Supporting Information

Structural evolution and reaction pathways in ring-opening polymerization for mono-benzoxazines based on phenol-aniline/cyclohexylamine

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Contents:

Materials

Phenol (⩾ 99%), aniline (⩾ 99.5%), cyclohexylamine (CHA) (⩾ 98%), paraformaldehyde (⩾95%), formaldehyde (37 wt. % aqueous), toluene (⩾99.5%), and chloroform (⩾99%) were purchased from Kermel Chemical Reagent Co., Ltd, China. All chemicals were used as received.

Synthesis of benzoxazines

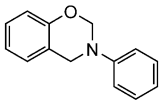
Phenol-aniline-based benzoxazine (PH-a). In a 250 mL three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, 9.3 mL (0.1 mol) of aniline and 6.0 g (0.2 mol) of paraformaldehyde in 40 mL of toluene were stirred at 0 °C for 60 min. Subsequently, 9.4 mL (0.1 mol) of phenol was added to the reaction solution, and the temperature was gradually raised to 80 °C and maintained for 5 h. Thereafter, the solvent was removed by distillation under vacuum to get a solid crude product, which was dissolved in approximately 30 mL of chloroform. The chloroform solution was washed several times with a 1.5 mol/L NaOH aqueous solution and deionized water, respectively, followed by evaporation of the chloroform under reduced pressure. Subsequently, the reaction mixture was subjected to a silica gel (200–300 mesh) column chromatography followed by elution with a dichloromethane/petroleum ether mixture (1/2 in volume) to afford fraction of the product. The product was dried at 65 °C in a vacuum oven for 24 h. Finally, a pale yellow solid product was obtained, and the yield was approximately 78%.

Phenol-cyclohexylamine-based benzoxazine (PH-cha). In a 250 mL three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, 10 mL (0.1 mol) of cyclohexylamine and 17 mL (0.2 mol) of formaldehyde in 40 mL of toluene were stirred at 0 °C for 60 min. Subsequently, 9.4 mL (0.1 mol) of phenol was added to the reaction solution, and the temperature was gradually raised to 75 °C and maintained for 3 h. Thereafter, the solvent was removed by distillation under vacuum to get a solid crude product, which was dissolved in approximately 30 mL of chloroform. The chloroform solution was washed several times with a 1.5 mol/L NaOH aqueous solution, a 0.1 mol/L HCl aqueous solution, and deionized water, respectively, followed by evaporation of the chloroform under reduced pressure. Subsequently, the reaction mixture was subjected to a silica gel (200–300 mesh) column chromatography followed by elution with an ethyl acetate/petroleum ether mixture (1/5 in volume) to afford fraction of the product. The product was dried at 65

°C in a vacuum oven for 24 h. Finally, a pale yellow solid was obtained, and the yield was approximately 48%.

^{1}H and ^{13}C NMR, FTIR, and MS data of benzoxazines

PH-a



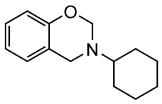
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.68 (s, 2H, Ar–C*H*$_2$–N), 5.41 (s, 2H, N–C*H*$_2$–O), 6.88 (d, 1H, Ar–H), 6.95 (t, 1H, Ar–H), 7.00 (t, 1H, Ar–H), 7.06 (d, 1H, Ar–H), 7.17 (s, 1H, Ar–H), 7.19 (s, 2H, Ar–H), and 7.33 (t, 2H, Ar–H).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 50.50 (Ar–*C*H_2–N), 79.56 (O–*C*H_2–N), 117.08 (Ar–H), 118.36 (Ar–H), 120.94 (Ar–H), 121.04 (Ar–CH_2–N), 121.54 (Ar–H), 126.88 (Ar–H), 127.99 (Ar–H), 129.40 (Ar–H), 148.51 (Ar–N), and 154.51 (Ar–O).

FTIR (KBr, cm^{-1}): 3025 (νC–H of aromatic ring), 2953 (ν_sC–H of CH_2), 2923 (ν_{as}C–H of CH_2), 2853 (ν_sC–H of CH_2), 1600, 1583, and 1489 (aromatic C═C), 1455 (C–H scissoring bending of CH_2), 1374, 1338, and 1297 (CH_2 wagging), 1253 (CH_2 twisting), 1227 (ν_{as}C–O–C in oxazine ring), 1157, 1113, and 1086 (ν_{as}C–N–C in oxazine ring), 1032 (ν_sC–O–C in oxazine ring), 944 (O–C–N stretching mode of the oxazine ring with minor contribution of the C–H out-of-plane bending), 971 (aromatic C–H in-plane bending), 851, 752, and 693 (aromatic C–H out-of-plane bending), and 589 (CCC in-plane bending)

MS (ESI, *m*/*z*): $[M+H]^+$ calcd for $C_{14}H_{13}NO$, 212.1070; found, 212.1072.

PH-cha



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.26–1.98 (m, 10H, C*H*$_2$ of cyclohexyl group), 2.72 (s, 1H, C*H* of cyclohexyl group), 4.10 (s, 2H, Ar–C*H*$_2$–N), 5.00 (s, 2H, O–C*H*$_2$–N), 6.75 (d, 1H, Ar–H), 6.85 (t, 1H, Ar–H), 6.95 (d, 1H, Ar–H), and 7.11 (t, 1H, Ar–H).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 25.56, 25.97, and 31.66 (*C*H_2 of cyclohexyl group), 58.74 (*C*H of cyclohexyl group), 47.45 (Ar–*C*H_2–N), 80.33 (O–*C*H_2–N), 116.56 (Ar–H), 120.32 (Ar–H), 121.81 (Ar–CH_2–N), 127.03 (Ar–H), 127.47 (Ar–H), and 155.19 (Ar–O–CH_2).

FTIR (KBr, cm^{-1}): 3018 (νC–H of aromatic ring), 2928 (ν_{as}C–H of CH_2), 2854 (ν_sC–H of CH_2), 1609, 1584, and 1489 (aromatic C═C), 1455 (C–H scissoring

bending of CH_2), 1378, 1358, and 1332 (CH_2 wagging), 1259 (CH_2 twisting), 1225 (ν_{as}C–O–C in oxazine ring), 1187, 1146, and 1128 (ν_{as}C–N–C in oxazine ring), 1105 and 1032 (ν_{s}C–O–C in oxazine ring), 920 (O–C–N stretching mode of the oxazine ring with minor contribution of the C–H out-of-plane bending), 994, 974, and 903 (aromatic C–H in-plane bending), 842, 752, and 706 (aromatic C–H out-of-plane bending), and 587 (CCC in-plane bending).

MS (ESI, *m*/*z*): $[M+H]^+$ calcd for $C_{14}H_{19}NO$, 218.1539; found, 218.1537. $[M+Na]^+$ calcd for $C_{14}H_{19}NO$, 240.1359; found, 240.1360.

Thermal treatment of benzoxazine monomers

Each benzoxazine monomer was put in a glass bottle (diameter 25 mm and height 25 mm) with a ground glass stopper. Partially polymerized samples of PH-a and PH-cha were prepared by isothermally heating PH-a at 190 °C for 60 min and PH-cha at 170 °C for 20 min and are referred to as PH-a-190-60 and PH-cha-170-20, respectively, and the samples obtained by isothermally heating PH-a at 220 °C for 35 min and PH-cha at 180 °C for 35 min are referred to as PH-a-220-35 and PH-cha-180-35, respectively, where the numbers indicate the polymerization temperature and time, respectively.

Preparation of polybenzoxazines

First, PH-a or PH-cha was put into a steel mold preheatd in an over at 90 °C, and the mold was put into a vacuum oven. Then, for PH-a, the vacuum oven was step-heated to 130, 140, 150, 160, 170, 180, and 190 °C and hold at each temperature for 1 h, thereafter, hold at 200 °C for 6 h; whereas for PH-cha, the vacuum oven was step-heated to 120, 130, 140, 150, 160, 170, and 180 °C and held at each temperature for 1 h, and then at 190 °C for 6 h.

Measurements

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired in a Zhongke-Niujin BUXI-I 400 NMR spectrometer with an operating frequency of 400 MHz. Deuterated chloroform ($CDCl_3$) was used as the solvent and tetramethylsilane (TMS) as the internal standard.

The FTIR spectra of PH-a and PH-cha and their thermal treated products were obtained in the transmittance mode using a Nicolet 380 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA) with a deuterated triglycine sulfate (DTGS) detector. The spectral resolution was 4 cm^{-1}, and the number of scans was 32. Samples were dissolved in chloroform and the solution was coated on a KBr disk. By evaporating the solvent at 50 °C in a vacuum oven, a thin uniform film was formed. Thereafter, the disk was heated isothermally in a static air oven and removed periodically to be scanned.

A TA instruments Q2000 differential scanning calorimeter was used to monitor the thermal behavior of PH-a and PH-cha, operating at a heating rate of 10 °C/min in a nitrogen flow of 50 mL/min. The amount of benzoxazine samples used was about 4 mg.

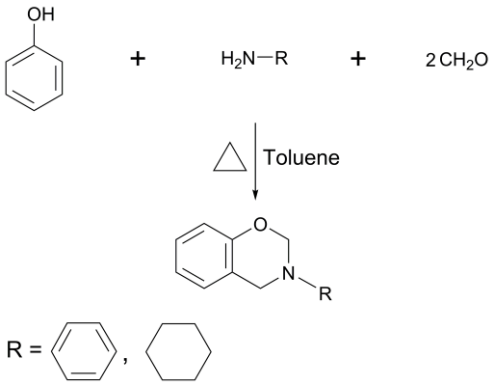
Dynamic mechanical analysis (DMA) was performed using a TA instruments Q800 dynamic mechanical analyzer at a heating rate of 5°C/min under multi-frequency-strain mode. The dimensions of rectangular specimens were nominally 15.0 mm × 6.0 mm × 1.0 mm.

Thermogravimetric analysis was performed with a TA instruments Q50 thermogravimeter operating at a heating rate of 10 °C/min in a nitrogen flow of 50 mL/min. The amount of benzoxazine samples used was about 5 mg.

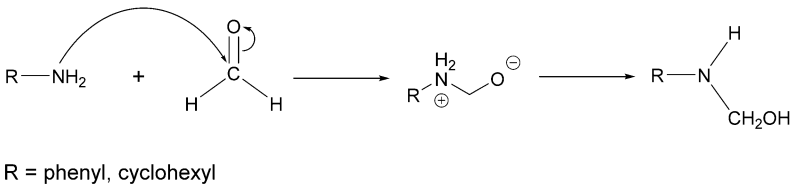
Mass spectra were obtained on a Bruker electrospray ionization–quadrupole–time-of-flight mass spectrometer (ESI-Q-TOF MS) operating in positive ion mode. The capillary voltage was maintained at +4000 V with the end plate offset at –500 V. The pressure for the nebulizer gas was set at 0.3 bar, the drying gas temperature at 200 °C, and the drying gas flow at 4.0 L/min. The detection was carried out within a mass range of 50–2000 mass-to-charge ratio (*m*/*z*). The MS data were processed through Compass DataAnalysis software (Version 4.4; Bruker Daltonics, Germany). The molecular weight, m/z, and theoretical isotopic profile of the molecular ions were calculated using the IsotopePattern tool (Bruker Daltonics, Germany).

Computational method

All the Computations were carried out by the Gaussian 09 package. The B3LYP functional and 6-311G(d,p) basis set were used to get the optimized geometries for reactant, intermediates, transition states, and products. The subsequent frequency computations at the same level were performed, where zero numbers of imaginary frequency were obtained for reactant, intermediates, and products, and only one numbers of imaginary frequency was obtained for transition states, indicating the true minima and saddle points on the potential energy surface.



Scheme S1. Synthesis reactions of PH-a and PH-cha.



Scheme S2. Formation mechanism of carbinolamine intermediate in synthesis of PH-a and PH-cha.

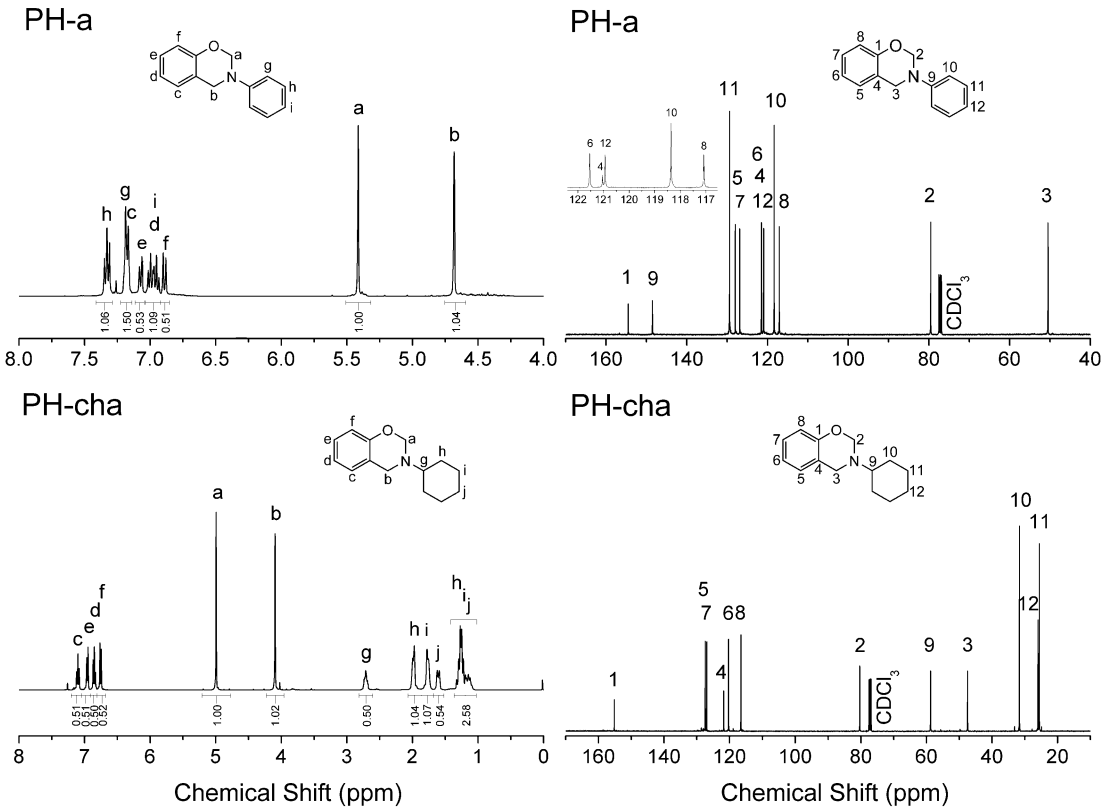


Figure S1. ^{1}H and ^{13}C NMR spectra of PH-a and PH-cha.

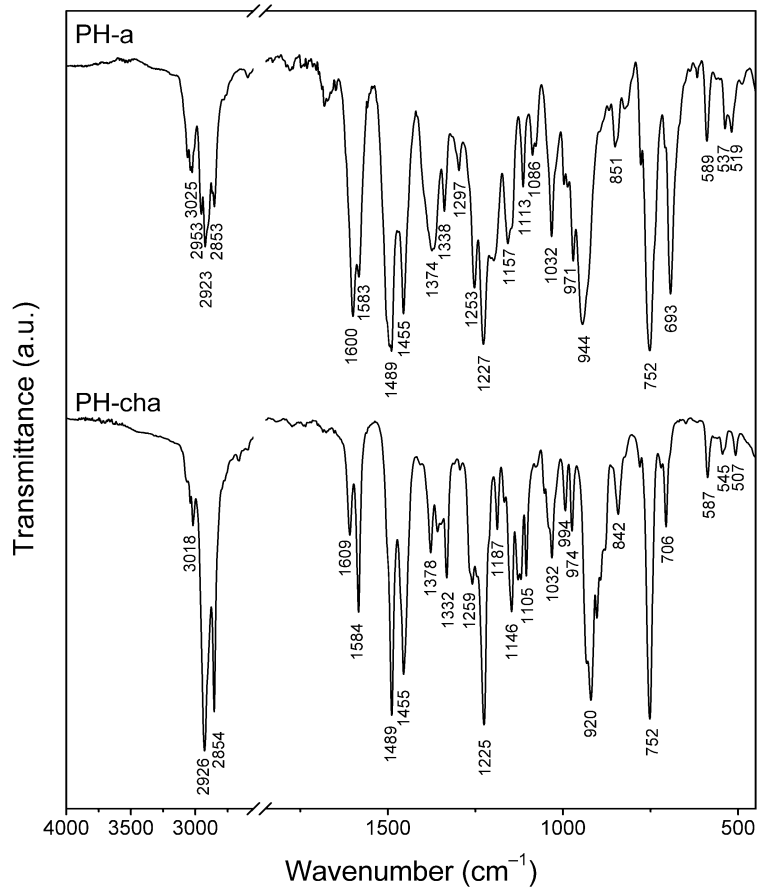


Figure S2. FTIR spectra of PH-a and PH-cha.

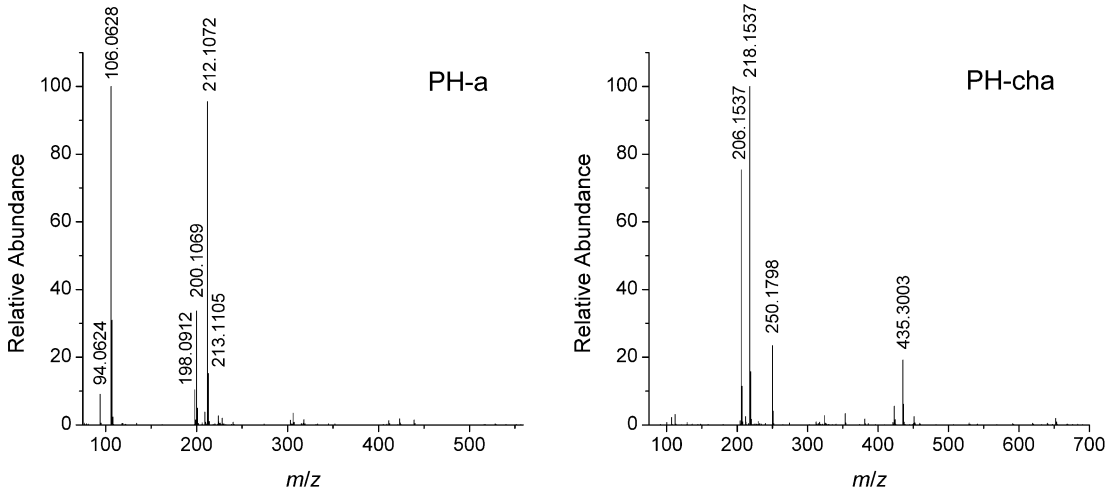


Figure S3. Positive ion ESI mass spectra of PH-a and PH-cha.

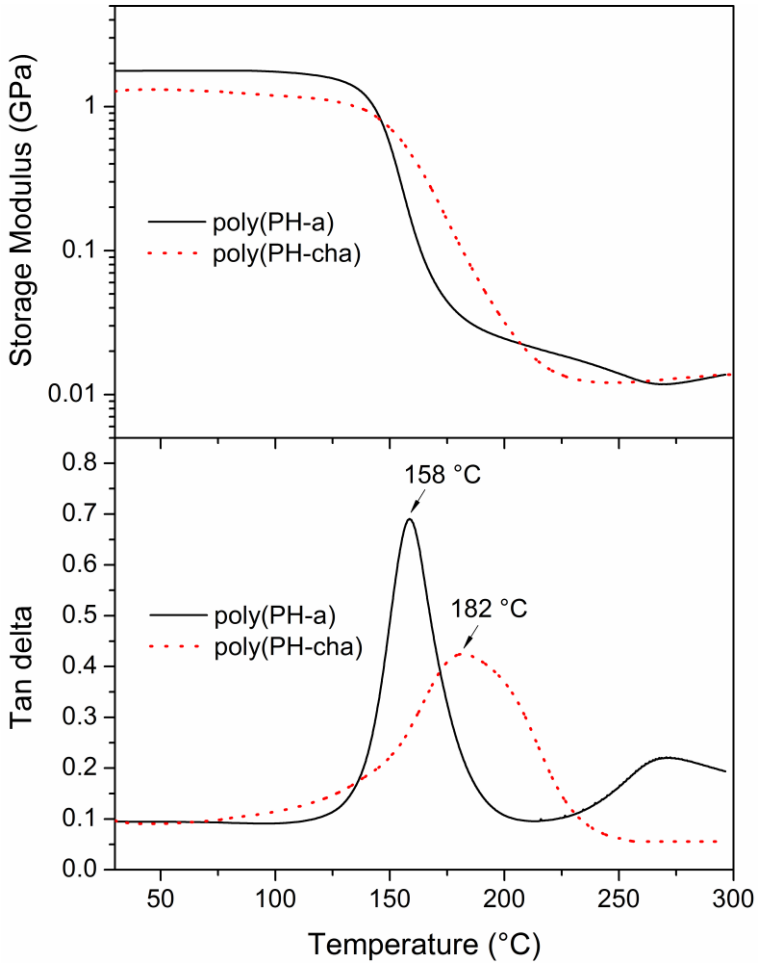


Figure S4. DMA curves of poly(PH-a) and poly(PH-cha).

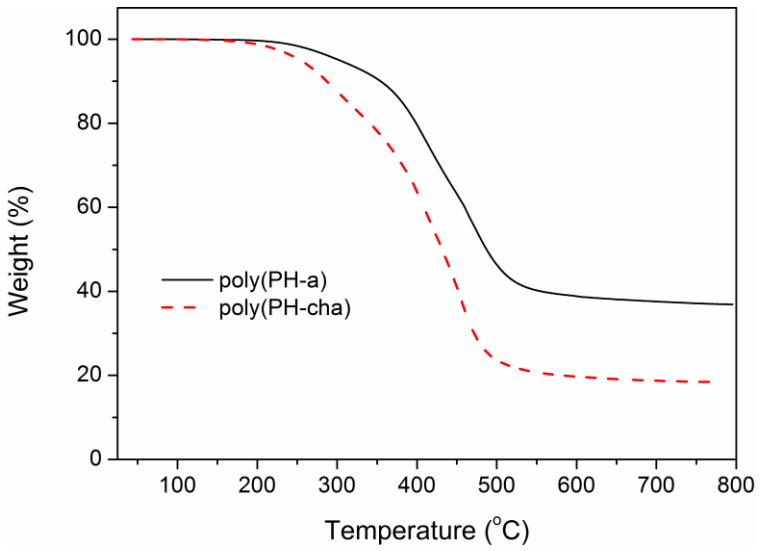


Figure S5. TG curves of poly(PH-a) and poly(PH-cha).

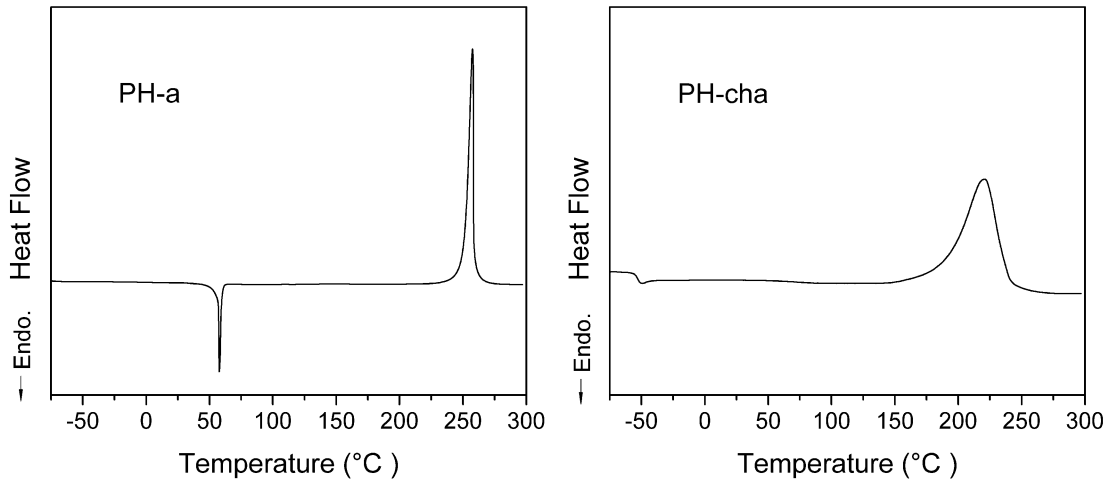


Figure S6. DSC curves of PH-a and PH-cha.

