

Time and Concentration-Dependent Reactivity of Cys, Hcy and GSH on the Diels-Alder-Grafted 1,3,5-Tris Conjugate of Calix[6]arene To Bring Selectivity for Cys: Spectroscopy and Microscopy, and Its Reactivity in Cells

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SI01. Characterization of P₁	2
SI02. Characterization of P₂	3
SI03. Characterization of P₃	5
SI04. Characterization of P₄	6
SI05. Characterization of L₁	8
SI06. Fluorescence studies of L₁ with amino acids	10
SI07. Characterization of P₆	12
SI08. Characterization of P₇	13
SI09. Characterization of P₈	15
SI10. Characterization of P₉	16
SI11. Characterization of P₁₀	18
SI12. Characterization of L₂	19
SI13. Parametric details of the 2D NMR experiments carried out with P₁₀ and L₂	21
SI14. Fluorescence studies of L₂ with amino acids	22
SI 15. SEM images of L₂ with GSH	23

SI01. Characterization of P₁:

CPR-3-SV-279-1H.1.1.1r
CPR-3-SV-279-1H

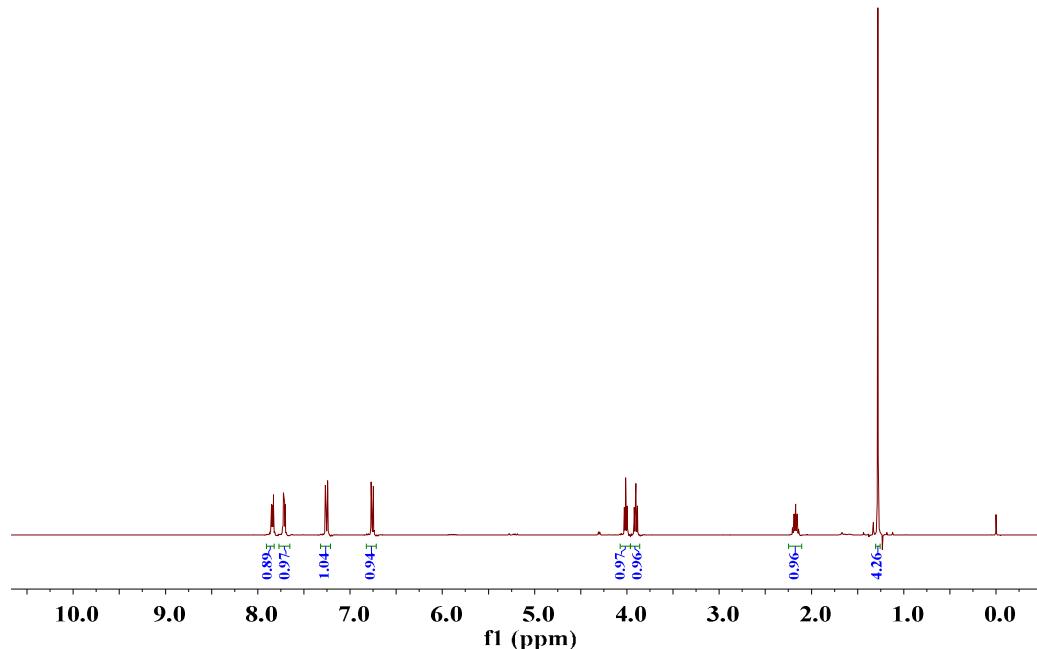


Figure S01. ¹H NMR spectrum (CDCl₃, 400 MHz) of P₁.

CPR-3-SV-315-13C.2.1.1r
CPR-3-SV-315-13C

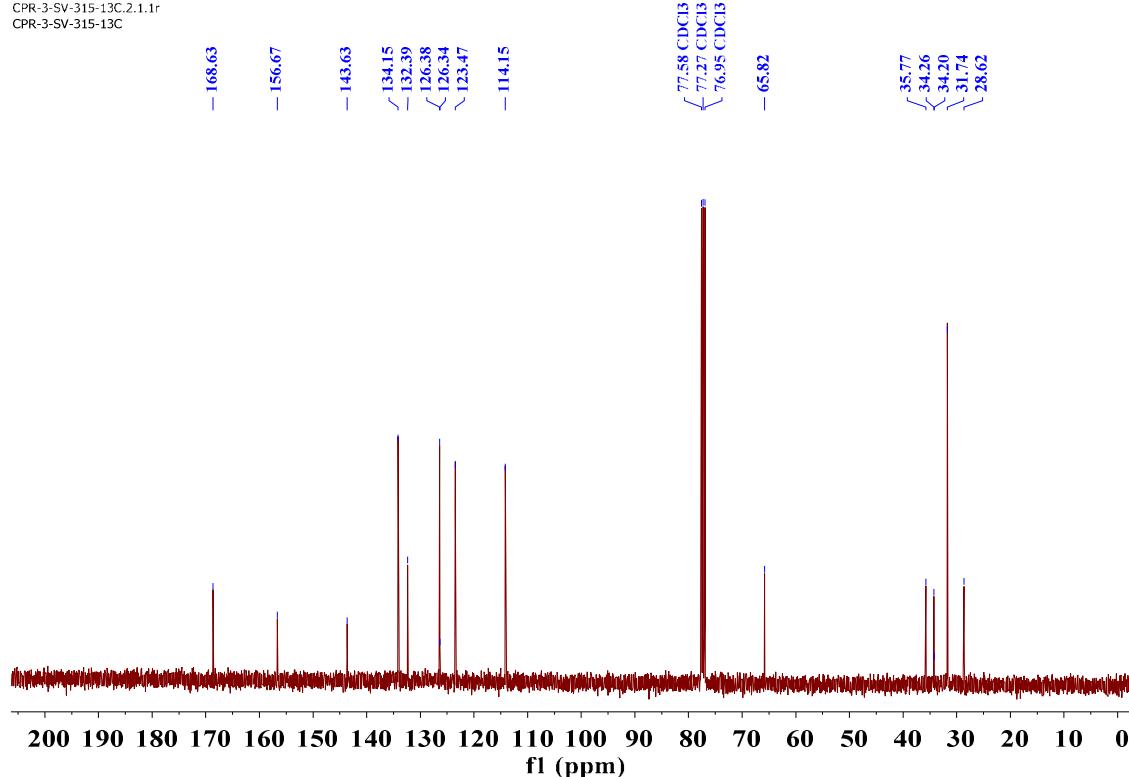


Figure S02. ¹³C NMR spectrum (CDCl₃, 100 MHz) of P₁

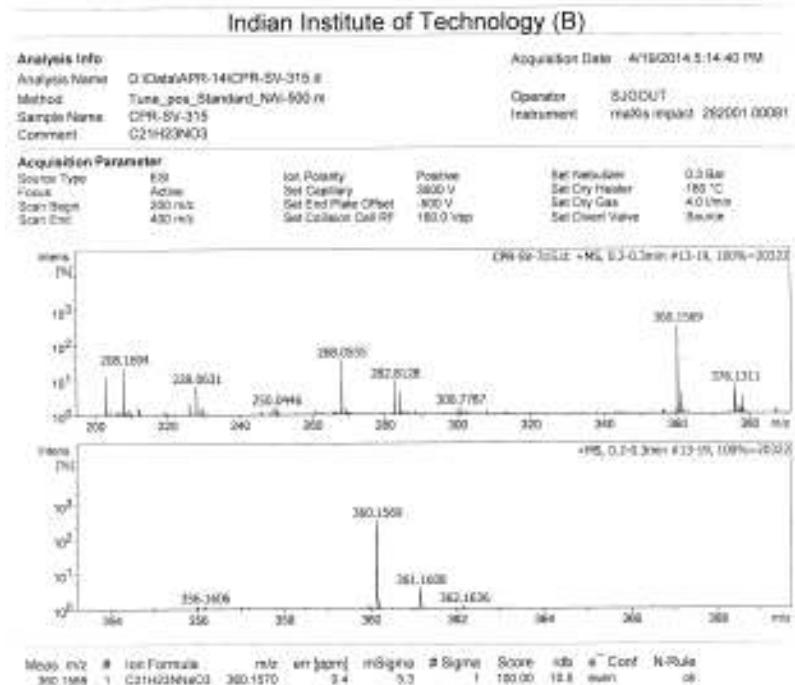


Figure S03. HRMS spectrum of **P₁**.

SI02. Characterization of **P₂**:

CPR-3-SV-DPROTE-1H.1.1.1r
CPR-3-SV-DPROTE-1H

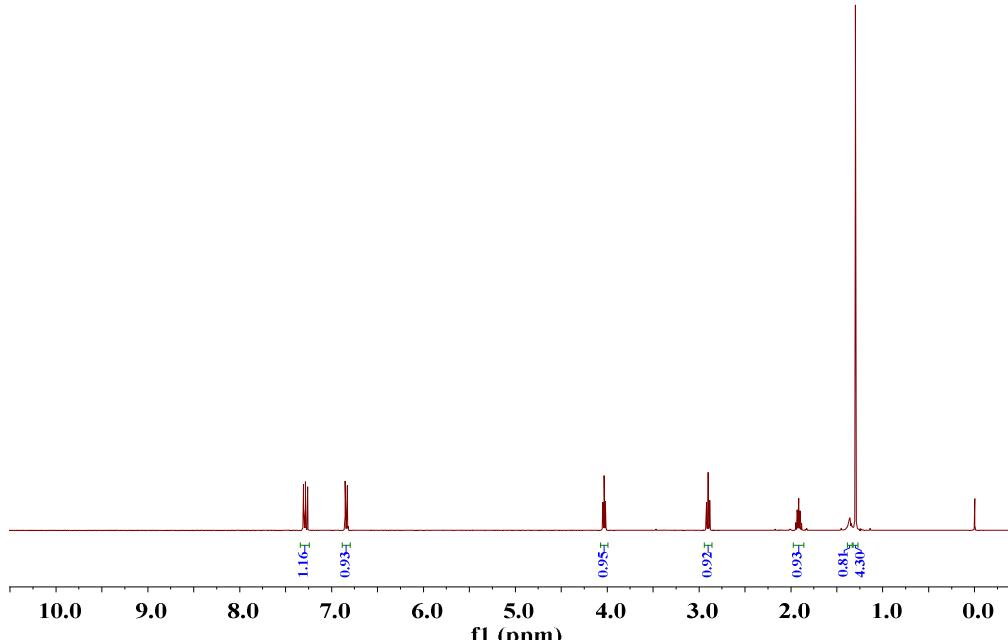


Figure S04. ¹H NMR spectrum (CDCl₃, 400 MHz) of **P₂**.

