Supporting Information

One-Pot Synthesis of Core-Modified Meso Aryl Calix[5]phyrin and N-Fused [24]pentaphyrin:

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Experimental

General

All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran and n-hexane were purified and distilled by standard procedure. Electronic spectra were recorded on Perkin-Elmer Lambda 20 UV/Vis spectrophotometer. Proton NMR spectra were obtained on a 400 MHz JEOL spectrometer in $CDCl_3$. FAB-MS spectra were obtained on a JEOL-SX-120/DA6000 spectrometer. Thiophene diol, Selenophene diol and Tetrapyrrane are synthesized using methods described in reference in the manuscript and stored under inert atmosphere.

Syntheses:

7: A mixture of **4** (0.133g, 0.35 mmol) and tetrapyrrane **6** (0.28g, 0.35mmol) were dissolved in dry dichloromethane (200 ml) and stirred under nitrogen atmosphere for 5 min. *Para*-toluenesulfonic acid (PTSA) (0.02g, 0.1 mmol) was added and the stirring was continued for 90 min. DDQ (0.16g, 0.7 mmol) was added and the reaction mixture was further stirred for 90 min. The solvent was evaporated in vacuum. The residue was purified by chromatography on a basic alumina column, first green band which was eluted with dichloromethane/petroleum ether (1:5) gave **7** in (0.025g, 11.2%); ^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ = 11.15 (brs, NH, 2H), 7.75 (m, 2H), 7.14 (d, J = 4.1Hz, 2H), 7.03 (s, 2H), 6.99 (s, 2H), 6.92 (d, J = 4.3Hz, 2H), 6.51 (d, J = 4.4Hz, 2H), 4.0 (s, 1H), 2.35 (s, 6H), 2.12 (s, 6H), 2.05 (s, 6H); FAB-MS: m/z (%): 1141 (100) [M^+]; UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$): 386 (2.1), 466 (4.1), 494 (4.6), 708 (1.1). elemental analysis: calcd (%) for $C_{61}H_{35}F_{15}N_4S$: C 64.21, H 3.09, N 4.91; found: C 64.25, H 2.89, N 4.15.

8: A mixture of **5** (0.16g, 0.38 mmol) and tetrapyrrane **6** (0.3g, 0.38mmol) were dissolved in dry dichloromethane (200 ml) and stirred under nitrogen atmosphere for 5 min. *Para*-toluenesulfonic acid (PTSA) (0.021g, 0.1 mmol) was added and the stirring was

continued for 90 min. DDQ (0.15 g, 0.76 mmol) was added and the reaction mixture was further stirred for 90 min. The solvent was evaporated in vacuum. The residue was purified by chromatography on a basic alumina column, first green band which was eluted with dichloromethane/petroleum ether (1:5) gave **8** in (0.035g, 13.4%); ^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ = 9.04 (brs, NH, 2H), 7.9 (m, 2H), 7.36 (s, 2H), 7.09 (m, 4H), 7.03(s, 2H), 6.96 (d, J = 4.4Hz, 2H), 6.68 (d, J = 4.5Hz, 2H), 2.56 (s, 1H), 2.43(s, 6H), 2.14 (s, 6H), 2.1 (s, 6H); FAB-MS: m/z (%): 1187.85(70) [M^+]; UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$): 412 (5.5), 490 (7.5), 691 (2.5). elemental analysis: calcd (%) for $C_{61}H_{35}F_{15}N_4Se$: C 61.68, H 2.97, N 4.72; found: C 62.32, H 2.76, N 4.45.

9: The second orange band (after the green fraction **7**) which was eluted with dichloromethane/petroleum ether (2:3) gave **9** in (0.07g, 14.6%); ^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ = 18.02 (brs, 1H, NH), 14.39 (m, 1H), 13.31 (d, J = 3.8Hz, 1H), 12.97 (d, J = 3.8Hz, 4H), 6.63 (d, J = 9Hz, 4H, Ar-H), 4.75 (dd, J = 4.8Hz, 2H), 4.64 (m, 1H), 4.59 (m, 2H), 4.03 (d, J = 6Hz, 1H), 2.33(s, 6H), 2.21 (s, 6H), 2.1 (s, 6H); FAB-MS: m/z (%): 1139.5(70) [M^+]; UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$): 436 (4.6), 470 (5.2), 498 (6.4). elemental analysis: calcd (%) for $C_{61}H_{33}F_{15}N_4S$: C 64.33, H 2.92, N 4.92; found: C 63.75, H 2.65, N 4.35.

10: The second orange band (after the green fraction **8**) which was eluted with dichloromethane/petroleum ether (2:3) gave **10** in (0.065g, 15.2%); ^{1}H NMR (300 MHz, $CDCl_3$, 25° C, TMS): δ = 17.83 (brs, 1H, NH), 13.74 (m, 1H), 12.46 (d, J = 3.8Hz, 1H), 12.16 (d, J = 3.8Hz, 4H), 6.64 (d, J = 9Hz, 4H, Ar-H), 4.97 (brs, 1H, NH), 4.9 (dd, J = 4.8Hz, 2H), 4.79 (m, 1H), 4.73 (m, 2H), 4.21 (d, J = 6Hz, 1H), 2.15(s, 6H), 2.13 (s, 6H), 2.1 (s, 6H); FAB-MS: m/z (%): 1187.85(70) [M^+]; UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$): 426 (6.1), 466 (6.9), 492 (8.3). elemental analysis: calcd (%) for $C_{61}H_{33}F_{15}N_4Se$: C 61.78, H 2.80, N 4.72; found: C 61.35, H 2.73, N 4.25.

