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Supporting Information

Grafting Self-Immolative Poly(Benzyl Ether)s Toward Sustainable Adhesive Thermosets with Reversible Bonding and Triggered De-Bonding Capabilities

Byeongjun Choi,[†] Ji Woo Kim,[†] Geunyoung Choi,[†] Songah Jeong,[†] Eunpyo Choi,[‡] and Hyungwoo Kim*[,†]

[†]School of Polymer Science and Engineering, Chonnam National University, 77 Yong-bong-ro, Buk-gu, Gwangju 61186, Korea
[‡]School of Mechanical Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, Korea; Korea Institute of Medical Microrobotics (KIMIRo), Gwangju 61011, Korea

*Corresponding author e-mail: kimhw@jnu.ac.kr

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General Experimental

All reactions were performed in flame-dried glassware under a positive pressure of nitrogen unless otherwise noted. Air-and moisture-sensitive liquids were transferred by syringe or stainless steel cannula. Compound **2** was prepared as reported by Thimm, Funke, Meyer, and Müller.[S1] Compound **4** was prepared as reported by Yeung, Kim, Mohapatra, and Phillips.[S2] Compound **10** was prepared as reported by Kim, Mohapatra, and Phillips.[S3] Compound **19** was prepared as reported previously by Chaumette, Laufersweiler, and Parquette.[S4]

Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker Ascend 400 MHz NMR spectrometers at 25 °C processed with MestReNova software. Proton

chemical shift are expressed in part per million (ppm, δ scale) and are referenced to tetramethylsilane ($(CH_3)_4Si$ 0.00 ppm) or to residual protium in the solvent ($CDCl_3$, δ 7.26 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad peak), integration. Carbon nuclear magnetic resonance (^{13}C NMR) were recorded using a Bruker Ascend 400 MHz NMR spectrometer at 25 °C. Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$, δ 77.06 ppm).

Molecular weights of polymers were analyzed by gel permeation chromatography (GPC) using an Shimadzu Prominence LC-20A instrument equipped with a differential refractive index detector (RID-20A) and an auto-sampler unit (SIL-20A). The column configuration consisted of a guard column (GVP-ODS, Shimadzu), a Phenogel linear column (pore size range 100–100000 Å; particle diameter, 5 μm; size, 300 mm × 7.5 mm; Phenomenex) and a Phenogel column with a pore size of 100 Å (particle diameter, 5 μm; size, 300 mm × 7.5 mm; Phenomenex). HPLC-grade THF was used as eluent with a flow rate of 1 mL min^{-1} at 25 °C.

The lap shear test and 180º peel test were performed using a universal testing machine (UTM) (MCT-2150, A&D, Japan) with a 500-N load cell at 25 °C in the air. (i) The shear test was performed under the following conditions: The sample was applied in-between glasses and heated in an oven at 120°C for 4 hours. Then, the glued joint was mounted in an UTM and elongated at 10 mm min^{-1}. The stress–strain curves were recorded until detached. (ii) The peel test was performed under the following conditions: The sample was applied between a tape strip and a glass substrate and heated in an oven at 120 °C for

4 hours. The end of the adhered strip was pulled back at an angle of 180° with a speed of 300 mm min^{-1}. The force–displacement curves were recorded until detached. Each strength was measured in quintuplicate and reported on average.

Thermogravimetric analysis (TGA) was performed using TGAQ50 (TA Instruments). Samples were measured up to 800 °C at a heating rate of 10 °C min^{-1} under an N_2 atmosphere.

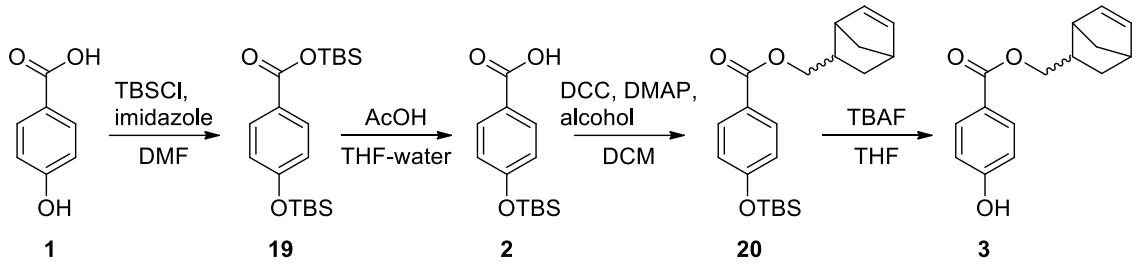
Differential scanning calorimetry (DSC) was performed to investigate thermal transition of samples using DSC823e (Mettler Toledo). The samples were measured at heating and cooling rates of 10 °C min^{-1} under an N_2 atmosphere.

High-resolution mass spectrometry (HRMS) was performed using a JMS-T200GC (JEOL) time-of-flight mass spectrometer in a field desorption mode (Waters).

The dynamic thermal properties were measured by a dynamic mechanical analyzer (DMA 2980, TA Instruments). The rectangular specimen was prepared to have a size of 13 mm × 5.38 mm × 0.47 mm. The storage modulus (G′) and loss factor (tan δ, the ratio of the loss modulus to the storage modulus) were measured at a constant shear strain of 0.5% from 0.01 Hz to 30 Hz at 25 ºC

Synthetic Procedures

The functional initiator



Scheme S1. Synthetic route to the functional initiator **3**.

Synthesis of 19: To a solution of **1** (500 mg, 3.62 mmol, 1.0 equiv) and *tert*-butyldimethylsilyl chloride (1.65 g, 10.93 mmol, 3.0 equiv) in DMF (7.5 mL) was added 1*H*-imidazole (0.74 g, 10.93 mmol, 3.0 equiv). After stirring for 20 h at 25 °C, the reaction mixture was diluted with diethyl ether and washed with water (50 mL) and brine (50 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was further purified by flash column chromatography eluting with dichloromethane. The desired product was obtained as a clear oil (992.7 mg, 3.22 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.7 Hz, 2 H), 6.85 (d, J = 8.7 Hz, 2 H), 1.02 (s, 9 H), 0.99 (s, 9H), 0.36 (s, 6 H), 0.23 (s, 6 H). The ^{1}H NMR spectrum of this compound was matched with the previous data.[S4]

Synthesis of 2: To a solution of **19** (1.0 g, 3.22 mmol, 1.0 equiv) in THF (10 mL) and water (2.2 mL) was added acetic acid (8.63 mL, 10.62 mmol, 3.0 equiv). After stirring for 20 h at 25 °C, the reaction mixture was diluted with diethyl ether and washed with water (50 mL) and brine (50 mL). The combined organic layer was dried over Na_2SO_4, filtered,

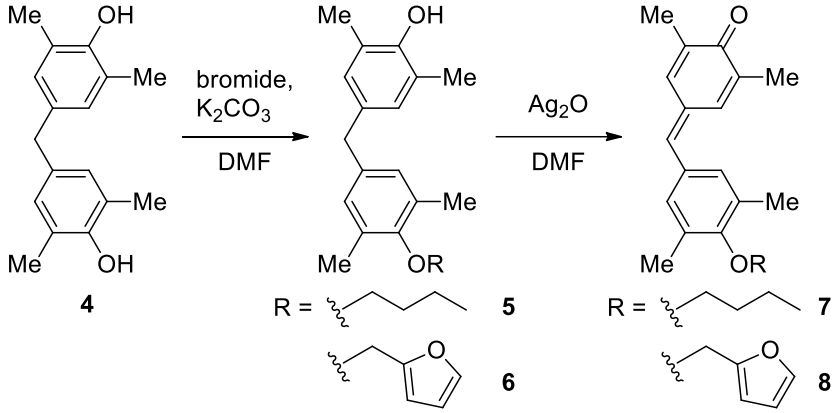
and concentrated under reduced pressure. The residue mixture was purified by flash column chromatography (elution with 2% MeOH in DCM) and further purified by re-crystallization from MeCN. The desired product was obtained as a colorless needle (1.48 g, 2.76 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.7 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 0.99 (s, 9 H), 0.24 (s, 6 H). The ^{1}H NMR spectrum of this compound was matched with the previous data.[S1]

Synthesis of 20: 5-Norbornene-2-methanol (380 mg, 3.06 mmol, 1.2 equiv) and **2** (642.8 mg, 2.55 mmol, 1.0 equiv) were dissolved in dry DCM (30 mL). After adding 4-dimethylaminopyridine (31.8 mg, 0.26 mmol, 0.1 equiv) and *N*,*N*'-dicyclohexylcarbodiimide (631.4 mg, 3.06 mmol, 1.2 equiv), the mixture was stirred for 24 h at 25 °C. Then, the resulting product was washed with water (50 mL), a saturated aqueous $NaHCO_3$ solution (50 mL), and brine (50 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was briefly passed through a short flash silica column eluting with hexanes and used without further isolation. A white powder (322.4 mg, 0.91 mmol, 45%).

Synthesis of 3: To a solution of **20** (322.4 mg, 0.91 mmol, 1.0 equiv) in THF (15 mL) was added tetra-*n*-butylammonium fluoride (232.9 mg, 0.91 mmol, 1.0 equiv). The reaction mixture was stirred for 5 h at 25 °C. Then, the resulting product was diluted with ethyl acetate and washed with water (50 mL) and brine (50 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue mixture was purified by flash column chromatography (elution with 10% ethyl acetate in

hexanes) to afford a white powder (100.14 mg, 0.41 mmol, 45%). IR (cm^{-1}): 3300, 2960, 1672, 1587, 1514, 1273, 1165, 980, 700 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.95 (m, 2 H), 6.88–6.85 (m, 2 H), 6.20–5.98 (m, 2 H), 4.40–3.83 (m, 2 H), 2.97–2.80 (m, 2 H), 2.54 (s, 1 H), 1.92–1.87 (m, 1.4 H), 1.49–1.27 (m, 2 H), 0.66–0.63 (m, 0.6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.50, 160.78, 137.77, 137.05, 136.24, 132.02, 122.15, 115.43, 69.22, 68.57, 49.43, 45.03, 44.00, 43.75, 42.25, 41.65, 38.02, 29.60, 28.96; HRMS (TOF MS FD+): Calcd. for $C_{15}H_{16}O_3$ (M^+) 244.10940 *m*/*z*, found: 244.10950 *m*/*z*.

The quinone methide monomers



Scheme S2. Synthetic route to the quinone methide monomers **7** and **8**.

Synthesis of 5: The compound **4** (2 g, 7.8 mmol, 1.0 equiv) and 1-bromobutane (0.85 mL, 7.8 mmol, 1.0 equiv) were dissolved in DMF (20 mL). After adding K_2CO_3 (1.18 g, 8.6 mmol, 1.1 equiv), the suspension was stirred for 24 h at 25 °C. After dilution with ethyl acetate, the mixture was washed with water (50 mL), saturated aqueous NH_4Cl (50 mL), and brine (50 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (elution with 10% ethyl acetate in hexanes) to afford a yellow oil (1.71 g, 5.48 mmol,

70%). IR (cm^{-1}): 3454, 2919, 1484, 1193, 980; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (s, 4 H), 3.74–3.72 (m, 4 H), 2.22 (d, J = 6.9 Hz, 12 H), 1.76 (q, J = 6.7 Hz, 2 H), 1.52 (q, J = 7.4 Hz, 2 H), 0.99 (t, J = 7.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.22, 150.39, 136.72, 132.98, 130.62, 129.04, 122.94, 71.97, 40.63, 32.47, 19.33, 16.22, 15.86, 13.95; HRMS (TOF MS FD+): Calcd. for $C_{21}H_{28}O_2$ (M^+) 312.20838 *m*/*z*, found: 312.20852 *m*/*z*.

