Supplementary Material

Supramolecular Brush Polymer Prepared from 1,3,4-Oxadiazole and Cyanobutoxy Functionalised Pillar[5]arene for Detecting Cu^{2+}

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Table of Contents

1. General Information

$3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5$-octamethoxy-1,3,5,7,9(1,4)-pentabenzen eacyclodecaphane-$1^2,1^5$-diylbis(trifluoromethane sulfonate) (**5**)[1,2] was prepared according to the procedures reported in literature. All other reagents were of commercially available and used without further treatment. The solvents used were of analytical grade. Pyridine, tetrahydrofuran, dichloromethane and acetonitrile were predried and distilled over sodium in benzophenome or calcium hydride. Column chromatography was performed using 200-300 mesh silica gels. ^{1}H NMR spectra were collected on a Bruker-400 instrument and chemical shifts are reported in ppm relative to the residual deuterated solvents. Proton decoupled ^{13}C NMR spectra were recorded at 101 MHz on the same spectrometer. High-resolution mass spectra (HRMS) were performed at the central laboratory of Nankai University with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. The melting points were collected on an X-4 digital display melting point instrument without correction. Scanning electron microscopy investigations were carried out on a ZEISS MERLIN Compact instrument with operating voltage as 1.00 kV. UV/Vis spectra were recorded on a SPECTROD 210 PLUS UV/Vis spectrophotometer. Steady-state emission spectra were recorded on a Cary Eclip Se spectrophotometer.

2. Synthesis

Synthesis of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoic acid (2) This compound was prepared according to the reported procedures[2] with minor modification as follows. A solution of 3-boronobenzoic acid (1.66 g, 10 mmol) and 2,3-dimethylbutane-2,3-diol (1.42 g, 12 mmol) in 30 mL of toluene was refluxed and stirred for 12 h under nitrogen atmosphere. After cooling, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 4:1) as an eluent to afford **2** as white solid. Yield, 92%. M.p. 191.5 – 192.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.79, 139.97, 136.59, 132.82, 128.72, 127.89, 84.19, 24.87. HRMS (ESI) calcd for $C_{13}H_{17}BO_4$ $[M+Na]^+$ 271.1118, found 271.1118.

Synthesis of N'-(dimethylamino)benzoyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzohydrazide (3) To a round-bottom flask (100 mL) were added **2** (1.98 g, 8 mmol), oxalyl

dichloride (2.03 g, 16 mmol), DMF (2 drops) and dry dichloromethane (20 mL). The reaction mixture was stirred for 2 h at room temperature. The solvent and excessive oxalyl dichloride were removed under reduced pressure to afford 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoyl chloride. Then, 4-(dimethylamino)benzohydrazide (1.43 g, 8 mmol), triethylamine (808 mg, 8 mmol) and dry dichloromethane (20 mL) were added dropwise to the as-formed benzoyl chloride. The mixture was stirred at room temperature for 2h, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using dichloromethane/ethyl acetate (v/v = 2:1) as an eluent to afford **3** as white solid. 2.1 g, 61% yield. mp 229.8 – 231.7 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.37 – 10.20 (m, 2H), 8.27 (s, 1H), 8.03 (s, 1H), 7.83 (s, 3H), 7.54 (s, 1H), 6.74 (s, 2H), 2.98 (s, 6H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.09, 165.75, 152.52, 137.51, 133.64, 132.59, 130.43, 128.99, 128.14, 119.07, 110.89, 84.03, 39.74, 24.76. HRMS (ESI) calcd for $C_{13}H_{17}BO_4$ $[M+Na]^+$ 432.2071, found 432.2070.

Synthesis of N,N-dimethyl-4-(5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)aniline (4) To a round-bottom flask (100 mL) were added **3** (409 mg, 1 mmol), N,N-Diisopropylethylamine (0.26 g, 2 mmol), 4-methylbenzenesulfonyl chloride TsCl (0.57 g, 3 mmol) and acetonitrile (10 mL). The reaction mixture was stirred for 12 h at 40 °C. Then, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 10:1) as an eluent to afford **4** as white solid. 0.21 g, 62% yield. mp 185.7 – 187.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.23 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 8.9 Hz, 2H), 7.95 (d, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 8.9 Hz, 2H), 3.06 (s, 6H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.26, 163.52, 152.54, 137.43, 132.75, 129.44, 128.37, 128.29, 123.83, 111.54, 110.96, 84.16, 40.07, 24.88. HRMS (ESI) calcd for $C_{22}H_{26}BN_3O_3$ $[M+H]^+$ 392.2140, found 392.2139.

Synthesis of 1^5-(3-(5-(4-(dimethylamino)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl trifluoromethane sulfonate (6) To a Schlenk flask were added **4** (0.35 g, 1.0 mmol), **5** (1.0 g，1.0 mmol), sodium carbonate (0.54 g, 5.1 mmol), and $Pd(PPh_3)_4$ (0.31 g, 0.27 mmol) as a catalyst in a solution mixture of tetrahydrofuran (30 mL) and water (10 mL). The reaction mixture was stirred for 18 h at 80 ºC under nitrogen atmosphere. The solvent was removed in vacuo, the solid residue was

extracted by ethyl acetate twice (2×10 mL). The organic phase was combined and dried with anhydrous $MgSO_4$, filtered and concentrated at reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 15:1) as an eluent to afford **6** as white solid. 0.9 g, 80% yield. mp 134.1 – 135.8 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 8.05 – 7.93 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.11 (s, 1H), 6.82 – 6.73 (m, 7H), 6.70 (s, 1H), 6.64 (s, 1H), 5.93 (s, 1H), 3.88 (s, 2H), 3.84 – 3.82 (m, 6H), 3.74 (s, 3H), 3.71 (s, 2H), 3.69 – 3.66 (m, 9H), 3.64 (s, 3H), 3.61 (s, 3H), 3.47 (s, 3H), 3.44 (s, 3H), 3.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.40, 163.22, 152.38, 150.98, 150.89, 150.77, 150.67, 150.61, 150.57, 150.16, 147.79, 141.77, 139.64, 133.86, 132.08, 130.71, 129.45, 128.87, 128.80, 128.28, 128.23, 127.71, 127.32, 126.62, 125.17, 124.73, 124.38, 122.57, 120.19, 117.00, 114.33, 114.11, 114.01, 113.98, 113.85, 113.64, 113.31, 112.98, 111.53, 110.65, 55.94, 55.82, 55.74, 55.65, 55.59, 55.47, 55.16, 55.11, 40.00, 32.62, 31.58, 31.42, 29.86, 29.44, 29.24, 22.46, 14.05. ^{19}F NMR (377 MHz, $CDCl_3$) δ −73.77. HRMS (ESI) calcd for $C_{60}H_{58}F_3N_3O_{12}S$ $[M+Na]^+$ 1124.3591, found 1124.3588.

