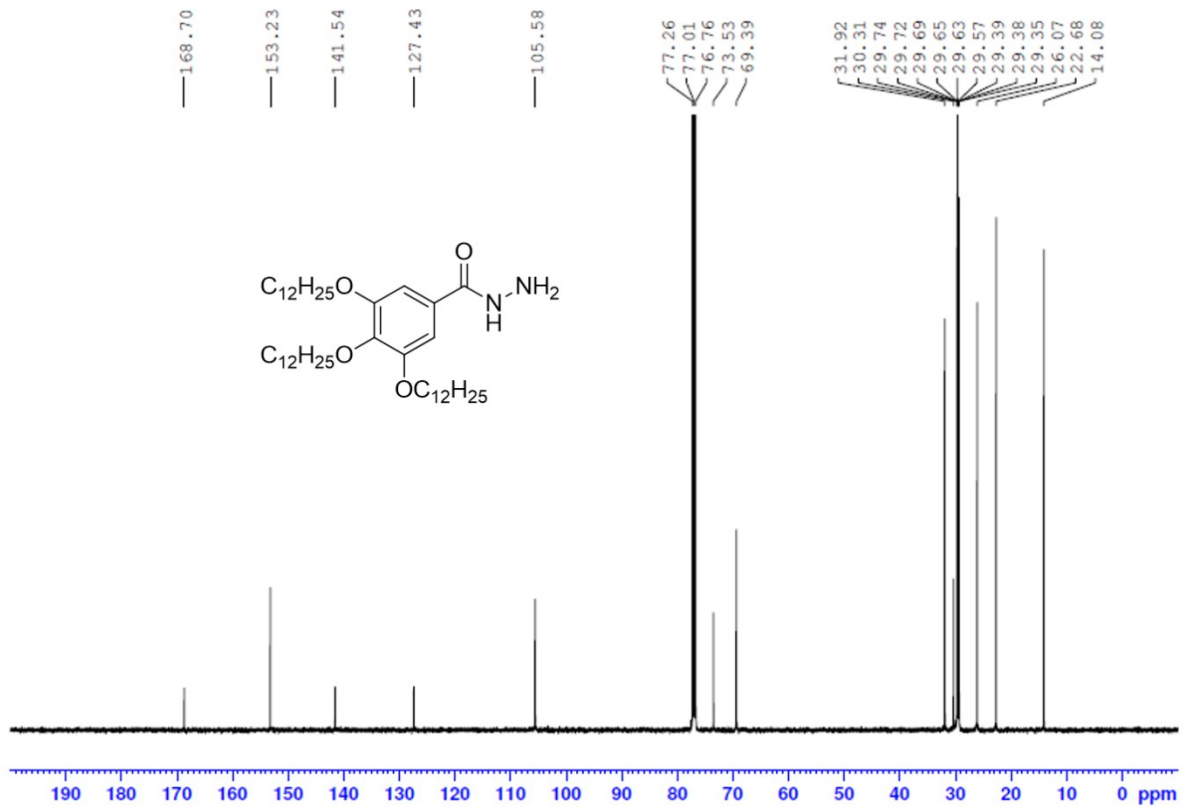


Figure S14. ^{13}C-NMR spectrum of **H12** recorded in $CDCl_3$ (125 MHz)

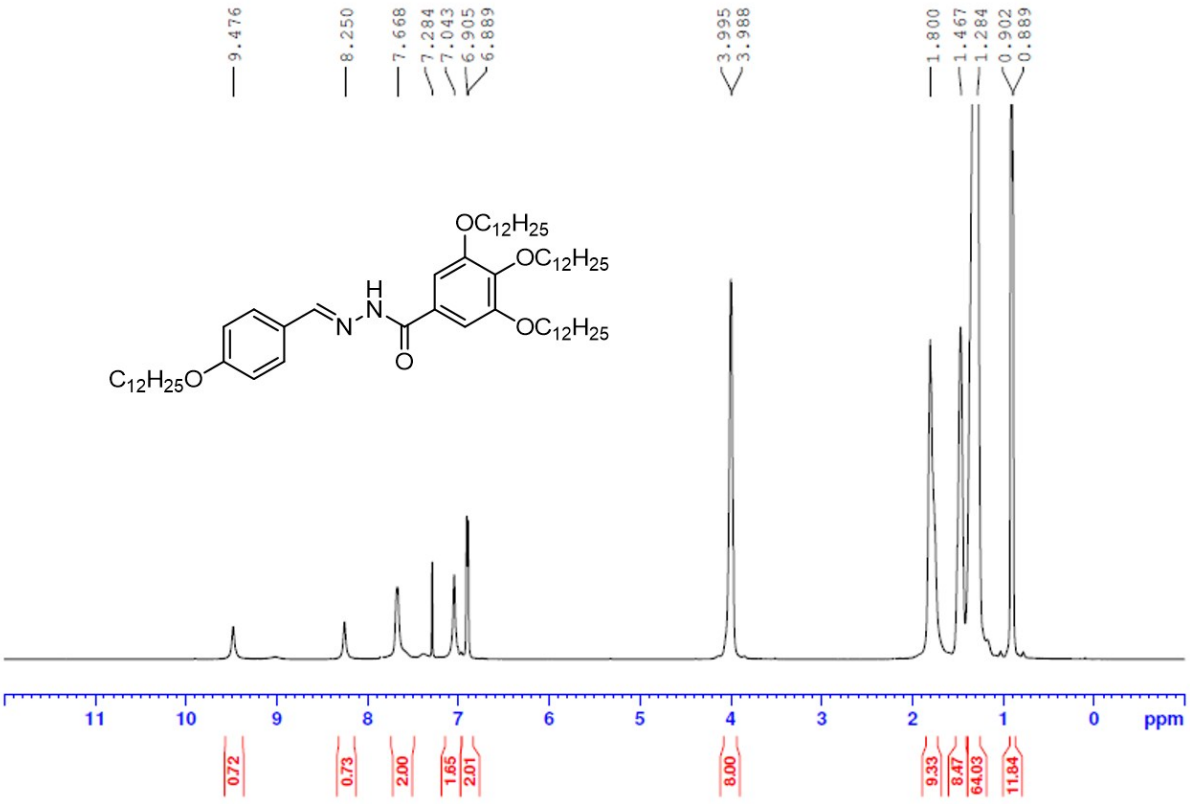


Figure S15. ^{1}H-NMR spectrum of **Hz1** recorded in $CDCl_3$ (500 MHz)

