Macrocycles of higher *ortho*-phenylenes: Assembly and folding

Supporting Information

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Experimental NMR assignments of key compounds

NMR spectra were acquired on Bruker Avance 500 and 600 MHz spectrometers. The protons of interest are in slow conformational exchange at room temperature. In general, however, the signals for the aromatic protons of *o*-phenylenes sharpen at lower temperatures,[1] so characterization was done at 0 ℃ in $CDCl_3$. The chemical shift assignments below are based on analysis of the 2D NMR spectra (COSY, HSQC, and HMBC). Smaller signals were associated with minor conformers (as opposed to impurities), which could be confirmed by examination of the EXSY spectra.

o-Phenylene hexamers

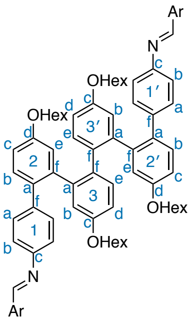


Figure S1. Labeling of *o*-phenylene hexamers.

oP^6(M)

Proton	^{1}H (ppm)	^{13}C (ppm)
1a	6.50	129.3
1b	6.83	120.3
1c		149.0
1f		139.6
2a		131.9
2b	6.96	130.2
2c	6.74	113.3
2d		157.9
2e	5.96	116.2
2f		140.9
3a		140.4
3b	6.70	116.4
3c		157.2
3d	6.37	113.6
3e	5.75	132.8
3f		133.1

Table S1. Experimental ^{1}H and ^{13}C chemical shifts of **oP^6(M)**, major conformer.

oP^6(DPB)$_{3+3}$

Proton	^{1}H (ppm)	^{13}C (ppm)
1a	6.49	129.4
1b	6.84	120.3
1c		148.3
1f		139.9
2a		131.3
2b	6.97	130.2
2c	6.74	113.3
2d		158.0
2e	5.94	115.9
2f		140.8
3a		140.6
3b	6.70	116.2
3c		157.1
3d	6.35	113.5
3e	5.69	132.6
3f		132.9

Table S2. Experimental ^{1}H and ^{13}C chemical shifts of **oP^6(DPB)$_{3+3}$**, major conformer.

o-Phenylene decamers

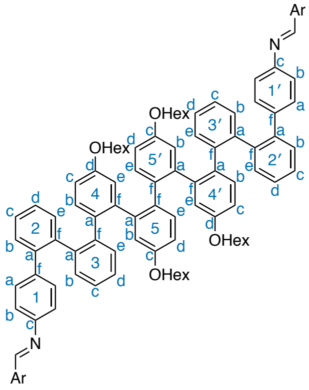


Figure S2. Labeling of *o*-phenylene decamers.

oP^{10}(M)

Proton	^{1}H (ppm)	^{13}C (ppm)
1a	6.27	128.8
1b	6.71	119.8
1c		149.0
1f		139.5
2a		138.4
2b	6.85	128.4
2c	7.01	125.2
2d	6.78	126.8
2e	6.13	130.9
2f		139.9
3a		138.5
3b	6.93	129.9
3c	7.04	125.3
3d	6.74	126.7
3e	5.87	130.6
3f		141.4
4a		131.3
4b	5.49	131.3
4c	6.02	112.7
4d		156.8
4e	5.34	115.2
4f		140.3
5a		139.9
5b	5.31	115.6
5c		156.8
5d	6.16	113.1
5e	5.78	131.3
5f		132.6

Table S3. Experimental ^{1}H and ^{13}C chemical shifts of **oP^{10}(M)**, major conformer.

oP^{10}(DPB)$_{2+2}$

Proton	^{1}H (ppm)	^{13}C (ppm)	Proton	^{1}H (ppm)	^{13}C (ppm)
1a	7.18	130.4	1a′	6.52	129.6
1b	7.07	120.6	1b′	6.89	120.4
1c		149.3	1c′		149.0
1f		140.0	1f′		140.2
2a		139.9	2a′		138.8
2b	7.47	130.5	2b′	7.03	129.2
2c	7.21	126.8	2c′	7.16	126.4
2d	6.94	126.8	2d′	7.01	127.3
2e	6.82	130.6	2e′	6.47	131.8
2f		139.9	2f′		140.0
3a		137.8	3a′		140.2
3b	6.61	132.0	3b′	7.23	131.1
3c	6.68	125.4	3c′	7.34	126.8
3d	6.56	125.3	3d′	7.09	127.7
3e	4.74	133.6	3e′	6.26	133.4
3f		138.6	3f′		140.7
4a		131.3	4a′		133.5
4b	6.63	132.1	4b′	5.73	131.8
4c	6.32	114.2	4c′	6.20	114.7
4d		156.2	4d′		157.4
4e	5.92	115.3	4e′	5.38	115.9
4f		139.6	4f′		141.0
5a		138.4	5a′		141.7
5b	6.15	115.4	5b′	5.44	116.5
5c		156.3	5c′		158.1
5d	6.33	114.8	5d′	6.78	113.1
5e	5.97	133.0	5e′	6.89	132.6
5f		133.4	5f′		132.8

Table S4. Experimental ^{1}H and ^{13}C chemical shifts of **oP^{10}(DPB)$_{2+2}$**, major *o*-phenylene conformer.

Proton	^{1}H (ppm)	^{13}C (ppm)
1a	6.15	131.0
1b	6.93	119.8
1c		149.3
1f		139.9
2a		140.3
2b	7.18	130.4
2c	7.14	126.2
2d	6.84	125.9
2e	6.35	131.3
2f		138.5
3a		137.9
3b	6.39	131.7
3c	6.64	125.1
3d	6.70	126.2
3e	6.13	132.2
3f		141.0
4a		132.3
4b	6.87	132.6
4c	6.72	112.8
4d		157.8
4e	5.67	116.7
4f		141.2
5a		141.7
5b	5.42	116.4
5c		157.4
5d	6.37	114.9
5e	6.17	133.8
5f		133.6

Table S5. Experimental ^{1}H and ^{13}C chemical shifts of **oP^{10}(DPB)$_{2+2}$**, minor (2nd most populated) *o*-phenylene conformer.

oP^{10}(DPB)$_{3+3}$

Proton	^{1}H (ppm)	^{13}C (ppm)
1a	6.28	129.1
1b	6.73	120.0
1c		148.5
1f		140.1
2a		138.1
2b	6.86	128.8
2c	7.02	125.8
2d	6.78	127.2
2e	6.14	131.4
2f		140.0
3a		138.4
3b	6.94	130.5
3c	7.05	125.4
3d	6.74	127.4
3e	5.87	130.8
3f		141.1
4a		131.2
4b	5.48	131.6
4c	6.01	112.7
4d		156.8
4e	5.34	115.4
4f		140.8
5a		140.0
5b	5.31	115.6
5c		156.8
5d	6.15	113.4
5e	5.78	131.6
5f		132.5

Table S6. Experimental ^{1}H and ^{13}C chemical shifts of **oP^{10}(DPB)$_{3+3}$**, major conformer.

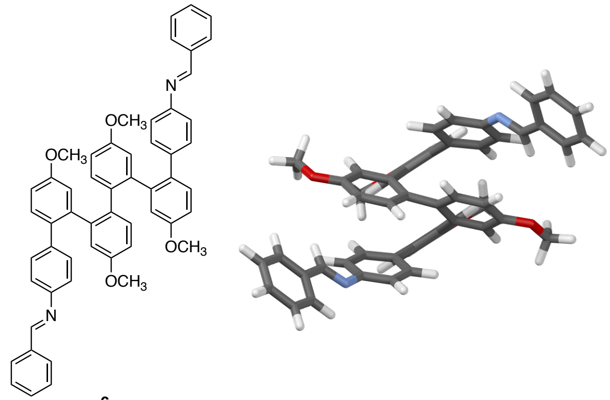
Computational

Ab initio geometry optimizations were carried out at the PCM(CHCl$_3$)/B97-D/cc-pVDZ or (gas-phase) B97-D/cc-pVDZ levels. We have previously found that the B97-D functional[2] with the TZV(2d,2p) basis set does a good job of predicting the relative conformational energies of *o*-phenylenes;[3] the cc-pVDZ basis set was found to qualitatively reproduce these results with a substantial decrease in the computational cost (roughly fivefold for hexa(*o*-phenylenes)). For the purposes of this study only relative energies were needed. All optimized conformer geometries were verified to have 0 imaginary frequencies by vibrational frequency analysis.

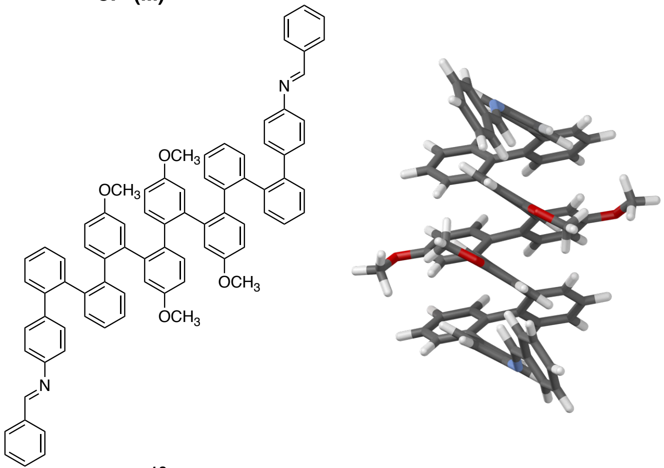
Predictions of ^{1}H isotropic shieldings were carried out on the optimized geometries at the GIAO/PCM(CHCl$_3$)/-WP04/6-31G(d) level,[4] a method that has been shown to give good results for organic compounds[5] and which we have used extensively in the analysis of *o*-phenylenes.[3]

Cartesian coordinates for all optimized geometries are provided in a separate ASCII file to facilitate reuse.

Model compounds **oP^{6}(M)′** *and* **oP^{10}(M)′**



oP^{6}(M)′



oP^{10}(M)′

Figure S3. Optimized geometries of model compounds **oP^{6}(M)′** and **oP^{10}(M)′** (PCM(CHCl$_3$)/B97-D/cc-pVDZ).

Selected conformations of interest for **oP^{10}(M)′** were optimized (e.g., ones that could have been good fits within a [2+2] macrocycle). The AAAABBB conformer is more stable than other examples (BAAAAAB, AAABBBA) that were predicted to be more stable for deca(*o*-phenylene) (Figure 7 in the main text), indicating that the alkoxy groups do exert a significant (likely steric) effect.

Compound	Conformer	Energy (E_h)	IF
oP^{6}(M)′	AAA	−2493.051854	0
	AAB	−2493.030303	0
	BAB	−2493.030538	0
	ABB	−2493.025230	0
	BBB	−2493.020050	0
oP^{10}(M)′	AAAAAAA	−3416.678350	0
	AAAAAAB	−3416.671740	0
	AAAABBB	−3416.671038	0
	BAAAAAB	−3416.666774	0
	BAAABBB	−3416.659711	0
	AAABBBA	−3416.664004	0

Table S7. Computational data for model compounds (PCM(CHCl$_3$)/B97-D/cc-pVDZ). IF = number of imaginary frequencies.

Position	AAA	AAB	BAB	ABB	BBB
1a	25.90	25.64	26.33	26.10	25.13
1b	25.70	25.46	25.50	25.77	25.36
2b	25.50	25.11	25.18	25.48	25.02
2c	25.71	25.74	25.48	25.57	25.69
2e	26.49	26.85	25.80	25.78	26.06
3b	25.97	25.85	26.55	25.62	26.30
3d	26.00	25.51	25.75	25.85	25.91
3e	26.49	25.45	25.00	25.47	25.32
3e′	26.49	26.53	25.00	26.00	25.32
3d′	26.00	26.09	25.75	26.17	25.91
3b′	25.97	26.64	26.55	26.28	26.30
2e′	26.49	26.53	25.80	27.83	26.06
2c′	25.71	25.71	25.48	26.10	25.69
2b′	25.50	25.18	25.18	25.14	25.02
1b′	25.70	25.48	25.50	25.33	25.36
1a′	25.90	26.18	26.33	25.09	25.13

Table S8. Calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//PCM($CHCl_3$)/B97-D/cc-pVDZ) ^{1}H isotropic shieldings for **oP^6(M)′** conformers.

Position	AAAAAAA	AAAAAAB	AAAABBB	AAABBBA	BAAAAAB	BAAABBB
1a	26.04	25.96	25.88	25.85	25.88	26.13
1b	25.79	25.76	25.67	25.69	25.22	25.53
2b	25.57	25.49	25.35	25.32	25.11	25.09
2c	25.33	25.28	25.21	25.12	25.25	25.19
2d	25.54	25.40	25.37	25.29	25.66	25.53
2e	26.18	25.89	25.84	25.11	26.07	25.69
3b	25.59	25.36	25.22	24.99	25.97	25.80
3c	25.38	25.27	25.01	25.02	25.75	25.46
3d	25.56	25.53	25.16	25.57	25.68	25.22
3e	26.37	26.24	25.74	26.62	26.16	25.50
4b	26.75	26.71	26.44	26.75	25.62	25.28
4c	26.17	26.17	26.18	26.16	25.67	25.70
4e	27.09	26.81	27.05	26.18	26.67	27.19
5b	27.07	26.77	26.87	26.87	26.94	27.15
5d	26.35	26.00	25.77	26.37	26.02	25.77
5e	26.54	26.06	25.65	26.18	25.66	25.25
5e′	26.54	26.13	26.41	26.40	25.66	25.64
5d′	26.35	16.27	26.07	26.47	26.02	25.73
5b′	27.07	27.29	26.34	28.25	26.94	26.13
4e′	27.09	27.02	26.96	27.86	26.67	26.53
4c′	26.17	25.73	26.17	26.25	25.67	26.10
4b′	26.75	25.70	25.40	26.11	25.62	25.35
3e′	26.37	26.34	27.16	25.95	26.16	27.25
3d′	25.56	25.73	25.77	25.72	25.68	25.63
3c′	25.38	25.78	25.69	25.28	25.75	25.57
3b′	25.59	26.04	25.77	24.94	25.97	25.67
2e′	26.18	26.18	25.47	25.10	26.07	25.35
2d′	25.54	25.73	25.33	24.93	25.66	25.30
2c′	25.33	25.33	25.04	24.99	25.25	25.01
2b′	25.57	25.25	24.89	25.38	25.11	24.88
1b′	25.79	25.54	25.08	25.29	25.22	25.20
1a′	26.04	26.19	25.08	25.79	25.88	25.05

Table S9. Calculated (GIAO/PCM(CHCl$_3$)/WP04/6-31G(d)//PCM(CHCl$_3$)/B97-D/cc-pVDZ) ^{1}H isotropic shieldings for **oP^{10}(M)′** conformers.

Hexa(o-phenylene) library

The conformers listed in Table S10 represent all possible backbone folding states of the parent hexa(*o*-phenylene), as determined by the previously established folding model.[3] Briefly, the 5 conformers were obtained by beginning with the 8 (2^3) possible A/B configurations of the three key biaryl bonds, then removing the sterically forbidden "ABA" sequence and all those made redundant by symmetry (e.g., AAB vs BAA).

Bite angles β were calculated between the vectors joining C$_{1\mathrm{f}}$–C$_{1\mathrm{c}}$ ($\vec{v}_1 = \vec{r}_{1\mathrm{f}} - \vec{r}_{1\mathrm{c}}$) and C$_{1'\mathrm{f}}$–C$_{1'\mathrm{c}}$ ($\vec{v}_2 = \vec{r}_{1'\mathrm{f}} - \vec{r}_{1'\mathrm{c}}$) (see Figure S1 for labels):

$$\beta = \arccos(\vec{v}_1 \cdot \vec{v}_2) \tag{1}$$

where $\vec{r}_n$ is the position vector of atom *n*.

Conformer	Energy (E_h)	IF	Bite angle
AAA	-1386.591693	0	68.5°
AAB	-1386.588501	0	83.8°
ABB	-1386.583259	0	112.5°
BAB	-1386.585872	0	132.3°
BBB	-1386.578840	0	76.7°

Table S10. Energies and bite angles for parent hexa(*o*-phenylene) conformers (B97-D/cc-pVDZ). IF = number of imaginary frequencies.

Position	AAA	AAB	ABB	BAB	BBB
1a	25.98	25.68	25.83	26.41	25.09
1b	25.55	25.27	25.35	25.48	25.17
1c	25.43	25.16	25.28	25.37	25.19
2b	25.46	25.19	25.48	25.26	24.97
2c	25.27	25.34	25.03	25.08	25.11
2d	25.48	25.62	24.93	25.22	25.34
2e	26.01	26.41	24.98	25.16	25.26
3b	25.33	25.33	24.84	25.80	25.57
3c	25.21	24.94	25.15	25.46	25.52
3d	25.57	24.93	25.51	25.13	25.50
3e	26.53	25.36	25.53	24.84	25.21
3e′	26.51	26.61	25.92	24.85	25.21
3d′	25.56	25.64	25.69	25.13	25.49
3c′	25.22	25.71	25.60	25.46	25.51
3b′	25.33	25.98	25.80	25.79	25.58
2e′	26.00	25.94	28.13	25.16	25.26
2d′	25.48	25.55	25.77	25.21	25.34
2c′	25.27	25.15	25.26	25.07	25.09
2b′	25.46	25.18	25.14	25.26	24.97
1c′	25.43	25.29	25.31	25.37	25.19
1b′	25.55	25.37	25.29	25.48	25.18
1a′	25.98	26.34	25.28	26.41	25.09

Table S11. Calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//B97-D/cc-pVDZ) ^{1}H isotropic shieldings for parent hexa(*o*-phenylene) conformers.

Deca(o-phenylene) library

The conformers listed in Table S12 represent all possible backbone folding states of the parent *o*-phenylene decamer, as determined by the previously established folding model.[3] Briefly, the 37 conformers were obtained by beginning with the 128 (2^7) possible A/B configurations of the seven backbone bonds, then removing all configurations with a sterically forbidden “ABA” sequence and all those made redundant by symmetry (e.g., ABAAAAA vs AAAAABA).

Bite angles β were calculated as for the hexa(*o*-phenylene) library.

Conformer	Energy (E_h)	IF	Bite angle
AAAAAAA	−2310.203764	0	69.0°
BABBBAB	−2310.199732	0	132.4°
AAAAAAB	−2310.199604	0	142.1°
AAABBAA	−2310.197536	0	135.2°
AABBBAB	−2310.196905	0	62.7°
AABBAAB	−2310.195677	0	29.5°
AAAABBA	−2310.195634	0	133.0°
AAAAABB	−2310.195608	0	123.3°
BAAAAAB	−2310.195023	0	29.5°
AAABBAB	−2310.194569	0	44.1°
AABBBAA	−2310.193917	0	119.4°
BAABBAB	−2310.193267	0	133.0°
BAAAABB	−2310.192991	0	59.0°
ABBAAAB	−2310.192670	0	10.3°
AAABBBA	−2310.192665	0	7.7°
ABBBABB	−2310.191453	0	81.7°
AAAABBB	−2310.191206	0	18.2°
AABBABB	−2310.190977	0	68.8°
ABBBAAB	−2310.190406	0	160.8°
ABBAABB	−2310.190368	0	84.2°
ABBABBA	−2310.190225	0	35.1°
BAAABBB	−2310.188127	0	150.4°
BBAAABB	−2310.188020	0	140.7°
AABBBBA	−2310.187997	0	16.7°
BABBABB	−2310.187683	0	131.0°
AAABBBB	−2310.187260	0	141.3°
BBAABBB	−2310.185783	0	76.3°
ABBABBB	−2310.185776	0	144.0°
ABBBBAB	−2310.185189	0	148.1°
BAABBBB	−2310.184992	0	50.1°
AABBBBB	−2310.183291	0	155.4°
BBBABBB	−2310.183040	0	78.5°
ABBBBBA	−2310.182188	0	157.0°
BABBBBB	−2310.180505	0	35.1°
BBABBBB	−2310.177474	0	111.6°
ABBBBBB	−2310.177471	0	59.9°
BBBBBBB	−2310.172733	0	84.0°

Table S12. Energies and bite angles for parent deca(*o*-phenylene) conformers (B97-D/cc-pVDZ). IF = number of imaginary frequencies.

Position	AAAAAAA	AAAAAAB	AAAAABB	AAAABBA	AAAABBB	AAABBAA	AAABBAB	AAABBBA
1a	26.21	26.12	26.05	26.02	25.93	25.81	25.83	25.81
1b	25.69	25.64	25.56	25.60	25.50	25.54	25.50	25.48
1c	25.58	25.51	25.42	25.47	25.37	25.44	25.41	25.40
2b	25.68	25.60	25.53	25.60	25.53	25.35	25.36	25.36
2c	25.43	25.35	25.29	25.35	25.30	25.10	25.10	25.14
2d	25.64	25.53	25.54	25.49	25.44	25.25	25.27	25.34
2e	26.16	25.99	26.03	25.99	25.93	25.65	25.67	25.65
3b	25.51	25.37	25.41	25.22	25.18	25.17	25.12	24.96
3c	25.33	25.28	25.22	25.06	24.98	25.41	25.29	24.91
3d	25.60	25.62	25.45	25.32	25.23	25.74	25.64	25.22
3e	26.39	26.28	26.15	25.95	25.84	26.75	26.72	26.54
4b	26.81	26.71	26.48	26.56	26.41	26.73	26.74	26.65
4c	25.94	25.82	25.54	25.92	25.69	25.72	25.71	25.65
4d	25.88	25.66	25.45	25.90	25.63	25.26	25.35	25.26
4e	26.51	26.26	25.99	26.78	26.60	25.50	25.69	25.60
5b	26.49	26.16	26.15	26.48	26.36	26.30	26.38	26.27
5c	25.78	25.44	25.67	25.61	25.52	25.63	25.72	25.73
5d	25.75	25.41	25.79	25.22	25.18	25.78	26.01	25.82
5e	26.30	25.95	26.71	25.54	25.49	27.79	27.78	26.00
5e′	26.30	26.13	26.29	26.32	26.19	26.34	26.46	26.29
5d′	25.75	25.84	25.57	25.79	25.64	25.86	25.77	25.88
5c′	25.78	25.88	25.25	26.08	25.70	25.82	25.42	25.95
5b′	26.49	26.75	25.58	28.25	25.76	26.14	25.41	28.22
4e′	26.53	26.46	26.43	26.41	26.28	27.39	27.35	27.42
4d′	25.88	25.69	25.75	25.93	25.86	25.70	25.47	25.50
4c′	25.94	25.33	25.76	25.90	25.70	25.67	25.17	25.65
4b′	26.81	25.67	25.75	26.27	25.56	26.67	24.98	26.03
3e′	26.38	26.42	26.28	27.39	27.48	25.41	24.92	25.89
3d′	25.60	25.72	25.86	25.72	25.73	24.99	25.20	25.75
3c′	25.33	25.78	25.71	25.30	25.64	25.03	25.53	25.28
3b′	25.50	26.13	25.91	25.02	25.73	25.46	25.91	24.92
2e′	26.17	26.39	27.69	25.08	25.56	26.67	25.30	25.02
2d′	25.63	25.78	25.57	25.00	25.54	25.86	25.31	24.94
2c′	25.44	25.31	25.22	25.14	25.22	25.52	25.20	25.00
2b′	25.67	25.36	25.16	25.66	25.05	25.30	25.40	25.44
1c′	25.57	25.33	25.33	25.55	25.21	25.22	25.49	25.07
1b′	25.69	25.40	25.34	25.60	25.19	25.32	25.64	25.09
1a′	26.21	26.33	25.31	26.12	25.20	25.74	26.61	25.79

Table S13. Calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//B97-D/cc-pVDZ) ^{1}H isotropic shieldings for parent deca(*o*-phenylene) conformers.

Position	AAABBBB	AABBAAB	AABBABB	AABBBAA	AABBBAB	AABBBBA	AABBBBB	ABBAAAB
1a	25.75	25.67	25.76	25.73	25.80	25.69	25.68	25.98
1b	25.46	25.26	25.34	25.33	25.36	25.27	25.30	25.46
1c	25.39	25.19	25.24	25.21	25.23	25.18	25.17	25.42
2b	25.31	25.24	25.24	25.12	25.58	25.16	25.13	25.55
2c	25.07	25.40	25.34	24.96	26.79	25.22	25.20	25.09
2d	25.22	25.76	25.70	25.11	24.78	25.53	25.45	24.98
2e	25.53	26.53	26.62	26.28	26.91	26.51	26.40	25.04
3b	24.97	25.46	25.41	25.30	25.46	25.34	25.31	24.98
3c	25.11	25.05	25.00	24.93	25.05	25.00	24.98	25.25
3d	25.45	24.99	25.03	24.94	25.03	24.99	24.96	25.67
3e	26.56	25.33	25.51	25.40	25.48	25.35	25.31	27.58
4b	26.61	26.52	26.81	26.61	26.74	26.59	26.59	26.12
4c	25.64	25.77	25.81	25.80	25.72	25.63	25.61	25.78
4d	25.23	26.16	26.10	25.90	25.77	25.63	25.63	25.80
4e	25.51	27.78	27.90	25.96	26.02	25.69	25.61	25.93
5b	26.22	26.00	26.08	25.99	26.10	25.98	25.90	28.13
5c	25.58	25.80	25.56	25.66	25.81	25.75	25.67	25.88
5d	25.59	25.78	25.34	25.58	25.88	25.65	25.52	25.46
5e	25.62	26.08	25.31	27.69	27.70	25.66	25.35	25.83
5e′	26.23	27.42	27.71	27.69	27.98	27.83	27.66	25.32
5d′	25.83	25.61	25.61	25.58	25.67	25.82	25.67	25.42
5c′	25.63	25.75	25.21	25.67	25.40	25.99	25.54	25.75
5b′	25.51	26.18	24.97	25.99	25.29	28.18	25.40	26.92
4e′	27.37	25.28	24.89	25.97	25.71	25.64	25.46	27.02
4d′	25.54	24.96	25.15	25.91	25.53	25.67	25.61	25.80
4c′	25.55	25.00	25.44	25.80	25.14	25.77	25.56	25.43
4b′	25.35	25.38	25.53	26.60	24.89	26.02	25.25	25.34
3e′	25.49	26.32	25.25	25.40	24.88	25.57	25.25	25.79
3d′	25.64	25.82	25.44	24.95	25.14	25.45	25.41	25.38
3c′	25.61	25.60	25.62	24.94	25.45	25.15	25.48	25.56
3b′	25.63	25.67	25.96	25.31	25.76	24.87	25.58	25.85
2e′	25.30	25.99	27.87	26.29	25.11	25.02	25.25	25.81
2d′	25.28	25.62	25.86	25.12	25.19	24.94	25.34	25.65
2c′	25.05	25.25	25.37	24.94	24.94	25.04	25.12	25.24
2b′	24.94	25.26	25.23	25.12	26.15	25.49	24.95	25.25
1c′	25.20	25.23	25.33	25.20	25.19	25.29	25.22	25.27
1b′	25.19	25.45	25.34	25.34	25.32	25.34	25.16	25.36
1a′	25.11	26.44	25.37	25.73	26.23	25.87	25.04	26.32

Table S14. Calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//B97-D/cc-pVDZ) ^{1}H isotropic shieldings for parent deca(*o*-phenylene) conformers (cont.).

Position	ABBAABB	ABBABBA	ABBABBB	ABBBAAB	ABBBABB	ABBBBAB	ABBBBBA	ABBBBBB
1a	25.88	26.05	25.99	25.57	26.26	25.89	25.88	25.83
1b	25.44	25.49	25.43	25.10	25.85	25.33	25.29	25.28
1c	25.40	25.41	25.39	25.07	26.28	25.30	25.24	25.24
2b	25.59	25.64	25.58	25.36	25.65	25.52	25.47	25.47
2c	25.11	25.16	25.08	25.00	25.14	25.06	25.01	25.02
2d	24.99	25.05	24.95	24.90	25.00	24.96	24.89	24.90
2e	24.99	25.19	25.10	24.98	25.13	25.07	25.03	24.98
3b	24.91	25.11	25.03	24.83	24.92	24.89	24.87	24.81
3c	25.30	25.43	25.35	25.25	25.24	25.26	25.20	25.14
3d	26.09	26.02	25.92	25.66	25.61	25.71	25.55	25.51
3e	27.69	27.96	27.74	25.68	25.87	25.81	25.59	25.53
4b	26.02	26.29	26.08	25.95	26.16	26.07	25.98	25.97
4c	25.82	25.72	25.63	25.73	25.87	25.79	25.66	25.69
4d	25.82	25.47	25.40	26.10	25.96	25.67	25.50	25.54
4e	26.13	25.48	25.32	27.85	27.77	25.71	25.46	25.39
5b	27.81	28.23	28.10	28.33	28.21	28.23	28.09	28.03
5c	25.75	25.92	25.83	25.96	25.85	26.04	25.99	25.90
5d	25.70	25.33	25.28	25.88	25.47	26.02	25.78	25.61
5e	26.25	25.12	25.05	26.13	25.33	27.75	25.67	25.37
5e′	25.32	25.11	24.90	25.50	25.74	25.77	25.67	25.48
5d′	24.99	25.34	25.15	25.61	25.50	25.60	25.77	25.60
5c′	25.01	25.92	25.47	25.77	25.18	25.39	26.00	25.58
5b′	25.38	28.22	25.57	26.17	24.89	25.19	28.09	25.33
4e′	26.37	25.48	25.29	25.31	24.87	25.51	25.47	25.28
4d′	25.78	25.48	25.42	24.96	25.13	25.36	25.50	25.45
4c′	25.53	25.72	25.56	24.96	25.41	25.12	25.68	25.49
4b′	25.26	26.29	25.60	25.26	25.41	24.84	26.00	25.21
3e′	26.02	27.96	27.78	26.18	25.09	24.81	25.58	25.25
3d′	25.77	26.02	25.99	25.26	25.31	25.14	25.56	25.50
3c′	25.68	25.43	25.75	25.34	25.43	25.49	25.17	25.55
3b′	25.83	25.11	25.82	25.60	25.48	25.82	24.83	25.58
2e′	27.80	25.20	25.58	25.98	27.75	25.22	25.00	25.22
2d′	25.91	25.06	25.48	25.61	25.67	25.27	24.93	25.34
2c′	25.21	25.16	25.17	25.24	25.13	25.05	25.01	25.11
2b′	25.03	25.62	25.04	25.26	25.02	25.17	25.45	24.93
1c′	25.32	25.41	25.29	25.38	25.19	25.40	25.27	25.18
1b′	25.31	25.49	25.33	25.61	25.22	25.53	25.28	25.18
1a′	25.22	26.05	25.36	26.47	25.20	26.41	25.89	25.06

Table S15. Calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//B97-D/cc-pVDZ) ^{1}H isotropic shieldings for parent deca(*o*-phenylene) conformers (cont.).

Position	BAAAAAB	BAAAABB	BAAABBB	BAABBAB	BAABBBB	BABBABB	BABBBAB	BABBBBB
1a	26.10	26.31	26.28	26.49	26.38	26.49	26.74	26.38
1b	25.29	25.43	25.31	25.52	25.52	25.49	25.44	25.46
1c	25.23	25.35	25.26	25.29	25.33	25.39	25.19	25.36
2b	25.27	25.27	25.17	25.27	25.24	25.28	27.32	25.15
2c	25.27	25.20	25.17	25.26	25.18	25.06	25.53	25.04
2d	25.75	25.62	25.55	25.63	25.61	25.25	25.43	25.23
2e	26.28	26.12	25.70	26.01	25.95	25.21	25.38	25.14
3b	26.02	25.99	25.84	25.62	25.54	25.88	26.00	25.77
3c	25.73	25.69	25.50	25.53	25.36	25.54	25.54	25.43
3d	25.70	25.58	25.29	25.77	25.46	25.20	25.21	25.12
3e	26.26	26.10	25.60	26.37	26.08	24.97	24.93	24.82
4b	25.53	25.31	25.19	25.37	25.25	25.02	24.94	24.80
4c	25.20	24.98	25.21	25.03	24.93	25.33	25.18	25.09
4d	25.46	25.32	25.52	25.08	24.94	25.83	25.49	25.38
4e	26.22	25.97	26.83	25.43	25.25	27.62	25.82	25.41
5b	26.45	26.59	26.83	26.28	26.09	25.29	25.41	25.12
5c	25.60	25.80	25.66	25.83	25.62	25.21	25.51	25.33
5d	25.56	25.85	25.36	25.83	25.41	25.26	25.96	25.45
5e	25.83	26.63	25.25	27.53	25.20	25.36	27.94	25.47
5e′	25.83	25.95	25.60	26.17	25.95	27.48	27.94	27.57
5d′	25.55	25.28	25.27	25.66	25.70	25.79	25.96	25.89
5c′	25.60	24.95	25.47	25.40	25.55	25.29	25.50	25.64
5b′	26.45	25.25	25.53	25.28	25.41	25.01	25.42	25.43
4e′	26.22	26.04	25.77	27.65	27.59	25.00	25.83	25.49
4d′	25.45	25.56	25.75	26.01	26.00	25.24	25.48	25.59
4c′	25.20	25.63	25.57	25.25	25.59	25.48	25.18	25.57
4b′	25.53	25.63	25.40	24.97	25.29	25.48	24.94	25.34
3e′	26.26	26.08	27.52	24.87	25.39	25.22	24.93	25.51
3d′	25.69	25.73	25.65	25.19	25.64	25.38	25.21	25.68
3c′	25.74	25.64	25.59	25.52	25.63	25.49	25.54	25.62
3b′	26.02	25.89	25.69	25.88	25.63	25.87	26.00	25.61
2e′	26.28	27.67	25.42	25.22	25.27	27.80	25.39	25.31
2d′	25.75	25.61	25.42	25.25	25.31	25.72	25.44	25.37
2c′	25.26	25.25	25.17	25.10	25.08	25.27	25.54	25.14
2b′	25.27	25.14	24.96	25.31	24.92	25.16	27.31	25.01
1c′	25.23	25.32	25.17	25.46	25.21	25.31	25.19	25.23
1b′	25.29	25.34	25.14	25.59	25.19	25.31	25.45	25.21
1a′	26.10	25.30	25.12	26.55	25.09	25.31	26.74	25.13

Table S16. Calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//B97-D/cc-pVDZ) ^1H isotropic shieldings for parent deca(*o*-phenylene) conformers (cont.).

Position	BBAAABB	BBAABBB	BBABBBB	BBBABBB	BBBBBBB
1a	25.23	25.19	25.17	25.26	25.07
1b	25.26	25.27	25.21	25.28	25.17
1c	25.27	25.32	25.24	25.36	25.16
2b	25.07	24.99	25.11	24.95	24.95
2c	25.17	25.24	25.39	25.09	25.07
2d	25.50	25.91	25.87	25.38	25.33
2e	27.64	27.66	27.33	25.49	25.20
3b	25.75	25.75	25.86	25.80	25.58
3c	25.58	25.64	25.72	25.71	25.53
3d	25.70	25.74	25.36	25.93	25.45
3e	25.71	25.95	25.04	27.60	25.17
4b	25.48	25.16	25.40	25.46	25.19
4c	25.44	25.32	25.34	25.52	25.47
4d	25.30	25.45	25.10	25.33	25.46
4e	25.65	26.10	24.82	25.15	25.19
5b	25.18	25.22	24.64	25.50	25.25
5c	25.24	24.94	25.03	25.38	25.48
5d	25.67	24.94	25.25	25.10	25.45
5e	26.87	25.25	25.50	24.81	25.20
5e′	26.86	26.14	25.21	24.81	25.20
5d′	25.67	25.55	25.43	25.10	25.46
5c′	25.24	25.35	25.55	25.39	25.48
5b′	25.18	25.23	25.47	25.51	25.25
4e′	25.65	25.96	26.94	25.14	25.19
4d′	25.30	25.71	26.21	25.33	25.46
4c′	25.45	25.56	25.80	25.52	25.47
4b′	25.48	25.36	25.51	25.46	25.19
3e′	25.70	27.68	25.33	27.59	25.17
3d′	25.71	26.08	25.30	25.94	25.44
3c′	25.58	25.62	25.40	25.72	25.51
3b′	25.76	25.63	25.63	25.78	25.58
2e′	27.64	25.37	25.97	25.50	25.21
2d′	25.50	25.49	26.16	25.39	25.32
2c′	25.17	25.17	25.34	25.09	25.08
2b′	25.07	25.03	25.21	24.94	24.95
1c′	25.28	25.18	25.22	25.36	25.16
1b′	25.26	25.17	25.21	25.28	25.17
1a′	25.23	25.14	25.22	25.27	25.07

Table S17. Calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//B97-D/cc-pVDZ) ^{1}H isotropic shieldings for parent deca(*o*-phenylene) conformers (cont.).

Macrocycles $\mathbf{oP^6(DPB)_{3+3}'}$ *and* $\mathbf{oP^{10}(DPB)_{3+3}'}$

The model macrocycles $\mathbf{oP^6(DPB)_{3+3}'}$ and $\mathbf{oP^{10}(DPB)_{3+3}'}$ were optimized as follows: First, the imines were oriented by considering the structures in Chart S1. PES scans were performed about the indicated bonds at the PCM($CHCl_3$)/B97-D/cc-pVDZ level for the AAA, AAB, AAAABBB (both ends), and BAAAAAB backbone configurations. The local minima were then optimized free of constraints, and the lowest-energy geometries in each case were used to build the macrocycles. These models were first optimized at the PM7 level then at the PCM($CHCl_3$)/B97-D/cc-pVDZ level to obtain the final geometries.

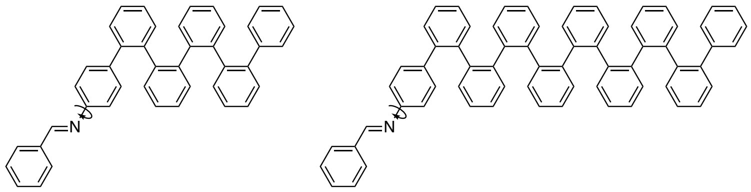


Chart S1. Model structures used to determine optimum imine orientations.

We stress that this method does not guarantee that we obtain the global conformational energy minimum for the macrocycles; in some cases, the preference for a specific imine orientation by the model compounds (Chart S1) is small (<0.1 kcal/mol). That said, the geometries should provide a useful perspective on the fit of the *o*-phenylenes to the macrocycles: assuming it is consistent between each *o*-phenylene moiety, the exact imine orientation has no effect on β.

Conformer	Energy (E_h)	IF
Homochiral-$(AAA)_3$	−6558.611585	0
Heterochiral-$(AAA)_3$	−6558.611734	0
Homochiral-$(AAA)_2(AAB)$	−6558.605894	0

Table S18. Energies for optimized **oP^6(DPB)$_{3+3}$**$'$. IF = number of imaginary frequencies.

Conformer	Energy (E_h)	IF
Homochiral-antiparallel-$(AAAABBB)_2$	−6219.626291	0
Homochiral-(AAAABBB)(BAAAAAB)	−6219.630339	0
Homochiral-$(BAAAAAB)_2$	−6219.635096	0

Table S19. Energies for optimized **oP^{10}(DPB)$_{2+2}$**$'$. IF = number of imaginary frequencies.

Experimental vs computational NMR comparisons

*Major conformers of **oP^6(M)** and **oP^{10}(M)***

Comparisons between the experimental chemical shifts of **oP^6(M)**/**oP^{10}(M)** and models **oP^6(M)$'$**/**oP^{10}(M)$'$** were made as previously reported.[1,5,6] The comparison is made on the basis of the RMS deviation between the computed chemical shifts (obtained by scaling the isotropic shieldings relative to the experimental chemical shifts) and the experimental shifts.[5] In both cases, the best fit is to the (expected) perfectly folded AAA/AAAAAAA conformers. Confidence in the matches was assessed using a non-parametric method reported previously.[1,7] This method is similar to the approach used for $\Delta\delta$ below and uses the same Python program. Using this method, the AAA conformer of **oP^6(M)$'$** is a better match to the experimental data than AAB at the >99.9% confidence level, and the AAAAAAA conformer of **oP^{10}(M)$'$** is a better match to the experimental data than AAAAAAB at the >99.99% confidence level. The RMSDs are also consistent with previous analyses of *o*-phenylenes (<0.15 ppm).

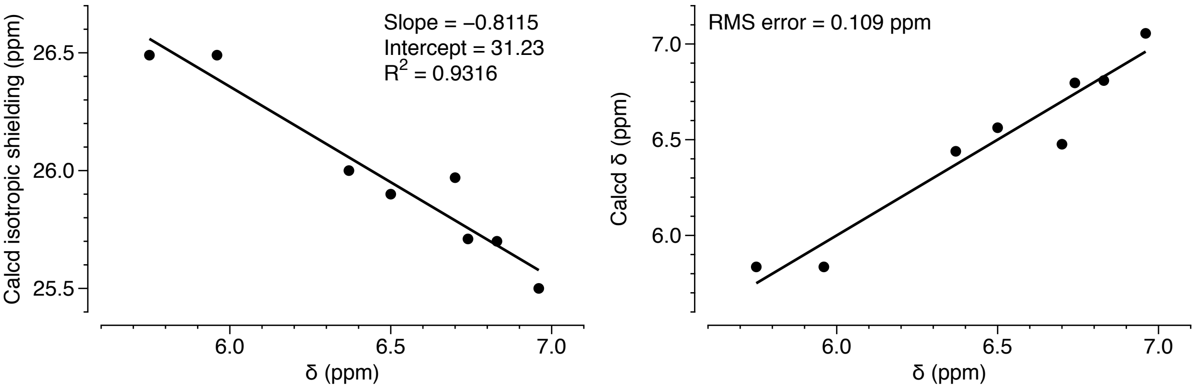


Figure S4. Left: Comparison of calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//PCM($CHCl_3$)/B97-D/cc-pVDZ) isotropic shieldings of **oP^6(M)$'$** vs experimental chemical shifts of **oP^6(M)**. Right: Scaled calculated chemical shifts vs experimental chemical shifts.

