

Supporting Information

Supramolecular helical nanofibers assembled from a pyridinium- functionalized methyl glycyrrhetate amphiphile

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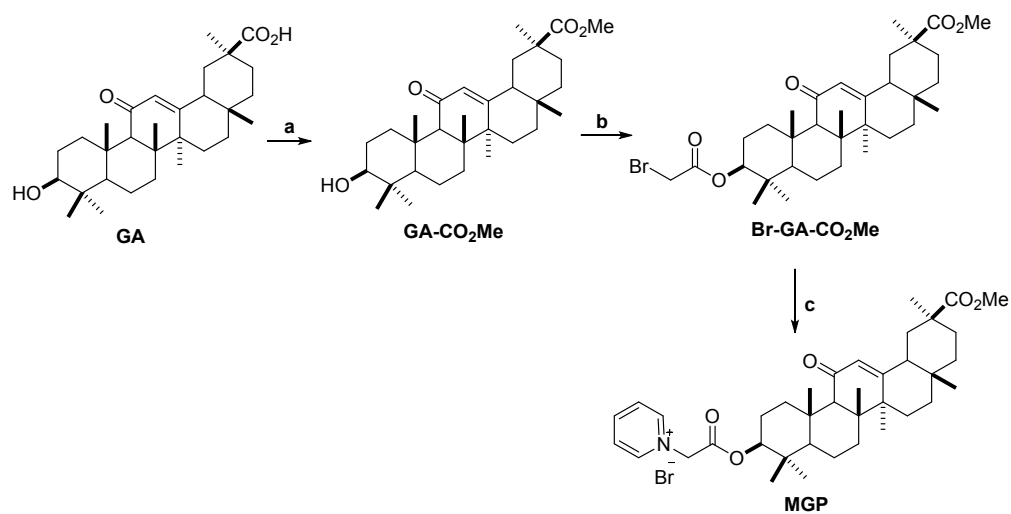
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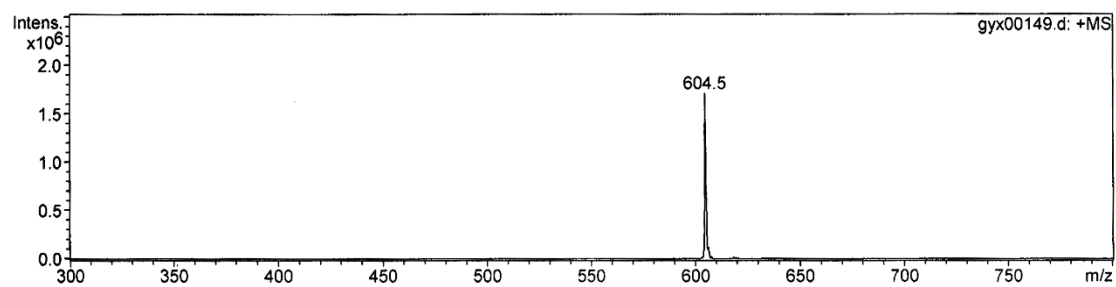
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1. Synthesis and structure characterization of MGP

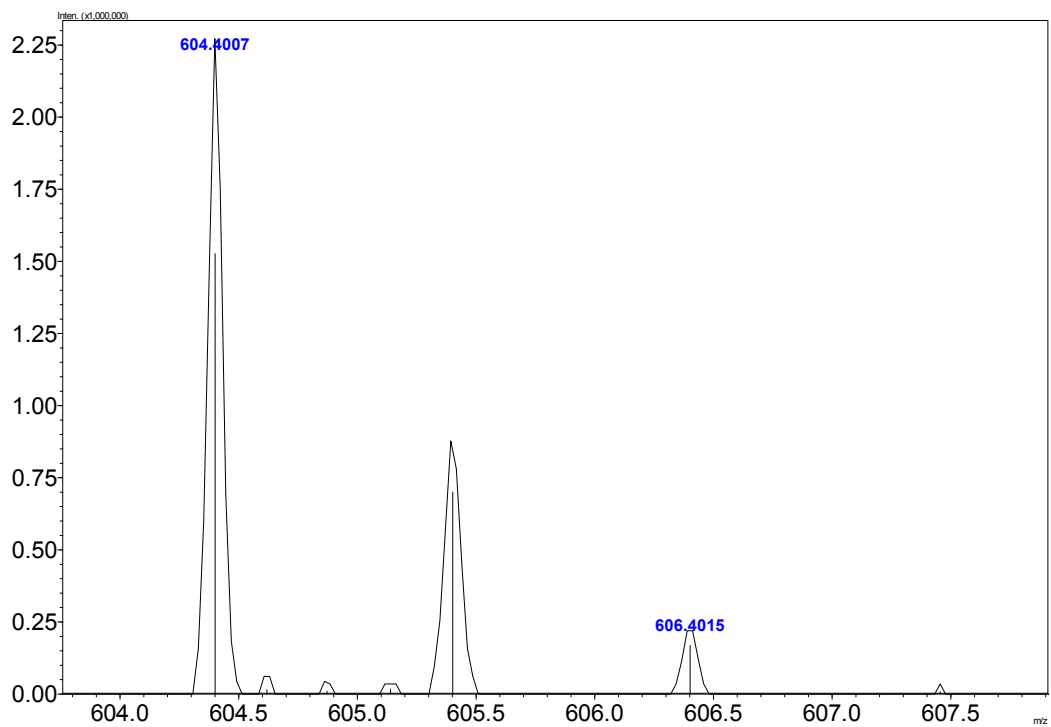


Scheme S1 (a) CH₃I, DMF, r.t., 20 h, 98 %; (b) BrCOCH₂Br, K₂CO₃, dry DCM, r.t., 12 h, 90 %; (c) Pyridine, r.t., 10 h, 92 %.

