Supporting Information

Role of Chirality and Macroring in Imprinted Polymers with Enantiodiscriminative Power

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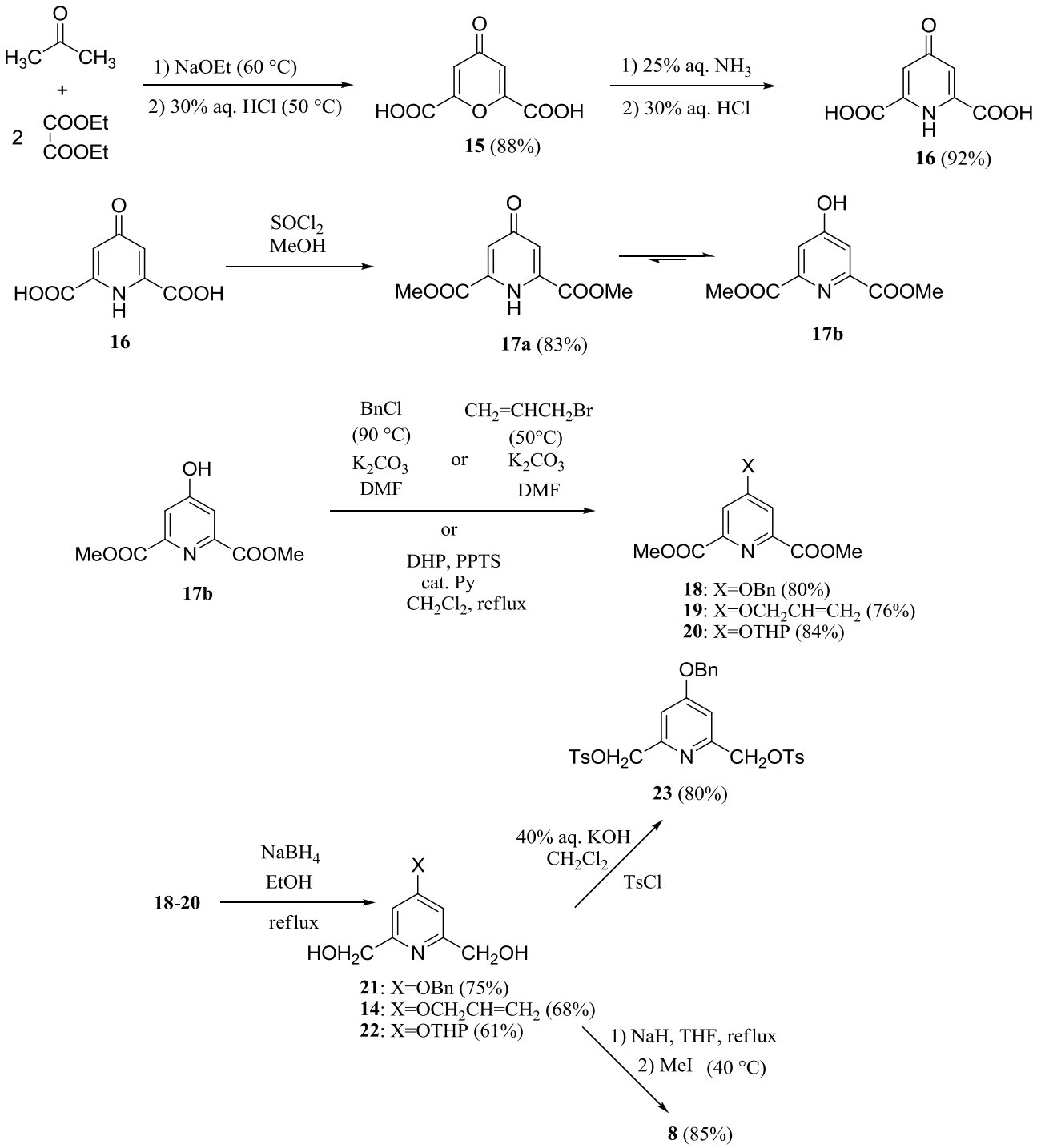
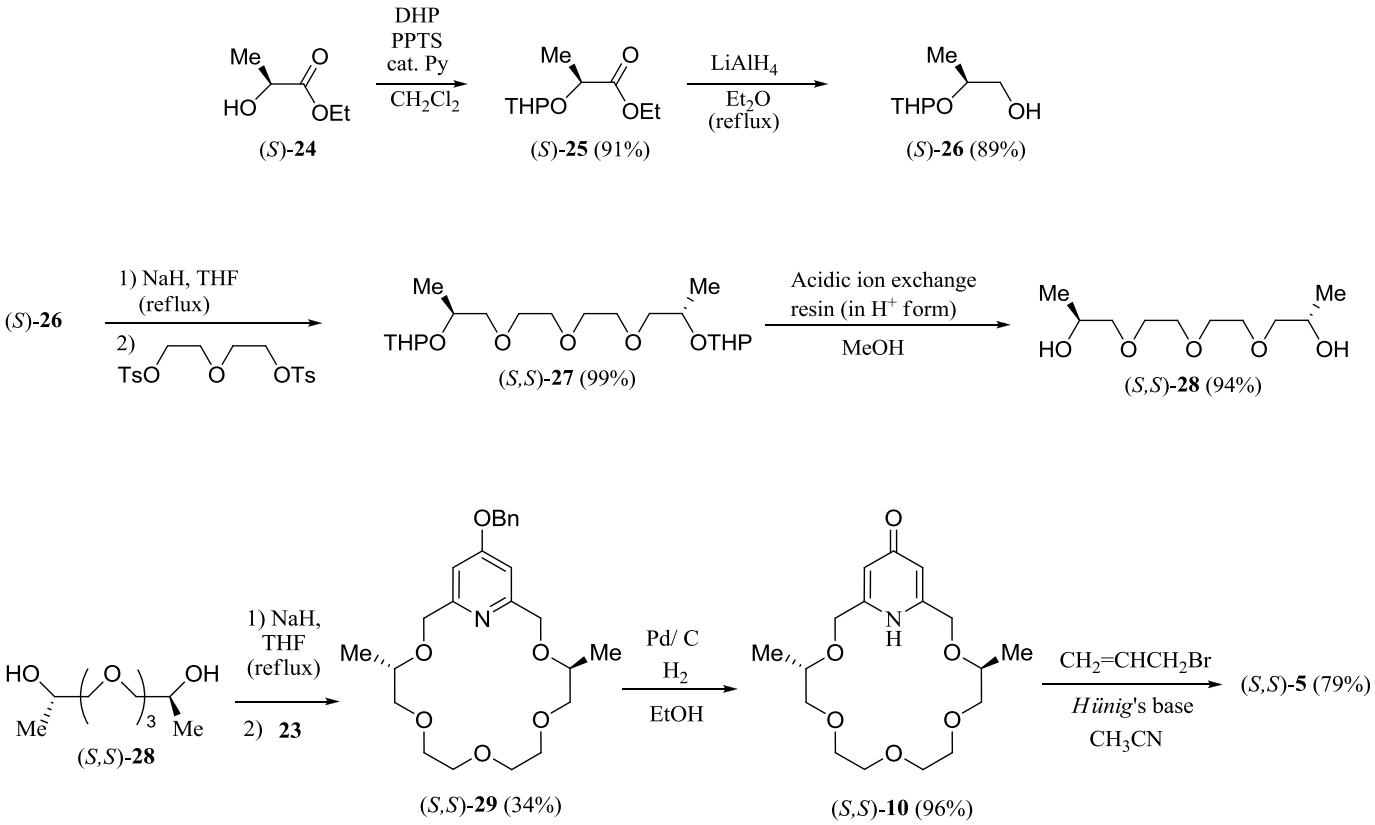
Detailed syntheses of functional monomers

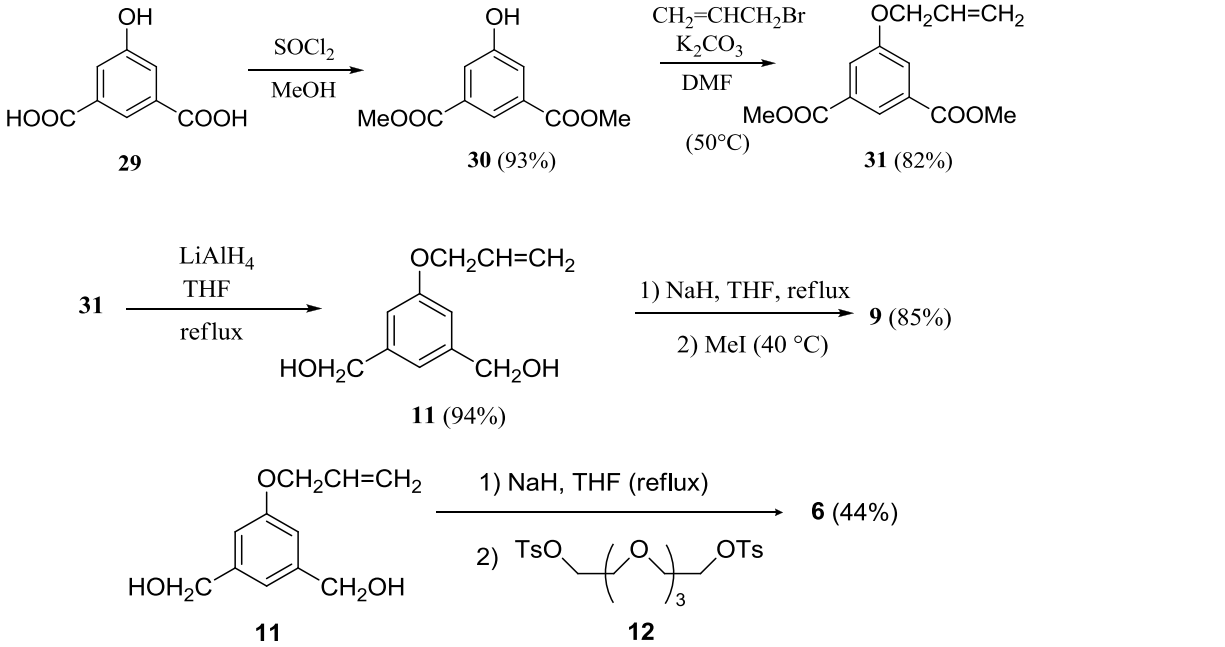
Functional monomers (*S*,*S*)-**5**–**9** were synthesized as shown in **Scheme S1–S4.**



