Electronic Supplementary Material (ESI) for Green Chemistry.


Supporting Information

# Programmable One Cycle-One Disaccharide Unit Modular Synthesis of Hyaluronan and Chondroitin Hybrid Glycans

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## Supplementary Figures

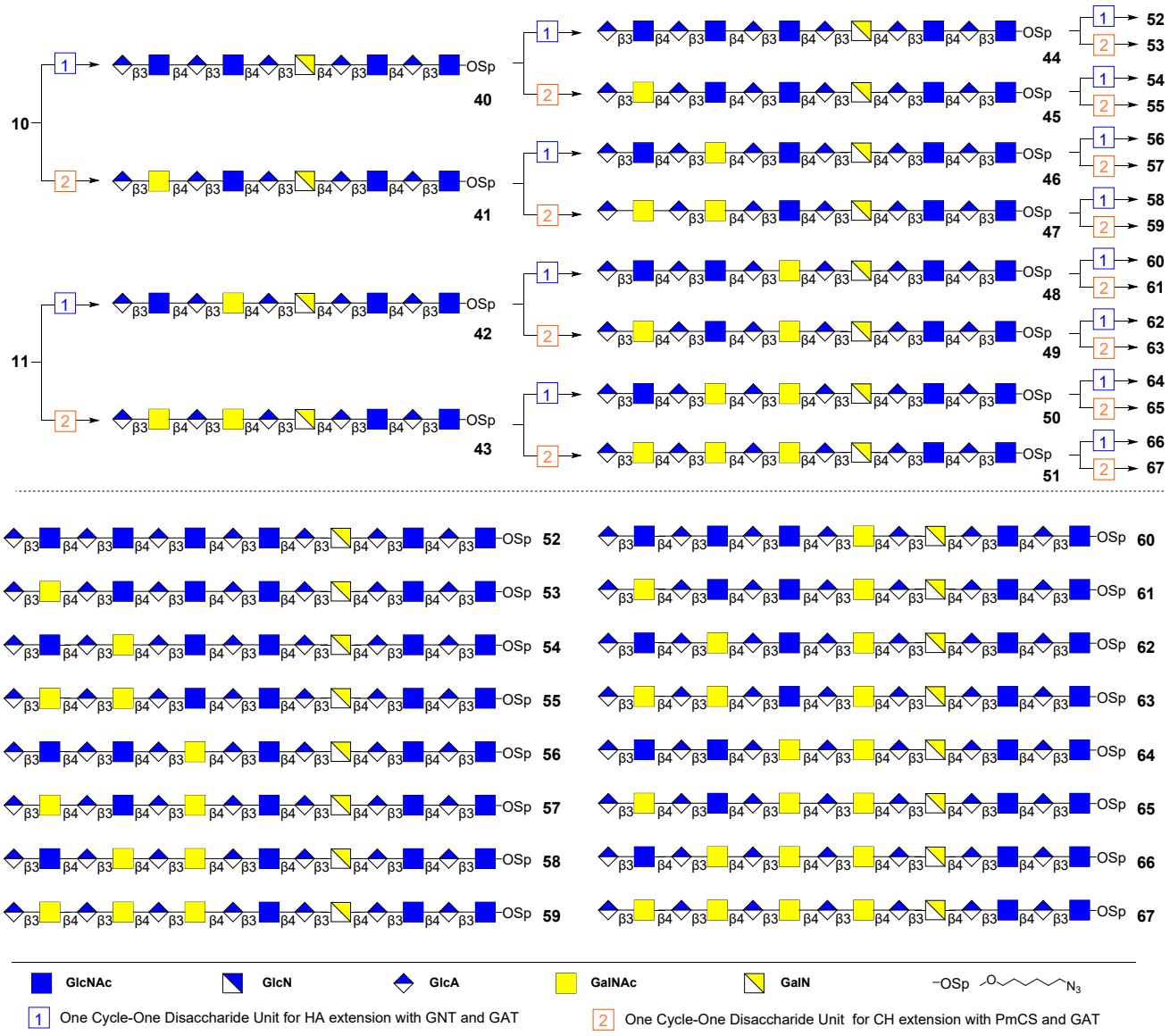



**Fig. S1**. The Scheme for the synthesis of HA and CH hybrid glycans with GalN.

## Experimental Procedures

### General Information

All sugar nucleotides were prepared as previously reported.[1] The starting acceptor HA4 **1** with azido group was provided by Professor Zhongjun Li from Peking University.[2,3] Thin layer chromatography (TLC) was performed on silica gel plates 60 F254 (Merck, Billerica MA). Plates were visualized under UV light and/or by treatment with *p*-anisaldehyde sugar stain followed by heating. DEAE Sepharose Fast Flow (GE, Piscataway, NJ) was used for ion exchange chromatography. Gel filtration chromatography was performed using a column packed with BioGel P-2/P-4/P-6 Fine resins (Bio-Rad, Hercules Hercules, CA). $^{1}$H NMR (600 MHz) and $^{13}$ C NMR (150 MHz) spectra were recorded on Bruker AVANCE-600 spectrometer at 25 ℃. NMR spectra were calibrated using solvent signals ($^{1}$H: δ 4.79 for $D_2O$). High resolution electrospray ionization mass spectra (ESI-MS) were obtained at the Core Facilities for Life and Environmental Sciences in Shandong University. Microscale thermophoresis (MST) was conducted using an NT.115 MST instrument (Nano Temper Technologies GmbH) equipped with red and blue filter sets.

Enzymes with single catalytic activity GAT (β1,3-GlcA transferase) and GNT (β1,4-GlcNAc transferase)[4] were obtained from hyaluronan synthase (PmHAS)[5] by site directed mutagenesis at Asp$^{196}$ and Asp$^{477}$. *Pasteurella Multocida* chondroitin synthase (PmCS)[6] is 90% similar with PmHAS at the nucleotide and amino acid levels. All recombinant strains harboring corresponding genes were cloned and stored in our laboratory.

In detail, PmHAS$^{1–703}$ (GenBank: AF036004.2), PmCS $^{46–695}$ (GenBank: AF195517.2 ), GNT (PmHAS$^{1–703}$ D196N mutant), and GAT (PmHAS$^{1–703}$ D477K mutant) were synthesized by BGI Tech Solutions company and clone into the expression plasmid pET-15b with NdeI and XhoI as restriction sites.

The resulting recombinant constructs were transformed into *Escherichia coli* BL21 (DE3) strains and maintained on lysogeny broth (LB) medium with ampicillin selection. All of the strains were cultured in LB medium with 100 μg/mL ampicillin at 37 ℃ under vigorous shaking at 220 rpm. When $OD_{600}$ reached 0.6-0.8, 0.2 mM Isopropyl β-D-1-thiogalactopyranoside (IPTG) was added and cultured at 16 ℃ for 20 h. Cells were harvested by centrifuging at 8, 000 rpm for 10 min. Protein purification were performed

by utilizing Ni-NTA Sepharose affinity resin according to the protocol. The purified fraction was dialyzed with a Millipore Amicon ultra 10 K centrifugal filter to remove imidazole and other components.

The theoretical Mw of *N*-His6 labeled PmHAS is 83 kDa, and the theoretical Mw of GNT and GAT is the same as that of PmHAS. The theoretical Mw of *N*-His6 labeled PmCS is 80 kDa. As shown in Figure S2, the size of target protein after affinity purification by Ni column is consistent with the theoretical value.

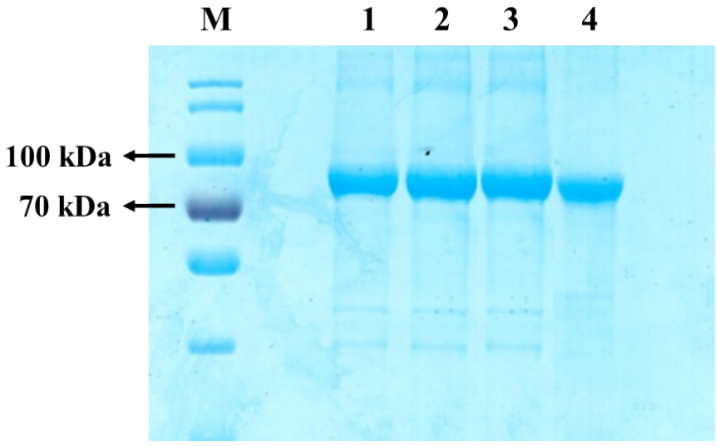
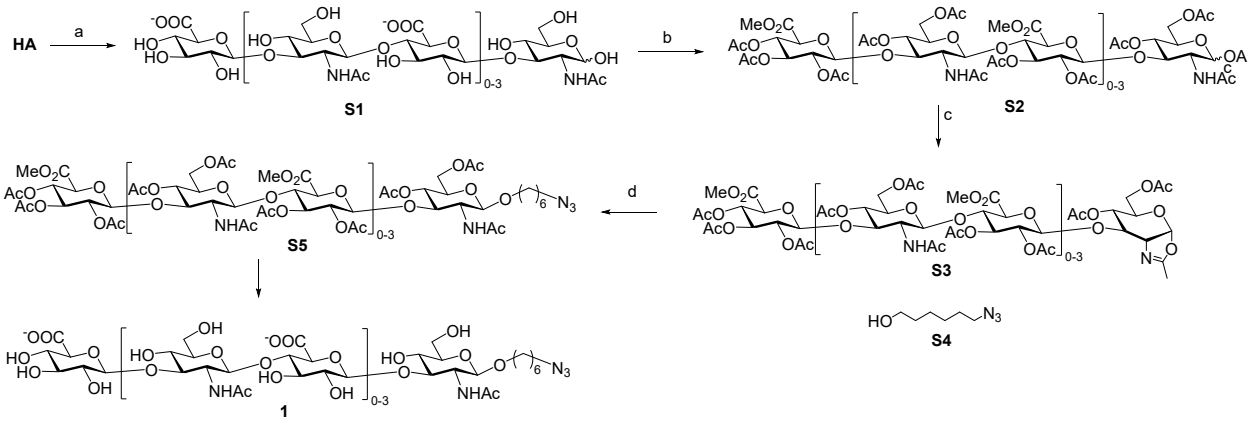



**Fig. S2**. SDS-PAGE profile of enzymes in this study

M: Marker, 1: PmHAS, 2: GNT, 3: GAT, 4: PmCS

## General procedures for one cycle-one disaccharide unit reactions

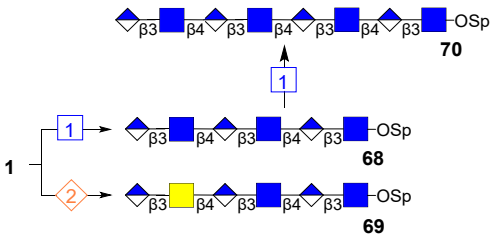
## Synthesis of compound 1




Reagent and condition: (a) BTH, 37 °C, pH 5.0, 0.15 M NaCl, 14 d; (b) i: AcCl, MeOH, 4 °C, 4 d; ii: $Ac_2O$, pyridine, RT, 20 h, 42 % over three steps; (c) TMSBr, $BF_3{\cdot}OEt_2$, 1,2-DCE, RT, overnight, 70%; (d) 6-azido hexanol, $CuCl_2$, $CHCl_3$, reflux, 10 h, 95 %; (e) 0.20 N HCl(MeOH), 10 °C, 36 h.

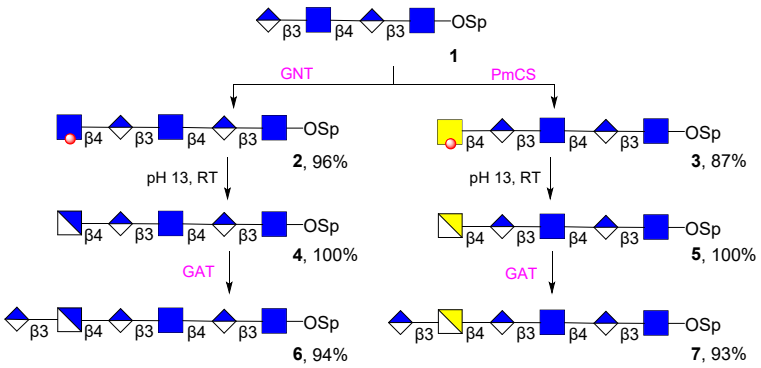
Sodium hyaluronate was digested by hyaluronidase from bovine (BTH) to give crude product S1, then S1 was protected with two different protected group to generate compound S2. The S2 was further modified to get S3 and then coupled with compound S4 to form S5. S5 was deprotected to give compound 1. Please refer to J. Org. Chem. 2018, 83, 22, 14069–14077 for detail procedure.

**Synthesis of 68, 69, and 70**




The reaction was conducted at 37 ℃ in a final volume of 10 mL containing 50 mM Tris-HCl (pH 7.5), 20 mM $MgCl_2$, 10 mM HA4 **1** and 12 mM UDP-GlcNAc and 2 mg/mL GN-T (or 12 mM UDP-GalNAc and 2 mg/mL PmCS). The reaction was monitored by TLC (ethyl acetate: methanol: water: acetic acid=5: 2: 2:0.5) with *p*-anisaldehyde sugar stain followed by heating. The reaction was quenched by boiling at 100 °C for 5 min. Then the mixture was added with 12 mM UDP-GlcA and 2 mg/mL GA-T monitored by TLC. The mixture was quenched by boiling at 100 °C for 5 min. The supernatant was centrifuged at 12,000 rpm for 5 min followed by purification via gel filtration chromatography.

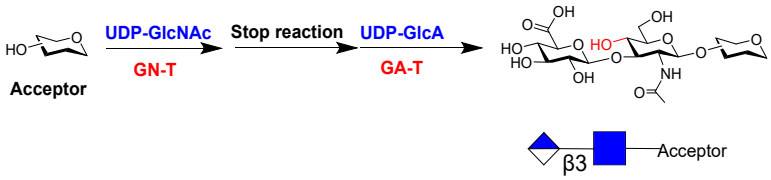
**Synthesis of 6 and 7**




The reaction was conducted at 37 ℃ in a final volume of 10 mL containing 50 mM Tris-HCl (pH 7.5), 20 mM $MgCl_2$, 10 mM HA4 **1** and 12 mM UDP-GlcNAc and 2 mg/mL GN-T

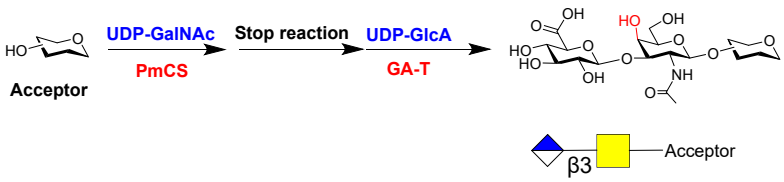
(or 12 mM UDP-GalNAc and 2 mg/mL PmCS). The reaction was monitored by TLC (ethyl acetate: methanol: water: acetic acid=5: 2: 2:0.5) with *p*-anisaldehyde sugar stain followed by heating. The reaction was quenched by boiling at 100 °C for 5 min. To convert the GlcNTFA/GalNTFA residue to GlcN/GalN residue, NaOH solution was added to mixture to reach the final concentration of 0.1 M. TLC were used to monitor the degree of the detrifluoroacetylation reaction. Upon the completion of detrifluoroacetylation, the pH of the reaction mixture was adjusted to 7.0. Then the mixture was added with 12 mM UDP-GlcA and 2 mg/mL GA-T monitored by TLC. The mixture was quenched by boiling at 100 °C for 5 min. The supernatant centrifuged at 12,000 rpm for 5 min was purified by gel filtration chromatography.

**Synthesis of HA disaccharide repeat unit**




The reaction was conducted at 37 ℃ containing 50 mM Tris-HCl (pH 7.5), 20 mM $MgCl_2$, 10 mM acceptor and 12 mM UDP-GlcNAc and 2 mg/mL GN-T. The reaction was monitored by TLC (ethyl acetate: methanol: water: acetic acid=5: 2: 2: 0.5 for octasaccharides, 5: 2: 3: 1 for decasaccharide, n-butanol: methanol: ammonia: water=5: 5: 2: 1 for other oligosaccharides) with *p*-anisaldehyde sugar stain followed by heating. The reaction was quenched by boiling at 100 °C for 5 min. Then the mixture was added with 12 mM UDP-GlcA and 2 mg/mL GA-T monitored by TLC. The mixture was quenched by boiling at 100 °C for 5 min. The supernatant centrifuged at 12,000 rpm for 5 min was purified by gel filtration chromatography.

**Synthesis of CH disaccharide repeat unit**



The reaction was conducted at 37 ℃ containing 50 mM Tris-HCl (pH 8.0), 20 mM $MgCl_2$, 10 mM acceptor and 12 mM UDP-GalNAc and 2 mg/mL PmCS. The reaction was monitored by TLC (ethyl acetate: methanol: water: acetic acid=5: 2: 2: 0.5 for hexasaccharides and octasaccharides, 5: 2: 3: 1 for decasaccharide, n-butanol: methanol: ammonia: water=5: 5: 2: 1 for other hybrid oligosaccharides) with *p*-anisaldehyde sugar stain followed by heating. The reaction was quenched by boiling at 100 °C for 5 min. Similarly, the mixture was added with 12 mM UDP-GlcA and 2 mg/mL GA-T monitored by TLC. The mixture was quenched by boiling at 100 °C for 5 min. The supernatant centrifuged at 12,000 rpm for 5 min was purified by gel filtration chromatography.

**General methods for compound purification**

The reaction mixture for compounds **6-11** and **68-70** were concentrated and purified by a BioGel P-2 gel filtration column (2.5 cm×100 cm, water as eluent), respectively. The reaction mixture for compounds **12-15 and 40-43** were concentrated and purified by a BioGel P-4 gel filtration column (2.5 cm×100 cm, water as eluent), respectively. Similarly, the reaction mixture for compound **16-39 and 52-68** were concentrated and purified by a BioGel P-4 gel filtration column (1.6 cm×100 cm, water as eluent), respectively.

DEAE ion exchange chromatography was applied to separate acceptor and product under a gradient of 0.02 M NaCl in the condition that the acceptors couldn’t transform into the corresponding product thoroughly. The collected products were lyophilized and then characterized by ESI-MS and NMR, respectively.

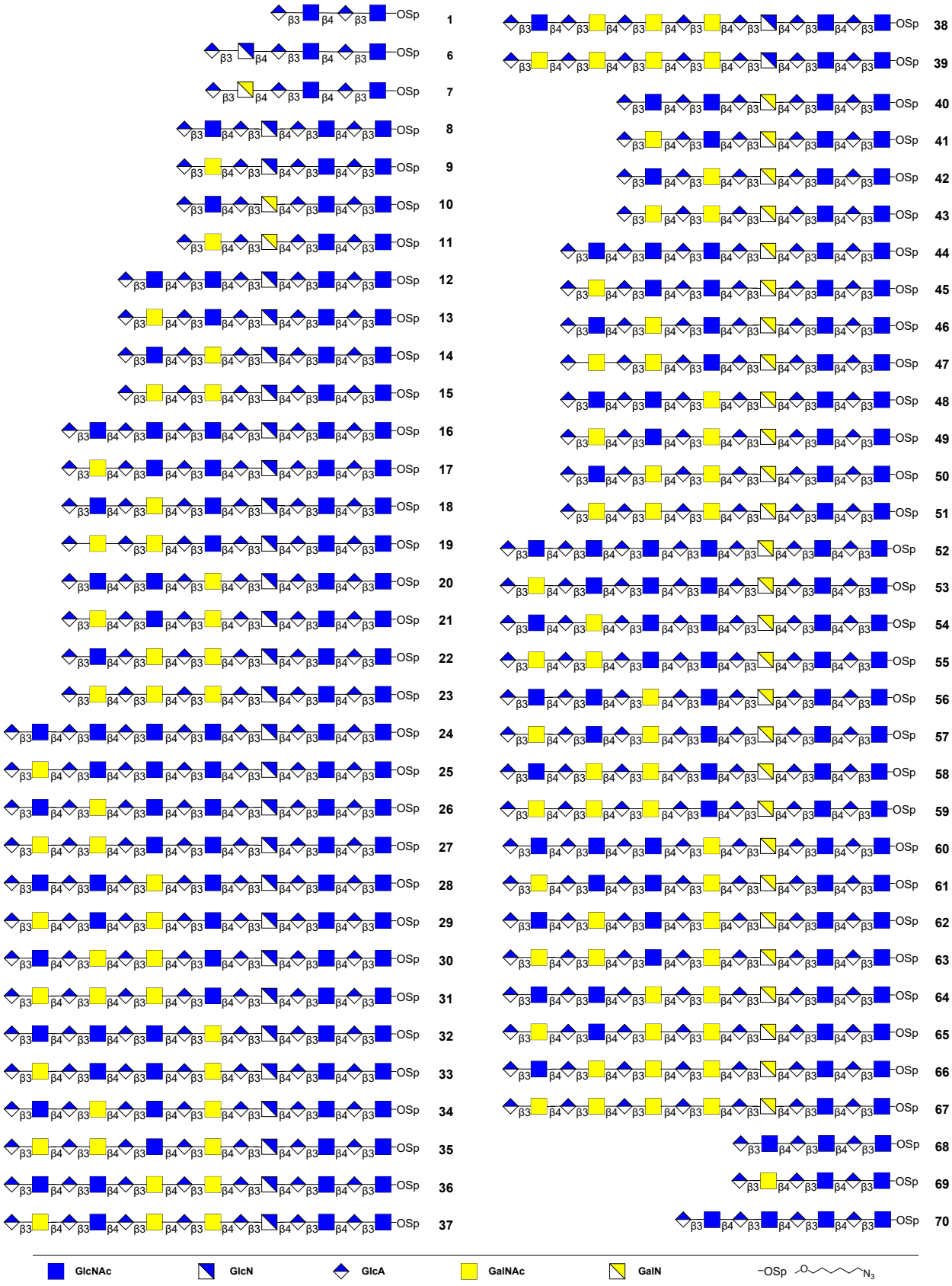
## Table S1 Hybrid oligosaccharides synthesized in this work

| Entry | Compound | Yield(%)[a] | Amount(mg)[b] |
|---|---|---|---|
| **6** | H*HH | 62 | 295.6 |
| **7** | C*HH | 50 | 180.7 |
| **8** | HH*HH | 67 | 123.4 |
| **9** | CH*HH | 62 | 118.7 |
| **10** | HC*HH | 69 | 83.4 |
| **11** | CC*HH | 67 | 80.9 |
| **12** | HHH*HH | 56 | 37.8 |
| **13** | CHH*HH | 71 | 40.5 |
| **14** | HCH*HH | 71 | 40.6 |
| **15** | CCH*HH | 70 | 39.8 |
| **16** | HHHH*HH | 79 | 18.3 |
| **17** | CHHH*HH | 75 | 17.2 |
| **18** | HCHH*HH | 69 | 16.5 |
| **19** | CCHH*HH | 82 | 19.3 |
| **20** | HHCH*HH | 75 | 17.2 |
| **21** | CHCH*HH | 79 | 18.6 |
| **22** | HCCH*HH | 76 | 17.6 |
| **23** | CCCH*HH | 81 | 19.0 |
| **24** | HHHHH*HH | 67 | 1.9 |
| **25** | CHHHH*HH | 60 | 1.7 |
| **26** | HCHHH*HH | 71 | 1.4 |
| **27** | CCHHH*HH | 68 | 1.3 |
| **28** | HHCHH*HH | 80 | 2.3 |
| **29** | CHCHH*HH | 72 | 2.0 |
| **30** | HCCHH*HH | 76 | 2.2 |
| **31** | CCCHH*HH | 70 | 2.0 |
| **32** | HHHCH*HH | 79 | 2.2 |
| **33** | CHHCH*HH | 66 | 1.9 |
| **34** | HCHCH*HH | 90 | 2.6 |
| **35** | CCHCH*HH | 69 | 1.9 |
| **36** | HHCCH*HH | 85 | 2.4 |
| **37** | CHCCH*HH | 66 | 1.9 |
| **38** | HCCCH*HH | 84 | 2.3 |

| Entry | Compound | Yield(%)[a] | Amount(mg)[b] |
|---|---|---|---|
| **39** | CCCCH*HH | 60 | 1.7 |
| **40** | HHC*HH | 66 | 27.8 |
| **41** | CHC*HH | 71 | 29.9 |
| **42** | HCC*HH | 72 | 29.6 |
| **43** | CCC*HH | 71 | 29.1 |
| **44** | HHHC*HH | 73 | 14.7 |
| **45** | CHHC*HH | 72 | 14.2 |
| **46** | HCHC*HH | 76 | 15.5 |
| **47** | CCHC*HH | 50 | 10.7 |
| **48** | HHCC*HH | 73 | 14.7 |
| **49** | CHCC*HH | 62 | 12.5 |
| **50** | HCCC*HH | 68 | 13.2 |
| **51** | CCCC*HH | 66 | 12.8 |
| **52** | HHHHC*HH | 90 | 2.6 |
| **53** | CHHHC*HH | 72 | 2.0 |
| **54** | HCHHC*HH | 81 | 2.3 |
| **55** | CCHHC*HH | 69 | 1.9 |
| **56** | HHCHC*HH | 75 | 2.2 |
| **57** | CHCHC*HH | 85 | 1.6 |
| **58** | HCCHC*HH | 78 | 2.2 |
| **59** | CCCHC*HH | 66 | 1.9 |
| **60** | HHHCC*HH | 76 | 2.2 |
| **61** | CHHCC*HH | 52 | 1.5 |
| **62** | HCHCC*HH | 73 | 2.1 |
| **63** | CCHCC*HH | 50 | 1.4 |
| **64** | HHCCC*HH | 86 | 2.4 |
| **65** | CHCCC*HH | 71 | 2.0 |
| **66** | HCCCC*HH | 72 | 2.1 |
| **67** | CCCCC*HH | 50 | 1.8 |
| **68** | HHH | 90 | 25.6 |
| **69** | CHH | 82 | 23.3 |
| **70** | HHHH | 85 | 22.0 |

[a] Yield calculated from extract product and theoretical amount. [b] Lyophilized pure product isolated from one cycle-one disaccharide unit reaction system.

H: GlcAβ1,3GlcNAc,  C: GlcAβ1,3GalNAc,  H*: GlcAβ1,3GlcN,  C*: GlcAβ1,3GalN,  .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GlcN
GlcA
GalNAc
GalN
OSp
O
N3

**Fig. S3 Summary of synthesizd glycans in this work**

**Compound 6, H*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.76 (d, *J* = 8.5 Hz, 1H), 4.68 (d, *J* = 7.9 Hz, 1H), 4.57 (d, *J* = 8.5 Hz, 1H), 4.55-4.47 (m, 3H), 3.97-3.89 (m, 6H), 3.8-3.44 (m, 23H), 3.40-3.20 (m, 5H), 2.08-2.00 (m, 6H), 1.65-1.53 (m, 4H), 1.43-1.31 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.41, 174.90, 174.83, 174.49, 174.16, 103.09, 102.68, 102.07, 100.91, 100.56, 99.14, 82.98, 82.27, 82.08, 80.21, 79.98, 76.36, 75.81, 75.36, 75.28, 74.42, 74.02, 73.56, 73.00, 72.68, 72.43, 72.34, 72.03, 71.48, 70.41, 68.57, 68.44, 67.87, 60.69, 60.49, 60.23, 54.90, 54.55, 54.21, 51.11, 28.40, 27.96, 25.54, 24.62, 22.48, 22.20.

ESI-MS (negative ion): Calcd for $C_{46}H_{74}N_6O_{33}$: 1238.4297, $[M-H]^-$ 1237.4224, $[M-2H]^{2-}$ 618.2076; Found $[M-H]^-$ 1237.4080, $[M-2H]^{2-}$ 618.2001.

**Compound 7, C*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.75 (d, *J* = 8.4 Hz, 1H), 4.67 (d, *J* = 7.8 Hz, 1H), 4.58 (d, *J* = 8.5 Hz, 1H), 4.56-4.47 (m, 3H), 4.29 (d, *J* = 2.7 Hz, 1H), 4.07 (dd, *J* = 10.9, 2.2 Hz, 1H), 3.95-3.43 (m, 27H), 3.42-3.31 (m, 5H), 2.07-2.00 (m, 6H), 1.66-1.54 (m, 4H), 1.44-1.29 (m, 4H).$^{13}$C NMR (151 MHz, $D_2O$) δ 175.81, 174.90, 174.86, 174.49, 174.17, 103.35, 103.09, 102.67, 100.91, 100.55, 99.42, 82.98, 82.27, 80.25, 79.97, 79.80, 76.35, 75.36, 75.21, 74.28, 74.12, 73.56, 72.87, 72.43, 72.24, 71.63, 70.41, 70.41, 68.58, 68.44, 66.59, 61.22, 60.84, 60.69, 60.50, 59.45, 54.55, 54.21, 52.09, 51.11, 28.40, 27.95, 25.54, 24.62, 22.48, 22.19.

ESI-MS (negative ion): Calcd for $C_{46}H_{74}N_6O_{33}$: 1238.4297, $[M-H]^-$ 1237.4224, $[M-2H]^{2-}$ 618.2076; Found $[M-H]^-$ 1237.4411, $[M-2H]^{2-}$ 618.2741.

**Compound 8, HH*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.71 (d, *J* = 8.4 Hz, 1H), 4.69 (d, *J* = 7.9 Hz, 1H), 4.61-4.55 (m, 2H), 4.54-4.46 (m, 4H), 3.95-3.85 (m, 8H), 3.85-3.70 (m, 15H), 3.67-3.45 (m, 15H), 3.40-3.15 (m, 6H) , 2.06-2.00 (m, 9H), 1.65-1.53 (m, 4H), 1.43-1.30 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.47, 174.92, 174.91, 174.81, 174.49, 174.16, 174.02, 103.09, 102.97, 102.70, 102.30, 100.92, 100.56, 100.50, 99.25, 83.05, 82.99, 82.25, 80.22, 79.99, 79.62, 76.55, 76.37, 75.85, 75.70, 75.39, 75.36, 75.29, 74.49, 74.01, 73.60, 73.57, 72.86, 72.70, 72.42, 72.34, 71.69, 70.41, 68.57, 68.53, 68.44, 67.77, 60.70, 60.53, 60.49, 60.21, 55.02, 55.02, 54.55, 54.22, 51.11, 28.40, 27.95, 25.54, 24.62, 22.46, 22.46, 22.19.

ESI-MS (negative ion): Calcd for $C_{60}H_{95}N_7O_{44}$: 1617.5411, $[M-2H]^{2-}$ 807.7633; Found $[M-2H]^{2-}$ 807.7479.

**Compound 9, CH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.67-4.58 (m, 2H), 4.50-4.38 (m, 6H), 4.09 (d, *J* = 3.0 Hz, 1H), 3.93 (dd, *J* = 10.7, 8.6 Hz, 1H), 3.86-3.36 (m, 37H), 3.31-3.22 (m, 5H), 1.99-1.87 (m, 9H), 1.57-1.41 (m, 4H), 1.35-1.21 (m, 4H).$^{13}$C NMR (151 MHz, $D_2O$) δ 175.96, 174.97, 174.91, 174.80, 174.50, 174.16, 174.08, 104.12, 103.10, 102.71, 102.33, 102.32, 100.92, 100.80, 100.56, 82.97, 82.26, 80.32, 80.25, 79.99, 79.30, 76.53, 76.37, 76.11, 75.84, 75.36, 75.29, 75.29, 75.00, 74.54, 74.02, 73.72, 73.57, 72.82, 72.72, 72.43, 72.34, 71.79, 70.42, 68.58, 68.44, 67.77, 67.69, 61.10, 60.70, 60.50, 60.23, 59.49, 55.09, 54.55, 54.22, 51.12, 51.04, 28.40, 27.96, 25.54, 24.62, 22.49, 22.49, 22.20.

ESI-MS (negative ion): Calcd for $C_{60}H_{95}N_7O_{44}$: 1617.5411, $[M-2H]^{2-}$ 807.7633; Found $[M-2H]^{2-}$ 807.7658.

**Compound 10, HC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.76 (d, *J* = 8.0 Hz, 1H), 4.67 (d, *J* = 7.8 Hz, 1H), 4.60-4.55 (m, 2H), 4.54-4.47 (m, 4H), 4.26 (d, *J* = 2.8 Hz, 1H), 4.10 (dd, *J* = 11.0, 2.8 Hz, 1H), 3.95-3.90 (m, 5H), 3.88-3.83 (m, 2H), 3.81-3.71 (m, 15H), 3.68-3.45 (m, 14H), 3.43-3.31 (m, 6H), 2.06-2.01 (m, 9H), 1.64-1.54 (m, 4H), 1.42-1.33 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.44, 174.91, 174.87, 174.49, 174.39, 174.15, 103.43, 103.09, 102.95, 102.65, 100.91, 100.55, 100.51, 98.74, 83.01, 82.95, 82.28, 80.12, 79.96, 79.72, 79.20, 76.43, 76.34, 75.70, 75.38, 75.36, 75.29, 74.11, 74.09, 73.56, 73.48, 72.69, 72.66, 72.43, 72.23, 72.23, 72.04, 71.68, 70.42, 68.58, 68.51, 68.51, 68.45, 66.66, 62.47, 60.79, 60.70, 60.52, 60.52, 54.55, 54.21, 52.04, 51.12, 28.40, 27.96, 25.54, 24.62, 22.48, 22.20.

ESI-MS (negative ion): Calcd for $C_{60}H_{95}N_7O_{44}$: 1617.5411, $[M-2H]^{2-}$ 807.7633, $[M-3H]^{3-}$ 538.1731; Found $[M-2H]^{2-}$ 807.7479, $[M-3H]^{3-}$ 538.1735.

**Compound 11, CC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.76 (d, *J* = 8.1 Hz, 1H), 4.68 (d, *J* = 7.8 Hz, 1H), 4.58 (d, *J* = 8.5 Hz, 1H), 4.55-4.47 (m, 5H), 4.26 (d, *J* = 2.8 Hz, 1H), 4.18 (d, *J* = 3.1 Hz, 1H), 4.10 (dd, *J* = 11.0, 2.8 Hz, 1H), 4.05-3.89 (m, 5H), 3.86-3.55 (m, 24H), 3.53-3.45 (m, 6H), 3.44-3.31 (m, 6H), 2.07-1.99 (m, 9H), 1.64-1.54 (m, 4H), 1.43-1.30 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.90, 174.97, 174.91, 174.86, 174.49, 174.43, 174.14, 104.11, 103.41, 103.09, 102.65, 100.91, 100.82, 100.55, 98.74, 83.01, 82.29, 80.25, 80.11, 79.96, 79.41, 79.18, 76.40, 76.33, 76.10, 75.36, 75.29, 74.99, 74.11, 73.59, 73.57,

72.71, 72.61, 72.43, 72.24, 71.78, 70.42, 68.58, 68.46, 67.66, 66.66, 61.09, 60.80, 60.70, 60.51, 54.56, 54.21, 52.05, 51.12, 51.02, 28.40, 27.96, 25.55, 24.63, 22.50, 22.48, 22.21.

ESI-MS (negative ion): Calcd for $C_{60}H_{95}N_7O_{44}$: 1617.5411, $[M-2H]^{2-}$ 807.7633; Found $[M-2H]^{2-}$ 807.7663.

**Compound 12, HHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.75 (d, *J* = 7.8 Hz, 1H), 4.69 (d, *J* = 7.9 Hz, 1H), 4.60-4.56 (m, 3H), 4.55-4.46 (m, 5H), 3.97-3.88 (m, 8H), 3.88-3.82 (m, 4H), 3.82-3.71 (m, 17H), 3.70-3.45 (m, 19H), 3.40-3.31 (m, 6H), 2.06-2.00 (m, 12H), 1.64-1.54 (m, 4H), 1.43-1.30 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.47, 174.93, 174.93, 174.91, 174.82, 174.50, 174.16, 173.99, 173.99, 103.17, 103.10, 103.10, 102.98, 102.70, 102.27, 102.25, 100.92, 100.56, 100.51, 83.08, 83.00, 82.58, 82.56, 82.26, 80.18, 79.99, 79.99, 79.91, 79.91, 79.63, 76.57, 76.37, 76.29, 75.87, 75.70, 75.38, 75.36, 75.29, 74.44, 74.43, 74.01, 73.59, 73.57, 73.55, 72.86, 72.70, 72.47, 72.47, 72.43, 72.34, 71.69, 70.42, 68.58, 68.52, 68.45, 68.42, 68.42, 67.77, 67.77, 60.70, 60.51, 60.19, 54.97, 54.55, 54.29, 54.22, 51.12, 28.40, 27.96, 25.54, 24.62, 22.48, 22.46, 22.20.

ESI-MS (negative ion): Calcd for $C_{74}H_{116}N_8O_{55}$: 1996.6526, $[M-2H]^{2-}$ 997.3190, $[M-3H]^{3-}$ 664.5436; Found $[M-2H]^{2-}$ 997.3172, $[M-3H]^{3-}$ 664.5428.

**Compound 13, CHH*HH:** $^1$H NMR (600 MHz, $D_2O$) 4.69 (d, *J* = 7.8 Hz, 1H), 4.62-4.42 (m, 8H), 4.18 (d, *J* = 2.9 Hz, 1H), 4.04-3.47 (m, 47H), 3.42-3.29 (m, 6H), 2.13-1.98 (m, 12H), 1.65-1.53 (m, 4H), 1.42-1.33 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.61, 175.12, 175.05, 174.98, 174.68, 174.63, 174.31, 174.18, 104.46, 104.26, 103.23, 103.11, 102.81, 102.17, 101.06, 100.93, 100.69, 100.66, 83.15, 82.41, 81.38, 81.37, 81.32, 80.49, 80.44, 80.23, 80.13, 79.43, 79.13, 76.70, 76.51, 76.25, 76.04, 75.85, 75.85, 75.50, 75.50, 75.43, 75.43, 75.11, 74.48, 74.13, 74.02, 73.83, 73.71, 72.86, 72.83, 72.65, 72.57, 72.48, 71.93, 71.83, 70.56, 69.92, 68.72, 68.65, 68.59, 67.87, 67.83, 61.23, 60.84, 60.66, 60.31, 54.99, 54.70, 54.35, 51.26, 51.13, 28.54, 28.10, 25.69, 24.77, 22.62, 22.34.

ESI-MS (negative ion): Calcd for $C_{74}H_{116}N_8O_{55}$: 1996.6526, $[M-2H]^{2-}$ 997.3190, $[M-3H]^{3-}$ 664.5436; Found $[M-2H]^{2-}$ 997.3260.

**Compound 14, HCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.77 (d, *J* = 8.1 Hz,1H), 4.71 (d, *J* = 7.9 Hz, 1H), 4.61-4.45 (m, 8H), 4.12 (d, *J* = 5.1 Hz, 1H), 4.04-3.96 (m, 2H), 3.94-3.90

(m, 5H), 3.88-3.46 (m, 39H), 3.41-3.25 (m, 7H), 2.06-1.99 (m, 12H), 1.66-1.54 (m, 4H), 1.44-1.29 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.47, 174.98, 174.91, 174.84, 174.54, 174.49, 174.17, 174.04, 104.32, 104.12, 103.09, 102.97, 102.67, 102.03, 100.92, 100.79, 100.55, 100.52, 83.01, 82.27, 81.24, 81.23, 81.18, 80.35, 80.30, 80.09, 79.99, 79.29, 78.99, 76.56, 76.37, 76.11, 75.90, 75.71, 75.71, 75.36, 75.36, 75.29, 75.29, 74.97, 74.34, 73.99, 73.88, 73.69, 73.57, 72.72, 72.69, 72.51, 72.43, 72.34, 71.79, 71.69, 70.42, 69.78, 68.58, 68.51, 68.45, 67.73, 67.69, 61.09, 60.70, 60.52, 60.17, 54.85, 54.56, 54.21, 51.12, 50.99, 28.40, 27.96, 25.55, 24.63, 22.48, 22.20.

ESI-MS (negative ion): Calcd for $C_{74}H_{116}N_8O_{55}$: 1996.6526, $[M-2H]^{2-}$ 997.3190, $[M-3H]^{3-}$ 664.5436; Found $[M-2H]^{2-}$ 997.3180, $[M-3H]^{3-}$ 664.5439.

**Compound 15, CCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.71 (d, *J* = 8.0 Hz, 1H), 4.63-4.44 (m, 8H), 4.17 (d, *J* = 2.0 Hz, 1H), 4.12 (d, *J* = 2.0 Hz, 1H), 3.96-3.87 (m, 3H), 3.95-3.89 (m, 5H), 3.83-3.46 (m, 37H), 3.39-3.28 (m, 7H), 2.06-1.99 (m, 12H), 1.66-1.52 (m, 4H), 1.43-1.31 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.72, 174.98, 174.95, 174.89, 174.79, 174.49, 174.40, 174.02, 173.86, 104.30, 104.12, 103.08, 102.65, 101.92, 100.91, 100.84, 100.82, 100.58, 98.36, 83.03, 82.29, 80.77, 80.31, 80.28, 79.99, 79.68, 79.68, 79.28, 76.41, 76.41, 76.22, 76.16, 76.00, 75.92, 75.36, 75.27, 75.27, 74.97, 74.20, 73.97, 73.68, 73.57, 72.69, 72.69, 72.67, 72.42, 72.42, 72.33, 71.76, 70.41, 68.57, 68.45, 67.72, 67.67, 61.43, 61.06, 60.69, 60.49, 60.13, 59.30, 54.74, 54.55, 54.20, 51.11, 51.01, 46.66, 28.40, 27.95, 25.54, 24.62, 22.48, 22.47, 22.46, 22.20.

ESI-MS (negative ion): Calcd for $C_{74}H_{116}N_8O_{55}$: 1996.6526, $[M-2H]^{2-}$ 997.3190, $[M-3H]^{3-}$ 664.5436; Found $[M-2H]^{2-}$ 997.3188, $[M-3H]^{3-}$ 664.5446.

**Compound 16, HHHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.75 (d, *J* = 7.8 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.61-4.44 (m, 10H), 3.96-3.88 (m, 8H), 3.88-3.45 (m, 48H), 3.35-3.24 (m, 8H), 2.09-1.99 (m, 15H), 1.65-1.54 (m, 4H), 1.45-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1186.8731, $[M-3H]^{3-}$ 790.2475, $[M-4H]^{4-}$ 592.9336.

**Compound 17, CHHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.61 (d, *J* = 7.9 Hz, 1H), 4.52-4.35 (m, 10H), 4.09 (d, *J* = 2.9 Hz, 1H), 3.94-3.38 (m, 56H), 3.31-3.21 (m, 7H), 1.97-1.87 (m, 15H), 1.59-1.40 (m, 4H), 1.34-1.19 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3712, $[M-3H]^{3-}$ 791.2461, $[M-4H]^{4-}$ 593.1838.

**Compound 18, HCHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 7.8 Hz, 1H), 4.61-4.45 (m, 10H), 4.12 (d, *J* = 2.6 Hz, 1H), 4.02-3.48 (m, 56H), 3.42-3.30 (m, 7H), 2. (m, 15H), 1.65-1.54 (m, 4H), 1.43-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-3H]^{3-}$ 791.9118, $[M-4H]^{4-}$ 593.1837.

**Compound 19, CCHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 8.2 Hz, 1H), 4.60-4.45 (m, 10H), 4.18 (d, *J* = 2.0 Hz, 1H), 4.13 (d, *J* = 2.2 Hz, 1H), 4.04-3.98 (m, 2H), 3.95 -3.47 (m, 53H), 3.41-3.30 (m, 7H), 2.09-1.93 (m, 15H), 1.64-1.54 (m, 4H), 1.41-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3727, $[M-3H]^{3-}$ 791.2464, $[M-4H]^{4-}$ 593.1839.

