ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Reactivity of Decafluorobenzophenone and decafluoroazobenzene towards aromatic diamines: a pratical entry to Donor-Acceptor systems

Paolo Coghi,*[a], Antonio Papagni,*[a] Riccardo Po,[b] Anna Calabrese,[b] Alessandra Tacca,[b] and Alberto Savoini [b] and Milda Stuknyte[c]

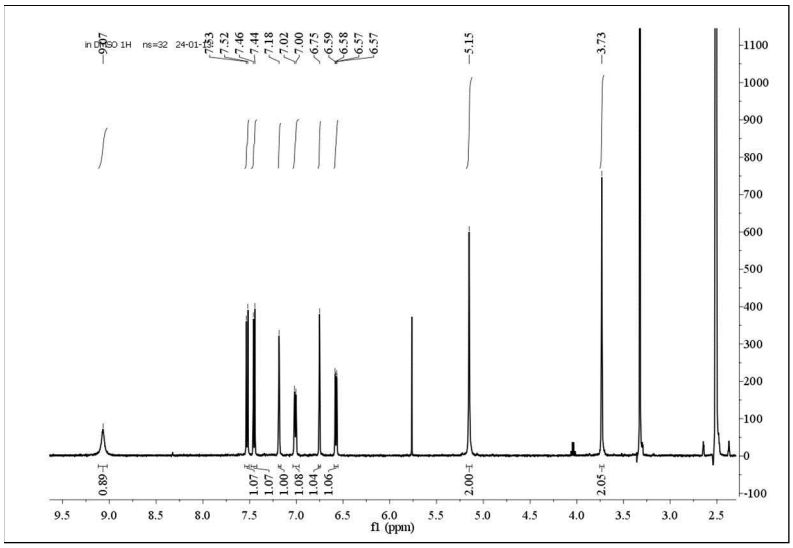
[a] Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Via R.Cozzi, 53 Milano, Italy Fax: +39-0264485400
E-mail: antonio.papagni@mater.unimib.it; paolo.coghi@unimib.it

[b] Centro Ricerche per le Energie non Convenzionali – IstitutoEni Donegani,Eni SpA, Via Fauser 4, 28100 Novara, Italy

[c] Department of Food, Environmental and Nutritional Sciences (DeFENS), Packaging Division, University of Milan, via Celoria, 2 - 20133 Milano, Italy

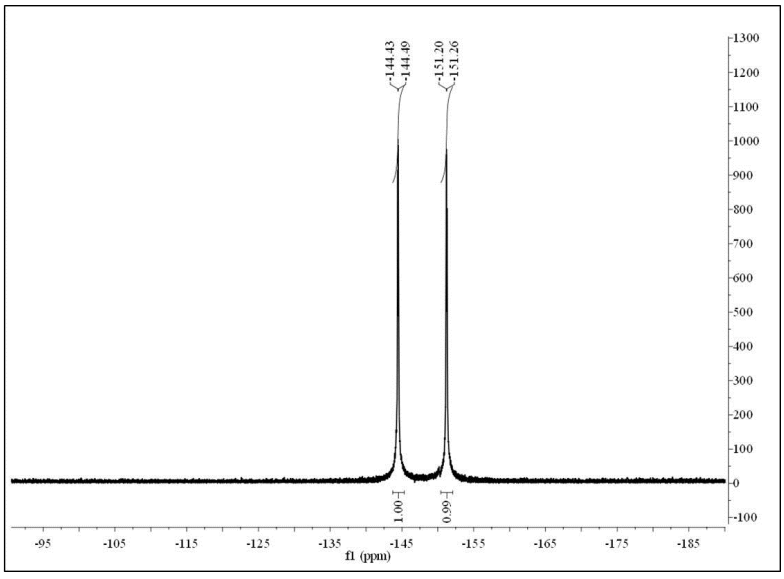
^{1}H NMR spectrum of A in DMSO

4-4'(2,7 diaminofluoren)-yl-2,3,5,6,2',3',5',6'-octafluorobenzophenone (A)



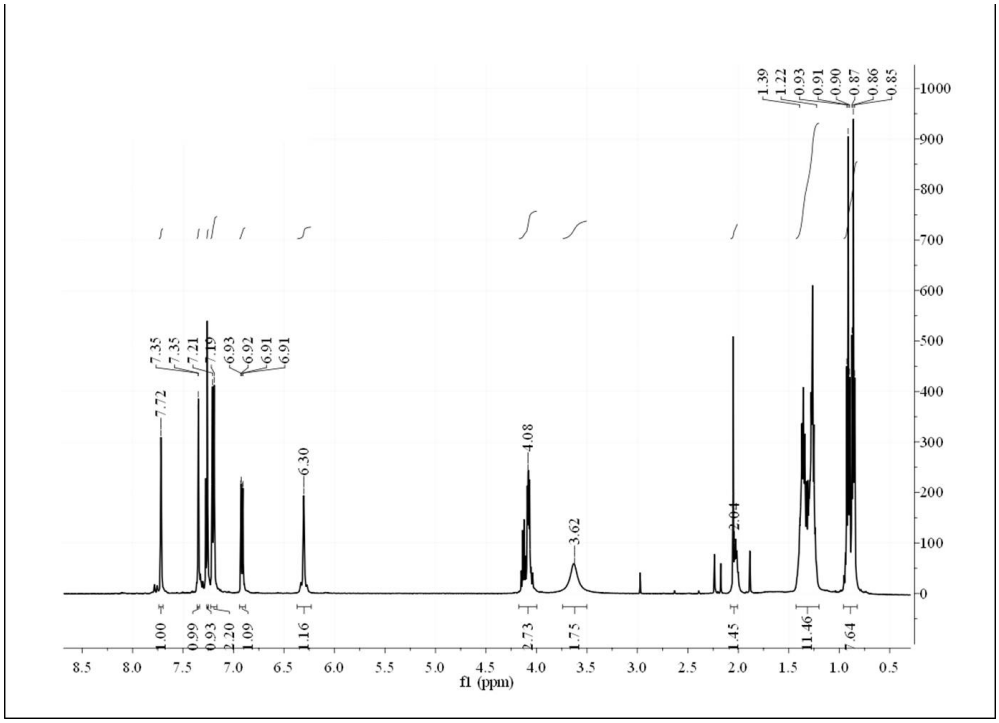
^{19}F NMR spectrum of A in DMSO

4-4'(2,7 diaminofluoren)-yl-2,3,5,6,2',3',5',6'-octafluorobenzophenone (A)



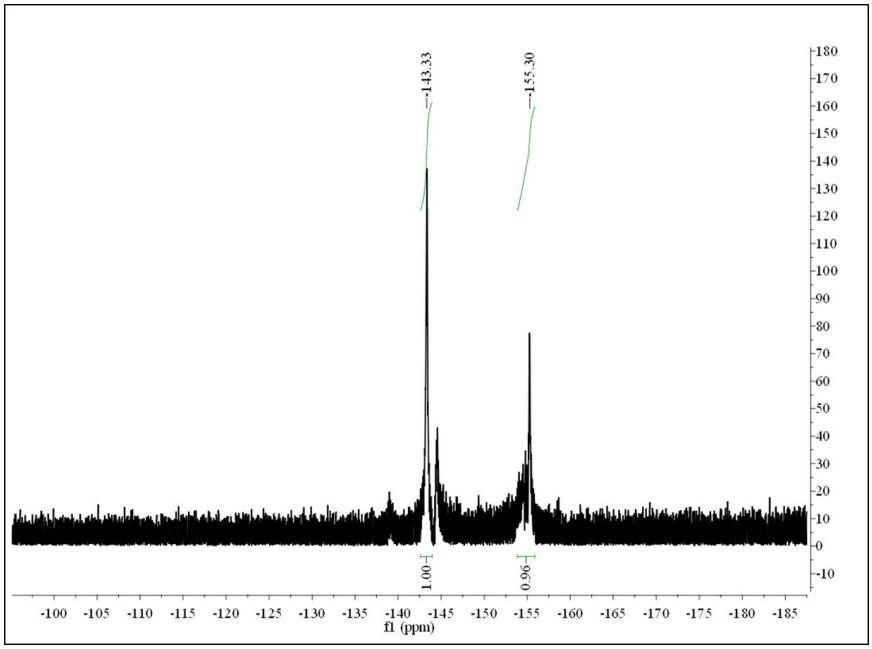
^{1}H NMR spectrum of B in $CDCl_3$

4-4'-[3,6-Diamino-N-(2-ethylhexyl)carbazo)-yl]-2,3,5,6,2',3',5',6'-octafluorobenzophenone (B)

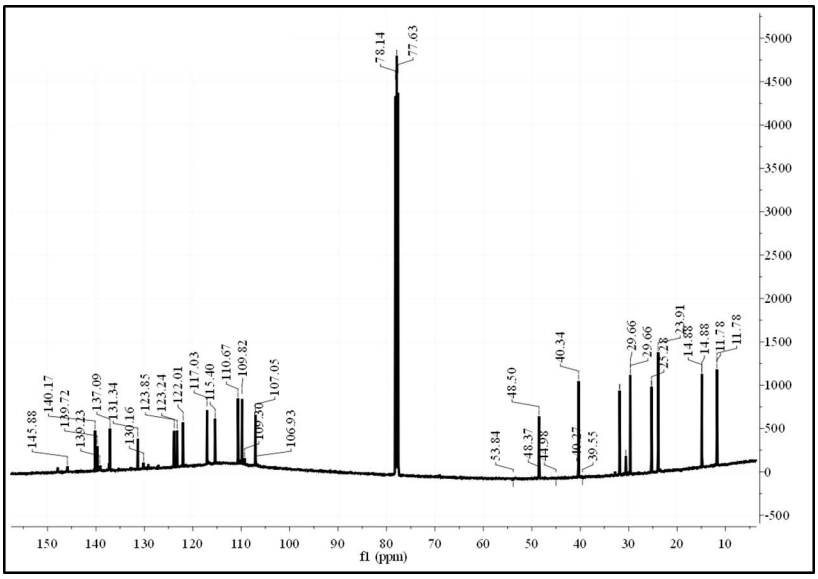


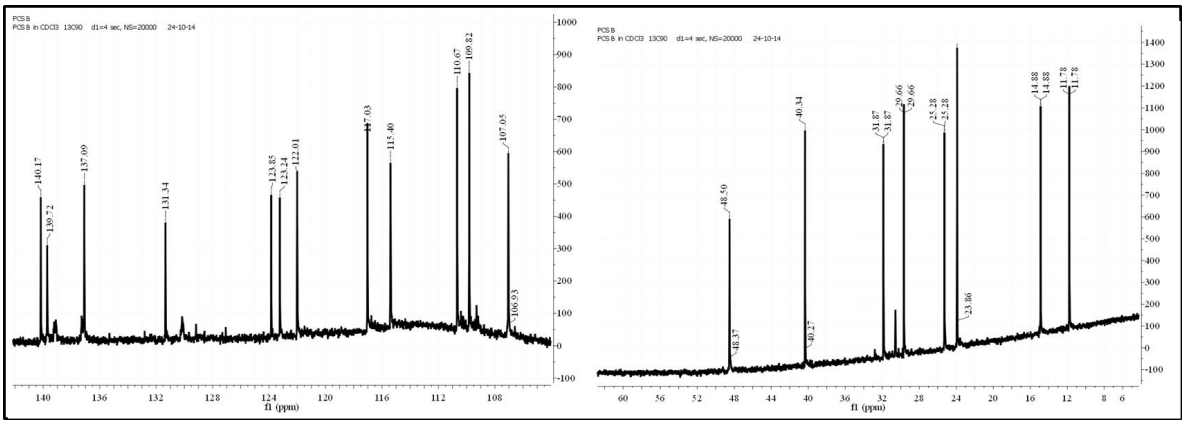
^{19}F NMR spectrum of B in DMSO

4-4'-[3,6-Diamino-N-(2-ethylhexyl)carbazo)-yl]-2,3,5,6,2',3',5',6'-octafluorobenzophenone (B)