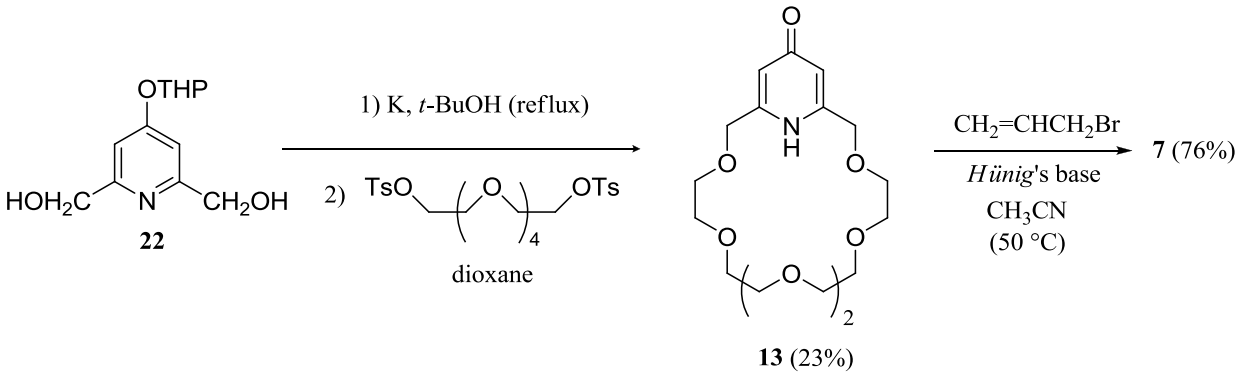
Scheme S1. Synthesis of functional monomer **8** and intermediate **23**.



Scheme S2. Synthesis of functional monomer (*S*,*S*)-**5**.



Scheme S3. Syntheses of functional monomer **6** and **9**.



Scheme S4. Synthesis of functional monomer **7.**

Adsorption Isotherm

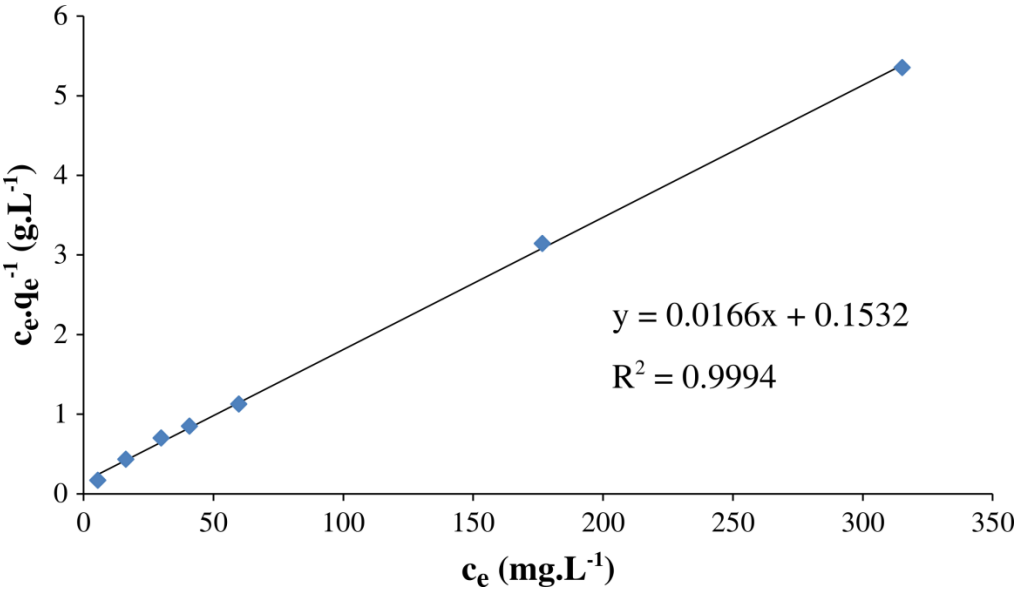


Figure S1. Typical isotherm fitted to the Langmuir model. 20 mL of 6-12 mM Rac-**1** in acetonitrile/methanol (1/4) per gram $IP1^A$ was loaded.

IR Spectra of functional monomers

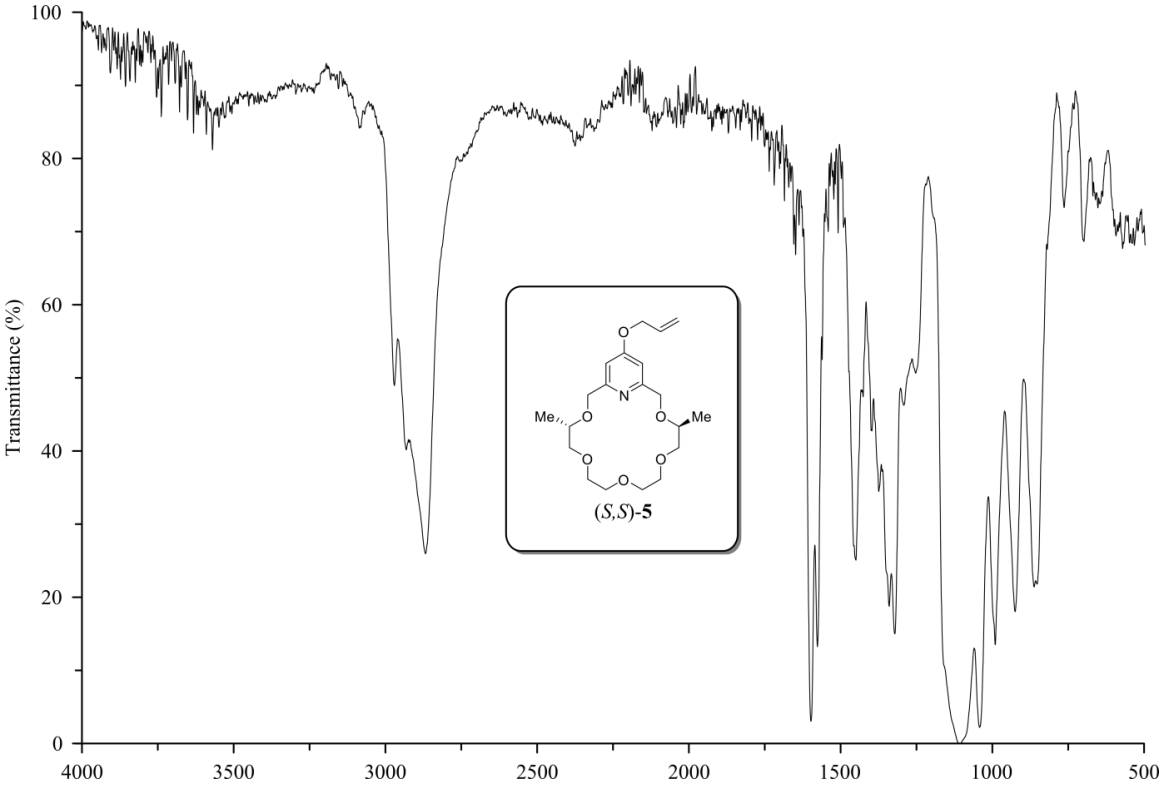


Figure S2. IR spectum of (4*S*,14*S*)-(+)-19-allyloxy-4,14-dimethyl-3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1] heneicosa-1(*21*),17,19-triene [(*S*,*S*)-**5**].

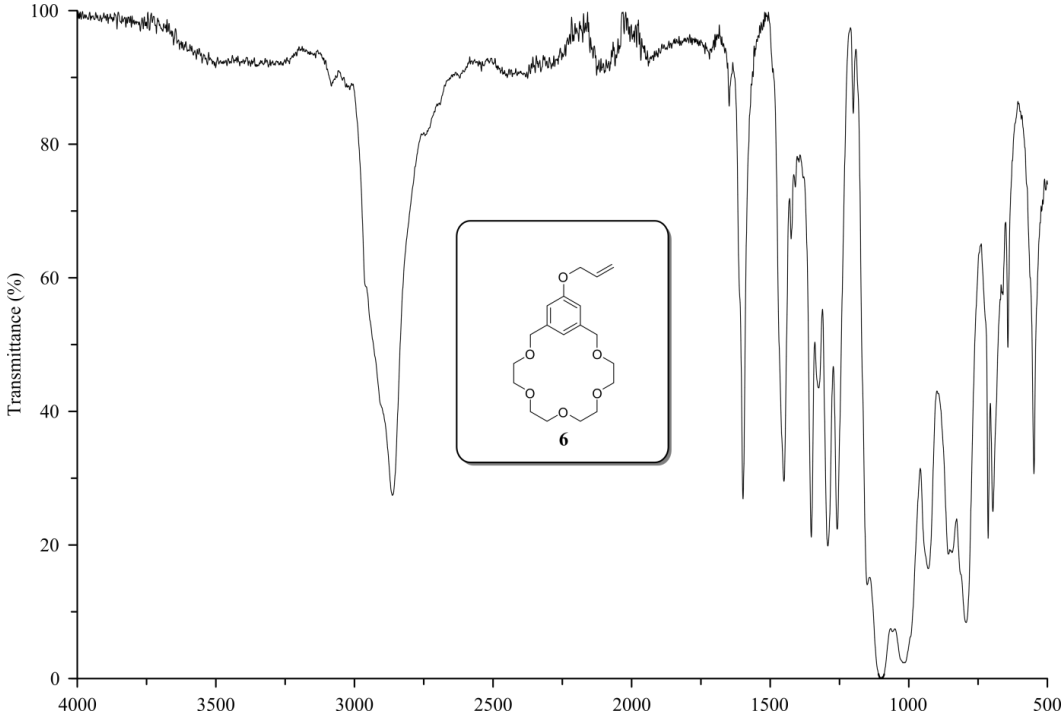


Figure S3. IR spectrum of 19-allyloxy-3,6,9,12,15-pentaoxabicyclo[15.3.1] heneicosa-1(*21*),17,19-triene (**6**).