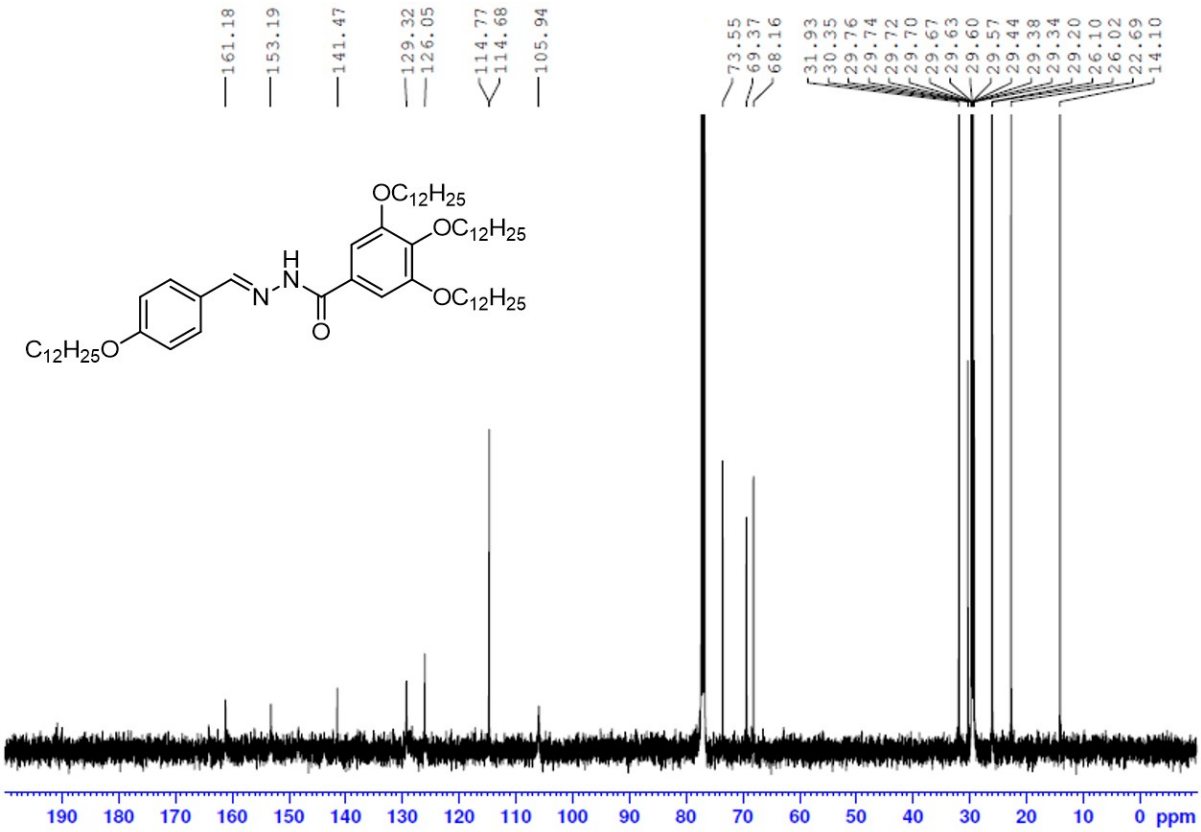


Figure S16. ^{13}C-NMR spectrum of **Hz1** recorded in $CDCl_3$ (125 MHz)

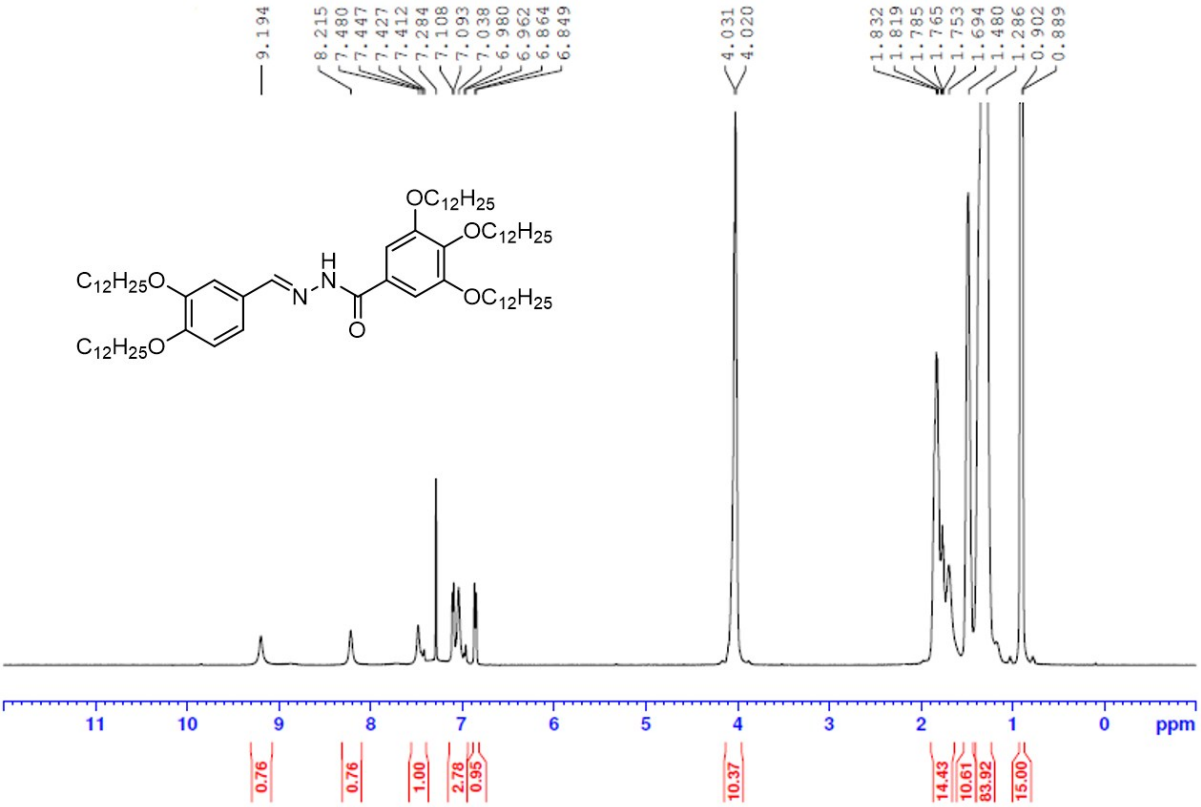


Figure S17. ^{1}H-NMR spectrum of **HZ2** recorded in $CDCl_3$ (500 MHz)

