

SUPPORTING INFORMATION**A General Approach to Sequence-Controlled Polymers Using Macrocyclic ROMP**

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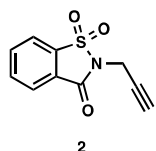
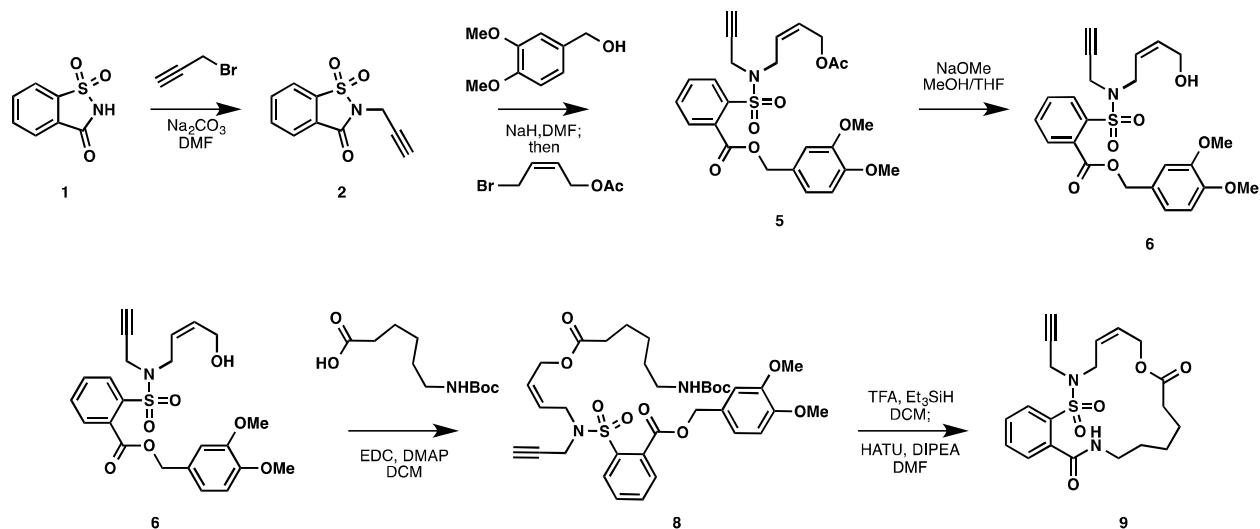
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General procedures. All reactions were carried out under an argon atmosphere with dry solvents using anhydrous conditions unless otherwise stated. Dry dichloromethane (CH_2Cl_2), *N,N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were obtained by passing these previously degassed solvents through activated alumina columns. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as the visualizing agent and an acidic mixture of anisaldehyde, ceric ammonium molybdate, or basic aqueous potassium permanganate (KMnO_4), and heat as developing agents. E. Merck silica gel (60, particle size 0.043–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker Avance 500 MHz and Varian VNMRs 600 MHz instruments and calibrated using residual undeuterated solvent as an internal reference (CHCl_3 @ 7.26 ppm ^1H NMR, 77.16 ppm ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra (MS) were recorded on a time-of-flight mass spectrometer by chemical ionization (CI) or matrix assisted laser desorption/ionization (MALDI) using a 2,5 dihydroxy benzoic acid (DHB) matrix. Gel permeation chromatography (GPC) was performed on a Waters Alliance 2695 separation module with a Waters 2414 differential refractometer eluting with DMF containing 0.1% LiBr.

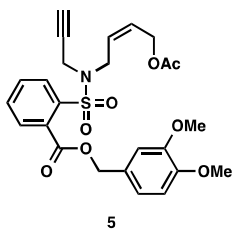
Experimental Procedures

Scheme S1 - Synthesis of monomer 9



2: Saccharin (20.0 g, 109 mmol) was added to a dry, argon flushed round bottom flask and was dissolved in dry DMF (110 mL, 1M). Sodium carbonate (11.6 grams, 109 mmol, 1.0 eq) was added portion wise [Note: CO₂ evolution] followed by propargyl bromide (18.2 mL, 80 wt% in PhMe, 164 mmol, 1.5 eq). The flask was placed into a preheated 80 °C oil bath and the reaction mixture was stirred for 14 hours. The flask was then poured into water (800 mL) with vigorous stirring. The heterogeneous mixture was filtered directly and dried *in vacuo* to give **2**. Alternatively, the filtered product was dissolved in ethyl acetate (250 mL), washed with brine (100 mL), dried over Na₂SO₄ and concentrated *in vacuo* to give **2** as a tan crystalline solid (23.4 grams, 97% yield). Characterization matched that reported by Mabrouir et. al. *Tetrahedron Letters* **2007**, 48, 443-447.

Note: Use of potassium carbonate gives a mixture of regioisomeric alkylated products. Lithium carbonate also gave exclusive *N*-alkylation, but is slower.



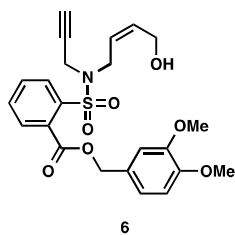
5: Veratryl alcohol (1.52 g, 9.04 mmol) was added to a dry, argon flushed round bottom flask, dissolved in dry DMF (14 mL) and cooled to 0 °C in an ice bath. Sodium hydride (380 mg, 9.5 mmol, 1.05 eq) was added portion wise [Note: H₂ evolution] and the reaction mixture was stirred for 30 minutes. Compound **2** (2.00 g,

9.04 mmol, 1 equiv) was added dropwise in DMF (4 mL). After 10 minutes, full conversion of the starting material was observed by TLC and acetoxy allyl bromide¹ (2.24 g, 11.7 mmol, 1.3 equiv) was added to the reaction mixture. After warming to room temperature and stirring for 30 minutes, the reaction was poured into water (100 mL) and extracted with ethyl acetate (2x 100 mL). The organic layer was washed with brine (100 mL), dried over Na₂SO₄ and concentrated *in vacuo* to give an oil. Diethyl ether (100 mL) was added to this oil and the flask was placed in a refrigerator (4 °C) overnight. The resulting crystals are filtered and further washed with diethyl ether. Drying *in vacuo* give **5** (3.10 grams, 68% yield) as tan crystals.

MS (m/z): calcd for C₂₄H₂₇NO₈SNa, [M+Na]⁺, 524.1355; found, 524.141;

¹H NMR (500 MHz, CDCl₃): δ 7.91 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.49 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.99 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.80 – 5.72 (m, 1H), 5.59 – 5.50 (m, 1H), 5.32 (s, 2H), 4.63 (dd, *J* = 6.9, 1.4 Hz, 2H), 4.11 (d, *J* = 2.4 Hz, 2H), 4.04 (dd, *J* = 7.3, 1.5 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 2.11 (t, *J* = 2.4 Hz, 1H), 2.04 (s, 3H).

¹³C NMR (CDCl₃, 126 MHz): δ 170.8, 167.8, 149.4, 149.2, 137.1, 133.5, 132.7, 130.4, 129.3, 129.2, 128.7, 128.2, 127.7, 121.7, 112.3, 111.1, 77.1, 73.9, 68.5, 59.8, 56.1, 56.0, 43.3, 36.1, 21.0.



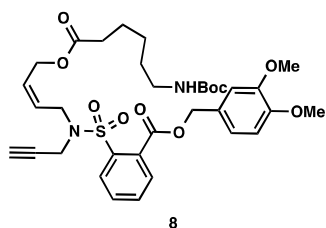
6: Compound **5** (3.00 g, 5.98 mmol, 1 eq) was dissolved in dry THF (30 mL) and then further diluted with methanol (30 mL). Sodium methoxide (600 μL, 1M in MeOH, 0.1 eq; freshly prepared) was added drop wise at room temperature. After 75 minutes, the starting material was fully consumed by TLC and the reaction was quenched with sat. aq NH₄Cl (1.0 mL). The solvents were removed under vacuum

and the resulting oil was partitioned between ethyl acetate and brine. The organic layer was separated, dried over Na₂SO₄ and concentrated *in vacuo* to give **6** (2.75 grams, quant.) as a thick yellow oil.

MS (m/z): calcd for C₂₃H₂₅NO₇SNa, [M+Na]⁺, 482.1249; found, 482.146;

¹H NMR (500 MHz, CDCl₃): δ 7.92 – 7.85 (m, 1H), 7.60 – 7.52 (m, 2H), 7.49 – 7.45 (m, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.98 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 5.81 (dtt, *J* = 11.1, 6.8, 1.4 Hz, 1H), 5.42 (dtt, *J* = 10.3, 7.4, 1.5 Hz, 1H), 5.30 (s, 2H), 4.17 (d, *J* = 6.7 Hz, 2H), 4.11 (d, *J* = 2.4 Hz, 2H), 4.00 (d, *J* = 7.3 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.14 (t, *J* = 2.4 Hz, 1H), 1.89 (s, 1H, O-H).

^{13}C NMR (CDCl_3 , 126 MHz): δ 167.92, 149.39, 149.13, 137.05, 134.41, 133.40, 132.67, 130.39, 129.14, 128.62, 127.64, 125.43, 121.73, 112.34, 111.05, 77.31, 73.83, 68.51, 58.03, 56.05, 56.00, 43.15, 36.11.

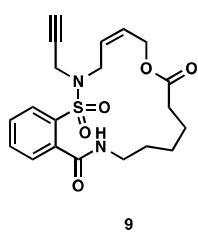


8: Compound **6** (2.75 g, 5.98 mmol, 1 eq) and *N*-Boc-5-aminovaleric acid (1.66 g, 7.18 mmol, 1.2 eq) were dissolved in dry DCM (30 mL). EDC (1.39 g, 8.95 mmol, 1.5 eq) was added to the reaction mixture at room temperature followed by DMAP•TsOH (88 mg, 0.3 mmol 0.05 eq). After 14 hours, the reaction mixture was diluted with DCM (100 mL), washed with 1N HCl (50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The resulting oil was purified by column chromatography (25% to 50% EtOAc in hexanes) to give **8** (3.77 g, 94% yield) as a white foam.

MS (m/z): calcd for $\text{C}_{34}\text{H}_{44}\text{N}_2\text{O}_{10}\text{SNa}$, $[\text{M}+\text{Na}]^+$, 695.2614; found, 695.149;

^1H NMR (600 MHz, CDCl_3): δ 7.90 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.56 (pd, $J = 7.4, 1.5$ Hz, 2H), 7.48 (dd, $J = 7.0, 2.0$ Hz, 1H), 7.02 (d, $J = 1.9$ Hz, 1H), 6.98 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.83 (d, $J = 8.2$ Hz, 1H), 5.78 – 5.71 (m, 1H), 5.57 – 5.50 (m, 1H), 5.31 (s, 2H), 4.63 (dd, $J = 6.8, 1.4$ Hz, 2H), 4.54 (br-s, 1H), 4.10 (d, $J = 2.4$ Hz, 2H), 4.04 (d, $J = 7.3$ Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.08 (br-s, 2H), 2.28 (t, $J = 7.5$ Hz, 2H), 2.11 (t, $J = 2.4$ Hz, 1H), 1.60 (p, $J = 7.5$ Hz, 2H), 1.49 – 1.43 (m, 2H), 1.42 (s, 9H), 1.35 – 1.27 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz): δ 173.3, 167.8, 156.0, 149.4, 149.2, 137.0, 133.5, 132.7, 130.4, 129.4, 129.2, 128.7, 128.1, 127.7, 121.7, 112.3, 111.0, 79.2, 77.1, 73.9, 68.5, 59.6, 56.0, 56.0, 43.3, 40.5, 36.0, 34.1, 29.8, 28.5, 26.4, 24.6.



9: Compound **8** (3.70 g, 5.5 mmol, 1 eq) was dissolved in dry DCM (21 mL) and triethylsilane (8.8 mL, 55 mmol, 10 eq) was added followed by TFA (5.5 mL, 72 mmol, 13 eq). The reaction mixture was stirred for 2 hours at room temperature, then diluted with toluene (100 mL) and concentrated *in vacuo* to give the intermediate amino acid.

This was directly dissolved in DMF (1.0 L) and HATU (4.18 g, 11.0 mmol, 2 eq) was added at room temperature. After stirring the reaction mixture for 30 minutes, diisopropylethylamine (4.8 mL, 27.5 mmol, 5 eq) was added. After 36 hours, the reaction mixture was concentrated *in vacuo* and

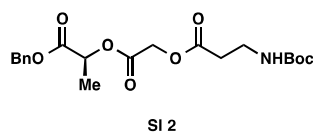
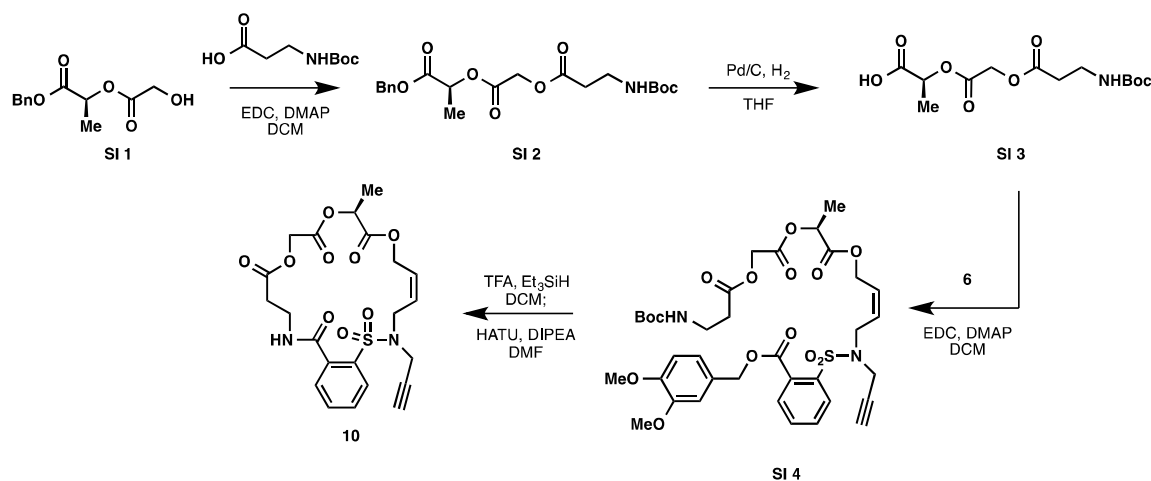
diluted with ethyl acetate (100 mL). The organic layer was washed with 1N HCl (3x 50 mL), 0.5N NaOH (2x 50 mL) and brine (50 mL). The combined organics were dried over Na₂SO₄, concentrated *in vacuo* and the resulting foam was purified by column chromatography (25% to 50% EtOAc in hexanes to 50% EtOAc/5% DCM in hexanes) to give **9** (1.63 g, 73% yield) as a white solid.

MS (m/z): calcd for C₂₀H₂₅N₂O₅S, [M+H]⁺, 405.1484; found, 405.1467;

¹H NMR (600 MHz, 9:1 CDCl₃:MeOD): δ 7.82 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.53 (td, *J* = 7.5, 1.3 Hz, 1H), 7.48 – 7.42 (m, 2H), 5.88 – 5.76 (m, 2H), 4.56 (d, *J* = 6.4 Hz, 2H), 4.08 (d, *J* = 5.3 Hz, 2H), 4.03 (d, *J* = 2.4 Hz, 2H), 3.32 (t, *J* = 6.3 Hz, 2H), 3.30 (s, 2H), 2.35 – 2.27 (m, 2H), 2.23 (t, *J* = 2.5 Hz, 1H), 1.70 – 1.60 (m, 2H), 1.57 – 1.47 (m, 2H), 1.43 – 1.32 (m, 2H).

¹³C NMR (CDCl₃:MeOD, 151 MHz): δ 174.43, 168.22, 136.64, 136.45, 132.83, 130.32, 129.73, 129.64, 128.46, 127.41, 76.61, 74.47, 59.12, 43.03, 40.16, 36.49, 34.10, 28.10, 26.14, 24.59.

Scheme S2 – Synthesis of monomer 10



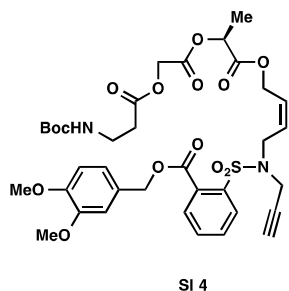
SI 2: Compound **SI 1**² (940 mg, 3.95 mmol, 1 eq) and *N*-Boc-β-alanine (897 mg, 4.74 mmol, 1.2 eq) were dissolved in dry DCM (13 mL). EDC (797 g, 5.13 mmol, 1.3 eq) was added to the reaction mixture at room temperature followed by DMAP (48 mg, 0.39 mmol, 0.1 eq). After 15 hours, the reaction mixture was diluted with DCM (50 mL), washed with 1N HCl (25 mL), brine (25 mL), dried over Na₂SO₄ and concentrated *in*

vacuo. The resulting oil was purified by column chromatography (10% to 25% EtOAc in hexanes) to give **SI 2** (1.19 g, 74% yield) as a white foam.

MS (*m/z*): calcd for C₂₀H₂₇NO₈Na, [M+Na]⁺, 432.1634; found, 432.124;

¹H NMR (500 MHz, CDCl₃): δ 7.40 – 7.31 (m, 5H), 5.24 (q, *J* = 7.1 Hz, 1H), 5.19 (d, *J* = 4.6 Hz, 2H), 5.13 (br-s, 1H), 4.76 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 16.0 Hz, 1H), 3.44 (q, *J* = 6.1 Hz, 2H), 2.63 (dd, *J* = 6.5, 5.1 Hz, 2H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.43 (s, 9H).

¹³C NMR (CDCl₃, 151 MHz): δ 171.8, 169.9, 167.3, 155.9, 135.2, 128.7, 128.6, 128.3, 79.5, 69.6, 67.4, 60.6, 36.3, 34.6, 28.5, 17.0.



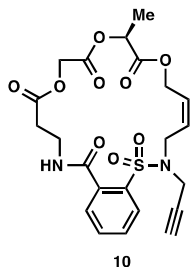
SI 4: Compound **SI 2** (1.13 g, 2.75 mmol, 1 eq) was dissolved in dry THF (9 mL) and Pd/C (113 mg, 10 wt%) was added to the reaction mixture at room temperature. Hydrogen gas was bubbled through the reaction mixture for 10 minutes then vigorously stirred 1 hour under a hydrogen atmosphere (balloon pressure). The reaction mixture was purged with argon for 10 minutes, filtered through celite and concentrated to give carboxylic acid **SI 3** that was used

directly in the next reaction. **SI 3** (2.75 mmol) and **6** (1.26 g, 2.75 mmol, 1.0 eq) were dissolved in dry DCM (14 mL) and EDC (640 mg, 4.12 mmol, 1.5 eq) was added to the reaction mixture at room temperature, followed by DMAP (34 mg, 0.28 mmol, 0.1 eq). After 15 hours, the reaction mixture was diluted with DCM (50 mL), washed with 1N HCl (25 mL), brine (25 mL), dried over Na₂SO₄ and concentrated *in vacuo*. The resulting oil was purified by column chromatography (40% to 60% EtOAc in hexanes) to give **SI 4** (1.60 g, 77% yield) as a white foam.

MS (*m/z*): calcd for C₃₆H₄₄N₂O₁₄SNa, [M+Na]⁺, 783.2411; found, 783.174;

¹H NMR (500 MHz, CDCl₃): δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.26 (s, 1H), 7.01 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.73 (dtd, *J* = 12.4, 7.2, 1.6 Hz, 1H), 5.61 – 5.52 (m, 1H), 5.29 (s, 2H), 5.14 (q, *J* = 7.0 Hz, 1H), 5.10 (br-s, 1H), 4.77 – 4.62 (m, 4H), 4.08 (s, 2H), 4.02 (d, *J* = 7.3 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.40 (t, *J* = 6.3 Hz, 2H), 2.60 (t, *J* = 6.1 Hz, 2H), 2.13 (t, *J* = 2.5 Hz, 1H), 1.48 (d, *J* = 7.1 Hz, 1H), 1.40 (s, 9H).

¹³C NMR (CDCl₃, 151 MHz): δ 171.6, 169.7, 167.7, 167.1, 155.7, 149.3, 149.0, 136.8, 133.3, 132.6, 130.3, 129.0, 128.8, 128.5, 128.3, 127.6, 121.6, 112.2, 110.9, 79.3, 74.0, 69.3, 68.3, 60.6, 60.4, 55.9, 55.9, 43.1, 36.1, 36.0, 34.4, 28.3, 16.8.



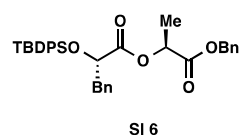
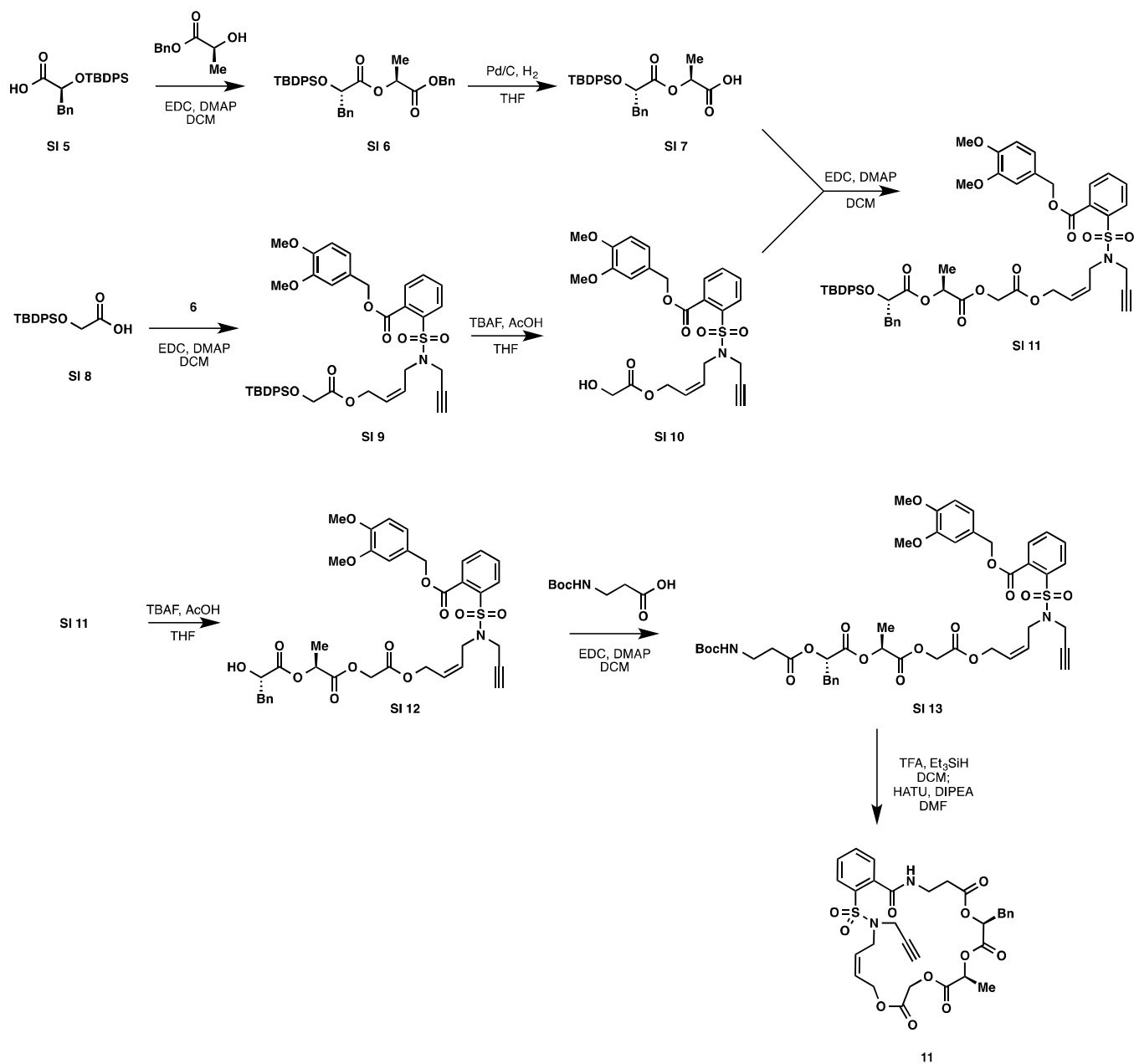
9: Compound **SI 4** (1.25 g, 1.64 mmol, 1 eq) was dissolved in dry DCM (6.5 mL) and triethylsilane (2.6 mL, 16 mmol, 10 eq) was added followed by TFA (1.65 mL, 21 mmol, 13 eq). The reaction mixture was stirred for 2 hours at room temperature, then diluted with toluene (50 mL) and concentrated *in vacuo* to give the intermediate amino acid. This was directly dissolved in DMF (325 mL) and HATU (1.25 g, 3.29 mmol, 2 eq) was added at room temperature. After stirring the reaction mixture for 30 minutes, diisopropylethylamine (1.4 mL, 8.0 mmol, 5 eq) was added. After 36 hours, the reaction mixture was concentrated *in vacuo* and diluted with ethyl acetate (100 mL). The organic layer was washed with 1N HCl (3x 50 mL), 0.5N NaOH (2x 50 mL) and brine (50 mL). The combined organics were dried over Na₂SO₄, concentrated *in vacuo* and the resulting foam was purified by column chromatography (50% to 75% EtOAc in hexanes) to give **9** (423 mg, 52% yield) as a white foam.