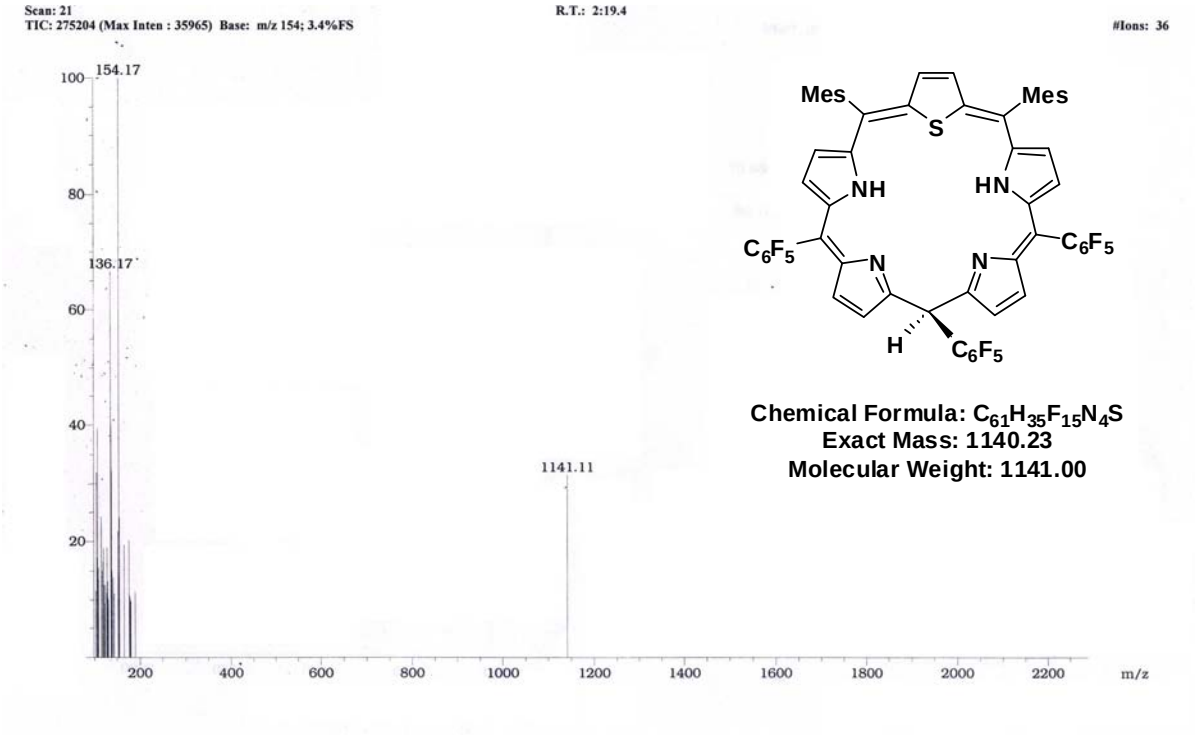


Figure 1: FAB Mass Spectrum of 7

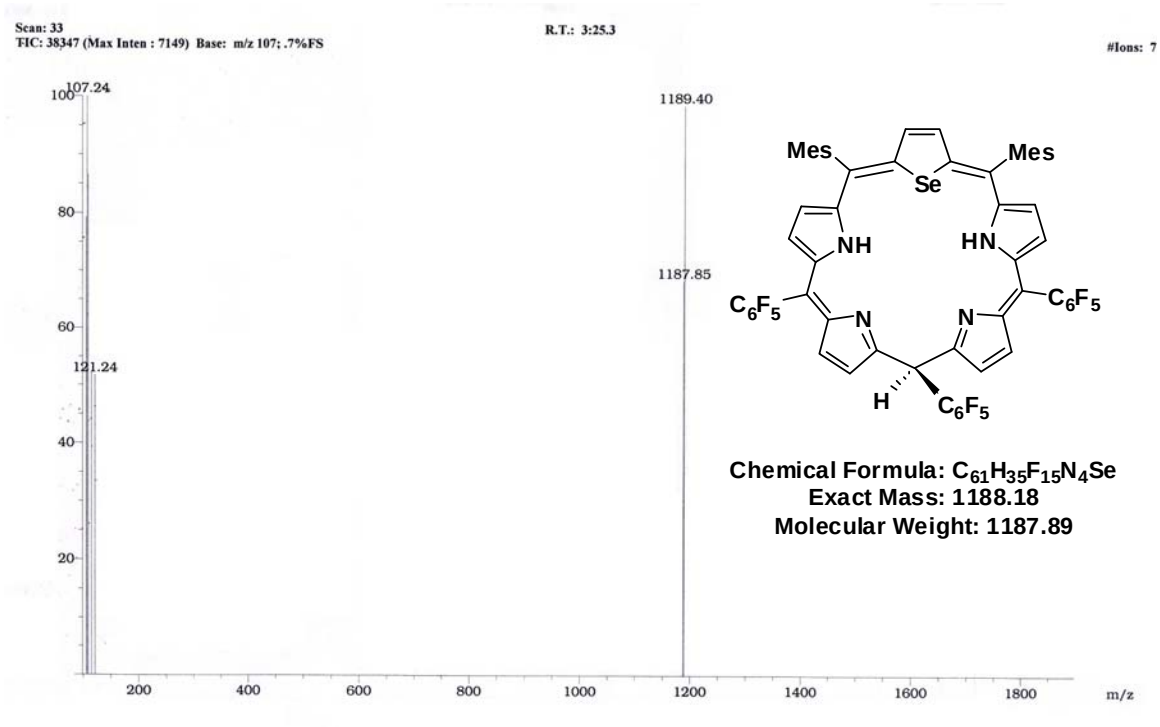


Figure 2: FAB Mass Spectrum of 8

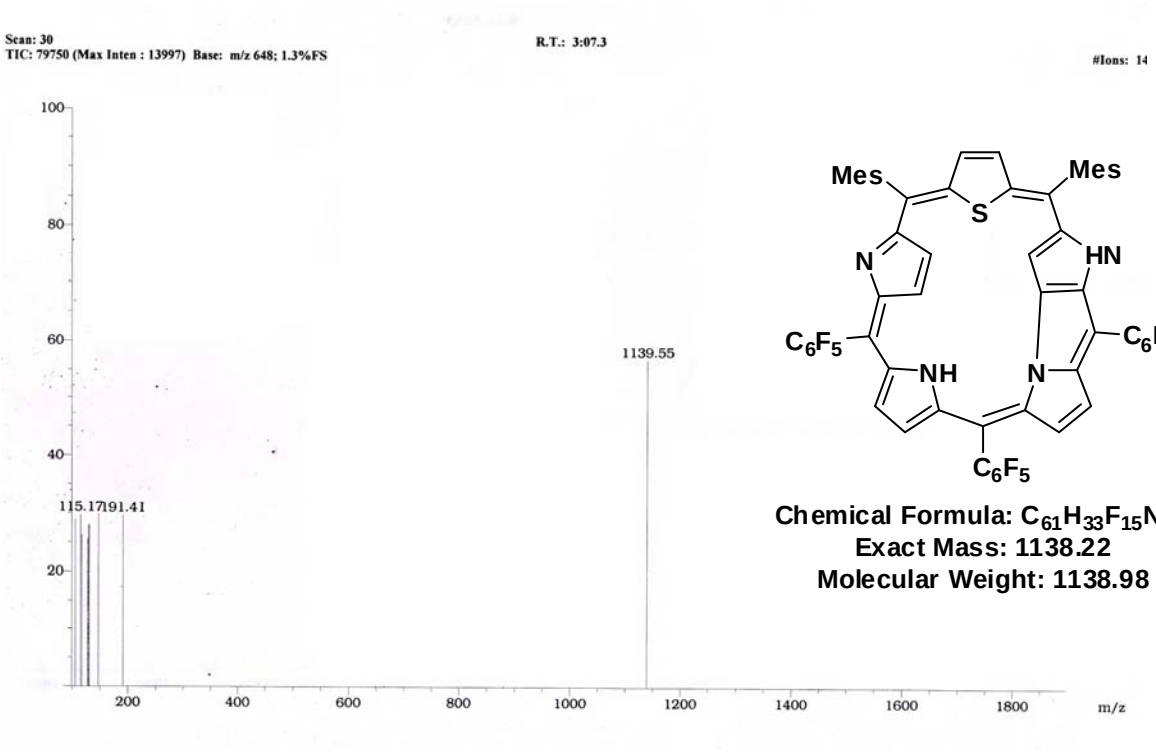


Figure 3: FAB Mass Spectrum of 9

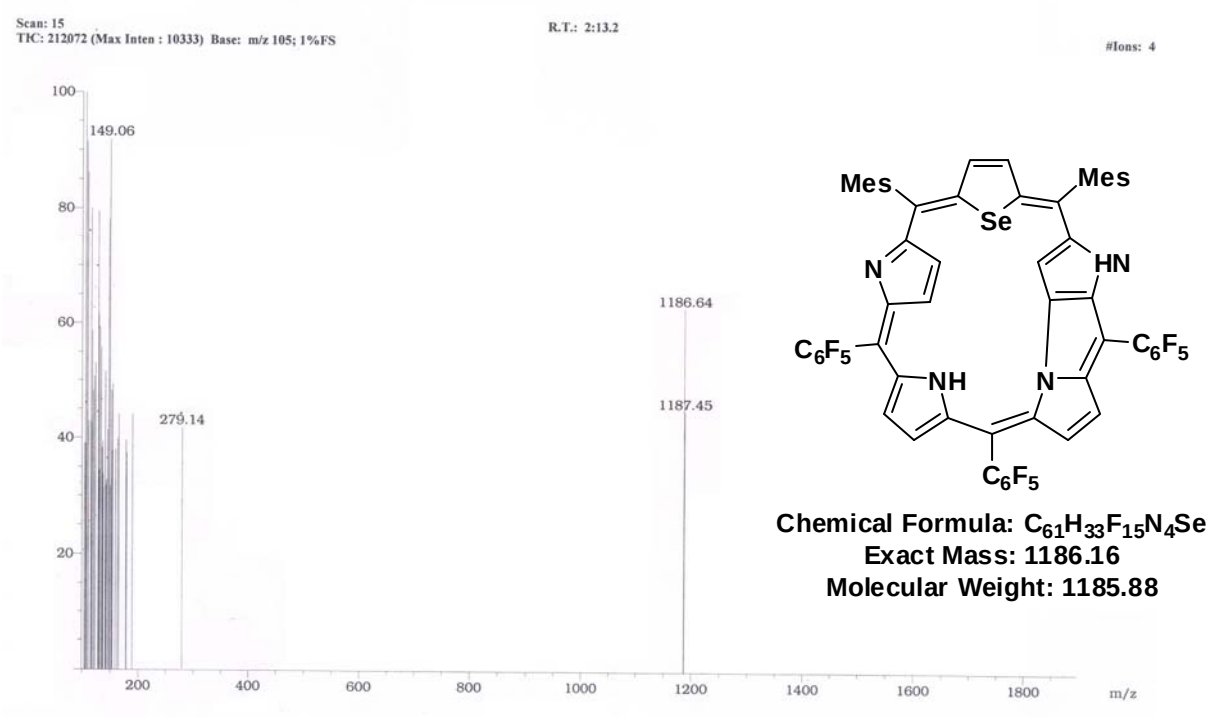


Figure 4: FAB Mass Spectrum of 10

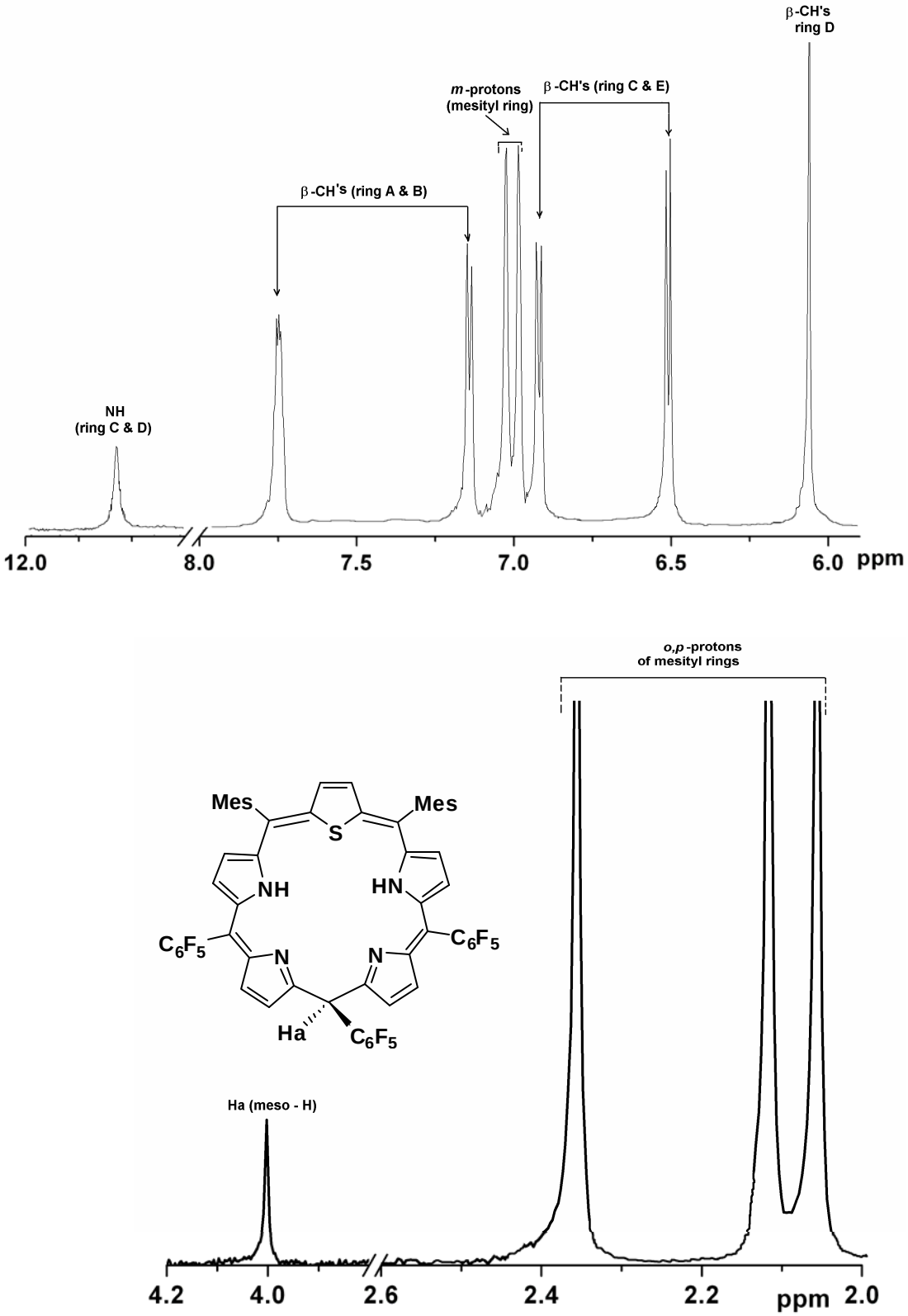