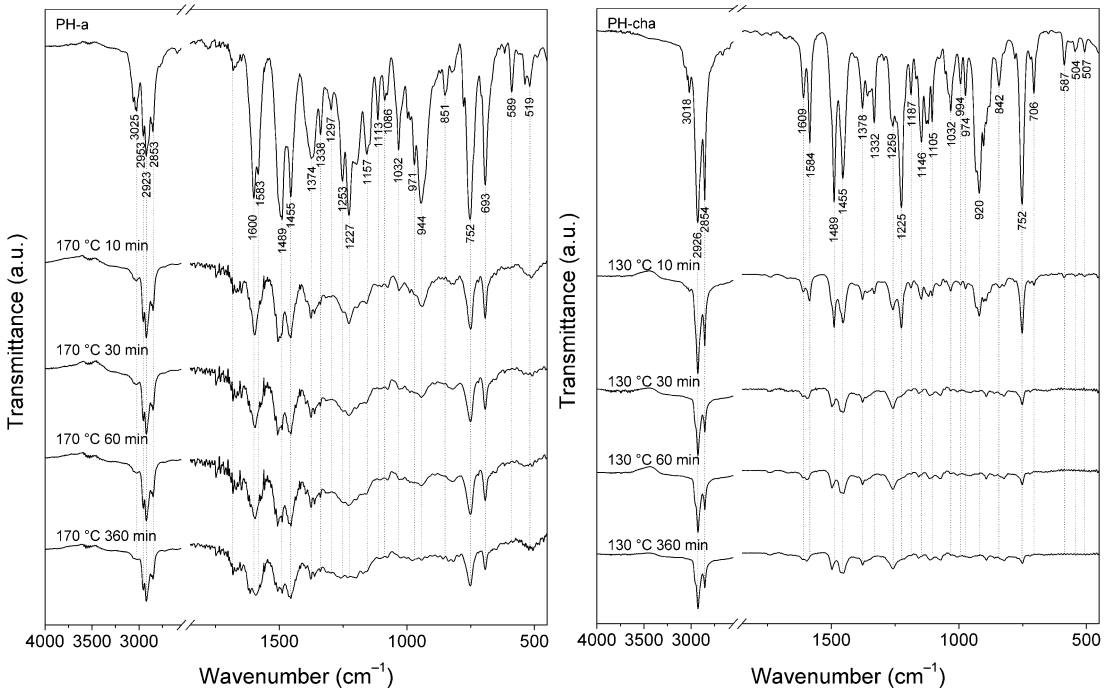


Figure S7. FTIR spectra of thermally treated products of PH-a and PH-cha.

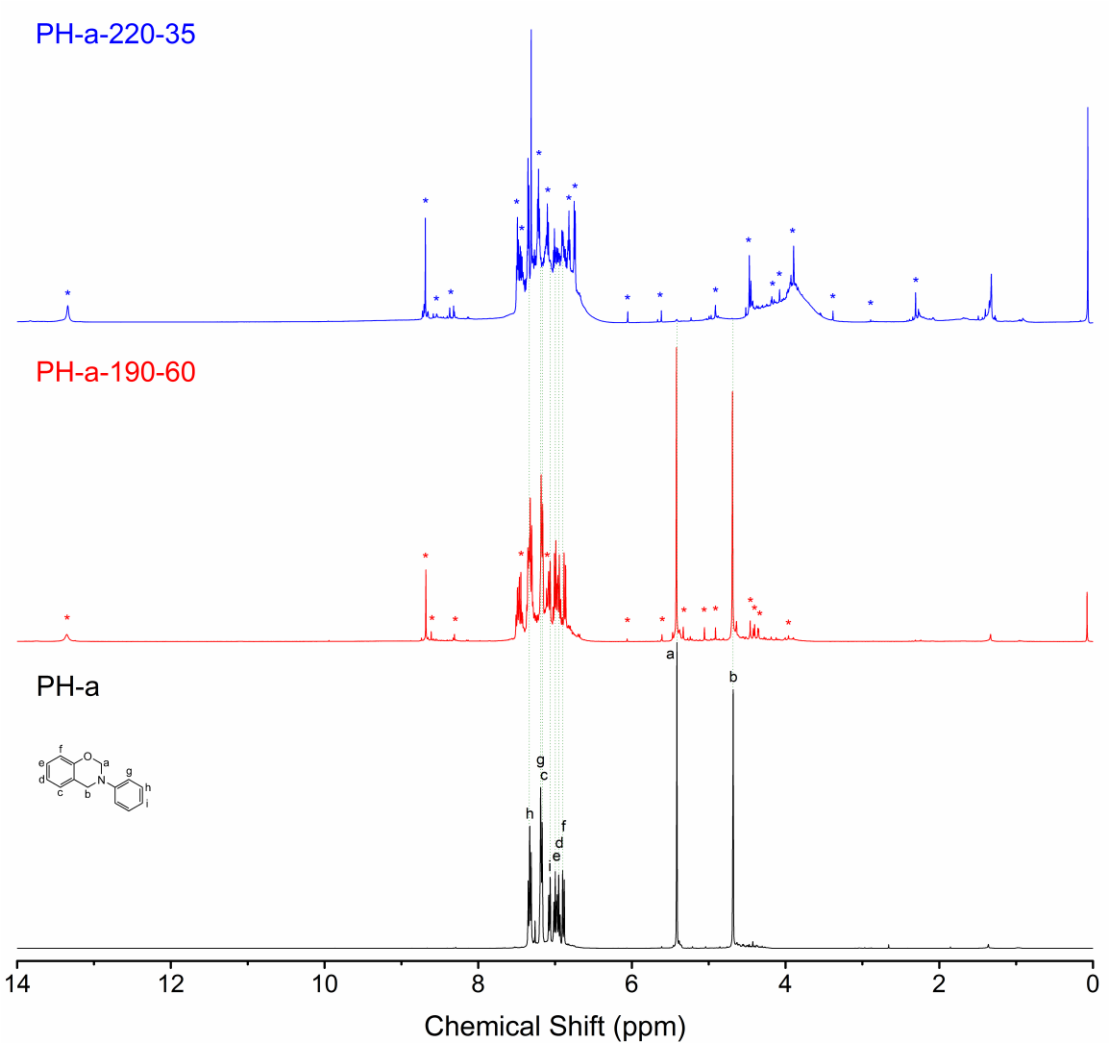


Figure S8. ^{1}H NMR spectra of PH-a, PH-a-190-60, and PH-a-220-35.

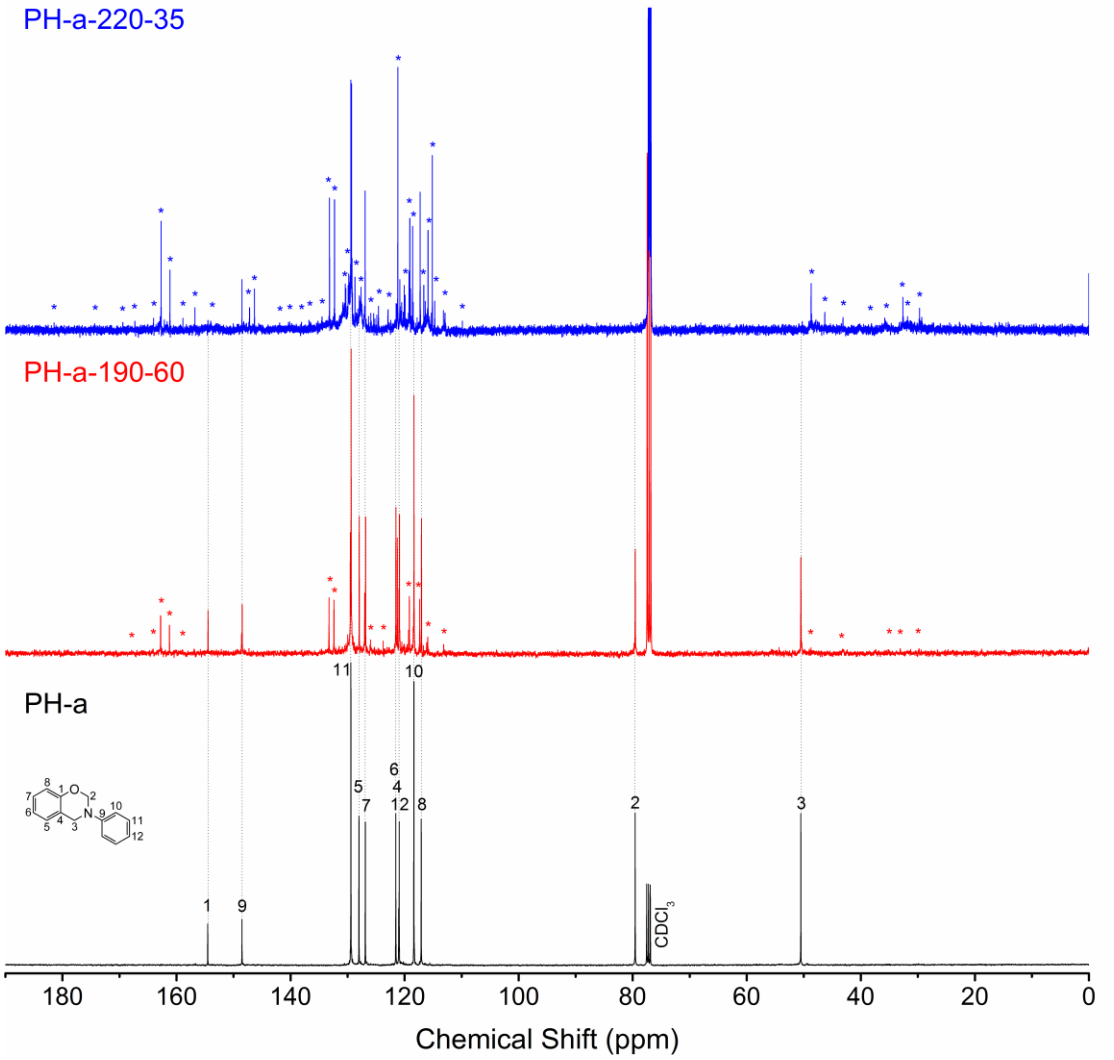


Figure S9. ^{13}C NMR spectra of PH-a, PH-a-190-60, and PH-a-220-35.

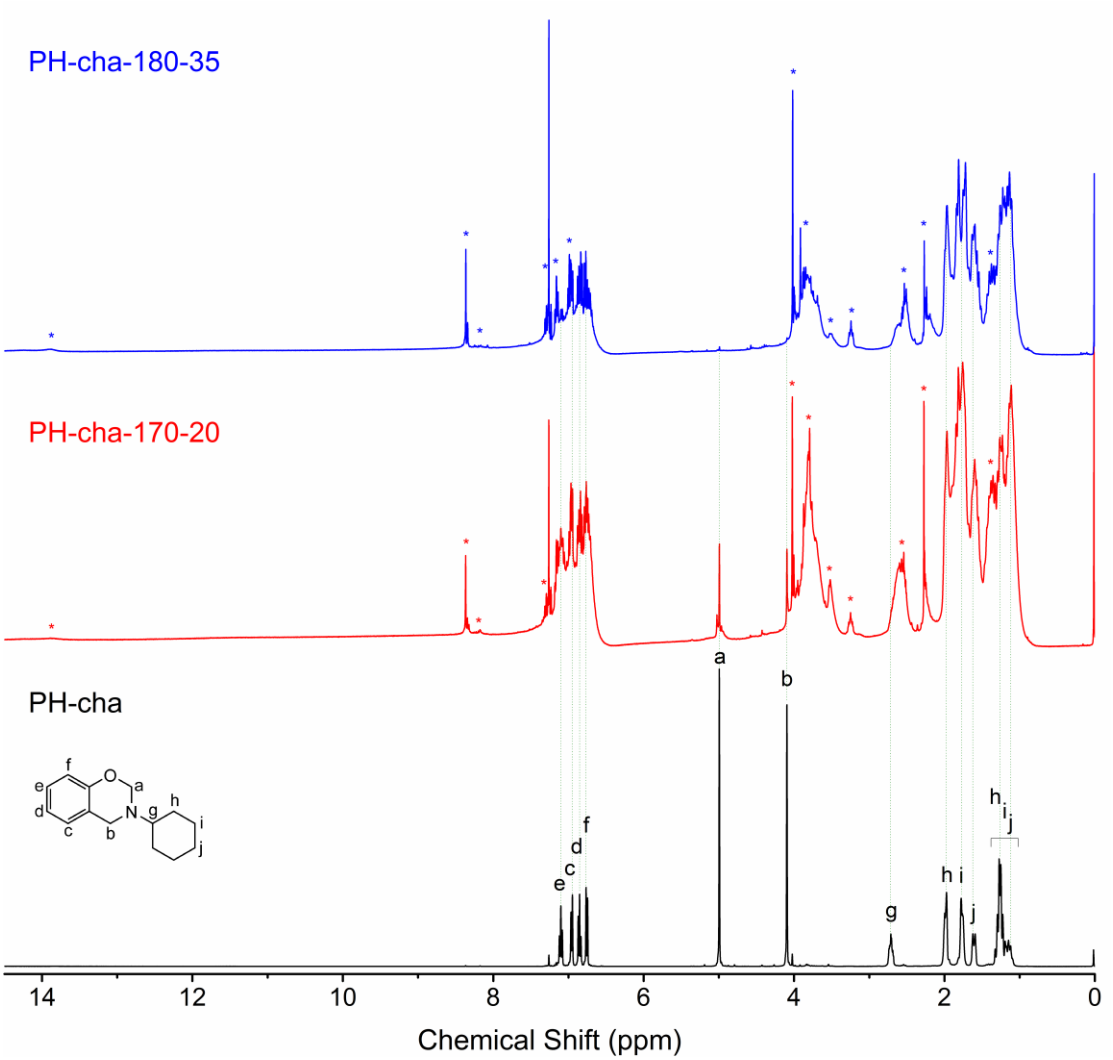


Figure S10. ^{1}H NMR spectra of PH-cha, PH-cha-170-20, and PH-cha-180-35.

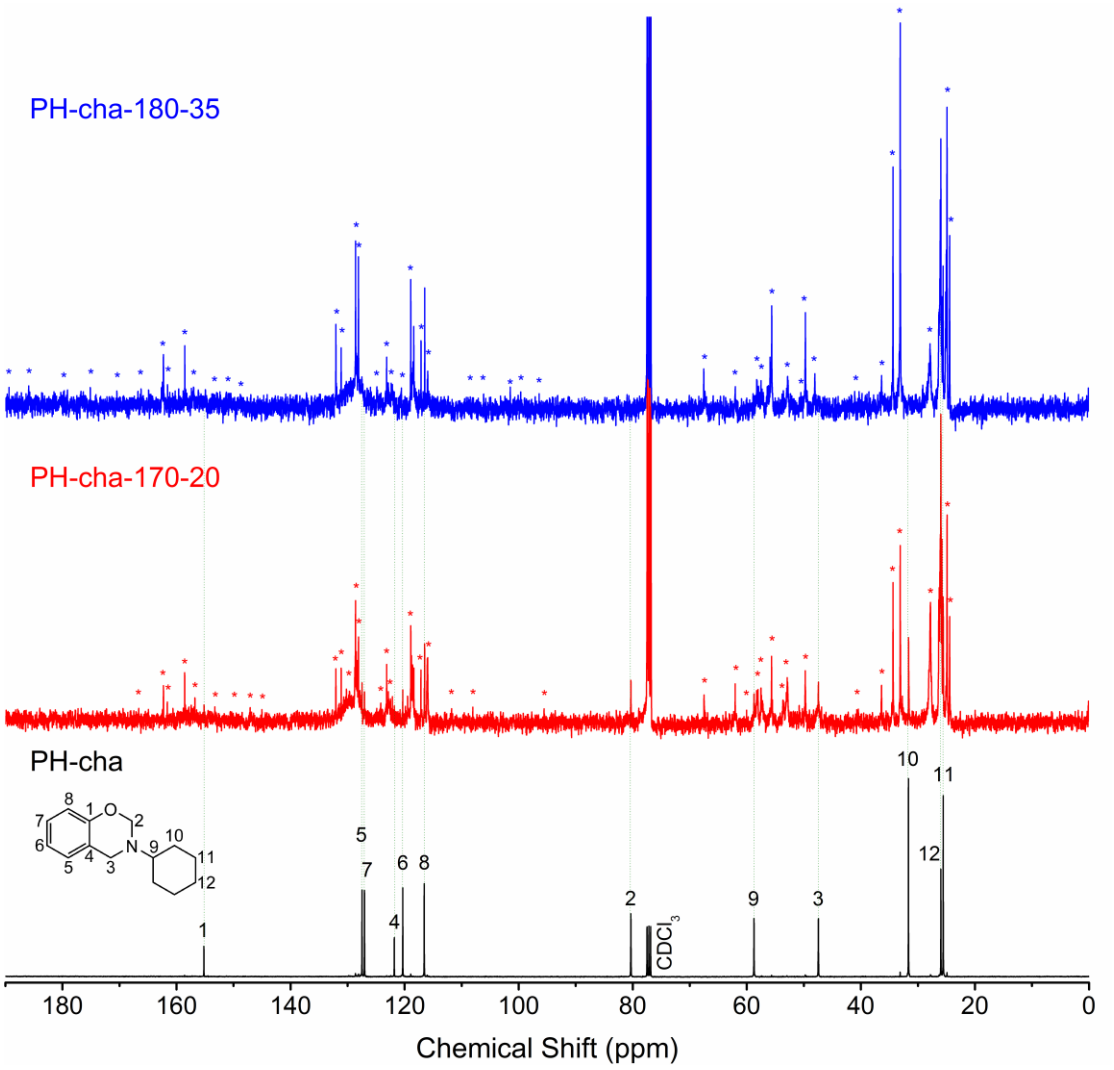
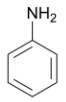
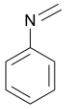


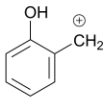
Figure S11. ^{13}C NMR spectra of PH-cha, PH-cha-170-20, and PH-cha-180-35.



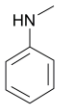
Formula: C_6H_7N
MW: 93.0573
m/z^C: 94.0651
m/z^F: 94.0647



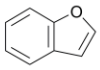
Formula: C_7H_7N
MW: 105.0573
m/z^C: 106.0651
m/z^F: 106.0650*



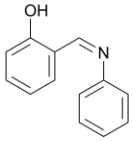
Formula: $C_7H_7O^+$
MW: 107.0491
m/z^C: 107.0491
m/z^F: 107.0488*



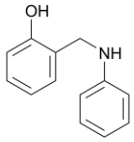
Formula: C_7H_9N
MW: 107.0729
m/z^C: 108.0808
m/z^F: 108.0783



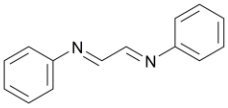
Formula: C_8H_6O
MW: 118.0413
m/z^C: 119.0491
m/z^F: 119.0488*



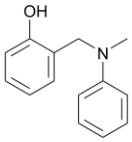
Formula: $C_{13}H_{11}NO$
MW: 197.0835
m/z^C: 198.0913
m/z^F: 198.0910*
m/z^C: 220.0733 $[M+Na]^+$
m/z^F: 220.0729 $[M+Na]^+$



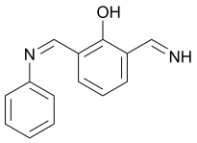
Formula: $C_{13}H_{13}NO$
MW: 199.0992
m/z^C: 200.1070
m/z^F: 200.1067*
m/z^C: 222.0889 $[M+Na]^+$
m/z^F: 222.0892 $[M+Na]^+$



Formula: $C_{14}H_{12}N_2$
MW: 208.0995
m/z^C: 209.1073
m/z^F: 209.1071



Formula: $C_{14}H_{15}NO$
MW: 213.1148
m/z^C: 214.1226
m/z^F: 214.1214*



Formula: $C_{14}H_{12}N_2O$
MW: 224.0944
m/z^C: 225.1022
m/z^F: 225.1071

m/z^C: calculated mass-to-charge ratio
m/z^F: found mass-to-charge ratio
*: Isotopologue

Figure S12. The confirmed fragments in PH-a-220-35.

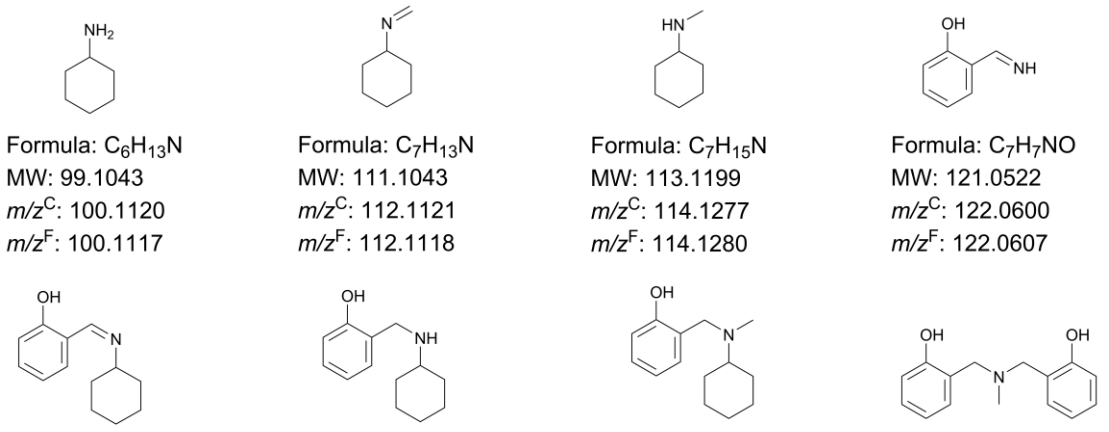


Figure S13. The confirmed fragments in PH-cha-180-35.

