Supporting Information

Organic Fluorophores Substituted Polyaza-[7]helicenes derived from 1,10-Phenanthroline: To Study The Chromophoric effect on Fluorescence Efficiency

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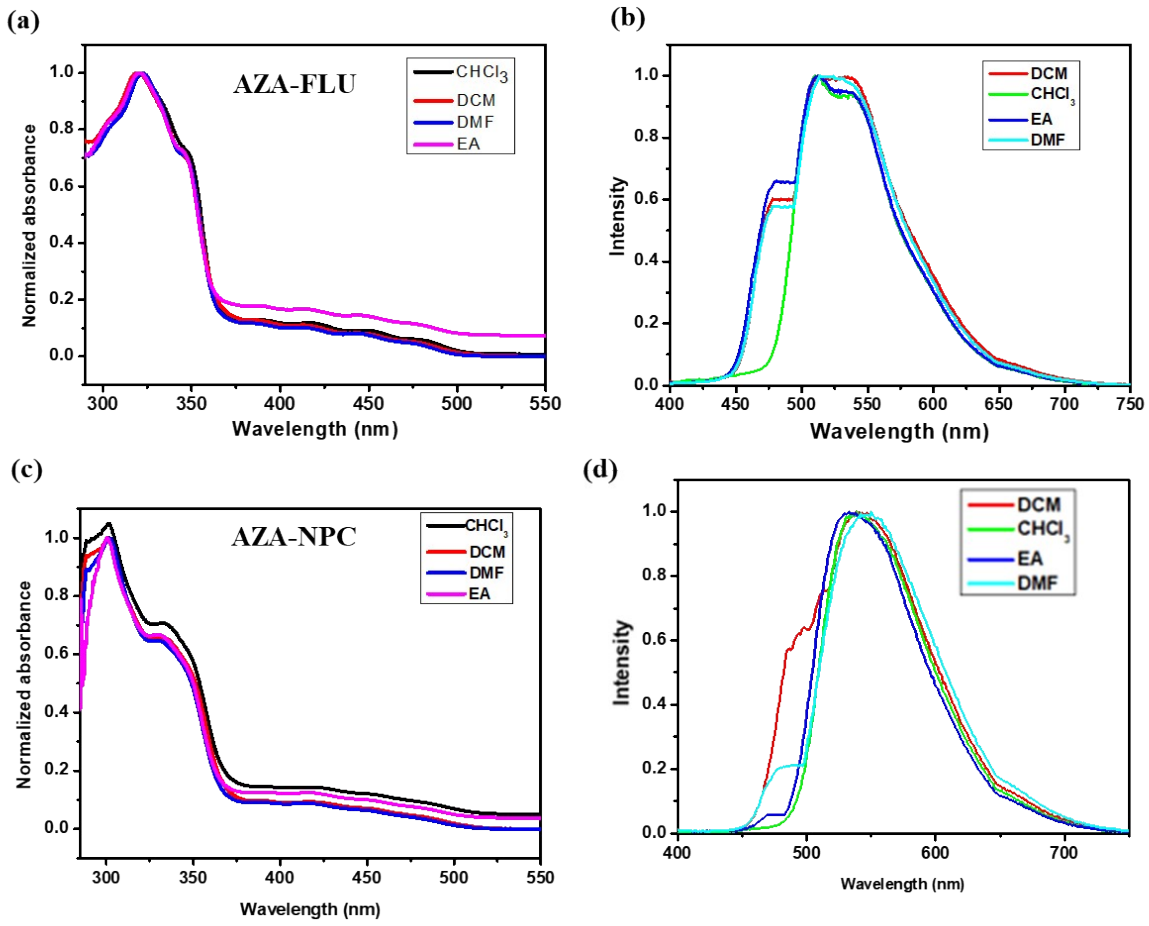

Figure S1. Solvatochromism study: (a-b) UV-visible absorption and (c-d) photoluminescence spectra of AZA-FLU and AZA-NPC in different organic solvents such as $CHCl_3$, DCM, DMF and EA.

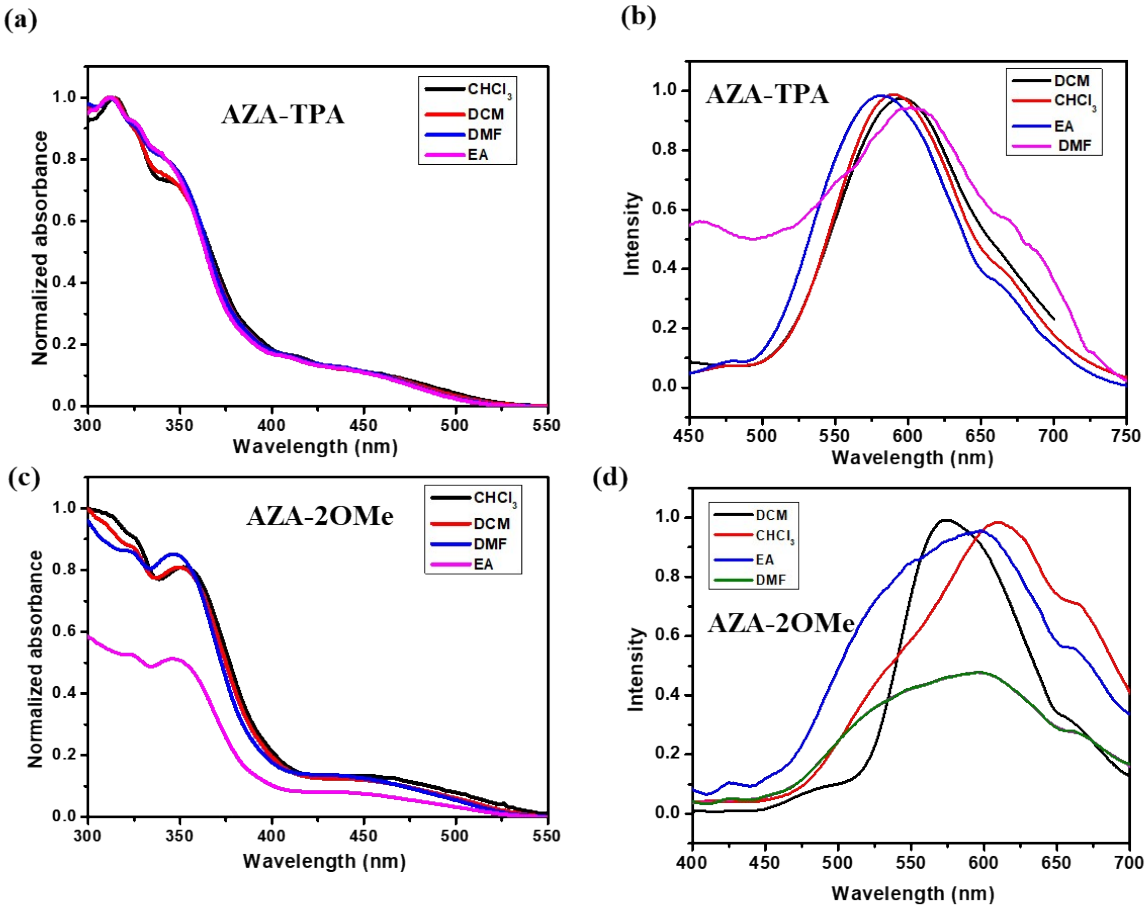

Figure S2. Solvatochromism study: (a-b) UV-visible absorption and (c-d) photoluminescence spectra of AZA-TPA and AZA-2OMe in different organic solvents such as $CHCl_3$, DCM, DMF and EA.

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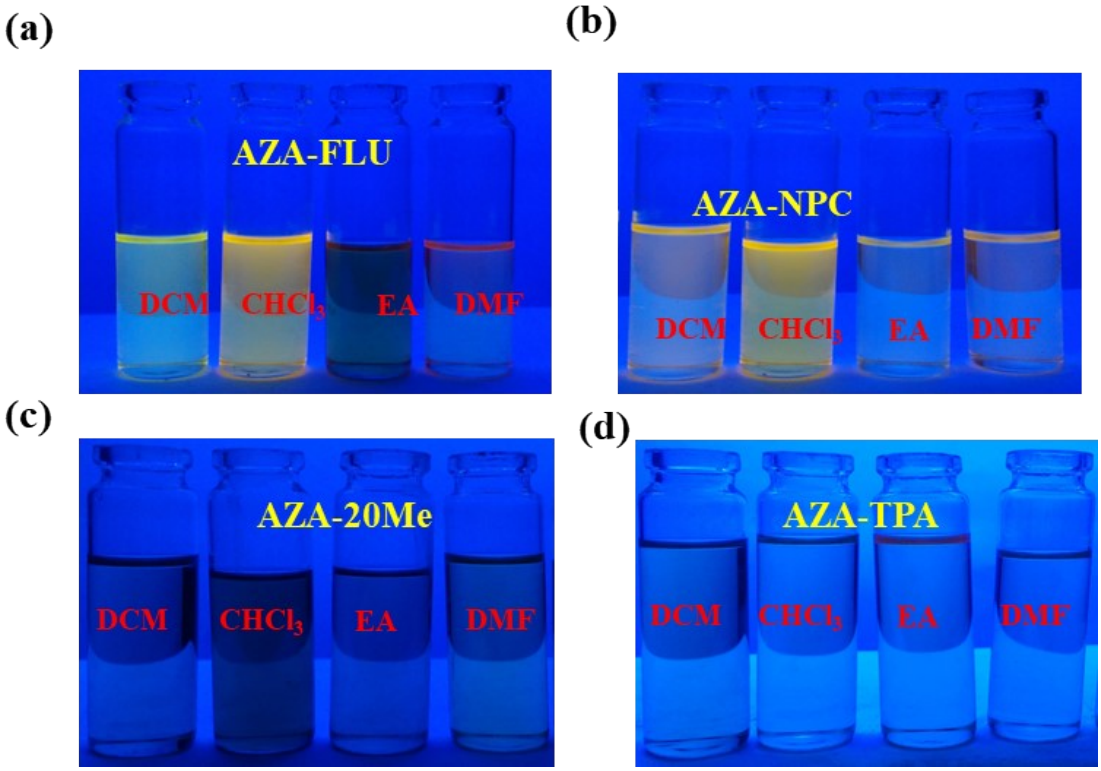


Figure S3. Fluorescence changes of (a) AZA-FLU, (b) AZA-NPC, (c) AZA-2OMe, and (d) AZA-TPA in different organic solvents including DCM, $CHCl_3$, EA and DMF (non-polar to polar).

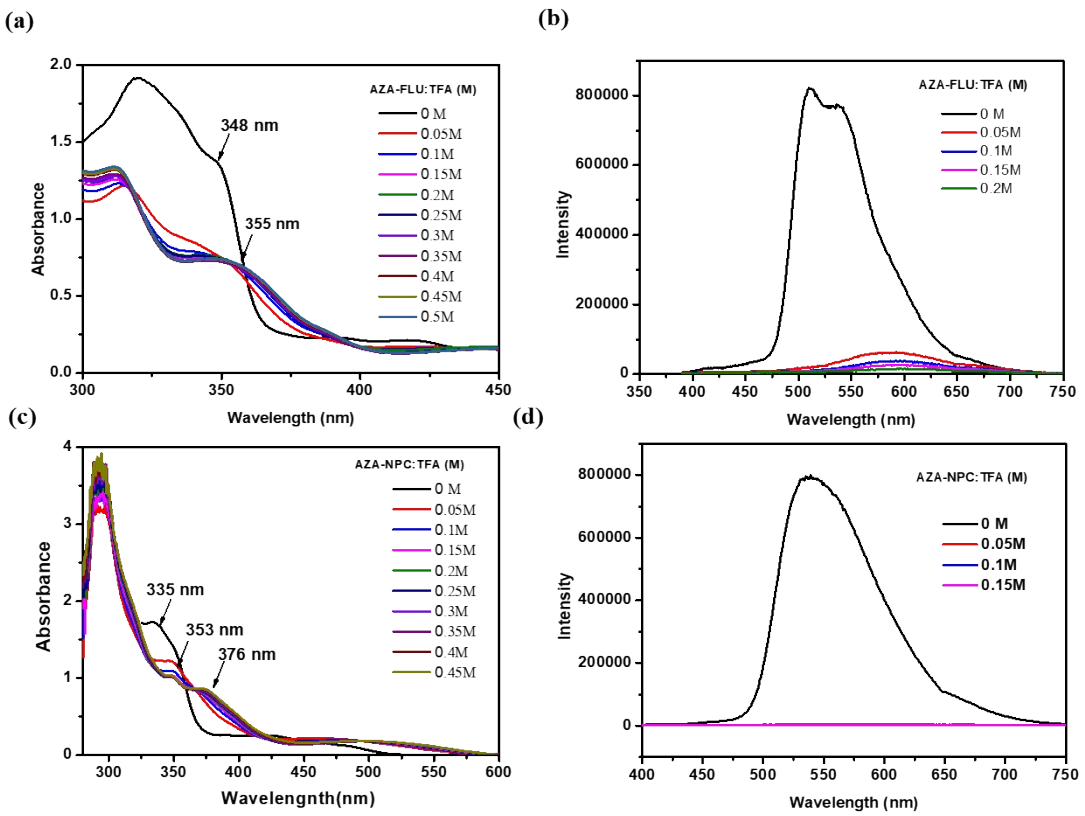


Figure S4. The basic nature analysis of aza-[7]helicenes with trifluoroacetic acid (TFA): (a-c) UV-visible absorption and (b-c) fluorometric titration study of AZA-FLU and AZA-NPC while successive addition of TFA.