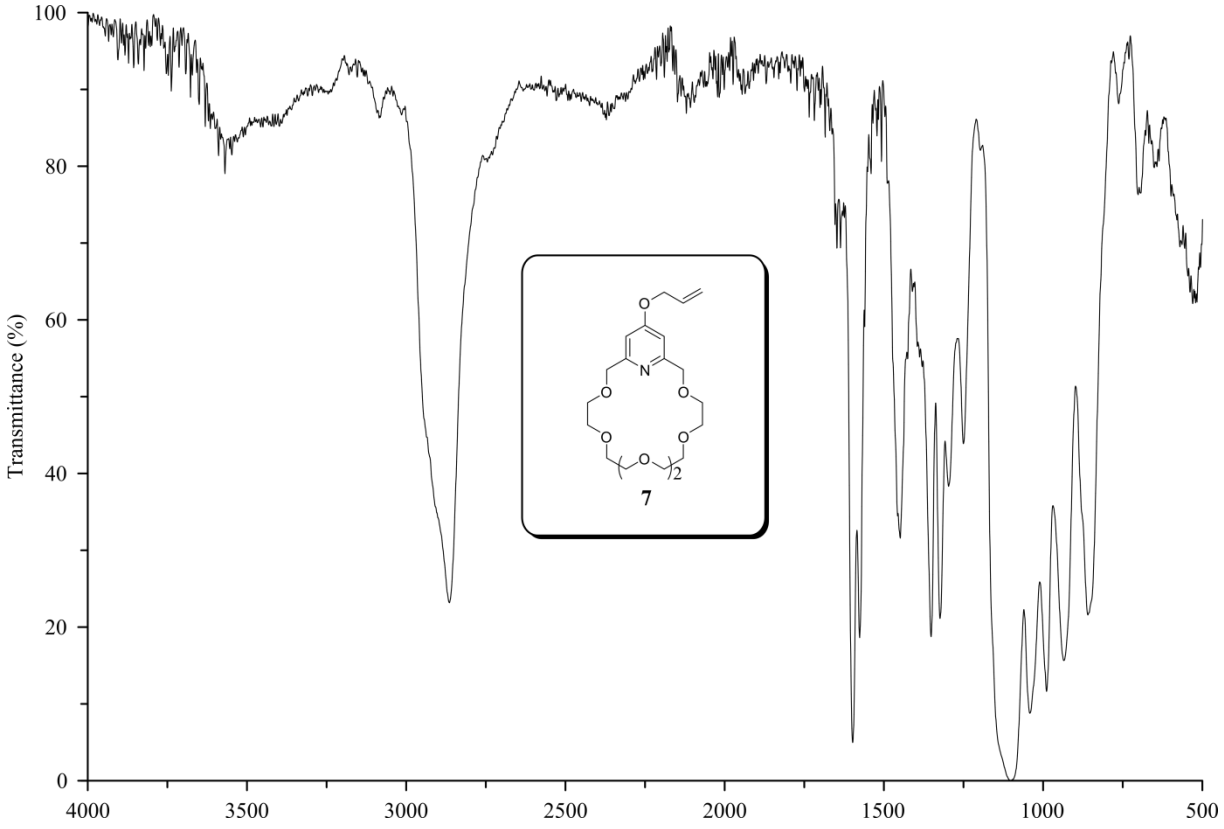


Figure S4. IR spectrum of 22-allyloxy-3,6,9,12,15,18-hexaoxa-24-azabicyclo[18.3.1]tetracosa-20,22,24-triene (**7**).

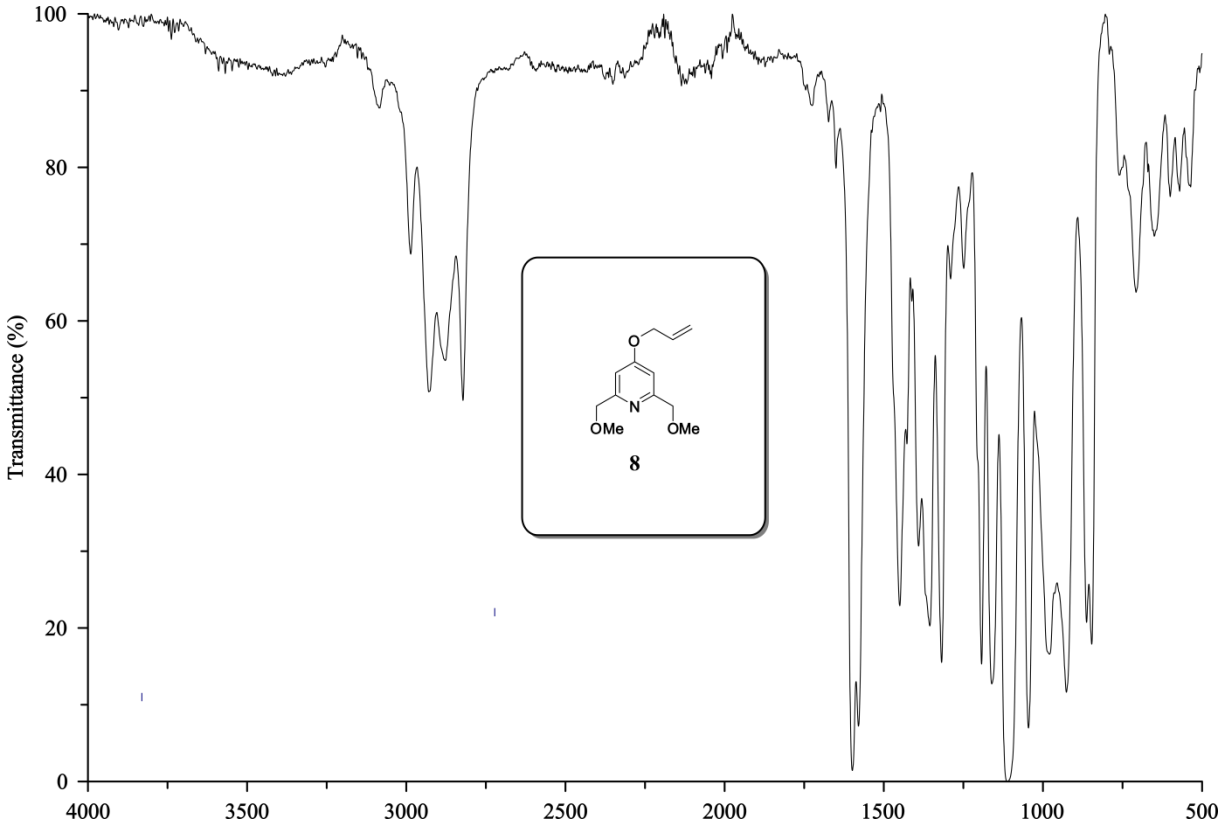


Figure S5. IR spectrum of 4-(allyloxy)-2,6-bis(methoxymethyl)pyridine (**8**).

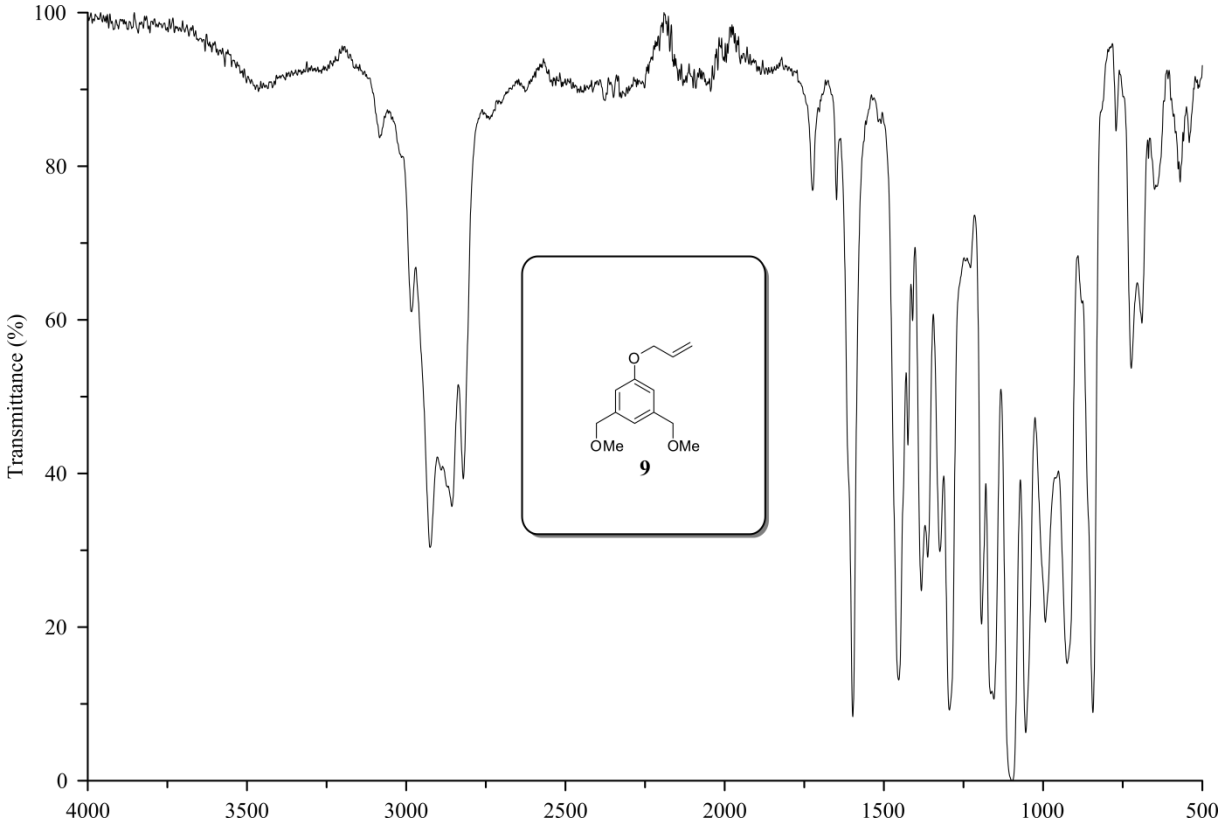


Figure S6. IR spectrum of 1-(allyloxy)-3,5-bis(methoxymethyl)benzene (**9**).

