Electronic Supplementary Material (ESI) for ChemComm.

An Unusual Macrocyclization Reagent for Highly Selective One-Pot Synthesis of Strained Macrocyclic Aromatic Hexamers†

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Supporting Information

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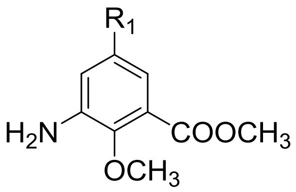
1. General remarks

^{1}H NMR and ^{13}C NMR data were obtained on a Bruker AMX300 or 600 (300 or 600 MHz) nuclear resonance spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectra as 0.00 ppm (chloroform, 7.26 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from tetramethylsilane using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. All reagents were purchased from Acros, Aldrich, and Alfa Aesar without further purification in advance before use.

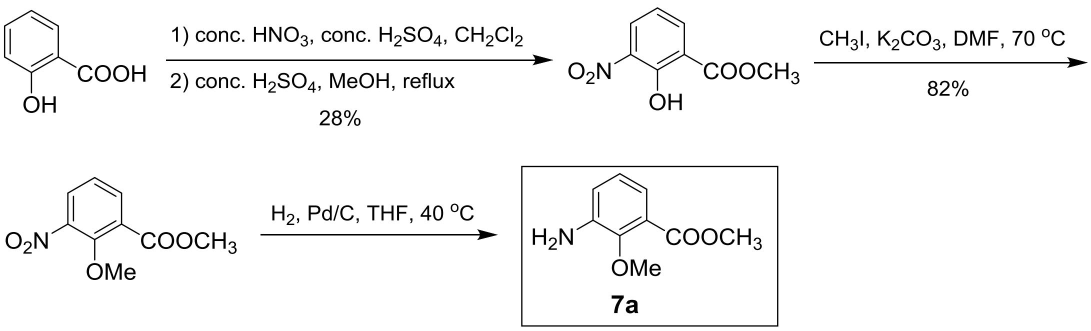
2. Synthesis of monomeric amino esters 7a-7d have been reported in the following journal articles

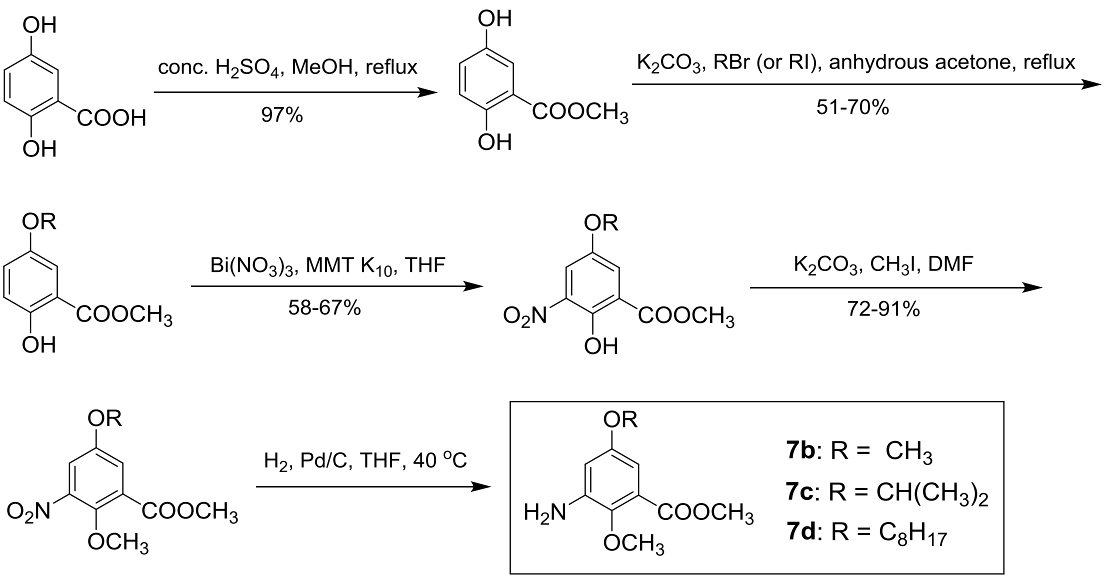


7a: R_1 = H
7b: R_1 = OMe
7c: R_1 = $OCH(CH_3)_2$
7d: R_1 = OC_8H_{17}

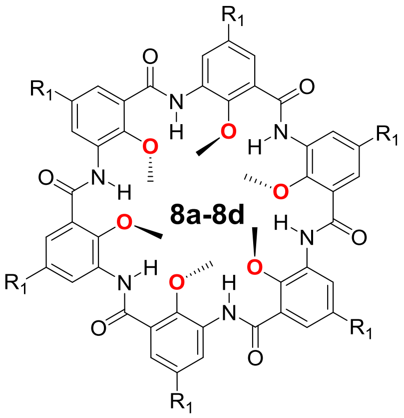
For synthesis of **7a**, see: B. Qin, X. Y. Chen, X. Fang, Y. Y. Shu, Y. K. Yip, Y. Yan, S. Y. Pan, W. Q. Ong, C. L. Ren, H. B. Su and H. Q. Zeng, *Org. Lett.* 2008, **10**, 5127.

For synthesis of **7b-7d**, see: Y. Yan, B. Qin, C. L. Ren, X. Y. Chen, Y. K. Yip, R. J. Ye, D. W. Zhang, H. B. Su and H. Q. Zeng, *J. Am. Chem. Soc.* 2010, **132**, 5869.





