Electronic supporting information

Synthesis and Characterization of Thiol-Stabilized Gold Nanoparticles Appended to Bis(pyrazole) pyridine for Fabrication of Rectangular Nano/Microstripes and Their Spin Crossover and SERS Studies

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This supporting information contains:

General experimental methods:

^{1}H and ^{13}C NMR spectroscopic data were recorded on a Bruker DPX 400 spectrometer with solvent proton as internal standard. Deuterated solvents $CDCl_3$-d_1, and DMSO-d_6 were obtained from Aldrich. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light.

Materials: Citrazinicacid, $(COCl)_2$, I_2, trifloro acetic acid, tetramethylammonium chloride, $[Pd(PPh_3)_4]$, Tosylchloride, LiBr, $HAuCl_4$. H_2O, $NaBH_4$, TOAB, $Fe(ClO_4)_2$. H_2O were obtained from Aldrich. K_2CO_3, LiOH, NaOH, thio urea, Cu(I)I, PPh_3 obtained from Avra Synthesis, Hyderabad, India. THF, Triethylamine, benzene, dichloromethane, hexane, pet-ether, $CHCl_3$ and methanol solvents were obtained from Finar Chemicals Limited, Ahmedabad, India. All solvent was used after distillation. Methanol, HCl and NaN_3 obtained from Merck. $MgSO_4$ and $Na_2S_2O_3$ were purchased from SRL chemicals.pvt. limited, Hyderabad.

Instrumentation details:

^{1}H and ^{13}C NMR spectroscopy data were recorded on a Bruker DPX 500 MHz spectrometer with solvent proton as an internal standard ($CDCl_3$-$d1$ = 7.26 ppm). LC mass spectrometry was performed on Shimadzu LCMS-2010A mass spectrometer. ESI-Mass spectrometry was performed on Bruker maXis ESI-TOF spectrometer. IR spectra were recorded on a JASCO FT/IR-5300 or Nicolet 5700 FT-IR instrument equipped with ATR attachment. Elemental analysis was recorded on a C H N analysis Thermo Finnigan Flash EA 1112 analyzer instrument. UV-Visible absorption spectra were recorded on a spectrophotometer Cary-100, Varian. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light.

Bulk Magnetic Studies: The temperature dependent magnetic susceptibility of complex I in the powder state was measured on a Quantum Design vibrating sample magnetometer (VSM-SQUID) setup in the temperature range of 340 ↔ 2 K at continuous cooling (↓) and heating (↑) cycles with an applied direct current (DC) magnetic field of 0.5 T. Heating and cooling rate of the sample was kept at a 10 K interval in sweep mode.

TEM measurement: It was carried out on Tecnai G2 FEI F12 instrument at an accelerating voltage of 120 kV. Carbon coated TEM grids (200 Mesh Type B) were purchased from Ted Pella Inc. U.S.A.

3.2.4. Method for Patterning. Micro patterning of complex **10** was carried out by drop casting 20 μL of a 2 mg/mL solution of complex I in acetonitrile (Aldrich, ≥ 99% purity) on glass substrate. The

substrate was cleaned by sonication for 2 min in electronic-grade water (Milli-Q-pure quality), 2 min in acetone (Aldrich chromatography quality), and then with 2-propanol (Aldrich spectroscopic-grade quality). Before micro patterning the solution of compound I was filtered through a Whatman filter paper.

Poly(dimethylsiloxane) (PDMS) stamps for lithography: Elastomeric PDMS (Sylgard 184 Down Corning) stamps were prepared by replica molding of a structured master (NTMDT AFM test gratings-TGZ3). The curing process was carried out at 60 °C for 6 h. Once cured, the replica was carefully peeled-off from the master and used as such for micropatterning techniques.

Atomic Force Microscopy (AFM): AFM imaging was carried out on NT-MDT Model Solver Pro M microscope using a class 2R laser of 650 nm wavelength having maximum output of 1 mW. All calculations and image processing was carried out by a software NOVA 1.0.26.1443 provided by the manufacturer. The images were recorded in a semicontact mode using a noncontact silicon cantilever (NSG10-DLC) tip purchased from NT-MDT, Moscow. The dimension of the tip is as follows: cantilever length = 100 (±5) μm, cantilever width 35 (±5) μm, and cantilever thickness = 1.7−2.3 μm, resonate frequency = 190−325 kHz, force constant = 5.5−22.5 N/m, chip size = 3.6 × 1.6 × 0.4 mm, reflective side = Au, tip height = 10−20 μm, tip curvature radius = 1−3 nm, and aspect ratio 3:1−5:1.

Confocal Raman micro spectroscopy studies. Raman spectra of the samples were recorded on a WI-Tec confocal Raman spectrometer equipped with a Peltier-cooled CCD detector. Using a 600 grooves/mm grating BLZ = 500 nm, the accumulation time was typically 10 s and integration time was typically 2.0000 s. Ten accumulations was performed for acquiring a single spectrum. For imaging the integration time was typically 2.000 s, keeping in mind that the x or y resolution is ~250 nm four points per line and four line per image was taken for imaging of a 1 μm × 1 μm area. A He−Ne 633 nm laser was used as an excitation source for the Raman scattering. All measurements were done at ambient conditions.

SERS Experiments: Experiments were conducted using complex 10 coated on silicon wafer, as the SERS substrate. Complex 9 was used as the analyte molecule; 10 μL of 0.4 μM solution of complex 9 in methanol was spread uniformly on the substrate and dried under ambient atmosphere. A WITec model Alpha 300 R Raman microscope was used for recording the Raman spectra, with 0.5 s integration time and 10 accumulations, through a 100× aperture (NA = 0.89). A 633 nm He-Ne laser with 12 m Watt power was used as the excitation source. The laser intensity was maintained constant in all measurements; a 100 μm detecting fiber was used to collect the spectra. A Raman spectrum for the bulk material used as the reference was recorded using a small amount of complex **9** powdered placed on the Si wafer.