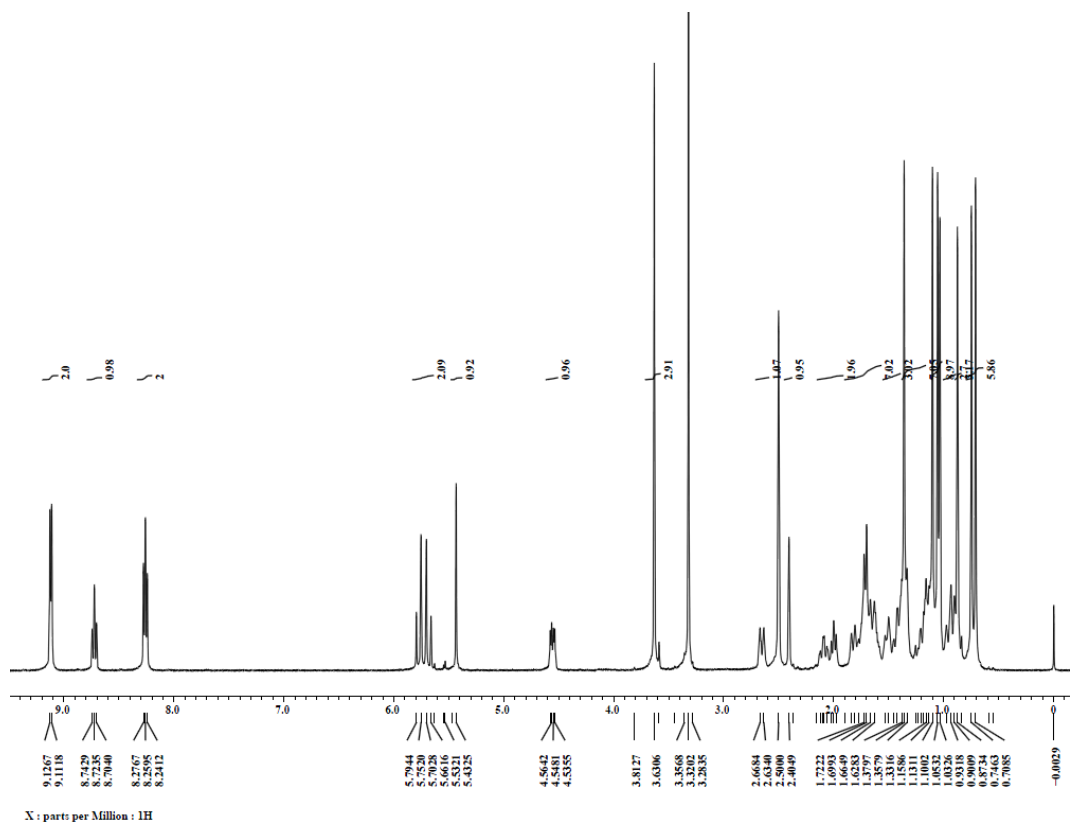
(1) ESI-MS (+) spectrum of MGP



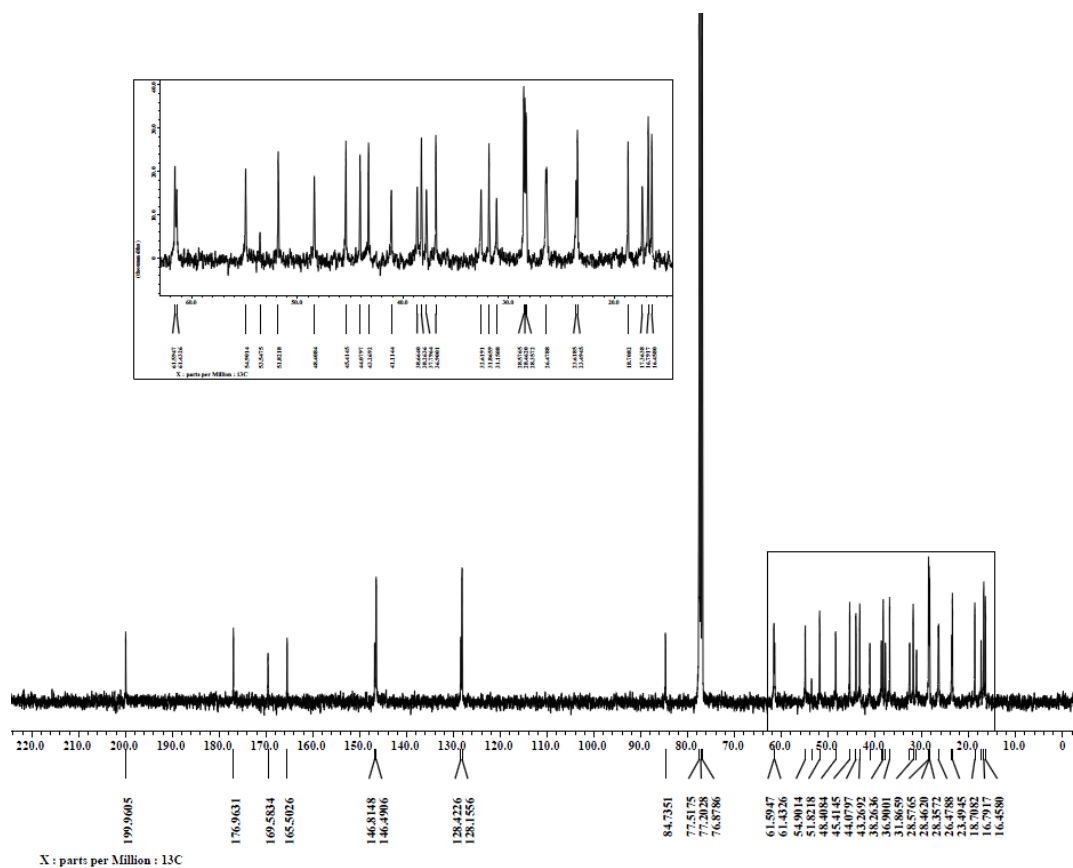
(2) HRMS (ESI) spectrum of **MGP**



(3) ^1H NMR spectrum of **MGP** (400 MHz, $\text{DMSO}-d_6$)



(4) ^{13}C NMR spectrum of **MGP** (100 MHz, CDCl_3)



2. Self-assembly behaviors of **MGP**

Entry	Mixed solvents (v/v)	MGC (mg mL^{-1})	State
1	chloroform/toluene =1:2	1.0	Gel
2	chloroform/ <i>o</i> -xylene =1:2	1.0	Gel
3	chloroform/ <i>m</i> -xylene =1:2	1.0	Gel
4	chloroform/ <i>p</i> -xylene =1:2	1.0	Gel
5	chloroform/mesitylene =1:2	1.0	Gel
6	chloroform/chlorobenzene =1:2	1.0	Gel
7	chloroform/bromobenzene =1:2	1.0	Gel
8	chloroform/ <i>o</i> -dichlorobenzene =1:2	1.0	Gel

Table S1 Self-assembly behaviors of **MGP** in various mixed solvents

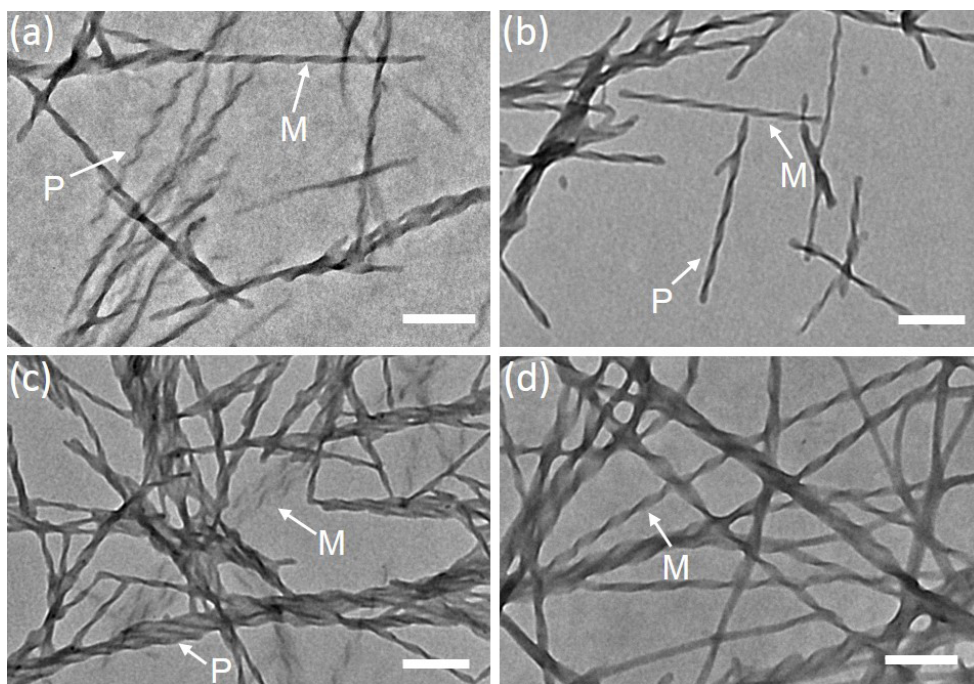


Fig. S1 TEM images of **MGP** assemblies in other mixed solvents of chloroform and (a) *p*-xylene, (b) chlorobenzene, (c) bromobenzene, (d) toluene (12 mM, chloroform/aromatic solvent = 1:2, v/v). Scale bar is 200 nm.

Mixed solvents	Handedness	Width/nm	Pitch/nm
chloroform/toluene	left	40	124
chloroform/ <i>o</i> -xylene	right/left	28	121
chloroform/ <i>m</i> -xylene	right/left	28	117
chloroform/ <i>p</i> -xylene	right/left	34	124
chloroform/mesitylene	left	29	118
chloroform/chlorobenzene	right/left	35	120
chloroform/bromobenzene	right/left	29	126
chloroform/ <i>o</i> -dichlorobenzene	right	29	115

Table S2 The parameters of helical fibers assembled from **MGP** in different chloroform/aromatic solvents (the width and pitch are average values)

3. CD spectra of MGP in mixed solvents

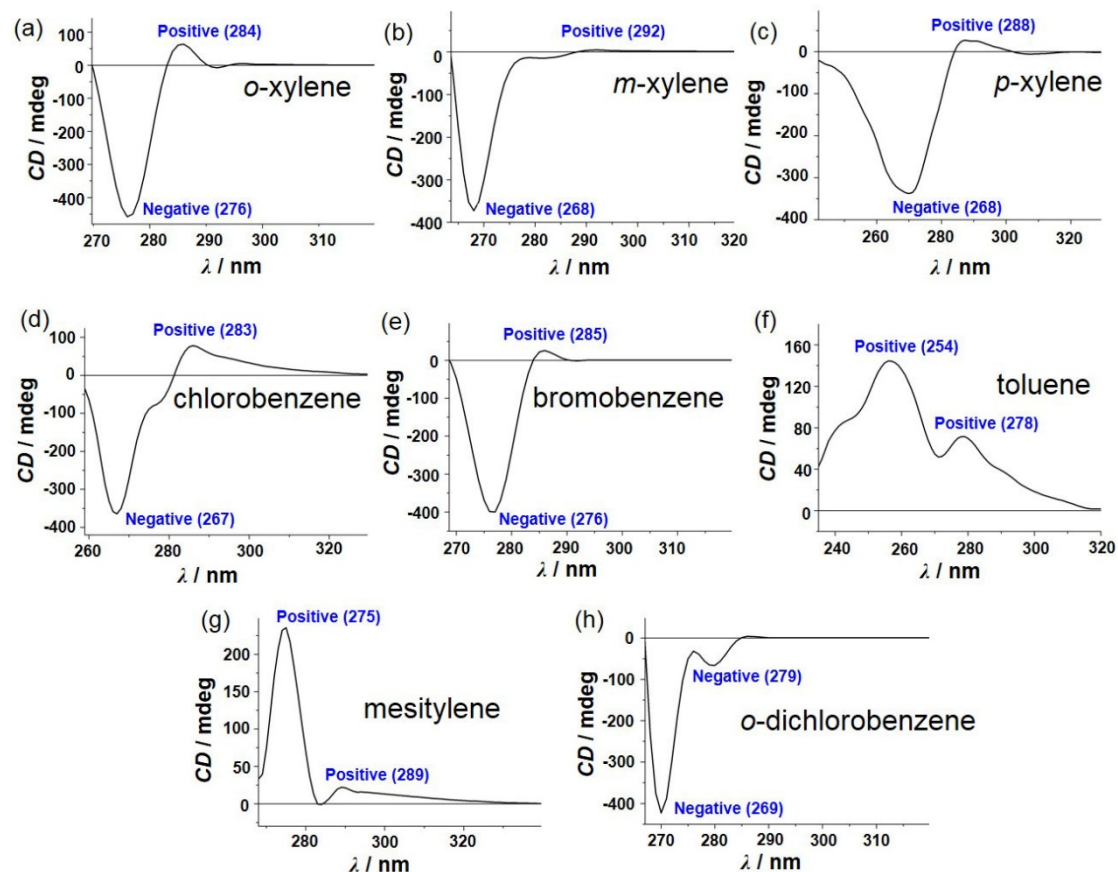


Fig. S2 CD spectra of **MGP** assemblies in different mixed solvents

(chloroform/aromatic solvent = 1:2, v/v, 1.5×10^{-3} M): (a) *o*-xylene, (b) *m*-xylene, (c) *p*-xylene, (d) chlorobenzene, (e) bromobenzene, (f) toluene, (g) mesitylene, (h) *o*-dichlorobenzene.