3. ^{1}H NMR, ^{13}C NMR, and (HR)MS of hexamers 8a, 8c and 8d



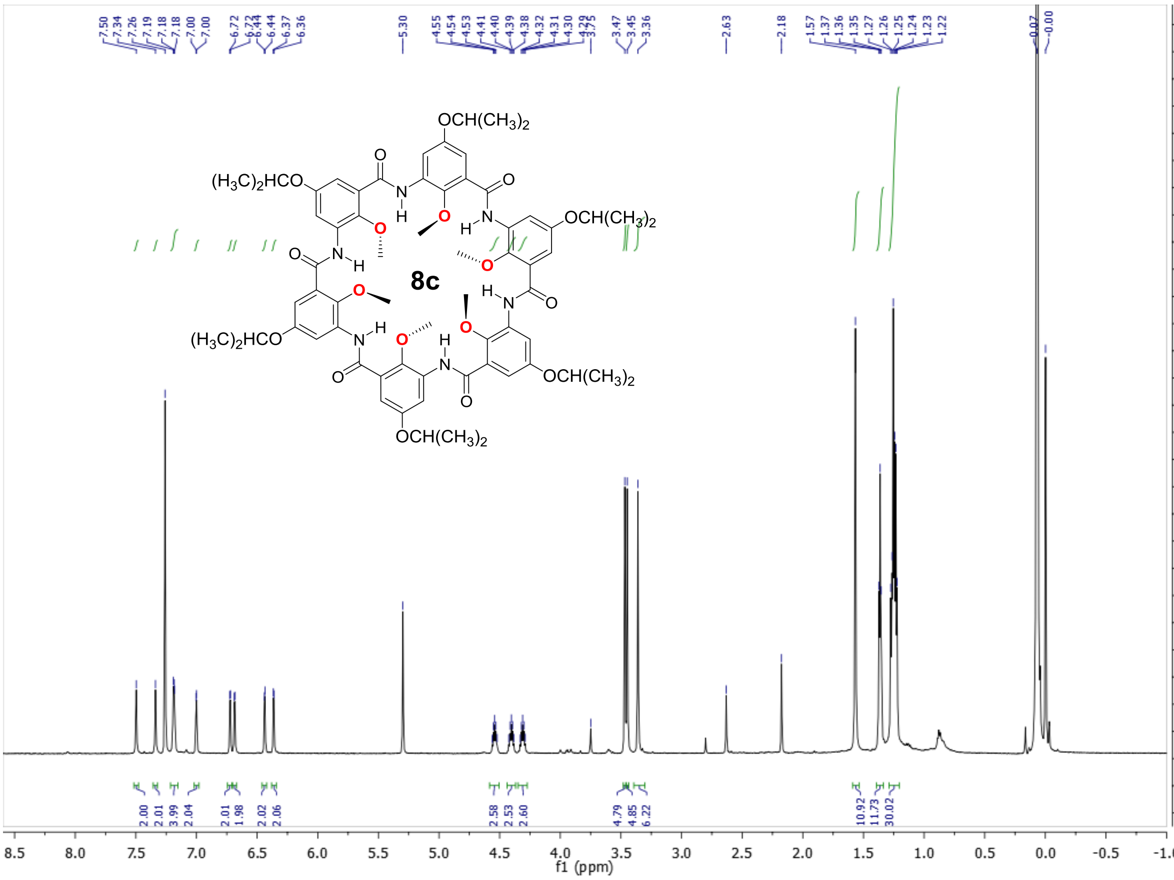
8a: R_1 = H
8c: R_1 = $OCH(CH_3)_2$
8d: R_1 = OC_8H_{17}

For ^{1}H NMR, ^{13}C NMR, and (HR)MS of hexamer **8a**, see Y. Liu, B. Qin and H. Q. Zeng, *Sci. China Chem.* 2012, **55**, 55.

Due to their highly distorted backbones as evidenced from the computationally determined structure of **8a** (Fig 2c of the text), the ^{1}H signals for the six aromatic units in both **8c** and **8d** split into three individual sets of signals. The same splitting is applicable to other proton signals from amide bonds and interior and exterior side chains as well as the ^{13}C NMR.

Hexamer 8c: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.34 (s, 2H), 7.21 – 7.15 (m, 4H), 7.00 (d, *J* = 2.7 Hz, 2H), 6.72 (d, *J* = 2.6 Hz, 2H), 6.69 (d, *J* = 2.7 Hz, 2H), 6.44 (d, *J* = 2.6 Hz, 2H), 6.36 (d, *J* = 2.5 Hz, 2H), 4.54 (dt, *J* = 12.1, 6.0 Hz, 3H), 4.40 (dt, *J* = 11.9, 5.9 Hz, 3H), 4.31 (dt, *J* = 12.0, 5.9 Hz, 3H), 3.47 (s, 5H), 3.45 (s, 5H), 3.36 (s, 6H), 1.57 (s, 11H), 1.36 (t, *J* = 5.6 Hz, 12H), 1.25 (td, *J* = 12.0, 6.0 Hz, 30H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.77, 169.49, 168.27, 153.93, 152.96, 152.60, 148.24, 143.95, 143.06, 132.25, 131.97, 131.51, 130.57, 130.11, 128.57, 123.95, 117.99, 115.37, 114.26, 113.90, 112.38, 71.06, 70.87, 70.79, 61.43, 61.35, 61.08, 53.78, 53.39, 29.68, 29.26, 22.12, 21.95, 21.85, 21.65. HRMS-EI: calculated for $[M+Na]^+$ ($C_{66}H_{78}N_6O_{18}K$): *m/z* 1265.5270, found: *m/z* 1265.5075.