MS (m/z): calcd for C₂₂H₂₅N₂O₉S, [M+H]⁺, 493.1281; found, 493.1299;

¹H NMR (500 MHz, CDCl₃): δ 7.78 (dd, *J* = 7.7, 2.6 Hz, 1H), 7.50 (td, *J* = 7.4, 2.7 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.34 (dd, *J* = 7.5, 2.4 Hz, 1H), 7.31 – 7.26 (m, 1H), 5.78 – 5.71 (m, 1H), 5.67 – 5.58 (m, 1H), 4.88 (qd, *J* = 7.0, 2.6 Hz, 1H), 4.72 (dd, *J* = 16.2, 2.7 Hz, 1H), 4.49 (dd, *J* = 16.3, 2.9 Hz, 1H), 4.14 (d, *J* = 18.4 Hz, 1H), 3.92 (d, *J* = 18.6 Hz, 1H), 3.88 (dd, *J* = 16.1, 6.1 Hz, 1H), 3.73 (dd, *J* = 15.4, 7.6 Hz, 1H), 3.68 – 3.58 (m, 2H), 2.64 (dt, *J* = 9.1, 6.4, 3.0 Hz, 2H), 2.23 (d, *J* = 2.6 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 126 MHz): δ 171.56, 169.85, 168.56, 168.02, 136.54, 135.65, 133.00, 130.88, 129.83, 128.85, 128.70, 126.83, 76.83, 74.64, 70.00, 60.37, 59.83, 42.74, 36.16, 35.52, 33.36, 16.34.

Scheme S3 – Synthesis of monomer 11



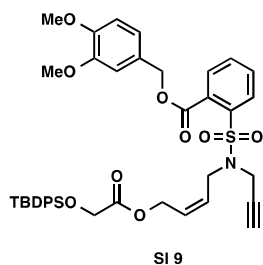
SI 6: Compound SI 5³ (4.85 g, 12.0 mmol, 1.2 eq) and (*S*)-benzyl lactate (1.80 g, 10.0 mmol, 1.0 eq) were dissolved in dry DCM (40 mL) and EDC (2.33 g, 15.0

mmol, 1.5 eq) was added to the reaction mixture at room temperature followed by DMAP (61 mg, 0.5 mmol, 0.05 eq). After 15 hours, the reaction mixture was diluted with DCM (50 mL), washed with 1N HCl (25 mL), brine (25 mL), dried over Na₂SO₄ and concentrated *in vacuo*. The resulting oil was purified by column chromatography (0% to 10% Et₂O in hexanes) to give **SI 6** (3.27 g, 58% yield) as a colorless oil.

MS (*m/z*): calcd for C₃₅H₃₈O₅SiNa, [M+Na]⁺, 589.7588; found, 589.263;

¹H NMR (500 MHz, CDCl₃): δ 7.69 – 7.65 (m, 2H), 7.48 – 7.29 (m, 12H), 7.29 – 7.25 (m, 6H), 5.19 (d, *J* = 12.3 Hz, 1H), 5.13 (d, *J* = 12.3 Hz, 1H), 4.77 (q, *J* = 7.1 Hz, 1H), 4.46 (dd, *J* = 8.6, 3.9 Hz, 1H), 3.11 (dd, *J* = 13.7, 3.9 Hz, 1H), 2.97 (dd, *J* = 13.7, 8.6 Hz, 1H), 1.23 (d, *J* = 7.1 Hz, 3H), 1.07 (s, 9H).

¹³C NMR (CDCl₃, 151 MHz): δ 172.0, 170.3, 137.3, 136.3, 135.9, 135.4, 133.1, 133.0, 130.2, 129.8, 129.6, 128.7, 128.5, 128.3, 128.3, 127.5, 126.7, 73.6, 68.6, 67.1, 41.4, 26.9, 19.3, 16.7.

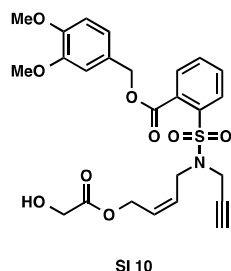


SI 9: Compound **SI 8**³ (1.13 g, 3.3 mmol, 1.1 eq) and **6** (1.38 g, 3.0 mmol, 1.0 eq) were dissolved in dry DCM (15 mL) and EDC (605 mg, 3.9 mmol, 1.3 eq) was added to the reaction mixture at room temperature followed by DMAP (44 mg, 0.15 mmol, 0.05 eq). After 15 hours, the reaction mixture was diluted with DCM (50 mL), washed with 1N HCl (25 mL), brine (25 mL), dried over Na₂SO₄ and concentrated *in vacuo*. The resulting oil was purified by column chromatography (10% to 30% EtOAc in hexanes) to give **SI 9** (1.82 g, 80% yield) as a colorless oil.

MS (*m/z*): calcd for C₄₁H₄₅NO₉SSiNa, [M+Na]⁺, 778.9438; found, 778.204;

¹H NMR (500 MHz, CDCl₃): δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 6.7 Hz, 4H), 7.56 (p, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.1 Hz, 4H), 7.04 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 5.76 – 5.65 (m, 1H), 5.59 – 5.49 (m, 1H), 5.32 (s, 2H), 4.67 (d, *J* = 6.8 Hz, 2H), 4.25 (s, 2H), 4.09 (d, *J* = 2.1 Hz, 2H), 4.03 (d, *J* = 7.3 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 2.06 (t, *J* = 2.5 Hz, 1H), 1.09 (s, 9H).

¹³C NMR (CDCl₃, 125 MHz): δ 170.9, 167.8, 149.4, 149.1, 137.0, 135.6, 133.4, 132.8, 132.6, 130.4, 130.0, 129.1, 128.9, 128.6, 128.4, 127.9, 127.7, 121.7, 112.3, 111.0, 77.0, 73.9, 68.4, 62.2, 59.8, 56.0, 56.0, 43.2, 36.0, 26.7, 19.3.

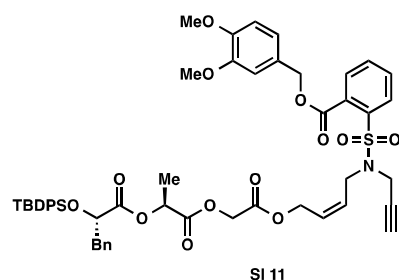


SI 10: Compound **SI 9** (1.8 g, 2.38 mmol, 1.0 eq) was dissolved in dry THF (8 mL) and acetic acid (410 μ L, 7.17 mmol, 3 eq) was added to the reaction mixture at room temperature followed by TBAF (3.6 mL, 1M in THF, 3.6 mmol, 1.5 eq). After 4 hours, the reaction mixture was diluted with ethyl acetate (50 mL), washed with sat. aq sodium bicarbonate (25 mL), brine (25 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The resulting oil was purified by column chromatography (33% to 66% EtOAc in hexanes to 100% EtOAc to 5% DCM in EtOAc) to give **SI 10** (1.06 g, 86% yield) as a white solid.

MS (m/z): calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_9\text{SNa}$, $[\text{M}+\text{Na}]^+$, 540.5388; found, 540.109;

^1H NMR (400 MHz, CDCl_3): δ 7.92 – 7.85 (m, 1H), 7.60 – 7.51 (m, 2H), 7.47 (ddd, $J = 7.0, 2.5, 1.5$ Hz, 1H), 7.01 (d, $J = 1.9$ Hz, 1H), 6.98 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.82 (dd, $J = 8.3, 1.2$ Hz, 1H), 5.81 – 5.69 (m, 1H), 5.61 – 5.52 (m, 1H), 5.30 (s, 2H), 4.73 (dd, $J = 7.1, 1.5$ Hz, 2H), 4.13 (d, $J = 2.8$ Hz, 2H), 4.08 (d, $J = 2.3$ Hz, 2H), 4.03 (d, $J = 7.1$ Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.61 (br-s, 1H), 2.12 (t, $J = 2.4$ Hz, 1H).

^{13}C NMR (CDCl_3 , 126 MHz): δ 173.0, 167.8, 149.3, 149.1, 136.8, 133.4, 132.7, 130.4, 129.2, 129.0, 128.6, 128.3, 127.6, 121.7, 112.3, 111.0, 77.0, 74.0, 68.4, 60.6, 60.5, 56.0, 56.0, 43.2, 36.1.



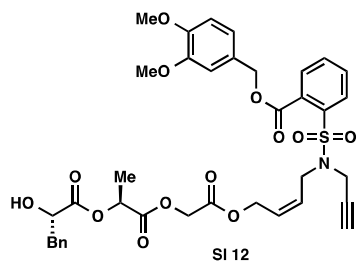
SI 11: Compound **SI 6** (1.41 g, 2.49 mmol, 1 eq) was dissolved in dry THF (9 mL) and Pd/C (140 mg, 10 wt%) was added to the reaction mixture at room temperature. Hydrogen gas was bubbled through the reaction mixture for 10 minutes then vigorously stirred for 24 hours under a hydrogen atmosphere (balloon pressure). The reaction mixture was bubbled with argon for 10 minutes, filtered through celite and concentrated to give carboxylic acid **SI 7** that was used directly in the next reaction. Compound **SI 7** (1.0 g, 1.93 mmol, 1.0 eq) and Compound **SI 10** (1.01 g, 2.12 mmol, 1.1 eq) were dissolved in dry DCM (15 mL) and EDC (599 mg, 3.9 mmol, 2 eq) was added to the reaction mixture at room temperature followed by DMAP \cdot TsOH (57 mg, 0.19 mmol, 0.1 eq). After 18 hours, the reaction mixture was diluted with DCM (50 mL), washed with 1N HCl (25 mL), brine (25 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The resulting oil was purified by column chromatography (30% to 50% EtOAc in hexanes) to give **SI 11** (1.80 g, 95% yield) as a white foam.

Compound **SI 7** (1.0 g, 1.93 mmol, 1.0 eq) and Compound **SI 10** (1.01 g, 2.12 mmol, 1.1 eq) were dissolved in dry DCM (15 mL) and EDC (599 mg, 3.9 mmol, 2 eq) was added to the reaction mixture at room temperature followed by DMAP \cdot TsOH (57 mg, 0.19 mmol, 0.1 eq). After 18 hours, the reaction mixture was diluted with DCM (50 mL), washed with 1N HCl (25 mL), brine (25 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The resulting oil was purified by column chromatography (30% to 50% EtOAc in hexanes) to give **SI 11** (1.80 g, 95% yield) as a white foam.

MS (*m/z*): calcd for C₂₅H₂₇NO₉SNa, [M+Na]⁺, 999.1678; found, 998.325;

¹H NMR (600 MHz, CDCl₃): δ 7.90 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.49 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.37 – 7.31 (m, 3H), 7.30 – 7.26 (m, 3H), 7.25 – 7.20 (m, 6H), 7.04 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.74 (dt, *J* = 11.1, 6.9, 1.5 Hz, 1H), 5.65 – 5.52 (m, 1H), 5.32 (s, 2H), 4.70 (m, 3H), 4.65 (d, *J* = 16.0 Hz, 1H), 4.50 (d, *J* = 15.9 Hz, 1H), 4.42 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.09 (d, *J* = 2.5 Hz, 2H), 4.03 (d, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 3.10 (dd, *J* = 13.7, 4.0 Hz, 1H), 2.95 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.12 (t, *J* = 2.4 Hz, 1H), 1.23 (d, *J* = 7.1 Hz, 3H), 1.01 (s, 9H).

¹³C NMR (CDCl₃, 151 MHz): δ 172.0, 169.9, 167.8, 166.9, 149.4, 149.1, 137.1, 136.9, 136.3, 135.9, 133.4, 133.1, 132.9, 132.7, 130.4, 130.2, 129.8, 129.6, 129.2, 129.0, 128.7, 128.3, 128.3, 127.7, 127.5, 126.7, 121.7, 112.3, 111.0, 76.9, 74.1, 73.5, 68.5, 68.3, 60.9, 60.6, 56.0, 56.0, 43.2, 41.3, 36.1, 26.8, 19.2, 16.6.



SI 12: Compound **SI 11** (1.80 g, 1.84 mmol, 1.0 eq) was dissolved in dry THF (6 mL) and acetic acid (316 μL, 5.5 mmol, 3 eq) was added to the reaction mixture at room temperature followed by TBAF (2.75 mL, 1M in THF, 2.75 mmol, 1.5 eq). After 3 hours, the reaction mixture was diluted with ethyl acetate (50 mL), washed with sat. aq sodium bicarbonate (25

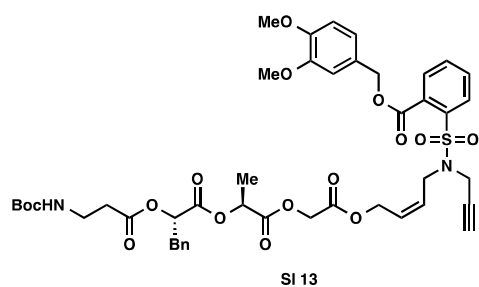
mL), brine (25 mL), dried over Na₂SO₄ and concentrated *in vacuo*. The resulting oil was purified by column chromatography (33% to 66% EtOAc in hexanes) to give **SI 12** (1.10 g, 81% yield) as a white foam.

MS (*m/z*): calcd for C₃₇H₃₉NO₁₃SNa, [M+Na]⁺, 760.2040; found, 760.107;

¹H NMR (600 MHz, CDCl₃): δ 7.88 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.55 (pd, *J* = 7.5, 1.6 Hz, 2H), 7.47 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.28 – 7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.98 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 5.78 – 5.69 (m, 1H), 5.61 – 5.52 (m, 1H), 5.30 (s, 2H), 5.24 (q, *J* = 7.1 Hz, 1H), 4.75 – 4.69 (m, 3H), 4.59 (d, *J* = 15.9 Hz, 1H), 4.46 (dd, *J* = 7.8, 4.2 Hz, 1H), 4.08 (d, *J* = 2.6 Hz, 2H), 4.02 (dd, *J* = 7.5, 1.5 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.21 (dd, *J* = 14.1, 4.2 Hz, 1H), 2.95 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.15 (t, *J* = 2.4 Hz, 1H), 1.55 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (CDCl₃, 151 MHz): δ 173.3, 169.6, 167.6, 166.7, 149.2, 149.0, 136.7, 136.5, 133.2, 132.6,

130.3, 129.5, 129.0, 128.9, 128.5, 128.3, 128.0, 127.5, 126.7, 121.5, 112.1, 110.9, 76.8, 74.0, 71.2, 69.0, 68.3, 61.0, 60.5, 55.8, 55.8, 43.0, 40.3, 35.9, 16.8.



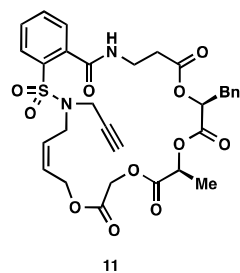
SI 13: Compound **SI 12** (1.09 g, 1.48 mmol, 1.0 eq) and *N*-Boc- β -alanine (364 mg, 1.92 mmol, 1.3 eq) were dissolved in dry DCM (15 mL) and EDC (605 mg, 3.9 mmol, 1.3 eq) was added to the reaction mixture at room temperature followed by DMAP•TsOH (44 mg, 0.15 mmol, 0.1 eq). After 18 hours, the reaction mixture was diluted with DCM (50 mL), washed with 1N HCl (25 mL),

brine (25 mL), dried over Na₂SO₄ and concentrated *in vacuo*. The resulting oil was purified by column chromatography (25% to 50% EtOAc in hexanes) to give **SI 13** (1.31 g, 97% yield) as a white foam.

MS (m/z): calcd for C₄₅H₅₂N₂O₁₆SNa, [M+Na]⁺, 931.9855; found, 931.292;

¹H NMR (600 MHz, CDCl₃): δ 7.90 – 7.81 (m, 1H), 7.57 – 7.49 (m, 2H), 7.45 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.21 (dt, *J* = 8.0, 1.9 Hz, 3H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.96 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.75 – 5.68 (m, 1H), 5.58 – 5.51 (m, 1H), 5.28 (s, 2H), 5.26 – 5.18 (m, 2H), 4.94 (t, *J* = 6.0 Hz, 1H), 4.76 – 4.66 (m, 3H), 4.55 (d, *J* = 15.9 Hz, 1H), 4.06 (d, *J* = 2.5 Hz, 2H), 4.00 (d, *J* = 7.3 Hz, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.34 – 3.21 (m, 3H), 3.06 (dd, *J* = 14.5, 9.7 Hz, 1H), 2.64 – 2.36 (m, 2H), 2.13 (t, *J* = 2.4 Hz, 1H), 1.54 (d, *J* = 7.1 Hz, 3H), 1.38 (s, 9H).

¹³C NMR (CDCl₃, 151 MHz): δ 171.51, 169.50, 168.89, 167.61, 166.67, 155.68, 149.21, 148.97, 136.69, 135.80, 133.25, 132.59, 130.29, 129.21, 129.03, 128.91, 128.49, 128.46, 128.06, 127.51, 127.03, 121.54, 112.13, 110.89, 79.14, 76.79, 74.02, 72.69, 68.99, 68.27, 60.97, 60.47, 55.85, 55.81, 43.01, 36.91, 36.02, 35.95, 34.46, 28.31, 16.73.



11: Compound **13** (1.30 g, 1.43 mmol, 1 eq) was dissolved in dry DCM (5.7 mL) and triethylsilane (2.3 mL, 14.4 mmol, 10 eq) was added followed by TFA (1.4 mL, 18.6 mmol, 13 eq). The reaction mixture was stirred for 2 hours at room temperature, then diluted with toluene (50 mL) and concentrated *in vacuo* to give the intermediate amino acid. This was directly dissolved in DMF (282 mL) and HATU (1.09 g, 2.87

mmol, 2 eq) was added at room temperature. After stirring the reaction mixture for 30 minutes,

diisopropylethylamine (1.24 mL, 7.2 mmol, 5 eq) was added. After 36 hours, the reaction mixture was concentrated *in vacuo* and diluted with ethyl acetate (100 mL). The organic layer was washed with 1N HCl (3x 50 mL), 0.5N NaOH (2x 50 mL) and brine (50 mL). The combined organics were dried over Na₂SO₄, concentrated *in vacuo* and the resulting foam was purified by column chromatography (25% to 50% EtOAc in hexanes) to give **11** (682 mg, 74% yield) as a white foam.

MS (m/z): calcd for C₃₁H₃₂N₂O₁₁SNa, [M+Na]⁺, 663.1625; found, 663.028;

¹H NMR (600 MHz, 9:1 CDCl₃:MeOD): δ 7.85 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.51 (td, *J* = 7.5, 1.3 Hz, 1H), 7.47 (td, *J* = 7.7, 1.5 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 3H), 5.79 – 5.67 (m, 2H), 5.20 (dd, *J* = 9.1, 4.1 Hz, 1H), 5.14 (q, *J* = 7.0 Hz, 1H), 4.67 – 4.61 (m, 2H), 4.58 (ddd, *J* = 12.7, 4.7, 1.9 Hz, 1H), 4.48 (d, *J* = 15.7 Hz, 1H), 4.07 – 3.93 (m, 4H), 3.65 (ddd, *J* = 13.3, 7.0, 6.0 Hz, 1H), 3.57 (ddd, *J* = 13.6, 7.0, 5.9 Hz, 1H), 3.25 (s, 2H), 3.19 (dd, *J* = 14.5, 4.0 Hz, 1H), 3.07 (dd, *J* = 14.5, 9.1 Hz, 1H), 2.72 (ddd, *J* = 16.2, 7.0, 5.9 Hz, 1H), 2.54 (ddd, *J* = 16.2, 6.9, 6.0 Hz, 1H), 2.14 (t, *J* = 2.4 Hz, 1H), 1.39 (d, *J* = 7.0 Hz, 3H).

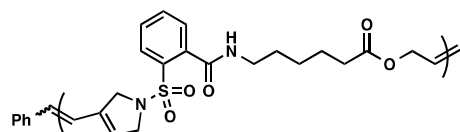
¹³C NMR (9:1 CDCl₃:MeOD, 151 MHz): δ 171.6, 169.6, 168.7, 168.3, 166.9, 136.6, 136.2, 135.6, 132.9, 130.5, 129.8, 129.3, 129.2, 129.0, 128.5, 127.1, 127.0, 77.1, 74.1, 73.2, 69.0, 61.3, 60.1, 43.2, 36.9, 36.4, 35.5, 33.6, 16.6.

Polymerization General Procedure

A stock solution 3,5 dichloropyridine is prepared in degassed DCM:MeOH (9:1) at either 20 or 40 mM depending on the substrate. The macrocyclic monomer (0.1 mmol) is added to an 8 mL vial (Fisher #14-959-25A) equipped with a stir bar, placed under an argon atmosphere, dissolved in the stock solution (200 μL) and cooled to 0 °C in an ice bath. In a separate vial, a solution of Grubbs 3rd generation catalyst⁴ is prepared using the stock solution and 50 μL is rapidly transferred to the stirred reaction mixture using a microliter syringe.

At the given time, the polymerization is stopped by addition of ethyl vinyl ether (250 μL, 20% v/v in DCM). The reaction mixture is taken out of the ice bath, further diluted with DCM (2 mL) and allowed to stir open to air. The reaction is then concentrated, dissolved in 9:1 CDCl₃/MeOD to determine conversion by ¹H-NMR, and precipitated 2x into diethyl ether. The precipitated polymer is then characterized using

GPC, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.

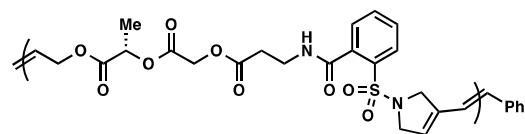


P-9: Prepared following the general procedure.

Physical state: light gray solid;

$^1\text{H NMR}$ (600 MHz, 9:1 $\text{CDCl}_3:\text{MeOD}$): (major isomer) δ 7.77 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.52 (td, $J = 7.5, 1.3$ Hz, 1H), 7.47 (td, $J = 7.7, 1.4$ Hz, 1H), 7.42 (dd, $J = 7.6, 1.4$ Hz, 1H), 6.26 (d, $J = 15.9$ Hz, 1H), 5.64 – 5.61 (m, 1H), 5.49 (dt, $J = 15.9, 6.1$ Hz, 1H), 4.51 (d, $J = 6.1$ Hz, 2H), 4.26 – 4.18 (m, 4H), 3.34 – 3.27 (m, 2H), 2.26 (t, $J = 7.4$ Hz, 2H), 1.57 (dp, $J = 19.4, 7.3$ Hz, 4H), 1.34 (tt, $J = 7.2, 5.5$ Hz, 2H).

$^{13}\text{C NMR}$ (9:1 $\text{CDCl}_3:\text{MeOD}$, 151 MHz): (major isomer) δ 173.6, 168.6, 136.8, 135.9, 135.1, 132.7, 129.7, 129.5, 128.7, 126.6, 126.1, 124.2, 64.2, 54.9, 53.4, 40.0, 34.0, 28.6, 26.4, 24.4.

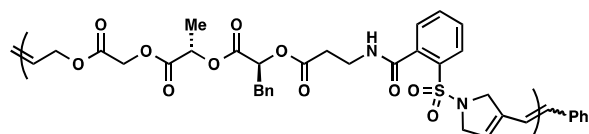


P-10: Prepared following the general procedure.

Physical state: light gray solid;

$^1\text{H NMR}$ (600 MHz, 9:1 $\text{CDCl}_3:\text{MeOD}$): (major isomer) δ 7.85 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.51 (td, $J = 7.5, 1.3$ Hz, 1H), 7.47 (td, $J = 7.7, 1.5$ Hz, 1H), 7.36 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 3H), 5.79 – 5.67 (m, 2H), 5.20 (dd, $J = 9.1, 4.1$ Hz, 1H), 5.14 (q, $J = 7.0$ Hz, 1H), 4.67 – 4.61 (m, 2H), 4.58 (ddd, $J = 12.7, 4.7, 1.9$ Hz, 1H), 4.48 (d, $J = 15.7$ Hz, 1H), 4.07 – 3.93 (m, 4H), 3.65 (ddd, $J = 13.3, 7.0, 6.0$ Hz, 1H), 3.57 (ddd, $J = 13.6, 7.0, 5.9$ Hz, 1H), 3.25 (s, 2H), 3.19 (dd, $J = 14.5, 4.0$ Hz, 1H), 3.07 (dd, $J = 14.5, 9.1$ Hz, 1H), 2.72 (ddd, $J = 16.2, 7.0, 5.9$ Hz, 1H), 2.54 (ddd, $J = 16.2, 6.9, 6.0$ Hz, 1H), 2.14 (t, $J = 2.4$ Hz, 1H), 1.39 (d, $J = 7.0$ Hz, 3H).

$^{13}\text{C NMR}$ (9:1 $\text{CDCl}_3:\text{MeOD}$, 151 MHz): (major isomer) δ 171.6, 169.6, 168.7, 168.3, 166.9, 136.6, 136.2, 135.6, 132.9, 130.5, 129.8, 129.3, 129.2, 129.0, 128.5, 127.1, 127.0, 77.1, 74.1, 73.2, 69.0, 61.3, 60.1, 43.2, 36.9, 36.4, 35.5, 33.6, 16.6.