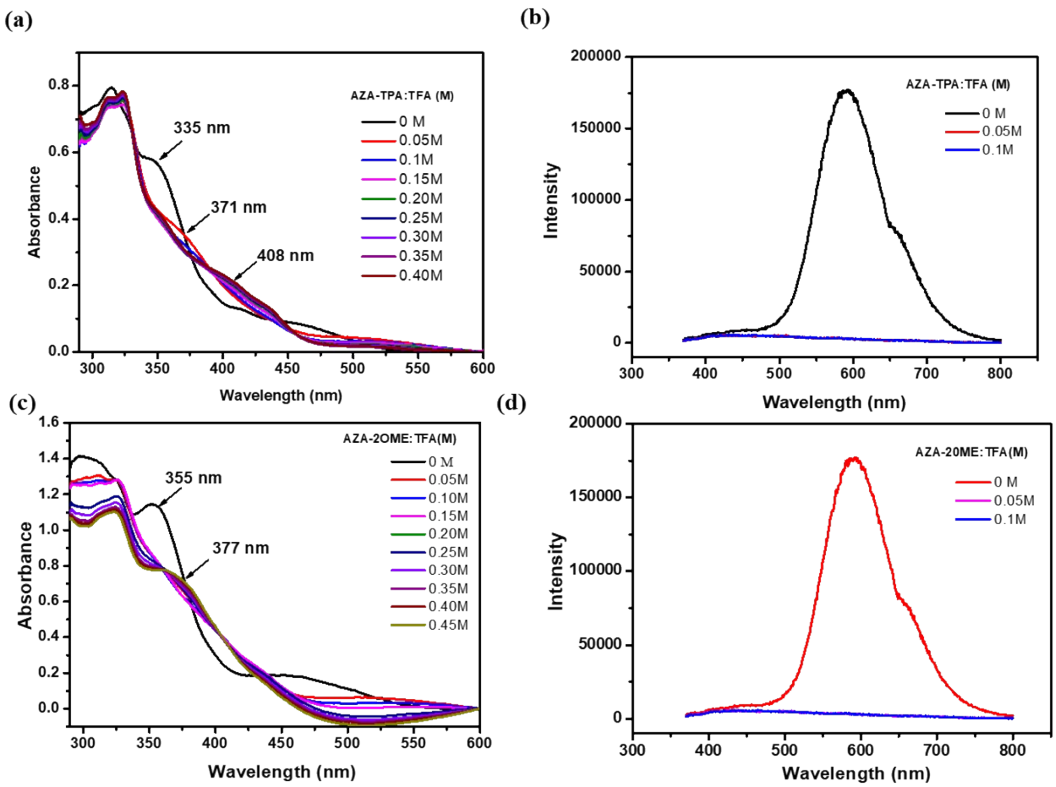


Figure S5. The basic nature analysis of aza-[7]helicenes with trifluoroacetic acid (TFA): (a-c) UV-visible absorption and (b-c) photoluminescence titration study of AZA-TPA and AZA-2OMe while successive addition of TFA.

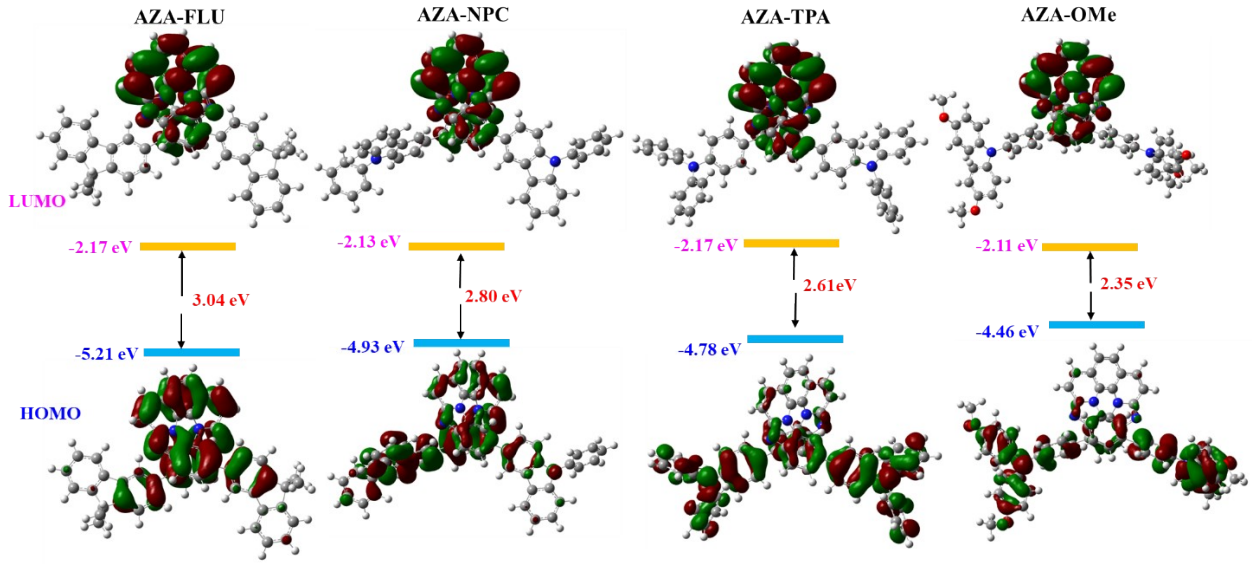


Figure S6. The band gap (E_g) difference between the AZA-FLU, AZA-NPC, AZA-TPA and AZA-2OMe obtained from the DFT calculations.

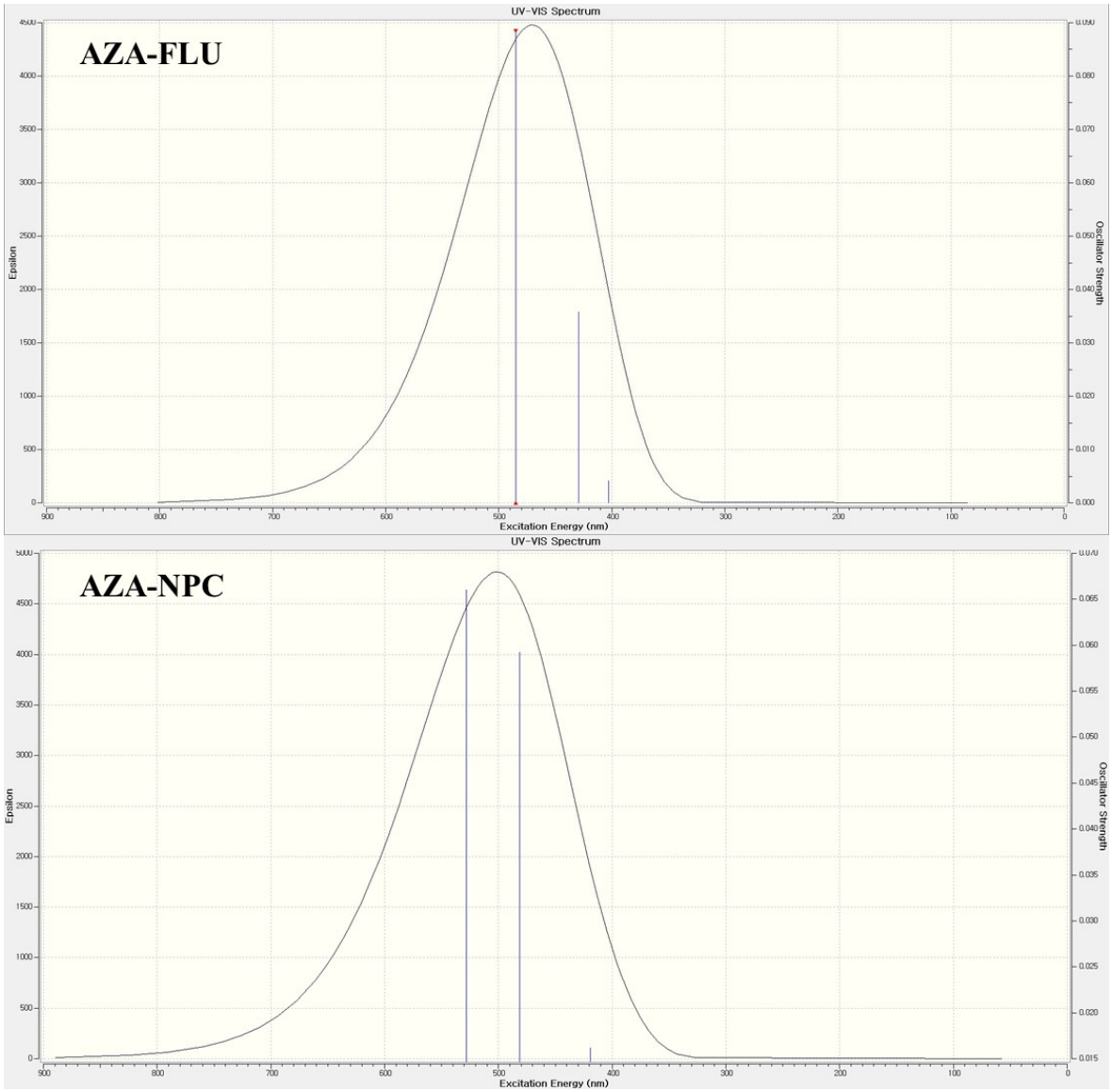


Figure S7. The theoretical UV-vis absorption spectra and TDDFT calculated energy transition with oscillator strength show with a vertical line of AZA-FLU and AZA-NPC.

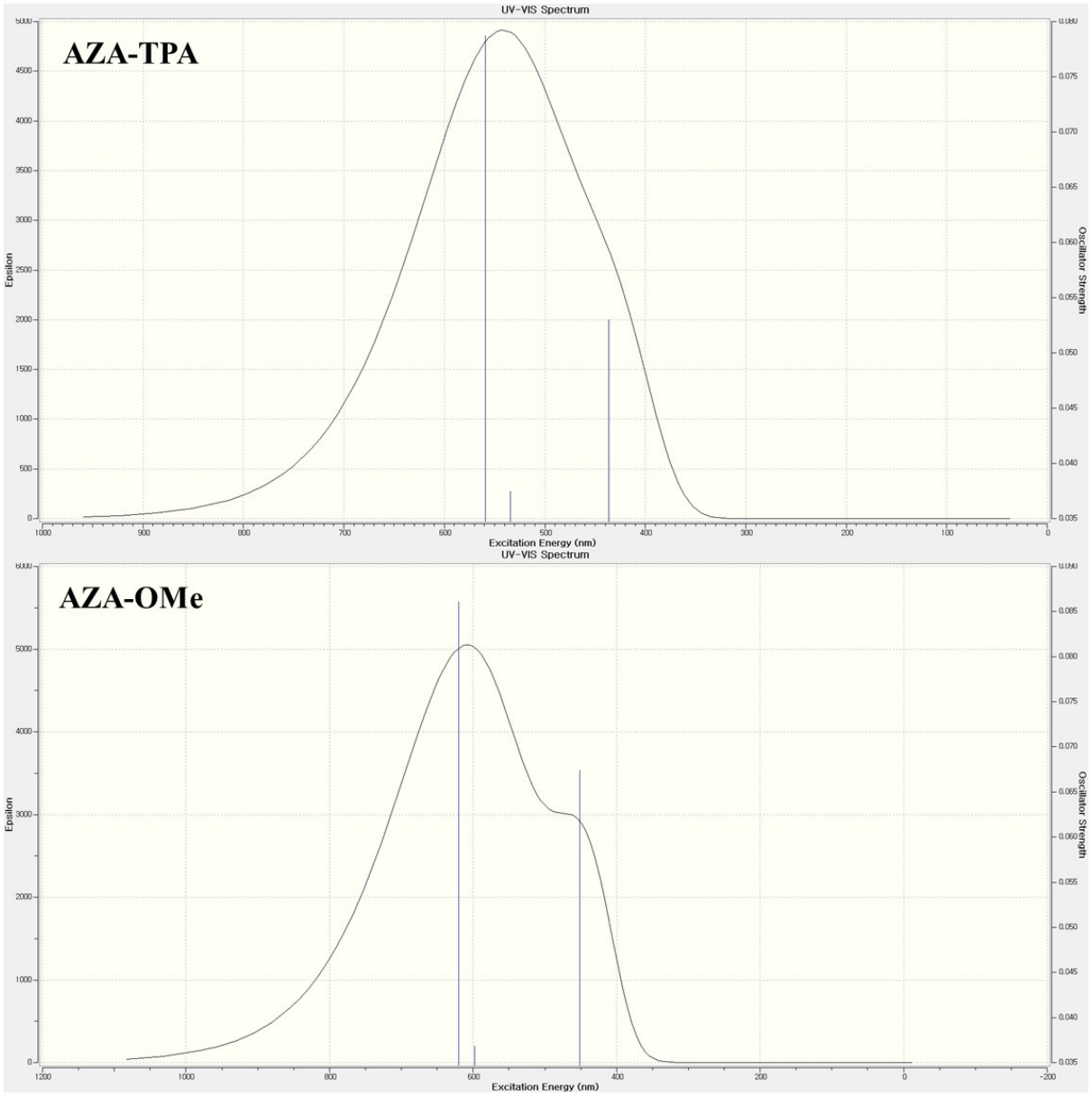


Figure S8. The theoretical absorption spectra and TDDFT calculated energy transitions with oscillator strength show a vertical line of AZA-TPA and AZA-OMe.