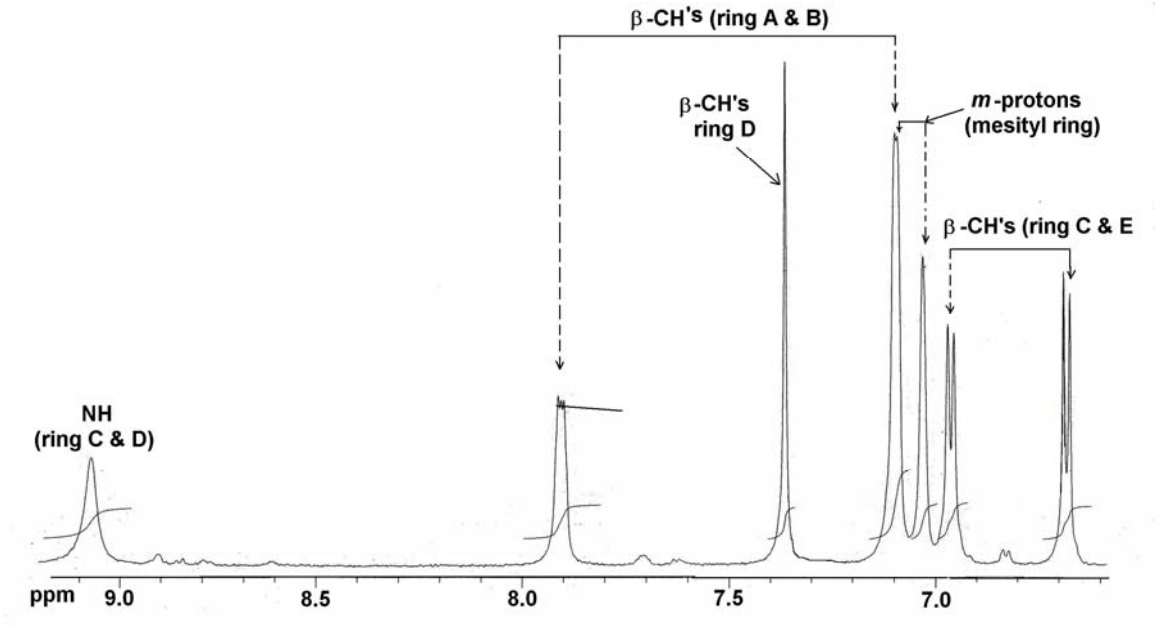


Figure 5: ^{1}H NMR spectrum of 7 in CD_2Cl_2 at 298 K

(assignments marked are obtained from ^{1}H-^{1}H COSY spectrum)



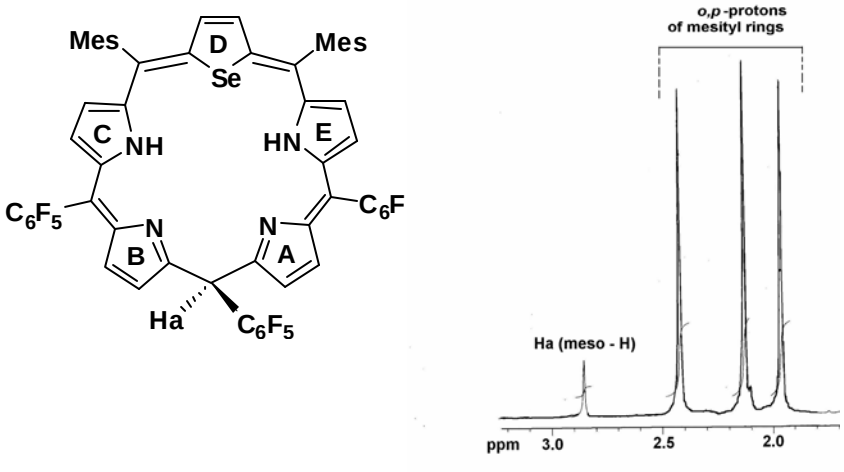


Figure 6: ^{1}H NMR spectrum of 8 in CD_2Cl_2 at 298 K
(assignments marked are obtained from ^{1}H-^{1}H COSY spectrum)