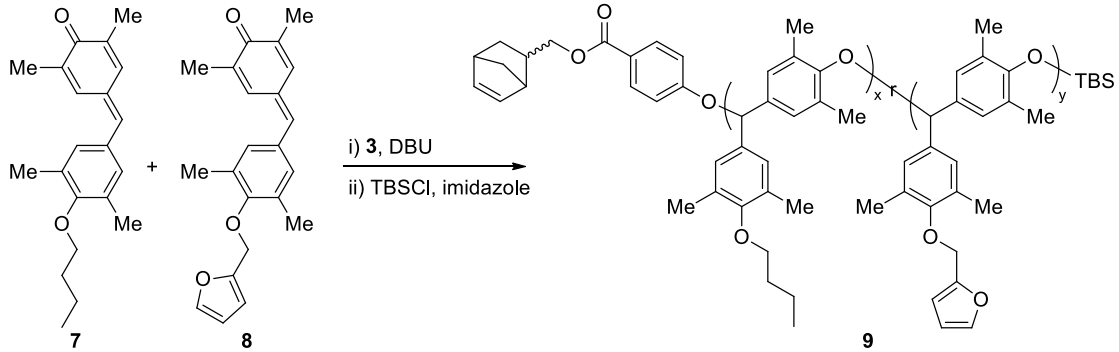
Synthesis of 6: This compound was synthesized following a similar manner for **5** except for using 2-(bromomethyl)furan instead of 1-bromobutane. *Quantities of reagents*: **4** (1.1 g, 4.25 mmol, 1.0 equiv), 2-(bromomethyl)furan (0.75 g, 4.25 mmol, 1.1 equiv), and K_2CO_3 (645.71 mg, 4.67 mmol, 1.1 equiv). A yellow oil (919.74 mg, 2.73 mmol, 64%). IR (cm^{-1}): 3120, 2950, 1600, 1480, 1220, 916 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1 H), 6.82 (d, J = 5.8 Hz, 4 H), 6.37–6.34 (m, 2 H), 4.74 (s, 2 H), 3.72 (s, 2 H), 2.22 (d, J = 2.3 Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.77, 151.43, 150.68, 143.12, 137.55, 133.06, 131.12, 129.32, 123.31, 110.66, 109.9, 66.18, 40.65, 16.39; HRMS (TOF MS FD+): Calcd. for $C_{22}H_{24}O_3$ (M^+) 336.17200 *m*/*z*, found: 336.17252 *m*/*z*.

Synthesis of 7: To a solution of **5** (1.1 g, 3.38 mmol, 1.0 equiv) in diethly ether (20 mL) was added Ag_2O (1.3 g, 5.60 mmol, 1.7 equiv). After stirring for 18 h at 25 °C, the resulting product was filtered using gravity to remove the metal particles. A yellow filtrate was concentrated via rotary evaporation and purified by re-crystallization from *n*-hexane. A yellowish orange powder (776 mg, 2.5 mmol, 74%). IR (cm^{-1}): 2912, 2361, 1554, 980, 930 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1 H), 7.15 (s, 2 H), 7.07 (s, 1 H), 7.03 (s, 1 H), 3.82 (t, J = 6.5 Hz, 2 H), 2.33 (s, 6 H), 2.06 (d, J = 6.9 Hz, 6 H), 1.82 (t, J = 7.5 Hz, 2 H), 1.55

(t, J = 7.5 Hz, 2 H), 1.01 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.25, 157.69, 143.18, 139.18, 137.23, 135.24, 131.67, 131.37, 130.84, 72.30, 32.51, 19.36, 16.96, 16.46, 16.24, 13.99; HRMS (TOF MS FD+): Calcd. for $C_{21}H_{26}O_2$ (M^+) 310.19273 *m*/*z*, found: 310.19279 *m*/*z*.

Synthesis of 8: This compound was synthesized following a similar manner for **7** except for using **6** instead of **5** and omitting re-crystallization. *Quantities of reagents*: **6** (1.0 g, 3.54 mmol, 1.0 equiv), Ag_2O (1.3 g, 5.60 mmol, 1.7 eq). A yellowish orange powder (734 mg, 2.2 mmol, 62%). IR (cm^{-1}): 3119, 2912, 2350, 1560, 1217, 972, 921 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1 H), 7.48 (s, 1 H), 7.15 (s, 2 H), 7.07 (s, 1 H), 7.03 (s, 1 H), 4.84 (s, 2 H), 2.30 (s, 6 H), 2.07 (d, J = 7.8 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.23, 156.77, 150.66, 143.19, 142.88, 137.27, 135.29, 131.97, 131.39, 130.97, 110.57, 109.71, 66.10, 16.91, 16.36, 16.03; HRMS (TOF MS FD+): Calcd. for $C_{22}H_{22}O_3$ (M^+) 334.15635 *m*/*z*, found: 334.15615 *m*/*z*.

The poly(benzyl ether)-based macro-monomers

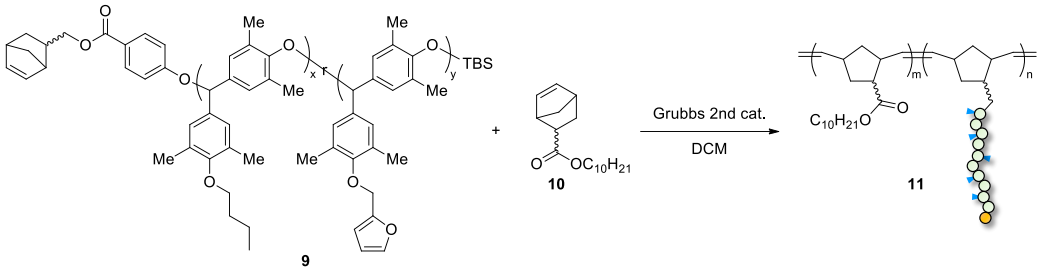


Scheme S3. Synthetic route to the poly(benzyl ether) **9**.

Synthesis of 9: To a round–bottom flask were added **7** (200 mg, 0.64 mmol, 1.0 equiv), **8** (220.16 mg, 0.64 mmol, 1.00 equiv), and dry DCM (2 mL). After cooling to 0 °C, a solution of **3** (0.314 mg, 1.28 μmol, 0.002 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.2 μL, 1.28 μmol, 0.002 equiv) in DCM (0.1 mL) was added in one portion to initiate polymerization. The reaction mixture was stirred for 4 h at 0 °C, to which *tert*-butyldimethylsilyl chloride (96.5 mg, 0.64 mmol, 1.0 equiv) and 1*H*-imidazole (43.5 mg, 0.64 mmol, 1.0 equiv) were added in sequence. After stirring for 24 h at 25 °C, the resulting product was isolated by the addition of MeOH and filtration. After re-dissolving in DCM and re-precipitating in MeOH twice, the desired product was obtained as a white powder (396.1 mg, 94%). M_n, 27 kDa; M_w, 34 kDa; $Đ$, 1.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1 H), 6.87 (br s, 8 H), 6.33 (s, 1 H), 6.29 (s, 1 H), 5.52 (s, 2 H), 4.74 (s, 2 H), 3.72 (s, 2 H), 2.25–2.17 (br m, 12 H), 1.85–1.83 (br m, 12 H), 1.75 (br m, 2 H), 1.53–1.50 (br m, 2 H), 1.02–0.96 (m, 3 H).

Synthesis of control poly(benzyl ether) 14: This polymer was prepared following a similar manner for **9** without the addition of the monomer **8**. *Quantities of reagents*: **7** (200 mg, 0.64 mmol, 1.0 equiv), **3** (0.16 mg, 0.64 μmol, 0.001 equiv), DBU (0.1 μL, 0.64 μmol, 0.001 equiv), *tert*-butyldimethylsilyl chloride (96.5 mg, 0.64 mmol, 1.00 equiv), 1*H*-imidazole (43.5 mg, 1.0 equiv, 0.64 mmol). A white powder (90%). M_n, 44 kDa; M_w, 50 kDa; $Đ$, 1.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (br s, 4 H), 5.52 (s, 1 H), 3.72 (m, 2 H), 2.24–2.16 (br m, 6 H), 1.85–1.83 (br m, 6 H), 1.76 (br m, 2 H), 1.53–1.50 (br m, 2 H), 1.02–0.96 (m, 3 H).

The graft copolymers via ROMP



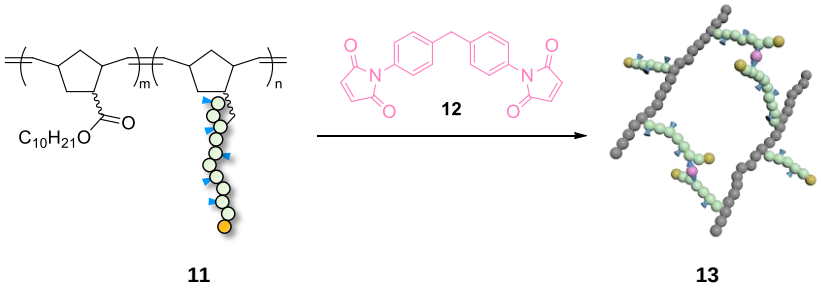
Scheme S3. Synthetic route to the graft copolymer **11**.

Synthesis of 11: To a round–bottom flask were added **9** (25 mg, 0.93 μmol, 0.001 equiv), **10** (259.7 mg, 0.93 mmol, 0.999 equiv) and dry DCM (2 mL). (0.1 mol% **9** was incorporated.) Then, a solution of Grubbs catalyst 2nd generation (7.9 mg, 0.01 eq, 9.3 μmol) in DCM (1 mL) was added in one portion to the reaction mixture. After polymerization for 24 h at 25 °C, ethyl vinyl ether (0.44 mL, 4.6 mmol, 5.0 equiv) was added to quench the reaction. The resulting mixture was stirred for additional 1 hour and purified by precipitation by adding MeOH. After re-dissolving in DCM and reprecipitating in MeOH twice, the desired product was obtained as a gray solid (217.5 mg, 75%). M_n, 237 kDa; M_w, 388 kDa; *Đ*, 1.64. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 0.001 H), 6.87 (br s, 0.008 H), 6.33 (s, 0.001 H), 6.29 (s, 0.001 H), 5.52 (s, 0.002 H), 5.44–5.21 (br m, 2.002 H), 4.74 (s, 0.002 H), 3.99 (br m, 2 H), 3.72 (s, 0.002 H), 2.25–2.17 (br m, 0.012 H), 1.85–1.83 (br m, 0.012 H), 1.75 (br m, 0.002 H), 1.53–1.50 (br m, 0.002 H), 1.02–0.96 (m, 0.003 H).

For comparison, the different molar ratios of **9** was adjusted, such as 1 or 0.05 mol%, when synthesizing **11** following a similar manner above. The desired products were obtained as a gray solid (66–75%).

Control graft copolymer 15: This polymer was prepared following a similar manner for **11** except for using **14** instead of **9**. *Quantities of reagents*: **10** (300 mg, 1.07 mmol, 0.999 equiv), **14** (16.05 mg, 1.07 μmol, 0.001 equiv), Grubbs catalyst 2nd generation (9.09 mg, 10.7 μmol, 0.01 equiv), ethyl vinyl ether (0.51 mL, 5.35 mmol, 5.0 equiv). A gray solid (83%). M_n, 272 kDa; M_w, 331 kDa; $Đ$, 1.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (br s, 0.004 H), 5.52 (s, 0.002 H), 5.44–5.21 (br m, 2.002 H), 4.00 (br m, 2 H), 3.73 (s, 0.002 H), 2.25–2.17 (br m, 0.006 H), 1.85–1.83 (br m, 0.006 H), 1.75 (br m, 0.002 H), 1.53–1.50 (br m, 0.002 H), 1.02–0.96 (m, 0.003 H).

The network formation via Diels–Alder reaction



Scheme S4. Synthetic route to the network **13**.

Synthesis of 13: The compound **11** (100 mg, 0.38 μmol, 1.0 equiv) and 4,4'-bismaleimidodiphenylmethane (**12**) (2.58 mg, 7.2 μmol, 19 equiv) were dissolved in dry DCM (3 mL). The mixture was transferred to a Teflon mold and dried for one day. After which, sequential heating 4 hours at 120 °C in an oven afforded the desired network. A quantitative yield.

For comparison, other control networks were prepared following a similar manner for **13** except for using different bismaleimide linkers such as *N*,*N*′-1,4-phenylenedimaleimide (**17**) or *N*,*N*′-1,3-phenylenedimaleimide (**18**) at the same molar ratio, instead of **12**.