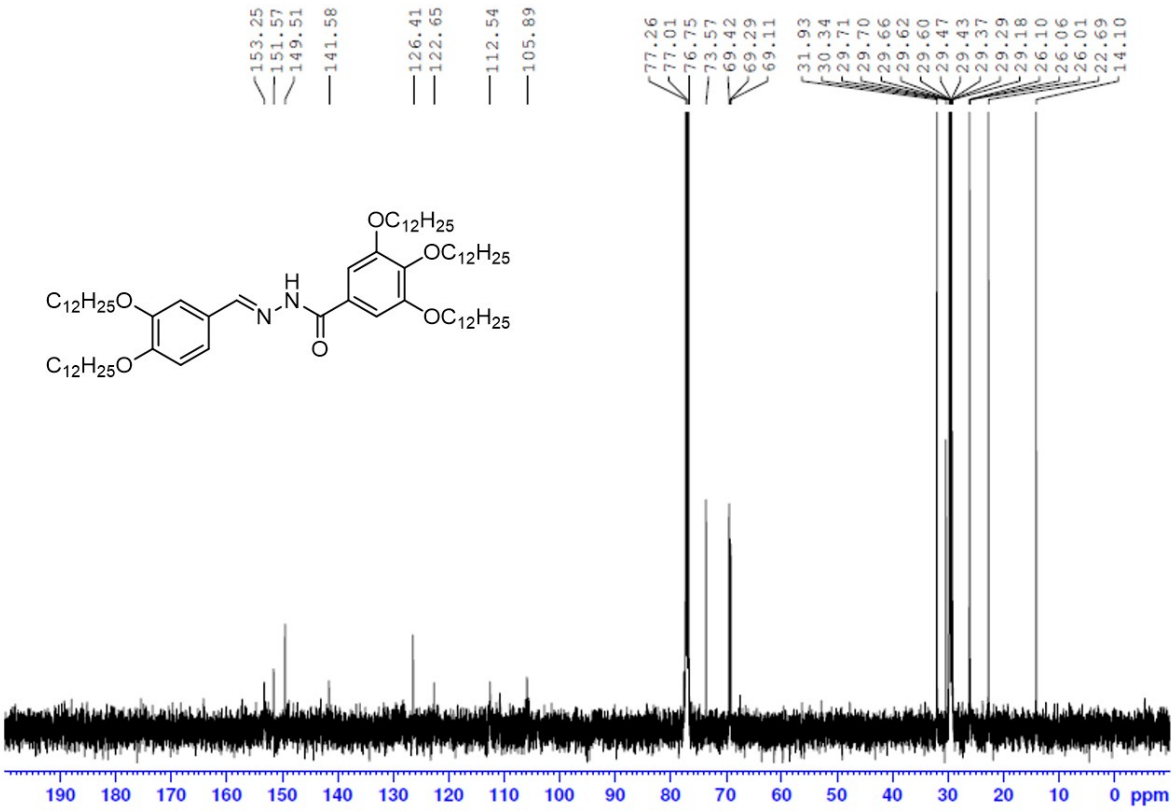


Figure S18. ^{13}C-NMR spectrum of **Hz2** recorded in $CDCl_3$ (125 MHz)

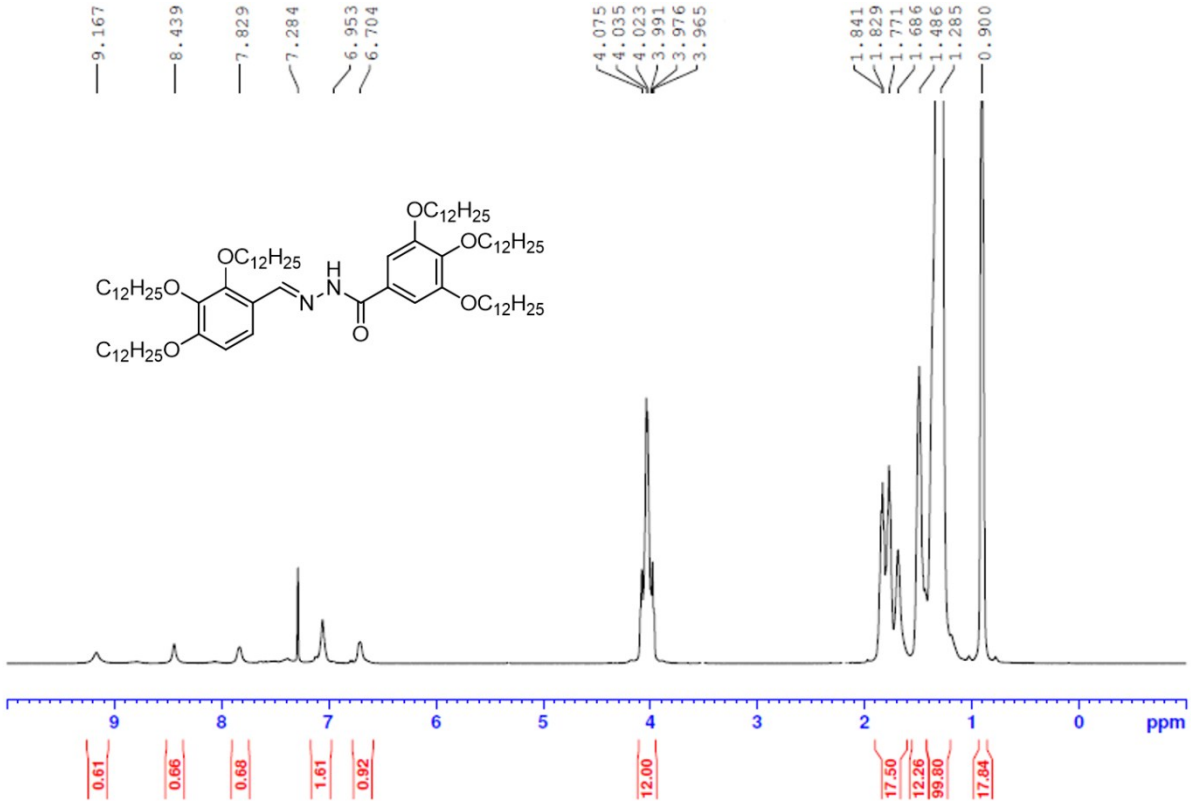


Figure S19. ^{1}H-NMR spectrum of **HZ3** recorded in $CDCl_3$ (500 MHz)

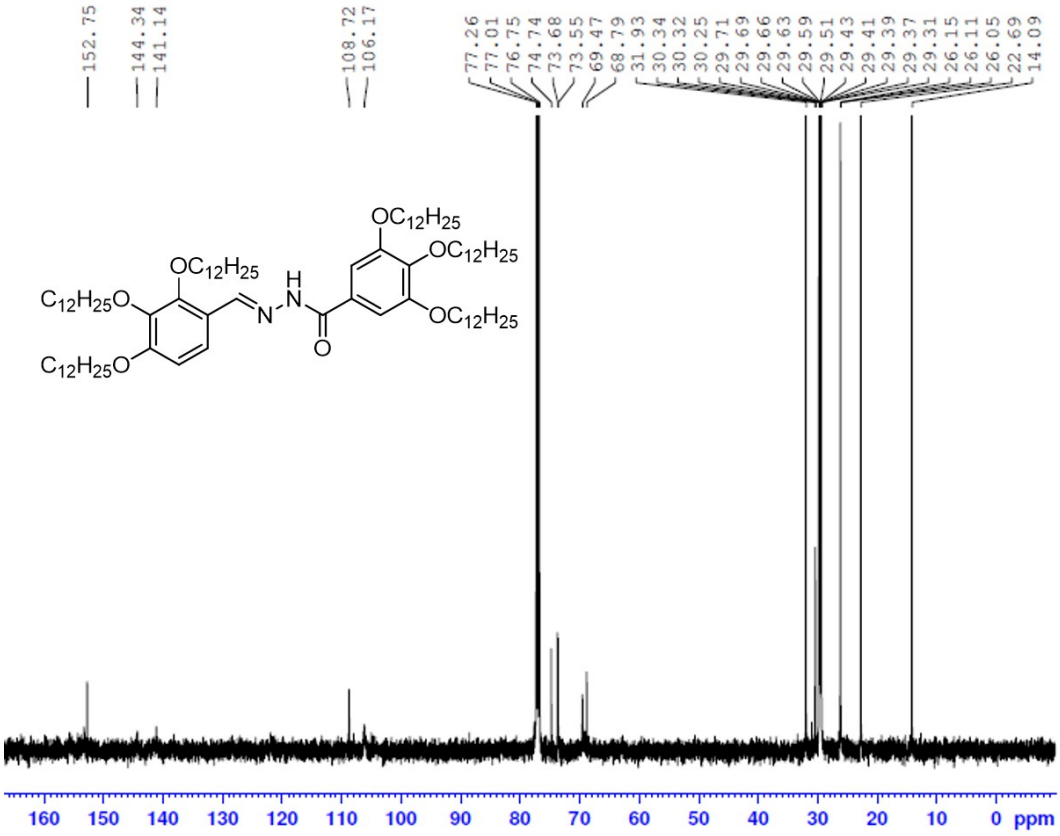


Figure S20. ^{13}C-NMR spectrum of **HZ3** recorded in $CDCl_3$ (125 MHz)