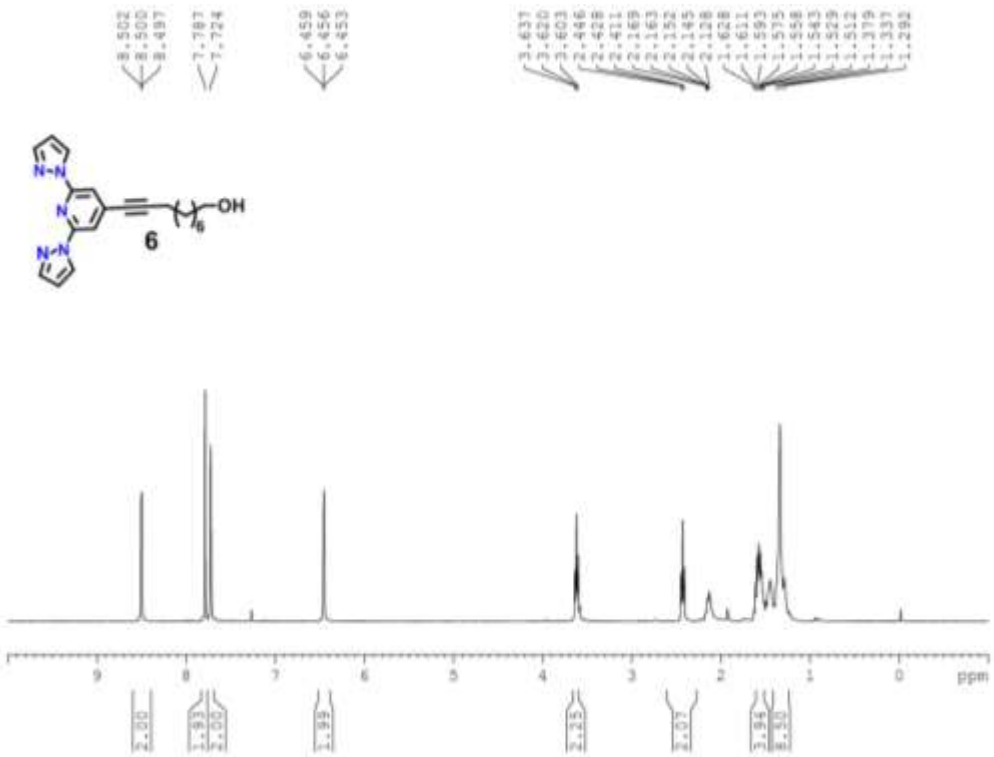

Fig. S1 ^{1}H-NMR Spectrum of compound 6

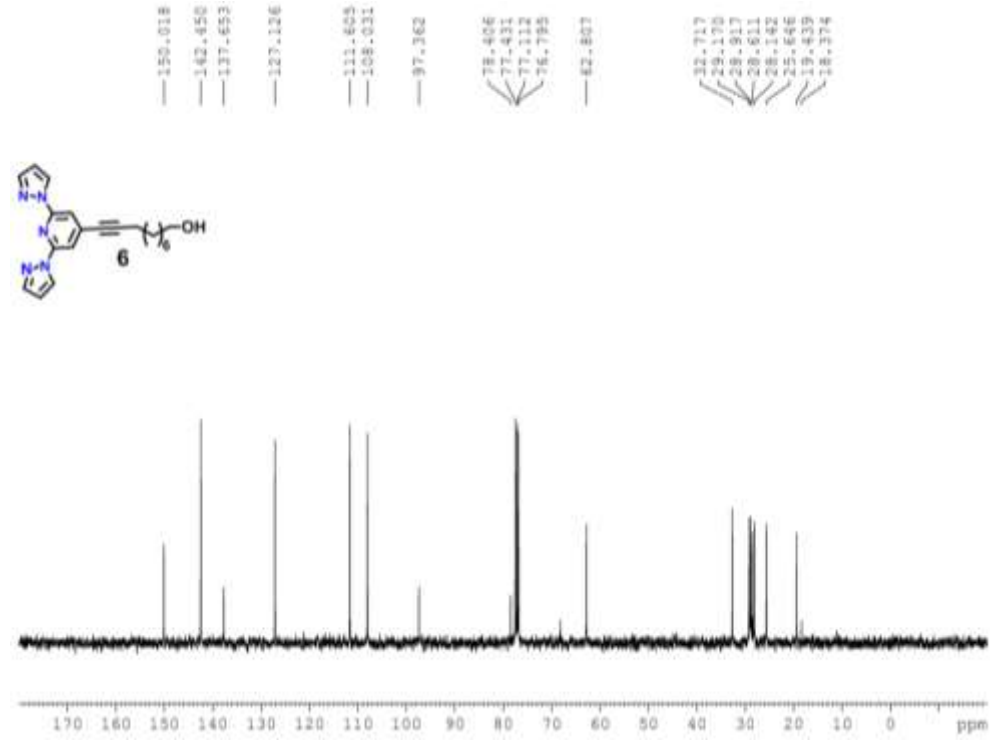

Fig. S2 ^{13}C-NMR Spectrum of compound 6

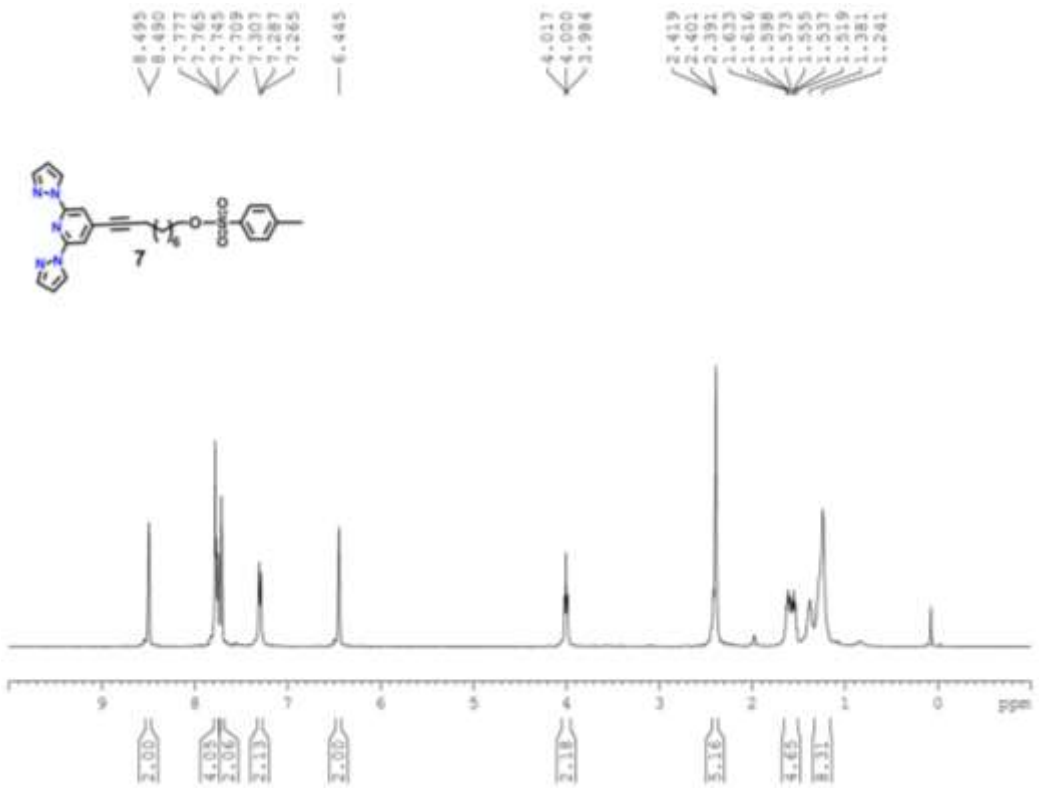

Fig. S3 ^{1}H-NMR Spectrum of compound 7

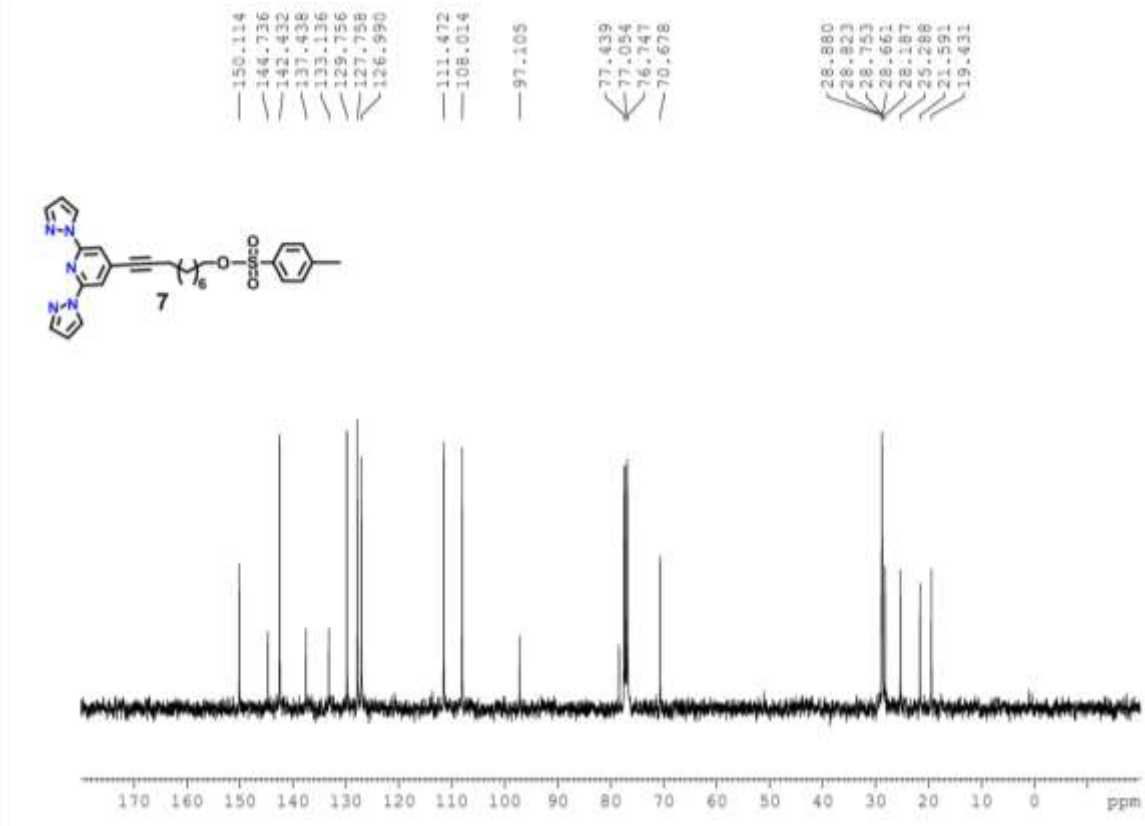

Fig. S4 ^{13}C-NMR Spectrum of compound 7

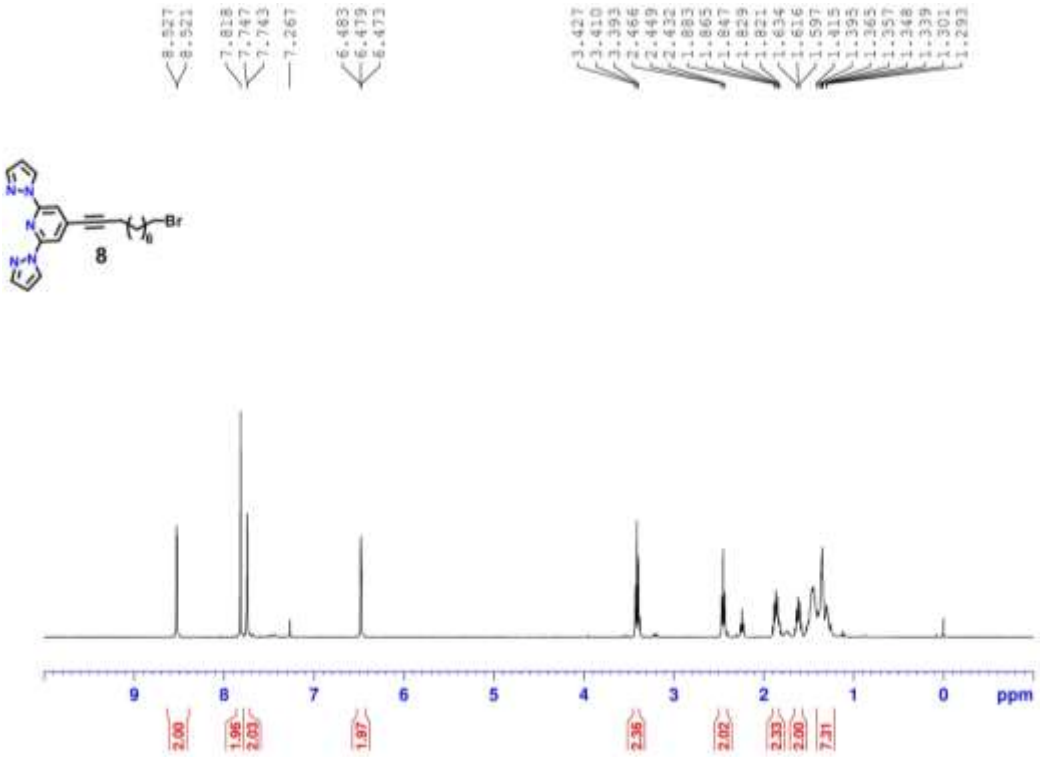

Fig. S5 ^{1}H-NMR Spectrum of compound 8

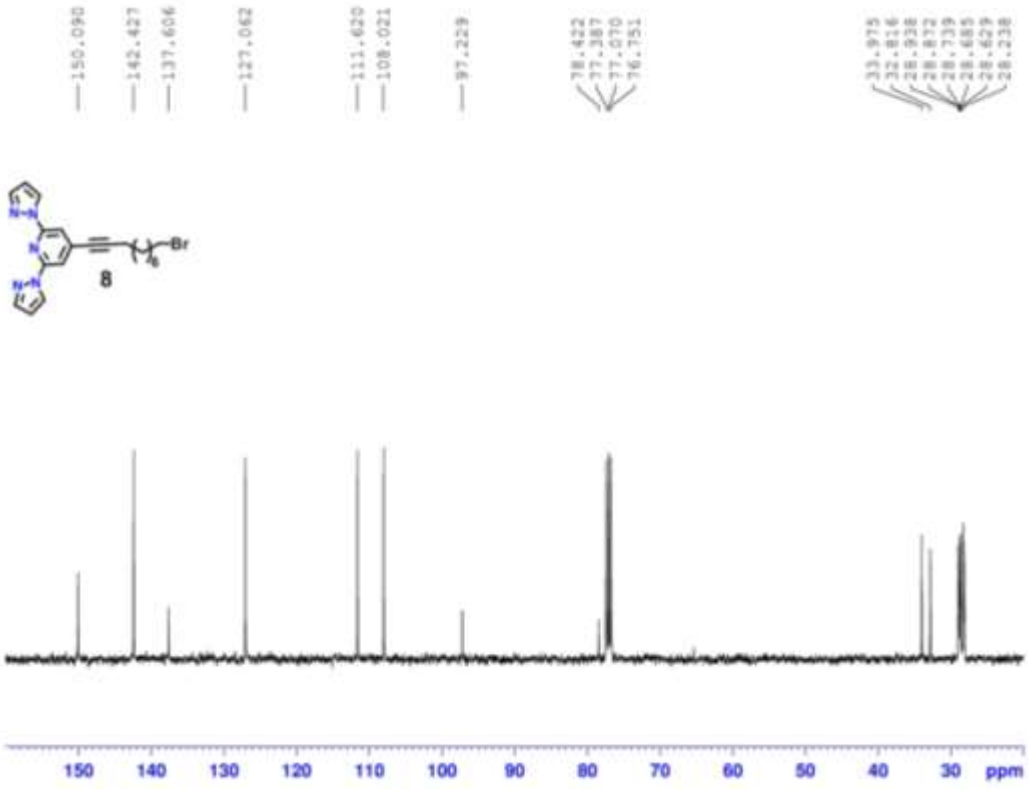