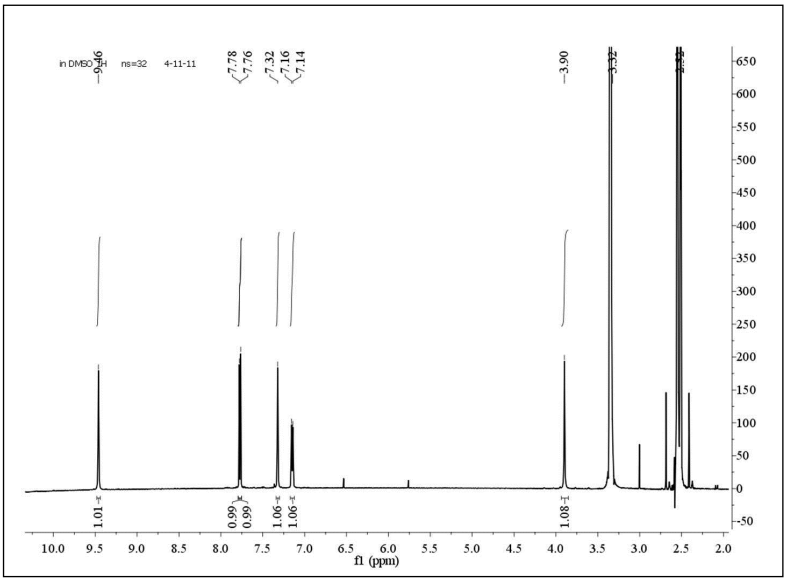
^{13} C - NMR spectrum of B in $CDCl_3$





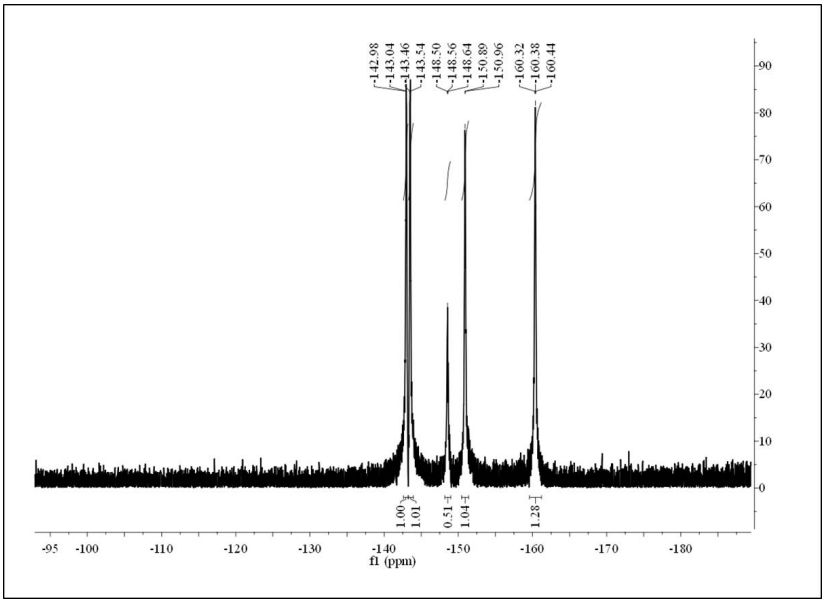
^{1}H NMR spectrum of C in DMSO

(4,4'-(9H-fluorene-2,7-diyl)bis(azanediyl)bis(2,3,5,6-tetrafluoro-4,1-phenylene))bis((perfluorophenyl)methanone) (C)



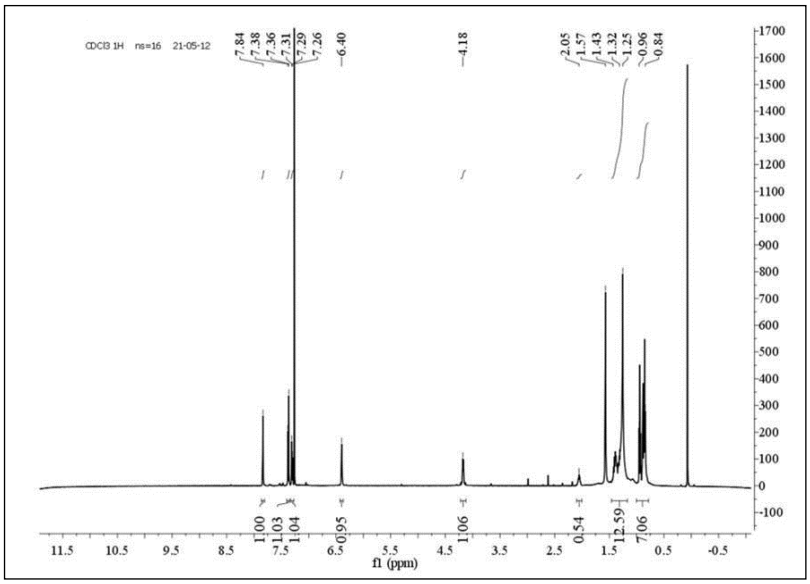
^{19}F NMR spectrum of C in DMSO

(4,4'-(9H-fluorene-2,7-diyl)bis(azanediyl)bis(2,3,5,6-tetrafluoro-4,1-phenylene))bis((perfluorophenyl)methanone) (C)



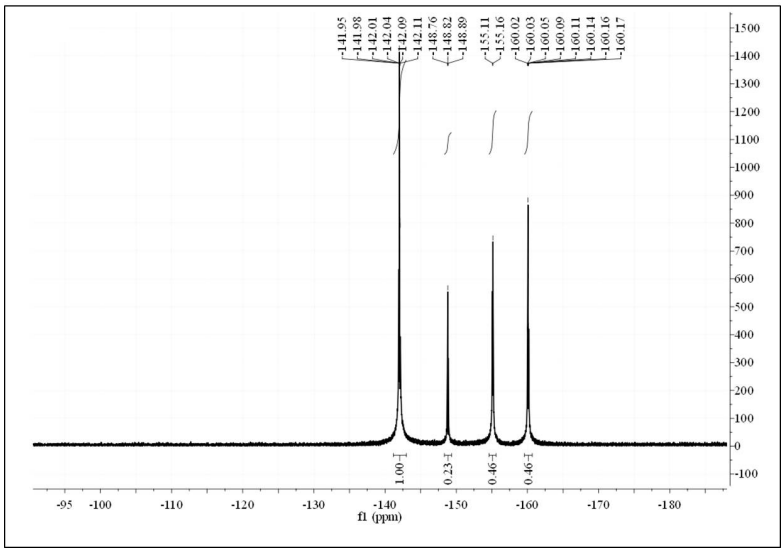
^{1}H NMR spectrum of D in $CDCl_3$

(4,4'-(9-(2-ethylhexyl)-9H-carbazole-3,6-diyl)bis(azanediyl)bis(2,3,5,6-tetrafluoro-4,1-phenylene))bis((perfluorophenyl)methanone) (D)



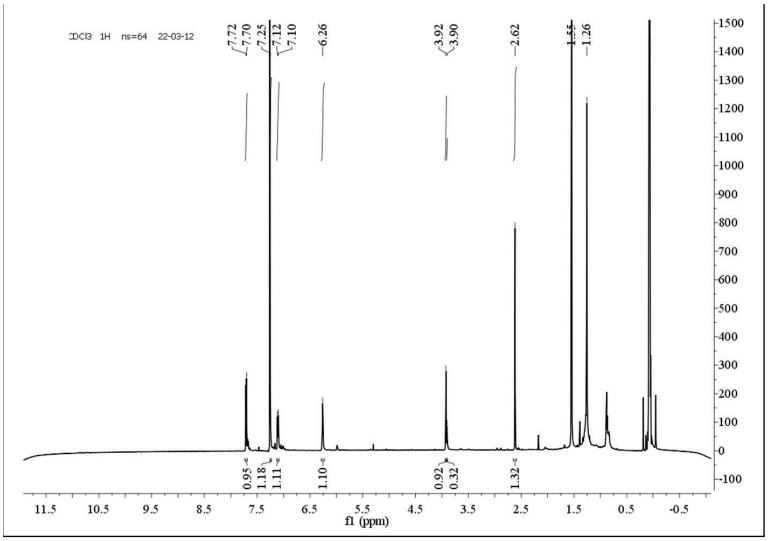
^{19}F NMR spectrum of D in DMSO

(4,4'-(9-(2-ethylhexyl)-9H-carbazole-3,6-diyl)bis(azanediyl)bis(2,3,5,6-tetrafluoro-4,1-phenylene))bis((perfluorophenyl)methanone) (D)



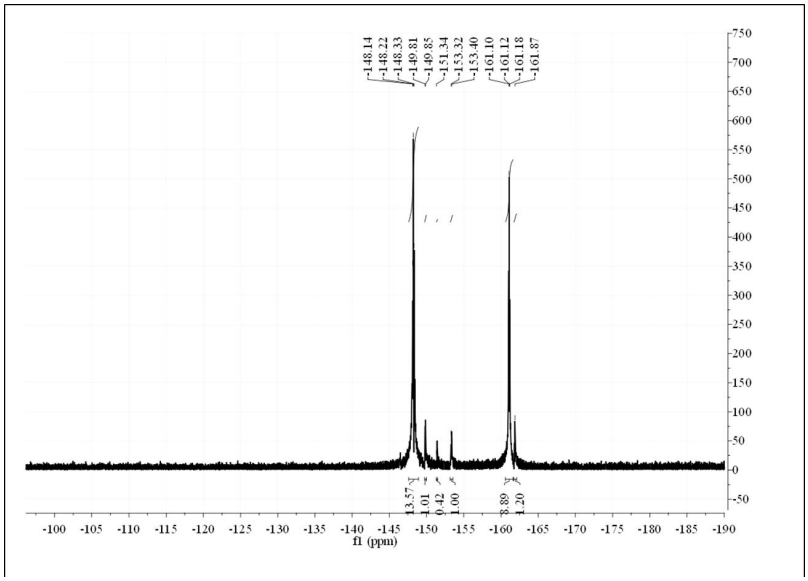
^{1}H NMR spectrum of E in $CDCl_3$

N^2-methyl-N^2,N^7-bis(2,3,5,6-tetrafluoro-4-((Z)-(perfluorophenyl)diazenyl)phenyl)-9H-fluorene-2,7-diamine (E)



