Electronic Supplementary Information (ESI)

Annulating thiazolium cations via direct double C–H activation strategy: Rh–N,S-heterocyclic carbene is the key

Champak Dutta, Arppitha Baby Sainaba and Joyanta Choudhury*

Organometallics & Smart Materials Laboratory, Department of Chemistry,
Indian Institute of Science Education and Research Bhopal, Bhopal 462 066, India
E-mail: joyanta@iiserb.ac.in

CONTENTS

1. General methods and materials

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400 and 500MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H spectra, 77.2 ppm for $^{13}C\{^{1}H\}$ spectra; CH_3CN: δ = 1.94 ppm for ^{1}H spectra, 1.3 ppm for $^{13}C\{^{1}H\}$ spectra; DMSO: 2.5 ppm for ^{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 doublet), dt (doublet of triplets), ddd (doublet of doublet of doublets), m (multiplet). ESI mass spectrometry 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 different low temperatures for each crystal. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents and $RhCl_3.xH_2O$ were purchased from Aldrich. $[RhCp^*Cl_2]_2$[1] was synthesized according to reported procedure.

2. General procedure for the synthesis of thiazolium salts:

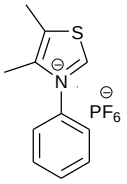
The synthesis of thiazolium salts were performed similar to the reported procedure[2], following two steps as given below:

Step 1. In an oven dried round-bottomed flask 50 mmol aniline (4.56 mL) is dissolved in 20 mL DMSO. To this, 2 g (50 mmol) freshly crushed NaOH is added and stirred for 15 min. at 27 °C. Then, 3.02 mL (50 mmol) CS_2 is added slowly in ice bath and stirred for 60 min at 27 °C. To this mixture 3-chloro-2-butanone is added in ice bath, slowly and stirred. After 1h, the reaction mixture is diluted with 200 mL distilled water and kept in refrigerator for 30 min. Later water phase is decanted and remaining solid dissolved in 125 mL of EtOH. To this, 1.5 mL of concentrated HCl (35%) is added and solution is refluxed at 100 °C for 1 h. The product crystallizes after one night of standing at 5 °C in refrigerator. The solid obtained is washed with 20 mL EtOH and dried under high vacuum.

Step 2. 10 mmol of the above compound in 25 mL AcOH is slowly treated with 3.06 mL H_2O_2 (30 mmol) and the solution is stirred for 30 min. Then the solvent is removed *in vacuo* and the remaining oil is dissolved in 20 mL MeOH. A mixture of 40 mL of MeOH/water (1:1) and 5.52 g of KPF_6 (30 mmol) were added to it. The dispersion is stirred at 27 °C for 16 h. Finally the solid obtained is filtered off, and remaining solution added to 100 mL water and extracted with 50 mL DCM first, followed by another extraction with 100 mL of DCM. The combined organic layer is dried over Na_2SO_4. The solvent is evaporated and dissolved in 2 mL DCM and precipitated with slow addition of diethyl ether and dried in high vacuum. Similarly, using various substituted anilines other thiazolium salts were synthesized.

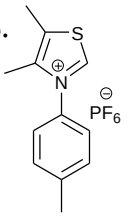
The compound 1k was synthesized similarly by following a reported procedure.[3]

4,5-dimethyl-3-phenylthiazol-3-ium hexafluorophosphate (1a)[2]: Yield = 61%.



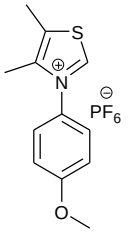
^{1}H NMR (400 MHz, DMSO) δ 10.26 (s, 1H), 7.71-7.69 (br, m, 5H), 2.59 (s, 3H), 2.21 (s, 3H). HRMS (ESI, positive ion): M^+ = 190.0673 (calculated 190.0685 for $[C_{11}H_{12}NS]^+$).

4,5-dimethyl-3-(p-tolyl)thiazol-3-ium hexafluorophosphate (1b)[2]: Yield = 46%.



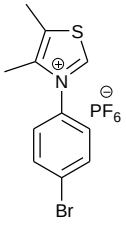
^{1}H NMR (400 MHz, CDCl3) δ 9.39 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H), 2.47 (s, 3H), 2.26 (s, 3H). HRMS (ESI, positive ion): M^+ = 204.0841 (calculated 204.0841 for $[C_{12}H_{14}NS]^+$).

3-(4-methoxyphenyl)-4,5-dimethylthiazol-3-ium hexafluorophosphate(1c)[2]: Yield = 58%.



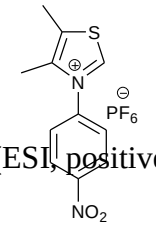
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 8.9 Hz, 2*H), 3.90 (s, 3H), 2.60 (s, 3H), 2.28 (s, 3H). HRMS (ESI, positive ion): M^+ = 220.0791 (calculated 220.0791 for $[C_{12}H_{14}NOS]^+$)

3-(4-bromophenyl)-4,5-dimethylthiazol-3-ium hexafluorophosphate(1d)[2]:



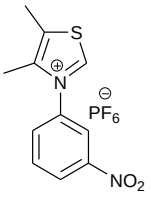
Yield = 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 2.60 (s, 3H), 2.27 (s, 3H). HRMS (ESI, positive ion): M^+ =267.9784 (calculated 267.9790 for $[C_{11}H_{11}BrNS]^+$).

4,5-dimethyl-3-(4-nitrophenyl)thiazol-3-ium hexafluorophosphate (1e):



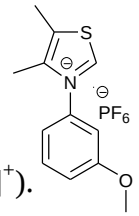
Yield = 57%. ^{1}H NMR (400 MHz, DMSO) δ 10.32 (s, 1H), 8.54 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 3H), 2.59 (s, 3H), 2.23 (s, 3H). HRMS (ESI, positive ion): M+ =235.0546 (calculated 235.0336 for $[C_{11}H_{11}N_2O_2S]^+$).

4,5-dimethyl-3-(3-nitrophenyl)thiazol-3-ium hexafluorophosphate (1f):



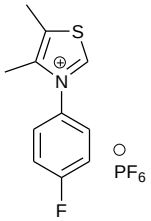
Yield = 60%. ^{1}H NMR (500 MHz, DMSO) δ 10.30 (s, 1H), 8.72 (t, *J* = 2.1 Hz, 1H), 8.56 (dd, *J* = 8.0, 2.4 Hz, 1H), 8.18 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.99 (t, *J* = 8.2 Hz, 1H), 2.59 (s, 3H), 2.22 (s, 3H). HRMS (ESI, positive ion): M+ =235.0530 (calculated 235.0536 for $[C_{11}H_{11}N_2O_2S]^+$).

4,5-dimethyl-3-(3-methoxyphenyl)thiazol-3-ium hexafluorophosphate (1g)[2]:



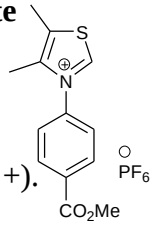
Yield = 63 %. ^{1}H NMR (400 MHz, DMSO) δ 10.24 (s, 1H), 7.60 (t, *J* = 8.1 Hz, 1H), 7.35 (s, 1H), 7.31 – 7.21 (m, 2H), 3.83 (s, 3H), 2.58 (s, 3H), 2.22 (s, 3H). HRMS (ESI, positive ion): M^+ = 220.0782 (calculated 220.0791 for $[C_{12}H_{14}NOS]^+$).

4,5-dimethyl-3-(4-fluorophenyl)thiazol-3-ium hexafluorophosphate(1h)[2]:

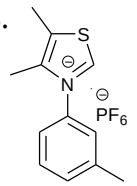


Yield = 65 %. ^{1}H NMR (400 MHz, DMSO) δ 10.25 (s, 1H), 7.83 – 7.76 (m, 2H), 7.61 – 7.54 (m, 2H), 2.58 (s, 3H), 2.20 (s, 3H). HRMS (ESI, positive ion): M^+ = 208.0577 (calculated 208.0591 for $[C_{11}H_{11}FNS]$+).

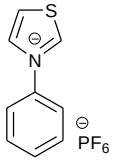
3-(4-benzoic acid methyl ester)-4,5-dimethylthiazol-3-ium hexafluorophosphate (1i)[2]: Yield = 60 %. ^{1}H NMR (400 MHz, DMSO) δ 10.30 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 2.59 (s, 3H), 2.21 (s, 3H). HRMS (ESI, Positive ion): M+ = 248.0743 (calculated 248.0740 for $[C_{13}H_{14}NO_2S]$+).



4,5-dimethyl-3-(m-tolyl)thiazol-3-ium hexafluorophosphate (1j)[2]: Yield = 58 %. ^{1}H NMR (400 MHz, DMSO) δ 10.23 (s, 1H), 7.72 – 7.36 (m, 5H), 2.58 (s, 3H), 2.43 (s, 3H), 2.21 (s, 3H). HRMS (ESI, positive ion): M^+ = 204.0838 (calculated 204.0841 for $[C_{12}H_{14}NS]^+$).

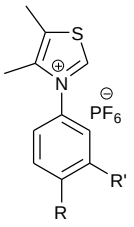
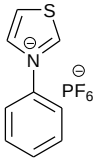
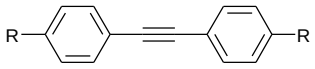
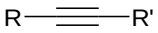


3-phenyl-3-thiazolium hexafluorophosphate (1k)[3]: Yield = 65 %. ^{1}H NMR



(400 MHz, DMSO) δ 10.61 (s, 1H), 8.98 (d, *J* = 3.7 Hz, 1H), 8.57 – 8.52 (m, 1H), 7.88-7.89 (m, 2H), 7.75 – 7.68 (m, 3H). HRMS (ESI, positive ion): M+ =162.0352 (calculated 162.0372 for [C9H8NS]+).

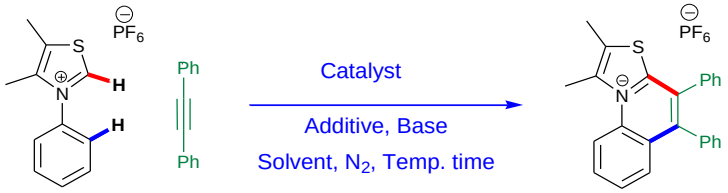
3: Table for thiazolium salts and internal alkynes used:

Thiazolium salt	Internal Alkyne
R'= H, R= H, **1a**; Me, **1b**; OMe, **1c**; Br, **1d**; NO_2, **1e** R'= H, R= F, **1h**; CO_2Me, **1i** R'= NO_2, R= H, **1f,** R'= OMe, R= H**, 1g** R'= Me, R= H, **1j**  **1k**, 	1. R= H, **2a**; Me, **2b**; OMe, **2c**; SMe, **2d**; *t*-Bu, **2e;** -CHO, **2f**.  2. R=R'= n-Pr, **2g**; R=R'= Et, **2h** R= Ph, R'= Et, **2i** R= Ph, R'= Me, **2j** 

4. Optimization of the reaction conditions:

To an oven dried Schlenk tube, **1a** (0.1 mmol), NaOAc (0.5 mmol), $[RhCp^*Cl_2]_2$ (0.003 mmol), AgOTf (0.25 mmol) and **2a** (0.1 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 solvent (2.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 27 °C in dark. After certain time, the whole reaction mixture was passed through a short Celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/MeOH solvent mixture wherever separation required. For optimization studies, NMR spectroscopic yields were calculated against 1,3,5-trimethoxybenzene (TMB) as internal standard. Conditions were varied as shown in Table S1 to optimize the catalytic protocol.

Table S1: Optimization studies[a]



1a, 0.1 mmol **2a**, 0.1 mmol **3a**

Entry	Catalyst	Additives (equiv.)	Solvent (Temp., °C)	Time (h)	Yield (%)[b]
1	$[RhCp^*Cl_2]_2$	NaOAc (5) + AgOTf (2.5)	DCE (100)	24	quantitative (isolated 94)
2	$[RhCp^*Cl_2]_2$	NaOAc (5) + AgOTf (2.5)	DCE (27)	24	98
3	$[RhCp^*Cl_2]_2$	NaOAc (5) + AgOTf (2.5)	DCE (27)	12	78
4	**$[RhCp^*Cl_2]_2$**	**NaOAc (5) + AgOTf (2.5)**	**DCE (27)**	**18**	**92 (isolated 90)**
5	[c]$[RhCp^*Cl_2]_2$	NaOAc (5) + AgOTf (2.5)	DCE (27)	24	20
6	-	NaOAc (5) + AgOTf (2.5)	DCE (27)	18	Not detected
7	$[RhCp^*Cl_2]_2$	AgOTf	DCE (27)	18	Not detected
8	$[RhCp^*Cl_2]_2$	-	DCE (27)	18	Not detected
9	$[RhCp^*Cl_2]_2$	Cs_2CO_3 (1.5) + AgOTf (2.5)	DCE (27)	24	30
10	$[RhCp^*Cl_2]_2$	NaOAc(5) + AgOTf (2.5)	DCM (27)	18h	89
11	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	MeOH (80)	24h	50

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), catalyst (0.003 mmol), Additives (as mentioned above), degassed solvent (2.0 mL), N_2 atmosphere, Temperature; 27±2 °C unless noted otherwise. [b]crude yields are shown. [c]1 mol% of catalyst was used.

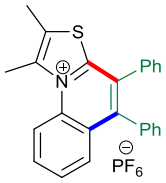
5. General procedure for the annulation reactions

To an oven dried Schlenk tube, **1** (0.1 mmol), NaOAc (0.5 mmol), $[RhCp^*Cl_2]_2$ (0.003 mmol), AgOTf (0.25 mmol) and **2** (0.1 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 DCE (2.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 27 °C in dark. After 18 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated

under reduced pressure. The final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/MeOH solvent mixture wherever separation required.

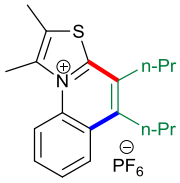
6. Experimental characterization data for the products (3a-3ac)

1,2-dimethyl-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3a):



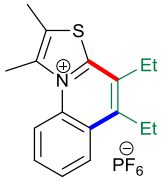
Yield = 90%, 46.1 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 9.0 Hz, 1H), 8.04 – 7.95 (m, 1H), 7.83 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.15 (m, 10H), 3.17 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 159.3, 146.6, 141.0, 137.0, 135.3, 135.0, 132.9, 132.6, 131.6, 130.8, 130.8, 130.7, 130.4, 130.1, 130.1, 129.9, 129.4, 129.2, 120.1, 18.5, 13.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.6 (d, *J* = 712.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -145.19 (hept, *J* = 712.6 Hz). HRMS (ESI, positive ion): M^+ = 367.1366 (calculated 367.1389 for $[C_{25}H_{21}NS]^+$).

1,2-dimethyl-4,5-dipropylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3b):



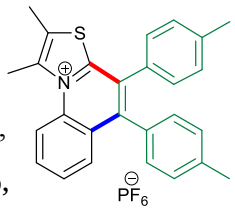
Yield = 92%, 40.7mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.8 Hz, 1H), 8.27 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.97 – 7.91 (m, 1H), 7.86 (t, *J* = 7.4 Hz, 1H), 3.18 – 3.12 (m, 2H), 3.09 (s, 3H), 3.04 – 2.98 (m, 2H), 2.66 (s, 3H), 1.74 (ddd, *J* = 21.5, 14.9, 6.4 Hz, 4H), 1.12 (dt, *J* = 14.5, 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 146.4, 139.5, 135.4, 131.2, 130.4, 129.3, 129.2, 127.2, 126.5, 119.2, 33.9, 30.9, 23.9, 22.2, 18.2, 14.6, 14.4, 13.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.4 (d, *J* = 712.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.71 (hept, *J* = 712.5 Hz). HRMS (ESI, positive ion): M^+= 298.1679 (calculated 298.1629 for $[C_{19}H_{24}NS]^+$).

4,5-diethyl-1,2-dimethylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3c):

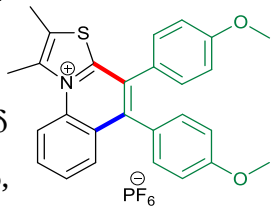


Yield = 90%, 37.3 mg,^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.9 Hz, 1H), 8.31 (d, *J* = 8.3 Hz, 1H), 7.99 – 7.91 (m, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 3.23 (q, *J* = 7.6 Hz, 2H), 3.12 – 3.04 (m, 5H), 2.67 (s, 3H), 1.42 – 1.33 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 156.1, 147.7, 139.6, 135.5, 131.3, 130.4, 130.4, 129.4, 127.1, 126.5, 119.3, 25.2, 22.1, 18.3, 14.7, 13.4, 13.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.85 (d, *J* = 712.57 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.66 (hept, *J* = 712.56 Hz). HRMS (ESI, positive ion): M^+= 270.1299 (calculated 270.1311 for $[C_{17}H_{20}NS]^+$).

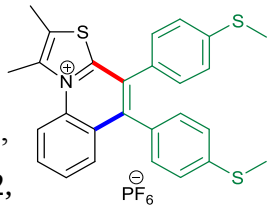
1,2-dimethyl-4,5-di*p*-tolyl-3a*H*-thiazolo[3,2-a]quinoline hexafluorophosphate (3d): Yield = 79%, 42.6 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 9.0 Hz, 1H), 8.00 (t, *J* = 7.4 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.13 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.20 (s, 3H), 2.63 (s, 3H), 2.37 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 146.2, 140.0, 140.0, 139.2, 136.2, 131.9, 131.7, 131.1, 130.7, 130.7, 130.1, 130.0, 130.0, 129.7, 129.4, 129.1, 128.6, 119.0, 21.5, 21.5, 18.2, 13.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.37 (d, *J* = 712.8 Hz).^{31}P NMR (202 MHz, $CDCl_3$) δ -144.85 (hept, *J* = 712.8 Hz). HRMS (ESI, positive ion): M^+ = 394.1595 (calculated 395.1624 for $[C_{27}H_{24}NS]^+$).



4,5-bis(4-methoxyphenyl)-1,2-dimethyl-3a*H*-thiazolo[3,2-a]quinolone hexafluorophosphate (3e): Yield = 90% , 57.3 mg, ^{1}H NMR (500 MHz, CD_3CN) δ 9.00 (d, *J* = 8.9 Hz, 1H), 8.05 (t, *J* = 7.3 Hz, 1H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.96 (dd, *J* = 8.5, 3.9 Hz, 4H), 3.80 (s, 6H), 3.15 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 161.4, 161.0, 159.8, 146.7, 140.9, 136.9, 132.6, 132.5, 132.4, 132.3, 131.5, 130.5, 130.0, 129.5, 127.5, 127.0, 120.0, 115.4, 114.8, 56.1, 56.1, 18.5, 13.5. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M^+ = 426.1500 (calculated 426.1522 for $[C_{27}H_{24}NO_2S]^+$).

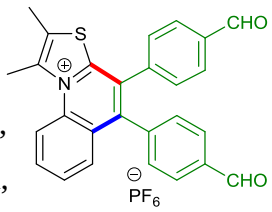


1,2-dimethyl-4,5-bis(4-(methylthio)phenyl)-3a*H*-thiazolo[3,2-a]quinolone hexafluoro phosphate (3f): Yield = 89% , 54 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.8 Hz, 1H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.25-7.19 (m, 6H), 7.12 (d, *J* = 7.7 Hz, 2H), 3.17 (s, 3H), 2.62 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 145.7, 141.6, 140.7, 140.1, 136.2, 132.0, 131.8, 130.5, 130.2, 130.0, 129.9, 129.8, 129.2, 129.1, 128.5, 126.4, 125.8, 119.0, 18.2, 15.1, 15.0, 13.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.43 (d, *J* = 713.0 Hz). ^{31}P (202 MHz, $CDCl_3$) -134.87- -156.00 (hept, *J* =712.9). HRMS (ESI, positive ion): M^+ = 458.1053 (calculated 458.1065 for $[C_{27}H_{24}NS_3]^+$).

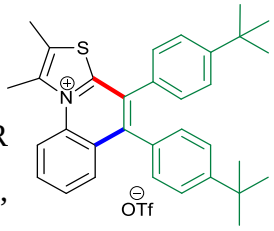


4,5-bis(4-formylphenyl)-1,2-dimethylthiazolo[3,2-a]quinolizin-10-ium hexafluorophopsphate (3g): Yield: 90%, 51.8 mg, ^{1}H NMR (400 MHz, CD_3CN) δ 10.02 (d, *J* = 3.3 Hz, $2H_{aldehyde}$), 9.06 (d, *J* = 9.0 Hz, 1H), 8.12 (ddd, *J* = 8.8, 7.1, 1.6 Hz, 1H), 7.95 – 7.90 (m,

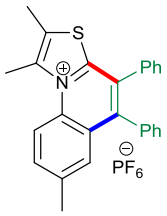
4H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.80 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 3.19 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 193.1 (C_{CHO}), 193.0 (C_{CHO}), 158.3, 145.5, 141.4, 140.5, 140.3, 138.2, 137.6, 137.0, 134.8, 133.4, 133.1, 131.8, 131.0, 130.5, 130.5, 130.38, 130.3, 128.6, 120.3, 18.5, 13.6. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M+= 422.1209 (calculated 422.1193 for $[C_{27}H_{20}NO_2S]^+$).



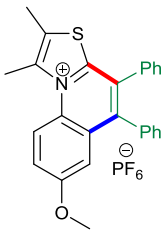
4,5-bis(4-tert-butylphenyl)-1,2-dimethyl-3aH-thiazolo[3,2-a]quinoline trifluoromethane sulphonate (3h): Yield = 81 %, 50.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (d, *J* = 9.0 Hz, 1H), 8.04 (t, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.34 (dd, *J* = 8.3, 2.1 Hz, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.27 (s, 3H), 2.67 (s, 3H), 1.29 (s, 6H), 1.28 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 153.1, 152.4, 146.4, 140.2, 136.2, 131.9, 131.8, 131.0, 130.8, 130.7, 130.0, 130.0, 129.6, 129.1, 128.4, 126.1, 125.4, 119.4, 34.9, 34.8, 31.3, 31.2, 18.5, 13.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.30(s). HRMS (ESI, positive ion): M^+ = 478.2554 (calculated 478.2563 for $[C_{33}H_{36}NS]^+$).



1,2,7-trimethyl-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3i): Yield = 81%, 42.5 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 9.1 Hz, 1H), 7.80 (d, *J* = 9.1 Hz, 1H), 7.56 (s, 1H), 7.40 – 7.28 (m, 6H), 7.24 (dd, *J* = 5.4, 3.8 Hz, 2H), 7.18 (dd, *J* = 6.4, 2.8 Hz, 2H), 3.16 (s, 3H), 2.59 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 145.8, 139.8, 139.9, 134.6, 134.0, 133.8, 133.5, 131.8, 130.5, 130.0, 129.9, 129.8, 129.3, 129.1, 129.0, 128.6, 128.4, 118.71, 21.5, 18.0, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.3 (d, *J* = 712.81 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.83 (hept, *J* = 712.78 Hz). HRMS (ESI, positive ion): M^+= 380.1472 (calculated 380.1467 for $[C_{26}H_{22}NS]^+$).

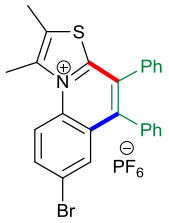


7-methoxy-1,2-dimethyl-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3j): Yield = 78%, 42.2 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 9.7 Hz, 1H), 7.58 (dd, *J* = 9.7, 2.7 Hz, 1H), 7.36 – 7.29 (m, *J* = 3.2 Hz, 6H), 7.28 – 7.23 (m, *J* = 5.3 Hz, 2H), 7.22 – 7.17 (m, *J* = 2.6 Hz, 2H), 7.11 (d,

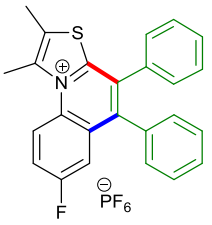


J = 2.7 Hz, 1H).3.75 (s,3H), 3.15(s,3H), 2.59(s,3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 155.6, 145.3, 139.7, 134.1, 133.9, 131.9, 131.2, 130.8, 130.4, 130.0, 129.9, 129.8, 129.3, 129.2, 128.7, 121.1, 120.6, 110.5, 55.9, 18.1, 13.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.31 (d, *J* = 712.94 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.82 (hept, *J* = 712.75 Hz). HRMS (ESI, positive ion): M^+= 396.1430 (calculated 396.1417for $[C_{26}H_{22}NOS]^+$).

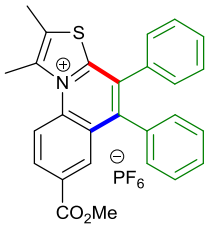
7-bromo-1,2-dimethyl-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3k): Yield = 92%, 54.2 mg, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 9.5 Hz, 1H), 8.06 (dd, *J* = 9.4, 2.3 Hz, 1H), 7.94 (d, *J* = 2.3 Hz, 1H), 7.39 – 7.33 (m, 6H), 7.28 (dt, *J* = 3.8, 2.2 Hz, 2H), 7.22 (d, *J* = 1.8 Hz, 1H), 7.21 – 7.20 (m, 1H), 3.17 (s, 3H), 2.63 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 144.9, 140.2, 135.1, 134.7, 133.7, 133.1, 132.5, 131.9, 131.8, 130.1, 130.0, 129.9, 129.8, 129.5, 129.4, 128.8, 123.6, 120.6, 18.4, 13.6.^{19}F NMR (471 MHz, $CDCl_3$) δ -75.11 (d, *J* = 713.2 Hz).. ^{31}P NMR (202 MHz, $CDCl_3$) δ -132.62 – -157.69 (hept *J*= 713.0 Hz). HRMS (ESI, positive ion): M^+= 444.0444 (calculated 444.0422for $[C_{25}H_{19}NBrS]^+$).



7-fluoro-1,2-dimethyl-4,5-diphenyl-thiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3l): Yield = 90%, 47.6 mg, ^{1}H NMR (400 MHz, CD_3CN) δ 9.08 (dd, *J* = 9.7, 4.4 Hz, 1H), 7.89 – 7.80 (m, 1H), 7.51 – 7.41 (m, 7H), 7.36 (d, *J* = 5.7 Hz, 2H), 7.29 (d, *J* = 3.7 Hz, 2H), 3.16 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 163.2, 160.7, 159.0, 145.7, 141.1, 135.1, 134.5, 133.8, 133.5, 132.5, 131.6, 131.5, 130.8, 130.8, 130.7, 130.1, 129.5, 123.2, 123.1, 121.1, 120.8, 115.0, 114.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.91 (d, *J* = 713.0 Hz), -100.38 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -145.19 (hept, *J* = 712.8 Hz). HRMS (ESI, positive ion): M+= 384.1213 (calculated 384.1217 for $[C_{25}H_{19}NFS]^+$).

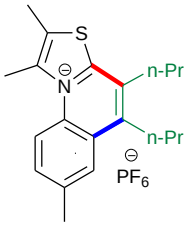


7-(methoxycarbonyl)-1,2-dimethyl-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3m): Yield = 86 %, 48.9 mg, ^{1}H NMR (400 MHz, CD_3CN) δ 9.11 (d, *J* = 9.3 Hz, 1H), 8.54 (dd, *J* = 9.3, 1.9 Hz, 1H), 8.38 (d, *J* = 1.8 Hz, 1H), 7.49 – 7.42 (m, 6H), 7.36 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.31 (dd, *J* = 6.3, 2.9 Hz, 2H), 3.89 (s, 3H), 3.18 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 165.9, 160.6, 146.6, 141.3, 138.8, 135.0, 134.5, 133.6, 132.5, 131.8,

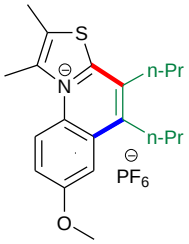


131.6, 131.3, 130.9, 130.9, 130.7, 130.3, 130.2, 129.5, 129.2, 120.9, 53.5, 18.5, 13.5. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M+= 424.1363 (calculated 424.1366 for $[C_{27}H_{22}NO_2S]^+$).

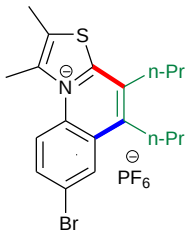
1,2,7-trimethyl-4,5-dipropylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3n) Yield=78%, 35.6 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 9.0 Hz, 1H), 8.00 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 3.20 – 3.11 (m, 2H), 3.09 (s, 3H), 3.05 – 2.96 (m, 2H), 2.67 (s, 3H), 2.63 (s, 3H), 1.73 (td, *J* = 14.4, 7.1 Hz, 4H), 1.14 (dt, *J* = 17.9, 7.2 Hz, 6H).^{13}C NMR (400 MHz, $CDCl_3$) δ 155.4, 146.1, 139.8, 139.4, 133.8, 132.8, 130.2, 129.2, 127.4, 125.8, 119.0, 34.0, 30.9, 23.9, 22.2, 21.7, 18.2, 14.6, 14.5, 13.3.^{19}F NMR (376 MHz, $CDCl_3$) δ -73.79 (d, *J* = 712.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.62 (hept, *J* = 712.52 Hz). HRMS (ESI, positive ion): M^+= 312.1792 (calculated 312.1780for $[C_{20}H_{26}NS]^+$).



7-methoxy-1,2-dimethyl-4,5-dipropylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3o): Yield= 80%, 37.8 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 9.7 Hz, 1H), 7.58 (dd, *J* = 9.7, 2.8 Hz, 1H), 7.53 (d, *J* = 2.7 Hz, 1H), 4.01 (s, 3H), 3.15 – 3.10 (m, 2H), 3.10 (s, 3H), 3.03 – 2.97 (m, 2H), 2.68 (s, 3H), 1.82 – 1.70 (m, 4H), 1.15 (dt, *J* = 14.6, 7.3 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 154.2, 145.5, 139.4, 130.4, 130.3, 129.5, 129.3, 121.0, 120.1, 107.7, 56.1, 34.1, 31.1, 23.5, 22.3, 18.3, 14.8, 14.5, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.79 (d, *J* = 712.56 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.66 (hept, *J* = 712.59 Hz). HRMS (ESI, positive ion): M^+= 328.1746 (calculated 328.1730for $[C_{20}H_{26}NOS]^+$).

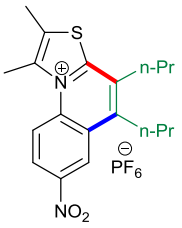


7-bromo-1,2-dimethyl-4,5-dipropylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3p): Yield = 92%, 47.9 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 9.2 Hz, 1H), 8.30 (s, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 3.14 – 3.08 (m, 2H), 3.06 (s, 3H), 3.04 – 2.97 (m, 2H), 2.66 (s, 3H), 1.83 – 1.66 (m, 4H), 1.13 (dt, *J* = 14.0, 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 144.9, 139.9, 134.3, 133.9, 131.0, 130.2, 128.8, 128.6, 123.4, 121.1, 34.0, 30.8, 23.8, 22.2, 18.1, 14.6, 14.4,

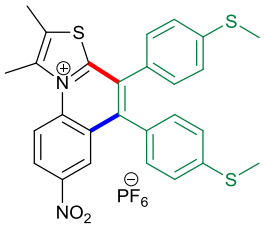


13.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.79 (d, *J* = 712.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.83 (hept, *J* = 712.6 Hz). HRMS (ESI, positive ion): M^+ = 376.0807 (calculated 376.0729 for $[C_{19}H_{23}BrNS]^+$).

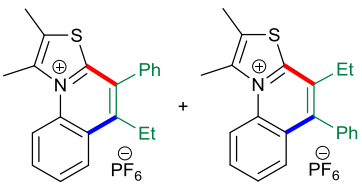
1,2-dimethyl-7-nitro-4,5-dipropylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3q): Yield = 91%, 44.4 mg, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 2.2 Hz, 1H), 9.00 (d, *J* = 9.7 Hz, 1H), 8.59 (dd, *J* = 9.6, 2.2 Hz, 1H), 3.28 – 3.16 (m, 2H), 3.15 – 3.01 (m, 5H), 2.67 (s, 3H), 1.78 (dq, *J* = 14.8, 7.2 Hz, 4H), 1.18 (t, *J* = 7.3 Hz, 3H), 1.12 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 146.3, 146.2, 140.5, 137.9, 131.7, 131.4, 127.9, 124.2, 122.0, 121.7, 34.1, 31.1, 24.1, 22.1, 18.1, 14.6, 14.5, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.79 (d, *J* = 712.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -131.98- -158.39 (hept, *J* = 712.6 Hz). HRMS (ESI, positive ion): M^+ = 343.1479 (calculated 343.1475 for $[C_{19}H_{23}N_2O_2S]^+$).



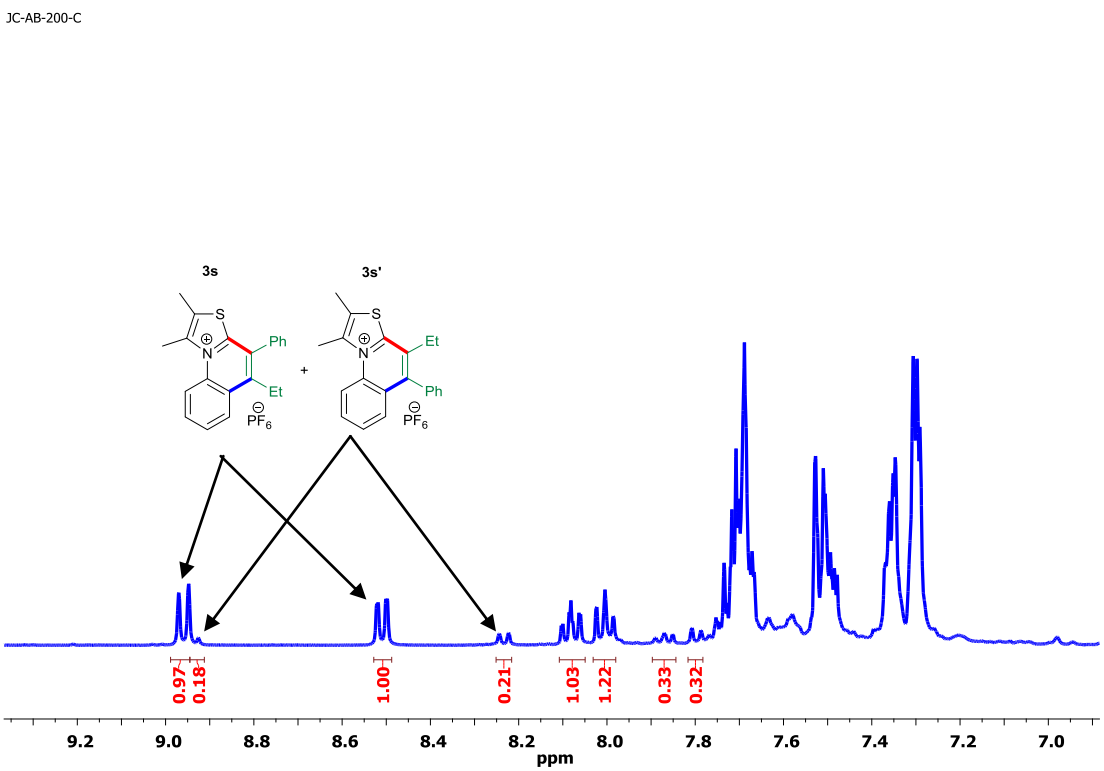
1,2-dimethyl-4,5-bis(4-(methylthio)phenyl)-7-nitro-3aH-thiazolo[3,2-a]quinoline hexafluorophosphate (3r): Yield = 80% , 51.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 9.6 Hz, 1H), 8.64 (d, *J* = 2.5 Hz, 1H), 8.60 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.23 – 7.16 (m, 6H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.10 (s, 3H), 2.59 (s, 3H), 2.50 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 146.1, 145.4, 142.0, 141.5, 140.6, 138.4, 132.8, 132.1, 130.5, 129.9, 129.2, 129.0, 128.4, 126.2, 125.8, 124.9, 124.7, 121.0, 17.8, 14.8 (two peaks merged), 13.4. ^{31}P NMR (202 MHz, $CDCl_3$) δ -145.33 (hept, *J* = 713.3 Hz).^{19}F NMR (471 MHz, $CDCl_3$) δ -74.53 (d, *J* = 713.3 Hz). HRMS (ESI, positive ion): M^+ = 503.0911 (calculated 503.916 for $[C_{27}H_{23}N_2O_2S_3]^+$).



5-ethyl-1,2-dimethyl-4-phenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate + 4-ethyl-1,2-dimethyl-5-phenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3s + 3s′, 1: 0.18): Total Yield = 94% , 43.5 mg, ^{1}H NMR for **3s** (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 9.0 Hz, 1H), 8.37 (d, *J* = 7.6 Hz, 1H), 8.05 – 7.98 (m, 1H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.46 – 7.40 (m, 2H), 3.12 (s, 3H), 3.01 (q, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR for **3s** (101 MHz, $CDCl_3$) δ 157.8, 148.2, 139.6, 136.2, 134.1, 131.8, 131.5, 130.5, 130.4, 130.1, 129.4, 129.3, 127.1, 127.0, 119.4, 23.3, 18.2,



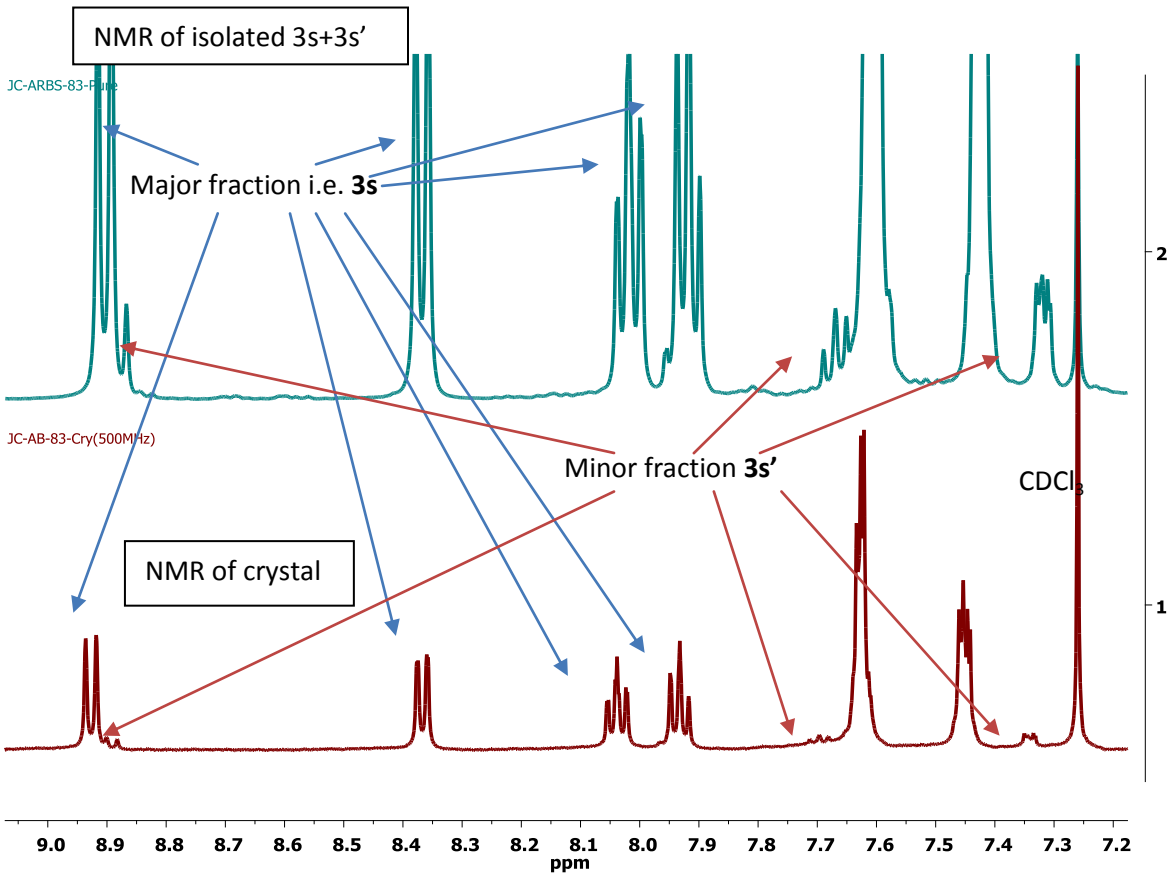
14.9, 13.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.13 (d, *J* = 712.71 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.81 (hept, *J* = 712.75 Hz). HRMS (ESI, positive ion): M^+= 318.1295 (calculated 318.1311 for $[C_{21}H_{20}NS]^+$).



Partial ^{1}H NMR spectrum of a crude reaction mixture containing **3s+ 3s′** (500 MHz, CD_3CN).

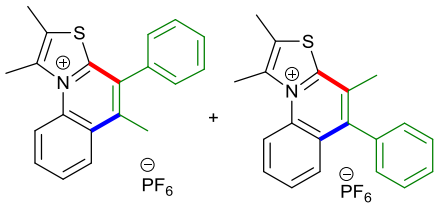
*Note: The ratio of **3s** to **3s′** was calculated from crude NMR analysis. **3s′** was not fully characterized because of less presence in the product mixture. The structural confirmation of major fraction is indirectly supported by corresponding SC-XRD and ^{1}H NMR analysis.*

Crystallographic confirmation of major region-isomer of 3s and 3s': After crystal data collection, few crystals were picked out carefully and ^{1}H NMR analysis was performed. The data shows similar pattern as purified sample NMR. In this case too, the major fraction was **3d**. Hence, it indirectly confirms that **3d** crystallizes and is present in major amount in the product mixture.