Table S1 Solvatochromism values of aza-[7]helicenes in different solvents.

Helicenes	UV-visible absorption λ_{max} (nm)					Emission spectra λ_{em} (nm)				
	$CHCl_3$	DCM	DMF	EA	TOL	$CHCl_3$	DCM	DMF	EA	TOL
AZA-FLU	481	480	476	480	455	535	534	545	536	544
AZA-NPC	482	482	478	483	454	539	545	550	535	543
AZA-20ME	486	485	480	484	458	591	613	591	590	576
AZA-TPA	481	481	481	480	480	593	598	606	585	558

Table S2 Time-resolved photoluminescence decay fitting parameters.

Helicenes	τ_1/ns	α_1 (%)	τ_2/ns	α_z (%)	τ_3/ns	α_3 (%)
AZA-FLU	5 .69	1.41	11.44	88.57	0.01	10.02
AZA-NPC	7.76	2.76	15.5	92.51	0.01	4.73
AZA-20ME	0.005	99.47	3.46	0.36	7.26	0.18
AZA-TPA	0.003	100	4.71	0.00	8.42	0.00

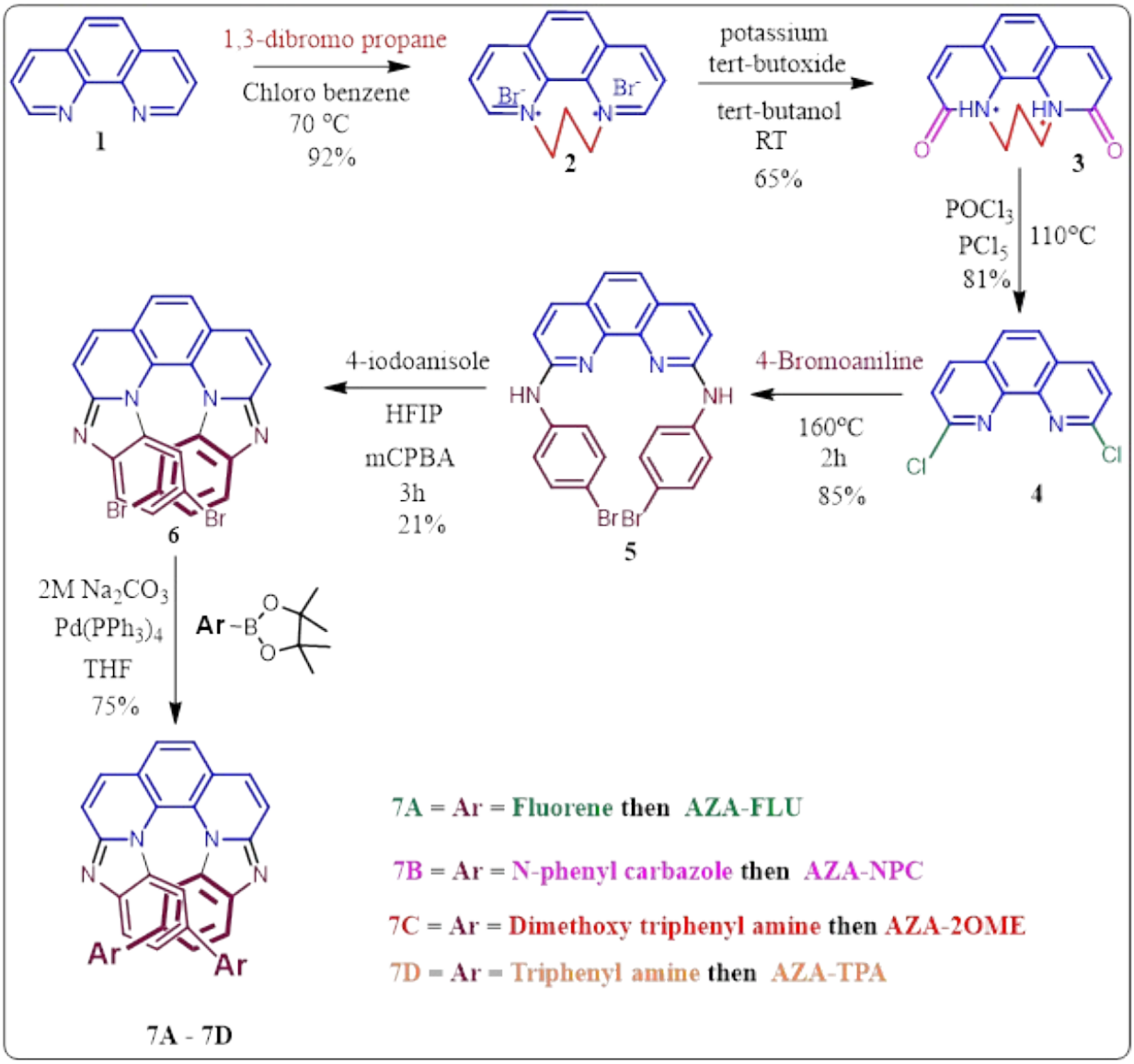
α_1 = amplitude of the components, τ = life Time

1. Experimental Section:

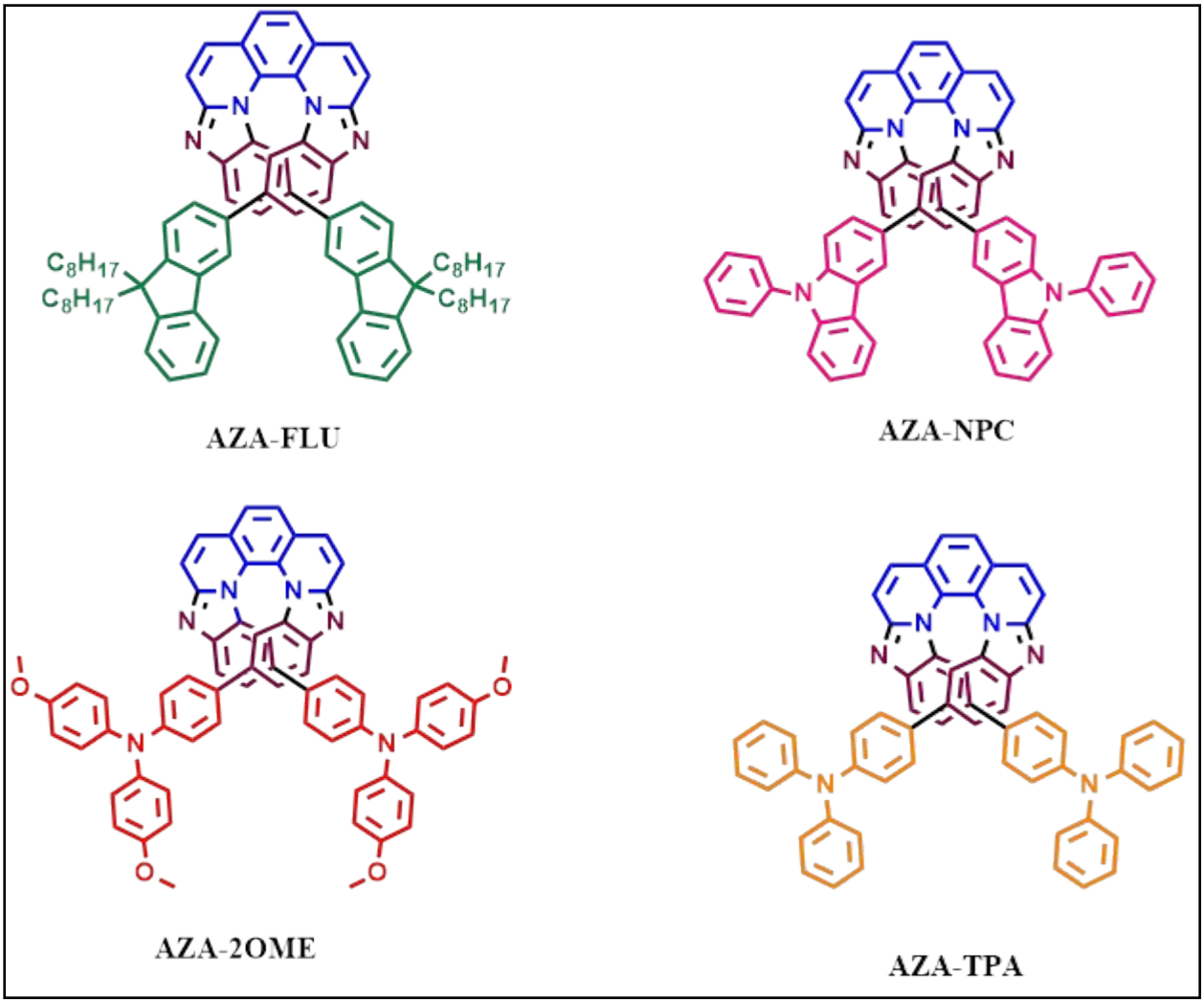
2. Materials and methods

All starting materials were purchased directly from commercial sources and used as such without any further purification. All the required solvents were distilled by following standard procedure and dried under vacuum. Nuclear magnetic resonance (NMR) was used for measuring the ^{1}H and ^{13}C spectra to measure the 1H and 13C spectra0 and 500 MHz, using tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were measured by the Shimadzu LCMS-2010 EV model with ESI probe and the final compounds are also characterized by using MALDI-TOF. The UV-visible absorption spectrophotometer was used to record absorption spectra in chloroform ($CHCl_3$) solution and thin film state. Cyclic voltammetry was performed on CH-Instruments with a three-electrode system consisting of Ag/AgCl electrode, a working electrode and a platinum wire counter-electrode. The redox electronic potentials of the dyes were measured in chloroform ($CHCl_3$) containing 0.1 M Bu_4NHClO_4 at a scan rate of 100 mV s^{-1}.

3. Synthesis



Scheme-S1: Synthetic procedure for AZA-FLU, AZA-NPC, AZA-TPA and AZA-2OMe.



6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium (2).

This compound was prepared by the previous reported procedure.[1] To a round bottom flask (100 ml) was charged with of 1, 10-phenanthroline monohydrate (10.00 g, 55.49 mmol) in chloro-benzene (40 mL) was heated at 70 °C with magnetic stirring. After forming the homogenous solution, 1,3-dibromopropane (22.40g, 110.98 mmol) was added slowly in drop wise manner over 15 minutes, and then the temperature was raised to 120 °C and continued reaction up to 4 h. During the process, a yellow color solid precipitate was observed from the reaction mixture. Then the reaction crude was allowed to room temperature and the yellow powder was collected from the filtration. Further the desired product was washed with hexane

and dried in high vacuum. Which could use for next step without purification to yield the product-2 (92%).

(4R,8R)-3,9-dioxo-4,5,6,7,8,9-hexahydro-3H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium (3)

This compound was prepared by the previous reported procedure.[1]In a 100 ml round bottom flask was charged with compound-2 (2.7 g, 12.15 mmol) and tert-butanol (40 ml). The reaction mixture was sonicated at room temperature over 15 minutes and then heated at 40^{o}C with magnetic stirring. Then potassium tert-butoxide (5.84 g, 60.77 mmol) was added over 10 minutes. After performing the reaction for 4 h, then allowed the crude material cooled to room temperature. The subsequent precipitated solid was collected by work up using chloroform solution. The combined extracted material was dried over Na_2SO_4 and evaporated to give the required product as a brown color solid, which could use for next step without purification to yield the product-3 (65%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 9.5 Hz, 1H), 7.36 (s, 1H), 6.80 (d, J = 9.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.83, 132.14, 123.14, 122.85, 122.75, 45.76, 29.73, 25.74. MS (ESI): Calculated for $C_{15}H_{14}N_2O_4$ (M^+): 254.10 Found: 253.0

2, 9-dichloro-1,10-phenanthroline (4)

This compound was prepared by the previous reported procedure.[1] To a 100 ml round bottom flask were charged with compound-3 (2 g, 8.26 mmol), $POCl_3$ (30 mL) and PCl_5 (4.18g, 19.00 mmol). Then the reaction mixture was degassed for 20 minutes and refluxed at 110 ^{o}C under inert atmosphere over 8 h. After completion of the reaction, the excess $POCl_3$ was removed off under distillation process. The resultant material was decomposed with ice. The desired crude was exacted by base mediated work up using EtOAc as a solvent. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (2:3) are elutes to give compound as a light yellow color solid to yield the product-4 (81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 1H), 7.83 (s, 1H), 7.65 (d, J = 8.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.95, 144.92, 138.78, 127.73, 126.26, 124.92. MS (ESI): Calculated for $C_{12}H_6Cl_2N_2$ (M^+): 249 Found: 249.

