Electronic Supplementary Material (ESI) for ChemComm.


# Electronic Supplementary Information (ESI)

## Orchestrated Catalytic Double Rollover Annulation:Rapid Access to N-Enriched Cationic and Neutral PAHs

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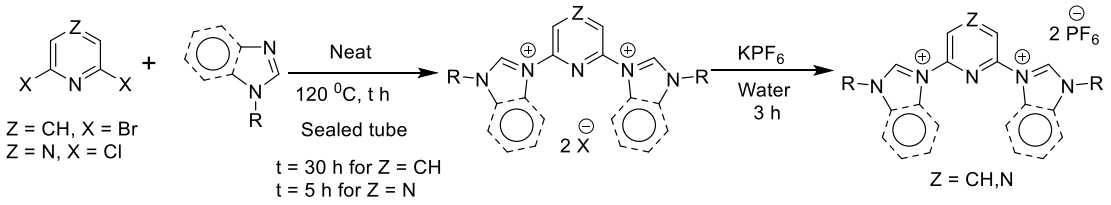
## 1. General Methods and Materials

$^{1}H$, $^{13}C\{^{1}H\}$, $^{19}F$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker AVANCE III 400 and 500 MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts ($\delta$) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: $\delta$ = 7.26 ppm for $^{1}H$ spectra, 77.2 ppm for $^{13}C\{^{1}H\}$ spectra; $CH_3CN$: $\delta$ = 1.94 ppm for $^{1}H$ spectra, 1.3 ppm for $^{13}C\{^{1}H\}$ spectra; DMSO: 2.50 ppm for $^{1}H$ spectra, 39.5 ppm for $^{13}C\{^{1}H\}$ spectra). All coupling constants ($J$) are expressed in hertz (Hz) and only given for $^{1}H$–$^{1}H$ couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublet of doublets), m (multiplet). ESI mass spectroscopy was performed on a Bruker microTOF QII spectrometer. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at low temperatures. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents, $RhCl_3.xH_2O$ and other chemicals were purchased from Aldrich. $[Cp^*RhCl_2]_2$[S1] and $[Cp^*Co(CO)I_2]$[S2] were synthesized according to reported procedure.

## 2. General Procedure for the Synthesis of Imidazolium Substituted Pyridines/Pyrazines[S3]




A mixture of 2,6-dibromopyridine or 2,6-dichloropyrazine (5 mmol) and N-alkylimidazole (15 mmol) was stirred in a sealed tube at 120 °C for 30 h (for pyridines) or 5 h (for pyrazines). After completion, THF (10 mL) was added to the mixture and the resulting solid residue was filtered and washed with THF (10 mL x 5) and diethyl ether (20 mL). The solid product was dried under vacuum to give an off-white powder. Next, this halide salt was dissolved in minimum amount of distilled water and an aqueous solution of $KPF_6$ (20 mmol) was added dropwise with vigorous stirring. After 3 h, the resulting white precipitate was filtered, washed with distilled water (20 mL x 3) and diethyl ether (20 mL x 2) to yield the desired product.

**2,6-*Bis*(1-methylimidazolium) pyridine hexafluorophosphate (1a):** Yield: 81%. $^1$H NMR (500 MHz, DMSO-$d_6$): δ 10.25 (s, 2H), 8.73 (s, 2H), 8.61 (d, *J* = 16.2 Hz, 1H), 8.18 (t, *J* = 8.9 Hz, 2H), 8.09 (s, 2H), 4.01 (s, 6H). HRMS (ESI, positive ion): $M^{2+}$ = 120.5664 (calculated = 120.5658 for $[C_{13}H_{15}N_5]^{2+}$).

**2,6-*Bis*(1-methylimidazolium) pyrazine hexafluorophosphate (1b):** A mixture of 2,6-dichloropyrazine (300 mg, 2.0 mmol) and N-methylimidazole (0.5 mL, 6.1 mmol) was stirred in a sealed tube at 120 °C for 3 h. The work up procedure was similar as mentioned above for synthesis of **1a**. Yield: 82%. $^1$H NMR (500 MHz, DMSO-$d_6$): δ 10.30 (s, 2H), 9.49 (s, 2H), 8.75 (d, *J* = 1.8 Hz, 2H), 8.09 (s, 2H), 4.04 (s, 6H). HRMS (ESI, positive ion): $M^{2+}$ = 121.0625 (calculated = 121.0634 for $[C_{12}H_{14}N_6]^{2+}$).

**1,1'-(pyridine-2,6-diyl)bis(3-butyl-1H-imidazol-3-ium) hexafluorophosphate (1c):** Yield: 50%. $^1$H NMR (400 MHz, $CD_3CN$): *δ* 9.60 (s, 2H), 8.41 (t, *J* = 8.1 Hz, 1H), 8.22 (t, *J* = 1.8 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.69 – 7.63 (m, 2H), 4.30 (t, *J* = 7.3 Hz, 4H), 1.93 (d, *J* = 2.5 Hz, 4H), 1.41 (dd, *J* = 15.1, 7.5 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 6H). HRMS (ESI, positive ion): $M^{2+}$ = 162.6125 (calculated = 162.6128 for $[C_{19}H_{27}N_5]^{2+}$).

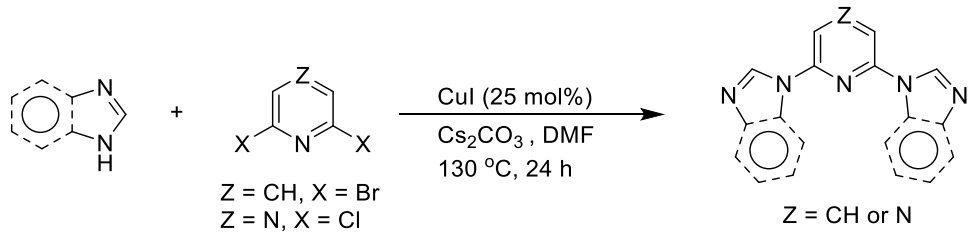
**3,3'-(pyridine-2,6-diyl)bis(1-methyl-1H-benzo[*d*]imidazol-3-ium) hexafluorophosphate (1d):** Yield: 83%. $^1$H NMR (500 MHz, DMSO-$d_6$): *δ* 10.63 (s, 2H), 8.78 (t, *J* = 8.1 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 8.1 Hz, 2H), 8.24 (d, *J* = 8.3 Hz, 2H), 7.87 (t, *J* = 7.7

Hz, 2H), 7.80 (t, *J* = 7.8 Hz, 2H), 4.31 (s, 6H). HRMS (ESI, positive ion): $M^{2+}$ = 170.5804 (calculated = 170.5815 for $[C_{21}H_{19}N_5]^{2+}$).

**1,1'-(pyrazine-2,6-diyl)bis(3-methyl-1H-benzo[d]imidazol-3-ium) hexafluorophosphate (1e):** Yield: 70%. $^1$H NMR (400 MHz, DMSO-$d_6$): δ 10.72 (s, 2H), 9.57 (s, 2H), 8.44 (d, *J* = 8.4 Hz, 2H), 8.24 (d, *J* = 8.2 Hz, 2H), 7.86 (t, *J* = 7.7 Hz, 2H), 7.80 (t, *J* = 7.8 Hz, 2H), 4.30 (s, 6H). HRMS (ESI, positive ion): $M^{2+}$ = 171.0780 (calculated = 171.0791 for $[C_{20}H_{18}N_6]^{2+}$).

**1,1'-(pyrazine-2,5-diyl)bis(3-methyl-1H-imidazol-3-ium) hexafluorophosphate (1f):** Yield: 70%. $^1$H NMR (500 MHz, DMSO-$d_6$): *δ* 10.18 (s, 2H), 9.37 (s, 2H), 8.62 (s, 2H), 8.05 (s, 2H), 4.03 (s, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$): *δ* 36.58, 119.42, 125.18, 134.97, 136.34, 143.05. HRMS (ESI, positive ion): $M^{2+}$ = 121.0606 (calculated = 121.0634 for $[C_{12}H_{14}N_6]^{2+}$).

### 3. Synthesis of 2,6-*bis*-(benz)imidazolyl pyridines/pyrazines[S4]




A mixture of CuI (1.04 mmol), $Cs_2CO_3$ (16.6 mmol), imidazole/benzimidazole (12.6 mmol), and 2,6-dibromopyridine or 2,6-dichloropyrazine (4.2 mmol) in dry DMF (9 mL) was stirred at room temperature for 30 min. in a sealed tube and then allowed to be stirred at 130 °C for 24 h. After completion, it was cooled to room temperature. To it $CH_2Cl_2$ (40 mL) was added and it was washed with $H_2O$ (20 mL x 2) by solvent extraction procedure. The $CH_2Cl_2$ layer was collected and concentrated under reduced pressure. The resulting residue was subjected to column chromatography (silica gel, 1-2% MeOH in $CHCl_3$) to isolate the desired product.

**2,6-di(1H-imidazol-1-yl)pyridine (1g):** Yield: 85%. $^1$H NMR (400 MHz, $CDCl_3$) *δ* 8.38 (s, 2H), 7.97 (t, *J* = 8.0 Hz, 1H), 7.67 (s, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 2H). HRMS (ESI, positive ion): $[M+H]^+$ = 212.0936 (calculated = 212.0931 for $[C_{11}H_{10}N_5]^+$).

**2,6-di(1H-imidazol-1-yl)pyrazine (1h):** Yield: 62%. $^1$H NMR (500 MHz, $CDCl_3$) *δ* 8.72 (s, 2H), 8.42 (s, 2H), 7.71 (t, *J* = 1.4 Hz, 2H), 7.30 (dd, *J* = 1.3, 0.8 Hz, 2H). HRMS (ESI, positive ion): $[M+H]^+$ = 213.0863 (calculated = 213.0883 for $[C_{10}H_9N_6]^+$).

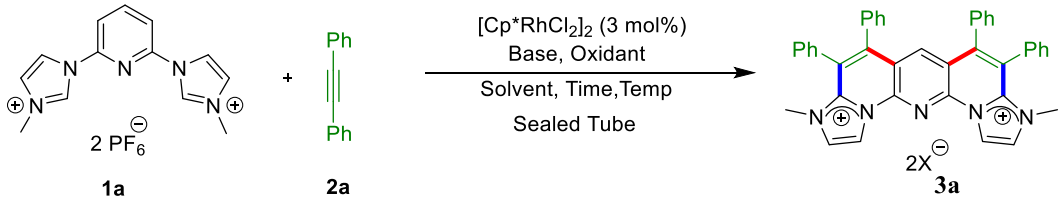
**2,6-bis(1H-benzo[d]imidazol-1-yl)pyridine (1i):** Yield: 80%. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.17 (s, 2H), 8.41 – 8.31 (m, 1H), 8.28 (s, 2H), 7.98 (d, $J$ = 7.0 Hz, 2H), 7.85 (s, 2H), 7.38 (s, 4H). HRMS (ESI, positive ion): $[M+H]^+$ = 312.1249 (calculated = 312.1244 for $[C_{19}H_{14}N_5]^+$).

**2,5-di(1H-imidazol-1-yl)pyrazine (1j):** Yield: 72%. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.63 (s, 2H), 8.38 (bs, 2H), 7.67 (t, $J$ = 1.4 Hz, 2H), 7.29 (bs, 2H), 7.26 (s, 2H). HRMS (ESI, positive ion): $[M+H]^+$ = 213.0867 (calculated = 213.0883 for $[C_{10}H_9N_6]^+$).

## 4. Optimization of the Reaction Conditions

To an oven dried sealed tube, **1a** (0.05 mmol), catalyst (3 mol%), **2a** (0.11 mmol) and additives were loaded. To this mixture, dry and degassed DCE (2.0 mL) was added and the reaction mixture was left with stirring at 120 ºC in dark. After a certain time, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (10 mL x 3). The combined filtrate was concentrated under reduced pressure and the whole crude mixture was subjected to $^1$H NMR spectroscopy in DMSO-$d_6$ for checking the yield by using 1,3,5-trimethoxybenzene as internal standard.

**Table S1:** Optimization Studies [a]




| No | Catalyst (mol%) | Base (equiv.) | Solvent | Oxidant (equiv.) | Temp. ( ºC) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|---|---|
| **1.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (10) | DCE | AgOTf (5) | 120 | 24 | 94 |
| **2.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (10) | DCE | AgOTf (5) | 120 | 12 | 93 |
| **3.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | DCE | AgOTf (2.5) | 120 | 12 | 52 |
| **4.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | DCE | AgOTf (5) | 120 | 6 | 68 |
| **5.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | DCE | AgOTf (5) | 120 | 12 | 93 |
| 6. | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | DCE | AgOAc (5) | 120 | 12 | Trace |
| **7.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | DCE | $Cu(OAc)_2.H_2O$ (5) | 120 | 12 | Mix. (~50) |
| **8.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | MeOH | $Cu(OAc)_2.H_2O$ (5) | 120 | 12 | Trace |
| **9.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | MeOH | $Cu(BF_4)_2$ (5) | 120 | 12 | Trace |
| **10.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | DCE | $Cu(BF_4)_2$ (5) | 120 | 12 | ~30 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **11.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | DCE | AgOTf (5) | 30 | 24 | Nd |
| **12.** | $[RhCp^*Cl_2]_2$ (2) | NaOAc (5) | DCE | AgOTf (5) | 120 | 12 | 65 |
| **13.** | $[RhCp^*Cl_2]_2$ (3) | KOAc (5) | DCE | AgOTf (5) | 120 | 12 | 88 |
| **14.** | $[RhCp^*Cl_2]_2$ (3) | $NaHCO_3$ (5) | DCE | AgOTf (5) | 120 | 12 | 40 |
| **15.** | $[RhCp^*Cl_2]_2$ (3) | $K_2CO_3$ (5) | DCE | AgOTf (5) | 120 | 12 | 22 |
| **16.** | -- | NaOAc (5) | DCE | AgOTf (5) | 120 | 12 | Nd |
| **17.** | $[RhCp^*Cl_2]_2$ (3) | -- | DCE | AgOTf (5) | 120 | 12 | Nd |
| **18.** | $[RhCp^*Cl_2]_2$ (3) | NaOAc (5) | DCE | -- | 120 | 12 | Nd |
| **19.** | $[CoCp^*COI_2]$ (6) | NaOAc (5) | DCE | -- | 120 | 12 | Nd |

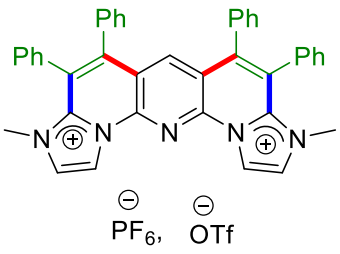
[a] Reaction conditions: **1a** (0.05 mmol), **2a** (0.11 mmol), catalyst (0.0015 mmol), additives (as mentioned), DCE (2.0 mL). [b] Crude product was detected by $^1H$ NMR spectroscopy by using 1,3,5-tri-methoxybenzene as internal standard. Nd = Not detected.

## 5. General Catalytic Procedure of Annulation Reactions for Scheme 2A, Main Article

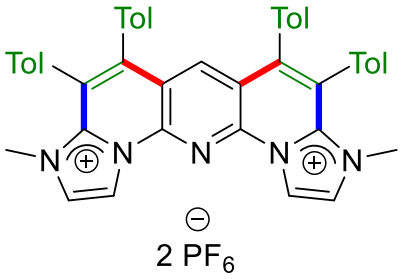
To an oven dried sealed tube, **1** (0.1 mmol), NaOAc (0.5 mmol), $[RhCp^*Cl_2]_2$ (0.003 mmol), AgOTf (0.5 mmol) and **2** (0.21 mmol) were loaded. To this mixture, dry and degassed DCE (2.0 mL) was added and the reaction mixture was left with stirring at 120 °C in dark. After 12 h stirring, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (20 mL x 2). The combined filtrate was concentrated under reduced pressure. Final product was separated and purified by alumina column chromatography, using $CHCl_3$/MeOH (95:5) as eluent.

## 6. Experimental Characterization Data of the Products (3a-3r) (*vide* Scheme 2B in main article)

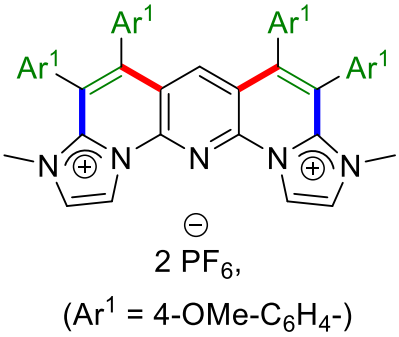
**3,9-Dimethyl-4,5,7,8-tetraphenyl-3,9-dihydroimidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridium Salt (3a):** Yield = 90%. $^1$H NMR (500 MHz, DMSO-$d_6$, 298K): $\delta$ 9.80 (d, $J$ = 2.2 Hz, 2H), 8.52 (d, $J$ = 2.2 Hz, 2H), 7.94 (s, 1H), 7.42 (m, $J$ = 5.1, 3.0 Hz, 10H), 7.20 (s, 6H), 7.09 (m, $J$ = 6.5, 3.0 Hz, 4H), 3.39 (s, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$, 298K): $\delta$ 143.9, 141.0, 140.3, 139.3, 132.5, 131.7, 131.3, 130.2, 130.0, 129.2, 129.0, 128.9, 128.6, 125.5, 119.6, 114.8, 38.3. $^{19}$F NMR (471 MHz, DMSO-$d_6$) $\delta$ -70.25 (d, $J$ = 711.6 Hz), -77.76. $^{31}$P NMR (202 MHz, DMSO-$d_6$, 298K): $\delta$ -144.3 (hept, $J$ = 711.37 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 296.6292 (calculated =296.6284 for $[C_{41}H_{31}N_5]^{2+}$).



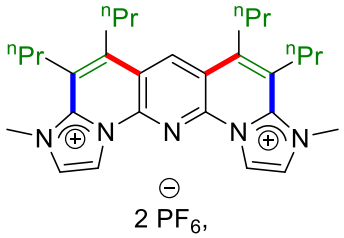

**3,9-Dimethyl-4,5,7,8-tetra-*p*-tolyl-3H-imidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridium Salt (3b):** Yield = 80%. $^1$H NMR (500 MHz, DMSO-$d_6$, 298K): $\delta$ 9.75 (d, $J$ = 2.2 Hz, 2H), 8.50 (d, $J$ = 2.2 Hz, 2H), 7.81 (s, 1H), 7.32 (d, $J$ = 8.0 Hz, 4H), 7.24 (d, $J$ = 7.9 Hz, 4H), 7.07 (d, $J$ = 7.9 Hz, 4H), 6.95 (d, $J$ = 8.0 Hz, 4H), 3.39 (s, 6H), 2.31 (s, 6H), 2.24 (s, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$, 298K): $\delta$ 143.6, 140.9, 140.9, 139.7, 139.1, 139.0, 138.0, 130.7, 129.7, 129.7, 129.1, 128.7, 128.4, 124.8, 119.5, 114.2, 37.7, 20.9, 20.6. $^{19}$F NMR (471 MHz, DMSO-$d_6$, 298K): $\delta$ -70.20 (d, $J$ = 711.3 Hz). $^{31}$P NMR (202 MHz, DMSO-$d_6$, 298K): $\delta$ -144.23 (hept, $J$ = 711.4 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 324.6613 (calculated = 324.6597for $[C_{45}H_{39}N_5]^{2+}$).



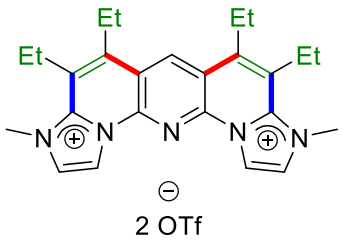
**4,5,7,8-Tetrakis(4-methoxyphenyl)-3,9-dimethyl-3,9 dihydroimidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridine-12,14-diium Salt (3c):** Yield = 63% $^{1}$H NMR (500 MHz, $CD_3CN$, 298K) $\delta$ 9.24 (d, $J$ = 2.3 Hz, 2H), 8.12 (s, 1H), 7.97 (d, $J$ = 2.3 Hz, 2H), 7.38 – 7.27 (m, 4H), 7.10 – 7.03 (m, 4H), 7.02 – 6.98 (m, 4H), 6.90 – 6.80 (m, 4H), 3.83 (s, 6H), 3.78 (s, 6H), 3.45 (s, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$, 298K) $\delta$ 161.6, 160.9, 146.2, 141.4, 141.0, 140.7, 133.2, 132.5, 129.,5 126.1, 125.8, 124.2, 121.3, 115.0, 114.8, 114.7, 56.2, 56.1, 39.2. $^{19}$F NMR (471 MHz, $CD_3CN$, 298K) $\delta$ -72.99 (d, $J$ = 706.8 Hz). $^{31}$P NMR (202 MHz, $CD_3CN$, 298K) $\delta$ -139.44 (d, $J$ = 706.7 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 356.6493 (calculated = 356.6496 for $[C_{45}H_{39}N_5O_4]^{2+}$).



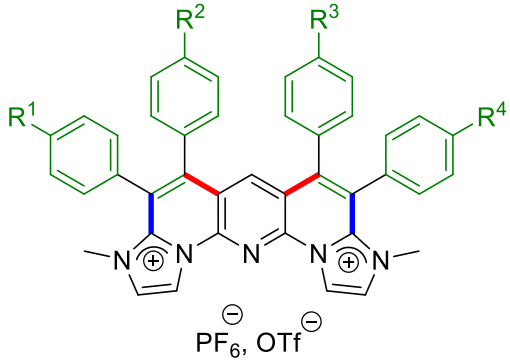

**3,9-Dimethyl-4,5,7,8-tetrapropyl-3,9-dihydroimidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridium Salt (3d):** Yield = 71%. $^{1}$H NMR (500 MHz, DMSO-$d_6$, 298K): $\delta$ 9.57 (d, $J$ = 2.0 Hz, 2H), 9.38 (s, 1H), 8.43 (d, $J$ = 2.1 Hz, 2H), 4.39 (s, 6H), 3.49 – 3.44 (m, 4H), 3.26 – 3.18 (m, 4H), 1.72 (tt, $J$ = 14.7, 7.4 Hz, 8H), 1.18 (dd, $J$ = 16.4, 7.4 Hz, 12H). $^{13}$C NMR (126 MHz, DMSO-$d_6$, 298K): $\delta$ 143.4, 140.4, 139.6, 137.1, 129.0, 124.9, 118.4, 114.3, 38.8, 29.3, 28.8, 24.7, 24.5, 14.5, 14.1. $^{19}$F NMR (471 MHz, DMSO-$d_6$, 298K): $\delta$ -70.20 (dd, $J$ = 711.3, 9.6 Hz). $^{31}$P NMR (202 MHz, DMSO-$d_6$, 298K): $\delta$ -144.22 (hept, $J$ = 711.5 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 228.6585 (calculated = 228.6597 for $[C_{29}H_{39}N_5]^{2+}$).




**4,5,7,8-Tetraethyl-3,9-dimethylimidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridine-3,9-diium Salt (3e):** Yield = 50%. $^{1}$H NMR (500 MHz, $CD_3CN$, 298K) $\delta$ 9.33 (s, 1H), 9.14 (d, $J$ = 2.3 Hz, 2H), 7.92 (d, $J$ = 2.3 Hz, 2H), 4.37 (s, 6H), 3.45 (q, $J$ = 7.6 Hz, 4H), 3.31 (q, $J$ = 7.6 Hz, 4H), 1.50 – 1.31 (m, 12H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 146.5, 141.6, 140.6, 137.4, 129.3, 126.9, 119.5, 114.6, 39.6, 21.9, 21.1, 15.6, 15.5. $^{19}$F NMR (376 MHz, $CD_3CN$) $\delta$ -79.31. HRMS (ESI, positive ion): $M^{2+}$ = 200.6292 (calculated = 200.6284 for $[C_{25}H_{31}N_5]^{2+}$).

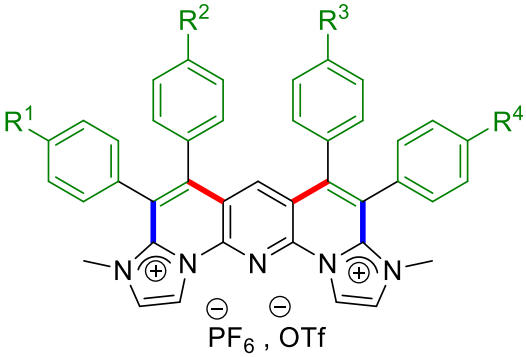


**3,9-Dimethyl-4,8-diphenyl-5,7-di-p-tolyl-3,9-dihydroimidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridine-12,14-diium Salts (3f):** Yield = 50% (a mixture of three regioisomers in **3f**/**3f'**/**3f"** = 2/1/1 ratio determined by $^{1}$H NMR spectroscopy). $^{1}$H NMR (400 MHz, DMSO, 298K) $\delta$ 9.79 (s, 2H), 8.53 (s, 2H), 7.92 – 7.83 (m, 1H), 7.45 (bs, 6H), 7.35 – 7.30 (m, 2H), 7.23 (d, $J$ = 6.0 Hz, 4H), 7.05 (m, 4H), 6.99 – 6.94 (m, 2H), 3.41 (d, $J$ = 4.0 Hz, 3H), 3.39 (s, 3H), 2.31 (s, 3H), 2.22 (d, $J$ = 8.2 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO, 298K) $\delta$ 144.0, 143.9, 143.9, 141.2, 140.2, 140.2, 139.5, 139.5, 139.4, 138.6, 138.5, 133.1, 133.1, 131.9, 131.3, 131.2, 130.1, 130.1, 130.1, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.8, 128.7, 128.6, 125.5, 125.4, 125.2, 125.2, 122.4, 119.9, 119.9, 119.8, 114.8, 114.7, 38.4, 38.3, 21.4, 21.1. $^{31}$P NMR (202 MHz, DMSO, 298K) $\delta$ -138.99 (d, $J$ = 711.3 Hz). $^{19}$F NMR (471 MHz, DMSO, 298K) $\delta$ -70.29 (d, $J$ = 711.4 Hz), -77.75 (s). HRMS (ESI, positive ion): $M^{2+}$ = 310.6459 (calculated = 310.6441 for $[C_{43}H_{35}N_5]^{2+}$).




$R^1 = R^4 = H$, $R^2 = R^3 = CH_3$ (**3f**)
$R^1 = R^3 = H$, $R^2 = R^4 = CH_3$ (**3f'**)
$R^1 = R^4 = CH_3$, $R^2 = R^3 = H$ (**3f"**)

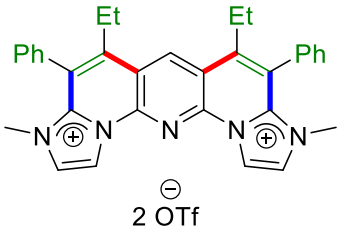
**3,9-Dimethyl-4,8-diphenyl-5,7-bis(4-(trifluoromethyl)phenyl)-3,9-dihydroimidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridine-12,14-diium Salt (3g):** Yield = 53% (a mixture of three regioisomers in **3g**/**3g'**/**3g"** = 4/1.5/1 ratio determined by $^{1}$H NMR spectroscopy). $^{1}$H NMR (500 MHz, $CD_3CN$) $\delta$ 9.46 (m, 3H), 8.04 (s, 1H), 8.01 (m, 3H), 7.81 (s, 1H), 7.79 (s, 1H), 7.70 (m, 5H), 7.50 (m, 7H), 7.46 – 7.40 (m, 5H), 7.36 (m, 4H), 7.24 – 7.19 (m, 5H), 7.12 (m, 2H), 3.38 (m, 9H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 146.1, 146.0, 144.0, 143.9, 142.6, 141.9, 141.5, 141.3, 141.3, 140.2, 140.2, 140.0, 138.1, 138.0, 136.8, 133.4, 133.4, 133.0, 132.9, 132.0, 132.0, 131.9, 131.9, 131.7, 131.0, 130.9, 130.8, 129.9, 129.89, 129.7, 129.7, 129.6, 129.6, 129.5, 129.2, 129.2, 129.0, 126.8, 126.6, 126.5, 126.4, 126.4, 126.0, 126.0, 125.9, 125.0, 124.9,



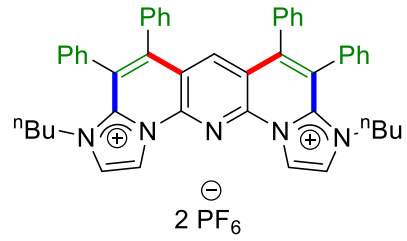

$R^1 = R^4 = CF_3$, $R^2 = R^3 = H$ (**3g**)
$R^1 = R^3 = CF_3$, $R^2 = R^4 = H$ (**3g'**)
$R^1 = R^4 = H$, $R^2 = R^3 = CF_3$ (**3g"**)

123.9, 123.8, 123.7, 123.3, 121.0, 120.8, 120.7, 120.5, 115.5, 115.4, 39.3, 39.1. HRMS (ESI, positive ion): $M^{2+}$ = 364.6146 (calculated = 364.6158 for $[C_{43}H_{29}F_6N_5]^{2+}$).

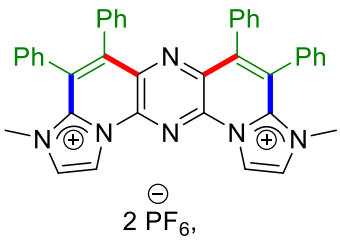
**5,7-Diethyl-3,9-dimethyl-4,8-diphenyl-3H-imidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridine-9,14-diium Salt (3h):** Yield = 78%. $^1$H NMR (400 MHz, DMSO-$d_6$, 298K): $\delta$ 9.69 (s, 2H), 9.61 (s, 1H), 8.41 (s, 2H), 7.70-7.71 (m, 6H), 7.62 (d, $J$ = 3.8 Hz, 4H), 3.32 (s, 6H), 3.15 (q, $J$ = 6.7 Hz, 4H), 1.21 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$, 298K): $\delta$ 145.7, 140.1, 138.9, 137.8, 131.8, 130.2, 130.1, 129.3, 128.1, 124.3, 121.9, 119.4, 117.6, 113.8, 37.4, 21.9, 15.2. $^{19}$F NMR (471 MHz, DMSO-$d_6$, 300K): $\delta$ -77.80 (s). HRMS (ESI, positive ion): $M^{2+}$ = 248.6272 (calculated = 248.6284 for $[C_{33}H_{31}N_5]^{2+}$).



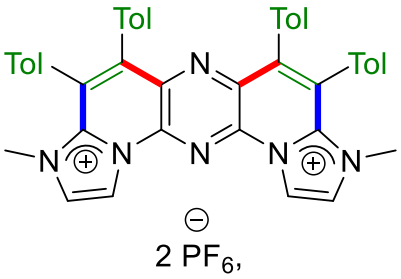

**3,9-Dibutyl-4,5,7,8-tetraphenyl-3,9-dihydroimidazo[1',2':1,6]pyrido[3,2-*g*]imidazo[1,2-*a*][1,8]naphthyridine-12,14-diium Salt (3i):** Yield=50%. $^1$H NMR (400 MHz, $CD_3CN$, 298K): $\delta$ 9.34 (s, 2H), 8.08 (s, 2H), 8.01 (s, 1H), 7.44 (bs, 10H), 7.29 – 7.18 (m, 6H), 7.10 (d, $J$ = 4.8 Hz, 4H), 3.84 – 3.59 (m, 4H), 1.61 (m, 4H), 0.98 (m, 4H), 0.77 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$, 298K): $\delta$ 146.2, 142.9, 141.3, 140.0, 133.6, 132.4, 131.6, 130.8, 129.8, 129.2, 128.1, 126.1, 120.9, 115.6, 50.9, 33.5, 20.3, 13.7. $^{19}$F NMR (471 MHz, $CD_3CN$, 298K): $\delta$ -72.98 (d, $J$ = 706.7 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 338.6751 (calculated = 338.6754 for $[C_{47}H_{43}N_5]^{2+}$).



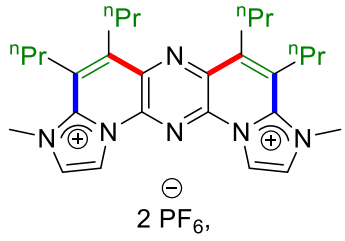

**3,9-Dimethyl-4,5,7,8-tetraphenyl-3H-imidazo[1',2':1,6]pyrido[2,3-*b*]imidazo[1',2':1,6]pyrido[3,2-*e*]pyrazine-9,14-diium Salt (3j):** Yield = 68%. $^1$H NMR (500 MHz, $CD_3CN$, 298K): $\delta$ 9.28 (d, $J$ = 2.3 Hz, 2H), 8.02 (d, $J$ = 2.3 Hz, 2H), 7.49 – 7.44 (m, 5H), 7.45 – 7.39 (m, 5H), 7.17 – 7.13 (m, 2H), 7.12 – 7.08 (m, 4H), 7.07 – 7.03 (m, 4H), 3.40 (s, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$, 298K): $\delta$ 146.3, 140.0, 137.9, 136.2, 132.7, 132.1, 131.8, 131.7, 130.9, 130.4, 130.2, 129.7, 129.2, 128.4, 115.9, 39.4. $^{19}$F NMR (471 MHz, $CD_3CN$, 298K): $\delta$ -73.01 (d, $J$ = 706.6 Hz). $^{31}$P NMR (202 MHz, $CD_3CN$, 298K): $\delta$ -144.68 (hept, $J$ = 706.6 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 297.1269 (calculated = 297.1260 for $[C_{40}H_{30}N_6]^{2+}$).



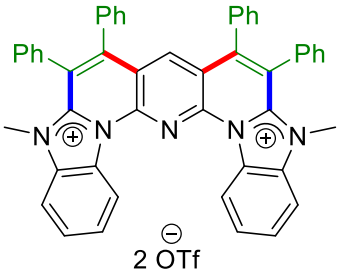
**3,9-Dimethyl-4,5,7,8-tetra-*p*-tolyl-3H-imidazo[1',2':1,6]pyrido[2,3-*b*]imidazo[1',2':1,6]pyrido[3,2-*e*]pyrazine-9,14-diium Salt (3k):** Yield = 51%. $^{1}$H NMR (400 MHz, $CD_3CN$, 298K): $\delta$ 9.21 (s, 2H), 7.98 (s, 2H), 7.29 (s, 8H), 6.95 (s, 8H), 3.38 (s, 6H), 2.37 (s, 6H), 2.27 (s, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$, 298K): $\delta$ 146.4, 141.3, 140.2, 139.1, 138.0, 136.0, 131.7, 131.6, 130.3, 130.1, 130.0, 129.1, 129.0, 118.6, 115.6, 39.3, 21.3, 21.3. $^{19}$F NMR (471 MHz, DMSO-$d_6$, 298K): $\delta$ -72.44 (d, $J$ = 706.6 Hz). $^{31}$P NMR (202 MHz, DMSO-$d_6$, 298K): $\delta$ -144.11 (hept, $J$ = 706.6 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 325.1586 (calculated = 325.1573 for $[C_{44}H_{38}N_6]^{2+}$).



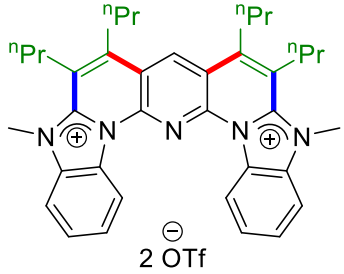

**3,9-Dimethyl-4,5,7,8-tetrapropyl-3H-imidazo[1',2':1,6]pyrido[2,3-*b*]imidazo[1',2':1,6]pyrido[3,2-*e*]pyrazine-9,14-diium Salt (3l):** Yield = 67%. $^{1}$H NMR (500 MHz, $CD_3CN$, 298K): $\delta$ 9.01 (d, $J$ = 2.3 Hz, 2H), 7.92 (d, $J$ = 2.3 Hz, 2H), 4.36 (s, 6H), 3.51 – 3.43 (m, 4H), 3.32 – 3.25 (m, 4H), 1.83 – 1.74 (m, 8H), 1.20 (td, $J$ = 7.3, 1.5 Hz, 12H). $^{13}$C NMR (126 MHz, $CD_3CN$, 298K): $\delta$ 146.6, 141.3, 137.0, 135.4, 130.2, 130.1, 115.1, 39.8, 30.2, 30.1, 25.1, 24.9, 14.9, 13.9. $^{19}$F NMR (471 MHz, $CD_3CN$, 298K): $\delta$ -72.97 (d, $J$ = 706.6 Hz). $^{31}$P NMR (202 MHz, $CD_3CN$, 298K): $\delta$ -144.66 (hept, $J$ = 706.6 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 229.1579 (calculated = 229.1573 for $[C_{28}H_{38}N_6]^{2+}$).



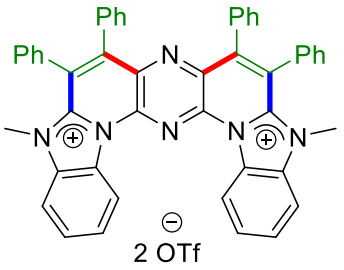

**5,11-Dimethyl-6,7,9,10-tetraphenyl-5H-benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine-11,18-diium Salt (3m):** Yield = 75% . $^{1}$H NMR (500 MHz, DMSO-$d_6$, 298K): $\delta$ 9.67 (d, $J$ = 8.3 Hz, 2H), 8.42 (d, $J$ = 8.4 Hz, 2H), 8.24 (t, $J$ = 7.6 Hz, 2H), 8.17 (t, $J$ = 7.8 Hz, 2H), 8.10 (s, 1H), 7.48 (s, 10H), 7.29 – 7.22 (m, 6H), 7.17 – 7.10 (m, 4H), 3.60 (s, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$, 298K): $\delta$ 148.7, 144.3, 143.2, 141.0, 134.3, 132.8, 132.0, 131.4, 130.2, 129.9, 129.1, 128.6, 128.5, 127.2, 125.6, 122.3, 119.8, 119.5, 117.2, 114.7, 34.9. $^{19}$F NMR (471 MHz, DMSO-$d_6$, 298K): $\delta$ -77.75 (s). HRMS (ESI, positive ion): $M^{2+}$ = 346.6468 (calculated = 346.6441 for $[C_{49}H_{35}N_5]^{2+}$).



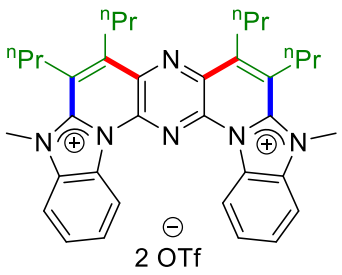
**5,11-Dimethyl-6,7,9,10-tetrapropyl-5H-benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine-11,18-diium Salt (3n):** Yield = 76%. $^{1}$H NMR (500 MHz, DMSO-d$_6$, 298K): $\delta$ 9.60 (s, 1H), 9.47 (d, $J$ = 8.1 Hz, 2H), 8.49 (d, $J$ = 8.1 Hz, 2H), 8.12 – 7.99 (m, 4H), 4.59 (s, 6H), 3.66 – 3.58 (m, 4H), 3.44 – 3.38 (m, 4H), 1.87 – 1.75 (m, 8H), 1.22 (q, $J$ = 6.9 Hz, 12H). $^{13}$C NMR (126 MHz, DMSO-d$_6$, 298K): $\delta$ 148.9, 145.0, 142.1, 136.5, 134.0, 129.0, 127.1, 126.7, 124.5, 121.9, 119.4, 117.6, 117.0, 114.0, 34.6, 29.6, 28.8, 24.4, 24.0, 14.1, 13.6. $^{19}$F NMR (471 MHz, DMSO-d$_6$, 298K): $\delta$ -77.75 (s). HRMS (ESI, positive ion): $M^{2+}$ = 278.6776 (calculated = 278.6754 for $[C_{37}H_{43}N_5]^{2+}$).




**5,11-Dimethyl-6,7,9,10-tetraphenyl-5,11 dihydrobenzo[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*]benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*e*]pyrazine-16,18-diium Salt (3o):** Yield = 69% $^{1}$H NMR (500 MHz, CD$_3$CN, 298K) $\delta$ 9.65 (d, $J$ = 8.5 Hz, 2H), 8.26 (ddd, $J$ = 8.4, 7.0, 1.3 Hz, 2H), 8.22 – 8.13 (m, 4H), 7.62 – 7.48 (m, 10H), 7.26 – 7.21 (m, 2H), 7.19 – 7.11 (m, 8H), 3.62 (s, 6H). $^{13}$C NMR (126 MHz, CD$_3$CN, 298K) $\delta$ 150.9, 144.4, 139.0, 136.9, 135.4, 132.8, 132.4, 132.0, 131.5, 131.2, 131.0, 130.1, 130.1, 130.0, 129.5, 128.5, 128.4, 115.2, 35.9. $^{31}$P NMR (202 MHz, CD$_3$CN, 298K) $\delta$ -146.47 (d, $J$ = 706.6 Hz). $^{19}$F NMR (471 MHz, CD$_3$CN, 298K) $\delta$ -72.33 (d, $J$ = 2.3 Hz), -73.08 (dd, $J$ = 706.6, 2.3 Hz), -73.83 (d, $J$ = 2.3 Hz). HRMS (ESI, positive ion): $M^{2+}$ = 347.1410 (calculated = 347.1417 for $[C_{48}H_{34}N_6]^{2+}$).

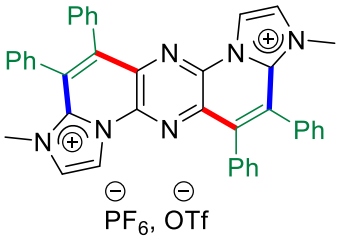



**5,11-Dimethyl-6,7,9,10-tetrapropyl-5,11 dihydrobenzo[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*]benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*e*]pyrazine-16,18-diium Salt (3p):** Yield = 70%. $^{1}$H NMR (500 MHz, CD$_3$CN, 298K) $\delta$ 9.46 (dd, $J$ = 7.1, 1.2 Hz, 2H), 8.26 (dd, $J$ = 7.4, 1.6 Hz, 2H), 8.11 (pd, $J$ = 7.4, 1.3 Hz, 4H), 4.59 (s, 6H), 3.67 – 3.60 (m, 4H), 3.49 (dd, $J$ = 9.7, 7.3 Hz, 4H), 1.91 (m, 8H), 1.29 (td, $J$ = 7.3, 1.7 Hz, 12H). $^{13}$C NMR (126 MHz, CD$_3$CN, 298K) $\delta$ 151.9,

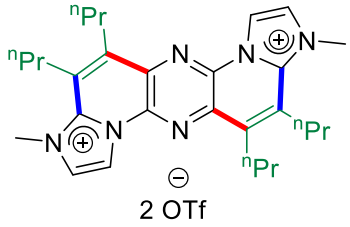


145.7, 138.2, 135.9, 135.2, 130.5, 130.0, 129.4, 128.4, 117.8, 115.0, 36.0, 30.9, 30.6, 25.1, 25.0, 15.0, 13.9. $^{19}$F NMR (376 MHz, $CD_3CN$, 298K) $\delta$ -73.07 (d, $J$ = 706.7 Hz), -79.37 (s). HRMS (ESI, positive ion): $M^{2+}$ = 279.1727 (calculated = 279.1730 for $[C_{36}H_{42}N_6]^{2+}$).

**3,10-Dimethyl-4,5,11,12-tetraphenylimidazo[1',2':1,6]pyrido[2,3-*b*]imidazo[1',2':1,6]pyrido[2,3-*e*]pyrazine-3,10-diium salt (3q):** Yield = 67% $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.41 (s, 2H), 8.36 (s, 2H), 7.48 (s, 8H), 7.43 (s, 8H), 7.33 (bs, 4H), 3.40 (s, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 143.5, 138.5, 136.9, 135.2, 132.5, 131.6, 131.1, 130.3, 130.2, 129.9, 129.1, 129.0, 128.8, 128.3, 122.4, 121.9, 119.8, 114.2, 38.5. $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ -70.29 (d, $J$ = 711.3 Hz), -77.77 (s). HRMS (ESI, positive ion): $M^{2+}$ = 297.1271 (calculated = 297.1260 for $[C_{40}H_{30}N_6]^{2+}$).




**3,10-Dimethyl-4,5,11,12-tetrapropylimidazo[1',2':1,6]pyrido[2,3-*b*]imidazo[1',2':1,6]pyrido[2,3-*e*]pyrazine-3,10-diium (3r):** Yield = 65% $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.93 (d, $J$ = 2.3 Hz, 2H), 7.94 (d, $J$ = 2.3 Hz, 2H), 4.37 (s, 6H), 3.54 – 3.43 (m, 4H), 3.34 – 3.24 (m, 4H), 1.87 – 1.71 (m, 8H), 1.23 – 1.13 (m, 12H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 145.6, 140.7, 137.1, 135.6, 131.9, 129.9, 114.9, 39.8, 30.3, 29.6, 25.1, 24.7, 14.6, 14.0. $^{19}$F NMR (376 MHz, $CD_3CN$) $\delta$ -79.30. HRMS (ESI, positive ion): $M^{2+}$ = 229.1580 (calculated = 229.1573 for $[C_{28}H_{38}N_6]^{2+}$).

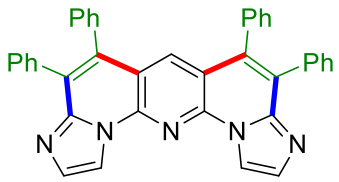


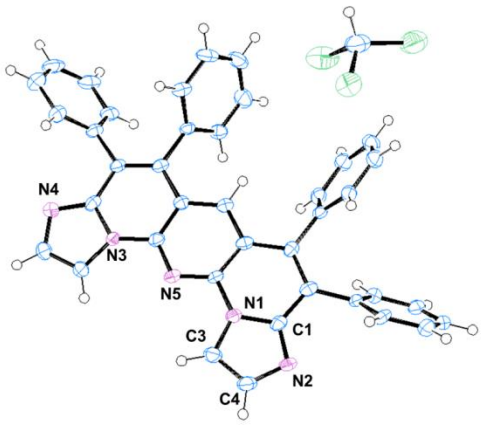
## 7. General Catalytic Procedure of Annulation Reactions for Scheme 2B, Main Article

In an oven dried sealed tube **1g-1i** (0.1 mmol), $[RhCp^*Cl_2]_2$ (3 mol%), **2a** (0.21 mmol) and $Cu(OAc)_2.H_2O$ (0.3 mmol) were taken .To this 2 mL of toluene was added and stirred at 140 ºC for 12 h. After the reaction time the mixture was cooled to room temperature and $CH_2Cl_2$ (15 mL) was added to this mixture followed by washing with saturated $K_2CO_3$ solution The organic layer was collected and the extraction was repeated by $CH_2Cl_2$ (10 mL x 2) and the organic layers were combined and evaporated to dryness. Final product was separated and purified by alumina column chromatography, using $CHCl_3$ as eluent.

## 8. Experimental Characterization Data of the Products (3s-3af) (*vide* Scheme 2B in main article)

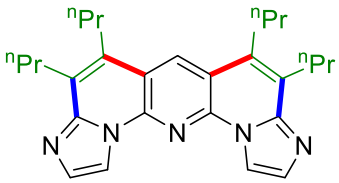
**4,5,7,8-Detraphenylimidazo[1',2':1,6]pyrido[3,2-g]imidazo[1,2-*a*][1,8]naphthyridine (3s):** Yield = 78%. $^1$H NMR (500 MHz, $CDCl_3$, 298K) $\delta$ 8.73 (d, $J$ = 1.4 Hz, 2H), 8.13 (s, 1H), 7.83 (d, $J$ = 1.3 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.30 – 7.27 (m, 6H), 7.18 – 7.15 (m, 6H), 7.05 – 7.03 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$, 298K) $\delta$ 145.3, 140.8, 138.4, 135.2, 134.8, 134.2, 133.4, 130.8, 130.7, 129.3, 128.0, 127.9, 127.8, 127.5, 117.6, 112.7. HRMS (ESI, positive ion): $[M+H]^+$ = 564.2163 (calculated = 564.2183 for $[C_{39}H_{26}N_5]^+$).



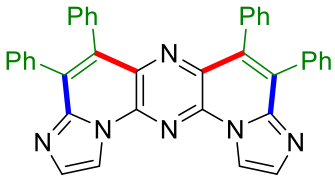




Molecular structure of product **3s** (50% probability level).

**4,5,7,8-Tetrapropylimidazo[1',2':1,6]pyrido[3,2-g]imidazo[1,2-*a*][1,8]naphthyridine (3t):** Yield = 72%. $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.60 (s, 1H), 8.39 (bs, 2H), 7.61 (d, $J$ = 1.1 Hz, 2H), 3.12 – 3.07 (m, 4H), 3.05 – 2.99 (m, 4H), 1.80 (dq, $J$ = 15.1, 7.4 Hz, 4H), 1.72 (dq, $J$ = 15.0, 7.4 Hz, 4H), 1.16 (t, $J$ = 7.3 Hz, 6H), 1.12 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ 14.7, 14.7, 23.4, 24.1, 30.2, 30.4, 112.2, 116.5, 128.9, 131.3, 131.8, 132.2, 140.2, 145.7. HRMS (ESI, positive ion): $[M+H]^+$ = 428.2821(calculated = 428.2809 for $[C_{27}H_{34}N_5]^+$).

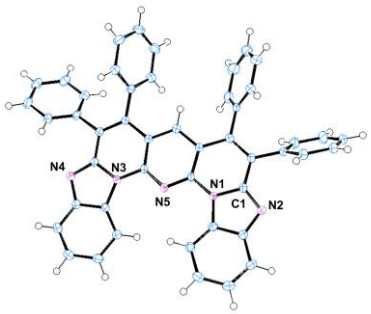



**4,5,7,8-Tetraphenylimidazo[1',2':1,6]pyrido[2,3-*b*]imidazo[1',2':1,6]pyrido[3,2-*e*]pyrazine (3u):** Yield = 78%. $^{1}$H NMR (500 MHz, $CDCl_3$, 298K) $\delta$ 8.68 (d, $J$ = 1.4 Hz, 2H), 7.80 (d, $J$ = 1.4 Hz, 2H), 7.39 (dt, $J$ = 3.9, 2.1 Hz, 4H), 7.37 – 7.22 (m, 6H), 7.16 – 7.07 (m, 2H), 7.03 (bs, 4H), 7.02 (bs, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$, 298K) $\delta$ 145.0, 135.5, 135.5, 134.9, 134.7, 134.1, 134.1, 133.1, 131.1, 130.9, 128.1, 128.0, 127.3, 126.9, 113.5. HRMS (ESI, positive ion): $[M+H]^+$ = 565.2110 (calculated = 565.2135 for $[C_{38}H_{25}N_6]^+$).



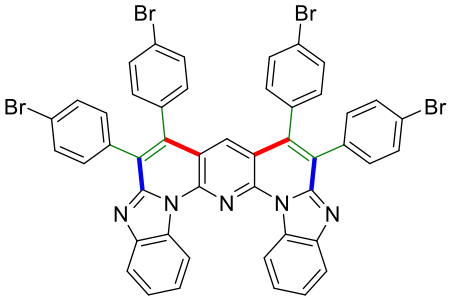

**6,7,9,10-Tetraphenylbenzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine (3v):** Yield = 80%. $^{1}$H NMR (500 MHz, $CDCl_3$, 298K) $\delta$ 9.60 (d, $J$ = 8.0 Hz, 2H), 8.11 (d, $J$ = 7.7 Hz, 2H), 8.05 (s, 1H), 7.74 – 7.69 (m, 2H), 7.68 – 7.63 (m, 2H), 7.44 – 7.37 (m, 4H), 7.34 – 7.26 (m, 6H), 7.21 – 7.14 (m, 6H), 7.06 (dd, $J$ = 6.4, 3.2 Hz, 4H). 13C NMR (126 MHz, $CDCl_3$) $\delta$ 149.5, 144.8, 144.2,138.8, 137.5, 135.2, 134.8, 130.9, 130.8, 130.4, 129.3, 128.0, 128.0, 127.9, 127.7, 125.5, 123.6, 120.9, 116.7, 116.1. HRMS (ESI, positive ion): $[M+H]^+$ = 664.2486 (calculated = 664.2496 for $[C_{47}H_{30}N_5]^+$).



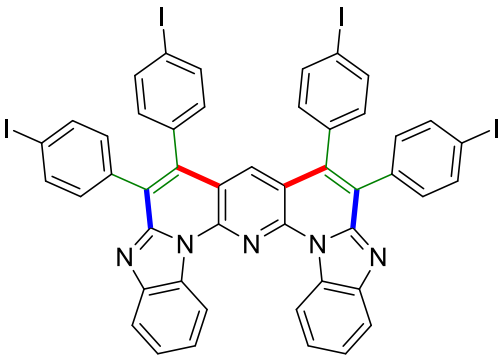




Molecular structure of product **3v** (50% probability level).

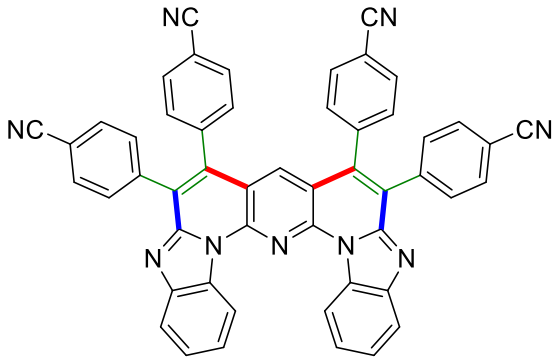
**6,7,9,10-Tetrakis(4-bromophenyl)benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine(3w):** Yield = 61%. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.54 (d, $J$ = 8.0 Hz, 2H), 8.15 (d, $J$ = 8.0 Hz, 2H), 7.87 (s, 1H), 7.78 – 7.70 (m, 2H), 7.72 – 7.64 (m, 2H), 7.49 (d, $J$ = 8.4 Hz, 4H), 7.43 (d, $J$ = 8.3 Hz, 4H), 7.30 (d, $J$ = 8.4 Hz, 4H), 6.93 (d, $J$ = 8.3 Hz, 4H).$^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 147.6, 144.1, 137.6, 135.1, 133.2, 133.0, 132.5, 132.0, 132.0, 131.9, 131.3, 130.9, 130.2, 126.9, 125.0, 123.5, 123.2, 120.7, 117.2, 116.1. HRMS (ESI, positive ion): $[M+H]^+$ = 979.8891 (calculated = 979.8875 for $[C_{47}H_{26}Br_4N_5]^+$).




**6,7,9,10-Tetrakis(4-iodophenyl)benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine (3x):** Yield = 63%. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.52 (d, $J$ = 8.1 Hz, 2H), 8.15 (t, $J$ = 6.3 Hz, 2H), 7.91 (s, 1H), 7.73 – 7.61 (m, 6H), 7.16 (d, $J$ = 8.4 Hz, 2H), 6.80 (d, $J$ = 8.3 Hz, 2H). $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 148.2, 144.2, 137.8, 137.7, 137.2, 134.0, 133.3, 132.7, 132.0, 130.8, 130.4, 128.9, 126.4, 124.5, 120.9, 116.7, 116.5, 116.0, 95.2, 94.6.HRMS (ESI, positive ion): $[M+H]^+$ = 1167.8340 (calculated = 1167.8361 for $[C_{47}H_{26}I_4N_5]^+$).

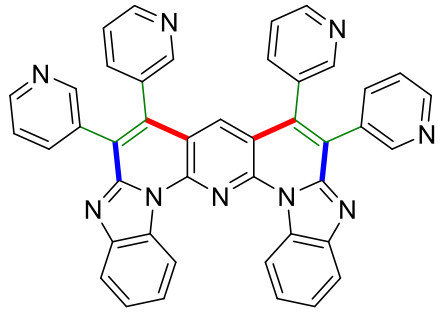



**4,4',4'',4'''-(Benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine-6,7,9,10-tetrayl)tetrabenzonitrile (3y):** Yield = 44%. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.81 (s, 1H), 9.54 (d, $J$ = 8.2 Hz, 1H), 9.08 (d, $J$ = 7.9 Hz, 1H), 8.30 (d, $J$ = 7.1 Hz, 1H), 8.21 – 8.01 (m, 2H), 7.81 – 7.77 (m, 1H), 7.74 (m, 3H), 7.65 (dd, $J$ = 8.3, 6.1 Hz, 3H), 7.62 – 7.57 (m, 3H), 7.51 (dd, $J$ = 8.2, 5.9 Hz, 2H), 7.40 (d, $J$ = 8.3 Hz, 2H), 7.22 (d, $J$ = 8.3 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 148.11, 147.97, 147.44, 145.70, 145.02, 144.81, 144.46, 140.30, 139.78, 139.53, 138.96, 138.92, 137.24, 137.06, 136.33, 133.04, 132.61, 132.59, 131.99, 131.77, 131.55, 130.88, 130.77, 129.63, 129.01, 126.84, 126.65, 126.21, 125.30, 125.17, 121.58, 121.16, 118.68, 118.63, 118.22, 117.66, 116.93, 116.40, 116.04, 113.57, 113.49,

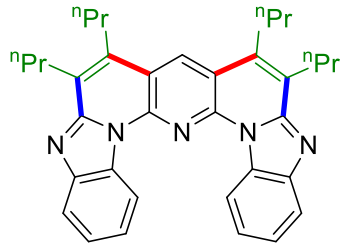


113.40, 113.06, 112.92.HRMS (ESI, positive ion): $[M+H]^+$ = 764.2345 (calculated = 764.2306 for $[C_{51}H_{26}N_9]^+$).

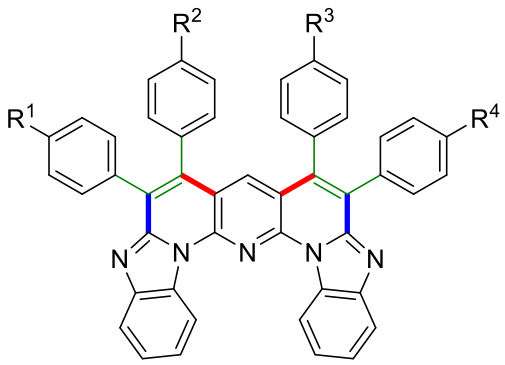
**6,7,9,10-Tetra(pyridin-3-yl)benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine (3z):** Yield = 72%. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.55 (d, $J$ = 8.1 Hz, 2H), 8.64 – 8.48 (m, 6H), 8.35 (d, 2H), 8.11 (d, $J$ = 8.0 Hz, 2H), 7.90 (d, $J$ = 6.2 Hz, 2H), 7.84 (s, 1H), 7.76 (dd, $J$ = 11.3, 4.1 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.49 (m, 2H), 7.38 (dd, $J$ = 7.7, 5.1 Hz, 2H) 7.24 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 151.1, 151.0, 150.8, 149.9, 149.8, 149.1, 148.5, 144.8, 139.0, 138.8, 138.0, 137.7, 136.2, 135.6, 130.8, 130.6, 130.5, 127.5, 126.3, 124.6, 123.5, 123.4, 122.9, 121.3, 116.3, 116.2.HRMS (ESI, positive ion): $[M+H]^+$ = 668.2300 (calculated = 668.2306 for $[C_{43}H_{26}N_9]^+$).



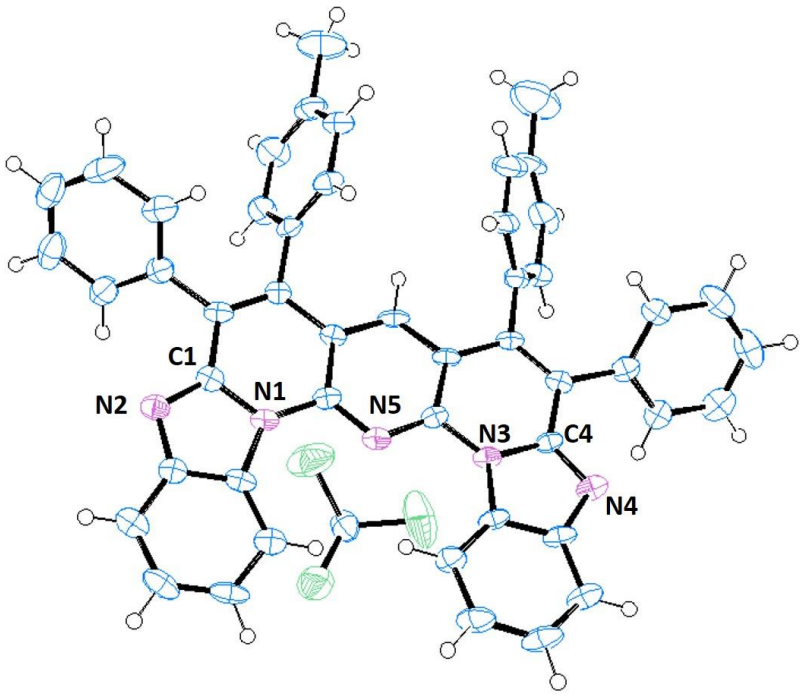
**6,7,9,10-Tetrapropylbenzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine (3aa):** Yield = 74%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 9.49 – 9.35 (m, 2H), 8.76 (s, 1H), 8.13 – 8.05 (m, 2H), 7.66 – 7.56 (m, 4H), 3.31 – 3.21 (m, 4H), 3.16 (dd, $J$ = 9.4, 6.9 Hz, 4H), 1.95 – 1.87 (m, 4H), 1.82 (dt, $J$ = 14.9, 7.6 Hz, 4H), 1.23 (t, $J$ = 7.3 Hz, 6H), 1.17 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ 149.3, 142.9, 135.5, 130.3, 128.3, 124.6, 122.4, 119.5, 115.48, 115.0, 77.2, 30.0, 29.9, 23.4, 22.6, 14.2, 14.0. HRMS (ESI, positive ion): $[M+H]^+$ = 528.3122 (calculated = 528.3122 for $[C_{35}H_{38}N_5]^+$).



**6,10-Diphenyl-7,9-di-p-tolylbenzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine(3ab):** Yield = 63% (a mixture of three regioisomers in **3ab**/**3ab'**/**3ab"** = 2/1/1 ratio determined by $^{1}$H NMR spectroscopy). $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.55 (d, $J$ = 8.0 Hz, 2H), 8.12 (d, $J$ = 7.8 Hz, 2H), 7.99 (s, 1H), 7.71 – 7.55 (m, 4H), 7.47 – 7.38 (m, 2H), 7.31 (m, 5H), 7.24 – 7.16 (m, 3H), 7.11 (dd, $J$ = 8.0, 2.3 Hz, 2H), 7.06 (m, 2H), 6.98 (t, $J$ = 8.5 Hz, 2H), 6.95 – 6.89 (m, 2H), 2.32 (s, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 149.4, 149.2, 144.1, 144.0, 139.6, 138.9, 138.2, 137.9, 137.9, 137.8, 137.6, 137.6, 137.5, 135.4, 135.3, 134.7, 132.1, 132.1, 131.6, 131.0, 130.9, 130.7, 130.6, 130.5, 130.4, 130.4, 129.2, 128.9, 128.9, 128.6, 128.1, 127.7, 127.6, 125.7, 125.7, 123.8, 123.7, 120.8, 120.7, 117.2, 117.1, 117.0, 116.9, 116.1, 21.5, 21.3. HRMS (ESI, positive ion): $[M+H]^+$ = 692.2805 (calculated = 692.2809 for $[C_{49}H_{34}N_5]^+$).

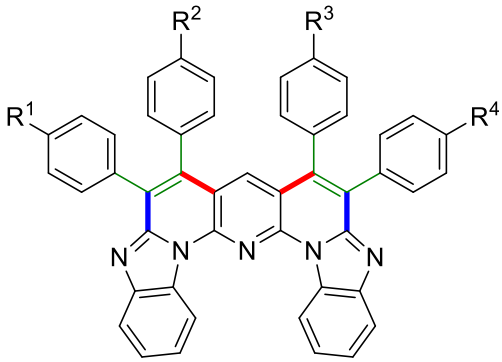



$R^1 = R^4 = H$, $R^2 = R^3 = CH_3$ (**3ab**)
$R^1 = R^3 = H$, $R^2 = R^4 = CH_3$ (**3ab'**)
$R^1 = R^4 = CH_3$, $R^2 = R^3 = H$ (**3ab"**)

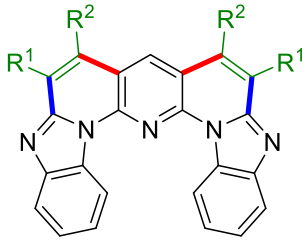



Molecular structure of product **3ab** (50% probability level).

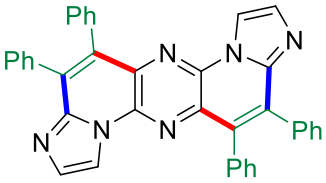
**7,9-Diphenyl-6,10-bis(4 (trifluoromethyl)phenyl)benzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine (3ac):** Yield = 65% (a mixture of three regioisomers in **3ac**/**3ac'**/**3ac"** = 4/1/1.2 ratio determined by $^{1}$H NMR spectroscopy). $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.54 (d, $J$ = 8.0 Hz, 4H), 8.11 (dd, $J$ = 12.3, 8.1 Hz, 4H), 8.04 (s, 1H), 7.82 (s, 1H), 7.78 (s, 1H), 7.72 – 7.60 (m, 8H), 7.58 – 7.51 (m, 10H), 7.46 (d, $J$ = 8.1 Hz, 2H), 7.43 – 7.31 (m, 8H), 7.25 – 7.17 (m, 10H), 7.08 – 6.97 (m, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 148.7, 144.5, 144.5, 144.4, 144.35, 144.2, 144.2, 139.6, 139.5, 139.1, 138.9, 138.5, 138.3, 138.1, 137.4, 136.3, 134.5, 134.5, 133.9, 131.5, 131.5, 131.0, 130.9, 130.9, 130.7, 130.6, 130.6, 130.4, 130.3, 130.2, 130.1, 130.0, 130.0, 129.9, 129.7, 128.7, 128.5, 128.5, 128.4, 128.0, 127.9, 126.0, 125.9, 125.3, 125.3, 125.2, 125.2, 125.1, 124.2, 124.1, 124.1, 123.1, 122.8, 121.0, 121.0, 120.9, 116.9, 116.7, 116.5, 116.1, 117.0. HRMS (ESI, positive ion): $[M+H]^+$ = 800.2256 (calculated = 800.2243 for $[C_{49}H_{28}F_6N_5]^+$).



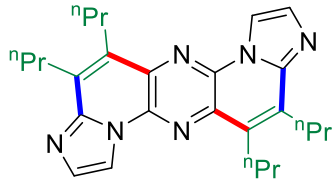

**7,9-Diethyl-6,10-diphenylbenzo[4',5']imidazo[1',2':1,6]pyrido[3,2-*g*]benzo[4,5]imidazo[1,2-*a*][1,8]naphthyridine (3ad):** Yield = 70% (a mixture of three regioisomers in 1.2/1 ratio determined by $^{1}$H NMR spectroscopy). $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.58 – 9.30 (m, 4H), 8.95 (s, 1H), 8.21 (s, 1H), 8.18 – 8.13 (m, 1H), 8.08 – 8.01 (m, 2H), 7.68 – 7.62 (m, 10H), 7.59 (m, 10H), 7.51 – 7.43 (m, 4H), 7.42 – 7.37 (m, 1H), 7.22 – 7.17 (m, 1H), 3.04 (m, 6H), 2.66 (m, 2H), 1.39 (m, 6H), 1.05 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 149.8, 149.4, 144.6, 144.6, 144.2, 143.4, 139.4, 139.2, 135.8, 135.6, 135.6, 134.4, 132.3, 130.7, 130.7, 129.9, 129.7, 129.8, 129.6, 129.5, 129.3, 129.1, 129.0, 128.9, 128.8, 128.6, 128.6, 128.5, 128.2, 125.6, 125.3, 125.3, 123.5, 123.4, 123.3, 120.8, 120.7, 120.2, 117.2, 116.2, 116.1, 116.0, 115.9, 115.2, 77.4, 77.2, 76.9, 22.9, 22.7, 22.5, 15.4, 14.8, 14.5. HRMS (ESI, positive ion): $[M+H]^+$ = 568.2502 (calculated = 568.2496 for $[C_{39}H_{30}N_5]^+$).