**Compound 20, HHCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.72 (d, *J* = 8.3 Hz, 1H ), 4.63-4.44 (m, 10H), 4.14 (d, *J* = 2.5 Hz, 1H), 4.03-3.48 (m, 56H), 3.43-3.32 (m, 7H), 2.09-1.99 (m, 15H), 1.67-1.54 (m, 4H), 1.43-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3757, $[M-3H]^{3-}$ 791.2455, $[M-4H]^{4-}$ 592.9334.

**Compound 21, CHCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.71 (d, *J* = 7.9 Hz, 1H), 4.62-4.43 (m, 10H), 4.20-4.10 (m, 2H), 4.08-3.45 (m, 55H), 3.43-3.29 (m, 7H), 2.11-1.93 (m, 15H), 1.69-1.52 (m, 4H), 1.44-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-3H]^{3-}$ 790.9113, $[M-4H]^{4-}$ 593.1831.

**Compound 22, HCCH*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.70 (d, *J* = 7.9 Hz, 1H), 4.60-4.44 (m, 10H), 4.12 (d, *J* = 2.0 Hz, 1H), 4.02-3.47 (m, 56H), 3.41-3.31 (m, 7H), 2.06-1.99 (m, 15H), 1.66-1.52 (m, 4H), 1.41-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-3H]^{3-}$ 790.9122, $[M-4H]^{4-}$ 592.9328.

**Compound 23, CCCH*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 7.8 Hz, 1H), 4.61-4.44 (m, 10H), 4.20-4.10 (m, 3H), 4.03-3.98 (m, 3H), 3.93-3.48 (m, 51H) 3.40-3.28 (m, 7H), 2.09-1.90 (m, 15H), 1.66-1.53 (m, 4H), 1.43-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3185, $[M-3H]^{3-}$ 791.2094.

**Compound 24, HHHHH*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 7.8 Hz, 1H), 4.61-4.44 (m, 13H), 3.97-3.45 (m, 66H), 3.41-3.31 (m, 8H), 2.08-1.93 (m, 18H), 1.62-1.53 (m, 5H), 1.36-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$ 917.6190; Found $[M-2H]^{2-}$ 1376.9346, $[M-3H]^{3-}$ 917.6222.

**Compound 25, CHHHH*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.66 (d, *J* = 7.8 Hz, 1H), 4.59-4.45 (m, 12H), 4.17 (d, *J* = 2.9 Hz, 1H), 4.05-3.43 (m, 65H), 3.40-3.29 (m, 8H), 2.05-2.00 (m, 18H), 1.64-1.53 (m, 4H), 1.43-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-3H]^{3-}$ 917.6190, $[M-4H]^{4-}$ 687.9624, $[M-5H]^{5-}$550.1685; Found $[M-3H]^{3-}$ 917.6172, $[M-4H]^{4-}$ 687.9614, $[M-5H]^{5-}$ 550.1681.

**Compound 26, HCHHH*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.8 Hz, 1H), 4.61-4.45 (m, 12H), 4.12 (d, *J* = 1.9 Hz, 1H), 4.02-3.47 (m, 65H), 3.39-3.28 (m, 8H), 2.06-1.95 (m, 18H), 1.65-1.53 (m, 4H), 1.41-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$ 917.6190; Found $[M-3H]^{3-}$ 917.6174, $[M-4H]^{4-}$ 687.9625, $[M-5H]^{5-}$ 550.1685.

**Compound 27, CCHHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.71 (d, *J* = 7.7 Hz, 1H), 4.63-4.44 (m, 12H), 4.18 (d, *J* = 2.9 Hz, 1H), 4.08-3.41 (m, 65H), 3.40-3.32 (m, 8H), , 2.07-1.98 (m, 18H), 1.67-1.54 (m, 4H), 1.41-1.33 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$ 917.6190; Found $[M-3H]^{3-}$ 917.6222, $[M-4H]^{4-}$ 687.9609, $[M-5H]^{5-}$ 550.1671.

**Compound 28, HHCHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.70 (d, *J* = 7.8 Hz, 1H ), 4.61-4.45 (m, 12H), 4.12 (d, *J* = 1.5 Hz, 1H), 4.02-3.46 (m, 65H),3.41-3.31 (m, 8H), 2.09-1.98 (m, 18H), 1.62-1.56 (m, 4H), 1.38-1.33 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$ 917.6190; Found $[M-3H]^{3-}$ 917.6226, $[M-4H]^{4-}$ 687.9661, $[M-5H]^{5-}$ 550.1715.

**Compound 29, CHCHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.70 (d, *J* = 8.0 Hz, 1H), 4.61-4.46 (m, 12H), 4.18 (d, *J* = 2.9 Hz, 1H), 4.12 (d, *J* = 1.9 Hz, 1H), 4.01-3.47 (m, 64H) , 3.42-3.31 (m, 8H), 2.08-1.99 (m, 18H), 1.62-1.54 (m, 4H), 1.42-1.34 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$ 917.6190; Found $[M-3H]^{3-}$ 917.6226, $[M-4H]^{4-}$ 687.9661, $[M-5H]^{5-}$ 550.1716.

**Compound 30, HCCHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 7.9 Hz, 1H), 4.63-4.46 (m, 12H), 4.16-4.10 (m, 2H), 4.02-3.46 (m, 64H), 3.35-3.30 (m, 8H), 2.09-1.99 (m, 18H), 1.65-1.52 (m, 4H), 1.42-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$ 917.6190; Found $[M-3H]^{3-}$ 917.6218, $[M-4H]^{4-}$ 687.9658, $[M-5H]^{5-}$ 550.1715.

**Compound 31, CCCHH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 7.8 Hz, 1H), 4.61-4.44 (m, 12H), 4.20-4.11 (m, 3H), 4.03-3.46 (m, 63H), 3.40-3.29 (m, 8H), 2.05-1.97 (m, 18H), 1.65-1.52 (m, 4H), 1.43-1.27 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$ 917.6190; Found $[M-3H]^{3-}$ 917.6166, $[M-4H]^{4-}$ 687.9614, $[M-5H]^{5-}$ 550.1678.

**Compound 32, HHHCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.68(d, *J* = 7.8 Hz, 1H), 4.60-4.44 (m, 12H), 4.13 (d, *J* = 2.5 Hz, 1H), 4.02-3.47 (m, 65H), 3.42-3.30 (m, 8H), 2.09-1.98 (m, 18H), 1.65-1.54 (m, 4H), 1.44-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$ 917.6190; Found $[M-3H]^{3-}$ 917.6235, $[M-4H]^{4-}$ 687.9665, $[M-5H]^{5-}$ 550.1720.

**Compound 33, CHHCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.3 Hz, 1H), 4.60-4.42 (m, 12H), 4.18 (d, *J* = 2.8 Hz, 1H), 4.13 (d, *J* = 1.8 Hz, 1H) 4.02-3.46 (m, 64H), , 3.40-3.29 (m, 8H), 2.07-1.99 (m, 18H), 1.65-1.55 (m, 4H), 1.41-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6230, $[M-4H]^{4-}$ 687.9670, $[M-5H]^{5-}$ 550.1723.

**Compound 34, HCHCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 7.8 Hz, 1H), 4.59-4.45 (m, 12H), 4.16-4.09 (m, 2H), 4.02-3.48 (m, 64H), 3.41-3.28 (m, 8H), 2.09-1.98 (m, 18H), 1.65-1.54 (m, 4H), 1.43-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6166, $[M-4H]^{4-}$ 687.9612, $[M-5H]^{5-}$ 550.1677.

**Compound 35, CCHCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.61 (d, *J* =7.5 Hz, 1H), 4.51-4.37 (m, 12H), 4.10-4.01 (m, 3H), 3.96-3.38 (m, 63H), 3.31-3.20 (m, 8H), 1.98-1.90 (m, 18H), 1.55-1.46 (m, 4H), 1.34-1.22 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6210, $[M-4H]^{4-}$ 687.9652, $[M-5H]^{5-}$ 550.1709.

**Compound 36, HHCCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.72 (d, *J* = 6.9 Hz, 1H), 4.62-4.44 (m, 12H), 4.13 (d, *J* = 2.8 Hz, 1H), 4.04-3.45 (m, 65H), 3.39-3.31 (m, 8H), 2.07-1.95 (m, 18H), 1.63-1.55 (m, 4H), 1.40-1.34 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6232, $[M-4H]^{4-}$ 687.9665, $[M-5H]^{5-}$ 550.1720.

**Compound 37, CHCCH*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.70 (d, *J* = 7.0 Hz, 1H), 4.60-4.46 (m, 13H), 4.18 (d, *J* = 2.9 Hz, 1H), 4.12 (d, *J* = 2.9 Hz, 1H), 4.01 (d, *J* = 8.4 Hz, 2H), 3.92 (dd, *J* = 10.4, 6.3 Hz, 7H), 3.87-3.45 (m, 55H), 3.41-3.30 (m, 8H), 2.07-1.99 (m, 18H), 1.65-1.54 (m, 4H), 1.41-1.33 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-2H]^{2-}$ 1376.9262 $[M-3H]^{3-}$ 917.6166, $[M-4H]^{4-}$ 687.9612, $[M-5H]^{5-}$ 550.1677.

**Compound 38, HCCCH*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.71 (d, *J* = 7.8 Hz, 1H), 4.62-4.45 (m, 12H), 4.14-4.09 (m, 3H), 4.02-3.47 (m, 63H), 3.42-3.31 (m, 8H), 2.08-1.97 (m, 18H), 1.66-1.54 (m, 4H), 1.43-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6230, $[M-4H]^{4-}$ 687.9663, $[M-5H]^{5-}$ 550.1717.

**Compound 39, CCCCH*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.72 (d, *J* = 8.0 Hz, 1H), 4.60-4.48 (m, 12H), 4.17 (d, *J* = 2.0 Hz, 1H), 4.15-4.10 (m, 3H), 4.03-3.46 (m, 62H), 3.39-3.31 (m, 8H), 2.07-1.98 (m, 18H), 1.66-1.52 (m, 4H), 1.41-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6234, $[M-4H]^{4-}$ 687.9667, $[M-5H]^{5-}$ 550.1722.

**Compound 40, HHC*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.75 (d, *J* = 7.5 Hz, 1H), 4.67 (d, *J* = 7.8 Hz, 1H), 4.62-4.45 (m, 8H), 4.26 (d, *J* = 2.2 Hz, 1H), 4.07 (d, *J* = 10.4 Hz, 1H), 3.95-3.71 (m, 29H), 3.68-3.46 (m, 16H), 3.42-3.30 (m, 7H), 2.08-2.00 (m, 12H), 1.66-1.53 (m, 4H), 1.43-1.31 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.47, 174.93, 174.93, 174.86, 174.50, 174.39, 174.39, 174.16, 174.16, 103.50, 103.16, 103.10, 102.99, 102.99, 102.67, 100.92, 100.56, 100.56, 100.52, 83.09, 83.03, 82.50, 82.27, 80.22, 79.98, 79.98, 79.93, 79.75, 76.46, 76.37, 76.30, 75.70, 75.38, 75.37, 75.37, 75.29, 74.17, 74.14, 73.57, 73.57, 73.48, 72.70, 72.47, 72.43, 72.24, 72.24, 71.69, 70.42, 68.58, 68.52, 68.52, 68.46, 68.42, 66.67, 60.81, 60.81, 60.71, 60.71, 60.51, 60.51, 54.56, 54.28, 54.22, 52.05, 51.12, 51.12, 28.41, 28.41, 27.96, 25.55, 25.55, 24.63, 22.48, 22.20..

ESI-MS (negative ion): Calcd for $C_{74}H_{116}N_8O_{55}$: 1996.6526, $[M-2H]^{2-}$ 997.3190, $[M-3H]^{3-}$ 664.5436; Found $[M-2H]^{2-}$ 997.3157, $[M-3H]^{3-}$ 664.5431.

**Compound 41, CHC*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 7.8 Hz, 1H), 4.61-4.48 (m, 8H), 4.26 (d, *J* = 2,6 Hz, 1H), 4.17 (d, *J* = 2.9 Hz, 1H), 4.11 (d, *J* = 2.9 Hz, 1H), 4.03 -3.48 (m, 44H), 3.43-3.32 (m, 7H), 2.07-1.98 (m, 12H), 1.67-1.54 (m, 4H), 1.43-1.32 (m, 5H).$^{13}$C NMR (151 MHz, $D_2O$) δ 175.02, 174.95, 174.88, 174.61, 174.49, 173.84, 173.54,

173.54, 173.37, 104.14, 103.43, 103.07, 103.03, 102.62, 100.96, 100.91, 100.66, 100.61, 98.69, 82.95, 82.37, 80.23, 79.99, 79.71, 79.67, 79.20, 75.94, 75.74, 75.66, 75.46, 75.36, 75.29, 75.22, 74.98, 74.10, 73.94, 73.68, 73.59, 73.47, 72.70, 72.63, 72.59, 72.36, 72.29, 72.21, 71.65, 71.28, 70.42, 68.56, 68.44, 68.35, 68.29, 67.67, 66.67, 61.16, 61.02, 60.78, 60.70, 60.50, 60.50, 54.54, 54.27, 54.23, 52.04, 51.12, 51.05, 28.40, 27.96, 25.55, 24.62, 24.62, 22.45, 22.45, 22.20.

ESI-MS (negative ion): Calcd for $C_{74}H_{116}N_8O_{55}$: 1996.6526, $[M-2H]^{2-}$ 997.3190, $[M-3H]^{3-}$ 664.5436; Found $[M-2H]^{2-}$ 997.3162.

**Compound 42, HCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69-4.57 (m, 2H), 4.55-4.38 (m, 8H), 4.18 (d, *J* = 2.1 Hz, 1H ), 4.06 (d, *J* = 2.9 Hz, 1H ), 4.01-3.90 (m, 2H), 3.88-3.38 (m, 43H), 3.34-3.21 (m, 7H), 2.02-1.88 (m, 12H), 1.59-1.45 (m, 4H), 1.39-1.21 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.44, 174.92, 174.84, 174.82, 174.51, 174.51, 174.44, 174.44, 174.13, 104.28, 104.28, 103.51, 103.05, 102.90, 102.61, 100.85, 100.72, 100.50, 100.45, 82.89, 82.86, 82.16, 80.24, 80.14, 80.12, 79.89, 79.30, 76.30, 76.27, 75.68, 75.26, 75.19, 74.88, 74.21, 74.19, 74.17, 74.04, 73.54, 73.46, 73.46, 72.59, 72.55, 72.40, 72.33, 72.14, 71.62, 70.35, 69.27, 68.46, 68.46, 68.39, 68.32, 67.63, 67.63, 66.60, 61.00, 60.76, 60.58, 60.58, 60.39, 54.47, 54.13, 54.13, 51.95, 51.03, 50.89, 28.32, 27.90, 25.47, 24.56, 22.38, 22.38, 22.11, 22.11.

ESI-MS (negative ion): Calcd for $C_{74}H_{116}N_8O_{55}$: 1996.6526, $[M-2H]^{2-}$ 997.3190, $[M-3H]^{3-}$ 664.5436; Found $[M-2H]^{2-}$ 997.3265.

**Compound 43, CCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.6 Hz, 1H), 4.60 (d, *J* = 7.7 Hz, 1H), 4.52-4.39 (m, 8H), 4.22-3.90 (m, 6H), 3.89-3.36 (m, 41H), 3.33-3.22 (m, 7H), 1.99-1.90 (m, 12H), 1.57-1.47 (m, 4H), 1.36-1.20 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.93, 174.92, 174.90, 174.84, 174.84, 174.57, 174.43, 174.42, 174.13, 104.26, 104.07, 103.87, 103.44, 103.44, 103.05, 102.60, 100.85, 100.73, 100.50, 82.89, 82.16, 80.23, 80.05, 79.88, 79.53, 79.28, 76.31, 76.26, 76.25, 76.07, 76.02, 75.32, 75.26, 75.19, 74.89, 74.09, 74.02, 73.58, 73.47, 73.46, 72.71, 72.61, 72.53, 72.35, 72.13, 71.77, 71.72, 70.97, 70.35, 68.45, 68.41, 68.33, 67.62, 67.59, 66.58, 61.31, 61.01, 60.74, 60.58, 60.38, 54.47, 54.14, 51.95, 51.03, 50.93, 50.89, 28.32, 28.32, 27.90, 25.47, 24.56, 22.40, 22.38, 22.10.

ESI-MS (negative ion): Calcd for $C_{74}H_{116}N_8O_{55}$: 1996.6526, $[M-2H]^{2-}$ 997.3190, $[M-3H]^{3-}$ 664.5436; Found $[M-2H]^{2-}$ 997.3262.

**Compound 44, HHHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.66 (d, *J* = 7.8 Hz, 1H), 4.62-4.44 (m, 10H), 4.25 (d, *J* = 2.9 Hz 1H), 3.97-3.42 (m, 55H), 3.41-3.30 (m, 8H), 2.08-1.99 (m, 15H), 1.64-1.54 (m, 4H), 1.42-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-3H]^{3-}$ 791.2461, $[M-4H]^{4-}$ 593.1836.

**Compound 45, CHHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.66 (d, *J* = 7.7 Hz, 1H), 4.60-4.45 (m, 10H), 4.26 (d, *J* = 2.8 Hz, 1H), 4.18 (d, *J* = 3.0 Hz, 1H), 4.09-3.96 (m, 2H), 3.94 -3.46 (m, 52H), 3.41-3.29 (m, 8H), 2.09-2.00 (m, 15H), 1.65-1.53 (m, 4H), 1.42-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3682, $[M-3H]^{3-}$ 790.9098, $[M-4H]^{4-}$ 592.9317.

**Compound 46, HCHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.8 Hz, 1H), 4.60-4.45 (m, 10H), 4.26 (d, *J* = 2.8 Hz, 1H), 4.15-4.05 (m, 2H), 4.02-3.46 (m, 53H), 3.43-3.29 (m, 8H), 2.09-1.98 (m, 15H), 1.66-1.54 (m, 4H), 1.45-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-3H]^{3-}$ 791.2460, $[M-4H]^{4-}$ 592.9326.

**Compound 47, CCHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.66 (d, *J* = 7.8 Hz, 1H), 4.62-4.44 (m, 10H), 4.28-3.98 (m, 5H), 3.95-3.46 (m, 51H), 3.42-3.31 (m, 8H), 2.05-2.01 (m, 15H), 1.67-1.53 (m, 4H), 1.43-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3746, $[M-3H]^{3-}$ 791.2470, $[M-4H]^{4-}$ 593.1841.

**Compound 48, HHCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.9 Hz, 1H), 4.62-4.44 (m, 10H), 4.26 (d, *J* = 2.9 Hz, 1H), 4.15-4.06 (m, 2H), 4.02-3.47 (m, 53H), 3.43-3.30 (m, 8H), 2.08-1.98 (m, 15H), 1.67-1.53 (m, 4H), 1.42-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-3H]^{3-}$ 790.9118, $[M-4H]^{4-}$ 593.1837.

**Compound 49, CHCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.68 (d, *J* = 7.8 Hz), 4.60-4.46 (m, 10H), 4.26-3.48 (m, 56H), 3.42-3.31 (m, 8H), 2.07-1.88 (m, 15H), 1.65-1.52 (m, 4H), 1.42-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3757, $[M-3H]^{3-}$ 790.2455, $[M-4H]^{4-}$ 592.9334.

**Compound 50, HCCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.68 (d, *J* = 7.9 Hz, 1H), 4.61-4.44 (m, 10H), 4.27 (d, *J* = 2.4 Hz, 1H), 4.14-3.48 (m, 55H), 3.42-3.29 (m, 8H), 2.06-1.99 (m, 15H), 1.65-1.53 (m, 4H), 1.42-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3710, $[M-3H]^{3-}$ 791.2450, $[M-4H]^{4-}$ 593.1822.

**Compound 51, CCCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.7 Hz, 1H), 4.60-4.45 (m, 10H), 4.17-3.40 (m, 56H), 3.42-3.30 (m, 8H), 2.08-1.98 (m, 15H), 1.66-1.54 (m, 4H), 1.43-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{88}H_{137}N_9O_{66}$: 2375.7641, $[M-2H]^{2-}$ 1186.8748, $[M-3H]^{3-}$ 790.9141, $[M-4H]^{4-}$ 592.9337; Found $[M-2H]^{2-}$ 1187.3714, $[M-3H]^{3-}$ 790.9121, $[M-4H]^{4-}$ 593.1840.

**Compound 52, HHHHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.71 (d, *J* = 7.7 Hz, 1H), 4.60-4.44 (m,13H), 4.24 (d, *J* = 2.4 Hz, 1H), 3.97-3.46 (m, 64H), 3.41-3.29 (m, 9H), 2.09-1.98 (m, 18H), 1.66-1.55 (m, 4H), 1.44-1.33 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6169, $[M-4H]^{4-}$ 687.9614, $[M-5H]^{5-}$ 550.1678.

**Compound 53, CHHHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.68-4.45 (m, 13H), 4.26-4.15 (m, 2H), 4.07-3.42 (m, 63H), 3.41-3.27 (m, 9H), 2.06-1.97 (m, 18H), 1.64-1.53 (m, 4H), 1.43-1.29 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6234, $[M-4H]^{4-}$ 687.9666, $[M-5H]^{5-}$ 550.1720.

**Compound 54, HCHHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.68-4.42 (m, 13H), 4.28-4.13 (m, 2H), 4.08-3.44 (m, 63H), 3.42-3.25 (m, 9H), 2.07-1.97 (m, 18H), 1.64-1.52 (m, 4H), 1.42-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6222, $[M-4H]^{4-}$ 687.9660, $[M-5H]^{5-}$ 550.1717.

**Compound 55, CCHHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.70 (d, *J* = 7.4 Hz, 1H), 4.61-4.45 (m, 13H), 4.19-4.11 (m, 2H), 4.03-3.46 (m, 64H), 3.42-3.31 (m, 8H), 2.07-1.99 (m, 18H), 1.66-1.55 (m, 4H), 1.42-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6207, $[M-4H]^{4-}$ 687.9646, $[M-5H]^{5-}$ 550.1705.

**Compound 56, HHCHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.72 (d, *J* = 7.6 Hz, 1H), 4.66 (d, *J* = 8.2 Hz, 1H), 4.60-4.44 (m, 12H), 4.25 (d, *J* = 2.6 Hz, 1H), 4.12 (d, *J* = 2.4 Hz, 1H), 4.07-3.46 (m, 63H), 3.40-3.32 (m, 9H), 2.07-1,97 (m, 18H), 1.63-1.55 (m,4H), 1.41-1.30 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6230, $[M-4H]^{4-}$ 687.9665, $[M-5H]^{5-}$ 550.1720.

**Compound 57, CHCHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.71-4.47 (m, 14H), 4.28-4.10 (m, 3H), 4.04-3.47 (m, 62H), 3.42-3.24 (m, 9H), 2.06-1.95 (m, 18H), 1.65-1.55 (m, 4H), 1.40-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6210, $[M-4H]^{4-}$ 687.9649, $[M-5H]^{5-}$ 550.1707.

**Compound 58, HCCHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69-4.45 (m, 13H), 4.28-3.47 (m, 65H), 3.41-3.27 (m, 9H), 2.06-1.99 (m, 18H), 1.66-1.51 (m, 4H), 1.42-1.29 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6229, $[M-4H]^{4-}$ 687.9665, $[M-5H]^{5-}$ 550.1720.

**Compound 59, CCCHC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ4.67-4.46 (m, 14H), 4.28-3.45 (m, 65H), 3.43-3.29 (m, 9H), 2.05-1.99 (m, 18H), 1.64-1.53 (m, 4H), 1.42-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6213, $[M-4H]^{4-}$ 687.9652, $[M-5H]^{5-}$ 550.1709.

**Compound 60, HHHCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.6 Hz, 1H), 4.61-4.44 (m, 12H), 4.28-4.14 (m, 2H), 4.04-3.45 (m, 63H), 3.41-3.29 (m, 9H), 2.06-1.98 (m, 18H), 1.64-1.54 (m, 4H), 1.42-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6204, $[M-4H]^{4-}$ 687.9644, $[M-5H]^{5-}$ 550.1704.

**Compound 61, CHHCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.66 (d, *J* = 7.7 Hz, 1H), 4.61-4.42 (m, 12H), 4.26-4.12 (m, 3H), 4.02-3.48 (m, 62H), 3.40-3.30 (m, 9H), 2.06-1.94 (m, 18H), 1.65-1.56 (m, 4H), 1.41-1.34 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6200, $[M-4H]^{4-}$ 687.9640, $[M-5H]^{5-}$ 550.1702.

**Compound 62, HCHCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69 (d, *J* = 7.5 Hz, 1H), 4.60-4.46 (m, 12H), 4.26 (d, *J* = 2.5 Hz, 1H), 4.12 (d, *J* = 1.4 Hz, 2H), 4.04-3.48 (m, 62H), 3.41-3.31 (m, 9H), 2.06-1.97 (m, 18H), 1.64-1.54 (m, 4H), 1.41-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6199, $[M-4H]^{4-}$ 687.9640, $[M-5H]^{5-}$ 550.1701.

**Compound 63, CCHCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.70-4.45 (m, 14H), 4.27-3.96 (m, 8H), 3.94-3.46 (m, 57H), 3.41-3.31 (m, 9H), 2.07-1.94 (m, 18H), 1.65-1.53 (m, 4H), 1.43-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6203, $[M-4H]^{4-}$ 687.9643, $[M-5H]^{5-}$ 550.1703.

**Compound 64, HHCCC*HH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.69-4.45 (m,14H), 4.29-3.44 (m, 65H), 3.43-3.31 (m, 9H), 2.06-2.00 (m, 18H), 1.64-1.54 (m, 4H), 1.45-1.30 (m, 4H)

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6222, $[M-4H]^{4-}$ 687.9658, $[M-5H]^{5-}$ 550.1713.

**Compound 65, CHCCC*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.7 Hz, 1H), 4.58-4.47 (m, 12H), 4.26-3.45 (m, 65H), 3.40-3.32 (m, 9H), 2.05-1.99 (m,18H), 1.65-1.53 (m, 4H), 1.43-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6209, $[M-4H]^{4-}$ 687.9648, $[M-5H]^{5-}$ 550.1706.

**Compound 66, HCCCC*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.67 (d, *J* = 7.4 Hz, 1H), 4.60-4.46 (m, 12H), 4.25-3.50 (m, 65H), 3.42-3.29 (m, 9H), 2.14-1.95 (m, 18H), 1.66-1.52 (m, 4H), 1.41-1.31 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6205, $[M-4H]^{4-}$ 687.9645, $[M-5H]^{5-}$ 550.1704.

**Compound 67, CCCCC*HH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.65 (d, *J* = 7.4 Hz, 1H), 4.60-4.44 (m, 12H), 4.26-3.47 (m, 65H), 3.39-3.28 (m, 9H), 2.06-1.96 (m, 18H), 1.65-1.52 (m, 4H), 1.42-1.32 (m, 4H).

ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 2754.8755, $[M-2H]^{2-}$ 1376.9322, $[M-3H]^{3-}$917.6190; Found $[M-3H]^{3-}$ 917.6222, $[M-4H]^{4-}$ 687.9658, $[M-5H]^{5-}$ 550.1713.

**Compound 68, HHH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.62-4.45 (m, 6H), 3.96-3.69 (m, 18H), 3.66-3.45 (m, 11H), 3.40-3.31 (m, 5H), 2.12-1.98 (m, 9H), 1.65-1.53 (m, 4H), 1.43-1.30 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) δ 175.41, 174.90, 174.83, 174.49, 174.16, 103.09, 102.68, 102.07, 100.91, 100.56, 99.14, 82.98, 82.27, 82.08, 80.21, 79.98, 76.36, 75.81, 75.36, 75.28, 74.42, 74.02, 73.56, 73.00, 72.68, 72.43, 72.34, 72.03, 71.48, 70.41, 68.57, 68.44, 67.87, 60.69, 60.49, 60.23, 54.90, 54.55, 54.21, 51.11, 28.40, 27.96, 25.54, 24.62, 22.48, 22.20.

ESI-MS (negative ion): Calcd for $C_{46}H_{74}N_6O_{33}$: 1280.4402, $[M-H]^{-}$ 1279.4324, $[M-2H]^{2-}$ 618.2076; Found $[M-H]^{-}$ 1279.4341, $[M-2H]^{2-}$ 639.2150.

**Compound 69, CHH:** $^{1}$H NMR (600 MHz, $D_2O$) δ 4.62-4.44 (m, 6H), 4.18 (d, *J* = 3.1 Hz, 1H), 4.06-3.29 (m, 33H), 2.15-1.91 (m, 9H), 1.68-1.52 (m, 4H), 1.44-1.30 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) 175.96, 174.98, 174.93, 174.50, 174.20, 174.13, 104.13, 103.14, 103.10, 100.93, 100.83, 100.58, 82.50, 82.24, 80.36, 80.00, 79.61, 79.61, 76.39, 76.29, 76.11, 75.37, 75.33, 75.29, 75.00, 73.66, 73.57, 72.72, 72.42, 71.80, 70.42, 68.58, 68.40,

67.69, 61.08, 60.70, 60.49, 54.56, 54.29, 51.12, 51.04, 28.41, 27.96, 25.55, 24.63, 22.50, 22.48, 22.20.

ESI-MS (negative ion): Calcd for $C_{46}H_{74}N_6O_{33}$: 1280.4402, $[M-2H]^{2-}$ 618.2076; Found $[M-2H]^{2-}$ 639.1968.

**Compound 70, HHHH:** $^1$H NMR (600 MHz, $D_2O$) δ 4.60-4.56 (m, 3H), 4.53 (d, *J* = 8.5 Hz, 1H), 4.50-4.45 (m, 4H), 3.97-3.89 (m, 5H), 3.88-3.71 (m, 19H), 3.64-3.57 (m, 4H), 3.56-3.45 (m, 10H), 3.42-3.30 (m, 6H), 2.08-1.98 (m, 12H), 1.66-1.55 (m, 4H), 1.42-1.31 (m, 4H). $^{13}$C NMR (151 MHz, $D_2O$) 175.34, 175.34, 174.93, 174.50, 174.04, 174.03, 174.00, 174.00, 103.16, 103.09, 102.97, 100.93, 100.60, 100.60, 100.55, 100.54, 83.06, 82.56, 82.49, 82.49, 82.25, 82.25, 80.01, 79.94, 79.91, 76.29, 76.29, 76.19, 75.65, 75.39, 75.37, 75.34, 75.28, 75.28, 73.57, 73.55, 72.69, 72.46, 72.46, 72.41, 71.67, 71.67, 70.42, 68.58, 68.51, 68.40, 68.40, 60.70, 60.49, 59.31, 54.56, 54.29, 54.22, 51.12, 28.41, 27.96, 25.55, 25.55, 24.63, 24.63, 22.47, 22.20.

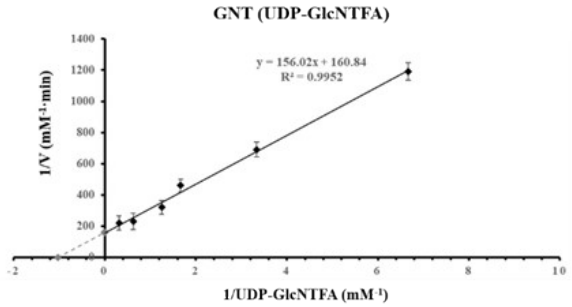
ESI-MS (negative ion): Calcd for $C_{102}H_{158}N_{10}O_{77}$: 1659.5517, $[M-2H]^{2-}$ 828.768; Found $[M-2H]^{2-}$ 828.7516.

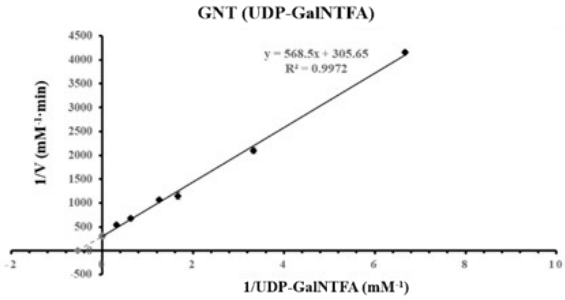
**Kinetic assays**

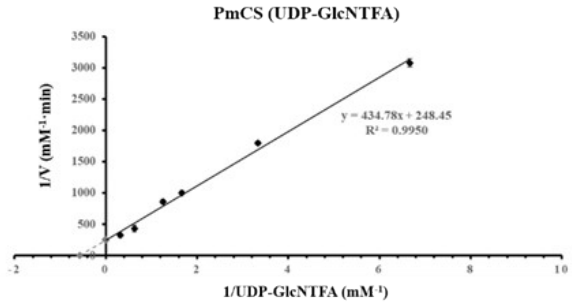
Enzymatic assays were carried out in 25 µL reactions that contained 100 mM Tris-HCl (pH 7.0), 1 mM $MgCl_2$, 2 mM acceptor, UDP-GlcNAc/GalNAc, UDP-GlcN/ GalN, UDP-GlcNTFA/GalNTFA or UDP-GlcA and various amounts of enzyme in a 96-well plate. Reactions were allowed to proceed for 30 min at 37 °C and the formation of byproduct UDP were measured by UDP-Glo™ glycosyltransferase assay (Promega Cat.#V6961). Michaelis-Menten kinetic parameters were obtained by varying the concentrations of donors (0.02, 0.04, 0.08, 0.15, 0.3, 0.6 mM) in the presence of a fixed concentration (2 mM) of acceptor. The double reciprocal lineweaver-burk plots were obtained from the average values of duplicate assay results.

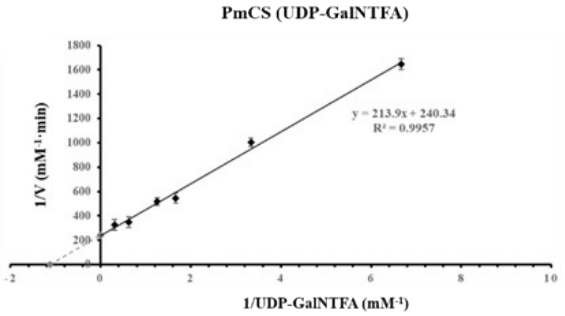
To convert the GlcNTFA/GalNTFA residue to GlcN/GalN residue, NaOH solution was added to compound **2** and **3** solution (10 mM) to reach a final concentration of 0.1 M. TLC were used to monitor the degree of the detrifluoroacetylation reaction. Upon the

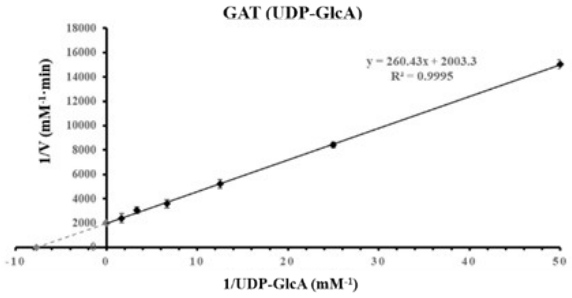
completion of detrifluoroacetylation, pH of the reaction mixture was adjusted to 7.0 followed by purification using a P2 column.

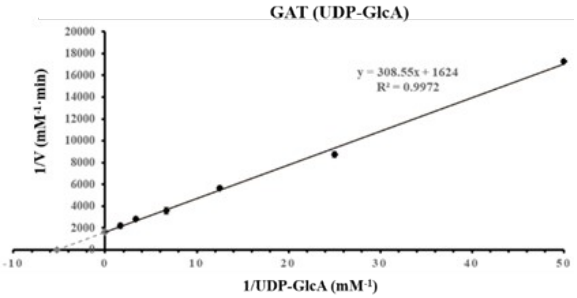


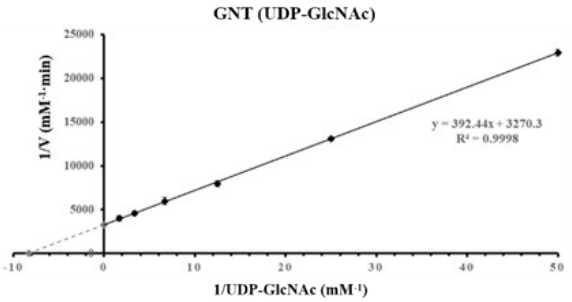



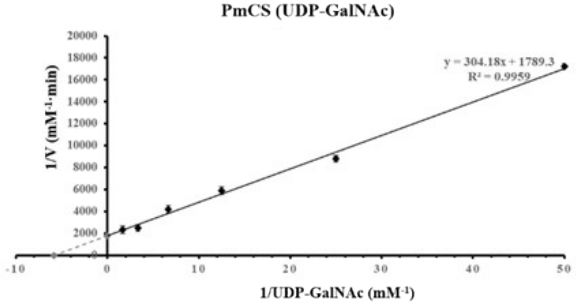



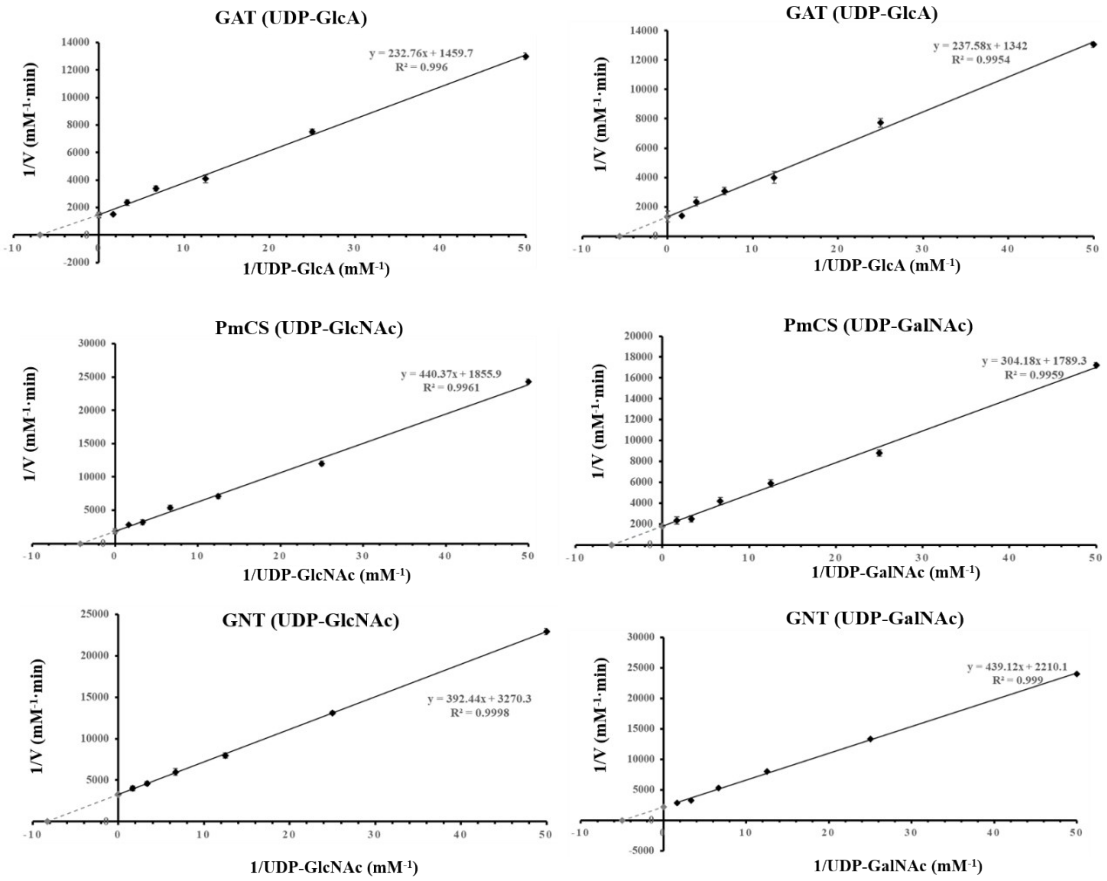



**Fig. S4**. The kinetic plots of GNT, GAT and PmCS measured using various substrates.

## Microarray Fabrication

Glycan microarray was printed according to the guidelines of MIRAGE. All glycans (Table S1) were prepared at a concentration of 100 mM in the printing buffer (150 mM phosphate, pH 8.5), and printed on dibenzocyclooctyne (DBCO)-activated glass slides (Z Biotech, LLC, Aurora, CO), each for 1 nL in replicates of 6. Non-contact printing was performed at room temperature with a humidity of 60% by a sciFLEXARRAYER S3 spotter (Scienion) with one PDC 70 Piezo Dispense Capillary, and 16 subarrays were printed on each slide. After overnight dehumidification, the slides were stored at -20 °C until use. Print buffer was printed as a negative control. In addition, biotin-PEG-azido (0.01mg/mL) was printed as a positive control. A marker containing Cy5 (0.01 mg/mL) was also printed in the replicates of six.

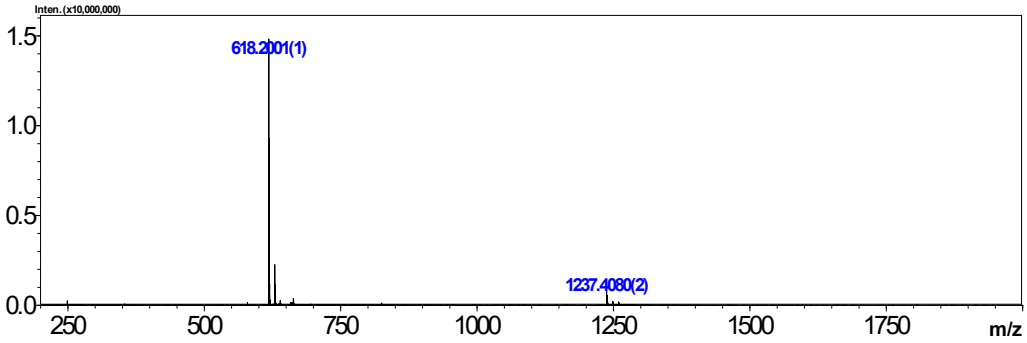
## Microarray Assay

Glycan microarray assay with hyaladherins was analyzed as follows: CD44 (Abcam, 202 mg/mL, 200 mL) and aggrecan (R&D System, 101 mg/mL, 200 mL) were pre-mixed with NHS-biotin (20 mg/mL, 2 mL) and were incubated at room temperature for 2 h, followed by dialysis with 10 K centrifugal filter to remove NHS-biotin and by-products. Degree-of-labelling (DOL, dye: protein radio) of labelled protein was measured and controlled between 0.5-1 to ensure that protein function was not affected by labeling. The labelling protein (12.5 mL, 25 mL, 50 mL and 100 mL) was diluted with PBS to 100 mL. The array slide was mounted with a ProPlate 16 Well Module, and 100 μL of 10 mg/mL BSA was added to each well and the slide was shaken for 30 min. Then the solution was discarded, then 100 μL labelled protein of different concentrations, or Biotin-labeled Stabilin-2 (R&D System, 12.5 mg/mL) were added to each well, and the slide was sealed and incubated at room temperature for 2 h. The slide was then washed gently by 200 mL buffer I (20 mM Tris-HCl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05 Tween-20, and 1% BSA) × 5 and buffer II (20 mM Tris-HCl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$ and 0.05 Tween-20) × 3. Cy5-streptavidin (1 μg/mL, 100 mL) was added to each well and the slide was sealed and incubated at room temperature for 1 h avoiding light. Finally, the slide was washed by 200 mL buffer I×5, buffer II× 3 and deionized water. After dried by brief centrifuge, the slide was scanned with a LuxScan-10K/A microarray scanner by recording the fluorescent signal of Cy5 and the collected data was analyzed with the LuxScan 3.0 software. The average relative fluorescence units (RFUs) and standard error measurement (SEM) were calculated and shown in bar graphs (SEM value as error bars).