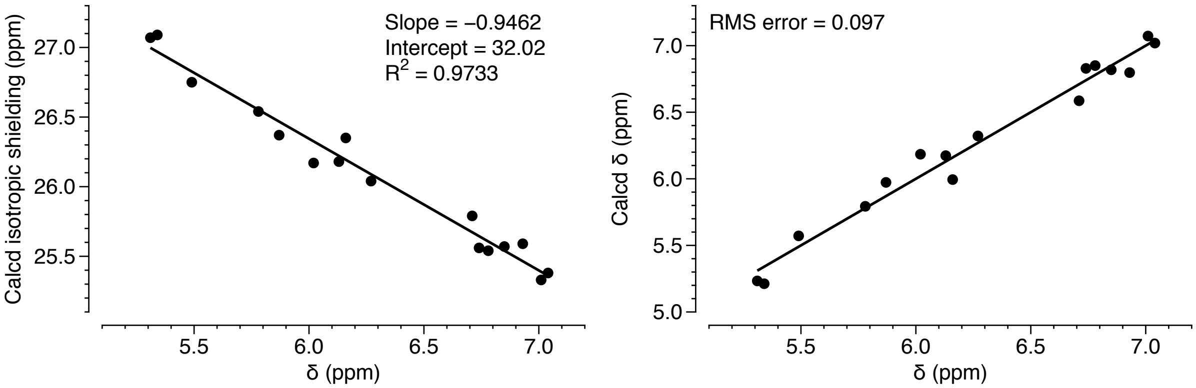


Figure S5. Left: Comparison of calculated (GIAO/PCM($CHCl_3$)/WP04/6-31G(d)//PCM($CHCl_3$)/B97-D/cc-pVDZ) isotropic shieldings of **oP^{10}(M)′** vs experimental chemical shifts of **oP^{10}(M)**. Right: Scaled calculated chemical shifts vs experimental chemical shifts.

Conformer	RMSD (ppm)
AAA	0.024
AAB	0.432
ABB	0.723
BAB	0.744
BBB	0.684

Table S20. RMSDs on $\Delta\delta^{exp}$ for **oP^6(DPB)$_{3+3}$** (vs **oP^6(M)**) compared to $\Delta\delta^{calc}$ for hexa(*o*-phenylene) (XXX vs AAA).

Conformer	RMSD (ppm)	Conformer	RMSD (ppm)
BBBAAAA	0.110	ABBAABB	0.707
BBBAAAB	0.368	ABBBAAA	0.707
BAAAAAA	0.441	BBABBBB	0.732
BAAAAAB	0.501	BBAABBA	0.747
AAAAAAA	0.513	ABBABBB	0.755
BBBBAAA	0.518	ABBBBAA	0.757
BBBAABB	0.548	AABBBAA	0.762
AAAAAAB	0.554	BBAABBB	0.763
BBAAAAA	0.561	BBABBAA	0.767
ABBAAAA	0.564	ABBBBBA	0.772
BAABBAA	0.573	ABBABBA	0.793
AAABBAA	0.575	BBABBBA	0.794
BBBBBAA	0.580	AABBAAA	0.796
AAABBBB	0.590	BBBBABB	0.796
BBBABBA	0.595	BBAAABB	0.799
BBBABBB	0.599	ABBBBBB	0.800
ABBAAAB	0.611	BABBAAA	0.809
BBBBAAB	0.621	ABBBAAB	0.816
AAABBBA	0.627	AABBBBB	0.822
BBBBBBA	0.634	AABBBBA	0.822
AAAAABB	0.639	AABBAAB	0.824
BAABBBB	0.645	BBABBAB	0.827
BAAAABB	0.649	BABBBBB	0.851
AAAABBB	0.654	BABBAAB	0.852
BBAAAAB	0.658	BABBBBA	0.859
BAABBBA	0.688	ABBBBAB	0.864
BBBBBBB	0.694	BABBBAA	0.899
BAAABBB	0.697	ABBBABB	0.951
BAAABBA	0.701	BABBABB	0.960
AAABBAB	0.702	AABBBAB	0.981
BAABBAB	0.703	AABBABB	0.992
AAAABBA	0.704	BABBBAB	1.081
BBBBBAB	0.706		

Table S21. RMSDs on $\Delta\delta^{\mathrm{exp}}$ for $\mathbf{oP^{10}(DPB)_{2+2}}$ (major conformer) (vs $\mathbf{oP^{10}(M)}$) compared to $\Delta\delta^{\mathrm{calc}}$ for deca(*o*-phenylene) (XXXXXXX vs AAAAAAA).

Conformer	RMSD (ppm)
BAAAAAB	0.132
AAAAAAB	0.337
BAAAABB	0.453
AAAAAAA	0.466
BAAABBB	0.470
AAAABBB	0.489
BAABBBB	0.506
AAAAABB	0.509
AAABBBB	0.555
BAABBAB	0.557
ABBAAAB	0.571
AABBAAB	0.572
AAAABBA	0.634
BABBBBB	0.635
AAABBAB	0.635
ABBBAAB	0.638
BBAABBB	0.641
BBBBBBB	0.641
AABBBBB	0.652
AAABBBA	0.655
ABBBBBB	0.660
AAABBAA	0.663
BBAAABB	0.671
BBBABBB	0.673
BBABBBB	0.680
ABBAABB	0.692
ABBBBBA	0.696
ABBBBAB	0.711
AABBBAA	0.714
AABBBBA	0.717
ABBABBB	0.733
BABBABB	0.741
ABBBABB	0.798
AABBABB	0.804
AABBBAB	0.806
ABBABBA	0.830
BABBBAB	0.854

Table S22. RMSDs on $\Delta\delta^{\mathrm{exp}}$ for **oP^{10}(DPB)$_{2+2}$** (minor conformer) (vs **oP^{10}(M)**) compared to $\Delta\delta^{\mathrm{calc}}$ for deca(*o*-phenylene) (XXXXXXX vs AAAAAAA).

Conformer	RMSD (ppm)
AAAAAAA	0.009
AAAAAAB	0.318
BAAAAAB	0.461
AAAAABB	0.470
AAABBAA	0.487
AAAABBB	0.492
AAAABBA	0.495
AAABBBA	0.559
AABBBAA	0.577
AABBAAB	0.580
AAABBBB	0.586
BAAAABB	0.611
ABBAAAB	0.623
AAABBAB	0.649
AABBBBA	0.659
BAAABBB	0.674
BAABBBB	0.708
ABBBAAB	0.708
AABBBBB	0.709
ABBBBBA	0.717
BAABBAB	0.725
ABBAABB	0.729
BBAAABB	0.758
AABBABB	0.784
BBAABBB	0.787
ABBBBBB	0.788
ABBABBA	0.798
ABBABBB	0.806
AABBBAB	0.808
ABBBBAB	0.812
BBABBBB	0.827
ABBBABB	0.833
BABBBBB	0.845
BBBABBB	0.848
BBBBBBB	0.872
BABBABB	0.878
BABBBAB	0.960

Table S23. RMSDs on $\Delta\delta^{\mathrm{exp}}$ for **oP^{10}(DPB)$_{3+3}$** (major conformer) (vs **oP^{10}(M)**) compared to $\Delta\delta^{\mathrm{calc}}$ for deca(*o*-phenylene) (XXXXXXX vs AAAAAAA).

The quality of the match between the experimental and computational $\Delta\delta$ values was judged in two ways. First, the absolute RMSD values for the matches, which are all <0.13 ppm, are consistent with the errors associated with previous comparisons between *o*-phenylene NMR assignments[1,6–8] and DFT predictions at the same level of theory.[5] Our typical cutoff for a good match is 0.15 ppm. Second, we made non-parametrized statistical comparisons in a similar way to previous reports.[1,7] Briefly, to compare the RMSD values for a “good” vs “bad” match, we compare the statistic

$$F = \frac{\left(\sum \Delta\delta^{\mathrm{exp}}_{\mathrm{good}} - \Delta\delta^{\mathrm{calc}}_{\mathrm{good}}\right)^2}{\left(\sum \Delta\delta^{\mathrm{exp}}_{\mathrm{bad}} - \Delta\delta^{\mathrm{calc}}_{\mathrm{bad}}\right)^2} \tag{2}$$

where the sums are over each assigned proton of the oligomers. The null hypothesis is $F = 1$. If true, we would be able to swap $\Delta\delta^{\mathrm{calc}}$ values without affecting F. So, permutations of the data are generated and the “true” F value is compared to this distribution. For example, if we are comparing $\Delta\delta^{\mathrm{exp}}$ for **oP^6(DPB)$_{3+3}$** to the predicted $\Delta\delta^{\mathrm{calc}}$ for the AAA geometry against the possible match to the AAB geometry, we calculate F for the genuine comparison and then generate a library of permutations ($2^{16} = 65,536$) where the good and bad $\Delta\delta^{\mathrm{calc}}$ values are swapped. The original F value was the 3rd lowest out of the entire library, thus we conclude that the match is significant with $p = 5 \times 10^{-5}$.

As there are 2^n swapping possibilities to be considered (where n is the number of chemical shift assignments), it is not always possible to explicitly consider all possible permutations in a reasonable time frame. We calculate all permutations if there are fewer than 2^{20} possibilities; otherwise, we generate a random selection of 2^{20} (1,048,576).

This analysis was done using the following Python program:

```
”””NMR comparison module.

Allows an experimental NMR spectrum to be compared to two calculated
spectra, one presumed to be a good match, the other not. Provides a
one-tailed, non-parametric statistical comparison by ranking the quality
of the good match vs a large sample of permutations, as described in
2010 JOC 8627. If it is possible to consider all possible permutations,
it will do so. Otherwise, a number of random permutations is considered
up to the constant max_swaps.

Requires 3 arguments:
    1. A text file with the experimental data. This is a simple list of
        numbers (1 per line).
    2. A text file with the proposed ”good” match to the data. The order
        of the numbers must match.
    3. A text file of the proposed ”bad” match.

Optional arguments:
    output_file: Filename for output.
    max_swaps (int): Maximum number of permutations that will be
        considered.
    direct: switches to the test_func_direct error function if no
        regression is needed.
”””

import sys
import scipy.stats
import numpy as np
import argparse


def test_func_reg(exp, calc1, calc2):
    ”””Quantify quality of match given an experimental spectrum and two
```

```
    calculated spectra. This function uses the standard error of a
    linear regression as its basis, and is appropriate for direct
    comparisons of spectra.

    Args:
        exp (list): The experimental spectrum as a list of chemical
            shifts.
        calc1 (list): The proposed ”good” spectrum.
        calc2 (list): The proposed ”bad” spectrum.

    Returns:
        The F-statistic comparing the variances on linear fits between
        the two calculated spectra and the experimental spectrum.
    ”””

    s1_regress = scipy.stats.linregress(exp, calc1)
    s2_regress = scipy.stats.linregress(exp, calc2)

    # The std error of the fit is stored as the 5th element of each
    # tuple.
    return s2_regress[4]**2/s1_regress[4]**2


def test_func_direct(exp, calc1, calc2):
    ”””Quantify quality of match given two sets of experimental data.
    This function uses the sum squared error and is appropriate for
    comparisons where the data will not be scaled by refitting after
    swaps have been made (e.g., changes in chemical shifts).

    ”””

    sq_err1 = [(exp[n] - calc1[n])**2 for n in range(len(exp))]
    sq_err2 = [(exp[n] - calc2[n])**2 for n in range(len(exp))]

    return sum(sq_err2)/sum(sq_err1)


def permute_spec(seed, s1, s2):
    ”””Permute two sets of data.

    Args:
        seed (int): Number used to seed the permutation. Will be
            converted into binary and then used as follows: 0=no swap,
            1=swap on an element by element basis.
        s1, s2 (lists): The sets to be permuted. Must be the same
            length.

    Returns:
        The new sets, as a tuple.
    ”””
```

```
    s1_new = []
    s2_new = []

    # Converts seed to a binary string with leading zeros, of matching
    # length to the lists.
    swap_key = ”{seed:0{length}b}”.format(seed=seed, length=len(s1))

    for n in range(len(s1)):
        if swap_key[n] == ”0”:
            s1_new.append(s1[n])
            s2_new.append(s2[n])
        elif swap_key[n] == ”1”:
            s1_new.append(s2[n])
            s2_new.append(s1[n])

    return s1_new, s2_new


def main():
    parser = argparse.ArgumentParser()
    parser.add_argument(
        ”exp_data”,
        help=”Datafile for experimental NMR spectrum”)
    parser.add_argument(
        ”good_match”,
        help=”Datafile for proposed good computational match”)
    parser.add_argument(
        ”bad_match”,
        help=”Datafile for proposed bad computational match”)
    parser.add_argument(
        ”-o”, ”--output_file”,
        help=”Output filename”)
    parser.add_argument(
        ”-m”, ”--max_swaps”,
        help=”Maximum number of permutations”,
        type=int, default=2**20)
    parser.add_argument(
        ”-d”, ”--direct”,
        help=”Use direct errors (no regression)”,
        action=”store_true”)
    args = parser.parse_args()

    max_swaps = args.max_swaps

    if args.direct:
        test_func = test_func_direct
    else:
        test_func = test_func_reg
```

```
exp = []   # The experimental data
set1 = []  # The first (better) comparison data
set2 = []  # The second comparison data

with open(args.exp_data) as exp_data_file:
    for line in exp_data_file:
        exp.append(float(line))

with open(args.good_match) as set1_data_file:
    for line in set1_data_file:
        set1.append(float(line))

with open(args.bad_match) as set2_data_file:
    for line in set2_data_file:
        set2.append(float(line))

# The error value for the original spectra.
comp_err = test_func(exp, set1, set2)

tests = [comp_err]  # Stores the results of the permutations

# Checks to see if it is possible to consider all possible
# permutations of the two spectra.
if 2**len(exp) <= max_swaps:
    all_possible = True
    num_considered = 2**len(exp)
    print(”Able to consider all {:,} possibilities.”.format(
            num_considered))
else:
    all_possible = False
    num_considered = max_swaps
    print(”Number of permutations considered capped at {:,}.”.format(
            num_considered))

# Used in a progress indicator.
increment = num_considered // 100

for n in range(1, num_considered):
    # Simple progress indicator.
    if n % increment == 0:
        sys.stdout.write(’\r’)
        sys.stdout.write(”Progress: {:4.0%}”.format(n/num_considered))
        sys.stdout.flush()

    # If considering all possible spectra, the seed for permute_spec
    # is simply n. Otherwise, a random integer is generated between
    # 00...0 and 11...1.
    if all_possible:
        s1_perm, s2_perm = permute_spec(n, set1, set2)
    else:
```

```
            ranseed = np.random.randint(2**len(exp))
            s1_perm, s2_perm = permute_spec(ranseed, set1, set2)

        tests.append(test_func(exp, s1_perm, s2_perm))

    # Finishes progress indicator.
    sys.stdout.write(”\n”)
    sys.stdout.flush()

    tests.sort(reverse=True)  # Sort tests list for ranking

    rank = tests.index(comp_err) + 1  # Rank of original F stat in total list

    output_text = ”Test function for true comparison: {}\n”.format(comp_err)
    output_text += ”Rank: {:,} out of {:,}\n”.format(rank, len(tests))
    output_text += ”p = {} ({:.4%})\n”.format(
            rank/len(tests), 1 - rank/len(tests))

    if args.output_file:
        with open(args.output_file, ’w’) as output_file:
            output_file.write(output_text)
    else:
        print(output_text)
```

Experimental

General

Unless otherwise noted, all starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Anhydrous solvents were obtained from an alumina column solvent purification system. Melting points were determined using a Thermal Analysis Q20 differential scanning calorimeter at a heating rate of 10 ℃/min. NMR spectra were measured for $CDCl_3$ solutions using Bruker Avance 500 and 600 MHz NMR spectrometers. Semi-preparative gel permeation chromatography (GPC) was performed using a Waters Breeze 2 HPLC equipped with a 19×300 mm Ultrastyragel 500 Å GPC column with toluene as the eluent.

Terephthalaldehyde **1** is commercially available. The dialdehyde linkers **2** and **3** were synthesized according to literature procedures.[9,10]

*o-Phenylene tetramer **5***

Compound **3**[11] (2.949 g, 5.58 mmol) was added to a dry round bottom flask and dissolved in DMF (125 mL). To the solution was added iodohexane (3.34 mL, 22.6 mmol) and K_2CO_3 (6.170 g, 44.64 mmol). The reaction, fitted with a condenser, was brought to 100 ℃ and stirred for 2 days. Once cooled to rt, the reaction was poured into water (50 mL) and extracted with EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes:EtOAc, 49:1) gave **5** as thick colorless oil (3.875 g, 80%): NMR spectra broadened due to slow conformational exchange, see Figures S6 (^{1}H) and S7 (^{13}C); HRMS (MALDI) calcd for $C_{48}H_{63}Br_2O_4$ ($[M-H]^+$) 861.309307, found 861.308761.

*o-Phenylene octamer **7***

A Schlenk vacuum tube was charged with **5** (772.1 mg, 0.893 mmol), 10-hydroxy-10,9-boroxarophenanthrene[12] (531.0 mg, 2.794 mmol), $Pd(PPh_3)_2Cl_2$ (132 mg, 0.188 mmol), and SPhos (87 mg, 0.212 mmol), then evacuated and back-filled with argon (3×). Anhydrous THF (16 mL) and triethylamine (4 mL) were added under a positive pressure of argon and the reaction mixture degassed by three freeze-pump-thaw cycles. The Schlenk tube was sealed and heated at 85 ℃ for 48 h, then cooled and diluted with EtOAc (10 mL) and 2 M HCl(aq) (10 mL). The aqueous layer was extracted with EtOAc (3 × 25 mL) and the combined organic layers washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes:EtOAc, 9:1) gave **6** as a white solid (see Figure S8 (^{1}H NMR spectrum)). Intermediate **6** was dissolved in CH_2Cl_2 (50 mL) and brought to 0 ℃. Pyridine (0.22 mL, 2.8 mmol) was added and the mixture allowed to stir at 0 ℃ for 10 min. Tf_2O (0.34 mL, 0.72 mmol) was added and the mixture stirred while warming to rt overnight. The reaction was quenched with HCl(aq) (10 mL), extracted with EtOAc (3 × 25 mL), and the combined organic layers washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes:toluene, 3:2) gave **7** as a white solid (668.5 mg, 57% over two steps): mp 121.8 ℃; NMR spectra broadened due to slow conformational exchange, see Figure S9 (^{1}H); HRMS (MALDI) calcd for $C_{74}H_{80}F_6O_{10}S_2$ (M^+) 1306.509712, found 1306.509162.

o-Phenylene hexamer ***oP^{6}(NH$_{2}$)***

A Schlenk vacuum tube was charged with **5** (466.7 mg, 0.540 mmol), 4-amino-phenylboronic acid pinacol ester (513.0 mg, 2.34 mmol), $Pd(PPh_3)_2Cl_2$ (121 mg, 0.172 mmol), SPhos (81.2 mg, 0.198 mmol), and Cs_2CO_3 (820 mg, 2.52 mmol), then evacuated and back-filled with argon (3×). Dry THF (10 mL) and water (2 mL) were added under a positive pressure of argon. The Schlenk tube was sealed and heated at 80 ℃ for 48 h, then cooled and diluted with EtOAc (10 mL) and water (10 mL). The aqueous layer was extracted with EtOAc (3 × 20 mL) and the combined organic layers washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (toluene:EtOAc, 9:1) gave **oP^{6}(NH$_{2}$)** as a light brown solid (369.2 mg, 77%): mp 217.9 ℃ (dec.); NMR spectra broadened due to slow conformational exchange, see Figures S10 (^{1}H), S11 (^{13}C), S12 (COSY), S13 (HSQC), S14 (HMBC), and S15 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{60}H_{76}N_2O_4$ (M^+) 888.580508, found 888.579960.

o-Phenylene decamer ***oP^{10}(NH$_{2}$)***

A Schlenk vacuum tube was charged with **7** (95.1 mg, 0.073 mmol), 4-amino-phenylboronic acid pinacol ester (86.4 mg, 0.394 mmol), $Pd(PPh_3)_2Cl_2$ (13.8 mg, 0.020 mmol), SPhos (10.8 mg, 0.026 mmol), and Cs_2CO_3 (106.1 mg, 0.326 mmol), then evacuated and back-filled with argon (3x). Dry THF (3 mL) and triethylamine (0.75 mL) were added under a positive pressure of argon. The Schlenk tube was sealed and heated at 85 ℃ for 48 h, then cooled, diluted with EtOAc (10 mL) and water (10 mL). The aqueous layer was extracted with EtOAc (3 × 20 mL) and the combined organic layers washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes:EtOAc, 4:1) gave **oP^{10}(NH$_{2}$)** as a light brown solid (45.4 mg, 52%): mp 218.8 ℃ (dec.); NMR spectra broadened due to slow conformational exchange, see Figures S16 (^{1}H), S17 (^{13}C), S18 (COSY), S19 (HSQC), S20 (HMBC), and S21 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{84}H_{92}N_2O_4$ (M^+) 1192.705708, found 1192.705161.

o-Phenylene hexamer ***oP^{6}(M)***

An oven-dried round bottom flask was charged with **oP^{6}(NH$_{2}$)** (57.9 mg, 0.108 mmol), benzaldehyde (21.9 µL, 0.198 mmol), and $CHCl_3$ (50 mL). To this, 3 Å molecular sieves were added, followed by TFA (1.23 mg, 0.011 mmol). The reaction mixture was allowed to stand at room temperature for overnight with occasional stirring, then quenched with NEt_3 (3 mL) and concentrated. Purification by flash chromatography (hexanes:EtOAc:NEt_3 45:4:1) gave **oP^{6}(M)** as a yellow solid (35.3 mg, 46%): mp 144.6 ℃; NMR spectra broadened due to slow conformational exchange, see Figures S22 (^{1}H), S23 (^{13}C), S24 (COSY), S25 (HSQC), S26 (HMBC), and S27 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{74}H_{84}N_2O_4$ (M^+) 1064.643108, found 1064.642561.

o-Phenylene decamer ***oP^{10}(M)***

An oven-dried round bottom flask was charged with **oP^{10}(NH$_{2}$)** (39.2 mg, 0.033 mmol), benzaldehyde (6.7 µL, 0.066 mmol), and $CHCl_3$ (22 mL). To this, 3 Å molecular sieves were added, followed by TFA (0.374 mg, 0.003 mmol). The reaction mixture was allowed to stand at room temperature for overnight with occasional stirring. Once the reaction was complete, it was quenched with NEt_3 (3 mL) and concentrated. Purification by flash chromatography (hexanes:EtOAc:NEt_3 23:1:1) gave **oP^{10}(M)** as a yellow solid (9.8 mg, 22%): mp 174.6℃; NMR spectra broadened due to slow conformational exchange, see Figures S28 (^{1}H), S29 (COSY), S30 (TOCSY), S31 (HSQC), S32 (HMBC), and S33 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{98}H_{99}N_2O_4$ ($[M-H]^+$) 1367.760483, found 1367.759936.

General procedure for macrocyclization

An oven-dried round bottom flask was charged with *o*-phenylene diamine (**oP^{6}(NH$_{2}$)** or **oP^{10}(NH$_{2}$)**) (1.1 equiv), dialdehyde linker (1.0 equiv), and $CHCl_3$ (to a dialdehyde concentration of 1.5 mM). To this, 3 Å molecular sieves were added, followed by TFA (0.10 equiv). The reaction mixture was allowed to stand at room temperature for 5 d (**oP^{6}(NH$_2$)**) or 11 d (**oP^{10}(NH$_2$)**) with occasional stirring.[a] Once the reaction was complete, it was quenched with NEt$_3$ (3 mL) and concentrated. The crude products were purified via GPC.

*Macrocycle **oP^{6}(Phen)$_{3+3}$***

From **oP^{6}(NH$_2$)** (30.0 mg, 0.034 mmol) and **1** (4.1 mg, 0.030 mmol) was obtained compound **oP^{6}(Phen)$_{3+3}$** (17.5 mg, 59%) as a yellow solid: mp 240.2 °C (dec.); NMR spectra broadened due to slow conformational exchange, see Figures S34 (^{1}H), S35 (COSY), S36 (HSQC), S37 (HMBC), and S38 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{204}H_{233}N_6O_{12}$ ($[M-H]^+$) 2958.780649, found 2958.780103.

*Macrocycle **oP^{6}(BIP)$_{3+3}$***

From **oP^{6}(NH$_2$)** (31.4 mg, 0.035 mmol) and **2** (6.7 mg, 0.032 mmol) was obtained compound **oP^{6}(BIP)$_{3+3}$** (13.7 mg, 40%) as a pale yellow solid: mp 226.5 °C (dec.); NMR spectra broadened due to slow conformational exchange, see Figures S39 (^{1}H), S40 (COSY), S41 (HSQC), S42 (HMBC), and S43 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{222}H_{245}N_6O_{12}$ ($[M-H]^+$) 3186.874549, found 3186.874004.

*Macrocycle **oP^{6}(DPB)$_{3+3}$***

From **oP^{6}(NH$_2$)** (31.4 mg, 0.035 mmol) and **3** (8.3 mg, 0.032 mmol) was obtained compound **oP^{6}(DPB)$_{3+3}$** (15.4 mg, 43%) as a pale yellow solid: mp 265.3 °C (dec.); NMR spectra broadened due to slow conformational exchange, see Figures S44 (^{1}H), S45 (COSY), S46 (HSQC), S47 (HMBC), and S48 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{234}H_{245}N_6O_{12}$ ($[M-H]^+$) 3330.874549, found 3330.874004.

*Macrocycles **oP^{10}(Phen)$_{2+2}$** and **oP^{10}(Phen)$_{3+3}$***

From **oP^{10}(NH$_2$)** (30.0 mg, 0.025 mmol) and **1** (3.1 mg, 0.023 mmol) was obtained compounds **oP^{10}(Phen)$_{2+2}$** (5.1 mg, 22%) and **oP^{10}(Phen)$_{3+3}$** (3.8 mg, 16%).

oP^{10}(Phen)$_{2+2}$

Yellow solid: NMR spectra broadened due to slow conformational exchange, see Figures S49 (^{1}H), S50 (COSY), S51 (HSQC), S52 (HMBC), and S53 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{184}H_{187}N_4O_8$ ($[M-H]^+$) 2580.434891, found 2580.434345.

oP^{10}(Phen)$_{3+3}$

Yellow solid: NMR spectra broadened due to slow conformational exchange, see Figures S54 (^{1}H), S55 (COSY), S56 (HSQC), S57 (HMBC), and S58 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{276}H_{282}N_6O_{12}$ (M^+) 3872.16353, found 3872.15204.

*Macrocycles **oP^{10}(BIP)$_{2+2}$** and **oP^{10}(BIP)$_{3+3}$***

From **oP^{10}(NH$_2$)** (30.1 mg, 0.025 mmol) and **2** (4.8 mg, 0.023 mmol) was obtained compounds **oP^{10}(BIP)$_{2+2}$** (7.7 mg, 31%) and **oP^{10}(BIP)$_{3+3}$** (3.9 mg, 16%).

oP^{10}(BIP)$_{2+2}$

Pale yellow solid: NMR spectra broadened due to slow conformational exchange, see Figures S59 (^{1}H), S60 (COSY), S61 (HSQC), S62 (HMBC), and S63 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{196}H_{195}N_4O_8$ ($[M-H]^+$) 2732.497491, found 2732.496946.

oP^{10}(BIP)$_{3+3}$

Yellow solid: NMR spectra broadened due to slow conformational exchange, see Figures S64 (^{1}H), S65 (COSY), S66 (HSQC), S67 (HMBC), and S68 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{294}H_{294}N_6O_{12}$ (M^+) 4100.25743, found 4100.24691.

*Macrocycles **oP^{10}(DPB)$_{2+2}$** and **oP^{10}(DPB)$_{3+3}$***

From **oP^{10}(NH$_2$)** (30.4 mg, 0.026 mmol) and **3** (6.0 mg, 0.023 mmol) was obtained compounds **oP^{10}(DPB)$_{2+2}$** (9.2 mg, 35%) and **oP^{10}(DPB)$_{3+3}$** (4.1 mg, 16%).

---

[a] The mixture was not stirred continuously to avoid breaking up the molecular sieves.

oP^{10}(DPB)$_{2+2}$

Pale yellow solid: NMR spectra broadened due to slow conformational exchange, see Figures S69 (^{1}H), S70 (COSY), S71 (TOCSY), S72 (HSQC), S73 (HMBC), and S74 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{204}H_{195}N_4O_8$ ([M − H]$^+$) 2828.497491, found 2828.466946.

oP^{10}(DPB)$_{3+3}$

Pale yellow solid: NMR spectra broadened due to slow conformational exchange, see Figures S75 (^{1}H), S76 (COSY), S77 (HSQC), S78 (HMBC), and S79 (NOESY/EXSY); HRMS (MALDI) calcd for $C_{306}H_{294}N_6O_{12}$ (M$^+$) 4244.25743, found 4244.25010.

Computational chemistry

DFT calculations were performed using Gaussian 09, rev. B.01.[13] All energy minima were verified to have 0 imaginary frequencies by vibrational frequency analysis. PM7 calculations were performed using MOPAC2016.[14]

NMR spectra

*o-Phenylene tetramer **5***

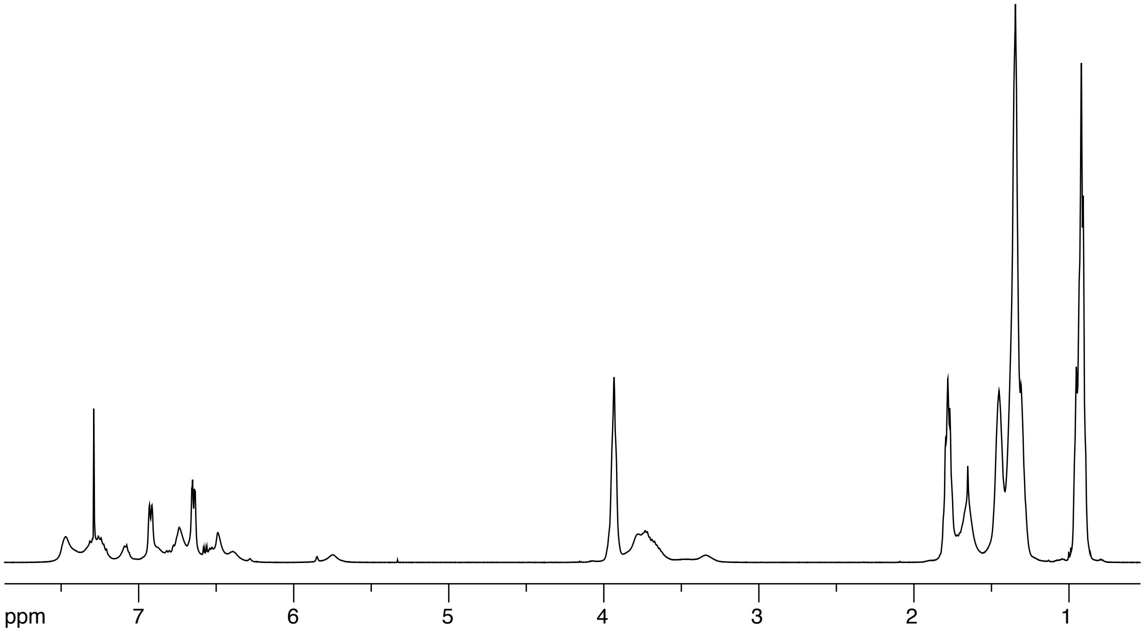


Figure S6. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 0 °C) of **5**.

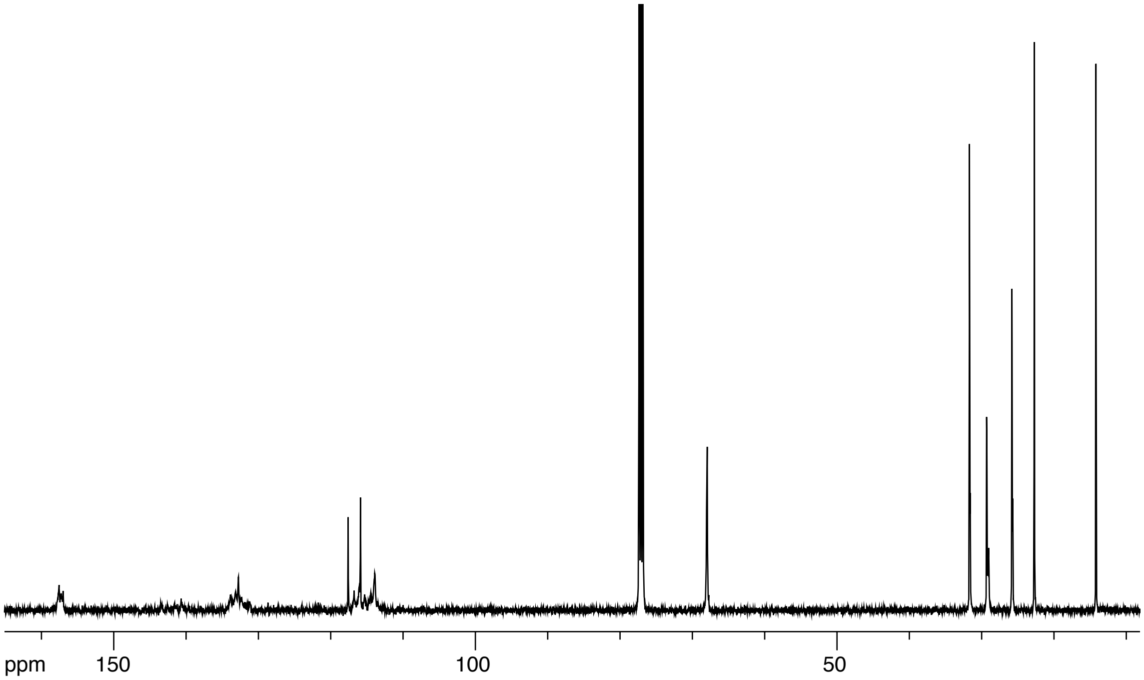


Figure S7. ^{13}C NMR spectrum (125 MHz, CDCl$_3$, 0 ℃) of **5**.

o-Phenylene octamers **6** and **7**

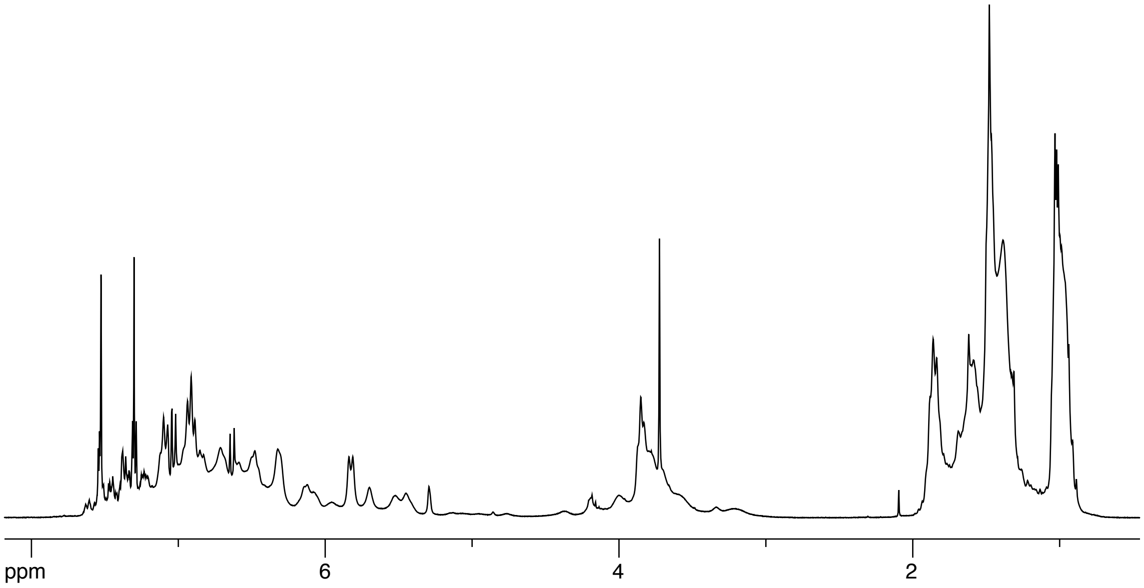


Figure S8. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 0 ℃) of **6**.

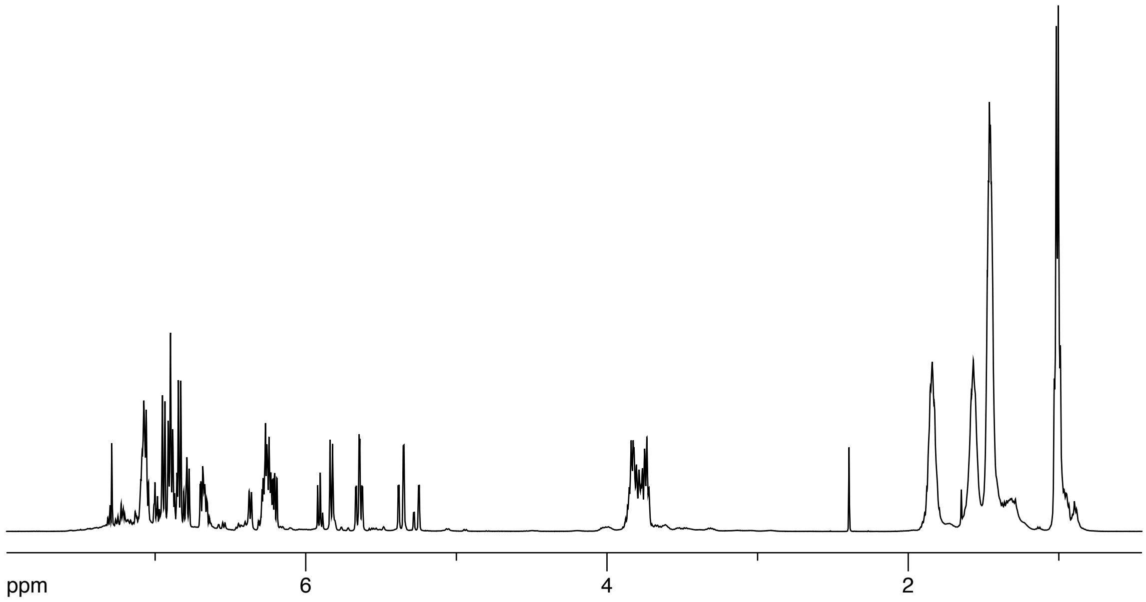


Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 0 ℃) of 7.

*o-Phenylene hexamer **oP^{6}(NH$_2$)***

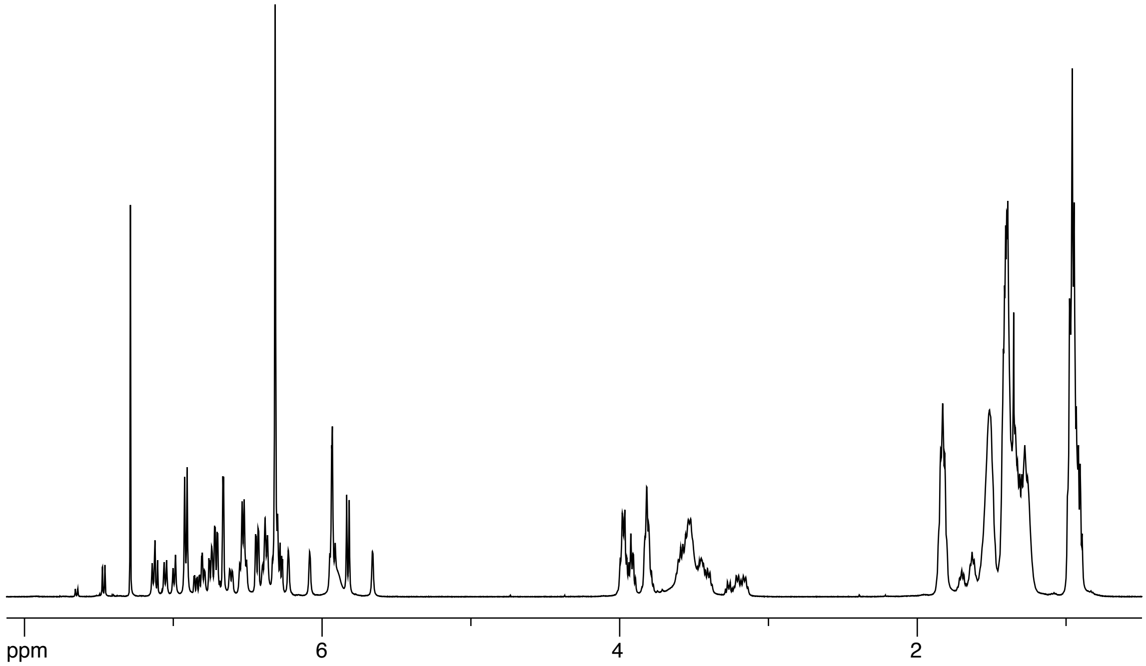


Figure S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{6}(NH$_2$)**.

