Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


# Supporting Information

## To

# Conversion of Amino-Terephthalonitriles to Multi-Substituted Single Benzene Fluorophores with Utility in Bioimaging

Tanya Raghava,[a] Anjan Chattopadhyay,[*a] Subhadeep Banerjee,[*a,b] Nivedita Sarkar[b]

[a]Department of Chemistry, Birla Institute of Technology and Science Pilani KK Birla Goa Campus, NH 17B, Bypass Road, Zuarinagar Goa-403726, India.

[b]Fluoresight Bioprobes Private Limited, BGIIES Bioncubator, BITS Pilani KK Birla Goa Campus, NH 17B Bypass Road, Zuarinagar, Goa 403726, India

subhadeepb@goa.bits-pilani.ac.in, anjan@goa.bits-pilani.ac.in

## Materials and methods

Solvents, reagents, and other materials were purchased from commercial suppliers and used without further purification. TLC: pre-coated silica gel thin layer sheets ALUGRAM Xtra SIL G/$UV_{254}$ (Macherey-Nagel) and detection by UV-lamp. Flash chromatography: silica gel 60 Å, 60-120 mesh from Loba Chemie Pvt. Ltd. NMR spectra were recorded on Bruker Avance Neo 500 MHz NMR spectrometer at Central Sophisticated Instrumentation Facility, Birla Institute of Technology and Science, Pilani, K.K. Birla, Goa Campus, India and Bruker 400 MHz NMR spectrometer at Birla Institute of Technology and Science, Pilani, Hyderabad Campus, India with DMSO-$d_6$ and $CDCl_3$ as internal standards. Chemicals shifts (δ) for $d_6$-DMSO are expressed in ppm relative to the residual DMSO signal at 2.50 ppm for $^1$H and at 39.65 ppm for $^{13}$C nuclei. Chemicals shifts (δ) for $CDCl_3$ are expressed in ppm relative to the residual $CHCl_3$ signal at 7.25 ppm for $^1$H and at 77 ppm for $^{13}$C nuclei. UV-visible spectra were recorded on a Jasco V-570 spectrophotometer; fluorescence spectra were recorded on a Jasco FP-8500 spectrofluorimeter in the Department of Chemistry, Birla Institute of Technology and Science, K.K. Birla, Goa campus, India. Liquid Chromatography-Mass spectrometry (LC-MS) data were obtained from Agilent triplequad 6460 instrument to determine the molecular mass of compounds in the electrospray ionization (ESI+) and (ESI-) modes at Central Sophisticated Instrumentation Facility, BITS Pilani, K.K. Birla, Goa, India. High-Resolution Mass Spectrometry (HRMS) data were obtained using Agilent Technologies 6545 Q-TOF LC/MS instrument at HRMS Facility at BITS Pilani, Pilani Campus.

## Experimental Procedures

**8-cyano-6,7-difluoro-1,2,3,4-tetrahydroquinoxaline-5-carboxamide**, **9**: Potassium hydroxide (89.26 mg, 1.59 mmol) was taken in a 100 mL round bottom flask and dissolved in 1 mL distilled water. To this ethanol (10 mL) was added followed by addition of 6,7-difluoro-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile **6** (70 mg, 0.318 mmol) to the above reaction mixture, which was kept at reflux for 5 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (40 mL) and washed with brine (5 × 25 mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using ethyl acetate as eluent. The yield of **9** was 20% (weight: 15 mg). $^1$H NMR (500 MHz, $d_6$-DMSO): δ 7.85-7.84 (m, 2H), 6.68 (s, 1H), 6.47 (s, 1H), 3.28 (m, 2H), 3.24 (m, 2H); $^{13}$C NMR (125 MHz, $d_6$-DMSO): δ 165.08, 136.07, 130.88, 113.27, 110.63, 82.95, 38.88; $^{19}$F NMR (470 MHz, $d_6$-DMSO): δ -153.31 (d, $^3J$ = 24.44 Hz ,1F), -154.88 (d, $^3J$ = 25.38 Hz, 1F). LCMS-ESI (+) (M+1): 238.90 and LCMS-ESI (-) (M-1): 236.80.

**6,7-difluoro-1,2,3,4-tetrahydroquinoxaline-5,8-dicarboxamide**, **10**: Potassium hydroxide (89.26 mg, 1.59 mmol) was taken in a 100 mL round bottom flask and dissolved in 1 mL distilled water. To this ethanol (10 mL) was added followed by addition of 6,7-difluoro-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile **6** (70 mg, 0.318 mmol) to the above reaction mixture, which was kept at reflux for 5 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (40 mL) and washed with brine (5 × 25 mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using ethyl acetate as eluent. The yield of **10** was 6 % (weight: 5 mg). $^{1}$H NMR (500 MHz, $d_6$-DMSO): δ 7.70 (m, 2H), 6.49 (s, 1H), 3.25 (s, 2H); $^{13}$C NMR (125 MHz, $d_6$-DMSO): δ 166.02, 137.97, 131.21, 107.65; $^{19}$F NMR (470 MHz, $d_6$-DMSO): δ -155.63 (s, 1F). LCMS-ESI (+) (M+1): 257.00.

**6,9-dimethyl-2,3,6,7,8,9-hexahydro-[1,4]dioxino[2,3-g]quinoxaline-5,10-dicarbonitrile**, **11**: Potassium hydroxide (226 mg, 4.03 mmol) was taken in a 100 mL round bottom flask and dissolved in 0.5 mL distilled water. To this ethylene glycol (8 mL) was added followed by addition of 6,7-difluoro-1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile **5** (100 mg, 0.40 mmol) to the above reaction mixture, which was kept at reflux for 1 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (50 mL) and washed with brine (6 × 25 mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using chloroform and petroleum ether (1:1) as eluent. The yield of **11** was 39% (weight: 42 mg). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 4.28 (s, 4H), 3.04 (s, 4H), 3.03 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.83, 137.81, 114.69, 96.32, 64.86, 46.78, 44.30. LCMS-ESI (+) (M+1): 271.1000. ESI-HRMS (+) (M+1) for $C_{14}H_{15}N_4O_2$ calculated: 271.1190, found: 271.1192.

**6,7-diethoxy-1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile**, **12**:
Potassium hydroxide (452.08 mg, 8.05 mmol) was taken in a 100 mL round bottom flask and dissolved in 1 mL distilled water. To this ethanol (20 mL) was added followed by addition of 6,7-difluoro-1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile **5** (200 mg, 0.805 mmol) to the above reaction mixture, which was kept at reflux for 6 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (70 mL) and washed with brine (8 × 25

mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using chloroform and petroleum ether (1:1) as eluent. The yield of **12** was 25 % (weight: 60 mg). $^{1}$H NMR (400 MHz, $d_6$-DMSO): δ 4.09 (q, $^{3}J$ = 8.00 Hz, 4H), 3.12 (s, 4H), 3.05 (s, 6H), 1.32 (t, $^{3}J$ = 8.00 Hz, 6H); $^{13}$C NMR (100 MHz, $d_6$-DMSO): δ 145.70, 140.75, 115.76, 101.57, 70.63, 46.60, 44.28, 15.85. LCMS-ESI (+) (M+1): 301.1995. ESI-HRMS (+) (M+1) for $C_{16}H_{21}N_4O_2$ calculated: 301.1660, found: 301.1661.

**8-cyano-6,7-diethoxy-1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5-carboxamide**, **13**: Potassium hydroxide (339.06 mg, 6.04 mmol) was taken in a 100 mL round bottom flask and dissolved in 1 mL distilled water. To this ethanol (20 mL) was added followed by addition of 6,7-difluoro-1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile **5** (150 mg, 0.60 mmol) to the above reaction mixture, which was kept at reflux for 24 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (60 mL) and washed with brine (7 × 25 mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using ethyl acetate as eluent. The yield of **13** was 27 % (weight: 52 mg). $^{1}$H NMR (500 MHz, $d_6$-DMSO): δ 7.66 (s, 1H), 7.50 (s, 1H), 4.09 (q, $^{3}J$ = 7.00 Hz, 2H), 3.93 (q, $^{3}J$ = 7.00 Hz, 2H), 3.12 (m, 2H), 3.06 (s, 3H), 2.94 (m, 2H), 2.75 (s, 3H), 1.32 (t, $^{3}J$ = 5.00 Hz, 3H), 1.24 (t, $^{3}J$ = 5.00 Hz, 3H); $^{13}$C NMR (125 MHz, $d_6$-DMSO): δ 167.85, 149.15, 141.55, 140.83, 133.55, 116.77, 96.48, 70.09, 47.05, 45.78, 44.36, 43.88, 15.99. LCMS-ESI (+) (M+1): 319.1800. ESI-HRMS (+) (M+1) for $C_{16}H_{23}N_4O_3$ calculated: 319.1770, found: 319.1766.

**6-fluoro-7-isopropoxy-1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile**, **14**: Potassium hydroxide (113.02 mg, 2.01 mmol) was taken in a 100 mL round bottom flask and dissolved in 0.5 mL distilled water. To this isopropanol (10 mL) was added followed by addition of 6,7-difluoro-1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile **5** (50 mg, 0.201 mmol) to the above reaction, which was kept at reflux for 6 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (30 mL) and washed with brine (5 × 25 mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using chloroform and petroleum ether (1:1) as eluent. The yield of **14** was 36 % (weight: 21 mg). $^{1}$H NMR (400 MHz, $d_6$-DMSO): δ 4.39 (m, 1H), 3.23 (m, 2H), 3.17 (s, 3H), 3.15 (m, 2H), 3.06

(s, 3H), 1.29 (d, $^{3}J$ = 8.00 Hz, 6H); $^{13}$C NMR (100 MHz, $d_6$-DMSO): δ 141.04, 140.73, 115.54, 114.12, 101.29, 78.80, 47.17, 46.94, 44.35, 43.73, 22.61. LCMS-ESI (+) (M+Acetonitrile): 329.20.

**6-fluoro-1,4-dimethyl-7-(octyloxy)-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile**, **17**: Potassium hydroxide (226.04 mg, 4.03 mmol) was taken in a 100 mL round bottom flask and dissolved in 1 mL distilled water. To this octanol (637 µL, 4.03 mmol) was added followed by addition of 6,7-difluoro-1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-5,8-dicarbonitrile **5** (100 mg, 0.40 mmol) to the above reaction mixture in 7 mL DMF, which was kept at reflux for 12 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (60 mL) and washed with brine (7 × 25 mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using ethyl acetate as eluent. The yield of **17** was 45 % (weight: 65 mg). $^{1}$H NMR (500 MHz, $d_6$-DMSO): δ 4.06 (t, $^{3}J$ = 7.50 Hz, 2H), 3.21 (m, 2H), 3.15 (s, 5H), 3.06 (s, 3H), 1.67 (m, 2H), 1.42 (m, 2H), 1.25 (m, 8H), 0.86 (t, $^{3}J$ = 7.50 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 147.05, 140.03, 139.41, 114.53, 113.26, 100.81, 75.44, 47.15, 46.95, 44.02, 43.56, 31.55, 29.68, 29.00, 25.42, 22.41, 13.95. LCMS-ESI (+) (M+1): 359.2004.

**10-cyano-6,9-dimethyl-2,3,6,7,8,9-hexahydro-[1,4]dioxino[2,3-g]quinoxaline-5-carboxamide**, **18**: Potassium hydroxide (62.34 mg, 1.11 mmol) was taken in a 100 mL round bottom flask and dissolved in 0.5 mL distilled water. To this isopropanol (10 mL) was added followed by addition of 6,9-dimethyl-2,3,6,7,8,9-hexahydro-[1,4]dioxino[2,3-g]quinoxaline-5,10-dicarbonitrile **11** (30 mg, 0.11 mmol) to the above reaction mixture and continued refluxing for 24 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (30 mL) and washed with brine (4 × 25 mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using ethyl acetate as eluent. The yield of **18** was 27 % (weight: 8.5 mg). $^{1}$H NMR (400 MHz, $d_6$-DMSO): δ 7.65 (s, 1H), 7.46 (s, 1H), 4.30 (m, 2H), 4.18 (m, 2H), 3.09 (m, 2H), 3.01 (s, 3H), 2.90 (m, 2H), 2.70 (s, 3H); $^{13}$C NMR (100 MHz, $d_6$-DMSO): δ 167.06, 141.58, 139.57, 133.17, 130.88, 127.39, 124.90, 116.28, 90.25, 65.38, 64.24, 47.10, 45.63, 44.49. LCMS-ESI (+) (M+1): 289.100. ESI-HRMS (+) (M+1) for $C_{14}H_{17}N_4O_3$ calculated: 289.1296, found: 289.1298.

**12-cyano-1,4-dimethyl-1,2,3,4-tetrahydrobenzo[5,6][1,4]dioxino[2,3-g]quinoxaline-5-carboxamide**, **20**: Potassium hydroxide (176.45 mg, 3.14 mmol) was taken in a 100 mL round bottom flask and dissolved in 0.5 mL distilled water. To this ethanol (10 mL) was added followed by addition of 1,4-dimethyl-1,2,3,4-tetrahydrobenzo[5,6][1,4]dioxino[2,3-g]quinoxaline-5,12-dicarbonitrile **19** (100 mg, 0.314 mmol) to the above reaction mixture and continued refluxing for 12 h monitored by TLC. After complete consumption of starting material, the reaction mixture was cooled to room temperature and then 6M HCl was added to reaction mixture till the pH became approximately 2. The reaction mixture was dissolved in ethyl acetate (30 mL) and washed with brine (7 × 25 mL). The combined organic extracts were dried over sodium sulphate and concentrated *in vacuo*. The crude compound was purified by column chromatography using ethyl acetate as eluent. The yield of **20** was 31 % (weight: 32 mg). $^{1}$H NMR (500 MHz, $d_6$-DMSO): δ 7.90 (s, 1H), 7.67 (s, 1H), 7.01 (m, 4H), 3.14 (m, 2H), 3.08 (s, 3H), 2.95 (m, 2H), 2.76 (s, 3H); $^{13}$C NMR (125 MHz, $d_6$-DMSO): δ 165.90, 141.40, 140.95, 138.43, 132.81, 130.48, 125.61, 125.00, 116.94, 115.17, 89.15, 47.09, 45.97, 44.17, 43.72. LCMS-ESI (+) (M+1) for $C_{18}H_{17}N_4O_3$ calculated: 337.1295, found:337.50.

**Cell culture and confocal imaging protocol for compound 17**

HeLa cells were procured from National Centre for Cell Sciences (Pune, India) and maintained in Dulbecco's Modified Eagle Medium (HiMedia), supplemented with 10% (v/v) Fetal Bovine Serum (HiMedia), antibiotics (Penicillin10000U/mL+ Streptomycin 10000µg/mL) (GIBCO) and maintained at 37ºC incubator with humidified atmosphere of $CO_2$ (5%) and air (95%). Cells were cultured in vented T-25 cell culture flasks.

For confocal imaging, HeLa cells ($8x10^3$) were seeded on a clean cover slip and grown overnight. Next day, cells were fixed with ice-cold methanol for 10 minutes and then washed with cold 1x PBS buffer (pH 7.4). The cells were then stained with 100 µM of compound **17** for 30 minutes. Then the cells were washed thrice with cold 1x PBS buffer (pH 7.4). To stain the nuclei, DAPI was added to the cells in fresh 1x PBS buffer for 10 minutes. The cover slip was mounted on clean glass slide with glycerol and viewed under confocal microscope at 80X magnification and 1% laser power. The excitation laser user for **17** was 488 nm with an emission window between 500-550 nm.

