

Strong Viscoelastic Glycerol Solutions Formed from Phenylalanine-Based Amine Oxide Surfactants

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1. Synthesis of Cn-Phe-AO

The detailed synthetic process, which is shown in Figure 1, is described as follows.

(1) Synthesis of Cn-Phe.

Fatty acid (0.1 mol) was added to a 500 mL three-necked flask. Thionyl chloride (SOCl_2 , 0.12 mol) was added dropwise at 35 °C, and the acidic gas generated during the reaction was absorbed by aqueous sodium hydroxide solution. The reaction was maintained for 3 hours until the system became clear and transparent, and no new bubbles were observed in the sodium hydroxide absorption solution, indicating that the reaction was deemed complete. Subsequently, residual SOCl_2 in the system was removed by reduced-pressure distillation, yielding a transparent yellow viscous liquid, which was the target product fatty acyl chloride.

Separately, dichloromethane was added to a 1000 mL three-necked flask as the solvent, followed by dissolving L-phenylalanine methyl ester hydrochloride (0.12 mol) and triethylamine (0.3 mol) therein with stirring until complete dissolution. The reaction system was cooled to -5 °C, and a dichloromethane solution of fatty acyl chloride (containing 0.1 mol fatty acyl chloride) was slowly added dropwise. After the addition was complete, the reaction was continued for another 2 hours.

After the reaction, the reaction mixture was transferred to a 1000 mL separating funnel, extracted 2–3 times with weakly acidic aqueous solution, and then washed three times with deionized water until the pH of the washing solution reached 3–4. The dichloromethane organic phase was collected and dried over anhydrous magnesium sulfate, and the desiccant was removed by suction filtration. The resulting filtrate was concentrated by reduced-pressure rotary evaporation to obtain Intermediate 1.

Yield : 89%

(2) Synthesis of Cn-Phe-2N.

To prepare Intermediate 2, Intermediate 1 (0.05 mol) and 3-dimethylamino-1-propylamine (0.15 mol) were sequentially added to a 500 mL single-necked flask. A small amount of potassium

hydroxide (KOH) was introduced as a catalyst, and the reaction was carried out at 105°C for 24 h. Upon completion of the reaction, excess 3-dimethylamino-1-propylamine in the system was removed via reduced-pressure distillation. The crude product was purified by recrystallization using acetone as the solvent, ultimately affording Intermediate 2 as a solid.

Yield: 66%

(3) Synthesis of the compound **Cn-Phe-AO**.

For the synthesis of the final product Cn-Phe-AO, Intermediate 2 (0.03 mol) and ethanol (300 mL) were charged into a 500 mL three-necked flask. A small amount of citric acid and EDTA-2Na were added as catalysts. The reaction system was maintained at 50 °C, and 30% hydrogen peroxide (H₂O₂, 0.09 mol) was added dropwise. After the completion of H₂O₂ addition, the reaction mixture was stirred continuously at 85 °C for 5 h, yielding the final product designated as Cn-Phe-AO.

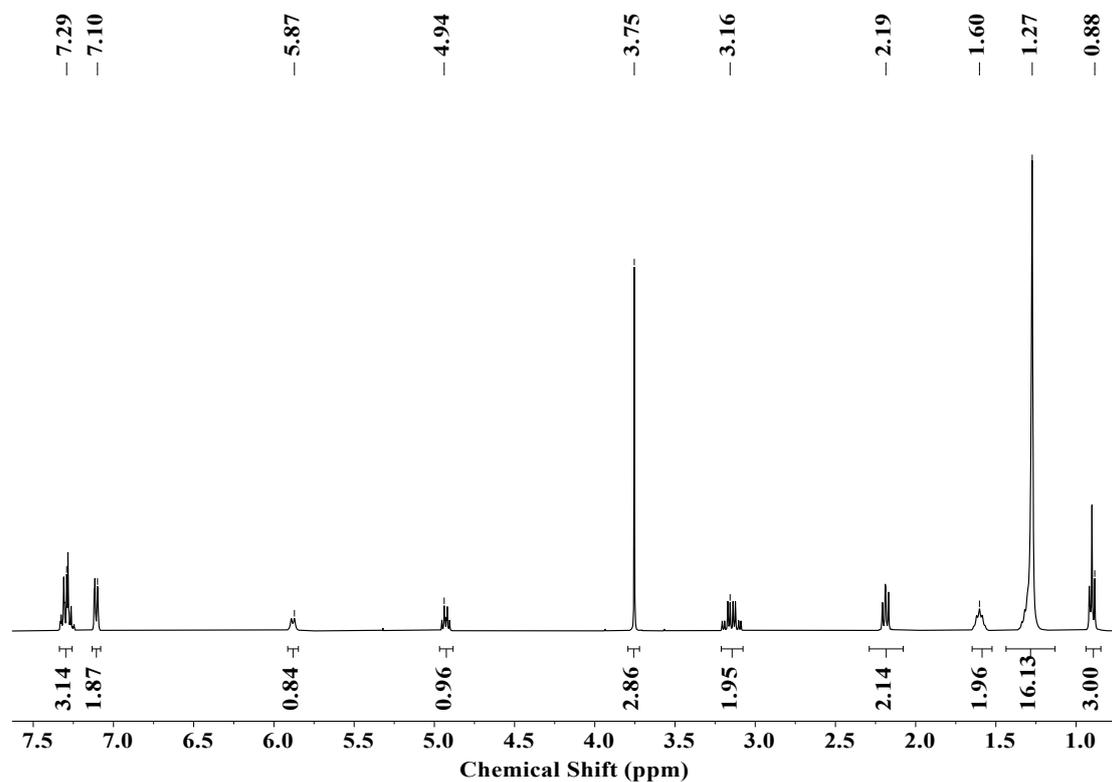
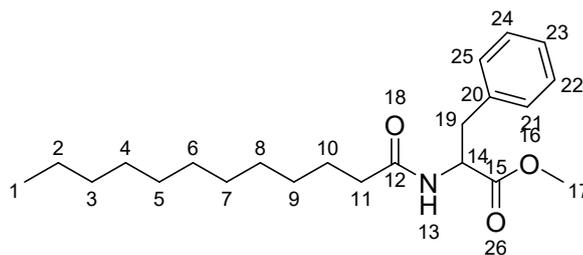


Figure S1a ¹H NMR spectrum of compound C12-Phe (CDCl₃).



¹H NMR (400 MHz, CDCl₃) 7.29(m, 3H, C21-H, C25-H,C23-H), 7.10(m, 2H, C24-H, C22-H),

5.87(s, 1H, N13-H), 4.94(m, 1H, C14-H), 3.75(s, 3H, C17-3H), 3.16(m, 3H, C19-3H), 2.19(m, 2H, C11-2H), 1.60(m, 2H, C10-2H), 1.27(m, 16H, C2-9-2H), 0.88(t, 3H, C1-3H).

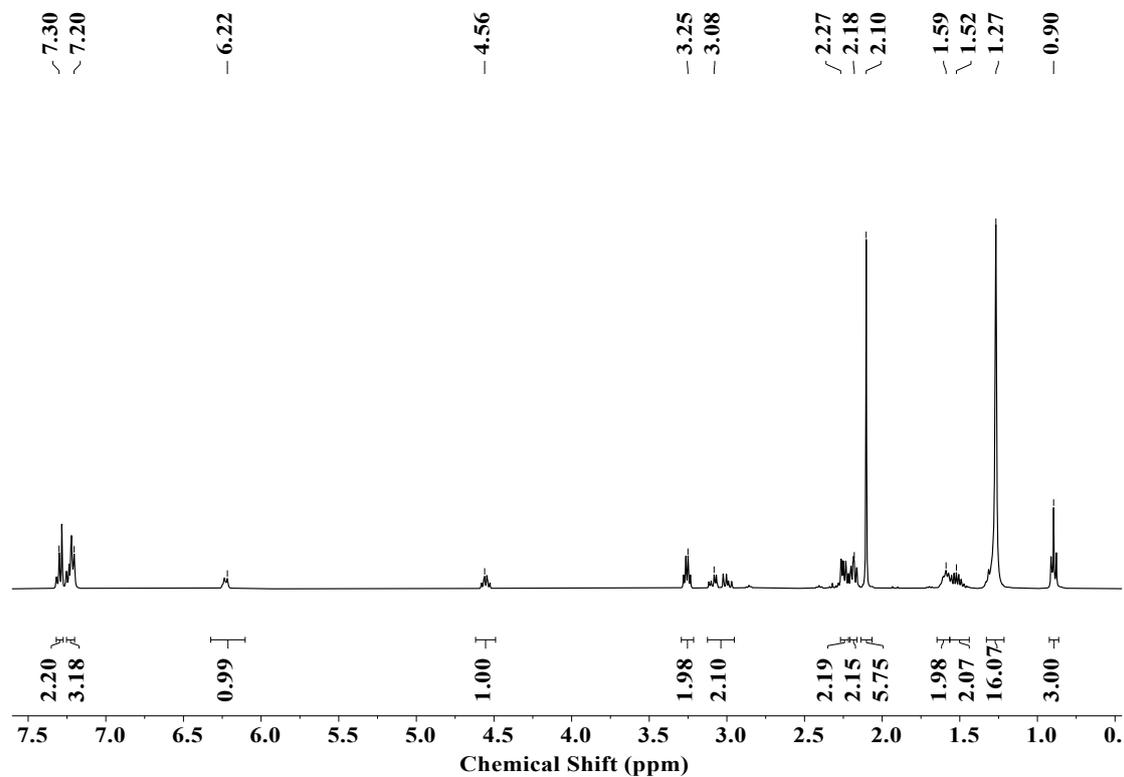
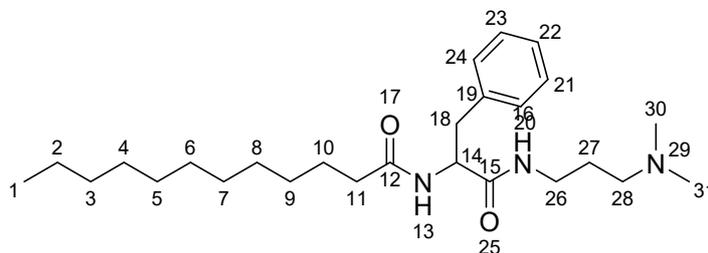


Figure S1b ^1H NMR spectrum of compound C12-Phe-2N (CDCl_3).



^1H NMR (400 MHz, CDCl_3) 7.30(m, 2H, C20-H,C24-H), 7.20(m, 3H, C21-H,C22-H C23-H), 6.22(s,1H,N13-H),4.56(t,1H,C14-H),3.25(m,2H,C18-2H),3.08(m,2H,C26-2H),2.27(m,2H,C28-2H),2.18(m,2H,C11-2H), 2.10 (s, 6H, C30-3H,C31-3H), 1.59(m, 2H, C27-2H), 1.52(m, 2H, C10-2H), 1.27(m, 16H, C2-9-2H), 0.9(t, 3H, C1-3H).