^{1}H- & ^{13}C-NMR Facsimilies

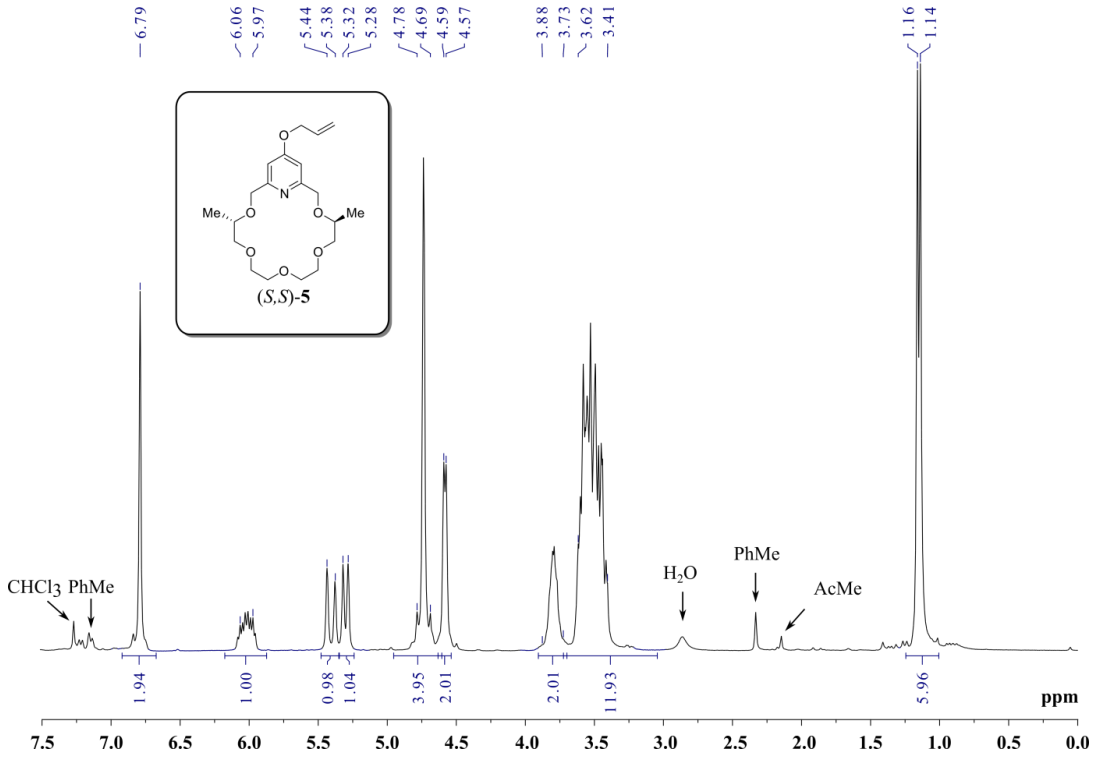


Figure S7. ^{1}H NMR spectrum of (4*S*,14*S*)-(+)-19-allyloxy-4,14-dimethyl-3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1] heneicosa-1(*21*),17,19-triene [(*S*,*S*)-**5**].

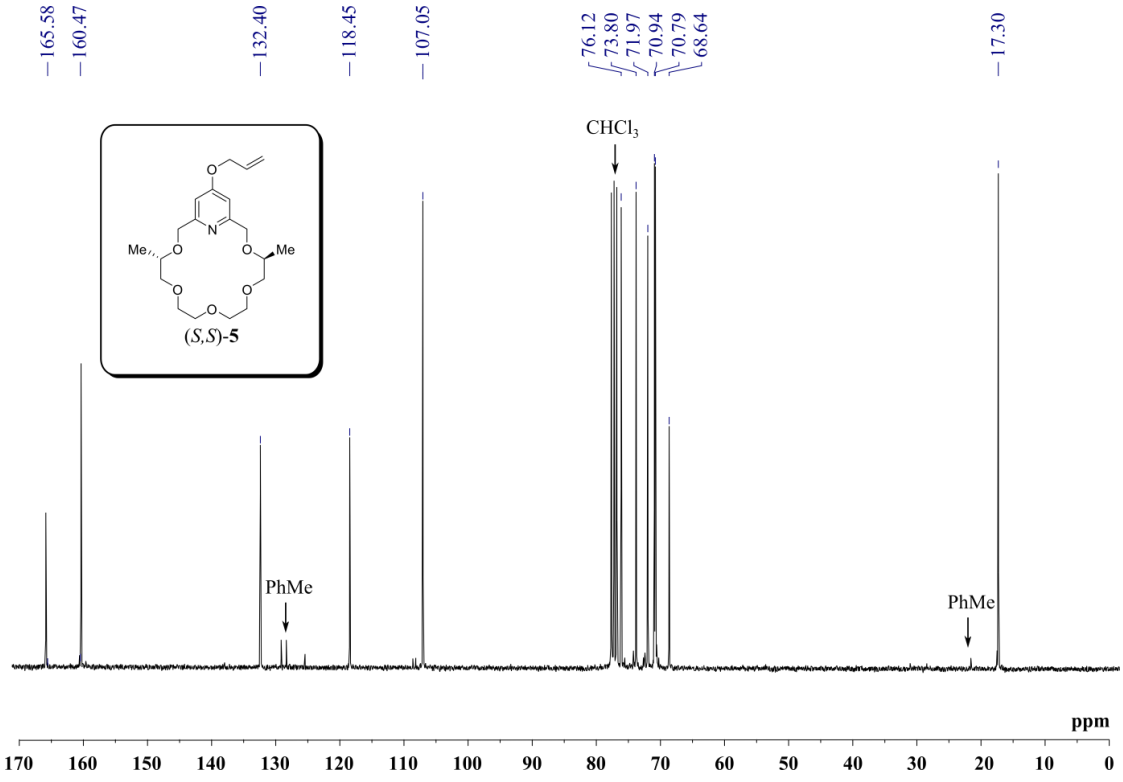


Figure S8. ^{13}C NMR spectrum of (4*S*,14*S*)-(+)-19-allyloxy-4,14-dimethyl-3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1] heneicosa-1(21),17,19-triene [(*S*,*S*)-**5**].

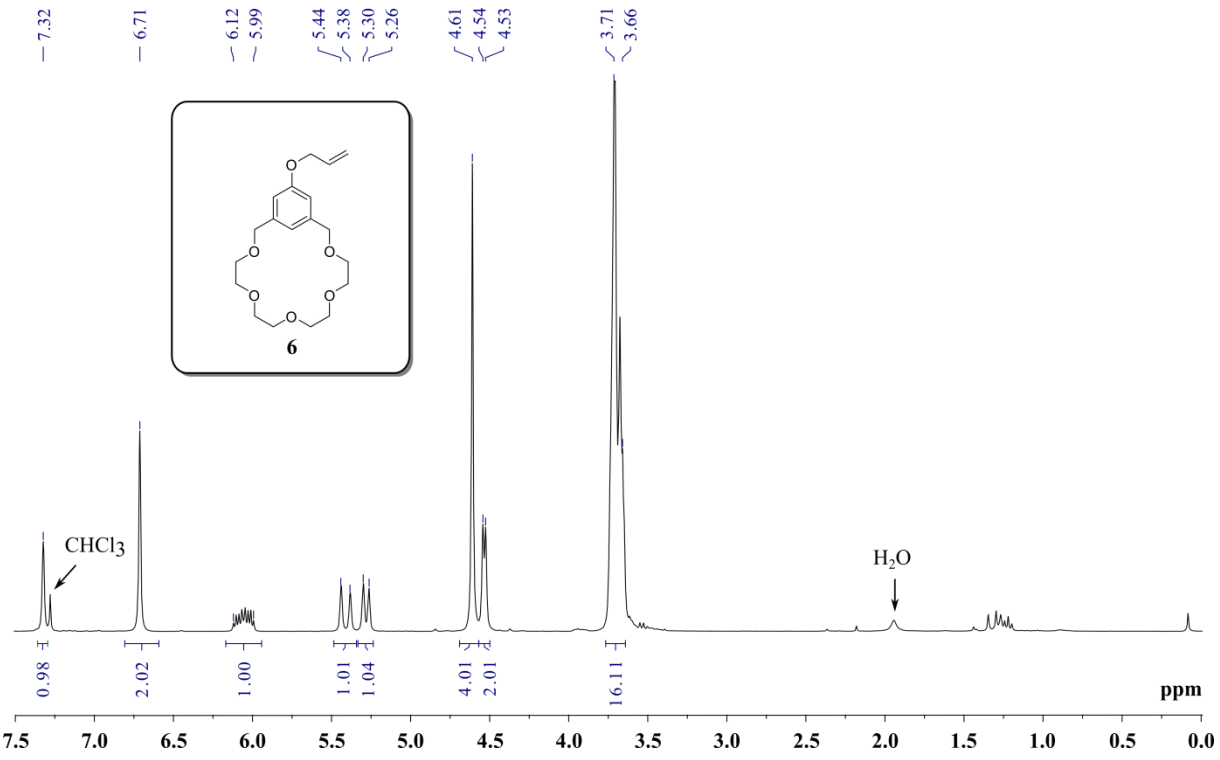


Figure S9. [1]H NMR spectrum of 19-allyloxy-3,6,9,12,15-pentaoxabicyclo[15.3.1] heneicosa-1(*21*),17,19-triene (**6**).

