Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Post Polymerization Modification of the Side Chain in Optically Active Polymer by Thiol-ene Reaction

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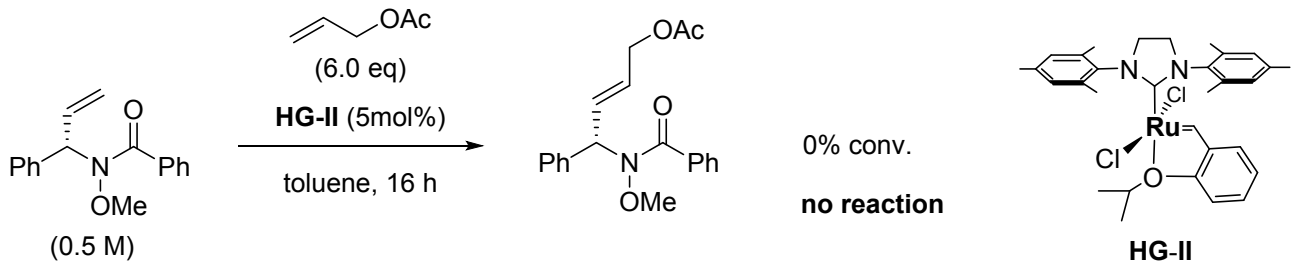
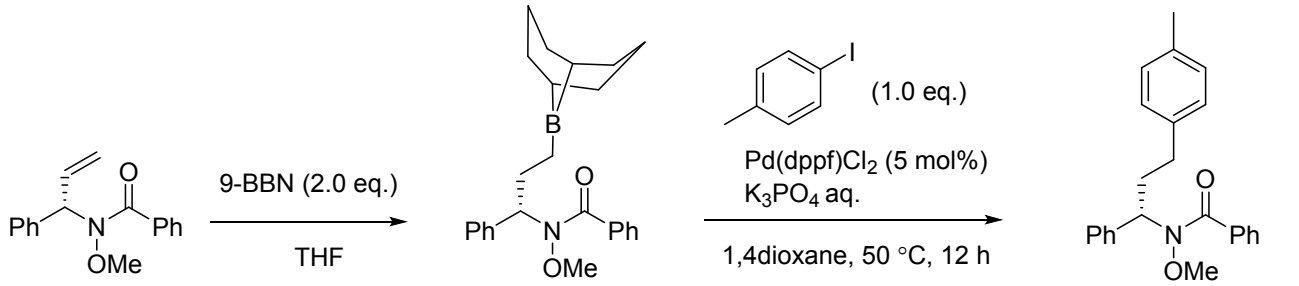
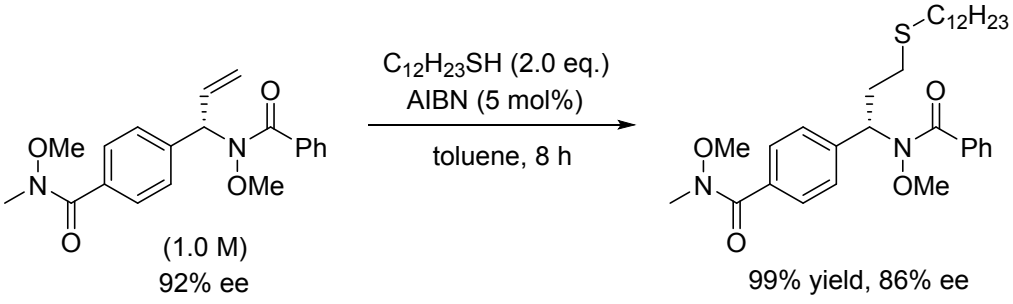
Cross Metathesis Reaction



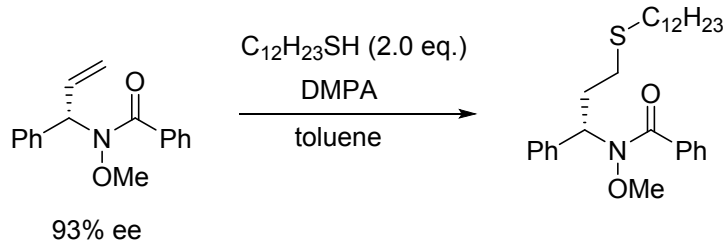
Suzuki Miyaura Coupling via Hydroboration of 9-BBN



Thiol-ene Reaction



Screening of the Reaction Conditions of Thiol-ene reaction using DMPA as Radical Initiator

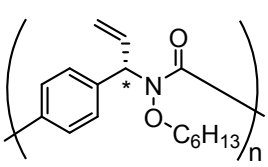


93% ee

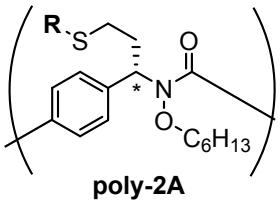
entry	**thiol** (eq.)	DMPA (mol%) [a]	concentration (M) of allylic compound	reaction time (h)	^{1}H NMR yield (%) [b]	ee (%)
1	1.2	5	1.0	16	65	-
2	1.2	20	1.0	16	83	-
3	1.2	20	0.50	16	69	-
4	2.0	20	1.0	16	quant.	92
5	2.0	20	1.0	1	91	-
6 [d]	4.0	20	1.0	1	quant.	92

[a] The equivalents and mol% was relative to C=C of **poly-1A**. [b] The NMR yield was determined from the integral intensity of the ^{1}H NMR signals of the crude product.

Solubility of Polymers [a]

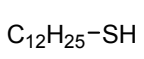


poly-1A

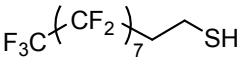


poly-2A

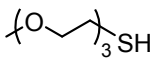
R =



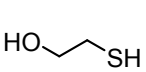
poly-2Aa



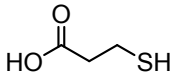
poly-2Ab



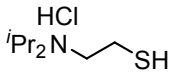
poly-2Ac



poly-2Ae



poly-2Af



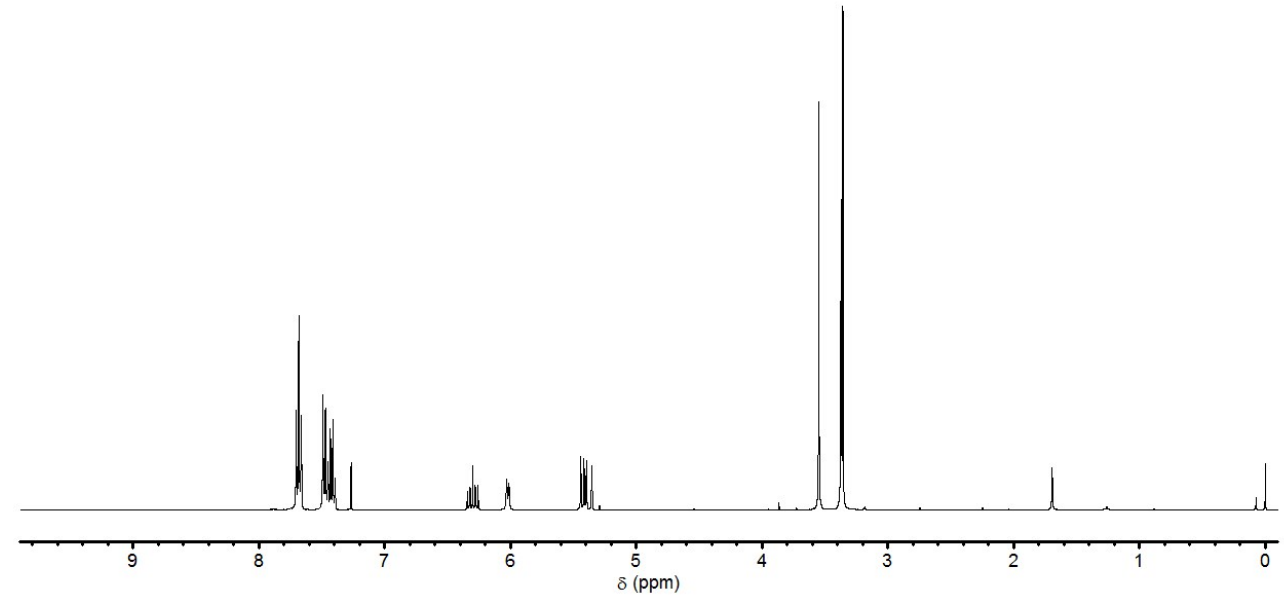
poly-2Ai

polymer	C_6F_6	Cyclohexane	$CHCl_3$	THF	MeCN	MeOH	Water
poly-1A	–	–	+	+	–	–	–
poly-2A(3a)	–	+	+	+	–	–	–
poly-2A(3b)	+	–	+	+	–	–	–
poly-2A(3c)	N.D.	–	+	+	+	–	–
poly-2A(3e)	N.D.	–	+	+	–	± + (EtOH)	–
poly-2A(3f)	N.D.	–	–	+	–	+	–
poly-2A(3i)	N.D.	–	+	–	+	+	+