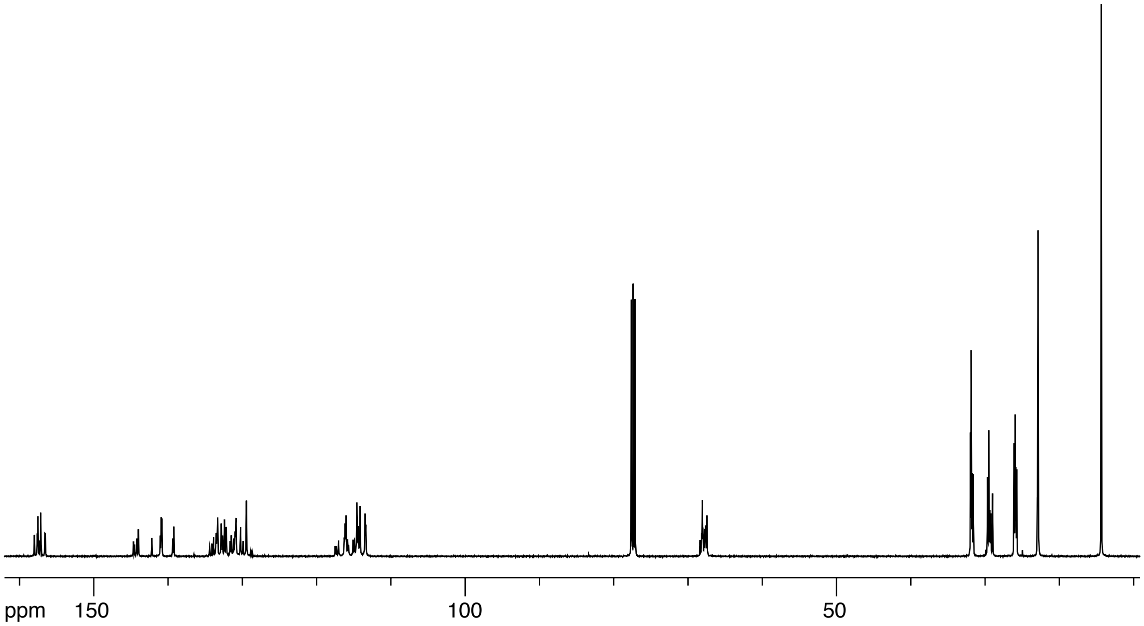


Figure S11. ^{13}C NMR spectrum (125 MHz, CDCl$_3$, 0 ℃) of **oP^6(NH$_2$)**.

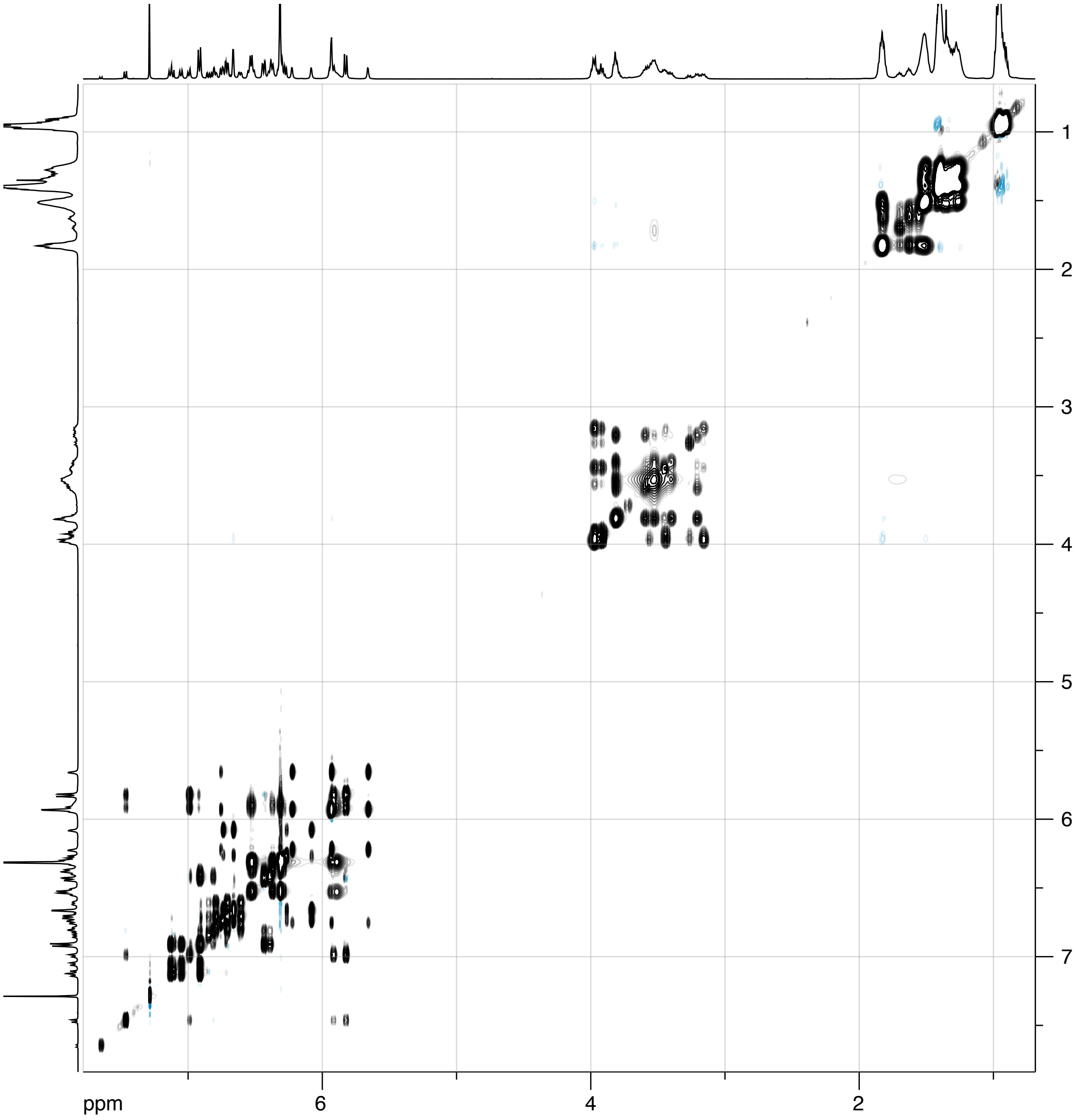


Figure S12. COSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^6(NH_2)$**.

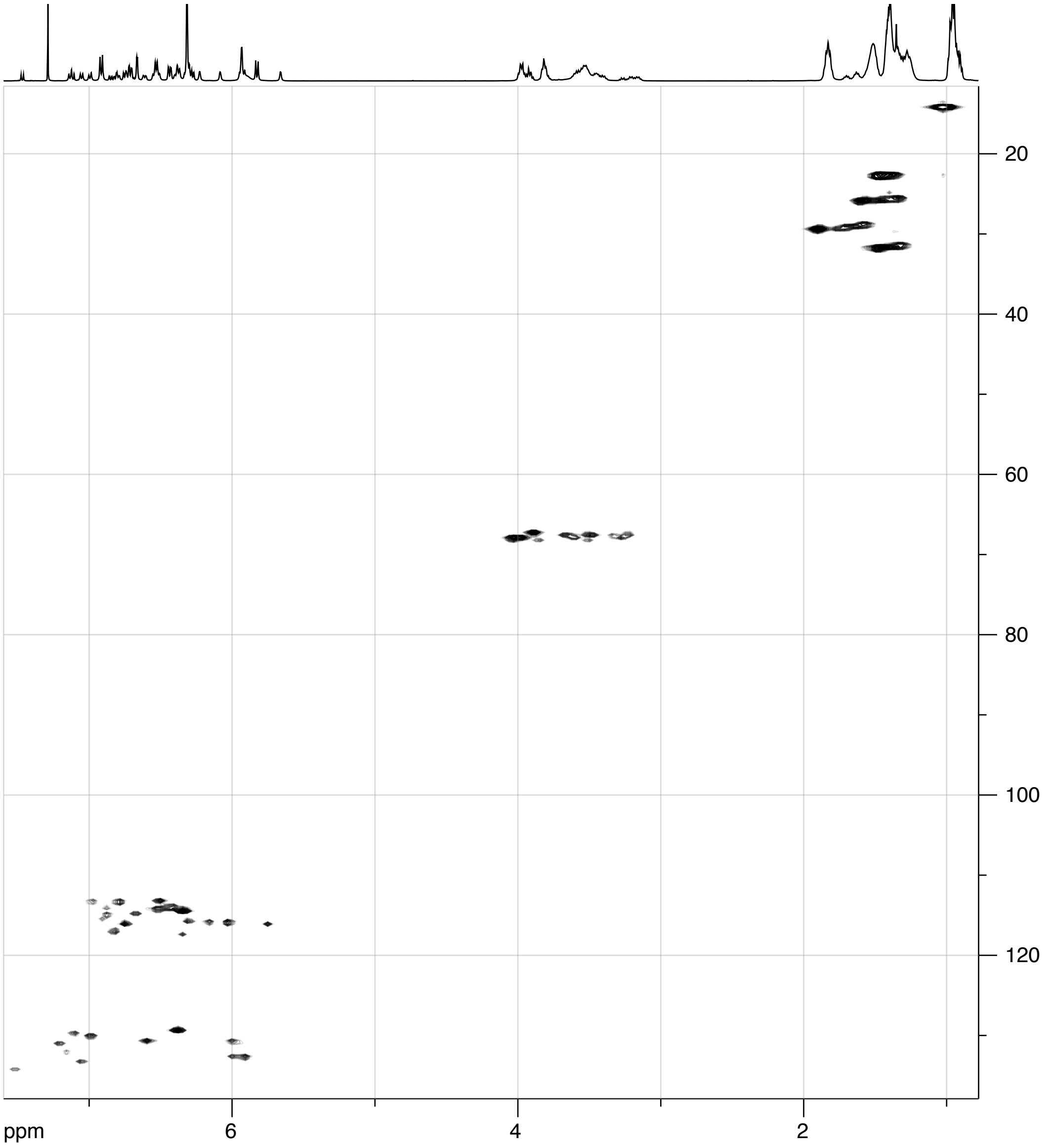


Figure S13. HSQC spectrum (500 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^6(NH_2)}$.

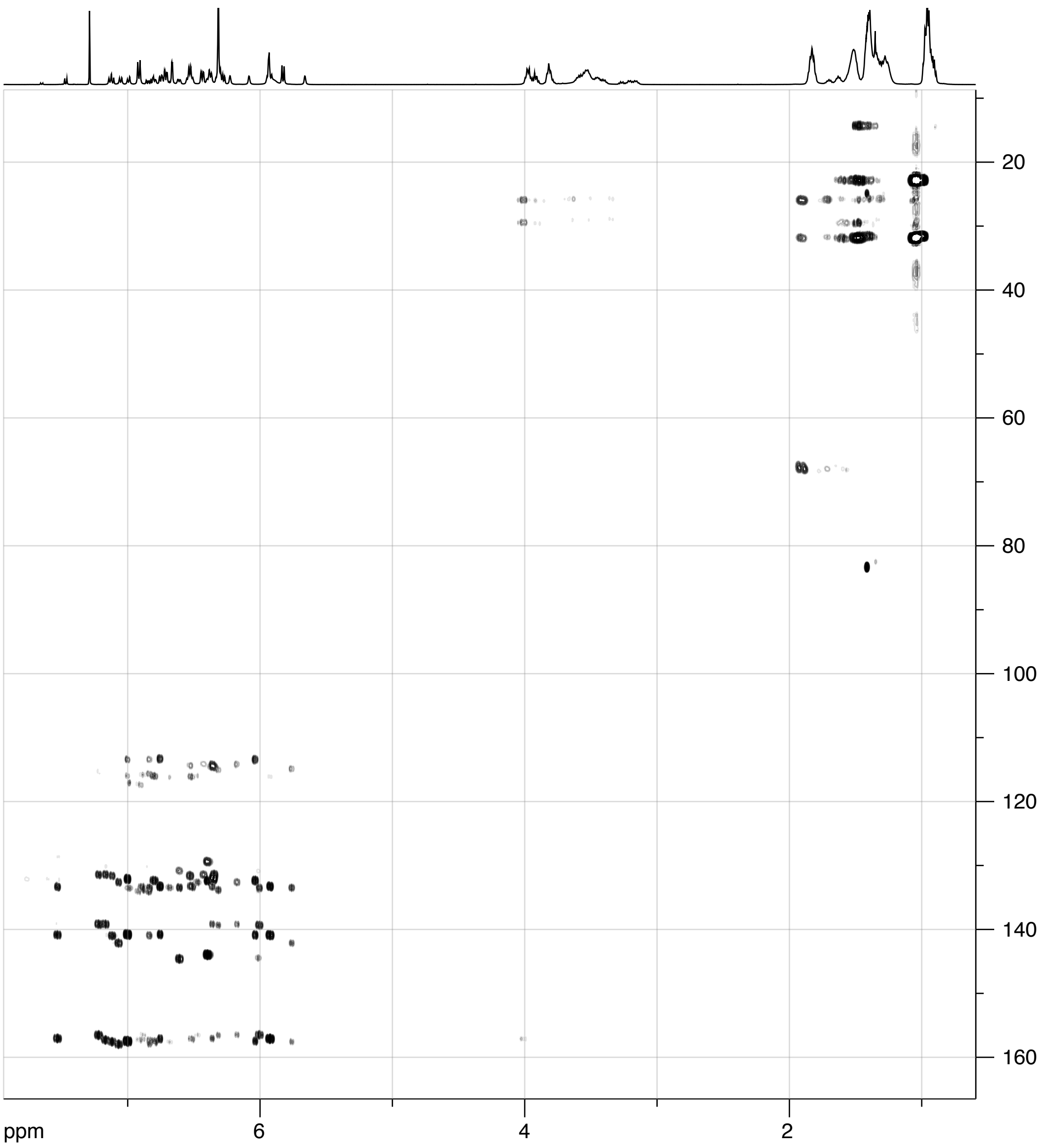


Figure S14. HMBC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^6(NH_2)$**.

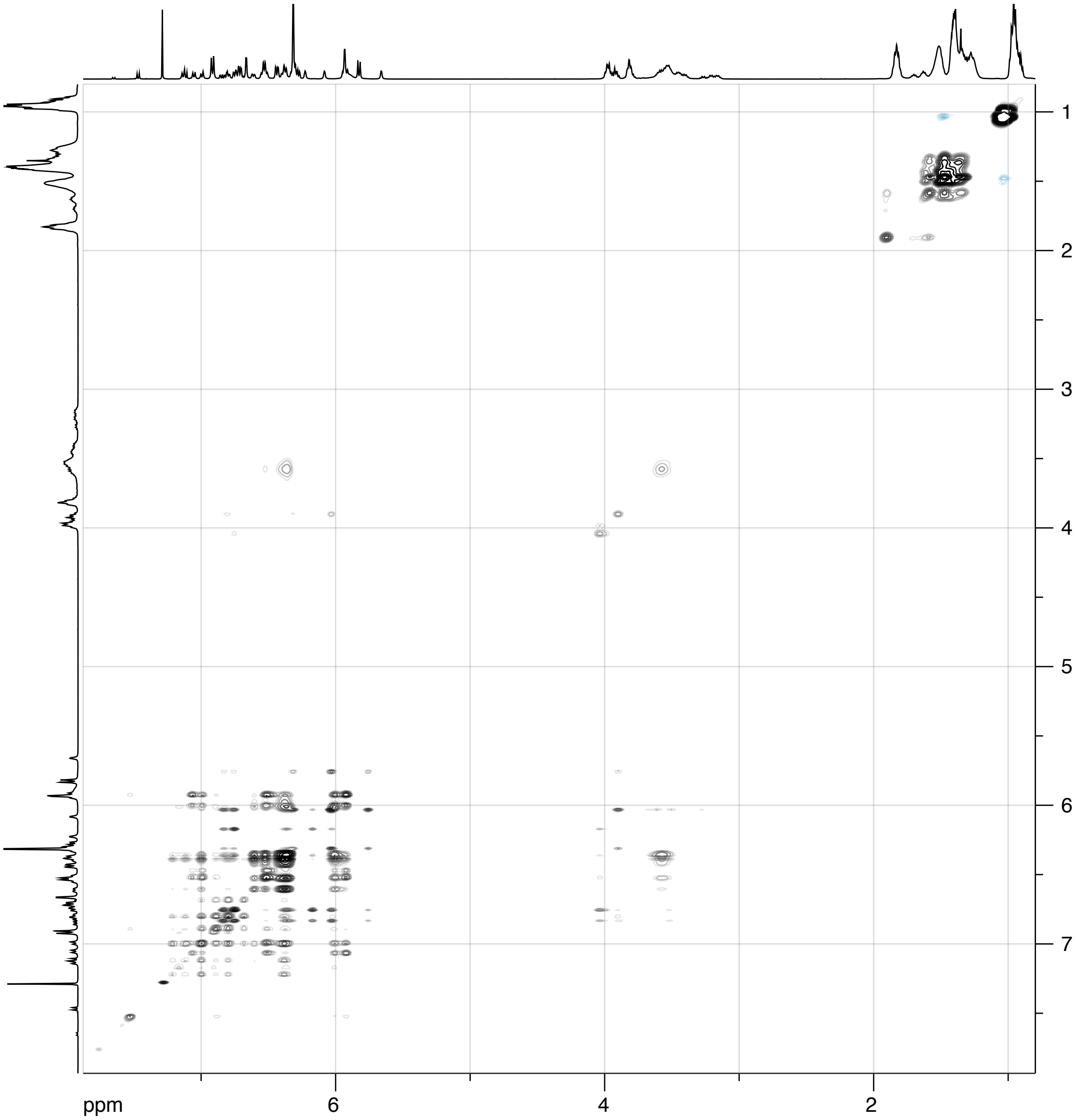


Figure S15. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^6(NH_2)$**.

o-Phenylene decamer ***oP***^{10}***(NH***$_2$***)***

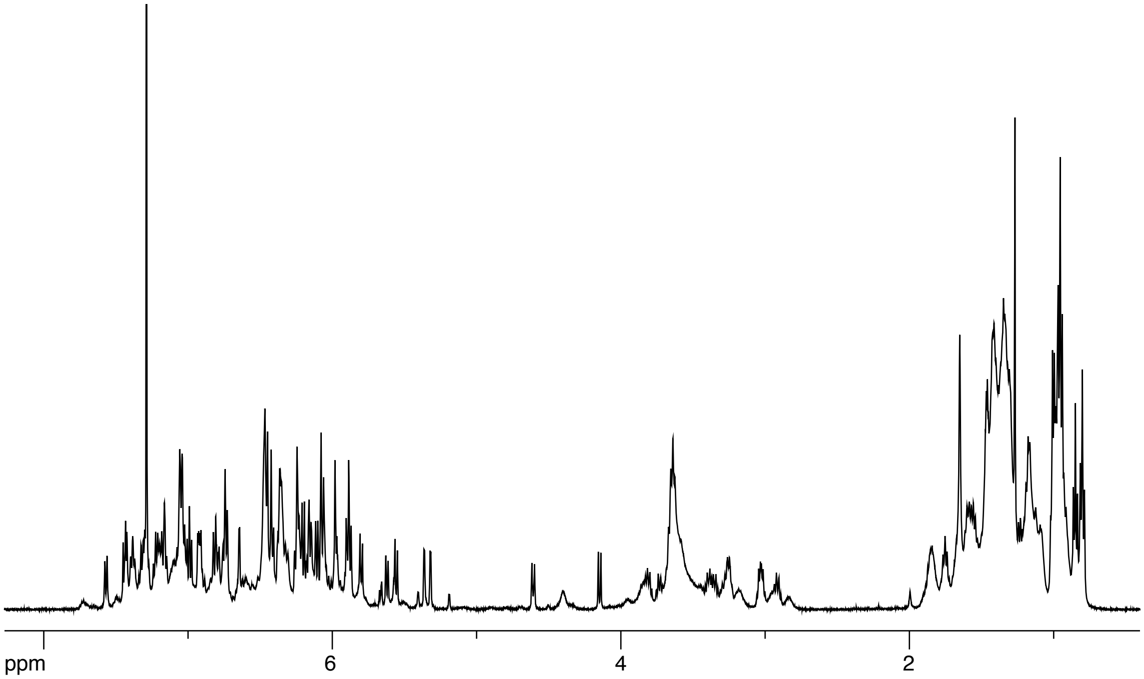


Figure S16. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 0 ℃) of **oP^{10}(NH$_2$)**.

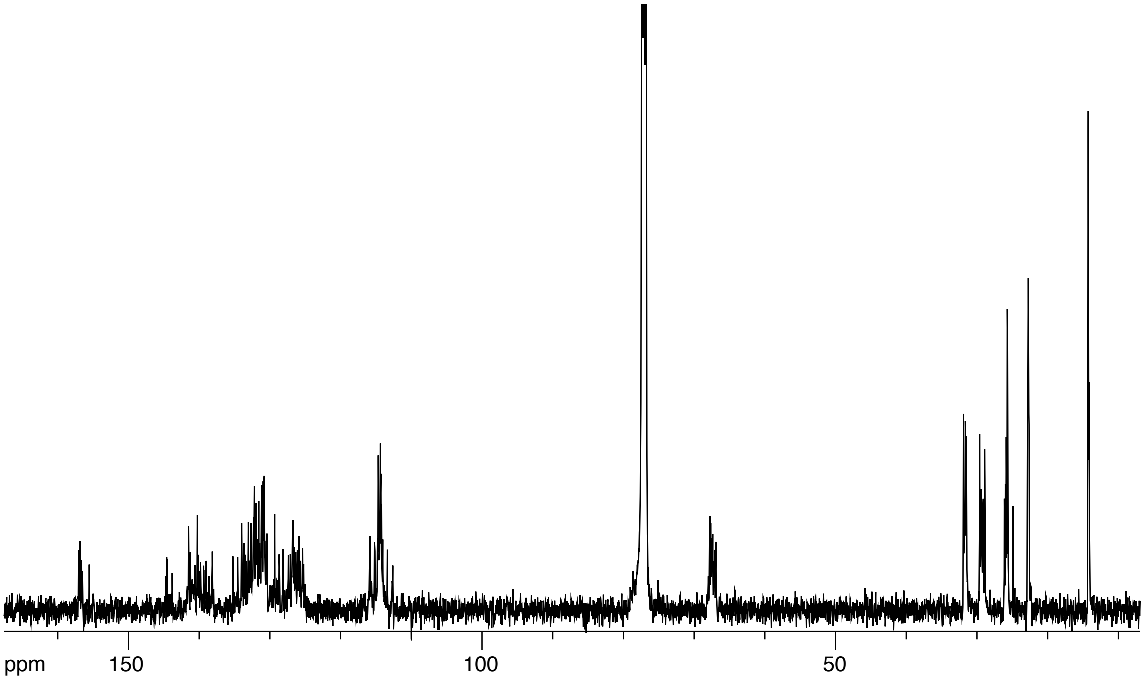


Figure S17. ^{13}C NMR spectrum (125 MHz, CDCl$_3$, 0 ℃) of **oP^{10}(NH$_2$)**.

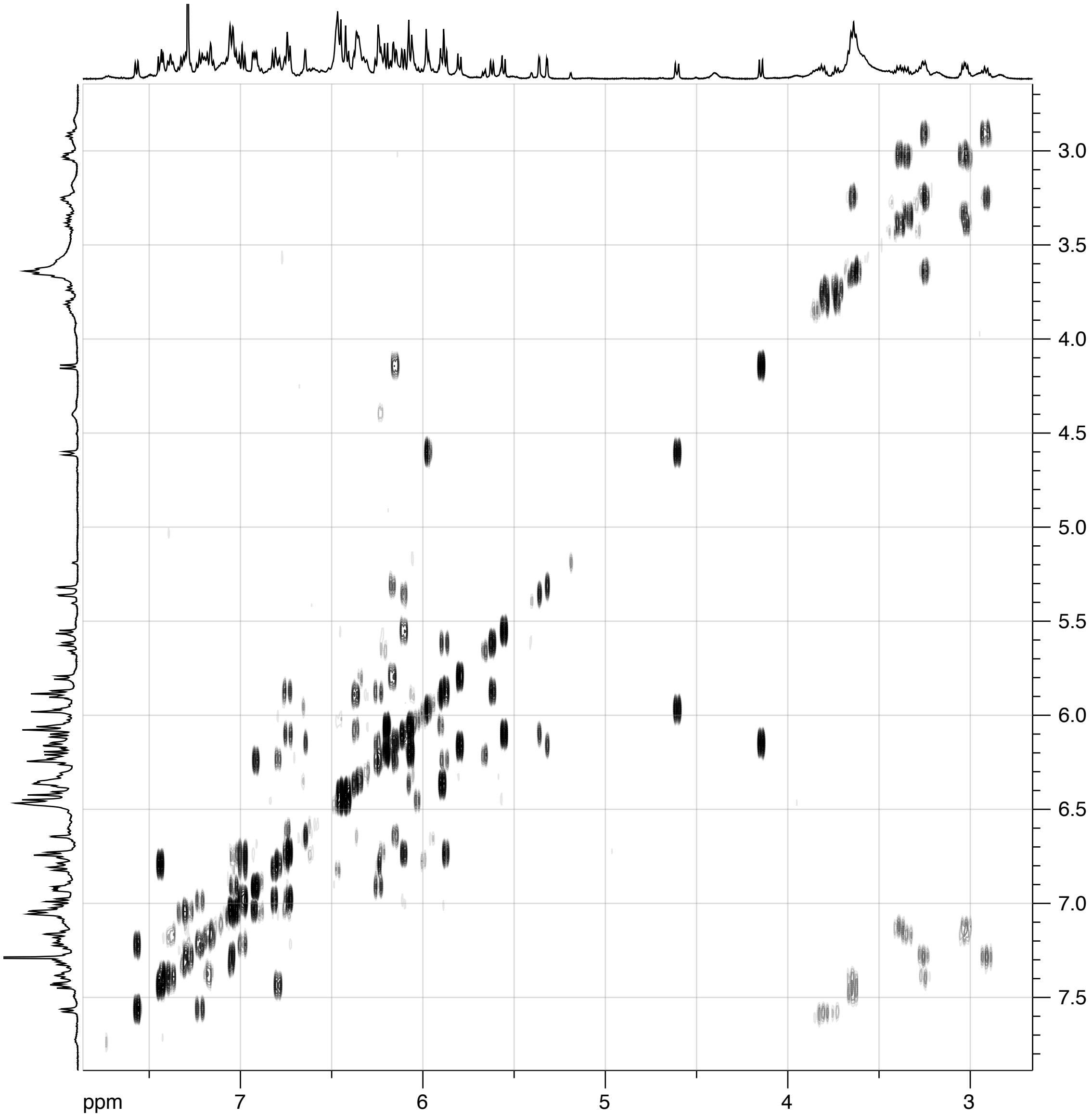


Figure S18. COSY spectrum (500 MHz, CDCl$_3$, 0 °C) of **oP^{10}(NH$_2$)**.

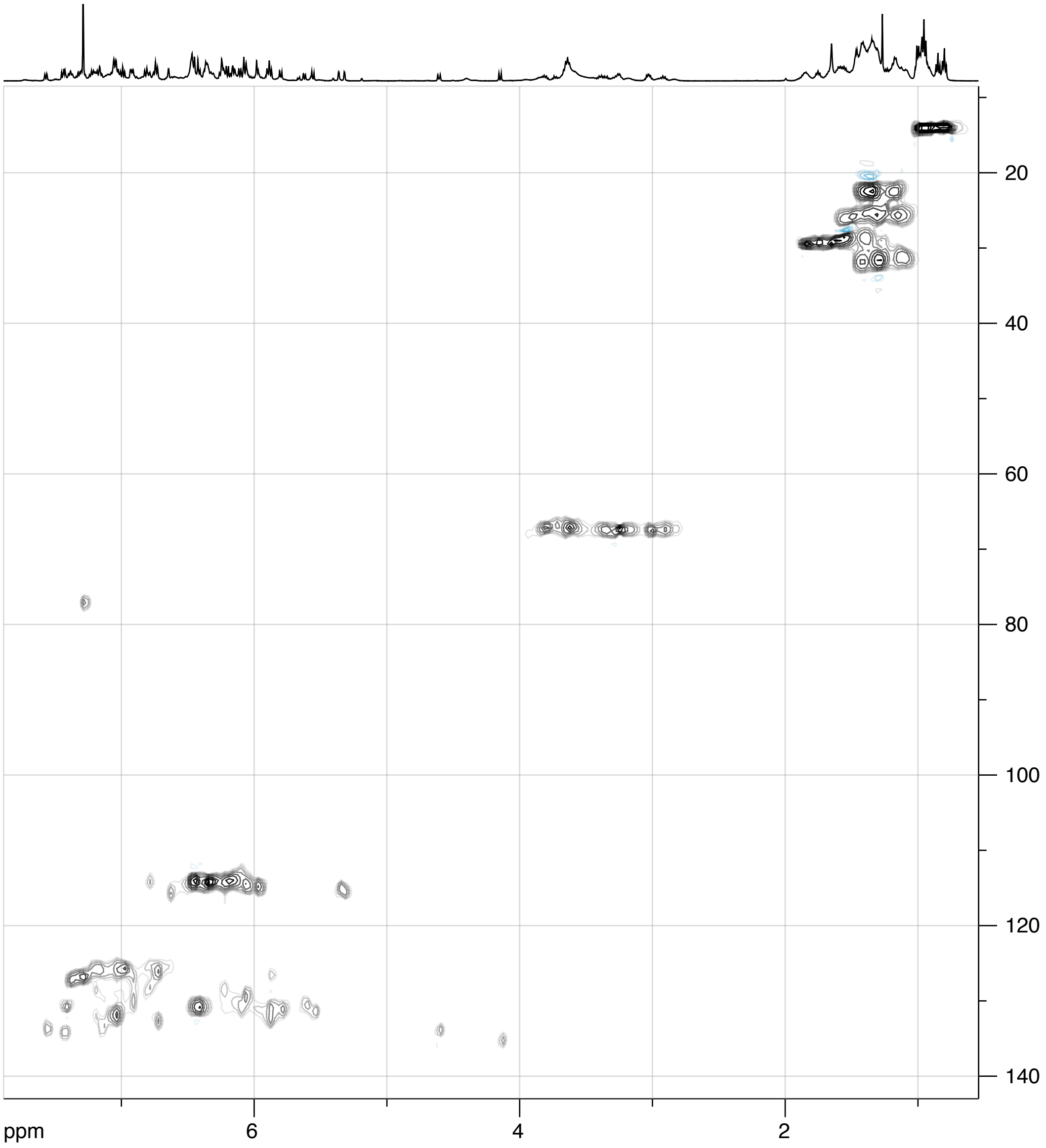


Figure S19. HSQC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(NH$_2$)**.

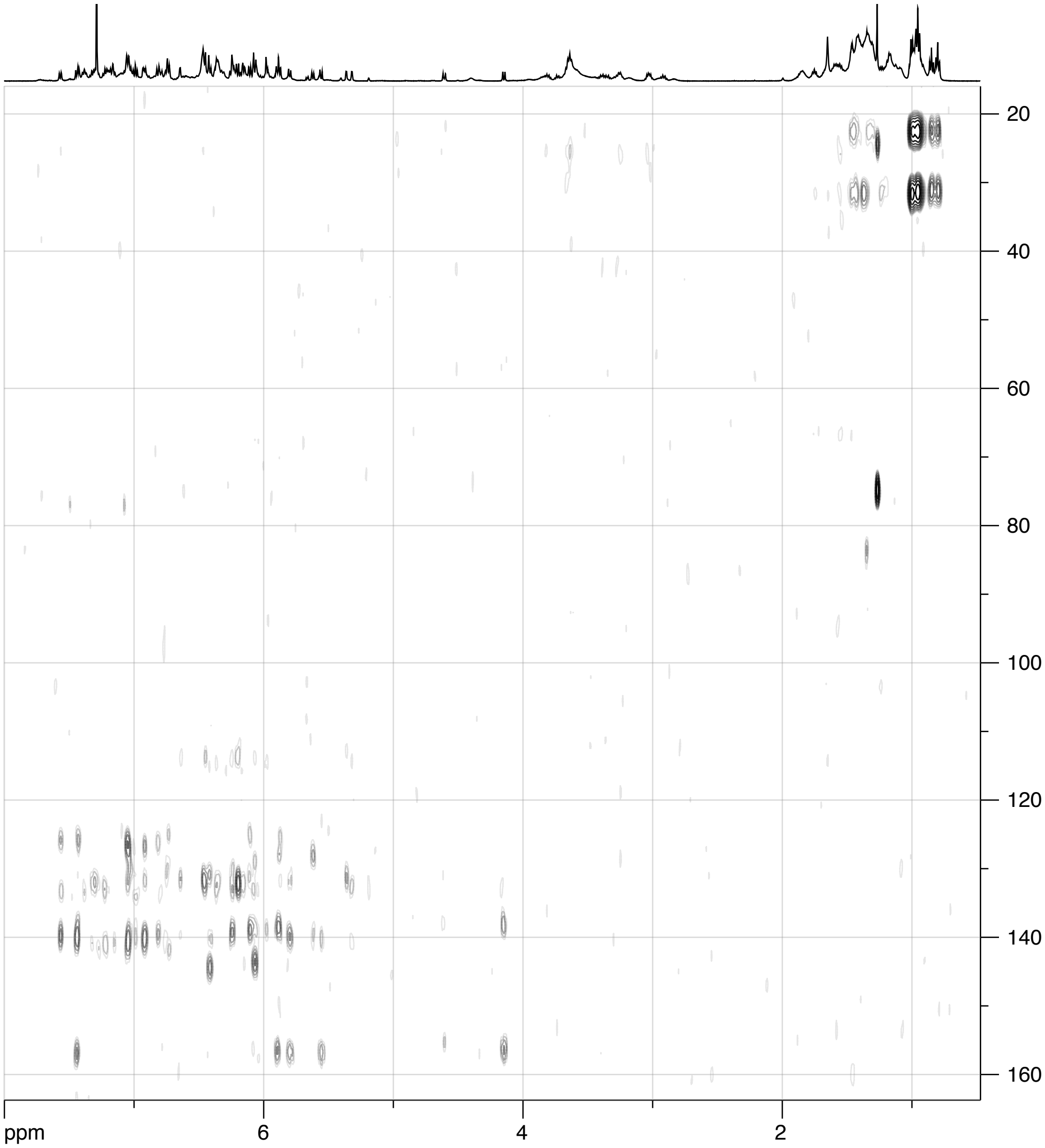


Figure S20. HMBC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(NH_2)$**.

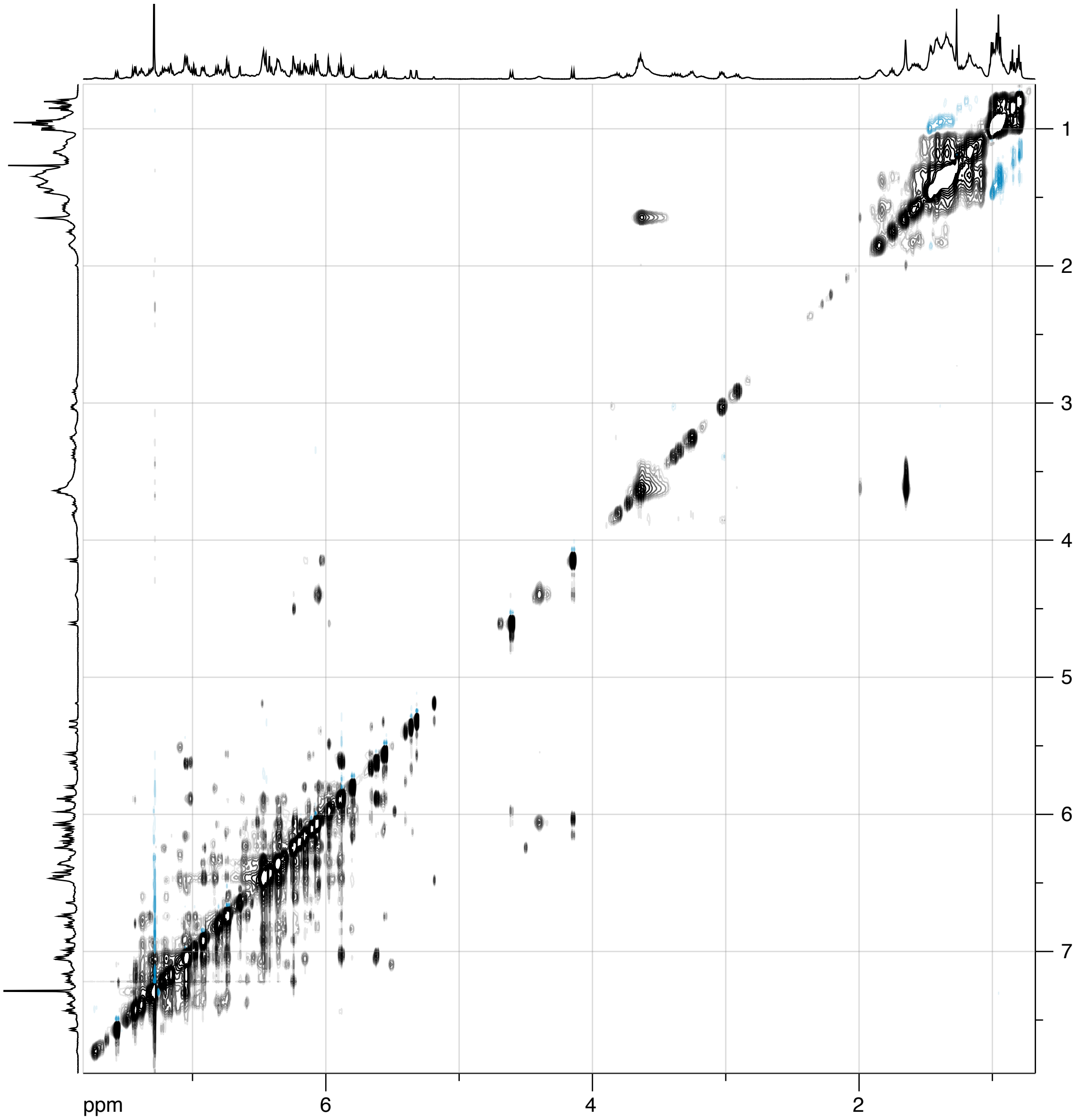


Figure S21. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(NH_2)$**.

o-Phenylene hexamer ***oP^6(M)***

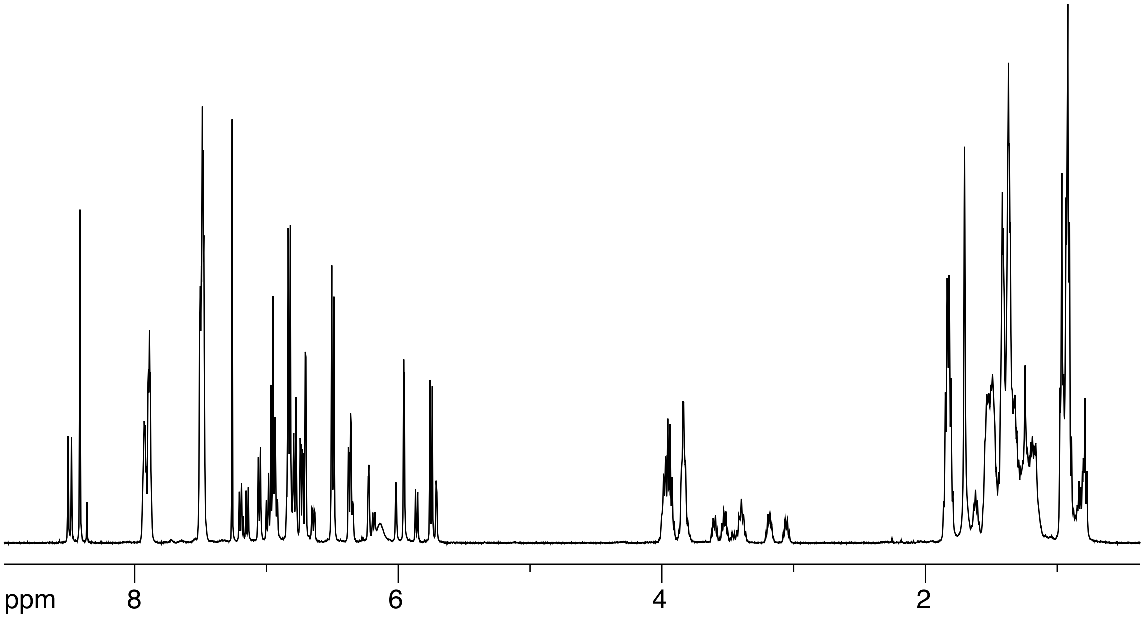


Figure S22. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^6(M)**.