Hexamer 8d: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.72 (s, 2H), 7.53 (s, 2H), 7.16 (d, *J* = 3.0 Hz, 2H), 6.97 (d, *J* = 2.9 Hz, 2H), 6.77 (d, *J* = 2.8 Hz, 2H), 6.71 (d, *J* = 2.9 Hz, 2H), 6.43 (d, *J* = 2.7 Hz, 2H), 6.38 (d, *J* = 2.7 Hz, 2H), 3.95 (m, 4H), 3.83 (m, 6H), 3.75 (dd, *J* = 15.4, 6.6 Hz, 2H), 3.44 (s, 6H), 3.41 (s, 6H), 3.35 (s, 6H), 1.80 (m, 4H), 1.70 (m, 8H), 1.46 (m, 5H), 1.33 (m, 57H), 0.89 (t, *J* = 6.7 Hz, 16H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.17, 169.70, 168.42, 155.21, 154.10, 153.82, 148.30, 143.87, 142.95, 132.36, 131.92, 131.55, 130.20, 128.64, 122.39, 116.42, 113.92, 112.18, 111.99, 110.98, 68.78, 68.74, 68.68, 61.59, 61.47, 61.17, 31.82, 29.39, 29.35, 29.24, 29.20, 26.01, 25.97, 22.65, 14.08. HRMS-EI: calculated for $[M+Na]^+$ ($C_{96}H_{138}N_6O_{18}K$): *m/z* 1685.9965, found: *m/z* 1685.9752.