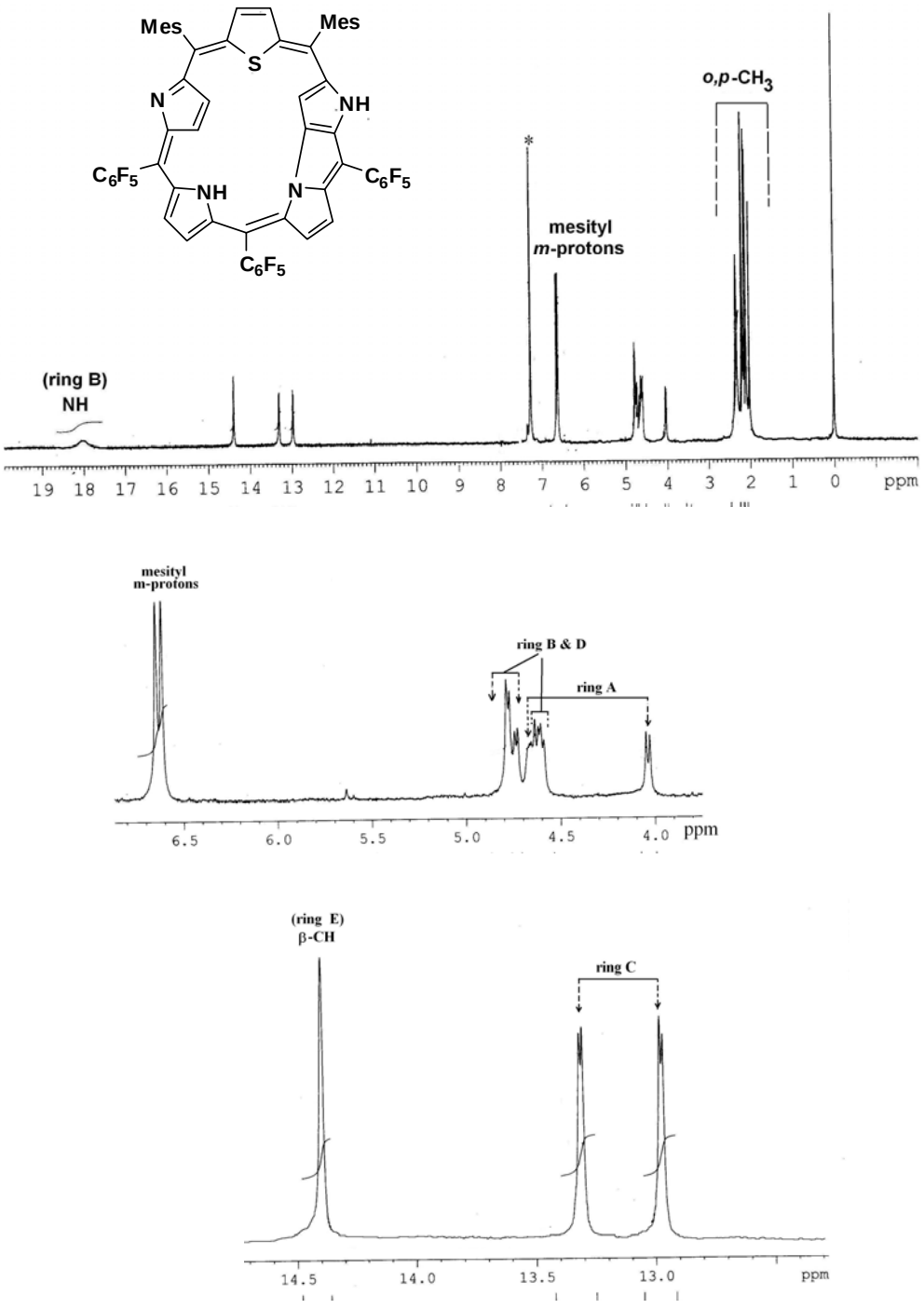


Figure 7: ^{1}H NMR spectrum of 9 in CD_2Cl_2 at 298 K

(assignments marked are obtained from ^{1}H-^{1}H COSY spectrum)

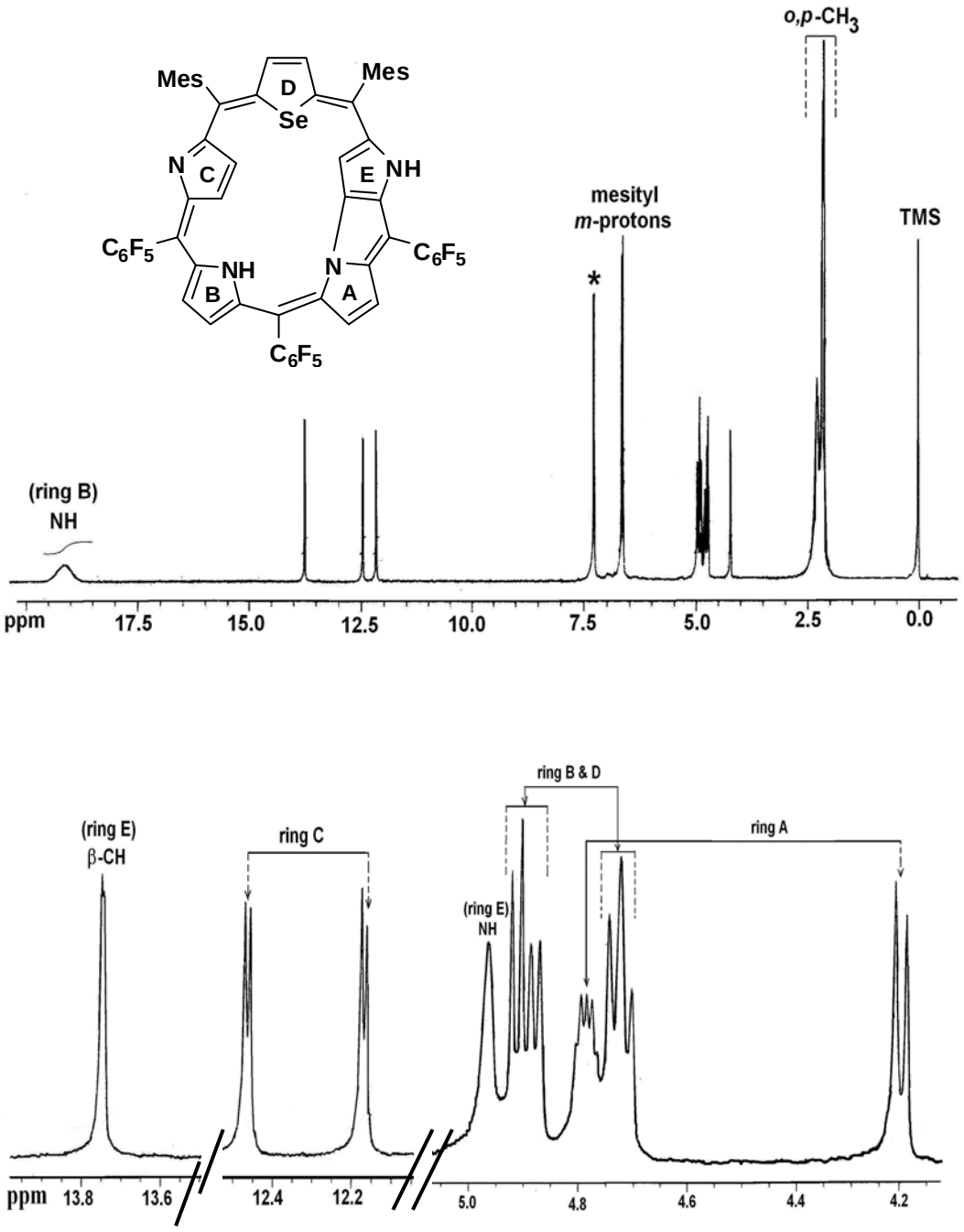


Figure 8: ^{1}H NMR spectrum of 10 in CD_2Cl_2 at 298 K
(assignments marked are obtained from ^{1}H-^{1}H COSY spectrum)