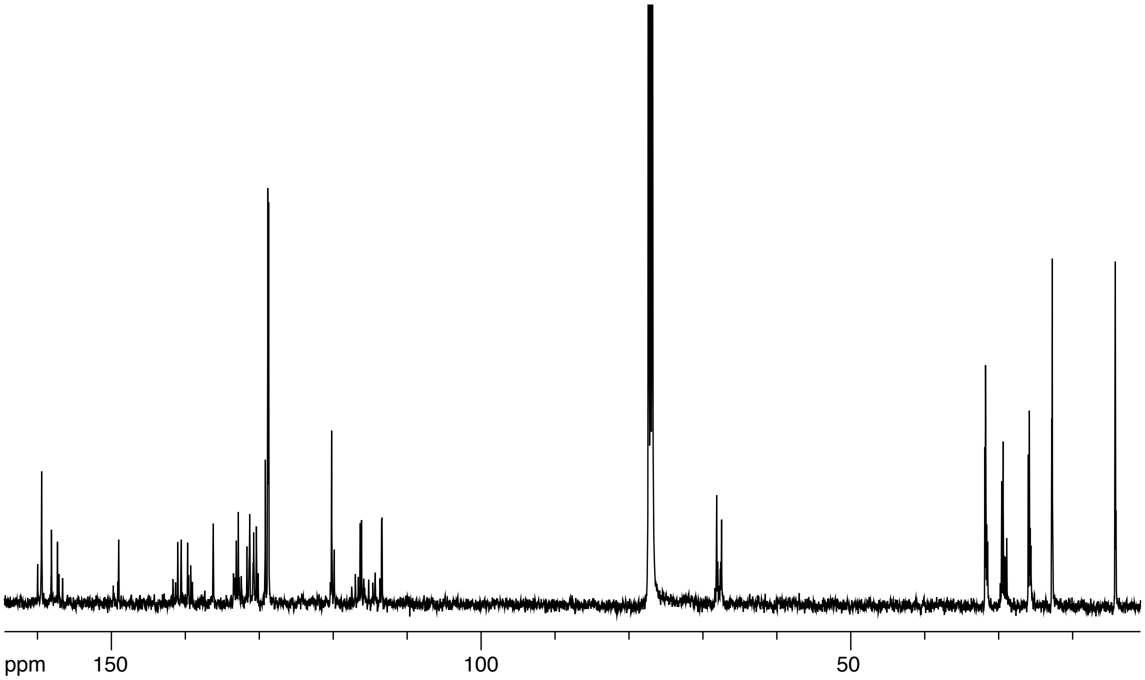


Figure S23. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 0 ℃) of **oP^6(M)**.

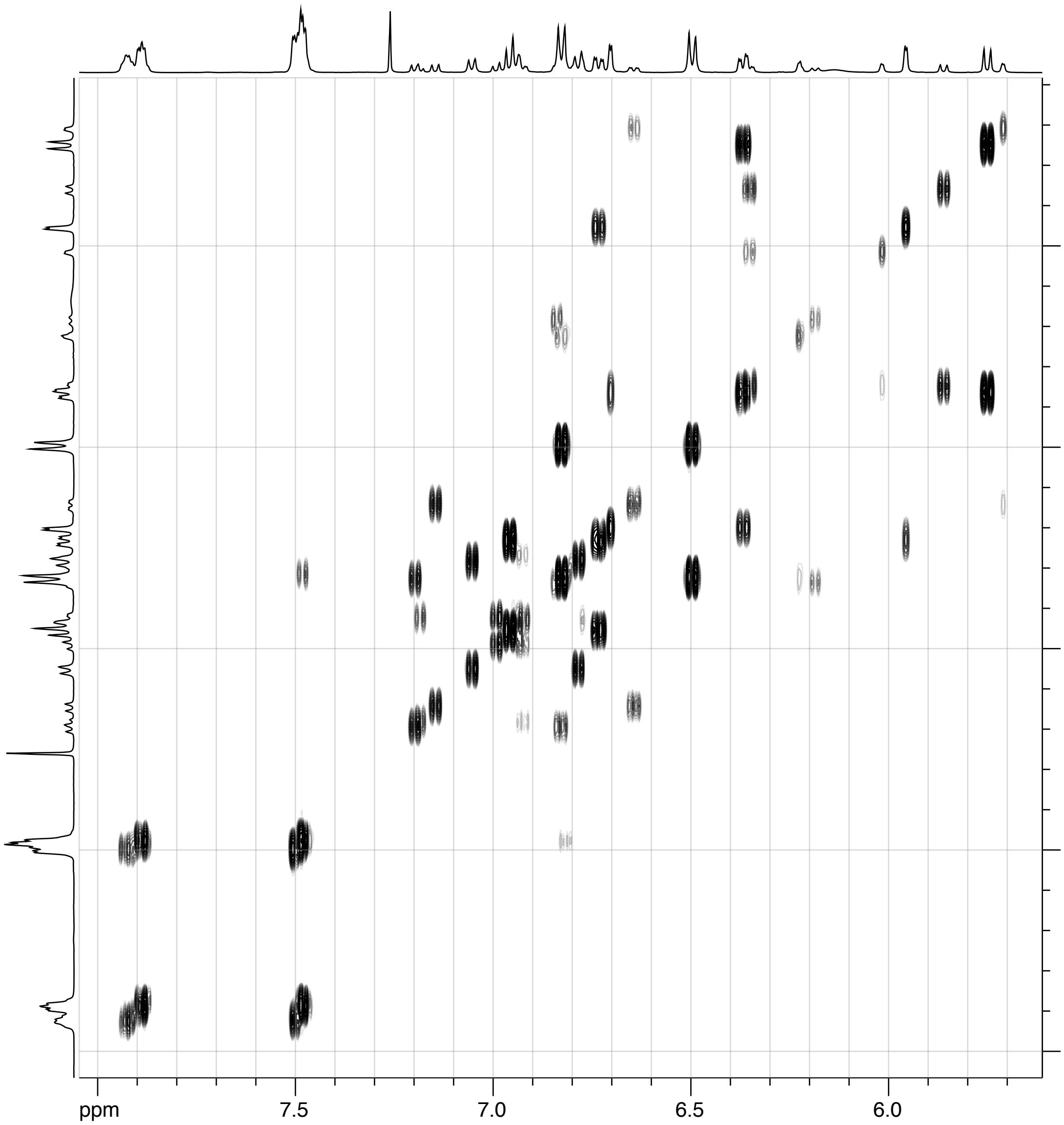


Figure S24. COSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^6(M)$**.

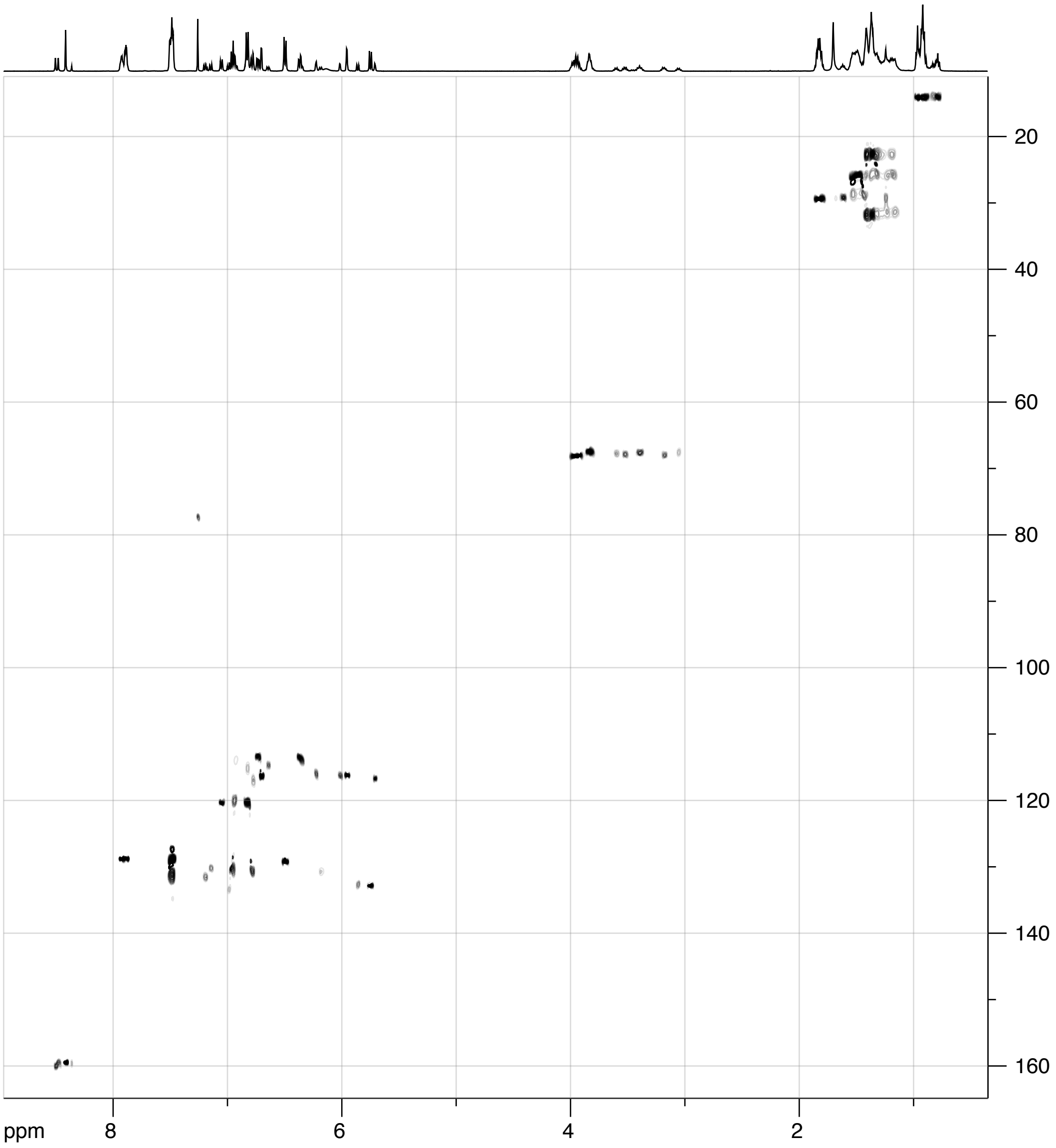


Figure S25. HSQC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^6(M)**.

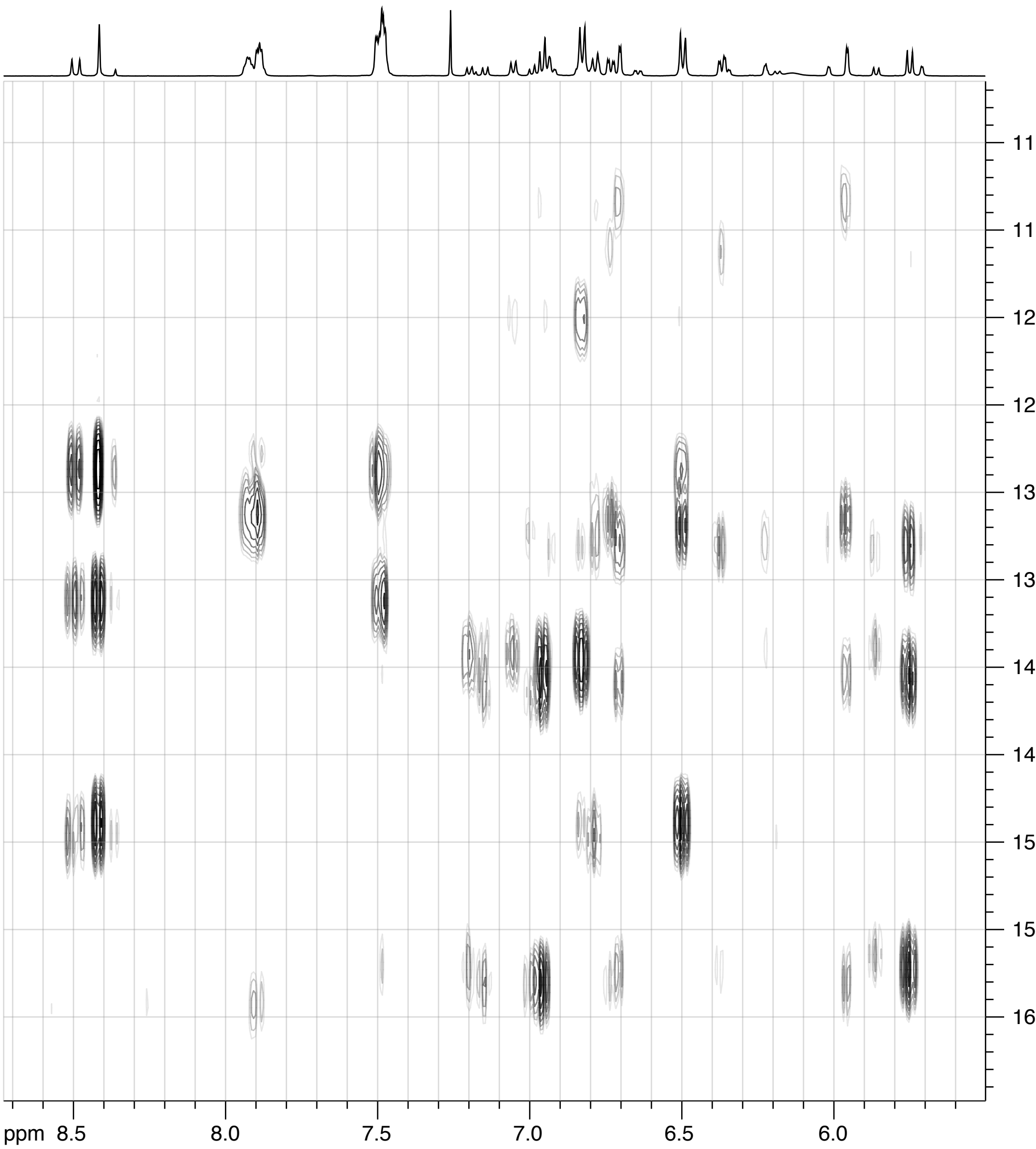


Figure S26. HMBC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^6(M)**.

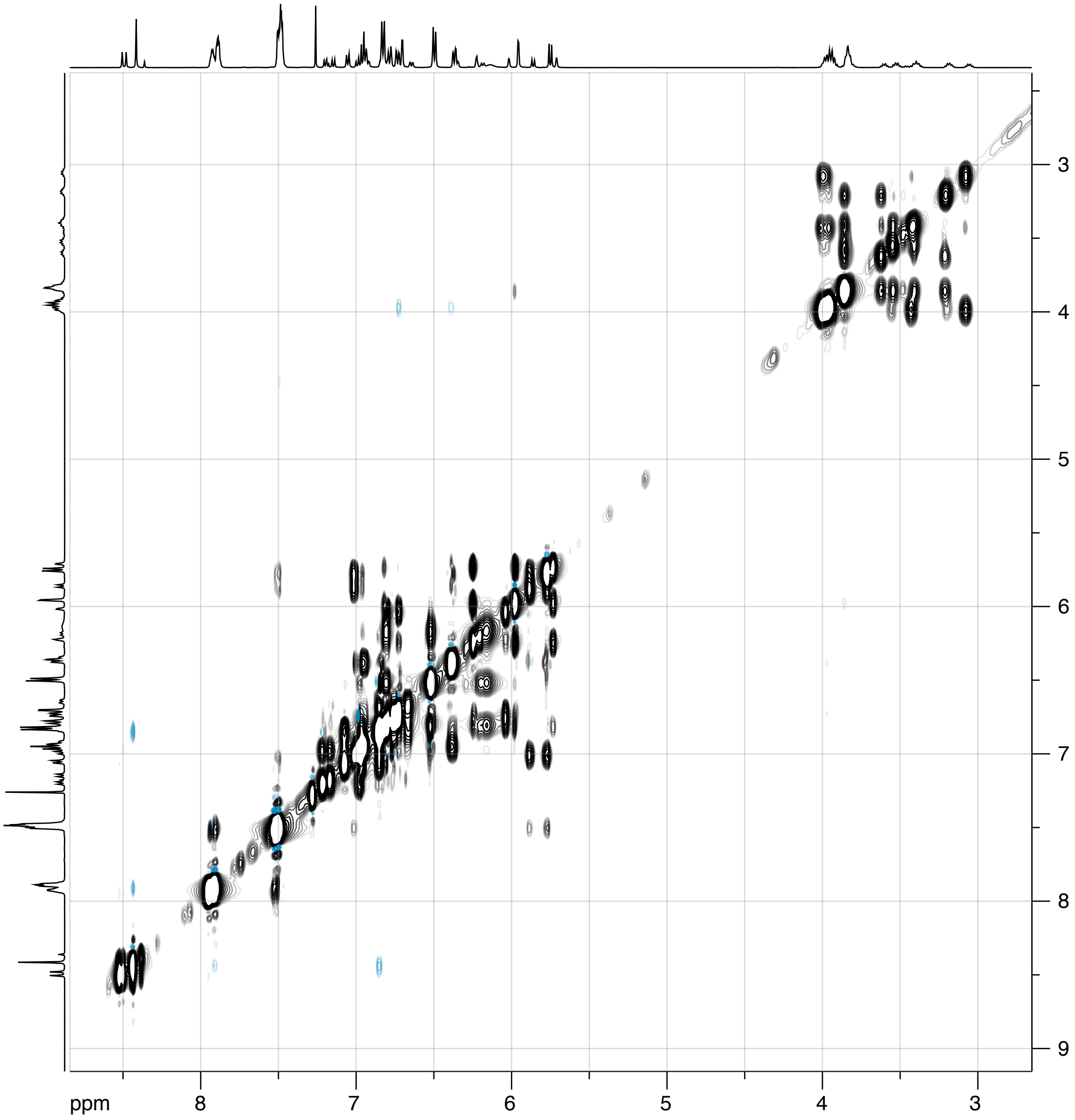


Figure S27. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^6(M)**.

o-Phenylene decamer ***oP^{10}(M)***

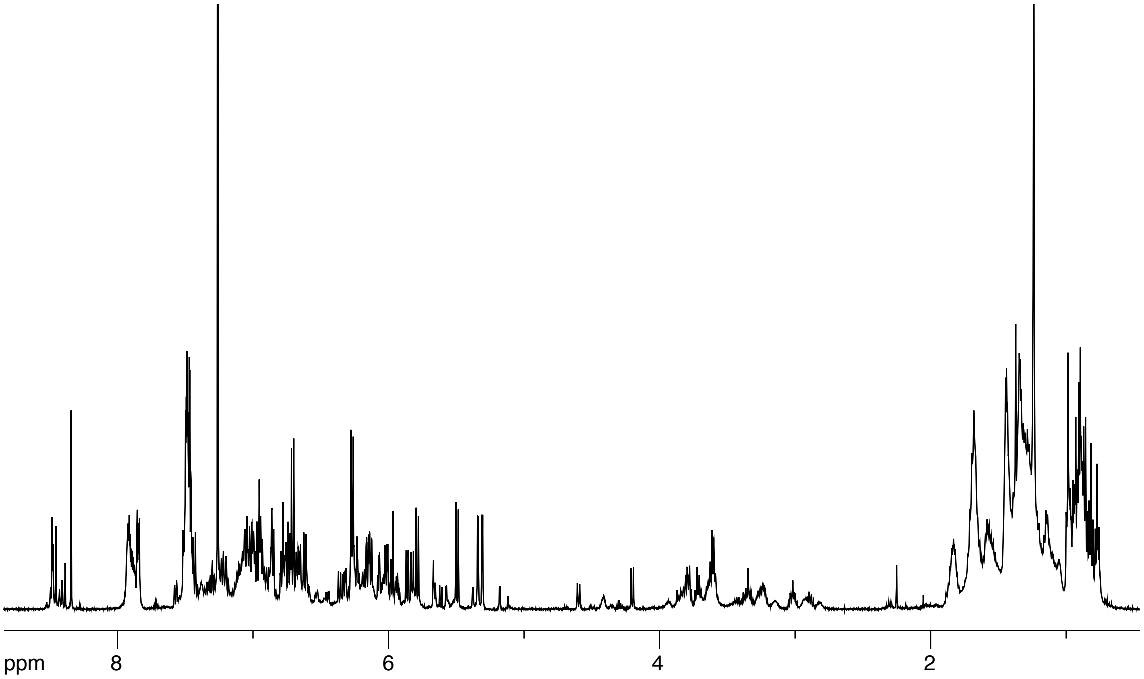


Figure S28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(M)**.

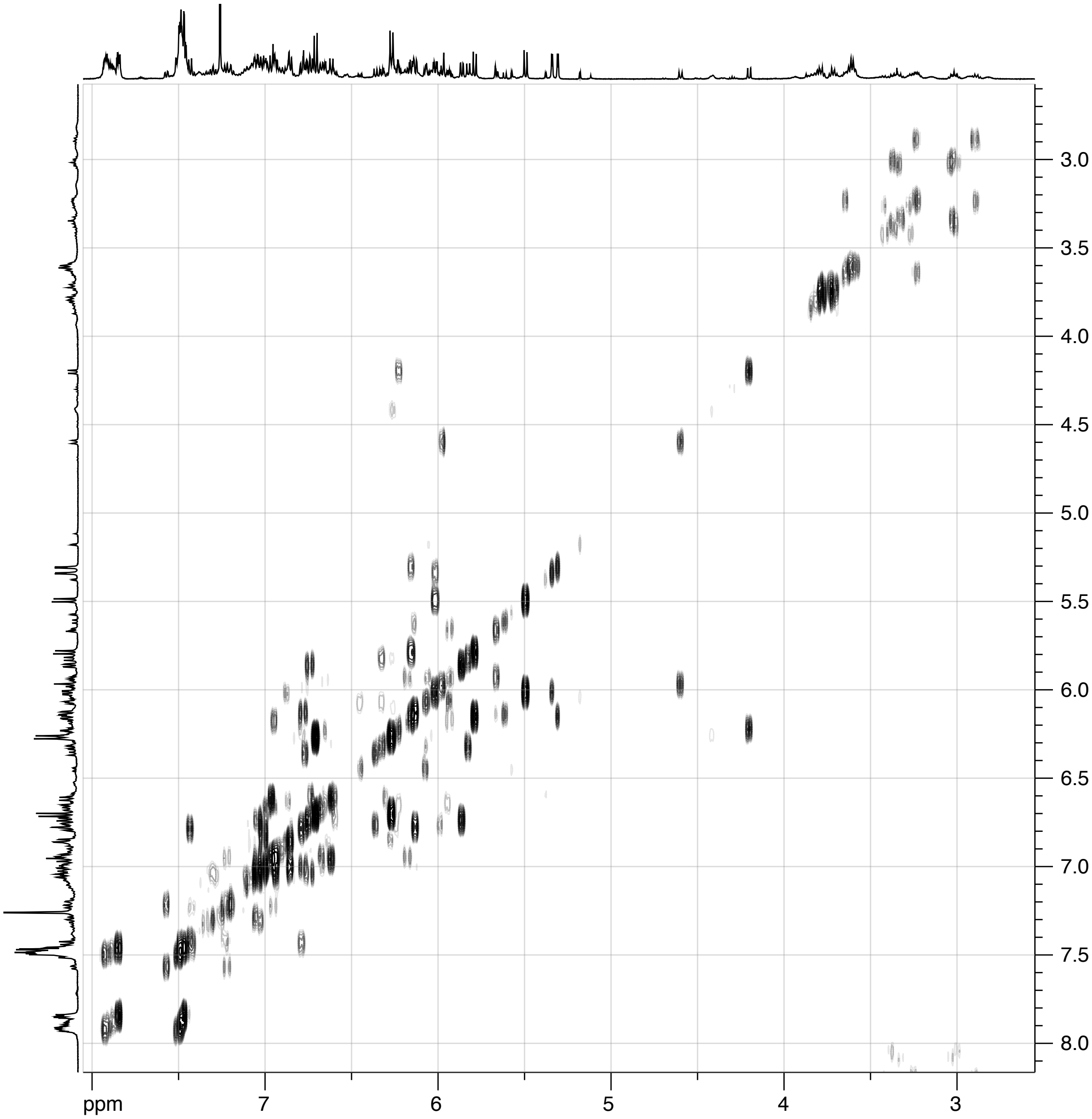


Figure S29. COSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(M)**.

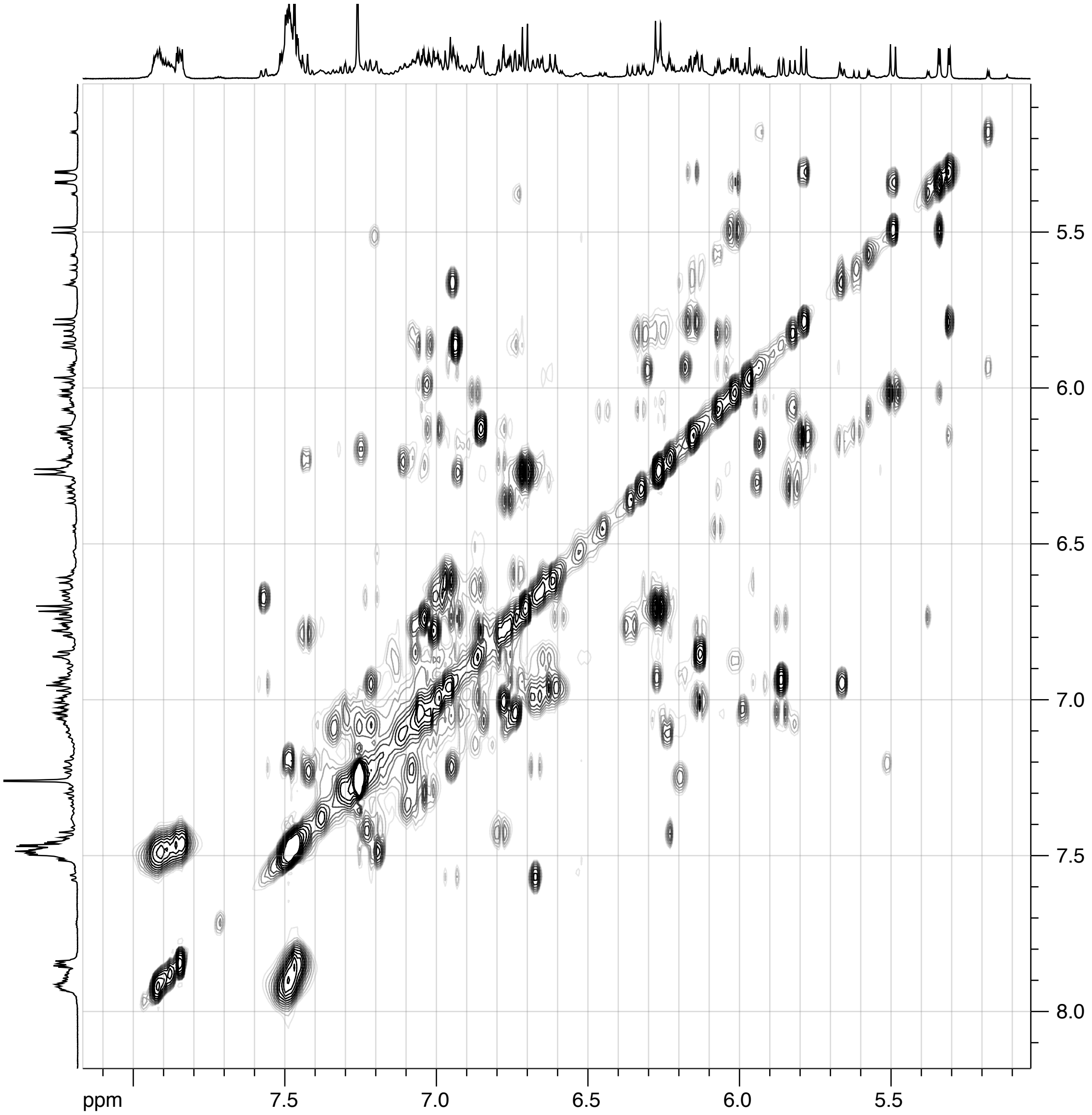


Figure S30. TOCSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(M)$**.

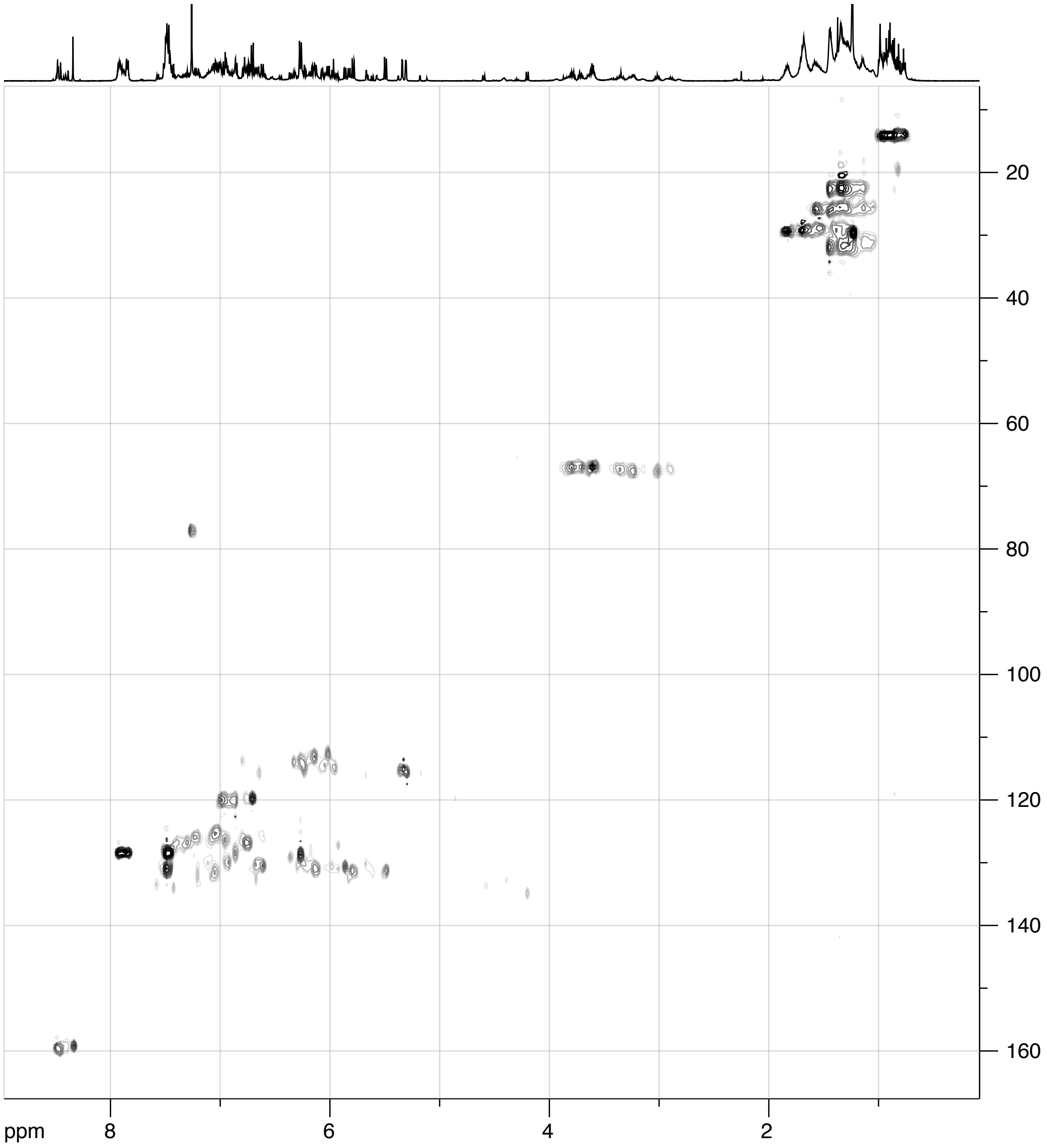


Figure S31. HSQC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(M)**.

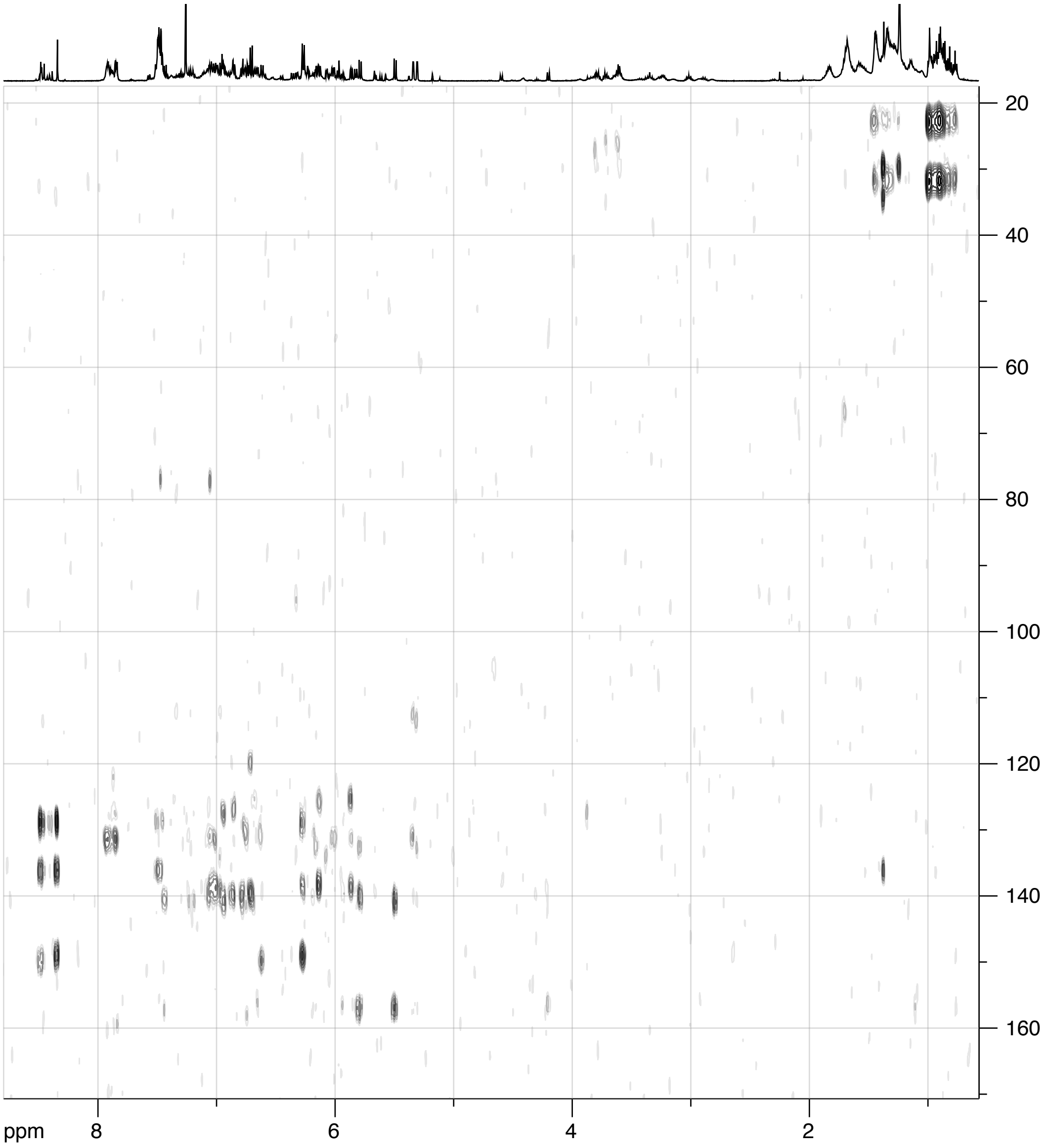


Figure S32. HMBC spectrum (500 MHz, CDCl$_3$, 0 ℃) of **oP^{10}(M)**.

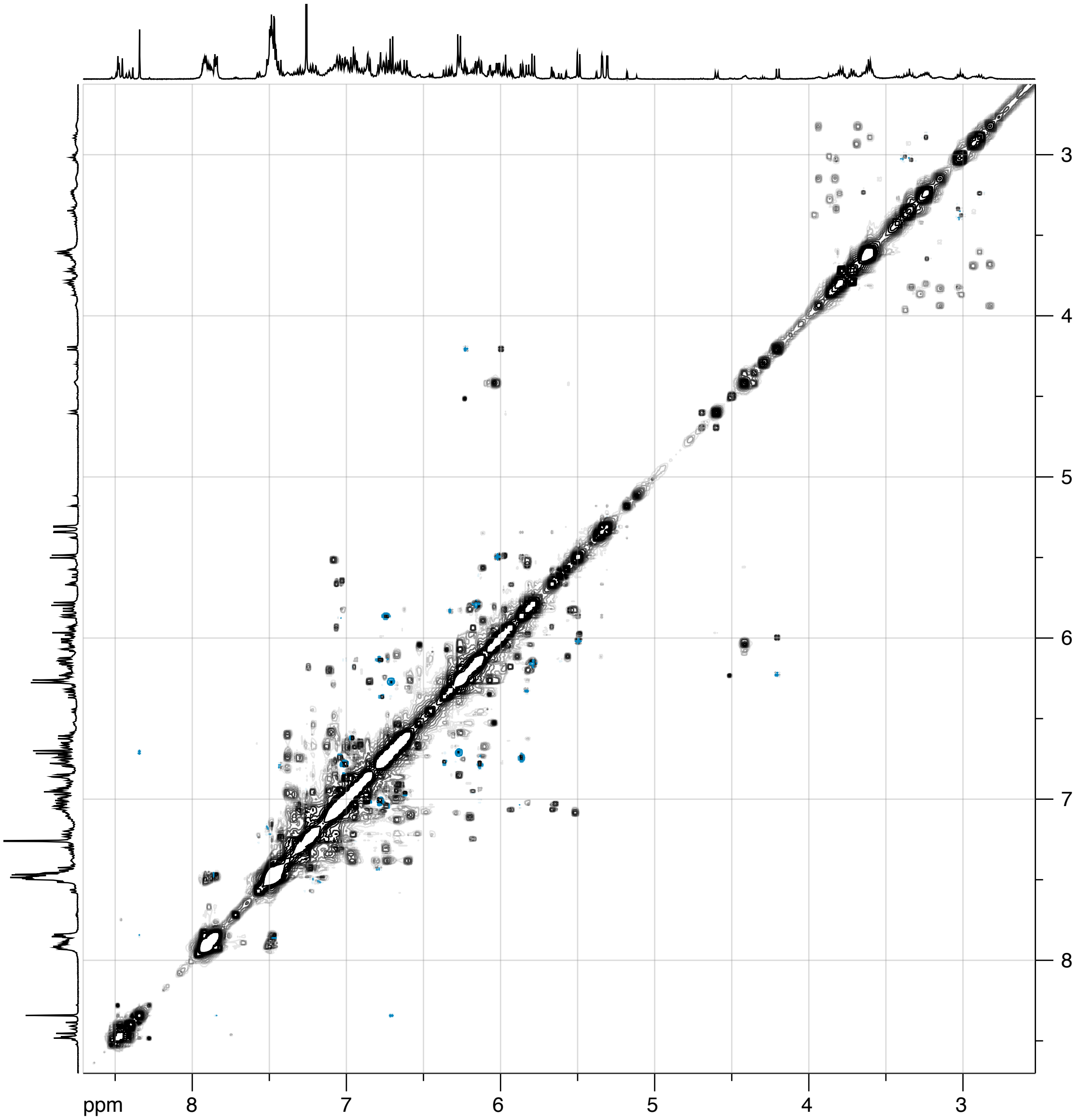


Figure S33. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(M)**.

*Macrocycle **oP^6(Phen)$_{3+3}$***

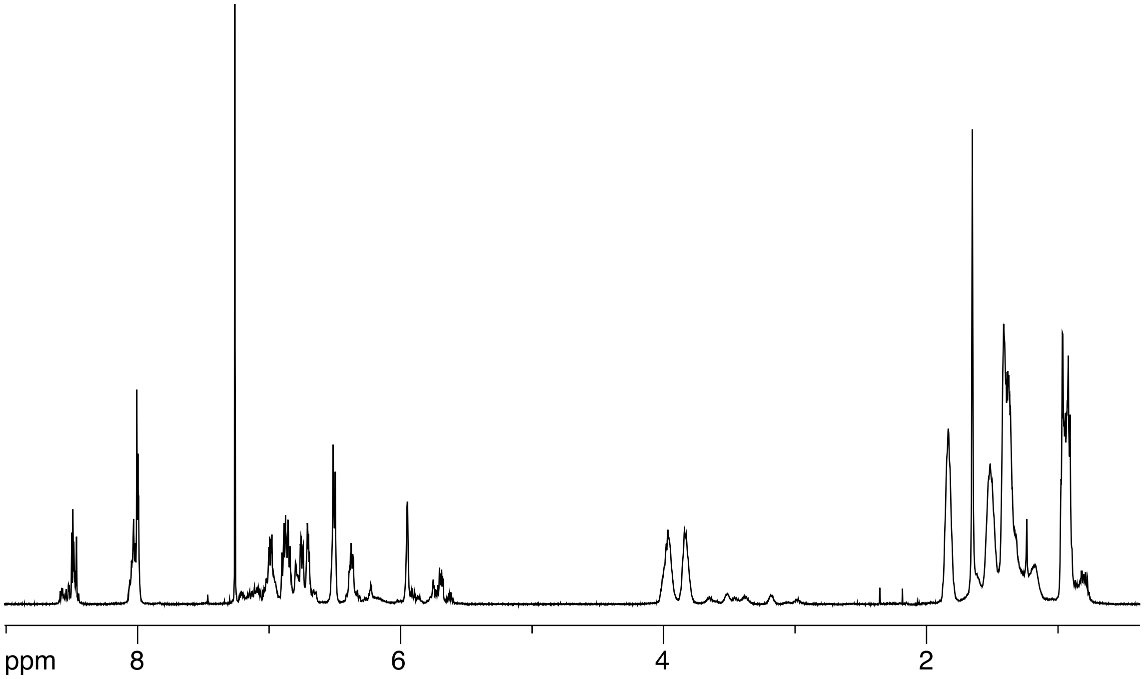


Figure S34. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 0 ℃) of **oP^6(Phen)$_{3+3}$**.