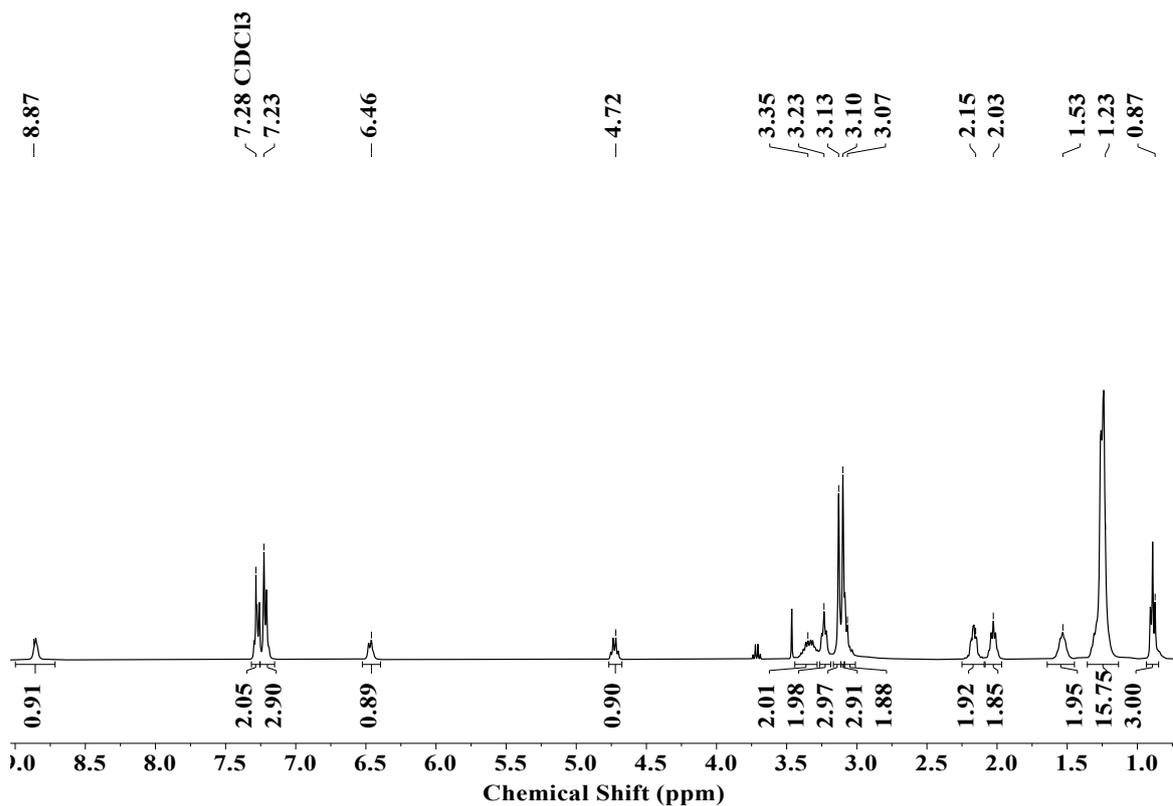
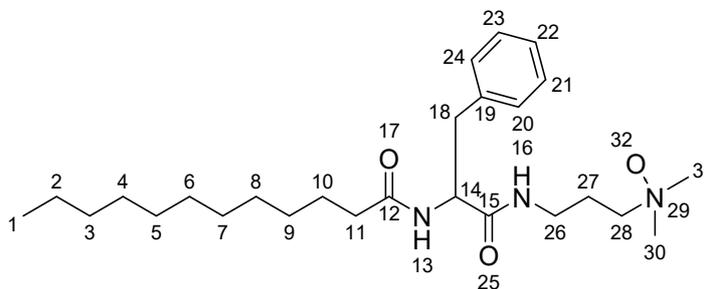


Figure S1c ^1H NMR spectrum of compound C12-Phe-AO(CDCl_3).



^1H NMR (400 MHz, CDCl_3) δ 8.87(d, 1H, N13-H), 7.28(t, 2H, C20-H, C24-H), 7.23(m, 3H, C21-H, C22-H, C23-H), 6.46(s, 1H, N13-H), 4.72(m, 1H, C14-H), 3.35(d, 2H, C18-2H), 3.23(t, 2H, C28-2H), 3.13(s, 3H, C30-3H), 3.10(s, 3H, C31-3H), 3.07(m, 2H, C26-2H), 2.15(t, 2H, C11-2H), 2.03(m, 2H, C27-2H), 1.53(m, 2H, C10-2H), 1.23(m, 16H, C2-9-2H), 0.87(t, 3H, C1-3H).

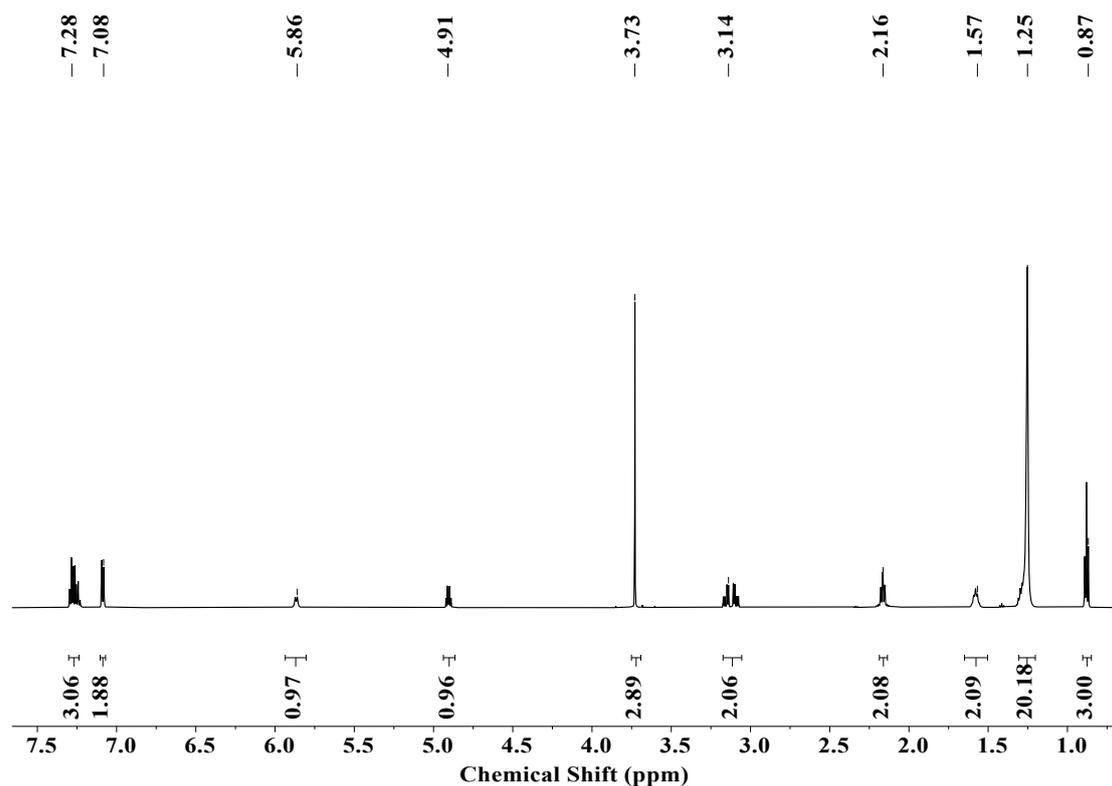
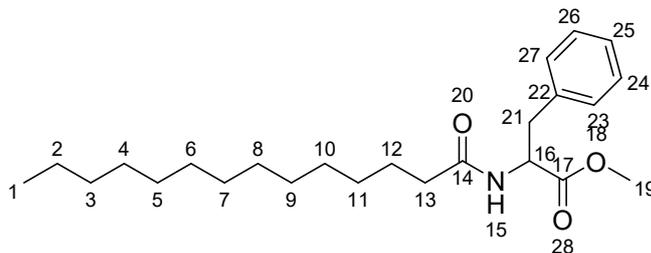


Figure S2a ^1H NMR spectrum of compound C14-Phe (CDCl_3).



^1H NMR (400 MHz, CDCl_3) 7.28(m, 3H, C23-H,C25-H,C27-H),7.08(m, 3H, C23-H,C27-H) 5.86(s, 1H, N15-H), 4.91(m, 1H, C16-H), 3.73(s, 3H, C19-3H), 3.14(m, 2H, C21-3H), 2.16(m, 2H, C13-2H), 1.57(m, 2H, C12-2H), 1.25(m, 20H, C2-11-2H), 0.87(t, 3H, C1-3H).

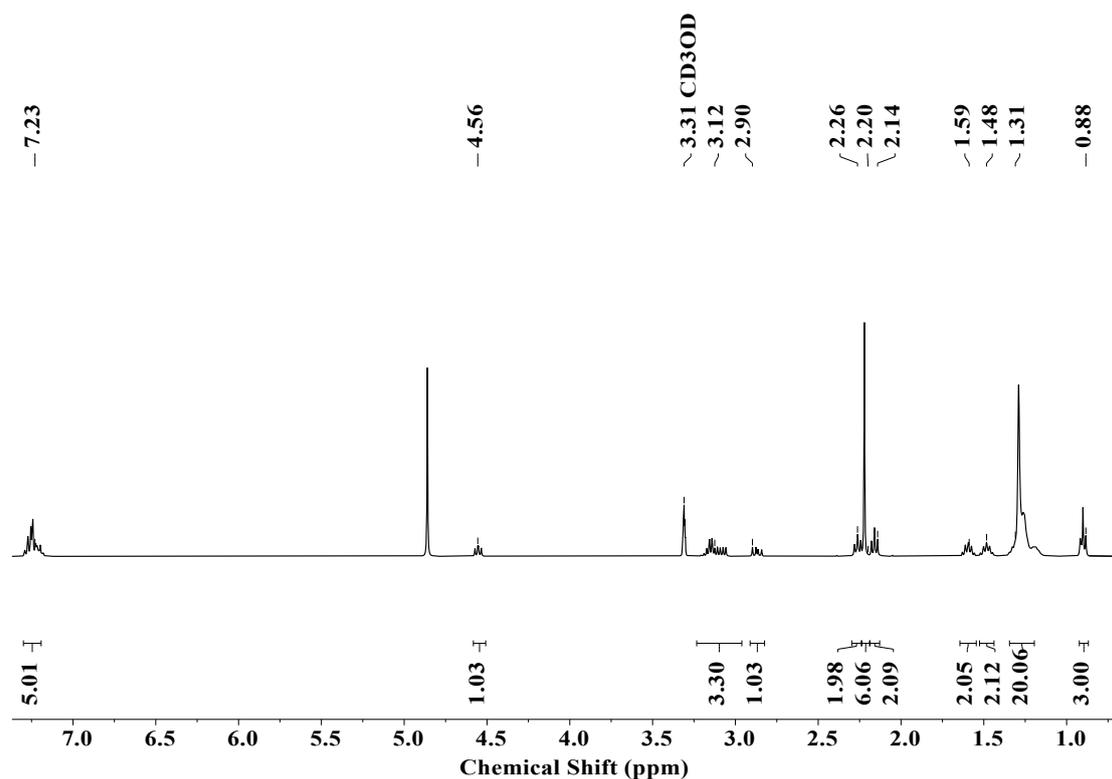
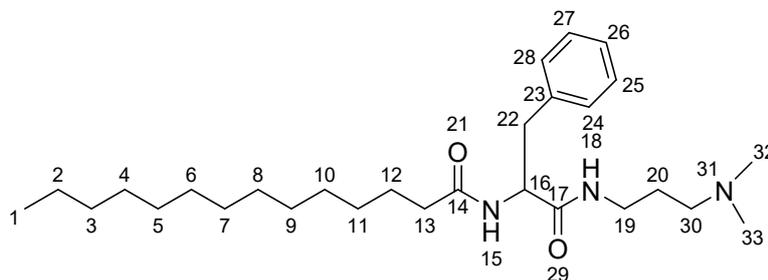


Figure S2b ^1H NMR spectrum of compound C14-Phe-2N(MeOD).



