# SUPPORTING INFORMATION FOR

# Selective and sensitive turn-on Fluorescent sensing of Arsenite based on Cysteine fused Tetraphenylethene with AIE characteristics in aqueous media

**Melek Baglan, Serdar Atılgan***

[a]*Department of Chemistry, Suleyman Demirel University, Isparta, 32000, Turkey*

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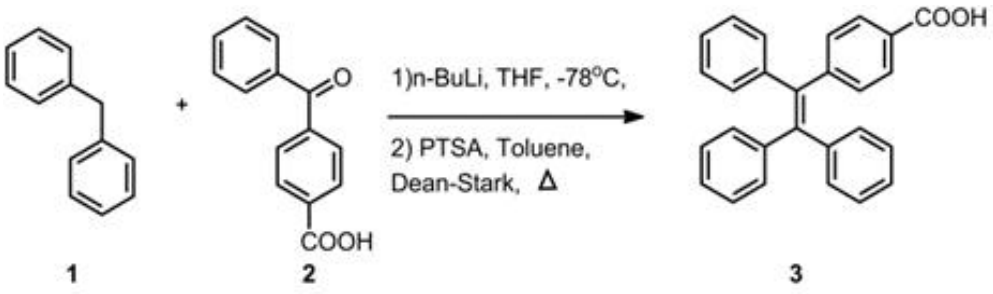
# S1. EXPERIMENTAL

## S1.1 GENERAL

All chemicals and solvents purchased from Aldrich were used without further purification. $^{1}$H NMR and $^{13}$C NMR spectra were recorded using a Bruker DPX-400 in DMSO with TMS as internal reference. The THF was further refluxed over metallic sodium in the presence of benzophenone until a persistent blue color was obtained and then it was distilled under an argon atmosphere. Absorption spectrometry was performed using a Shımadzu spectrophotometer. Steady state fluorescence measurements were conducted using a Shımadzu RF-5301PC spectrofluorometer. Column chromatography of all products was performed using Merck Silica Gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM). Reactions were monitored by thin layer chromatography using fluorescent coated aluminum sheets. Solvents were purchased from Sigma and solvents used for spectroscopy experiments were spectrophotometric grade. HRMS (high-resolution MS) was recorded on an Agilent 6210 time-of-flight LC/MS system. *N*-(1-methanesulfonyl)benzotriazole **4** was prepared according to literature procedures.[1] For NMR and Mass analysis, three equivalent of $As^{3+}$ was added to aqueous solution of **7** in water and after evaporation of solvent under ambient conditions at room temperature, the residue was used for both $^{1}$H-NMR and mass spectroscopy analysis. It was dissolved in DMSO for $^{1}$H-NMR analysis.

## S1.2 SYNTHESIS

### Synthesis of TPECOOH, 3

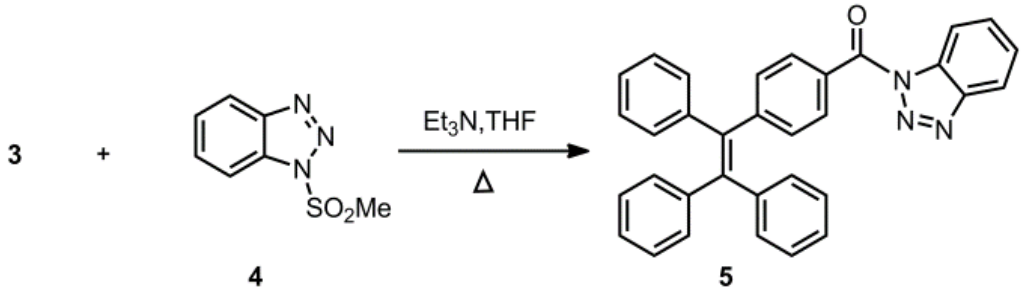



To a solutiom of diphenylmethane, **1** (2.02 g, 12 mmol) in dry tethrahyrofuran (20 ml) was added 4 ml of a 2.5 M solution of n-butyllithium in hexane (10 mmol) at 0ºC under an argon atmosphere. The resulting orange-red solution was stirred for 30 min at that temperature. Then, the mixture was cooled to -78 ºC. After stirring for one hour at that temperature benzylbenzoicacid, **2**, was added and the mixture was stirred for 6 h allowing the temperature to rise gradually to room temperature. The reaction was quenched with addition of an aqueous solution of ammonium chloride and the organic layer was extracted with EtOAc (3 X 250 mL) and the combined organic layers were washed with saturated brine solution and dried over anhydrous $MgSO_4$. The solvent was evaporated and the resulting

crude alcohol was subjected to acid catalyzed dehydration reaction in toluene with a catalyst, p-toluenesulfonic acid. The mixture was refluxed overnight and cooled to room temperature. The resulting brown residue was extracted with EtOAc (3 X 250 mL) and the crude product was purified by silica gel column chromatography using EtOAc as eluent to yield a light green powder, **3**. (4.15 g, 45%)