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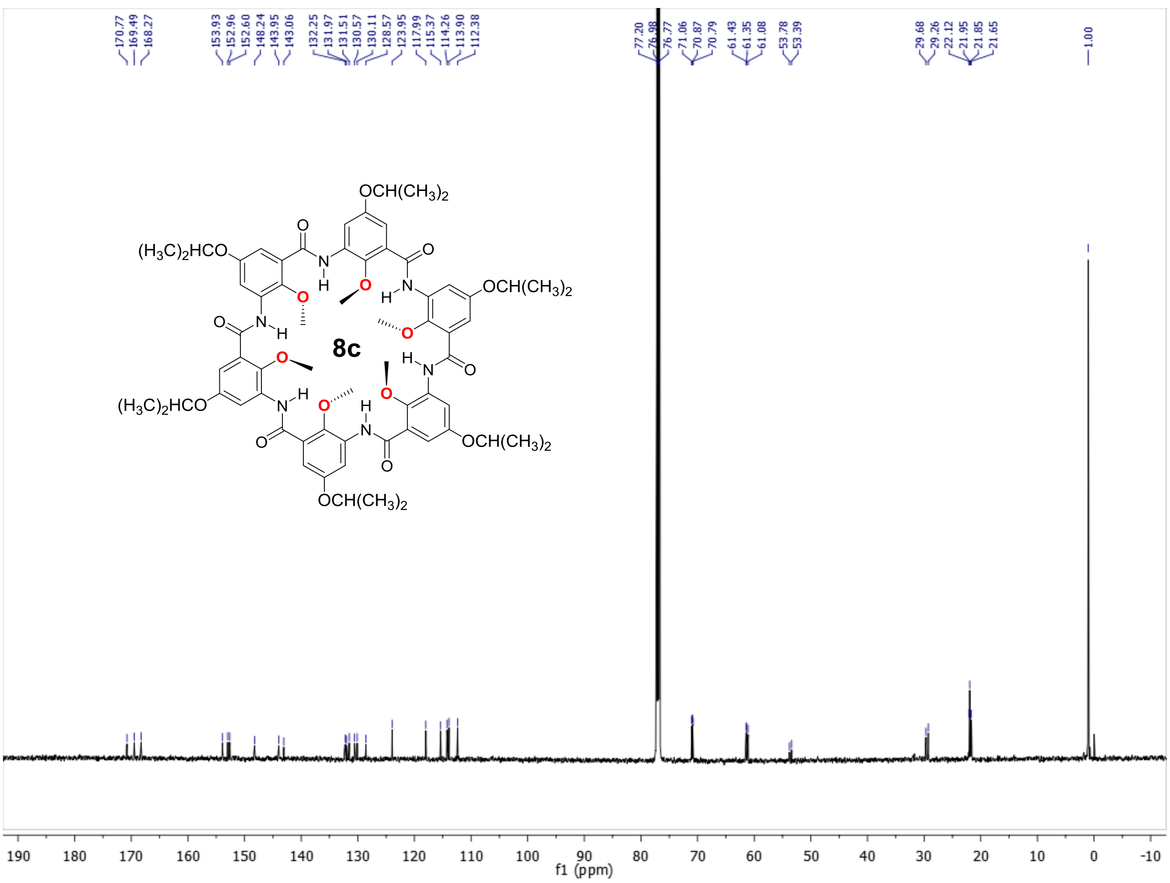
3.47 3.45 3.36
2.63
2.18
1.57 1.37 1.36 1.35 1.27 1.26 1.25 1.24 1.23 1.22
0.07 0.00
OCH(CH3)2
(H3C)2HCO
8c
2.00 2.01 3.99 2.04 2.01 1.98 2.02 2.06
2.58 2.53 2.60
4.79 4.85 6.22
10.92 11.73 30.02
f1 (ppm)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153.93 152.96 152.60 148.24 143.95 143.06
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77.20 76.98 76.77 71.06 70.87 70.79
61.43 61.35 61.08
53.78 53.39
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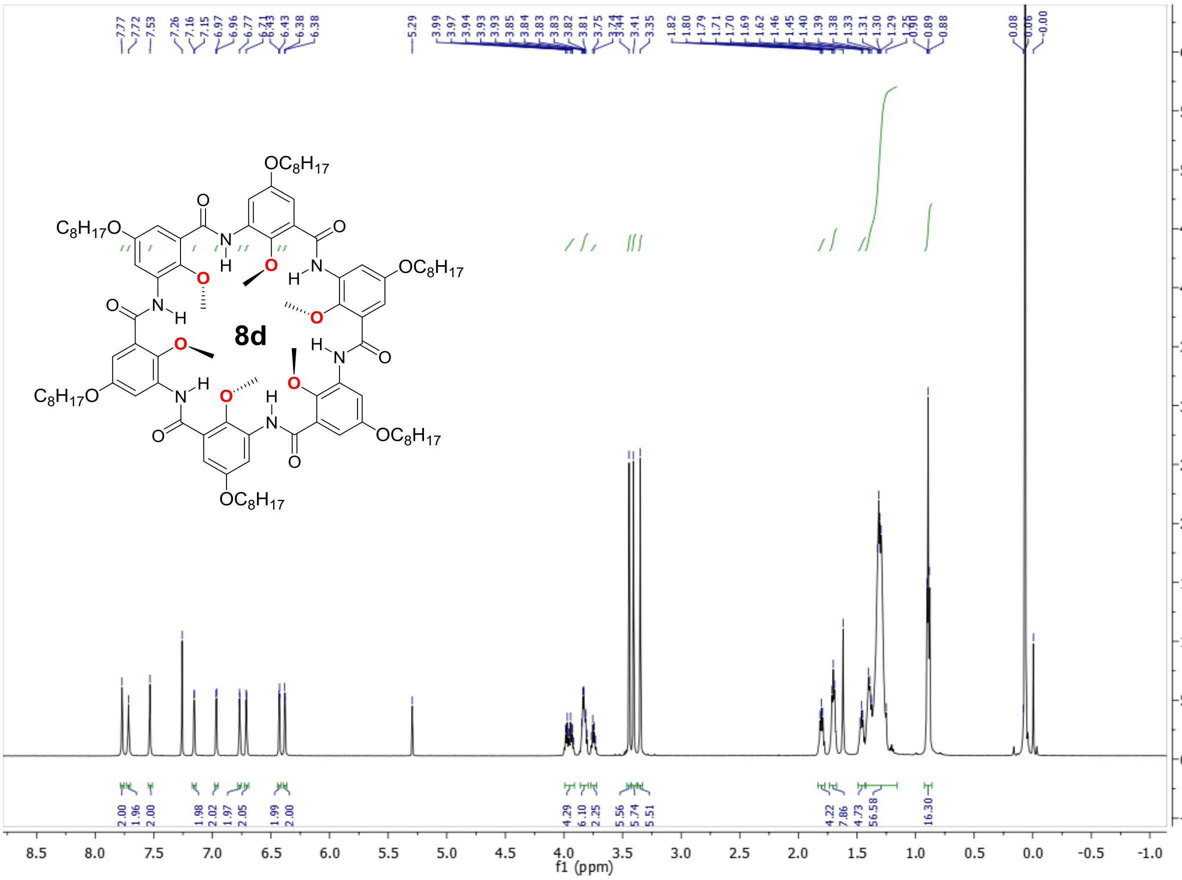
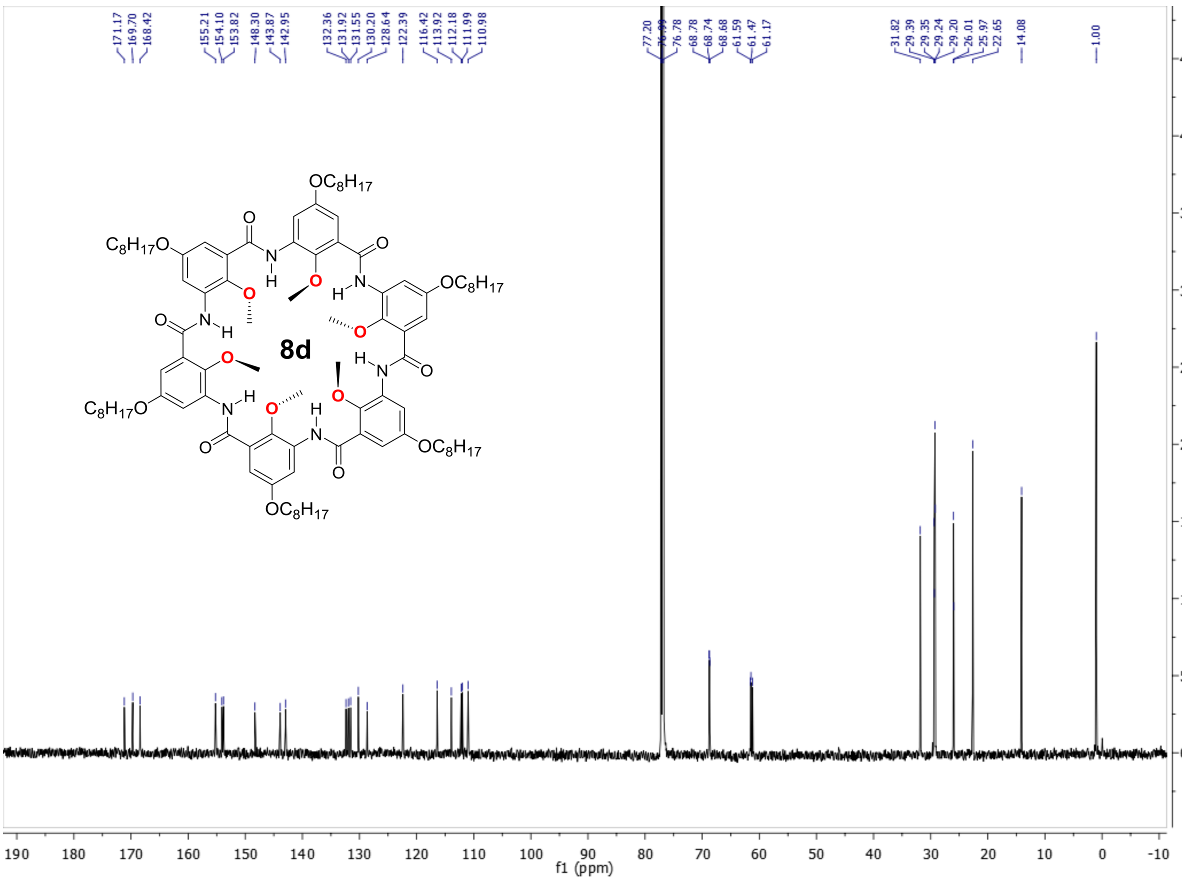
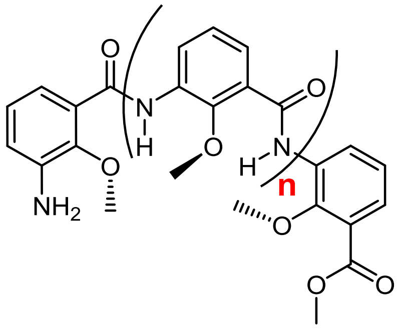
1.00
OCH(CH3)2
(H3C)2HCO
8c
f1 (ppm)