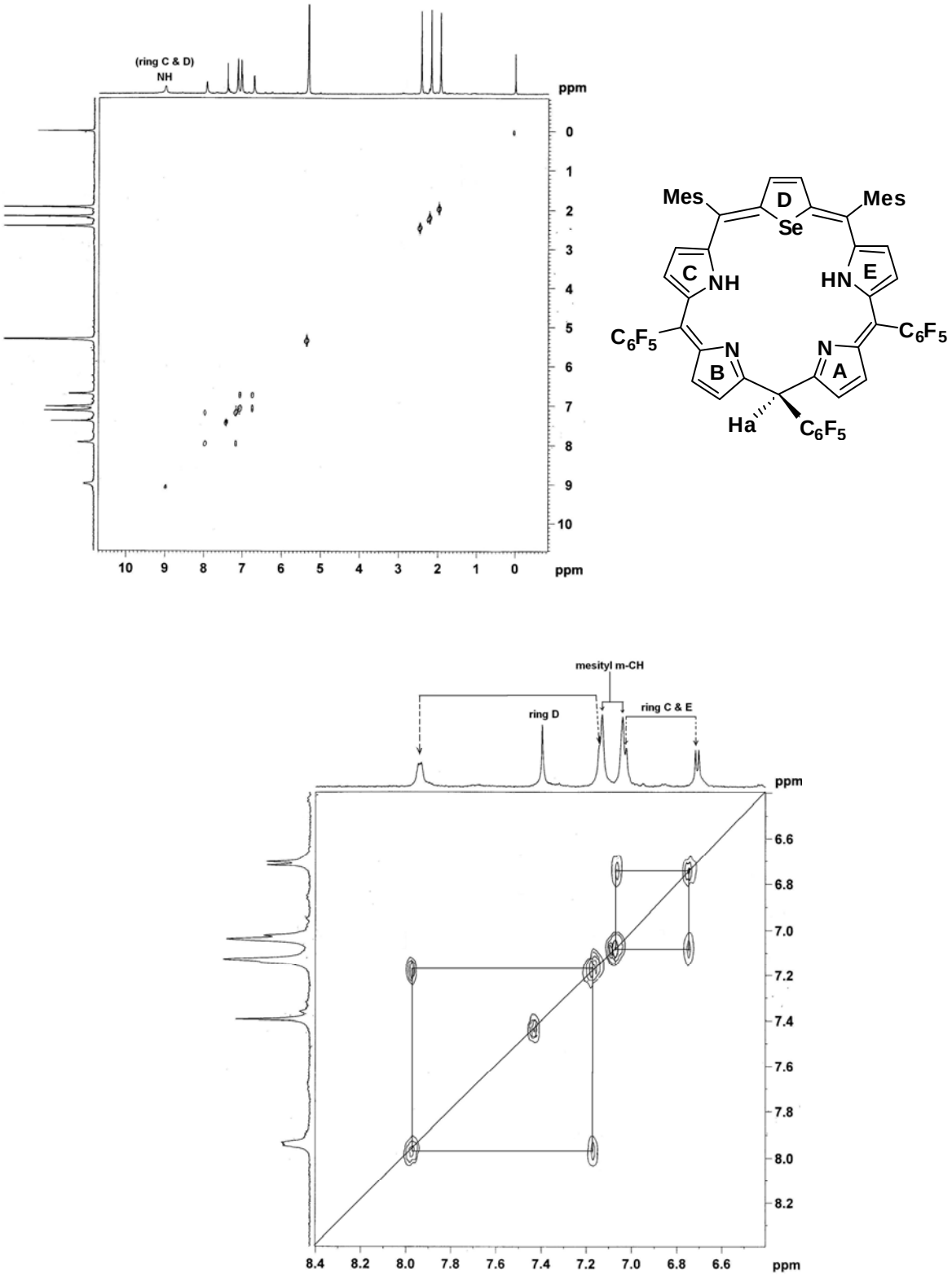


Figure 8: ^{1}H-^{1}H COSY spectrum of 8 in CD_2Cl_2 with assignments observed.

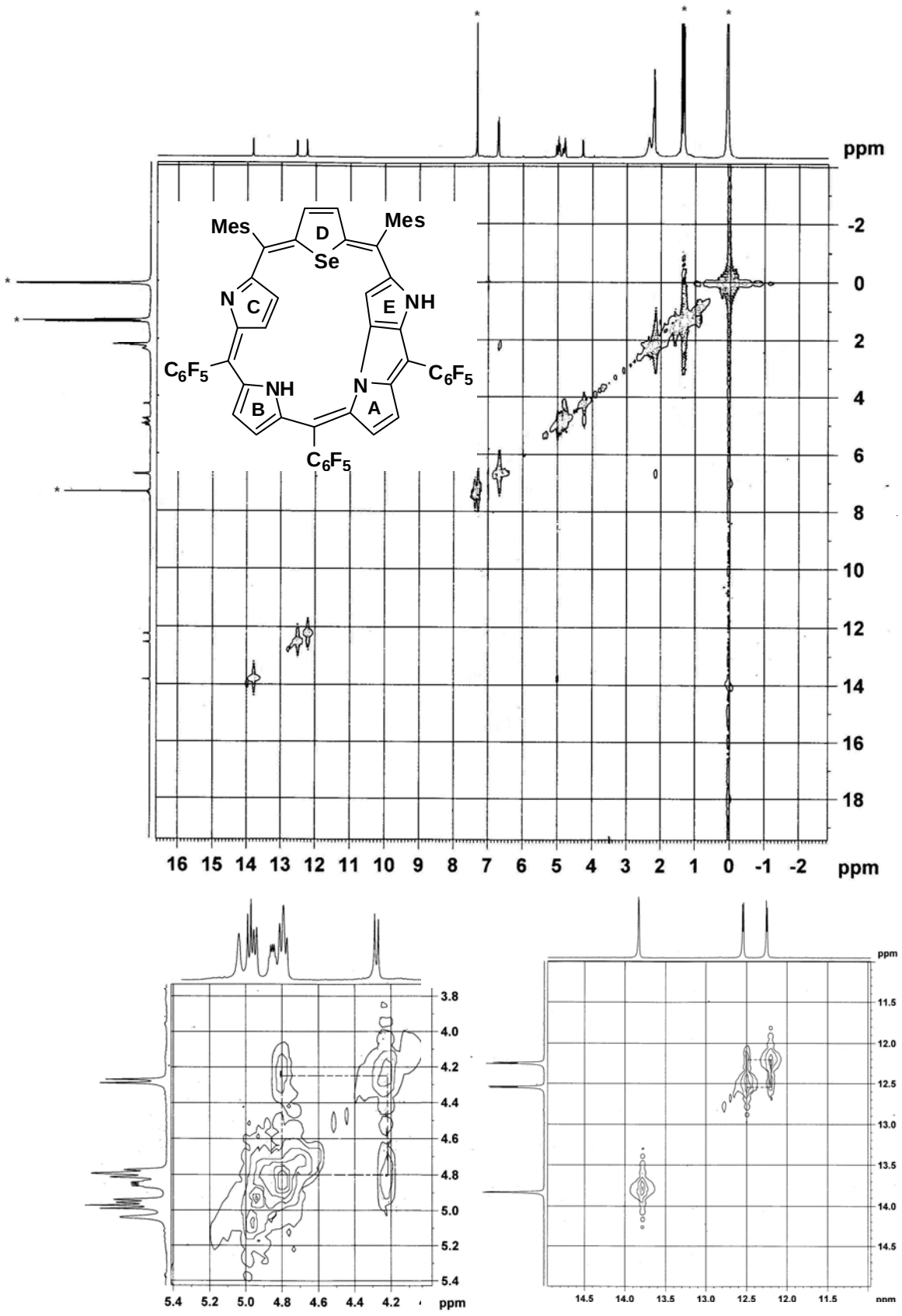


Figure 8: ^{1}H-^{1}H COSY spectrum of 10 in $CDCl_3$ with assignments observed.

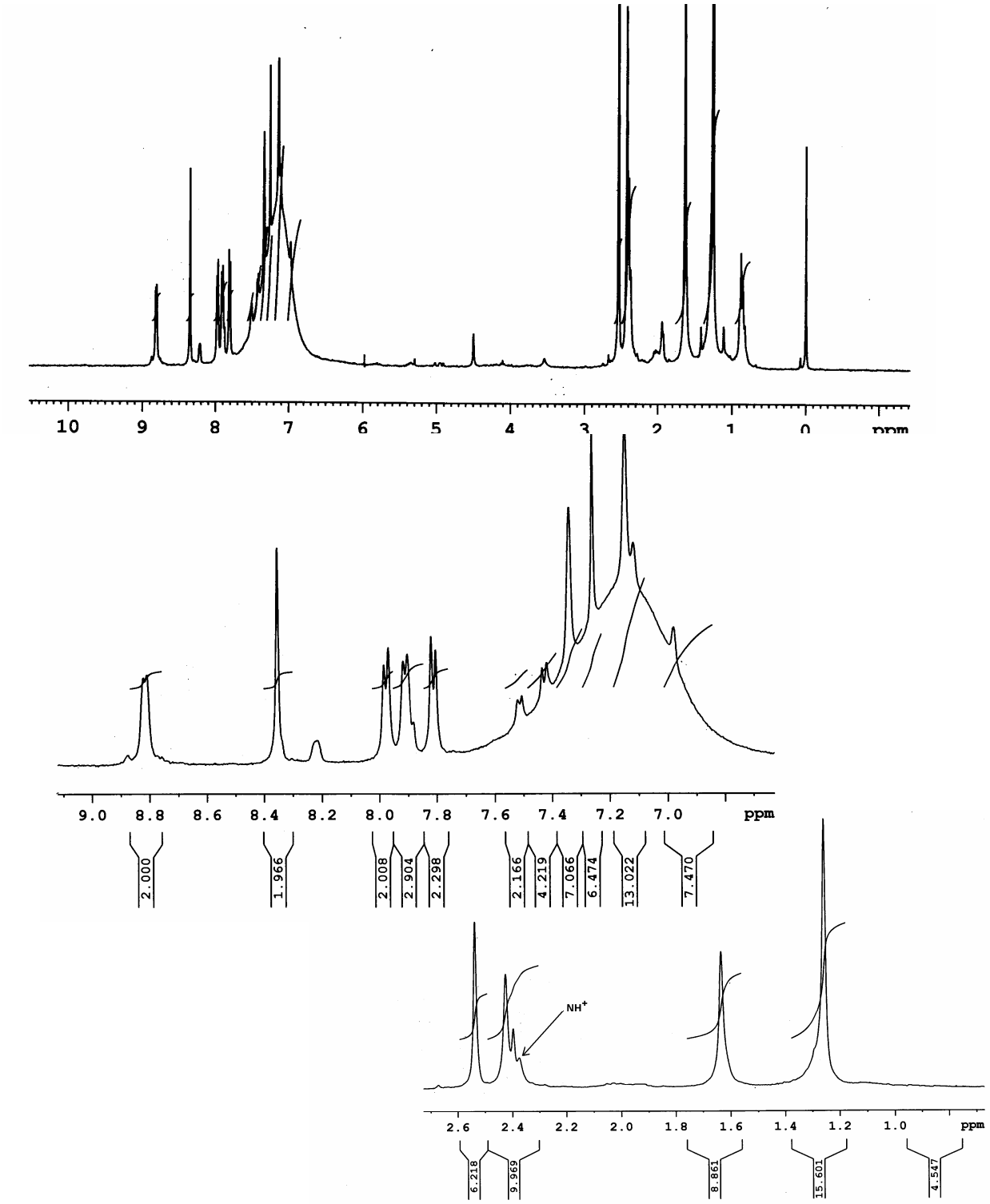


Figure 9: ^{1}H NMR spectrum of protonated form of 8 in $CDCl_3$ at 298 K

(Protonation experiments were carried out using diluted solution of TFA in $CDCl_3$ with 8)