N2,N9-bis(4-bromophenyl)-1,10-phenanthroline-2,9-diamine (5)

To a seal tube (10 ml) were charged with compound-4 (300 mg, 1.204 mmol) and 4-bromoaniline (2.07g, 12.04 mmol) was heated at 160 ºC for 2 h. After completion of reaction, it is allowed to cool 0 ºC and saturated aqueous $NaHCO_3$ solution was added. The desired crude was exacted by work up using EtOAc. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and then the organic solvents were completely removed by rotary evaporation. The crude material was purified by column chromatography using EtOAc and hexane (3:2) are elutes to give compound as a light yellow colour solid to yield the product-5 (85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.7 Hz, 1H), 7.48 (d, J = 15.6 Hz, 5H), 7.18 (d, J = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.15, 139.52, 138.29, 132.39, 124.37, 122.75, 121.94, 115.46, 111.53. MS(ESI): Calculated for $C_{24}H_{16}Br_2N_4(M^+)$: 520 Found: 521

10,15-dibromobenzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[2,1-k][1,10]phenanthroline (6)

To a stirred mixture of compound-5 (200 mg, 0.384 mmol), 4-iodoanisole (269 mg, 1.15 mmol), and HFIP (10 mL) was added. In portion wise manner mCPBA (200 mg, 0.11 mmol) was added over 2.5 hours, and then the reaction mixture was stirred for another 1 hour. The reaction was cooled to room temperature and by aqueous $NaHCO_3$ (20 mL) was added at 0 ºC. The resultant mixture was extracted with $CHCl_3$ and the organic layer was condensed under reduced pressure. The combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4 and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (4:1) are elutes to give compound as a yellow colour solid to yield product-6 (21%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 6H), 7.82 (d, J = 8.7 Hz, 2H), 7.35 – 7.27 (m, 2H), 5.94 (d, J = 1.7 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 139.21, 134.70, 133.46, 130.52, 129.77, 128.27, 125.43, 124.00, 120.84, 119.26, 115.54, 114.09. MALDI-TOF: Calculated for $C_{24}H_{16}Br_2N_4$ (M^+): 516.19 Found: 516.98.

10,15-bis(9,9-dioctyl-9H-fluoren-3-yl)benzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[2,1-k][1,10]phenanthroline 7A (AZA-FLU)

To a 50 ml round bottom flask was charged with starting compound-6 (100mg, 0.193 mmol), fluorene boronic ester (220 mg, 0.426 mmol), and 2M sodium carbonate (5 ml) were dissolved in THF (30ml). The respective amount of Pd $(PPh_3)_4$ catalyst was added to the degassed reaction mixture. The mixture was stirred for overnight, then after the completion of reaction the crude product was extracted with EtOAc and the organic layer was removed under reduced pressure. The combined organic layer was washed with NaCl solution and dried over anhydrous Na_2SO_4. The organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (3:2) are elutes to give compound as a bright yellow colour solid to yield compound-7A (75%). 1H NMR (400 MHz, CDCl3) δ 7.91 (dt, J = 22.7, 9.3 Hz, 8H), 7.57 (d, J = 8.1 Hz, 4H), 7.45 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 5.3 Hz, 2H), 7.24 (d, J = 3.5 Hz, 4H), 6.97 (d, J = 7.7 Hz, 2H), 6.67 (s, 2H), 6.27 (s, 2H), 2.31 (td, J = 14.8, 4.2 Hz, 4H), 2.11 (dd, J = 20.9, 9.8 Hz, 4H), 1.47 (d, J = 19.5 Hz, 5H), 1.15 – 0.95 (m, 42H), 0.75 – 0.65 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.59, 149.93, 147.41, 141.63, 139.83, 138.97, 134.83, 132.40, 128.77, 125.93, 125.45, 125.04, 124.17, 123.88, 121.90, 121.47, 120.79, 118.76, 118.23, 110.21, 54.47, 39.48, 30.81, 29.39, 28.32, 22.81, 21.58, 13.06. CHN calc. C, 86.72; H, 8.34; N, 4.93 found C, 86.95; H, 8.56; N, 4.99. HRMS Calculated for $C_{82}H_{94}N_4(M+H^+)$: 1135.7512 Found: 1135.7551

10,15-bis(9-phenyl-9H-carbazol-3-yl)benzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[2,1-k][1,10]phenanthroline 7B (AZA-NPC)

In a round bottom flask 50 ml was charged with compound-6 (138 mg, 0.267 mmol), N-phenylcarbazole boronicester (250 mg, 0.66 mmol), and 2M sodium carbonate (5 ml) in THF (30ml). Before going to addition of Pd $(PPh_3)_4$ catalysts, degassed the reaction mixture over 20 minutes. The reaction mixture has stirred for 12 h, after the completion of reaction the crude product was extracted with EtOAc and the organic layer was condensed rota evaporator. The combined organic layer was washed with brine solution and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (3:2) are elutes to give compound as an orange colour solid to yield the compound-7B (75%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 5.7 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.95 (s, 1H), 7.91 (d, J = 9.4 Hz,

1H), 7.59 (ddd, J = 20.6, 14.3, 6.0 Hz, 7H), 7.49 – 7.41 (m, 4H), 7.37 (d, J = 8.5 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 6.39 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.47, 142.35, 141.27, 140.03, 137.68, 135.99, 133.37, 129.98, 129.80, 127.45, 127.02, 126.41, 125.35, 125.53, 125.35, 125.03, 124.79 – 124.46, 124.23, 124.07, 123.91, 122.48, 121.40, 120.47, 119.56, 119.32, 119.23, 119.32, 118.86, 111.18, 109.78. CHN calc. C, 85.69; H, 4.31; N, 9.99; found C, 85.99; H, 4.51; N, 10.15. HRMS: Calculated for $C_{60}H_{36}N_6$(M+H$^+$): 841.3035, Found 841.3074.

4,4'-(benzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[2,1-k][1,10]phenanthroline-10,15-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) 7C (AZA-20ME)

To a round bottom flask (50 ml) was consisted with compound-6 (60 mg, 0.116 mmol), Dimethoxy triphenylamine boronicester (111 mg, 0.255 mmol), and 2M Na_2CO_3 (5 ml) in THF (30ml). The $Pd(PPh_3)_4$ catalysts was added to the degassed the reaction mixture. The mixture was stirred for overnight, then after the completion of reaction the crude product was extracted with EtOAc and the organic layer was condensed under reduced pressure. The combined organic layer was washed with NaCl solution and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (3:2) are elutes to give compound as a red colour solid to yield the compound -7C (75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (t, J = 4.7 Hz, 4H), 7.89 – 7.80 (m, 4H), 7.33 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.9 Hz, 8H), 6.87 (dd, J = 15.0, 8.8 Hz, 12H), 6.73 (d, J = 8.7 Hz, 4H), 6.14 (s, 2H), 3.83 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.99, 148.21, 147.90, 142.10, 140.78, 134.94, 133.27, 132.79, 129.42, 127.85, 126.82, 125.93, 125.01, 124.77, 124.62, 122.35, 120.41, 120.28, 120.08, 119.38, 114.81, 110.19, 55.53. CHN calc. C, 79.65; H, 5.01; N, 8.71; found C, 79.85; H, 5.21; N, 8.81. HRMS(ESI): Calculated for $C_{64}H_{48}N_6O_4$(M+H$^+$): 965.3859 Found 965.3809.

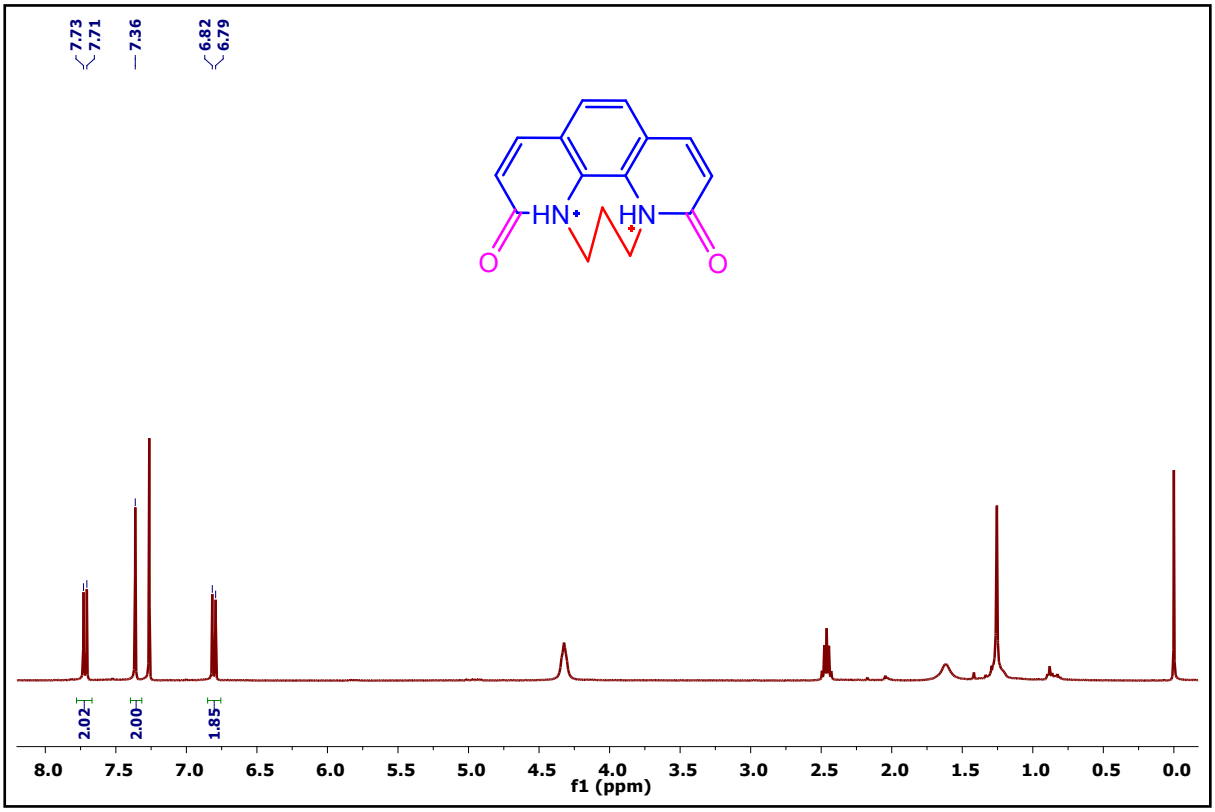
4,4'-(benzo[4,5]imidazo[1,2-a]benzo[4,5]imidazo[2,1-k][1,10]phenanthroline-10,15-diyl)bis(N,N-diphenylaniline) 7D (AZA-TPA)

In a 50 ml round bottom flask was charged with compound-6 (60 mg, 0.116 mmol), Triphenylamine boronicester (111 mg, 0.255 mmol), and 2M sodium carbonate (5 ml) in THF (25ml). The $Pd(PPh_3)_4$ catalyst was added to the degassed the reaction mixture. The mixture was stirred for 12 h, then after the completion of reaction the crude product was extracted with EtOAc. The combined organic layer was washed with brine and dried over anhydrous sodium

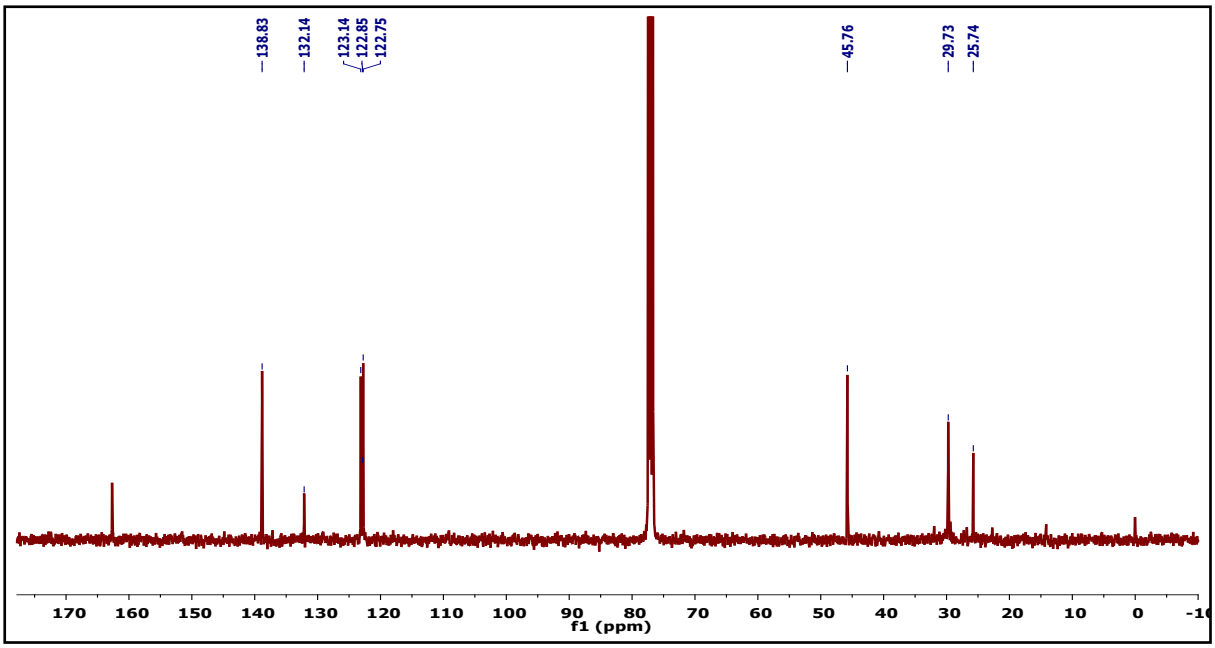
sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (3:2) are elutes to give compound as a red colour solid to yield compound-7D (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 10.9 Hz, 2H), 7.68 (dd, J = 11.0, 8.5 Hz, 2H), 7.55 (t, J = 6.7 Hz, 1H), 7.46 (dd, J = 16.7, 8.2 Hz, 2H), 7.28 (s, 2H), 7.21 (s, 2H), 7.06 (dd, J = 19.1, 7.3 Hz, 5H), 6.76 (t, J = 8.6 Hz, 1H), 6.04 (d, J = 34.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.28, 148.15, 147.62, 147.08, 134.66, 132.18, 132.08, 131.96, 130.34, 129.45, 129.32, 128.59, 128.47, 128.08, 127.97, 126.26, 125.15, 124.92, 124.60, 123.52, 123.05, 122.34, 122.10, 120.83, 120.17, 119.61, 119.18, 115.98, 114.88, 114.78, 109.92. CHN cacl. C, 85.28; H, 4.77; N, 9.95; found C, 85.48; H, 4.87; N, 9.99; HRMS(ESI): Calculated for $C_{60}H_{40}N_6(M+H^+)$: 844.3314 Found 844.3318.