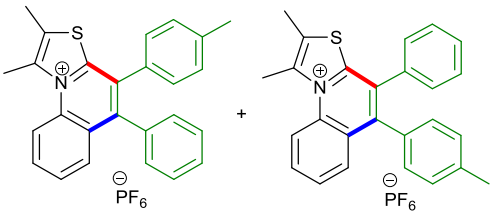


Comparative NMR analysis of **3s**+**3s'**product mixture with crystals of **3s**

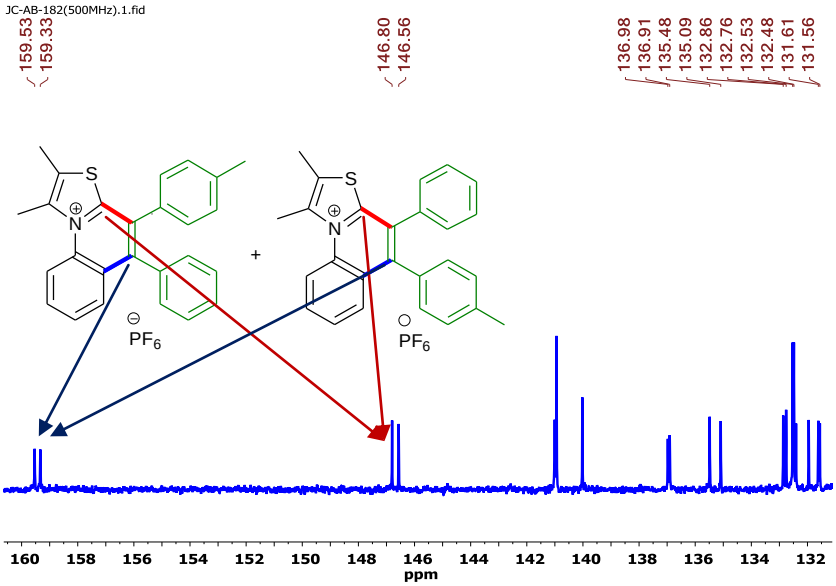
1,2,5-trimethyl-4-phenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate + 1,2,5-trimethyl-5-phenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3t + 3t′ , 1: 0.11): Total Yield = 89 %, 39.9 mg, ^{1}H NMR for **3z** (400 MHz, CD_3CN) δ 8.98 (d, *J* = 8.9 Hz, 1H), 8.49 (dd, *J* = 8.2, 0.9 Hz, 1H), 8.11 – 8.04 (m, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.68 (dd, *J* = 6.7, 4.5 Hz, 3H), 7.49 (dd, *J* = 6.4, 2.8 Hz, 2H), 3.11 (s, 3H), 2.62 (s, 3H), 2.58 (s, 3H). ^{13}C NMR for **3z** (101 MHz, CD_3CN) δ 143.8, 140.6, 136.5, 135.6, 132.5, 131.9, 131.6, 131.3, 130.8, 130.4, 130.1, 130.1, 128.9, 128.4, 120.2, 18.5, 17.2, 13.3. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M^+= 304.1128 (calculated 304.1154 for $[C_{20}H_{18}NS]^+$). *(Note: The ratio of **3t** to **3t′** was calculated from crude ^{1}H NMR spectrum analysis as similar to **3s** + **3s′** analysis. **3t′** could not be fully characterized because of less presence of it in the mixture.)*



1,2-dimethyl-5-phenyl-4-(p-tolyl)thiazolo[3,2-a]quinolin-10-ium hexafluorophosphate + 1,2-dimethyl-4-phenyl-5-(p-tolyl)thiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3u+ 3u′, 1:1): Total Yield = 94%, 49.4 mg, ^{1}H NMR (400 MHz, CD_3CN) δ 9.03 (d, *J* = 9.0 Hz, 1H), 8.06 (dd, *J* = 8.8, 4.7 Hz, 1H), 7.88 – 7.79 (m, 2H), 7.43 (dd, *J* = 7.4, 4.8 Hz, 3H), 7.35 (d, *J* = 5.5 Hz, 1H), 7.32 – 7.21 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 1H), 3.17 (s, 3H), 2.62 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 159.5, 159.3, 146.8, 146.6, 141.0, 140.9, 140.0, 137.0, 136.9, 135.5, 135.1, 132.9, 132.8, 132.5, 132.4, 132.0, 131.6, 131.6, 130.8, 130.7, 130.7, 130.5, 130.4, 130.1, 130.1, 130.0, 130.0, 129.9, 129.4, 129.4, 129.3, 120.1, 21.3, 21.2, 18.5, 13.5. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M^+= 380.1482 (calculated 380.1467 for $[C_{26}H_{22}NS]^+$).



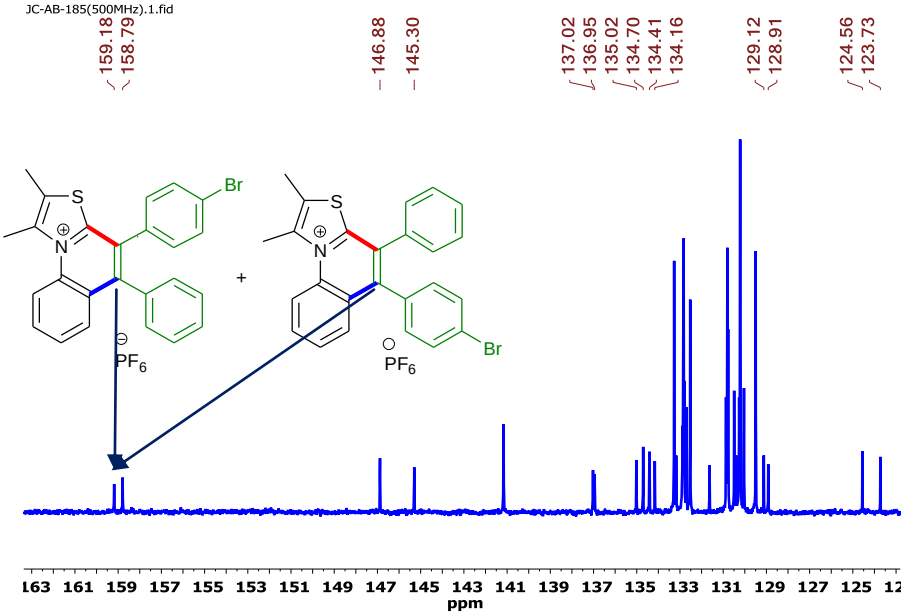
Note: The regio-isomers are not detectable by ^{1}H NMR analysis. However, two sets of carbon peaks in ^{13}C NMR indicates formation of the other isomer.



Partial ^{13}C{^{1}H} NMR spectrum of a mixture containing **3u**+ **3u′** (CD_3CN, 126 MHz)

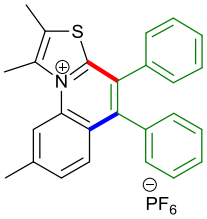
4-(4-bromophenyl)-1,2-dimethyl-5-phenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate + 5-(4-bromophenyl)-1,2-dimethyl-4-phenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3v + 3v′, 1:1): Total Yield = 89%, 52.5 mg, ^{1}H NMR (400 MHz, CD_3CN) δ 9.04 (d, *J* = 9.0 Hz, 1H), 8.09 (ddd, *J* = 8.8, 6.2, 2.4 Hz, 1H), 7.90 – 7.80 (m, 2H), 7.59 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.35 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.21 (d, *J* = 8.3 Hz, 1H), 3.17 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 159.2, 158.8, 146.9, 145.3, 141.2, 137.0, 136.9, 135.0, 134.71 134.4, 134.2, 133.3, 133.2, 132.9, 132.9, 132.8, 132.8, 132.7, 132.5, 131.6, 130.9, 130.8, 130.8, 130.5, 130.4, 130.3, 130.2, 130.0, 129.5, 129.1, 128.9, 124.5, 123.7, 120.1, 120.1,18.51, 13.5. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M+= 444.0396 (calculated 446.0416 for $[C_{25}H_{19}BrNS]^{+}$).

Note: The regio-isomers are not detectable by ^{1}H NMR. However, two sets of carbon peaks in ^{13}C NMR indicates formation of the other isomer.

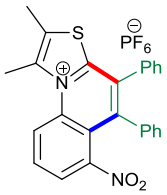


Partial ^{13}C{^{1}H} NMR spectrum of a mixture containing **3v**+ **3v′** (CD_3CN, 126 MHz)

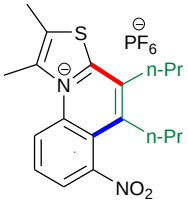
1,2,8-trimethyl-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3w): Yield = 80 %, 42.0 mg, ^{1}H NMR (400 MHz, CD_3CN) δ 8.80 (s, 1H), 7.77 – 7.58 (m, 2H), 7.50 – 7.39 (m, 6H), 7.35 (d, *J* = 4.5 Hz, 2H), 7.28 (d, *J* = 3.4 Hz, 2H), 3.19 (s, 3H), 2.73 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 159.2, 146.6, 144.4, 140.8, 137.2, 135.4, 135.1, 132.4, 131.7, 130.9, 130.8, 130.7, 130.6, 130.1, 130.1, 129.8, 129.3, 127.2, 119.5, 22.4, 18.5, 13.5. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M^+= 380.1468 (calculated 380.1467 for $[C_{26}H_{22}NS]^+$).



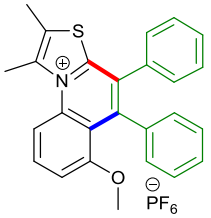
1,2-dimethyl-6-nitro-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3x): Yield = 86%, 47.9 mg, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (d, *J* = 1.9 Hz, 1H), 8.48 (dd, *J* = 9.1, 2.0 Hz, 1H), 8.05 (d, *J* = 9.1 Hz, 1H), 7.41 – 7.35 (m, 6H), 7.35 – 7.31 (m, 2H), 7.26 – 7.23 (m, 2H), 3.27 (s, 3H), 2.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 147.6, 145.3, 140.5, 135.4, 133.9, 133.6, 133.3, 132.9, 132.5, 131.8, 130.4, 130.1, 129.8, 129.6, 129.5, 128.9, 122.6, 114.8, 18.1, 13.7. ^{19}F (471 MHz, $CDCl_3$) δ -75.11 (d, *J* = 713.2 Hz). ^{31}P (202 MHz, $CDCl_3$) -134.87- -156.00 (hept, *J*=712.9). HRMS (ESI, positive ion): M^+ = 411.1170 (calculated 411.1162 for $[C_{25}H_{19}N_2O_2S]^+$).



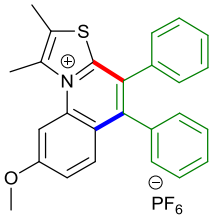
1,2-dimethyl-6-nitro-4,5-dipropylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3y): Yield = 89%, 43.5mg, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 1.6 Hz, 1H), 8.61 (dd, *J* = 9.2, 1.7 Hz, 1H), 8.45 (d, *J* = 9.2 Hz, 1H), 3.23 – 3.16 (m, 5H), 3.11 – 3.06 (m, 2H), 2.75 (s, 3H), 1.80 (ddd, *J* = 23.9, 16.0, 7.6 Hz, 4H), 1.21 – 1.13 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 147.1, 145.4, 140.3, 134.8, 133.1, 132.0, 131.3, 128.5, 122.7, 115.3, 34.5, 31.3, 29.8, 23.9, 22.3, 18.3, 14.7, 14.6, 13.7. ^{31}P NMR (202 MHz, $CDCl_3$) δ -132.62 – -159.74 (hept, *J* = 713.0Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.11 (d, *J* = 713.2 Hz). HRMS (ESI, positive ion): M^+ = 343.1480 (calculated 343.1475 for $[C_{19}H_{23}N_2O_2S]^+$).



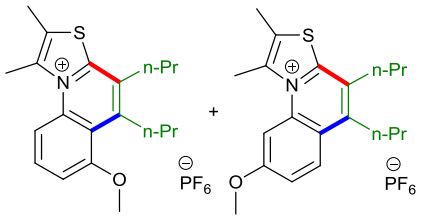
6-methoxy-1,2-dimethyl-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate + 8-methoxy-1,2-dimethyl-4,5-diphenylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3z + 3z′; 1: 0.6): Total Yield = 90%, 48.7 mg. ^{1}H NMR for **3z** (500 MHz, CD_3CN) δ 8.50 (d, *J* = 9.0 Hz, 1H), 7.99 (t, *J* = 8.6 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.26 – 7.21 (m, 5H), 7.10 (d, *J* = 7.5 Hz, 2H), 3.43 (s, 3H), 3.09 (s, 3H), 2.59 (s, 3H). ^{13}C NMR for **3z** (126 MHz, CD_3CN) δ 159.4, 159.2, 145.8, 140.8, 139.7, 138.2, 135.7, 133.5, 132.9, 131.7, 131.0, 130.3, 129.8, 129.0, 128.0, 119.9, 112.3, 111.9, 57.1, 18.6, 13.5. ^{19}F NMR for **3z** (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR for **3z** (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M^+= 328.1401 (calculated 396.1417 for $[C_{26}H_{22}NOS]^+$).



^{1}H NMR for **3z′** (400 MHz, CD_3CN) δ 8.34 (d, *J* = 2.2 Hz, 1H), 7.74 (d, *J* = 9.3 Hz, 1H), 7.46 (dd, *J* = 9.3, 2.3 Hz, 1H), 7.43 – 7.39 (m, 6H), 7.33 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.28 – 7.24 (m, 2H), 4.10 (s, 3H), 3.19 (s, 3H), 2.60 (s, 3H).^{13}C NMR for **3y'** (101 MHz, CD_3CN) δ 162.9, 159.4, 146.9, 140.1, 138.7, 135.5, 135.1, 132.1, 132.0, 130.9, 130.8, 130.6, 130.1, 129.9, 129.3, 123.5, 119.6, 102.75, 57.24, 18.23, 13.45. ^{19}F NMR for **3z′** (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR for **3z′** (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M^+= 328.1419 (calculated 396.1417 for $[C_{26}H_{22}NOS]^+$). *Note: The ratio of **3z** to **3z′** was calculated from crude ^{1}HNMR analysis.*

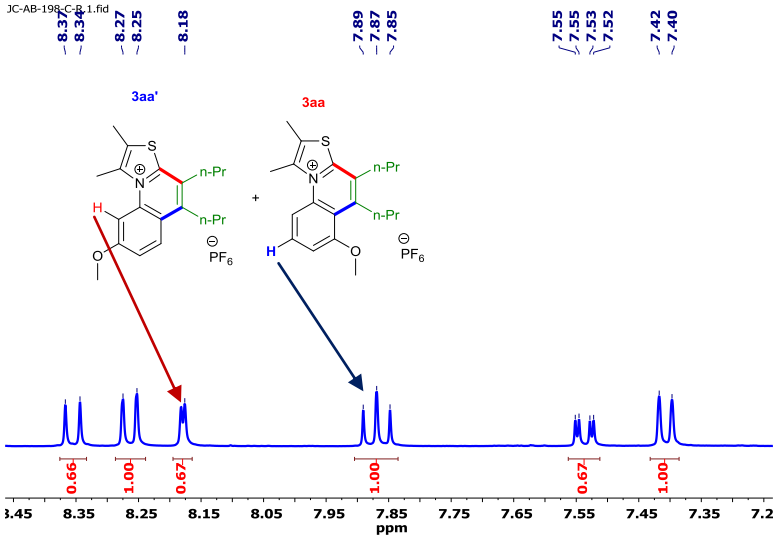


6-methoxy-1,2-dimethyl-4,5-dipropylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate + 8-methoxy-1,2-dimethyl-4,5-dipropylthiazolo[3,2-a]quinolin-10-ium hexafluorophosphate (3aa + 3aa′, 1: 0.67): Total yield = 82 %, 38.8 mg, ^{1}H NMR for **3aa** (500 MHz, CD_3CN) δ 8.26 (d, *J* = 8.9 Hz, 1H), 7.87 (t, *J* = 8.5 Hz,1H), 7.41 (d, *J* = 8.2 Hz, 1H), 4.09 (s, 3H), 3.43 – 3.35 (m, 2H), 3.04 – 2.99 (m, 2H), 2.95 (s, 3H), 2.63 (s, 3H), 1.73 (dd, *J* = 15.8, 7.6 Hz, 2H), 1.65 (dd, *J* = 15.5, 7.6 Hz, 2H), 1.13 (q, *J* = 7.6 Hz, 6H). ^{1}H NMR for **3aa′**) (500 MHz, CD_3CN) δ 8.36 (d, *J* = 9.3 Hz, 1H), 8.18 (br, s, 1H), 7.54 (d, *J* = 9.2 Hz, 1H), 4.06 (s, 3H), 3.19 (dd, *J* = 9.2, 7.1 Hz, 2H), 3.08 (s, 3H), 2.64 (s, 3H), 1.73 (dd, *J* = 15.8, 7.6 Hz, 2H, *merged with **3aa′***), 1.65 (dd, *J* = 15.5, 7.6 Hz, 2H, *merged with **3aa′***), 1.13 (q, *J* = 7.6 Hz, 6H, *merged with **3aa′***). ^{13}C NMR for **3aa′** (126 MHz, CD_3CN) δ

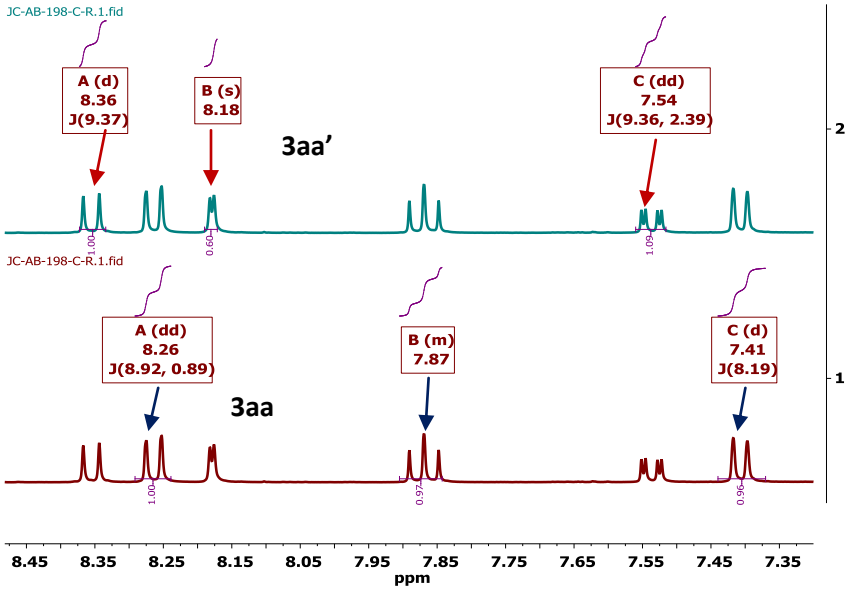


159.3, 157.7, 148.8, 140.4, 137.9, 132.0, 130.7, 129.9, 120.3, 112.8, 111.1, 34.7, 34.6, 25.4, 23.0, 18.7, 14.9, 14.5, 13.5. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M+= 328.1722 (calculated 328.1730 for $[C_{20}H_{26}NOS]^+$).

Note: The formation of the two regio-isomers are distinct with their characteristic proton NMR chemical shifts. The ratio of the isomers was calculated from crude NMR as shown below

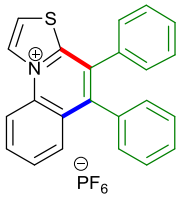


Partial ^{1}H NMR spectrum of a crude reaction mixture containing **3aa**+**3aa′** (400 MHz, CD_3CN)

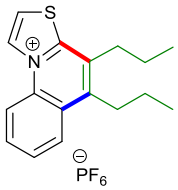


Comparative partial ^{1}H NMR spectral analysis of **3aa** and **3aa′**

4,5-diphenylbenzo[ij]thiazolo[3,2-a]quinolizin-10-ium hexafluorophopsphate (3ab): Yield = 84 %, 40.6 mg, ^{1}H NMR (500 MHz, CD_3CN) δ 9.31 (br, s, 1H), 8.71 (d, *J* = 8.6 Hz, 1H), 8.31 (d, *J* = 2.1 Hz, 1H), 8.17 (t, *J* = 7.8 Hz, 1H), 7.89 (dd, *J* = 20.7, 12.7 Hz, 2H), 7.46-7.40 (m, 8H), 7.31 (d, *J* = 4.1 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 160.1, 147.9, 135.2, 135.2, 134.7, 134.1, 131.7, 130.9, 130.8, 130.8, 130.7, 130.5, 130.4, 130.2, 130.0, 129.4, 127.9, 124.6. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz). HRMS (ESI, positive ion): M^+= 338.0998 (calculated 338.0998 for $[C_{23}H_{16}NS]^+$).



4,4-dipropylthiazolo[3,2-a]quinol-10-ium hexafluorophosphate (**3ac**): Yield = 81 %, 33.6 mg, ^{1}H NMR (400 MHz, CD_3CN) δ 9.15 (d, *J* = 4.4 Hz, 1H), 8.55 (d, *J* = 8.6 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 4.3 Hz, 1H), 8.10 – 8.04 (m, 1H), 7.96 (t, *J* = 7.7 Hz, 1H), 3.32 – 3.25 (m, 2H), 3.16 – 3.09 (m, 2H), 1.77 (ddd, *J* = 23.2, 15.7, 7.7 Hz, 4H), 1.15 (dd, *J* = 15.7, 7.4 Hz, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ 158.72, 148.82, 134.76, 133.18, 130.70, 130.49, 130.14, 128.02, 127.03, 122.74, 119.11, 34.34, 31.25, 24.93, 22.80, 14.49, 14.37. ^{19}F NMR (471 MHz, CD_3CN) δ -72.96 (d, *J* = 706.5 Hz). ^{31}P NMR (202 MHz, CD_3CN) δ -144.64 (hept, *J* = 706.5 Hz. HRMS (ESI, positive ion): M+= 270.1311 (calculated 270.1288 for $[C_{17}H_{20}NS]^+$)



7. Mechanistic studies:

7.1. Synthesis of the cyclometalated Rh(III) intermediate complex 4:

To an oven dried Schlenk tube, **1a** (0.05 mmol), Cs_2CO_3 (1.5 equiv.), $[RhCp^*Cl_2]_2$ (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 (5.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at reflux condition of 110 ^{o}C. After 24 h, the whole reaction mixture was passed through a short celite pad which was thereafter washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. The solid part was re-precipitated thrice using DCM/Diethyl ether solvent combination to obtain the desired complex **4**. Yield = 72%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 8.2 Hz, 1H), 2.71 (s, 3H), 2.34 (s, 3H), 1.75 (s, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.0 (d, $J_{Rh\text{-}C(NSHC)}$ = 53.6 Hz), 163.2 (d, $J_{Rh\text{-}}$

$_{C(Ph)}$ = 32.6 Hz), 150.5 (s), 138.2 (s), 137.7 (s), 128.1 (s), 126.4 (s), 122.4 (s), 114.2 (s), 99.2 (d, $J_{Rh\text{-}C(Cp^*)}$ = 4.8 Hz), 14.8 (s), 12.5 (s), 9.7 (s). HRMS (ESI, positive ion): M+ = 426.0763 (calculated 426.0757 for $[C_{21}H_{25}NSRh\text{-}Cl]^+$).

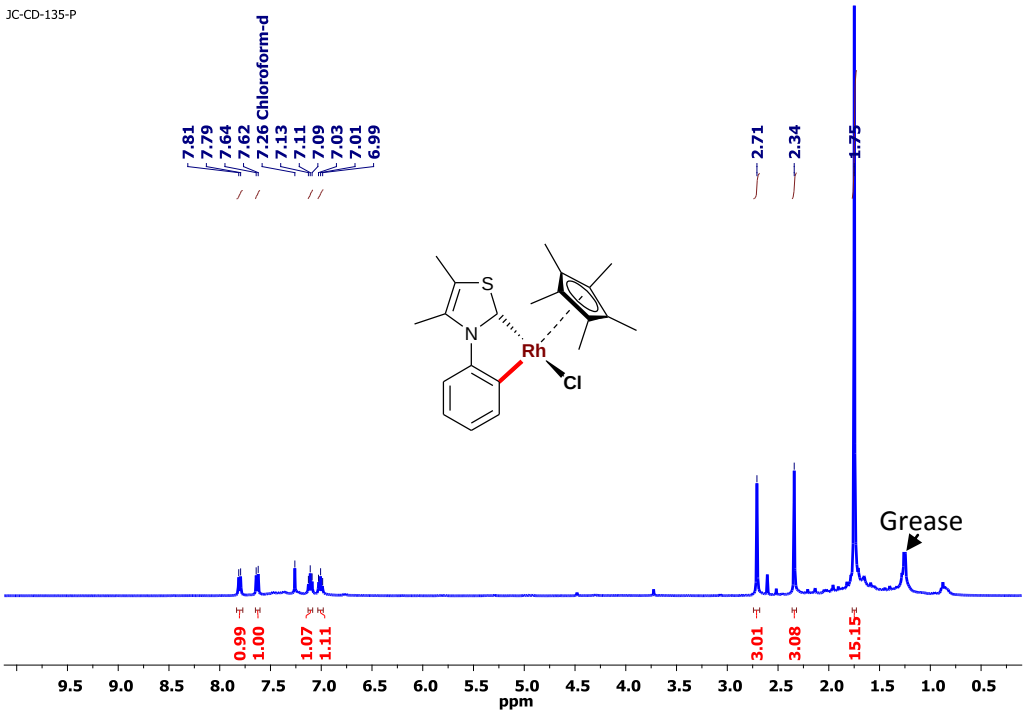


Fig. S1: ^{1}H NMR spectrum of complex **4** (400 MHz, $CDCl_3$)

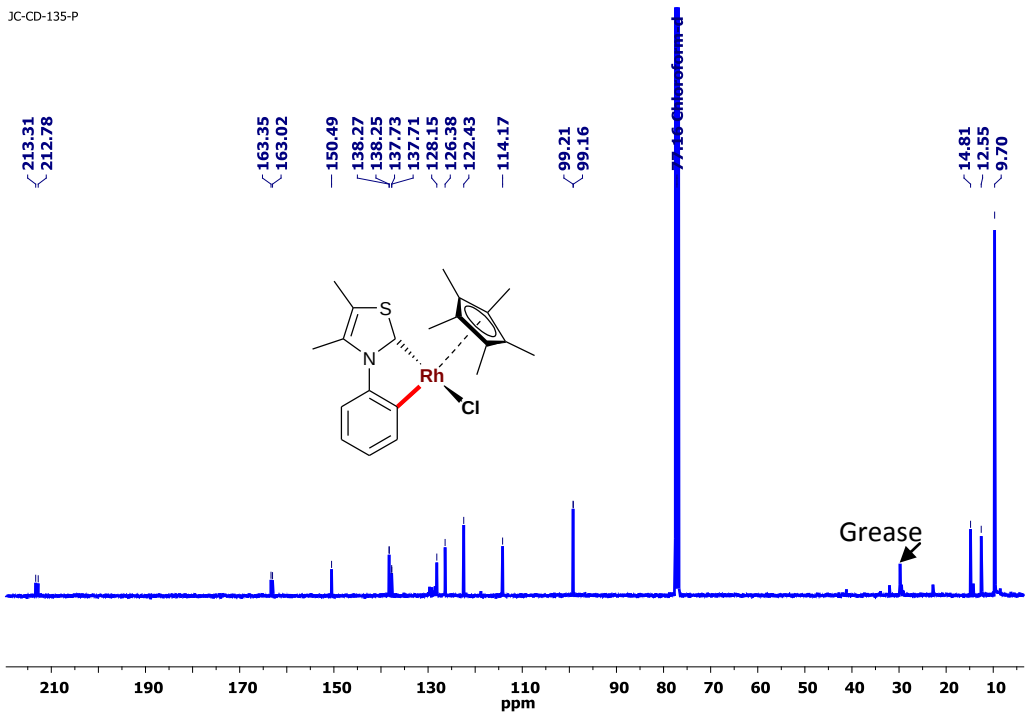


Fig. S2: $^{13}C\{^{1}H\}$ NMR spectrum of complex **4** (100 MHz, $CDCl_3$)

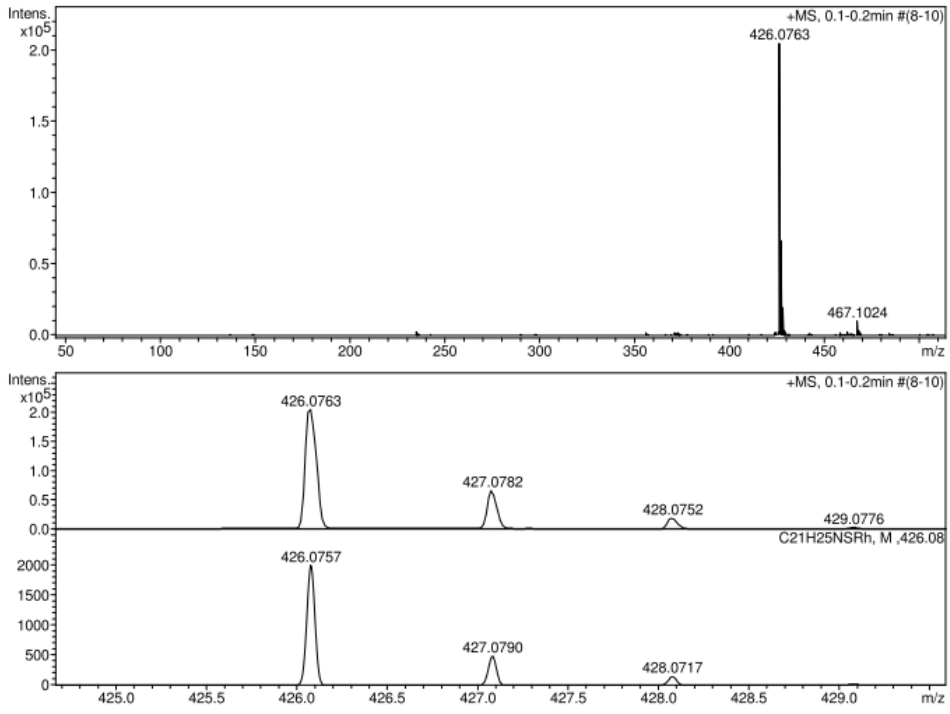


Fig.S3: ESI-HRMS (positive ion mode) spectrum of complex **4**

7.2. SC-XRD data analysis for complex 4.

The structure of this complex was characterised by single crystal X-ray diffraction study. A suitable single crystal of **4** was grown by layering of dichloromethane solution of **4** with hexane at room temperature. The details of the crystal data are provided in CIF file.

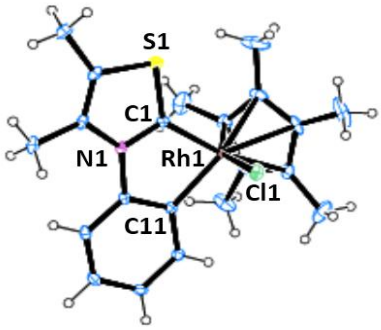
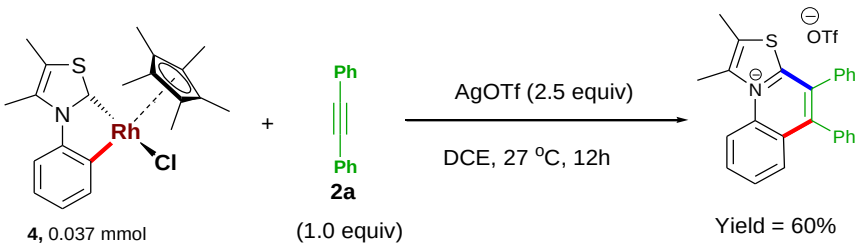


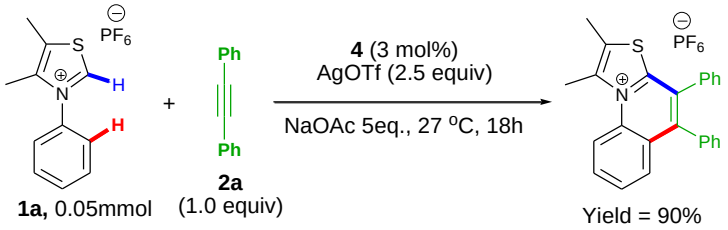
Fig. S4: Molecular structure of **4** (30% probability level). Selected bond lengths (Å) and bond angles (°): C_1–Rh_1 = 1.976(2); C_{11}–Rh_1 = 2.026(2); Cl_1–Rh_1 = 2.3845(6); C_1–N_1 = 1.353(3); C_1–S_1 = 1.698(2); N_1–C_1–S_1 = 109.15(15); C_1–Rh_1–C_{11} = 77.42(9); C_1–Rh_1–Cl_1 = 91.54(6), C_{11}–Rh_1–Cl_1 = 88.21(7).

7.3. Stoichiometric reaction of Rh(III) complex 4



In an oven dried Schlenk tube, a mixture of Complex **4** (17.0 mg, 0.037 mmol), AgOTf (23.6 mg, 0.092 mmol) and **2a** (6.5 mg, 0.037 mmol) in dry and degassed DCE (2.0 mL) were stirred at 27 °C under dark and N_2 atmosphere. After 12 h stirring, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/MeOH solvent mixture to get desired product (30.9 mg, 60%).

7.4. Reaction catalyzed by Rh(III) complex 4



To an oven dried Schlenk tube, **1a** (16.8 mg, 0.05 mmol), NaOAc (20.5 mg, 0.25 mmol), complex **4** (0.7 mg, 3 mol %), AgOTf (32.1 mg, 0.125 mmol) and **2a** (8.9 mg, 0.05 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 DCE (2.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After 18 h, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/MeOH solvent mixture, afforded **3a** (46.1 mg, 90%).

8. Computational studies:

Gaussian 09 software was used to carry out all the theoretical studies.[4] DFT calculations were performed with B3LYP exchange-correlation functional by using 6-31G (d) basis set for H, C, O, S and N atoms[5]. 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**, **3e** and **3x** are as below.

3a

```
 -----
 Symbolic Z-matrix:
 Charge =  1 Multiplicity = 1
 C                    -1.57978  -5.80543  -1.22278
 C                    -3.4638   -5.02452  -2.56624
 C                    -3.97846  -6.30722  -2.6085
 C                    -3.27483  -7.36032  -1.99696
 H                    -3.96771  -4.22616  -3.09287
 N                    -0.37116  -5.51059  -0.53986
 C                     0.23085  -4.29625  -0.76539
 C                     0.32475  -6.33982   0.41332
 C                     1.50824  -5.80169   0.81236
 C                    -1.6594   -3.40717  -1.9617
 C                    -0.35911  -3.23076  -1.47366
 C                     0.40431  -1.94869  -1.55568
 C                     1.59343  -1.87125  -2.30109
 C                    -0.03953  -0.79879  -0.8732
 C                     2.32317  -0.67909  -2.36953
 H                     1.94946  -2.74002  -2.84736
 C                     0.68618   0.38744  -0.93527
 H                    -0.95544  -0.83412  -0.29328
 C                     1.87488   0.45853  -1.68526
 H                     3.23028  -0.65273  -2.96032
 H                     0.3339    1.26194  -0.3989
 C                    -2.41117  -2.28765  -2.57754
 C                    -1.88778  -1.55896  -3.66201
 C                    -3.67869  -1.9174   -2.07296
 C                    -2.60433  -0.50651  -4.23454
 H                    -0.91988  -1.82223  -4.07289
 C                    -4.38495  -0.85402  -2.62643
 H                    -4.10031  -2.4509   -1.22688
 C                    -3.8565   -0.13975  -3.7181
 H                    -2.17572   0.01885  -5.07867
 H                    -5.34727  -0.57309  -2.21217
 C                    -2.25228  -4.72761  -1.88356
 H                    -4.89942  -6.5058   -3.14392
 H                    -3.64329  -8.37708  -2.07135
 C                    -2.08611  -7.1172   -1.32355
 H                    -1.54266  -7.95416  -0.92181
 C                     2.51574  -6.33503   1.78003
 H                     3.53453  -6.17864   1.41055
 H                     2.43937  -5.83585   2.75401
 H                     2.3885   -7.40856   1.93581
 C                    -0.26124  -7.58472   1.0215
 H                    -1.32831  -7.46864   1.22897
 H                    -0.12165  -8.47824   0.40327
 H                     0.23072  -7.77553   1.97666
 S                     1.80309  -4.17184   0.0714
```

```
 H                     2.37832   1.40268  -1.69154
 H                    -4.45497   0.66145  -4.09865

-----
3e
-----
 Symbolic Z-matrix:
 Charge =  1 Multiplicity = 1
 C                    -1.70012  -5.80494  -1.07761
 C                    -3.5216   -4.99501  -2.41001
 C                    -4.11789  -6.26711  -2.32931
 C                    -3.41689  -7.23277  -1.55538
 H                    -4.01574  -4.21375  -2.97072
 N                    -0.46643  -5.59079  -0.46882
 C                     0.18499  -4.36879  -0.54501
 C                     0.28083  -6.48778   0.30048
 C                     1.38728  -5.80798   0.70533
 C                    -1.62326  -3.42587  -1.84951
 C                    -0.37368  -3.25948  -1.26037
 C                     0.37978  -1.96746  -1.32932
 C                     1.46019  -1.82571  -2.22004
 C                     0.01118  -0.88568  -0.50997
 C                     2.16463  -0.61855  -2.28457
 H                     1.73975  -2.64954  -2.87109
 C                     0.72216   0.31784  -0.57508
 H                    -0.82992  -0.98165   0.16912
 C                     1.7993    0.45263  -1.45965
 H                     2.99072  -0.51293  -2.97935
 H                     0.43262   1.14814   0.05952
 C                    -2.2995   -2.30657  -2.56623
 C                    -1.75896  -1.7744   -3.75163
 C                    -3.49556  -1.76551  -2.05154
 C                    -2.40179  -0.7203   -4.40666
 H                    -0.84124  -2.18277  -4.15986
 C                    -4.12694  -0.70257  -2.70441
 H                    -3.915    -2.15512  -1.1284
 C                    -3.58261  -0.1795   -3.88338
 H                    -1.97839  -0.31897  -5.32083
 H                    -5.036    -0.28062  -2.29001
 C                    -2.29546  -4.71884  -1.77695
 H                    -5.05463  -6.51119  -2.7852
 H                    -3.8559   -8.20251  -1.44685
 C                    -2.24183  -7.0202   -0.95609
 H                    -1.70692  -7.75273  -0.38849
 C                     2.56672  -6.27198   1.5801
 H                     3.48073  -6.15963   1.03524
 H                     2.60636  -5.67833   2.46943
 H                     2.43256  -7.30036   1.84341
 C                    -0.19443  -7.92998   0.55697
 H                    -1.13479  -7.91022   1.0671
 H                    -0.30593  -8.44018  -0.37693
 H                     0.52722  -8.44158   1.15895
```

S	1.32901	-4.50827	0.19429
C	4.0598	2.15744	-2.67541
H	4.47325	3.14071	-2.59084
H	4.81149	1.43305	-2.44064
H	3.71365	2.00089	-3.67569
C	-3.68666	1.84107	-6.20735
H	-3.5457	1.05283	-6.91708
H	-4.35009	2.57444	-6.6159
H	-2.7435	2.2962	-5.98781
O	-4.38647	1.17518	-4.71227
O	2.69738	1.98722	-1.54261

3x

Symbolic Z-matrix:
Charge = 1 Multiplicity = 1

C	-1.61521	-5.92597	-1.26083
C	-3.3551	-5.40001	-2.87161
C	-3.80363	-6.70711	-2.82805
C	-3.15465	-7.6517	-2.04458
N	-0.50137	-5.53126	-0.4838
C	0.05633	-4.30515	-0.7148
C	0.18346	-6.26792	0.52691
C	1.31168	-5.62826	0.94477
C	-1.76154	-3.58461	-2.11224
C	-0.54429	-3.30525	-1.51289
C	0.14948	-1.98223	-1.59177
C	0.82615	-1.61143	-2.76343
C	0.1644	-1.11744	-0.48449
C	1.50299	-0.39385	-2.82629
H	0.82679	-2.27762	-3.62075
C	0.83626	0.10249	-0.55556
H	-0.36153	-1.39232	0.42633
C	1.50732	0.4643	-1.7252
H	2.02594	-0.11652	-3.73655
H	0.83341	0.76927	0.30152
C	-2.61672	-2.42269	-2.56134
C	-2.48729	-1.95203	-3.79852
C	-3.04555	-1.50336	-1.5677
C	-2.89909	-0.65336	-4.23876
H	-2.04692	-2.59564	-4.55262
C	-3.33431	-0.10043	-1.89831
H	-2.75681	-1.67935	-0.53216
C	-3.3367	0.3119	-3.33012
H	-2.83706	-0.30176	-5.26482
H	-3.51662	0.6411	-1.12611
C	-2.25546	-4.944	-2.08129
H	-3.46611	-8.69138	-2.04915
C	-2.04468	-7.26771	-1.28267
H	-1.50154	-8.02929	-0.75042

C	2.28822	-6.0771	1.99411
H	3.23393	-5.53502	1.90949
H	1.89419	-5.89802	3.00203
H	2.50884	-7.14364	1.89681
C	-0.32641	-7.52293	1.17703
H	-1.40595	-7.48367	1.34631
H	-0.09117	-8.43218	0.61241
H	0.15011	-7.62192	2.15458
S	1.51645	-4.07979	0.17302
H	2.03254	1.41329	-1.7782
H	-3.5733	1.32811	-3.63255
H	-4.63469	-6.98175	-3.46946
N	-3.8763	-4.5114	-3.91199
O	-3.08953	-4.60191	-4.91757
O	-4.98906	-3.83945	-3.92736

9. Fluorescence and UV-Visible studies:

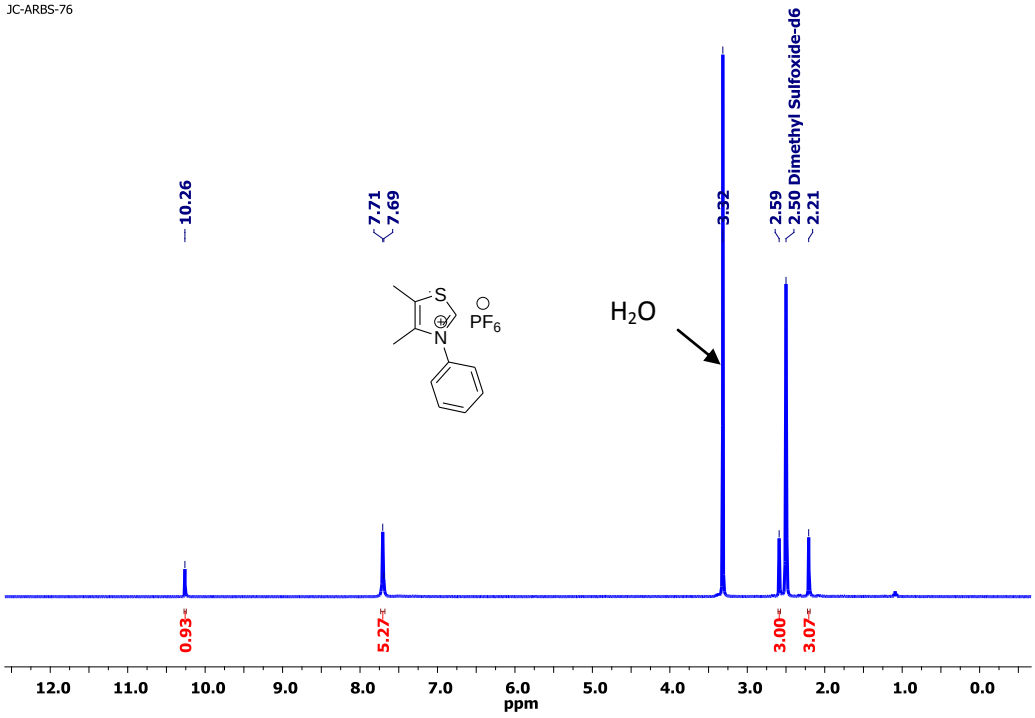
The UV-Visible absorption spectra were obtained with help of Cary 100 UV-Vis spectrophotometer using 1.0 cm quartz cuvettes at room temperature. The samples were prepared in acetonitrile of concentration 15 μM each.