**4,5,11,12-Tetraphenylimidazo[1',2':1,6]pyrido[2,3-*b*]imidazo[1',2':1,6]pyrido[2,3-*e*]pyrazine (3ae):** Yield = 84%.[1]H NMR (500 MHz, $CDCl_3$) $\delta$ 8.24 (d, $J$ = 1.4 Hz, 2H), 7.67 (d, $J$ = 1.4 Hz, 2H), 7.45 – 7.41 (m, 4H), 7.38 – 7.31 (m, 16H). [13]C NMR (126 MHz, $CDCl_3$) $\delta$ 144.3, 136.9, 135.3, 134.7, 134.7, 134.4, 133.9, 133.8, 132.0, 131.0, 128.4, 128.1, 127.8, 127.7, 113.7. HRMS (ESI, positive ion): $[M+H]^+$ = 565.2150 (calculated = 565.2135 for $[C_{38}H_{25}N_6]^+$).

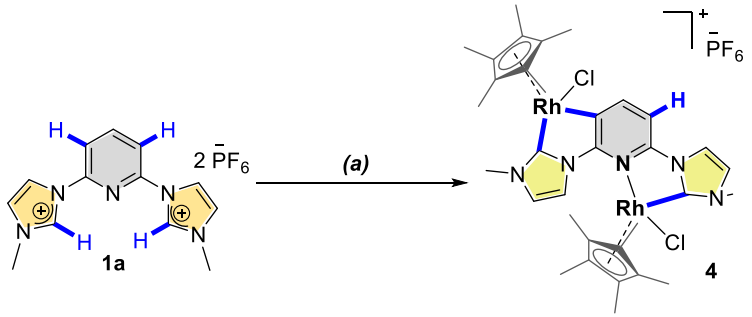



**4,5,11,12-Tetrapropylimidazo[1',2':1,6]pyrido[2,3-*b*]imidazo[1',2':1,6]pyrido[2,3-*e*]pyrazine (3af):** Yield = 80%. [1]H NMR (500 MHz, $CDCl_3$) $\delta$ 8.46 (d, $J$ = 1.2 Hz, 2H), 7.67 (d, $J$ = 1.2 Hz, 2H), 3.28 – 3.21 (m, 4H), 3.17 (dd, $J$ = 9.2, 6.9 Hz, 4H), 1.85 (dd, $J$ = 15.6, 7.6 Hz, 4H), 1.79 (dd, $J$ = 15.3, 7.5 Hz, 4H), 1.13 (tt, $J$ = 12.3, 6.2 Hz, 12H).[13]C NMR (126 MHz, $CDCl_3$) δ 145.2, 136.6, 135.1, 134.1, 133.7, 132.8, 112.9, 31.2, 29.2, 24.1, 23.6, 15.1, 15.0. HRMS (ESI, positive ion): $[M+H]^+$ = 429.2778 (calculated = 429.2761 for $[C_{26}H_{33}N_6]^+$).



## 9. Mechanistic Studies

### A. Synthesis of the 1st Rollover Intermediate 4:

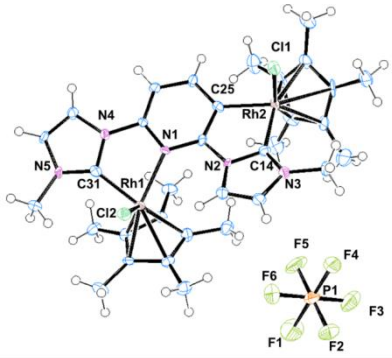



*(a)*: $[Cp^*RhCl_2]_2$ (x equiv.), NaOAc (10 equiv), DCE, reflux, 24 h

isolated yield of **4:** 63% (x = 1.0 equiv.); 30% (x = 0.5 equiv.)

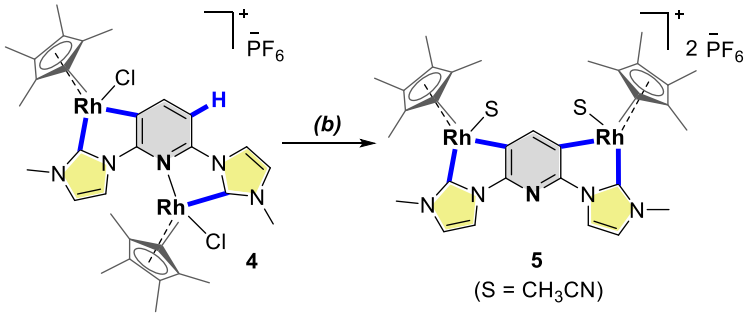
To an oven dried Schlenk tube, a mixture of **1a** (27 mg, 0.05 mmol), NaOAc (41 mg, 0.5 mmol) and $[Cp^*RhCl_2]_2$ (1.0 equiv. or 0.5 equiv.) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with $N_2$ gas. To this mixture, dry and degassed DCE (5 mL) was added under Schlenk technique. After 24 h of reflux, the reaction mixture was allowed to cool down to room temperature and the solution was passed through a short celite pad followed by washing with dichloromethane (3×10 mL). The combined filtrate was concentrated under reduced pressure. Next complex was purified by flash alumina column using $CH_2Cl_2$/MeOH (98:2) as eluent. Finally, reprecipitation using $CH_2Cl_2$/n-pentane gives the desired complex **4** (Yield = 63% or 30%) as orange solid after drying under reduced pressure.

$^1$H NMR (500 MHz, $CD_3CN$, 298K): $\delta$ 9.36 (d, $J$ = 2.0 Hz, 1H), 8.37 (d, $J$ = 7.8 Hz, 1H), 7.70 (d, $J$ = 2.0 Hz, 1H), 7.40 (m, 2H), 7.22 (d, $J$ = 2.0 Hz, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 1.78 (s, 15H), 1.41 (s, 15H). $^{31}$P NMR (202 MHz, $CD_3CN$, 298K): $\delta$ -139.40 (d, $J$ = 706.4 Hz). $^{19}$F NMR (471 MHz, $CD_3CN$, 298K): $\delta$ -72.94 (d, $J$ = 706.5 Hz). HRMS (ESI, positive ion): $M^+$ = 784.0916 (calculated = 784.0927 for $[C_{33}H_{42}Cl_2N_5Rh_2]^+$).




Molecular structure of intermediate **4** (50% probability level).

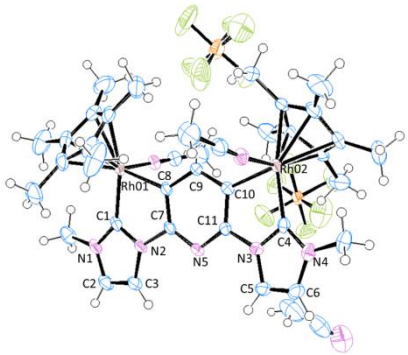
**B. Synthesis of the 2nd Rollover Intermediate 5**:




***(b)***: NaOAc (10 equiv), AgOTf (5 equiv), $CH_3CN$, 70 $^0$C, 12 h

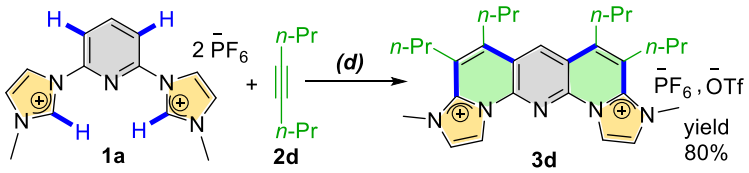
To an oven dried Schlenk tube, a mixture of **4** (47 mg, 0.05 mmol), NaOAc(41 mg, 0.50 mmol) and $AgPF_6$ (64 mg, 0.25 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with $N_2$ gas. To this mixture, dry and degassed $CH_3CN$ (2 mL) was added under Schlenk technique. After 12 h of heating, the reaction mixture was allowed to cool down to room temperature and the solution was passed through a short celite pad followed by washing with acetonitrile (3×5 mL). The combined filtrate was concentrated under reduced pressure and the solid formed was re-dissolved in minimum quantity of $CH_3CN$. To this solution diethyl ether (~5 times) was added and again all volatiles were evaporated. The resulting yellow solid was washed with cold pentane to afford the desired complex **5** (Yield= 71%) after drying under reduced pressure.

$^1$H NMR (500 MHz, $CD_3CN$, 298K) $\delta$ 8.39 (s, 1H), 7.87 (d, $J$ = 2.0 Hz, 2H), 7.38 (d, $J$ = 2.0 Hz, 2H), 4.05 (s, 6H), 1.79 (s, 30H). $^{13}$C NMR (126 MHz, $CD_3CN$, 298K): $\delta$ 177.9 (d, $J$ = 53.4 Hz),156.5, 155.3, 147.3 (d, $J$ = 34.1 Hz),126.1, 117.8, 101.26 (d, $J$ = 5.4 Hz), 39.1, 11.0 $^{31}$P NMR (202 MHz, $CD_3CN$, 298K) $\delta$ -139.39 (d, $J$ = 706.4 Hz). $^{19}$F NMR (471 MHz, $CD_3CN$, 298K) $\delta$ -72.89 (d, $J$ = 706.3 Hz). HRMS (ESI, positive ion): $M^{+2}$ = 356.5720 (calculated = 356.5731 for $[C_{33}H_{41}N_5Rh_2]^{2+}$).



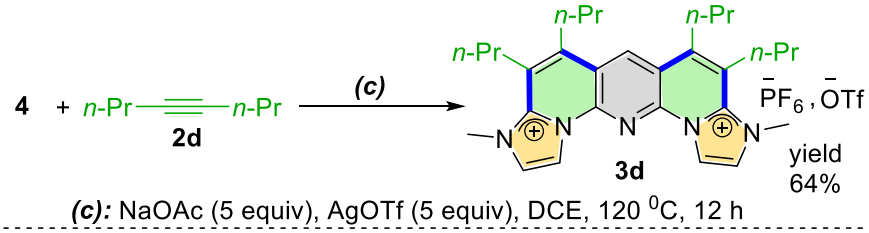

Molecular structure of intermediate **5** (50% probability level).

**C. Catalytic Reaction with Intermediate 4:**



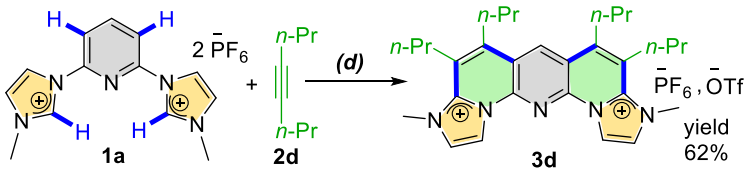

To an oven dried sealed tube, **1a** (26.5 mg, 0.05 mmol), NaOAc (21 mg, 0.25 mmol), **4** (0.0015 mmol), AgOTf (65 mg, 0.25 mmol) and **2d** (19 mg, 0.11 mmol) were loaded. To this mixture, dry and degassed DCE (2.0 mL) was added and the reaction mixture was left with stirring at 120 °C in dark. After 12 h, the whole reaction mixture was passed through a short celite pad which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated and purified by alumina column chromatography, using $CHCl_3$/MeOH (95:5) as eluent. Yield of **3d**= 80%.

**D. Stoichiometric Reaction with Intermediate 4:**




To an oven dried sealed tube, **4** (47 mg, 0.025 mmol), NaOAc (21 mg, 0.25 mmol), AgOTf (32 mg, 0.125 mmol) and **2d** (10 µL, 0.06 mmol) were loaded. To this mixture, dry and degassed DCE (1.5 mL) was added and the reaction mixture was left with stirring at 120 °C in dark. After 12 h, the whole reaction mixture was passed through a short celite pad which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated and purified by alumina column chromatography, using $CHCl_3$/MeOH (95:5) as eluent. Yield of **3d**= 64%.

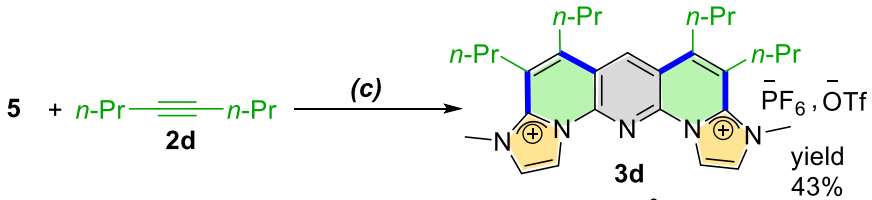
**E. Catalytic Reaction with Intermediate 5:**




***(d)*: 5** (3 mol%), NaOAc (5 equiv), AgOTf (5 equiv), DCE, 120 $^0$C, 12 h

To an oven dried sealed tube, **1a** (27 mg, 0.05 mmol), NaOAc (21 mg, 0.25 mmol), **5** (0.0015 mmol), AgOTf (64 mg, 0.25 mmol) and **2d** (19 µL, 0.12 mmol) were loaded. To this mixture, dry and degassed DCE (2.0 mL) was added and the reaction mixture was left with stirring at 120 °C in dark. After 12 h, the whole reaction mixture was passed through a short celite pad which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated and purified by alumina column chromatography, using $CHCl_3$/MeOH (95:5) as eluent. Yield of **3d**=62%.

**F. Stoichiometric Reaction with Intermediate 5:**




***(c):*** NaOAc (5 equiv), AgOTf (5 equiv), DCE, 120 $^0$C, 12 h

To an oven dried sealed tube, **5** (27 mg, 0.025 mmol), NaOAc (10 mg, 0.125 mmol), AgOTf (32 mg, 0.125 mmol) and **2d** (10.0 mg, 0.055 mmol) were loaded. To this mixture, dry and degassed DCE (2.0 mL) was added and the reaction mixture was left with stirring at 120 °C in dark. After 12 h, the whole reaction mixture was passed through a short celite pad which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated and purified by alumina column chromatography, using $CHCl_3$/MeOH (95:5) as eluent. Yield of **3d**= 43%.

## 10. Spectroscopic Measurements

Steady-state absorption spectra were recorded on SHIMADZU UV-1800 spectrophotometer. All steady-state fluorescence measurements were done on HORIBA Jobin Yvon Fluorolog spectrofluorimeter. The fluorescence and UV-Vis. spectra were recorded by using a 1 cm path length quartz cuvette. Both excitation and emission slit were kept at 1 nm while recording the fluorescence spectra. All the experiments were carried out at ambient temperature (298K).

Time-resolved fluorescence measurements were performed using a Hamamatsu MCP photomultiplier (R-3809U-50). The time-correlated single photon counting (TCSPC) setup consists of an Ortec 9327 pico-timing amplifier and using pulse Diode laser ($\lambda_{ex}$ 405 nm) with fwhm ~143 ps with a setup target 10,000 counts. The instrument response function (IRF) was measured before and after fluorescence lifetime measurement using a dilute suspension of Ludox (colloidal silica, purchased from Sigma-Aldrich). The emission polarizer was positioned at the magic angle (54.7º) polarization with respect to excitation polarizer. The single exponential fitting function was employed by iterative deconvolution method using supplied software EzTime (HORIBA Scientific, v3.2.9.6). The general form of the fitting function was

$$I(t) = I(0) \sum \alpha_i \exp(-{}^{t}/_{\tau_i})$$

where I(t) and I(0) are the fluorescence intensity at time t and 0 respectively, t is the time $\alpha_i$ and $\tau_i$ are the contributing amplitude and its corresponding lifetime. The quality of the fitted data was judged from the reduced chi-squared value ($\chi^2$), calculated using the IBH software provided with the instrument. All the measurements were carried out at ambient temperature (298K).

## 11. Cell Culture and Imaging Studies

**A. Materials and Instruments:** Dulbecco's Modified Eagle Medium (DMEM), Trypsin, Antibiotic cocktail and Fetal Bovine Serum (FBS) were purchased from HiMedia (USA). LysoTracker Red and MitoTracker Red were purchased from Thermo Fisher SCIENTIFIC (USA). The 35 mm glass bottom imaging dishes were obtained from Ibidi (Germany, Cat#

81158). All the confocal microscopy imaging were performed with an Olympus FV3000 Confocal Laser Scanning Microscope (LSM). The image processing was done with the help of cellSens software (Olympus).

**B. Culture Method:** BHK-21 and CHO cells were obtained from NCCS, Pune, India and were grown in a 25 $cm^2$ cell culture flask (Corning, USA) using DMEM (phenol red free) containing 10% (v/v) FBS and 1% (v/v) antibiotic cocktail in 5% $CO_2$ at 37 ºC in a $CO_2$ incubator. For imaging purpose, cells were grown to 75% - 80% confluency in the 35 mm glass bottom imaging dishes ($170 \pm 5\ \mu$m) in DMEM with 10% FBS. The cells were washed twice with PBS (pH 7.4) containing 5 mM $MgCl_2$. Then the cells were co-incubated with 5 $\mu$M of the dye of interest and 300 nM of LysoTracker Red/MitoTracker Red (whichever applicable) for 15 minutes and washed with PBS (pH 7.4) twice before imaging.

**C. MTT Assay:** Around 10,000 of cell per well were seeded in a 96 well-plate and grown for 24 h in the aforementioned condition. After that, the dye of interest was added according to the concentration from a concentrated stock in DMSO. The added amount of DMSO was not more than 2 $\mu$L. After 24 h of incubation, 20 $\mu$L of MTT dye solution (5 mg/ mL in PBS buffer) was added to each well and incubated for 4 h. The media was removed gently from each well and 200 $\mu$L DMSO was added to each well and allowed to dissolve the purple color crystal for 30 min. The absorption at 570 nm was recorded in a microplate reader from BioTek (Synergy H1 Hybrid Multimode Reader).

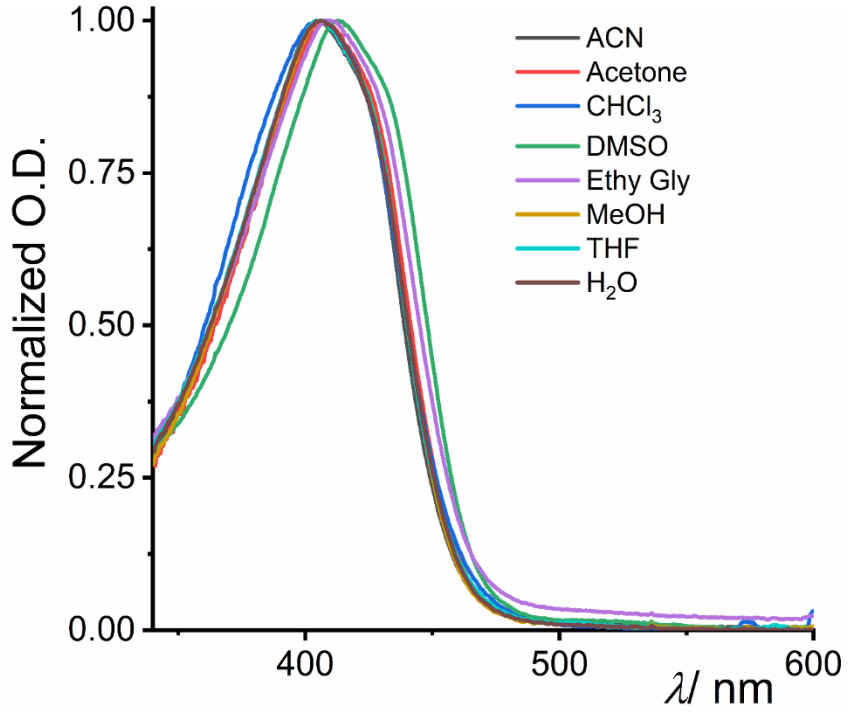
**D. Confocal Microscopy:** For fluorescence imaging, 488 and 561 nm excitation lasers were used. For 488 nm and 561 nm excitation, the emission windows were kept at 500-560 nm and 565-650 nm, respectively. The confocal aperture was kept at 0.81 Airy Disk (AU) while the dwell time was 4 $\mu$s/pixel.

**Table S2:** Solvent-dependent photophysical properties of **3j**

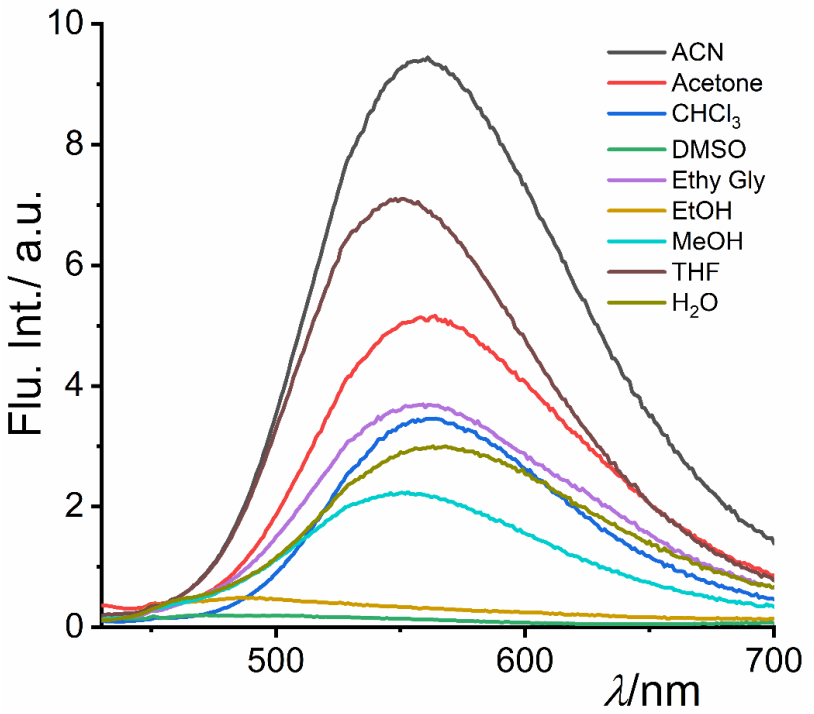
| Entry | Solvent | $\lambda_{abs}^{max}$ (nm) | $\lambda_{em}^{max}$ (nm) | $\Phi$ (%) | $\tau$ (ns) |
|---|---|---|---|---|---|
| 1 | ACN | 405 | 558 | 21.2 | 5.8 |
| 2 | Acetone | 406 | 560 | 11.3 | 4.9 |
| 3 | $CHCl_3$ | 404 | 560 | 12.6 | 3.5 |
| 4 | DMSO | 413 | 488 | 0.8 | 0.6 |
| 5 | Ethylene glycol | 409 | 560 | 10.4 | 4.7 |
| 6 | EtOH | 406 | 490 | 1.6 | 1.3 |
| 7 | MeOH | 406 | 550 | 6.3 | 2.4 |
| 8 | THF | 405 | 548 | 19.7 | 4.6 |
| 9 | Water | 406 | 565 | 9.8 | 4.1 |

**Table S3:** Solvent-dependent photophysical properties of **3s**

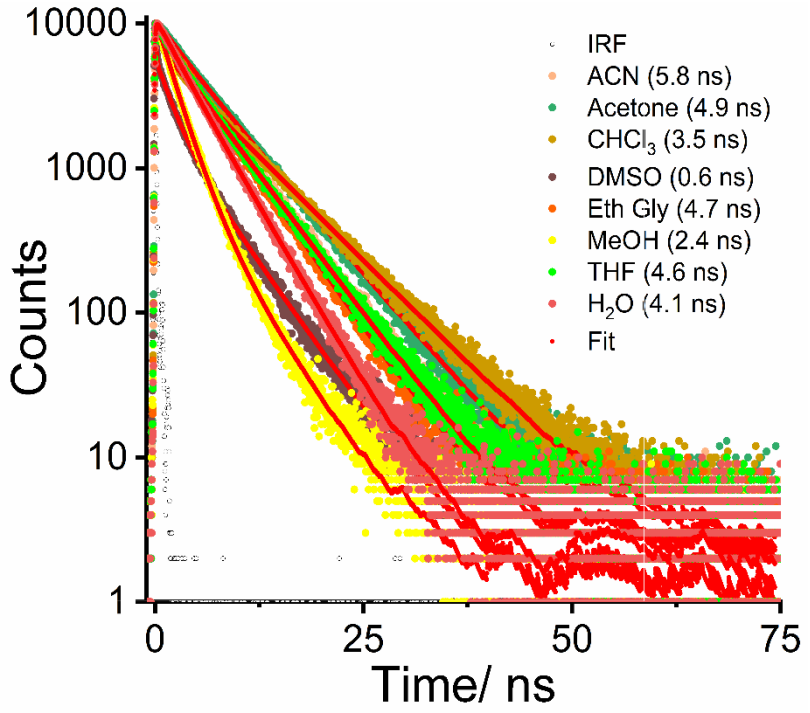
| Entry | Solvent | $\lambda_{abs}^{max}$ (nm) | $\lambda_{em}^{max}$ (nm) | $\Phi$ (%) | $\tau$ (ns) |
|---|---|---|---|---|---|
| 1 | ACN | 385 | 455 | 14.2 | 6.7 |
| 2 | Acetone | 388 | 455 | 15.6 | 6.4 |
| 3 | $CHCl_3$ | 380 | 455 | 10.3 | 3.9 |
| 4 | DMSO | 390 | 462 | 17.2 | 7.3 |
| 5 | EtOH | 385 | 452 | 22.8 | 6.4 |
| 6 | MeOH | 381 | 452 | 14.3 | 6.9 |
| 7 | THF | 390 | 455 | 18.1 | 6.6 |
| 8 | Water | 400 | 510 | 0.8 | 1.8 |



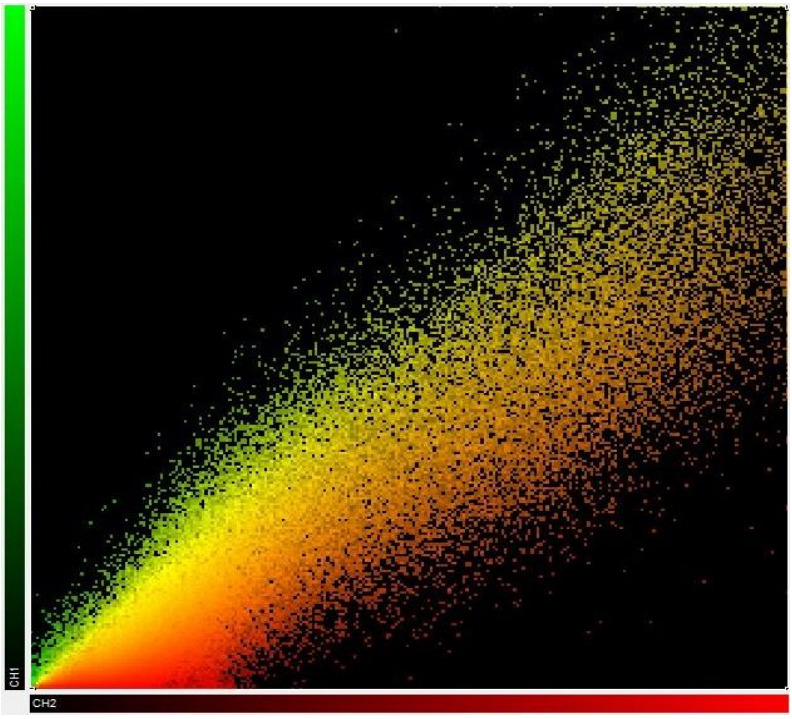

Absorption spectra of **3j** (2 $\mu$M) in different solvents



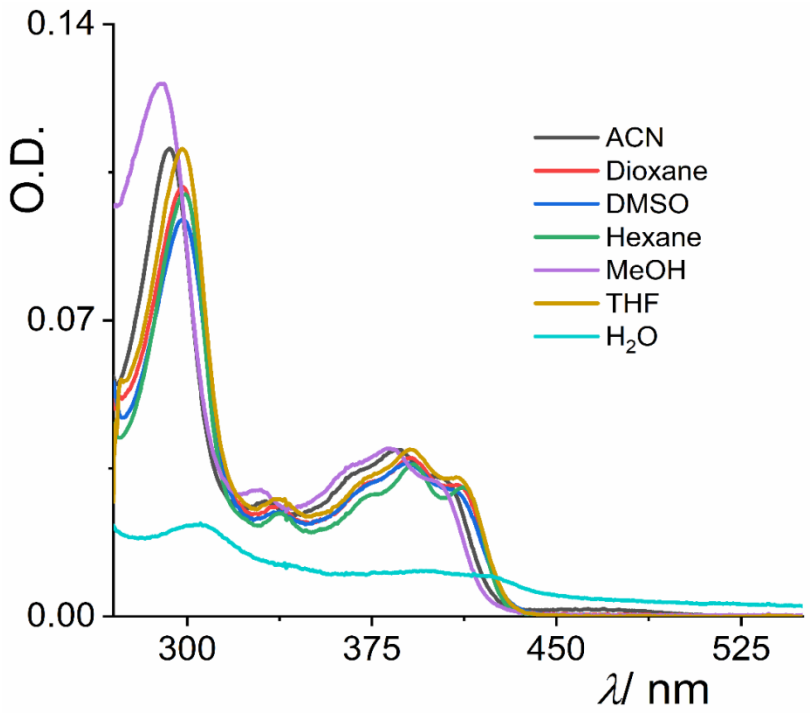

Emission spectra of **3j** (2 $\mu$M) in different solvents



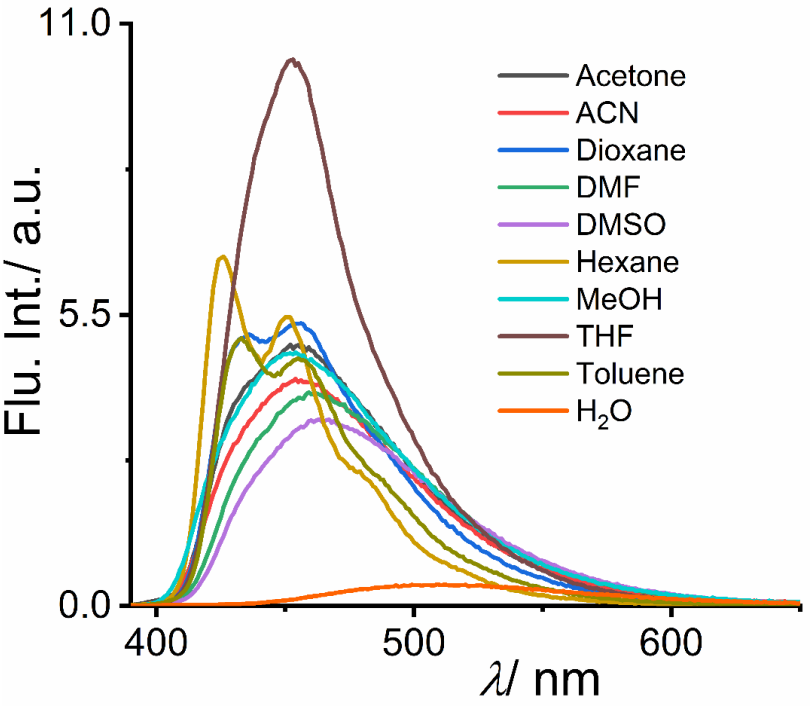

Fluorescence lifetime of **3j** (2 $\mu$M) in different solvents



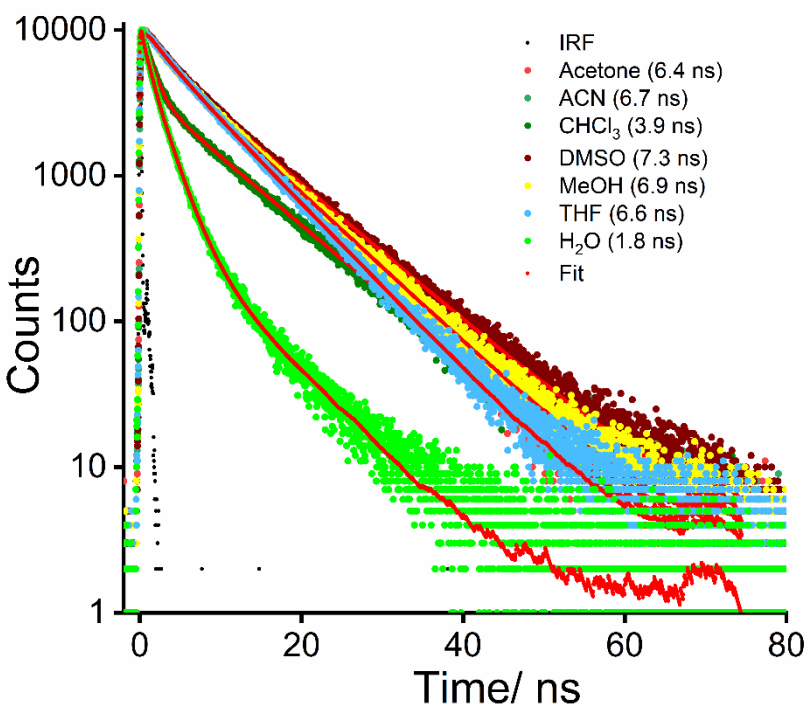

Scatter plot (**3j** and MitoTracker Red) obtained by fluorescence colocalization microscopy with Pearson's co-efficient 0.92±0.04



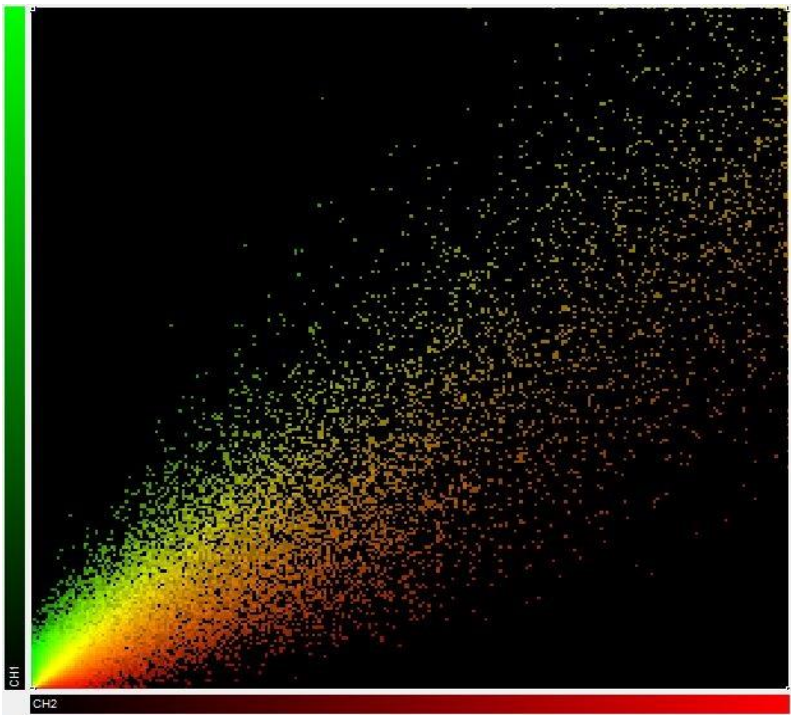

Absorption spectra of **3s** (5 $\mu$M) in different solvents




Emission spectra of **3s** (5 $\mu$M) in different solvents




Fluorescence lifetime of **3s** (5 $\mu$M) in different solvents




Scatter plot (**3s** and LysoTracker Red) obtained by fluorescence colocalization microscopy with Pearson's co-efficient 0.94±0.02

## 12. Computational Studies

Gaussian 09 software was used to carry out all the computational studies.[S5] DFT calculations were performed with B3LYP exchange-correlation functional by using 6-31G (d) basis set for H, C, and N atoms.[S6] Only gas phase calculations were performed to get optimized geometry of the structures. Frequency calculations were carried out to check the true minima of the optimized structures. For ground state optimized geometries, it showed 0 imaginary frequency. Later, images of HOMO and LUMO were obtained from optimized geometry to check electronic distributions and energy gap in between.

The x, y and z coordinates for the optimized structures of **3a**, **3b** and **3j** are as below

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**3a**

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Symbolic Z-matrix:

Charge = 2 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.46555 | -5.72544 | -1.35355 |
| C | -3.35376 | -4.95254 | -2.50499 |
| C | -3.98998 | -6.19177 | -2.32676 |
| C | -3.33221 | -7.21623 | -1.6405 |
| H | -3.85872 | -4.16921 | -3.03063 |
| N | -0.13411 | -5.41527 | -0.8645 |
| C | 0.49913 | -4.25168 | -1.01553 |
| C | 0.86686 | -6.06048 | -0.16519 |
| C | 2.00896 | -5.64812 | 0.19907 |
| H | 2.81722 | -6.09798 | 0.73689 |
| N | 1.79969 | -4.28513 | -0.41081 |
| C | 2.76558 | -3.1772 | -0.3894 |
| H | 3.7602 | -3.57139 | -0.37378 |

| | | | |
|---|---|---|---|
| H | 2.63496 | -2.57322 | -1.26292 |
| H | 2.60463 | -2.58055 | 0.4841 |
| C | -1.47269 | -3.39907 | -2.23513 |
| C | -0.21212 | -3.13059 | -1.76261 |
| C | 0.07804 | -1.88363 | -0.90674 |
| C | 1.37713 | -1.64034 | -0.44083 |
| C | -0.95702 | -0.9922 | -0.59381 |
| C | 1.64118 | -0.50561 | 0.33801 |
| H | 2.16742 | -2.32097 | -0.67976 |
| C | -0.69298 | 0.14253 | 0.18503 |
| H | -1.94891 | -1.17796 | -0.94955 |
| C | 0.60612 | 0.38582 | 0.65095 |
| H | 2.63307 | -0.31986 | 0.69375 |
| H | -1.48326 | 0.82316 | 0.42397 |
| H | 0.80772 | 1.25221 | 1.24561 |
| C | -2.03933 | -2.55804 | -3.39409 |
| C | -2.75908 | -3.17894 | -4.42383 |
| C | -1.83522 | -1.17181 | -3.419 |
| C | -3.27473 | -2.4136 | -5.47848 |
| H | -2.91492 | -4.23736 | -4.40481 |
| C | -2.35087 | -0.40647 | -4.47366 |
| H | -1.28568 | -0.69774 | -2.63278 |
| C | -3.07062 | -1.02737 | -5.5034 |
| H | -3.82427 | -2.88767 | -6.26471 |

| | | | |
|---|---|---|---|
| H | -2.19503 | 0.65195 | -4.49268 |
| H | -3.46433 | -0.44302 | -6.30865 |
| C | -2.11707 | -4.73971 | -2.02233 |
| N | -2.04985 | -6.97923 | -1.14618 |
| N | -3.97508 | -8.52403 | -1.44743 |
| C | -5.24553 | -8.876 | -1.89372 |
| C | -3.41327 | -9.61382 | -0.78877 |
| C | -4.33436 | -10.67026 | -0.81537 |
| H | -2.41554 | -9.56343 | -0.3547 |
| H | -4.19559 | -11.65711 | -0.38679 |
| N | -5.49592 | -10.20246 | -1.51595 |
| C | -6.7193 | -10.97129 | -1.78641 |
| H | -7.56185 | -10.45844 | -1.37169 |
| H | -6.84939 | -11.07438 | -2.84345 |
| H | -6.63714 | -11.94068 | -1.34094 |
| C | -6.1317 | -7.88012 | -2.66478 |
| C | -5.40673 | -6.42088 | -2.88525 |
| C | -7.51093 | -8.3709 | -3.14276 |
| C | -5.99317 | -5.19692 | -3.61301 |
| C | -7.41349 | -4.70913 | -3.27191 |
| C | -5.26364 | -4.54763 | -4.55257 |
| H | -4.27679 | -4.88655 | -4.78956 |
| C | -5.85008 | -3.32367 | -5.28032 |
| C | -7.99993 | -3.48517 | -3.99967 |

| | | | |
|---|---|---|---|
| H | -8.98677 | -3.14625 | -3.76267 |
| C | -8.58027 | -8.31554 | -2.3121 |
| H | -8.46589 | -7.92952 | -1.32073 |
| C | -7.67556 | -8.92648 | -4.56959 |
| C | -9.05479 | -9.41726 | -5.04757 |
| H | -9.16917 | -9.80328 | -6.03894 |
| C | -9.9595 | -8.80632 | -2.79008 |
| H | -6.83494 | -8.97268 | -5.22998 |
| H | -7.99428 | -5.2177 | -2.53101 |
| H | -10.8038 | -8.76262 | -2.13423 |
| C | -10.26995 | -9.35435 | -4.10363 |
| C | -7.14257 | -2.87978 | -4.96993 |
| H | -5.27408 | -2.81102 | -6.02215 |
| H | -6.95813 | -2.12529 | -5.64641 |
| H | -11.22225 | -9.88639 | -4.24528 |
| H | 0.96609 | -7.1415 | -0.34279 |

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**3b**

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Symbolic Z-matrix:

Charge = 2 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.46555 | -5.72544 | -1.35355 |
| C | -3.35376 | -4.95254 | -2.50499 |
| C | -3.98998 | -6.19177 | -2.32676 |
| C | -3.33221 | -7.21623 | -1.6405 |

| | | | |
|---|---|---|---|
| H | -3.85872 | -4.16921 | -3.03063 |
| N | -0.13411 | -5.41527 | -0.8645 |
| C | 0.49913 | -4.25168 | -1.01553 |
| C | 0.86686 | -6.06048 | -0.16519 |
| C | 2.00896 | -5.64812 | 0.19907 |
| H | 2.81722 | -6.09798 | 0.73689 |
| N | 1.79969 | -4.28513 | -0.41081 |
| C | 2.76558 | -3.1772 | -0.3894 |
| H | 3.7602 | -3.57139 | -0.37378 |
| H | 2.63496 | -2.57322 | -1.26292 |
| H | 2.60463 | -2.58055 | 0.4841 |
| C | -1.47269 | -3.39907 | -2.23513 |
| C | -0.21212 | -3.13059 | -1.76261 |
| C | 0.07804 | -1.88363 | -0.90674 |
| C | 1.37713 | -1.64034 | -0.44083 |
| C | -0.95702 | -0.9922 | -0.59381 |
| C | 1.64118 | -0.50561 | 0.33801 |
| H | 2.16742 | -2.32097 | -0.67976 |
| C | -0.69298 | 0.14253 | 0.18503 |
| H | -1.94891 | -1.17796 | -0.94955 |
| C | 0.60612 | 0.38582 | 0.65095 |
| H | 2.63307 | -0.31986 | 0.69375 |
| H | -1.48326 | 0.82316 | 0.42397 |
| C | -2.03933 | -2.55804 | -3.39409 |

| | | | |
|---|---|---|---|
| C | -2.75908 | -3.17894 | -4.42383 |
| C | -1.83522 | -1.17181 | -3.419 |
| C | -3.27473 | -2.4136 | -5.47848 |
| H | -2.91492 | -4.23736 | -4.40481 |
| C | -2.35087 | -0.40647 | -4.47366 |
| H | -1.28568 | -0.69774 | -2.63278 |
| C | -3.07062 | -1.02737 | -5.5034 |
| H | -3.82427 | -2.88767 | -6.26471 |
| H | -2.19503 | 0.65195 | -4.49268 |
| C | -2.11707 | -4.73971 | -2.02233 |
| N | -2.04985 | -6.97923 | -1.14618 |
| N | -3.97508 | -8.52403 | -1.44743 |
| C | -5.24553 | -8.876 | -1.89372 |
| C | -3.41327 | -9.61382 | -0.78877 |
| C | -4.33436 | -10.67026 | -0.81537 |
| H | -2.41554 | -9.56343 | -0.3547 |
| H | -4.19559 | -11.65711 | -0.38679 |
| N | -5.49592 | -10.20246 | -1.51595 |
| C | -6.7193 | -10.97129 | -1.78641 |
| H | -7.56185 | -10.45844 | -1.37169 |
| H | -6.84939 | -11.07438 | -2.84345 |
| H | -6.63714 | -11.94068 | -1.34094 |
| C | -6.1317 | -7.88012 | -2.66478 |
| C | -5.40673 | -6.42088 | -2.88525 |

| | | | |
|---|---|---|---|
| C | -7.51093 | -8.3709 | -3.14276 |
| C | -5.99317 | -5.19692 | -3.61301 |
| C | -7.41349 | -4.70913 | -3.27191 |
| C | -5.26364 | -4.54763 | -4.55257 |
| H | -4.27679 | -4.88655 | -4.78956 |
| C | -5.85008 | -3.32367 | -5.28032 |
| C | -7.99993 | -3.48517 | -3.99967 |
| H | -8.98677 | -3.14625 | -3.76267 |
| C | -8.58027 | -8.31554 | -2.3121 |
| H | -8.46589 | -7.92952 | -1.32073 |
| C | -7.67556 | -8.92648 | -4.56959 |
| C | -9.05479 | -9.41726 | -5.04757 |
| H | -9.16917 | -9.80328 | -6.03894 |
| C | -9.9595 | -8.80632 | -2.79008 |
| H | -6.83494 | -8.97268 | -5.22998 |
| H | -7.99428 | -5.2177 | -2.53101 |
| H | -10.8038 | -8.76262 | -2.13423 |
| C | -10.26995 | -9.35435 | -4.10363 |
| C | -7.14257 | -2.87978 | -4.96993 |
| H | -5.27408 | -2.81102 | -6.02215 |
| H | 0.96609 | -7.1415 | -0.34279 |
| C | -11.60317 | -10.0992 | -4.30194 |
| H | -12.40642 | -9.49778 | -3.93048 |
| H | -11.75324 | -10.29059 | -5.34394 |

| | | | |
|---|---|---|---|
| H | -11.57619 | -11.02676 | -3.7692 |
| C | -6.86681 | -1.7517 | -5.98136 |
| H | -6.23951 | -1.01239 | -5.52881 |
| H | -6.37706 | -2.15645 | -6.84231 |
| H | -7.79226 | -1.30249 | -6.27572 |
| C | -3.63726 | -0.18634 | -6.66236 |
| H | -3.96058 | -0.83537 | -7.4492 |
| H | -4.46761 | 0.39034 | -6.31183 |
| H | -2.87731 | 0.47036 | -7.03129 |
| C | 0.89628 | 1.63277 | 1.50682 |
| H | 1.27356 | 1.33032 | 2.46133 |
| H | 1.62334 | 2.24303 | 1.01299 |
| H | -0.00646 | 2.19135 | 1.64081 |

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**3j**

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Symbolic Z-matrix:

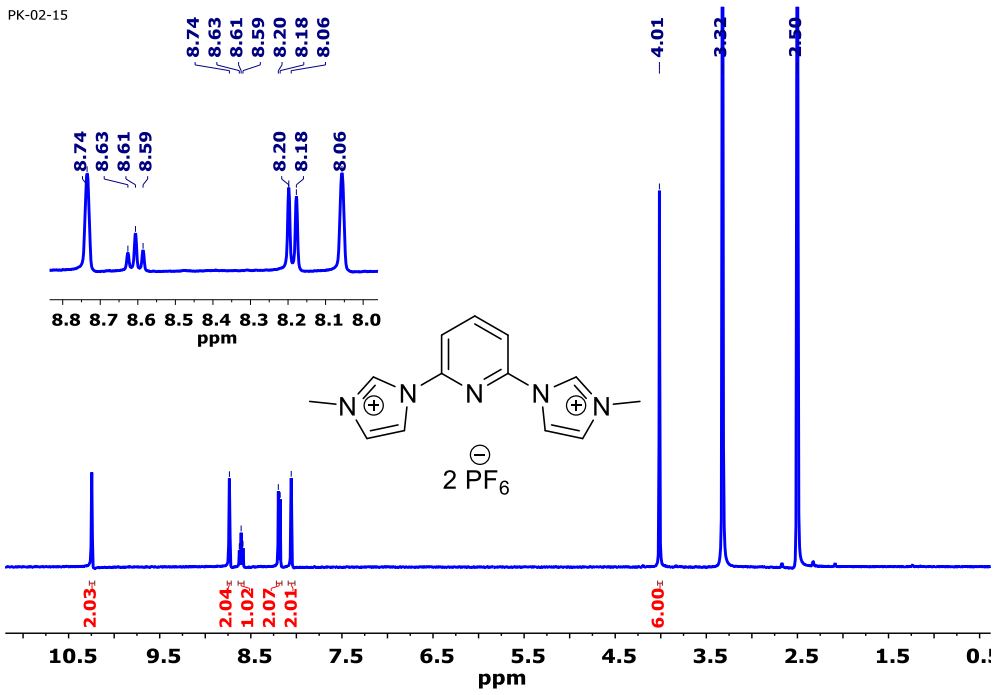
Charge = 2 Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.46555 | -5.72544 | -1.35355 |
| C | -3.98998 | -6.19177 | -2.32676 |
| C | -3.33221 | -7.21623 | -1.6405 |
| N | -0.13411 | -5.41527 | -0.8645 |
| C | 0.49913 | -4.25168 | -1.01553 |
| C | 0.86686 | -6.06048 | -0.16519 |
| C | 2.00896 | -5.64812 | 0.19907 |
| H | 2.81722 | -6.09798 | 0.73689 |
| N | 1.79969 | -4.28513 | -0.41081 |
| C | 2.76558 | -3.1772 | -0.3894 |
| H | 3.7602 | -3.57139 | -0.37378 |

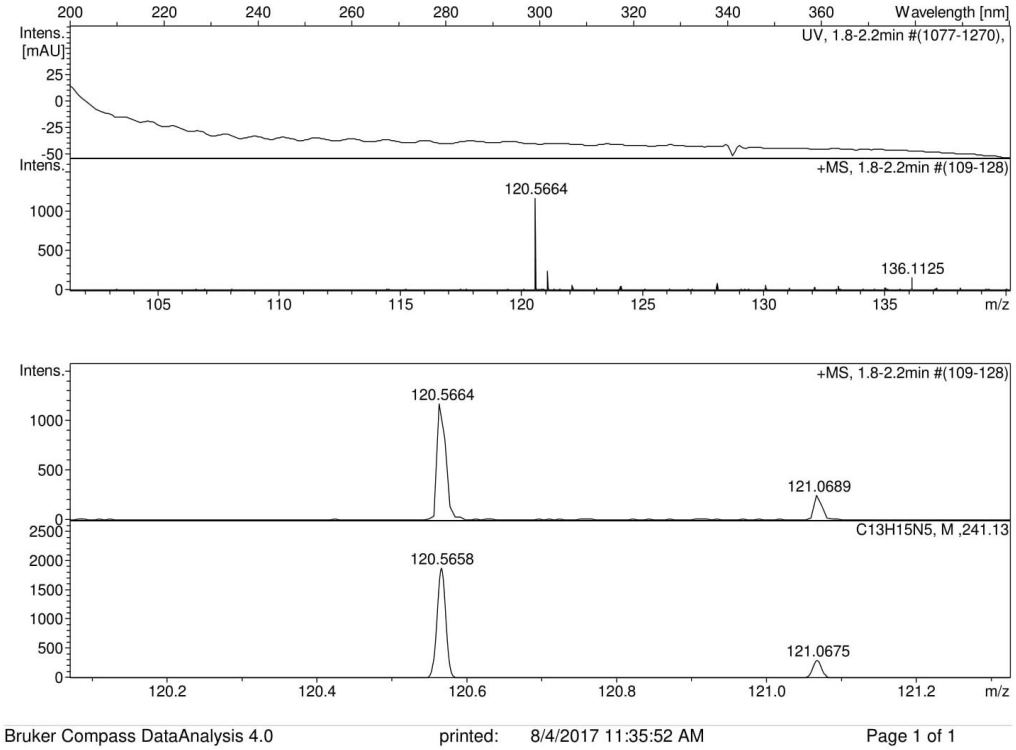
| | | | |
|---|---|---|---|
| H | 2.63496 | -2.57322 | -1.26292 |
| H | 2.60463 | -2.58055 | 0.4841 |
| C | -1.47269 | -3.39907 | -2.23513 |
| C | -0.21212 | -3.13059 | -1.76261 |
| C | 0.07804 | -1.88363 | -0.90674 |
| C | 1.37713 | -1.64034 | -0.44083 |
| C | -0.95702 | -0.9922 | -0.59381 |
| C | 1.64118 | -0.50561 | 0.33801 |
| H | 2.16742 | -2.32097 | -0.67976 |
| C | -0.69298 | 0.14253 | 0.18503 |
| H | -1.94891 | -1.17796 | -0.94955 |
| C | 0.60612 | 0.38582 | 0.65095 |
| H | 2.63307 | -0.31986 | 0.69375 |
| H | -1.48326 | 0.82316 | 0.42397 |
| H | 0.80772 | 1.25221 | 1.24561 |
| C | -2.03933 | -2.55804 | -3.39409 |
| C | -2.75908 | -3.17894 | -4.42383 |
| C | -1.83522 | -1.17181 | -3.419 |
| C | -3.27473 | -2.4136 | -5.47848 |
| H | -2.91492 | -4.23736 | -4.40481 |
| C | -2.35087 | -0.40647 | -4.47366 |
| H | -1.28568 | -0.69774 | -2.63278 |
| C | -3.07062 | -1.02737 | -5.5034 |
| H | -3.82427 | -2.88767 | -6.26471 |
| H | -2.19503 | 0.65195 | -4.49268 |
| H | -3.46433 | -0.44302 | -6.30865 |
| C | -2.11707 | -4.73971 | -2.02233 |
| N | -2.04985 | -6.97923 | -1.14618 |
| N | -3.97508 | -8.52403 | -1.44743 |
| C | -5.24553 | -8.876 | -1.89372 |
| C | -3.41327 | -9.61382 | -0.78877 |
| C | -4.33436 | -10.67026 | -0.81537 |
| H | -2.41554 | -9.56343 | -0.3547 |
| H | -4.19559 | -11.65711 | -0.38679 |

| | | | |
|---|---|---|---|
| N | -5.49592 | -10.20246 | -1.51595 |
| C | -6.7193 | -10.97129 | -1.78641 |
| H | -7.56185 | -10.45844 | -1.37169 |
| H | -6.84939 | -11.07438 | -2.84345 |
| H | -6.63714 | -11.94068 | -1.34094 |
| C | -6.1317 | -7.88012 | -2.66478 |
| C | -5.40673 | -6.42088 | -2.88525 |
| C | -7.51093 | -8.3709 | -3.14276 |
| C | -5.99317 | -5.19692 | -3.61301 |
| C | -7.41349 | -4.70913 | -3.27191 |
| C | -5.26364 | -4.54763 | -4.55257 |
| H | -4.27679 | -4.88655 | -4.78956 |
| C | -5.85008 | -3.32367 | -5.28032 |
| C | -7.99993 | -3.48517 | -3.99967 |
| H | -8.98677 | -3.14625 | -3.76267 |
| C | -8.58027 | -8.31554 | -2.3121 |
| H | -8.46589 | -7.92952 | -1.32073 |
| C | -7.67556 | -8.92648 | -4.56959 |
| C | -9.05479 | -9.41726 | -5.04757 |
| H | -9.16917 | -9.80328 | -6.03894 |
| C | -9.9595 | -8.80632 | -2.79008 |
| H | -6.83494 | -8.97268 | -5.22998 |
| H | -7.99428 | -5.2177 | -2.53101 |
| H | -10.8038 | -8.76262 | -2.13423 |
| C | -10.26995 | -9.35435 | -4.10363 |
| C | -7.14257 | -2.87978 | -4.96993 |
| H | -5.27408 | -2.81102 | -6.02215 |
| H | -6.95813 | -2.12529 | -5.64641 |
| H | -11.22225 | -9.88639 | -4.24528 |
| H | 0.96609 | -7.1415 | -0.34279 |
| N | -3.35376 | -4.95254 | -2.50499 |

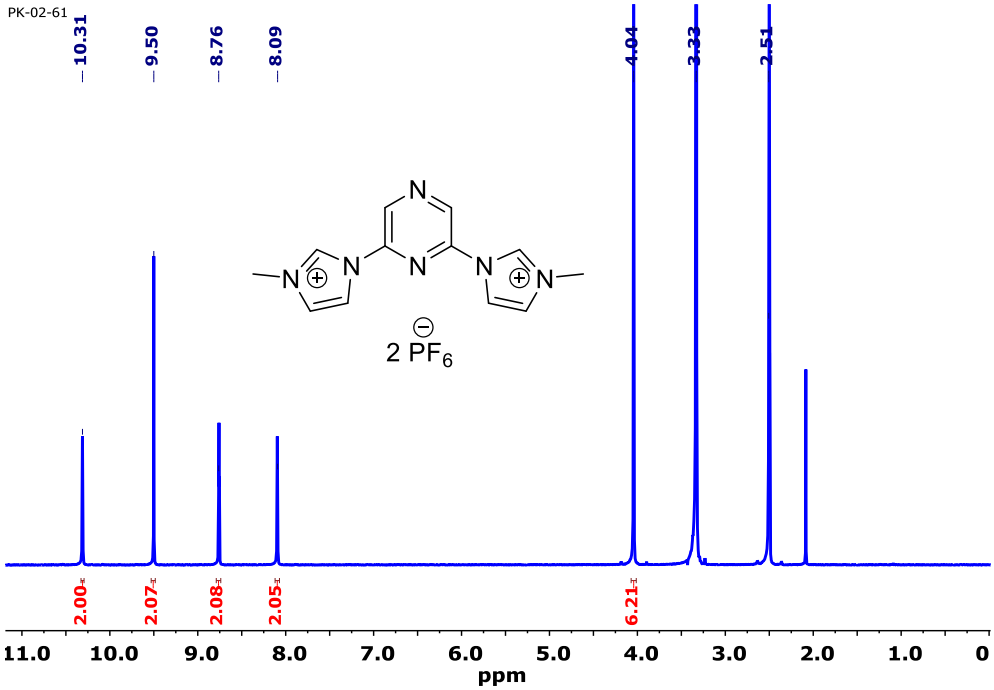
## 13. $^{1}H$, $^{13}C\{^{1}H\}$, $^{19}F$ & $^{31}P\{^{1}H\}$ NMR and ESI Mass Spectra



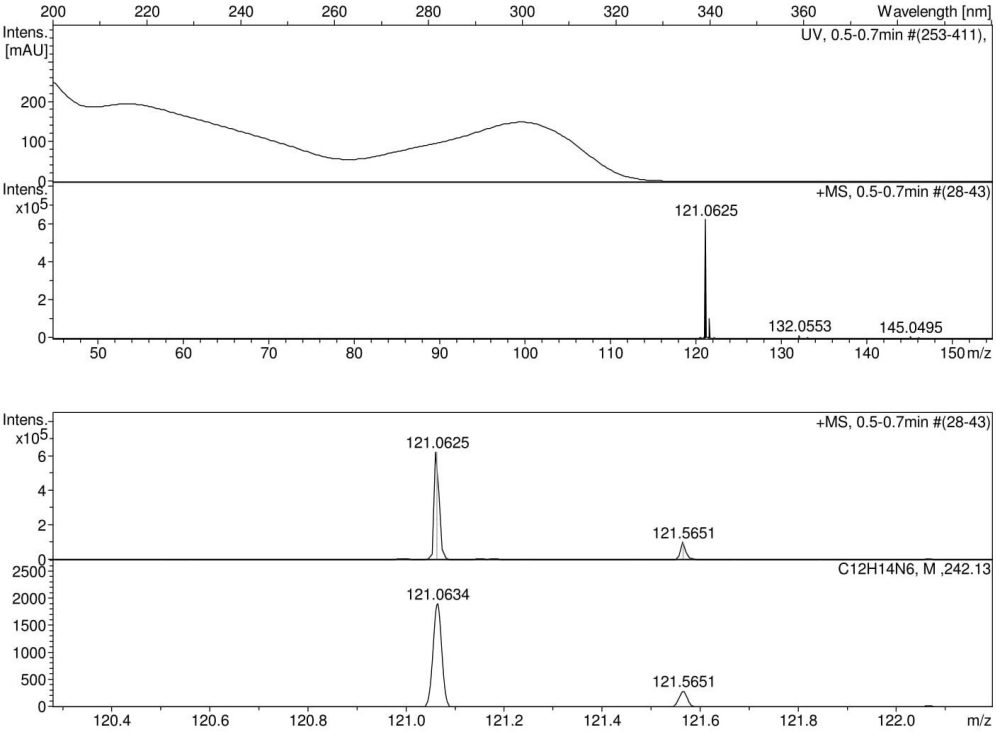

$^{1}H$ NMR spectrum of **1a** (500 MHz, DMSO-$d_6$, 298 K).



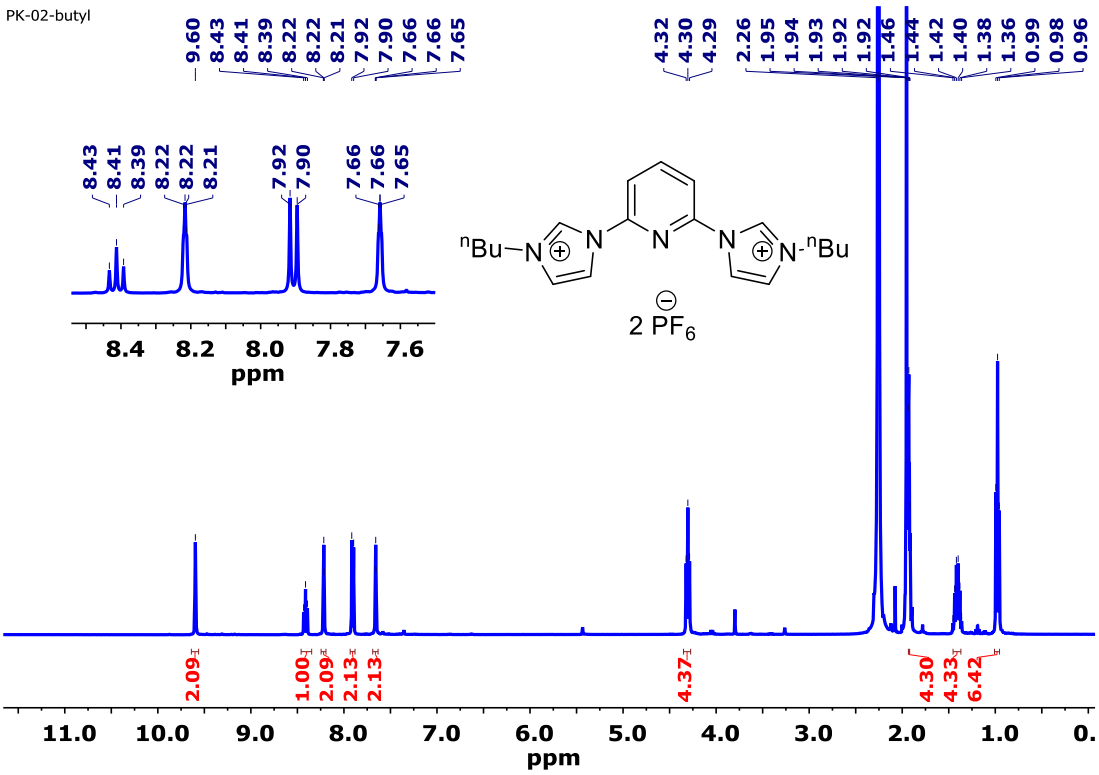

ESI-HRMS (positive ion mode) spectrum of **1a**.



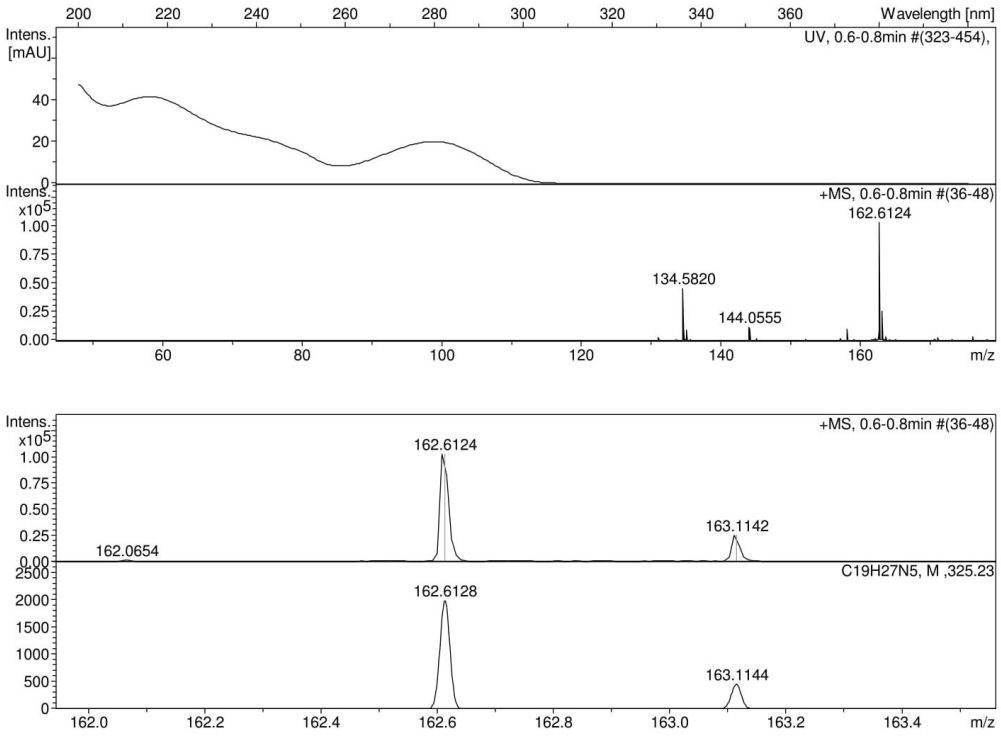

$^{1}$H NMR spectrum of **1b** (500 MHz, DMSO-$d_6$, 298K).



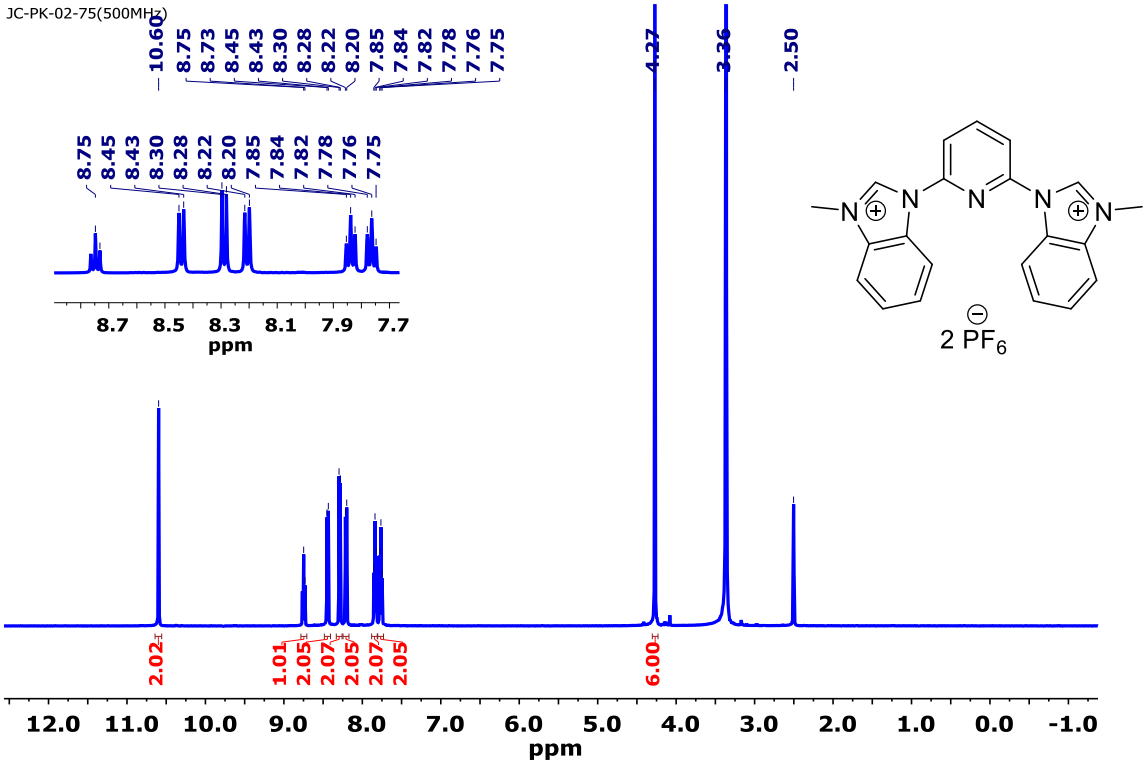

ESI-HRMS (positive ion mode) spectrum of **1b**.



