Supporting Information for

Metal Assisted Cyclomerization of Benzodipyrrins into Expanded Norroles, Aza-Heptalene and Acyclic Dimers

*Santosh C. Gadekar, Baddigam Kiran Reddy, Santosh P. Panchal and Venkataramanarao G. Anand**

Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune – 411008, Maharashtra, India

*Email: vg.anand@iiserpune.ac.in

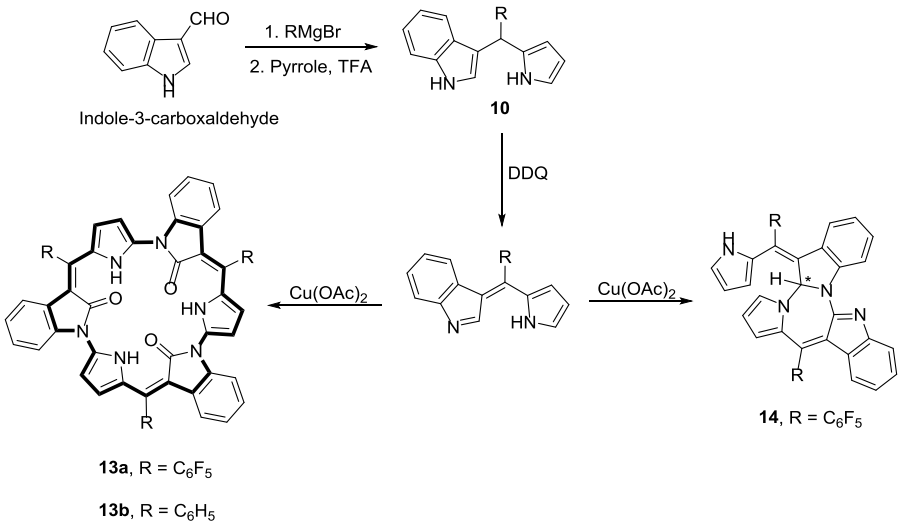
General Experimental Methods

All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry THF was obtained by refluxing and distillation over pressed Sodium metal. Column chromatography was performed on silica gel (230-400) in glass columns. ^{1}H NMR and ^{19}F NMR spectra were recorded either on a JEOL 400 MHz or Bruker 500 MHz spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $(CH_3)_2SO$ (δ = 2.50 ppm) or THF (δ = 1.73 ppm) or $(CH_3)_2CO$ (δ = 2.1 ppm) as internal reference for ^{1}H. High Resolution Mass spectra were obtained using WATERS G2 Synapt Mass Spectrometer. Electronic spectra were recorded on a Perkin-Elmer λ-900 ultraviolet−visible (UV−vis) spectrophotometer. Single crystals were grown in suitable organic solvent and Single crystal X-ray diffraction were performed at 100K on BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Quantum mechanical calculations were carried out on Gaussian 03 program suite using High Performance Computing Cluster facility of IISER PUNE. All calculations were carried out by Density Functional Theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G(d,p) basis set for all the atoms were employed in the calculations. To estimate the NICS(0) values at the center of the seven membered rings of molecular plane of all the macrocycles, the gauge independent atomic orbital(GIAO) method used based on the optimized geometries. The molecular structures obtained from single crystal analysis were used for geometry optimization.

Reference:

18. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Scheme 3a:



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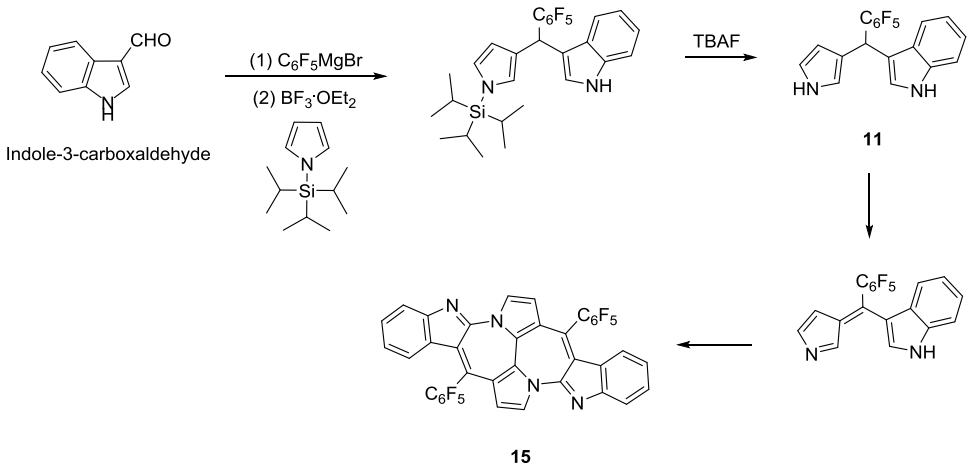

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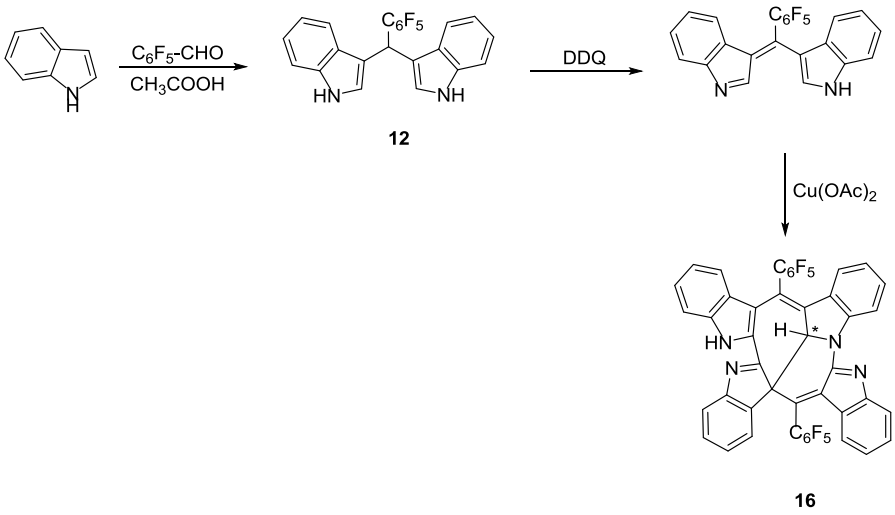
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CH3COOH
C6F5
HN
NH
12
DDQ
C6F5
N
NH
Cu(OAc)2
C6F5
HN
H
*
N
N
N
C6F5
16

Synthesis of N-Confused Monobenzo-Dipyrromethane (NCMB-DPM) 10

To a dissolved Indole-3-carboxaldehyde (1.00 g, 6.90 mmol, 1 equiv.) in 20 ml dry THF, pentafluorophenyl magnesium bromide (2.4 equiv.) was added and reaction mixture stirred overnight. The reaction was quenched with solution of saturated ammonium chloride and worked up with dichloromethane. Solvent were evaporated on rota evaporator. The carbinol (2.00 g, 6.39 mmol, 1 equiv.) obtained was condensed with pyrrole (22.00 ml, 319.49 mmol, 50 equiv.) using trifluoroacetic acid (0.05 ml, 0.64 mmol, 0.1 equiv.) in 100 ml round bottom flask under inert N_2 atmosphere. After 30 minute, 50 ml dichloromethane was added and organic layer extracted from 50 ml 0.1 N NaOH aqueous layer in dichloromethane, dried over sodium sulphate and solvent were evaporated in vacuo. The residue was chromatographed to get pure N-Confused Monobenzo Dipyrromethane (NCMB-DPM) **10** (1.30 gm, Yield = 56%).

^{1}H NMR (Acetone-d_6, 400MHz, 295K): δ = 6.00(m, 1H), 6.05(m, 1H), 6.15(s, 1H), 6.73(m, 1H), 6.97(m, 1H), 7.11(m, 2H), 7.26(d, J = 8.0 Hz, 1H), 7.41(d, J = 8.0 Hz, 1H), 9.95(bs, 1H, exchangeable with D_2O), 10.24(bs, 1H, exchangeable with D_2O); **^{13}C-NMR** (Acetone-d_6, 400MHz, 295K): δ = 31, 106, 107, 111, 113, 117, 118, 119, 121, 123, 126, 129 ppm; **HRMS** (EI): *m/z* calcd for $(C_{19}H_{11}F_5N_2\text{-}H)^+$ = 361.0764; observed = 361.0768

Synthesis of Expanded Norrole 13a

In 25 ml two neck round bottom flask, NCMB-DPM **10a** (0.50 g, 1.38 mmol, 1 equiv.) dissolved in 10 ml dry THF and DDQ (0.69 g, 3.04 mmol, 2.2 equiv.) was added under N_2 atmosphere. Copper(II) acetate (0.25 g, 1.3812 mmol, 1 equiv.) was added after 1 hour and reaction stirred overnight. Reaction mixture was directly chromatographed on silica gel (230-400 mesh) to get red colour **13a** (21 mg, 3.9%) in 10% ethyl acetate/n-hexane as eluent.

^{1}H NMR (THF-d_8, 400MHz, 295K): δ = 6.01(d, J = 8.0 Hz, 3H), 6.43(m, 3H), 6.68(m, 3H), 6.89(t, J = 8.0 Hz, 3H), 7.21(t, J = 8.0 Hz, 3H), 7.55(d, J = 8.0 Hz, 3H), 14.86(bs, 3H, exchangeable with D_2O); **^{13}C NMR** (THF-d_8, 400MHz, 295K)**:** δ = 103, 111, 115, 121, 122, 124, 125, 126, 127, 133, 138, 167 ppm; **^{19}F NMR** (THF-d_8, 376MHz, 295K): -162.27(t, J = 22.56 Hz, 6F), -154.56(t, J = 22.56 Hz, 3F), -142.51(d, J = 22.56 Hz, 6F); **HRMS** (EI): *m/z* calcd. for $(C_{57}H_{21}F_{15}N_6O_3)^+$ = 1122.1436, Observed = 1122.1387; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon)$L $mol^{-1}cm^{-1}$ = 271 nm (29580) and 440 nm (32211); **Crystal data:**$C_{62}H_{21}N_6F_{15}O_3$(M_r = 1182.85), monoclinic, space group *P 21/c (No.14)*, a = 8.6387(19), b = 14.094(3), c = 42.764(10)Å, α = 90.00, β = 91.418(5), γ = 90.00°, V = 5205(2)Å^3, Z = 4, ρ_{calcd} = 1.510 Mg/m^3, T = 100K, R_{int} (all data) = 0.1046, R_1(all data) = 0.1785, R_W (all data) = 0.2842, GOF = 1.554

Synthesis of Expanded Norrole 13b

NCMB-DPM **10b** (0.50 g, 1.84 mmol, 1 equiv.), DDQ (0.92 g, 4.04 mmol, 2.2 equiv.) and copper(II) acetate (0.33 g, 1.84 mmol, 1 equiv.) were reacted using similar protocol as mentioned above for **13a**. **13b** (19 mg, Yield 3.6%)

^{1}H NMR (Dichloromethane-d_2, 400MHz, 295K): δ = 5.50 (d, J = 8.0 Hz, 3H), 6.20 (m, 3H), 6.52 (m, 3H), 6.67 (t, J = 8.0 Hz, 3H), 7.08 (t, J = 8.0 Hz, 3H), 7.39 (m, 6H), 7.44(d, J = 8.0

Hz, 3H), 7.58 (m, 9H), 14.83(bs, 3H, exchangeable with D_2O); **HRMS** (EI): *m/z* calcd. for $(C_{57}H_{36}N_6O_3+H)^+$= 853.2927, Observed = 853.2905; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon)$L $mol^{-1}cm^{-1}$ = 271 nm (6177), 431 nm (11431); **Crystal data:**$C_{57}H_{36}N_6O_4$(M_r = 868.92), triclinic, space group *P -1 (No.2)*, *a* = 12.261(6), *b* = 13.380(6), *c* = 14.218(6)Å, α = 77.740(9), β = 81.518(10), γ = 89.721(12), V = 2253.5(18)$Å^3$, Z = 2, ρ_{calcd} = 1.281 Mg/m^3, *T* = 100K, R_{int} (all data) = 0.1061, R_1(all data) = 0.2447, R_W (all data) = 0.3764, GOF = 1.000

Synthesis of Acyclic Dimer 14

NCMB-DPM **10a** (0.20 g, 0.55 mmol, 1 equiv.) was dissolved in 200ml dry tetrahydrofuran in two neck 250ml round bottom flack under N_2 inert atmosphere and DDQ (0.28 g, 1.26 mmol, 2.2 equiv.) was added. After 1 hour copper(II) acetate (0.10 g, 0.56 mmol, 1 equiv.) added and reaction continued for overnight. Then reaction mixture was passed through a bed of basic alumina, a dark colour fraction obtained contains **13a** and **14**. The organic fraction was evaporated on rota evaporator to get crude reaction mixture which was further purified on silica gel (230-400 mesh) by column chromatography. First fraction gave red colour band **13a** (7 mg, 3.4%) and second band corresponds to **14** (8 mg, 4%).
^{1}H NMR (Acetone-d_6, 400MHz, 295K): δ = 5.62(s, 1H), 6.18(m, 1H), 6.32(m, 1H), 6.48(d, J = 8.0 Hz, 1H), 6.57(d, J = 8.0 Hz, 1H), 6.60(d, J = 8.0 Hz, 1H), 6.83(t, J = 8.0 Hz, 1H), 6.90-6.95(m, 2H), 7.02(s, 1H), 7.22(t, J = 8.0 Hz, 1H), 7.28(d, J = 8.0 Hz, 1H), 7.36-7.40(m, 2H), 8.23(d, J = 8.0 Hz, 1H), 10.10(bs, 1H, exchangeable with D_2O); **^{13}C NMR** (Acetone-d_6, 400MHz, 295K)**:** δ = 74, 111, 112, 116, 118, 121, 122, 124, 126, 127, 128, 129, 130, 143, 156, 158 ppm; **^{19}F NMR** (Acetone-d_6, 376MHz, 295K): -162.60(t, J = 22.56 Hz, 1F), -162.11(q, J = 22.56 Hz, 2F), -161.84(t, J = 22.56 Hz, 1F), -154.89 (d, J = 22.56 Hz, 1F), -154.65 (d, J = 18.80 Hz, 1F), -143.37 (d, J = 22.56 Hz, 1F), -142.75 (d, J = 22.56 Hz, 1F), -142.03 (d, J = 22.56 Hz, 1F) -141.88 (d, J = 22.56 Hz, 1F); **HRMS** (EI): *m/z* calcd. for $(C_{38}H_{16}N_4F_{10}+H)^+$= 719.1294, Observed = 719.1288; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon)$L $mol^{-1}cm^{-1}$ = 281 nm (16830), 325 nm (16658), 342 nm (16759), 391 nm (21354); **Crystal data:**$C_{41}H_{22}N_4F_{10}O$(M_r = 776.63), triclinic, space group *P -1 (No.2)*, *a* = 9.9304(18), *b* = 12.231(2), *c* = 14.545(3)Å, α = 75.314(4), β = 82.512(4), γ = 80.770(4)°, V = 1679.3(5)$Å^3$, Z = 2, ρ_{calcd} = 1.536 Mg/m^3, *T* = 100K, R_{int} (all data) = 0.0524, R_1(all data) = 0.1342, R_W (all data) = 0.1372, GOF = 0.941

Synthesis of Doubly N-Confused Monobenzo-Dipyrromethane (DNCMB-DPM) 11

The Indole-3-carboxaldehyde was reduced with pentafluorophenyl magnesium bromide to its carninol. Carbinol (2.50 g, 7.99 mmol, 1 equiv.) and 1-(triisopropylsilyl)pyrrole (4.45 g, 19.97 mmol, 2.5 equiv.) in 23 ml dry dichloromethane were stirred under N_2 at 0ºC for 10 min. Then $BF_3{\cdot}Et_2O$ (0.99 ml, 7.99 mmol, 1 equiv.) was added and reaction mixture stirred at 0ºC for 5 min. The reaction mixture was passed through basic alumina using dichloromethane as eluent and solvent evaporated in vacuo. The concentrated reaction mixture was directly subjected to excess of tetrabutyl ammonium fluoride (1 M in THF) for 90 min., deprotected reaction mixture quenched with water and extracted with dichloromethane. The combined organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue obtained was

purified by silica gel column chromatography using hexane/ethyl acetate eluent. The first fraction afforded NCMB-DPM **10a** (1.00 g, Yield = 35%) and second fraction gave Doubly N-Confused Monobenzo Dipyrromethane (DNCMB-DPM) **11** (1.40 g, Yield = 48%).
^{1}H NMR (Acetone-d_6, 400MHz, 295K): δ = 6.01(s, 1H), 6.17(s, 1H), 6.75(s, 1H), 6.79(m, 1H), 6.95(t, J = 8.0 Hz, 1H), 7.09(t, J = 8.0 Hz, 1H), 7.17(s, 1H), 7.29(d, J = 8.0 Hz, 1H), 7.39(d, J = 8.0 Hz, 1H), 9.97(bs, 1H, exchangeable with D_2O), 10.14(bs, 1H, exchangeable with D_2O); **^{13}C-NMR** (Acetone-d_6, 400MHz, 295K): δ = 31, 108, 111, 115, 116, 118, 119, 121, 122, 123, 127 ppm; **HRMS** (EI): *m/z* calcd for $(C_{19}H_{11}F_5N_2\text{-}H)^+$ = 361.0764; observed = 361.0769

Synthesis of Aza-Heptalene 15

The compound **15** was synthesized by applying similar procedure as used for **13a**. DNCMB-DPM **11** (0.70 g, 1.93 mmol, 1 equiv.) was oxidized to its dipyrrin using DDQ (0.97 g, 4.25 mmol, 2.2 equiv.) in 20 ml dry THF and further reaction with copper(II) acetate (0.35 g, 1.93 mmol, 1 equiv.) under goes oxidative cyclodimerization to compound **15** (7 mg, Yield = 1%).
^{1}H NMR (Dichloromethane-d_2, 400MHz, 295K): δ = 6.35(d, J = 8.0 Hz, 2H), 6.94(d, J = 4.0 Hz, 2H), 7.13(t, J = 8.0 Hz, 2H), 7.48(t, J = 8.0 Hz, 2H), 7.71(d, J = 8.0 Hz, 2H), 9.35(d, J = 4.0 Hz, 2H); **^{13}C NMR** (Dichloromethane-d_2, 400MHz, 295K)**:** δ = 114, 120, 121, 122, 123, 124, 125, 126, 128, 129, 152, 154 ppm; **^{19}F NMR** (Dichloromethane-d_2, 376MHz, 295K): -161.39(t, J = 18.80 Hz, 4F), -153.44(t, J = 18.80 Hz, 2F), -142.88(d, J = 18.80 Hz, 4F); **HRMS** (EI): *m/z* calcd. for $(C_{38}H_{12}N_4F_{10}+H)^+$ = 715.0981, Observed = 715.0965; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon)$L $mol^{-1}cm^{-1}$ = 322 nm (17900), 388 nm (14420), 503 nm (7460), 540 nm (7960); **Crystal data:**$C_{38}H_{12}N_4F_{10}$(M_r = 714.52), triclinic, space group *P -1(No.2)*, *a* = 6.799(3), *b* = 8.219(3), *c* = 13.376(4)Å, *α* = 82.308(9), *β* = 75.542(7), *γ* = 83.754(10)°, V = 715.1(4)$Å^3$, Z = 1, ρ_{calcd} = 1.659 Mg/m^3, *T* = 100K, R_{int} (all data) = 0.1119, R_1(all data) = 0.1656, R_W (all data) = 0.3393, GOF = 1.923

