Supporting Information

Controlled Polymerization of Levoglucosenone-Derived Enynes to Give Bio-Based Polymers with Tunable Degradation Rates and High Glass Transition Temperatures

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1. Supporting Figures and Extended Discussion

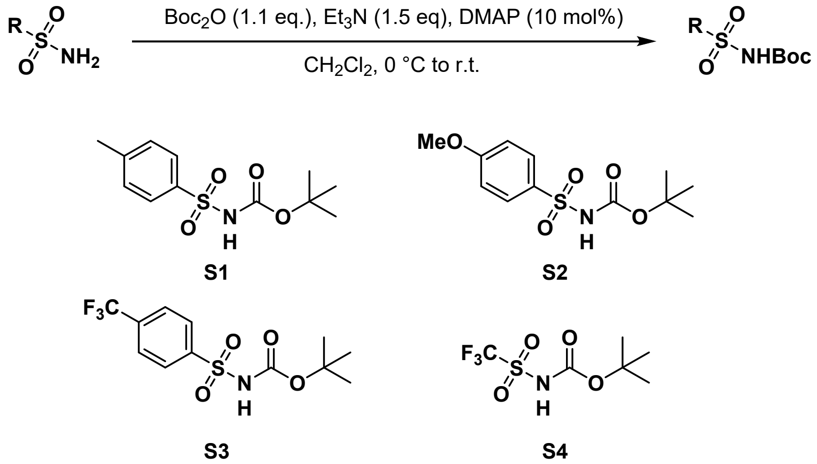


Figure S1. Synthesis of **S1** – **S4**.

Figure S1 *Discussion:*

Compounds **S1**,[1] **S2**,[2] **S3** and **S4**[3] were prepared as reported in literature.

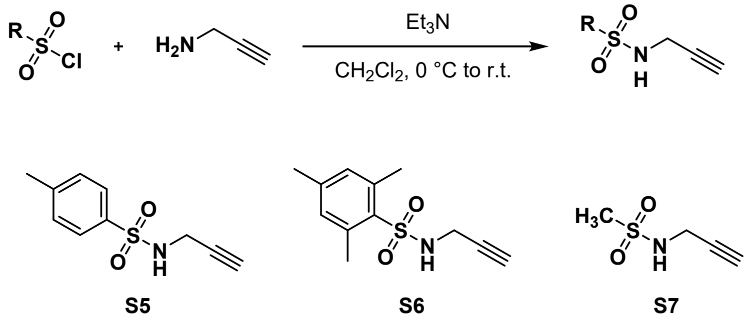


Figure S2. Synthesis of **S5** – **S7**.

Figure S2 *Discussion:*

Compounds **S5** – **S7** were prepared as reported in literature.[4]

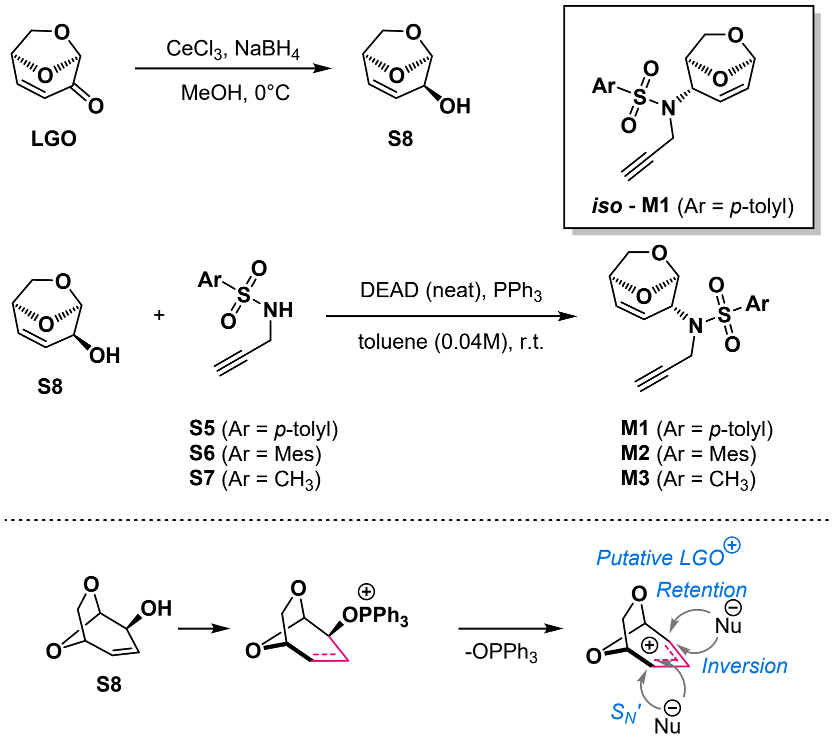


Figure S3. Synthesis of **M1** – **M3**, **epi-M2** and **iso-M1**.

Figure S3 *Discussion:*

Compounds **S8** was prepared as reported in literature.[5]

Monomers **M1** – **M3** were synthesized under optimized Mitsunobu conditions to minimize the minor diastereoisomer. The minor isomer could be separated by flash column chromatography.

The relative and absolute stereochemistry of **M2** was determined by X-ray crystallographic analysis (See **Section 8**). The stereochemistry of **M1** and **M3** was assigned in analogy to **M2**. We are confident in the stereochemical assignment by analogy as we could isolate also the ***iso*-M1**.

The ***iso*-M1** connectivity was assigned by 2D NMR analysis. The ***iso*-M1** stereochemistry was assigned by 2D NOESY analysis (see **Section 4.1**).

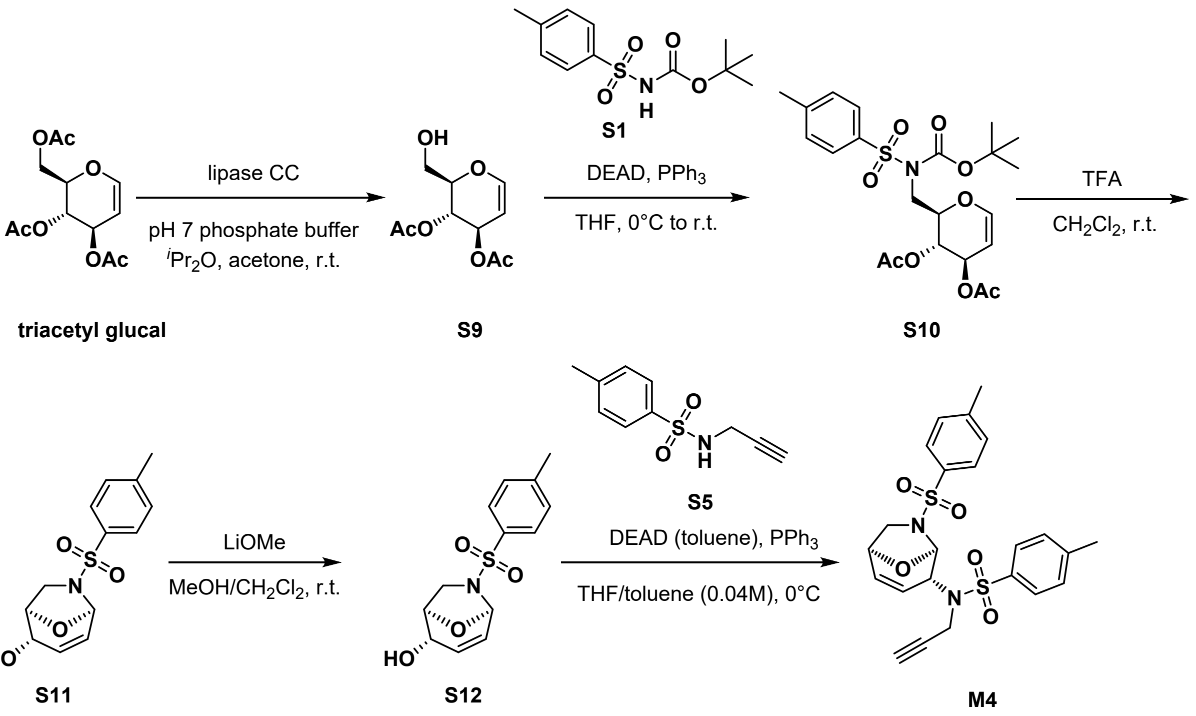


Figure S4. Synthesis of **M4**.

Figure S4 *Discussion:*

Compounds **S9** was prepared as reported in literature from commercially available **triacetyl glucal**.[6] Then, **S10** was synthesized under Mitsunobu conditions, followed by a TFA induced cascade Boc deprotection / cyclization to yield acetate **S11**. Then, it was hydrolyzed with LiOMe to give **S12**. Monomer **M4** was synthesized under optimized Mitsunobu conditions. The minor isomers could not be observed by crude ^{1}H NMR. The relative and absolute stereochemistry of **M4** was determined by X-ray crystallographic analysis (See **Section 8**).

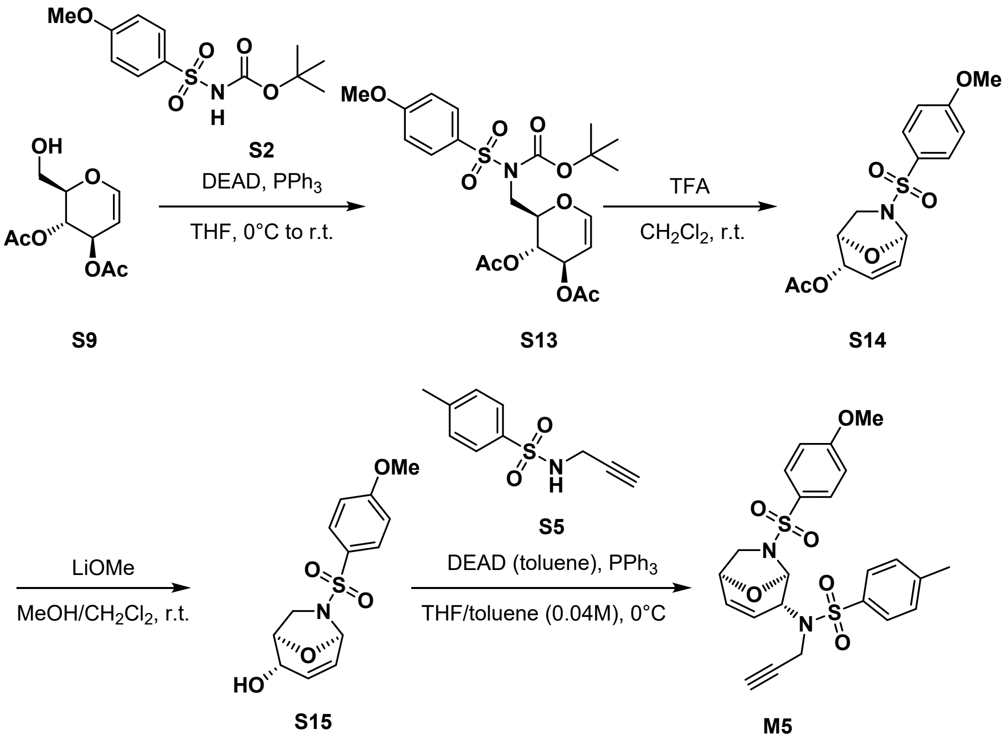


Figure S5. Synthesis of **M5**.

***Figure S5** Discussion:*

Compounds **S9** was prepared as reported in literature from commercially available **triacetyl glucal**.[6] Then, **S13** was synthesized under Mitsunobu conditions, followed by a TFA induced cascade Boc deprotection / cyclization to yield acetate **S14**. Then, it was hydrolyzed with LiOMe to give **S15**. Monomer **M5** was synthesized under optimized Mitsunobu conditions. The minor isomers could not be observed by crude ^{1}H NMR.

The stereochemistry of **M5** was assigned in analogy to **M4**.

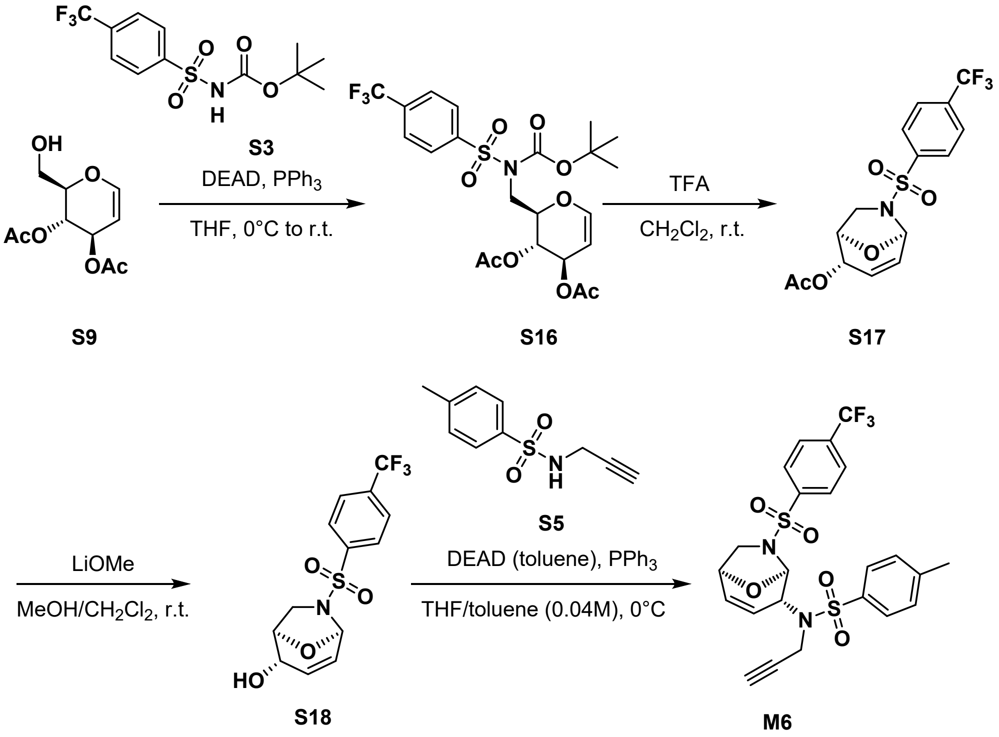


Figure S6. Synthesis of **M6**.

Figure S6 *Discussion:*

Compounds **S9** was prepared as reported in literature from commercially available **triacetyl glucal**.[6] Then, **S16** was synthesized under Mitsunobu conditions, followed by a TFA induced cascade Boc deprotection / cyclization to yield acetate **S17**. Then, it was hydrolyzed with LiOMe to give **S18**. Monomer **M6** was synthesized under optimized Mitsunobu conditions. The minor isomers could not be observed by crude ^{1}H NMR.

The stereochemistry of **M6** was assigned in analogy to **M4**.

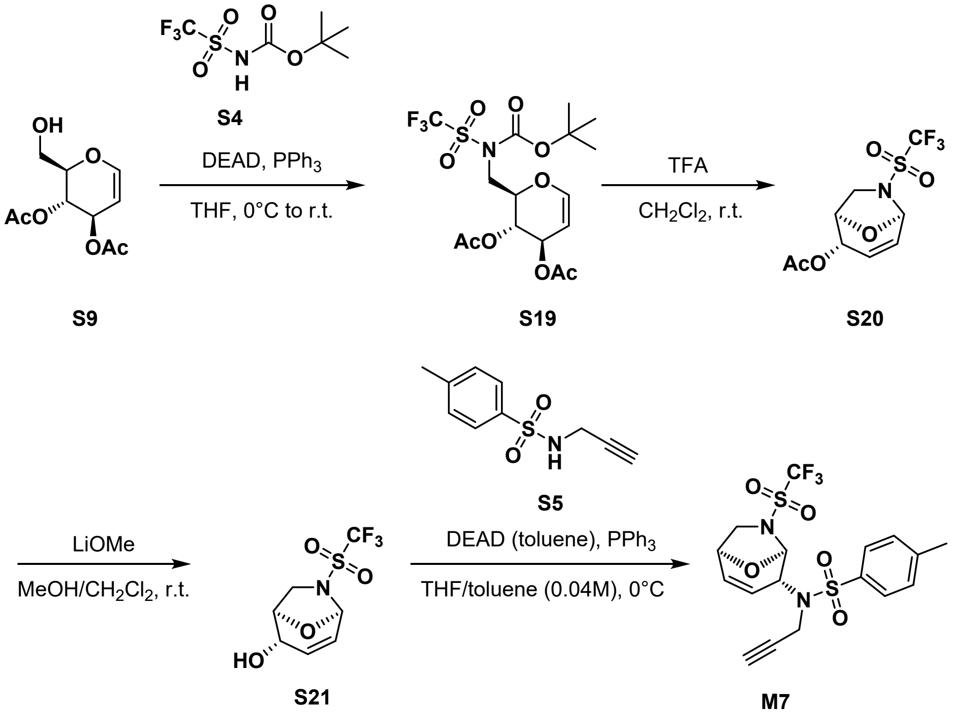
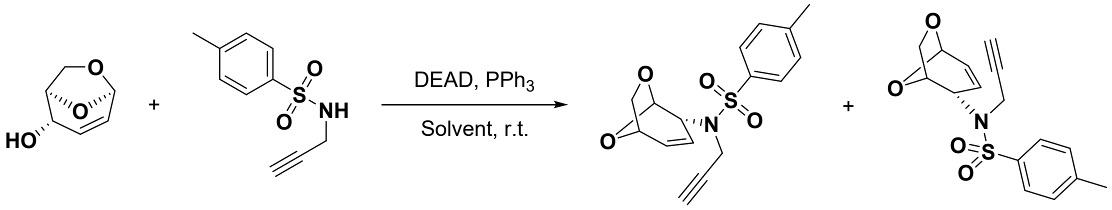


Figure S7. Synthesis of **M7**.

Figure S7 *Discussion:*

Compounds **S9** was prepared as reported in literature from commercially available **triacetyl glucal**.[6] Then, **S19** was synthesized under Mitsunobu conditions, followed by a TFA induced cascade Boc deprotection / cyclization to yield acetate **S20**. Then, it was hydrolyzed with LiOMe to give **S21**. Monomer **M7** was synthesized under optimized Mitsunobu conditions. The minor isomers could not be observed by crude ^{1}H NMR.

The stereochemistry of **M7** was assigned in analogy to **M4**.



S22 **S5** **M1** ***iso*-M1**

d.r. can be controlled by solvent variation

Figure S8. Synthesis of ***iso*-M1**.

Figure S8 *Discussion:*

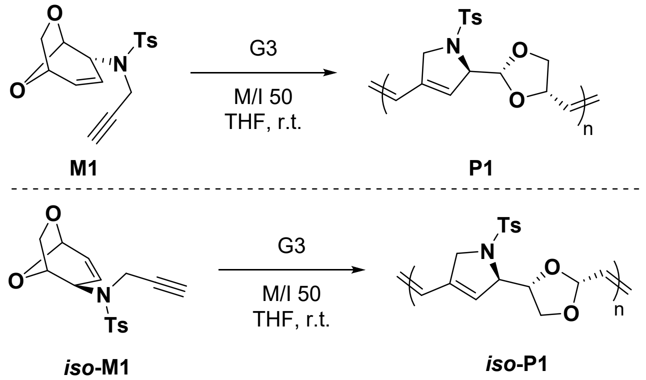
Compound **S22** was prepared as reported in literature.[6] To prepare an isomeric monomer to **M1**, we prepared ***iso*-LGOH** (**S22**) from **triacetly glucal**. By subjecting this to Mitsunobu conditions, we could tune the diastereomeric ratio (*d.r.*) between **M1** and ***iso*-M1**. We performed concentration and solvent screening (see **Table S1** below). A trend that followed the solvent polarity, measured by ET(30) value was observed.

Table S1. Optimization of Mitsunobu reaction for **M1** and *iso*-**M1** synthesis.

solvent	temp. (°C)	conc. (M)	**M1**	***iso*-M1**	solvent ET(30) values[7]
toluene	RT	0.04	1	1.5	< 34.7 (*o*-xylene)
THF	RT	0.1	2	1	37.4
THF	RT	0.04	2.3	1	37.4
EtOAc	RT	0.1	3	1	38.1
CH_2Cl_2	RT	0.04	6	1	40.7
CH_2Cl_2	0	0.04	25	1	40.7
acetone	RT	0.04	Reaction stalls		42.2
ACN	RT	0.1	No reaction		45.6

[a] *d.r.* was calculated from the crude mixture.

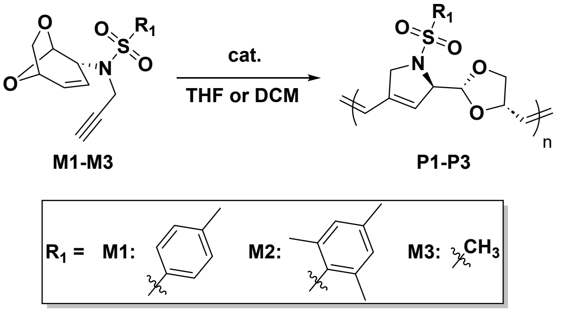
Table S2. Polymerization of **M1** and ***iso*-M1**.[a]



entry	monomer	conc. (M)	time (h)	conv. (%)[b]	yield (%)[c]	M_n (kDa)[d]	*Đ*[d]
1	**M1**	0.2	0.66	>99	92	12.8	1.32
2	***iso*-M1**	0.2	1.5	22	17	2.2	1.52

[a]Polymerization of M/I 50 was conducted in degassed THF at room temperature. [b]Determined by ^{1}H NMR analysis of the crude mixture. [c]Isolated yield. [d]Determined by THF size exclusion chromatography calibrated by polystyrene standards.

Table S3. Optimization of polymerization for dioxolane-containing monomers (**M1-M3**).[a]



entry	MX	M/I	temp. (°C)	conc. (M)	time (h)	conv. (%)[b]	yield (%)[c]	M_n (kDa)[d]	*Đ*[d]
1	M1	30	RT	0.2	0.5	>99	62	7.5	1.21
2	**M1**	**30**	**10**	**0.2**	**0.5**	**>99**	**79**	**9.1**	**1.06**
3	**M1**	**50**	**10**	**0.2**	**1**	**>99**	**99**	**14.5**	**1.14**
4	M1	75	10	0.2	1.5	>99	77	18.1	1.21
5	**M1**	**75**	**0**	**0.2**	**3**	**>99**	**73**	**19.8**	**1.16**
6	**M1**	**100**	**0**	**0.2**	**4**	**>99**	**83**	**24.1**	**1.23**
7	**M1**	**150**	**0**	**0.2**	**6**	**90**	**72**	**29.0**	**1.72**
8	M1	150	-10	0.2	16	87	58	25.0	1.82
9[e]	**M1**	**150**	**-10**	**0.2**	**16**	**95**	**87**	**35.6**	**1.45**
10	**M2**	**30**	**10**	**0.2**	**0.5**	**>99**	**61**	**8.4**	**1.13**
11	**M2**	**50**	**10**	**0.2**	**1**	**>99**	**92**	**15.5**	**1.21**

12	**M2**	**75**	**0**	**0.2**	**3**	**>99**	**85**	**24.0**	**1.29**
13	M2	100	0	0.2	4	>99	92	28.4	1.45
14	M2	100	-10	0.2	8	>99	81	25.0	1.33
15	**M2**	**100**	**-10**	**0.1**	**16**	**>99**	**98**	**28.3**	**1.39**
16	M2	150	-10	0.1	24	81	57	29.1	2.55
17[e]	M2	150	-10	0.1	24	74	55	26.5	2.45
18	M3	30	RT	0.2	0.5	>99	95	4.6	1.30
19[f]	**M3**	**30**	**RT**	**0.2**	**1**	**99**	**91**	**6.8**	**1.21**
20[f]	M3	50	RT	0.2	3.5	99	74	7.7	1.43
21[e]	M3	50	RT	0.2	2	98	98	8.8	1.49
22[e]	M3	50	0	0.2	8	>99	89	9.6	1.34
23[e,f]	**M3**	**50**	**0**	**0.2**	**8**	**>99**	**80**	**11.5**	**1.28**
24[e,f]	**M3**	**75**	**0**	**0.2**	**12**	**89**	**68**	**14.2**	**1.37**
25[e,f]	M3	100	0	0.2	20	>99	93	12.3	1.60

[a] Highlighted rows are used in **Table 1** of the *main text*. Polymerizations conducted with 15 mg of monomer in degassed THF (**M1** and **M2**). Due to the insolubility of **M3** in THF, degassed dichloromethane was used as solvent. [b] Determined by ^{1}H NMR analysis of the crude mixture. [c] Isolated yield. [d] Determined by THF size exclusion chromatography calibrated by polystyrene standards (**P1** and **P2**). Due to the insolubility of **P3** in THF, M_n of **P3** was determined by chloroform size exclusion chromatography calibrated by polystyrene standards. [e] G3-DIPP was used as catalyst. [f] 20 mol% of 3-chloropyridine was added as an additive.

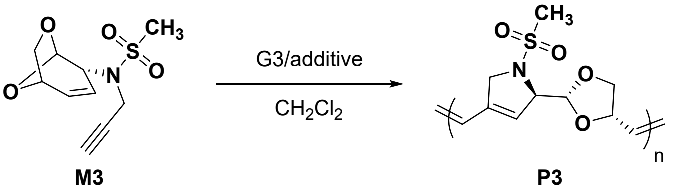
Table S3 *Discussion:*

We began by attempting the polymerization of **M1** at room temperature using G3 catalyst at 0.2 M concentration (entry 1). Decreasing the reaction temperature from RT to 10 °C improved the polymerization results, showing lower dispersity (entries 2 and 3). Also, we tried the polymerization of M/I 75 under the same conditions, showing a slightly higher dispersity of 1.21 (entry 4). Further decreasing the reaction temperature from 10 °C to 0 °C gave lower dispersity up to M/I 100 (entries 5 and 6). However, the polymerization of M/I 150 did not show a linear increase in M_n (entry 7). Thus, we decreased the reaction temperature to -10 °C and changed the catalyst to G3-DIPP, resulting in a linear increase of the M_n with moderate dispersity (entries 8 and 9).

For **M2**, we conducted the polymerization under the optimal conditions of **M1** (entries 10 – 12). Also, we tried the polymerization of M/I 100 under the same conditions, but it showed moderate dispersity (entry 13). After screening several reaction temperatures and monomer concentrations, we chose -10 °C and 0.1 M as an optimal conditions for M/I 100 and obtained lower dispersity (entries 14 and 15). We also tried the polymerization of M/I 150 under the same conditions using both G3 or G3-DIPP catalyst, which did not show improved polymerization results (entries 16 and 17).

For **M3**, we began the polymerization at room temperature using G3 catalyst at 0.2 M concentration (entry 18). We chose 3-chloropyridine as an additive after additive screening (**Table S4**). This resulted in higher M_n and lower dispersity (entry 19). We tried the polymerization of M/I 50 under the same conditions, but M_n did not increase significantly, and the dispersity broadened (entry 20). After attempting several combinations of G3-DIPP catalyst, additive, and lower temperature, we chose the combination of G3-DIPP and 20 mol% of 3-chloropyridine at 0 °C as optimal conditions (entries 21 – 23). Also, we tried the polymerization of M/I 75 under the same conditions, showing a linear increase of the M_n with moderate dispersity (entry 24). However, the M_n did not increase further from the polymerization of M/I 100 (entry 25).

Table S4. Optimization of polymerization for **M3**.[a]



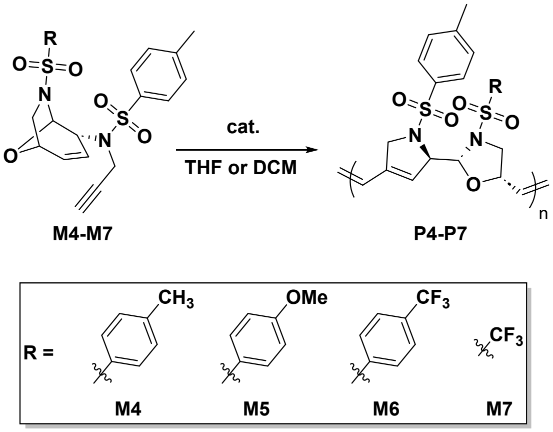
entry	M/I/Add	additive	temp. (°C)	conc. (M)	time (h)	conv. (%)[b]	yield (%)[c]	M_n (kDa)[d]	$Đ$[d]
1	30	-	RT	0.2	0.5	>99	95	4.6	1.30
2	30/1/6	pyridine	RT	0.2	1	99	63	4.2	1.21
3	30/1/6	3-ClPy	RT	0.2	1	99	91	6.8	1.21
4	30/1/6	3,5-Cl_2Py	RT	0.2	1	>99	85	4.7	1.30
5	30/1/6	4-OMePy	RT	0.2	1	16	-	1.3	1.23

[a]Polymerizations conducted with 15 mg of monomer and G3 catalyst in degassed dichloromethane. [b]Determined by ^{1}H NMR analysis of the crude mixture. [c]Isolated yield. [d]Determined by chloroform size exclusion chromatography calibrated by polystyrene standards.

***Table S4** Discussion:*

To stabilize the propagating carbene, we screened the various pyridine additives. Among them, 3-chloropyridine provided the highest M_n with lower dispersity.

Table S5. Optimization of polymerization for oxazolidine-containing monomers (**M4-M7**).[a]



entry	MX	M/I (additive)	temp. (°C)	conc. (M)	time (h)	conv. (%)[b]	yield (%)[c]	M_n (kDa)[d]	$Đ$[d]

1	**M4**	**30**	**RT**	**0.2**	**0.66**	**>99**	**85**	**9.4**	**1.08**
2	**M4**	**50**	**RT**	**0.2**	**1**	**>99**	**80**	**17.2**	**1.20**
3	**M4**	**75**	**10**	**0.2**	**4**	**>99**	**97**	**21.5**	**1.21**
4	M4	100	RT	0.2	2	99	99	30.3	1.52
5	**M4**	**100**	**10**	**0.2**	**5**	**>99**	**82**	**27.5**	**1.20**
6	M4	150	10	0.2	7.5	>99	97	44.6	1.38
7	**M4**	**150**	**0**	**0.2**	**15**	**>99**	**85**	**37.9**	**1.25**
8	M4	200	0	0.2	8	82	65	41.2	1.51
9	M4	200	0	0.1	22	>99	88	43.4	1.25
10	M4	200	0	0.3	6	82	65	41.2	1.51
11	**M4**	**200** **(5 mol% Cl$_2$Py)**	**0**	**0.1**	**20**	**99**	**87**	**51.2**	**1.20**
12	M4	300	0	0.1	30	86	73	58.8	1.79
13	M4	300 (20 mol% Py)	0	0.1	30	14	0	n.p.[e]	n.p. [e]
14	M4	300 (20 mol% ClPy)	0	0.1	30	17	1	12.9	1.27
15	M4	300 (20 mol% Cl$_2$Py)	0	0.1	30	60	56	54.9	1.47
16	M4	300 (10 mol% Cl$_2$Py)	0	0.1	30	80	72	64.3	1.62
17	**M4**	**300** **(5 mol% Cl$_2$Py)**	**0**	**0.1**	**30**	**85**	**76**	**65.4**	**1.41**
18	M4	300 (2.5 mol% Cl$_2$Py)	0	0.1	30	98	86	47.9	1.34
19	**M5**	**30**	**RT**	**0.2**	**0.66**	**>99**	**99**	**9.6**	**1.06**
20	**M6**	**30**	**RT**	**0.2**	**0.66**	**>99**	**84**	**11.2**	**1.09**
21	**M7**	**30**	**RT**	**0.2**	**0.66**	**58**	**48**	**11.2**	**1.64**
22	**M7**	**30**	**-10**	**0.2**	**12**	**>99**	**81**	**10.4**	**1.24**

[a]Highlighted rows are used in **Table 2** of the *main text*. Polymerizations conducted with 15 mg of monomer in degassed THF. [b]Determined by ^{1}H NMR analysis of the crude mixture. [c]Isolated yield. [d]Determined by THF size exclusion chromatography calibrated by polystyrene standards. [e]n.p.=not precipitated.

***Table S5** Discussion:*

We began by attempting the polymerization of **M4** at room temperature and 0.2 M concentration (entries 1, 2, and 4). The polymerization of M/I 100 showed a moderate dispersity of 1.52 (entry 4). Decreasing the temperature to 10 °C improved the polymerization result, providing a linearly increased M_n and lower dispersity not only for M/I 100 but also for M/I 75 (entries 3 and 5). For M/I 150, lower reaction temperature of 0 °C provided improved polymerization (entries 6 and 7). We also tried the polymerization of M/I 200 under the same conditions, but the conversion decreased to 82% with higher dispersity (entry 8). After the reaction concentration screening, 0.1 M concentration gave a full monomer conversion with lower dispersity of 1.25 (entries 8 – 10). Under the same conditions, we conducted the polymerization of M/I 300, resulting in a higher M_n but with 86% conversion (entry 12). After an extensive screening of the pyridine additives and their loadings, we chose addition of 5 mol% of 3,5-dichloropyridine as optimal conditions (entries

13 – 18). Based on these optimal conditions, we obtained a linear increase in M_n with low dispersity up to M/I 100 (entries 11 and 17).

2. General Information

Abbreviations

Ac, acetyl; ACN, acetonitrile; DCN, dichloromethane; DCTB, *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenyliden]malononitrile; DEAD, Diethyl azodicarboxylate; DIPP, diisopropyl; DMAP, 4-dimethylaminopyridine; DSC, differential scanning calorimetry; EA, ethyl acetate; EVE, ethyl vinyl ether; G3, Grubbs 3rd-generation catalyst; GC-HRMS, gas chromatography-high resolution mass spectrometry; ; M/I, monomer to initiator ratio; MALDI-TOF, matrix-assisted laser desorption/ionization-time of flight; MS, mass spectrometer/spectrometry; NMR, nuclear magnetic resonance; RI, refractive index; RT, room temperature; SEC, size exclusion chromatography; TFA, trifluoroacetic acid; TGA, thermogravimetric analysis; THF, tetrahydrofuran.

Chemicals

All commercially available reagents were used without further purification unless otherwise stated. For polymerizations, THF and chloroform were distilled from sodium and benzophenone and degassed by Ar bubbling for 10 min before use. Thin-layer chromatography (TLC) was carried out on precoated plates (Merck silica gel 60, F_{254}), and the spots were visualized with UV light or by charring the plates dipped in Cerium Ammonium Molybdate stain or $KMnO_4$ solution.

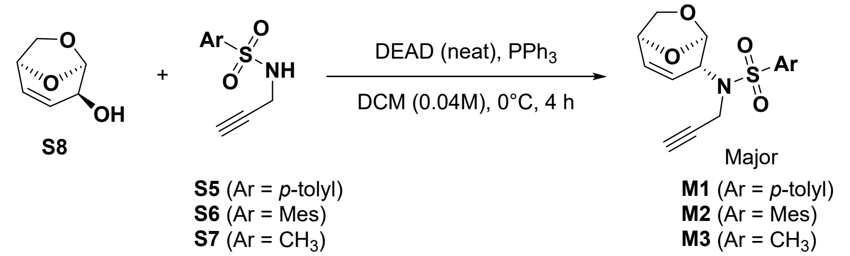
Instruments

NMR: ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 600 (600 MHz for ^1H and 150 MHz for ^{13}C), Varian/Oxford As-500 (500 MHz for ^1H and 125 MHz for ^{13}C), Agilent vrms-500 Magnetic Resonance System (499 MHz for ^1H and 126 MHz for ^{13}C), and Agilent 400-MR (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometers. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio-solvent as an internal standard ($CDCl_3$, ^1H: 7.26 ppm and ^{13}C: 77.16 ppm; CD_2Cl_2, ^1H: 5.32 ppm and ^{13}C: 54.00 ppm; CD_3CN, ^1H: 1.94 ppm and ^{13}C: 1.32 ppm). Abbreviations associated with the peak assignment are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; m, multiplet, dt, doublet of triplet; ddd, doublet of doublet of doublet; bs, broad singlet. **MS:** The molar masses were measured by Ultra High Resolution ESI Q-TOF mass spectrometer (Bruker, Germany) in the Sogang Center for Research Facilities. **SEC:** The SEC setup included a Waters 515 HPLC pump, Waters 2707 autosampler with a loop volume of 100 μL, and two Shodex gel permeation chromatography LF-804 size-exclusion columns maintained at 35 ºC. For molecular weight characterization a Wyatt OptiLab T-rEx refractive index detectors was used. The mobile phase consisted of HPLC-grade THF. Molecular weights were determined using a calibration curve prepared from polystyrene standards. **TGA:** Thermogravimetric analysis was completed with a TA Instruments Q50. **DSC:** Measurements of glass transition temperatures was completed with a TA DSC 2500. **MALDI-TOF:** MALDI-TOF spectra of the ground polymer were recorded on Bruker MALDI-TOF MS autoflex maX using DCTB as the matrix, soditum trifluoroacetate as the cationization agent. **XRD:** Single crystal X-ray diffraction was performed by SMART APEX (Bruker AXS) at Ewha Basic Science Research Institute.

3. Synthetic Protocols

3.1. Synthesis and Characterization of Monomer

3.1.1. M1-M3



General procedure:

To a stirred solution of **S8** (0.25 g, 1.95 mmol) in CH_2Cl_2 (49 mL) at 0 °C was added sulfonamide **SX** (1.95 mmol), PPh_3 (1.02 g, 3.90 mmol) and DEAD (0.61 mL, 3.90 mmol, neat). The mixture was stirred at 0 °C for 4h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to afford **M1** – **M3** as a white solid.

Monomers data:

M1: R_f = 0.50 (silica gel, hexane:EtOAc 7.5:2.5); FCC = (silica gel, hexane:Et_2O 9:1 to 7.5:2.5); yield = 0.47 g, 75%;

^1H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.69 (m, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 6.26 (ddd, *J* = 9.7, 4.9, 2.1 Hz, 1H), 5.57 – 5.41 (m, 2H), 4.72 (t, *J* = 4.5 Hz, 1H), 4.27 (dd, *J* = 18.5, 2.3 Hz, 1H), 4.12 (dd, *J* = 18.4, 2.4 Hz, 1H), 3.99 – 3.90 (m, 1H), 3.71 (d, *J* = 6.8 Hz, 1H), 3.68 – 3.58 (m, 1H), 2.43 (s, 3H), 2.13 (t, *J* = 2.4 Hz, 1H), 1.56 (d, *J* = 5.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 137.3, 132.5, 129.6, 127.6, 123.3, 102.2, 80.3, 72.1, 70.1, 54.7, 33.5, 21.6. ppm.

HRMS calcd. For $C_{16}H_{17}NO_4SNa^+$ $[M + Na]^+$ 342.0771, found 342.0774.