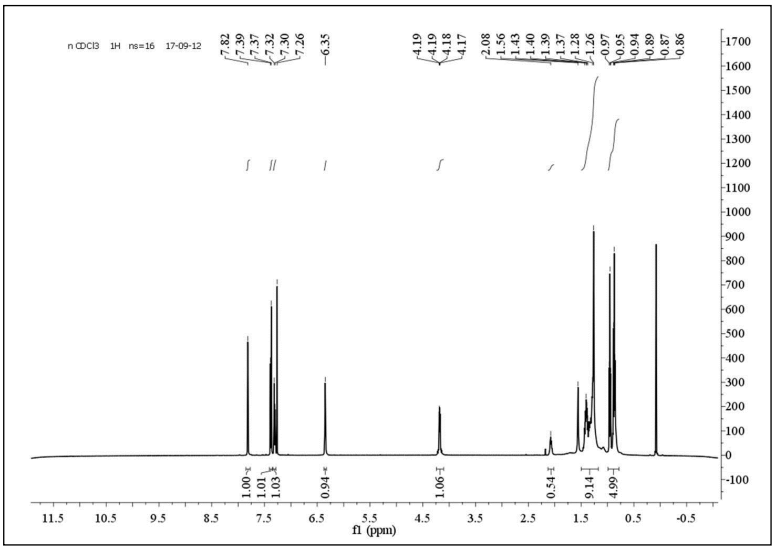
^{19}F NMR spectrum of E in DMSO

N^2-methyl-N^2,N^7-bis(2,3,5,6-tetrafluoro-4-((Z)-(perfluorophenyl)diazenyl)phenyl)-9H-fluorene-2,7-diamine (E)



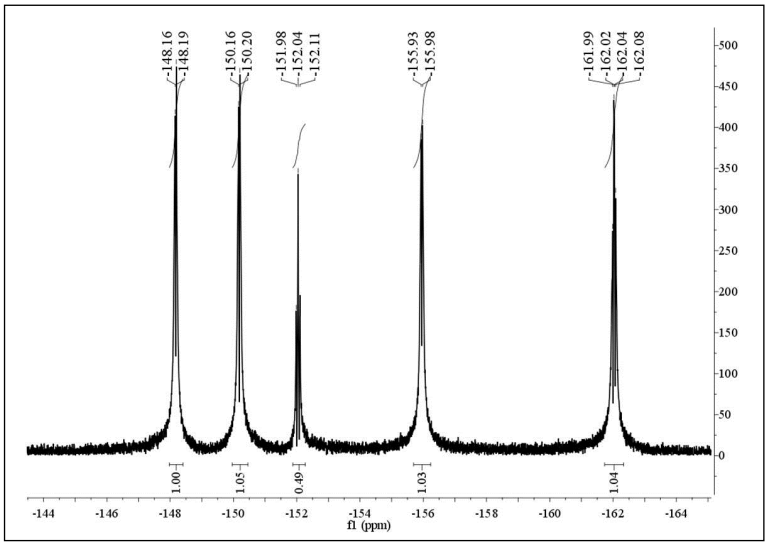
^{1}H NMR spectrum of F in $CDCl_3$

9-(2-ethylhexyl)-N^2,N^7-bis(2,3,5,6-tetrafluoro-4-((Z)-(perfluorophenyl)diazenyl)phenyl)-9H-carbazole-2,7-diamine (F)

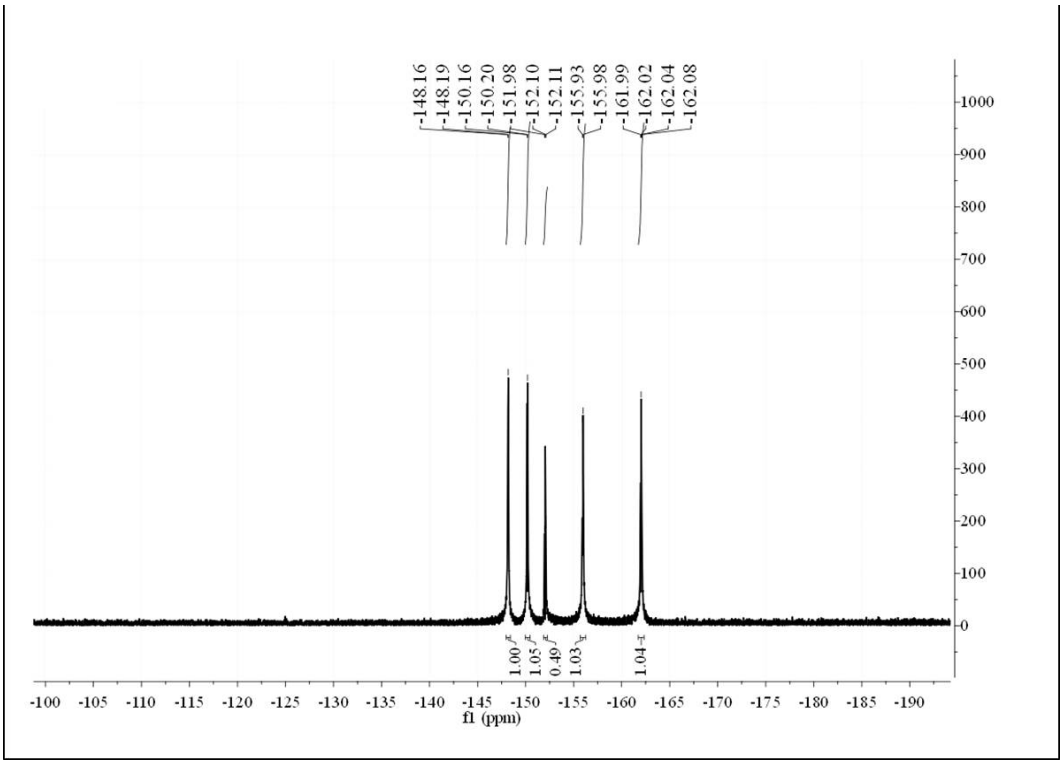


^{19}F NMR spectrum of F in DMSO

9-(2-ethylhexyl)-N^2,N^7-bis(2,3,5,6-tetrafluoro-4-((Z)-(perfluorophenyl)diazenyl)phenyl)-9H-carbazole-2,7-diamine (F)

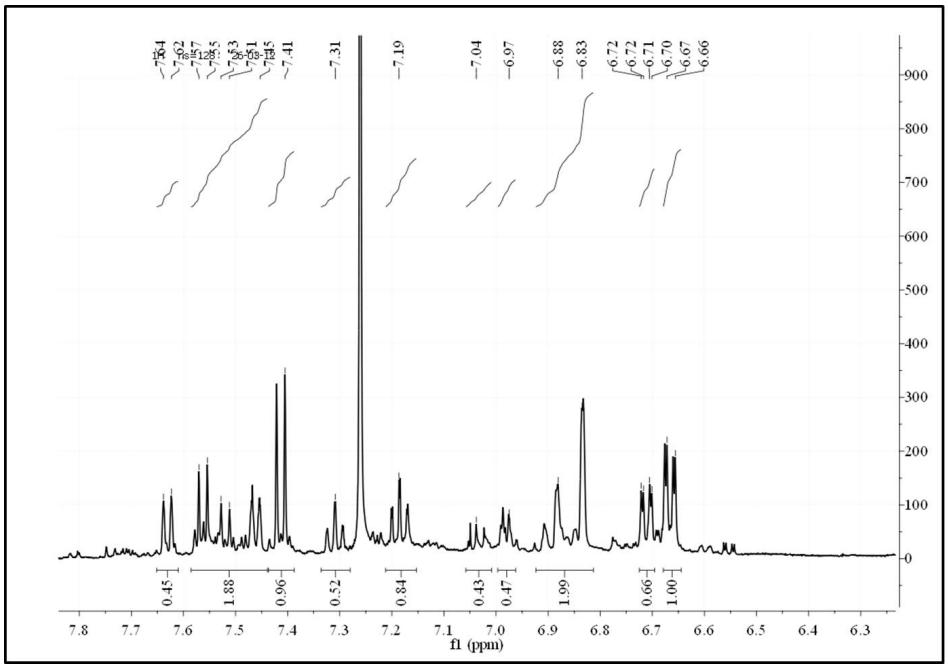


9-(2-ethylhexyl)-N2,N7-bis(2,3,5,6-tetrafluoro-4-((Z)-(perfluorophenyl)diazenyl)phenyl)-9H-carbazole-2,7-diamine (F)

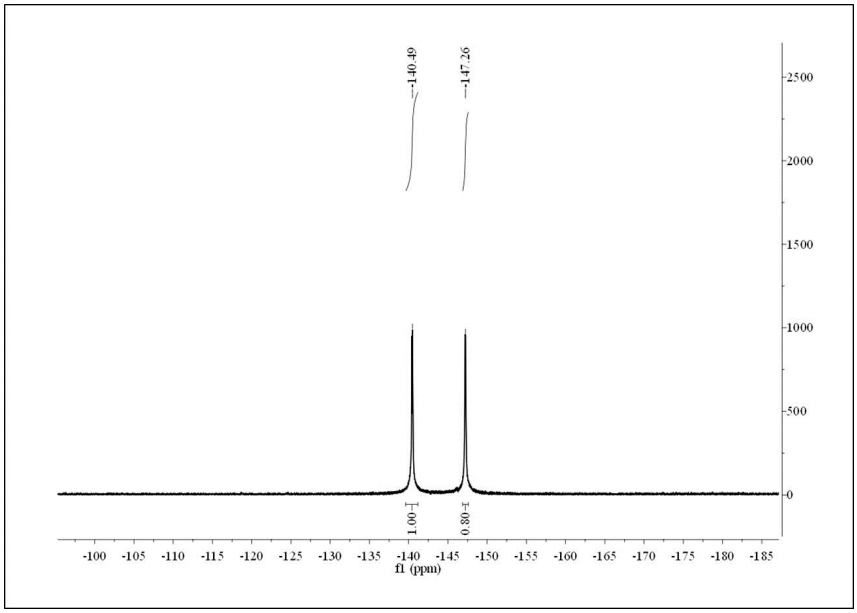


^{1}H NMR spectrum of G in $CDCl_3$

4-4'-(2,7 diaminofluorenyl)-2,3,5,6,2',3',5',6'-octafluoroazobenzene (G)