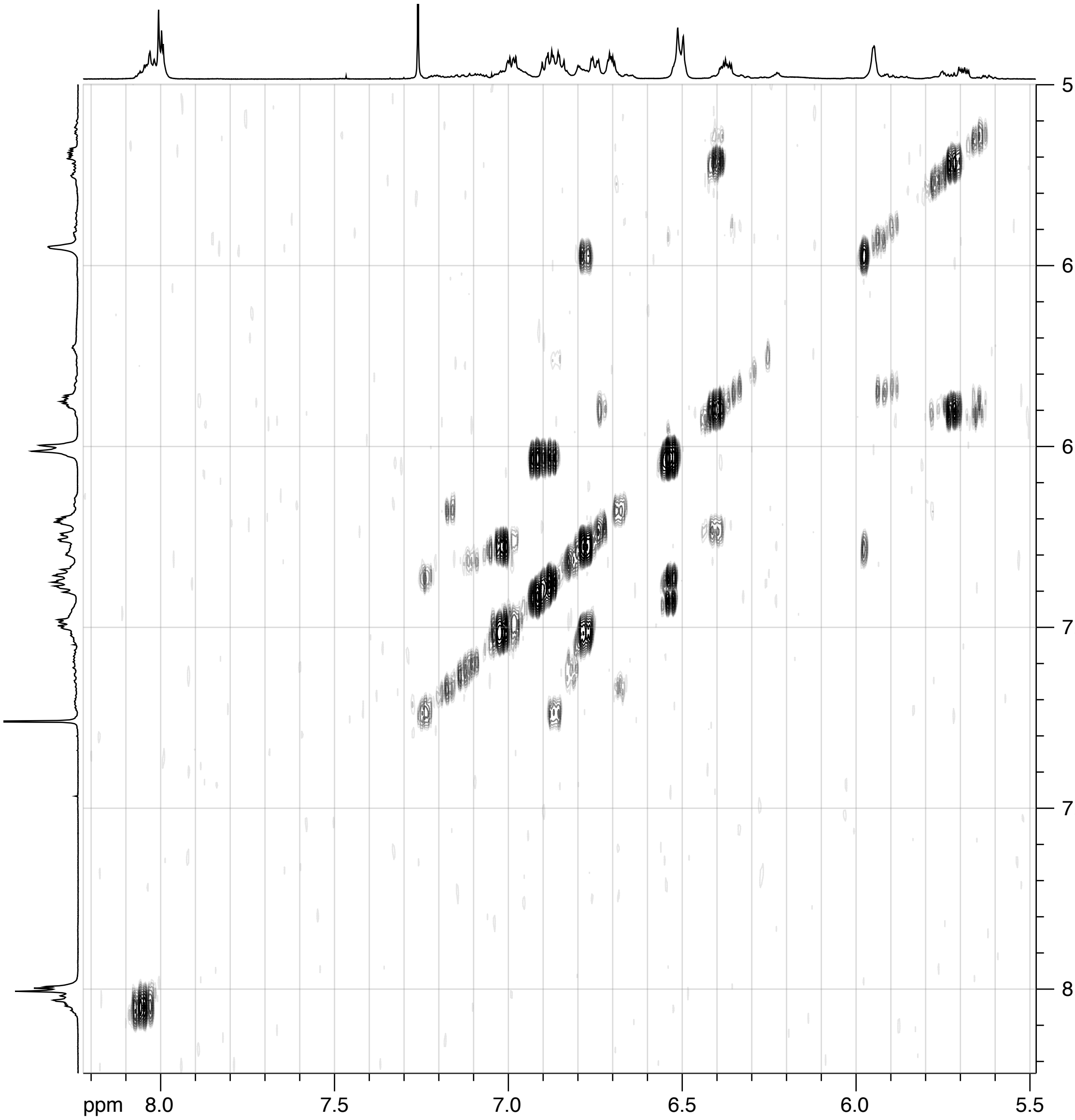


Figure S35. COSY spectrum (500 MHz, CDCl$_3$, 0 ℃) of **oP^6(Phen)$_{3+3}$**.

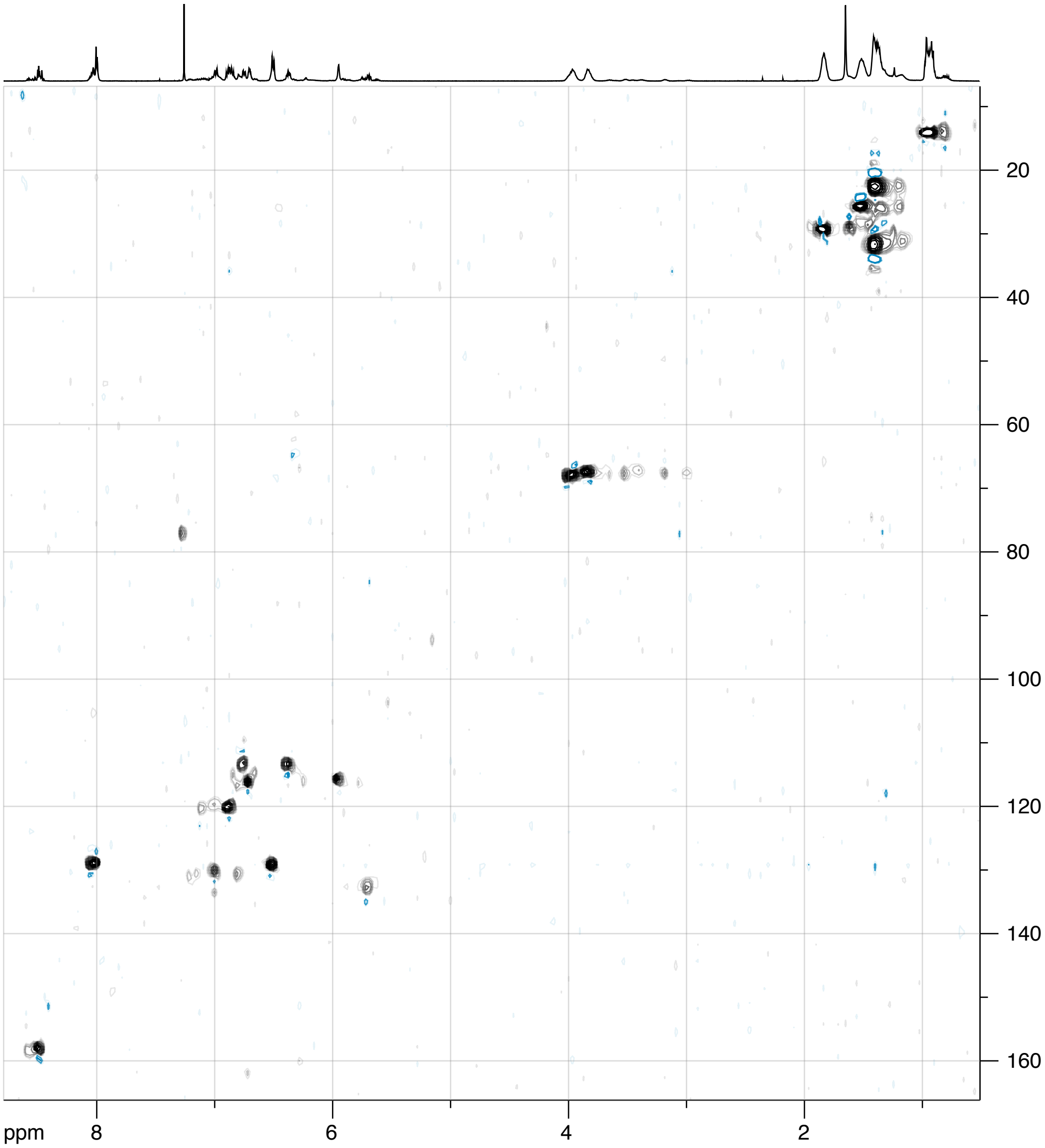


Figure S36. HSQC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^6(Phen)$_{3+3}$**.

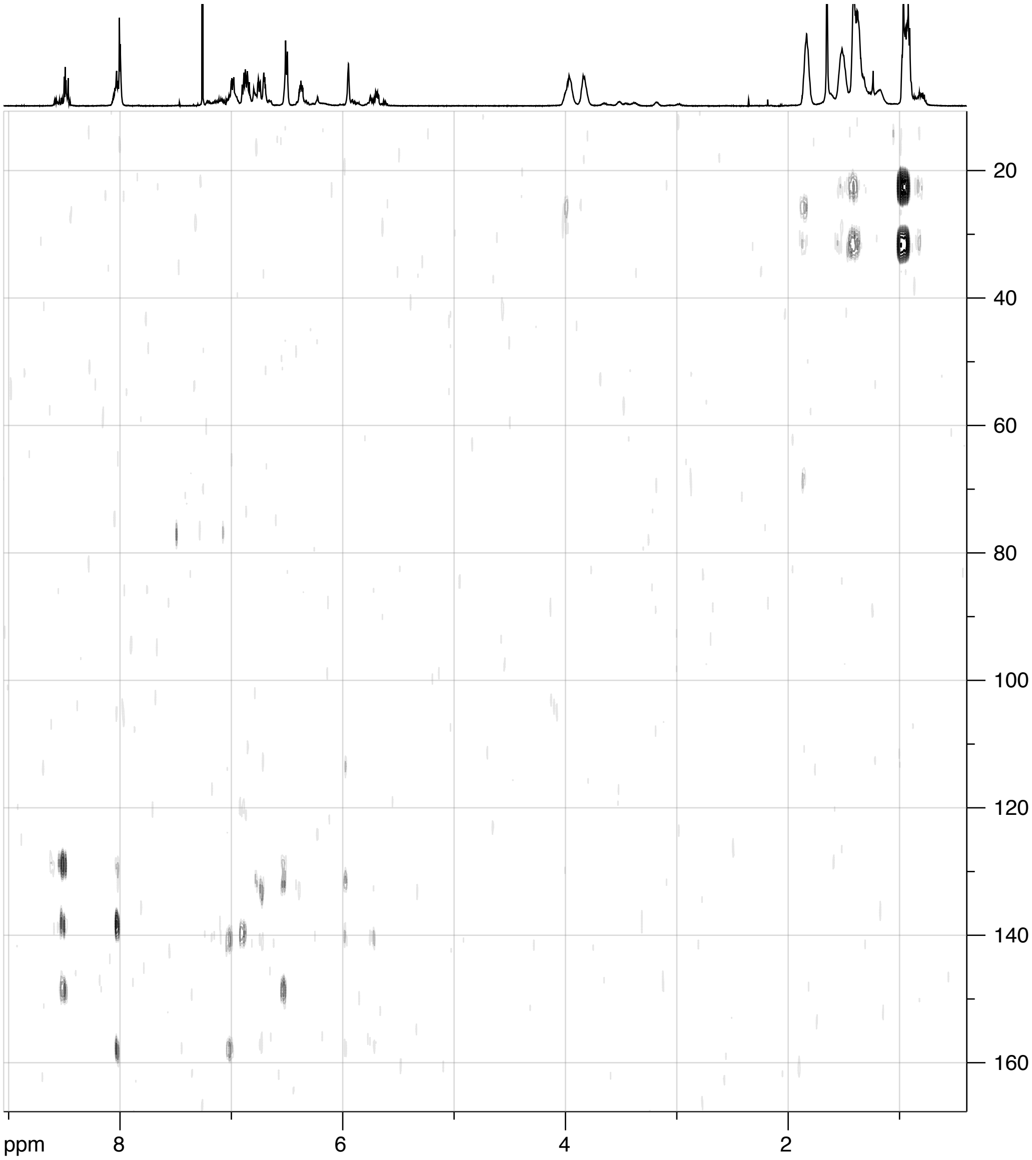


Figure S37. HMBC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^6(Phen)_{3+3}$**.

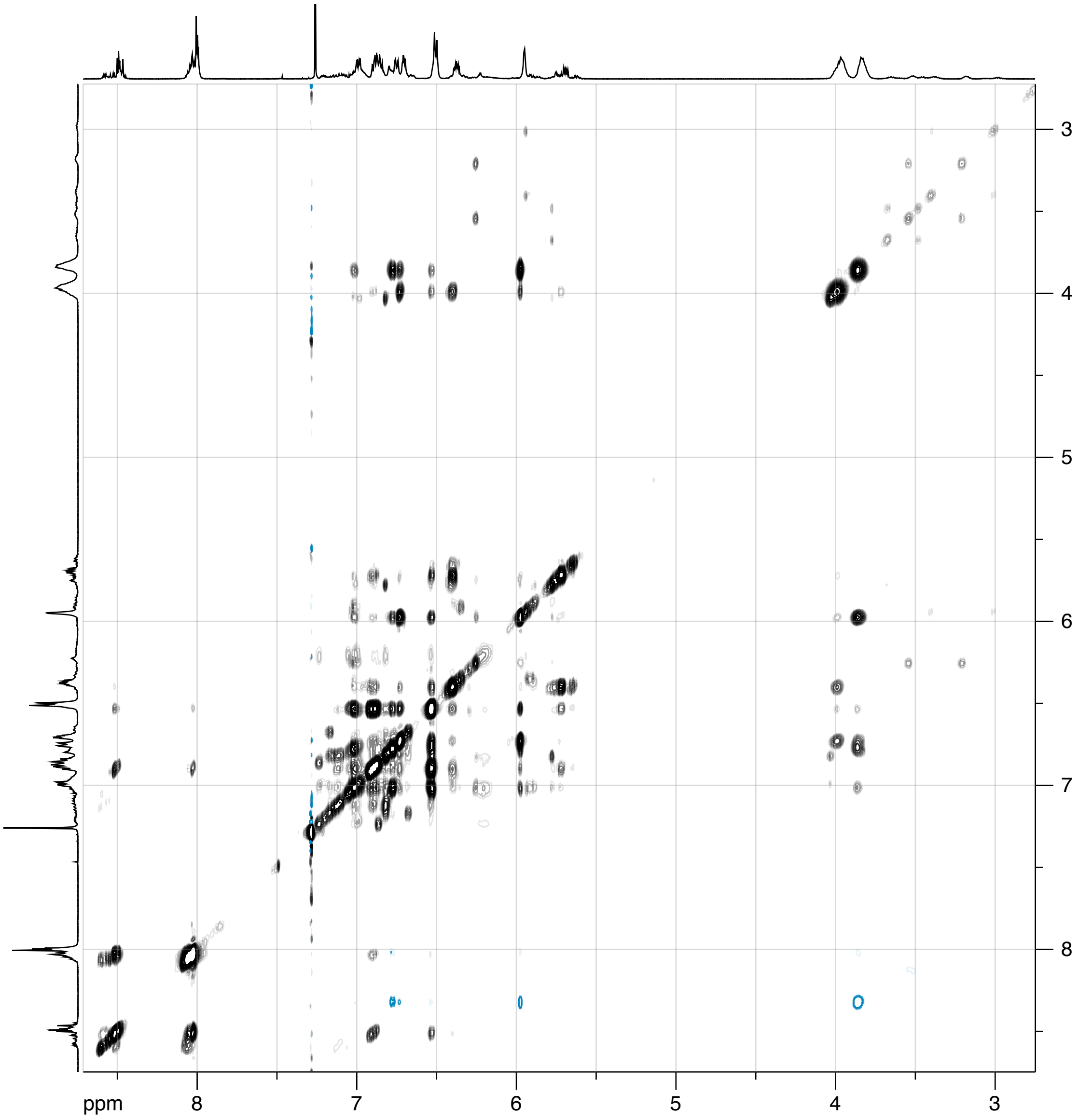


Figure S38. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^6(Phen)_{3+3}$**.

Macrocycle ***oP^{6}(BIP)$_{3+3}$***

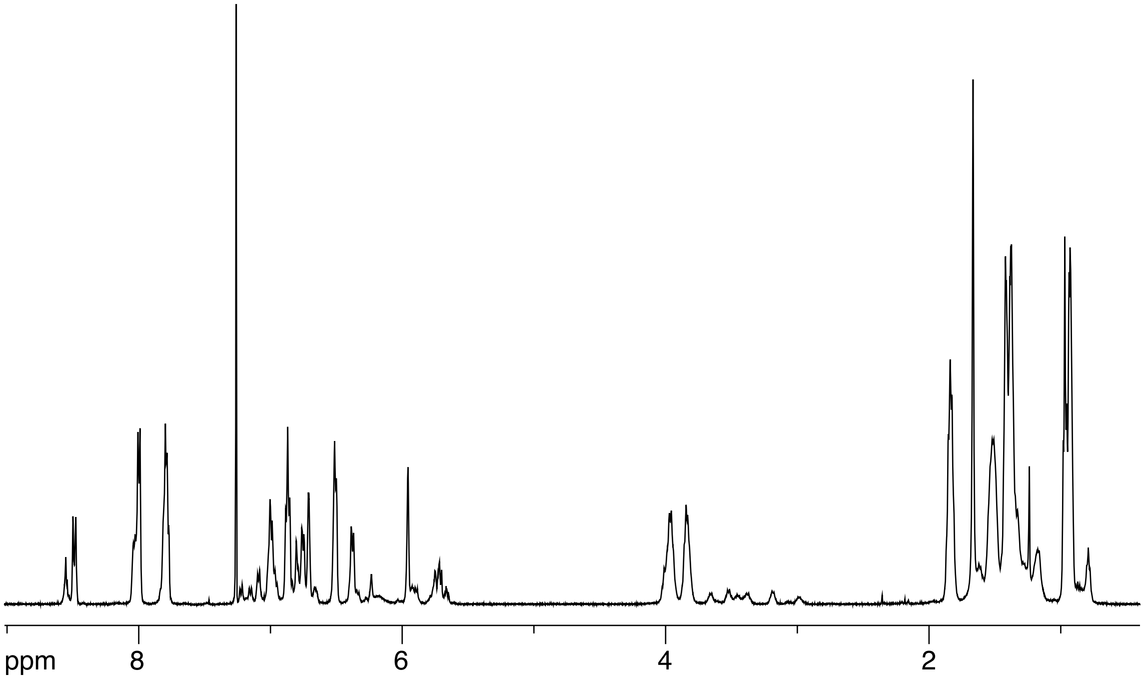


Figure S39. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 0 ℃) of **oP^{6}(BIP)$_{3+3}$**.

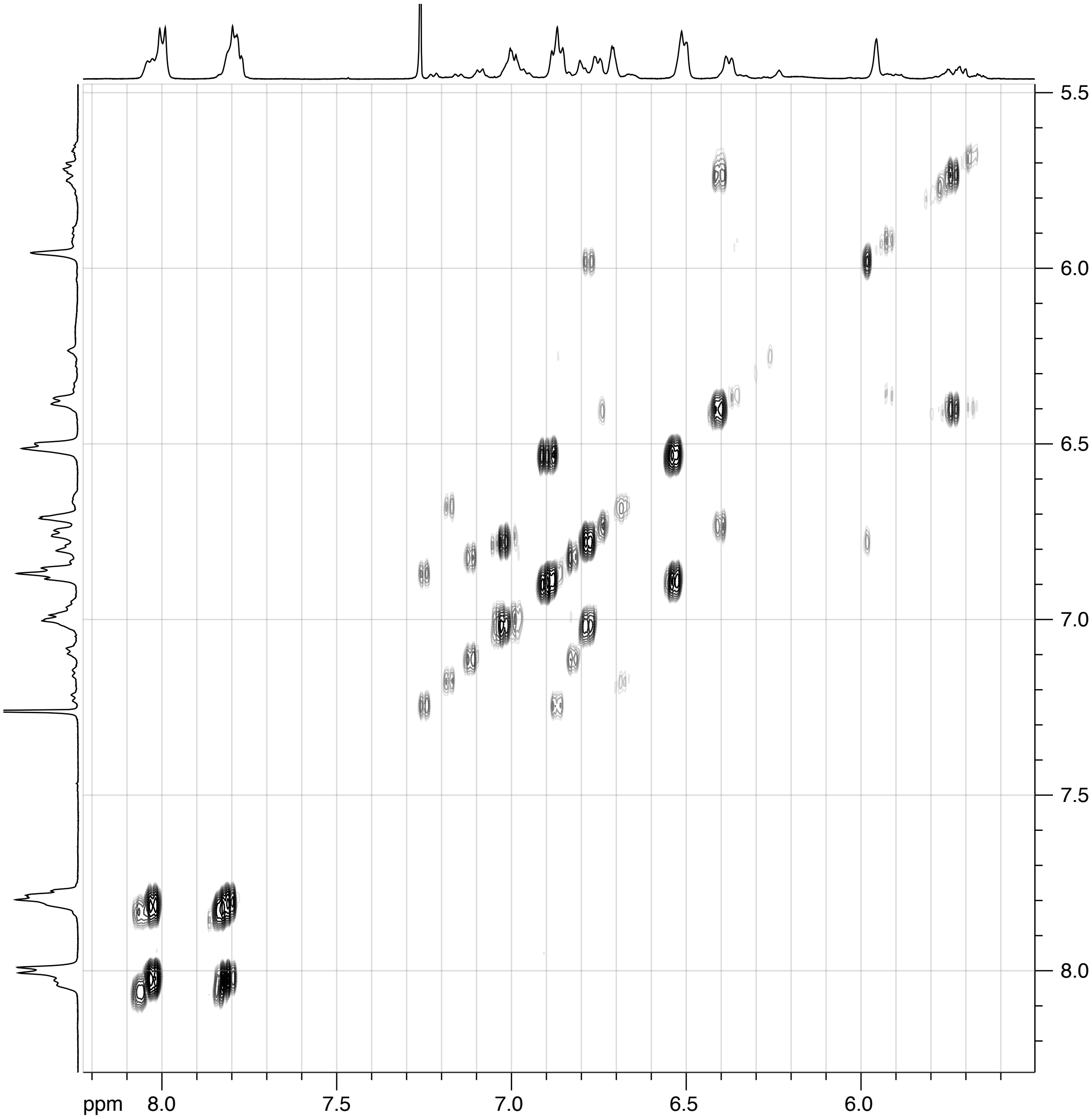


Figure S40. COSY spectrum (500 MHz, $CDCl_3$, 0 °C) of $\mathbf{oP^6(BIP)_{3+3}}$.

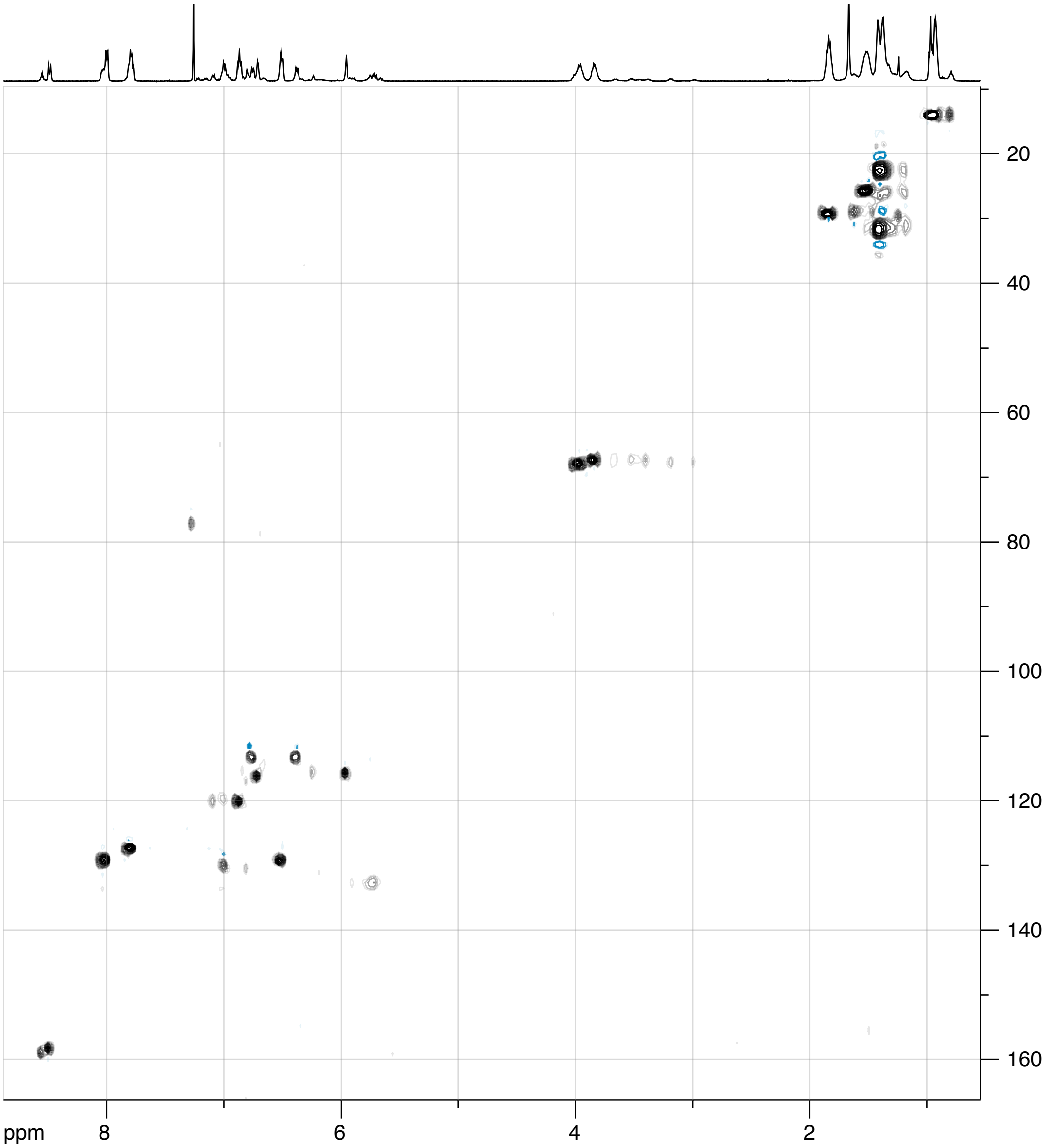


Figure S41. HSQC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^6(BIP)_{3+3}$**.

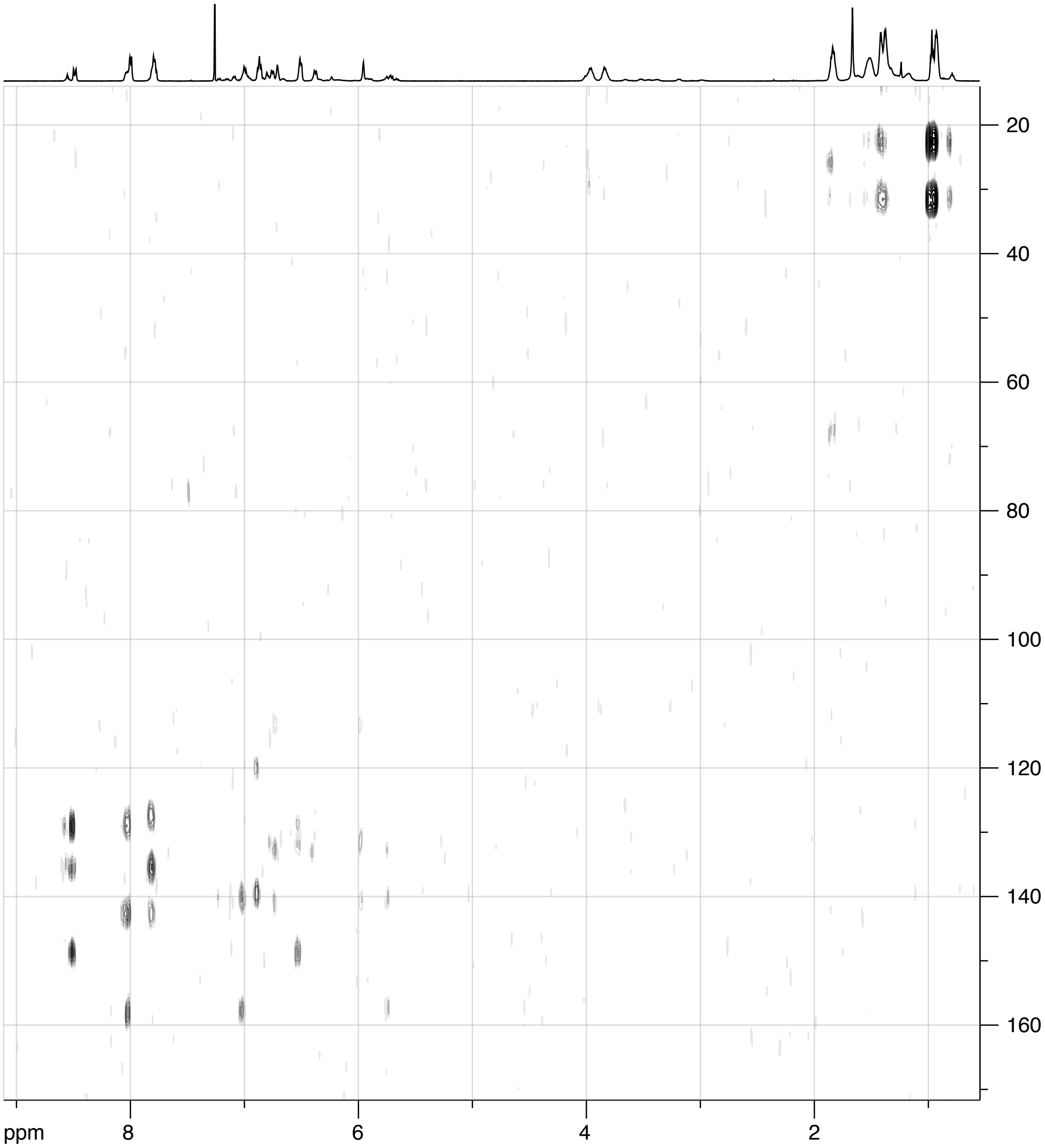


Figure S42. HMBC spectrum (500 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^6(BIP)_{3+3}}$.

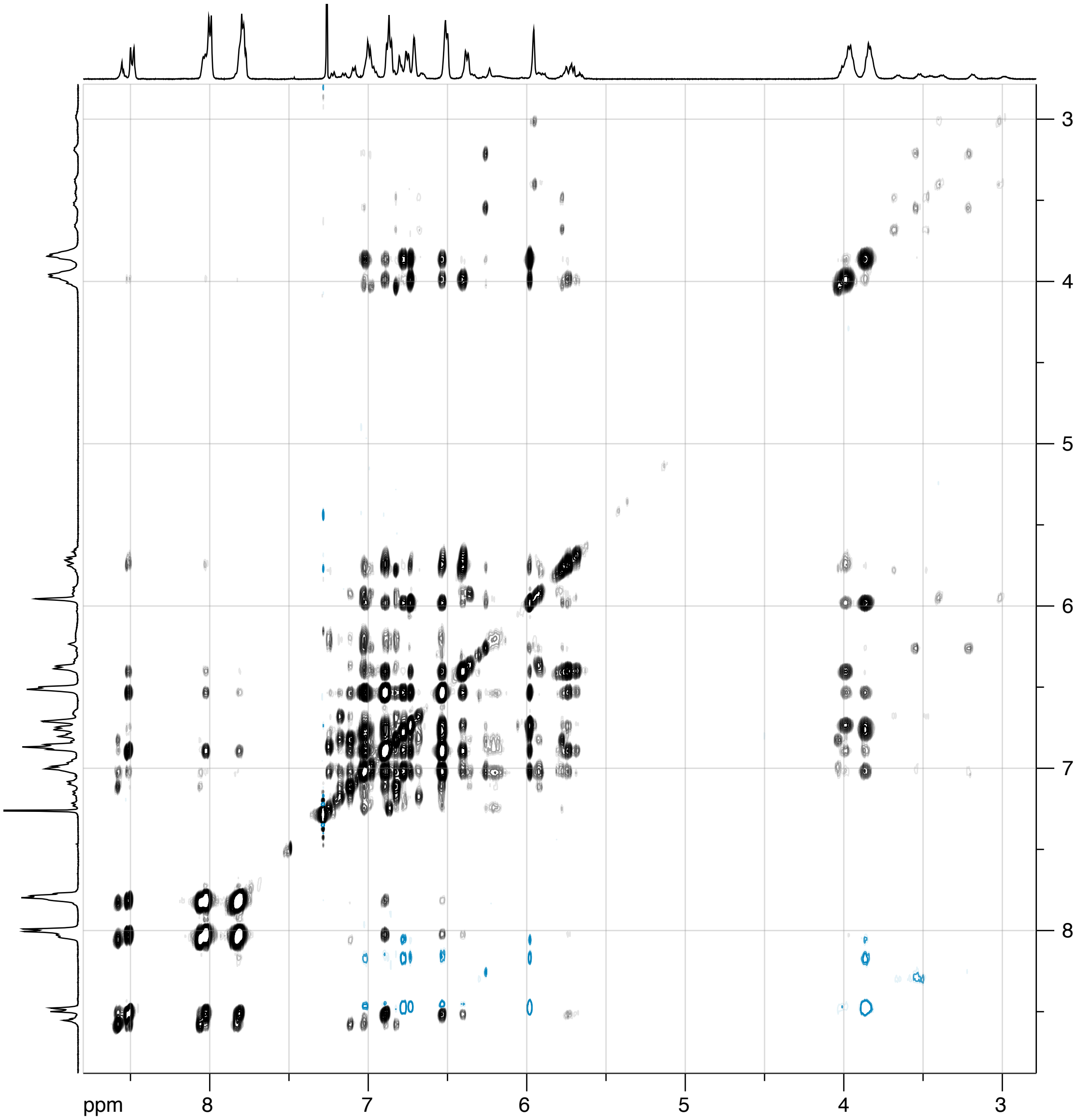


Figure S43. NOESY/EXSY spectrum (500 MHz, CDCl$_3$, 0 ℃) of $\mathbf{oP^6(BIP)_{3+3}}$.

Macrocycle ***oP^{6}(DPB)$_{3+3}$***

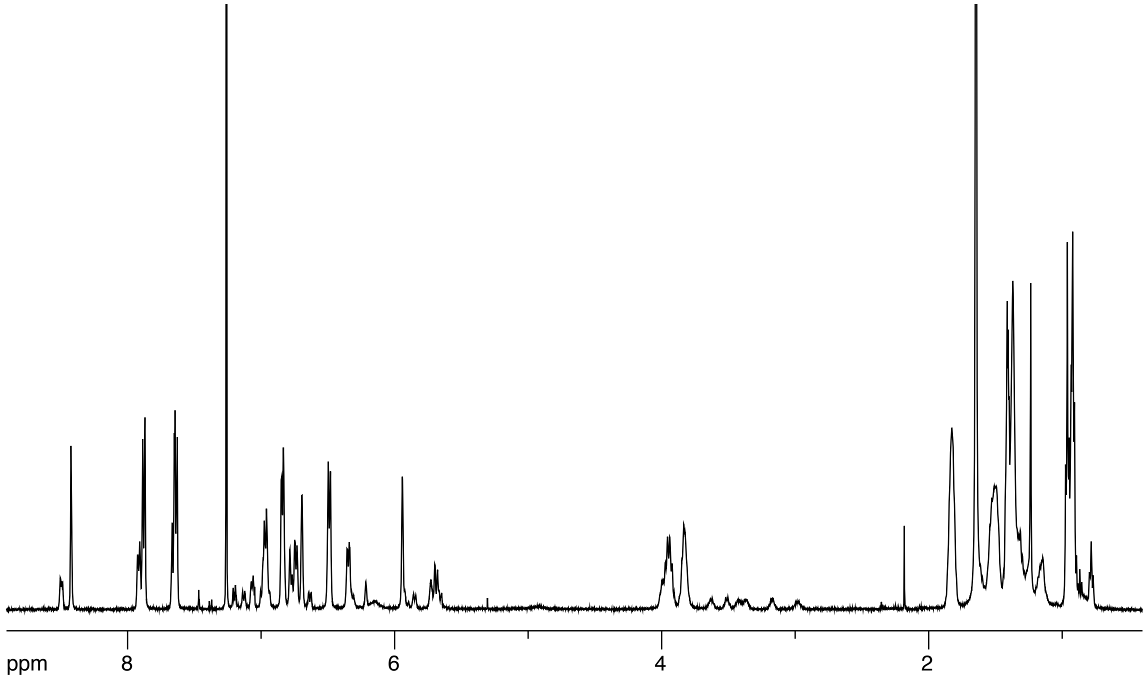


Figure S44. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{6}(DPB)$_{3+3}$**.

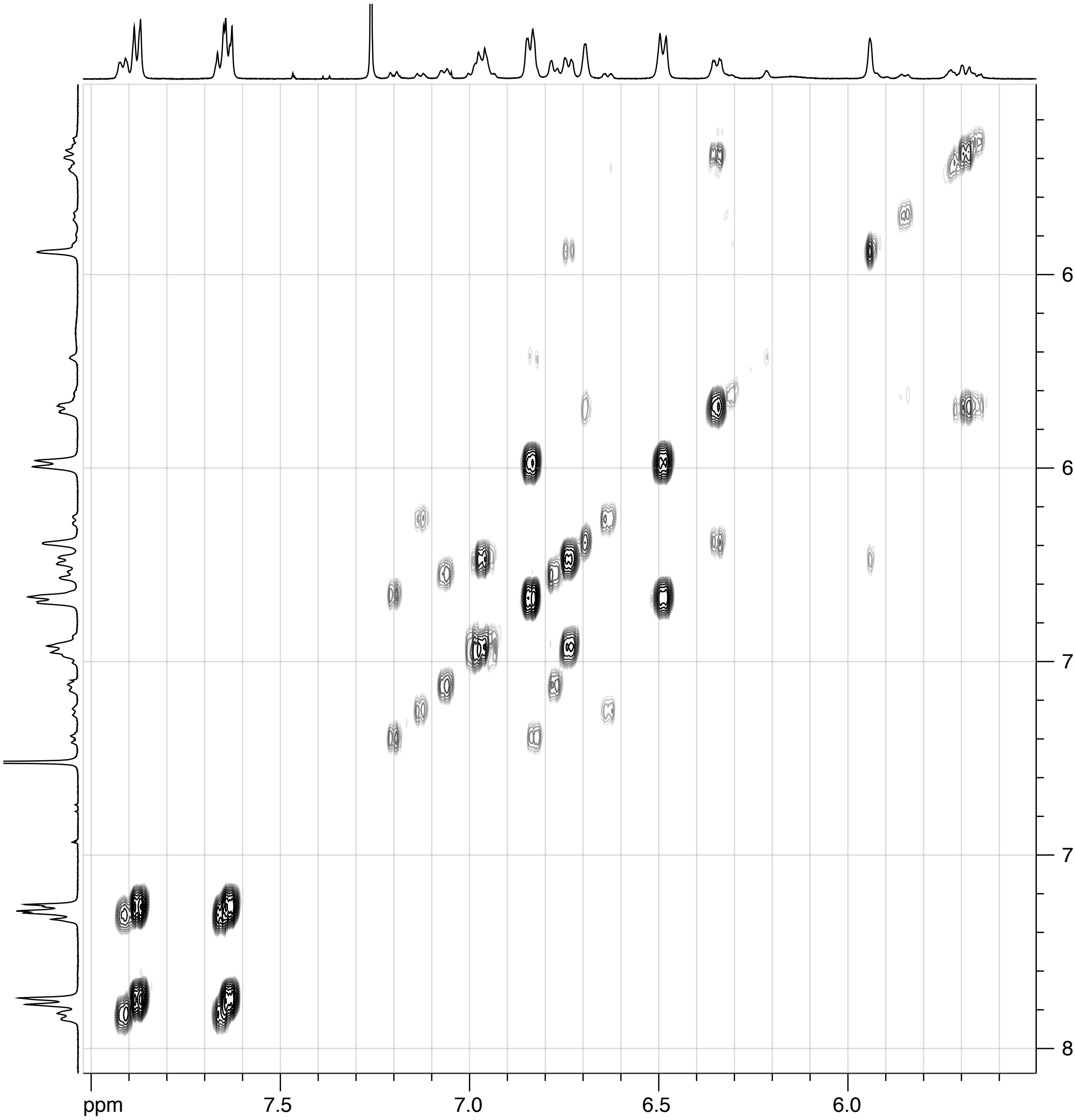


Figure S45. COSY spectrum (500 MHz, $CDCl_3$, 0 °C) of $\mathbf{oP^6(DPB)_{3+3}}$.