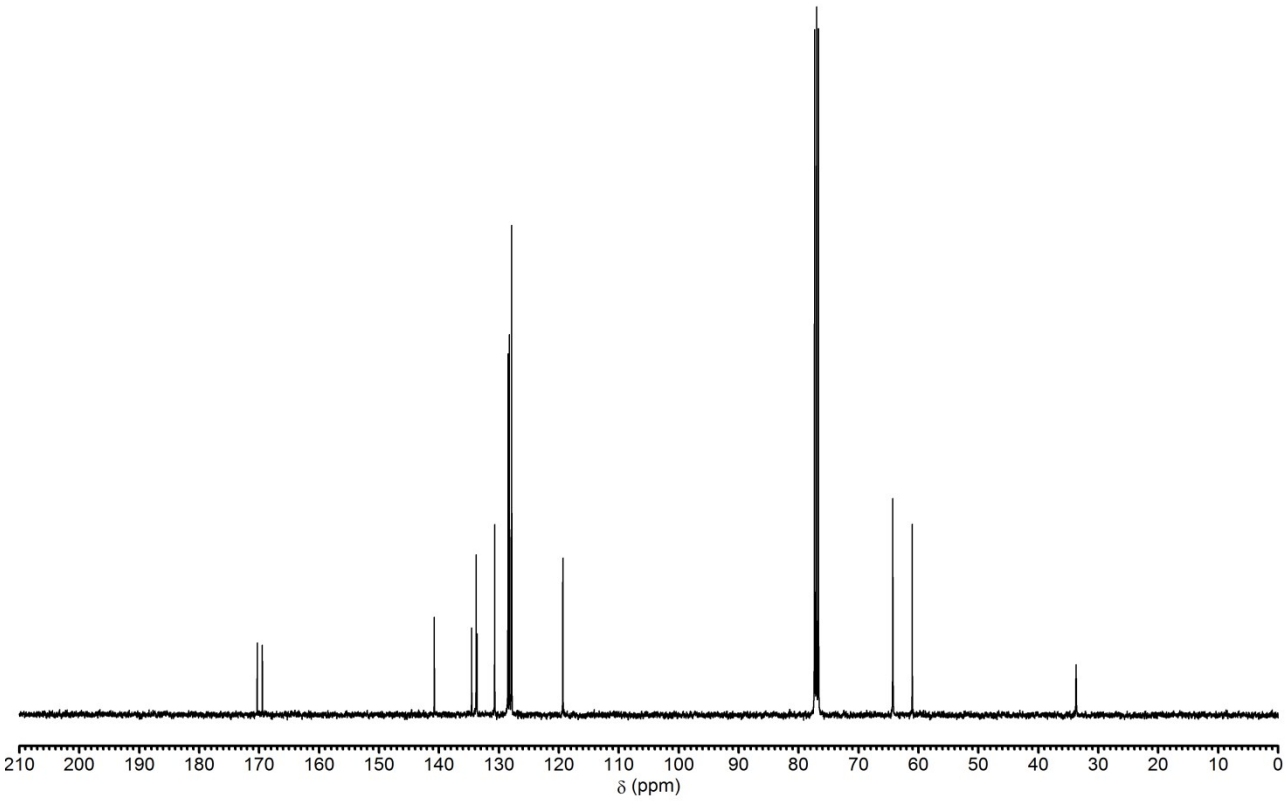
[a] Symbols: + soluble, ± partly soluble, – insoluble [(polymer, 1.0 mg) / (solvent, 1.0 mL)].

NMR Analysis

^{1}H NMR of (*R*)-4-[1-(*N*-methoxybenzamido)allyl]-*N*-methoxy-*N*-methylbenzamide (4)