Synthesis of 1^5-(3-(5-(4-(dimethylamino)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphan-12-ol (7) To a solution of **6** (0.44 g, 0.4 mmol) in THF (20mL) was added tetrabutylammonium fluoride (0.8 mL, 1M in THF) at 40 ºC; the mixture was stirred for 12 h. The reaction mixture was diluted with ethyl acetate, washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 2:1) as an eluent to afford **7** as white solid. 0.35 g, 89% yield. mp 152.4 – 153.9 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.25 (s, 1H), 7.06 (s, 1H), 7.01 (s, 1H), 6.83 (s, 1H), 6.81 (s, 2H), 6.79 (s, 1H), 6.77 (s, 1H), 6.74 (s, 1H), 6.69 (s, 1H), 6.68 (s, 1H), 6.47 (s, 1H), 6.42 (s, 1H), 3.90 (s, 3H), 3.85 – 3.81 (m, 11H), 3.79 (s, 2H), 3.70 – 3.69 (m, 6H), 3.67 – 3.66 (m, 6H), 3.60 (s, 3H), 3.19 (s, 3H), 3.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.20, 163.61, 153.77, 152.31, 151.85, 151.04, 150.87, 150.62, 150.53, 148.17, 143.28, 138.83, 132,83, 132.65, 131.22, 129.54, 128.63, 128.35, 128.23, 128.15, 128.01, 127.72, 125.92, 124.82, 124.44, 123.99, 117.76, 114.43, 114.29, 114.27, 113.82, 113.53, 113.42, 113.07, 111.51, 110.87, 60.30, 56.33, 55.96, 55.87, 55.80, 55.75, 55.73, 55.59, 55.16, 52.76, 39.98, 32.45, 31.76, 31.45, 30.45, 30.21, 29.68,

28.96, 22.59, 22.52, 20.95, 14.05. HRMS (ESI) calcd for $C_{59}H_{59}N_3O_{10}$ $[M+H]^+$ 970.4279, found 970.4276.

Synthesis of 5-((1^5-(3-(5-(4-(dimethylamino)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-12-yl)oxy) pentanenitrile (P5-OXD) A suspension of 7 (0.19 g, 0.2 mmol), 5-bromopentanenitrile (33 mg, 0.2 mmol) and potassium carbonate (0.11 g, 0.8 mmol) in acetonitrile (25 mL) was refluxed for 16 h under N_2 atmosphere. After cooling, the solvent was removed in vacuo, and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (v/v = 2:1) as an eluent to afford **P5-OXD** as white solid. 0.19 g, 90% yield. mp 138.7 – 140.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 2H), 7.99 – 7.97 (m, 2H), 7.49 (s, 1H), 7.40 (s, 1H), 7.15 (s, 1H), 6.93 – 6.69 (m, 10H), 6.21 (s, 1H), 3.83 – 3.57 (m, 36H), 3.08 (s, 6H), 1.26 (br, 2H), 0.90-0.87 (m, 2H), 0.57 (br, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.28, 163.51, 155.88, 152.25, 151.50, 150.38, 150.25, 150.08, 149.73, 142.99, 138.47, 132.99, 132.00, 128.86, 128.26, 127.94, 127.16, 126.85, 124.68, 124.12, 120.01, 119.58, 116.52, 113.88, 113.42, 112.78, 111.45, 110.78, 55.41, 39.97, 38.86, 38.63, 34.01, 31.76, 30.85, 30.58, 29.56, 29.39, 29.06, 28.95,27.84, 26.81, 22.86, 22.75, 22.57, 20.05, 19.07, 14.32, 14.07, 11.31. HRMS (ESI) calcd for $C_{64}H_{66}N_4O_{10}$ $[M+H]^+$ 1089.4416, found 1089.4413.

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2 N. L. Strutt, D. Fairen- Jimenez, J. Iehl, M. B. Lalonde, R. Q. Snurr, O. K. Farha, J. T. Hupp, J. F. Stoddart, *J. Am. Chem. Soc*., 2012, **134**, 17436–17439.

3 A. Kumar, G. Ye, Y. Ahmadibeni, K. Parang, *J. Org. Chem*., 2006, **71**, 7915–7918.

1. NMR Spectra

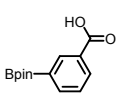

Figure S1 ^{1}H NMR spectrum of **2** in $CDCl_3$ (298K, * solvent peaks)

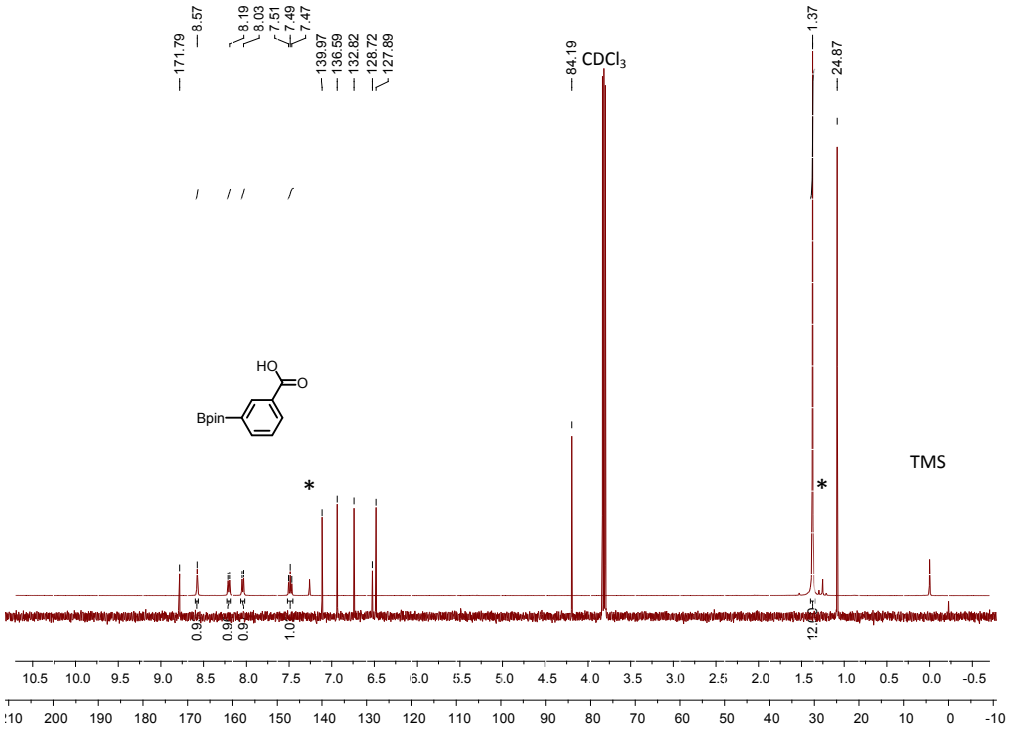

Figure S2 ^{13}C NMR spectrum of **2** in $CDCl_3$ (298K)