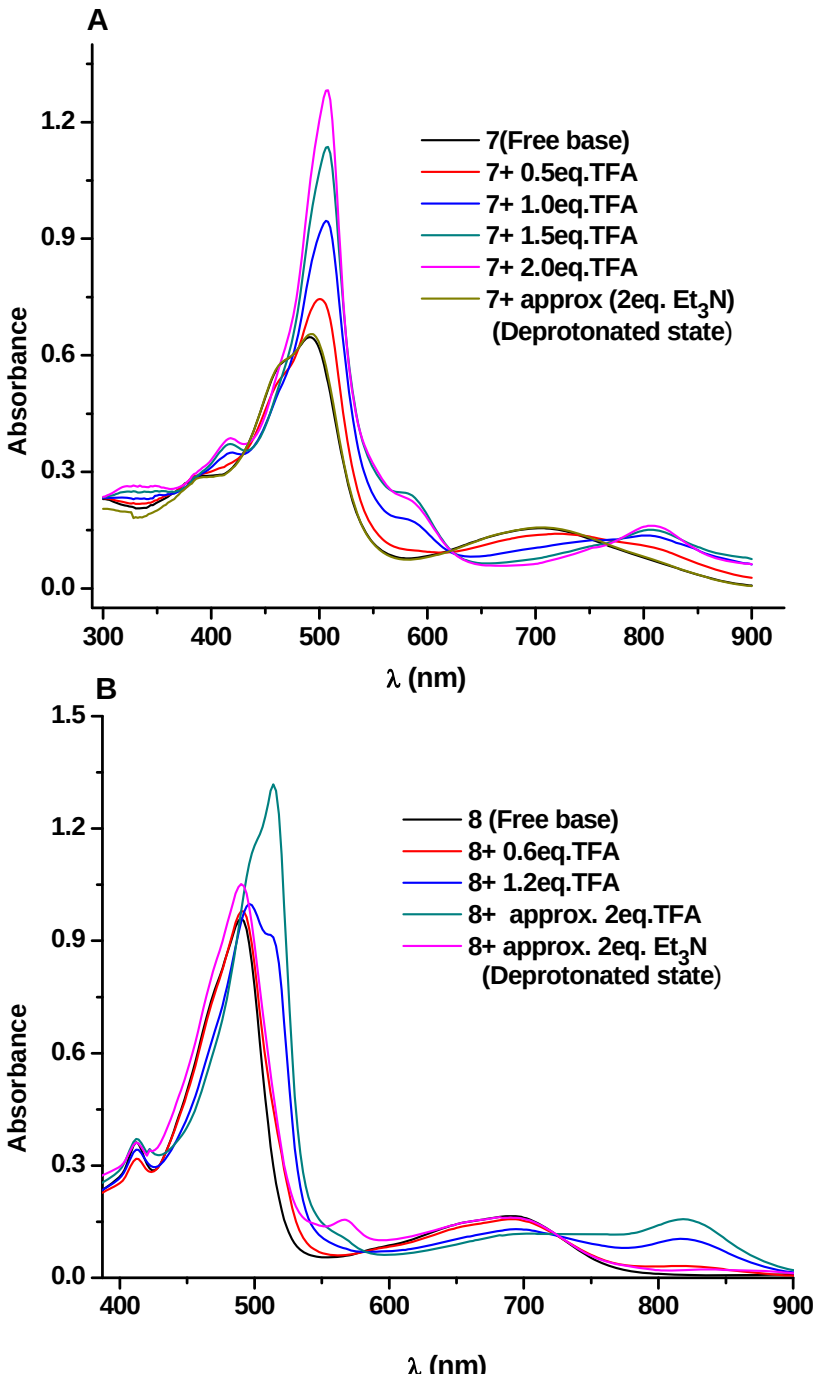


Figure 10: Electronic absorption spectra of (A) 7 (black), 7 with 0.28×10^{-4}M TFA (pink) and deprotonated 7 with 2eq. Et_3N (brown) (B) 8 (black), 8 with 0.23×10^{-4}M TFA (green) and deprotonated 8 with 2eq. Et_3N (pink) in CH_2Cl_2

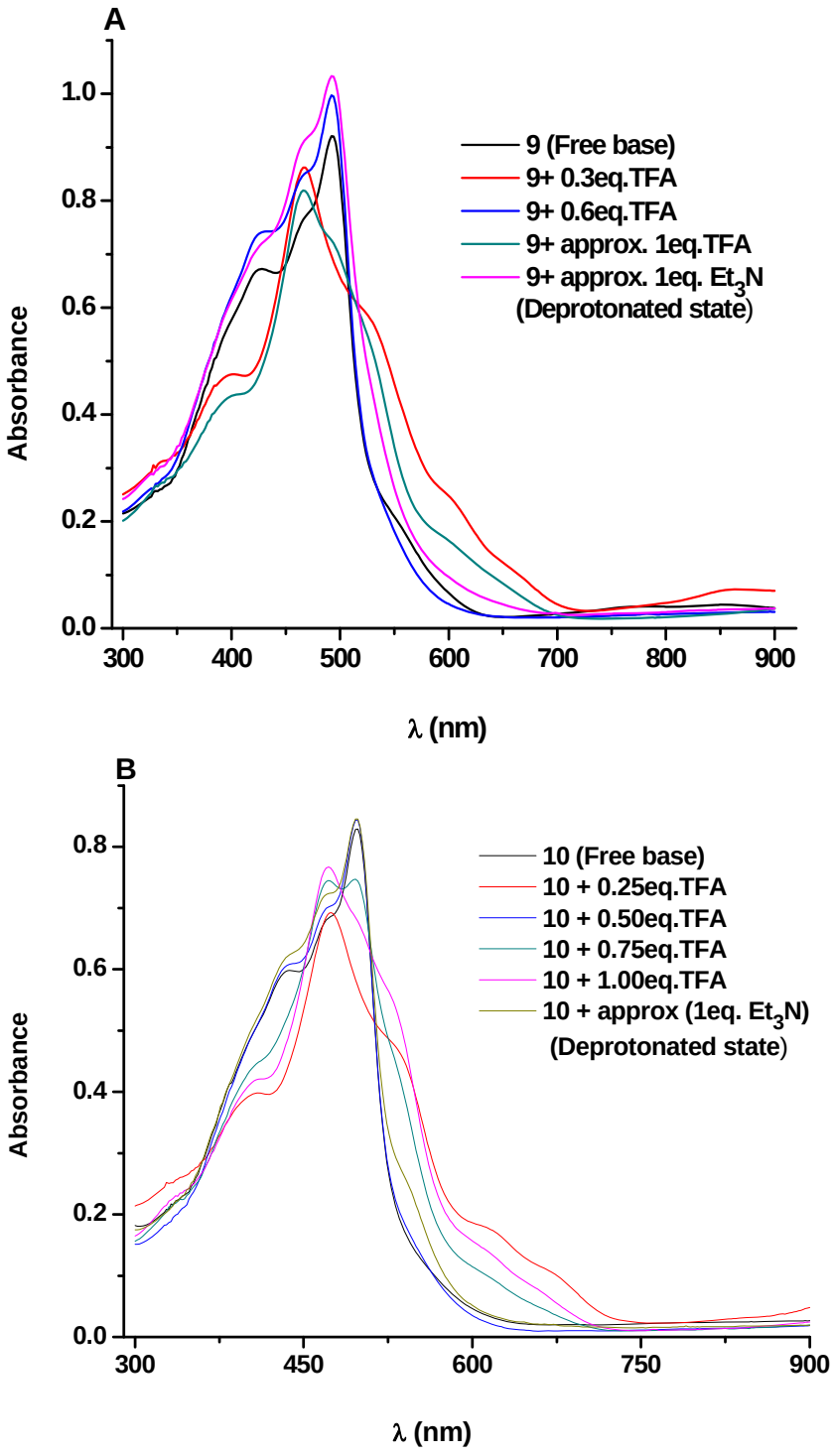


Figure 11: Electronic absorption spectra of (A) 9 (black), 9 with 0.06×10^{-4}M TFA (brown) and deprotonated 9 with 1eq.Et_3N (pink) (B) 10 (black), 10 with 0.14×10^{-4}M TFA (pink) and deprotonated 10 with 2eq. Et_3N (brown) in CH_2Cl_2