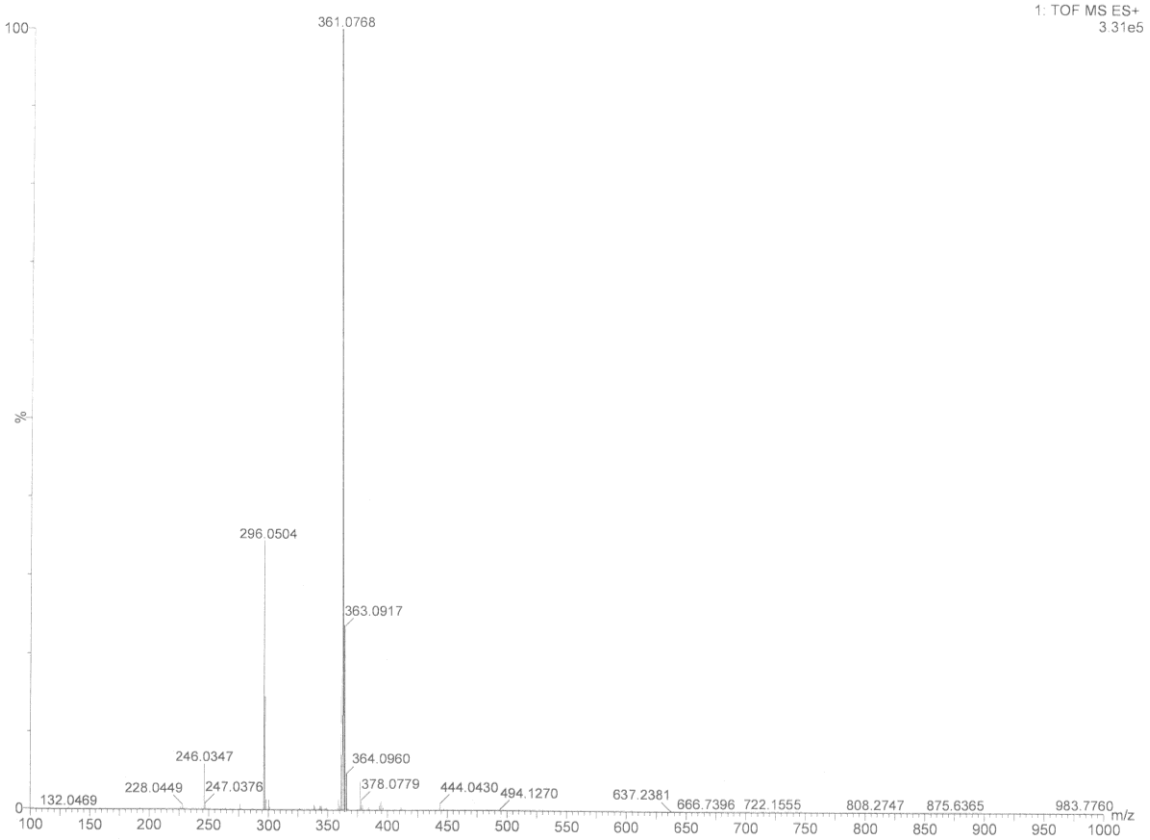
Synthesis of Doubly N-Confused Dibenzo-Dipyrromethane (DNCDB-DPM) 12

The Indole (2.34 g, 20.00 mmol, 2 equiv.) was condensed with pentafluorobenzaldehyde (1.96 g, 10.00 mmol, 1 equiv.) in 50 ml acetic acid by refluxing for 24 hours under inert N_2 atmosphere. Then the reaction mixture was evaporated and residue purified on silica gel (100-200 mesh). The colourless compound Doubly N-Confused Dibenzo Dipyrromethane (DNCDB-DPM) **12** (4.00 gm, Yield = 97%) was obtained.
^{1}H NMR (Acetone-d_6, 400MHz, 295K): δ = 6.37(s, 1H), 6.98(m, 2H), 7.14(m, 4H), 7.37(d, J = 8.0 Hz, 2H), 7.42(d, J = 8.0 Hz, 2H), 10.20(bs, 2H, exchangeable with D_2O); **^{13}C-NMR** (Acetone-d_6, 400MHz, 295K): δ = 29, 111, 114, 118, 119, 121, 124, 127, 137 ppm; **HRMS** (EI): *m/z* calcd for $(C_{23}H_{13}F_5N_2\text{-}H)^+$ = 411.0921; observed = 411.0923

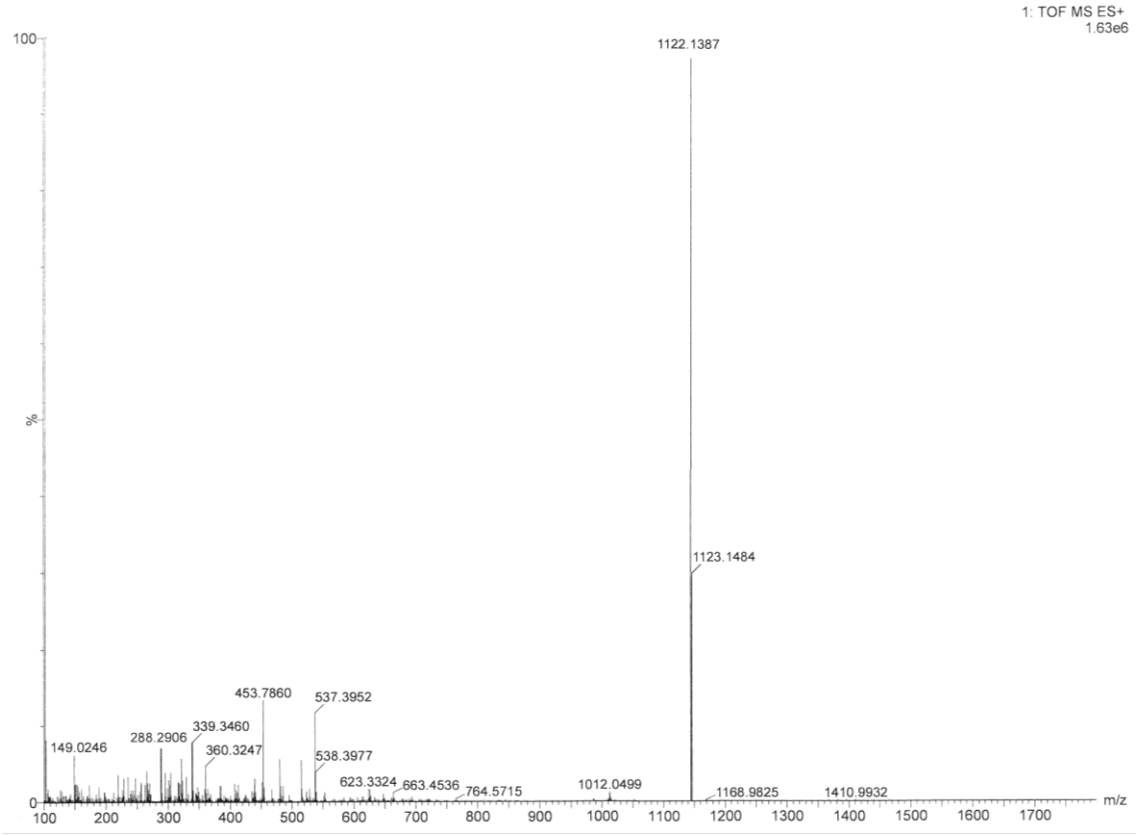
Synthesis of Acyclic Dimer 16

In a 250 ml round bottom flask, under inert atmosphere DNCDB-DPM **12** (1.66 g, 4.03 mmol, 1 equiv.) was dissolved in 100ml dry THF and DDQ (2.01 g, 8.86 mmol, 2.2 equiv.) was added. After 1 hour, copper(II) acetate (0.73 g, 4.03 mmol, 1 equiv.) was added and reaction continued for overnight. Then brown colour compound **16** (50 mg, 3%) was isolated by repetitive chromatographic purification.

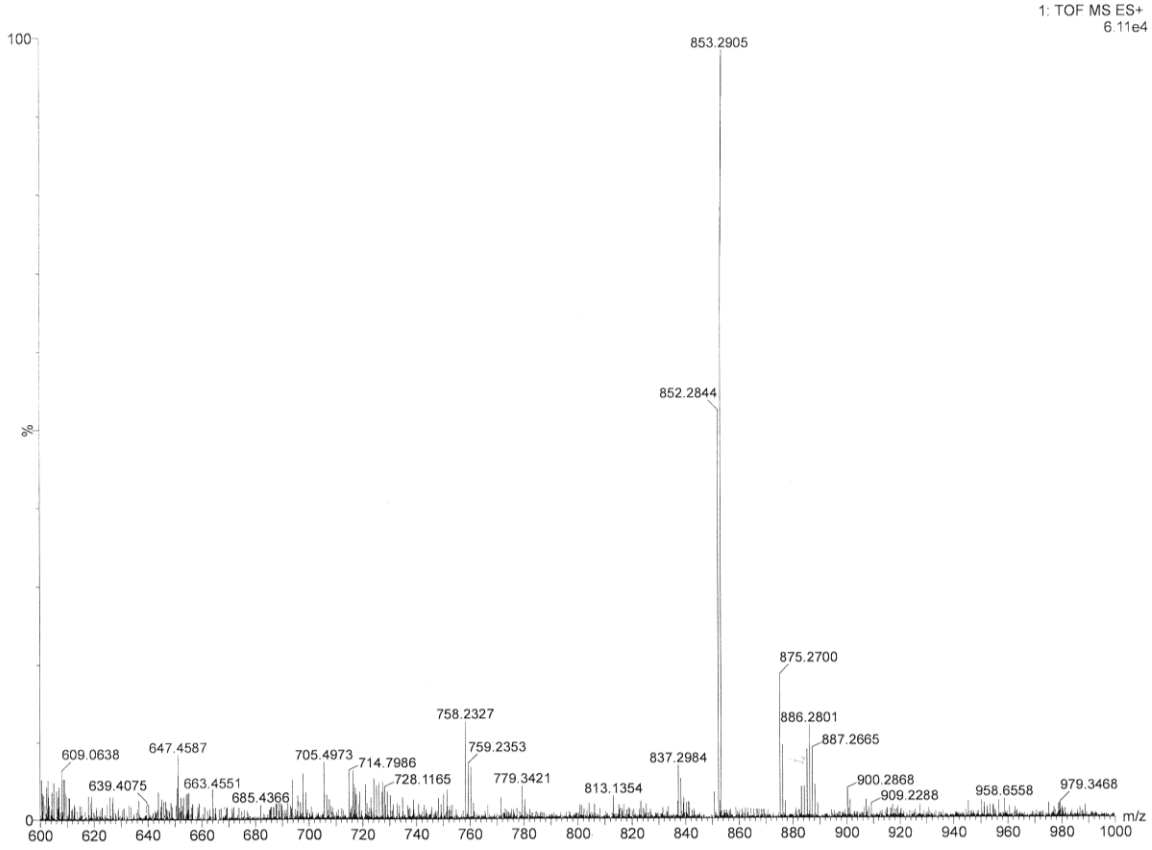
^{1}H NMR (Acetone-d_6, 400MHz, 295K): δ = 6.49(s, 1H), 6.62(d, J = 8.0 Hz, 1H), 6.76-6.82(m, 3H), 6.89(t, J = 8.0 Hz, 1H), 6.99(t, J = 8.0 Hz, 1H), 7.10-7.17(m, 2H), 7.26-7.35(m, 4H), 7.45-7.50(m, 2H), 7.60(d, J = 8.0 Hz, 1H), 8.26(d, J = 8.0 Hz, 1H), 11.81(bs, 1H, exchangeable with D_2O); **^{13}C NMR** (Acetone-d_6, 400MHz, 295K)**:** δ = 69, 108, 113, 114, 119, 121, 122, 125, 126, 128, 130, 131 ppm; **^{19}F NMR** (Acetone-d_6, 376MHz, 295K): -162.69(m, 3F), -159.37(t, J = 22.56 Hz, 1F), -155.28(t, J = 22.56 Hz, 1F), -153.05 (t, J = 22.56 Hz, 1F), -141.33 (d, J = 22.56 Hz, 1F), -140.89 (d, J = 22.56 Hz, 1F), -140.24 (d, J = 22.56 Hz, 1F), -136.88 (d, J = 22.56 Hz, 1F); **HRMS** (EI): *m/z* calcd. for $(C_{46}H_{18}N_4F_{10}+H)^+$= 817.1450, Observed = 817.1436; **UV-Vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon)$L $mol^{-1}cm^{-1}$ = 283 nm (1436), 338 nm (755); **Crystal data:**$C_{46}H_{18}N_4F_{10}$(M_r = 816.64), monoclinic, space group *P 21/n (No.14)*, a = 10.144(2), b = 12.998(3), c = 25.579(5)Å, α = 90.00, β = 96.312(4), γ = 90.00°, V = 3352.2(12)Å^3, Z = 4, ρ_{calcd} = 1.618 Mg/m^3, T = 100K, R_{int} (all data) = 0.0586, R_1(all data) = 0.1357, R_W (all data) = 0.1830, GOF = 0.972



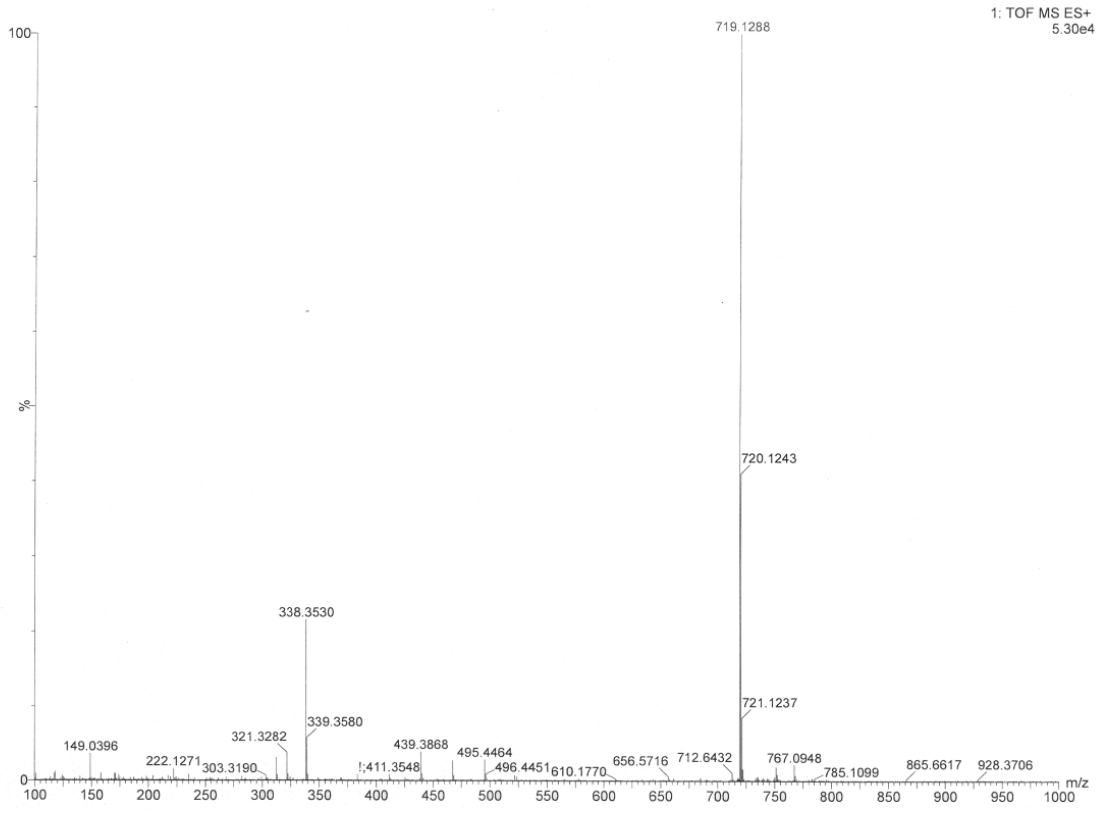
S1: HR-ESI-TOF mass spectrum of **10**.



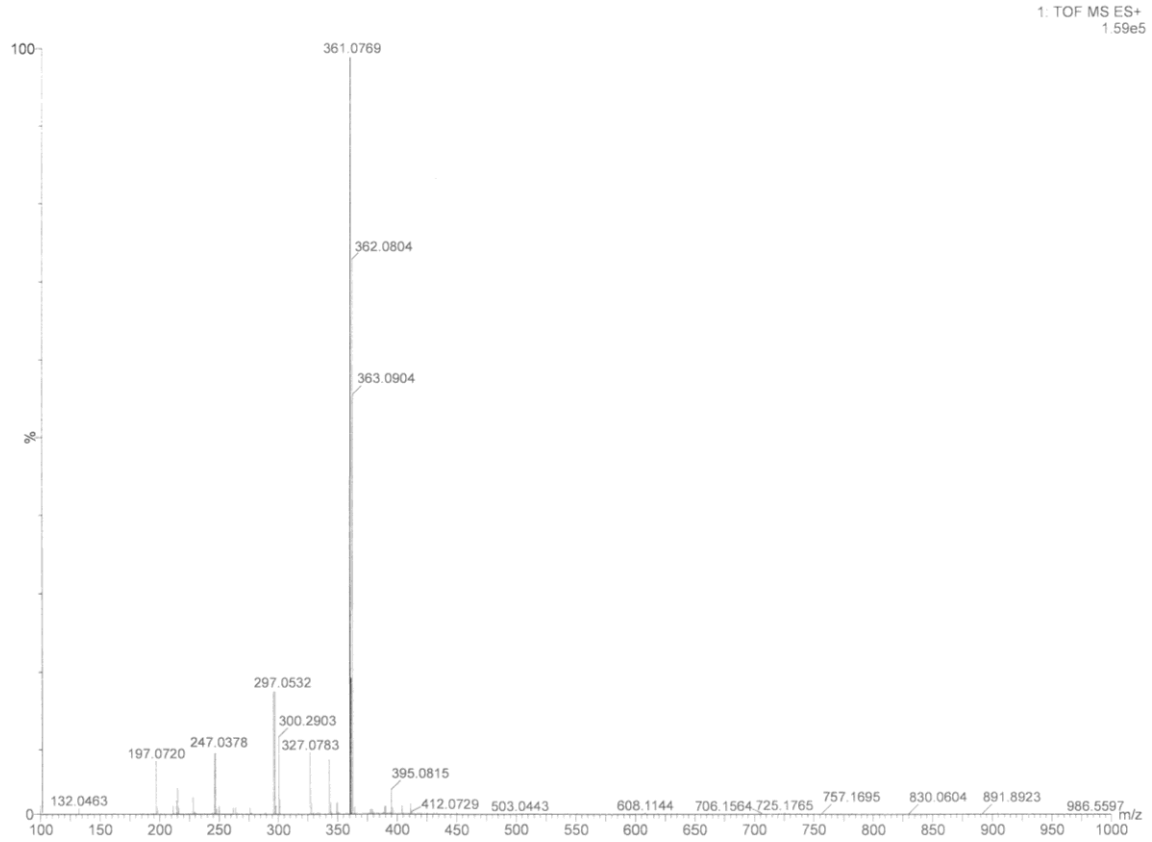
S2: HR-ESI-TOF mass spectrum of **13a**.