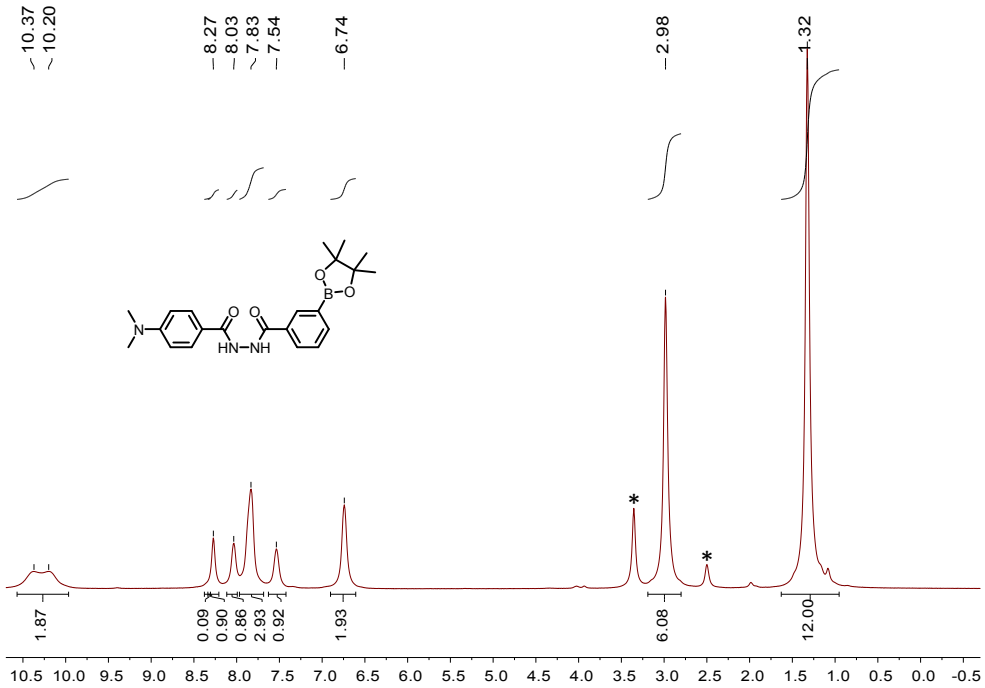

Figure S3 ^{1}H NMR spectrum of **3** in DMSO-d_6 (298K, * solvent peaks)

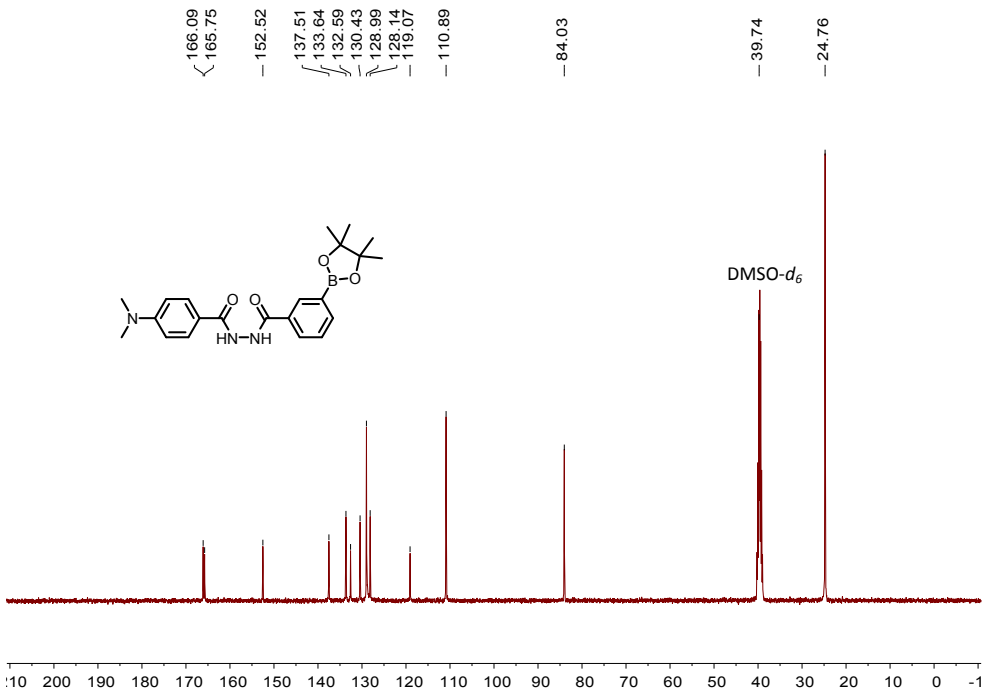

Figure S4 ^{13}C NMR spectrum of **3** in DMSO-d_6 (298K)

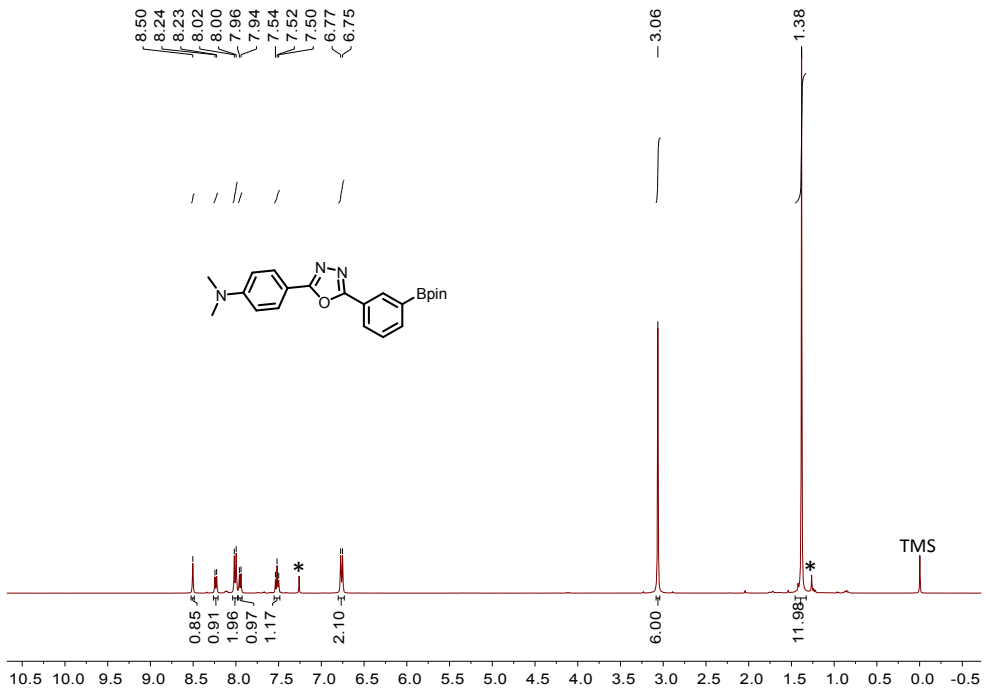

Figure S5 ^{1}H NMR spectrum of **4** in $CDCl_3$ (298K, * solvent peaks)