Fig. S6 ^{13}C-NMR Spectrum of compound 8

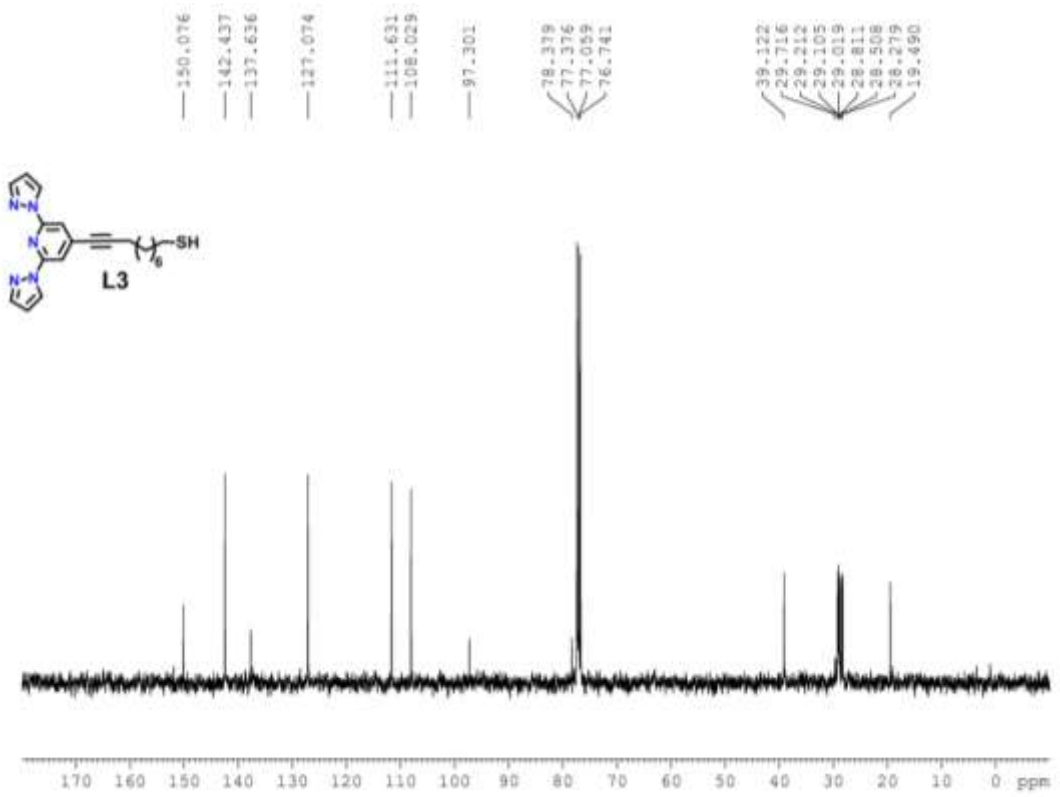

Fig. S7 ^{13}C-NMR Spectrum of L3

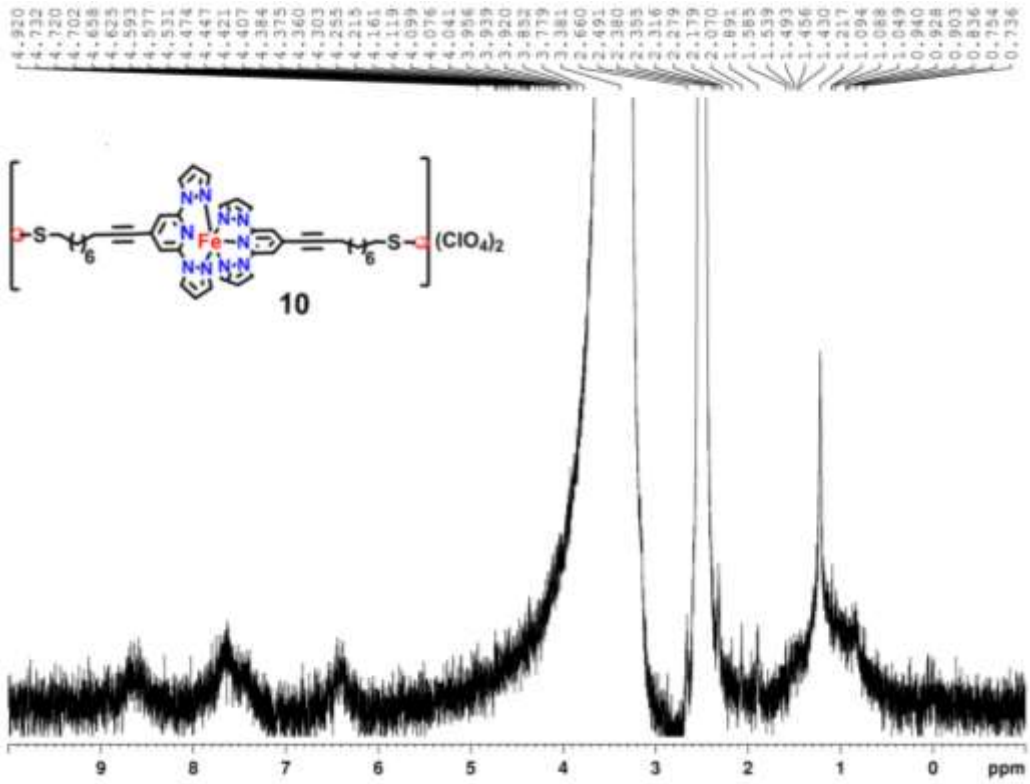

Fig. S8 ^{1}H-NMR Spectrum of compound 10

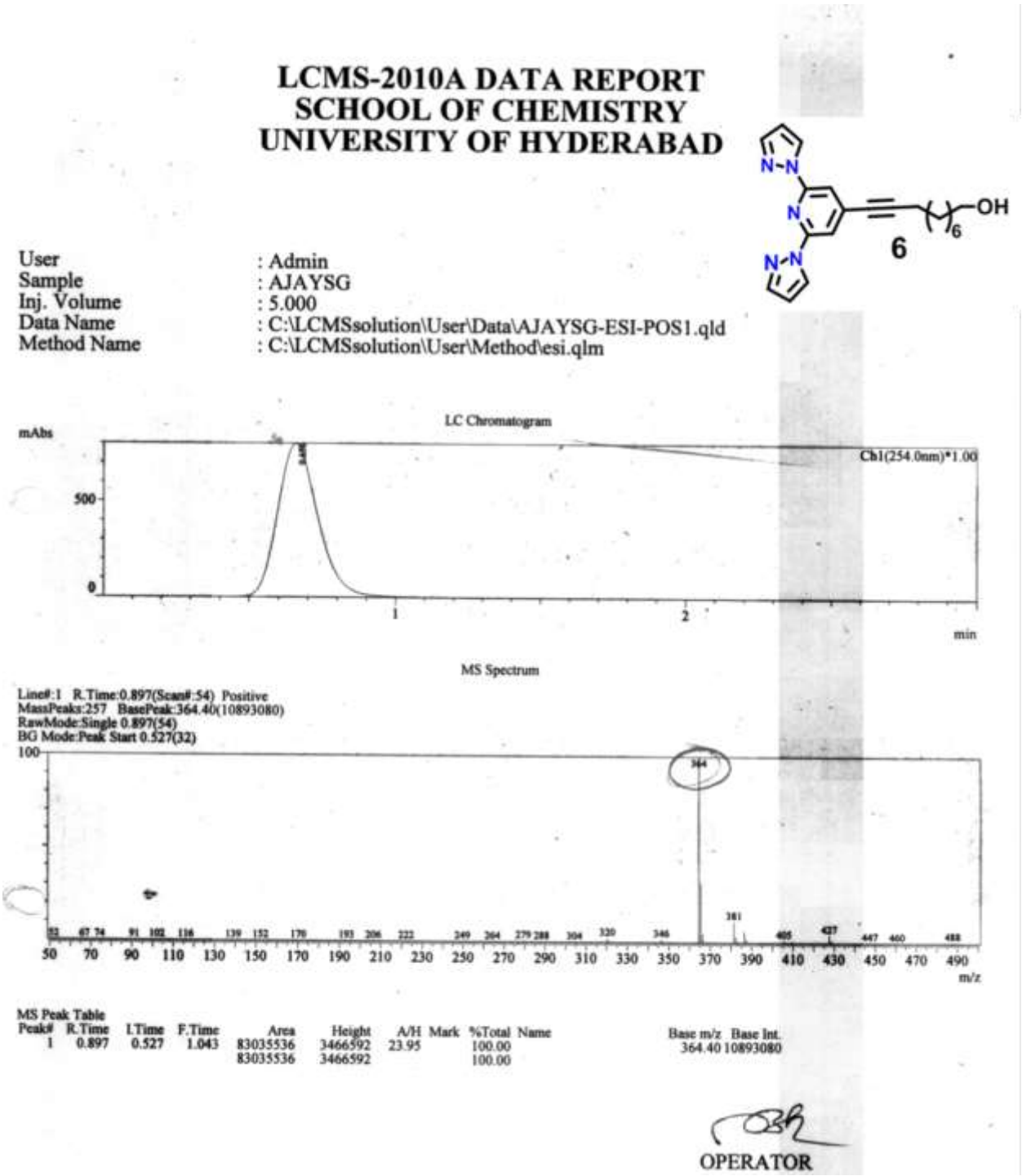

Fig. S9 LC-MS of compound 6

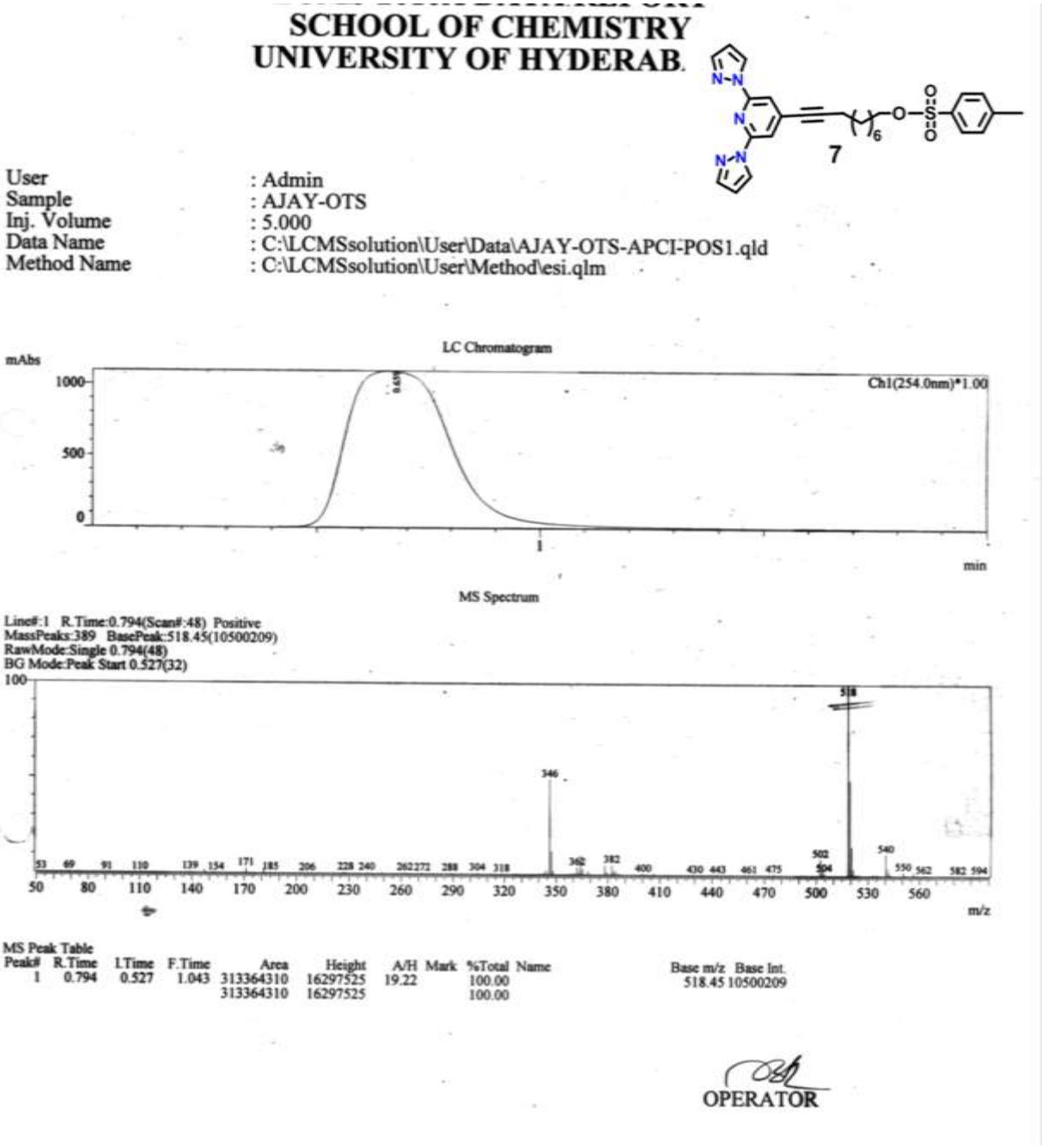

Fig. S10 LC-MS of compound 7

LCMS-2010A DATA REPORT
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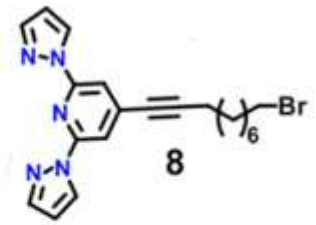