4. ^{1}H NMR, ^{13}C NMR, and (HR)MS of intermediate oligomers P2-P5

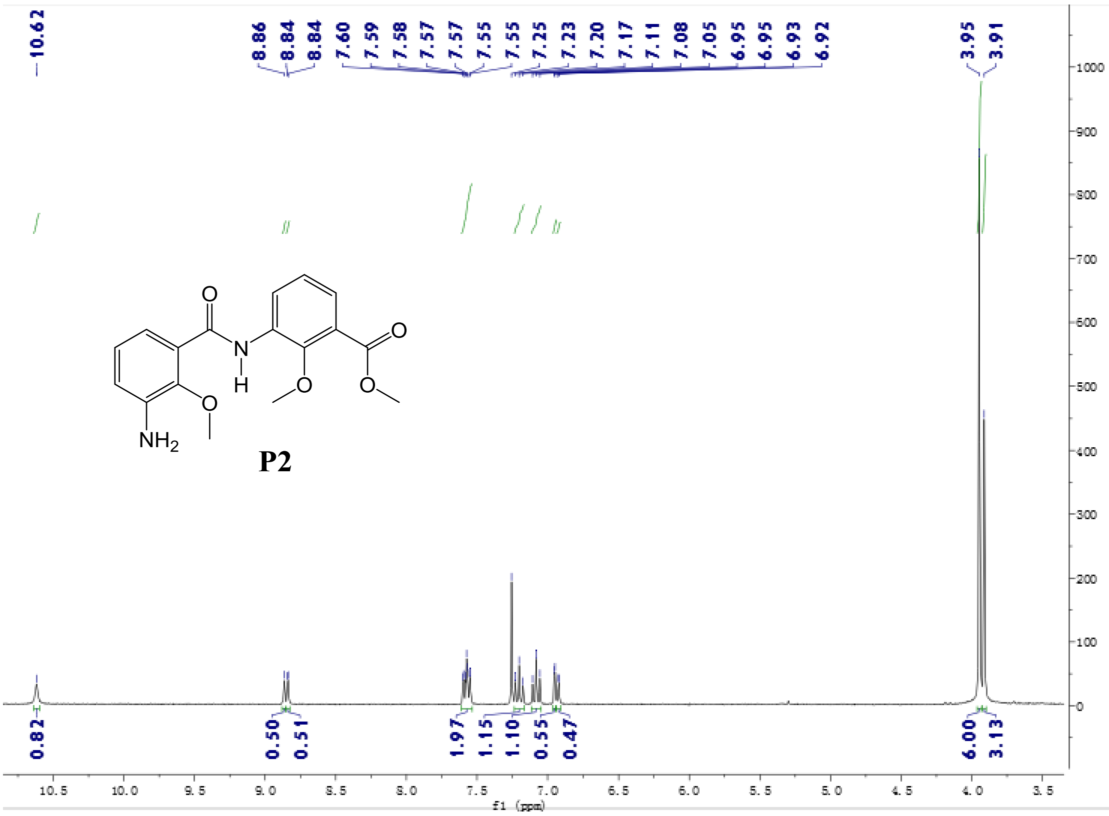


Dimer **P2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.62 (s, 1H), 8.86 (s, 1H), 8.84 (d, *J* = 1.6 Hz, 1H), 7.57 (ddd, *J* = 7.5, 5.8, 1.6 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 1.6 Hz, 1H), 6.93 (d, *J* = 1.6 Hz, 1H), 3.95 (s, 6H), 3.91 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.00, 162.56, 148.35, 144.18, 139.27, 132.51, 125.40, 124.75, 124.30, 123.72, 123.29, 122.47, 119.96, 118.83, 61.39, 59.79, 51.23. HRMS-EI: calculated for $[M+Na]^+$ ($C_{17}H_{18}N_2O_5Na$): *m/z* 353.1108, found: *m/z* 353.1125.

Trimer **P3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.54 (s, 1H), 10.38 (s, 1H), 8.88 – 8.81 (m, 2H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.60 (ddd, *J* = 9.6, 7.9, 1.6 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 1.6 Hz, 1H), 6.95 (d, *J* = 1.6 Hz, 1H), 3.97 (s, 3H), 3.96 (s, 3H), 3.96 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 164.87, 162.56, 162.03, 148.29, 146.27, 144.04, 139.25, 132.24, 131.74, 125.31, 125.29, 125.04, 124.91, 124.67, 124.50, 123.82, 123.68, 123.43, 122.44, 120.03, 119.03, 62.00, 61.42, 59.75, 51.28. HRMS-EI: calculated for $[M+Na]^+$ ($C_{25}H_{25}N_3O_7Na$): *m/z* 502.1585, found: *m/z* 502.1578.