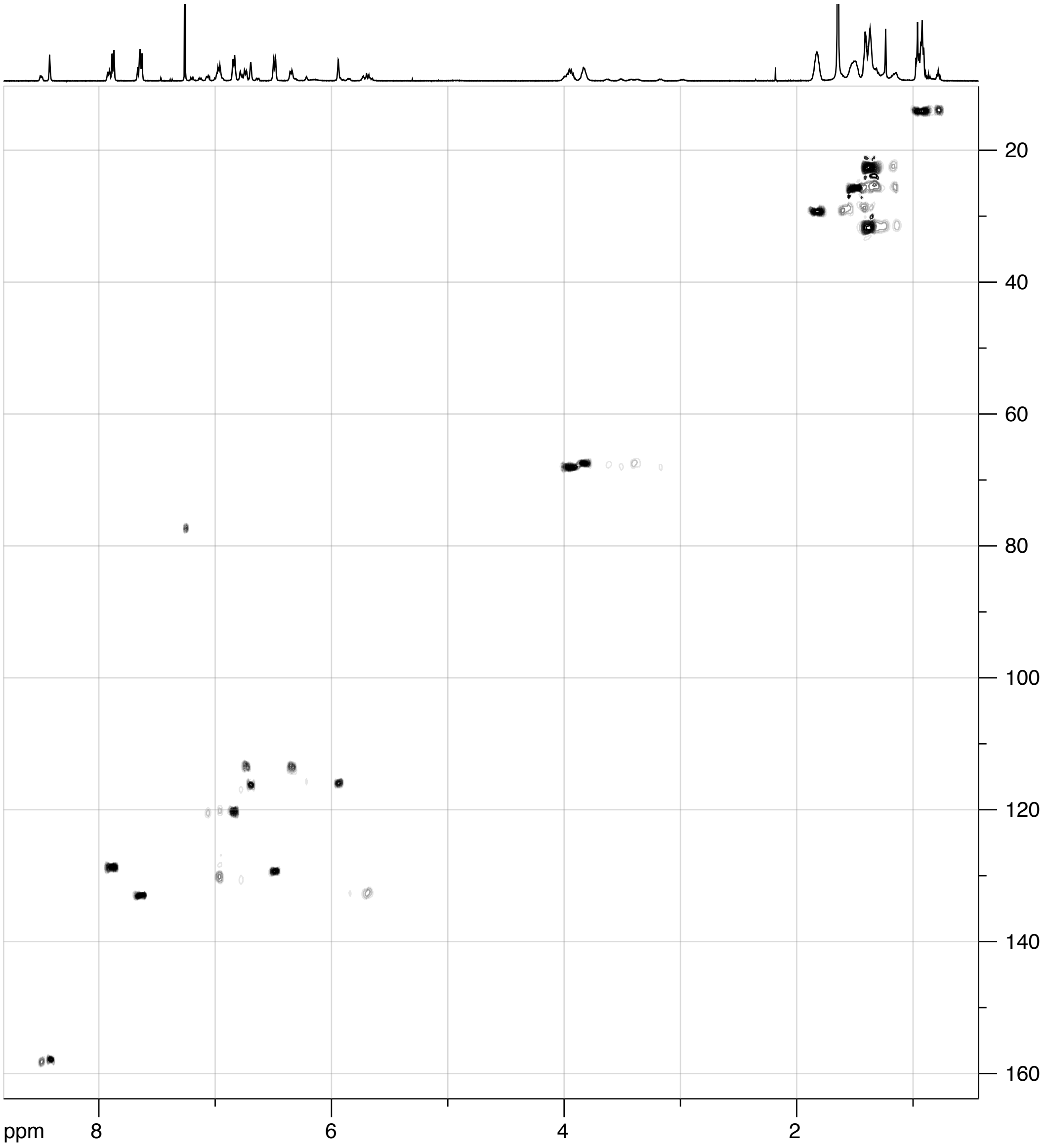


Figure S46. HSQC spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^6(DPB)$_{3+3}$**.

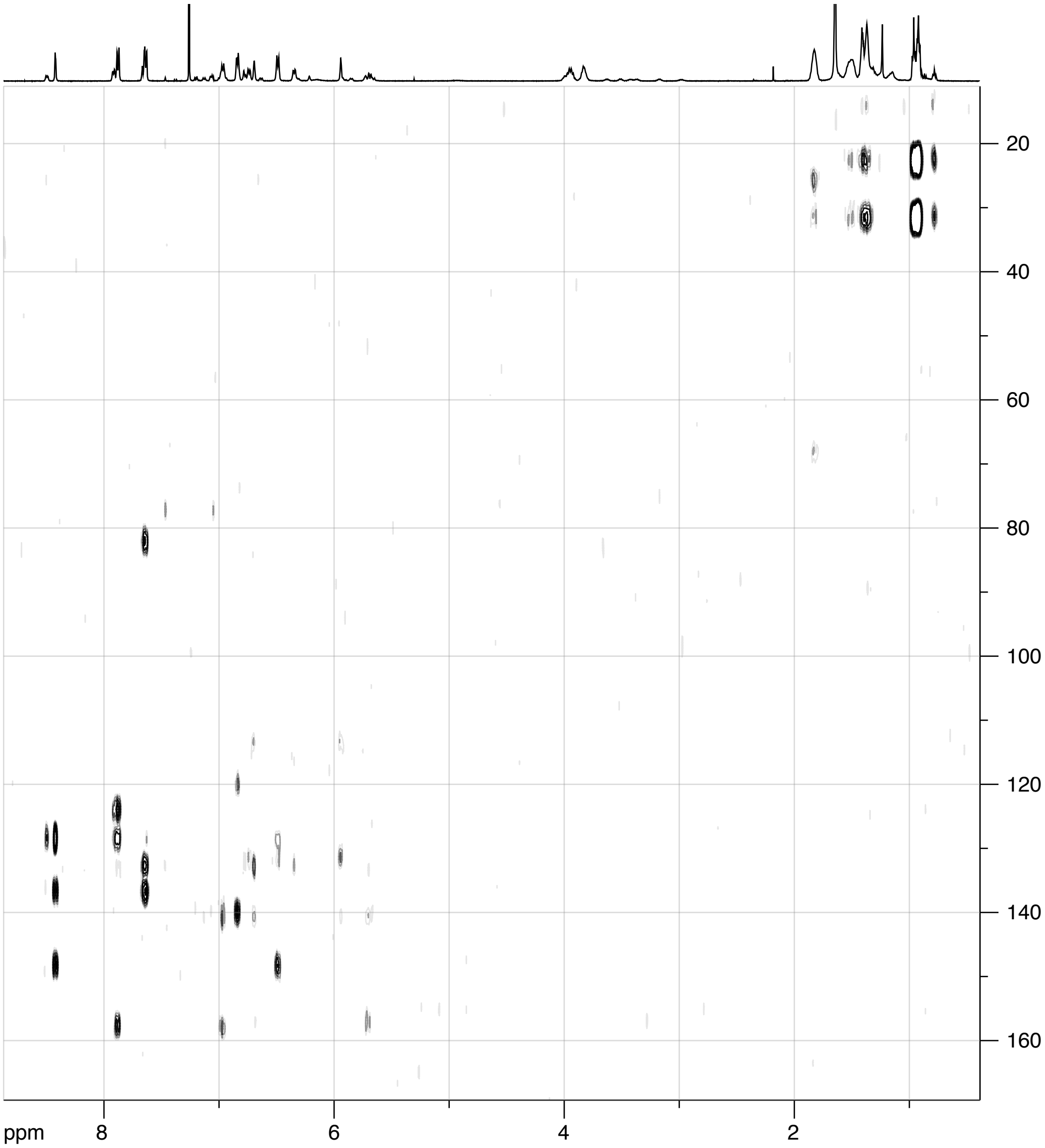


Figure S47. HMBC spectrum (500 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^6(DPB)_{3+3}}$.

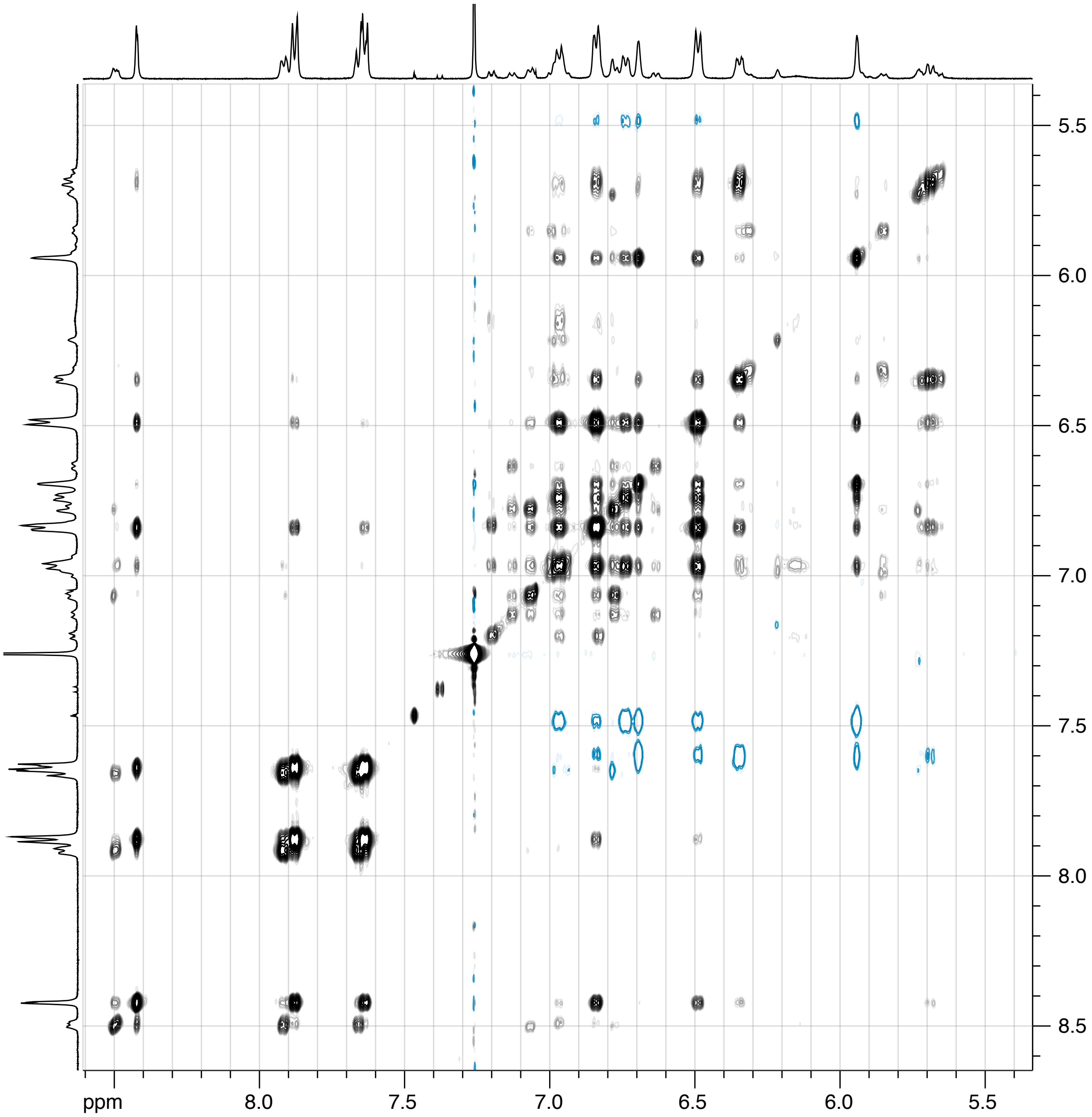


Figure S48. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^6(DPB)$_{3+3}$**.

Macrocycle ***oP^{10}(Phen)$_{2+2}$***

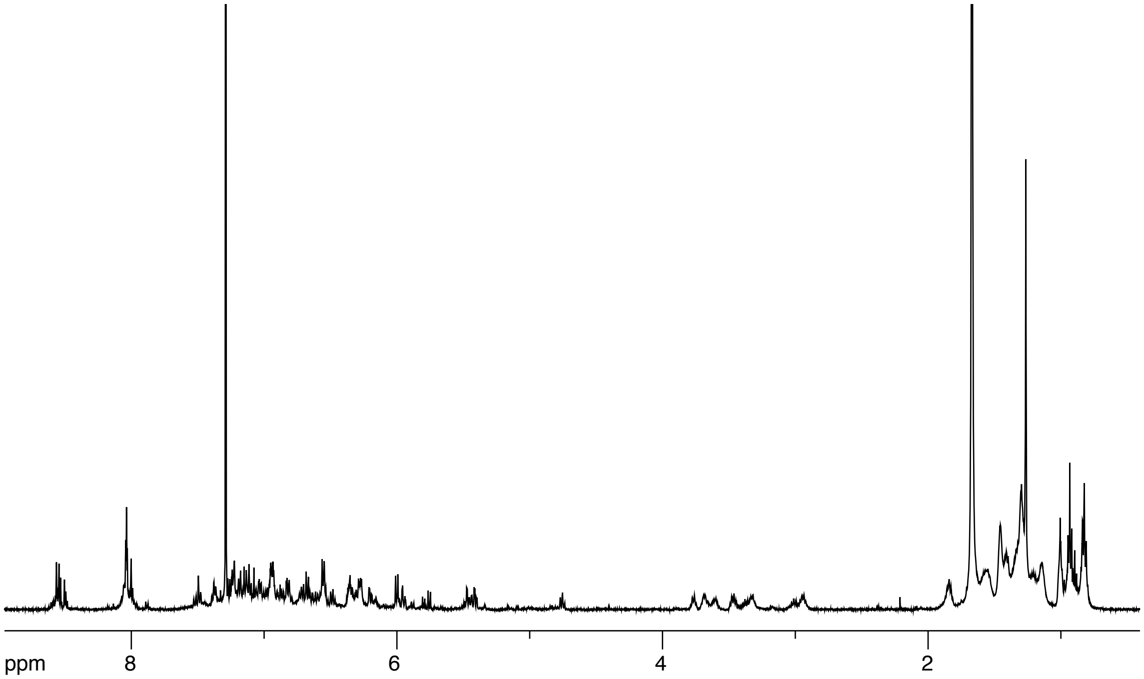


Figure S49. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(Phen)$_{2+2}$**.

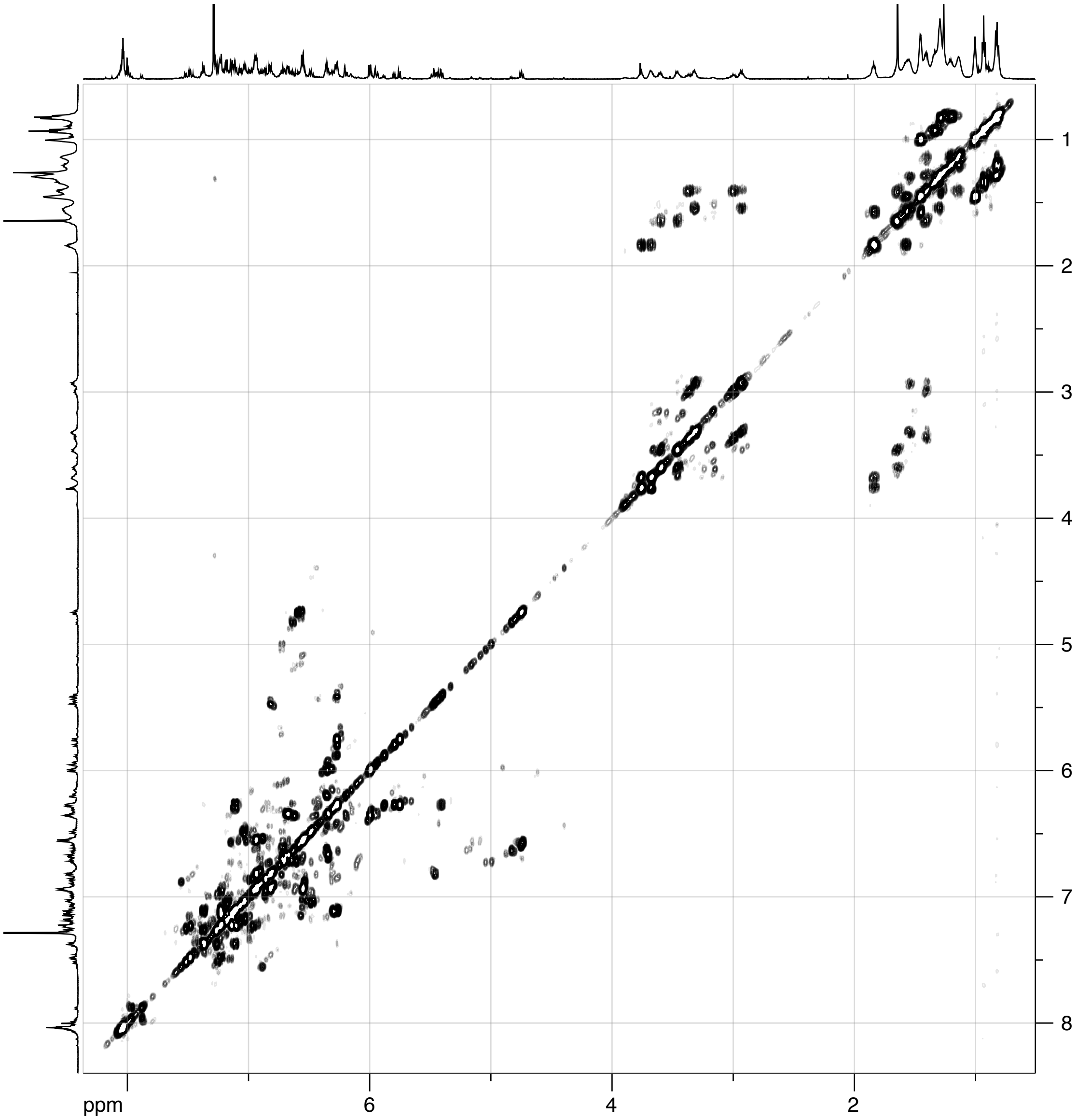


Figure S50. COSY spectrum (600 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(Phen)**$_{2+2}$.

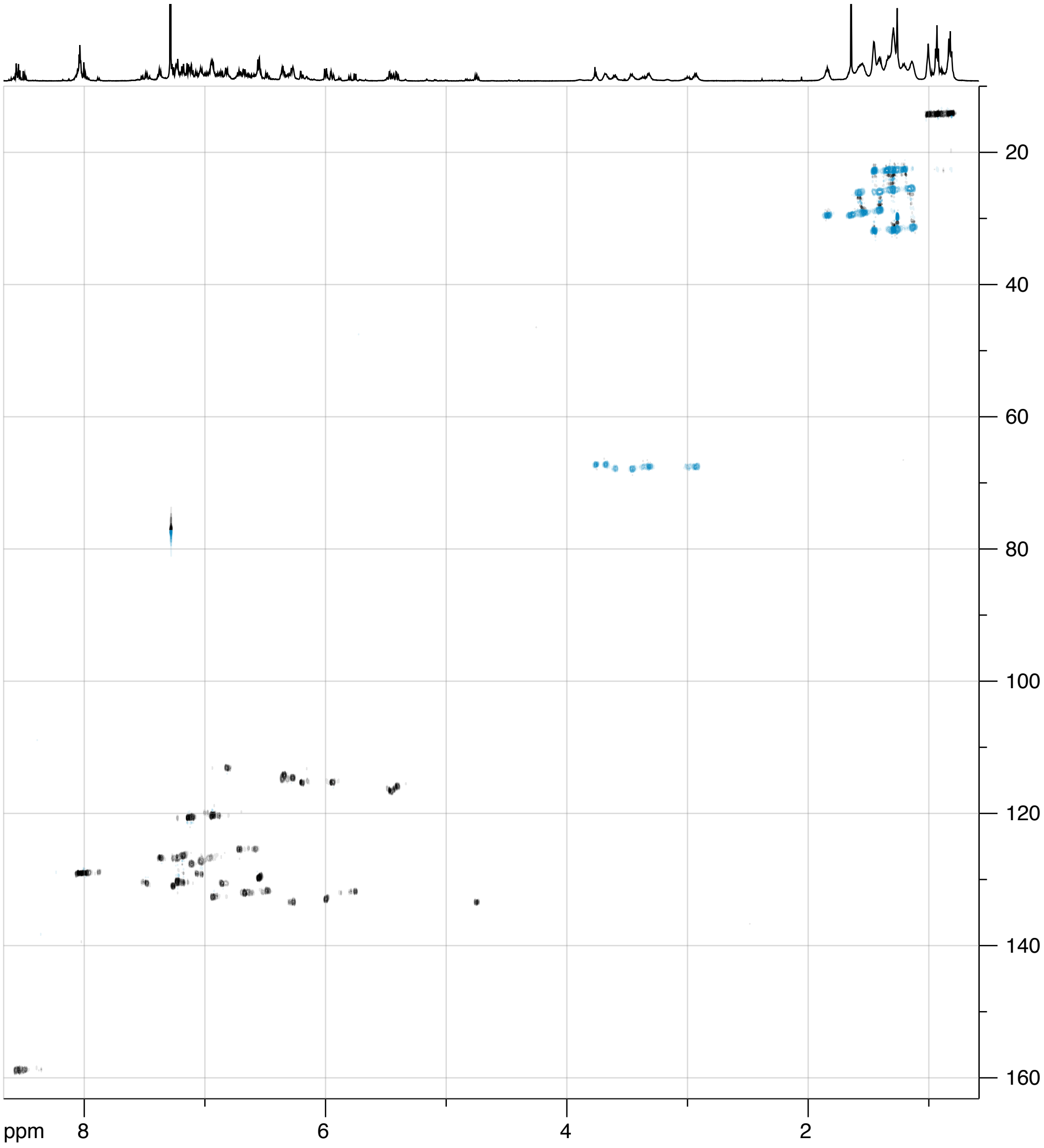


Figure S51. HSQC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(Phen)_{2+2}$**.

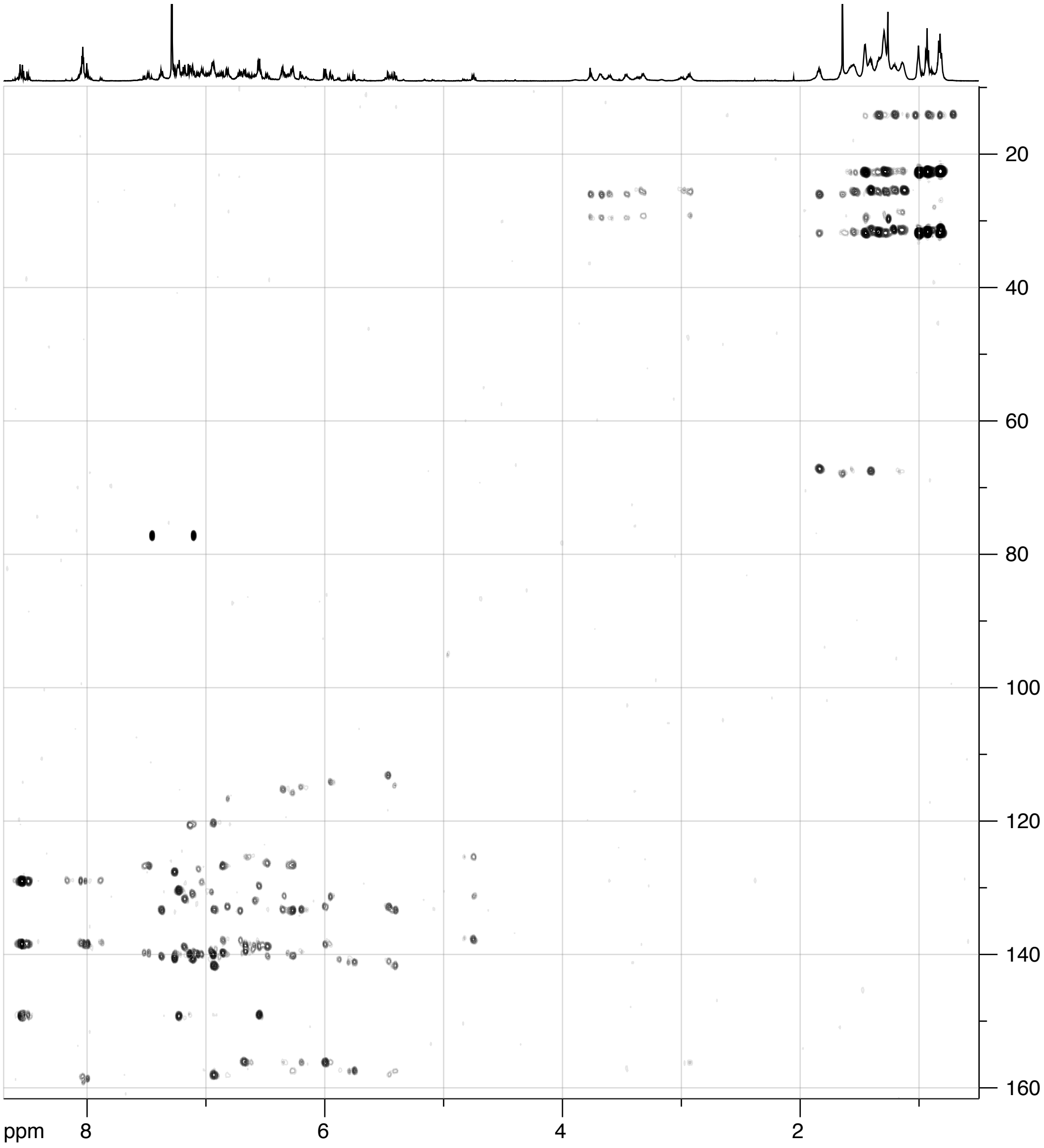


Figure S52. HMBC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(Phen)$_{2+2}$**.

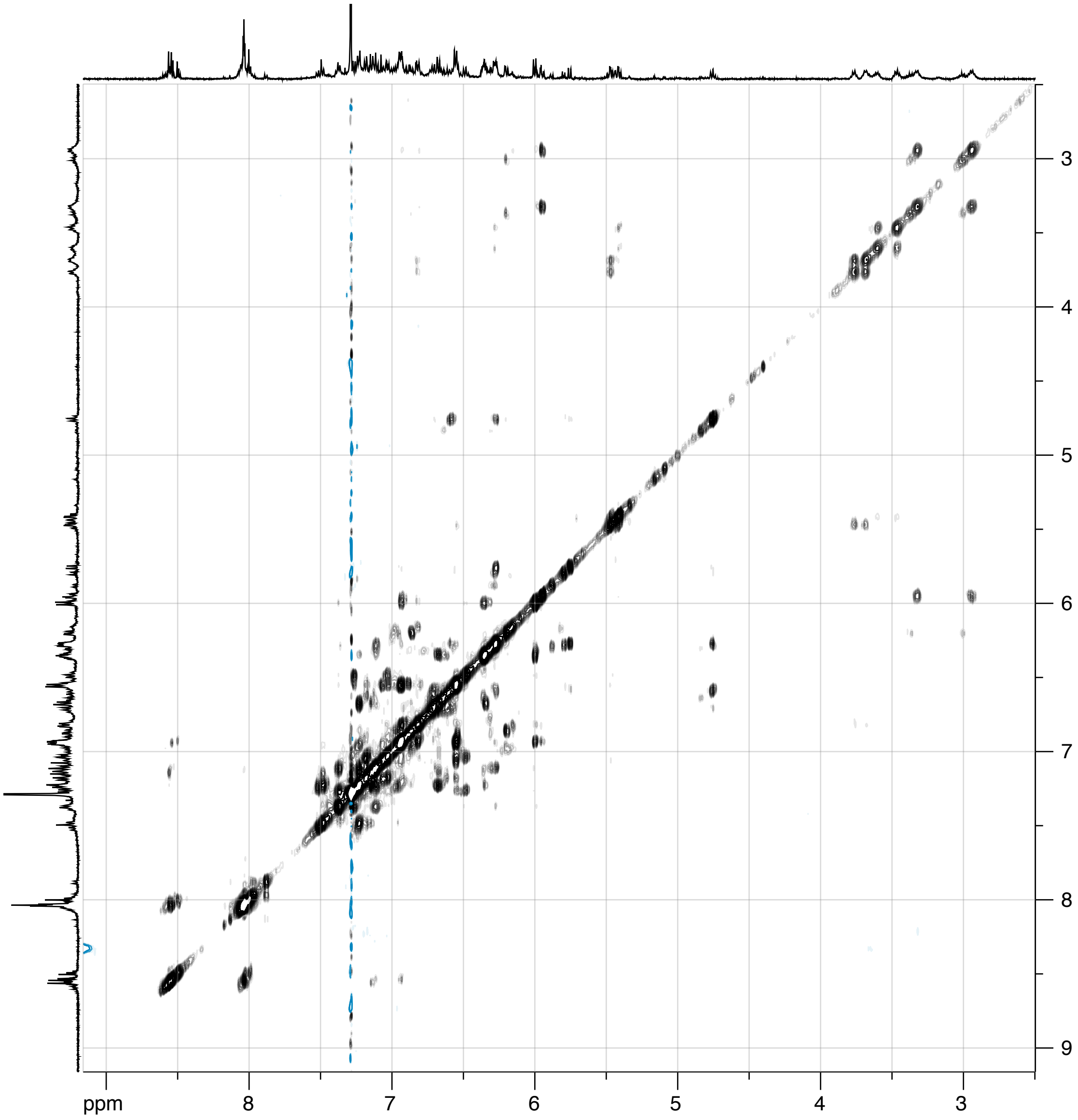


Figure S53. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(Phen)$_{2+2}$**.

Macrocycle ***oP^{10}(Phen)$_{3+3}$***

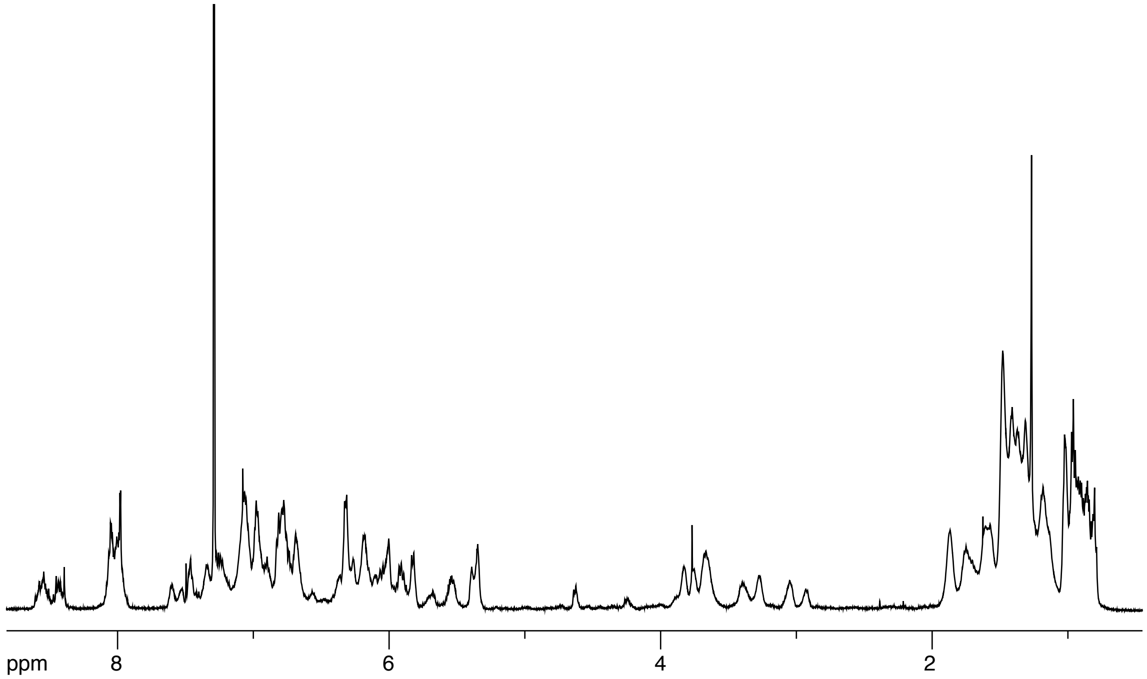


Figure S54. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 0 ℃) of **oP^{10}(Phen)$_{3+3}$**.

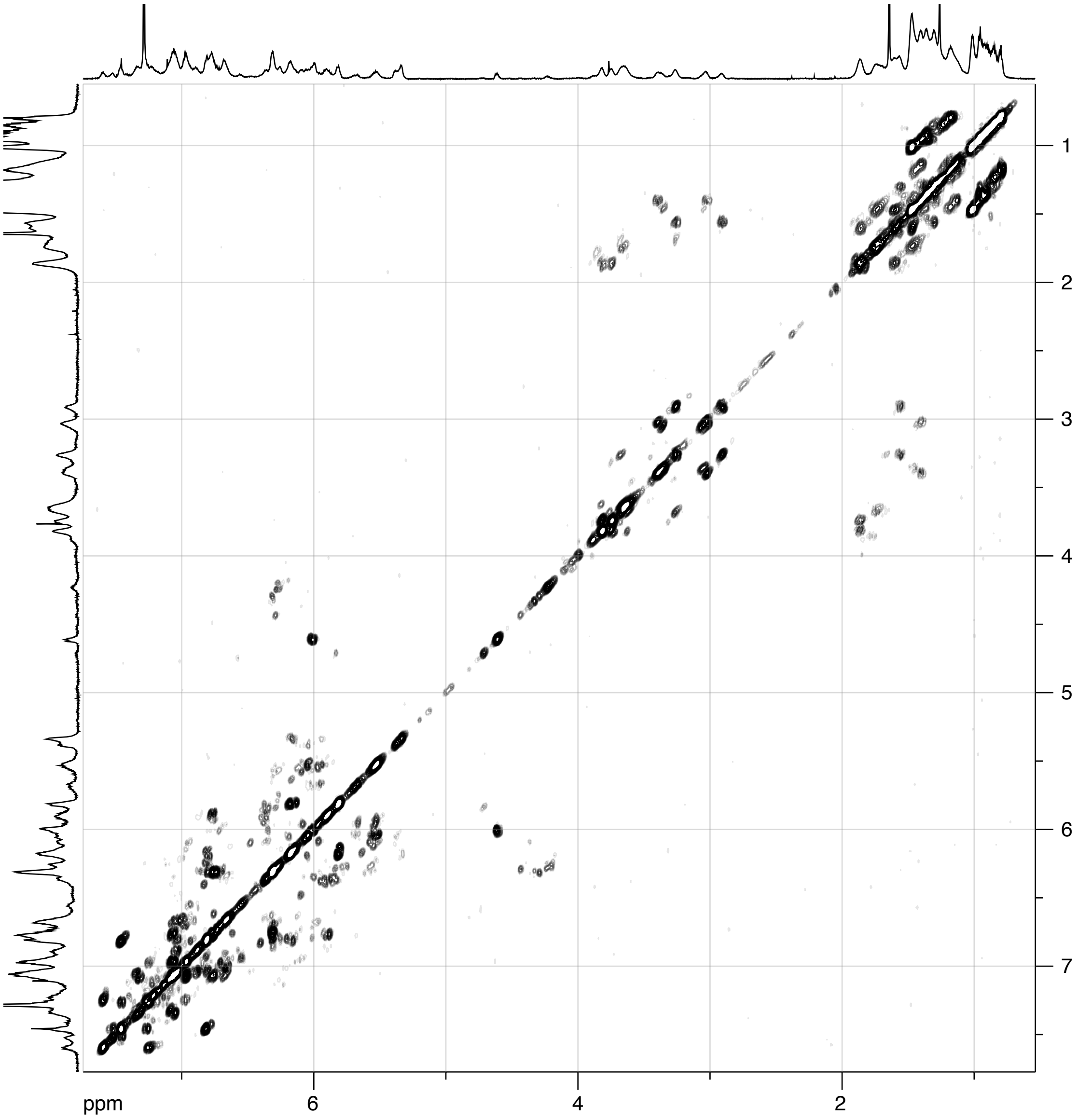


Figure S55. COSY spectrum (600 MHz, CDCl$_3$, 0 ℃) of **oP^{10}(Phen)**$_{3+3}$.

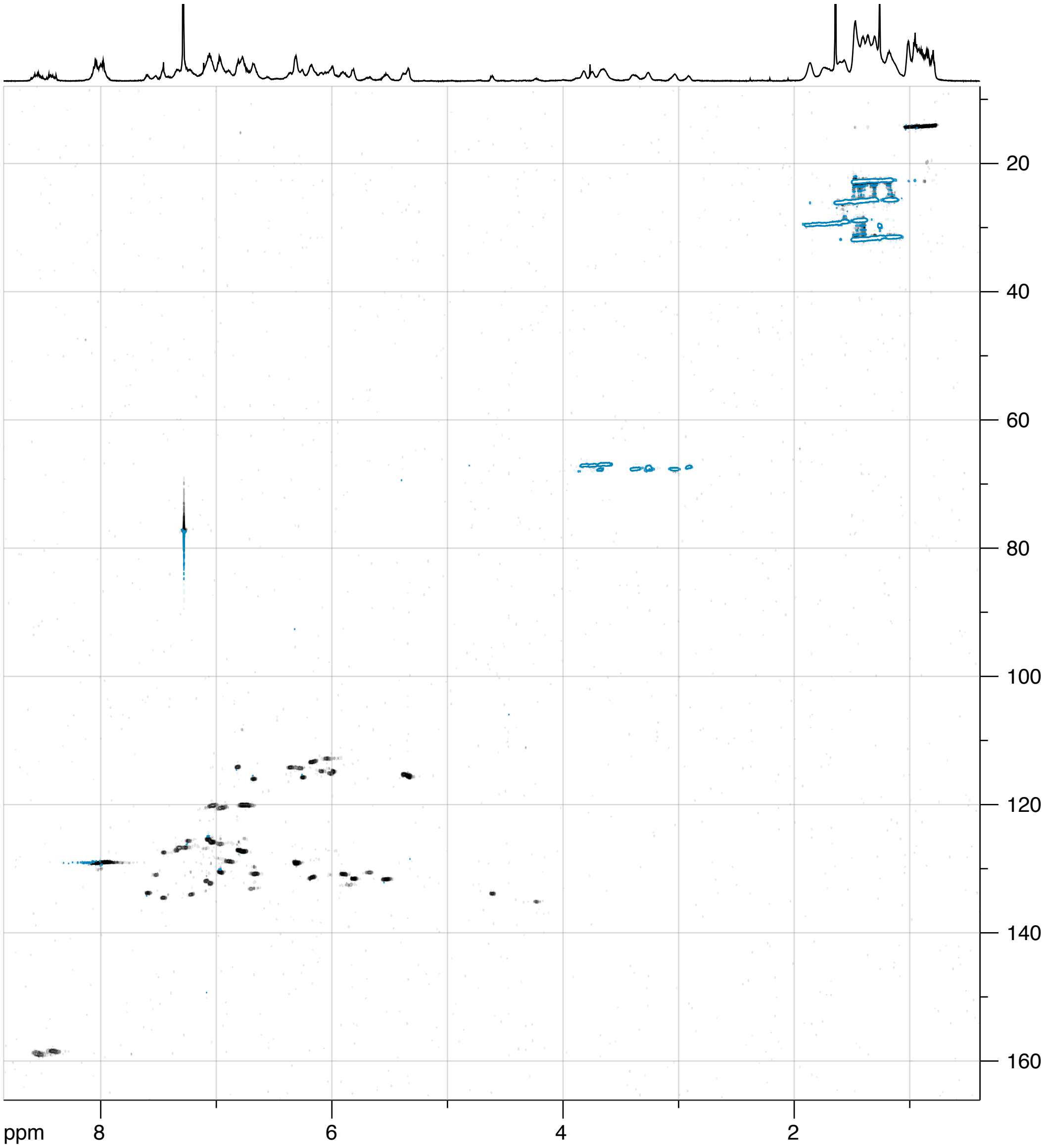


Figure S56. HSQC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(Phen)$_{3+3}$**.