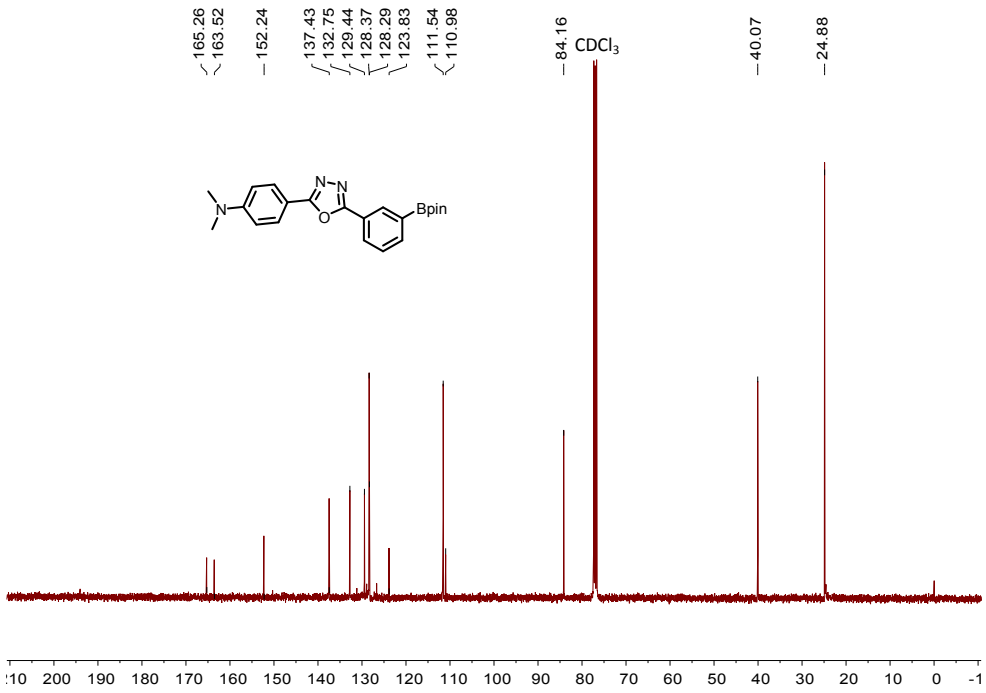

Figure S6 ^{13}C NMR spectrum of **4** in $CDCl_3$ (298K)

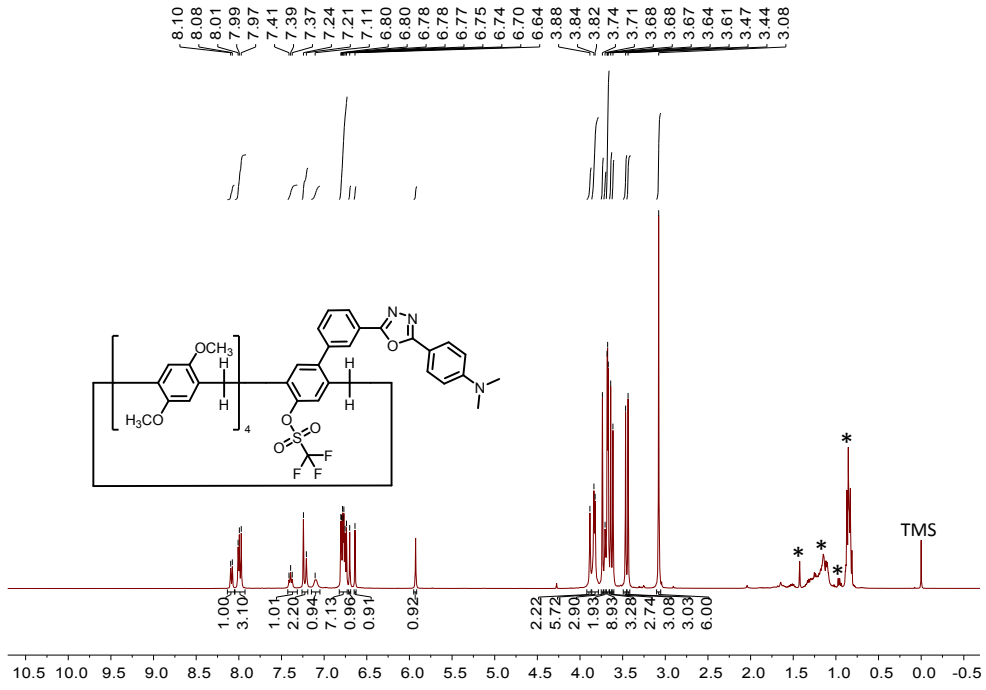

Figure S7 ^{1}H NMR spectrum of **6** in $CDCl_3$ (298K, * solvent peaks)

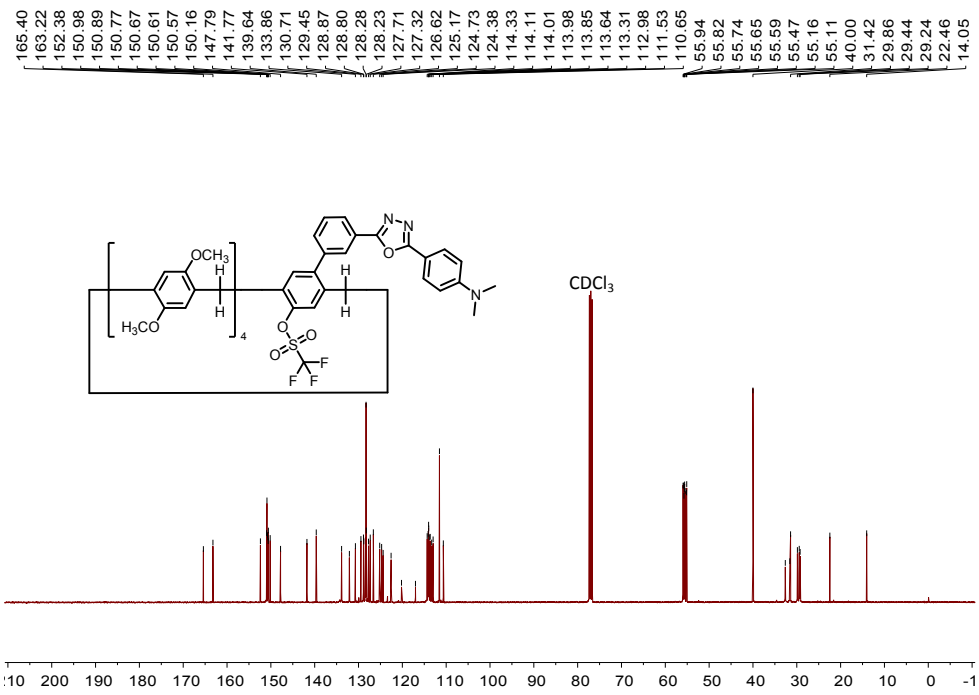

Figure S8 ^{13}C NMR spectrum of **6** in $CDCl_3$ (298K)