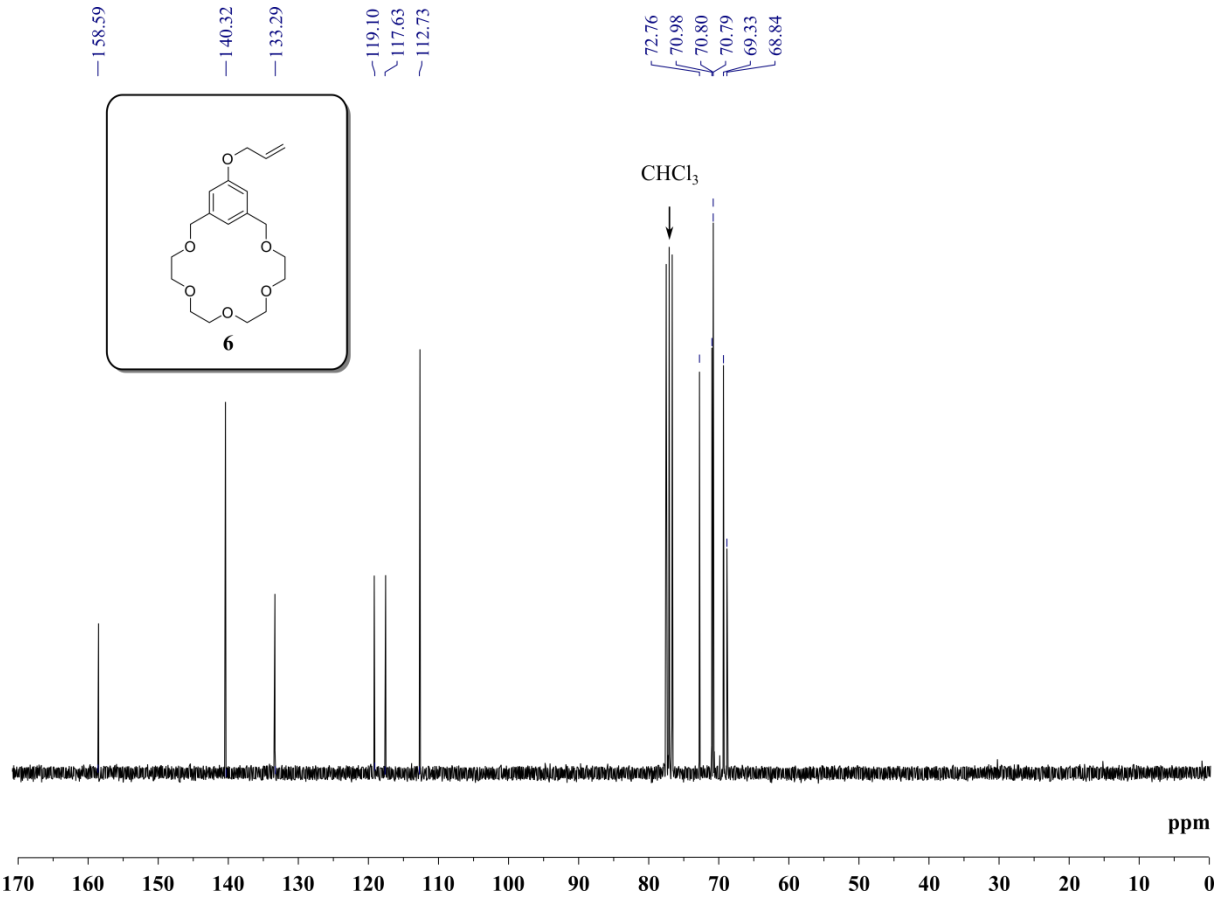


Figure S10. [13]C NMR spectrum of 19-allyloxy-3,6,9,12,15-pentaoxabicyclo[15.3.1] heneicosa-1(*21*),17,19-triene (**6**).

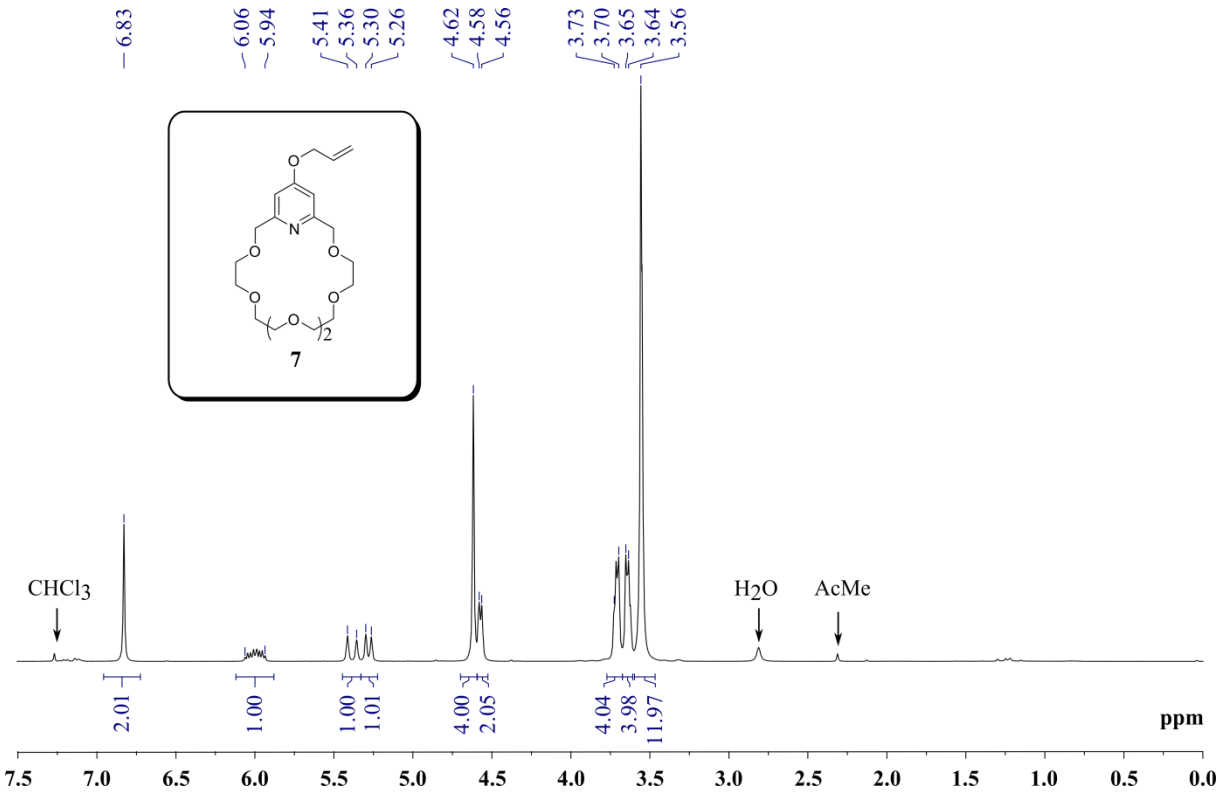


Figure S11. ^{1}H NMR spectrum of 22-allyloxy-3,6,9,12,15,18-hexaoxa-24-azabicyclo[18.3.1]tetracosa-20,22,24-triene (**7**).

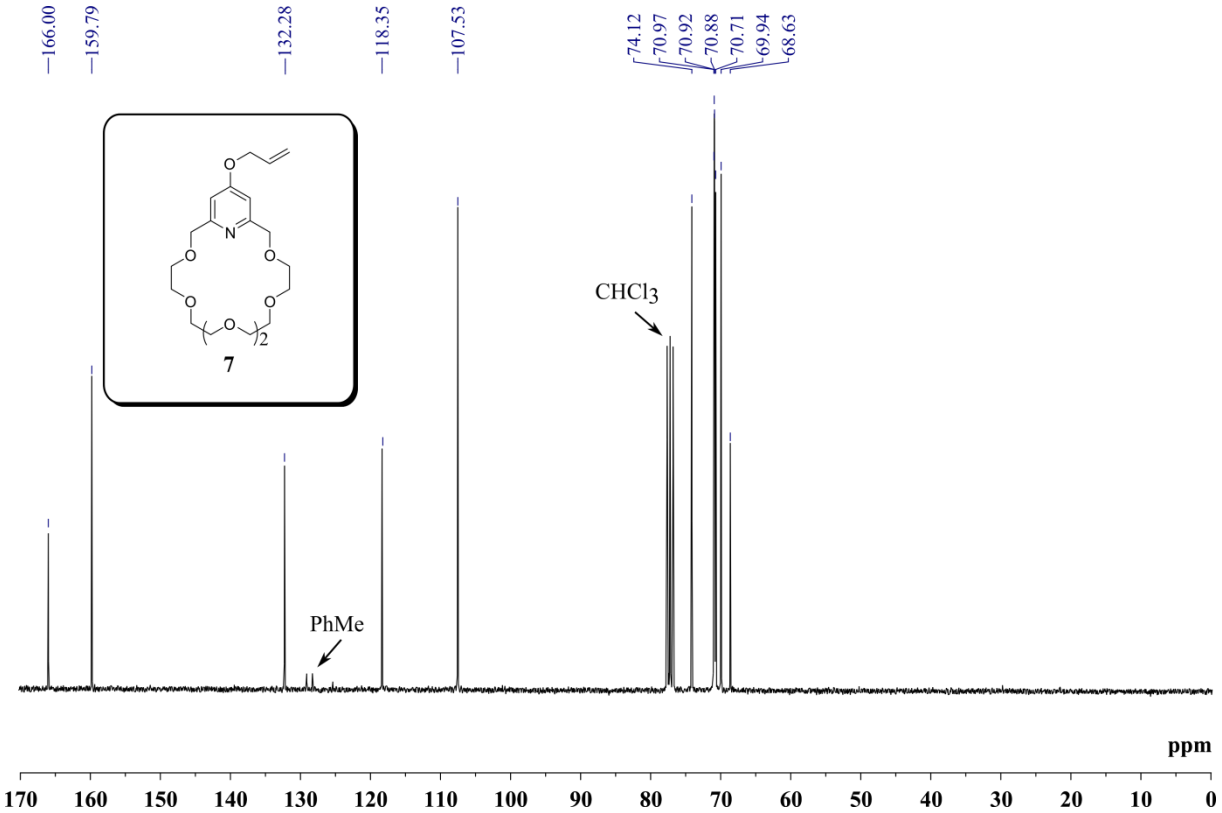


Figure S12. ^{13}C NMR spectrum of 22-allyloxy-3,6,9,12,15,18-hexaoxa-24-azabicyclo[18.3.1]tetracosa-20,22,24-triene (**7**).