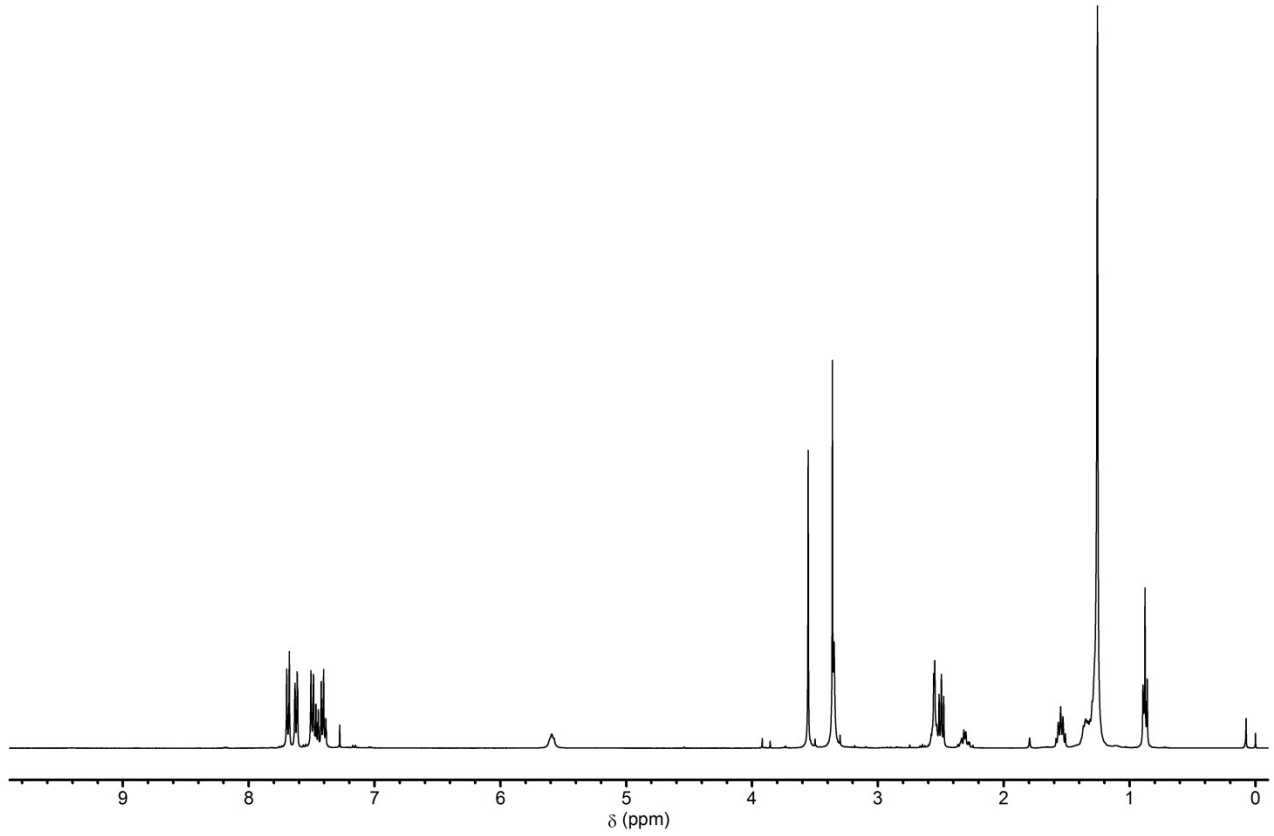


^{13}C NMR

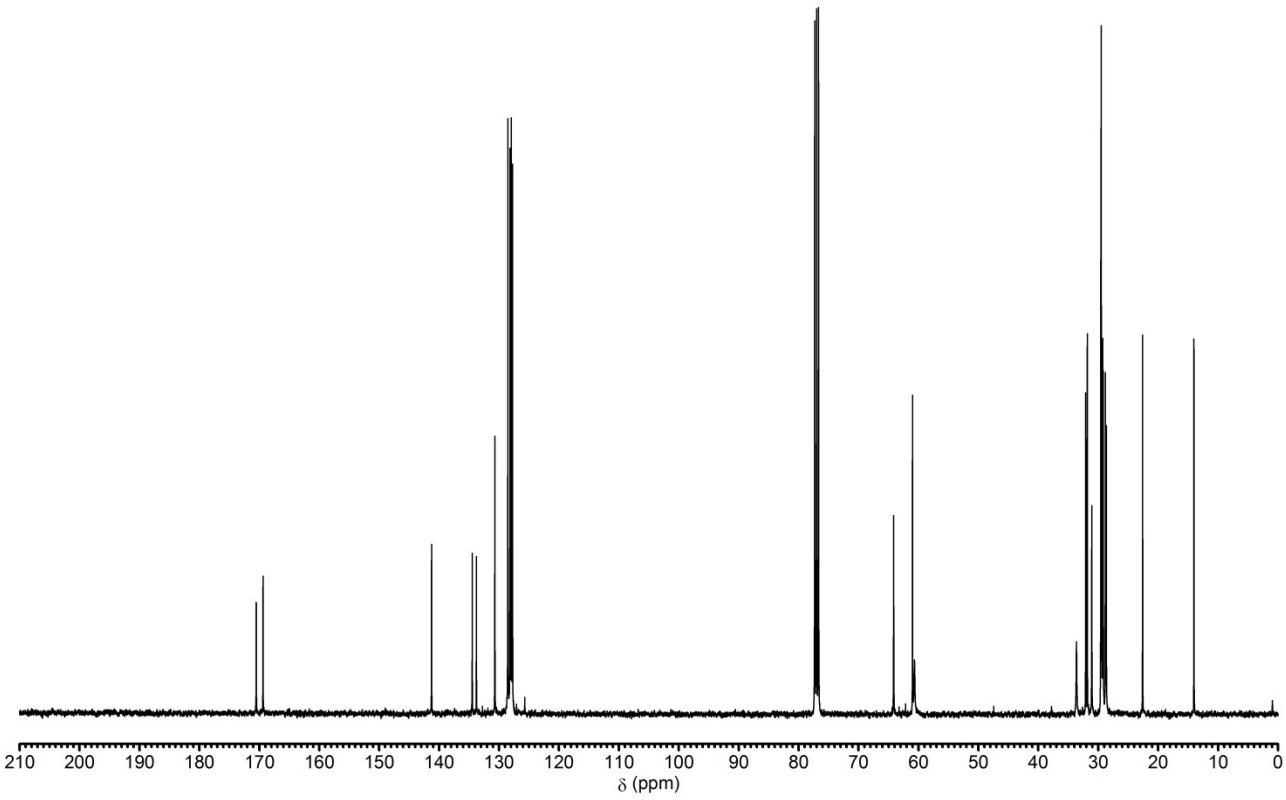


(*R*)-4-[3-(dodecylthio)-1-(*N*-methoxybenzamido)propyl]-*N*-methoxy-*N*-methylbenzamide (5a)

^{1}H NMR

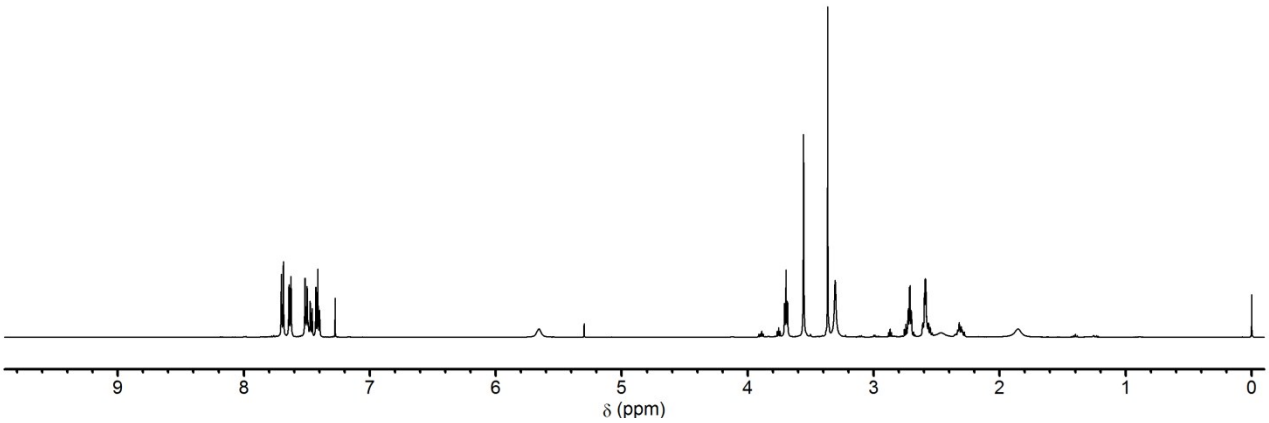


^{13}C NMR

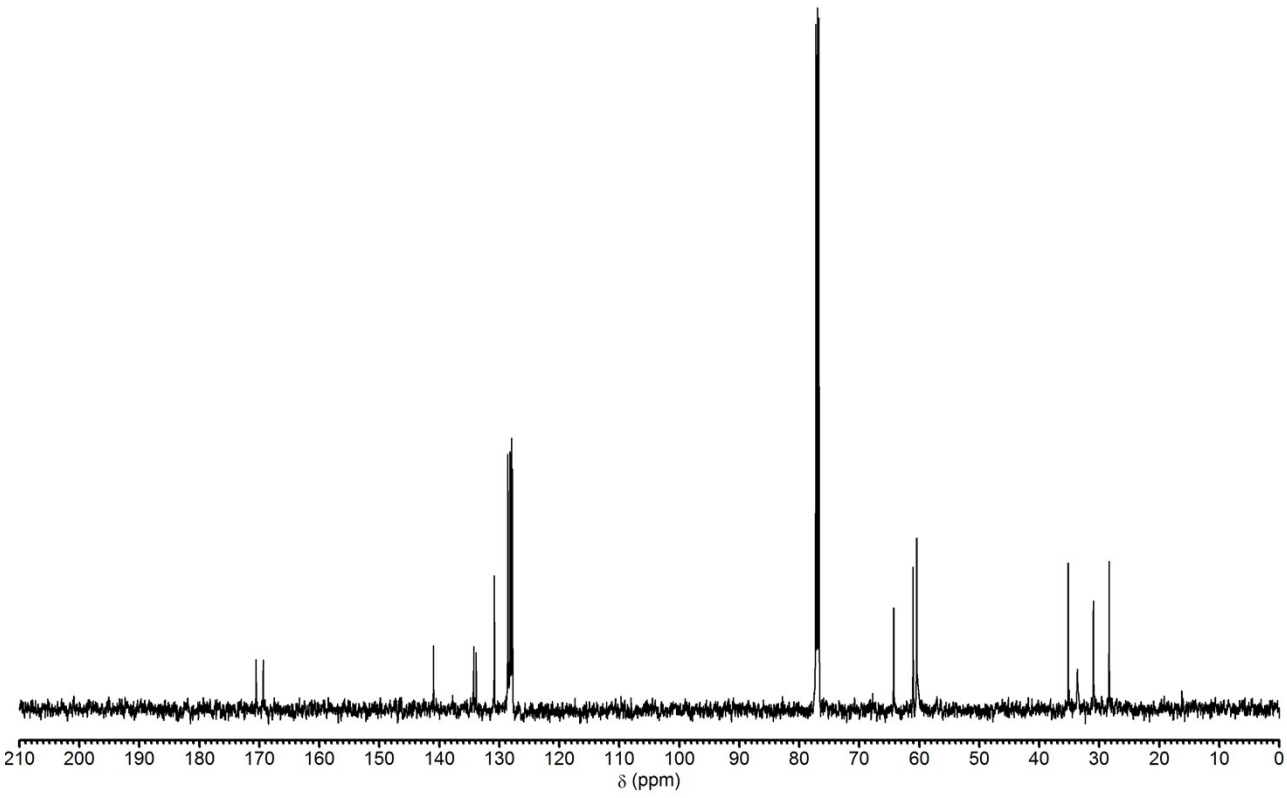


(*S*)-4-[3-(dodecylthio)-1-(*N*-methoxybenzamido)propyl]-*N*-methoxy-*N*-methylbenzamide (5b)