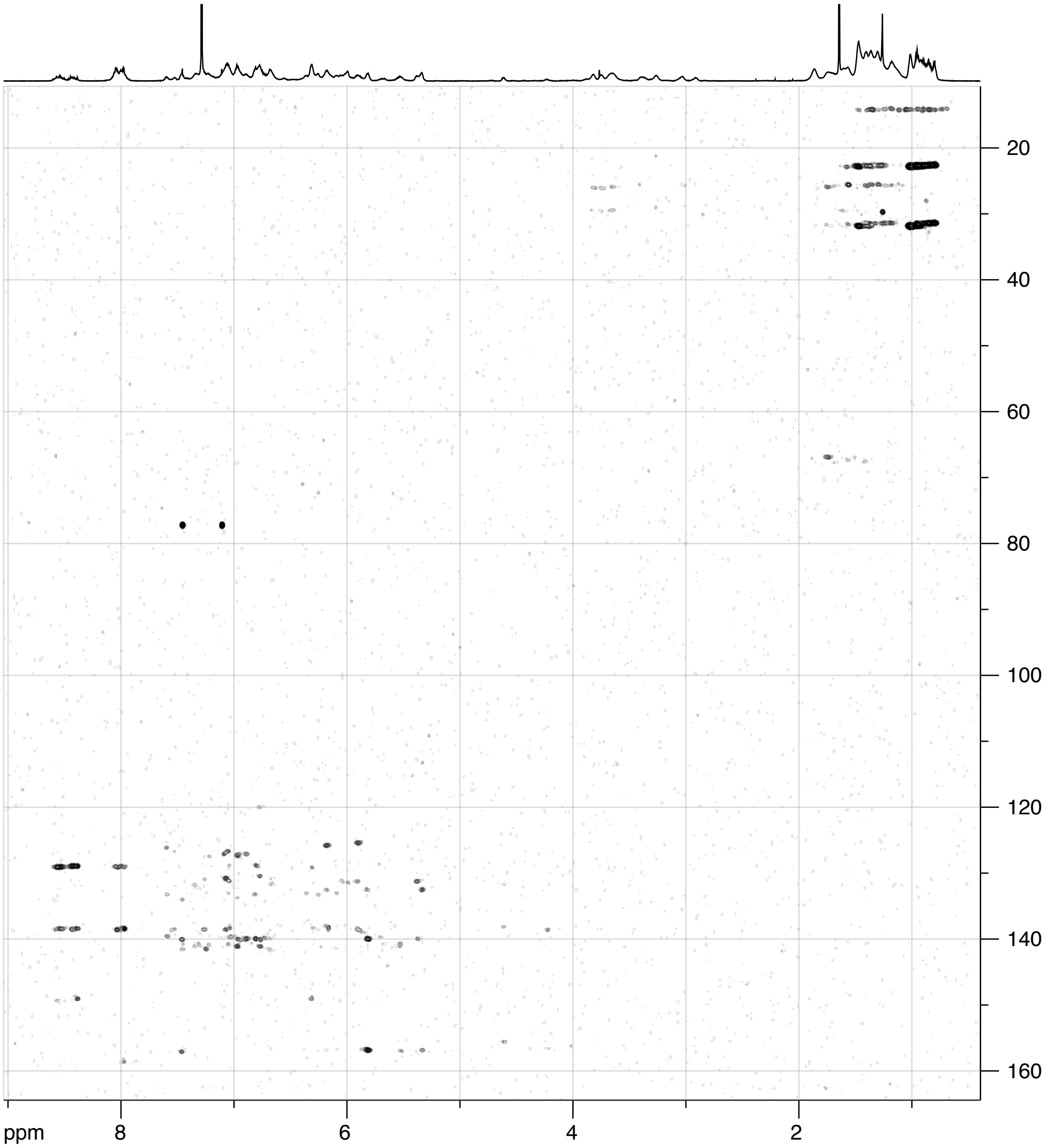


Figure S57. HMBC spectrum (600 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^{10}(Phen)_{3+3}}$.

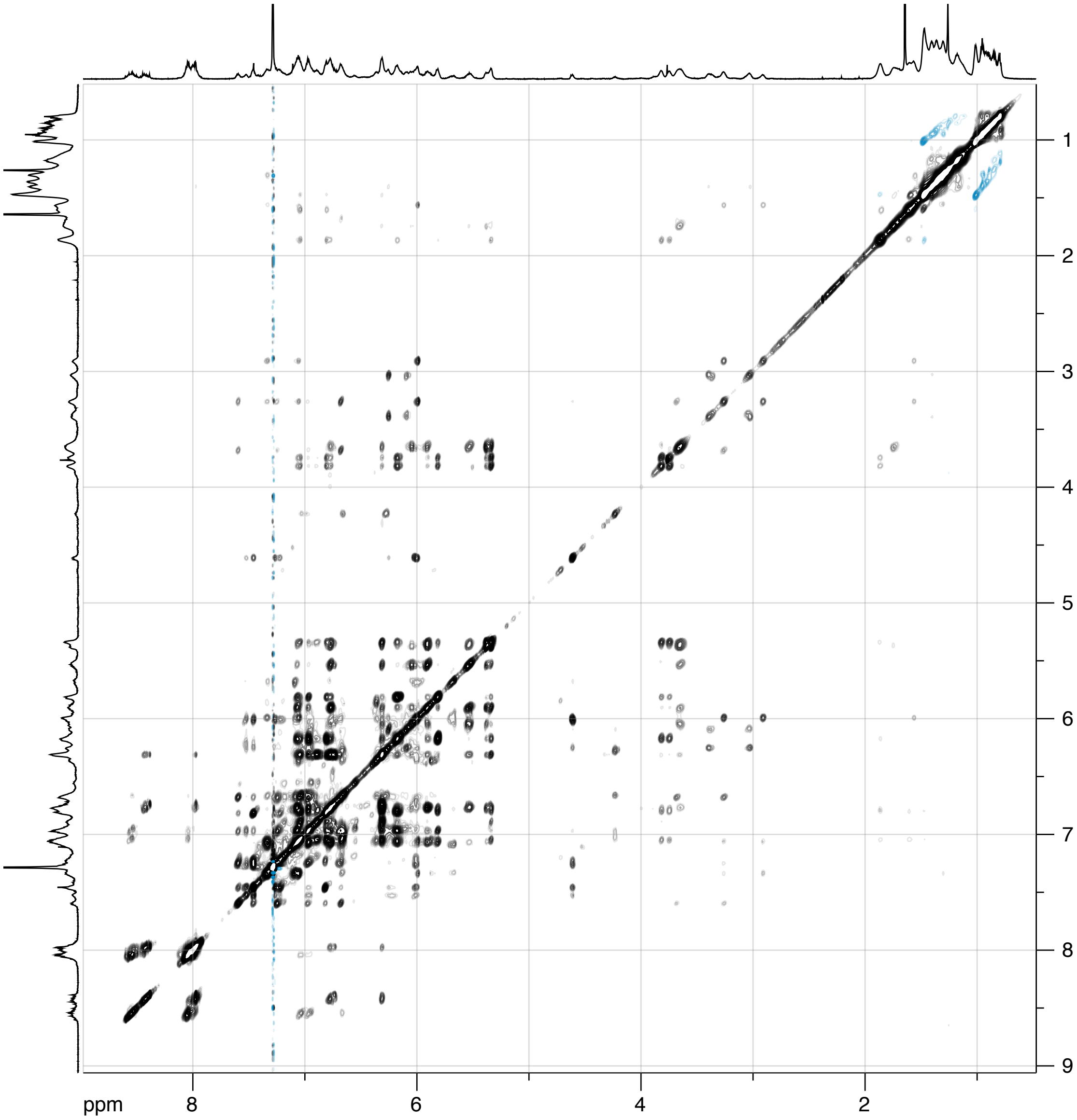


Figure S58. NOESY/EXSY spectrum (600 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(Phen)**$_{3+3}$.

***oP**$^{\textit{Macrocycle 10}}$**(BIP)**$_{\textit{2+2}}$*

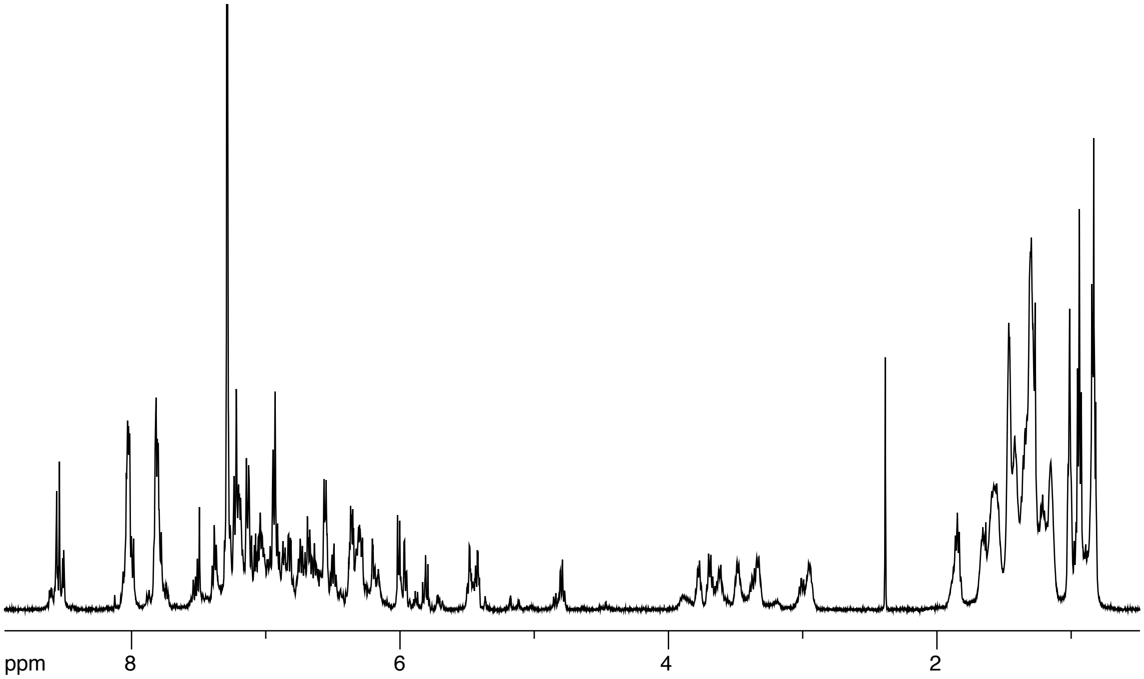


Figure S59. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(BIP)$_{2+2}$**.

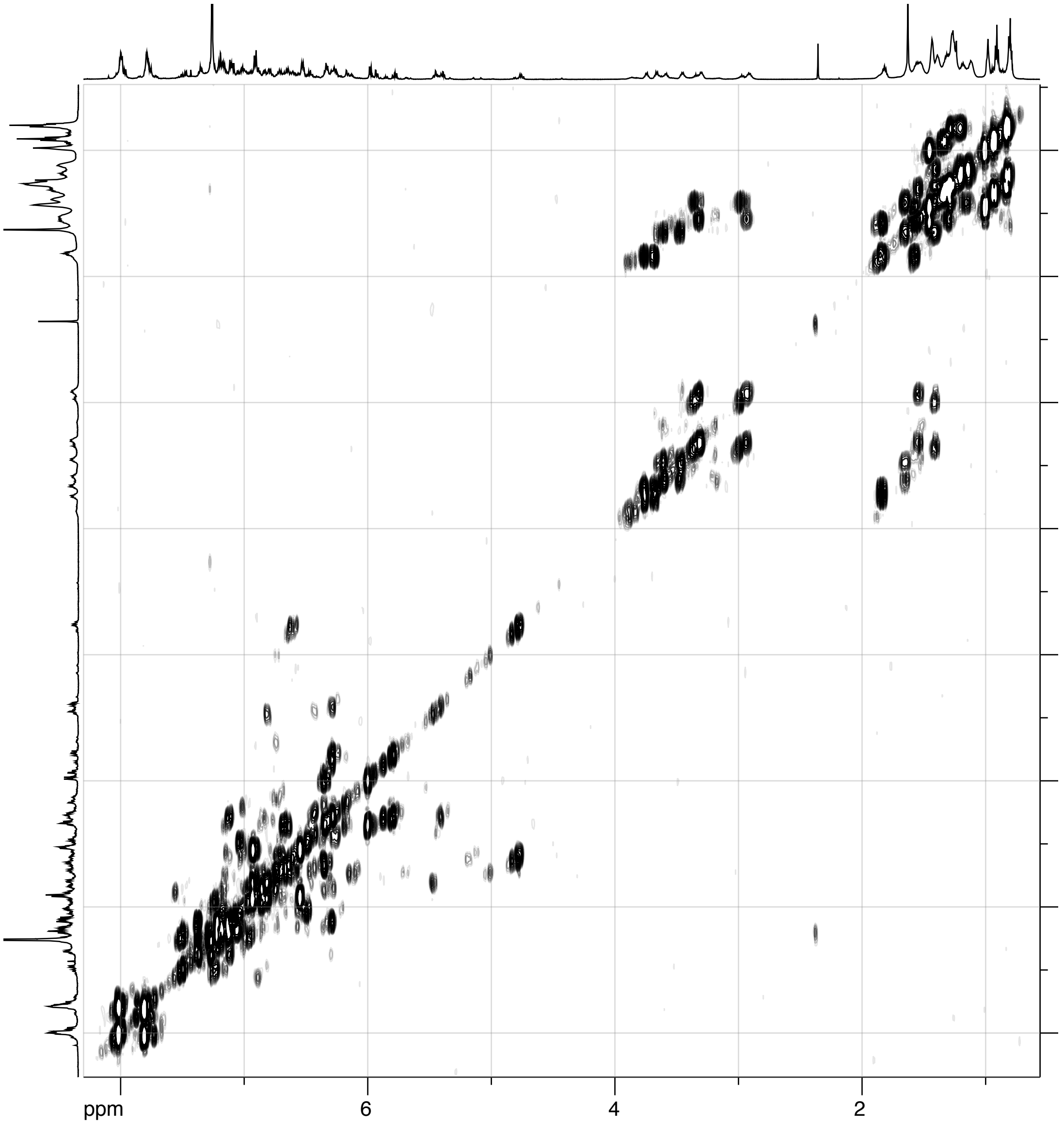


Figure S60. COSY spectrum (600 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^{10}(BIP)_{2+2}}$.

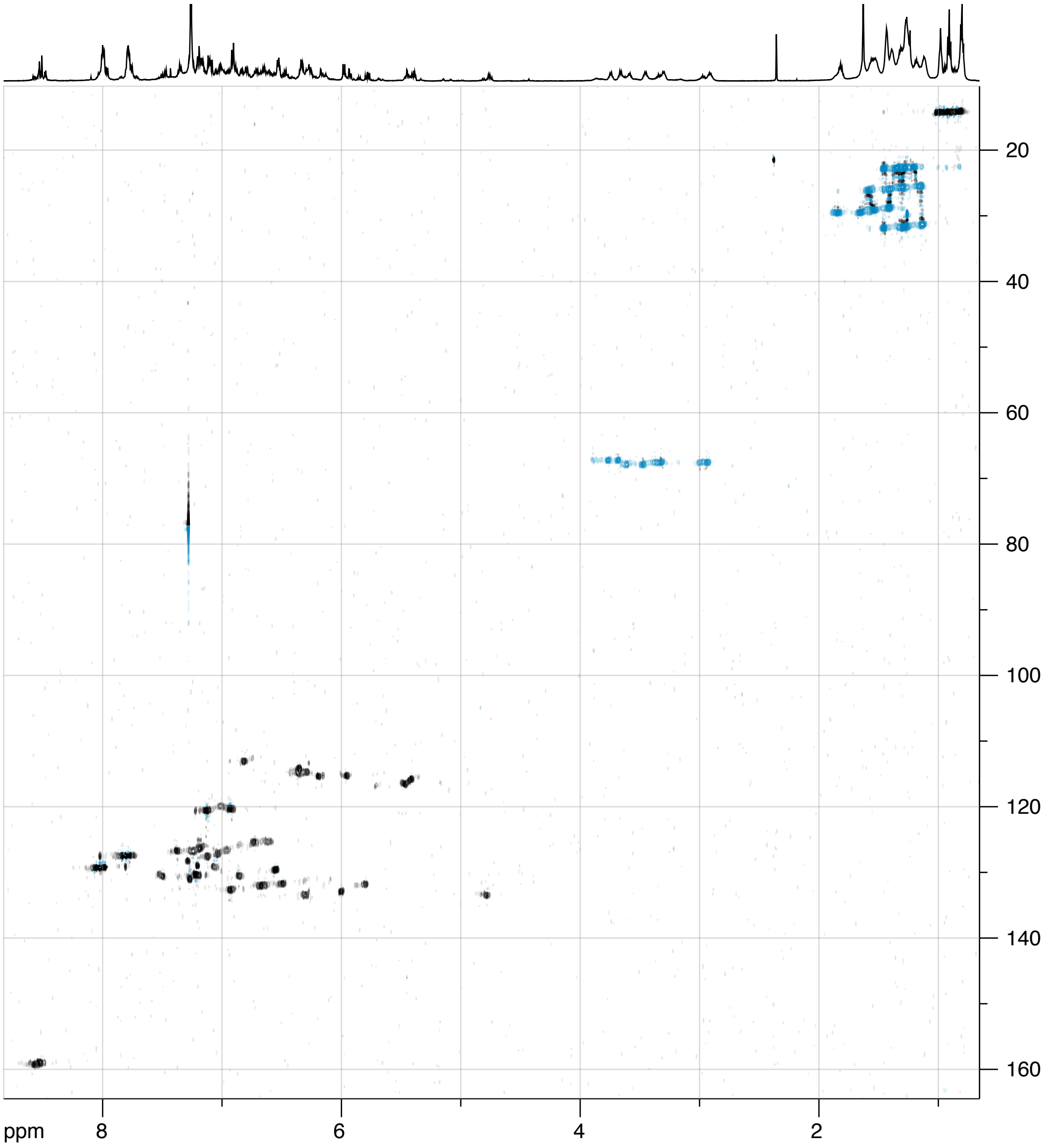


Figure S61. HSQC spectrum (600 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^{10}(BIP)_{2+2}}$.

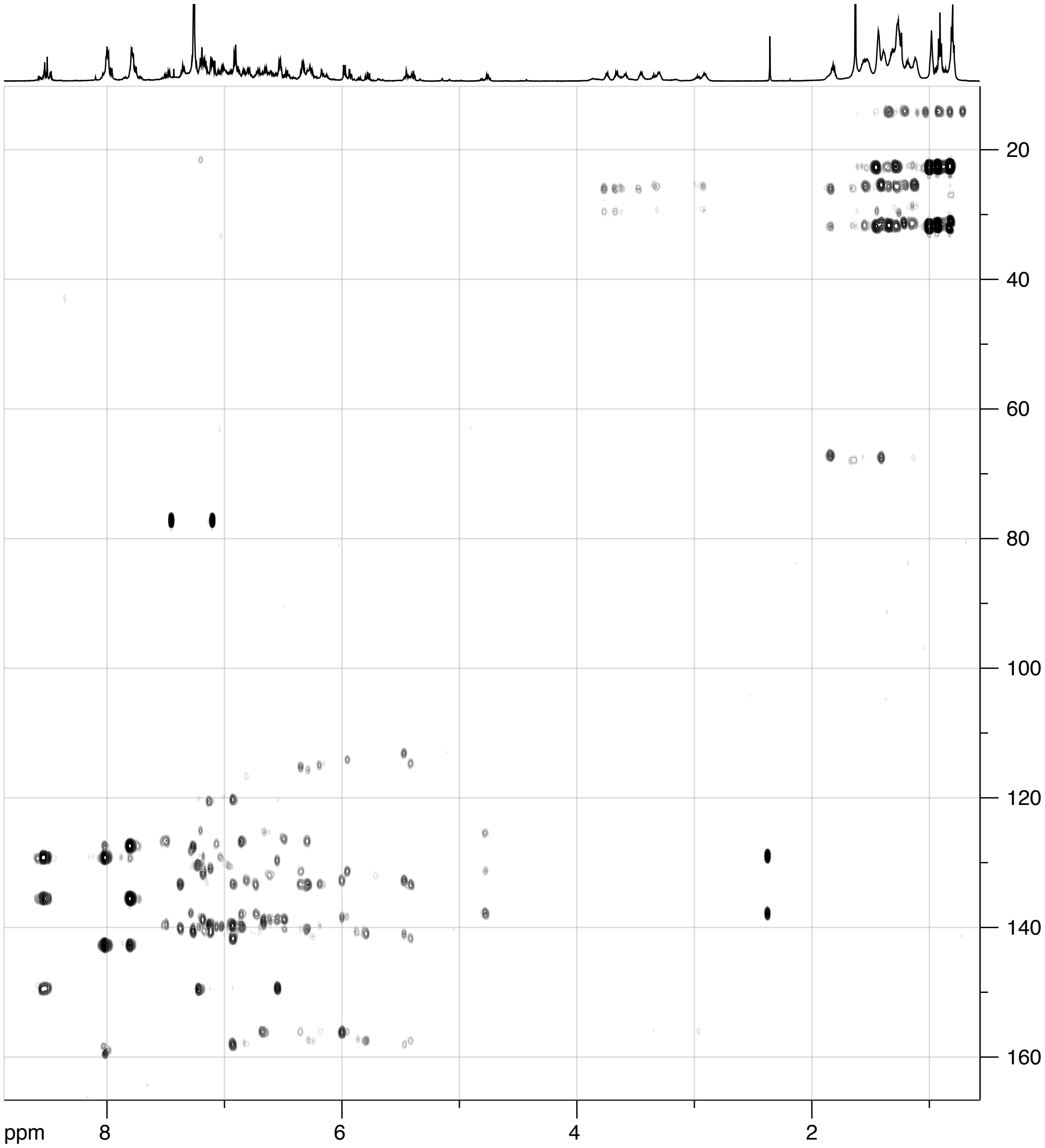


Figure S62. HMBC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(BIP)_{2+2}$**.

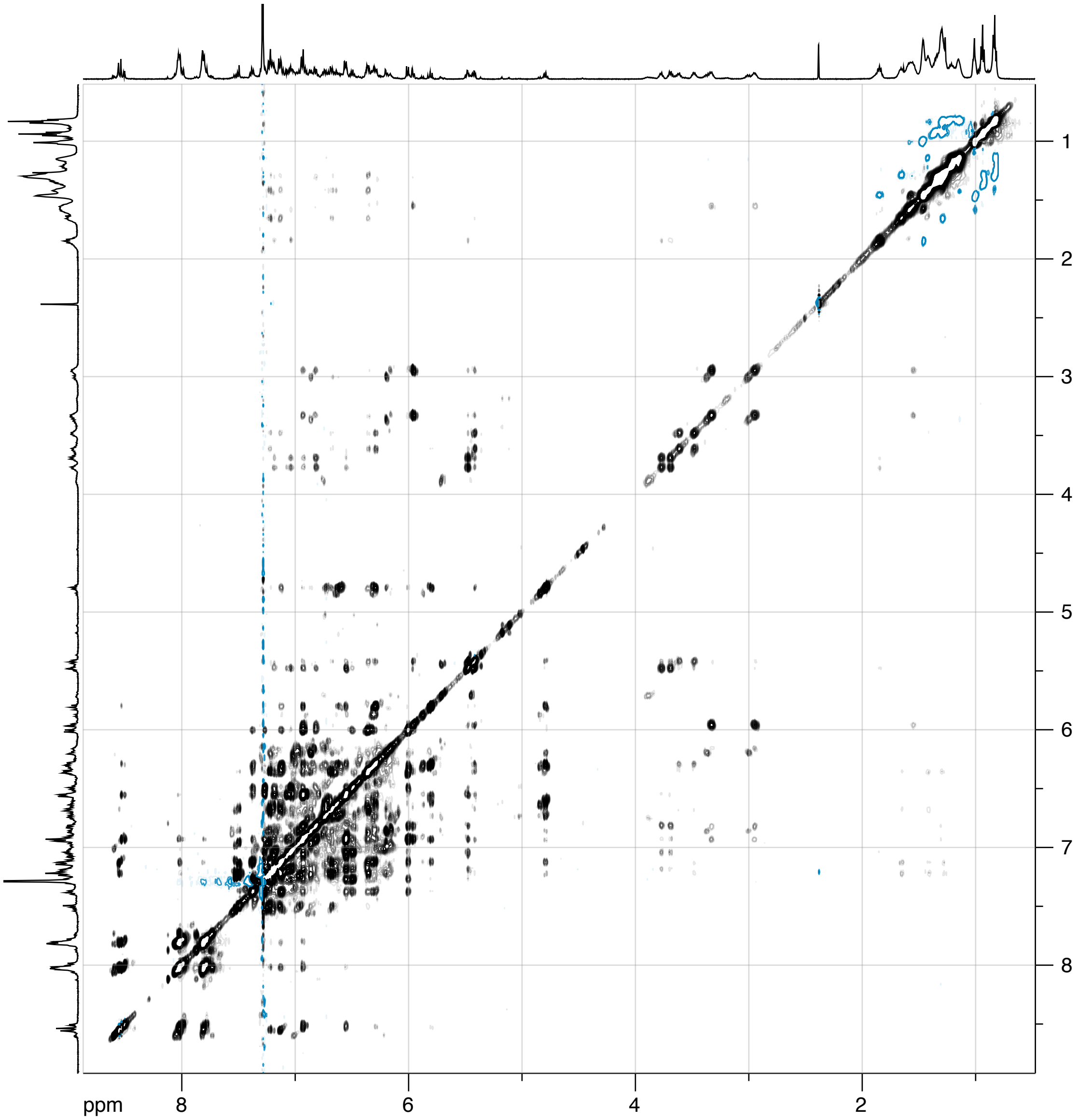


Figure S63. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^{10}(BIP)_{2+2}}$.

Macrocycle ***oP^{10}(BIP)$_{3+3}$***

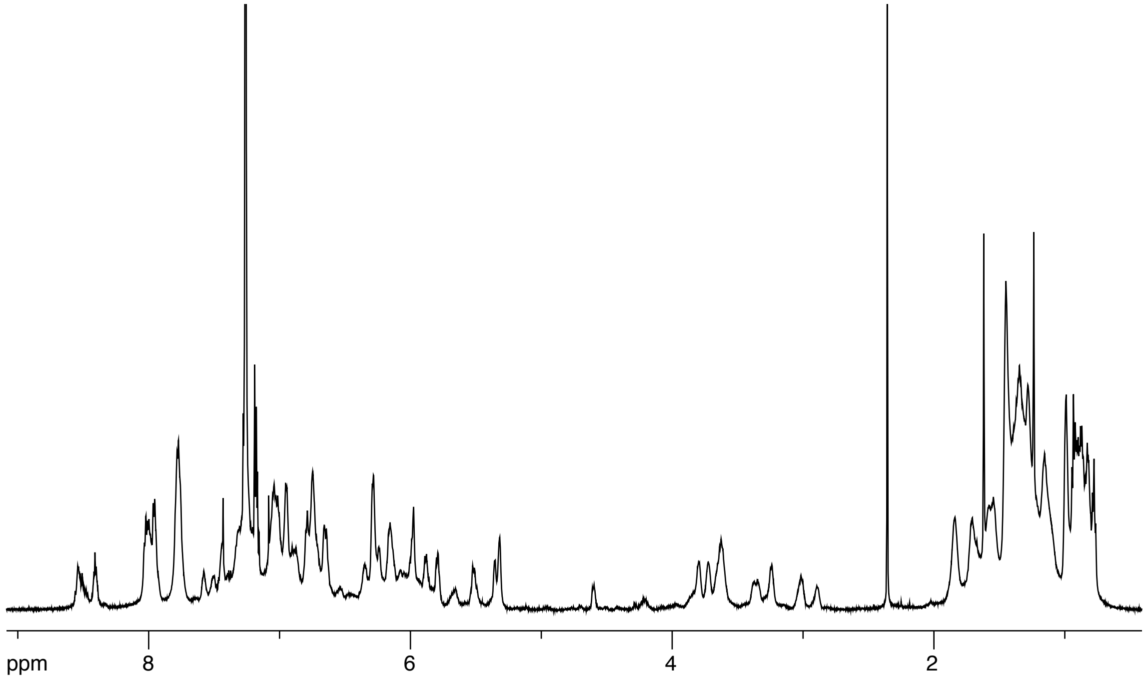


Figure S64. ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 0 °C) of **oP^{10}(BIP)$_{3+3}$**.

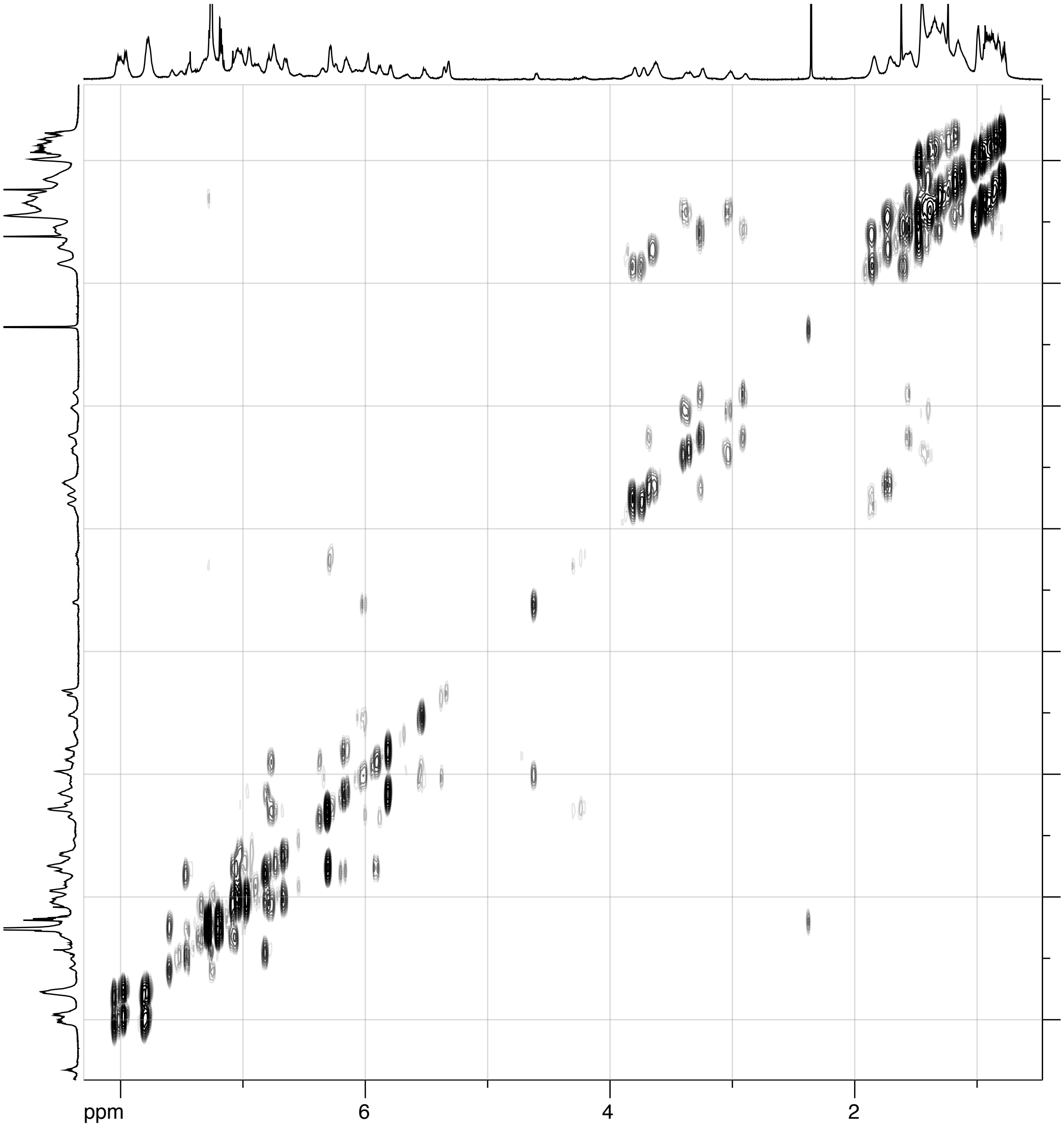


Figure S65. COSY spectrum (600 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^{10}(BIP)_{3+3}}$.

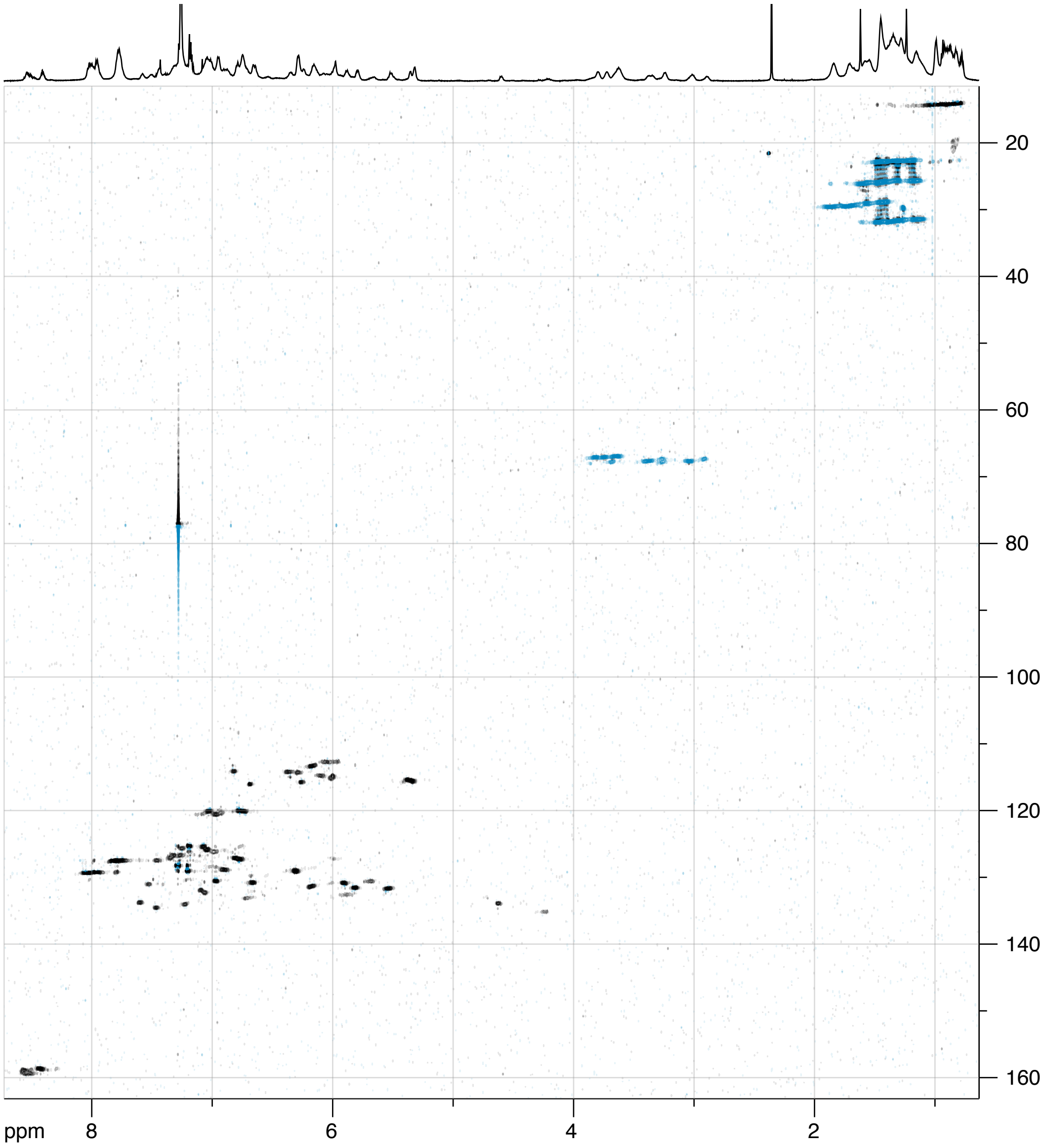


Figure S66. HSQC spectrum (600 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^{10}(BIP)_{3+3}}$.

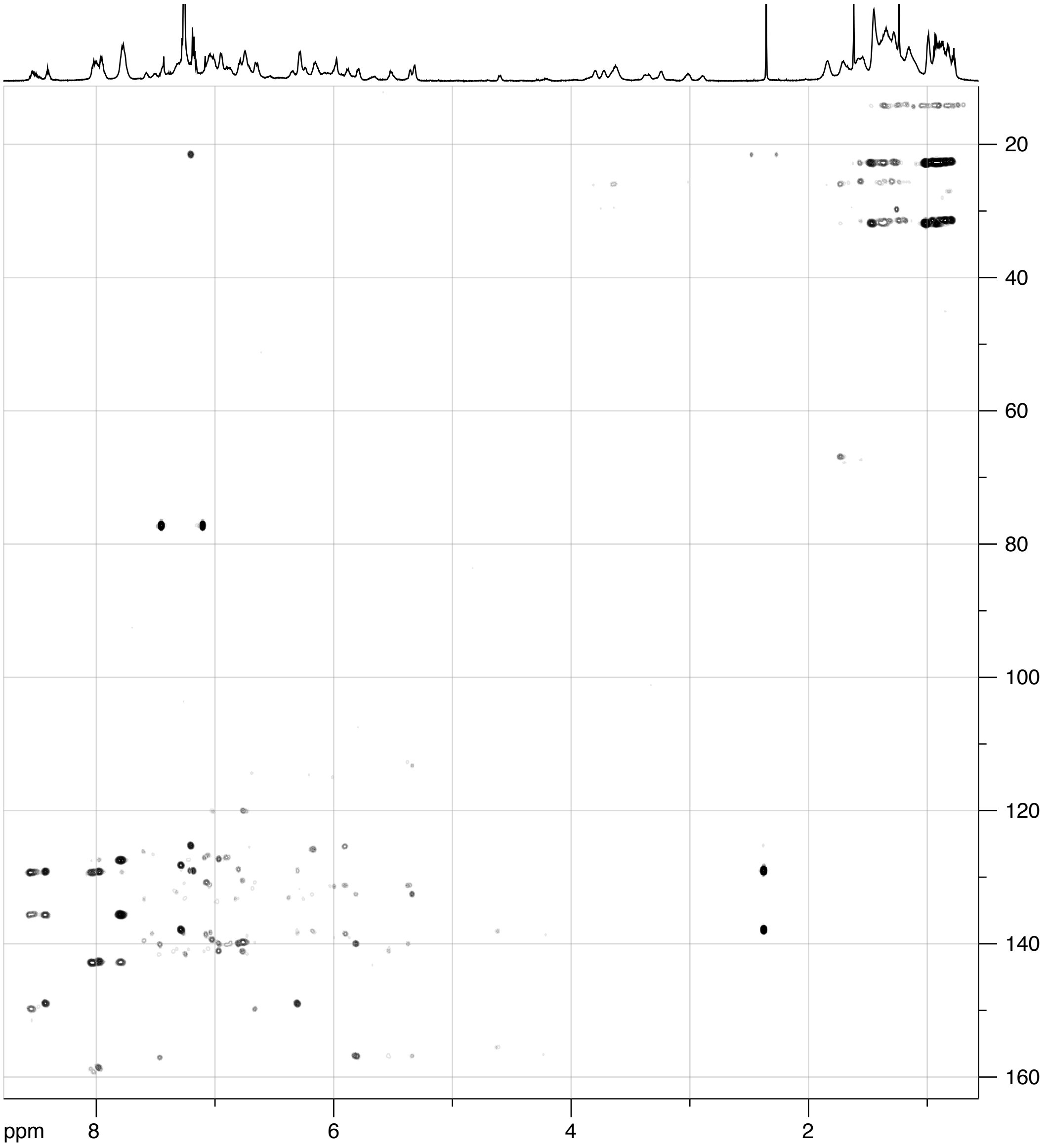


Figure S67. HMBC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(BIP)$_{3+3}$**.

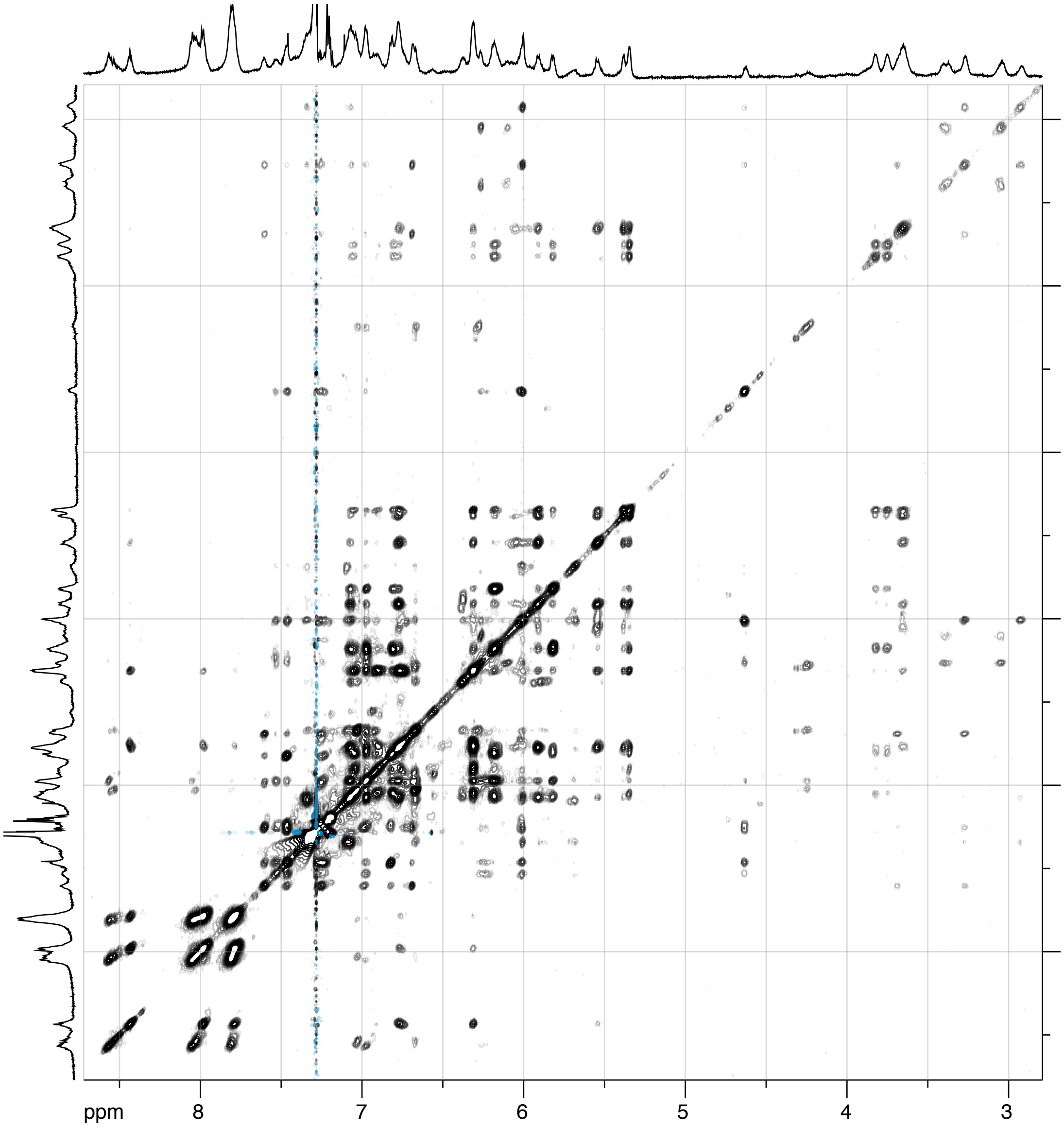


Figure S68. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(BIP)_{3+3}$**.