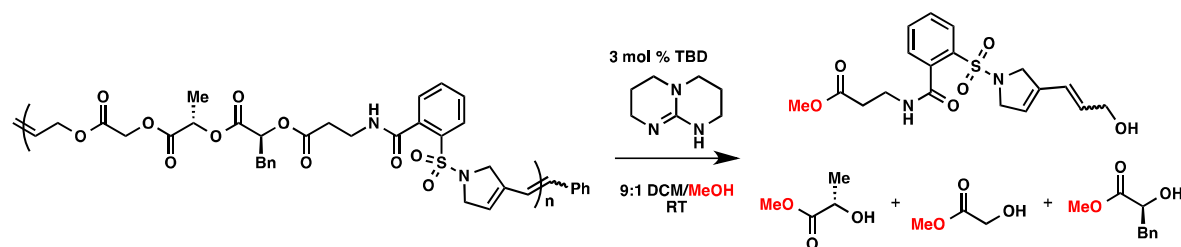
P-11: Prepared following the general procedure.

Physical state: light gray solid;

¹H NMR (600 MHz, 9:1 CDCl₃:MeOD): (major isomer) δ 7.85 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.51 (td, $J = 7.5, 1.3$ Hz, 1H), 7.47 (td, $J = 7.7, 1.5$ Hz, 1H), 7.36 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 3H), 5.79 – 5.67 (m, 2H), 5.20 (dd, $J = 9.1, 4.1$ Hz, 1H), 5.14 (q, $J = 7.0$ Hz, 1H), 4.67 – 4.61 (m, 2H), 4.58 (ddd, $J = 12.7, 4.7, 1.9$ Hz, 1H), 4.48 (d, $J = 15.7$ Hz, 1H), 4.07 – 3.93 (m, 4H), 3.65 (ddd, $J = 13.3, 7.0, 6.0$ Hz, 1H), 3.57 (ddd, $J = 13.6, 7.0, 5.9$ Hz, 1H), 3.25 (s, 2H), 3.19 (dd, $J = 14.5, 4.0$ Hz, 1H), 3.07 (dd, $J = 14.5, 9.1$ Hz, 1H), 2.72 (ddd, $J = 16.2, 7.0, 5.9$ Hz, 1H), 2.54 (ddd, $J = 16.2, 6.9, 6.0$ Hz, 1H), 2.14 (t, $J = 2.4$ Hz, 1H), 1.39 (d, $J = 7.0$ Hz, 3H).

¹³C NMR (9:1 CDCl₃:MeOD, 151 MHz): (major isomer) δ 171.6, 169.6, 168.7, 168.3, 166.9, 136.6, 136.2, 135.6, 132.9, 130.5, 129.8, 129.3, 129.2, 129.0, 128.5, 127.1, 127.0, 77.1, 74.1, 73.2, 69.0, 61.3, 60.1, 43.2, 36.9, 36.4, 35.5, 33.6, 16.6.

Scheme S4 - Methanolysis of P-11



P-11 (36.2k, \bar{M}_n : 1.26) is added to a 2-dram vial equipped with a stir bar, dissolved in 9:1 v/v DCM/MeOH (10 mg **P-11**/mL) and stirred at room temperature. A solution of TBD is added (2.6 mg/mL, 0.03 equiv/ester) is added under ambient conditions and the vial is capped. At the given time, the reaction is stopped by the addition of an AcOH solution (2 eq). A small aliquot is removed for GPC analysis and the remainder is concentrated *in vacuo* for ¹H-NMR.

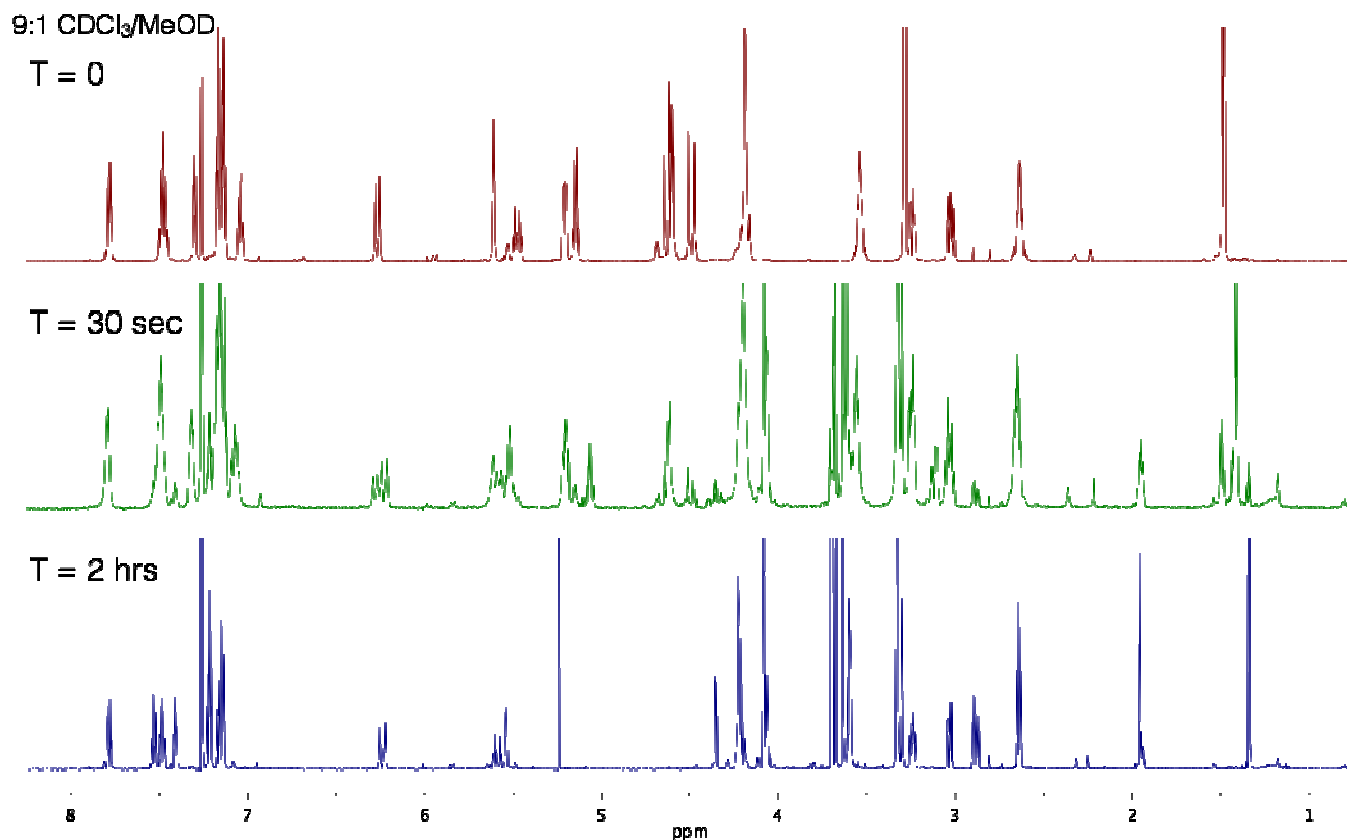
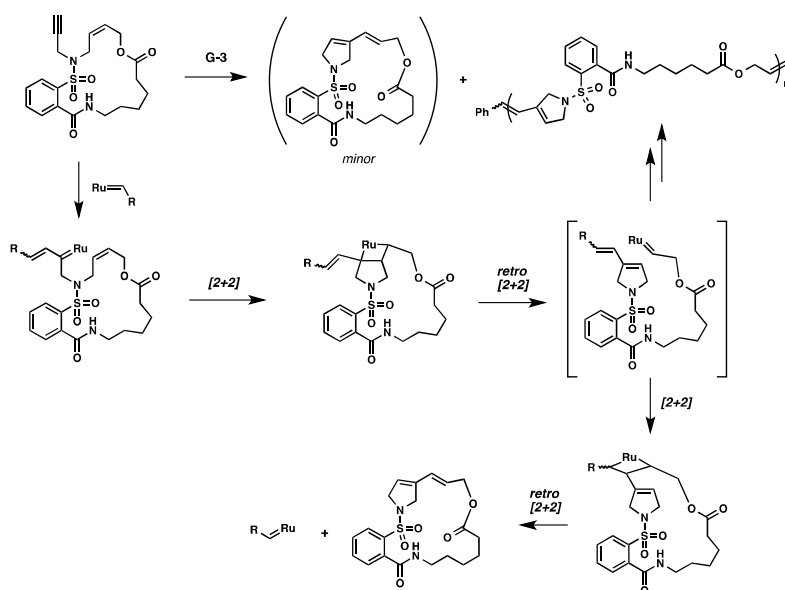
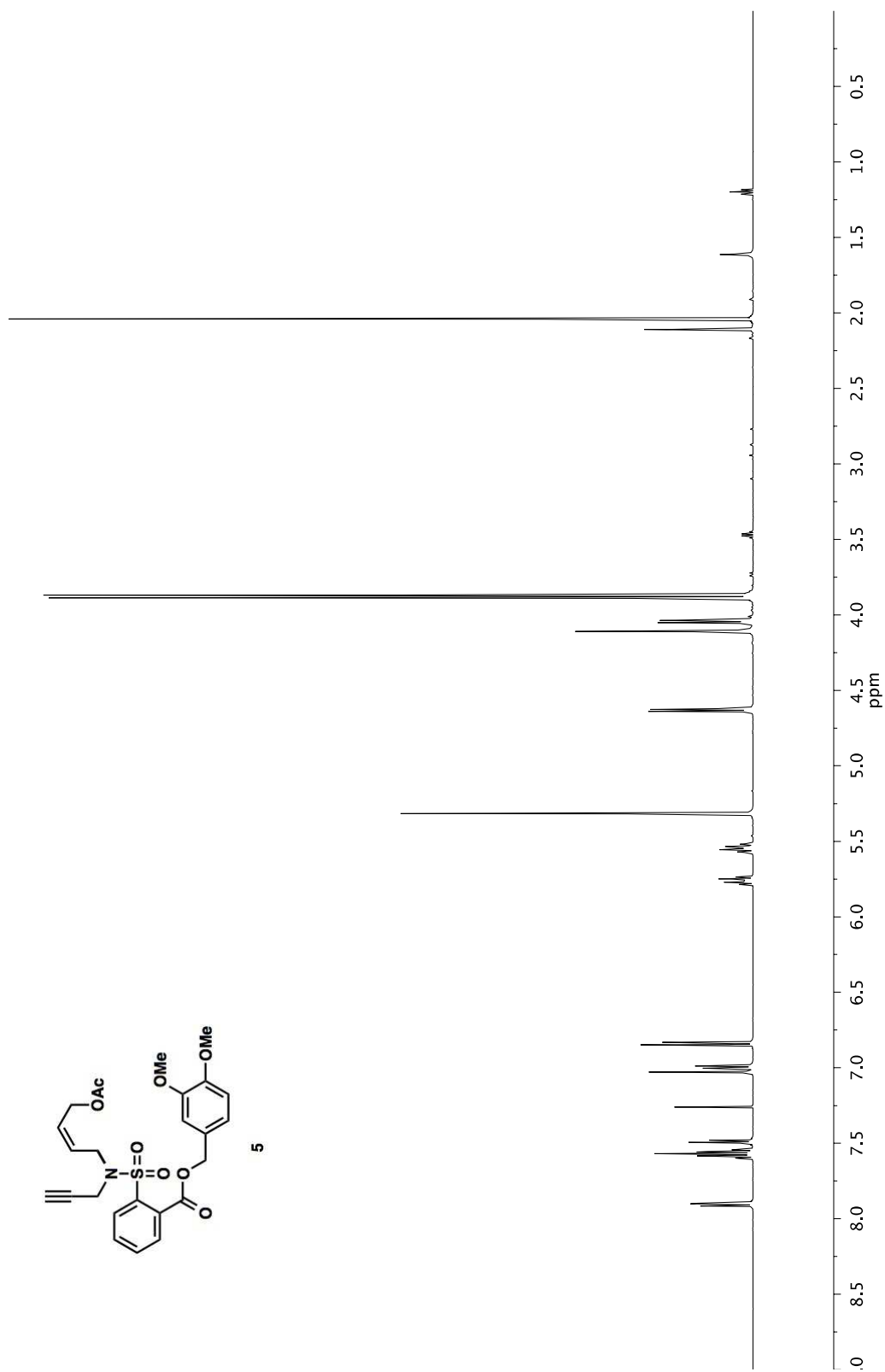


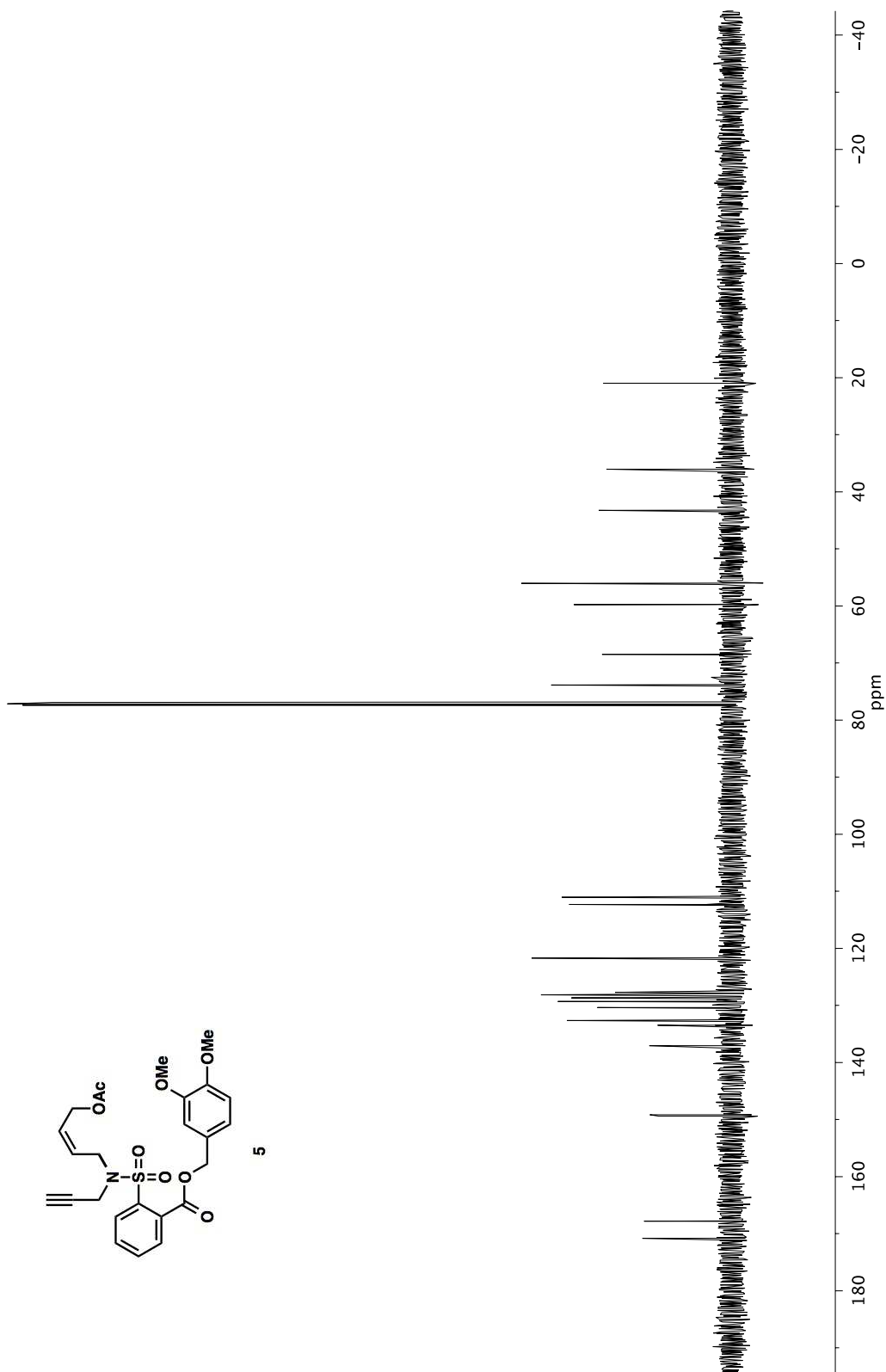
Figure S1 ¹H-NMR of methanolysis. T = 0, starting polymer; T = 30 seconds, variety of oligomeric species. Note the unresolved peaks; T = 2 hours, small molecule methyl esters. All of the peaks are sharp, well resolved and coincide with literature values for each of the known methyl esters.

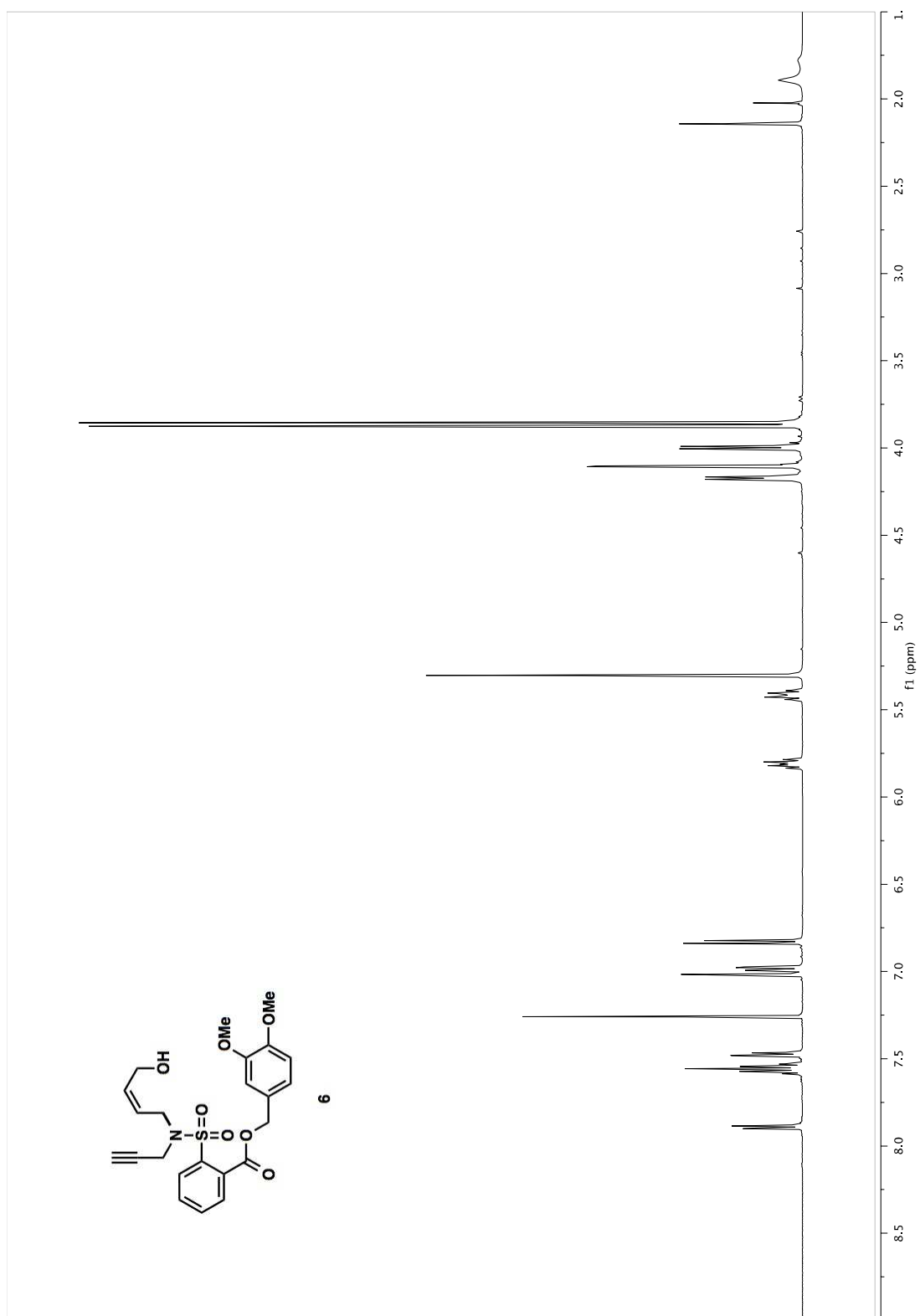
Scheme S5 Proposed Formation of Isomerized Monomers

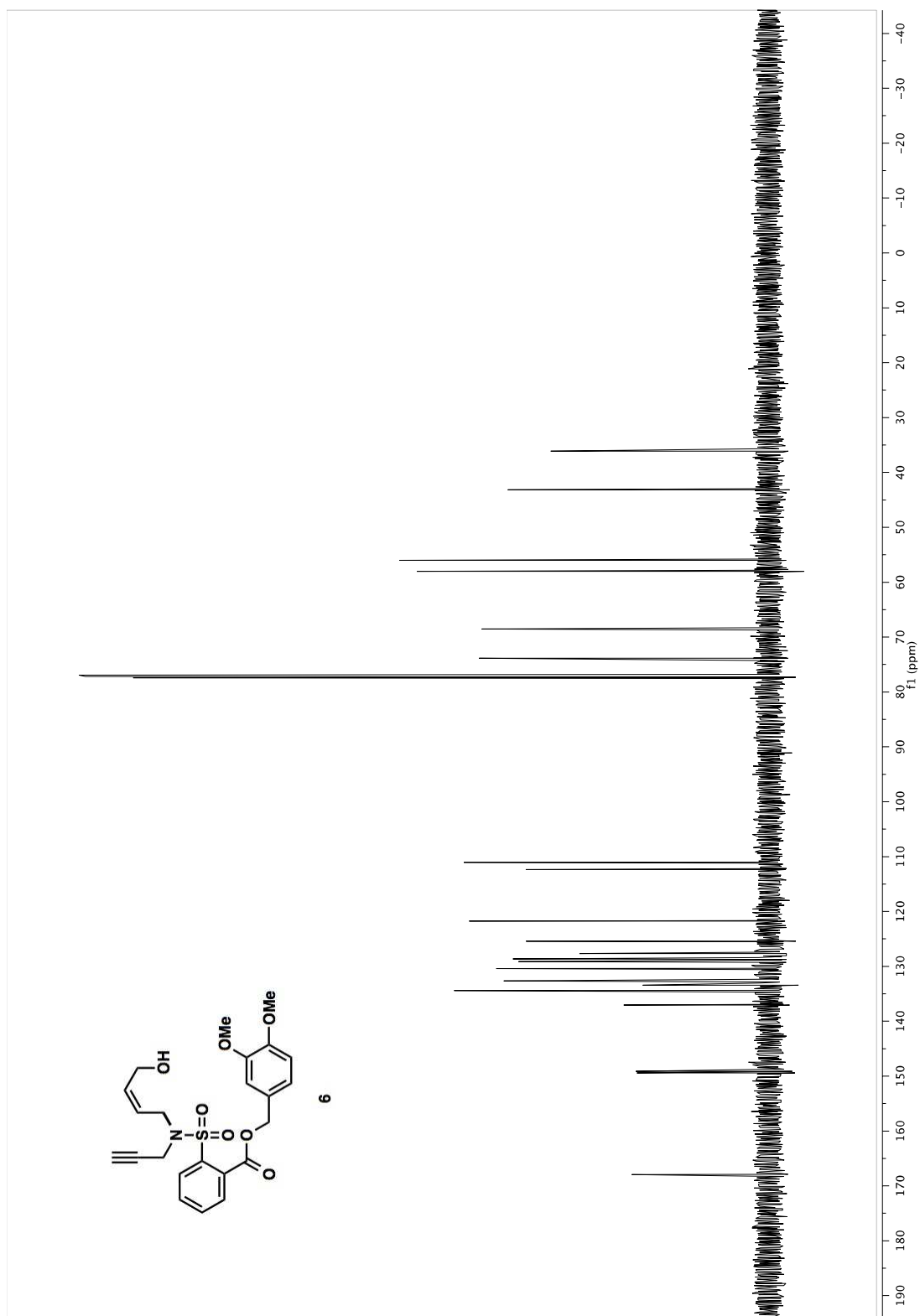


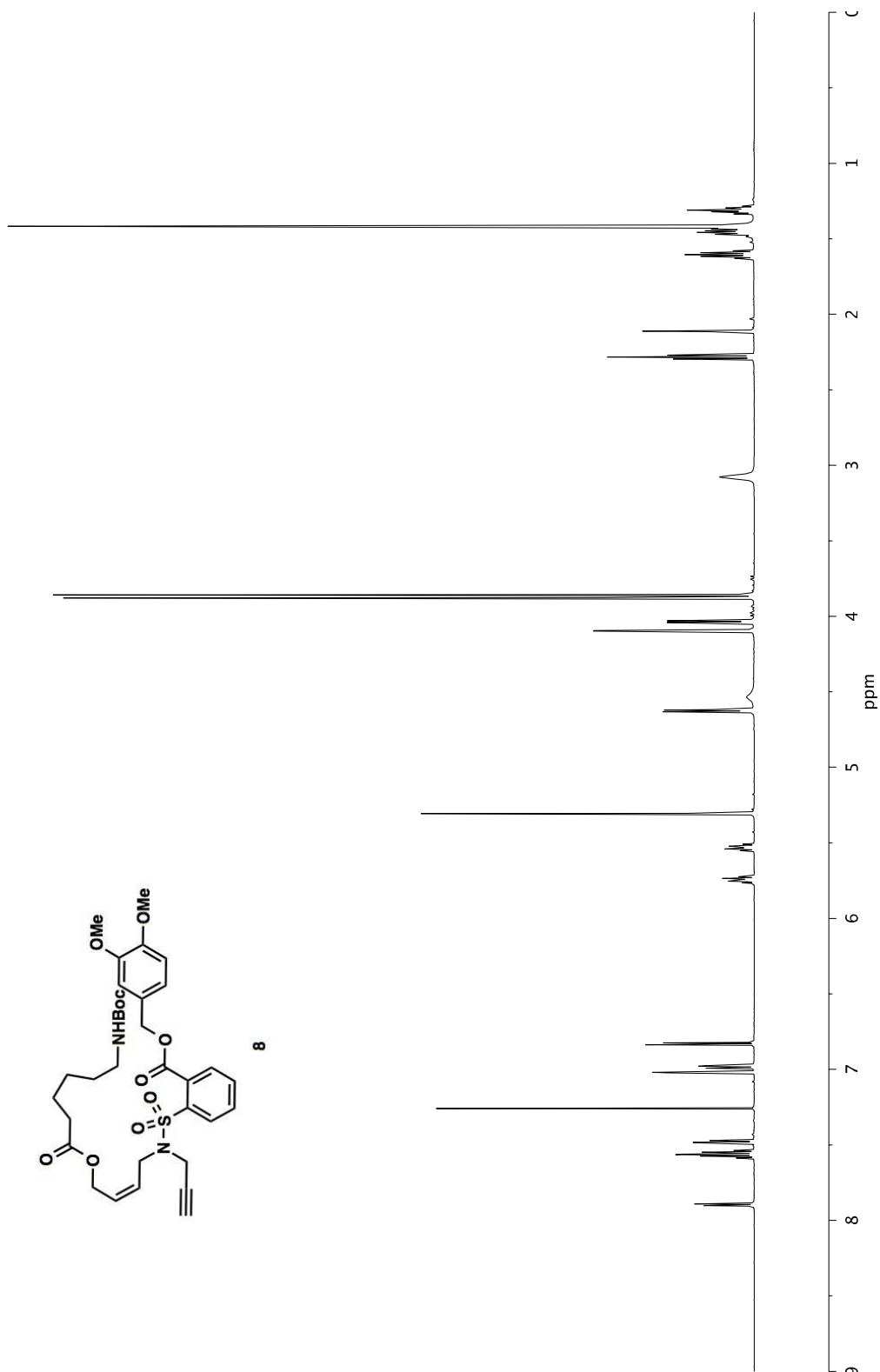
Small amounts (~15%) of the starting monomer are converted to a diene isomer during the course of the polymerization and do not appear to interfere with the polymerization process. The formation of this isomer is believed to occur through a polymerization intermediate (shown in brackets), but rather than undergoing propagation, it backbites into the neighboring diene. Dimer and trimer enyne byproducts are not observed, suggesting it is a proximity driven event that occurs after the initial ring opening, but before the ruthenium chain end can dissociate from the newly formed diene. It also is possible that this is an acid catalyzed process, though traditionally these reactions occur at elevated temperatures and with strongly acidic conditions.