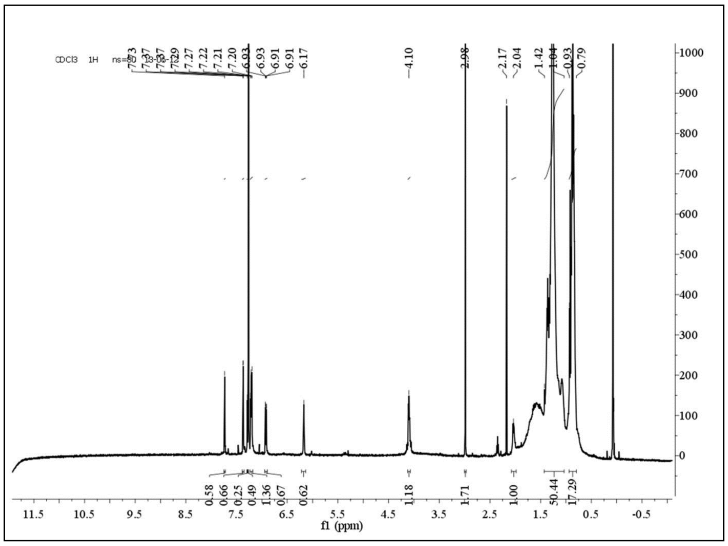


^{19}F NMR spectrum of G in DMSO

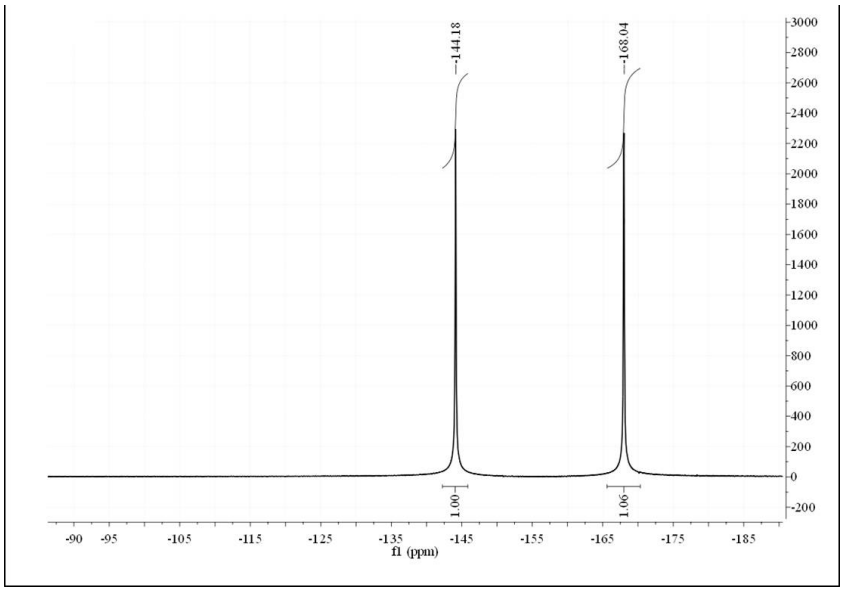


^{1}H NMR spectrum of H in $CDCl_3$

4-4'-[3,6-Diamino-N-(2-ethylhexyl)carbazo)-yl]- 2,3,5,6,2',3',5',6'-octafluoroazobenzene (H)

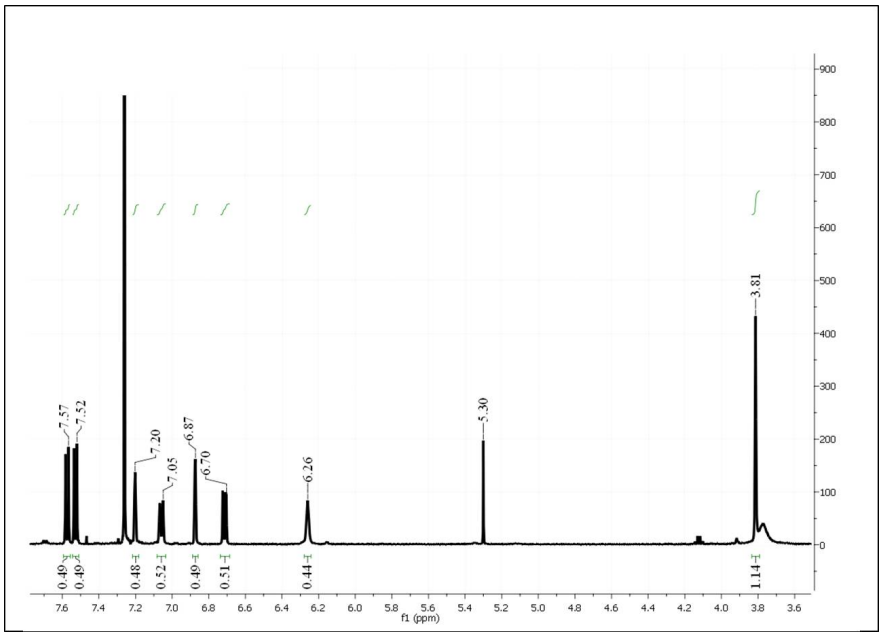


^{19}F NMR spectrum of H in DMSO

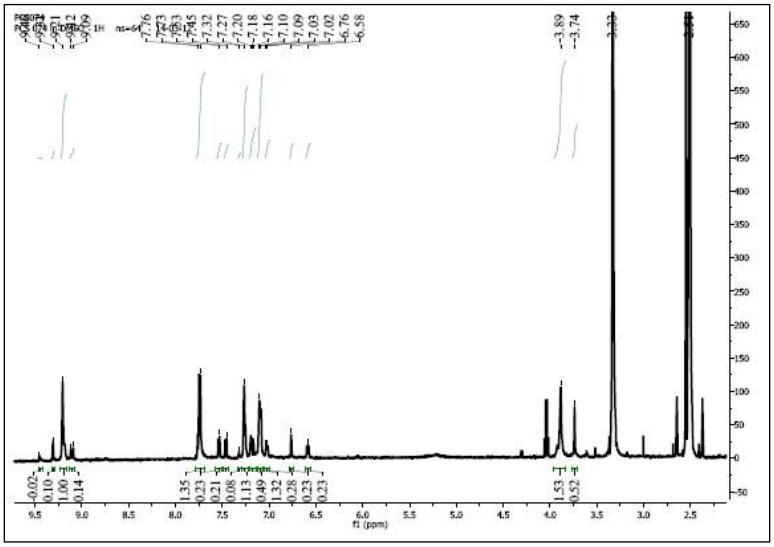


^{1}H NMR spectrum of I in $CDCl_3$

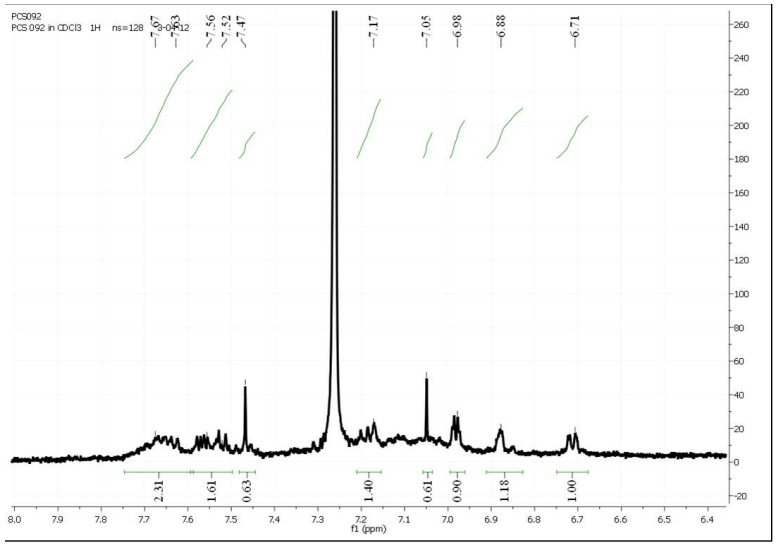
4-(2,7 diaminofluorenyl)-2,3,5,6,2',3', 4',5',6'-nonafluorobenzophenone (I)



^{1}H NMR spectrum of P1 in $CDCl_3$



^{1}H NMR spectrum of P2 in $CDCl_3$


PCS092
PCS 092 in CDCl3 1H ns=128 d1=2.12
7.67
7.63
7.56
7.52
7.47
7.17
7.05
6.98
6.88
6.71
2.31
1.61
0.63
1.40
0.61
0.90
1.18
1.00
f1 (ppm)

Electrochemical cyclic voltammetry

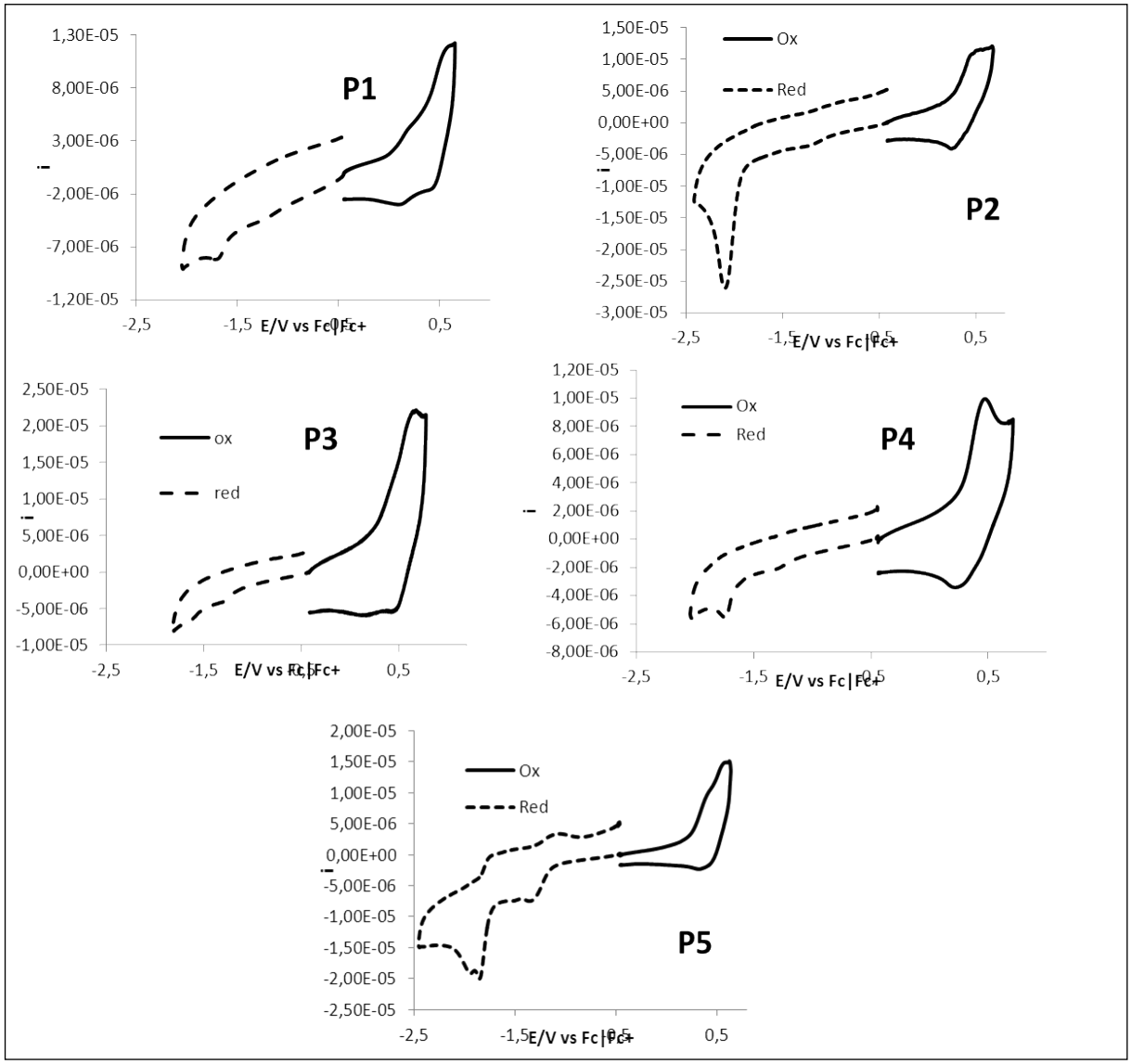


Figure S1 Cyclic voltammograms of samples solutions 0.2mg mL^{-1} in acetonitrile 0.1 M $TBATBF_4$ at a scan rate of 50 mV s^{-1}.