4. ^{1}H-NMR and ^{13}C-NMR Spectra

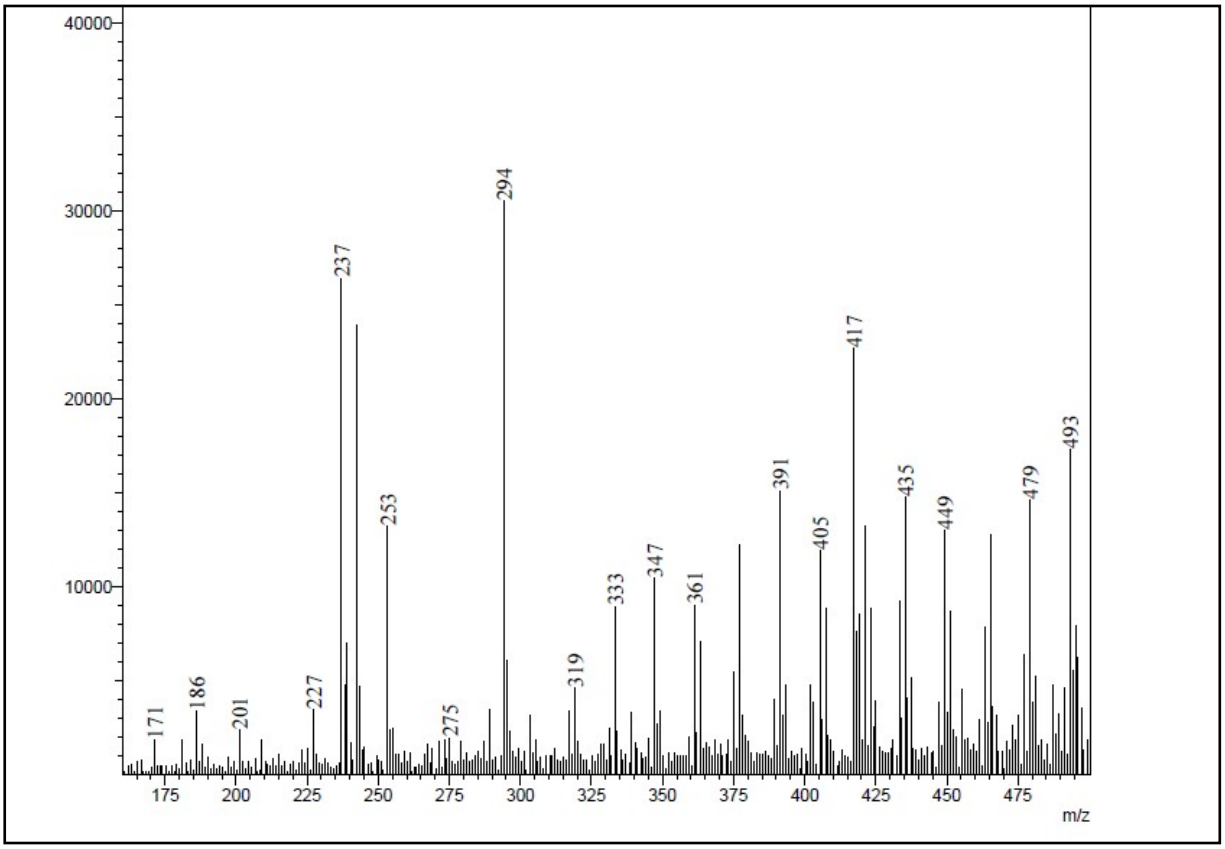
^{1}H-NMR of 3



^{13}C-NMR of 3



ESI spectra of 3



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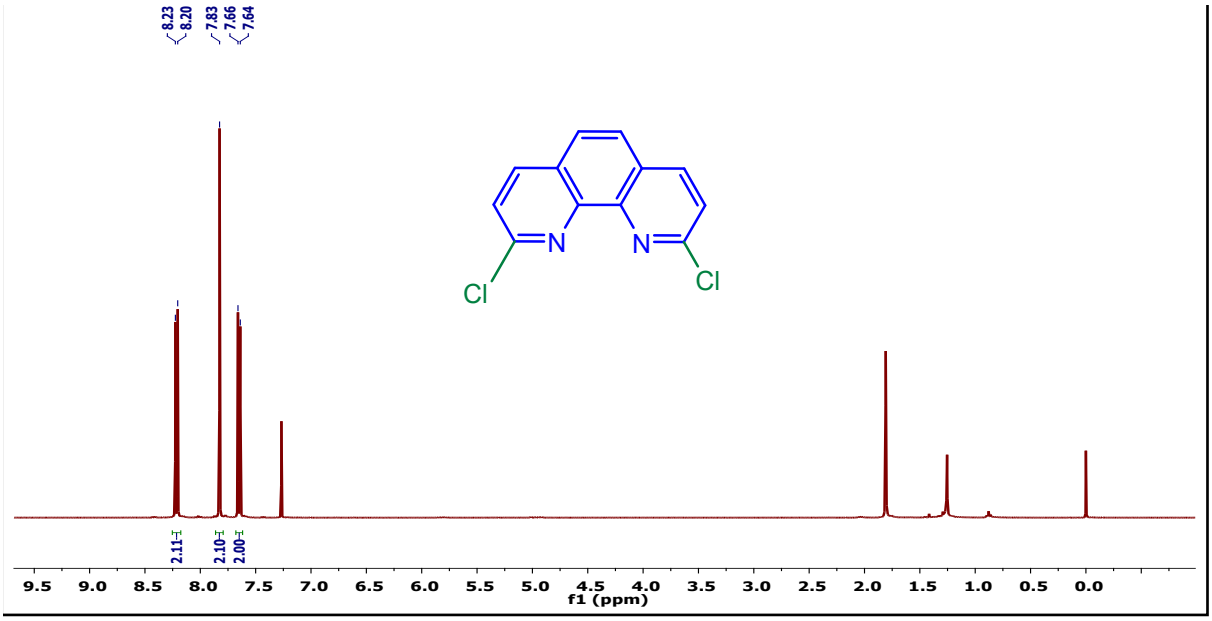

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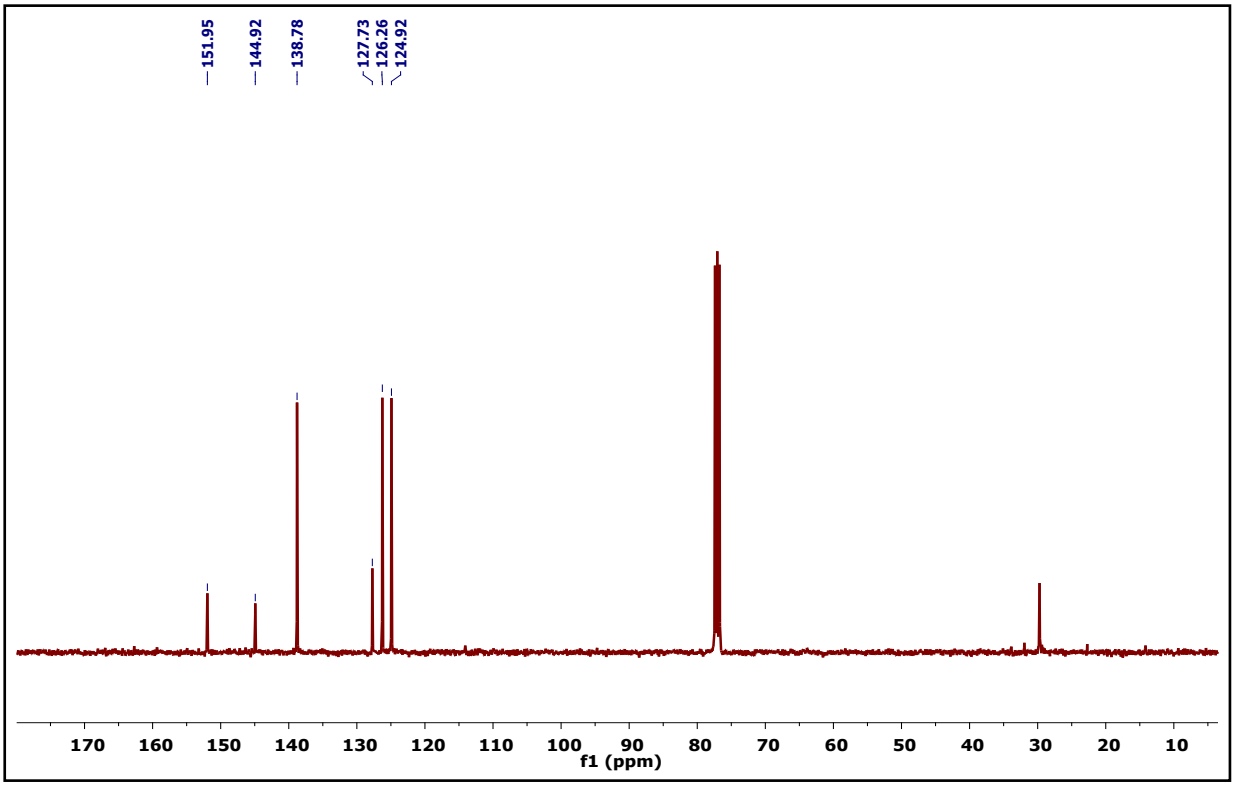
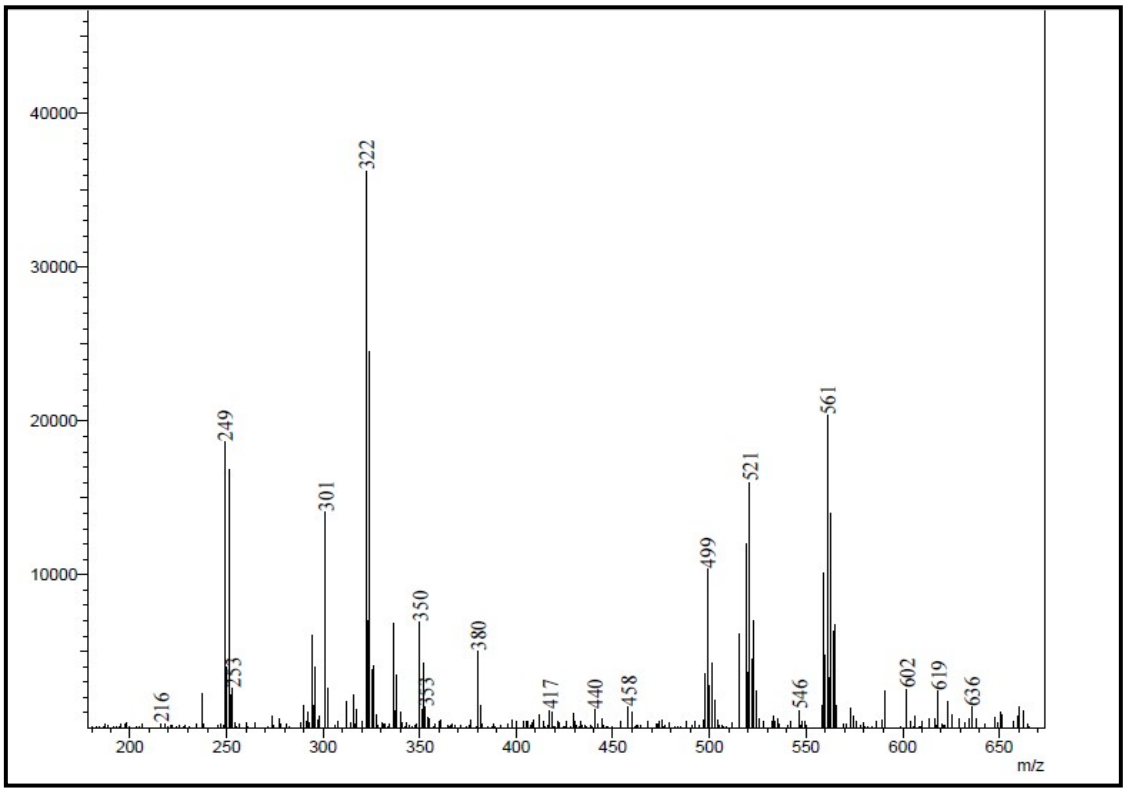
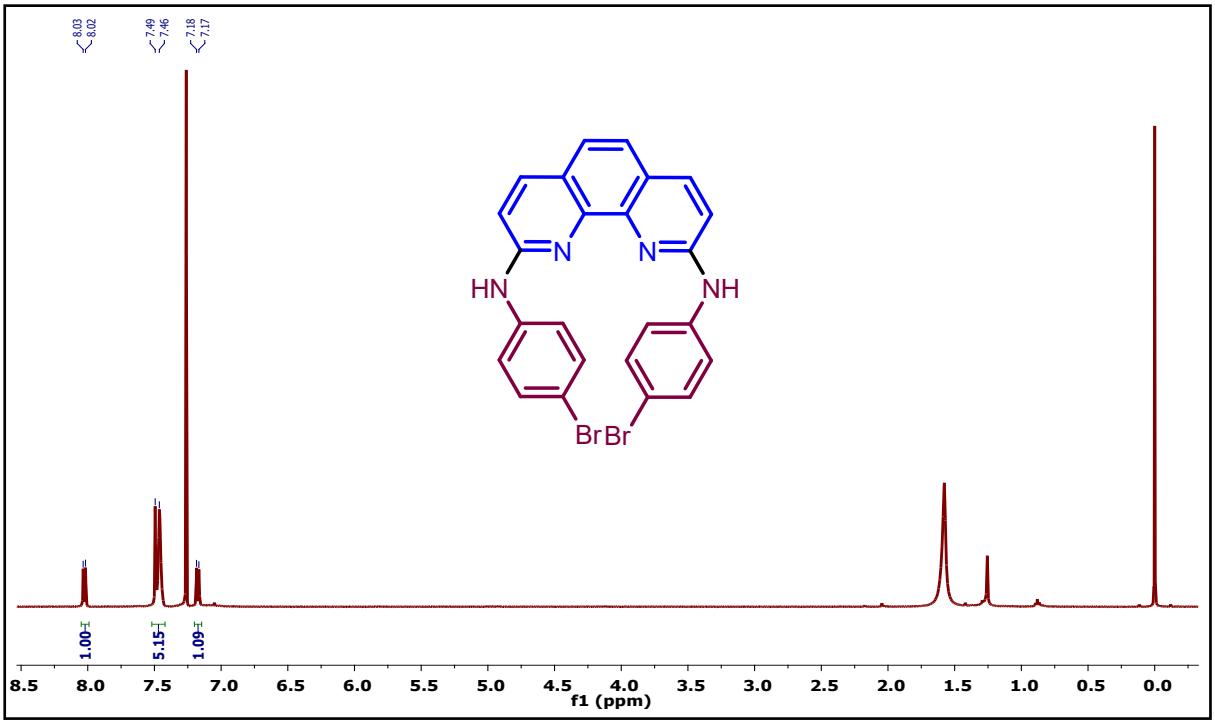