M2: R_f = 0.50 (silica gel, hexane:EtOAc 7.5:2.5); FCC = (silica gel, hexane:Et_2O 9:1 to 7.5:2.5); yield = 0.51 g, 75%;

^1H NMR (500 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.30 (ddd, *J* = 9.8, 4.7, 2.0 Hz, 1H), 5.67 (d, *J* = 2.4 Hz, 1H), 5.61 (ddd, *J* = 9.8, 3.8, 2.0 Hz, 1H), 4.75 (t, *J* = 4.4 Hz, 1H), 4.22 (dd, *J* = 18.3, 2.4 Hz, 1H), 4.03 (dd, *J* = 18.3, 2.4 Hz, 1H), 3.77 – 3.59 (m, 3H), 2.63 (s, 6H), 2.30 (s, 3H), 2.15 (t, *J* = 2.4 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 140.7, 132.8, 132.5, 132.3, 123.5, 102.2, 80.5, 71.6, 70.5, 54.4, 32.8, 23.0, 21.1 ppm.

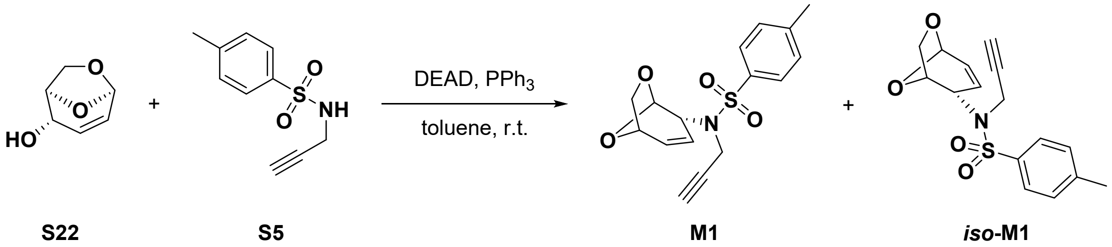
HRMS calcd. For $C_{18}H_{21}NO_4SNa^+$ $[M + Na]^+$ 370.1084, found 370.1085.

M3: R_f = 0.40 (silica gel, hexane:EtOAc 5:5); FCC = (silica gel, hexane:Et_2O 6:4 to 5:5); yield = 0.28 g, 58%;

^1H NMR (500 MHz, $CDCl_3$) δ 6.35 (ddd, *J* = 9.9, 4.7, 1.9 Hz, 1H), 5.74 (ddd, *J* = 9.8, 3.9, 2.1 Hz, 1H), 5.62 (d, *J* = 1.8 Hz, 1H), 4.78 (t, *J* = 4.5 Hz, 1H), 4.27 – 4.08 (m, 2H), 4.12 – 3.96 (m, 1H), 3.76 (d, J = 6.6 Hz, 1H), 3.70 (dd, J = 6.7, 4.1 Hz, 1H), 3.08 (s, 3H), 2.34 (t, J = 2.5 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.1, 123.6, 103.0, 80.7, 73.2, 70.8, 70.5, 55.1, 41.3, 33.9 ppm.

HRMS calcd. For $C_{10}H_{13}NO_4SNa^+$ $[M + Na]^+$ 266.0458, found 266.0461.

3.1.2. *iso*-M1



d.r. can be controlled by solvent variation

General procedure:

To a stirred solution of **S22** (0.25 g, 1.95 mmol) in toluene (49 mL) at RT was added sulfonamide **S5** (0.41 g, 1.95 mmol), PPh_3 (1.02 g, 3.90 mmol) and DEAD (0.61 mL, 3.90 mmol, neat). The mixture was stirred at RT for 4h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography with gravity to afford ***iso*-M1** as a white solid.

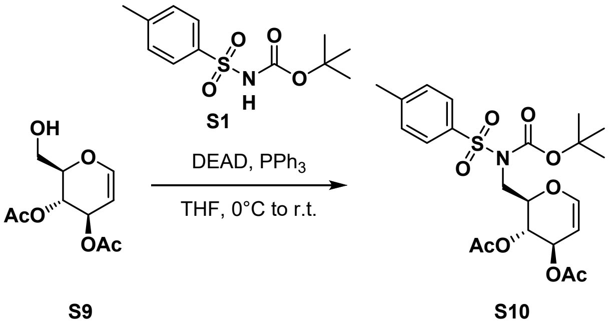
Monomers data:

***iso*-M1**: R_f = 0.51 (silica gel, hexane:EtOAc 7.5:2.5); FCC = (silica gel, hexane:Et_2O 9:1 to 7.5:2.5); yield = 0.26 g, 41%;

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.05 (dt, J = 9.8, 2.9 Hz, 1H), 5.73 – 5.63 (m, 1H), 5.46 (d, J = 3.4 Hz, 1H), 4.91 – 4.77 (m, 2H), 4.41 – 4.27 (m, 1H), 4.17 (dd, J = 8.7, 1.7 Hz, 1H), 4.07 (dd, J = 18.6, 2.4 Hz, 1H), 4.01 – 3.90 (m, 1H), 2.43 (s, 3H), 2.19 (q, J = 2.4, 1.9 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 135.8, 132.8, 129.8, 128.1, 124.2, 95.6, 79.2, 75.9, 74.0, 64.9, 58.1, 36.6, 21.7ppm.

HRMS calcd. For $C_{16}H_{17}NO_4SNa^+$ $[M + Na]^+$ 342.0771, found 342.0772.

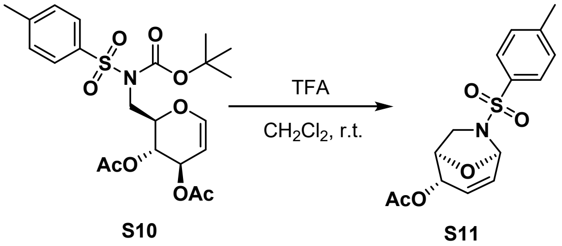
3.1.3. S10, S11, S12



To a stirred solution of **S9** (0.50 g, 2.17 mmol) in THF (22 mL) at 0 °C was added Boc-sulfonamide **S1** (0.56 g, 2.06 mmol), PPh_3 (0.85 g, 3.26 mmol) and DEAD (1.5 mL, 3.26 mmol, 2.2 M sol. in toluene). The mixture was stirred at room temperature for 2h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 7.5:2.5) to afford Boc-protected sulfonamide **S10** (0.92 g, 1.91 mmol, 88%) as a white solid. R_f = 0.70 (silica gel, hexane:EtOAc 6:4).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.75 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.52 (dd, *J* = 6.3, 1.2 Hz, 1H), 5.17 (td, *J* = 3.4, 2.7, 1.9 Hz, 1H), 5.10 (td, *J* = 4.2, 3.7, 1.1 Hz, 1H), 4.98 (ddd, *J* = 6.3, 4.2, 1.2 Hz, 1H), 4.54 – 4.48 (m, 1H), 4.45 (ddt, *J* = 9.9, 4.7, 1.5 Hz, 1H), 3.83 (dd, *J* = 14.8, 1.8 Hz, 1H), 2.44 (s, 3H), 2.10 (d, *J* = 16.2 Hz, 6H), 1.32 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 169.7, 150.8, 145.5, 144.2, 137.3, 129.3, 128.1, 98.1, 84.8, 74.1, 68.5, 65.2, 60.4, 45.3, 21.6, 20.9, 14.2 ppm.

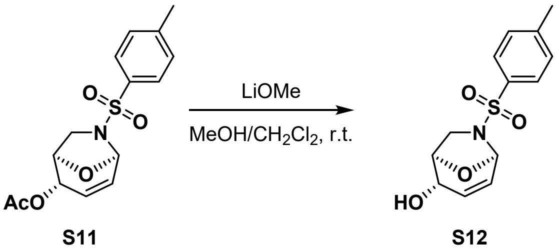
HRMS calcd. For $C_{22}H_{29}NO_9SNa^+$ $[M + Na]^+$ 506.1455, found 506.1457.



To a stirred solution of **S10** (0.92 g, 1.91 mmol) in CH_2Cl_2 (24 mL) at room temperature was added TFA (6 mL). The mixture was stirred at room temperature for 30 min. Then, it was diluted in CH_2Cl_2 (24 mL), cooled at 0 °C and quenched with Et_3N (11 mL, drop-wise addition). The resulting mixture was extracted with H_2O (30 mL), combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 6:4) to afford **S11** (0.44 g, 1.36 mmol, 71%) as a white solid. R_f = 0.5 (silica gel, hexane:EtOAc 6:4).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.65 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.29 (ddd, *J* = 9.6, 4.3, 1.0 Hz, 1H), 5.81 (d, *J* = 4.4 Hz, 1H), 5.78 (ddd, *J* = 9.6, 4.3, 1.8 Hz, 1H), 4.68 (dt, *J* = 4.3, 1.1 Hz, 1H), 4.44 (dq, *J* = 7.6, 1.8 Hz, 1H), 3.55 (dd, *J* = 11.7, 7.6 Hz, 1H), 3.13 (dd, *J* = 11.7, 2.0 Hz, 1H), 2.42 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 144.7, 134.5, 132.7, 130.2, 128.4, 122.9, 84.3, 75.5, 67.9, 46.5, 22.0, 21.3 ppm.

HRMS calcd. For $C_{15}H_{17}NO_5SNa^+$ $[M + Na]^+$ 346.0720, found 346.0721.

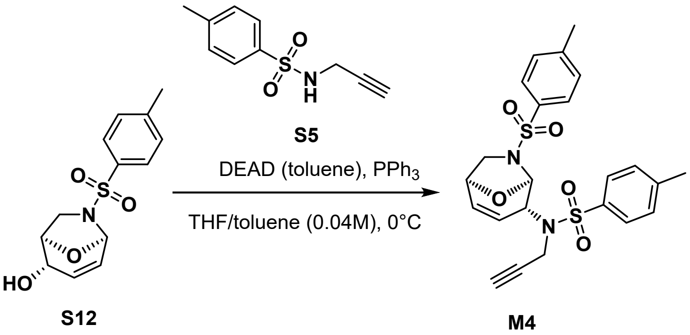


To a stirred solution of **S11** (0.44 g, 1.36 mmol) in MeOH/CH_2Cl_2 (4.5 mL, 1:1 ratio) at room temperature was added LiOMe (0.10 g, 2.72 mmol). The mixture was stirred at room temperature for 2h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 4:6) to afford alcohol **S12** (0.35 g, 1.23 mmol, 91%) as a white solid. R_f = 0.15 (silica gel, hexane:EtOAc 4:6).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (dt, *J* = 8.6, 0.9 Hz, 2H), 6.14 (ddt, *J* = 9.5, 4.2, 0.9 Hz, 1H), 5.98 – 5.81 (m, 1H), 5.74 (d, *J* = 4.3 Hz, 1H), 4.40 (dq, *J* = 7.5, 1.7 Hz, 1H), 3.62 – 3.42 (m, 2H), 3.06 (dd, *J* = 11.6, 2.2 Hz, 1H), 2.44 (s, 3H), 2.01 (d, *J* = 10.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.7, 134.9, 130.7, 130.3, 128.5, 126.8, 84.5, 78.5, 67.3, 46.2, 22.1 ppm.

HRMS calcd. For $C_{13}H_{15}NO_4SNa^+$ [M + Na]$^+$ 304.0614, found 304.0614.

3.1.4. M4

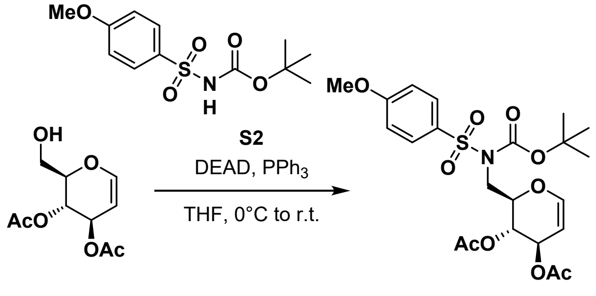


To a stirred solution of **S12** (0.35 g, 1.23 mmol) in toluene/THF (31 mL, 3:1 ratio) at 0 °C was added sulfonamide **S5** (0.23 g, 1.18 mmol), PPh$_3$ (0.62 g, 2.36 mmol) and DEAD (1.1 mL, 2.36 mmol, 2.2 M sol. in toluene). The mixture was stirred at 0 °C for 2h and concentrated under reduced pressure. The resulting residue was passed through a silica plug (ca. 20 mL, 1% acetone/CH$_2$Cl$_2$) and the filtrate concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 8:2 to 6:4) to afford **M4** (0.22 g, 0.50 mmol, 41%) as a white solid. R_f = 0.40 (silica gel, hexane:EtOAc 1:1).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.25 (ddd, *J* = 9.9, 4.5, 1.8 Hz, 1H), 5.65 (ddd, *J* = 9.8, 4.2, 1.8 Hz, 1H), 5.51 – 5.35 (m, 1H), 4.66 (t, *J* = 4.9 Hz, 1H), 4.32 (d, *J* = 4.1 Hz, 1H), 4.25 (dd, *J* = 18.5, 2.4 Hz, 1H), 4.14 (dd, *J* = 18.5, 2.4 Hz, 1H), 3.39 (d, *J* = 7.9 Hz, 1H), 3.09 (dd, *J* = 7.9, 5.3 Hz, 1H), 2.47 (d, *J* = 19.7 Hz, 6H), 2.10 (t, *J* = 2.4 Hz, 1H) ppm; ^{13}C NMR (126 MHz, CDCl$_3$) δ 144.1, 143.6, 136.9, 133.6, 132.3, 129.8, 129.5, 127.9, 127.5, 123.6, 89.2, 80.2, 72.3, 71.8, 55.4, 51.9, 33.6, 21.5 ppm.

HRMS calcd. For $C_{23}H_{24}N2O_5S_2Na^+$ [M + Na]$^+$ 495.1019, found 495.1024.

3.1.5. S13, S14, S15

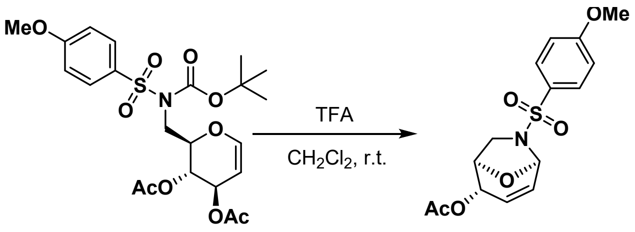


S9 **S13**

To a stirred solution of **S9** (0.50 g, 2.17 mmol) in THF (22 mL) at 0 °C was added Boc-sulfonamide **S2** (0.59 g, 2.06 mmol), PPh_3 (0.85 g, 3.26 mmol) and DEAD (1.5 mL, 3.26 mmol, 2.2 M sol. in toluene). The mixture was stirred at room temperature for 2h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 7.5:2.5) to afford Boc-protected sulfonamide **S13** (1.06 g, 2.13 mmol, 98%) as a white solid. R_f = 0.40 (silica gel, hexane:EtOAc 6:4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.85 (m, 2H), 7.00 – 6.88 (m, 2H), 6.51 (dd, *J* = 6.3, 1.2 Hz, 1H), 5.15 (td, *J* = 4.0, 1.2 Hz, 1H), 5.08 (t, *J* = 4.2 Hz, 1H), 4.96 (ddd, *J* = 6.2, 4.2, 1.1 Hz, 1H), 4.61 – 4.34 (m, 2H), 3.86 (s, 3H), 3.80 (dd, *J* = 14.6, 1.6 Hz, 1H), 2.08 (dd, *J* = 12.6, 1.5 Hz, 6H), 1.33 (d, *J* = 1.3 Hz, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 170.1, 163.8, 151.2, 145.9, 132.0, 130.9, 114.1, 98.5, 85.1, 74.6, 68.9, 65.6, 56.1, 45.7, 28.3, 21.5, 21.3 ppm.

HRMS calcd. For $C_{22}H_{29}NO_{10}SNa^+$ $[M + Na]^+$ 522.1404, found 522.1407.

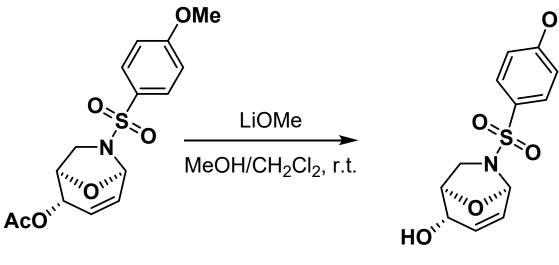


S13 **S14**

To a stirred solution of **S13** (1.06 g, 2.13 mmol) in CH_2Cl_2 (27 mL) at room temperature was added TFA (6.8 mL). The mixture was stirred at room temperature for 30 min. Then, it was diluted in CH_2Cl_2 (27 mL), cooled at 0 °C and quenched with Et_3N (12 mL, drop-wise addition). The resulting mixture was extracted with H_2O (30.0 mL), combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 6:4) to afford **S14** (0.35 g, 1.04 mmol, 49%) as a white solid. R_f = 0.5 (silica gel, hexane:EtOAc 6:4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.67 (m, 2H), 7.04 – 6.93 (m, 2H), 6.30 (dd, *J* = 9.6, 4.3 Hz, 1H), 5.89 – 5.72 (m, 2H), 4.76 – 4.65 (m, 1H), 4.44 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.86 (s, 3H), 3.54 (dd, *J* = 11.8, 7.6 Hz, 1H), 3.13 (dd, *J* = 11.9, 2.0 Hz, 1H), 2.05 (d, *J* = 1.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 163.3, 132.2, 130.0, 128.4, 122.3, 114.2, 83.9, 75.0, 67.4, 55.4, 46.0, 20.7ppm.

HRMS calcd. For C15$H_{17}NO_6SNa^+$ $[M + Na]^+$ 362.0669, found 362.0668.



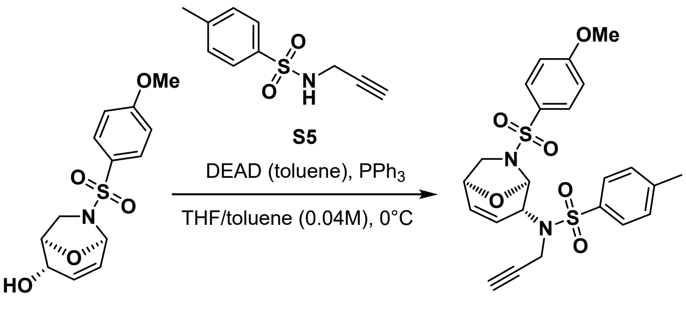
S14 **S15**

To a stirred solution of **S14** (0.35 g, 1.04 mmol) in MeOH/ CH_2Cl_2 (3.5 mL, 1:1 ratio) at room temperature was added LiOMe (79 mg, 2.08 mmol). The mixture was stirred at room temperature for 2h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 4:6) to afford alcohol **S15** (0.26 g, 0.88 mmol, 85%) as a white solid. R_f = 0.10 (silica gel, hexane:EtOAc 4:6).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.69 (m, 1H), 7.04 – 6.95 (m, 1H), 6.15 (dd, *J* = 9.5, 4.2 Hz, 1H), 5.85 (ddd, *J* = 9.5, 4.4, 1.8 Hz, 1H), 5.75 (d, *J* = 4.3 Hz, 1H), 4.40 (dq, *J* = 7.6, 1.8 Hz, 1H), 3.88 (s, 2H), 3.64 – 3.47 (m, 1H), 3.06 (dd, *J* = 11.7, 2.1 Hz, 1H), 1.96 (d, *J* = 10.7 Hz, 0H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 129.3, 126.7, 114.8, 84.5, 78.4, 67.3, 56.0, 46.1 ppm.

HRMS calcd. For $C_{13}H_{15}NO_5SNa^+$ $[M + Na]^+$ 320.0563, found 320.0564.

3.1.6. M5



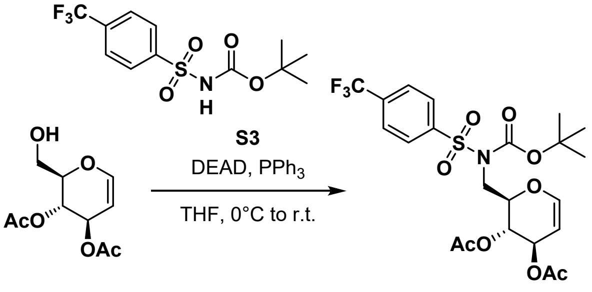
S15 **M5**

To a stirred solution of **S15** (0.26 g, 0.88 mmol) in toluene/THF (22 mL, 3:1 ratio) at 0 °C was added sulfonamide **S5** (0.17 g, 0.80 mmol), PPh_3 (0.420 g, 1.60 mmol) and DEAD (0.7 mL, 1.60 mmol, 2.2 M sol. in toluene). The mixture was stirred at 0 °C for 2h and concentrated under reduced pressure. The resulting residue was passed through a silica plug (ca. 20 mL, 1% acetone/CH_2Cl_2) and the filtrate concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 8:2 to 6:4) to afford **M5** (0.22 g, 0.46 mmol, 52%) as a white solid. R_f = 0.40 (silica gel, hexane:EtOAc 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.78 – 7.66 (m, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.07 – 6.92 (m, 2H), 6.30 – 6.16 (m, 1H), 5.69 – 5.54 (m, 1H), 5.43 (q, *J* = 1.4 Hz, 1H), 4.65 (t, *J* = 4.6 Hz, 1H), 4.27 (d, *J* = 3.7 Hz, 1H), 4.26 – 4.04 (m, 2H), 3.87 (d, *J* = 1.3 Hz, 3H), 3.43 – 3.30 (m, 1H), 3.07 (t, *J* = 6.9 Hz, 1H), 2.46 (s, 3H), 2.09 (dq, *J* = 2.3, 1.2 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 143.7, 136.9, 132.5, 129.7, 129.6, 128.0, 123.6, 114.4, 89.4, 80.3, 72.4, 71.9, 55.6, 55.5, 52.0, 33.7, 21.6 ppm.

HRMS calcd. For $C_{23}H_{24}N_2O_6S_2Na^+$ $[M + Na]^+$ 511.0968, found 511.0975.

3.1.7. S16, S17, S18

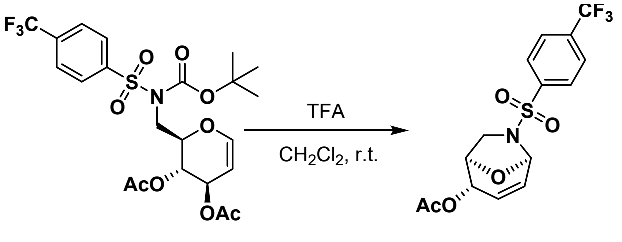


S9 **S16**

To a stirred solution of **S9** (0.50 g, 2.17 mmol) in THF (22 mL) at 0 °C was added Boc-sulfonamide **S3** (0.67 g, 2.06 mmol), PPh_3 (0.85 g, 3.26 mmol) and DEAD (1.5 mL, 3.26 mmol, 2.2 M sol. in toluene). The mixture was stirred at room temperature for 2h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 7.5:2.5) to afford Boc-protected sulfonamide **S16** (0.63 g, 1.17 mmol, 54%) as a white solid. R_f = 0.70 (silica gel, hexane:EtOAc 6:4).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 6.51 (dd, *J* = 6.3, 1.2 Hz, 1H), 5.18 (dd, *J* = 2.7, 1.2 Hz, 1H), 5.10 (ddd, *J* = 4.9, 3.7, 1.1 Hz, 1H), 5.00 (ddd, *J* = 6.3, 4.1, 1.1 Hz, 1H), 4.54 (dd, *J* = 15.1, 10.0 Hz, 1H), 4.43 (ddt, *J* = 10.1, 4.7, 1.8 Hz, 1H), 3.84 (dd, *J* = 15.1, 1.9 Hz, 1H), 2.11 (d, *J* = 15.2 Hz, 6H), 1.34 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $cdcl_3$) δ 170.3, 170.0, 150.7, 145.6, 144.1, 129.1, 126.2, 98.8, 86.0, 74.4, 68.8, 65.5, 45.8, 28.2, 21.5, 21.3 ppm.

HRMS calcd. For $C_{22}H_{26}F_3NO_9SNa^+$ $[M + Na]^+$ 560.1173, found 560.1176.

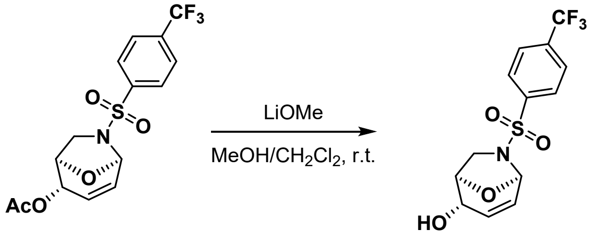


S16 **S17**

To a stirred solution of **S16** (0.63 g, 1.17 mmol) in CH_2Cl_2 (15 mL) at room temperature was added TFA (3.8 mL). The mixture was stirred at room temperature for 30 min. Then, it was diluted in CH_2Cl_2 (15 mL), cooled at 0 °C and quenched with Et_3N (6.9 mL, drop-wise addition). The resulting mixture was extracted with H_2O (30.0 mL), combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 7:3) to afford **S17** (0.29 g, 0.76 mmol, 65%) as an oil. R_f = 0.6 (silica gel, hexane:EtOAc 6:4).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 6.41 – 6.23 (m, 1H), 5.90 – 5.79 (m, 1H), 4.71 (dd, *J* = 2.7, 1.6 Hz, 2H), 4.48 (dq, *J* = 7.7, 1.8 Hz, 1H), 3.55 (ddd, *J* = 11.8, 7.5, 1.4 Hz, 1H), 3.19 (dd, *J* = 11.8, 2.0 Hz, 1H), 2.05 (d, *J* = 1.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 141.3, 135.5, 132.3, 127.9, 126.8, 124.6, 123.3, 122.4, 84.4, 75.7, 67.7, 46.6, 21.3 ppm.

HRMS calcd. For $C_{15}H_{14}F_3NO_5SNa^+$ $[M + Na]^+$ 400.0437, found 400.0441.



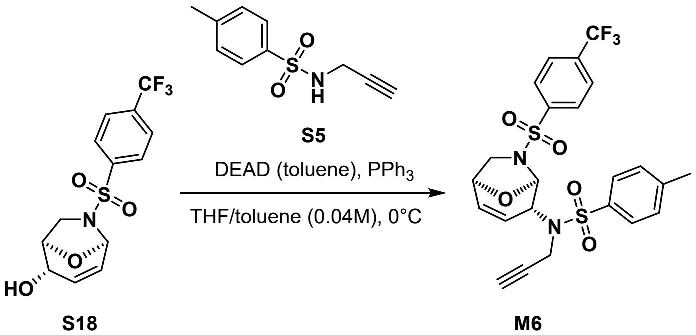
S17 **S18**

To a stirred solution of **S17** (0.29 g, 0.76 mmol) in MeOH/ CH_2Cl_2 (2.5 mL, 1:1 ratio) at room temperature was added LiOMe (57 mg, 1.52 mmol). The mixture was stirred at room temperature for 2h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 4:6) to afford alcohol **S18** (0.23 g, 0.68 mmol, 89%) as a white solid. R_f = 0.25 (silica gel, hexane:EtOAc 4:6).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 6.16 (dd, *J* = 9.6, 4.3 Hz, 1H), 5.89 (ddd, *J* = 9.6, 4.4, 1.8 Hz, 1H), 5.78 (d, *J* = 4.3 Hz, 1H), 4.45 (dq, *J* = 7.6, 1.8 Hz, 1H), 3.60 (d, *J* = 4.7 Hz, 1H), 3.54 (dd, *J* = 11.7, 7.6 Hz, 1H), 3.11 (dd, *J* = 11.6, 2.1 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 141.1, 129.8, 128.5, 127.6, 126.6, 126.3, 84.0, 78.1, 66.8, 45.7 ppm.

HRMS calcd. For $C_{13}H_{12}F_3NO_4SNa^+$ $[M + Na]^+$ 358.0331, found 358.0334.

3.1.8. M6



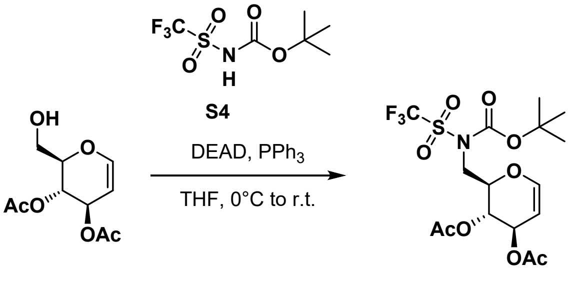
S18 **M6**

To a stirred solution of **S18** (0.23 g, 0.68 mmol) in toluene/THF (17 mL, 3:1 ratio) at 0 °C was added sulfonamide **S5** (0.13 g, 0.62 mmol), PPh_3 (0.32 g, 1.24 mmol) and DEAD (0.56 mL, 1.24 mmol, 2.2 M sol. in toluene). The mixture was stirred at 0 °C for 2h and concentrated under reduced pressure. The resulting residue was passed through a silica plug (ca. 20 mL, 0.5% acetone/CH_2Cl_2) and the filtrate concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 8:2 to 6:4) to afford **M6** (0.15 g, 0.29 mmol, 43%) as a white solid. R_f = 0.40 (silica gel, hexane:EtOAc 1:1).

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 4H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 6.24 (ddd, *J* = 9.8, 4.5, 1.8 Hz, 1H), 5.63 (ddd, *J* = 9.7, 4.1, 1.8 Hz, 1H), 5.52 – 5.45 (m, 1H), 4.70 (t, *J* = 4.9 Hz, 1H), 4.26 (d, *J* = 3.4 Hz, 1H), 4.24 – 4.08 (m, 2H), 3.41 (d, *J* = 7.9 Hz, 1H), 3.14 – 3.03 (m, 1H), 2.47 (s, 3H), 2.10 (t, *J* = 2.4 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 140.8, 140.5, 136.9, 132.3, 129.6, 128.0, 128.0, 126.5, 123.6, 89.6, 80.2, 72.4, 72.1, 55.3, 52.0, 33.8, 21.6 ppm.

HRMS calcd. For $C_{23}H_{21}F_3N_2O_5S_2Na^+$ [M + Na]$^+$ 549.0736, found 549.0738.

3.1.9. S19, S20, S21

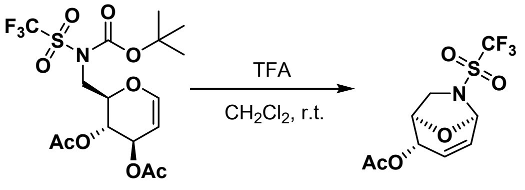


S9 **S19**

To a stirred solution of **S9** (0.50 g, 2.17 mmol) in THF (22 mL) at 0 °C was added Boc-sulfonamide **S4** (0.51 g, 2.06 mmol), PPh_3 (0.85 g, 3.26 mmol) and DEAD (1.5 mL, 3.26 mmol, 2.2 M sol. in toluene). The mixture was stirred at room temperature for 2h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 7.5:2.5) to afford Boc-protected sulfonamide **S19** (0.41 g, 0.89 mmol, 41%) as a white solid. R_f = 0.70 (silica gel, hexane:EtOAc 6:4).

^{1}H NMR (500 MHz, $CDCl_3$) δ δ 6.45 (dd, *J* = 6.3, 1.2 Hz, 1H), 5.16 (t, *J* = 4.0 Hz, 1H), 5.04 (t, *J* = 4.2 Hz, 1H), 4.95 (ddd, *J* = 6.3, 4.1, 0.9 Hz, 1H), 4.43 – 4.28 (m, 2H), 3.89 – 3.72 (m, 1H), 2.08 (d, *J* = 24.9 Hz, 6H), 1.54 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 169.7, 150.8, 145.5, 144.2, 137.3, 129.3, 128.1, 98.1, 84.8, 74.1, 68.5, 65.2, 60.4, 45.3, 21.6, 20.9, 14.2 ppm.

HRMS calcd. For $C_{16}H_{22}F_3NO_9SNa^+$ [M + Na]$^+$ 484.0860, found 484.0861.



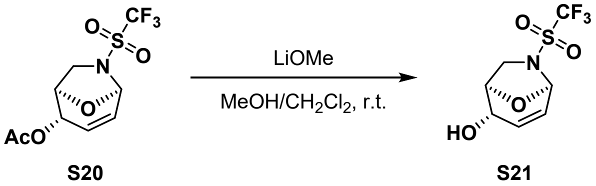
S19 **S20**

To a stirred solution of **S19** (0.41 g, 0.89 mmol) in CH_2Cl_2 (11 mL) at room temperature was added TFA (2.8 mL). The mixture was stirred at room temperature for 30 min. Then, it was diluted in

CH_2Cl_2 (11 mL), cooled at 0°C and quenched with Et_3N (5.1 mL, drop-wise addition). The resulting mixture was extracted with H_2O (30.0 mL), combined organic layer was washed with brine (5 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 7:3) to afford **S20** (0.150 g, 0.50 mmol, 56%) as an oil. R_f = 0.7 (silica gel, hexane:EtOAc 6:4).

^1H NMR (500 MHz, $CDCl_3$) δ 6.31 (dd, J = 9.6, 4.1 Hz, 1H), 5.92 (ddd, J = 9.6, 4.4, 1.8 Hz, 1H), 5.78 (d, J = 4.1 Hz, 1H), 4.95 – 4.88 (m, 1H), 4.84 (d, J = 4.3 Hz, 1H), 3.99 (dd, J = 10.9, 7.4 Hz, 1H), 3.28 (d, J = 10.8 Hz, 1H), 2.14 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 131.4, 123.6, 83.8, 76.2, 67.0, 46.7, 20.8 ppm.

HRMS calcd. For $C_9H_{10}F_3NO_5SNa^+$ $[M + Na]^+$ 324.0124, found 324.0129.

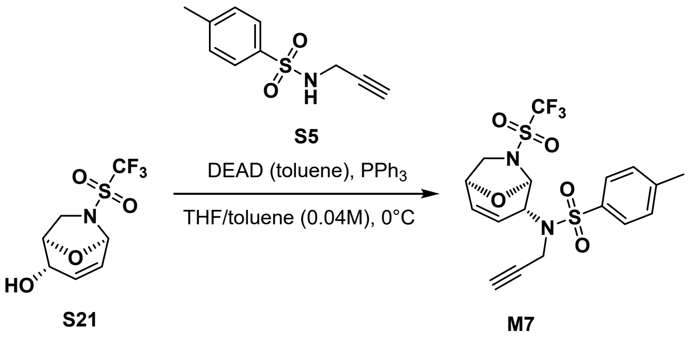


To a stirred solution of **S20** (0.150 g, 0.50 mmol) in MeOH/ CH_2Cl_2 (1.7 mL, 1:1 ratio) at room temperature was added LiOMe (38 mg, 1.0 mmol). The mixture was stirred at room temperature for 2h and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 4:6) to afford alcohol **S21** (84 mg, 0.33 mmol, 65%) as a white solid. R_f = 0.50 (silica gel, hexane:EtOAc 4:6).

^1H NMR (500 MHz, $CDCl_3$) δ 6.17 (dd, J = 9.5, 4.1 Hz, 1H), 5.99 (ddd, J = 9.5, 4.3, 1.7 Hz, 1H), 5.72 (d, J = 4.1 Hz, 1H), 4.89 (dq, J = 7.5, 1.8 Hz, 1H), 3.97 (dd, J = 10.8, 7.3 Hz, 1H), 3.74 (ddt, J = 10.7, 4.3, 1.1 Hz, 1H), 3.21 (d, J = 9.6 Hz, 1H), 2.13 (d, J = 10.8 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.2, 127.1, 83.8, 78.8, 66.5, 46.0 ppm.

HRMS calcd. For $C_7H_8F_3NO_4SNa^+$ $[M + Na]^+$ 282.0018, found 282.0018.

3.1.10. M7



To a stirred solution of **S21** (84 mg, 0.33 mmol) in toluene/THF (8.3 mL, 3:1 ratio) at 0°C was added sulfonamide **S5** (62 mg, 0.30 mmol), PPh_3 (0.16 g, 0.60 mmol) and DEAD (0.27 mL, 0.28 mmol, 2.2 M sol. in toluene). The mixture was stirred at 0°C for 2h and concentrated under reduced pressure. The resulting residue was passed through a silca plug (ca. 20 mL, 0.5%

acetone/CH_2Cl_2) and the filtrate concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, hexane:EtOAc 8:2 to 7:3) to afford **M7** (94 mg, 0.21 mmol, 63%) as a white solid. R_f = 0.70 (silica gel, hexane:EtOAc 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 6.31 (ddd, *J* = 10.0, 4.7, 1.9 Hz, 1H), 5.71 (ddd, *J* = 9.9, 4.0, 1.9 Hz, 1H), 5.60 (s, 1H), 4.92 (t, *J* = 5.0 Hz, 1H), 4.37 (s, 1H), 4.28 (dd, *J* = 18.4, 2.4 Hz, 1H), 4.10 (dd, *J* = 18.5, 2.5 Hz, 1H), 3.55 (t, *J* = 6.3 Hz, 1H), 3.45 (d, *J* = 8.1 Hz, 1H), 2.43 (s, 3H), 2.22 – 2.05 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.2, 132.2, 130.1, 128.2, 124.2, 122.0, 118.8, 90.6, 80.3, 73.1, 72.8, 55.0, 52.8, 34.1, 22.0 ppm.

HRMS calcd. For $C_{17}H_{17}F_3N2O_5S_2Na^+$ [M + Na]$^+$ 473.0423, found 473.0427.

3.2. Synthesis and Characterization of Polymers

3.2.1. General Procedure for Enyne Polymerization

A 4-mL sized screw-cap vial with septum was flame dried and charged with monomer (see below for scale) and a magnetic bar. The vial was purged with argon three times, and degassed anhydrous solvent was added. Initiator was dissolved in another 4-mL vial in the same solvent under Ar. The initiator solution was rapidly injected to the monomer solution at experimental temperature under vigorous stirring. Low reaction temperatures were regulated by electronically controlled circulating isopropanol bath (LC-LT212, LKLab). The reaction was quenched by excess EVE after the desired reaction time and precipitated using the conditions described below. Monomer conversion was calculated from the ^{1}H NMR spectrum of the crude mixture before precipitation.

3.2.2. P1

Following the general procedure provided in 3.2.1.: **M1** (20 mg, 0.063 mmol) in THF (213 μL), initiator (depending on feed ratio) in THF (100 μL). Precipitation conditions: Et_2O/*n*-hexane (1/1 ratio, 20.0 mL). **P1** was precipitated and filtered to give a white powder.

P1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dq), 7.31 (d), 6.30 (dq), 6.01 – 5.82 (m), 5.58 – 5.34 (m), 5.19 (t), 4.78 – 4.43 (m), 4.29 – 4.08 (m), 3.96 (dp), 3.67 – 3.37 (m), 2.70 – 2.28 (m) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 138.4, 137.1, 134.2, 130.7, 129.9, 127.5, 126.5, 125.3, 123.9, 105.1, 76.8, 73.5, 70.2, 68.9, 57.2, 54.9, 25.6, 21.6, 21.6 ppm.