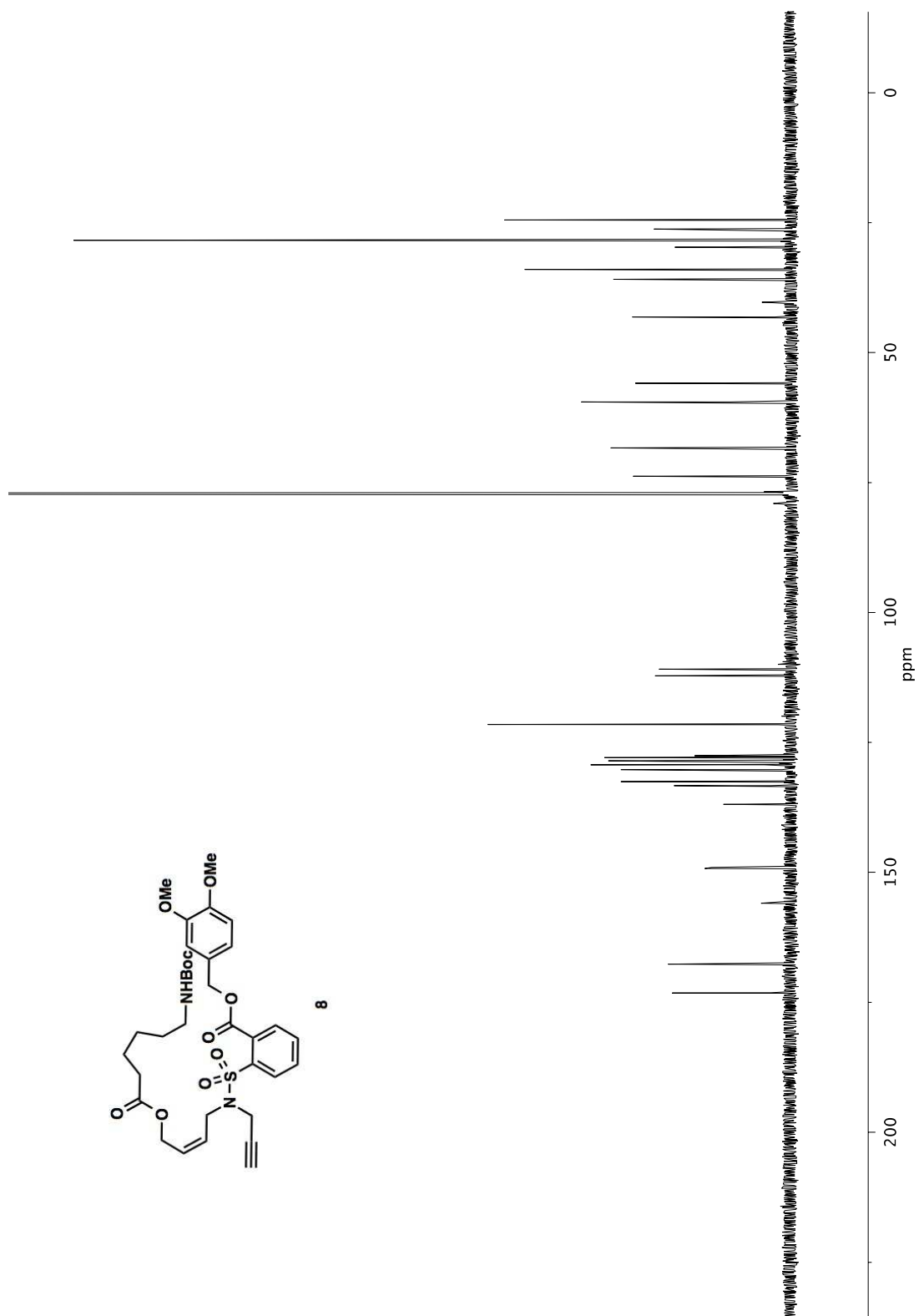
$^1\text{H-NMR}$ of **5**

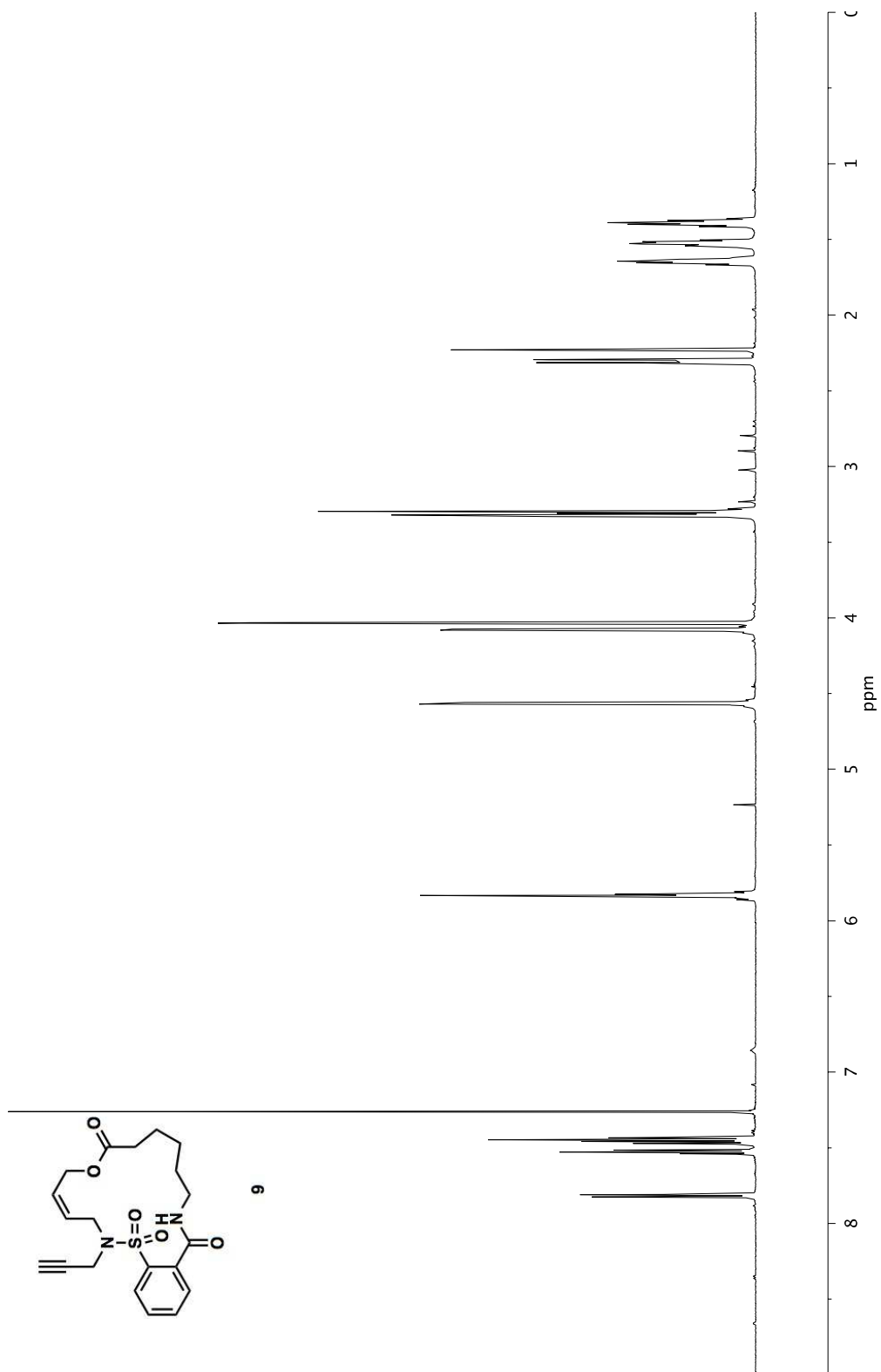
^{13}C -NMR of 5

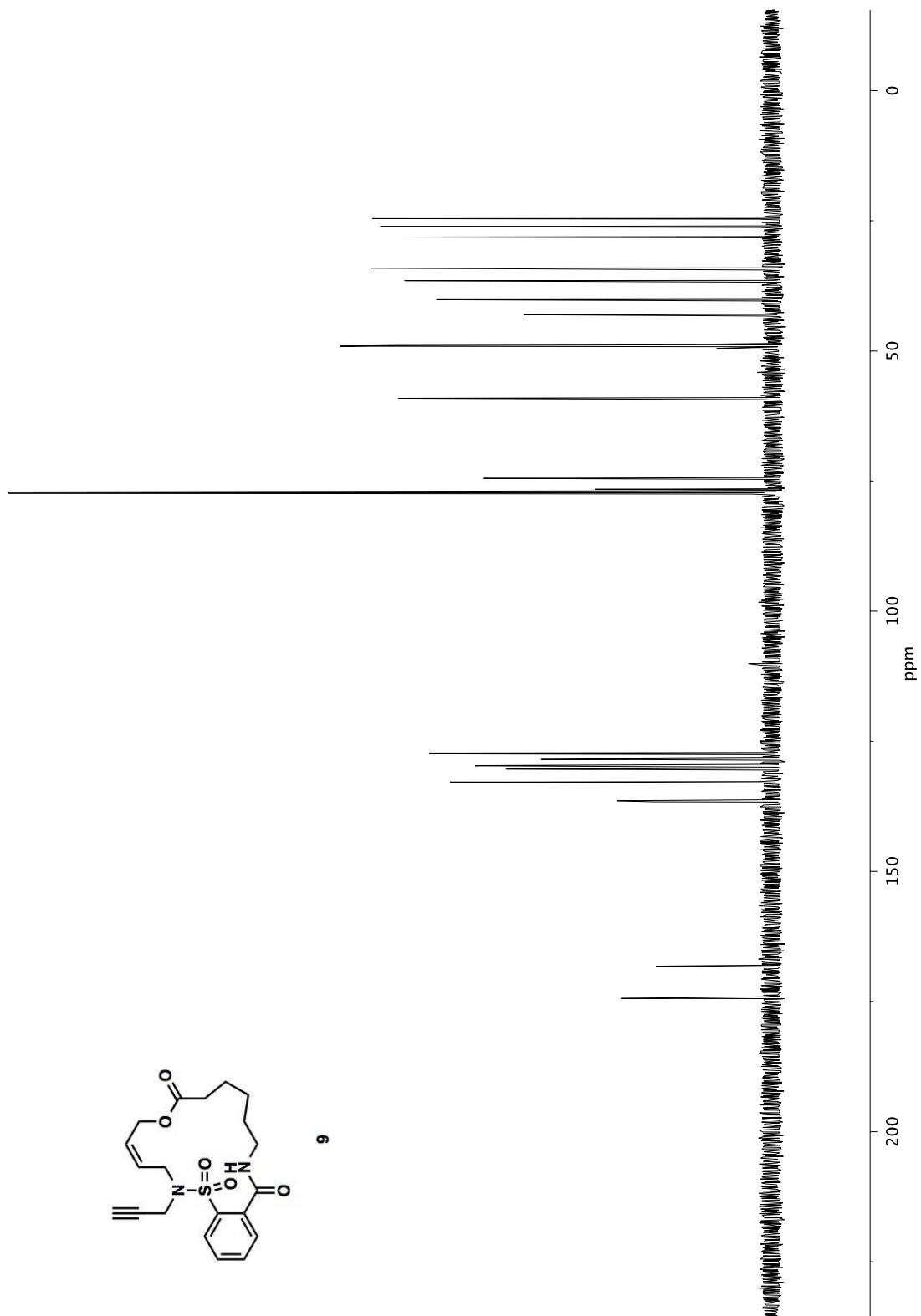
$^1\text{H-NMR}$ of **6**

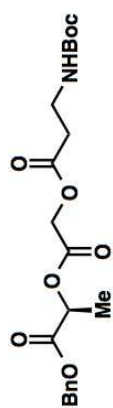
¹³C-NMR of 6

$^1\text{H-NMR}$ of **8**

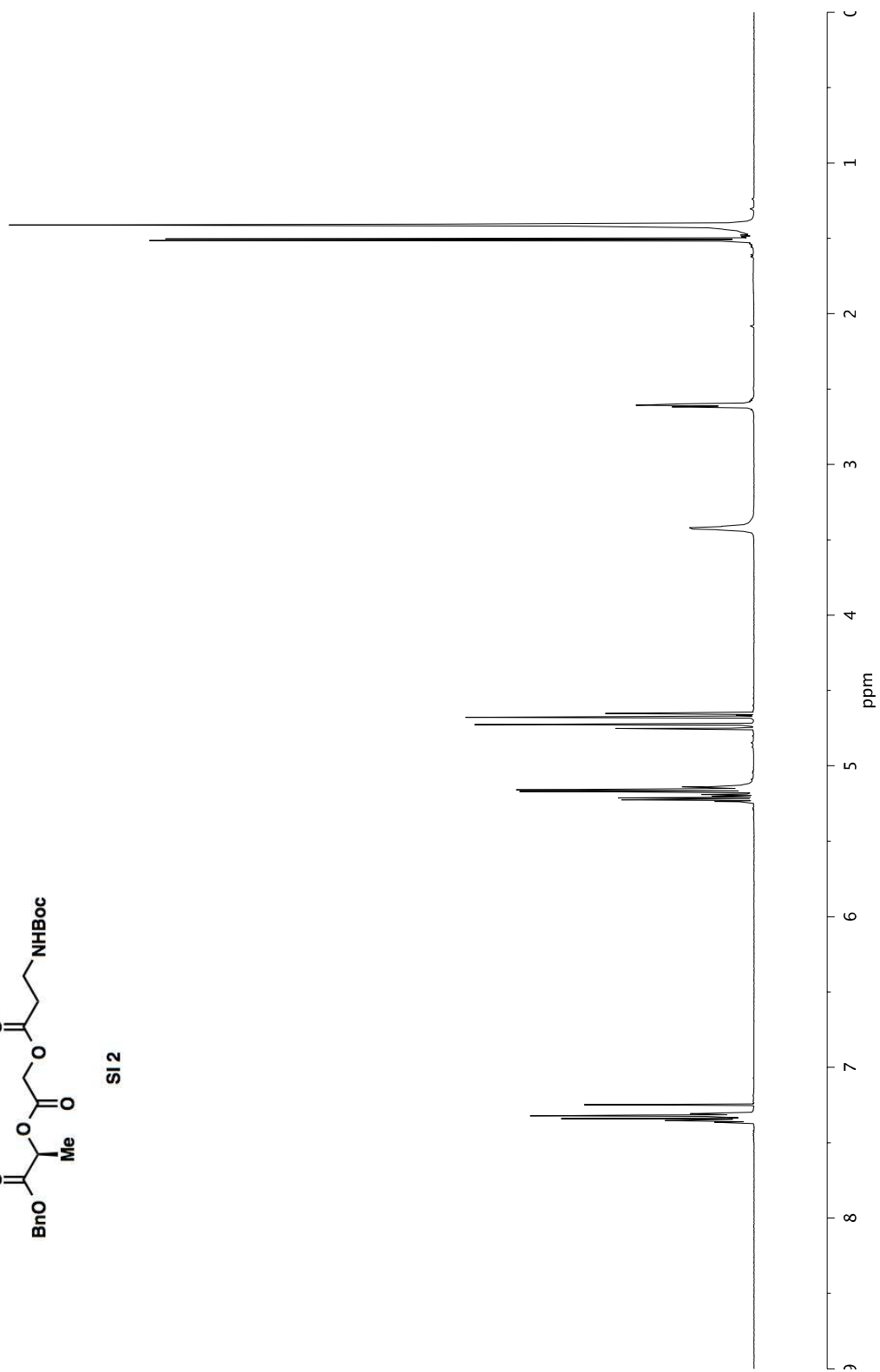
^{13}C -NMR of 8

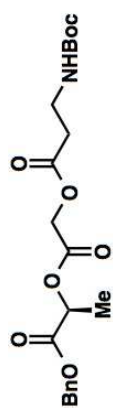
$^1\text{H-NMR}$ of **9**

^{13}C -NMR of 9

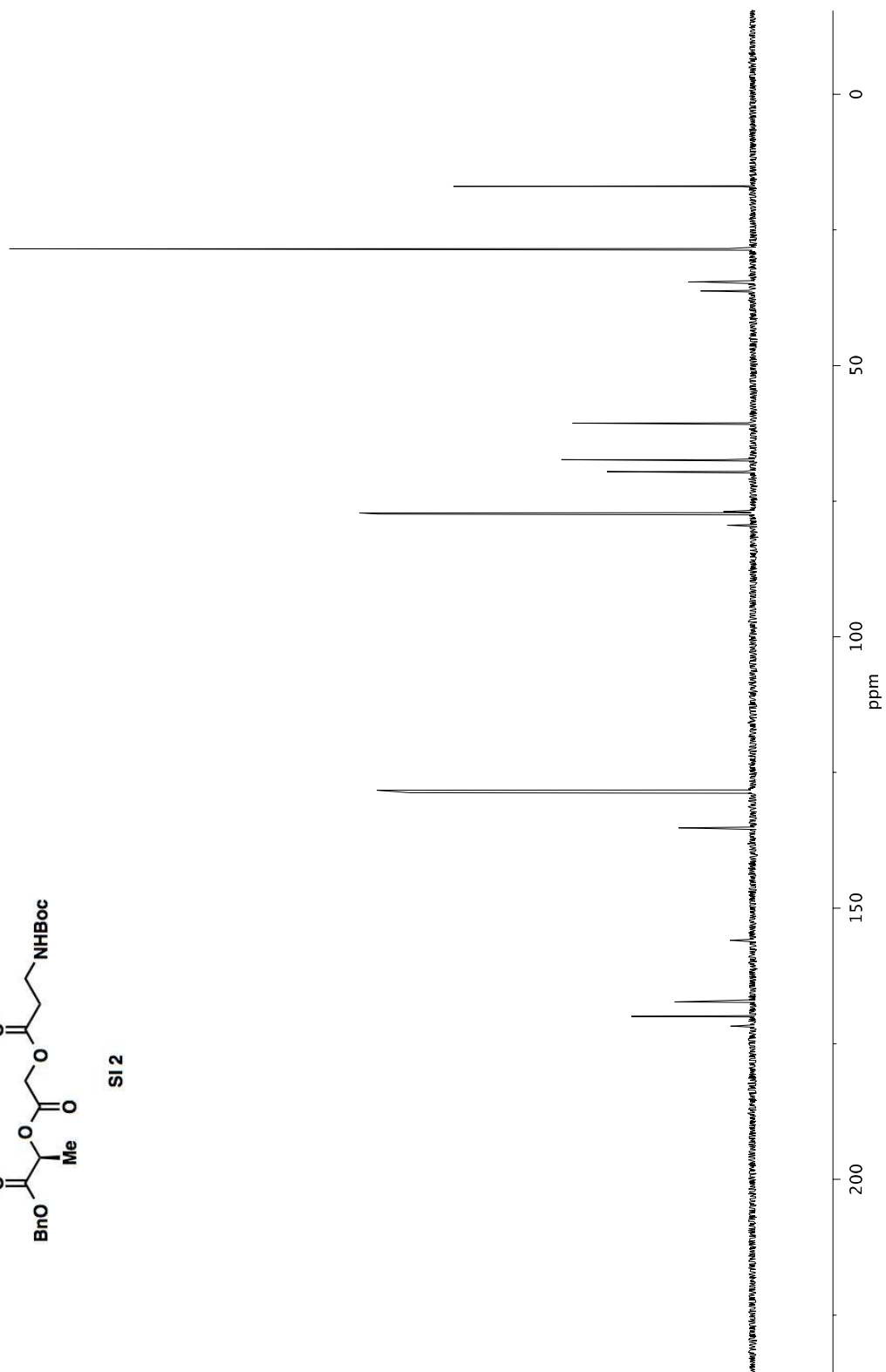
$^1\text{H-NMR}$ of SI 2

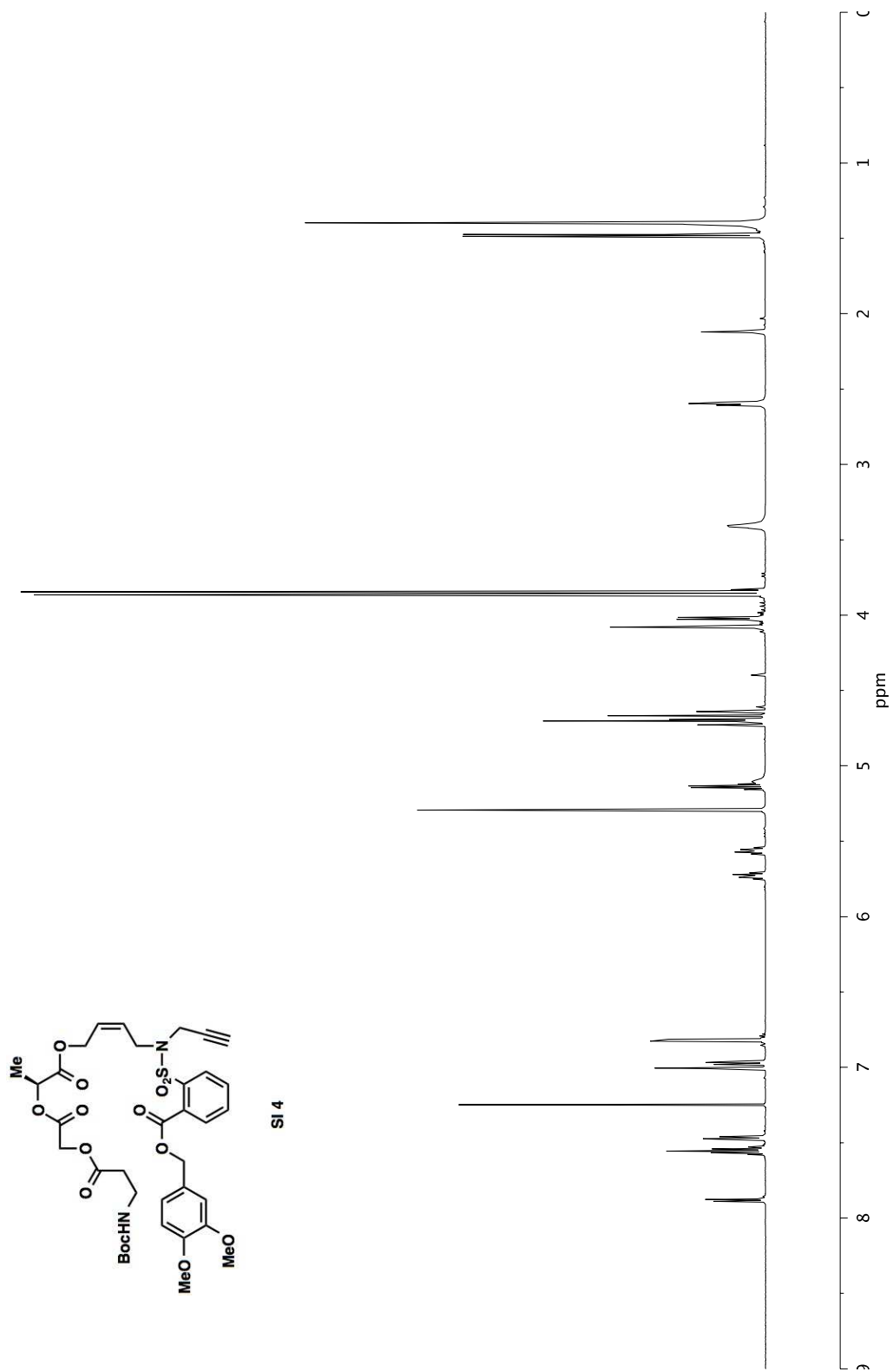