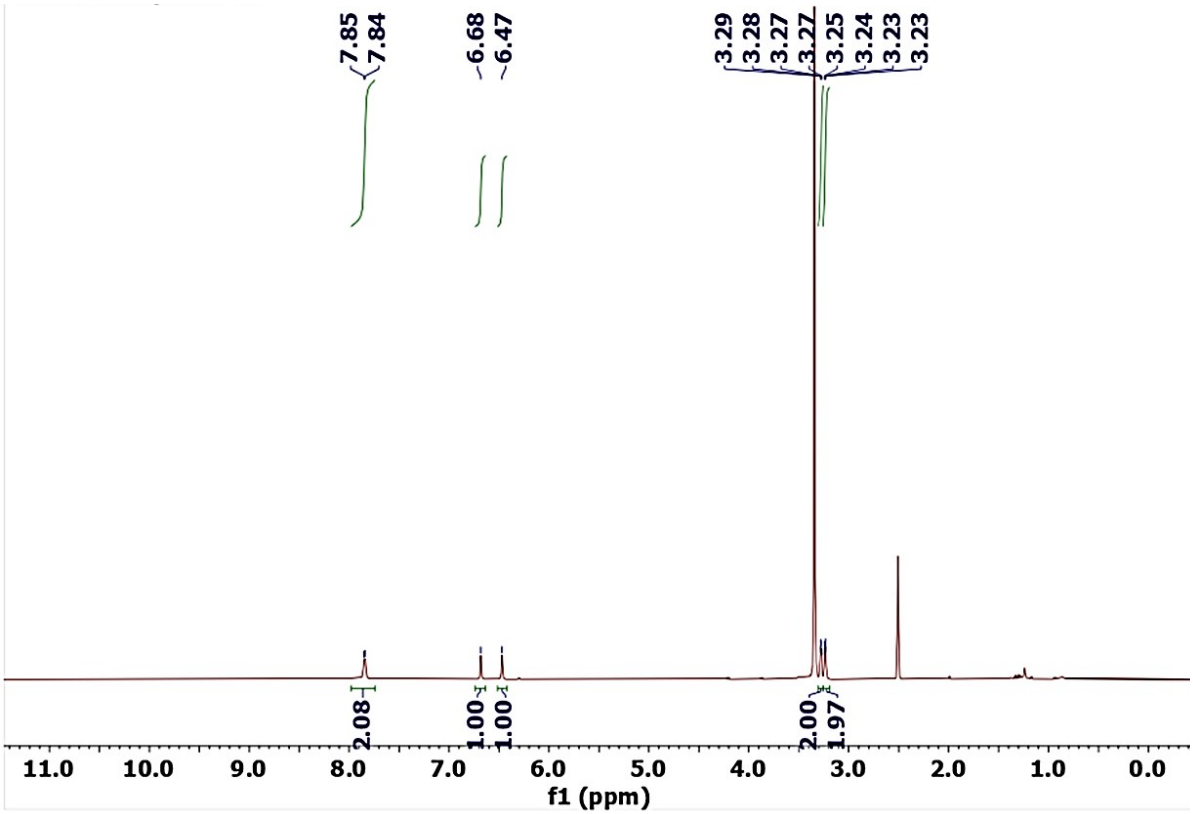



**Figure S1**: $^{1}H$ NMR spectrum (500 MHz) of compound **9** in DMSO-$d_6$.

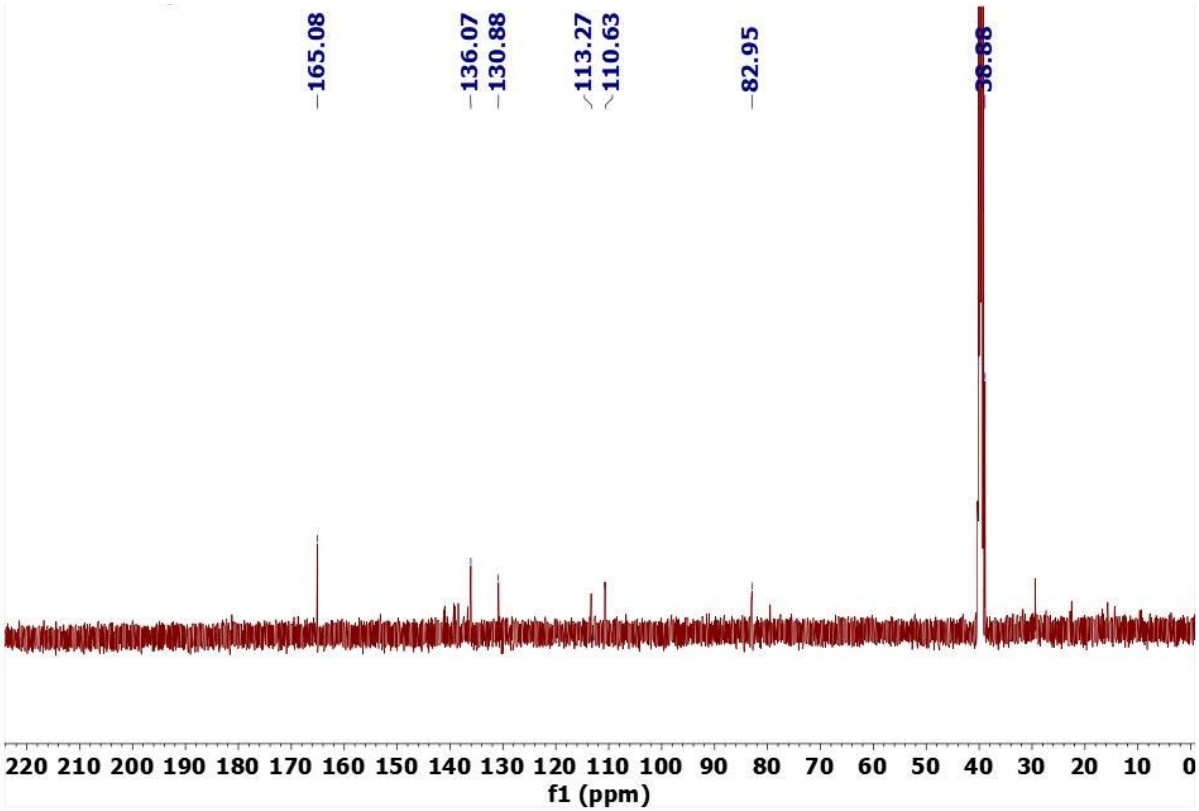



**Figure S2**: $^{13}C$ NMR spectrum (125 MHz) of compound **9** in DMSO-$d_6$

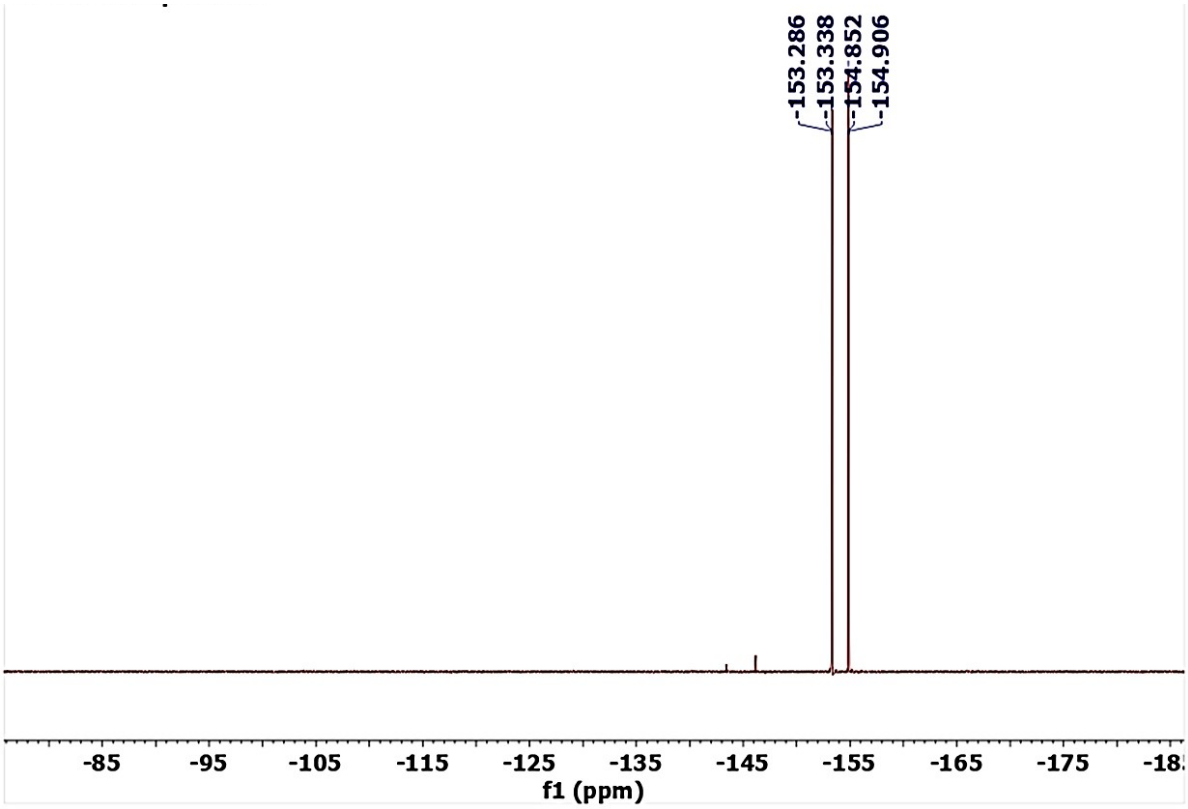



**Figure S3**: $^{19}F$ NMR spectrum (470 MHz) of compound **9** in DMSO-$d_6$.

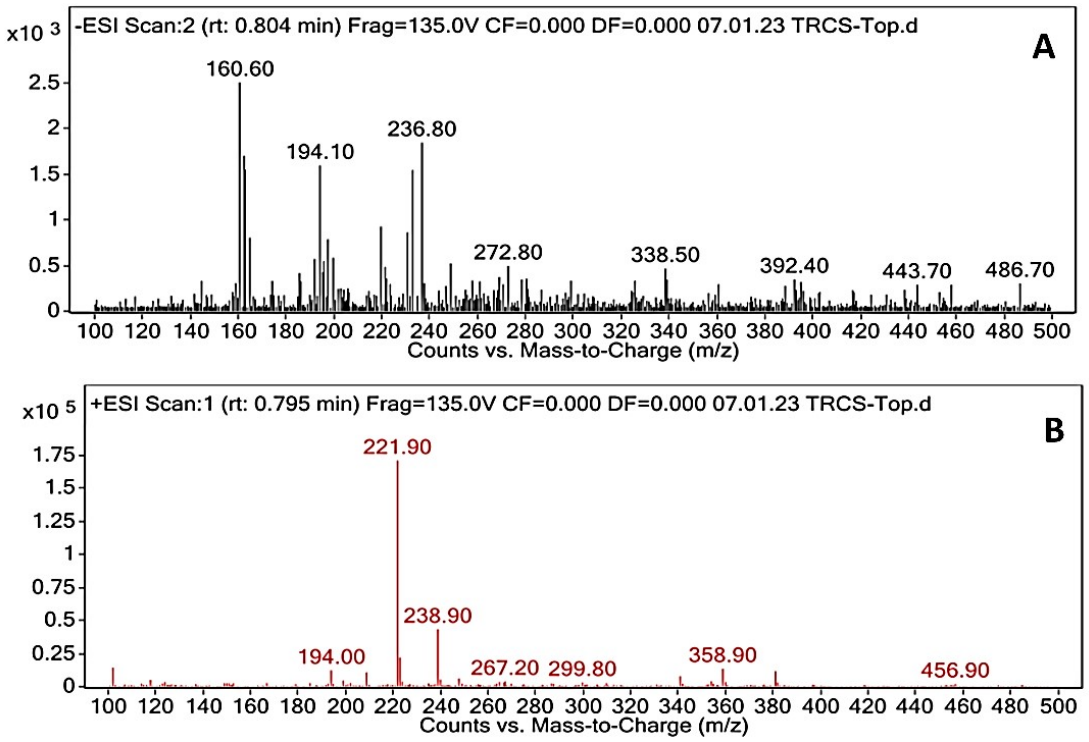



**Figure S4:** (A) LCMS-ESI (-) (M-1) compound **9** shows peak at 236.80. (B) LCMS-ESI (+) (M+1) of compound **9** shows peak at 238.90.