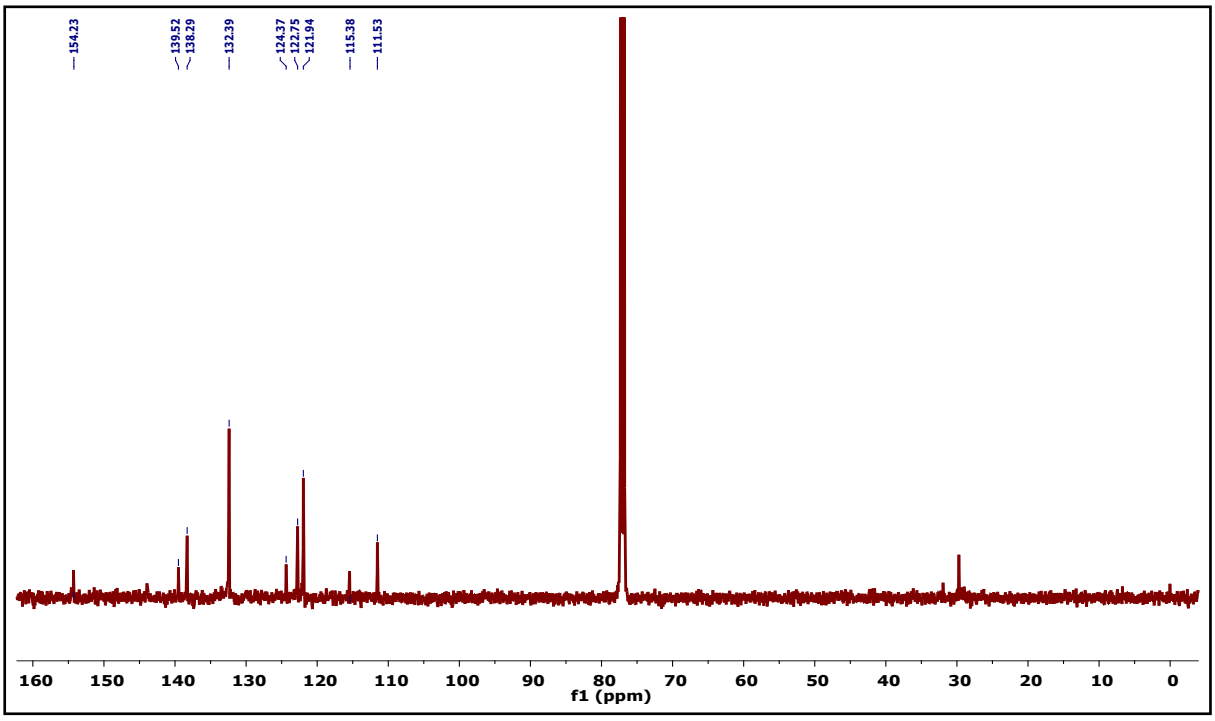
ESI spectra of 4



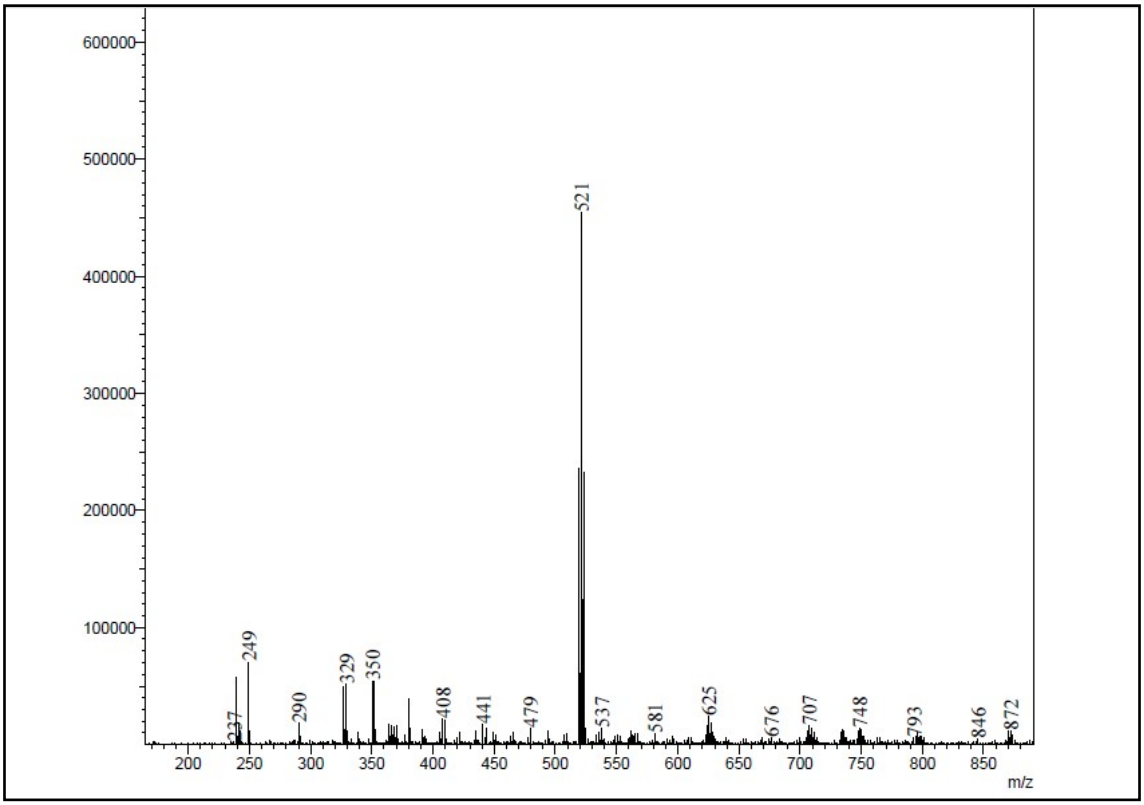
^{1}H-NMR of 5



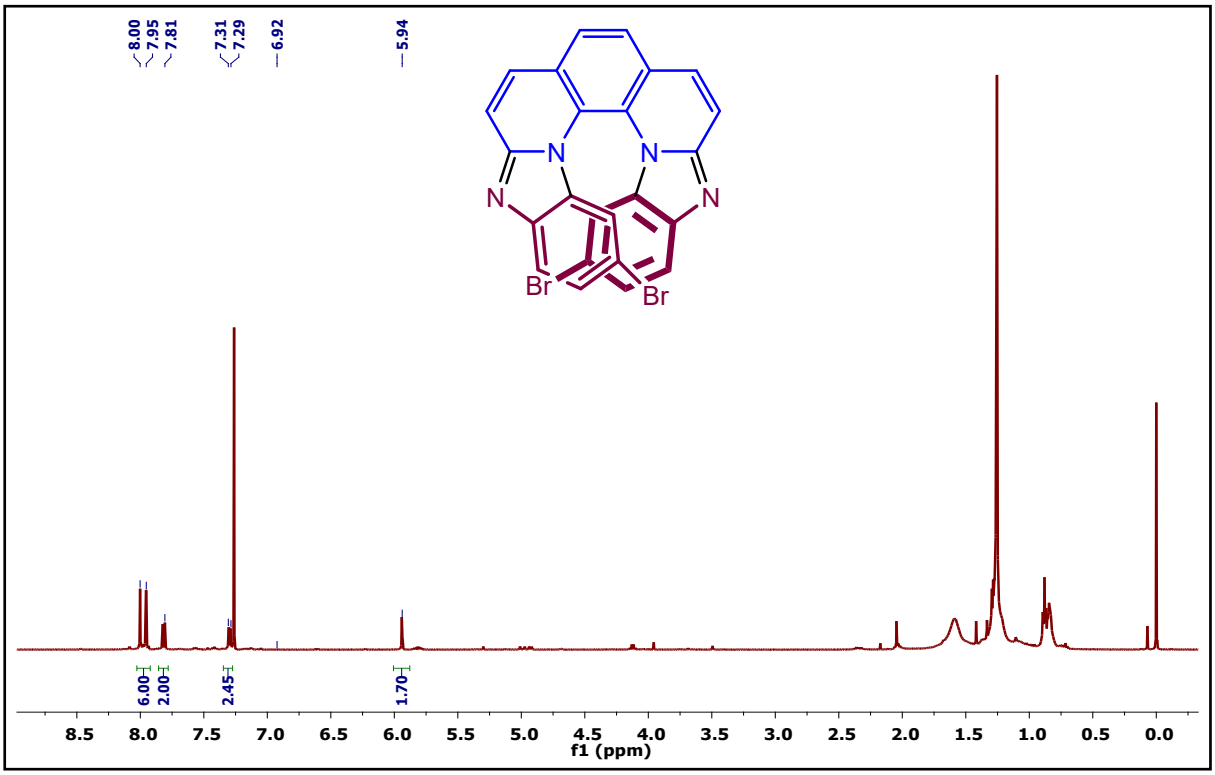
^{13}C-NMR of 5



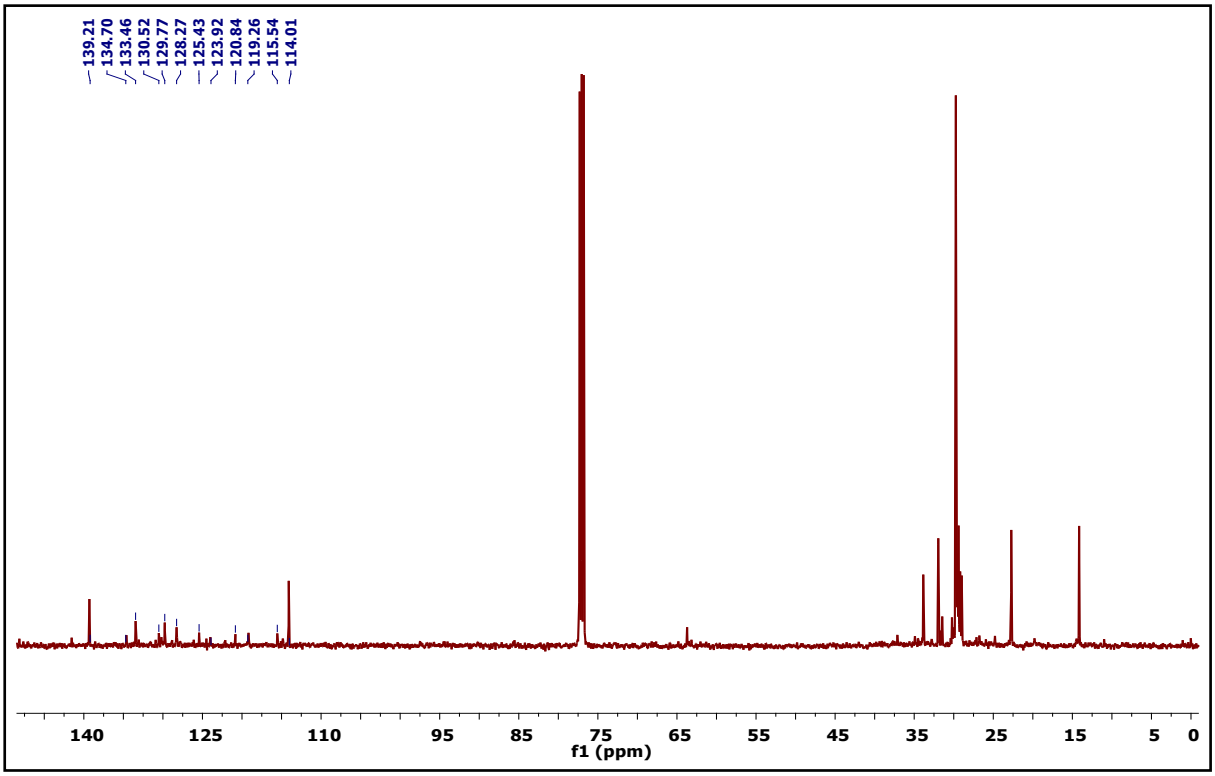
ESI spectra of 5