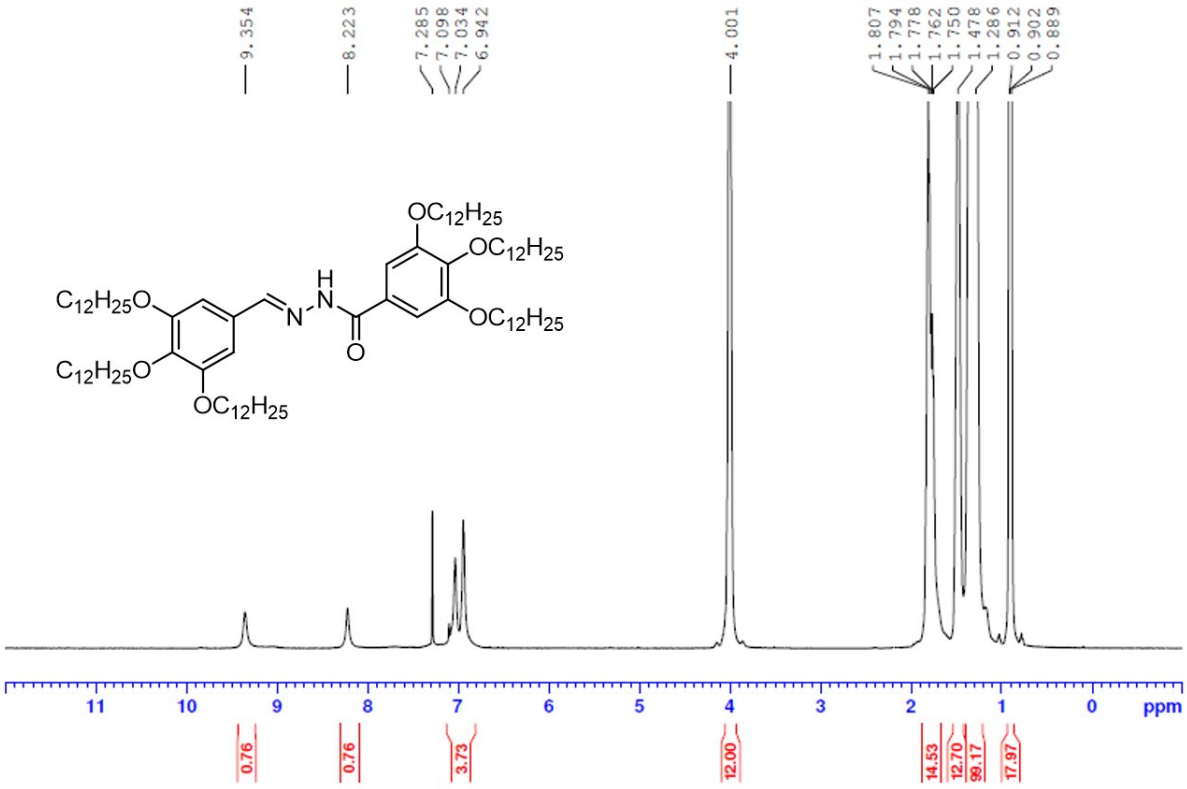


Figure S21. ^{1}H-NMR spectrum of **HZ4** recorded in $CDCl_3$ (500 MHz)

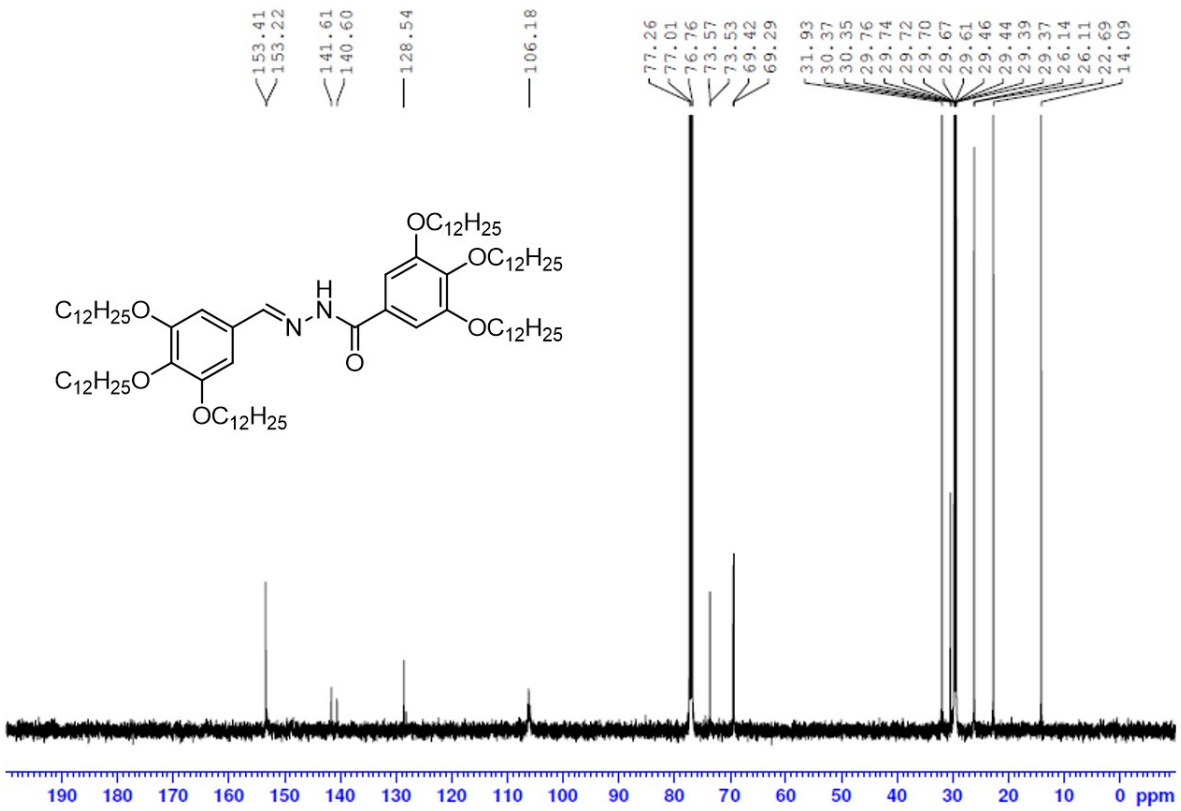


Figure S22. ^{13}C-NMR spectrum of **HZ4** recorded in $CDCl_3$ (125 MHz)