Quantitative Analyses on the Graft Copolymer

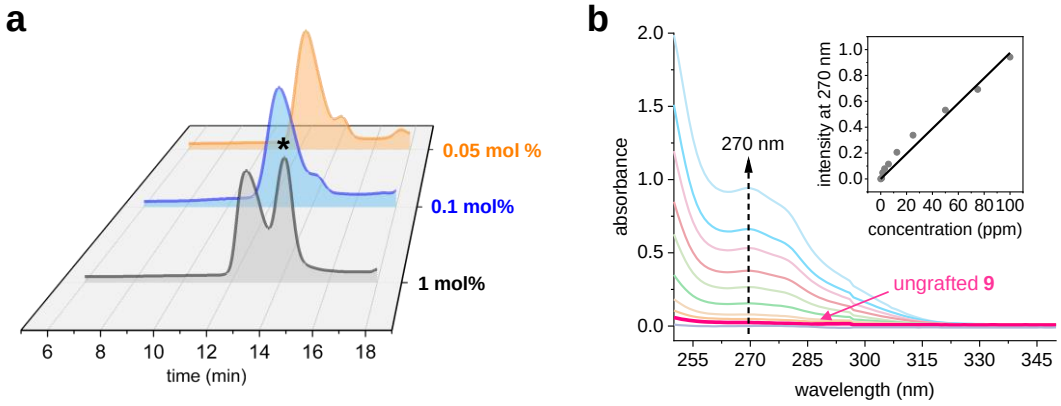


Figure S1. (a) Overlaid GPC chromatograms of the graft copolymer **11** when prepared using different amounts of **9** (black, 1 mol%; blue, 0.1 mol%; orange, 0.05 mol%). (b) Change in absorption spectrum of **9** with respect to its concentrations and the obtained calibration curve based on the peak at 270 nm (inset). The absorption spectrum of ungrafted **9** is shown for comparison (pink).

Measurement of ungrafted 9:

150 mg of **11** was dispersed in acetone (10 mL) and stored for 24 h at 23 °C. The suspension was syringe-filtered and the filtrate was analyzed using a UV–vis spectrometer to quantify the amount of ungrafted **9** referring to its calibration curve (the inset in Figure S1b).

Depolymerization Test

Depolymerization of the macromonomer 9:

To a solution of **9** (50 mg, 1.8 μmol, 1.0 equiv) in dry DCM (1 mL) was added TBAF (0.96 mg, 3.6 μmol, 2.0 equiv). After stirring for 1 hour at 25 °C, an aliquot was taken from the reaction mixture and measured by HRMS.

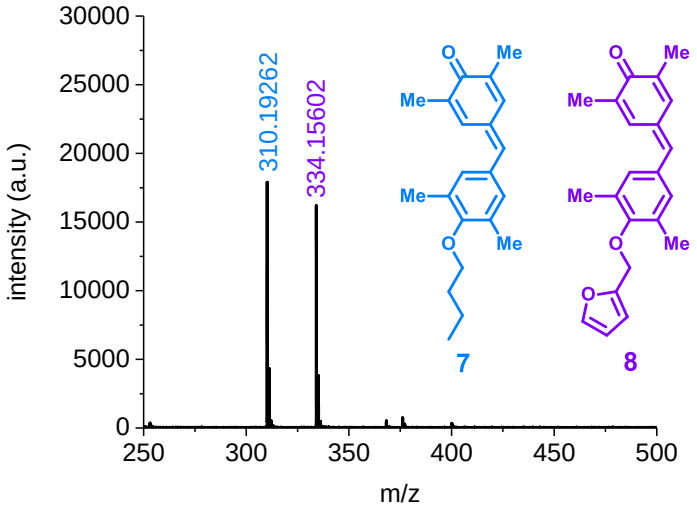


Figure S2. High-resolution mass spectrum of **9** after depolymerization. The inset shows the chemical structures of the monomers, **7** and **8**, for comparison.

Depolymerization of the graft copolymer 11:

To a solution of **11** (50 mg, 0.00021 mmol, 1.00 equiv) in dry DCM (1 mL) was added TBAF (1.1 mg, 0.0042 mmol, 20 equiv). After stirring for 1 hour at 25 °C, the resulting product was isolated by precipitation by adding MeOH and further purified by re-dissolving in DCM and reprecipitating in MeOH twice. The desired product was obtained as a colorless wax.

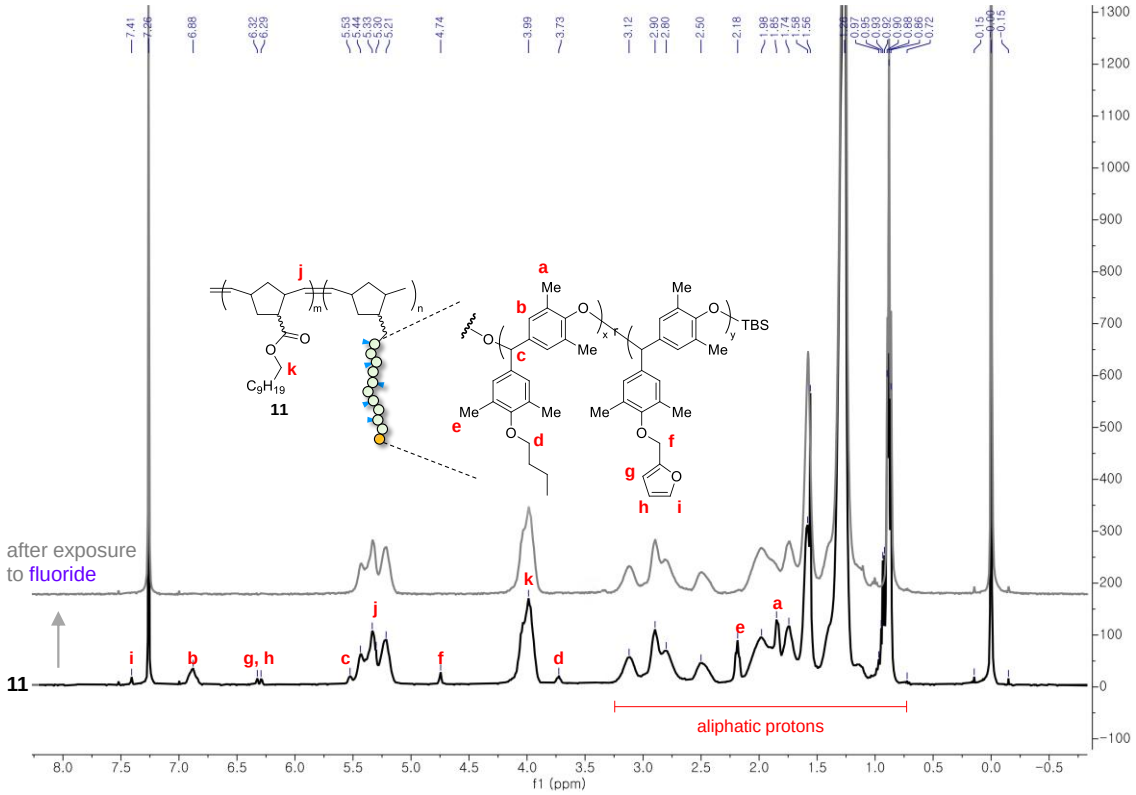


Figure S3. The obtained ^{1}H NMR spectra of **11** (black) and that after depolymerization in response to fluoride (gray). The inset shows the chemical structure of **11** with the assignment of proton peaks.

TGA and DSC Thermograms

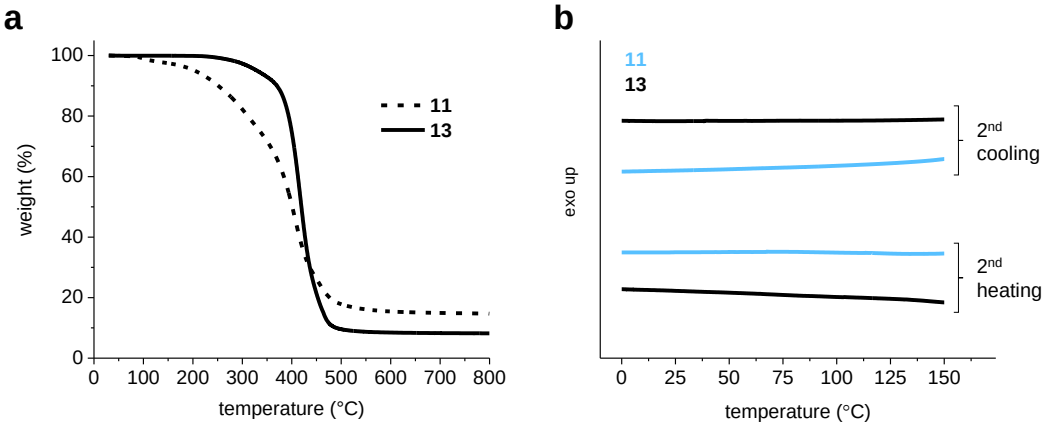


Figure S4. (a) TGA thermograms obtained from **11** and **13**. (b) DSC thermograms for **11** and **13** obtained during the second heating–cooling cycles.

Gel Content

For the test, each sample was soaked in various solvents for 16 h at 25 °C, washed, and dried in vacuum at 100 °C for 4 h. The gel content of the sample was calculated as follows:

$$\text{gel content (\%)} = \frac{m_1}{m_0} \times 100$$

where m_0 and m_1 indicate the initial mass and final mass, respectively.

Table S1. The obtained gel contents of the material after soaking in various solvents.

solvent	gel content (%)
Dichloromethane	87.8
N,*N*-Dimethylformamide	82.7
Water	100
Tetrahydrofuran	83.1
Ethanol	97.2

The Lap Shear and Peel Tests

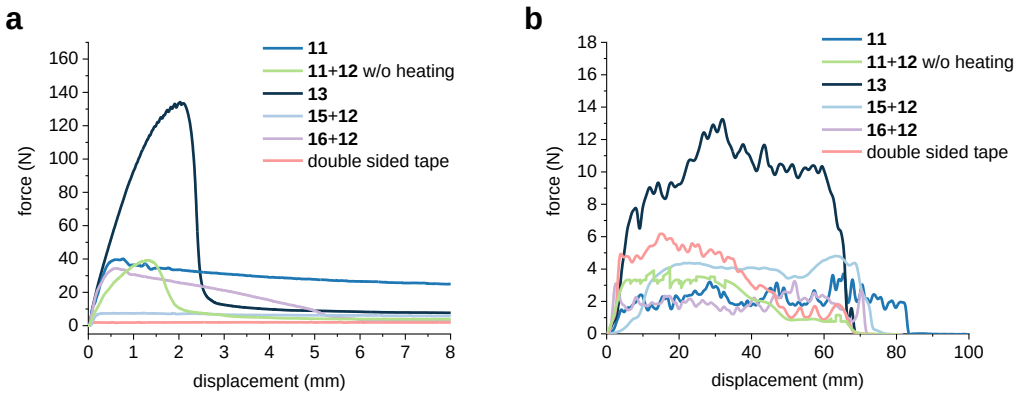


Figure S5. The representative load–displacement curves obtained from **11**, **13**, and the control samples, as measured by (a) lap shear test or (b) 180° peel test.

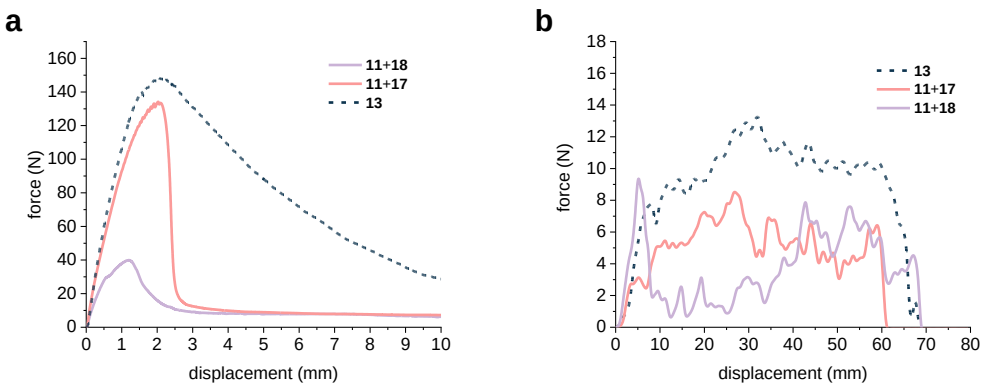


Figure S6. The representative load–displacement curves obtained from the samples of **11** cross-linked with different linkers, as measured by (a) lap shear test or (b) 180° peel test. The dotted line indicates the data from **13**.

DMA Results

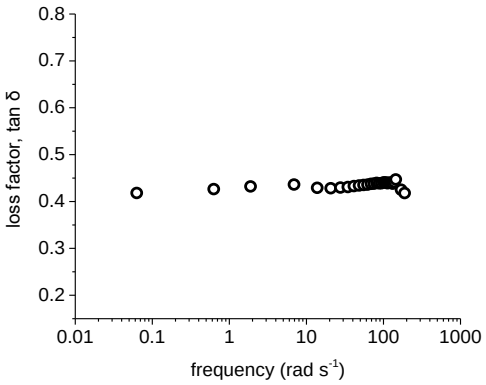


Figure S7. The estimated loss factor of **13** using DMA in the frequency sweep.