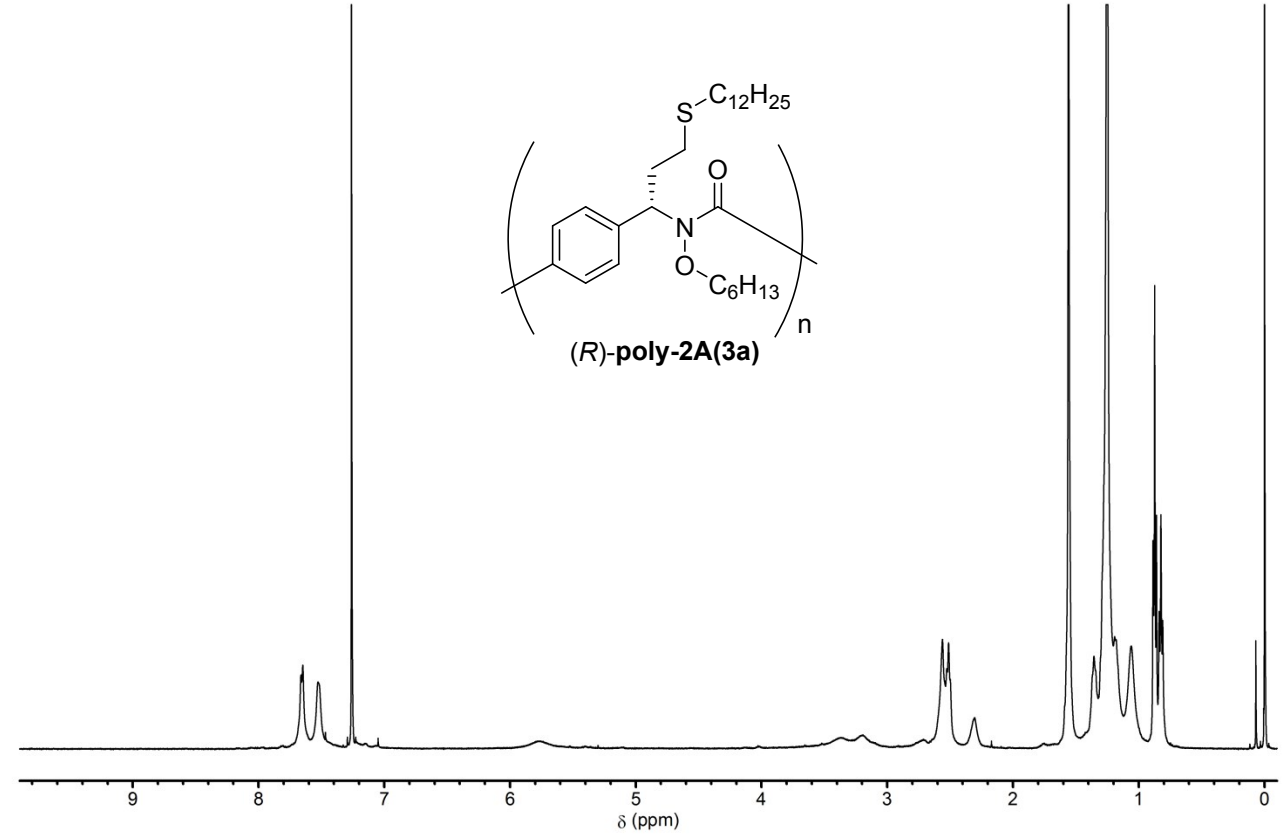
^{1}H NMR



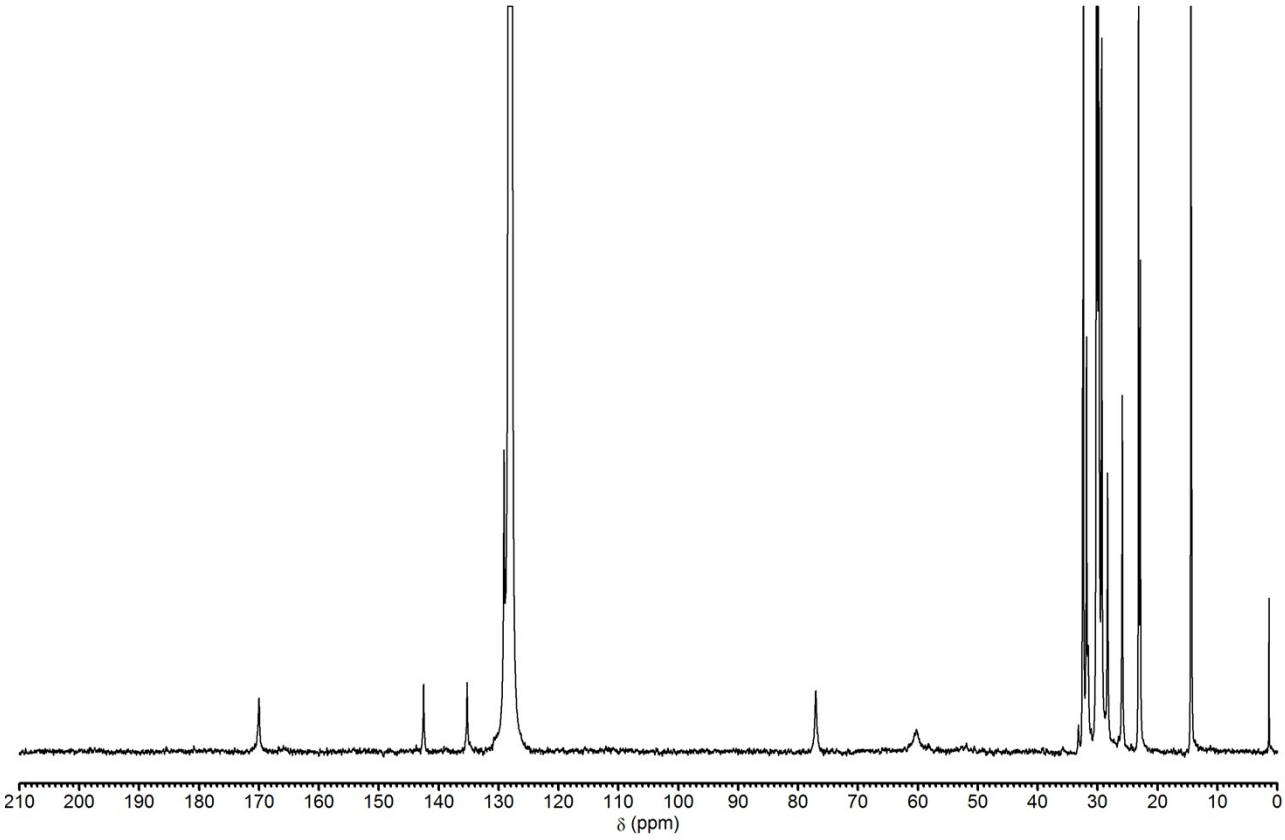
^{13}C NMR



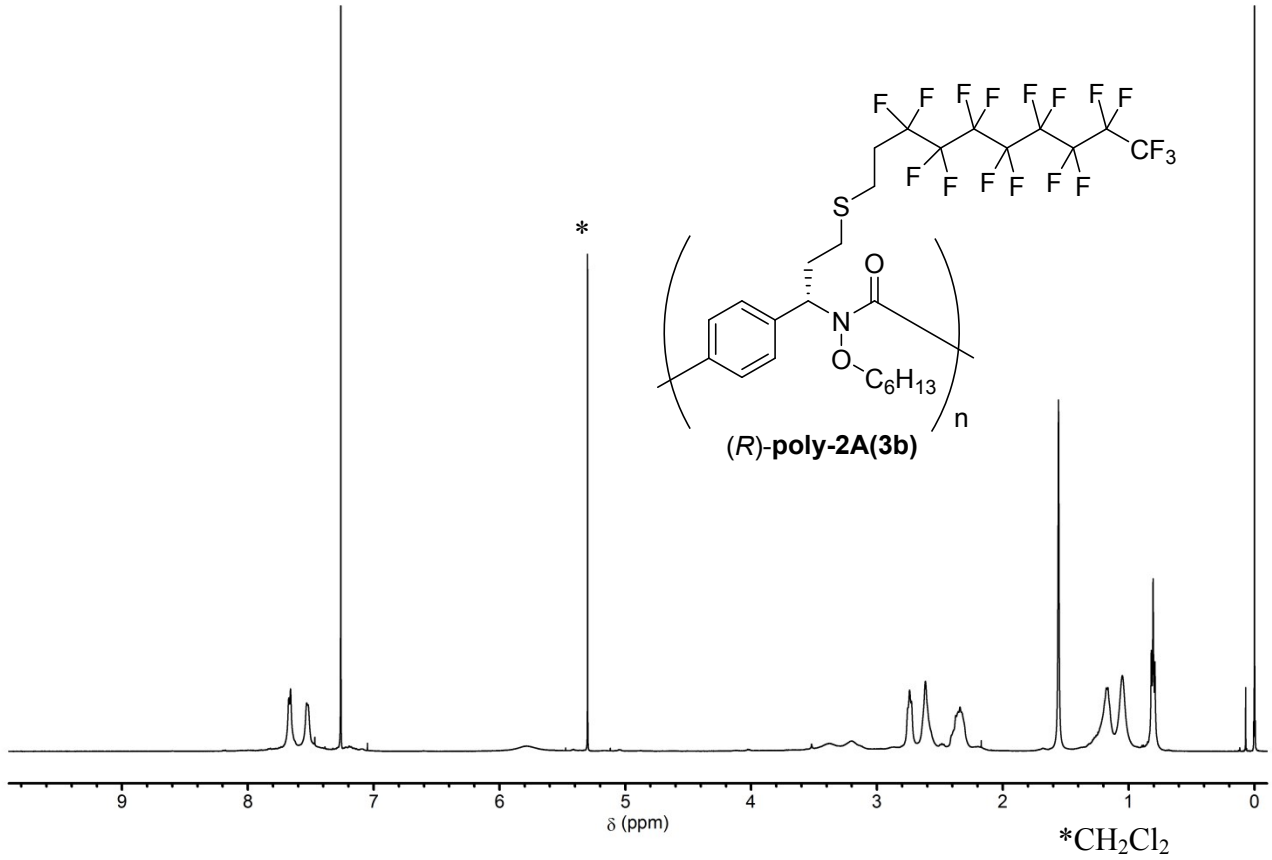