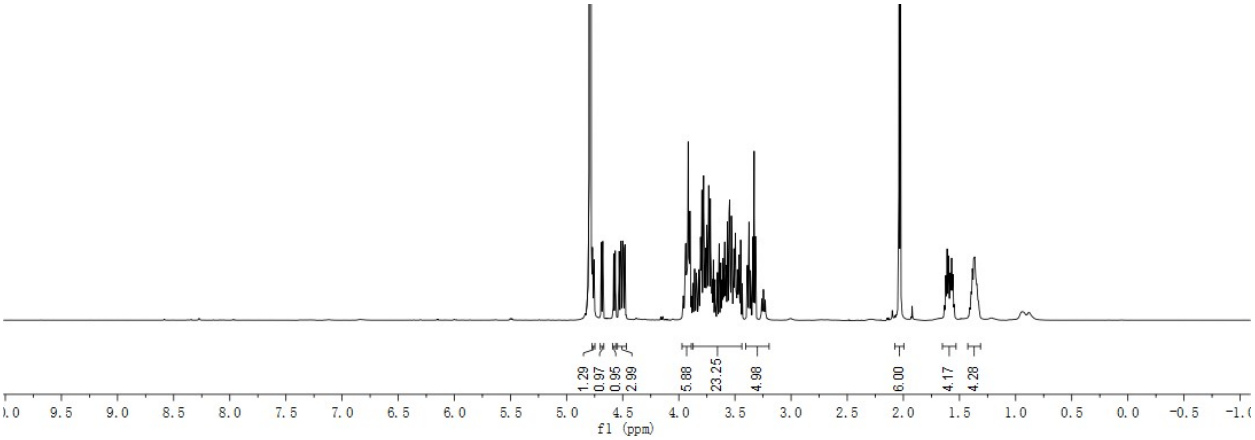
Glycan microarray involving A549 cells was analyzed as follows: A549 cells were cultured in RPMI Medium 1640 basic overnight at 37 ℃ and 5% $CO_2$. ~5 × $10^6$ cells were fixed in 2% paraformaldehyde for 20 min followed by incubation in PBS with NHS-biotin (0.2 mg/mL, 1 mL). Then the cells were washed three times with PBS to remove NHS-biotin and by-products. To reduce nonspecific cell adhesion, 100 mL BSA (10 mg/mL) was placed on the well, and the slide was incubated in a humid atmosphere for 2 h at 37 °C. Then the solution was removed, and 100 μL labelled cells (5 × $10^6$ cells) were added to each well, and the slide was sealed and incubated at room temperature for 2 h. After

incubation, the array slide was placed into a clean plastic container with PBS. The carrier containing the inverted slides was centrifuged at 200 × g for 20 min at 25 ℃ to remove nonadherent cells. The carrier was reimmersed in PBS and then placed gently in 4% paraformaldehyde for 30 min. Finally, Cy5-streptavidin (1 μg/mL, 100 mL) was added to the well and the slide incubated at room temperature for 30 min avoiding light and the slide was washed by deionized water. After dried by brief centrifuge, the slide was scanned with the microarray scanner by recording the fluorescent signal of Cy5.

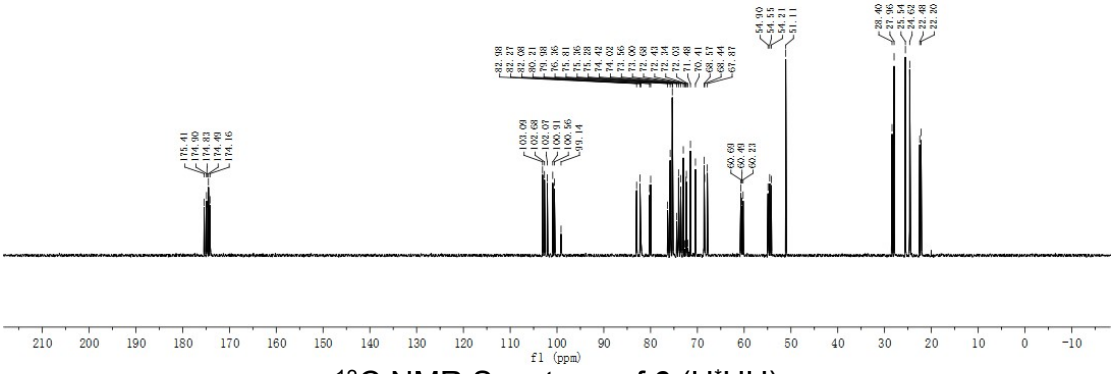
## ESI-MS and NMR Spectra of Synthesized Hybrid Oligosaccharides



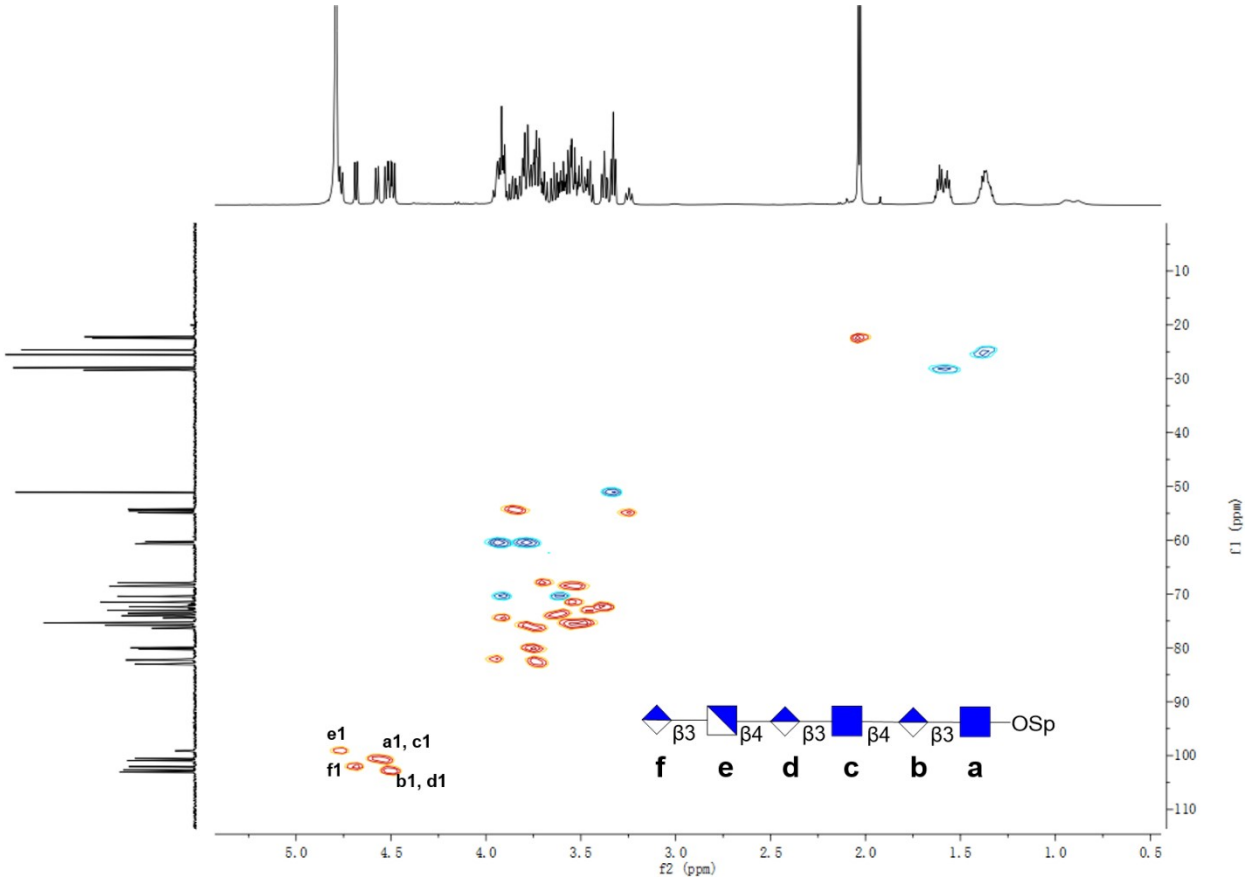

$^{-}$Q ESI-MS profile of **6** (H*HH)




$^{1}$H NMR Spectrum of **6** (H*HH)

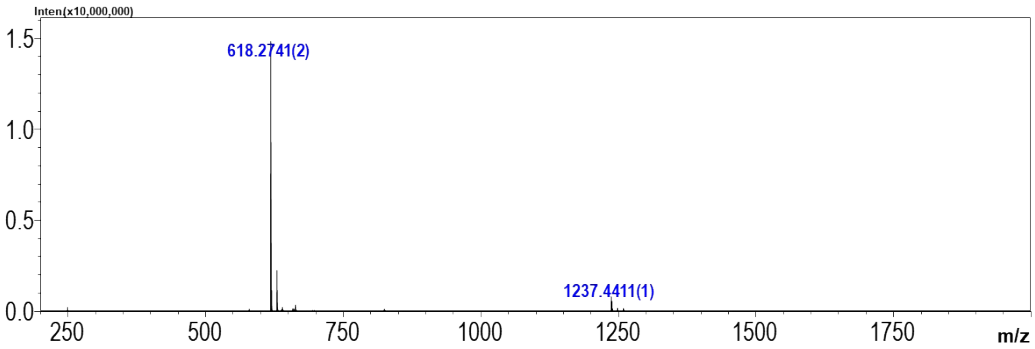



$^{13}$C NMR Spectrum of **6** (H*HH)

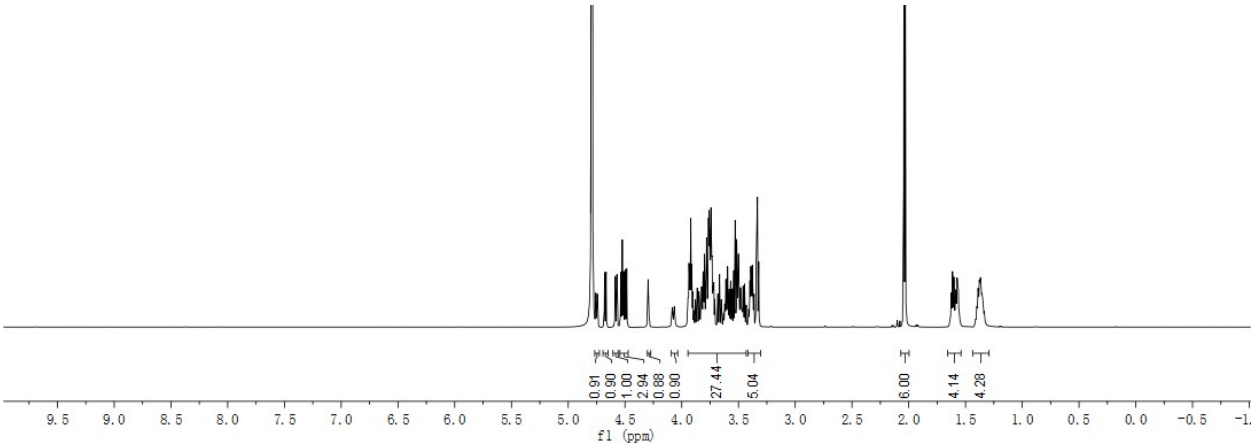



HSQC Spectrum of **6** (H*HH)

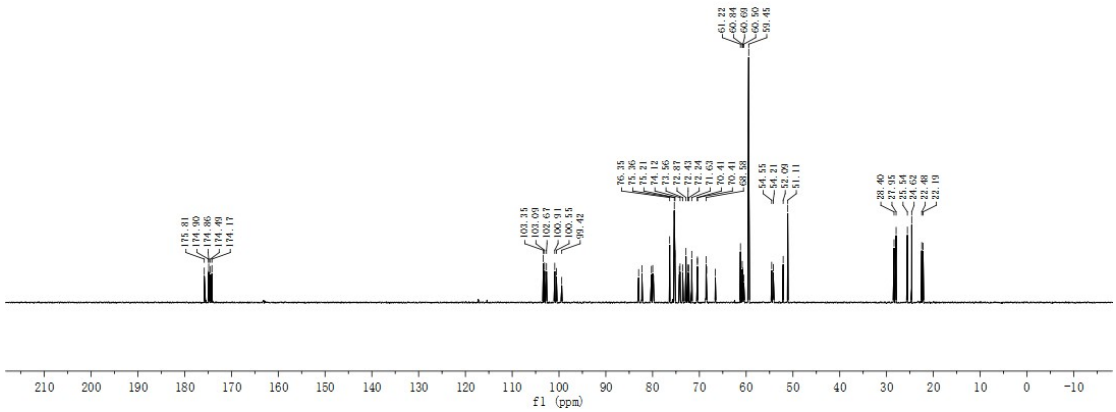
The anomeric signals are indicated.(bule: -CH2-)



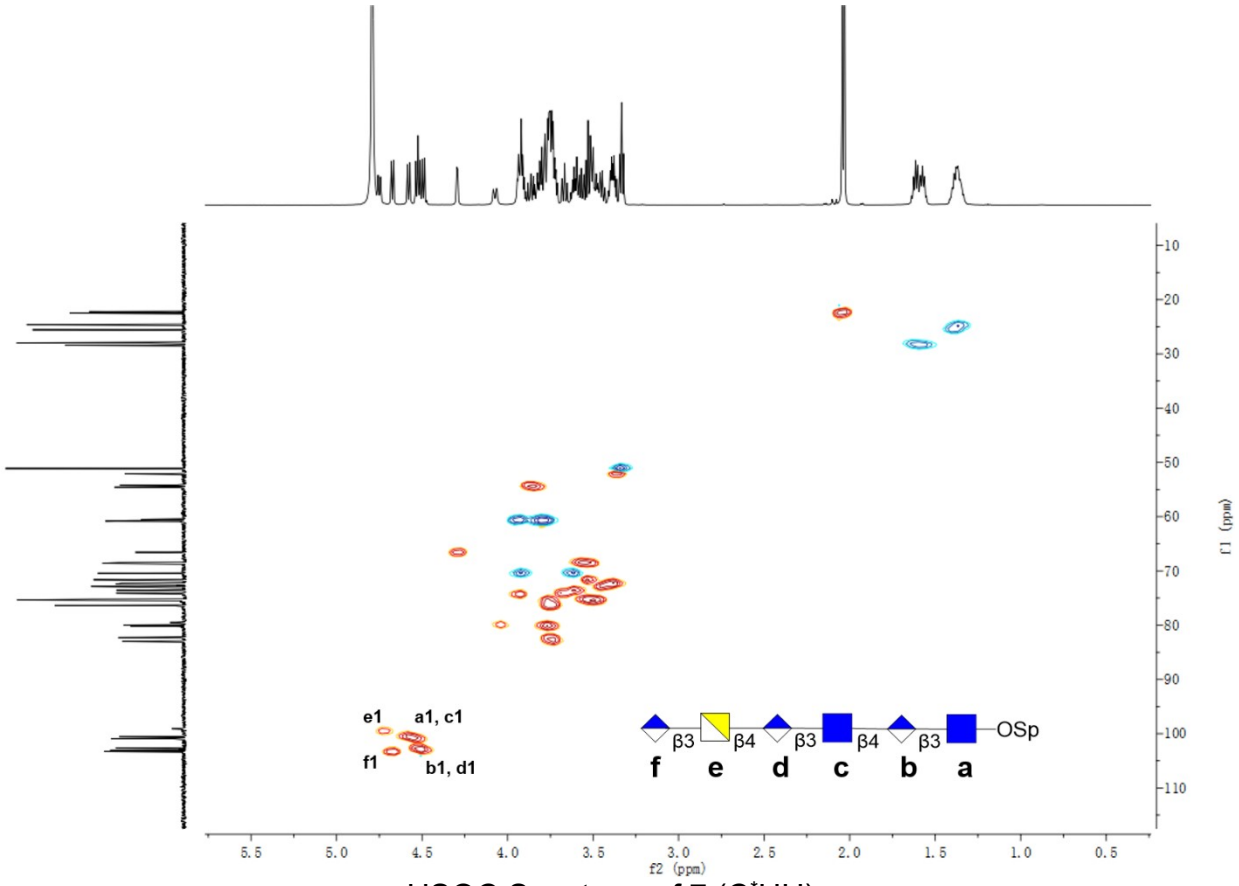

$^{-}$Q ESI-MS profile of **7** (C*HH)




$^{1}$H NMR Spectrum of **7** (C*HH)

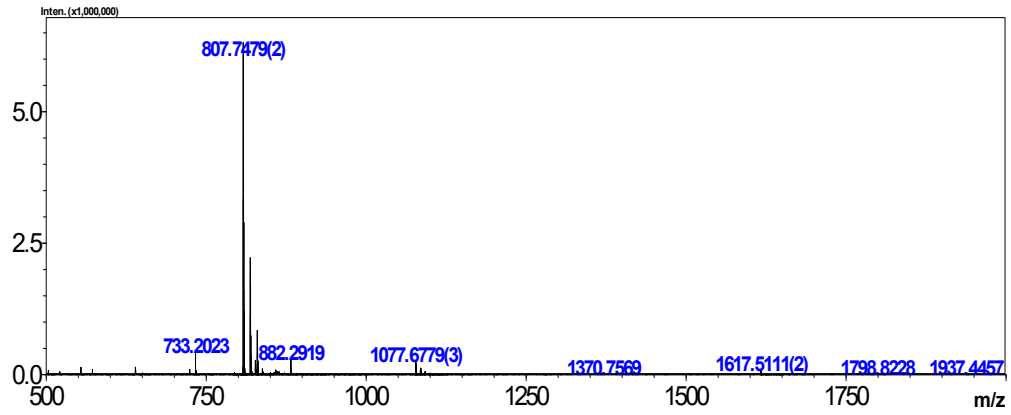



$^{13}$C NMR Spectrum of **7** (C*HH)

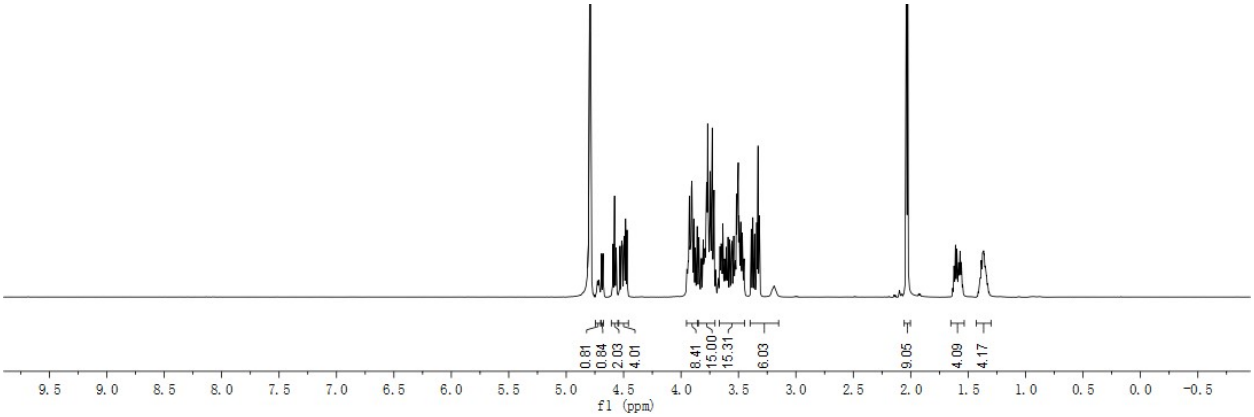



HSQC Spectrum of **7** (C*HH)

The anomeric signals are indicated. (bule: -CH2-)

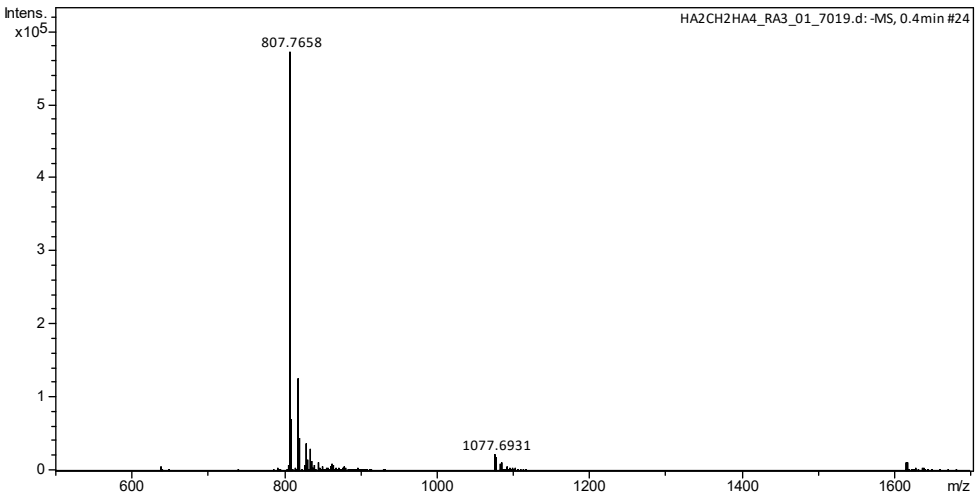



-Q ESI-MS profile of **8** (HH*HH)

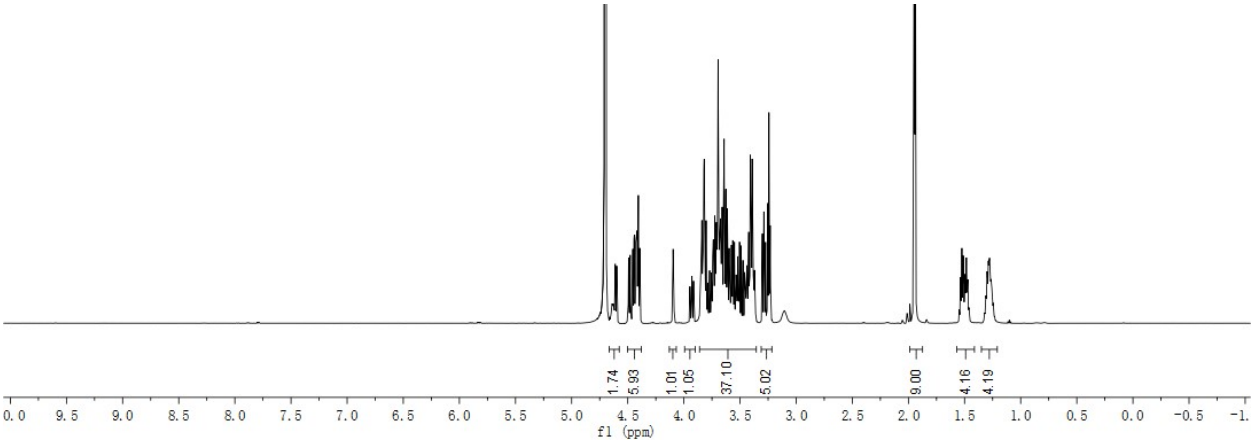



$^{1}$H NMR Spectrum of **8** (HH*HH)

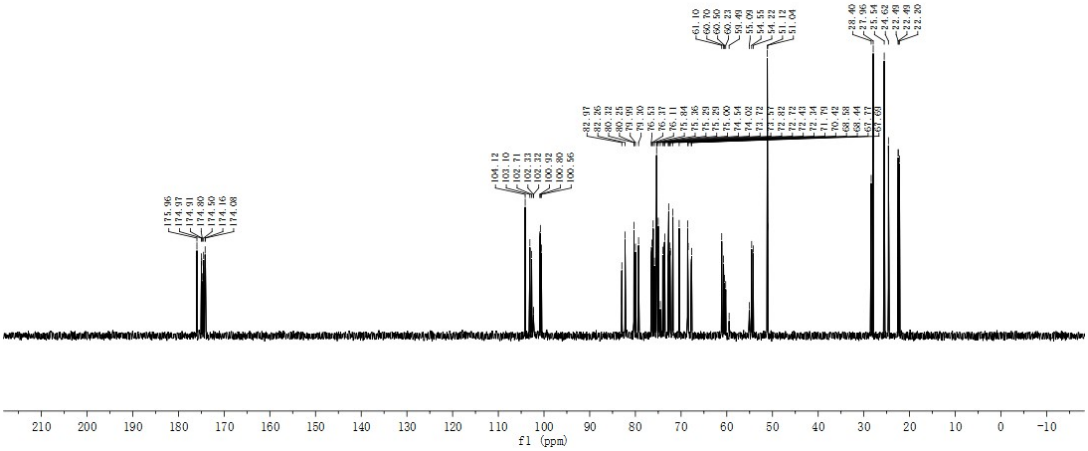
$^{13}$C NMR Spectrum of **8** (HH*HH)



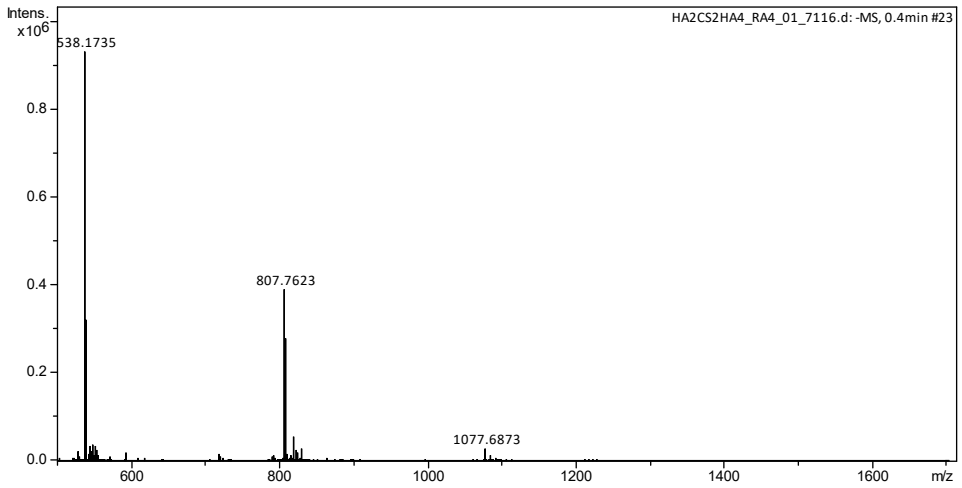

$^{-}$Q ESI-MS profile of **9** (CH$^{*}$HH)



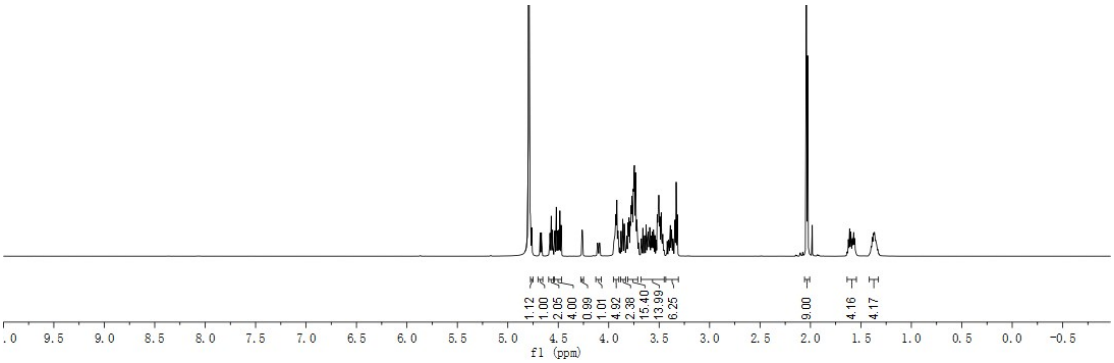

$^{1}$H NMR Spectrum of **9** (CH$^{*}$HH)



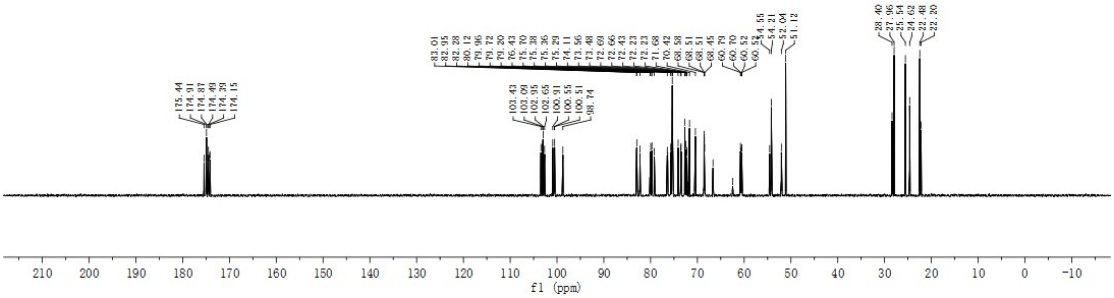

$^{13}$C NMR Spectrum of **9** (CH$^{*}$HH)



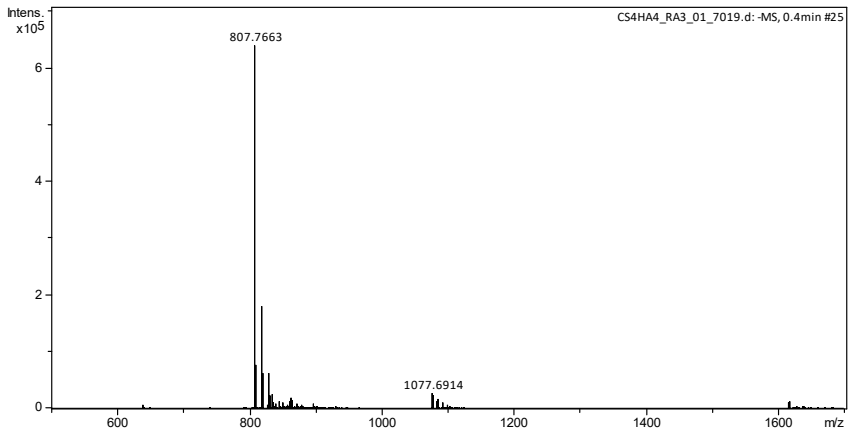

-Q ESI-MS profile of **10** (HC*HH)



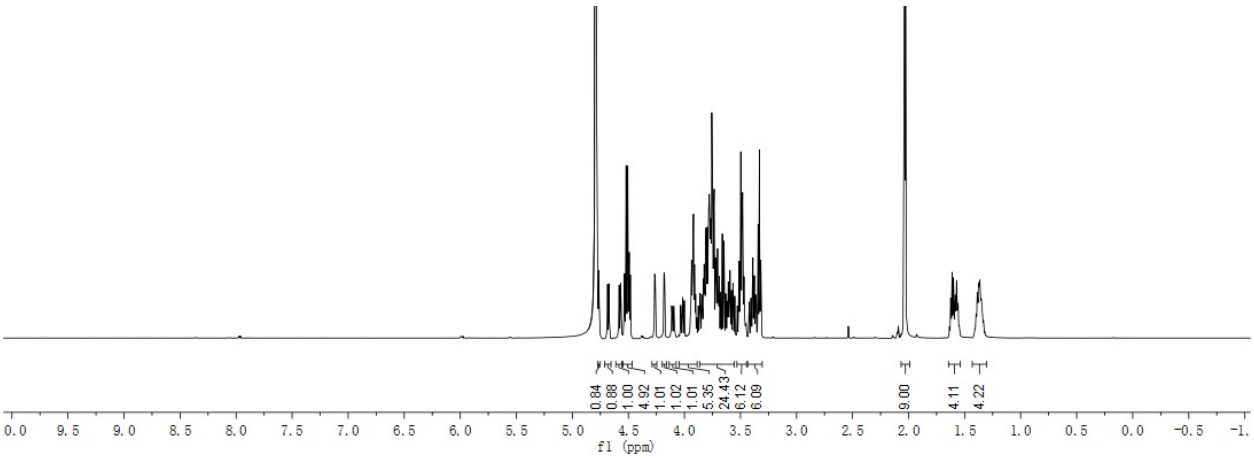

$^{1}$H NMR Spectrum of **10** (HC*HH)



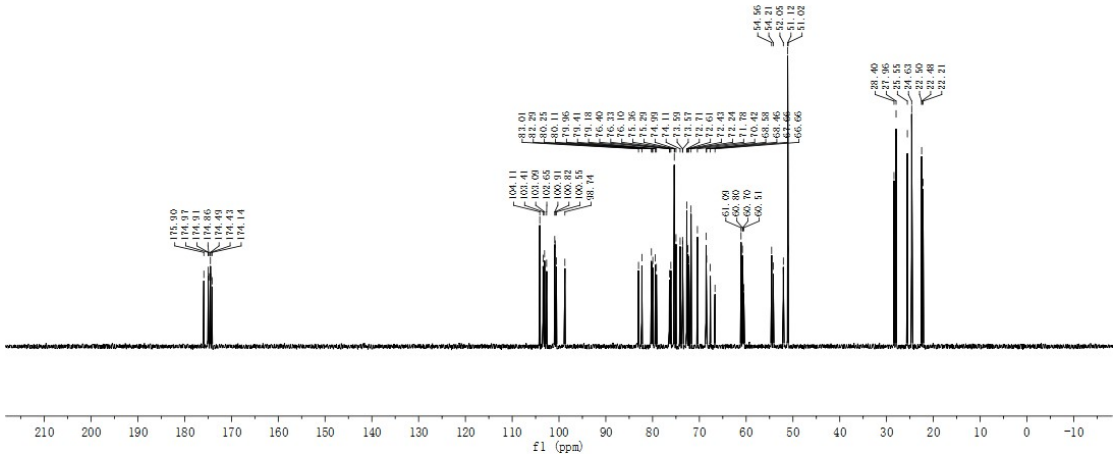

$^{1}$C NMR Spectrum of **10** (HC*HH)



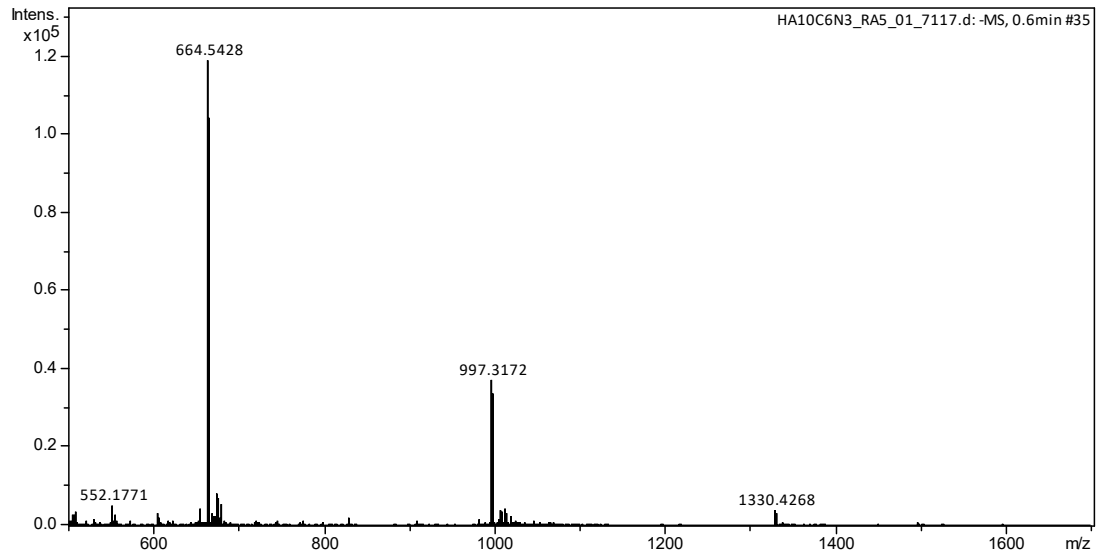

-Q ESI-MS profile of **11** (CC*HH)



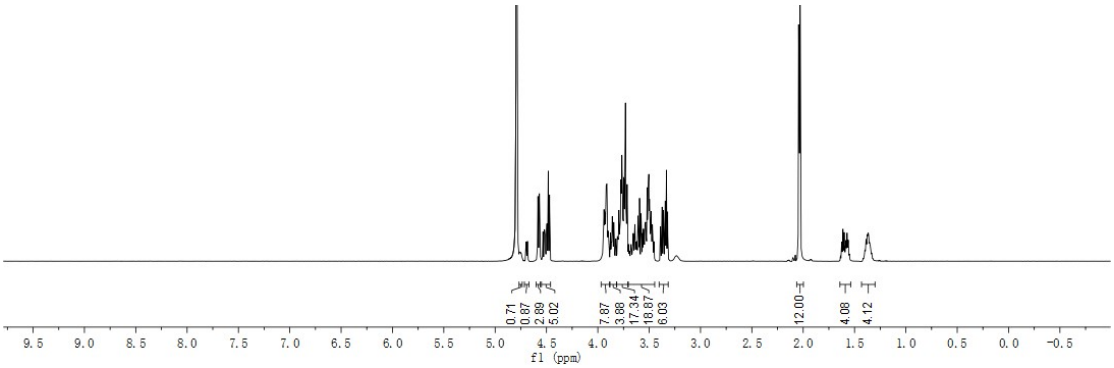

$^{1}$H NMR Spectrum of **11** (CC*HH**)**



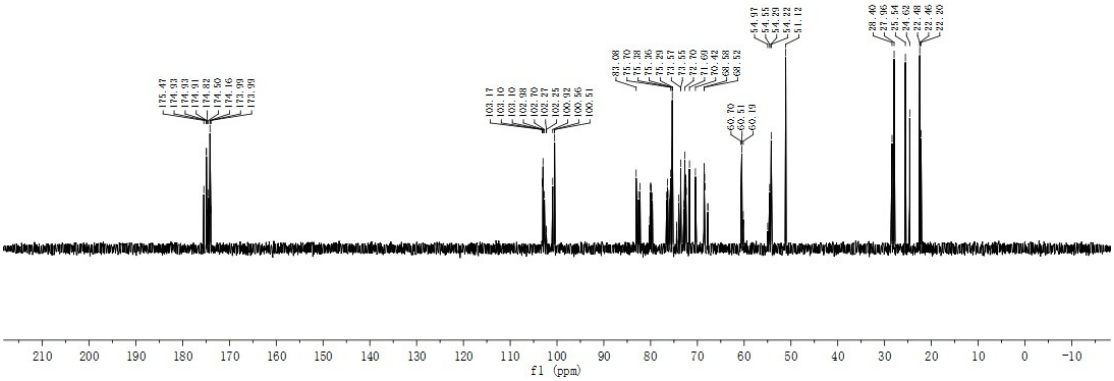

$^{1}$C NMR Spectrum of **11** (CC*HH**)**



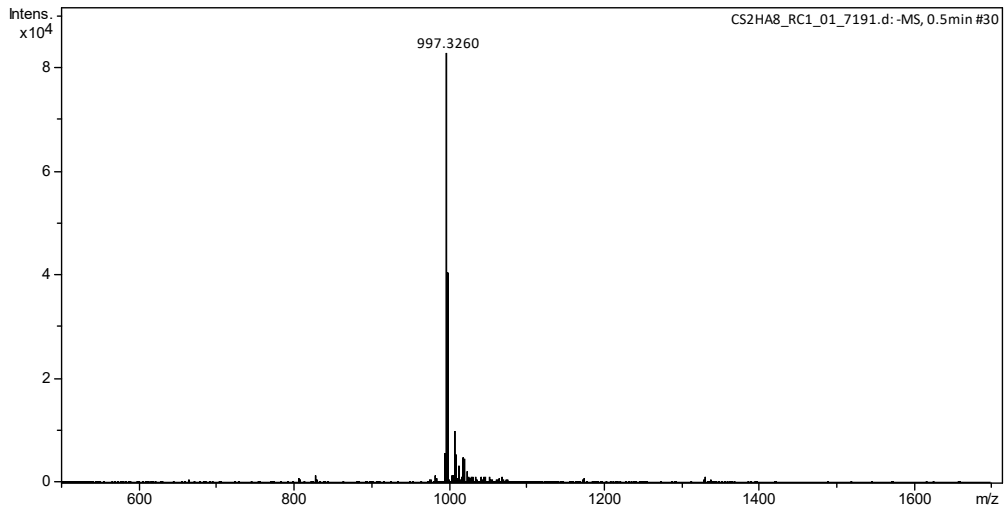

-Q ESI-MS profile of **12** (HHH*HH)



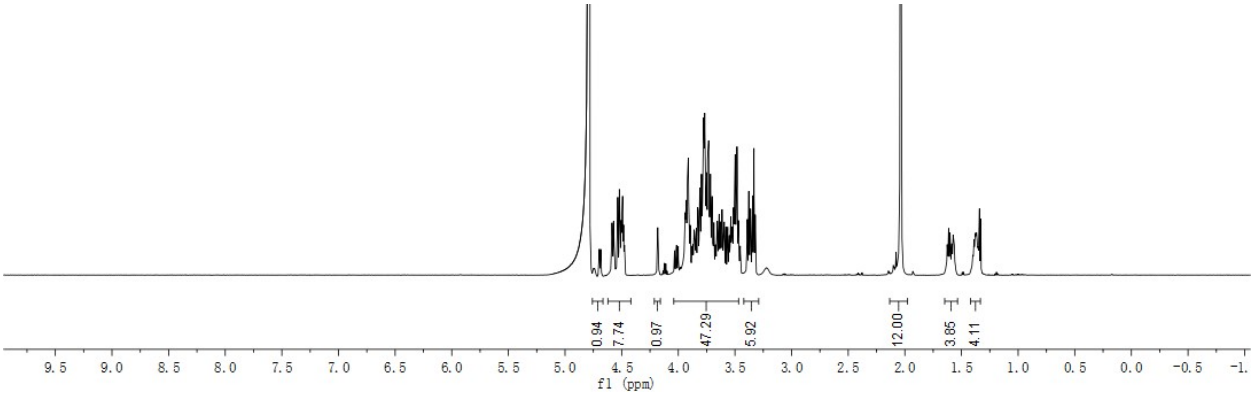

$^{1}$H NMR Spectrum of **12** (HHH*HH**)**



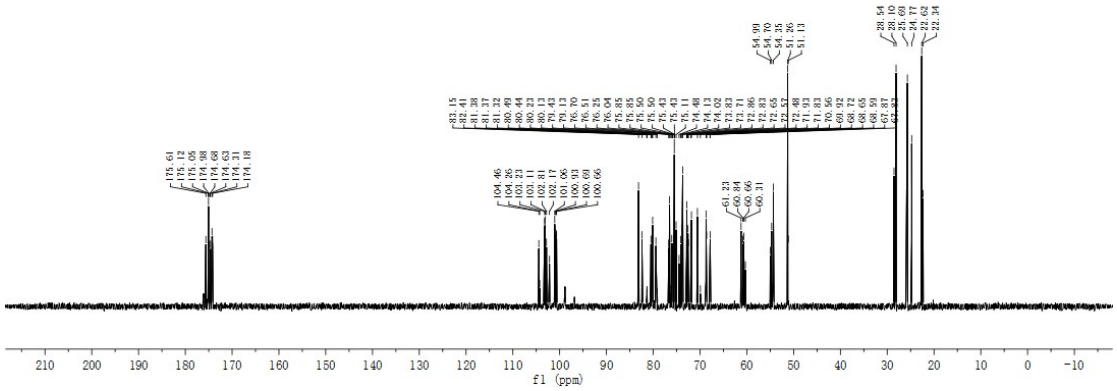

$^{1}$C NMR Spectrum of **12** (HHH*HH**)**



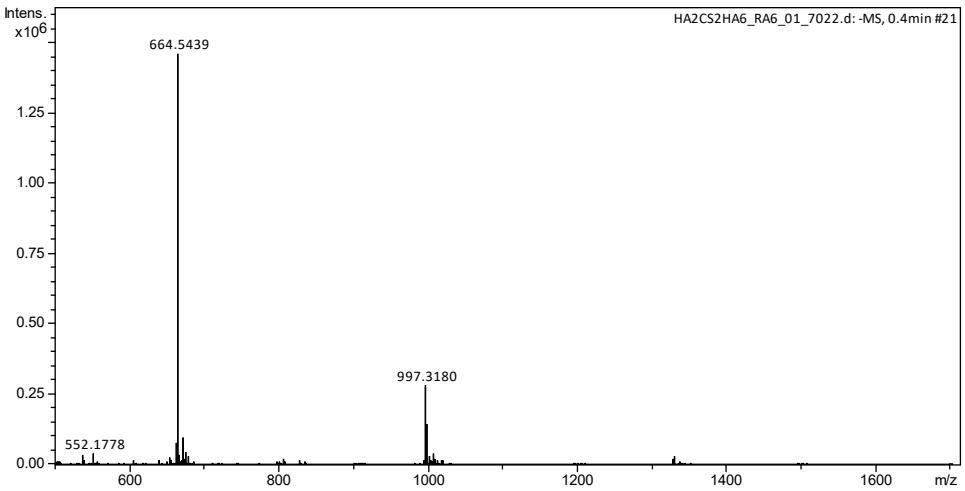

-Q ESI-MS profile of **13** (CHH*HH)