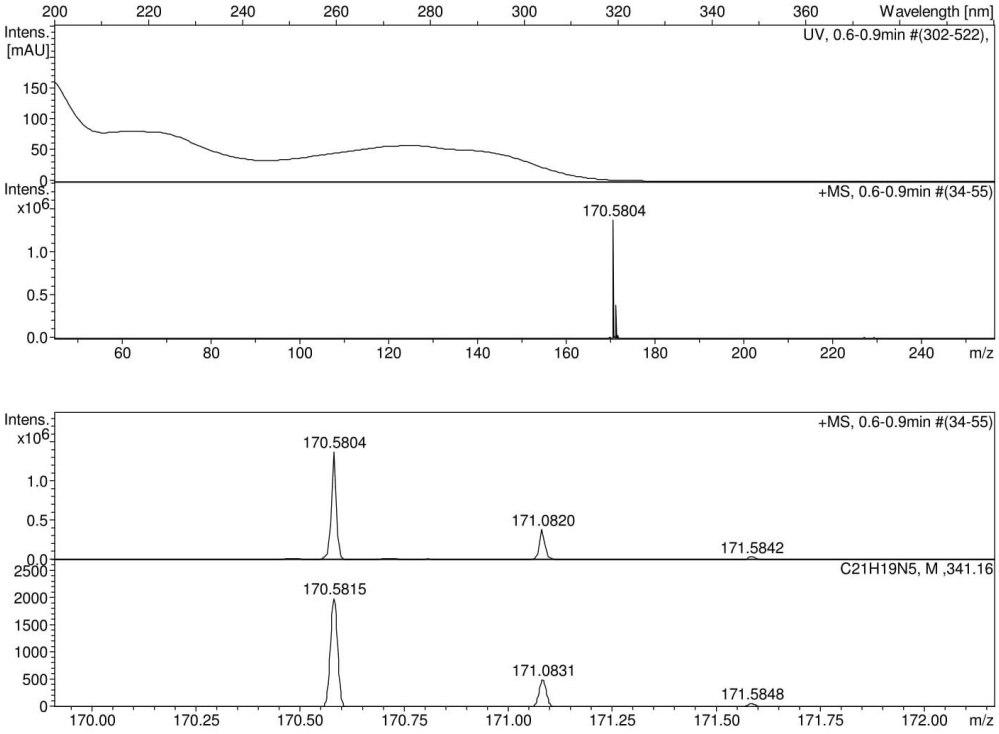

$^{1}$H NMR spectrum of **1c** (500 MHz, DMSO-$d_6$, 298 K).



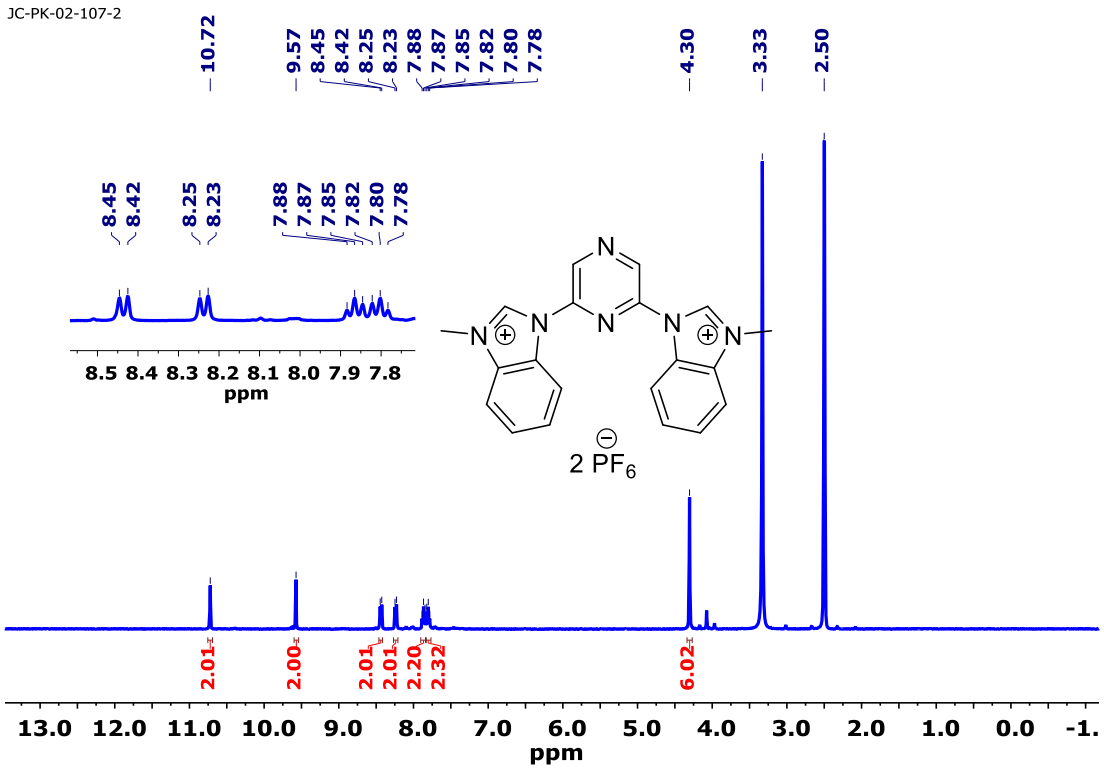

ESI-HRMS (positive ion mode) spectrum of **1c**



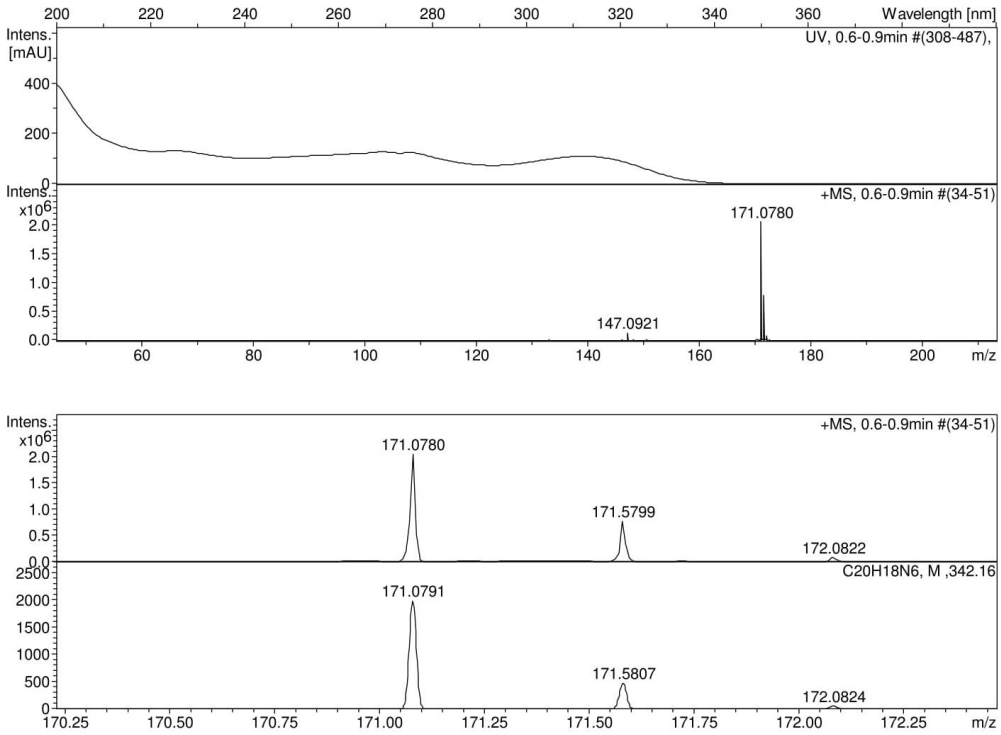

$^{1}$H NMR spectrum of **1d** (500 MHz, DMSO-$d_6$, 298 K).



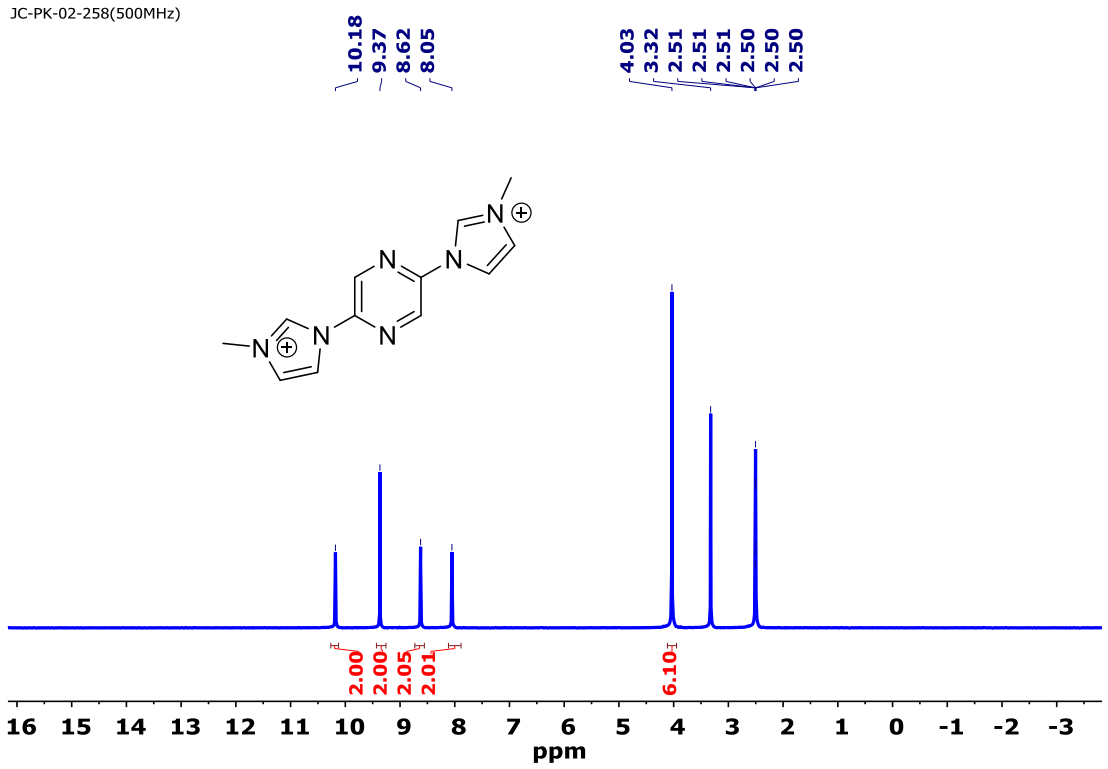

ESI-HRMS (positive ion mode) spectrum of **1d**



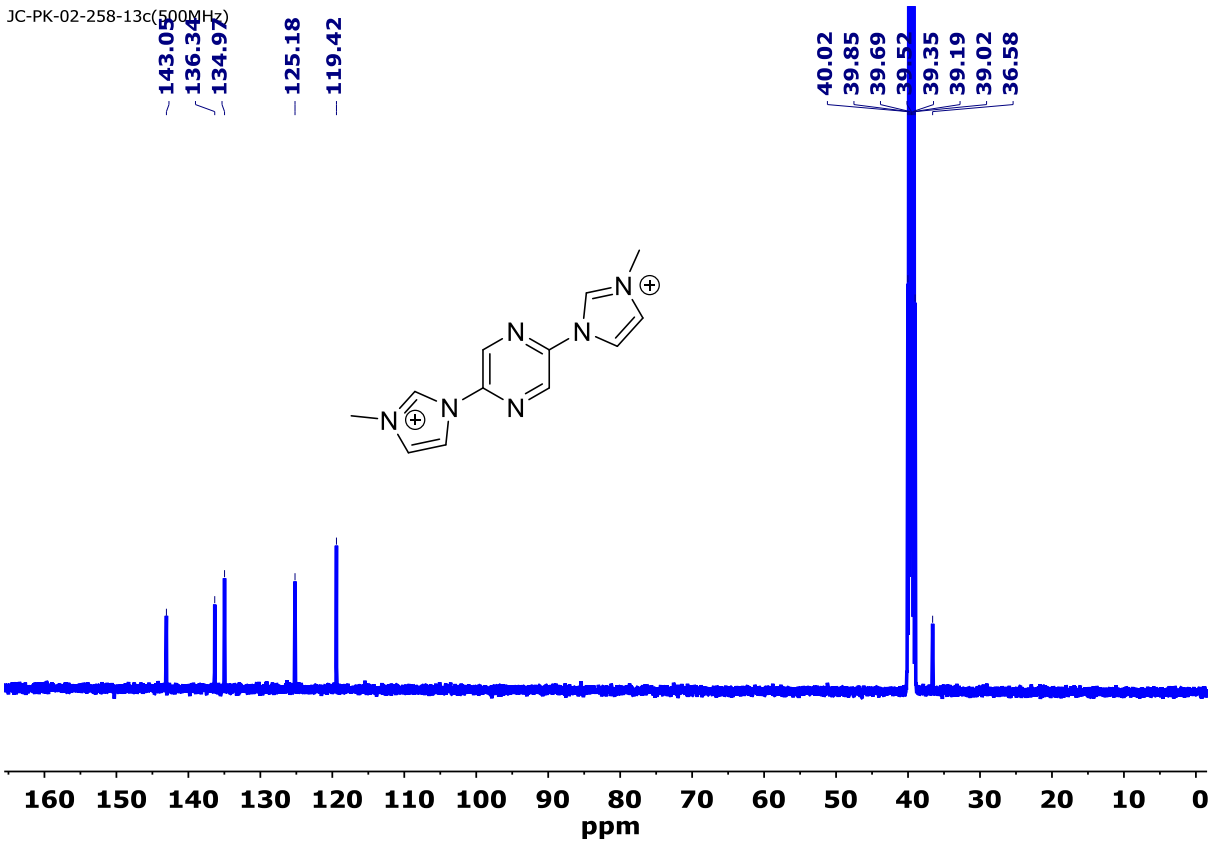

$^{1}$H NMR spectrum of **1e** (500 MHz, DMSO-$d_6$, 298 K)



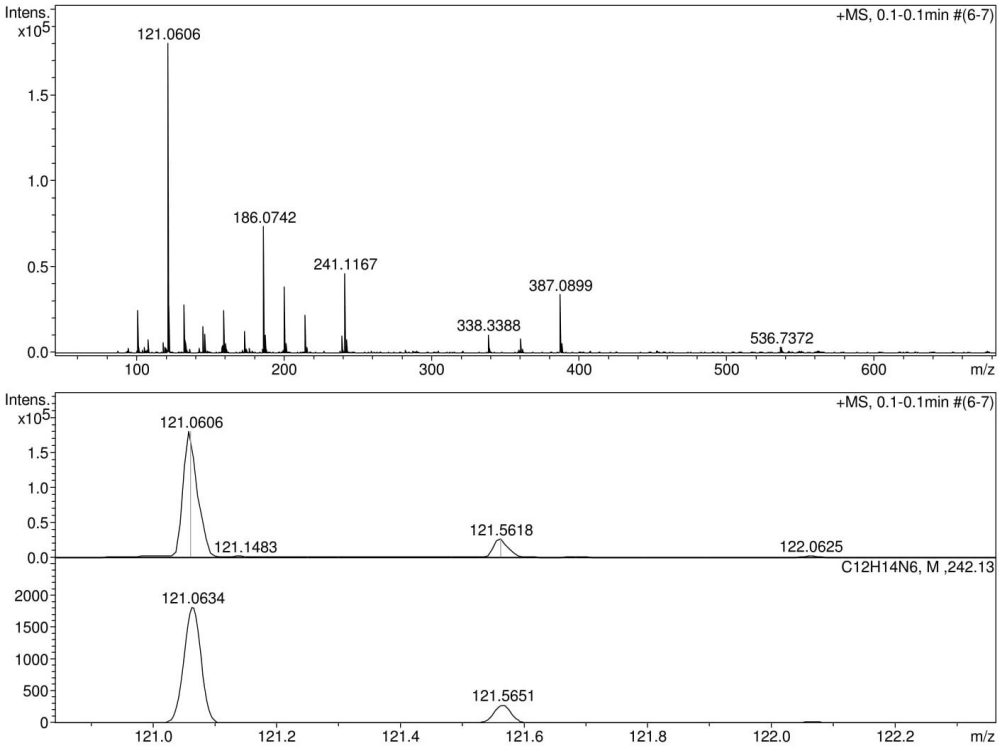

ESI-HRMS (positive ion mode) spectrum of **1e.**



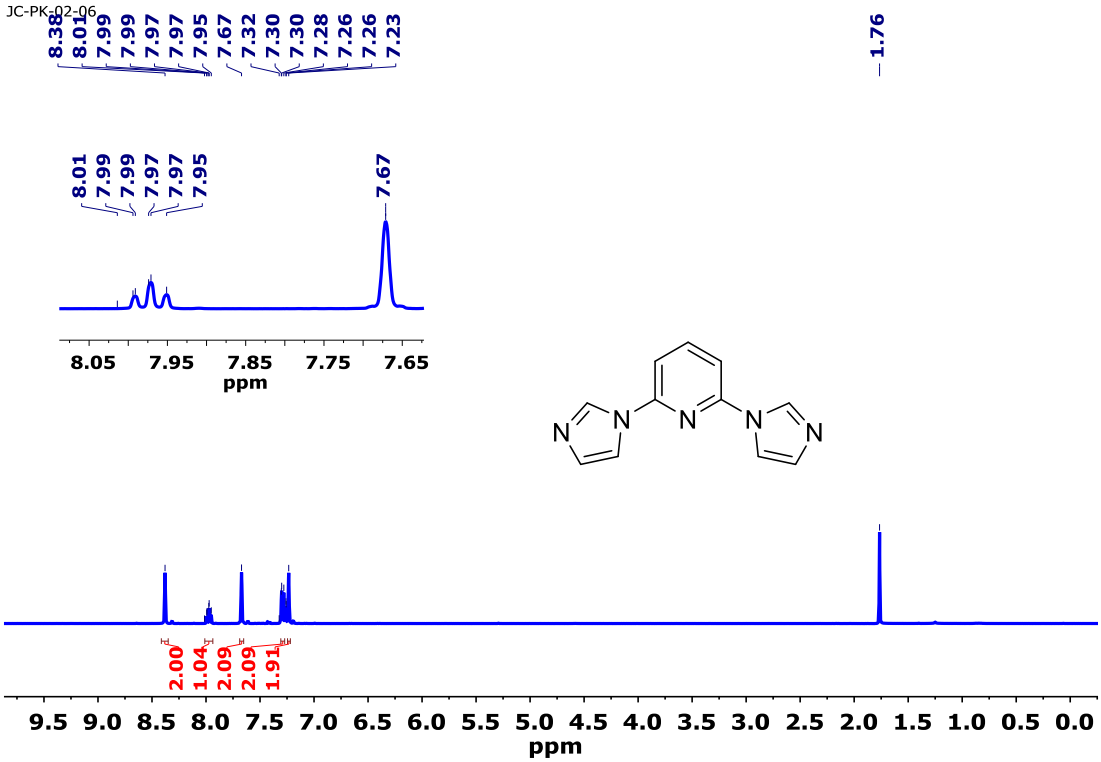

$^{1}$H NMR spectrum of **1f** (500 MHz, DMSO-d$_6$, 298 K).



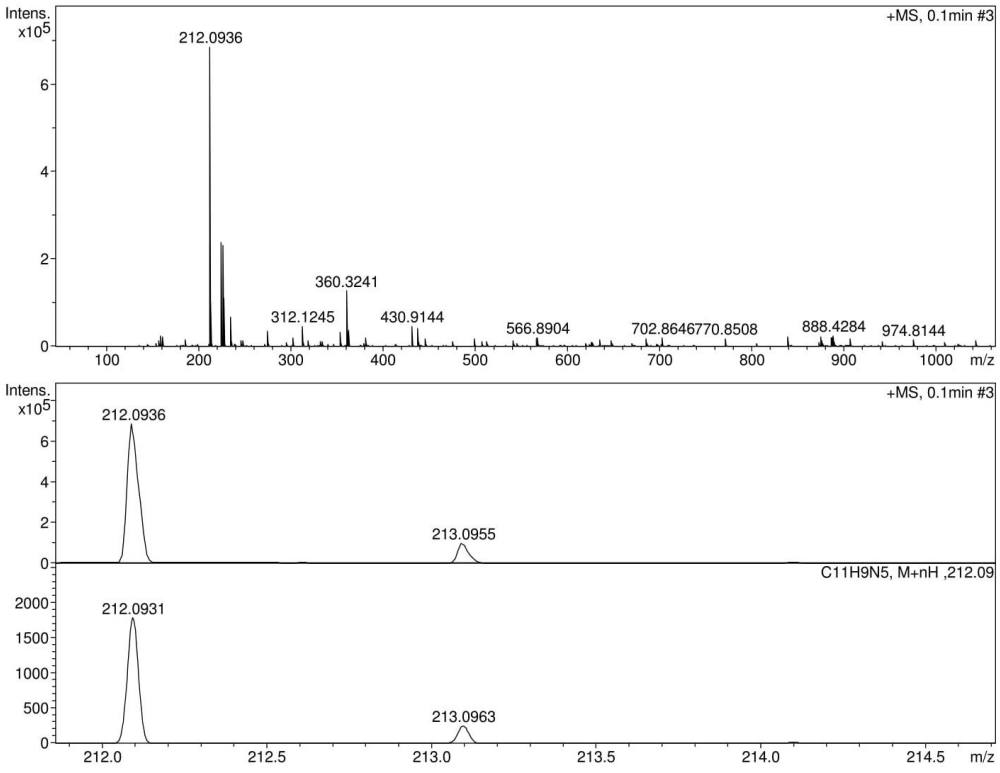

$^{13}$C{$^{1}$H} NMR spectrum of **1f** (126 MHz, DMSO-d$_6$, 298 K).



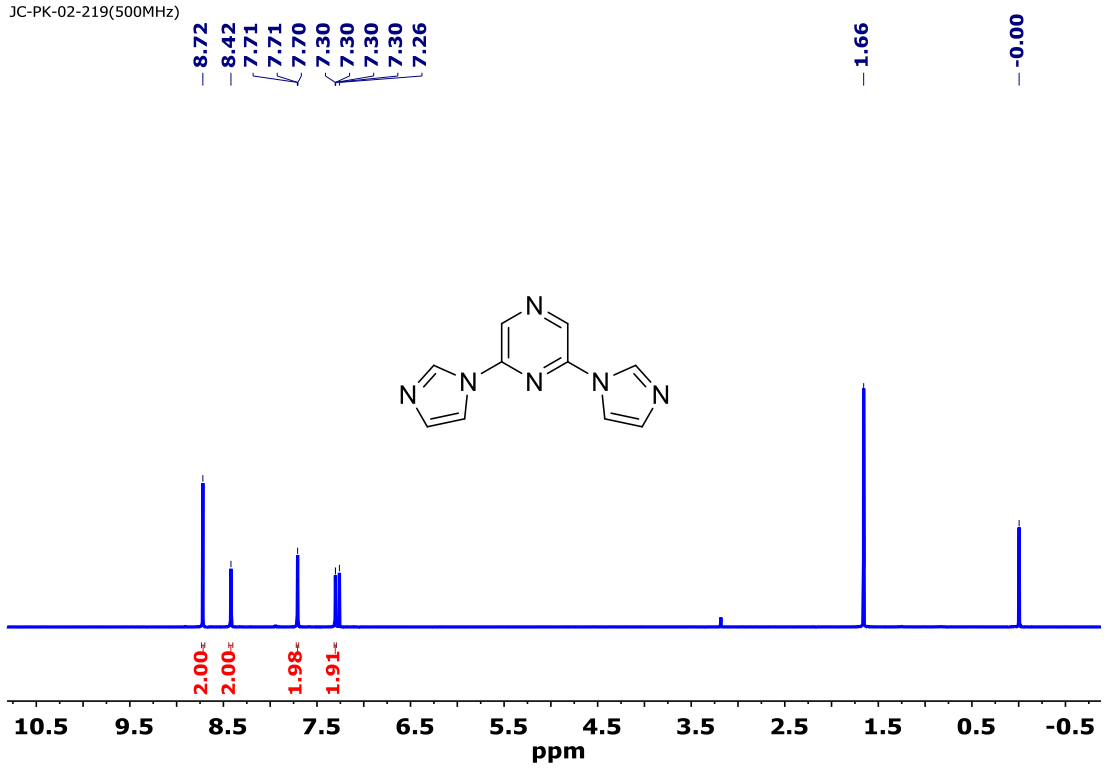

ESI-HRMS (positive ion mode) spectrum of **1f**



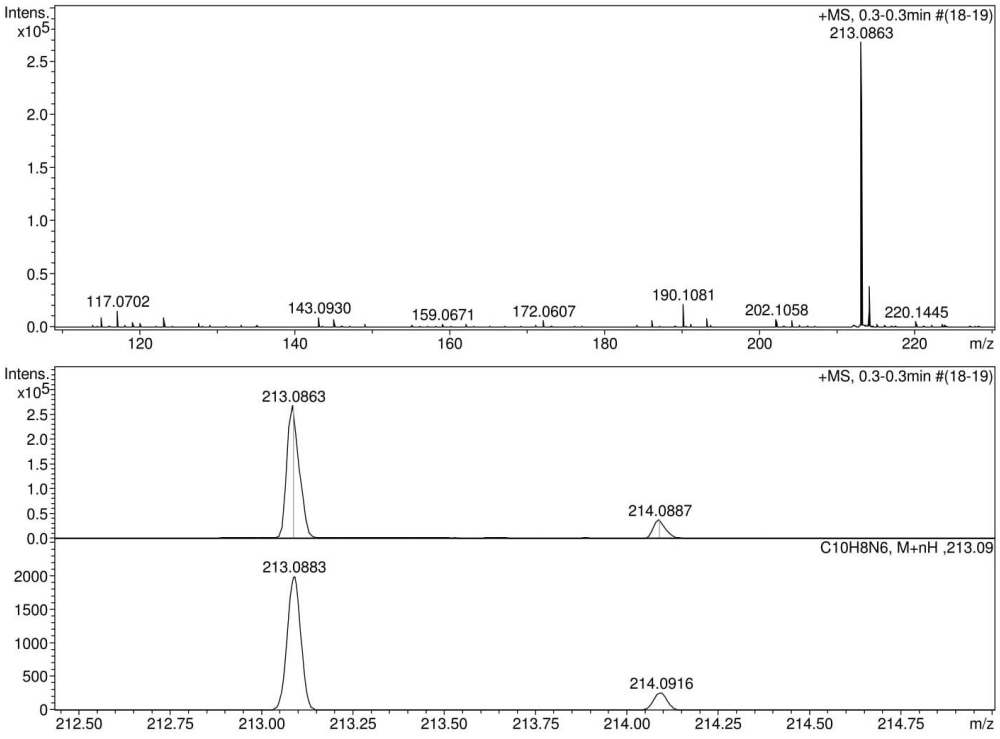

$^{1}$H NMR spectrum of **1g** (500 MHz, $CDCl_3$, 298 K).



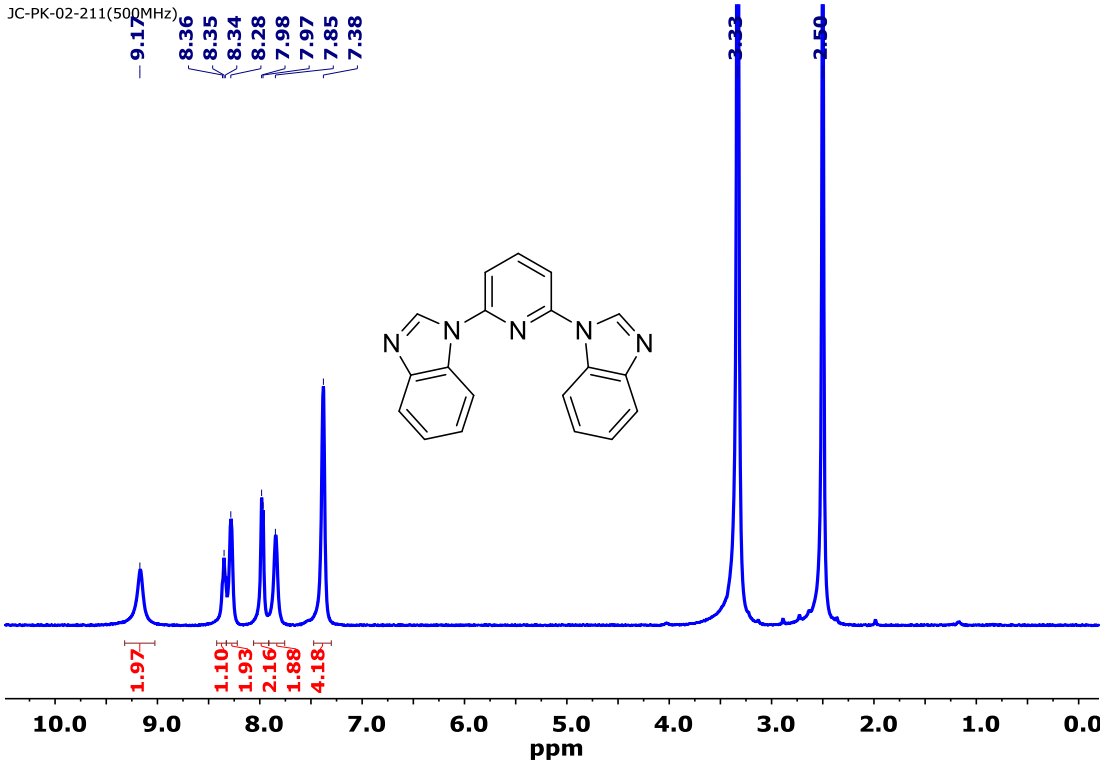

ESI-HRMS (positive ion mode) spectrum of **1g**



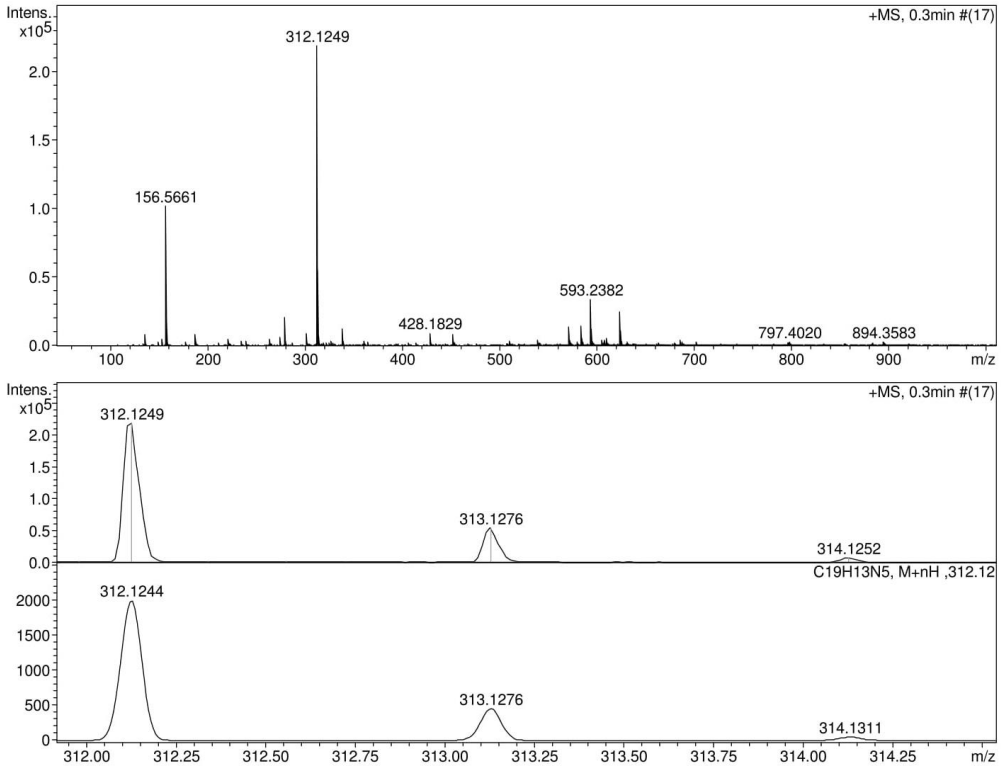

$^{1}$H NMR spectrum of **1h** (500 MHz, $CDCl_3$, 298K).



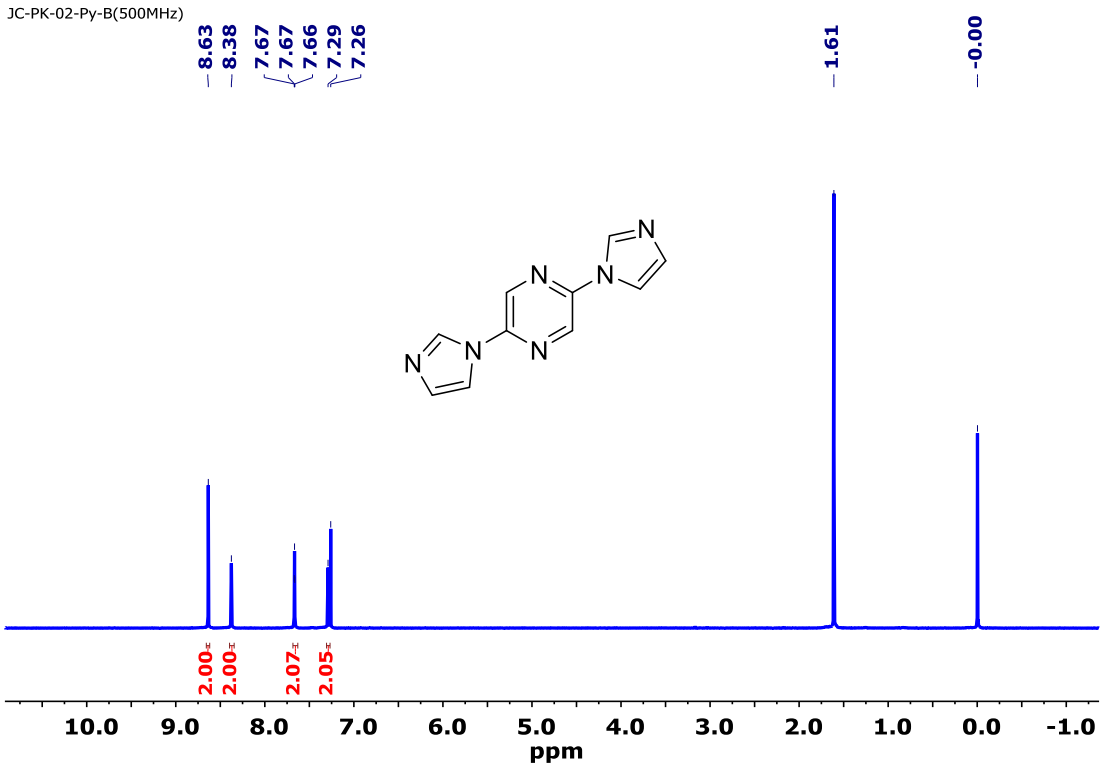

ESI-HRMS (positive ion mode) spectrum of **1h.**



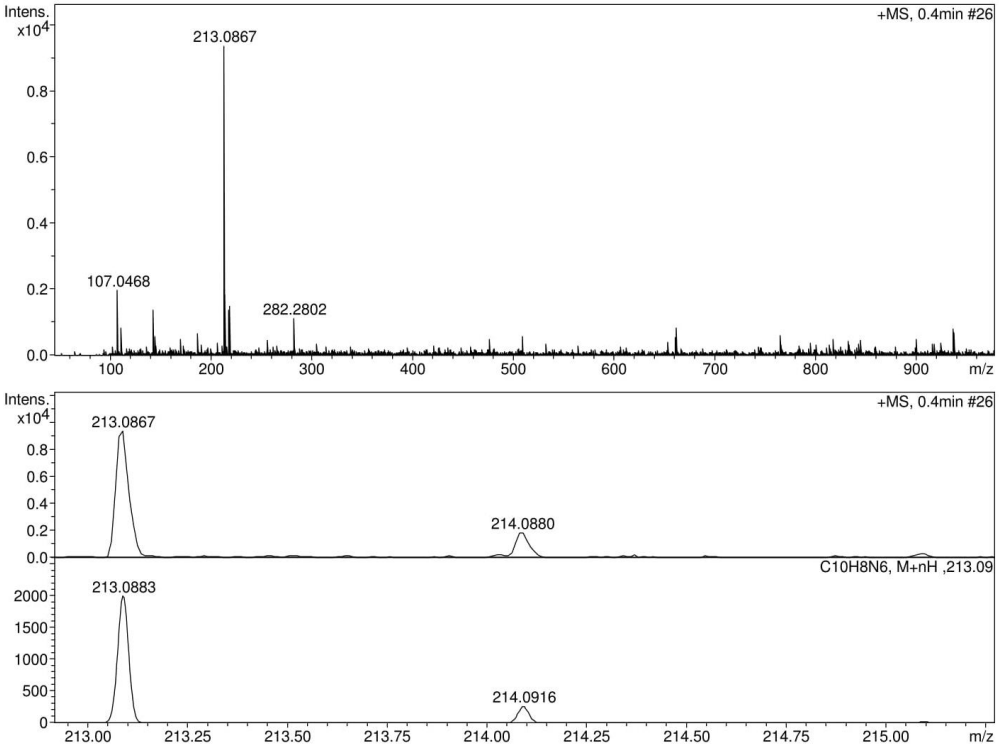

$^{1}$H NMR spectrum of **1i** (500 MHz, DMSO-$d_6$, 298K).



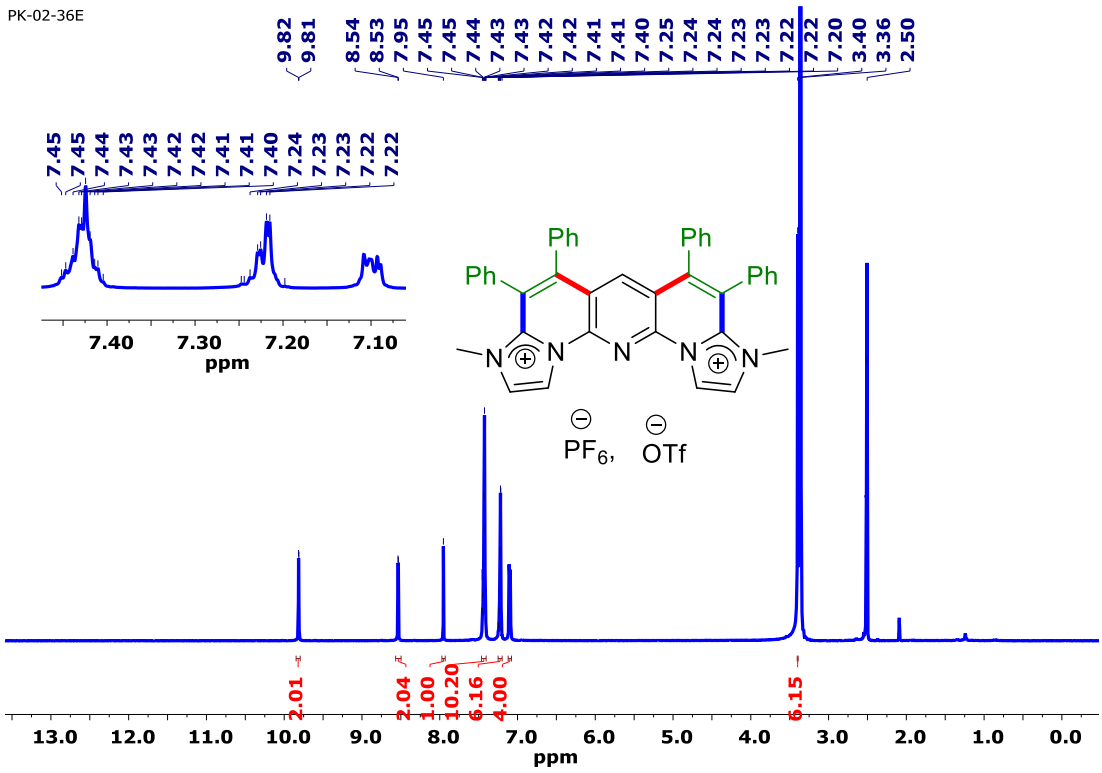

ESI-HRMS (positive ion mode) spectrum of **1i**



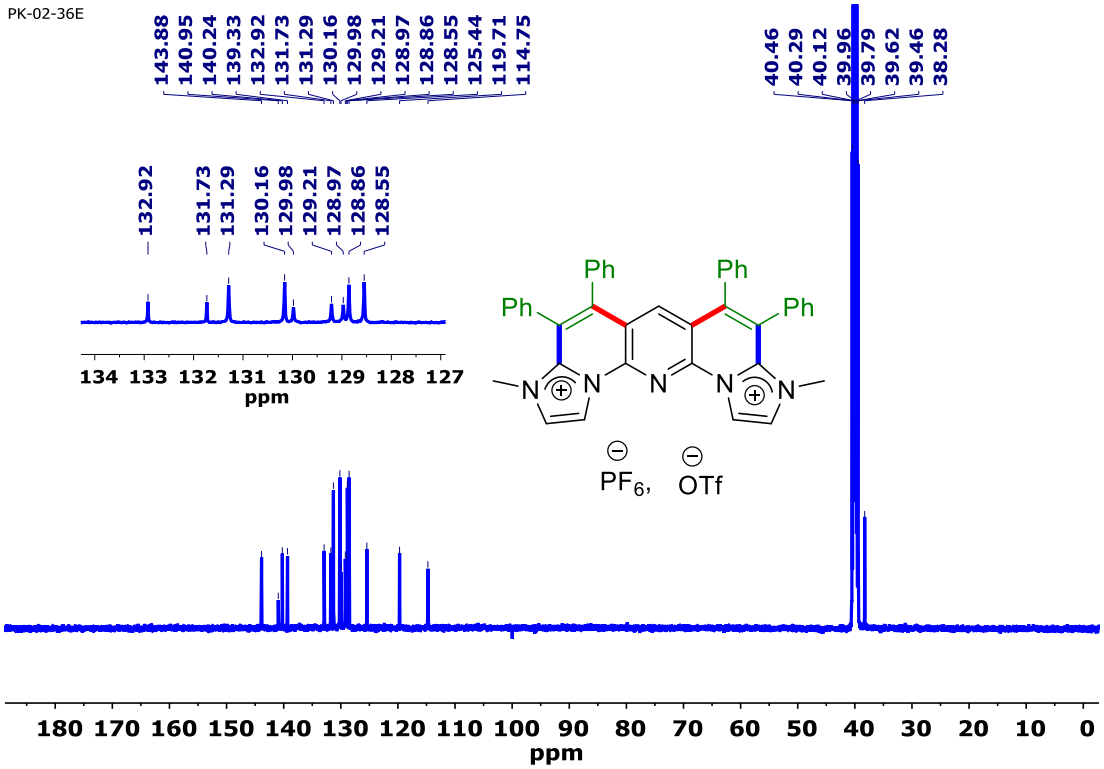

$^{1}$H NMR spectrum of **1j** (500 MHz, $CDCl_3$, 298 K).



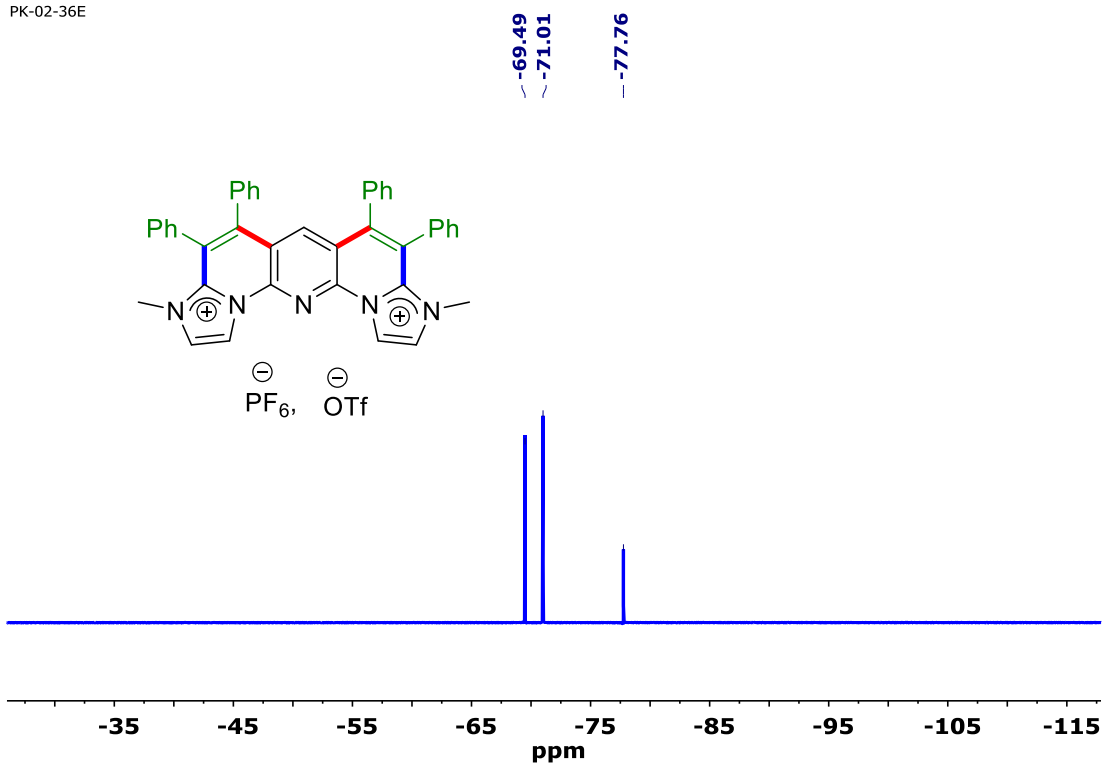

ESI-HRMS (positive ion mode) spectrum of **1j**



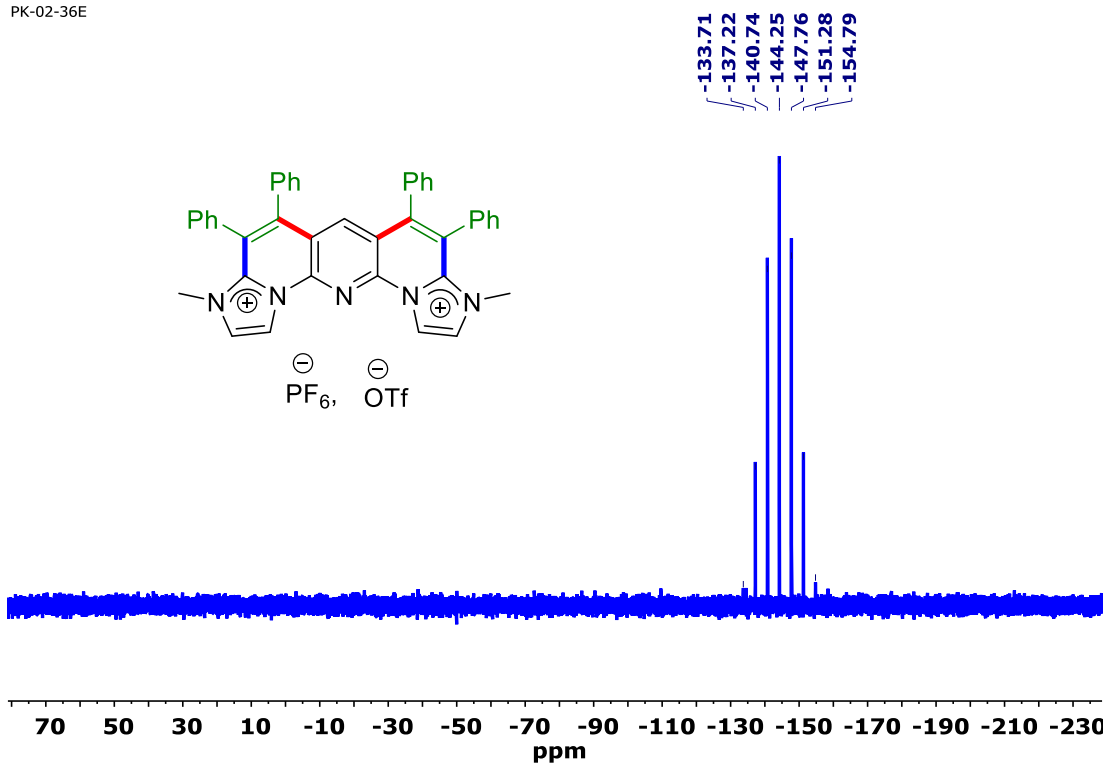

$^{1}$H NMR spectrum of **3a** (500 MHz, DMSO-$d_6$, 298 K).



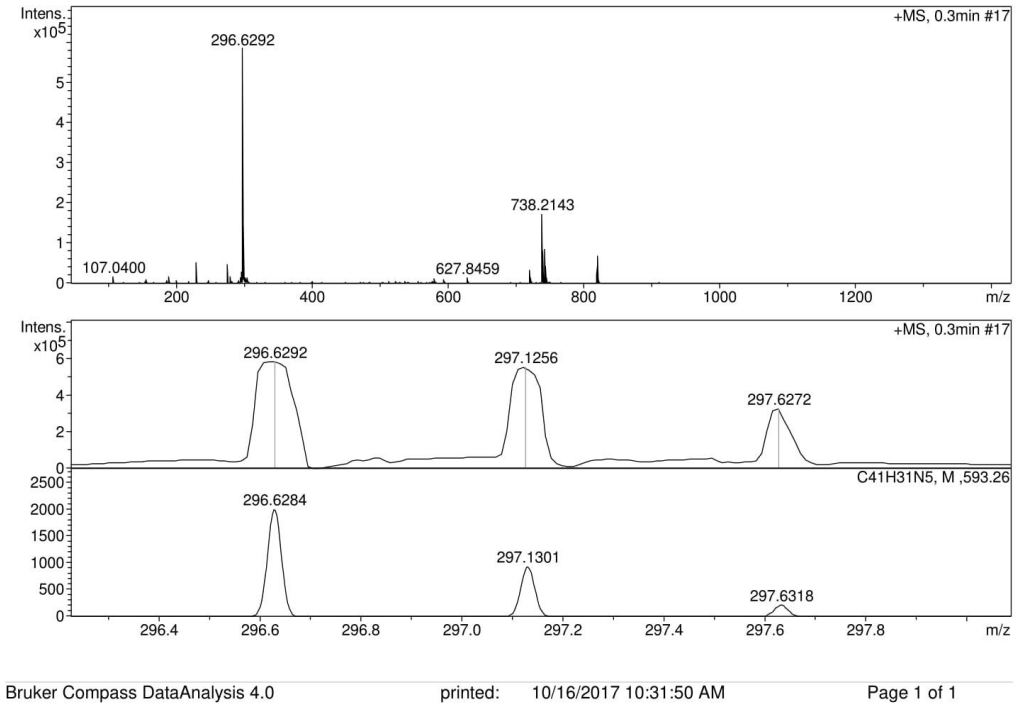

$^{13}$C{$^{1}$H} NMR spectrum of **3a** (126 MHz, DMSO-$d_6$, 298 K).



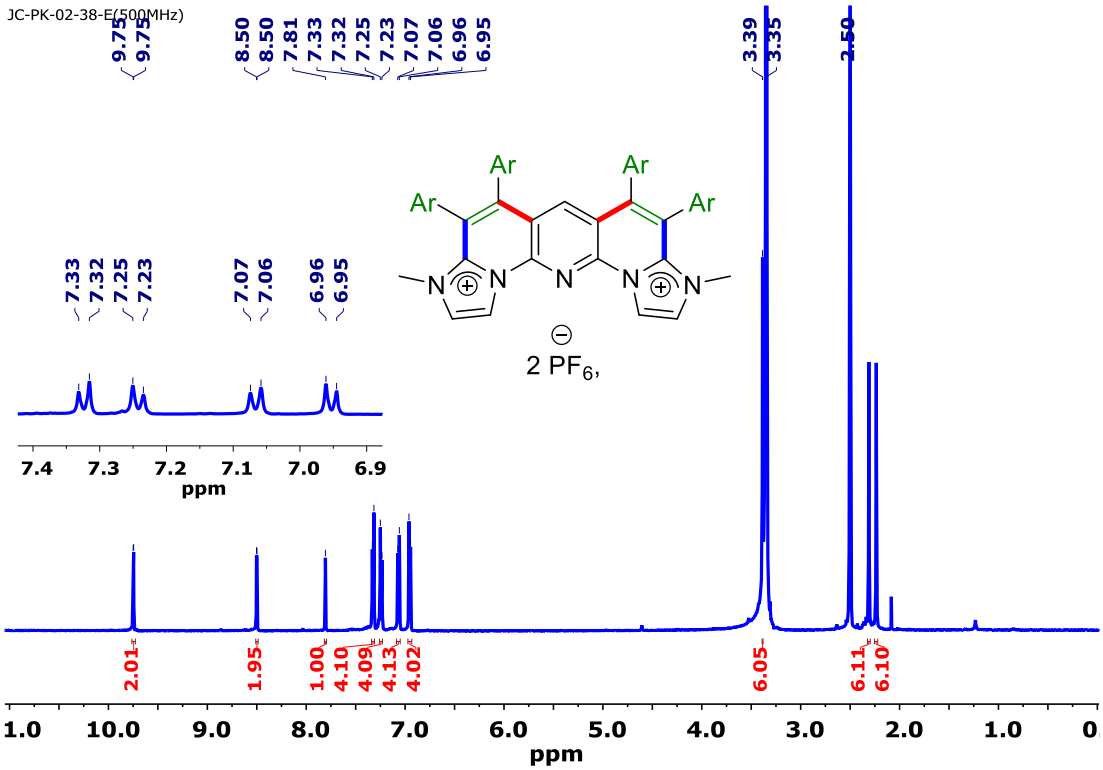

$^{19}$F NMR spectrum of **3a** (471 MHz, DMSO-$d_6$, 298 K).



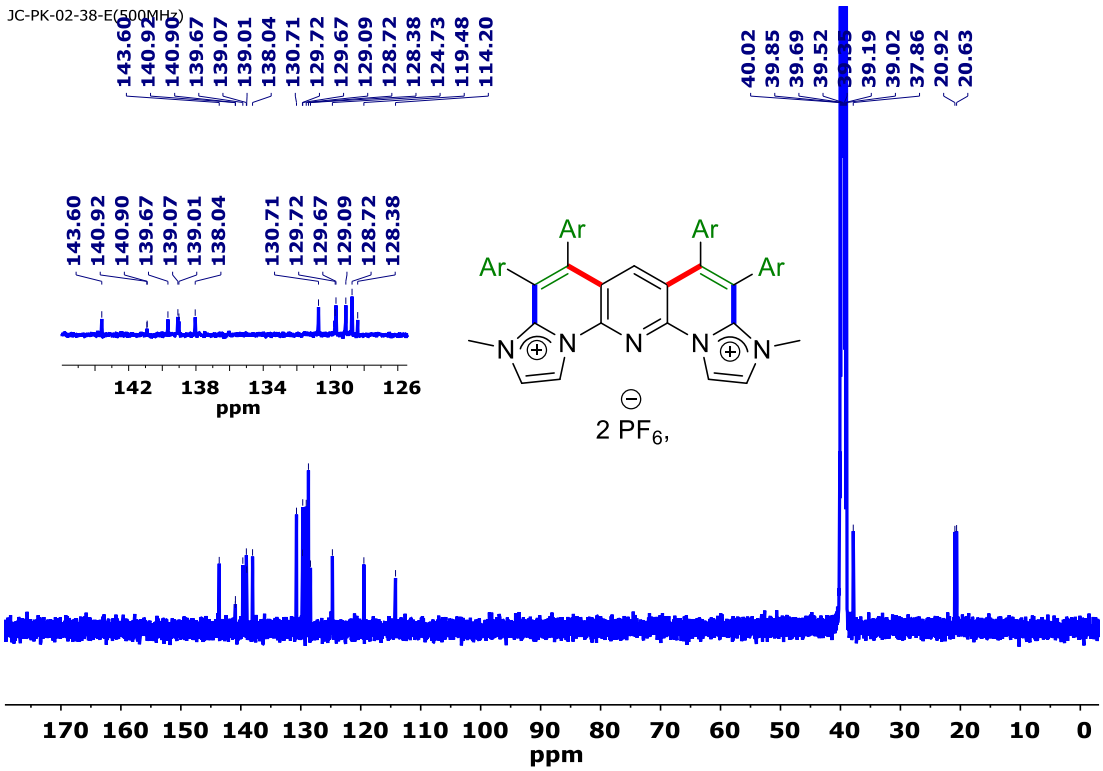

$^{31}$P NMR spectrum of **3a** (202 MHz, DMSO-$d_6$, 298 K).



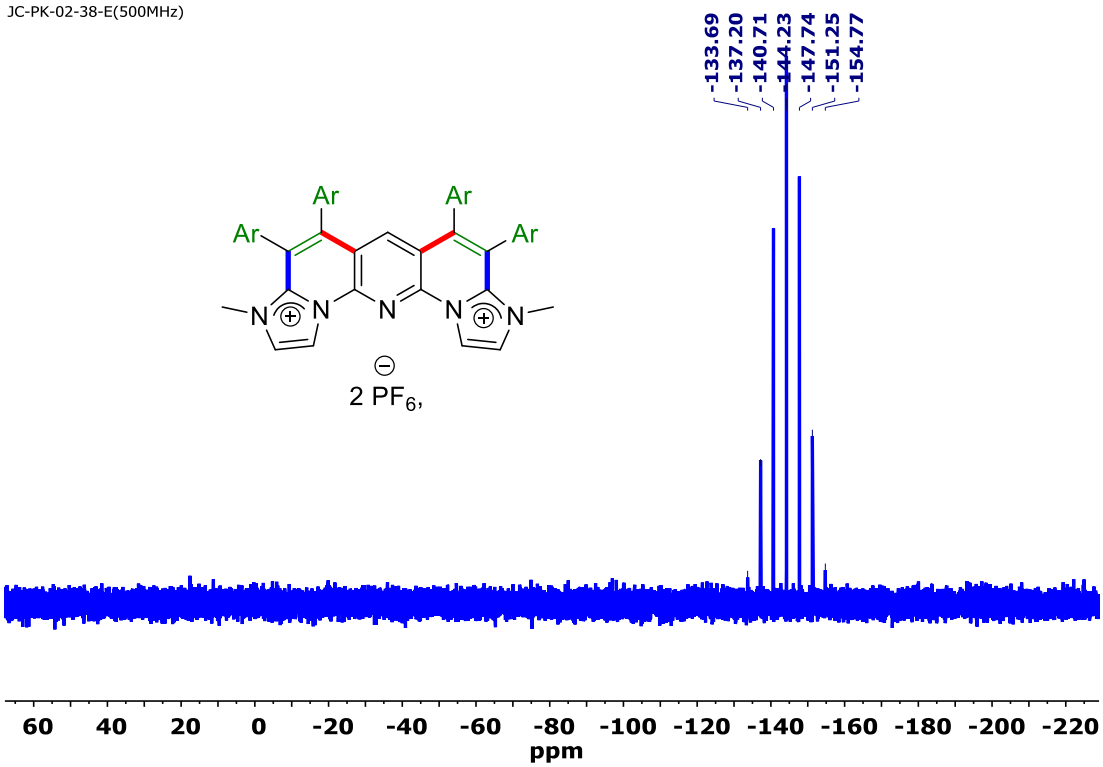

ESI-HRMS (positive ion mode) spectrum of **3a**



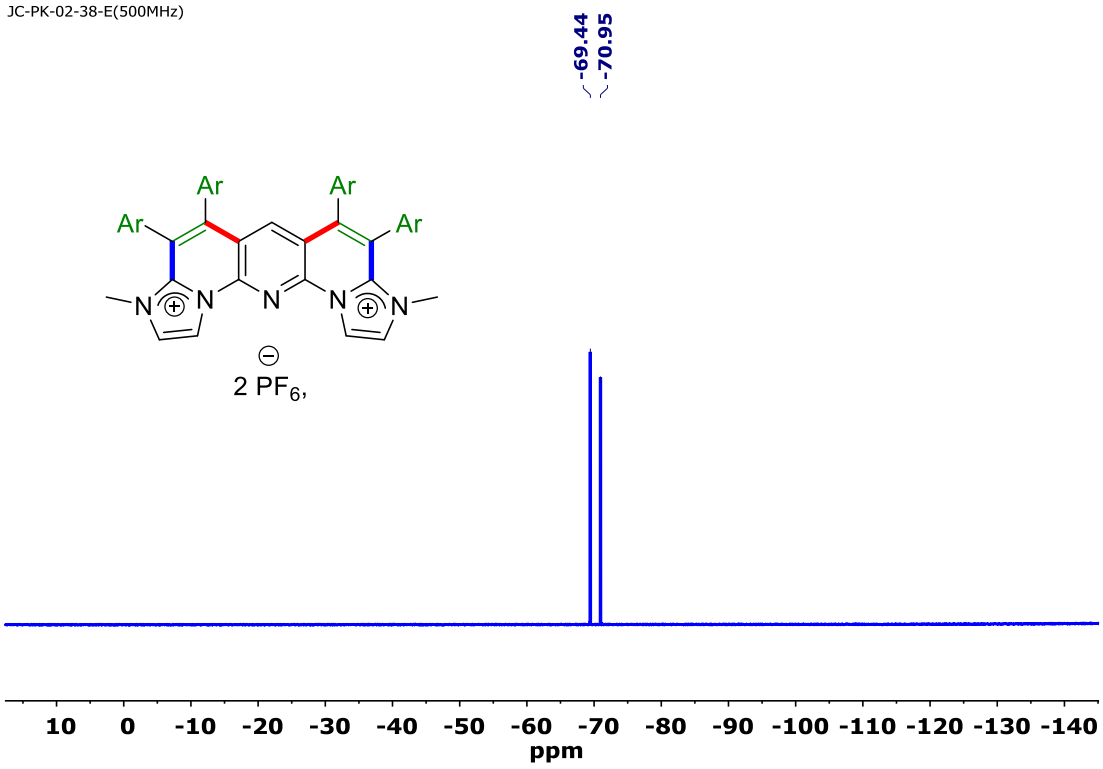

$^{1}$H NMR spectrum of **3b** (500 MHz, DMSO-$d_6$, 298 K).



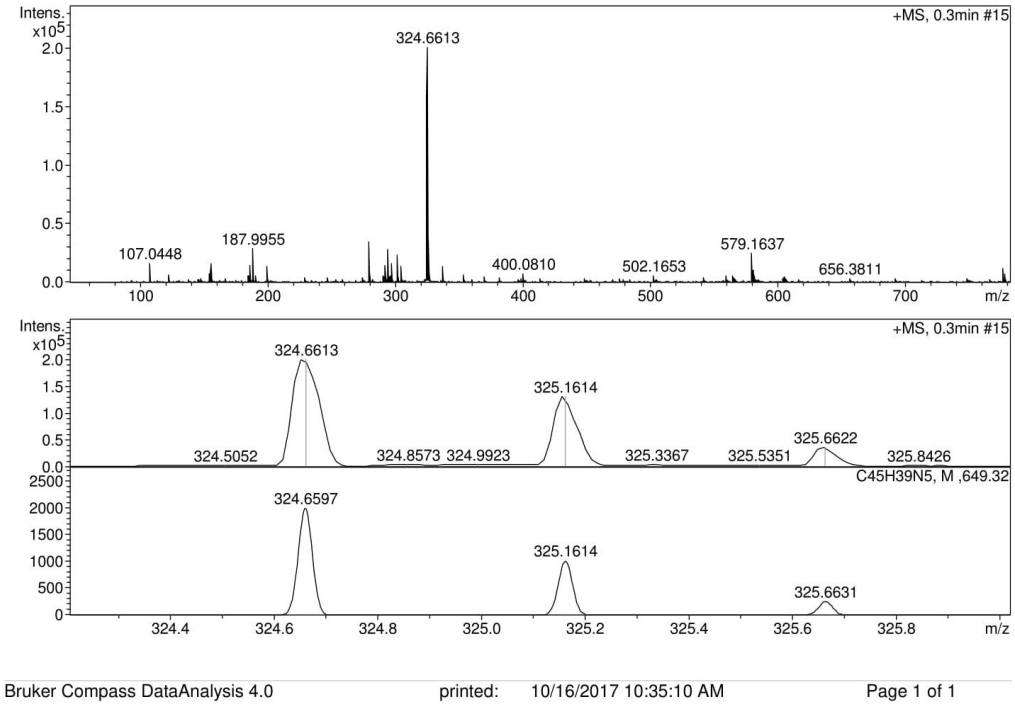

$^{13}C\{^{1}H\}$ NMR spectrum of **3b** (126 MHz, DMSO-$d_6$, 298K).



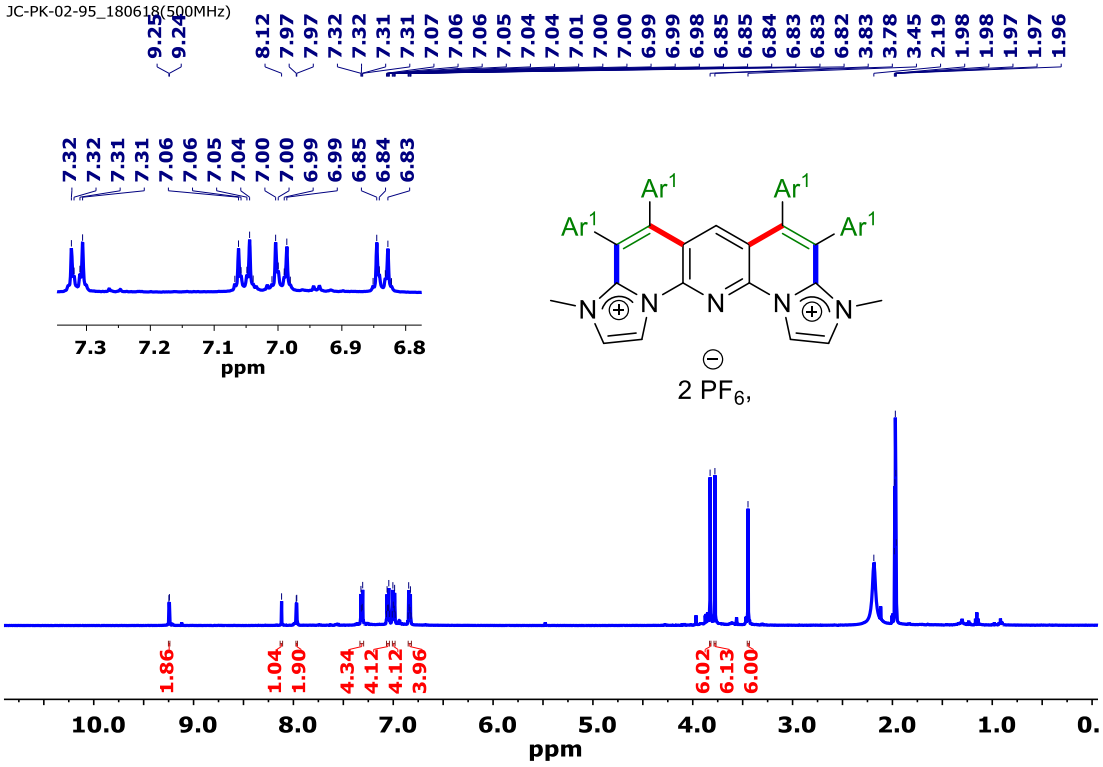

$^{31}P$ NMR spectrum of **3b** (202 MHz, DMSO-$d_6$, 298 K).



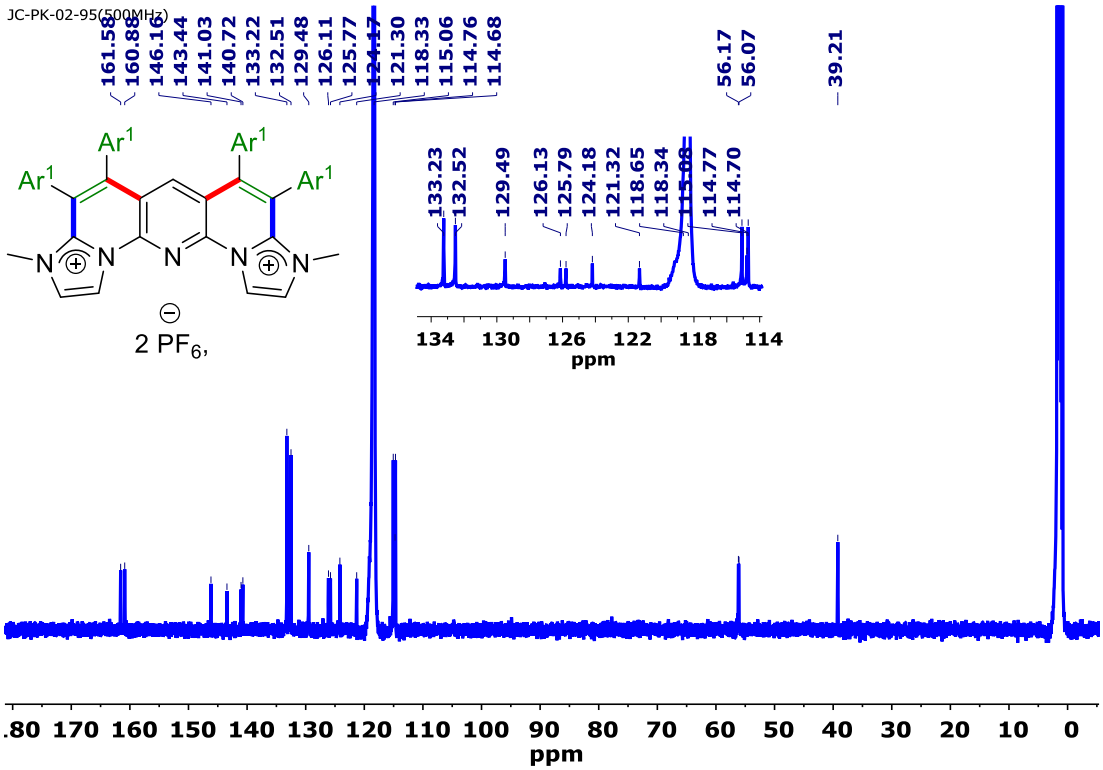

$^{19}$F NMR spectrum of **3b** (471 MHz, DMSO-$d_6$, 298K).