^{1}H NMR of poly-2A(3a)



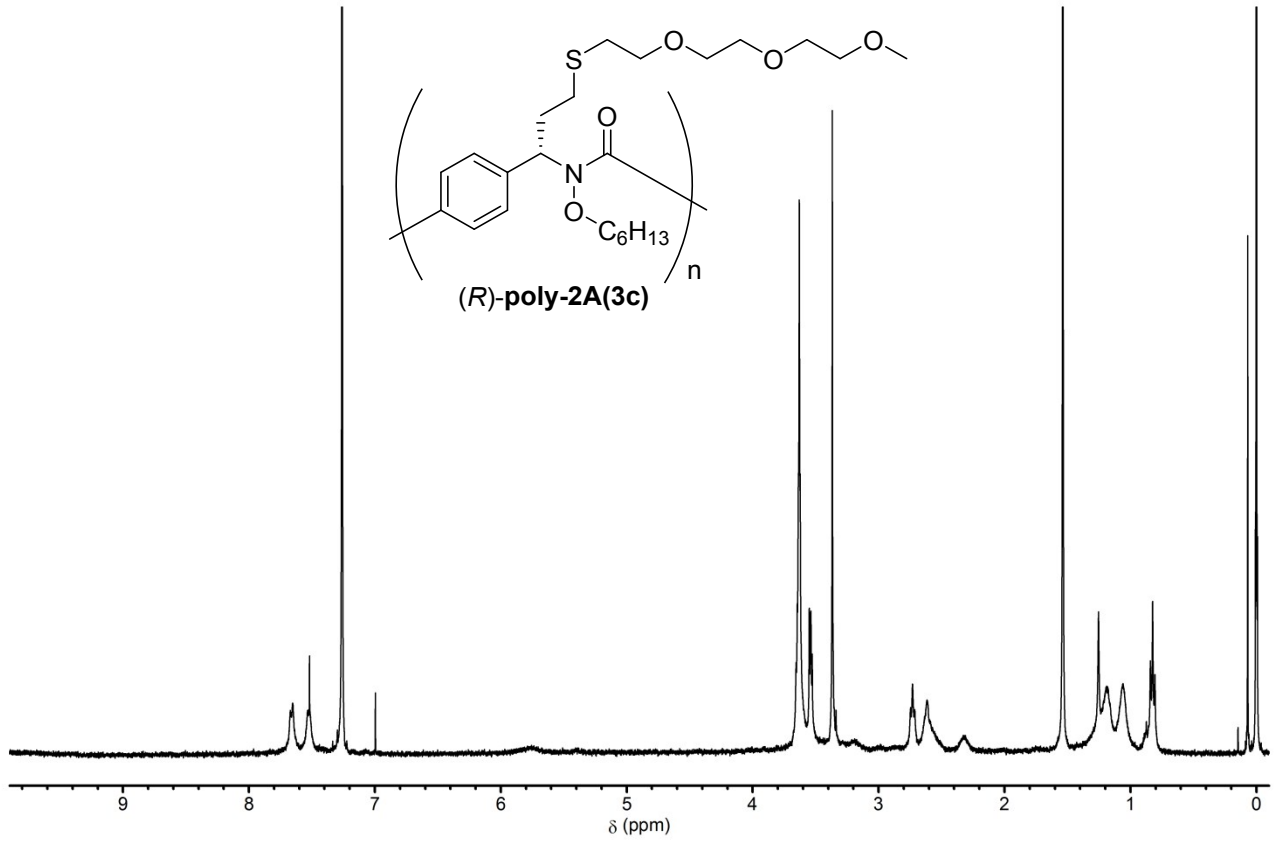
^{13}C NMR



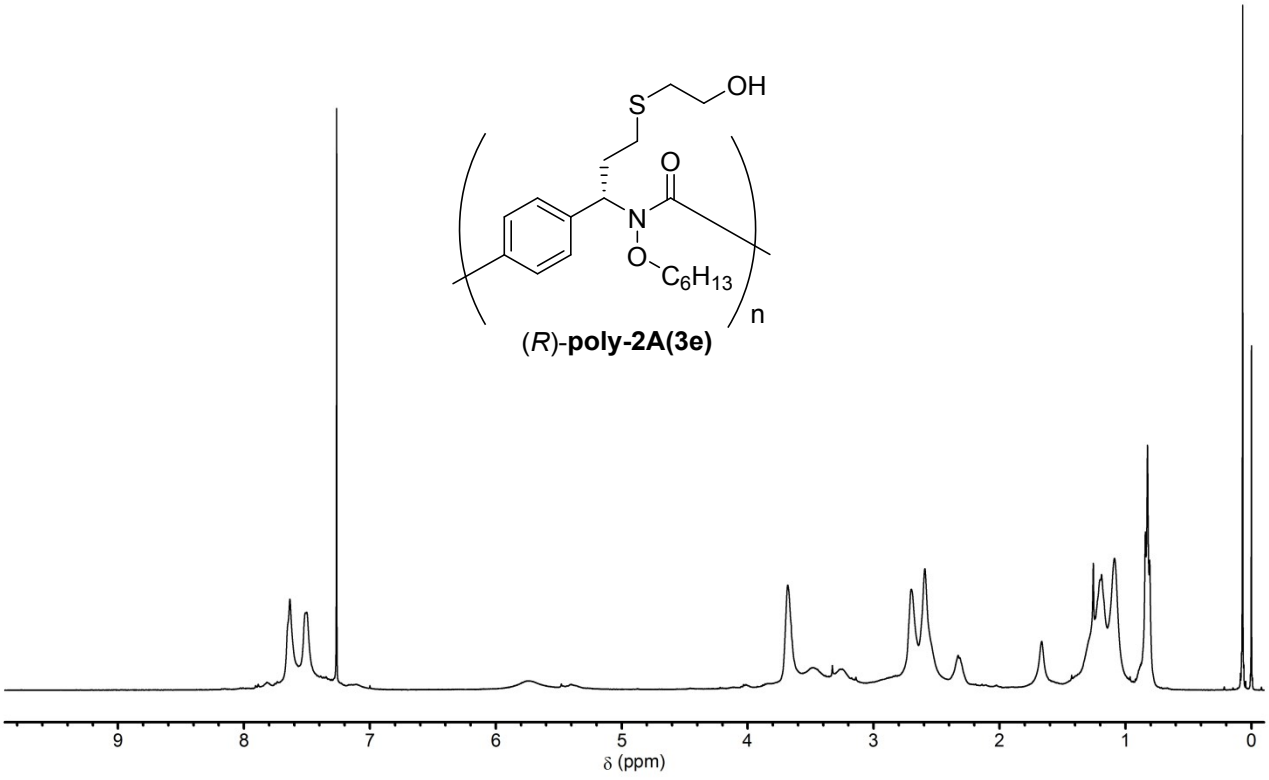
poly-2A(3b)