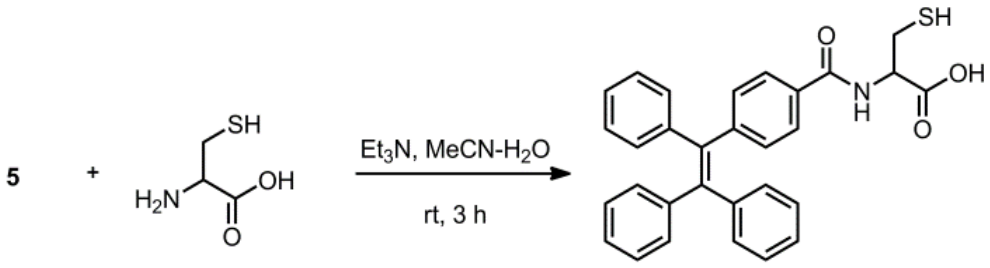
**$^1$H NMR (400 MHz, $CDCl_3$) δ**; 7.85-7.80 (d, 2H), 7.16-7.09 (m, 11H), 7.07-7.01 (m, 6H)
**$^{13}$C NMR (100 MHz, $CDCl_3$) δ**; 170.7, 149.6, 143.2, 143.1, 143.0, 142.7, 139.9, 131.4, 131.3, 131.2, 129.7, 127.9, 127.8, 127.7, 126.9, 126.8, 126.7 (overlapping has been observed for some aromatic carbon atoms)
**MALDI (TOF) m/z**: 376.14802 (calculated 376.14633, Δ=1.69 ppm)

**Synthesis of 1*H*-1,2,3-Benzotriazol-1-yl(TPE)methanone, 5**




A mixture of TPE-COOH, **3** (10.0 mmol) and 1-(methylsulfonyl)benzotriazole **4** (1.97 g, 10.0 mmol) and triethylamine (2.0 mL, 14.0 mmol) were refluxed in THF (50 mL) overnight. The solvent was evaporated and the residue was dissolved in chloroform (100 mL). The organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated to give a crude product. The crude product was used in the next step without any further purification.

**Synthesis of TPE-CYS, 7**




To a solution of L-cysteine **6** (2 mmol) and triethylamine (2 mmol) in $CH_3CN$-$H_2O$ (3:1, 8 mL) was added the corresponding **5** (2 mmol). The mixture was stirred at room temperature for 2 h. Solvent was removed under reduced pressure and ethyl acetate (10 mL) was added. The organic layer was washed with 2 N HCl and brine. After filtration and solvent

evaporation, the crude product was purified by silica gel column chromatography using n-$CH_3OH/CH_2Cl_2$ (v/v, 1:9) as eluent. Light brown powder of TPE-Cys was obtained in 92% yield (2.18 g).

**$^1$H-NMR** (400 MHz,$CDCl_3$) δ (ppm) 7.61 (s, 1H), 7.59 (s, 1H), 7.20-7.10 (m, 11H), 7.10-7.00 (m, 6H), 5.00(q, 1H), 3.30-3.00 ( m, 2H).

**$^{13}$C NMR (100 MHz, DMSO) δ**; 172.5, 166.5, 147.0, 143.4, 143.3, 143.2, 142.0, 140.2, 132.0, 131.2, 131.1, 131.0, 128.5, 128.4, 128.3, 127.4, 127.3, 127.2, 55.0, 52.2 (overlapping has been observed for some aromatic carbon atoms)

**MALDI (TOF) m/z**: 479.15614 (calculated 479.1551, Δ=1.04 ppm)

## References

1) Katritzky, A. R.; Shobana, N.; Pernak, J.; Afridi, A. S.; Fan,W. Q. *Tetrahedron* **1992**, *48*, 7817.

## S2 . ADDITIONAL DATA

### S2.1 Spectrophotometric studies

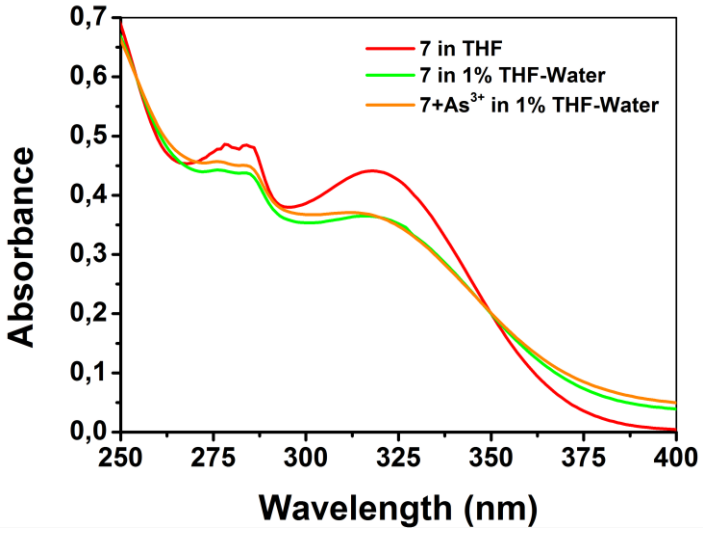



**Fig.S1.** UV/Vis absorption spectra of **7** (10 µM) in both THF and aqueous media and **7**+$As^{3+}$ in aqueous media