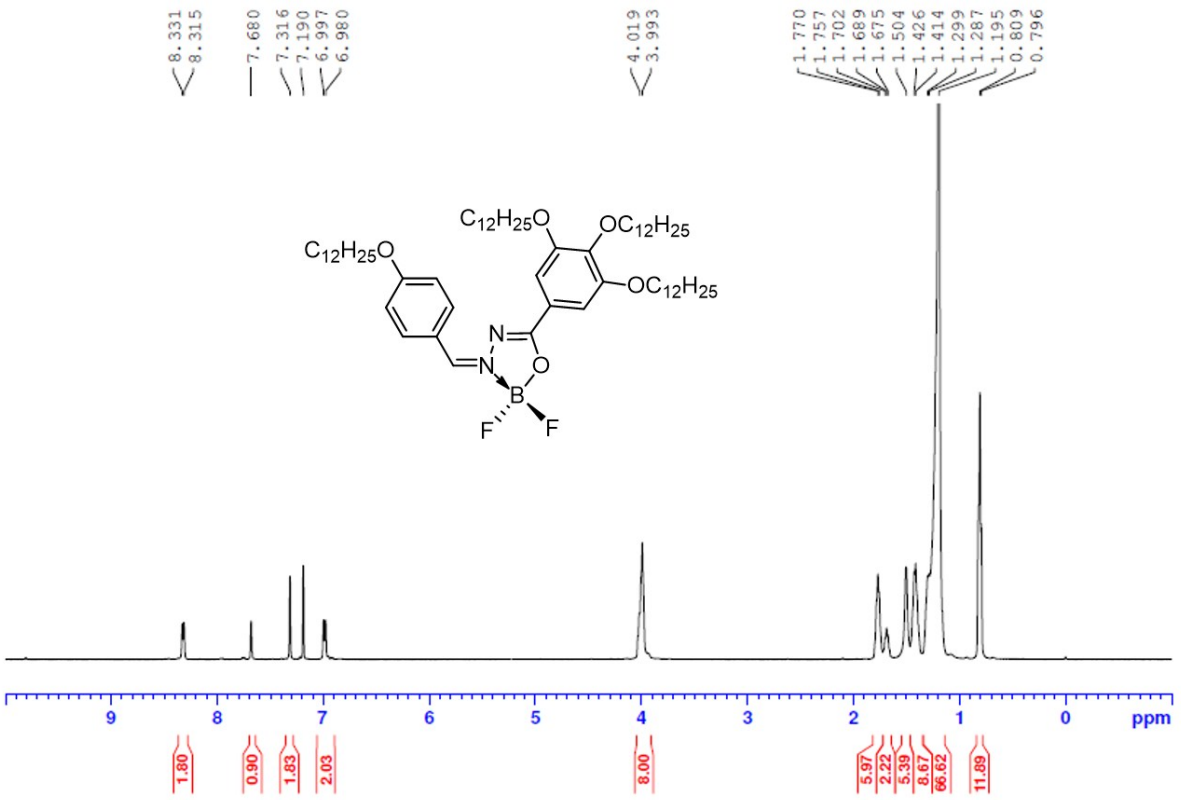


Figure S23. ^{1}H-NMR spectrum of **FB1** recorded in $CDCl_3$ (500 MHz)

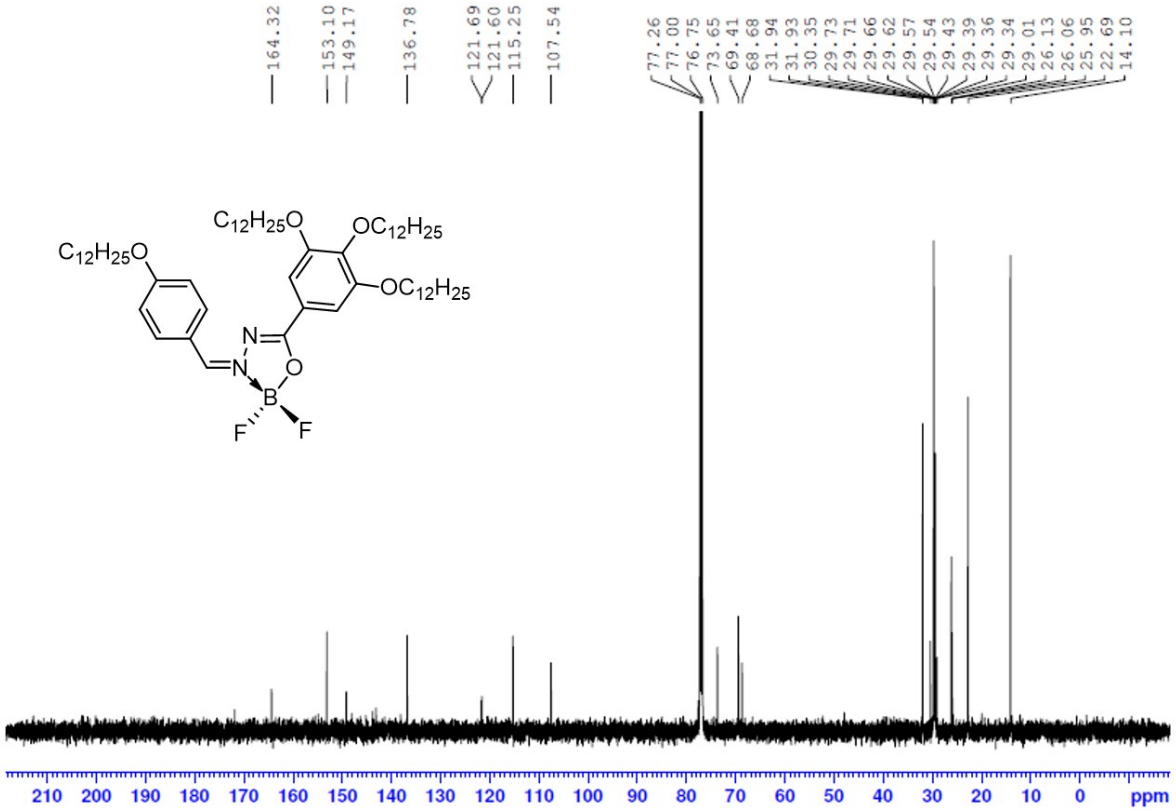


Figure S24. ^{13}C-NMR spectrum of **FB1** recorded in $CDCl_3$ (125 MHz)