^1H NMR (400 MHz, MeOD) 7.23(m, 5H, C24-H, C25-H, C26-H, C27-H, C28-H), 4.56(t, 1H, C16-H), 3.12(m, 2H, C22-2H), 2.90(m, 2H, C19-2H), 2.26(m, 2H, C30-2H), 2.2(s, 6H, C32-3H, C33-3H), 2.14 (t, 2H, C13-2H), 1.59(m, 2H, C20-2H), 1.48(m, 2H, C12-2H), 1.31(m, 20H, C2-11-2H), 0.88(t, 3H, C1-3H).

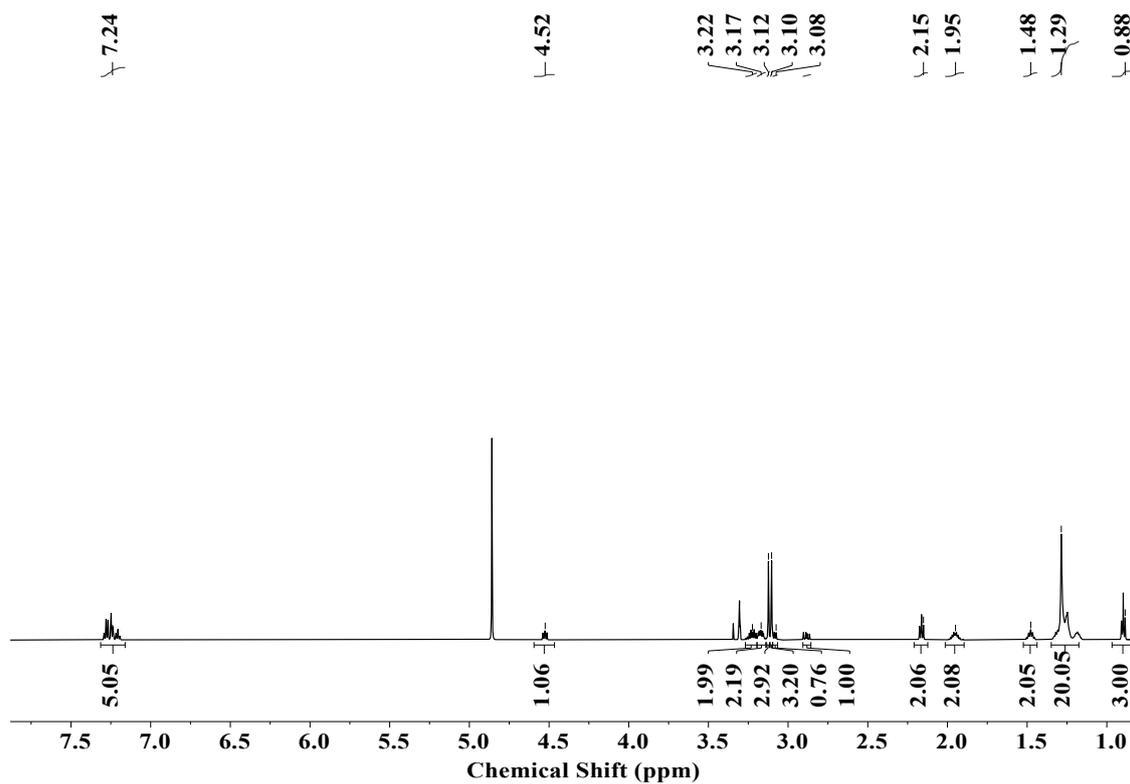
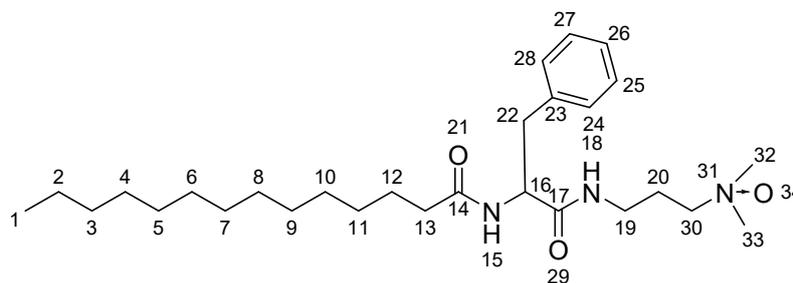


Figure S2c. ^1H NMR spectrum of compound C14-Phe-AO(MeOD)



^1H NMR (400 MHz, MeOD) δ 7.24(m, 5H, C24-28-H), 4.52 (m, 1H, C16-H), 3.22(m,2H,C22-2H),3.17 (m, 2H, C30-2H), 3.12(s, 3H, C32-3H), 3.10(s, 3H, C33-3H), 3.08(m, 2H, C19-2H), 2.16(t, 2H, C13-2H), 1.95(m, 2H, C20-2H), 1.48(m, 2H, C12-2H), 1.29(m, 20H, C2-11), 0.88(t, 3H, C1-3H).

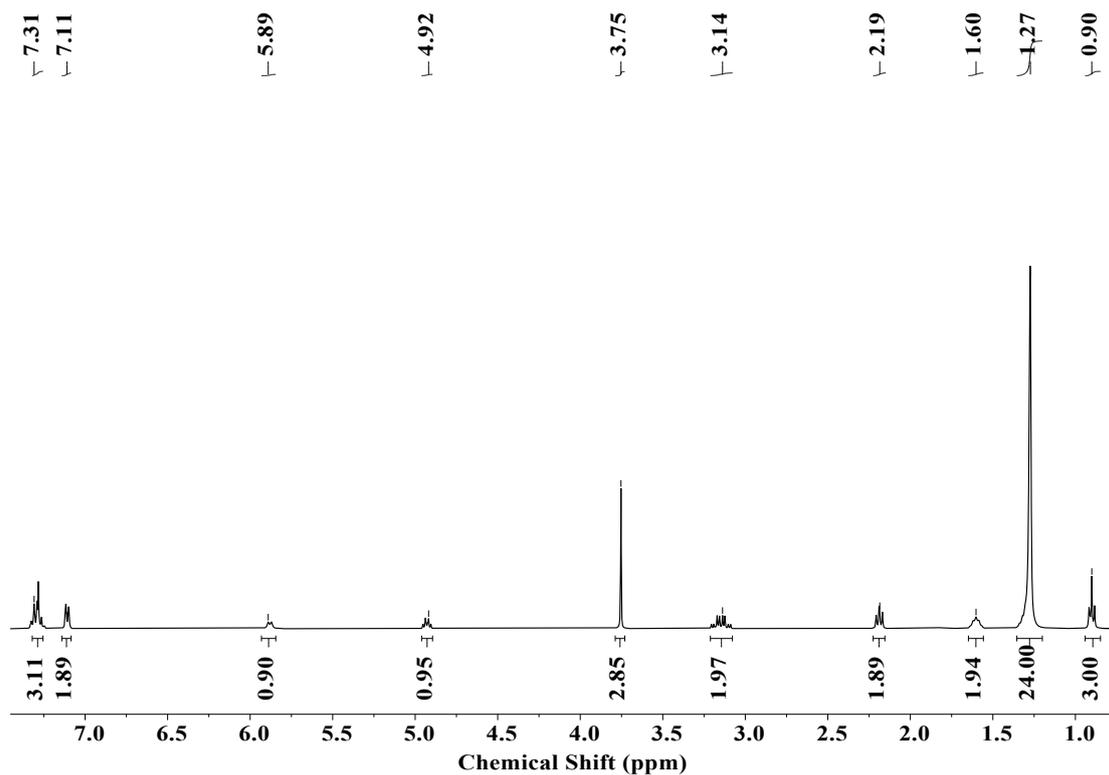
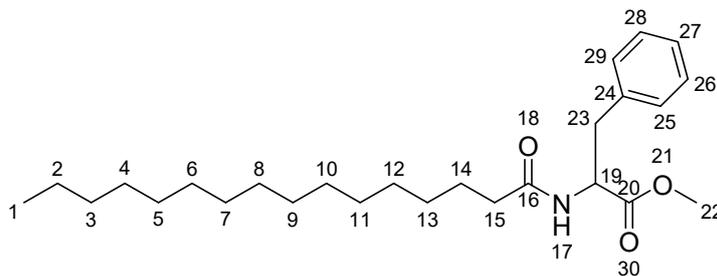


Figure S3a. ^1H NMR spectrum of compound C16-Phe (CDCl_3)



^1H NMR (400MHz, CDCl_3) δ 7.31(m, 3H, C25-H, C27-H, C29-H), 7.11(m, 2H, C26-H, C28-H), 5.89(s, 1H, N17-H), 4.92(m, 1H, C19-H), 3.75(s, 3H, C22-3H), 3.14(m, 2H, C23-2H), 2.19(t, 2H, C15-2H), 1.6(m, 2H, C14-2H), 1.27(m, 24H, C2-13-2H), 0.9(t, 3H, C1-3H).

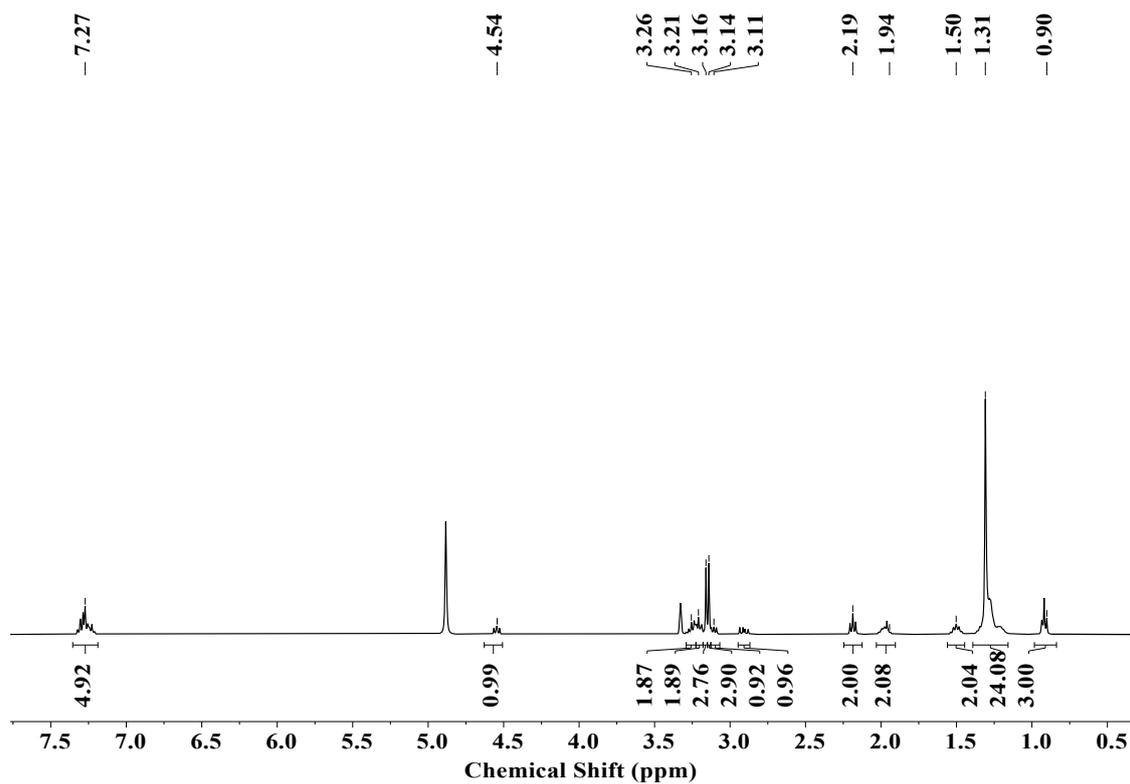
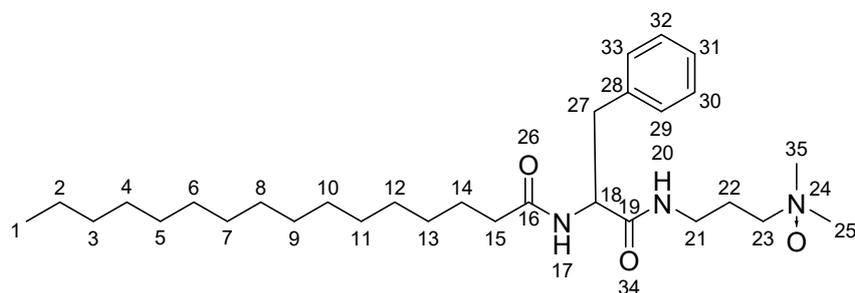