The fluorescence emission studies were performed on a Jobin Yvon Horiba Model Fluorolog-3-21. The sample solutions were made in acetonitrile of concentration 1 μM each. The excitation wavelength was 390 nm.

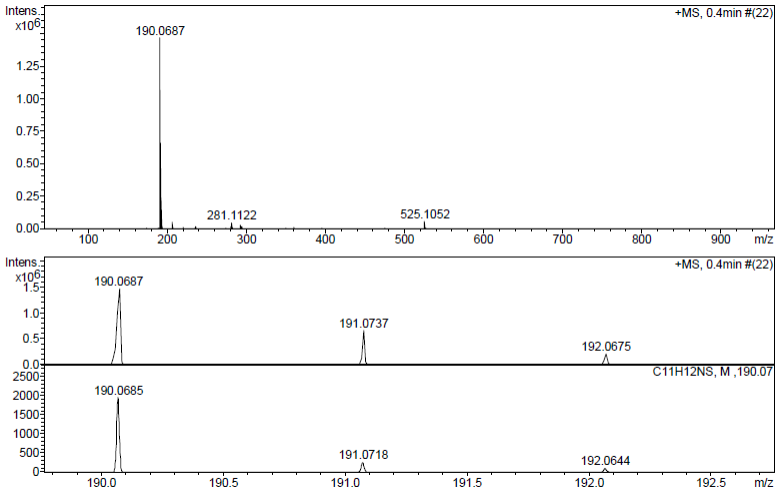
10. Cyclic voltammetric studies:

Cyclic Voltammetry (CV) experiments were performed on three electrode systems, in which Pt disk (1.0 mm diameter)/glassy carbon act as a working electrode: Pt wire as a counter electrode with reference electrode is saturated calomel electrode (SCE). All the samples were analysed in dry acetonitrile after proper degassing with argon gas before starting the experiment. 0.1 M solution of [Bu4N$^+$] PF_6^- in dry acetonitrile was used as supporting electrolyte. Ferrocene (E1/2, Fc/Fc+ = 0.433 V as SCE) was used as an external calibration standard for all the measurements. The scan rate was kept constant at either 30 mV/s for all the experiments. The samples were prepared at a concentration of 1.19 mM. Working electrode: glassy carbon, Reference electrode: SCE, Counter electrode: Pt wire.

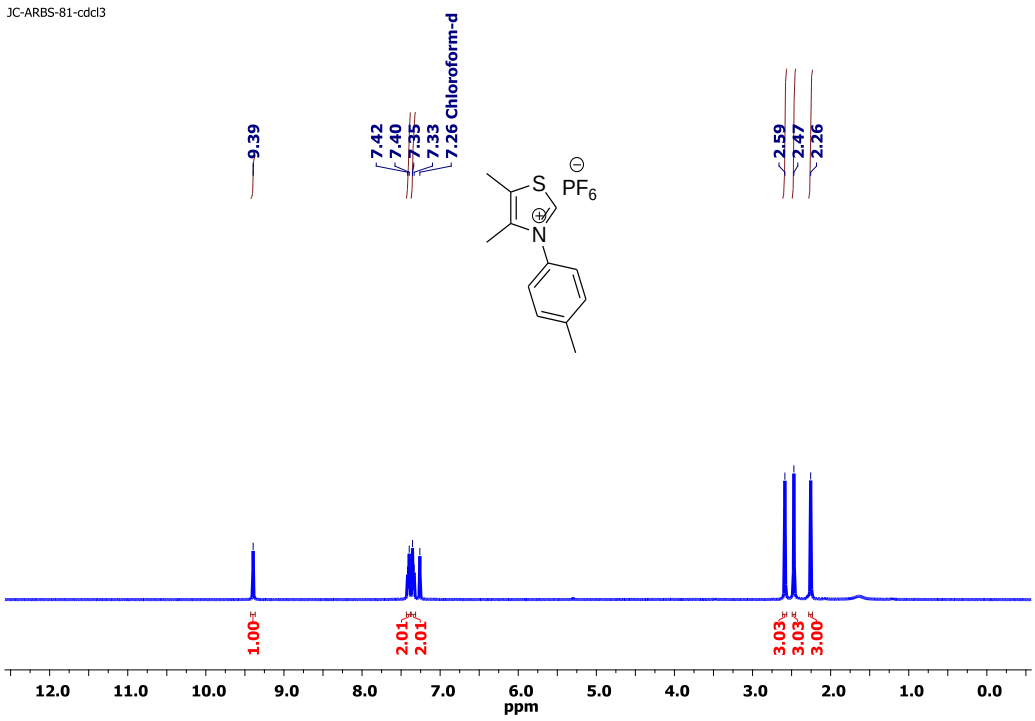
11. Spectral data for compounds 1a-1k:



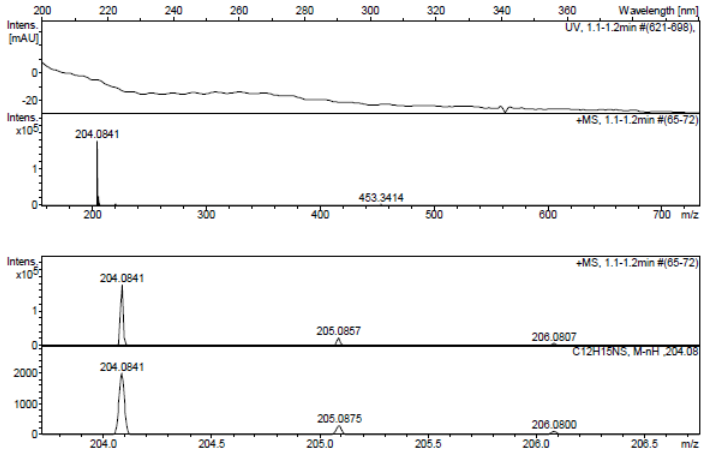
^{1}H NMR spectrum of **1a** (400 MHz, DMSO-d6)



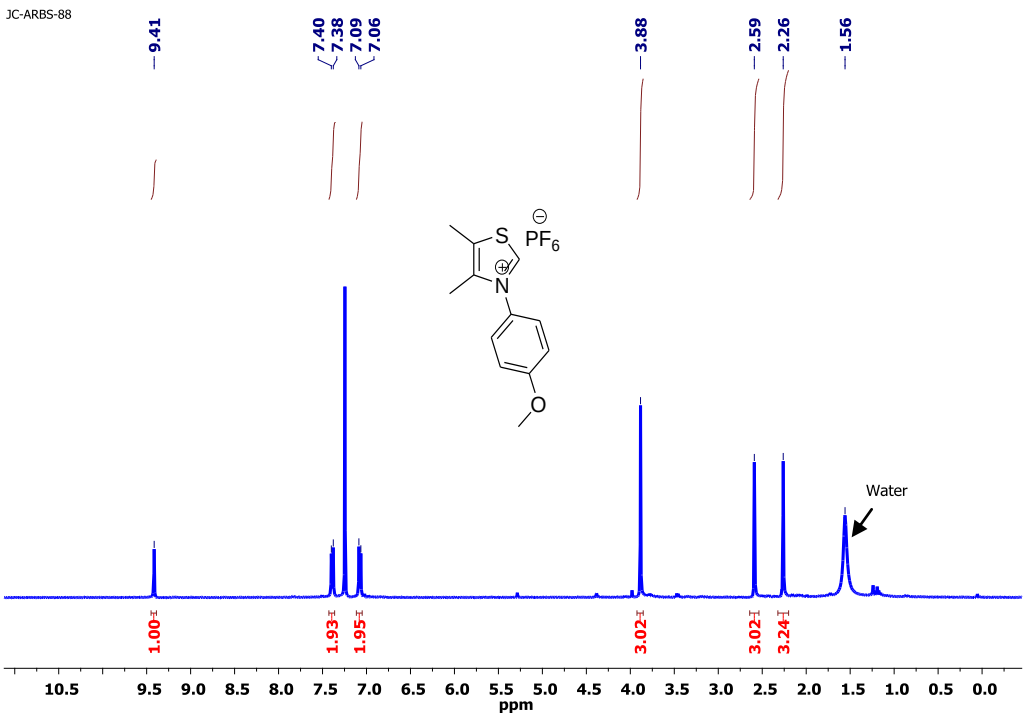
ESI-HRMS (positive ion mode) spectrum of **1a**



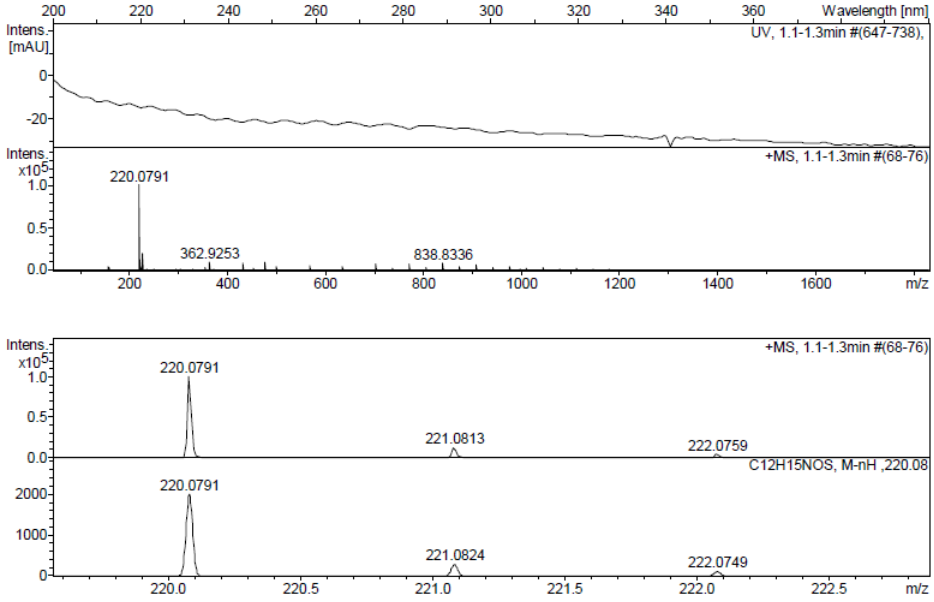
^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$).



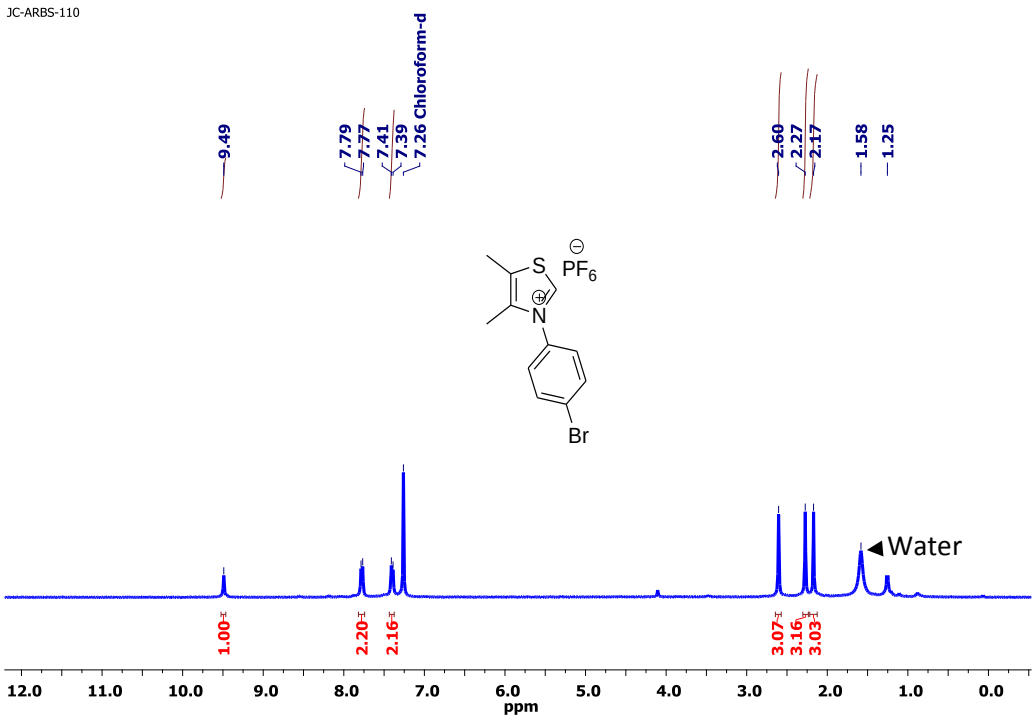
ESI-HRMS (positive ion mode) spectrum of **1b**



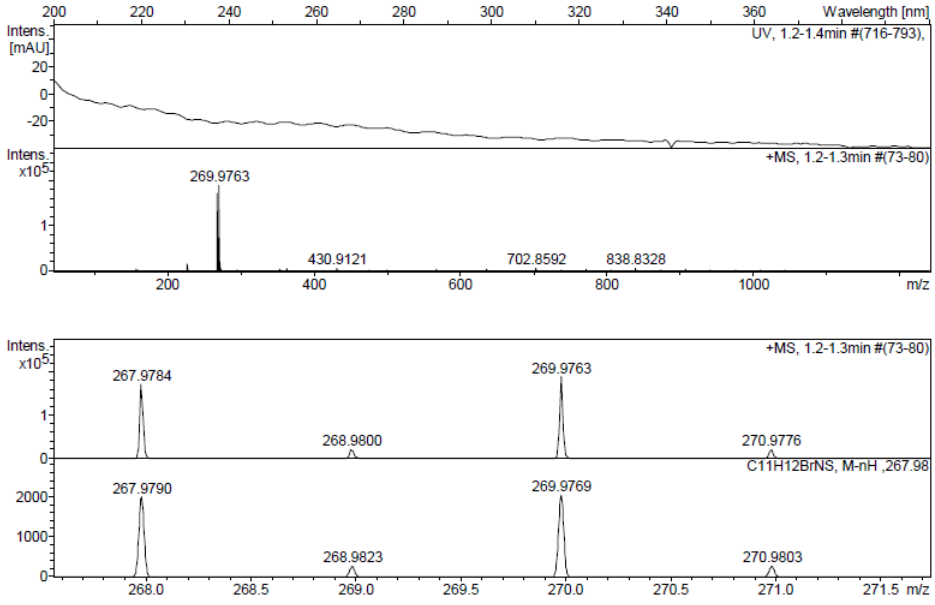
^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$).



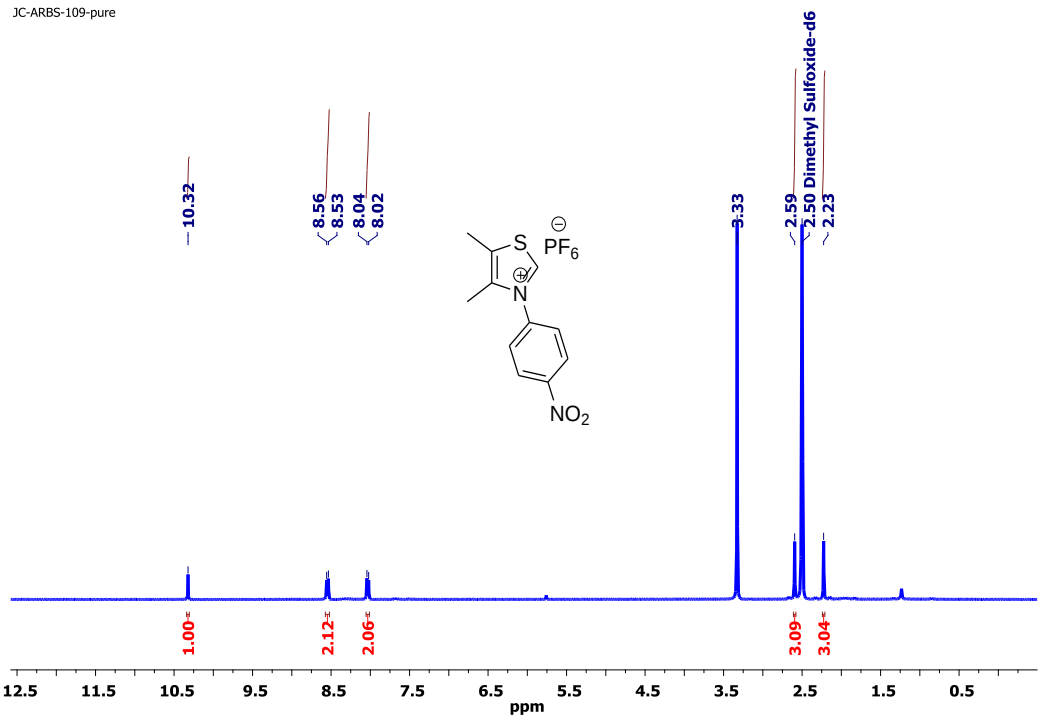
ESI-HRMS (positive ion mode) spectrum of **1c**



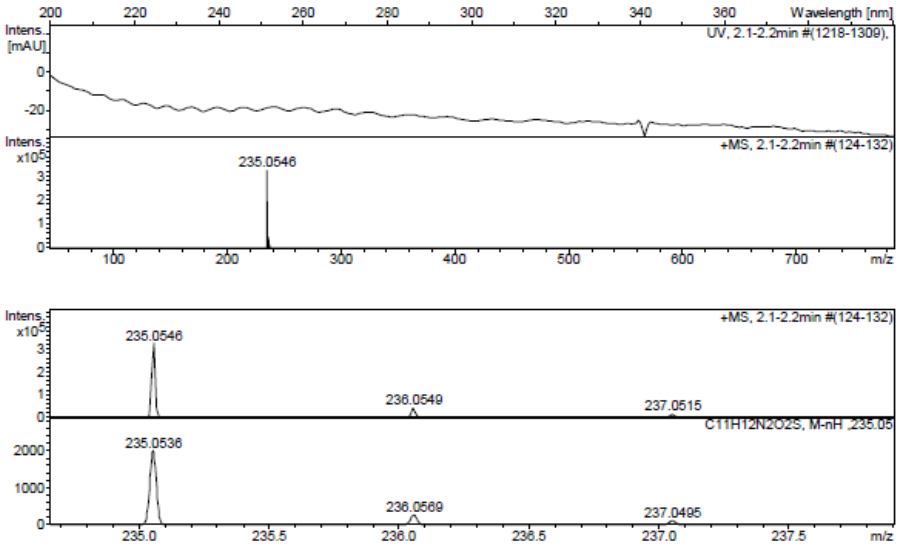
^{1}H NMR spectrum of **1d** (400 MHz, $CDCl_3$)



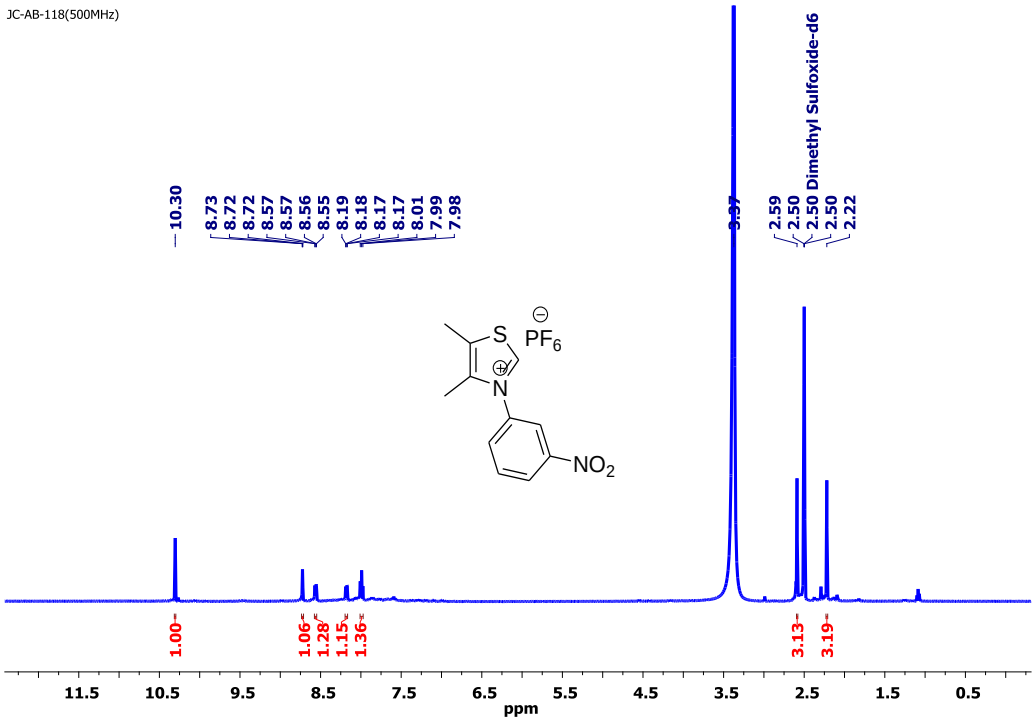
ESI-HRMS (positive ion mode) spectrum of **1d**.



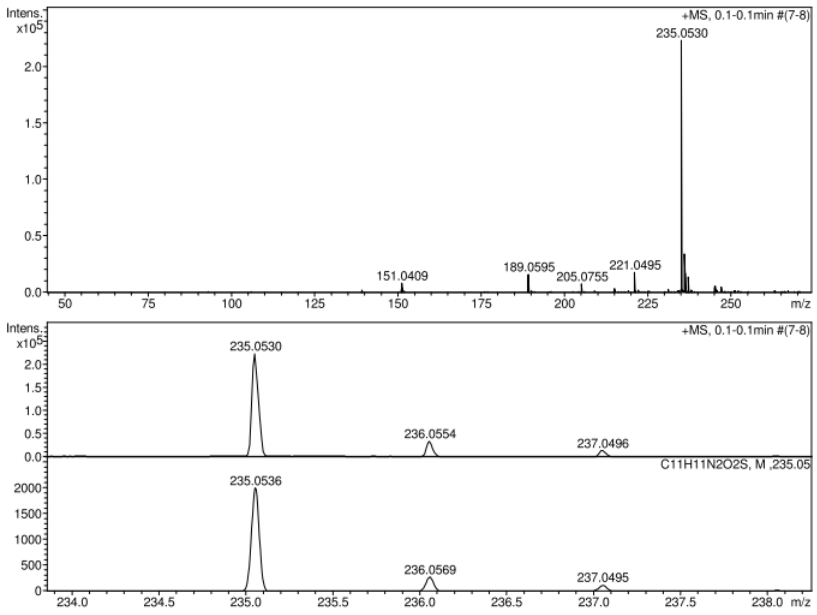
^{1}H NMR spectrum of **1e** (400 MHz, $CDCl_3$)



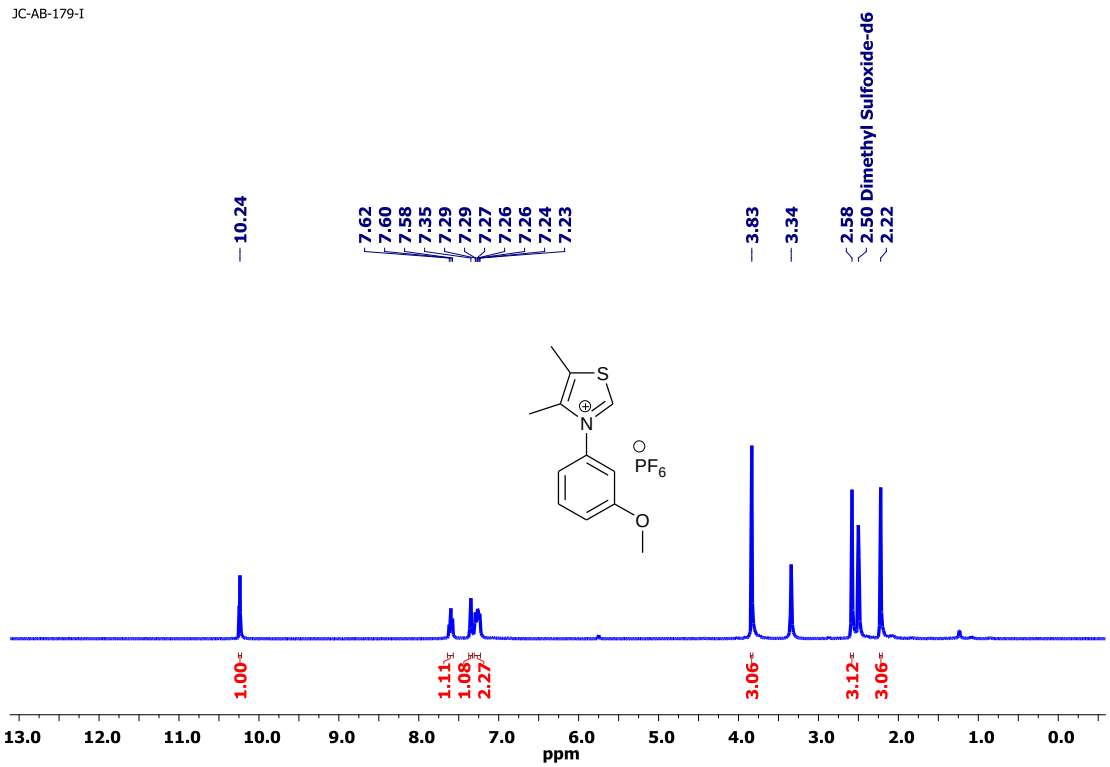
ESI-HRMS (positive ion mode) spectrum of **1e**.



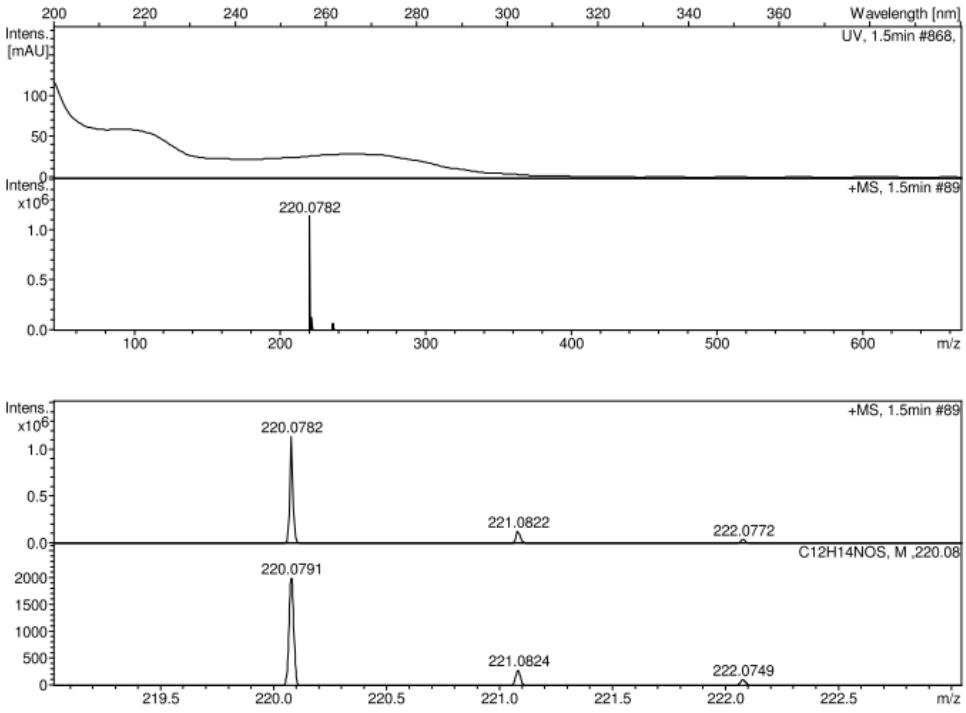
^{1}H NMR spectrum of **1f** (500 MHz, dmso-d6)



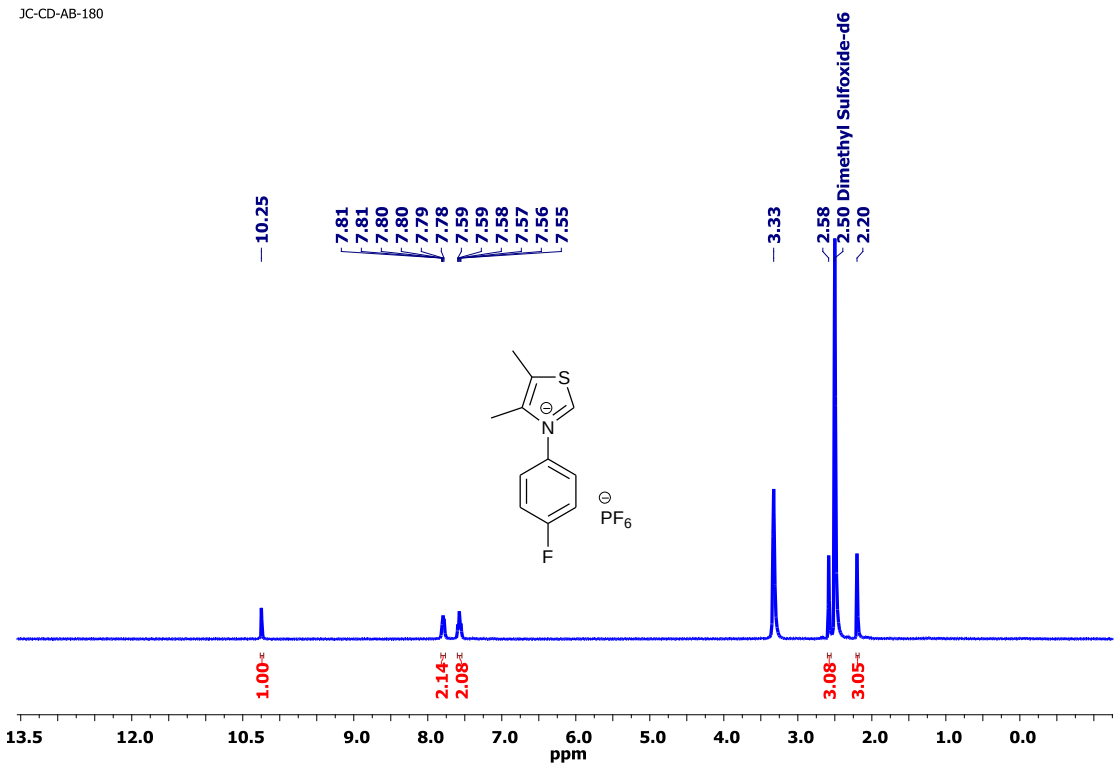
ESI-HRMS (positive ion mode) spectrum of **1f**



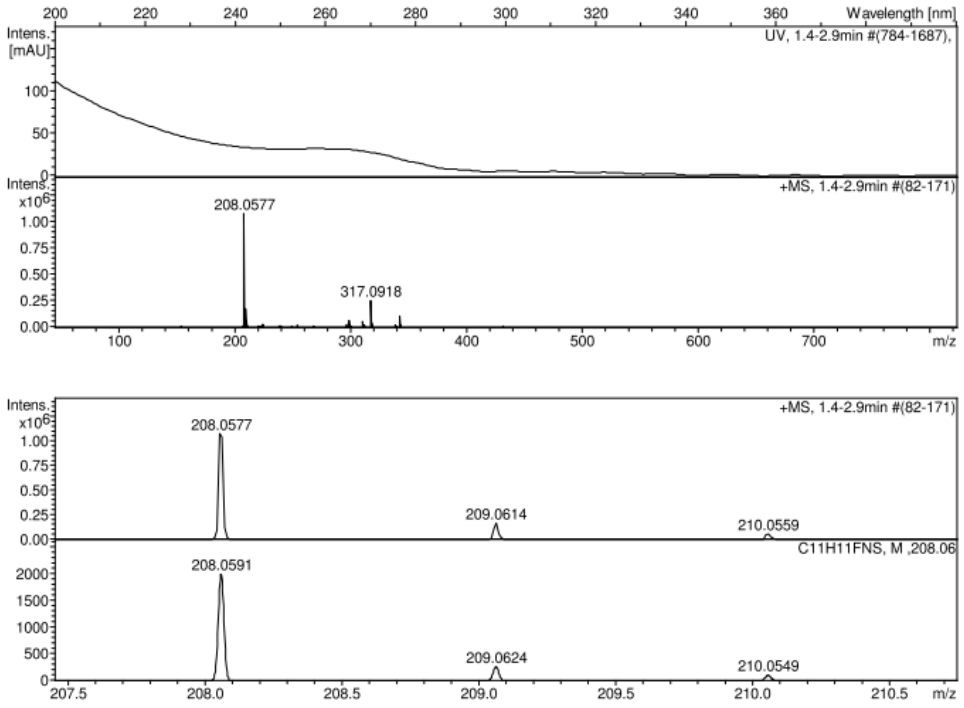
^{1}H NMR spectrum of **1g** (400 MHz, dmso-d6)



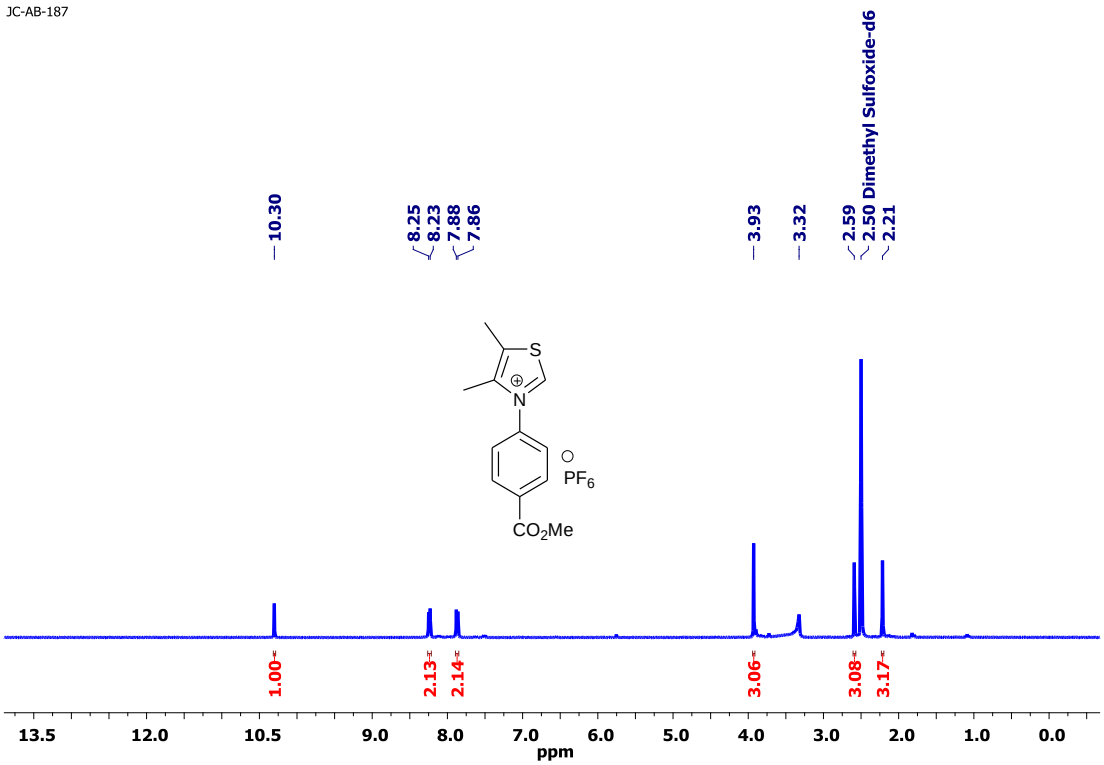
ESI-HRMS (positive ion mode) spectrum of **1g**



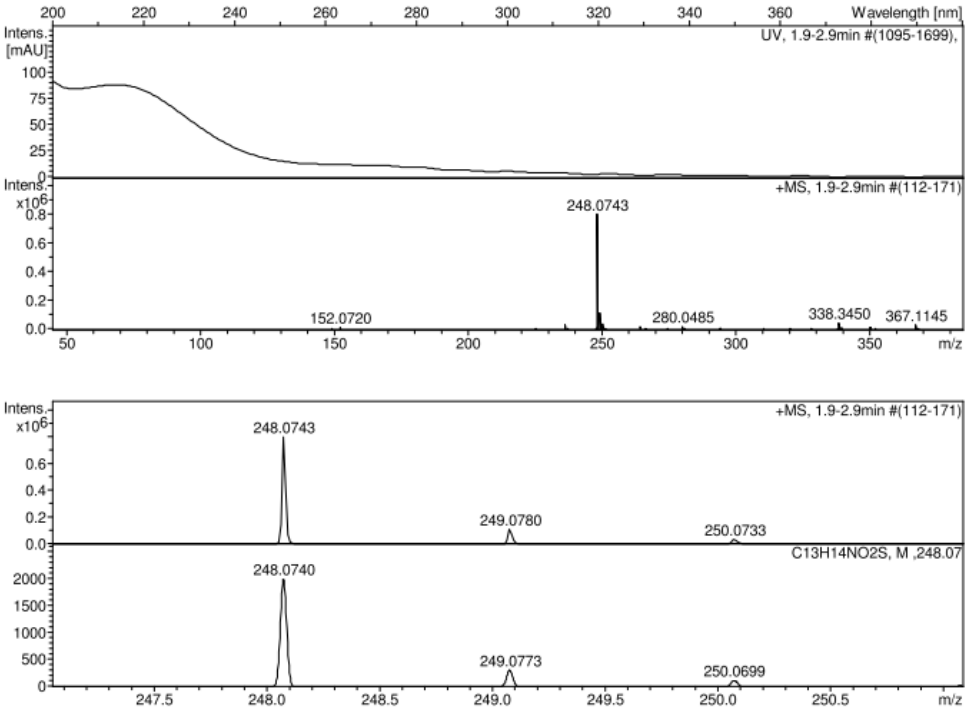
^{1}H NMR spectrum of **1h** (400 MHz, dmso-d6)



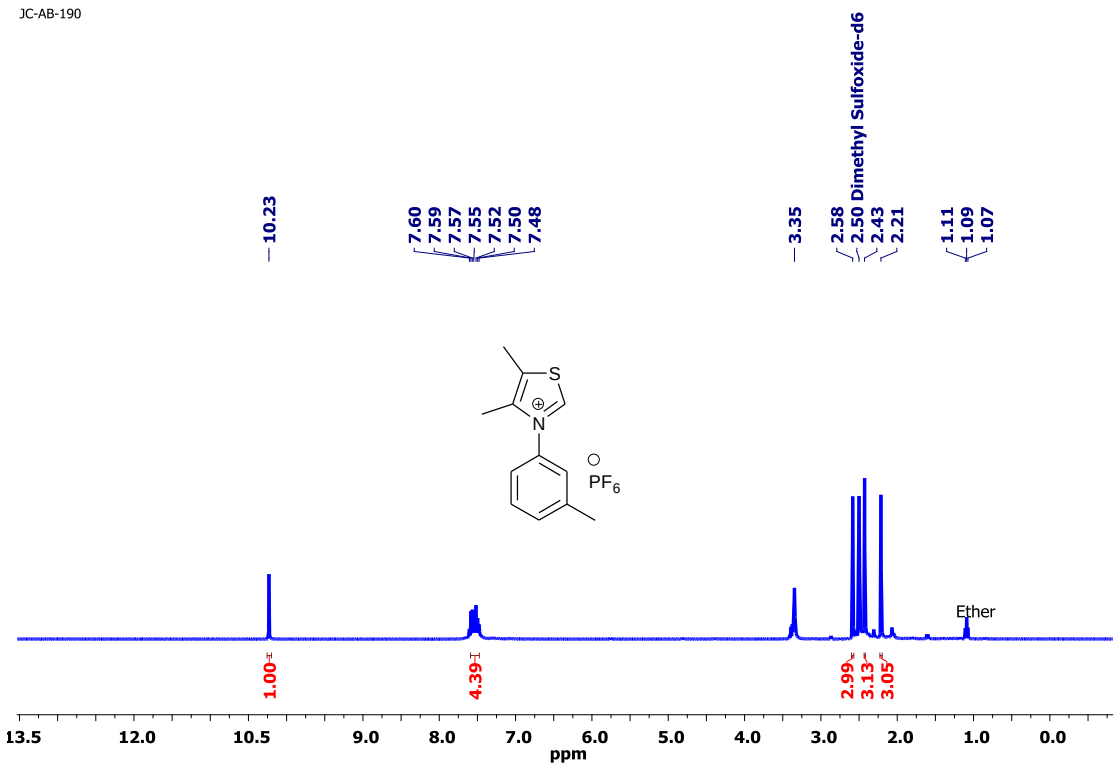
ESI-HRMS (positive ion mode) spectrum of **1h**



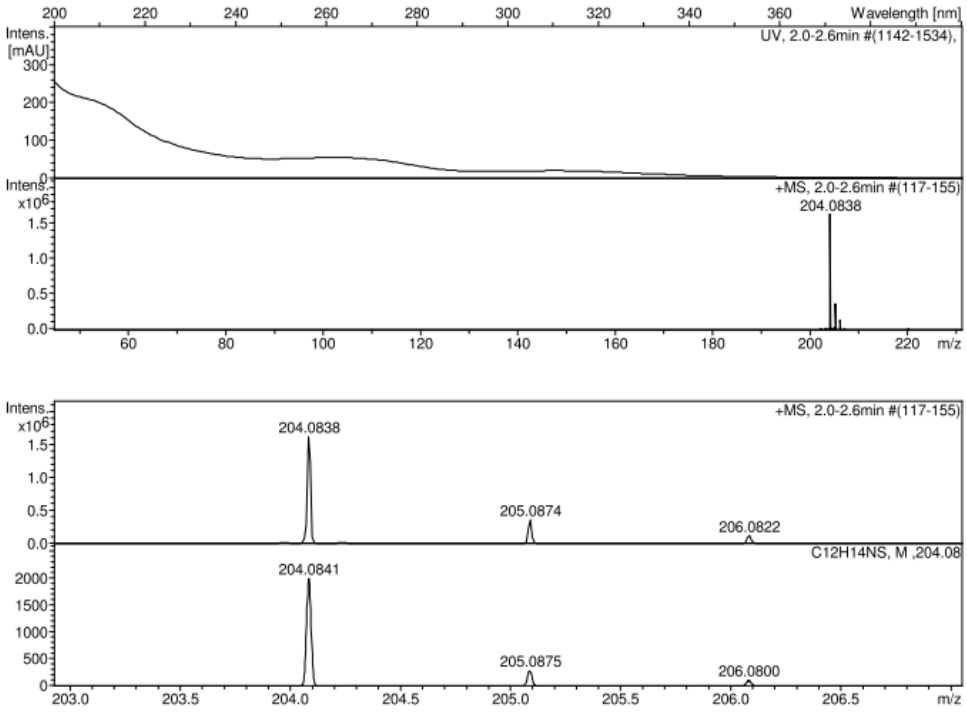
^{1}H NMR spectrum of **1i** (400 MHz, dmso-d6)