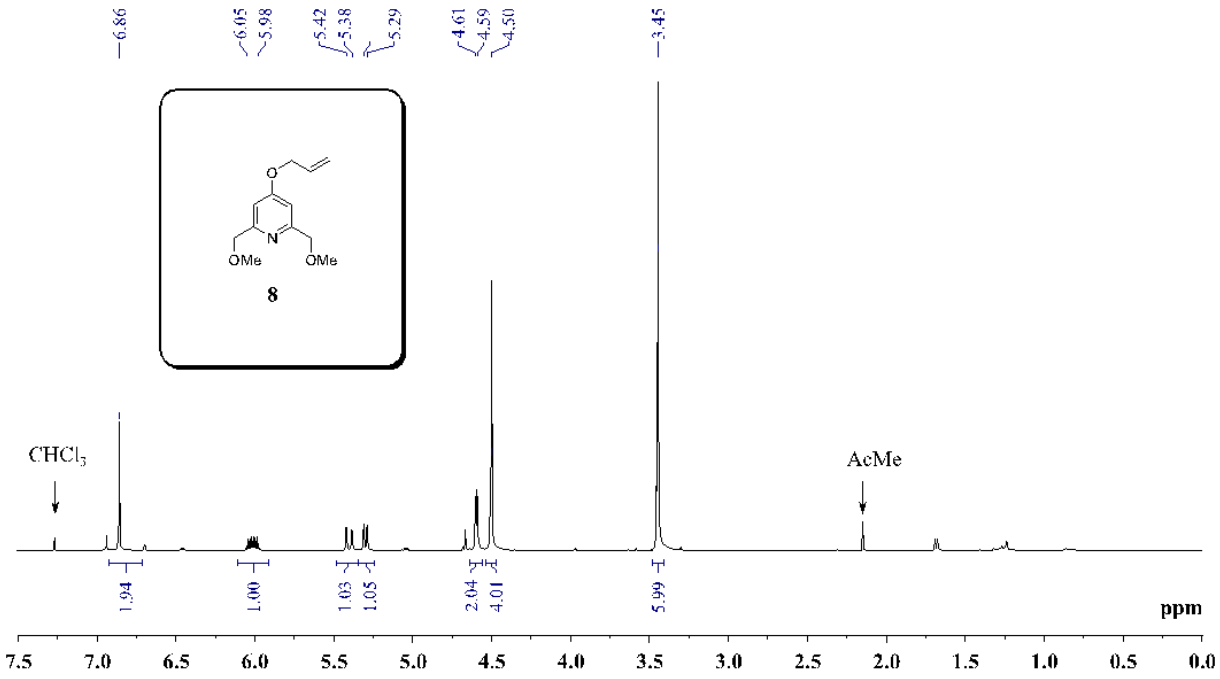


Figure S13. ^{1}H NMR spectrum of 4-(allyloxy)-2,6-bis(methoxymethyl)pyridine (**8**).

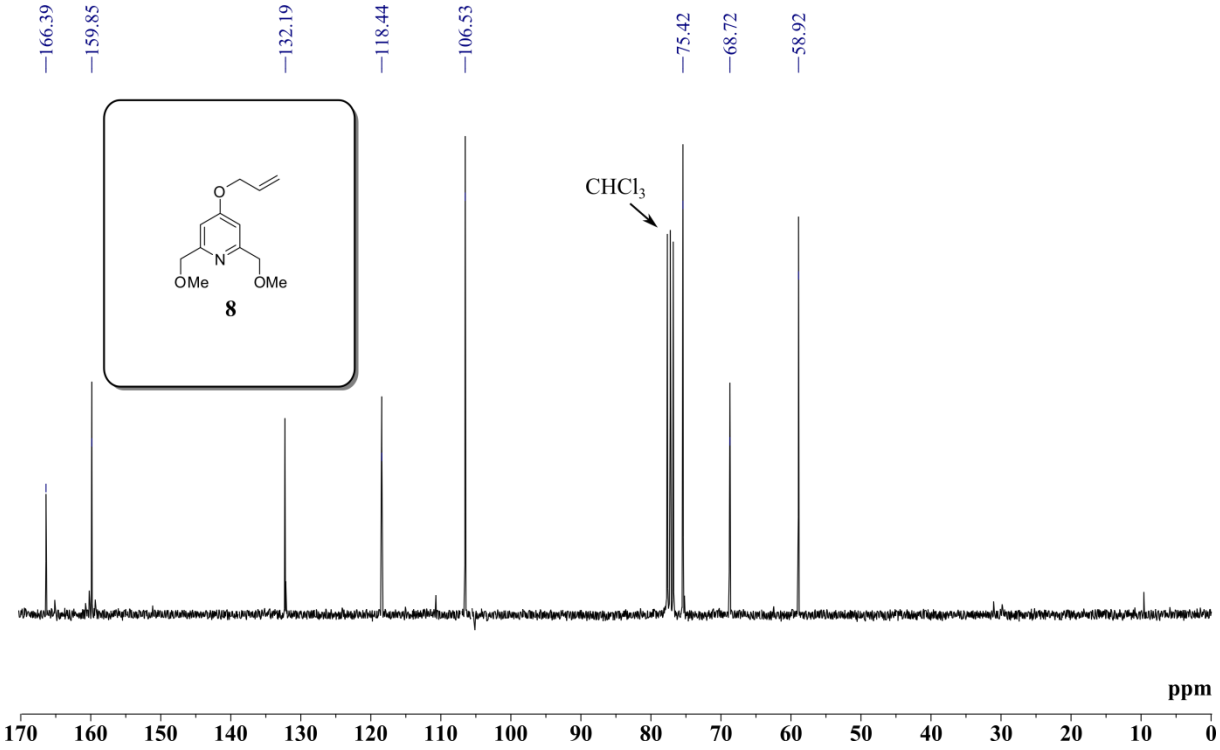


Figure S14. ^{13}C NMR spectrum of 4-(allyloxy)-2,6-bis(methoxymethyl)pyridine (**8**).

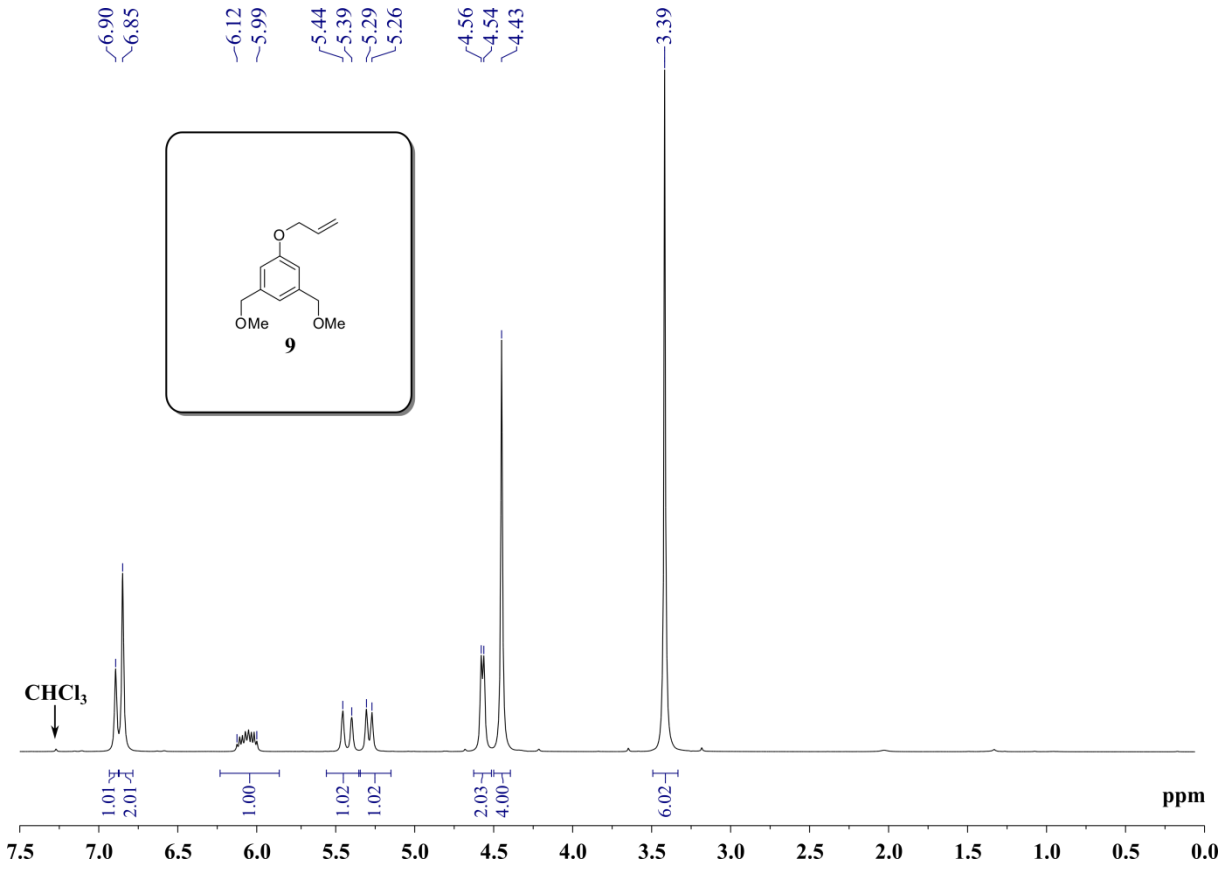


Figure S15. [1]H NMR spectrum of 1-(allyloxy)-3,5-bis(methoxymethyl)benzene (**9**).

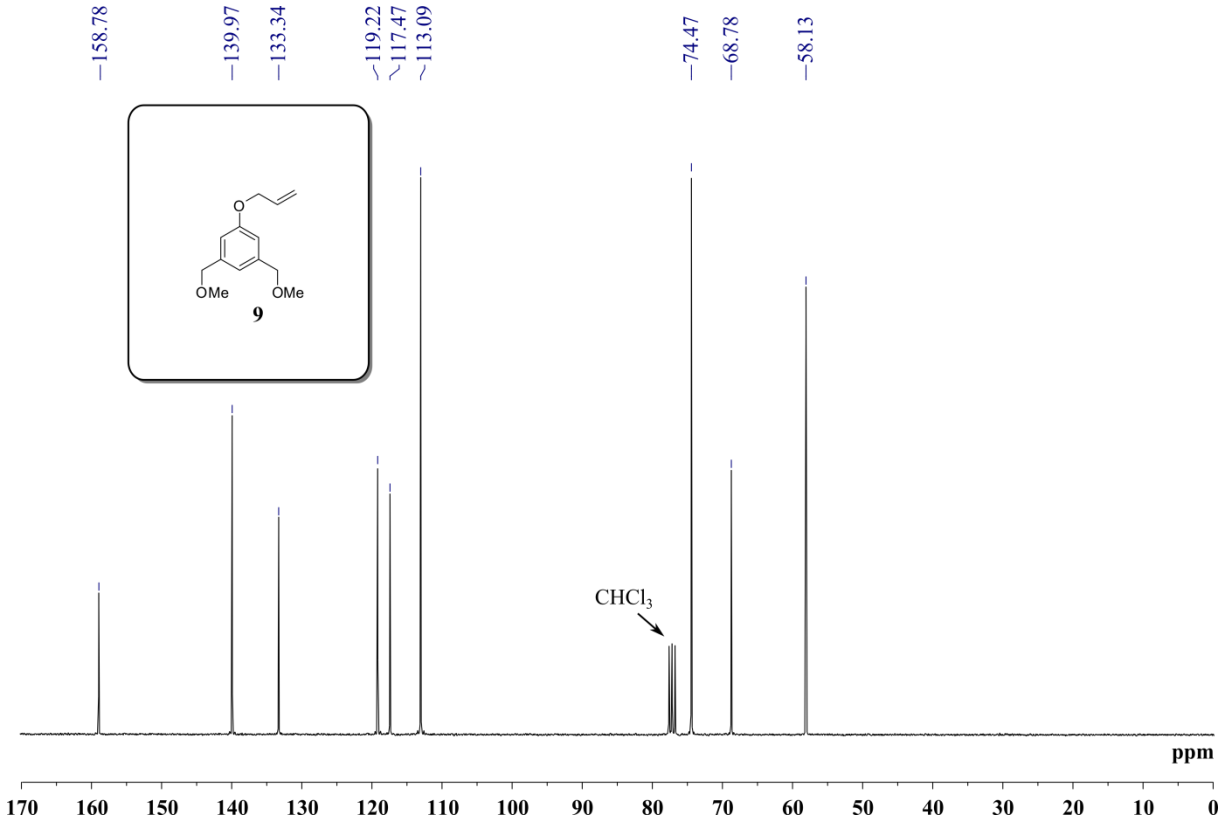


Figure S16. [13]C NMR spectrum of 1-(allyloxy)-3,5-bis(methoxymethyl)benzene (**9**).