3.2.3. P2

Following the general procedure provided in 3.2.1.: **M2** (20 mg, 0.058 mmol) in THF (188 μL), initiator (depending on feed ratio) in THF (100 μL). Precipitation conditions: Et_2O/*n*-hexane (1/1 ratio, 20.0 mL). **P2** was precipitated and filtered to give a white powder.

P2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d), 6.45 – 6.27 (m), 5.99 (d), 5.83 – 5.52 (m), 5.30 (s), 4.93 – 4.56 (m), 4.40 (s), 3.90 (d), 3.36 (s), 2.64 (s), 2.41 – 2.16 (m) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 140.8, 139.0, 138.9, 137.7, 132.4, 104.5, 73.9, 70.4, 67.9, 56.5, 54.2, 23.2, 21.4 ppm.

3.2.4. P3

Following the general procedure provided in 3.2.1.: **M3** (20 mg, 0.082 mmol) in CH_2Cl_2 (311 μL), initiator (depending on feed ratio) in CH_2Cl_2 (100 μL). Precipitation conditions: Et_2O/*n*-hexane (1/1 ratio, 20.0 mL). **P3** was precipitated and filtered to give a white powder.

P3: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.45 (q), 6.15 (q), 5.73 (q), 5.64 – 5.44 (m), 5.12 – 4.97 (m), 4.85 – 4.63 (m), 4.63 – 4.49 (m), 4.41 (d), 4.31 – 3.97 (m), 3.64 (q), 3.10 – 2.83 (m) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.7, 123.2, 105.2, 102.6, 72.8, 70.4, 70.1, 68.7, 68.1, 56.5, 54.7, 54.5, 40.9, 33.4 ppm.

3.2.5. P4

Following the general procedure provided in 3.2.1.: **M4** (20 mg, 0.042 mmol) in THF (112 μL), initiator (depending on feed ratio) in THF (100 μL). Precipitation conditions: Et_2O/*n*-hexane (1/1 ratio, 20.0 mL). **P4** was precipitated and filtered to give a white powder.

P4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.66 (m), 7.62 – 7.44 (m), 7.46 – 7.28 (m), 6.34 – 6.04 (m), 5.89 (d), 5.71 – 5.03 (m), 5.00 – 4.69 (m), 4.39 – 3.44 (m), 3.01 (d), 2.66 – 2.22 (m) ppm; ^{13}C NMR (126 MHz, CDCl3) δ 145.6, 145.0, 144.4, 137.0, 133.2, 130.8, 130.1, 127.9, 127.5, 91.9, 74.2, 70.4, 57.5, 55.5, 52.4, 25.4, 21.6 ppm.

3.2.6. P5

Following the general procedure provided in 3.2.1.: **M5** (20 mg, 0.041 mmol) in THF (105 µL), initiator (depending on feed ratio) in THF (100 µL). Precipitation conditions: Et_2O/*n*-hexane (1/1 ratio, 20.0 mL). **P5** was precipitated and filtered to give a white powder.

P5: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.56 (m), 7.42 – 7.28 (m), 7.21 – 6.92 (m), 6.27 – 5.75 (m), 5.64 – 4.99 (m), 4.83 (d), 4.37 – 3.42 (m), 2.97 (s), 2.41 (dt) ppm; ^{13}C NMR (126 MHz, CDCl3) δ 164.2, 163.8, 144.4, 137.0, 133.2, 130.1, 127.5, 115.4, 114.8, 91.9, 74.3, 70.6, 56.0, 55.8, 52.6, 21.7 ppm.

3.2.7. P6

Following the general procedure provided in 3.2.1.: **M6** (20 mg, 0.038 mmol) in THF (100 µL), initiator (depending on feed ratio) in THF (90 µL). Precipitation conditions: Et_2O/*n*-hexane (1/1 ratio, 20.0 mL). **P6** was precipitated and filtered to give a white powder.

P6: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 7.62 (m), 7.35 (d), 6.38 – 5.83 (m), 5.69 – 5.06 (m), 5.06 – 4.71 (m), 3.93 (dd), 3.05 (s), 2.61 – 2.27 (m) ppm; ^{13}C NMR (126 MHz, CDCl3) δ 144.5, 130.1, 128.7, 128.4, 127.4, 127.2, 126.8, 110.0, 91.7, 74.4, 70.3, 52.5, 21.5 ppm.

3.2.8. P7

Following the general procedure provided in 3.2.1.: **M7** (20 mg, 0.044 mmol) in THF (122 µL), initiator (depending on feed ratio) in THF (100 µL). Precipitation conditions: Et_2O/*n*-hexane (1/1 ratio, 20.0 mL). **P7** was precipitated and filtered to give a white powder.

P7: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d), 7.34 (t), 6.09 (d), 5.76 – 5.33 (m), 4.77 (d), 4.60 (d), 4.22 (d), 4.13 – 3.92 (m), 3.82 (s), 3.15 (s), 2.42 (d) ppm; ^{13}C NMR (126 MHz, CDCl3) δ 145.1, 133.3, 130.6, 127.9, 92.1, 75.6, 74.2, 69.9, 52.9, 22.0 ppm.

3.2.9. Block Copolymer Cascade Polymerization (P1-*b*-P6)

A 4-mL sized screw-cap vial with septum was flame dried and charged with **M1** (20 mg, 0.063 mmol) and a magnetic bar. The vial was purged with argon three times, degassed anhydrous THF (213 µL) was added and the solution cooled to 0 °C. Initiator **G3** (2.5 mg, 3.2 µmol) was dissolved in another 4-mL vial in THF (100 µL) under Ar. The initiator solution was rapidly injected in to the monomer solution at the same temperature under vigorous stirring. After 45 min, an aliquot (50 µL) was removed for analysis and a solution of **M6** (66 mg, 0.126 mmol) in THF (50 µL) was added rapidly. The reaction was stirred for 1.5 h before it was quenched by excess EVE. The polymer was precipitated in Et_2O:hexane (1:1, 20.0 mL). The obtained solids were filtered and dried *in vacuo*.

P1-*b*-**P6**: M_n ($Đ$) = 14.7 kDa (1.19); Yield (g/g) = 73%; ^{1}H NMR (499 MHz, $CDCl_3$) δ 8.44 – 7.54 (m, 14H), 7.30 (s, 6H), 6.30 (s, 1H), 5.92 (s, 2H), 5.45 (s, 4H), 5.19 (s, 4H), 4.82 (s, 2H), 4.59 (s, 2H), 4.40 – 3.36 (m, 11H), 3.07 (s, 2H), 2.40 ppm.

3.2.10. SEC Traces for Polymers

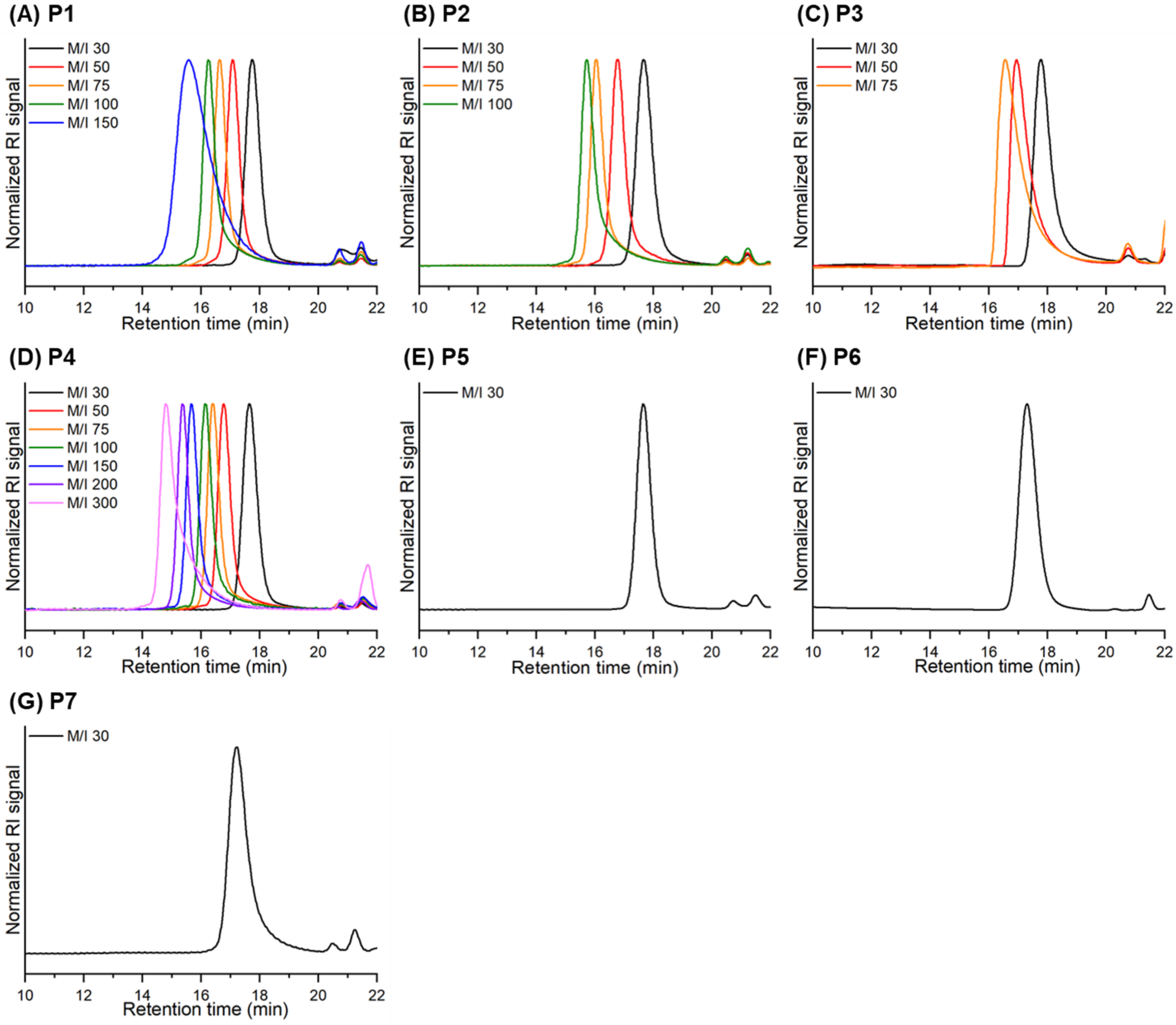


Figure S9. SEC traces of (A) **P1**, (B) **P2**, (C) **P3**, (D) **P4**, (E) **P5**, (F) **P6**, and (G) **P7**, which correspond to the entries in **Table 1** of the *main text*. Numbers in the legend indicate the targeted degree of polymerization.

3.2.11. Linear Plots of M_n versus M/I x conversion

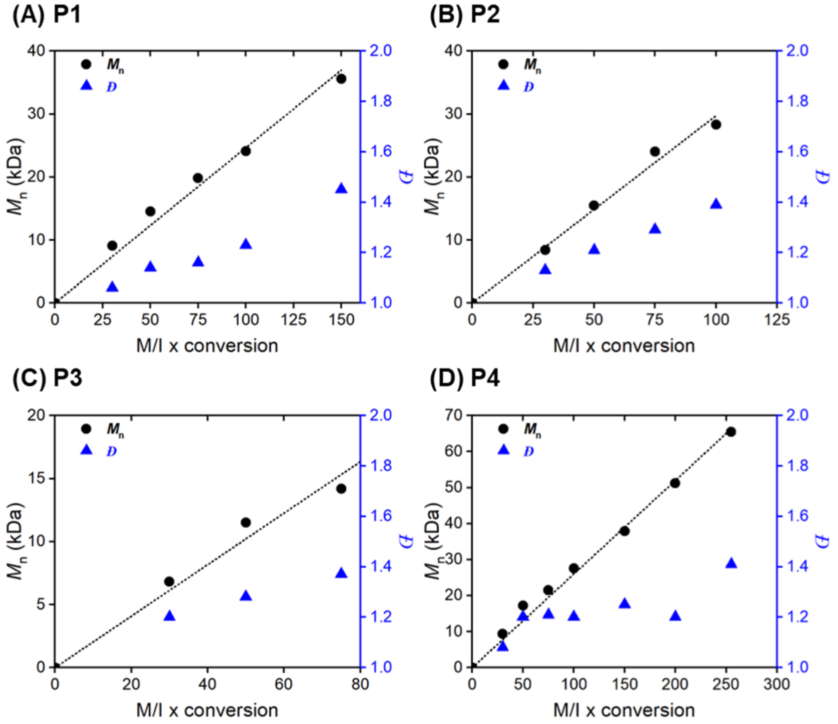
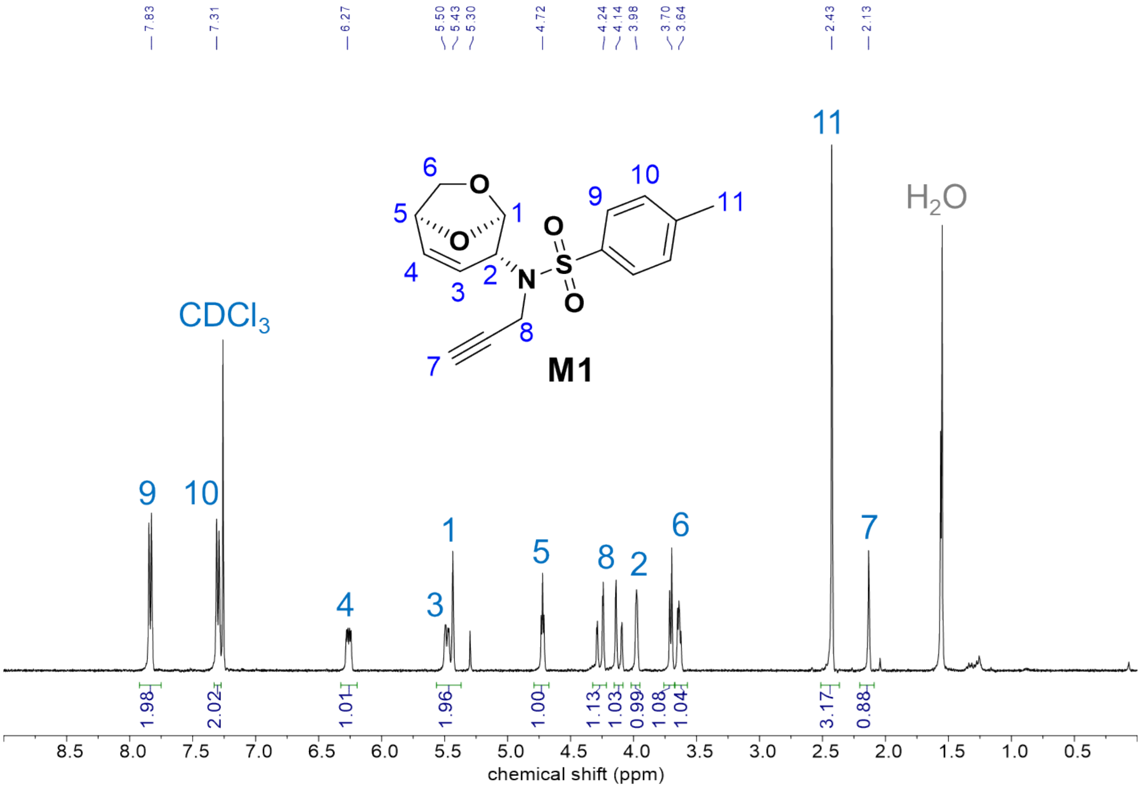


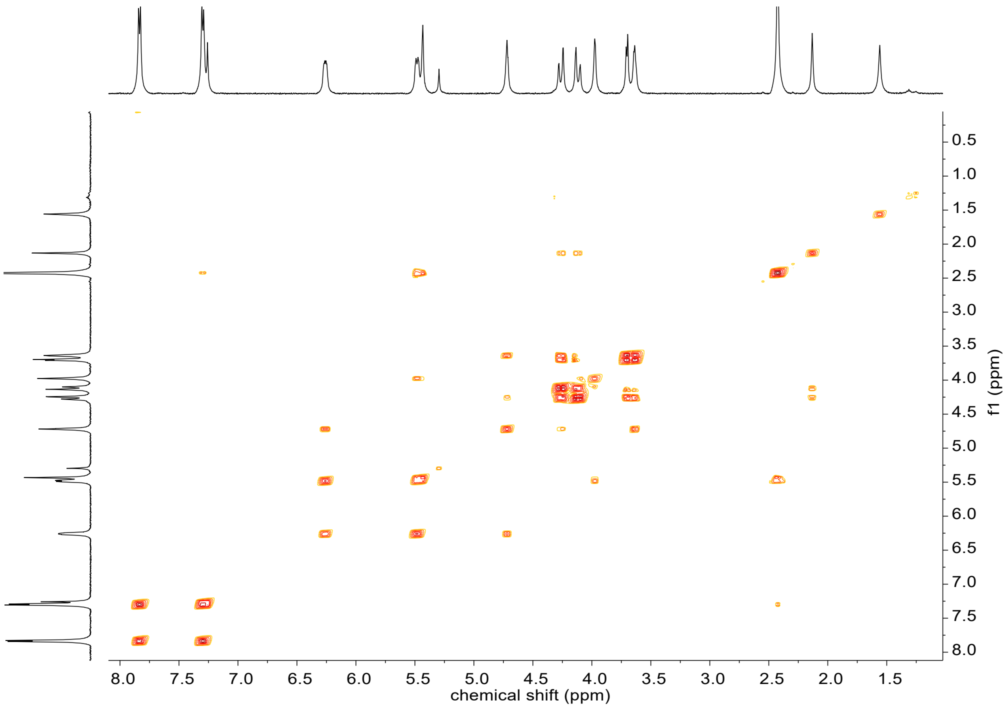
Figure S10. Linear plots of M_n versus M/I x conversion for (A) **P1**, (B) **P2**, (C) **P3**, and (D) **P4**, which correspond to the entries in **Table 1** of the *main text*. Black circles represent M_n values and blue triangles represent *Đ* values. Dashed lines are for visual aid only.

4. ^{1}H NMR assignment of Monomers and Polymers and ^{13}C NMR

4.1 Monomers

Monomer ^{1}H NMR spectra were assigned with the aid of 2D COSY and HSQC NMR spectroscopy.




0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.0
7.5
7.0
6.5
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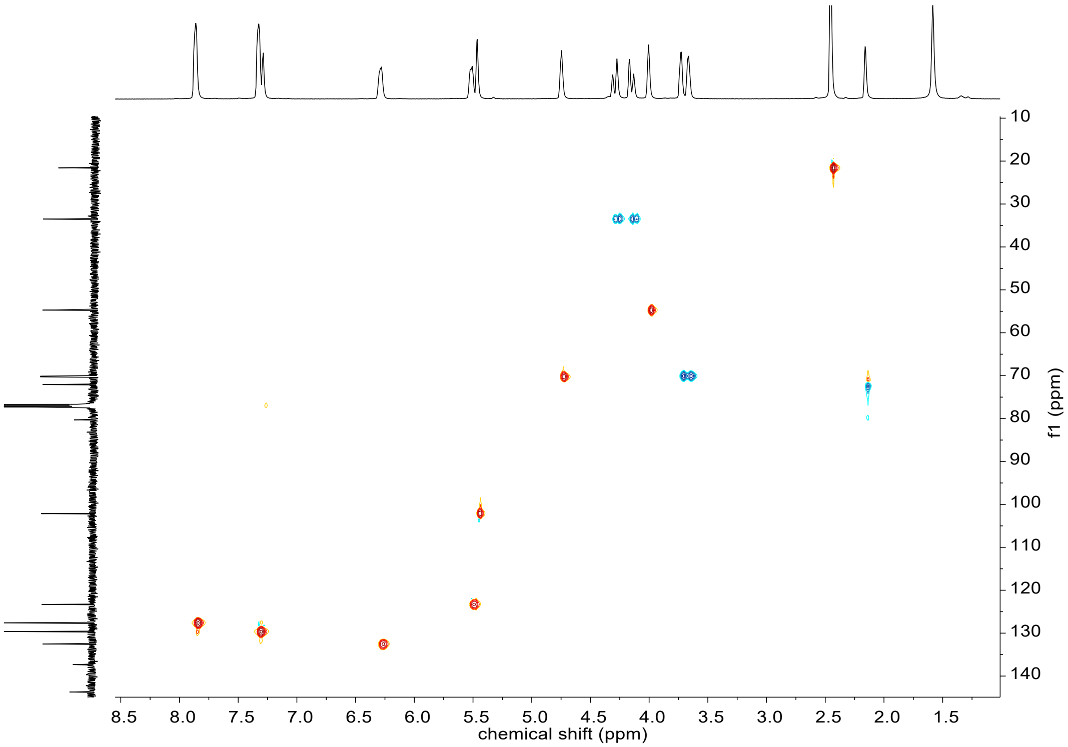
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
chemical shift (ppm)


10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
chemical shift (ppm)

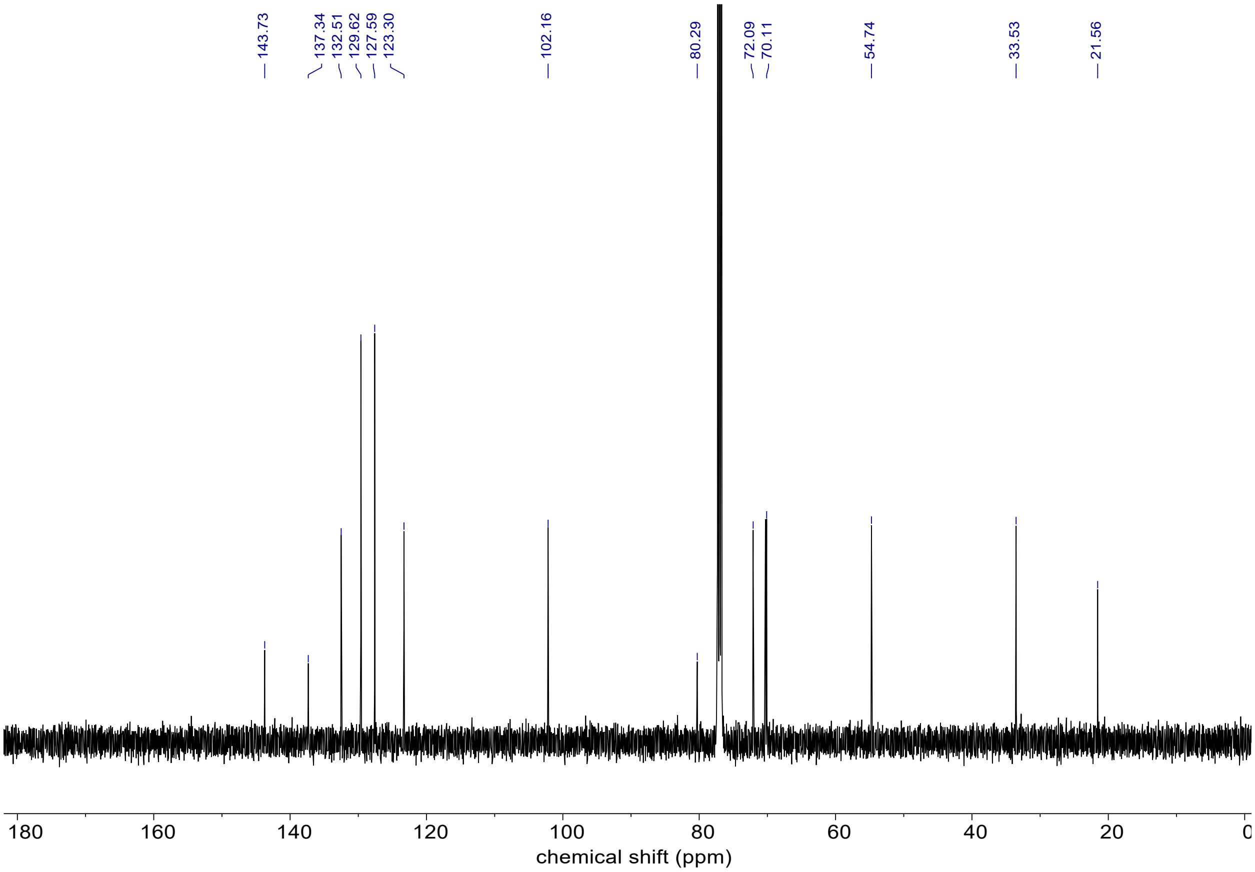
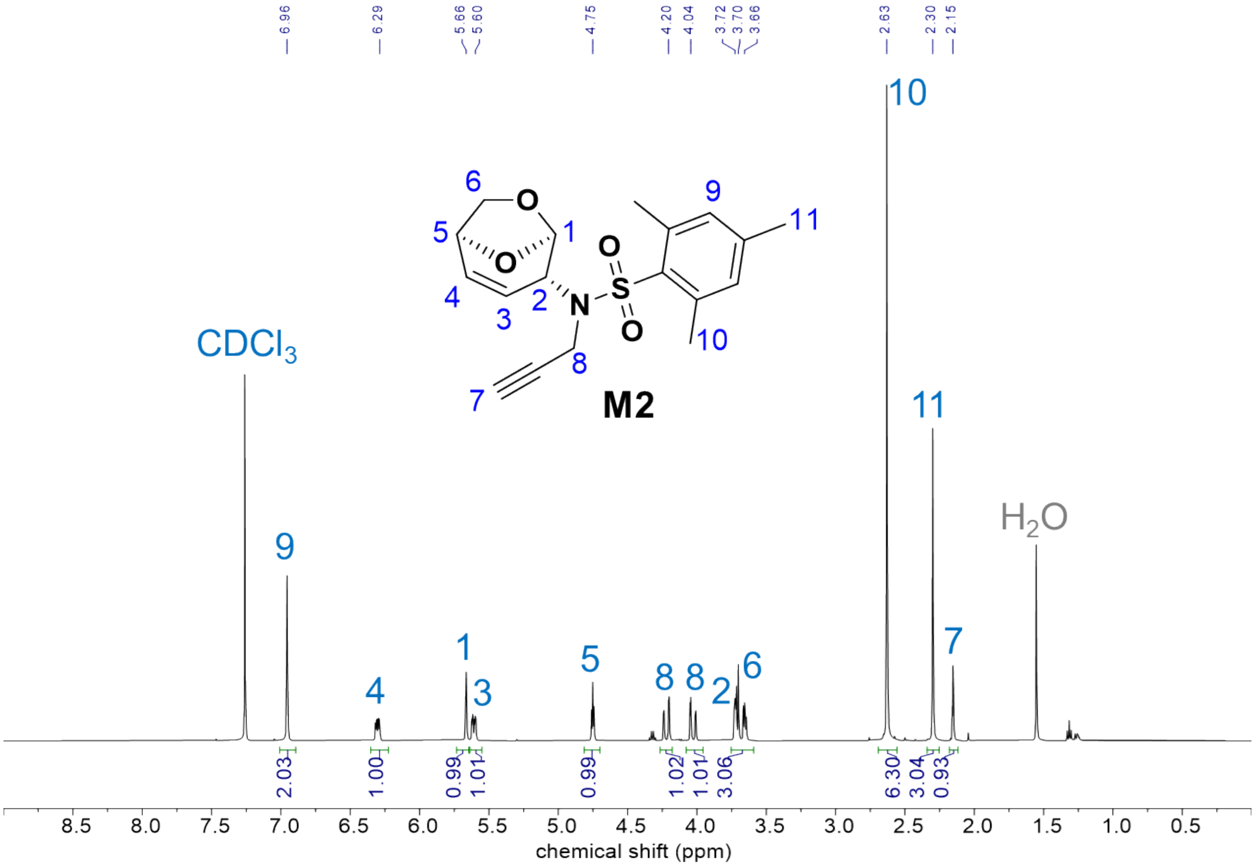
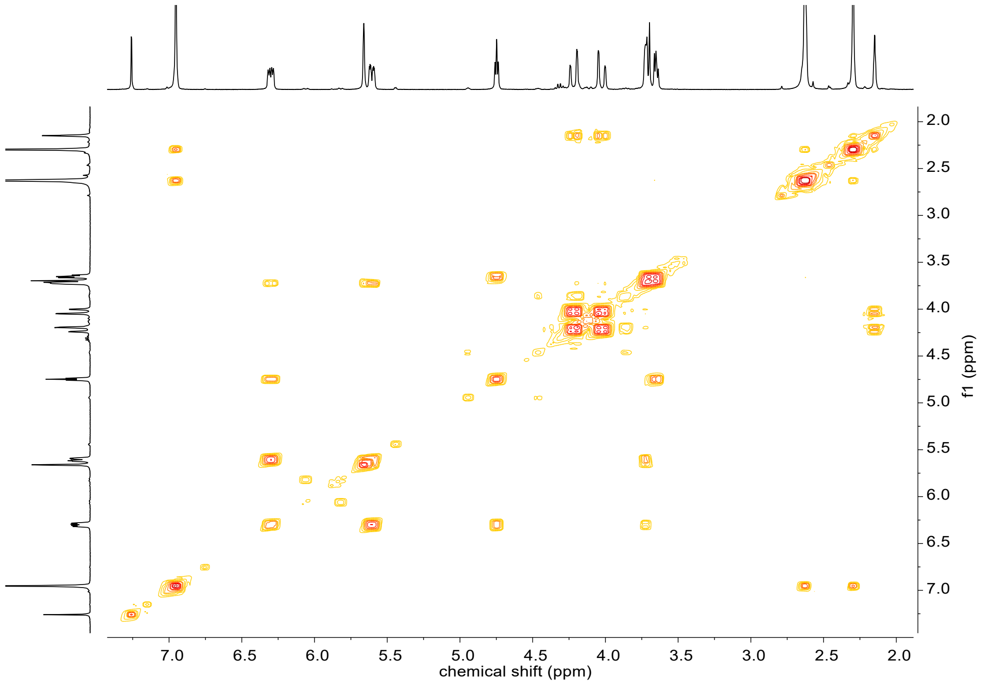


Figure S11. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **M1** [500 MHz, $CDCl_3$].


6.96
6.29
5.66
5.60
4.75
4.20
4.04
3.72
3.70
3.66
2.63
2.30
2.15
CDCl3
9
4
1
3
5
8
8
2
6
10
11
7
H2O
O
O
O
S
O
N
1
2
3
4
5
6
7
8
9
10
11
M2
2.03
1.00
0.99
1.01
0.99
1.02
1.01
3.06
6.30
3.04
0.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
chemical shift (ppm)

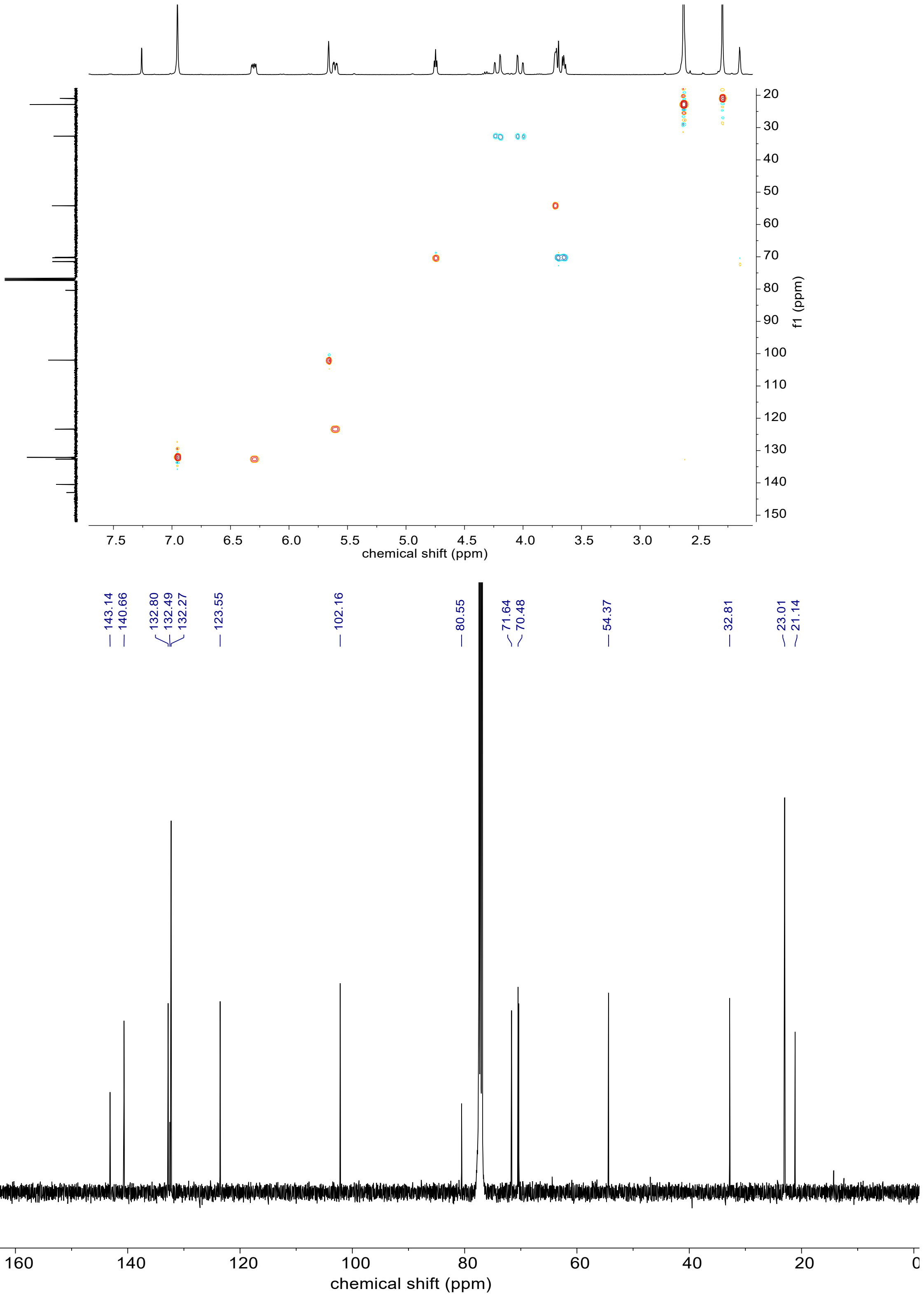
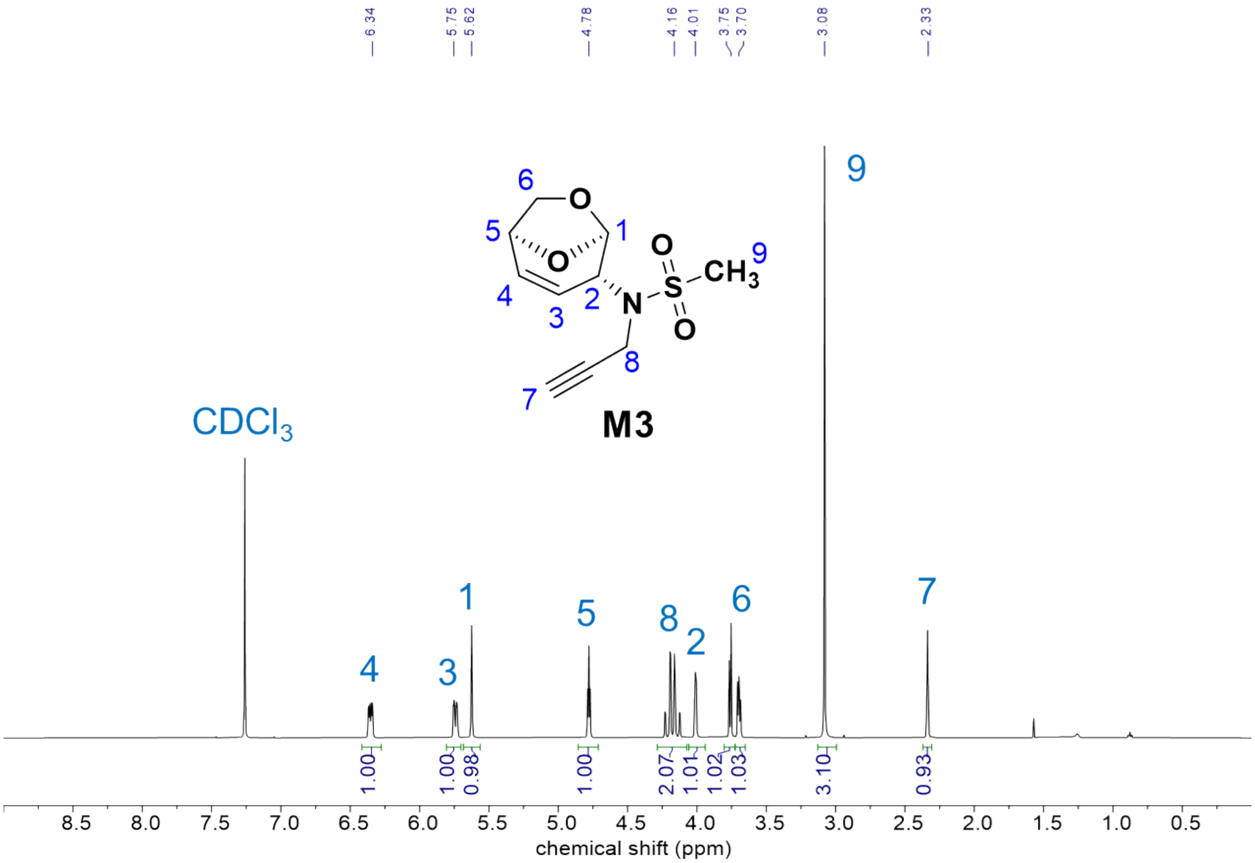
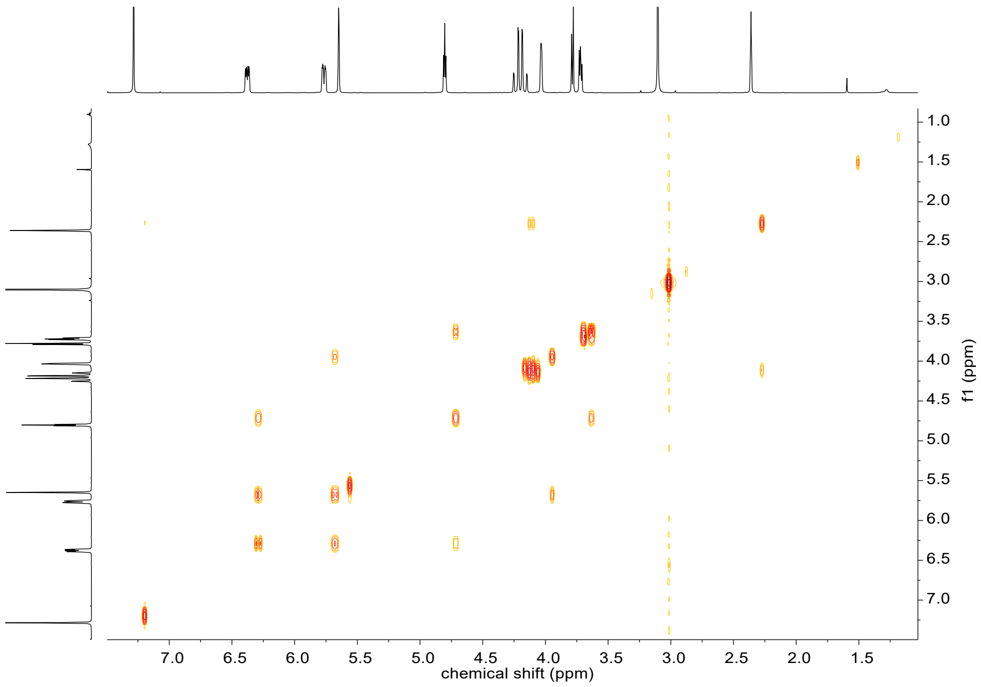


Figure S12. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **M2** [500 MHz, $CDCl_3$].