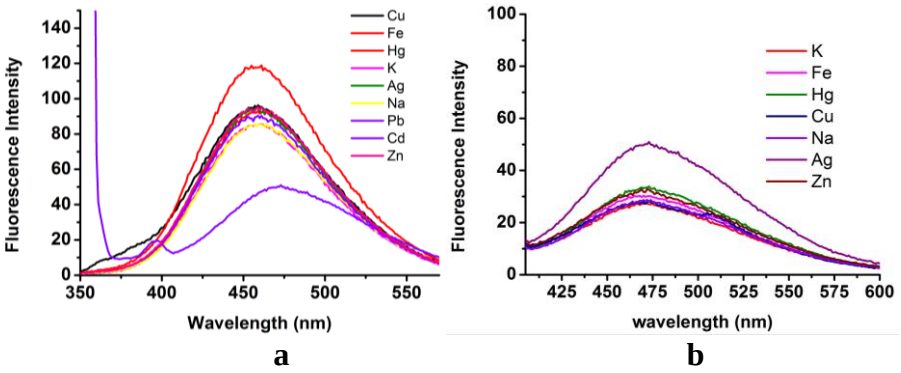



**Fig.S2.** Fluorescence emission change upon addition of a) 10 ppb b) 100 ppb of selected metal ions to the solution of 10μM **7** in 1:99 THF/$H_2O$ (Excitation wavelength was 330 nm)

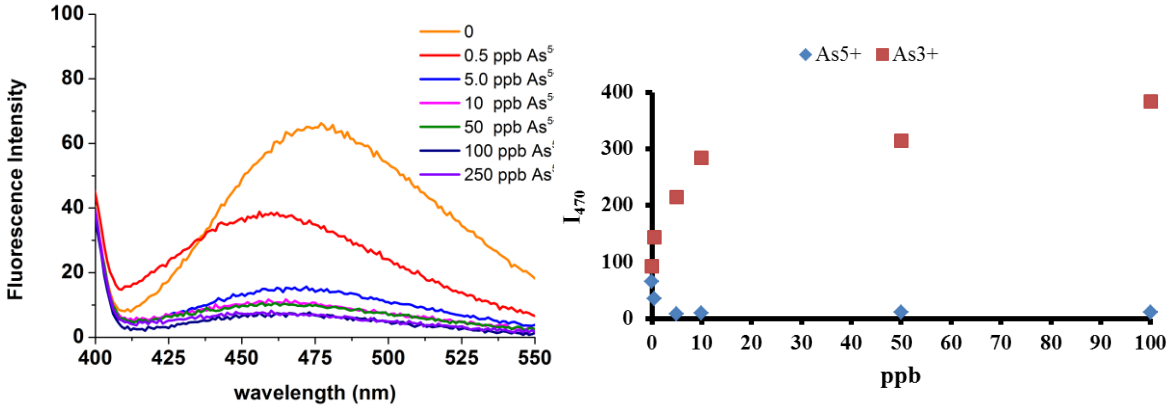



**Fig. S3.** a) Fluorescence intensity of 7 in 1%THF-$H_2O$ in the presence of different concentration of $As^{5+}$ b) Plot of the fluorescence intensity (470 nm) of **7** in 1%THF-$H_2O$ in the presence of different concentration of both $As^{3+}$ and $As^{5+}$ *vs* ppb level of analytes