SI 2

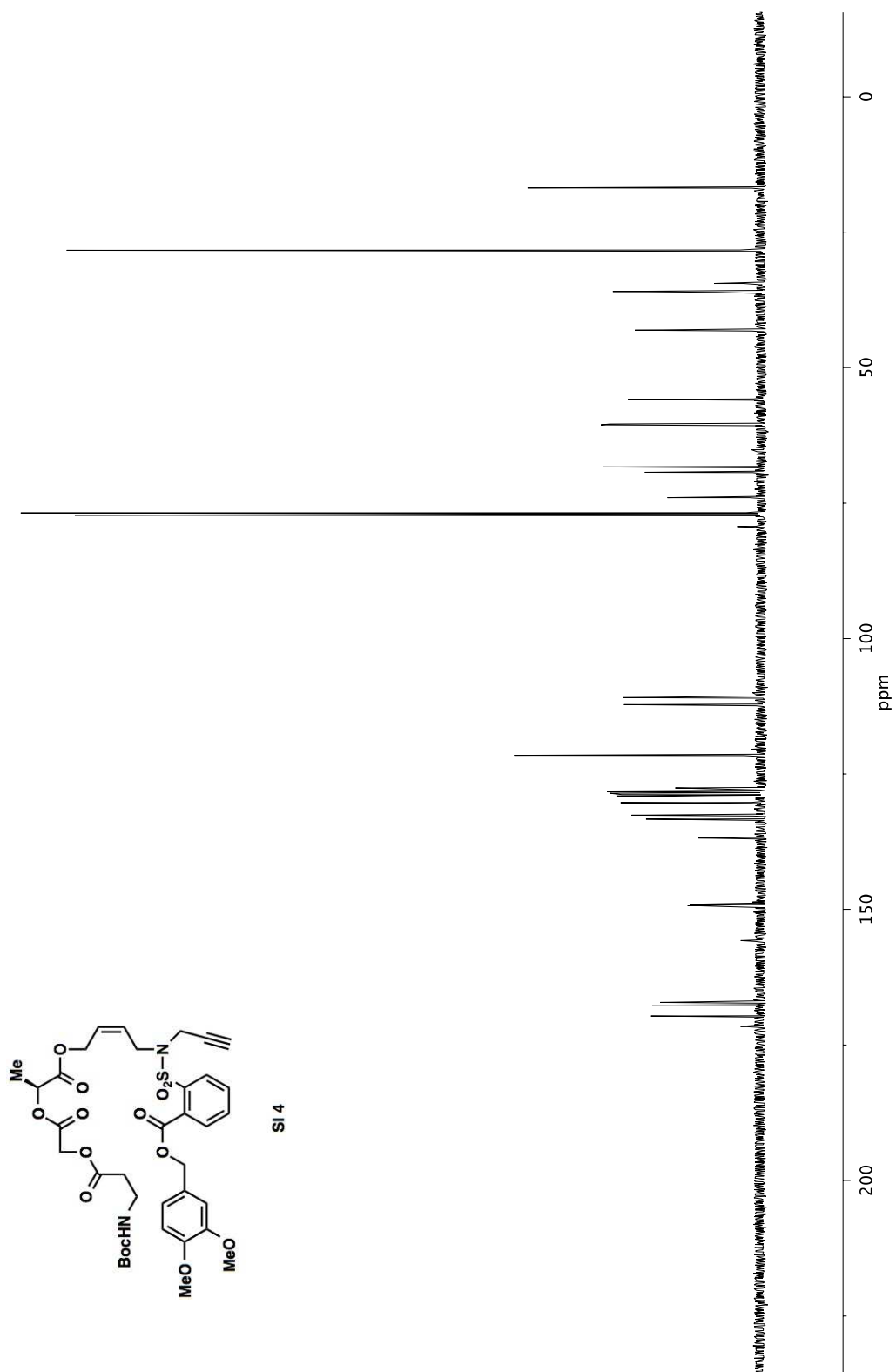


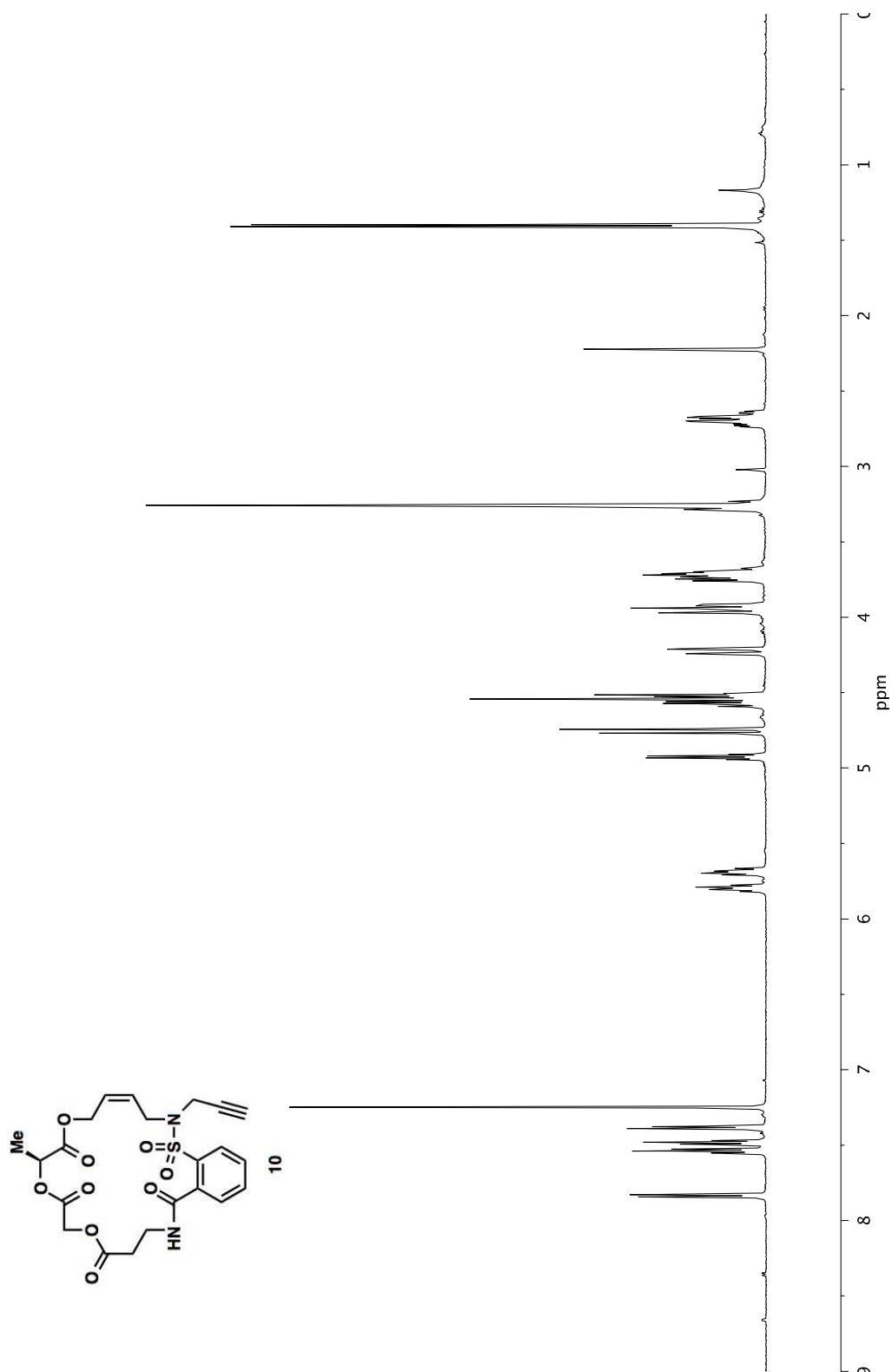
^{13}C -NMR of SI 2

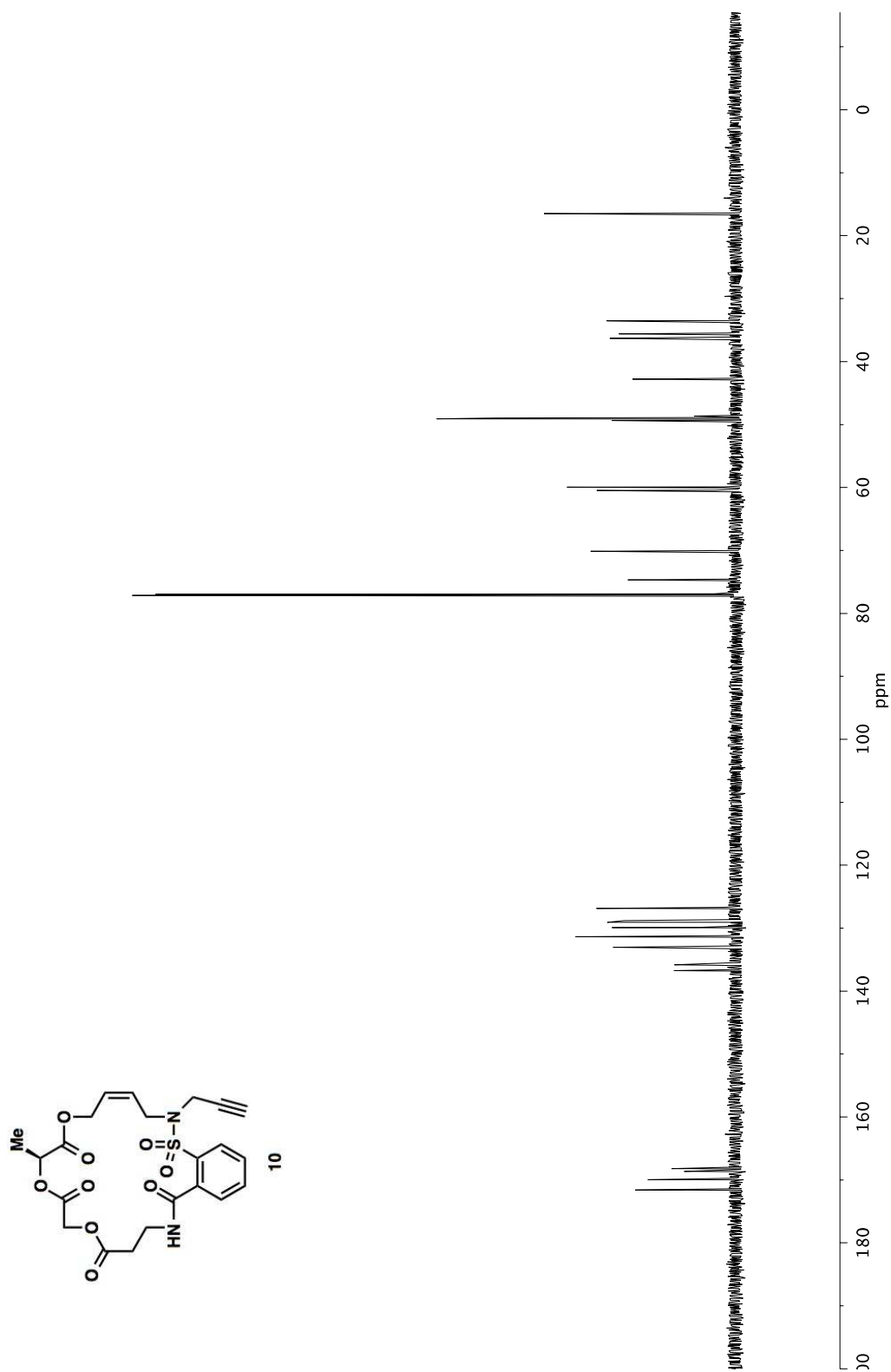
SI 2

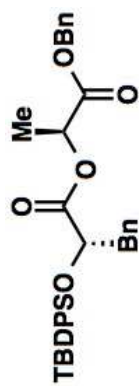


¹H-NMR of SI 4

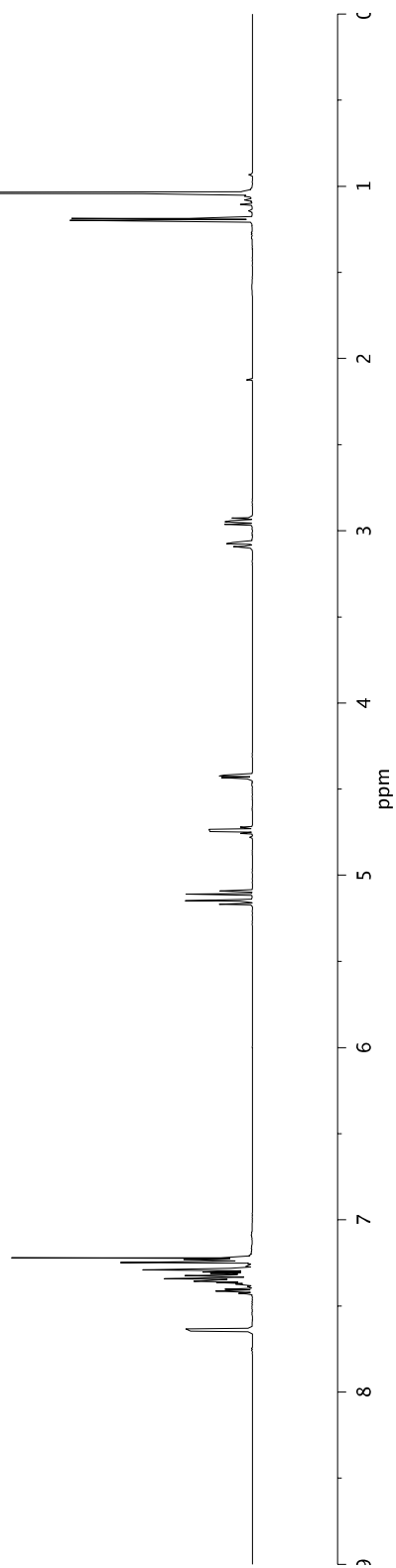
^{13}C -NMR of SI 4

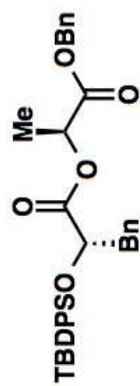
$^1\text{H-NMR}$ of 10

^{13}C -NMR of 10

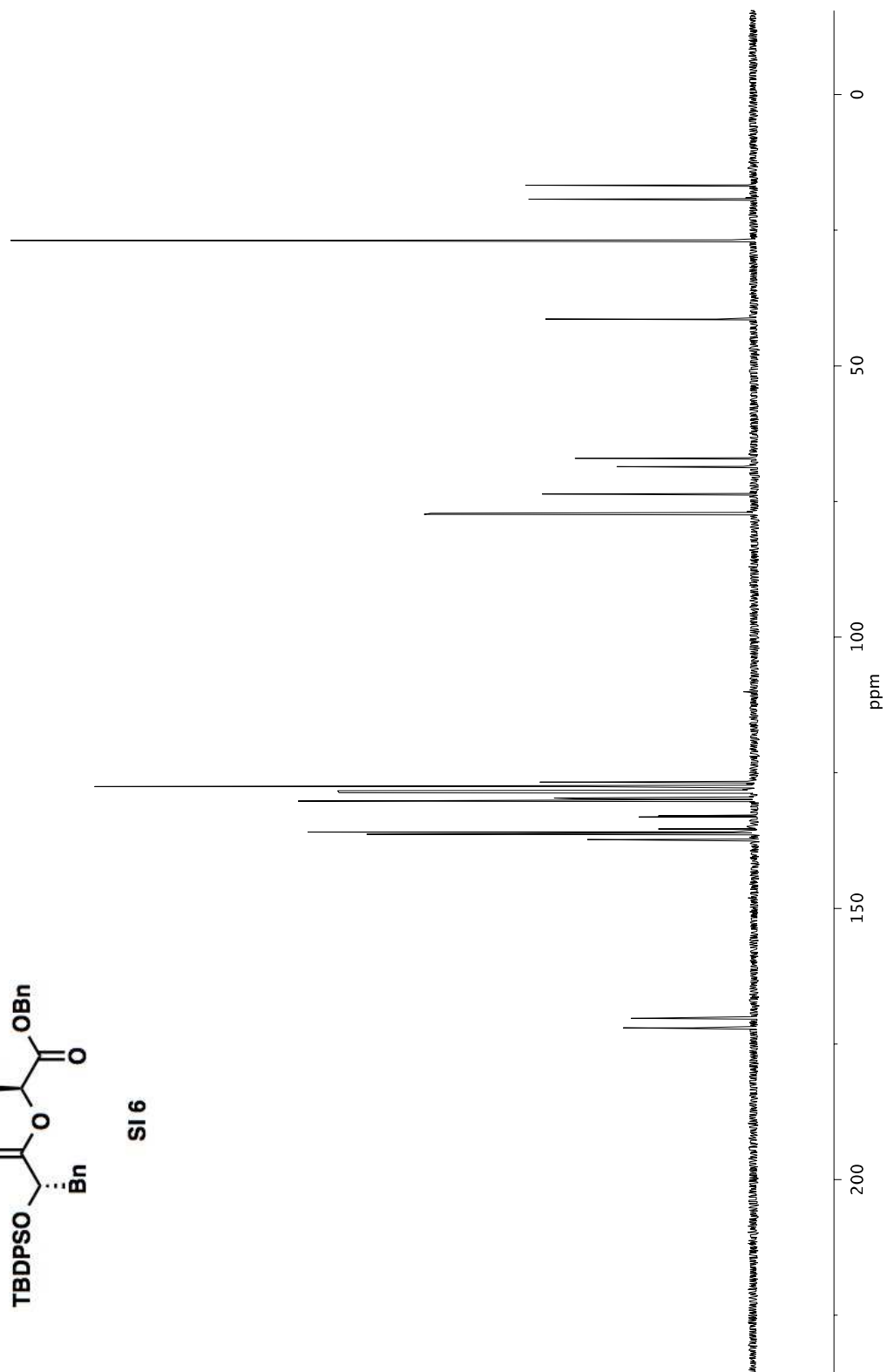
$^1\text{H-NMR}$ of SI 6

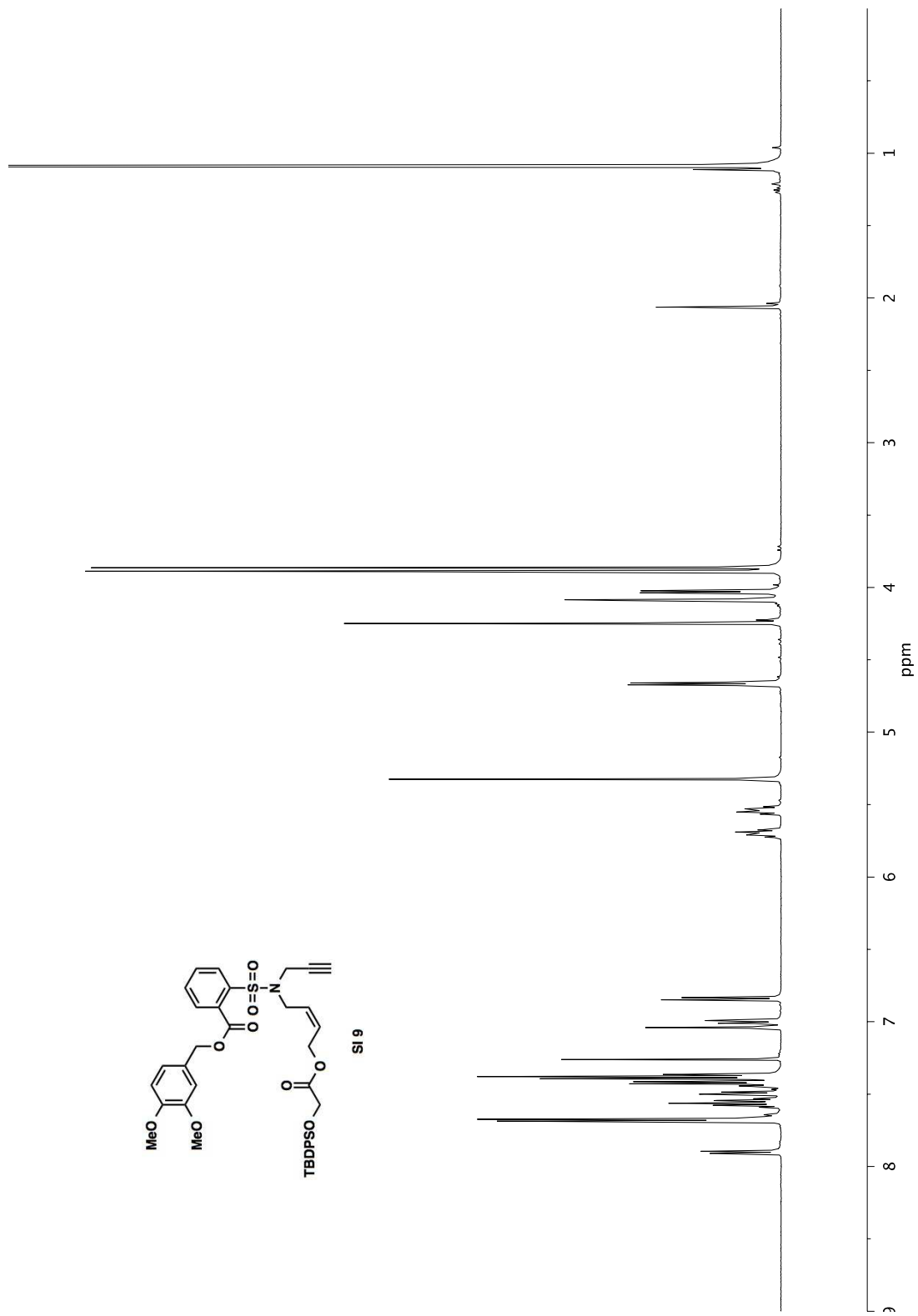
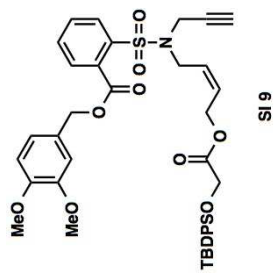
SI 6