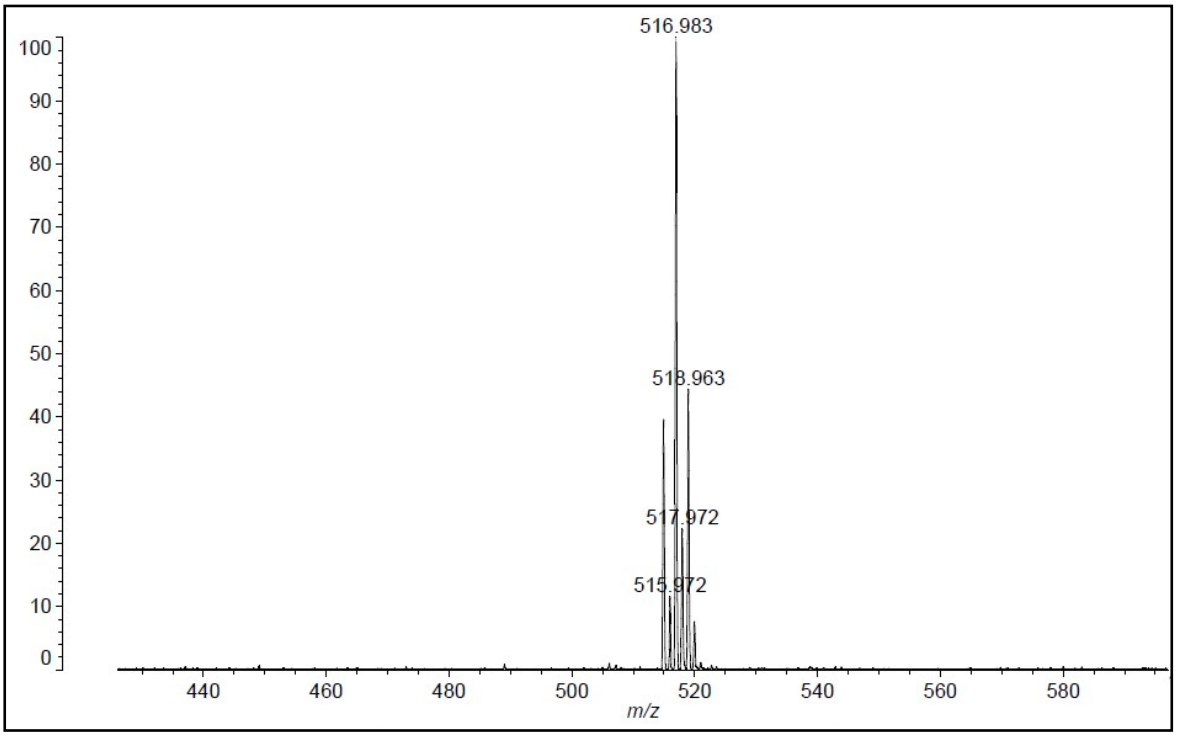
^{1}H-NMR of 6



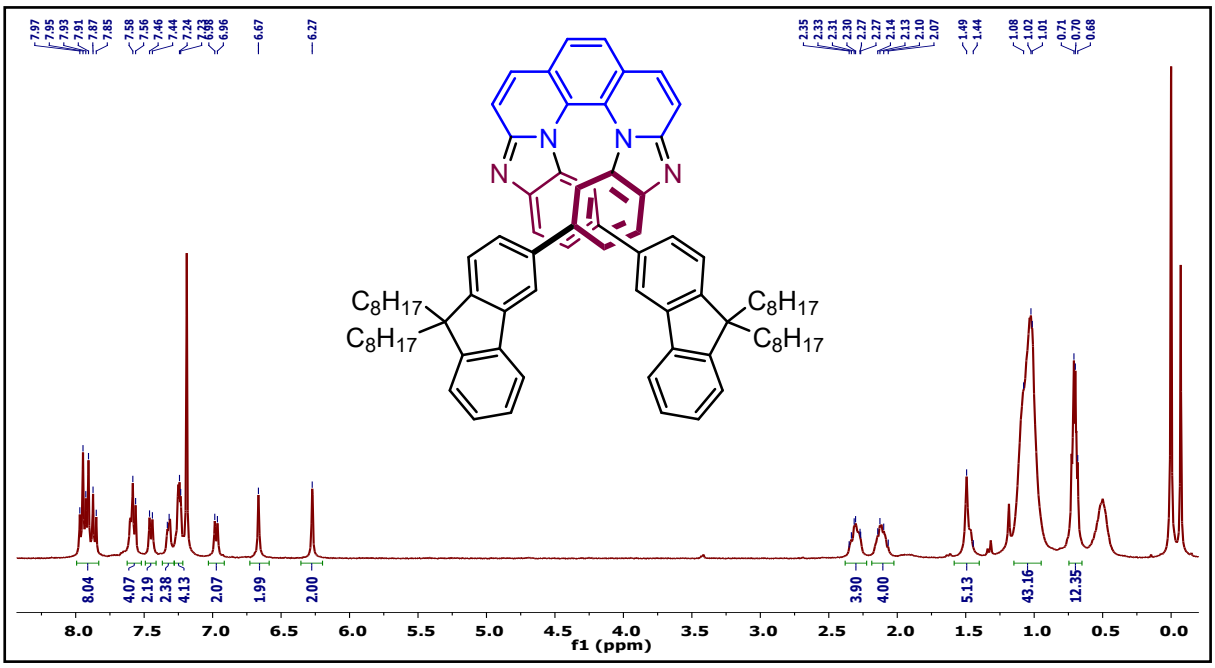
^{13}C-NMR of 6



MALDI-TOF spectra of 6



^{1}H-NMR of AZA-FLU



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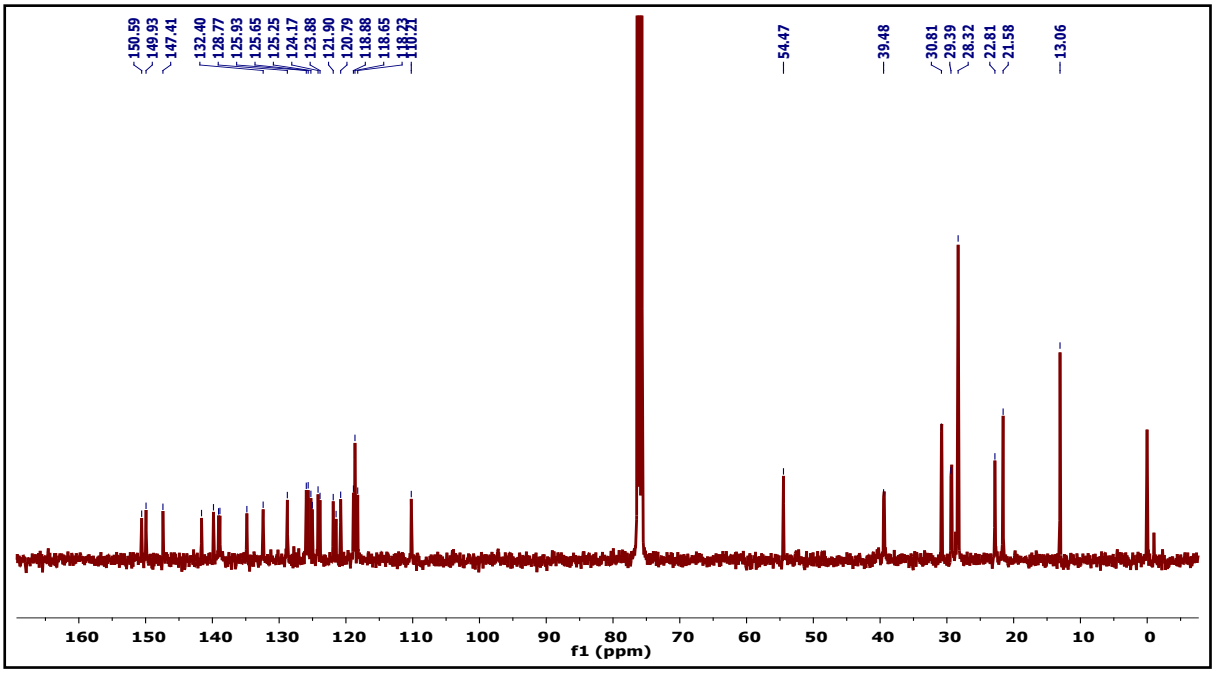