6.34
5.75
5.62
4.78
4.16
4.01
3.75
3.70
3.08
2.33
CDCl$_3$
M3
6
5
1
O
O
CH$_3$
9
S
4
2
N
3
O
8
7
1
5
8
2
6
9
4
3
7
1.00
1.00
0.98
1.00
2.07
1.01
1.02
1.03
3.10
0.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
chemical shift (ppm)

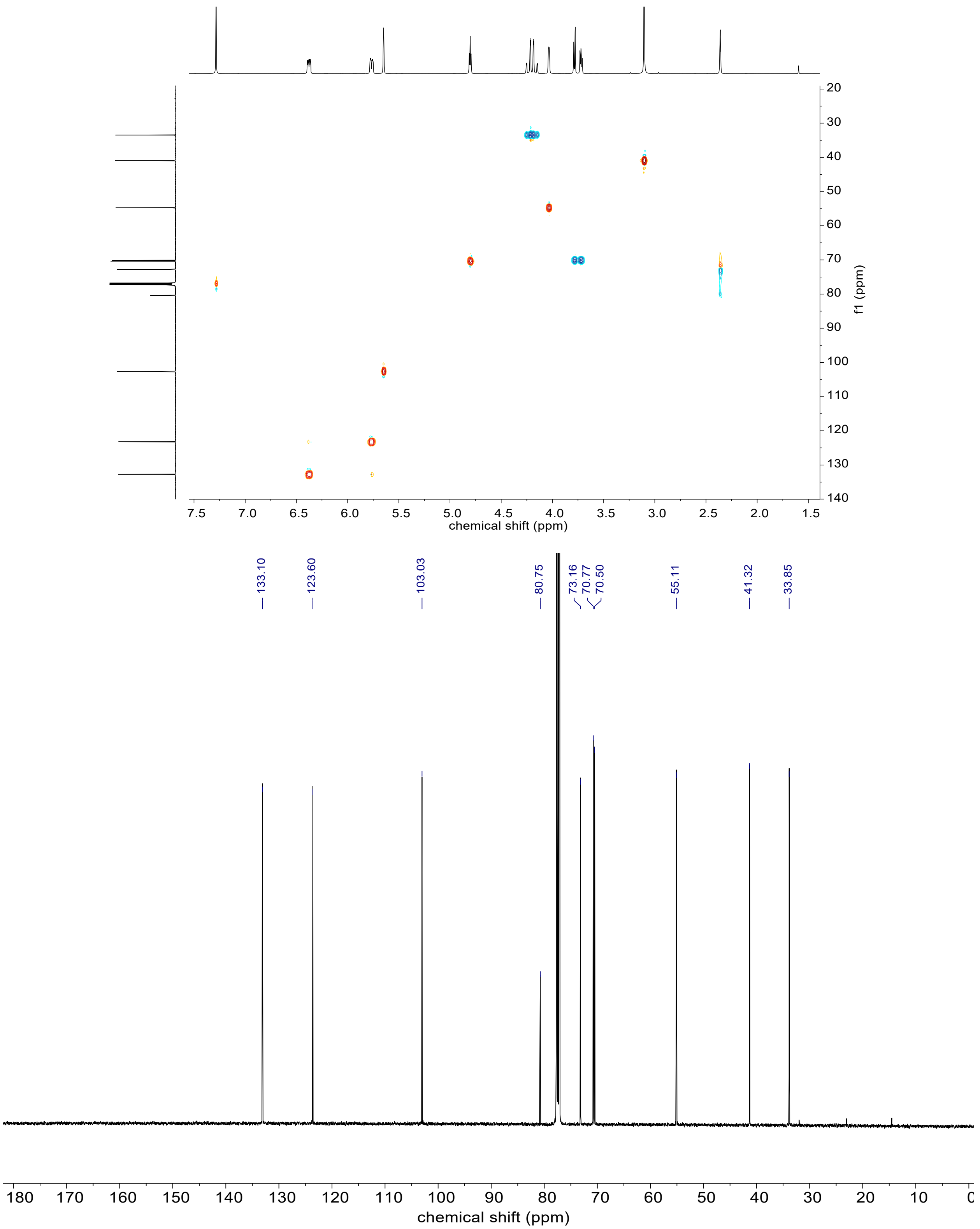
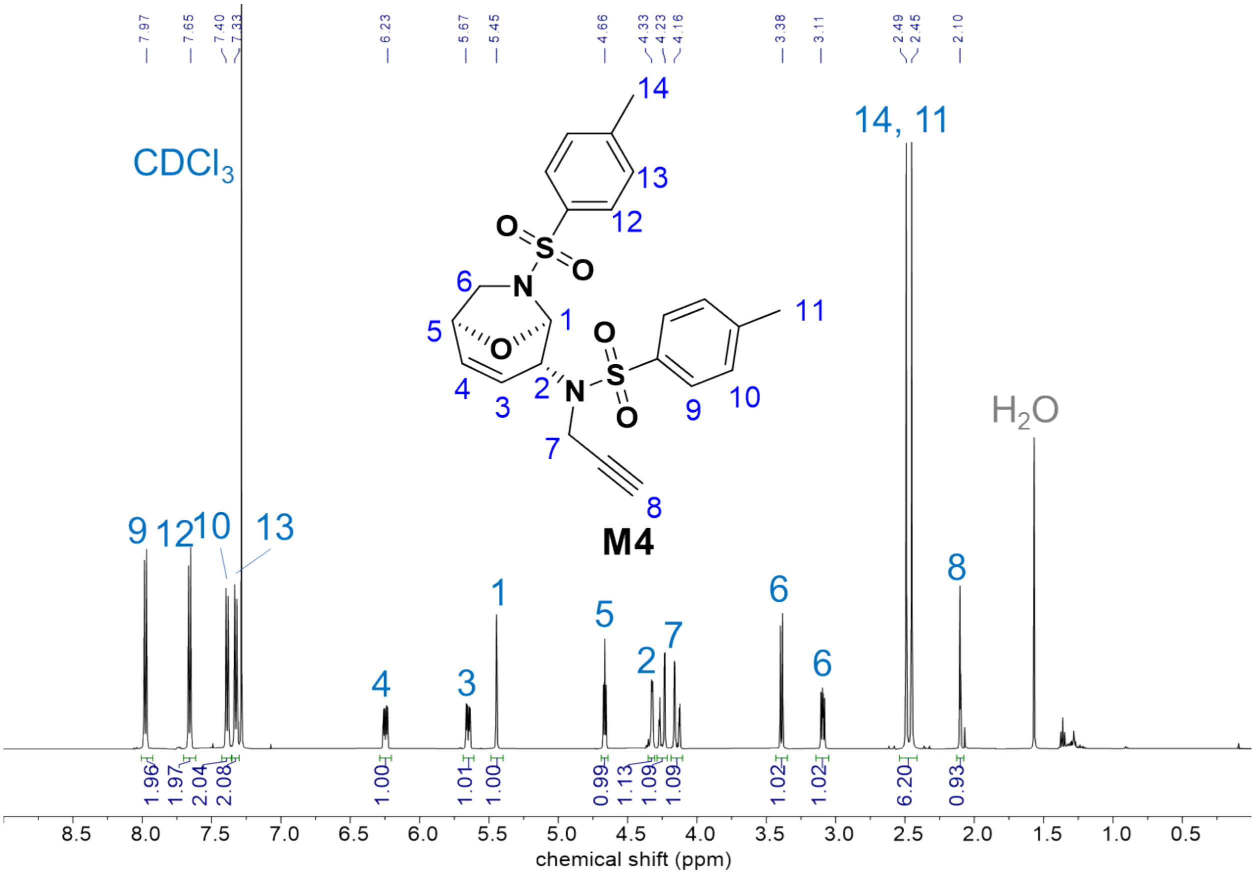
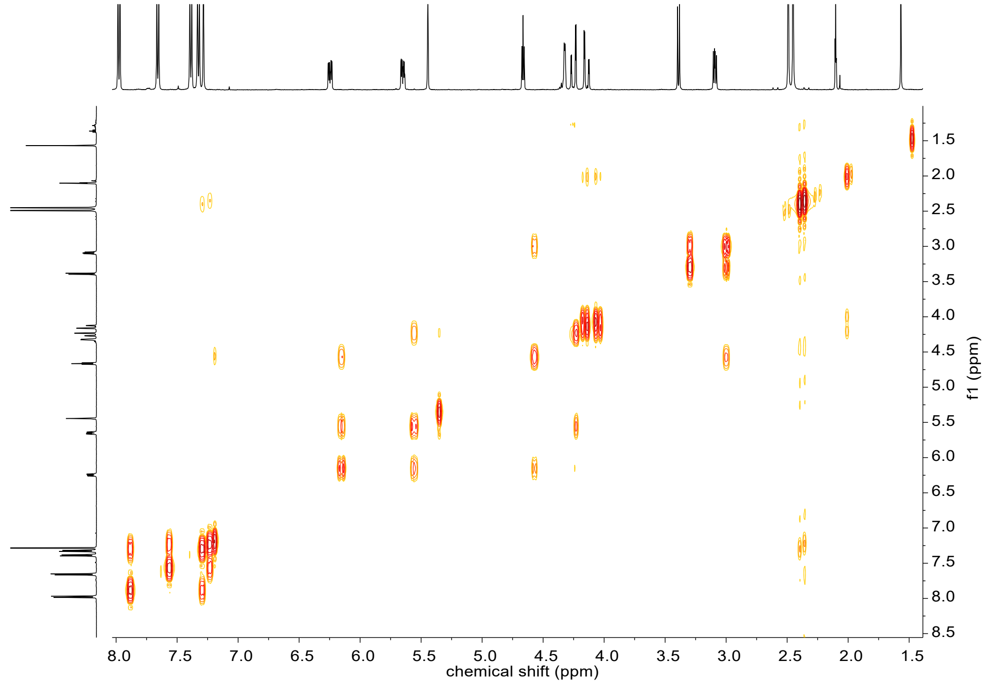


Figure S13. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **M3** [500 MHz, $CDCl_3$].


7.97
7.65
7.40
7.33
6.23
5.67
5.45
4.66
4.33
4.23
4.16
3.38
3.11
2.49
2.45
2.10
CDCl$_3$
14, 11
H_2O
9
12
10
13
4
3
1
5
2
7
6
6
8
1.96
1.97
2.04
2.08
1.00
1.01
1.00
0.99
1.13
1.09
1.09
1.02
1.02
6.20
0.93
M4
14
13
12
11
10
9
1
2
3
4
5
6
7
8
O
S
N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


f1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
chemical shift (ppm)

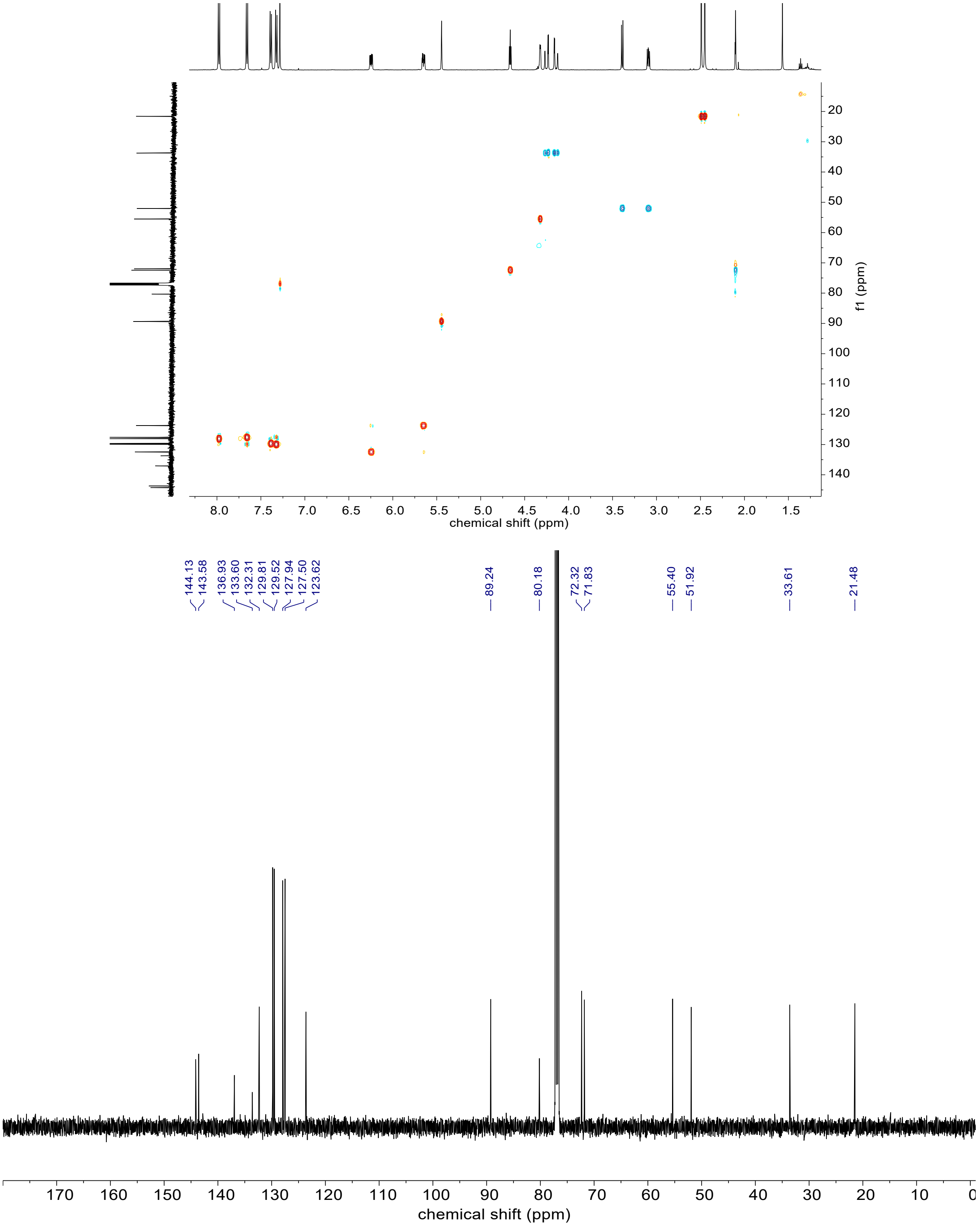
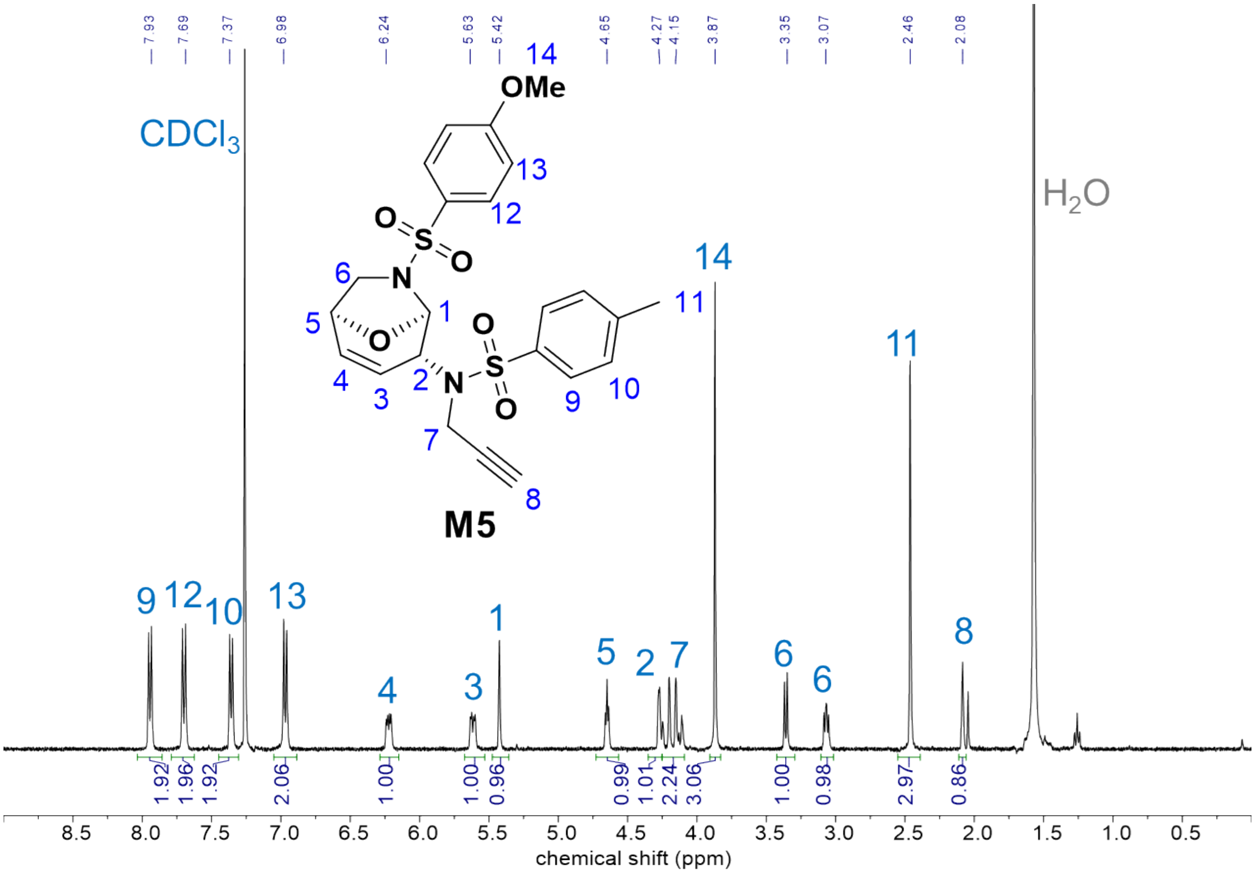
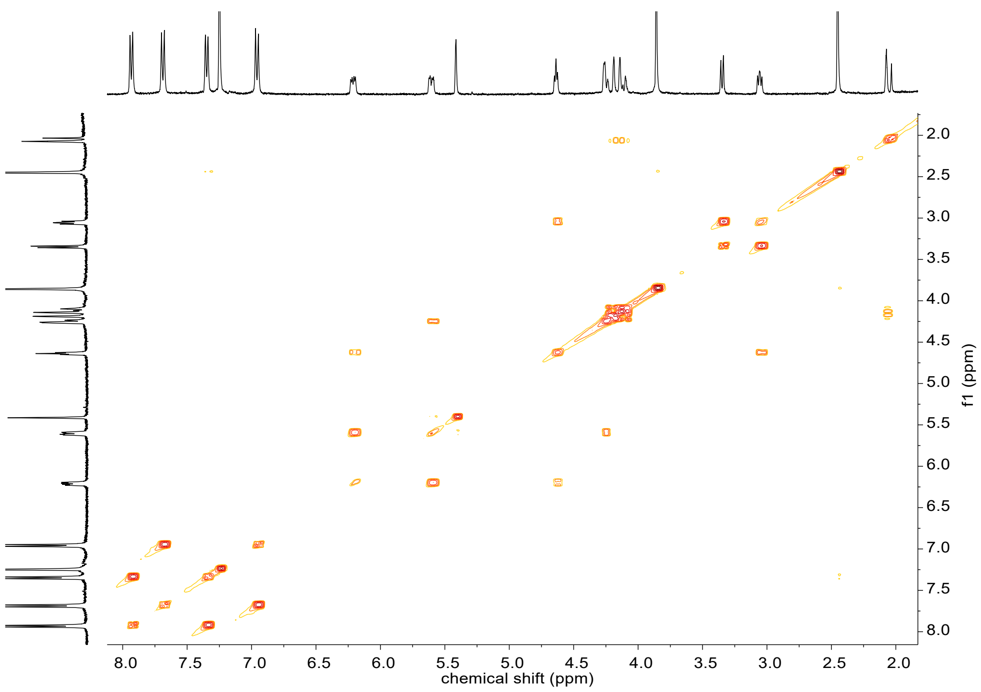


Figure S14. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **M4** [500 MHz, $CDCl_3$].


7.93
7.69
7.37
6.98
6.24
5.63
5.42
4.65
4.27
4.15
3.87
3.35
3.07
2.46
2.08
CDCl$_3$
H$_2$O
14
OMe
13
12
6
N
1
5
O
4
3
2
N
S
O
11
10
9
7
8
M5
9
12
10
13
4
3
1
5
2
7
14
6
6
11
8
1.92
1.96
1.92
2.06
1.00
1.00
0.96
0.99
1.01
2.24
3.06
1.00
0.98
2.97
0.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
chemical shift (ppm)
f1 (ppm)

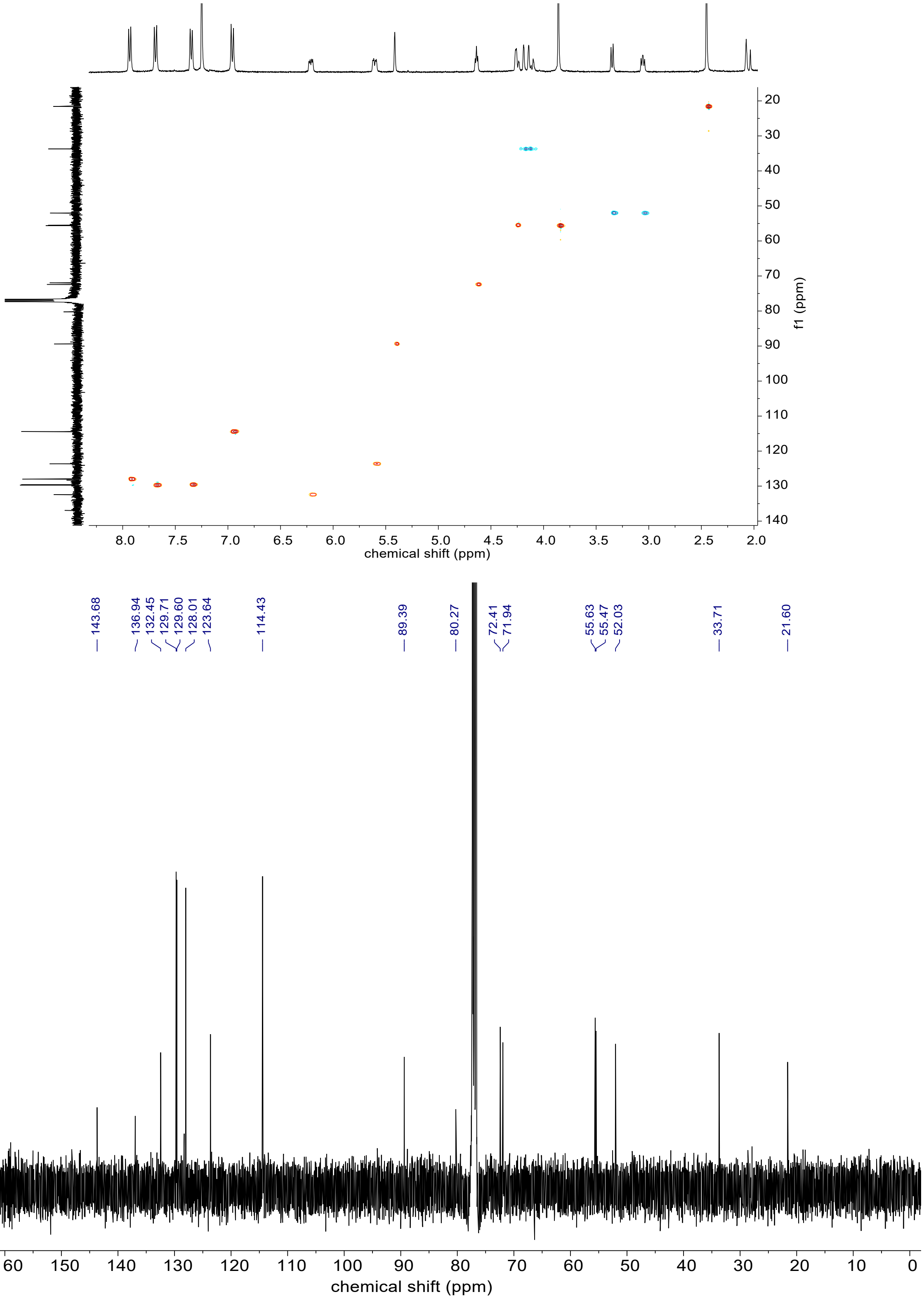
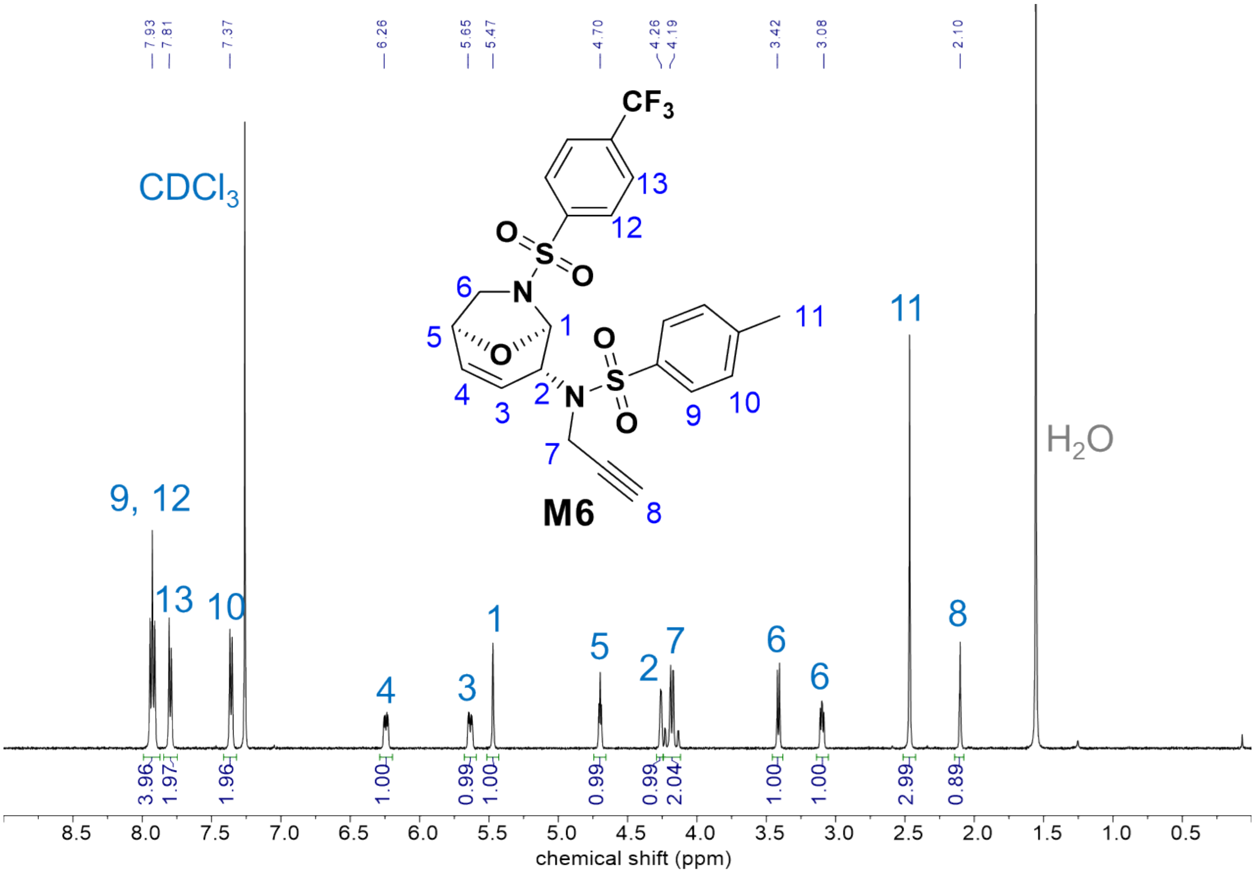
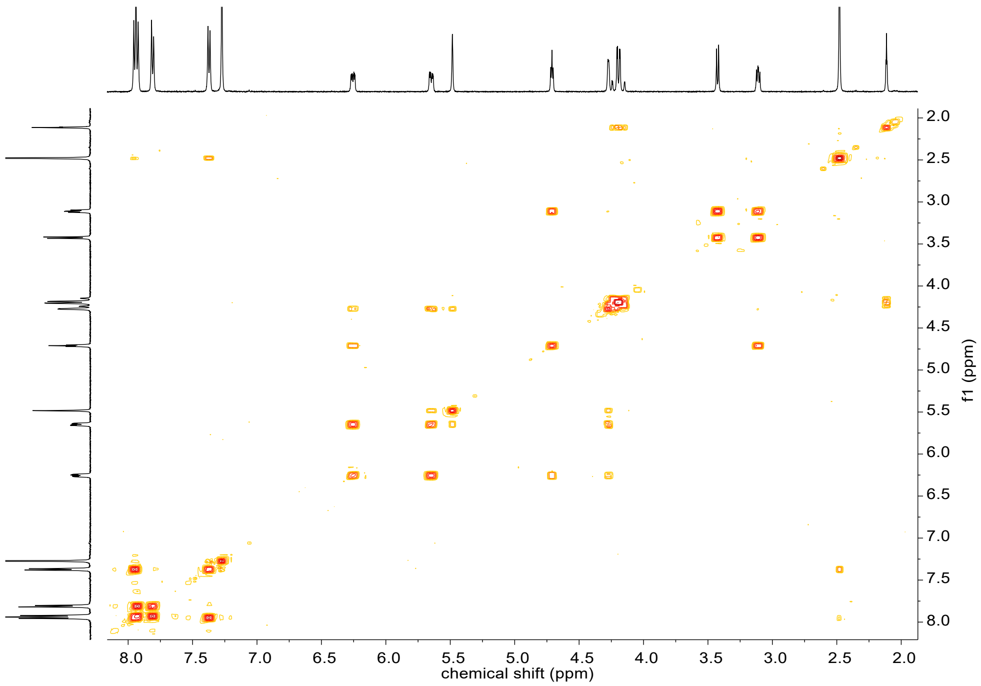


Figure S15. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **M5** [500 MHz, $CDCl_3$].


7.93
7.81
7.37
6.26
5.65
5.47
4.70
4.26
4.19
3.42
3.08
2.10
CDCl3
CF3
13
12
O
S
O
6
N
1
5
O
11
O
S
4
3
2
N
O
9
10
7
M6
8
H2O
9, 12
13
10
4
3
1
5
2
7
6
6
11
8
3.96
1.97
1.96
1.00
0.99
1.00
0.99
0.99
2.04
1.00
1.00
2.99
0.89
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
chemical shift (ppm)

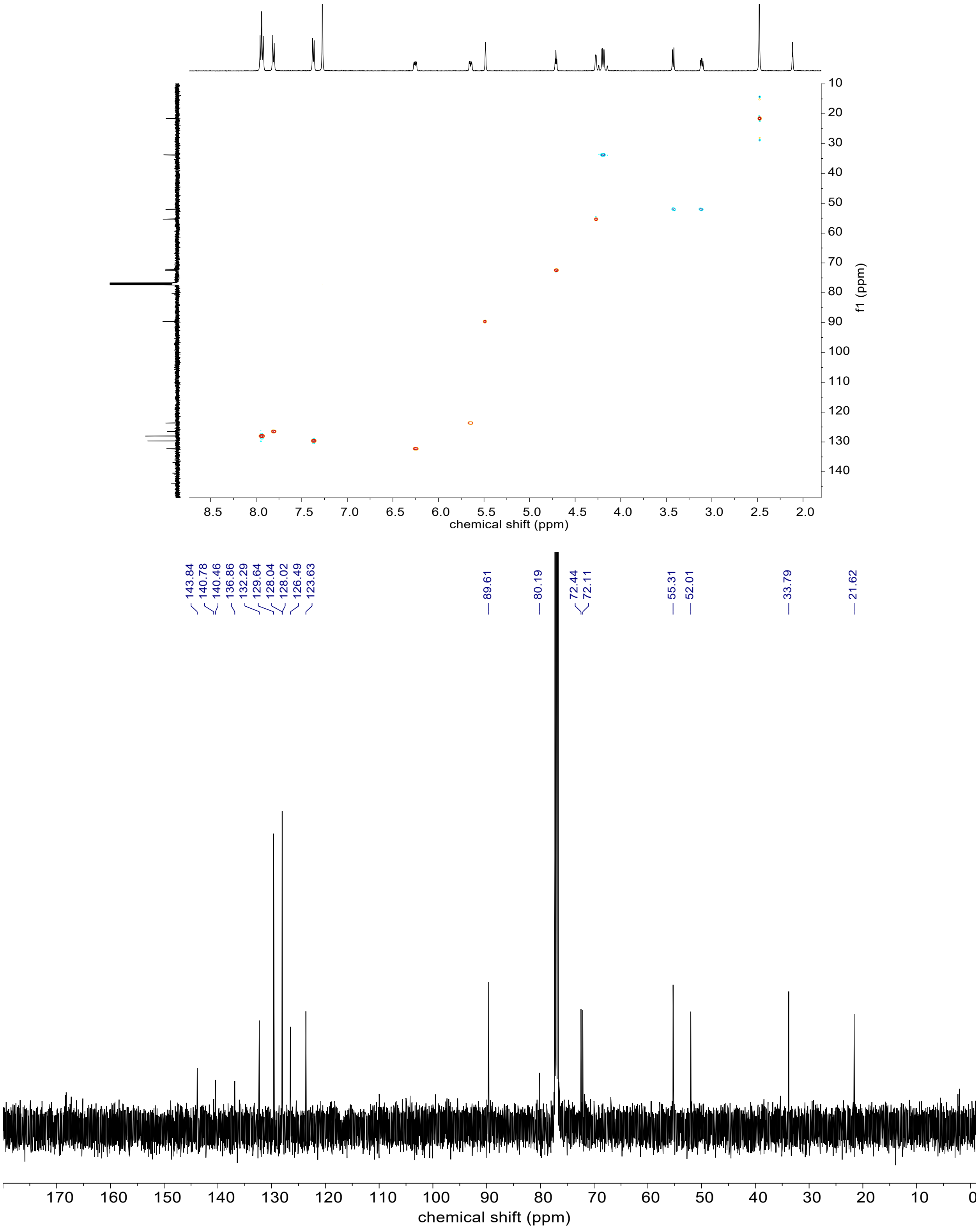
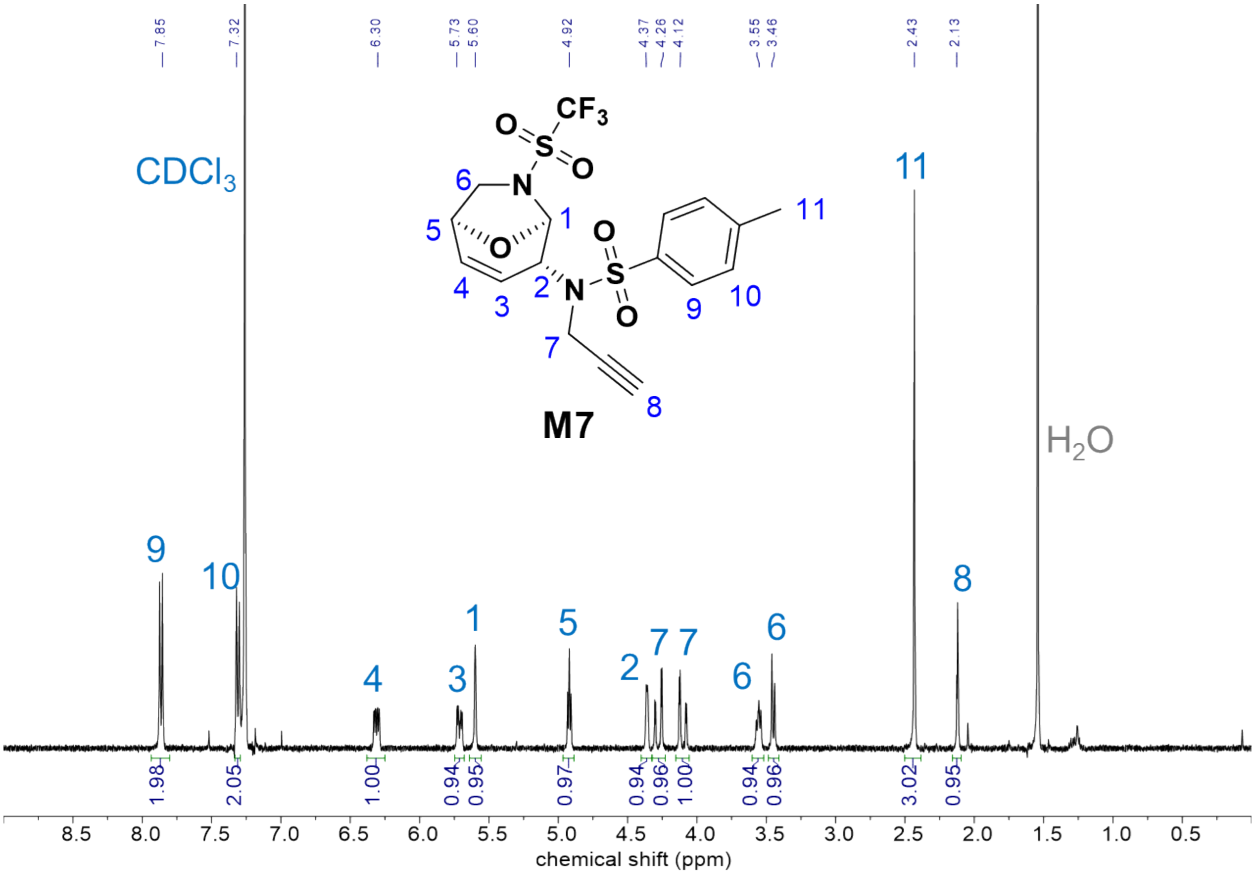
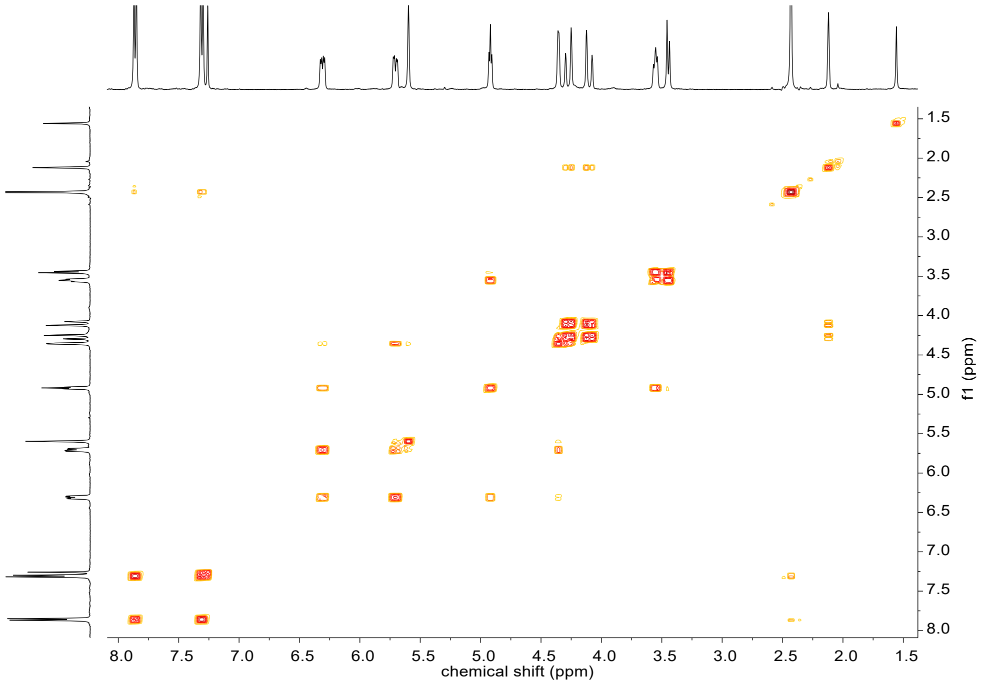


Figure S16. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **M6** [500 MHz, CDCl$_3$].