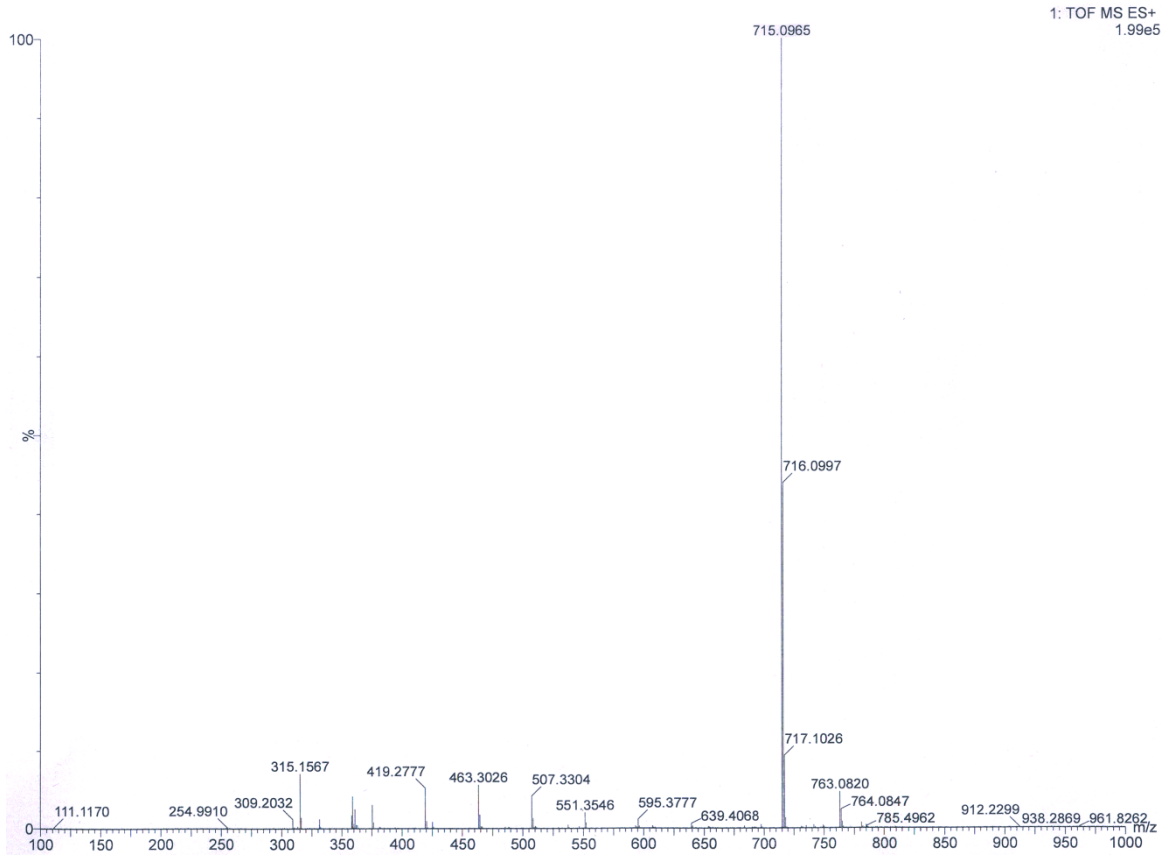
S3: HR-ESI-TOF mass spectrum of **13b**.



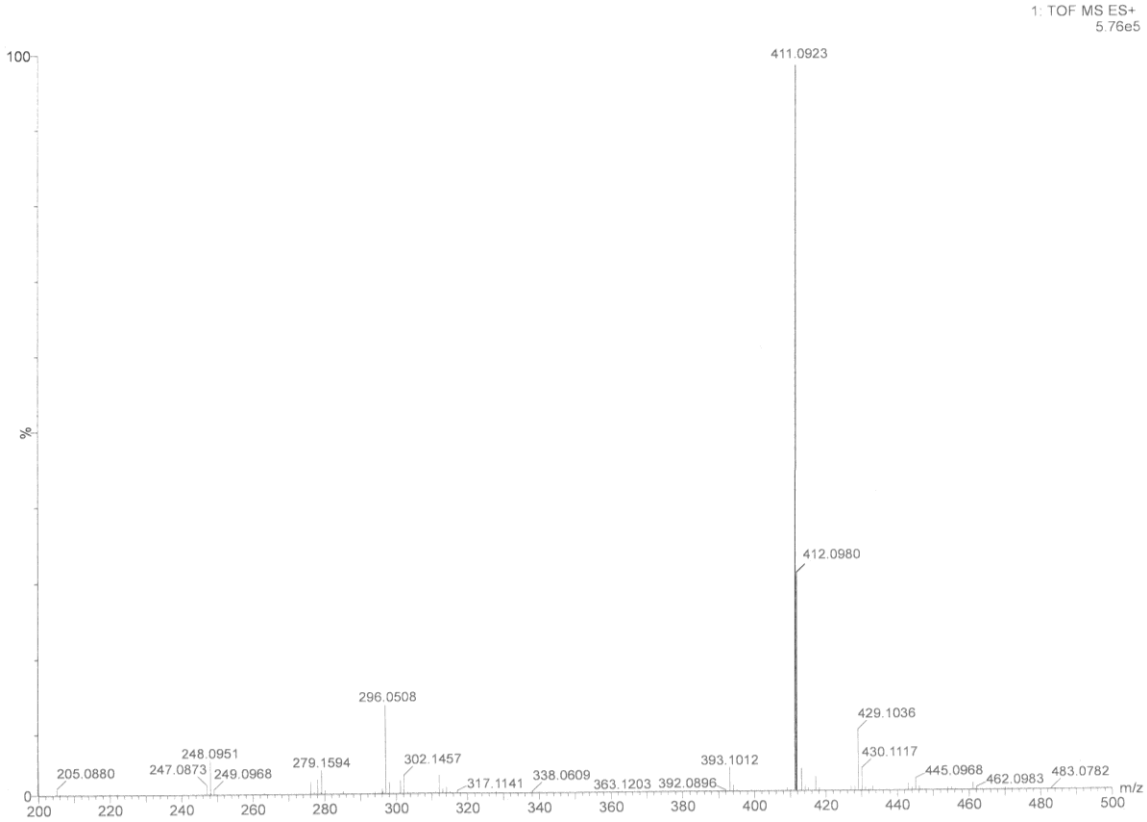
S4: HR-ESI-TOF mass spectrum of **14**.



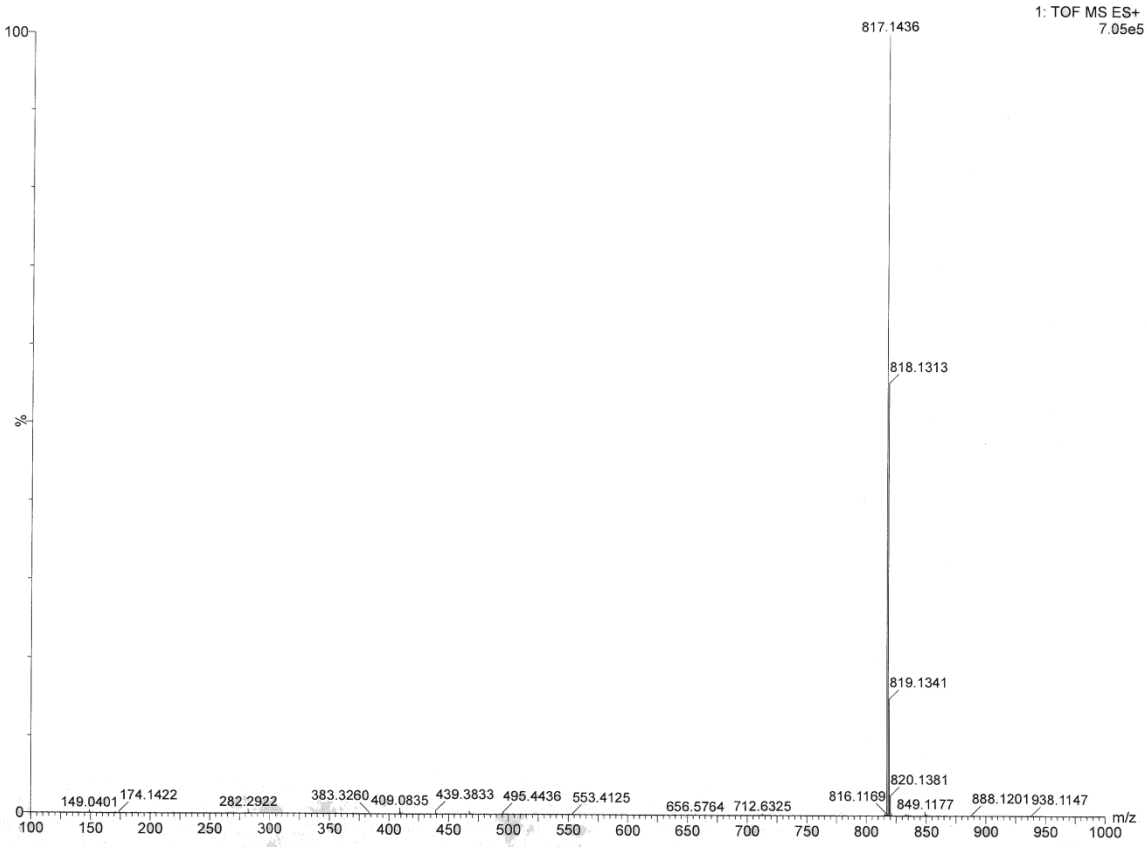
S5: HR-ESI-TOF mass spectrum of **11**.



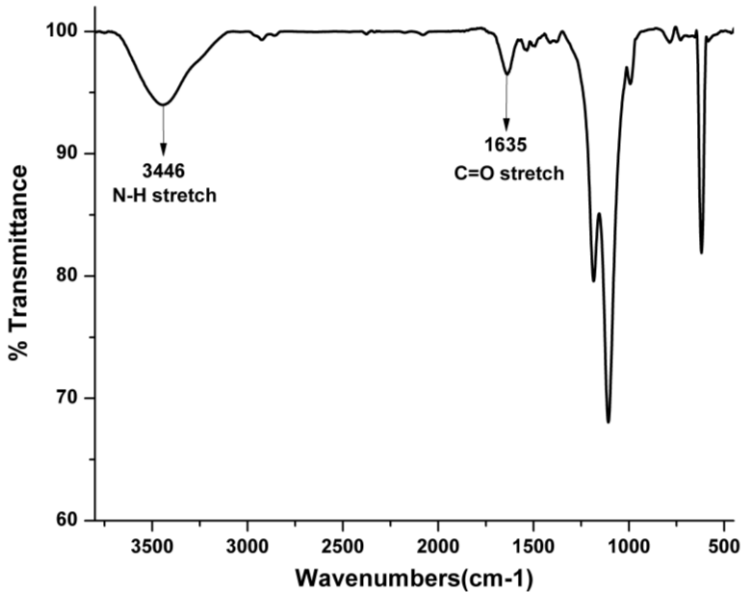
S6: HR-ESI-TOF mass spectrum of **15**.



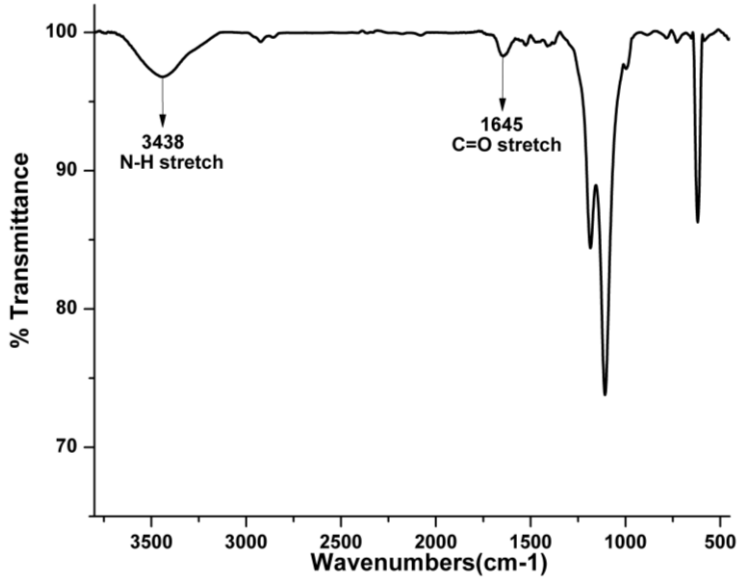
S7: HR-ESI-TOF mass spectrum of **12.**



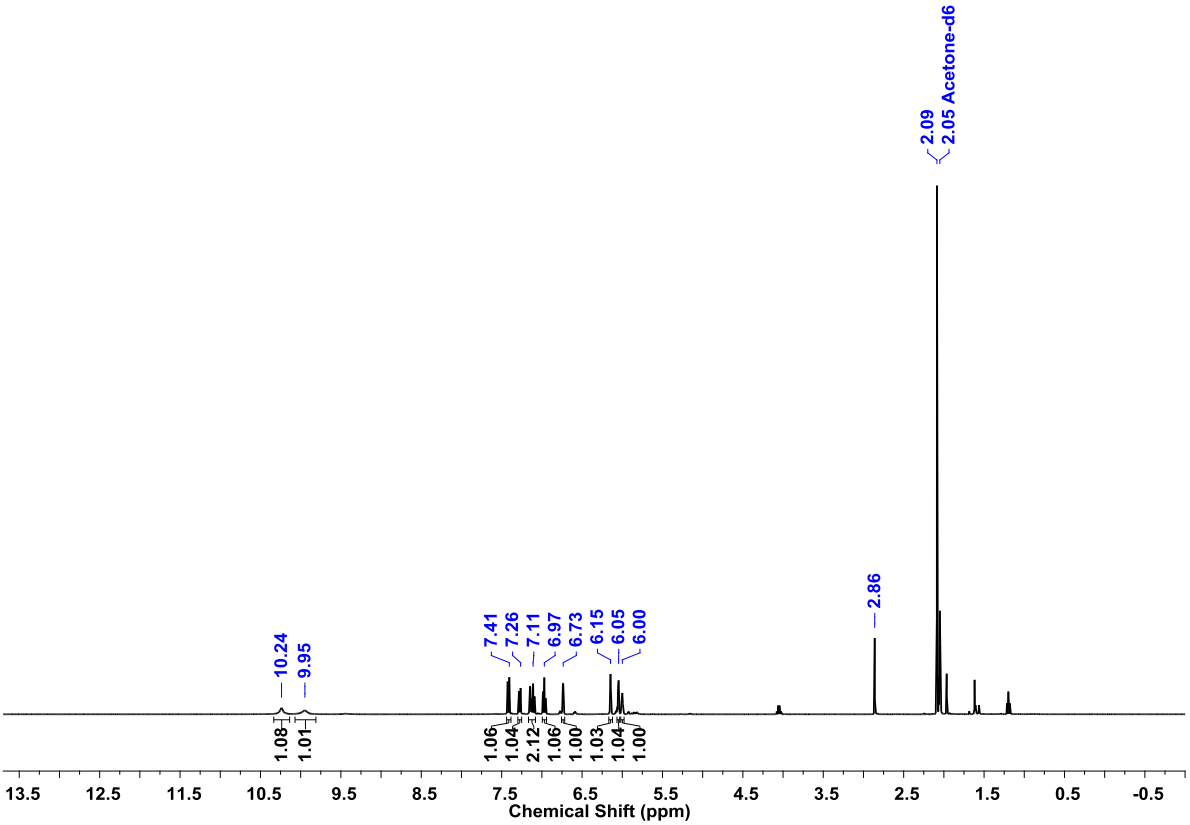
S8: HR-ESI-TOF mass spectrum of **16.**



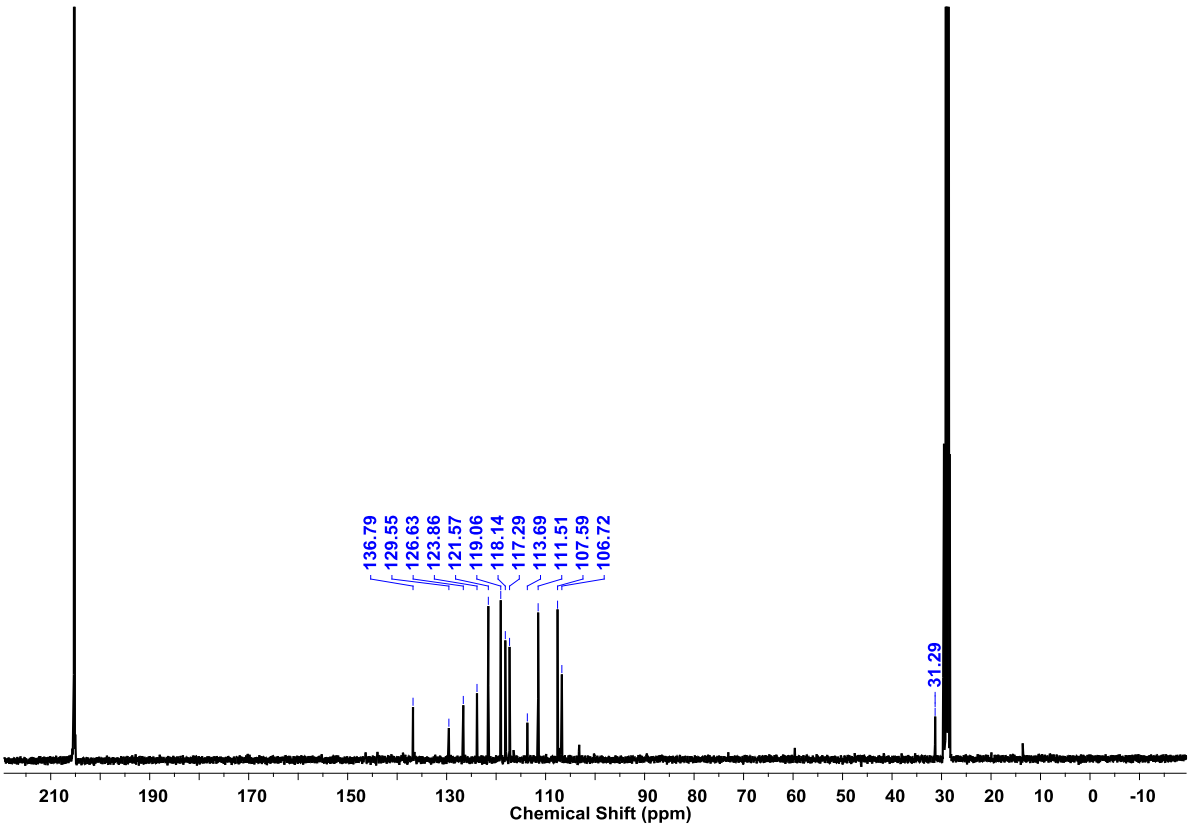
S9: IR spectrum of **13a**.



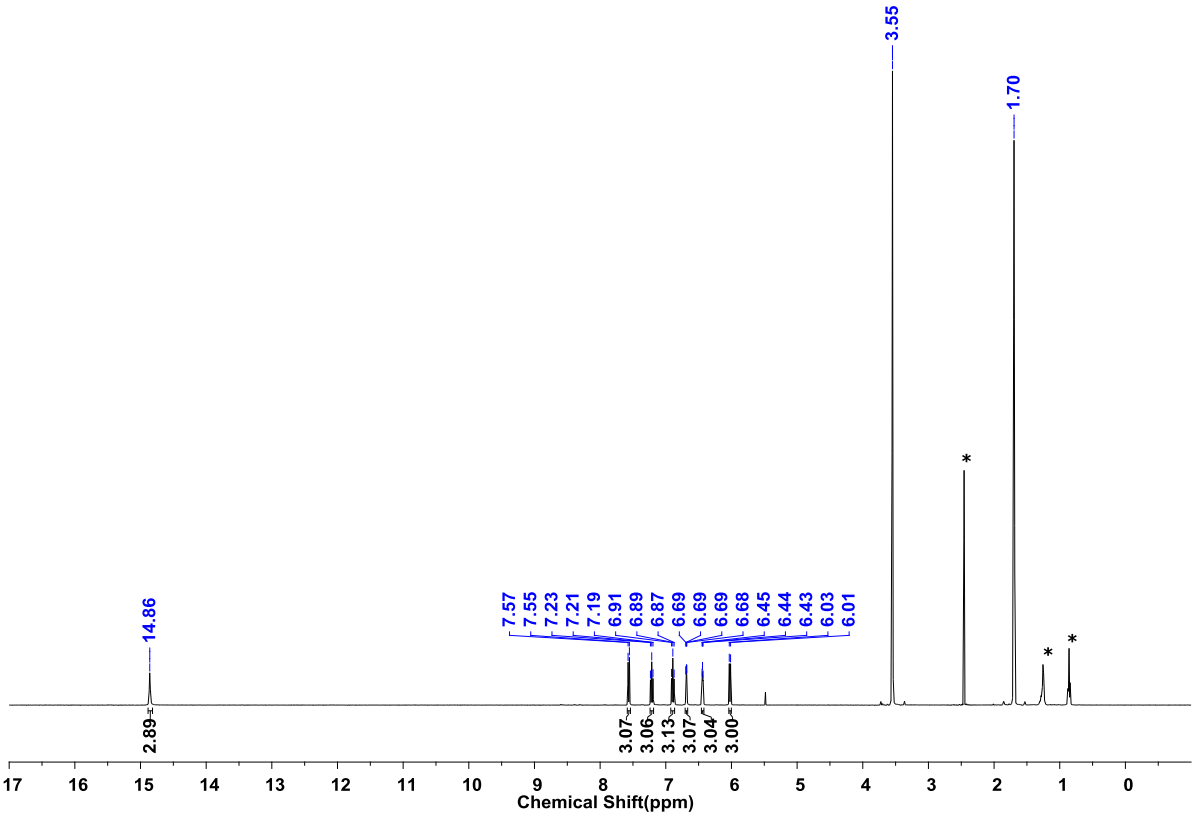
S10: IR spectrum of **13b**.