Figure S3c. ^1H NMR spectrum of compound C16-Phe-AO(MeOD)



^1H NMR (400 MHz, MeOD) δ 7.27(m, 5H, C29-33-H), 4.55(m, 1H, C18-H), 3.26 (m, 2H, C27-2H), 3.21(m, 2H, C23-2H), 3.16 (s, 3H, C25-3H), 3.14 (s, 3H, C35-3H), 3.11 (t, 2H, C21-2H), 2.19 (t, 2H, C15-2H), 1.94 (m, 2H, C22-2H), 1.50 (m, 2H, C14-2H), 1.31 (m, 24H, C2-13-2H), 0.90 (t, 3H, C1-3H).

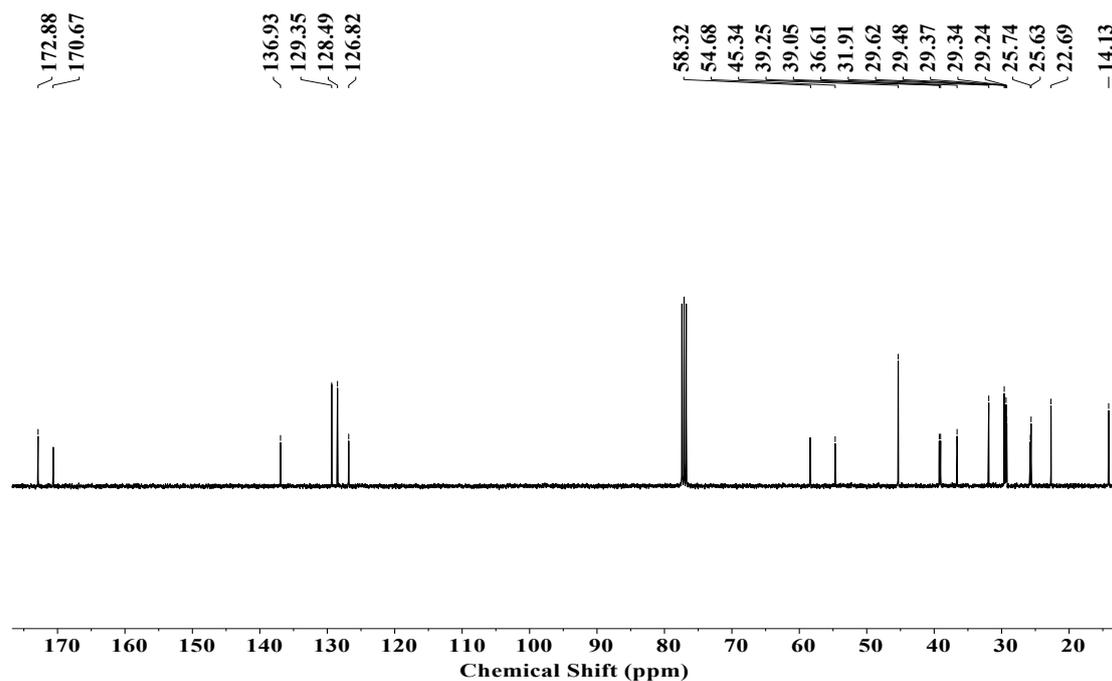


Figure S4a. ^{13}C NMR spectrum of compound C12-Phe-2N (CDCl_3).

^{13}C NMR (101 MHz, CDCl_3) δ 172.88, 170.67, 136.93, 129.35(2C), 128.49(2C), 126.82, 58.32, 54.68, 45.34(2C), 39.25, 39.05, 36.61, 31.91, 29.62(2C), 29.48, 29.37, 29.34, 29.24, 25.74, 25.63, 22.69, 14.13.

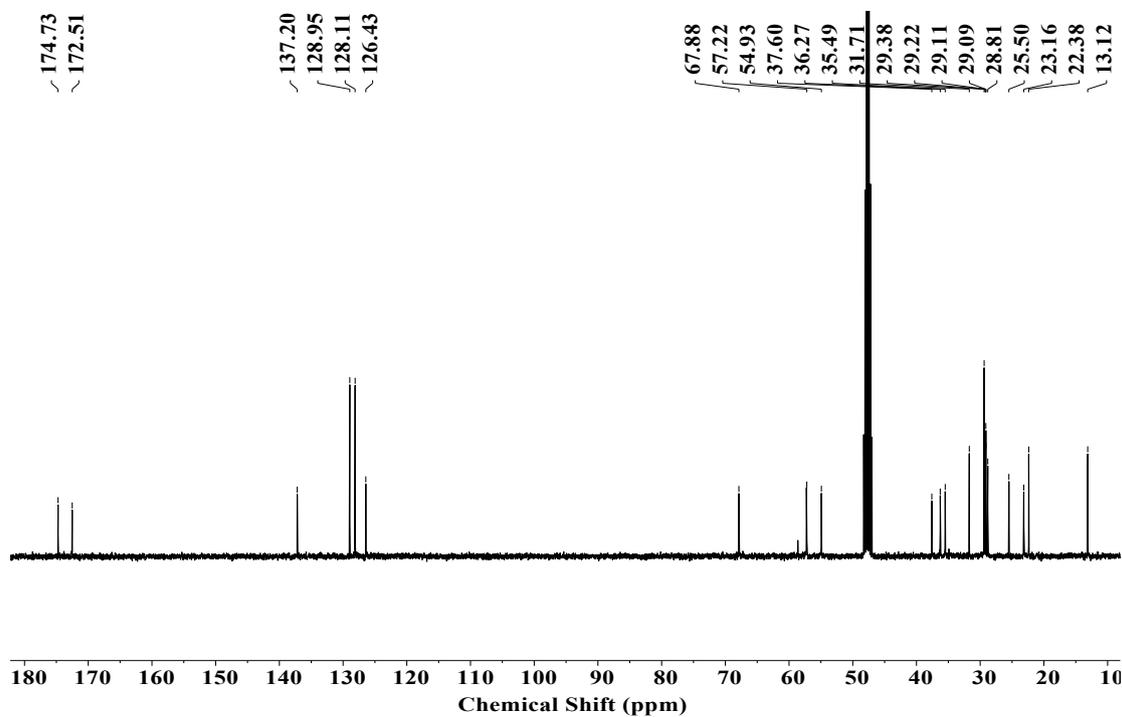


Figure S4b. ^{13}C NMR spectrum of compound C12-Phe-AO (MeOD)

^{13}C NMR (101 MHz, MeOD) δ 174.73, 172.51, 137.20, 128.95(2C), 128.11(2C), 126.43, 67.88,

57.22, 54.93, 37.60, 36.27, 35.49, 31.71, 29.38(2C), 29.22, 29.11(2C), 29.09, 28.81, 25.50, 23.16, 22.38, 13.12.

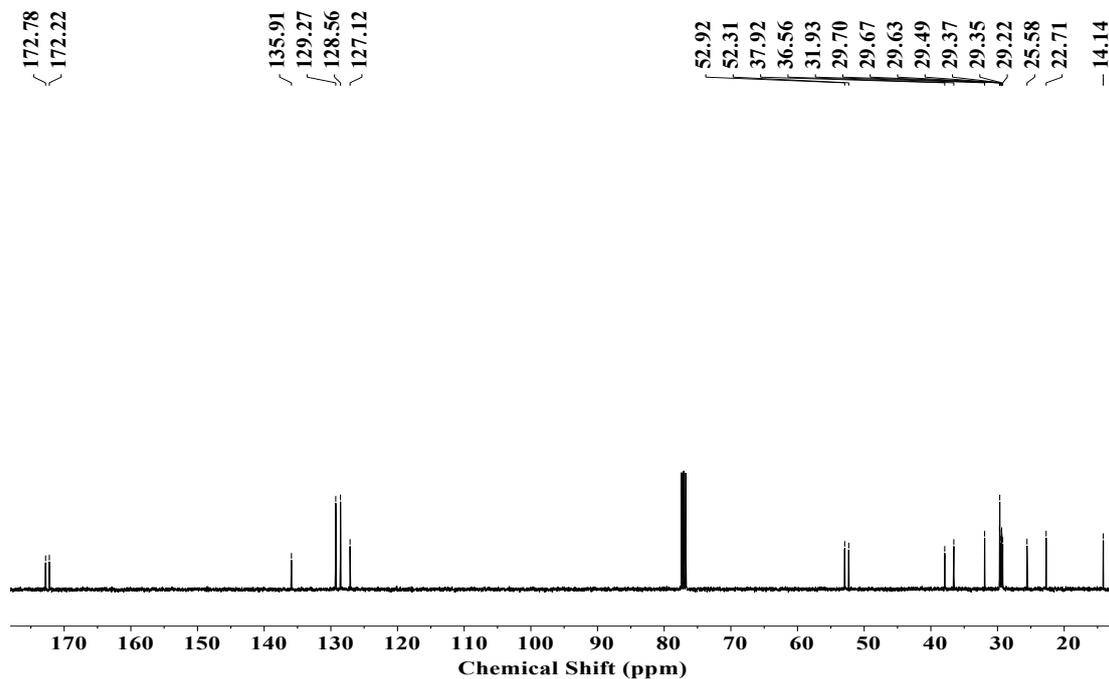


Figure S5a. ^{13}C NMR spectrum of compound C14-Phe (CDCl_3).

^{13}C NMR (101 MHz, CDCl_3) δ 172.78, 172.22, 135.91, 129.27(2C), 128.56(2C), 127.12, 52.92, 52.31, 37.92, 36.56, 31.93, 29.70, 29.67, 29.63(2C), 29.49, 29.37, 29.35, 29.22, 25.58, 22.71, 14.14.