Tetramer **P4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.44 (s, 1H), 10.23 (s, 1H), 10.20 (s, 1H), 8.86 (s, 1H), 8.84 (s, 1H), 7.94 – 7.86 (m, 2H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.59 (s, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 1.6 Hz, 1H), 6.97 (d, *J* = 1.6 Hz, 1H), 4.01 (s, 3H), 3.99 (s, 3H), 3.96 (d, *J* = 3.5 Hz, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 164.83, 162.70, 162.12, 162.01, 148.36, 146.21, 144.03, 139.31, 132.15, 131.69, 131.46, 125.45, 125.36, 125.25, 125.19, 125.04, 124.82, 124.77, 124.55, 124.17, 123.92, 123.87, 123.50, 122.34, 119.98, 119.05, 62.06, 61.97, 61.44, 59.79, 51.31. HRMS-EI: calculated for $[M+Na]^+$ ($C_{33}H_{32}N_4O_9Na$): *m/z* 651.2062, found: *m/z* 651.2026.

Pentamer **P5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.41 (s, 1H), 10.17 (s, 1H), 10.04 (s, 1H), 10.03 (s, 1H), 8.85 (d, *J* = 4.7 Hz, 2H), 7.93 – 7.87 (m, 4H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.43 – 7.37 (m, 4H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 7.8, 1.6 Hz, 1H), 4.04 (s, 6H), 3.99 (s, 3H), 3.98 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 171.09, 165.77, 163.74, 163.32, 163.13, 162.99, 149.22, 147.25, 147.23, 147.18, 144.94, 140.35, 133.10, 132.72, 132.39, 132.34, 126.56, 126.47, 126.45, 126.28, 126.25, 126.16, 125.88, 125.87, 125.84, 125.77, 125.54, 125.15, 124.94, 124.78, 124.48, 