4. TEM images of MGP under different concentrations

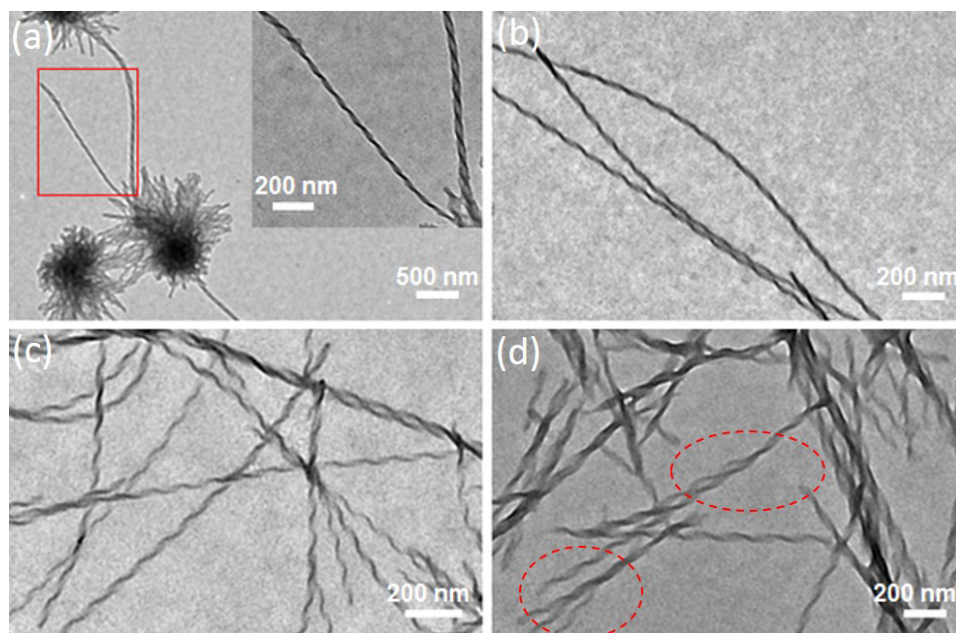


Fig. S3 TEM images of MGP in chloroform/*o*-xylene (1:2, v/v) under different concentrations. (a) 0.5 mg mL⁻¹, PG, insert refers to the magnified field inside the red line; (b) 1.0 mg mL⁻¹, G; (c) 3.0 mg mL⁻¹, G; (d) 5.0 mg mL⁻¹, G, dash circles show the coiling process of the helical fibers. G and PG are the abbreviations of gel and partial gel.

5. UV-Vis spectra of MGP under different concentrations

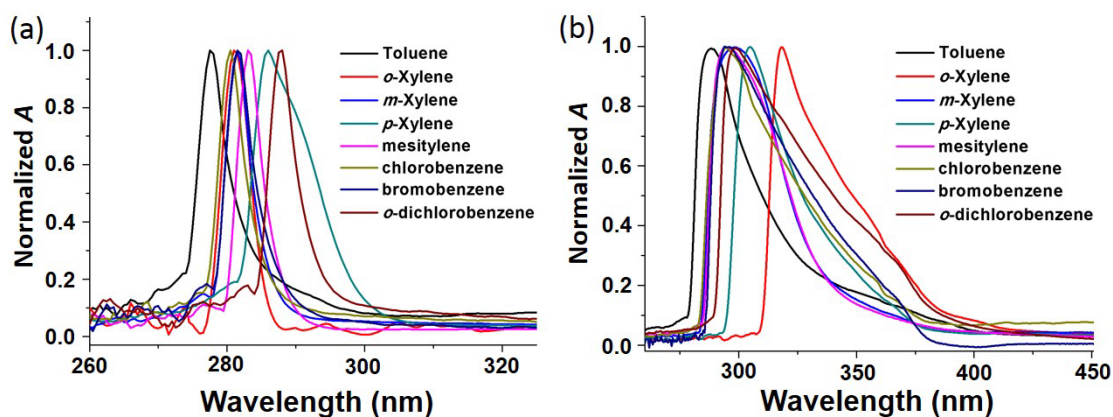


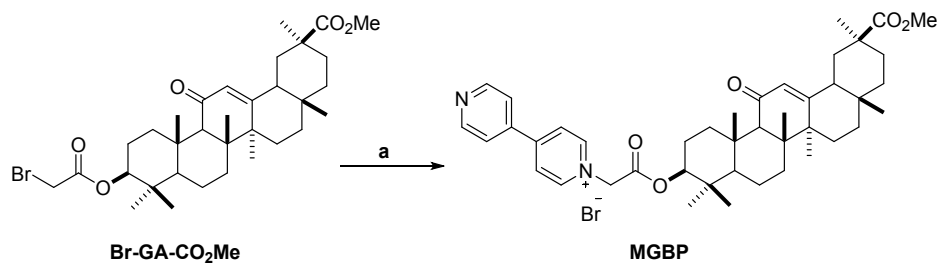
Fig. S4 Normalized UV-Vis spectra of MGP in mixed solvents (chloroform/aromatic solvent=1:2, v/v) under different concentrations: (a) 5.0×10^{-5} M, (b) 1.5×10^{-3} M.

Mixed solvents	λ_1 /nm	λ_2 /nm	$\Delta\lambda$ /nm
chloroform/toluene	277	288	11
chloroform/ <i>o</i> -xylene	280	318	38
chloroform/ <i>m</i> -xylene	281	297	16
chloroform/ <i>p</i> -xylene	285	305	20
chloroform/mesitylene	282	295	13
chloroform/chlorobenzene	280	295	15
chloroform/bromobenzene	281	294	13
chloroform/ <i>o</i> -dichlorobenzene	287	300	13

Table S3 The maximum absorption peaks of **MGP** in each solvent system under different concentrations (λ_1 : $C_1 = 5 \times 10^{-5}$ M, λ_2 : $C_2 = 1.5 \times 10^{-3}$ M, $\Delta\lambda = \lambda_2 - \lambda_1$)

6. Syntheses and structure characterizations of MGBP, C4-MGP, and C4-MOP

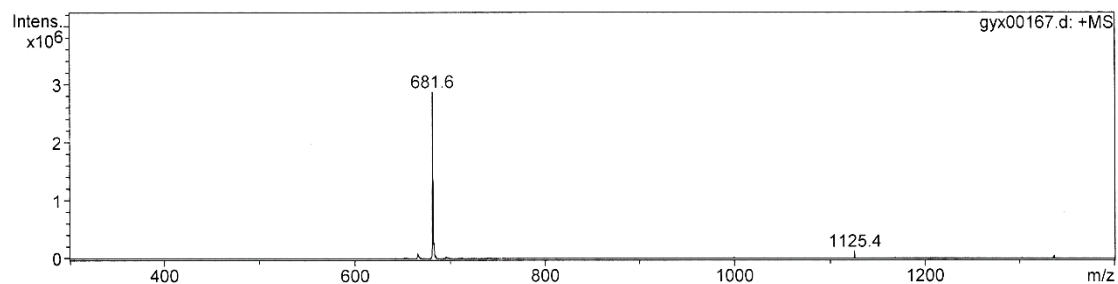
Synthesis of MGBP



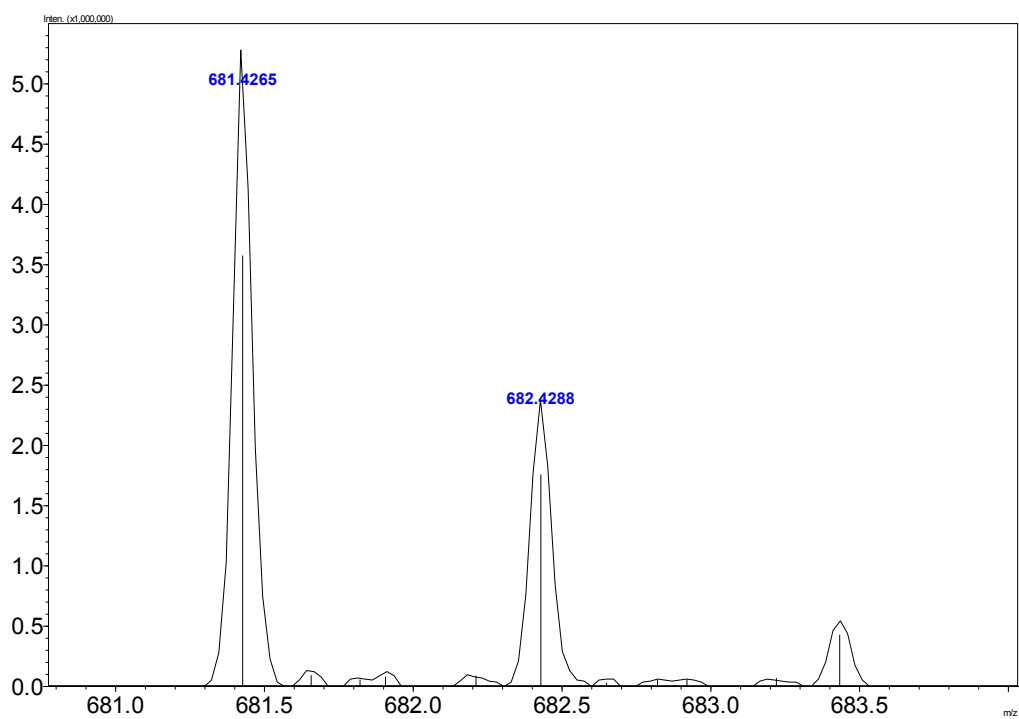
Scheme S2 (a) 4, 4'-bipyridine, dry CH_2Cl_2 , r.t., 24 h, 75 %.