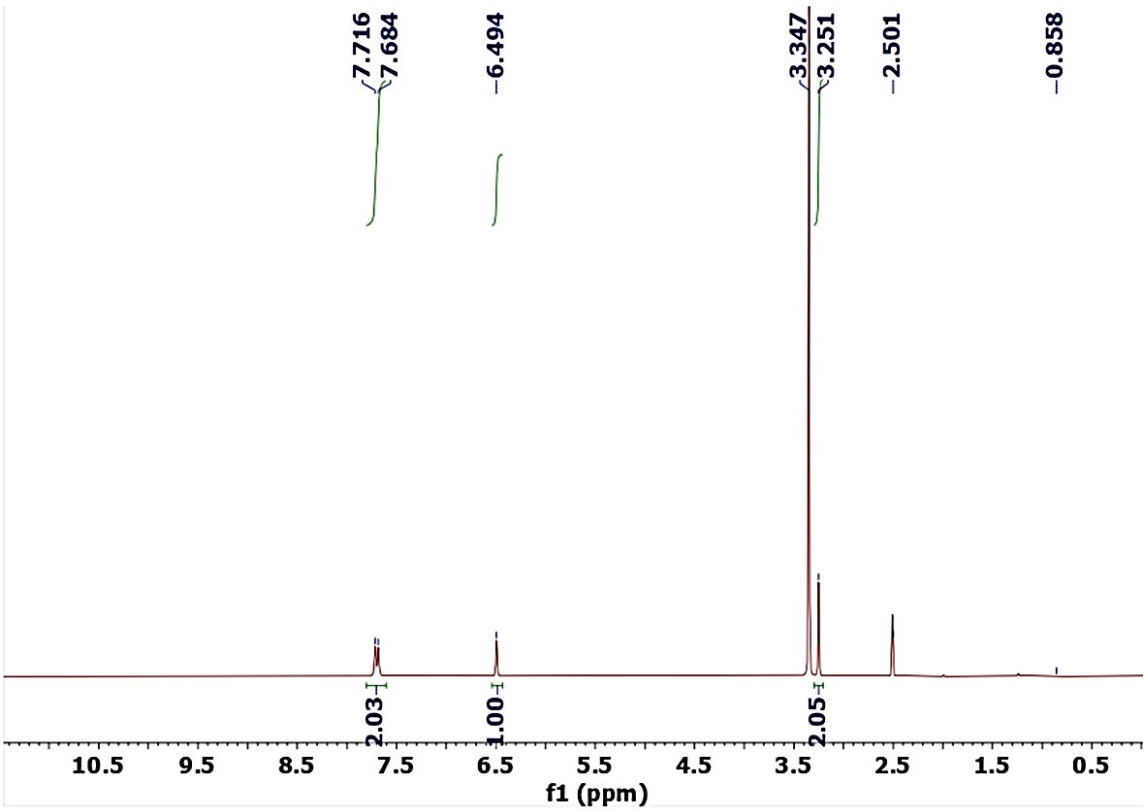



**Figure S5**: $^{1}$H NMR spectrum (500 MHz) of compound **10** in DMSO-$d_6$.

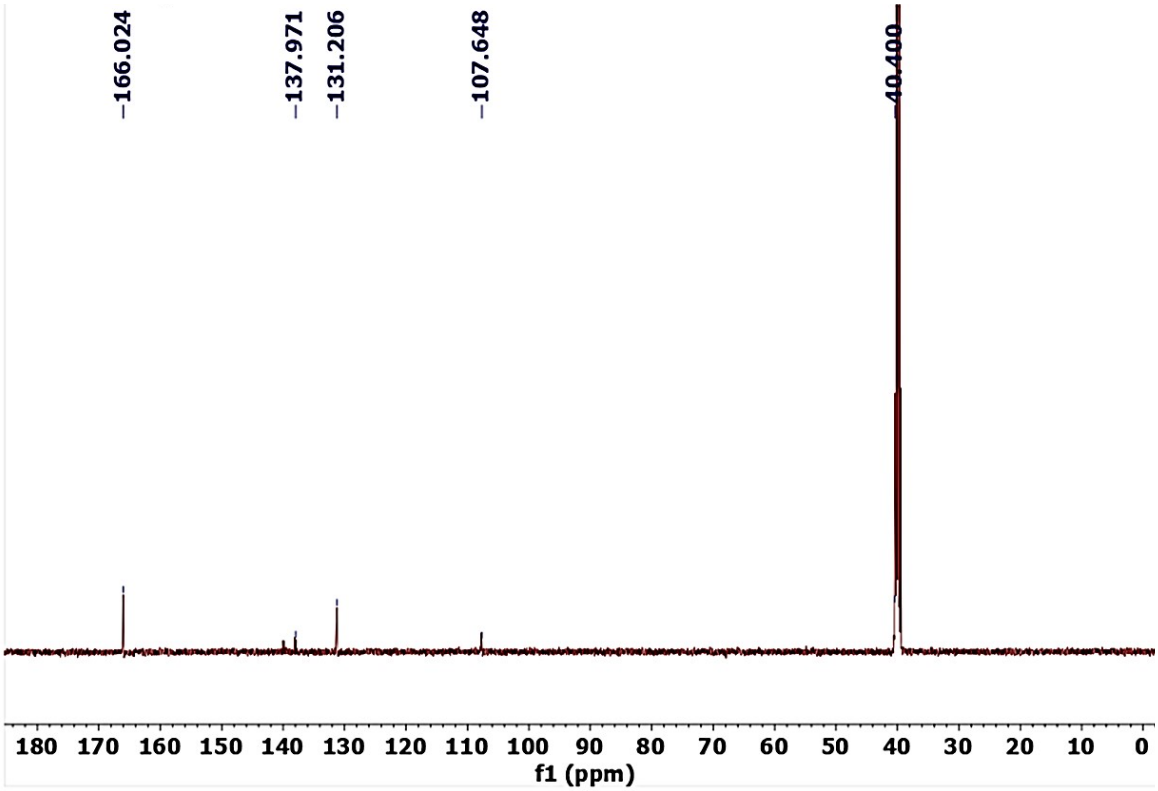



**Figure S6**: $^{13}C$ NMR spectrum (125 MHz) of compound **10** in DMSO-$d_6$.

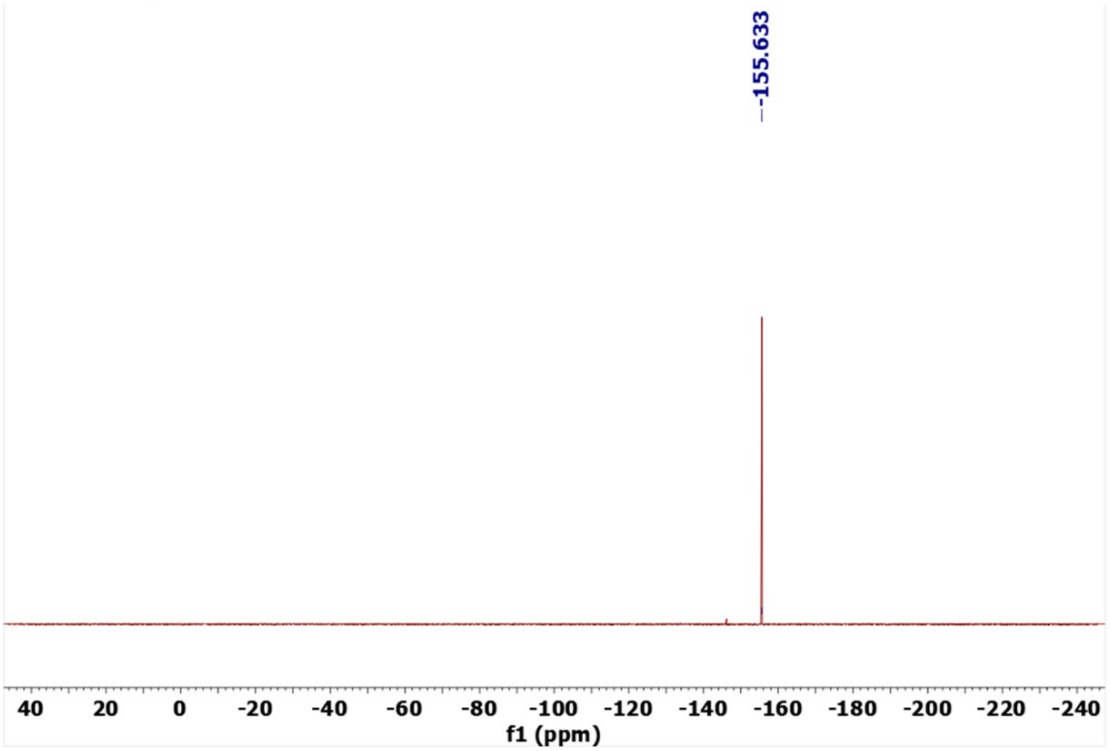



**Figure S7**: $^{19}F$ NMR spectrum (470 MHz) of compound **10** in DMSO-$d_6$.

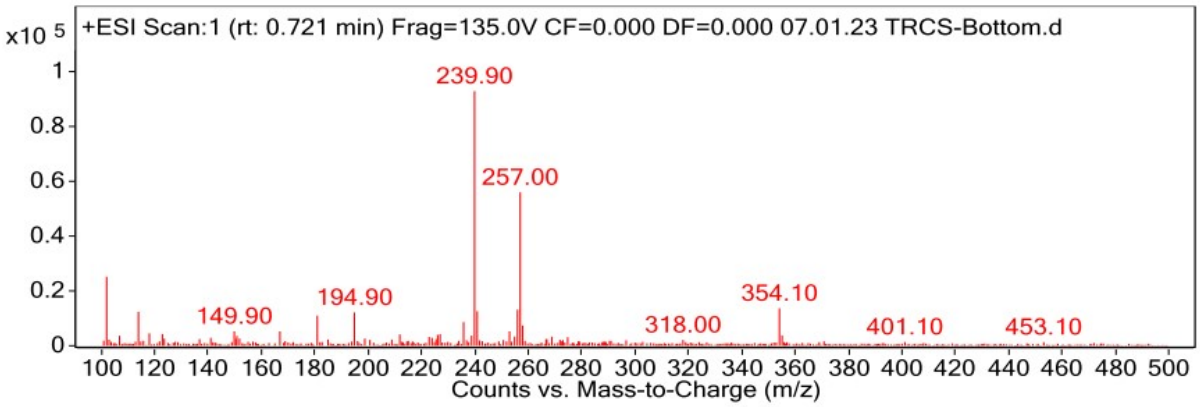



**Figure S8**: LCMS-ESI (+) of compound **10** shows peak at 257.00.

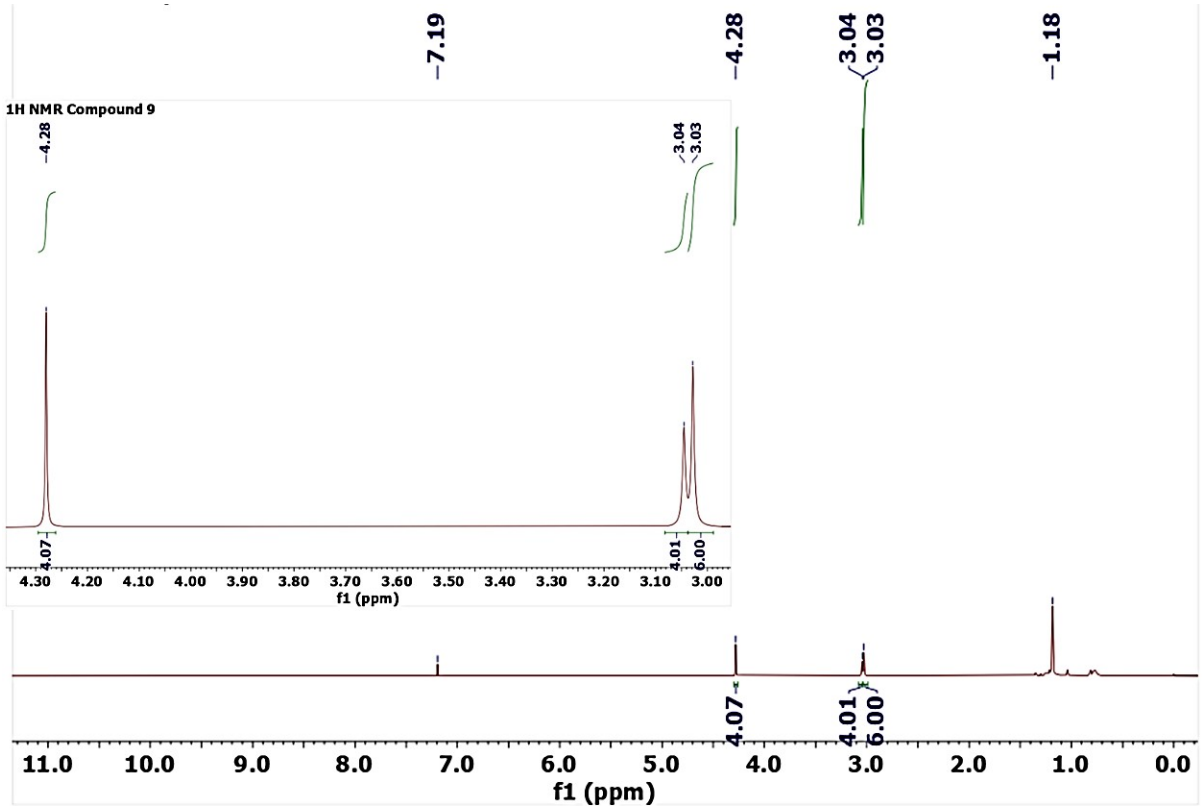



**Figure S9**: $^{1}$H NMR spectrum (400 MHz) of compound **11** in $CDCl_3$.

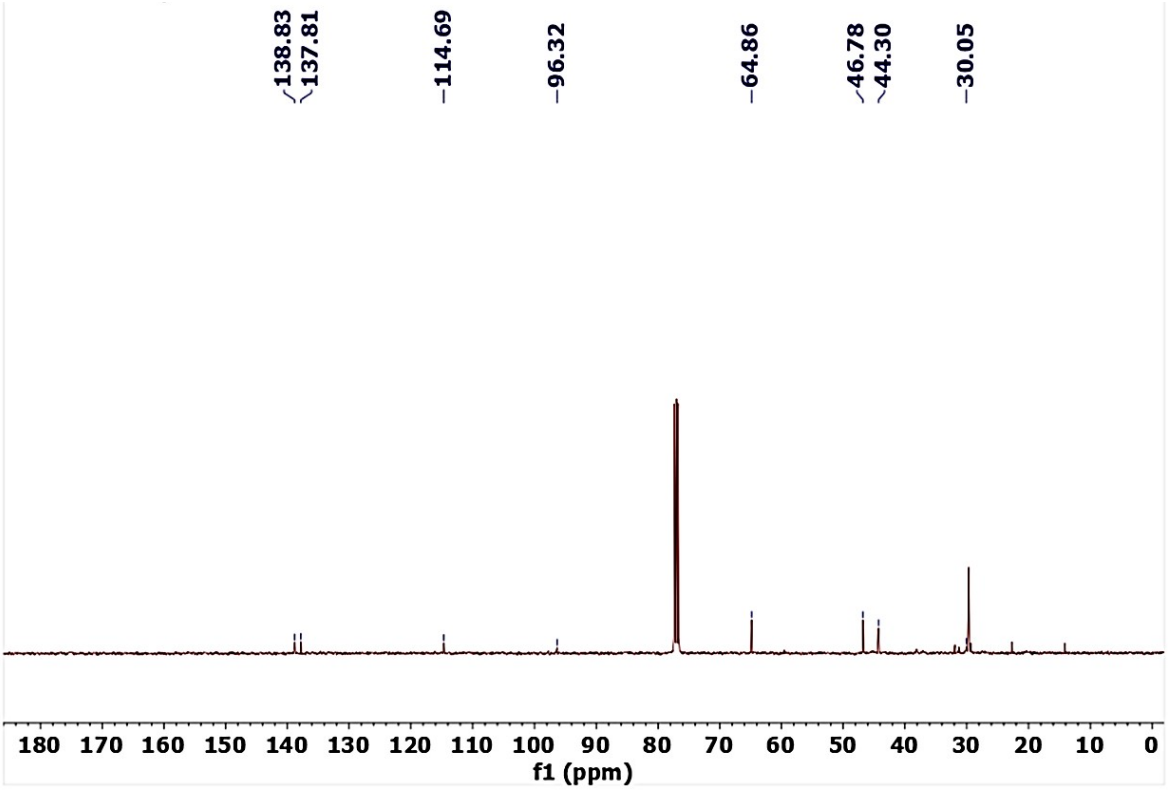



**Figure S10**: $^{13}C$ NMR spectrum (100 MHz) of compound **11** in $CDCl_3$.

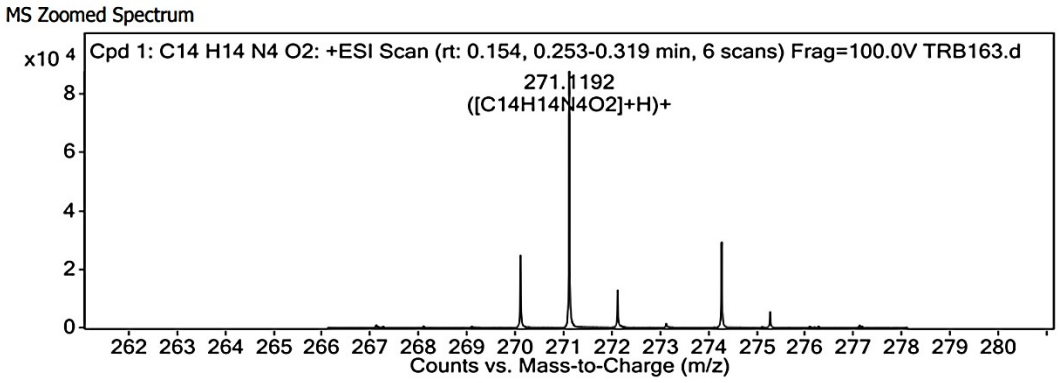



**Figure S11**: HRMS-ESI (+) of compound **11**.

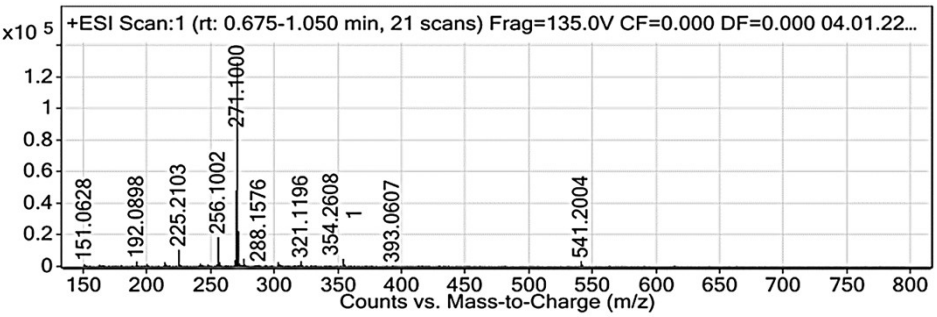



**Figure S12:** LCMS-ESI (+) (M+1) of compound **11** shows peak at 271.10.

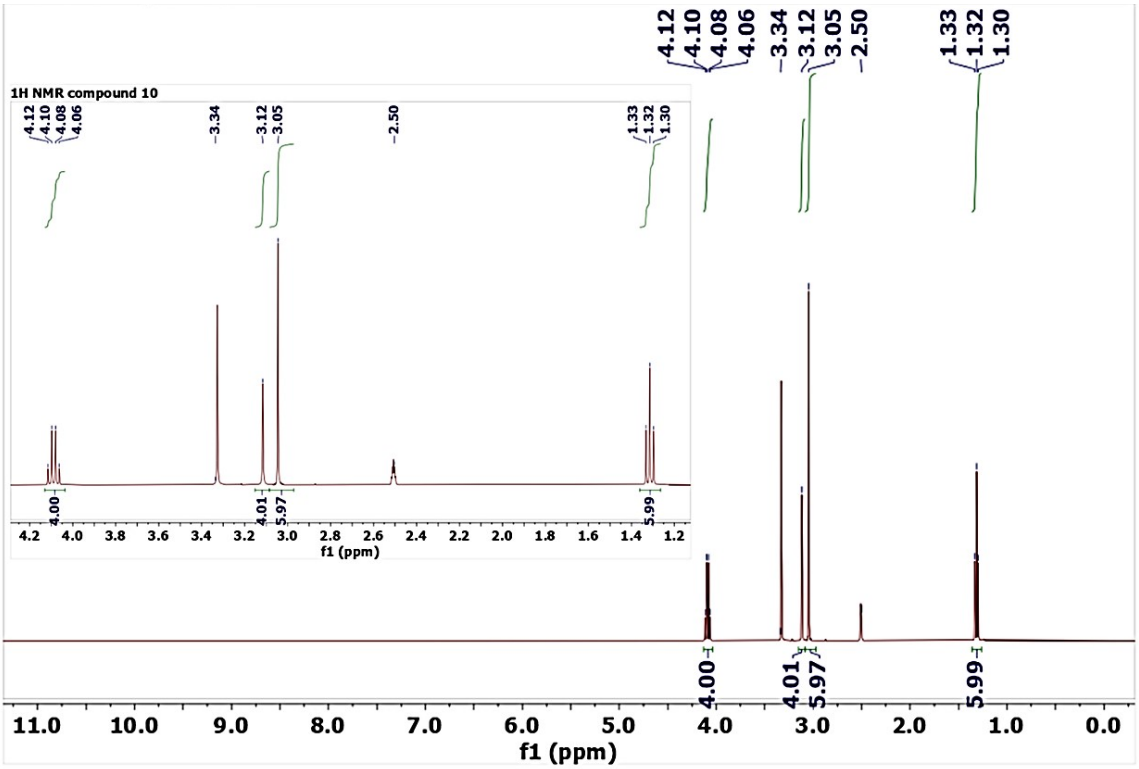



**Figure S13**: $^{1}H$ NMR spectrum (400 MHz) of compound **12** in DMSO-$d_6$.

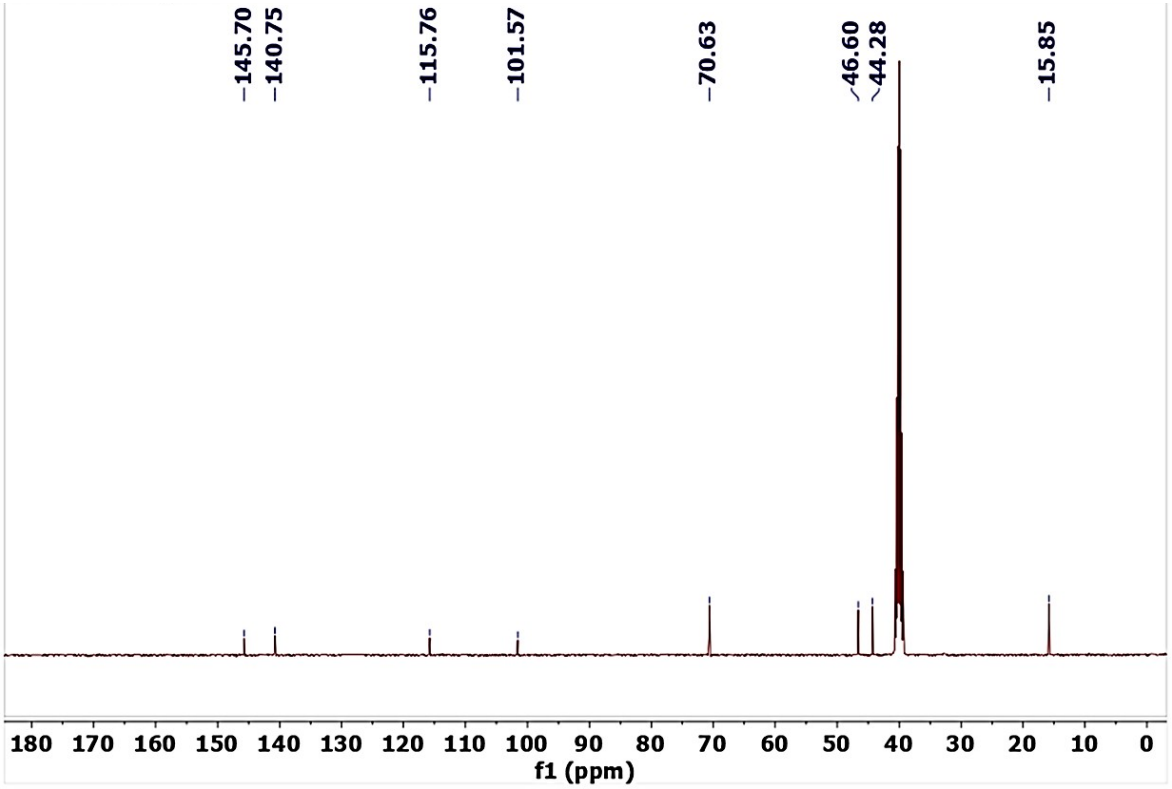