7.85
7.32
6.30
5.73
5.60
4.92
4.37
4.26
4.12
3.55
3.46
2.43
2.13
CDCl3
CF3
O
S
O
N
6
5
O
1
O
S
N
O
11
4
3
2
9
10
7
8
M7
H2O
9
10
4
3
1
5
2
7
7
6
6
11
8
1.98
2.05
1.00
0.94
0.95
0.97
0.94
0.96
1.00
0.94
0.96
3.02
0.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
chemical shift (ppm)

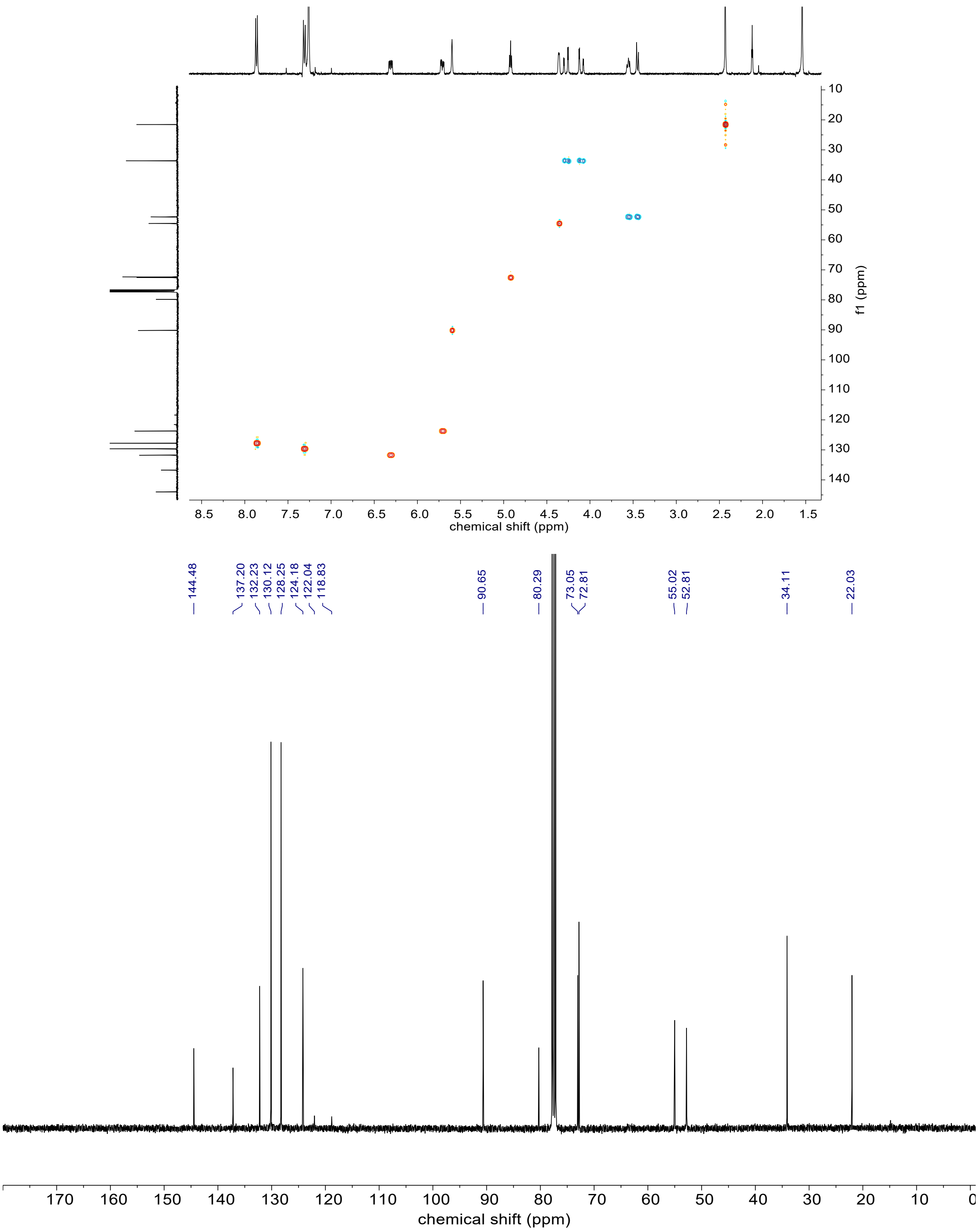
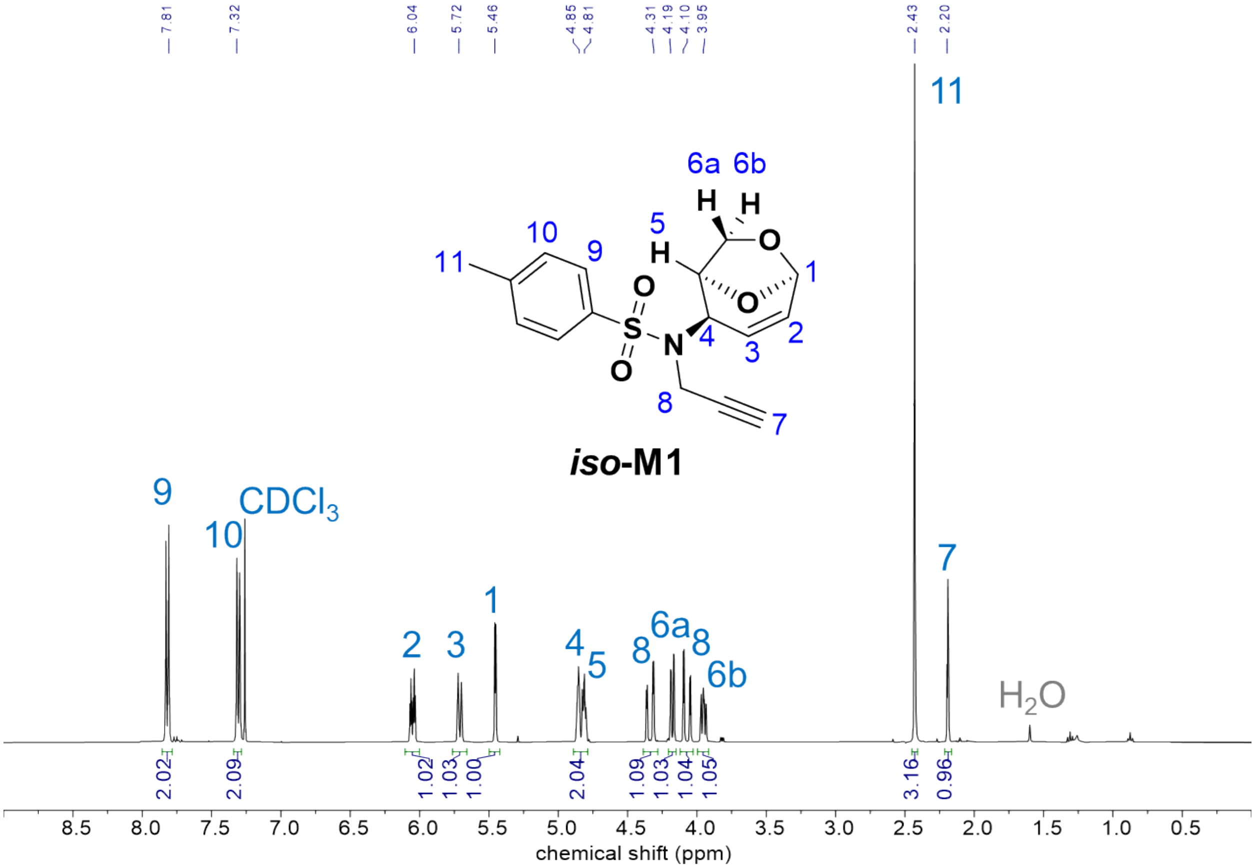
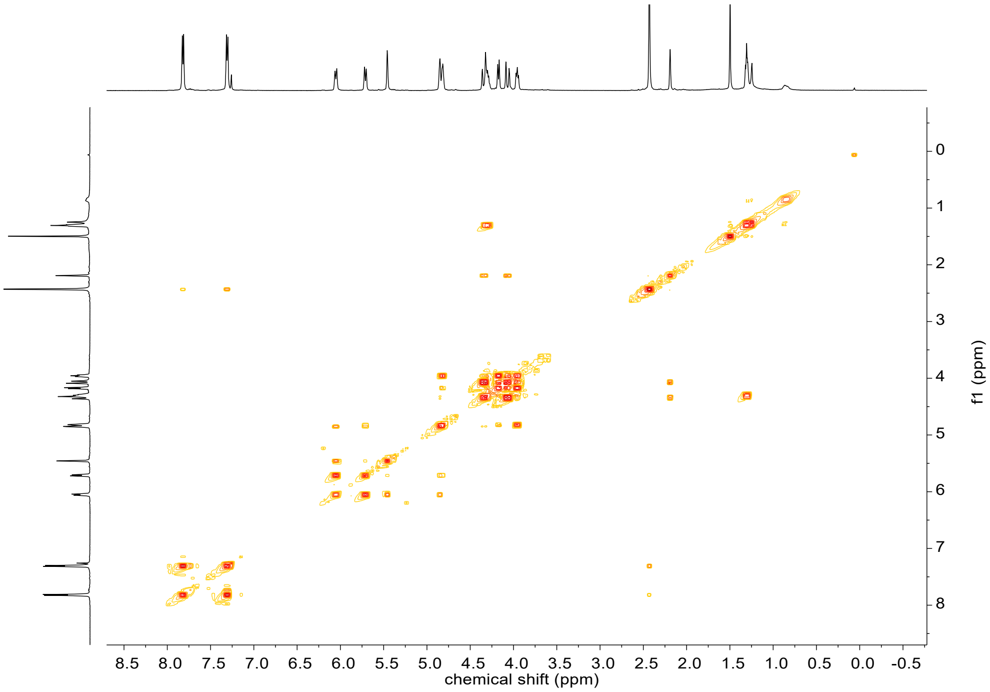


Figure S17. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **M7** [500 MHz, CDCl$_3$].


7.81
7.32
6.04
5.72
5.46
4.85
4.81
4.31
4.19
4.10
3.95
2.43
2.20
11
6a 6b
H H
5
H
O
10 9
1
O
S
O
N
4
3 2
O
8
7
iso-M1
9
CDCl$_3$
10
2 3
1
4 5
8 6a 8
6b
7
H$_2$O
2.02
2.09
1.02
1.03
1.00
2.04
1.09
1.03
1.04
1.05
3.16
0.96
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
chemical shift (ppm)


0
1
2
3
4
5
6
7
8
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
chemical shift (ppm)

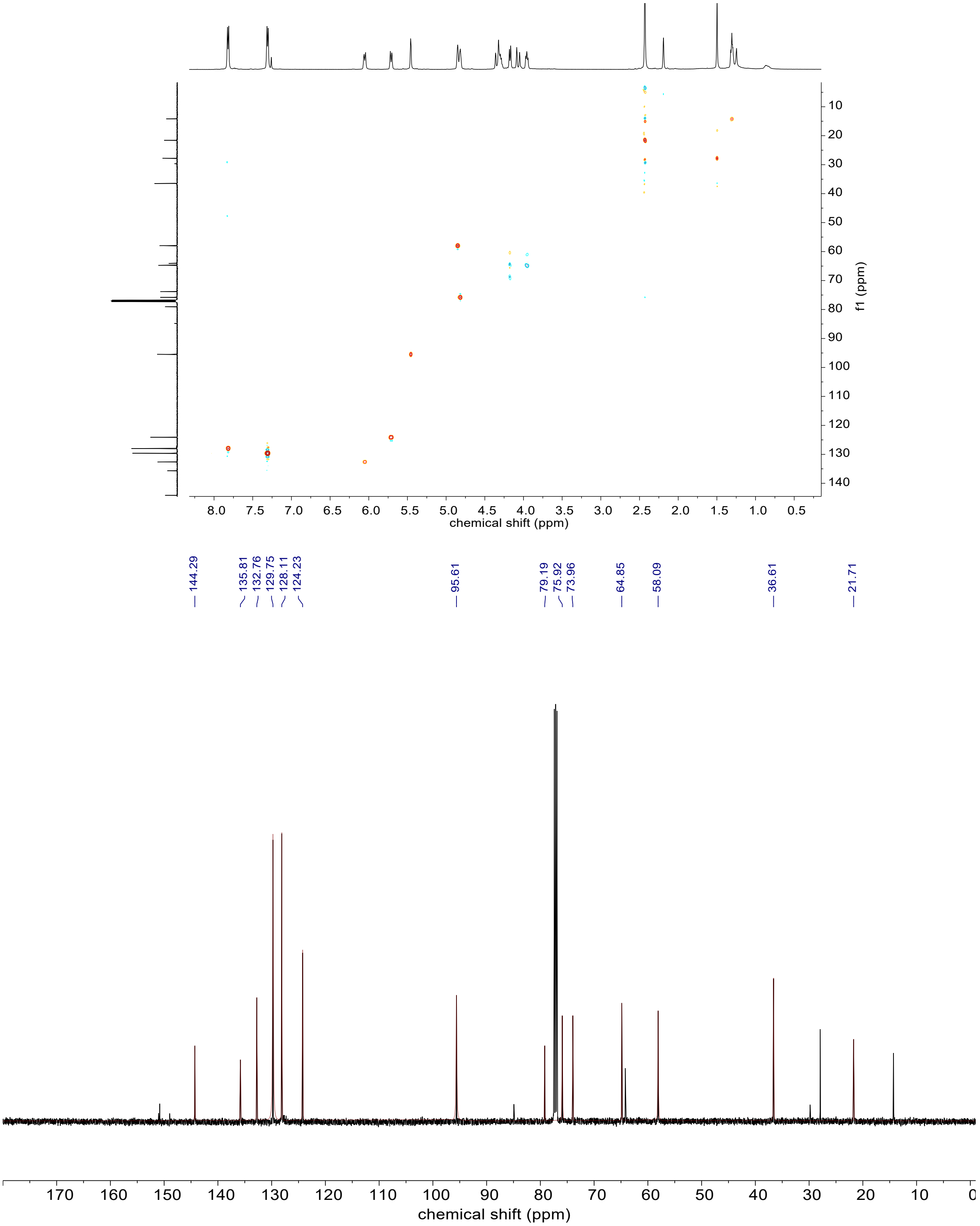


Figure S18. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for ***iso*-M1** [500 MHz, $CDCl_3$].

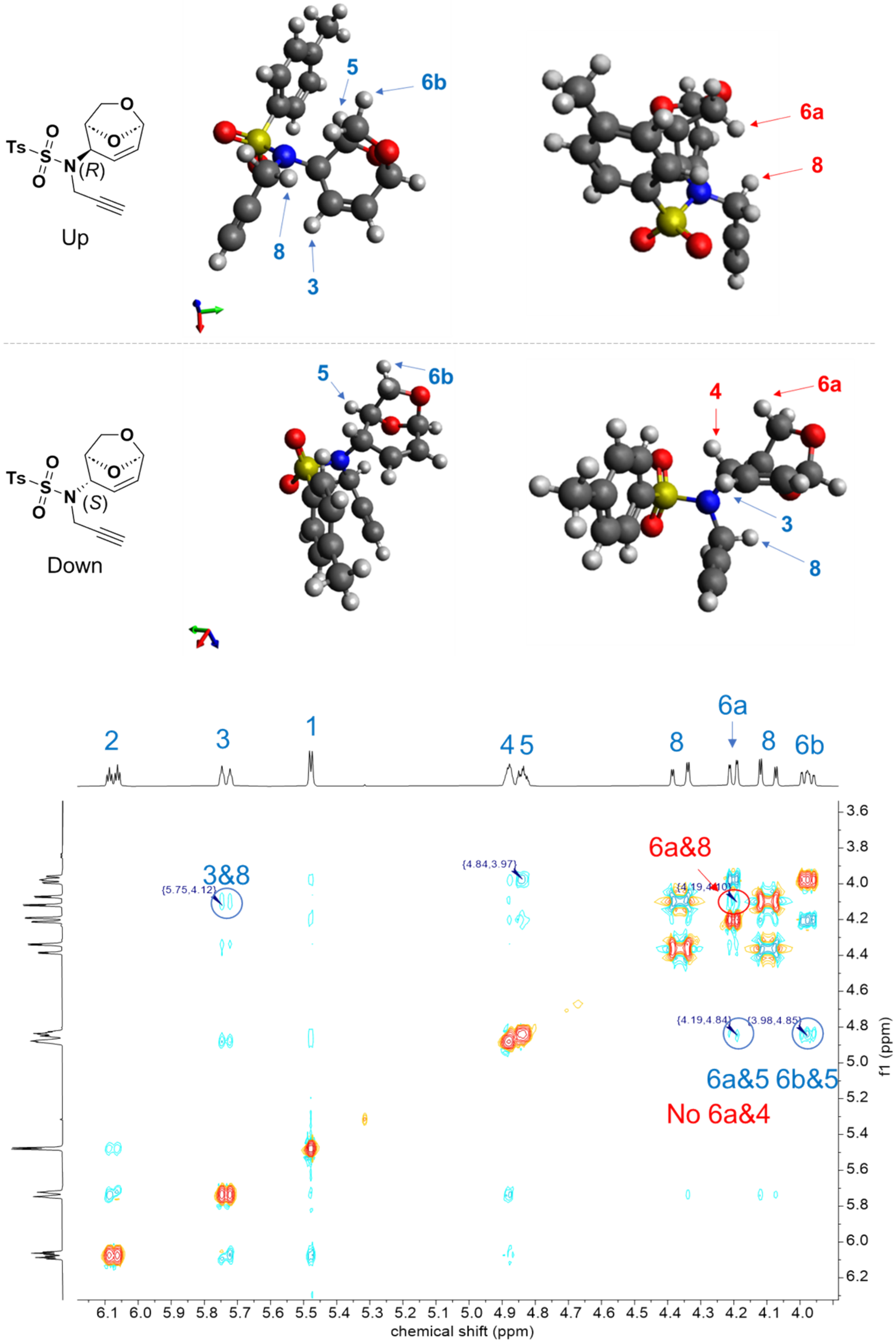
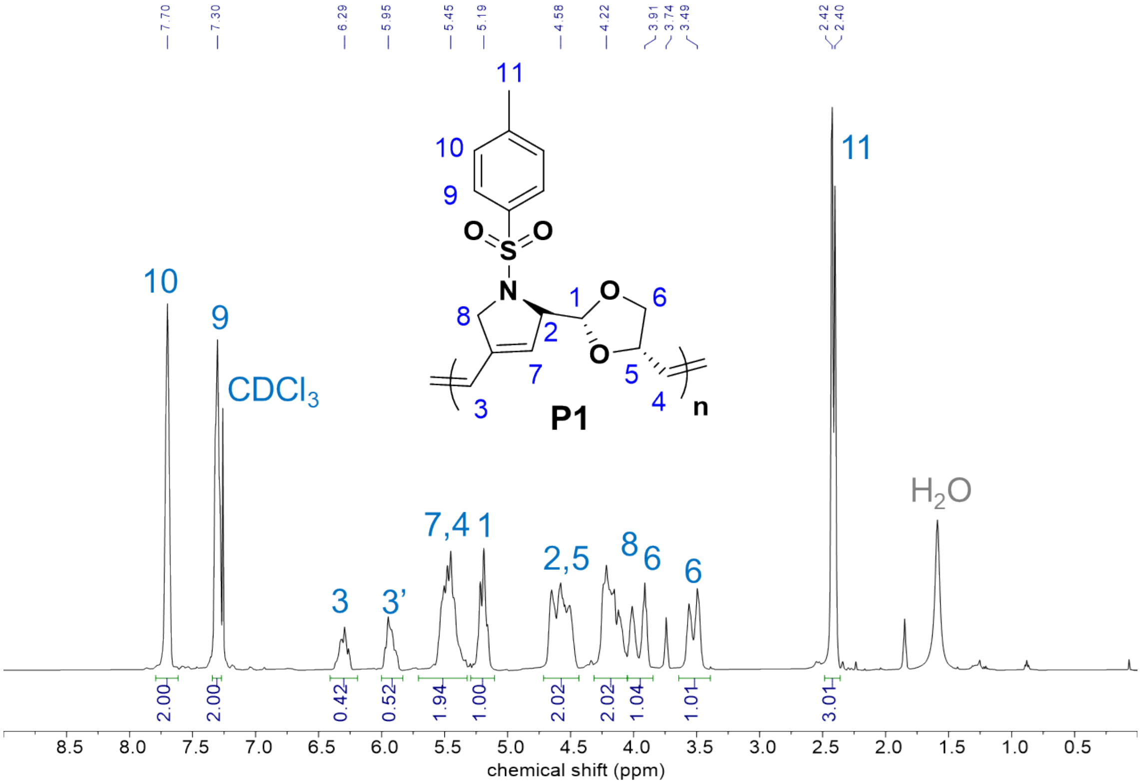
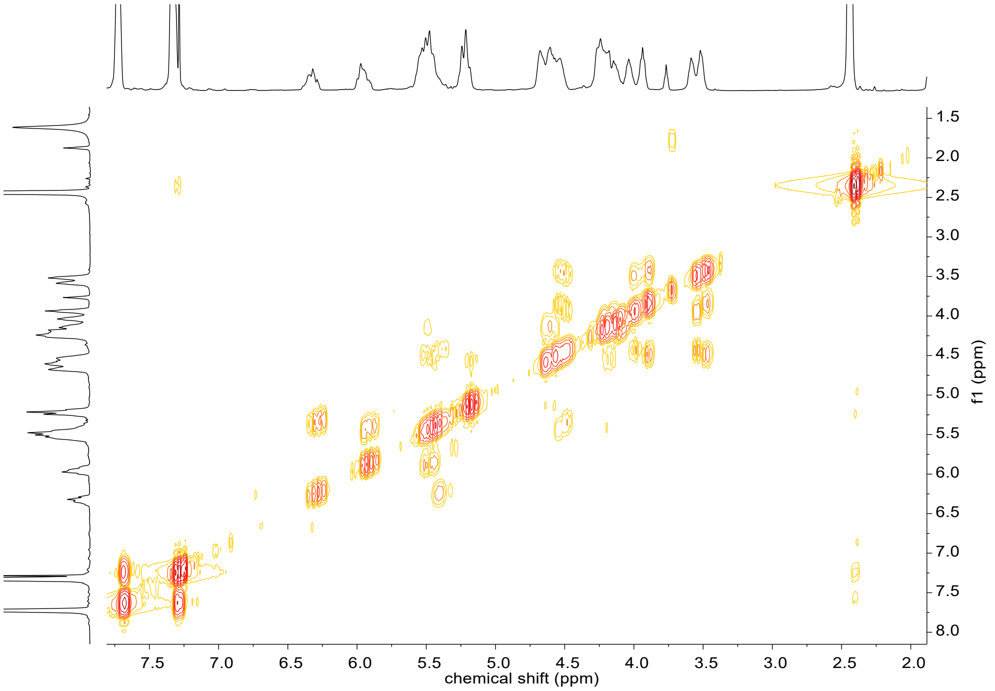


Figure S19. 3D structure of ***iso*-M1** (*R*) and **M1** (*S*) by geometry optimization (top). 2D-NOESY NMR spectra for ***iso*-M1** [500 MHz, $CDCl_3$].

4.2 Polymers

Polymers ^1H NMR spectra were assigned with the aid of 2D COSY and HSQC NMR spectroscopy.





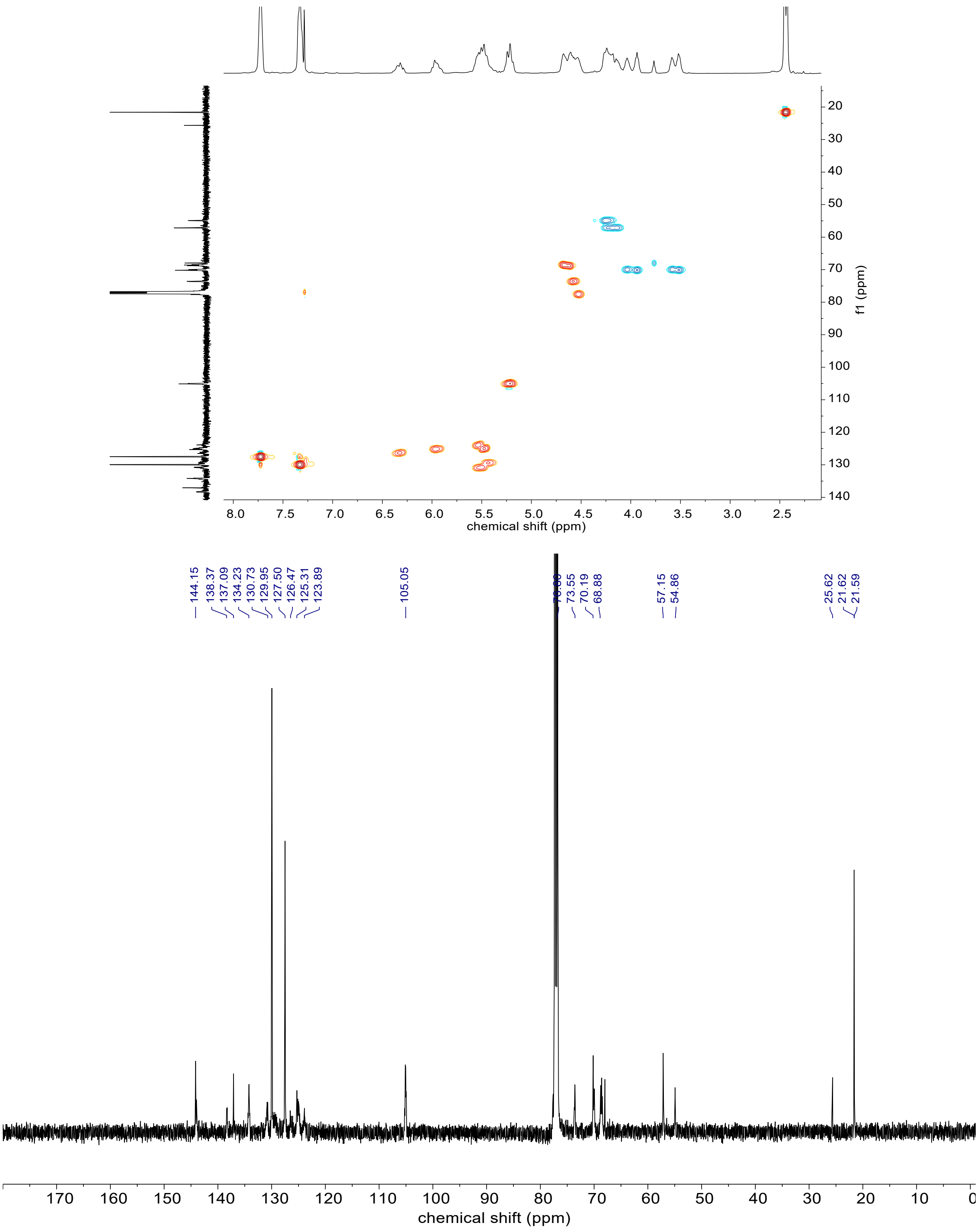
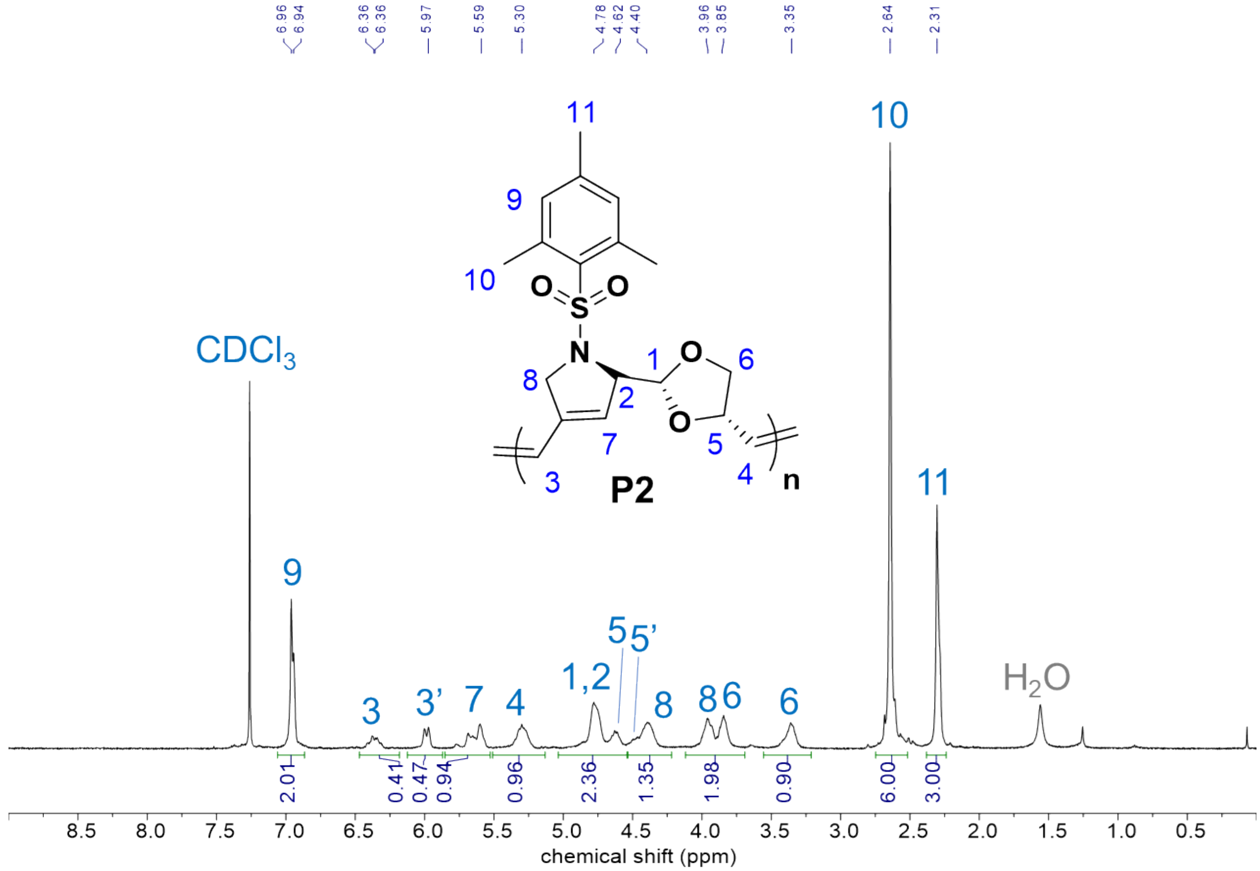
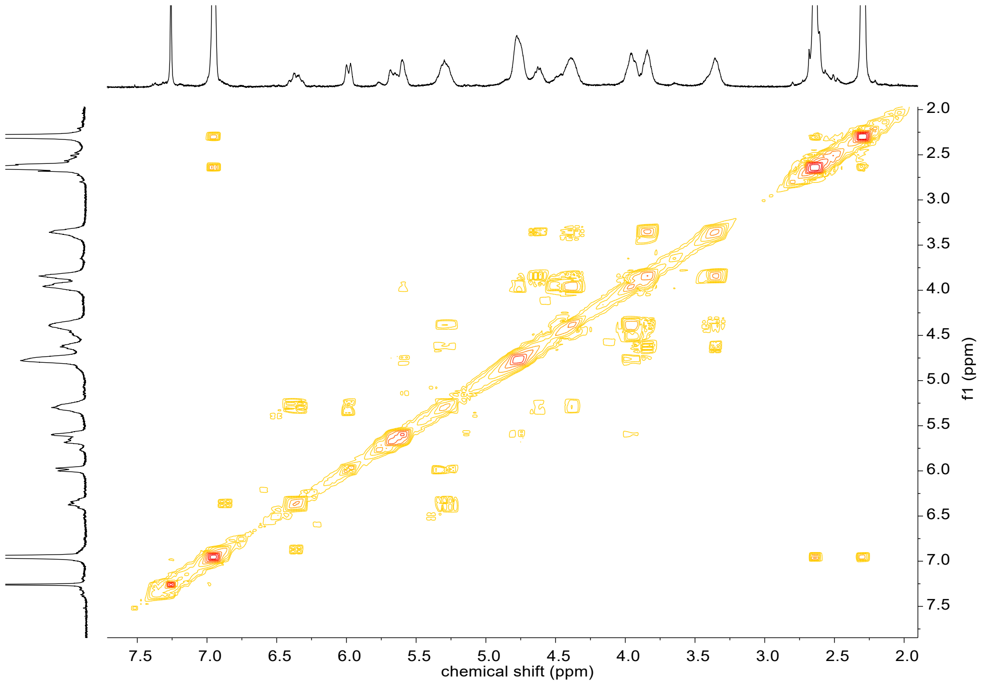


Figure S20. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **P1** [500 MHz, CDCl$_3$].