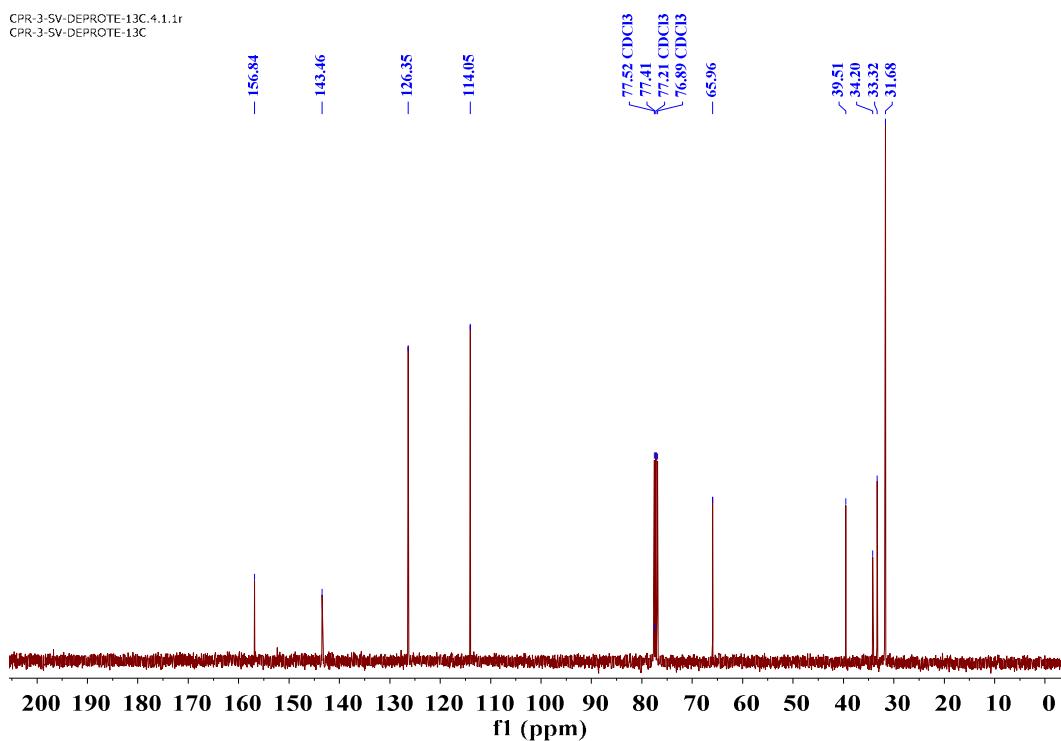


Figure S05. ^{13}C NMR spectrum (CDCl_3 , 100 MHz) of \textbf{P}_2 .



Figure S06. HRMS spectrum of \textbf{P}_2 .

SI03. Characterization of P₃

CPR-3-SV-319-1H,2,1,1r
CPR-3-SV-319-1H

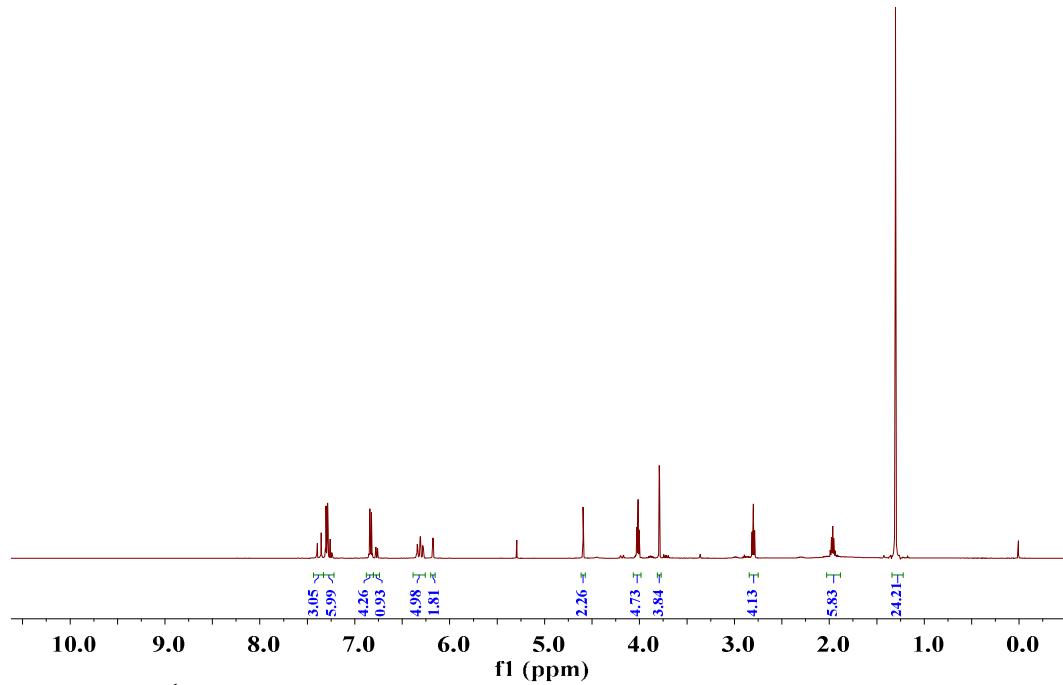


Figure S07. ¹H NMR spectrum (CDCl₃, 400 MHz) of P₃.

CPR-3-SV-319-13C,3.1.1r
CPR-3-SV-319-13C

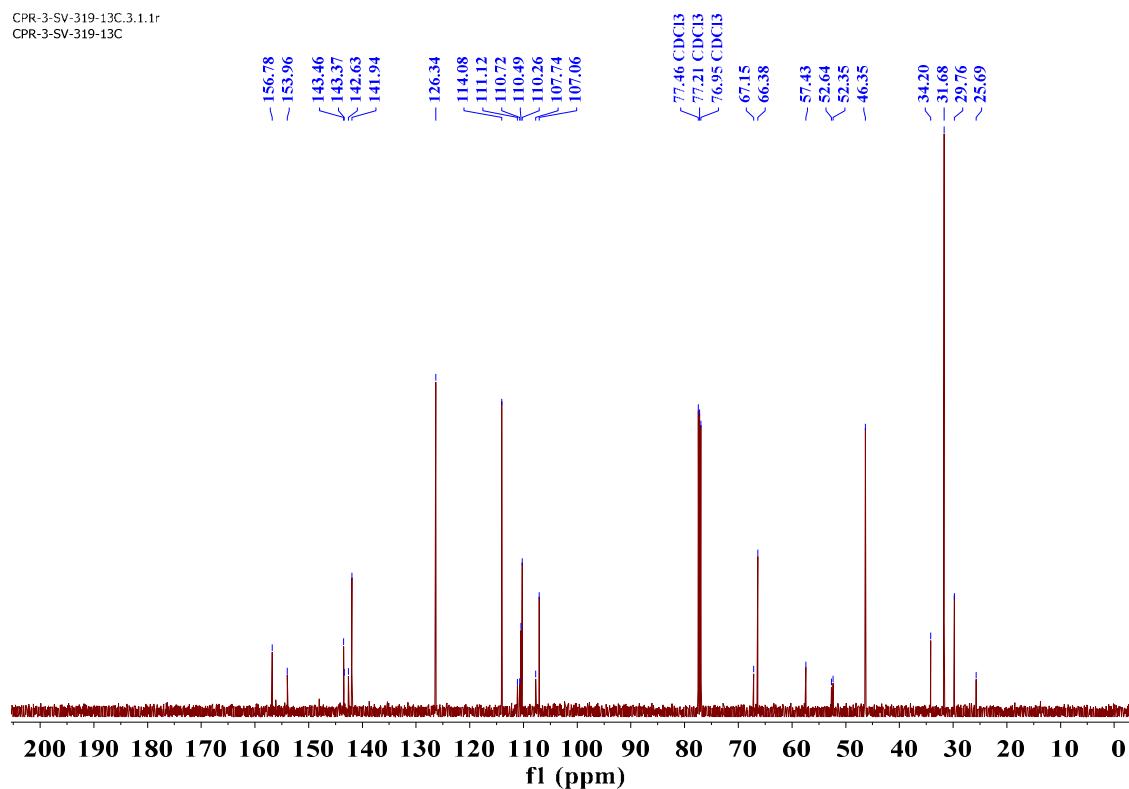


Figure S08. ¹³C NMR spectrum (CDCl₃, 100 MHz) of P₃.

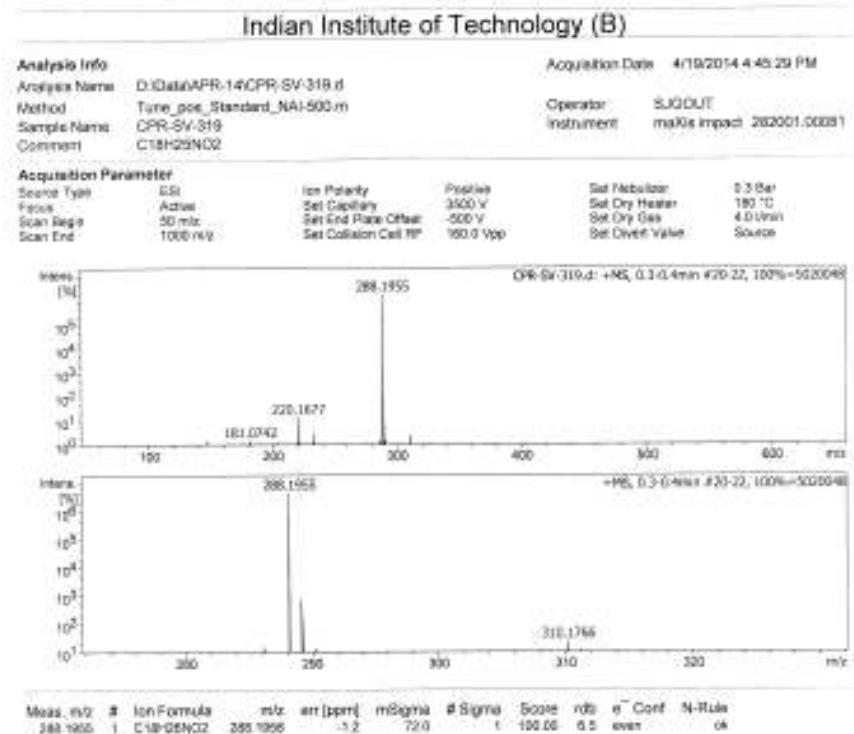


Figure S09. HRMS spectrum of P₃.

SI04. Characterization of P₄

pdata1
CPR-3-SV-285-1H

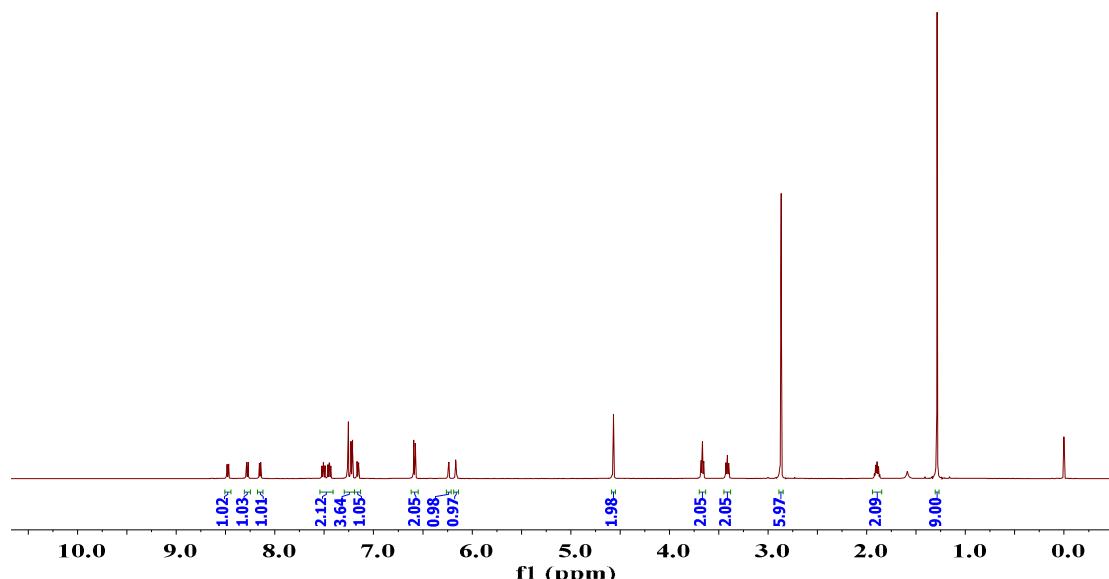


Figure S10. ¹H NMR spectrum (CDCl₃, 400 MHz) of P₄.