UV-Visible absorption and fluorescence spectra

Absorbtion spectra of triads A, B, C and D.

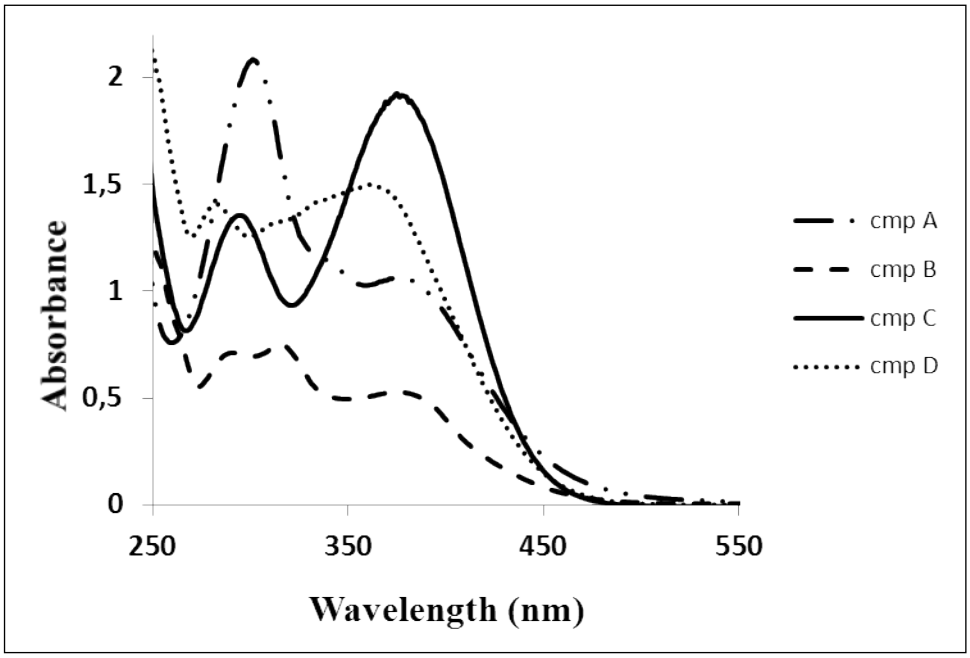


Figure S2 - Absorption spectra of selected monomers A, B, C and D(10^{-5}M CH_2Cl_2 solutions).

Absorbtion spectra of triads E, F, G and H.

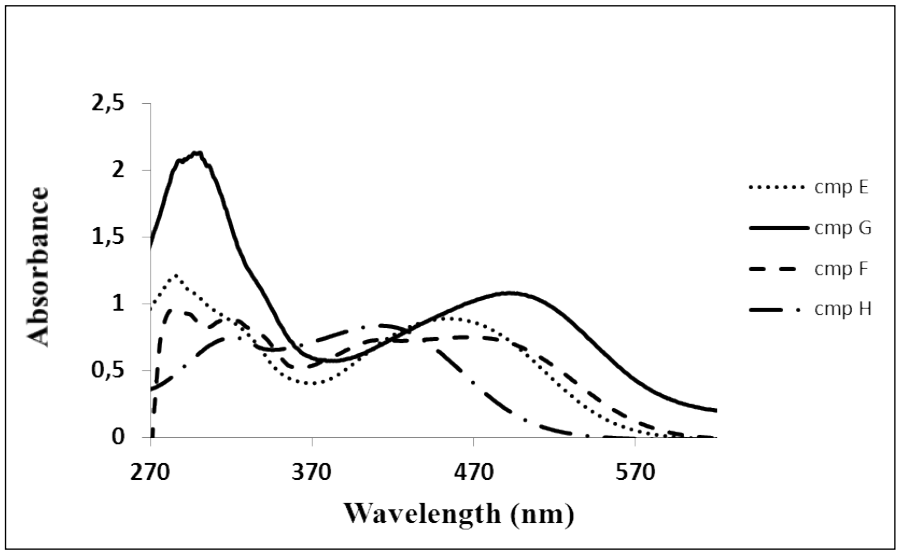


Figure S3 - Absorption spectra of selected monomers E, F, G and H(10^{-5}M CH_2Cl_2 solutions).

UV-Visible absorption of olygomers P1-P5.

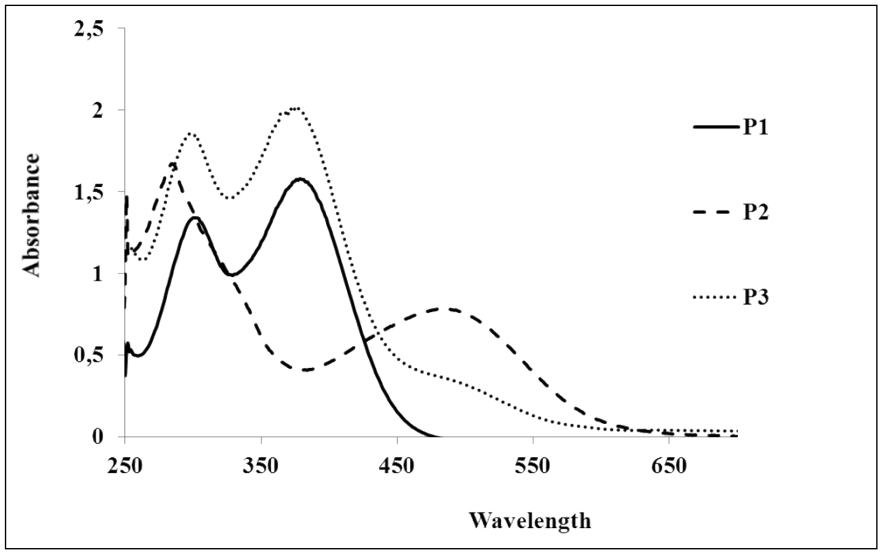


Figure S4 - Absorption spectra of polymers P1, P2 and P3 (10-5M CH2Cl2 solutions).The mixed Polymer P3 obtained from monomers C and G containing both the octafluorobenzophenone and octafluoroazobenzene shows an absorbance in solution which is practically the sum of absorbance of the polymer P1 and P2.

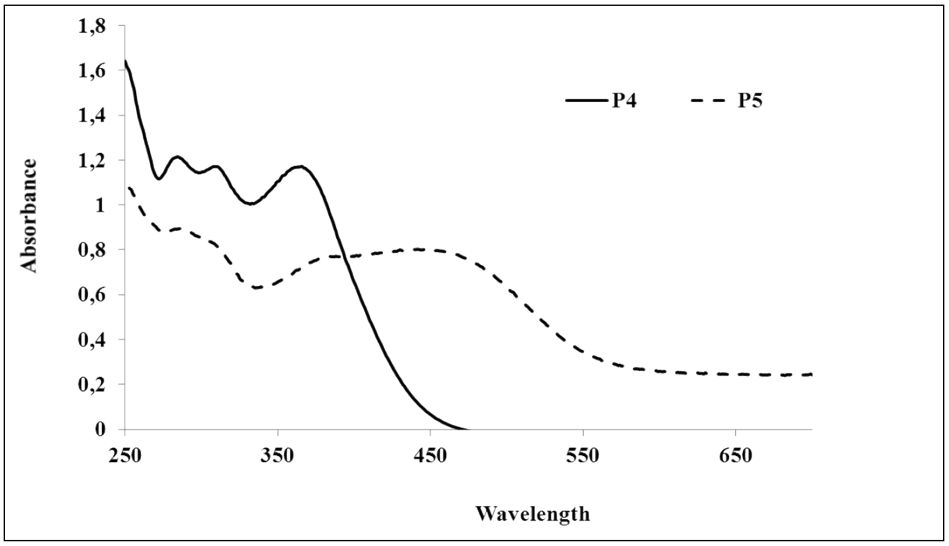


Figure S5 - Absorption spectra of selected polymers P4 and P5.

Fluorescence spectra of compound A, C and P1

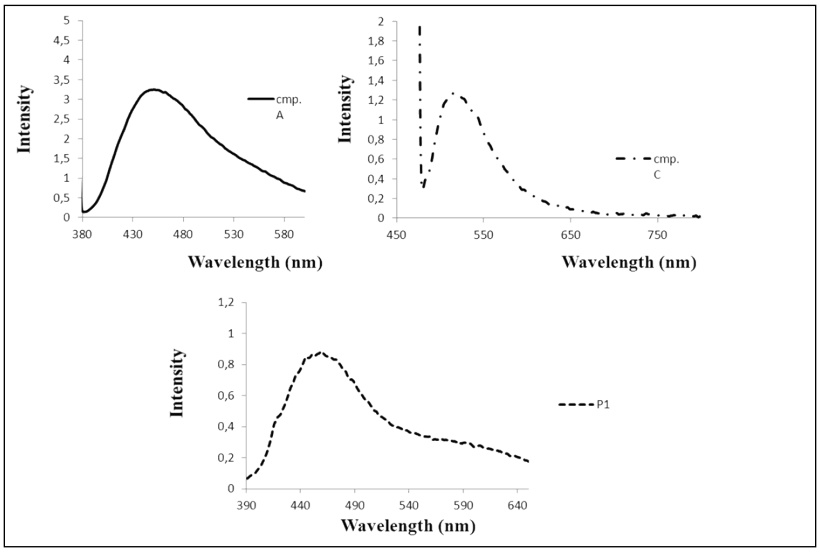


Figure S6. Fluorescence spectra of monomers A, C and polymer P1.