6.96
6.94
6.36
6.36
5.97
5.59
5.30
4.78
4.62
4.40
3.96
3.85
3.35
2.64
2.31
11
9
10
O
S
O
N
8
1
O
6
2
O
7
5
3
4
n
P2
CDCl$_3$
10
11
9
3
3’
7
4
1,2
5
5’
8
8
6
6
H$_2$O
2.01
0.41
0.47
0.94
0.96
2.36
1.35
1.98
0.90
6.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
chemical shift (ppm)

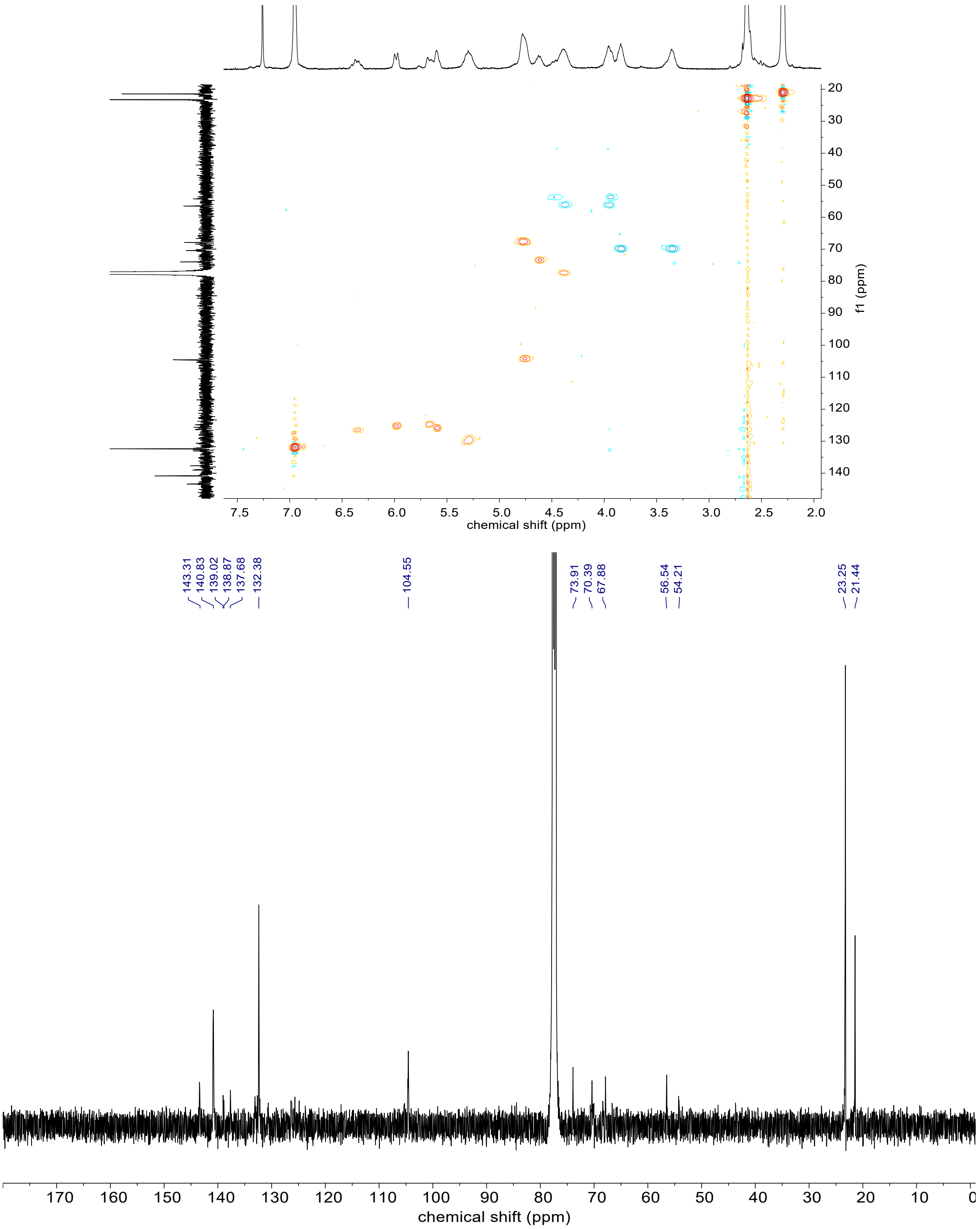
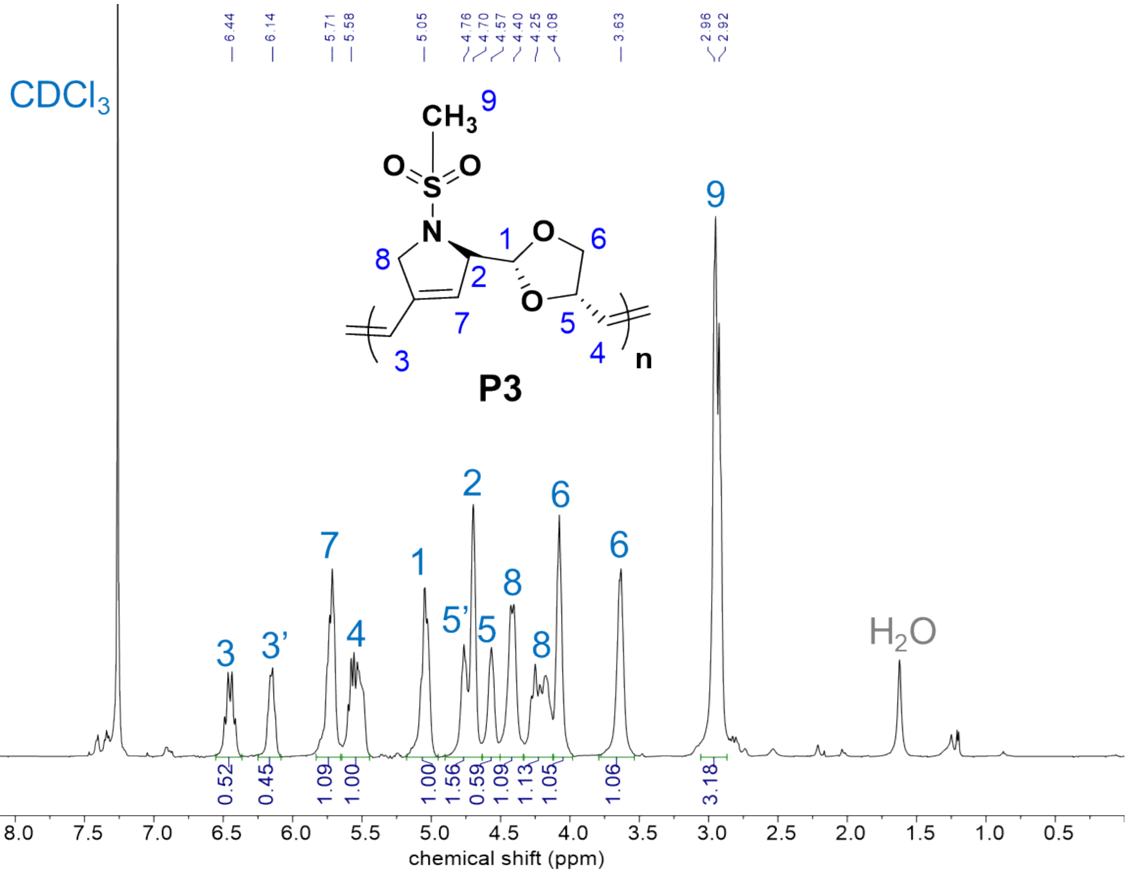
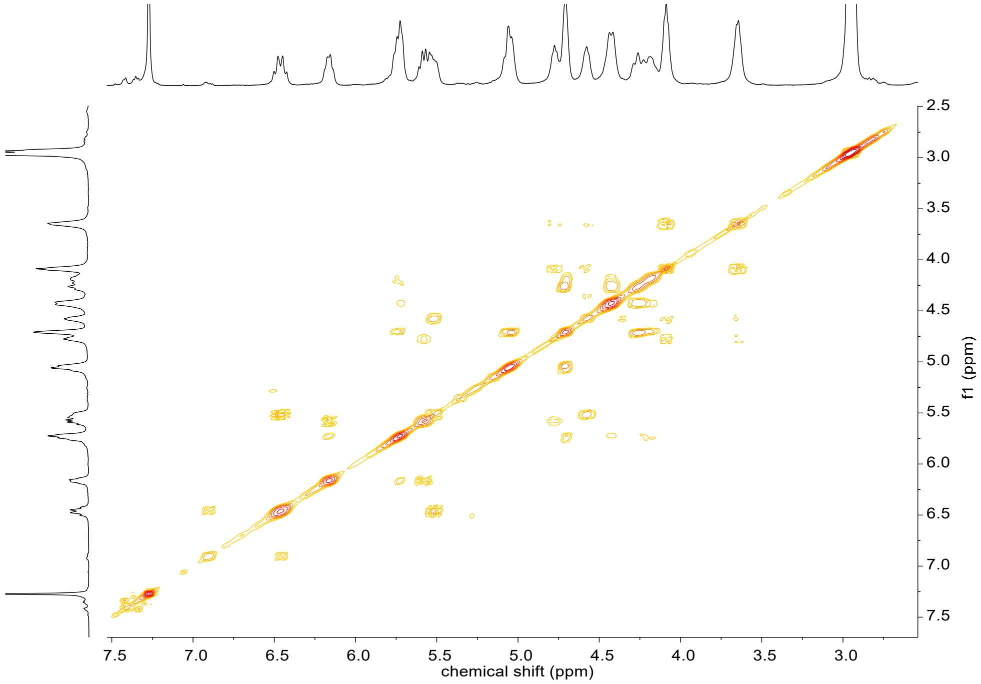


Figure S21. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **P2** [500 MHz, $CDCl_3$].



6.44
6.14
5.71
5.58
5.05
4.76
4.70
4.57
4.40
4.25
4.08
3.63
2.96
2.92
CDCl$_3$
CH$_3$ 9
O
S
O
N
8
1
2
O
6
O
5
7
3
4
n
P3
9
2
6
7
1
6
8
5'
5
3
3'
4
8
H$_2$O
0.52
0.45
1.09
1.00
1.00
1.56
0.59
1.09
1.13
1.05
1.06
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)



2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
chemical shift (ppm)

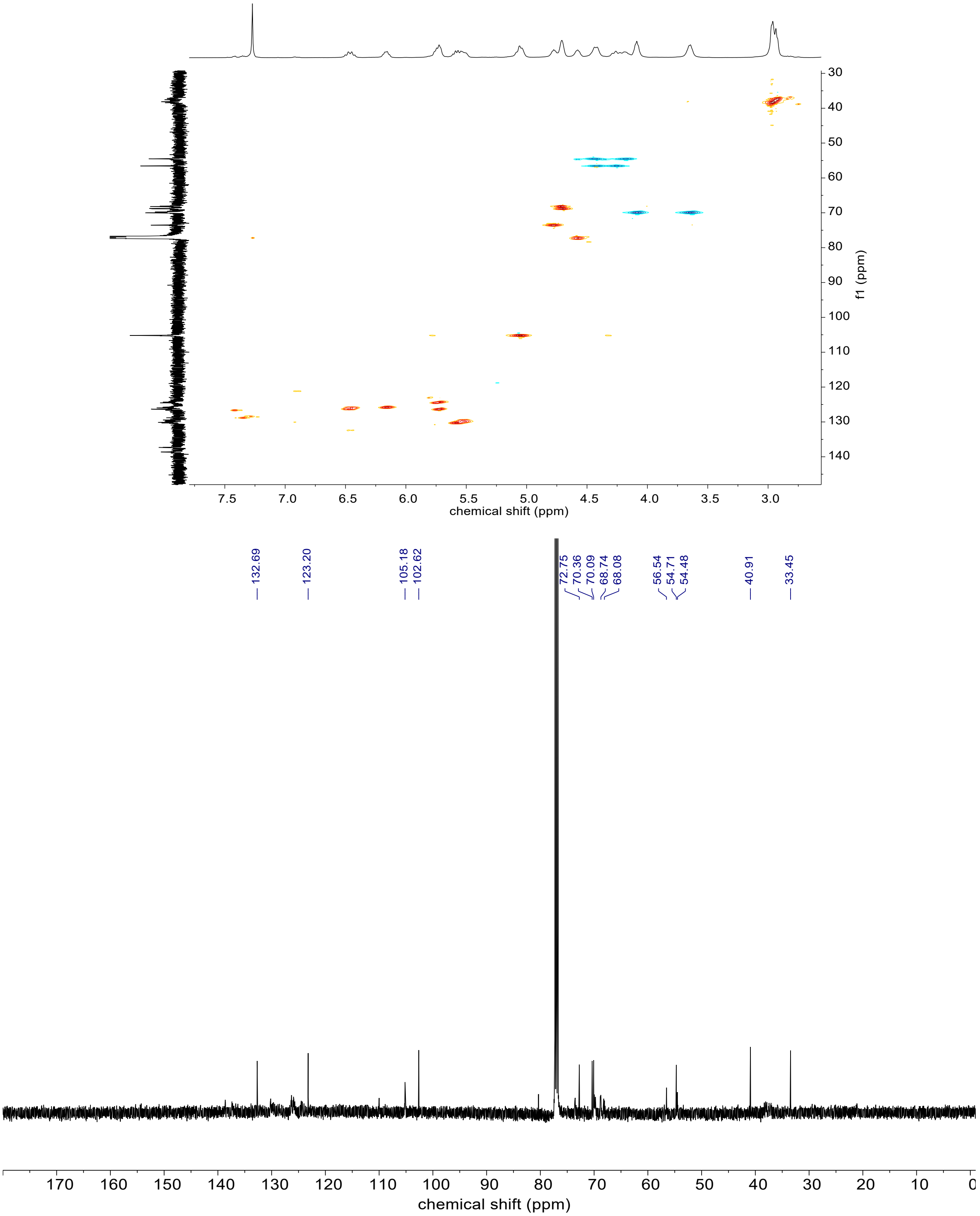
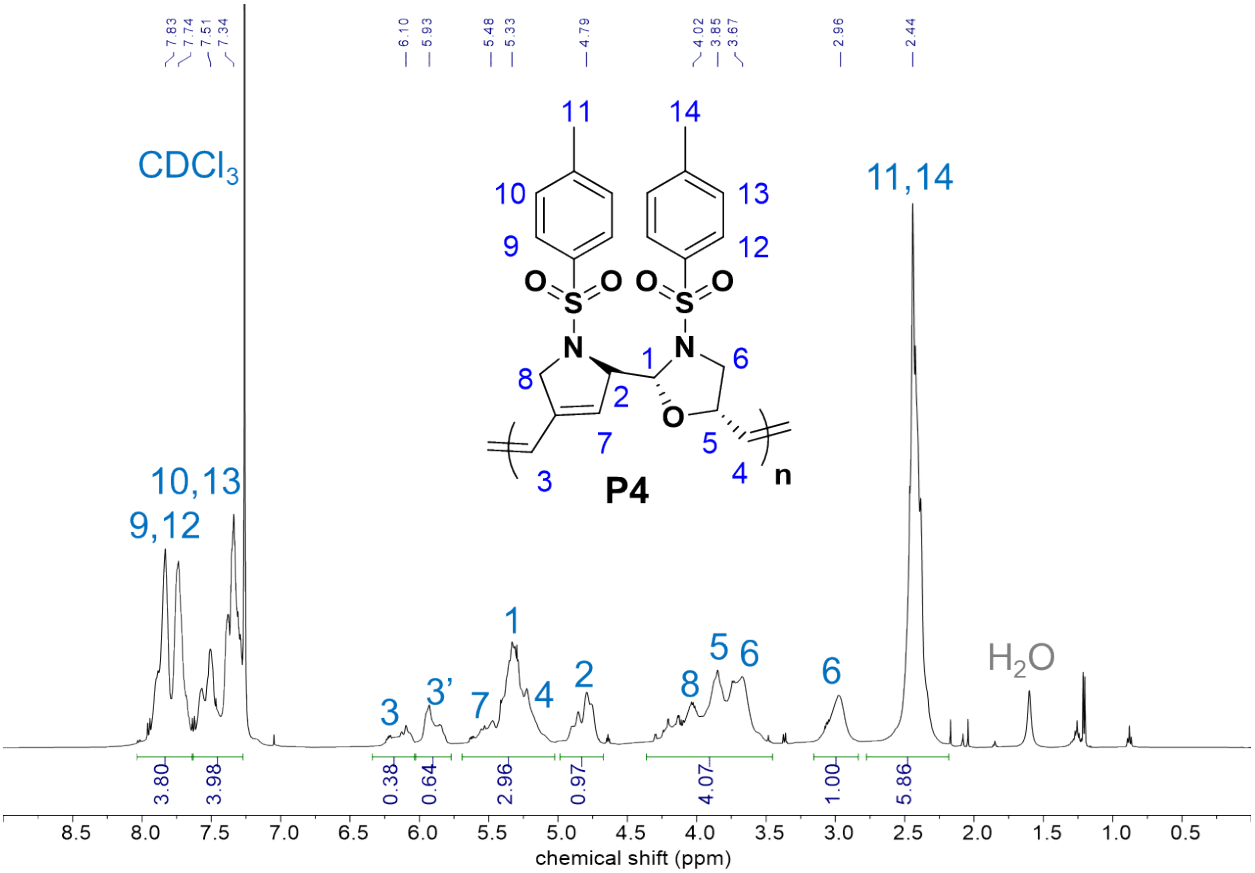
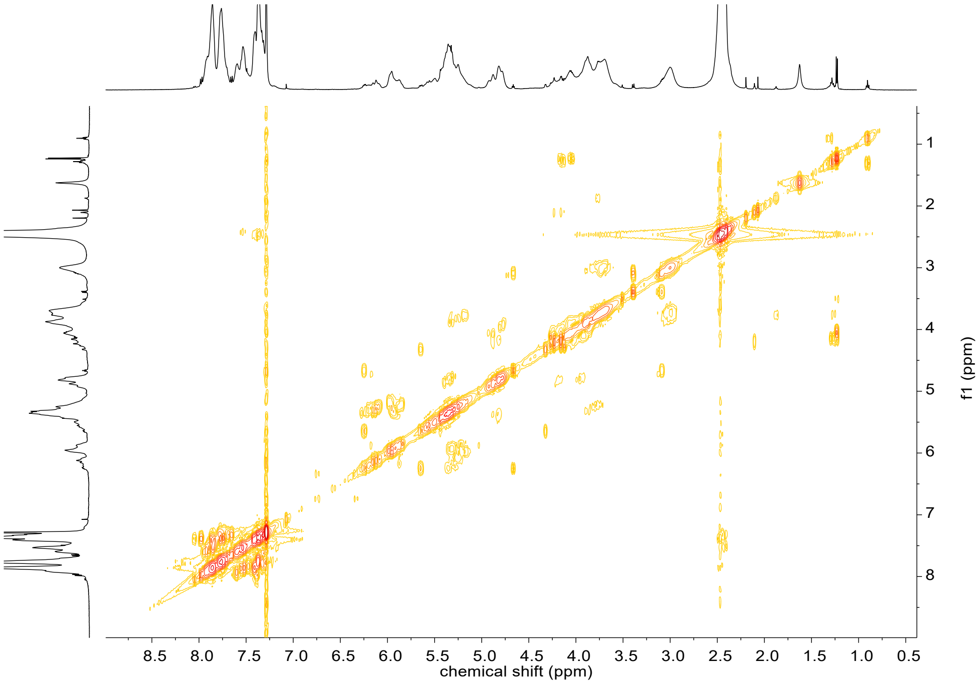


Figure S22. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **P3** [500 MHz, $CDCl_3$].


7.83
7.74
7.51
7.34
6.10
5.93
5.48
5.33
4.79
4.02
3.85
3.67
2.96
2.44
CDCl$_3$
11
14
10
13
9
12
O
S
O
O
S
O
N
N
8
1
6
2
O
7
5
3
4
n
P4
11,14
10,13
9,12
1
3
3'
7
4
2
8
5
6
6
H$_2$O
3.80
3.98
0.38
0.64
2.96
0.97
4.07
1.00
5.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


1
2
3
4
5
6
7
8
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
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chemical shift (ppm)

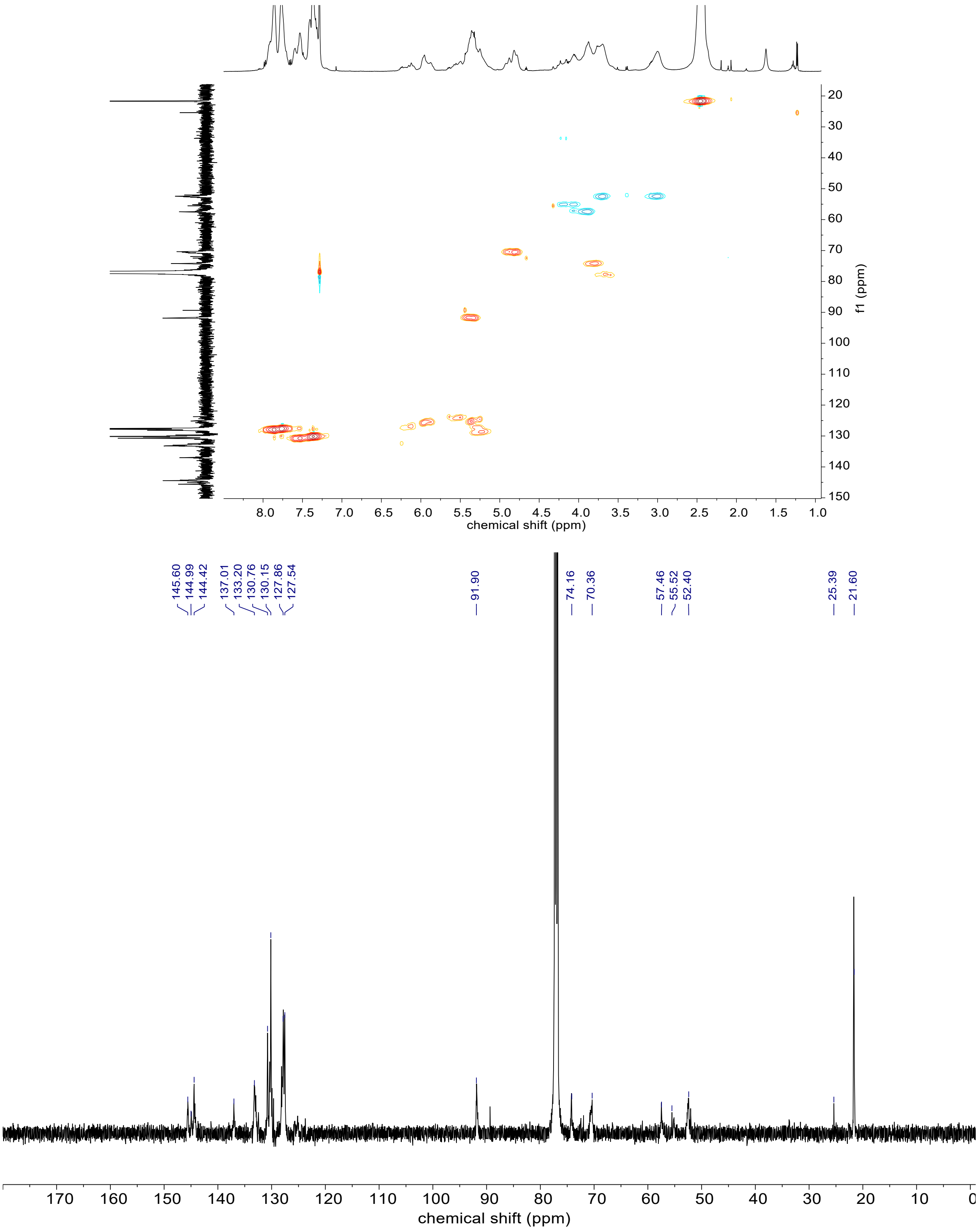
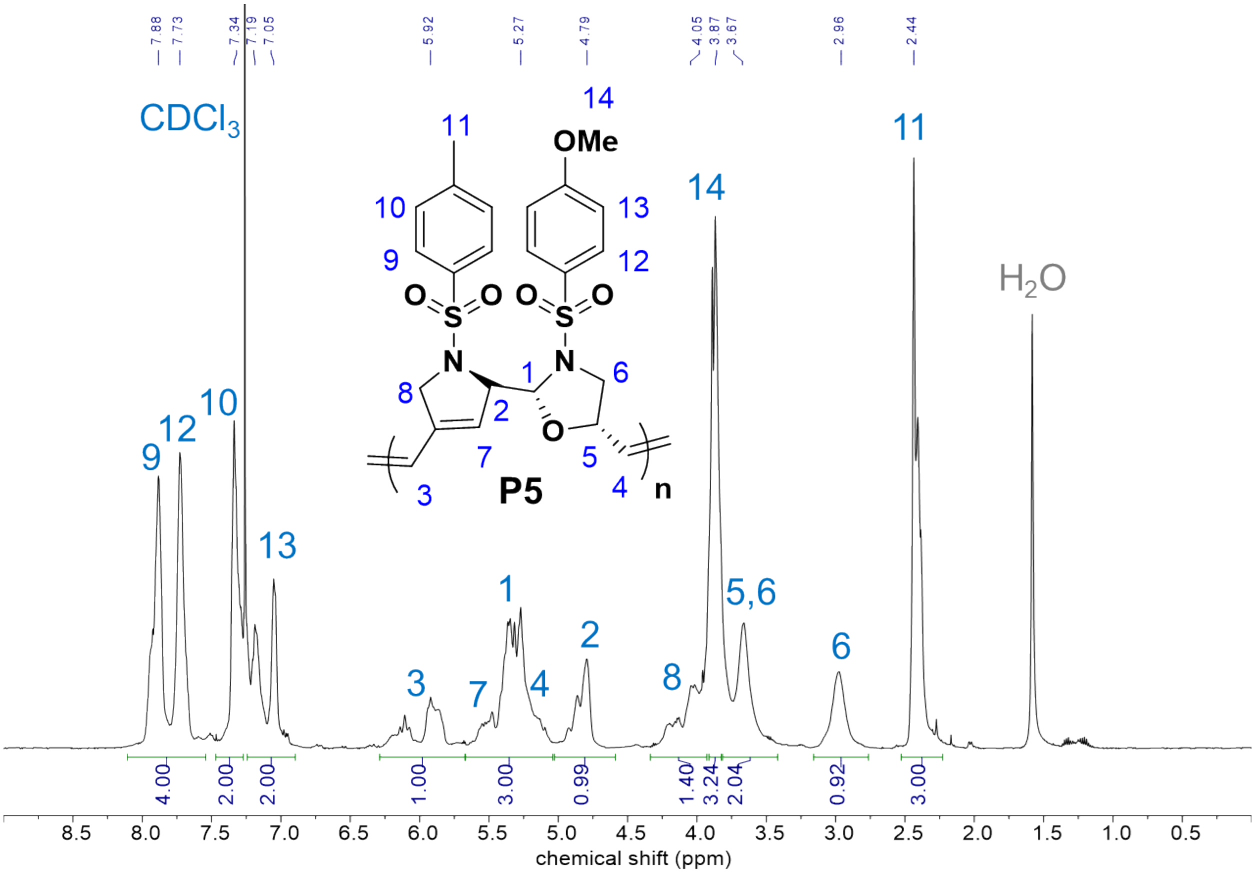
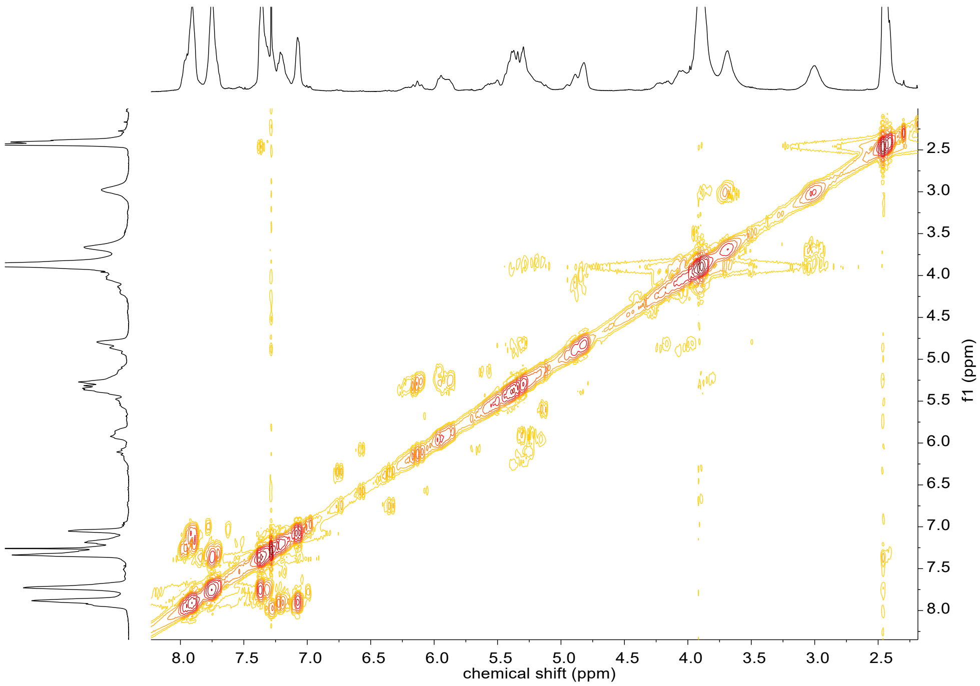


Figure S23. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **P4** [500 MHz, $CDCl_3$].


7.88
7.73
7.34
7.19
7.05
5.92
5.27
4.79
4.05
3.87
3.67
2.96
2.44
CDCl$_3$
11
14
OMe
10
13
9
12
O
S
N
8
1
2
6
7
5
3
4
n
P5
9
12
10
13
3
7
1
4
2
8
14
5,6
6
11
H$_2$O
4.00
2.00
2.00
1.00
3.00
0.99
1.40
3.24
2.04
0.92
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


8.0
7.5
7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
chemical shift (ppm)
f1 (ppm)

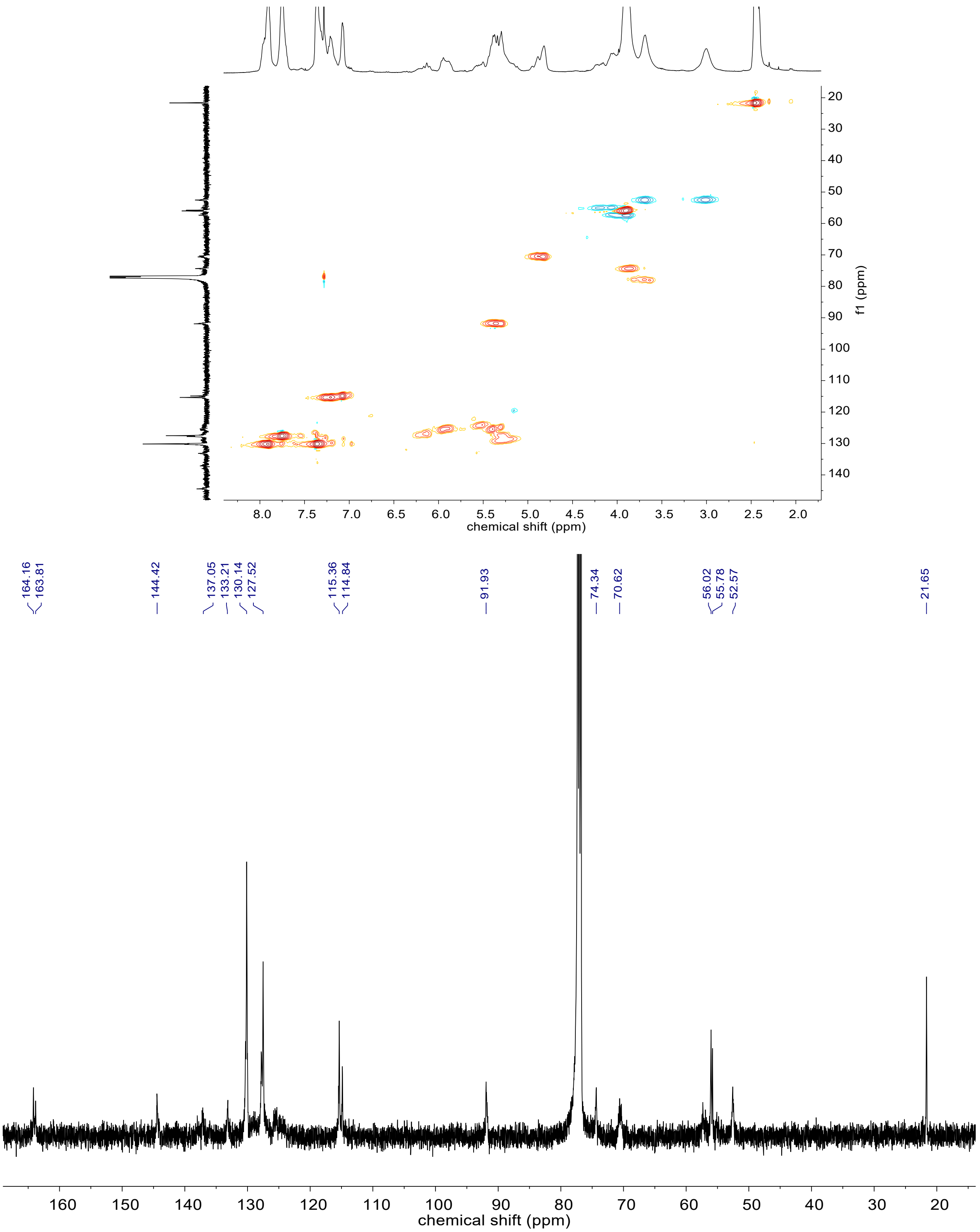
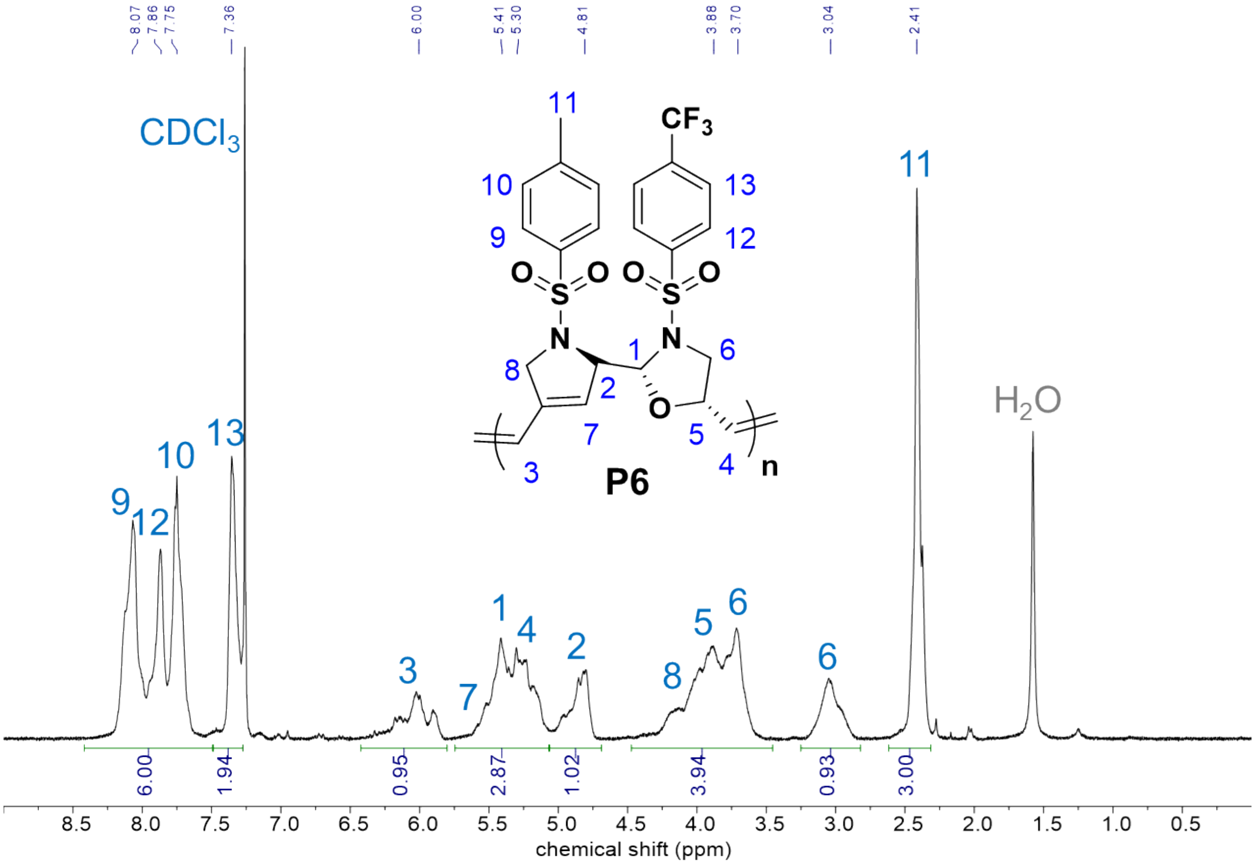
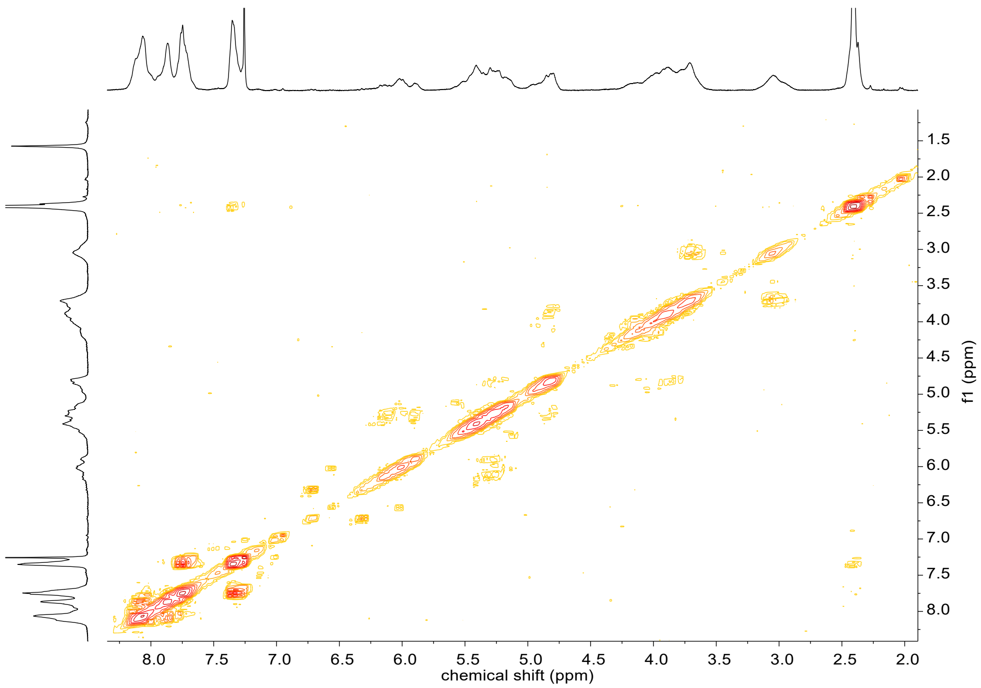


Figure S24. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **P5** [500 MHz, $CDCl_3$].