MGBP

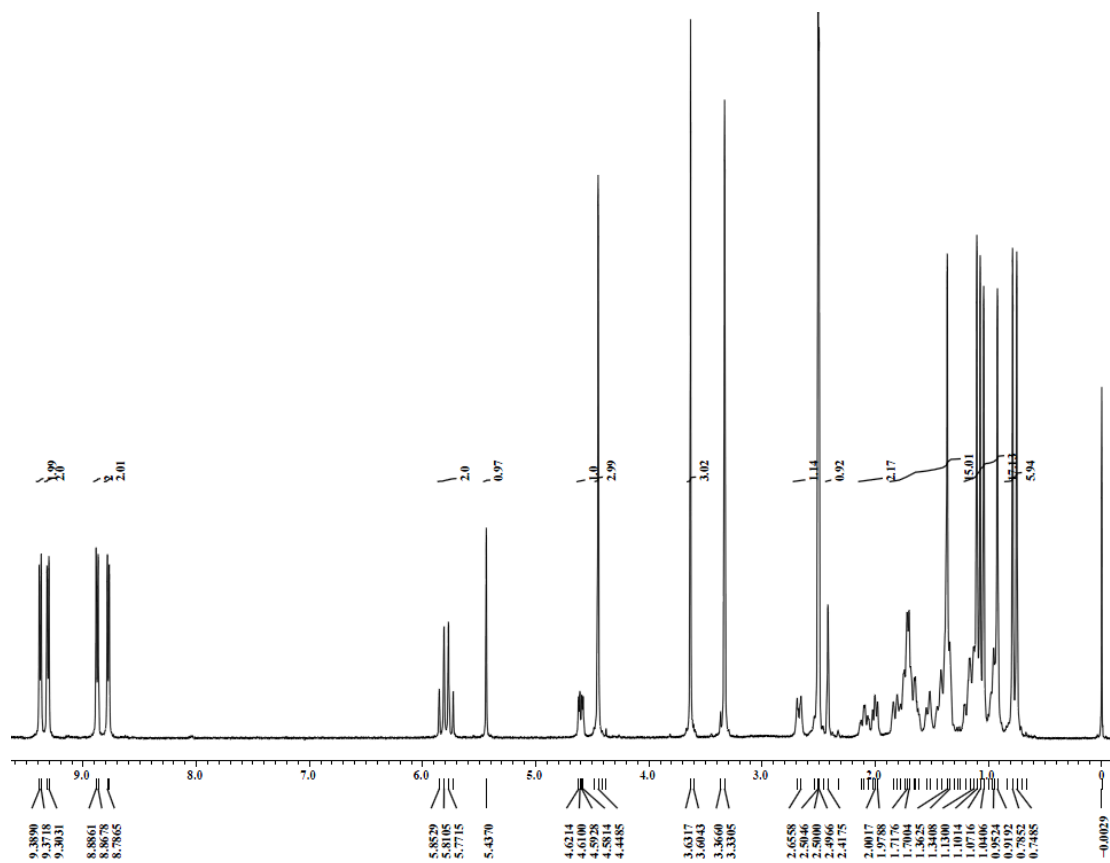
(1) ESI-MS (+) spectrum of MGBP



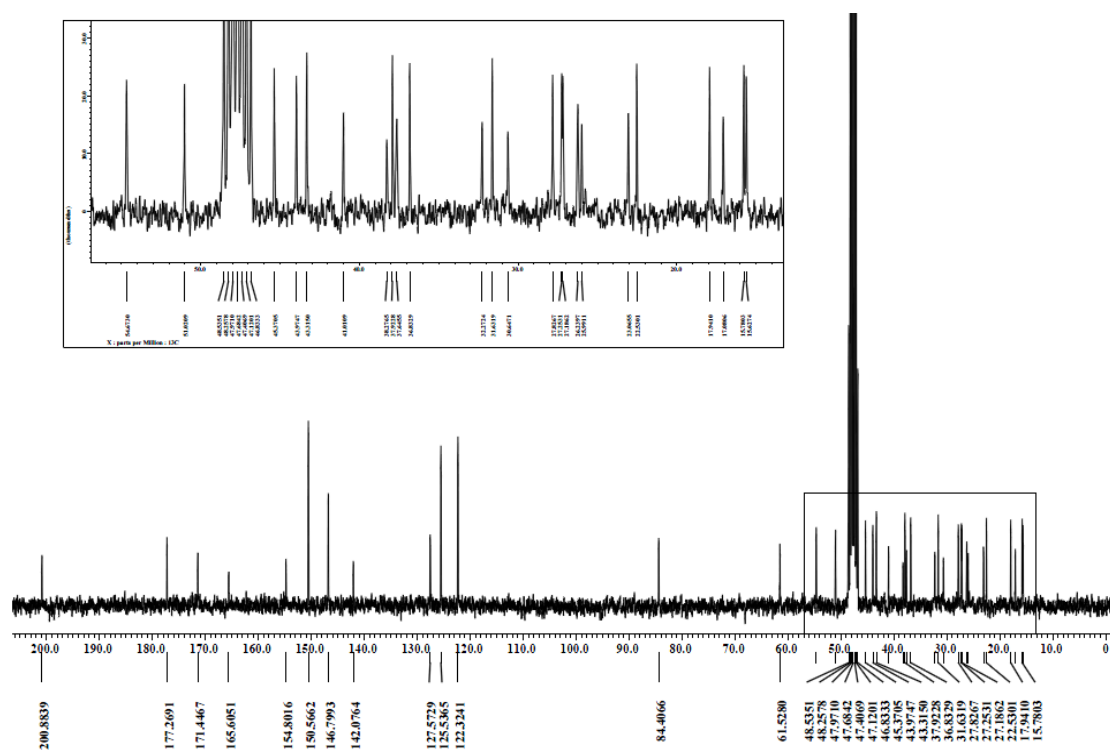
(2) HRMS (ESI) spectrum of MGBP



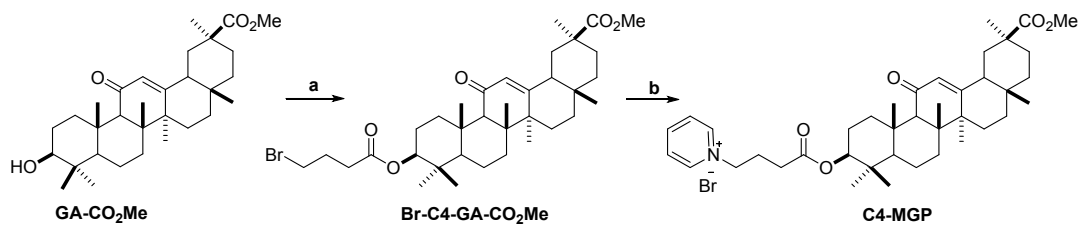
(3) ^1H NMR spectrum of MGBP (400 MHz, $\text{DMSO-}d_6$)



(4) ^{13}C NMR spectrum of **MGFP** (75 MHz, CD_3OD)



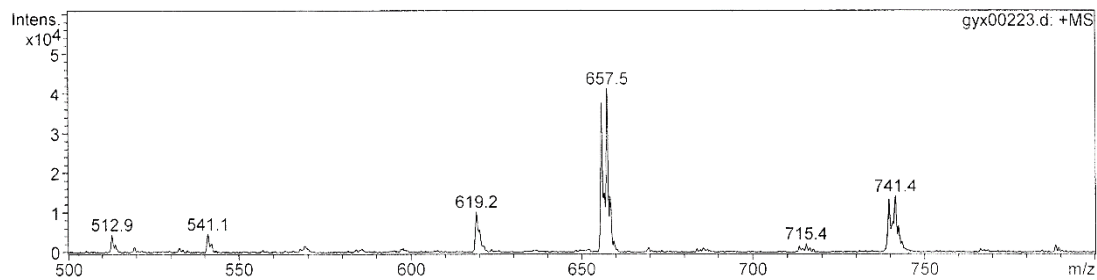
Synthesis of C4-MGP



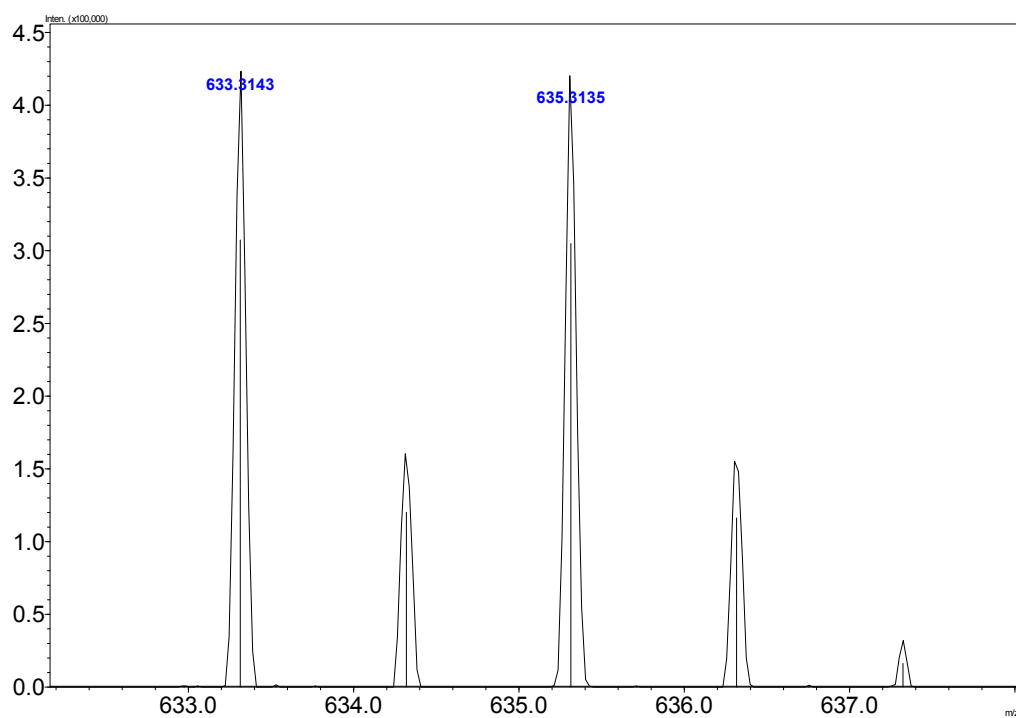
Scheme S3 (a) 4-Bromobutyric acid, DCC, DMAP, dry CH₂Cl₂, r.t., 20 h, 54 %; (b) Pyridine, r.t., 10 h, 64 %.