CPR-3-SV-285-13C.4.1.1r
CPR-3-SV-285-13C

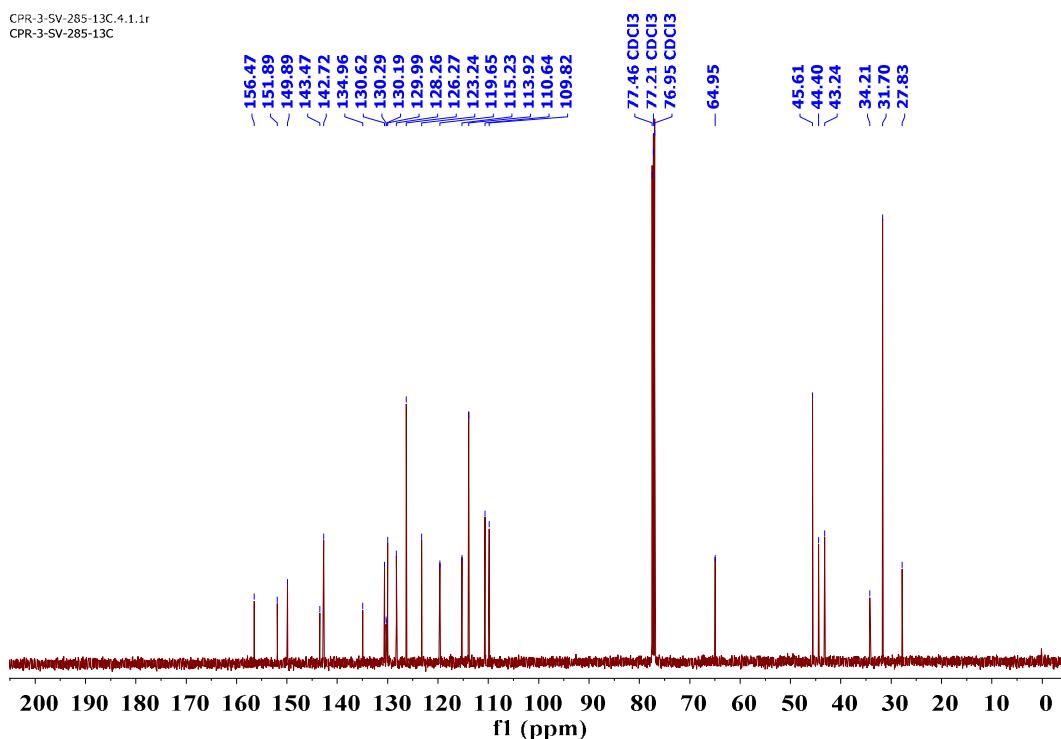


Figure S11. ¹³C NMR spectrum (CDCl₃, 100 MHz) of P₄.

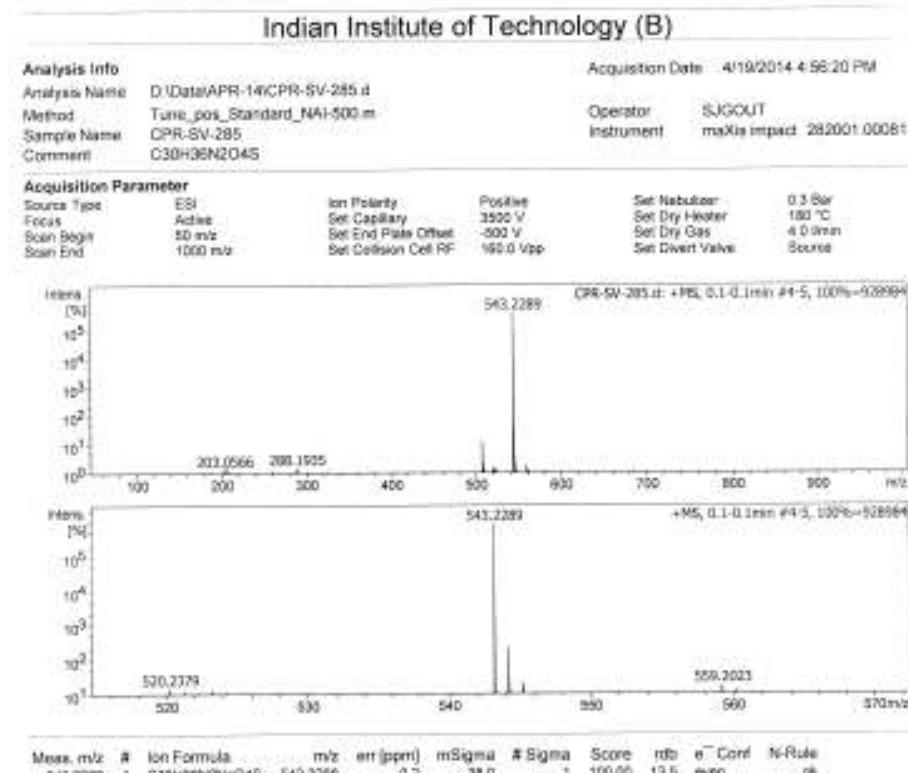


Figure S12. HRMS spectrum of P₄.

SI05. Characterization of L₁

CPR-3-SV-289-1H.2.1.1r
CPR-3-SV-289-1H

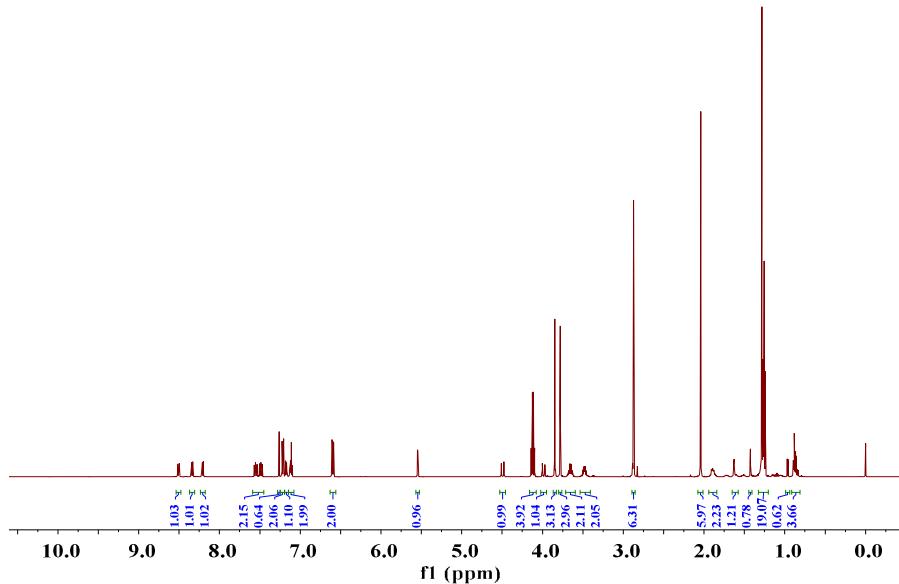


Figure S13. ¹H NMR spectrum (CDCl₃, 400 MHz) of L₁.