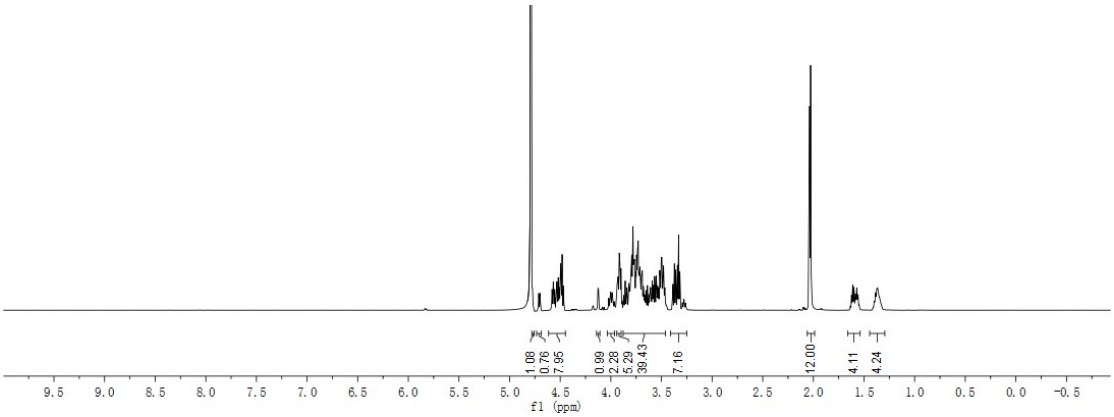

$^{1}$H NMR Spectrum of **13** (CHH*HH**)**



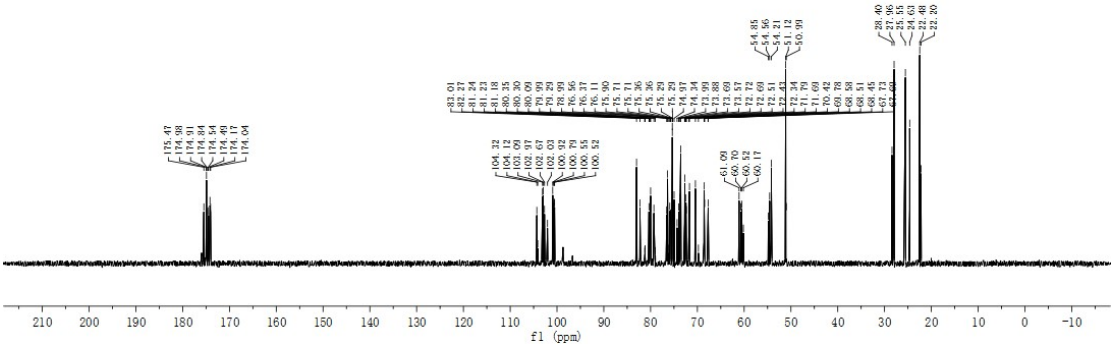

$^{1}$C NMR Spectrum of **13** (CHH*HH**)**



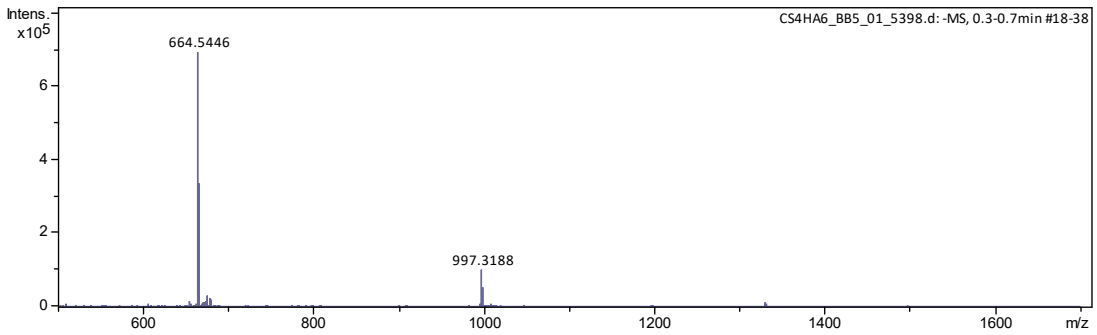

-Q ESI-MS profile of **14** (HCH*HH)



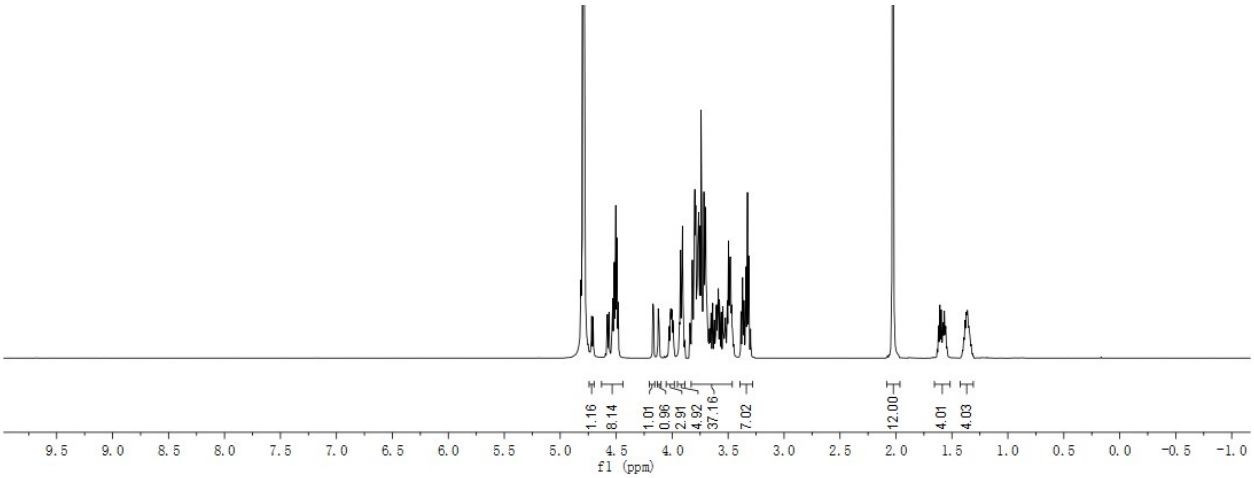

$^{1}$H NMR Spectrum of **14** (HCH*HH**)**



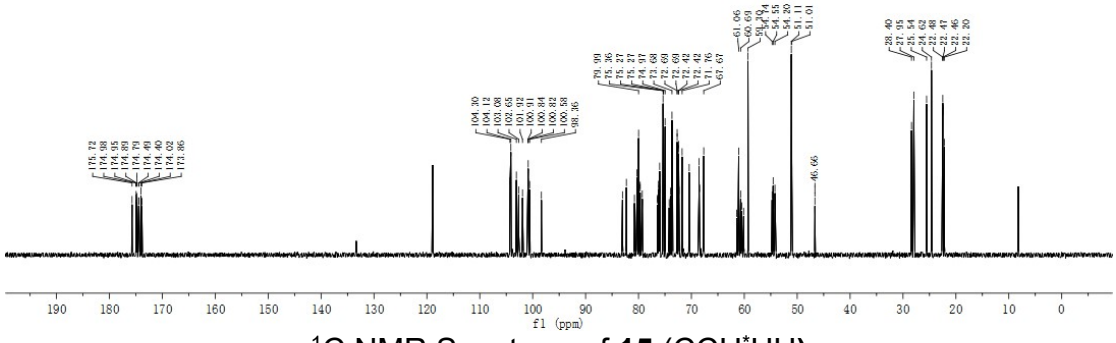

$^{1}$C NMR Spectrum of **14** (HCH*HH**)**



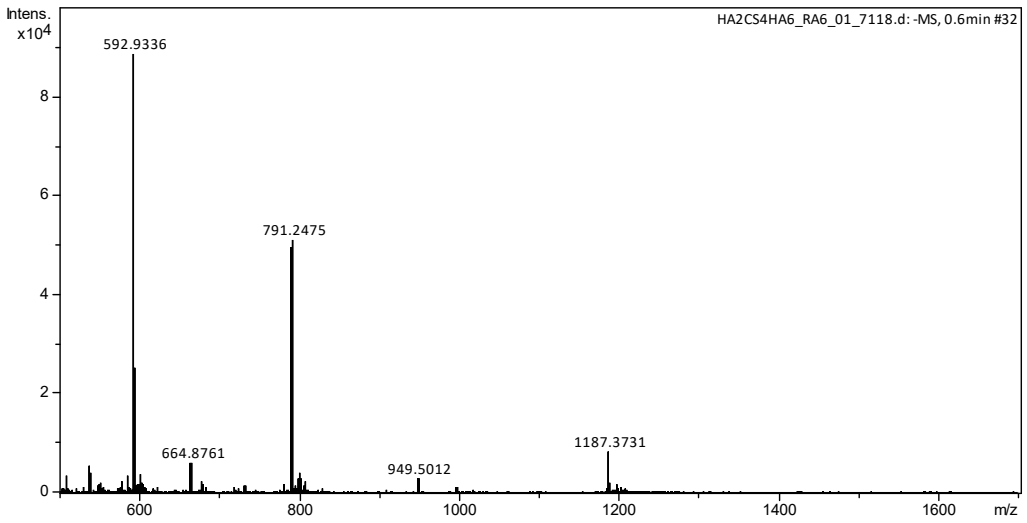

-Q ESI-MS profile of **15** (CCH*HH)



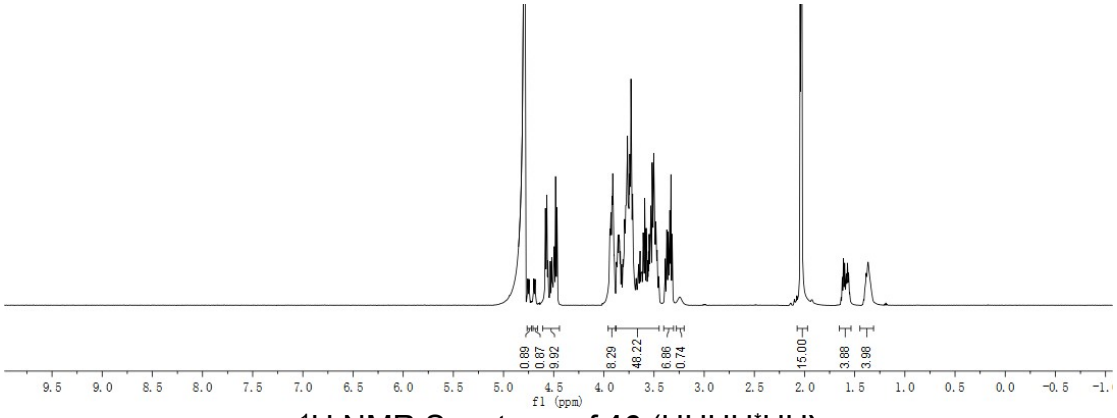

$^{1}$H NMR Spectrum of **15** (CCH*HH**)**



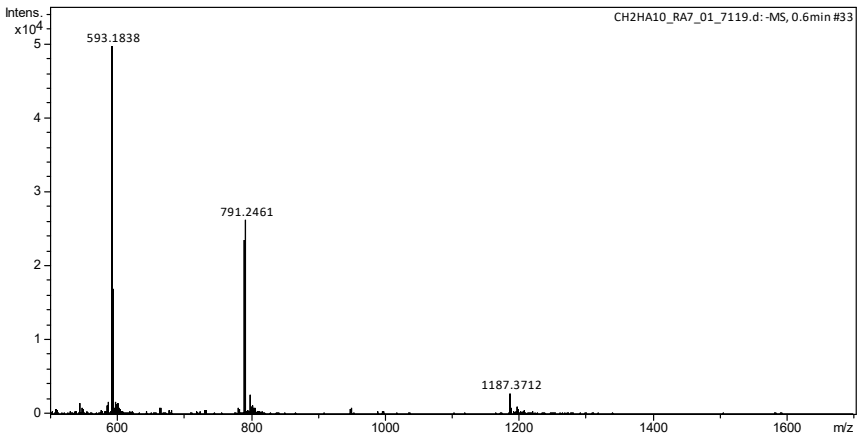

$^{1}$C NMR Spectrum of **15** (CCH*HH**)**



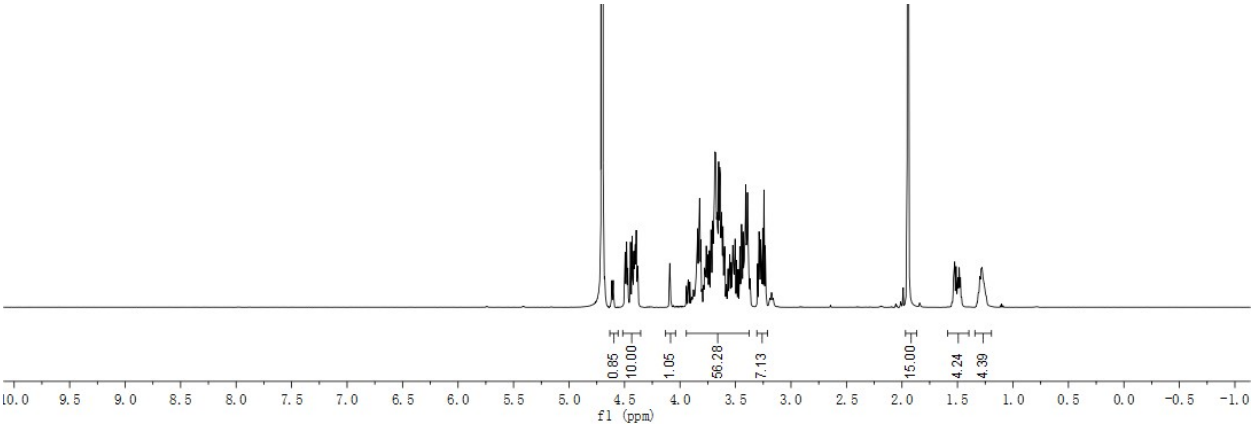

-Q ESI-MS profile of **16** (HHHH*HH)



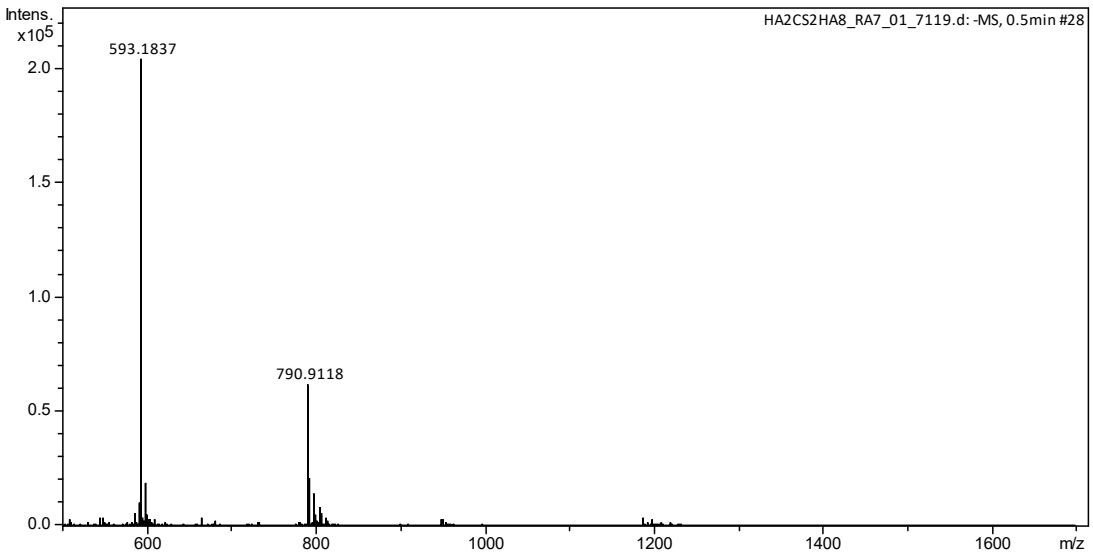

$^{1}$H NMR Spectrum of **16** (HHHH*HH**)**



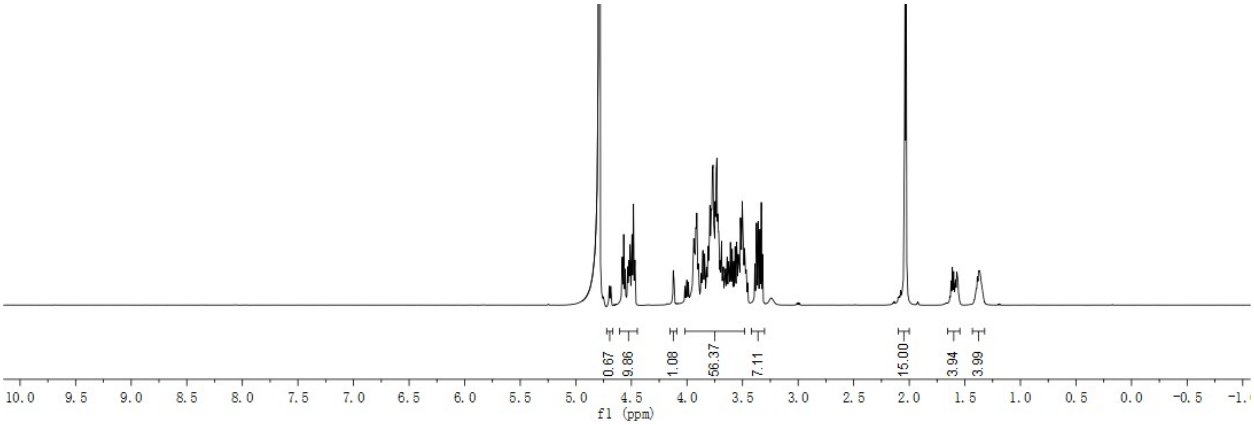

$^{-}$Q ESI-MS profile of **17** (CHHH$^{*}$HH)



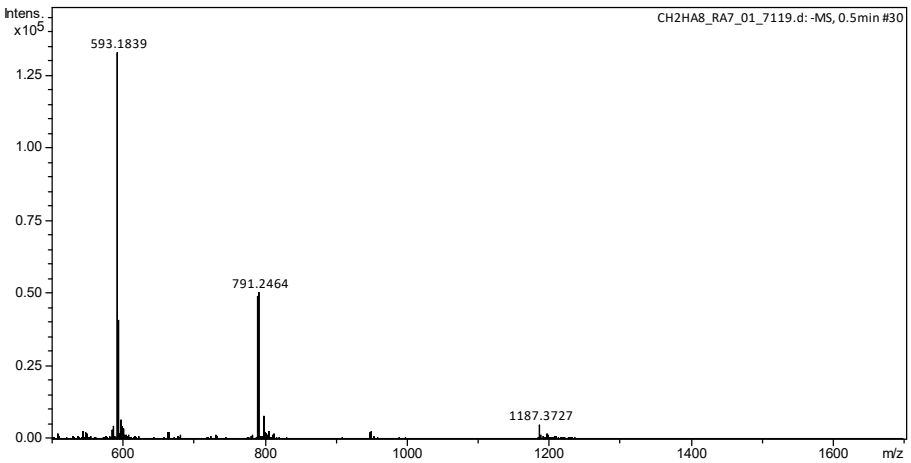

$^{1}$H NMR Spectrum of **17** (CHHH$^{*}$HH**)**



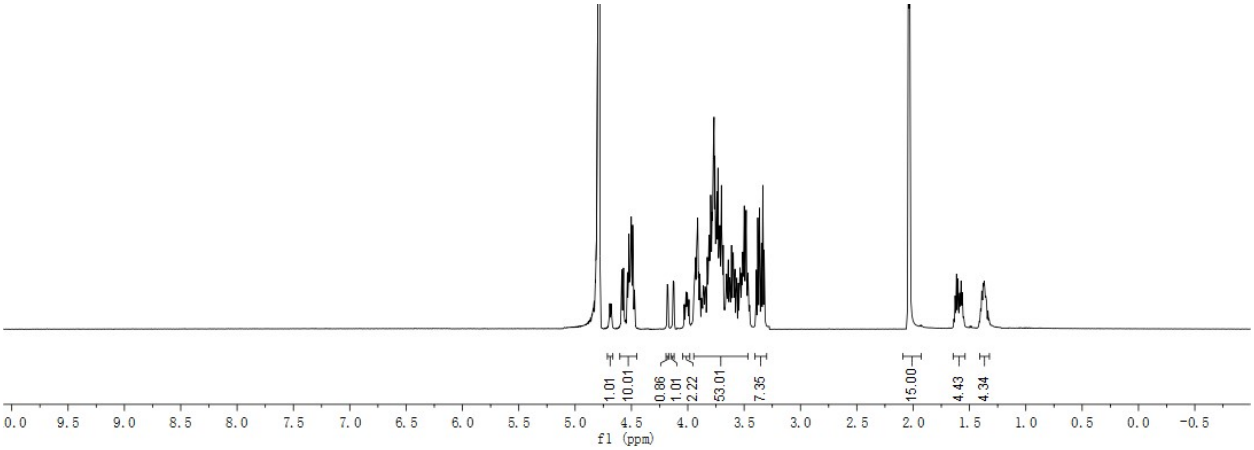

-Q ESI-MS profile of **18** (HCHH*HH)



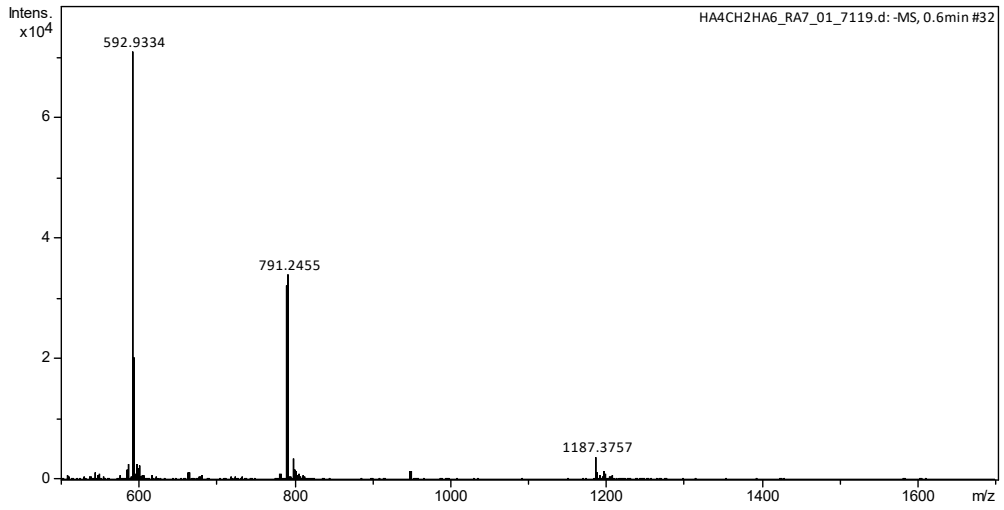

$^{1}$H NMR Spectrum of **18** (HCHH*HH**)**



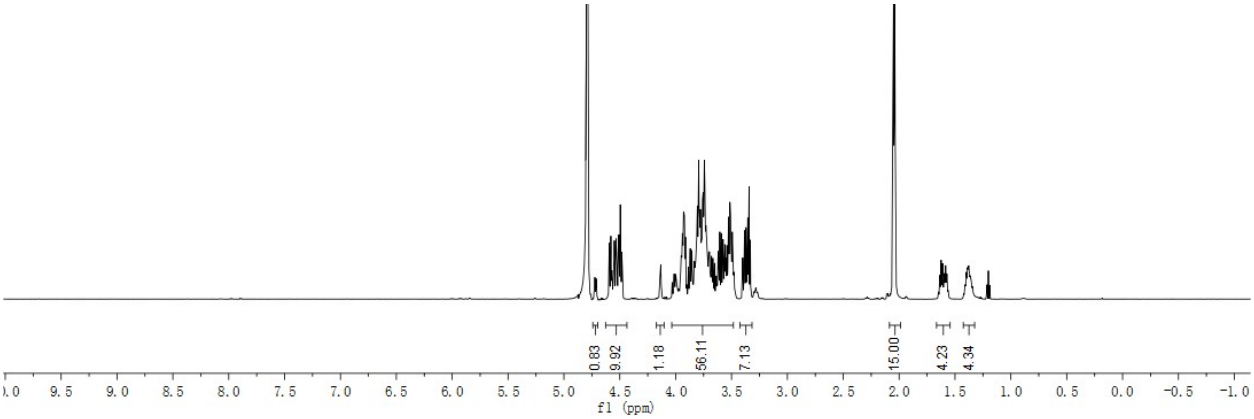

$^{-}$Q ESI-MS profile of **19** (CCHH$^{*}$HH)



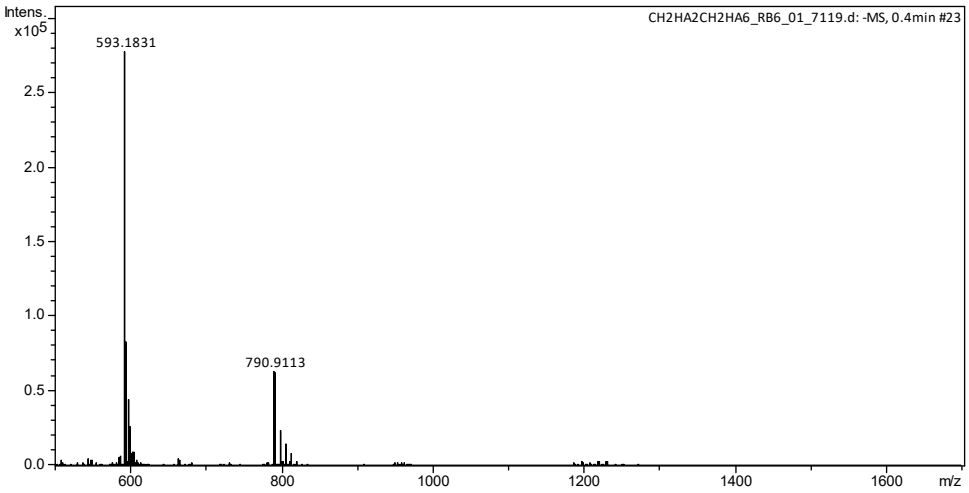

$^{1}$H NMR Spectrum of **19** (CCHH$^{*}$HH**)**



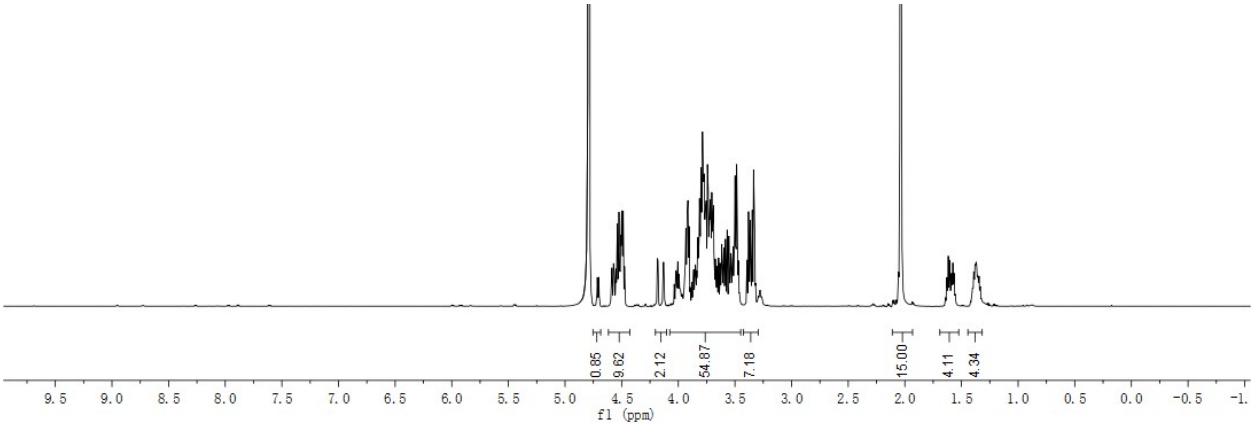

$^{-}$Q ESI-MS profile of **20** (HHCH$^{*}$HH)



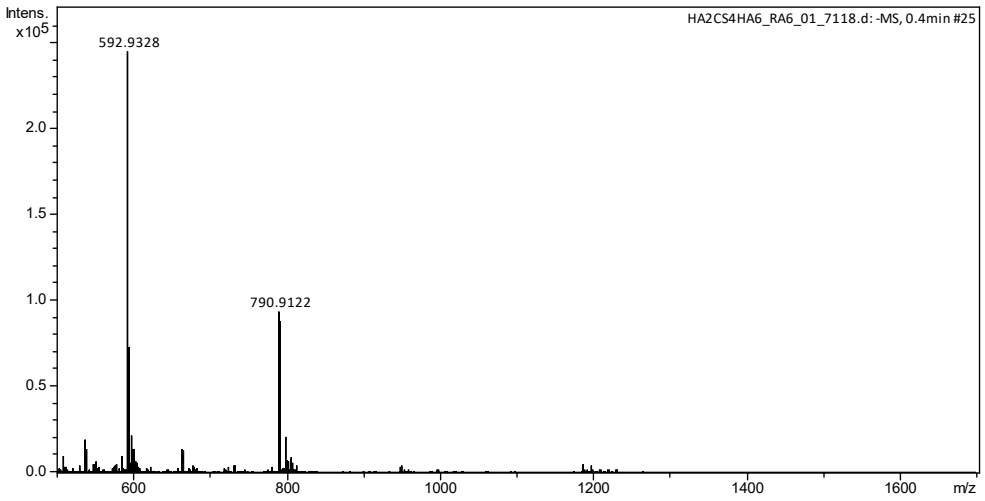

$^{1}$H NMR Spectrum of **20** (HHCH$^{*}$HH**)**



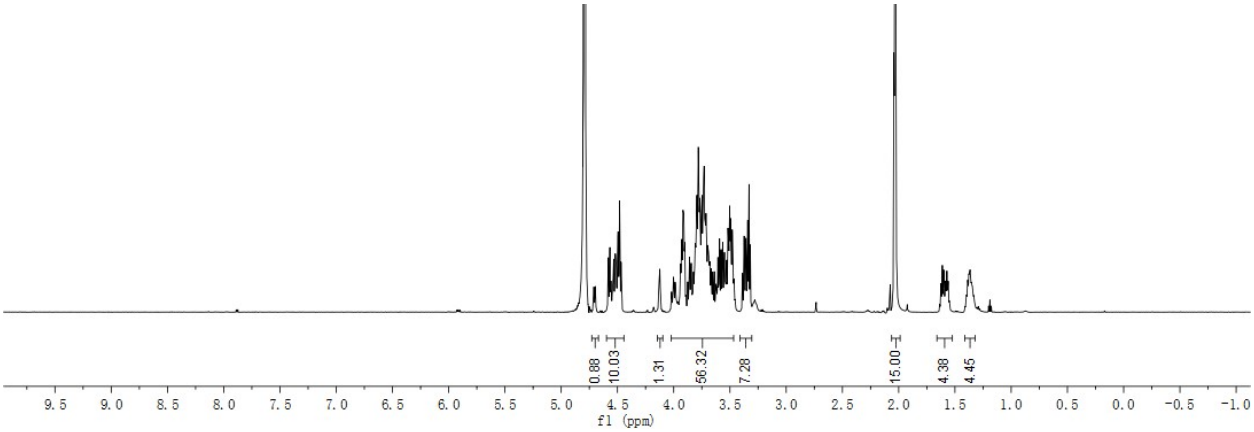

$^{-}$Q ESI-MS profile of **21** (CHCH$^{*}$HH)



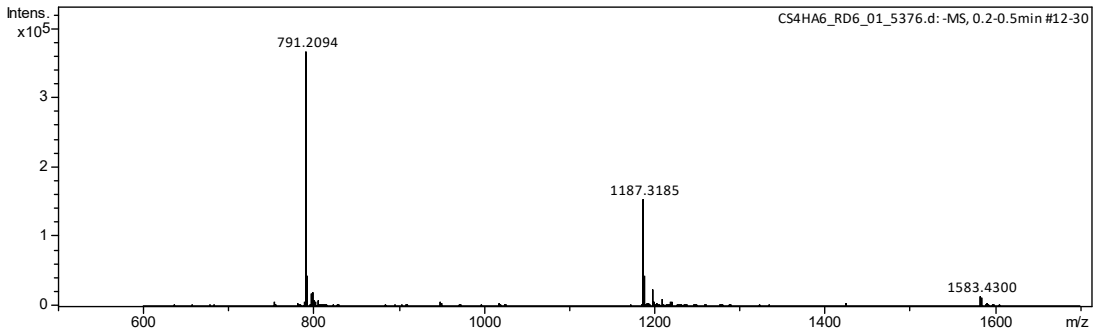

$^{1}$H NMR Spectrum of **21** (CHCH$^{*}$HH**)**



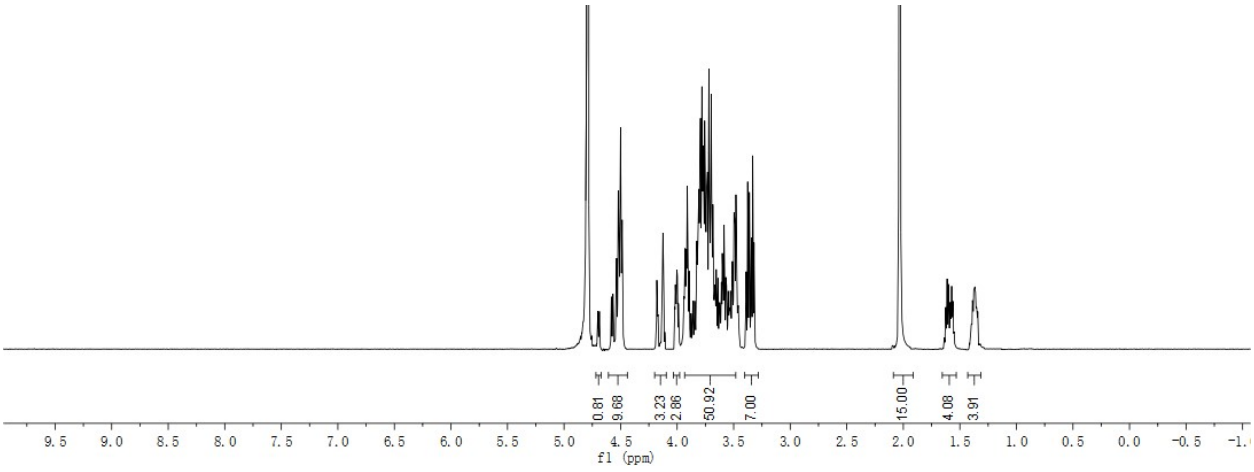

-Q ESI-MS profile of **22** (HCCH*HH)



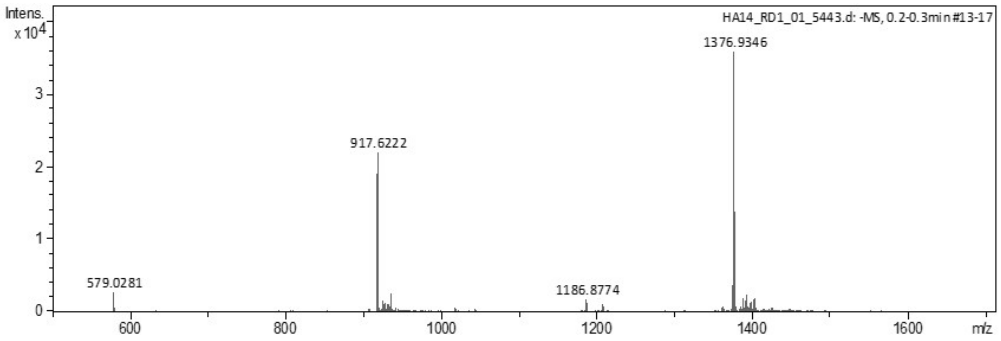

$^{1}$H NMR Spectrum of **22** (HCCH*HH**)**



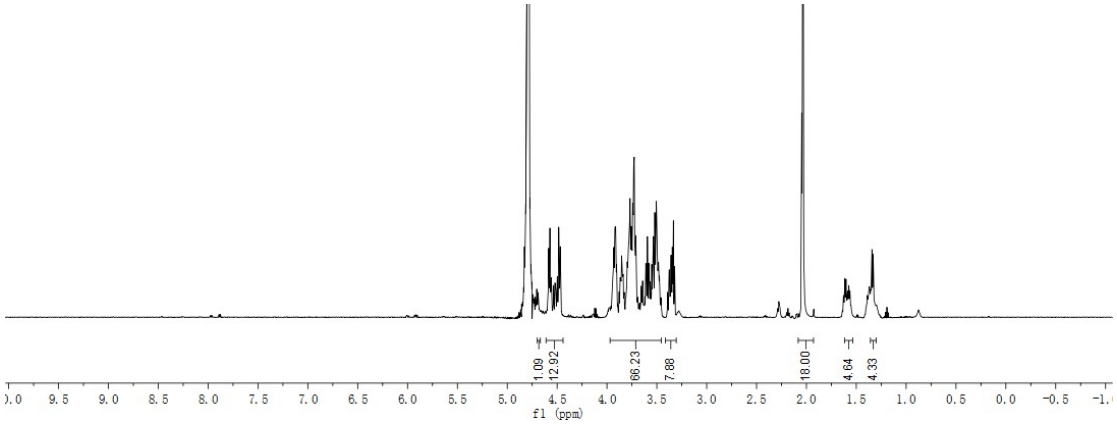

$^{-}$Q ESI-MS profile of **23** (CCCH$^{*}$HH)



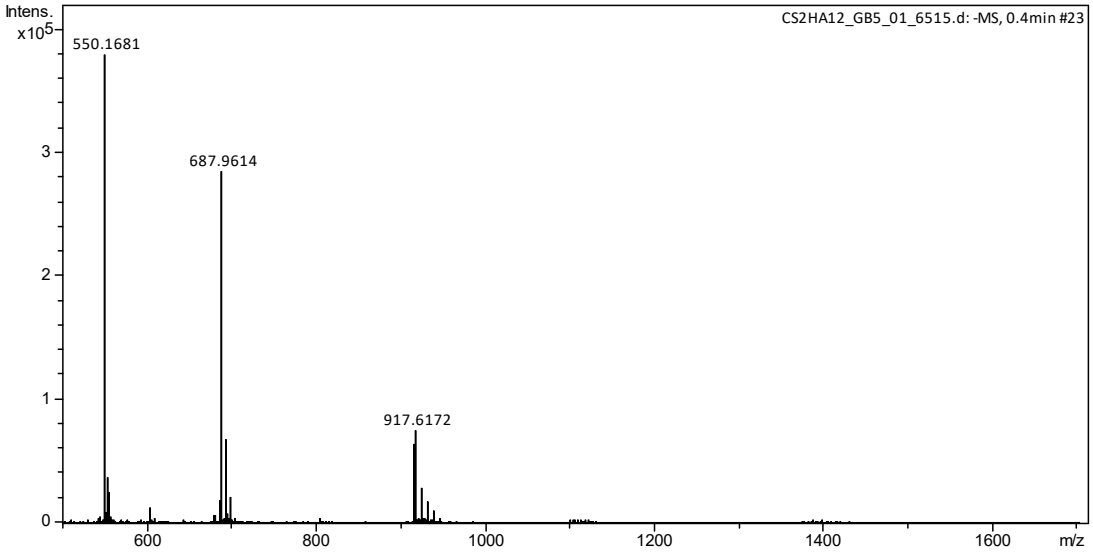

$^{1}$H NMR Spectrum of **23** (CCCH$^{*}$HH**)**



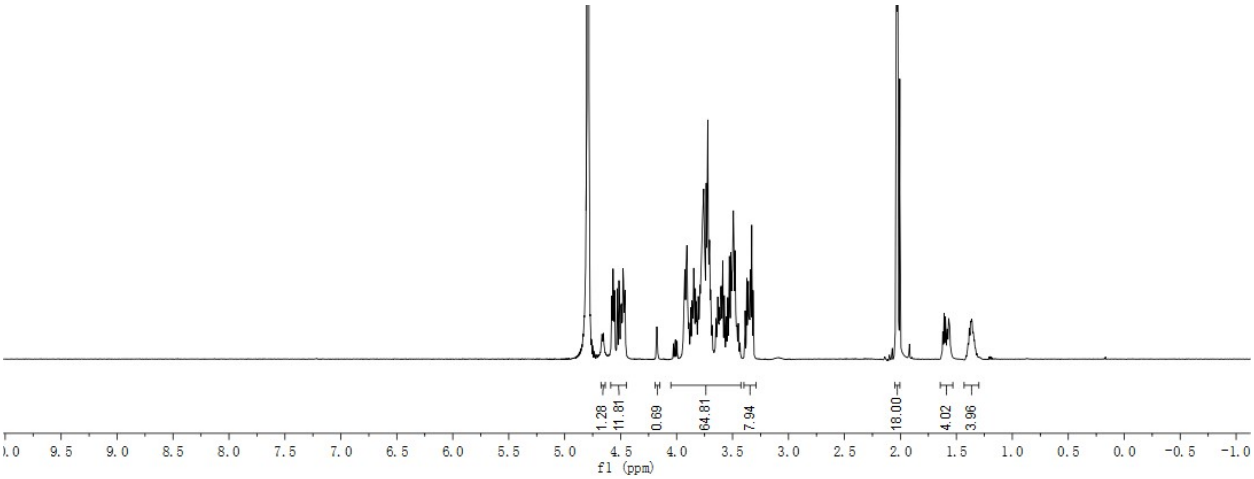

-Q ESI-MS profile of **24** (HHHHH*HH)