Fluorescence spectra of compounds E,G and P2

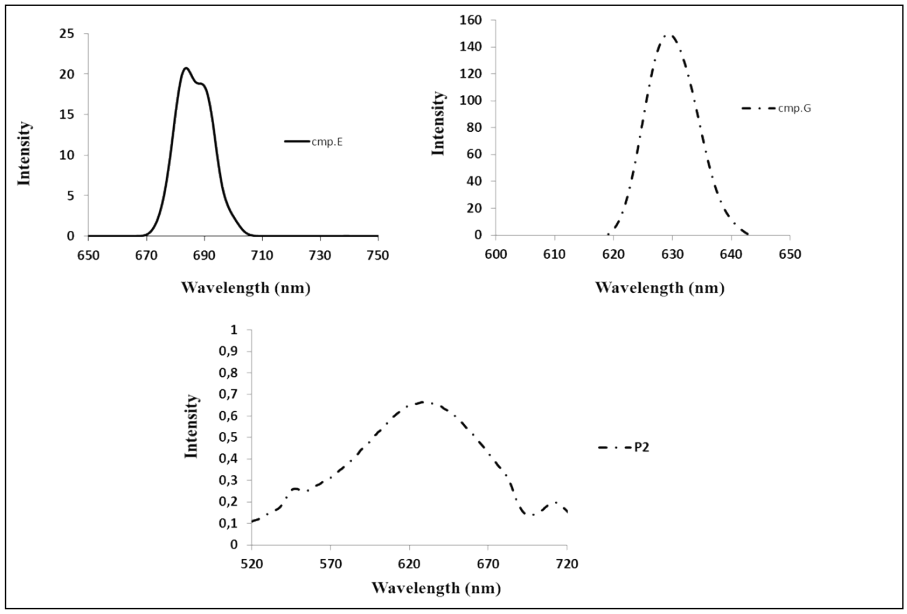


Figure S7. Fluorescence spectra of monomers E, G and polymer P2.

Fluorescence spectra of compound B, D and P3.

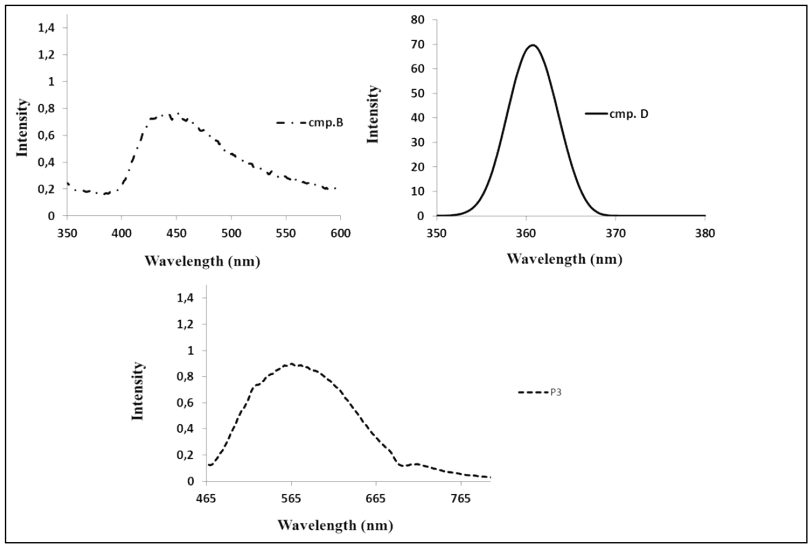


Figure S8. Fluorescence spectra of monomers B, D and polymer mixed P3.

Fluorescence spectra of compound F and H.

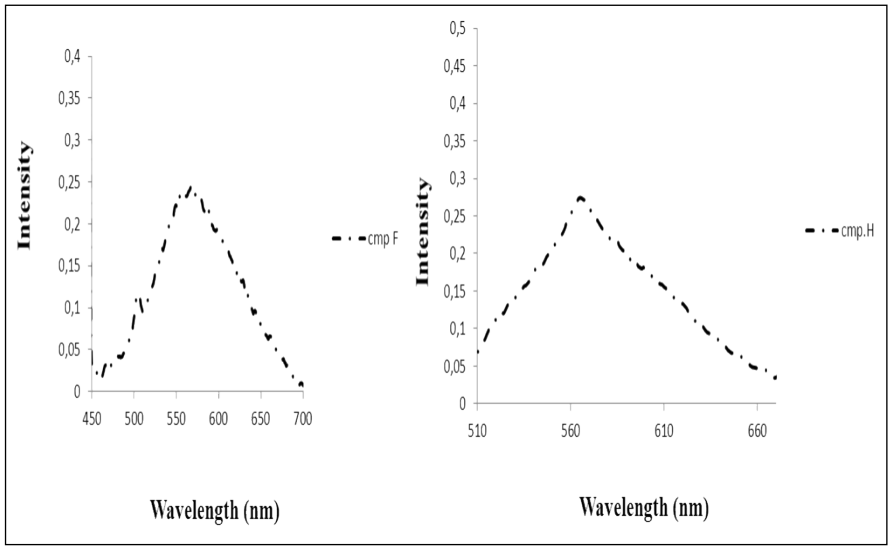


Figure S9. Fluorescence spectra of monomers E, G and polymer P2.

Gel permeation chromatography (GPC)

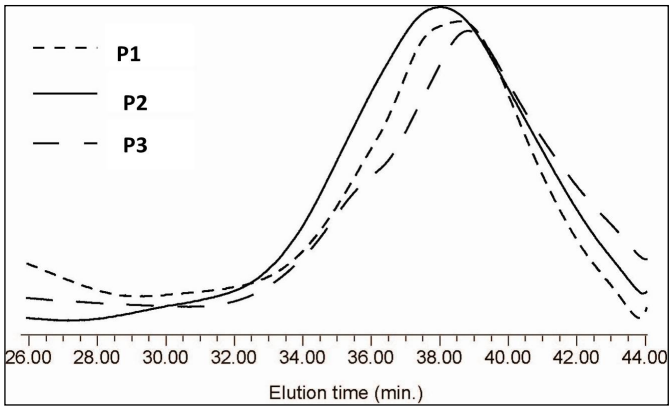


Figure S10 - **Gel permeation chromatography (GPC)** of polymer **P1, P2** and **P3**

polymer	Mn (Da)	Mw (Da)	Polydispersity
P1	940	2085	2.22
P2	1041	2263	2.17
P3	878	1885	2.15

MS spectra

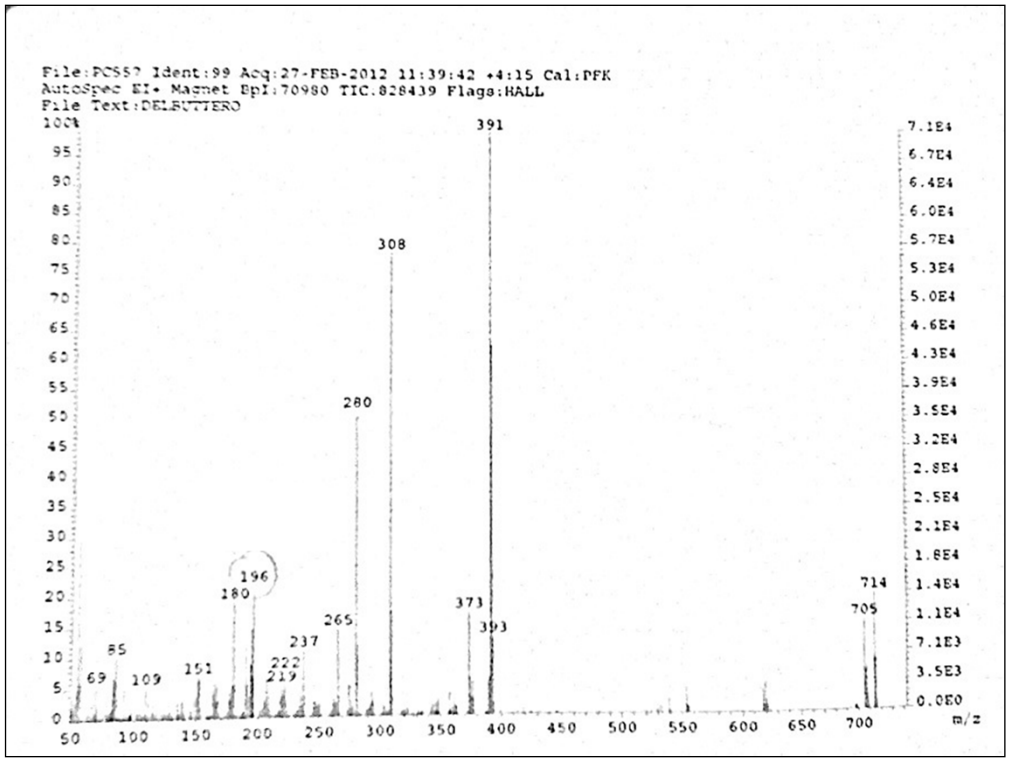
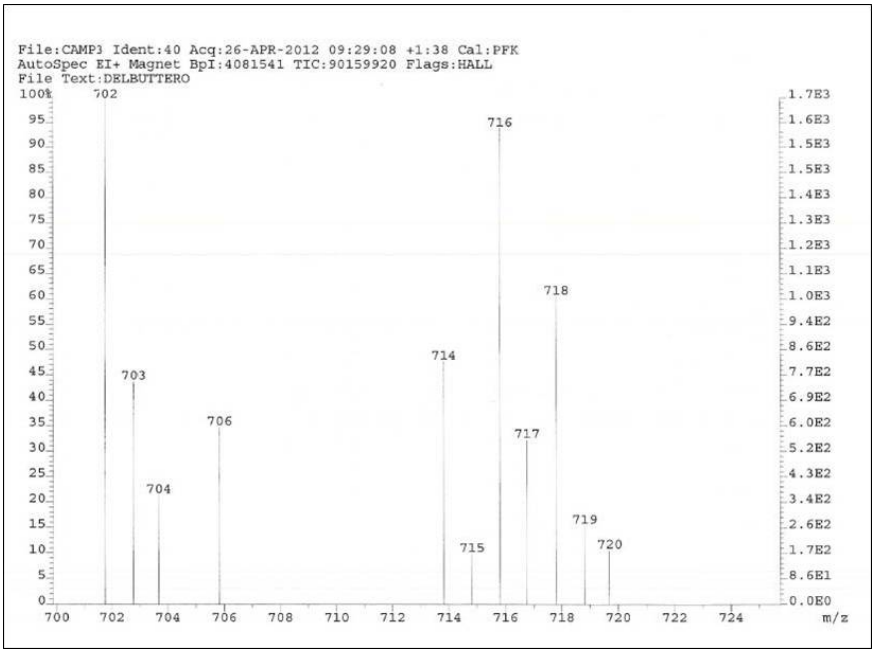