Investigation on Stimuli-Responsive Adhesive Strengths

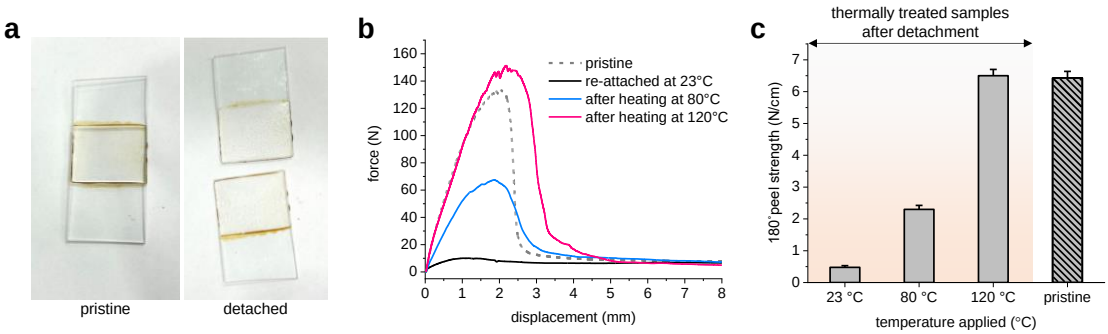


Figure S8. (a) Photographs of adherends of the pristine sample (left) and that after detachment by force (right). (b) The measured load–displacement curves of glass samples during the lap shear tests: (dotted gray) pristine, (black) reattached at 23 °C after detached by force, (sky blue) re-attached after thermal treatment at 80 °C for 4 h, and (pink) re-attached after thermal treatment at 120 °C for 4 h. (c) Change in the peel strength of the detached samples when treated at different temperatures. The data from the pristine sample for comparison.

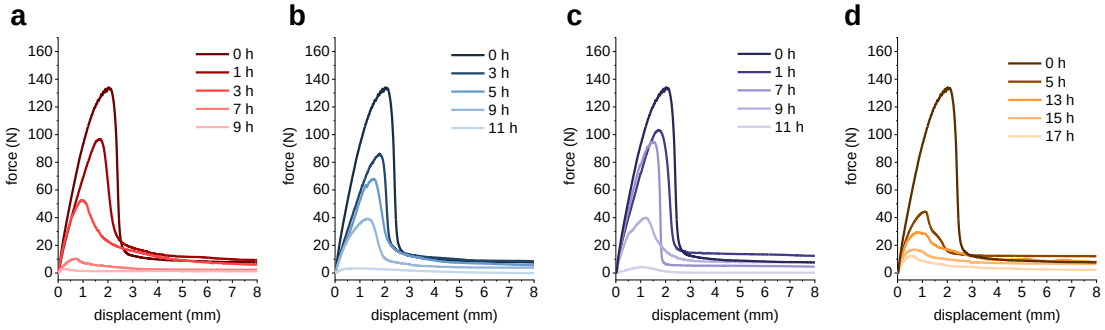


Figure S9. Change in the obtained load–displacement curves of the glued glasses as time elapsed when exposed to various concentrations of fluoride (a, 100 mM; b, 10 mM; c, 1 mM; d, 0.1 mM) at 25 °C.

NMR Spectra

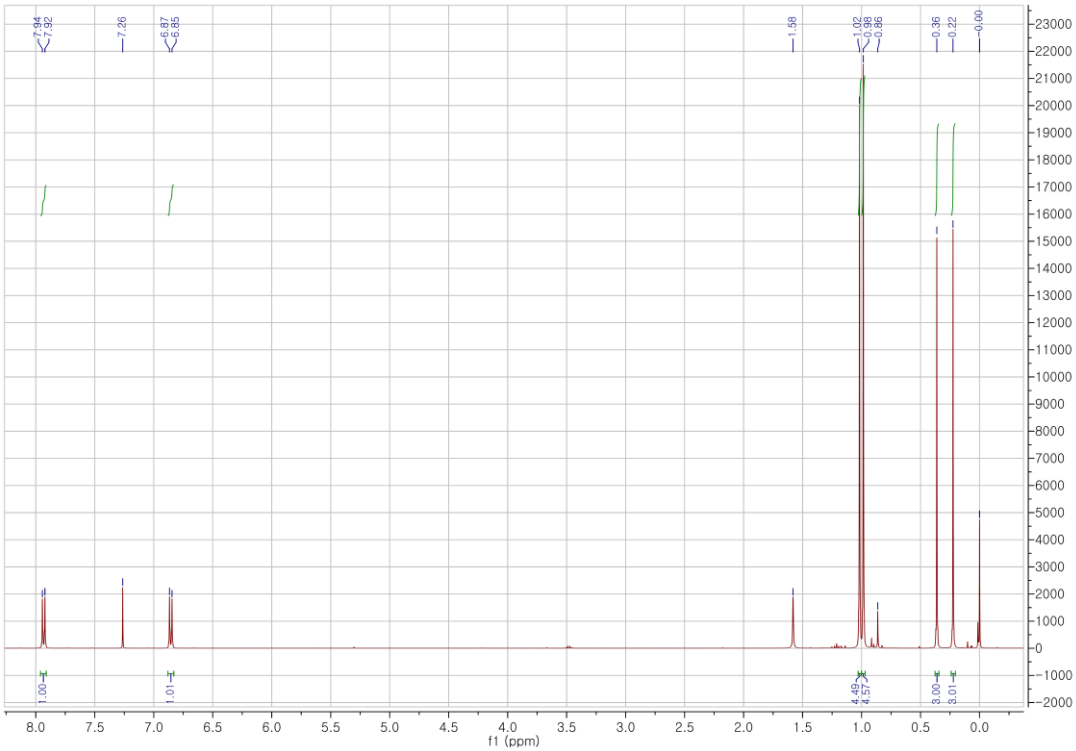


Figure S10. ^{1}H NMR spectrum of **19**.

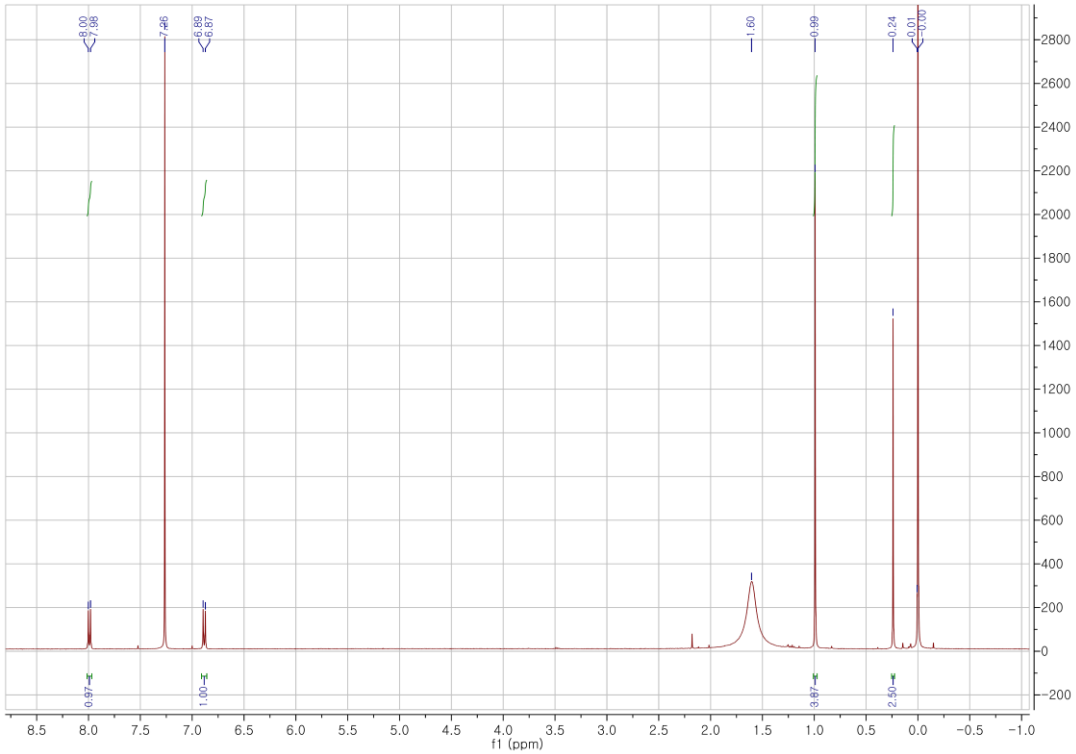


Figure S11. ^{1}H NMR spectrum of **2**.

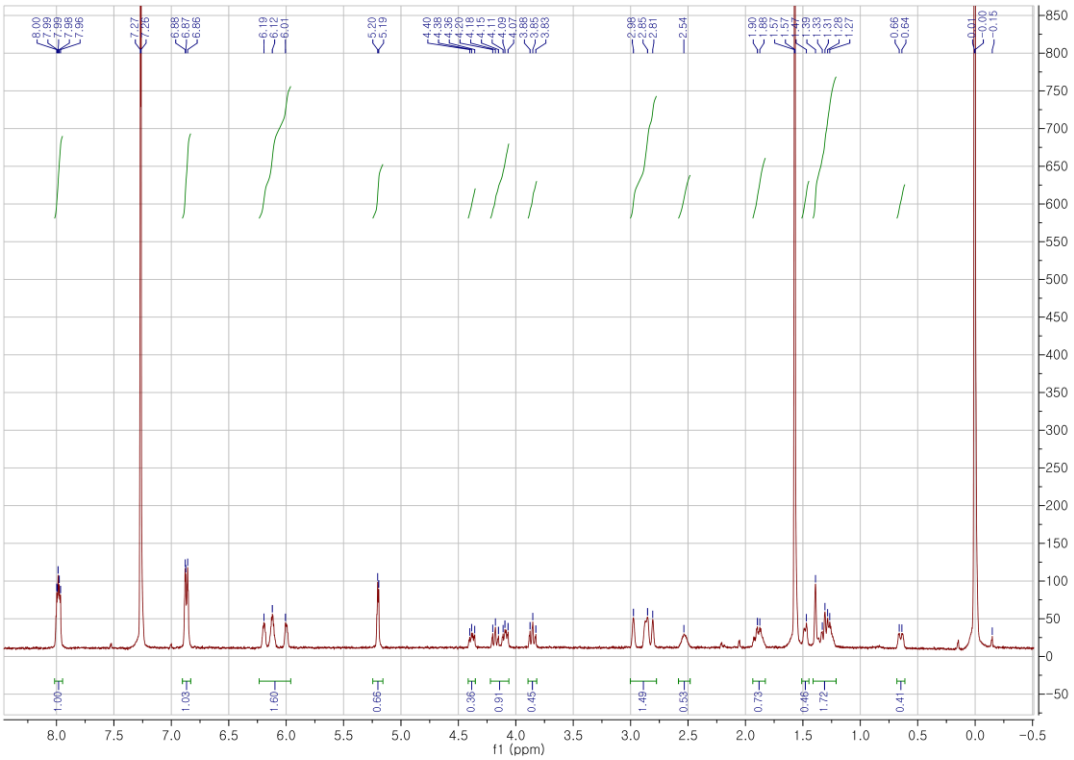


Figure S12. ^{1}H NMR spectrum of **3**.