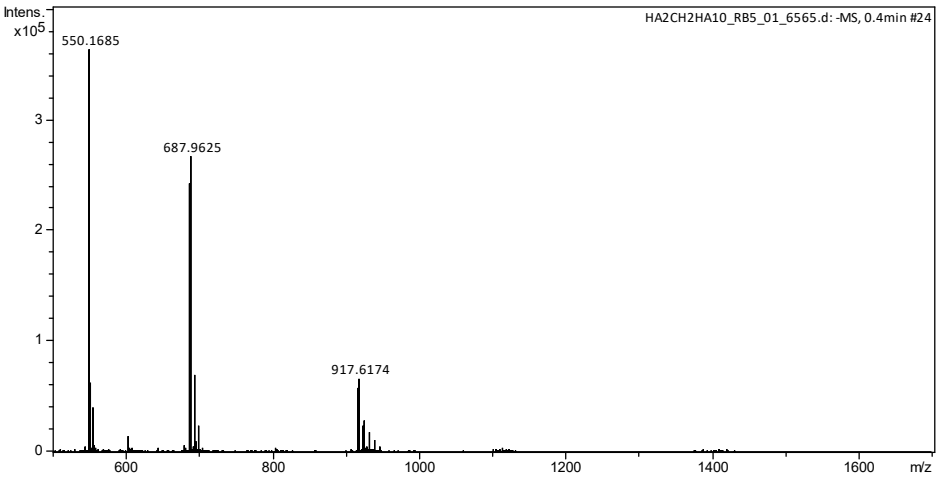

$^{1}$H NMR Spectrum of **24** (HHHHH*HH**)**



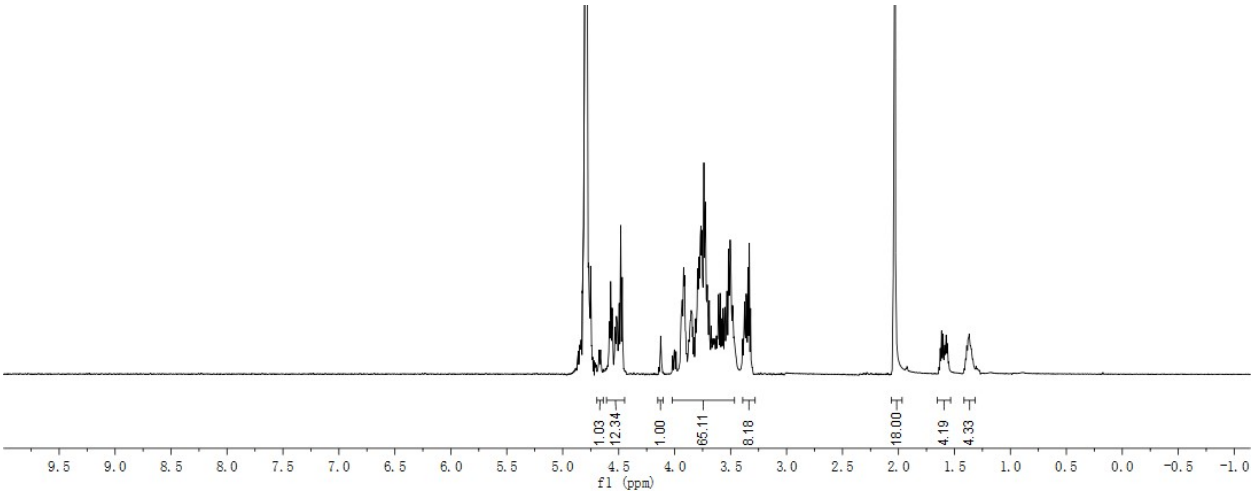

$^{-}$Q ESI-MS profile of **25** (CHHHH$^{*}$HH)



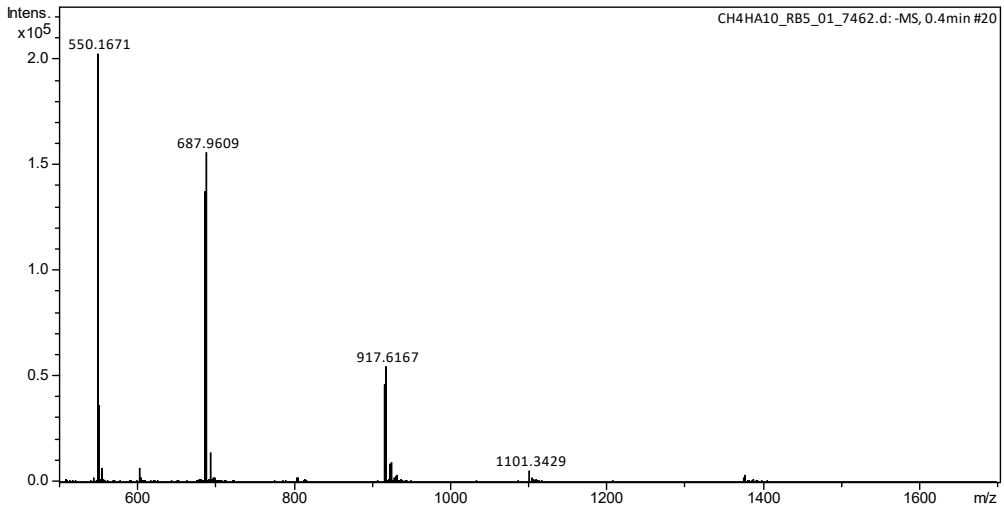

$^{1}$H NMR Spectrum of **25** (CHHHH$^{*}$HH**)**



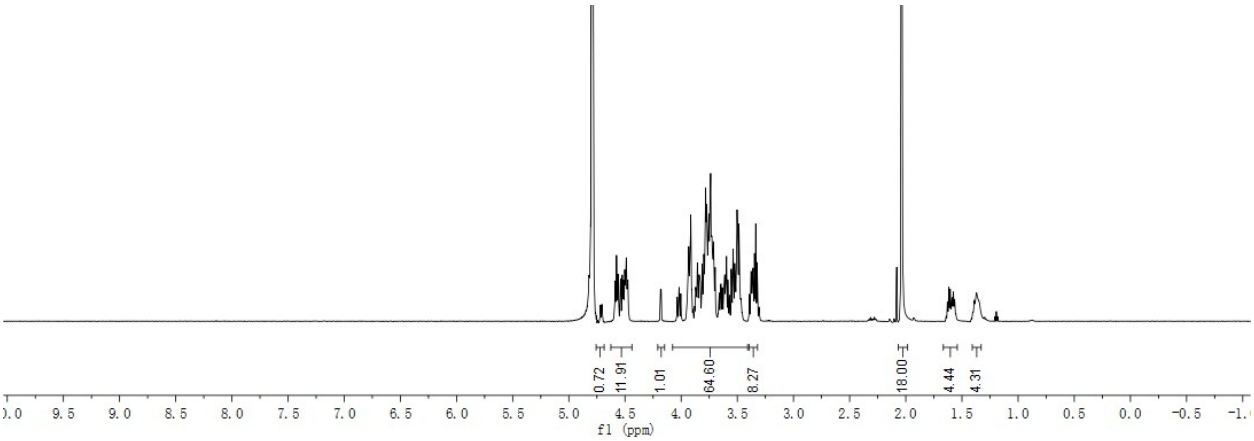

$^{-}$Q ESI-MS profile of **26** (HCHHH$^{*}$HH)



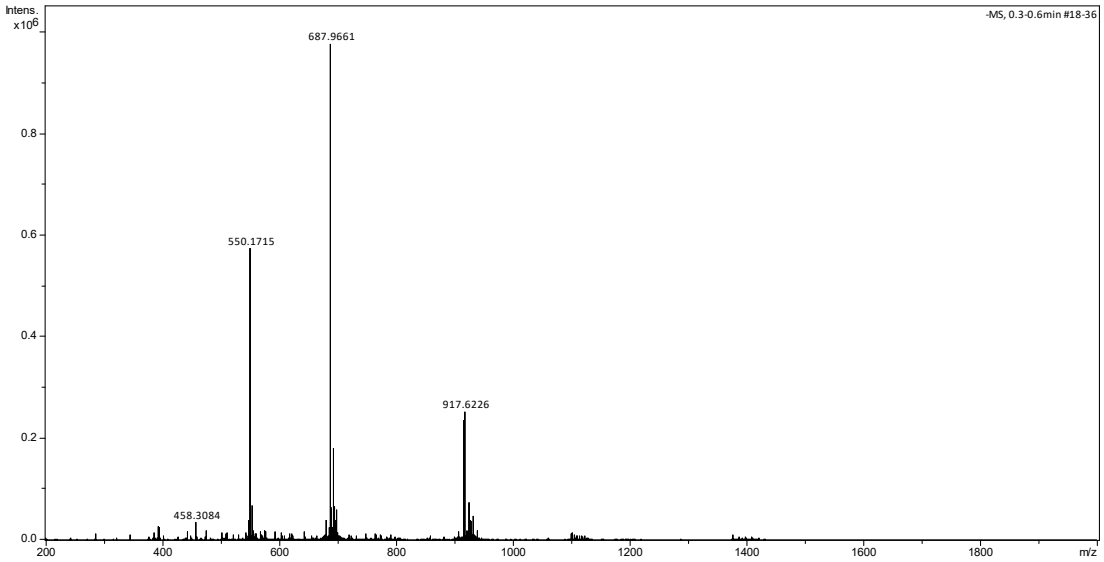

$^{1}$H NMR Spectrum of **26** (HCHHH$^{*}$HH**)**



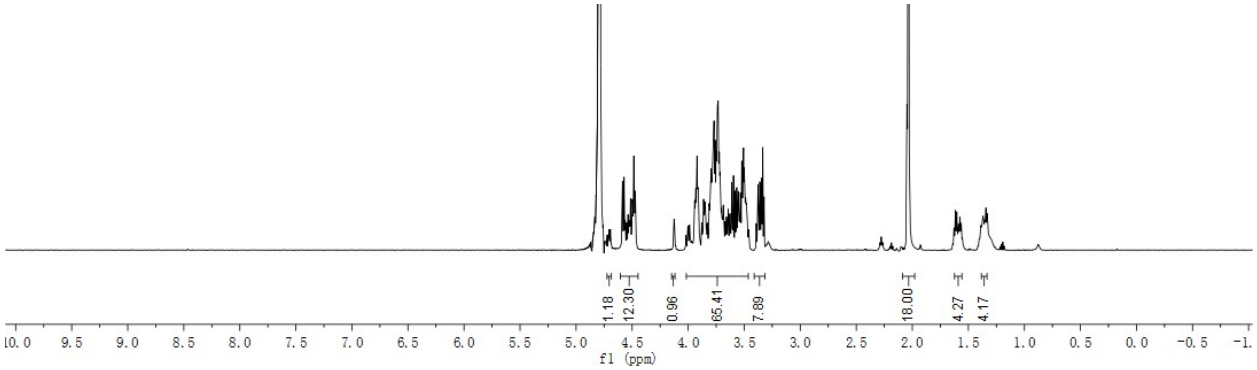

$^{-}$Q ESI-MS profile of **27** (CCHHH$^{*}$HH)



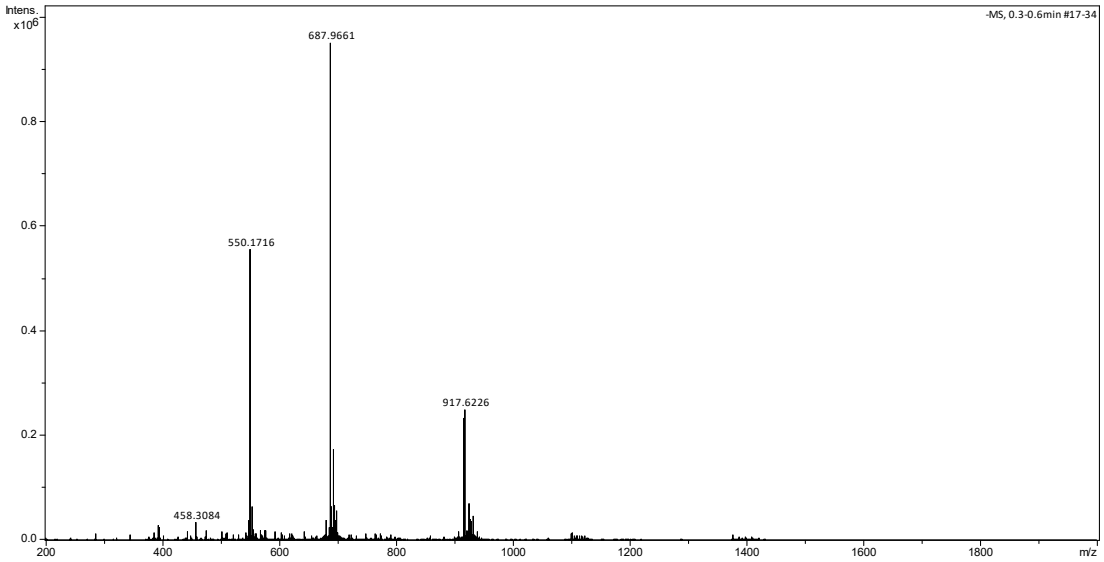

$^{1}$H NMR Spectrum of **27** (CCHHH$^{*}$HH**)**



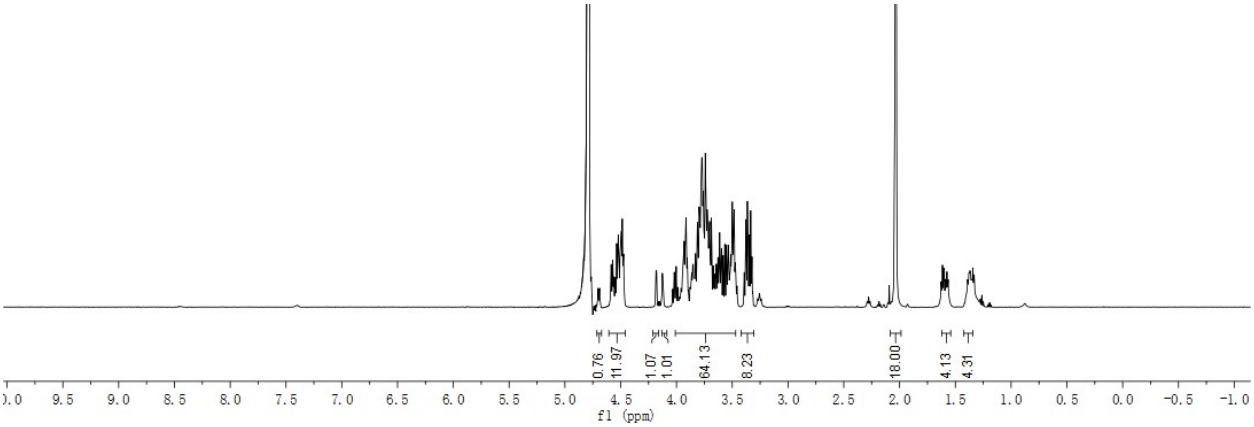

-Q ESI-MS profile of **28** (HHCHH*HH)



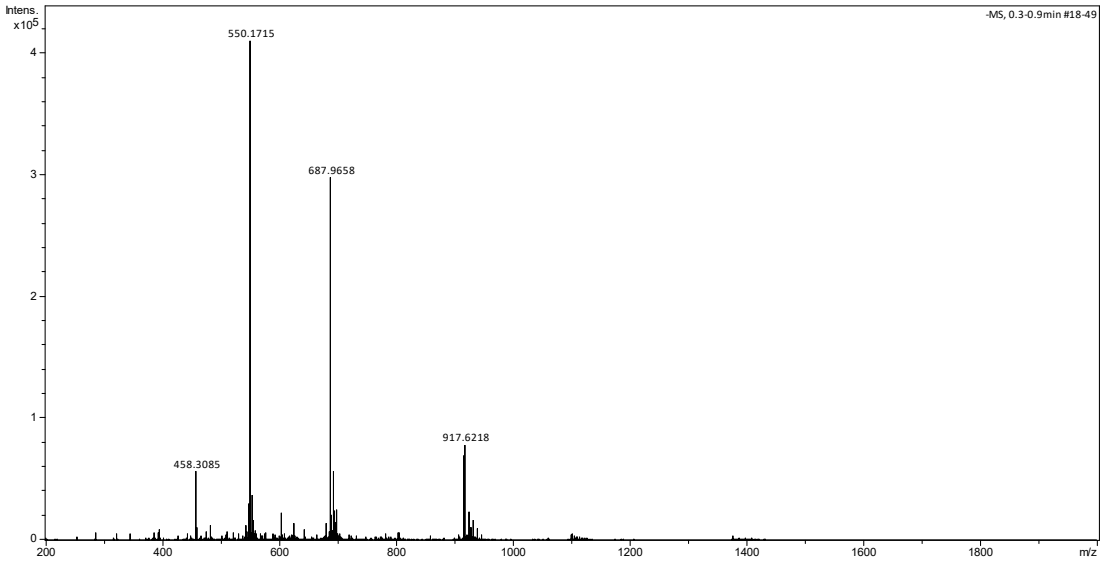

$^{1}$H NMR Spectrum of **28** (HHCHH*HH**)**



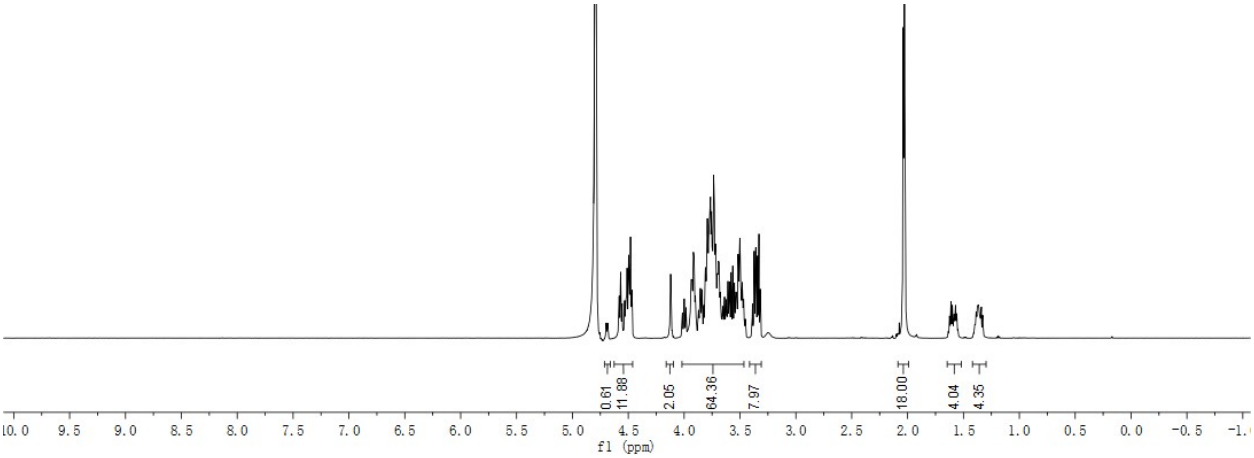

$^{-}$Q ESI-MS profile of **29** (CHCHH$^{*}$HH)



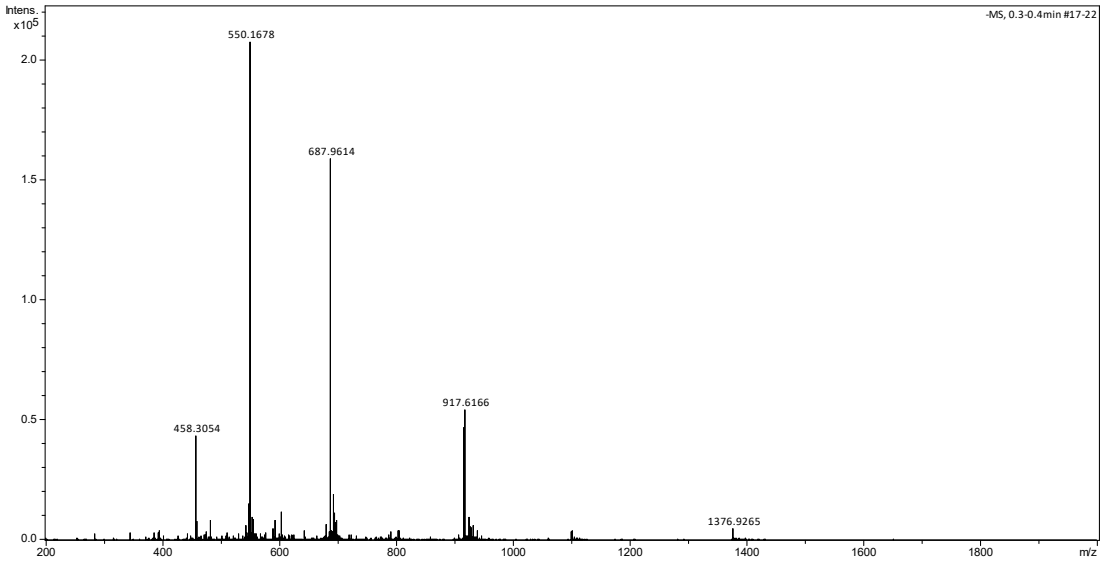

$^{1}$H NMR Spectrum of **29** (CHCHH$^{*}$HH**)**



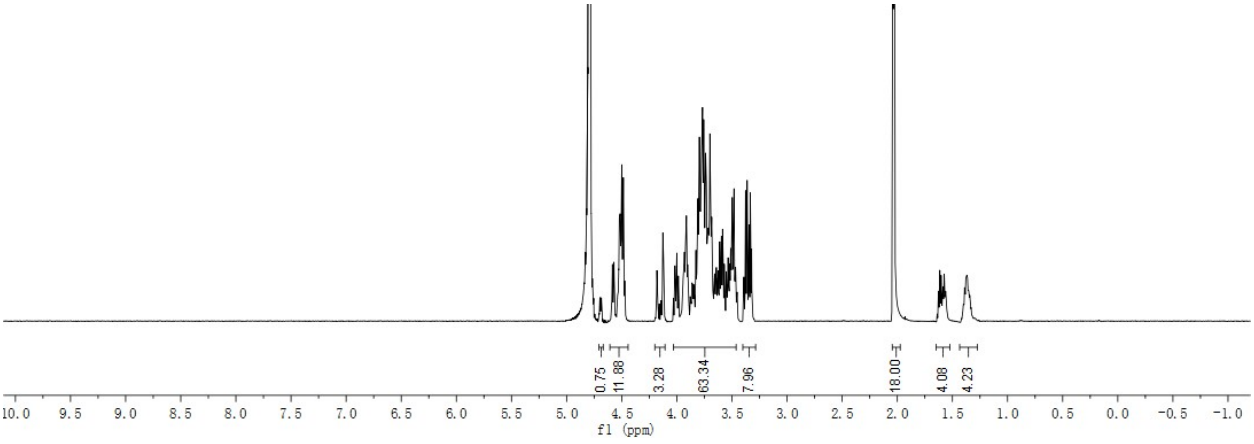

-Q ESI-MS profile of **30** (HCCHH*HH)



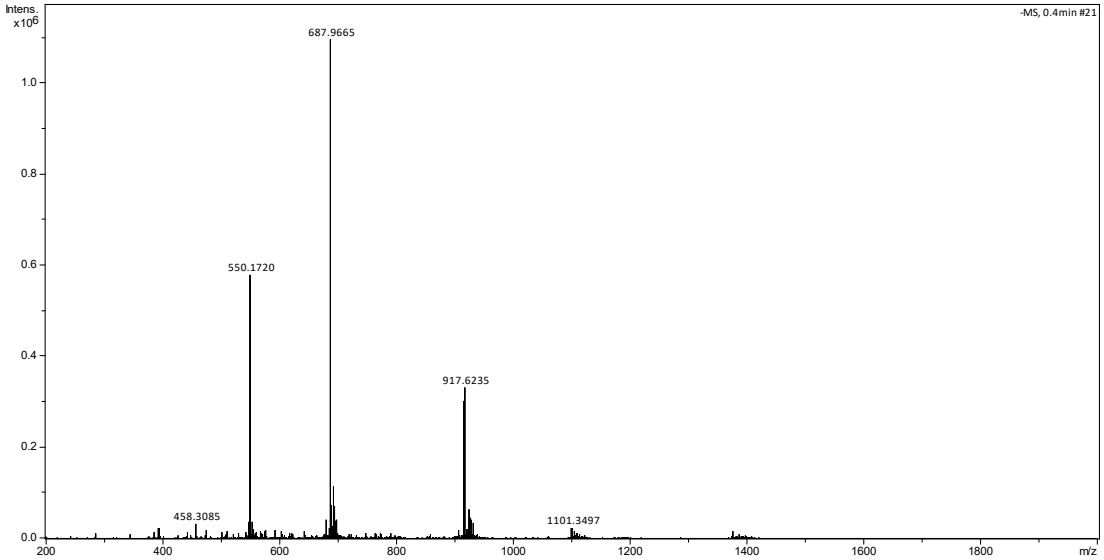

$^1$H NMR Spectrum of **30** (HCCHH*HH**)**



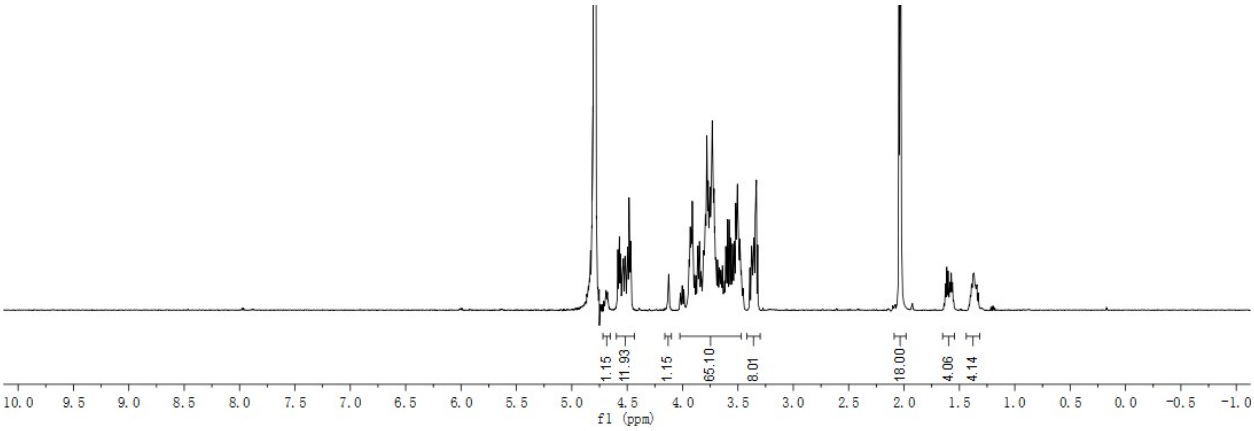

$^{-}$Q ESI-MS profile of **31** (CCCHH$^{*}$HH)



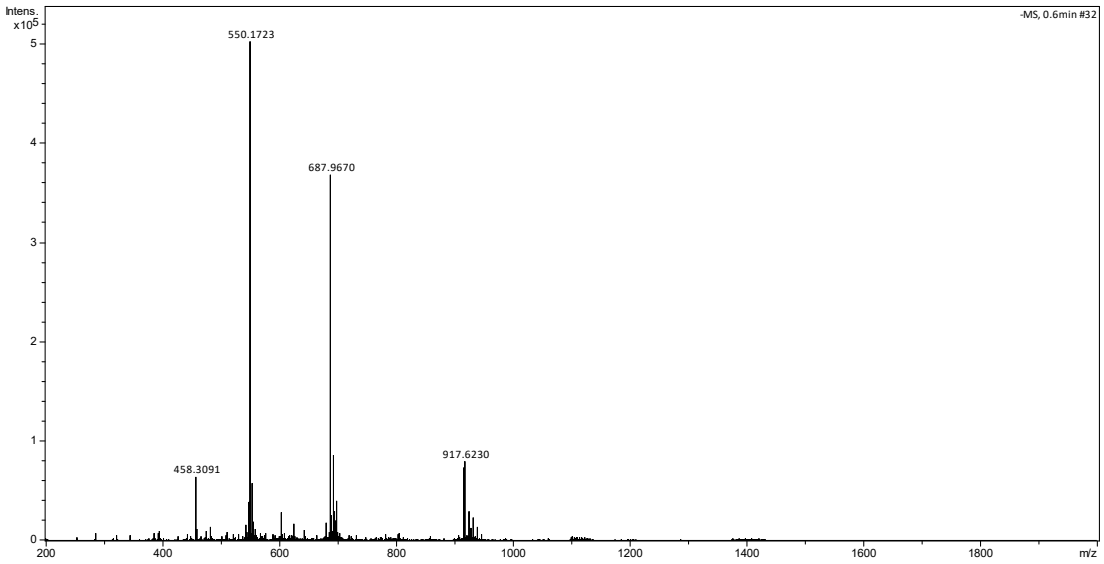

$^{1}$H NMR Spectrum of **31** (CCCHH$^{*}$HH**)**



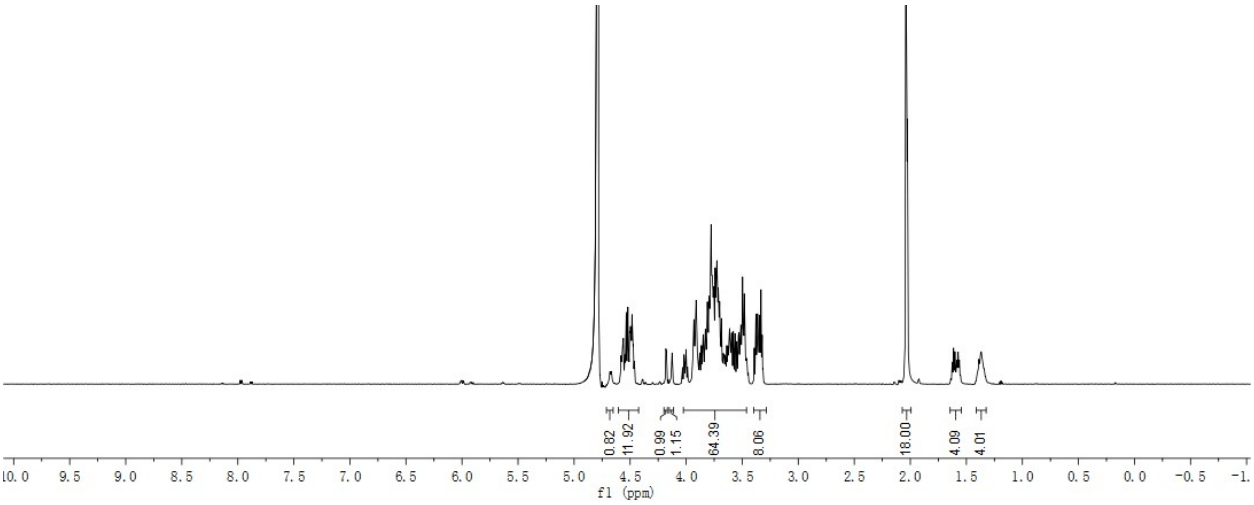

$^{-}$Q ESI-MS profile of **32** (HHHCH$^{*}$HH)



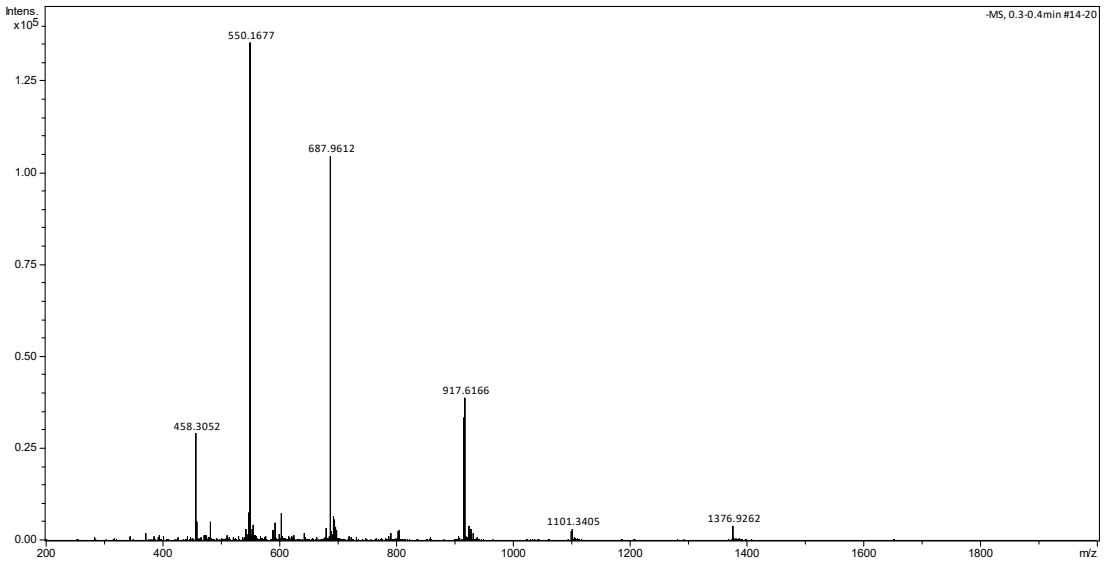

$^{1}$H NMR Spectrum of **32** (HHHCH$^{*}$HH**)**



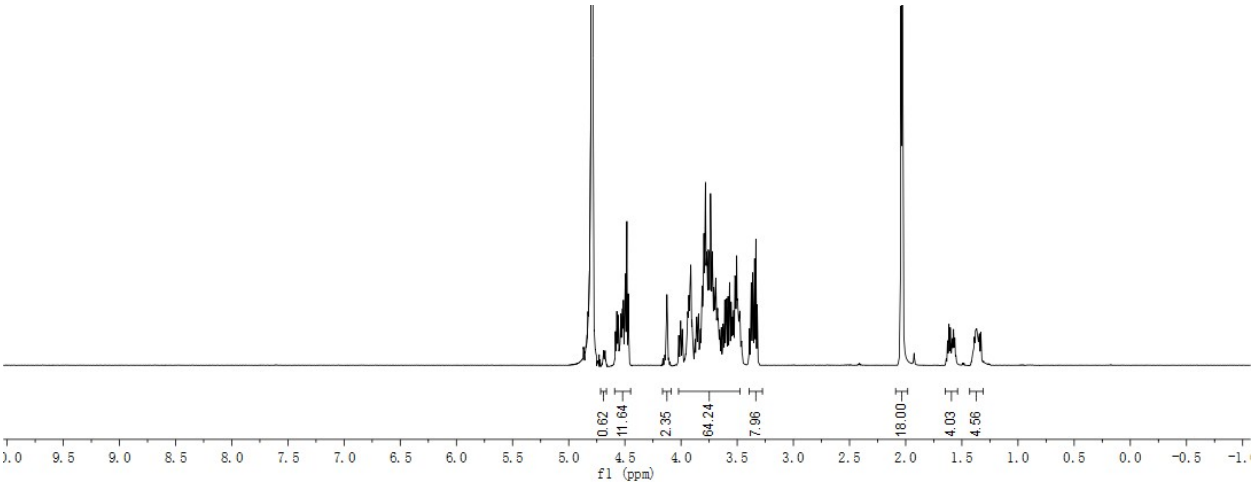

$^{-}$Q ESI-MS profile of **33** (CHHCH$^{*}$HH)



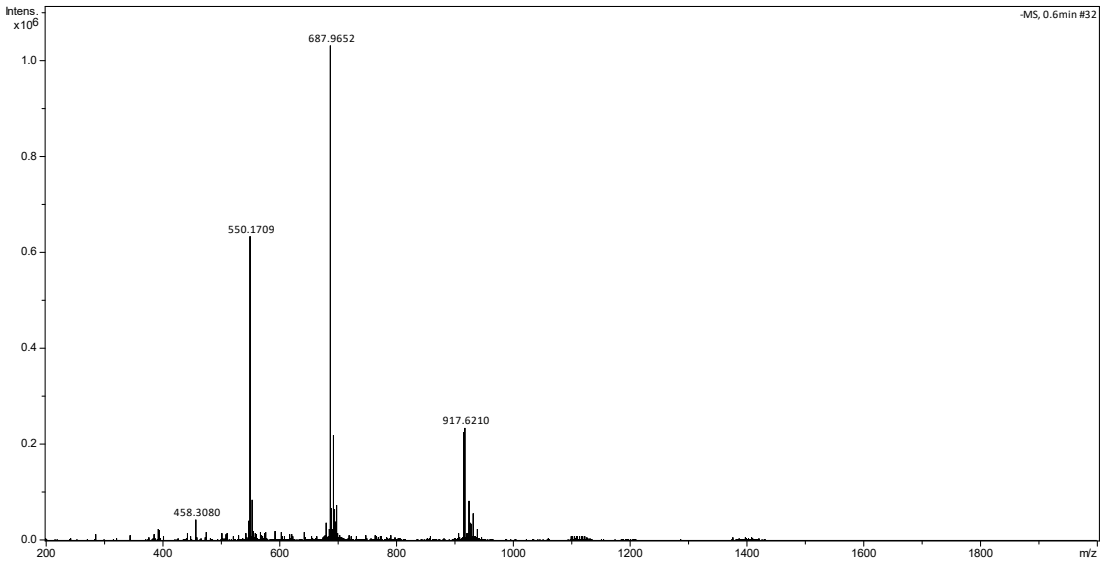

$^{1}$H NMR Spectrum of **33** (CHHCH$^{*}$HH**)**



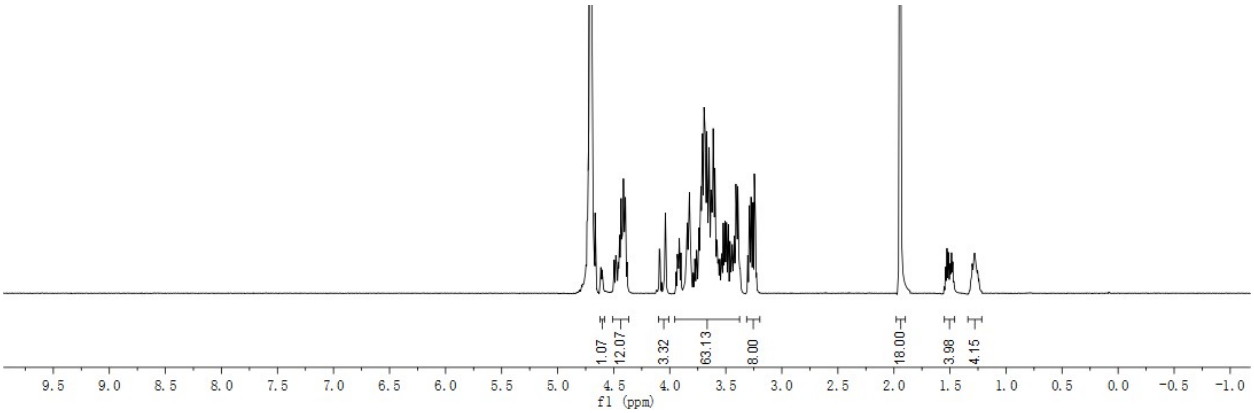

$^{-}$Q ESI-MS profile of **34** (HCHCH$^{*}$HH)



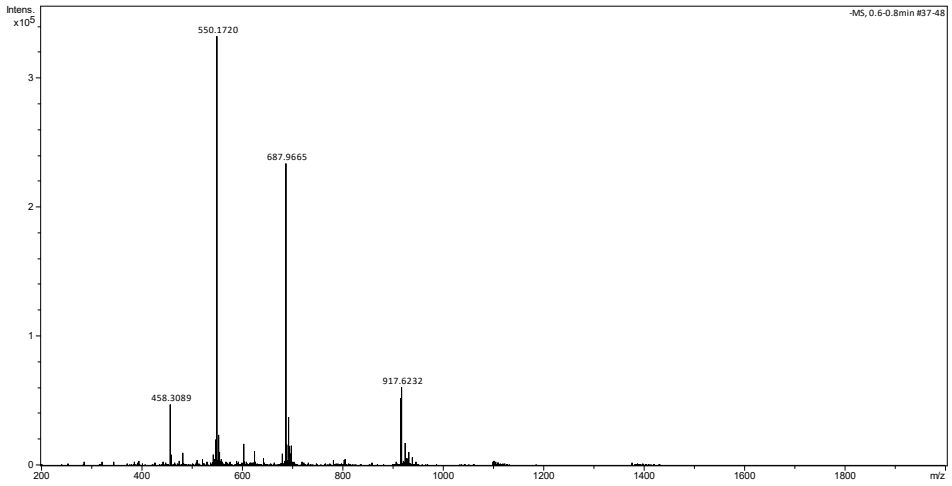

$^{1}$H NMR Spectrum of **34** (HCHCH$^{*}$HH**)**



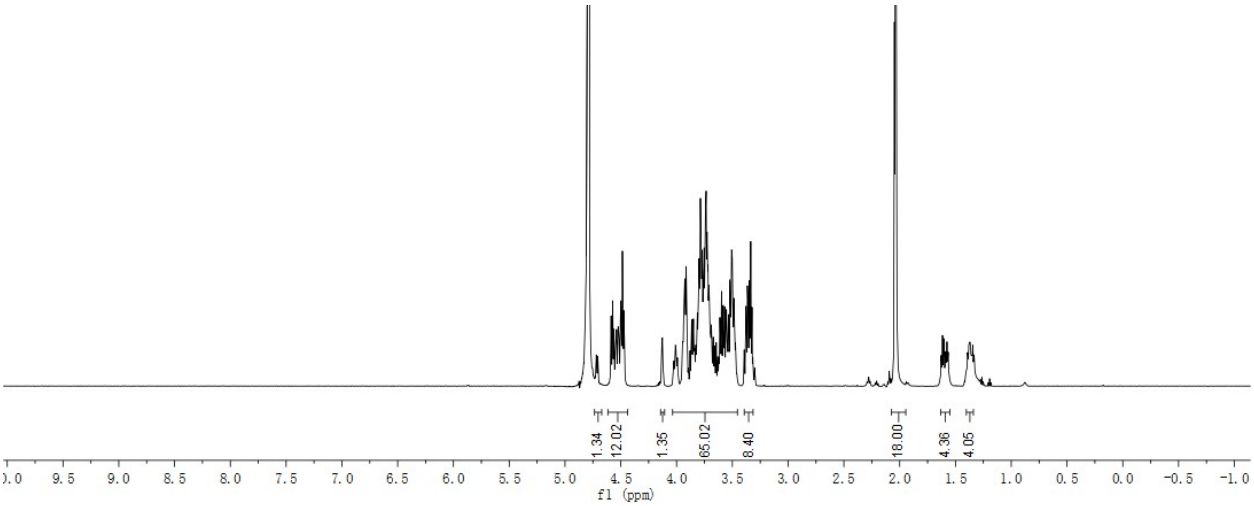

$^{-}$Q ESI-MS profile of **35** (CCHCH$^{*}$HH)



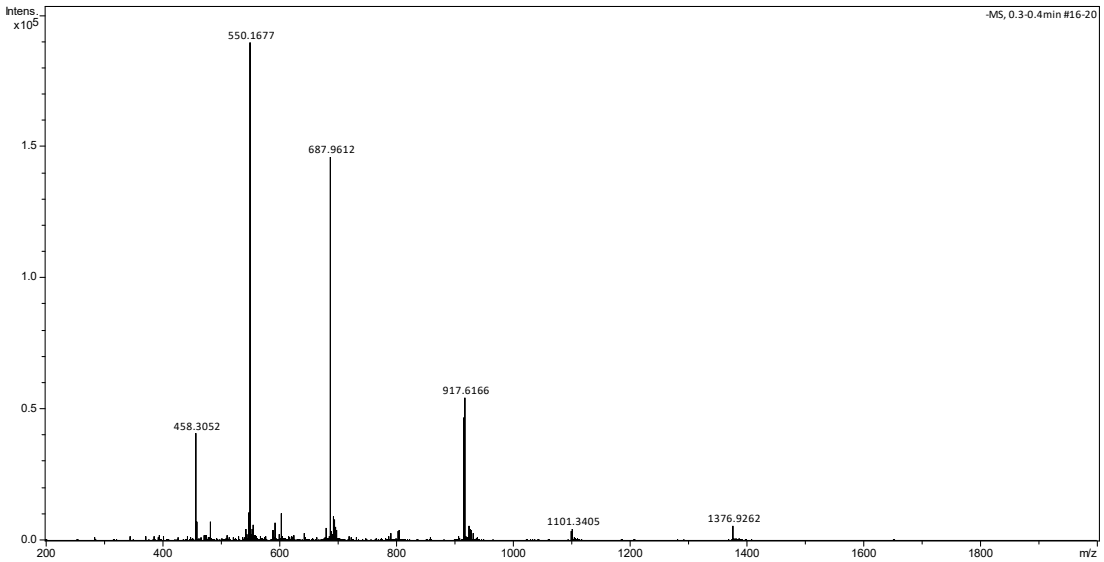

$^{1}$H NMR Spectrum of **35** (CCHCH$^{*}$HH**)**



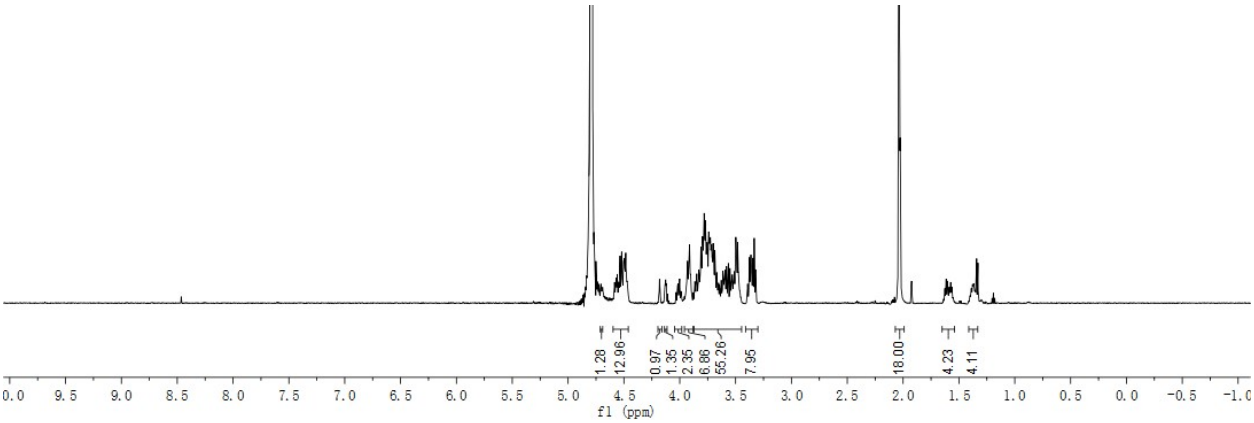

$^{-}$Q ESI-MS profile of **36** (HHCCH$^{*}$HH)