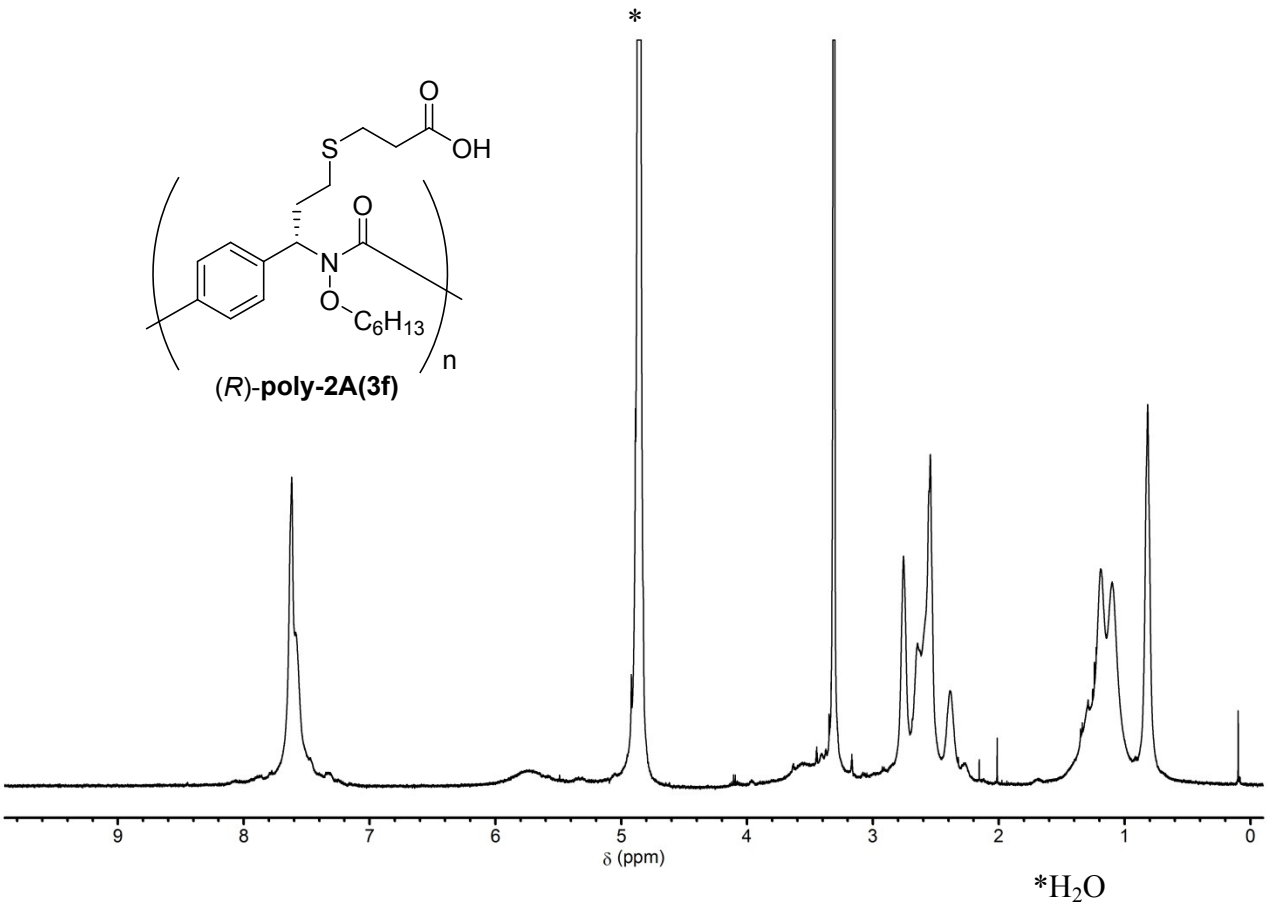
poly-2A(3c)



poly-2A(3e)

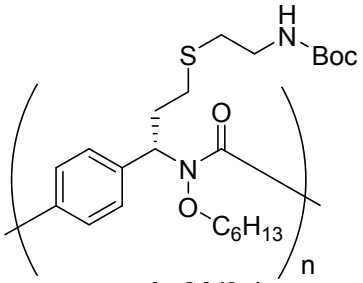


poly-2A(3f)



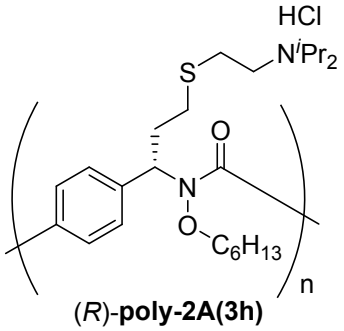
*H_2O

poly-2A(3g)



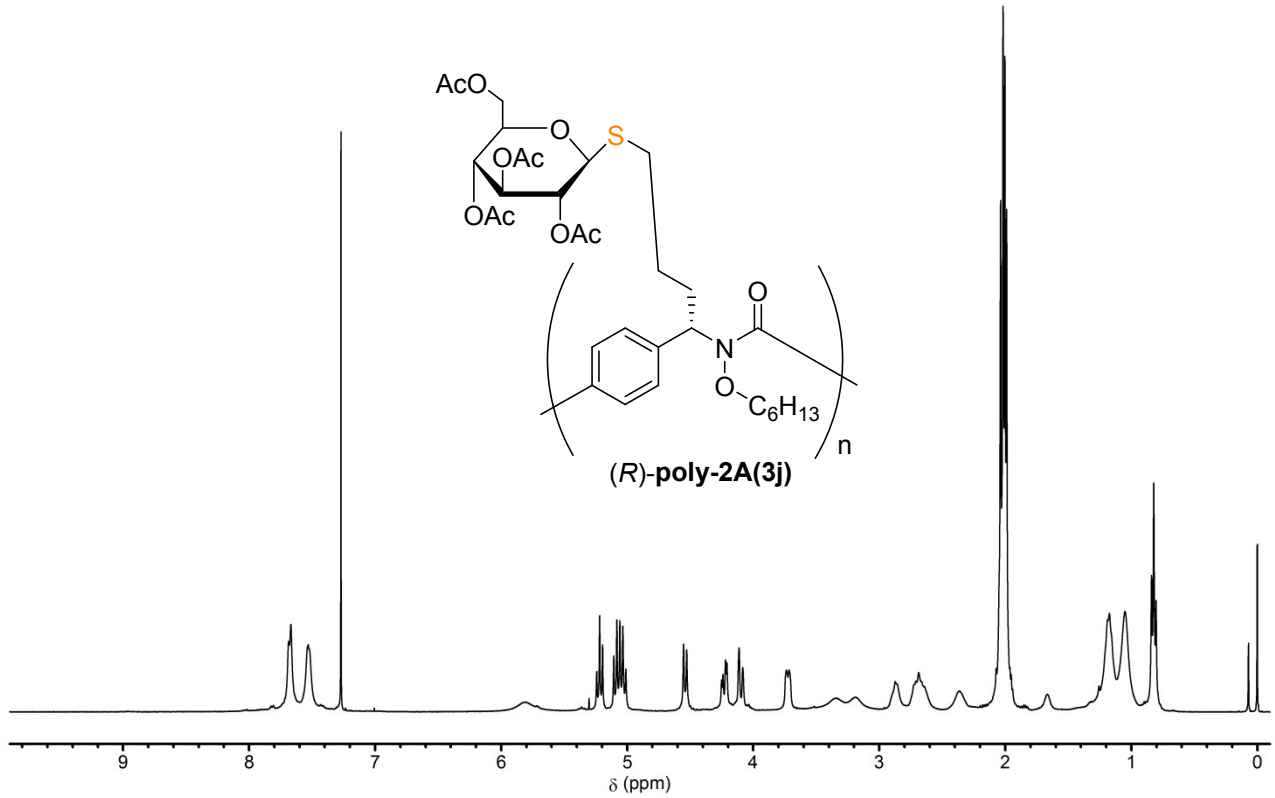
(*R*)-**poly-2A(3g)**

poly-2A(3h)