**Figure S14**: $^{13}C$ NMR spectrum (100 MHz) of compound **12** in DMSO-$d_6$.

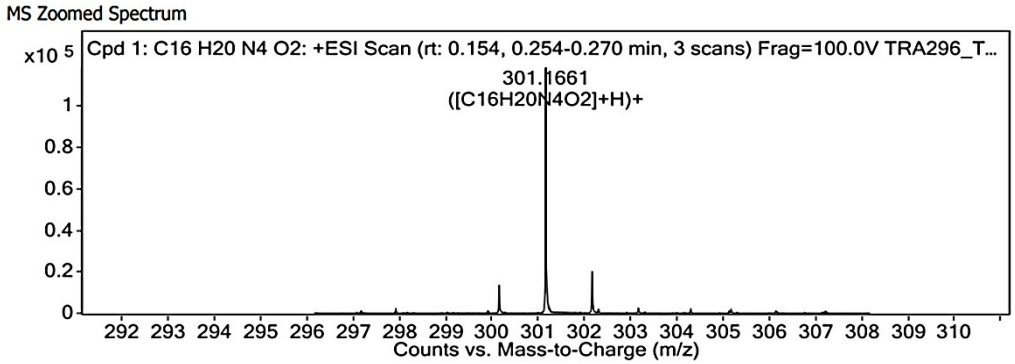



**Figure S15**: HRMS-ESI (+) of compound **12**.

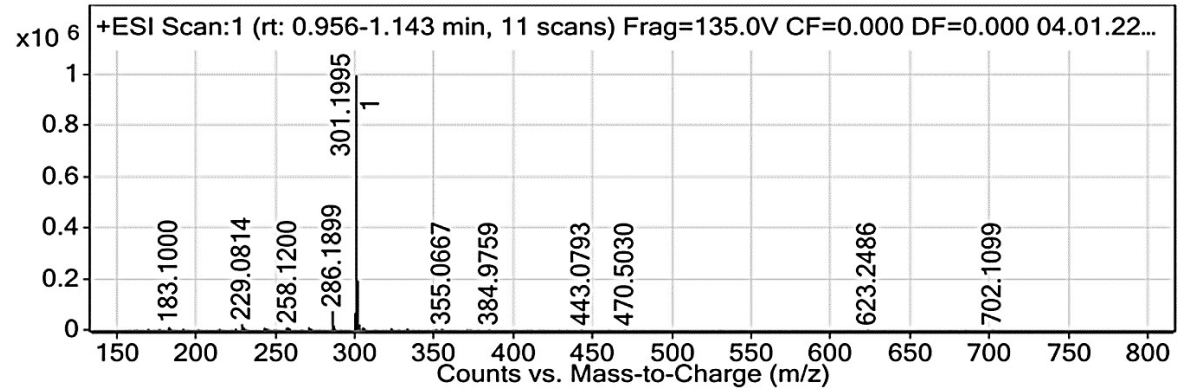



**Figure S16:** LCMS-ESI (+) (M+1) of compound **12** shows peak at 301.1995.

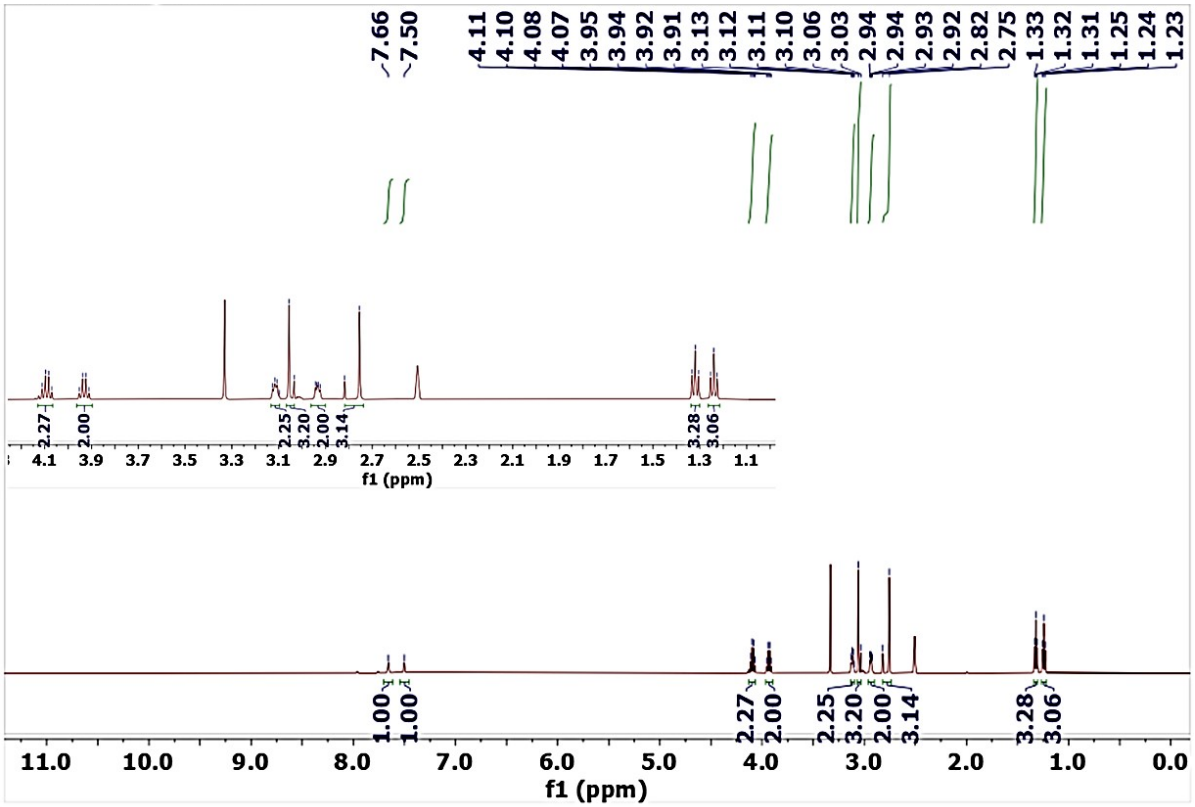



**Figure S17**: $^{1}$H NMR spectrum (500 MHz) of compound **13** in DMSO-$d_6$.

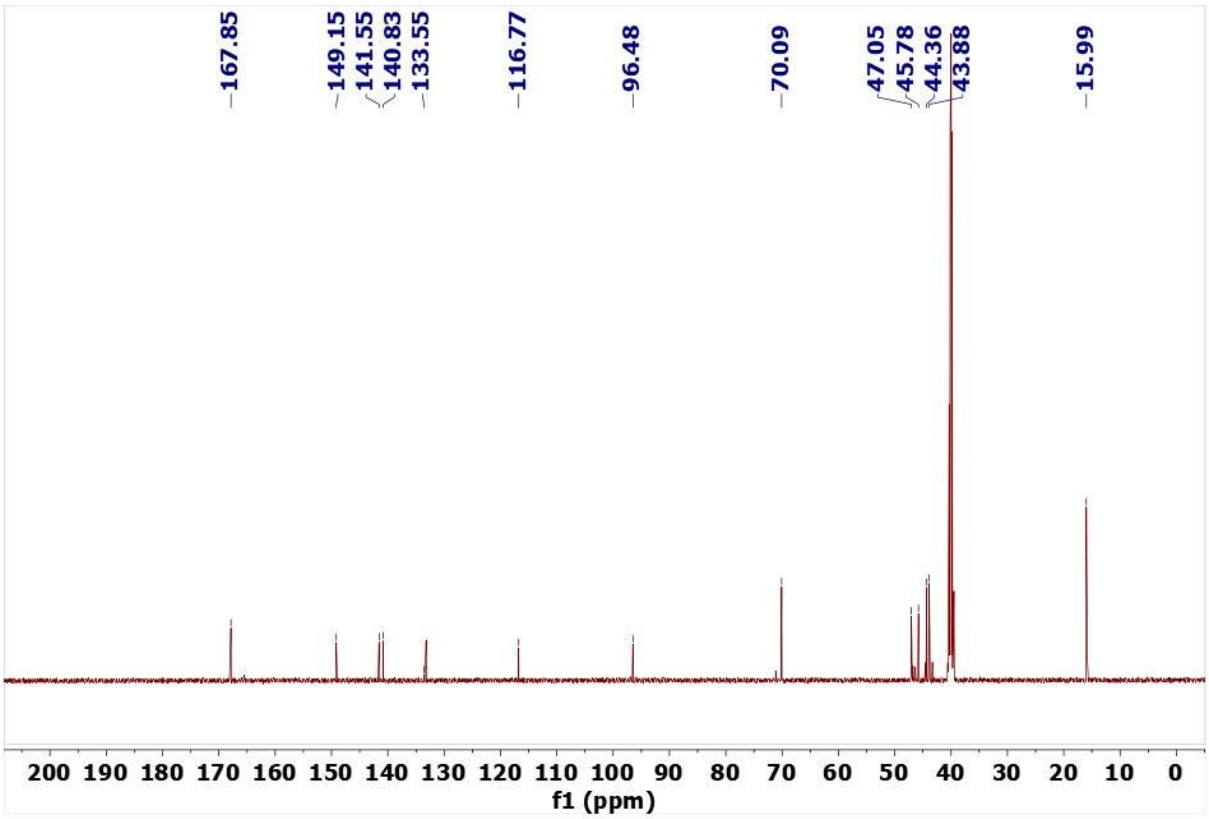



**Figure S18**: $^{13}$C NMR spectrum (125 MHz) of compound **13** in DMSO-$d_6$.

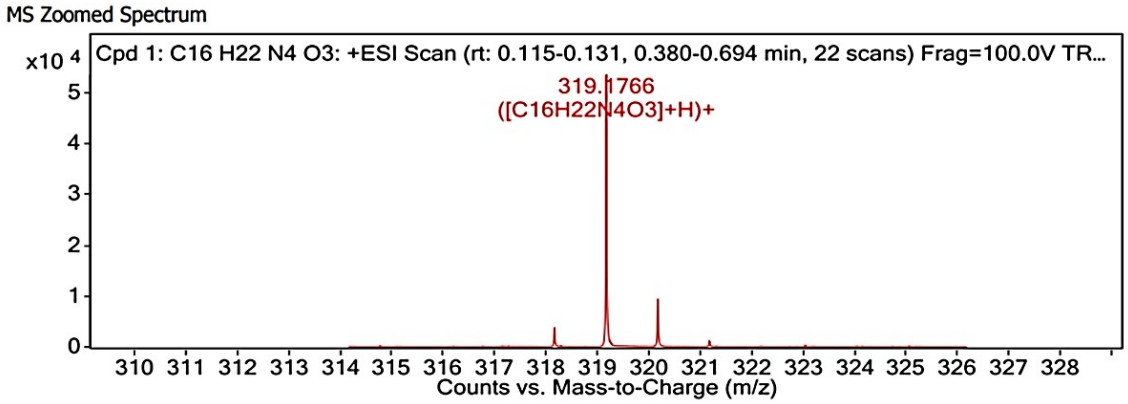



**Figure S19**: HRMS-ESI (+) of compound **13**.

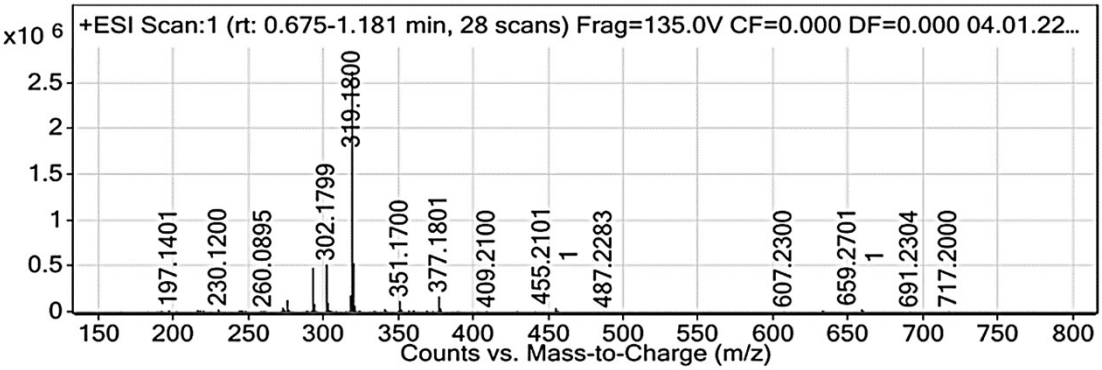



**Figure S20:** LCMS-ESI (+) (M+1) of compound **13** shows peak at 319.18.

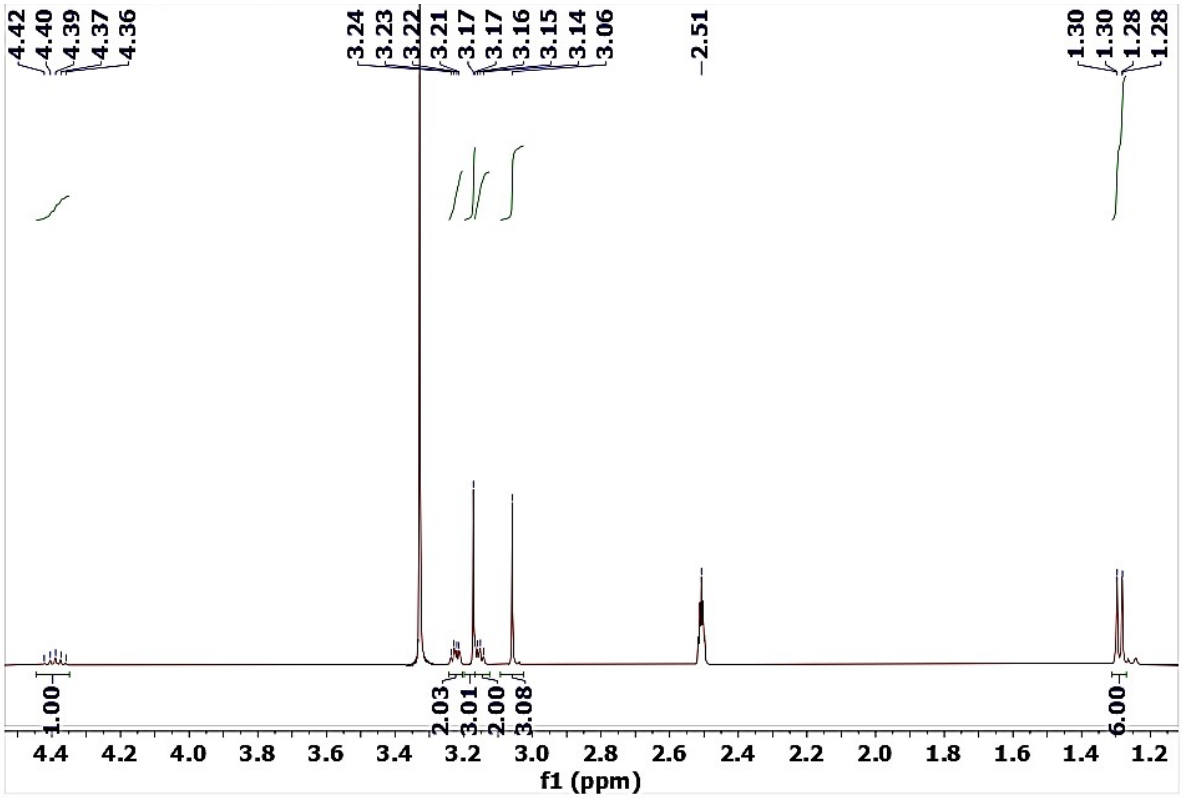



**Figure S21**: $^{1}H$ NMR spectrum (400 MHz) of compound **14** in DMSO-$d_6$.

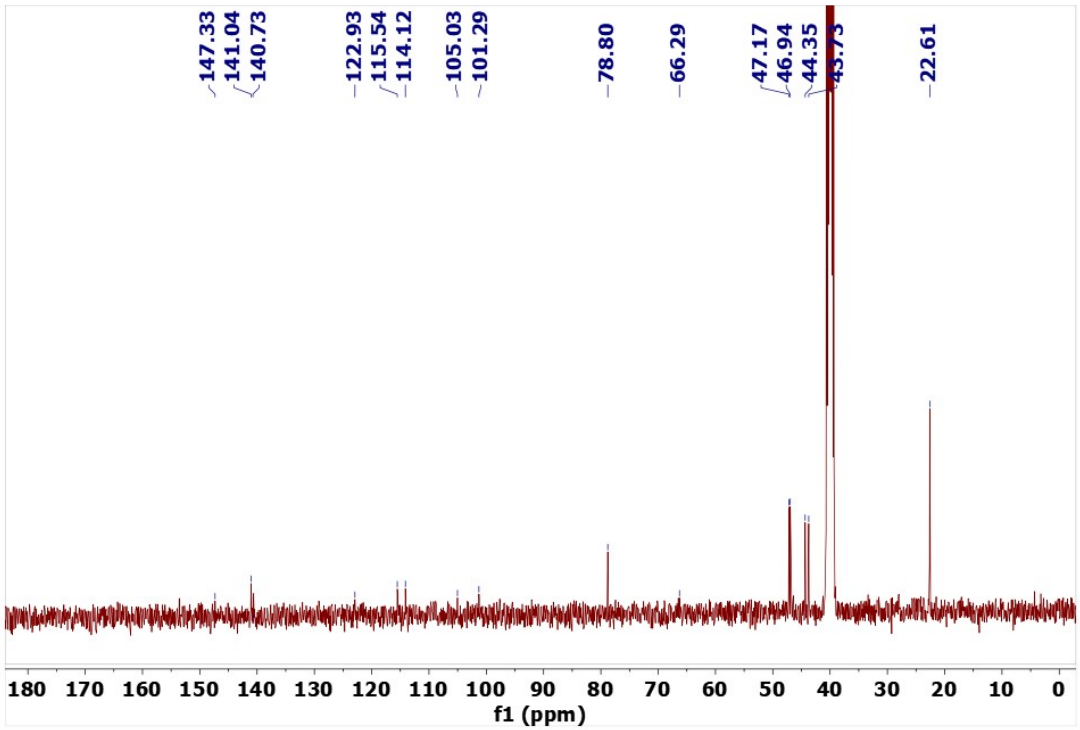
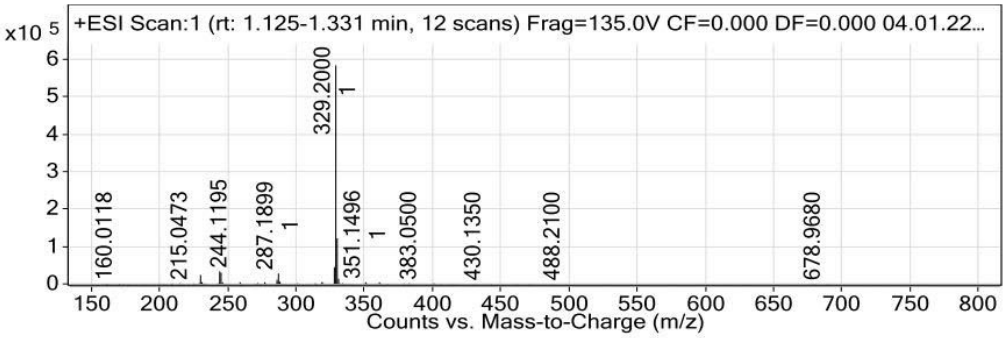