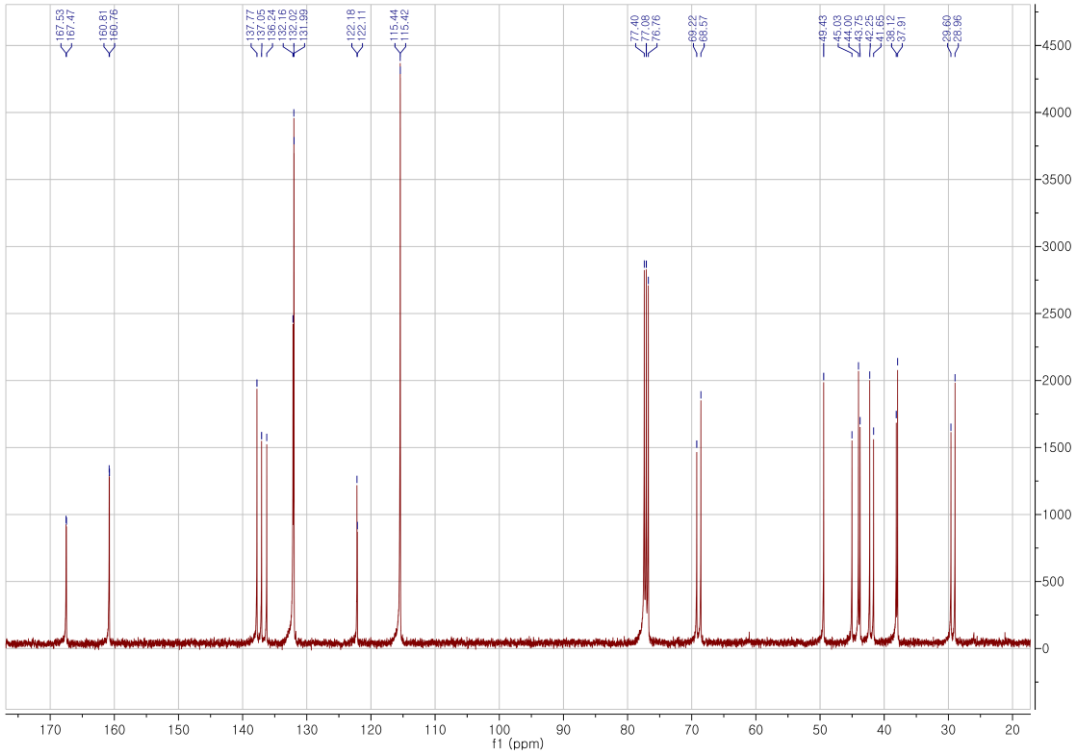


Figure S13. ^{13}C NMR spectrum of **3**.

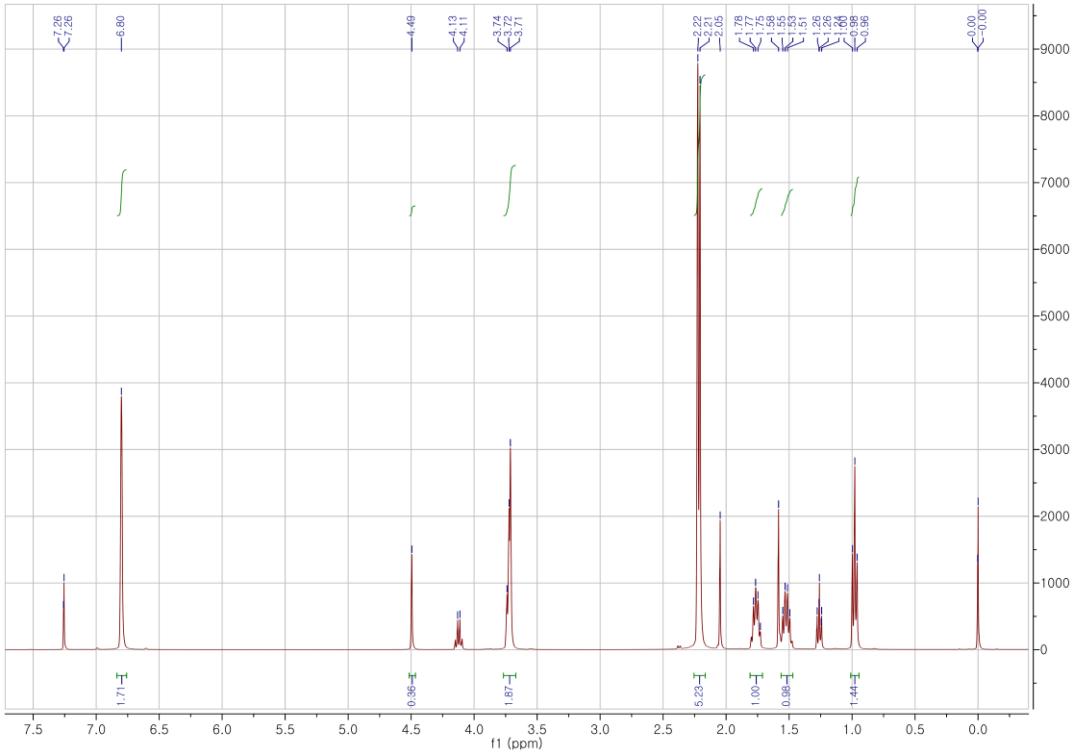


Figure S14. ^{1}H NMR spectrum of **5**.

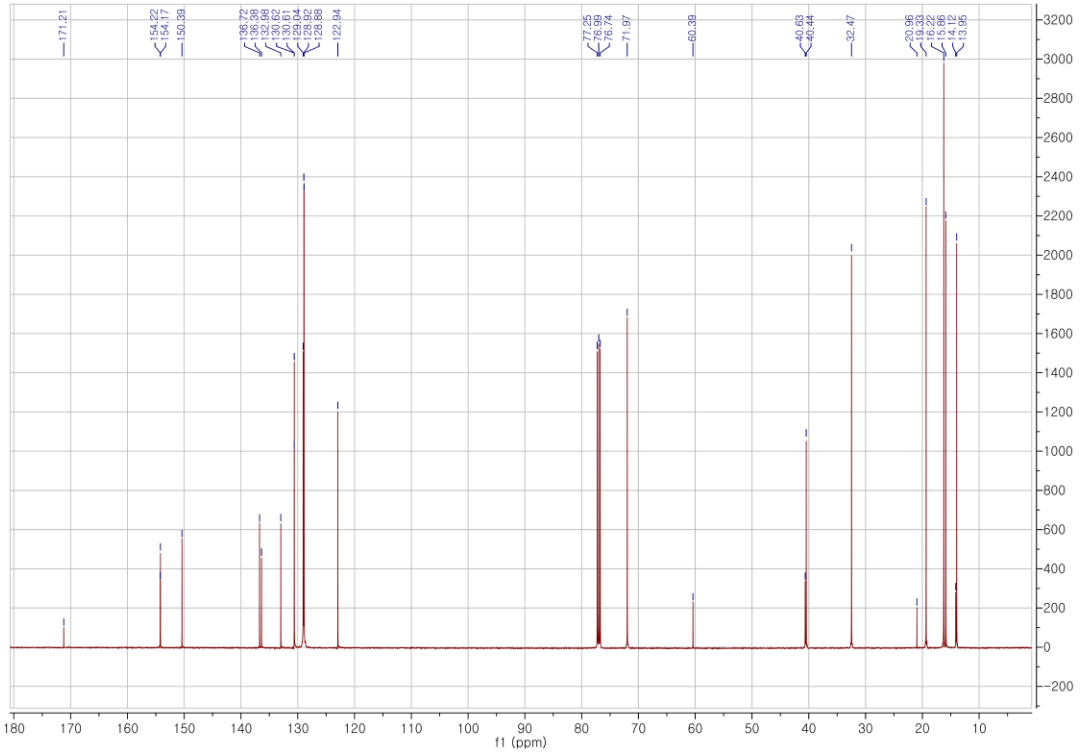


Figure S15. ^{13}C NMR spectrum of **5**.

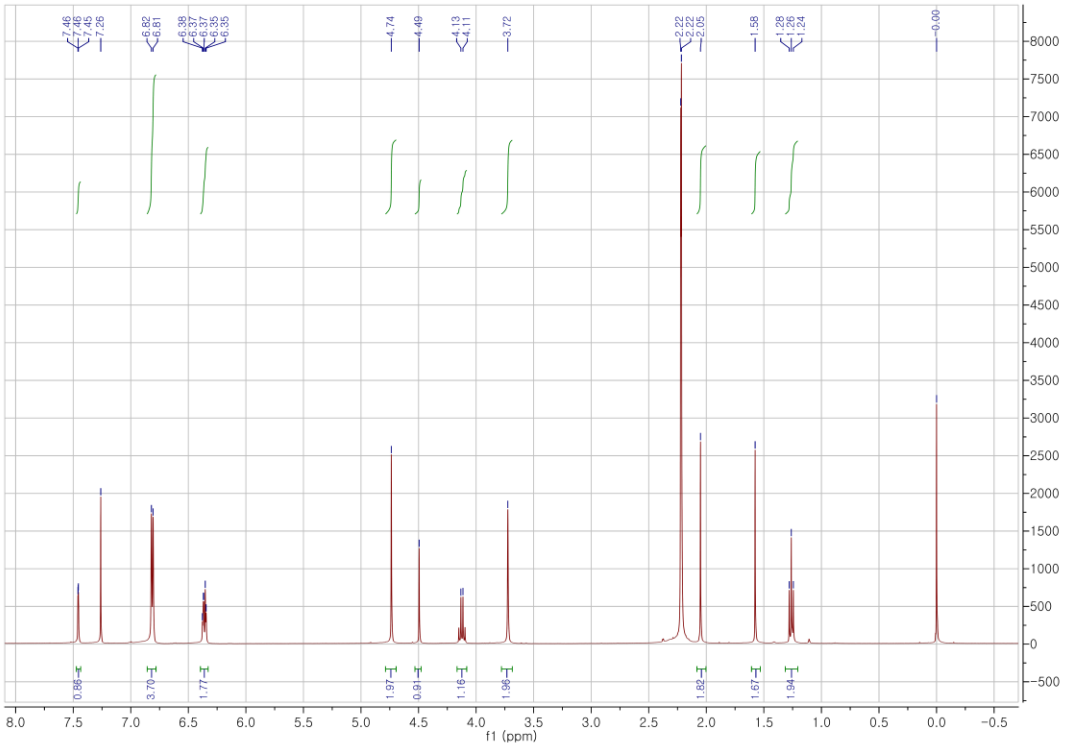


Figure S16. ^{1}H NMR spectrum of **6**.

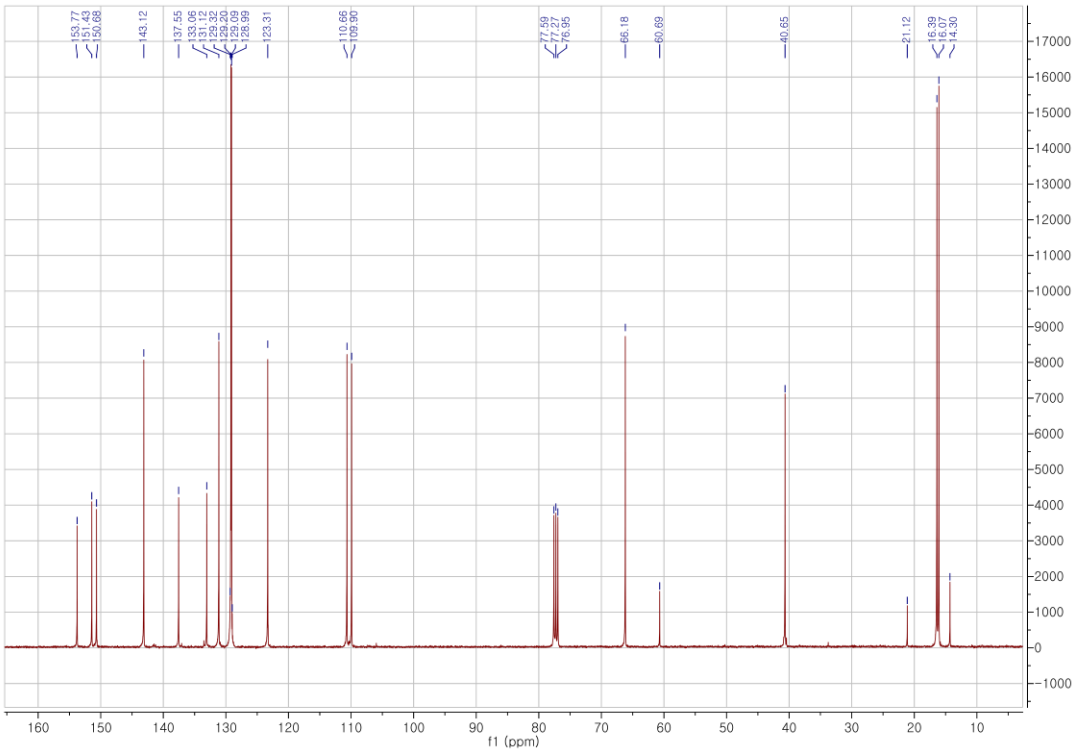


Figure S17. ^{13}C NMR spectrum of **6**.