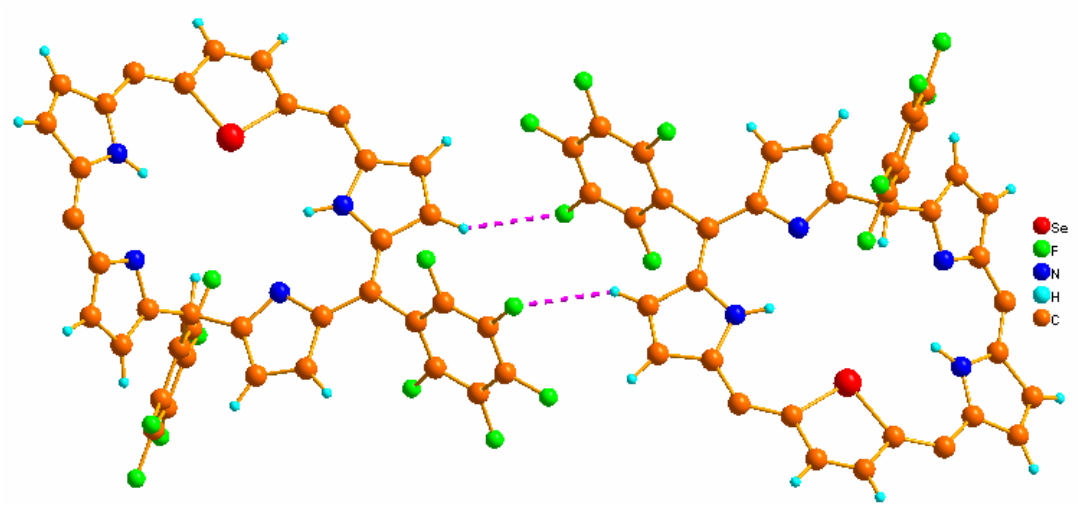


Figure 12 (a): View of a dimer through C—H---F interactions; C22—H22---F14; 2.59Å, 146.29(4)˚

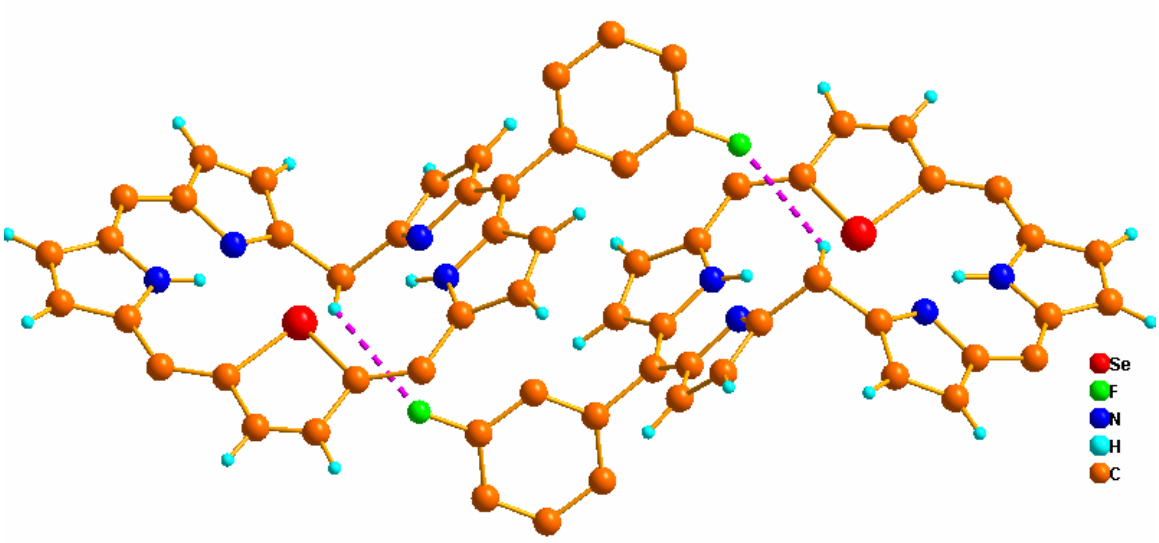


Figure 12 (b): View of a dimer through C—H---F interactions; C15—H15---F2; 2.816Å, 127.87(6)˚

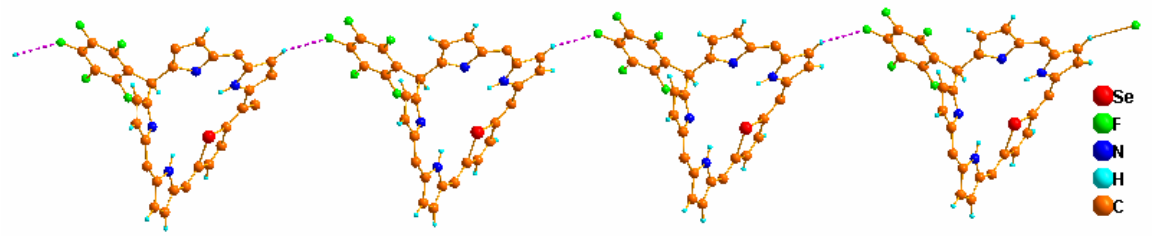


Figure 13 (a):One dimensional array through C—H---F interactions, C8—H8---F8; 2.696Å, 155.782˚

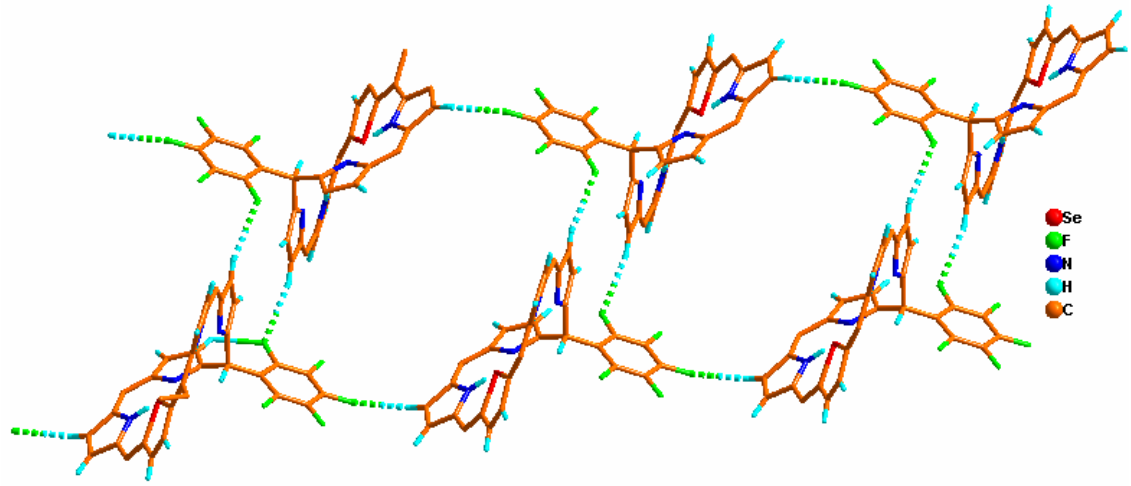


Figure 13 (b):Two dimensional helical structure through C—H---F interactions, C18—H18---F6; 2.738Å, 165.334˚ and C8—H8---F8; 2.696Å, 155.78(4)˚