**Figure S22**: $^{13}C$ NMR spectrum (100 MHz) of compound **14** in DMSO-$d_6$.




**Peak List**

| *m/z* | z | Abund |
|---|---|---|
| 230.1006 | | 23693.28 |
| 244.1195 | | 33606.69 |
| 245.1 | | 30215.23 |
| 286.1402 | | 11159.64 |
| 287.1899 | 1 | 27920.58 |
| 288.1902 | 1 | 5665.32 |
| 328.1704 | | 44659.61 |
| 329.2 | 1 | 583718.81 |
| 330.1999 | 1 | 121733 |
| 331.2091 | 1 | 13598.47 |

**Figure S23**: LCMS-ESI (+) of compound **14** (M+Acetonitrile at m/z 329.20).

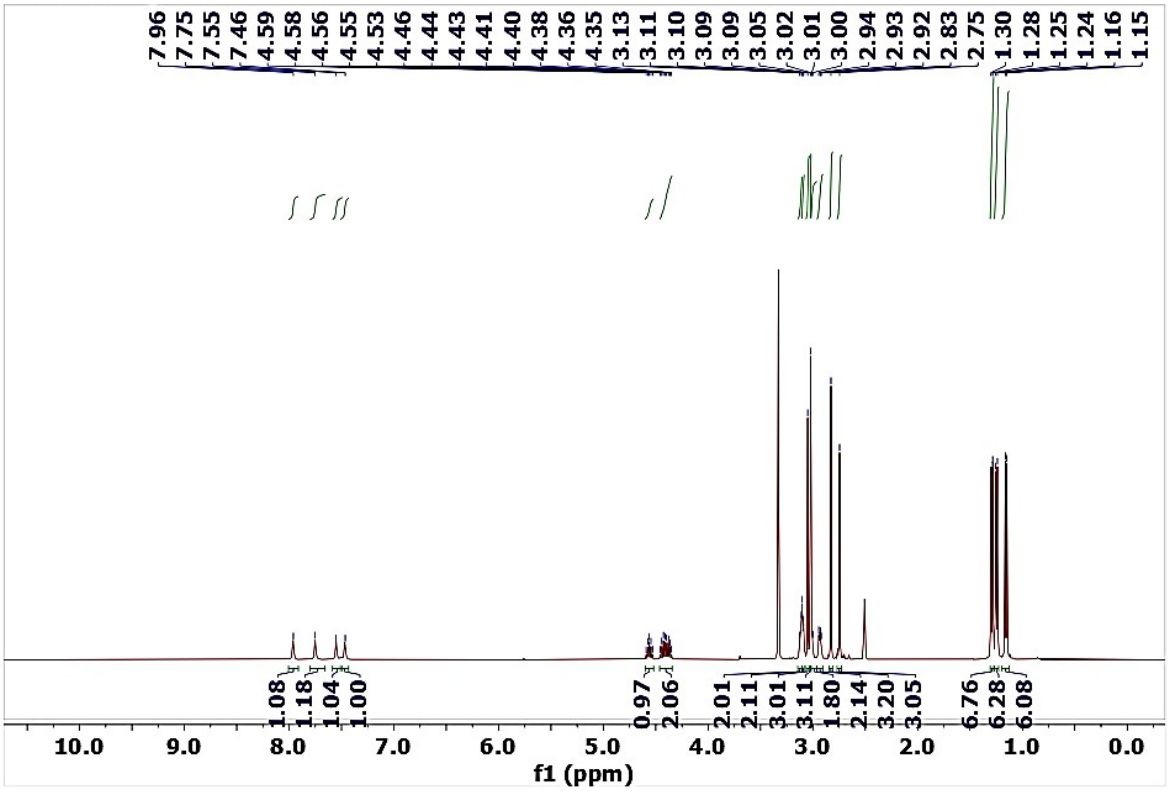



**Figure S24**: $^{1}$H NMR spectrum (400 MHz) of mixture of compounds **15** and **16** in DMSO-$d_6$.

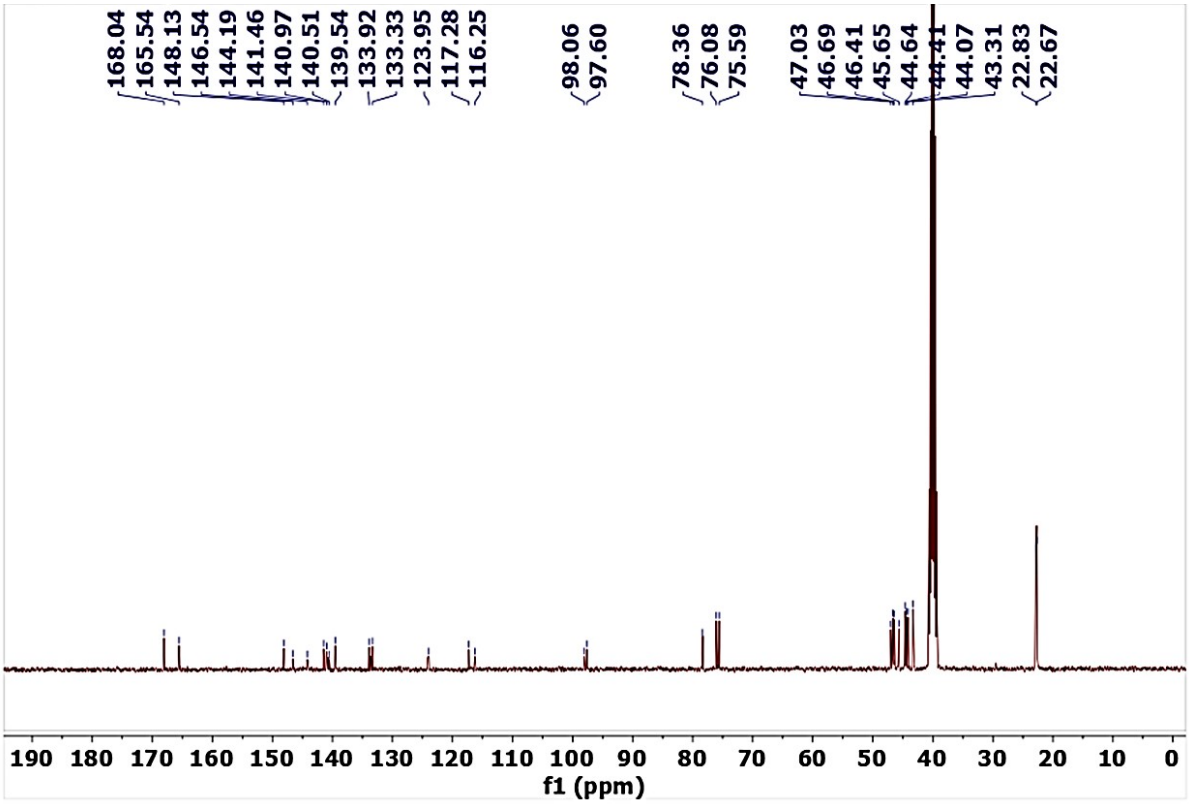
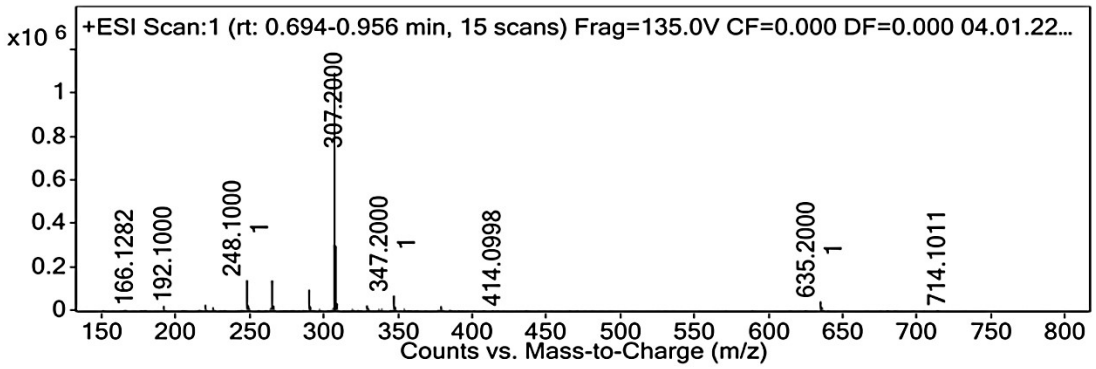



**Figure S25**: $^{13}$C NMR spectrum (100 MHz) of mixture of compounds **15** and **16** in DMSO-$d_6$.




**Peak List**

| m/z | z | Abund |
|---|---|---|
| 220.1 | | 23267.24 |
| 248.1 | 1 | 137386.03 |
| 265.1 | 1 | 136461.78 |
| 290.13 | 1 | 92912.64 |
| 307.09 | | 299718.91 |
| 307.2 | | 1094202.88 |
| 308.18 | | 295889.5 |
| 309.1399 | 1 | 31782.55 |
| 347.2 | 1 | 66131.76 |
| 635.2 | 1 | 39124.23 |