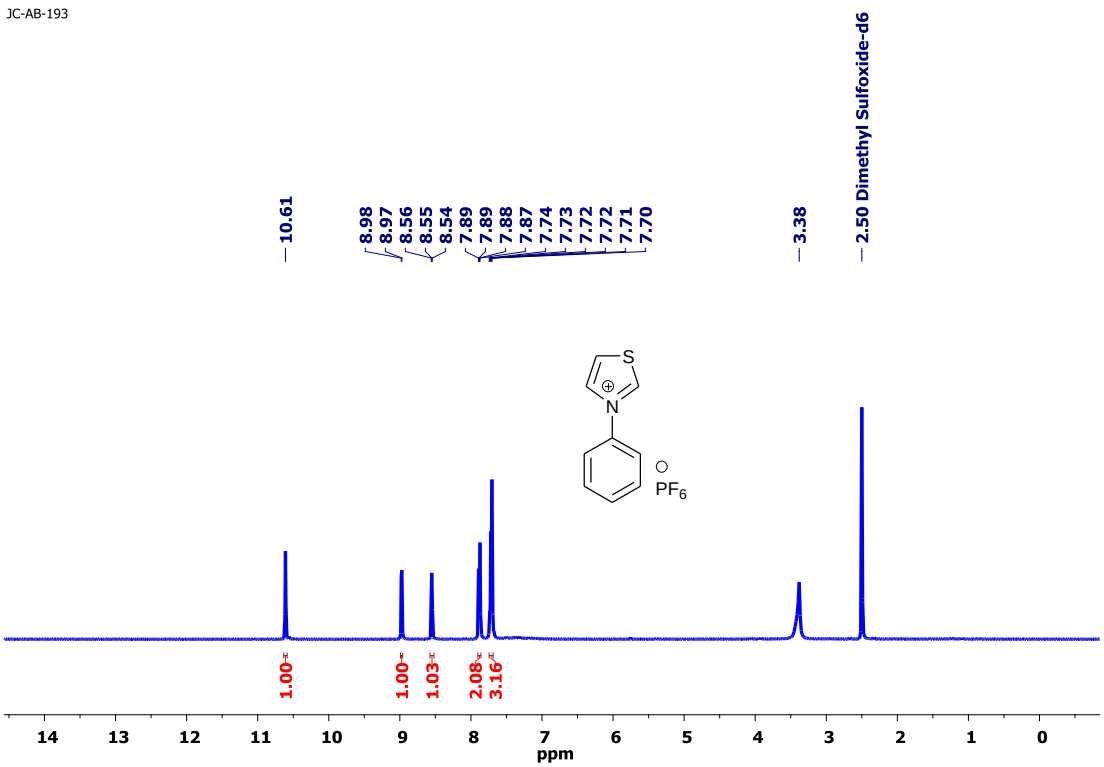
ESI-HRMS (positive ion mode) spectrum of **1i**



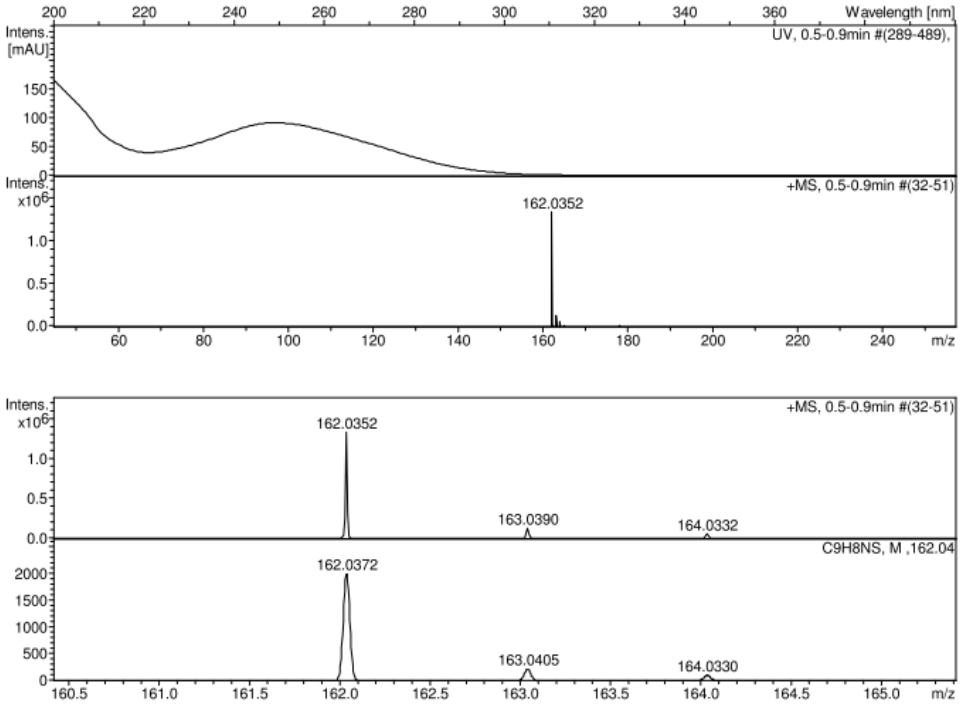
^{1}H NMR spectrum of **1j** (400 MHz, dmso-d6)



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

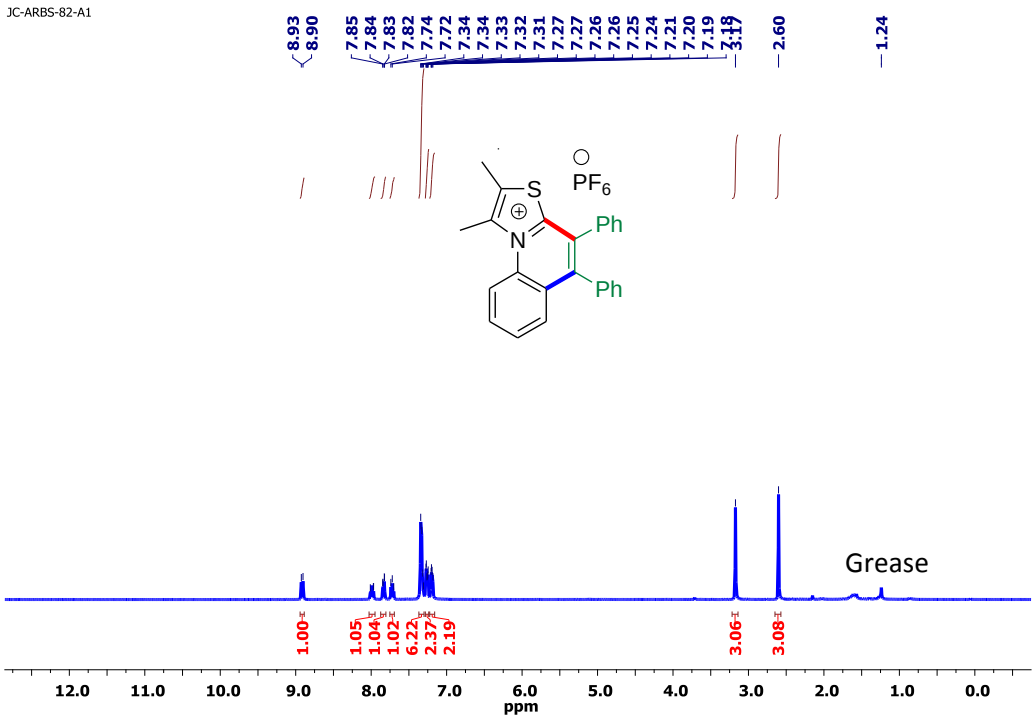


^{1}H NMR spectrum of **1k** (400 MHz, dmso-d6)

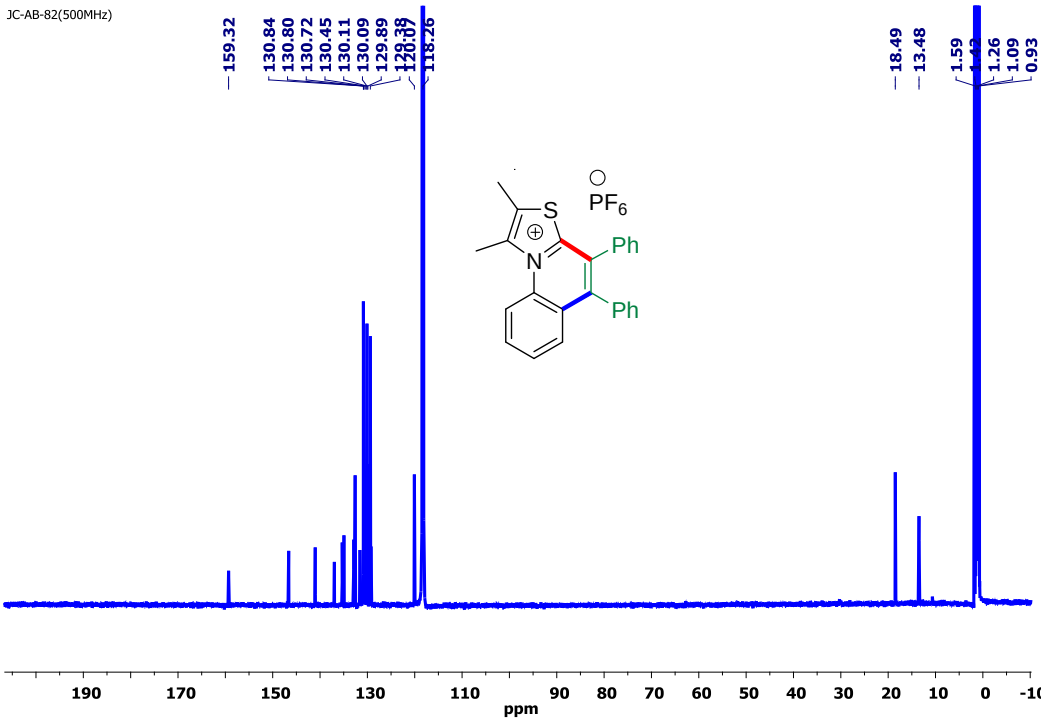


ESI-HRMS (positive ion mode) spectrum of **1k**

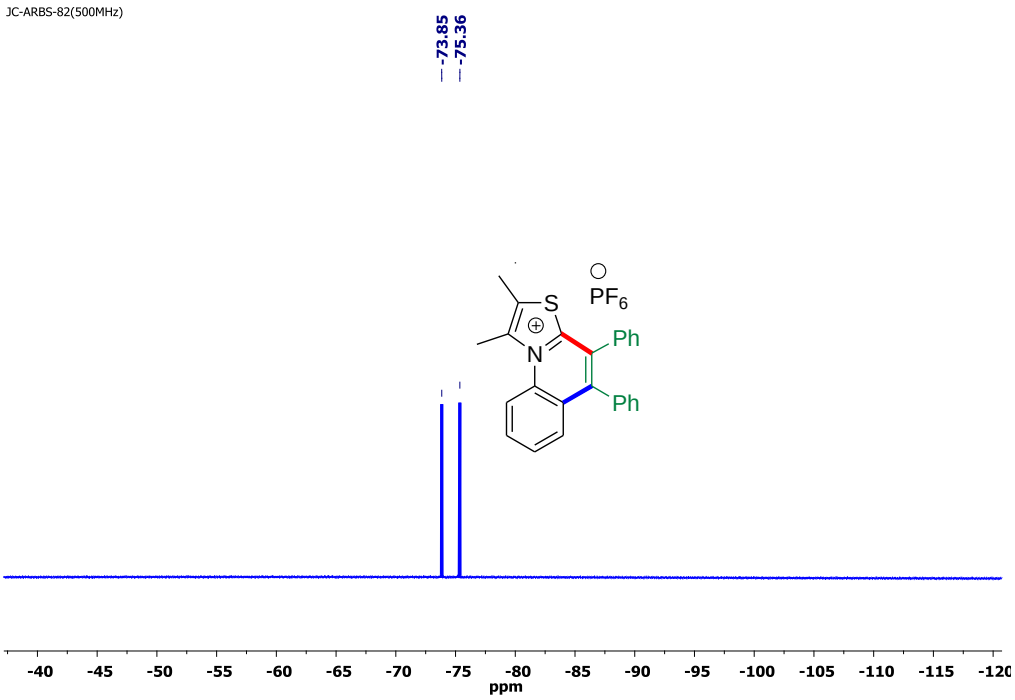
12. Spectral data for compounds 3a-3ac



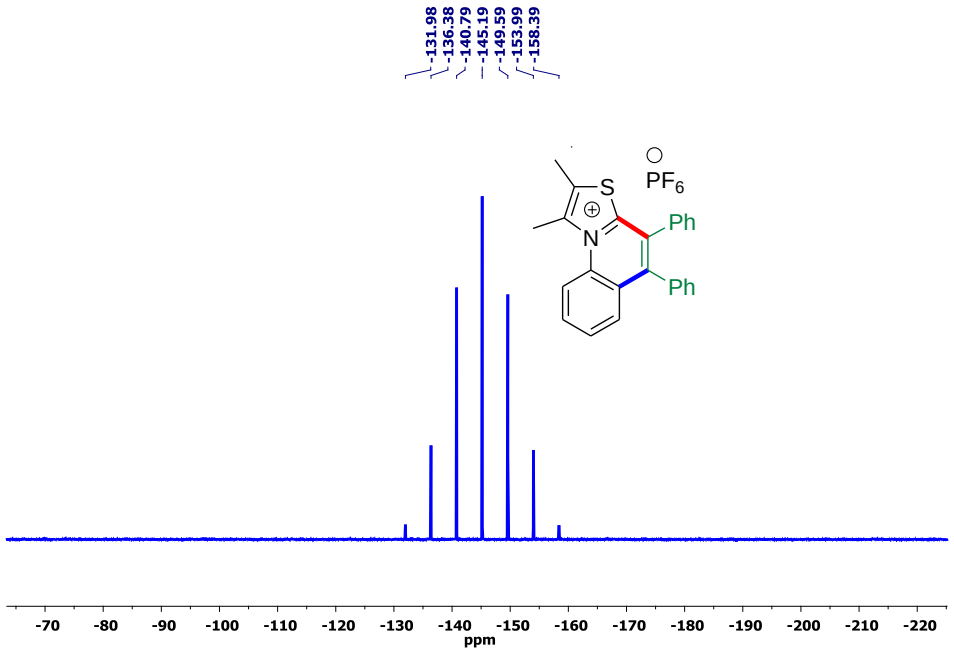
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



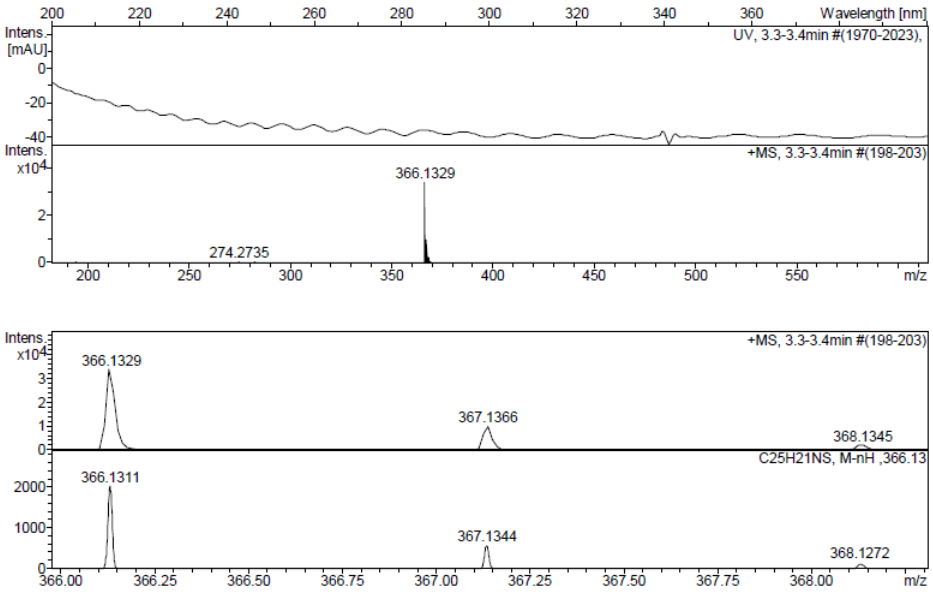
^{13}C{^{1}H} NMR spectrum of **3a** (126 MHz, CD_3CN).



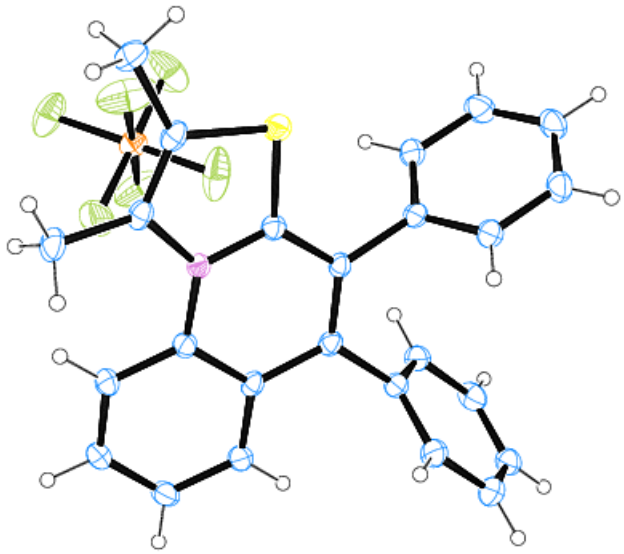
^{19}F NMR spectrum of **3a** (376 MHz, $CDCl_3$).



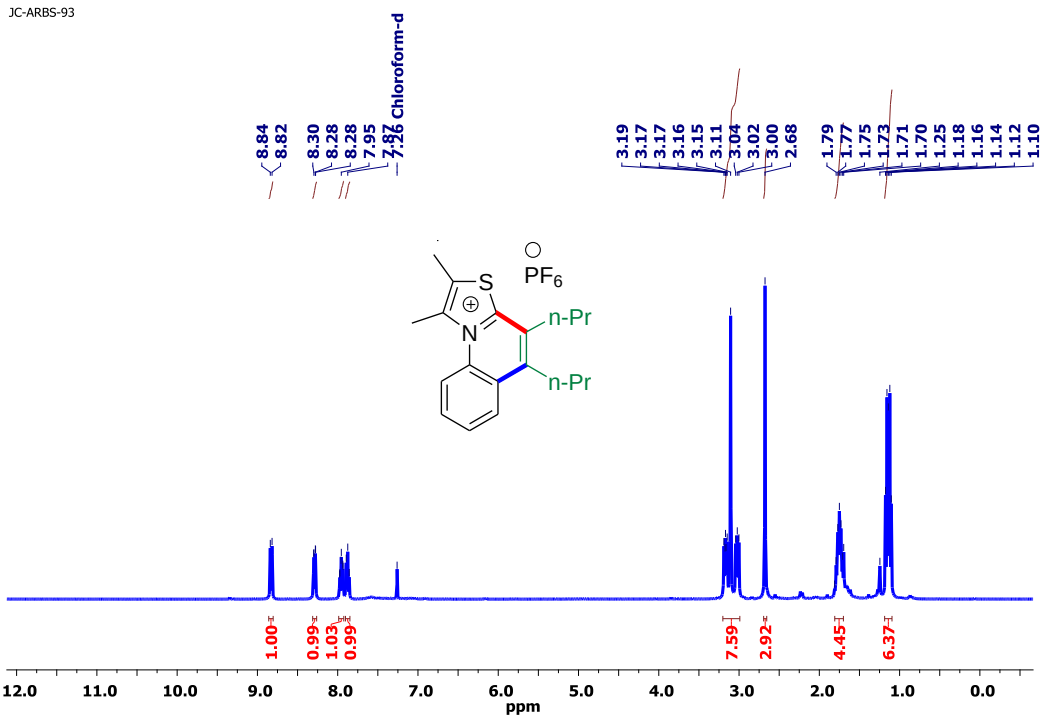
^{31}P NMR spectrum of **3a** (162 MHz, $CDCl_3$).



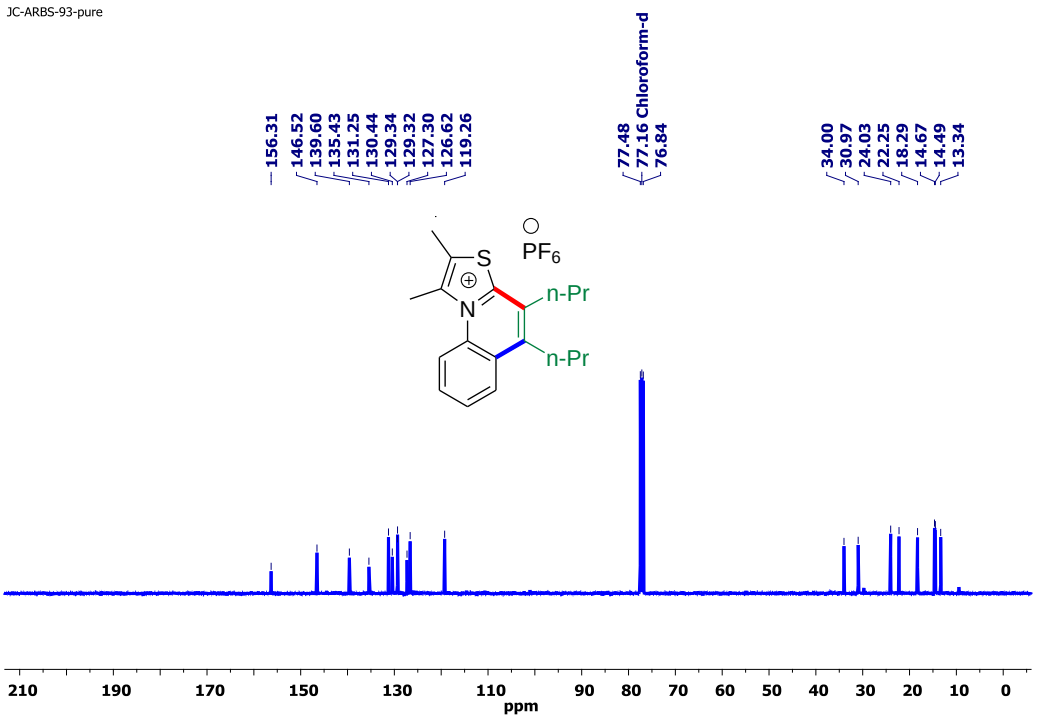
ESI-HRMS (positive ion mode) spectrum of **3a**



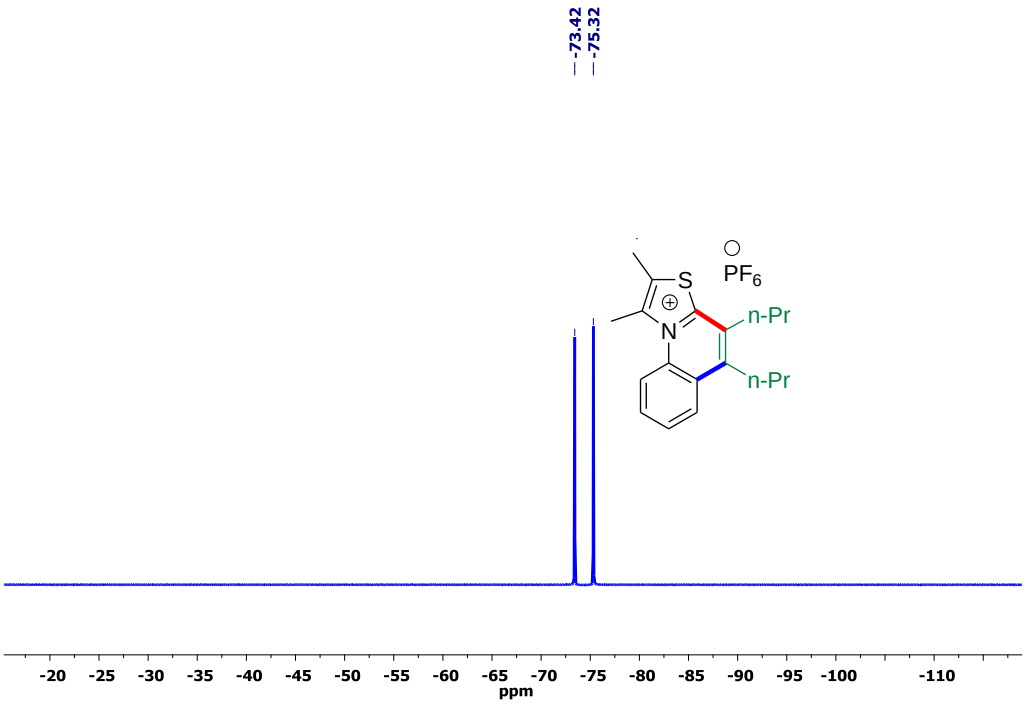
Single crystal XRD structure of **3a (30% probability ellipsoid)**



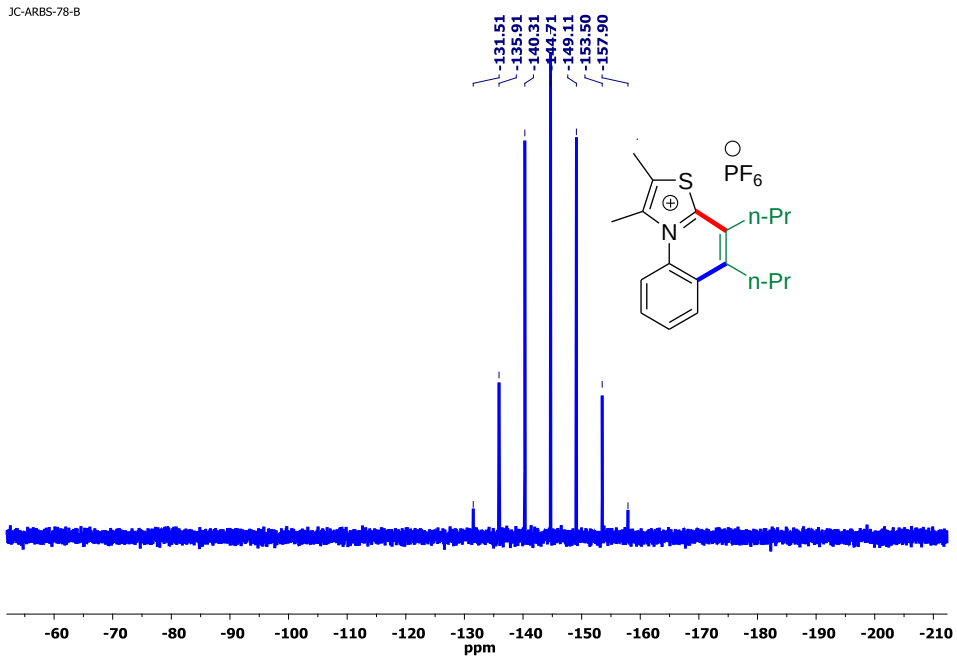
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$).



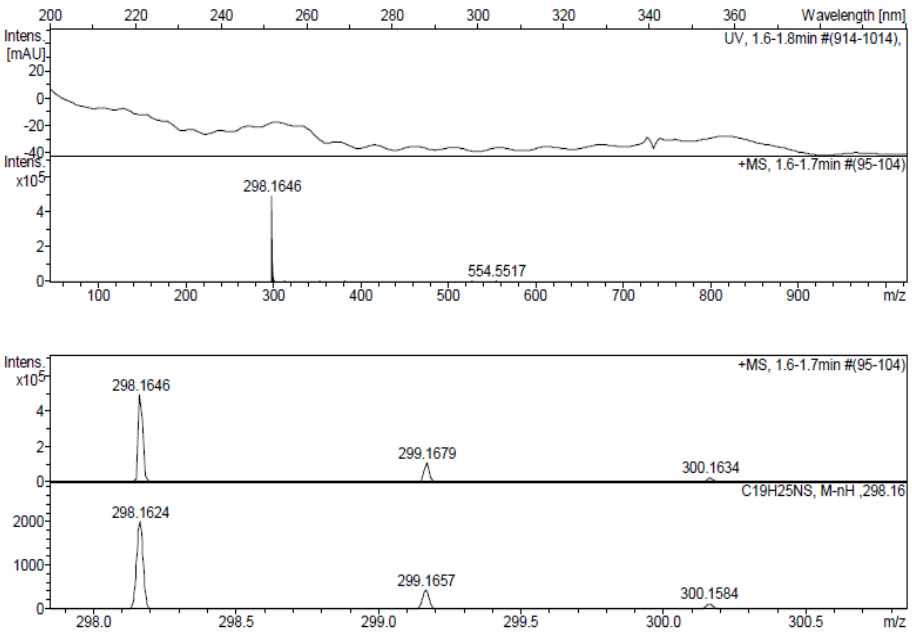
^{13}C{^{1}H} NMR spectrum of **3b** (101 MHz, $CDCl_3$)



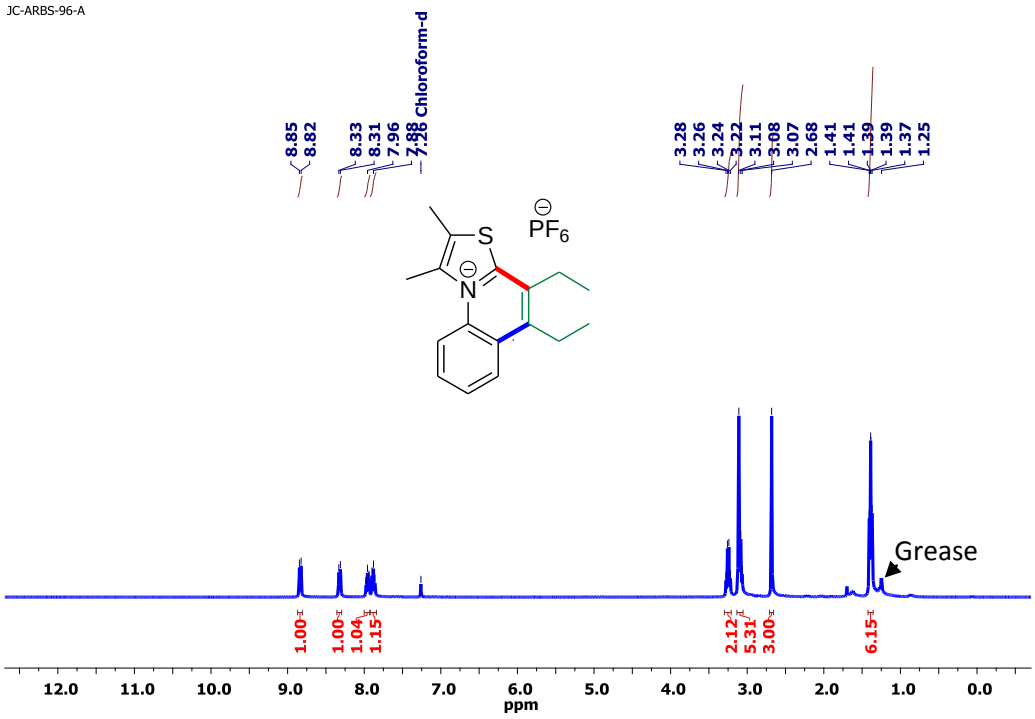
^{19}F NMR spectrum of **3b** (376 MHz, $CDCl_3$).



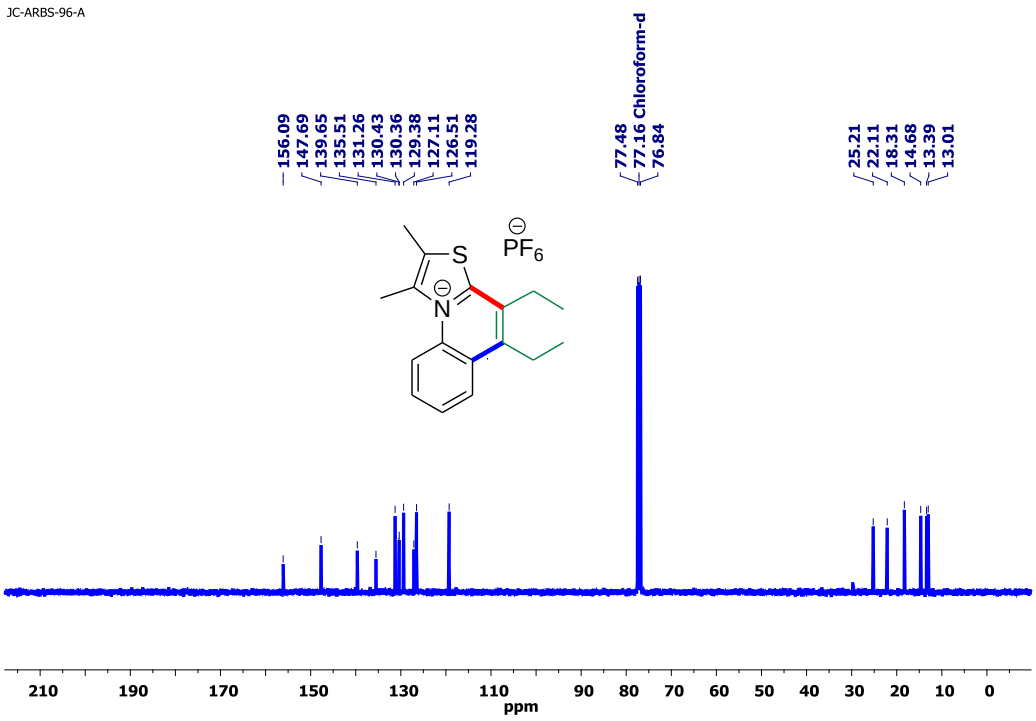
^{31}P NMR spectrum of **3b** (162 MHz, $CDCl_3$).



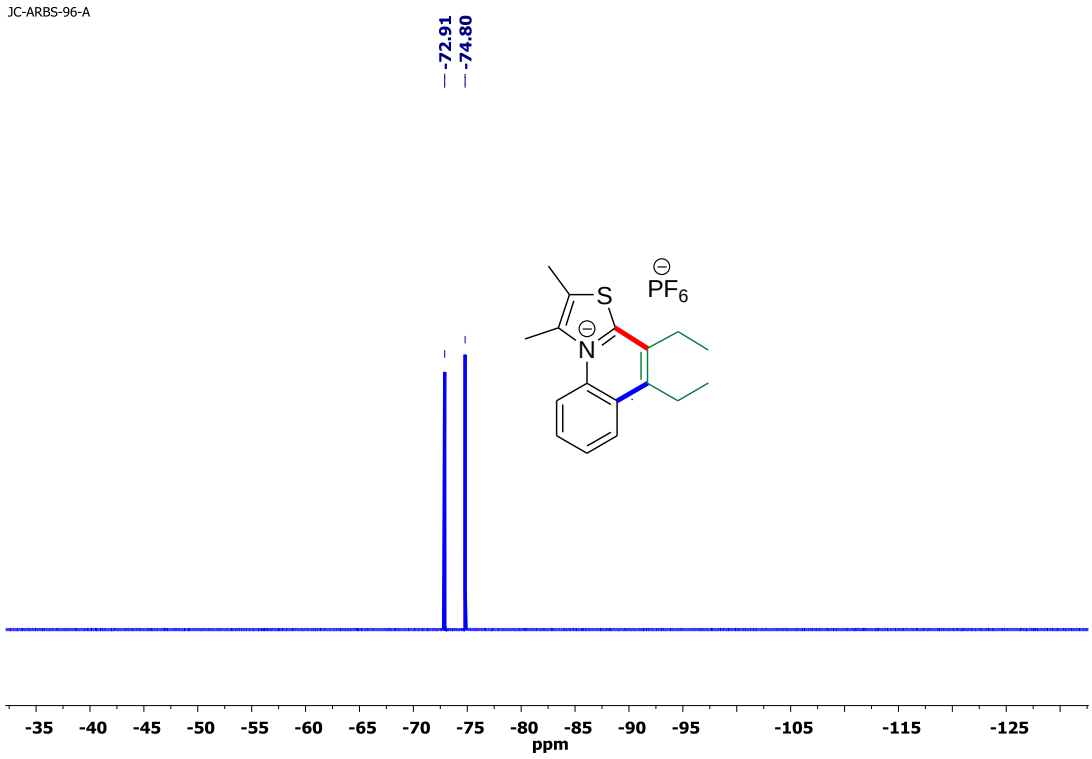
ESI-HRMS (positive ion mode) spectrum of **3b**



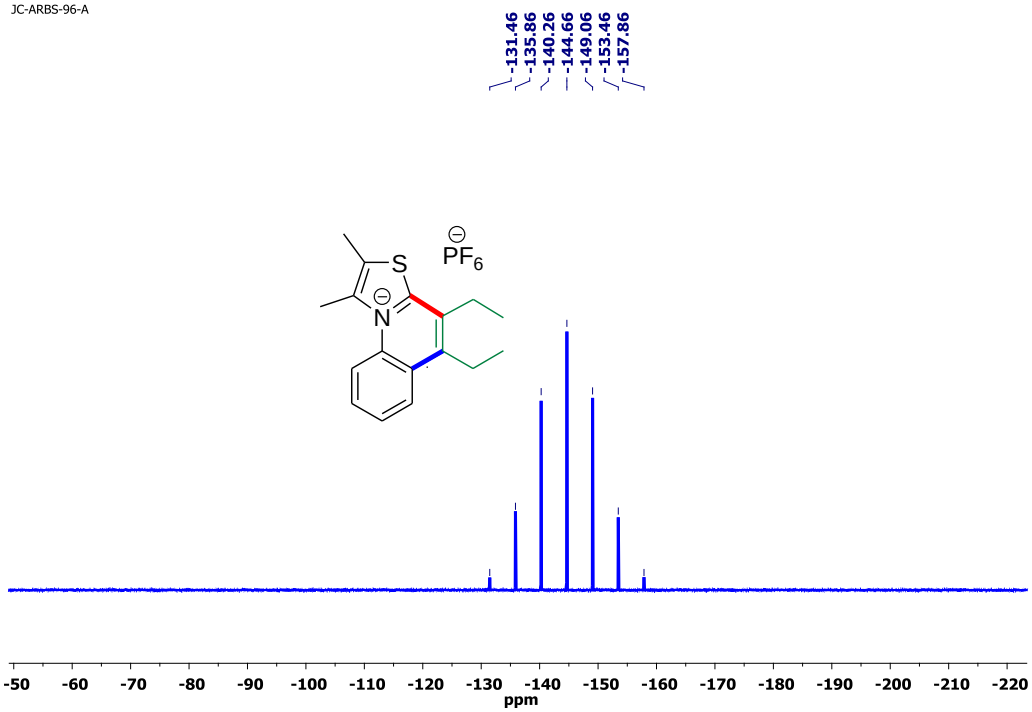
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$).



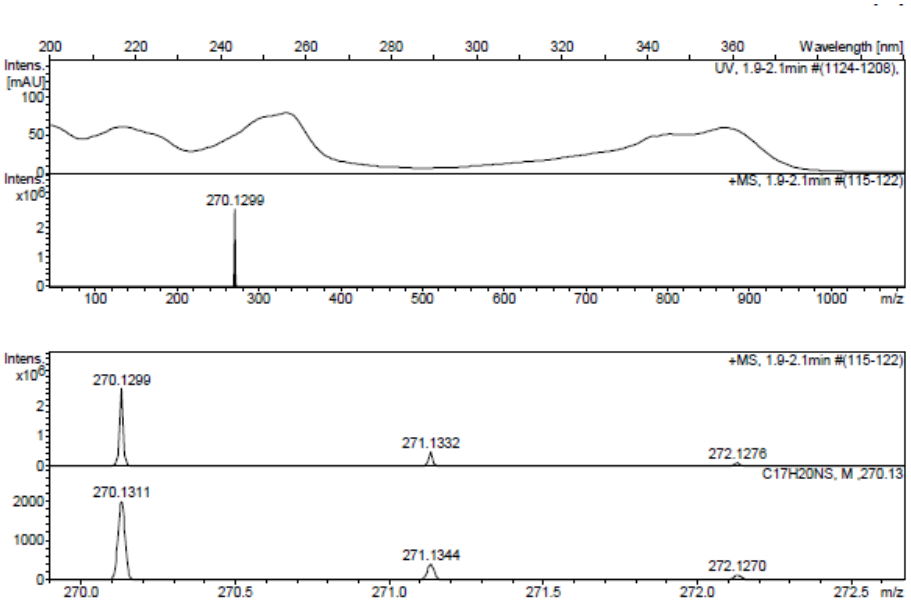
$^{13}C\{^{1}H\}$ NMR spectrum of **3c** (101 MHz, $CDCl_3$)



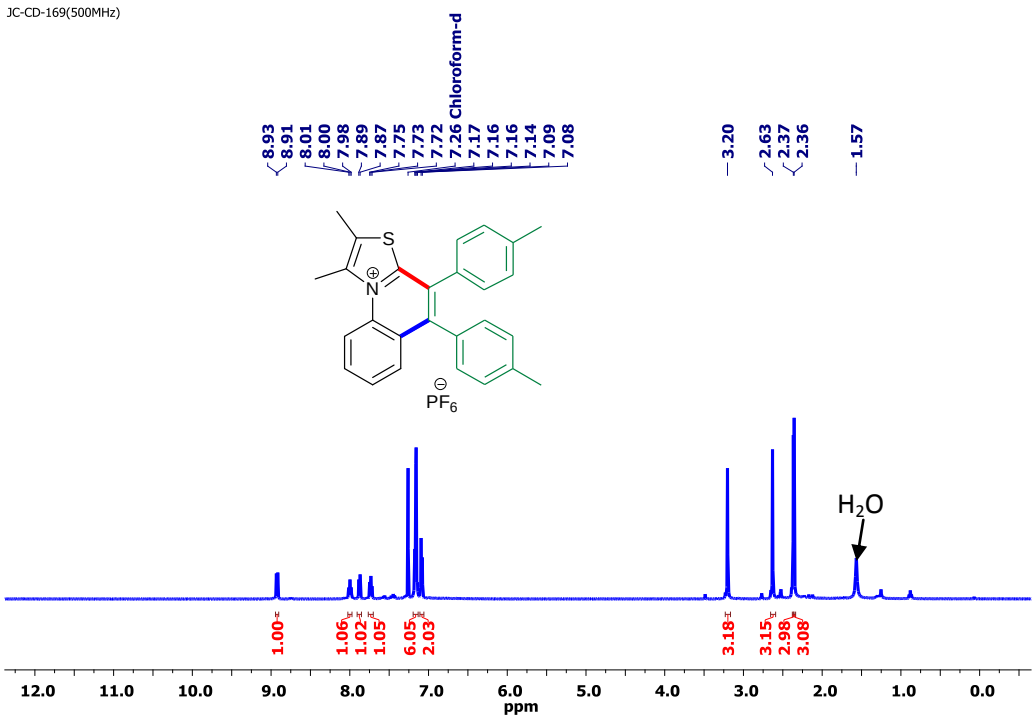
^{19} F NMR spectrum of **3c** (376 MHz, $CDCl_3$).