ESI Mass Spectra

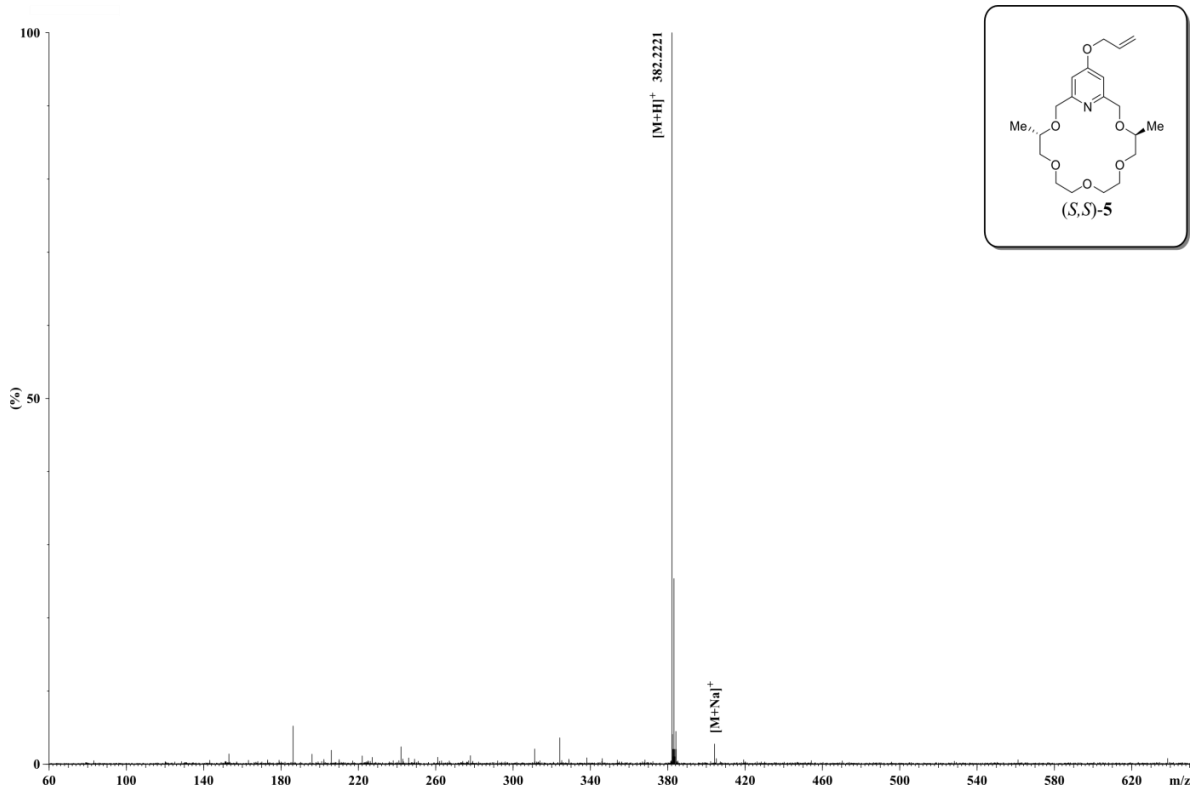


Figure S17. MS spectrum of (4*S*,14*S*)-(+)-19-allyloxy-4,14-dimethyl-3,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1] heneicosa-1(*21*),17,19-triene [(*S*,*S*)-**5**].

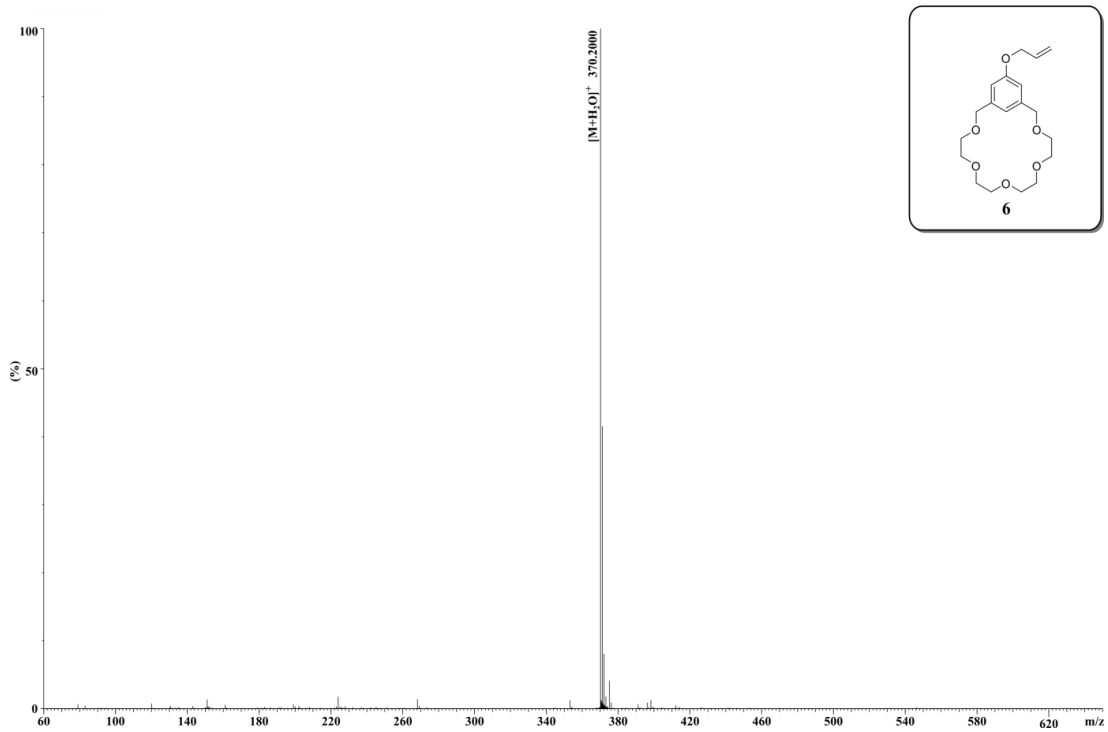


Figure S18. MS spectrum of 19-allyloxy-3,6,9,12,15-pentaoxabicyclo[15.3.1] heneicosa-1(*21*),17,19-triene (**6**).

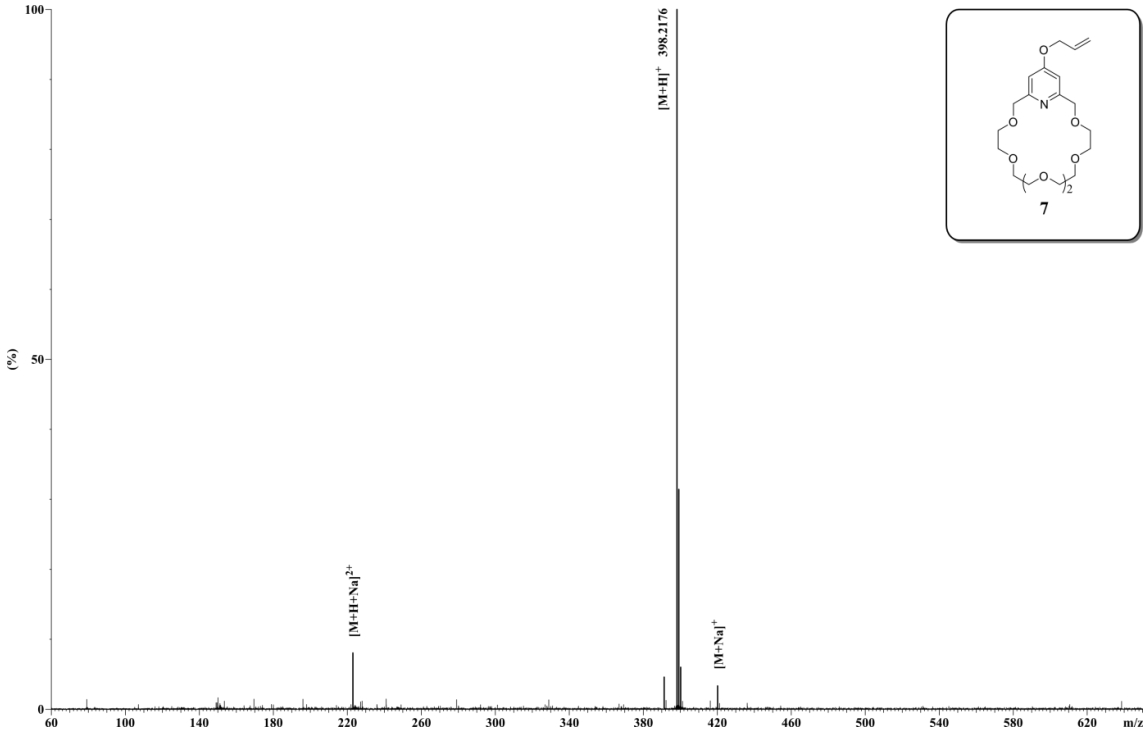


Figure S19. MS spectrum of 22-allyloxy-3,6,9,12,15,18-hexaoxa-24-azabicyclo[18.3.1]tetracosa-20,22,24-triene (**7**).