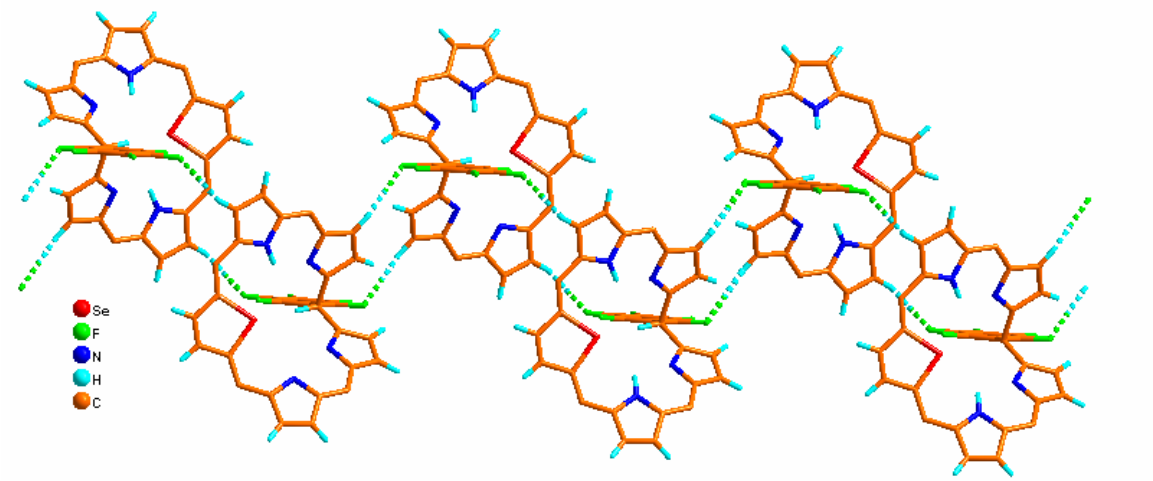


Figure 14 (a): Two dimensional network through C—H---F interactions, C18—H18---F6; 2.738Å, 165.334˚ and C23—H23---F9; 2.696Å, 161.13(4)˚

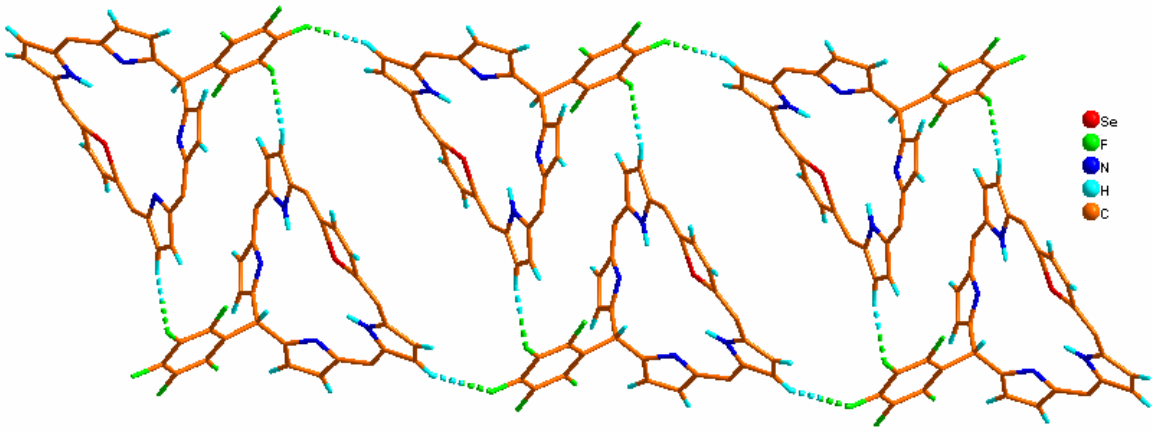


Figure 14 (b): Two dimensional network through C—H---F interactions, C8—H8---F9; 2.696Å, 155.78(4)˚ and C23—H23---F9; 2.696Å, 161.13(4)˚

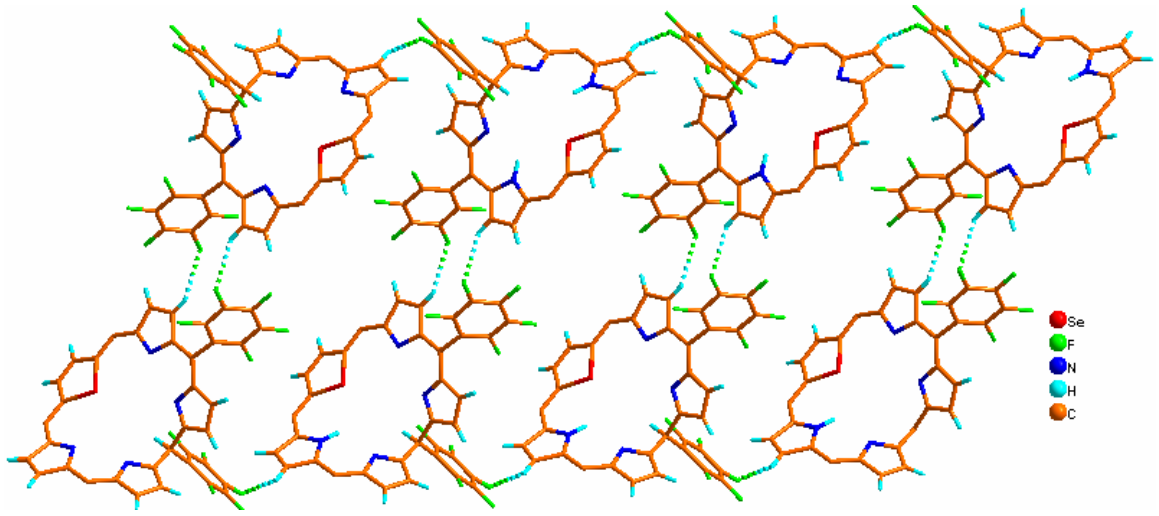


Figure 15 (a): Two dimensional network through C—H---F interactions, C8—H8---F9; 2.696Å, 155.78(4)˚ and C22—H22---F14; 2.592Å, 146.29(4)˚

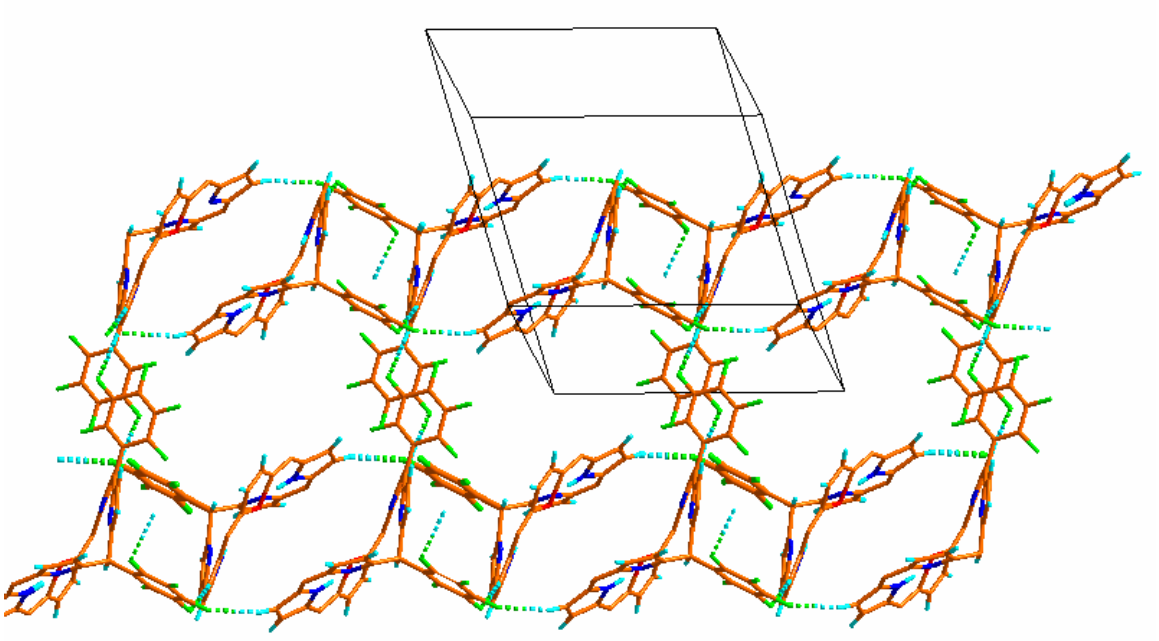


Figure 15 (b): View of 3D caged-like architecture through all combined C—H---F interactions

Table 1: Crystal data and structure refinement for 8

Identification code	25sepem	
Empirical formula	C_{67} H_{49} F_{15} N_4 Se	
Formula weight	1274.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.317 Å	α= 87.74°.
	b = 14.494 Å	β= 69.23°.
	c = 15.344 Å	γ = 74.18°.
Volume	2858.5 $Å^3$	
Z	2	
Density (calculated)	1.480 Mg/m^3	
Absorption coefficient	0.753 mm^{-1}	
F(000)	1296	
Crystal size	0.10 x 0.08 x 0.05 mm^3	
Theta range for data collection	1.97 to 26.00°.	
Index ranges	-16 ≤ h ≤ <=17, -17 ≤ k ≤ 17, -12 ≤ l ≤ 18	
Reflections collected	16276	
Independent reflections	11021 [R(int) = 0.0452]	
Completeness to theta = 26.00°	98.0 %	
Absorption correction	None	
Max. and min. transmission	0.9633 and 0.9285	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11021 / 0 / 721	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0803, wR2 = 0.1849	
R indices (all data)	R1 = 0.1277, wR2 = 0.2237	
Largest diff. peak and hole	1.302 and -0.716 $e.Å^{-3}$	