8.07
7.86
7.75
7.36
6.00
5.41
5.30
4.81
3.88
3.70
3.04
2.41
CDCl$_3$
11
CF$_3$
10
13
9
12
O
S
O
O
S
O
N
N
1
6
8
2
O
7
5
3
4
n
P6
9
12
10
13
3
7
1
4
2
8
5
6
6
11
H$_2$O
6.00
1.94
0.95
2.87
1.02
3.94
0.93
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)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2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
chemical shift (ppm)

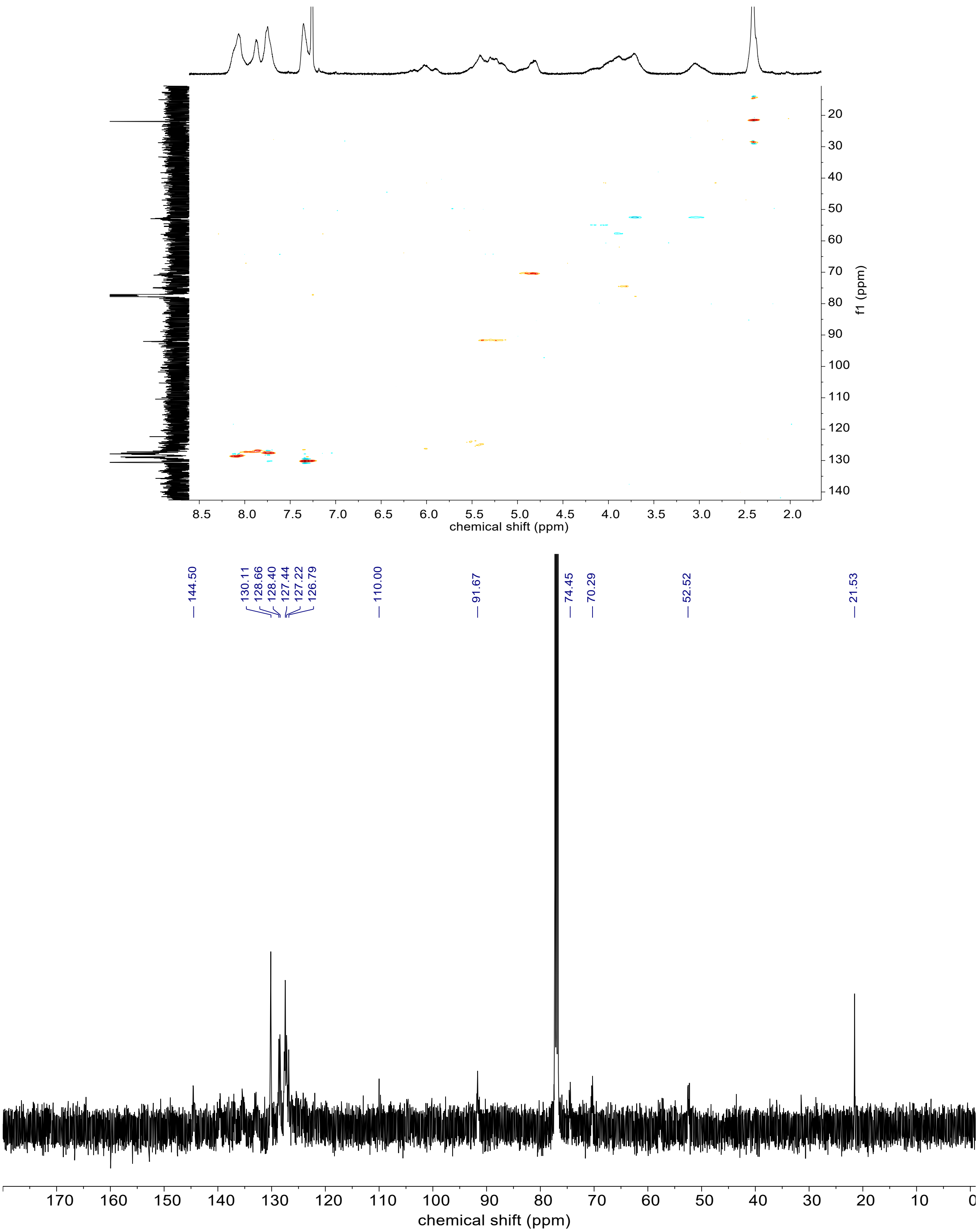
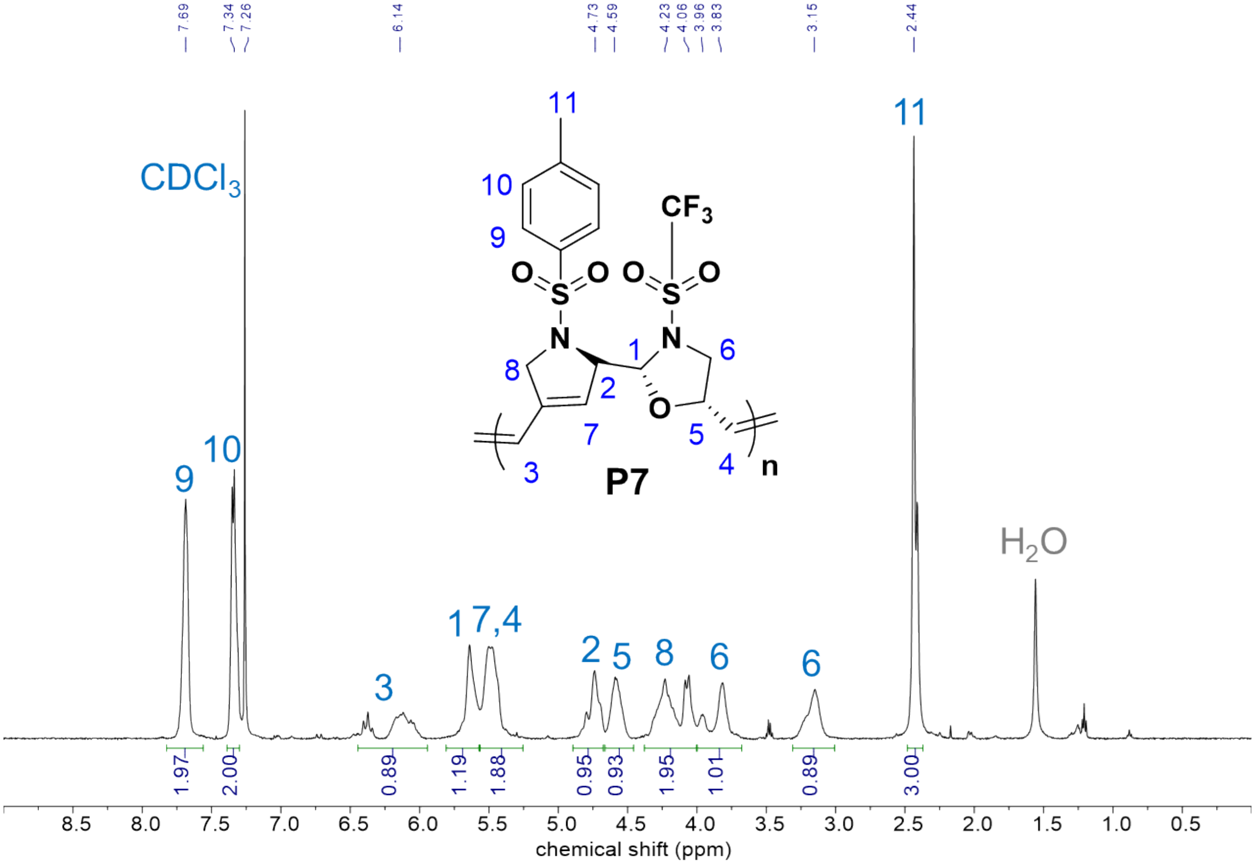
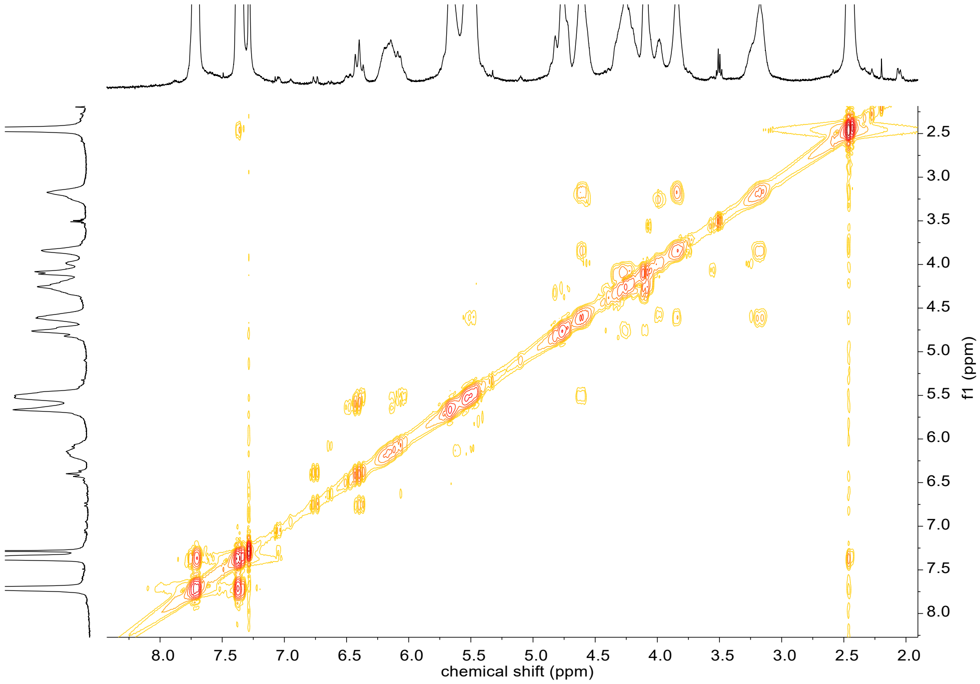


Figure S25. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **P6** [500 MHz, $CDCl_3$].


7.69
7.34
7.26
6.14
4.73
4.59
4.23
4.06
3.96
3.83
3.15
2.44
CDCl3
9
10
3
1
7,4
2
5
8
6
6
11
H2O
11
10
9
CF3
O
S
O
N
8
2
1
N
6
O
S
O
O
5
7
3
4
n
P7
1.97
2.00
0.89
1.19
1.88
0.95
0.93
1.95
1.01
0.89
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift (ppm)


2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.0
7.5
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4.0
3.5
3.0
2.5
2.0
chemical shift (ppm)

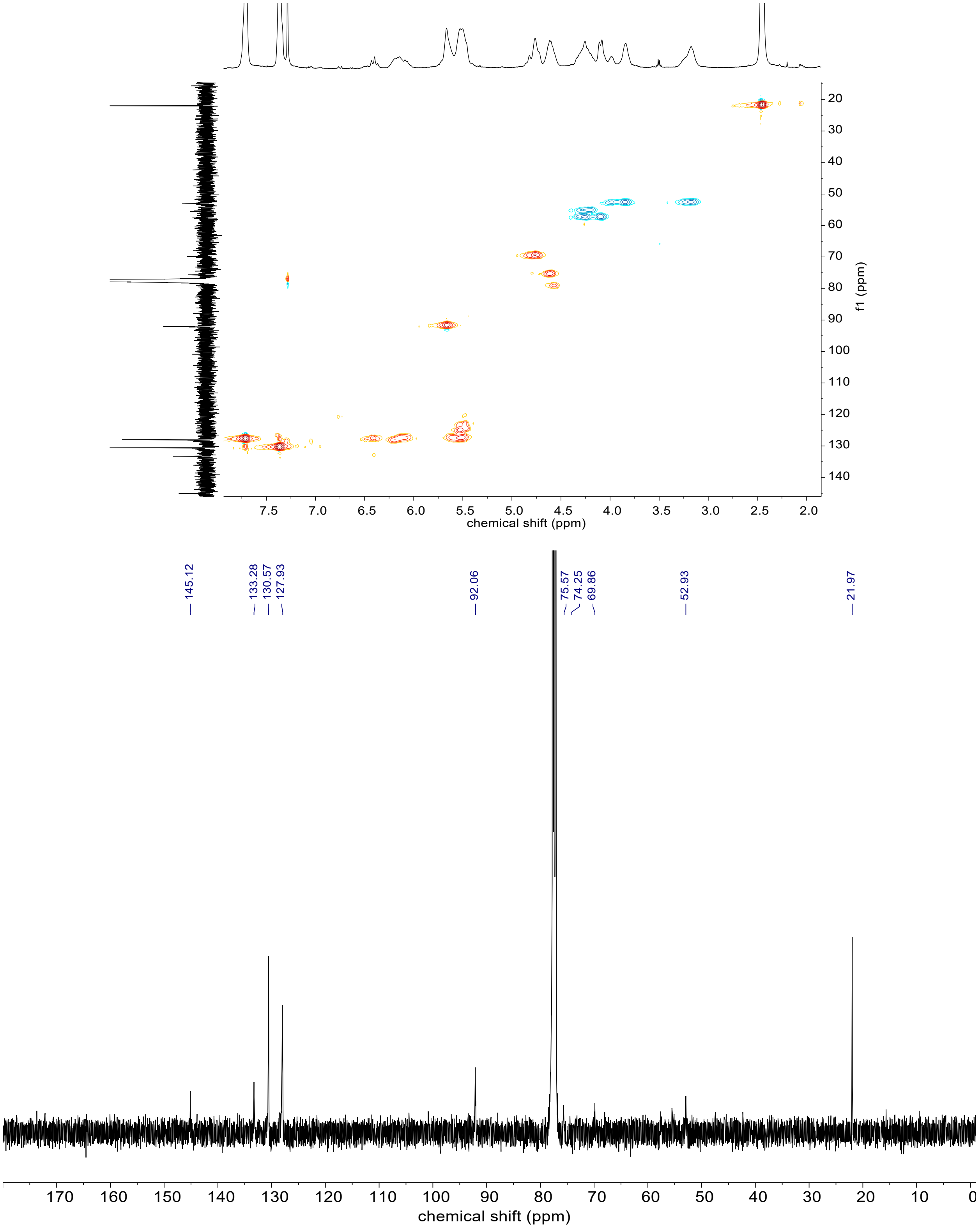


Figure S26. ^{1}H NMR, COSY NMR, HSQC NMR, and ^{13}C NMR spectra for **P7** [500 MHz, $CDCl_3$].

4.3 Block Copolymers

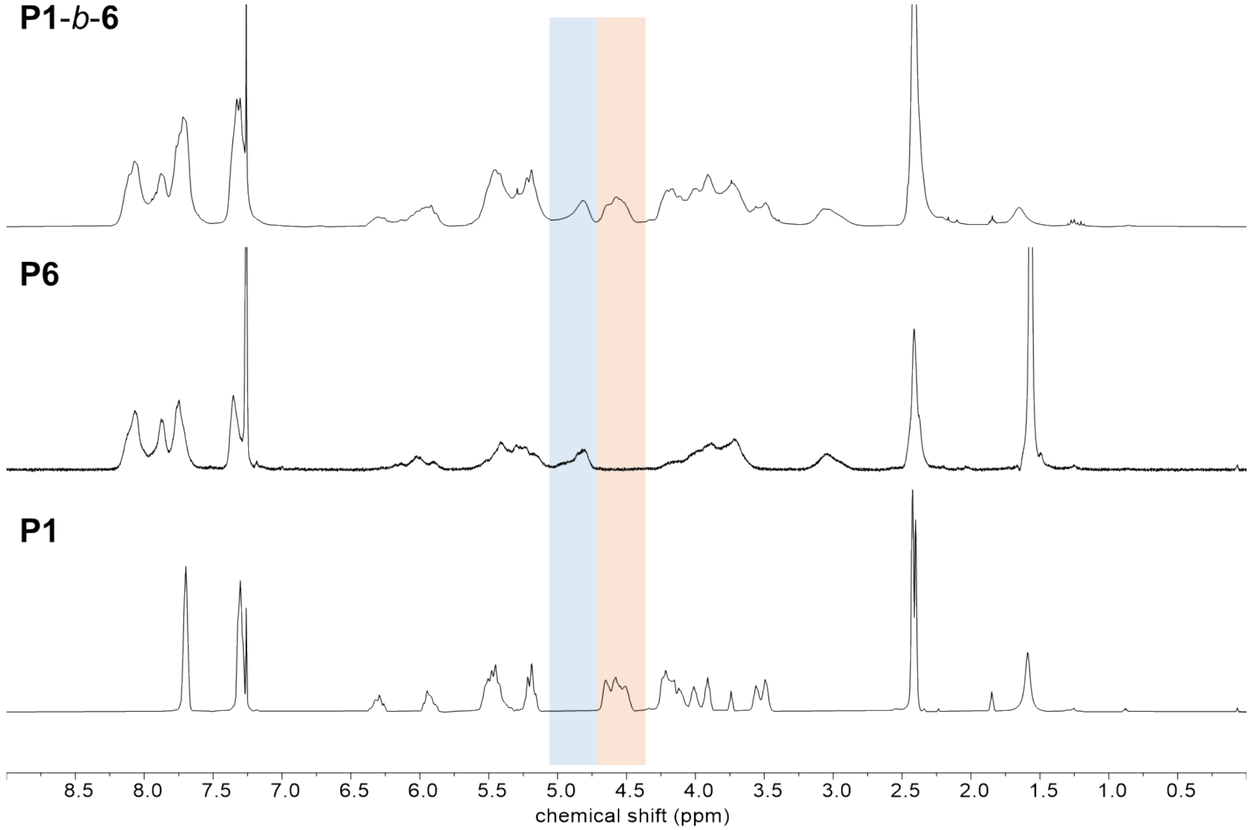


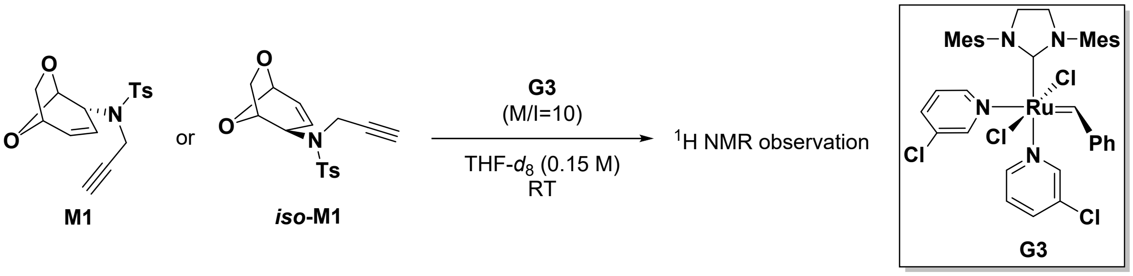
Figure S27. Stacked ^{1}H NMR spectra for **P1**, **P6**, and **P1**-*b*-**P6** [500 MHz, $CDCl_3$].

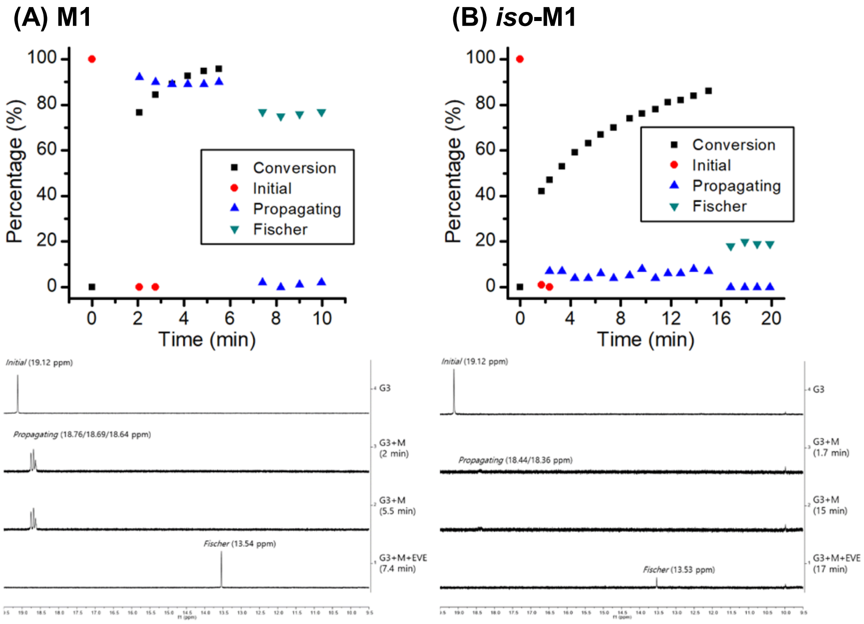
5. Kinetic Studies

5.1. General Procedure for *in situ* NMR Experiment

Initiator (0.009 mmol, 1 eq) and hexamethyldisilane (internal standard, one drop) were dissolved in deuterated solvent (500 µl). Initial benzylidene was measured by the integral ratio of initiator to hexamethyldisilane in ^{1}H NMR spectrum. (After the addition of 2 eq of the 3-chloropyridine additive) Monomer (0.090 mmol, 10 eq) solution in the deuterated solvent (100 µl) was added to the catalyst solution and mixed by shaking the NMR tube for 10 seconds. The reaction was monitored by ^{1}H NMR over time. The k_p values were obtained from the slope of linear ln [M]/[M]$_0$ *vs*. time graph.

5.2. M1 and *iso*-M1





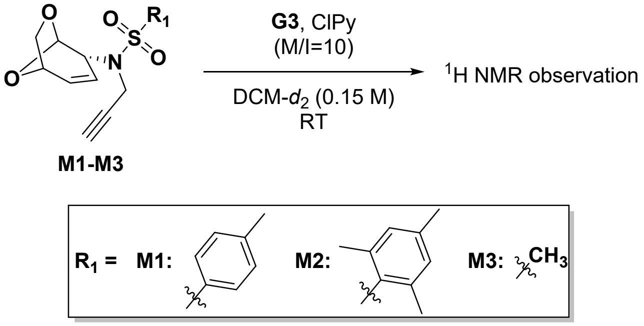
k_p = 0.051 k_p = 0.012

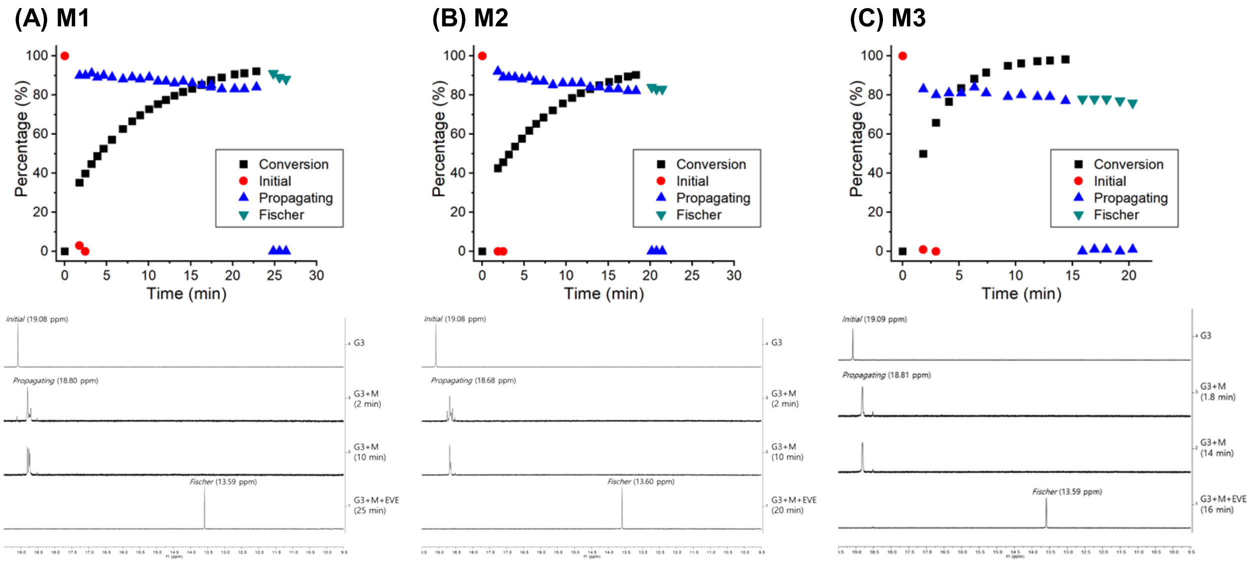
Figure S28. Plots of conversions and carbene changes monitored by *in situ* ^{1}H NMR during the polymerization of (A) **M1** and (B) ***iso*-M1**.

***Figure S28** Discussion:*

The kinetic studies of **M1** as well as **M2–M4** show continuous catalyst decomposition, likely due to the use of an NMR tube instead of a standard reaction setup. Without stirring, some propagating carbenes may have decomposed rather than reacting with monomers. Additionally, the reaction was carried out at room temperature, whereas lower temperatures are known to be optimal.

5.3. M1, M2, and M3





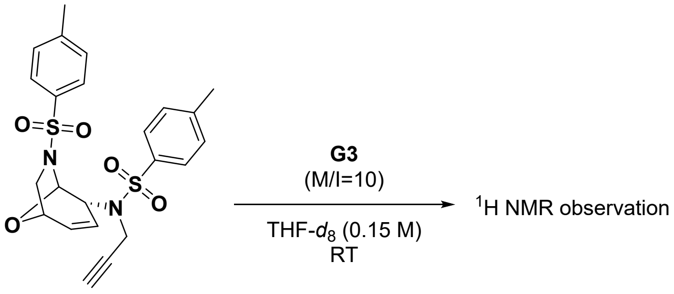
k_p = 0.108 k_p = 0.110 k_p = 0.318

Figure S29. Plots of conversions and carbene changes monitored by *in situ* ^{1}H NMR during the polymerization of (A) **M1**, (B) **M2**, and (C) **M3**.

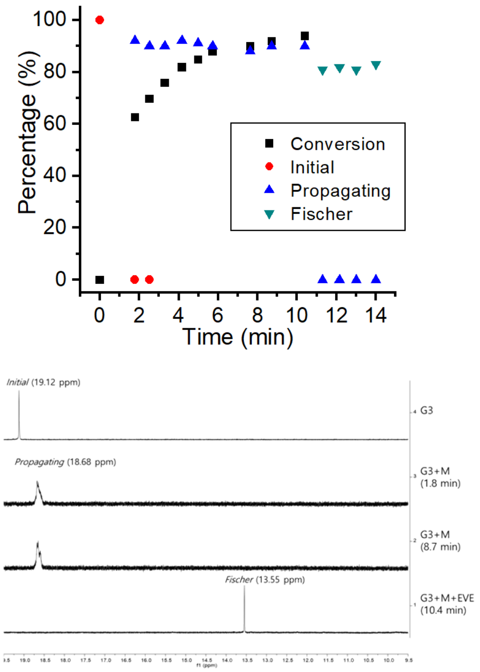
***Figure S29** Discussion:*

To understand the origin for the difficulty in controlling molecular weight even at lower M/I ratios for **M3**, we conducted *in situ* kinetic studies using ^{1}H NMR, and monitored changes in propagating carbene protons under conditions with additives (G3, 3-ClPy, M/I=10, DCM-d_2, 0.15 M, RT). The propagation rate of **M3** increases 2.94-fold as compared to the those exhibited by **M1** and **M2**, with relatively less propagating carbene observed (**M1** and **M2**: ca. 86%, **M3**: ca. 80%), suggesting the smaller steric methyl substituent, while allowing faster propagation, decreases the stability of the carbene.

5.3. M4



M4



$k_p = 0.29$

Figure S30. Plots of conversions and carbene changes monitored by *in situ* ^{1}H NMR during the polymerization of **M4**.

6. Degradation Studies

General procedure for **P1–P7** acidic degradation: dissolve polymer (ca. 0.02 M of repeat units) in a chloroform/MeOH mixture and adding 4M HCl (in dioxane) to achieve a final HCl concentration of 0.5 M at 40 °C. The degradation was monitored over time by taking aliquots for analysis. The aliquot was quenched with $NaHCO_3$ and dried under vacuum to analyze using NMR, SEC, and MALDI-TOF. Due to the overlap of peaks corresponding to the initial polymer and degradation products in the ^{1}H NMR spectra, degradation was monitored by normalized $M_{n,t}/M_{n,0}$ values from SEC analysis ($M_{n,0}$=initial molecular weight, $M_{n,t}$=molecular weight at time t in days).

Table S6. Degradation results for **P1** to **P7**.

polymer	**P1**	**P2**	**P3**	**P4**		**P5**	**P6**	**P7**
M/I	40	40	40	40	30	30	30	30
$M_{n,0}$ (kDa)[a]	10.8	13.0	8.1	11.9	6.7	8.5	9.7	9.6
$M_{n,14}$ (kDa)[a]	1.2	1.4	0.8	5.8	4.4	3.8	7.8	8.9
rate[b]	1.33	1.27	2.65	0.081	0.045	0.080	0.024	0.012

[a]Determined by THF size exclusion chromatography calibrated by polystyrene standards. $M_{n,0}$ refers to the initial molecular weight and $M_{n,14}$ refers to the final molecular weight after 14 days.
[b]Rate was obtained from the slope of linear ln ($M_n/M_{n,0}$) *vs.* time (day) graph

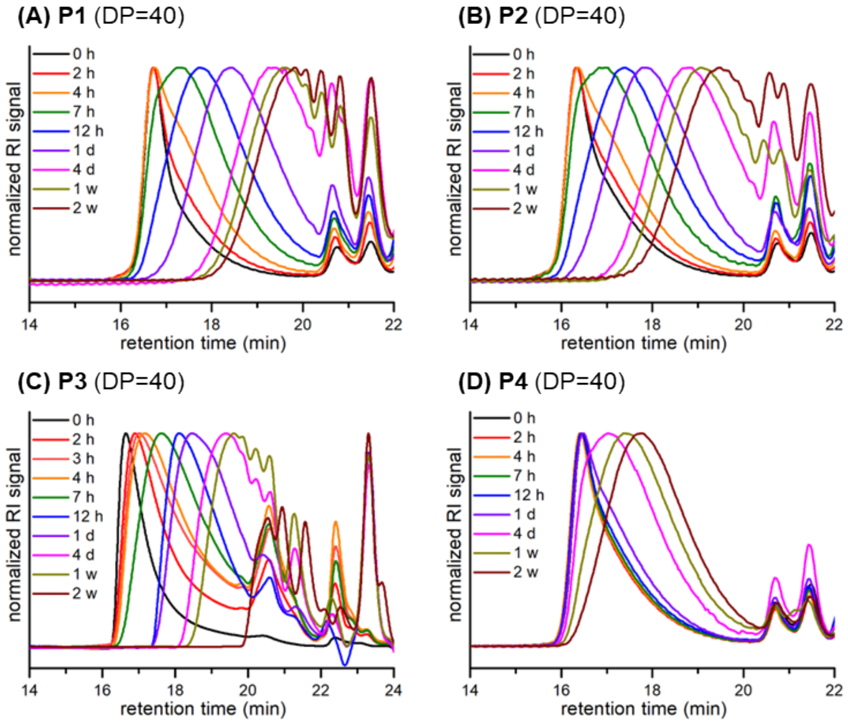


Figure S31. SEC traces of (A) **P1**, (B) **P2**, (C) **P3**, and (D) **P4** (DP=40) degradation under 0.5 M HCl acidic conditions. Numbers in the legend indicate the degradation time.

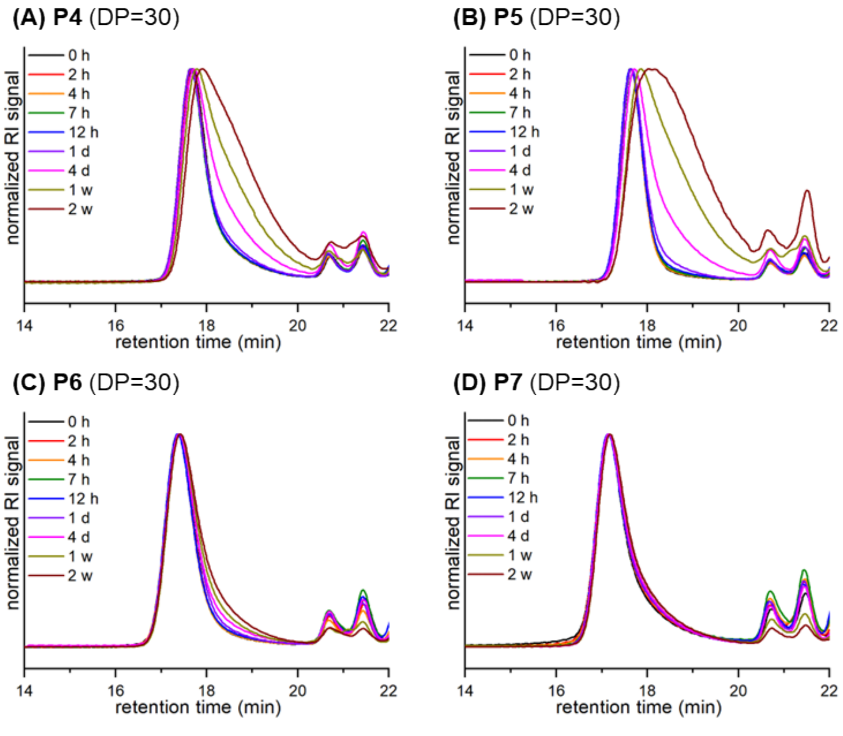


Figure S32. SEC traces of (A) **P4**, (B) **P5**, (C) **P6**, and (D) **P7** (DP=30) degradation under 0.5 M HCl acidic conditions. Numbers in the legend indicate the degradation time.

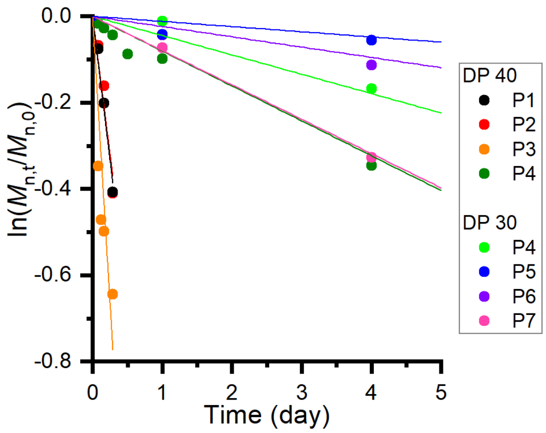


Figure S33. Normalized ln($M_{n,t}/M_{n,0}$) ($M_{n,0}$ = initial molecular weight, $M_{n,t}$ = molecular weight) *vs.* time t in days for **P1-P7**.

6.1. MALDI-TOF Analysis of Degraded Products and Proposed Degradation Mechanism

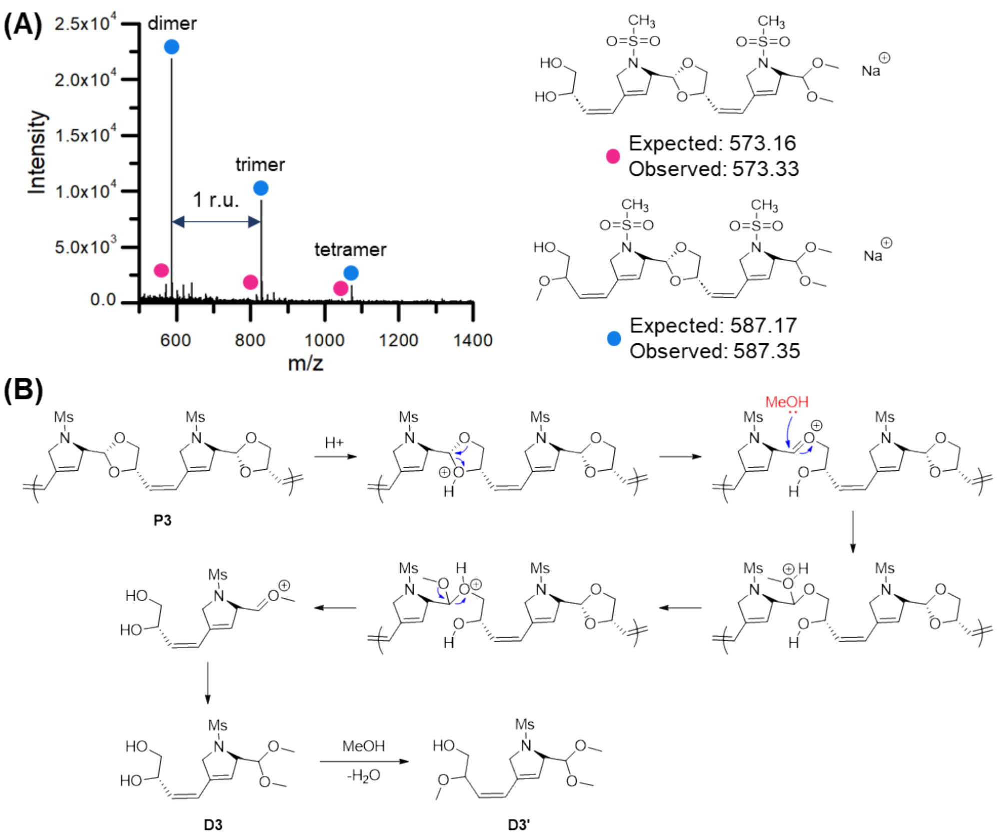


Figure S34. (A) MALDI-TOF analysis of the polymer degradation products of **P3**. (B) Proposed degradation mechanism.

7. Characterization of Polymer Thermal Properties

The thermal degradation temperature (T_d) and glass transition temperature (T_g) were measured for **P1–P7** using thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC), respectively. The results are shown in **Figure S35** and **S36** and summarized in **Table S7**.

TGA method: Heat at 10 °C/min to 600 °C. T_d values were calculated from the point exhibited 5% of weight loss.

DSC method: For **P1–P3**, first, heat at 50 °C/min from 25 to 100 °C. Second, cool at 50 °C/min from 100 to 0 °C. Third, heat at 50 °C/min from 0 to 180 °C. Fourth, cool at 50 °C/min from 180 to 0 °C. Fifth, heat at 50 °C/min from 0 to 230 °C. For **P4–P7**, first, heat at 50 °C/min from 25 to 100 °C. Second, cool at 50 °C/min from 100 to 0 °C. Third, heat at 150 °C/min from 0 to 180 °C. Fourth, cool at 50 °C/min from 180 to 0 °C. Fifth, heat at 150 °C/min from 0 to 250 °C. T_g values were calculated from the midpoint of the transition for the fifth step above (i.e., the third heating cycle).

Table S7. Summary of thermal properties for **P1–P7**.

polymer	M_n (kDa)	T_d (˚C)	T_g (˚C)
P1	5.0	285.0	158.5
P2	8.0	257.5	151.9
P3	4.4	244.2	174.9
P4	11.9	257.1	189.2
P5	8.1	283.6	152.6
P6	11.0	272.0	198.4
P7	11.2	266.4	187.1

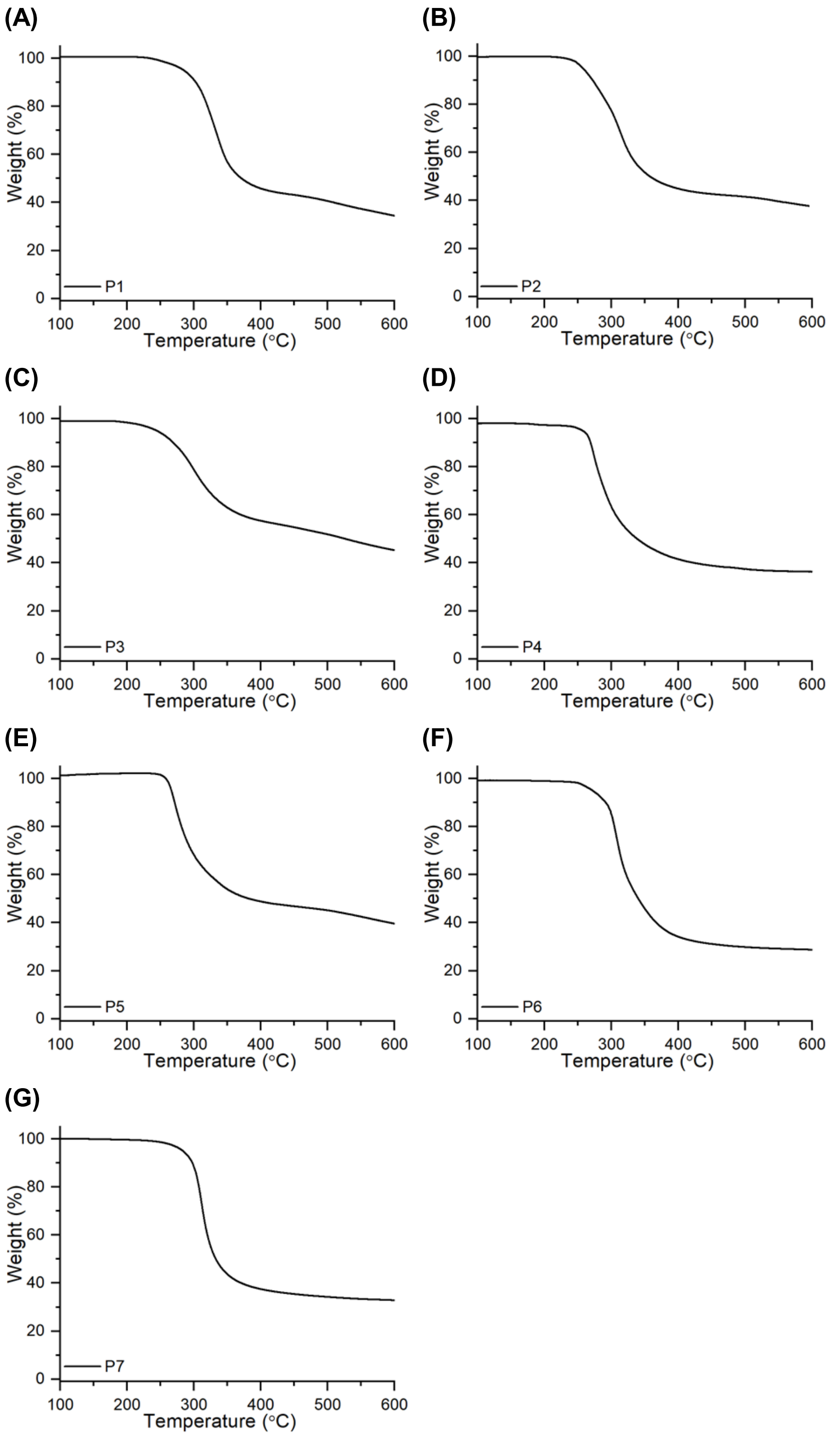


Figure S35. TGA curves for **P1–P7**.