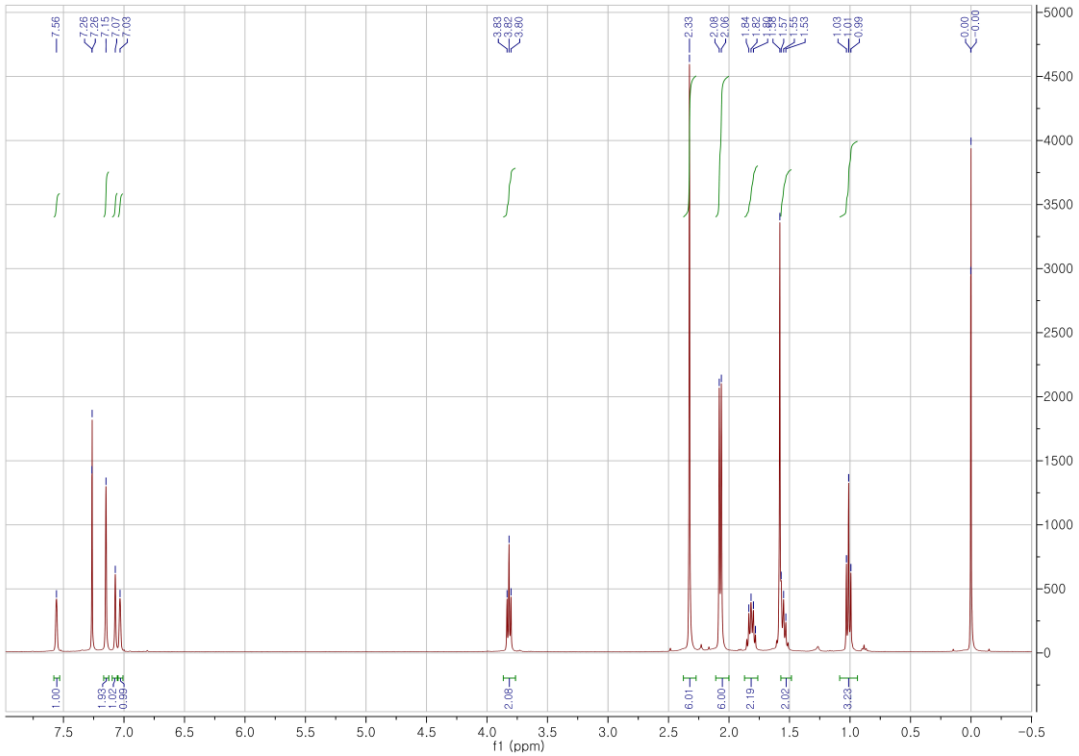


Figure S18. ^{1}H NMR spectrum of **7**.

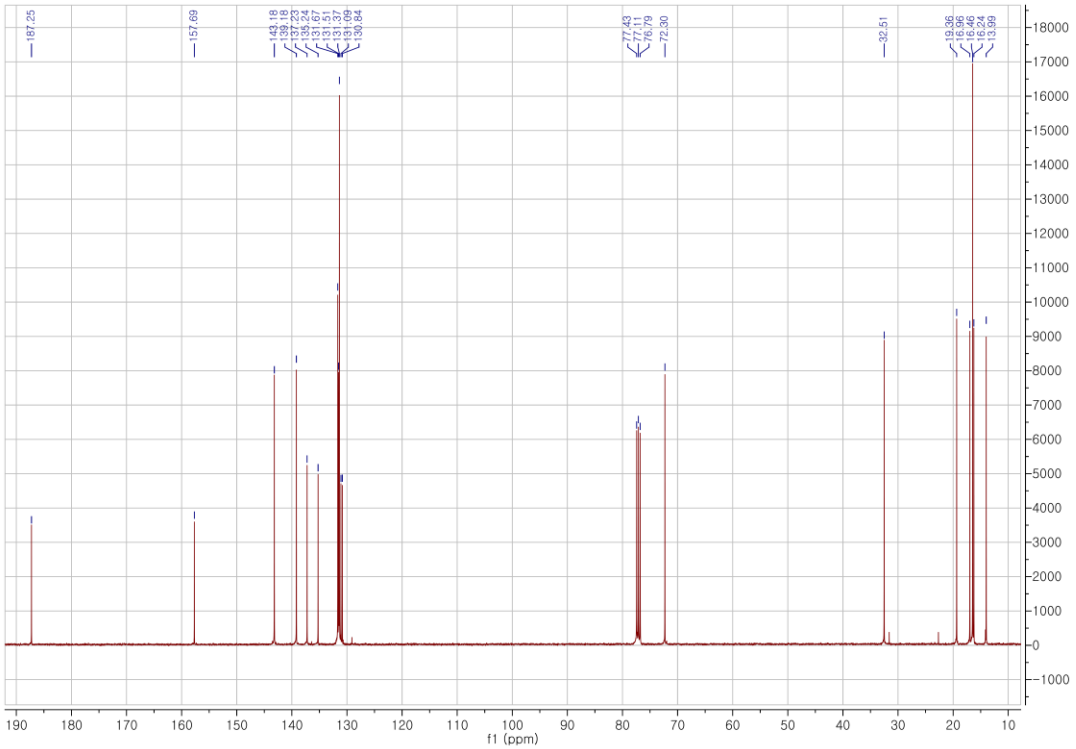


Figure S19. ^{13}C NMR spectrum of **7**.

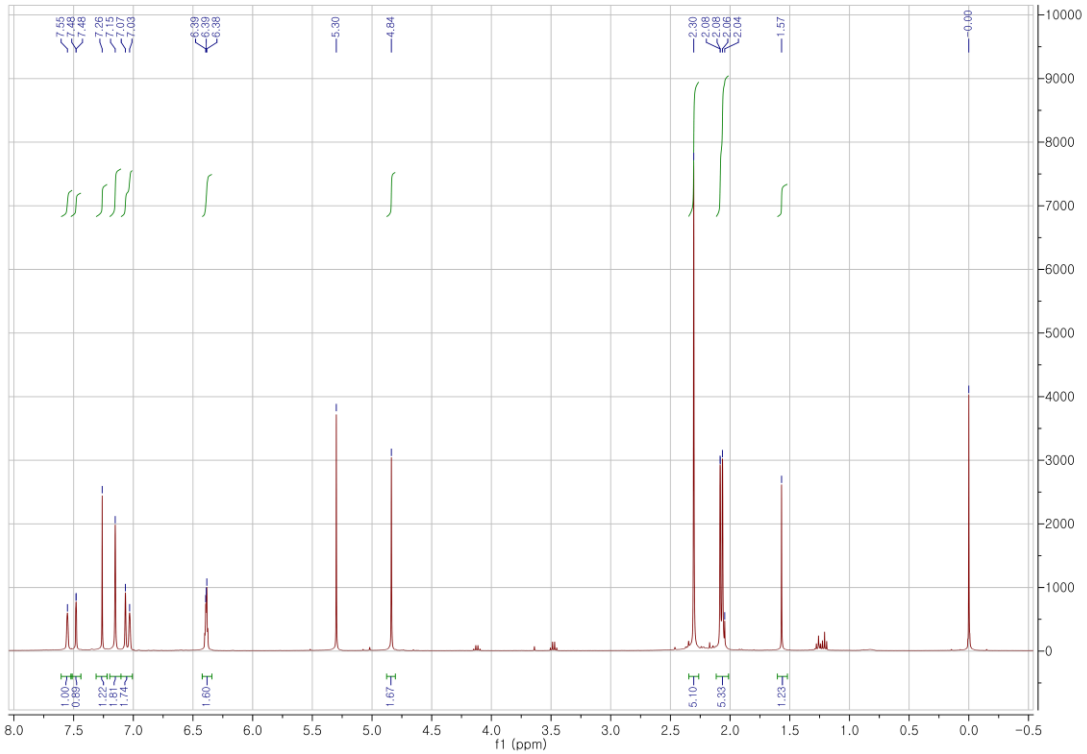


Figure S20. ^{1}H NMR spectrum of **8**.

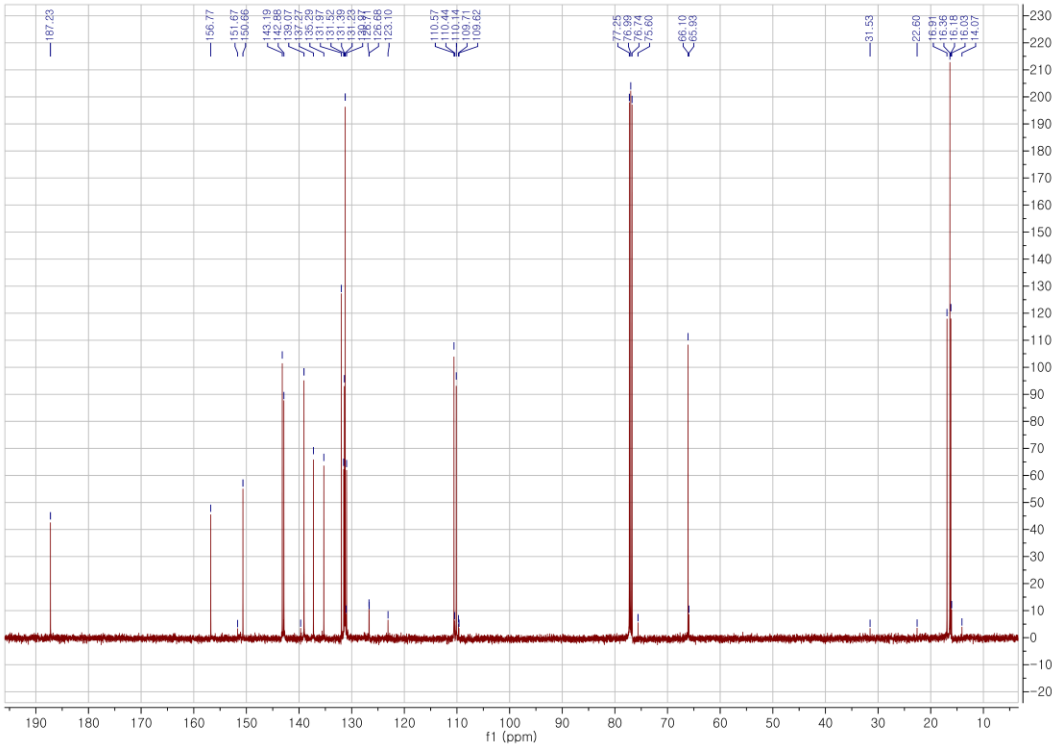


Figure S21. ^{13}C NMR spectrum of **8**.

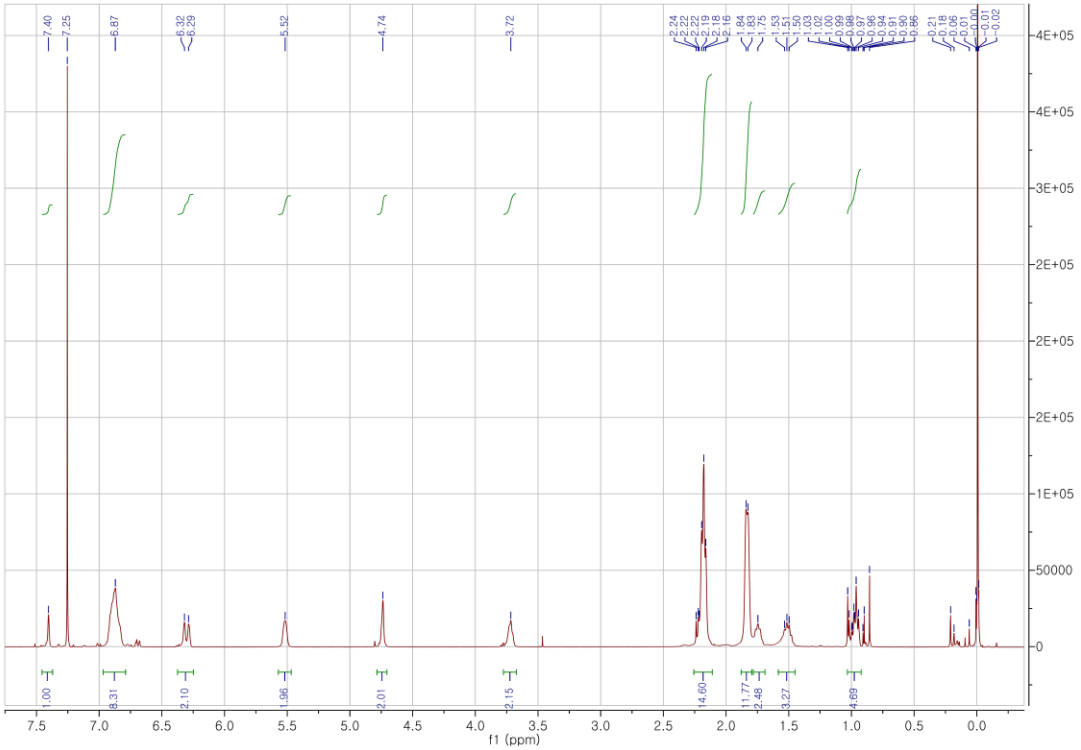


Figure S22. ^{1}H NMR spectrum of **9**.