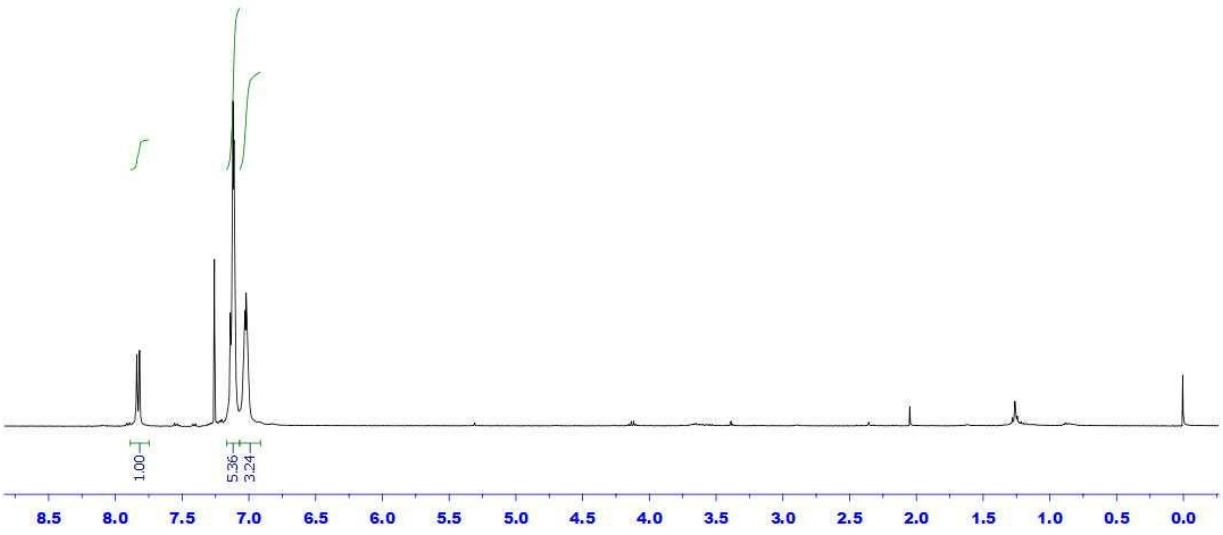



**Fig. S4** $^{1}$H NMR spectra of TPE-COOH**, 3**

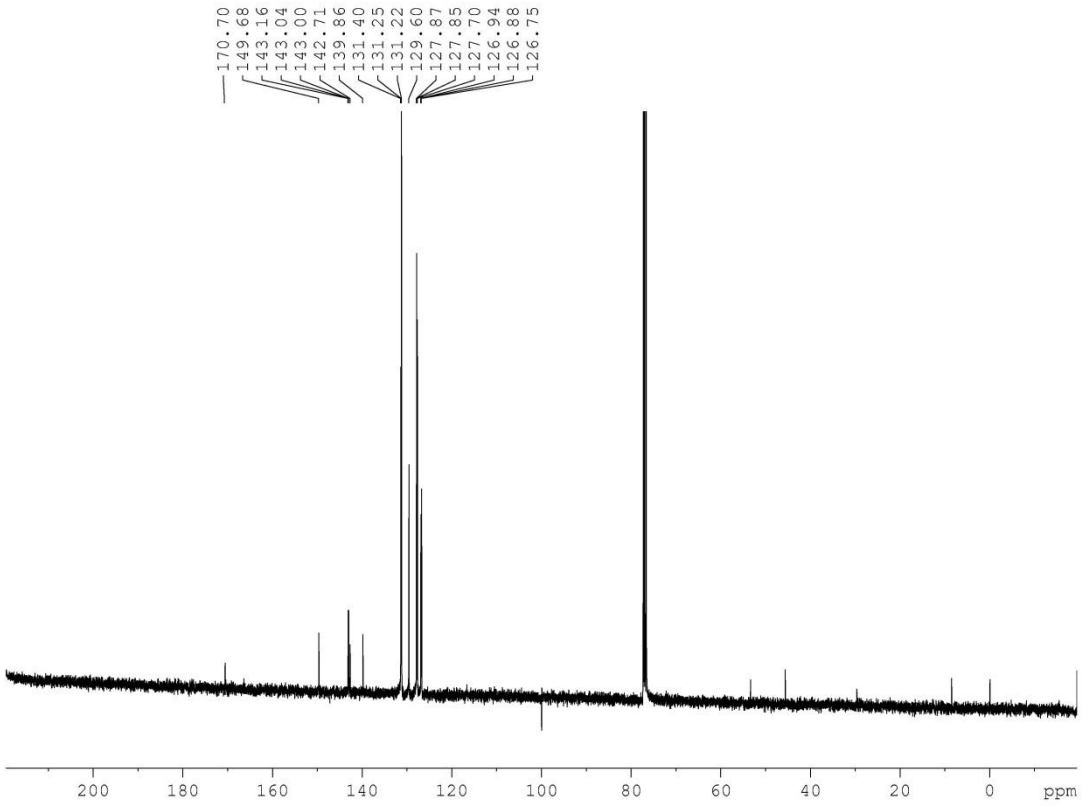



**Fig. S5** $^{13}$C NMR spectra of TPE-COOH**, 3**

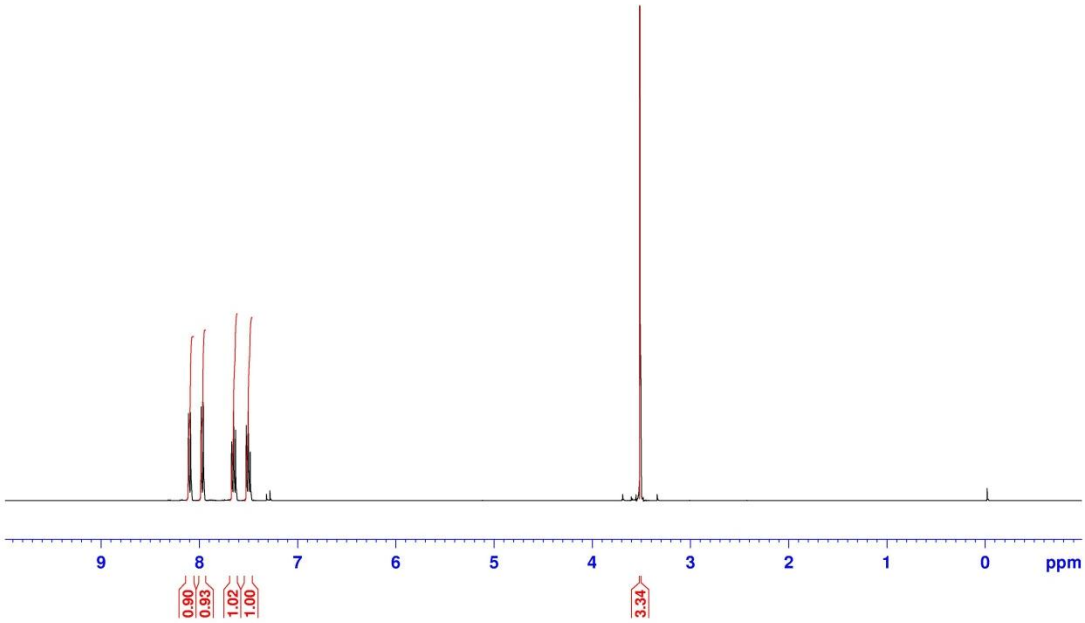



**Fig. S6** $^{1}$H NMR spectra of *N*-(1-methanesulfonyl)benzotriazole, **4**

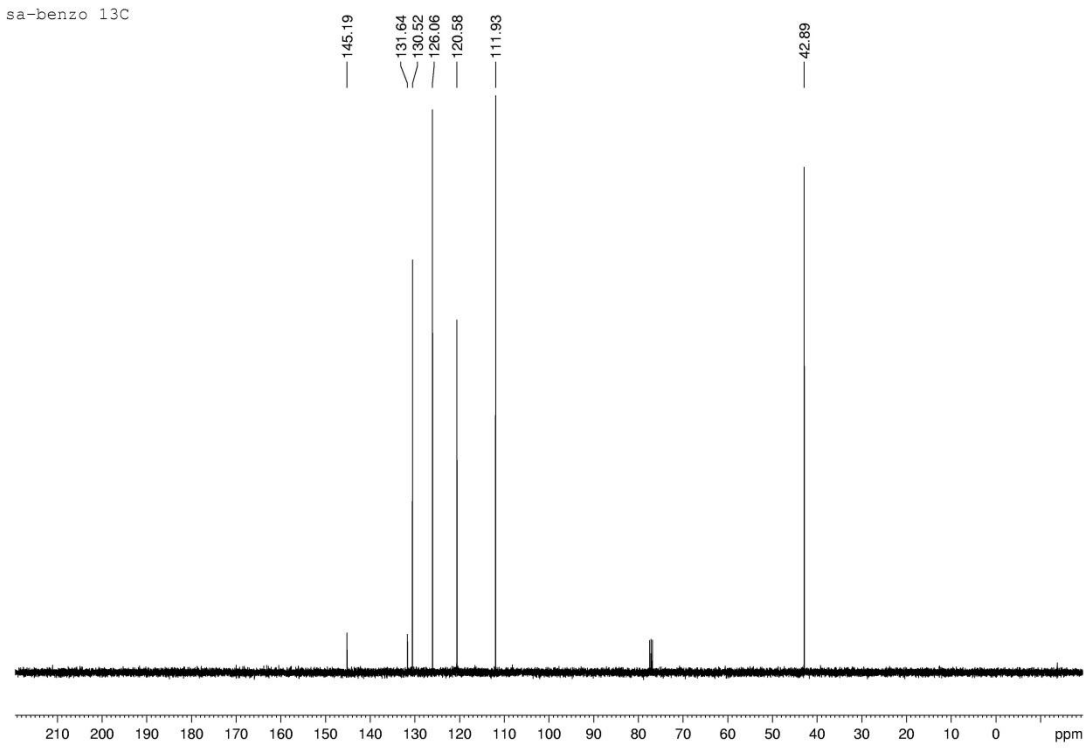



**Fig. S7** $^{13}$C NMR spectra of *N*-(1-methanesulfonyl)benzotriazole **4**

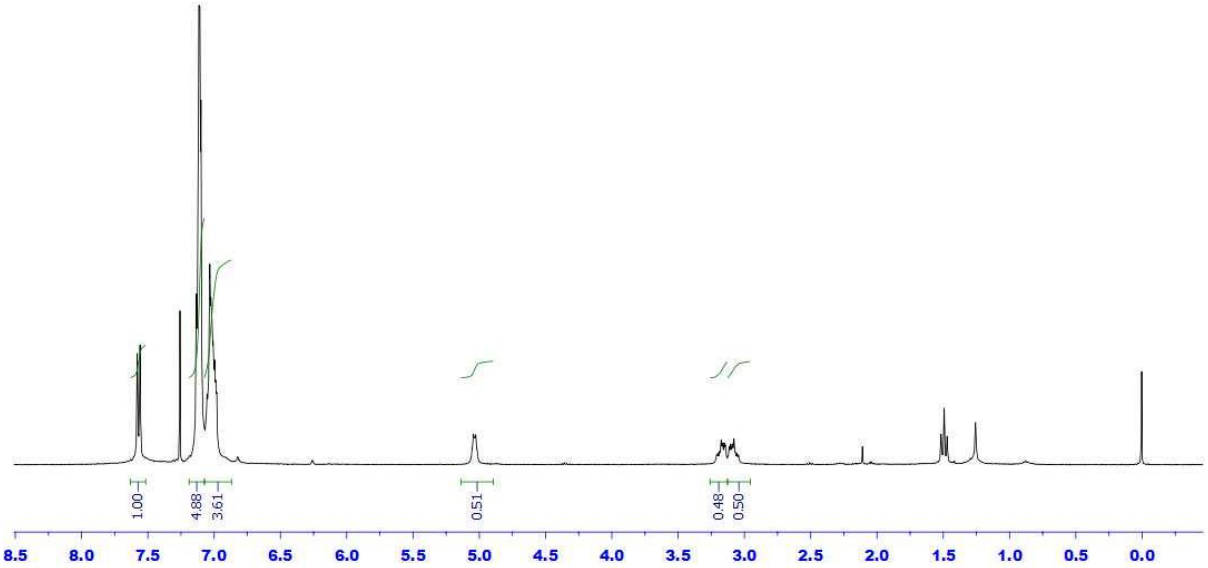



**Fig. S8** $^{1}$H NMR spectra of TPE-Cys **7** in $CDCl_3$

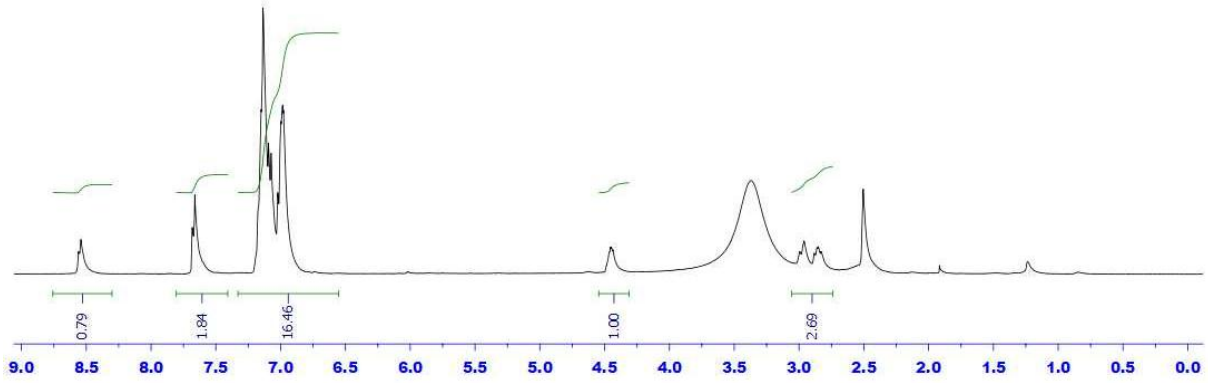