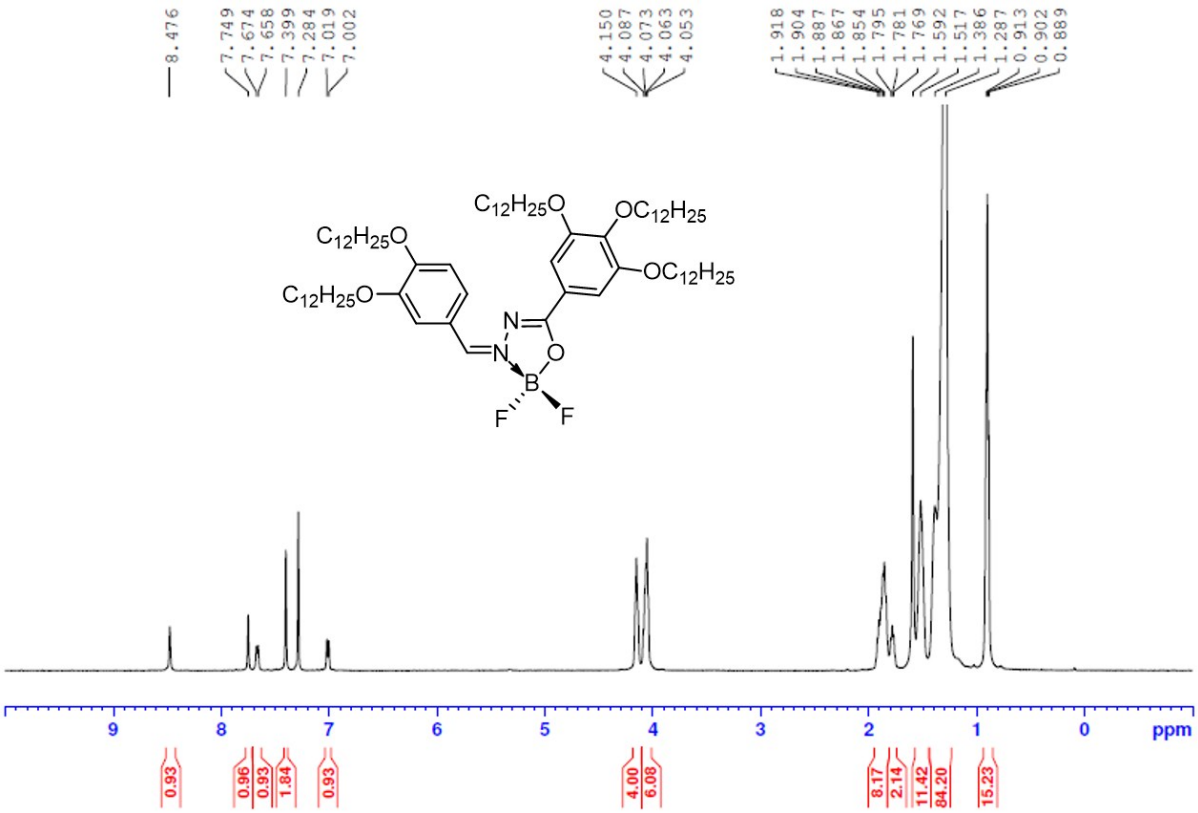


Figure S25. ^{1}H-NMR spectrum of **FB2** recorded in $CDCl_3$ (500 MHz)

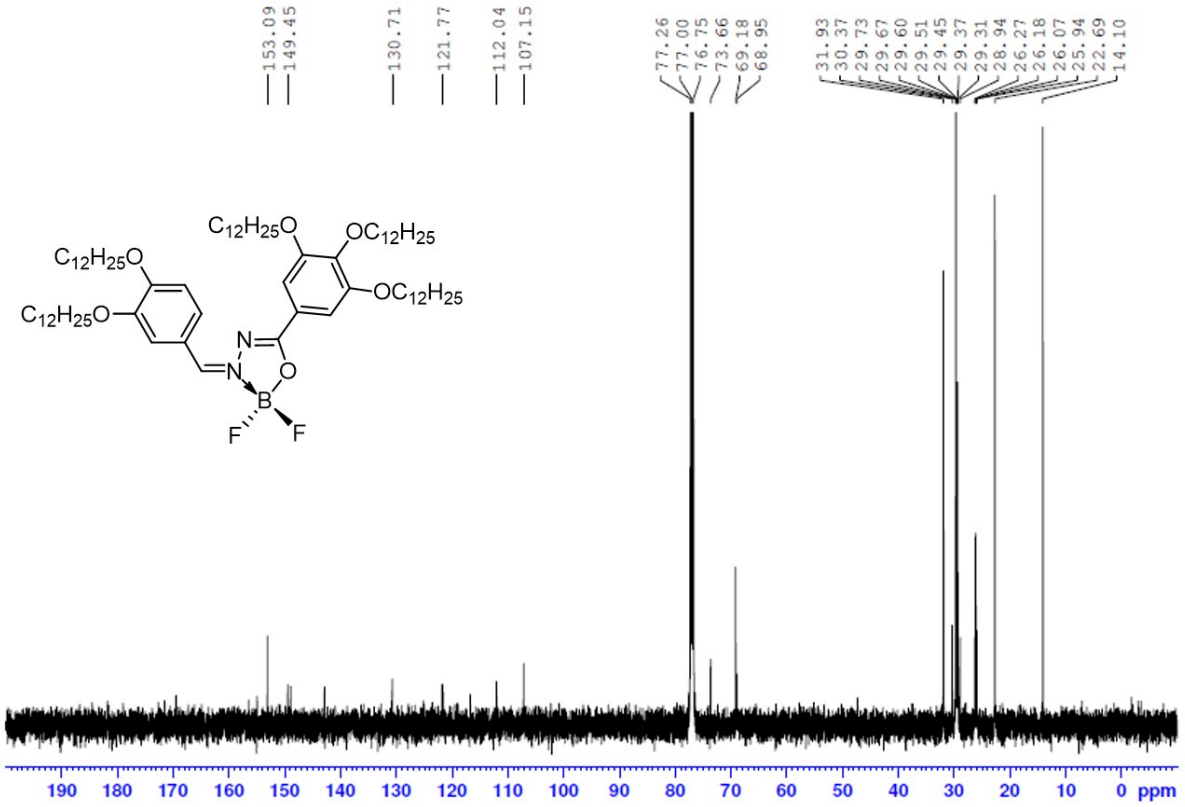


Figure S26. ^{13}C-NMR spectrum of **FB2** recorded in $CDCl_3$ (125 MHz)