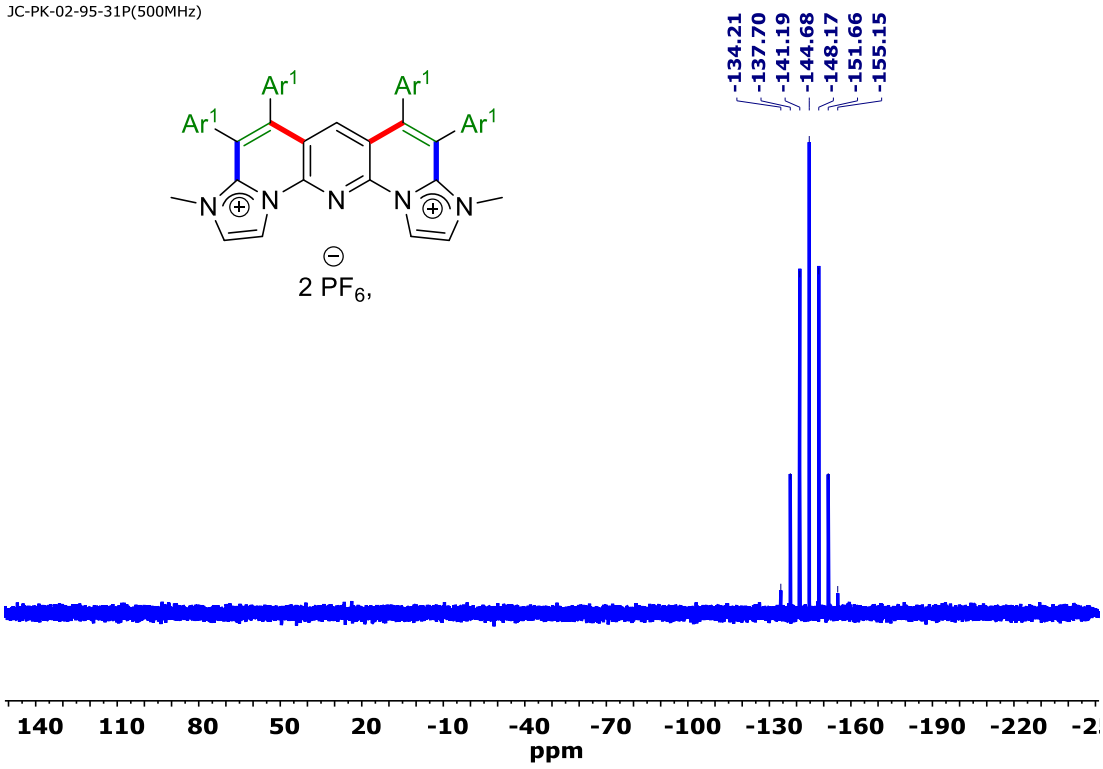

ESI-HRMS (positive ion mode) spectrum of **3b.**



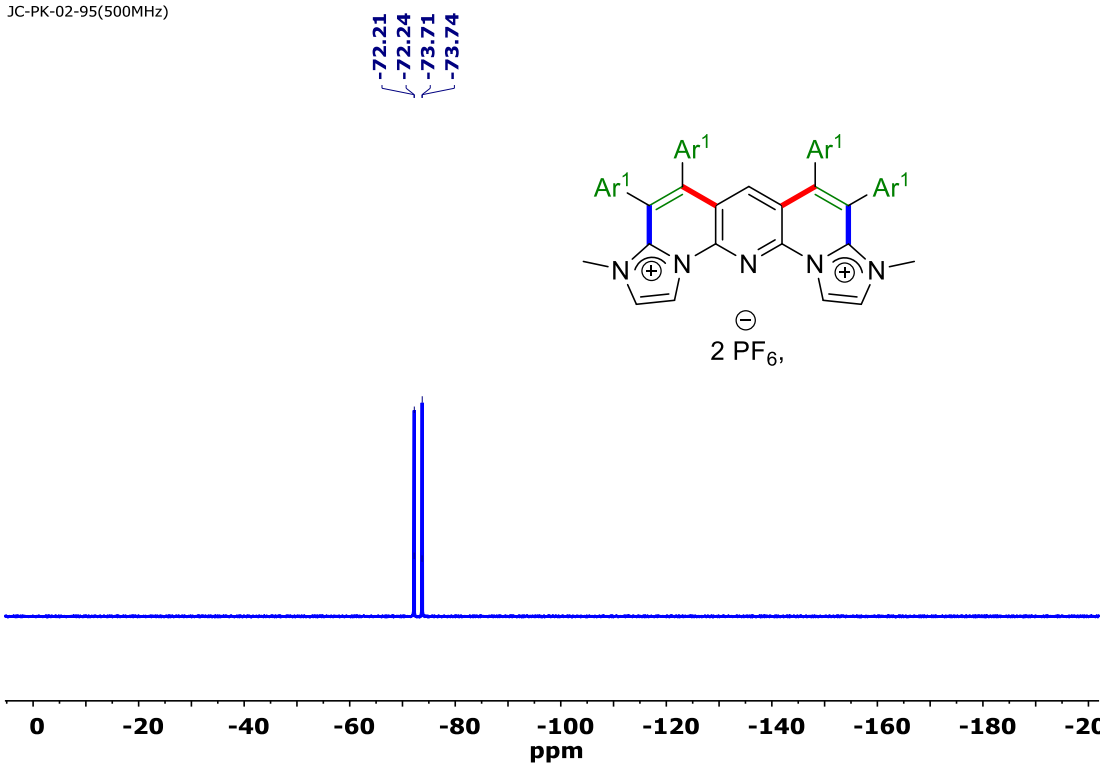

$^{1}$H NMR spectrum of **3c** (400 MHz, $CD_3CN$, 298 K).



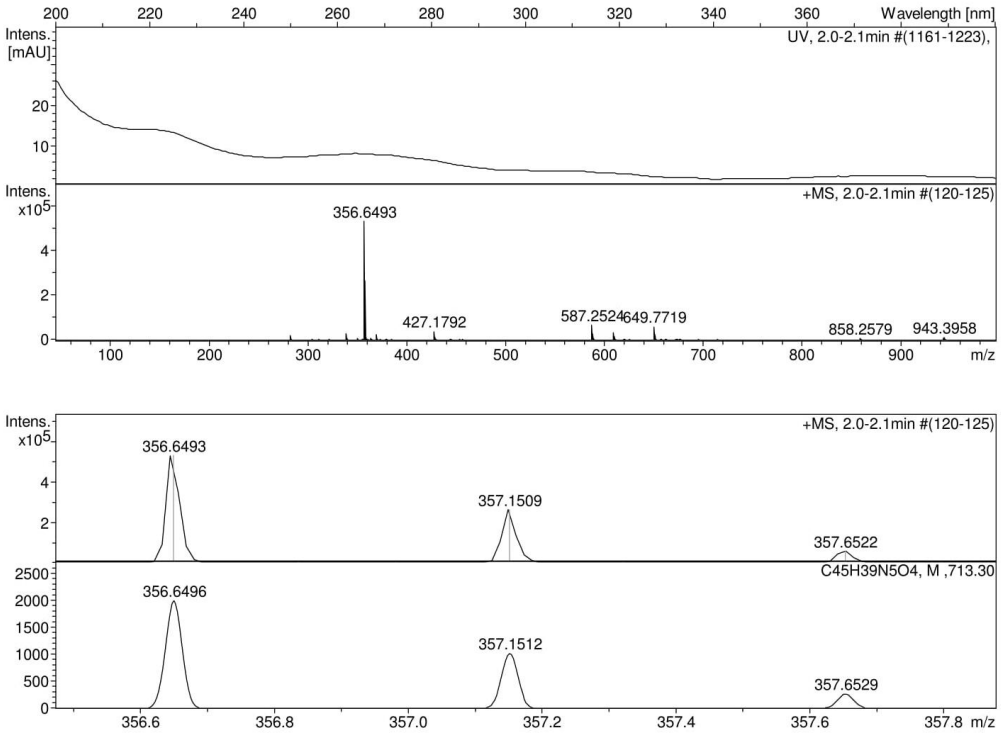

$^{13}$C{$^{1}$H} NMR spectrum of **3c** (126 MHz, $CD_3CN$, 298 K).



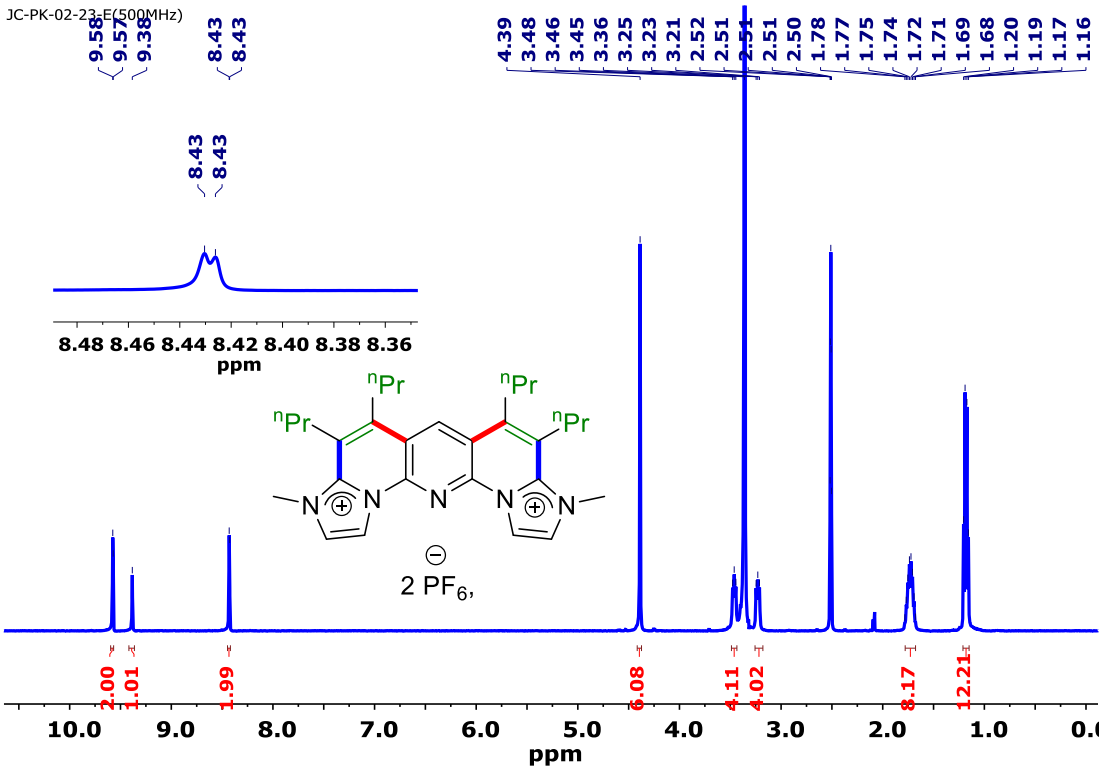

$^{31}$P NMR spectrum of **3c** (202 MHz, DMSO-$d_6$, 298 K).



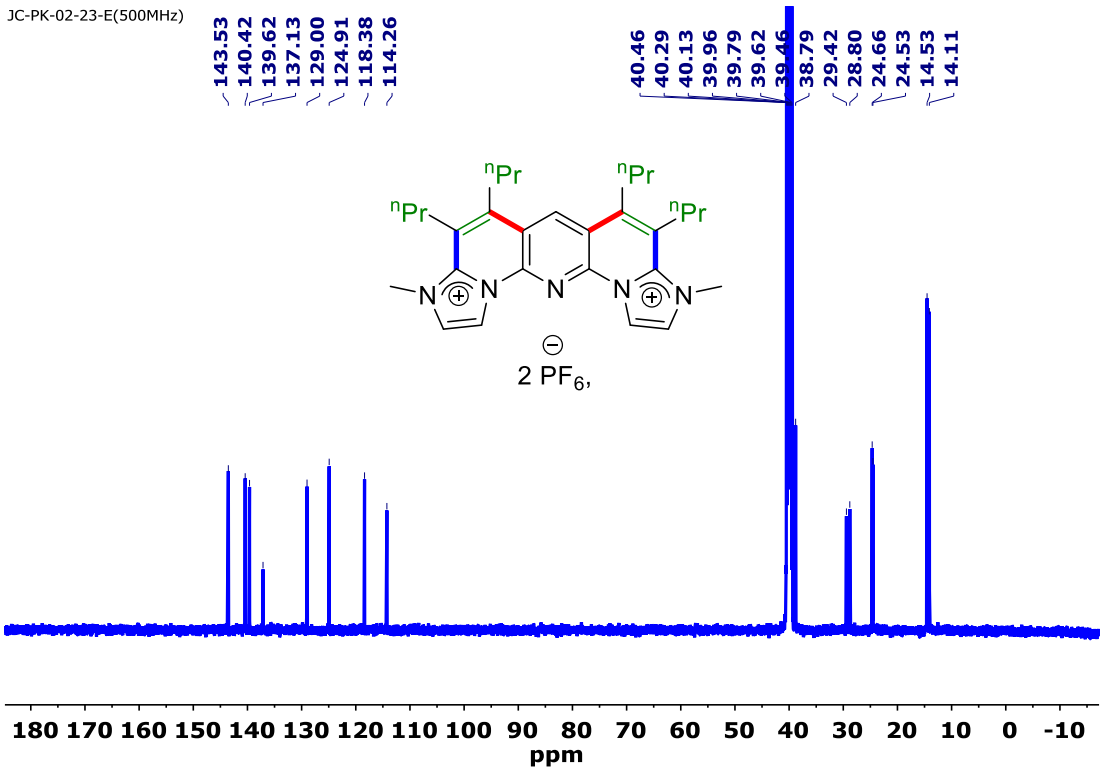

$^{19}$F NMR spectrum of **3c** (471 MHz, $CD_3CN$, 298 K).



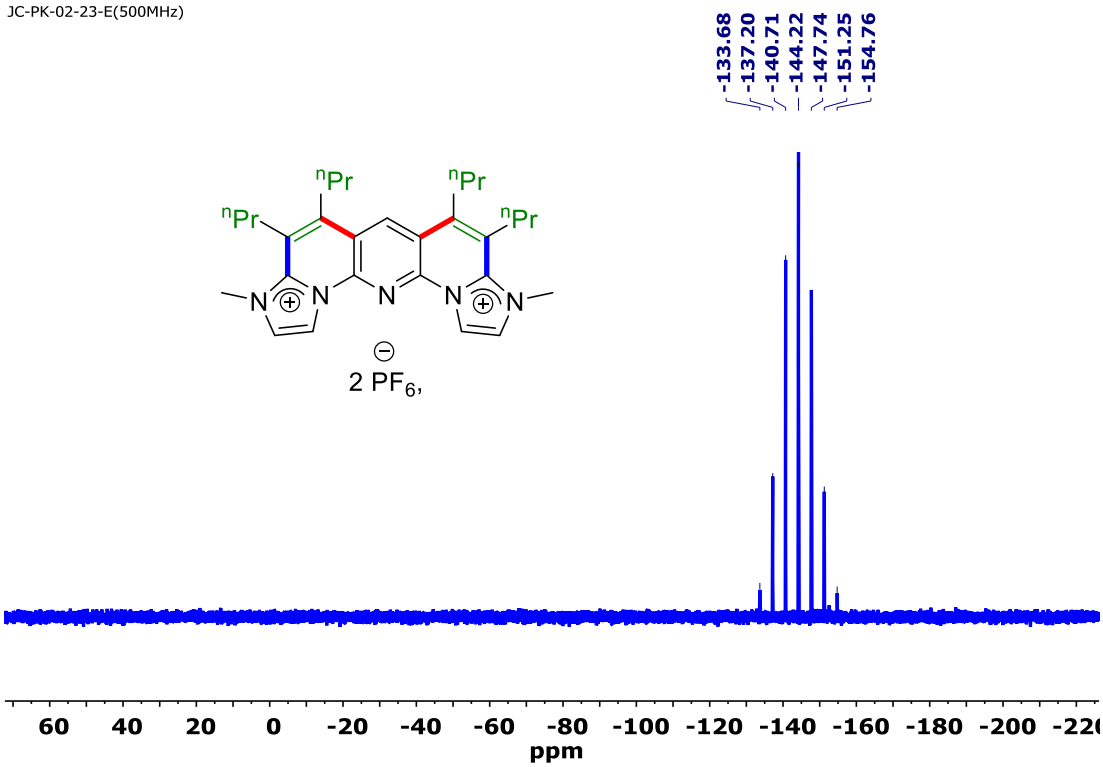

ESI-HRMS (positive ion mode) spectrum of **3c.**



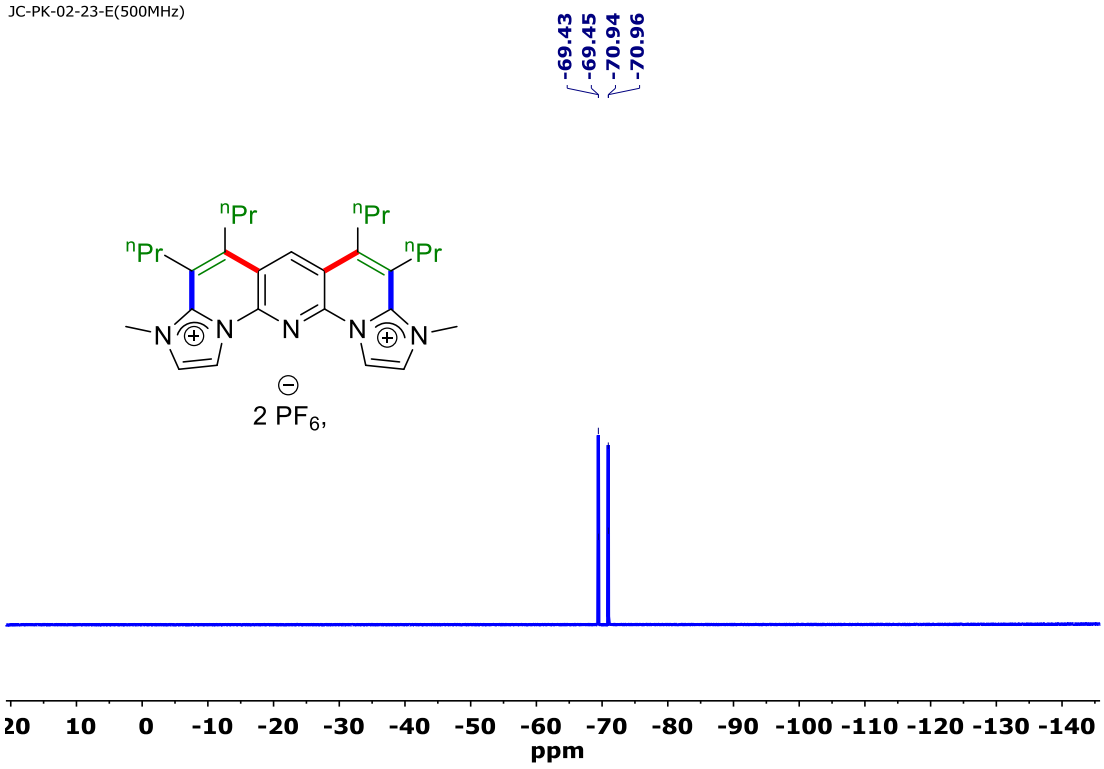

$^{1}$H NMR spectrum of **3d** (500 MHz, DMSO-d$_6$, 298K).



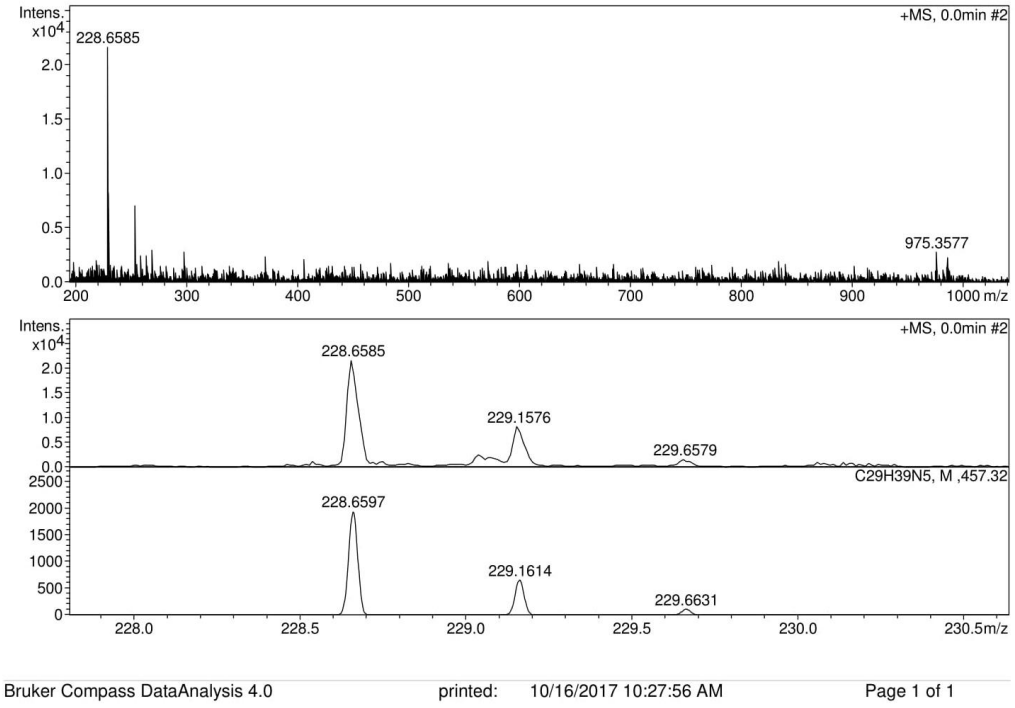

$^{13}C\{^{1}H\}$ NMR spectrum of **3d** (126 MHz, DMSO-$d_6$, 298 K).



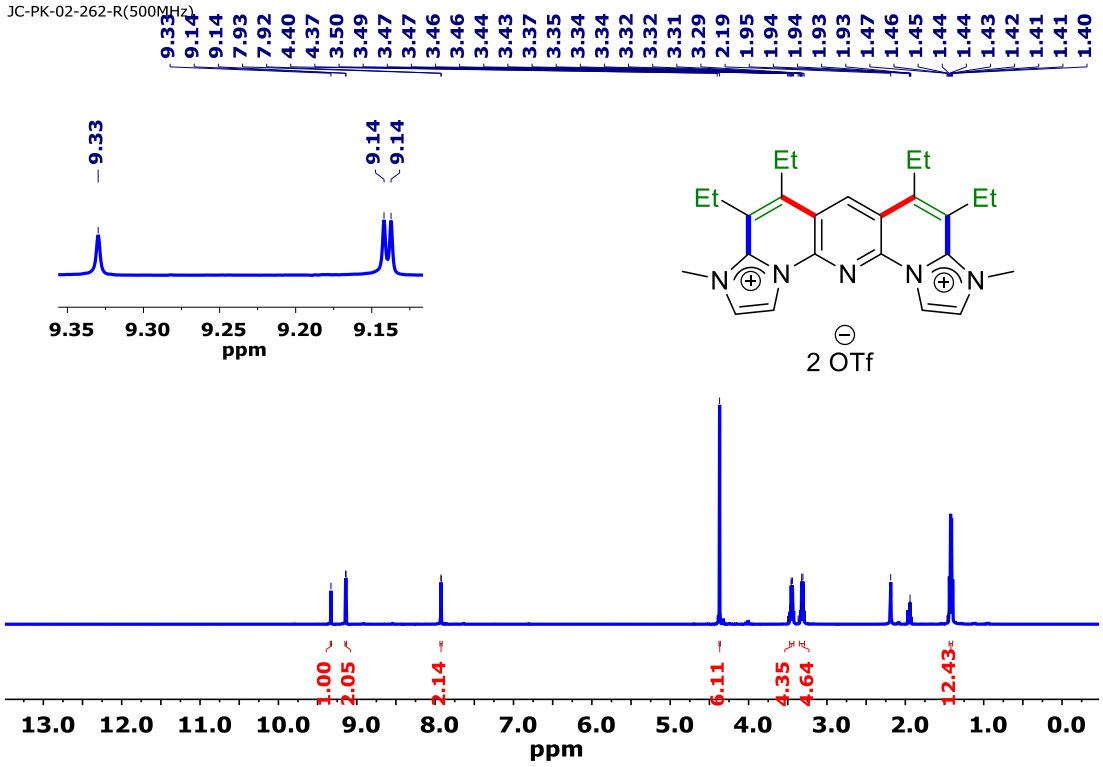

$^{31}P$ NMR spectrum of **3d** (202 MHz, DMSO-$d_6$, 298K).



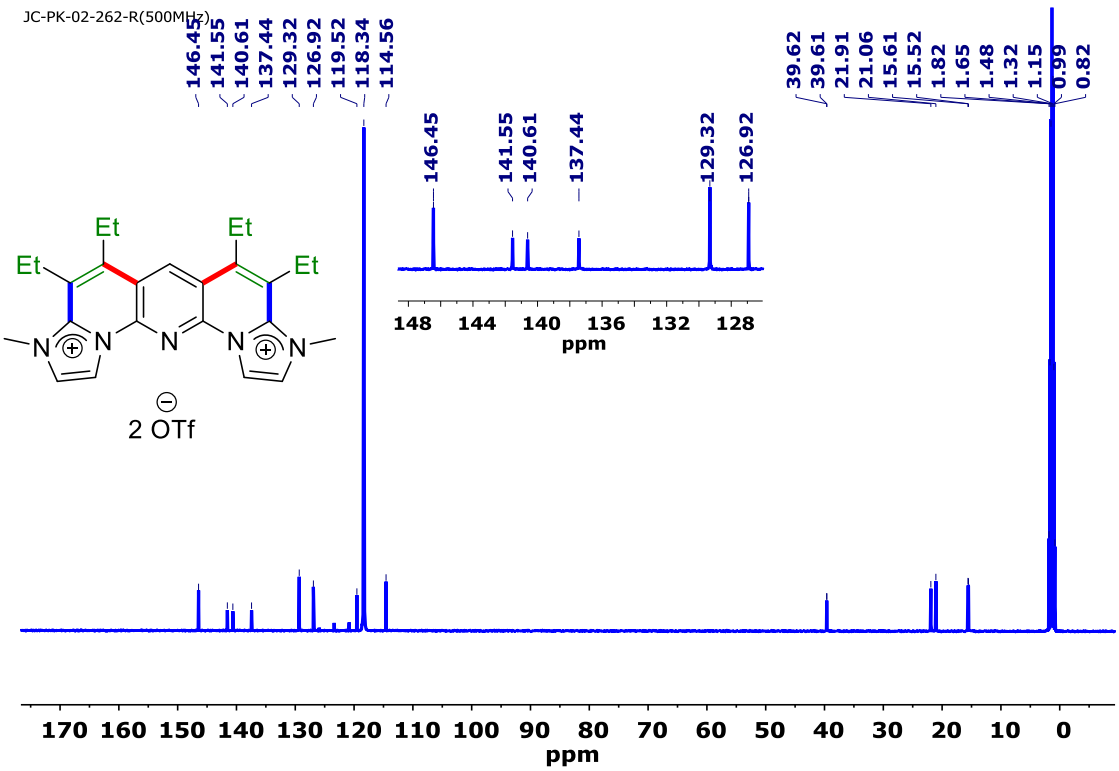

$^{19}$F NMR spectrum of **3d** (471 MHz, DMSO-$d_6$, 298 K).



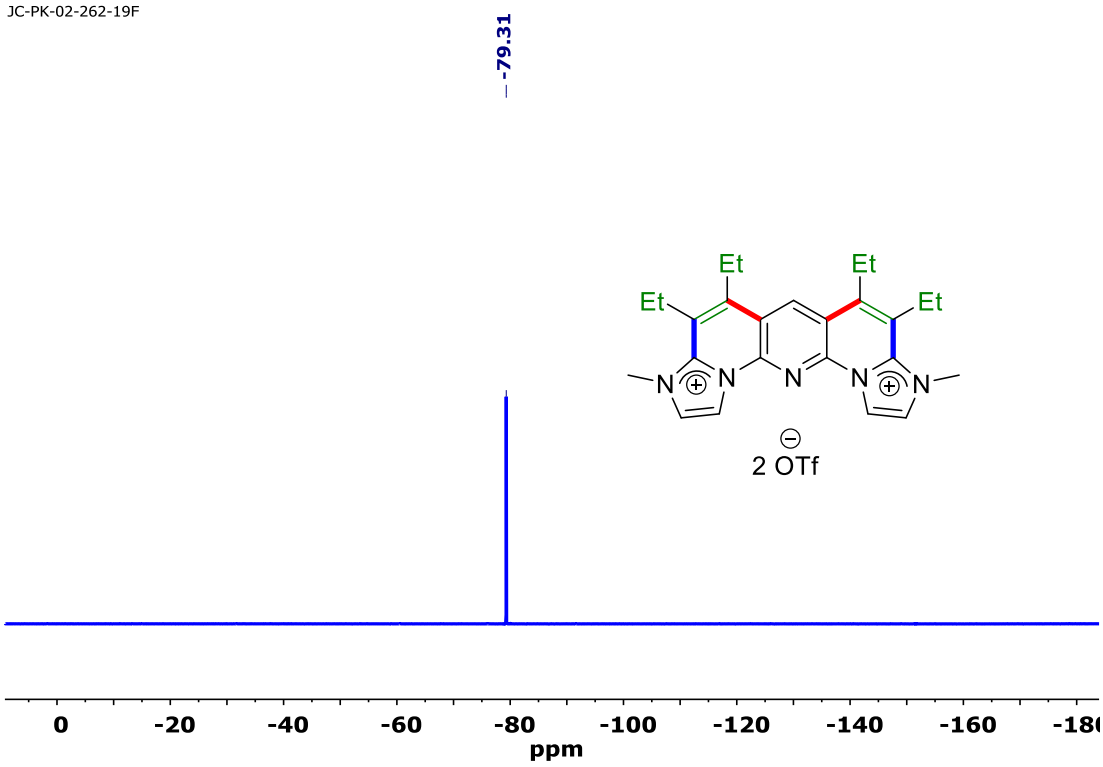

ESI-HRMS (positive ion mode) spectrum of **3d**



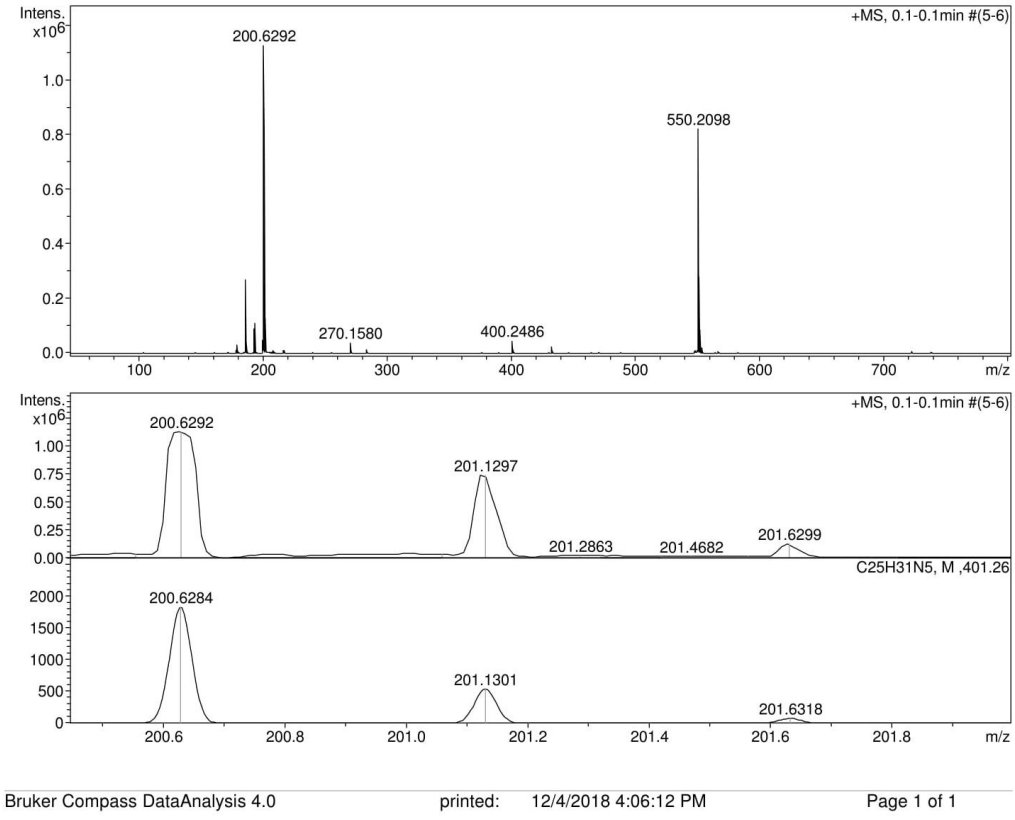

$^{1}$H NMR spectrum of **3e** (500 MHz, $CD_3CN$, 298 K).



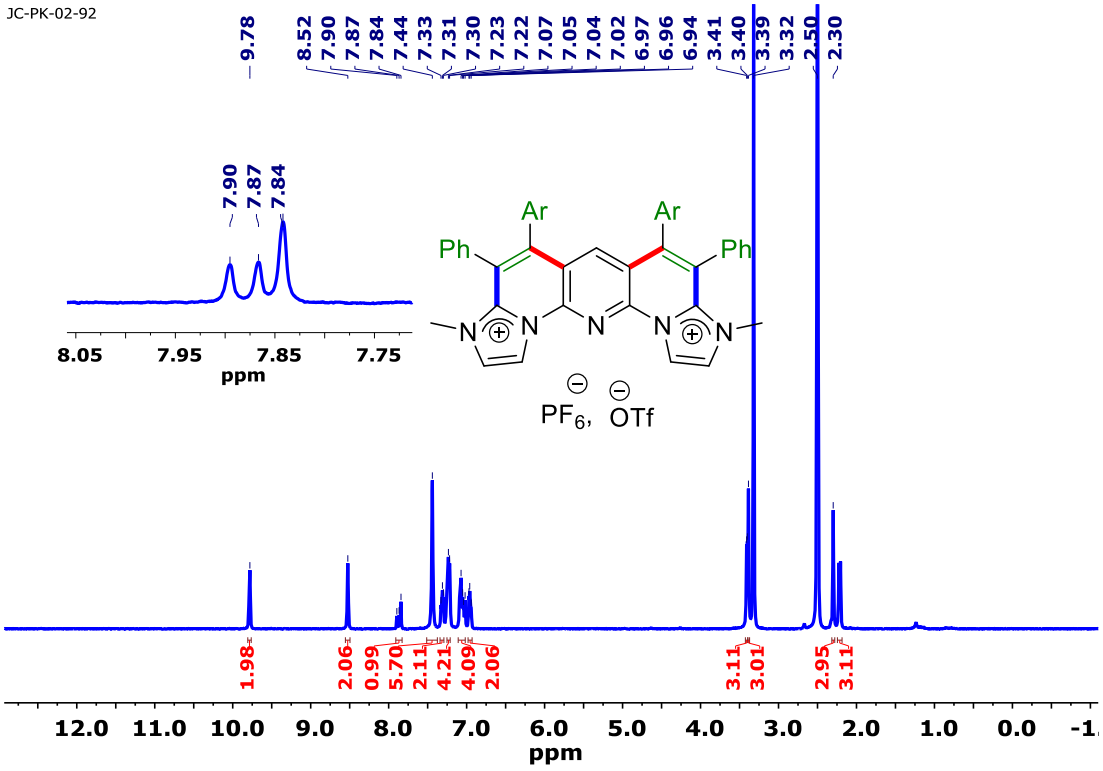

$^{13}$C{$^{1}$H} NMR spectrum of **3e** (126 MHz, $CD_3CN$, 298K).



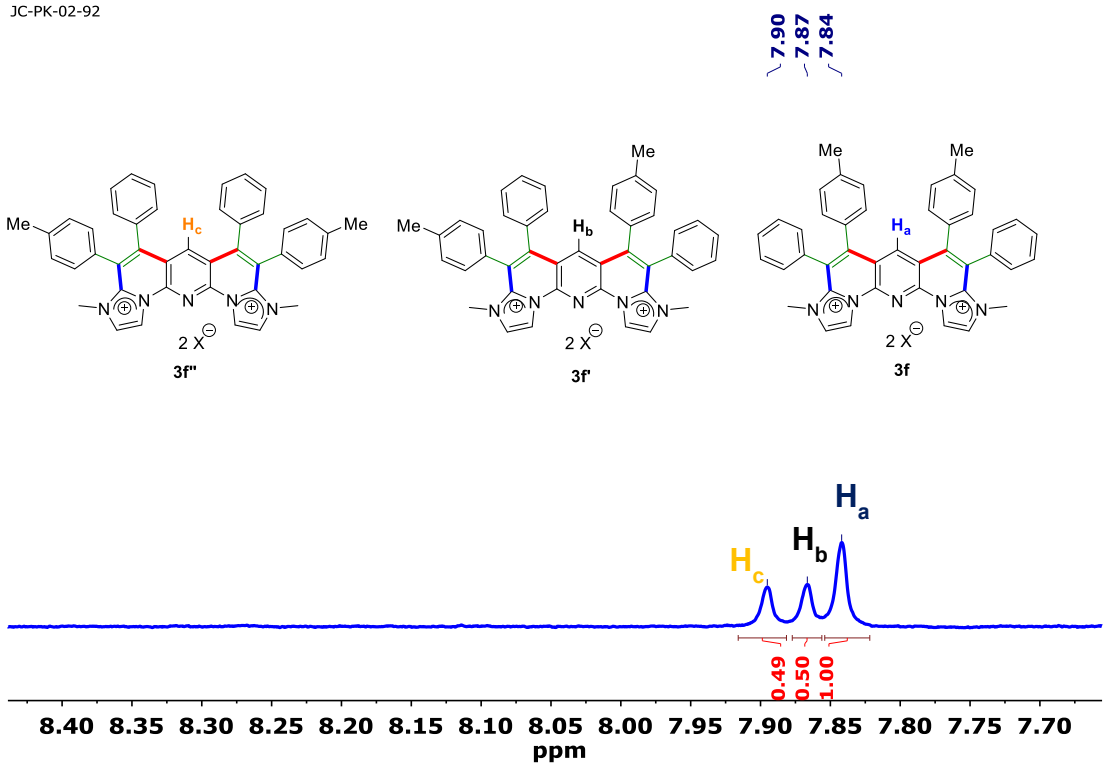

$^{19}$F NMR spectrum of **3e** (471 MHz, DMSO-$d_6$, 298K).



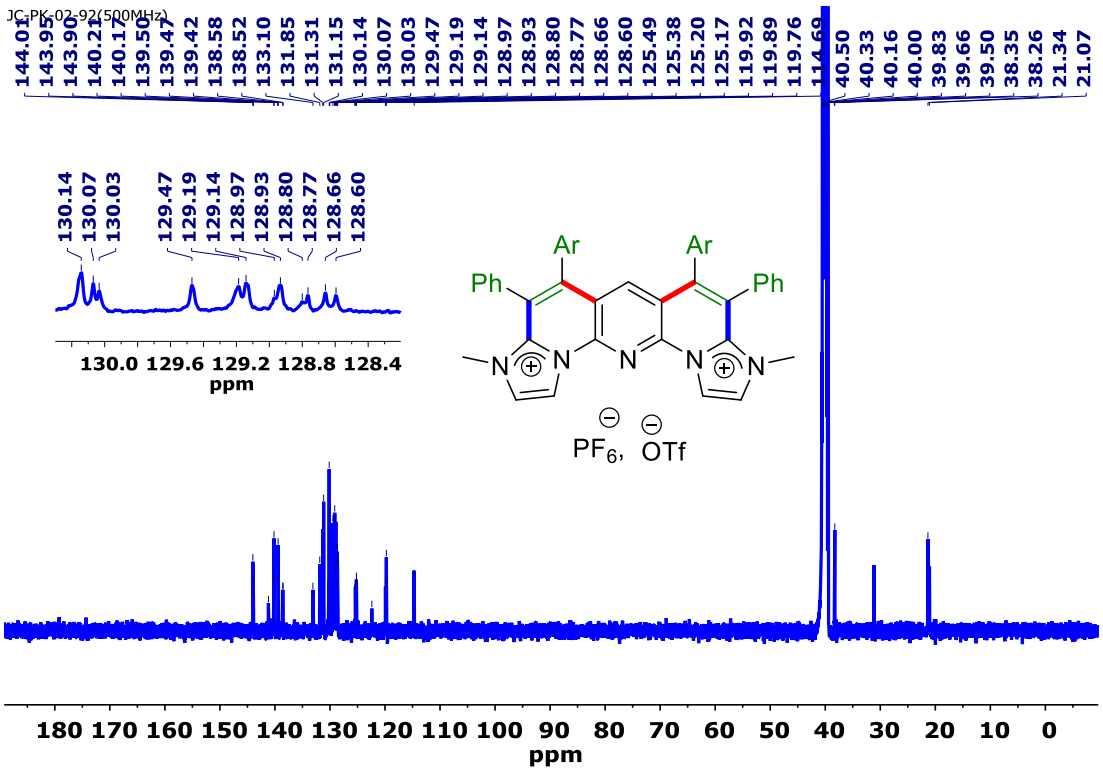

ESI-HRMS (positive ion mode) spectrum of **3e.**



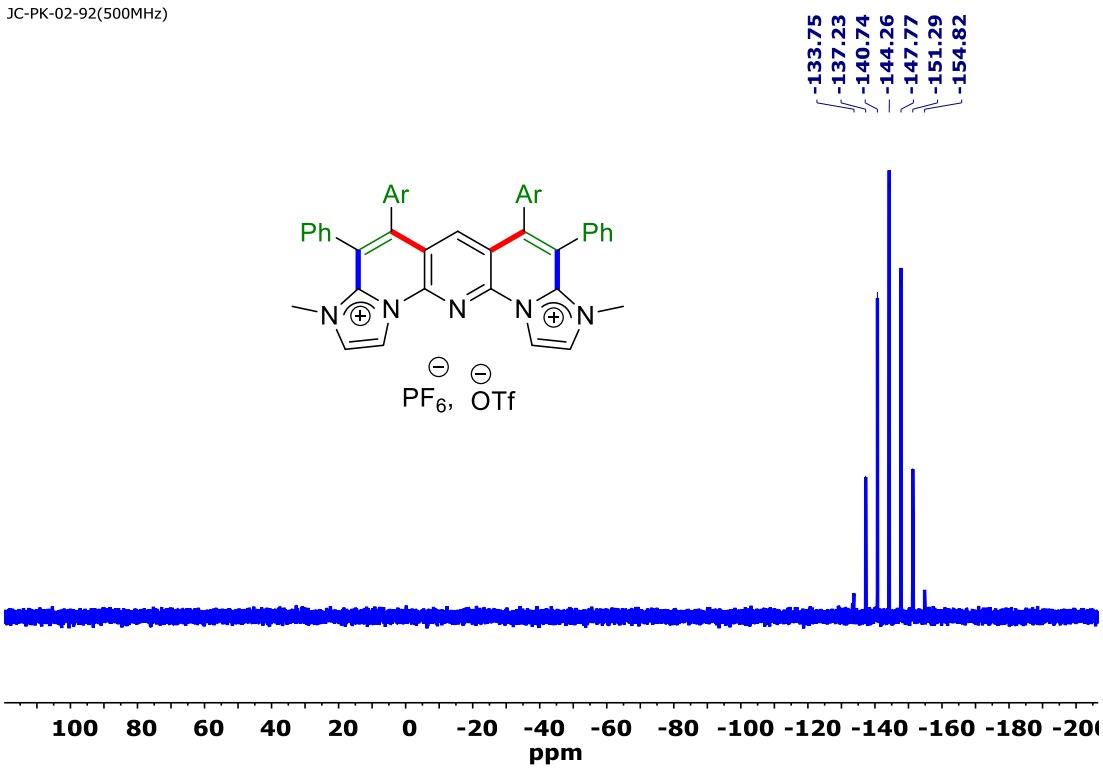

$^{1}$H NMR spectrum of **3f (**mixture of 3 isomers) (500 MHz, DMSO-$d_6$, 298 K).



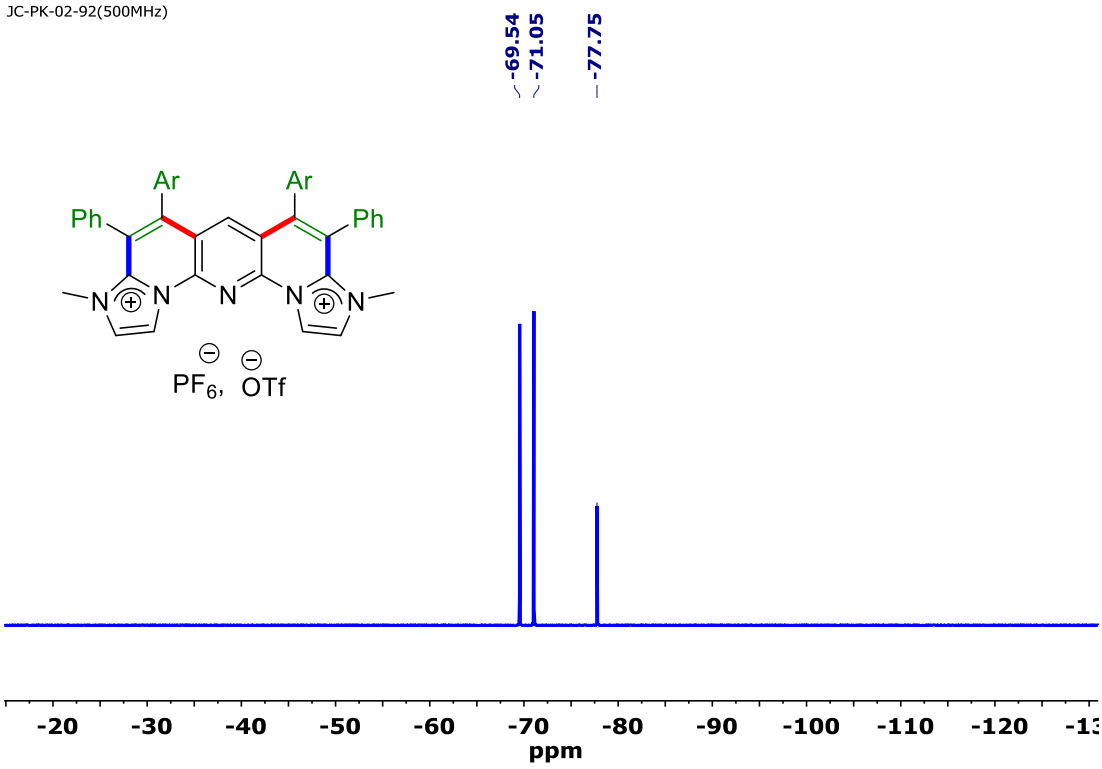

$^{1}$H NMR spectrum of **3f** (mixture of 3 isomers) (500 MHz, DMSO-$d_6$, 298 K).



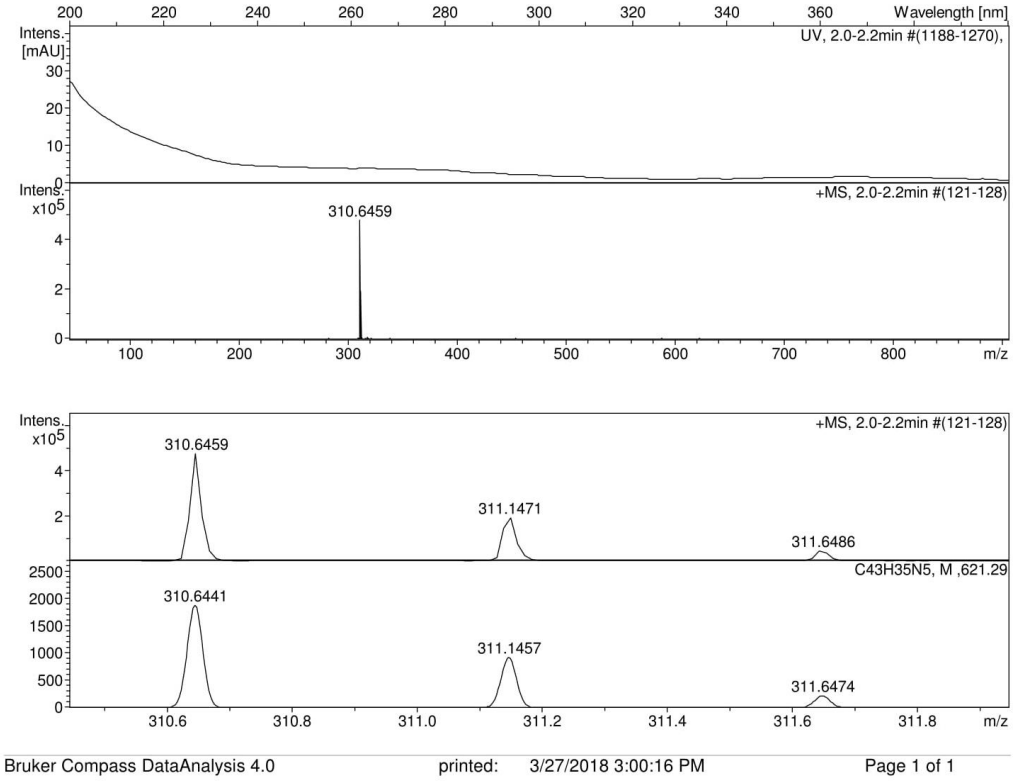

$^{13}C\{^{1}H\}$ NMR spectrum of **3f** (mixture of 3 isomers) (126 MHz, DMSO-$d_6$, 298 K).



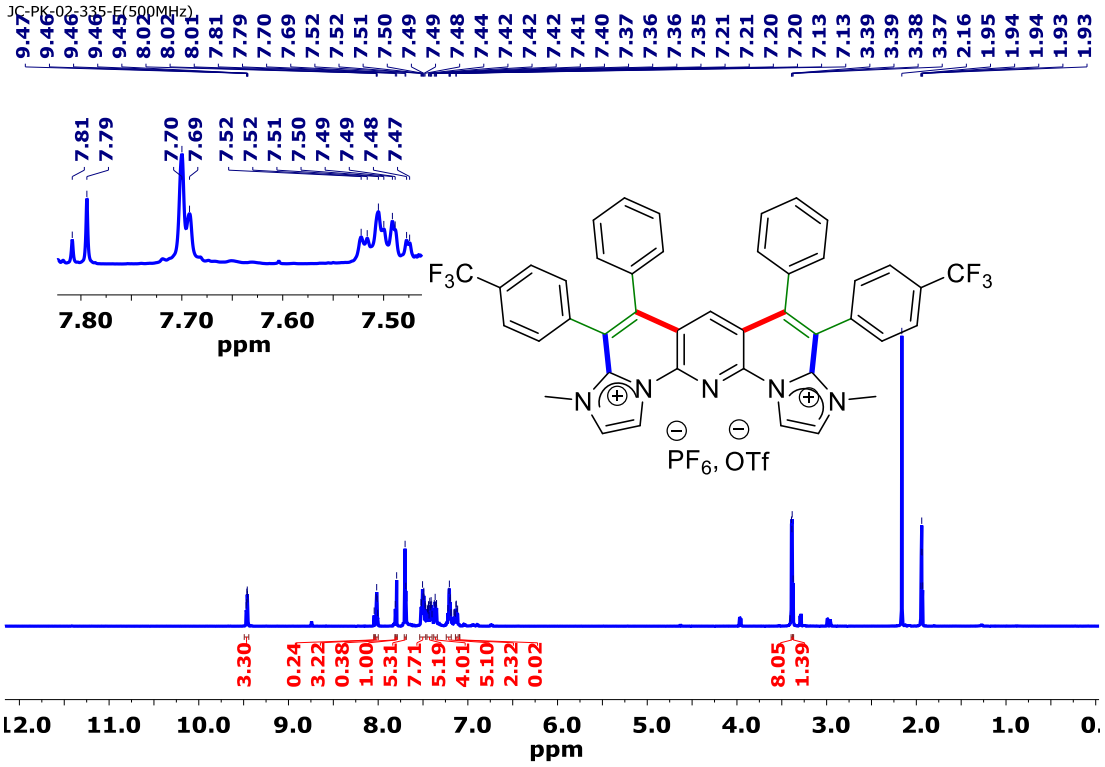

$^{31}P$ NMR spectrum of **3f** (mixture of 3 isomers) (202 MHz, DMSO-$d_6$, 298 K).



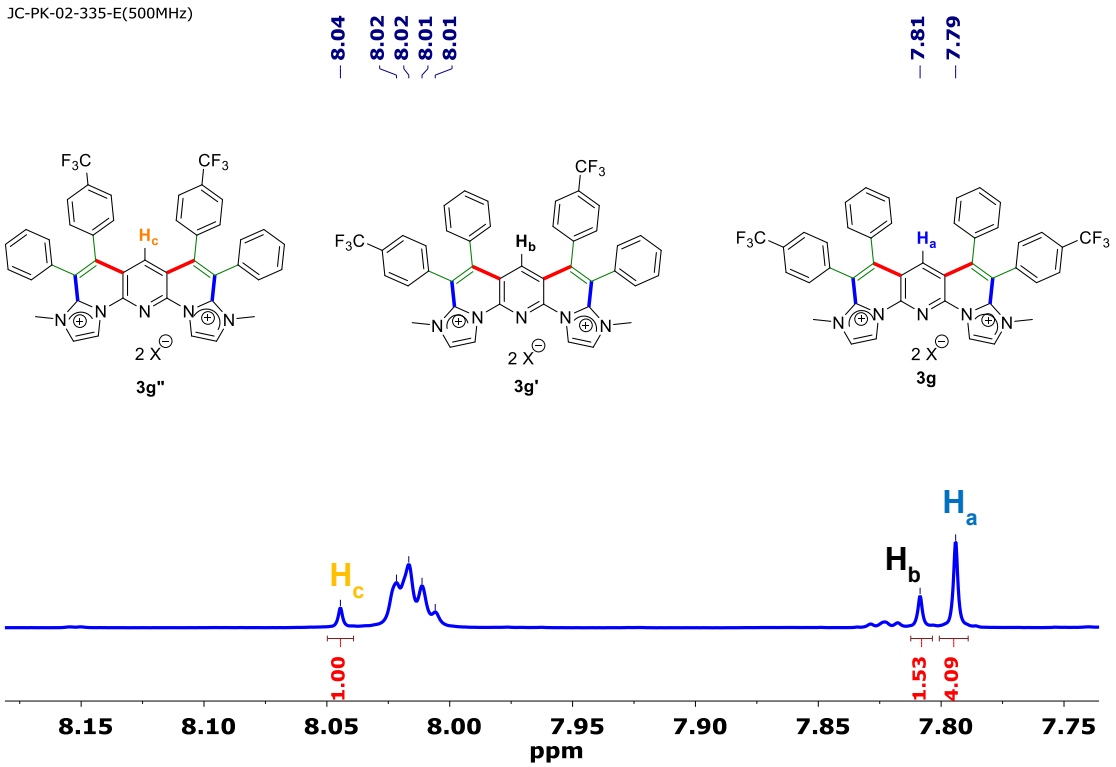

$^{19}$F NMR spectrum of **3f** (mixture of 3 isomers) (471 MHz, DMSO-$d_6$, 298 K).



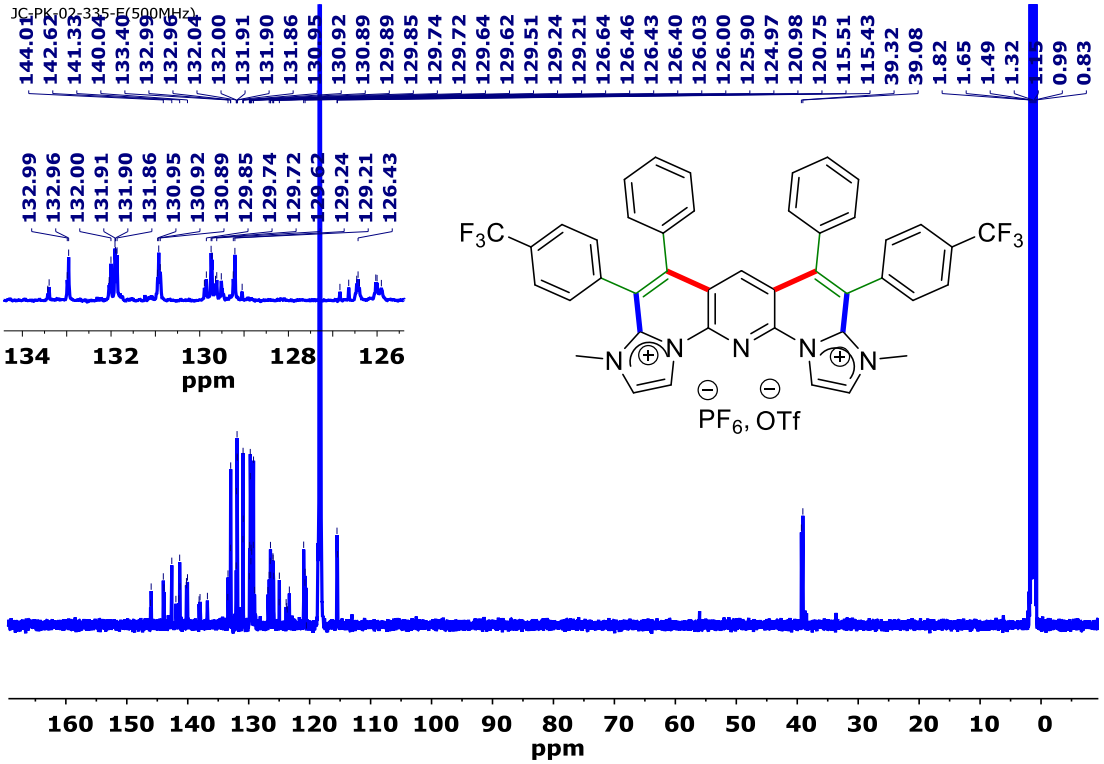

ESI-HRMS (positive ion mode) spectrum of **3f.**



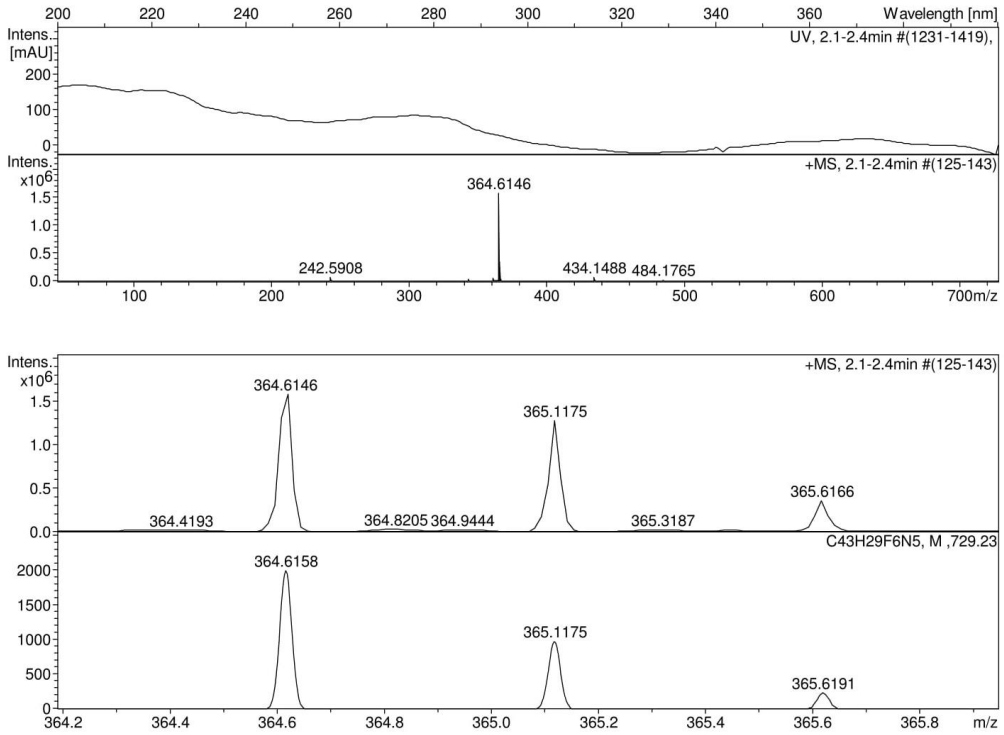

$^{1}$H NMR spectrum of **3g** (mixture of 3 isomers) (500 MHz, $CD_3CN$, 298 K).



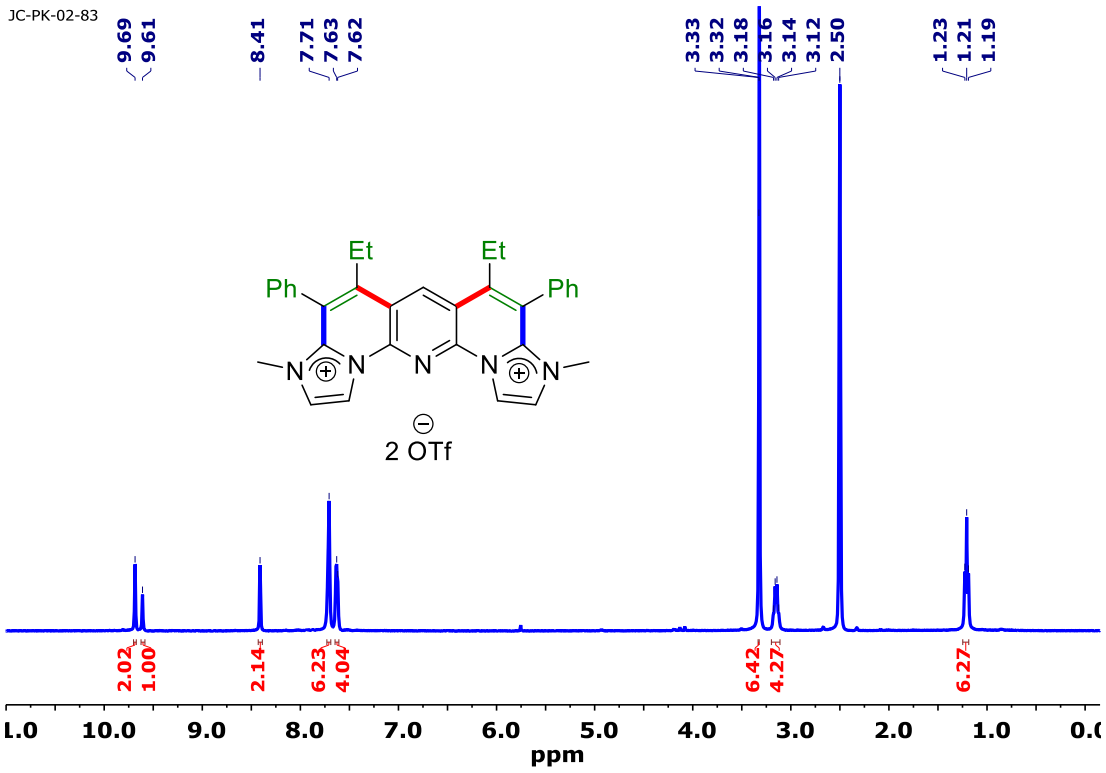

$^{1}$H NMR spectrum of **3g** (mixture of 3 isomers) (500 MHz, $CD_3CN$, 298 K).



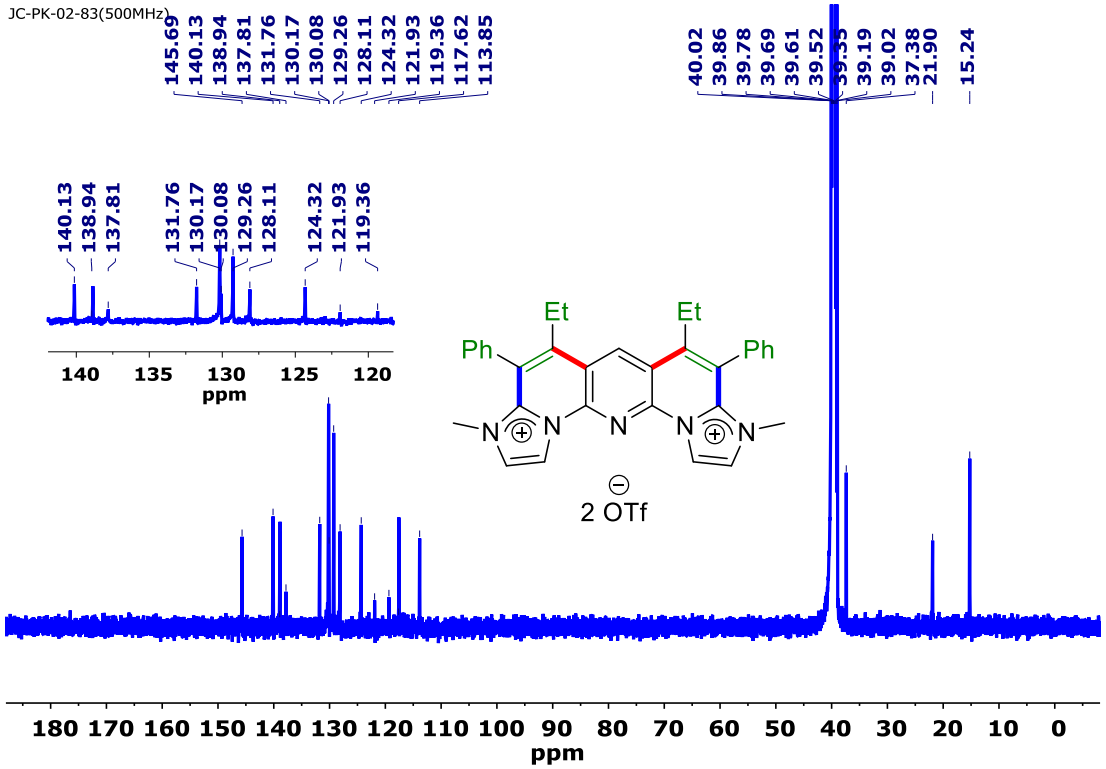

$^{13}C\{^{1}H\}$ NMR spectrum of **3g** (mixture of 3 isomers) (126 MHz, $CD_3CN$, 298 K).