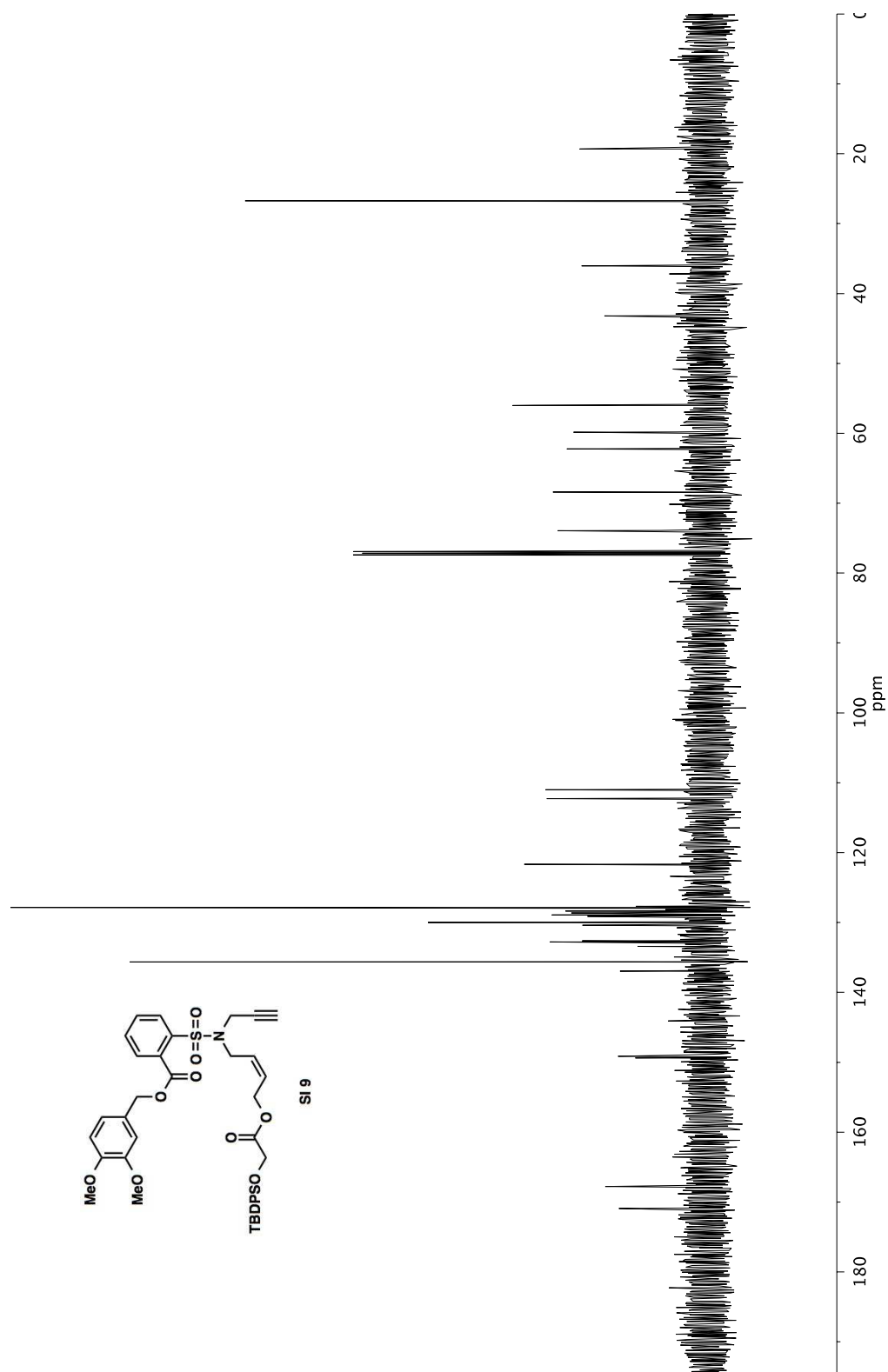


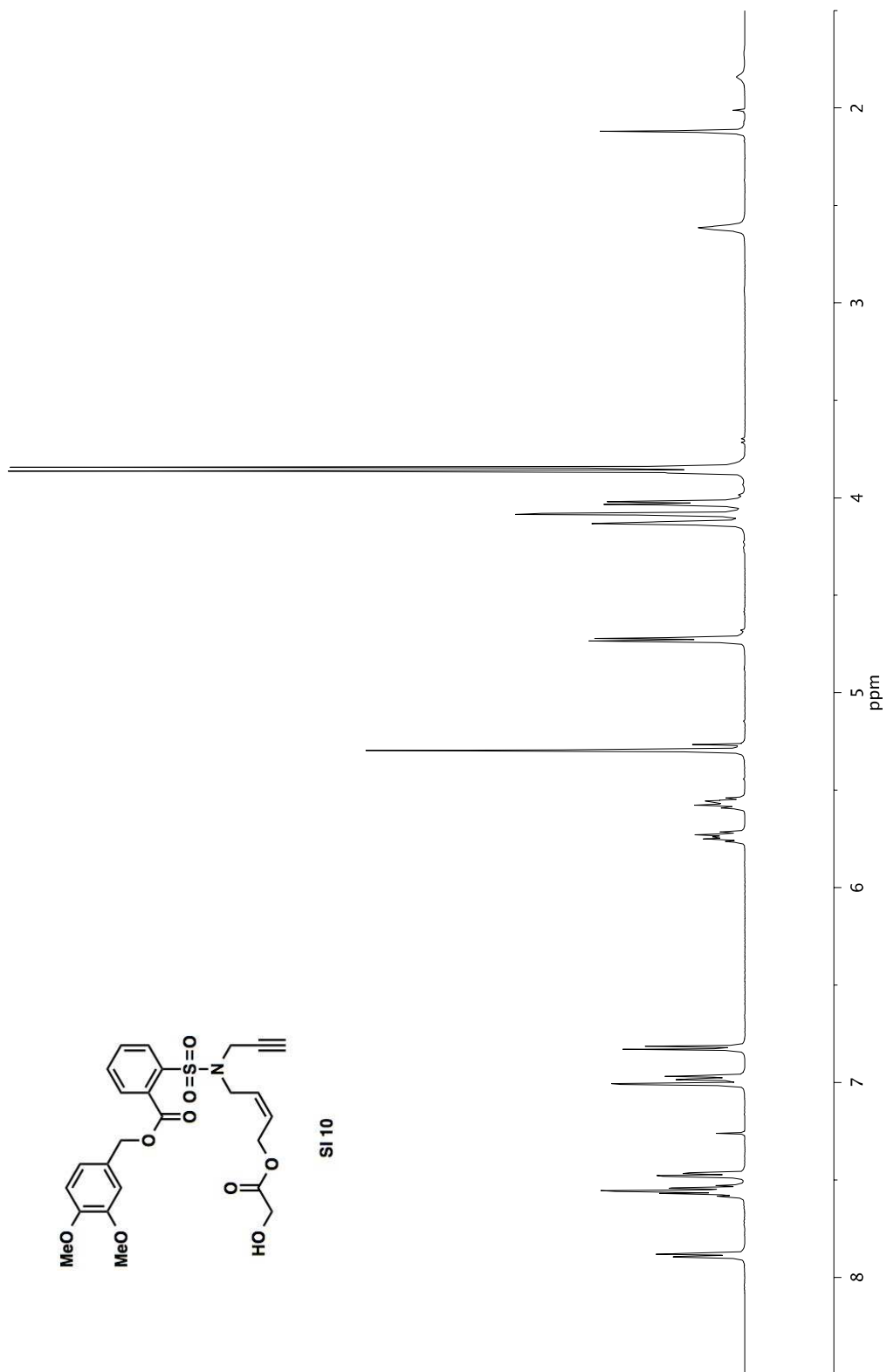
^{13}C -NMR of SI 6

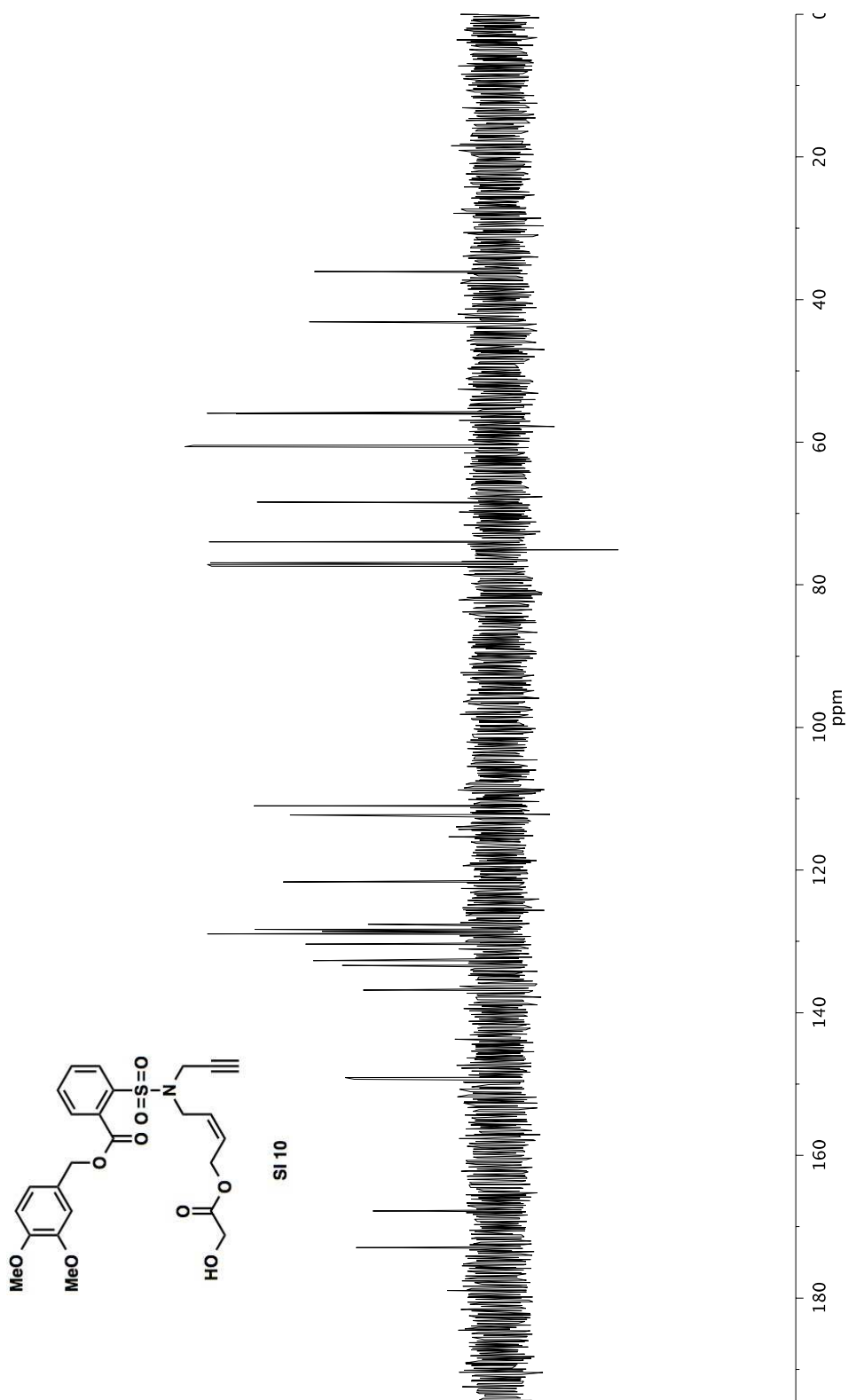
SI 6

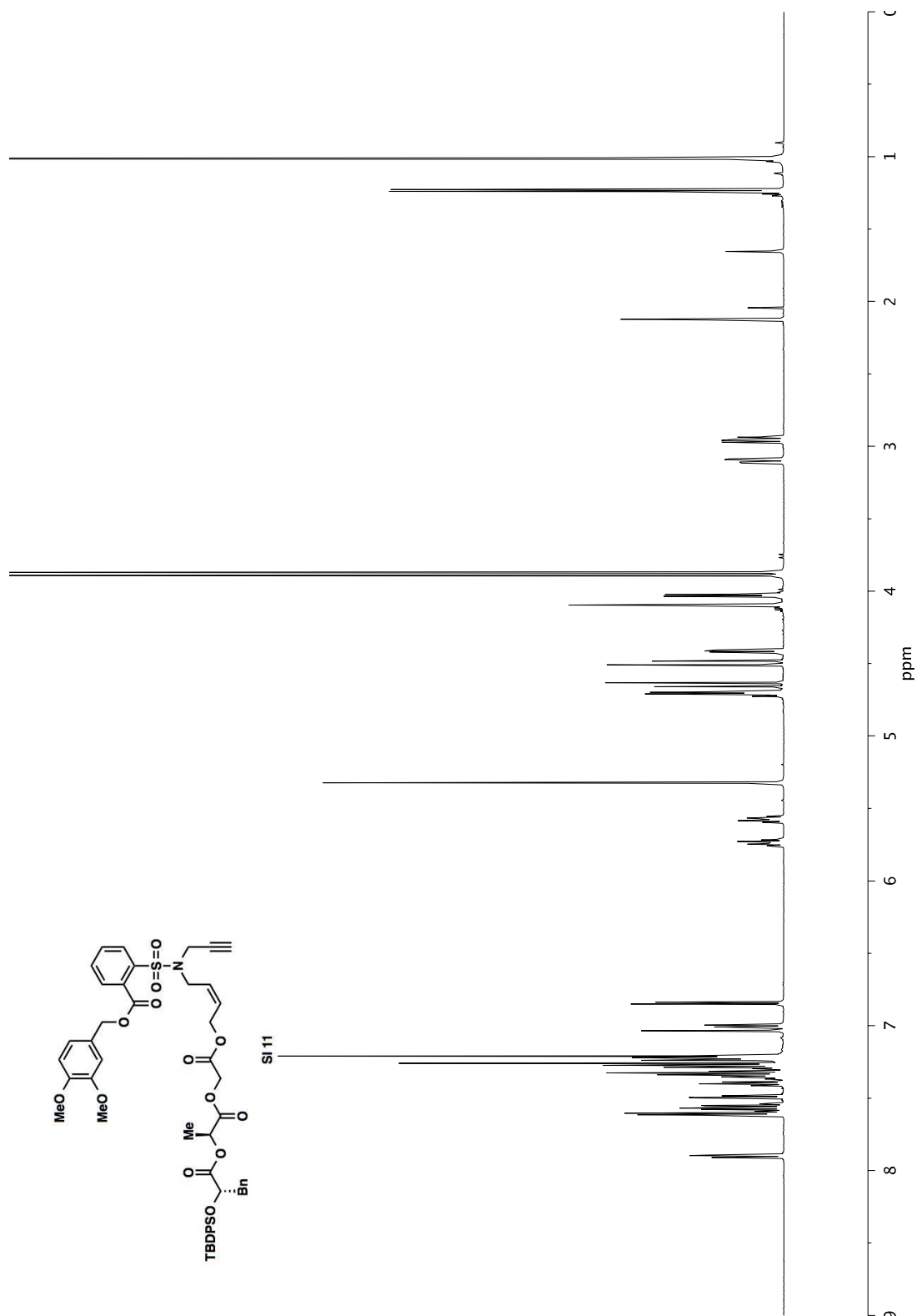


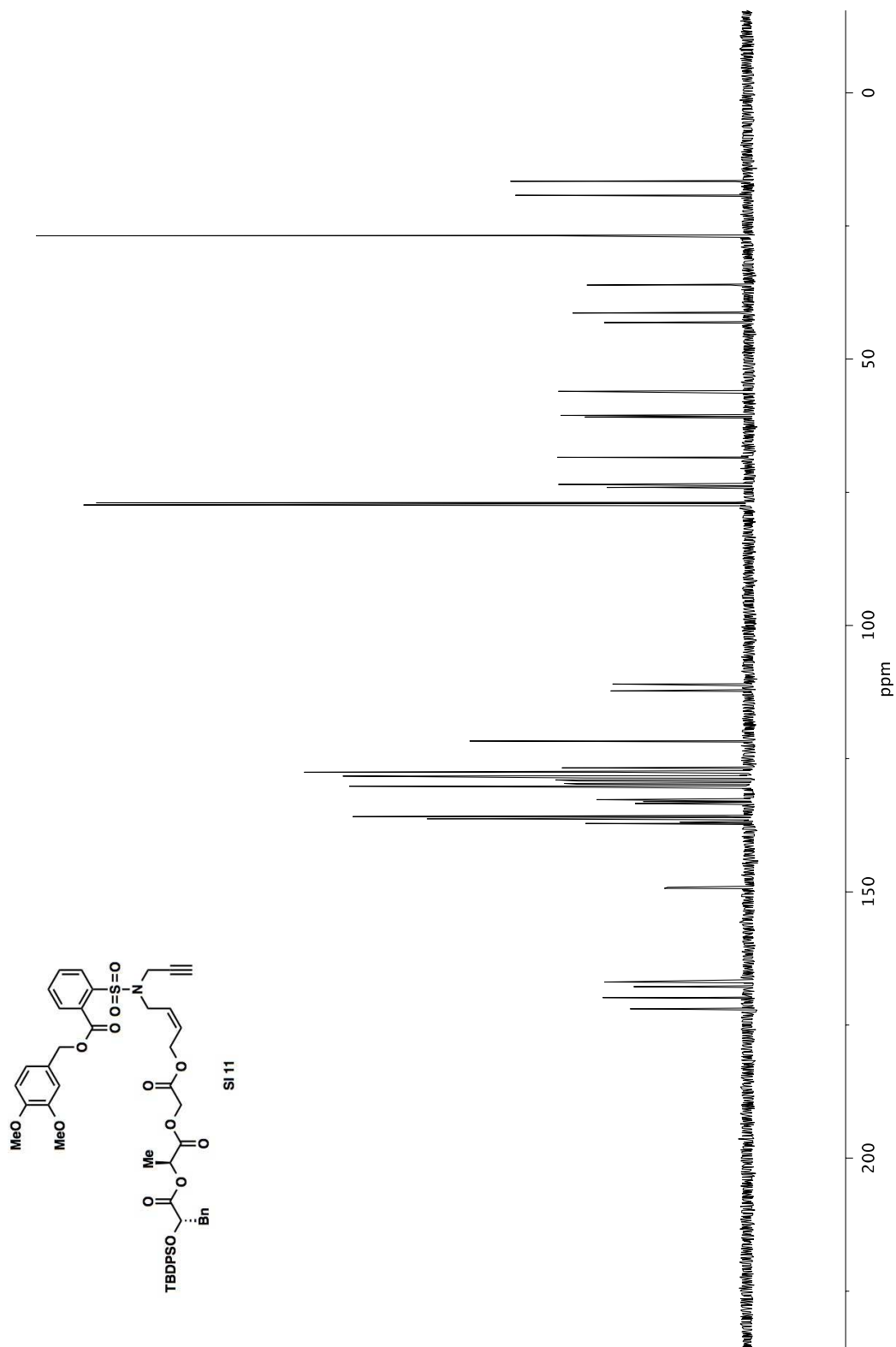
¹H-NMR of SI 9

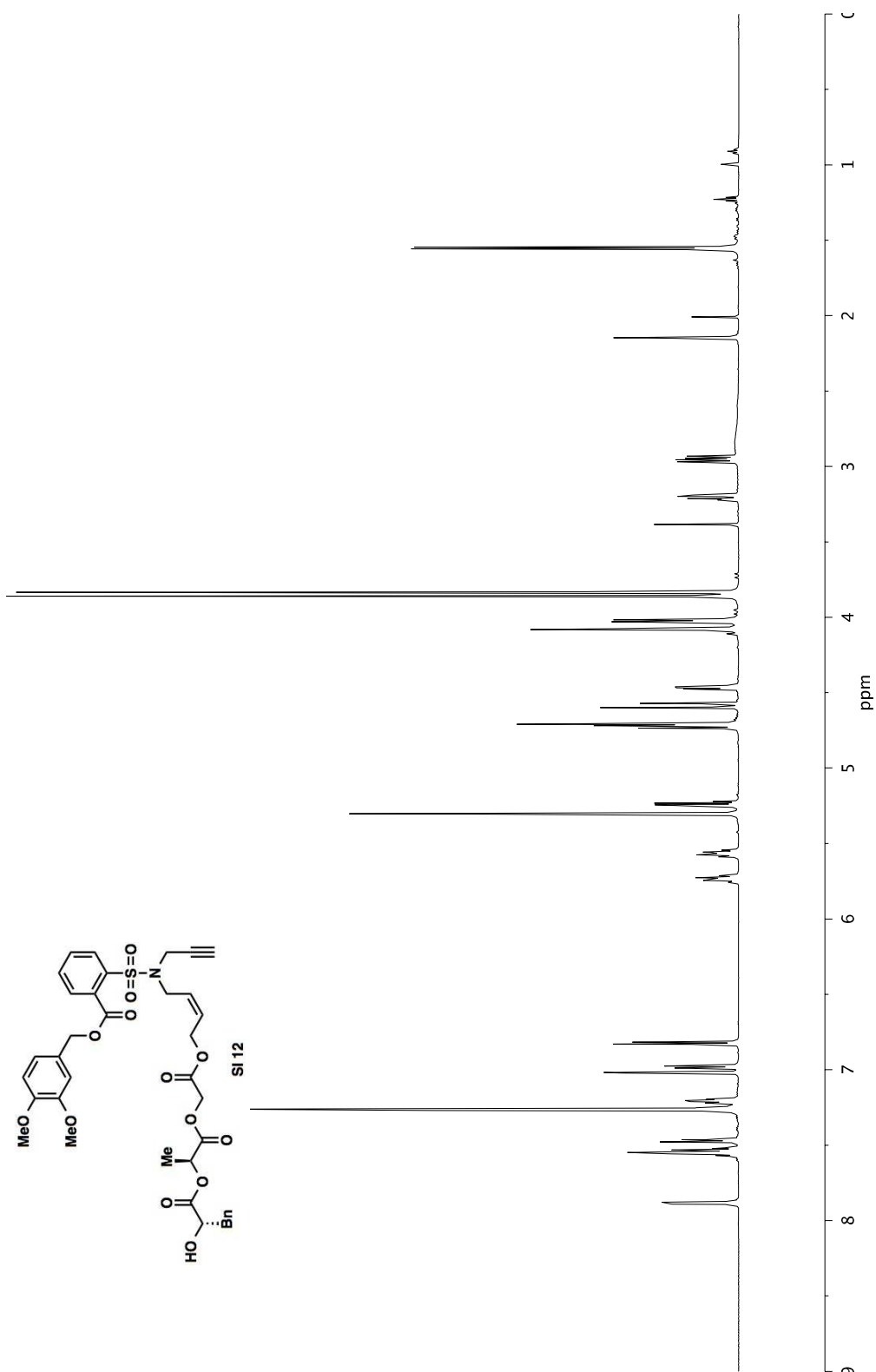
^{13}C -NMR of SI 9

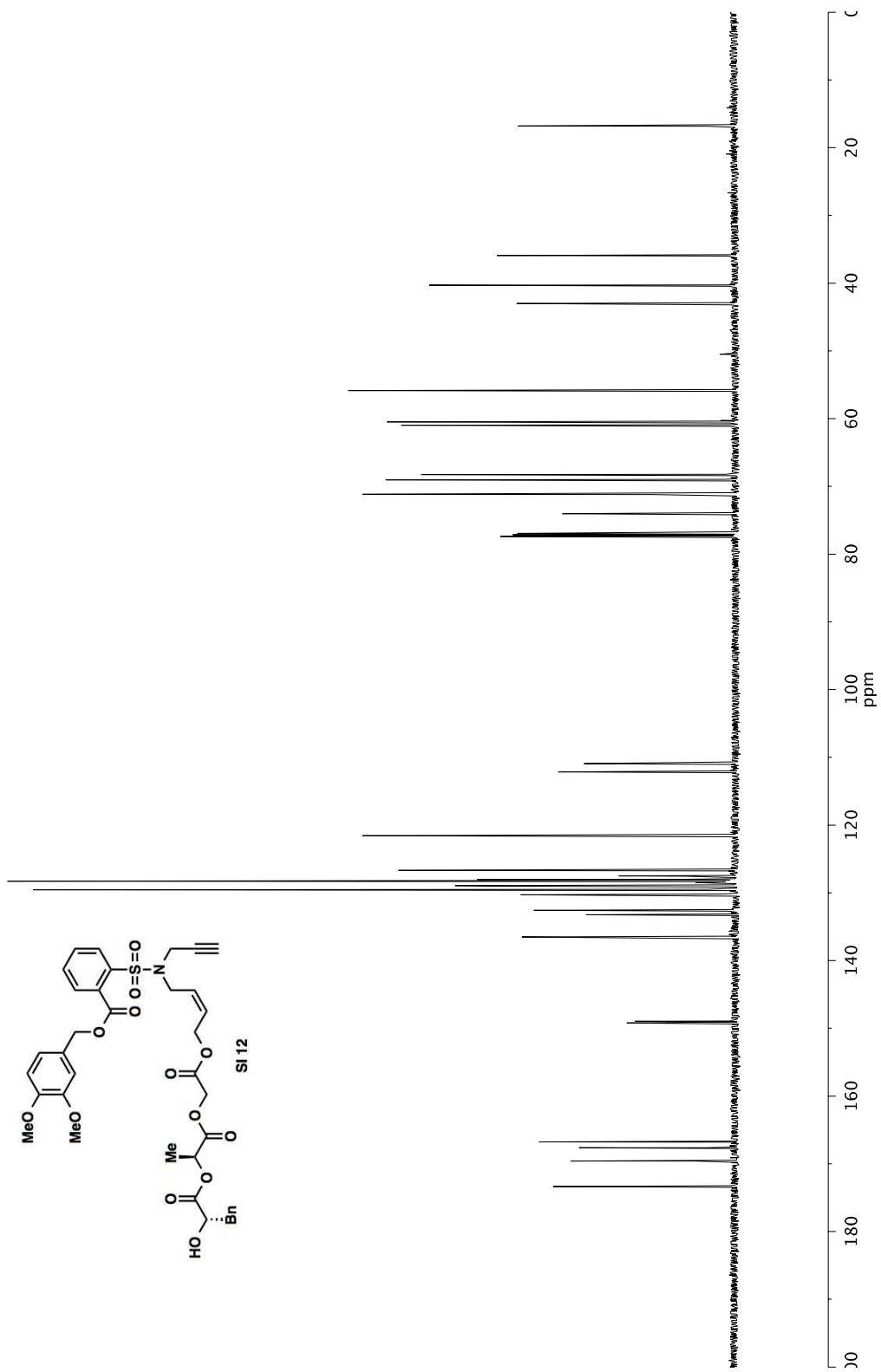
¹H-NMR of SI 10

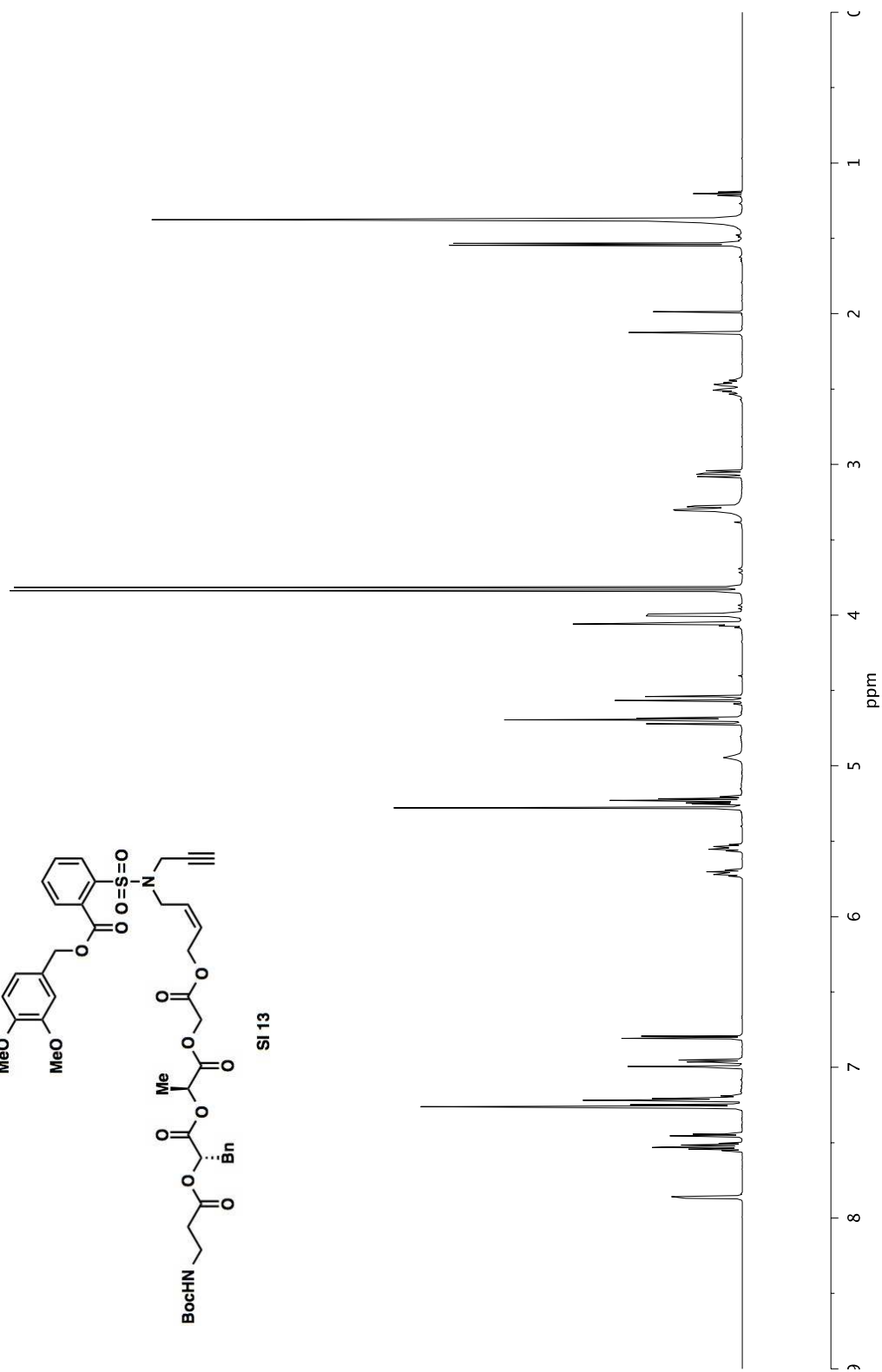
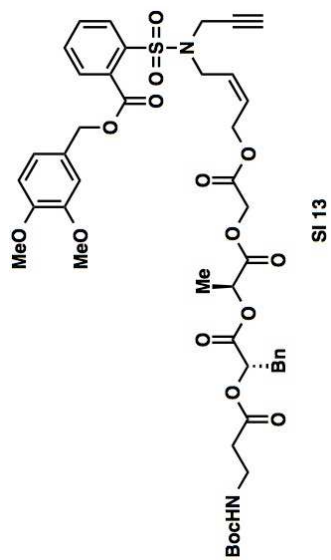
^{13}C -NMR of SI 10