**Figure S26**: LCMS-ESI (+) of compound mixture of compounds **15** and **16** shows peak at 307.20 and 347.20.

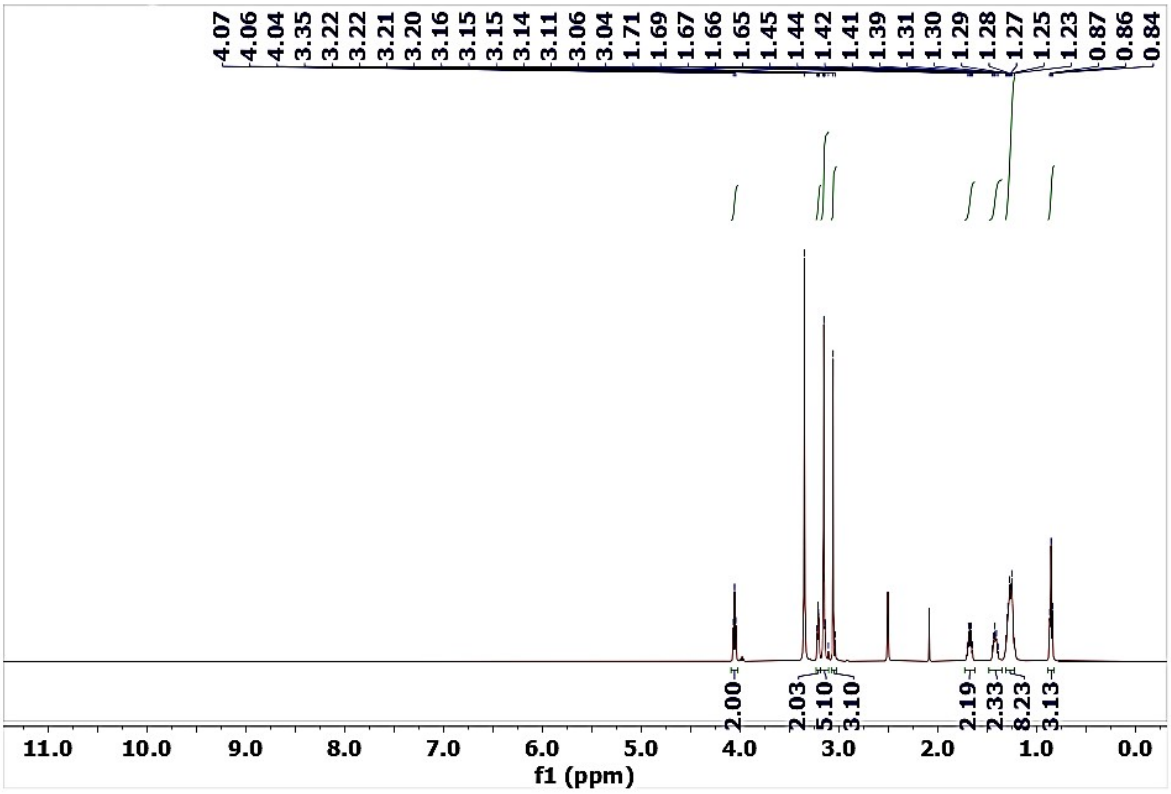



**Figure S27**: $^{1}$H NMR spectrum (500 MHz) of compound **17** in DMSO-$d_6$.

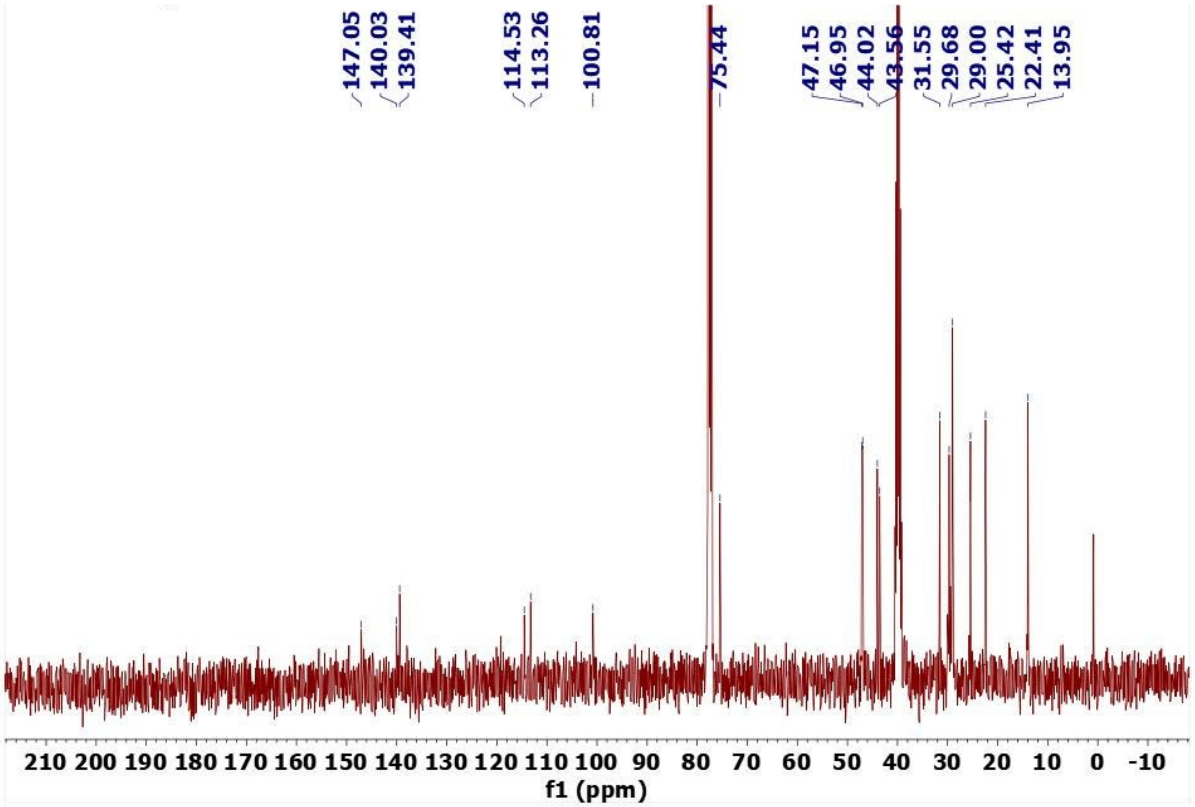



**Figure S28**: $^{13}C$ NMR spectrum (100 MHz) of compound **17** in $CDCl_3$.

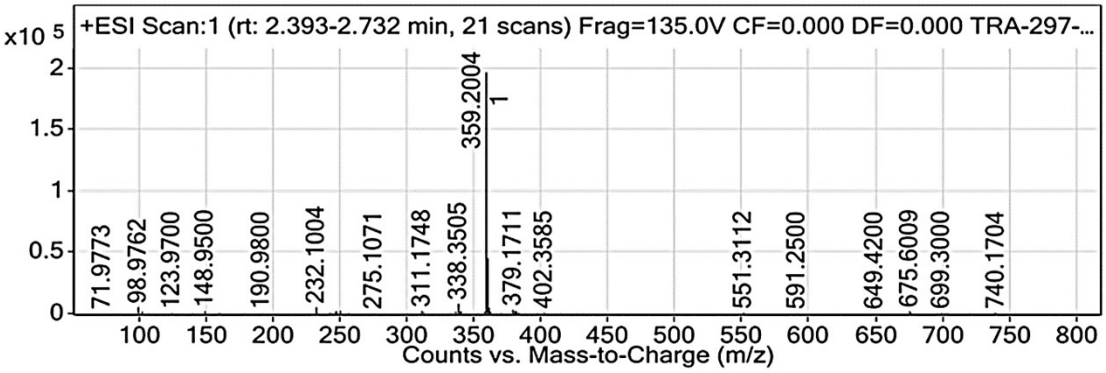



**Figure S29:** LCMS-ESI (+) (M+1) of compound **17** shows peak at 359.2004.

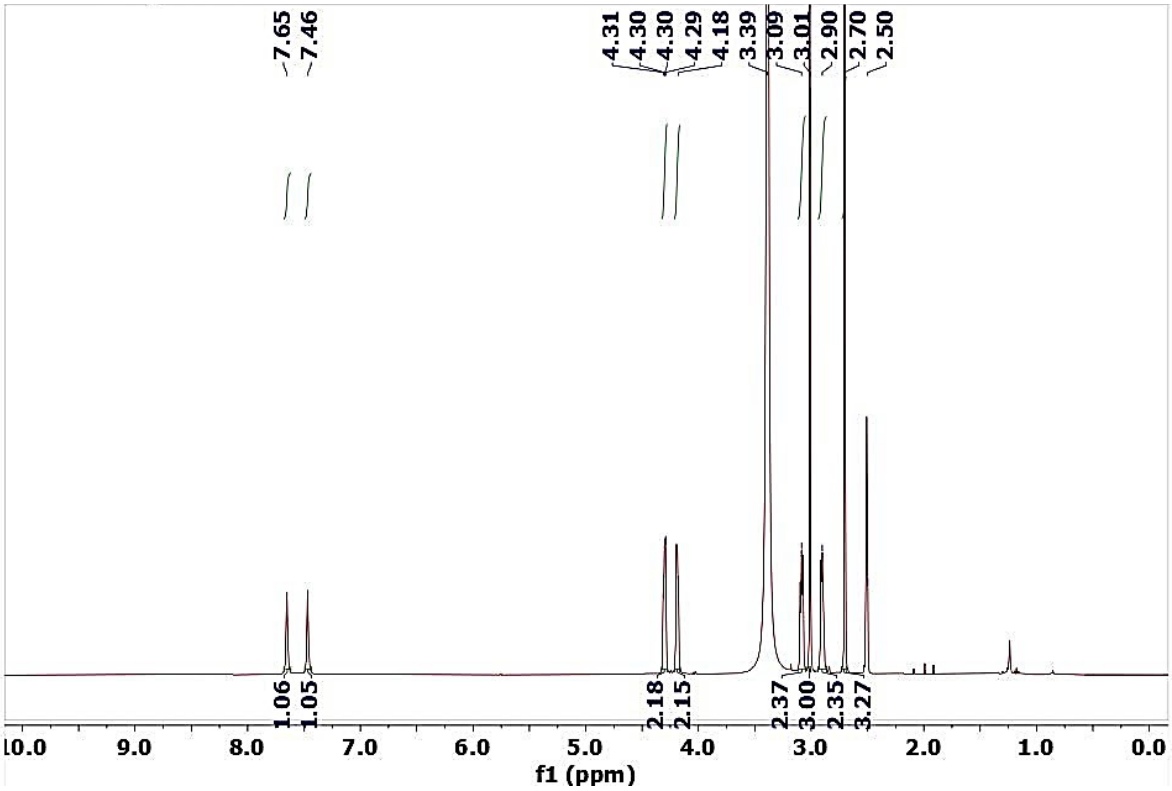



**Figure S30**: $^{1}H$ NMR spectrum (400 MHz) of compound **18** in DMSO-$d_6$.

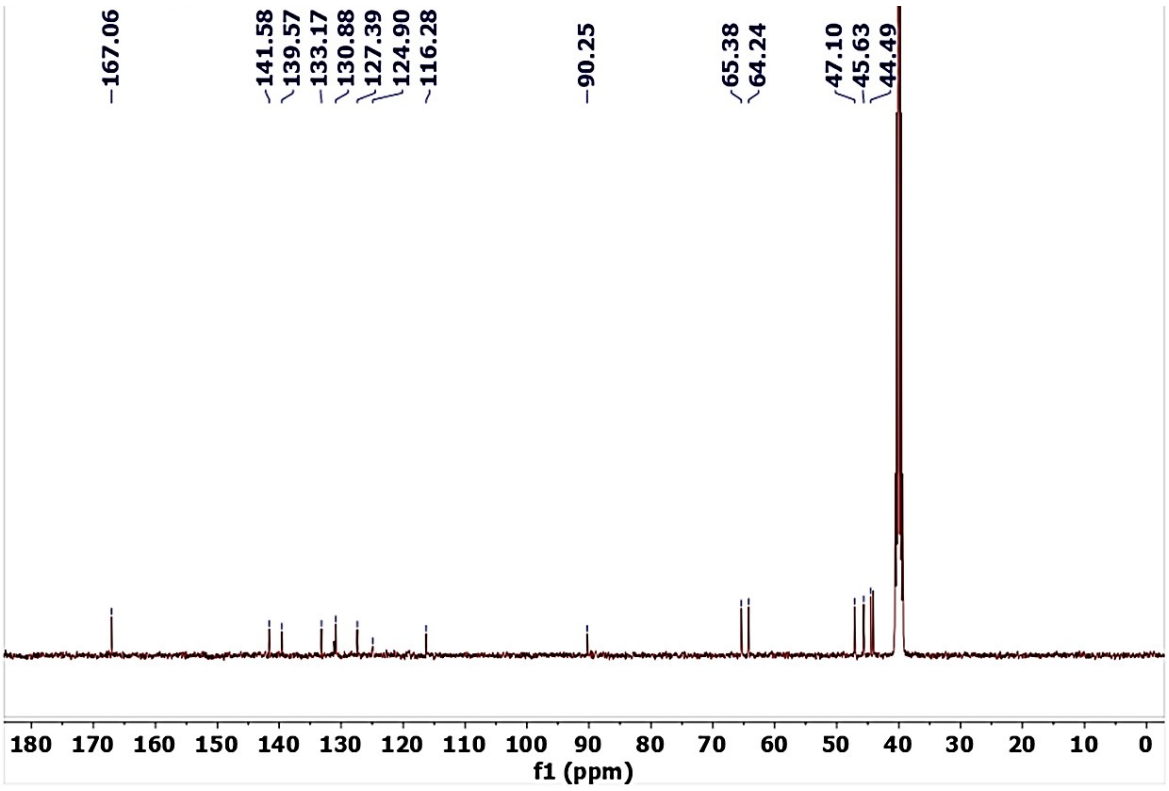



**Figure S31**: $^{13}C$ NMR spectrum (100 MHz) of compound **18** in DMSO-$d_6$.

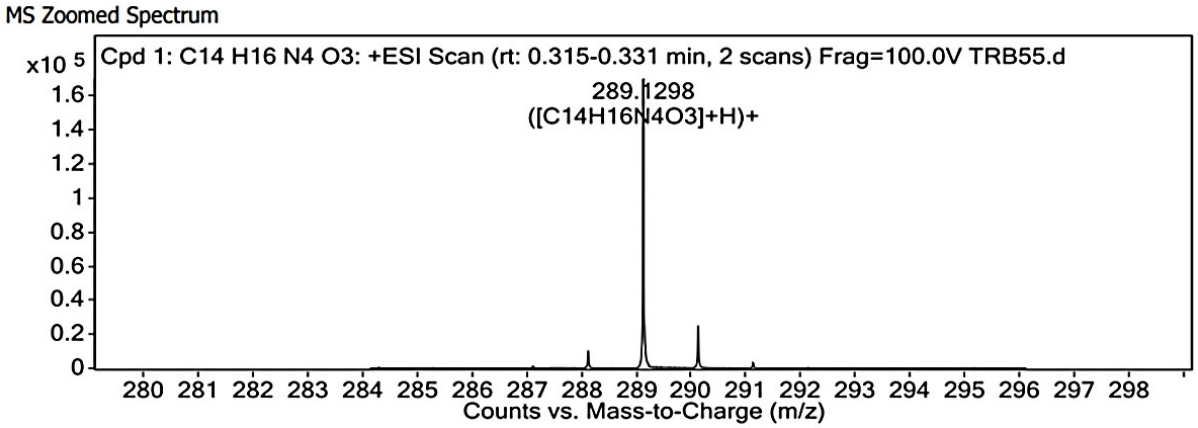



**Figure S32**: HRMS-ESI (+) of compound **18**.

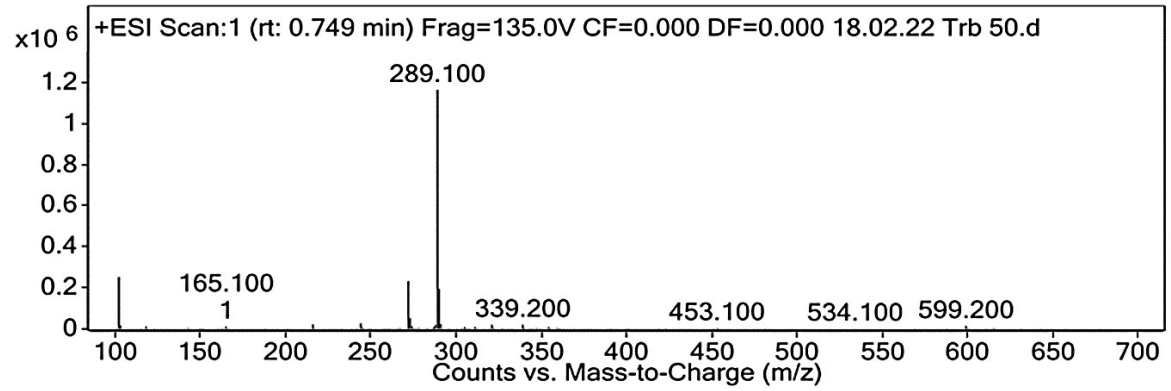



**Figure S33:** LCMS-ESI (+) (M+1) of compound **18** shows peak at 289.100.

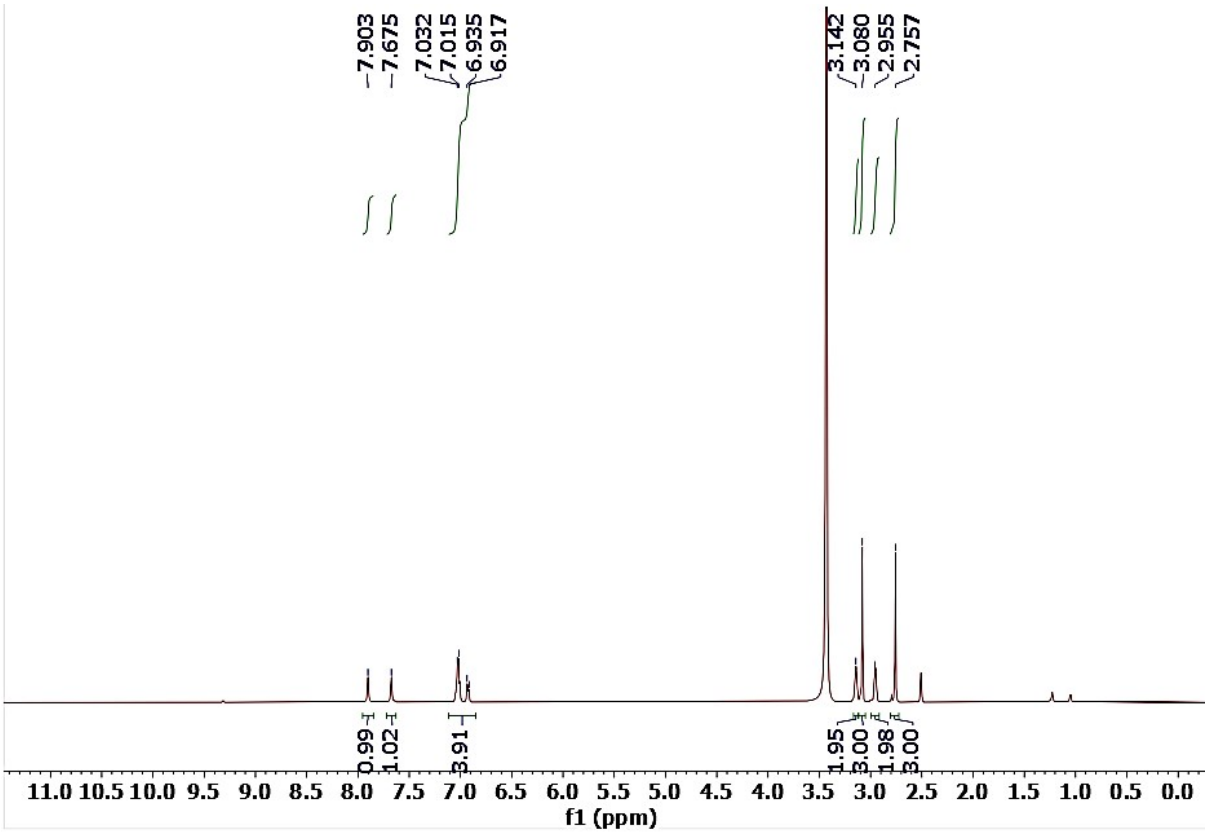



**Figure S34**: $^{1}H$ NMR spectrum (500 MHz) of compound **20** in DMSO-$d_6$.

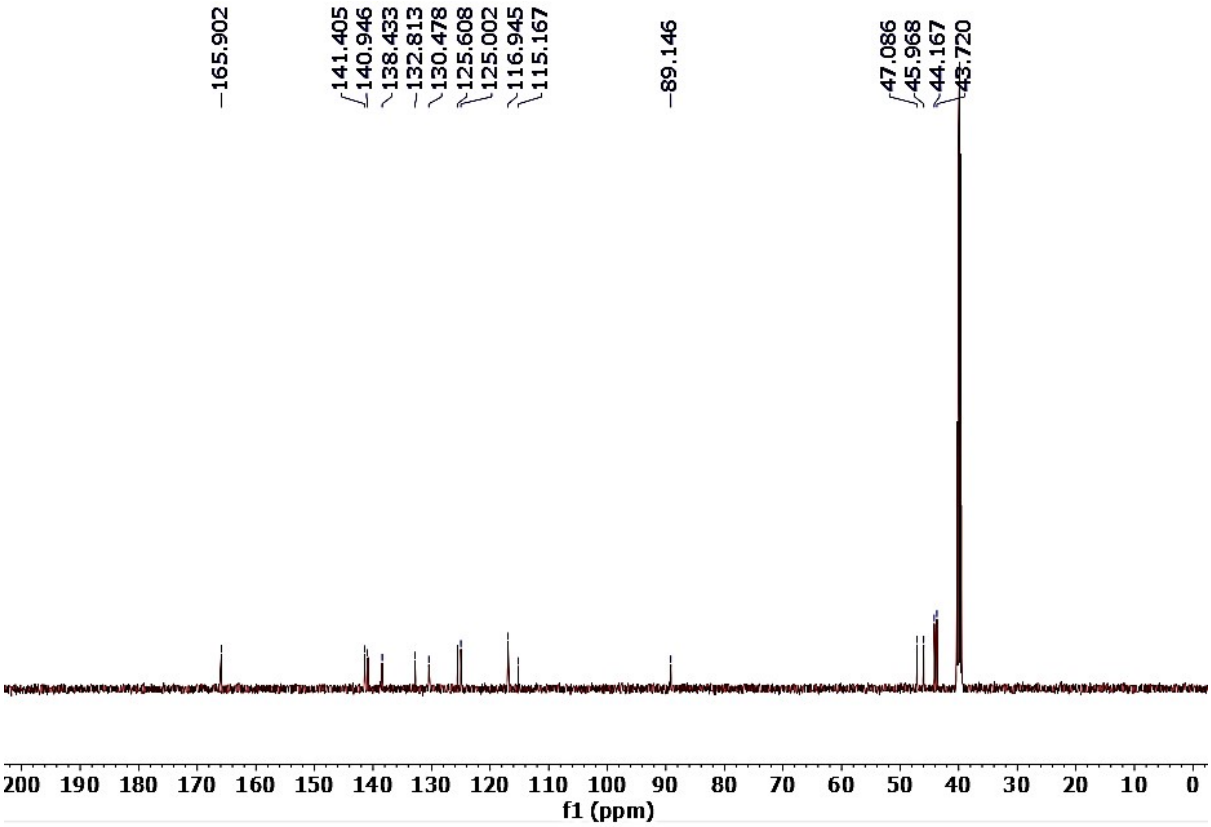



**Figure S35**: $^{13}C$ NMR spectrum (100 MHz) of compound **20** in $CDCl_3$.

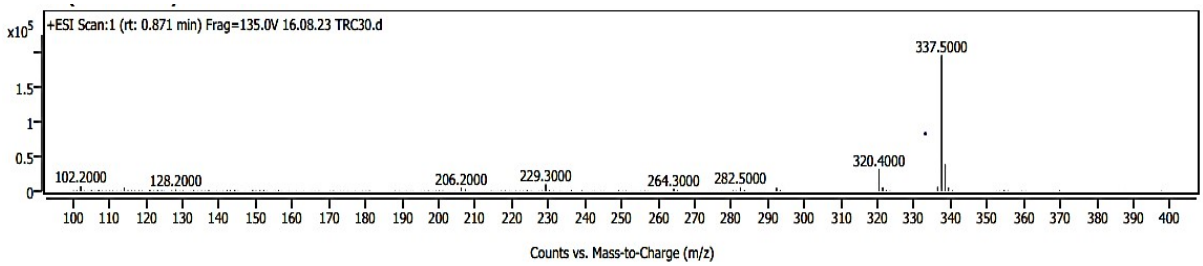