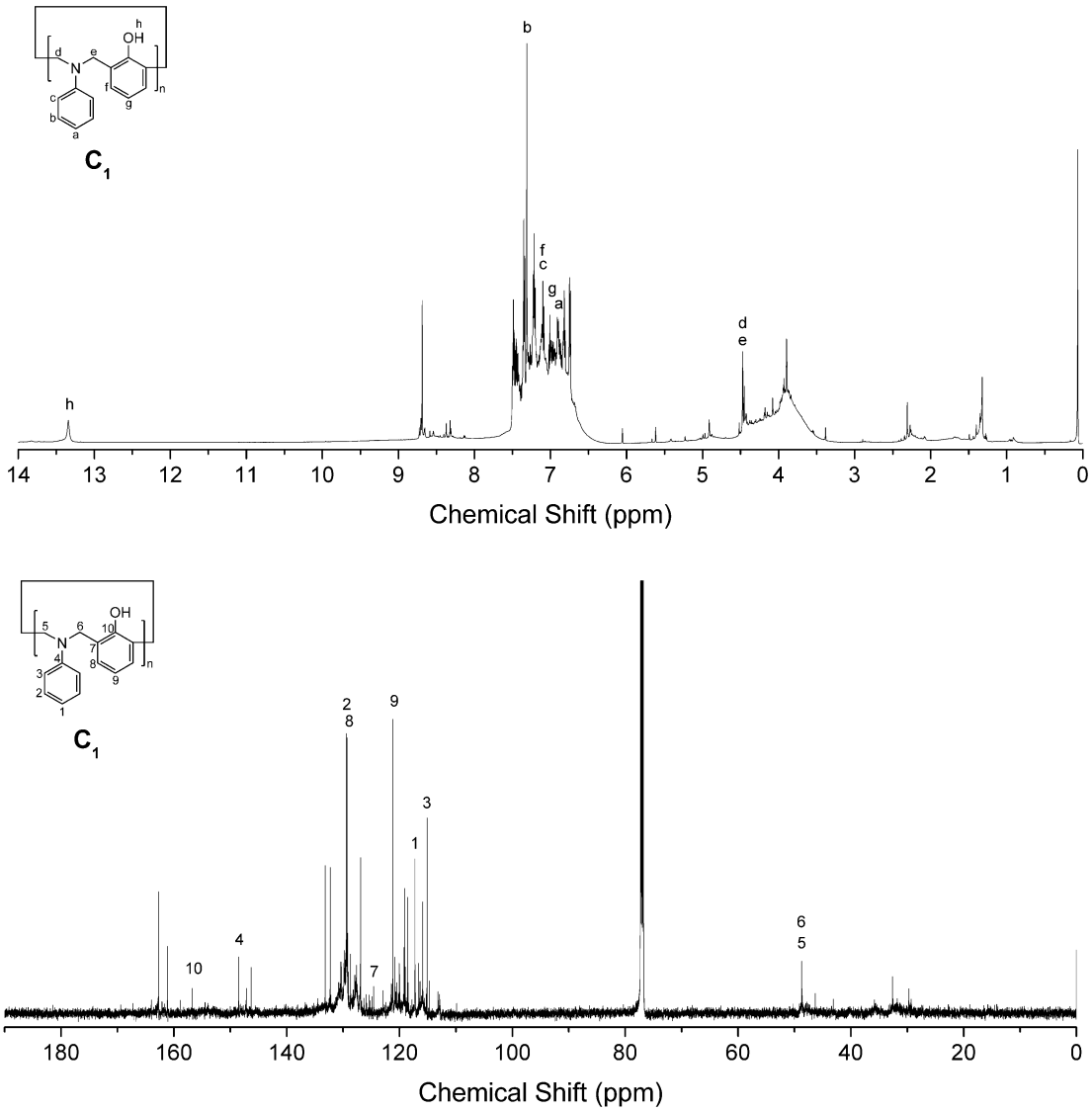


Figure S14. The proton and carbon assignments of the resonance signals of the identified products in PH-a-220-35.

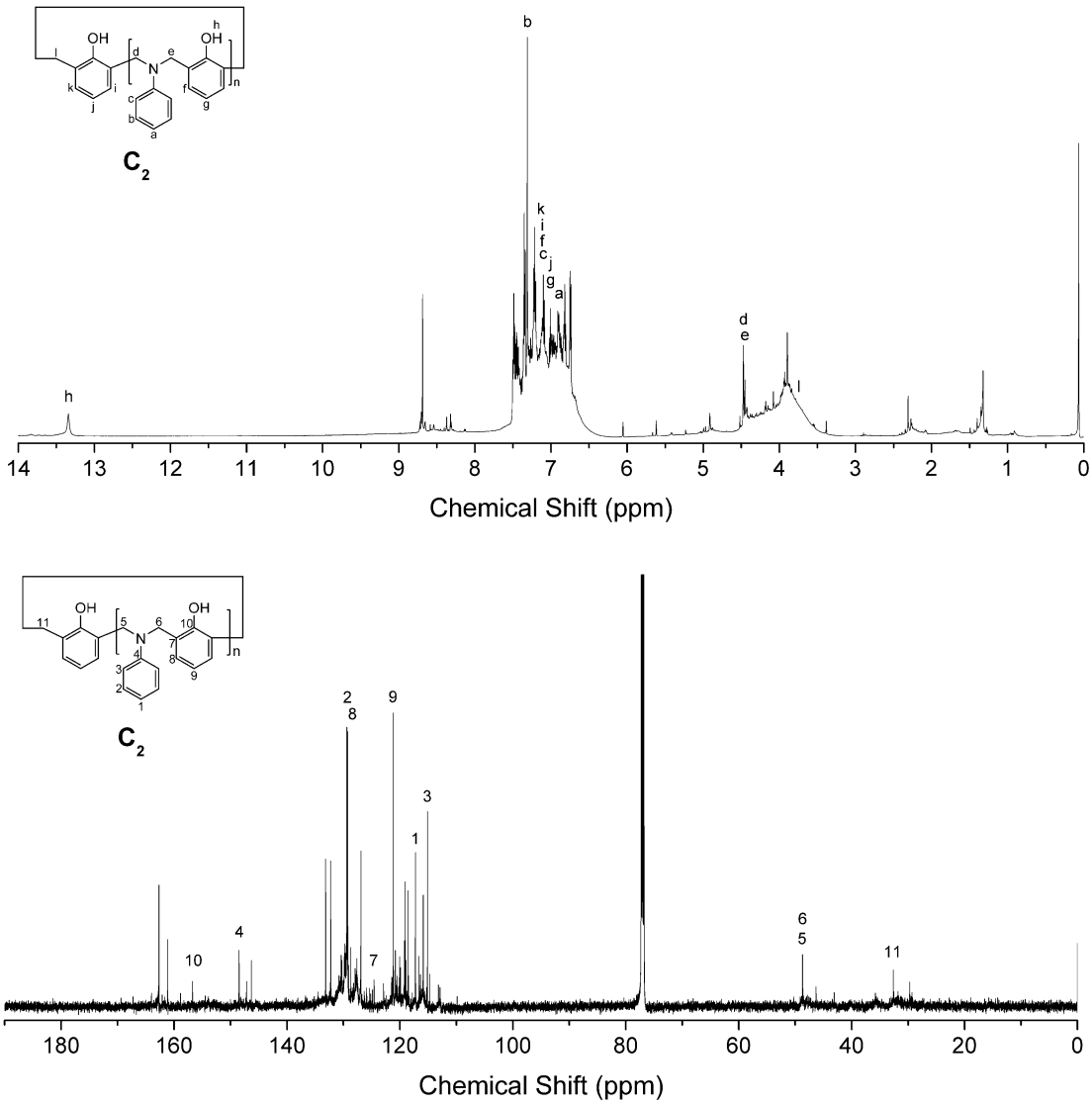


Figure S14. (continued).

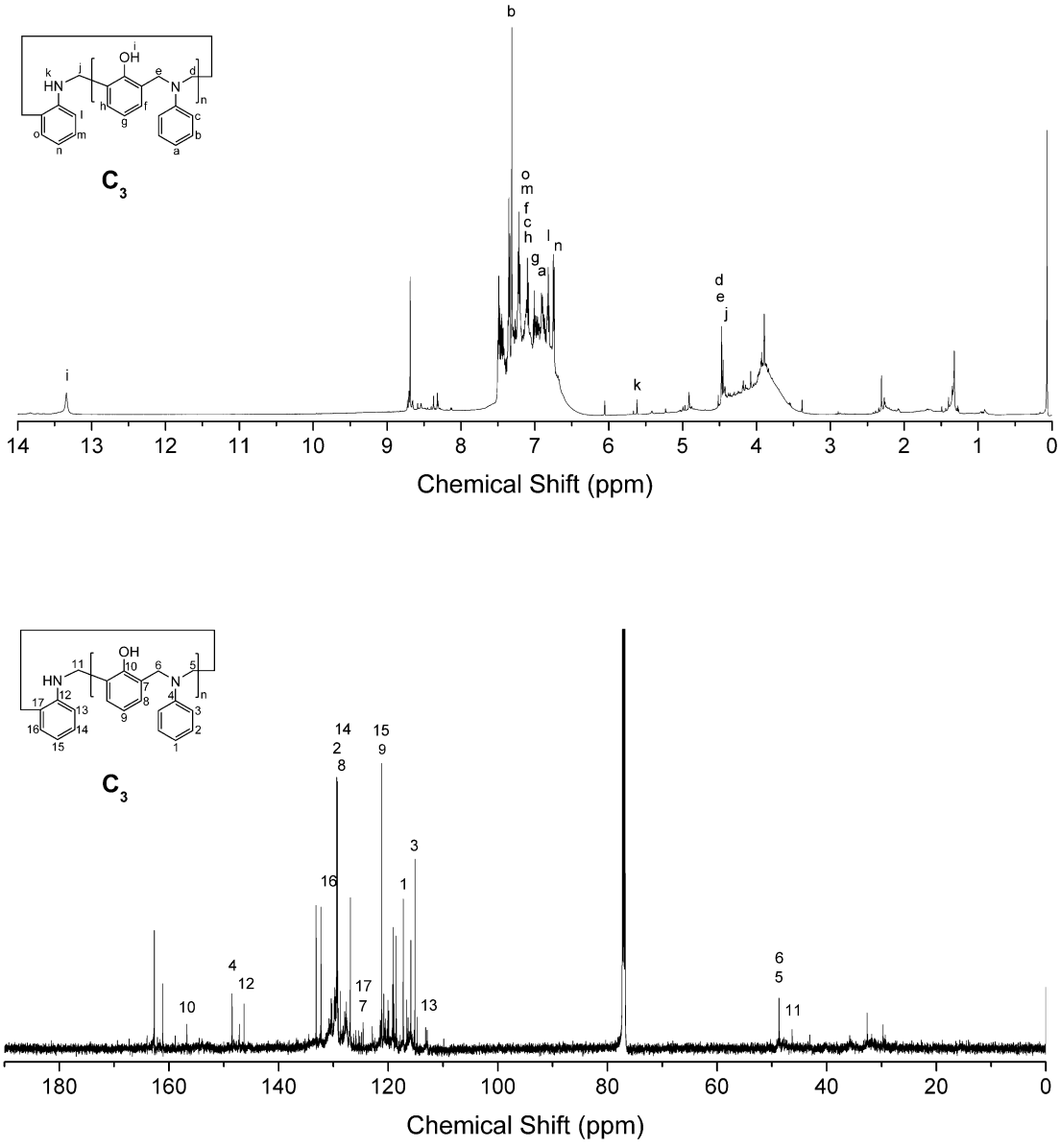


Figure S14. (continued).

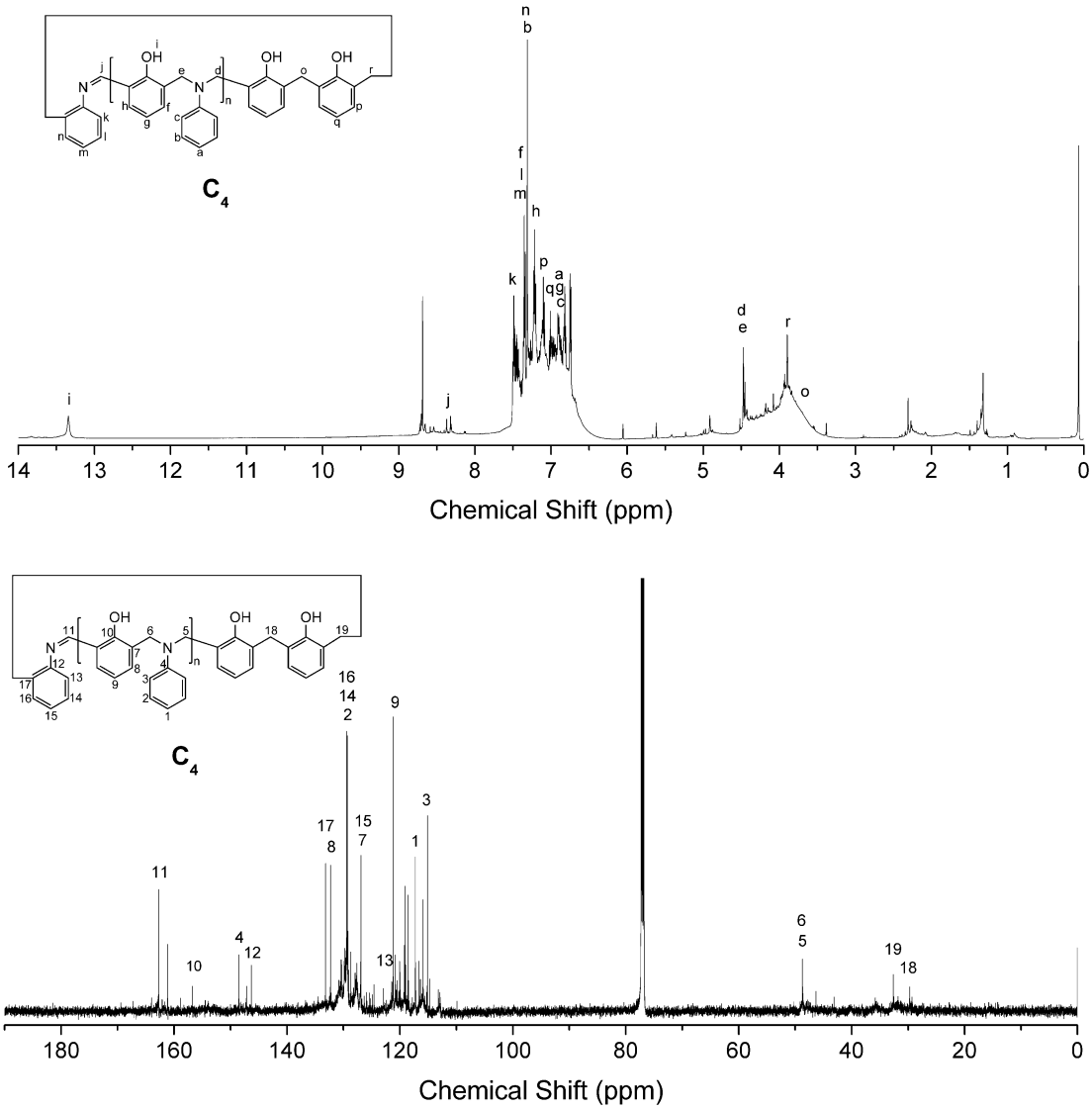


Figure S14. (continued).

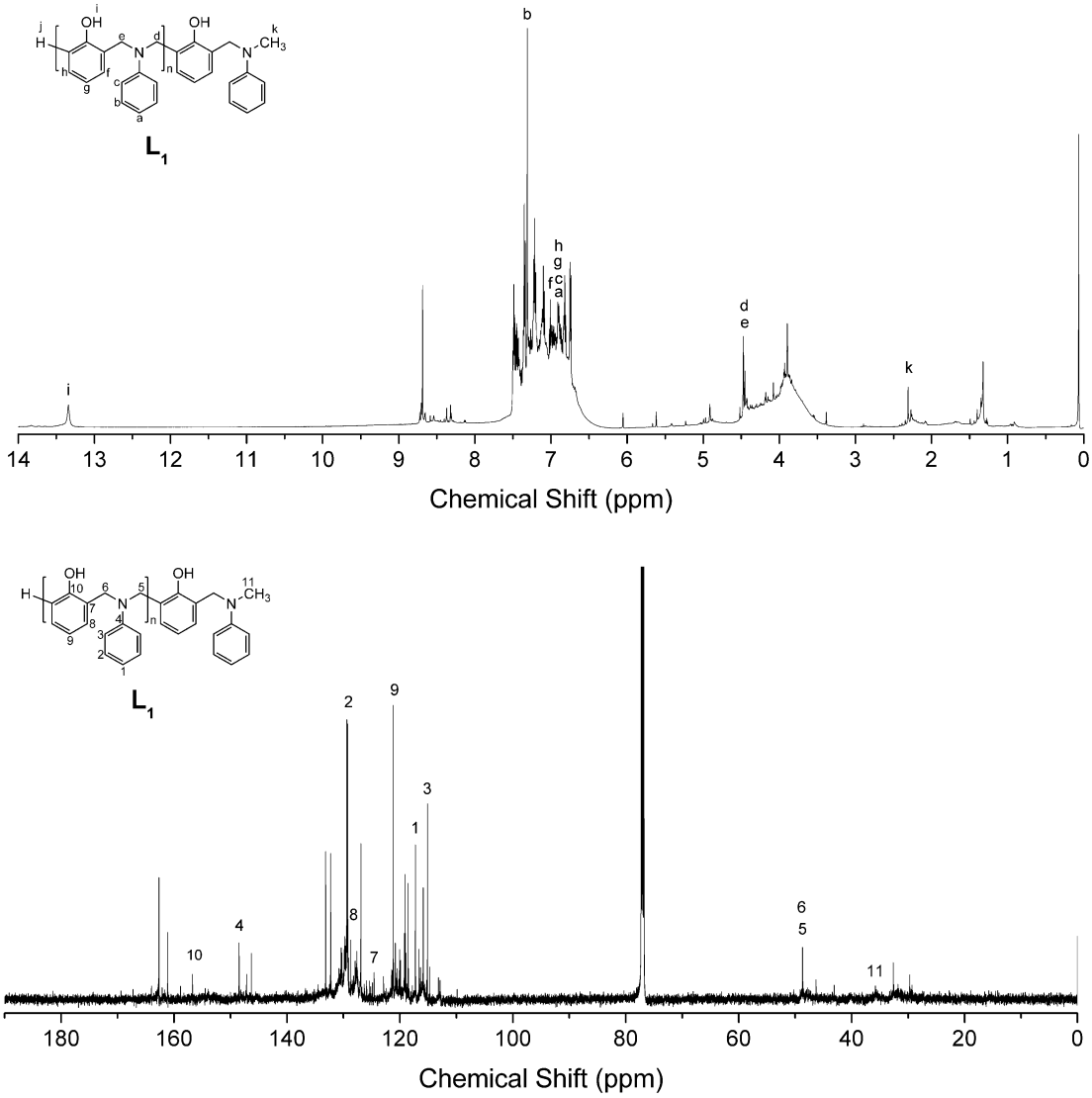


Figure S14. (continued).

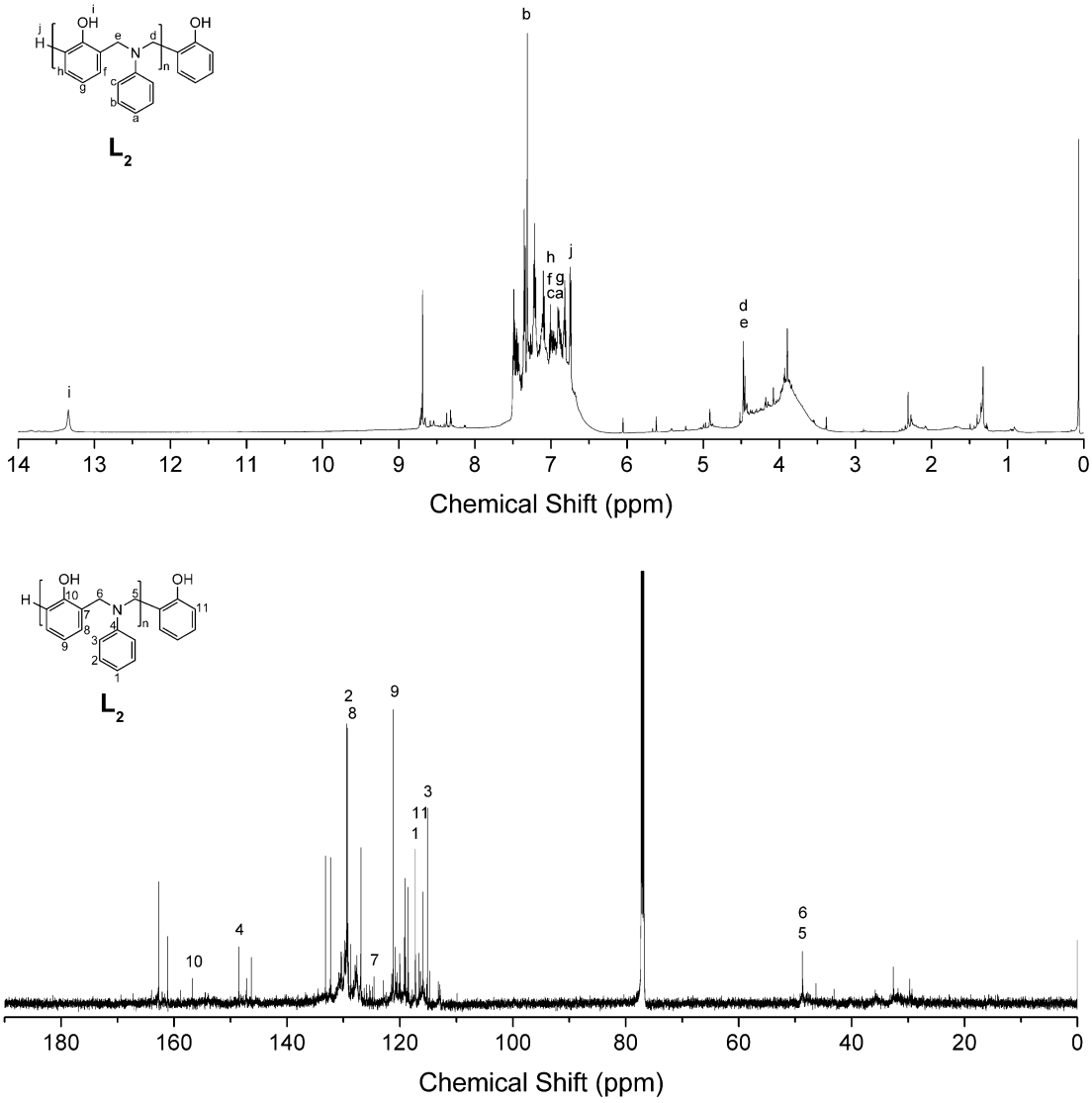


Figure S14. (continued).