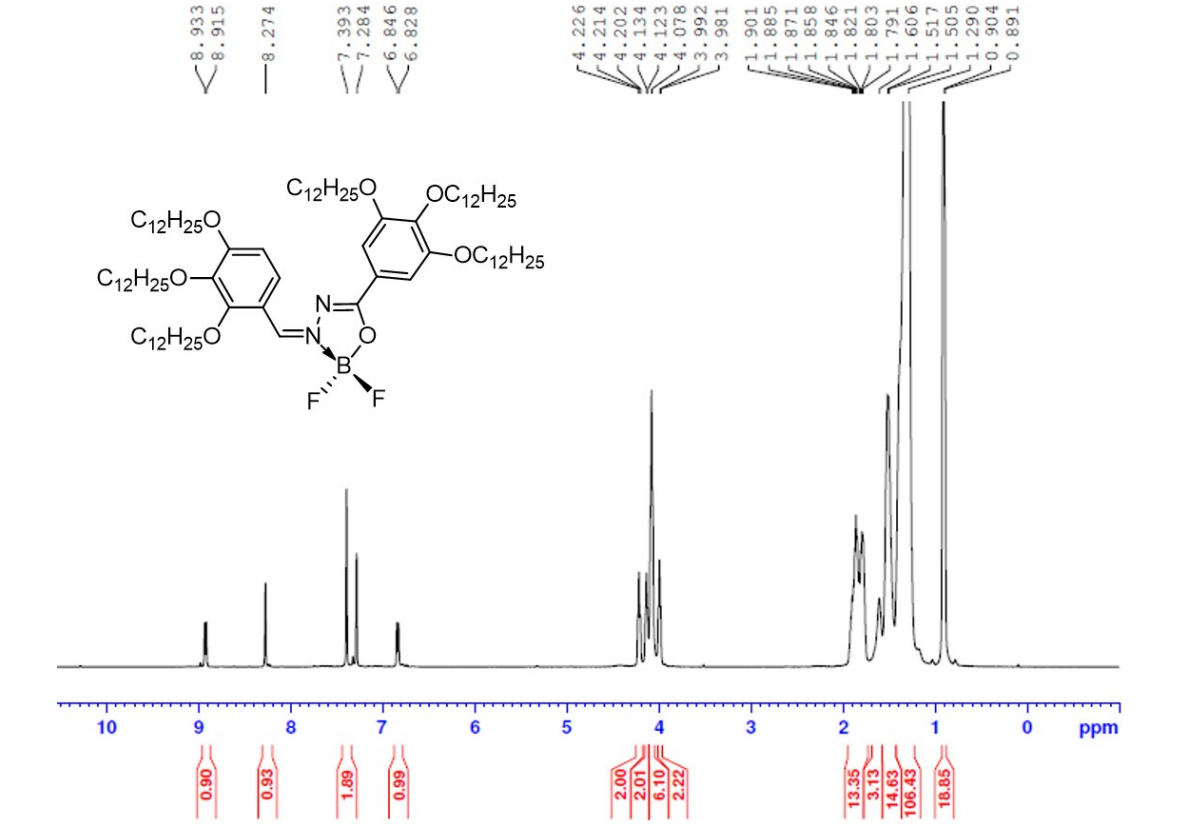


Figure S27. ^{1}H-NMR spectrum of **FB3** recorded in $CDCl_3$ (500 MHz)

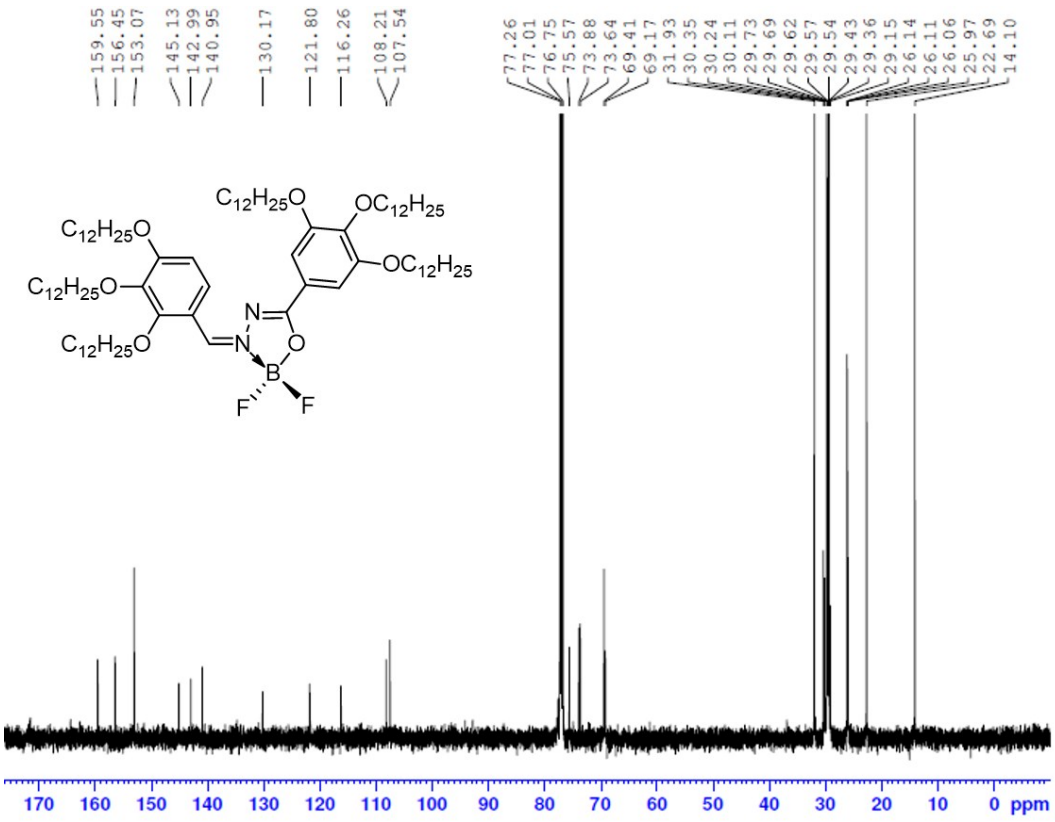


Figure S28. ^{13}C-NMR spectrum of **FB3** recorded in $CDCl_3$ (125 MHz)

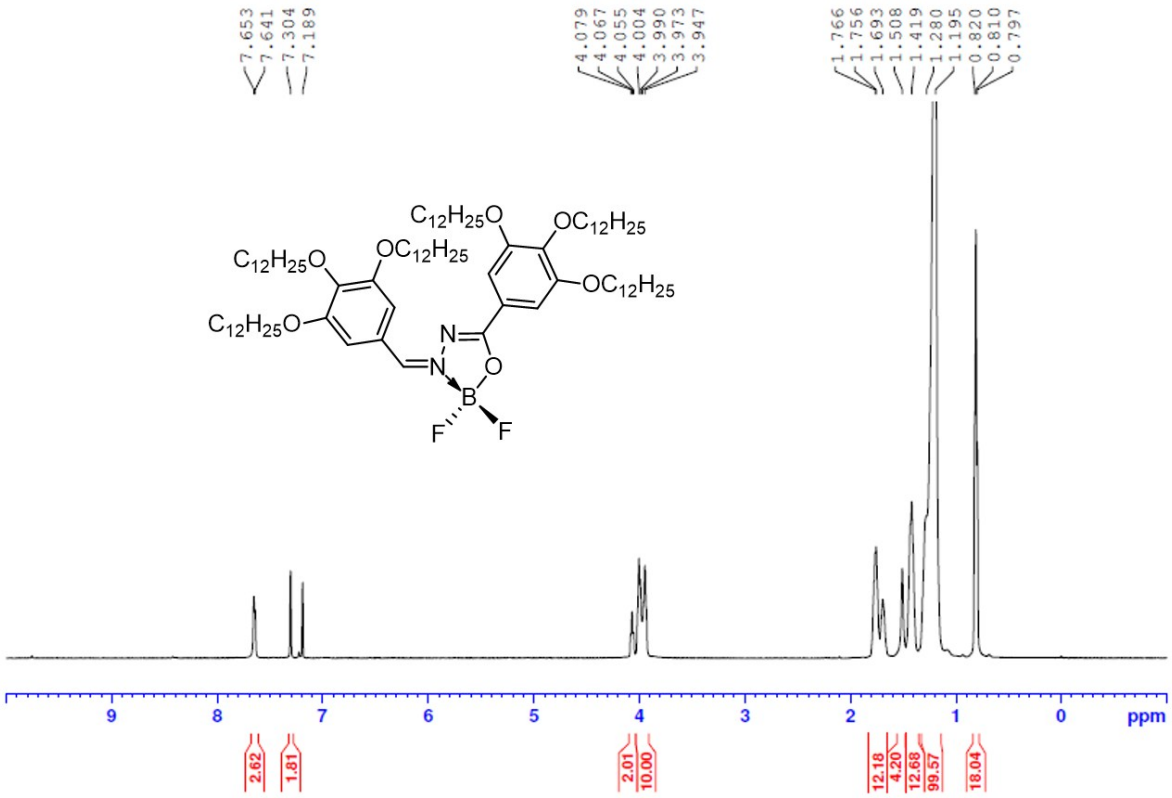


Figure S29. ^{1}H-NMR spectrum of **FB4** recorded in $CDCl_3$ (500 MHz)