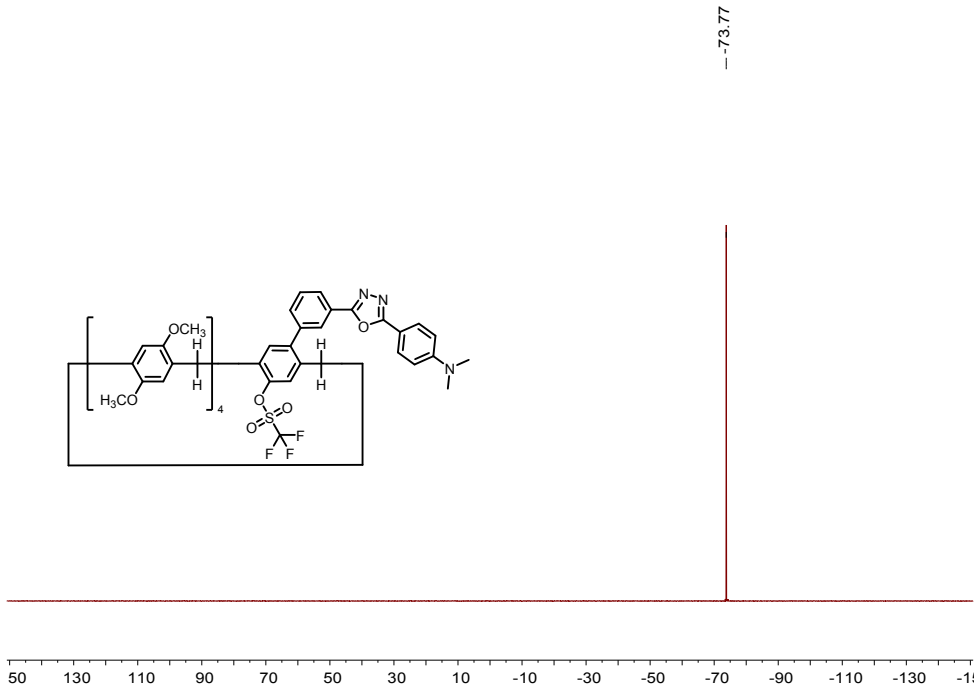

Figure S9 ^{19}F NMR spectrum of **6** in $CDCl_3$ (298K)

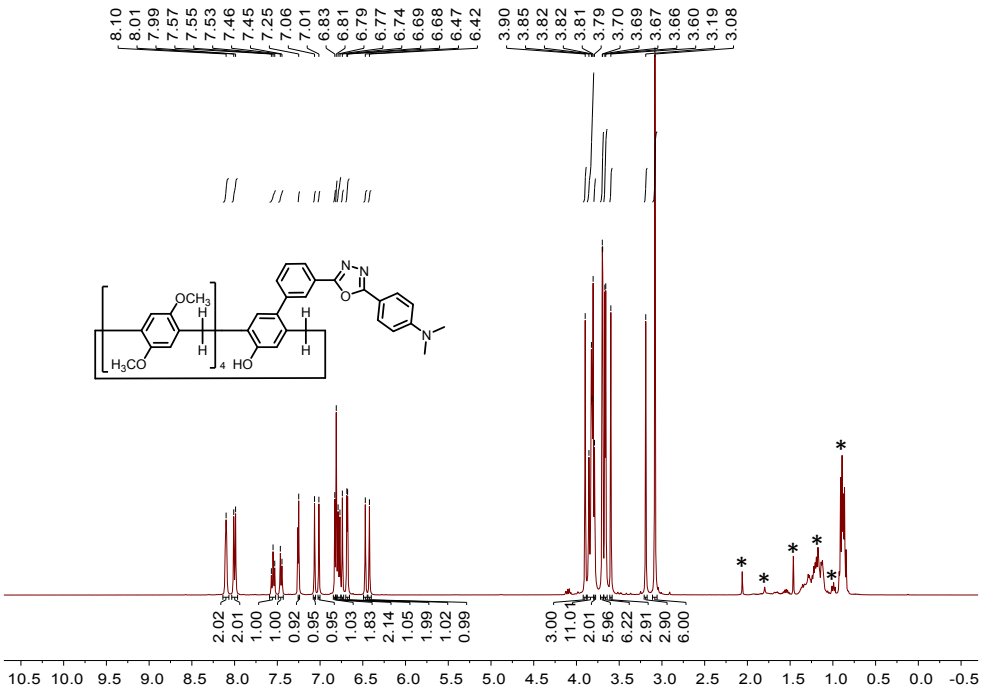

Figure S10 ^{1}H NMR spectrum of **7** in $CDCl_3$ (298K, * solvent peaks)

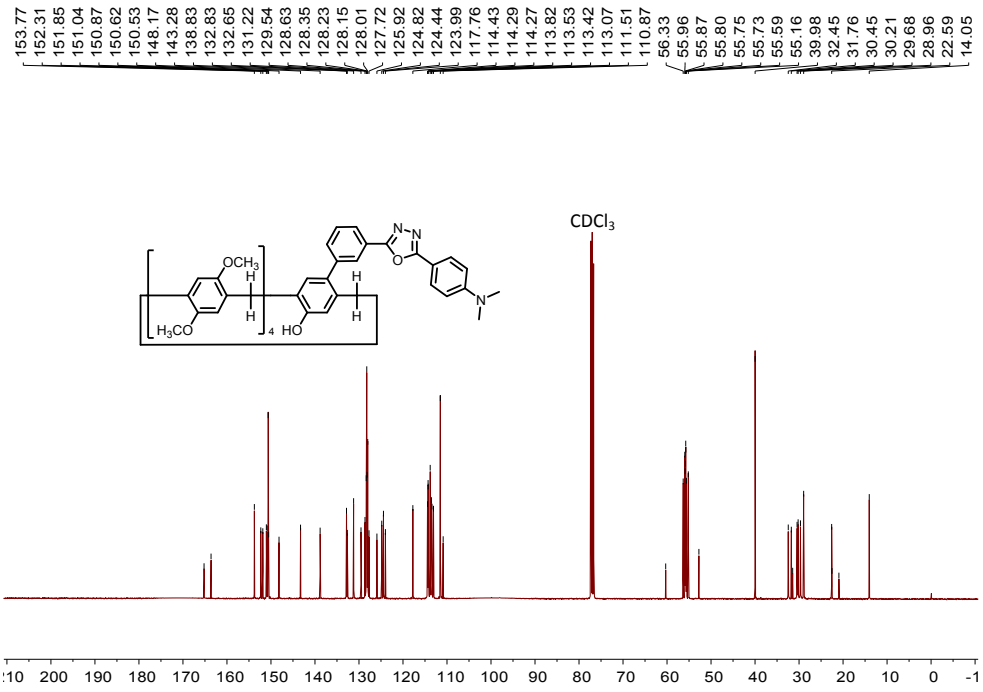

Figure S11 ^{13}C NMR spectrum of **7** in $CDCl_3$ (298K)

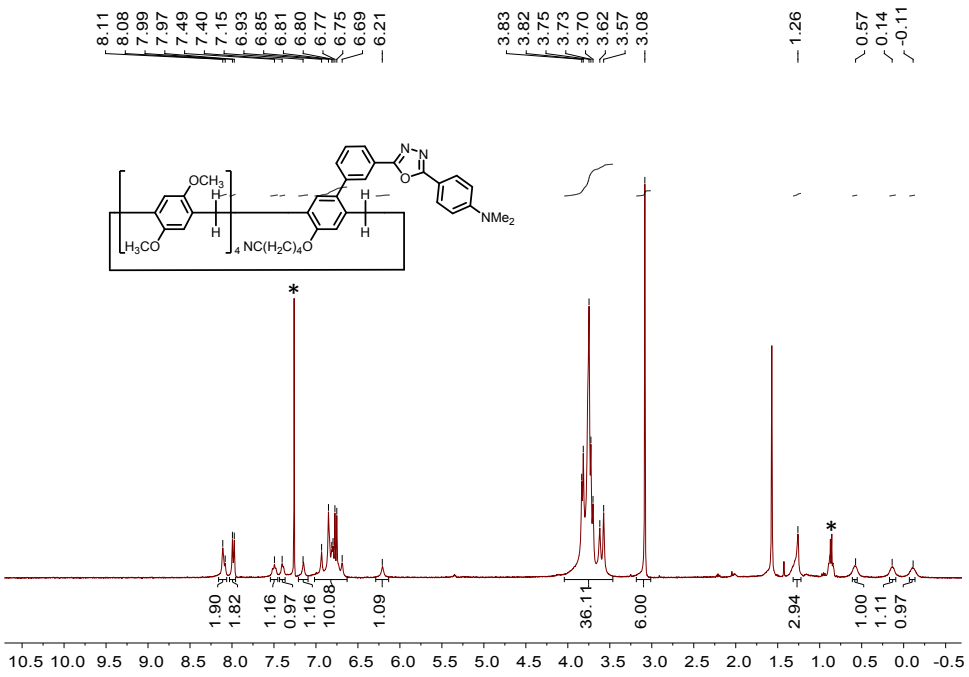

Figure S12 ^{1}H NMR spectrum of **P5-OXD** in $CDCl_3$ (298K, * solvent peaks)