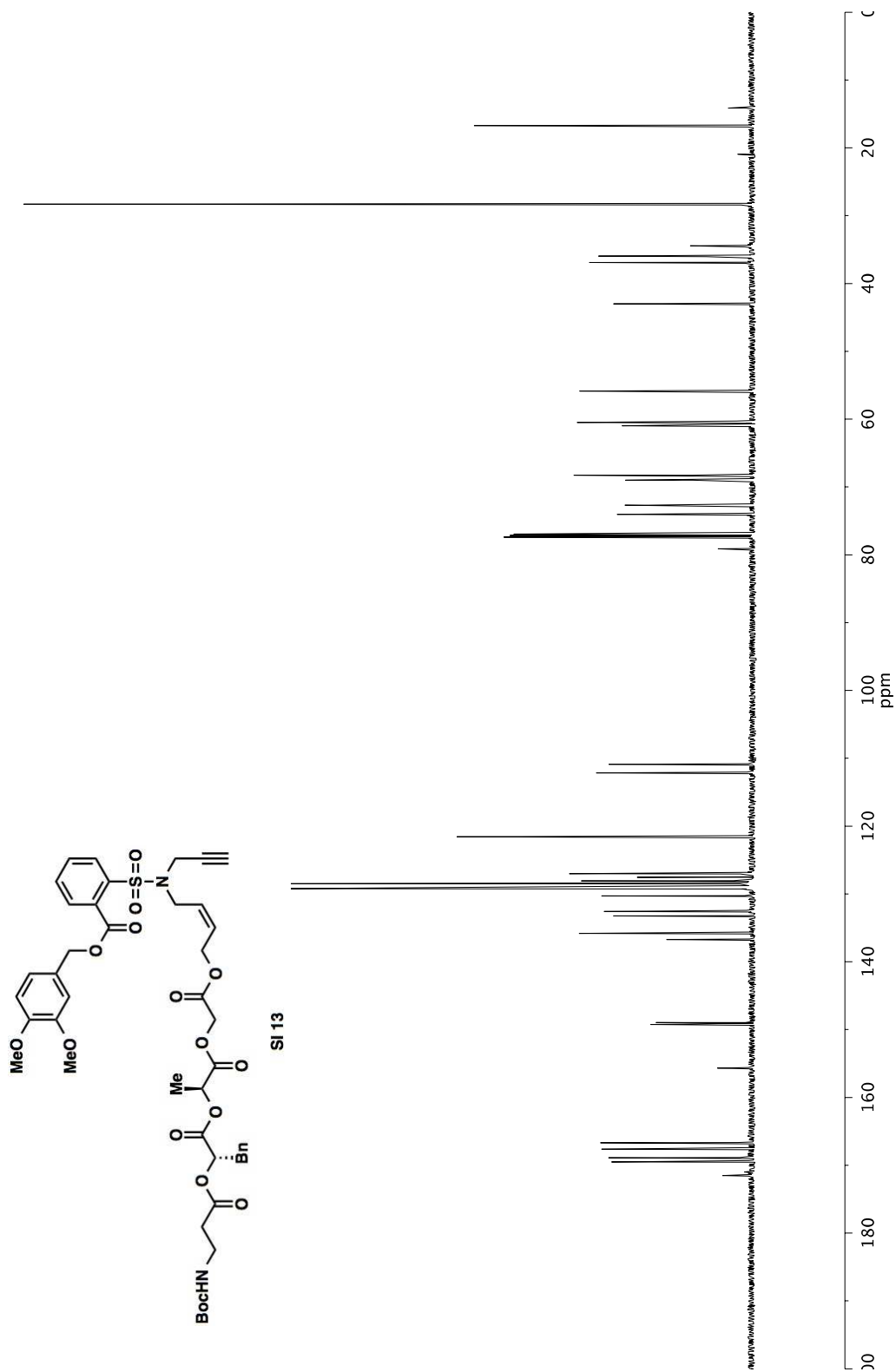
¹H-NMR of SI 11

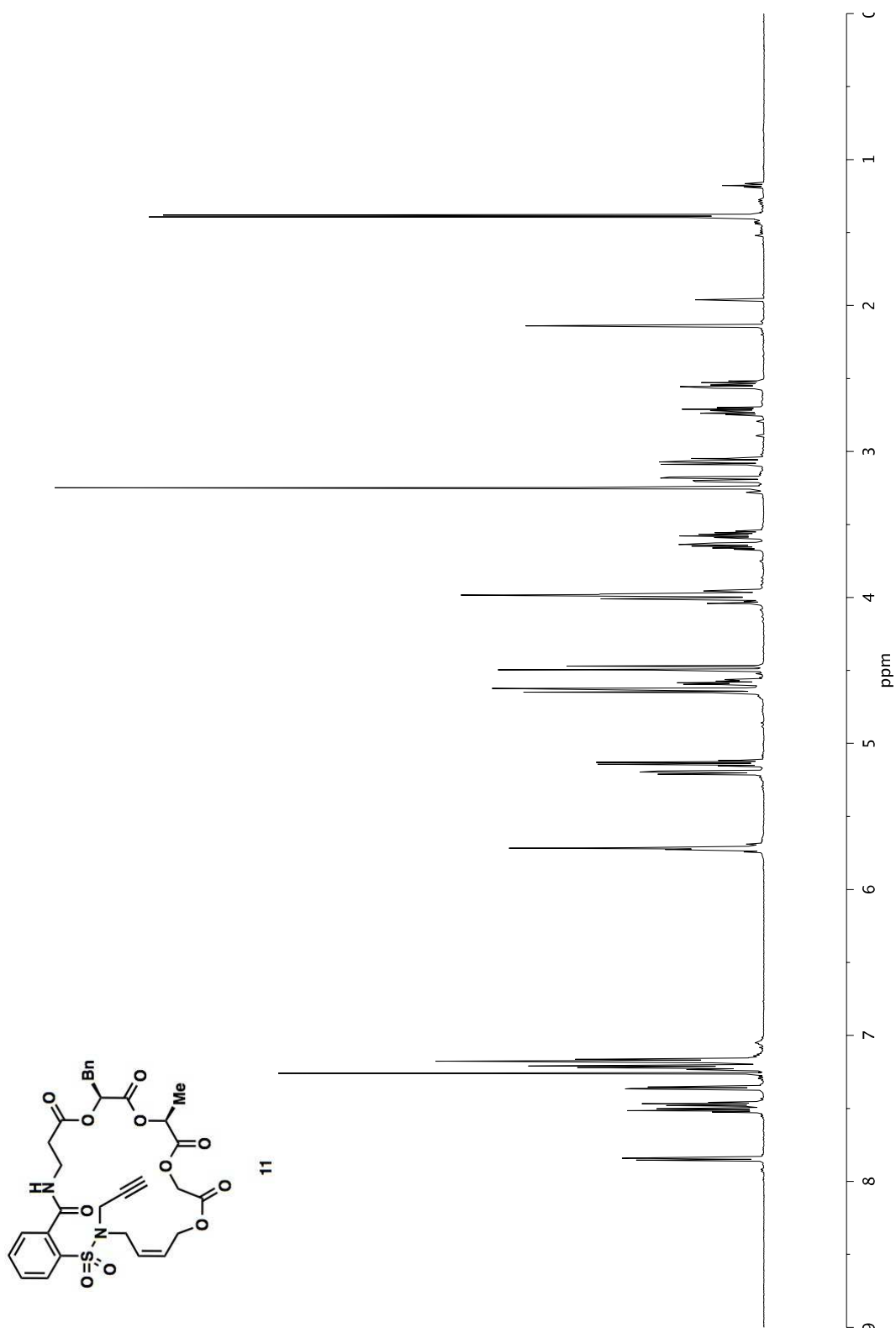
¹³C-NMR of SI 11

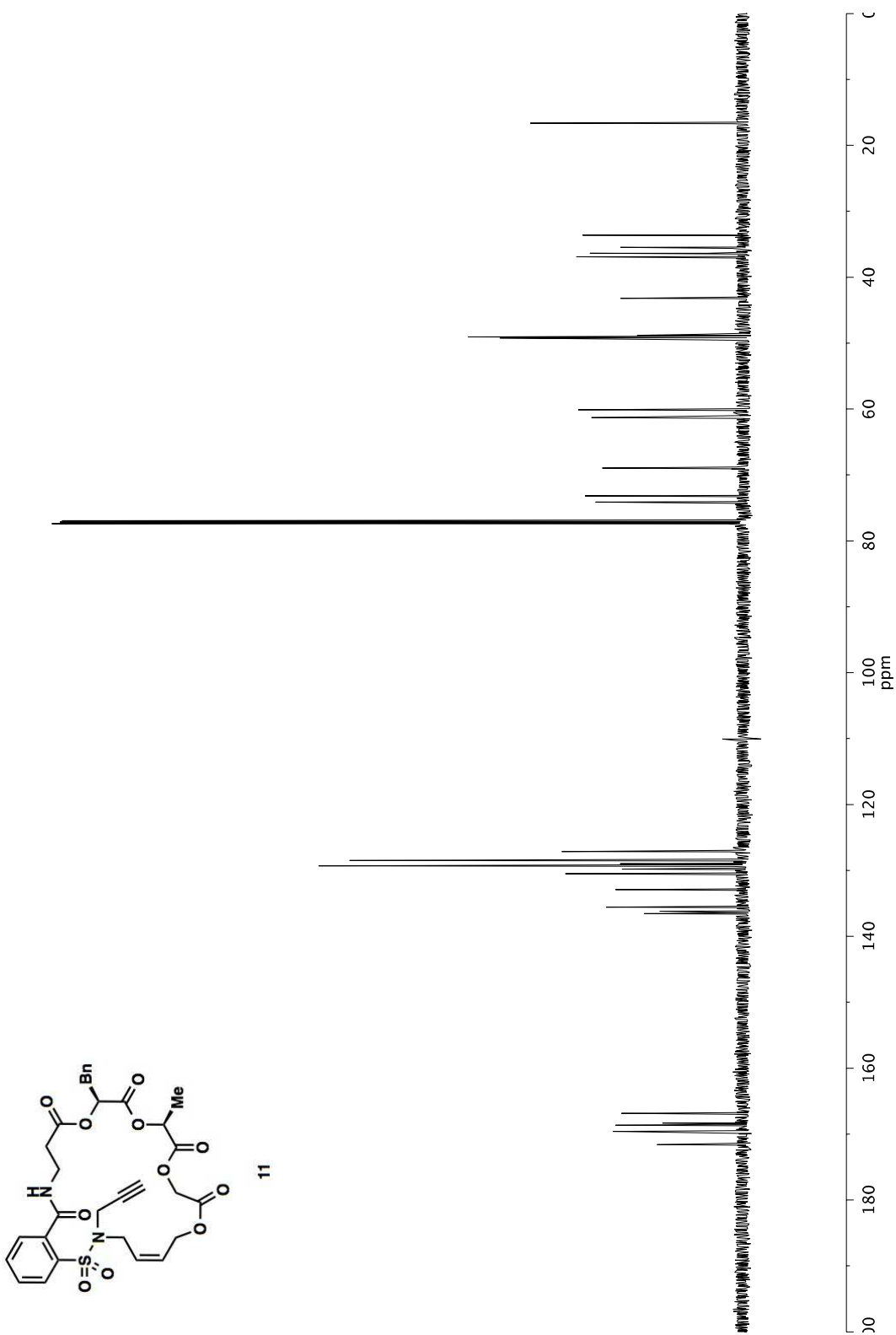
¹H-NMR of SI 12

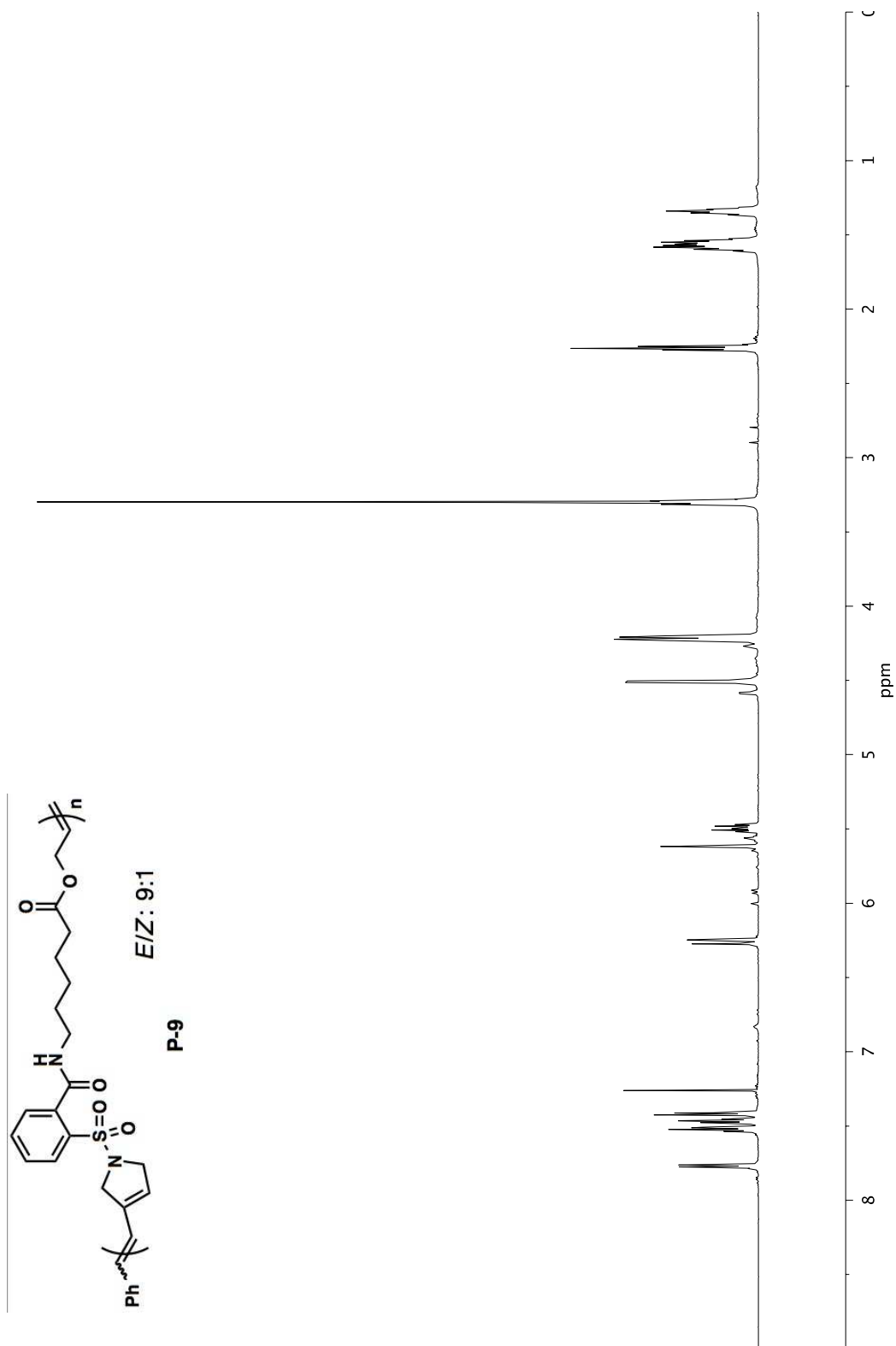
^{13}C -NMR of SI 12

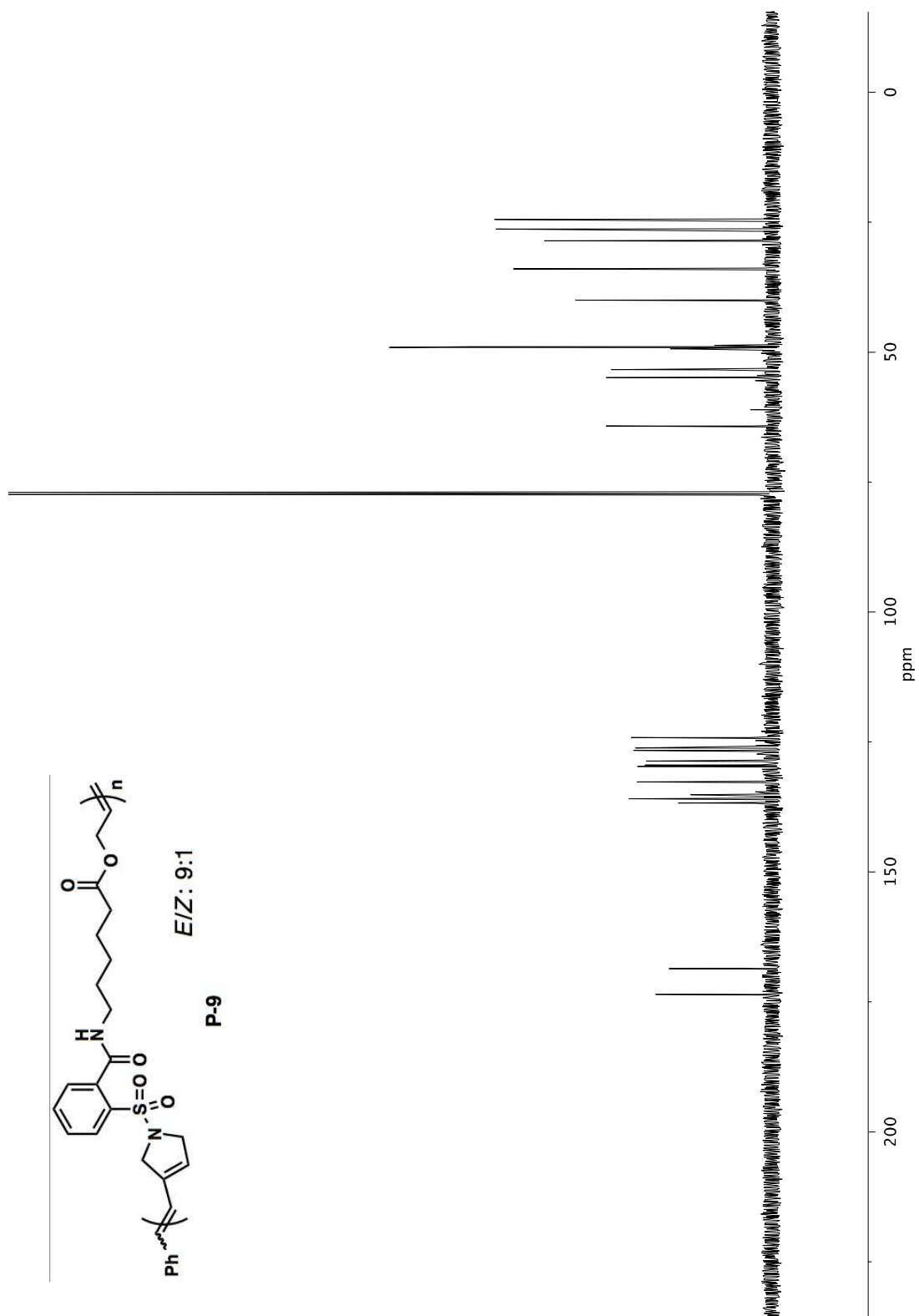
¹H-NMR of SI 13

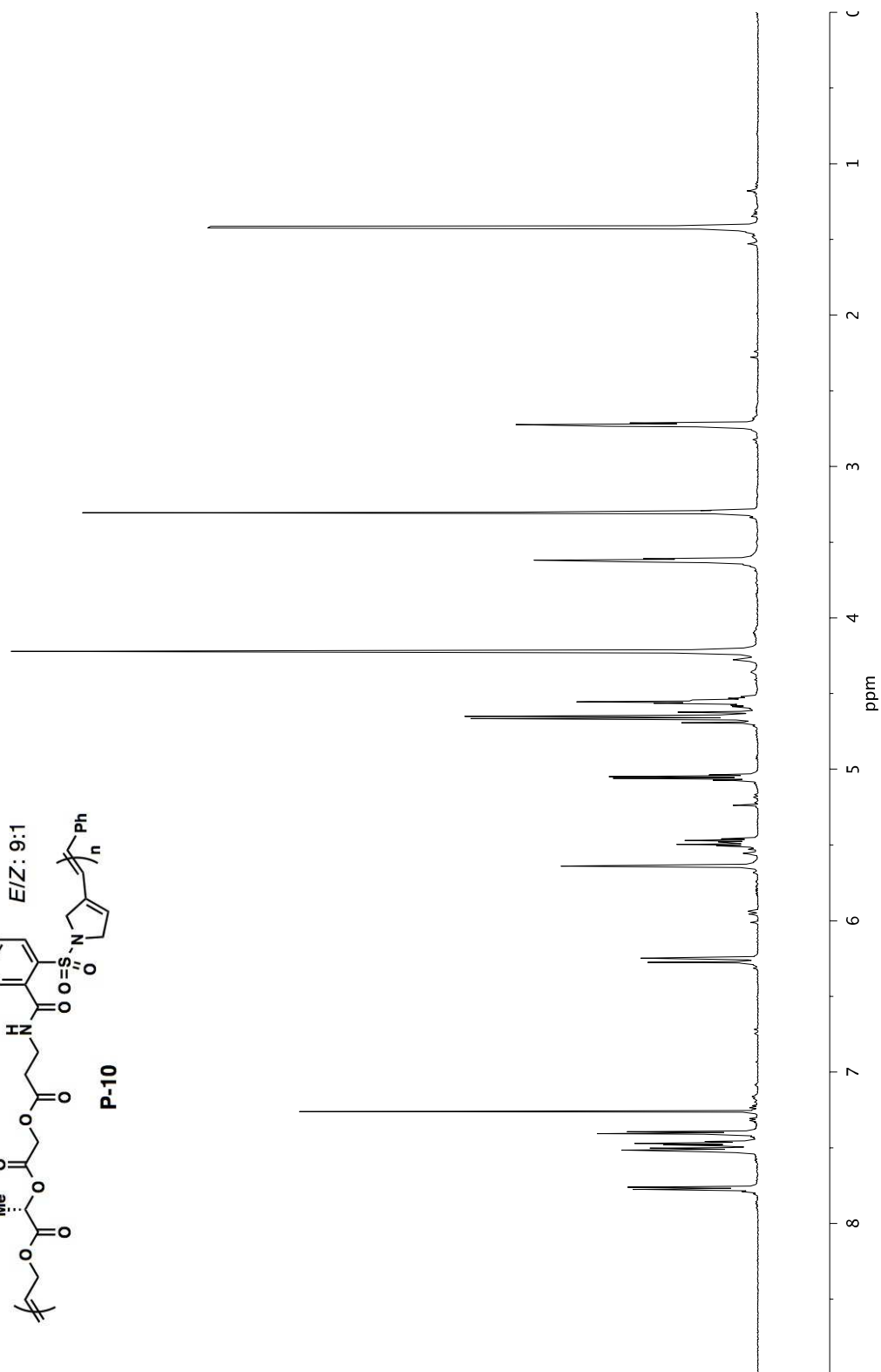
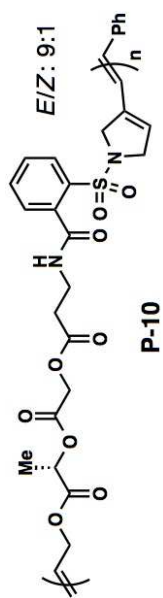
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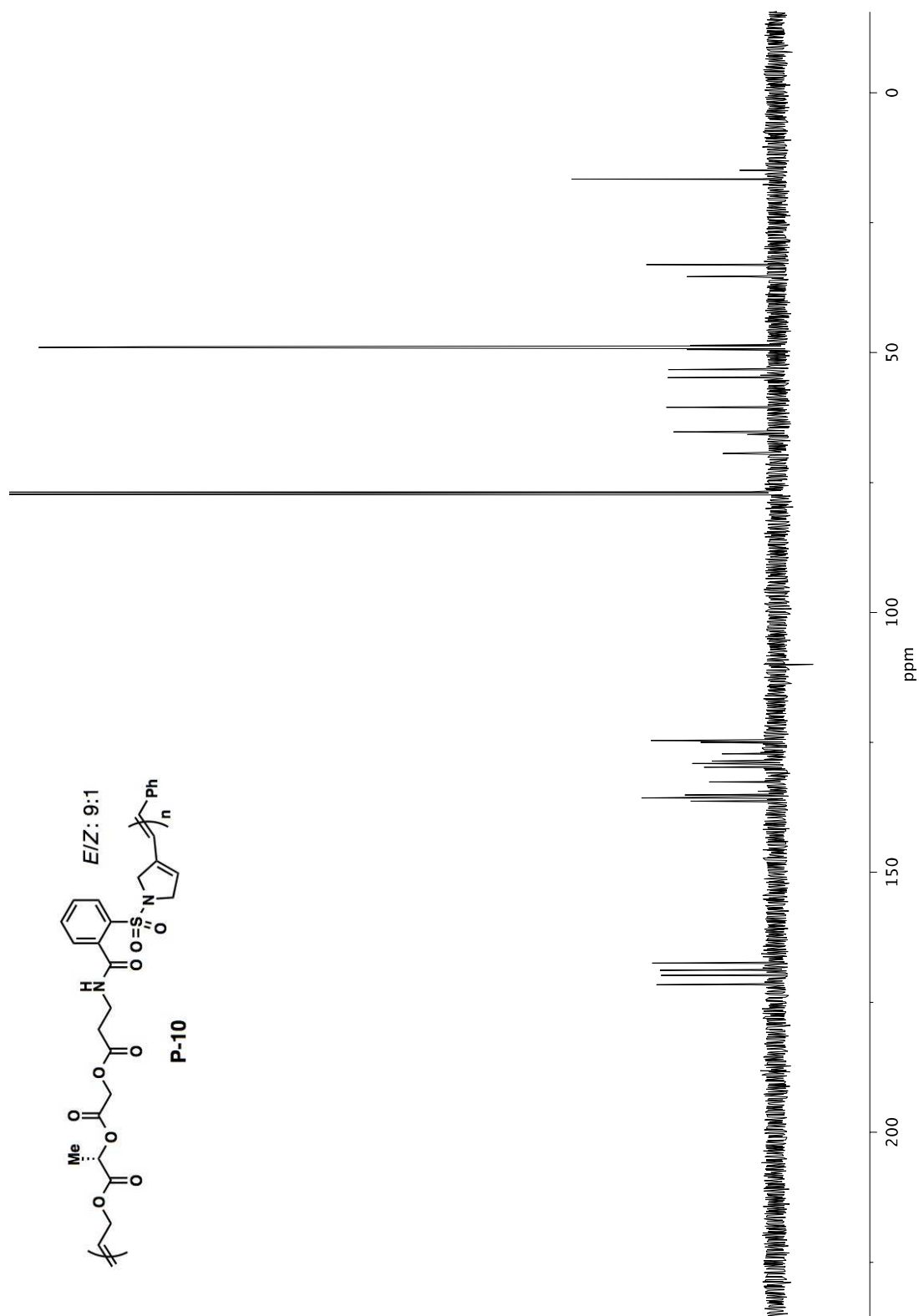
¹H-NMR of 11

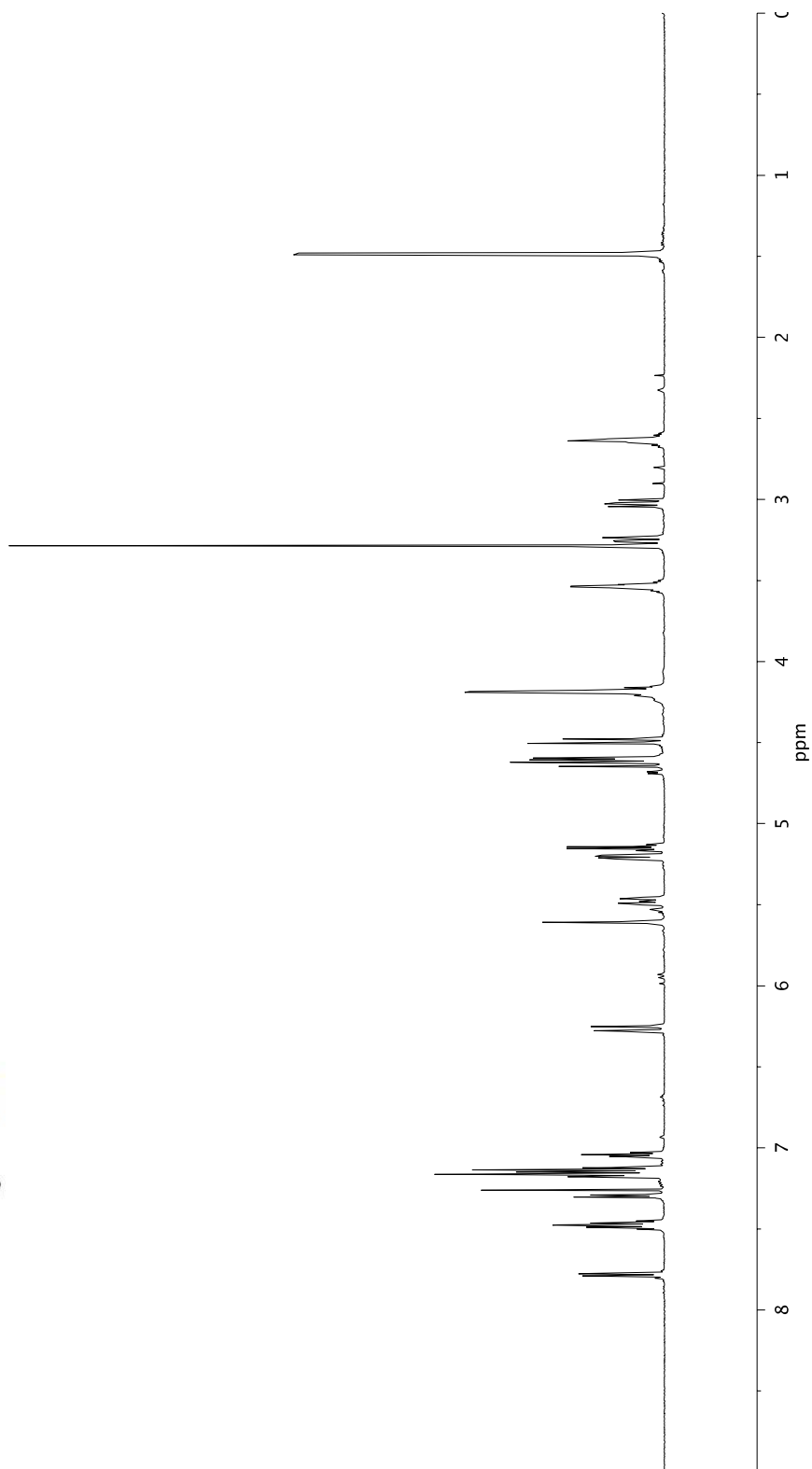
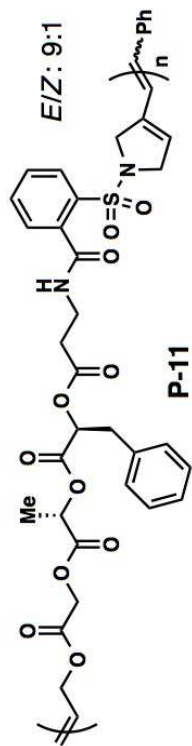
^{13}C -NMR of 11

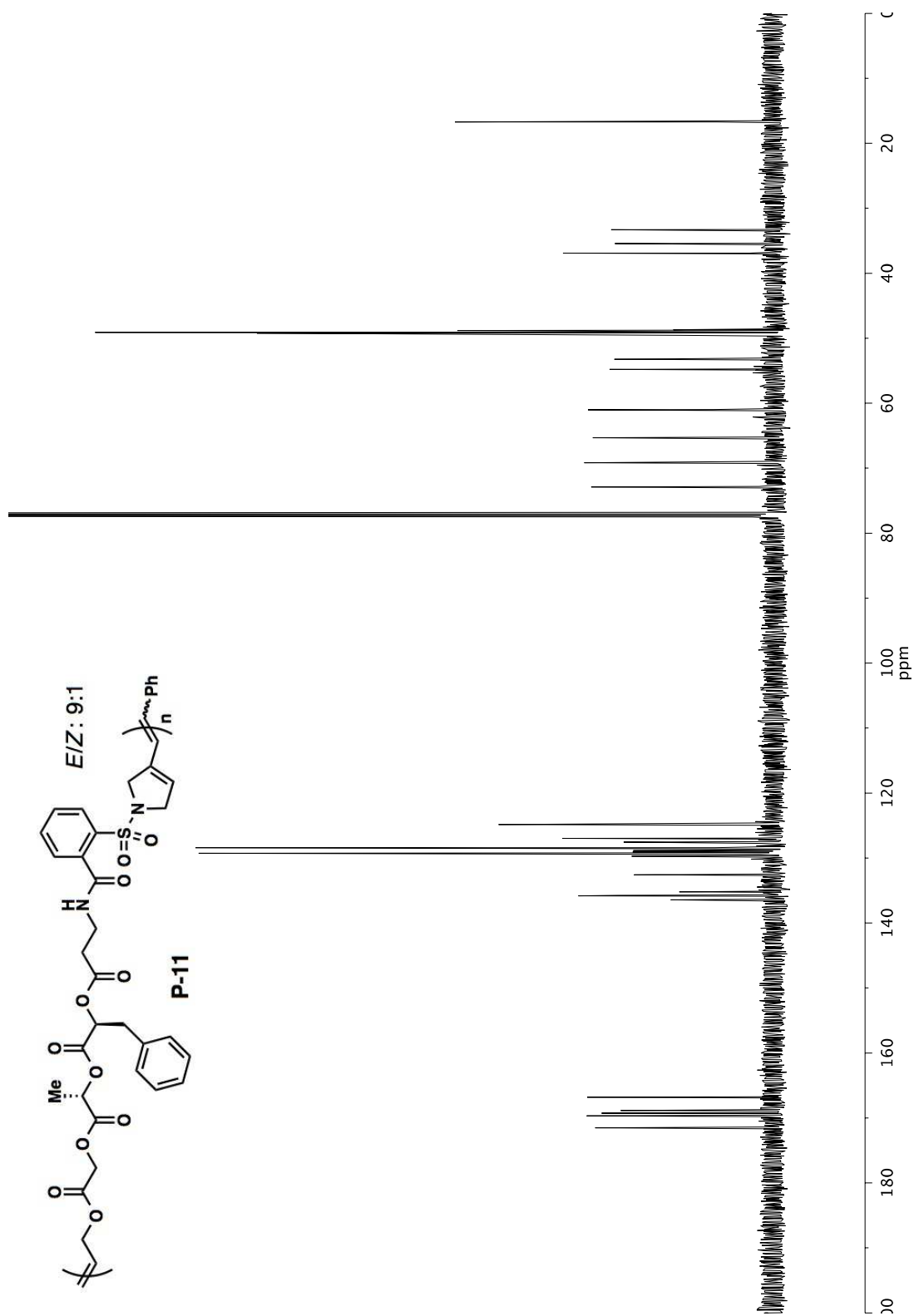
$^1\text{H-NMR}$ of P-9

^{13}C -NMR of P-9

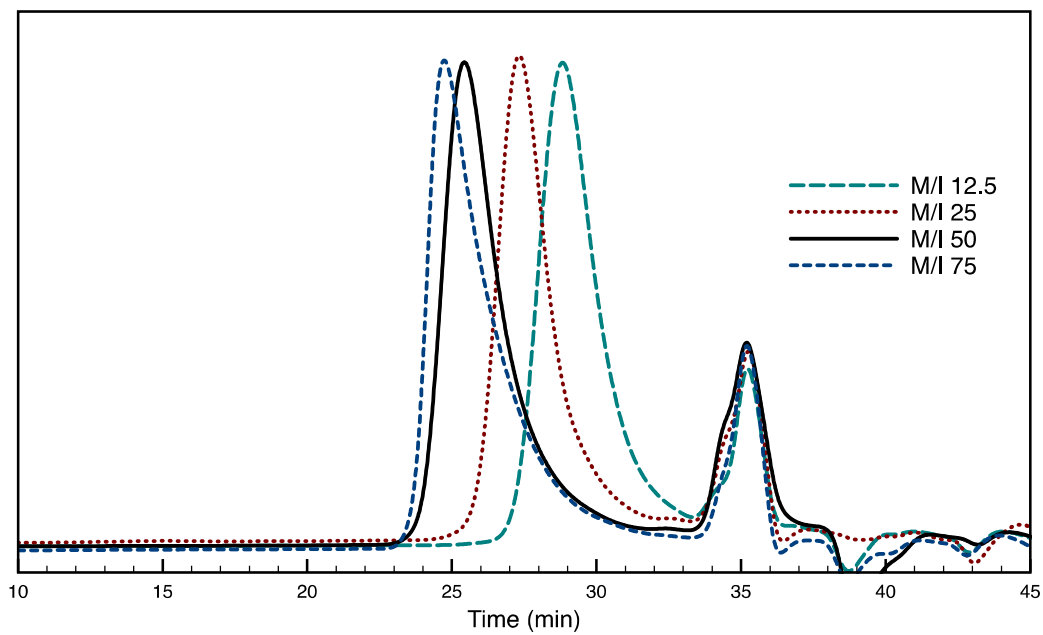
$^1\text{H-NMR}$ of P-10

^{13}C -NMR of P-10

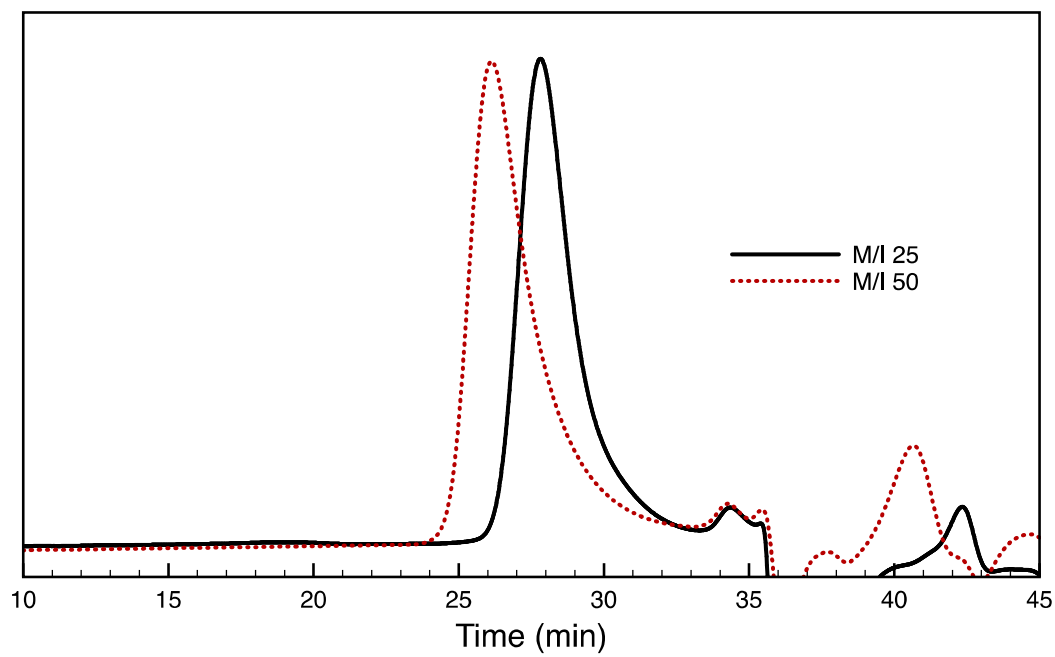