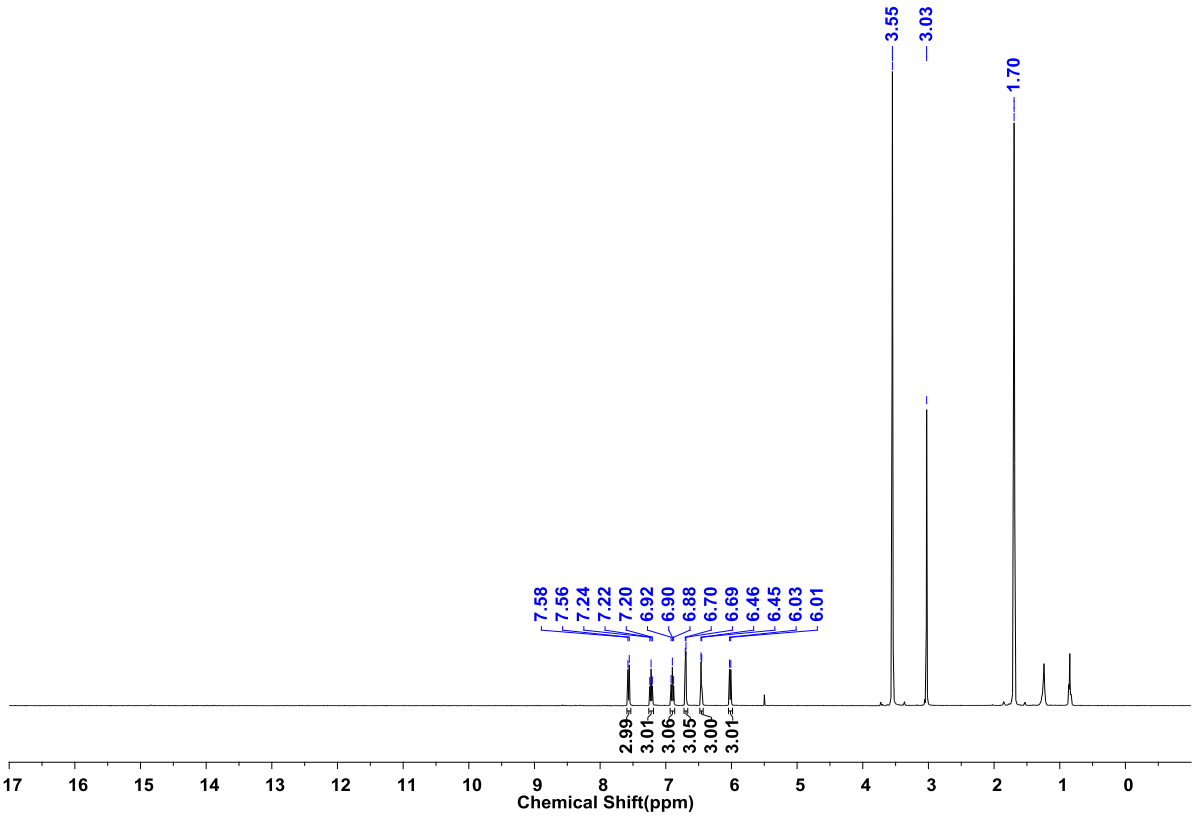
S11: ^{1}H-NMR spectrum of **10** in *Acetone-d_6* at 295K.



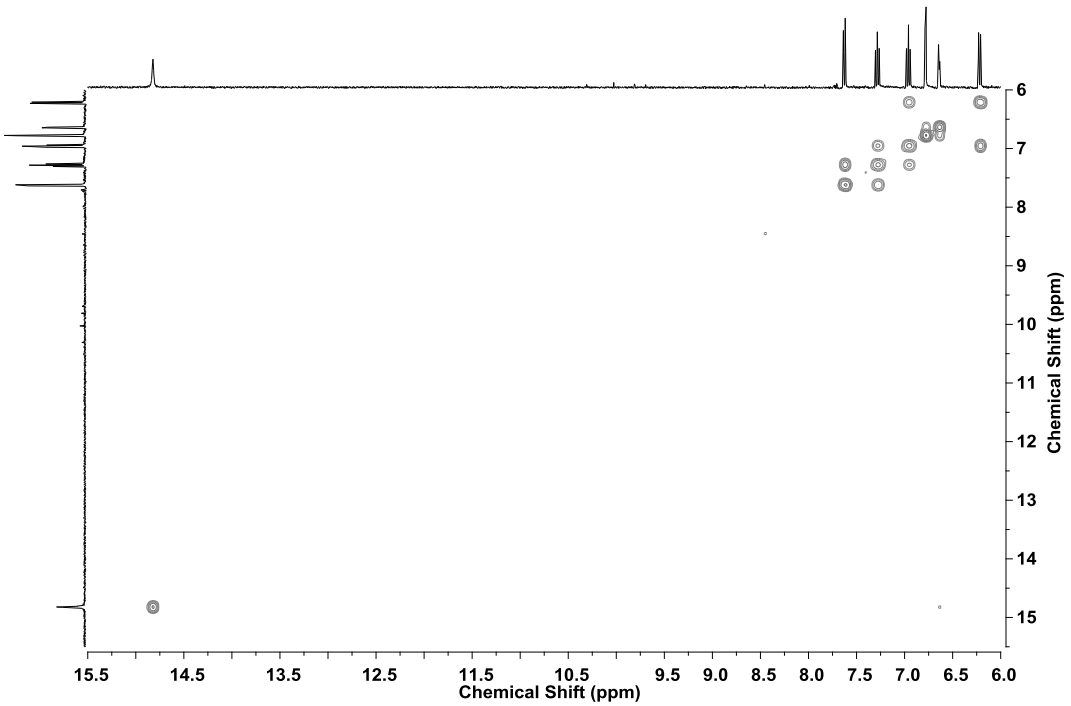
S12: ^{13}C-NMR spectrum of **10** in *Acetone-d_6* at 295K.



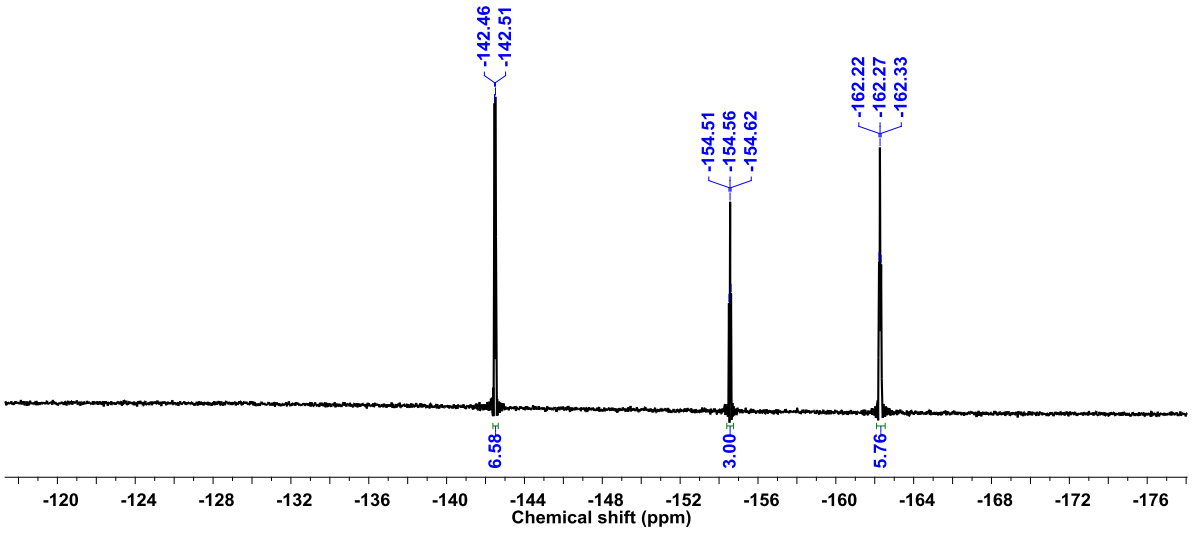
S13: ^{1}H-NMR spectrum of **13a** in *Tetrahydrofuran-d_8* at 295K.



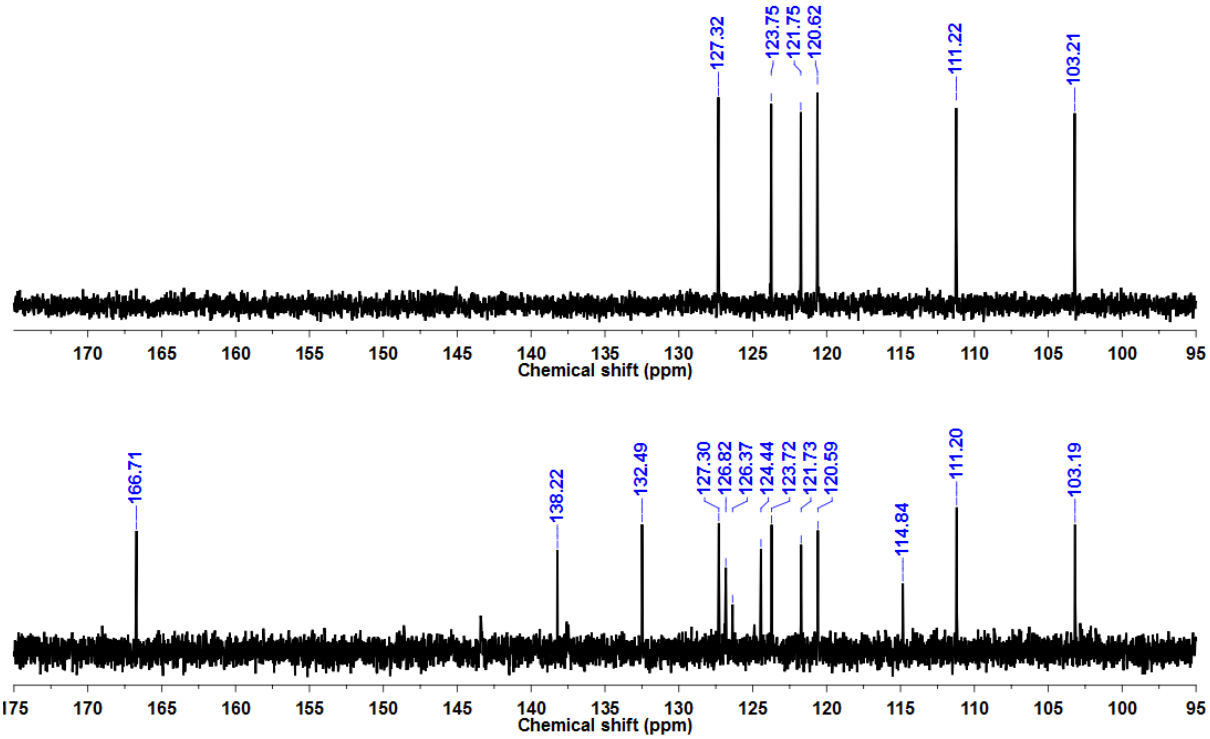
S14: ^{1}H-NMR spectrum of **13a** after D_2O exchange in *Tetrahydrofuran-d_8* at 295K



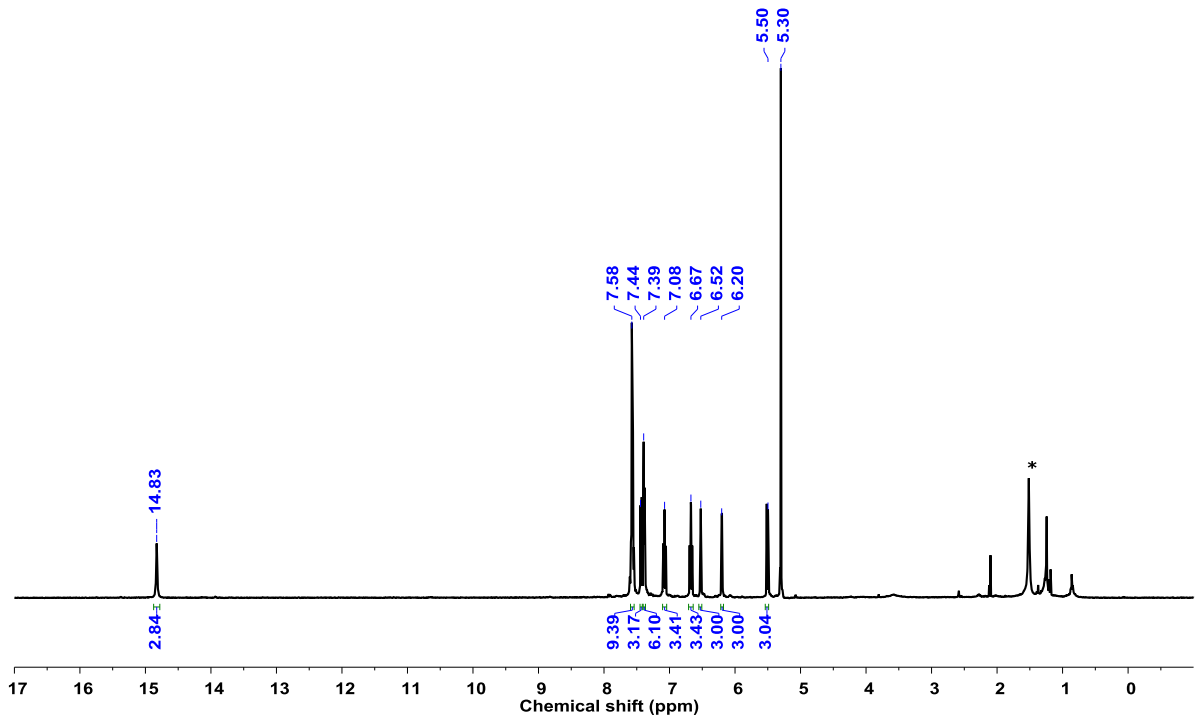
S15: ^{1}H-^{1}H COSY spectrum of **13a** in *Tetrahydrofuran-d_8* at 295K.



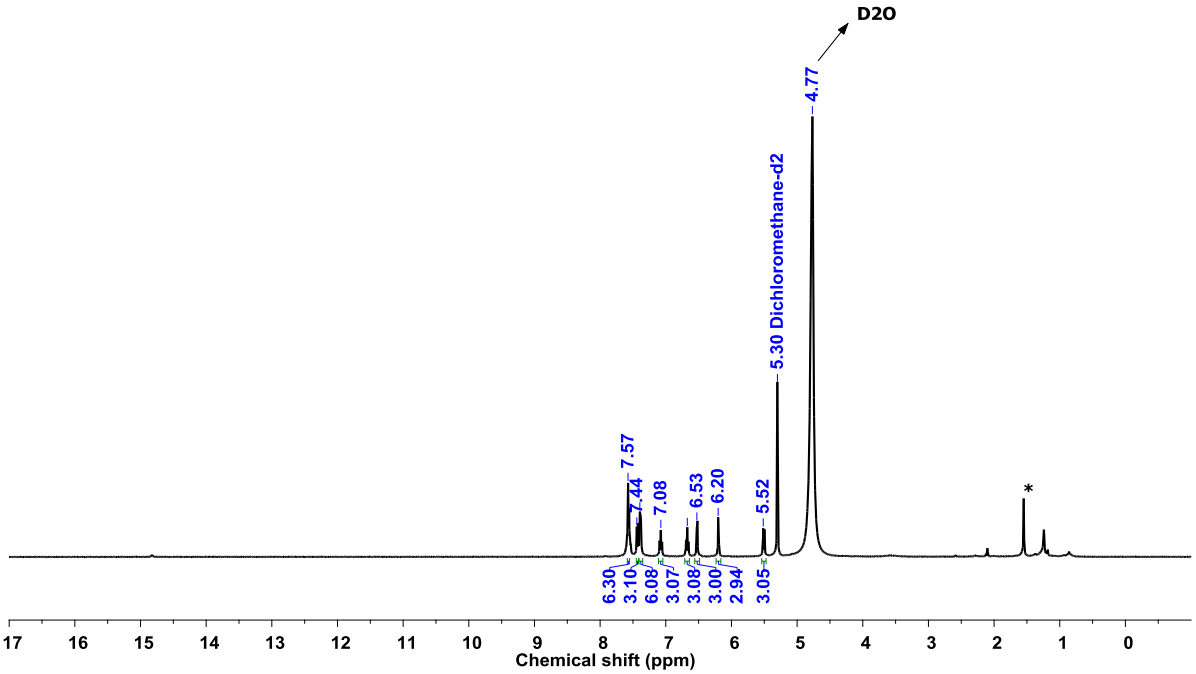
S16: ^{19}F-NMR spectrum of **13a** in *Tetrahydrofuran-d_8* at 295K.



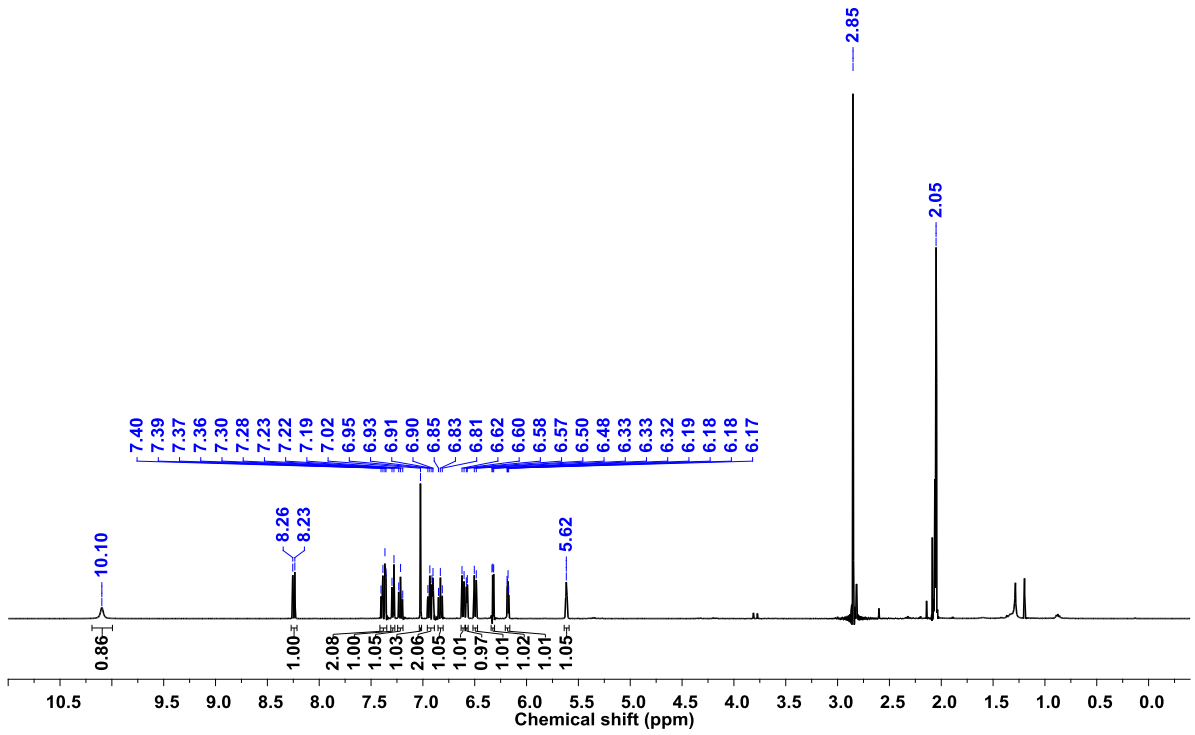
S17: (Top) DEPT-90 and (Bottom) ^{13}C-NMR COSY spectrum of **13a** in *Tetrahydrofuran-d_8* at 295K.