**Fig. S9** $^{1}$H NMR spectra of TPE-Cys **7** in DMSO

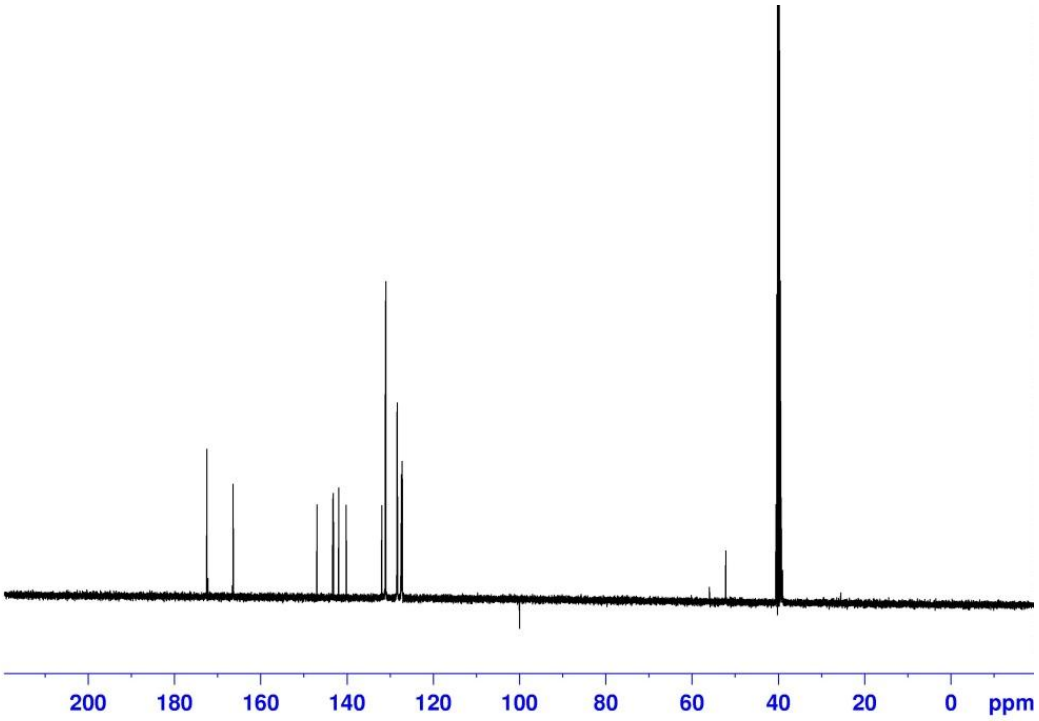



**Fig. S10** $^{13}$C NMR spectra of TPE-Cys **7** in DMSO

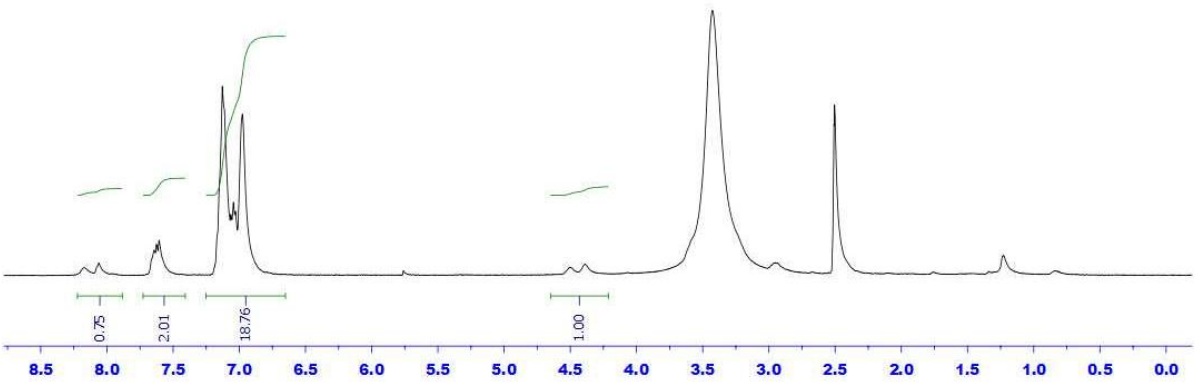



**Fig. S11** $^{1}$H NMR spectra of As(TPE-Cys)$_3$ in DMSO

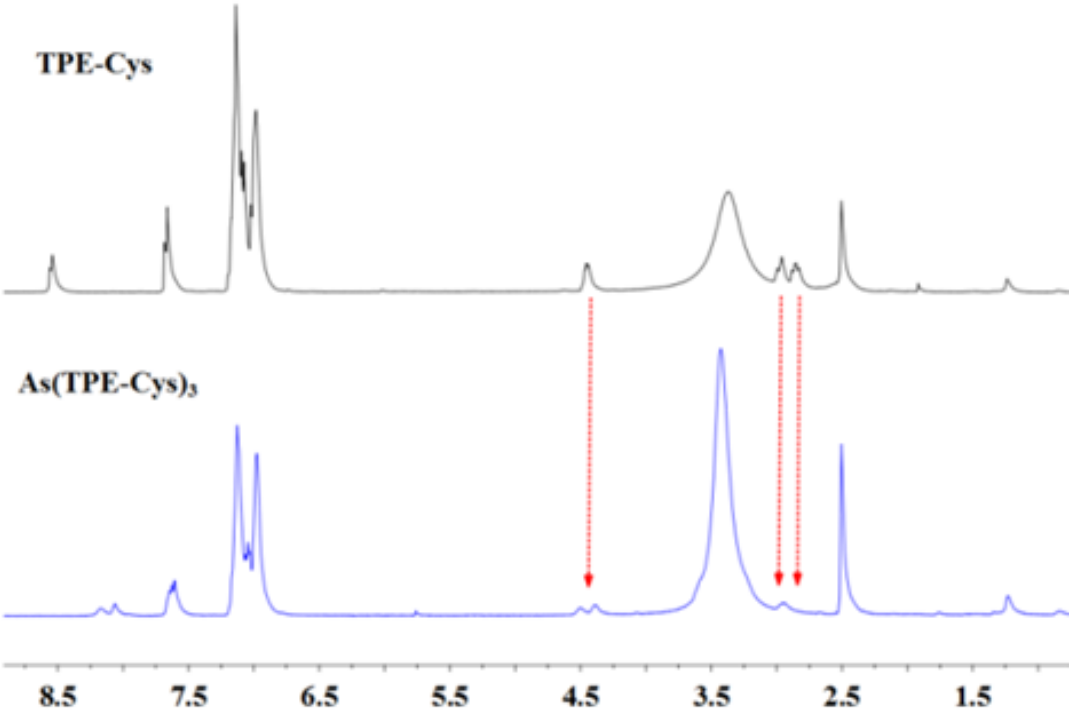