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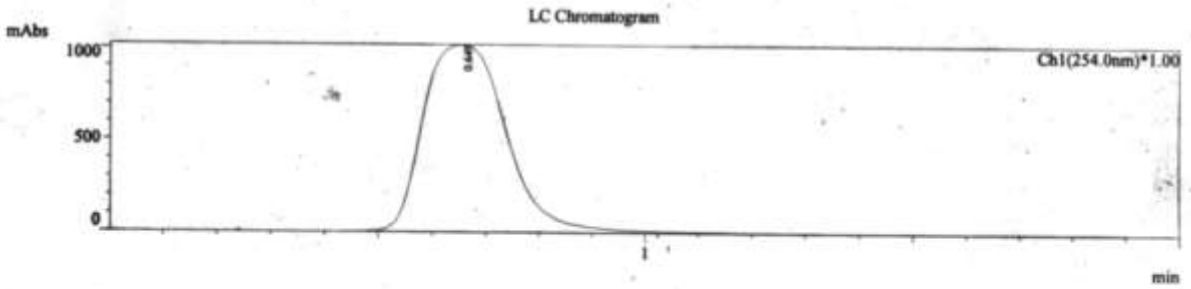

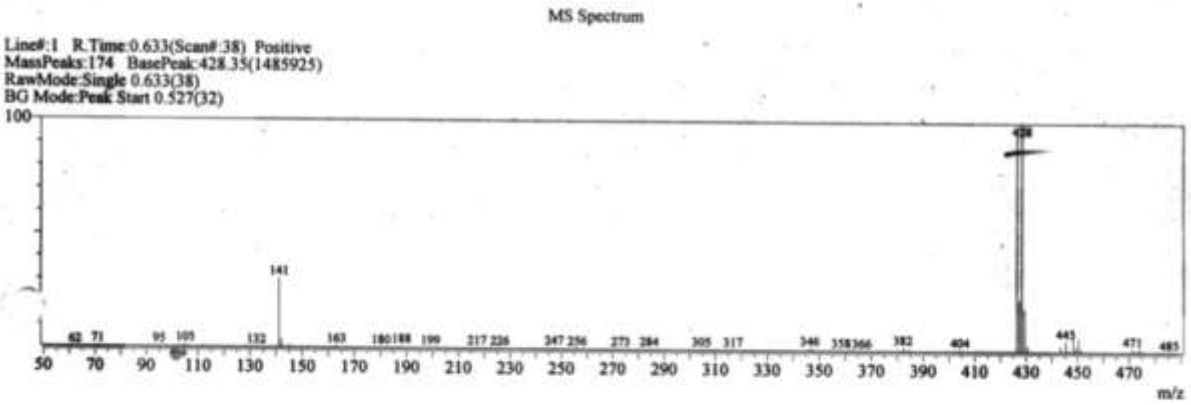

MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.633	0.527	0.743	28889768	4729383	6.10		100.00		428.35	1485925
				28889768	4729383			100.00			

OPERATOR

Fig. S11 LC-MS of compound 8

LCMS-2010A DATA REPORT
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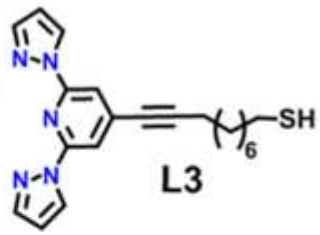