Br-C4-GA-CO₂Me

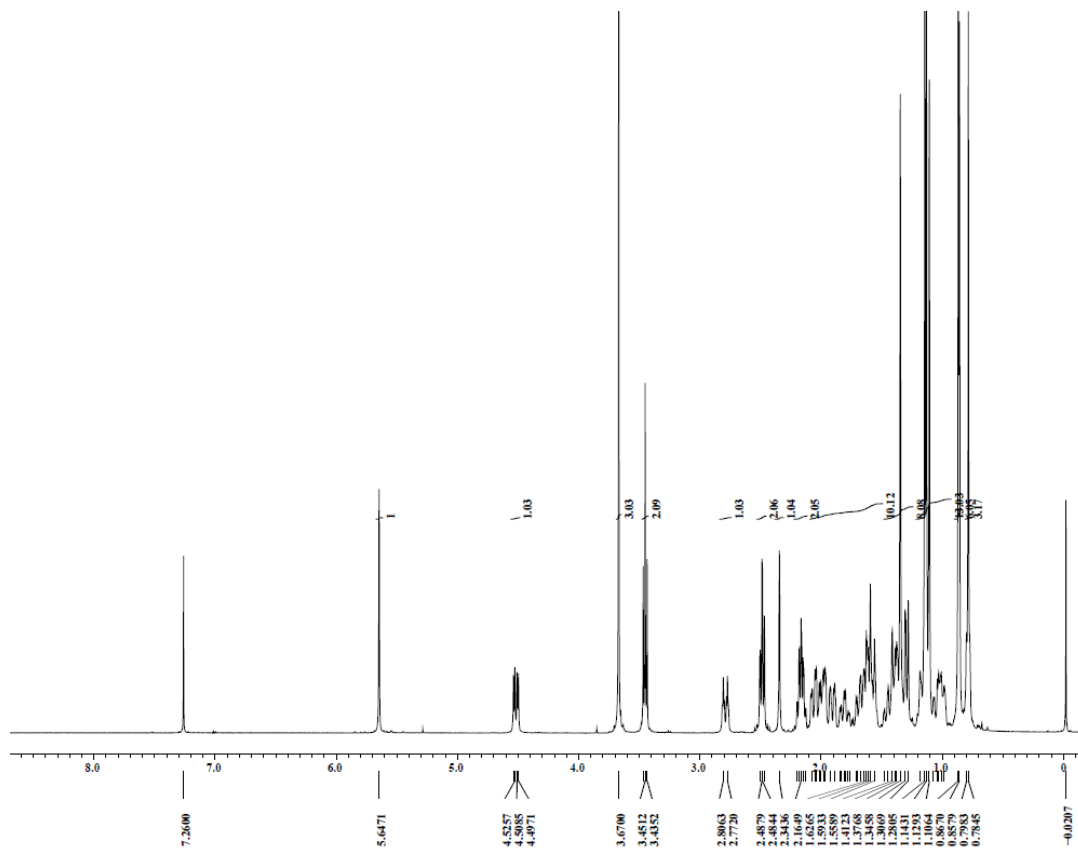
(1) ESI-MS (+) spectrum of Br-C4-GA-CO₂Me



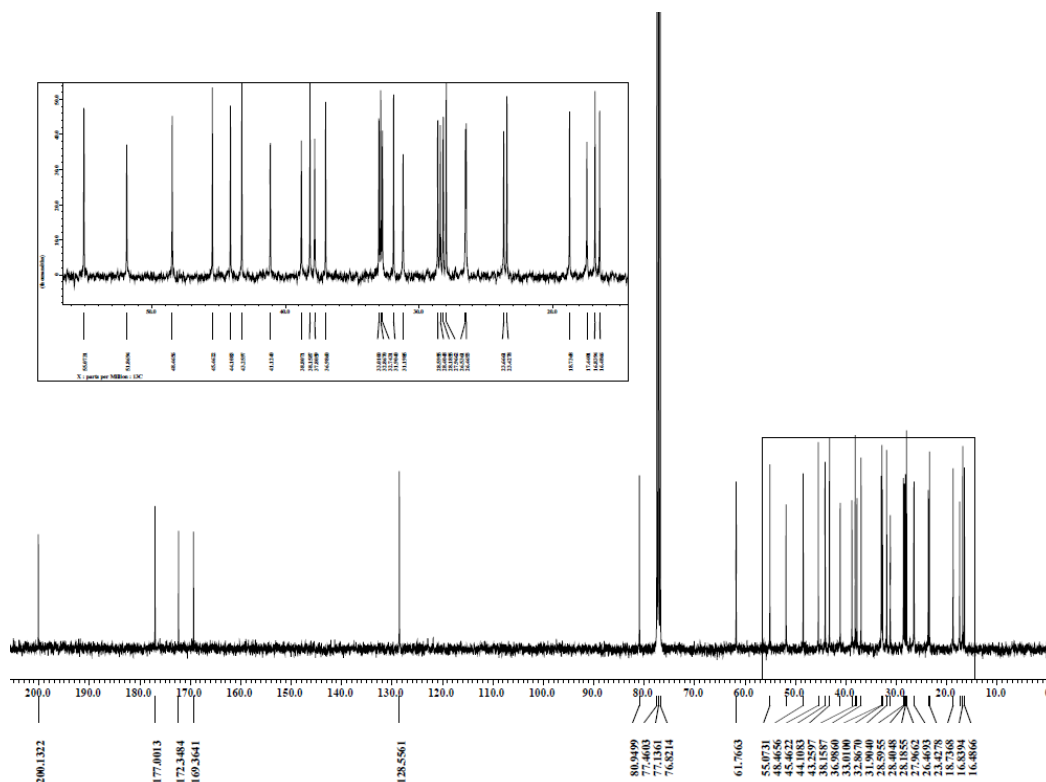
(2) HRMS (ESI) spectrum of Br-C4-GA-CO₂Me



(3) ^1H NMR spectrum of **Br-C4-GA-CO₂Me** (400 MHz, CDCl_3)

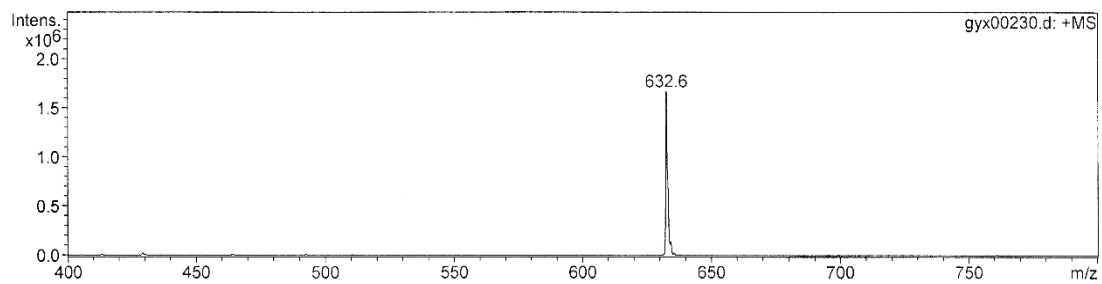


(4) ^{13}C NMR spectrum of **Br-C4-GA-CO₂Me** (100 MHz, CDCl_3)