$^1\text{H-NMR}$ of P-11

^{13}C -NMR of P-11

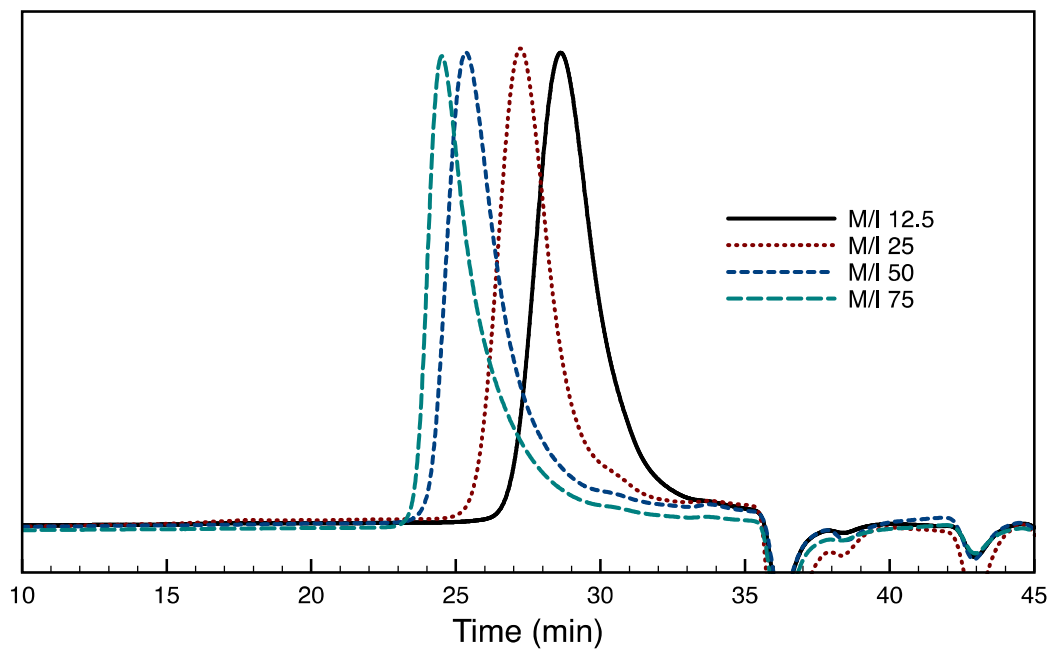
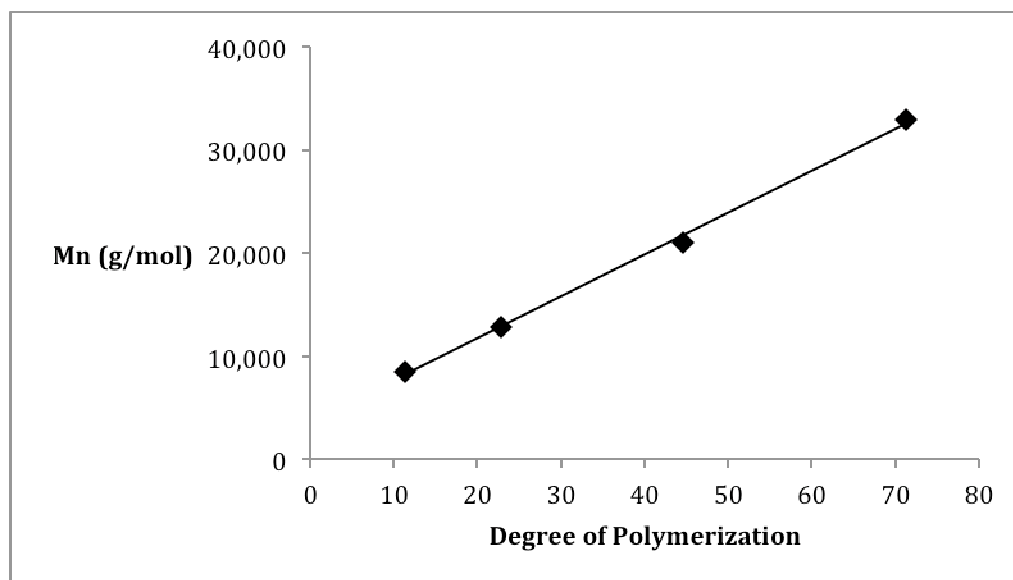
SEC-DMF of P-9

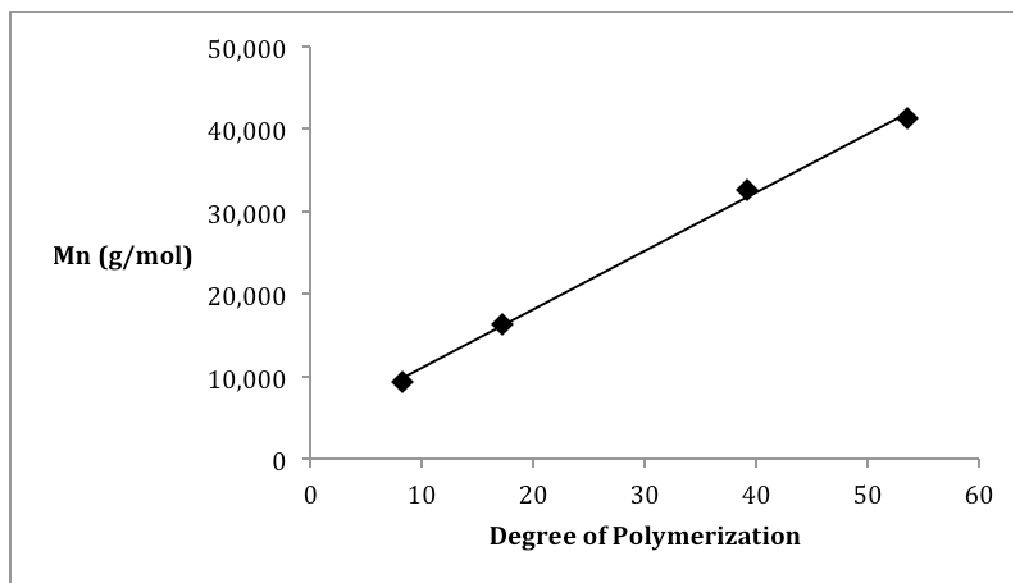


SEC-DMF of P-10



SEC-DMF of P-11

Degree of polymerization versus M_n for P-9

Degree of polymerization versus M_n for P-11**References**

1. Prepared according to: Mitchell, M.; Qaio, L.; Wong, C.-H., *Adv. Synth. Catal.* **2001**, *343*, 596.
2. Prepared according to: Stayshich, R. M.; Meyer, T. Y., *J. Am. Chem. Soc.* **2010**, *132*, 10920.
3. Prepared according to: Nicolaou, K. C.; Snyder, S. A.; Huang, X.; Simonsen, K. B.; Koumbis, A. E.; Bigot, A., *J. Am. Chem. Soc.*, **2004**, *126*, 10162.
4. Prepared according to: Park, H.; Choi, T.-L., *J. Am. Chem. Soc.* **2012**, *134*, 7270.