CPR-3-SV-289-13C.5.1.1r
CPR-3-SV-289-13C

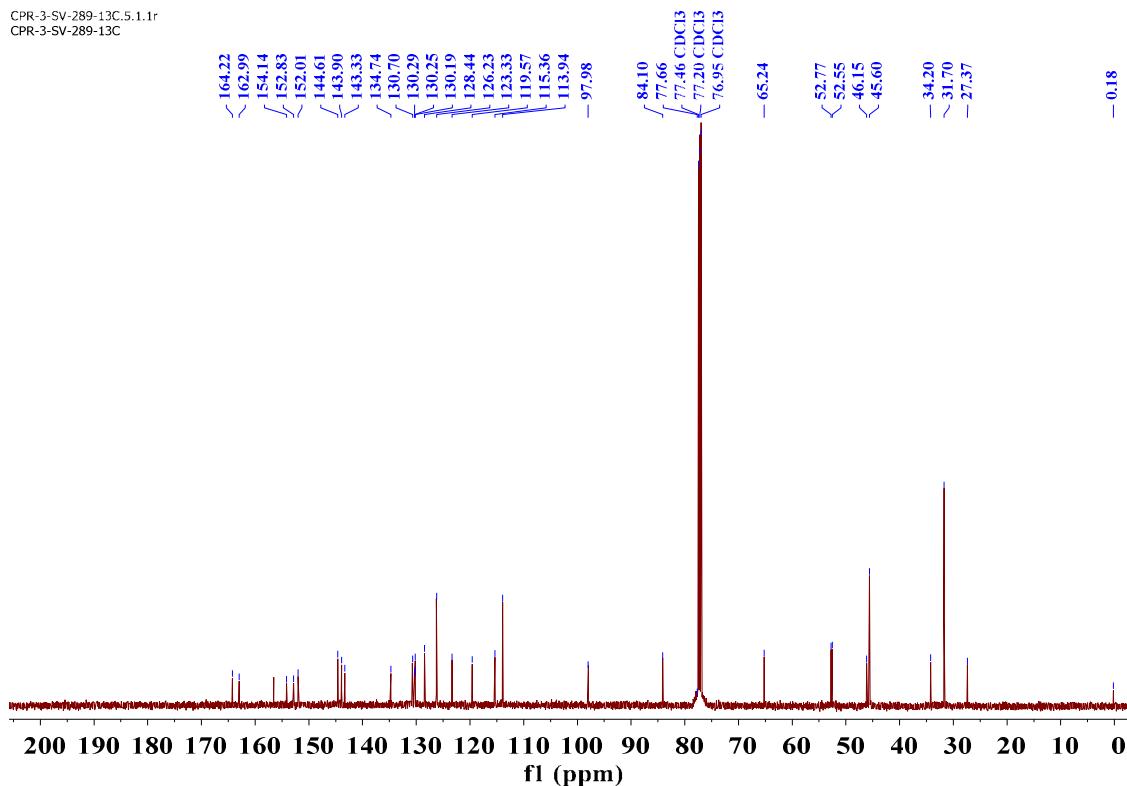


Figure S14. ¹³C NMR spectrum (CDCl₃, 125 MHz) of L₁

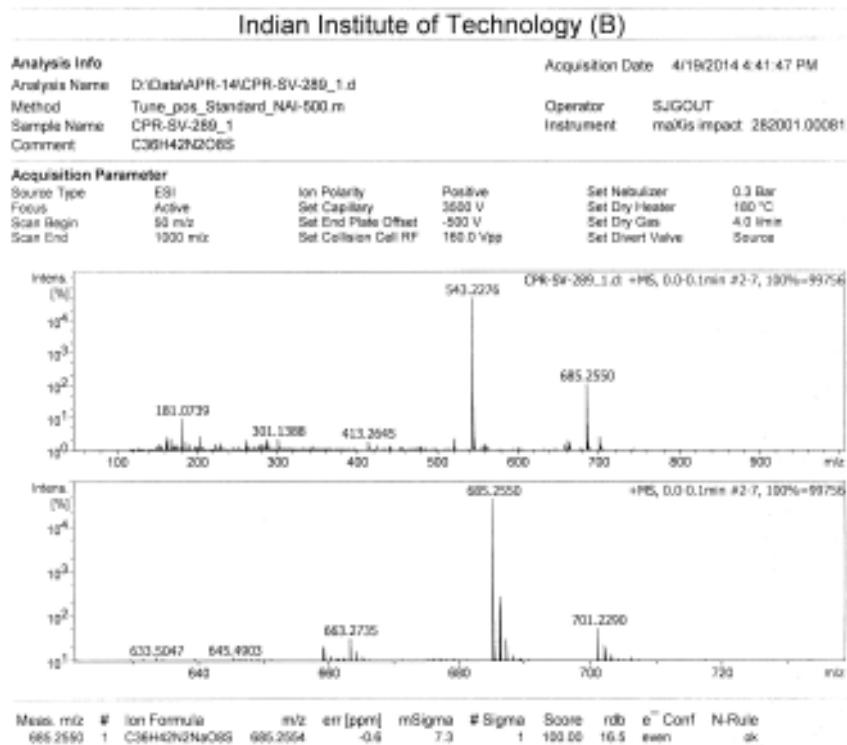
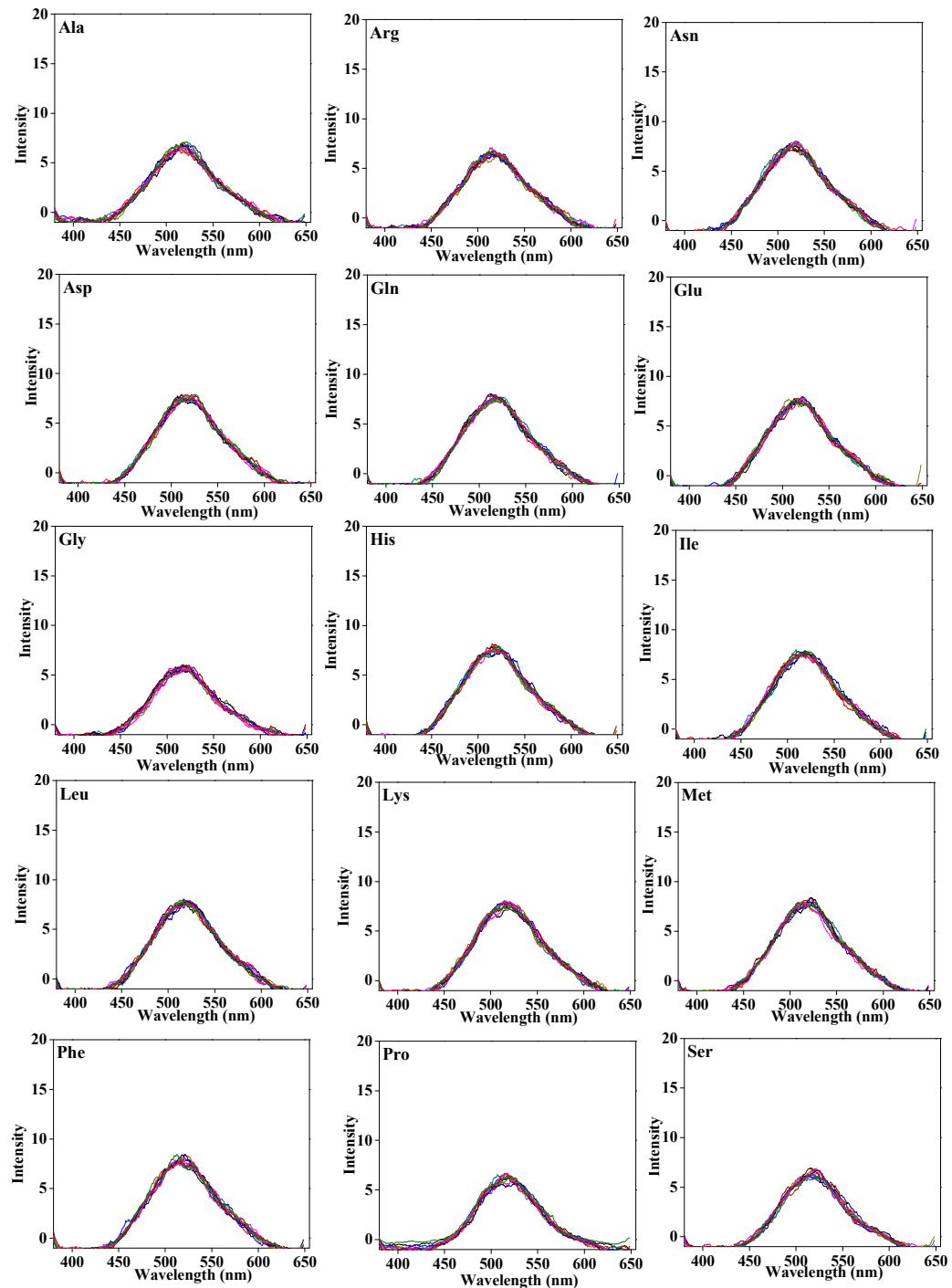


Figure S15. HRMS spectrum of L₁.

SI06. Fluorescence studies of L₁ with amino acids



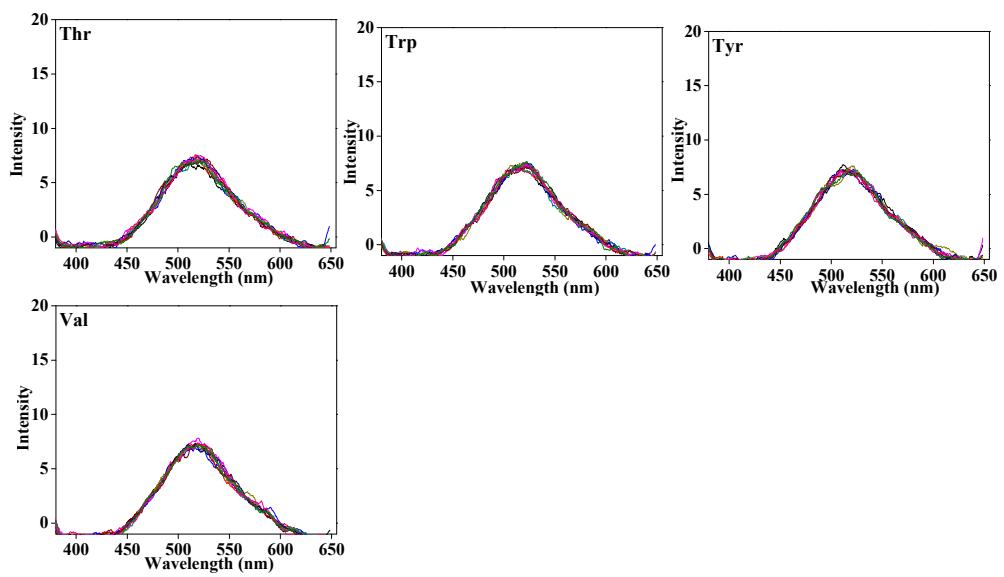


Figure S16. Fluorescence titration studies of **L** with amino acids.

SI07. Characterization of P₆

pdata/1
CPR-3-SV-TOCH3-1H

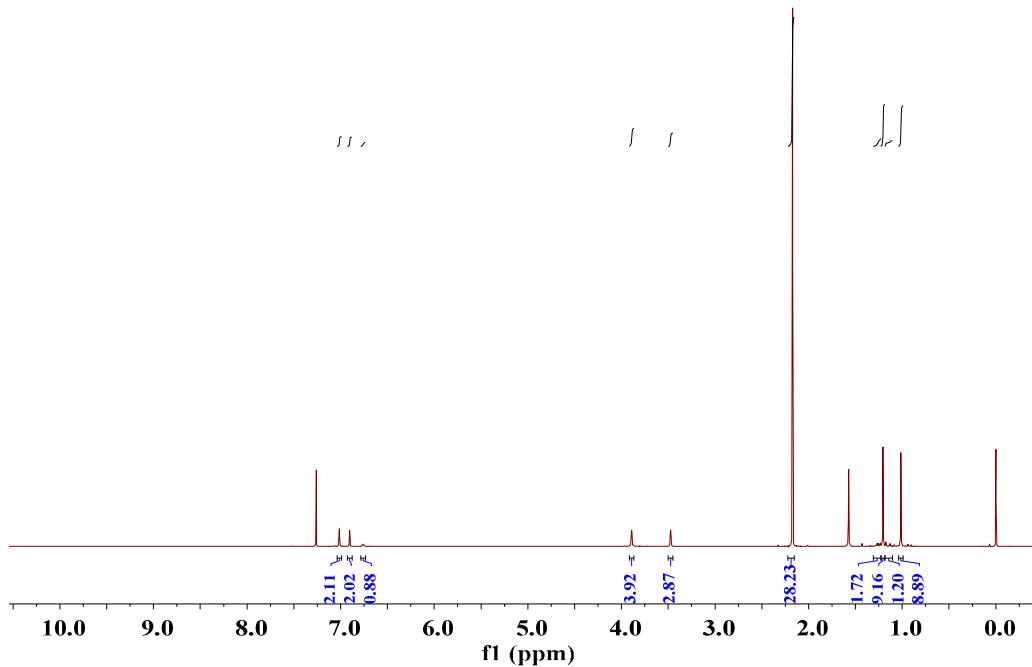


Figure S17. ¹H NMR spectrum (CDCl_3 , 400 MHz) of P₆.

pdata/1
CPR-3-SV-TOMe-13C

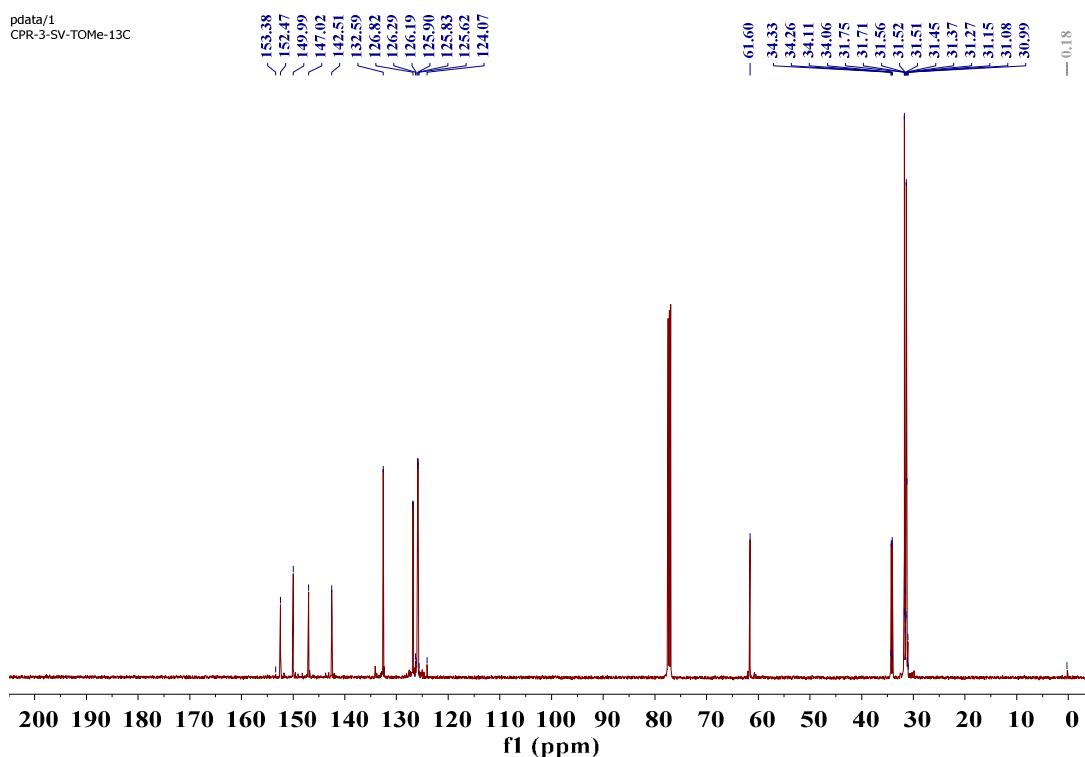


Figure S18. ¹³C NMR spectrum (CDCl_3 , 125 MHz) of P₆.