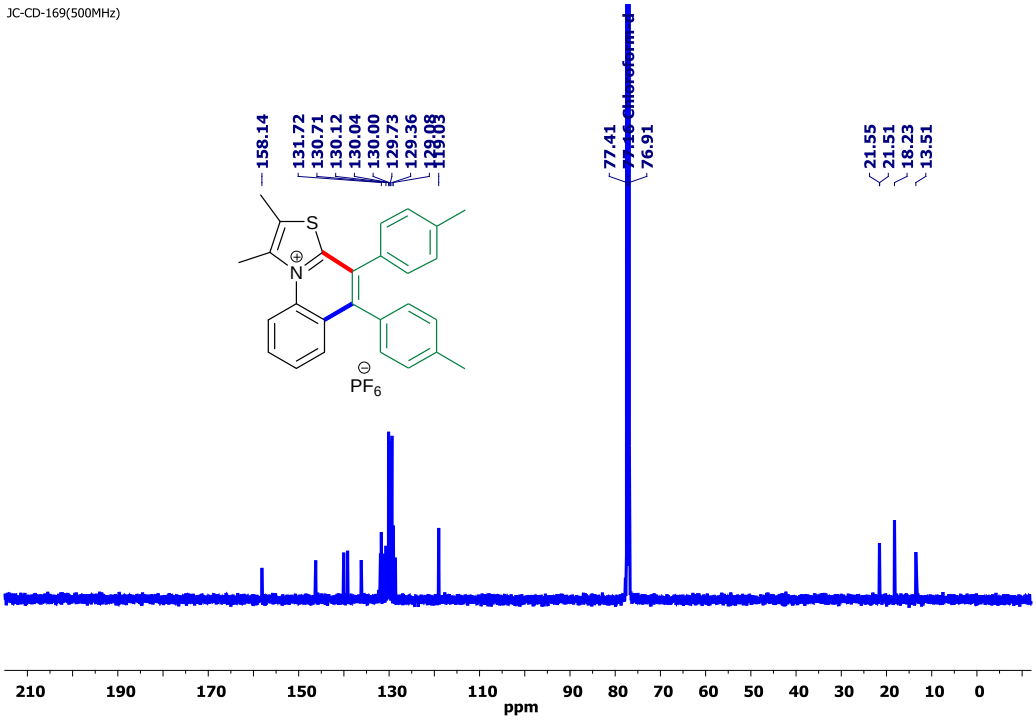
^{31}P NMR spectrum of **3c** (162 MHz, $CDCl_3$).



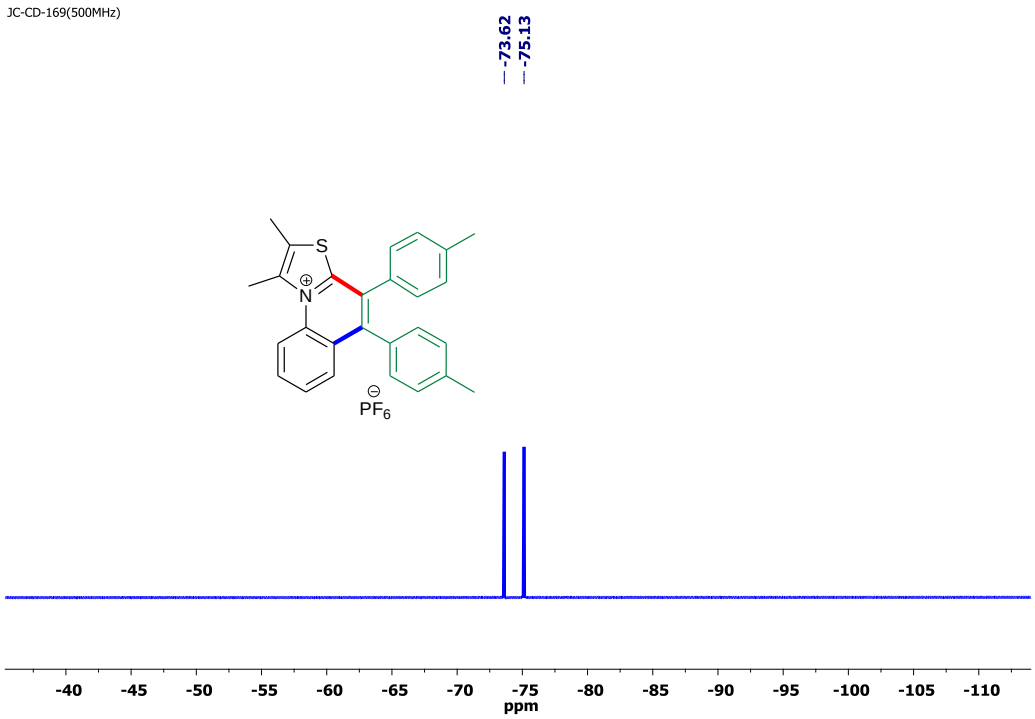
ESI-HRMS (positive ion mode) spectrum of **3c**



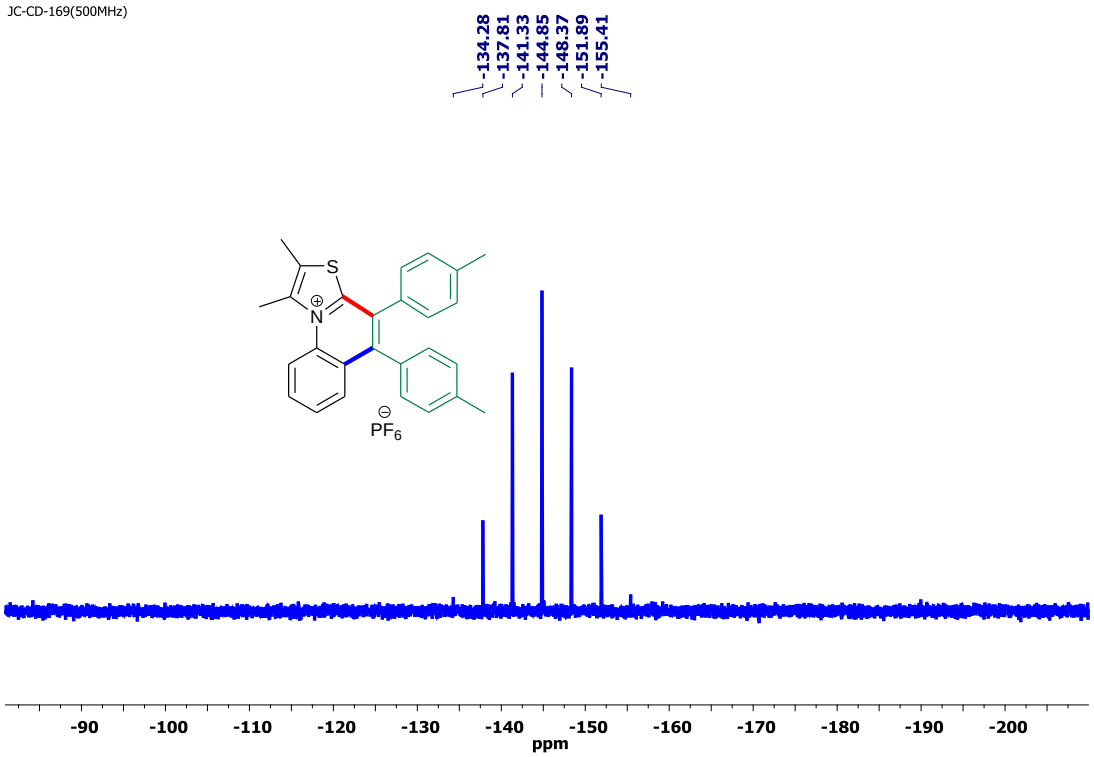
^{1}H NMR spectrum of **3d** (500 MHz, $CDCl_3$).



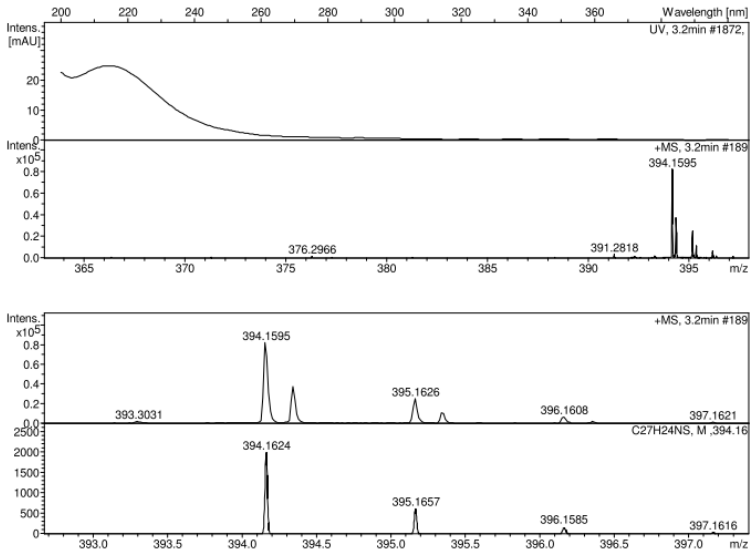
^{13}C{^{1}H} NMR spectrum of **3d** (125 MHz, CD_3CN).



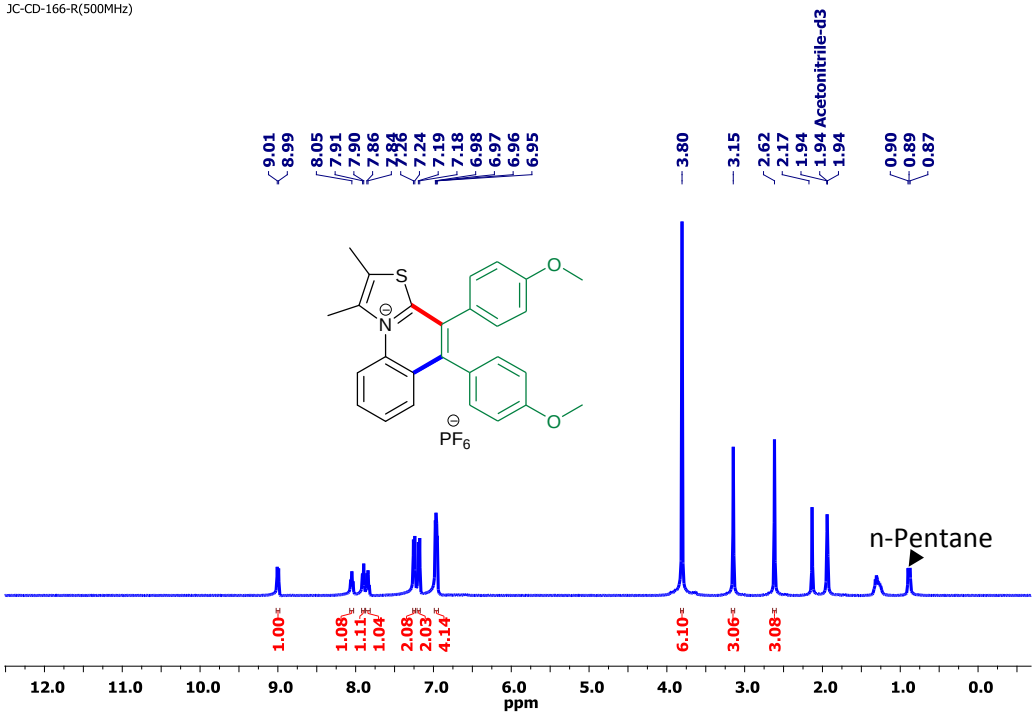
^{19}F NMR spectrum of **3d** (471 MHz, $CDCl_3$)



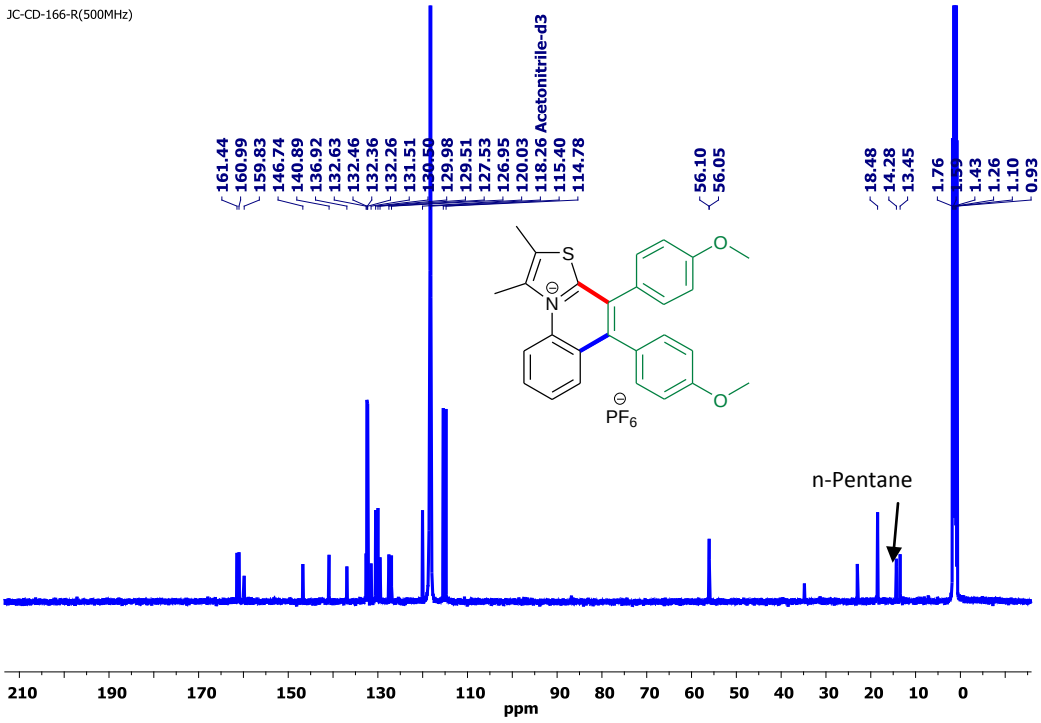
^{31}P NMR spectrum of **3d** (202 MHz, $CDCl_3$)



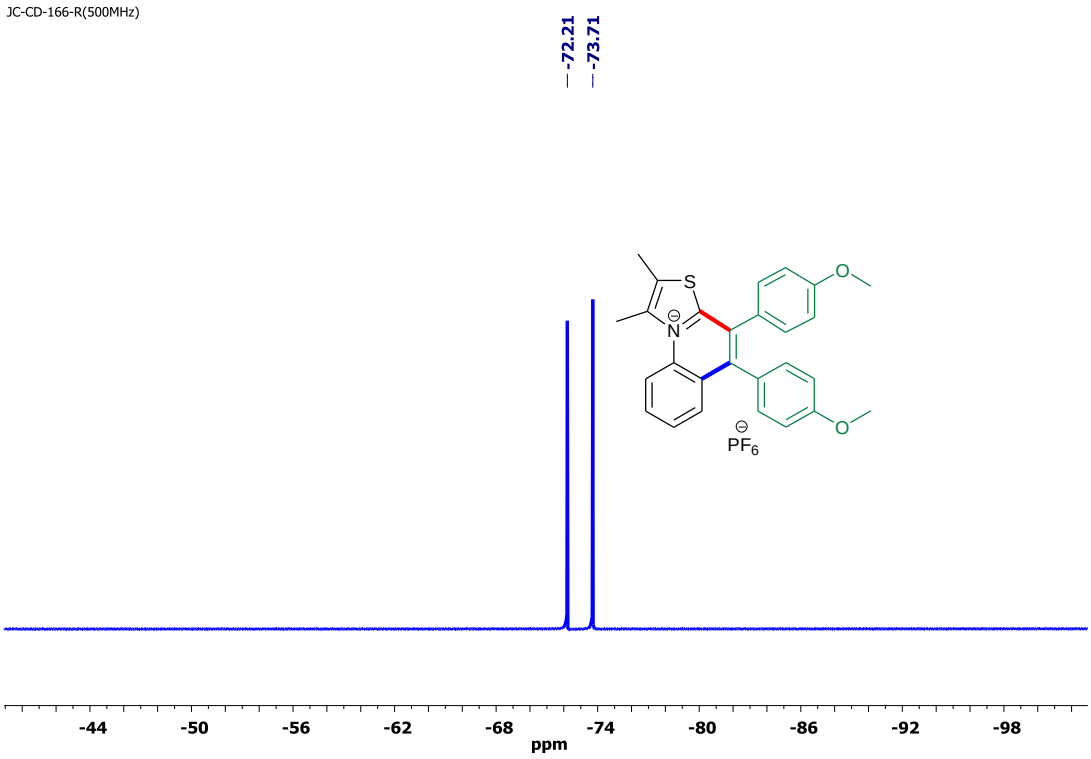
ESI-HRMS (positive ion mode) spectrum of **3d**



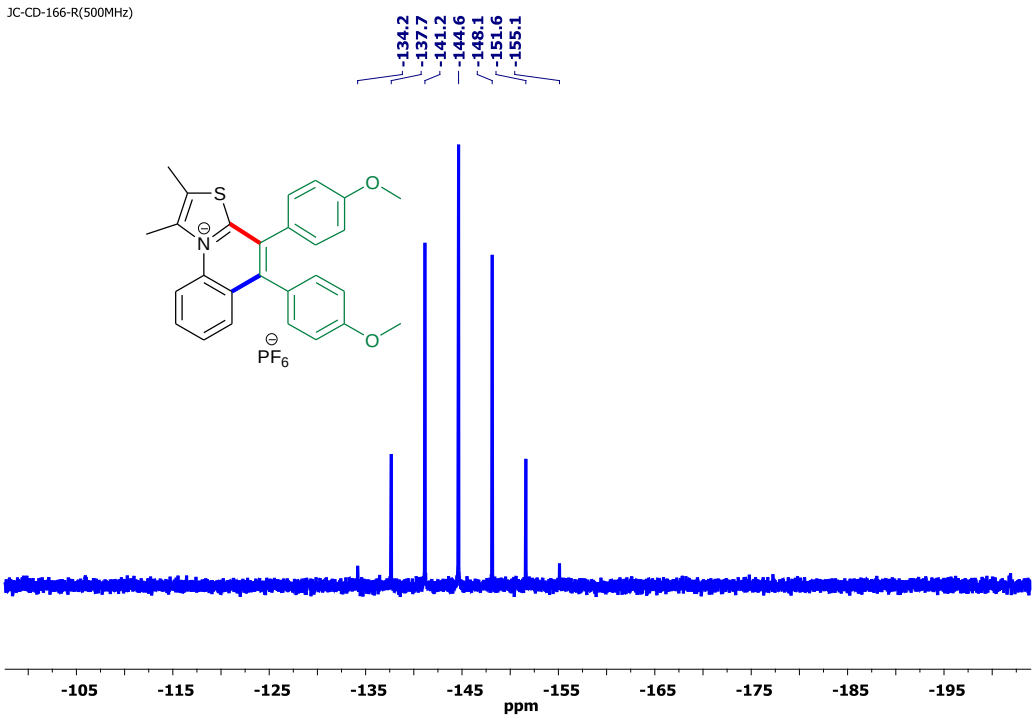
^{1}H NMR spectrum of **3e** (500 MHz, CD_3CN).



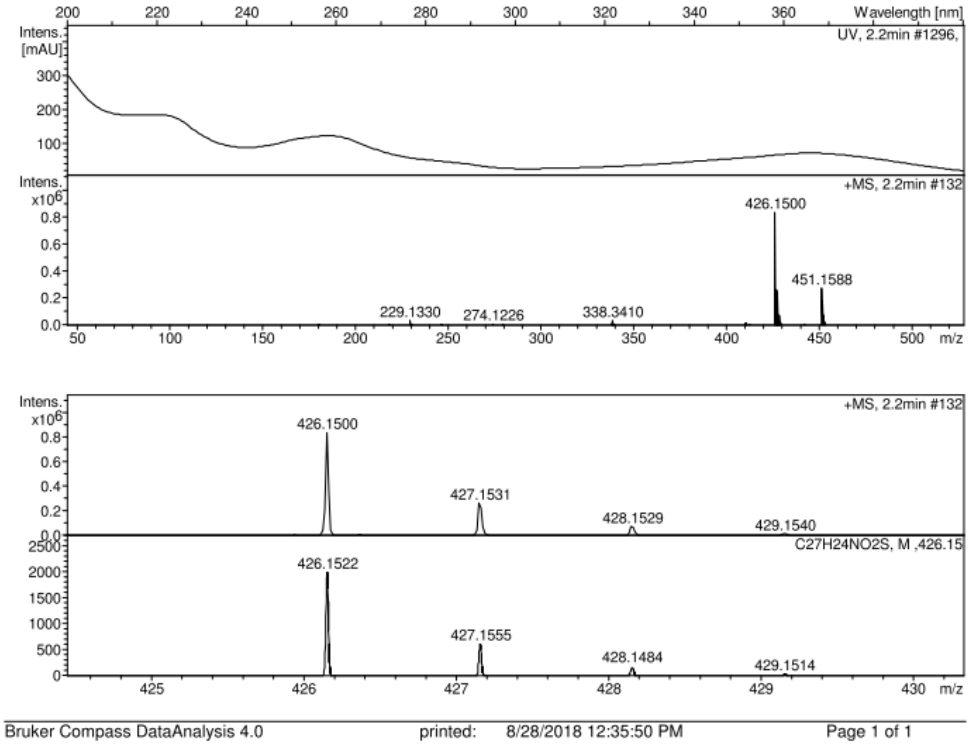
$^{13}C\{^{1}H\}$ NMR spectrum of **3e** (125 MHz, CD_3CN).



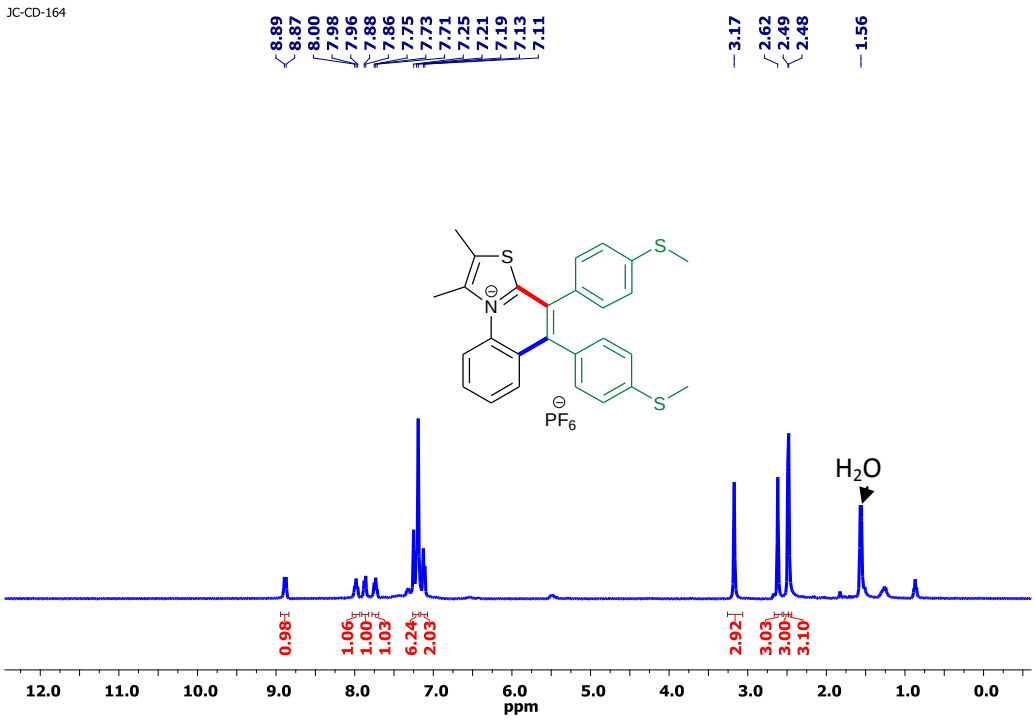
^{19}F NMR spectrum of **3e** (471 MHz, CD_3CN)



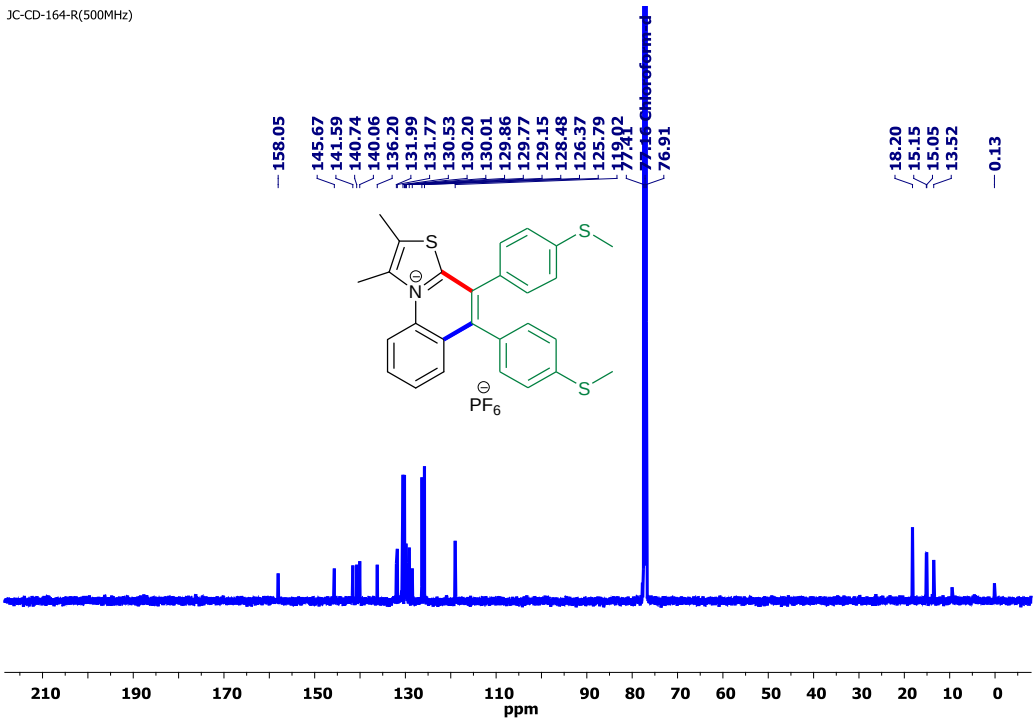
^{31}P NMR spectrum of **3e** (202 MHz, CD_3CN)



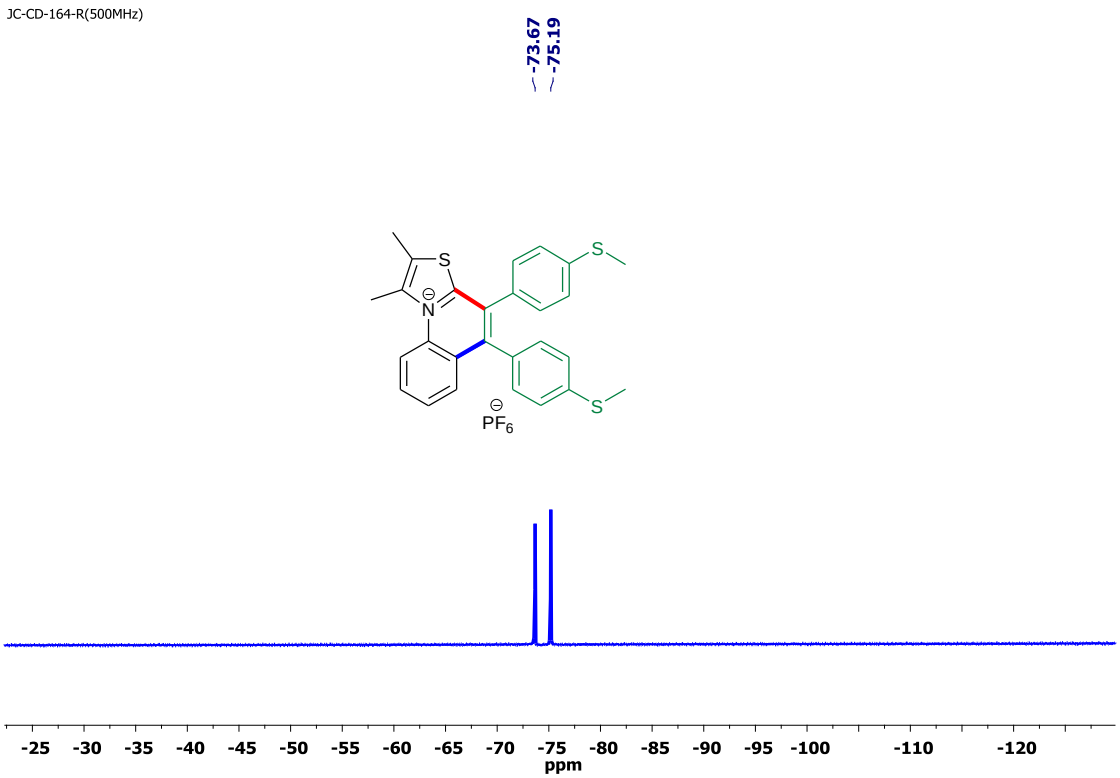
ESI-HRMS (positive ion mode) spectrum of **3e**



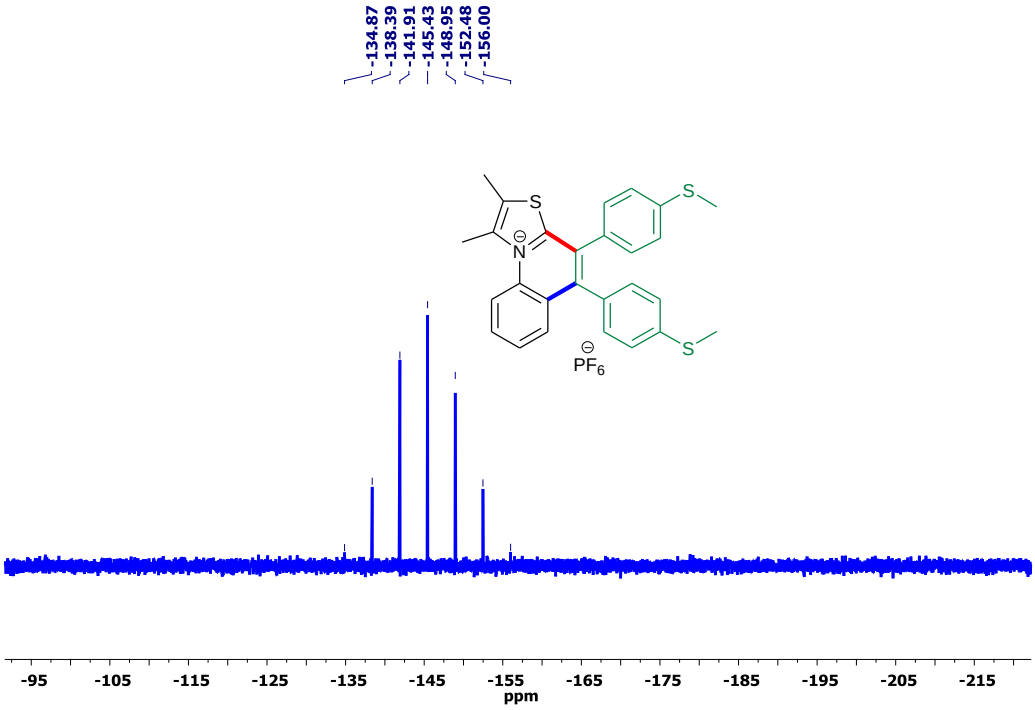
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$).



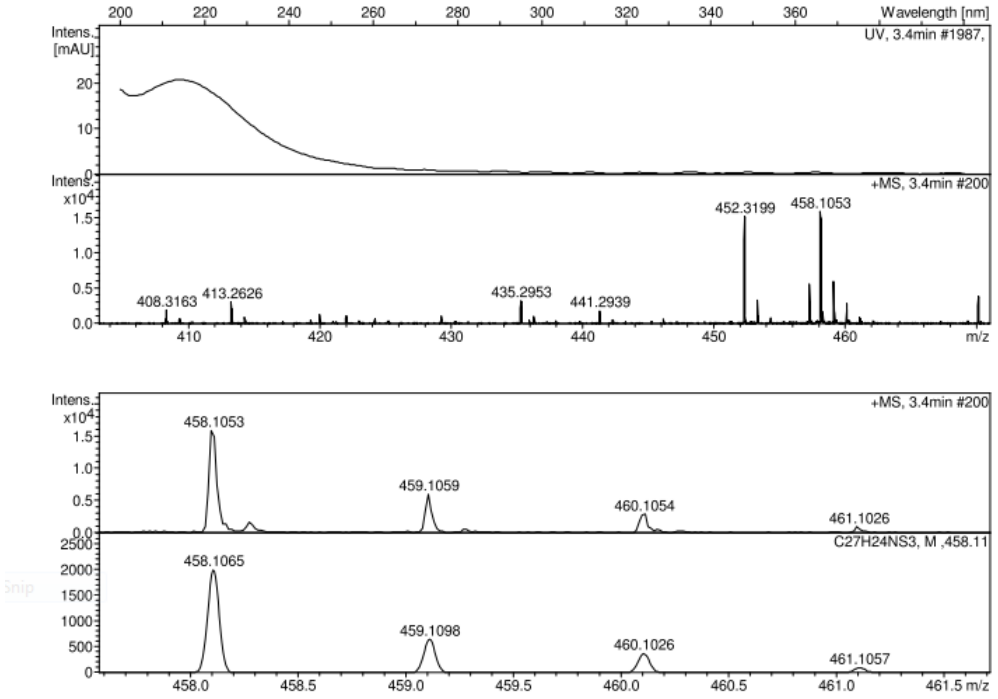
^{13}C{^{1}H} NMR spectrum of **3f** (125 MHz, $CDCl_3$)



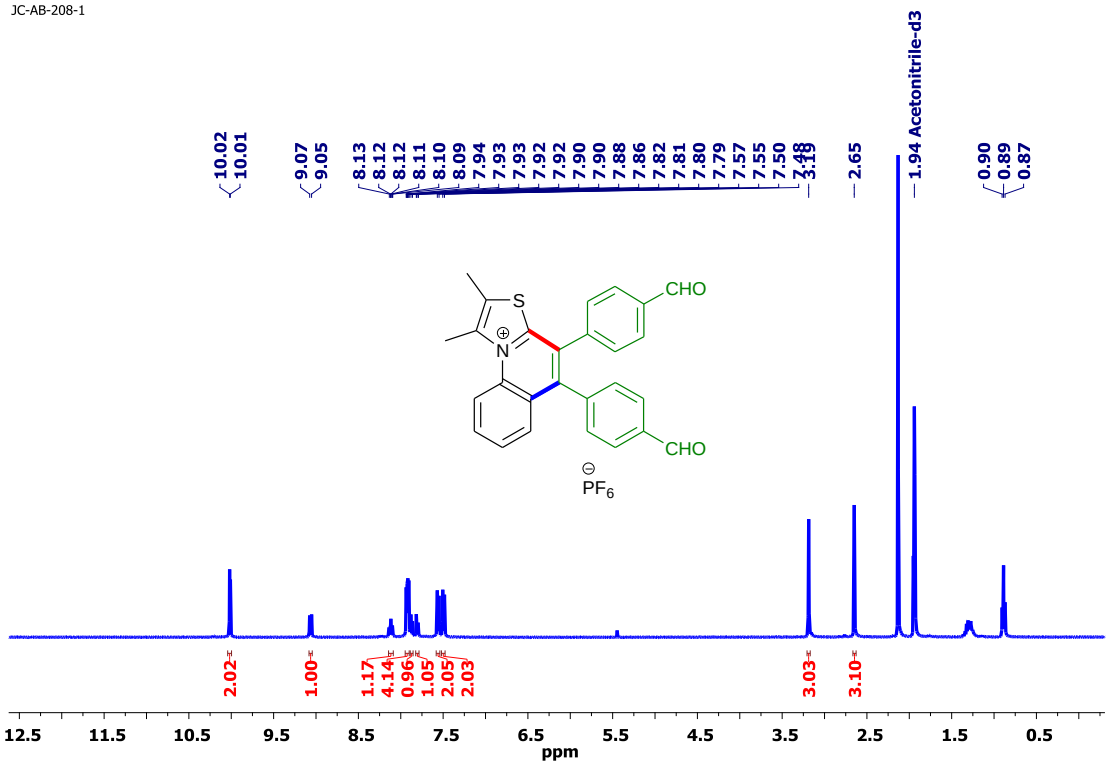
^{19}F NMR spectrum of **3f** (471 MHz, $CDCl_3$)



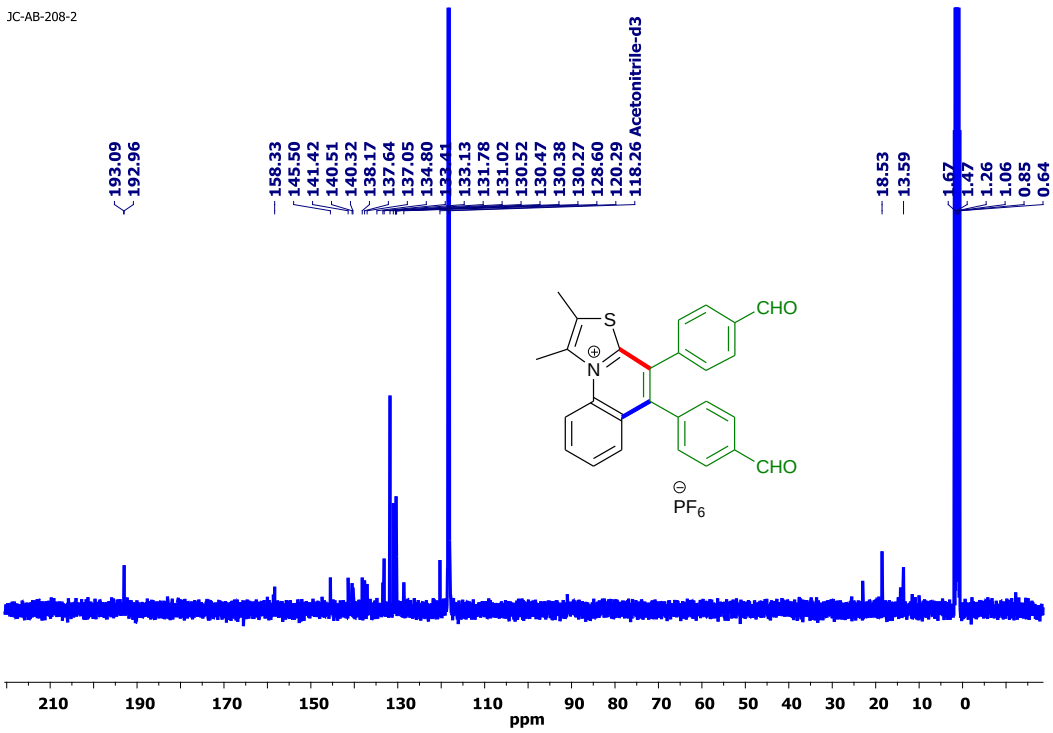
^{31}P NMR spectrum of **3f** (202 MHz, $CDCl_3$)



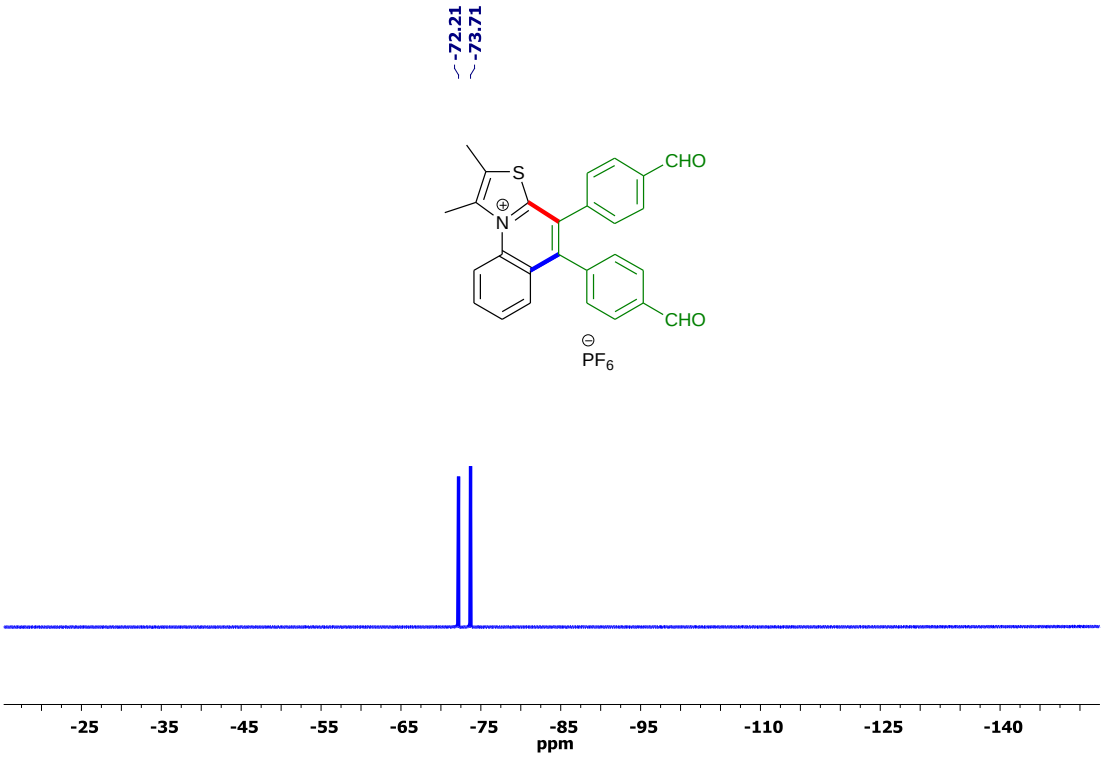
ESI-HRMS (positive ion mode) spectrum of **3f**