Figure S11 – **MS spectra of A**



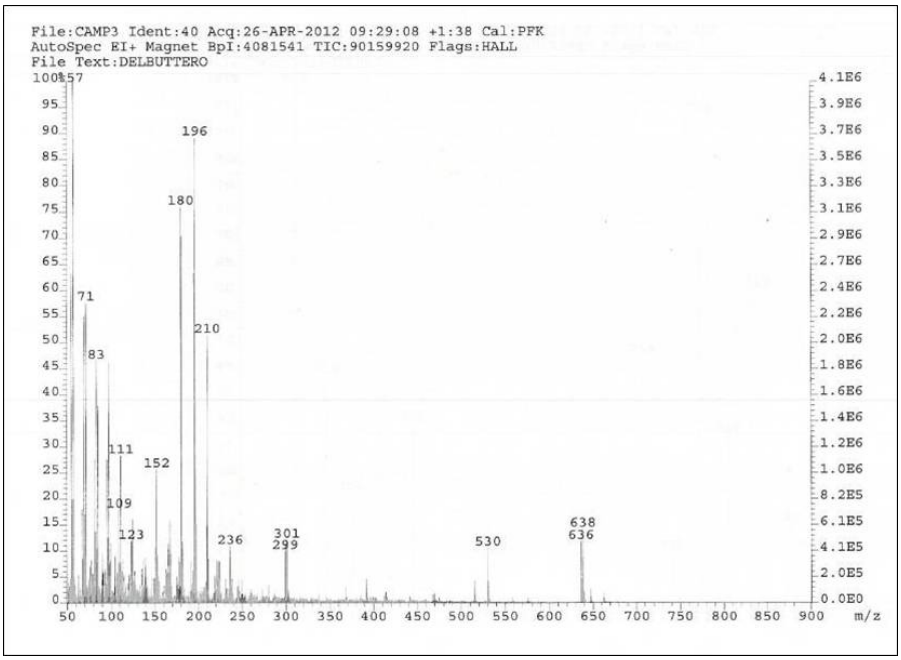
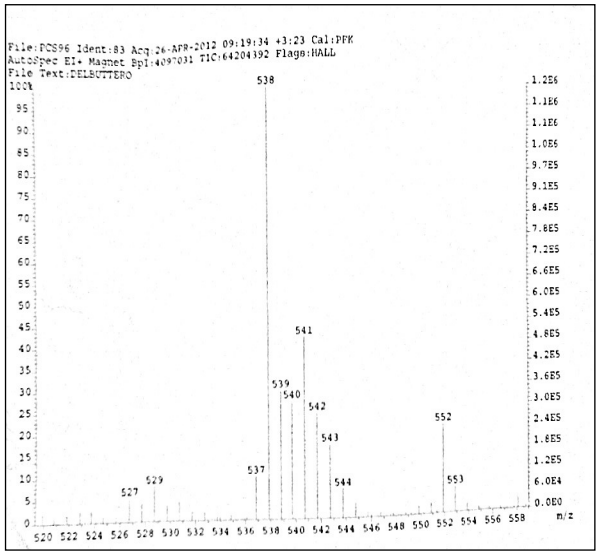


Figure S12 – **MS spectra of G**



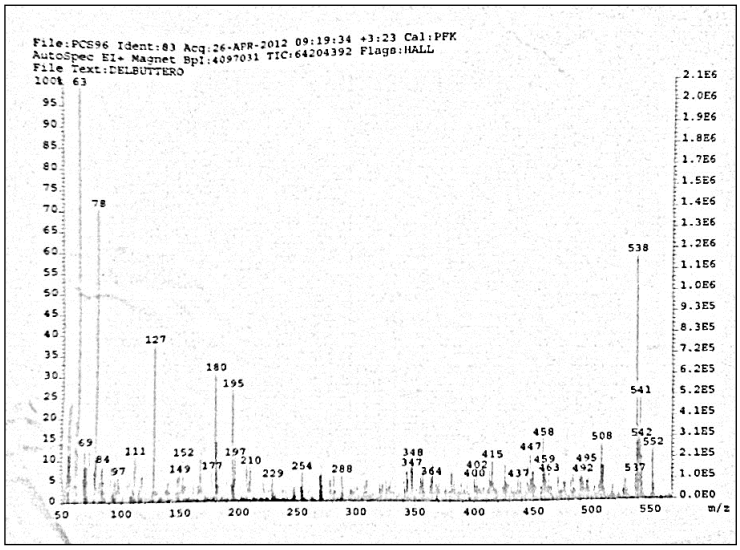
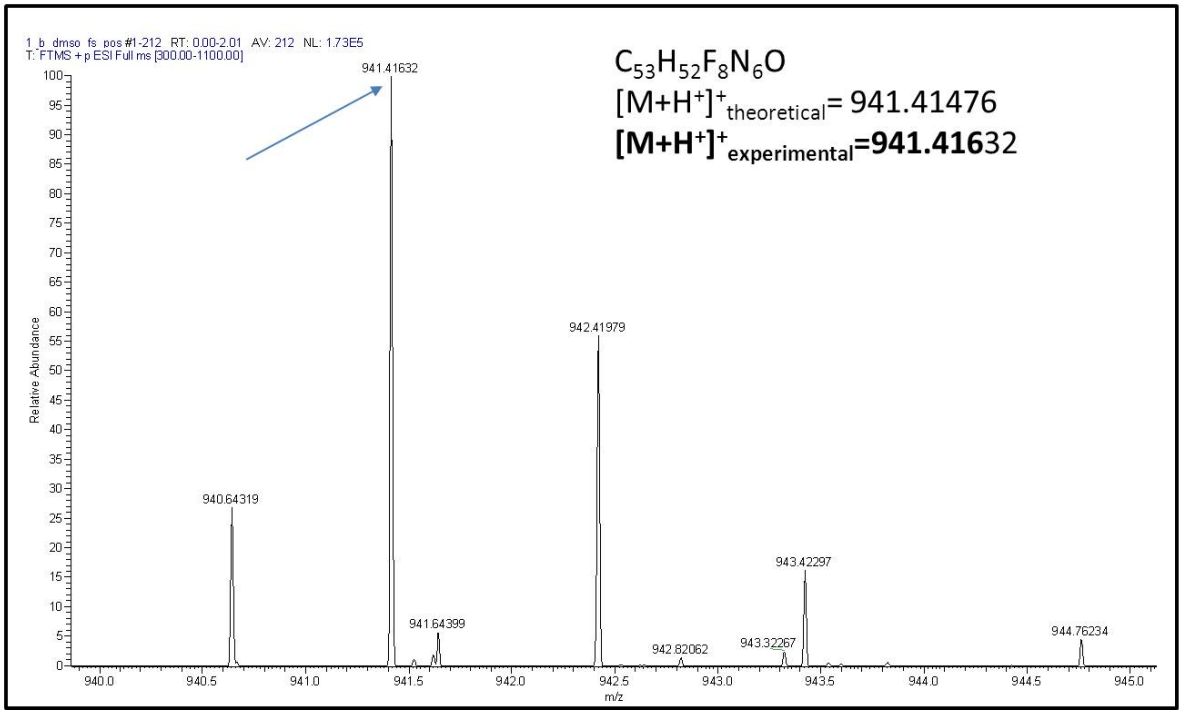


Figure S13 – **MS spectra of I**

ESI-HR-MS (S14)