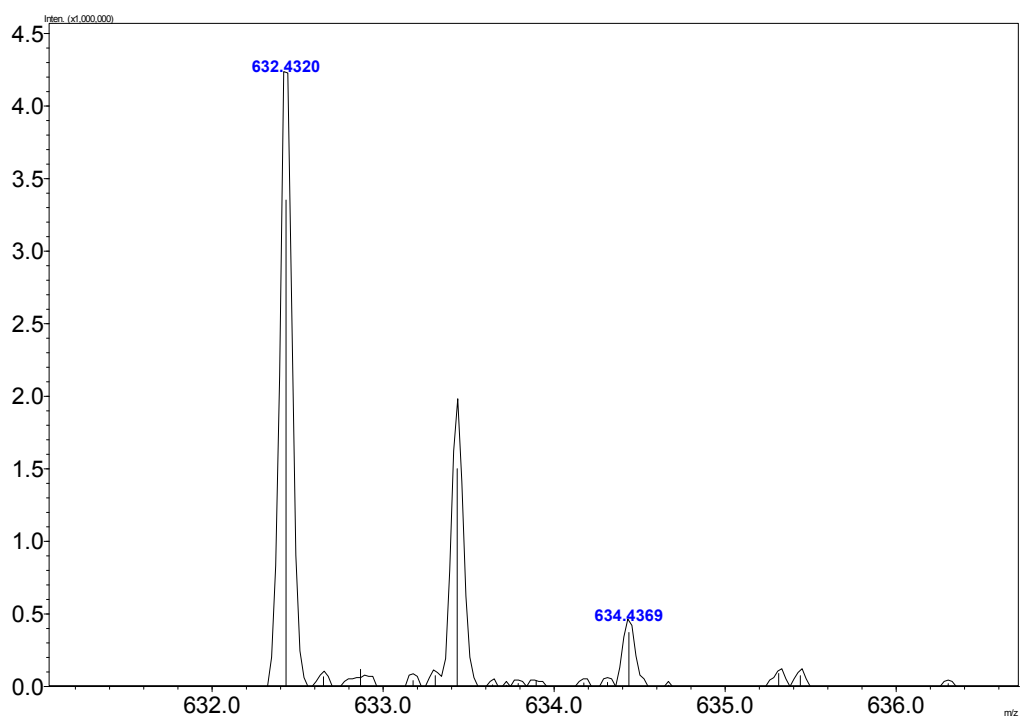


C4-MGP

(1) ESI-MS (+) spectrum of C4-MGP

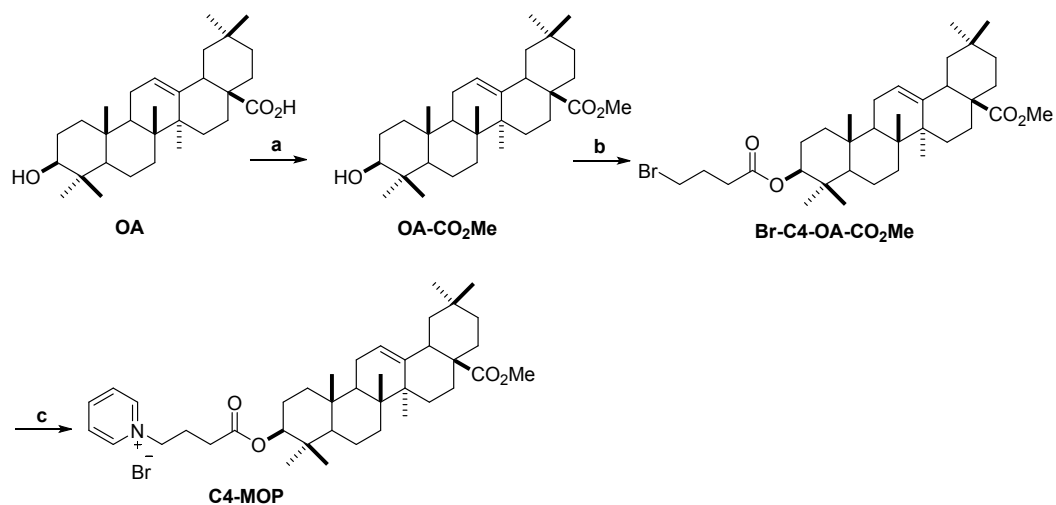


(2) HRMS (ESI) spectrum of C4-MGP



(3) ¹H NMR spectrum of C4-MGP (400 MHz, DMSO-*d*₆)

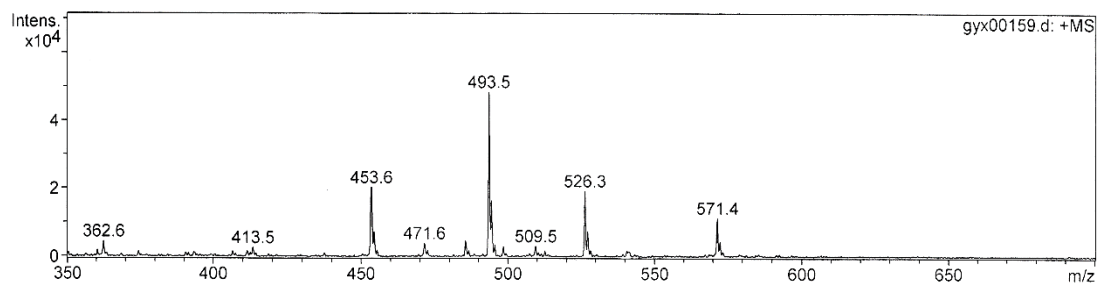
Synthesis of C4-MOP



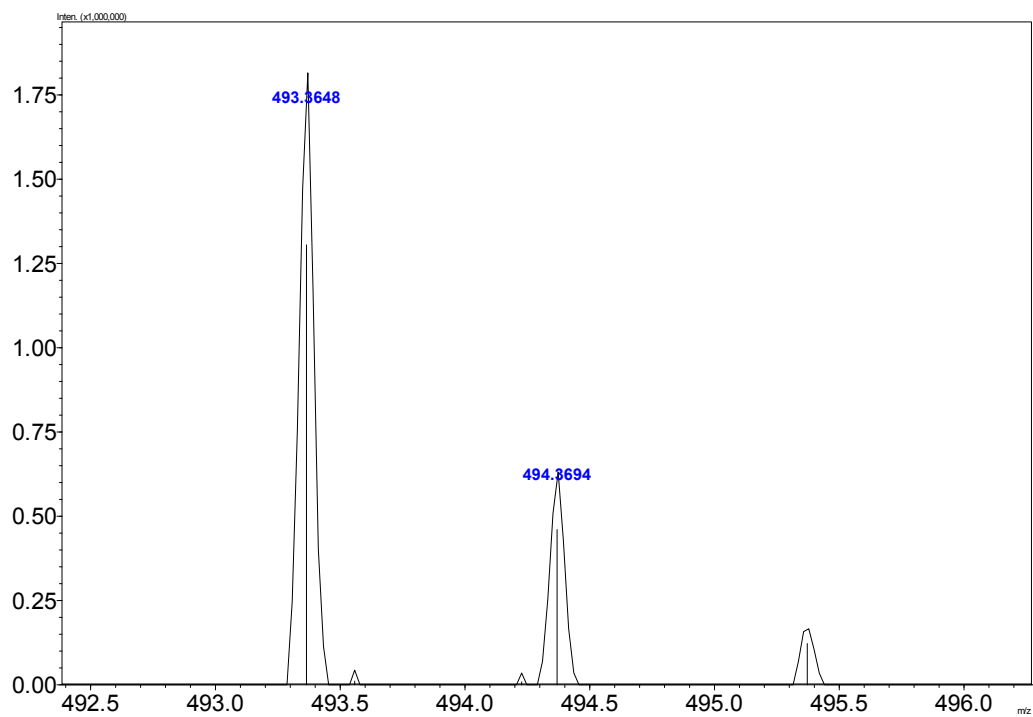
Scheme S4 (a) CH₃I, DMF, r.t., 20 h, 97 %; (b) 4-Bromobutyric acid, DCC, DMAP, dry DCM, r.t., 20 h, 58 %; (c) Pyridine, r.t., 12 h, 60 %.