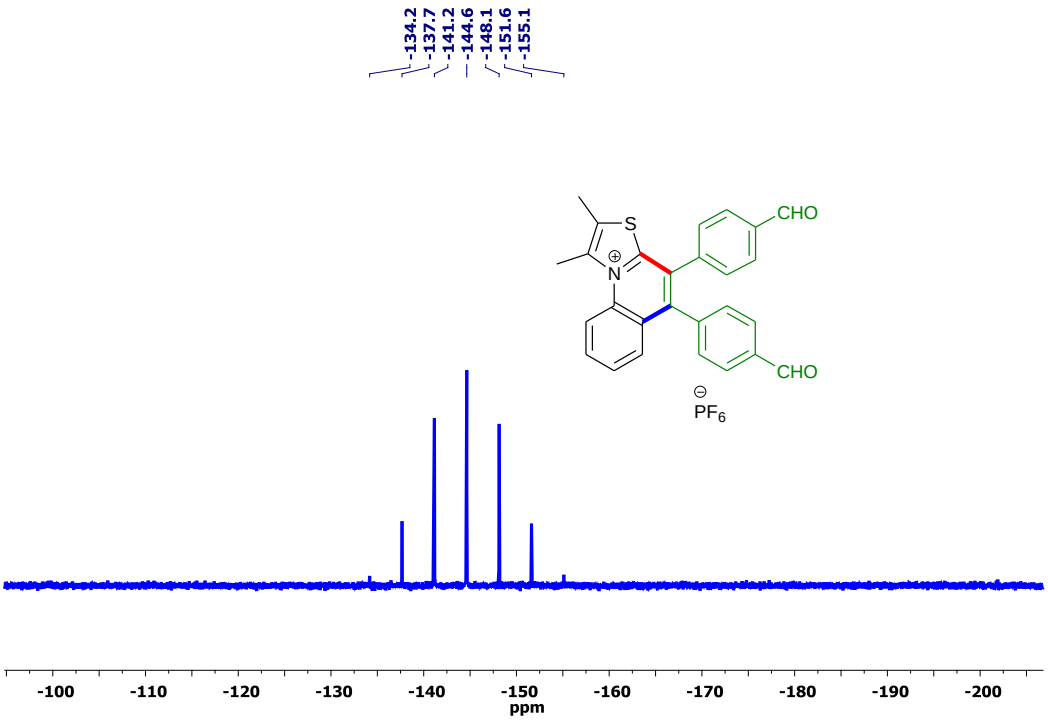
^{1}H NMR spectrum of **3g** (400 MHz, CD_3CN)



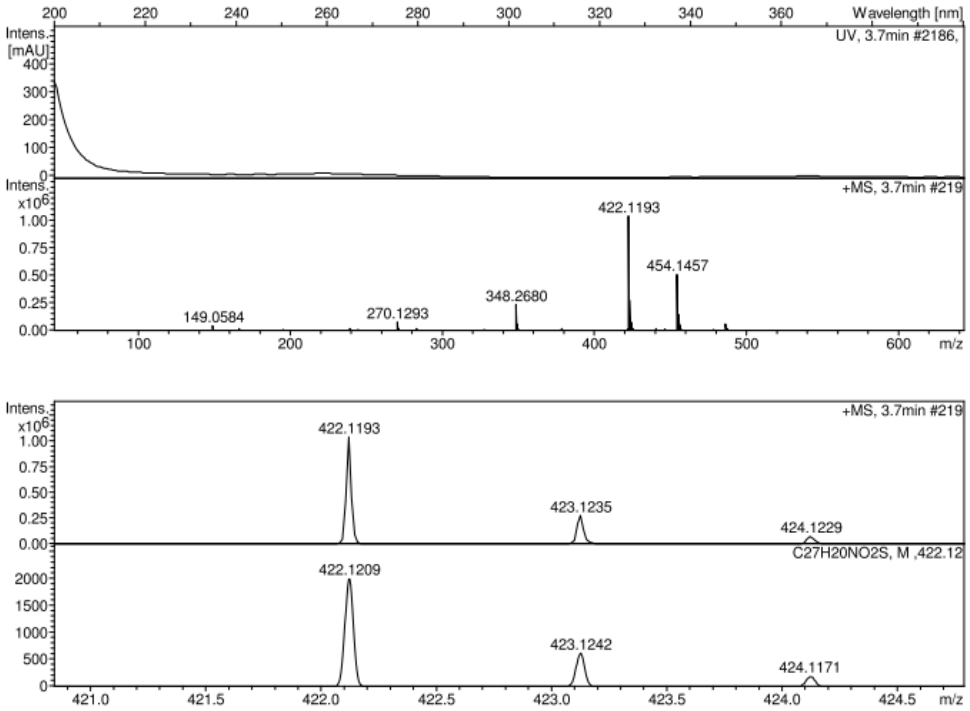
$^{13}C\{^{1}H\}$ NMR spectrum of **3g** (100 MHz, CD_3CN)



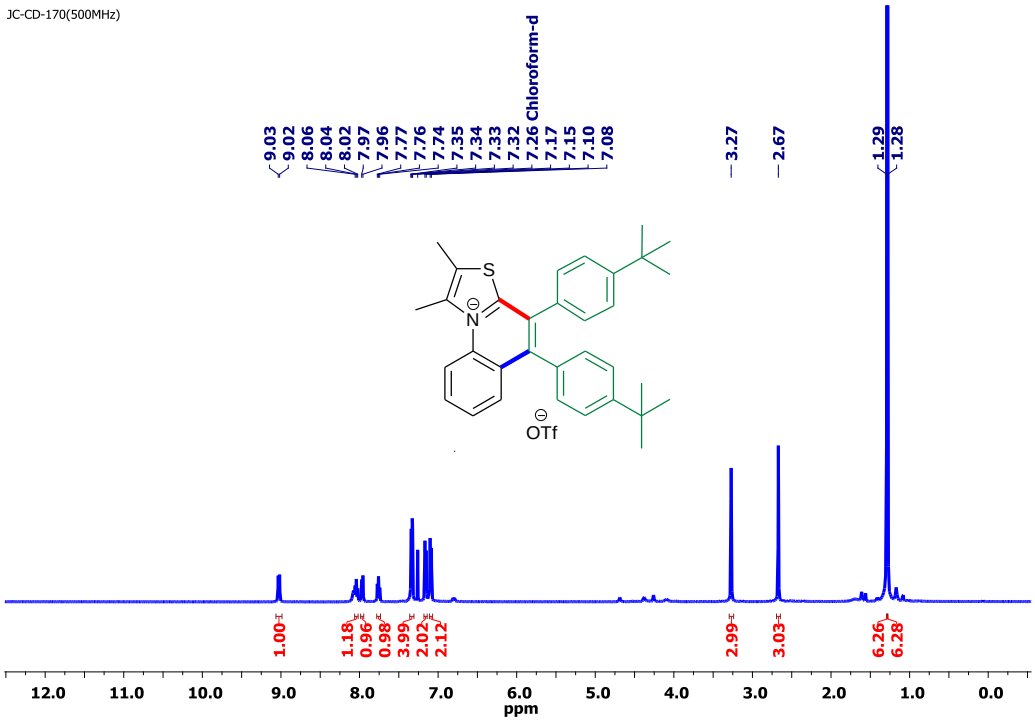
^{31}P NMR spectrum of **3g** (202 MHz, CD_3CN)



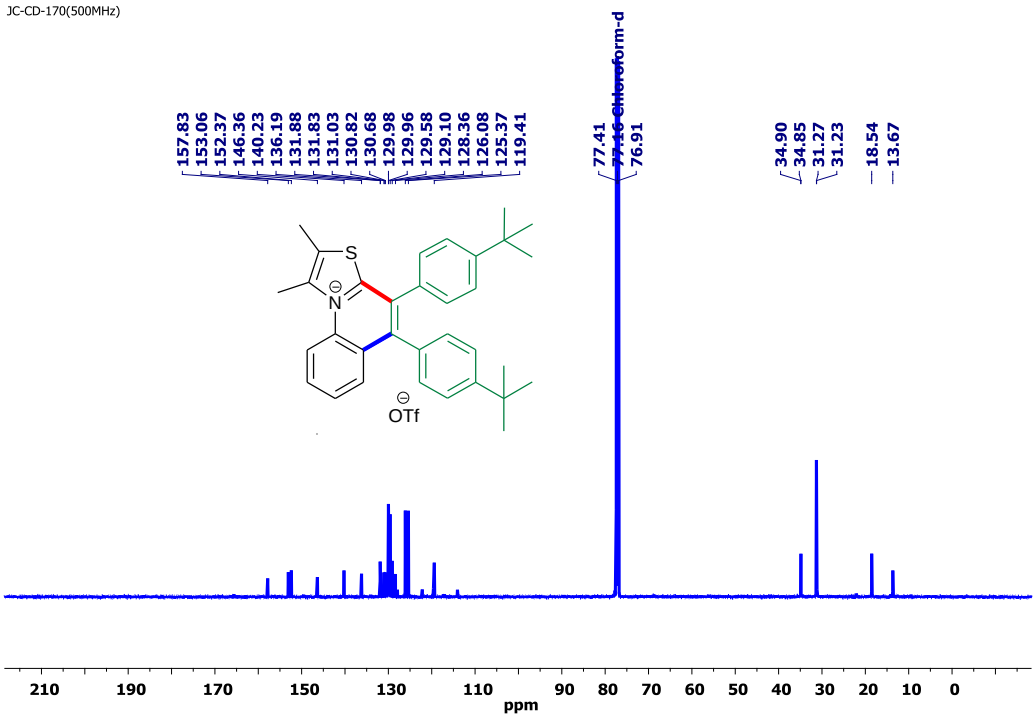
^{31}P NMR spectrum of **3g** (202 MHz, CD_3CN)



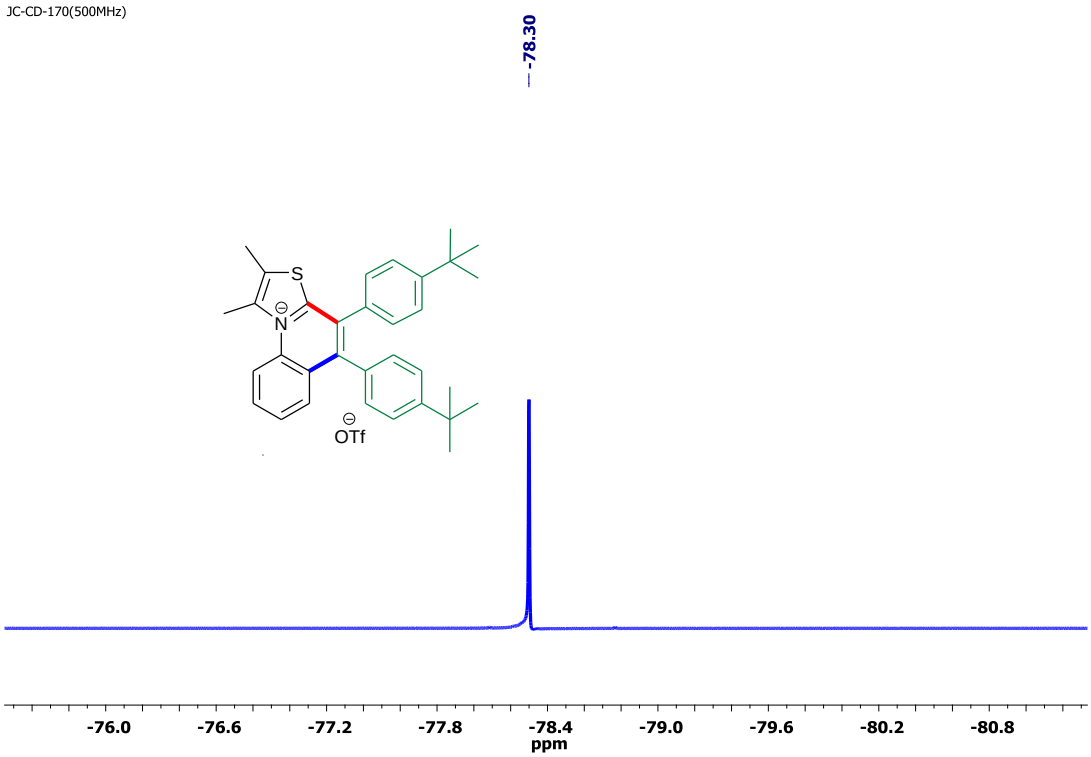
ESI-HRMS (positive ion mode) spectrum of **3g**



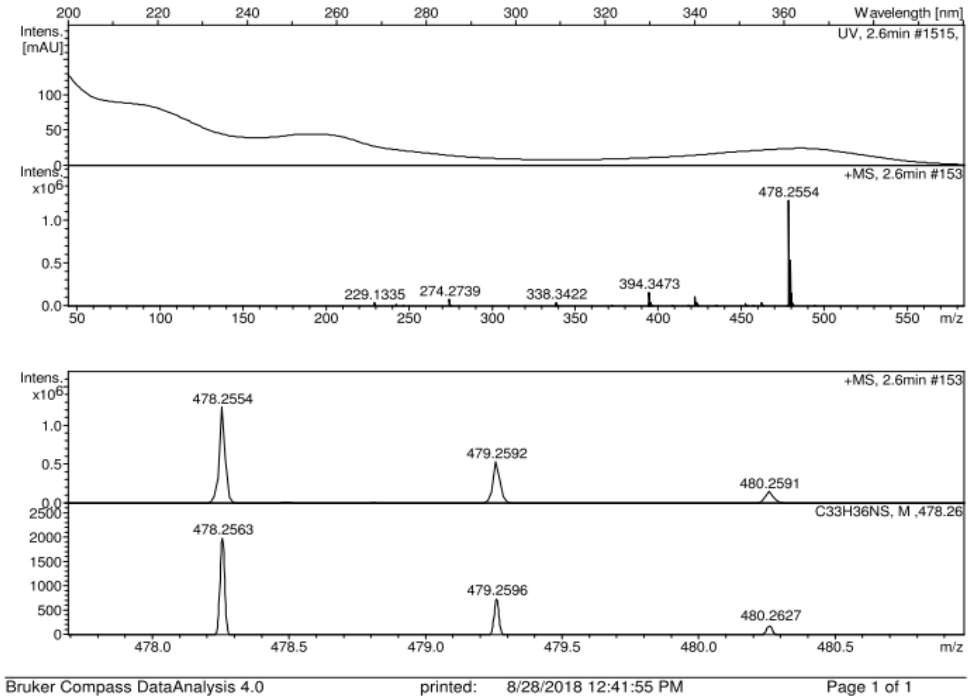
^{1}H NMR spectrum of **3h** (125 MHz, CD_3CN)



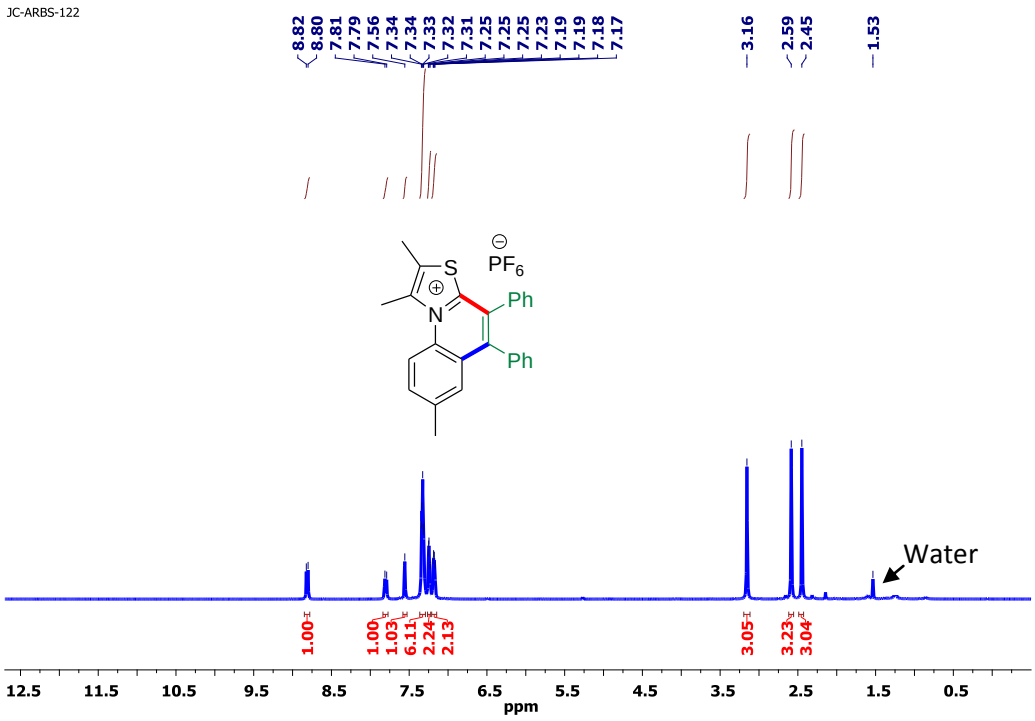
^{13}C{^{1}H} NMR spectrum of **3h** (125 MHz, $CDCl_3$).



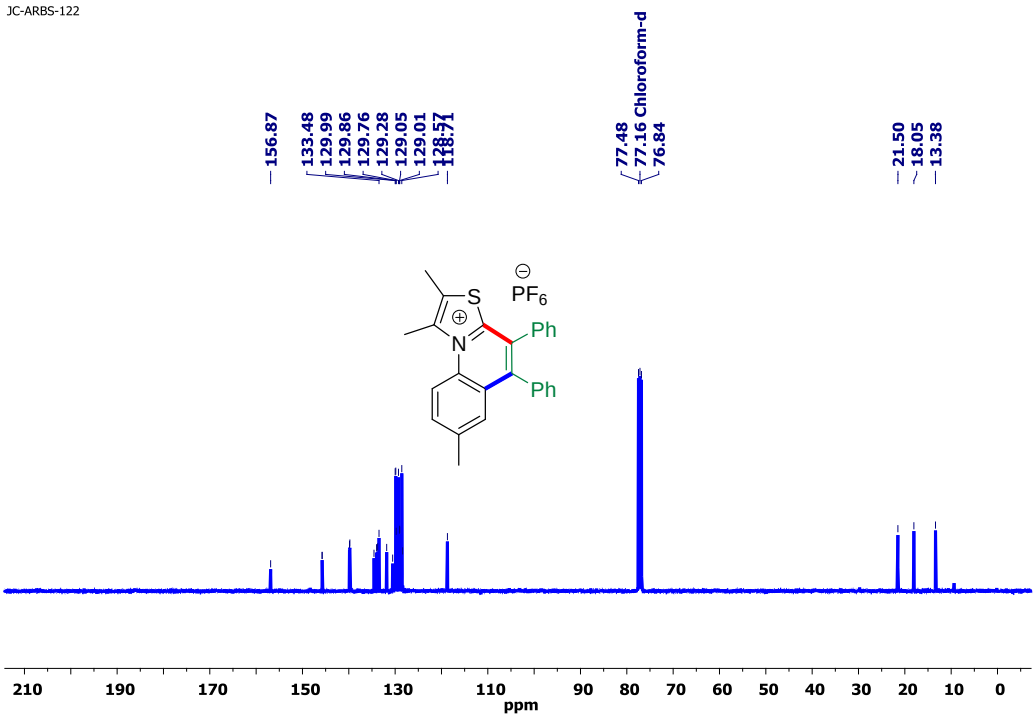
^{19}F NMR spectrum of **3h** (471 MHz, $CDCl_3$)



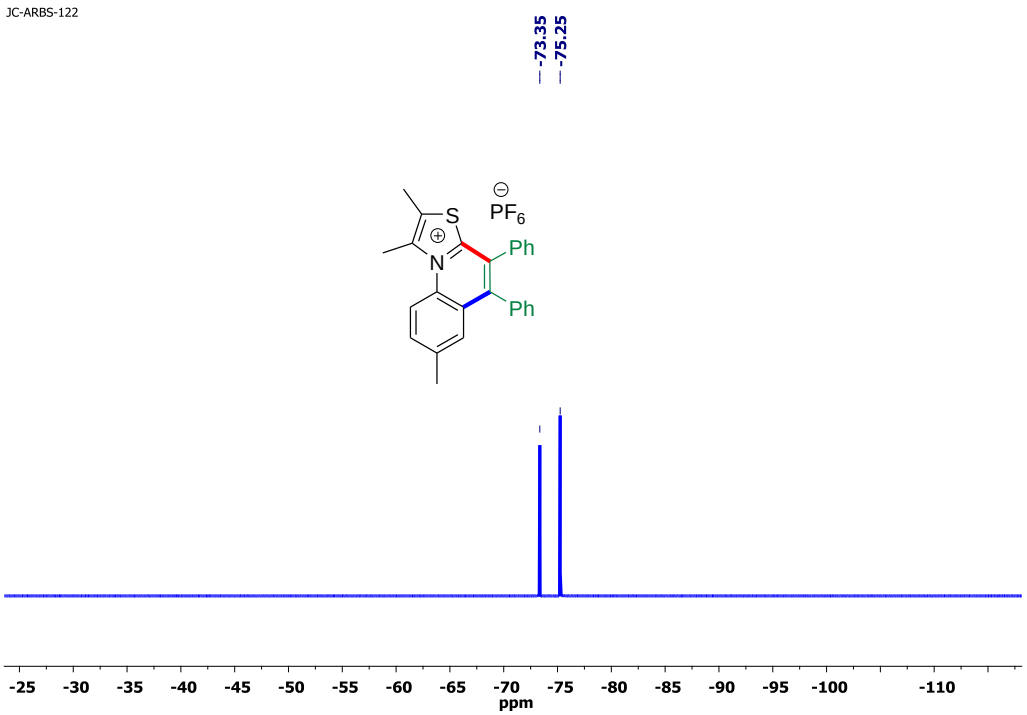
ESI-HRMS (positive ion mode) spectrum of **3h**



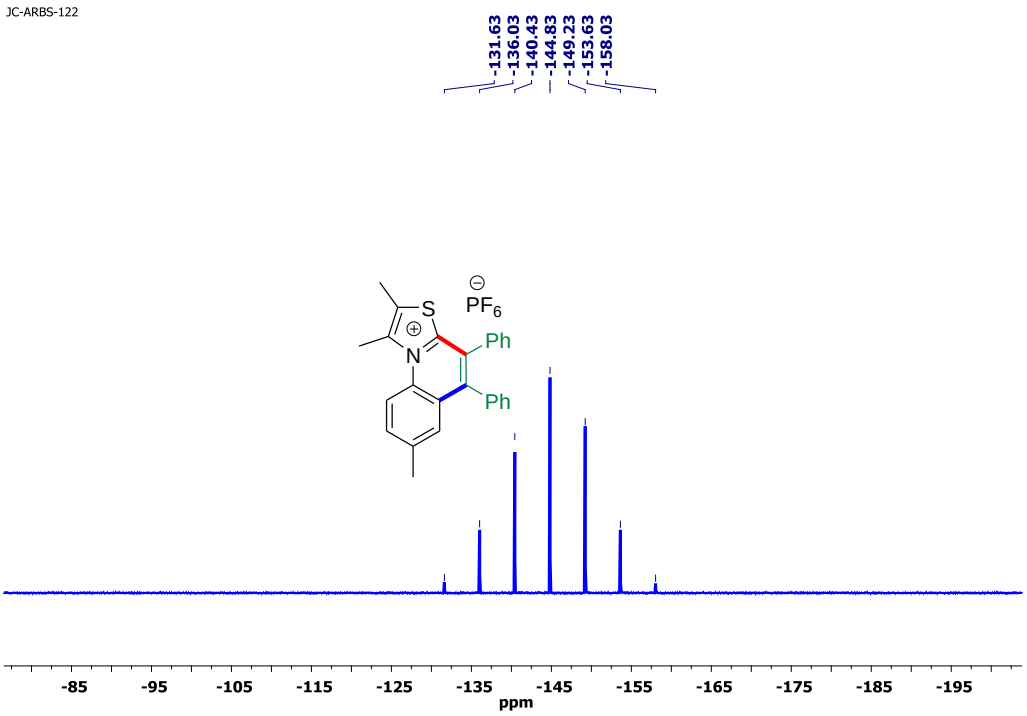
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$).



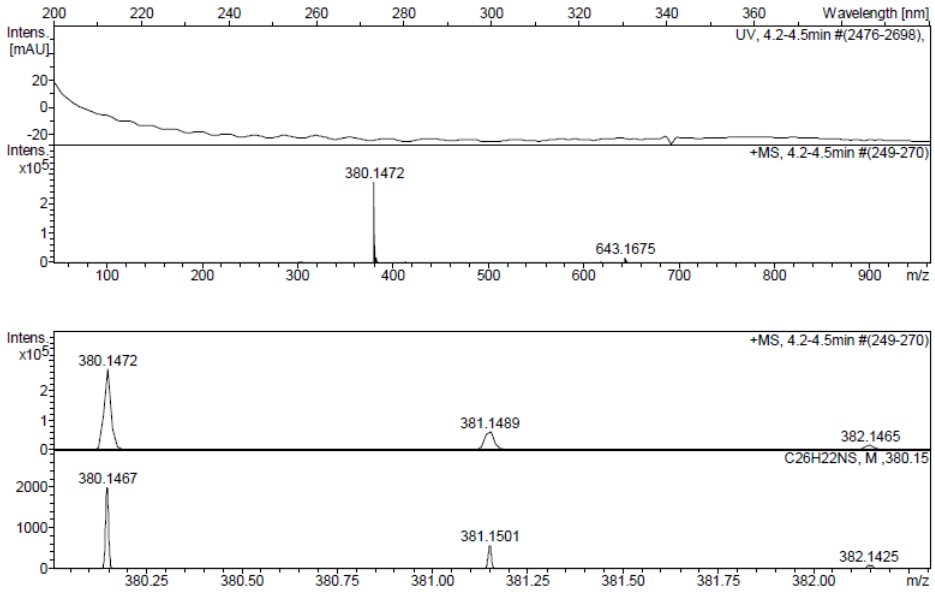
^{13}C{^{1}H} NMR spectrum of **3i** (101 MHz, $CDCl_3$



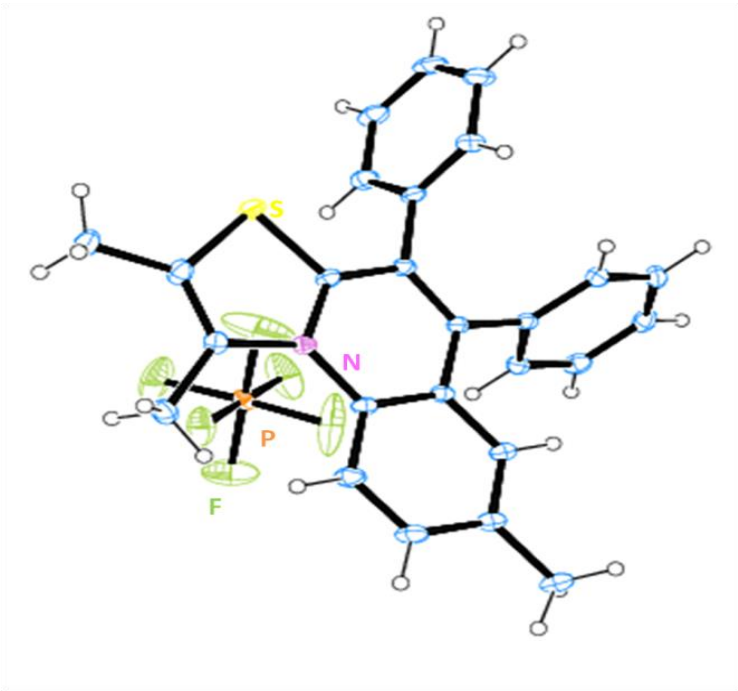
^{19}F NMR spectrum of **3i** (376 MHz, $CDCl_3$).



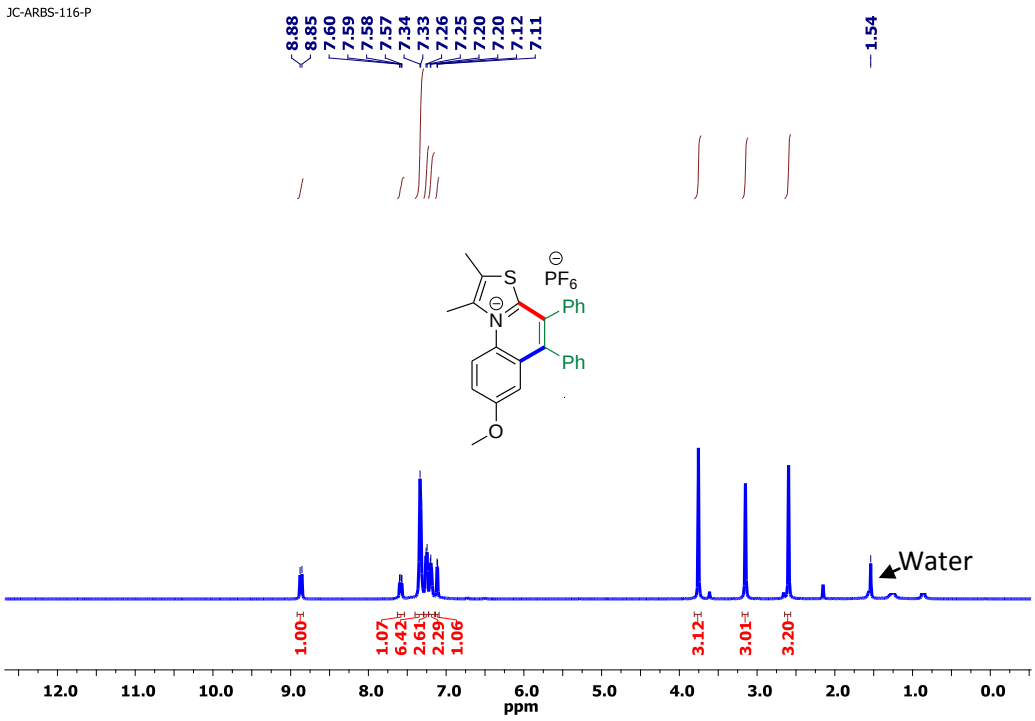
^{31}P NMR spectrum of **3i** (162 MHz, $CDCl_3$)



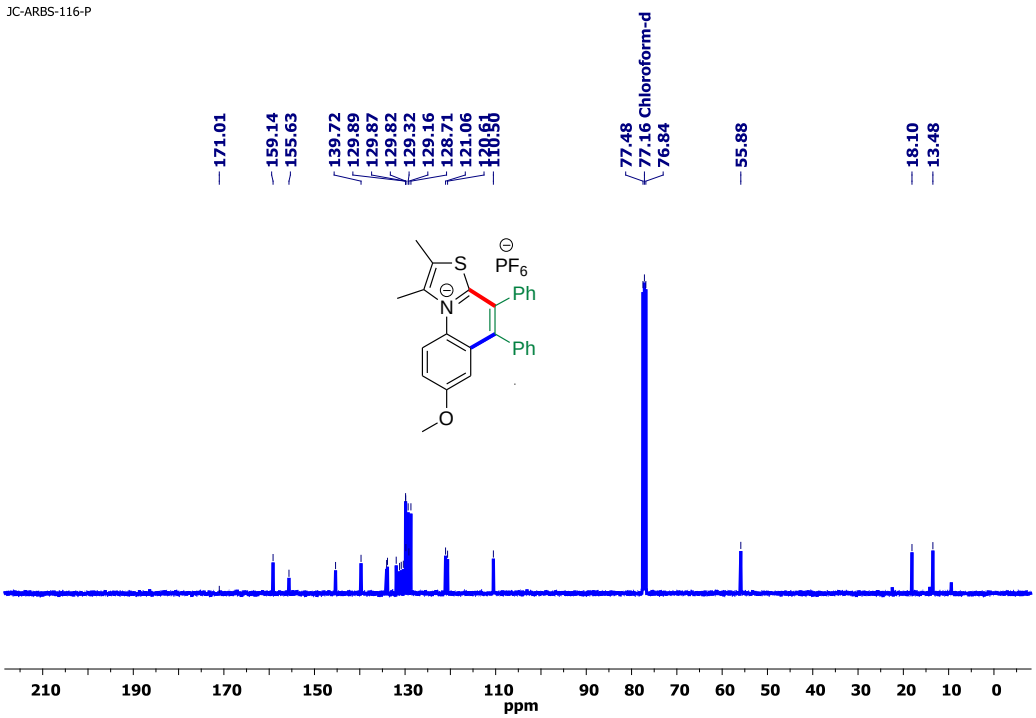
ESI-HRMS (positive ion mode) spectrum of **3i**



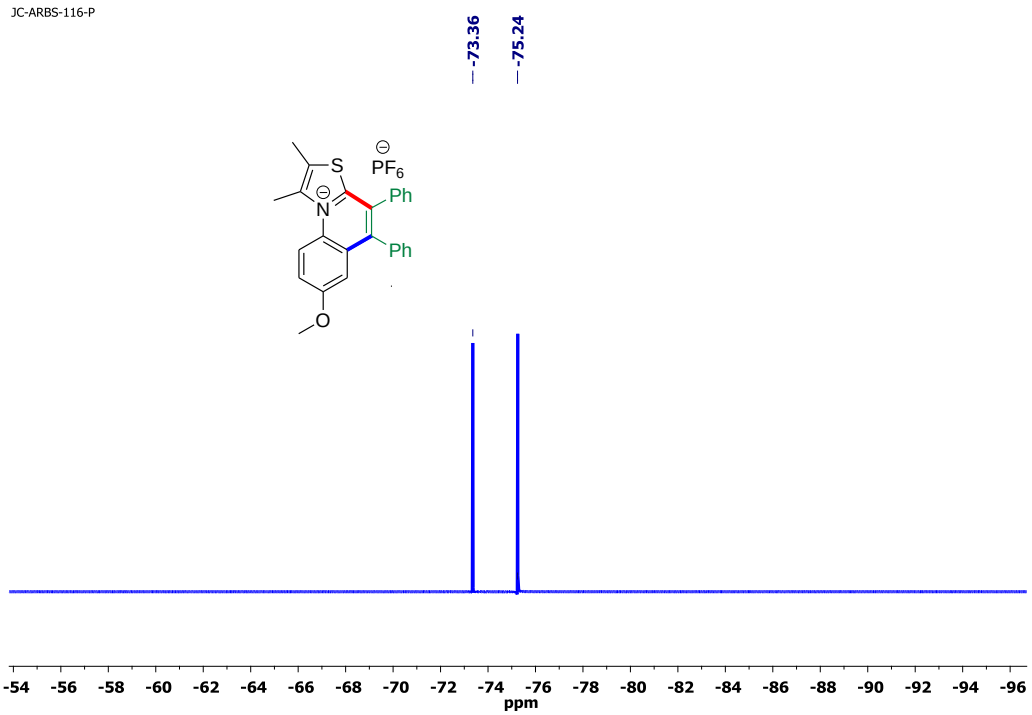
Single crystal XRD structure of **3i (30% probability ellipsoid)**



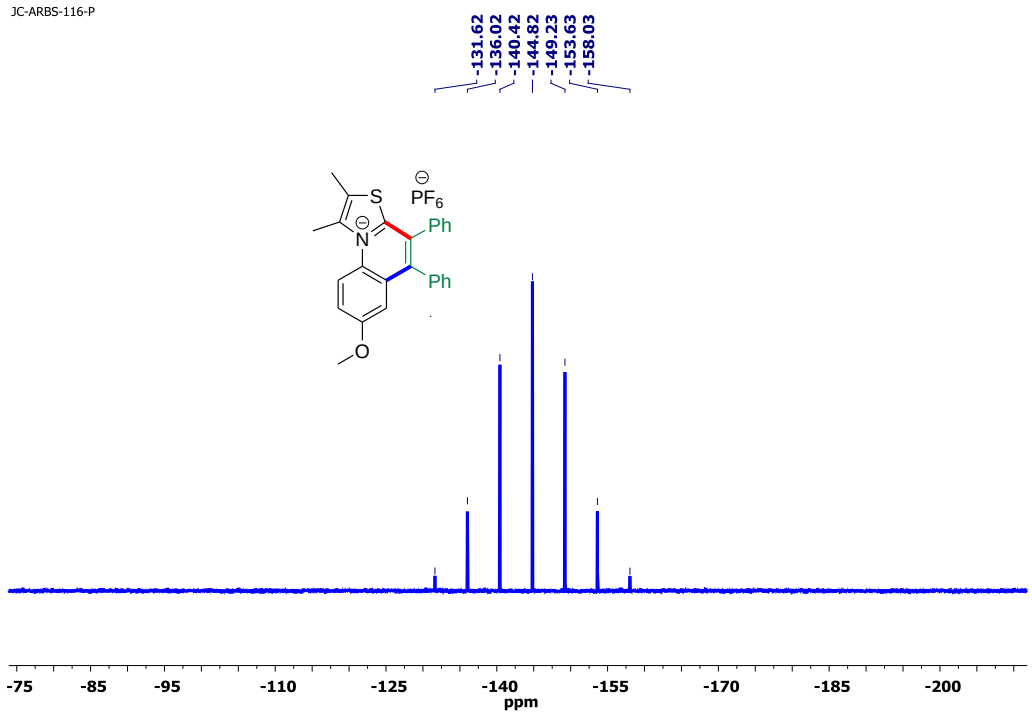
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$).



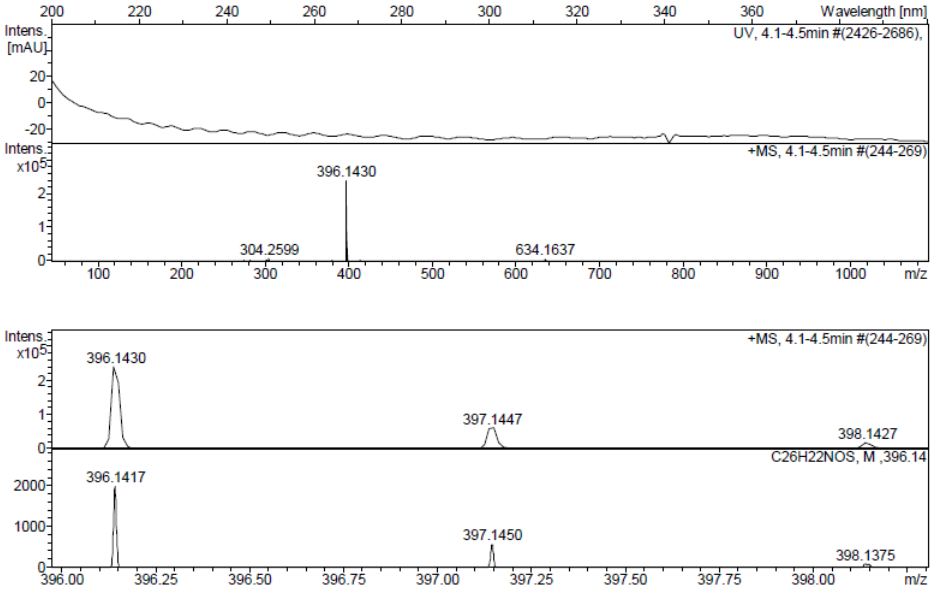
^{13}C{^{1}H} NMR spectrum of **3j** (101 MHz, $CDCl_3$)



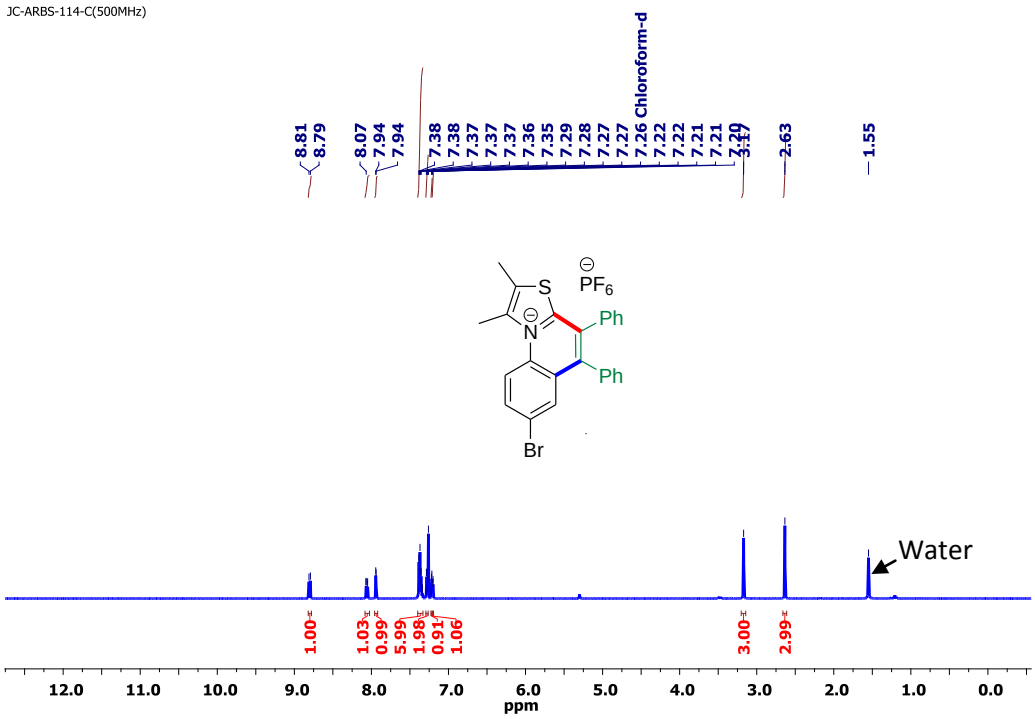
^{19}F NMR spectrum of **3j** (376 MHz, $CDCl_3$).



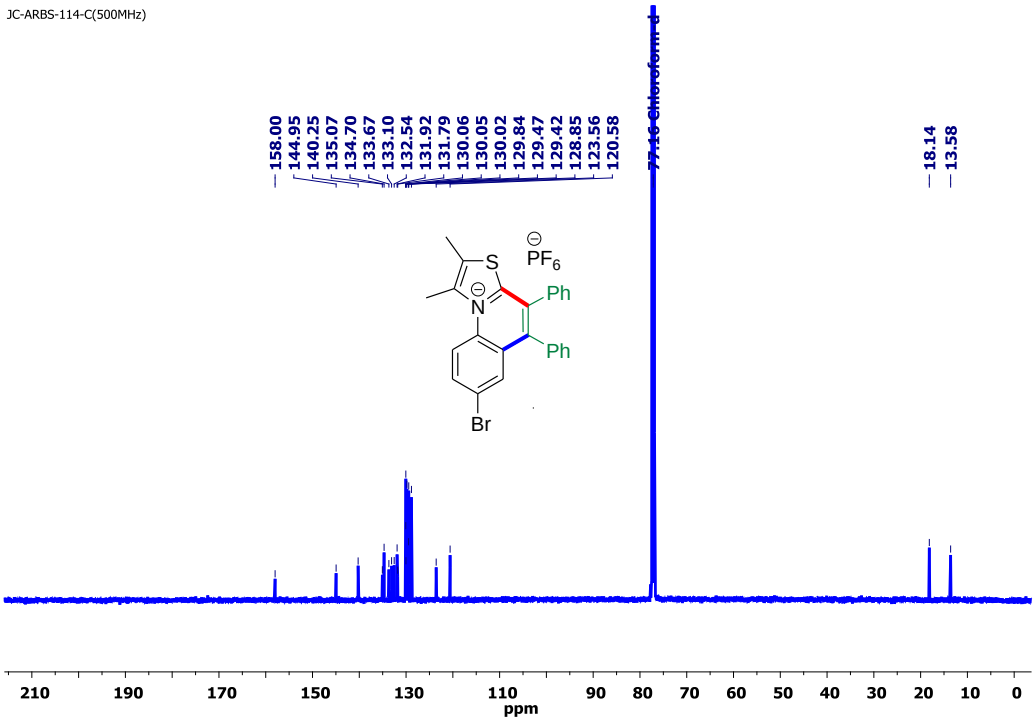
^{31}P NMR spectrum of **3j** (162 MHz, $CDCl_3$).