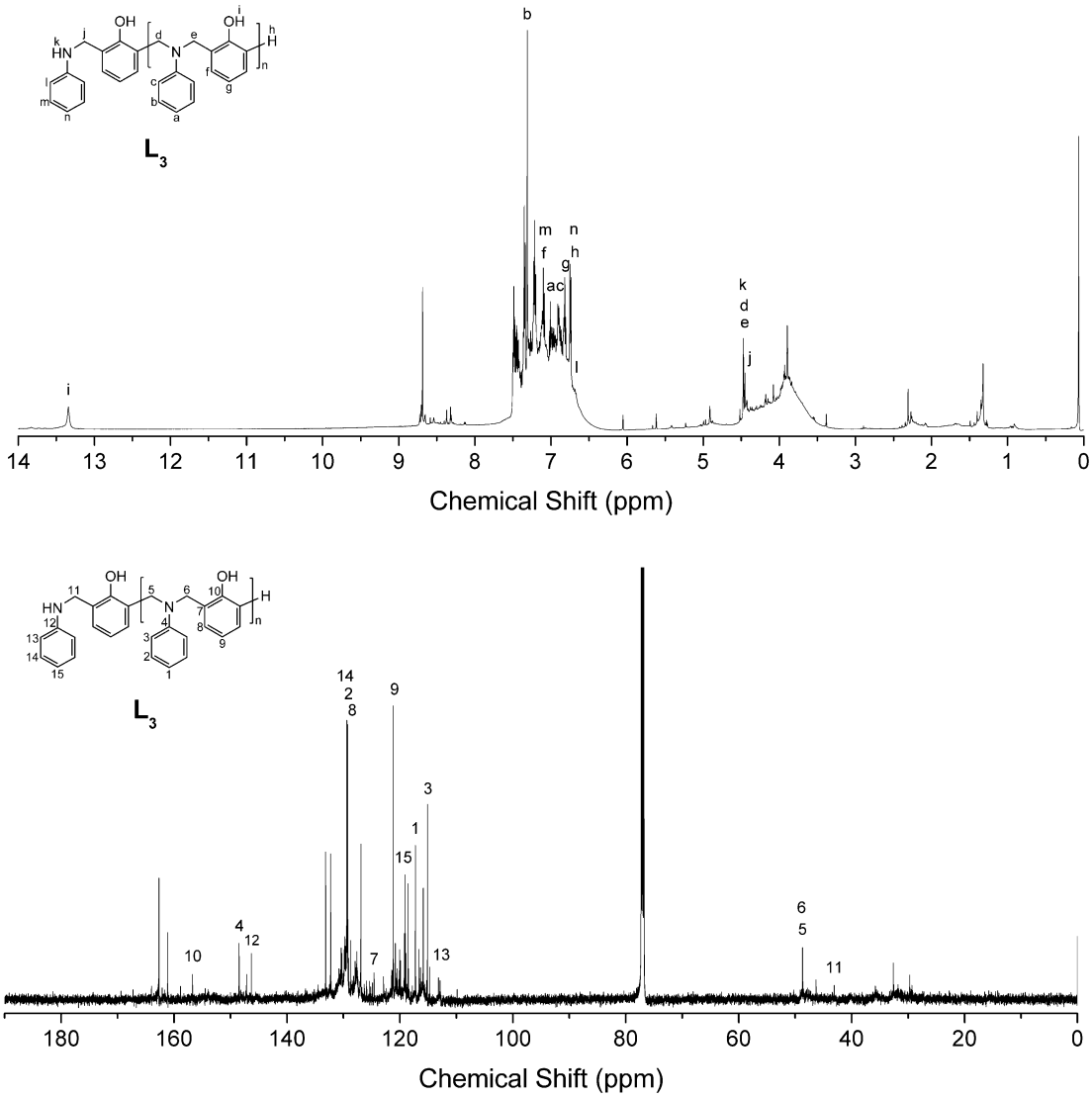


Figure S14. (continued).

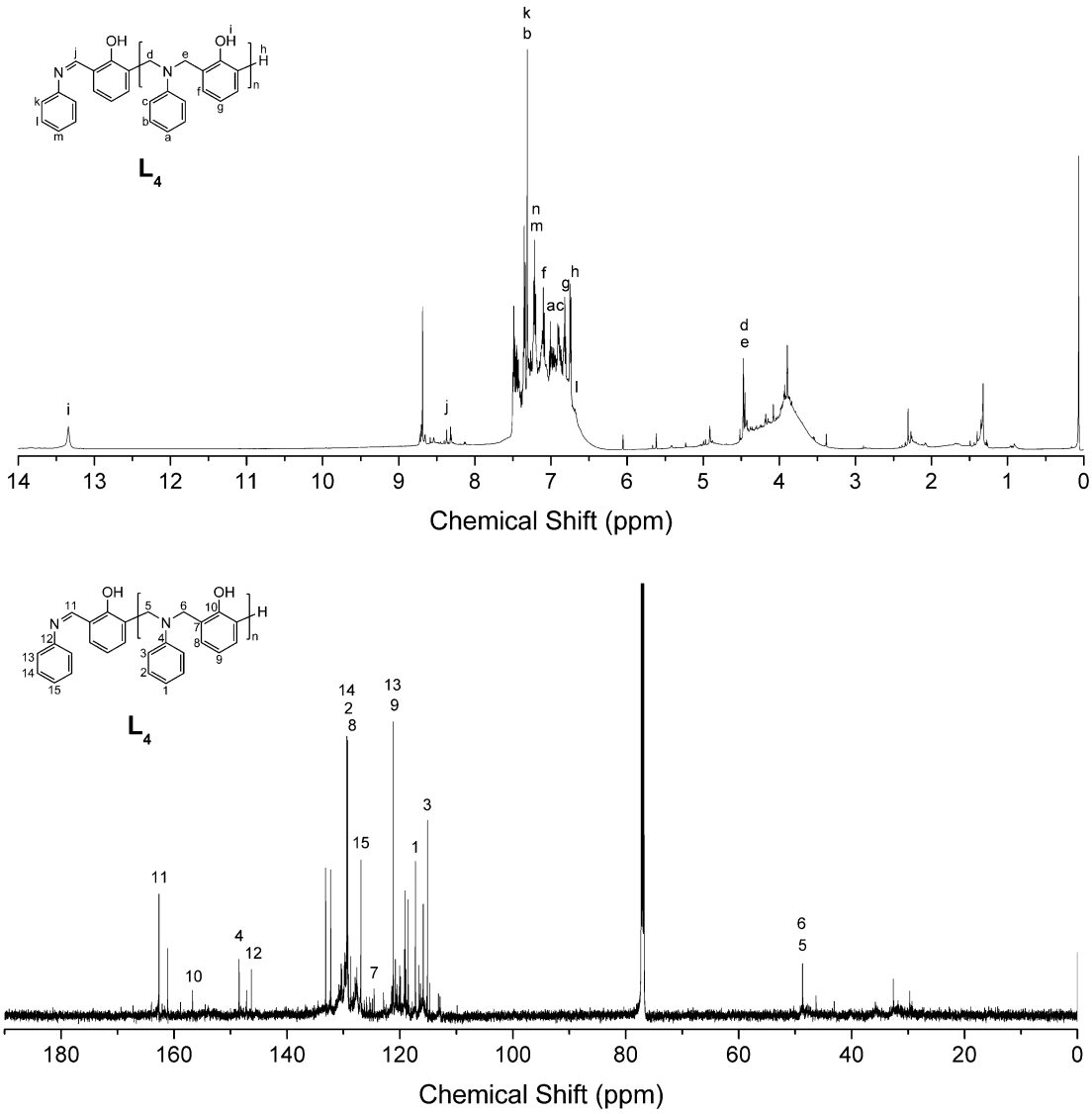


Figure S14. (continued).

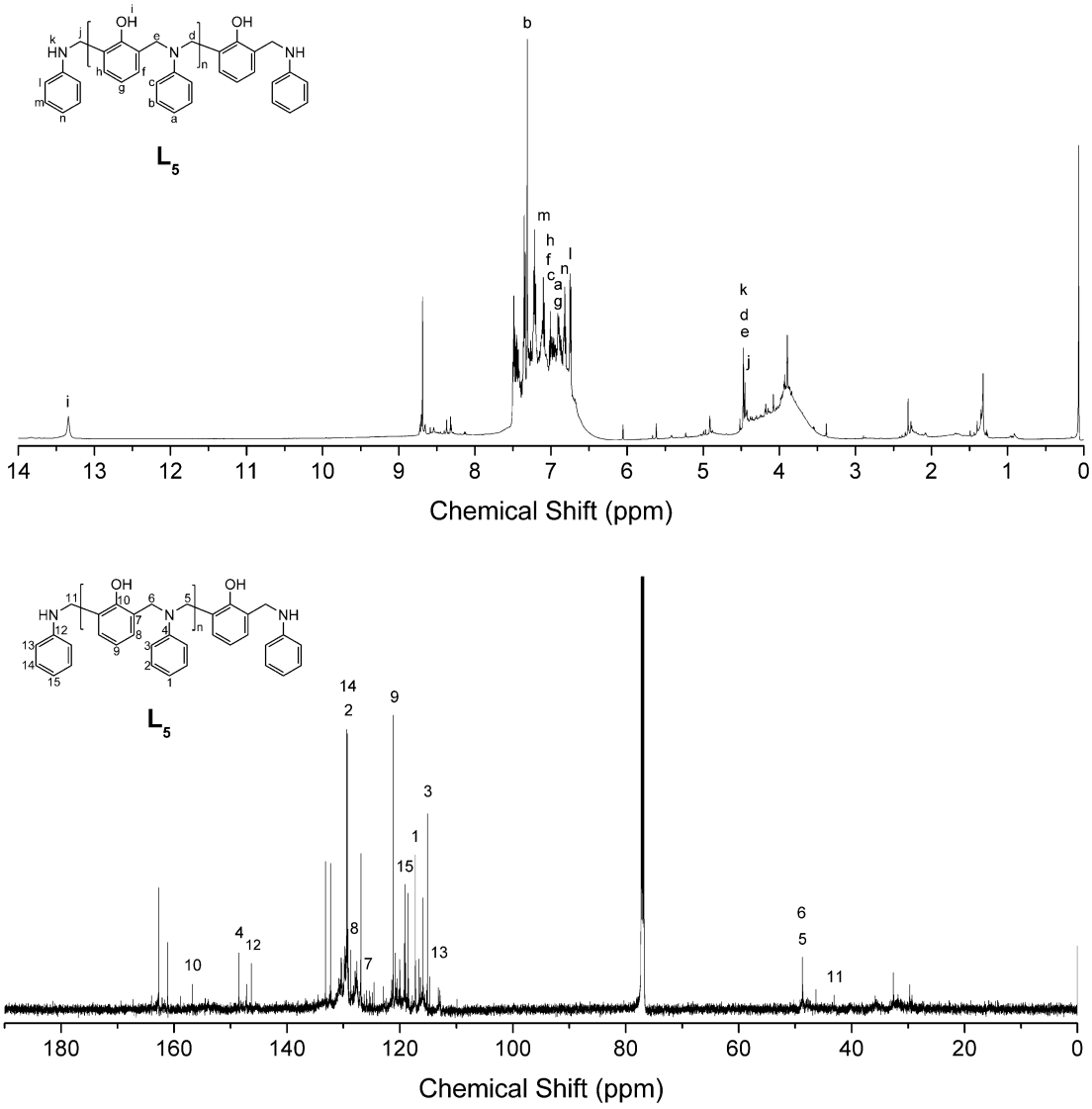


Figure S14. (continued).

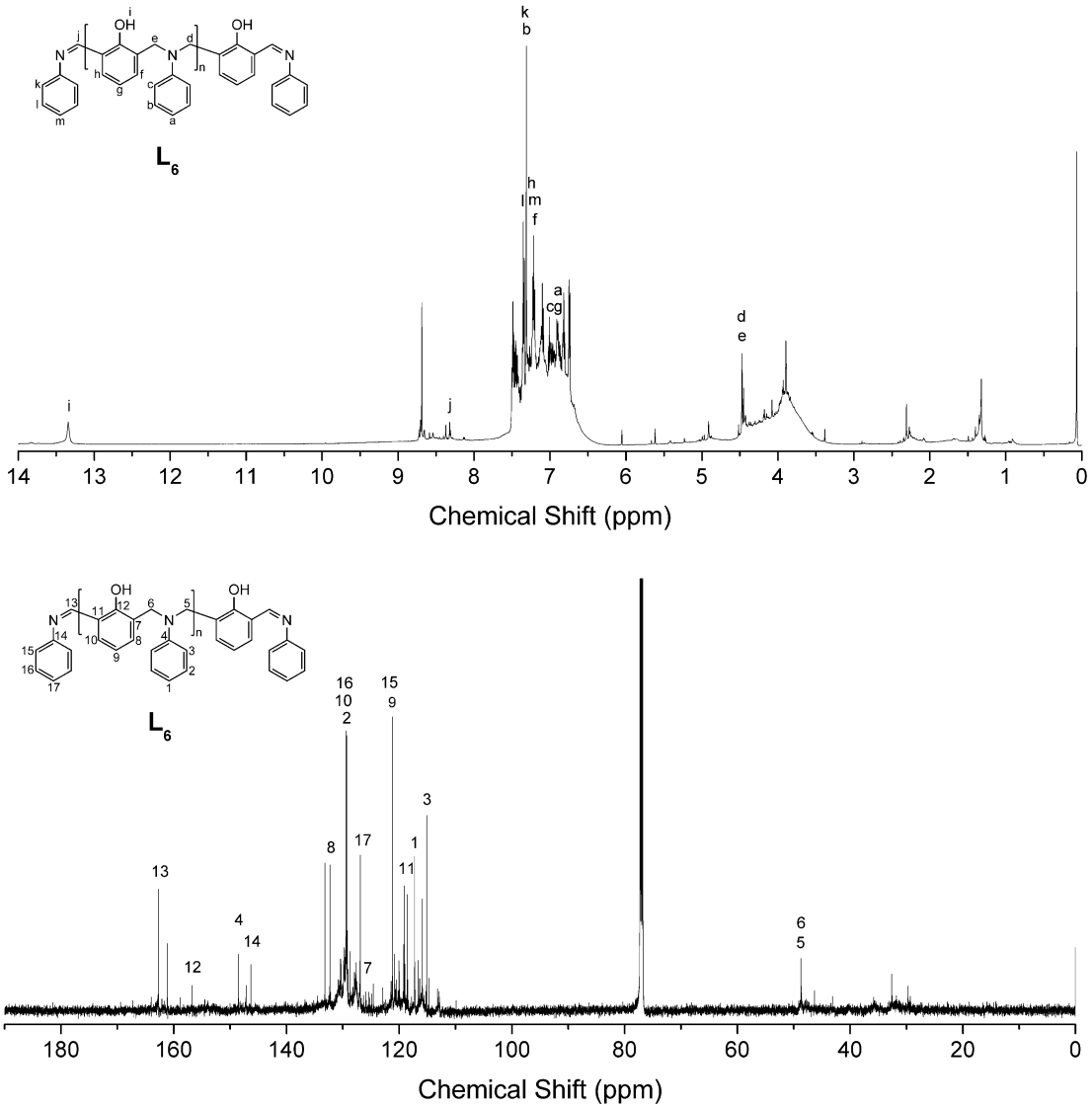


Figure S14. (continued).

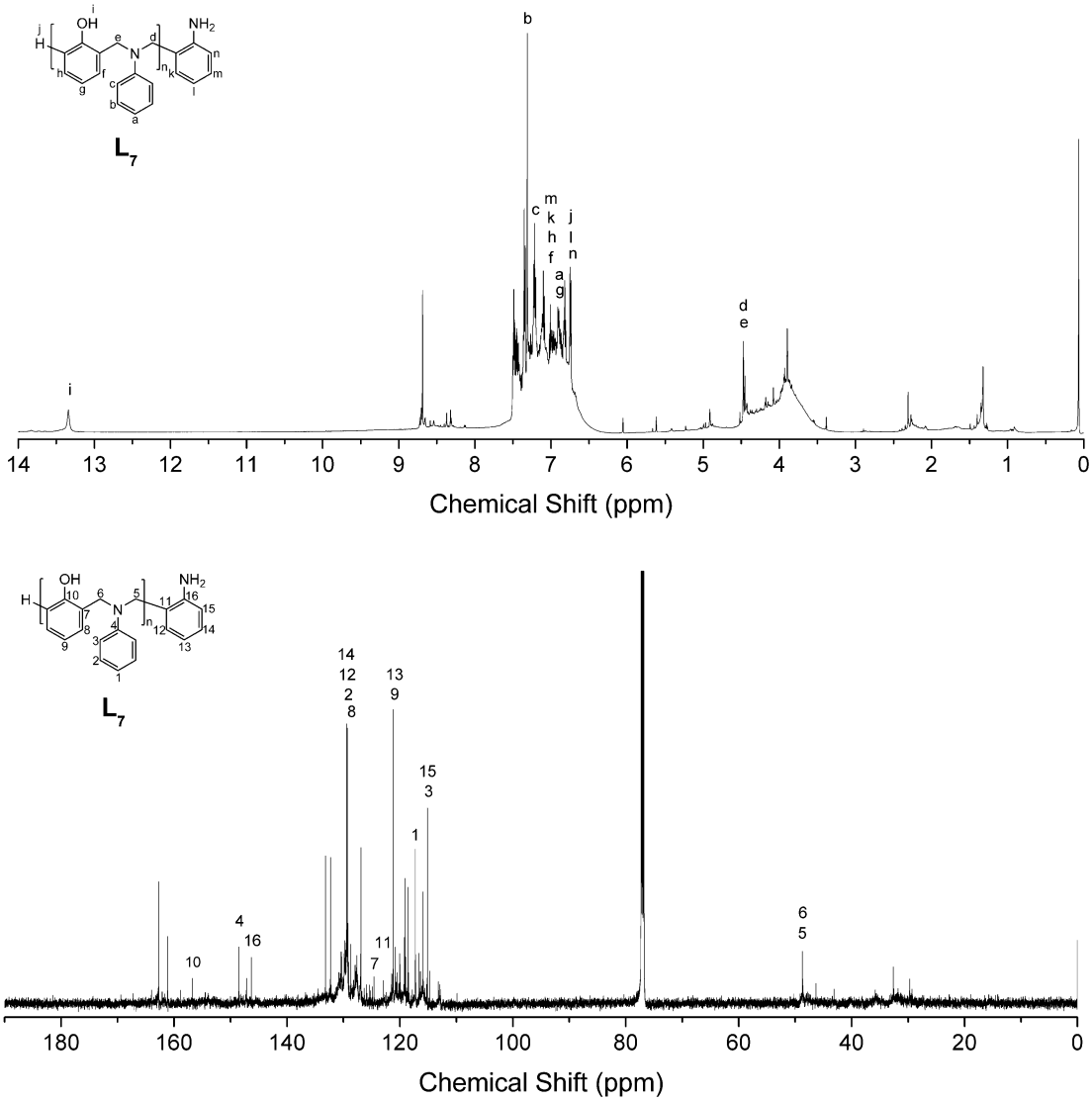


Figure S14. (continued).

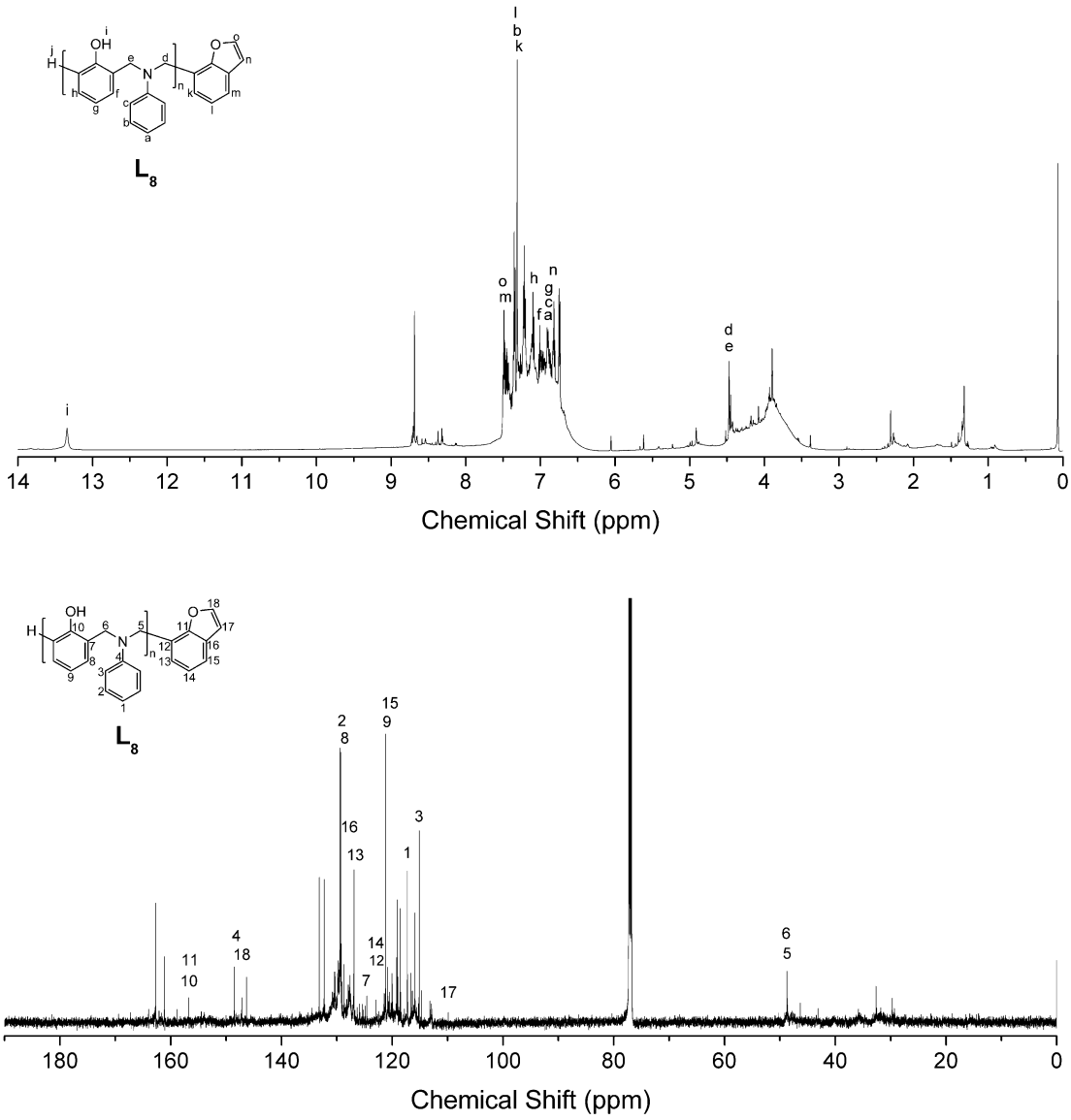


Figure S14. (continued).

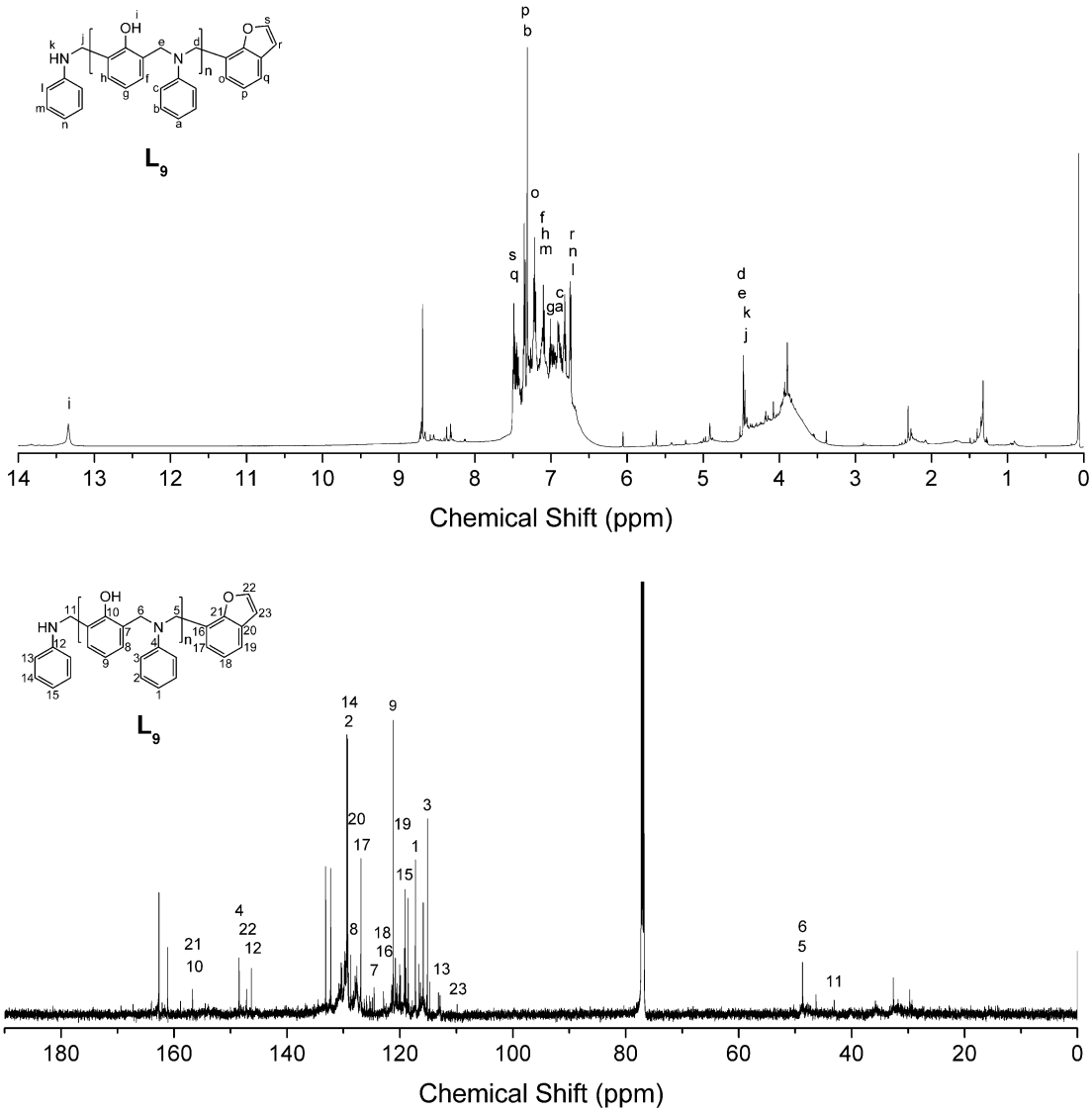


Figure S14. (continued).