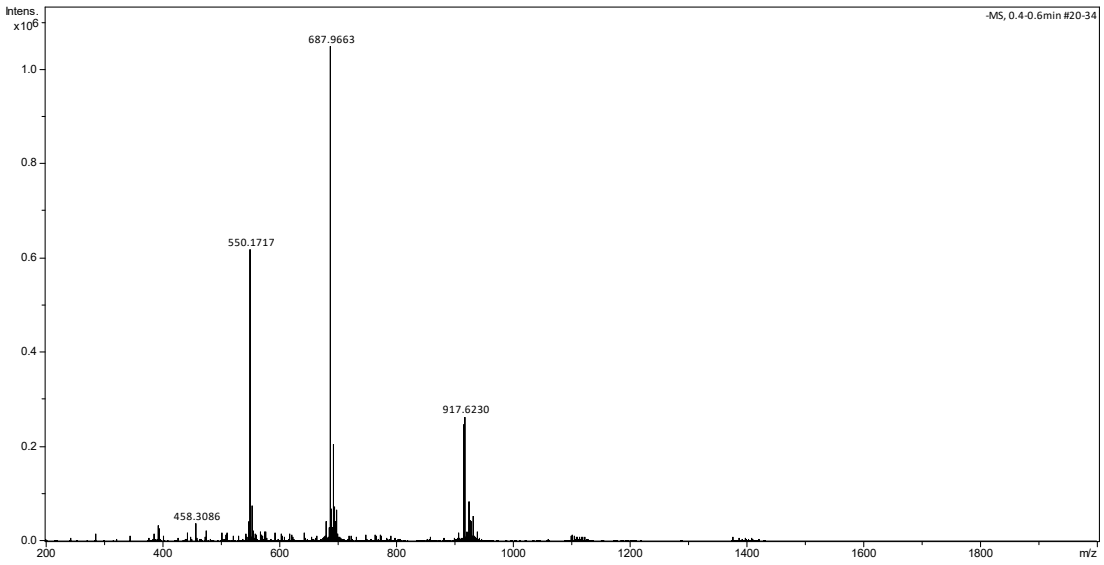

$^{1}$H NMR Spectrum of **36** (HHCCH$^{*}$HH**)**



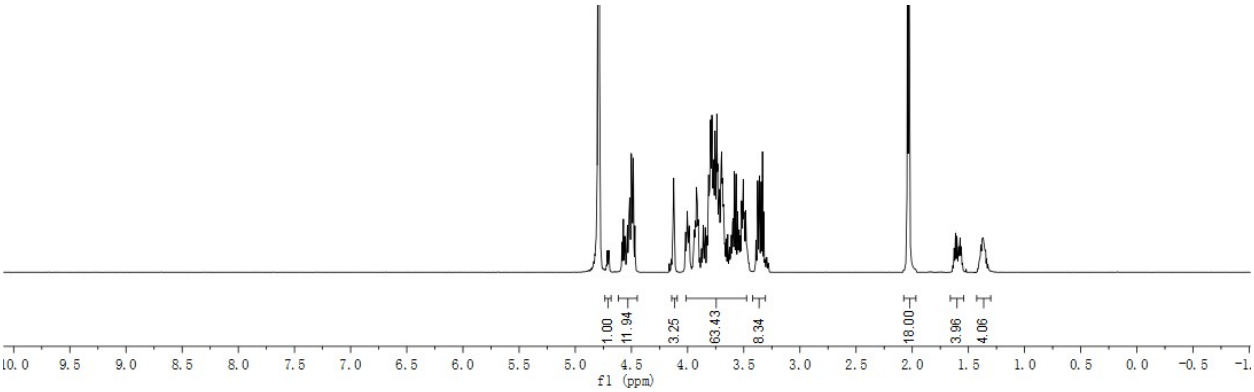

$^{-}$Q ESI-MS profile of **37** (CHCCH$^{*}$HH)



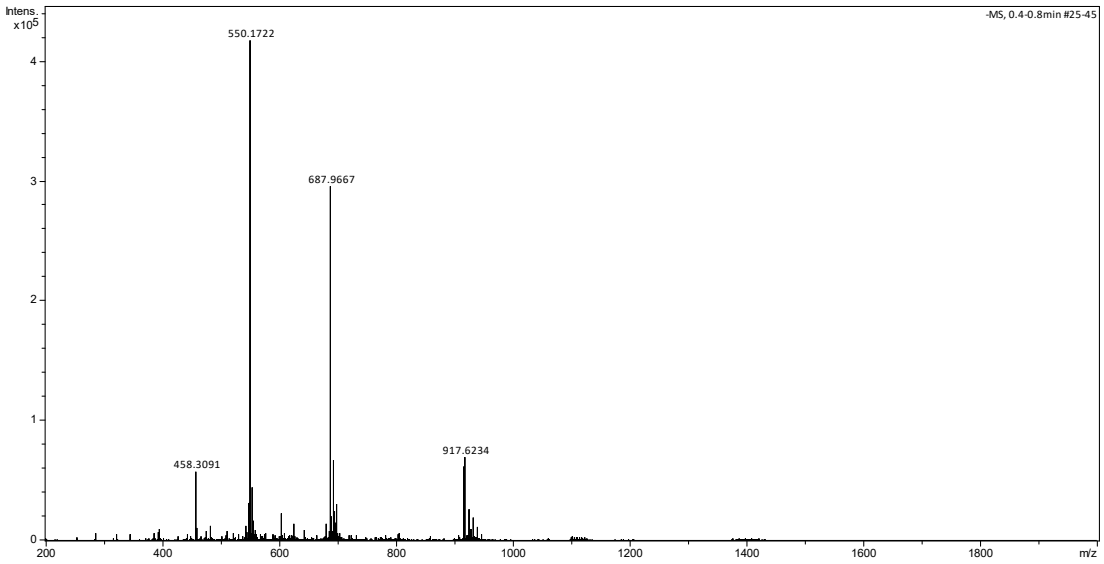

$^{1}$H NMR Spectrum of **37** (CHCCH$^{*}$HH**)**



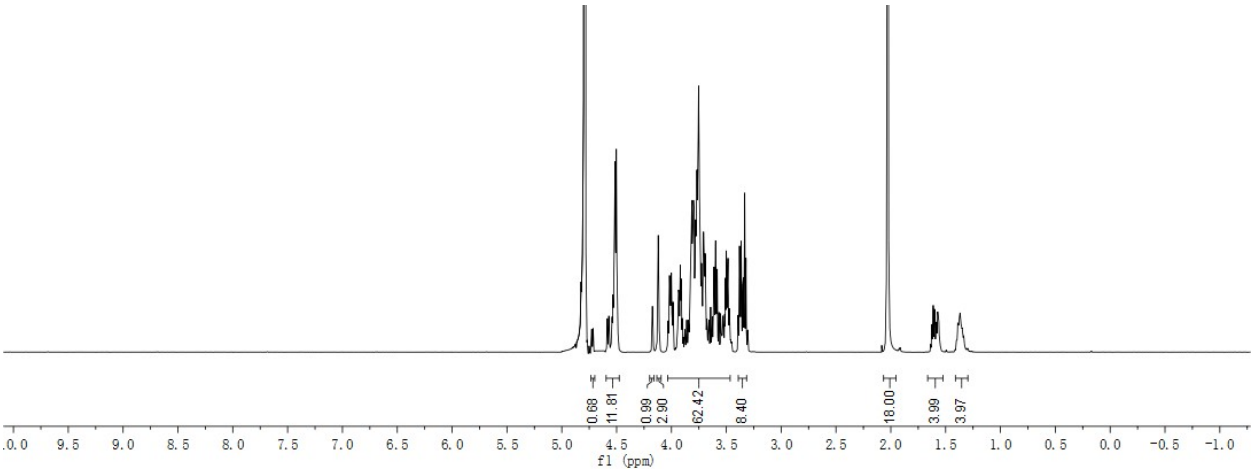

$^{-}$Q ESI-MS profile of **38** (HCCCH$^{*}$HH)



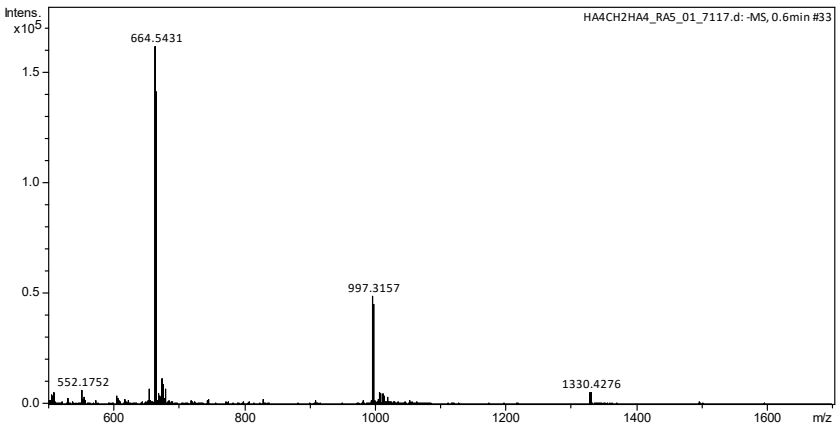

$^{1}$H NMR Spectrum of **38** (HCCCH$^{*}$HH**)**



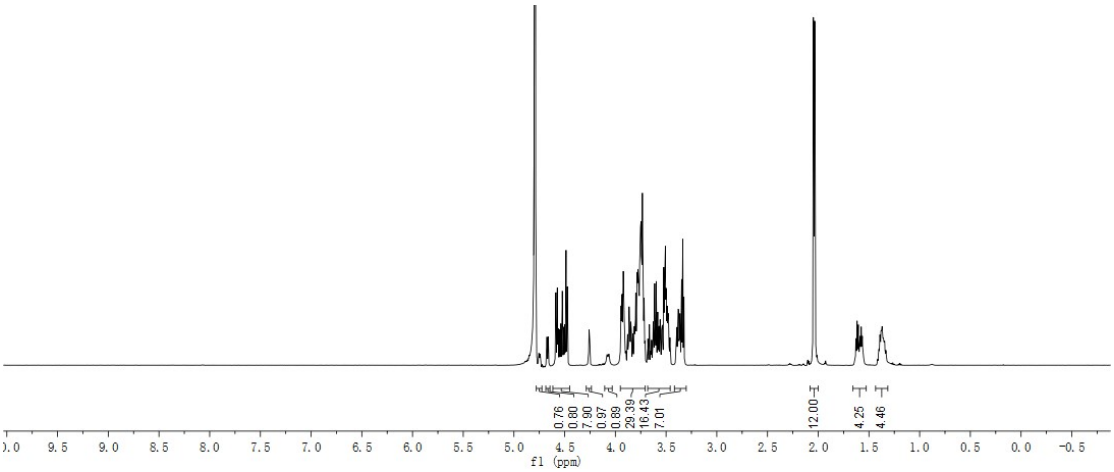

$^{-}$Q ESI-MS profile of **39** (CCCCH$^{*}$HH)



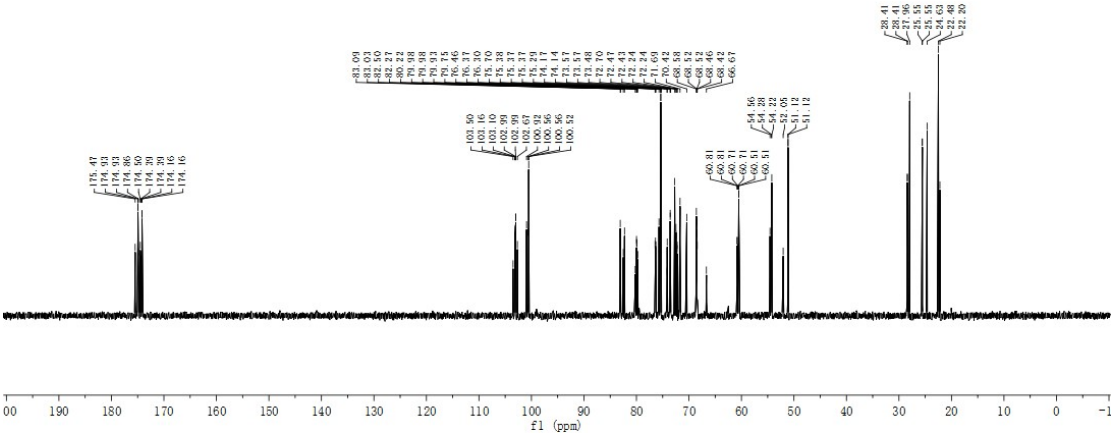

$^{1}$H NMR Spectrum of **39** (CCCCH$^{*}$HH**)**



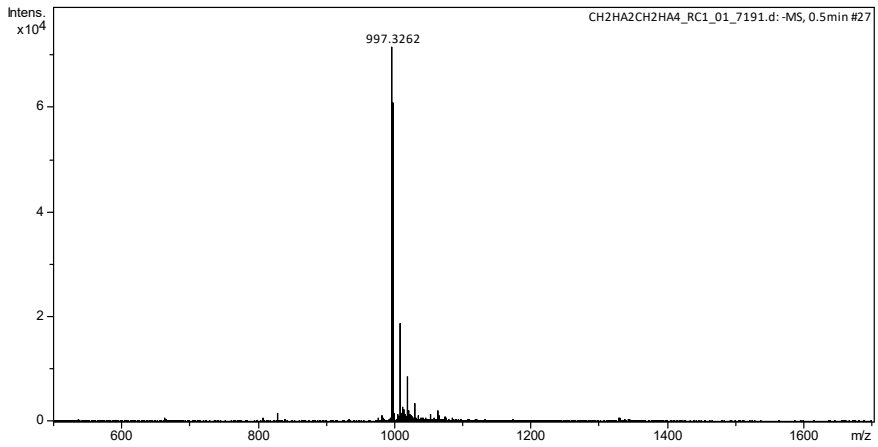

-Q ESI-MS profile of **40** (HHC*HH)



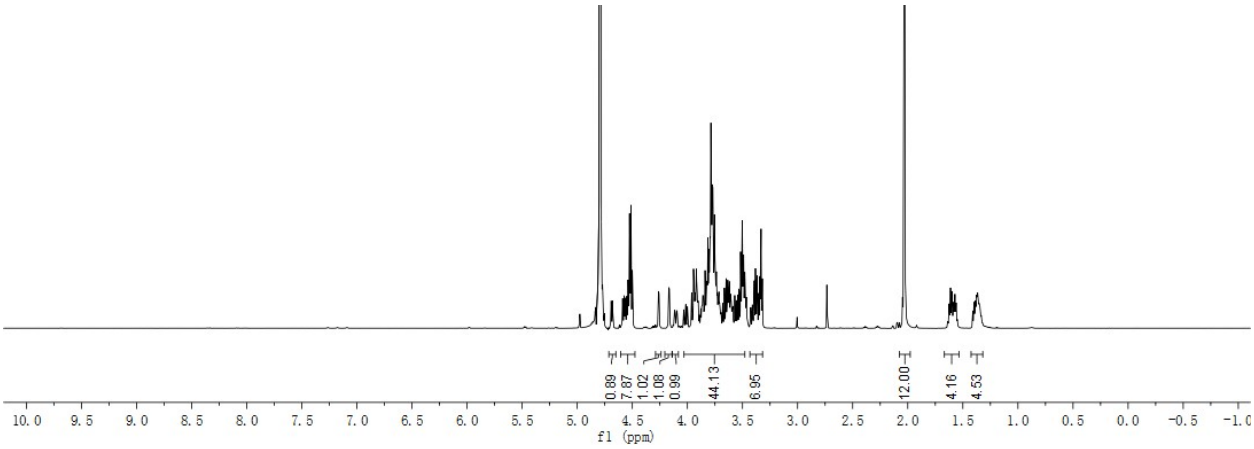

$^{1}$H NMR Spectrum of **40** (HHC*HH**)**



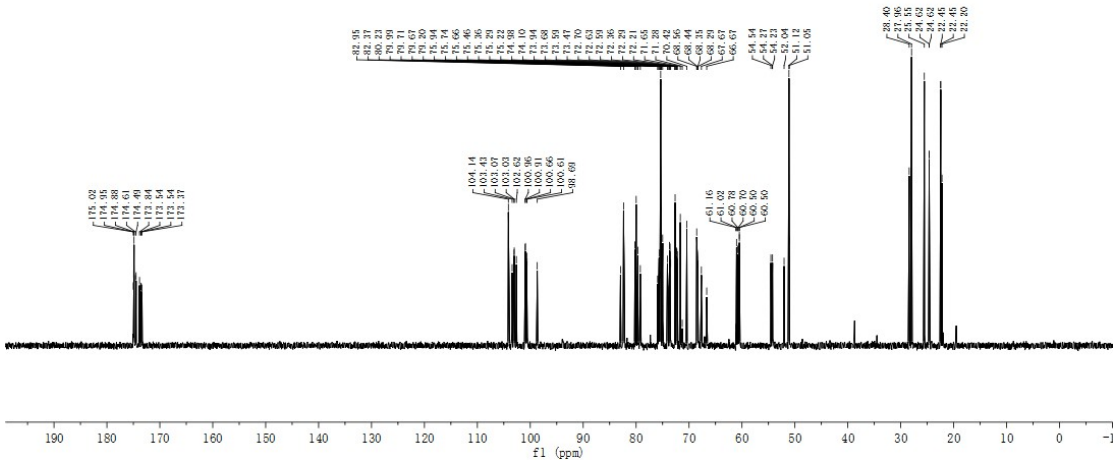

$^{1}$C NMR Spectrum of **40** (HHC*HH**)**



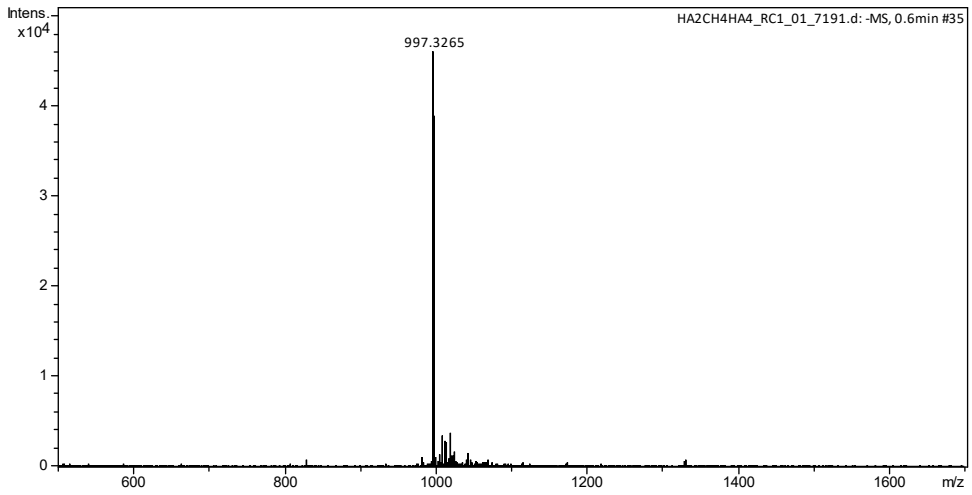

$^{-}$Q ESI-MS profile of **41** (CHC$^{*}$HH)



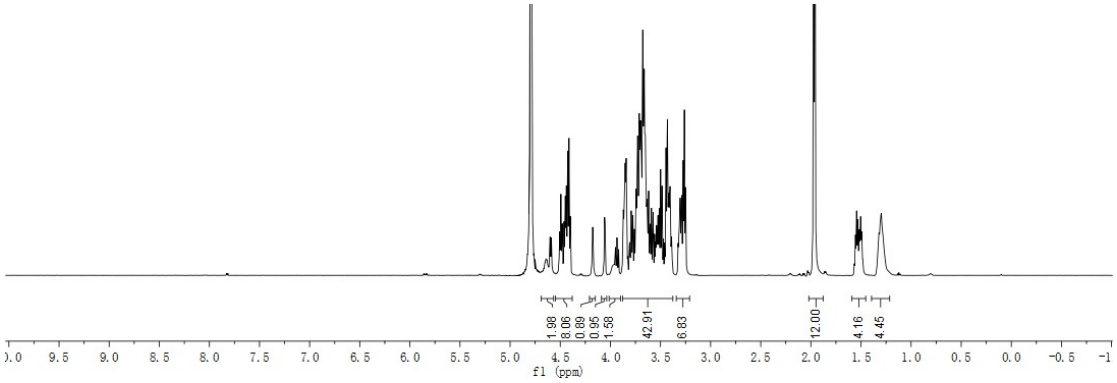

$^{1}$H NMR Spectrum of **41** (CHC$^{*}$HH**)**



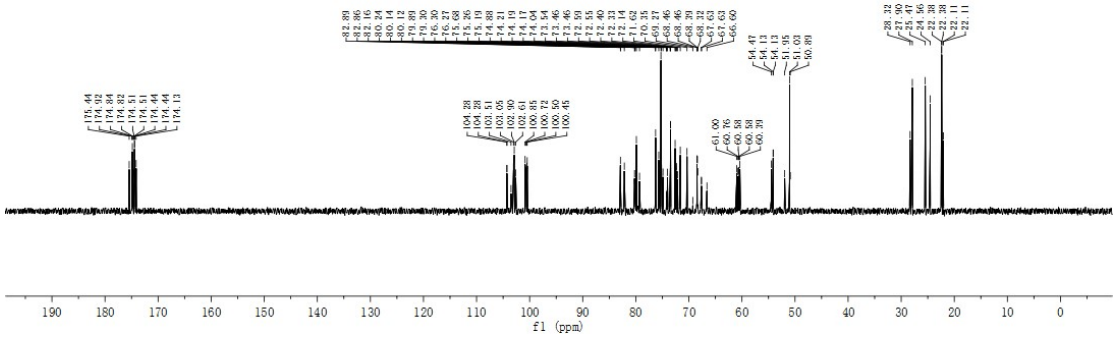

$^{1}$C NMR Spectrum of **41** (CHC$^{*}$HH**)**



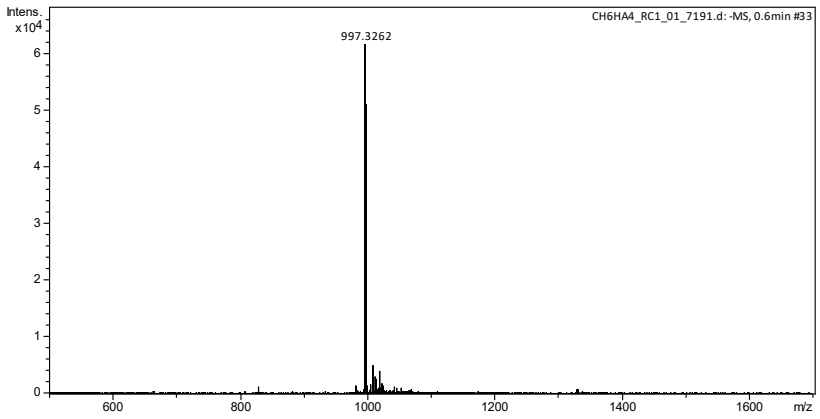

$^{-}$Q ESI-MS profile of **42** (HCC$^{*}$HH)



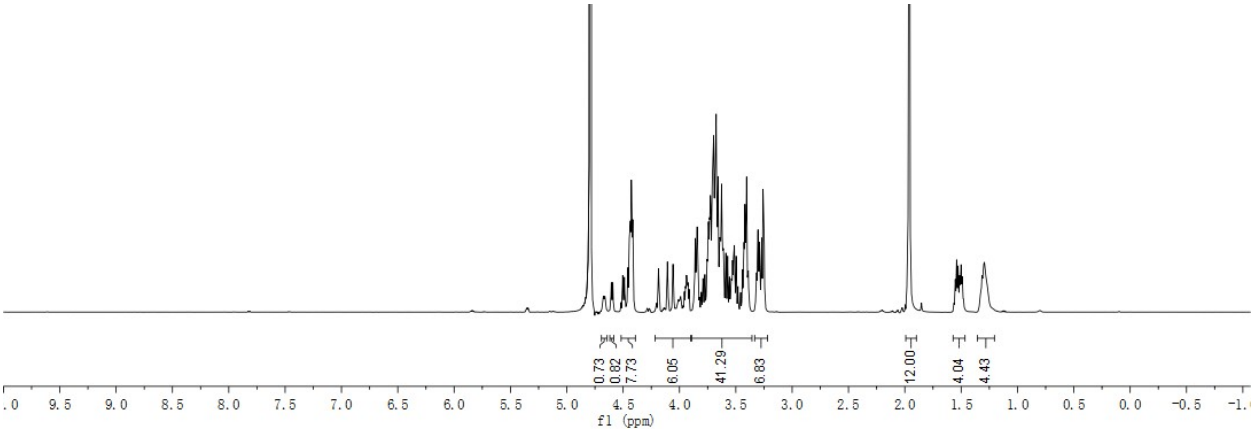

$^{1}$H NMR Spectrum of **42** (HCC$^{*}$HH**)**



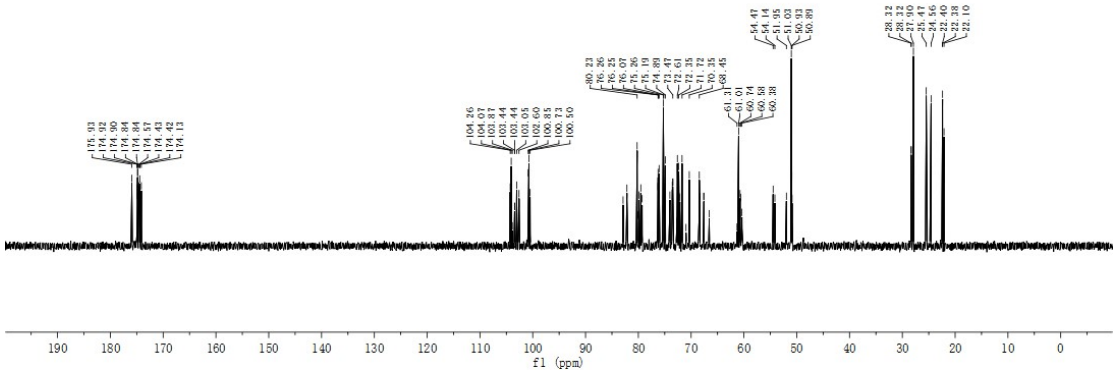

$^{1}$C NMR Spectrum of **42** (HCC$^{*}$HH**)**



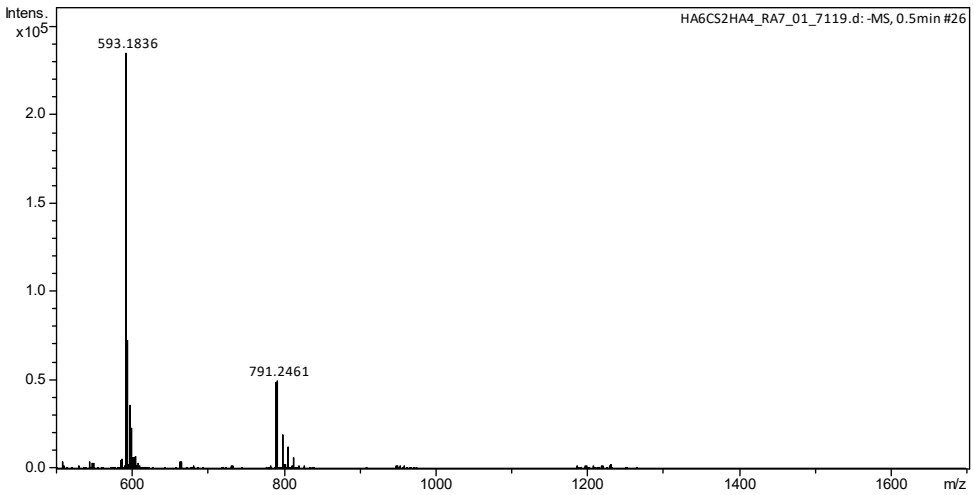

-Q ESI-MS profile of **43** (CCC*HH)



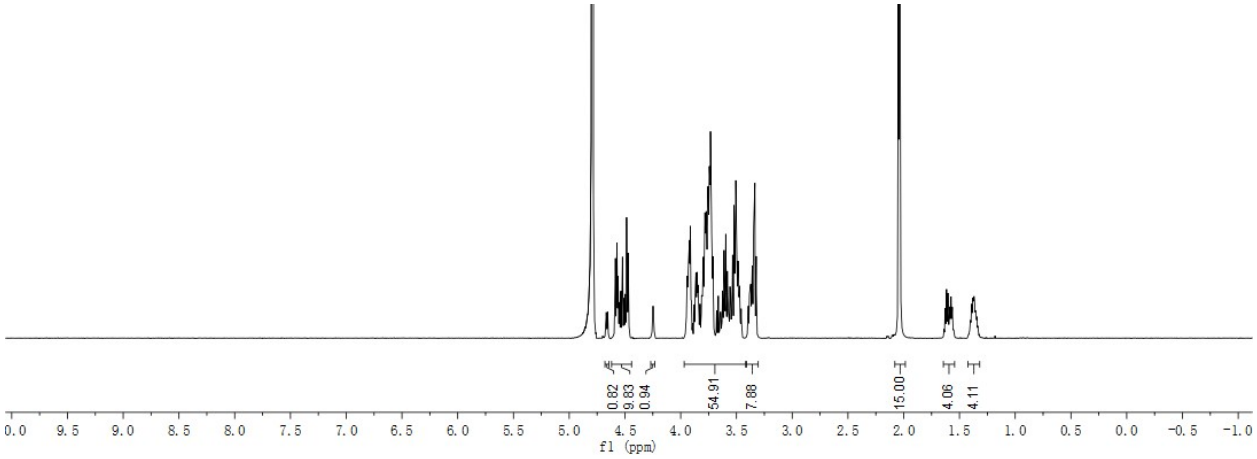

$^{1}$H NMR Spectrum of **43** (CCC*HH**)**



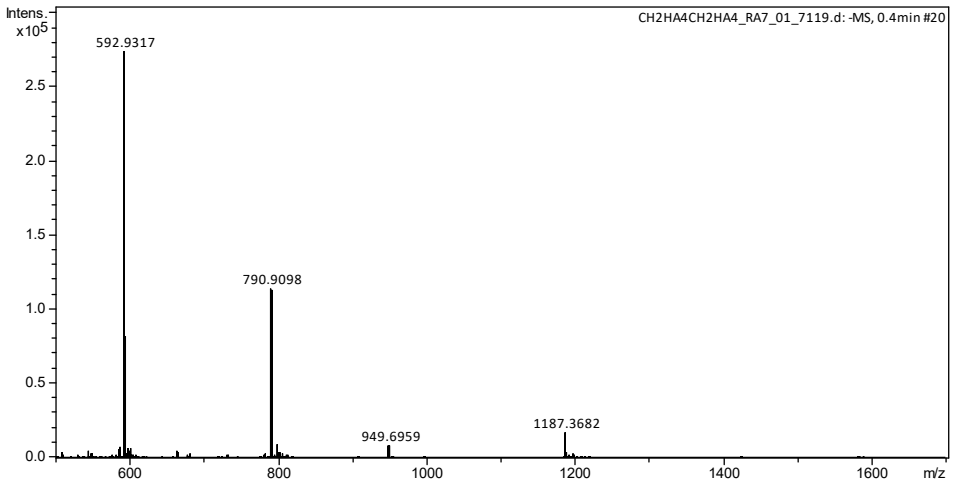

$^{1}$C NMR Spectrum of **43** (CCC*HH**)**



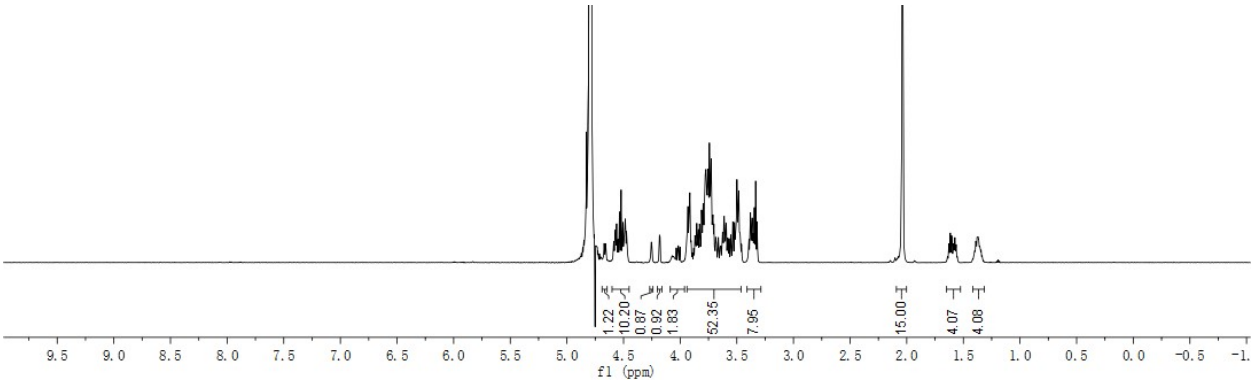

$^{-}$Q ESI-MS profile of **44** (HHHC$^{*}$HH)



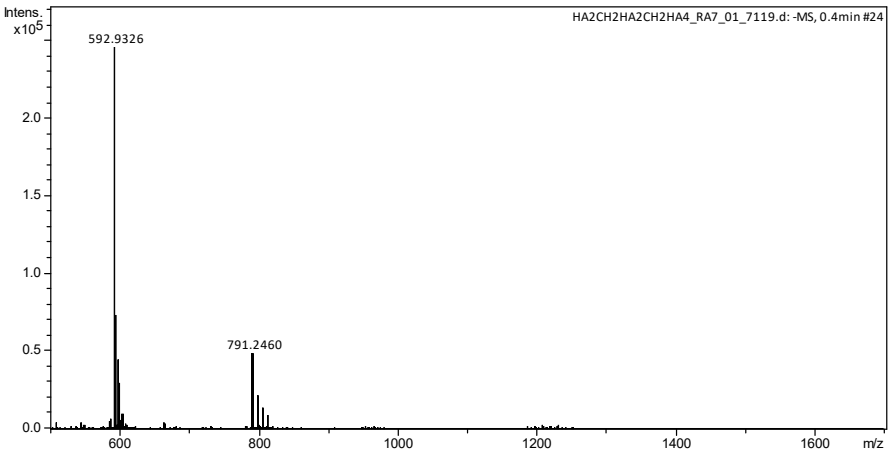

$^{1}$H NMR Spectrum of **44** (HHHC$^{*}$HH**)**



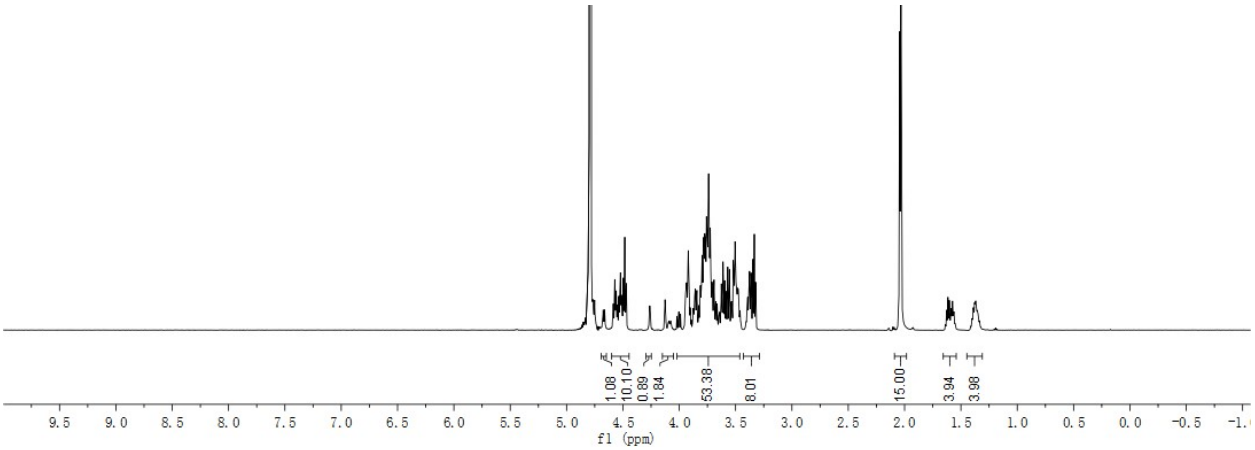

$^{-}$Q ESI-MS profile of **45** (CHHC$^{*}$HH)



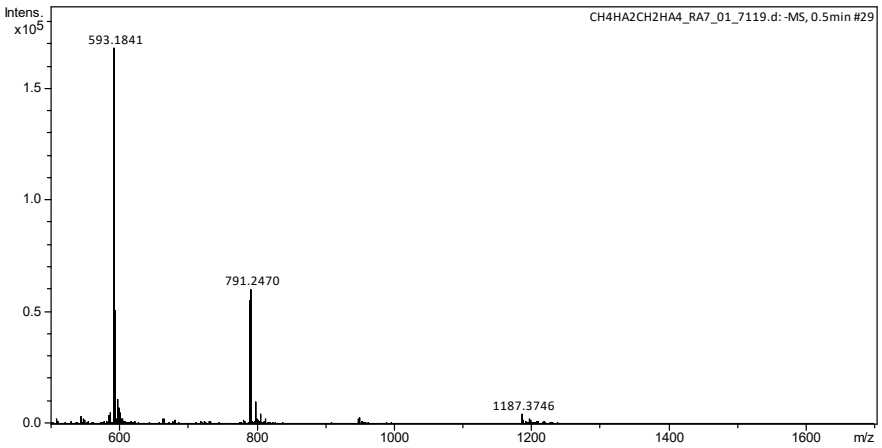

$^{1}$H NMR Spectrum of **45** (CHHC$^{*}$HH**)**



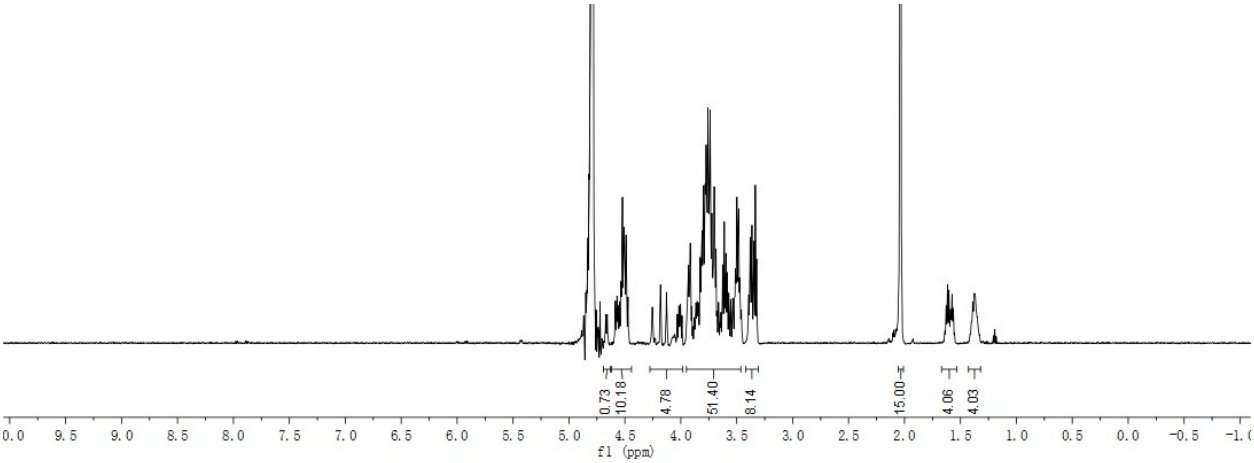

$^{-}$Q ESI-MS profile of **46** (HCHC$^{*}$HH)



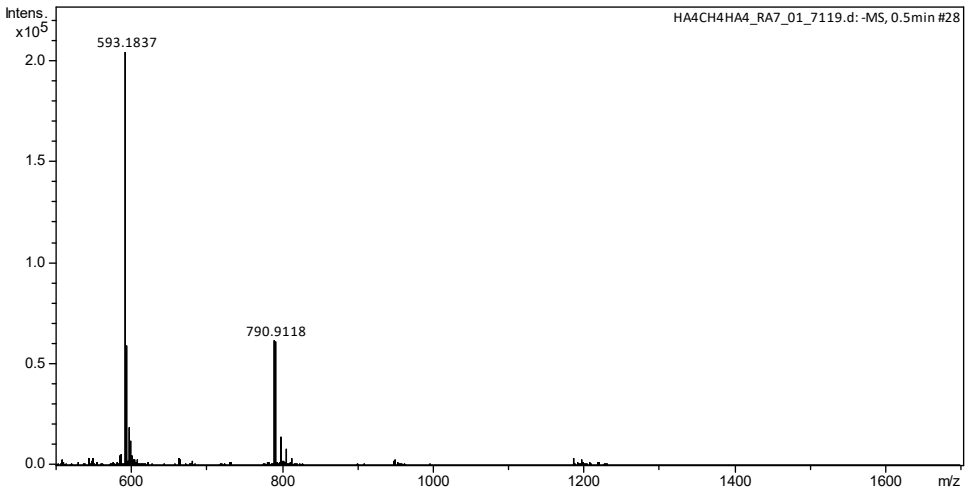

$^{1}$H NMR Spectrum of **46** (HCHC$^{*}$HH**)**



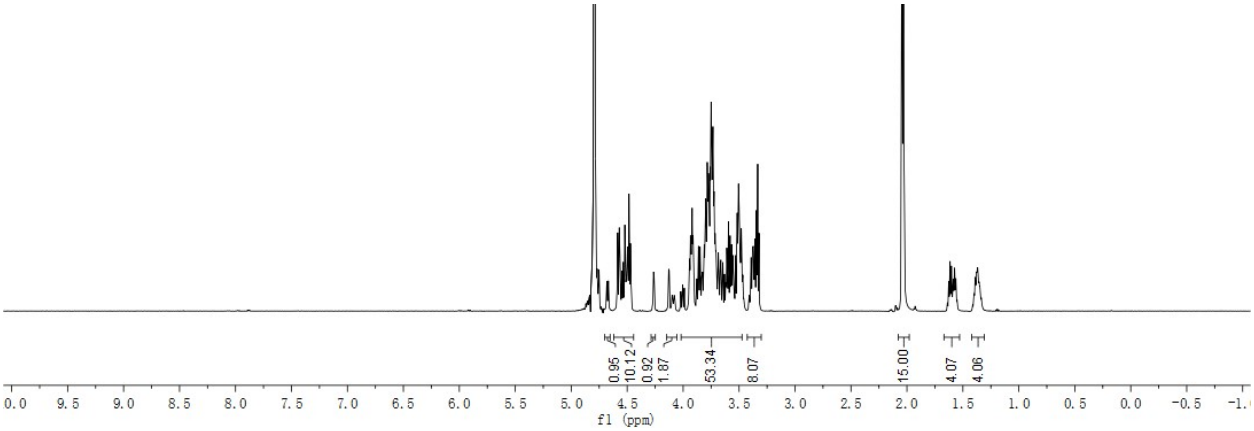

$^{-}$Q ESI-MS profile of **47** (CCHC$^{*}$HH)