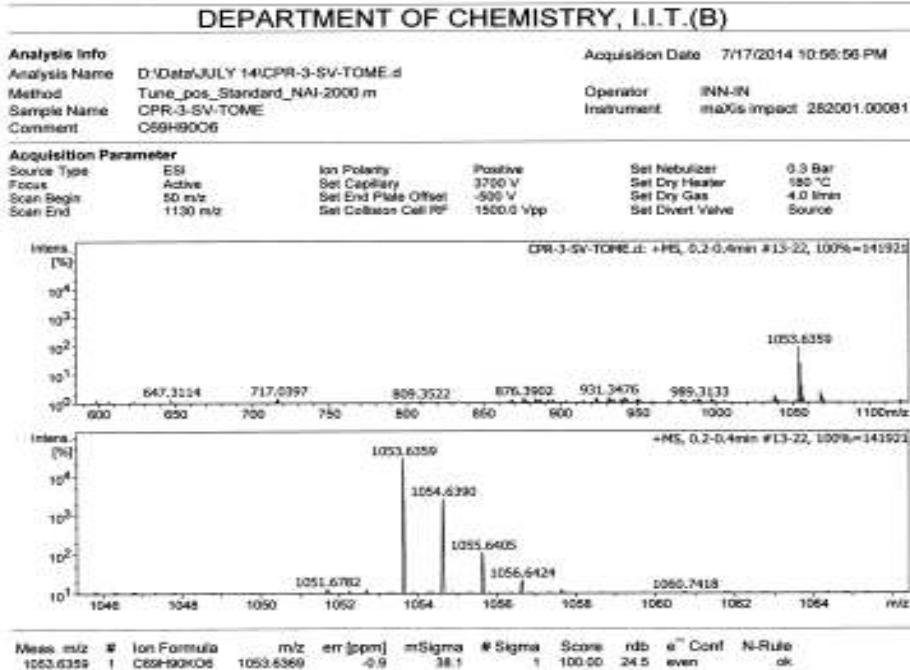


Figure S19. HRMS spectrum of **P₆**.

SI08. Characterization of P₇

CPR-3-SV-135-1H.6.1.1r
CPR-3-SV-135-1H

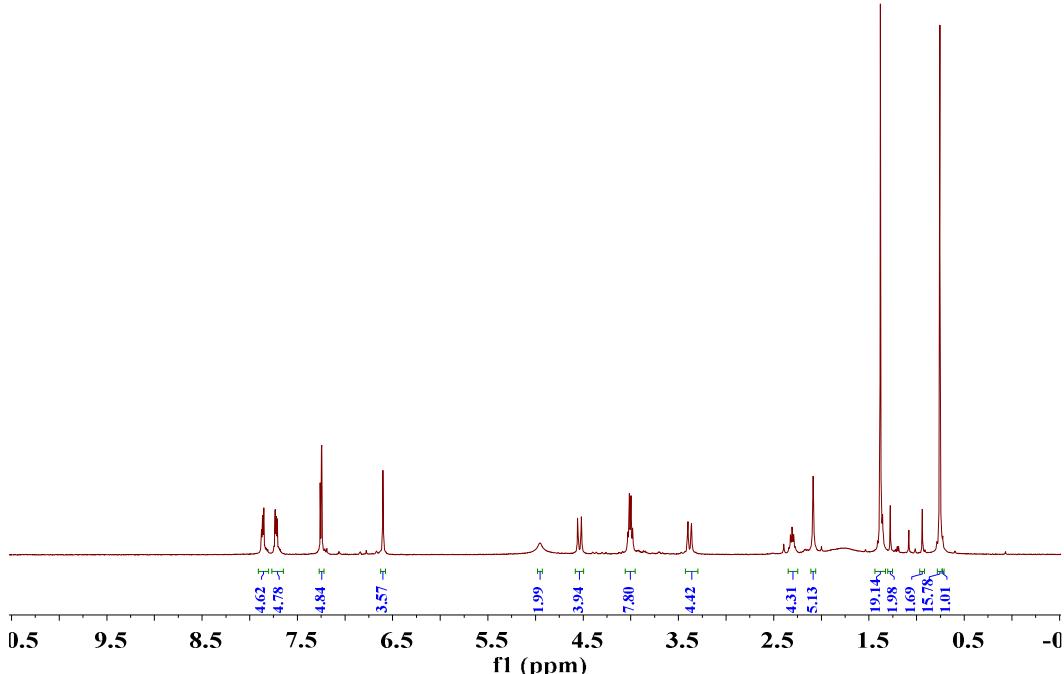


Figure S20. ¹H NMR spectrum (CDCl₃, 400 MHz) of **P₇**.

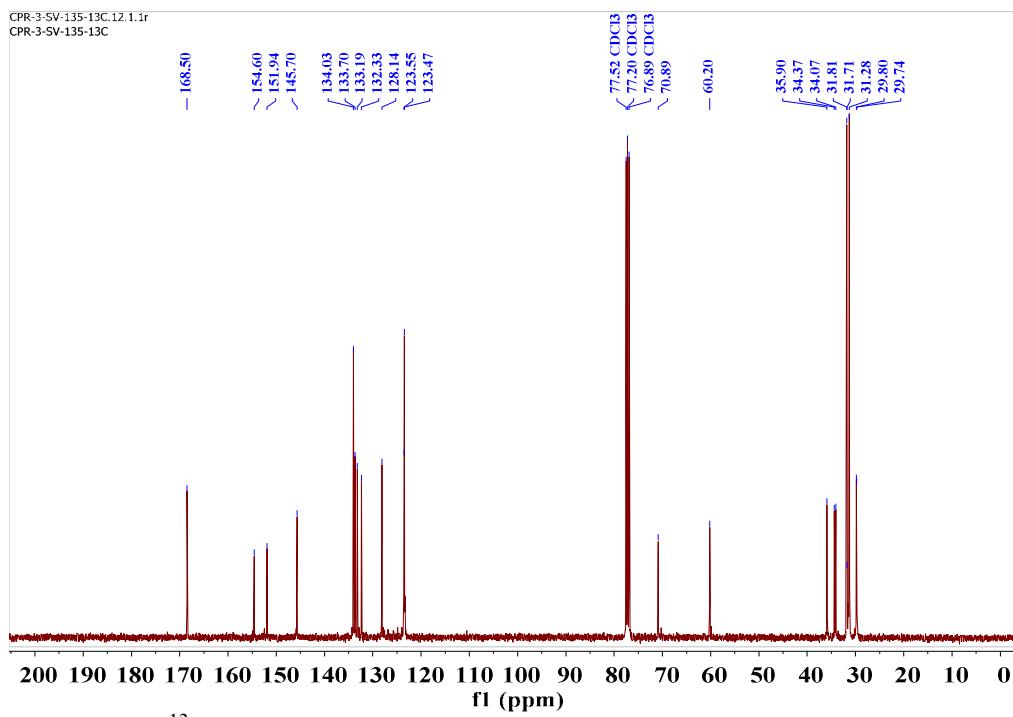


Figure S21. ^{13}C NMR spectrum (CDCl_3 , 100 MHz) of P_7

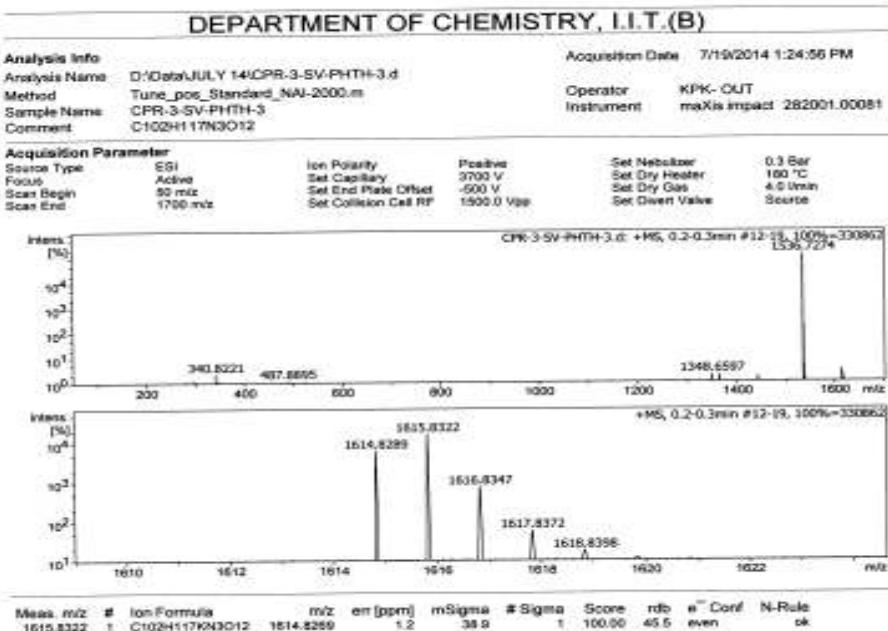


Figure S22. HRMS spectrum of P_7 .

SI9. Characterization of P₈

CPR-3-SV-148-1H.17.1.1r
CPR-3-SV-148-1H

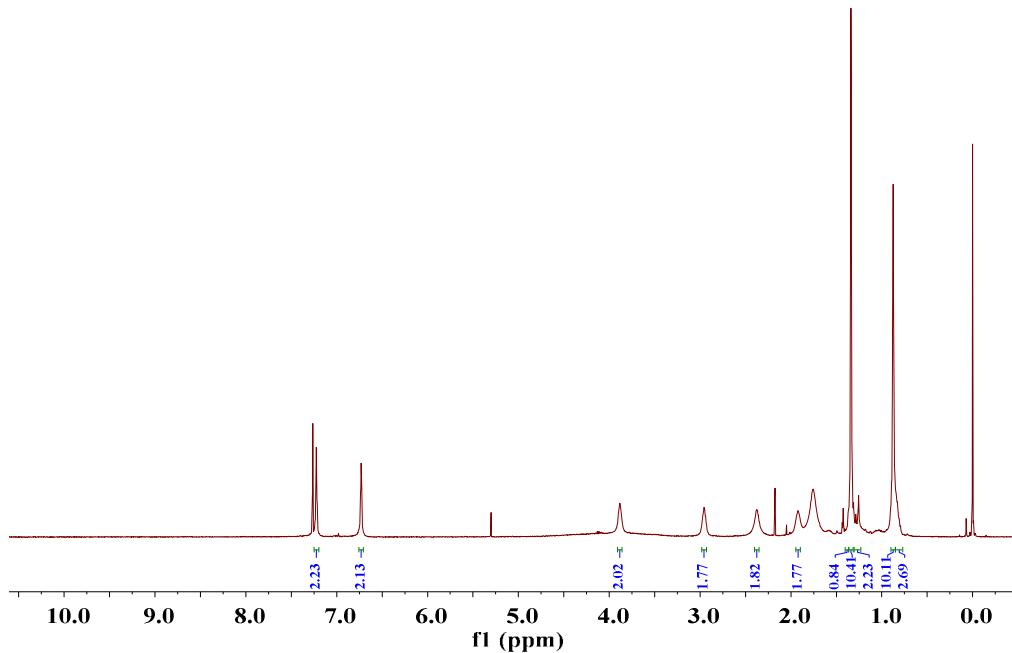


Figure S23. ¹H NMR spectrum (CDCl₃, 400 MHz) of P₈.