TRIAD B

Zoomed-in (940–945 m/z) ESI-HR-MS spectrum



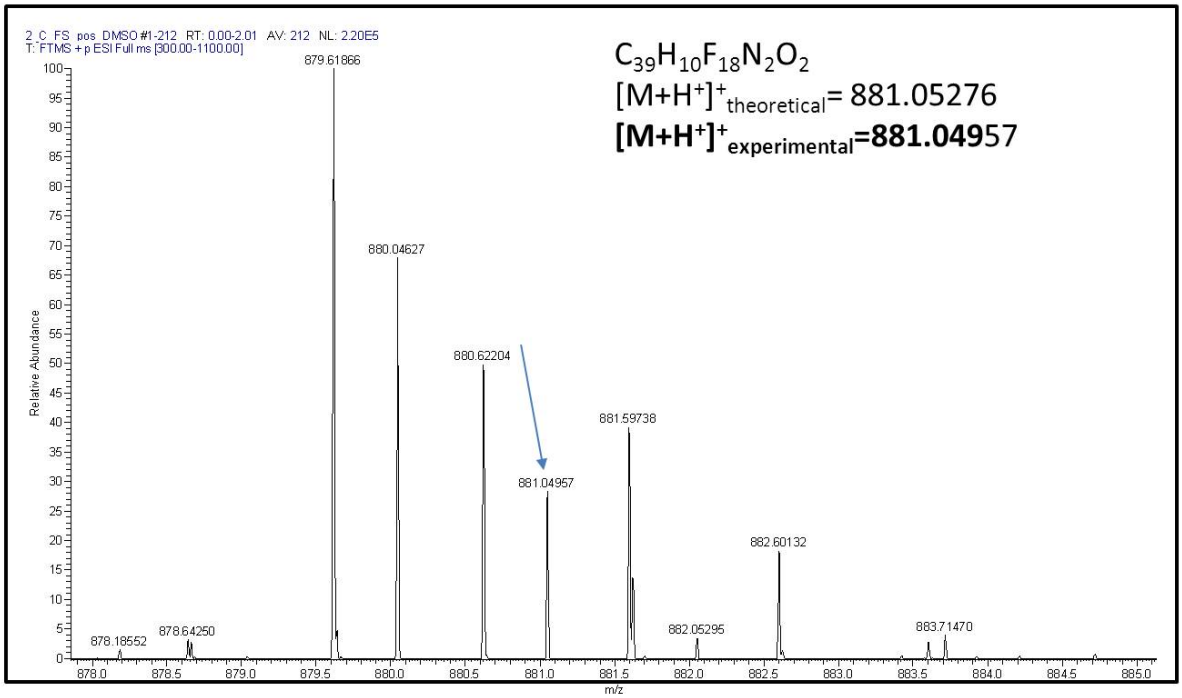
$C_{53}H_{52}F_8N_6O$

$[M+H^+]^+_{theoretical}$ = 941.41476

$[M+H^+]^+_{experimental}$=941.41632

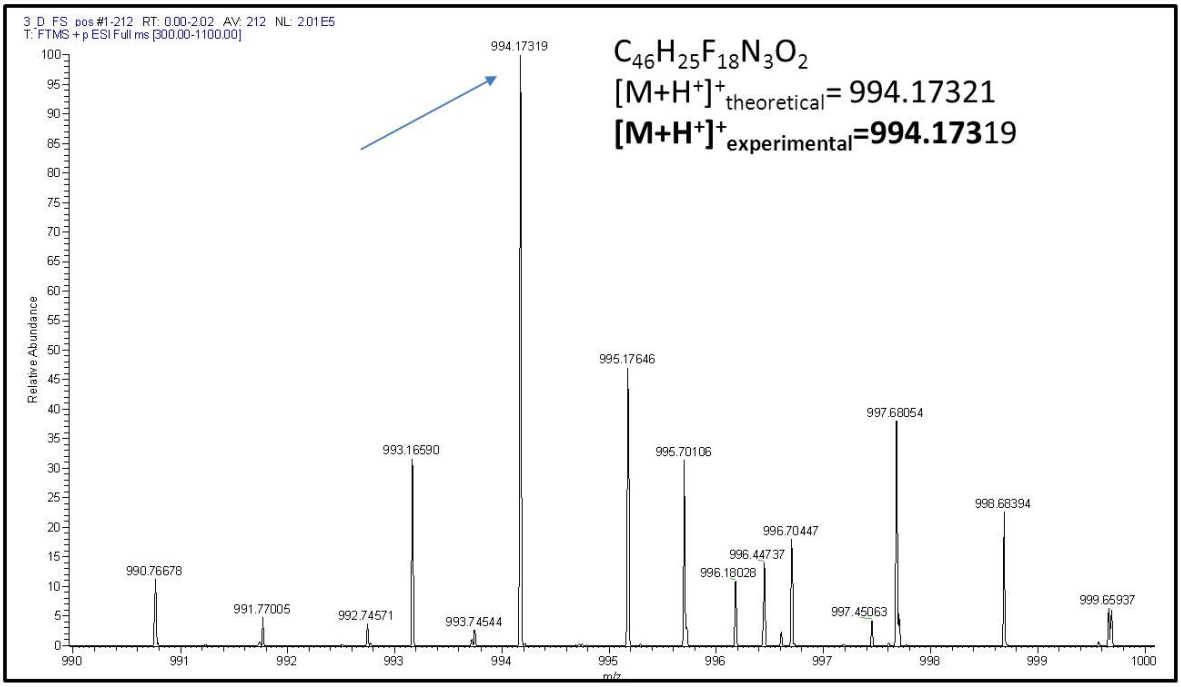
TRIAD C

Zoomed-in (878–885 m/z) ESI-HR-MS spectrum



TRIAD D

Zoomed-in (900–1000 m/z) ESI-HR-MS spectrum



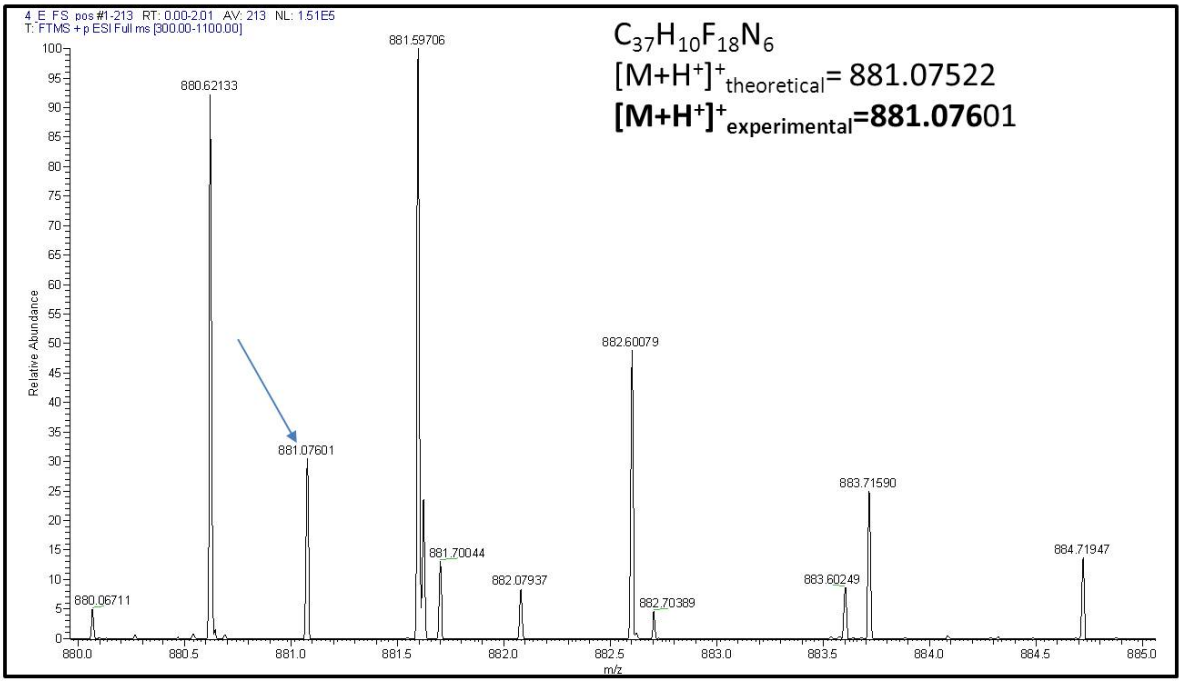
$C_{46}H_{25}F_{18}N_3O_2$

$[M+H^+]^+_{theoretical}$= 994.17321

$[M+H^+]^+_{experimental}$=994.17319

TRIAD E

Zoomed-in (880–885 m/z) ESI-HR-MS spectrum



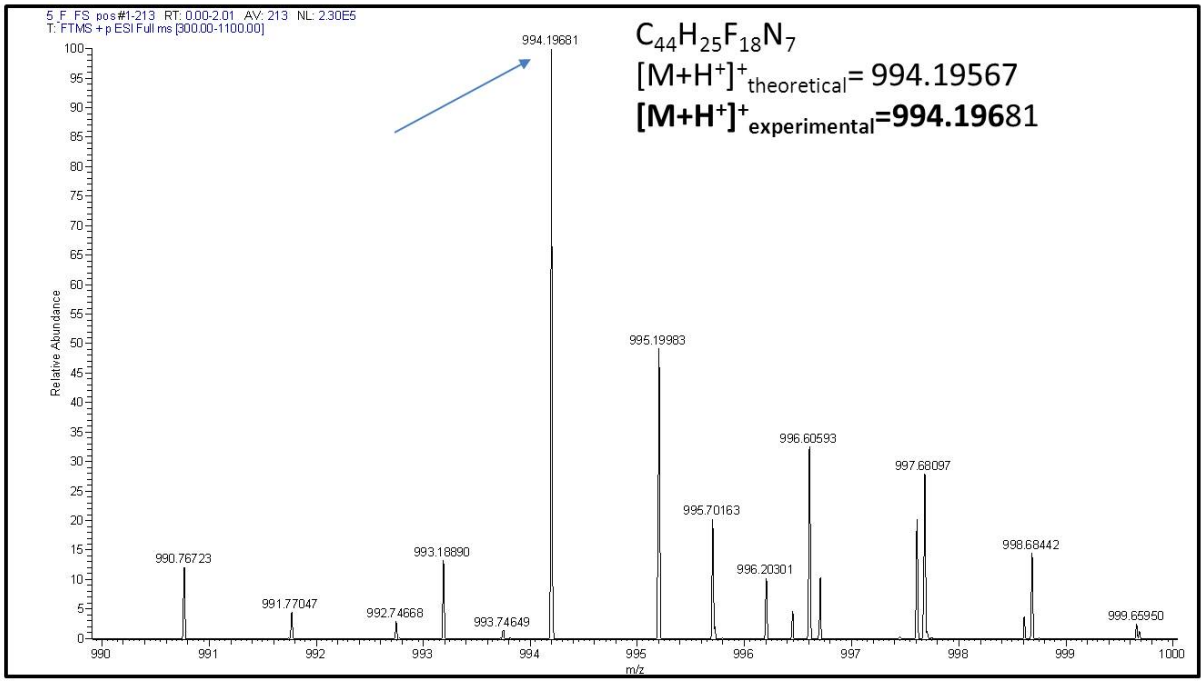
$C_{37}H_{10}F_{18}N_6$

$[M+H^+]^+_{theoretical}$= 881.07522

$[M+H^+]^+_{experimental}$=881.07601

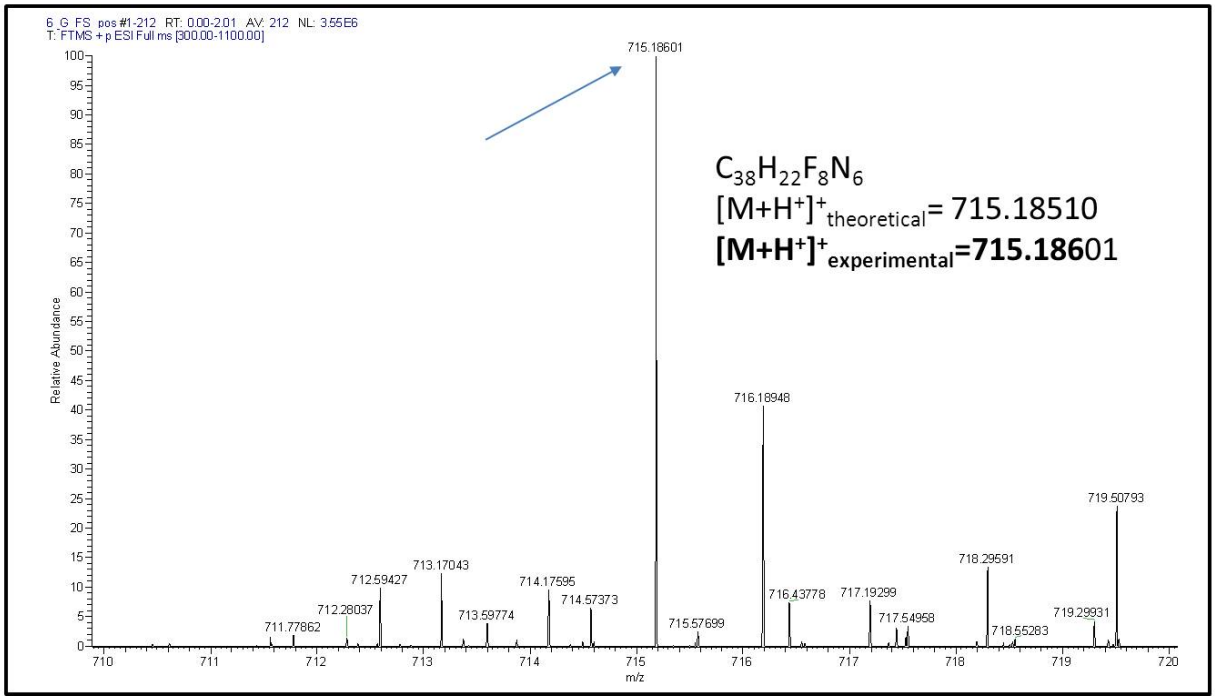
TRIAD F

Zoomed-in (990–1000 m/z) ESI-HR-MS spectrum



TRIAD G

Zoomed-in (710–720 m/z) ESI-HR-MS spectrum



TRIAD H

Zoomed-in (940–945 m/z) ESI-HR-MS spectrum