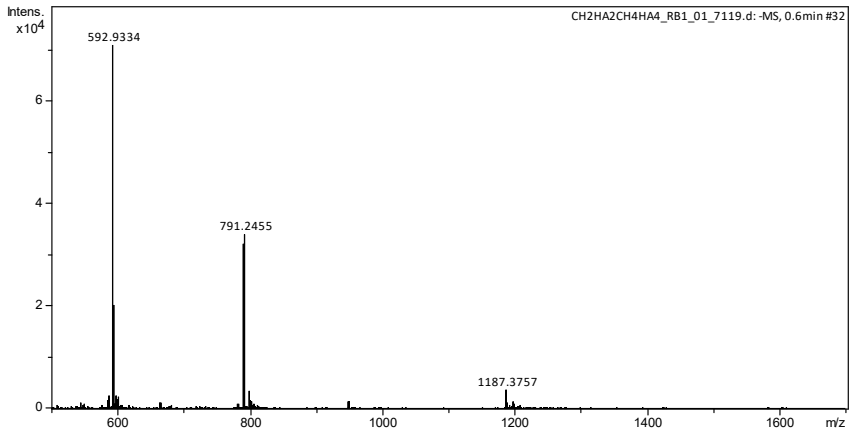

$^{1}$H NMR Spectrum of **47** (CCHC$^{*}$HH**)**



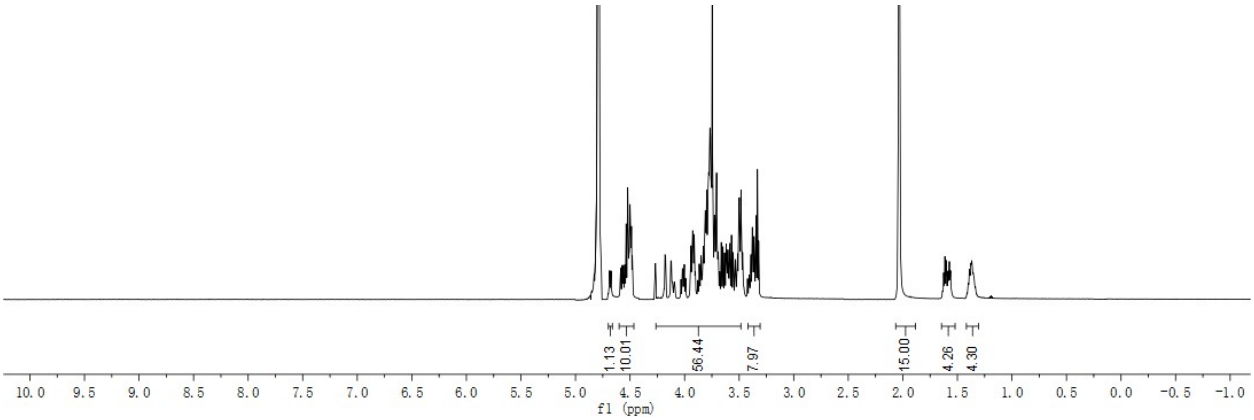

$^{-}$Q ESI-MS profile of **48** (HHCC$^{*}$HH)



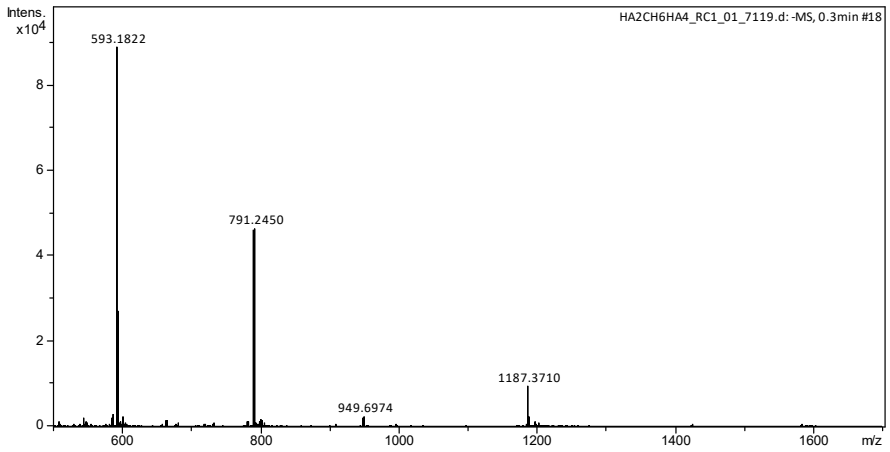

$^{1}$H NMR Spectrum of **48** (HHCC$^{*}$HH**)**



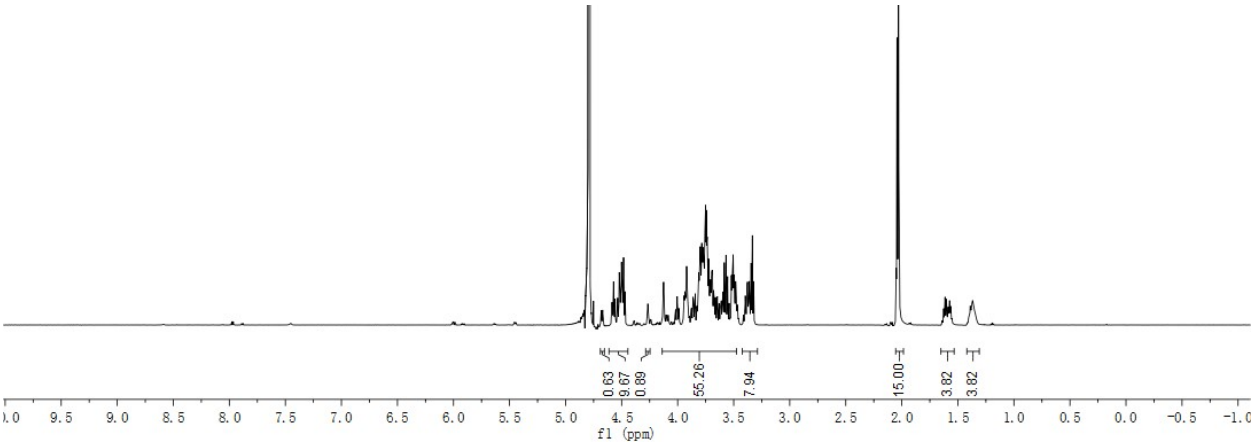

$^{-}$Q ESI-MS profile of **49** (CHCC$^{*}$HH)



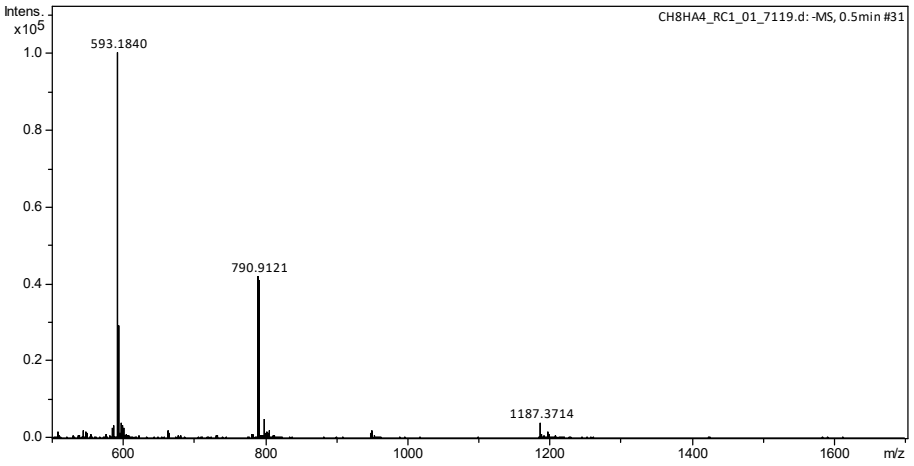

$^{1}$H NMR Spectrum of **49** (CHCC$^{*}$HH**)**



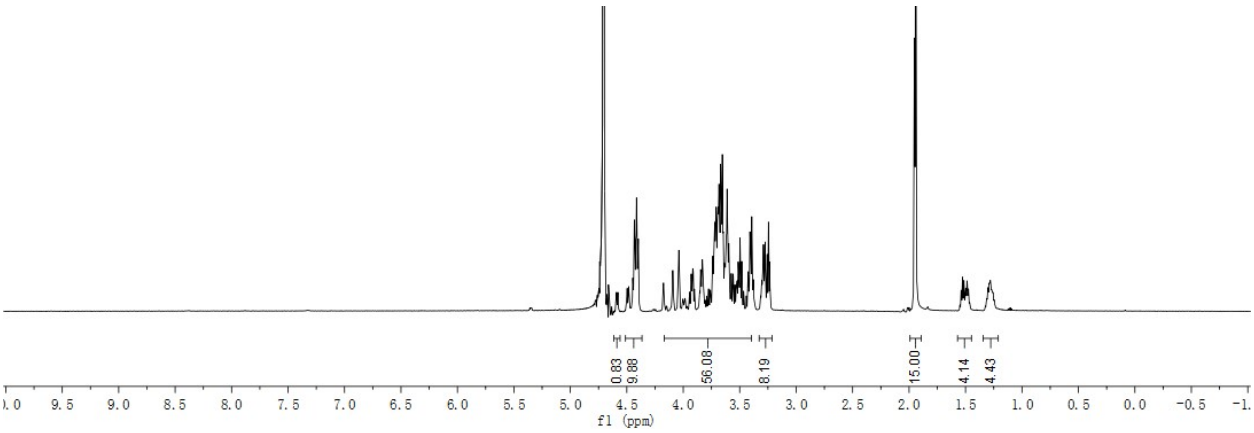

$^{-}$Q ESI-MS profile of **50** (HCCC$^{*}$HH)



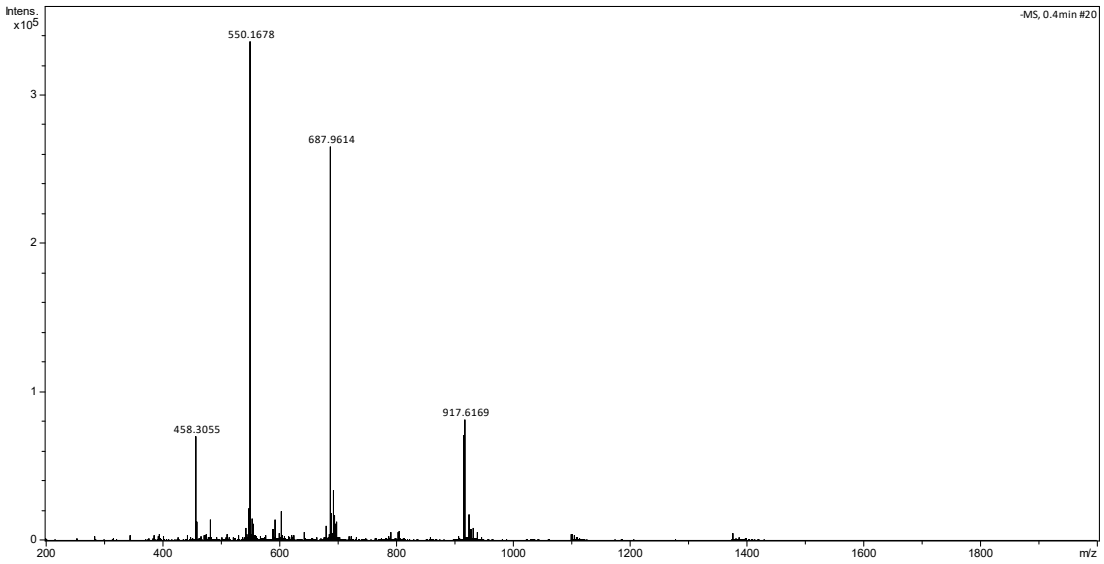

$^{1}$H NMR Spectrum of **50** (HCCC$^{*}$HH**)**



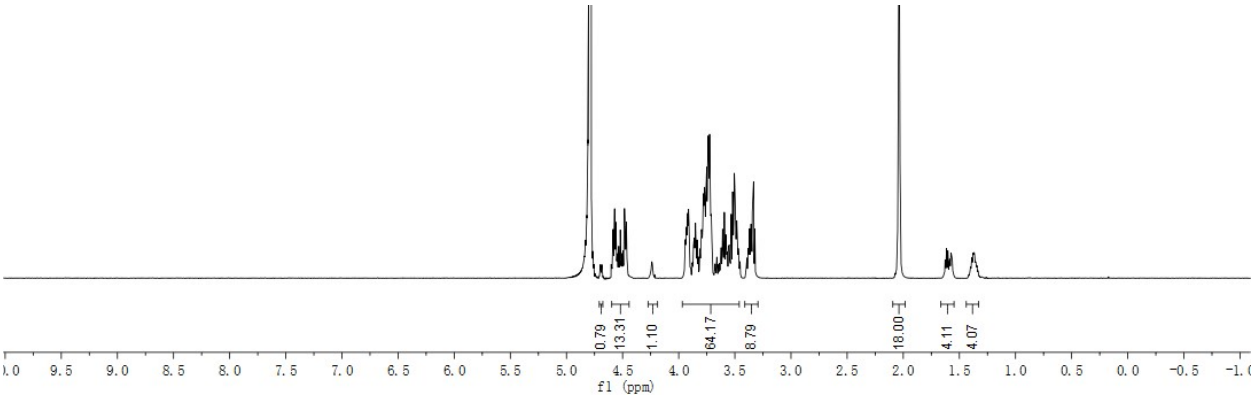

$^{-}$Q ESI-MS profile of **51** (CCCC$^{*}$HH)



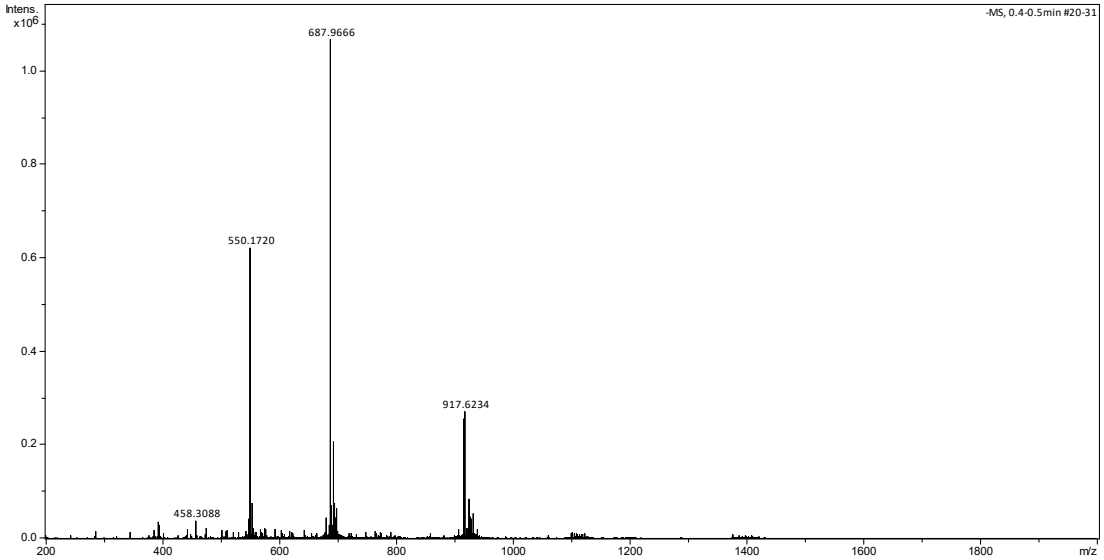

$^{1}$H NMR Spectrum of **51** (CCCC$^{*}$HH**)**



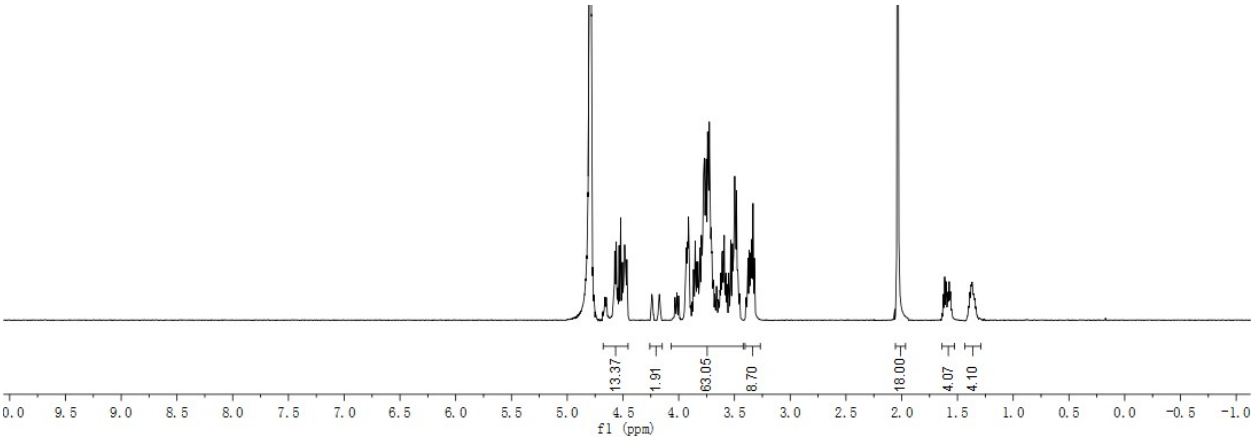

$^{-}$Q ESI-MS profile of **52** (HHHHC$^{*}$HH)



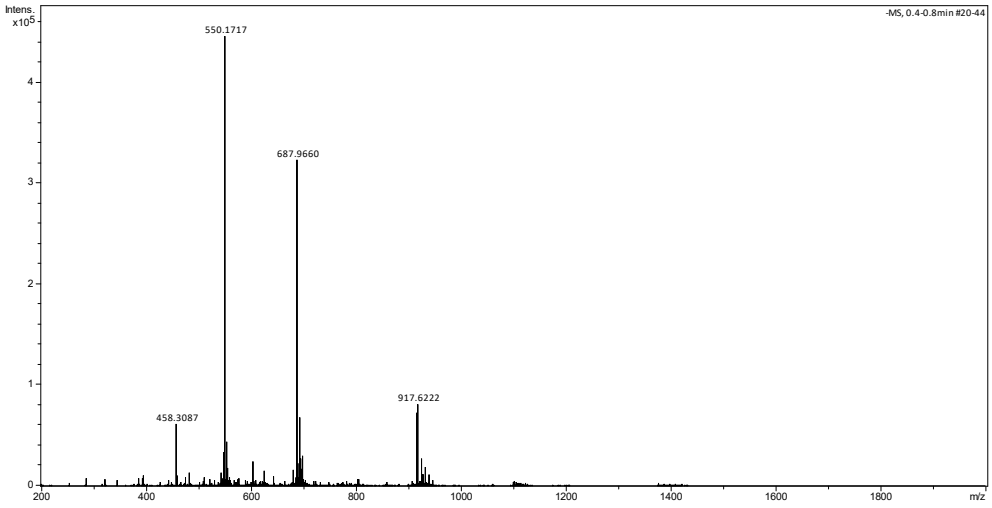

$^{1}$H NMR Spectrum of **52** (HHHHC$^{*}$HH**)**



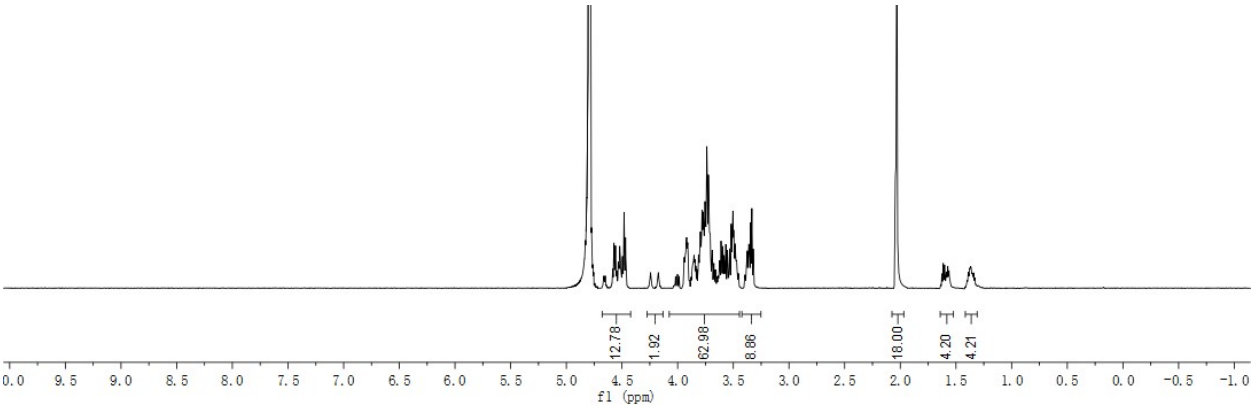

$^{-}$Q ESI-MS profile of **53** (CHHHC*HH)



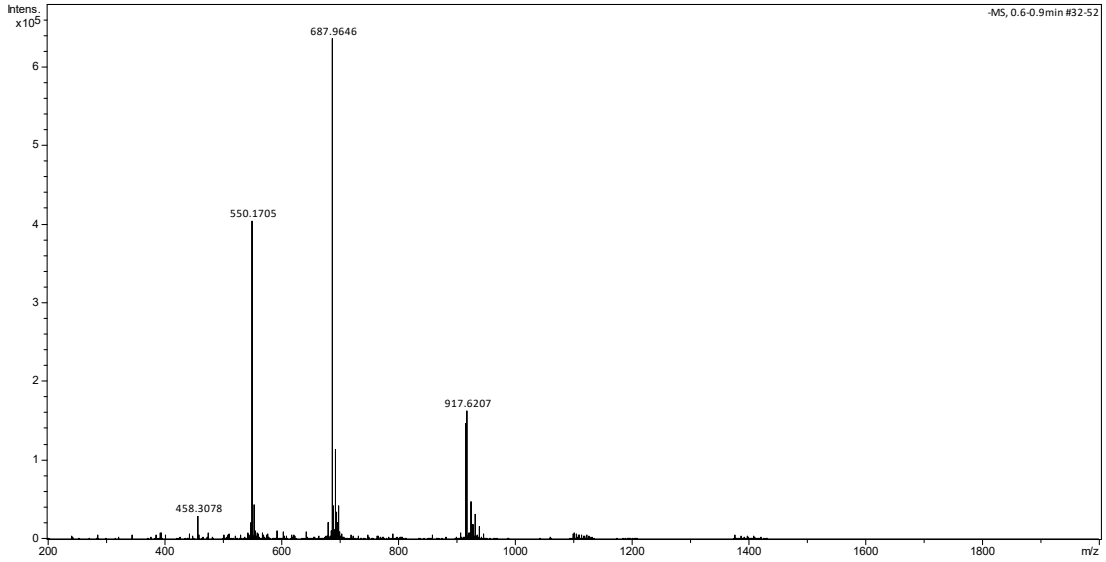

$^{1}$H NMR Spectrum of **53** (CHHHC*HH**)**



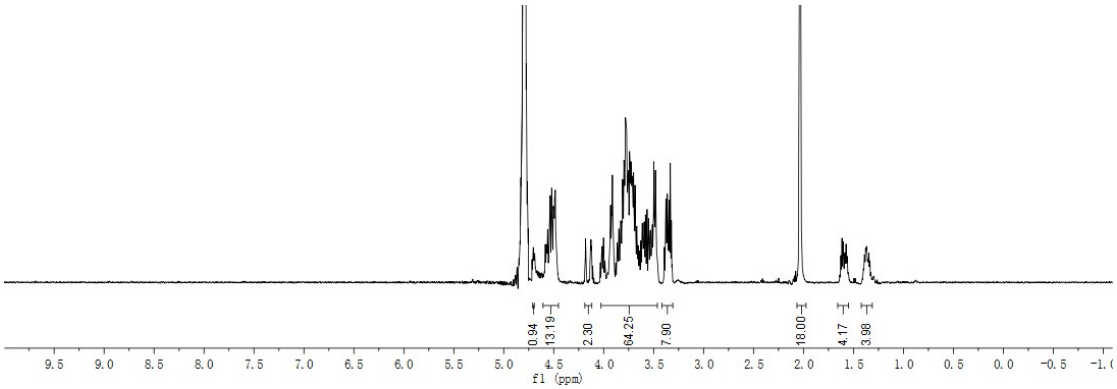

$^{-}$Q ESI-MS profile of **54** (HCHHC$^{*}$HH)



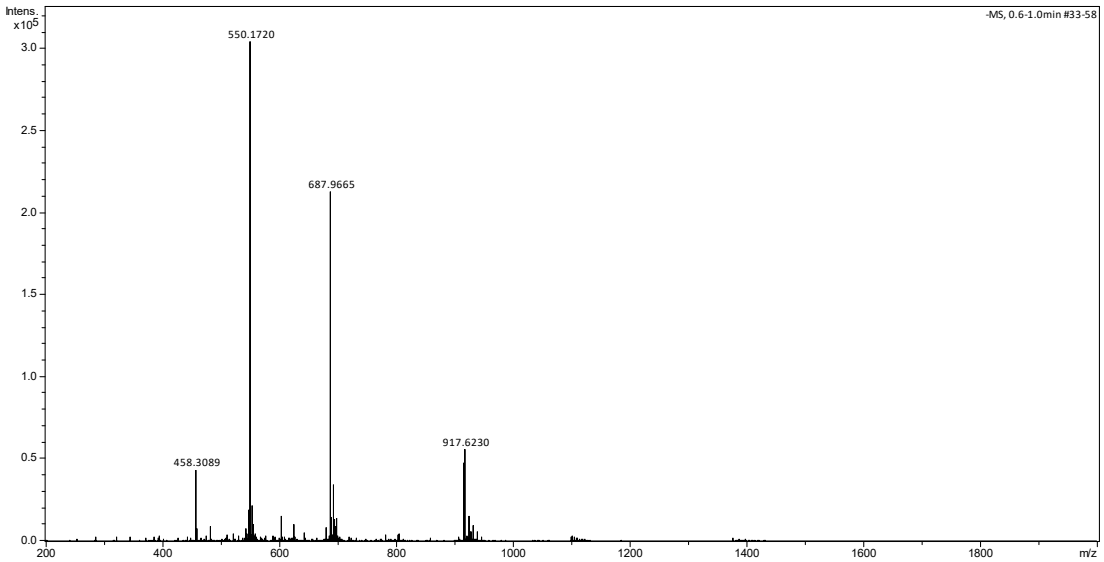

$^{1}$H NMR Spectrum of **54** (HCHHC$^{*}$HH**)**



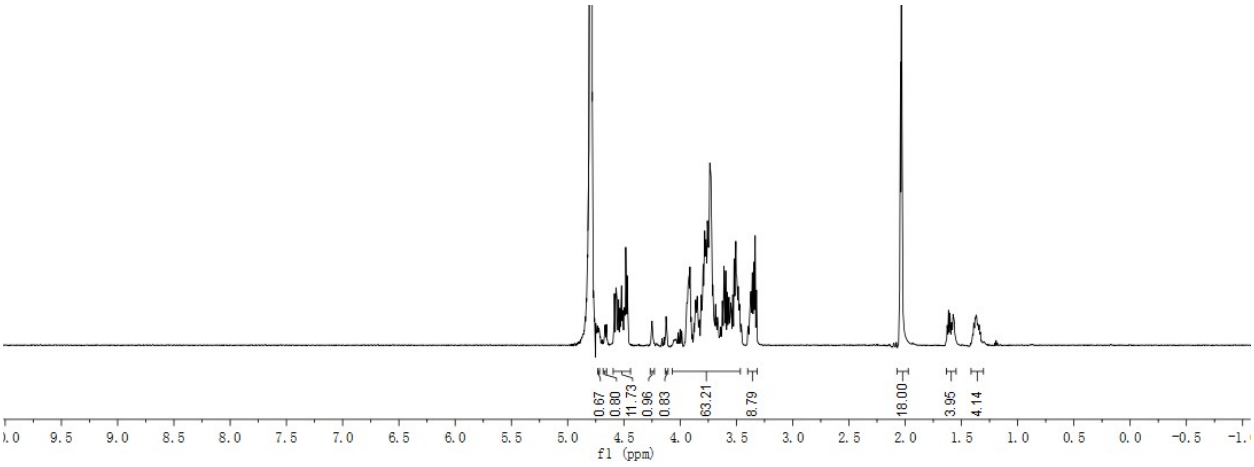

$^{-}$Q ESI-MS profile of **55** (CCHHC$^{*}$HH)



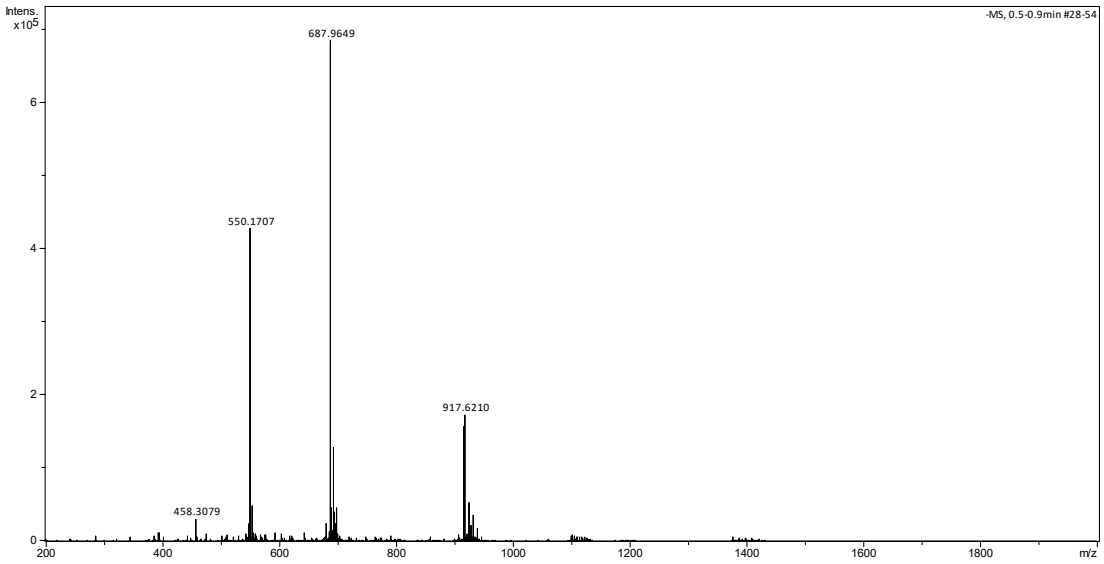

$^{1}$H NMR Spectrum of **55** (CCHHC$^{*}$HH**)**



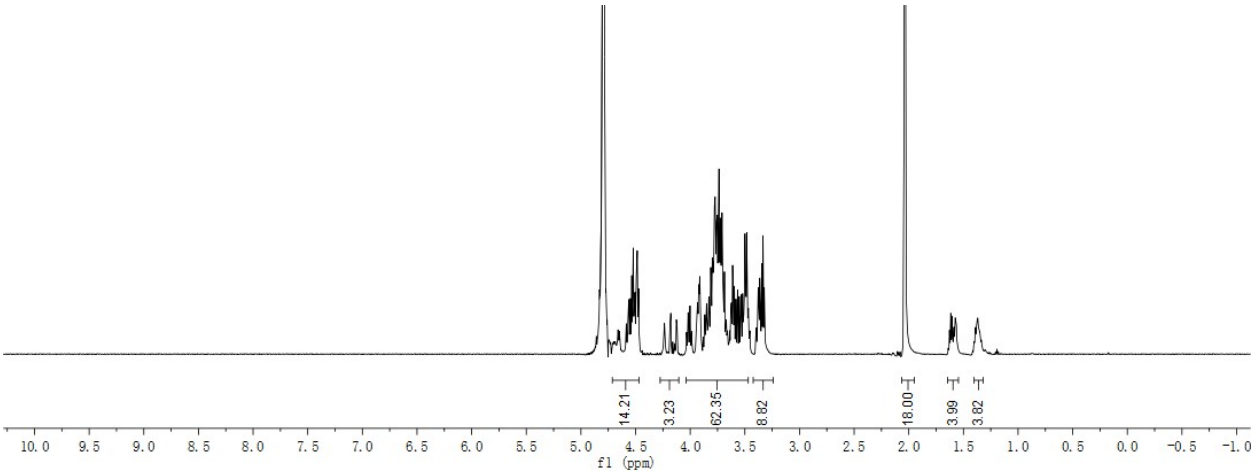

$^{-}$Q ESI-MS profile of **56** (HHCHC$^{*}$HH)



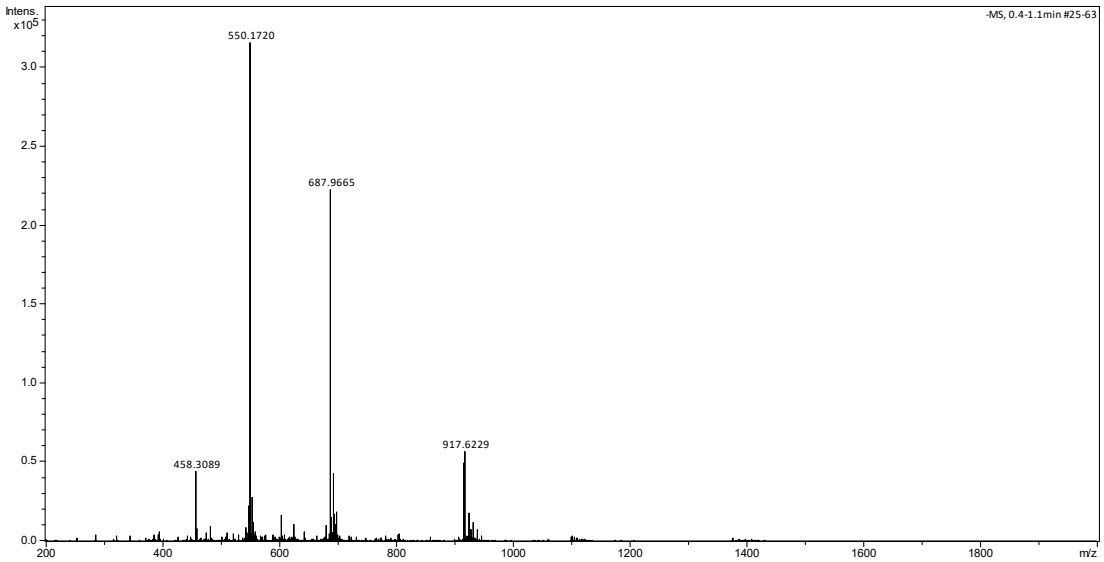

$^{1}$H NMR Spectrum of **56** (HHCHC$^{*}$HH**)**



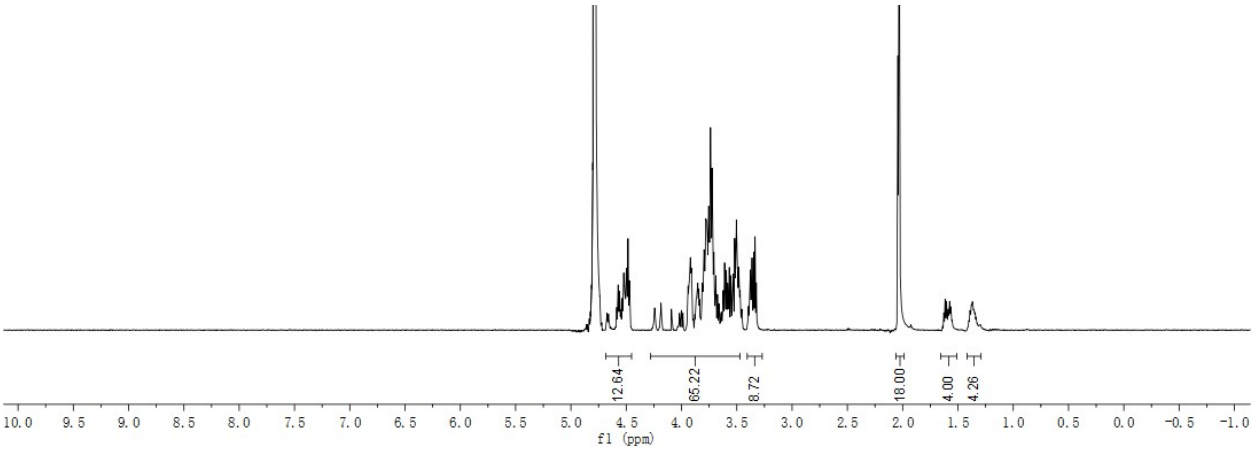

$^{-}$Q ESI-MS profile of **57** (CHCHC$^{*}$HH)



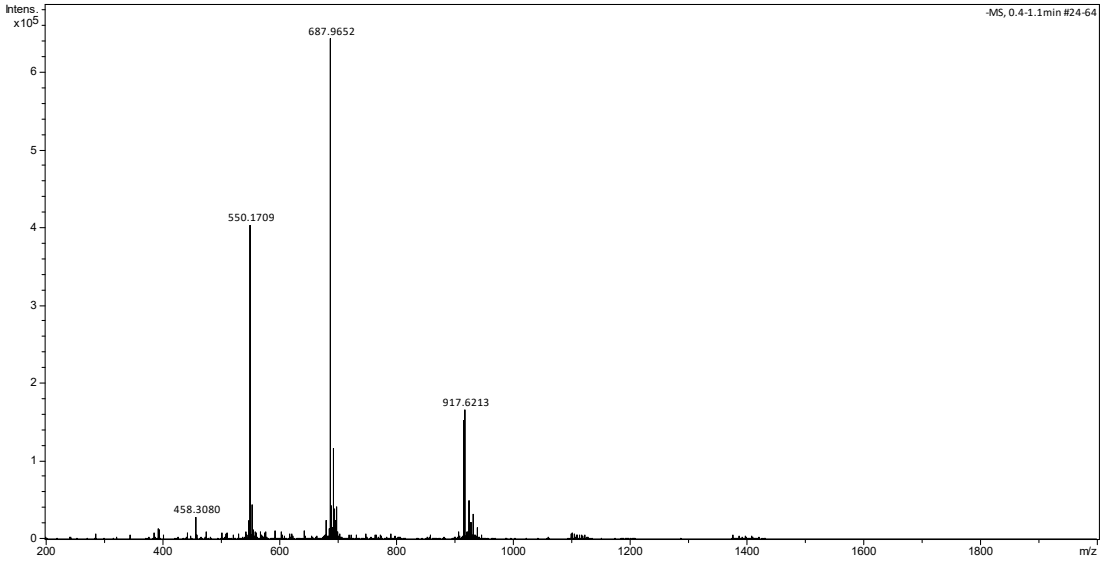

$^{1}$H NMR Spectrum of **57** (CHCHC$^{*}$HH**)**



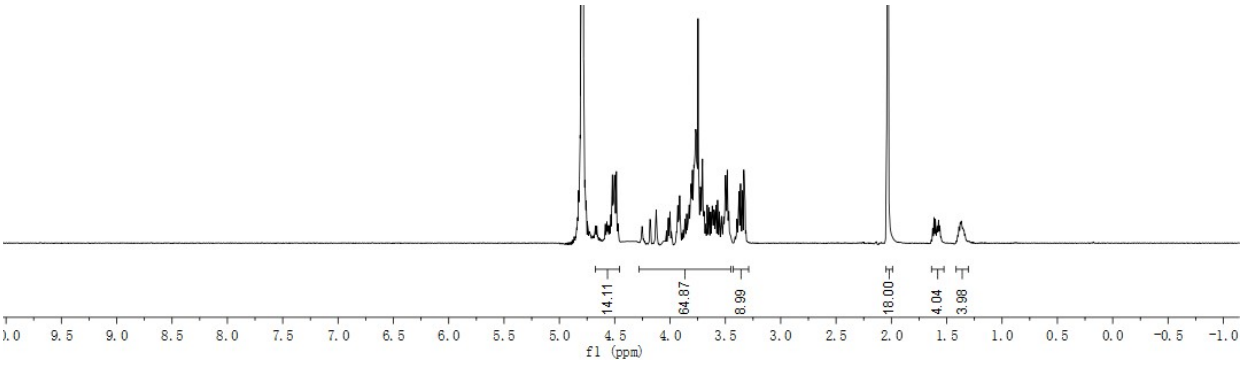

$^{-}$Q ESI-MS profile of **58** (HCCHC$^{*}$HH)



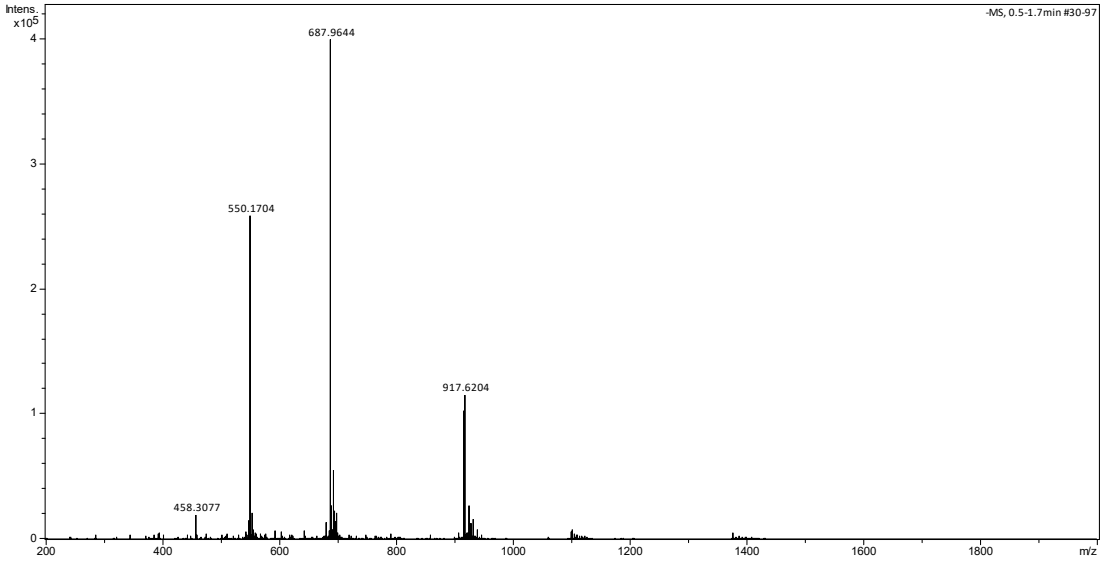

$^{1}$H NMR Spectrum of **58** (HCCHC$^{*}$HH**)**



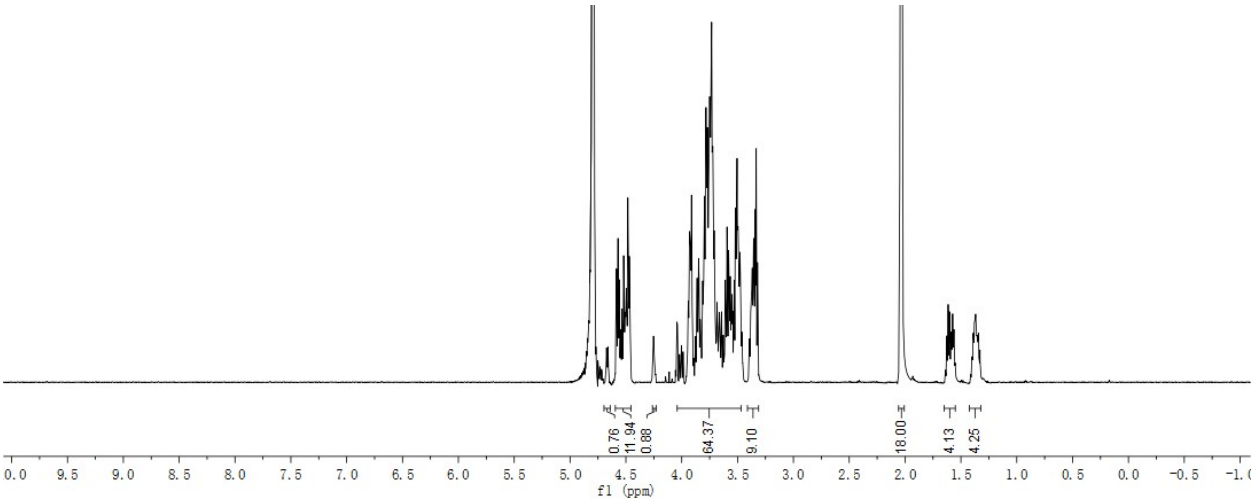

$^{-}$Q ESI-MS profile of **59** (CCCHC$^{*}$HH)