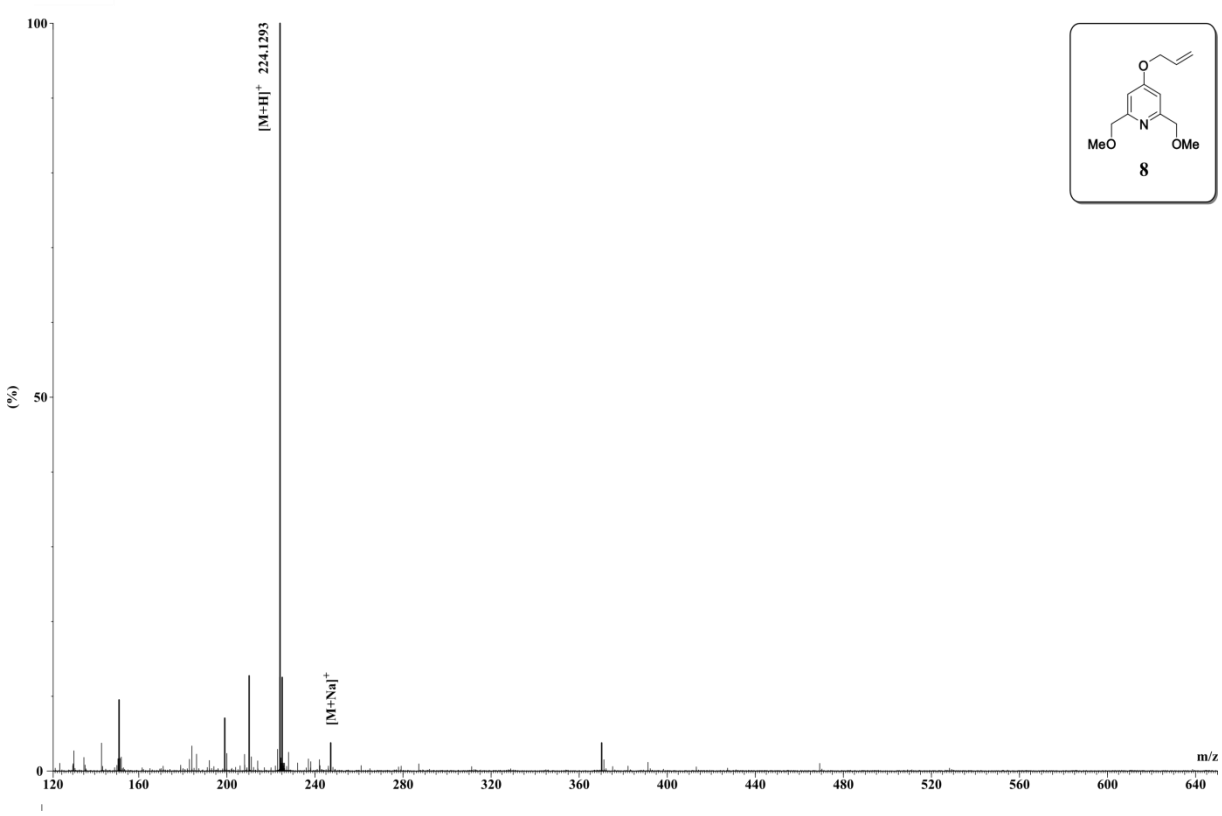


Figure S20. MS spectrum of 4-(allyloxy)-2,6-bis(methoxymethyl)pyridine (**8**).

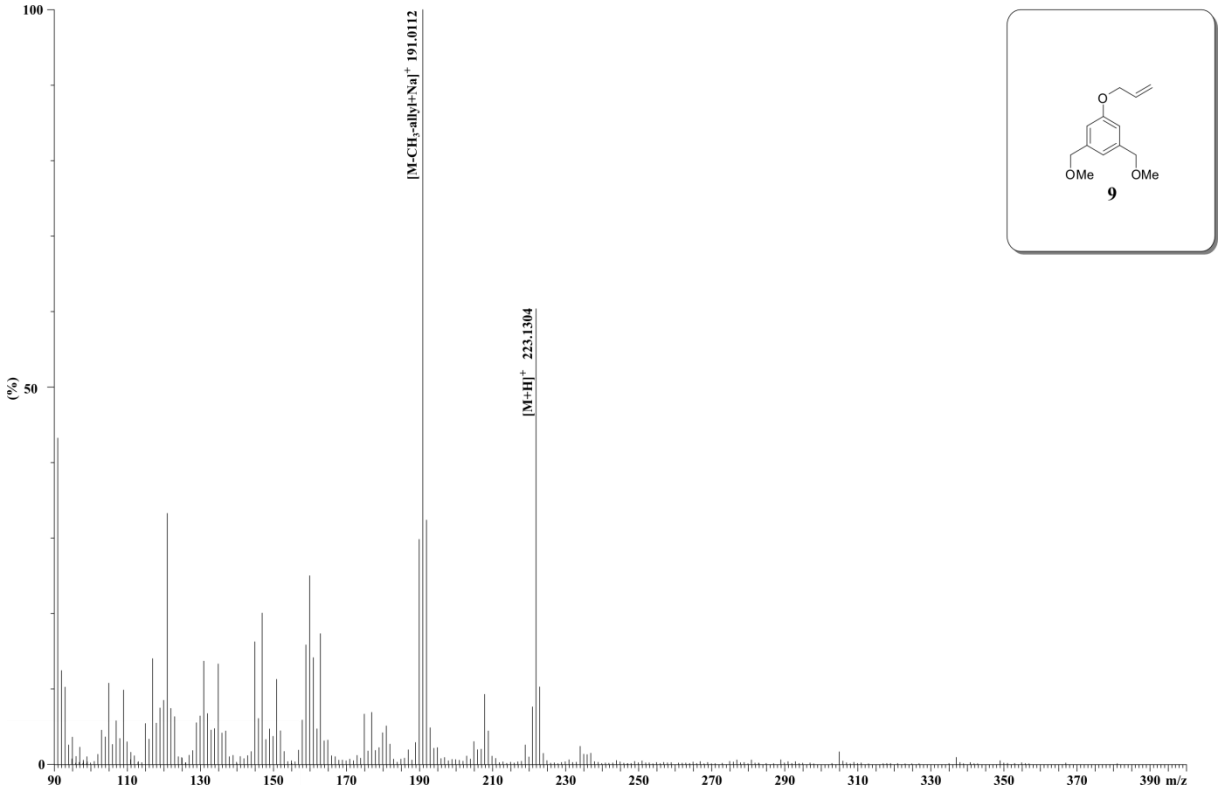


Figure S21. MS spectrum of 1-(allyloxy)-3,5-bis(methoxymethyl)benzene (**9**).

Table S1. Fitting results for kinetic data*

Analyte Released	Polymer	pH	First order model		Higuchi model		Hixson–Crowell model		Korsmeyer–Peppas model		
			k_1 (h^{-1})	R^2 (-)	k_2 ($h^{-0.5}$)	R^2 (-)	k_3 (h^{-1})	R^2 (-)	k_4 (h^{-n})	n (-)	R^2 (-)
		6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	IP1[A]	8	0.188±0.005	0.9452	0.232±0.005	0.9838	0.053±0.001	0.9299	0.375±0.026	0.3763±0.0310	0.9810
		10	0.602±0.184	0.9513	0.116±0.000	0.9502	0.085±0.015	0.8953	0.905±0.020	0.0576±0.0011	0.9696
		6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
(*R*)-**1**	IP1[B]	8	0.189±0.016	0.9112	0.224±0.006	0.9609	0.053±0.004	0.8978	0.396±0.031	0.3517±0.0169	0.9572
		10	0.411±0.104	0.7686	0.094±0.001	0.8834	0.062±0.007	0.7232	0.910±0.028	0.0440±0.0052	0.8392
		6	0.714±0.124	0.9915	0.319±0.001	0.9201	0.121±0.012	0.9612	0.6762±0.0216	0.2835±0.0067	0.9496
	CP1	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		6	0.595±0.086	0.9955	0.449±0.032	0.9569	0.123±0.013	0.9775	0.489±0.024	0.5006±0.0392	0.9537
	IP1[A]	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		6	0.710±0.181	0.9944	0.372±0.000	0.9436	0.127±0.019	0.9806	0.608±0.024	0.3546±0.0195	0.9568
(*S*)-**1**	IP1[B]	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		6	0.594±0.118	0.9680	0.319±0.001	0.9201	0.121±0.012	0.9612	0.676±0.022	0.2835±0.0067	0.9496
	CP1	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Analyte Released	Polymer	pH	First order model		Higuchi model		Hixson–Crowell model		Korsmeyer–Peppas model		
			k_1 (h^{-1})	R^2 (-)	k_2 ($h^{-0.5}$)	R^2 (-)	k_3 (h^{-1})	R^2 (-)	k_4 (h^{-n})	n (-)	R^2 (-)
		6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	IP2[A]	8	0.213±0.019	0.9369	0.221±0.023	0.9824	0.053±0.001	0.9301	0.476±0.004	0.2771±0.0333	0.9841
		10	0.907±0.227	0.9889	0.111±0.005	0.9457	0.105±0.011	0.9284	0.931±0.022	0.0534±0.0129	0.9829
		6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
(*R*)-**1**	IP2[B]	8	0.207±0.006	0.9430	0.217±0.011	0.9827	0.055±0.001	0.9267	0.464±0.006	0.2830±0.0141	0.9861
		10	1.189±0.898	0.9815	0.108±0.001	0.8983	0.115±0.041	0.9122	0.934±0.035	0.0469±0.0057	0.9142
		6	0.726±0.212	0.9942	0.258±0.032	0.9353	0.114±0.025	0.9668	0.743±0.014	0.2110±0.0243	0.9712
	CP2	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		6	0.681±0.150	0.9902	0.4027±0.0016	0.9495	0.128±0.016	0.9786	0.568±0.031	0.4030±0.0227	0.9594
	IP2[A]	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
(*S*)-**1**	IP2[B]	8	0.165±0.027	0.9636	0.158±0.023	0.9780	0.043±0.005	0.9532	0.498±0.029	0.2092±0.0504	0.9975
		10	0.955±0.223	0.9899	0.107±0.012	0.9445	0.108±0.016	0.9291	0.937±0.009	0.0520±0.0165	0.9802
		6	0.794±0.166	0.9984	0.332±0.003	0.9381	0.131±0.016	0.9757	0.673±0.018	0.2916±0.0129	0.9659
	CP2	8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
		10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

*In all cases zero-order model gave R^2 smaller than 0.7