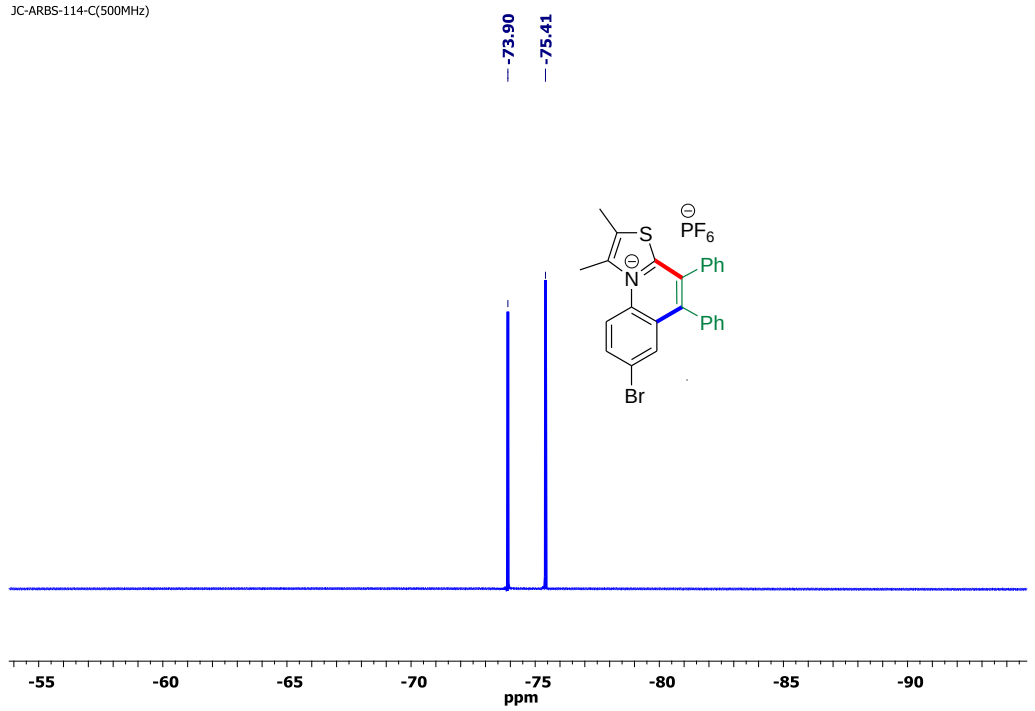
ESI-HRMS (positive ion mode) spectrum of **3j**



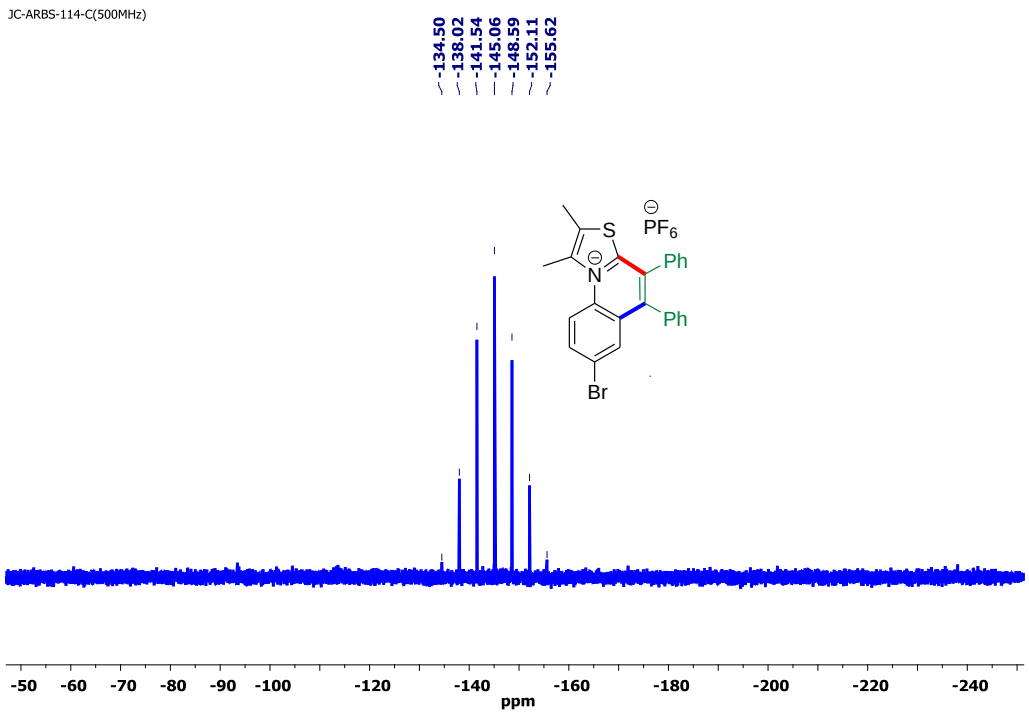
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$).



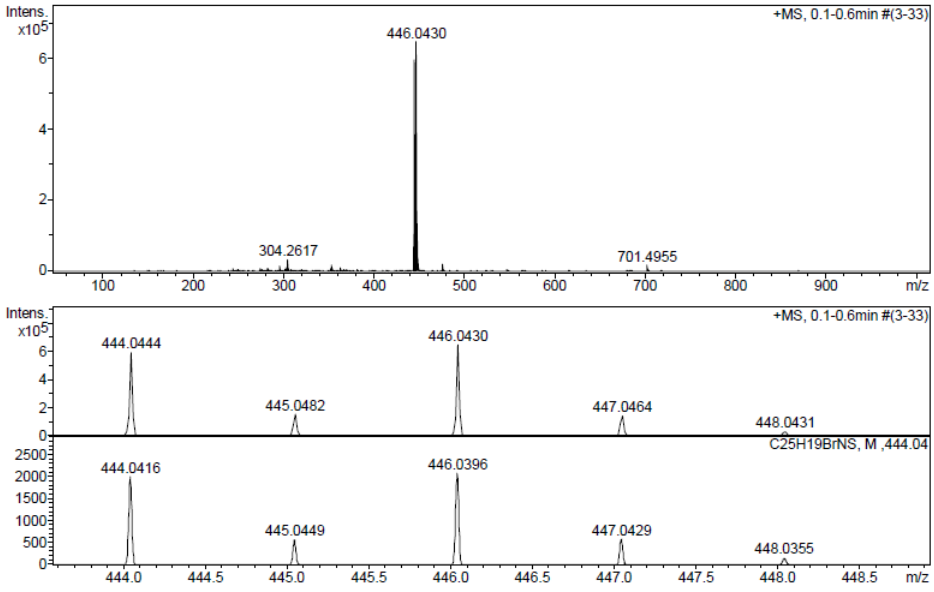
$^{13}C\{^{1}H\}$ NMR spectrum of **3k** (101 MHz, $CDCl_3$)



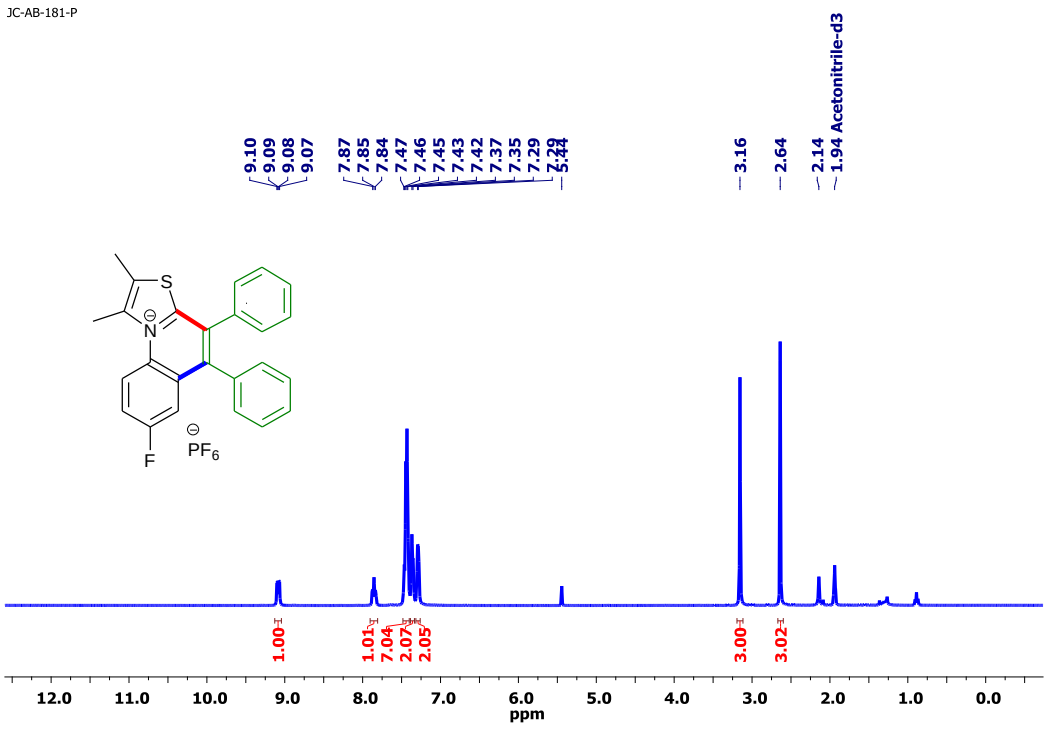
^{19} F NMR spectrum of **3k** (376 MHz, $CDCl_3$).



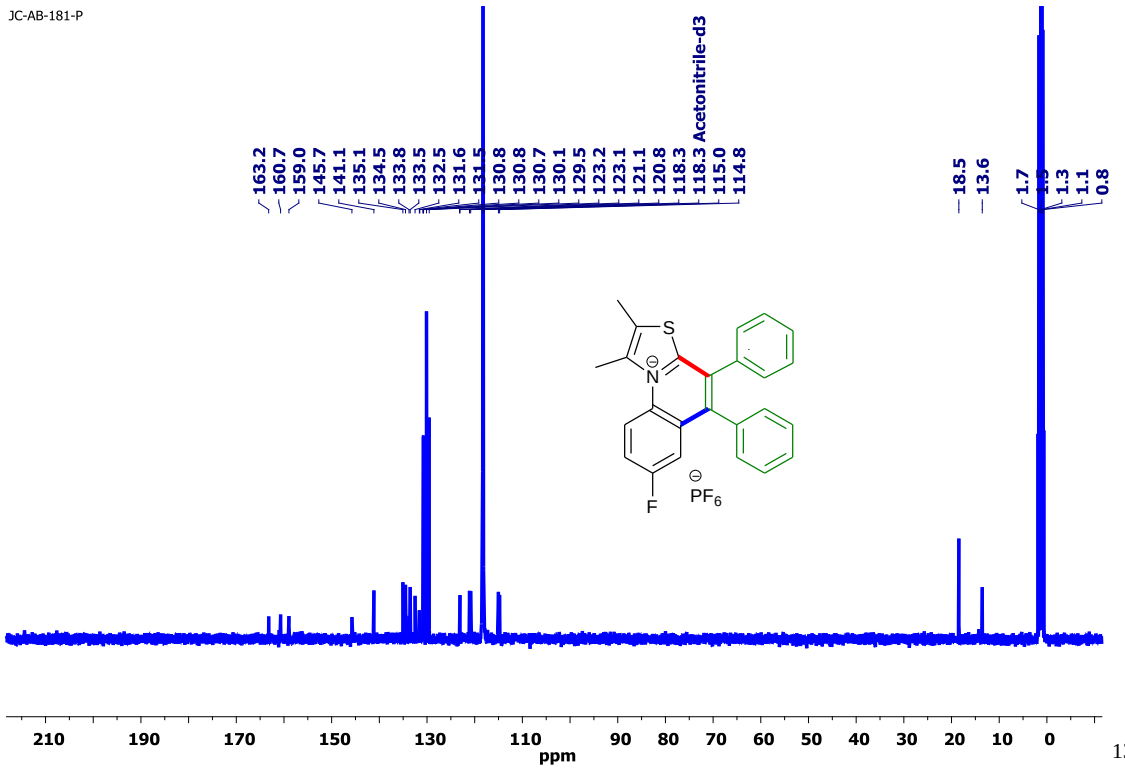
^{31}P NMR spectrum of **3k** (162 MHz, $CDCl_3$).



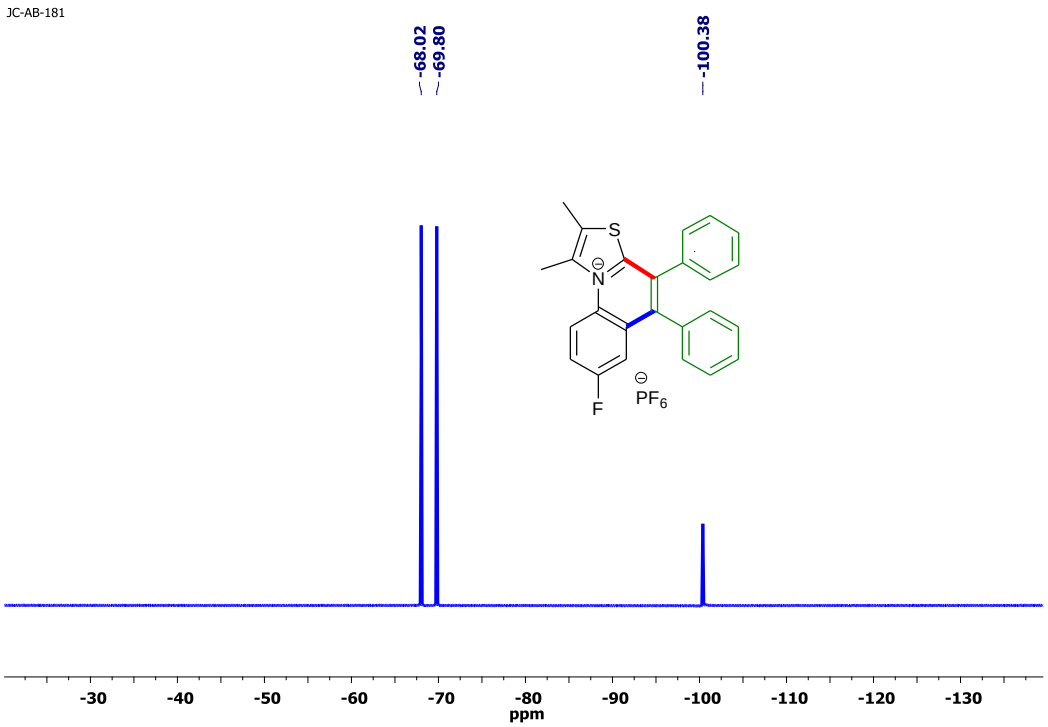
ESI-HRMS (positive ion mode) spectrum of **3k**



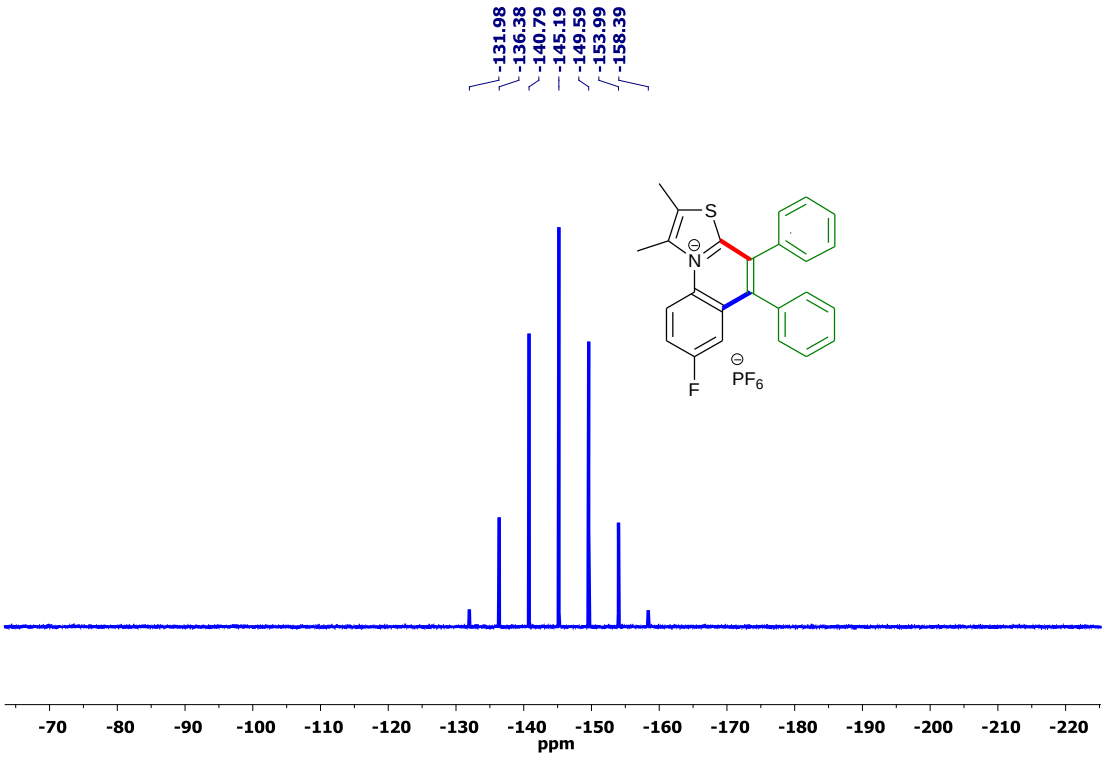
^{1}H NMR spectrum of **3l** (400 MHz, CD_3CN)



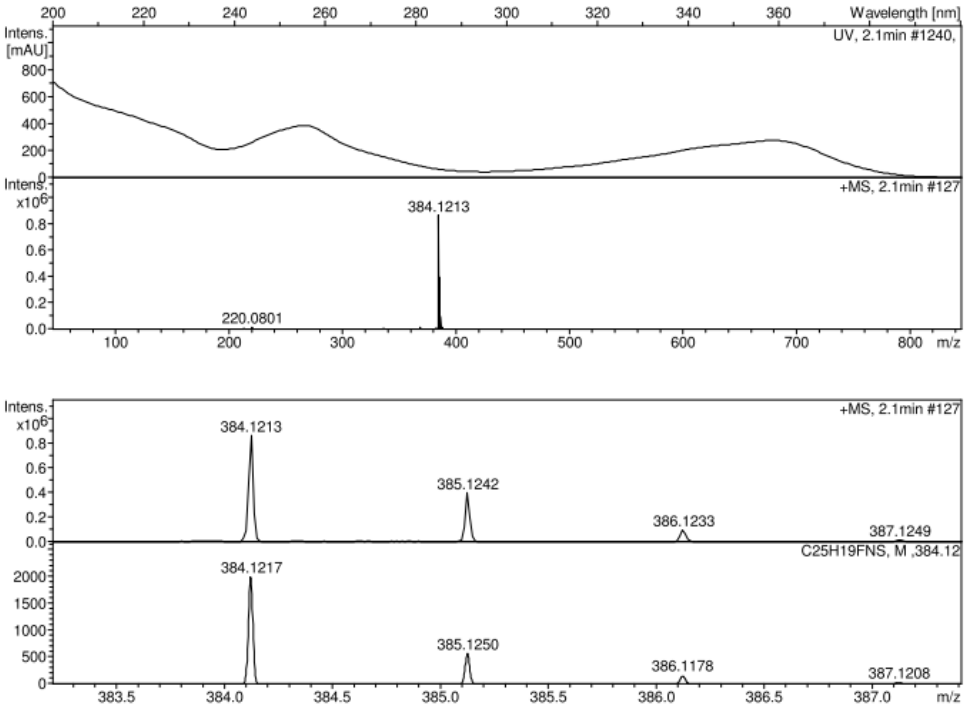
^{13}C{^{1}H} NMR spectrum of **3l** (100 MHz, CD_3CN)



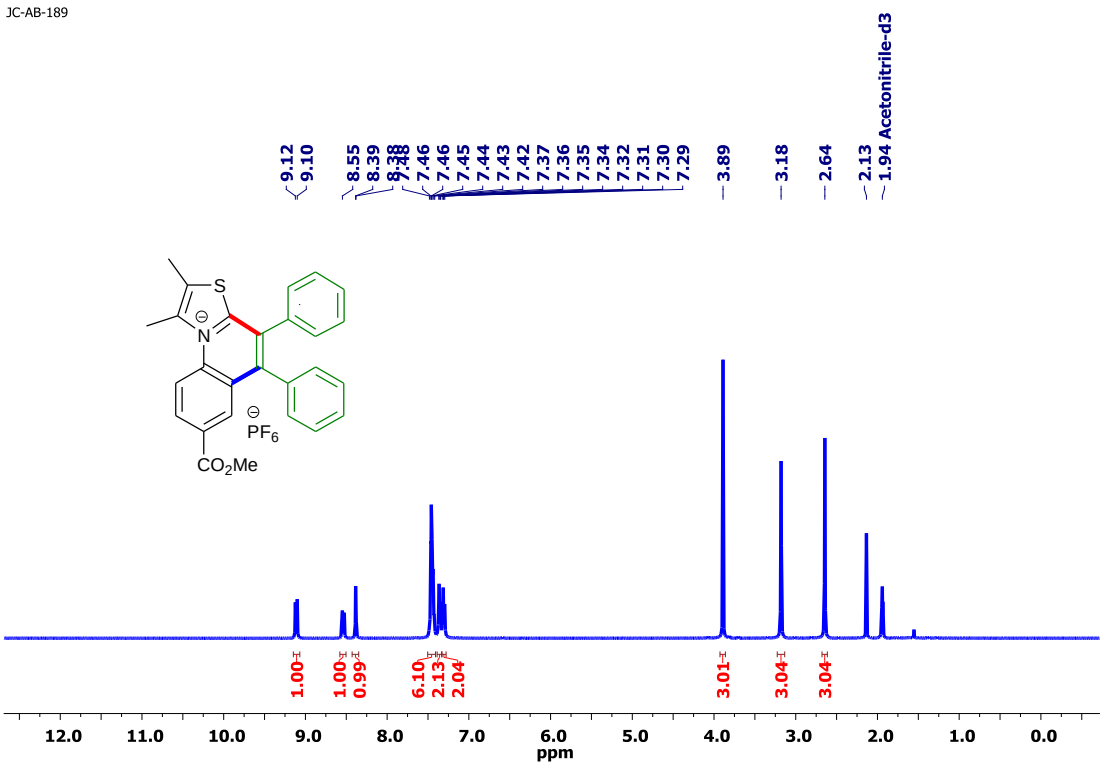
^{19}F NMR spectrum of **3l** (376 MHz, $CDCl_3$)



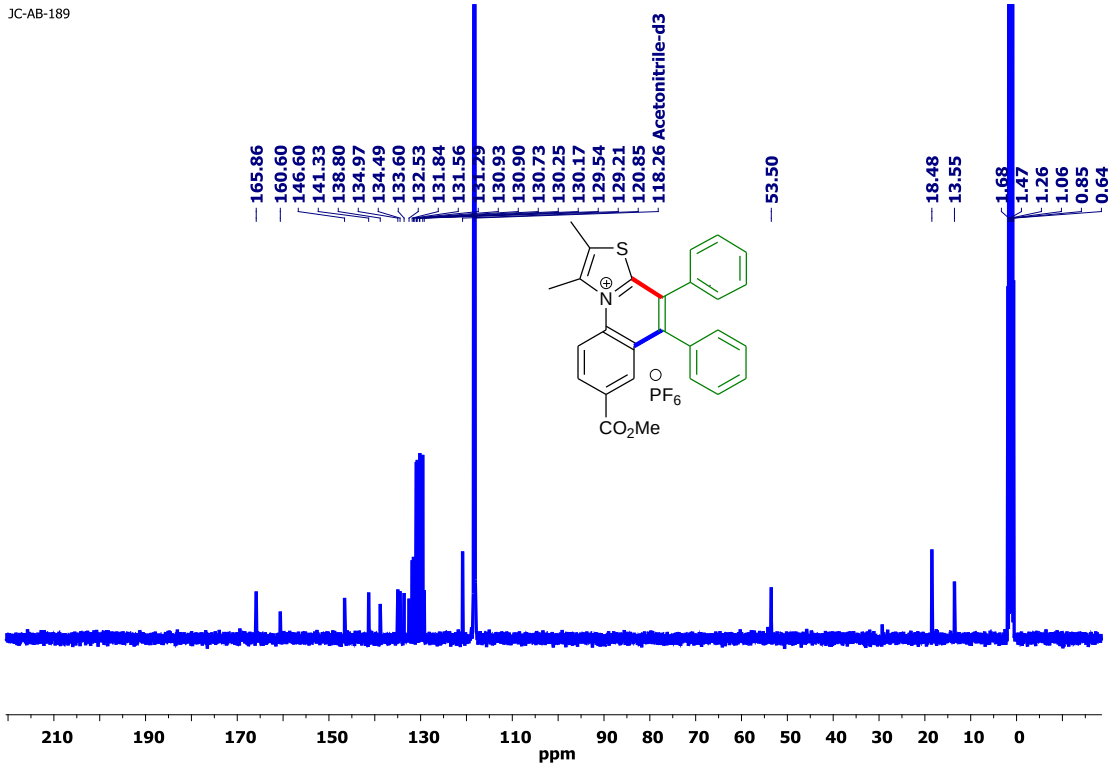
^{31}P NMR spectrum of **3l** (162 MHz, $CDCl_3$)



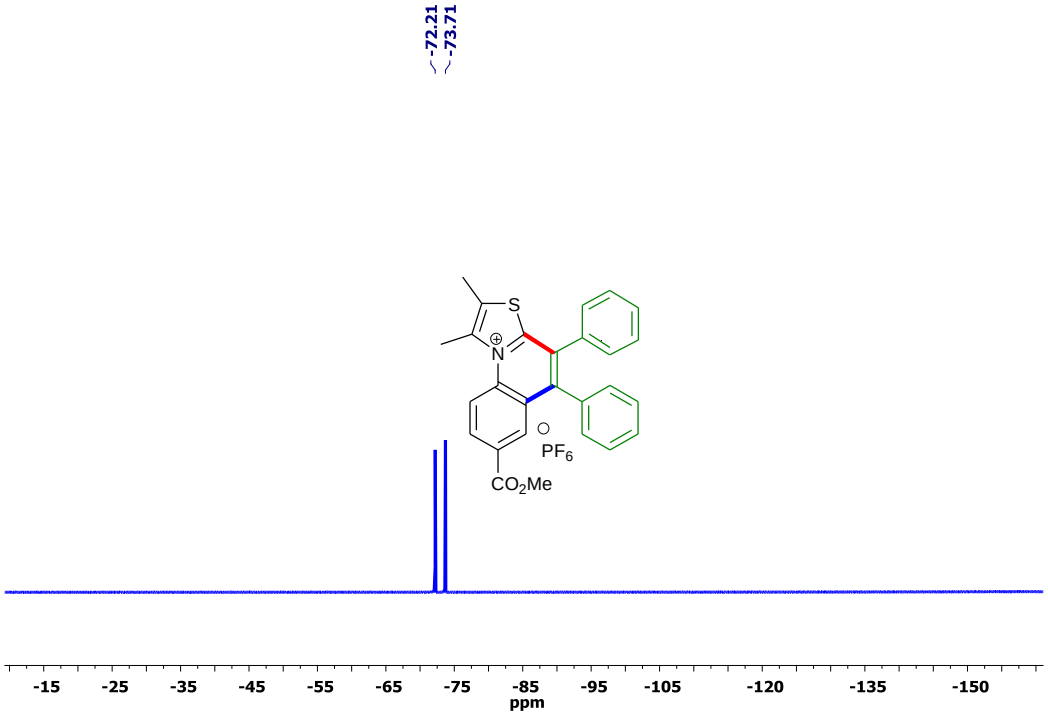
ESI-HRMS (positive ion mode) spectrum of **3l**



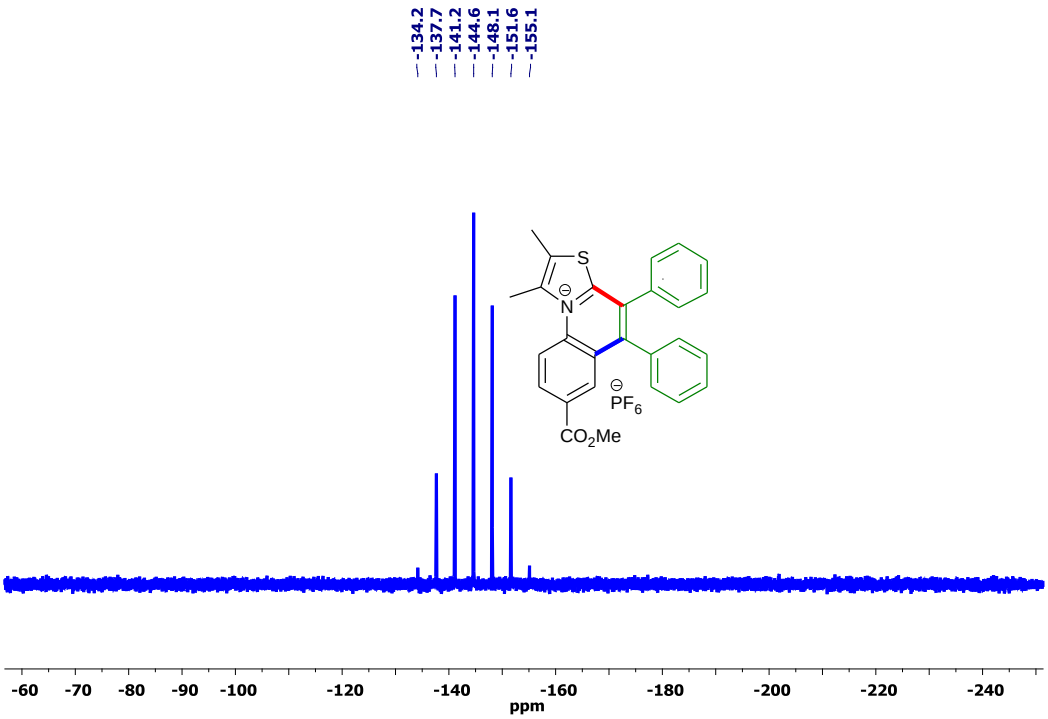
^{1}H NMR spectrum of **3m** (400 MHz, CD_3CN)



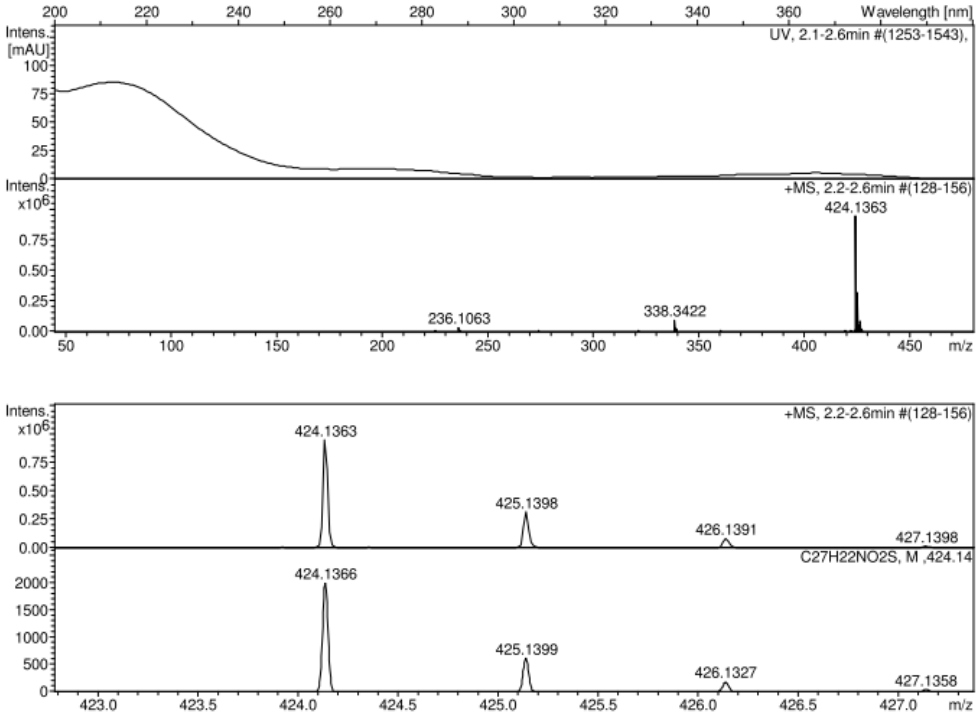
$^{13}C\{^{1}H\}$ NMR spectrum of **3m** (100 MHz, CD_3CN)



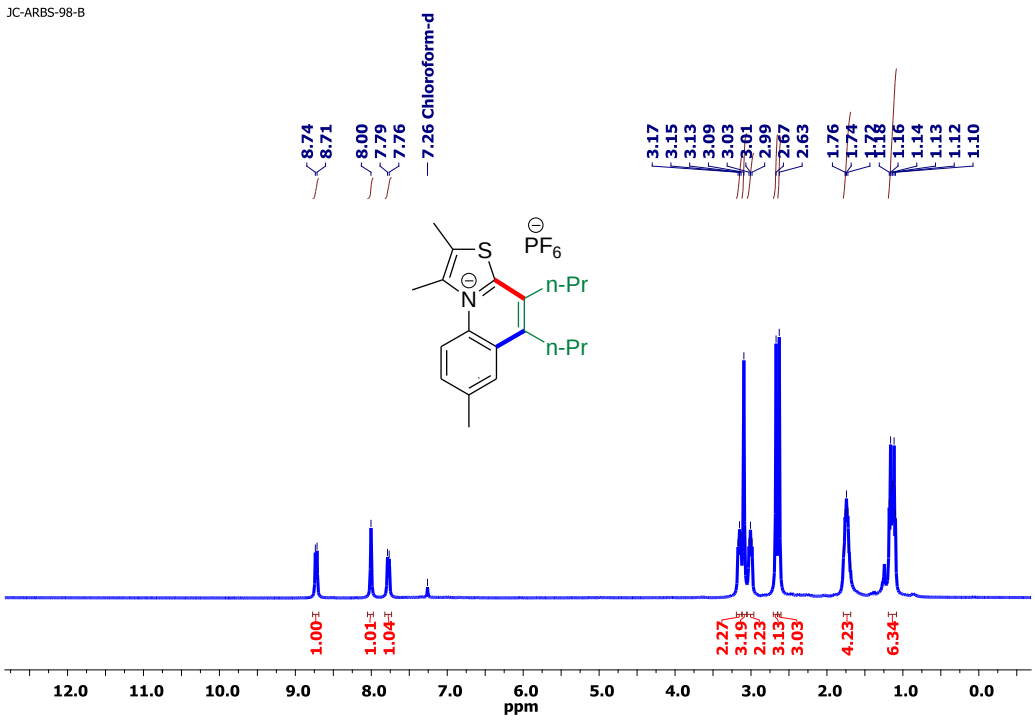
^{19}F NMR spectrum of **3m** (471 MHz, CD_3CN)



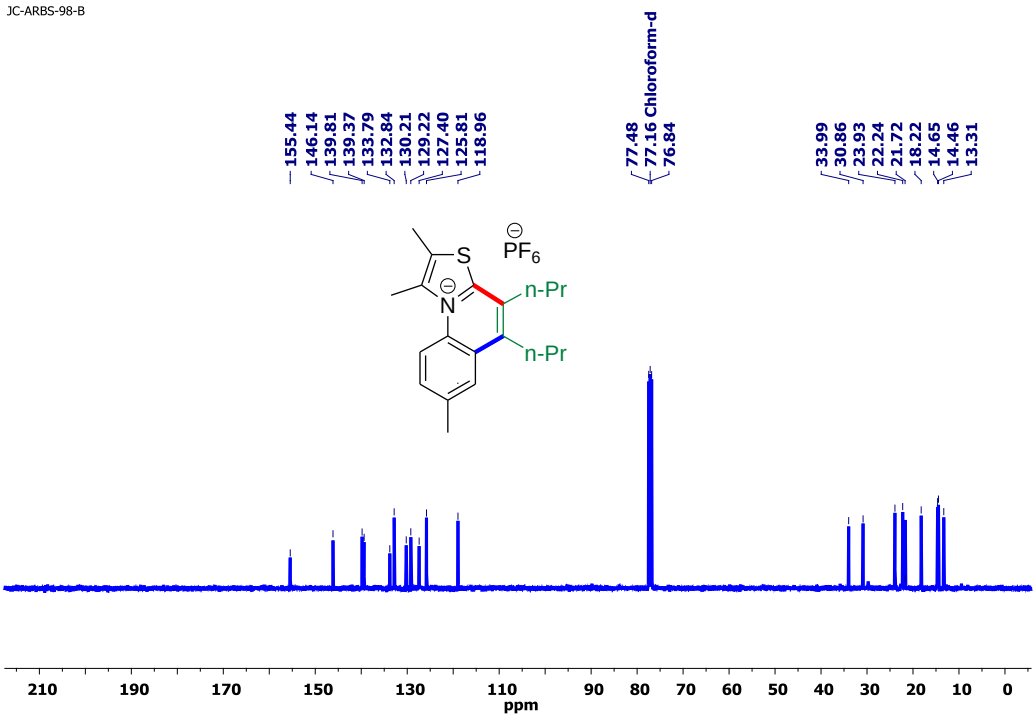
^{31}P NMR spectrum of **3m** (202 MHz, CD_3CN)



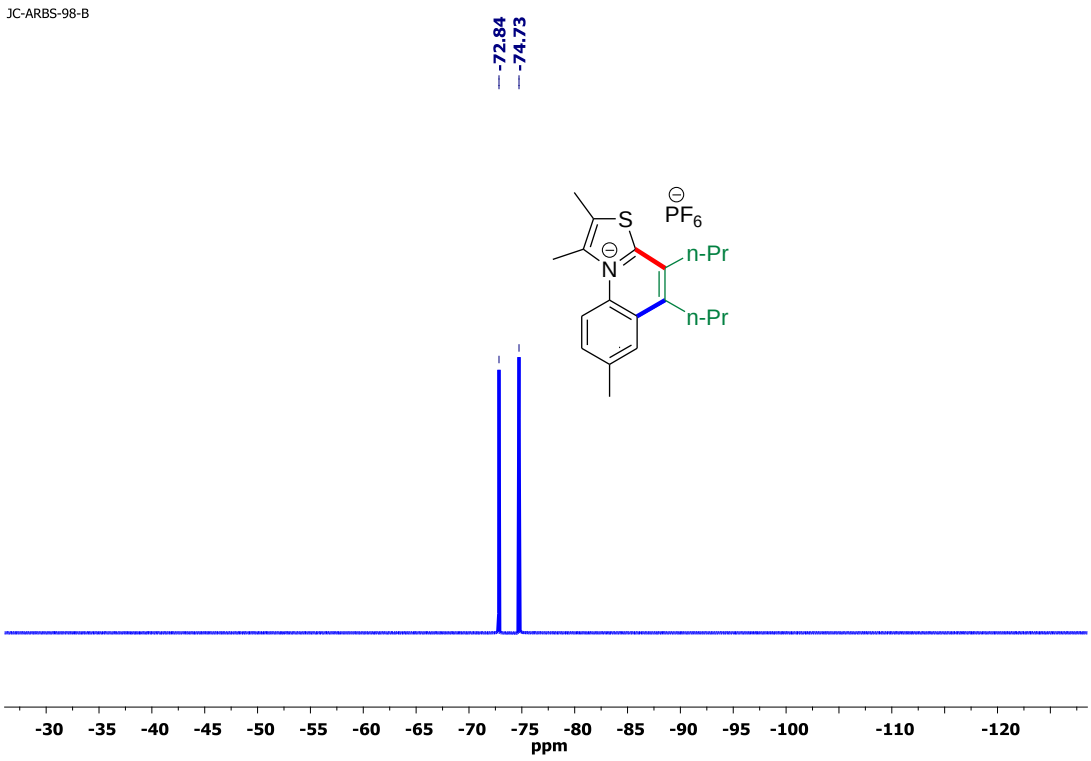
ESI-HRMS (positive ion mode) spectrum of **3m**



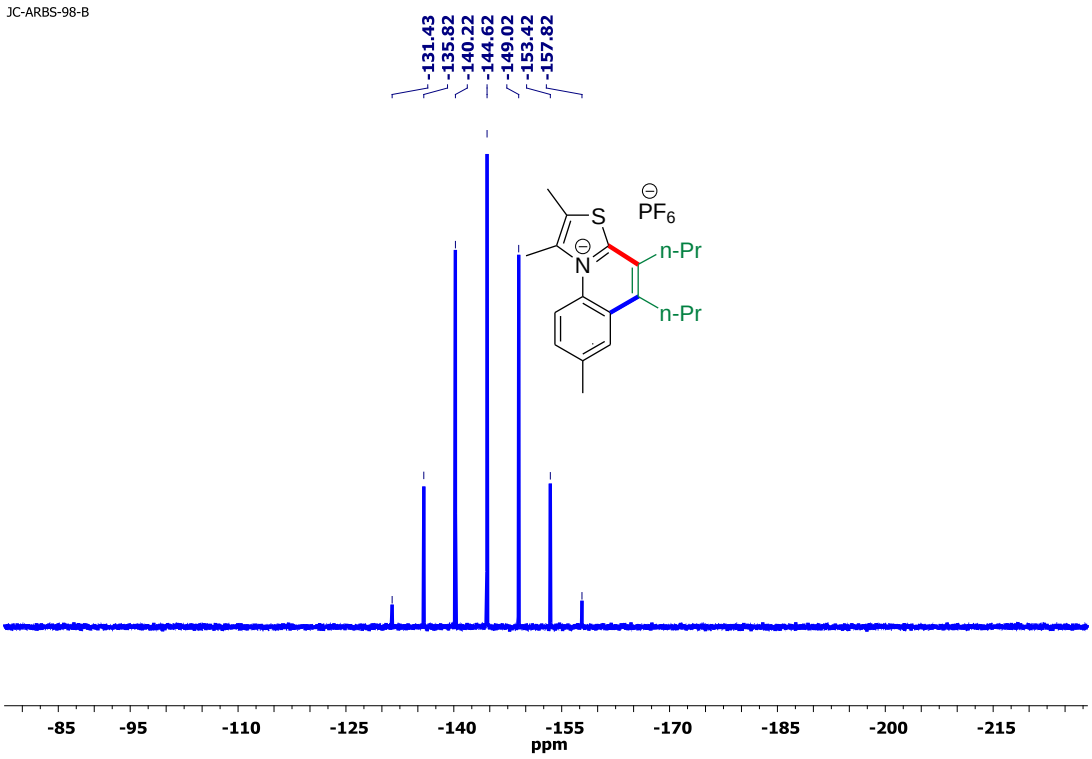
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$).