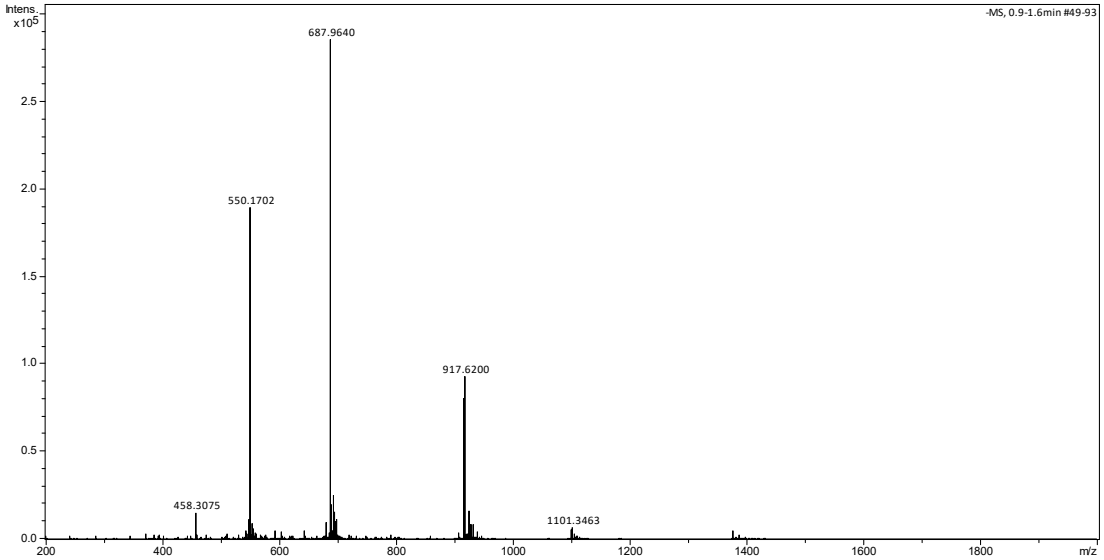
$^{1}$H NMR Spectrum of **59** (CCCHC$^{*}$HH**)**



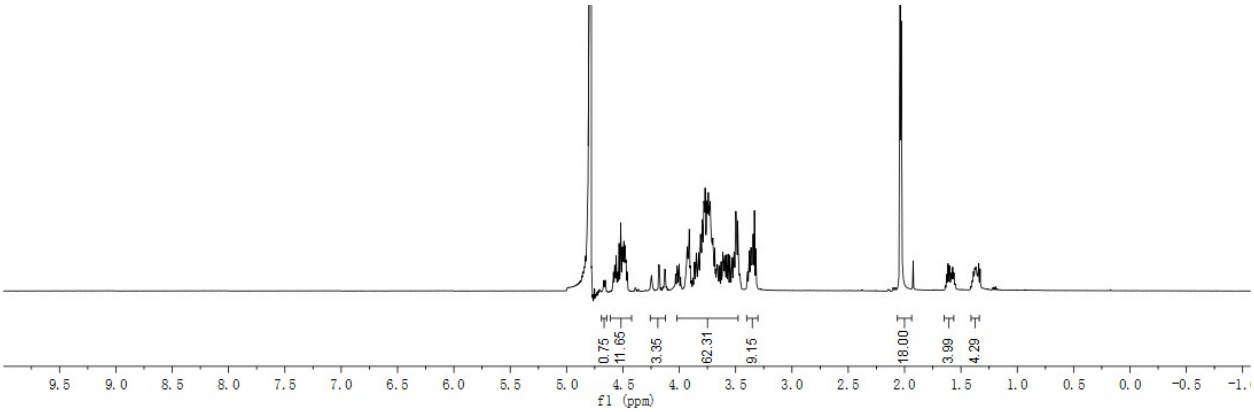

$^{-}$Q ESI-MS profile of **60** (HHHCC$^{*}$HH)



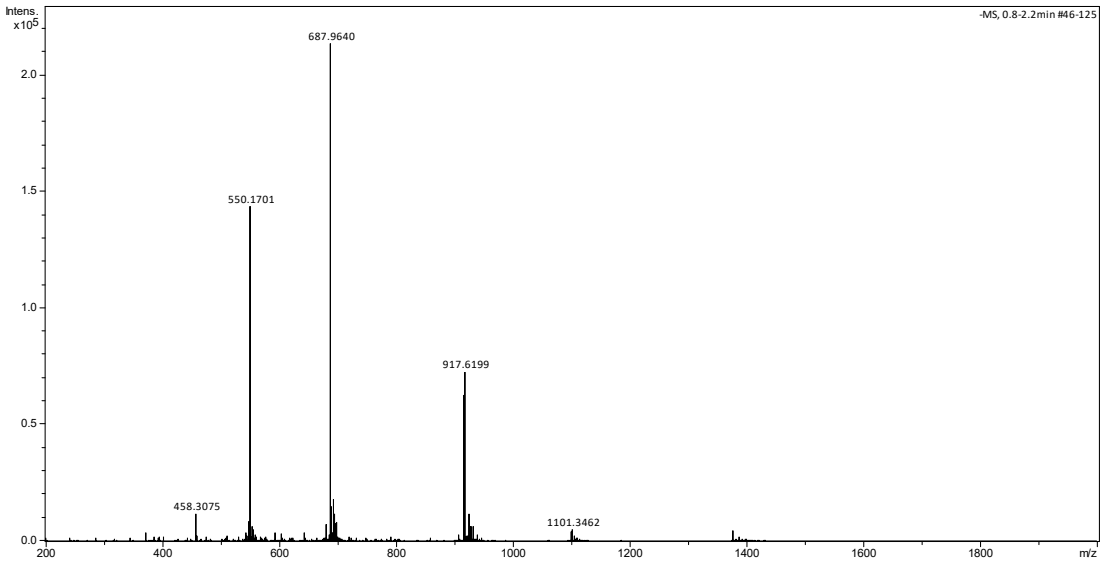

$^{1}$H NMR Spectrum of **60** (HHHCC$^{*}$HH**)**



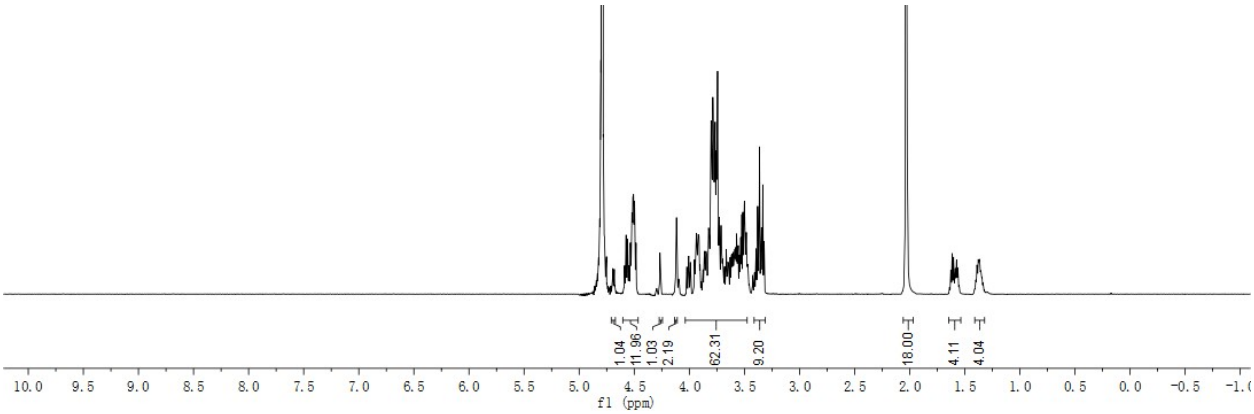

$^{-}$Q ESI-MS profile of **61** (CHHCC$^{*}$HH)



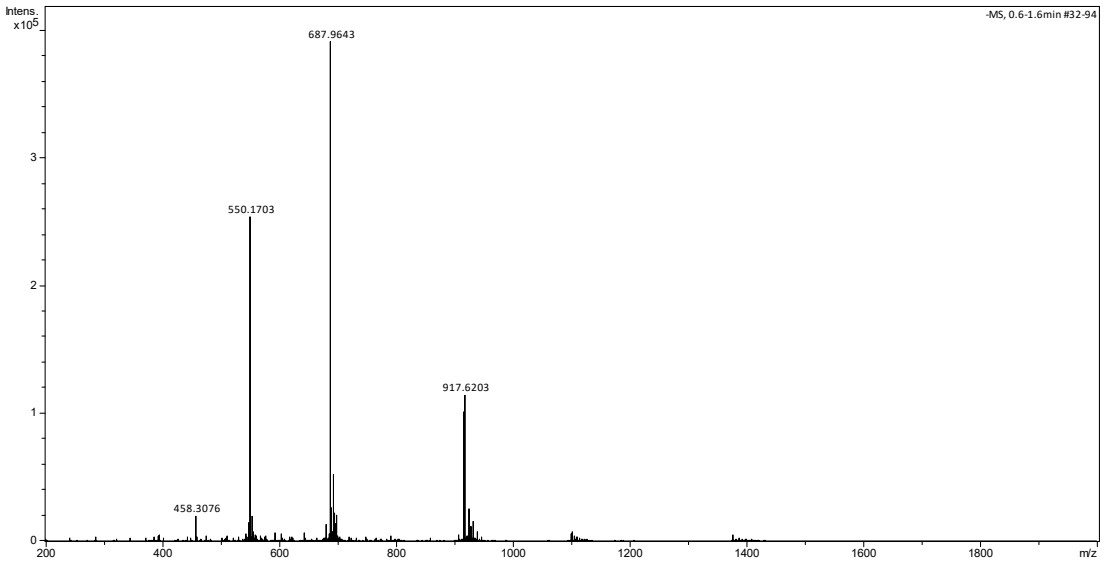

$^{1}$H NMR Spectrum of **61** (CHHCC$^{*}$HH**)**



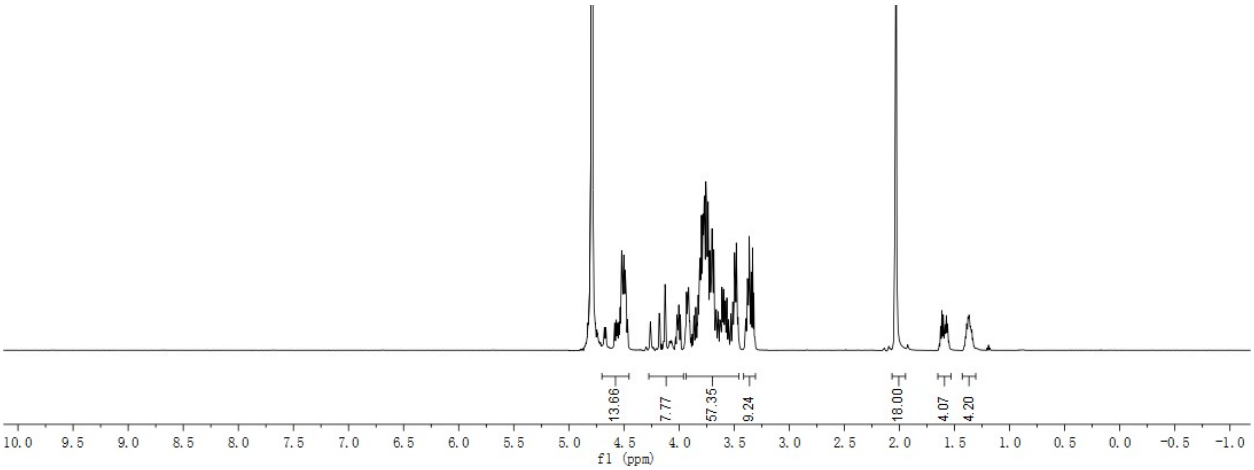

$^{-}$Q ESI-MS profile of **62** (HCHCC$^{*}$HH)



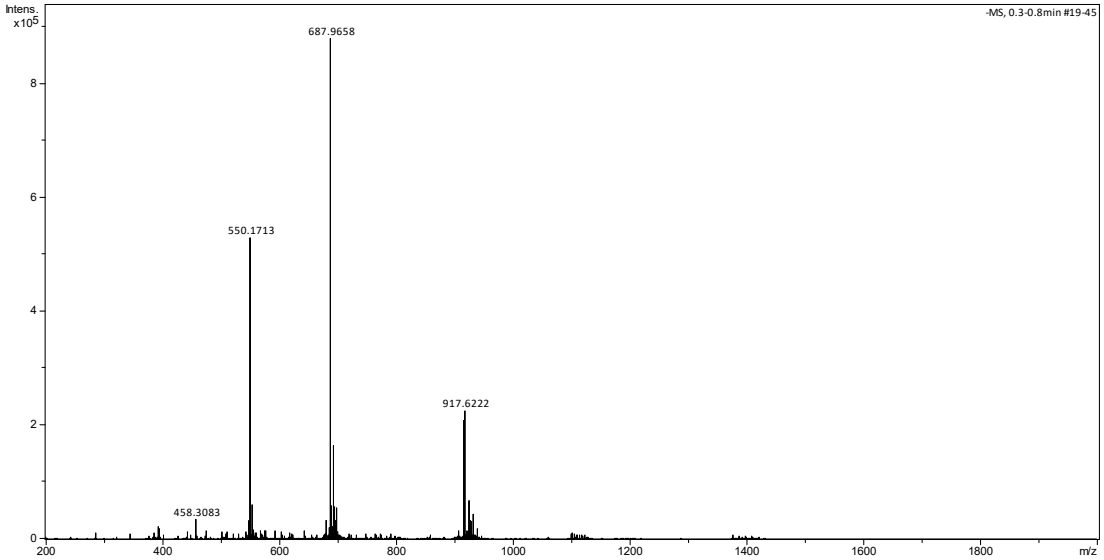

$^{1}$H NMR Spectrum of **62** (HCHCC$^{*}$HH**)**



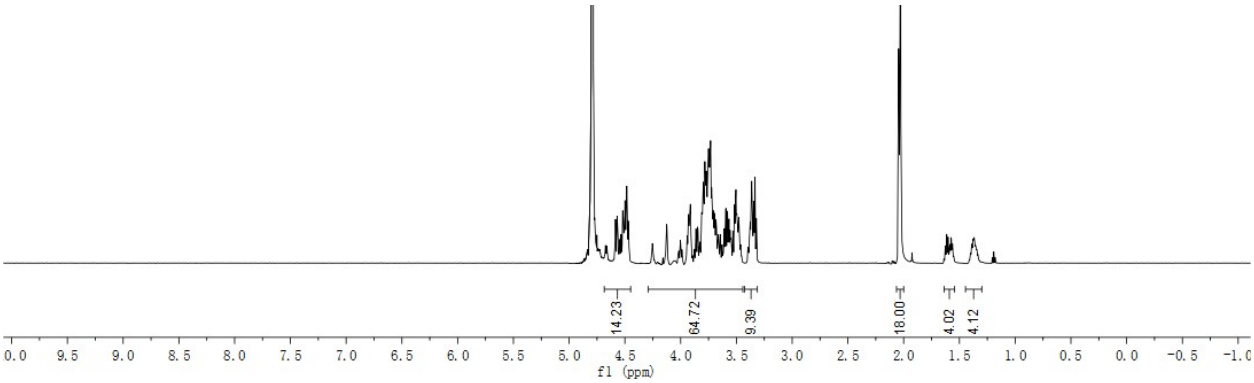

$^{-}$Q ESI-MS profile of **63** (CCHCC$^{*}$HH)



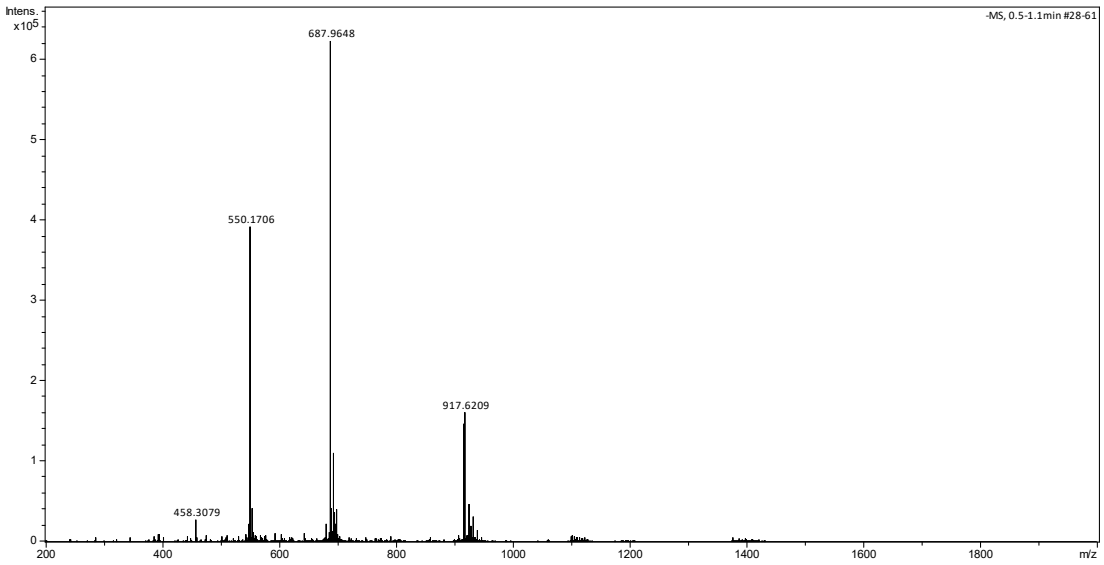

$^{1}$H NMR Spectrum of **63** (CCHCC$^{*}$HH**)**



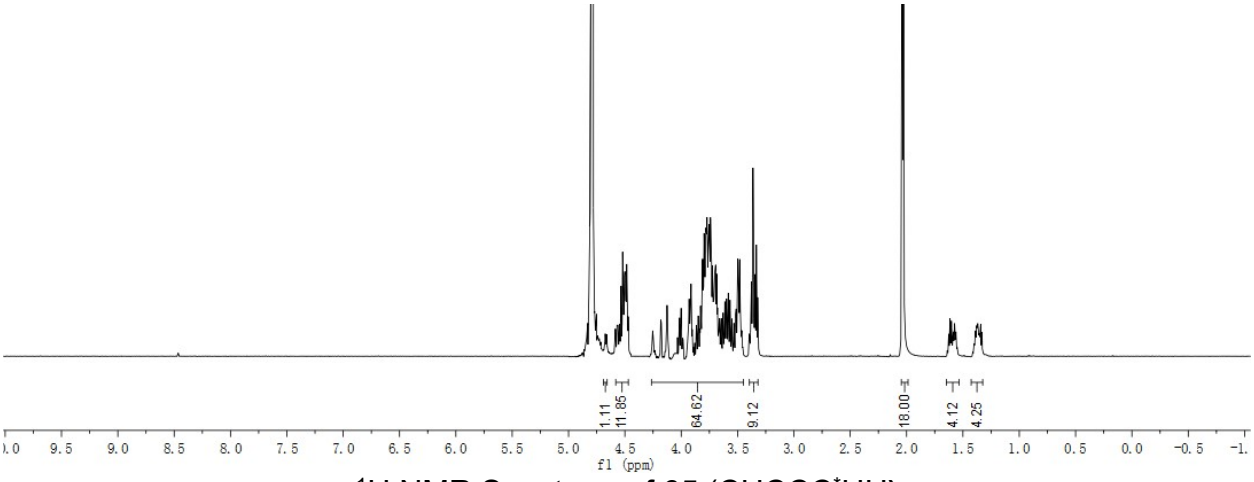

$^{-}$Q ESI-MS profile of **64** (HHCCC$^{*}$HH)



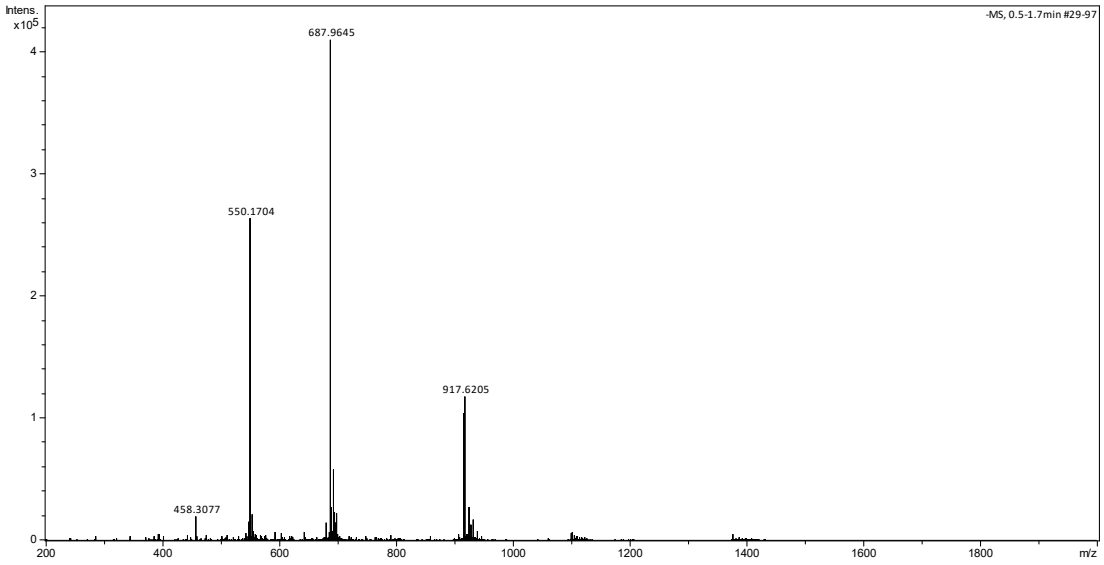

$^{1}$H NMR Spectrum of **64** (HHCCC$^{*}$HH**)**



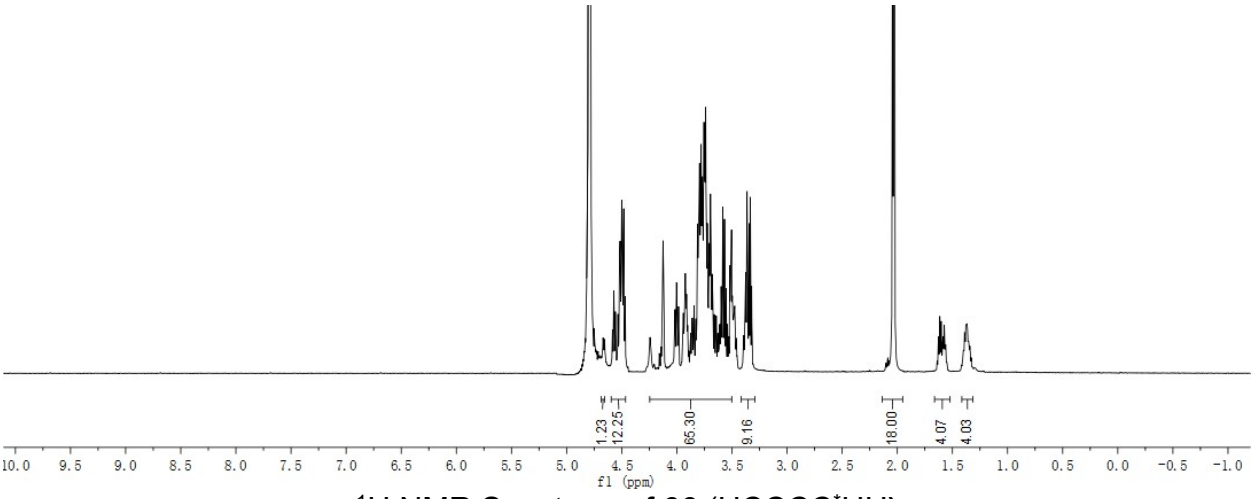

$^{-}$Q ESI-MS profile of **65** (CHCCC$^{*}$HH)



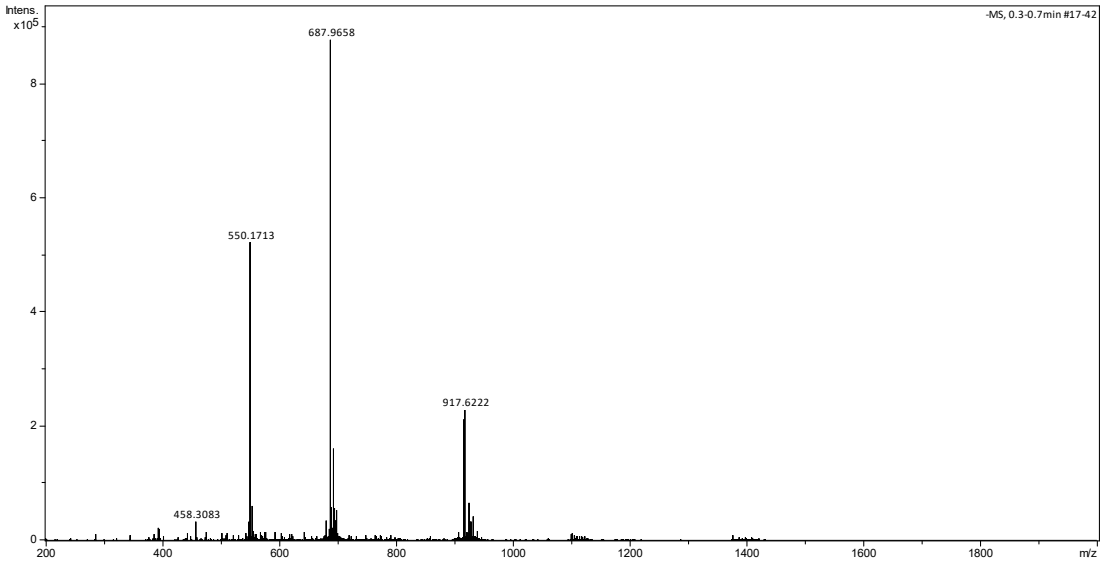

$^{1}$H NMR Spectrum of **65** (CHCCC$^{*}$HH**)**



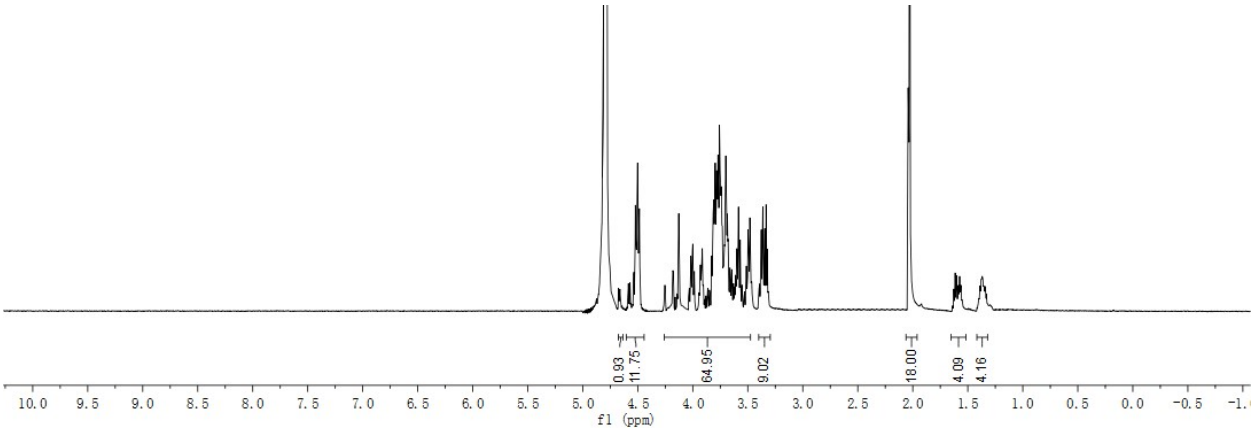

$^{-}$Q ESI-MS profile of **66** (HCCCC$^{*}$HH)



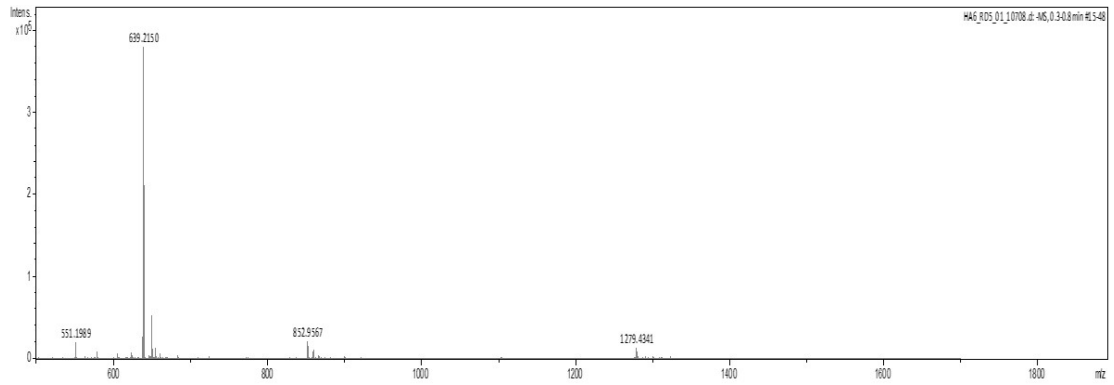

$^{1}$H NMR Spectrum of **66** (HCCCC$^{*}$HH**)**



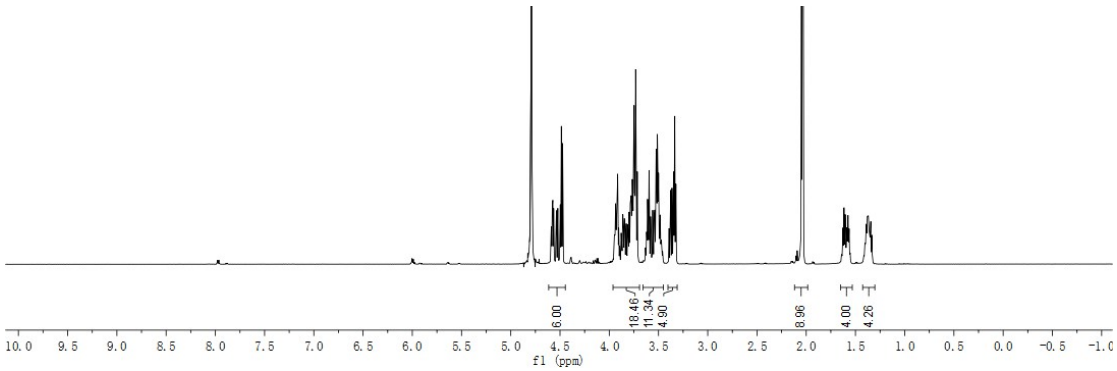

$^{-}$Q ESI-MS profile of **67** (CCCCC$^{*}$HH)



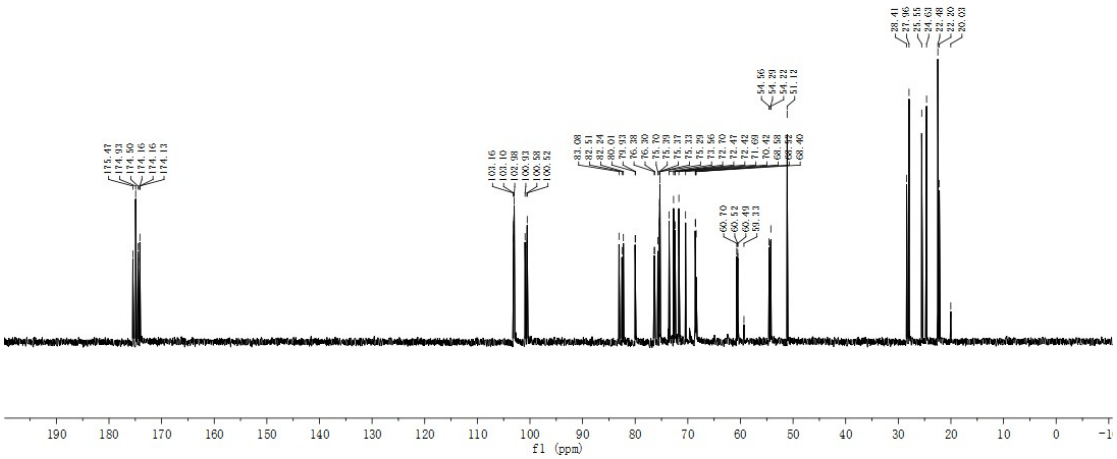

$^{1}$H NMR Spectrum of **67** (CCCCC$^{*}$HH**)**



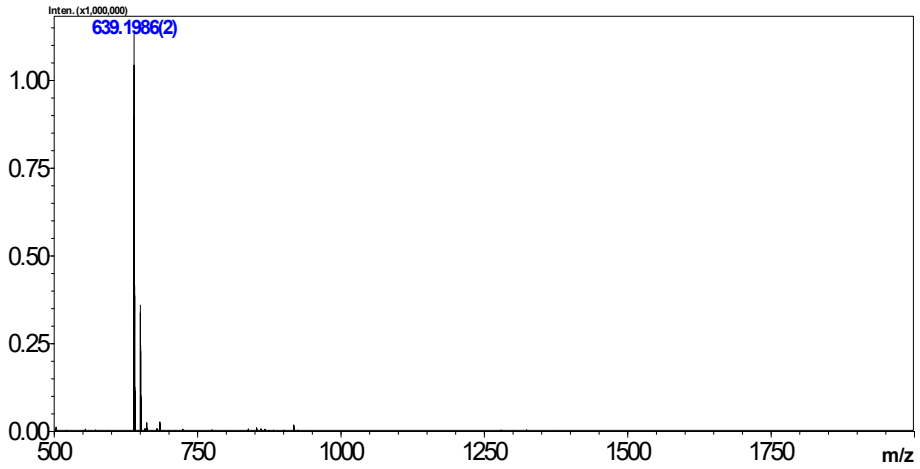

$^{-}$Q ESI-MS profile of **68** (HHH)



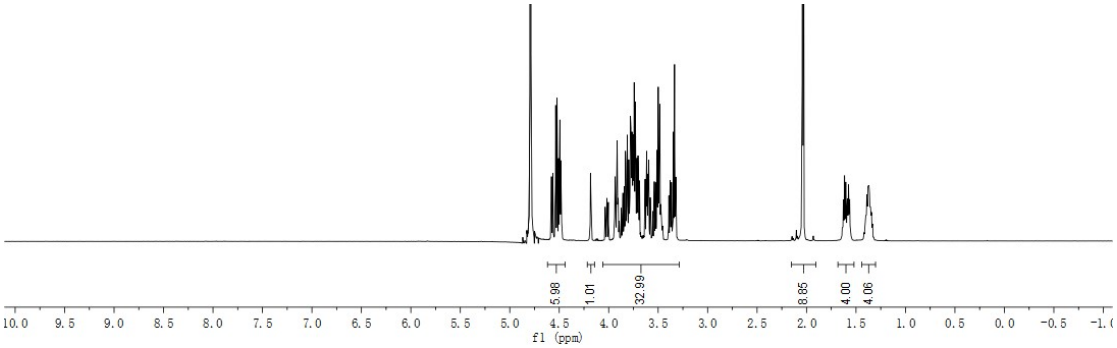

$^{1}$H NMR Spectrum of **68** (HHH)



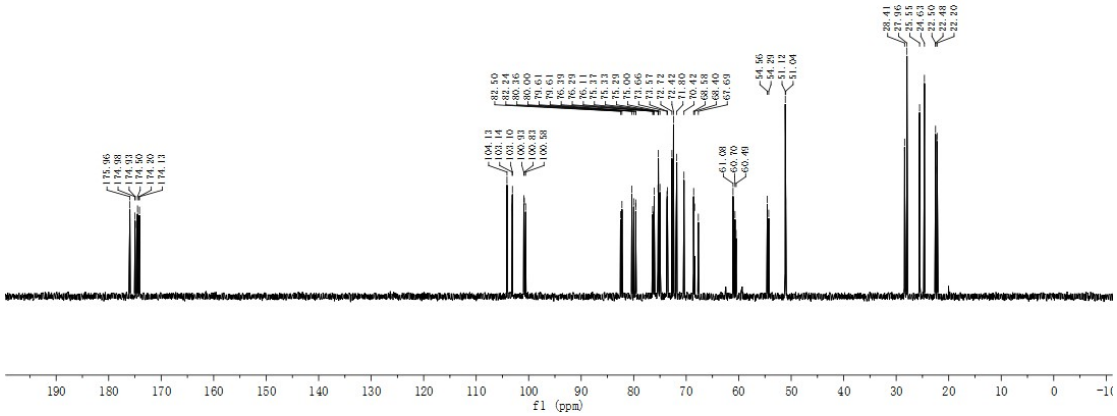

$^{13}$C NMR Spectrum of **68** (HHH)



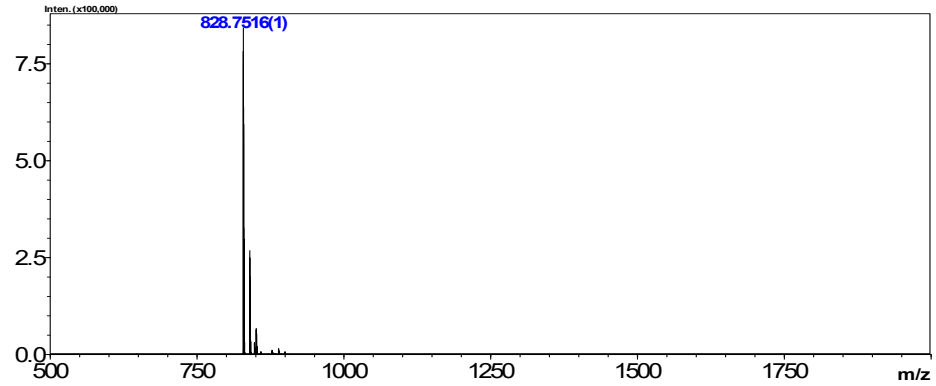

$^{-}$Q ESI-MS profile of **69** (CHH)



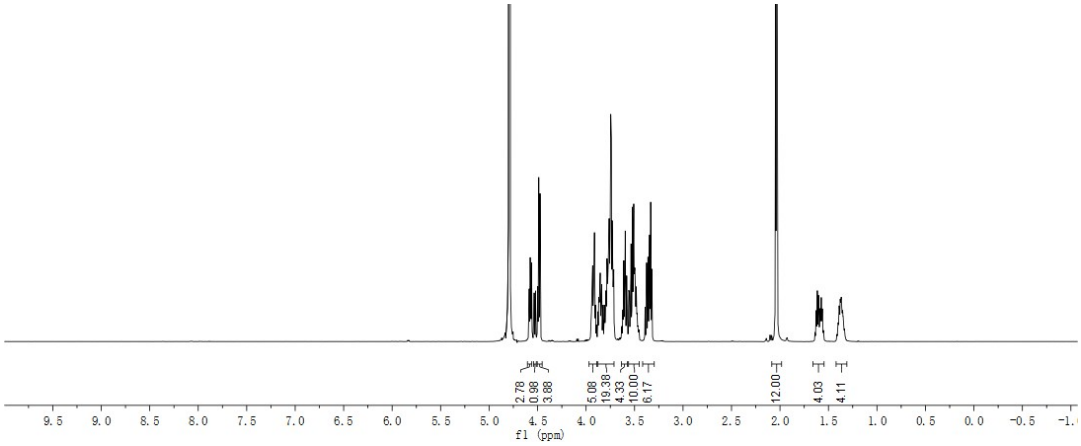

$^{1}$H NMR Spectrum of **69** (CHH)



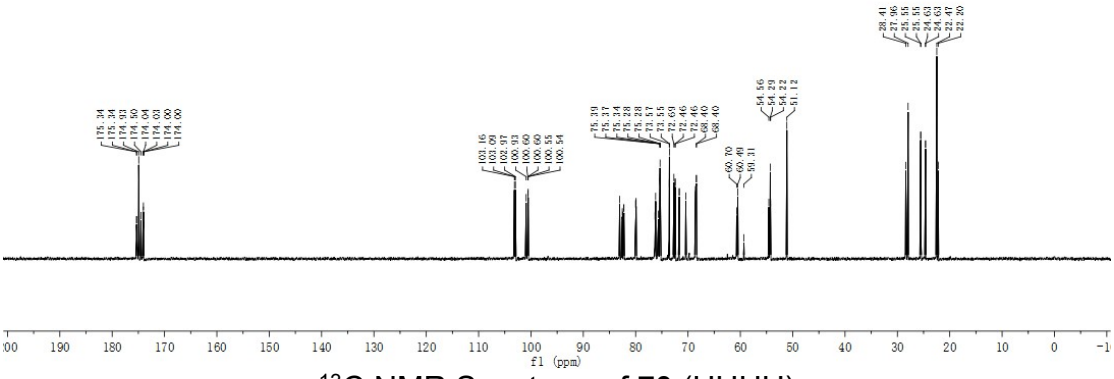

$^{13}$C NMR Spectrum of **69** (CHH)




-Q ESI-MS profile of **70** (HHHH)




$^{1}$H NMR Spectrum of **70** (HHHH)




$^{13}$C NMR Spectrum of **70** (HHHH)

# References


1. Li, S.; Wang, S. S.; Wang, Y. Q.; Qu, J. Y.; Liu, X. W.; Wang, P. G.; Fang, J. Q., Gram-scale production of sugar nucleotides and their derivatives. *Green Chem* **2021,** *23* (7), 2628-2633.
2. Yao, W.; Zhu, Y.; Zhang, X.; Sha, M.; Meng, X.; Li, Z., Semisynthesis of Chondroitin Sulfate E Tetrasaccharide from Hyaluronic Acid. *J Org Chem* **2018,** *83* (22), 14069-14077.
3. Yao, W.; Chen, M.; Dou, X.; Jin, H.; Zhang, X.; Zhu, Y.; Sha, M.; Liu, Z.; Meng, X.; Zhang, L.; Zhu, S.; Li, Z., Unravel a neuroactive sHA sulfation pattern with neurogenesis activity by a library of defined oligosaccharides. *Eur J Med Chem* **2019,** *163*, 583-596.
4. Jing, W.; DeAngelis, P. L., Dissection of the two transferase activities of the Pasteurella multocida hyaluronan synthase: two active sites exist in one polypeptide. *Glycobiology* **2000,** *10* (9), 883-9.
5. DeAngelis, P. L.; Jing, W.; Drake, R. R.; Achyuthan, A. M., Identification and molecular cloning of a unique hyaluronan synthase from Pasteurella multocida. *J Biol Chem* **1998,** *273* (14), 8454-8.
6. DeAngelis, P. L.; Padgett-McCue, A. J., Identification and molecular cloning of a chondroitin synthase from Pasteurella multocida type F. *J Biol Chem* **2000,** *275* (31), 24124-9.