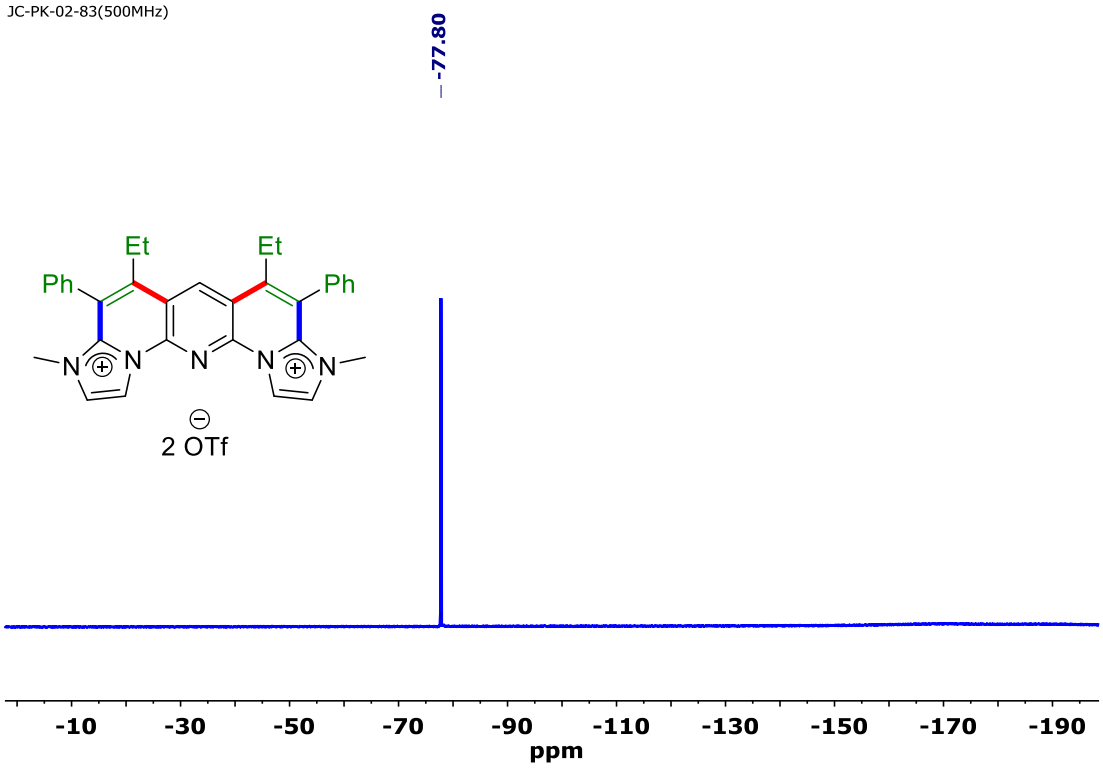

ESI-HRMS (positive ion mode) spectrum of **3g**.



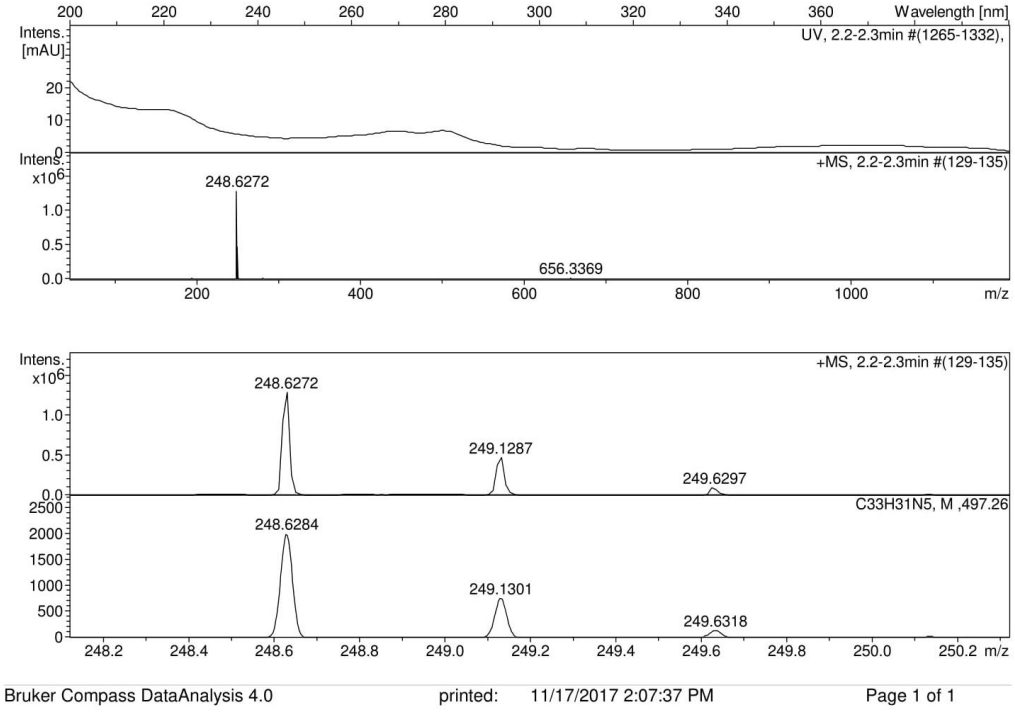

$^{1}$H NMR spectrum of **3h** (500 MHz, DMSO-d$_6$, 298 K).



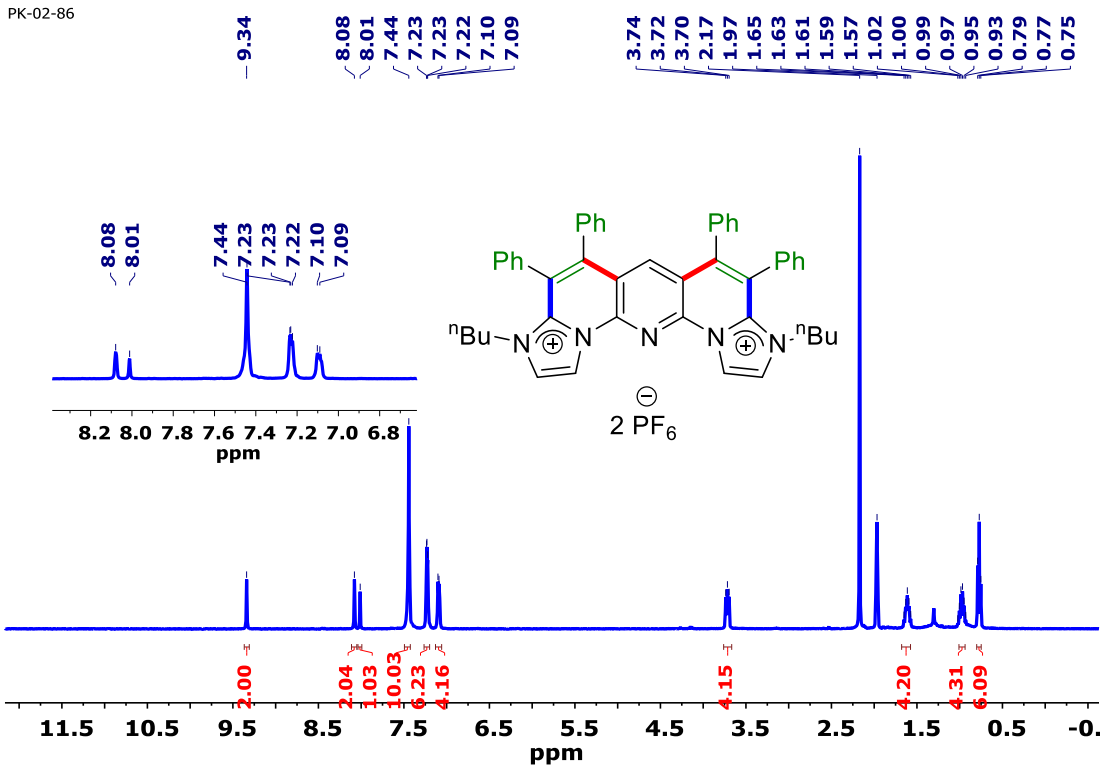

$^{13}$C{$^{1}$H} NMR spectrum of **3h** (126 MHz, DMSO-d$_6$, 298 K).



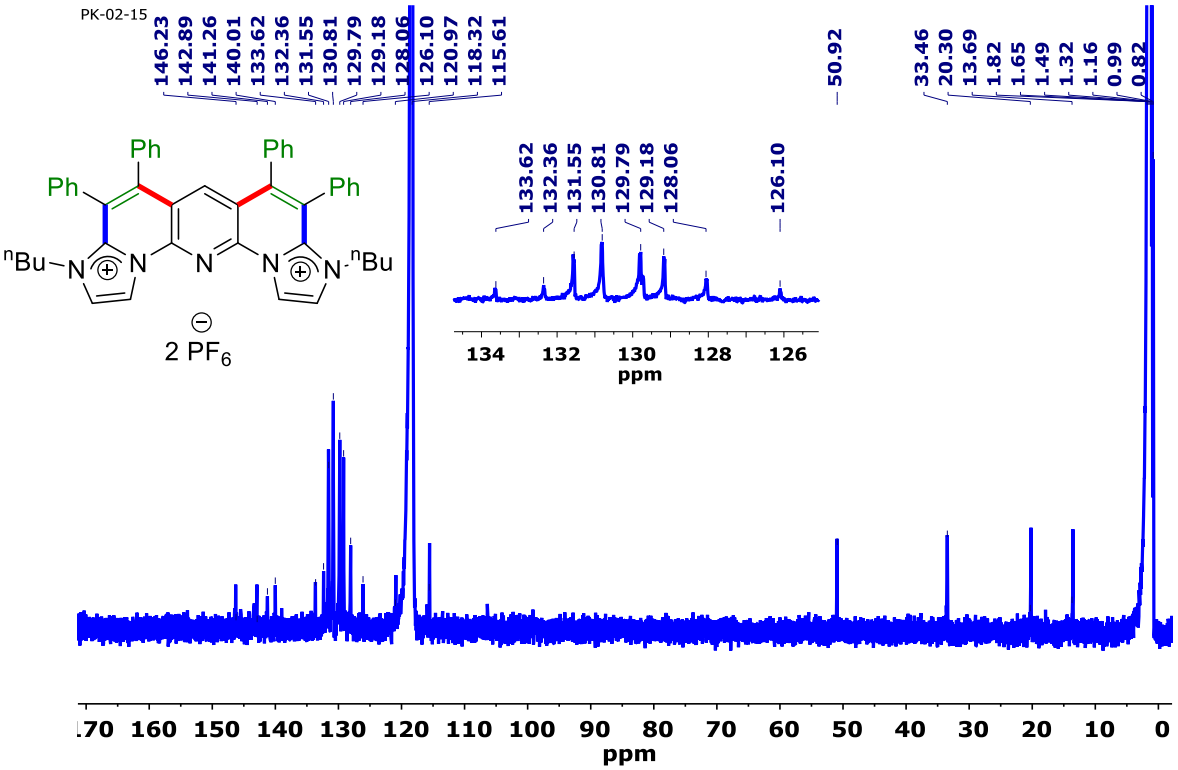

$^{19}$F NMR spectrum of **3h** (471 MHz, DMSO-$d_6$, 298K).



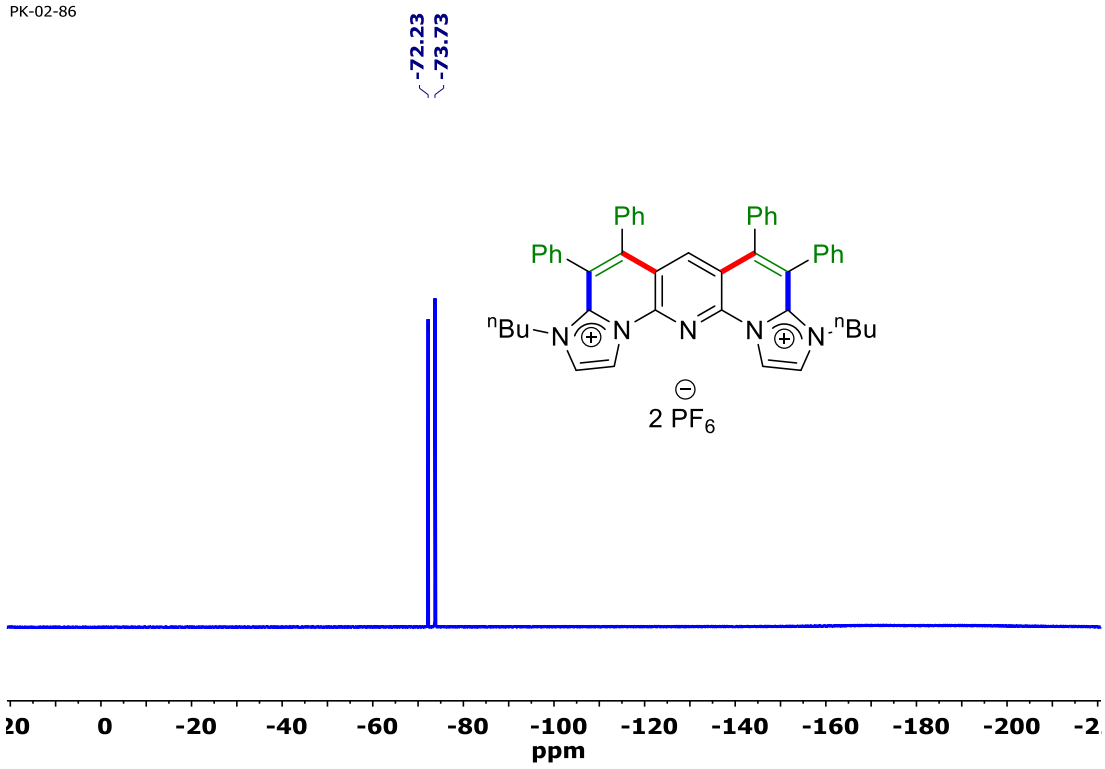

ESI-HRMS (positive ion mode) spectrum of **3h.**



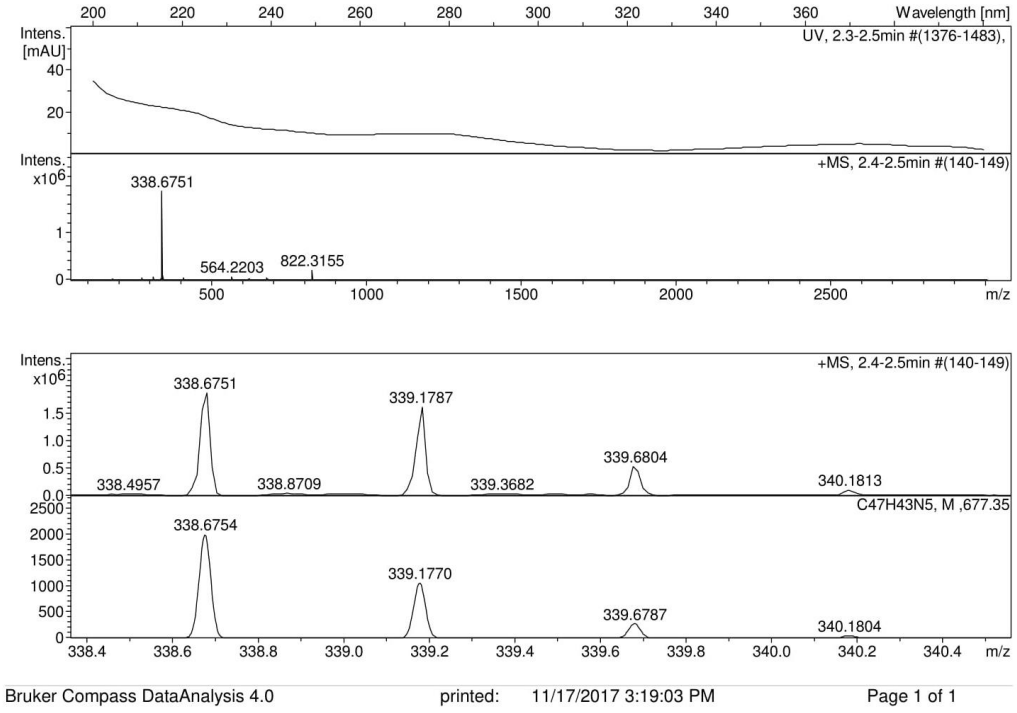

$^{1}$H NMR spectrum of **3i** (400 MHz, $CD_3CN$, 298K).



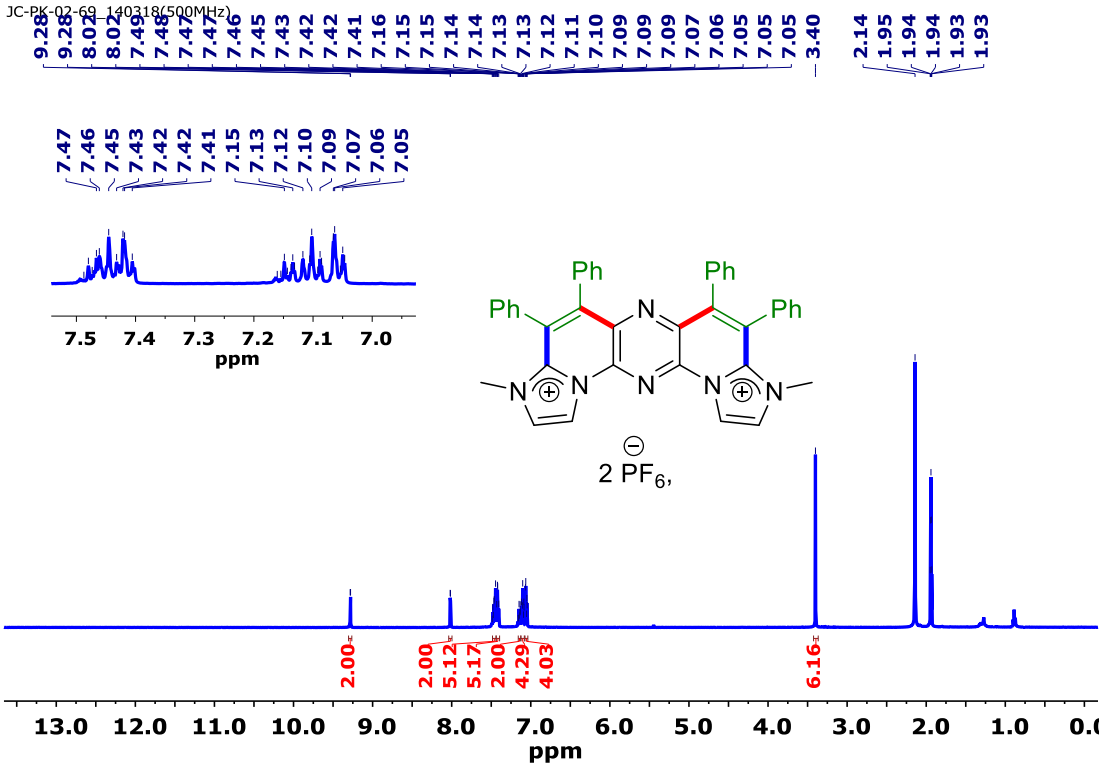

$^{13}$C{$^{1}$H} NMR spectrum of **3i** (126 MHz, $CD_3CN$, 298 K).



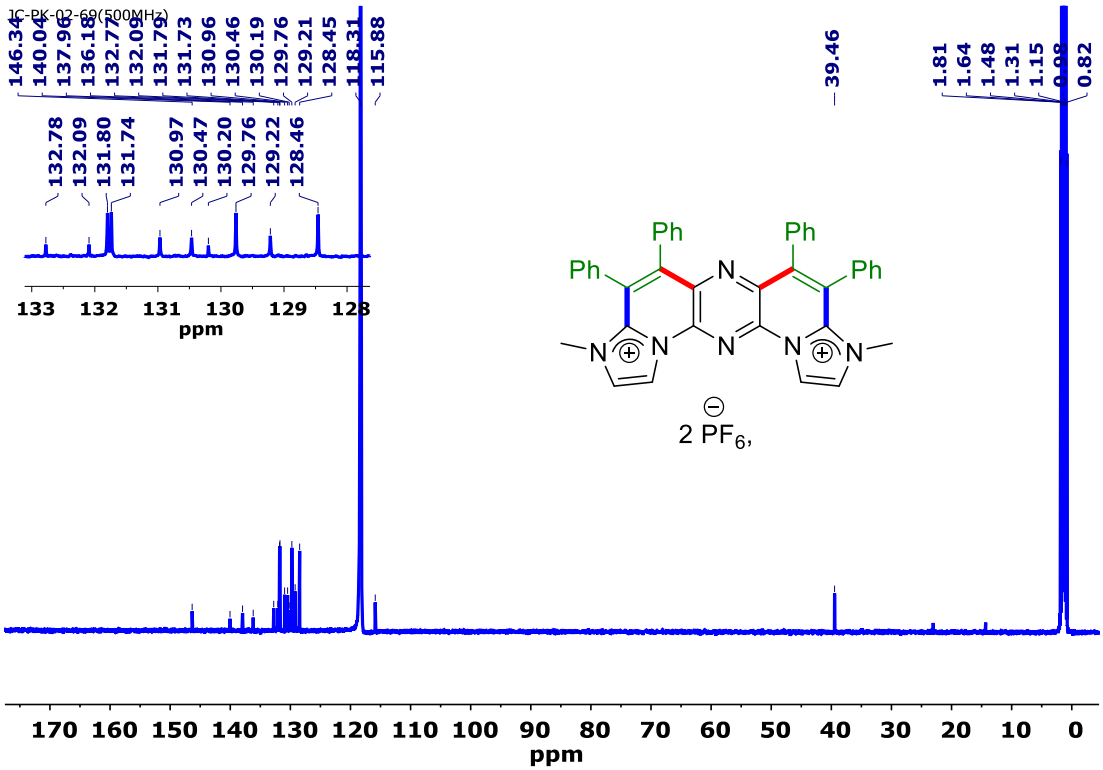

$^{19}$F NMR spectrum of **3i** (471 MHz, $CD_3CN$, 298 K).



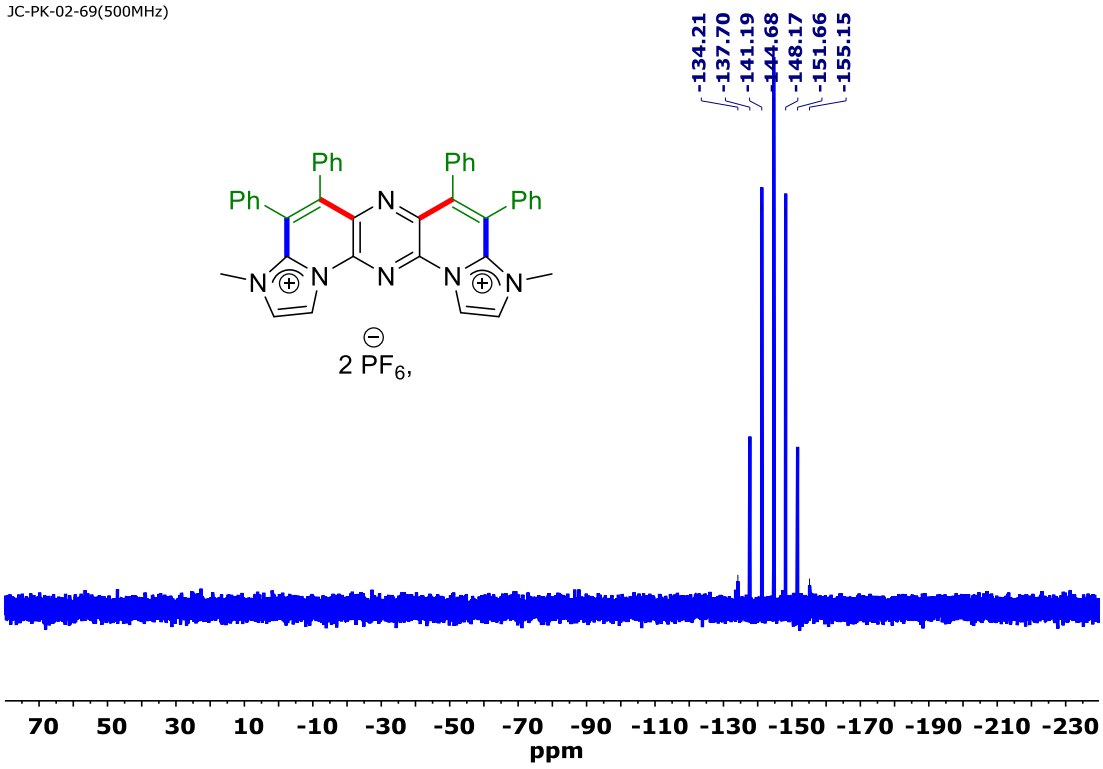

ESI-HRMS (positive ion mode) spectrum of **3i.**



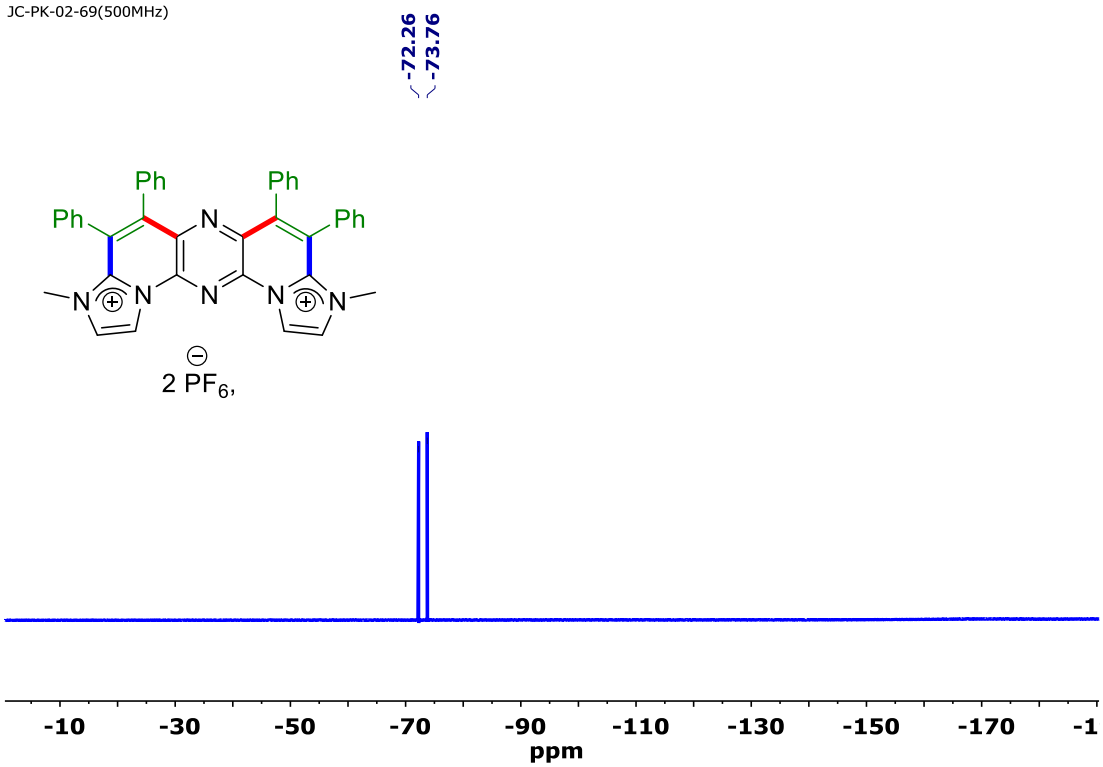

$^{1}$H NMR spectrum of **3j** (500 MHz, $CD_3CN$, 298K).



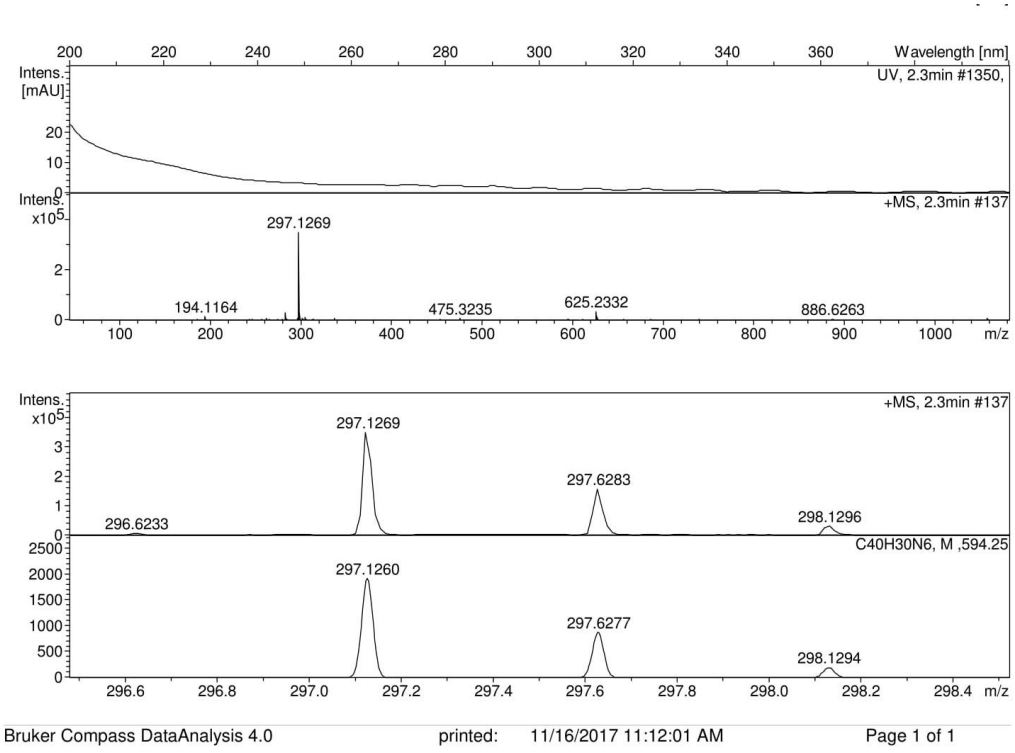

$^{13}$C{$^{1}$H} NMR spectrum of **3j** (126 MHz, $CD_3CN$, 298 K).



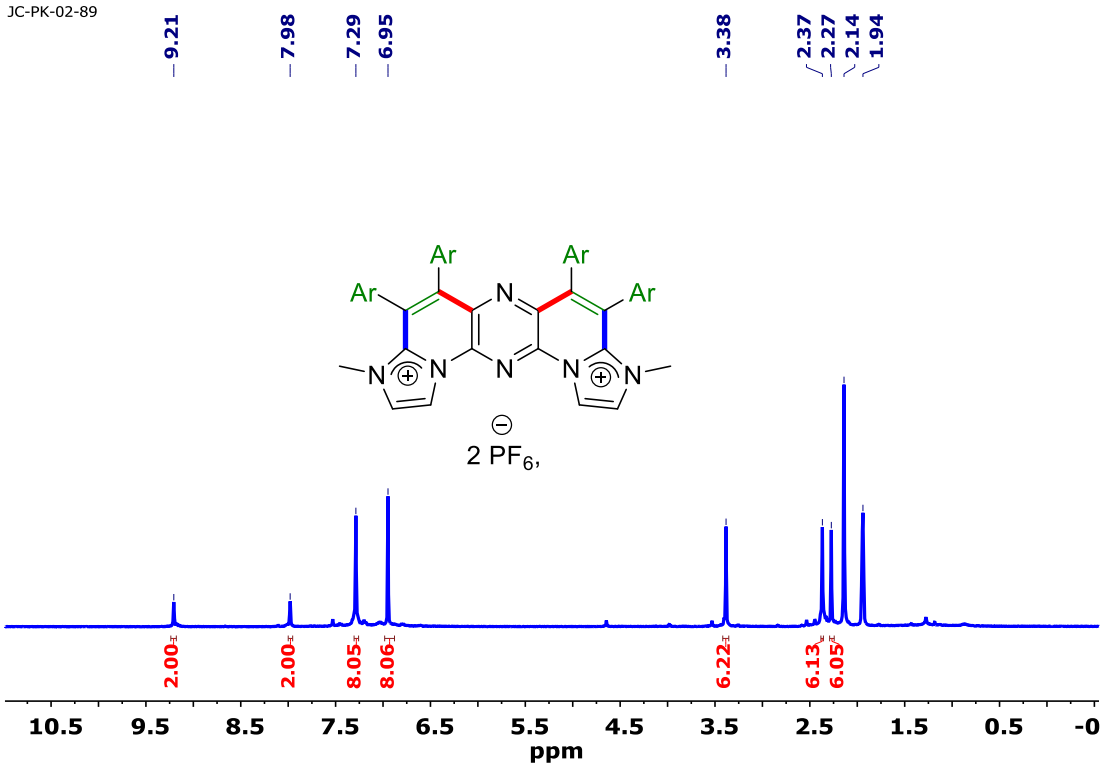

$^{31}$P NMR spectrum of **3j** (202 MHz, $CD_3CN$, 298 K).



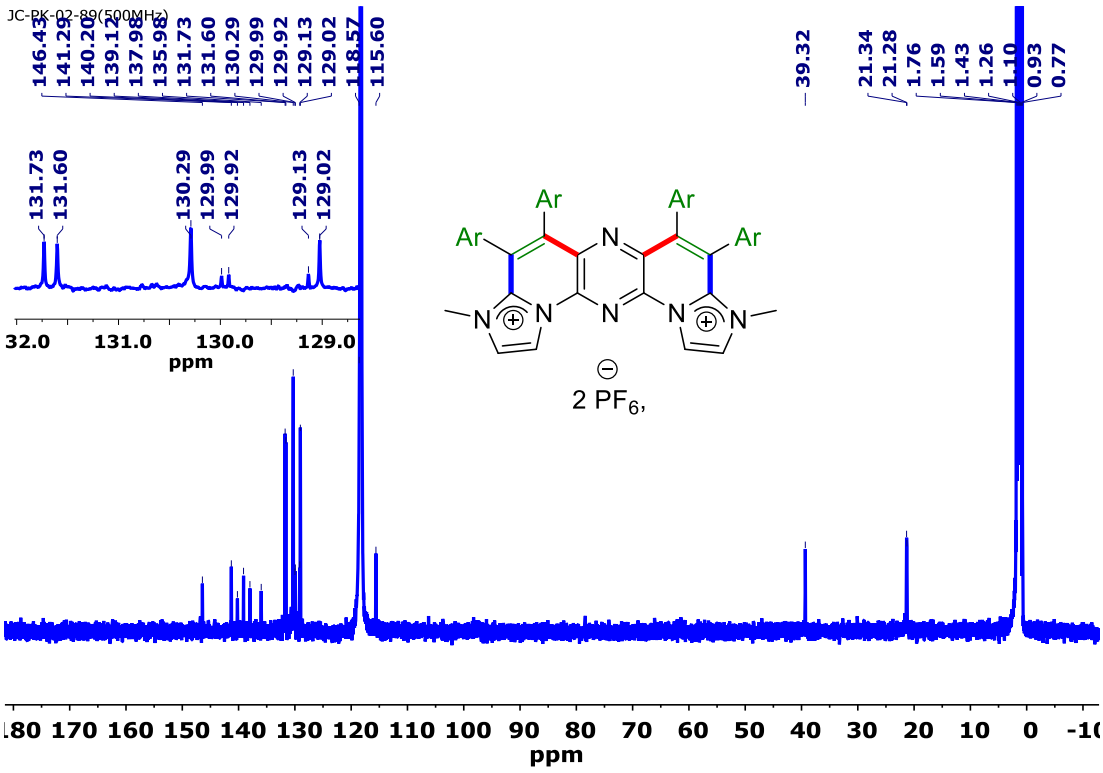

$^{19}$F NMR spectrum of **3j** (471 MHz, $CD_3CN$, 298K).



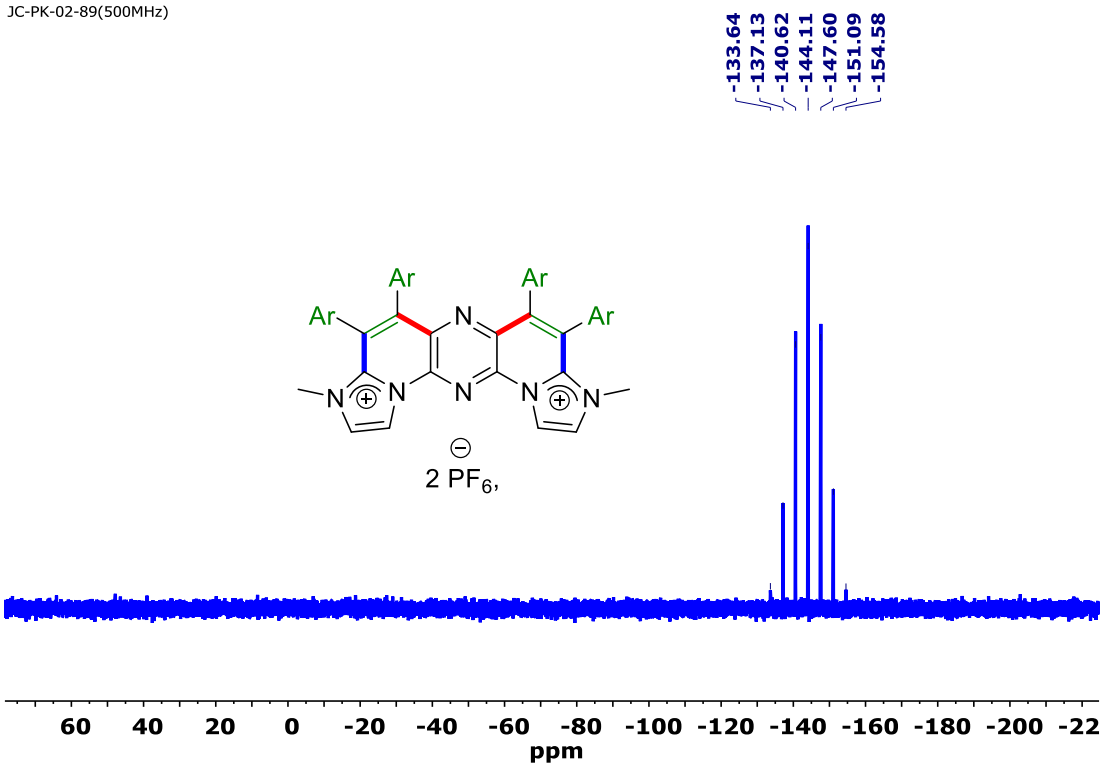

ESI-HRMS (positive ion mode) spectrum of **3j**.



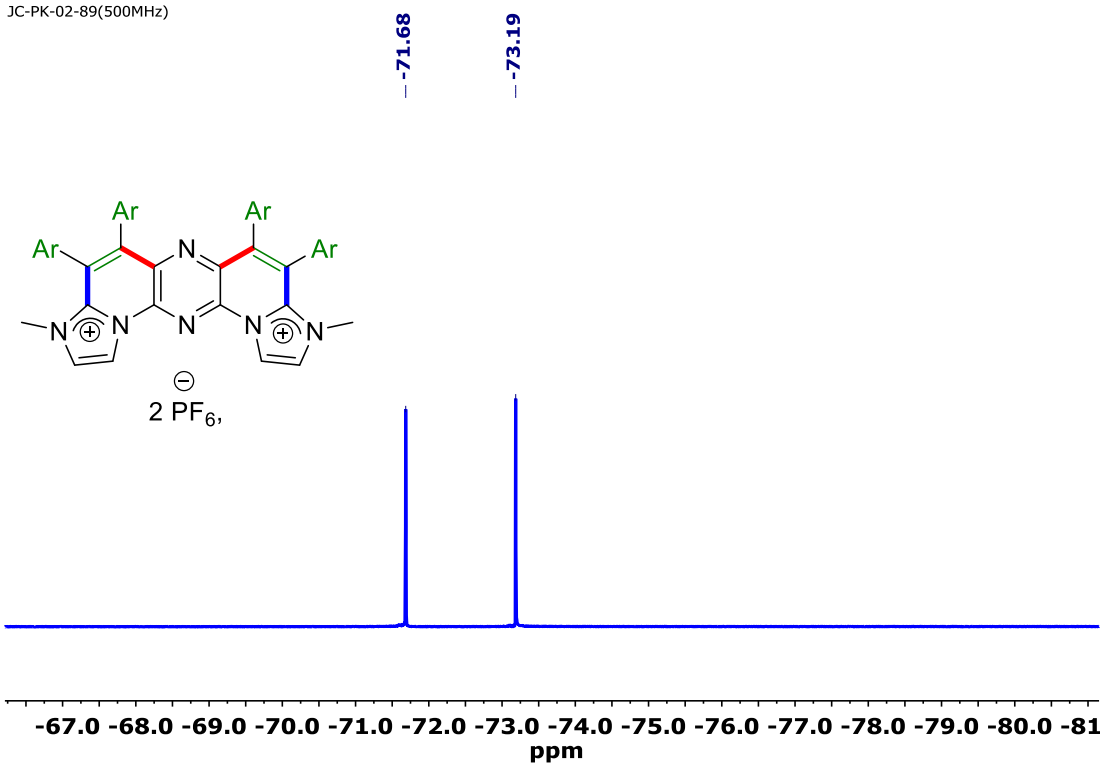

$^{1}$H NMR spectrum of **3k** (400 MHz, $CD_3CN$, 298 K).



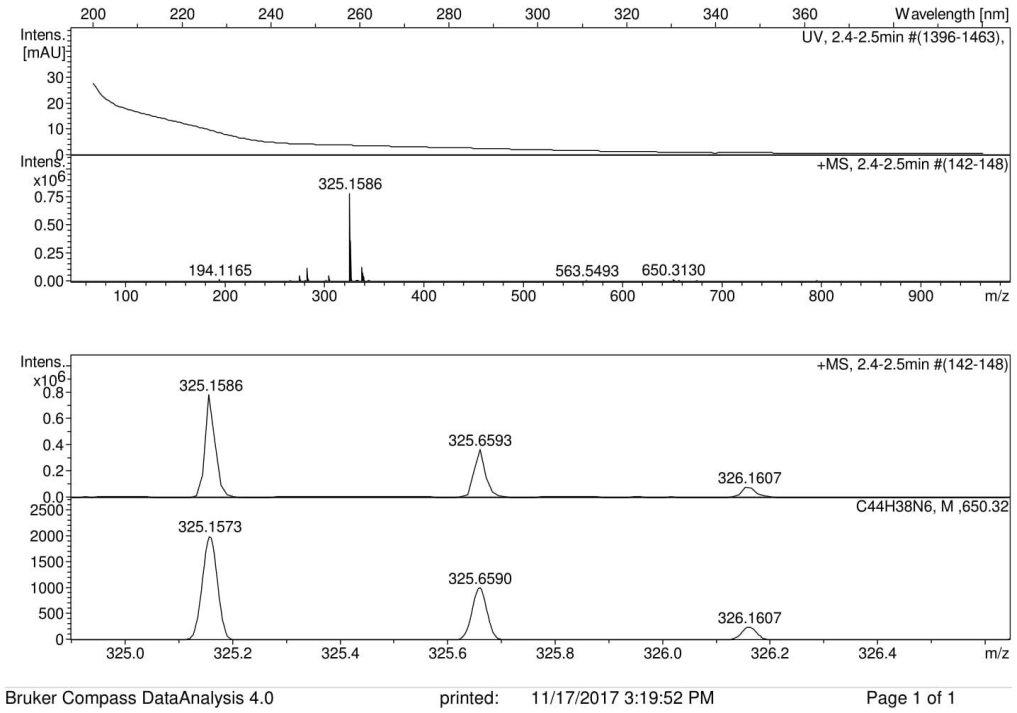

$^{13}C\{^{1}H\}$ NMR spectrum of **3k** (126 MHz, DMSO-$d_6$, 298 K).



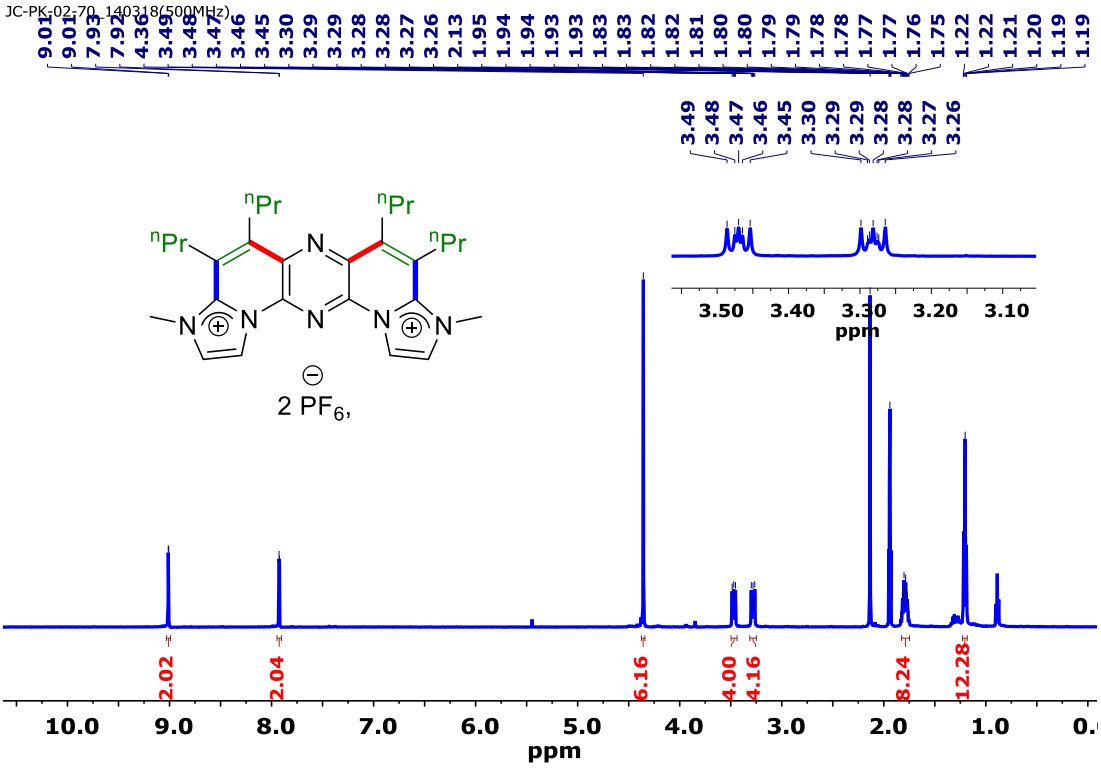

$^{31}P$ NMR spectrum of **3k** (202 MHz, DMSO-$d_6$, 298K).



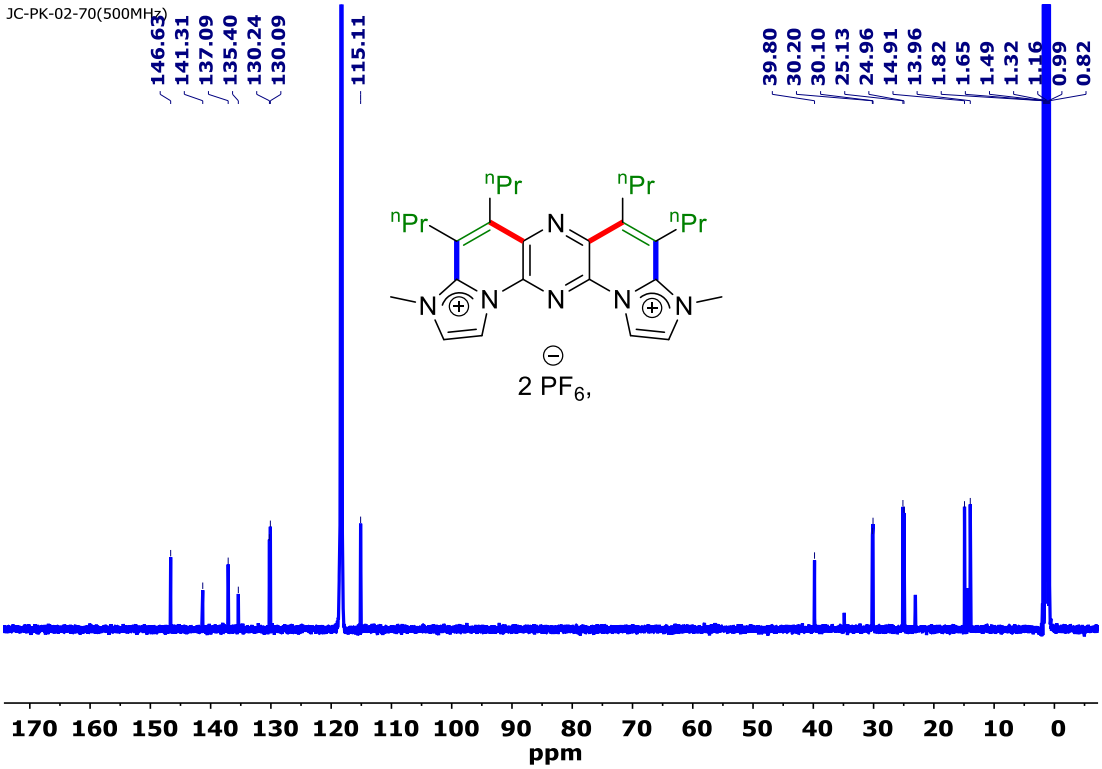

$^{19}$F NMR spectrum of **3k** (471 MHz, DMSO-$d_6$, 298 K).



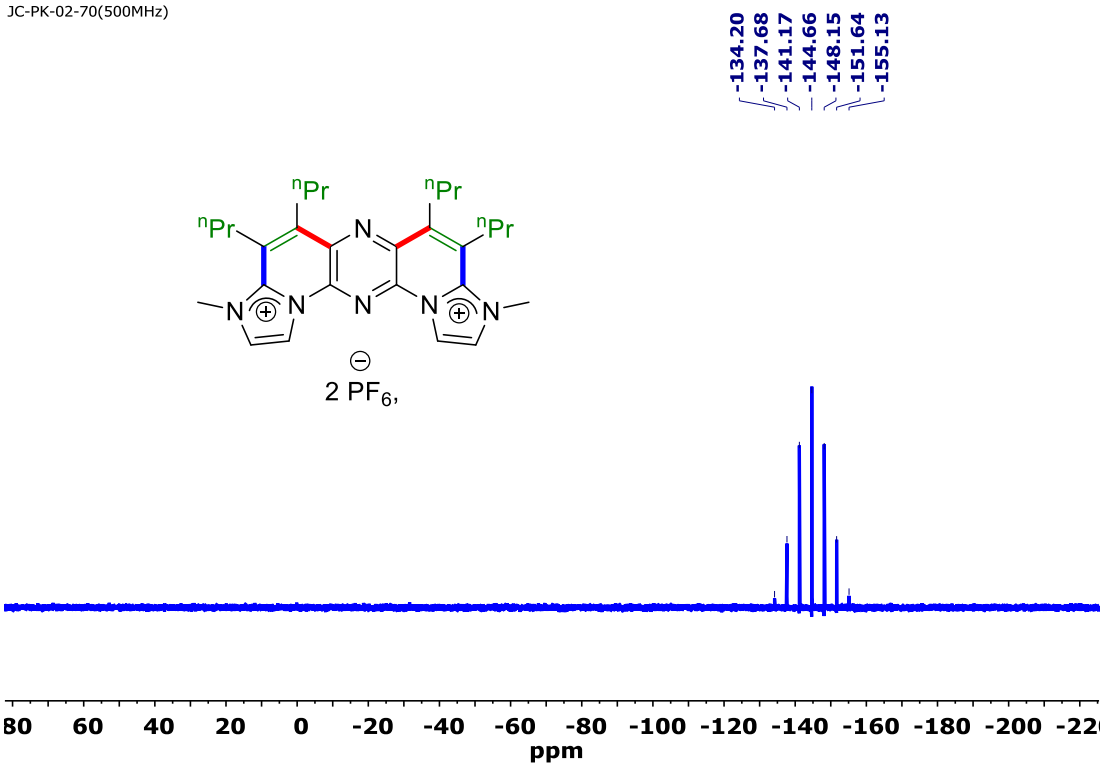

ESI-HRMS (positive ion mode) spectrum of **3k**.



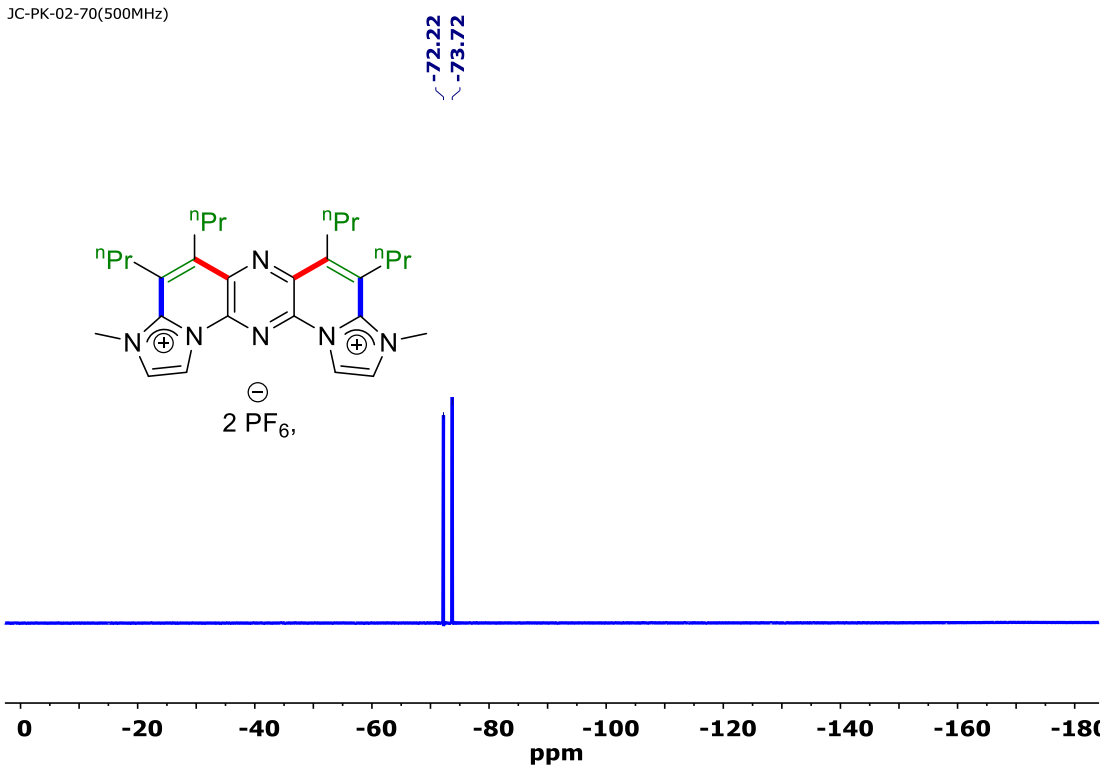

$^{1}$H NMR spectrum of **3l** (500 MHz, $CD_3CN$, 298 K).



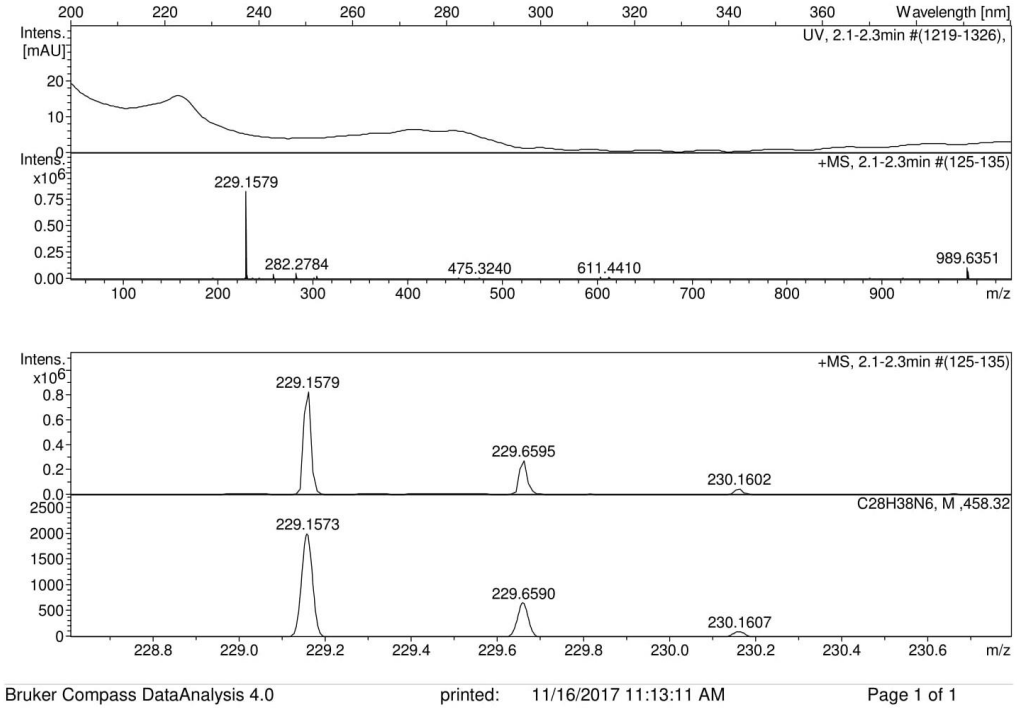

$^{13}$C{$^{1}$H} NMR spectrum of **3l** (126 MHz, $CD_3CN$, 298K).



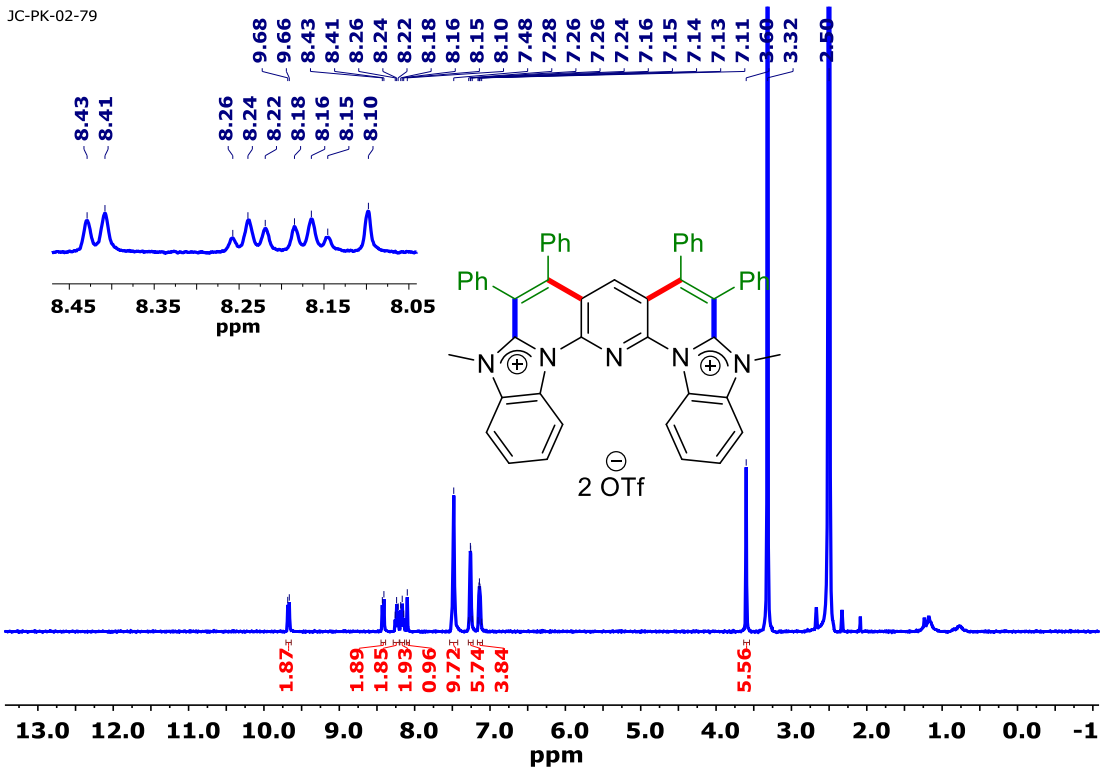

$^{31}$P NMR spectrum of **3l** (202 MHz, $CD_3CN$, 298 K).



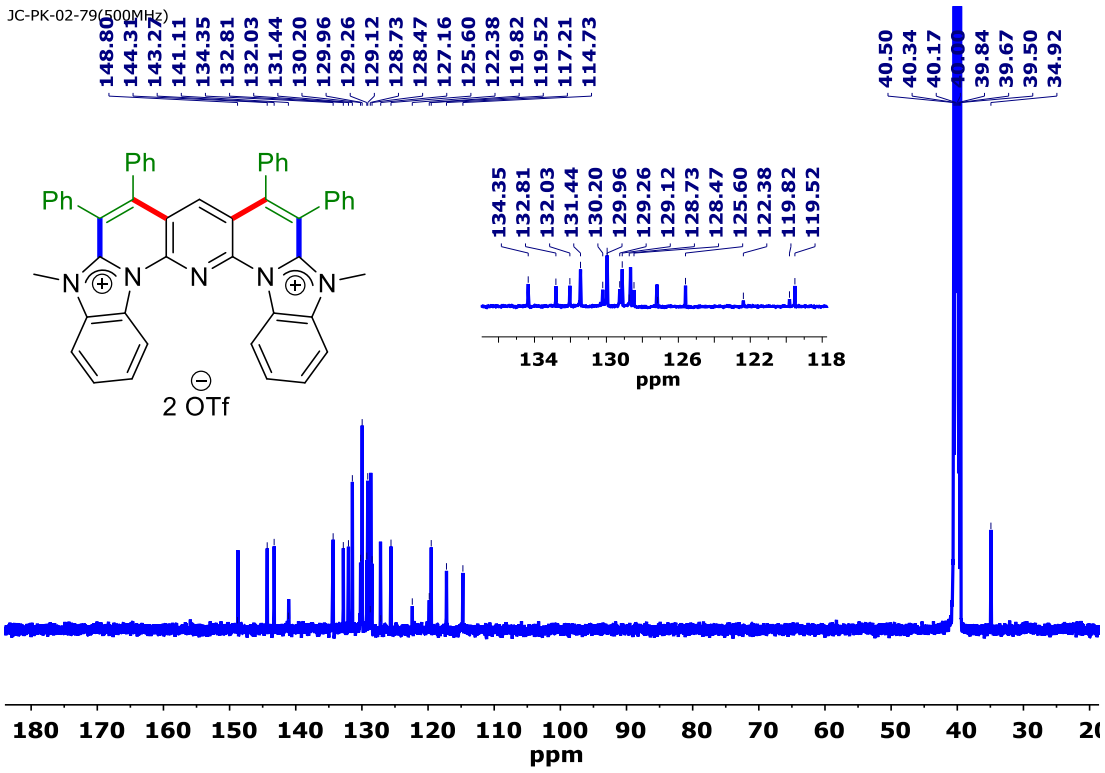

$^{19}$F NMR spectrum of **3l** (471 MHz, $CD_3CN$, 298 K).



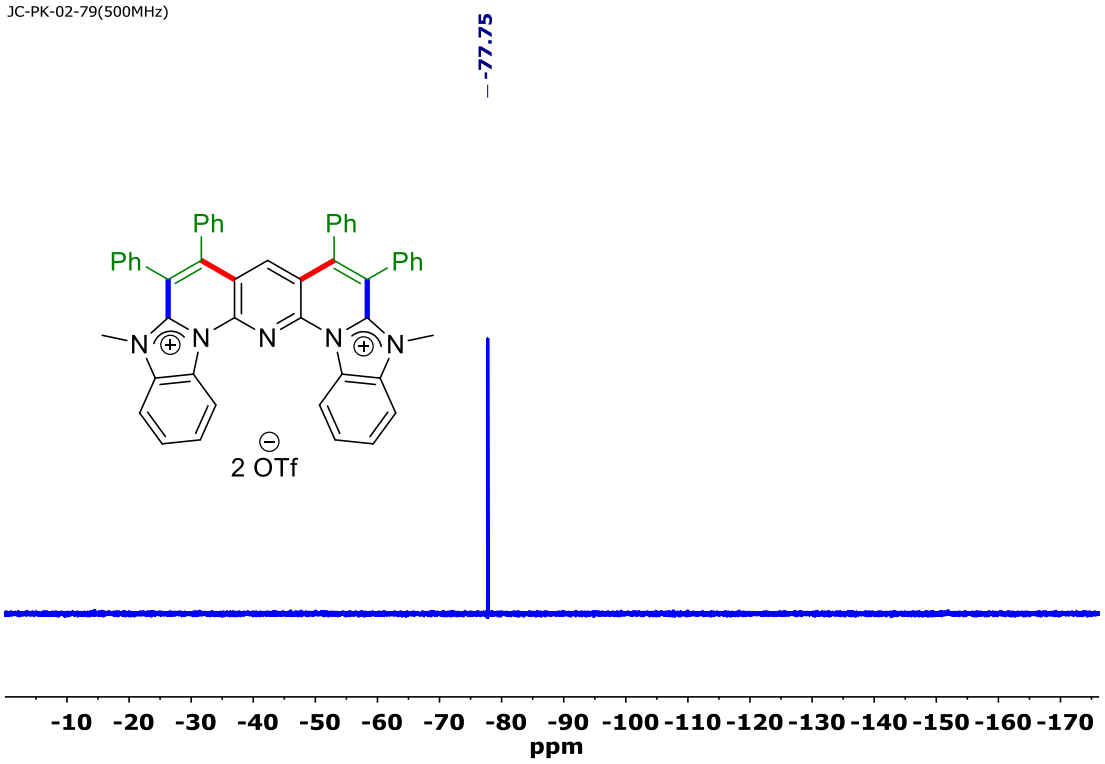

ESI-HRMS (positive ion mode) spectrum of **3l.**



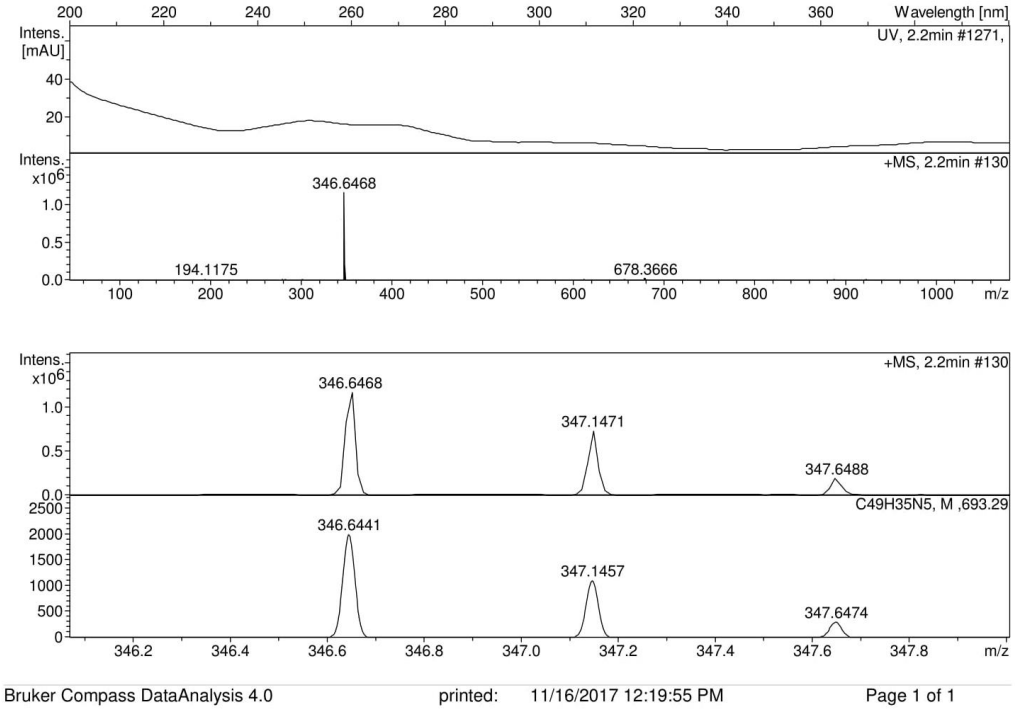

$^{1}$H NMR spectrum of **3m** (500 MHz, DMSO-$d_6$, 298 K).



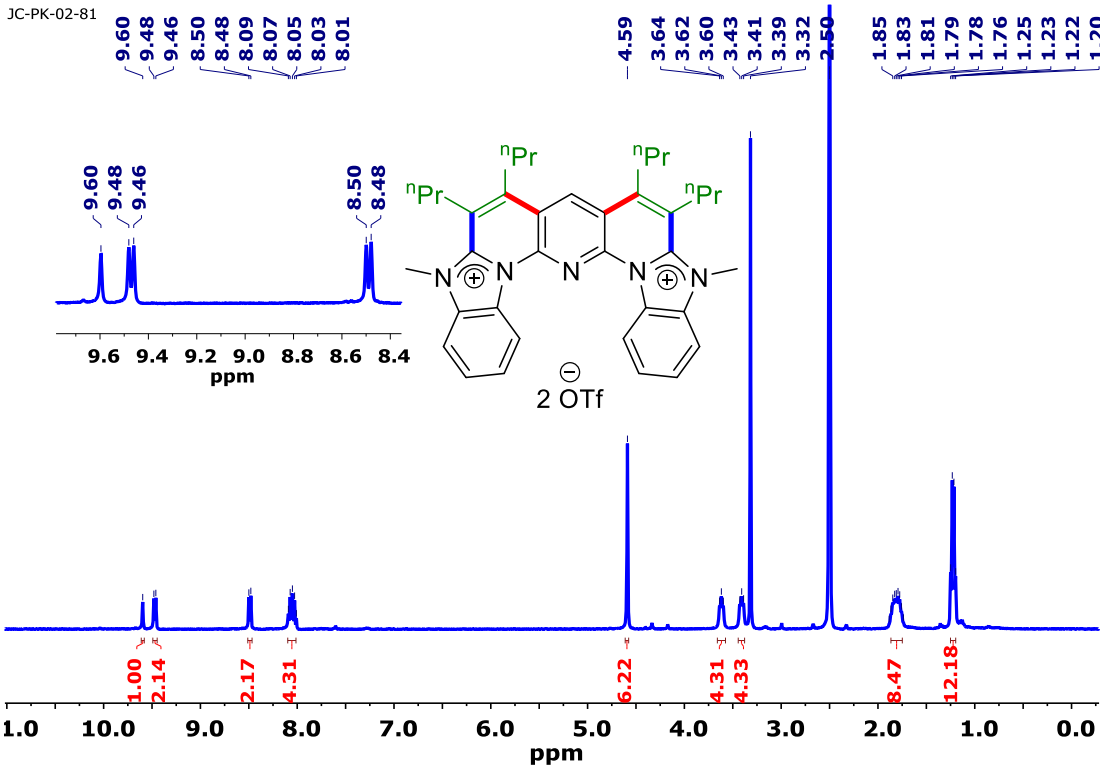

$^{13}C\{^{1}H\}$ NMR spectrum of **3m** (126 MHz, DMSO-$d_6$, 298K).