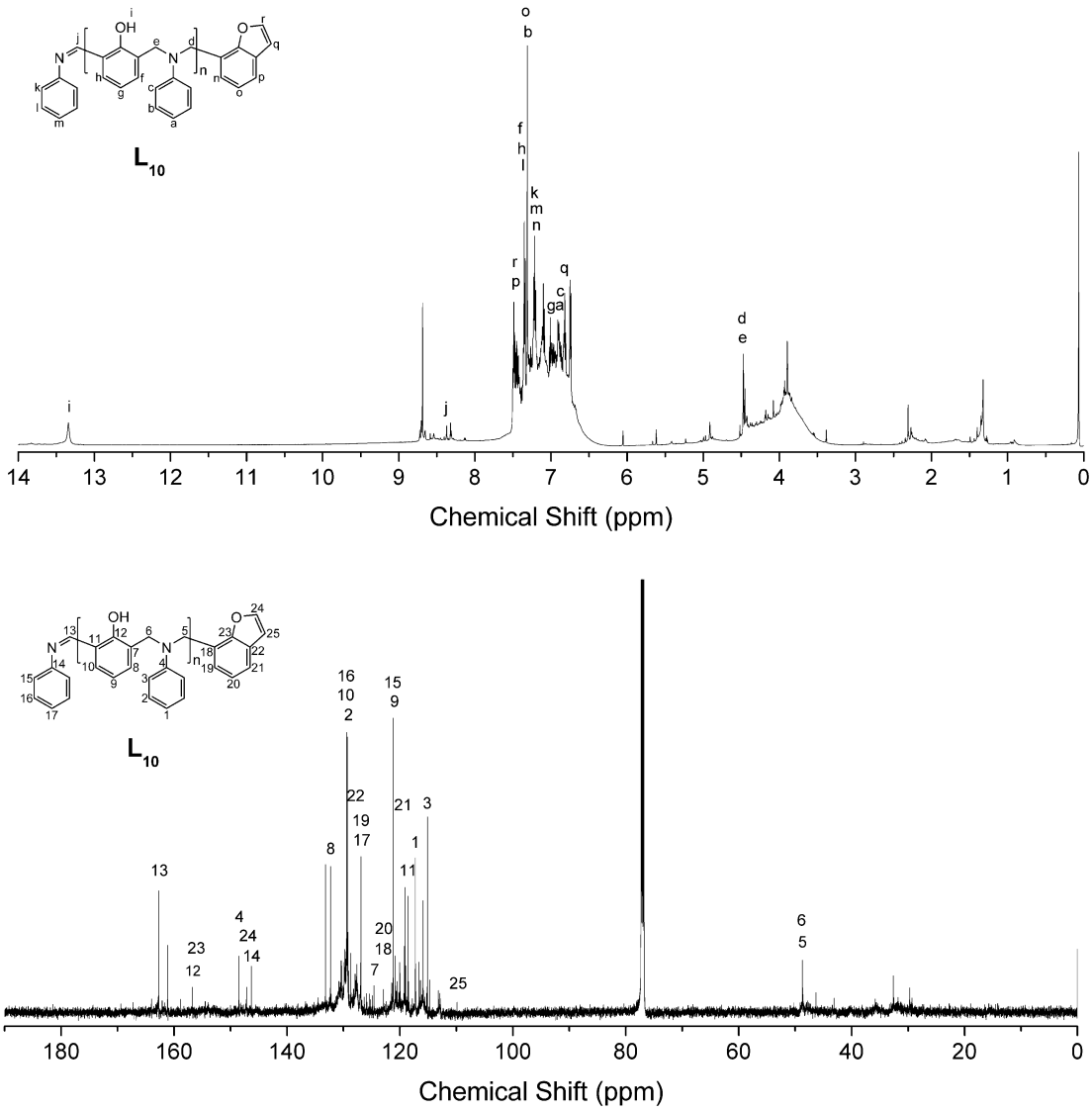


Figure S14. (continued).

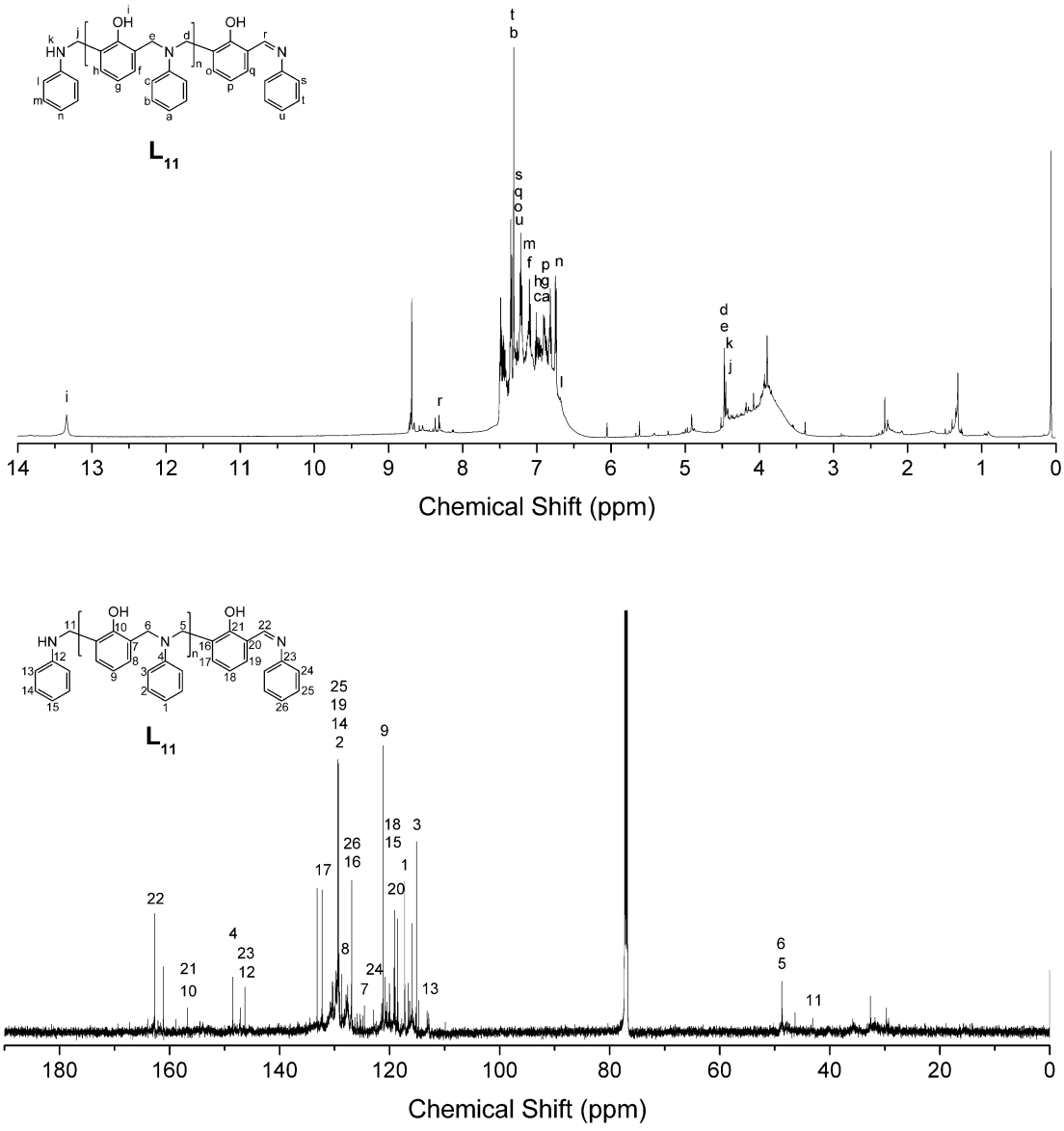


Figure S14. (continued).

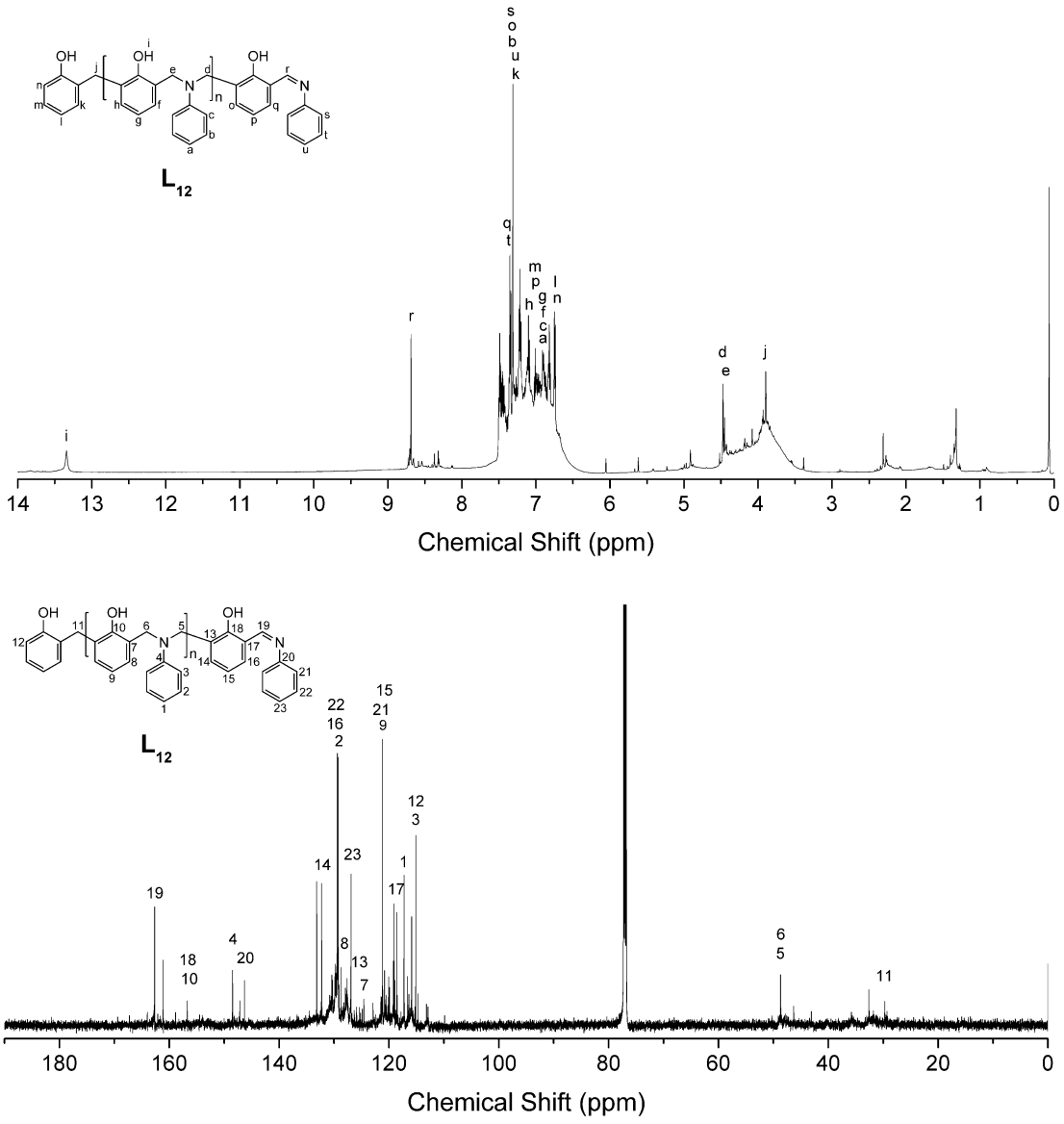


Figure S14. (continued).

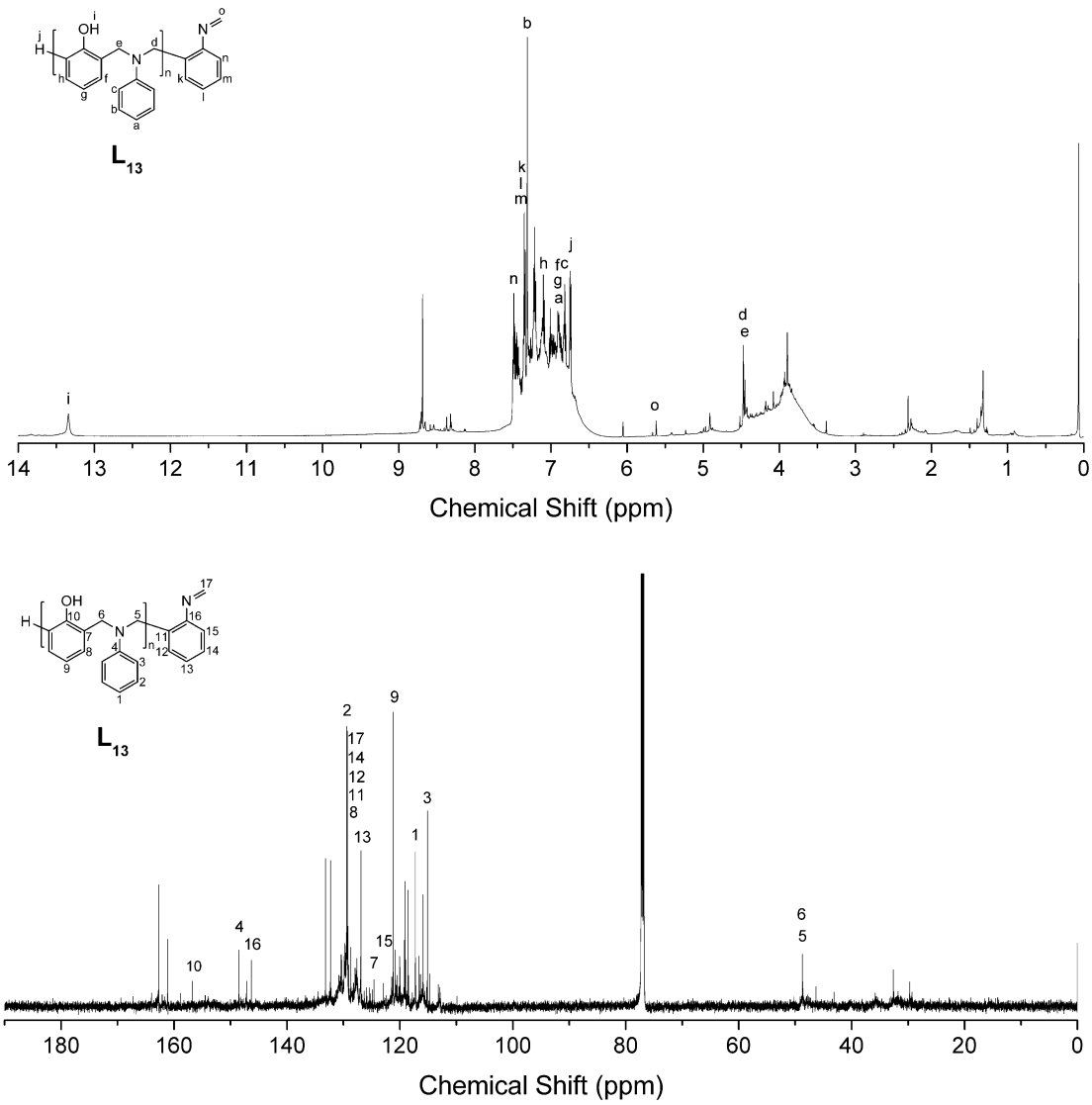


Figure S14. (continued).

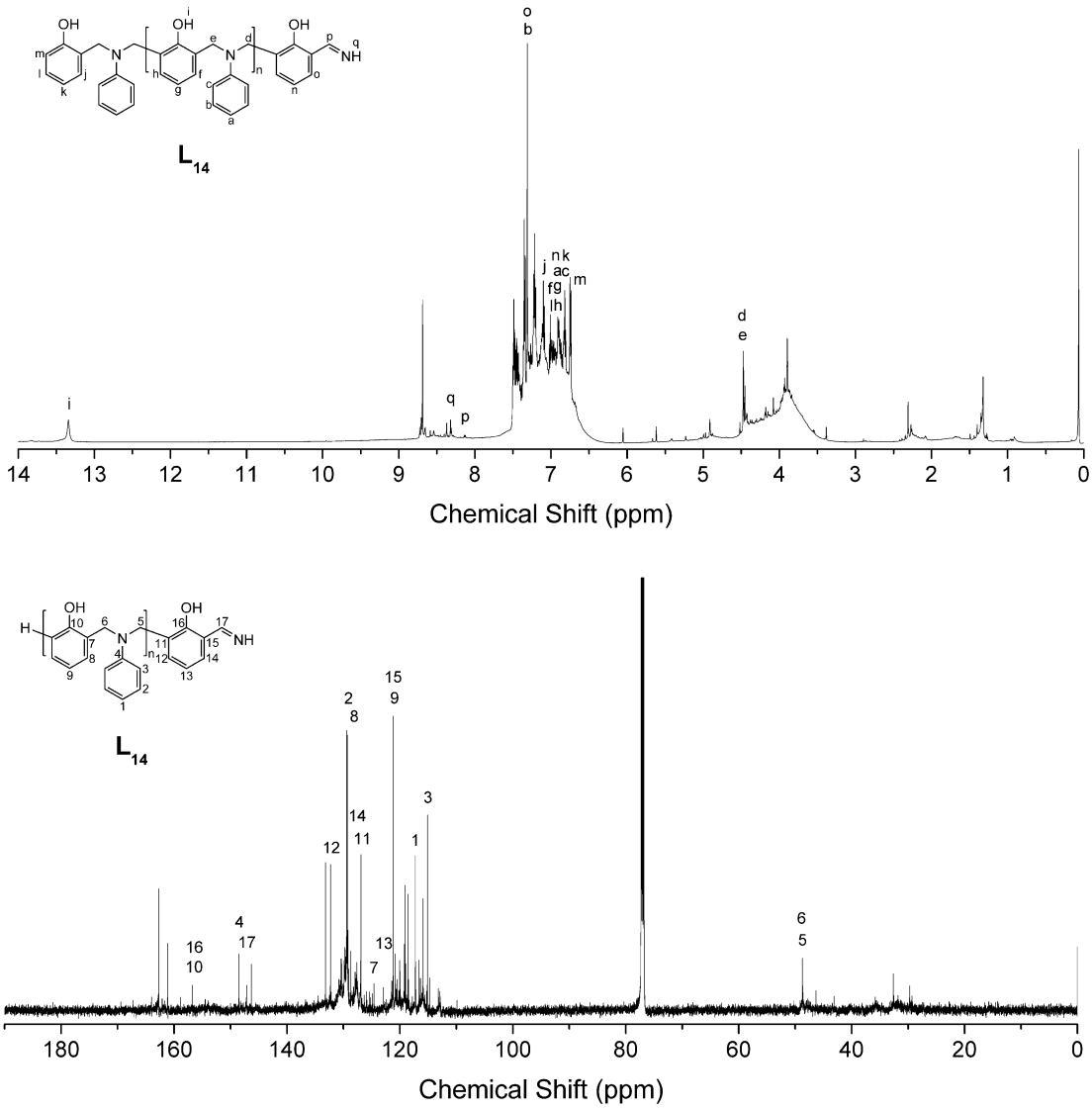


Figure S14. (continued).

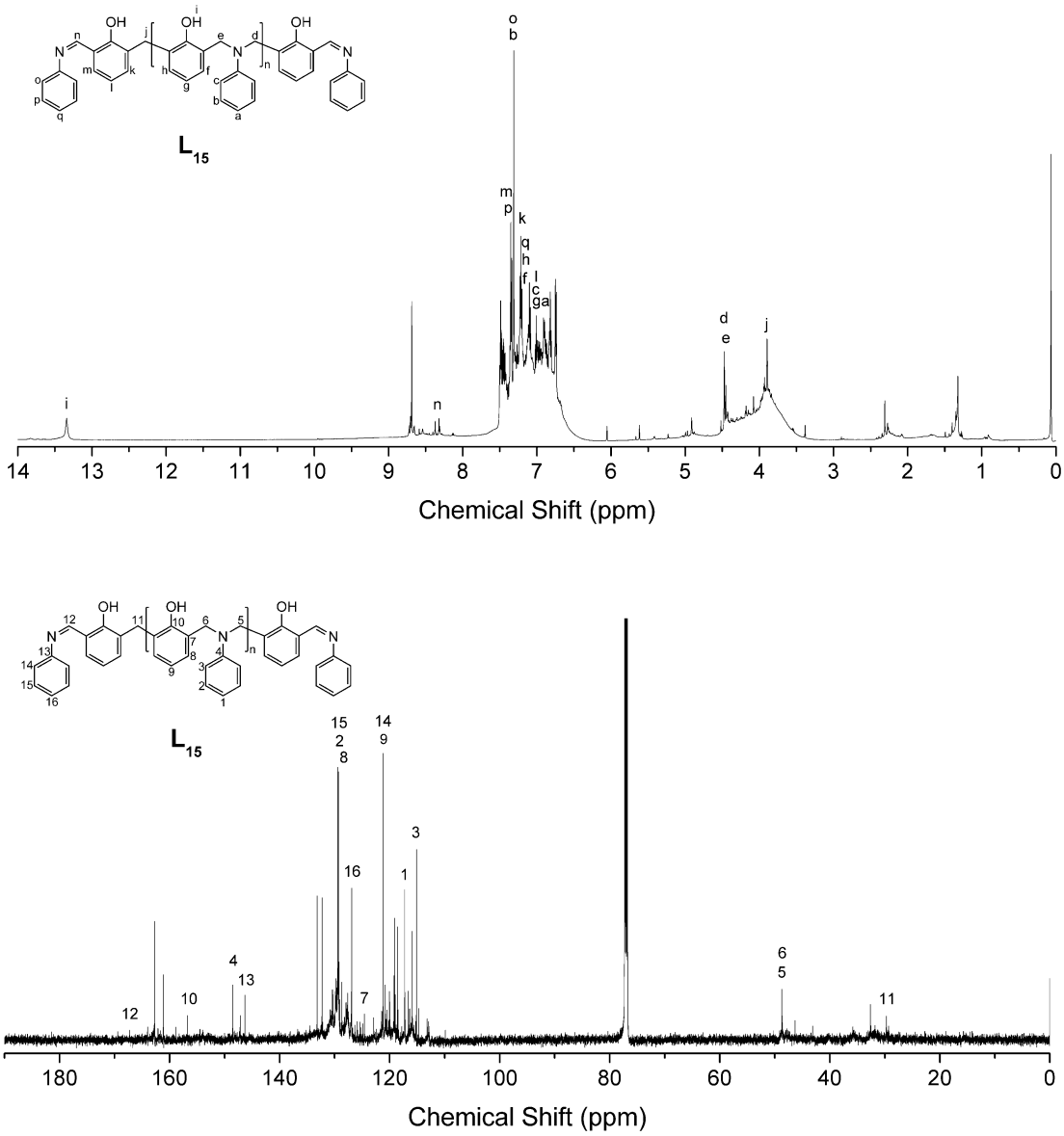


Figure S14. (continued).