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Inj. Volume : 5.000
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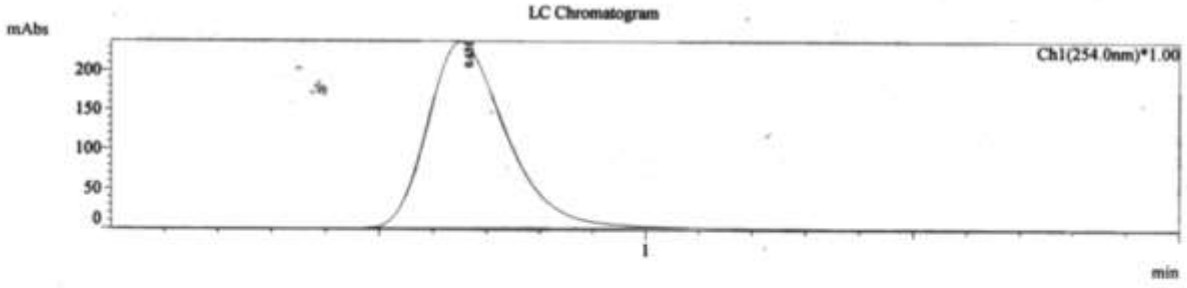
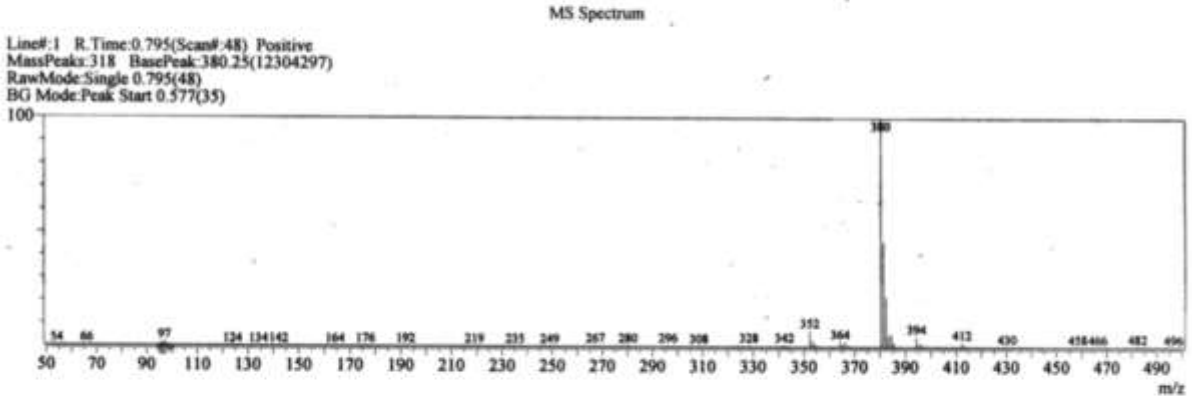


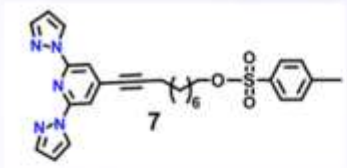


MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.795	0.577	1.010	304473890	24751492	12.30		100.00		380.25	12304297
				304473890	24751492			100.00			