OA-CO₂Me

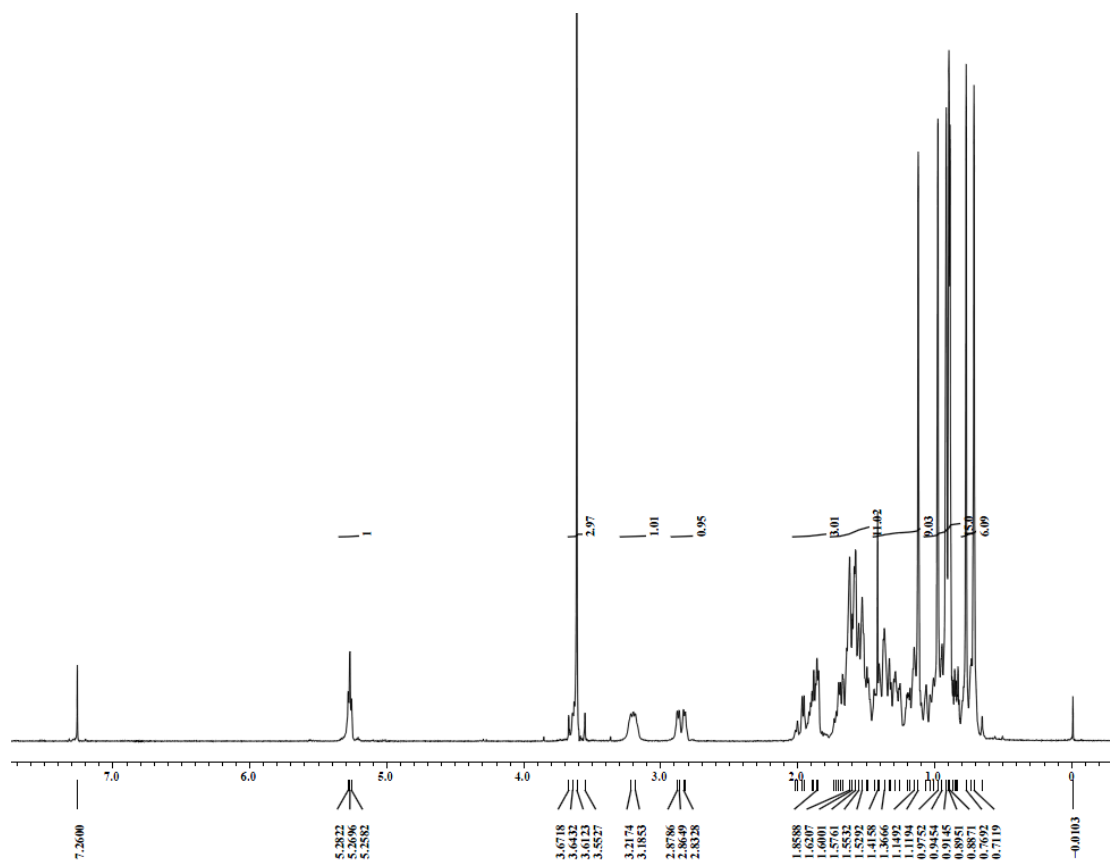
(1) ESI-MS (+) spectrum of OA-CO₂Me



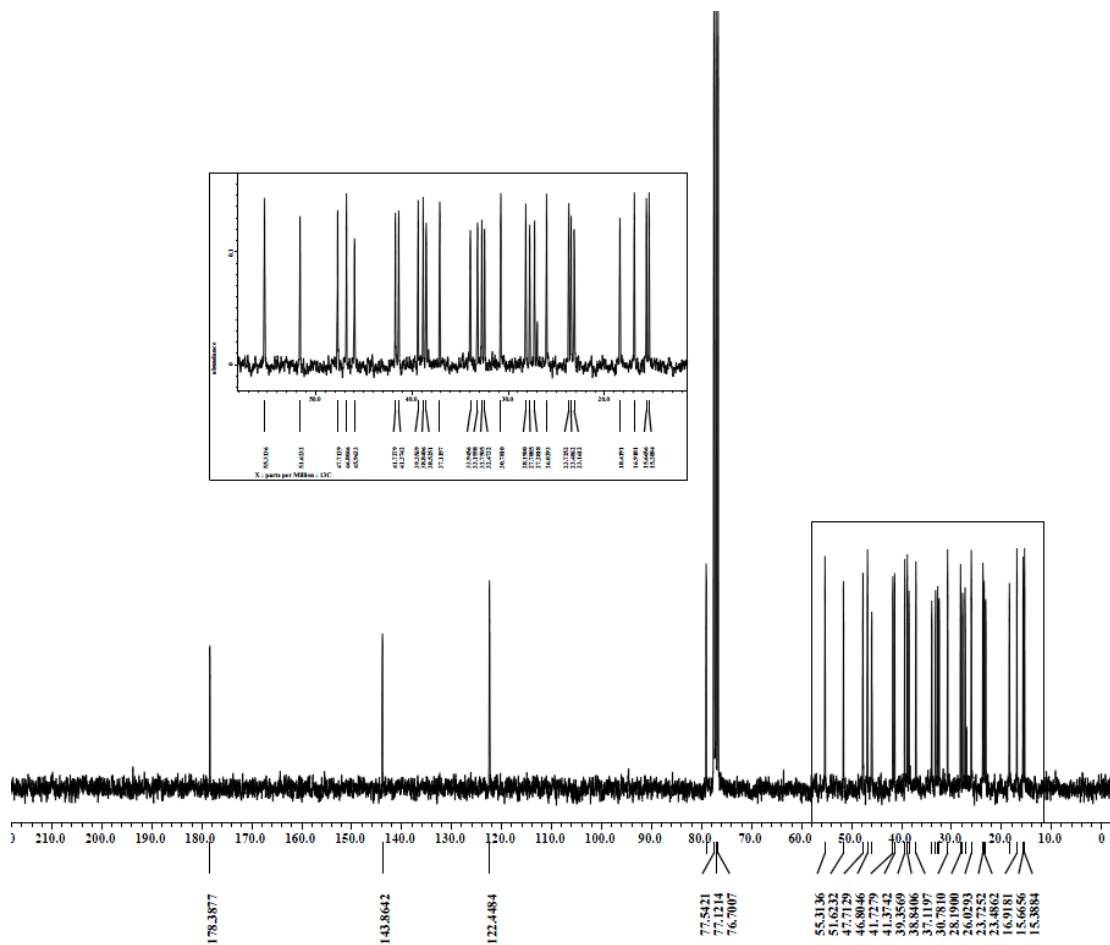
(2) HRMS (ESI) spectrum of OA-CO₂Me



(3) ^1H NMR spectrum of **OA-CO₂Me** (300 MHz, CDCl₃)

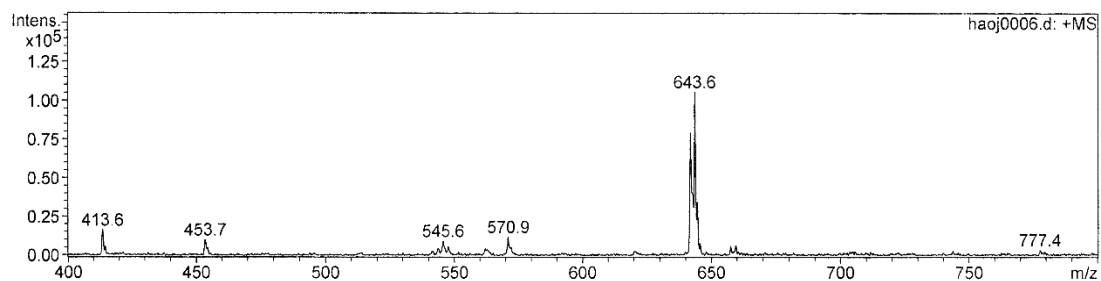


(4) ^{13}C NMR spectrum of **OA-CO₂Me** (75 MHz, CDCl_3)

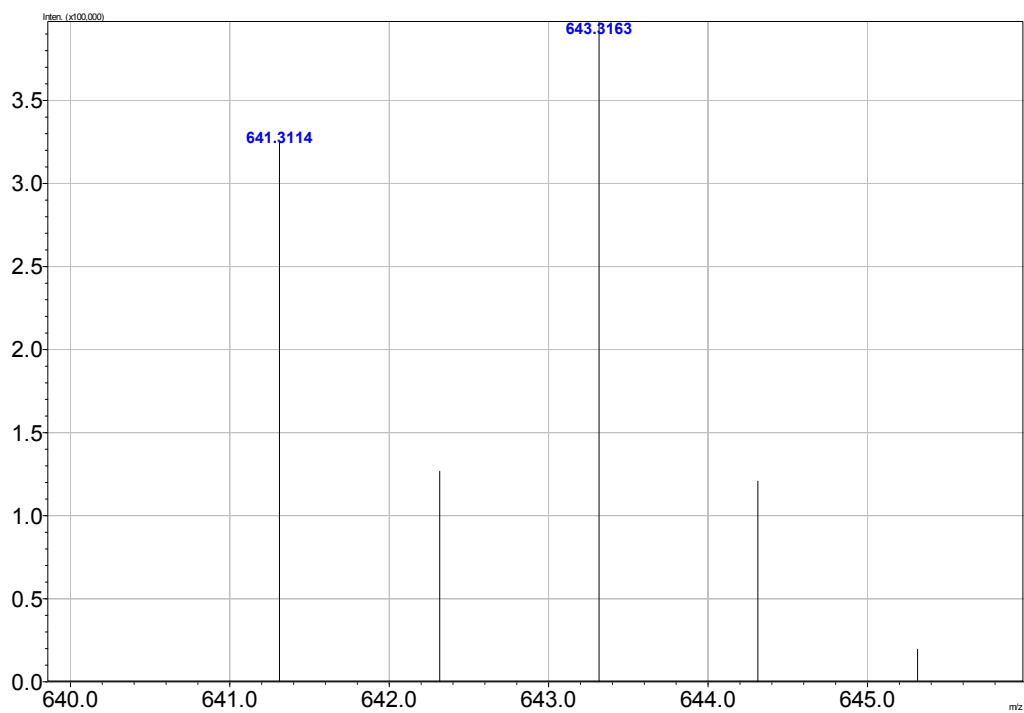


Br-C4-OA-CO₂Me

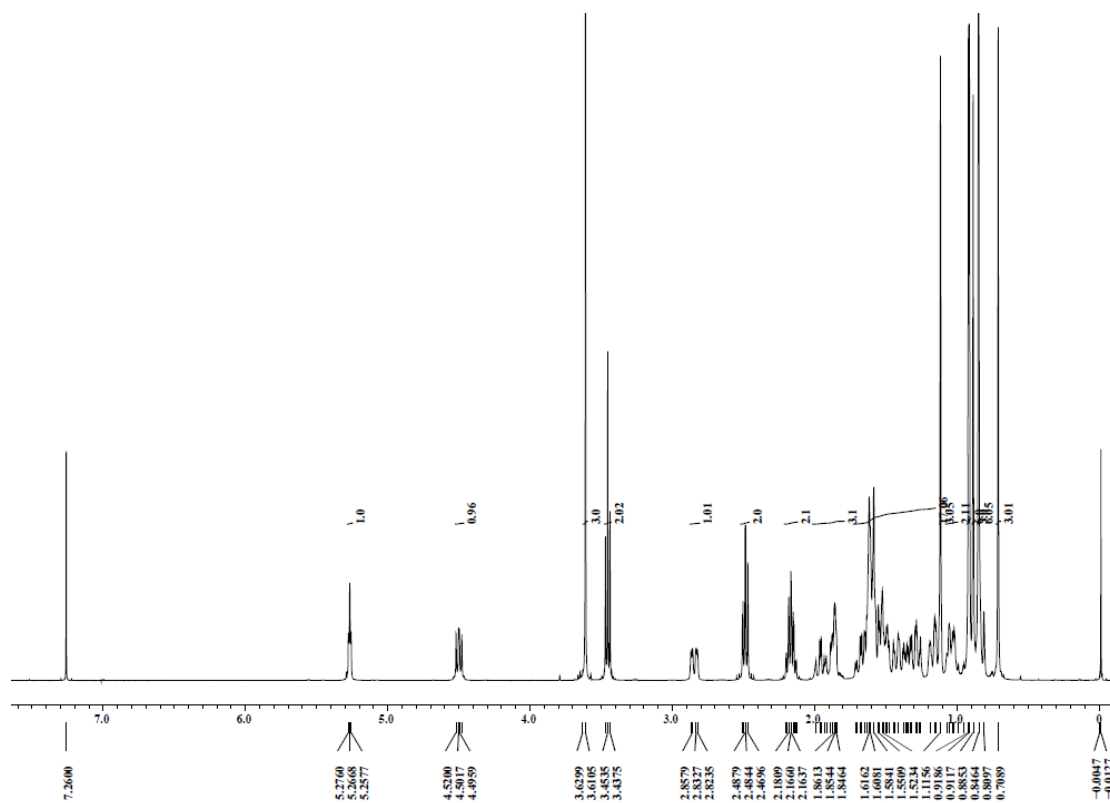
(1) ESI-MS (+) spectrum of **Br-C4-OA-CO₂Me**