***oP**^Macrocycle 10^**(DPB)**_2+2_*

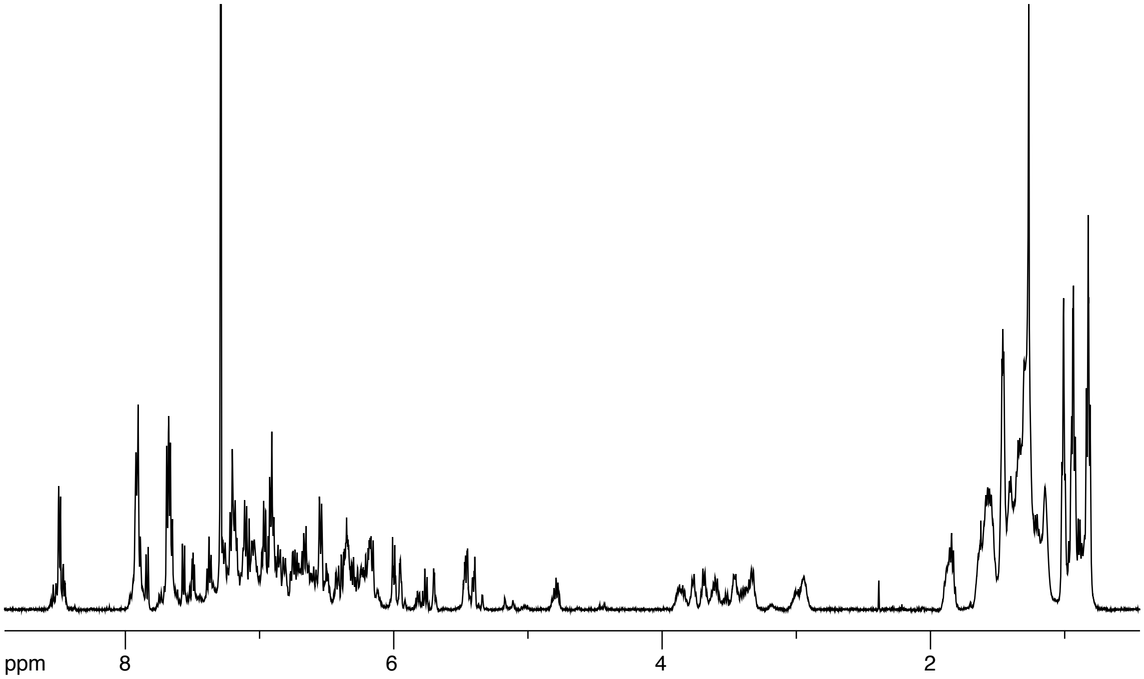


Figure S69. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 0 ℃) of **oP^{10}(DPB)$_{2+2}$**.

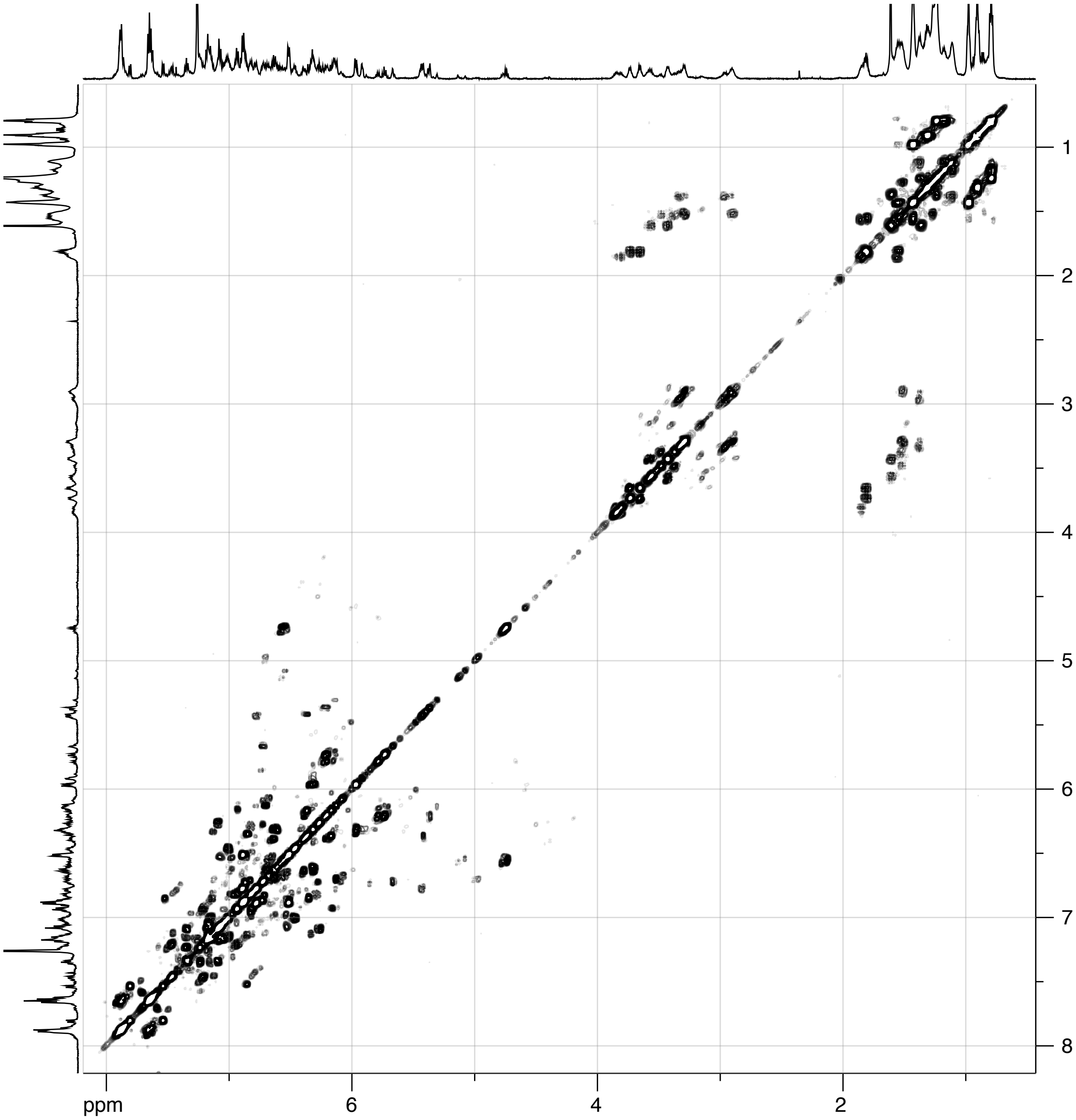


Figure S70. COSY spectrum (600 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(DPB)$_{2+2}$**.

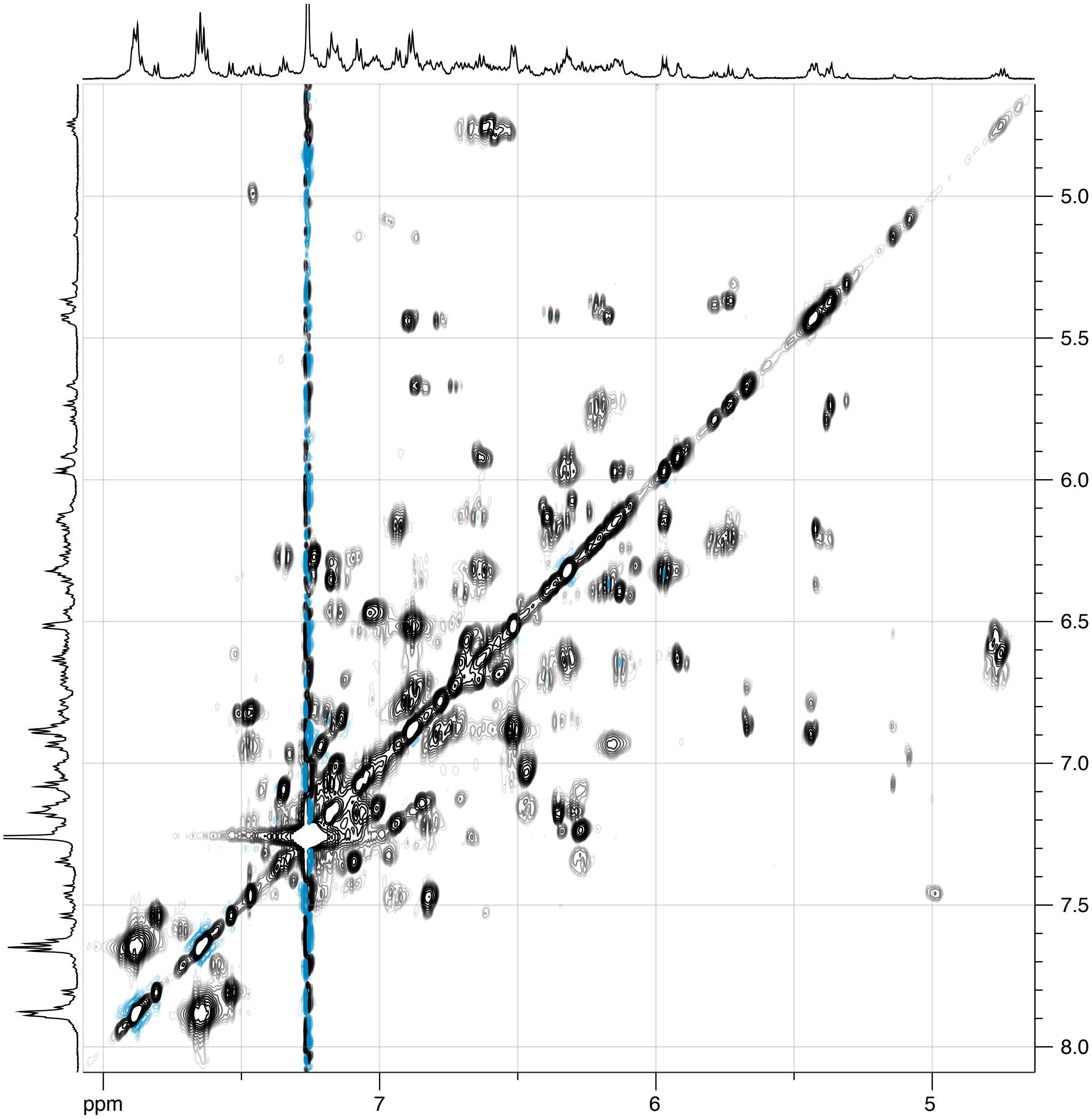


Figure S71. TOCSY spectrum (600 MHz, $CDCl_3$, 0 °C) of $\mathbf{oP^{10}(DPB)_{2+2}}$.

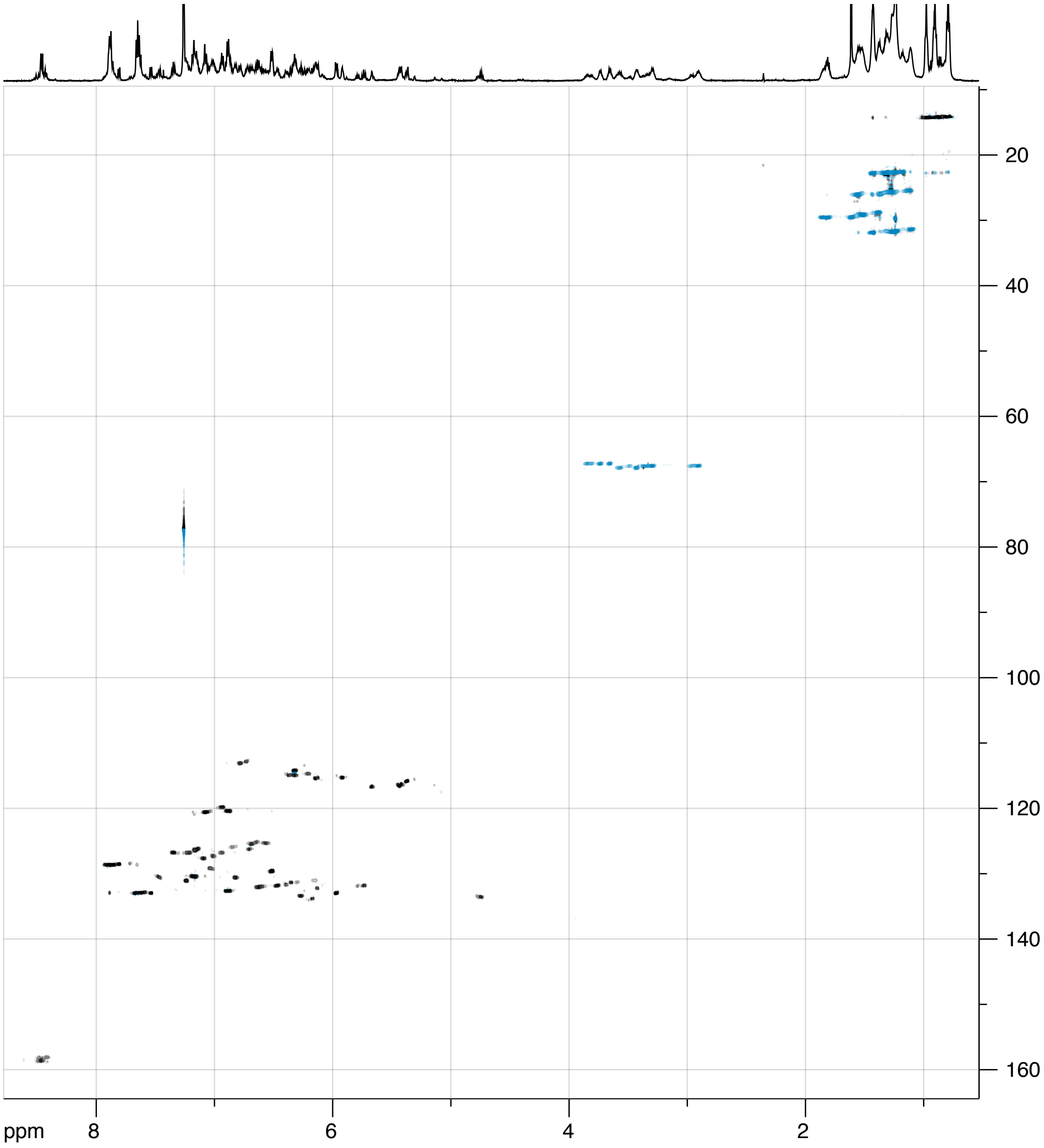


Figure S72. HSQC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(DPB)_{2+2}$**.

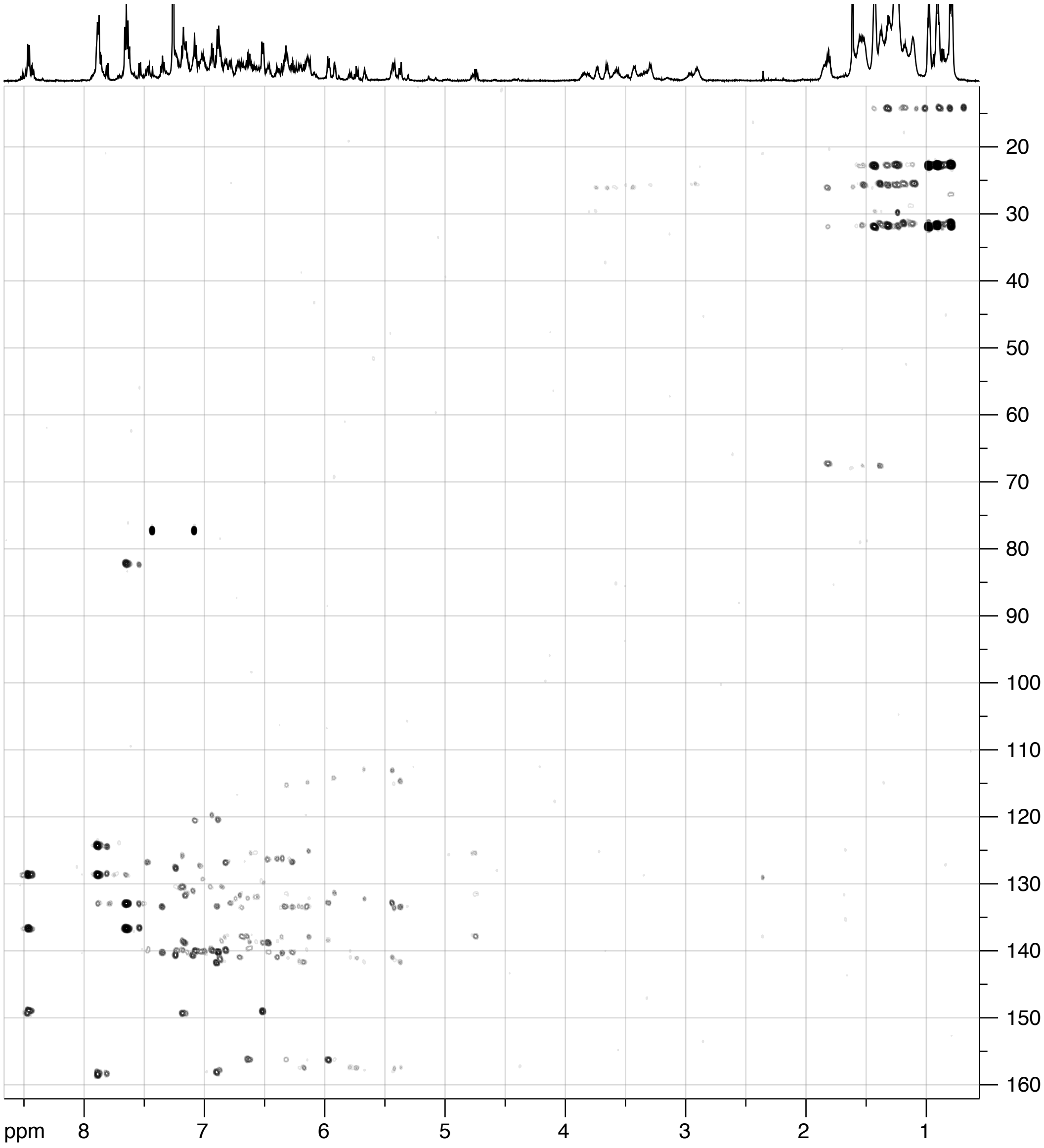


Figure S73. HMBC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(DPB)_{2+2}$**.

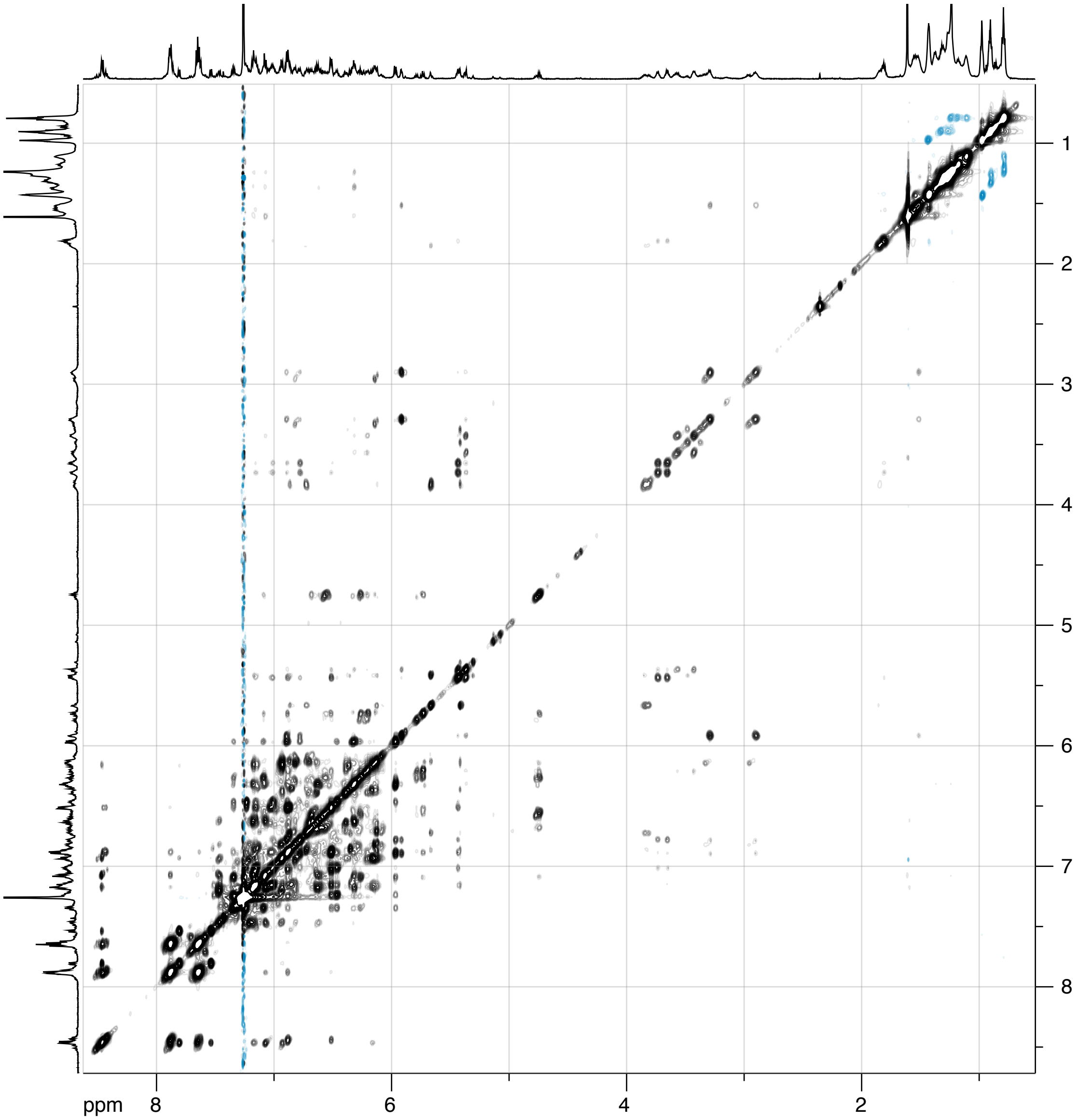


Figure S74. NOESY/EXSY spectrum (600 MHz, $CDCl_3$, 0 ℃) of **oP^{10}(DPB)**$_{2+2}$.

*Macrocycle **oP^{10}(DPB)$_{3+3}$***

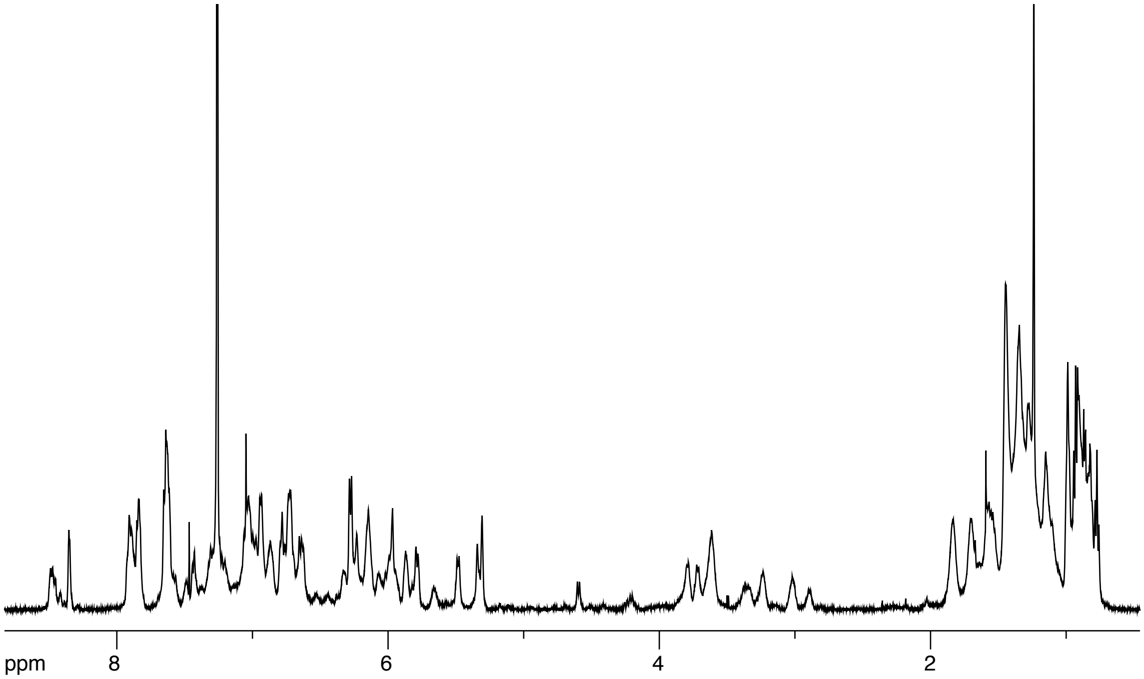


Figure S75. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 0 ℃) of **oP^{10}(DPB)$_{3+3}$**.

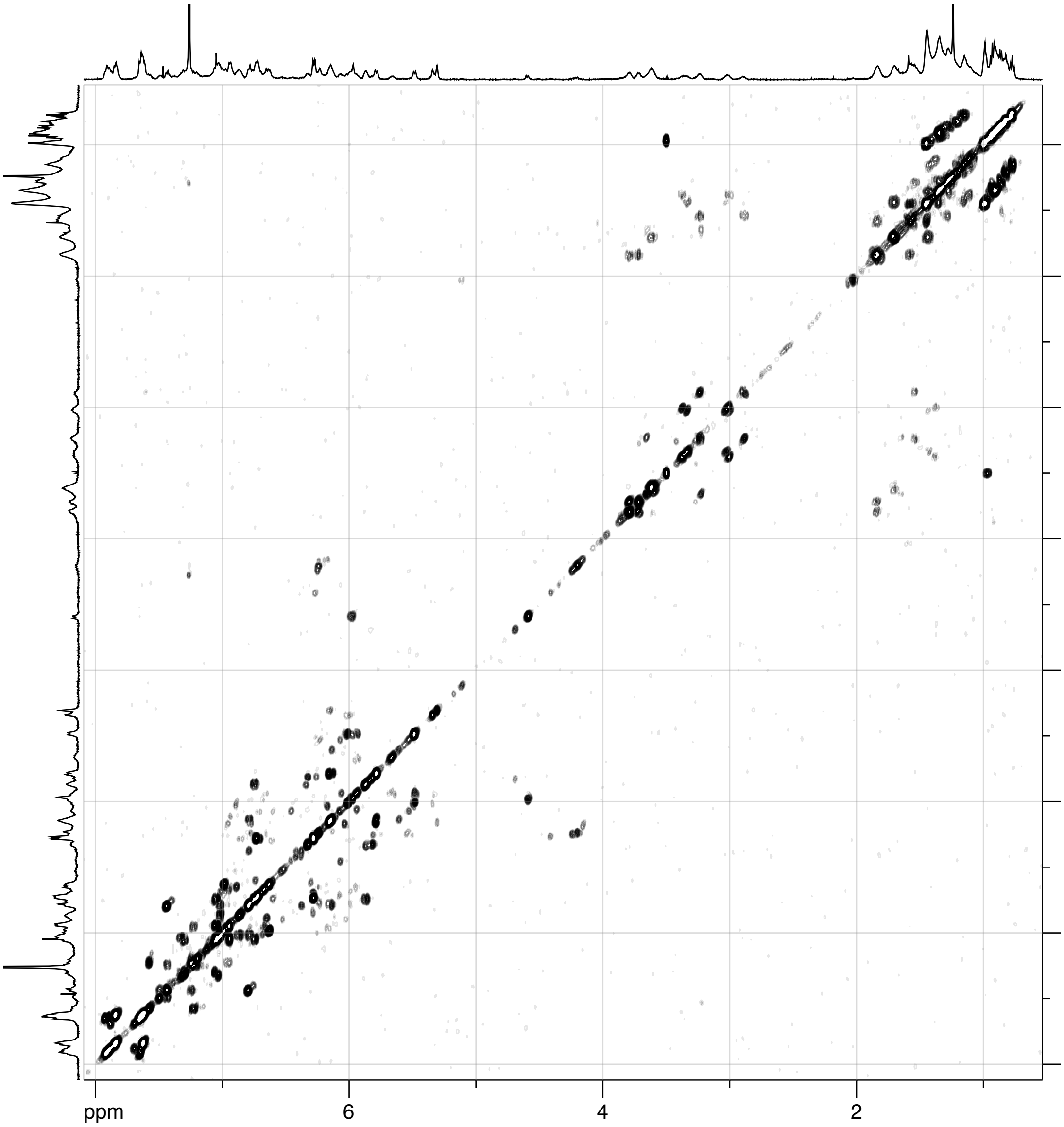


Figure S76. COSY spectrum (600 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(DPB)_{3+3}$**.

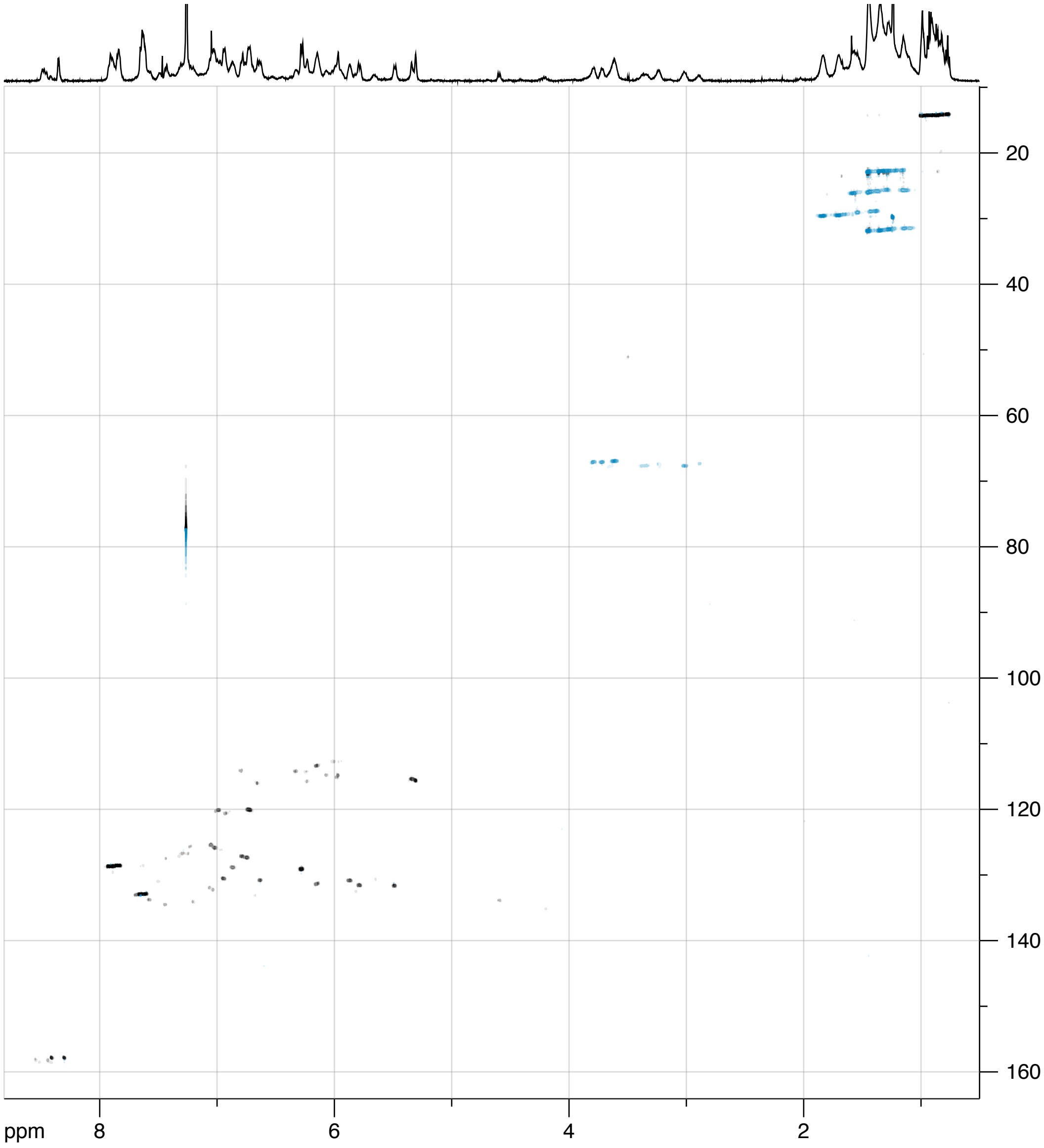


Figure S77. HSQC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(DPB)_{3+3}$**.

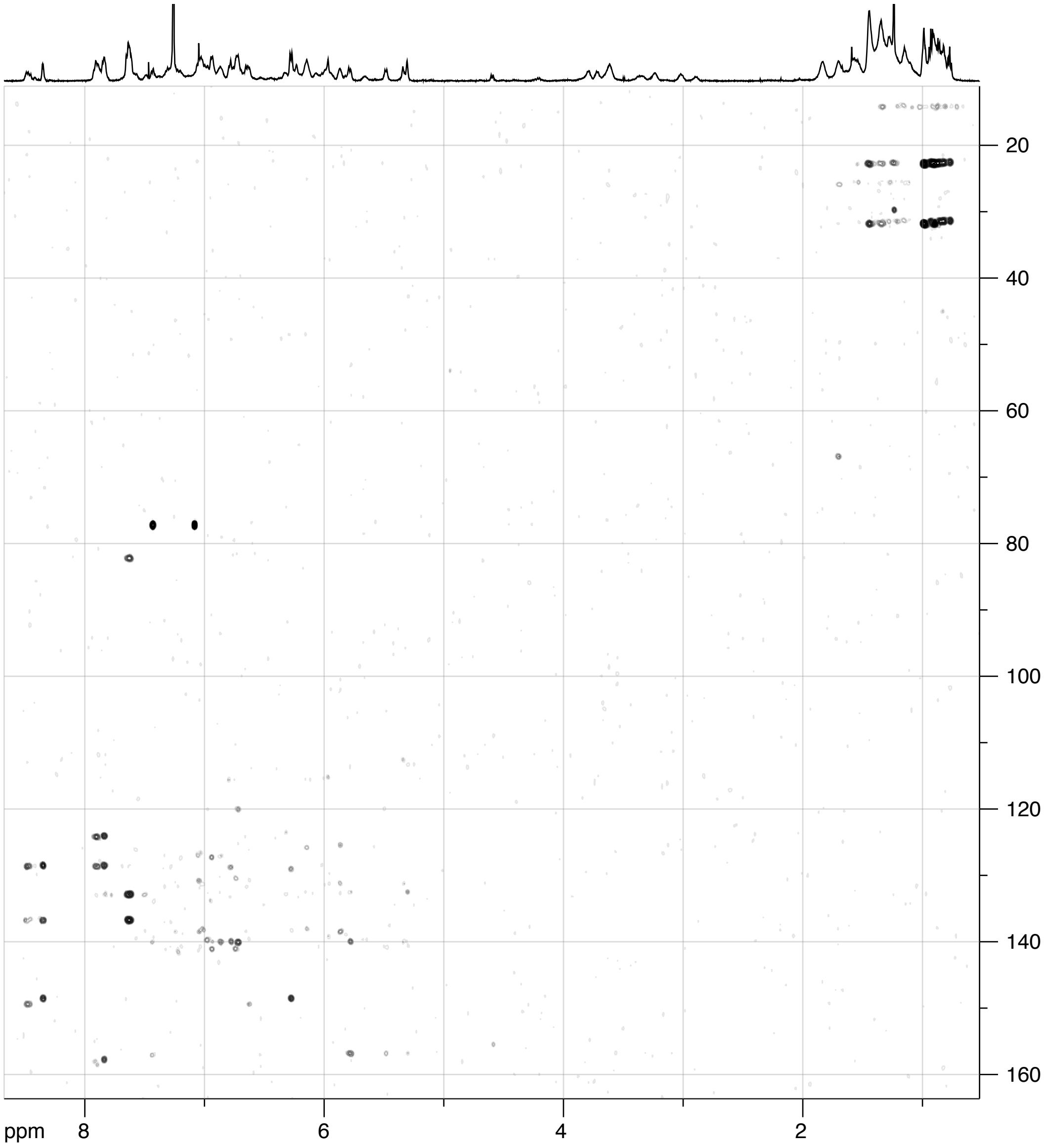


Figure S78. HMBC spectrum (600 MHz, $CDCl_3$, 0 ℃) of **$oP^{10}(DPB)_{3+3}$**.

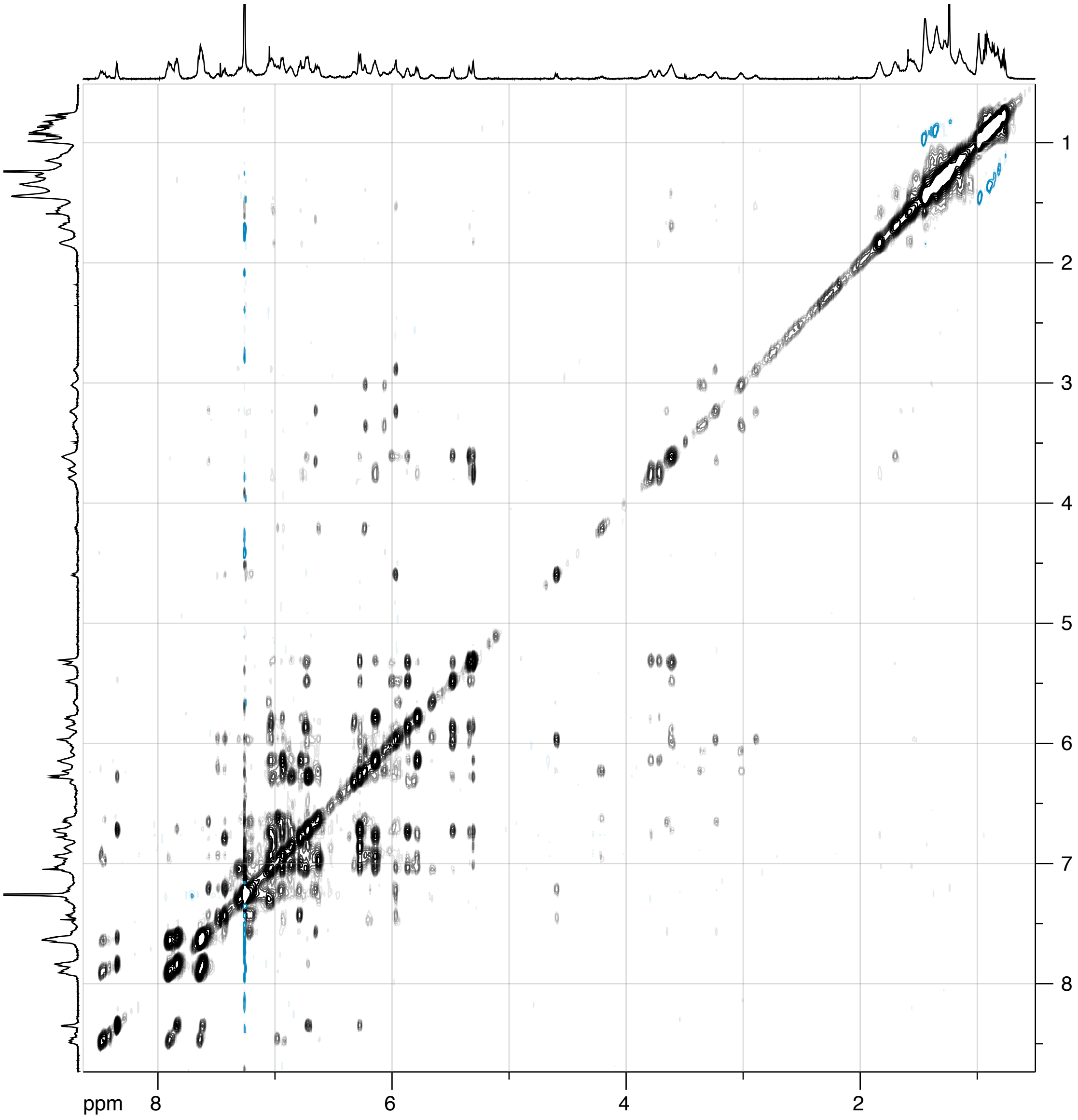


Figure S79. NOESY/EXSY spectrum (500 MHz, $CDCl_3$, 0 ℃) of $\mathbf{oP^{10}(DPB)_{3+3}}$.

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