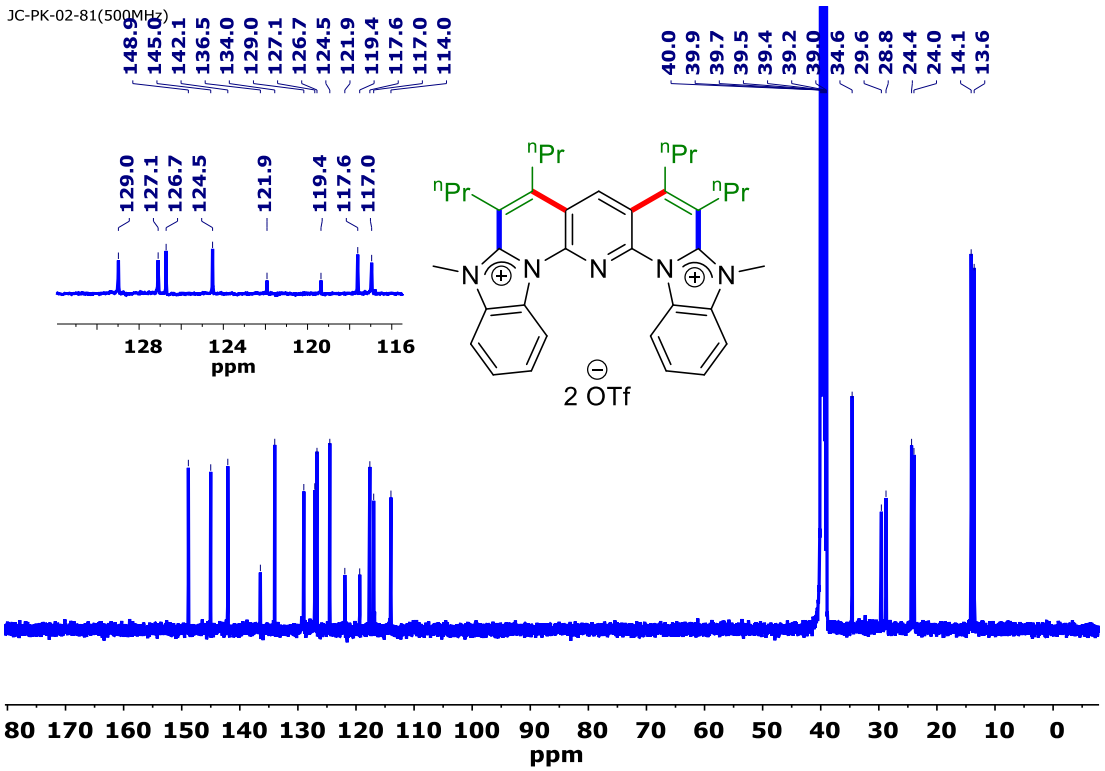

$^{19}F$ NMR spectrum of **3m** (471 MHz, DMSO-$d_6$, 298 K).



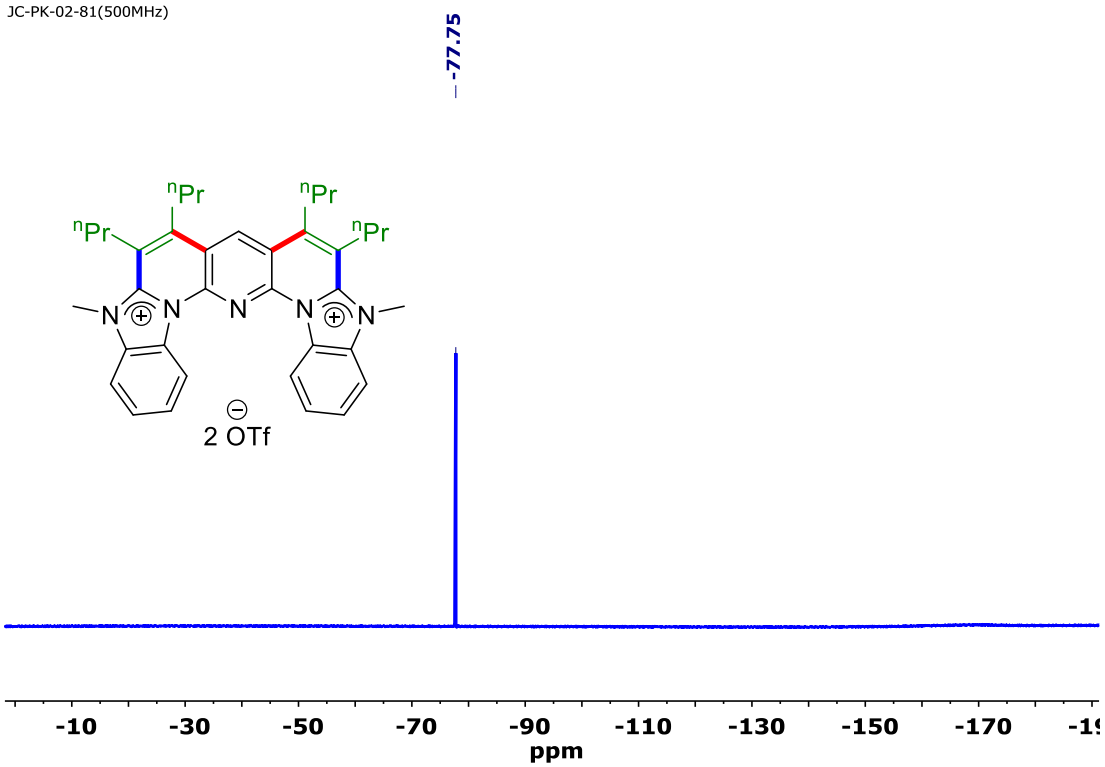

ESI-HRMS (positive ion mode) spectrum of **3m**.



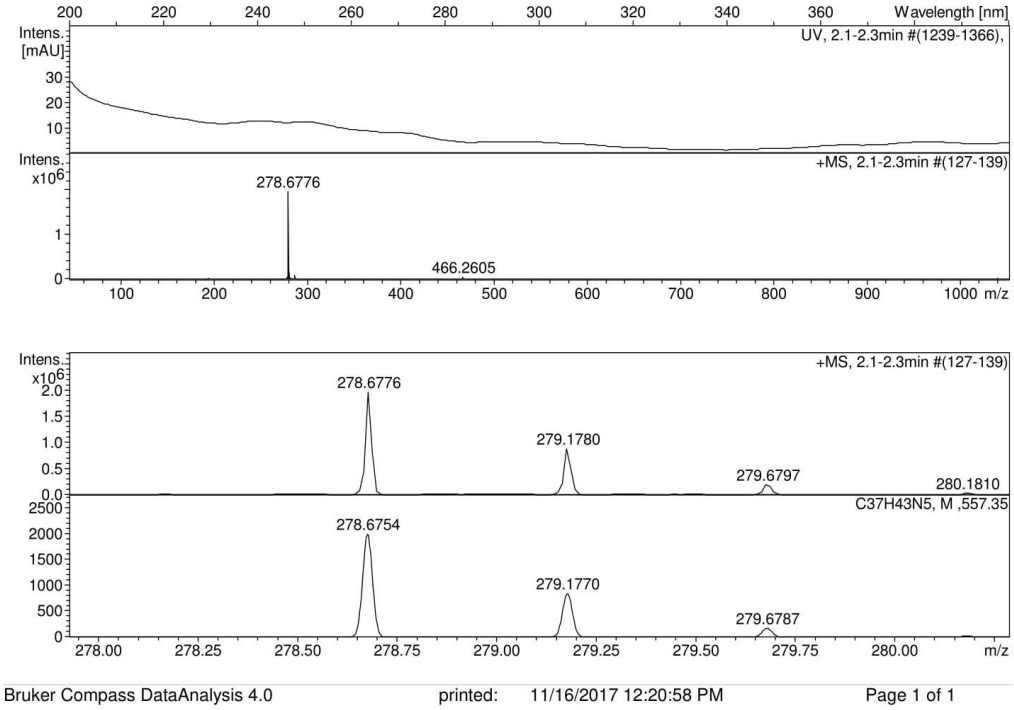

$^{1}$H NMR spectrum of **3n** (500 MHz, DMSO-$d_6$, 298K).



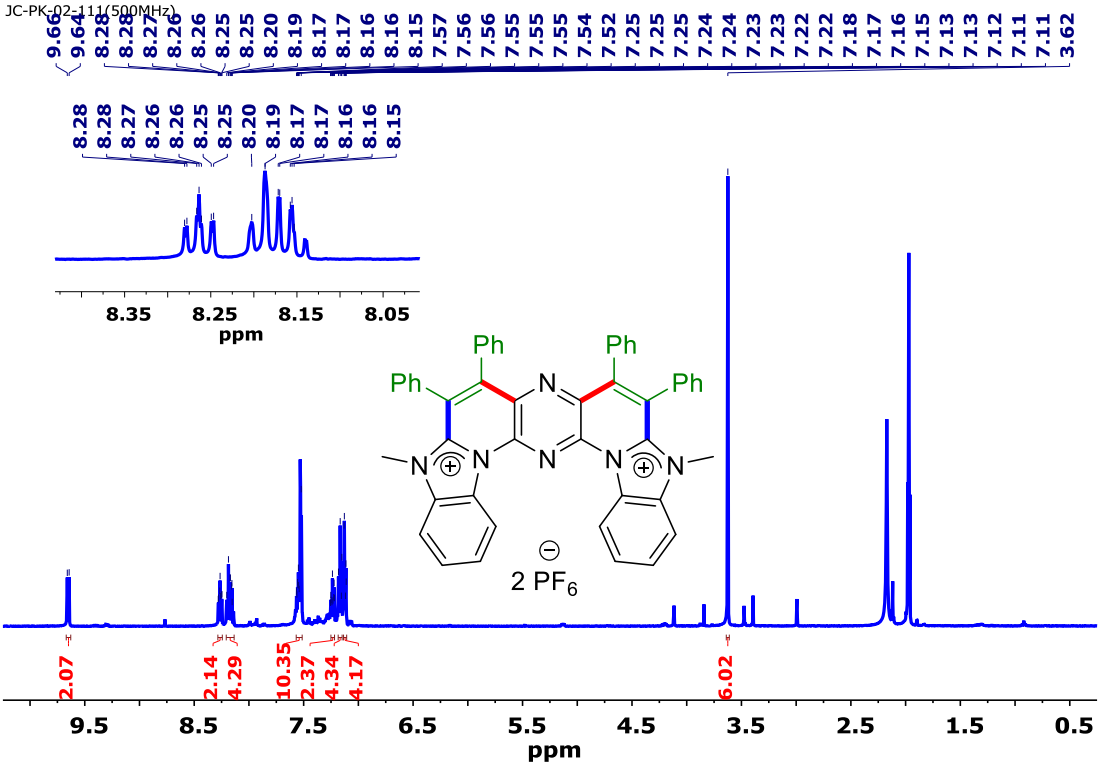

$^{13}C\{^{1}H\}$ NMR spectrum of **3n** (126 MHz, DMSO-$d_6$, 298 K).



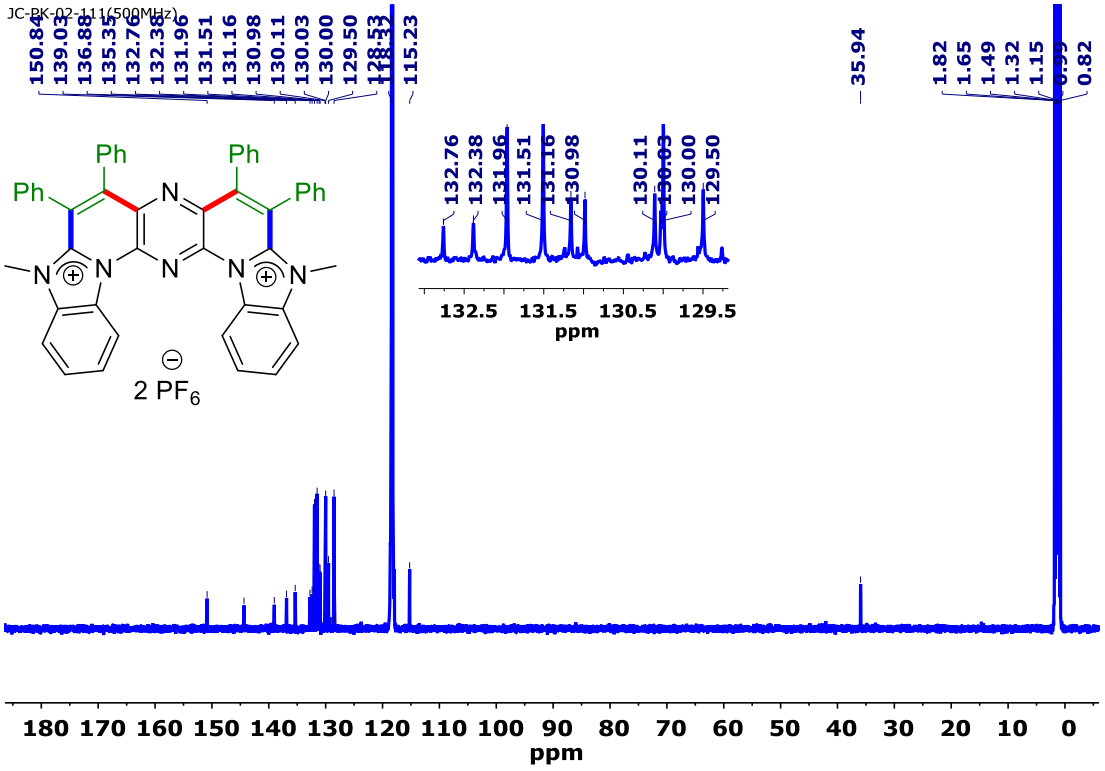

$^{19}F$ NMR spectrum of **3n** (471 MHz, DMSO-$d_6$, 298 K).



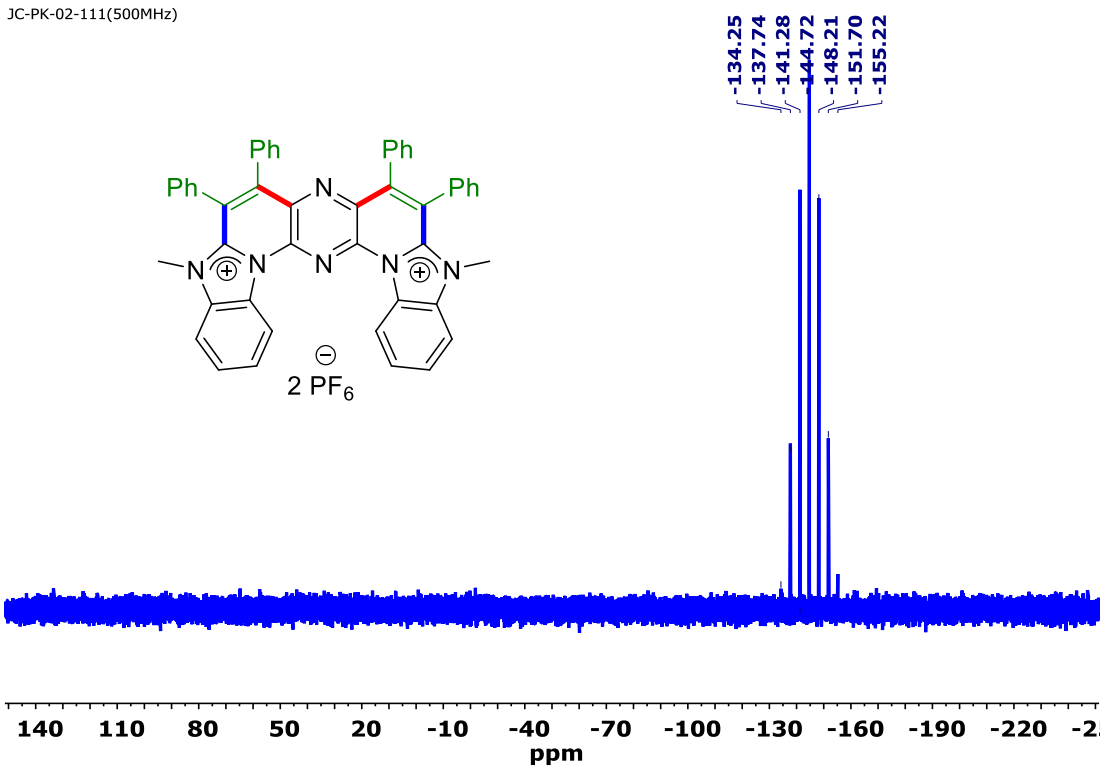

ESI-HRMS (positive ion mode) spectrum of **3n**.



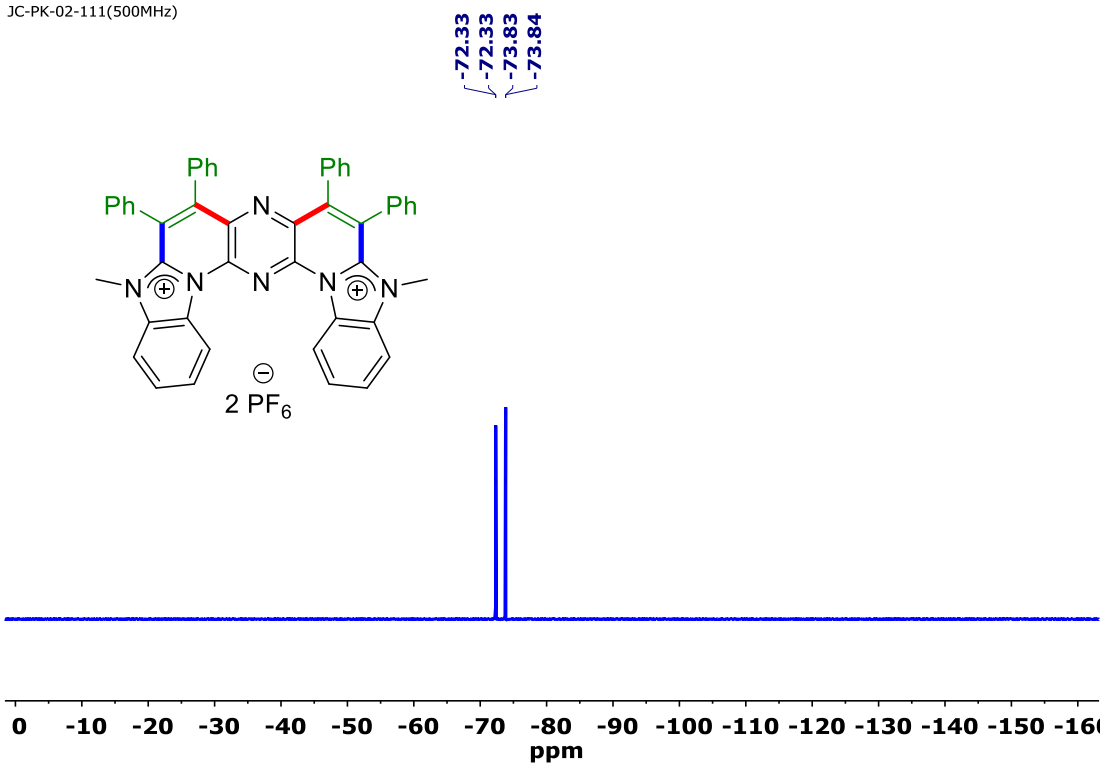

$^{1}$H NMR spectrum of **3o** (500 MHz, $CD_3CN$, 298 K).



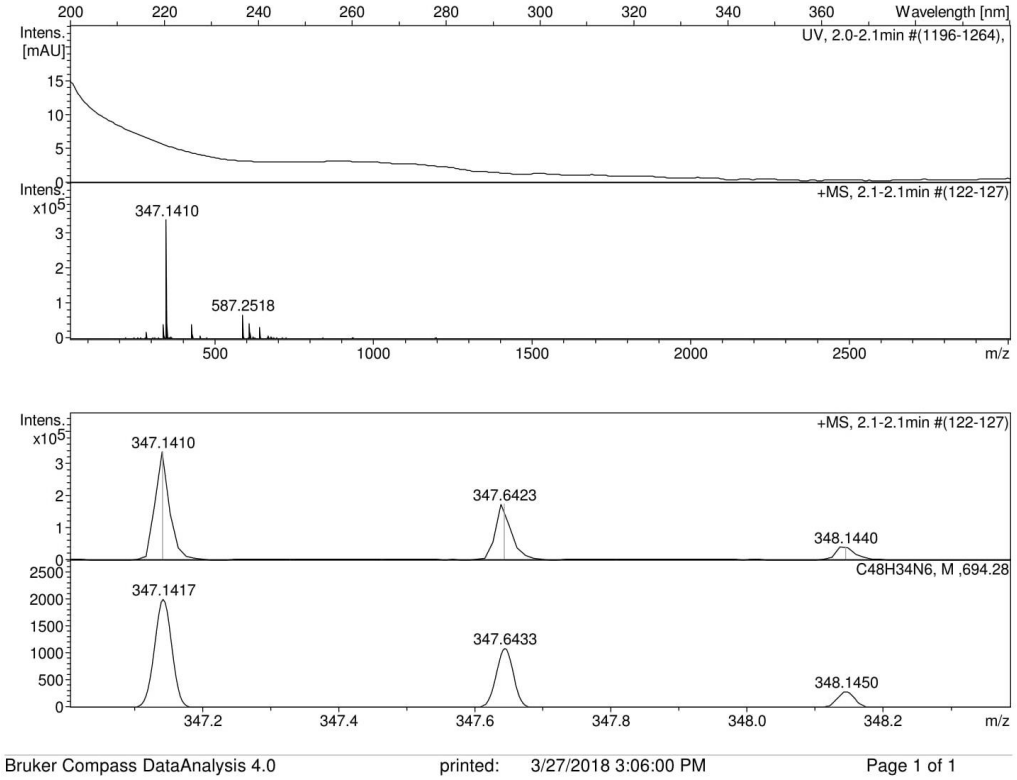

$^{13}C\{^{1}H\}$ NMR spectrum of **3o** (126 MHz, $CD_3CN$, 298 K).



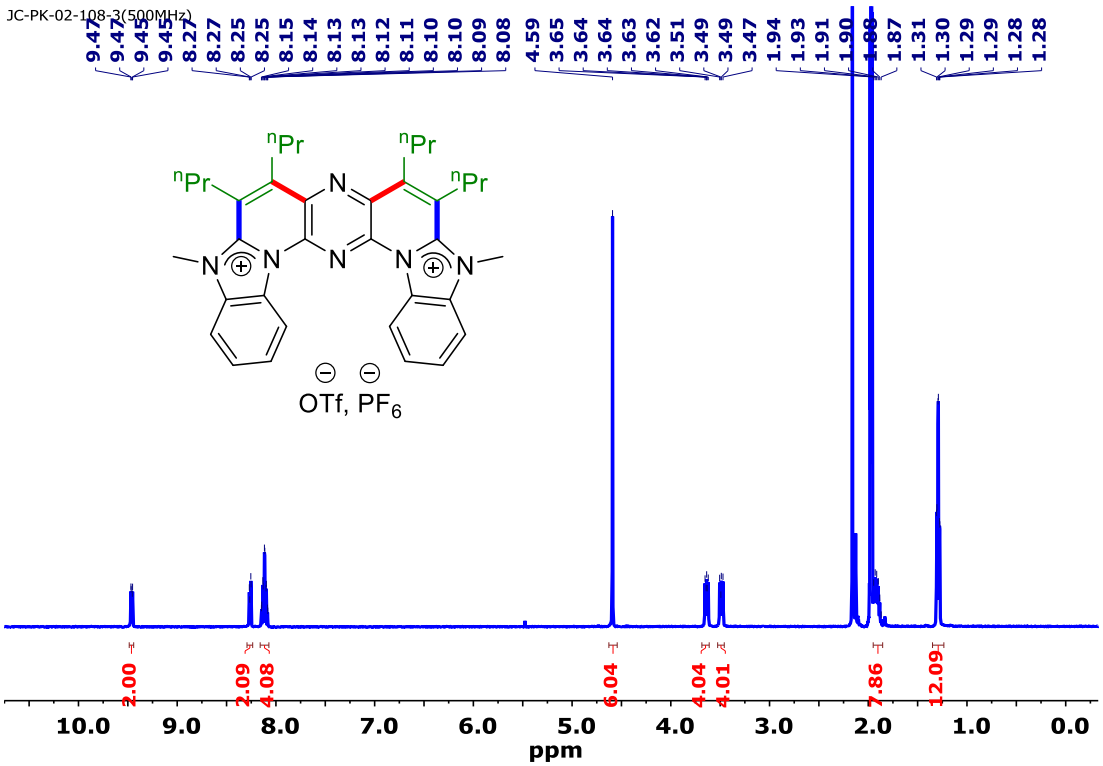

$^{31}P$ NMR spectrum of **3o** (202 MHz, $CD_3CN$, 298K).



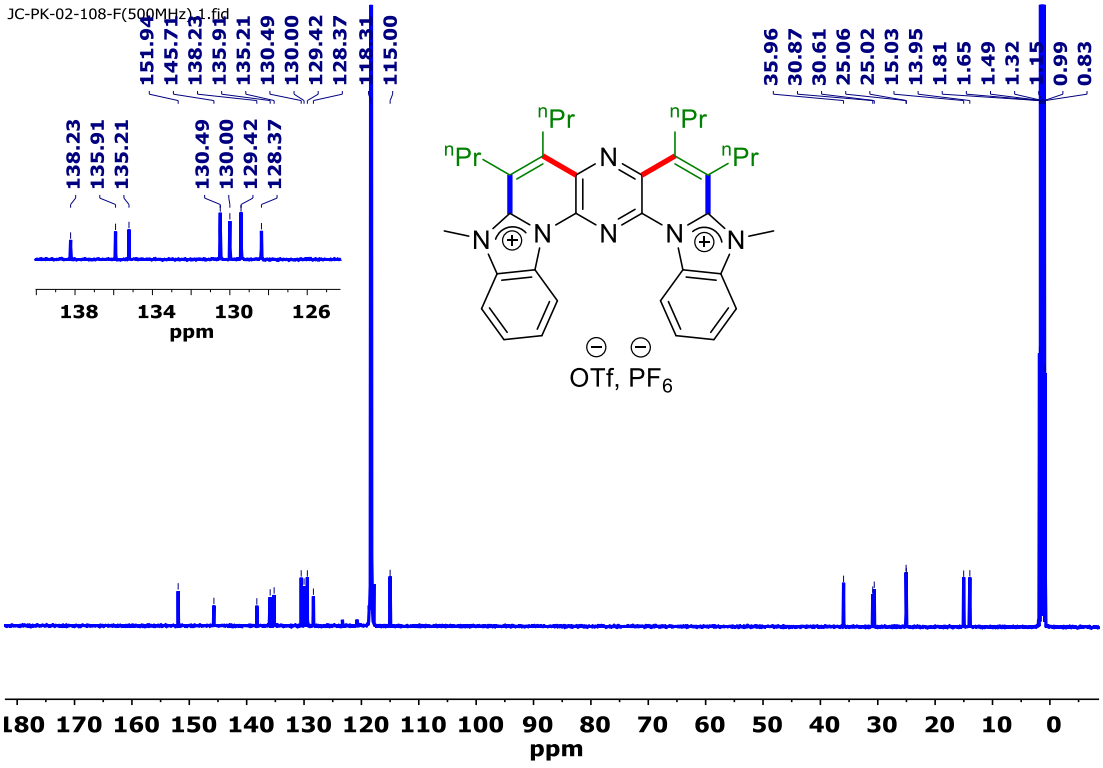

$^{19}$F NMR spectrum of **3o** (471 MHz, $CD_3CN$, 298 K).



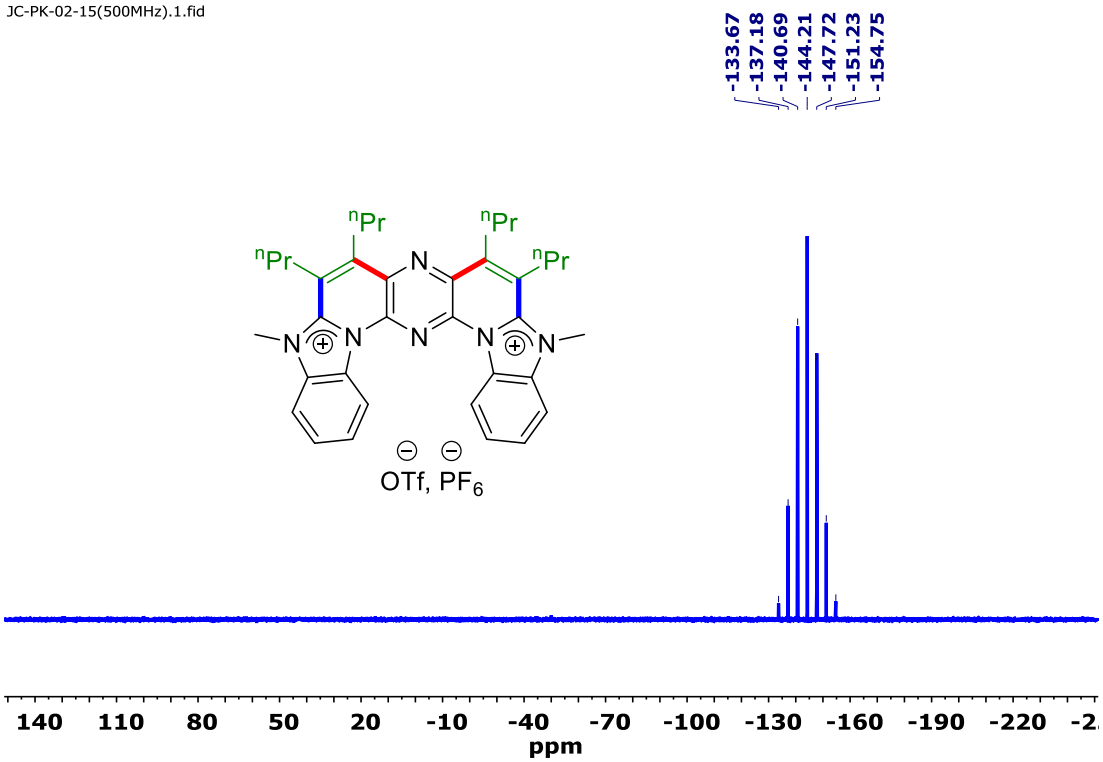

ESI-HRMS (positive ion mode) spectrum of **3o**.



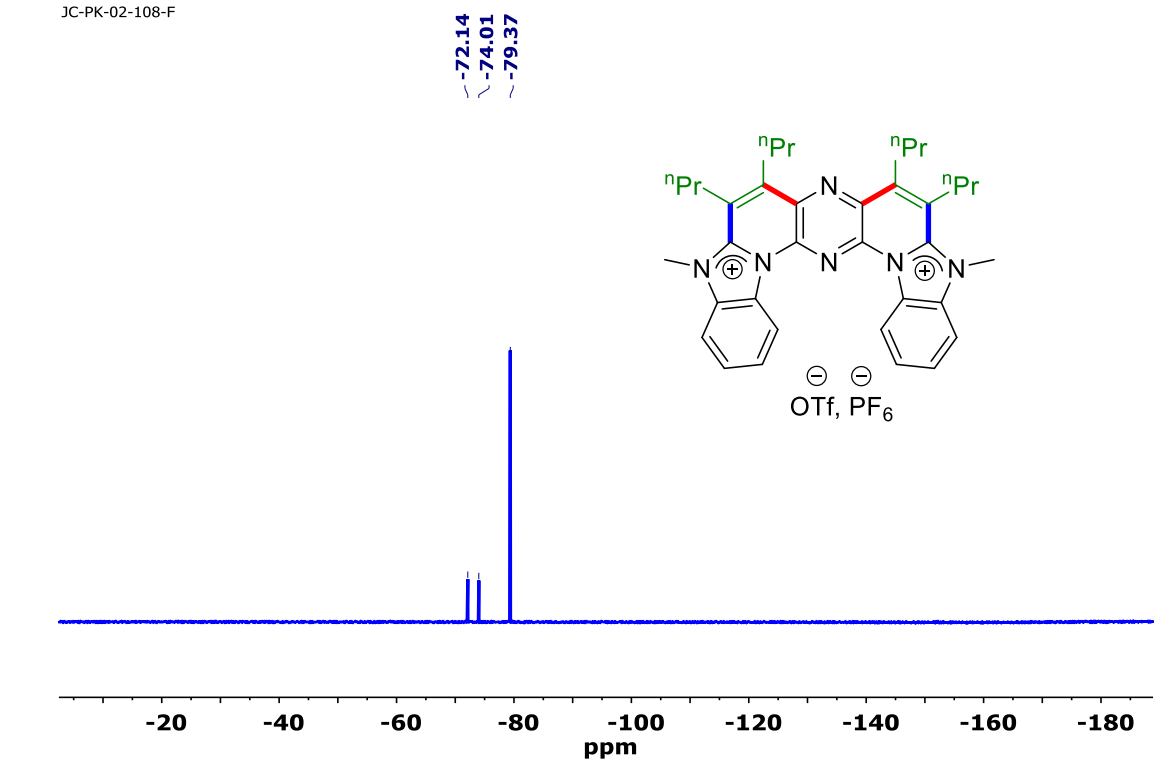

$^{1}$H NMR spectrum of **3p** (500 MHz, $CD_3CN$, 298 K).



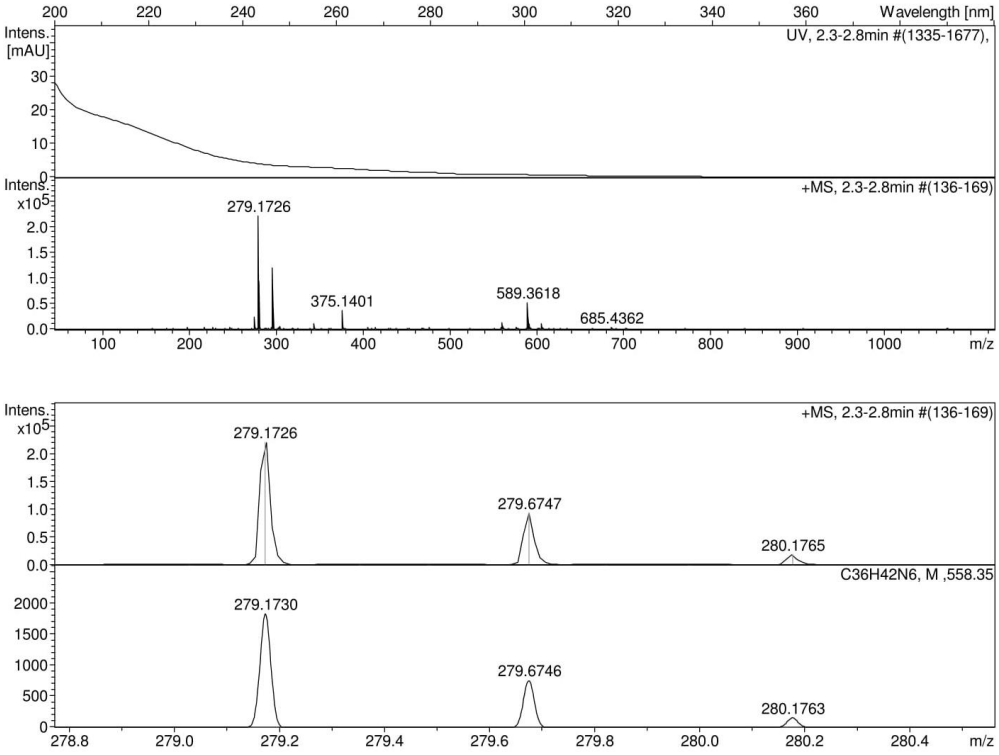

$^{13}$C{$^{1}$H} NMR spectrum of **3p** (126 MHz, $CD_3CN$, 298 K).



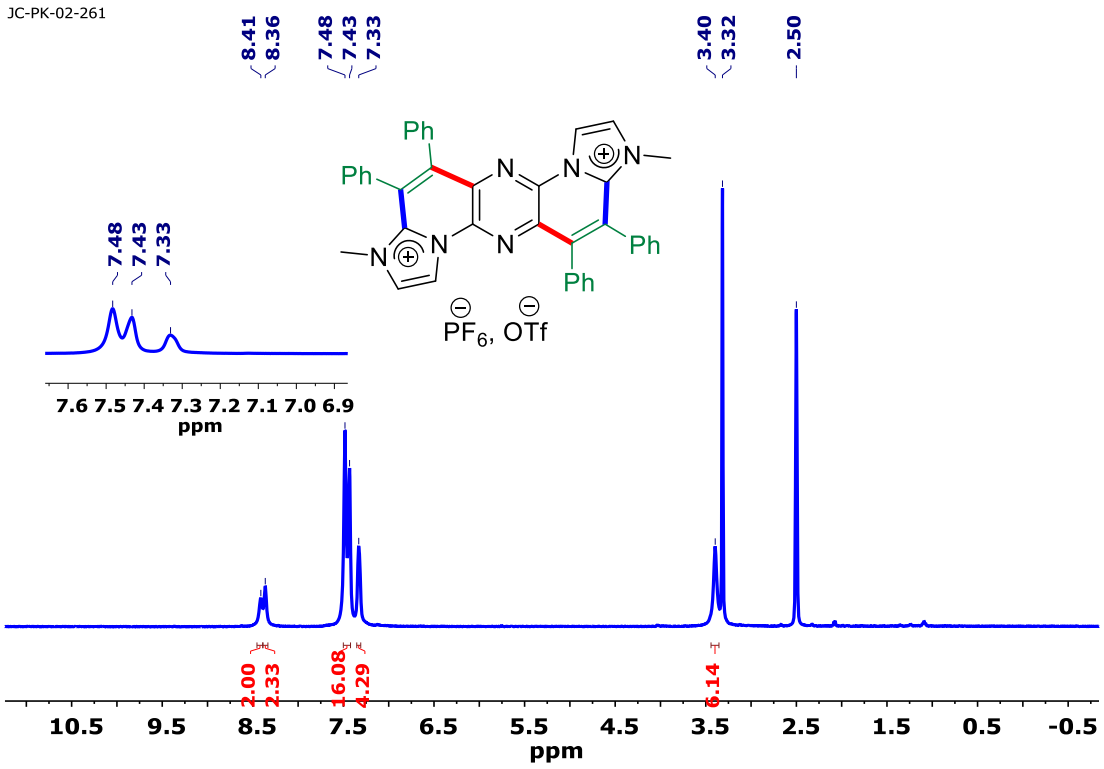

$^{31}$P NMR spectrum of **3p** (202 MHz, $CD_3CN$, 298 K).



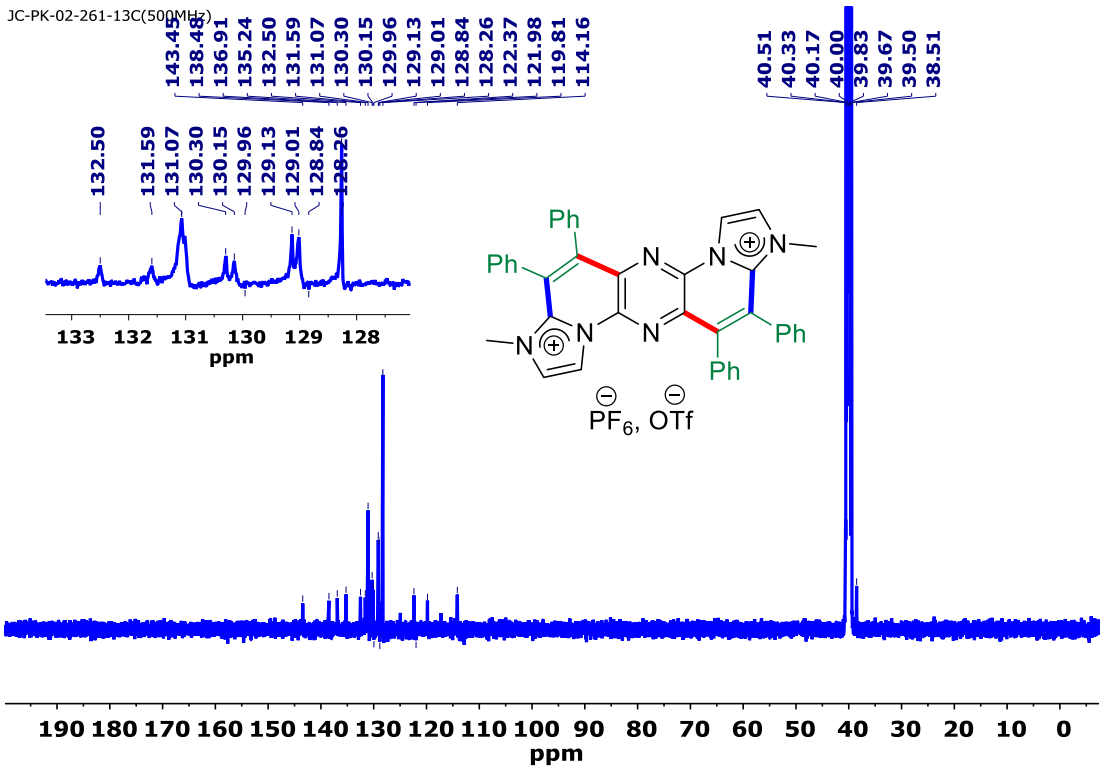

$^{19}$F NMR spectrum of **3p** (471 MHz, $CD_3CN$, 298 K).



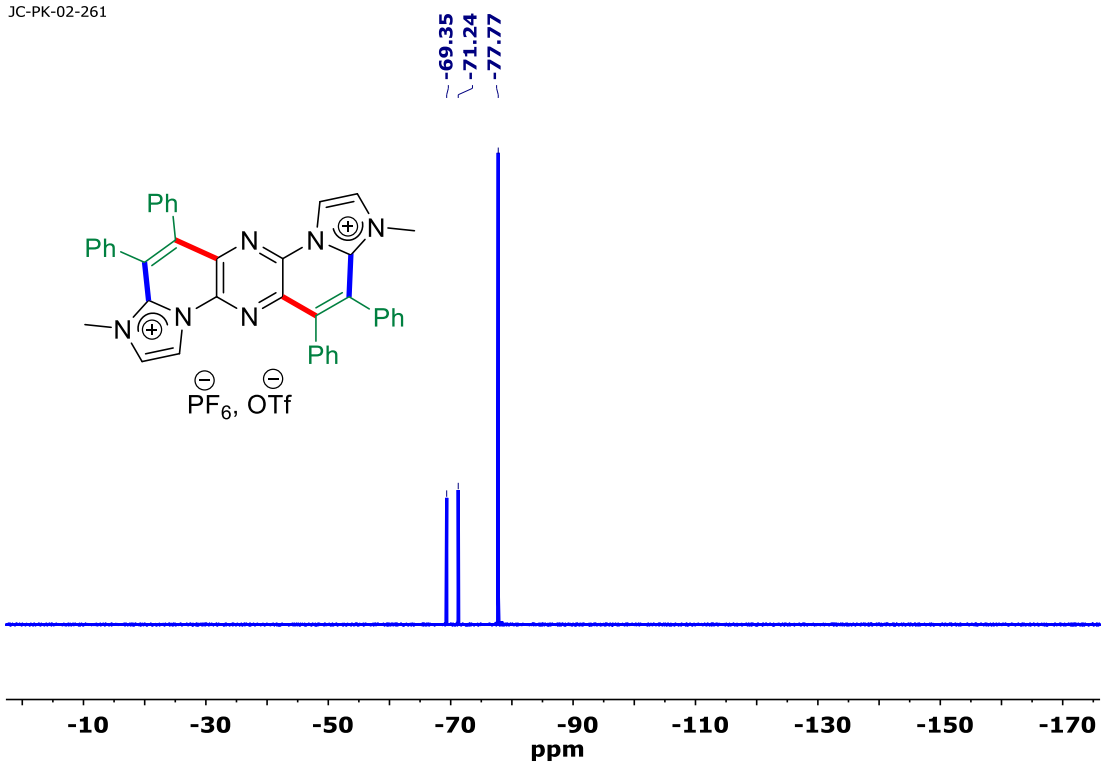

ESI-HRMS (positive ion mode) spectrum of **3p**.



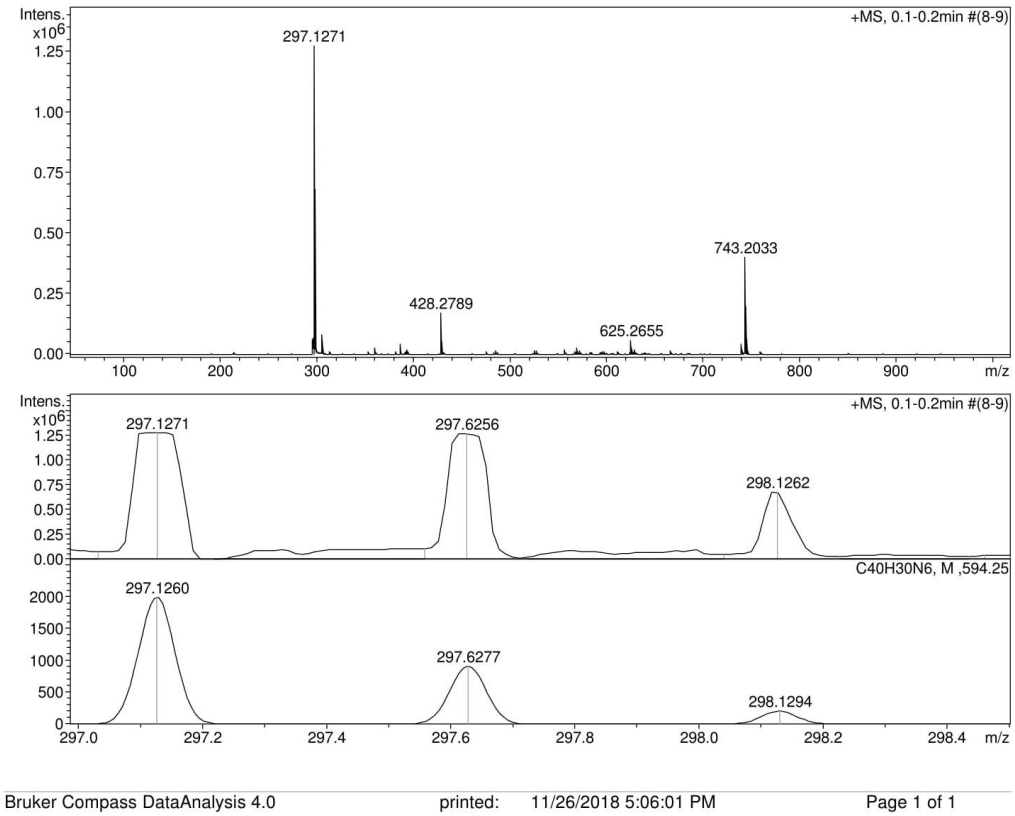

$^{1}$H NMR spectrum of **3q** (500 MHz, DMSO-$d_6$, 298 K).



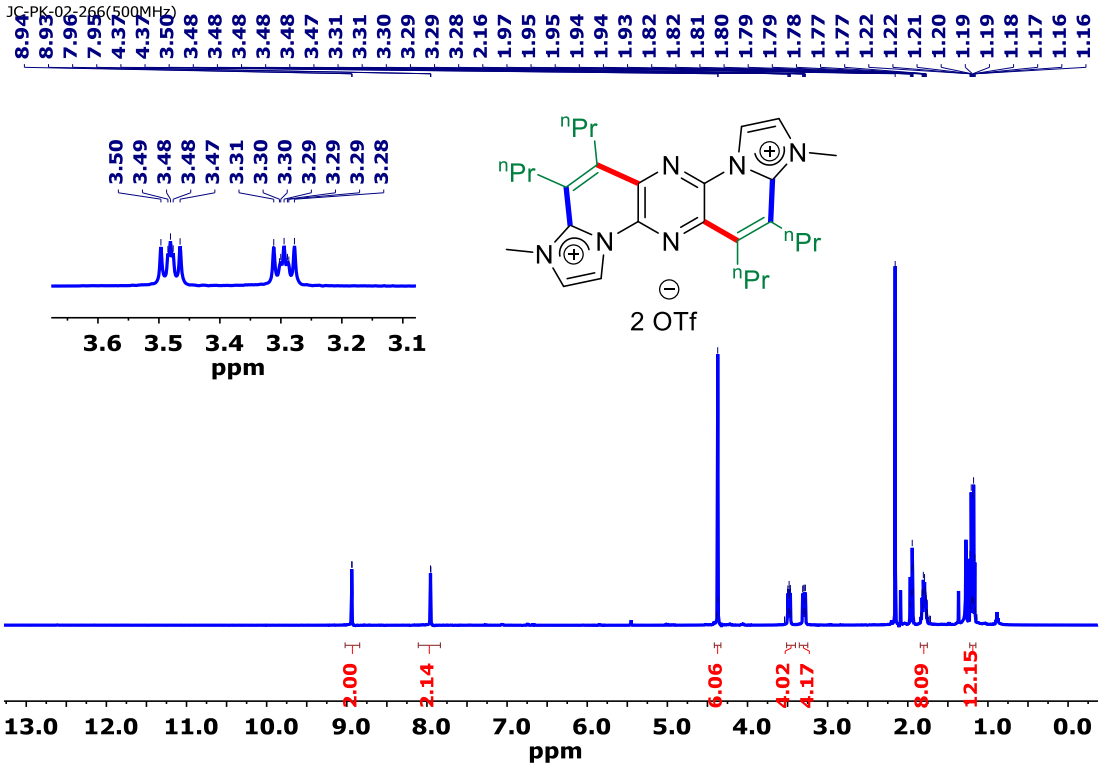

$^{13}C\{^{1}H\}$ NMR spectrum of **3q** (126 MHz, DMSO-$d_6$, 298 K).



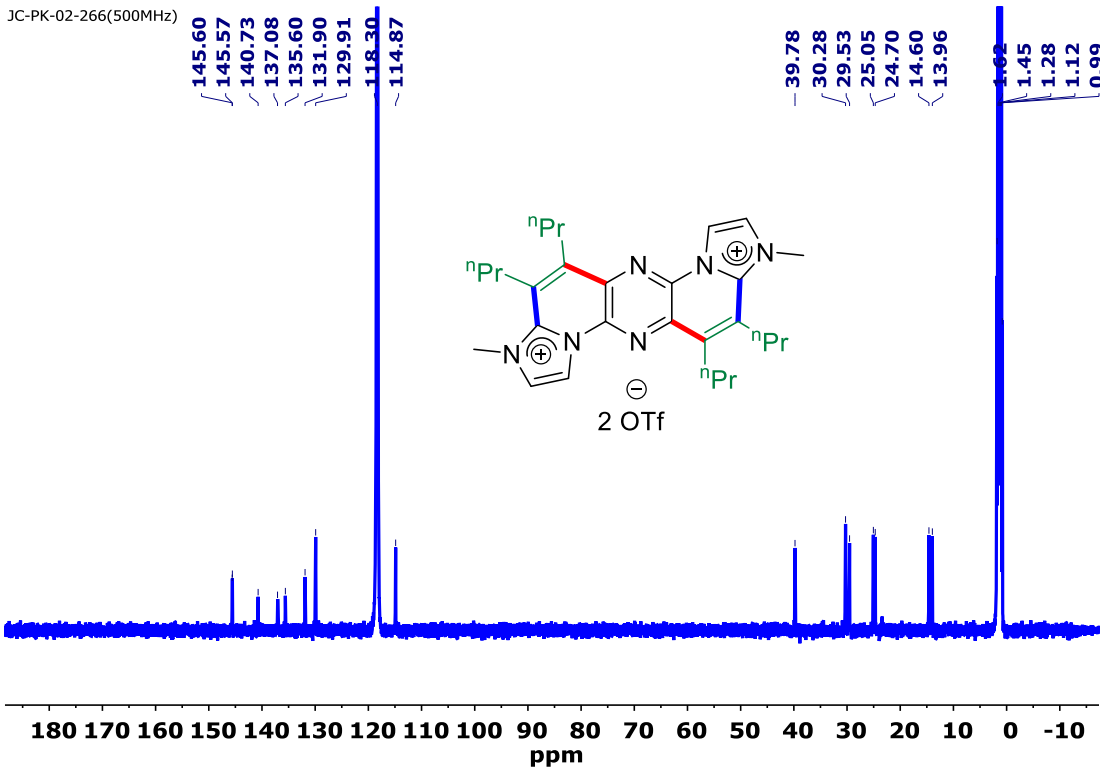

$^{19}F$ NMR spectrum of **3q** (376 MHz, DMSO-$d_6$, 298 K).



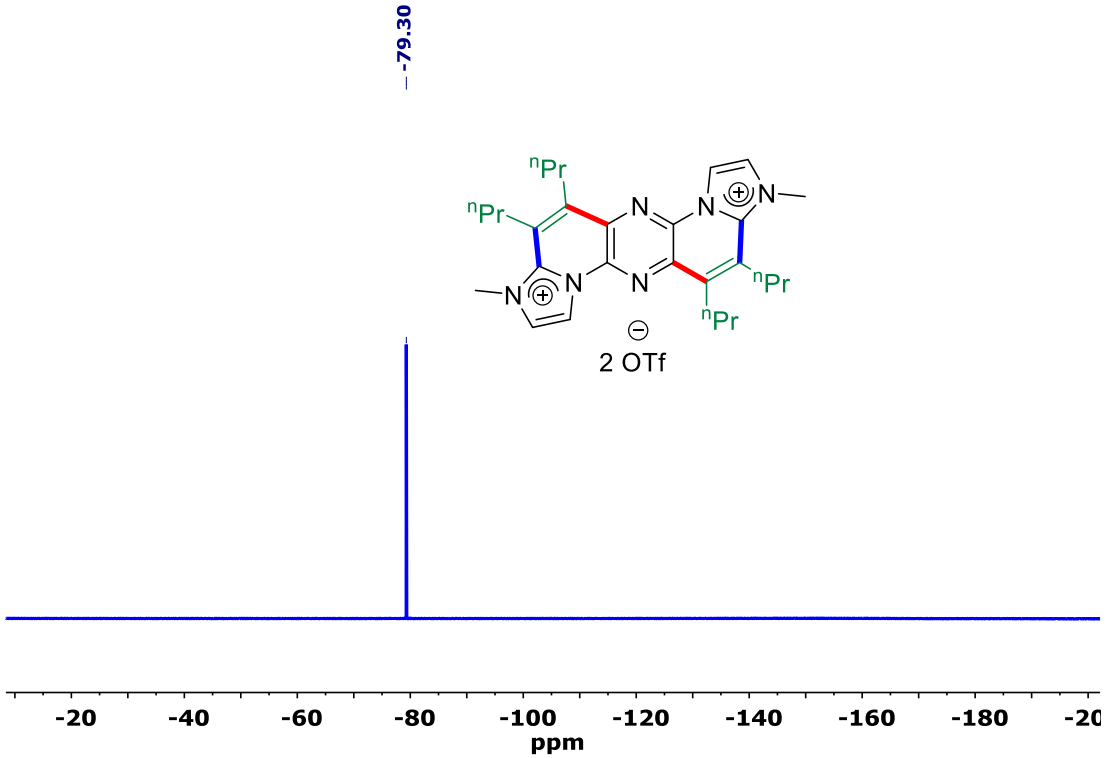

ESI-HRMS (positive ion mode) spectrum of **3q**.



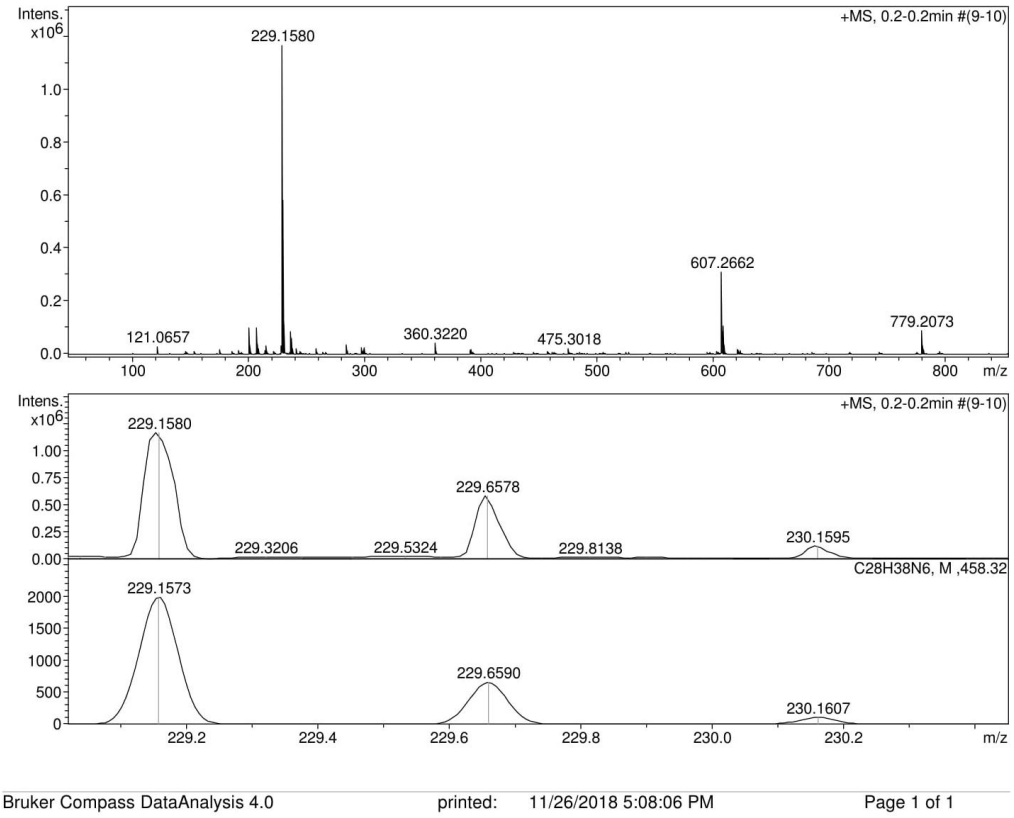

$^1$H NMR spectrum of **3r** (500 MHz, $CD_3CN$, 298 K).



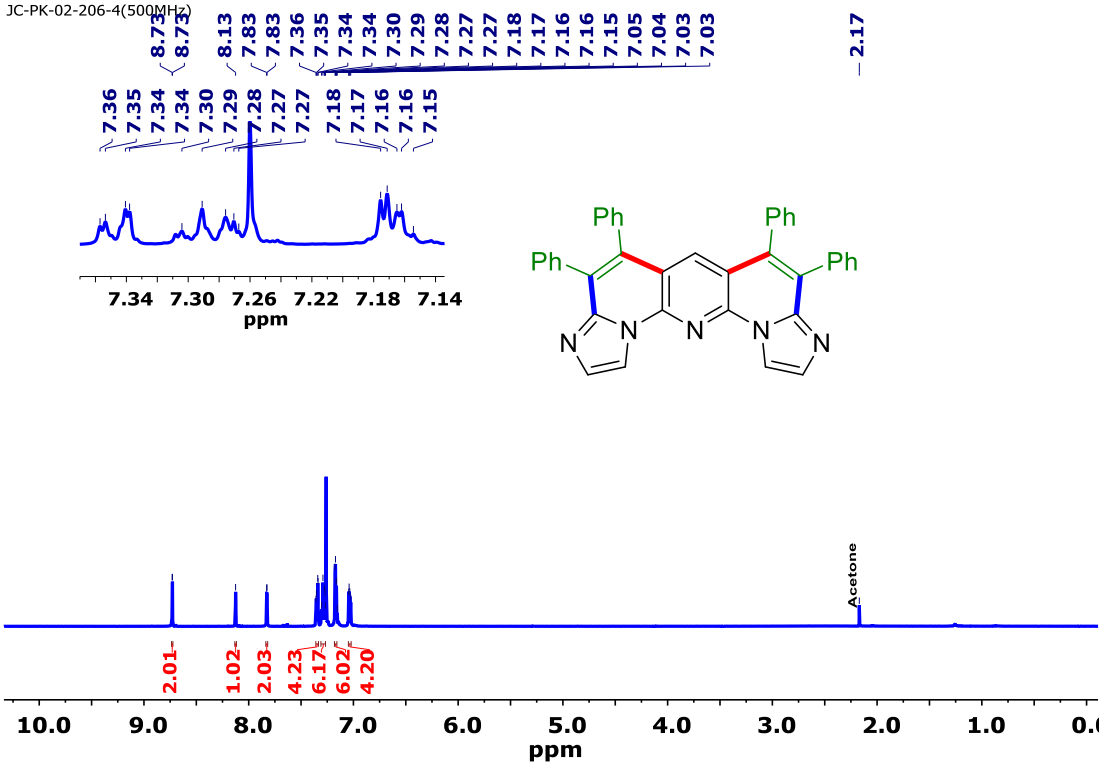

$^{13}C\{^{1}H\}$ NMR spectrum of **3r** (126 MHz, $CD_3CN$, 298 K).



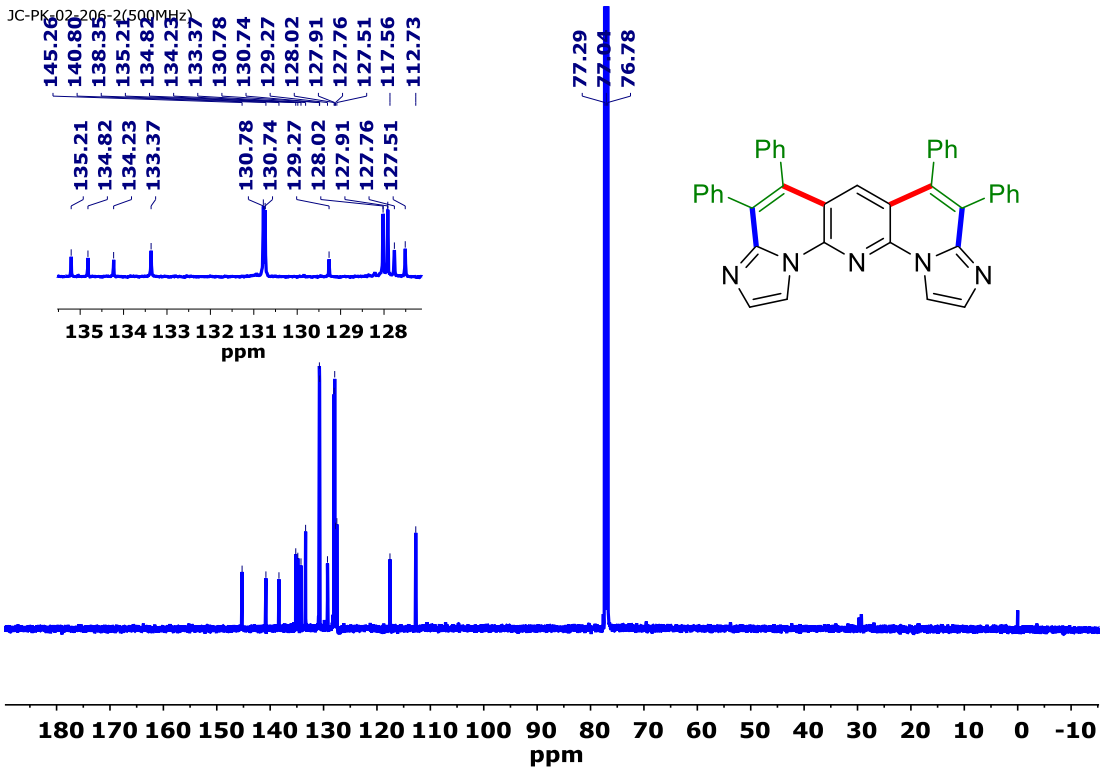

$^{19}F$ NMR spectrum of **3r** (376 MHz, DMSO-$d_6$, 298 K).



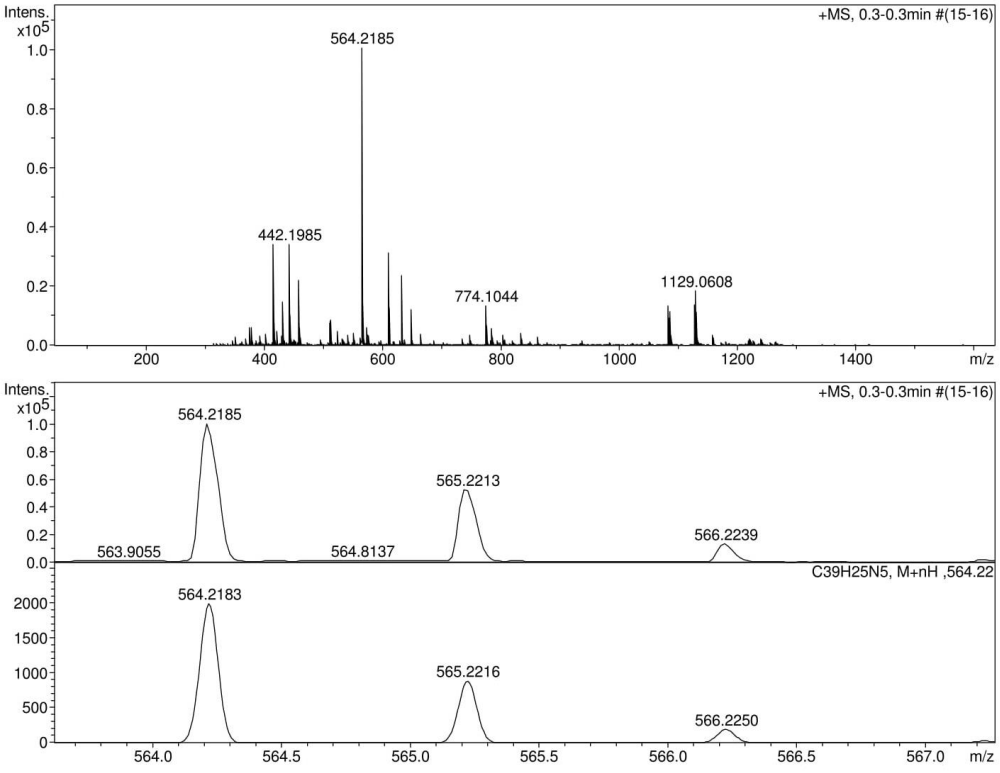

ESI-HRMS (positive ion mode) spectrum of **3r**.