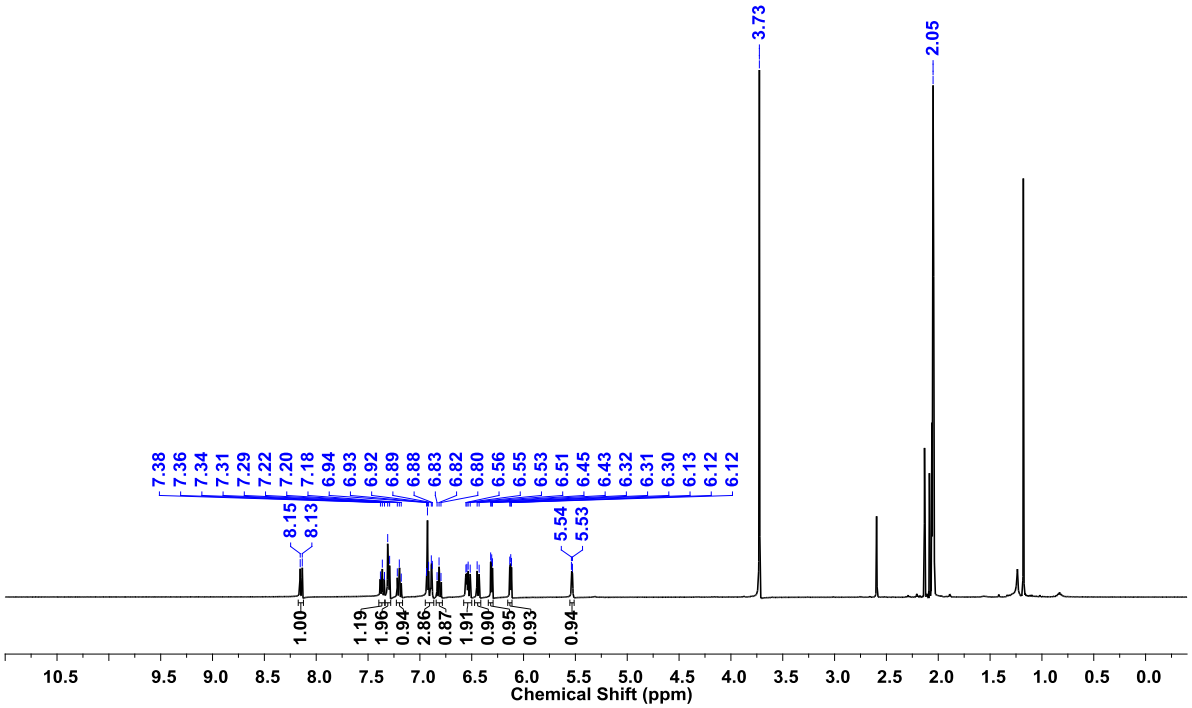
S18: ^{1}H-NMR spectrum of **13b** in *Dichloromethane-d_2* at 295K.



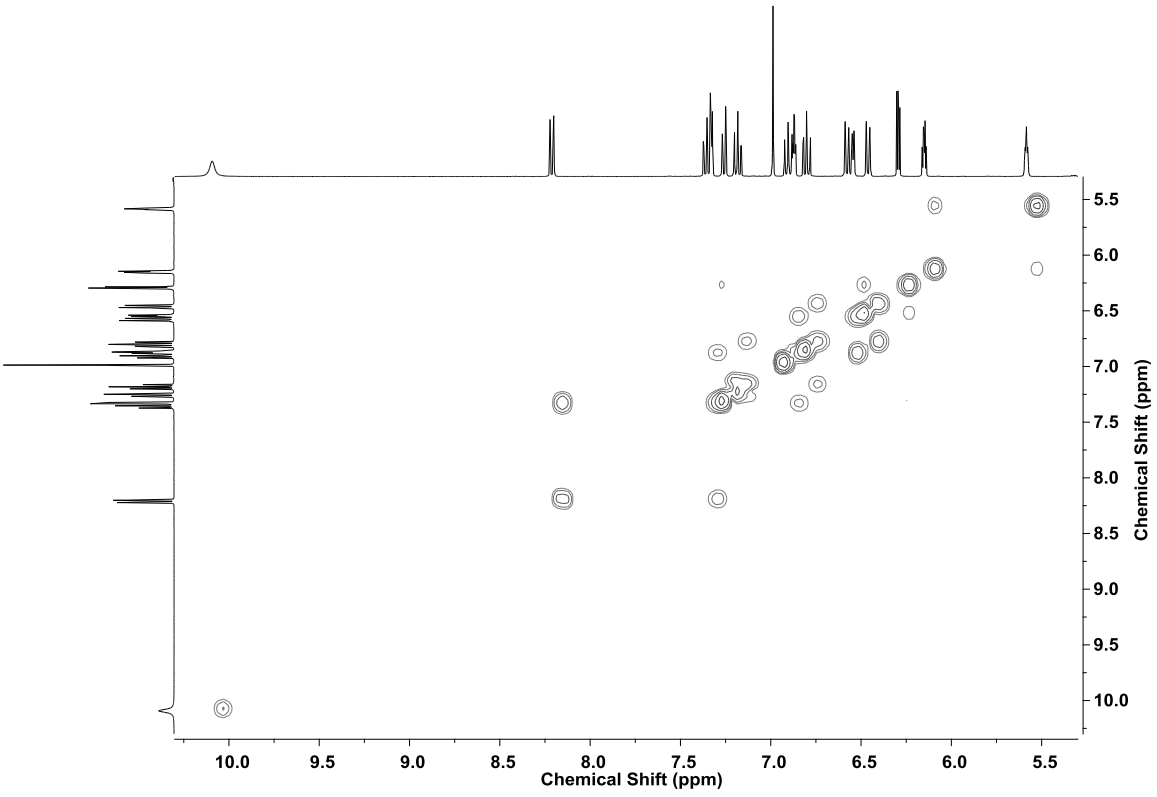
S19: ^{1}H-NMR spectrum of **13b** after D_2O exchange in *Dichloromethane-d_2* at 295K.



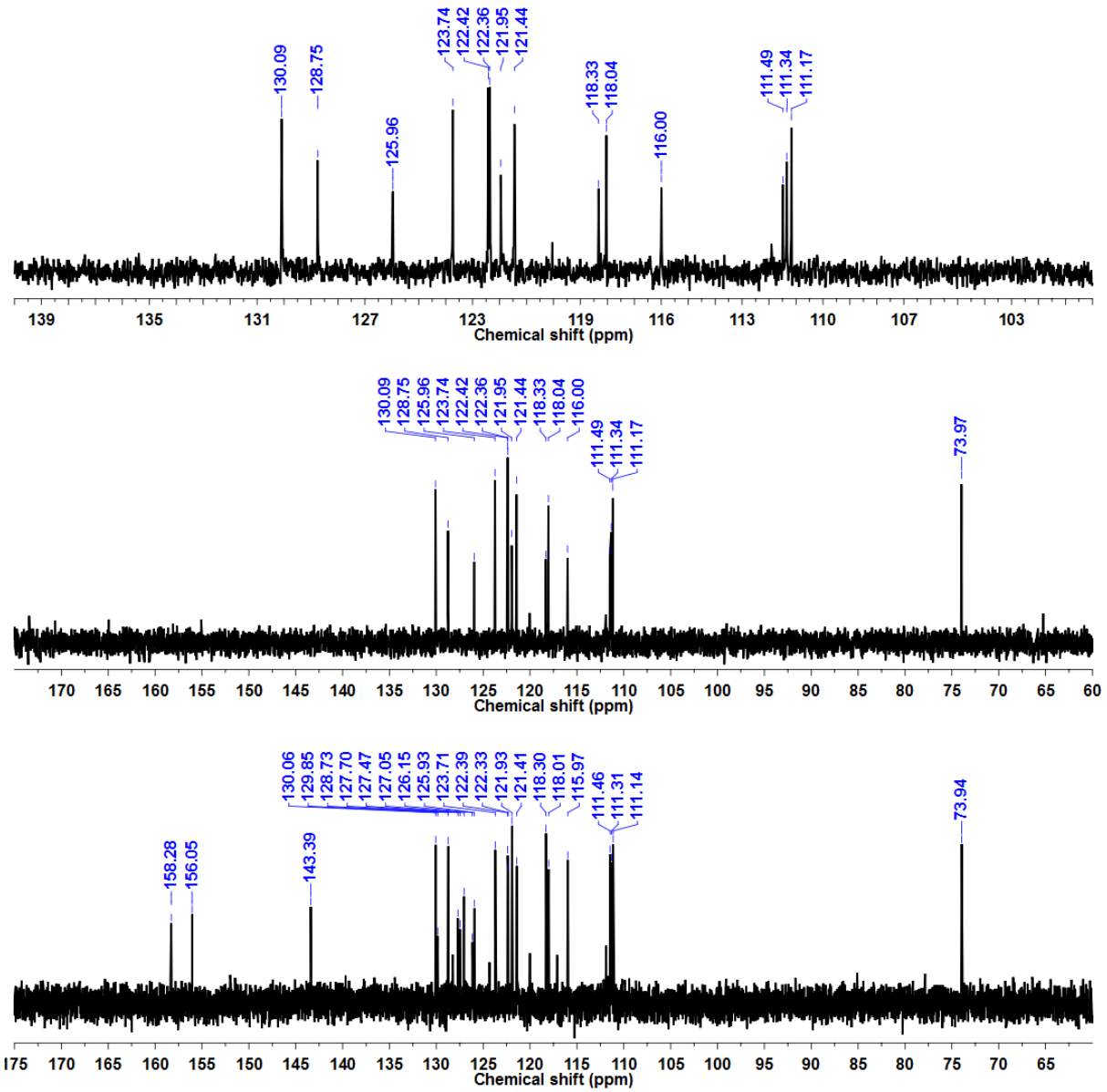
S20: ^{1}H-NMR spectrum of **14** in *Acetone-d_6* at 295K.



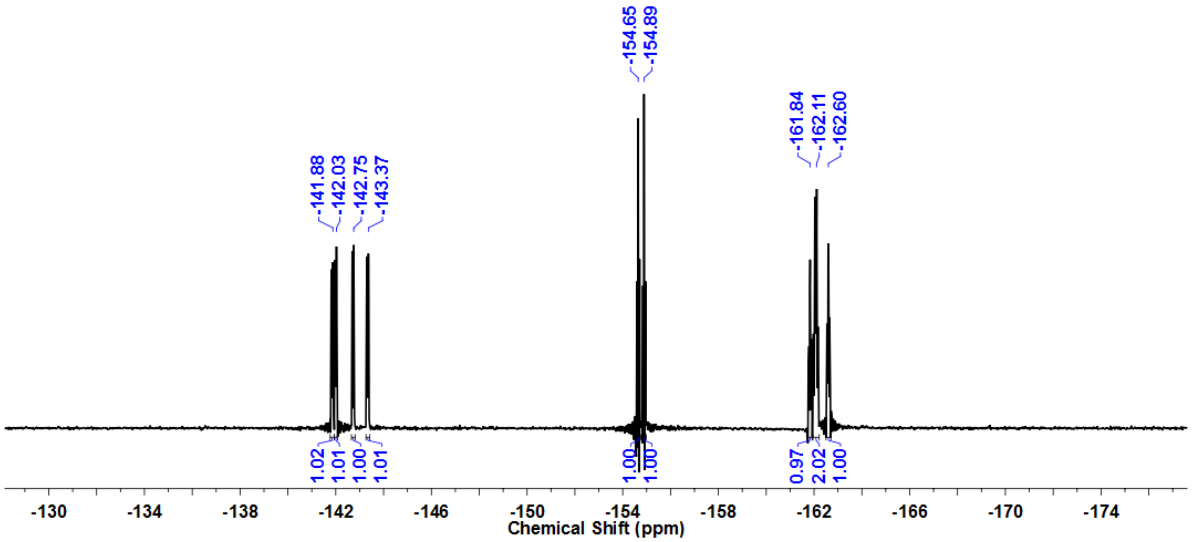
S21: ^{1}H-NMR spectrum of **14** after D_2O exchange in *Acetone-d_6* at 295K.



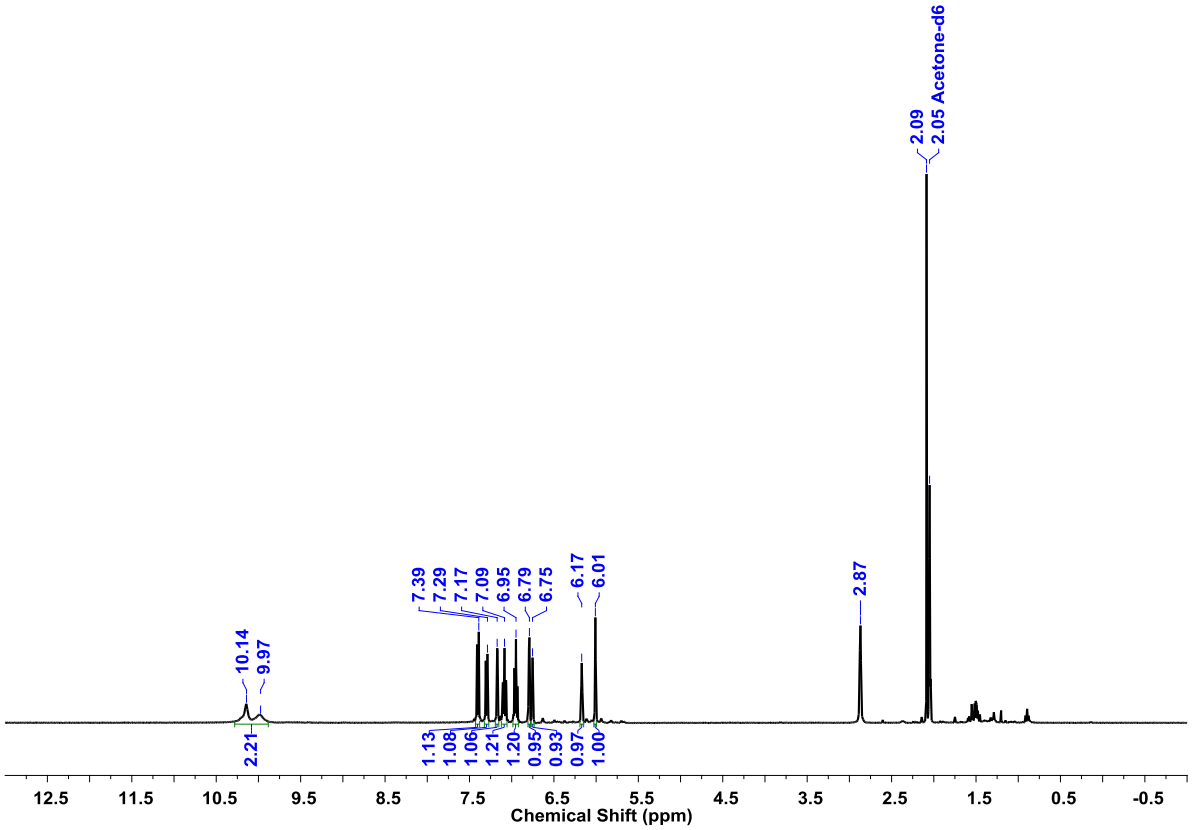
S22: ^{1}H-^{1}H COSY spectrum of **14** in *Acetone-d_6* at 295K.



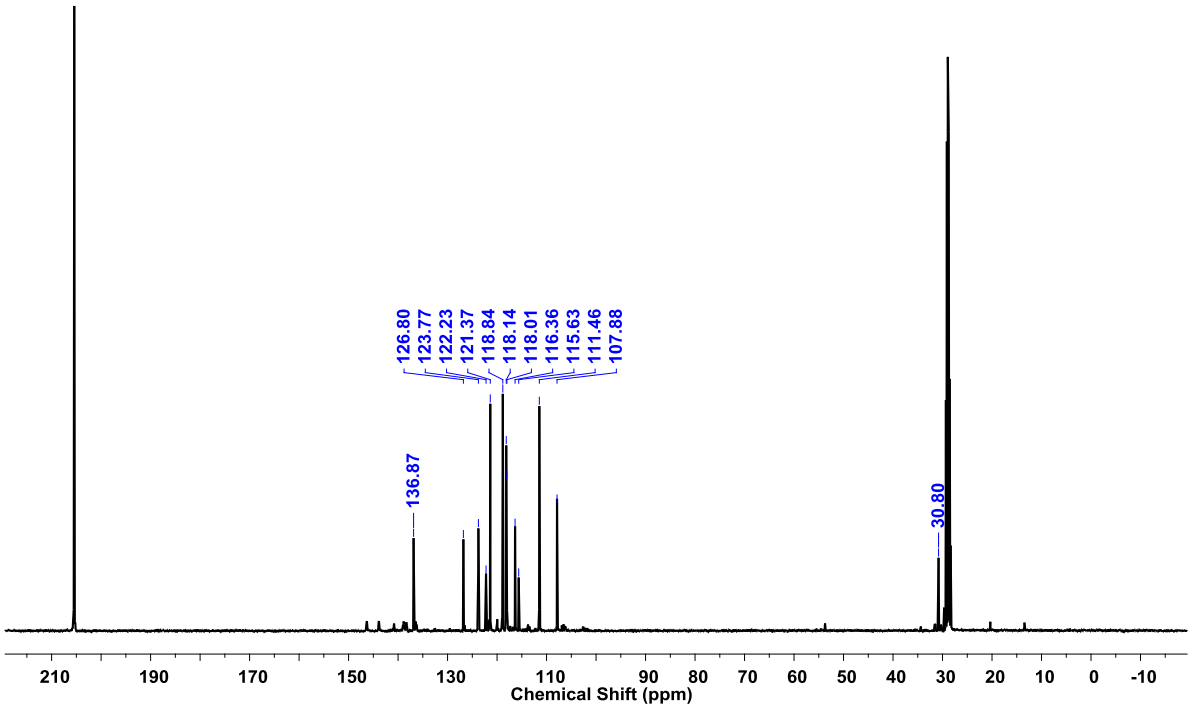
S23: (Top) Zoomed-DEPT-90, (Middle) DEPT-90 and (Bottom**)** ^{13}C-NMR spectrum of **14** in *Acetone-d_6* at 295K.