OPERATOR

Fig. S12 LC-MS of L3



FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

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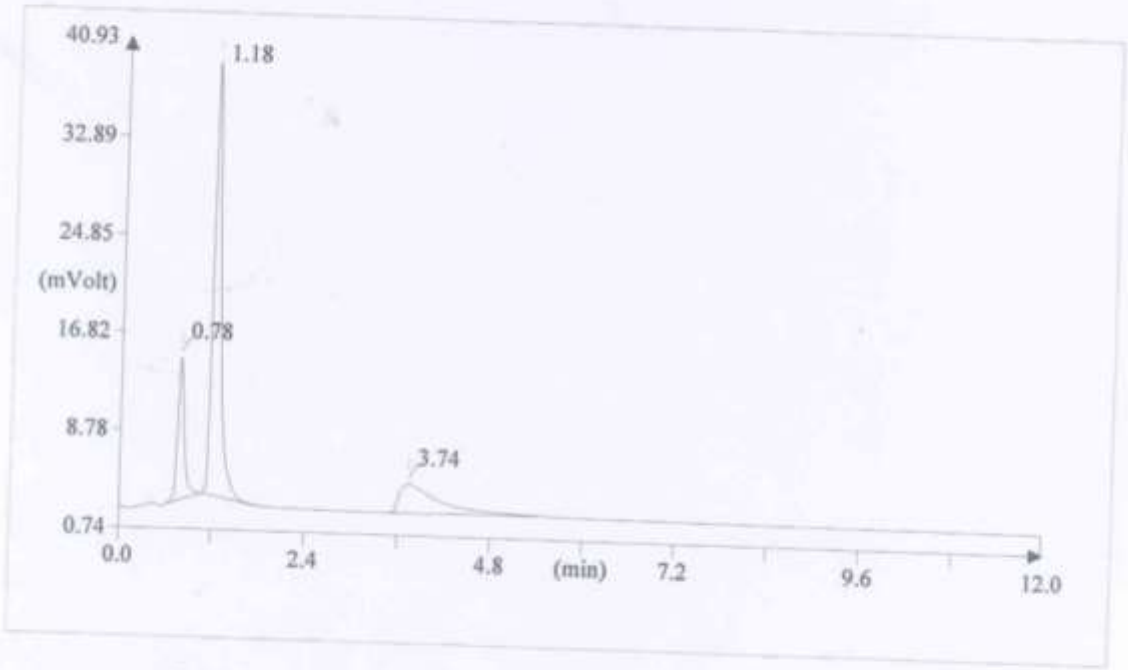
Sample weight:	1.112



Element Name	Element %	Ret. Time
Nitrogen	13. 45	0. 78
Carbon	64. 87	1. 18
Hydrogen	6. 12	3. 74