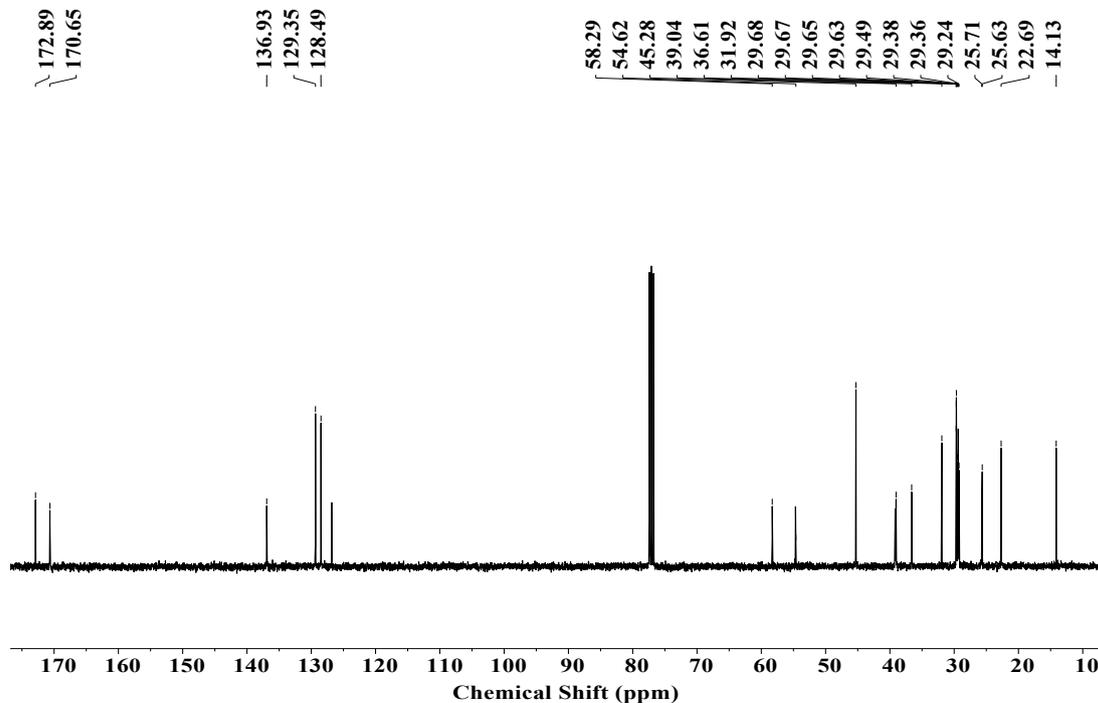


Figure S5b. ^{13}C NMR spectrum of compound C14-Phe-2N (CDCl_3)

^{13}C NMR (101 MHz, CDCl_3) δ 172.89, 170.65, 136.93, 129.35(2C), 128.49(2C), 58.29, 54.62,

45.28, 39.04, 36.61, 31.92, 29.68, 29.67, 29.65, 29.63(2C), 29.49(2C), 29.38(2C), 29.36, 29.24, 25.71, 25.63, 22.69, 14.13.

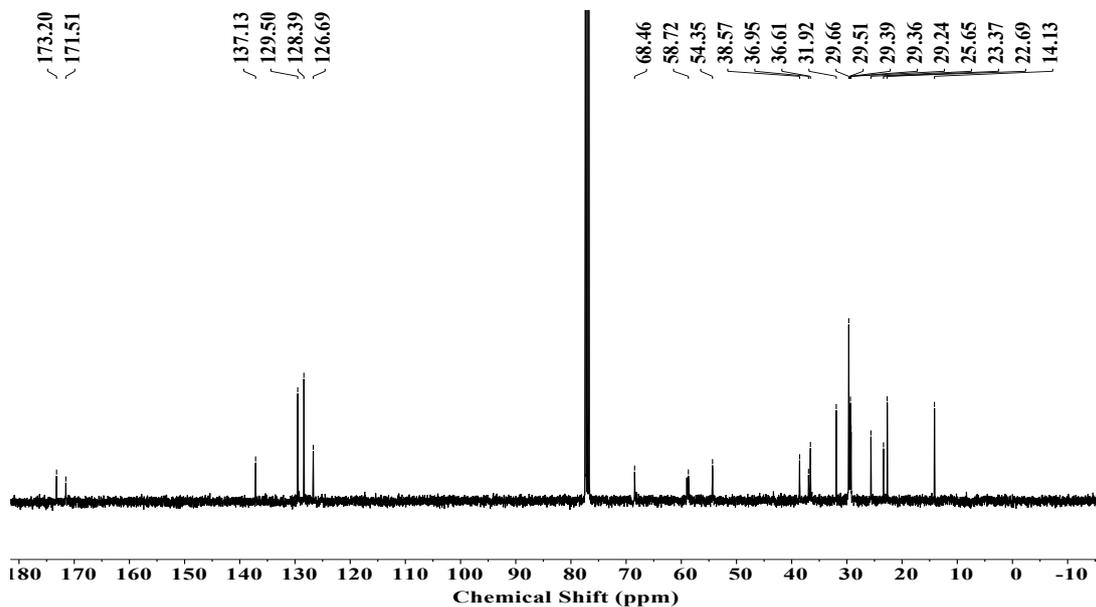


Figure S5c. ^{13}C NMR spectrum of compound C14-Phe-AO (CDCl_3)

^{13}C NMR (101 MHz, CDCl_3) δ 173.20, 171.51, 137.13, 129.50(2C), 128.39(2C), 126.69, 68.46, 58.72, 54.35, 38.57, 36.95, 36.61, 31.92, 29.66, 29.51(2C), 29.39(2C), 29.36(2C), 29.24(2C), 25.65, 23.37, 22.69, 14.13.

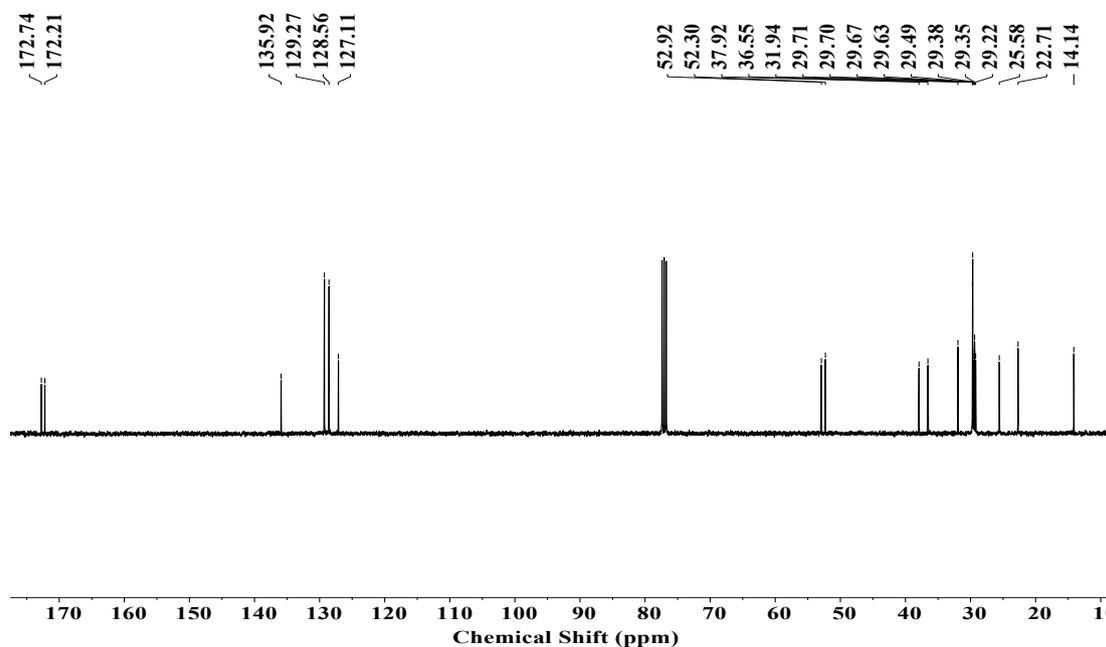


Figure S6a. ^{13}C NMR spectrum of compound C16-Phe (CDCl_3)

^{13}C NMR (101 MHz, CDCl_3) δ 172.74, 172.21, 135.92, 129.27(2C), 128.56(2C), 127.11, 52.92, 52.30, 37.92, 36.55, 31.94, 29.71, 29.70, 29.67(2C), 29.63(2C), 29.49, 29.38, 29.35, 29.22, 25.58,

22.71, 14.14.

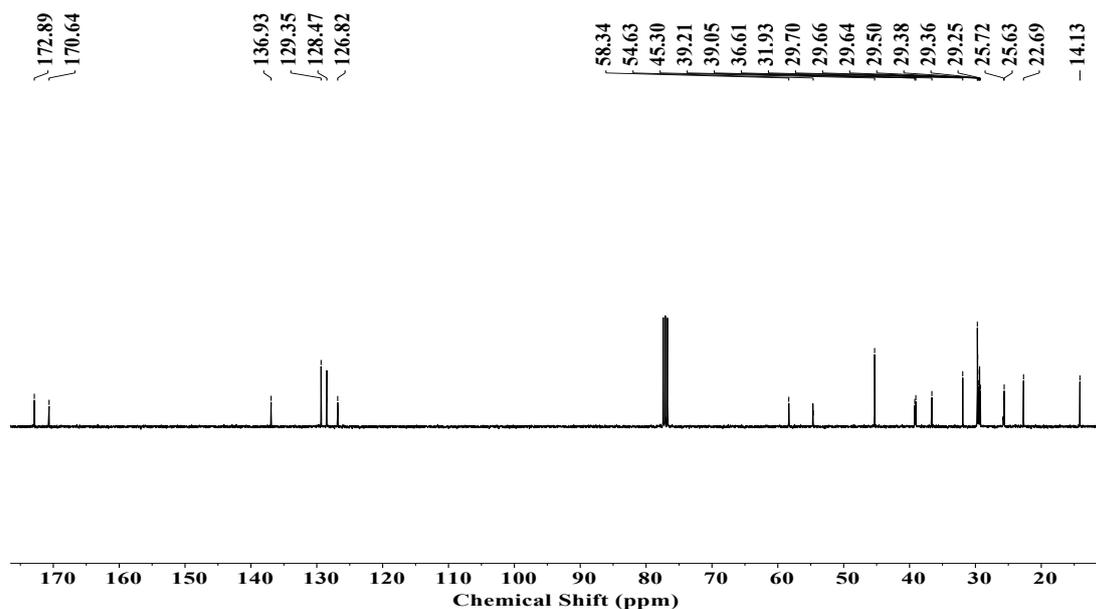


Figure S6b. ^{13}C NMR spectrum of compound C16-Phe-2N (CDCl_3)

^{13}C NMR (101 MHz, CDCl_3) δ 172.89, 170.64, 136.93, 129.35(2C), 128.47(2C), 126.82, 58.34, 54.63, 45.30, 39.21, 39.05, 36.61, 31.93, 29.70, 29.66, 29.64(2C), 29.50(2C), 29.38(2C), 29.36(2C), 29.25, 25.72, 25.63, 22.69, 14.13.