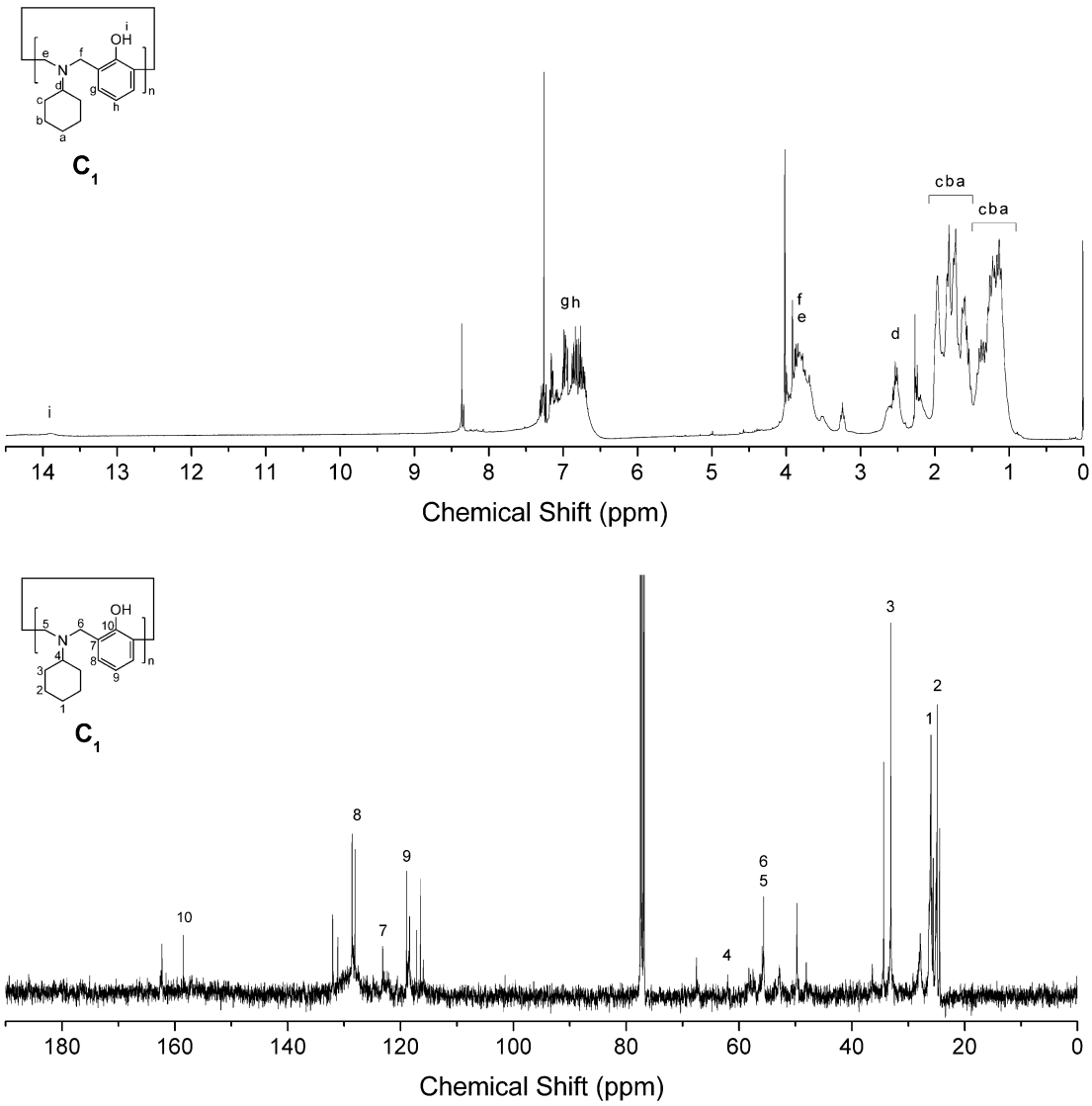


Figure S15. The proton and carbon assignments of the resonance signals of the identified products in PH-cha-180-35.

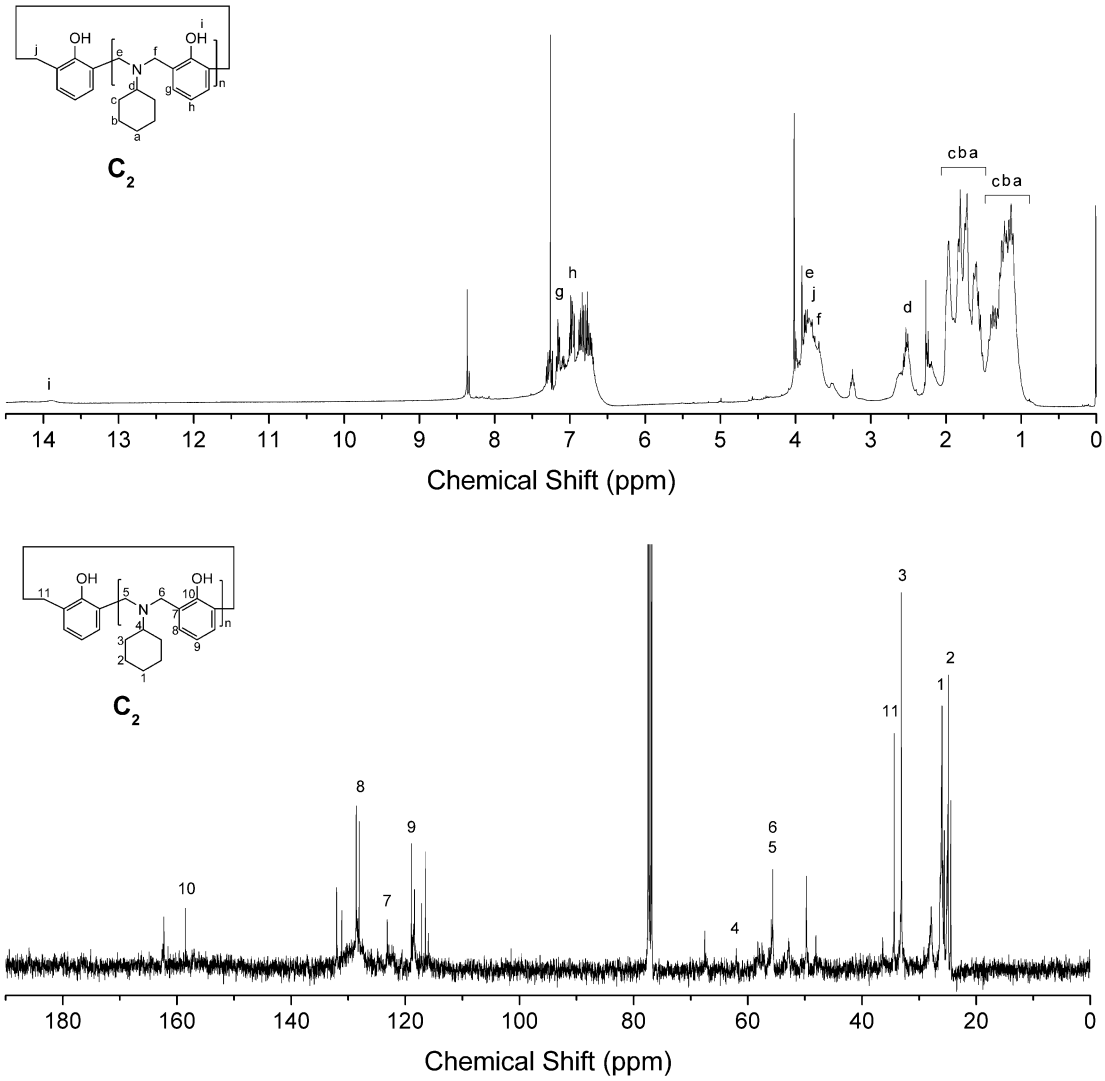


Figure S15. (continued).

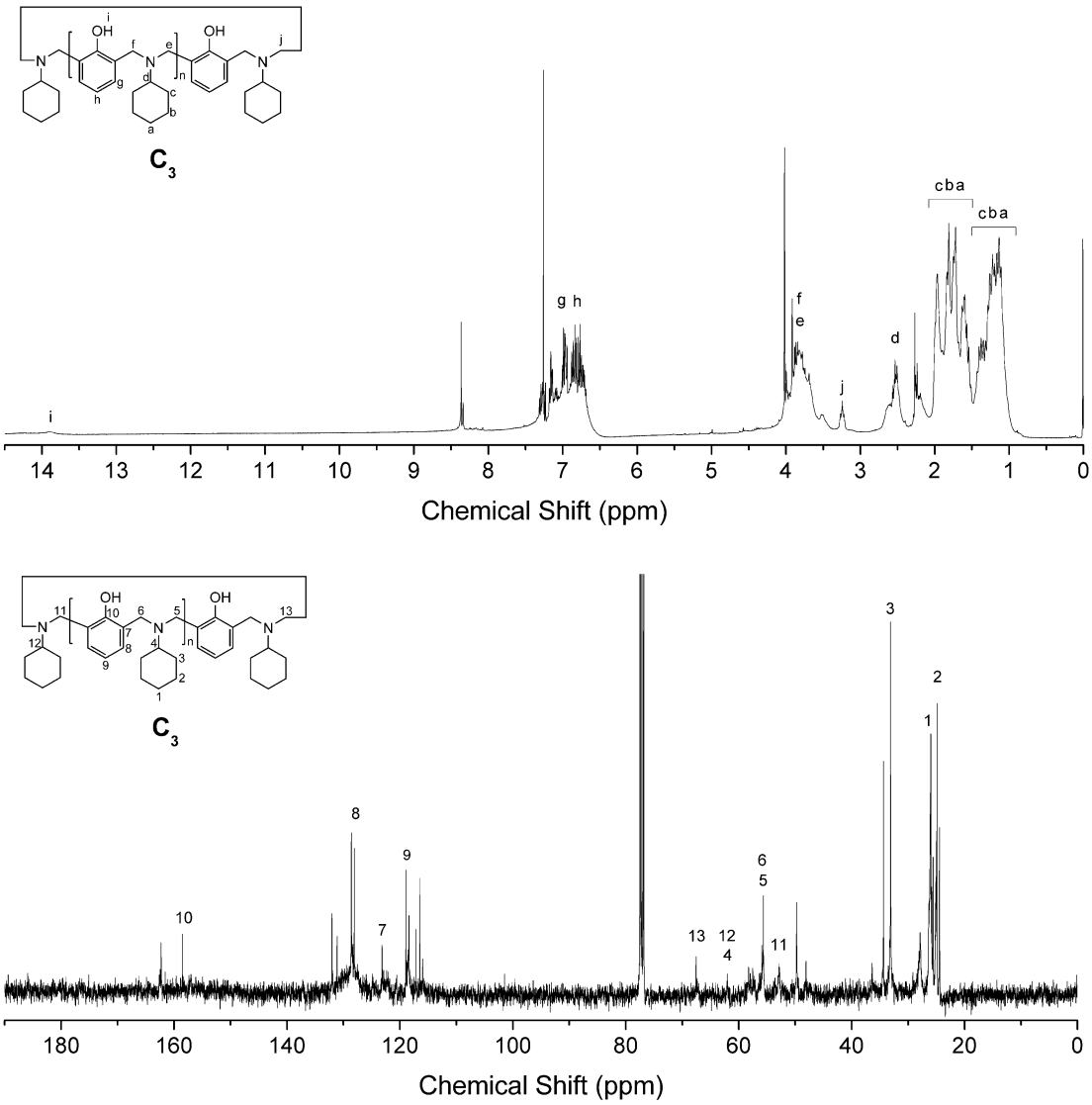


Figure S15. (continued).

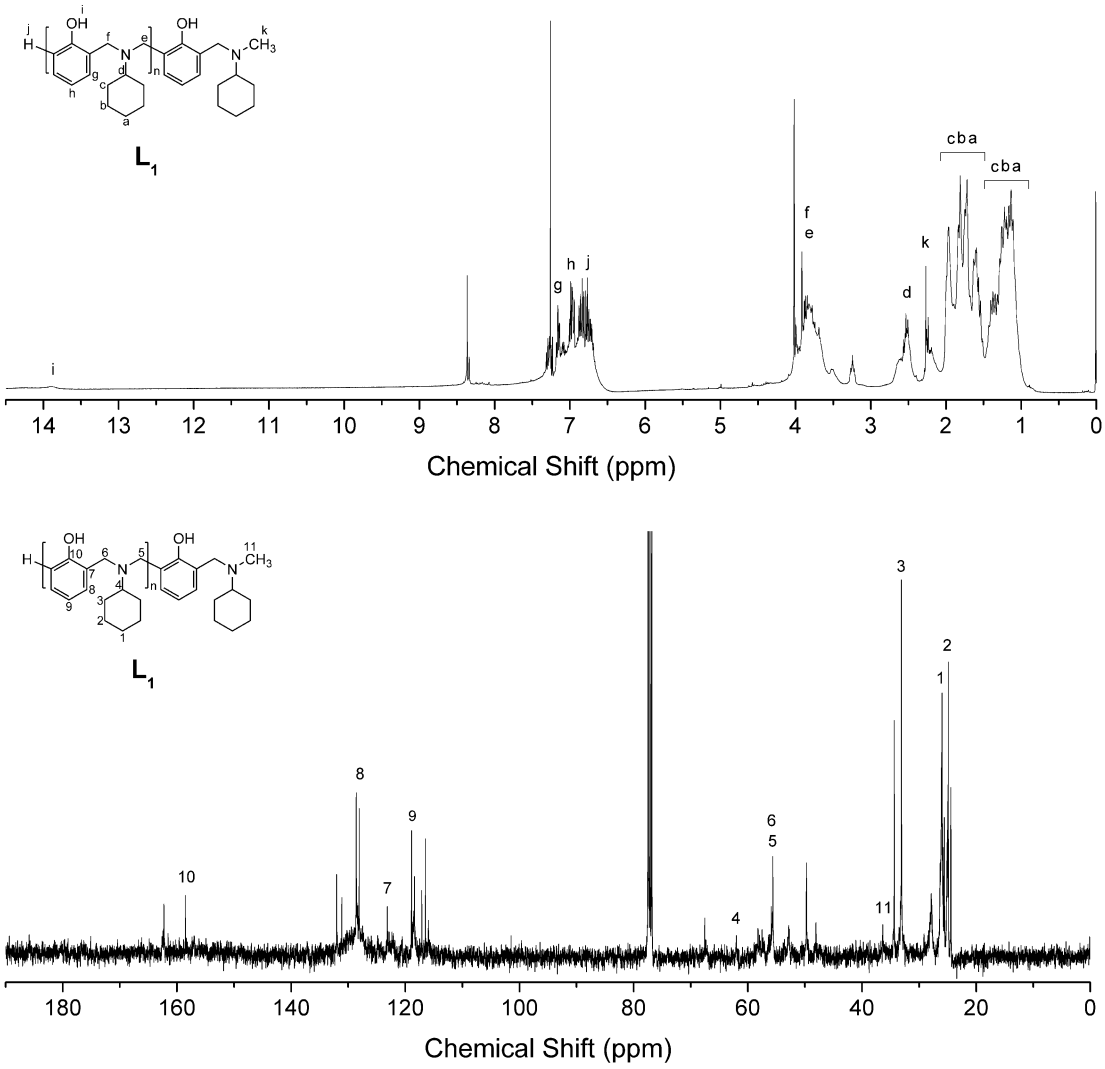


Figure S15. (continued).

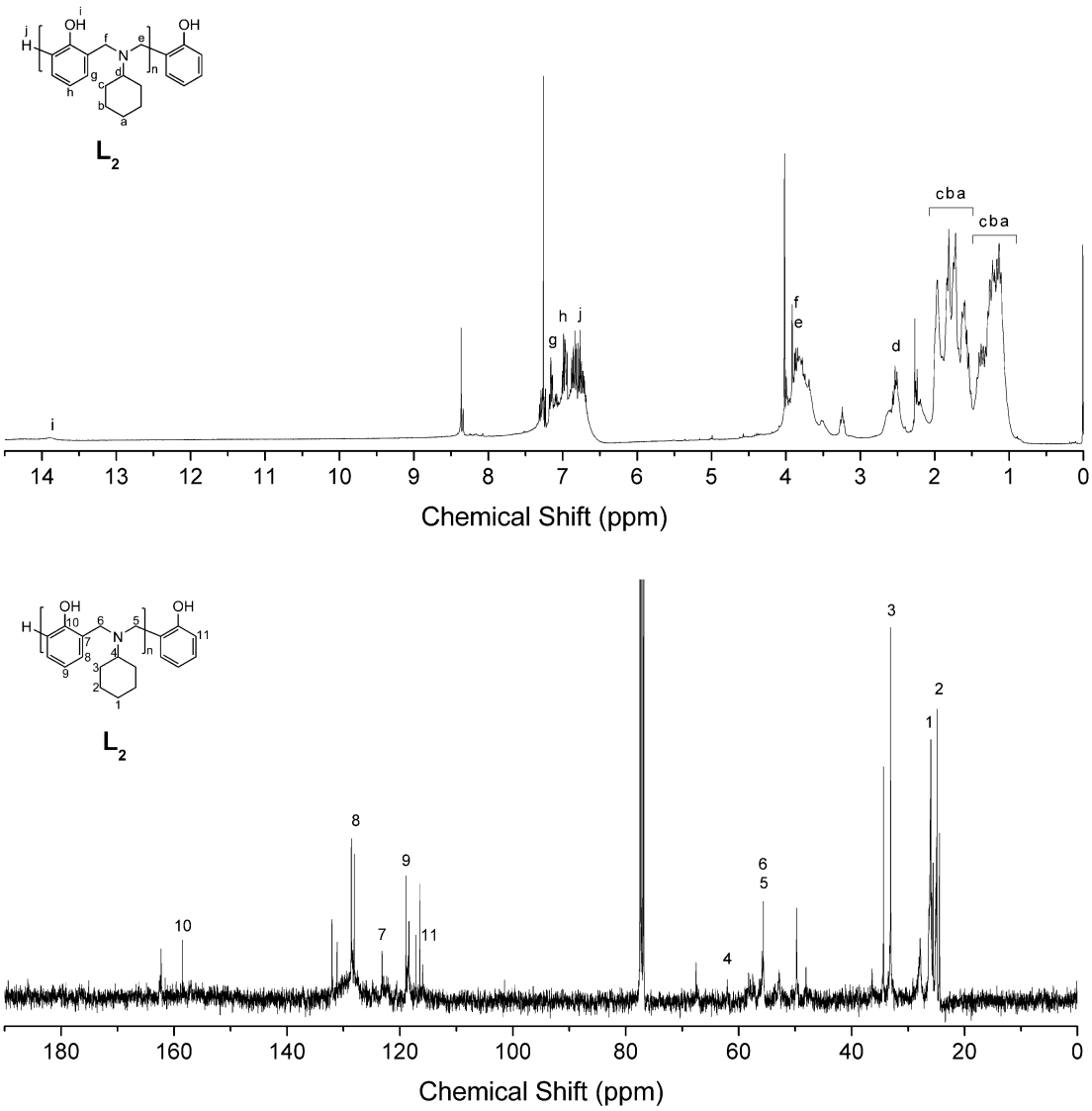


Figure S15. (continued).

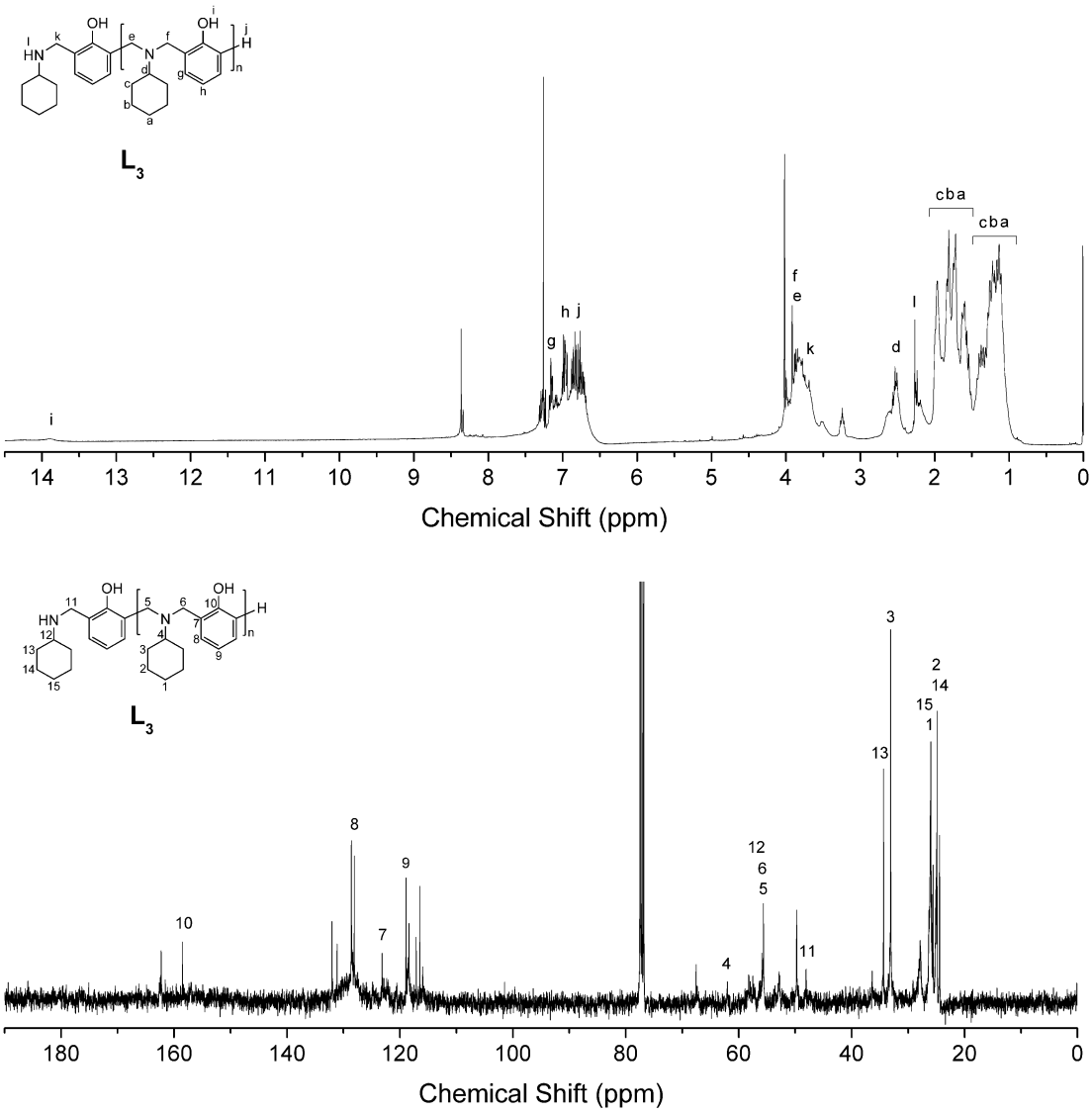


Figure S15. (continued).