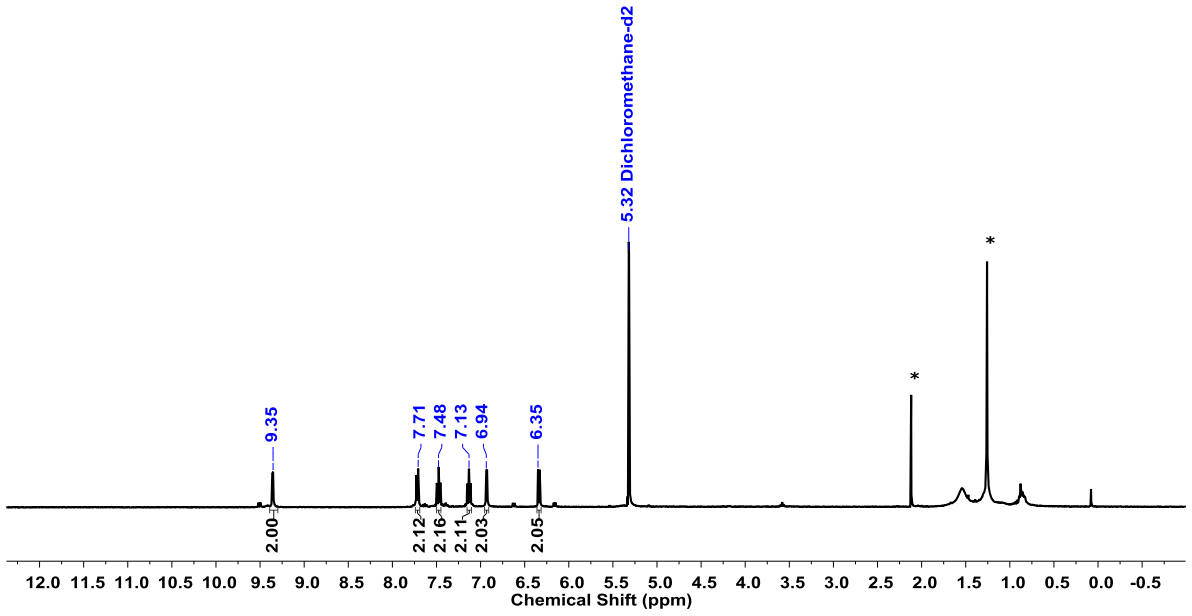
S24: ^{19}F-NMR spectrum of **14** in *Acetone-d_6* at 295K.



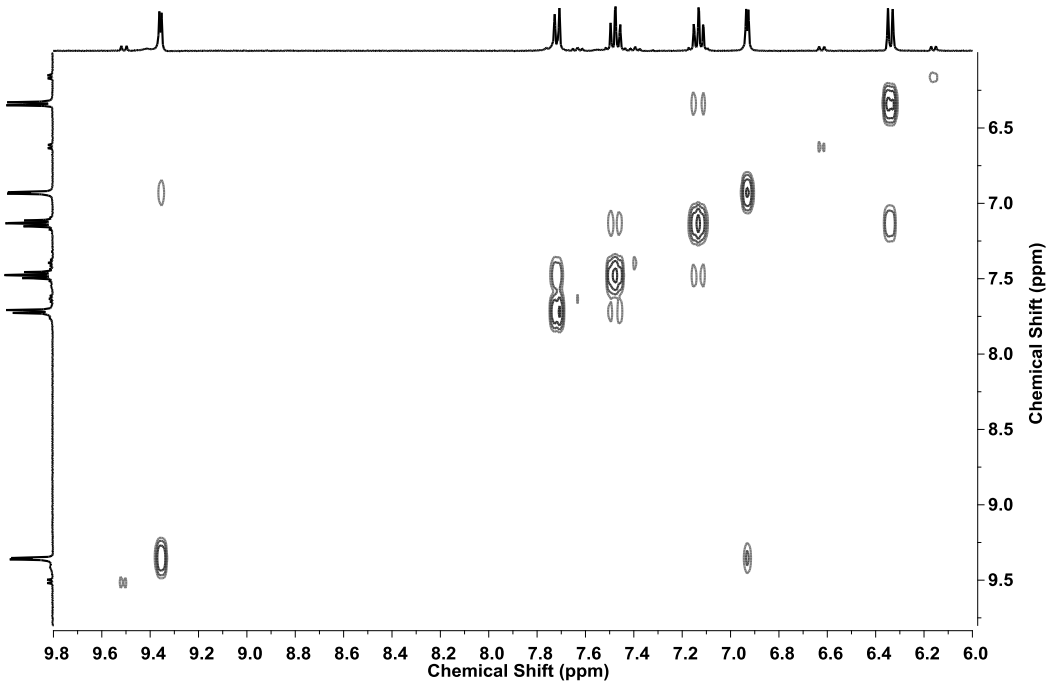
S25: ^{1}H-NMR spectrum of **11** in *Acetone-d_6* at 295K.



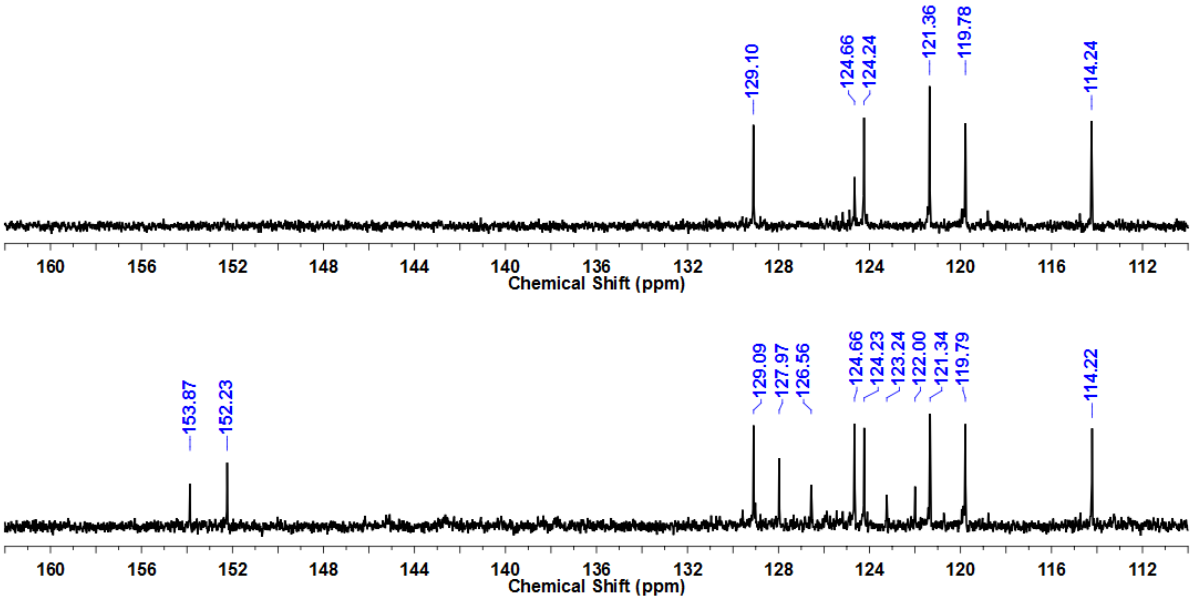
S26: ^{13}C-NMR spectrum of **11** in *Acetone-d_6* at 295K.



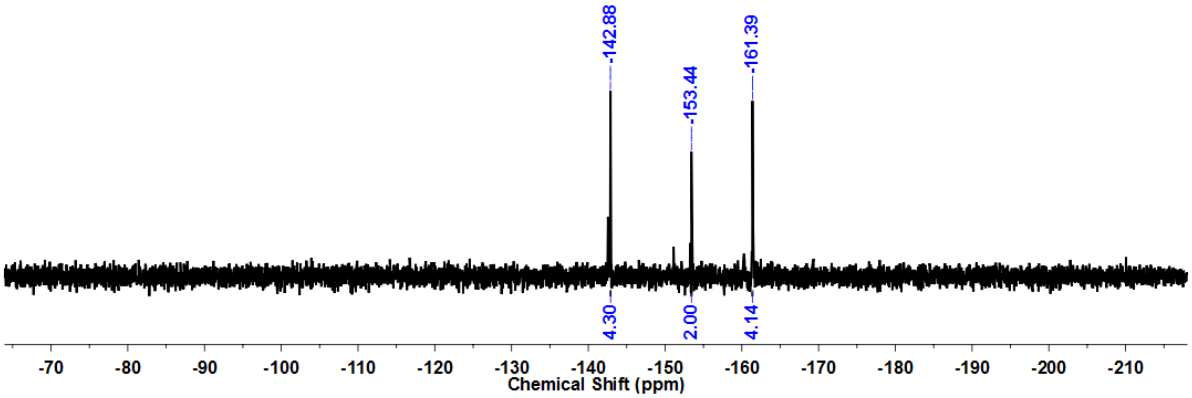
S27: ^{1}H-NMR spectrum of **15** in *Dichloromethane-d_2* at 295K.



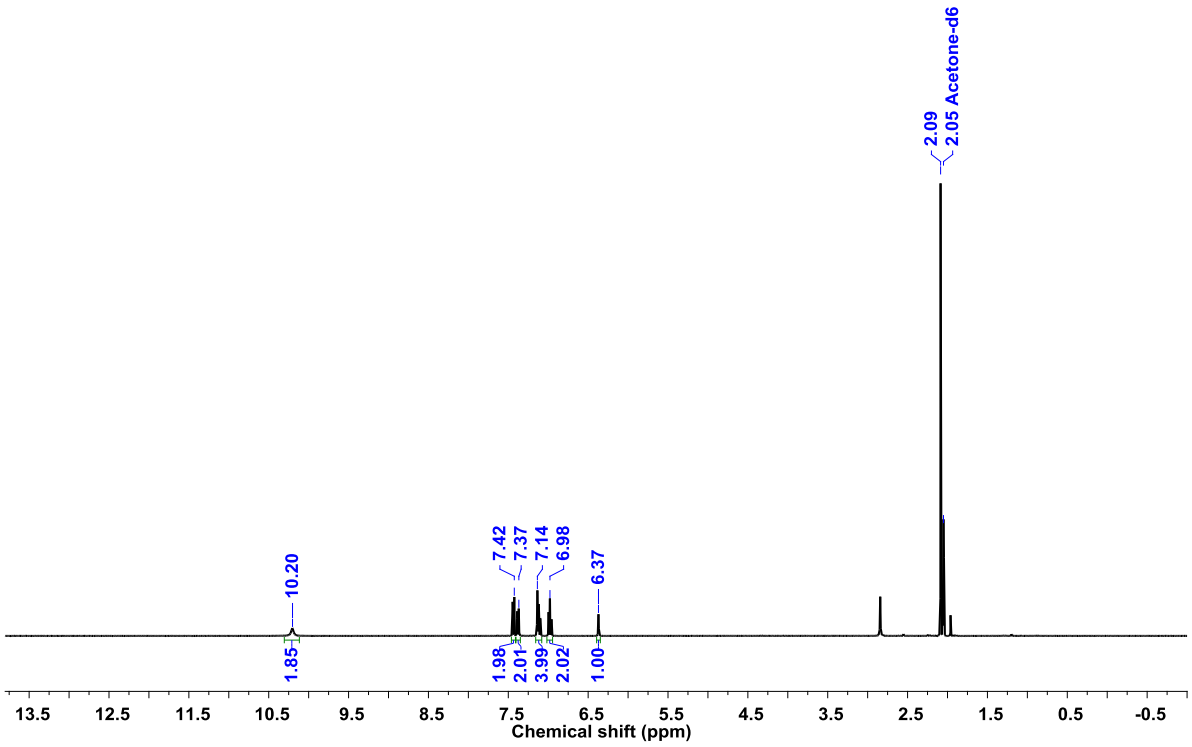
S28: ^{1}H-^{1}H COSY spectrum of **15** in *Dichloromethane-d_2* at 295K.



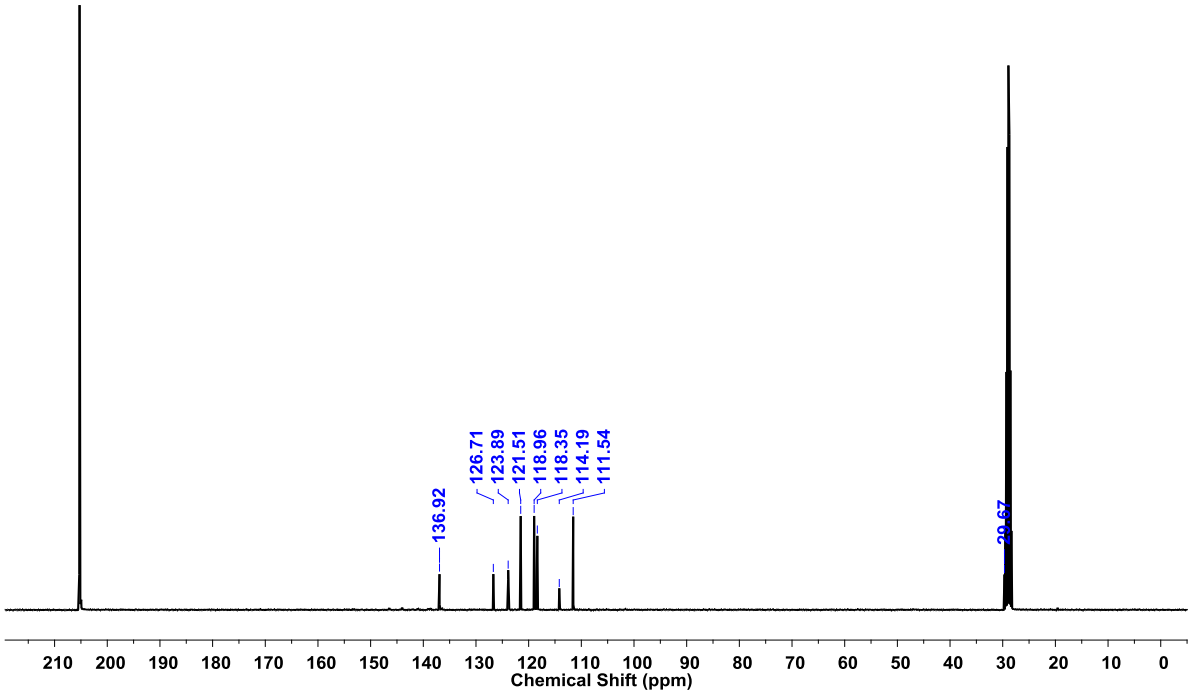
S29: (Top) DEPT-90 and (Bottom**)** ^{13}C-NMR spectrum of **15** in *Dichloromethane-d_2* at 295K.



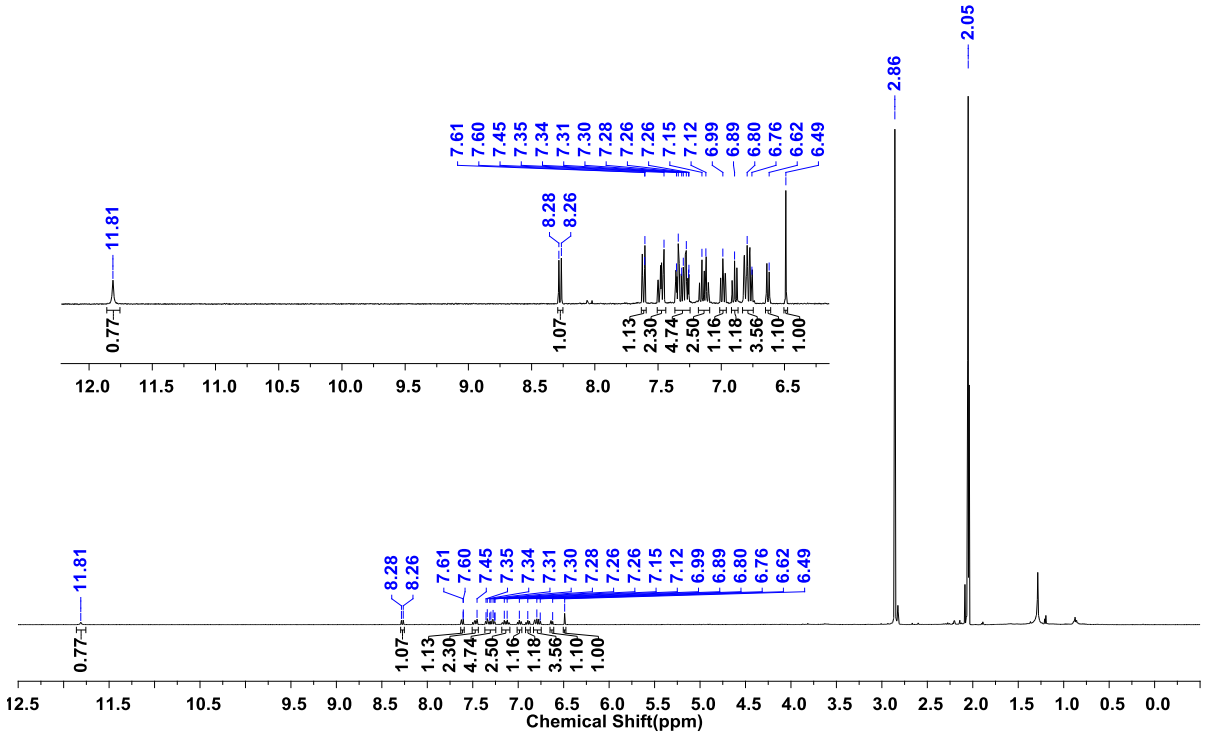
S30: ^{19}F-NMR spectrum of **15** in *Dichloromethane-d_2* at 295K.



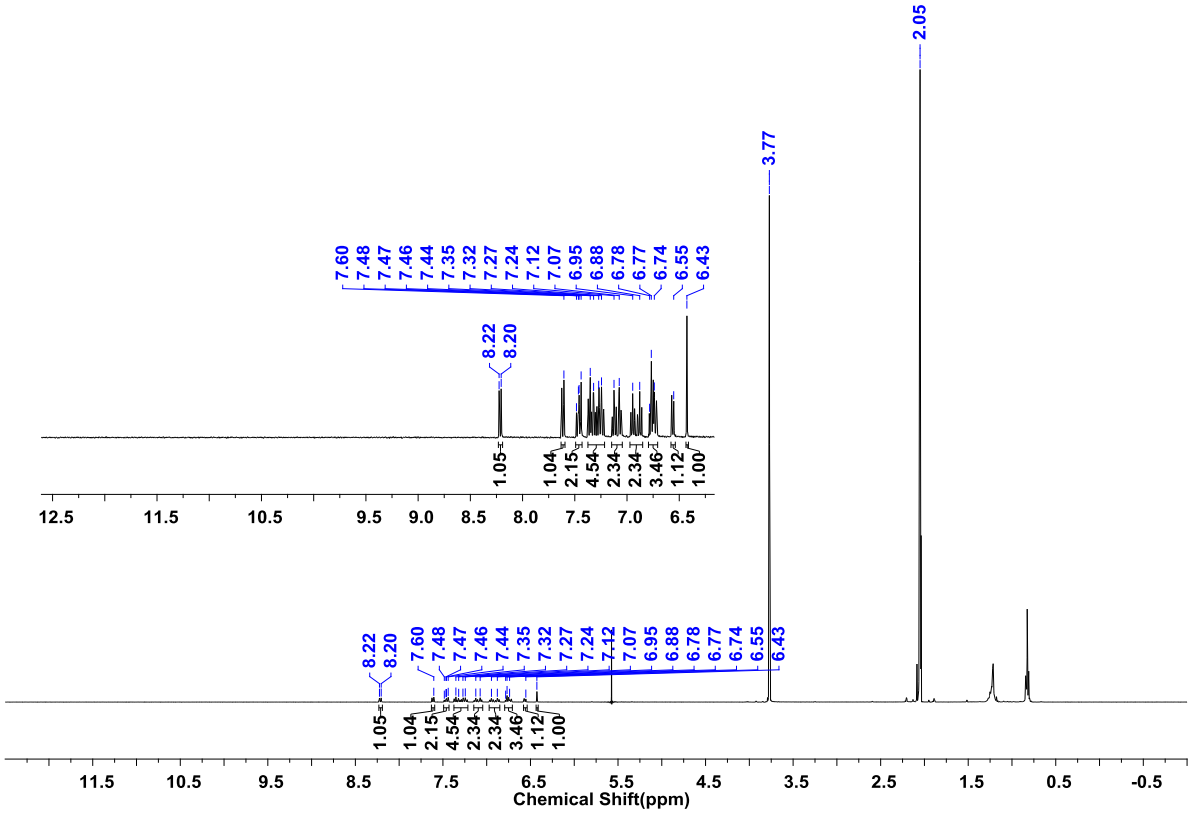
S31: ^{1}H-NMR spectrum of **12** in *Acetone-d_6* at 295K.