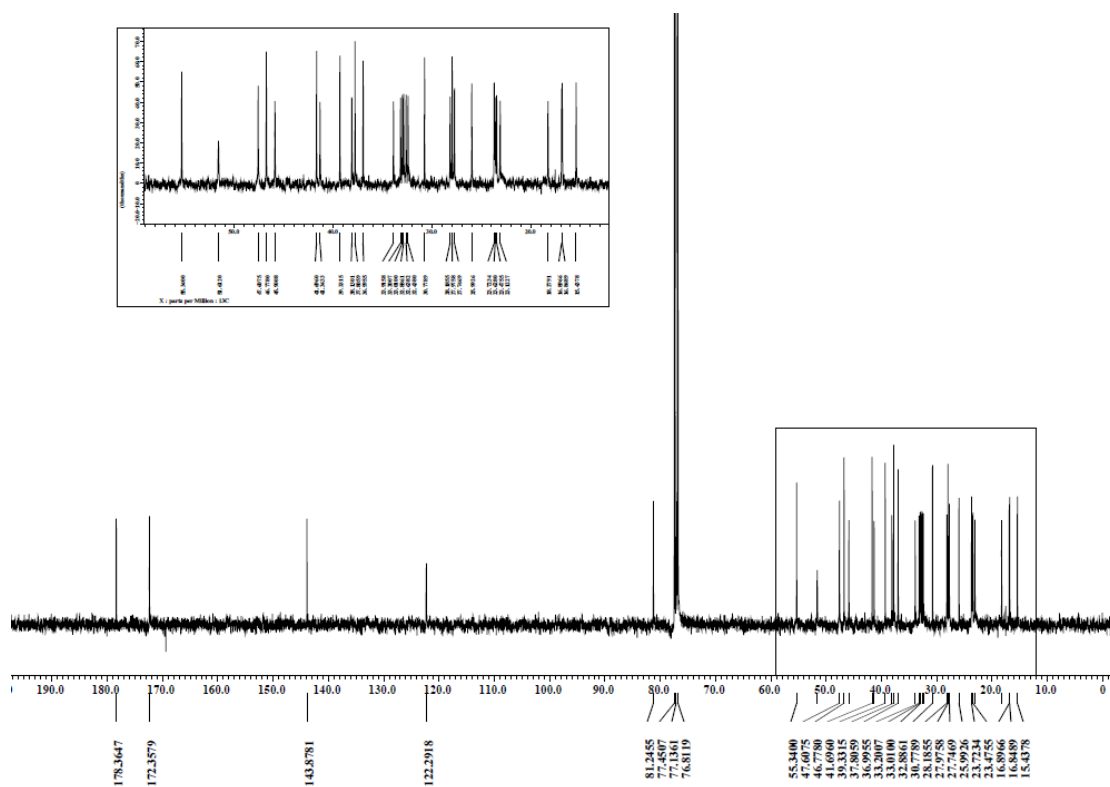
(2) HRMS (ESI) spectrum of **Br-C4-OA-CO₂Me**



(3) ¹H NMR spectrum of **Br-C4-OA-CO₂Me** (400 MHz, CDCl₃)

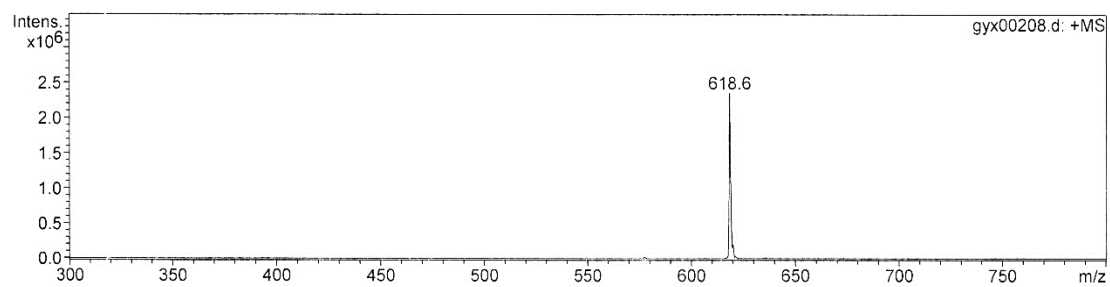


(4) ^{13}C NMR spectrum of **Br-C4-OA-CO₂Me** (100 MHz, CDCl_3)

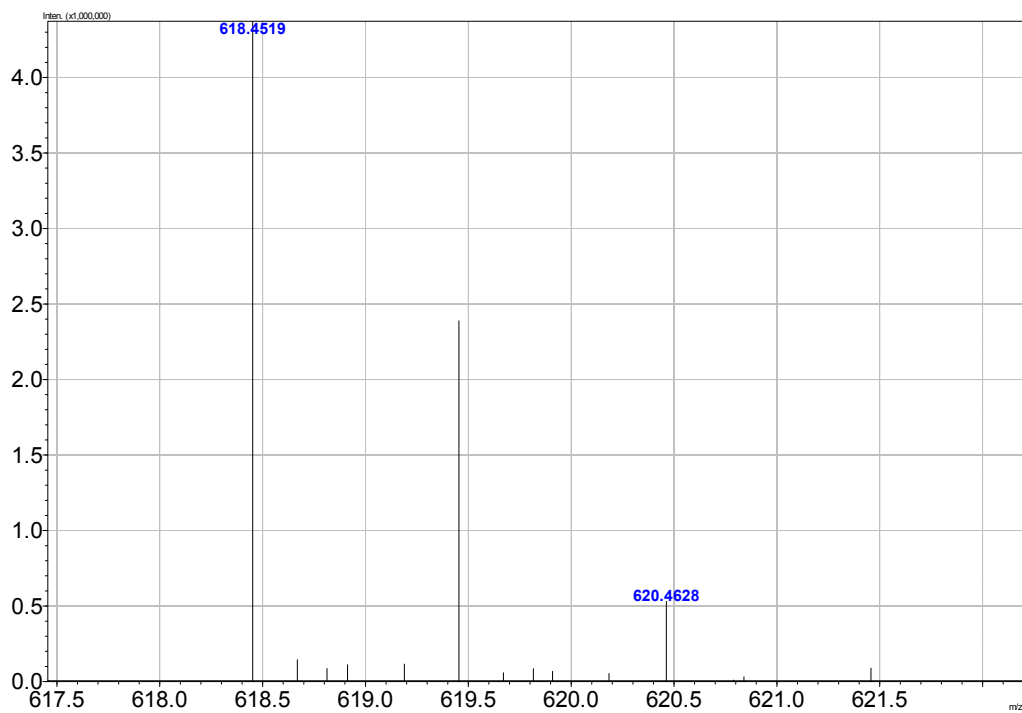


C4-MOP

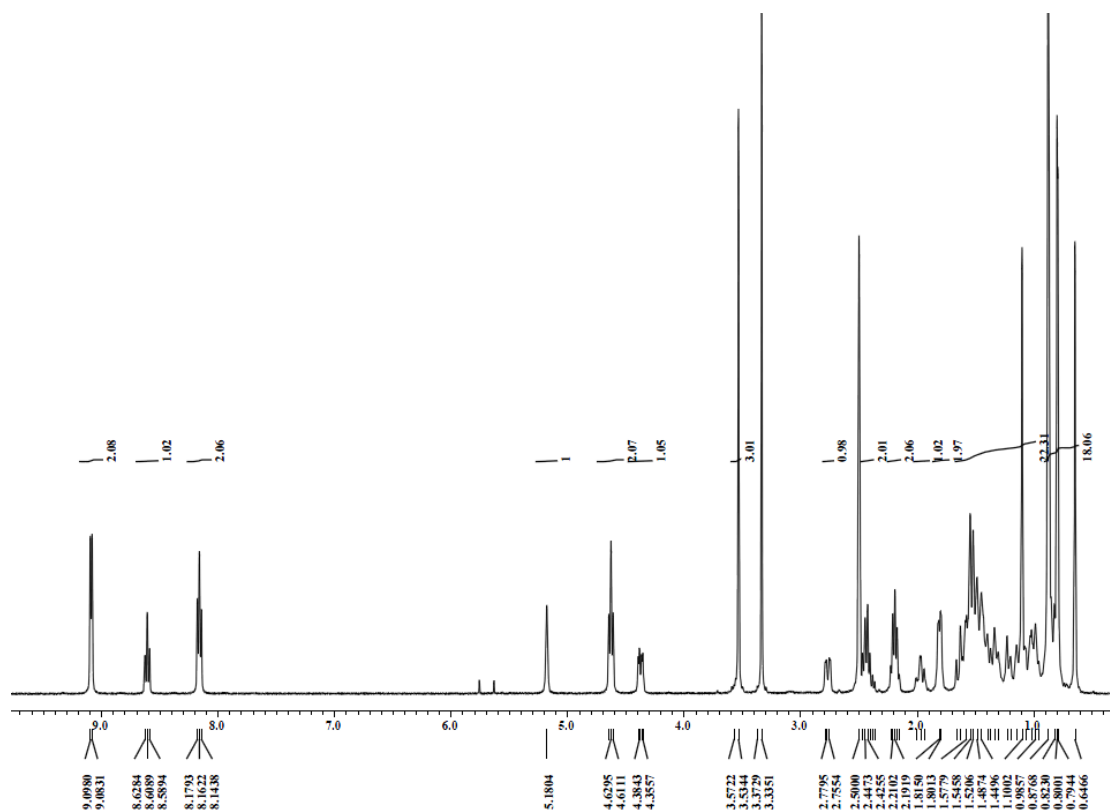
(1) ESI-MS (+) spectrum of **C4-MOP**



(2) HRMS (ESI) spectrum of **C4-MOP**



(3) ^1H NMR spectrum of **C4-MOP** (400 MHz, $\text{DMSO-}d_6$)



(4) ^{13}C NMR spectrum of **C4-MOP** (100 MHz, CDCl_3)