**Fig. S12.** $^{1}$H-NMR spectra (400 MHz, DMSO, rt) of 7 and As(TPE-Cys)$_3$

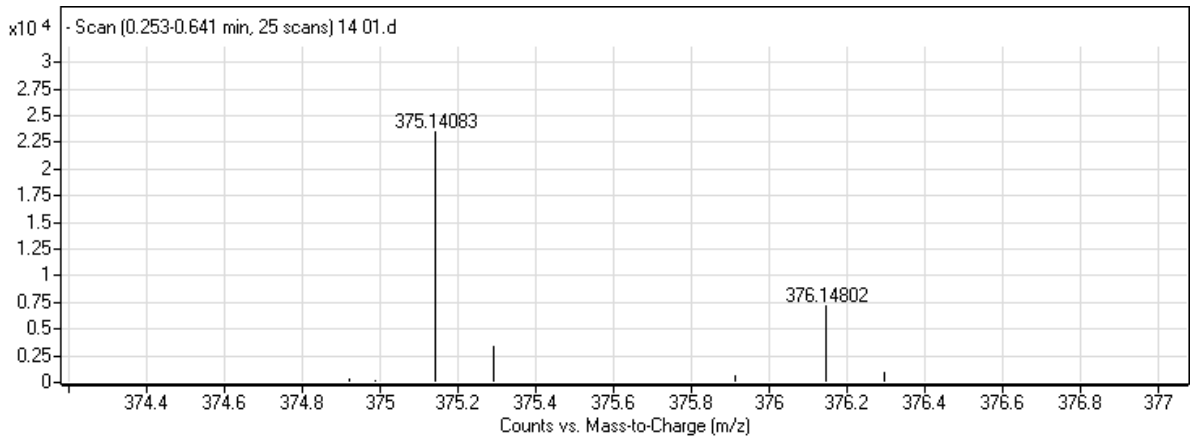



**Figure S13** MALDI-TOF Analysis of the compound **3** (calculated mass: 376.14633, measured mass: 376.14802, Formula: $C_{27}H_{20}O_2$)