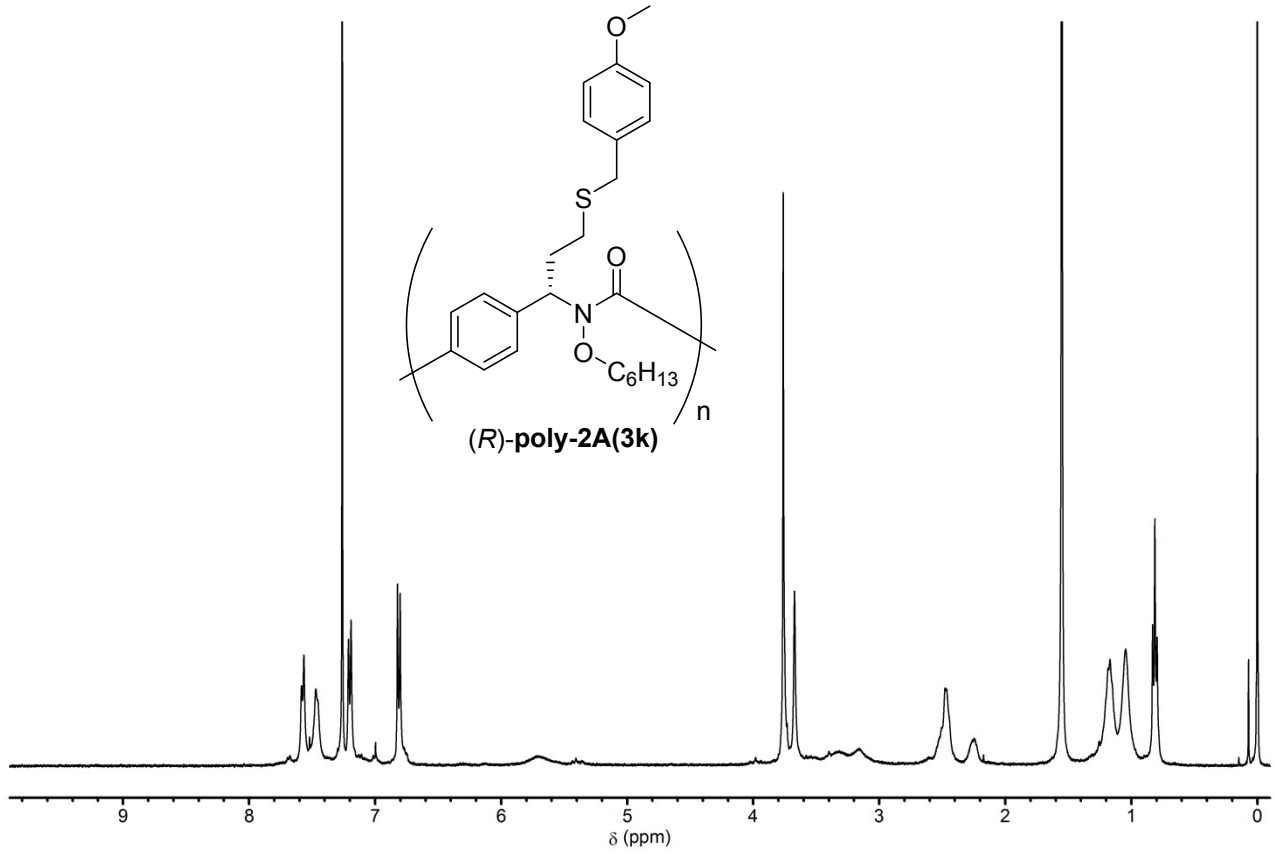


(*R*)-**poly-2A(3h)**

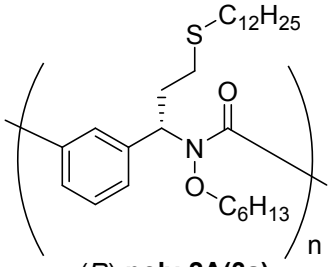
poly-2A(3j)


AcO
O
S
OAc
OAc
OAc
O
N
O
C_6H_{13}
n
(*R*)-**poly-2A(3j)**
9
8
7
6
5
4
3
2
1
0
δ (ppm)

poly-2A(3k)

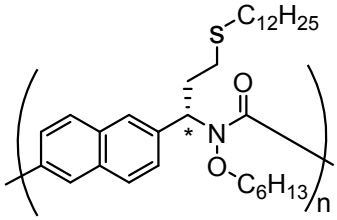

O
S
O
N
O
C_6H_{13}
n
(*R*)-**poly-2A(3k)**
9
8
7
6
5
4
3
2
1
0
δ (ppm)

poly-2B(3a)

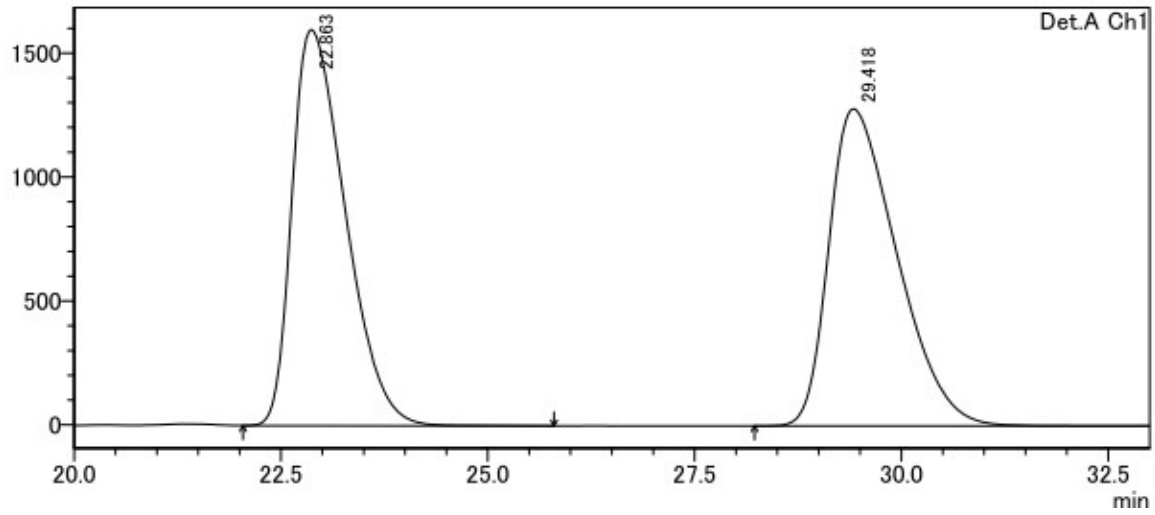


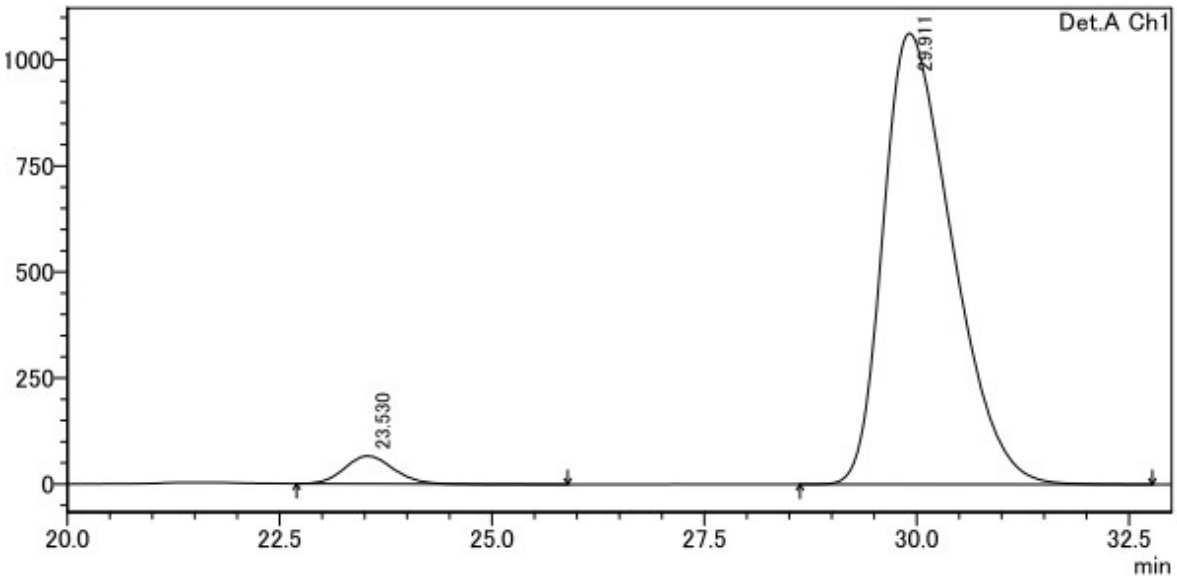
(*R*)-**poly-2A(3a)**

poly-2C(3a)