CPR-3-SV-148-13C.12.1.1r
CPR-3-SV-148-13C

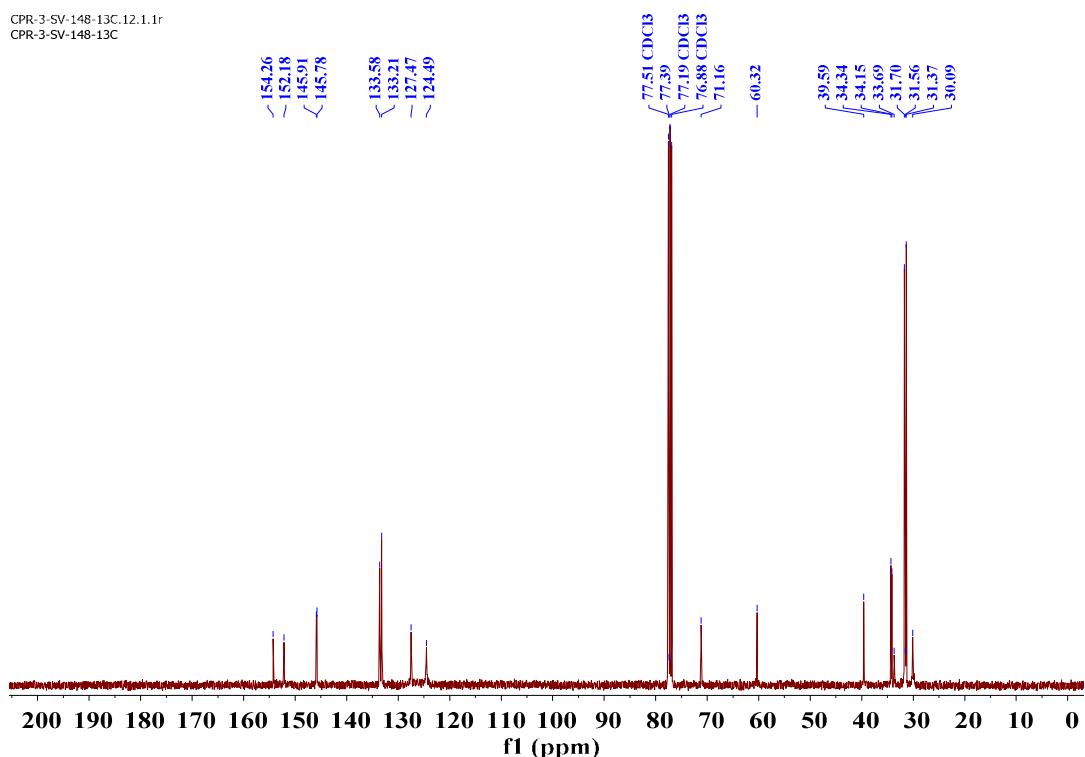


Figure S24. ¹³C NMR spectrum (CDCl₃, 100 MHz) of P₈.

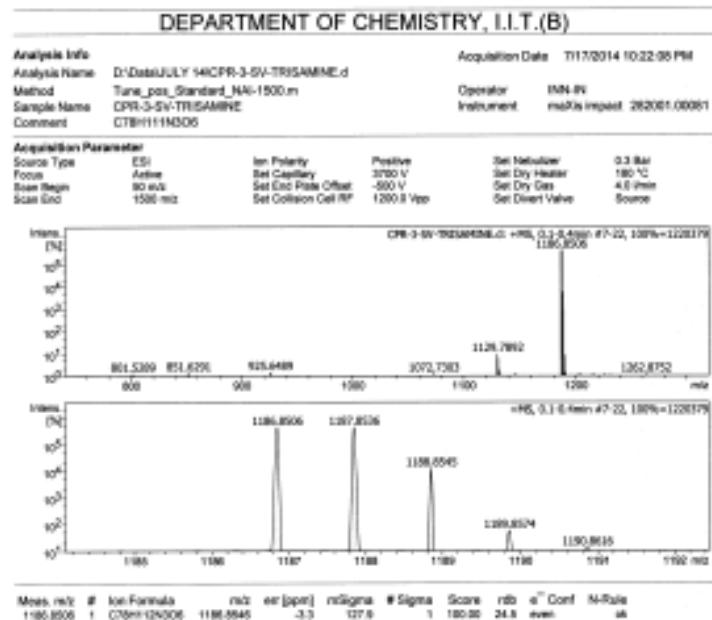


Figure S25. HRMS spectrum of **P₈**.

SI10. Characterization of **P₉**

CPR-3-SV-153-1-1H.5.1.1r
CPR-3-SV-153-1-1H

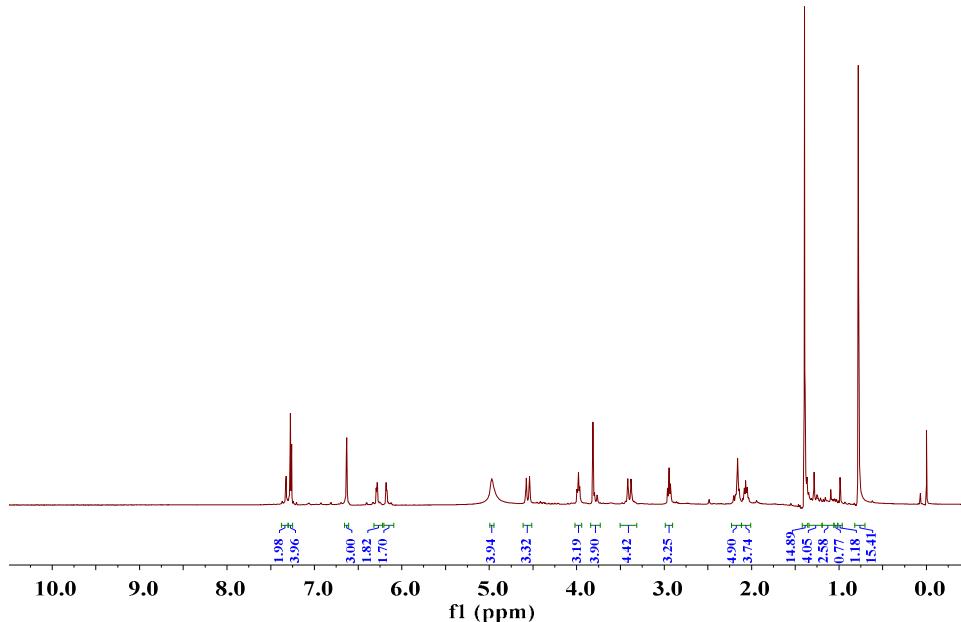


Figure S26. ¹H NMR spectrum (CDCl₃, 400 MHz) of **P₉**.

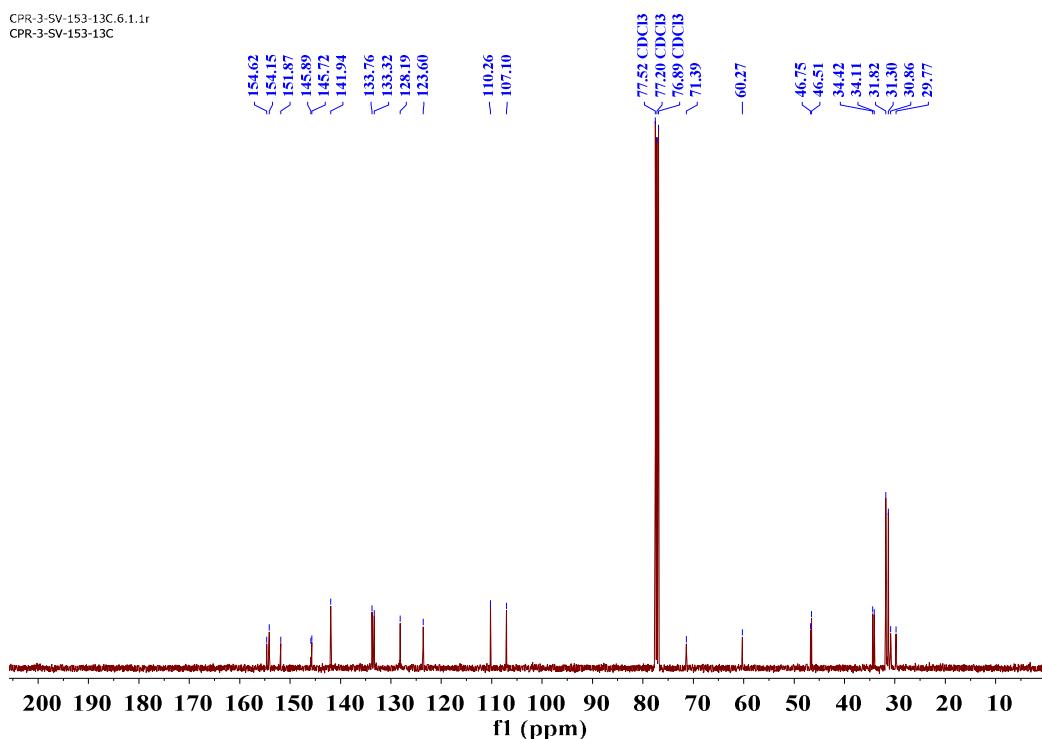


Figure S27. ^{13}C NMR spectrum (CDCl_3 , 100 MHz) of \textbf{P}_9 .

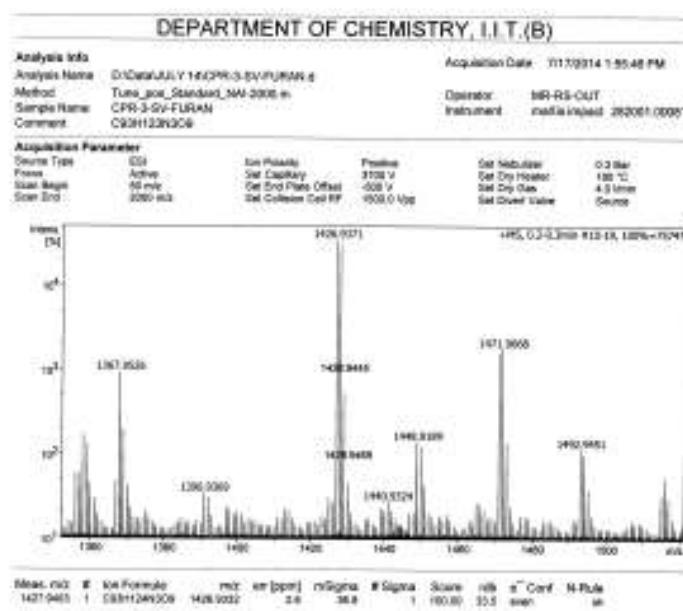


Figure S28. HRMS spectrum of \textbf{P}_9 .

SI11. Characterization of P₁₀

CPR-3-SV-263-1H.1.1.1r
CPR-3-SV-263-1H

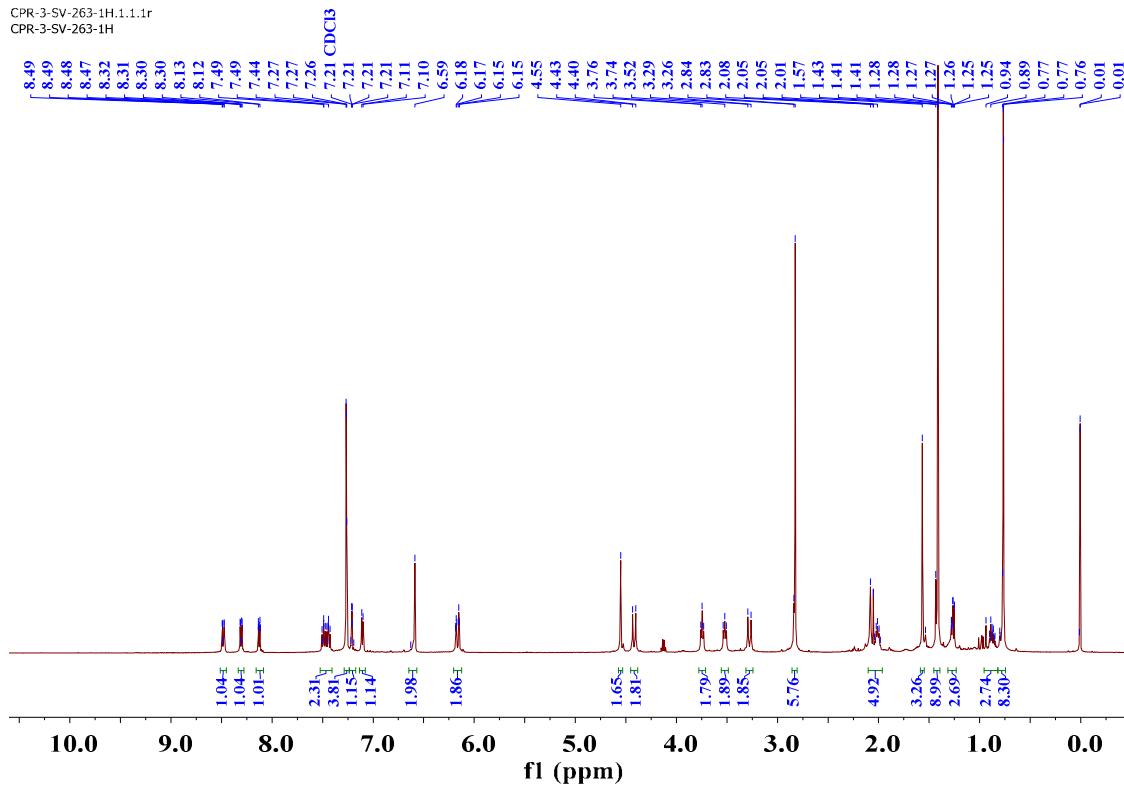


Figure S29. ^1H NMR spectrum (CDCl_3 , 500 MHz) of **P₁₀**.