123.47, 120.88, 120.01,63.03, 62.42, 60.87, 60.36, 52.29, 21.02, 14.19. HRMS-EI: calculated for $[M+Na]^+$ ($C_{41}H_{39}N_5O_{11}Na$): *m/z* 800.2538, found: *m/z* 800.2582.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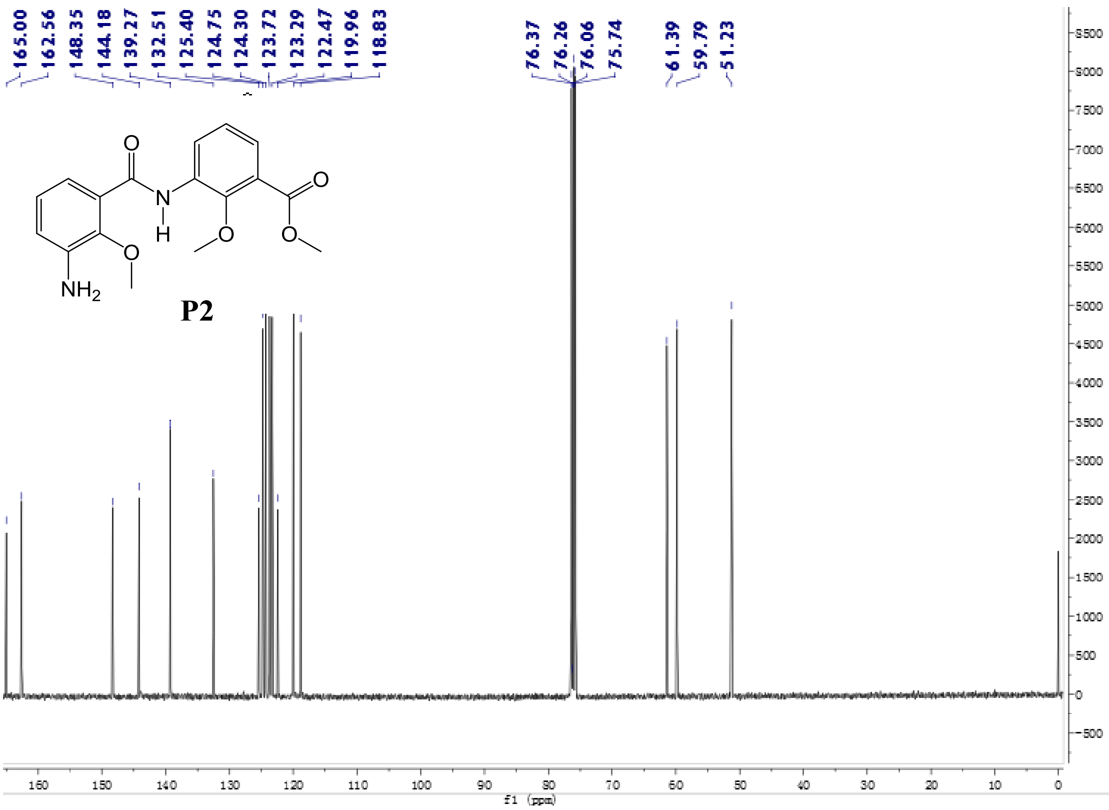
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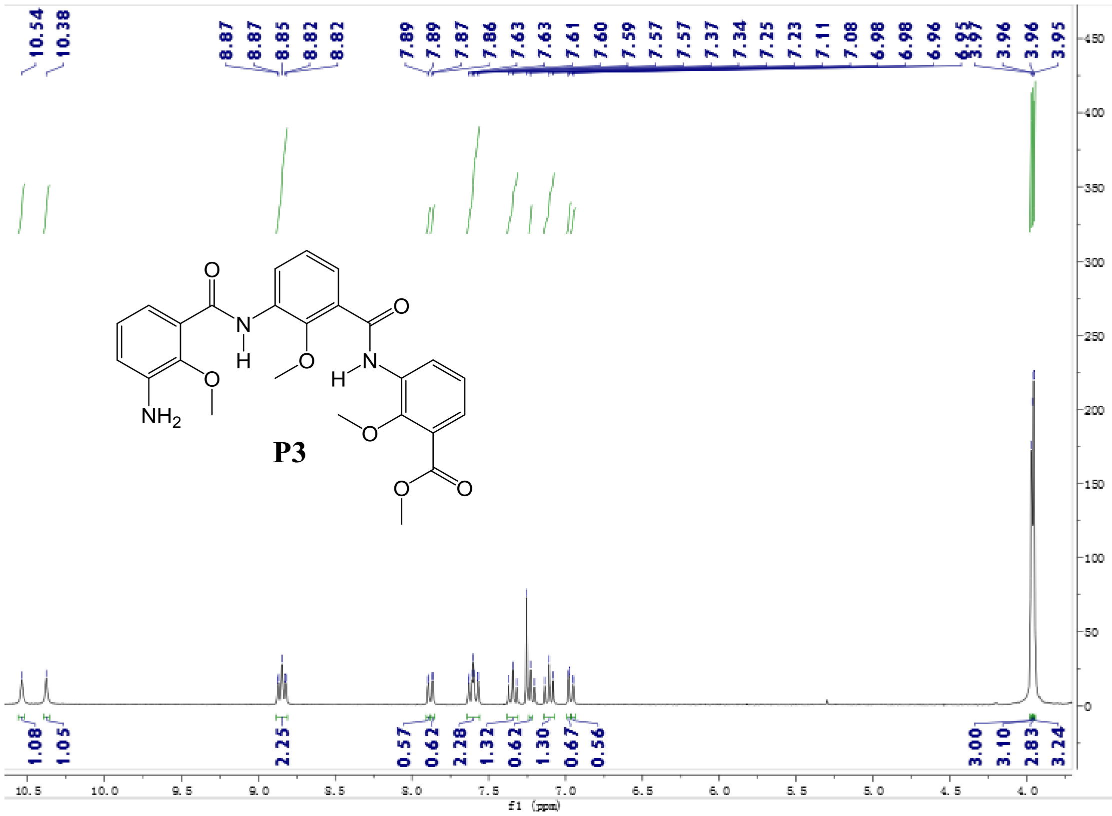
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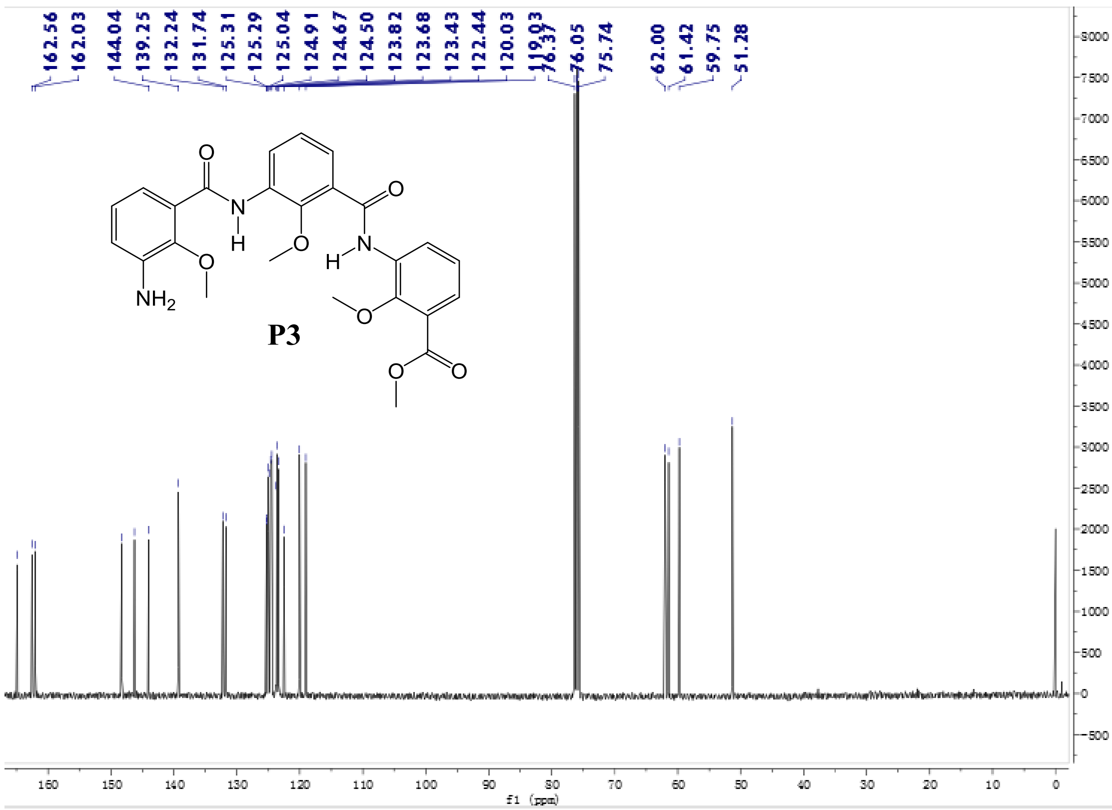
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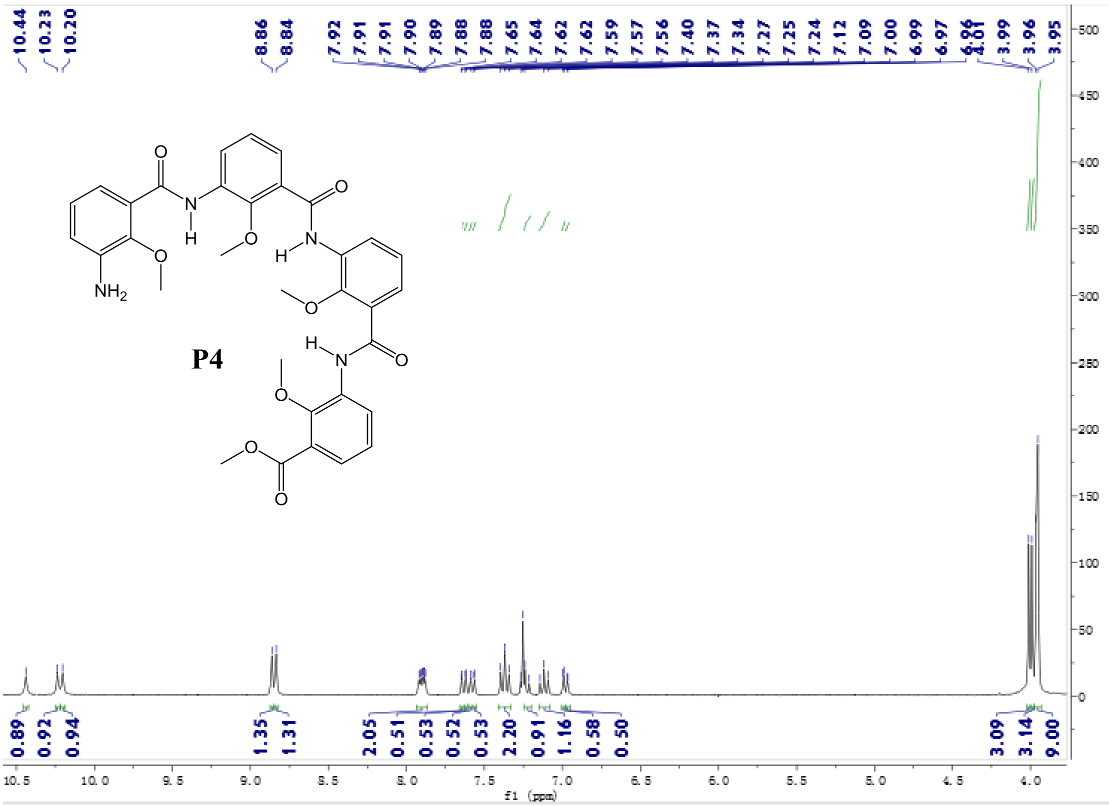
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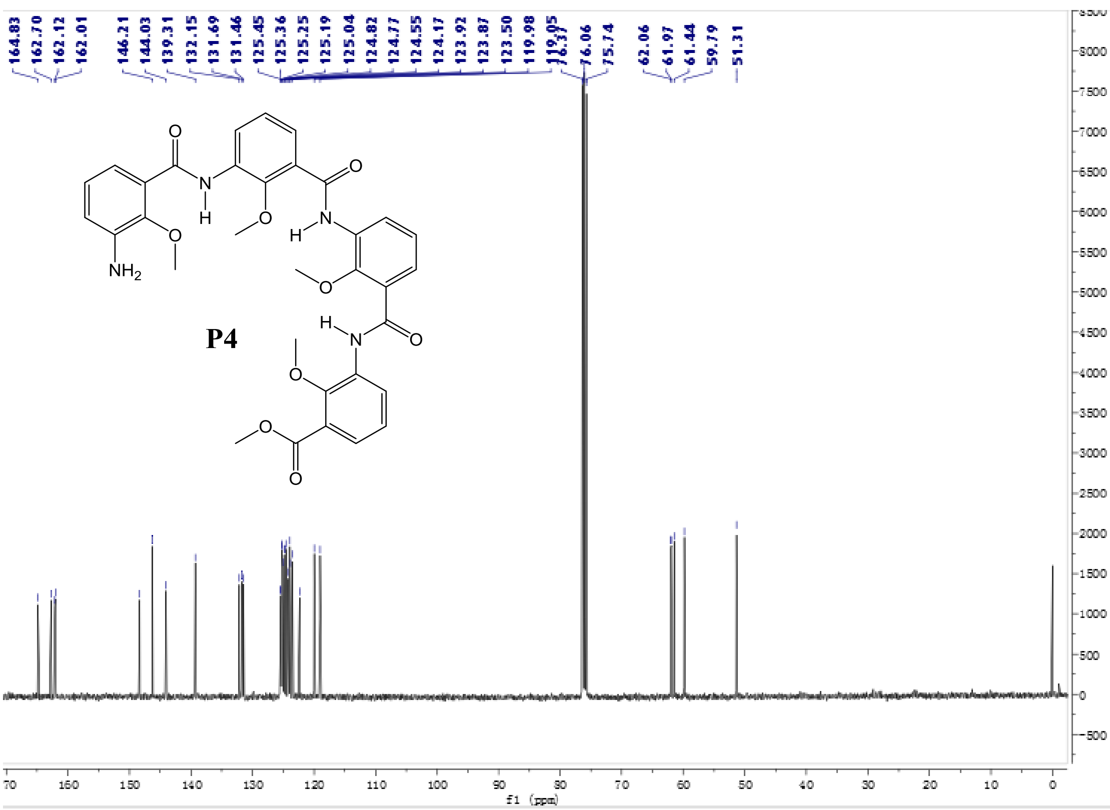
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