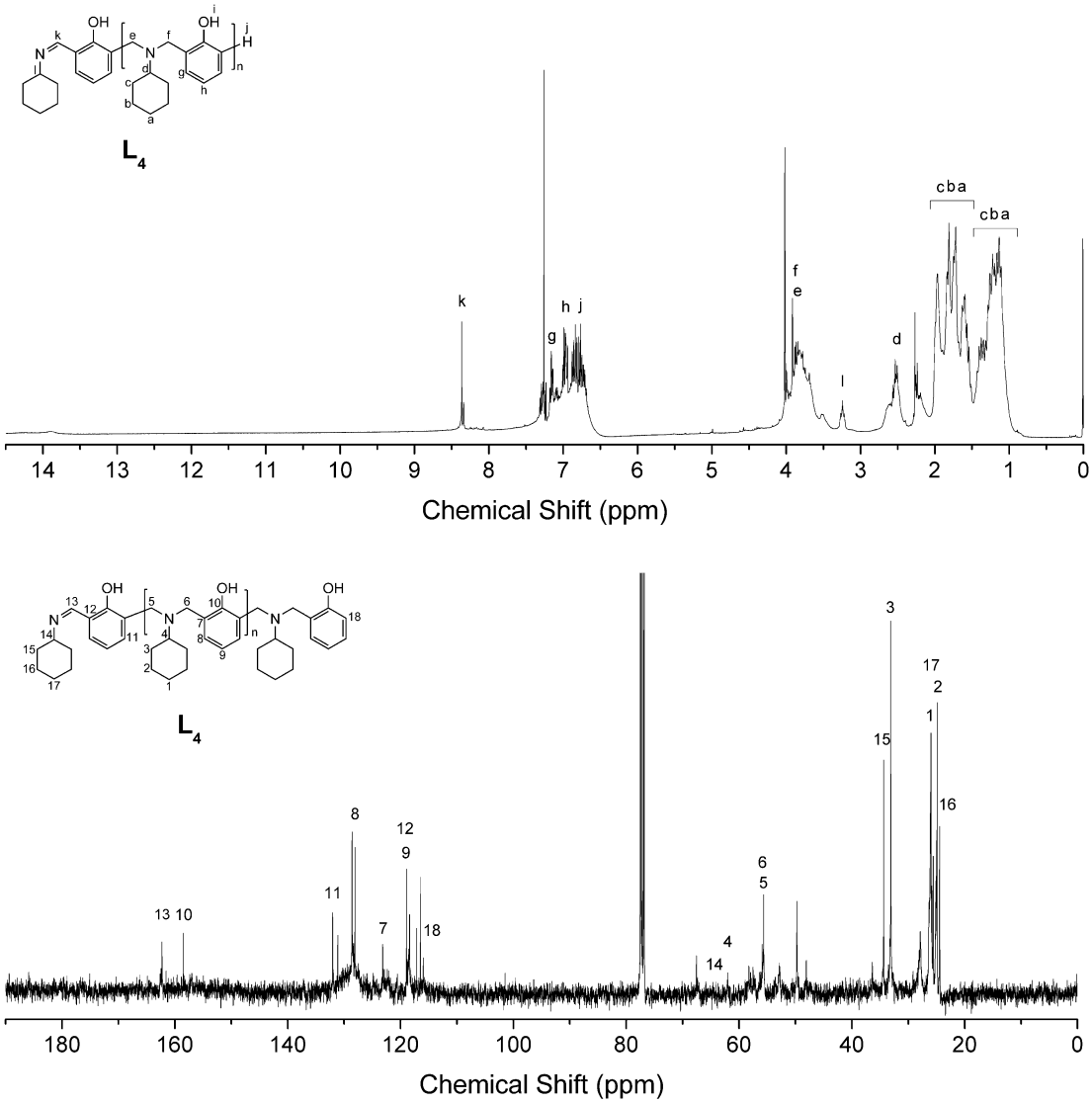


Figure S15. (continued).

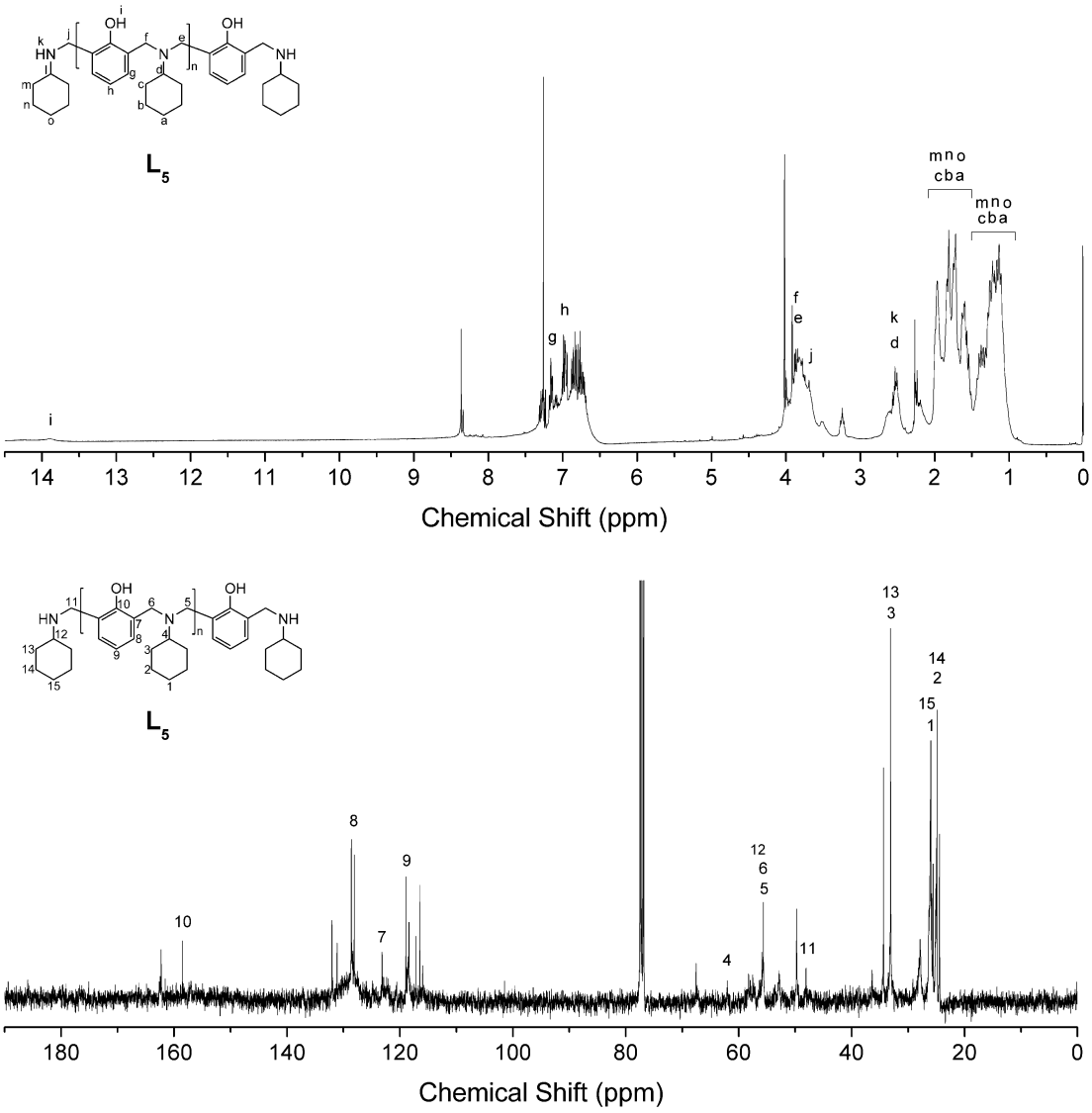


Figure S15. (continued).

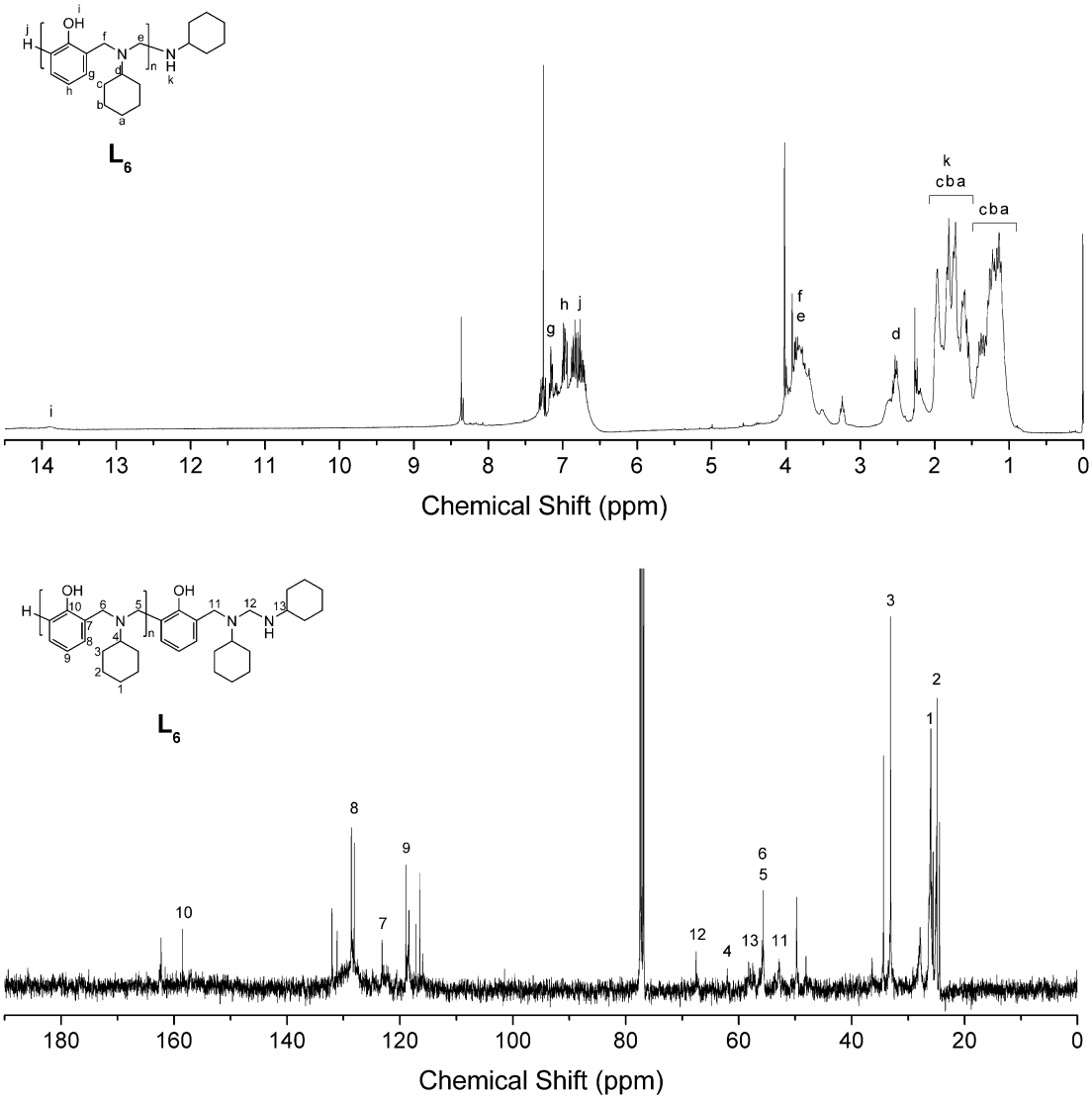


Figure S15. (continued).

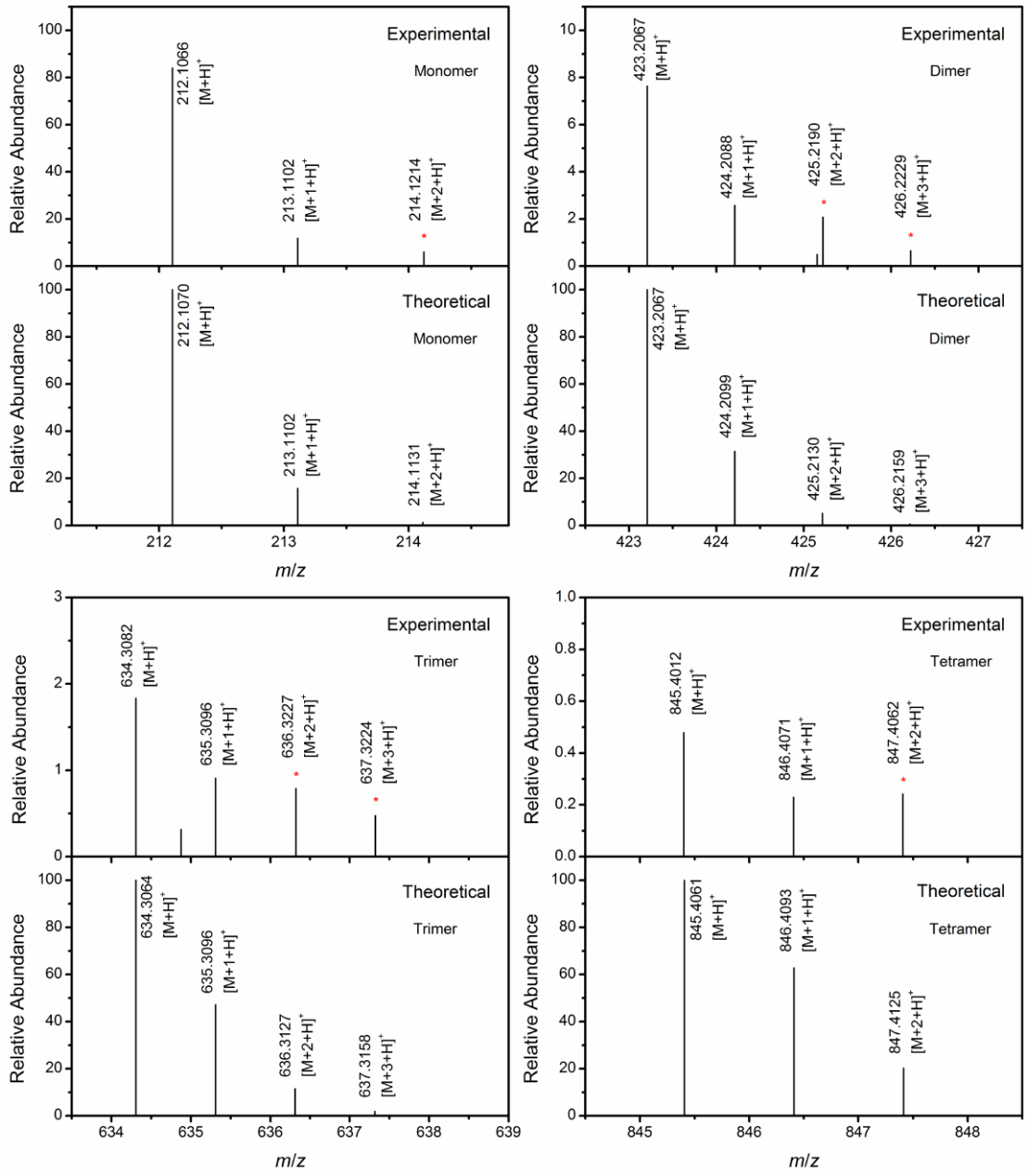


Figure S16. Experimental and theoretical isotopic distribution patterns for monomer, dimer, trimer, and tetramer in PH-a-220-35.

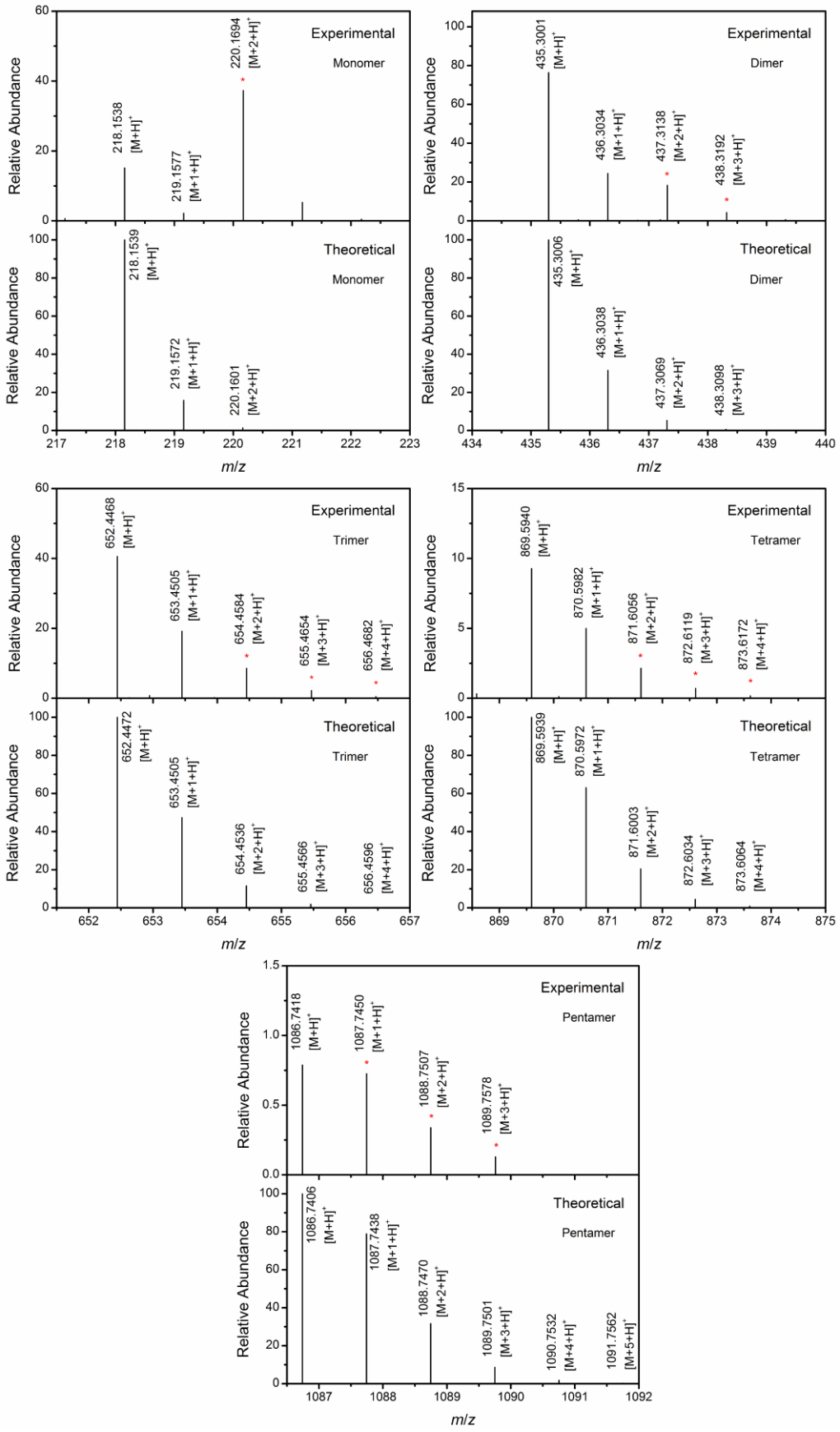


Figure S17. Experimental and theoretical isotopic distribution patterns for monomer, dimer, trimer, tetramer, and pentamer in PH-cha-180-35.