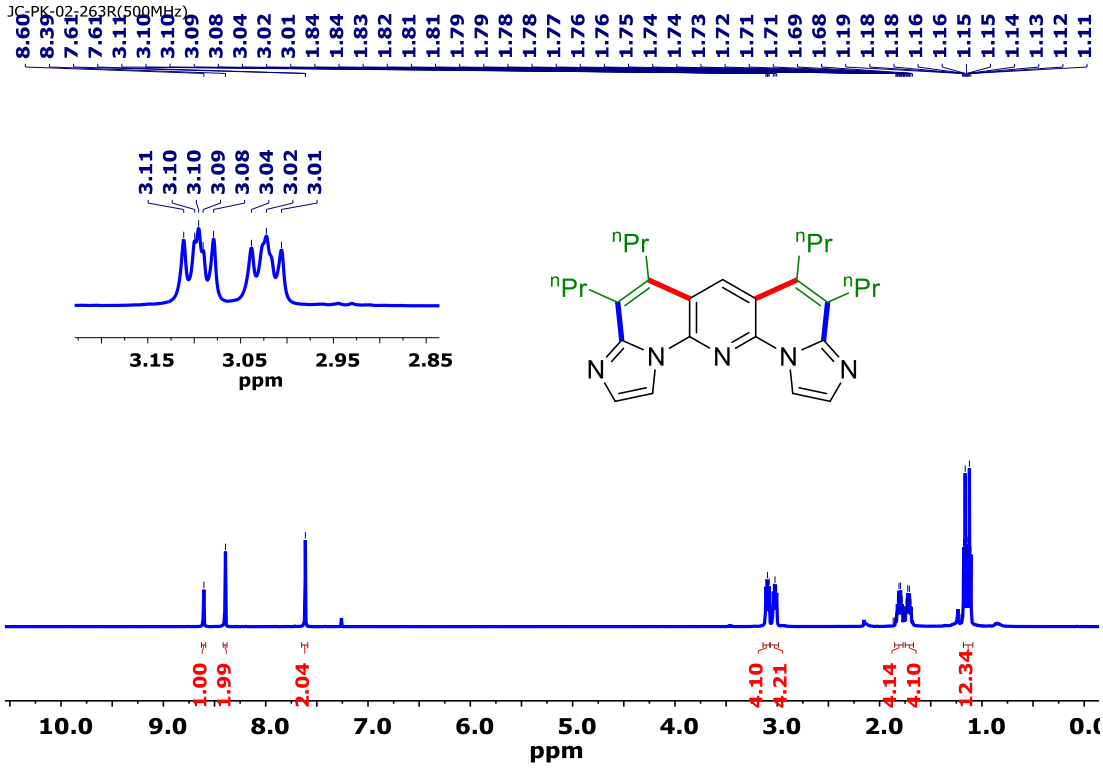

$^{1}$H NMR spectrum of **3s** (500 MHz, $CDCl_3$, 298 K).



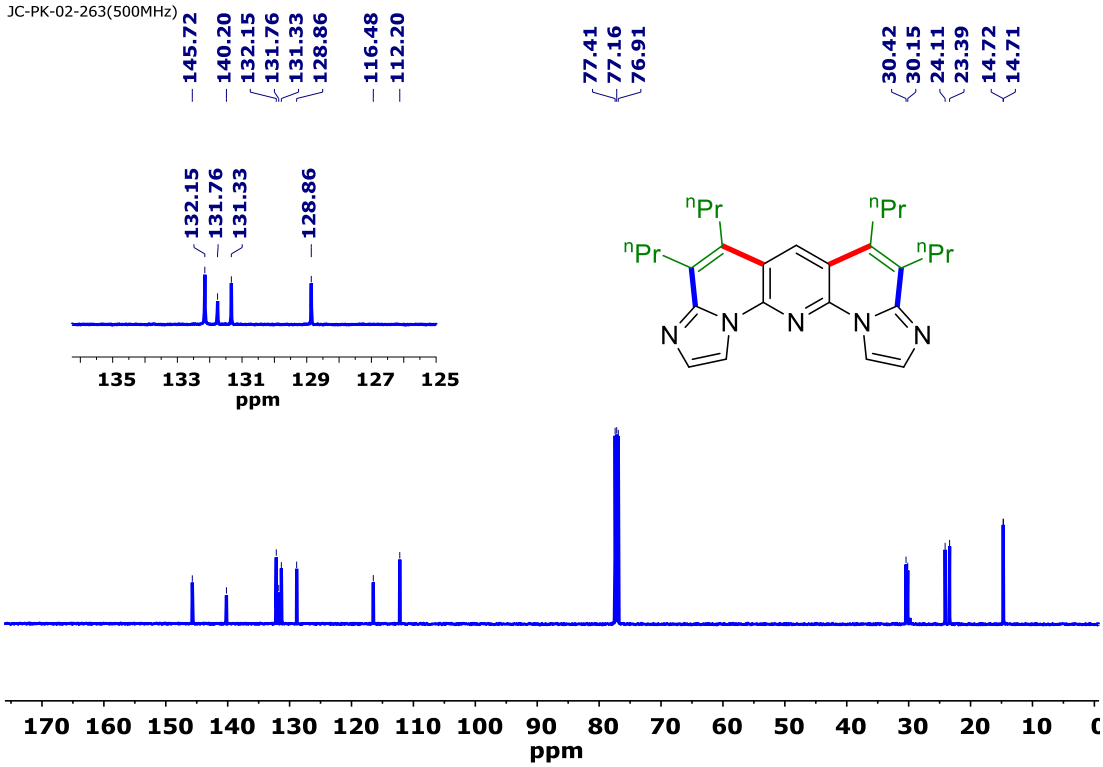

$^{13}C\{^{1}H\}$ NMR spectrum of **3s** (126 MHz, $CDCl_3$, 298 K).



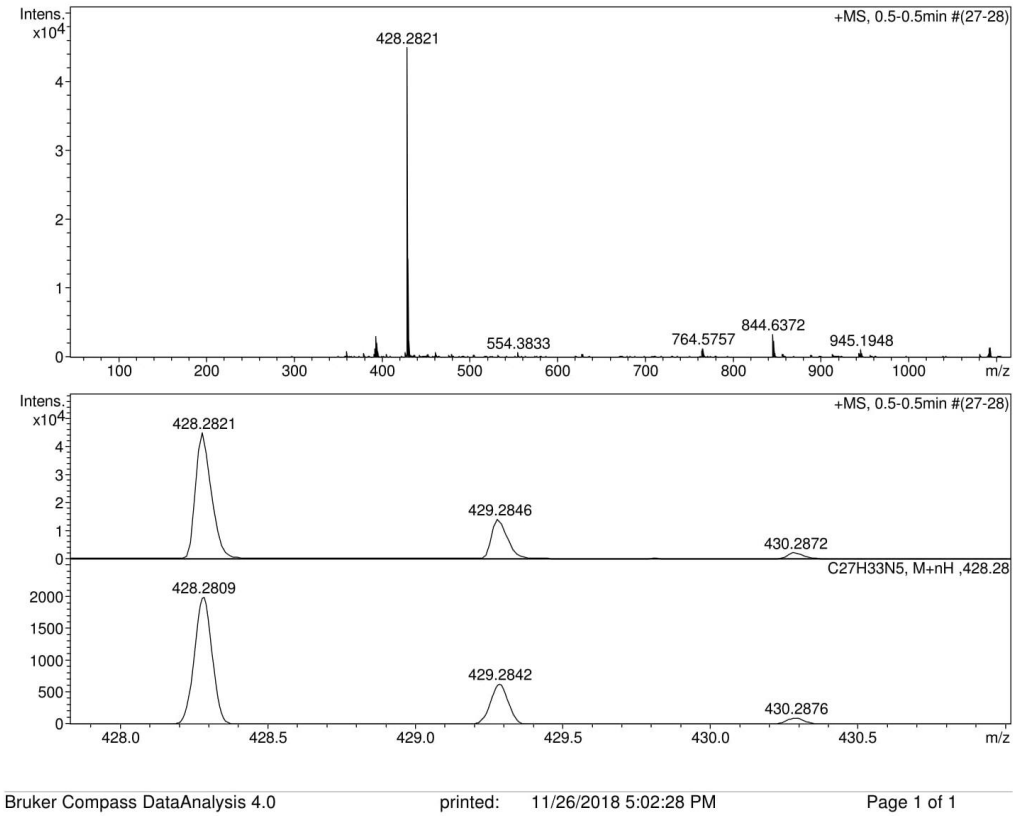

ESI-HRMS (positive ion mode) spectrum of **3s**.



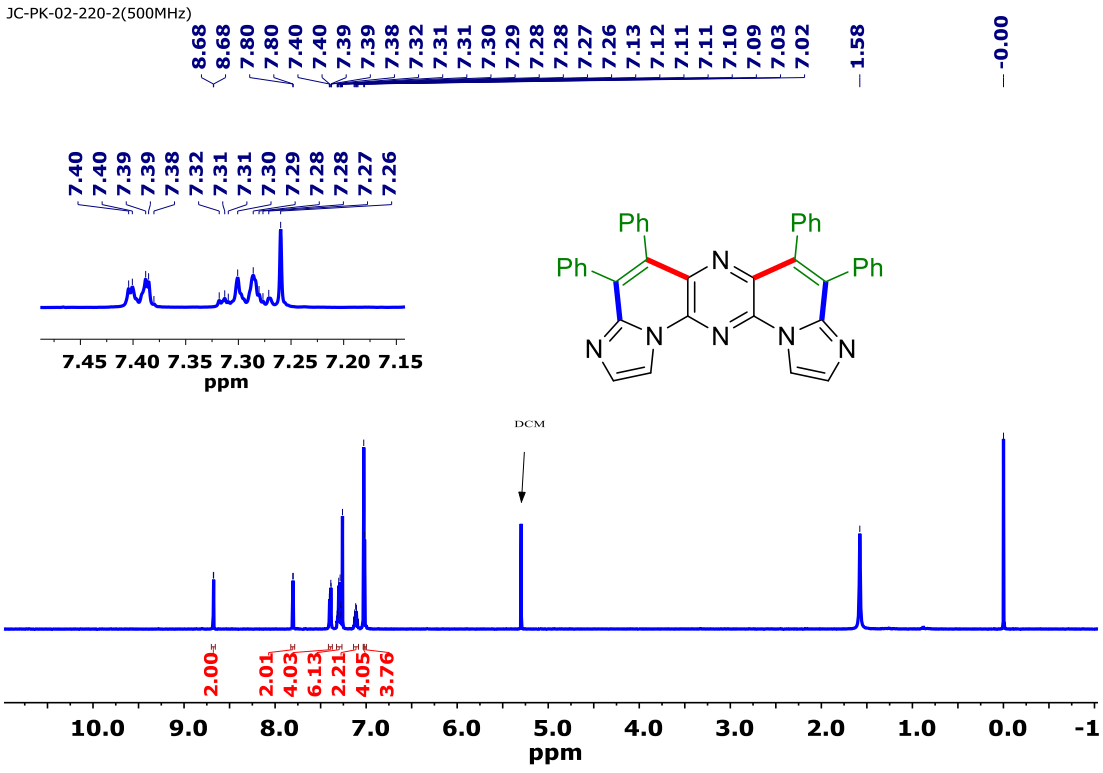

$^{1}$H NMR spectrum of **3t** (500 MHz, $CDCl_3$, 298 K).



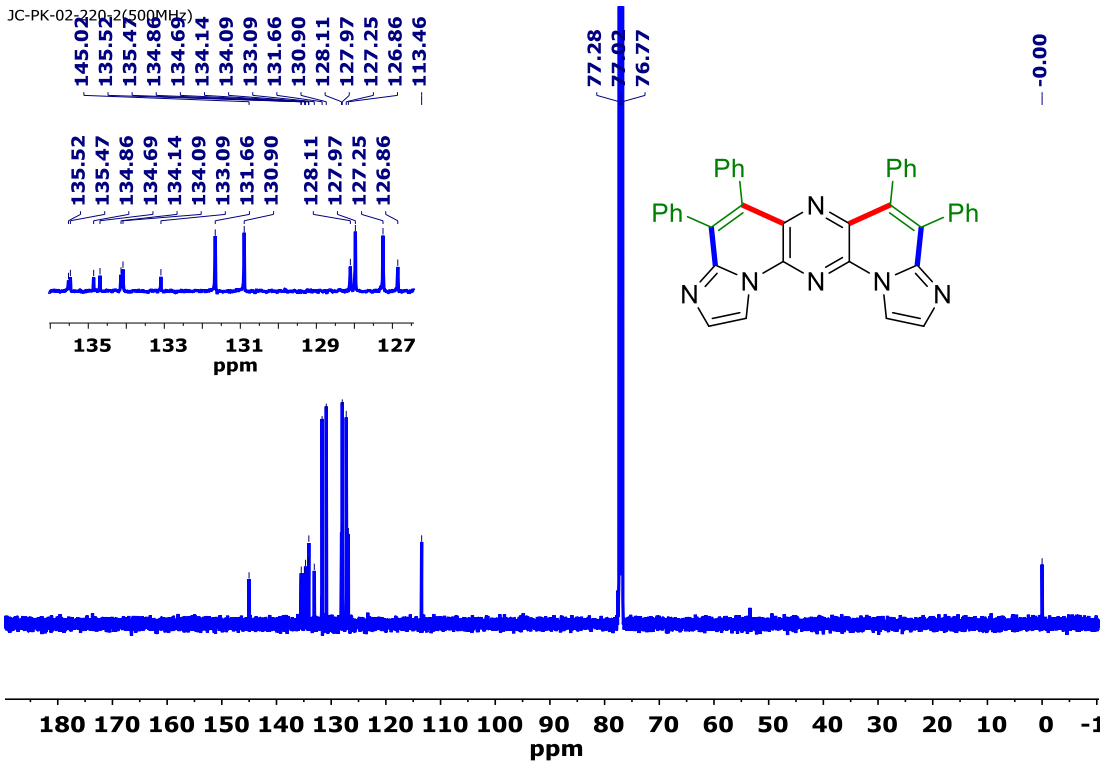

$^{13}$C{$^{1}$H} NMR spectrum of **3t** (126 MHz, $CDCl_3$, 298 K).



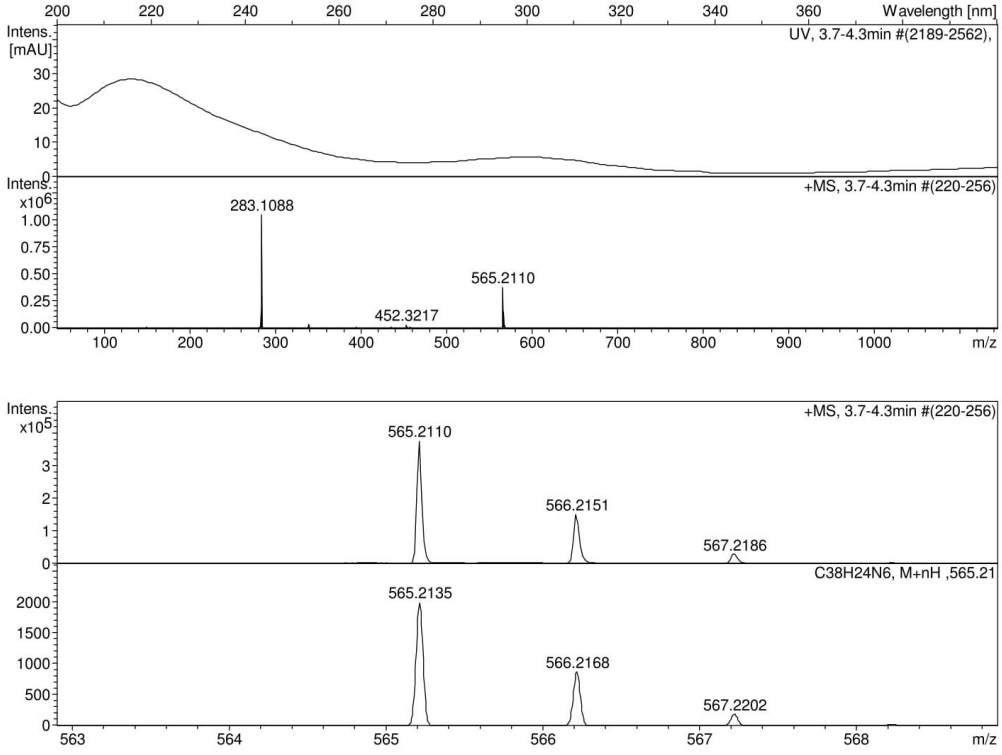

ESI-HRMS (positive ion mode) spectrum of **3t**.



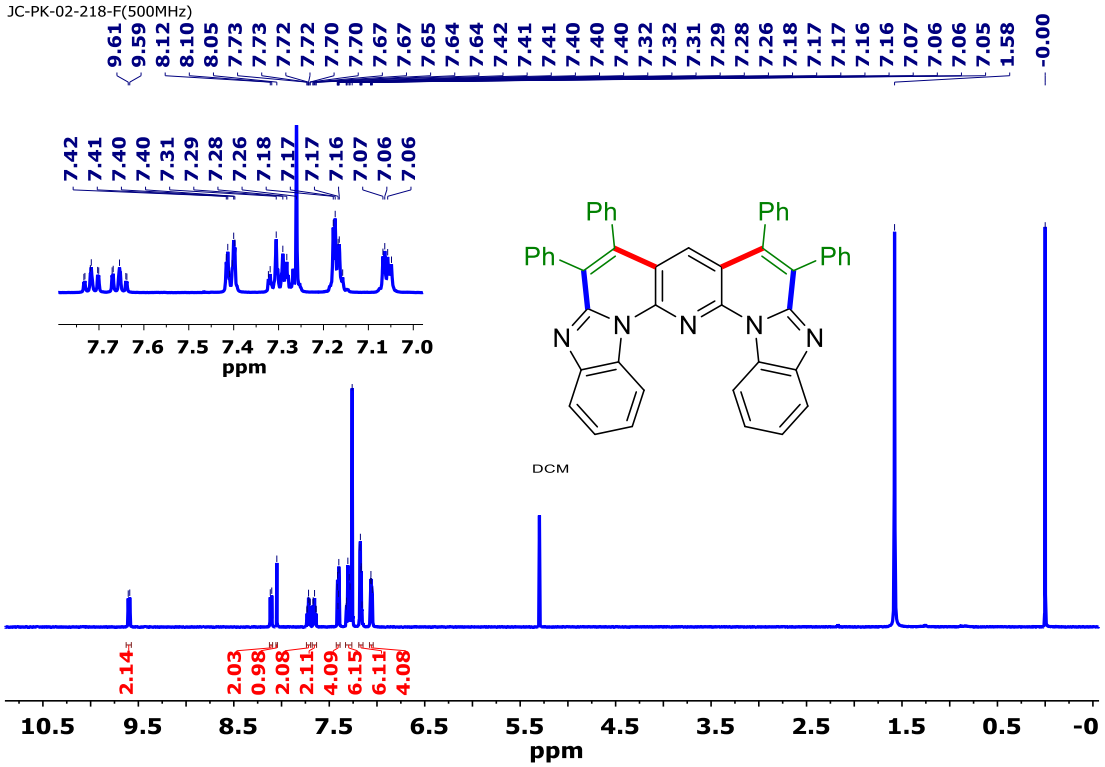

$^{1}$H NMR spectrum of **3u** (500 MHz, $CDCl_3$, 298 K).



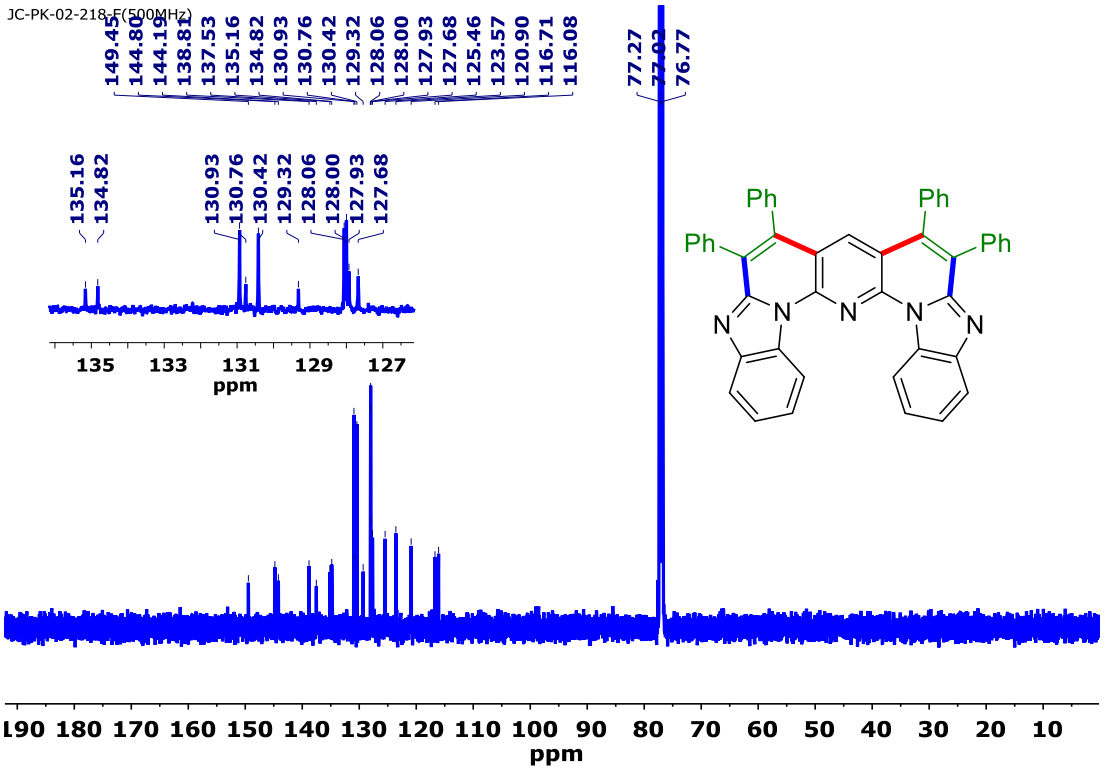

$^{13}C\{^{1}H\}$ NMR spectrum of **3u** (126 MHz, $CDCl_3$, 298 K).



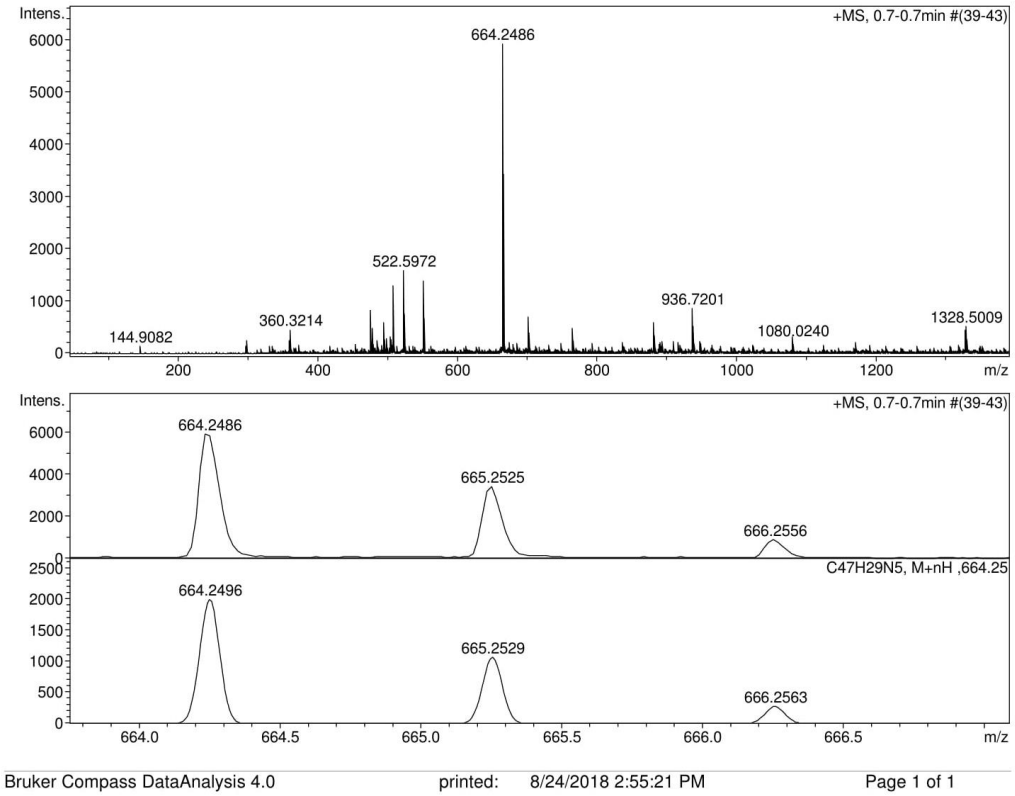

ESI-HRMS (positive ion mode) spectrum of **3u**.



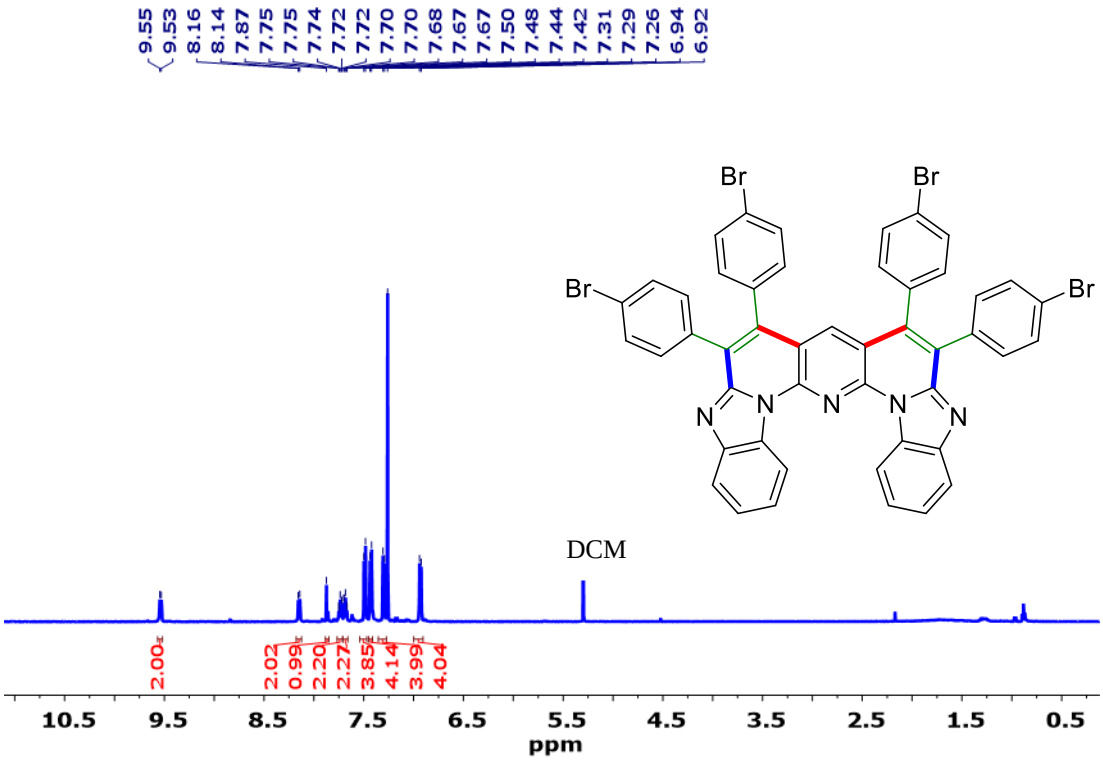

$^{1}$H NMR spectrum of **3v** (500 MHz, $CDCl_3$, 298 K).



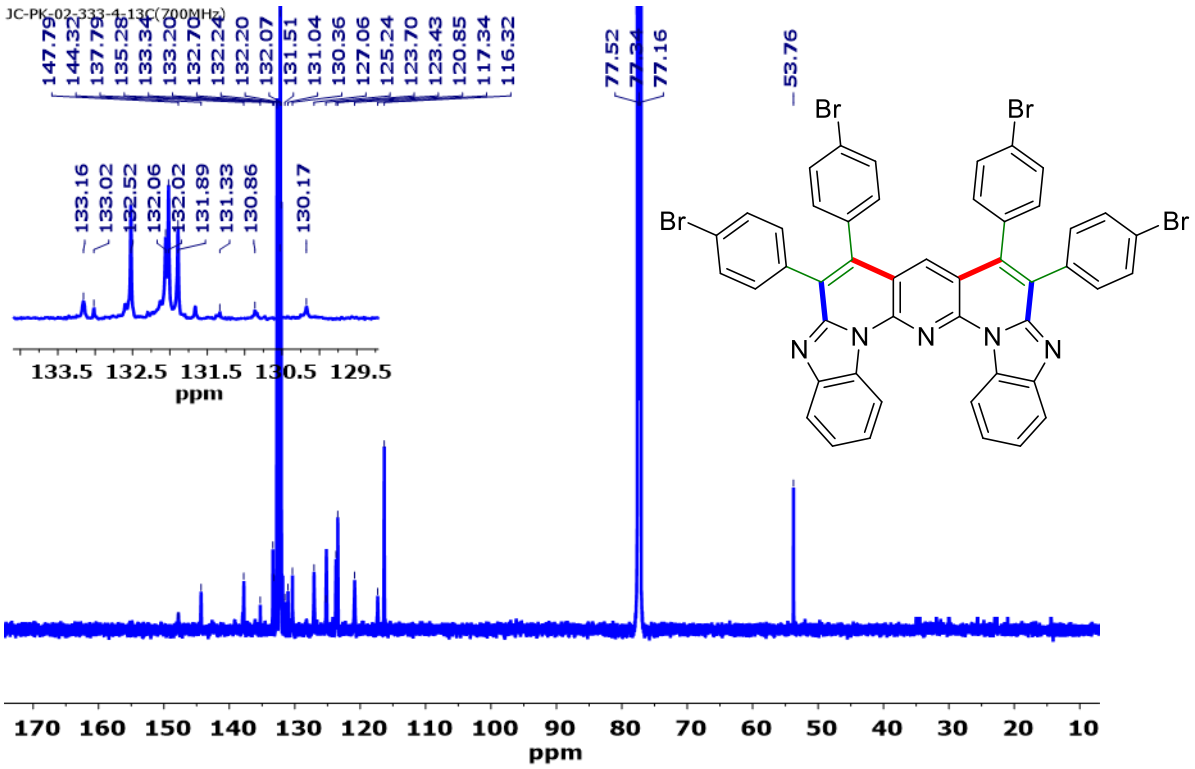

$^{13}$C{$^{1}$H} NMR spectrum of **3v** (126 MHz, $CDCl_3$, 298 K).



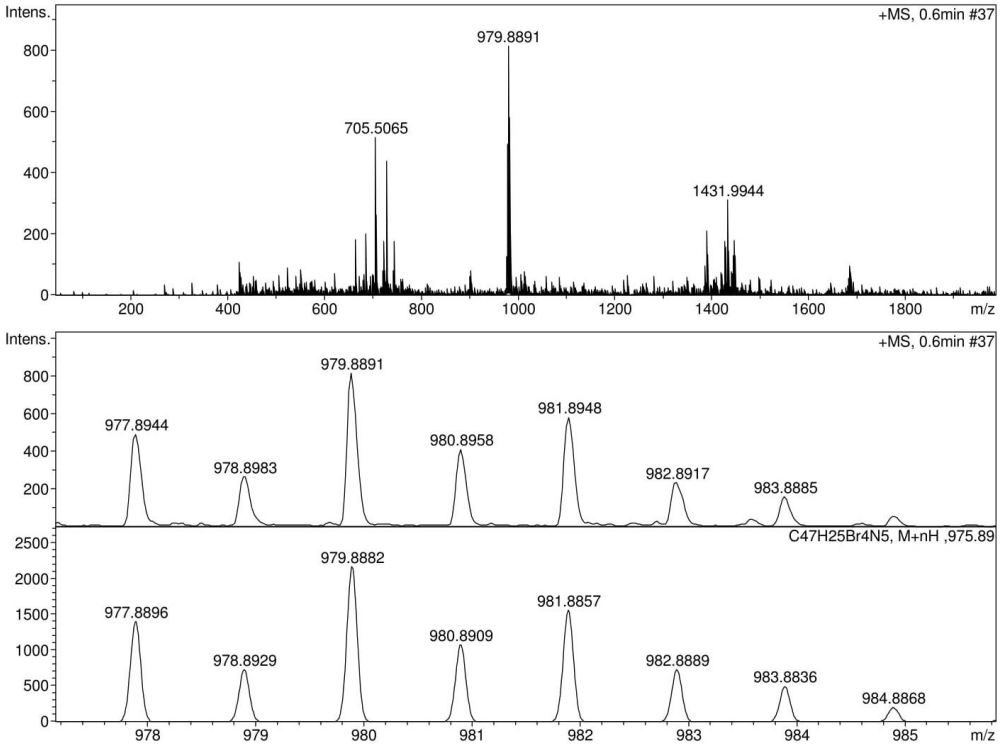

ESI-HRMS (positive ion mode) spectrum of **3v**.



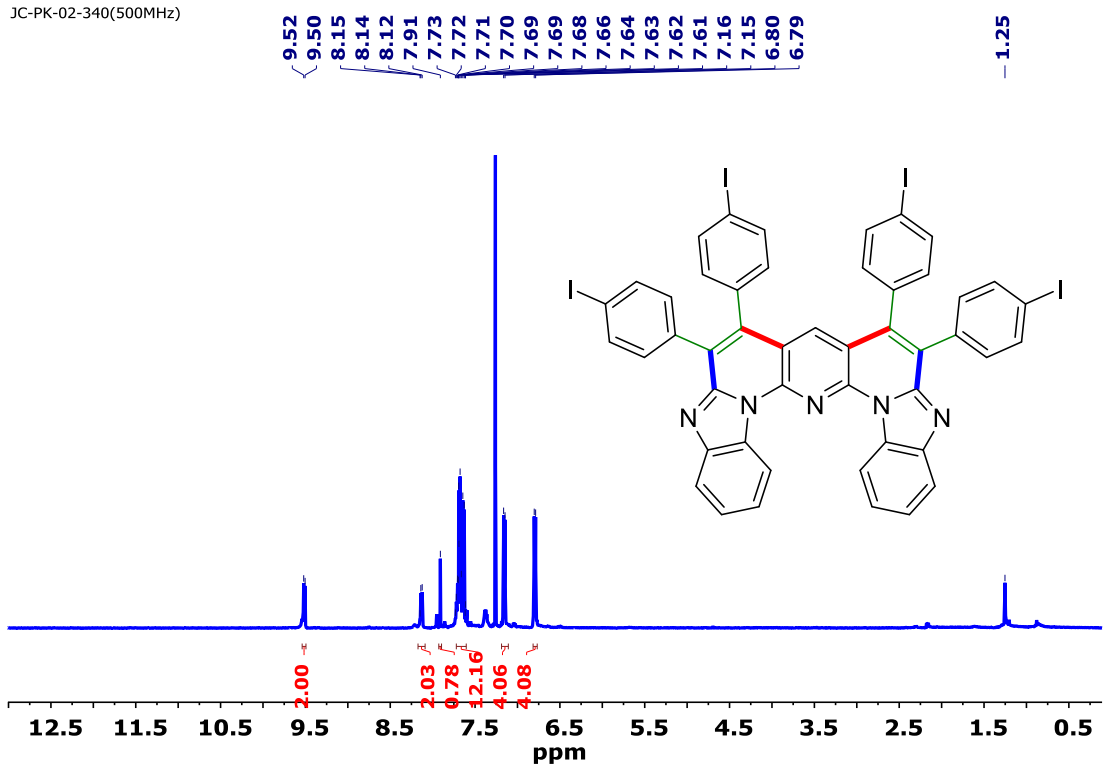

$^{1}$H NMR spectrum of **3w** (500 MHz, $CDCl_3$, 298 K).



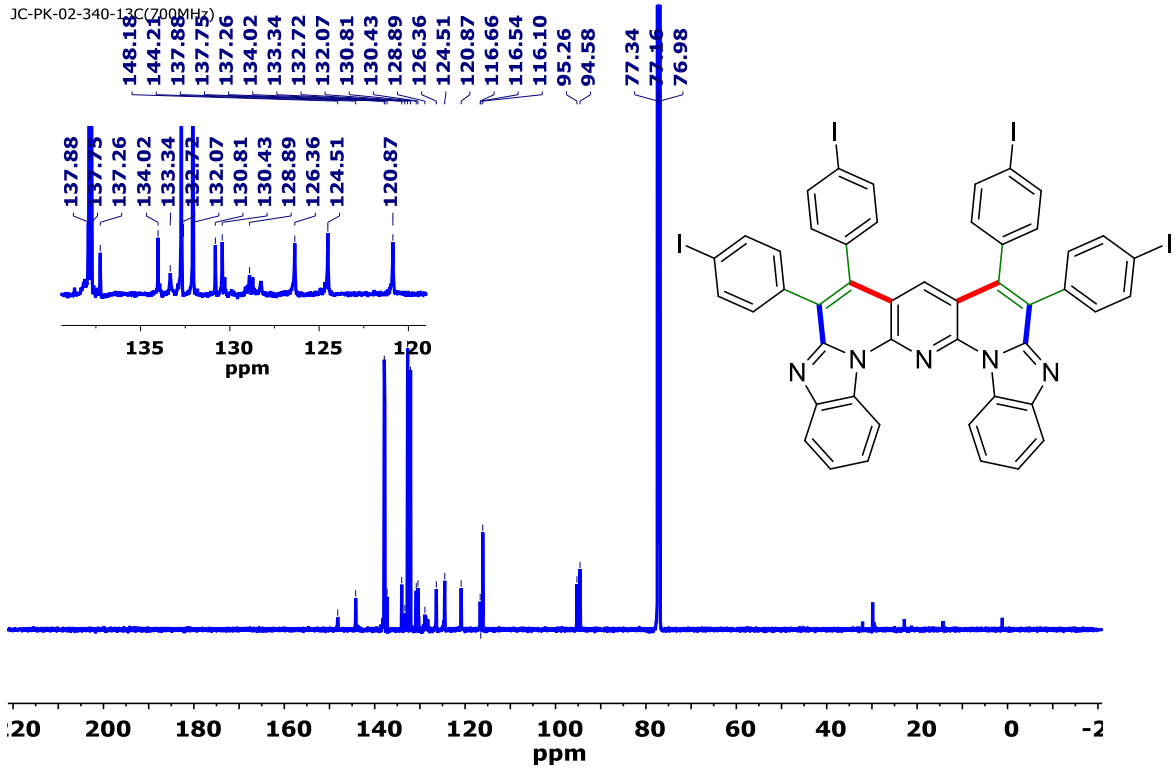

$^{13}C\{^{1}H\}$ NMR spectrum of **3w** (176 MHz, $CDCl_3$, 298 K).



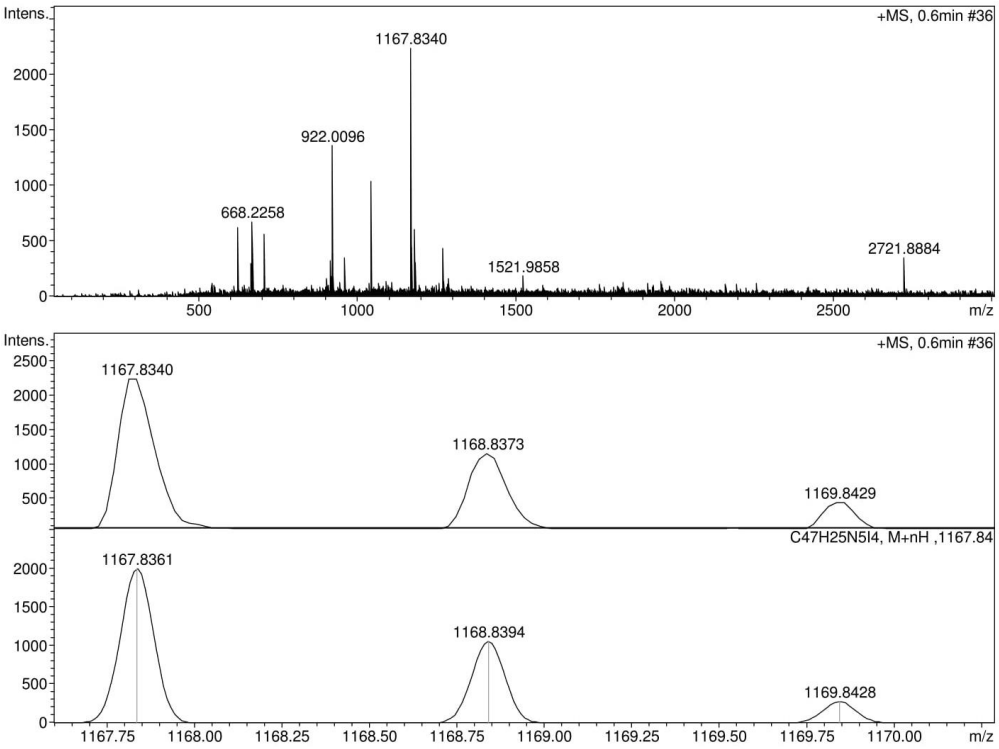

ESI-HRMS (positive ion mode) spectrum of **3w**.



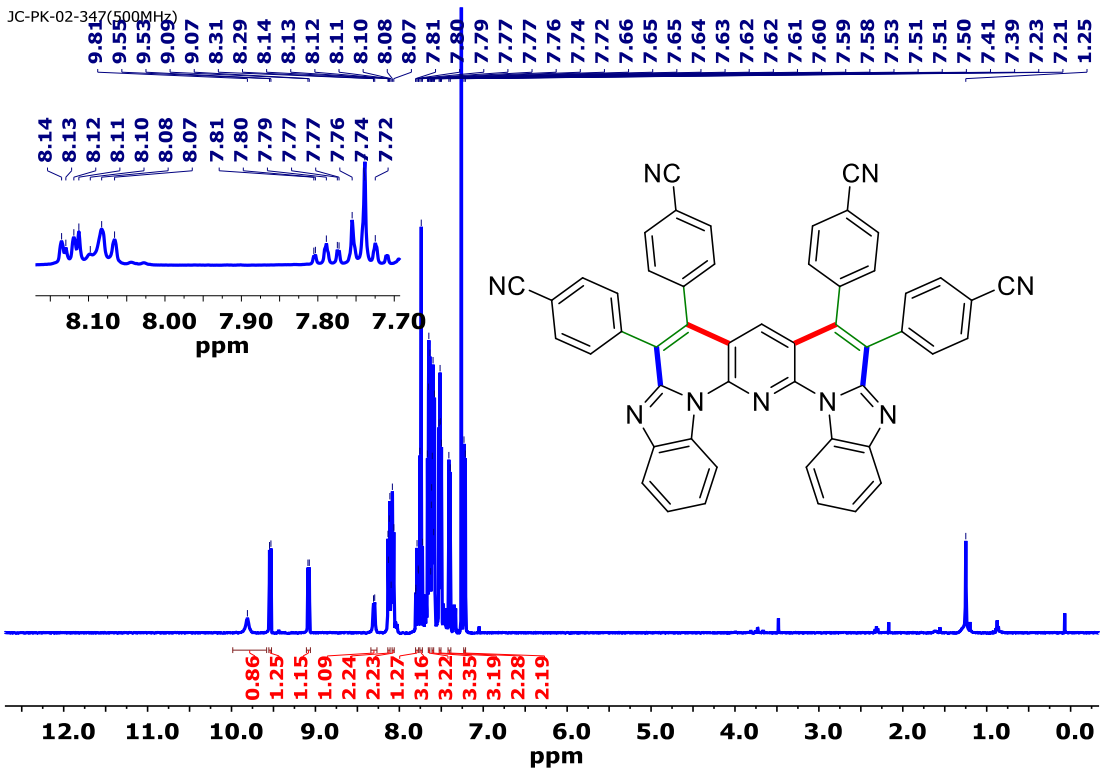

$^{1}$H NMR spectrum of **3x** (500 MHz, $CDCl_3$, 298 K).



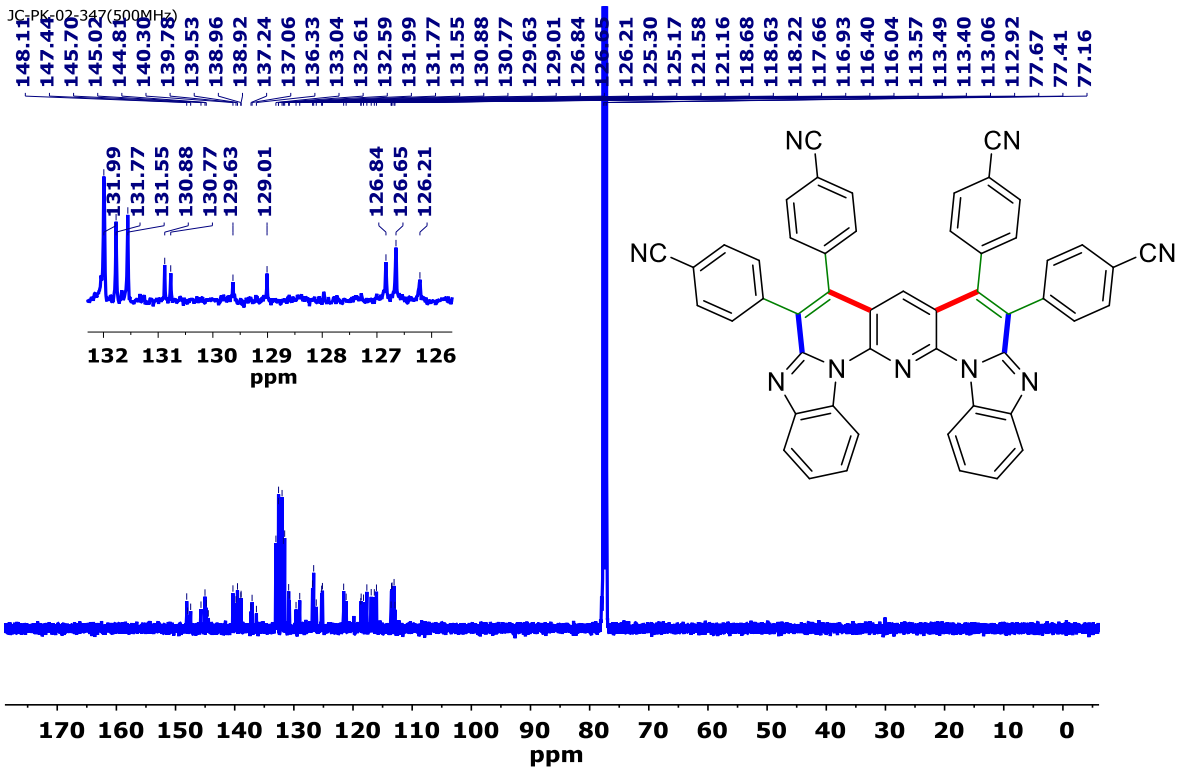

$^{13}$C{$^{1}$H} NMR spectrum of **3x** (176 MHz, $CDCl_3$, 298 K).



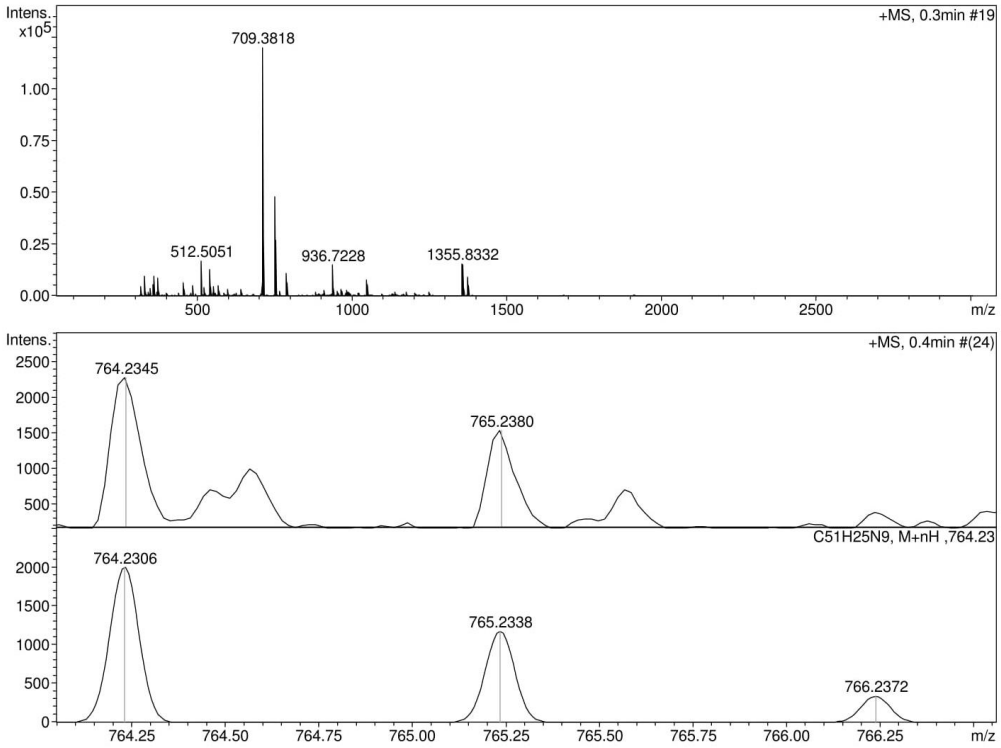

ESI-HRMS (positive ion mode) spectrum of **3x**.



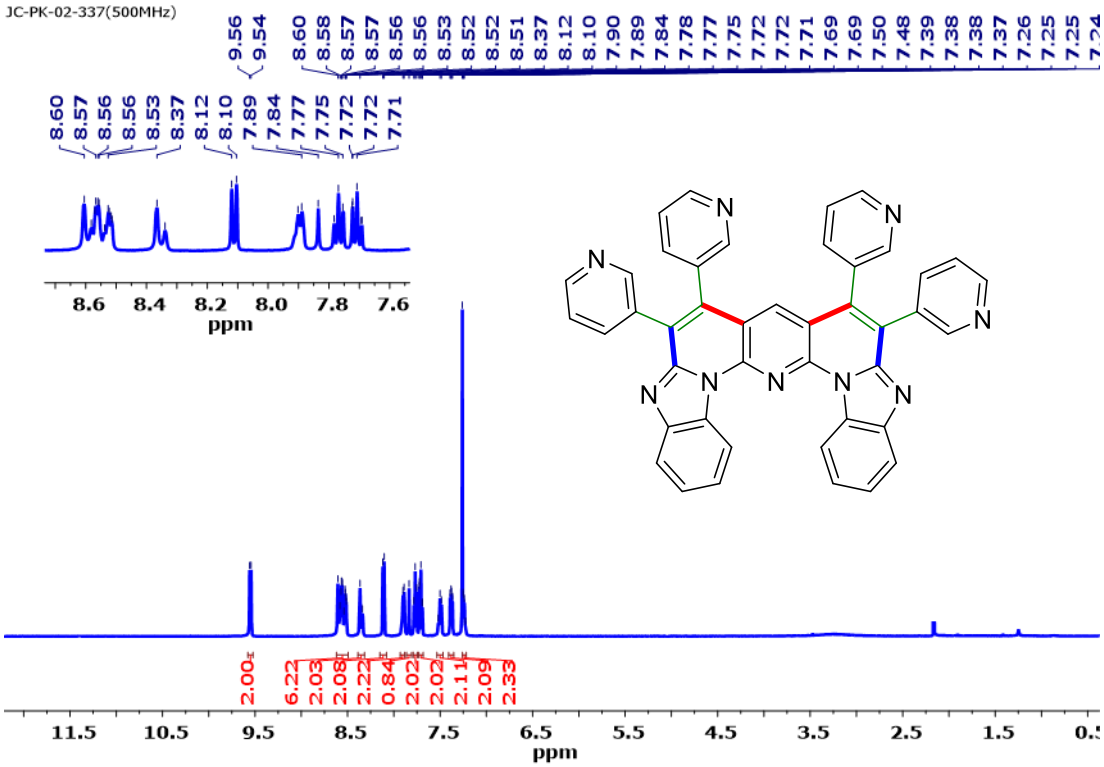

$^{1}$H NMR spectrum of **3y** (500 MHz, $CDCl_3$, 298 K).



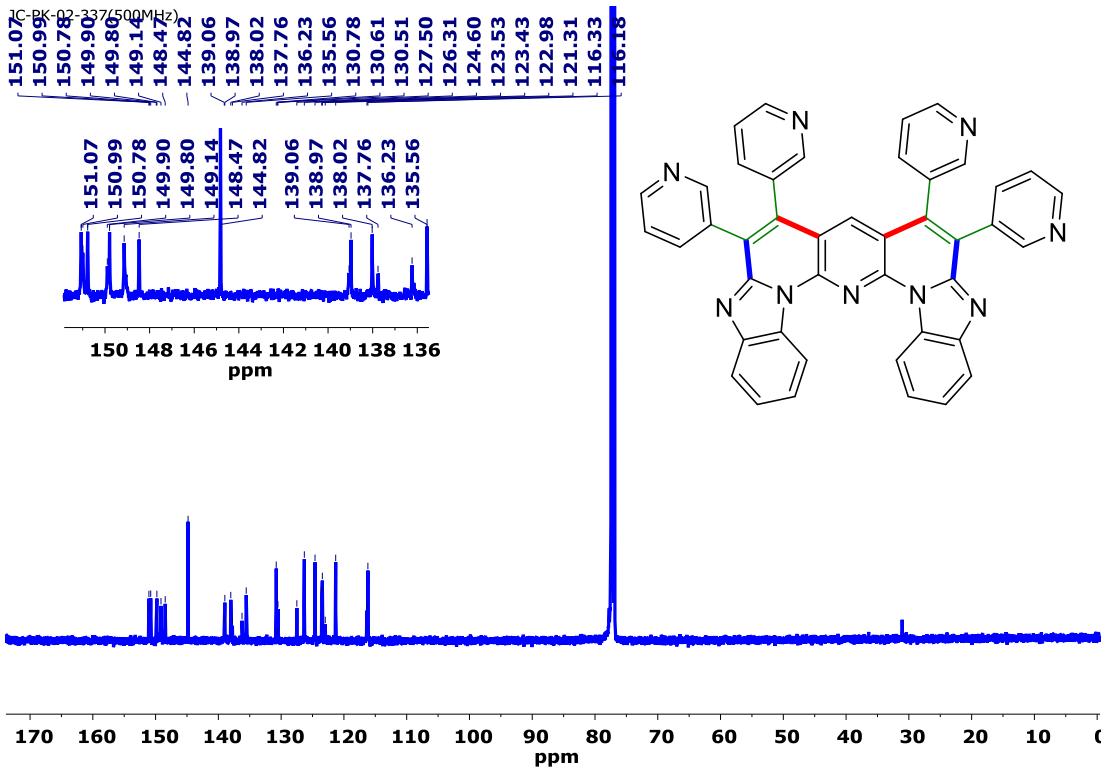

$^{13}C\{^{1}H\}$ NMR spectrum of **3y** (126 MHz, CDCl3, 298 K).



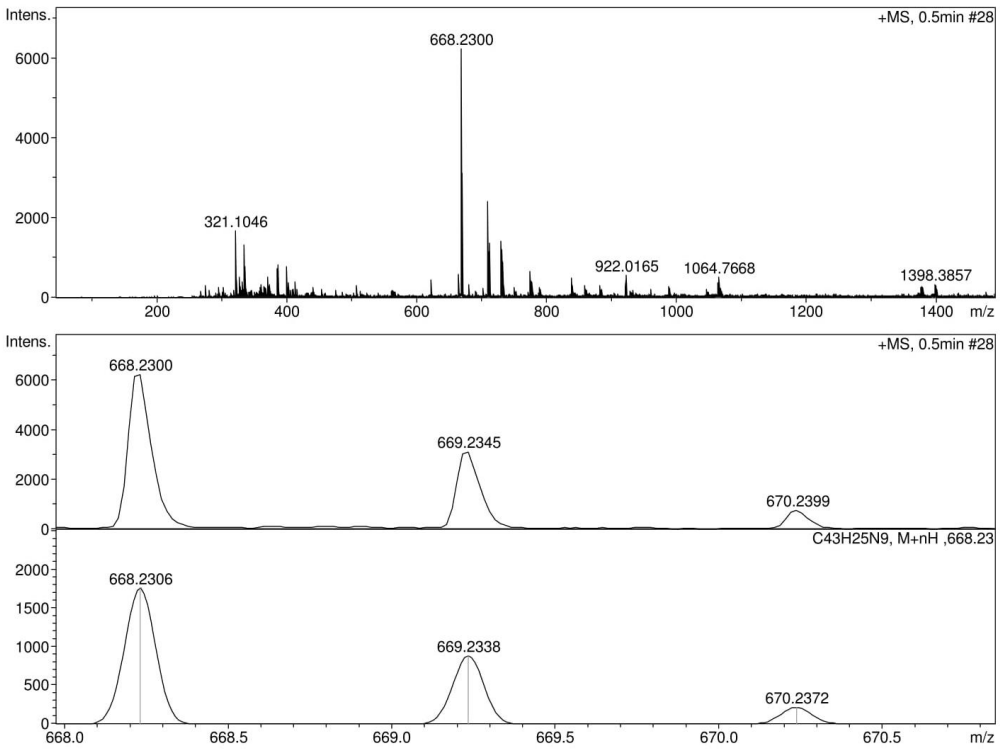

ESI-HRMS (positive ion mode) spectrum of **3y**.



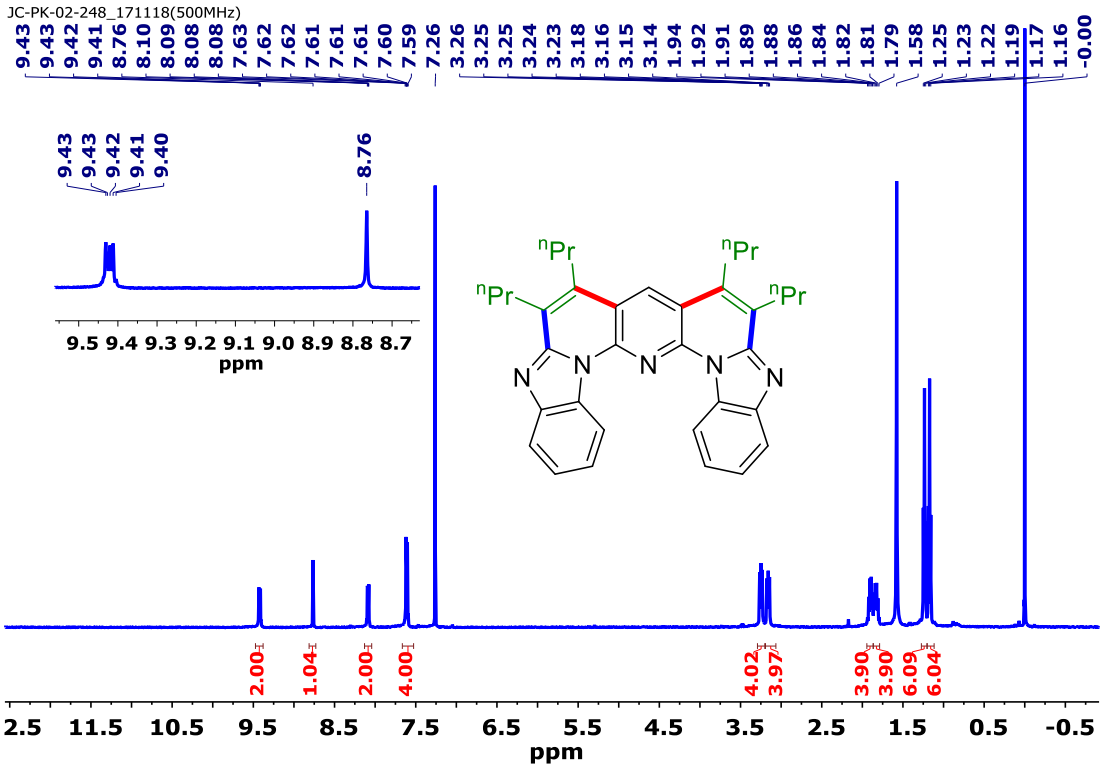

$^{1}$H NMR spectrum of **3z** (500 MHz, $CDCl_3$, 298 K).



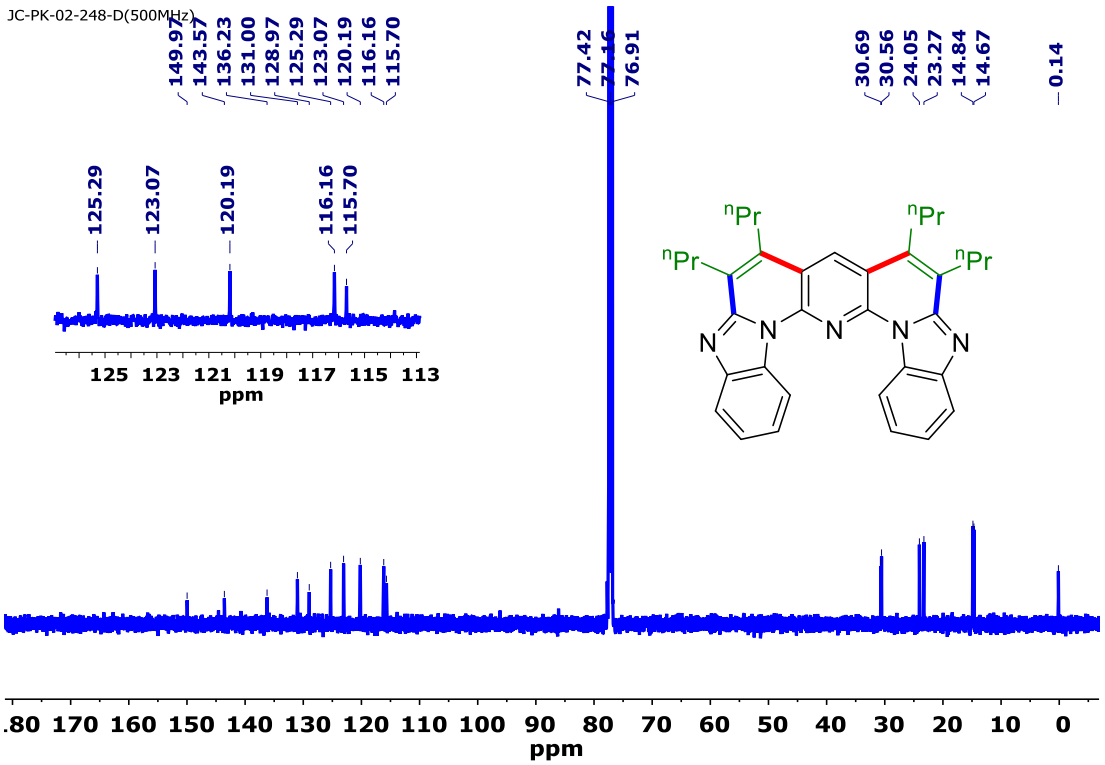

$^{13}C\{^{1}H\}$ NMR spectrum of **3z** (126 MHz, CDCl3, 298 K).



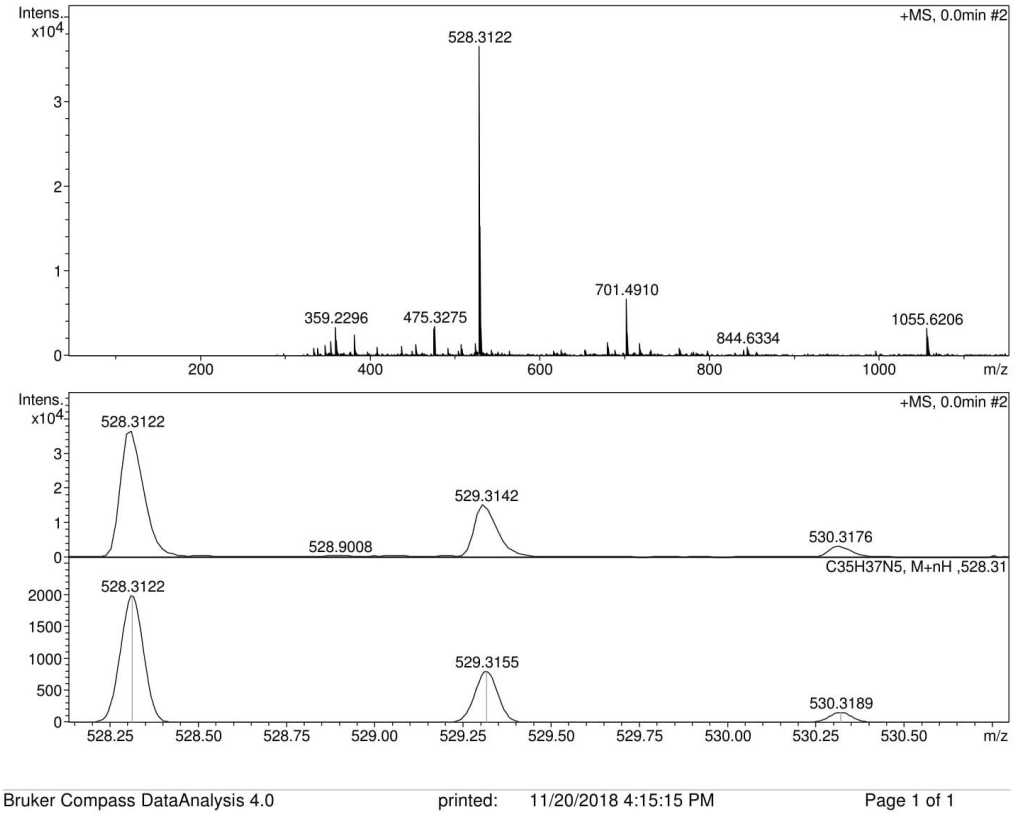

ESI-HRMS (positive ion mode) spectrum of **3z**.



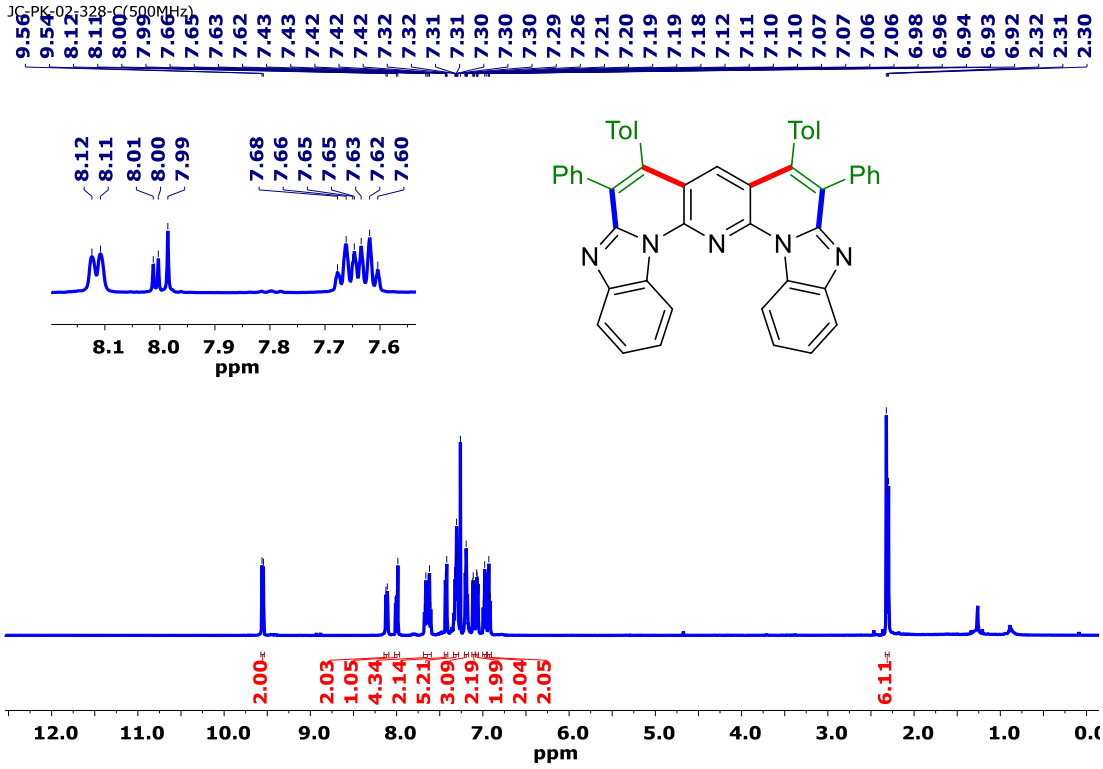

$^{1}$H NMR spectrum of **3aa** (500 MHz, $CDCl_3$, 298 K).