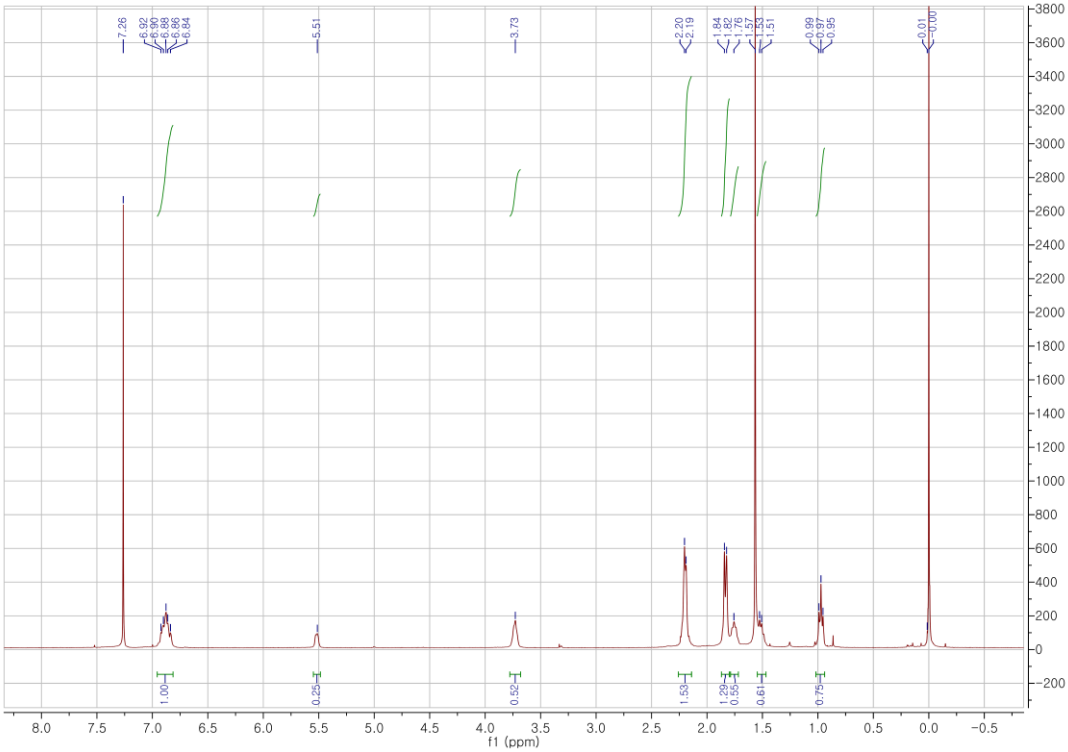


Figure S23. ^{1}H NMR spectrum of **14**.

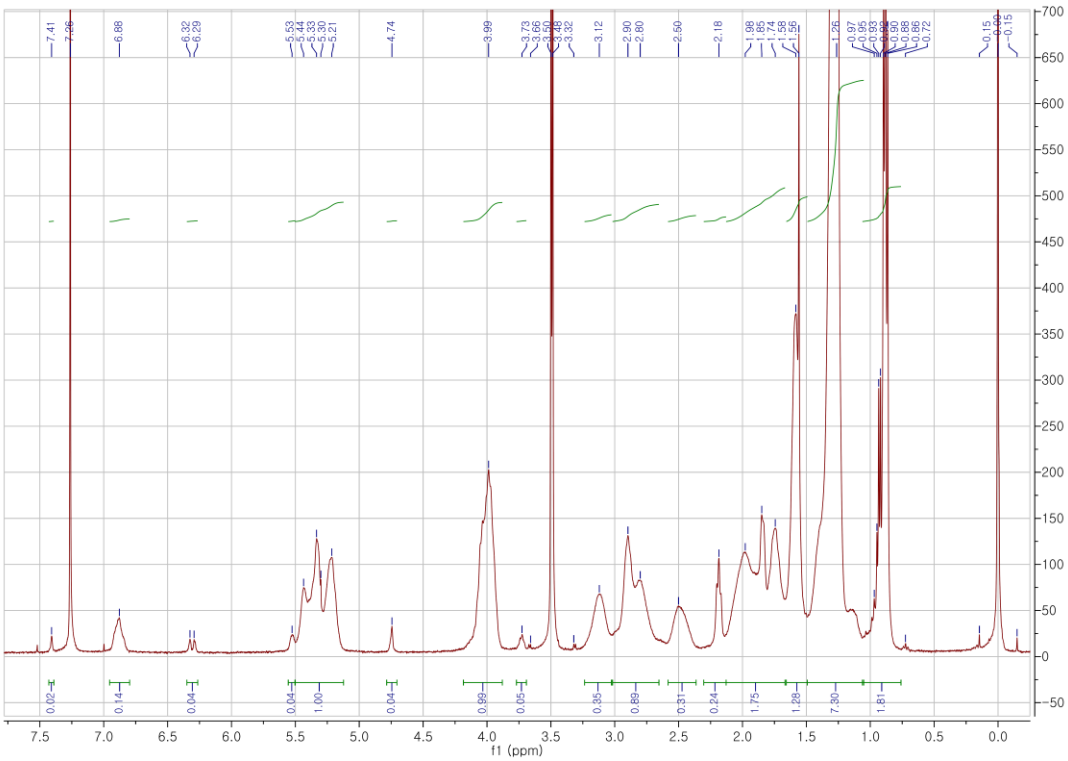


Figure S24. ^{1}H NMR spectrum of **11**.

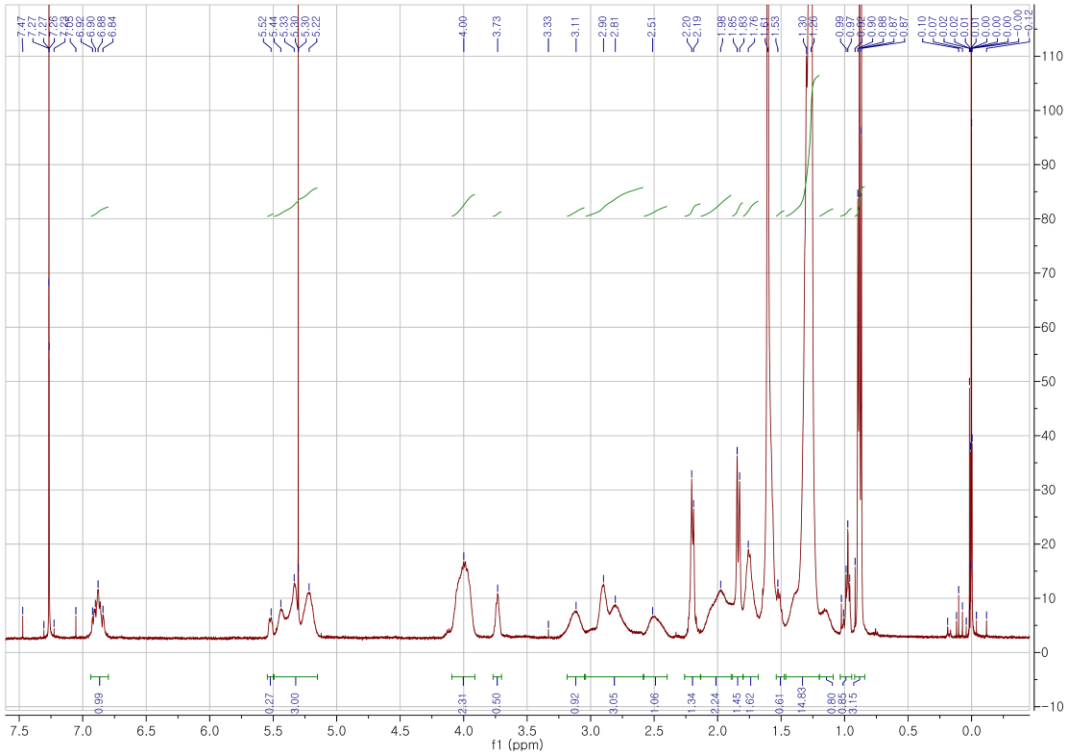
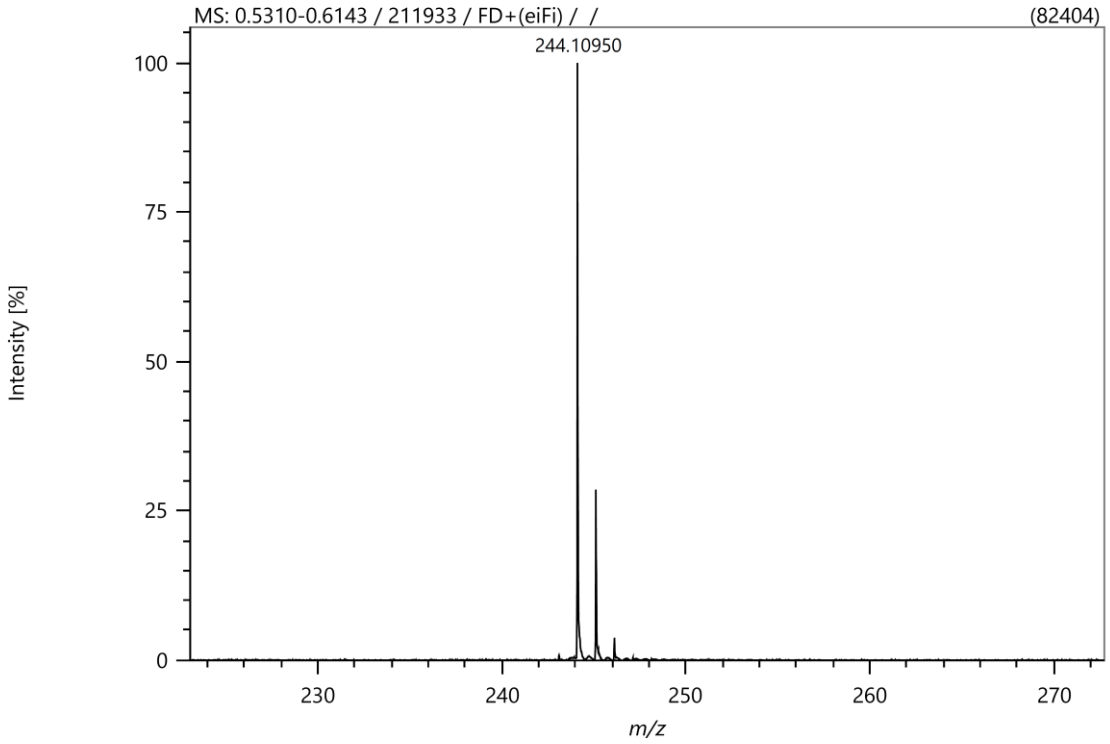


Figure S25. ^{1}H NMR spectrum of **15**.