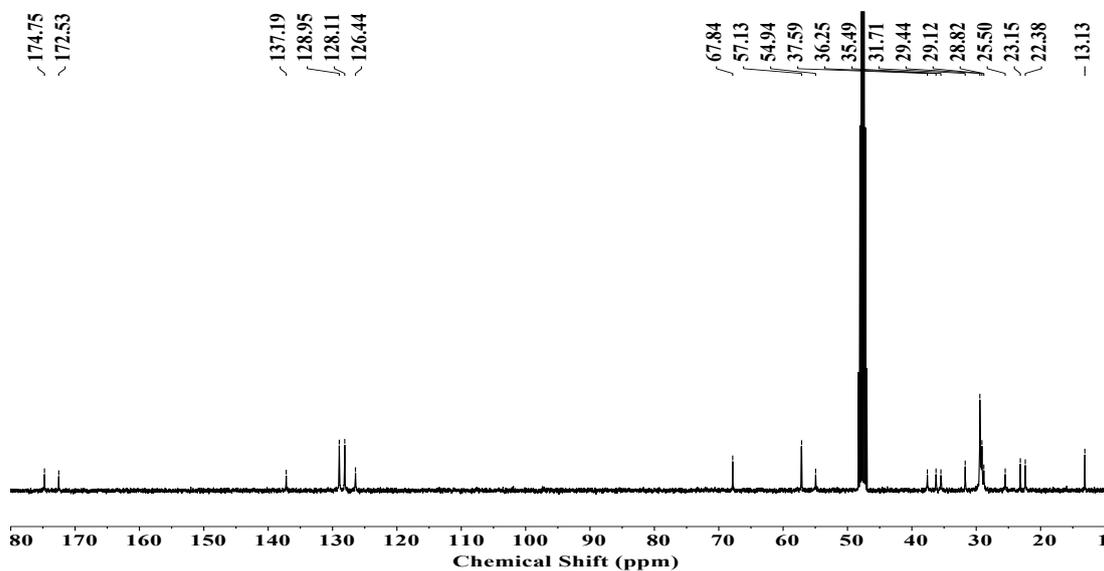


Figure S6c. ^{13}C NMR spectrum of compound C16-Phe-AO (MeOD)

^{13}C NMR (101 MHz, MeOD) δ 174.75, 172.53, 137.19, 128.95(2C), 128.11(2C), 126.44, 67.84, 57.13(2C), 54.94, 37.59, 36.25, 35.49, 31.71, 29.44(6C), 29.12(2C), 28.82(2C), 25.50, 23.15, 22.38, 13.13.