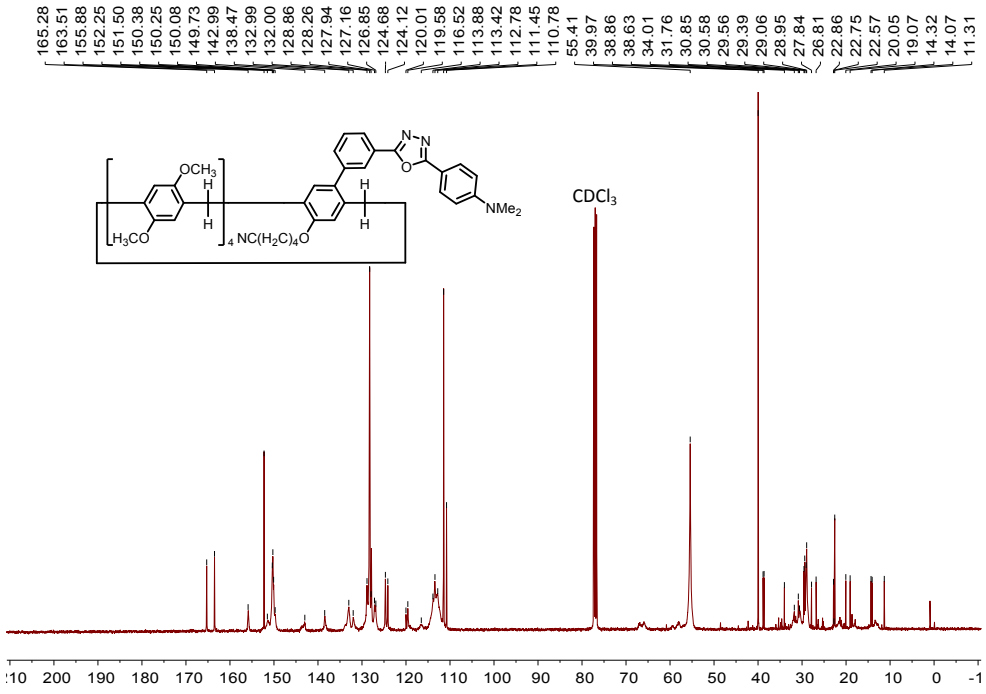

Figure S13 ^{13}C NMR spectrum of **P5-OXD** in $CDCl_3$ (298K)