Fig. S13 Elemental analysis of compound 7

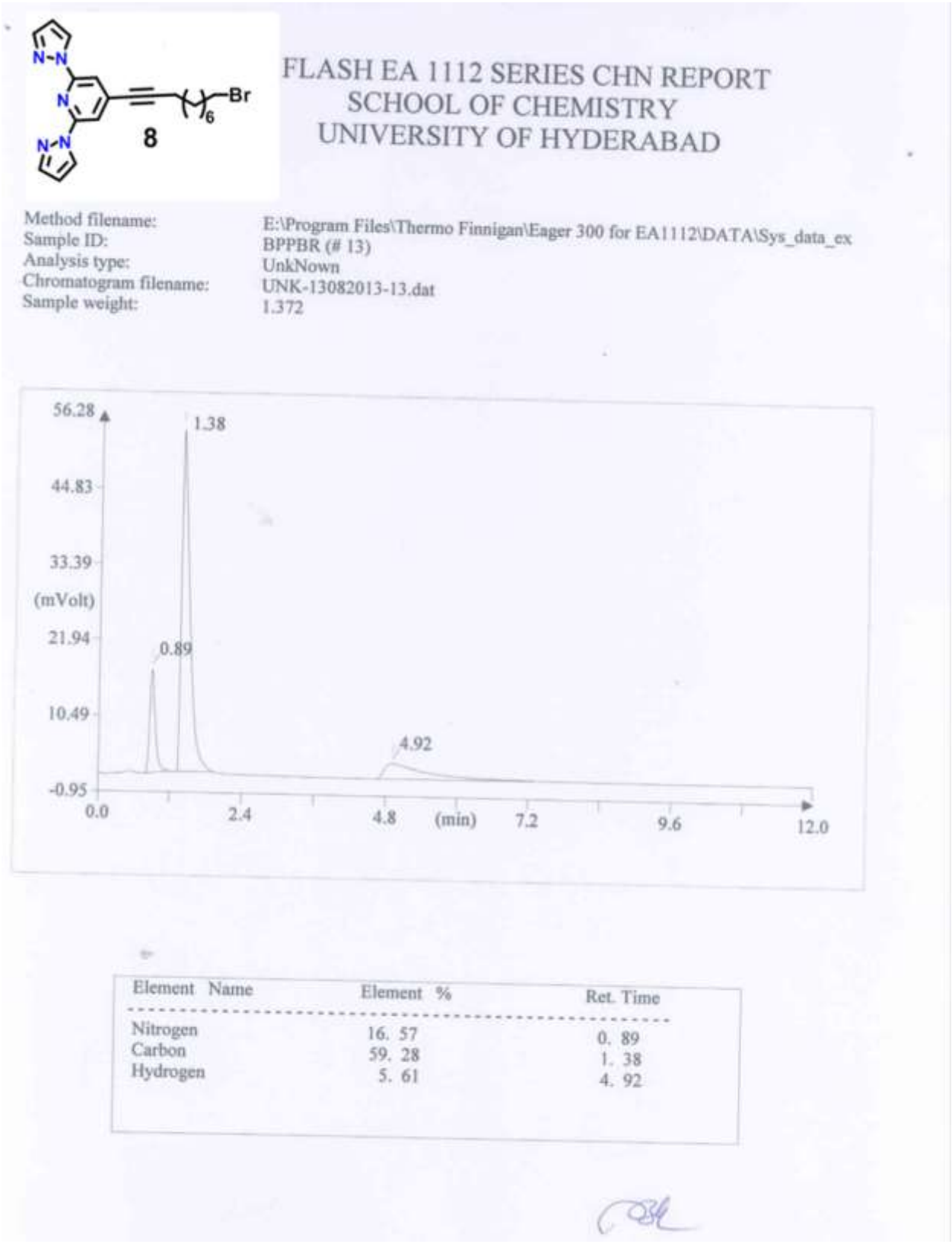


Fig. S14 Elemental analysis of compound 8

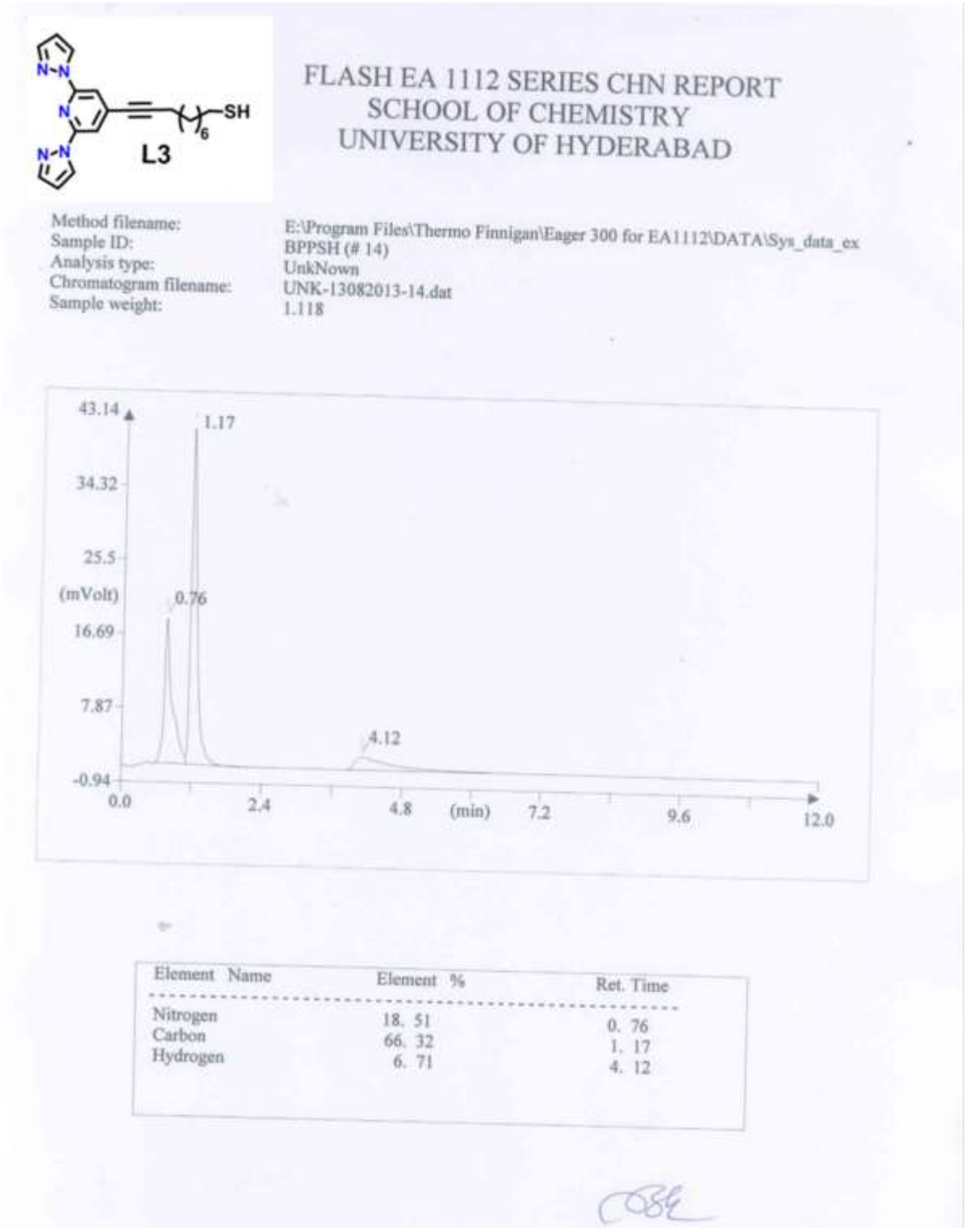


Fig. S15 Elemental analysis of L3

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

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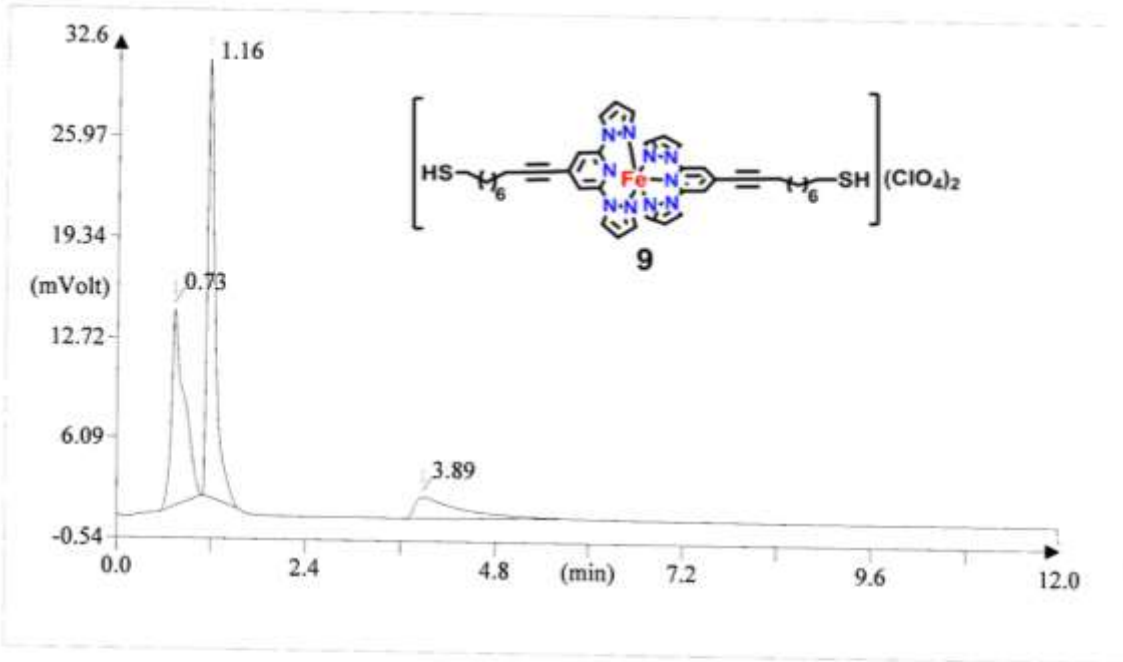

Element Name	Element %	Ret. Time
Nitrogen	13. 76	0. 73
Carbon	49. 85	1. 16
Hydrogen	4. 91	3. 89