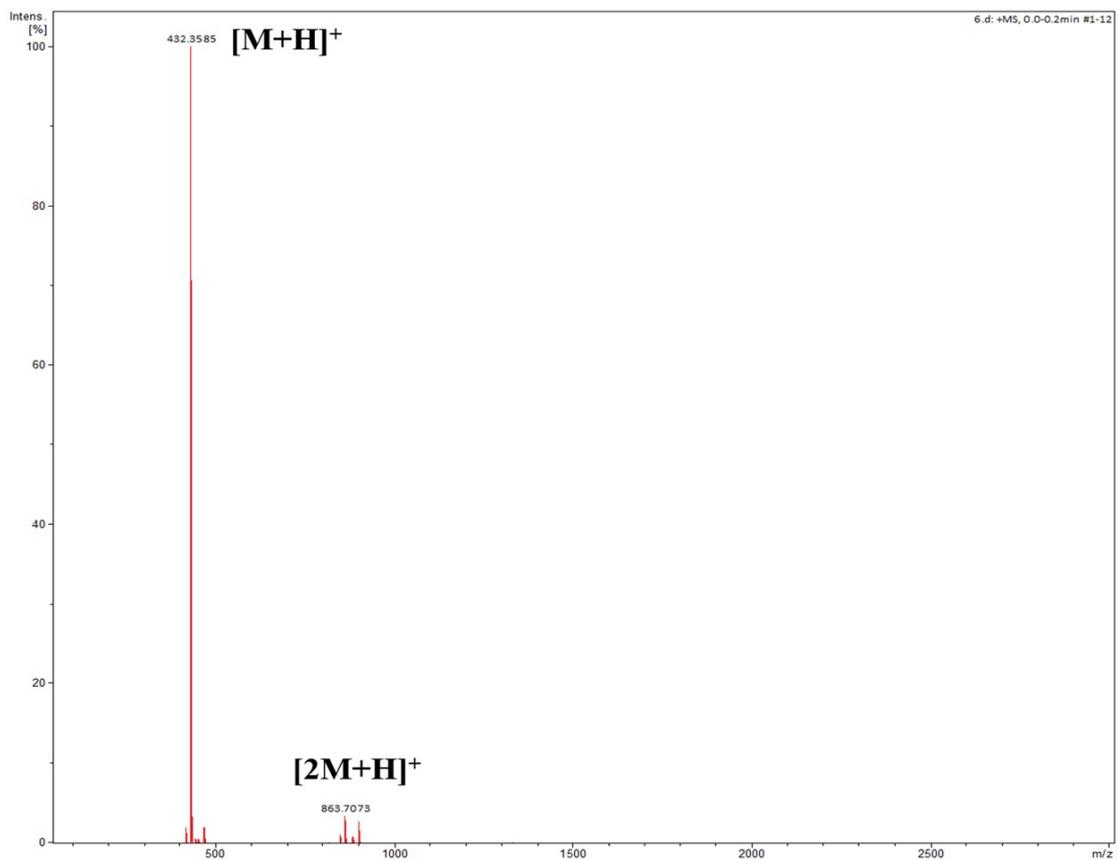


Figure S7a. HRMS of C12-Phe-2N

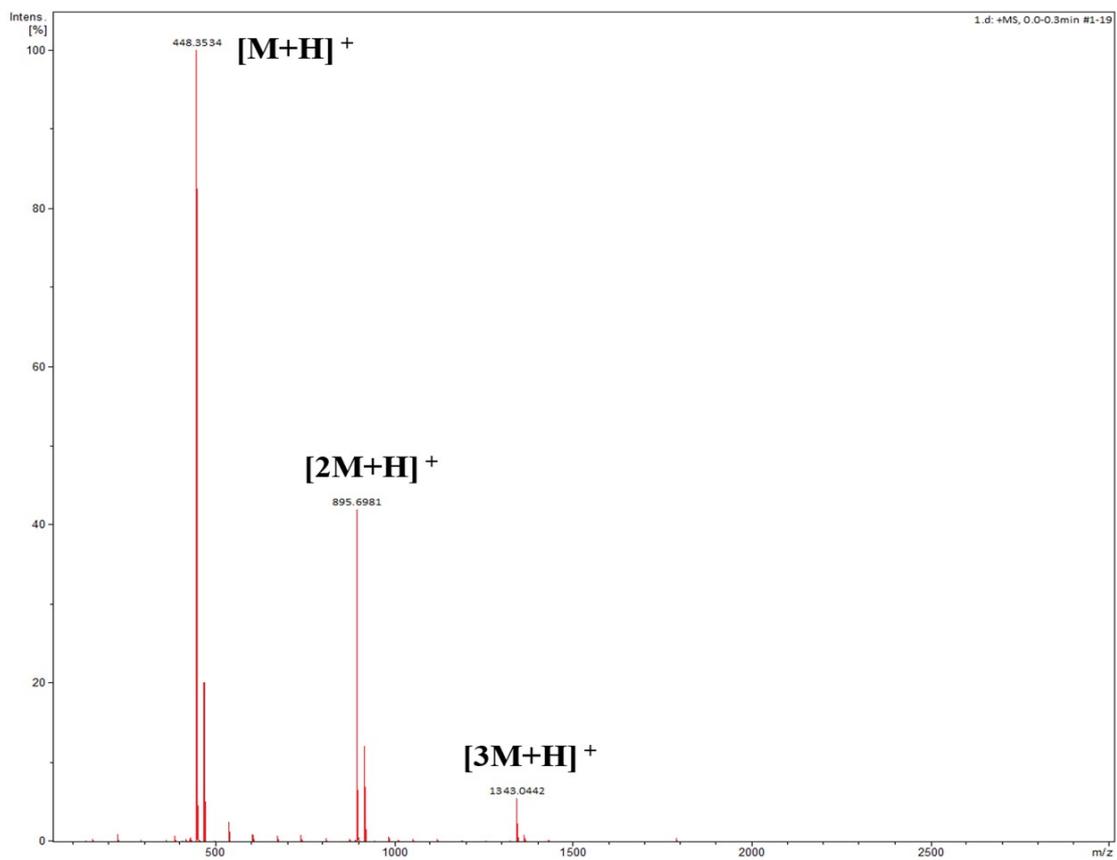


Figure S7b. HRMS of C12-Phe-AO

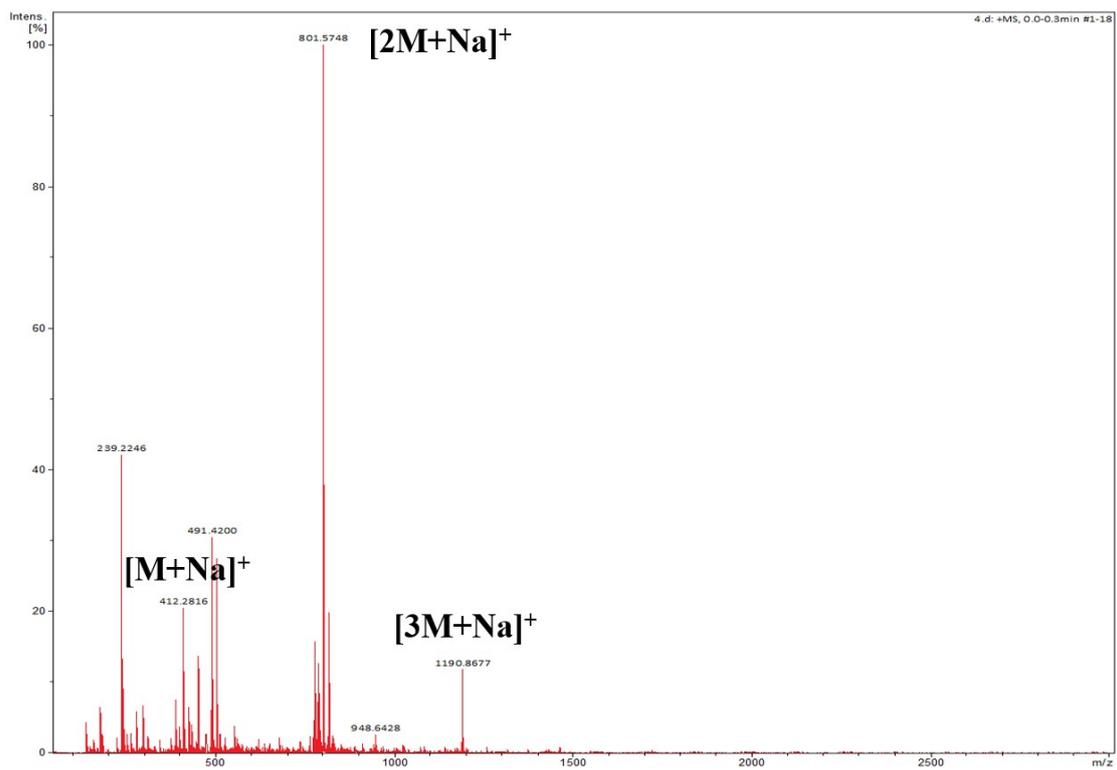


Figure S8a. HRMS of C14-Phe

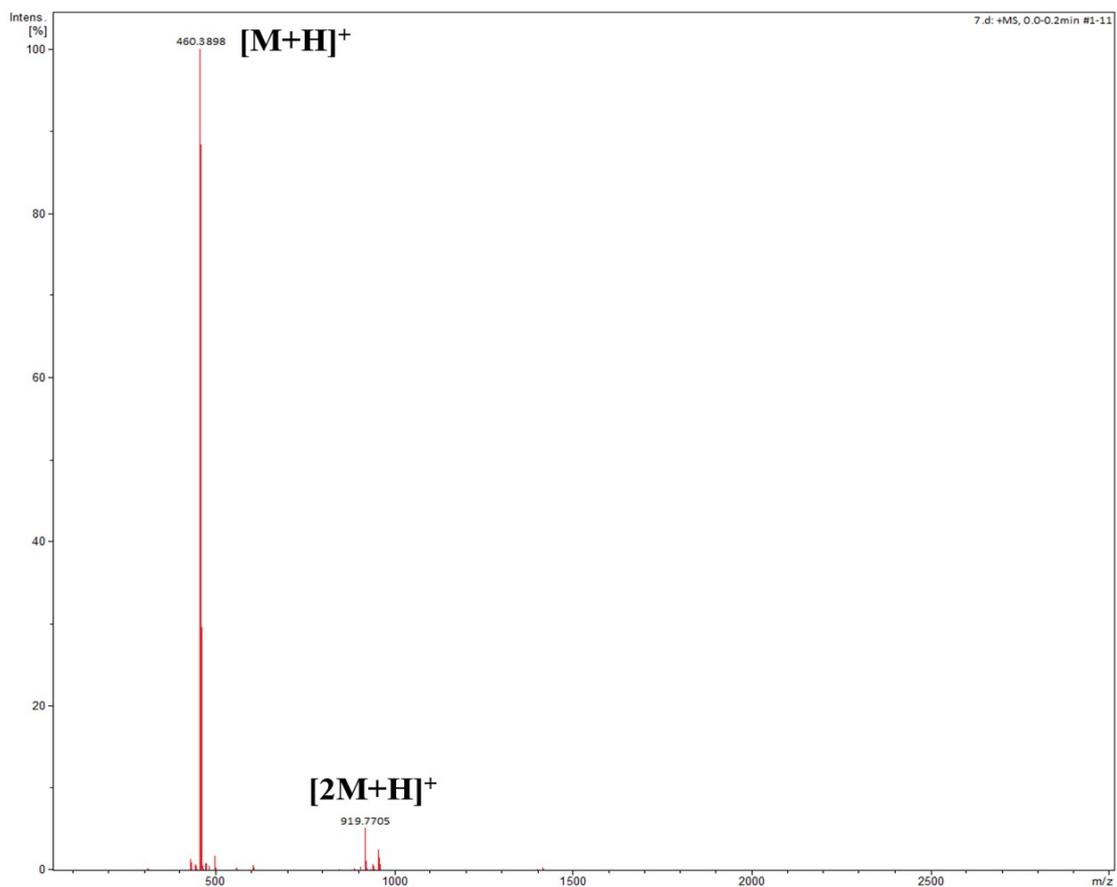


Figure S8b. HRMS of C14-Phe-2N

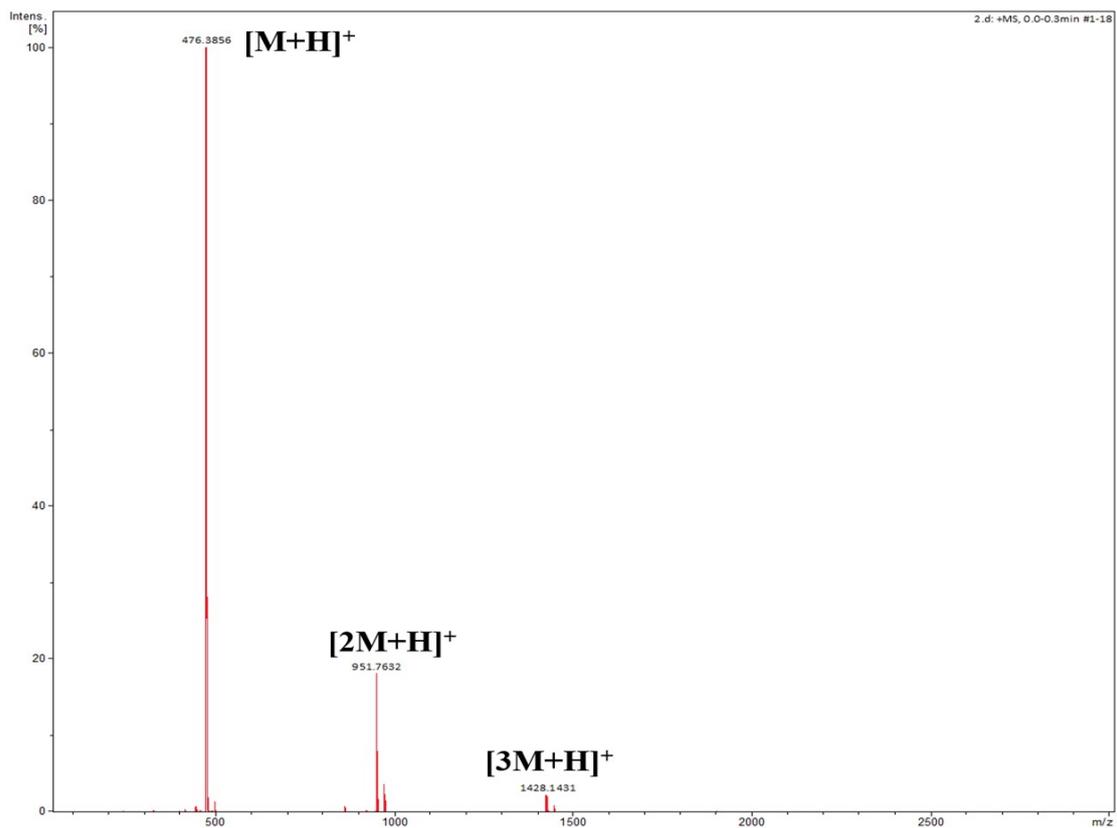


Figure S8c. HRMS of C14-Phe-AO

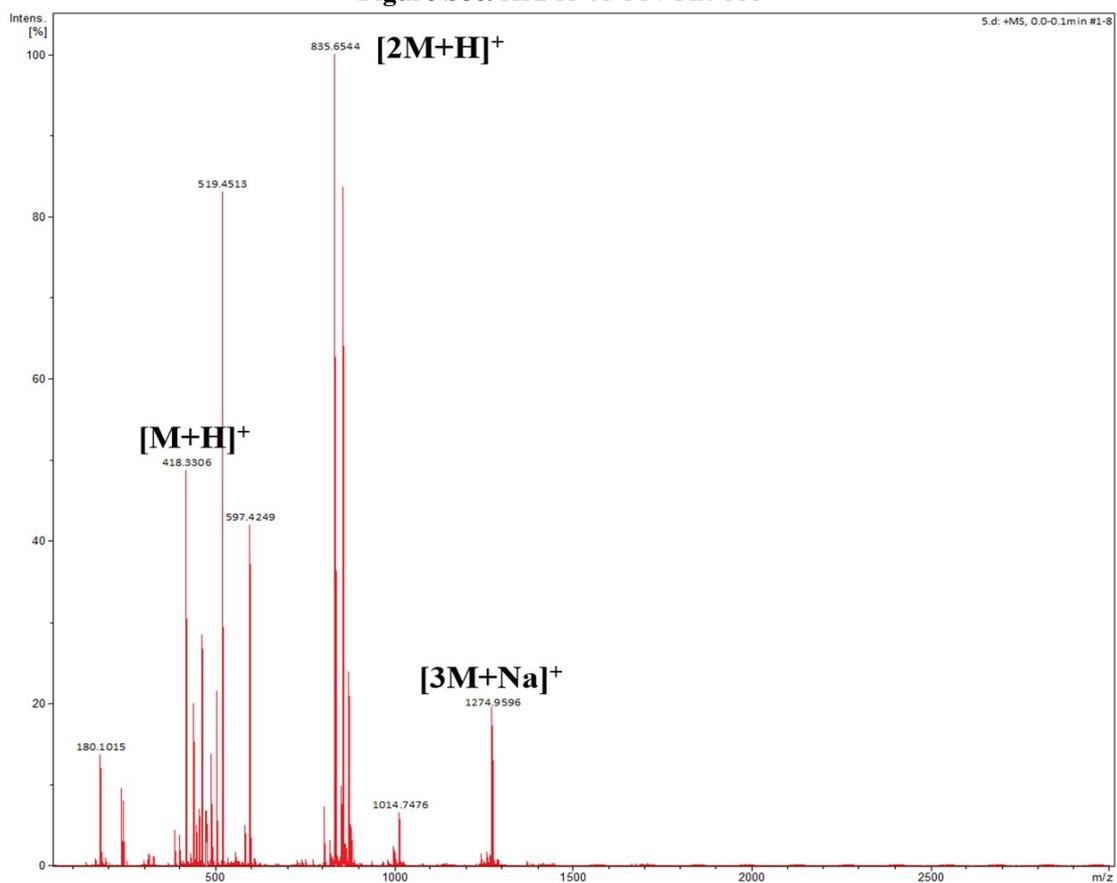


Figure S9a. HRMS of C16-Phe

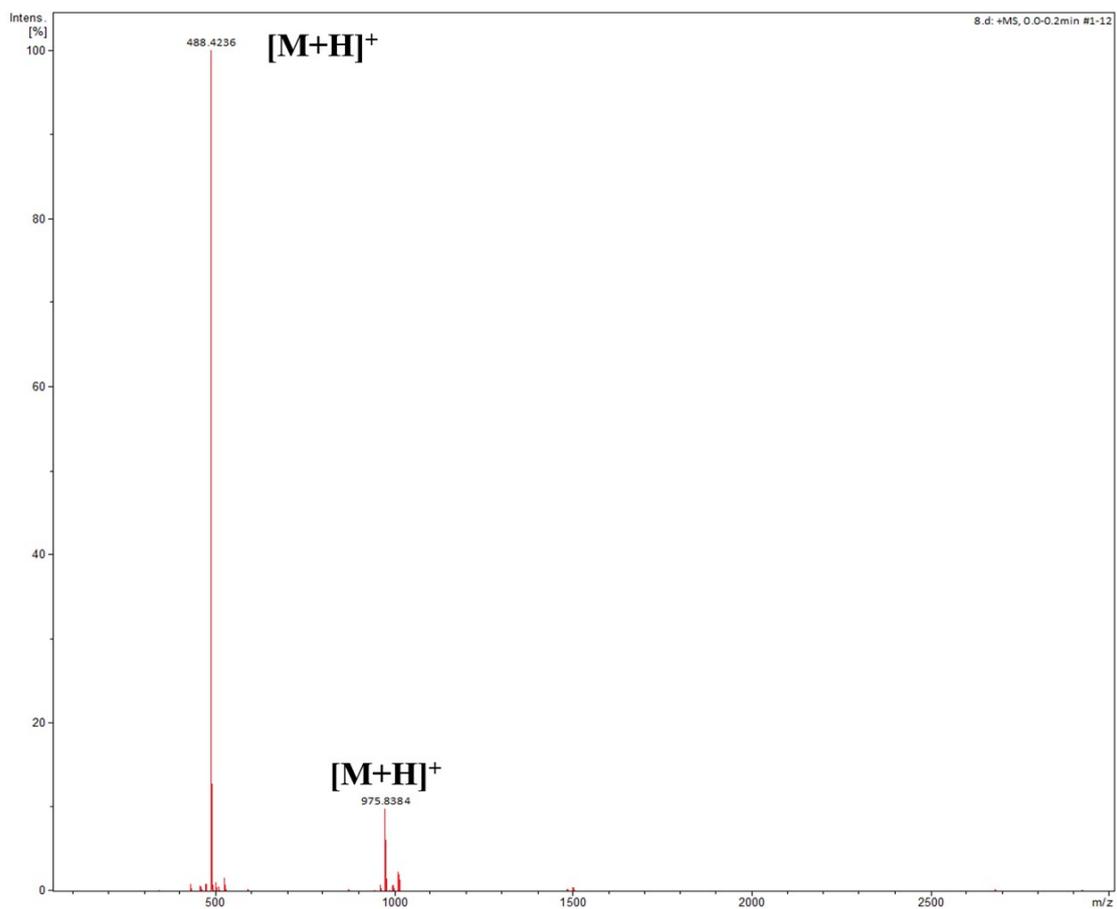


Figure S9b. HRMS of C16-Phe-2N

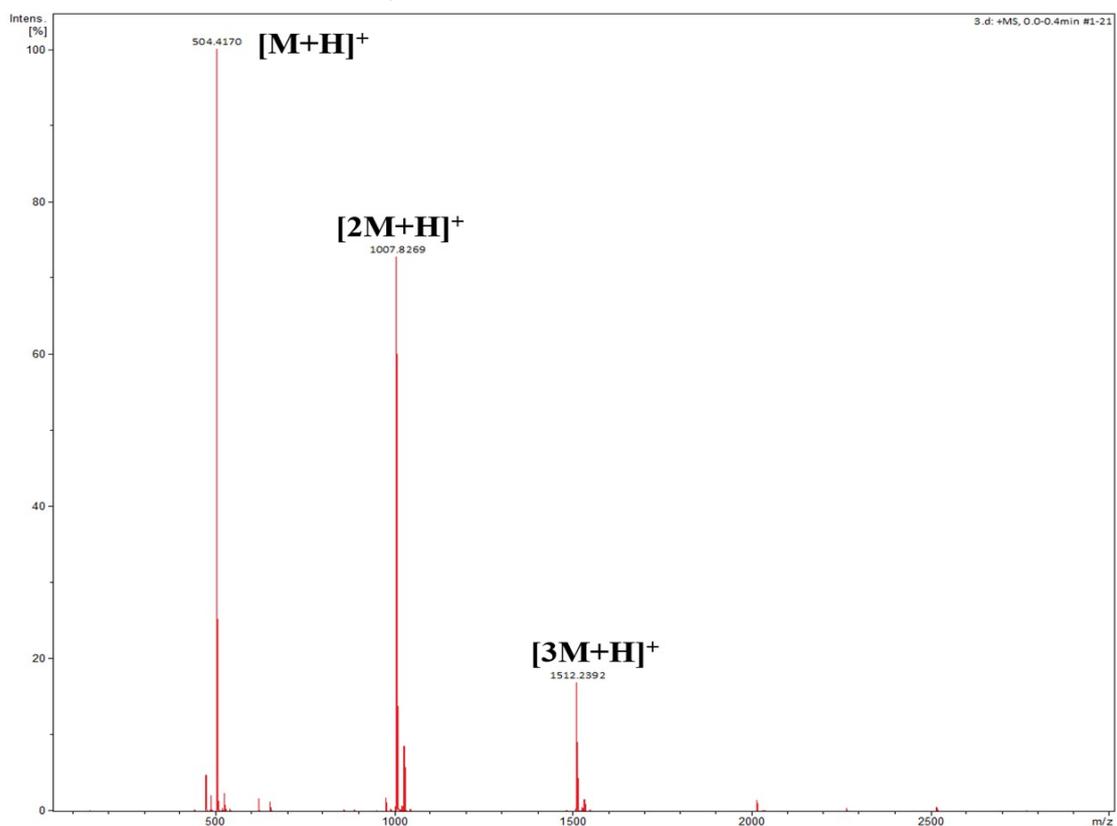


Figure S9c. HRMS of C16-Phe-AO

2. The physical appearance of glycerol solutions

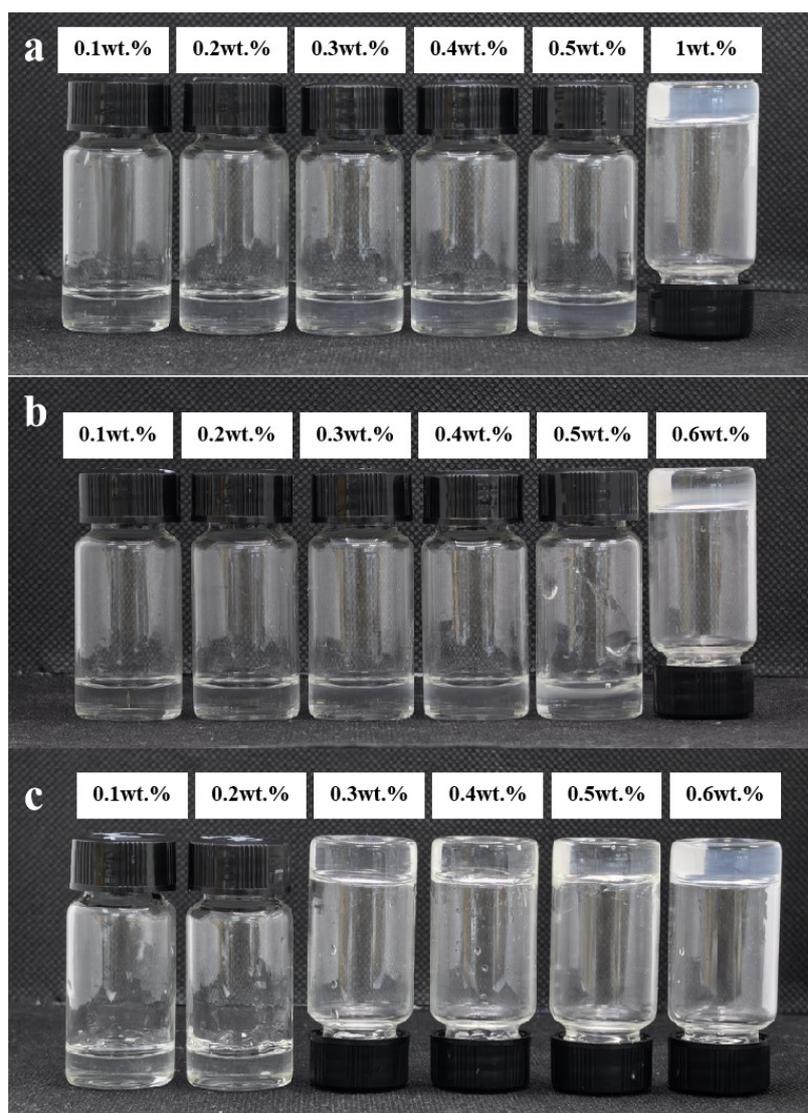


Figure S10. The physical appearance of Cn-Phe-AO(a:C12-Phe-AO, b:C14-Phe-AO, c:C16-Phe-AO) glycerol solutions

Table S1. Aggregation behavior of classical surfactants in glycerol. (S: solution; G: Gel; I: soild precipitation)