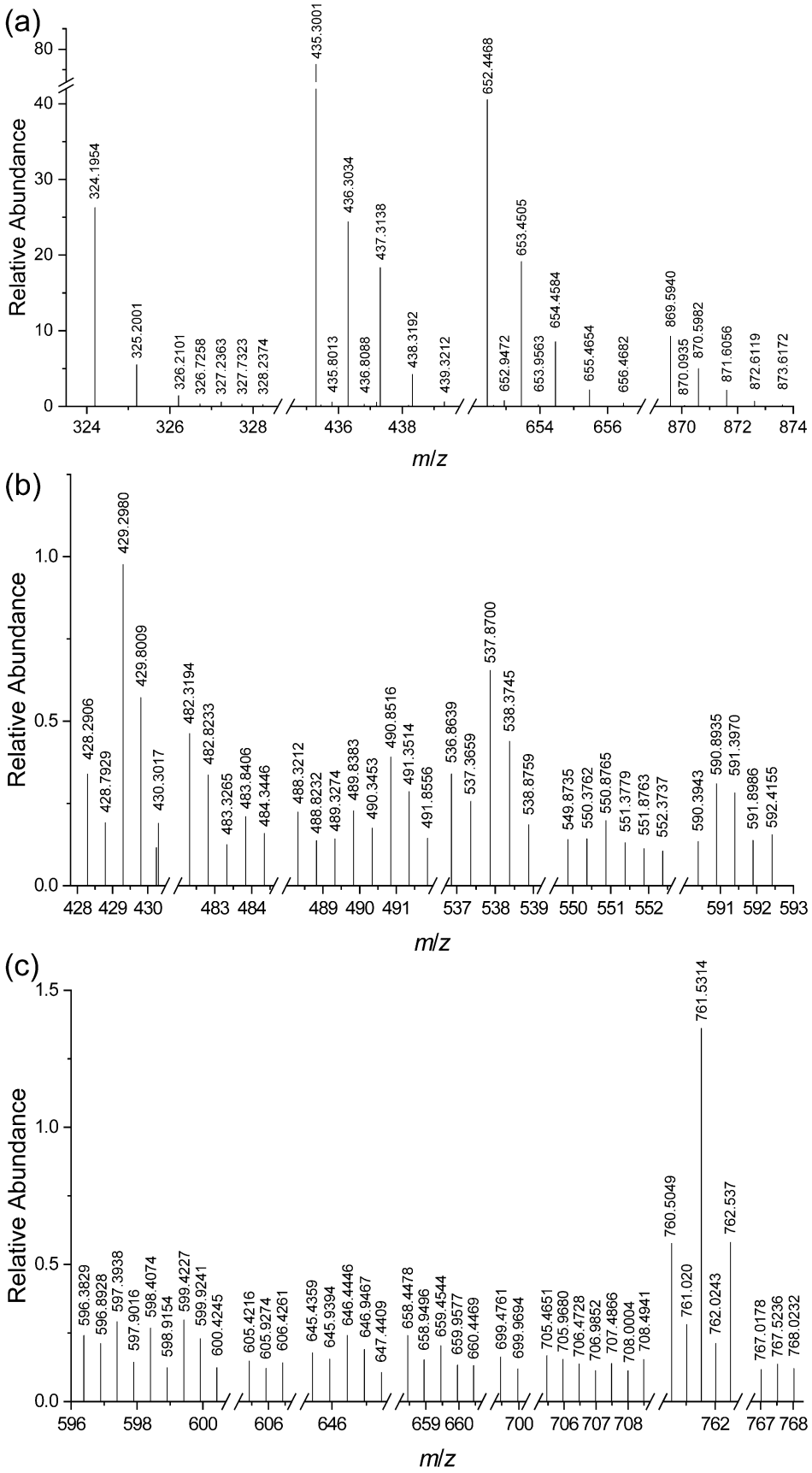
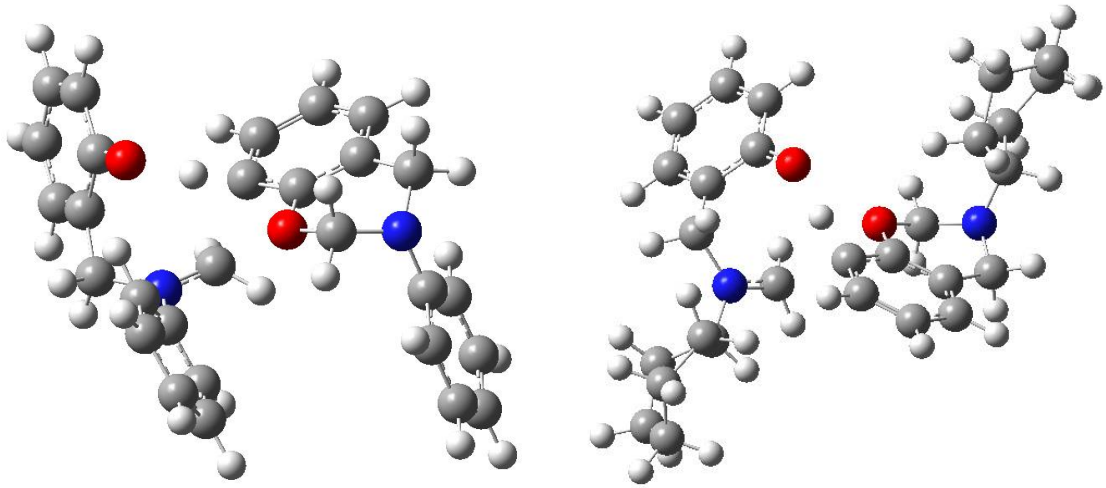
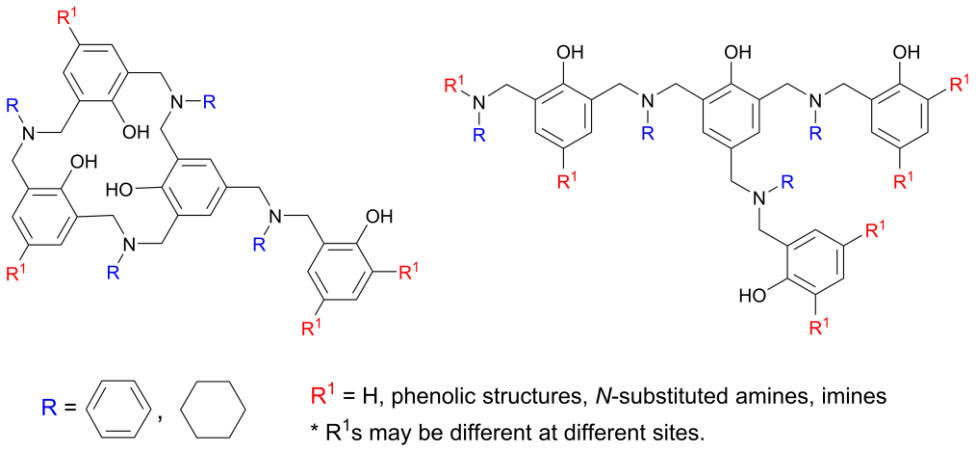


Figure S18. Isotopic distribution of doubly charged ions in the ESI mass spectrum of PH-cha-180-35.



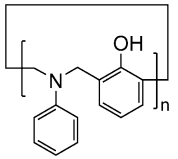
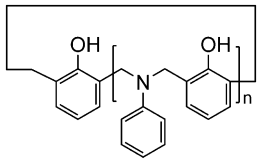
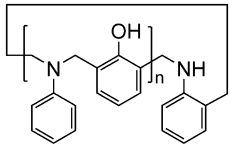
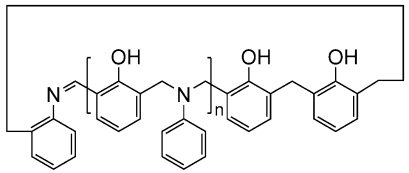
(a) (b)

Figure S19. The optimized transition state (**TS**) structures at B3LYP/6-311G(d,p) level for polymerization systems of (a) PH-a and (b) PH-cha.



Scheme S3. Possible crosslinking ways in PH-a and PH-cha systems.

Table S1. Mass results for cyclic products in PH-a-220-35 and the proposed assignments.

Mass series	$[M+H]^+$ (found)	$[M+H]^+$ (calcd)	$[M+Na]^+$ (found)	$[M+Na]^+$ (calcd)	M (Da)	Empirical formula	Chemical structure	n	Ring size
C_1	212.1066[a]	212.1070	234.0892	234.0889	211.0992	$C_{14}H_{13}NO$		1	-
	423.2067[a]	423.2067	445.1875	445.1886	422.1989	$C_{28}H_{26}N_2O_2$		2	12
	634.3082[a]	634.3064	-	656.2884	633.2986	$C_{42}H_{39}N_3O_3$		3	18
	845.4012	845.4061	-	867.3881	844.3983	$C_{56}H_{52}N_4O_4$		4	24
C_2	318.1498	318.1489	340.1325	340.1308	317.1410	$C_{21}H_{19}NO_2$		1	10
	529.2578	529.2485	-	551.2305	528.2407	$C_{35}H_{32}N_2O_3$		2	16
	740.3581	740.3483	-	762.3302	739.3405	$C_{49}H_{45}N_3O_4$		3	22
	951.4461	951.4480	-	973.4299	950.4402	$C_{63}H_{58}N_4O_5$		4	28
C_3	317.1620	317.1648	-	339.1468	316.1570	$C_{21}H_{20}N_2O$		1	10
	528.2628	528.2646	-	550.2465	527.2567	$C_{35}H_{33}N_3O_2$		2	16
	739.3589	739.3642	741.3617	741.3642	738.3564	$C_{49}H_{46}N_4O_3$		3	22
C_4	316.1335	316.1332	338.1162	338.1152	315.1254	$C_{21}H_{17}NO_2$		0	12
	527.2382	527.2329	-	549.2149	526.2251	$C_{35}H_{30}N_2O_3$		1	18
	738.3464	738.3326	-	760.3146	737.3248	$C_{49}H_{43}N_3O_4$		2	24

[a]: Isotopologue

Table S2. Mass results for linear products in PH-a-220-35 and the proposed assignments.

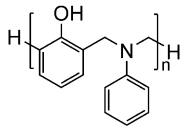
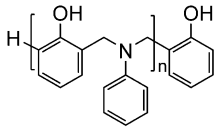
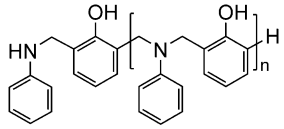
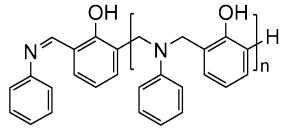
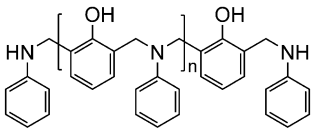
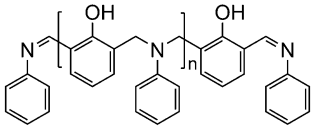
Mass series	$[M+H]^+$ (found)	$[M+H]^+$ (calcd)	$[M+Na]^+$ (found)	$[M+Na]^+$ (calcd)	M (Da)	Empirical formula	Chemical structure	n
L_1	214.1214[a]	214.1226	-	236.1046	213.1148	$C_{14}H_{15}NO$		1
	425.2190[a]	425.2224	-	447.2043	424.2145	$C_{28}H_{28}N_2O_2$		2
	636.3227	636.3221	-	658.3040	635.3142	$C_{42}H_{41}N_3O_3$		3
	847.4062	847.4218	-	869.4037	846.4140	$C_{56}H_{54}N_4O_4$		4
L_2	306.1501	306.1489	328.1345	328.1308	305.1410	$C_{20}H_{19}NO_2$		1
	517.2580	517.2485	-	539.2305	516.2407	$C_{34}H_{32}N_2O_3$		2
	728.3598	728.3483	-	750.3302	727.3405	$C_{48}H_{45}N_3O_4$		3
	939.4587	939.4480	-	961.4299	938.4402	$C_{62}H_{58}N_4O_5$		4
L_3	411.2059[a]	411.2067	433.1892[a]	433.1886	410.1989	$C_{27}H_{26}N_2O_2$		1
	622.3069[a]	622.3064	644.2935	644.2884	621.2986	$C_{41}H_{39}N_3O_3$		2
	833.4067[a]	833.4061	-	855.3881	832.3983	$C_{55}H_{52}N_4O_4$		3
L_4	409.1881[a]	409.1911	431.1751[a]	431.1730	408.1832	$C_{27}H_{24}N_2O_2$		1
	620.2926[a]	620.2908	642.2836	642.2727	619.2829	$C_{41}H_{37}N_3O_3$		2
	831.3930[a]	831.3905	-	853.3724	830.3827	$C_{55}H_{50}N_4O_4$		3
L_5	305.1636	305.1648	327.1443	327.1468	304.1570	$C_{20}H_{20}N_2O$		0
	516.2617	516.2646	538.2434	538.2465	515.2567	$C_{34}H_{33}N_3O_2$		1
	727.3593	727.3643	-	749.3462	726.3564	$C_{48}H_{46}N_4O_3$		2
	938.4570	938.4640	-	960.4459	937.4562	$C_{62}H_{59}N_5O_4$		3
L_6	301.1361	301.1335	323.1126	323.1155	300.1257	$C_{20}H_{16}N_2O$		0
	512.2326	512.2333	-	534.2152	511.2254	$C_{34}H_{29}N_3O_2$		1
	723.3328	723.3330	-	745.3149	722.3251	$C_{48}H_{42}N_4O_3$		2

Table S2. (continued).

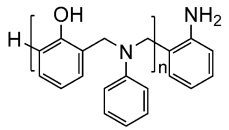
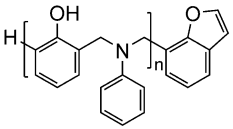
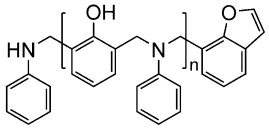
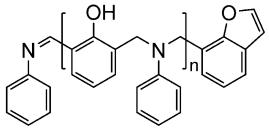
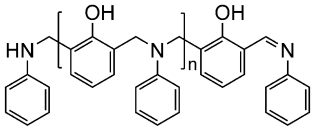
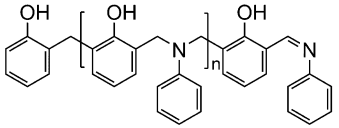
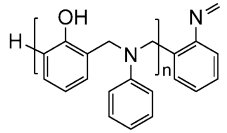
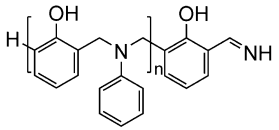
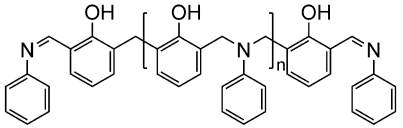
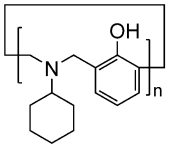
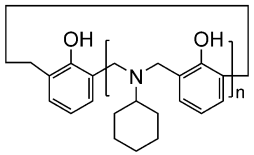
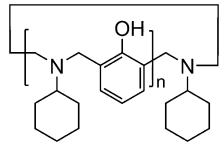
Mass series	$[M+H]^+$ (found)	$[M+H]^+$ (calcd)	$[M+Na]^+$ (found)	$[M+Na]^+$ (calcd)	M (Da)	Empirical formula	Chemical structure	n
L_7	305.1636	305.1648	327.1443	327.1468	304.1570	$C_{20}H_{20}N_2O$		1
	516.2617	516.2646	538.2434	538.2465	515.2567	$C_{34}H_{33}N_3O_2$		2
	727.3593	727.3643	-	749.3462	726.3564	$C_{48}H_{46}N_4O_3$		3
	938.4570	938.4640	-	960.4459	937.4562	$C_{62}H_{59}N_5O_4$		4
L_8	330.1509	330.1489	-	352.1308	329.1410	$C_{22}H_{19}NO_2$		1
	541.2583	541.2486	-	563.2205	540.2407	$C_{36}H_{32}N_2O_3$		2
	752.3517	752.3483	-	774.3302	751.3405	$C_{50}H_{45}N_3O_4$		3
L_9	224.1070	224.1070	-	246.0889	223.0992	$C_{15}H_{13}NO$		0
	435.2065	435.2067	-	457.1886	434.1989	$C_{29}H_{26}N_2O_2$		1
	646.2977	646.3064	-	668.2884	645.2986	$C_{43}H_{39}N_3O_3$		2
L_{10}	222.0892	222.0913	-	244.0733	221.0835	$C_{15}H_{11}NO$		0
	433.1892[a]	433.1911	-	455.1730	432.1832	$C_{29}H_{24}N_2O_2$		1
	644.2935	644.2908	-	666.2727	643.2829	$C_{43}H_{37}N_3O_3$		2
L_{11}	303.1488	303.1492	-	325.1311	302.1414	$C_{20}H_{18}N_2O$		0
	514.2481	514.2489	-	536.2308	513.2411	$C_{34}H_{31}N_3O_2$		1
	725.3459	725.3486	-	747.3306	724.3408	$C_{48}H_{44}N_4O_3$		2
	936.4465	936.4483	-	958.4303	935.4405	$C_{62}H_{57}N_5O_4$		3
L_{12}	304.1355	304.1332	326.1157	326.1152	303.1254	$C_{20}H_{17}NO_2$		0
	515.2378	515.2329	537.2239	537.2149	514.2251	$C_{34}H_{30}N_2O_3$		1
	726.3418	726.3326	-	748.3146	725.3248	$C_{48}H_{43}N_3O_4$		2
	937.4424	937.4323	-	959.4143	936.4245	$C_{62}H_{56}N_4O_5$		3

Table S2. (continued).

Mass series	$[M+H]^+$ (found)	$[M+H]^+$ (calcd)	$[M+Na]^+$ (found)	$[M+Na]^+$ (calcd)	M (Da)	Empirical formula	Chemical structure	n
L_{13}	317.1620	317.1648	-	339.1468	316.1570	$C_{21}H_{20}N_2O$		1
	528.2628	528.2646	-	550.2465	527.2567	$C_{35}H_{33}N_3O_2$		2
	739.3589	739.3643	-	761.3462	738.3564	$C_{49}H_{46}N_4O_3$		3
L_{14}	333.1602[a]	333.1598	355.1424	355.1417	332.1519	$C_{21}H_{20}N_2O_2$		1
	544.2598[a]	544.2595	566.2365	566.2414	543.2516	$C_{35}H_{33}N_3O_3$		2
	755.3601	755.3592	-	777.3411	754.3514	$C_{49}H_{46}N_4O_4$		3
	966.4638	966.4589	-	988.4408	965.4511	$C_{63}H_{59}N_5O_5$		4
L_{15}	407.1765	407.1754	-	429.1937	406.1676	$C_{27}H_{22}N_2O_2$		0
	618.2785	618.2751	-	640.2571	617.2673	$C_{41}H_{35}N_3O_3$		1
	829.3786	829.3748	-	851.3568	828.3670	$C_{55}H_{48}N_4O_4$		2

[a]: Isotopologue

Table S3. Mass results for cyclic products in PH-cha-180-35 and the proposed assignments.

Mass series	$[M+H]^+$ (found)	$[M+H]^+$ (calcd)	$[M+2H]^{2+}$ (found)	$[M+Na]^+$ (found)	$[M+Na]^+$ (calcd)	M (Da)	Empirical formula	Chemical structure	n	Ring size
C_1	218.1538[a]	218.1539	-	240.1353[a]	240.1359	217.1461	$C_{14}H_{19}NO$		1	-
	435.3001[a]	435.3006	-	457.2831[a]	457.2825	434.2928	$C_{28}H_{38}N_2O_2$		2	12
	652.4468[a]	652.4473	326.7258	674.4299	674.4292	651.4394	$C_{42}H_{57}N_3O_3$		3	18
	869.5940[a]	869.5939	435.3001	-	891.5759	868.5861	$C_{56}H_{76}N_4O_4$		4	24
	1086.7418[a]	1086.7406	543.8732	-	1108.7225	1085.7328	$C_{70}H_{95}N_5O_5$		5	30
	-	1303.8873	652.4468	-	1325.8692	1302.8791	$C_{84}H_{114}N_6O_6$		6	36
	-	1520[b]	761.0202	-	1542[b]	1520.0261	$C_{98}H_{133}N_7O_7$		7	42
	-	1737[b]	869.5940	-	1759[b]	1737.1728	$C_{112}H_{152}N_8O_8$		8	48
C_2	324.1954[a]	324.1958	-	346.1784[a]	346.1777	323.1880	$C_{21}H_{25}NO_2$		1	10
	541.3435[a]	541.3424	-	-	563.3244	540.3346	$C_{35}H_{44}N_2O_3$		2	16
	758.4900[a]	758.4891	379.7459	-	780.4711	757.4813	$C_{49}H_{63}N_3O_4$		3	22
	975.6370[a]	975.6358	488.3212	-	997.6177	974.6280	$C_{63}H_{82}N_4O_5$		4	28
	-	1192.7825	596.8928	-	1214.7644	1191.7746	$C_{77}H_{101}N_5O_6$		5	34
	-	1409.9291	705.4651	-	1431.9111	1408.9213	$C_{91}H_{120}N_6O_7$		6	40
C_3	329.2585[a]	329.2587	-	351.2394	351.2406	328.2509	$C_{21}H_{32}N_2O$		1	8
	546.4051[a]	546.4054	-	-	568.3873	545.3976	$C_{35}H_{51}N_3O_2$		2	14
	763.5528[a]	763.5520	-	-	785.5340	762.5442	$C_{49}H_{70}N_4O_3$		3	20
	980.6976[a]	980.6987	490.8516	-	1002.6807	979.6909	$C_{63}H_{89}N_5O_4$		4	26
	-	1197.8454	599.4227	-	1219.8273	1196.8309	$C_{77}H_{108}N_6O_5$		5	32
	-	1414.9921	708.0004	-	1436.9740	1413.9863	$C_{91}H_{127}N_7O_6$		6	38

[a]: Isotopologue

[b]: Nitrogen rule

Table S4. Mass results for linear products in PH-cha-180-35 and the proposed assignments.

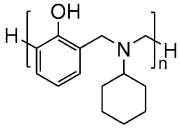
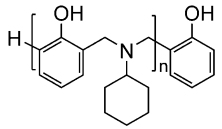
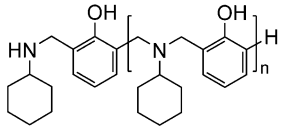
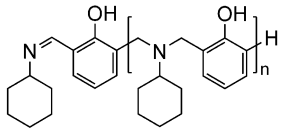
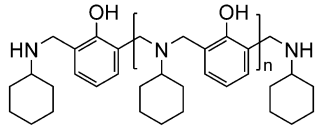
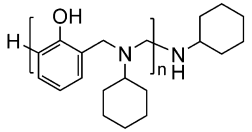
Mass series	$[M+H]^+$ (found)	$[M+H]^+$ (calcd)	$[M+2H]^{2+}$ (found)	$[M+Na]^+$ (found)	$[M+Na]^+$ (calcd)	M (Da)	Empirical formula	Chemical structure	n
L_1	220.1694[a]	220.1696	-	-	242.1515	219.1617	$C_{14}H_{21}NO$		1
	437.3138[a]	437.3163	-	-	459.2982	436.3084	$C_{28}H_{40}N_2O_2$		2
	654.4584	654.4629	327.7323	-	676.4448	653.4551	$C_{42}H_{59}N_3O_3$		3
	871.6056[a]	871.6096	436.3034	-	893.5915	870.6018	$C_{56}H_{78}N_4O_4$		4
	1088.7507[a]	1088.7562	544.8774	-	1110.7382	1087.7484	$C_{70}H_{97}N_5O_5$		5
	-	1305.9029	653.4505	-	1327.8849	1304.8951	$C_{84}H_{116}N_6O_6$		6
	-	1522[b]	762.0243	-	1544[b]	1522.0418	$C_{98}H_{135}N_7O_7$		7
L_2	312.1954[a]	312.1958	-	334.1786	334.1778	311.1880	$C_{20}H_{25}NO_2$		1
	529.3420[a]	529.3425	265.1732	-	551.3244	528.3346	$C_{34}H_{44}N_2O_3$		2
	746.4904[a]	746.4891	373.7461	-	768.4711	745.4813	$C_{48}H_{63}N_3O_4$		3
	963.6381[a]	963.6358	482.3194	-	985.6177	962.2680	$C_{62}H_{82}N_4O_5$		4
	-	1180.7824	590.8935	-	1202.7644	1179.7746	$C_{76}H_{101}N_5O_6$		5
	-	1397.9291	699.4761	-	1419.9111	1396.9213	$C_{90}H_{120}N_6O_7$		6
L_3	423.2998[a]	423.3006	212.1531	445.2865	445.2825	422.2928	$C_{27}H_{38}N_2O_2$		1
	640.4463[a]	640.4472	320.7260	662.4321	662.4292	639.4394	$C_{41}H_{57}N_3O_3$		2
	857.5935[a]	857.5939	429.2980	-	879.5758	856.5861	$C_{55}H_{76}N_4O_4$		3
	1074.7401[a]	1074.7406	537.8700	-	1096.7225	1073.7328	$C_{69}H_{95}N_5O_5$		4
	-	1291.8872	646.4446	-	1313.8692	1290.8794	$C_{83}H_{114}N_6O_6$		5
L_4	421.2844[a]	421.2850	-	-	443.2669	420.2771	$C_{27}H_{36}N_2O_2$		1
	638.4321[a]	638.4316	-	-	660.4136	637.4238	$C_{41}H_{55}N_3O_3$		2
	855.5797[a]	855.5783	428.2906	-	877.5602	854.5704	$C_{55}H_{74}N_4O_4$		3
	1072.7224[a]	1072.7249	536.8639	-	1094.7069	1071.7171	$C_{69}H_{93}N_5O_5$		4
	-	1289.8716	645.4359	-	1311.8536	1288.8638	$C_{83}H_{112}N_6O_6$		5

Table S4. (continued).

Mass series	$[M+H]^+$ (found)	$[M+H]^+$ (calcd)	$[M+2H]^{2+}$ (found)	$[M+Na]^+$ (found)	$[M+Na]^+$ (calcd)	M (Da)	Empirical formula	Chemical structure	n
L_5	317.2578[a]	317.2587	-	339.2403	339.2407	316.2509	$C_{20}H_{32}N_2O$		0
	534.4039[a]	534.4054	-	556.3748	556.3873	533.3976	$C_{34}H_{51}N_3O_2$		1
	751.5531	751.5521	-	773.5177	773.5340	750.5442	$C_{48}H_{70}N_4O_3$		2
L_6	317.2578[a]	317.2587	-	339.2403	339.2407	316.2509	$C_{20}H_{32}N_2O$		1
	534.4039[a]	534.4054	-	556.3748	556.3873	533.3976	$C_{34}H_{51}N_3O_2$		2
	751.5531	751.5521	-	773.5177	773.5177	750.5442	$C_{48}H_{70}N_4O_3$		3

[a]: Isotopologue

[b]: Nitrogen rule