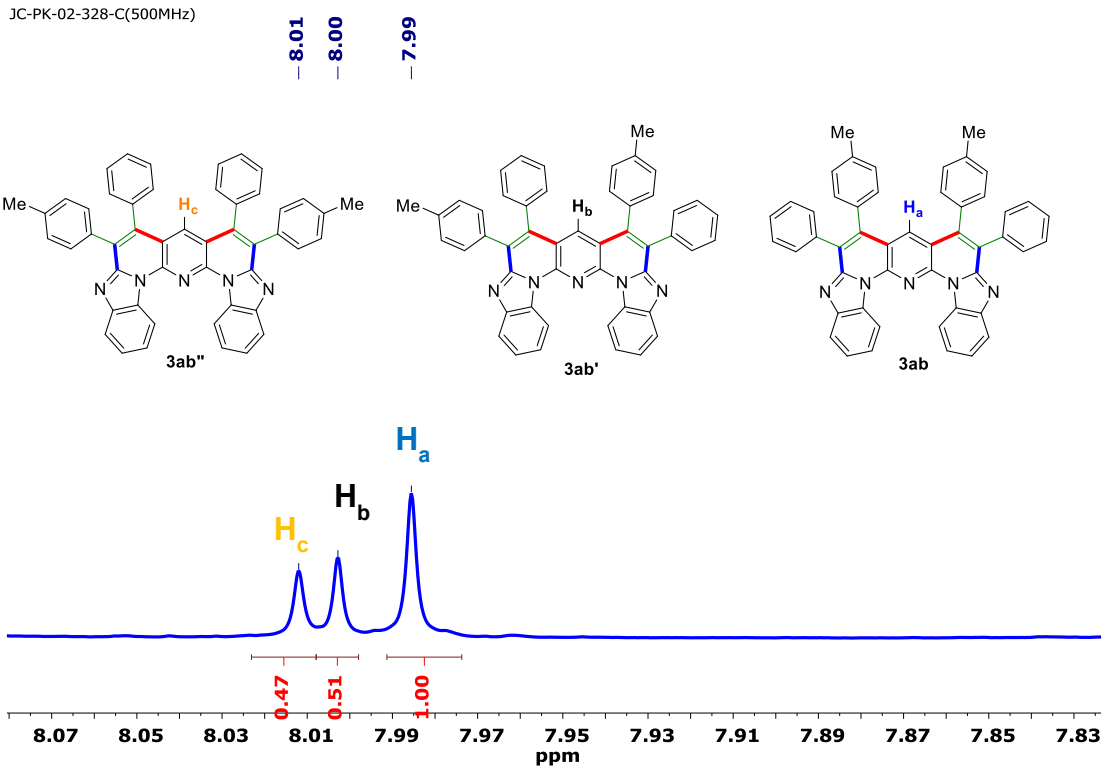

$^{13}C\{^{1}H\}$ NMR spectrum of **3aa** (126 MHz, $CDCl_3$, 298 K).



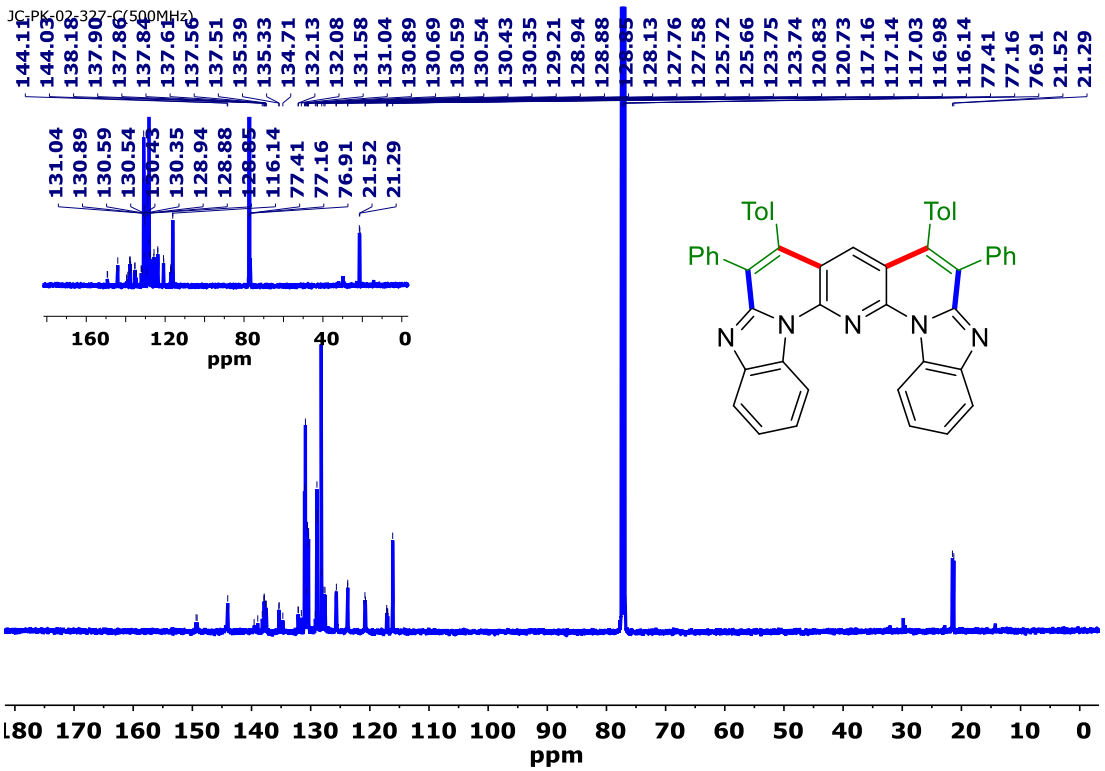

ESI-HRMS (positive ion mode) spectrum of **3aa**.



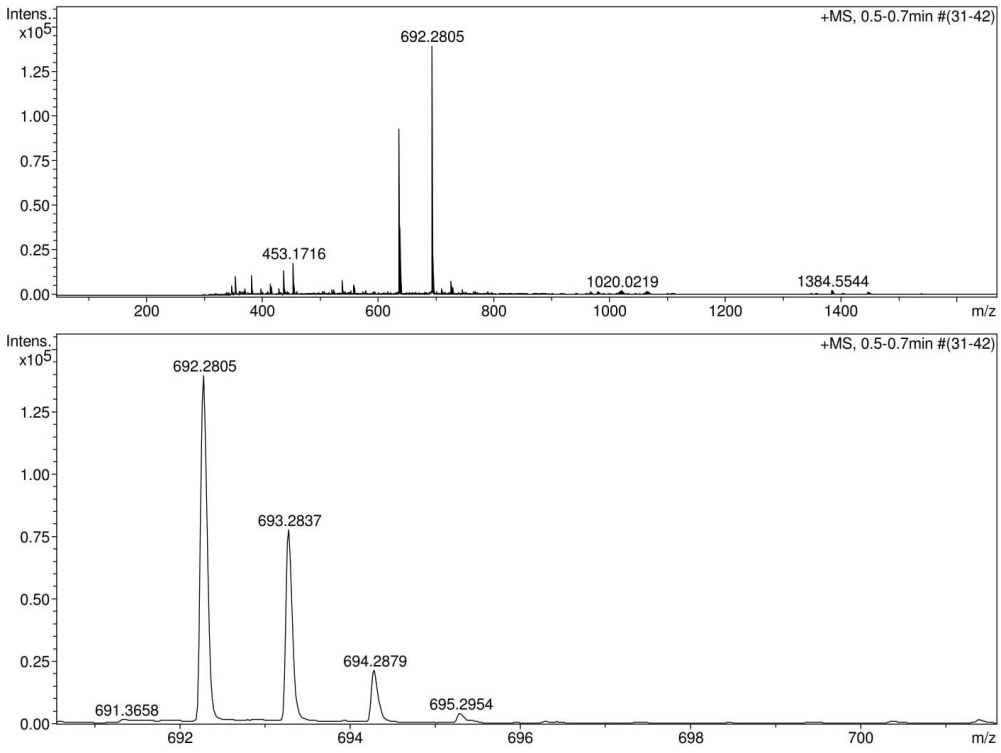

$^{1}$H NMR spectrum of **3ab** (mixture of 3 isomers) (500 MHz, $CDCl_3$, 298 K).



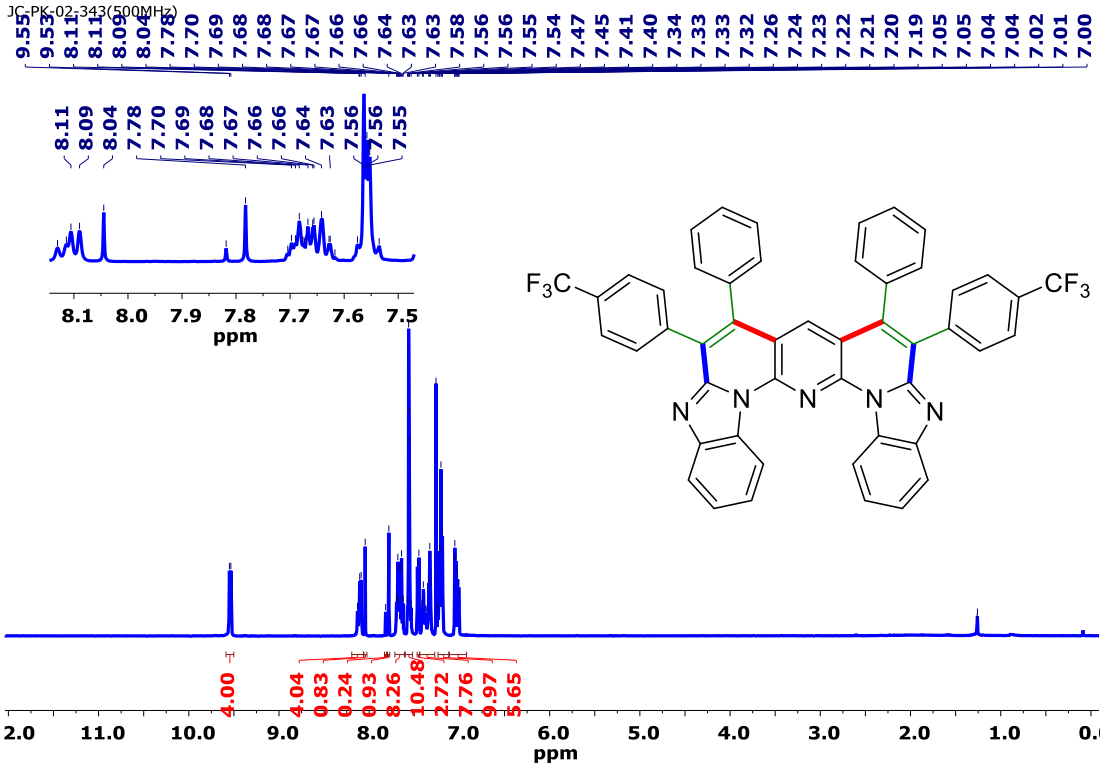

$^{1}$H NMR spectrum of **3ab** (mixture of 3 isomers) (500 MHz, $CDCl_3$, 298 K).



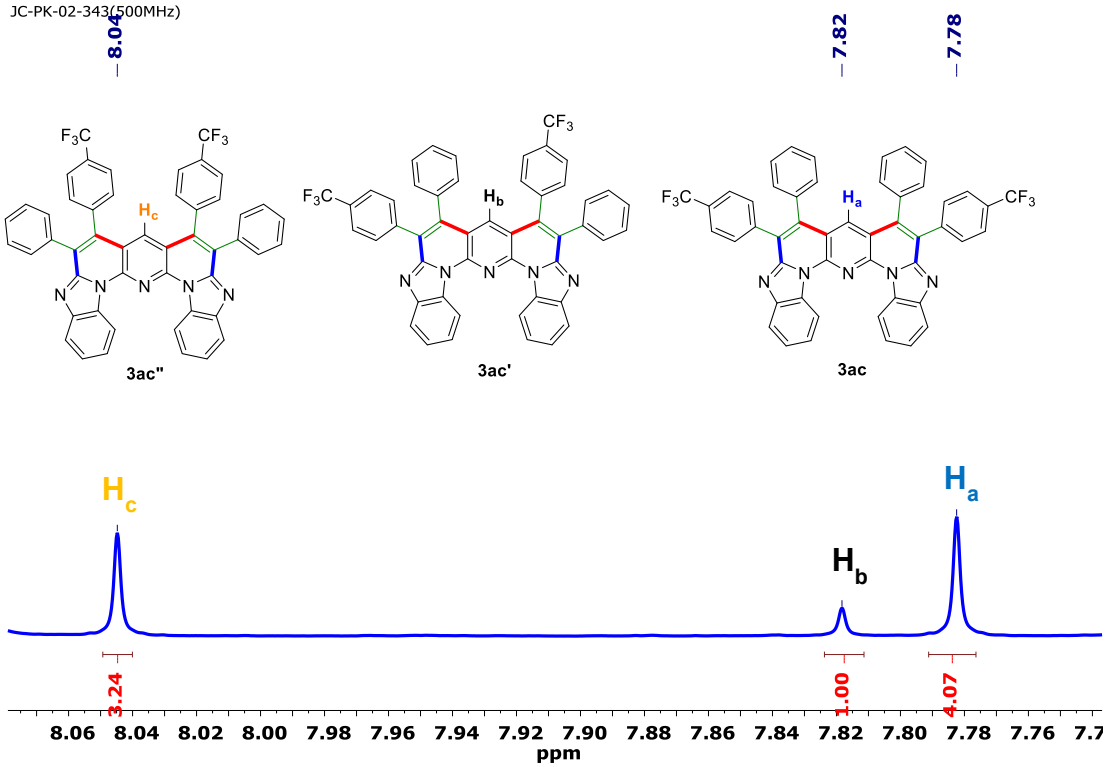

$^{13}C\{^{1}H\}$ NMR spectrum of **3ab** (mixture of 3 isomers) (126 MHz, $CDCl_3$, 298 K).



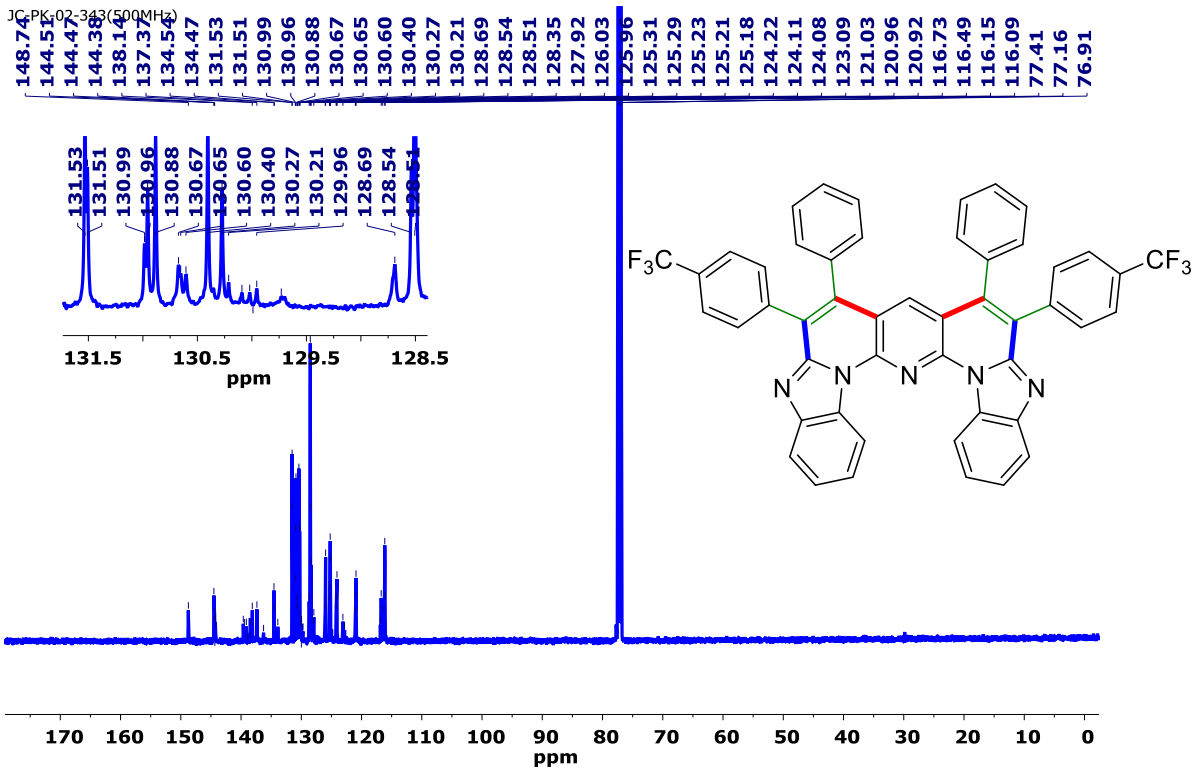

ESI-HRMS (positive ion mode) spectrum of **3ab**.



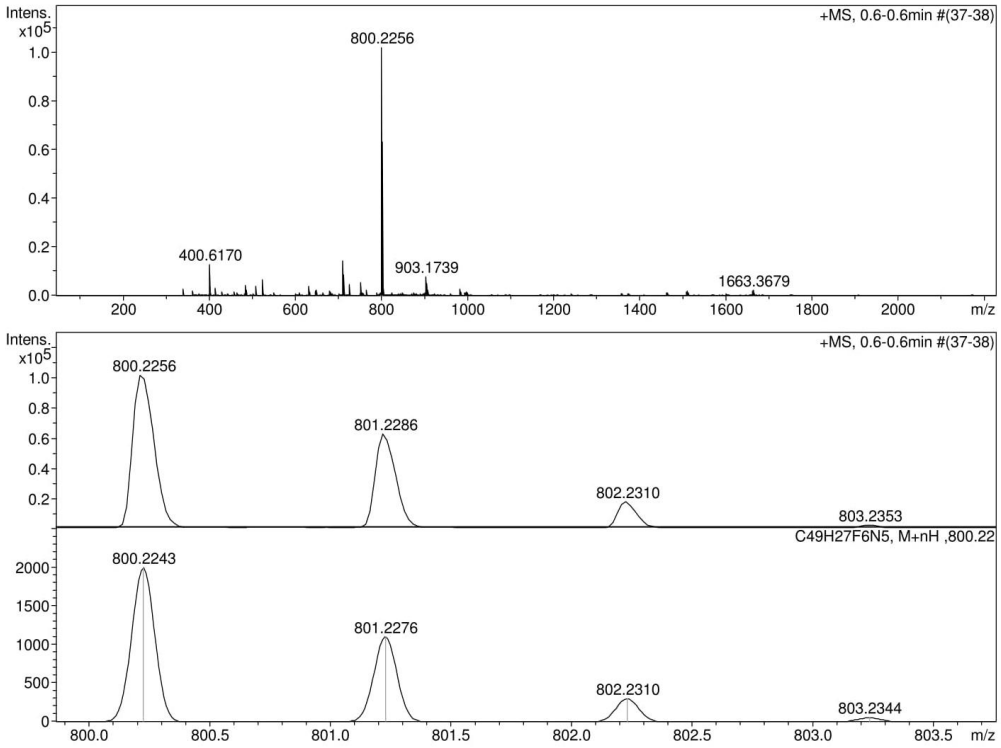

$^{1}$H NMR spectrum of **3ac** (mixture of 3 isomers) (500 MHz, $CDCl_3$, 298 K).



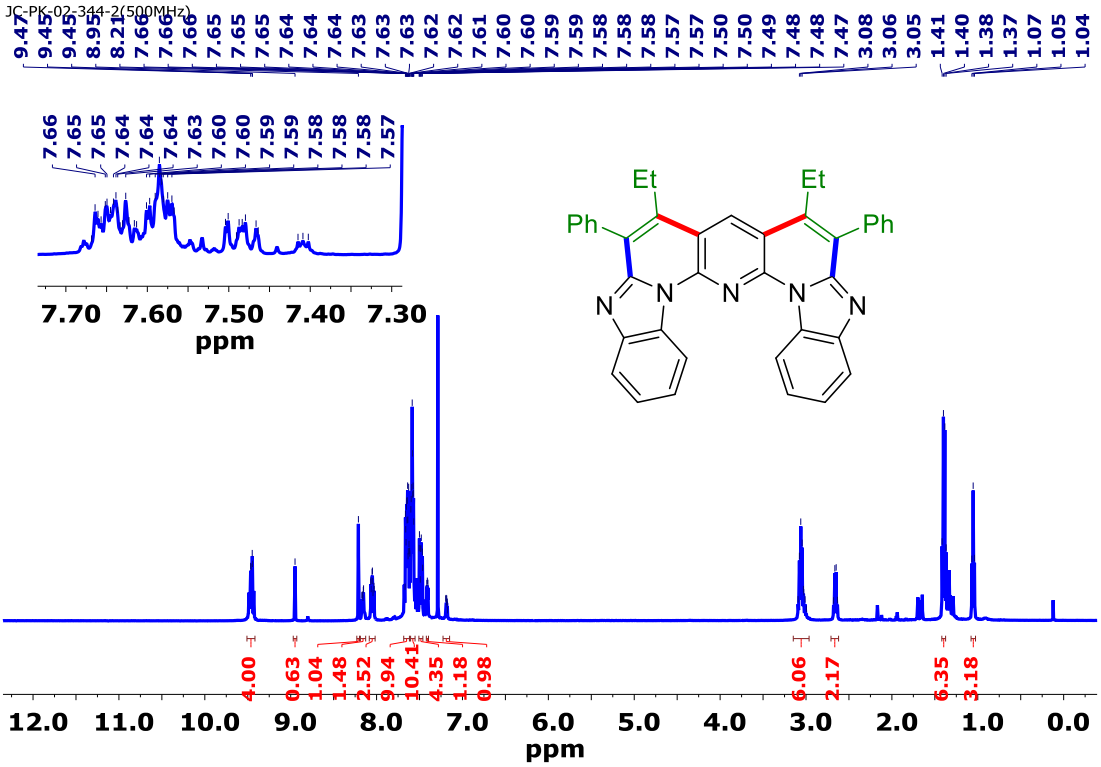

$^{1}$H NMR spectrum of **3ac** (mixture of 3 isomers) (500 MHz, $CDCl_3$, 298 K).



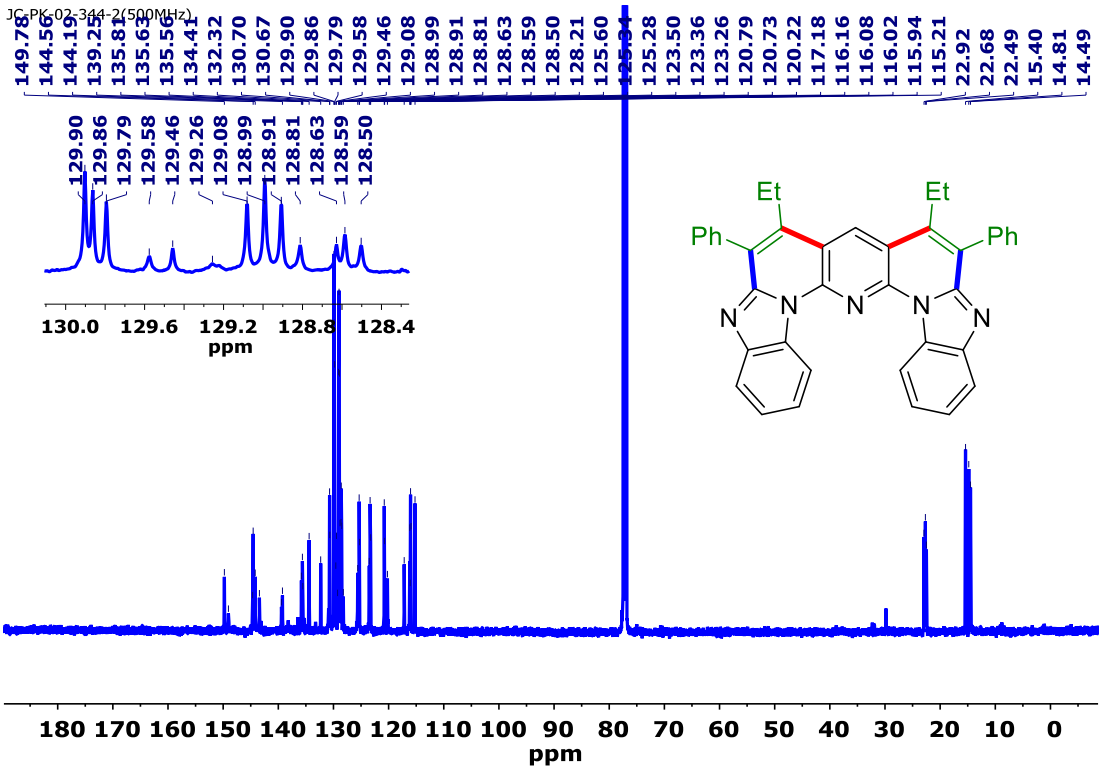

$^{13}C\{^{1}H\}$ NMR spectrum of **3ac** (mixture of 3 isomers) (126 MHz, $CDCl_3$, 298 K).



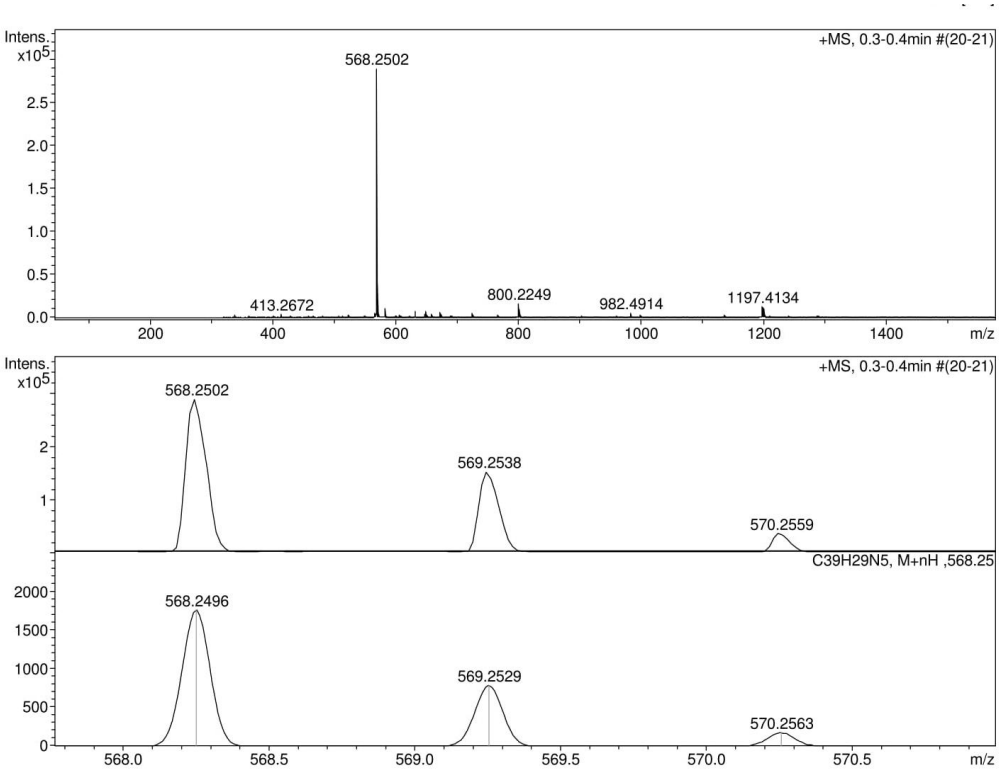

ESI-HRMS (positive ion mode) spectrum of **3ac**.



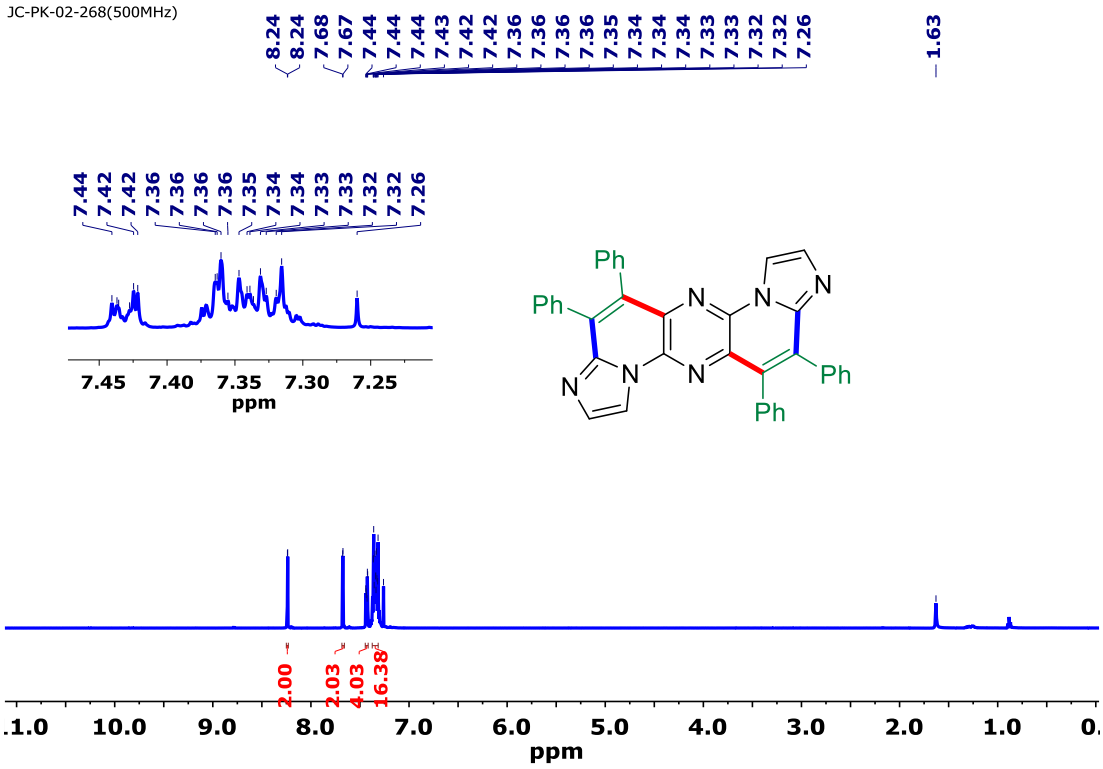

$^{1}$H NMR spectrum of **3ad** (mixture of two isomers) (500 MHz, $CDCl_3$, 298 K).



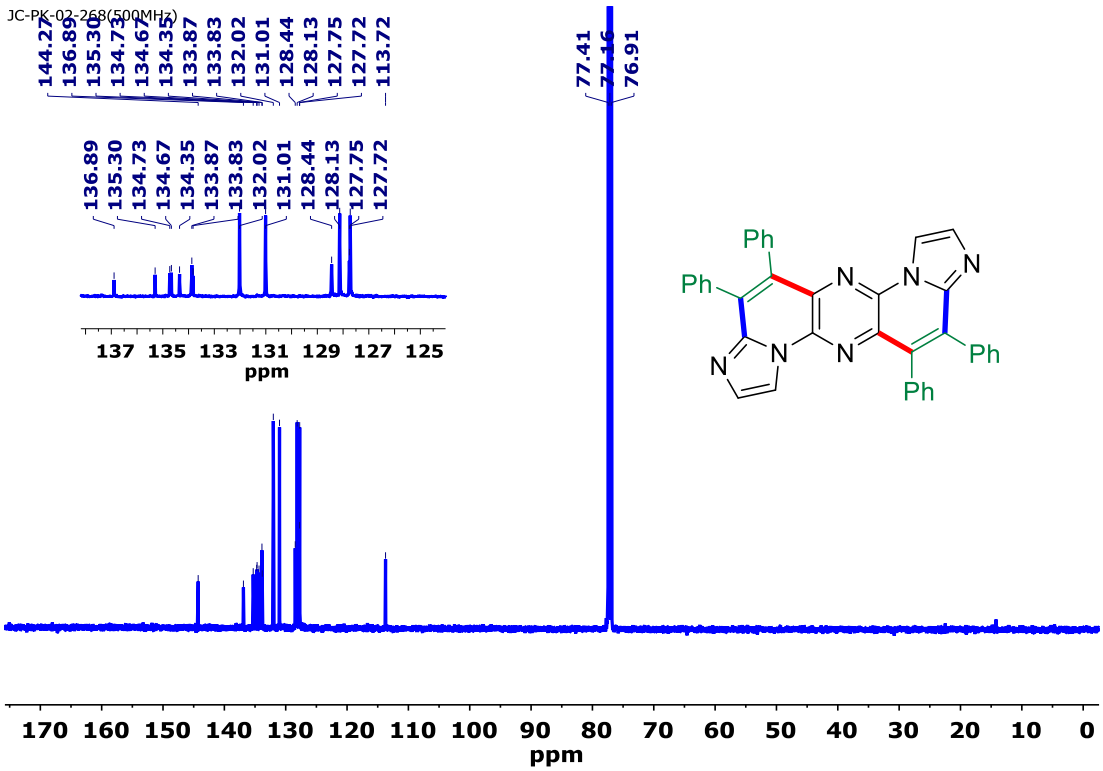

$^{13}$C{$^{1}$H} NMR spectrum of **3ad** (mixture of two isomers) (126 MHz, $CDCl_3$, 298 K).



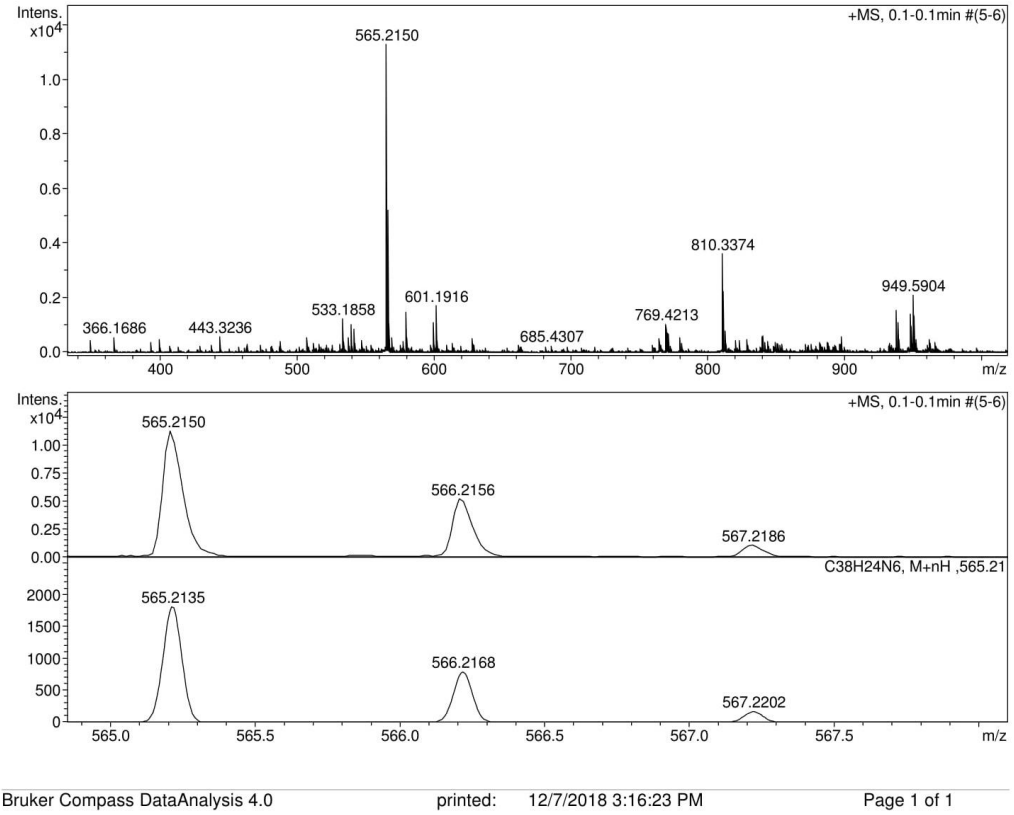

ESI-HRMS (positive ion mode) spectrum of **3ad**.



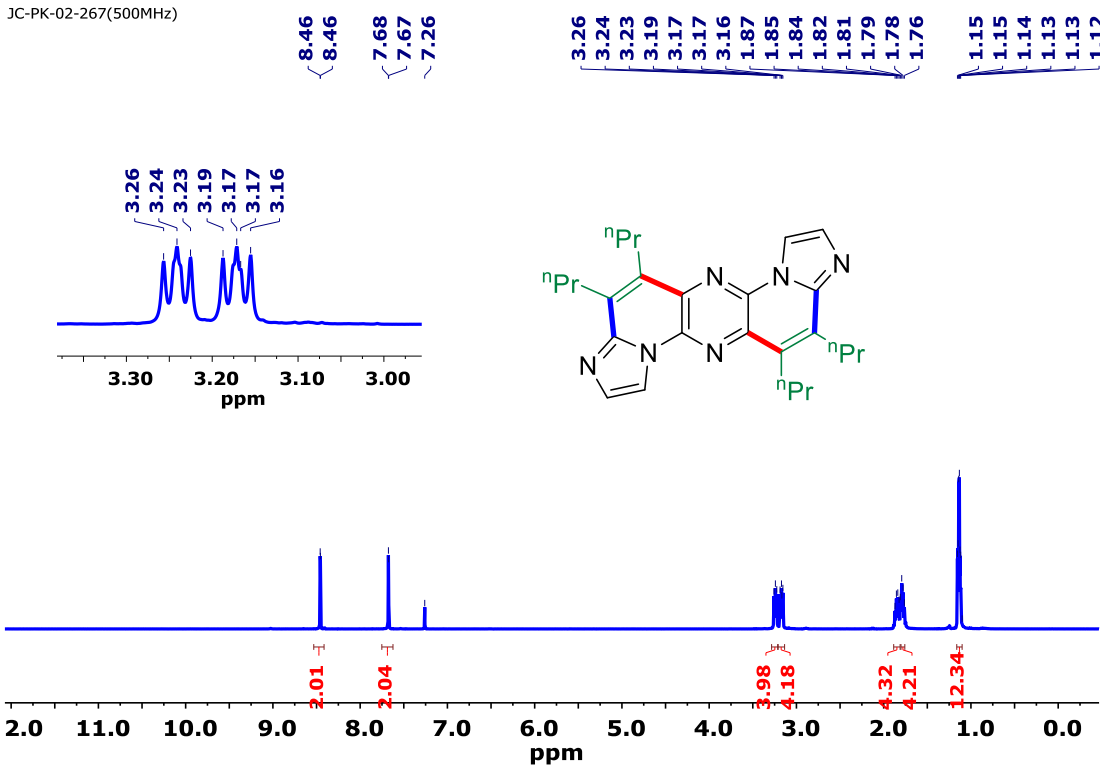

$^1$H NMR spectrum of **3ae** (500 MHz, $CDCl_3$, 298 K).



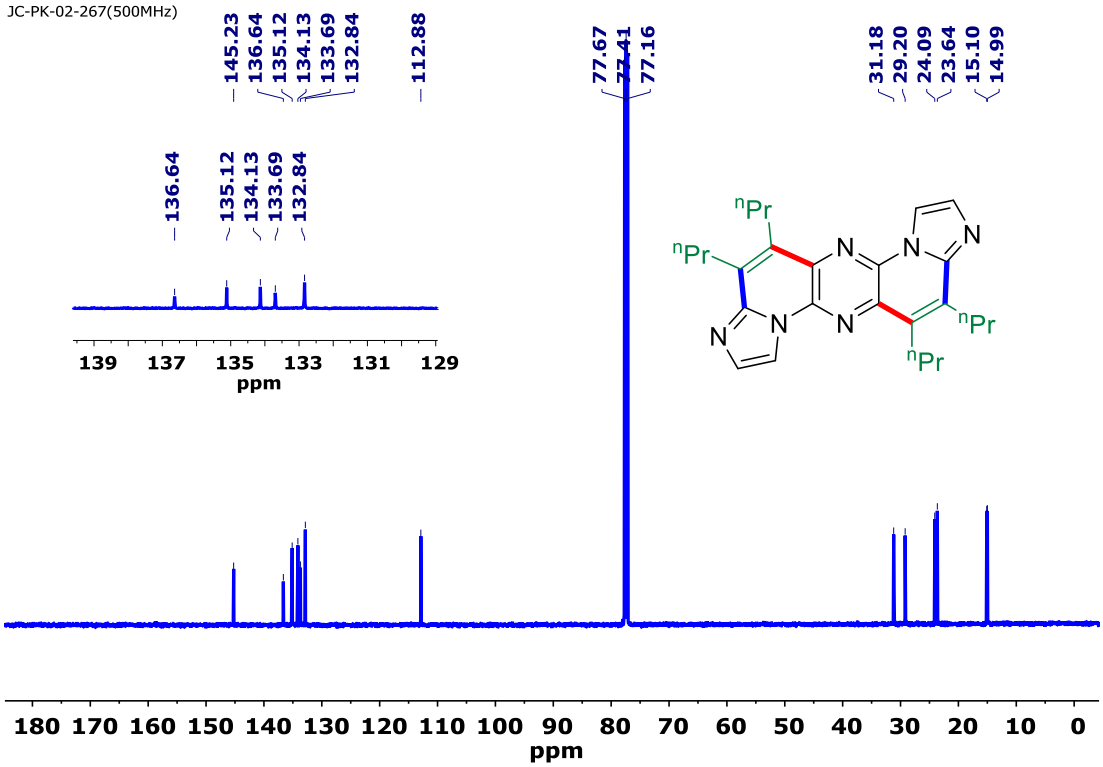

$^{13}C\{^{1}H\}$ NMR spectrum of **3ae** (126 MHz, $CDCl_3$, 298 K).



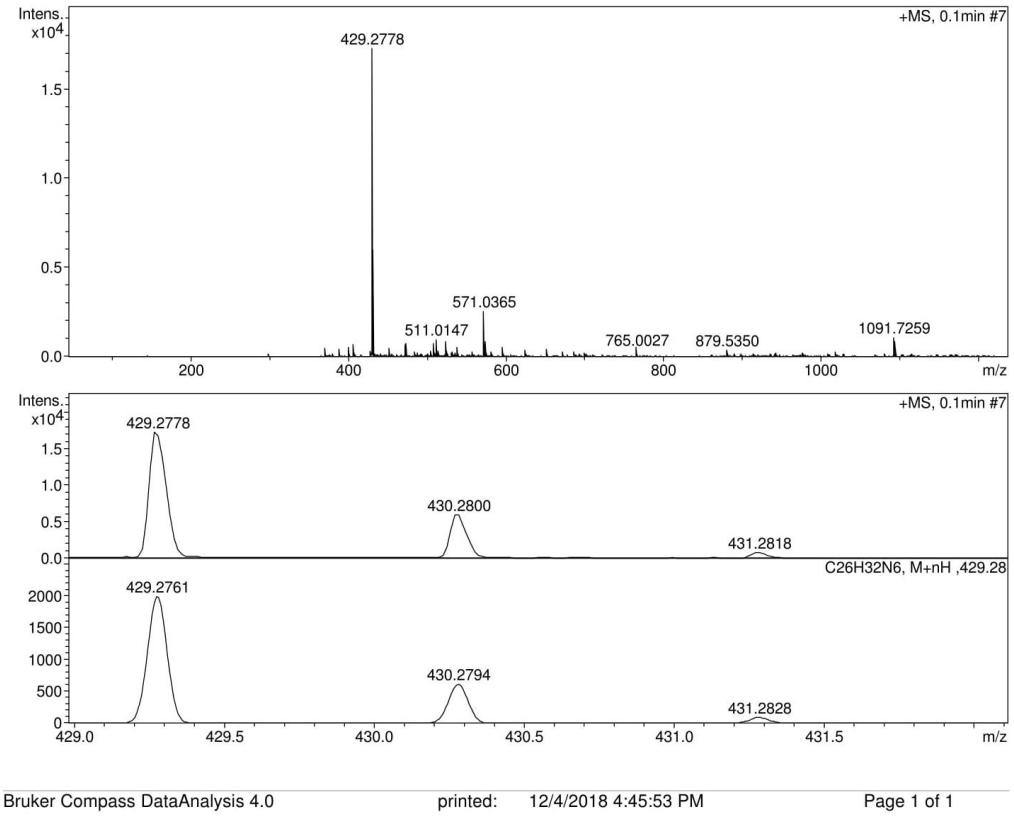

ESI-HRMS (positive ion mode) spectrum of **3ae**.



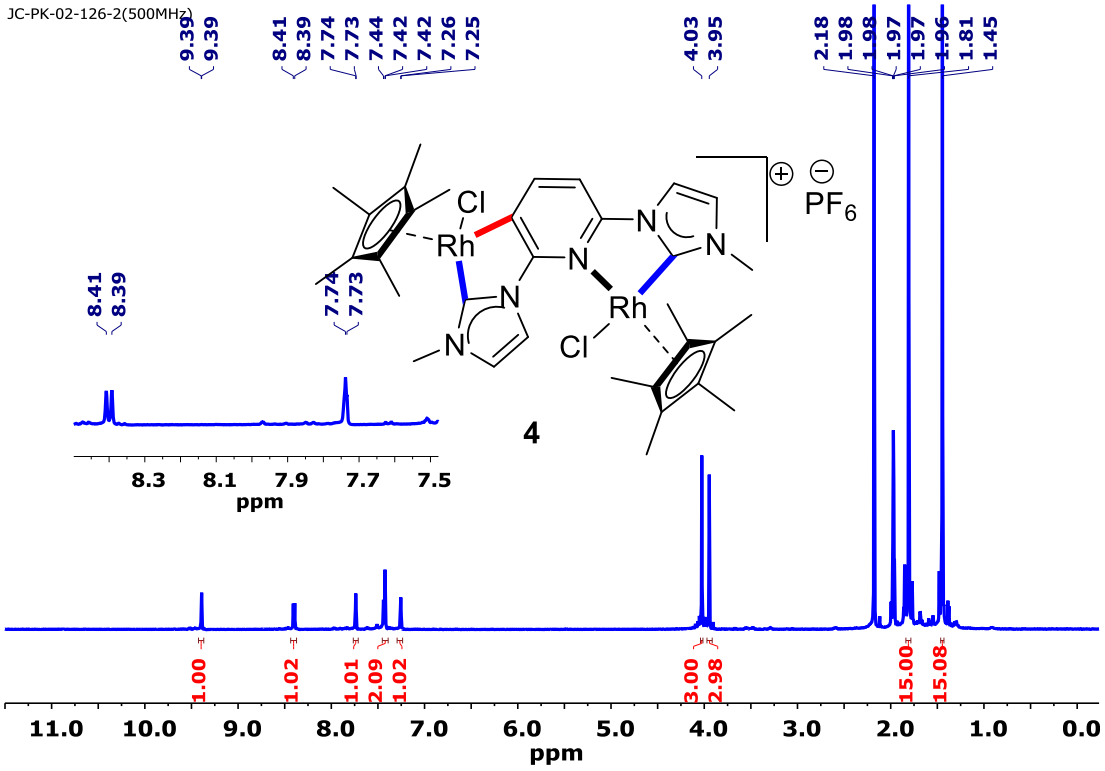

$^{1}$H NMR spectrum of **3af** (500 MHz, $CDCl_3$, 298 K).



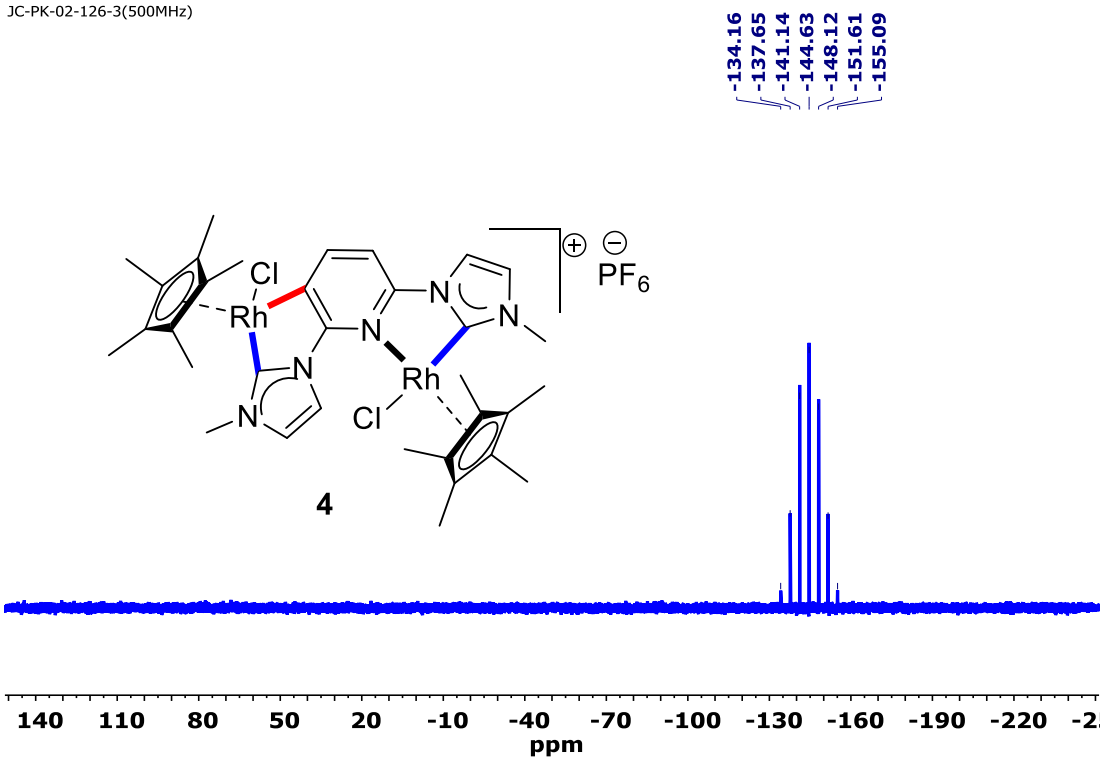

$^{13}$C{$^{1}$H} NMR spectrum of **3af** (126 MHz, $CDCl_3$, 298 K).



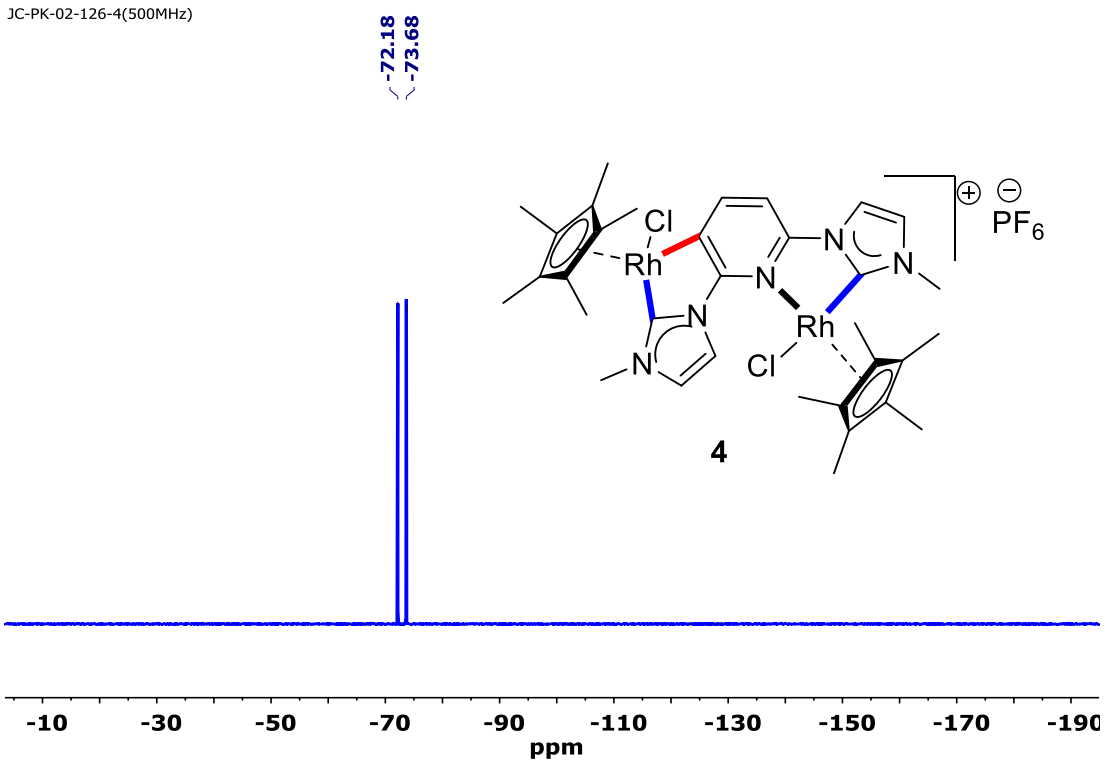

ESI-HRMS (positive ion mode) spectrum of **3af**.



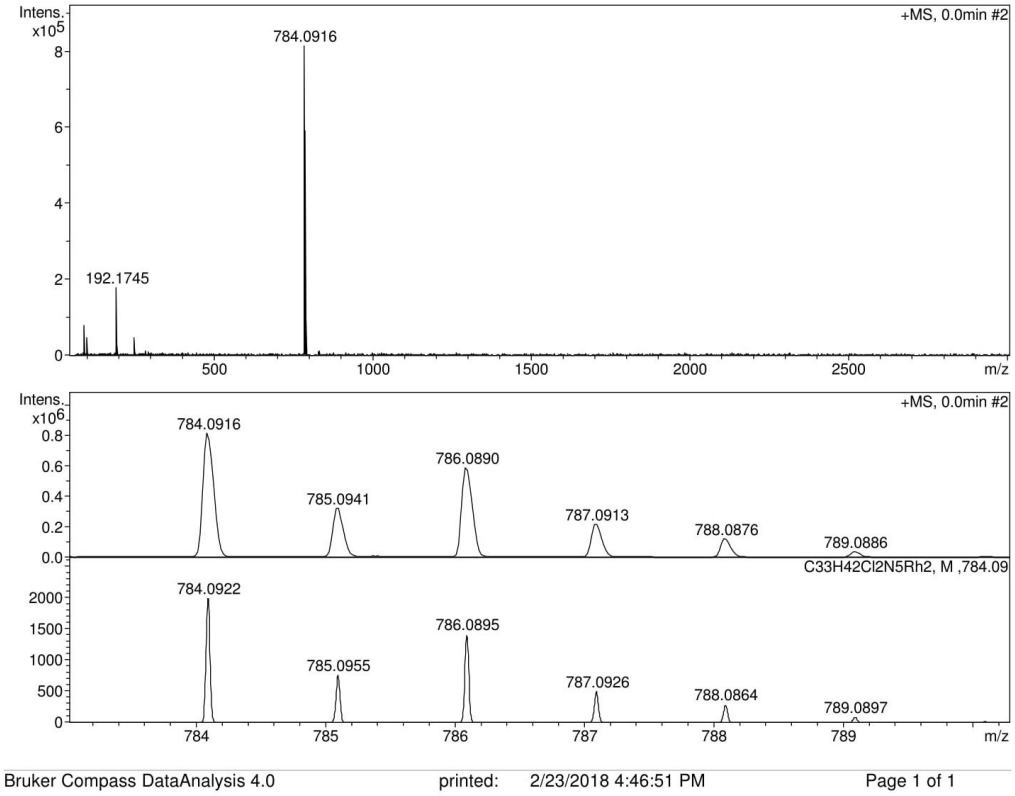

$^{1}$H NMR spectrum of **4** (500 MHz, $CD_3CN$, 298 K).



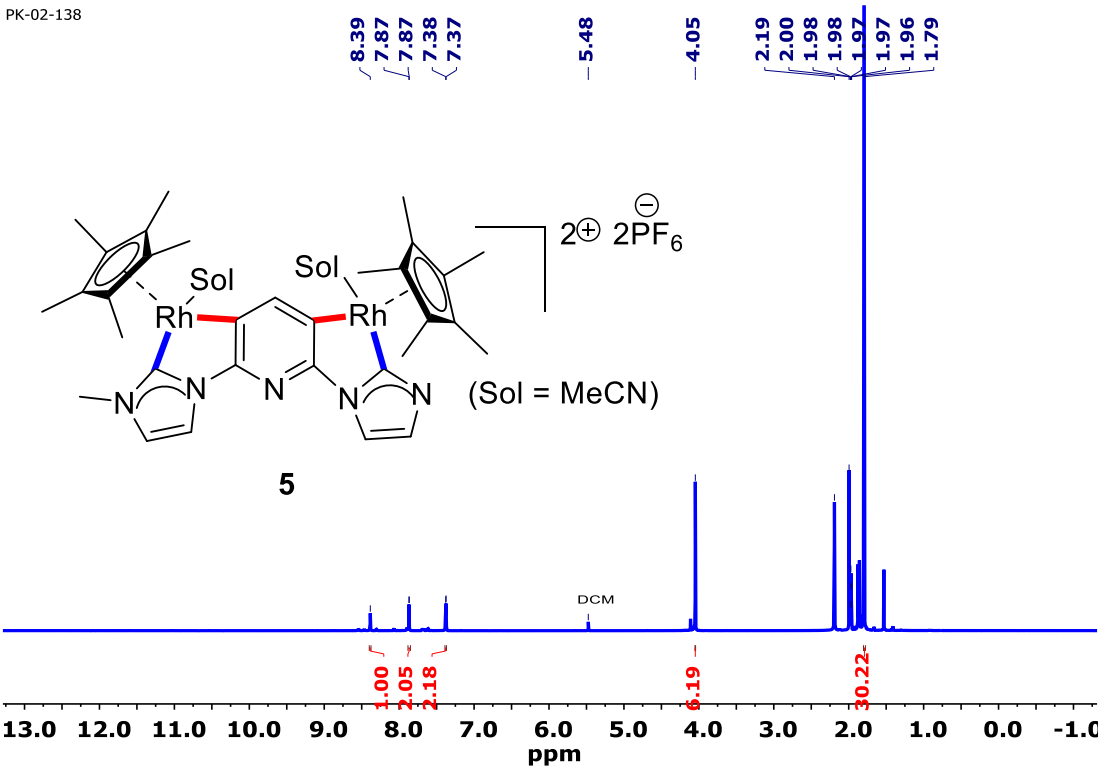

$^{31}$P NMR spectrum of **4** (202 MHz, $CD_3CN$, 298K).



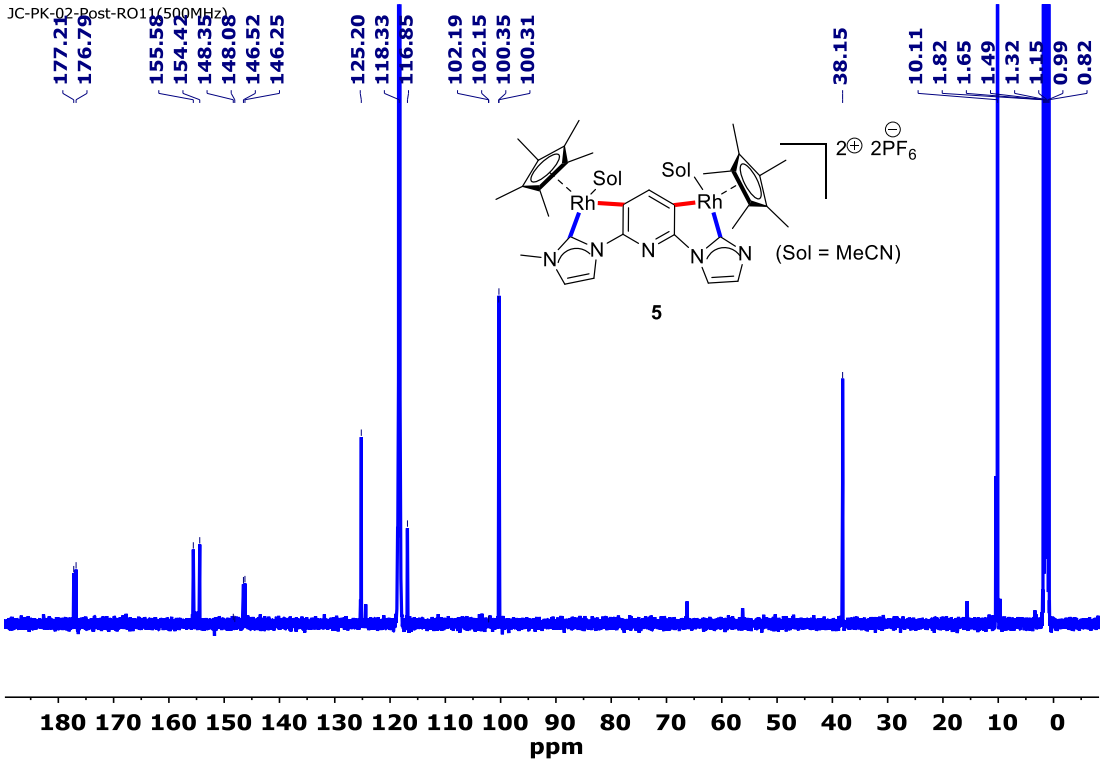

$^{19}$F NMR spectrum of **4** (471 MHz, $CD_3CN$, 298 K).



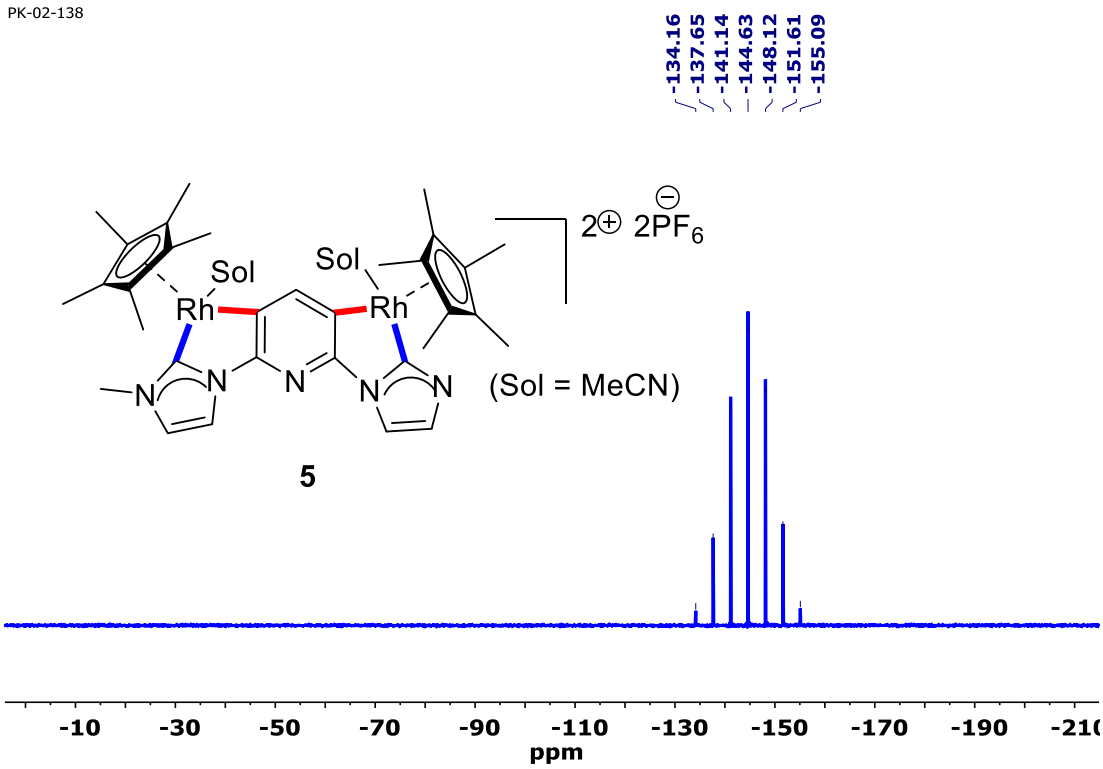

ESI-HRMS (positive ion mode) spectrum of **4**.



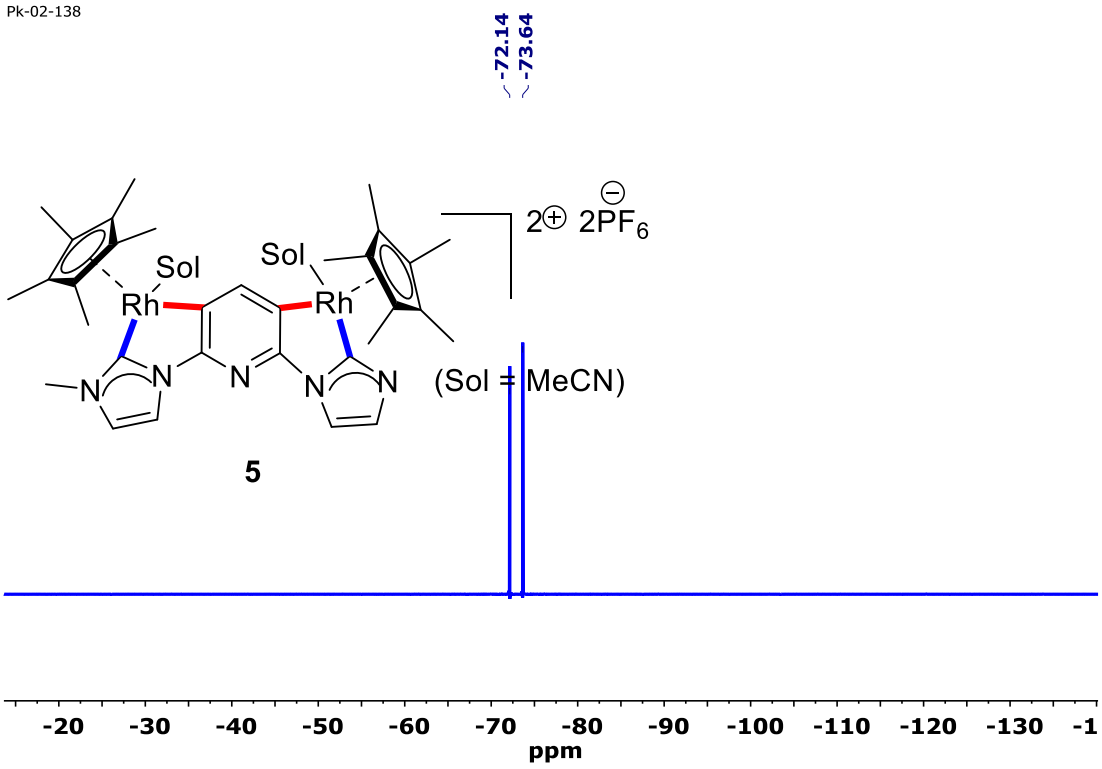

$^{1}$H NMR spectrum of **5** (500 MHz, $CD_3CN$, 298 K).



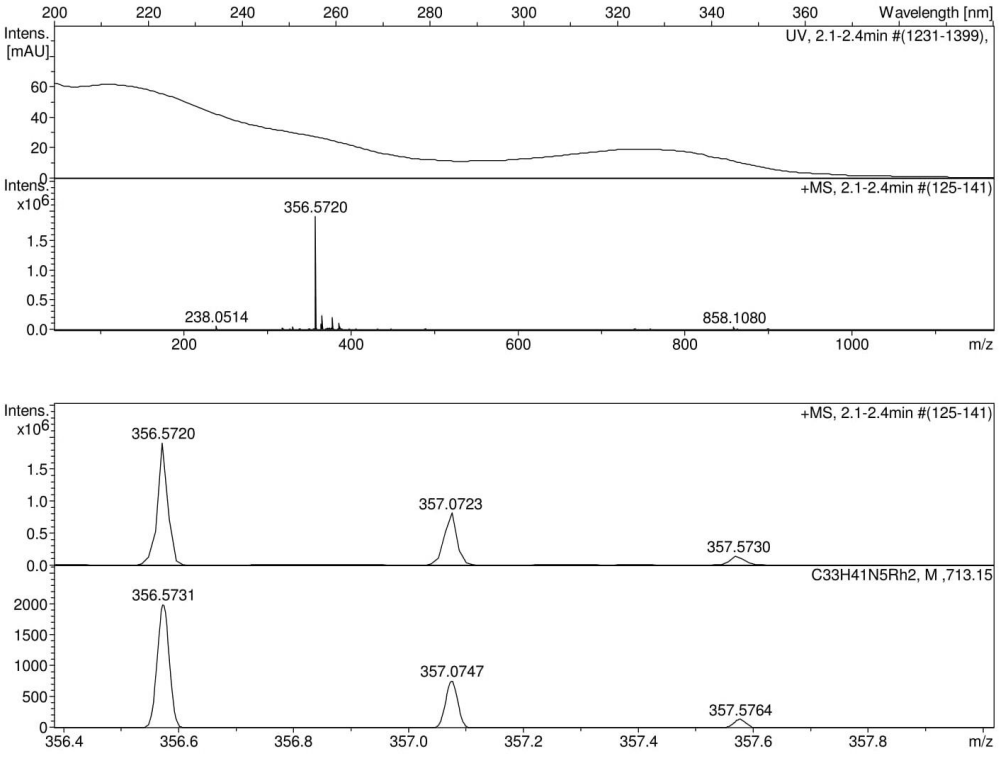

$^{13}C\{^{1}H\}$ NMR spectrum of **5** (126 MHz, $CD_3CN$, 298 K).




$^{31}P$ NMR spectrum of **5** (202 MHz, $CD_3CN$, 298 K).




$^{19}$F NMR spectrum of **5** (471 MHz, $CD_3CN$, 298 K).




ESI-HRMS (positive ion mode) spectrum of **5**.

## 14. References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