Types of surfactants	0.5wt.%	1wt.%
DTAB	I/20mM	I/40mM
TTAB	I/18mM	I/36mM
CTAB	I/17mM	I/17mM
SDS	S/21.8mM	S/43.6mM

SDBS	S/18mM	S/36mM
Sodium Laurate	S/28mM	S/56mM
Sodium Myristate	S/25mM	I/50mM
Sodium Palmitate	I/22mM	I/44mM

3.Surface Tensions of Cn-Phe-AO in Water and Glycerol

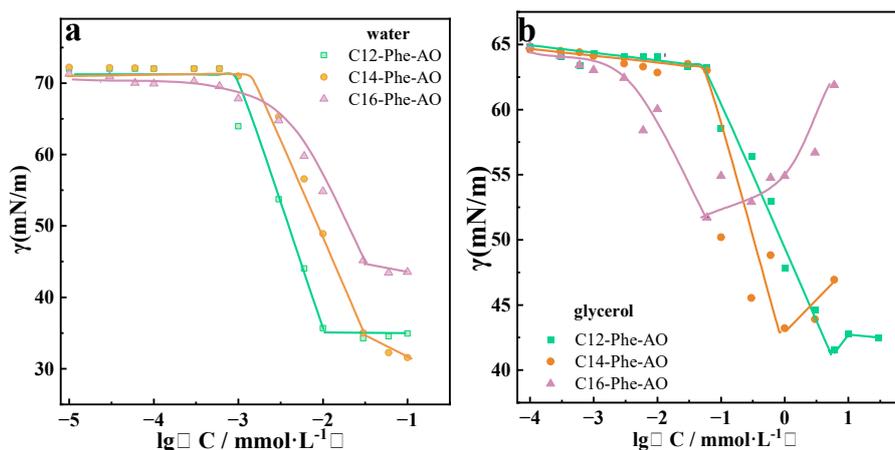


Figure S11. Equilibrium surface tension of Cn-Phe-AO (n=12,14,16) at different concentrations in water (a) and glycerol (b).

4.Rheological Behavior of C16-Phe-AO in 1, 3-propanediol solutions

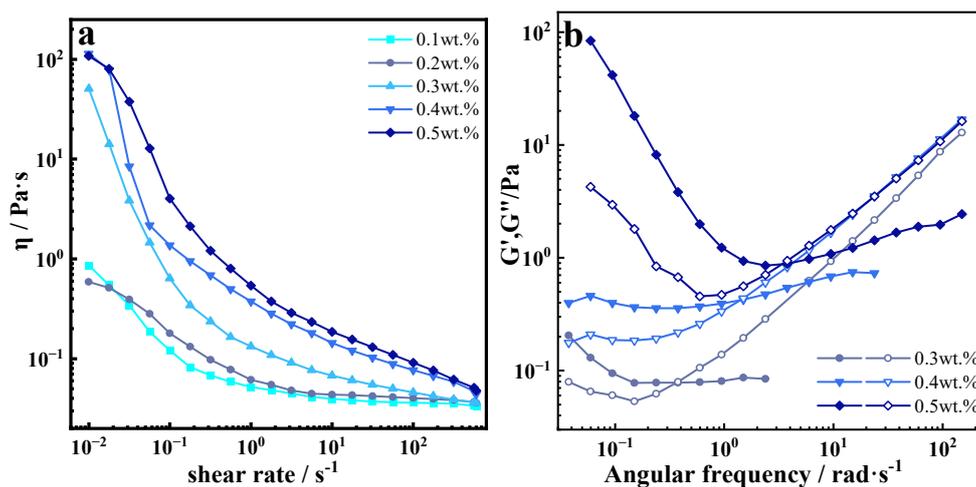


Figure S12. (a) Viscosity of 1,3-propanediol solution as a function of shear rate at different concentrations of C16-Phe-AO at 25°C; (b) Storage modulus G' (filled symbol) and loss modulus G'' (open symbol) as a function of oscillation frequency at different concentrations of C16-Phe-AO 1,3-propanediol solution at 25°C.