CPR-3-SV-154-13C

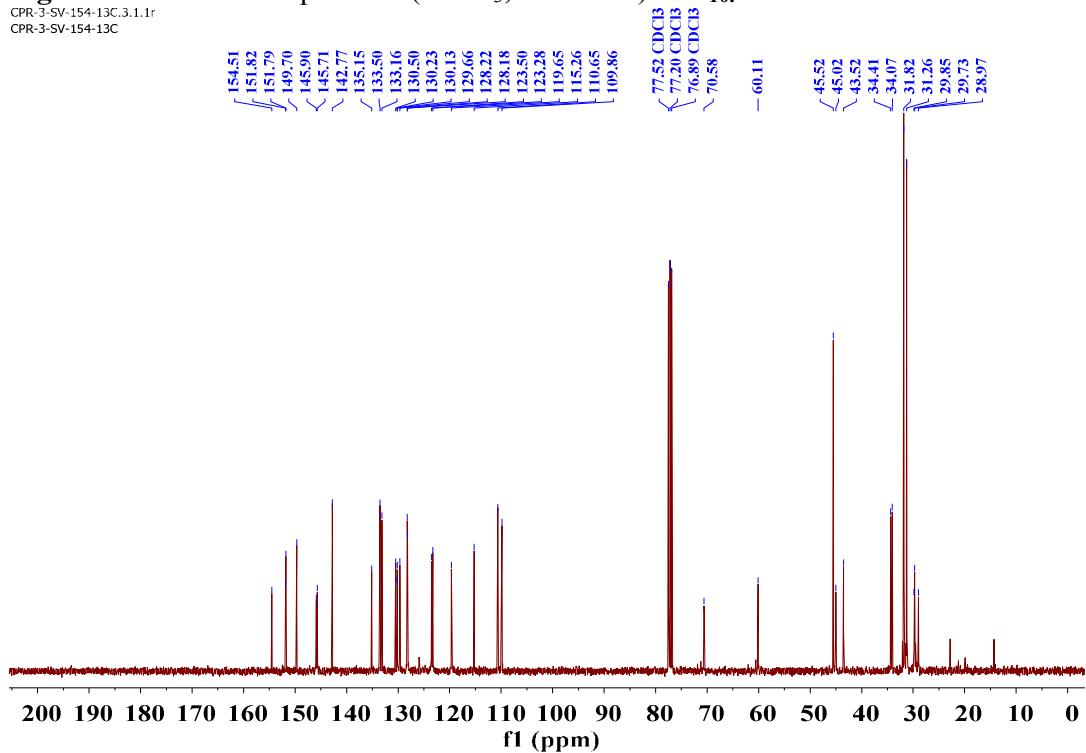


Figure S30. ^{13}C NMR spectrum (CDCl_3 , 125 MHz) of **P₁₀**.

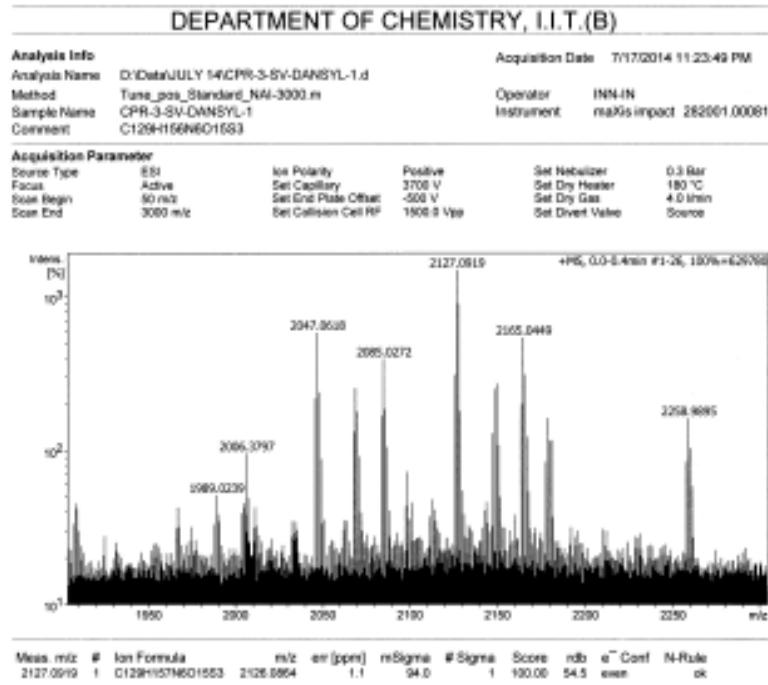


Figure S31. HRMS spectrum of \mathbf{P}_{10} .

SI12. Characterization of \mathbf{L}_2

CPR-3-SV-265-1H.3.1.1r
 CPR-3-SV-265-1H

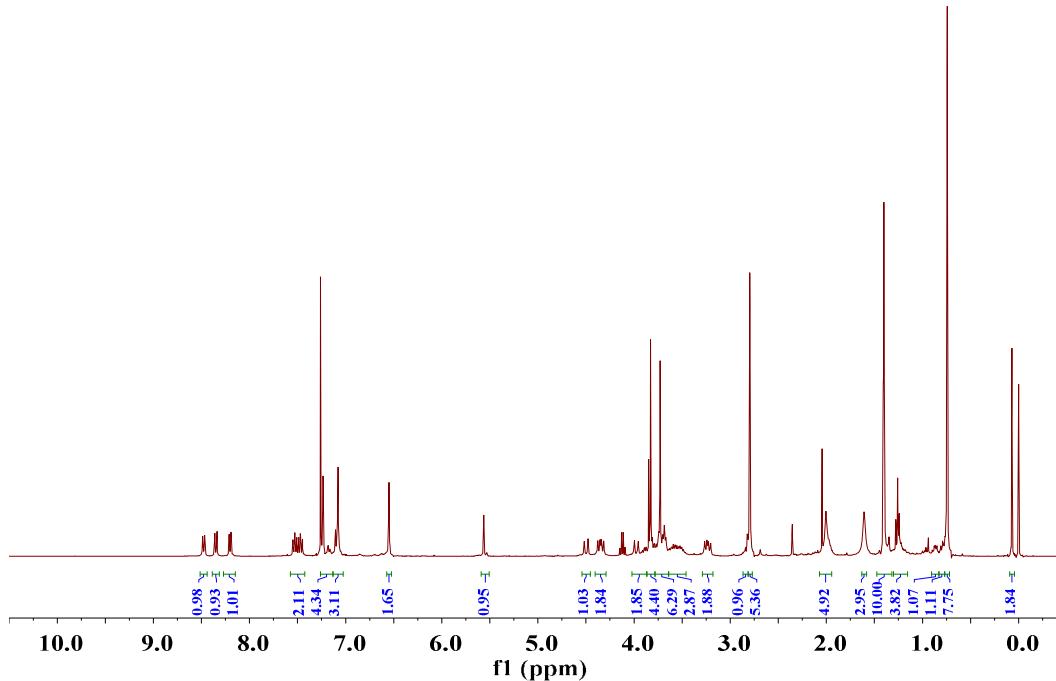


Figure S32. ^1H NMR spectrum (CDCl_3 , 400 MHz) of \mathbf{L}_2 .

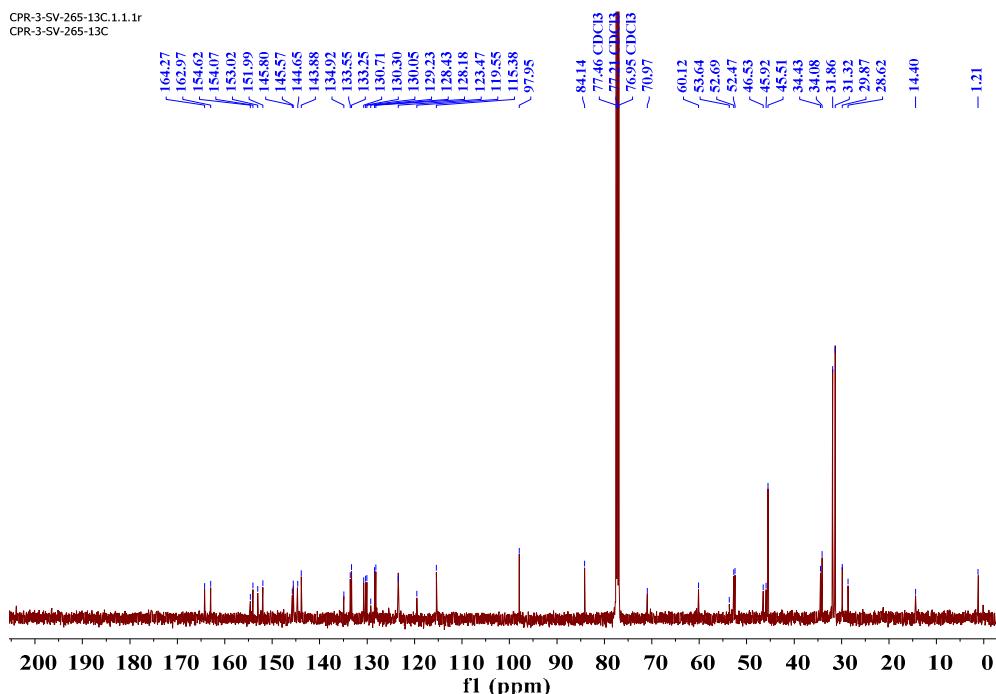


Figure S33. ^{13}C NMR spectrum (CDCl_3 , 100 MHz) of L_2 .

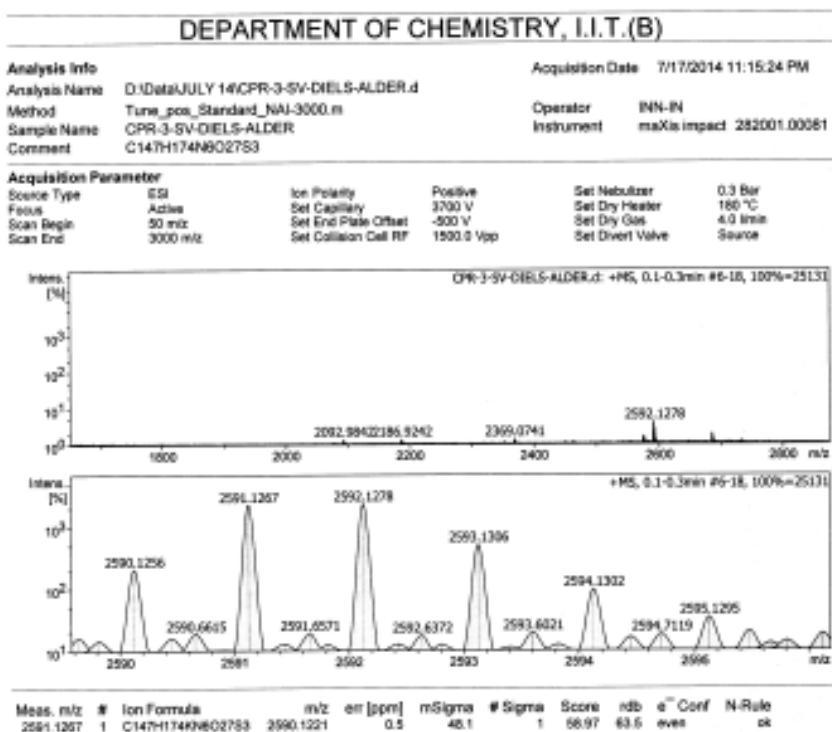


Figure S34. HRMS spectrum of L_2 .