**Figure S36:** LCMS-ESI (+) (M+1) of compound **20** shows peak at 337.50.

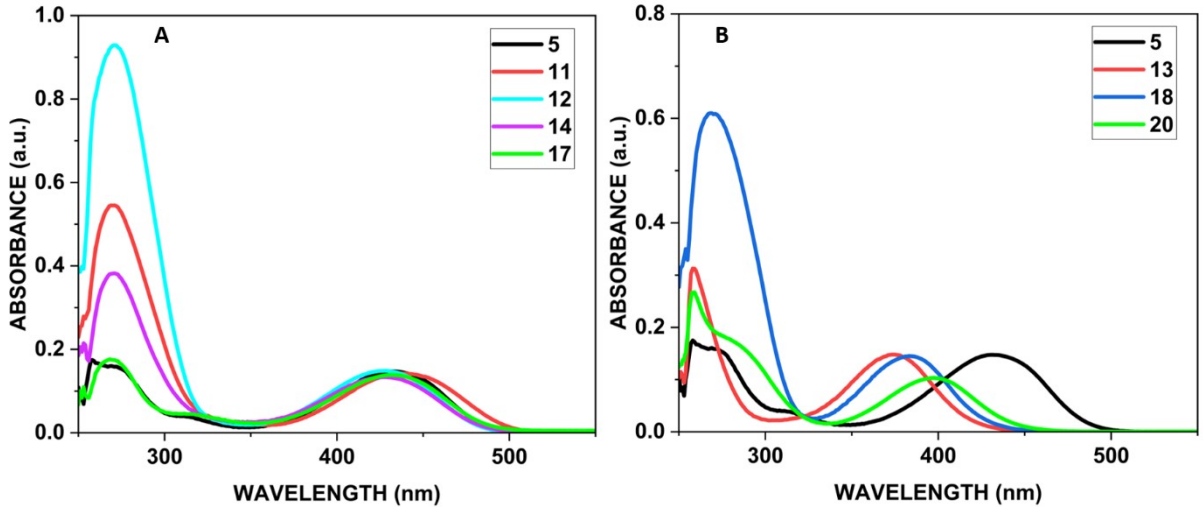



**Figure S37:** UV-Visible spectra (A) of compounds **5**, **11**, **12**, **14**, and **17** in DMSO and UV-Visible spectra (B) of compounds **5**, **13**, **18**, and **20** in DMSO.

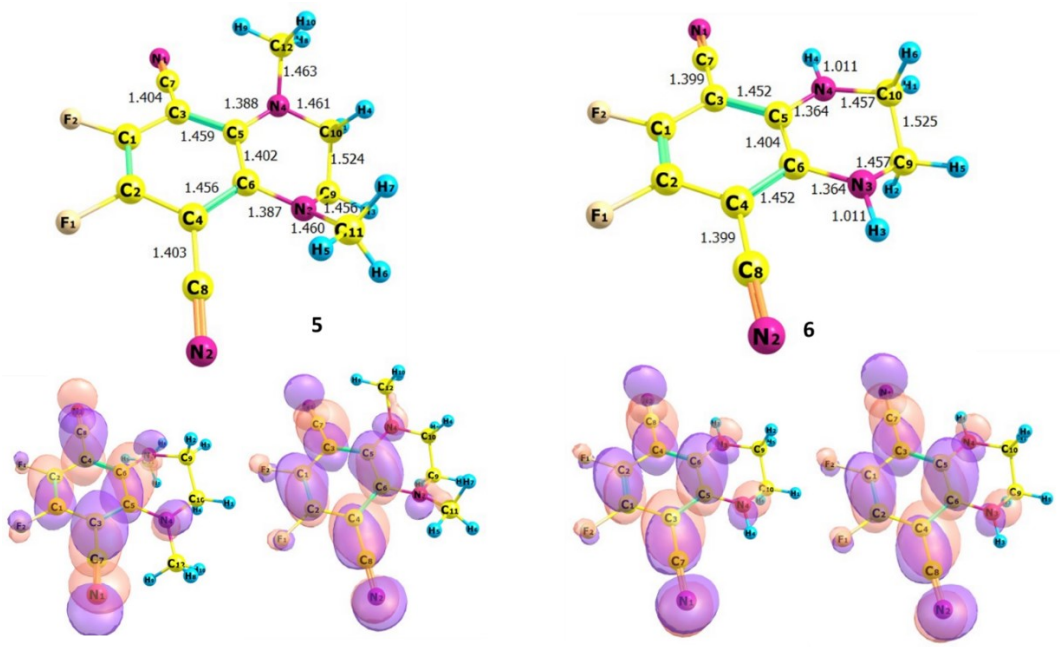



**Figure S38**: Excited state geometries and frontier molecular orbitals of compound **5** and **6.**

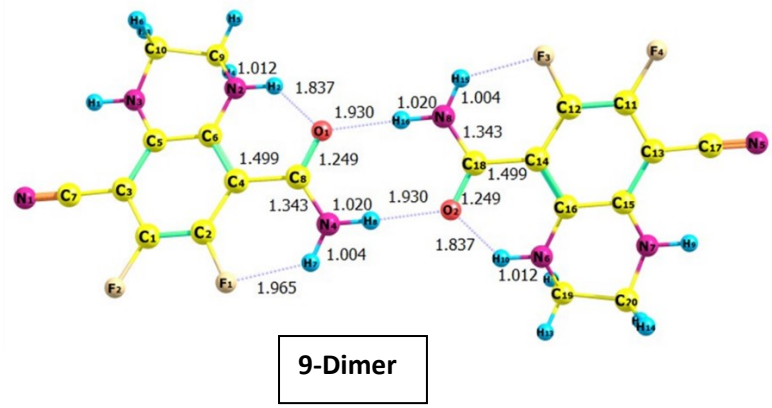



**Figure S39**: Ground state geometries of dimer of compound **9**.

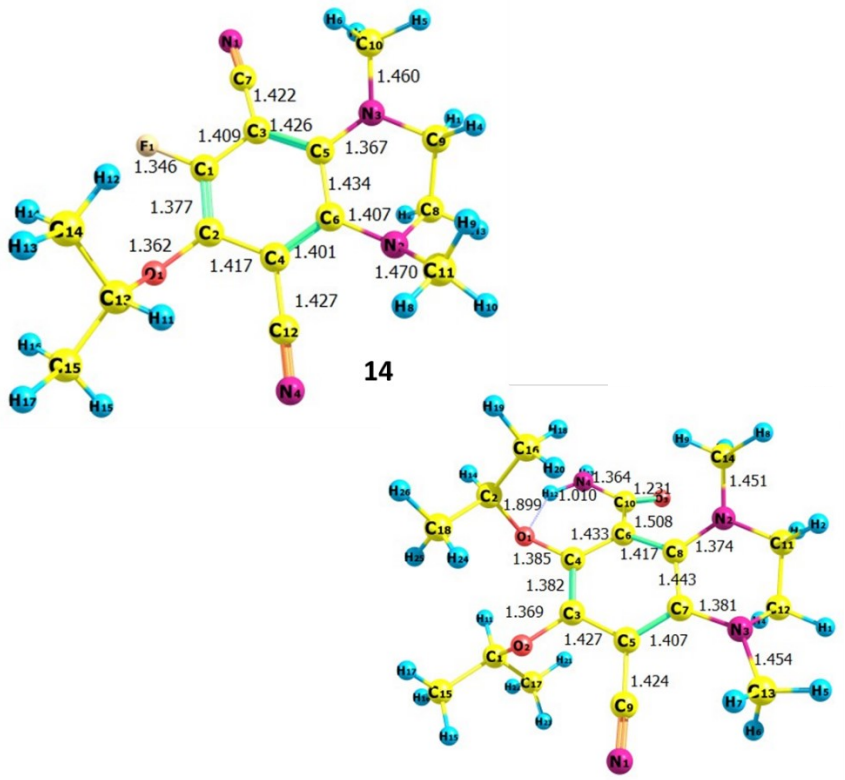



**Figure S40**: Ground state geometries of compounds **14** and **16**.

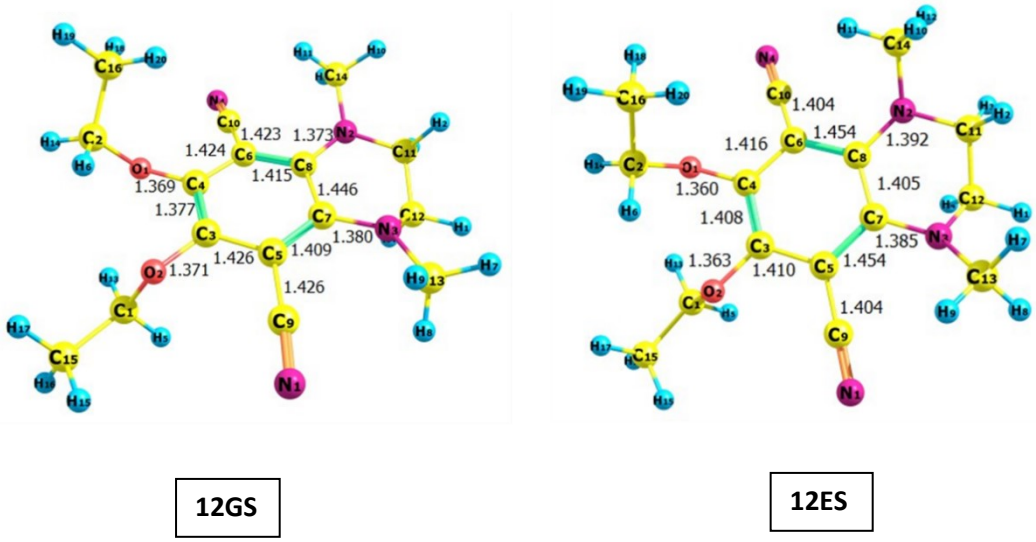
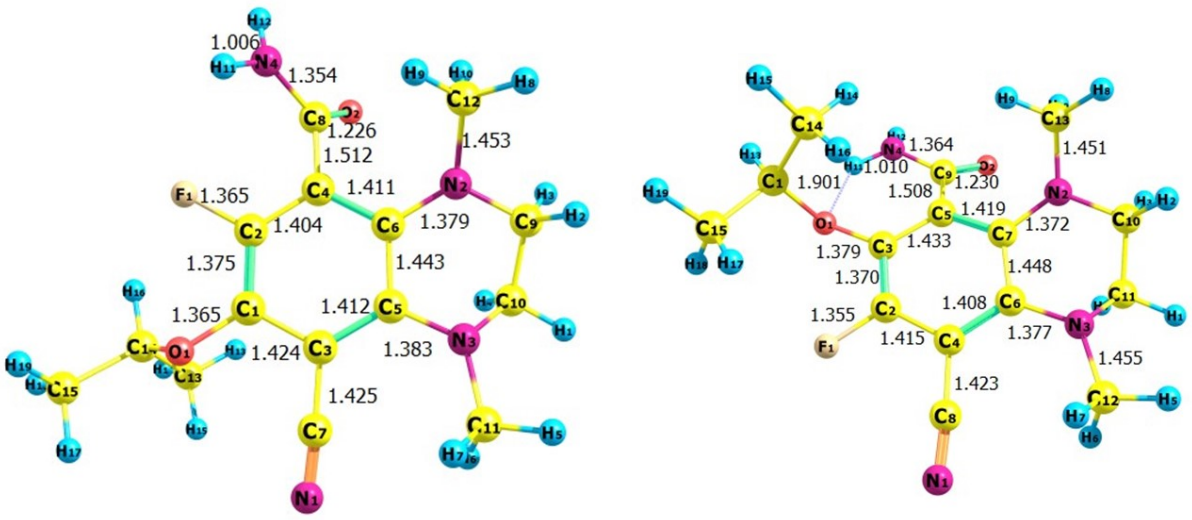



**Figure S41:** Ground state (GS) and excited state (ES) geometries of compound **12.**




**15a,** Energy = -1052.5676 Hartree **15b,** Energy = -1052.5590 Hartree

First one more stable by 5.4 kcal/mol

**Figure S42.** Ground state geometries of compounds **15a** and **15b**.

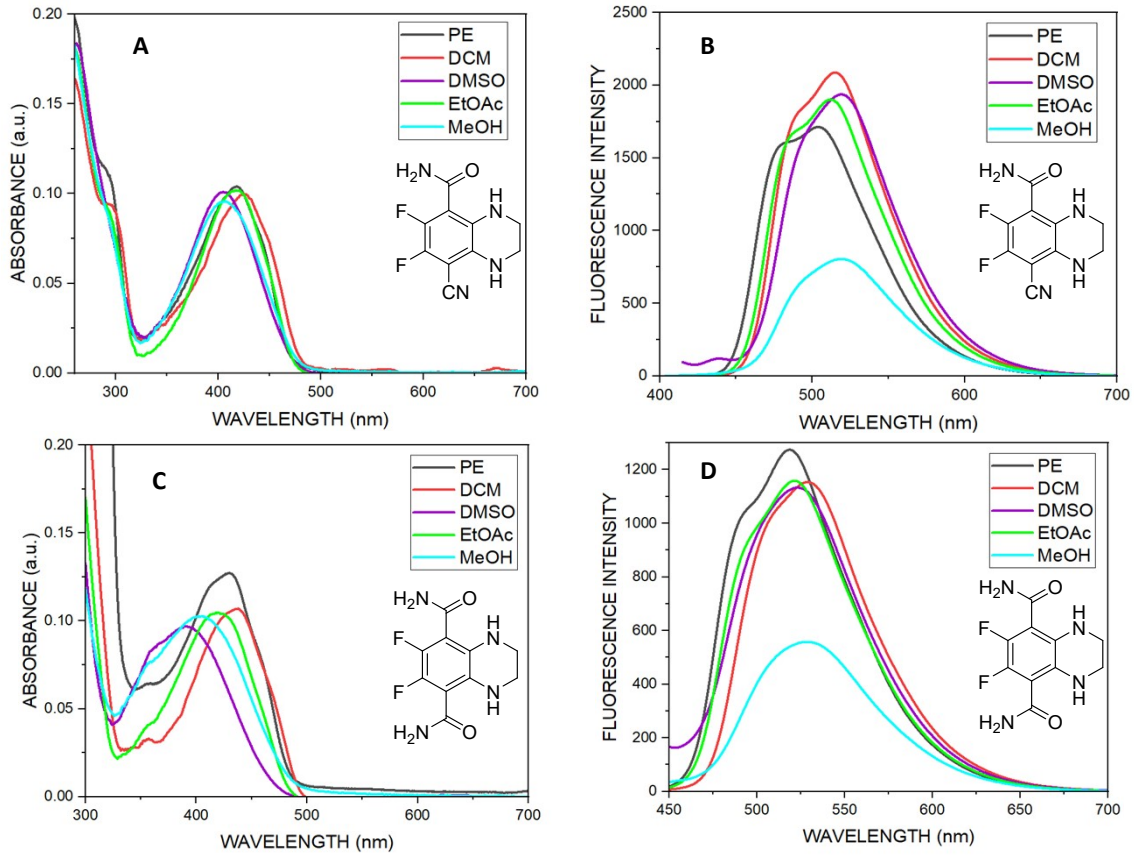



**Figure S43:** Solvatochromism plots for absorption spectra of compounds **9 (A)**, **10 (C)**, and fluorescence spectra of compounds **9 (B)**, and **10 (D)**.