HPLC analysis of 4



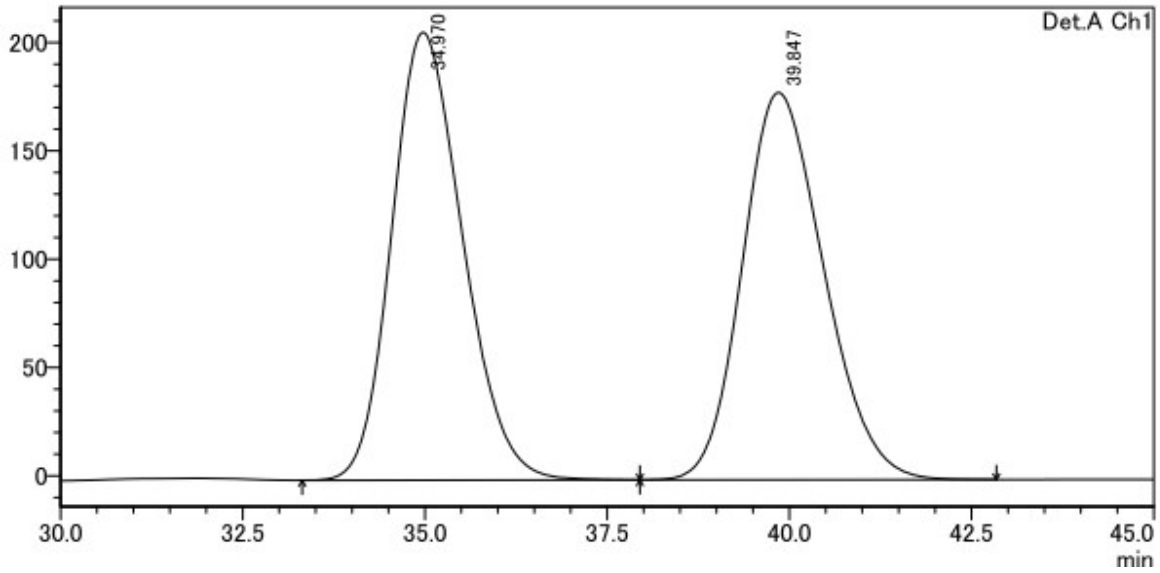


Peak Table

UV-Vis Ch1 230nm

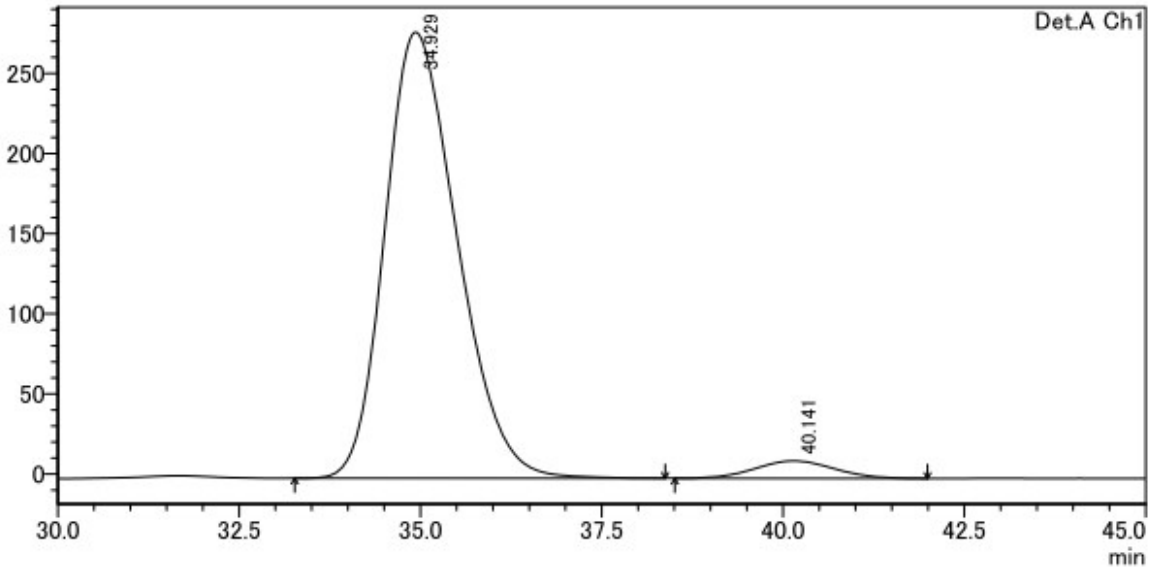
Peak	Retention Time	Area	High	Area Percent
1	23.530	2604890	65805	4.168
2	29.911	59891381	1063271	95.832
合計		62496271	1129076	100.000

HPLC analysis of 5a



UV-Vis Ch1 230nm

Peak	Retention Time	Area	High	Area Percent
1	34.970	14021037	206631	50.193
2	39.847	13913158	178709	49.807
合計		27934195	385340	100.000



UV-Vis Ch1 230nm

Peak	Retention Time	Area	High	Area Percent
1	34.929	19294228	278316	95.881
2	40.141	828830	10937	4.119
合計		20123059	289252	100.000

4. UV and CD Spectra

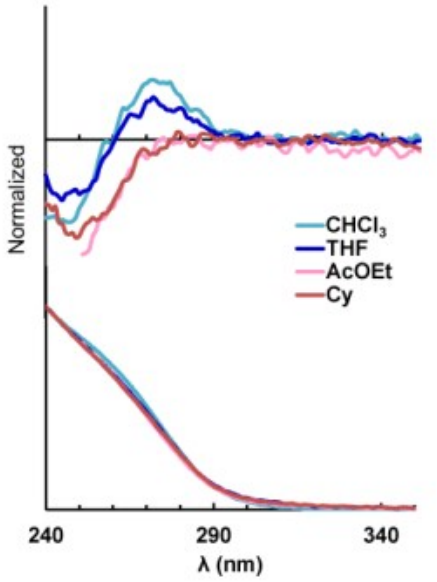


Fig. S1. CD and UV spectra of **poly-2A(3a)** in $CHCl_3$, THF, ethyl acetate (AcOEt), and cyclohexane (Cy) at 25 ºC.

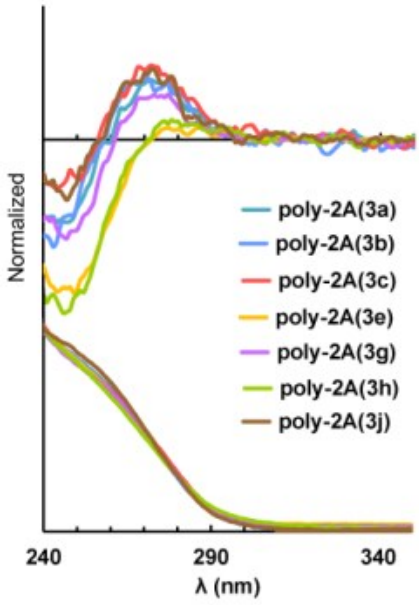


Fig. S2. CD and UV spectra of **poly-2A(3a)**, and **poly-2A(3b)**, **poly-2A(3c)**, **poly-2A(3e)**, **poly-2A(3g)**, **poly-2A(3g)**, **poly-2A(3h)**, and **poly-2A(3j)** in $CHCl_3$, THF, ethyl acetate (AcOEt), and cyclohexane (Cy) at 25 ºC.