HRMS Data

Spectrum



Elemental Composition

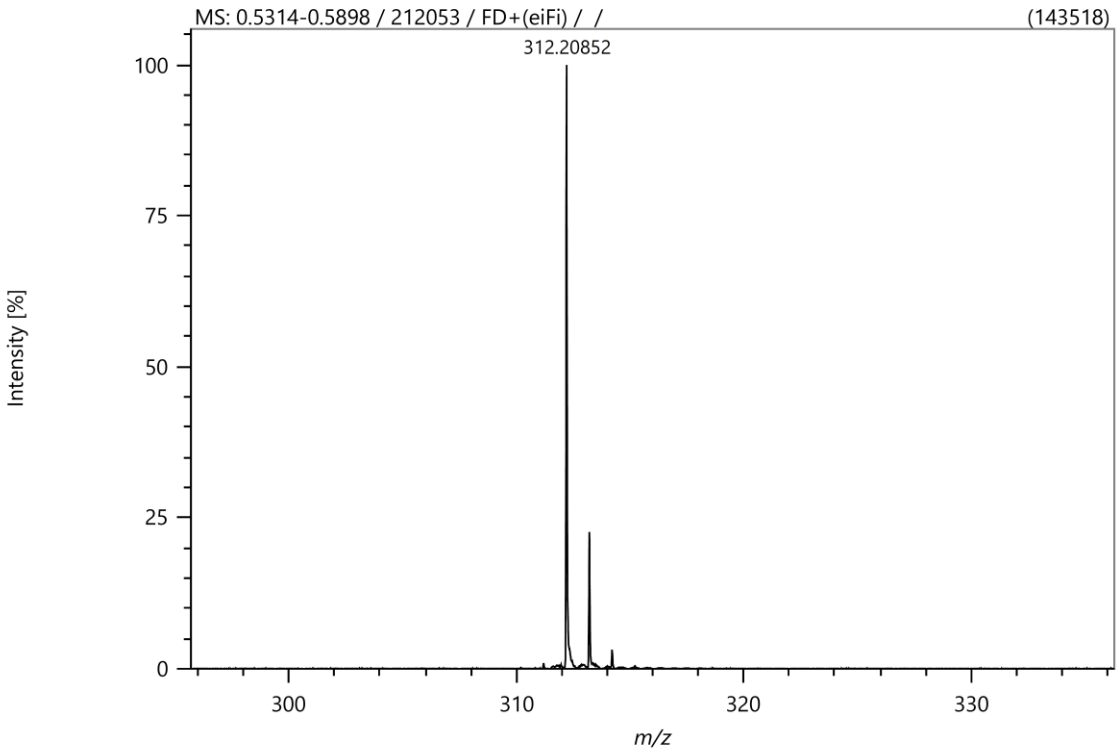
Parameters		Elements Set 1:			
Tolerance:	30.00 mDa	Symbol	C	H	O
Electron:	Odd/Even	Min	9	9	1
Charge:	+1	Max	15	16	3
DBE:	-90.0 - 90.0				

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
244.10950	82404.48	C15 H16 O3	244.10940	0.10	0.41	8.0

Figure S26. HRMS spectrum of **3**.

Spectrum



Elemental Composition

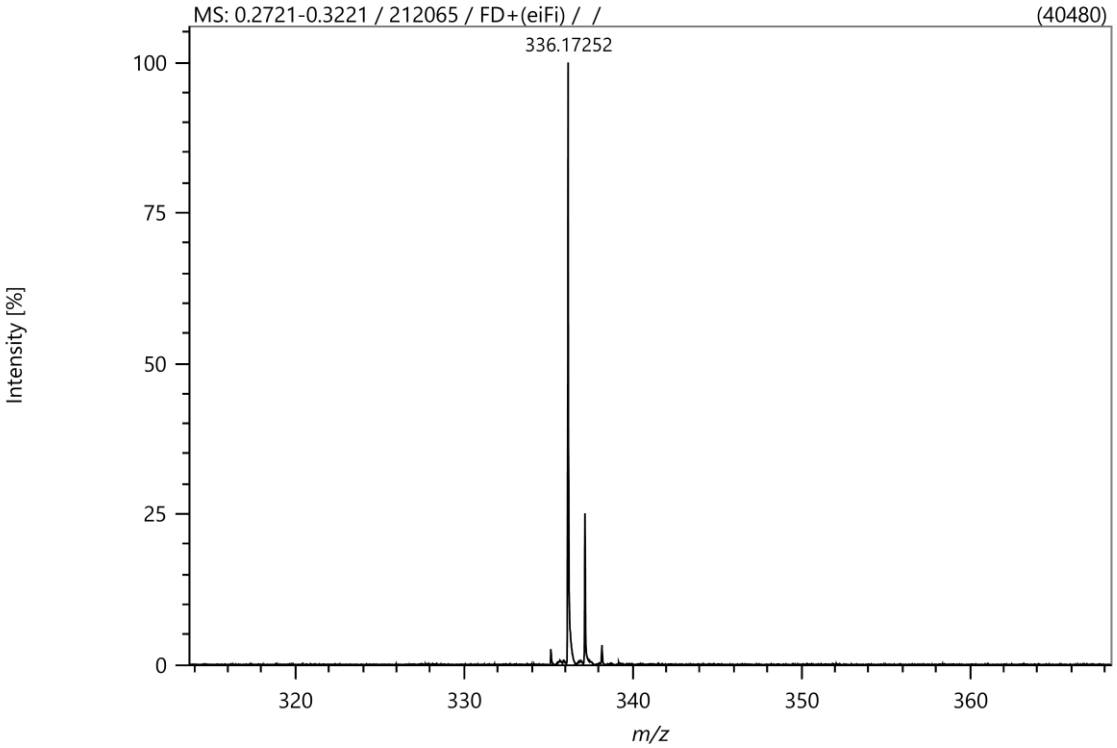
Parameters		Elements Set 1:			
Tolerance:	30.00 mDa	Symbol	C	H	O
Electron:	Odd/Even	Min	14	14	1
Charge:	+1	Max	21	28	2
DBE:	-90.0 - 90.0				

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
312.20852	143518.50	C21 H28 O2	312.20838	0.14	0.45	8.0

Figure S27. HRMS spectrum of **5**.

Spectrum



Elemental Composition

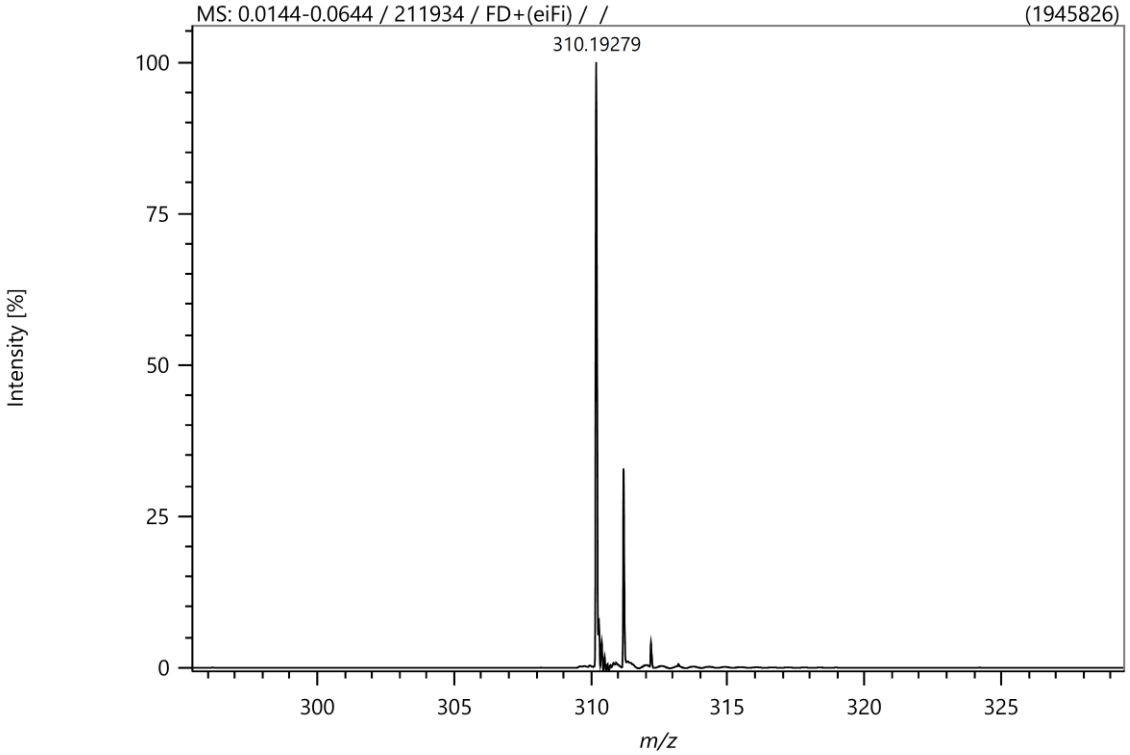
Parameters		Elements Set 1:			
Tolerance:	30.00 mDa	Symbol	C	H	O
Electron:	Odd/Even	Min	14	14	1
Charge:	+1	Max	22	24	3
DBE:	-90.0 - 90.0				

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
336.17252	40479.75	C22 H24 O3	336.17200	0.52	1.55	11.0

Figure S28. HRMS spectrum of **6**.

Spectrum



Elemental Composition

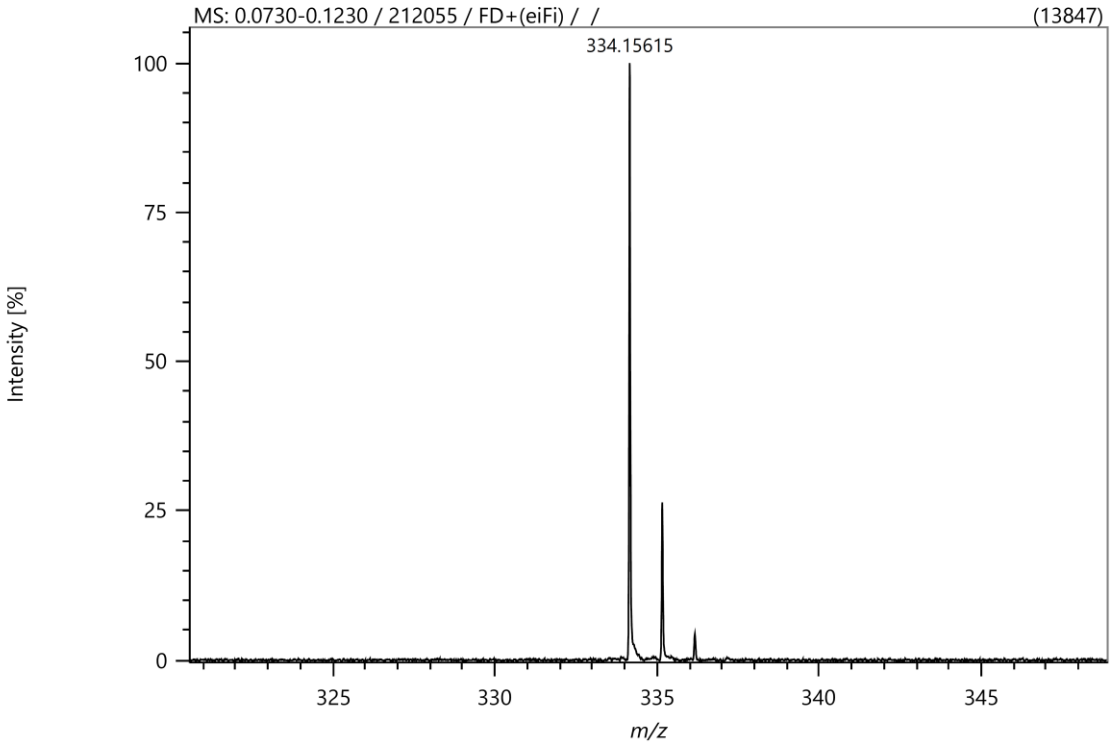
Parameters		Elements Set 1:			
Tolerance:	30.00 mDa	Symbol	C	H	O
Electron:	Odd/Even	Min	9	9	1
Charge:	+1	Max	21	26	2
DBE:	-90.0 - 90.0				

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
310.19279	1945826.05	C21 H26 O2	310.19273	0.06	0.20	9.0

Figure S29. HRMS spectrum of **7**.

Spectrum



Elemental Composition

Parameters		Elements Set 1:			
Tolerance:	30.00 mDa	Symbol	C	H	O
Electron:	Odd/Even	Min	14	14	1
Charge:	+1	Max	22	22	3
DBE:	-90.0 - 90.0				

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
334.15615	13846.54	C22 H22 O3	334.15635	-0.20	-0.59	12.0

Figure S30. HRMS spectrum of **8**.

References

S1. Thimm, D.; Funke, M.; Anne, M.; Müller, C. E. *J. Med. Chem*. **2013**, 56, 7084−7099.

S2. Yeung, K.; Kim, H.; Mohapatra, H.; Phillips, S. T. *J. Am. Chem. Soc*. **2015**, 137, 5324−5327.

S3. Kim, H.; Mohapatra, H.; Phillips, S. T. *Angew. Chem. Int. Ed*. **2015**, 54, 13063–13067.

S4. Chaumette, J.-L.; Laufersweiler, M. J.; Parquette, J. R. *J. Org. Chem*. 1998, 63, 9399–9405.