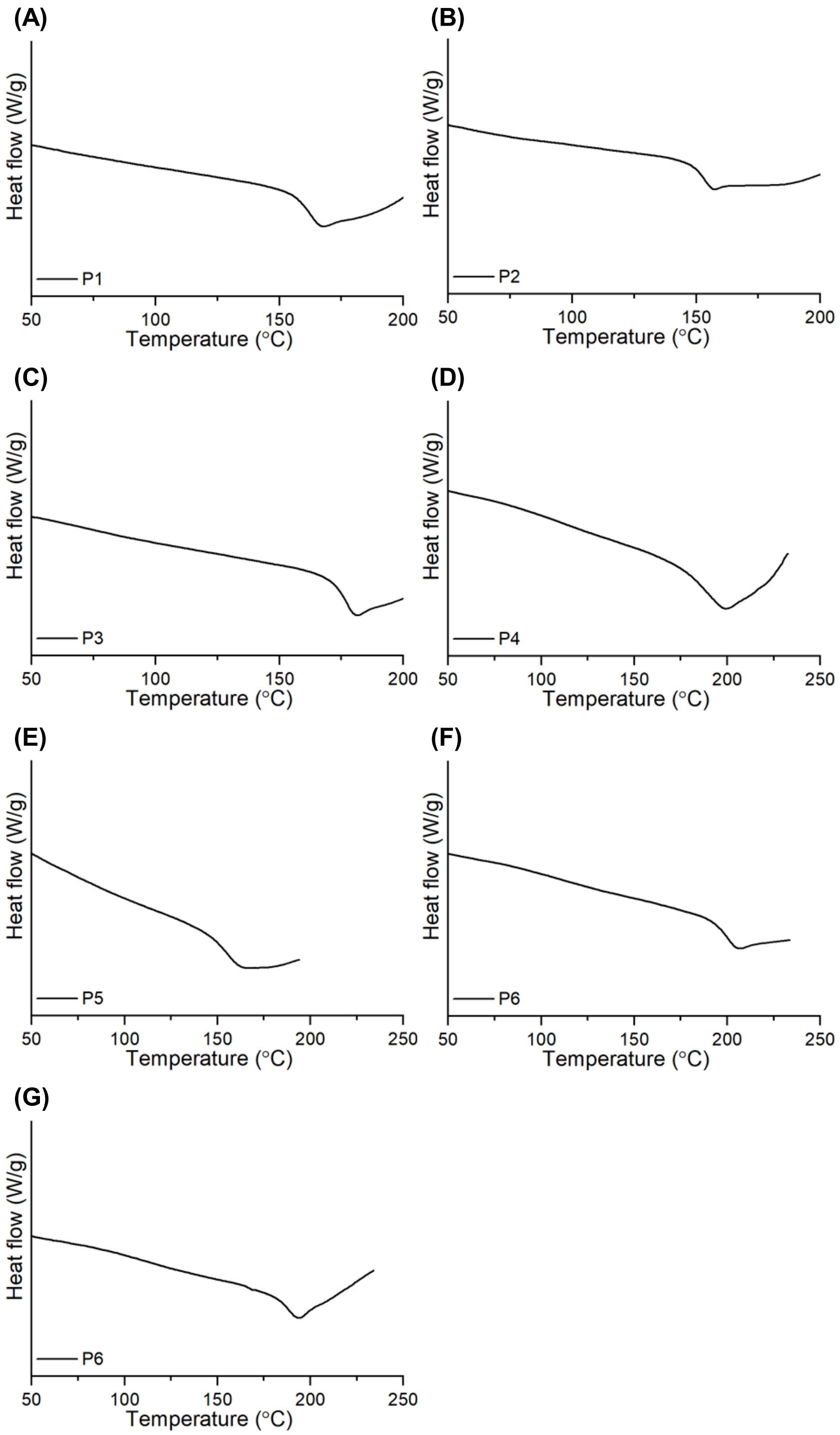


Figure S36. DSC curves for **P1**–**P7**.

8. X-Ray Crystallographic Data

8.1. Crystal Structure Determination of M2

Single crystals of **M2** were obtained by diffusion of hexane vapor into a chloroform solution of this material at RT. A colorless block-like specimen of $C_{17}H_{20}N_2O_4S$, approximate dimensions 0.060 mm x 0.100 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table S8. Data collection details for **M2**.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Phi	60.527	18.54	31.54	0.00	54.74	1.00	360	10.00	0.71073	50	30.0	n/a
Omega	60.527	18.54	-174.46	51.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Omega	60.527	18.54	-174.46	0.00	54.74	1.00	206	10.00	0.71073	50	30.0	n/a
Phi	60.527	18.54	-174.46	0.00	54.74	1.00	360	10.00	0.71073	50	30.0	n/a
Phi	60.527	0.00	0.00	0.00	54.74	360.00	1	108.00	0.71073	50	30.0	n/a

A total of 1133 frames were collected. The total exposure time was 3.17 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 50709 reflections to a maximum θ angle of 28.29° (0.75 Å resolution), of which 4227 were independent (average redundancy 11.996, completeness = 99.3%, R_{int} = 4.59%, R_{sig} = 2.20%) and 3965 (93.80%) were greater than 2σ(F^2). The final cell constants of a = 8.0830(4) Å, b = 11.2048(6) Å, c = 18.8269(8) Å, volume = 1705.12(14) Å^3, are based upon the refinement of the XYZ-centroids of 9420 reflections above 20 σ(I) with 5.484° < 2θ < 56.38°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.930. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9690 and 0.9870.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{17}H_{20}N_2O_4S$. The final anisotropic full-matrix least-squares refinement on F^2 with 220 variables converged at R1 = 3.80%, for the observed data and wR2 = 10.01% for all data. The goodness-of-fit was 1.031. The largest peak in the final difference electron density synthesis was 0.406 e$^-$/Å^3 and the largest hole was -0.327 e$^-$/Å^3 with an RMS deviation of 0.042 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.357 g/cm^3 and F(000), 736 e$^-$.

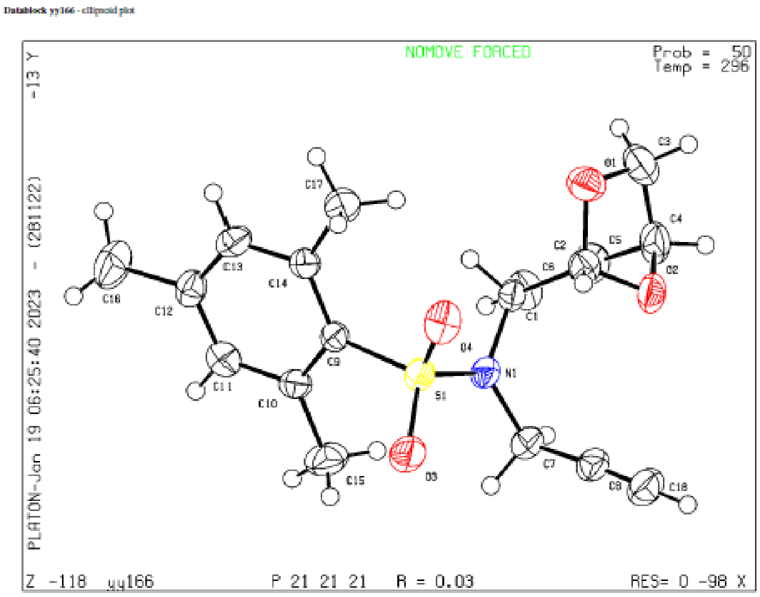


Figure S37. ORTEP of the molecular structure of **M2** shows thermal ellipsoids at the 50% probability level. **CCDC 2418634**.

Table S9. Sample and crystal data for **M2**.

Chemical formula	$C_{17}H_{20}N_2O_4S$	
Formula weight	348.41 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.100 x 0.150 mm	
Crystal habit	colorless block	
Crystal system	orthorhombic	
Space group	P 2_1 2_1 2_1	
Unit cell dimensions	a = 8.0830(4) Å	α = 90°
	b = 11.2048(6) Å	β = 90°
	c = 18.8269(8) Å	γ = 90°
Volume	1705.12(14) $Å^3$	
Z	4	
Density (calculated)	1.357 g/cm^3	
Absorption coefficient	0.213 mm^{-1}	
F(000)	736	

Table S10. Data collection and structure refinement for **M2**.

Theta range for data	2.12 to 28.29°

collection		
Index ranges	-10≤h≤10, -14≤k≤14, -25≤l≤24	
Reflections collected	50709	
Independent reflections	4227 [R(int) = 0.0459]	
Coverage of independent reflections	99.3%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9870 and 0.9690	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4227 / 0 / 220	
Goodness-of-fit on F^2	1.031	
Final R indices	3965 data; $I>2\sigma(I)$	R_1 = 0.0380, wR_2 = 0.0980
	all data	R_1 = 0.0412, wR_2 = 0.1001
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0588P)^2+0.3694P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.04(2)	
Largest diff. peak and hole	0.406 and -0.327 eÅ^{-3}	
R.M.S. deviation from mean	0.042 eÅ^{-3}	

Table S11. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **M2**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.7287(3)	0.4042(2)	0.36869(11)	0.0281(4)
C2	0.6902(3)	0.4806(2)	0.43434(12)	0.0334(5)
C3	0.8520(4)	0.4258(3)	0.52897(14)	0.0519(8)
C4	0.7137(4)	0.3377(3)	0.51345(14)	0.0462(7)
C5	0.7645(4)	0.2479(2)	0.45910(15)	0.0430(6)
C6	0.7664(3)	0.2788(2)	0.39152(14)	0.0379(6)
C7	0.4429(3)	0.3472(2)	0.32199(14)	0.0374(5)
C8	0.3152(3)	0.4130(2)	0.36042(13)	0.0345(5)
C9	0.8035(3)	0.4546(2)	0.20214(11)	0.0272(4)
C10	0.7810(3)	0.3541(2)	0.15754(12)	0.0309(5)
C11	0.9090(3)	0.3216(2)	0.11299(13)	0.0339(5)
C12	0.0597(3)	0.3799(2)	0.11306(13)	0.0354(5)
C13	0.0818(3)	0.4725(2)	0.16020(13)	0.0340(5)
C14	0.9574(3)	0.5137(2)	0.20501(11)	0.0286(4)
C15	0.6273(4)	0.2788(3)	0.15625(18)	0.0498(7)
C16	0.1943(4)	0.3437(3)	0.06221(19)	0.0599(9)
C17	0.0006(4)	0.6180(2)	0.25224(16)	0.0416(6)
N1	0.6017(3)	0.40781(19)	0.31329(10)	0.0331(4)
N2	0.2045(4)	0.4601(3)	0.39067(15)	0.0617(7)
O1	0.8425(2)	0.50611(18)	0.46991(10)	0.0441(4)
O2	0.5933(2)	0.41696(1	0.48292(9)	0.0418(4)

	x/a	y/b	z/c	U(eq)
		8)		
O3	0.4861(2)	0.5056(2)	0.20682(10)	0.0485(5)
O4	0.6741(3)	0.61857(15)	0.28338(10)	0.0422(5)
S1	0.63008(7)	0.50789(5)	0.25108(3)	0.03109(15)

Table S12. Bond lengths (Å) for **M2**.

C1-N1	1.464(3)	C1-C6	1.500(3)
C1-C2	1.536(3)	C1-H1	0.98
C2-O2	1.400(3)	C2-O1	1.430(3)
C2-H2	0.98	C3-O1	1.433(4)
C3-C4	1.519(5)	C3-H3A	0.97
C3-H3B	0.97	C4-O2	1.438(3)
C4-C5	1.493(4)	C4-H4	0.98
C5-C6	1.319(4)	C5-H5	0.93
C6-H6	0.93	C7-C8	1.461(4)
C7-N1	1.462(3)	C7-H7A	0.97
C7-H7B	0.97	C8-N2	1.185(4)
C9-C14	1.411(3)	C9-C10	1.416(3)
C9-S1	1.781(2)	C10-C11	1.381(3)
C10-C15	1.502(4)	C11-C12	1.382(4)
C11-H11	0.93	C12-C13	1.377(4)
C12-C16	1.505(4)	C13-C14	1.391(3)
C13-H13	0.93	C14-C17	1.509(3)
C15-H15A	0.96	C15-H15B	0.96
C15-H15C	0.96	C16-H16A	0.96
C16-H16B	0.96	C16-H16C	0.96
C17-H17A	0.96	C17-H17B	0.96
C17-H17C	0.96	N1-S1	1.6376(19)
O3-S1	1.4317(19)	O4-S1	1.426(2)

Table S13. Bond angles (°) for **M2**

N1-C1-C6	111.9(2)	N1-C1-C2	114.57(19)
C6-C1-C2	109.44(18)	N1-C1-H1	106.8
C6-C1-H1	106.8	C2-C1-H1	106.8
O2-C2-O1	106.11(19)	O2-C2-C1	110.8(2)
O1-C2-C1	108.29(19)	O2-C2-H2	110.5
O1-C2-H2	110.5	C1-C2-H2	110.5
O1-C3-C4	102.7(2)	O1-C3-H3A	111.2
C4-C3-H3A	111.2	O1-C3-H3B	111.2
C4-C3-H3B	111.2	H3A-C3-H3B	109.1
O2-C4-C5	109.2(2)	O2-C4-C3	100.0(2)
C5-C4-C3	111.6(2)	O2-C4-H4	111.8
C5-C4-H4	111.8	C3-C4-H4	111.8
C6-C5-C4	119.1(2)	C6-C5-H5	120.4
C4-C5-H5	120.4	C5-C6-C1	121.4(2)
C5-C6-H6	119.3	C1-C6-H6	119.3

C8-C7-N1	116.2(2)	C8-C7-H7A	108.2
N1-C7-H7A	108.2	C8-C7-H7B	108.2
N1-C7-H7B	108.2	H7A-C7-H7B	107.4
N2-C8-C7	175.5(3)	C14-C9-C10	120.6(2)
C14-C9-S1	121.14(17)	C10-C9-S1	118.19(17)
C11-C10-C9	118.3(2)	C11-C10-C15	117.5(2)
C9-C10-C15	124.2(2)	C10-C11-C12	122.3(2)
C10-C11-H11	118.8	C12-C11-H11	118.8
C13-C12-C11	118.1(2)	C13-C12-C16	121.3(3)
C11-C12-C16	120.6(3)	C12-C13-C14	123.2(2)
C12-C13-H13	118.4	C14-C13-H13	118.4
C13-C14-C9	117.3(2)	C13-C14-C17	116.6(2)
C9-C14-C17	126.2(2)	C10-C15-H15A	109.5
C10-C15-H15B	109.5	H15A-C15-H15B	109.5
C10-C15-H15C	109.5	H15A-C15-H15C	109.5
H15B-C15-H15C	109.5	C12-C16-H16A	109.5
C12-C16-H16B	109.5	H16A-C16-H16B	109.5
C12-C16-H16C	109.5	H16A-C16-H16C	109.5
H16B-C16-H16C	109.5	C14-C17-H17A	109.5
C14-C17-H17B	109.5	H17A-C17-H17B	109.5
C14-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	C7-N1-C1	121.52(19)
C7-N1-S1	121.44(17)	C1-N1-S1	115.51(16)
C2-O1-C3	106.5(2)	C2-O2-C4	101.35(19)
O4-S1-O3	117.80(13)	O4-S1-N1	108.98(11)
O3-S1-N1	106.86(11)	O4-S1-C9	108.42(11)
O3-S1-C9	109.45(11)	N1-S1-C9	104.52(10)

Table S14. Anisotropic atomic displacement parameters (Å^2) for **M2**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0266(11)	0.0316(10)	0.0261(10)	0.0040(8)	0.0036(8)	0.0028(9)
C2	0.0334(12)	0.0330(11)	0.0338(11)	-0.0029(9)	0.0006(9)	0.0068(10)

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C3	0.0497(17)	0.075(2)	0.0313(13)	-0.0087(12)	-0.0055(12)	0.0177(16)
C4	0.0448(15)	0.0661(18)	0.0278(11)	0.0138(11)	0.0045(11)	0.0111(14)
C5	0.0446(15)	0.0388(13)	0.0456(14)	0.0142(11)	-0.0008(12)	0.0065(12)
C6	0.0459(15)	0.0302(11)	0.0376(12)	-0.0022(9)	0.0017(11)	0.0094(11)
C7	0.0312(12)	0.0433(13)	0.0378(13)	-0.0005(10)	0.0049(10)	-0.0085(11)
C8	0.0268(11)	0.0419(12)	0.0347(12)	0.0068(10)	0.0052(10)	-0.0025(10)
C9	0.0262(11)	0.0307(10)	0.0246(10)	0.0071(8)	-0.0010(8)	0.0011(8)
C10	0.0295(11)	0.0331(11)	0.0301(11)	0.0040(9)	-0.0045(9)	-0.0040(10)
C11	0.0378(13)	0.0326(11)	0.0312(12)	-0.0011(9)	-0.0016(10)	-0.0003(10)
C12	0.0339(12)	0.0376(12)	0.0345(12)	0.0075(9)	0.0042(10)	0.0063(10)
C13	0.0262(11)	0.0369(12)	0.0389(12)	0.0079(9)	0.0006(9)	-0.0031(9)
C14	0.0295(11)	0.0292(10)	0.0270(10)	0.0075(8)	-0.0025(8)	-0.0032(9)
C15	0.0377(14)	0.0499(16)	0.0618(18)	-0.0103(13)	-0.0013(14)	-0.0141(13)
C16	0.0482(18)	0.0644(19)	0.067(2)	-0.0073(16)	0.0227(16)	0.0068(16)
C17	0.0446(14)	0.0399(12)	0.0402(12)	-0.0019(12)	0.0014(12)	-0.0140(10)
N1	0.0282(10)	0.0431(10)	0.0280(9)	0.0087(8)	0.0016(8)	-0.0058(8)
N2	0.0493(16)	0.0729(18)	0.0630(16)	0.0126(14)	-0.0010(14)	-0.0018(14)
O1	0.0398(10)	0.0484(10)	0.0442(10)	-0.0098(8)	-0.0055(8)	0.0009(9)
O2	0.0343(10)	0.0597(11)	0.0314(8)	0.0033(8)	0.0101(7)	0.0122(9)
O3	0.0292(9)	0.0757(14)	0.0406(10)	0.0149(10)	-0.0033(7)	0.0107(10)
O4	0.0481(11)	0.0297(8)	0.0488(10)	0.0044(7)	0.0099(9)	0.0098(8)
S1	0.0268(3)	0.0370(3)	0.0294(3)	0.0084(2)	0.0019(2)	0.0053(2)

Table S15. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **M2**.

	x/a	**y/b**	**z/c**	**U(eq)**
H1	0.8302	0.4363	0.3477	0.034
H2	0.6346	0.5547	0.4204	0.04
H3A	0.8332	0.4672	0.5735	0.062
H3B	0.9585	0.3861	0.5307	0.062
H4	0.6726	0.2997	0.5569	0.055
H5	0.7944	0.1711	0.4727	0.052
H6	0.7916	0.2218	0.3573	0.045
H7A	0.4004	0.3278	0.2752	0.045

	x/a	**y/b**	**z/c**	**U(eq)**
H7B	0.4623	0.2725	0.3467	0.045
H11	0.8933	0.2582	0.0818	0.041
H13	1.1848	0.5093	0.1622	0.041
H15A	0.6462	0.2092	0.1276	0.075
H15B	0.5376	0.3242	0.1365	0.075
H15C	0.5997	0.2549	0.2038	0.075
H16A	1.2134	0.2594	0.0661	0.09
H16B	1.2942	0.3860	0.0736	0.09
H16C	1.1613	0.3627	0.0146	0.09
H17A	1.1181	0.6305	0.2515	0.062
H17B	0.9655	0.6015	0.2999	0.062
H17C	0.9457	0.6884	0.2353	0.062

8.2. Crystal Structure Determination of M4

Single crystals of **M4** were obtained by diffusion of hexane vapor into a chloroform solution of this material at RT. A colorless block-like specimen of $C_{23}H_{24}N_2O_5S_2$, approximate dimensions 0.100 mm x 0.150 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table S16. Data collection details for **M4**.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
Omega	60.551	18.54	-173.86	-105.00	54.74	1.30	158	10.00	0.71073	50	30.0	n/a
Omega	60.551	18.54	-173.86	102.00	54.74	1.30	158	10.00	0.71073	50	30.0	n/a
Omega	60.551	27.81	-164.59	0.00	54.74	1.30	158	10.00	0.71073	50	30.0	n/a
Omega	60.551	18.54	-173.86	153.00	54.74	1.30	158	10.00	0.71073	50	30.0	n/a
Omega	60.551	18.54	-173.86	0.00	54.74	1.30	158	10.00	0.71073	50	30.0	n/a
Omega	60.551	18.54	-173.86	-156.00	54.74	1.30	158	10.00	0.71073	50	30.0	n/a
Phi	60.551	18.54	31.54	0.00	54.74	1.30	277	10.00	0.71073	50	30.0	n/a
Phi	60.551	18.54	-174.46	0.00	54.74	1.30	277	10.00	0.71073	50	30.0	n/a
Phi	60.551	0.00	0.00	0.00	54.74	360.00	1	108.00	0.71073	50	30.0	n/a

A total of 1503 frames were collected. The total exposure time was 4.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 118465 reflections to a maximum θ angle of 28.31° (0.75 Å resolution), of which 5747 were independent (average redundancy 20.613, completeness = 99.5%, R_{int} = 5.25%, R_{sig} = 1.95%) and 5351 (93.11%) were greater than 2σ(F^2). The final cell constants of a = 8.4134(6) Å, b = 14.6866(11) Å, c = 18.7432(13) Å, volume = 2316.0(3) Å^3, are based upon the refinement of the XYZ-centroids of 9512 reflections above 20 σ(I) with 5.157° < 2θ < 56.17°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.924. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9610 and 0.9740.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{23}H_{24}N_2O_5S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 291 variables converged at R1 = 3.38%, for the observed data and wR2 = 8.40% for all data. The goodness-of-fit was 1.097. The largest peak in the final difference electron density synthesis was 0.248 e^-/Å^3 and the largest hole was -0.216 e^-/Å^3 with an RMS deviation of 0.035 e^-/Å^3. On the basis of the final model, the calculated density was 1.355 g/cm^3 and F(000), 992 e^-.

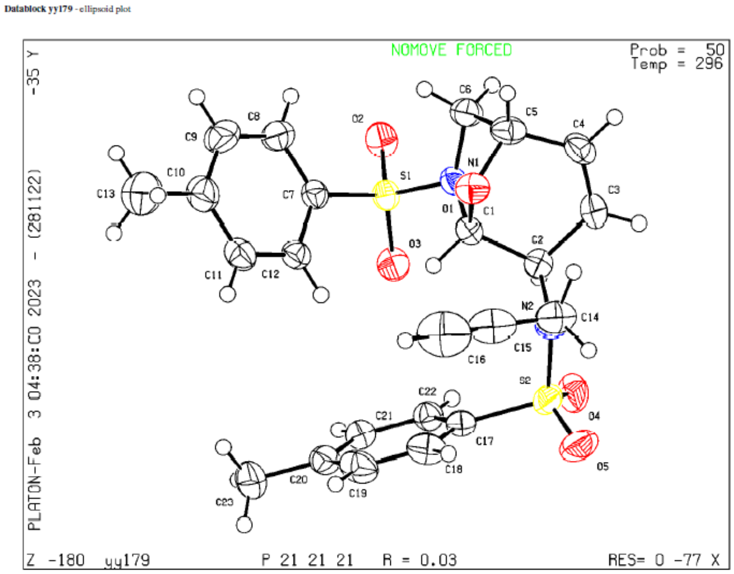


Figure S38. ORTEP of the molecular structure of **M4** showing thermal ellipsoids at the 50% probability level. **CCDC 2418635**.

Table S17. Sample and crystal data for **M4**.

Chemical formula	$C_{23}H_{24}N_2O_5S_2$	
Formula weight	472.56 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.150 x 0.150 mm	
Crystal habit	colorless block	
Crystal system	orthorhombic	
Space group	$P\ 2_12_12_1$	
Unit cell dimensions	a = 8.4134(6) Å	α = 90°
	b = 14.6866(11) Å	β = 90°
	c = 18.7432(13) Å	γ = 90°
Volume	2316.0(3) $Å^3$	
Z	4	
Density (calculated)	1.355 g/cm^3	
Absorption coefficient	0.267 mm^{-1}	
F(000)	992	

Table S18. Data collection and structure refinement for **M4**.

Theta range for data collection	1.76 to 28.31°
Index ranges	-11≤h≤11, -19≤k≤19, -24≤l≤24
Reflections collected	118465
Independent reflections	5747 [R(int) = 0.0525]

Coverage of independent reflections	99.5%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9740 and 0.9610	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	Σ $w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5747 / 0 / 291	
Goodness-of-fit on F^2	1.097	
Final R indices	5351 data; $I>2\sigma(I)$	R_1 = 0.0338, wR_2 = 0.0822
	all data	R_1 = 0.0376, wR_2 = 0.0840
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0459P)^2+0.2967P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.000(15)	
Largest diff. peak and hole	0.248 and -0.216 eÅ^{-3}	
R.M.S. deviation from mean	0.035 eÅ^{-3}	

Table S19. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **M4**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
S1	0.56912(6)	0.40501(4)	0.41755(3)	0.03186(12)
S2	0.13061(7)	0.44356(5)	0.20757(3)	0.04081(15)
O1	0.1881(2)	0.50978(11)	0.44405(9)	0.0388(4)
O3	0.5884(2)	0.39205(11)	0.34246(9)	0.0411(4)
O2	0.6402(2)	0.34330(12)	0.46692(10)	0.0429(4)
N1	0.3777(2)	0.39983(13)	0.43223(9)	0.0329(4)
O5	0.0071(2)	0.48371(18)	0.16555(10)	0.0633(6)
O4	0.1728(2)	0.35014(14)	0.19851(11)	0.0542(5)
N2	0.0774(2)	0.45604(14)	0.29042(10)	0.0375(4)
C22	0.4508(3)	0.46369(15)	0.19256(11)	0.0348(5)
C3	0.0416(3)	0.35716(17)	0.39416(14)	0.0414(5)
C6	0.3193(3)	0.3983(2)	0.50700(12)	0.0408(5)
C20	0.5823(3)	0.60674(16)	0.16961(12)	0.0409(5)
C12	0.6218(3)	0.58373(16)	0.38565(12)	0.0344(4)
C4	0.0409(3)	0.37224(19)	0.46385(14)	0.0437(6)
C1	0.2721(3)	0.46194(15)	0.39129(12)	0.0310(4)
C21	0.5885(3)	0.51373(16)	0.18080(12)	0.0376(5)
C11	0.6709(3)	0.67109(17)	0.40137(14)	0.0419(5)
C14	0.9695(3)	0.5298(2)	0.31171(14)	0.0493(6)
C2	0.1597(2)	0.40357(16)	0.34622(12)	0.0323(4)
C5	0.1539(3)	0.43953(18)	0.49551(12)	0.0402(5)
C17	0.3059(3)	0.50738(17)	0.19281(11)	0.0344(5)
C18	0.2963(3)	0.60039(19)	0.18154(14)	0.0459(6)
C23	0.7316(4)	0.6612(2)	0.15756(18)	0.0596(8)
C8	0.6914(3)	0.53641(19)	0.50472(14)	0.0461(6)
C10	0.7298(4)	0.69291(19)	0.46856(16)	0.0504(7)
C7	0.6323(3)	0.51642(15)	0.43747(12)	0.0315(4)
C19	0.4344(4)	0.64873(17)	0.17029(15)	0.0501(6)
C15	0.0410(4)	0.6199(2)	0.31763(16)	0.0576(8)
C9	0.7408(4)	0.6243(2)	0.51909(16)	0.0566(8)
C13	0.7816(6)	0.7894(2)	0.4854(2)	0.0802(12)
C16	0.0889(6)	0.6934(3)	0.3216(2)	0.0844(12)

Table S20. Bond lengths (Å) for **M4**.

S1-O2	1.4266(18)	S1-O3	1.4295(17)
S1-N1	1.6352(18)	S1-C7	1.760(2)
S2-O4	1.427(2)	S2-O5	1.431(2)

S2-N2	1.6266(19)	S2-C17	1.769(2)
O1-C1	1.404(3)	O1-C5	1.441(3)
N1-C6	1.485(3)	N1-C1	1.487(3)
N2-C14	1.469(3)	N2-C2	1.473(3)
C22-C17	1.378(3)	C22-C21	1.389(3)
C22-H22	0.93	C3-C4	1.325(4)
C3-C2	1.503(3)	C3-H3	0.93
C6-C5	1.533(3)	C6-H6A	0.97
C6-H6B	0.97	C20-C21	1.383(3)
C20-C19	1.389(4)	C20-C23	1.506(4)
C12-C11	1.380(3)	C12-C7	1.389(3)
C12-H12	0.93	C4-C5	1.494(4)
C4-H4	0.93	C1-C2	1.531(3)
C1-H1	0.98	C21-H21	0.93
C11-C10	1.391(4)	C11-H11	0.93
C14-C15	1.457(5)	C14-H14A	0.97
C14-H14B	0.97	C2-H2	0.98
C5-H5	0.98	C17-C18	1.385(4)
C18-C19	1.378(4)	C18-H18	0.93
C23-H23A	0.96	C23-H23B	0.96
C23-H23C	0.96	C8-C9	1.382(4)
C8-C7	1.386(3)	C8-H8	0.93
C10-C9	1.386(4)	C10-C13	1.515(4)
C19-H19	0.93	C15-C16	1.155(5)
C9-H9	0.93	C13-H13A	0.96
C13-H13B	0.96	C13-H13C	0.96
C16-H16	0.93		

Table S21. Bond angles (°) for **M4**.

O2-S1-O3	120.43(11)	O2-S1-N1	105.89(10)
O3-S1-N1	105.75(10)	O2-S1-C7	109.04(11)
O3-S1-C7	107.36(10)	N1-S1-C7	107.75(10)
O4-S2-O5	120.75(14)	O4-S2-N2	106.88(11)
O5-S2-N2	106.20(12)	O4-S2-C17	106.45(12)
O5-S2-C17	107.51(13)	N2-S2-C17	108.61(11)
C1-O1-C5	102.34(16)	C6-N1-C1	107.35(17)
C6-N1-S1	119.05(15)	C1-N1-S1	118.23(14)
C14-N2-C2	118.95(18)	C14-N2-S2	120.84(17)
C2-N2-S2	119.31(15)	C17-C22-C21	119.5(2)
C17-C22-H22	120.3	C21-C22-H22	120.3
C4-C3-C2	121.1(2)	C4-C3-H3	119.5
C2-C3-H3	119.5	N1-C6-C5	99.34(17)
N1-C6-H6A	111.9	C5-C6-H6A	111.9

N1-C6-H6B	111.9	C5-C6-H6B	111.9
H6A-C6-H6B	109.6	C21-C20-C19	118.1(2)
C21-C20-C23	121.0(3)	C19-C20-C23	120.9(2)
C11-C12-C7	119.6(2)	C11-C12-H12	120.2
C7-C12-H12	120.2	C3-C4-C5	120.0(2)
C3-C4-H4	120.0	C5-C4-H4	120.0
O1-C1-N1	104.14(17)	O1-C1-C2	110.97(18)
N1-C1-C2	108.09(17)	O1-C1-H1	111.1
N1-C1-H1	111.1	C2-C1-H1	111.1
C20-C21-C22	121.0(2)	C20-C21-H21	119.5
C22-C21-H21	119.5	C12-C11-C10	121.0(2)
C12-C11-H11	119.5	C10-C11-H11	119.5
C15-C14-N2	115.8(2)	C15-C14-H14A	108.3
N2-C14-H14A	108.3	C15-C14-H14B	108.3
N2-C14-H14B	108.3	H14A-C14-H14B	107.4
N2-C2-C3	110.52(18)	N2-C2-C1	112.93(19)
C3-C2-C1	109.43(18)	N2-C2-H2	107.9
C3-C2-H2	107.9	C1-C2-H2	107.9
O1-C5-C4	109.6(2)	O1-C5-C6	101.25(18)
C4-C5-C6	111.9(2)	O1-C5-H5	111.3
C4-C5-H5	111.3	C6-C5-H5	111.3
C22-C17-C18	120.7(2)	C22-C17-S2	119.45(18)
C18-C17-S2	119.9(2)	C19-C18-C17	118.9(3)
C19-C18-H18	120.6	C17-C18-H18	120.6
C20-C23-H23A	109.5	C20-C23-H23B	109.5
H23A-C23-H23B	109.5	C20-C23-H23C	109.5
H23A-C23-H23C	109.5	H23B-C23-H23C	109.5
C9-C8-C7	118.9(2)	C9-C8-H8	120.6
C7-C8-H8	120.6	C9-C10-C11	118.3(2)
C9-C10-C13	121.2(3)	C11-C10-C13	120.5(3)
C8-C7-C12	120.5(2)	C8-C7-S1	119.87(18)
C12-C7-S1	119.61(17)	C18-C19-C20	121.9(2)
C18-C19-H19	119.1	C20-C19-H19	119.1
C16-C15-C14	176.0(4)	C8-C9-C10	121.7(3)
C8-C9-H9	119.1	C10-C9-H9	119.1
C10-C13-H13A	109.5	C10-C13-H13B	109.5
H13A-C13-H13B	109.5	C10-C13-H13C	109.5
H13A-C13-H13C	109.5	H13B-C13-H13C	109.5
C15-C16-H16	180.0		

Table S22. Anisotropic atomic displacement parameters (Å^2) for **M4**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0288(2)	0.0296(2)	0.0372(3)	-0.0006(2)	0.0013(2)	0.0002(2)
S2	0.0343(3)	0.0585(4)	0.0296(3)	-0.0075(3)	-0.0005(2)	-0.0072(3)
O1	0.0472(9)	0.0326(8)	0.0367(8)	-0.0034(7)	0.0015(7)	0.0052(7)
O3	0.0432(9)	0.0389(9)	0.0412(9)	-0.0074(7)	0.0064(7)	-0.0006(7)
O2	0.0372(8)	0.0360(9)	0.0553(10)	0.0077(8)	-0.0026(8)	0.0035(7)
N1	0.0269(8)	0.0373(9)	0.0346(9)	0.0046(8)	0.0017(7)	-0.0018(8)
O5	0.0417(10)	0.1108(19)	0.0375(9)	0.0026(11)	-0.0091(8)	-0.0027(11)
O4	0.0583(11)	0.0523(11)	0.0518(11)	-0.0238(9)	0.0147(9)	-0.0210(9)
N2	0.0322(8)	0.0493(11)	0.0310(9)	-0.0015(8)	0.0027(8)	0.0059(8)
C22	0.0394(12)	0.0308(10)	0.0344(11)	0.0009(9)	-0.0001(9)	-0.0005(9)
C3	0.0320(11)	0.0439(13)	0.0483(14)	0.0012(11)	0.0027(10)	-0.0077(10)
C6	0.0377(11)	0.0515(14)	0.0332(11)	0.0068(11)	0.0017(9)	0.0004(11)
C20	0.0539(14)	0.0369(12)	0.0318(11)	-0.0004(9)	0.0000(10)	-0.0105(11)
C12	0.0349(10)	0.0364(11)	0.0320(10)	0.0002(9)	0.0043(9)	-0.0024(9)
C4	0.0330(12)	0.0520(14)	0.0461(13)	0.0101(11)	0.0092(10)	-0.0019(10)
C1	0.0294(10)	0.0304(11)	0.0331(10)	0.0032(8)	0.0028(8)	-0.0015(8)
C21	0.0389(12)	0.0391(11)	0.0348(11)	0.0005(9)	-0.0014(9)	-0.0020(10)
C11	0.0469(14)	0.0354(12)	0.0433(13)	0.0018(10)	0.0072(10)	-0.0043(10)
C14	0.0370(12)	0.0697(18)	0.0413(13)	0.0040(12)	0.0032(10)	0.0201(12)
C2	0.0299(10)	0.0332(10)	0.0337(10)	-0.0036(9)	0.0017(8)	0.0024(9)

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C5	0.0410(12)	0.0483(13)	0.0312(11)	0.0013(10)	0.0061(9)	0.0094(11)
C17	0.0378(11)	0.0391(12)	0.0264(10)	-0.0016(9)	0.0023(9)	-0.0022(10)
C18	0.0518(14)	0.0455(14)	0.0403(13)	0.0046(11)	0.0045(11)	0.0134(13)
C23	0.069(2)	0.0511(16)	0.0582(17)	0.0023(14)	0.0010(15)	-0.0259(15)
C8	0.0560(15)	0.0442(14)	0.0382(13)	0.0030(11)	-0.0068(11)	-0.0067(12)
C10	0.0632(17)	0.0385(14)	0.0496(15)	-0.0068(12)	0.0052(13)	-0.0134(12)
C7	0.0280(9)	0.0327(11)	0.0336(10)	-0.0009(9)	0.0034(8)	-0.0012(8)
C19	0.0730(18)	0.0310(12)	0.0463(14)	0.0069(10)	0.0045(14)	-0.0012(13)
C15	0.0691(19)	0.0570(18)	0.0468(15)	0.0004(13)	0.0031(13)	0.0313(15)
C9	0.077(2)	0.0521(16)	0.0406(14)	-0.0070(12)	-0.0108(13)	-0.0138(14)
C13	0.121(3)	0.0475(18)	0.072(2)	-0.0107(16)	-0.008(2)	-0.028(2)
C16	0.118(4)	0.053(2)	0.082(3)	-0.0039(18)	0.004(2)	0.026(2)

Table S23. Anisotropic Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **M4**.

	x/a	**y/b**	**z/c**	**U(eq)**
H22	0.4565	0.4012	0.2002	0.042
H3	-0.0323	0.3172	0.3746	0.05
H6A	0.3843	0.4357	0.5382	0.049
H6B	0.3135	0.3369	0.5258	0.049
H12	0.5820	0.5700	0.3406	0.041
H4	-0.0298	0.3410	0.4930	0.052
H1	0.3341	0.5035	0.3613	0.037
H21	0.6863	0.4842	0.1804	0.045

	x/a	y/b	z/c	U(eq)
H11	0.6645	0.7160	0.3665	0.05
H14A	-0.1163	0.5330	0.2772	0.059
H14B	-0.0770	0.5142	0.3574	0.059
H2	0.2232	0.3563	0.3227	0.039
H5	0.1117	0.4654	0.5398	0.048
H18	0.1983	0.6297	0.1816	0.055
H23A	0.7516	0.6989	0.1984	0.089
H23B	0.7188	0.6988	0.1161	0.089
H23C	0.8195	0.6205	0.1505	0.089
H8	0.6977	0.4915	0.5396	0.055
H19	0.4284	0.7113	0.1629	0.06
H9	0.7824	0.6377	0.5638	0.068
H13A	0.6896	0.8275	0.4902	0.12
H13B	0.8474	0.8119	0.4475	0.12
H13C	0.8406	0.7898	0.5293	0.12
H16	0.1275	0.7526	0.3249	0.101

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