Fig. S15 Elemental analysis of compound 9

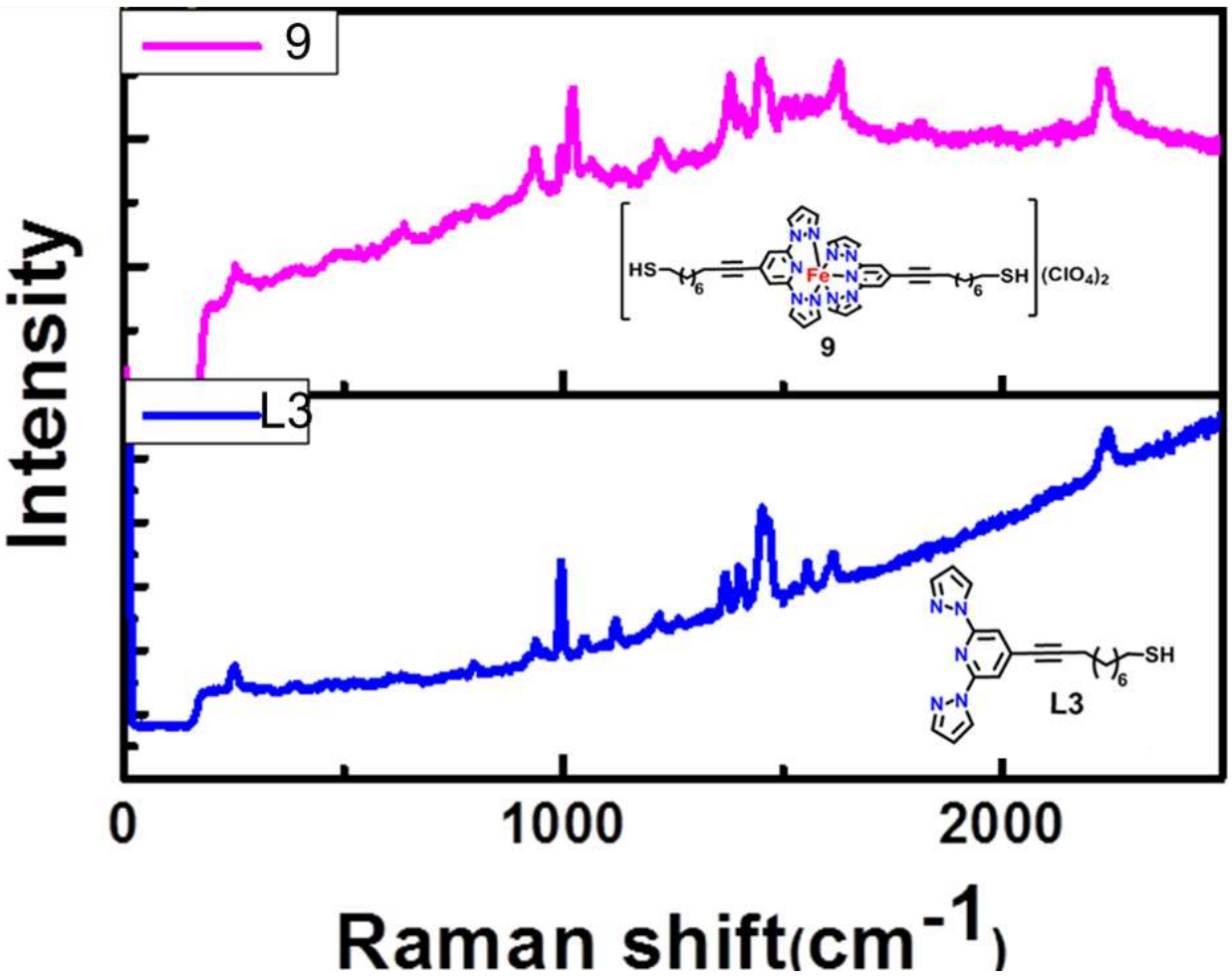

Fig. S16 Raman spetra of L3 and 9

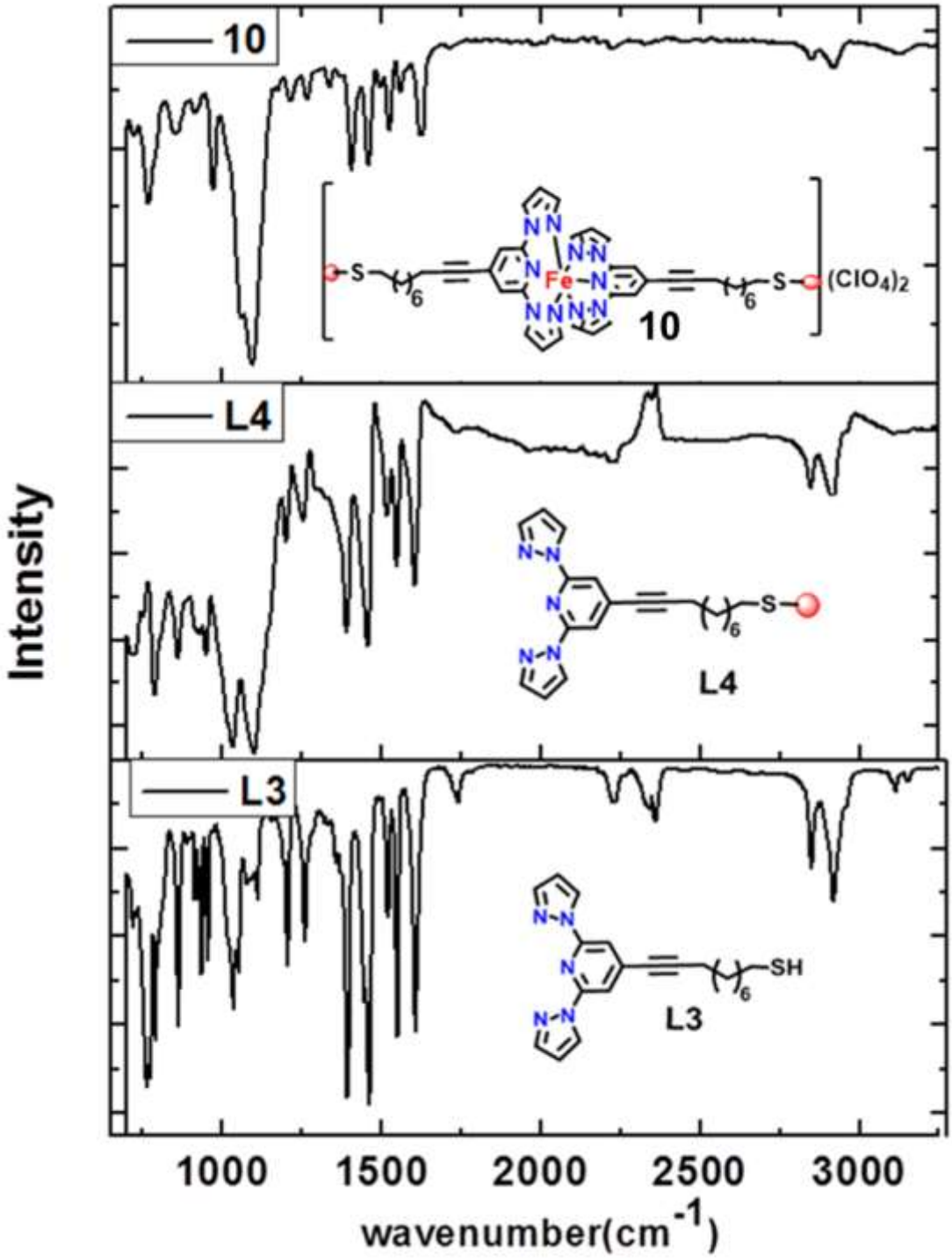

Fig. S17 FT-IR Spectra of 10, L3, and L4

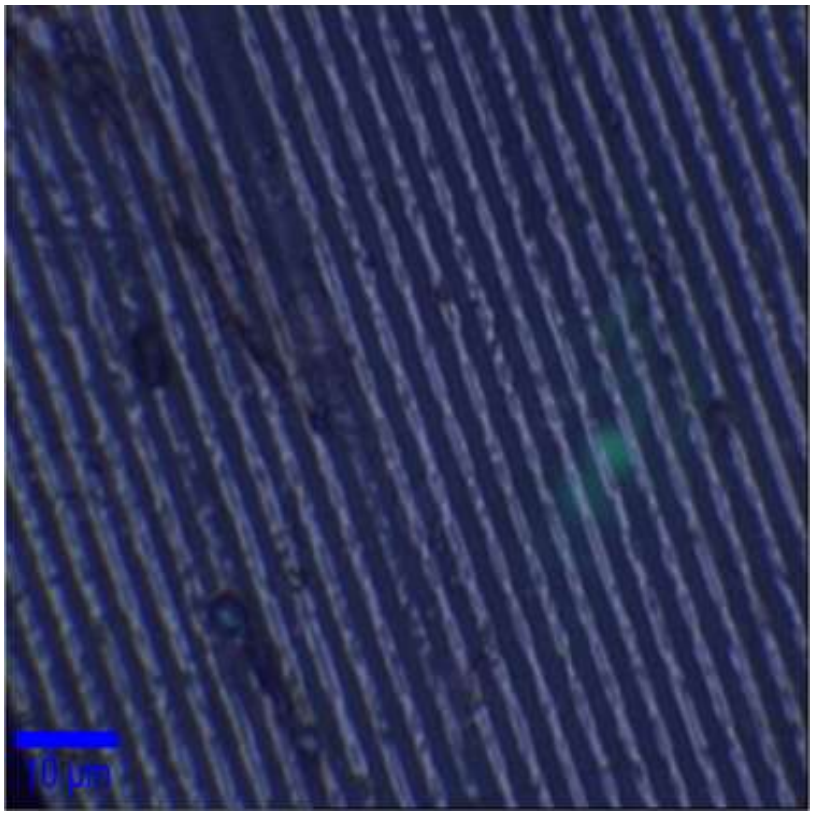

Fig. S18 Confocal Raman image of rectangle microstripes

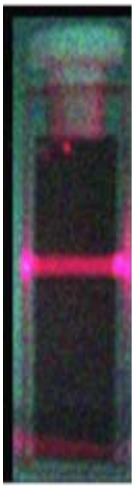

Fig. S19 Tyndall effect of L4 solution

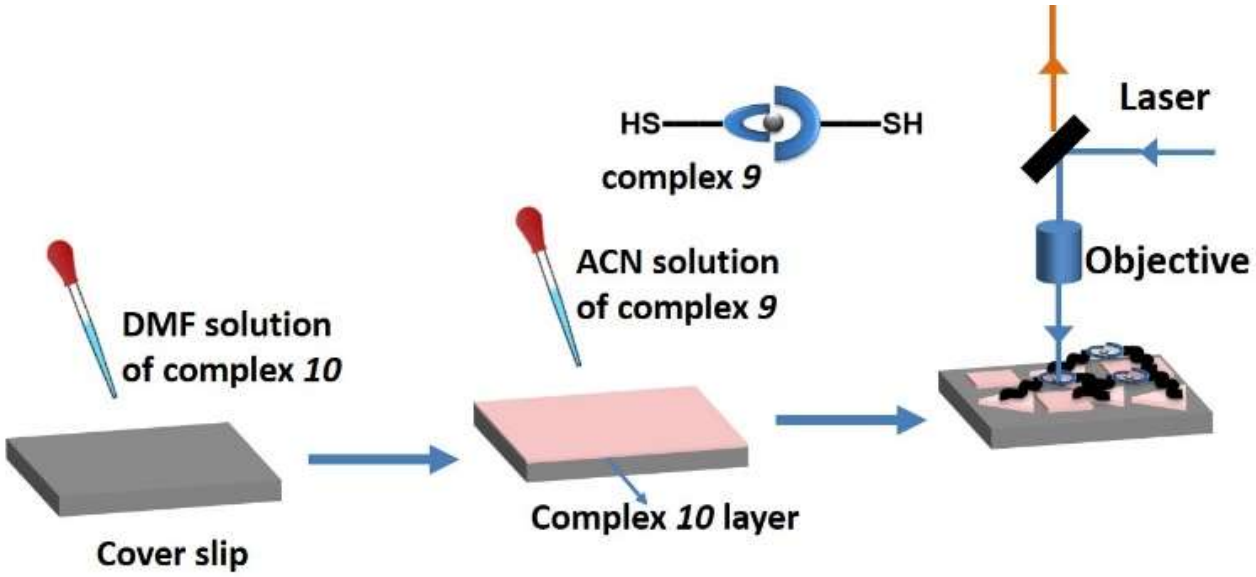

Fig. S20: Graphical representation of preparation of anlyte for SERS experiment.