SI13. Parametric details of the 2D NMR experiments carried out with P_{10} and L_2

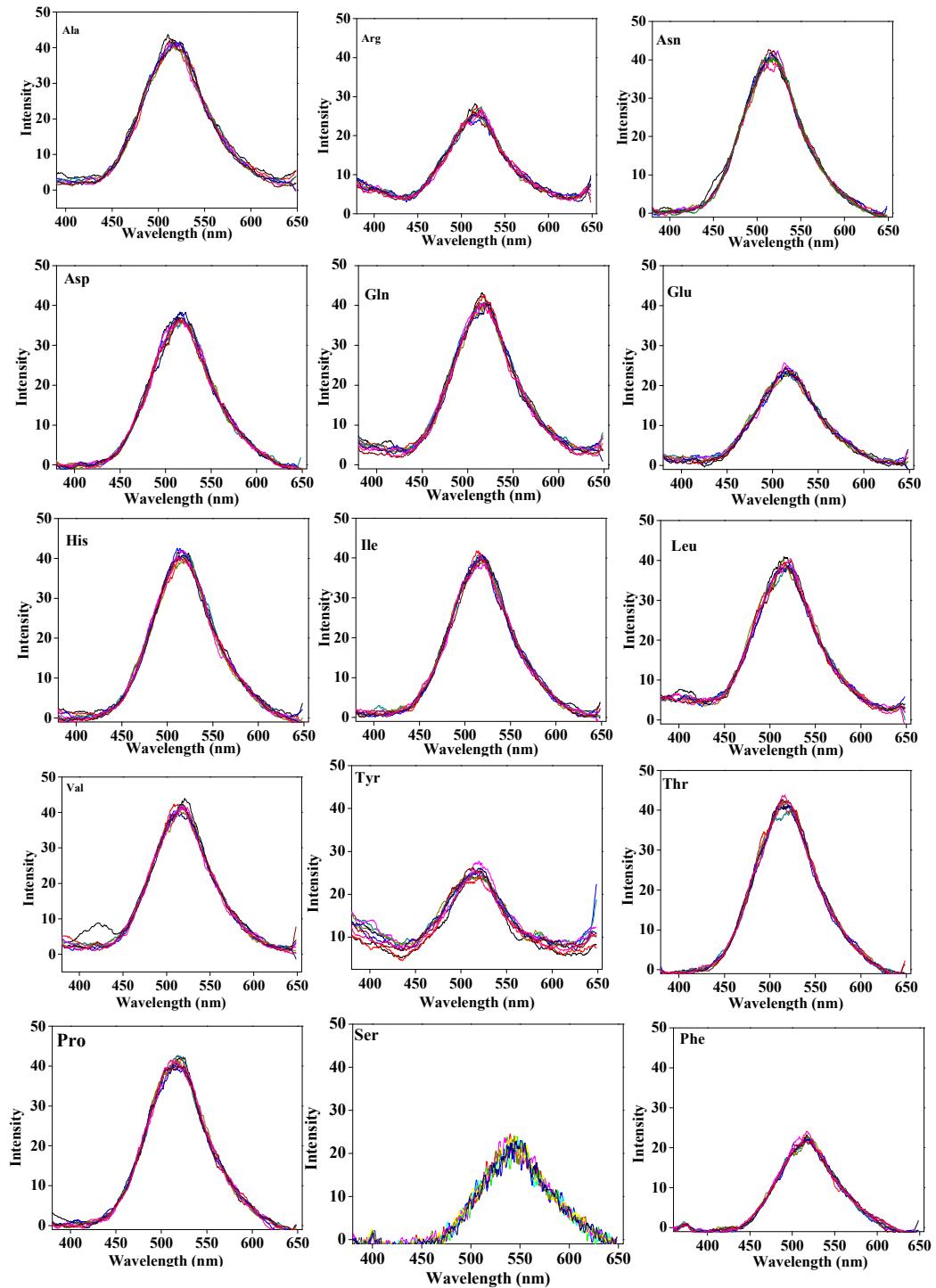
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Date_     20140904                     PROCNO   1
Time_     9.31
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PROBHD  5 mm PABBO BB/
PULPROG  cosyppgf
TD       2048
SOLVENT  CDC13
NS      16
DS      16
SWH    3881.988 Hz
FIDRES  0.2638324 sec
AQ      90.5
RG      1.895502 Hz
DW      128.800 usec
DE      6.50 usec
TE      295.7 K
D0      0.00000300 sec
D1      1.00000000 sec
D13     0.00000400 sec
D16     0.00020000 sec
IN0      0.00025760 sec
F2 - Acquisition Parameters
Date_   20131002
Time_   14.29
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG noesyppph
TD       2048
SOLVENT CDC13
NS      16
DS      32
SWH    3759.398 Hz
FIDRES 2.164367 Hz
AQ      0.2723840 sec
RG      61.42
DW      112.800 usec
DE      6.50 usec
TE      295.7 K
D0      0.00000300 sec
D1      1.00000000 sec
D13     0.30000001 sec
D16     0.00020000 sec
IN0      0.00026580 sec
F2 - Acquisition Parameters
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PULPROG cosyppppf
TD       2048
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NS      16
DS      8
SWH    4432.624 Hz
FIDRES 2.164367 Hz
AQ      0.2723840 sec
RG      197.27
DW      112.800 usec
DE      6.50 usec
TE      295.7 K
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D13     0.00000400 sec
D16     0.00020000 sec
IN0      0.0002560 sec
F2 - Acquisition Parameters
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PULPROG noesyppph
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DS      32
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AQ      0.2273280 sec
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DE      6.50 usec
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D1      1.0000000 sec
D13     0.30000001 sec
D16     0.00020000 sec
IN0      0.00022200 sec
===== CHANNEL f1 =====
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NUC1    1H
P0      14.75 usec
P1      14.75 usec
PL1     -1.00 dB
PL1W   10.56200695 W
SF01   400.1318998 MHz
===== GRADIENT CHANNEL =====
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GP21    10.00 %
P16     1000.00 usec
P16    1000.00 usec
F1 - Acquisition parameters
TD      230
SFO1   500.133 MHz
TD      230
SFO1   16.357510 Hz
FIDRES 7.522 ppm
SW      8.863 ppm
FnMODE TPII
SW      9.702 ppm
FnMODE QF
SI      2048
SF      400.1300098 MHz
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SSB    0
LB      0.00 Hz
GB      0
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SF      500.1300044 MHz
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WDW    QSINE
SSB    2
LB      0 Hz
GB      0
PC      1.50
F1 - Processing parameters
SI      1024
MC2    QF
SF      500.1300119 MHz
WDW    QSINE
SSB    0
LB      0 Hz
GB      0
PC      1.50
F1 - Processing parameters
SI      1024
MC2    QF
SF      500.1300119 MHz
WDW    QSINE
SSB    2
LB      0 Hz
GB      0
PC      1.50

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Figure S35. 2D NMR details for P_{10} and L_2 (a) & (b) COSY and NOESY for P_{10} ; (c) & (d) COSY and NOESY for L_2 .

SI14. Fluorescence studies of L₂ with amino acids



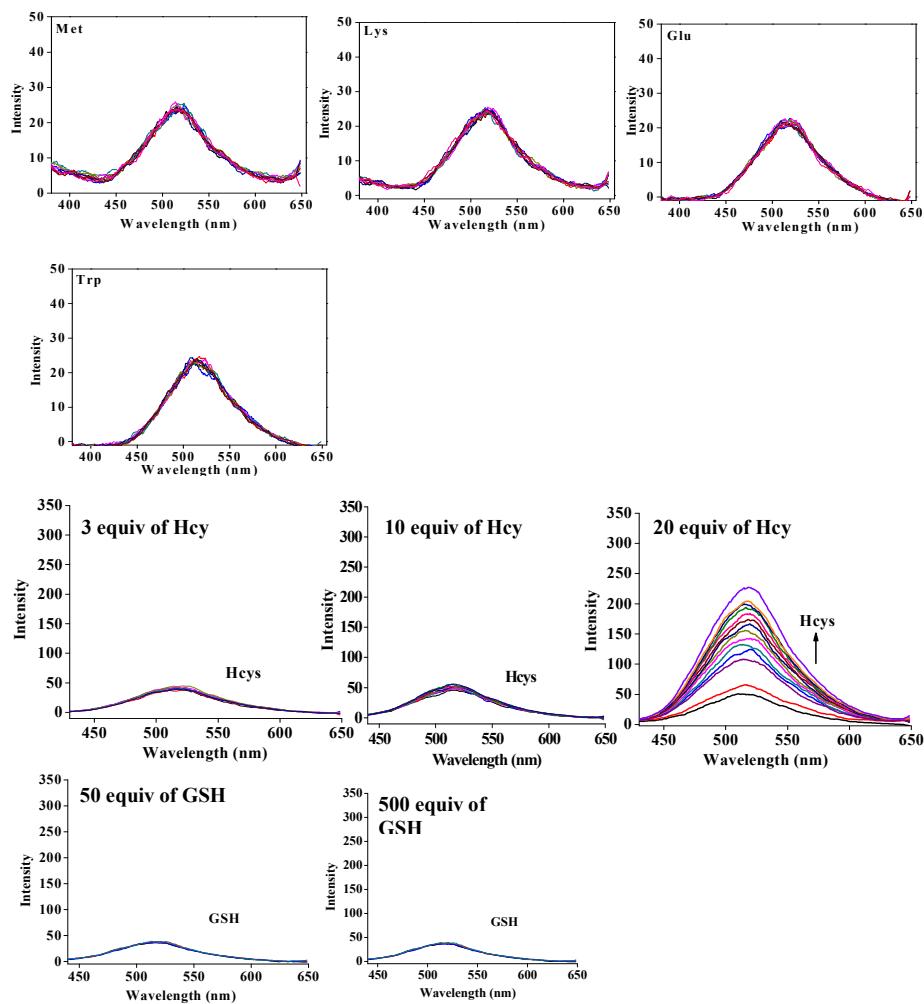


Figure S36. Fluorescence titration studies of \mathbf{L}_2 with amino acids.

SI 15. SEM images of \mathbf{L}_2 with GSH

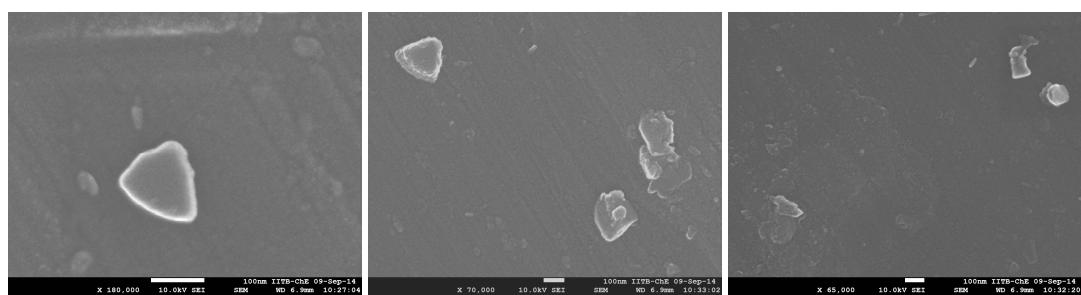


Figure S37. SEM images of \mathbf{L}_2 with the reaction of GSH (1:5).