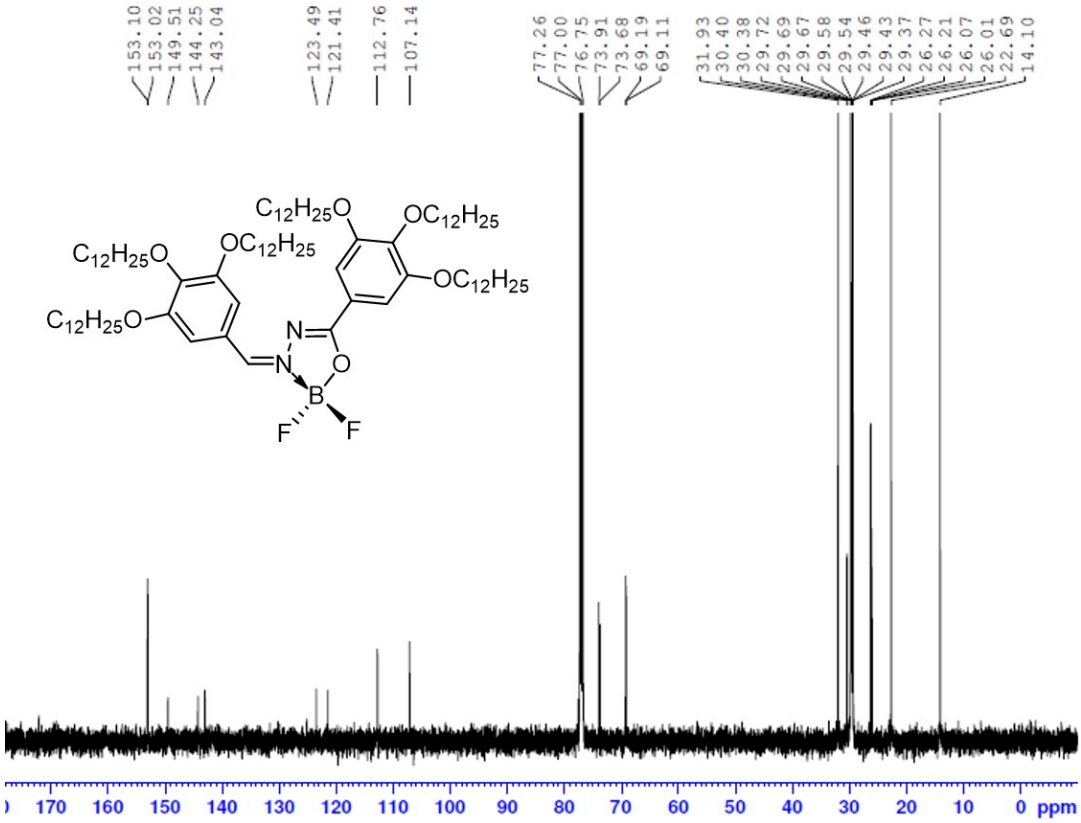


Figure S30. ^{13}C-NMR spectrum of **FB4** recorded in $CDCl_3$ (125 MHz)

6. DSC thermogram

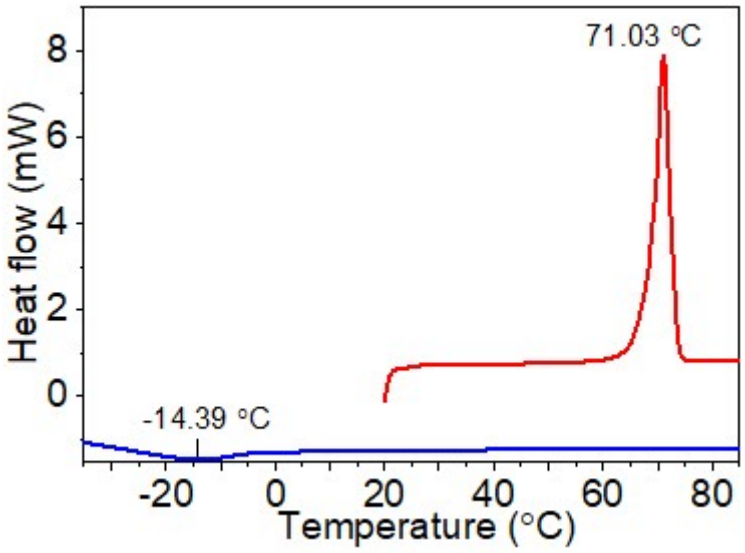


Figure S31. DSC thermogram of **HZ1**

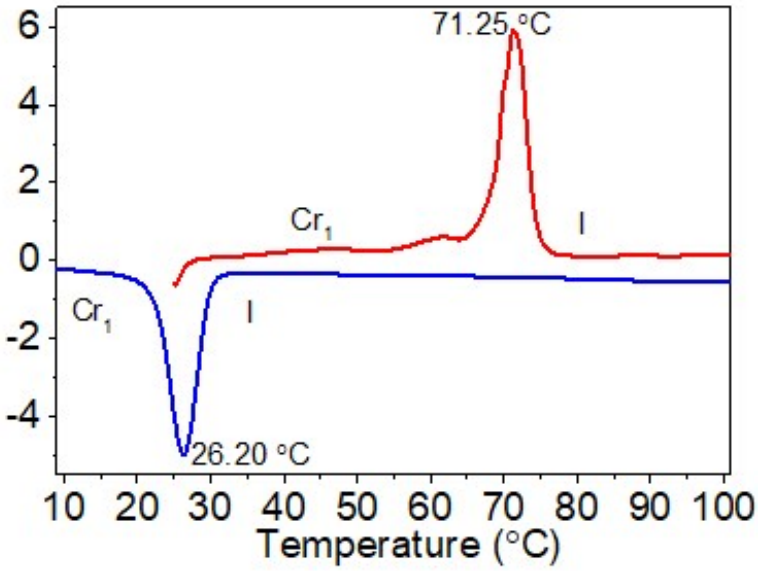


Figure S32. DSC thermogram of **FB1**

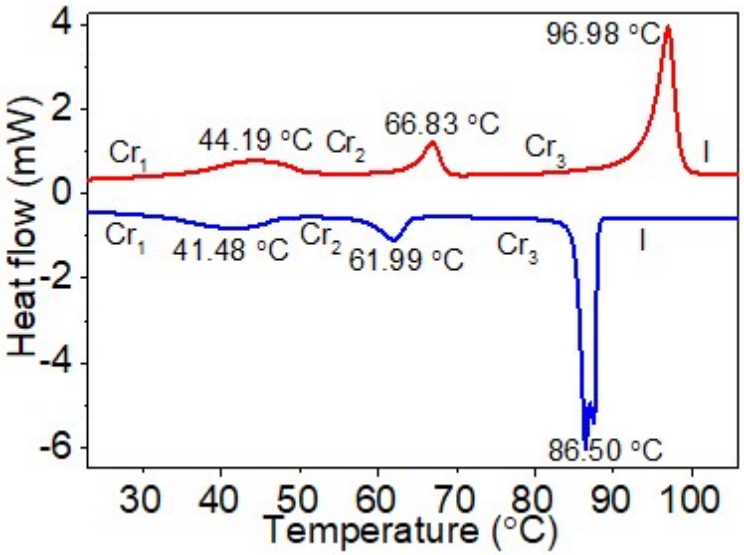


Figure S33. DSC thermogram of **FB3**