2. HR-ESI-MS Spectra

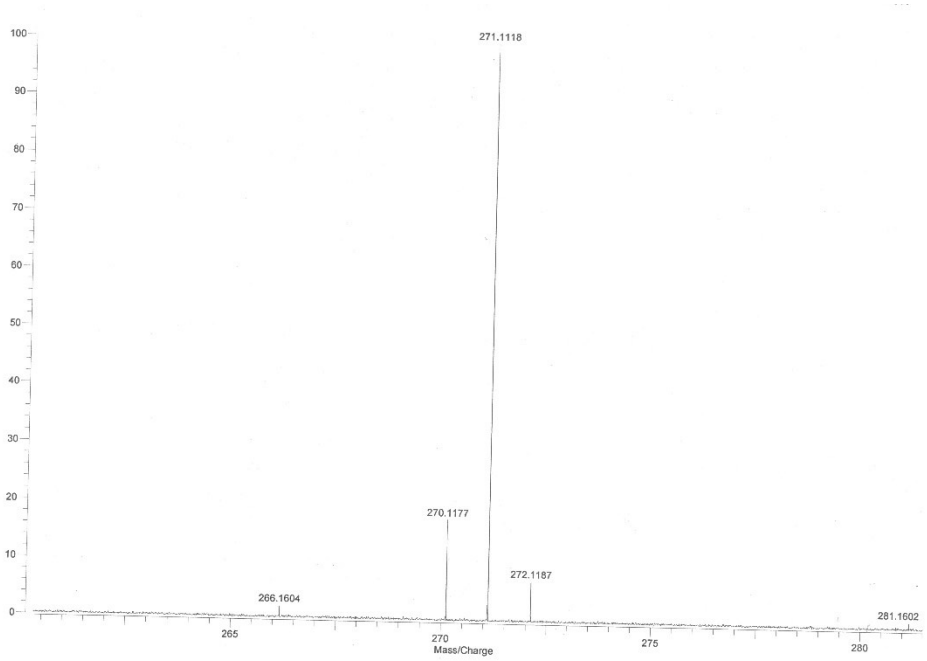

Figure S14 HRESIMS of **2**

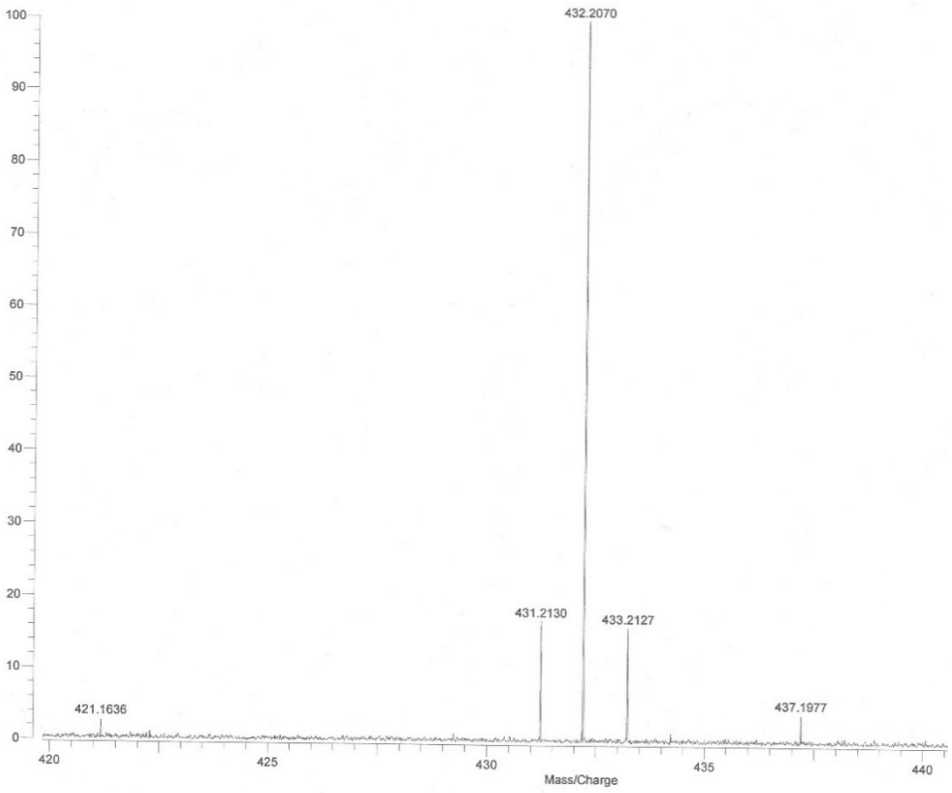

Figure S15 HRESIMS of **3**

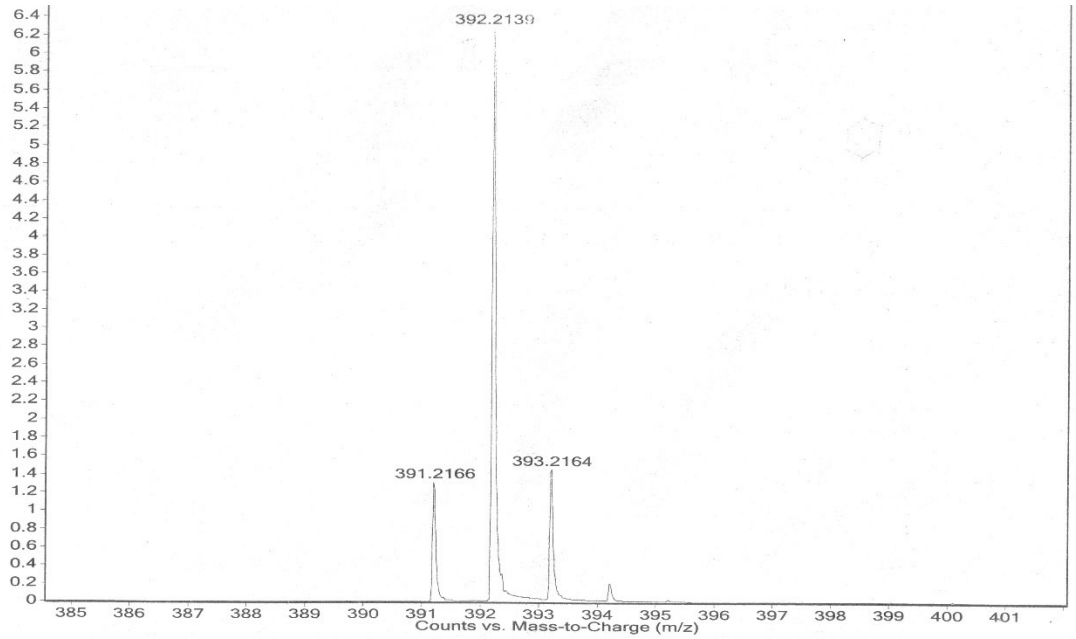

Figure S16 HRESIMS of **4**

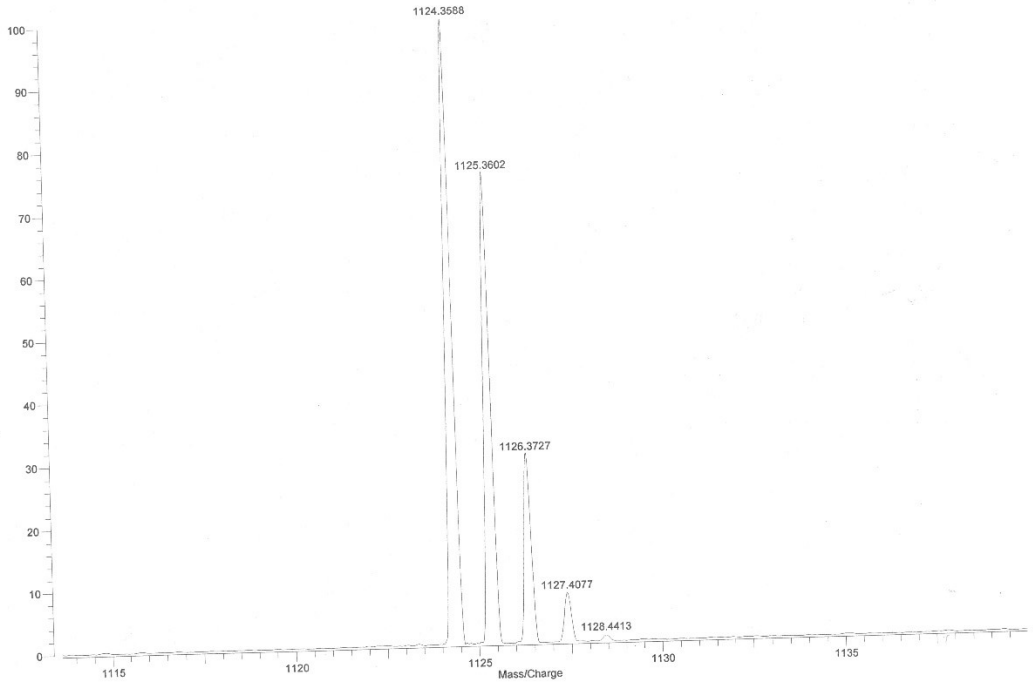

Figure S17 HRESIMS of **6**