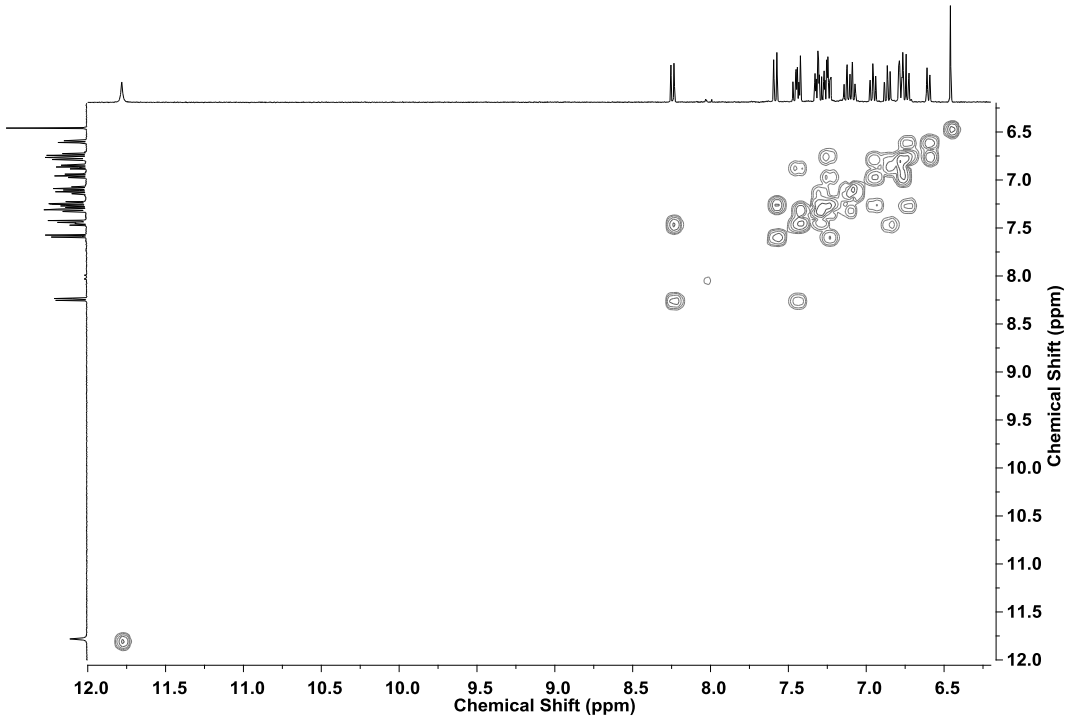
S32: ^{13}C-NMR spectrum of **12** in *Acetone-d_6* at 295K.



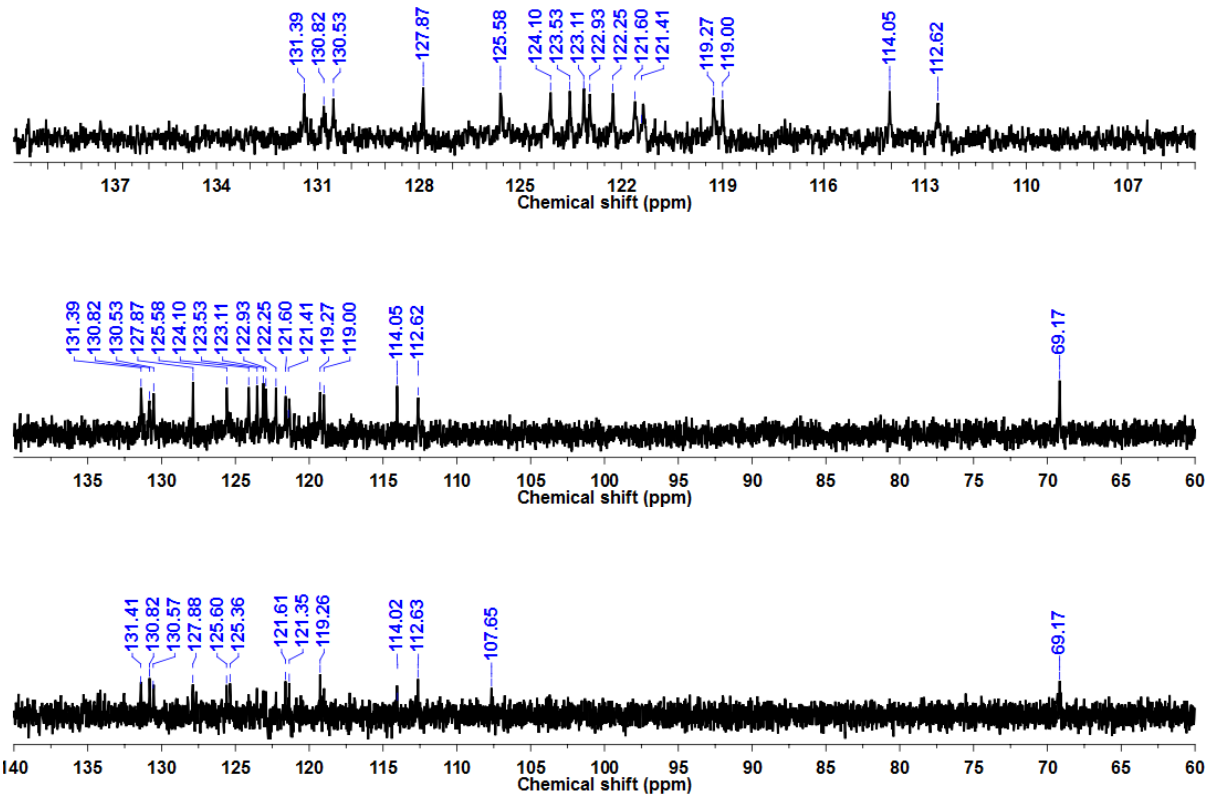
S33: ^{1}H-NMR spectrum of **16** in *Acetone-d_6* at 295K.



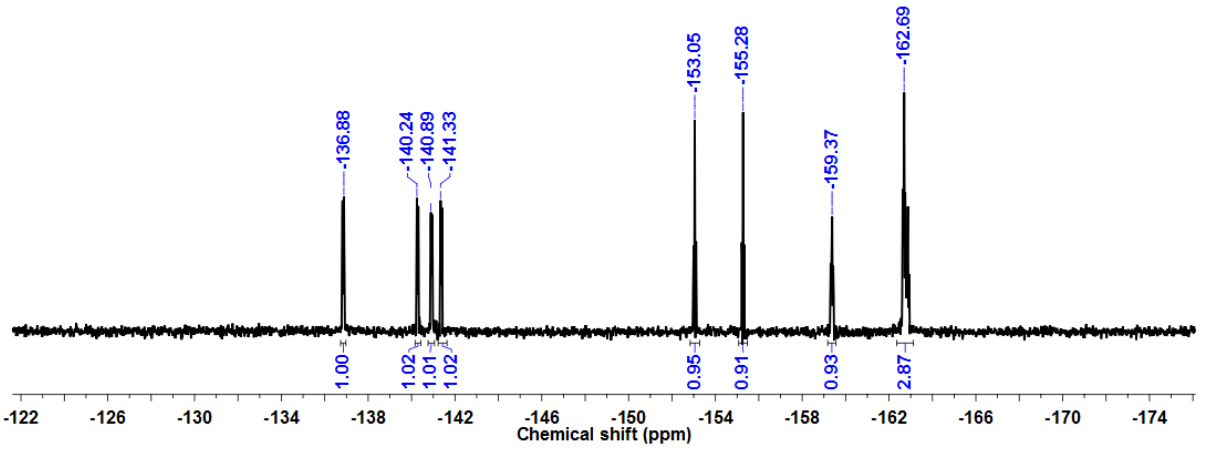
S34: ^{1}H-NMR spectrum of **16** after D_2O exchange in *Acetone-d_6* at 295K



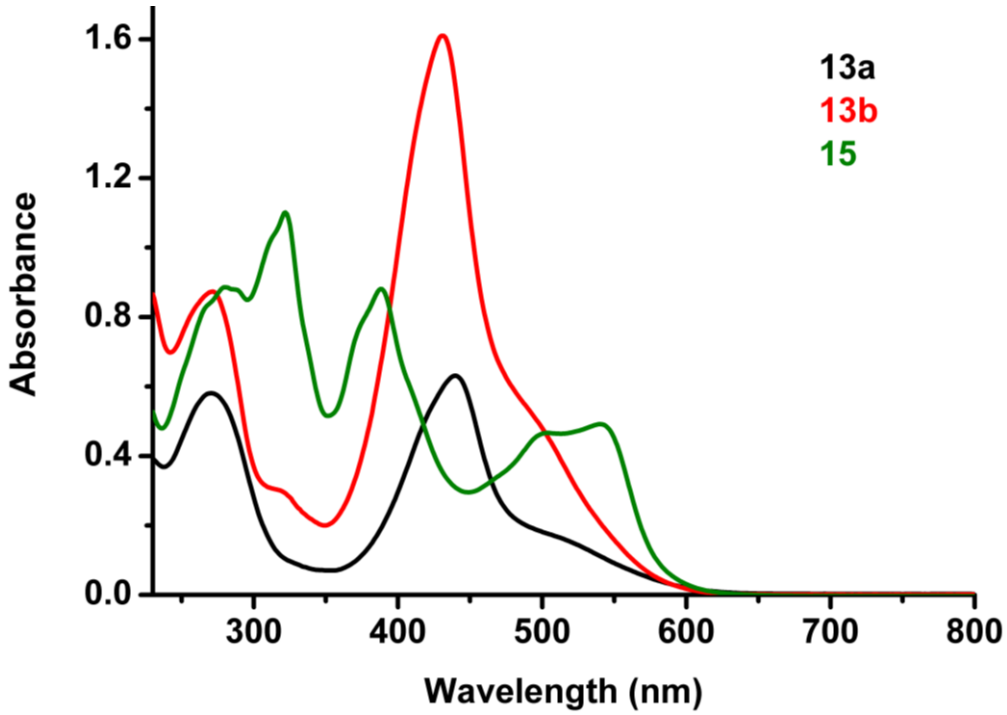
S35: ^{1}H-^{1}H COSY spectrum of **16** in *Acetone-d_6* at 295K.



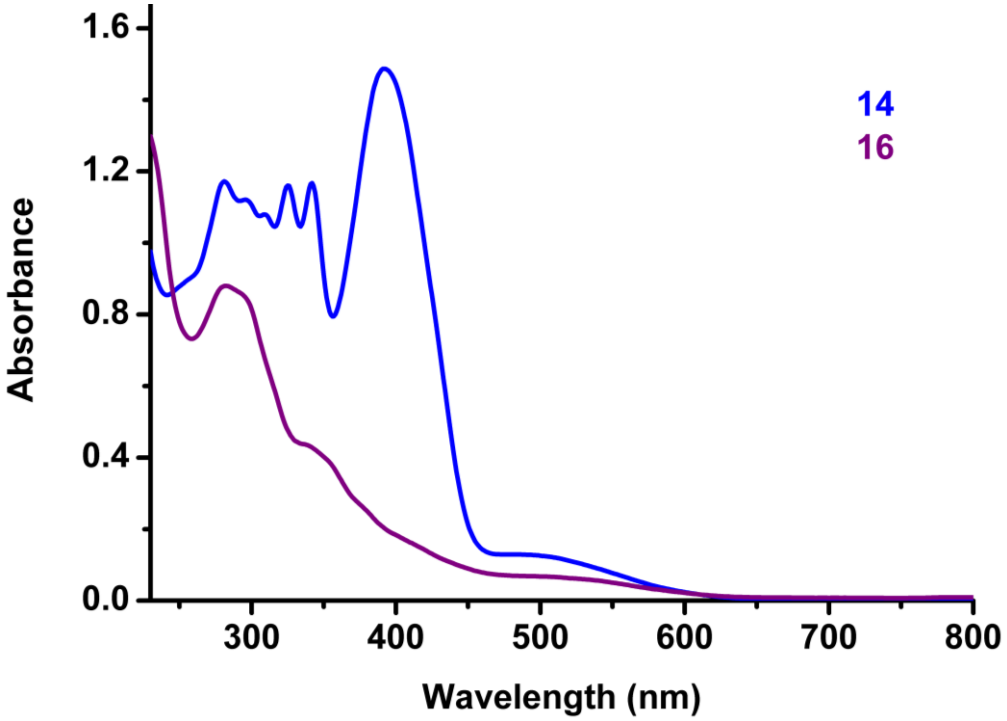
S36: (Top) Zoomed-DEPT-90, (Middle) DEPT-90 and (Bottom**)** ^{13}C-NMR COSY spectrum of **16** in *Acetone-d_6* at 295K.



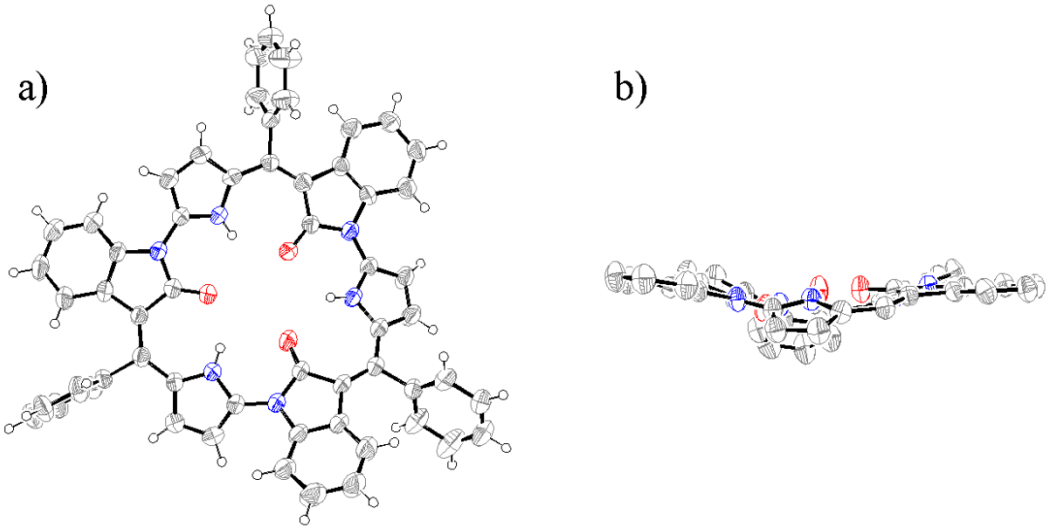
S37: ^{19}F-NMR spectrum of **16** in *Acetone-d_6* at 295K.



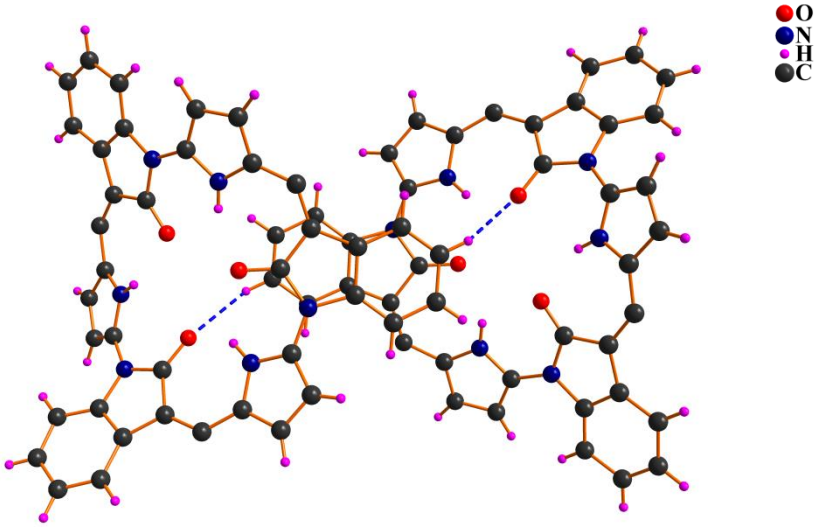
S38: Absorption spectrum of **13a**, **13b** and **15** recorded for 10^{-6} M solutions in dichloromethane (CH_2Cl_2).



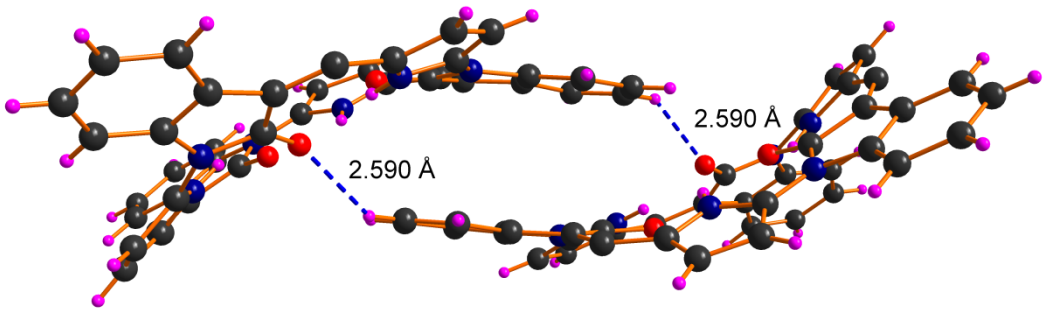
S39: Absorption spectrum of **14** and **16** recorded for 10^{-6} M solutions in CH_2Cl_2



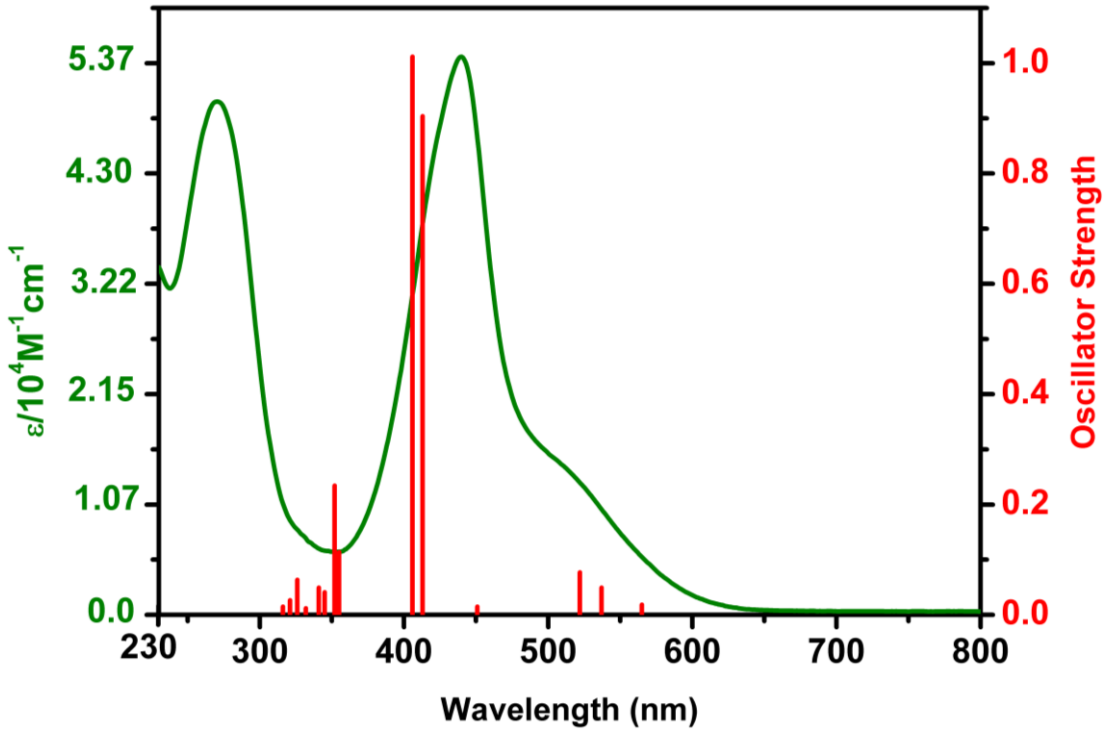
S40: ORTEP drawings of **13b**, The thermal ellipsoids are scaled to the 50% probability level, a) top view, b) side view.



S41: View 1-Hydrogen bonded dimer of **13a**. *meso*-pentafluorophenyl groups are omitted for clarity. Hydrogen-bonding interactions are indicated by broken lines.