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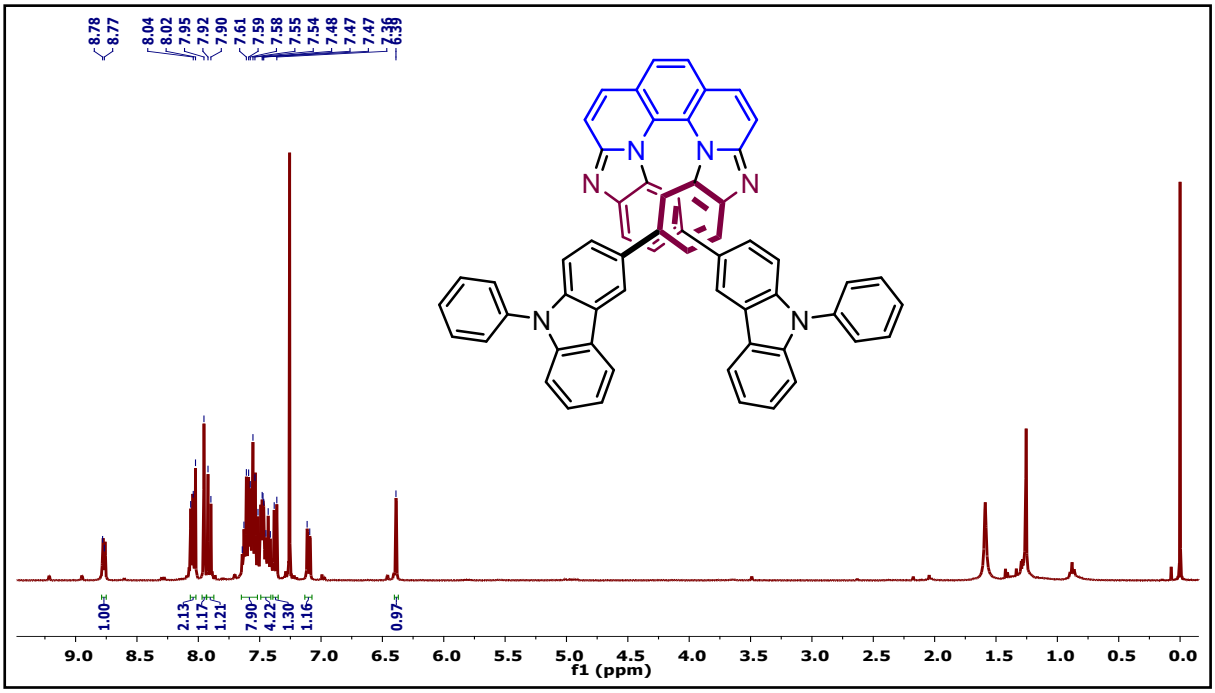
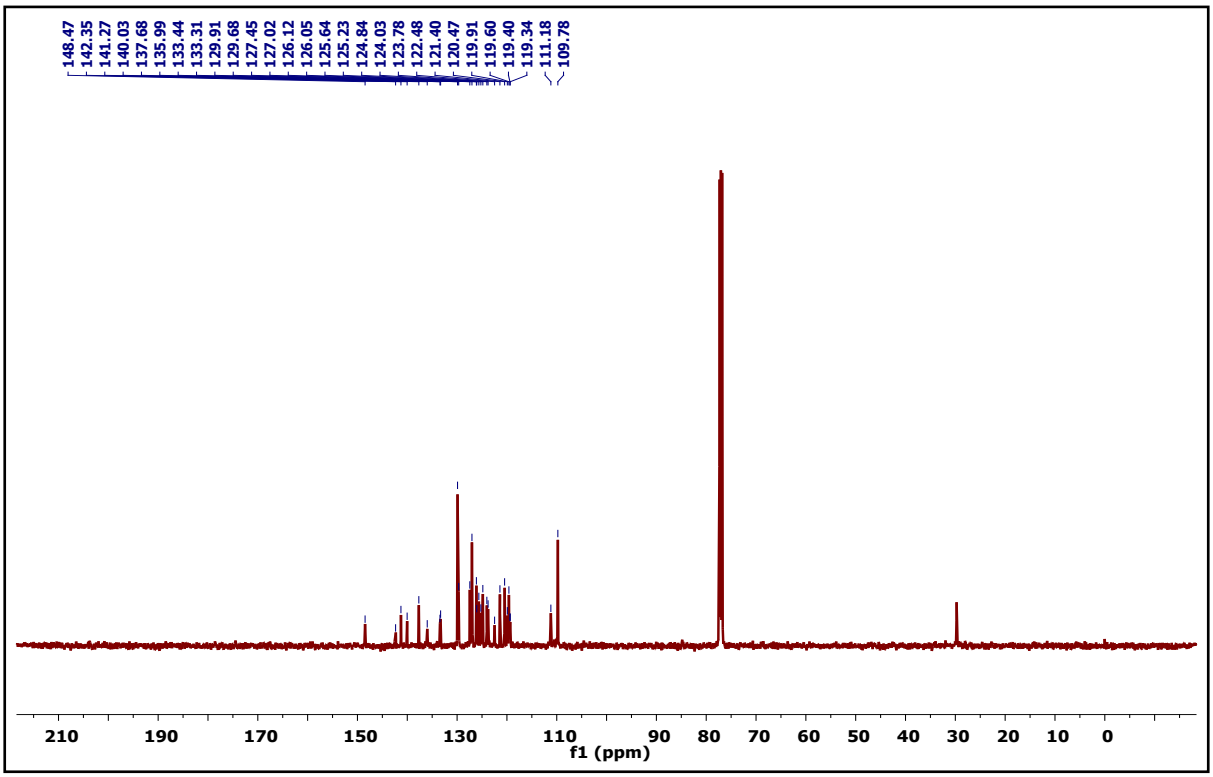
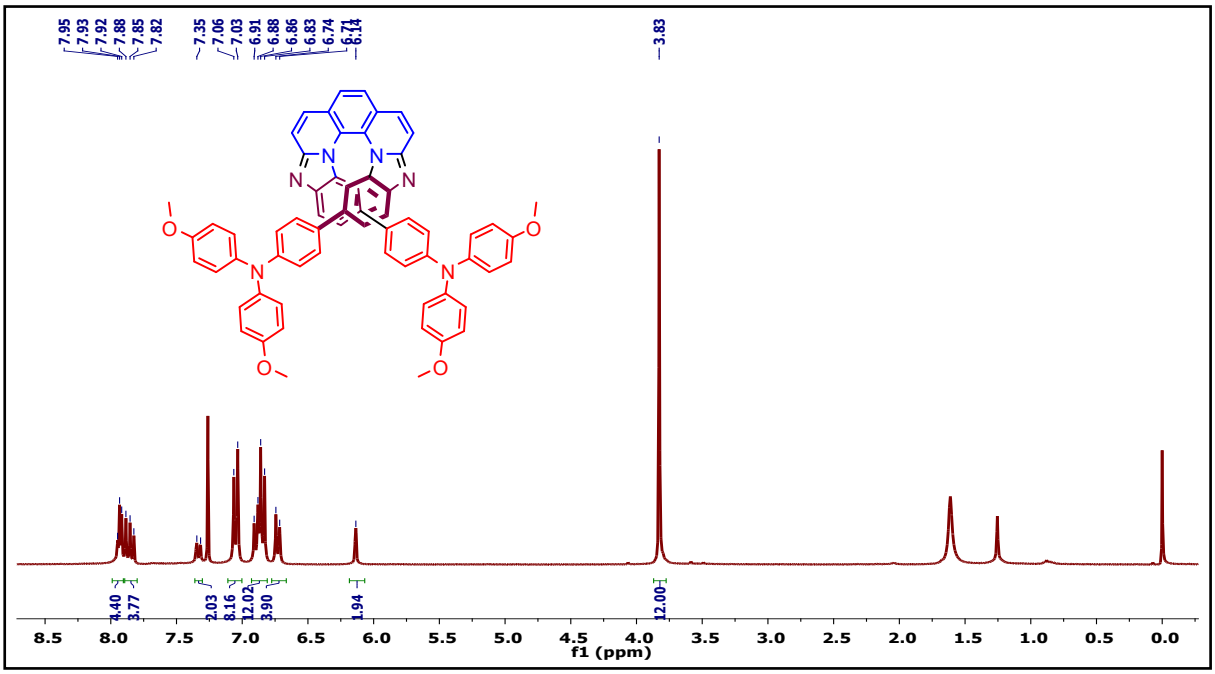


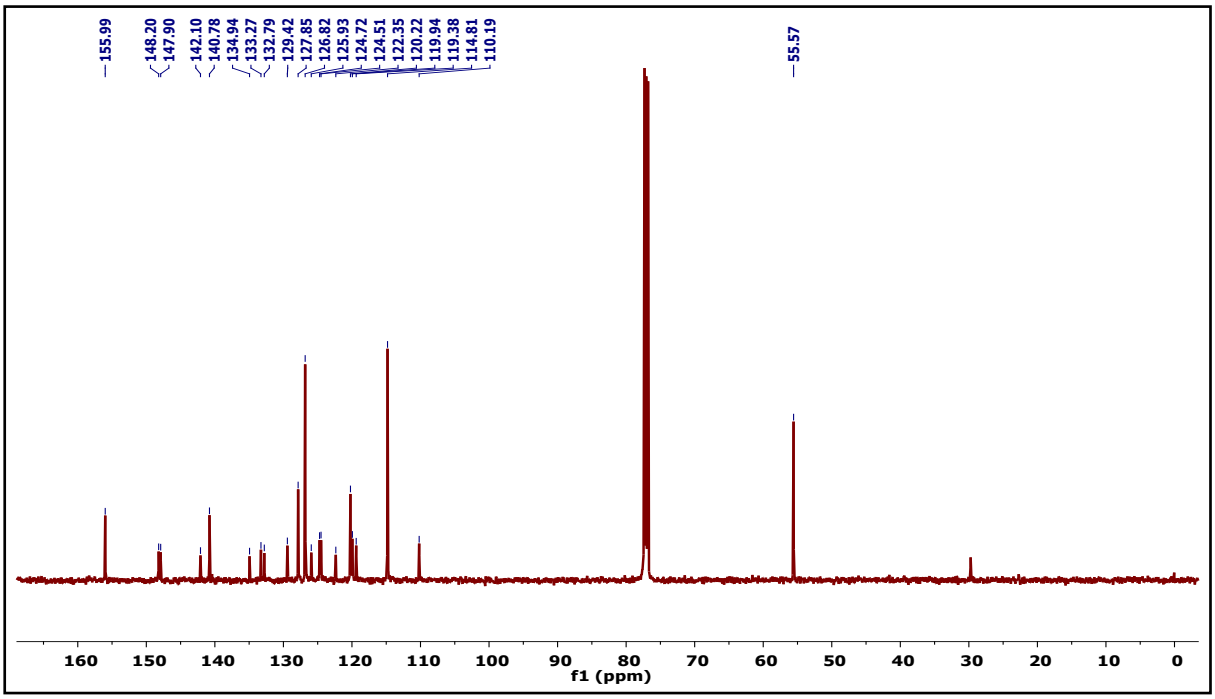
^{13}C-NMR of AZA-NPC



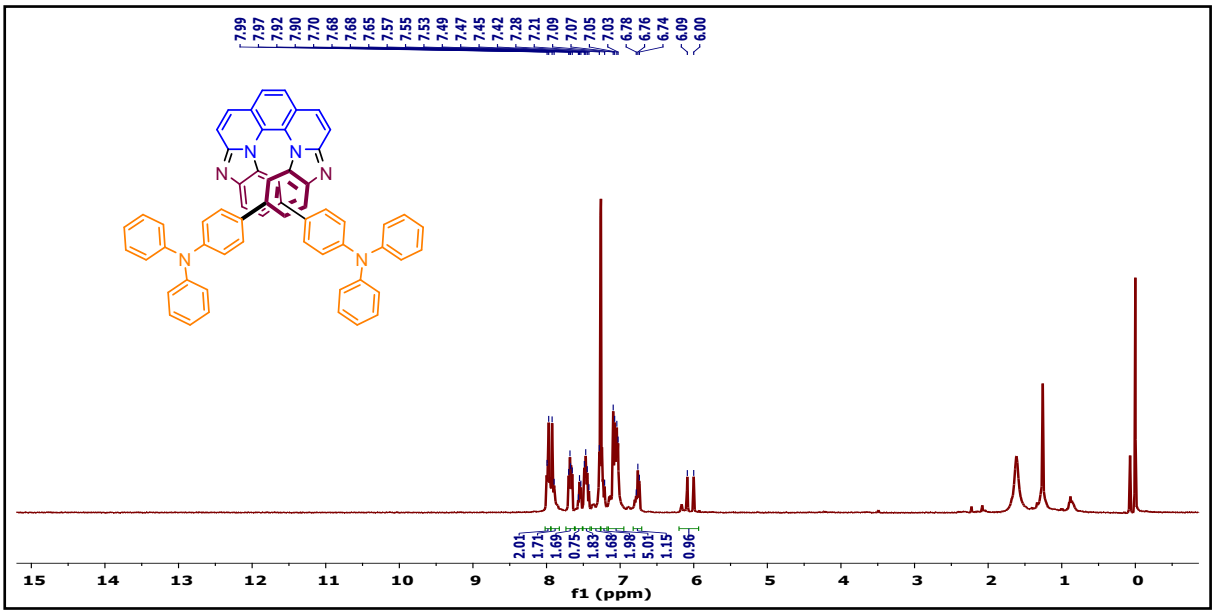
^{1}H-NMR of AZA-2OME



^{13}C-NMR of AZA-2OMe



^{1}H-NMR of AZA-TPA



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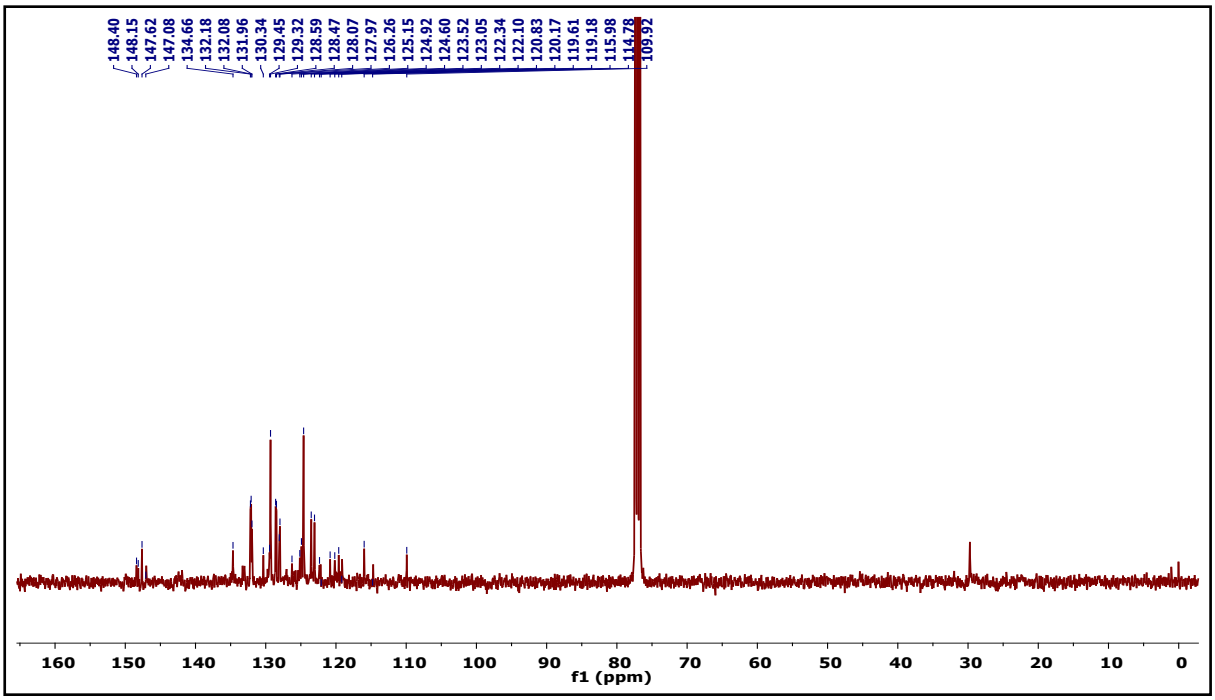

5. References

1. *H. C. Guo, R. H. Zheng and H. J. Jiang, Organic Preparations and Procedures International* ,2012, **4948**, 2–7.