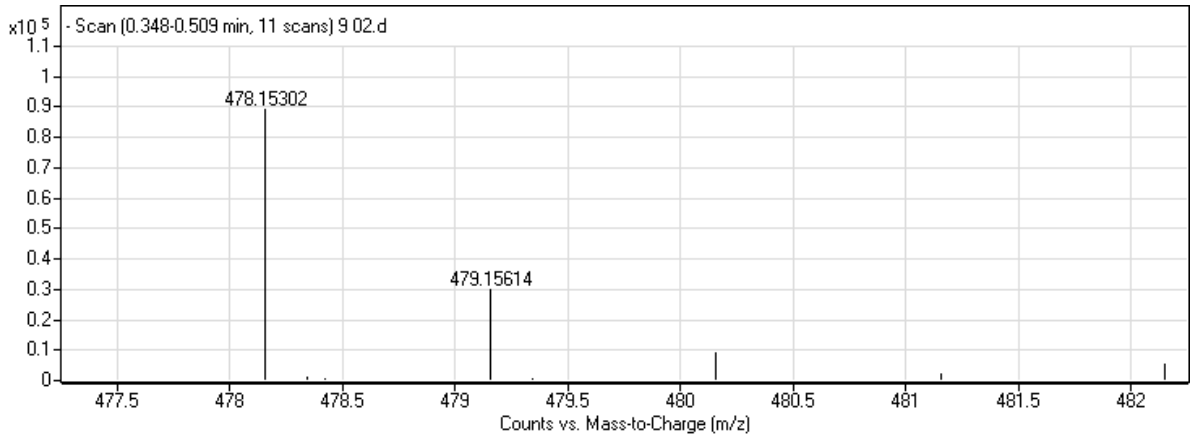



**Figure S14** MALDI-TOF Analysis of the compound **7**(calculated mass: 479.1551, measured mass: 479.15614, Formula: $C_{30}H_{25}NO_3S$)

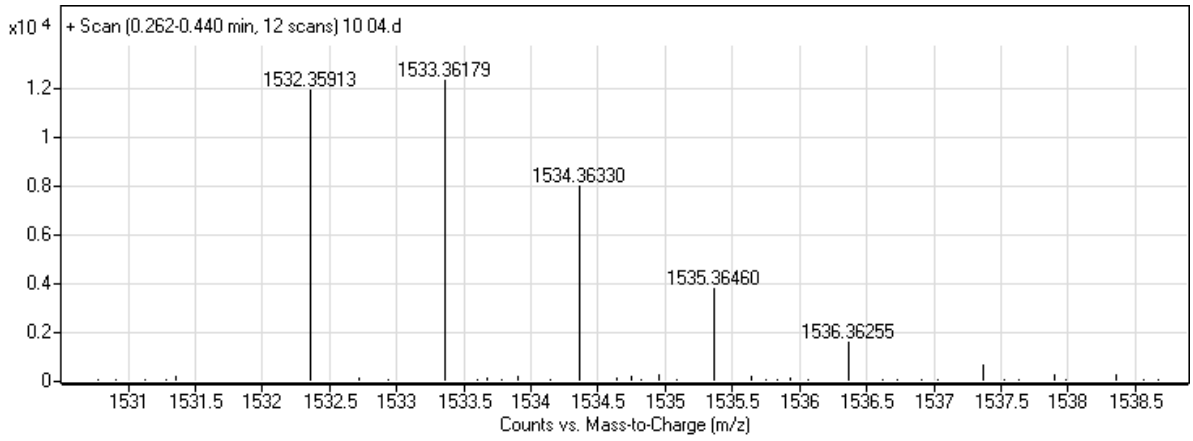



**Figure S15** MALDI-TOF Analysis of the As(TPE-Cys)$_3$ complex

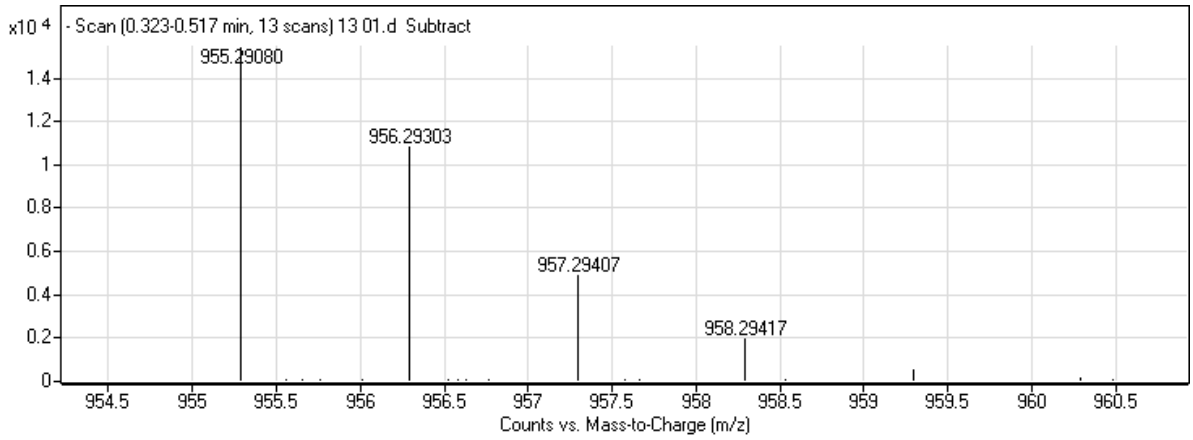



**Figure S16** MALDI-TOF Analysis of the TPE-Cys-Cys-TPE