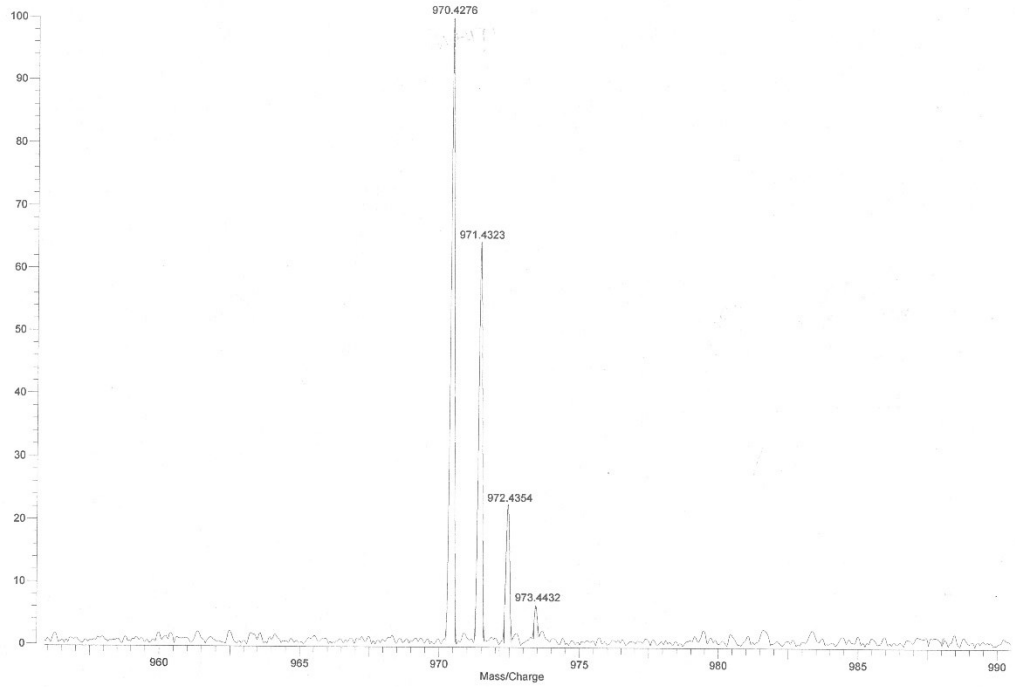

Figure S18 HRESIMS of **7**

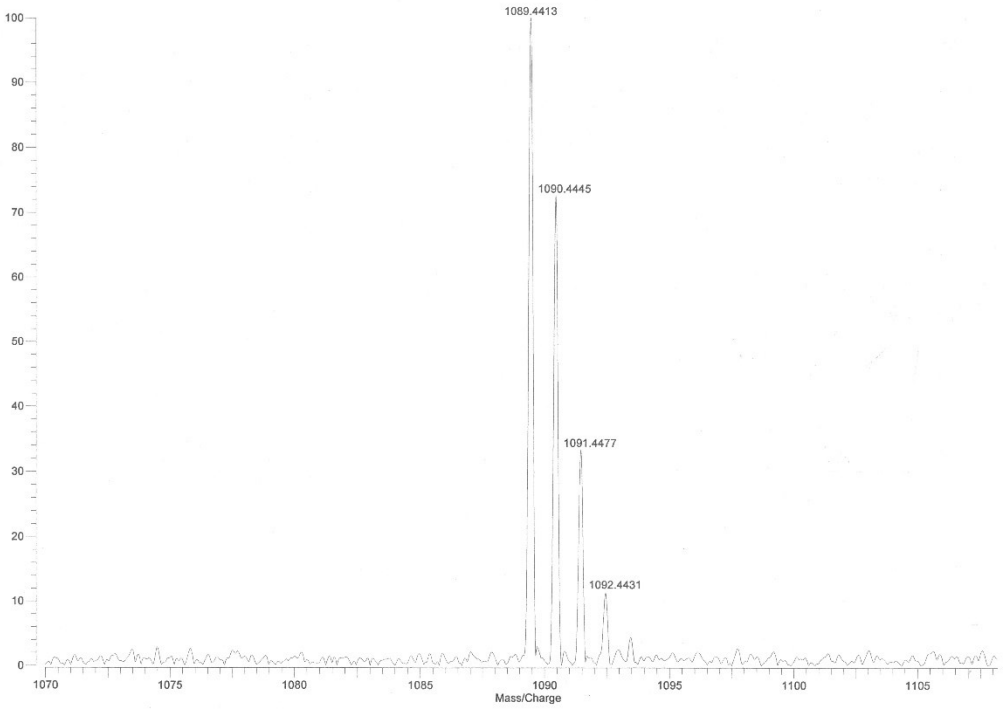

Figure S19 HRESIMS of **P5-OXD**

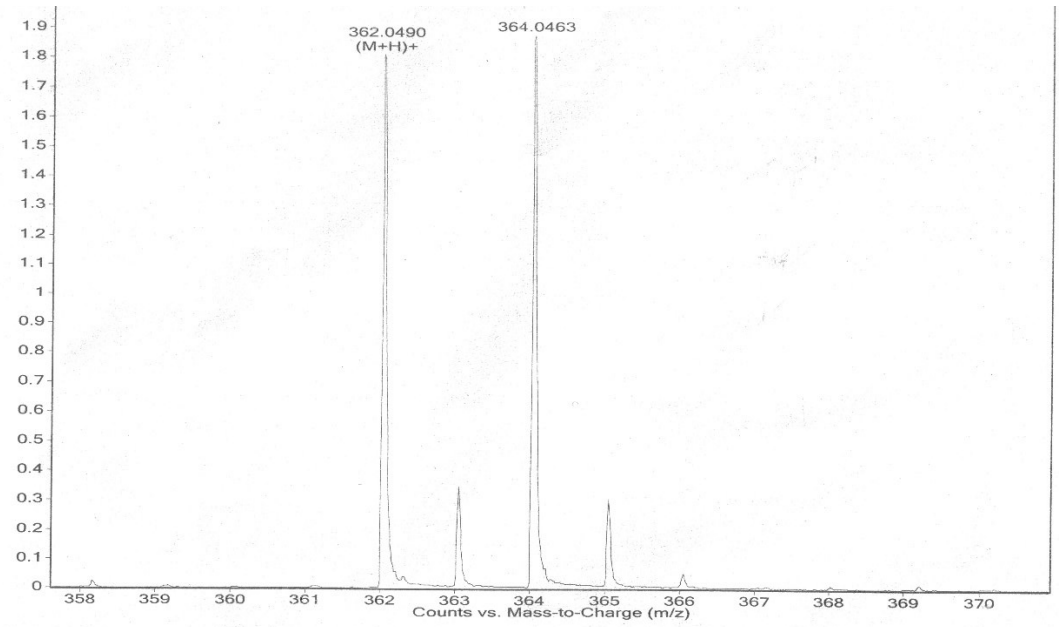

Figure S20 HRESIMS of **8**

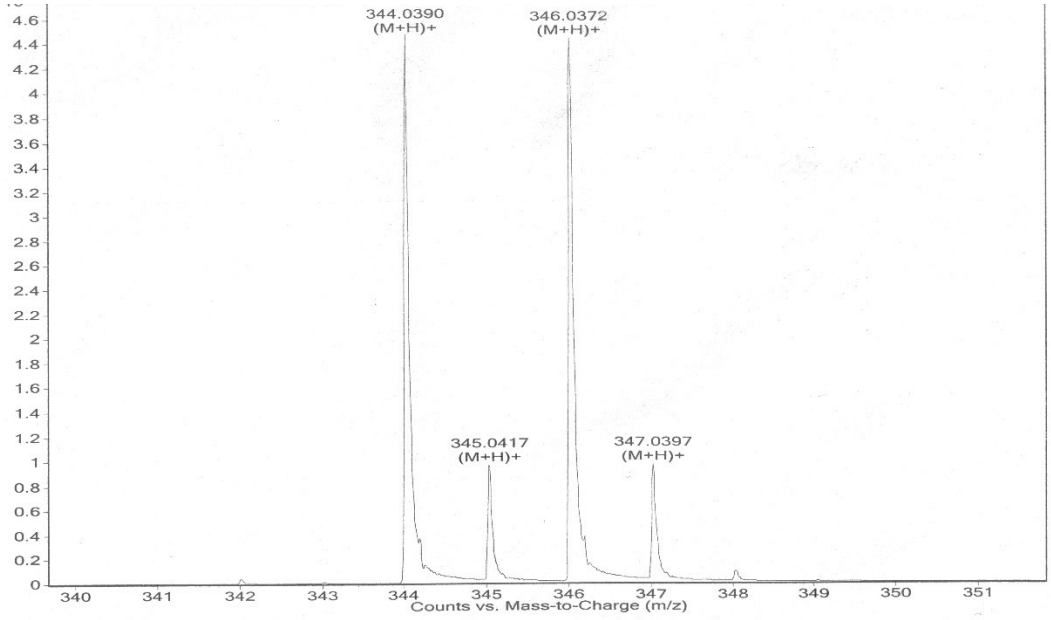

Figure S21 HRESIMS of **9**