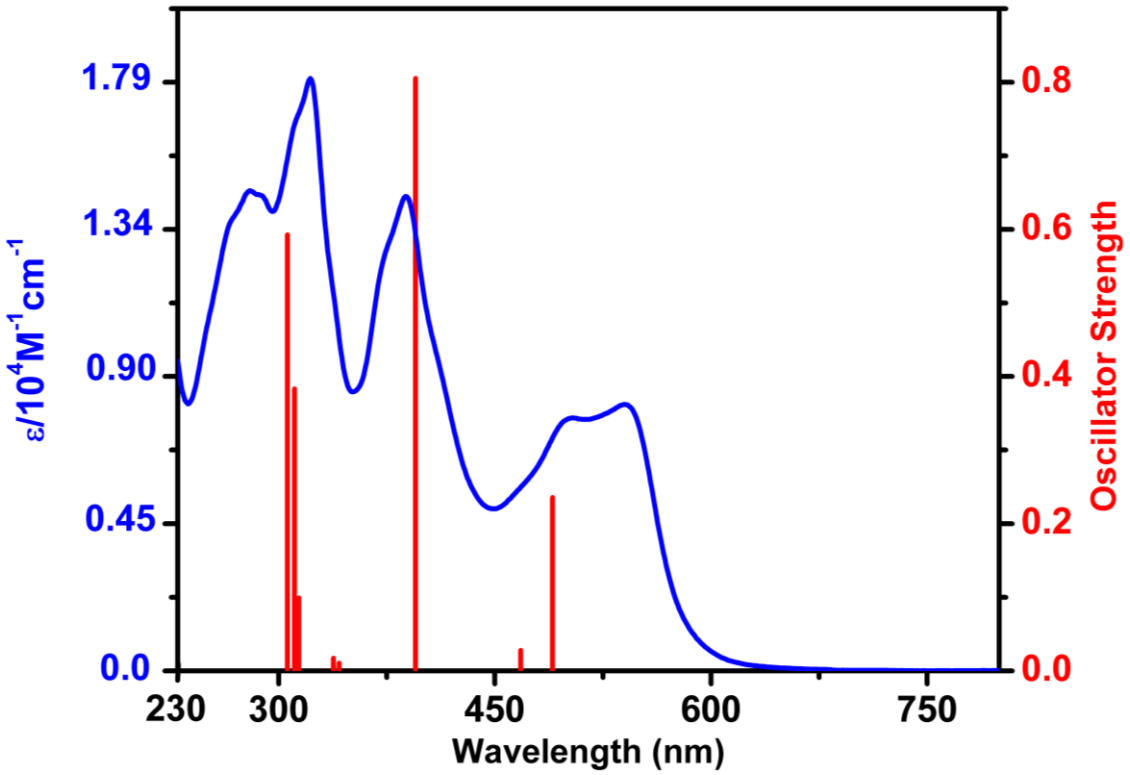
S42: View 2-Hydrogen bonded dimer of **13a**. *meso*-pentafluorophenyl groups are omitted for clarity. Hydrogen-bonding interactions are indicated by broken lines.



S43: The steady state absorption spectra (green line) recorded in CH_2Cl_2 and theoretical vertical excitation energies (red bar) for **13a** obtained from TD-DFT calculations carried out at the B3LYP/6-31G(d,p) level .

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength(f)	Major contribs
17698.34608	565.0245483	0.0184	H-2→LUMO (25%), HOMO→LUMO (62%)
18621.05072	537.0266238	0.0493	H-2→LUMO (42%), H-1→LUMO (18%),HOMO→LUMO (30%)
19158.21968	521.9691687	0.077	H-2→LUMO (22%), H-1→LUMO (63%)
22183.62624	450.7829284	0.0148	H-2→L+2 (57%), H-1→L+2 (31%)
24173.40976	413.6776772	0.9041	H-2→L+1 (65%)
24622.66368	406.1299025	1.0199	H-2→L+2 (24%), H-1→L+1 (12%), H-1→L+2 (19%), HOMO→L+2 (31%)
28152.17024	355.2124016	0.114	H-5→LUMO (35%), H-4→LUMO (12%), H-3→L+1 (45%)
28382.8464	352.3254806	0.2344	H-4→LUMO (56%), H-3→L+2 (23%)
28990.18608	344.9443192	0.0409	H-5→LUMO (47%), H-3→L+1 (41%)
29371.68896	340.4639077	0.0494	H-4→LUMO (25%), H-3→L+2 (66%)
30111.30448	332.1011883	0.012	HOMO→L+5 (94%)
30692.83424	325.8089469	0.0635	H-2→L+3 (70%), H-1→L+3 (21%)
31171.12432	320.8097307	0.0263	H-5→L+1 (28%), H-4→L+1 (36%)
31640.54224	316.0502094	0.0148	H-10→LUMO (14%), H-9→LUMO (31%)

S44: Selected TD-DFT (B3LYP/6-31g (d, p)) calculated energies, oscillator strengths and compositions of the major electronic transitions for **13a**.



S45: The steady state absorption spectra (green line) recorded in CH_2Cl_2 and theoretical vertical excitation energies (red bar) for **15** obtained from TD-DFT calculations carried out at the B3LYP/6-31G(d,p) level .

Energy(cm^{-1})	Wavelength (nm)	Osc. Strength(f)	Major contribs
20414.0336	489.8590938	0.2356	H-1→L+1 (10%), HOMO→LUMO (85%)
21371.42032	467.9146192	0.0279	H-2→LUMO (75%), H-1→L+1 (23%)
25330.0168	394.7885262	0.8053	H-2→LUMO (19%), H-1→L+1 (63%), HOMO→LUMO (12%)
29217.636	342.2590383	0.0105	H-4→LUMO (45%), H-3→L+1 (16%), HOMO→L+2 (36%)
29558.00432	338.317834	0.0174	H-4→LUMO (18%), H-3→L+1 (75%)
31829.27728	314.1761565	0.0992	H-6→LUMO (37%), H-5→L+1 (16%), H-4→LUMO (16%), HOMO→L+2 (26%)
32143.02912	311.1094466	0.3833	H-6→LUMO (20%), H-5→L+1 (12%), H-2→L+2 (39%), HOMO→L+2 (17%)
32643.09632	306.3434884	0.5928	H-6→LUMO (12%), H-2→L+2 (51%), HOMO→L+2 (10%)

S46: Selected TD-DFT (B3LYP/6-31g (d, p)) calculated energies, oscillator strengths and compositions of the major electronic transitions for **15**.

S47: Coordinates Table for optimized structure **13a**

Sr. No.	Atom	X	Y	Z
1	F	0.213508	-6.590796	1.251191
2	F	4.772095	3.59816	-2.203248
3	F	3.958442	5.064927	2.224687
4	F	-6.282329	1.971498	-2.074764
5	F	3.294269	-5.077448	-2.017728
6	F	6.785958	5.393962	-2.423715
7	F	-8.261676	1.842382	3.002386
8	F	-5.701338	1.092513	2.540364
9	F	1.02288	-9.133126	0.826967
10	F	4.089931	-7.623336	-2.437265
11	F	5.973412	6.856118	1.997687
12	F	-8.843667	2.71672	-1.606488
13	F	-9.843178	2.646681	0.930337
14	F	2.967564	-9.66054	-1.012986
15	F	7.388218	7.033603	-0.327769
16	O	1.20643	-1.258725	0.094619
17	O	-1.792041	-0.335823	-0.589484
18	O	0.468095	1.819369	0.507246
19	N	-0.81523	-2.964416	-0.342757
20	H	-0.414616	-2.073123	-0.034712
21	N	3.305166	-1.526372	1.036939
22	N	-0.425654	3.813493	-0.23216
23	N	-2.244534	2.23186	-0.206468
24	H	-1.710818	1.369309	-0.376032
25	N	2.921409	0.82736	0.66702
26	H	1.896357	0.807083	0.608969
27	N	-3.095311	-2.233951	-0.637187
28	C	0.056508	5.065308	-0.671652
29	C	-5.92086	1.499074	0.217773

30	C	4.076386	-2.60764	1.524471
31	C	1.728722	-5.749801	-0.368257
32	C	3.664322	1.988481	0.489725
33	C	1.467411	5.07294	-0.572864
34	C	-0.030841	-4.073037	-0.636014
35	C	-2.061591	-3.144995	-0.851501
36	C	2.092114	-2.010498	0.501169
37	C	-6.455776	1.485462	1.507244
38	C	5.082897	0.246006	0.85511
39	H	5.972114	-0.354789	0.944953
40	C	-4.463153	-2.559757	-0.489773
41	C	-3.612123	2.220132	0.030019
42	C	-4.495511	1.097525	-0.038171
43	C	-2.912738	-0.847549	-0.512219
44	C	4.2984	4.284942	0.013648
45	C	5.019481	1.616221	0.622882
46	H	5.864607	2.280611	0.535262
47	C	5.669629	6.058548	0.968498
48	C	0.649252	2.970948	0.106934
49	C	-1.766472	3.487692	-0.042327
50	C	3.75626	-0.218436	0.878954
51	C	-6.749258	1.928074	-0.820732
52	C	3.180719	3.289254	0.146094
53	C	6.084982	5.311616	-1.288018
54	C	-4.244325	-0.244936	-0.285977
55	C	3.43018	-3.819013	1.186703
56	C	-5.199036	-1.365523	-0.306297
57	C	1.165006	-6.817607	0.337054
58	C	1.288378	-4.333818	-0.14299
59	C	1.892039	3.749437	-0.087524
60	C	2.177546	-3.485215	0.497981
61	C	2.569495	-8.403883	-0.805639
62	C	-2.106486	-4.377853	-1.516747
63	H	-2.950244	-4.781033	-2.052471
64	C	2.720543	-6.053881	-1.305809
65	C	-0.845447	-4.956689	-1.37079
66	H	-0.542819	-5.921441	-1.747837
67	C	3.996807	-5.018288	1.63414
68	H	3.525906	-5.969228	1.425041
69	C	-7.198884	-2.728601	-0.167575
70	H	-8.276486	-2.794988	-0.055903
71	C	1.575916	-8.132915	0.132813
72	C	3.143141	-7.361693	-1.53069
73	C	-3.973015	3.547928	0.349284
74	H	-4.968188	3.887082	0.590501
75	C	5.176037	-4.994432	2.38164

76	H	5.611268	-5.9297	2.71924
77	C	-2.826413	4.33692	0.313522
78	H	-2.74784	5.387091	0.543964
79	C	-8.06959	2.311114	-0.594604
80	C	-6.588556	-1.472682	-0.160402
81	H	-7.209092	-0.597757	-0.037883
82	C	5.782796	-3.783702	2.717074
83	H	6.685564	-3.775867	3.319696
84	C	-7.772324	1.865342	1.75848
85	C	4.636694	5.129583	1.07255
86	C	5.22796	-2.569595	2.30132
87	H	5.669656	-1.630814	2.607929
88	C	-8.581166	2.277304	0.7012
89	C	5.04808	4.389916	-1.159824
90	C	6.393785	6.149777	-0.218312
91	C	1.42202	7.321429	-1.478802
92	H	1.95829	8.212648	-1.78919
93	C	-5.053798	-3.816952	-0.463106
94	H	-4.461109	-4.718312	-0.540222
95	C	-0.668382	6.130009	-1.192323
96	H	-1.742913	6.07266	-1.308
97	C	-6.439836	-3.890538	-0.301556
98	H	-6.921695	-4.862938	-0.280121
99	C	2.141032	6.231028	-0.984589
100	H	3.217405	6.301519	-0.936353
101	C	0.032743	7.270729	-1.591643
102	H	-0.513142	8.116474	-1.99781

S48: Coordinates Table for optimized structure **13b**

Sr. No.	Atom	X	Y	Z
1	O	-0.883093	1.670894	0.563681
2	O	-0.97071	-1.47949	-0.095039
3	O	1.81662	0.047921	-0.499436
4	N	1.385952	-2.732785	-0.405049
5	H	0.794651	-1.950802	-0.106913
6	N	3.481864	-1.542104	-0.542149
7	N	-0.374734	3.815728	-0.116033
8	N	1.726299	2.635893	-0.026157
9	H	1.390832	1.687862	-0.243815
10	N	-2.986037	-2.196936	0.795949
11	N	-3.082498	0.196744	0.508097
12	H	-2.07363	0.388374	0.50055
13	C	-4.981503	-4.959907	2.357231
14	H	-5.877189	-5.154579	2.93915

15	C	-4.679564	-3.646165	1.98629
16	H	-5.308593	-2.825465	2.305353
17	C	-3.530699	-3.425789	1.234865
18	C	-2.647208	-4.470036	0.877505
19	C	-1.474257	-3.868099	0.228623
20	C	-0.40693	-4.508536	-0.388979
21	C	0.859346	-3.96374	-0.784219
22	C	2.667277	-2.63288	-0.846444
23	C	3.015907	-0.225671	-0.381162
24	C	4.184461	0.623088	-0.069409
25	C	4.156862	1.980924	0.230783
26	C	5.460035	2.652521	0.570291
27	C	6.216885	3.278042	-0.428482
28	H	5.861536	3.263608	-1.454375
29	C	7.42202	3.906667	-0.111466
30	H	8.002757	4.384154	-0.89527
31	C	7.877921	3.92396	1.208129
32	H	8.815482	4.413435	1.454695
33	C	-7.515544	4.761794	-0.365365
34	H	-8.443929	5.315724	-0.468773
35	C	-7.045255	3.978263	-1.420936
36	H	-7.606234	3.920104	-2.349151
37	C	-5.852957	3.265014	-1.287442
38	H	-5.486333	2.655472	-2.107658
39	C	-5.111613	3.337494	-0.10047
40	C	-3.823799	2.575808	0.053726
41	C	-2.63577	3.281291	-0.106756
42	C	-1.275298	2.76742	0.15595
43	C	-1.073185	4.949533	-0.582477
44	C	-0.549932	6.146096	-1.057969
45	H	0.519	6.311522	-1.101229
46	C	-1.443701	7.12206	-1.506646
47	H	-1.058349	8.066477	-1.878779
48	C	-2.818131	6.883431	-1.486865
49	H	-3.505009	7.647724	-1.837551
50	C	-3.32995	5.66517	-1.033593
51	H	-4.397805	5.5062	-1.054708
52	C	-2.4594	4.668784	-0.570591
53	C	0.99368	3.761531	0.140922
54	C	1.839234	4.796214	0.57144
55	H	1.534309	5.800605	0.818197
56	C	3.121466	4.25694	0.650167
57	H	4.016816	4.77861	0.948803
58	C	3.056044	2.894655	0.282029
59	C	5.347947	-0.281222	-0.079538
60	C	4.879803	-1.590722	-0.339371

61	C	1.874024	-4.627497	-1.501747
62	H	1.791275	-5.61495	-1.927894
63	C	2.996827	-3.798901	-1.550293
64	H	3.931839	-3.997535	-2.048246
65	C	-0.555615	-5.969563	-0.698294
66	C	-1.492822	-6.386628	-1.654506
67	H	-2.103636	-5.643437	-2.157239
68	C	-1.641288	-7.739219	-1.957931
69	H	-2.365723	-8.046456	-2.706402
70	C	-0.864221	-8.695369	-1.300723
71	H	-0.985253	-9.749498	-1.532223
72	C	0.071206	-8.29023	-0.346975
73	H	0.678863	-9.028046	0.168788
74	C	0.232081	-6.935125	-0.054387
75	H	0.961792	-6.619884	0.684851
76	C	-4.134771	-6.011087	2.001795
77	H	-4.376738	-7.025708	2.303115
78	C	-2.964544	-5.773656	1.27744
79	H	-2.306926	-6.599379	1.041651
80	C	-3.691244	-1.003112	0.662309
81	C	-4.041456	1.190907	0.343224
82	C	-5.295471	0.547424	0.424776
83	H	-6.25255	1.035061	0.330492
84	C	-5.083575	-0.816038	0.611868
85	H	-5.832659	-1.588597	0.658433
86	C	-1.689578	-2.409667	0.273403
87	C	5.714032	-2.702314	-0.327024
88	H	5.321365	-3.700572	-0.464914
89	C	7.078159	-2.500074	-0.100832
90	H	7.74779	-3.354646	-0.090129
91	C	7.576239	-1.214692	0.110089
92	H	8.639354	-1.065411	0.272252
93	C	6.722811	-0.109101	0.131378
94	H	7.13974	0.869288	0.316487
95	C	5.916571	2.683777	1.89419
96	H	5.329114	2.205783	2.672147
97	C	7.120536	3.314608	2.21045
98	H	7.465814	3.330079	3.240064
99	C	-5.593583	4.119776	0.956952
100	H	-5.024151	4.176226	1.879631
101	C	-6.789146	4.826718	0.825307
102	H	-7.152246	5.42907	1.65291

S49: Coordinates Table for optimized structure **15**

Sr. No.	Atom	X	Y	Z
1	F	4.276985	0.692353	-2.366604
2	F	4.275215	0.69878	2.366264
3	F	6.713836	1.874871	-2.364499
4	N	-0.287117	1.868262	0.000365
5	N	-1.911726	3.52292	-0.00011
6	F	7.94148	2.466468	-0.001213
7	F	6.71221	1.881108	2.362755
8	C	-1.641123	2.24616	-0.000126
9	C	0.34804	0.618257	0.000124
10	C	2.867441	-0.012317	0.000234
11	C	1.752645	0.883359	0.000242
12	C	1.905619	2.303454	0.000493
13	H	2.840371	2.840909	0.00054
14	C	-4.037468	4.808556	-0.001187
15	H	-3.525841	5.765201	-0.000865
16	C	0.672232	2.870302	0.000586
17	H	0.34718	3.89588	0.000736
18	C	-3.304208	3.624699	-0.000722
19	C	-6.065074	3.469659	-0.002706
20	H	-7.149627	3.42045	-0.003531
21	C	2.829148	-1.383692	0.000536
22	C	-5.429484	4.718408	-0.002159
23	H	-6.02786	5.624573	-0.002537
24	C	-3.931559	2.352783	-0.001126
25	C	4.212242	0.651538	-0.000125
26	C	4.8601	0.972315	-1.194456
27	C	-5.329831	2.282274	-0.002243
28	H	-5.857302	1.337384	-0.002739
29	C	4.859275	0.975504	1.193804
30	C	6.114006	1.579191	-1.207516
31	C	6.741929	1.882324	-0.000874
32	C	6.113173	1.582375	1.206146
33	F	-4.276989	-0.692348	2.366604
34	F	-4.275211	-0.698786	-2.366263
35	F	-6.71384	-1.874866	2.364498
36	N	0.287117	-1.868261	-0.000362
37	N	1.911726	-3.522919	0.000113
38	F	-7.94148	-2.466468	0.00121
39	F	-6.712206	-1.881113	-2.362756
40	C	1.641123	-2.24616	0.000128
41	C	-0.34804	-0.618257	-0.000122
42	C	-2.867441	0.012317	-0.000233
43	C	-1.752645	-0.883358	-0.000239

44	C	-1.905619	-2.303454	-0.000489
45	H	-2.840371	-2.840909	-0.000534
46	C	4.037468	-4.808555	0.001187
47	H	3.525841	-5.765201	0.000868
48	C	-0.672233	-2.870302	-0.000581
49	H	-0.347181	-3.895879	-0.00073
50	C	3.304208	-3.624699	0.000723
51	C	6.065074	-3.469659	0.0027
52	H	7.149626	-3.42045	0.003521
53	C	-2.829148	1.383692	-0.000536
54	C	5.429484	-4.718407	0.002156
55	H	6.02786	-5.624572	0.002533
56	C	3.931559	-2.352782	0.001125
57	C	-4.212242	-0.651538	0.000125
58	C	-4.860102	-0.972313	1.194456
59	C	5.329831	-2.282273	0.002237
60	H	5.857302	-1.337384	0.00273
61	C	-4.859272	-0.975507	-1.193804
62	C	-6.114008	-1.579189	1.207515
63	C	-6.741929	-1.882325	0.000873
64	C	-6.113171	-1.582378	-1.206147