**Table S1** Absorption peak positions

| Compounds | Predicted peak position | Experimental peak position |
|---|---|---|
| **12** | 438 (0.29) H-L (0.70) | 428 |
| **13** | 375(0.20) H-L (0.70) | 374 |
| **14** | 431 (0.15), H-L(0.70) | 427 |
| **9** | 424 (0.22), H-L (0.70) | 406 |
| **10** | 429 (0.22), H-L (0.70) | 392 |

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**Table S2** Fluorescence peak positions

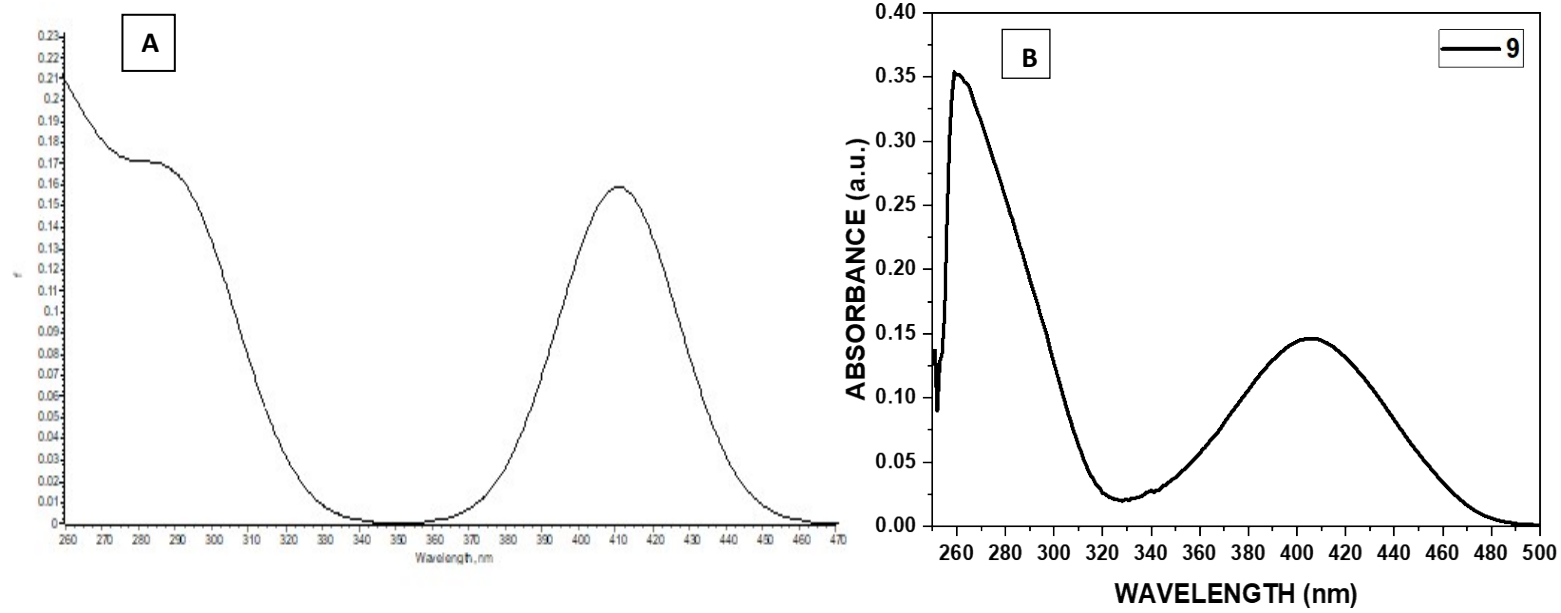
| Compounds | Predicted peak position | Experimental peak position |
|---|---|---|
| **12** | 548 | 537 |
| **13** | 571 | 546 |
| **9** | 510 | 519 |
| **10** | 525 | 523 |

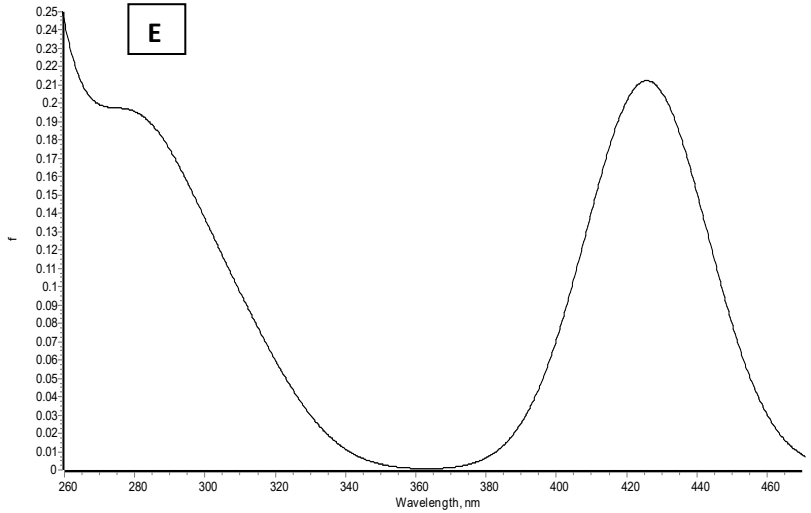
| **5** | | | **12** | | | **13** | | | **14** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MO NO. | Energy (eV) | | MO NO. | Energy (eV) | | MO NO. | Energy (eV) | | MO NO. | Energy (eV) | |
| 62 | -7.954494912 | HOMO-2 | 78 | -0.27937 | HOMO-2 | 83 | -7.122364184 | HOMO-2 | 74 | -7.783061832 | HOMO-2 |
| 63 | -6.799634608 | HOMO-1 | 79 | -0.23797 | HOMO-1 | 84 | -6.304383488 | HOMO-1 | 75 | -6.67772664 | HOMO-1 |
| 64 | -5.772124592 | HOMO | 80 | -0.19476 | HOMO | 85 | -5.12802602 | HOMO | 76 | -5.66817628 | HOMO |
| 65 | -2.420199704 | LUMO | 81 | -0.07228 | LUMO | 86 | -1.74018182 | LUMO | 77 | -2.291760952 | LUMO |
| 66 | -0.530354084 | LUMO+1 | 82 | -0.01111 | LUMO+1 | 87 | -0.13197626 | LUMO+1 | 78 | -0.453345256 | LUMO+1 |
| 67 | -0.002993276 | LUMO+2 | 83 | 0.01464 | LUMO+2 | 88 | 0.50749634 | LUMO+2 | 79 | 0.198100448 | LUMO+2 |
| **6** | | | **9** | | | **10** | | | | | |
| MO NO. | Energy (eV) | | MO NO. | Energy (eV) | | MO NO. | Energy (eV) | | | | |
| 54 | -8.659275352 | HOMO-2 | 83 | -7.122364184 | HOMO-2 | 64 | -7.450263964 | HOMO-2 | | | |
| 55 | -6.957734004 | HOMO-1 | 84 | -6.304383488 | HOMO-1 | 65 | -6.562349456 | HOMO-1 | | | |
| 56 | -5.704367708 | HOMO | 85 | -5.12802602 | HOMO | 66 | -5.170204 | HOMO | | | |
| 57 | -2.286046516 | LUMO | 86 | -1.74018182 | LUMO | 67 | -1.798142528 | LUMO | | | |
| 58 | -0.266129448 | LUMO+1 | 87 | -0.13197626 | LUMO+1 | 68 | 0.0748319 | LUMO+1 | | | |
| 59 | -0.045443372 | LUMO+2 | 88 | 0.50749634 | LUMO+2 | 69 | 0.394023968 | LUMO+2 | | | |

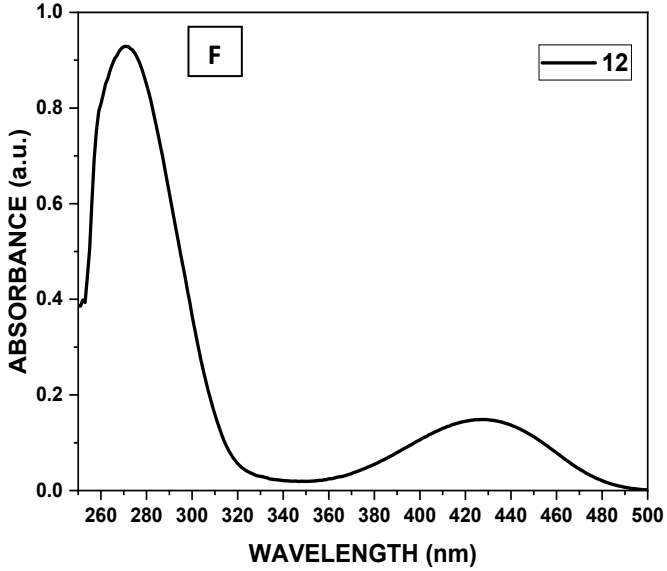
**Table S3**. Energies of Molecular Orbitals

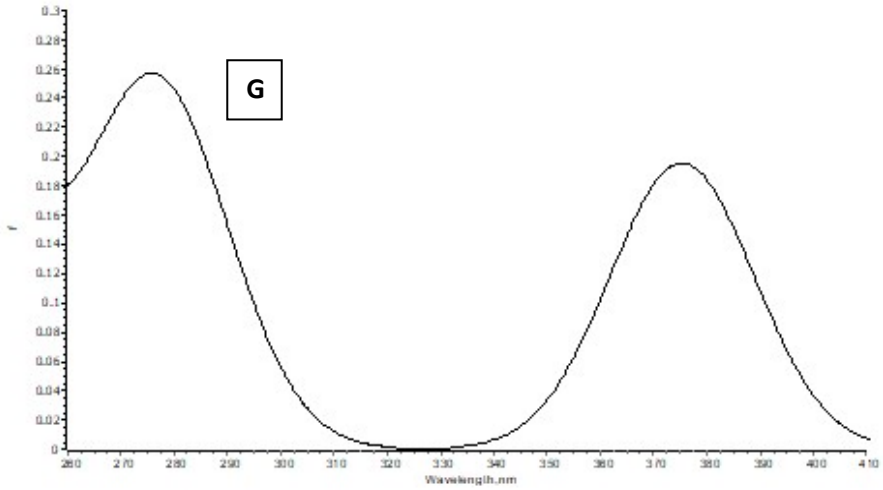
**Table S4**. Absorption peak positions

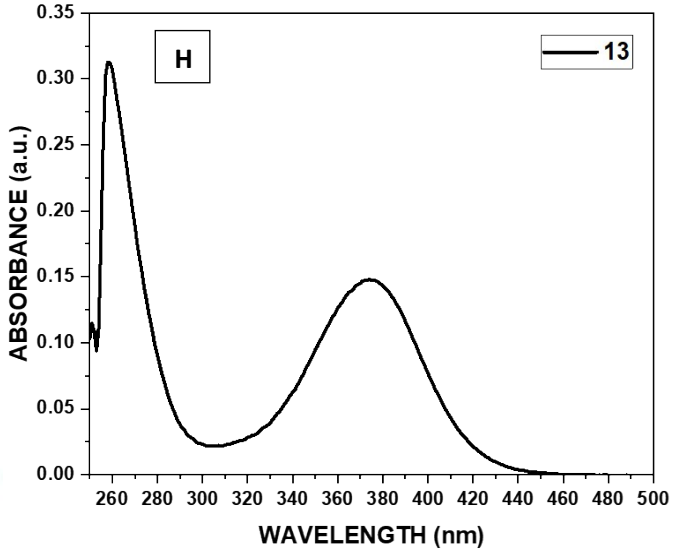
| | Theoretically predicted absorption peak at TDDFT level | | | Experimental peak position |
|---|---|---|---|---|
| Compounds | Predicted longest wave length absorption peak position ($S_0$-$S_1$ transition at optimized $S_0$) | Oscillator strengths of $S_0$-$S_1$ transitions | Excitations dominating the $S_0$-$S_1$ transitions (contribution) | |
| **12** | 426 | 0.22 | H→L (0.70) | 428 |
| **13** | 375 | 0.20 | H→L (0.70) | 374 |
| **14** | 431 | 0.15 | H→L (0.70) | 427 |
| **9** | 411 | 0.16 | H→L (0.70) | 406 |
| **10** | 416 | 0.15 | H→L (0.70) | 392 |


A
B
9
ABSORBANCE (a.u.)
WAVELENGTH (nm)
C
D
10
ABSORBANCE (a.u.)
WAVELENGTH (nm)
Wavelength, nm


E
f
Wavelength, nm


F
12
ABSORBANCE (a.u.)
WAVELENGTH (nm)


G
f
Wavelength,nm


H
13
ABSORBANCE (a.u.)
WAVELENGTH (nm)

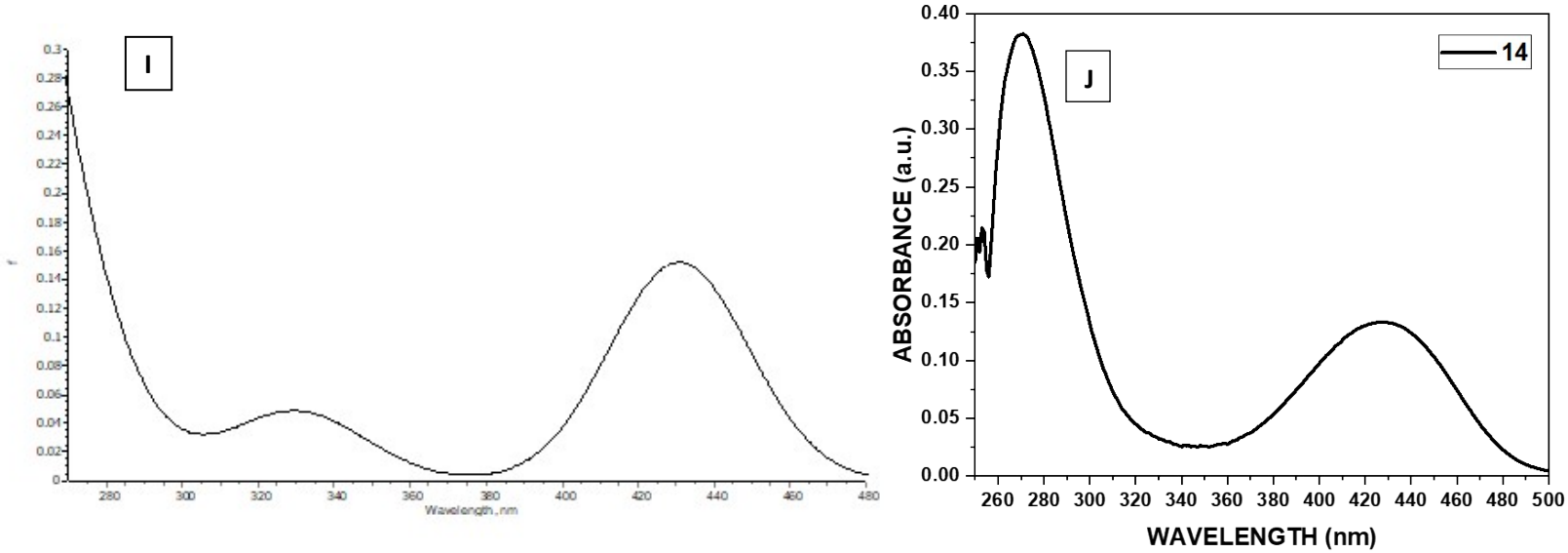



**Figure S44:** Left graphs (A), (C), (E), (G), (I) shows the TDDFT calculated absorption spectra and the right graphs (B), (D), (F), (H), (J) shows the experimental absorption spectra of compounds **9**, **10**, **12**,**13**, and **14** respectively.