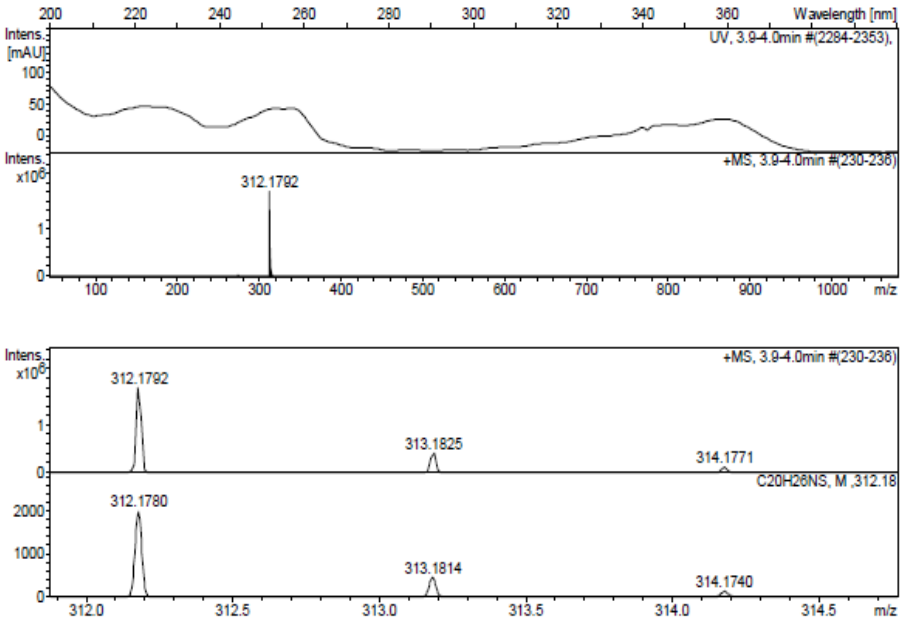
^{13}C{^{1}H} NMR spectrum of **3n** (101 MHz, $CDCl_3$



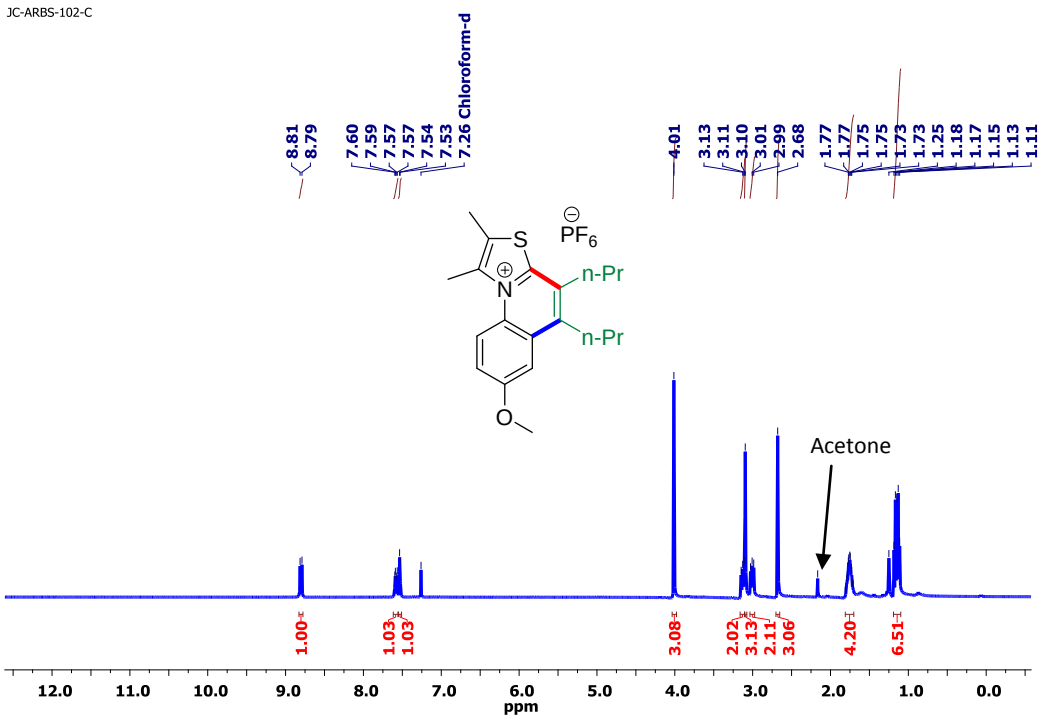
^{19}F NMR spectrum of **3n** (376 MHz, $CDCl_3$).



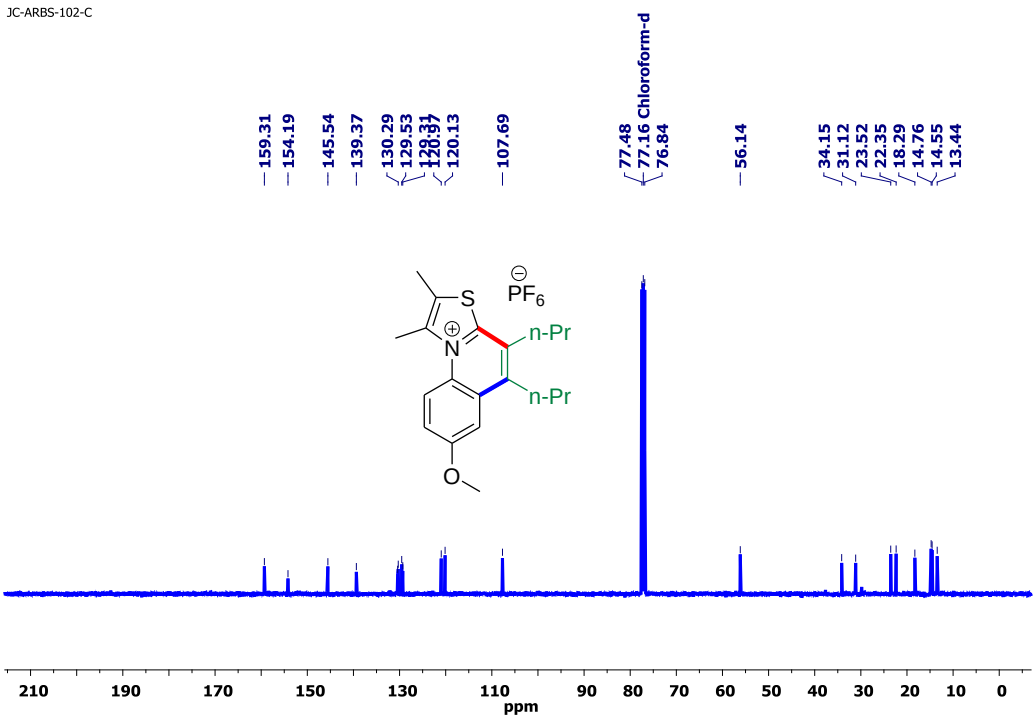
^{31}P NMR spectrum of **3n** (162 MHz, $CDCl_3$)



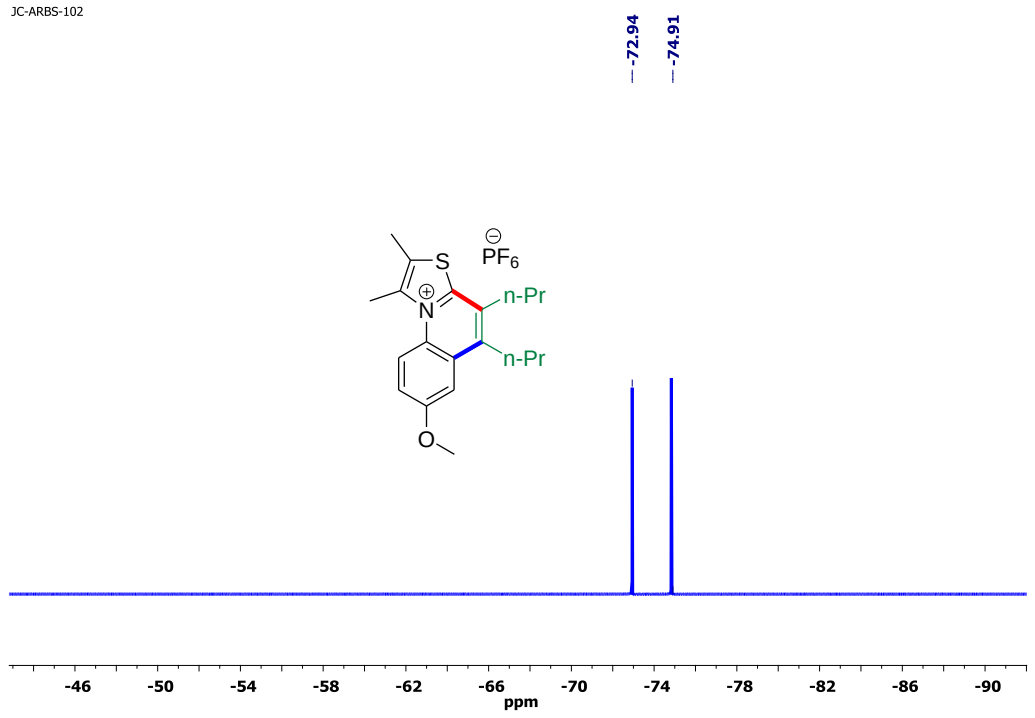
ESI-HRMS (positive ion mode) spectrum of **3n**



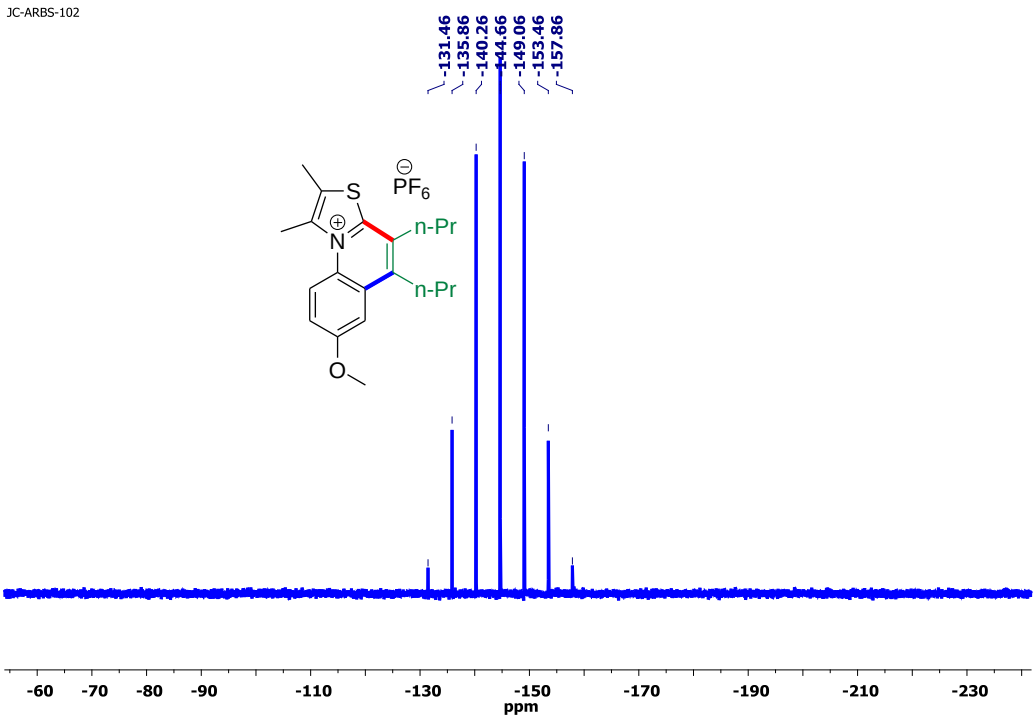
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



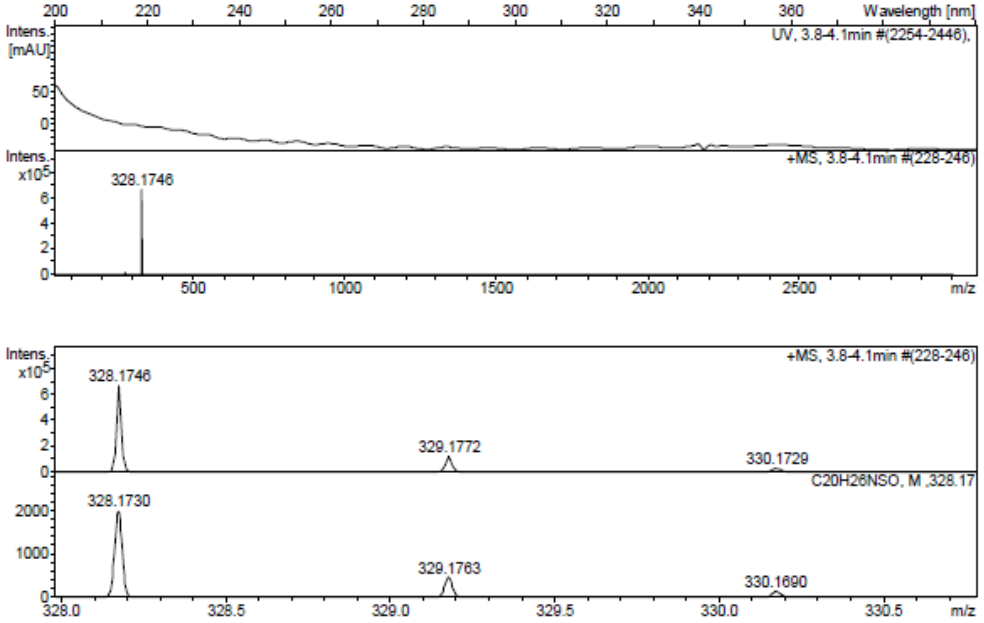
$^{13}C\{^{1}H\}$ NMR spectrum of **3o** (101 MHz, $CDCl_3$)



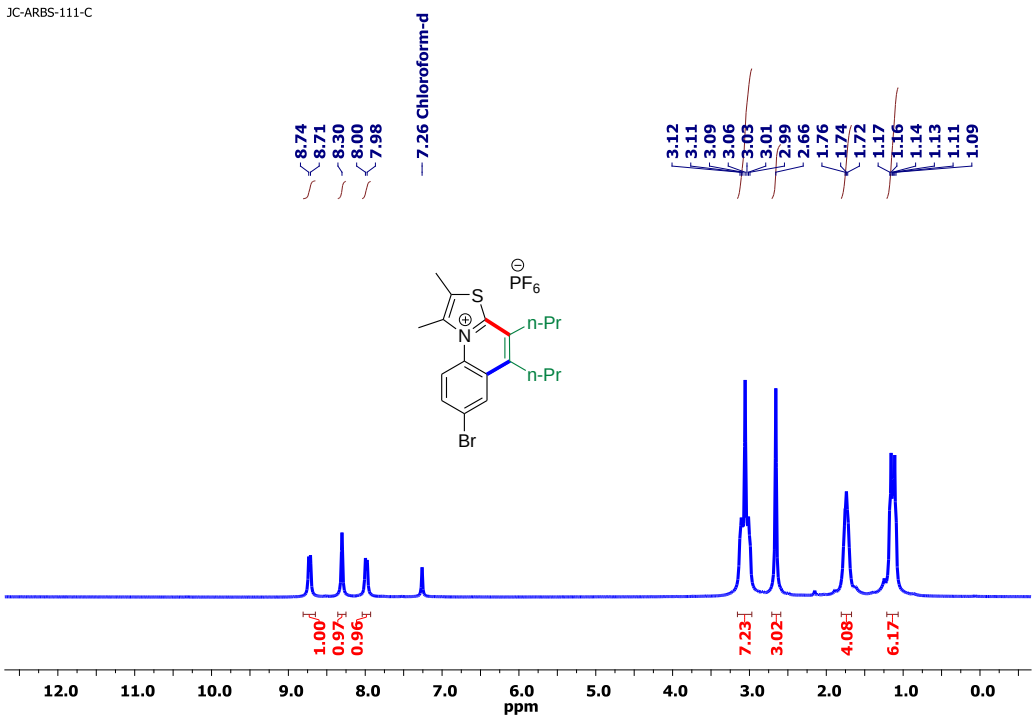
^{19} F NMR spectrum of **3o** (376 MHz, $CDCl_3$).



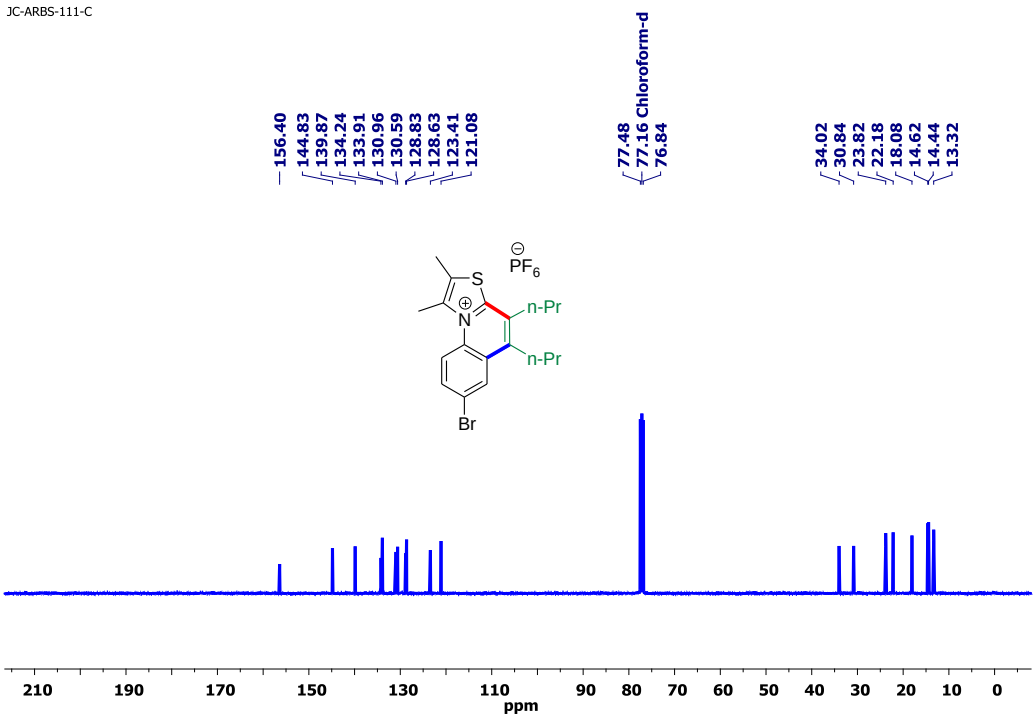
^{31}P NMR spectrum of **3o** (162 MHz, $CDCl_3$).



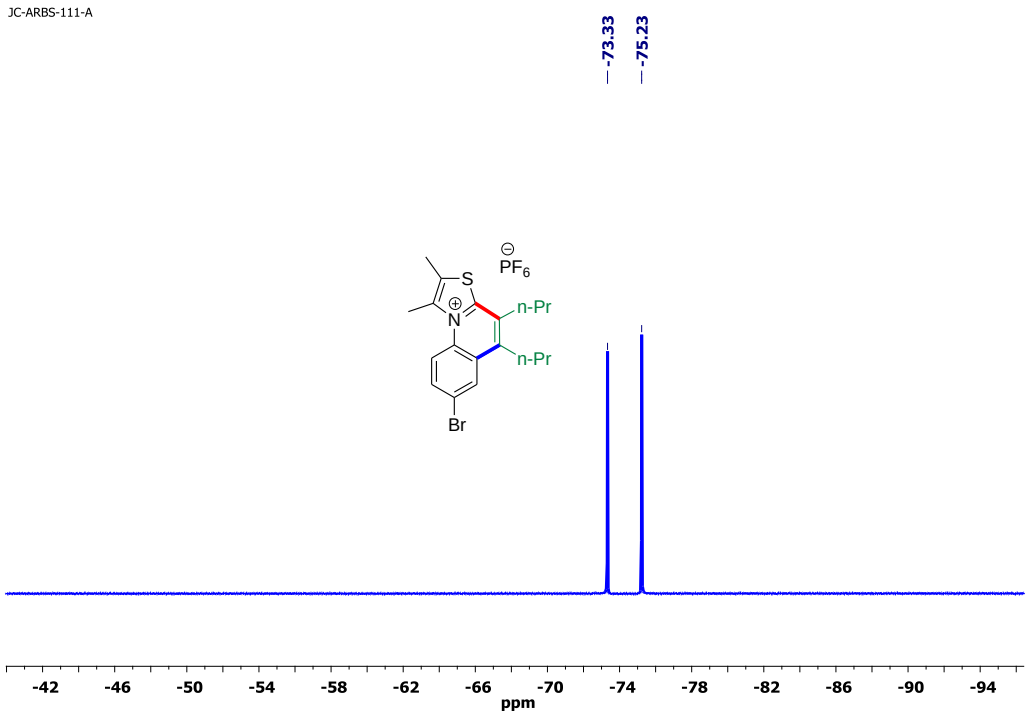
ESI-HRMS (positive ion mode) spectrum of **3o**



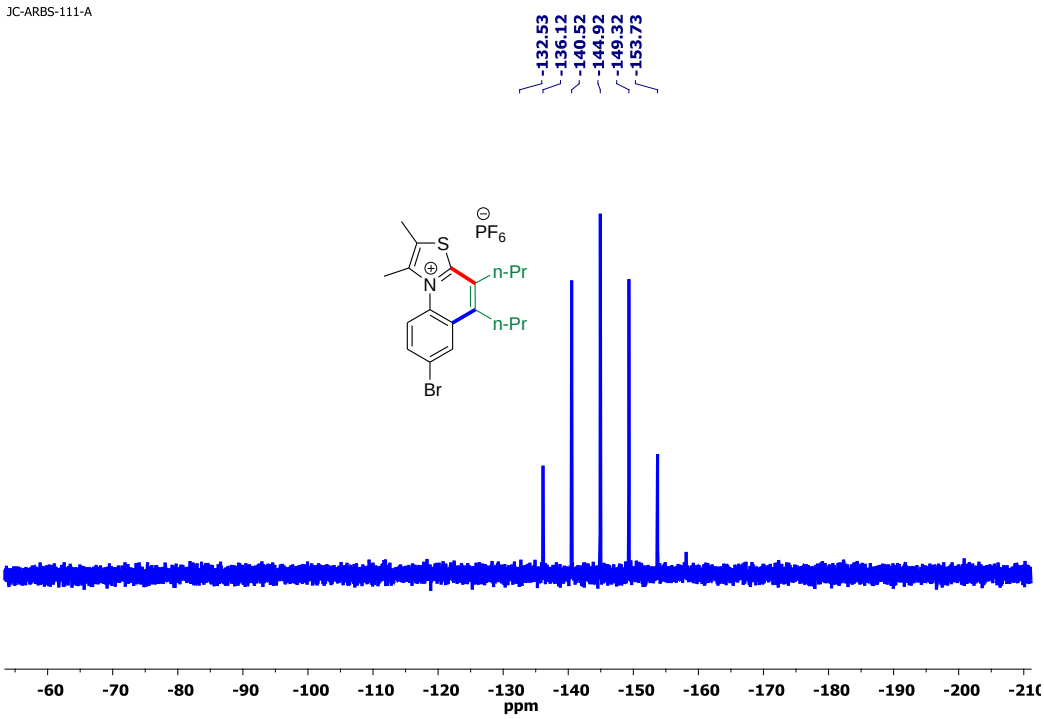
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$).



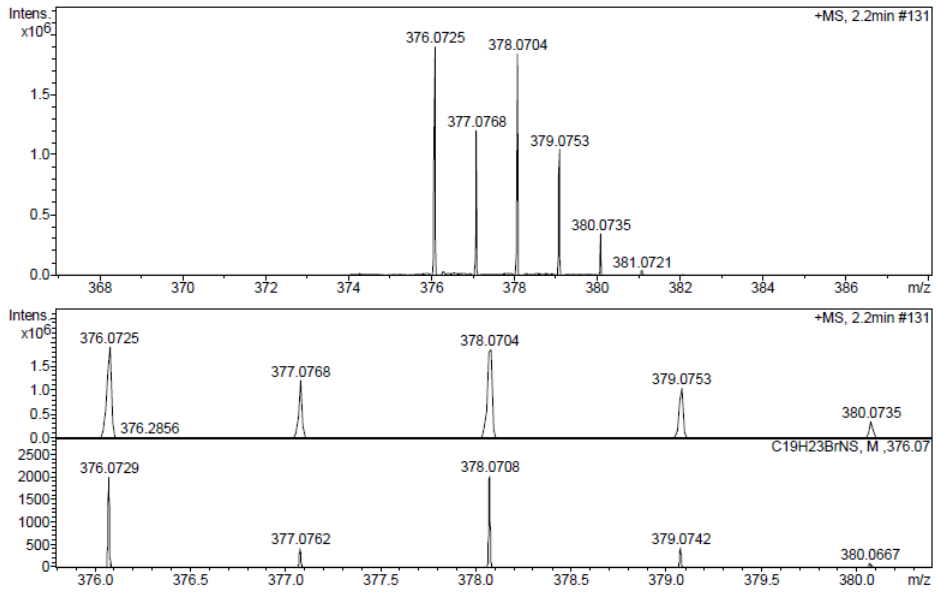
^{13}C{^{1}H} NMR spectrum of **3p** (101 MHz, $CDCl_3$)



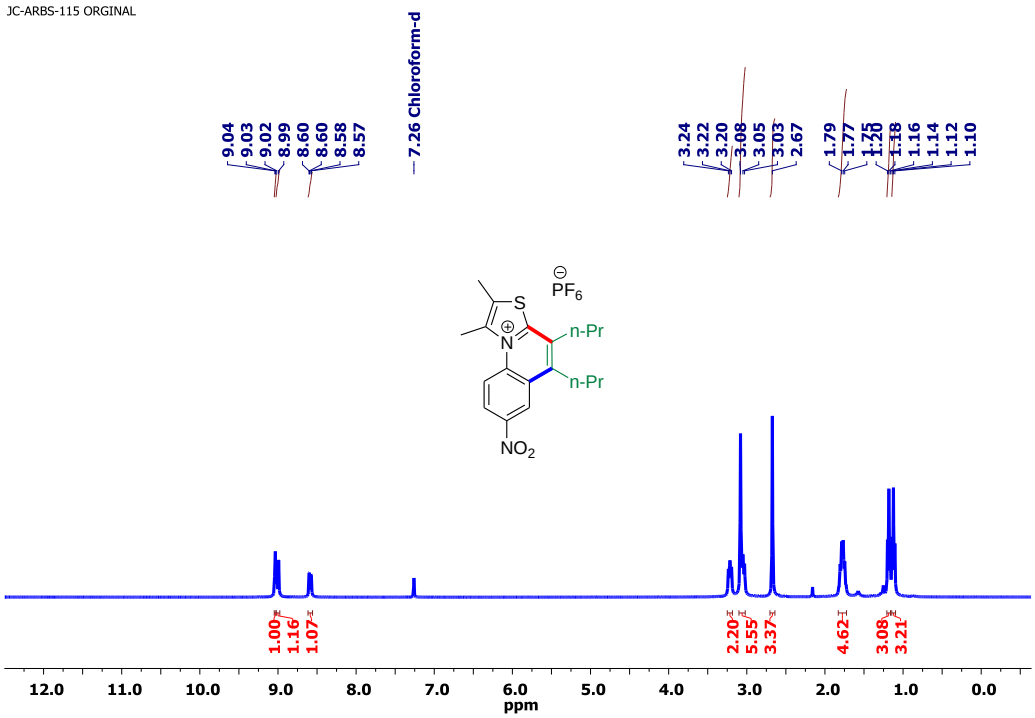
^{19} F NMR spectrum of **3p** (376 MHz, $CDCl_3$).



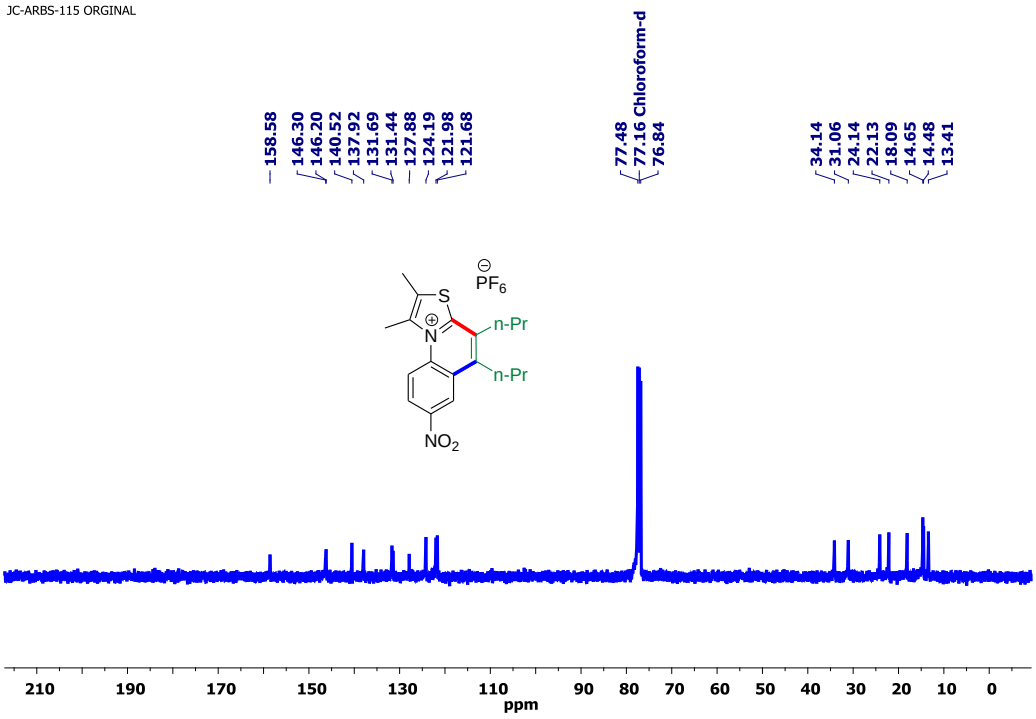
^{31}P NMR spectrum of **3p** (162 MHz, $CDCl_3$).



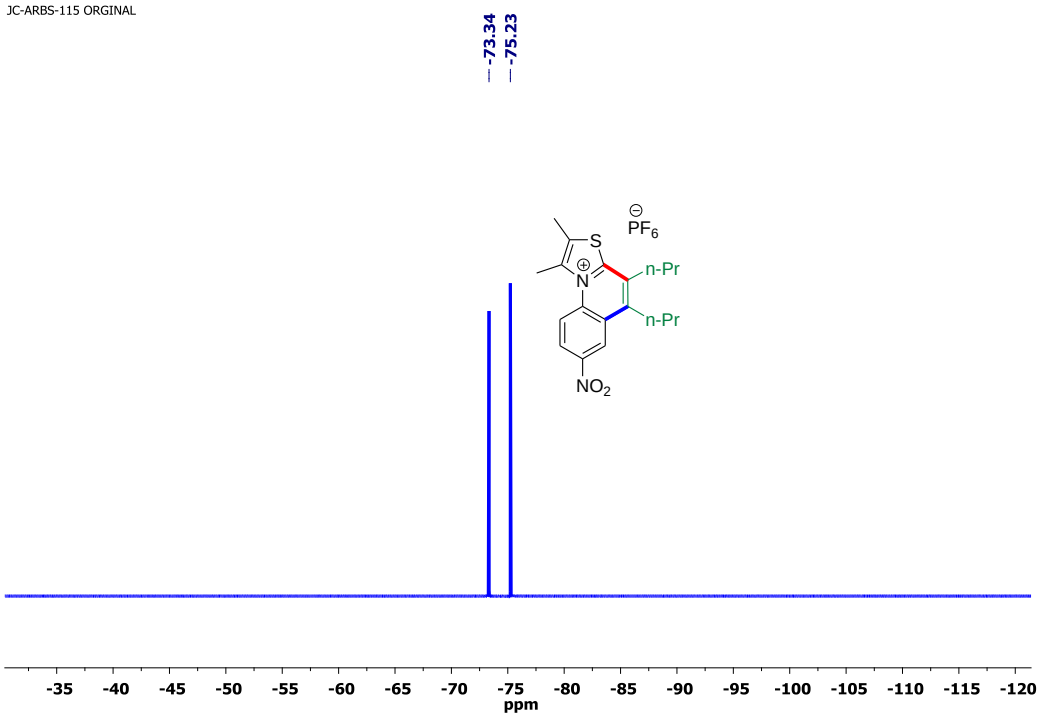
ESI-HRMS (positive ion mode) spectrum of **3p**



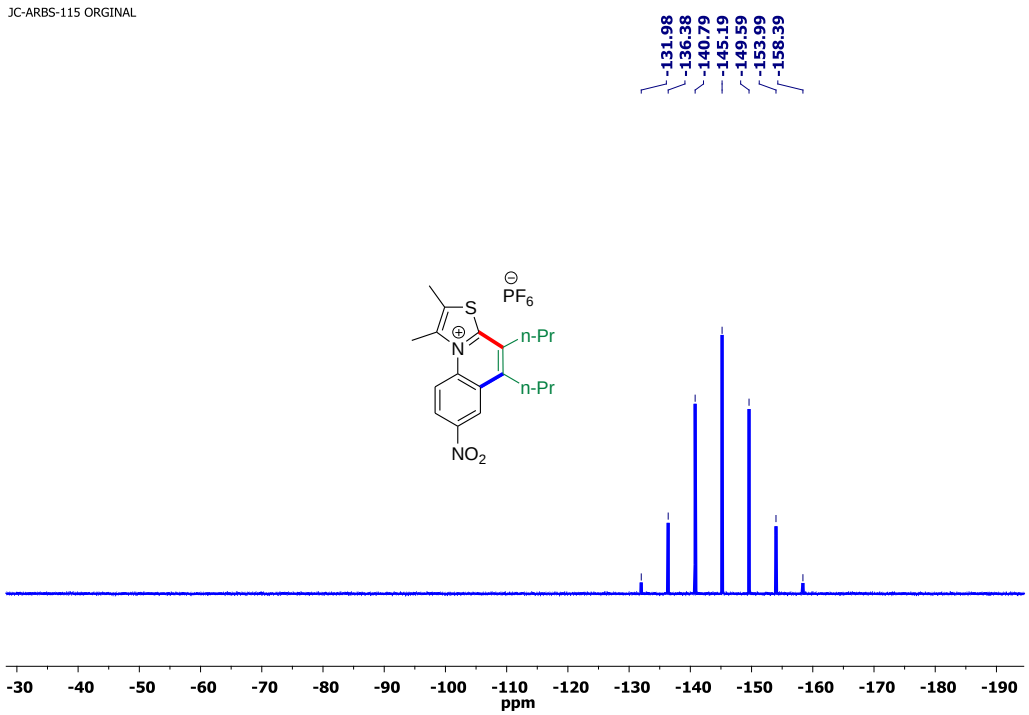
^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)



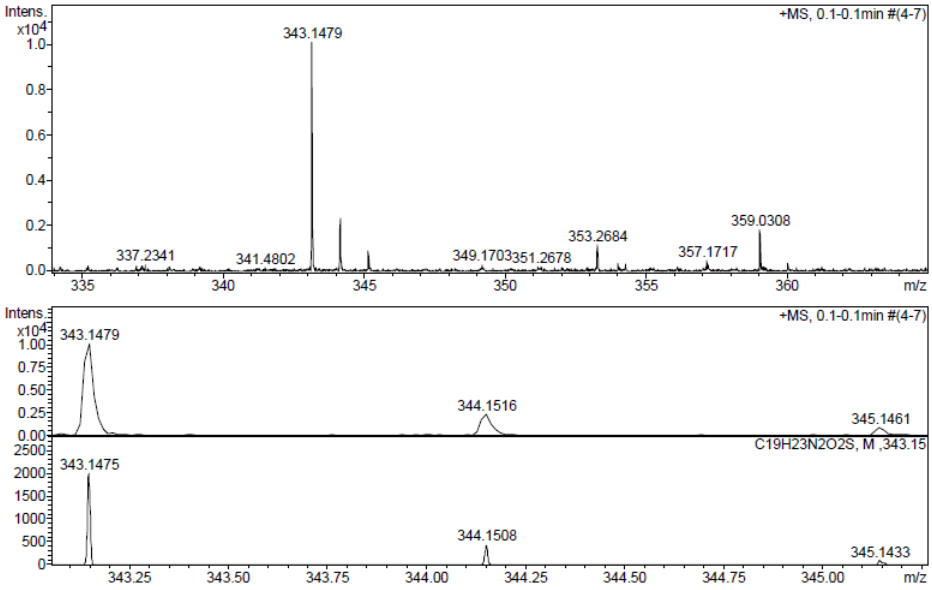
$^{13}C\{^{1}H\}$ NMR spectrum of **3q** (101 MHz, $CDCl_3$)



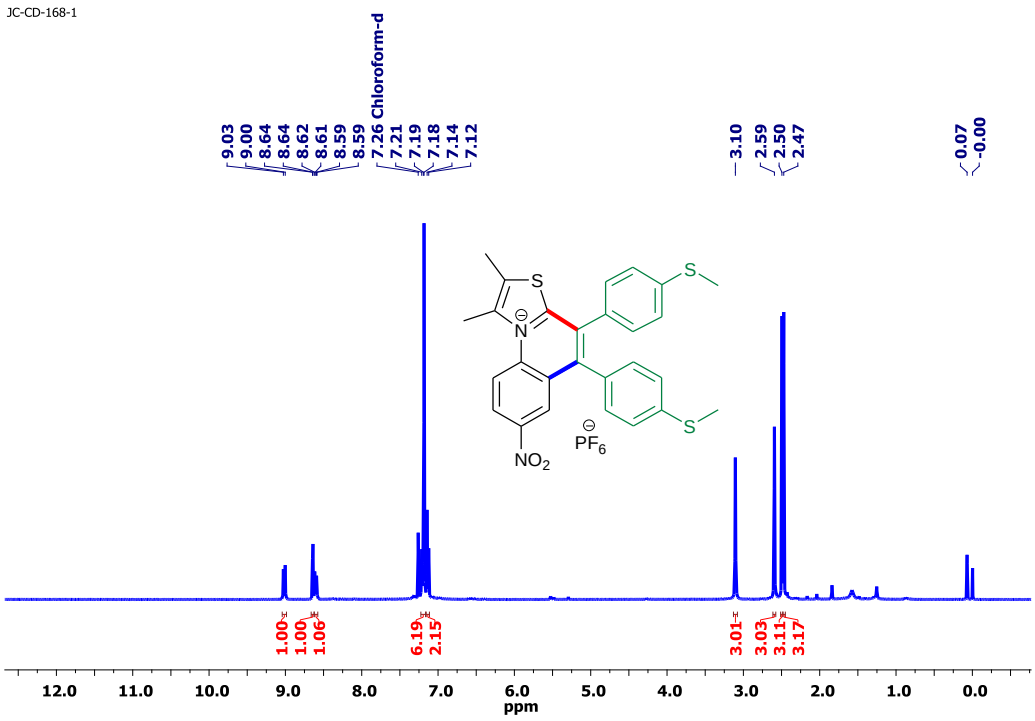
^{19} F NMR spectrum of **3q** (376 MHz, $CDCl_3$).



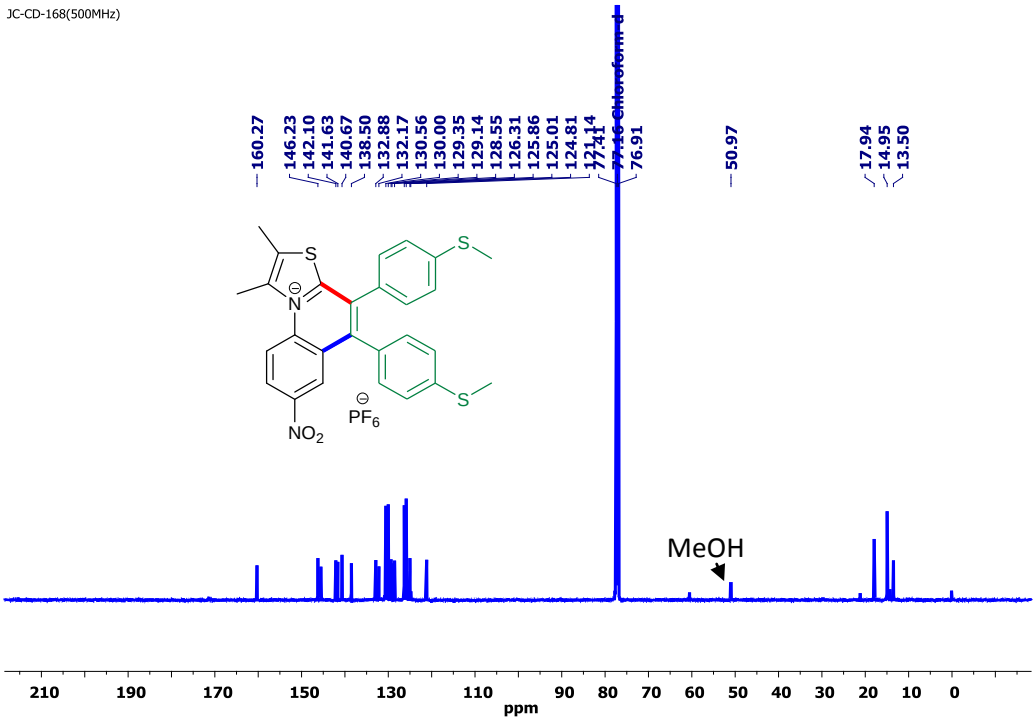
^{31}P NMR spectrum of **3q** (162 MHz, $CDCl_3$)



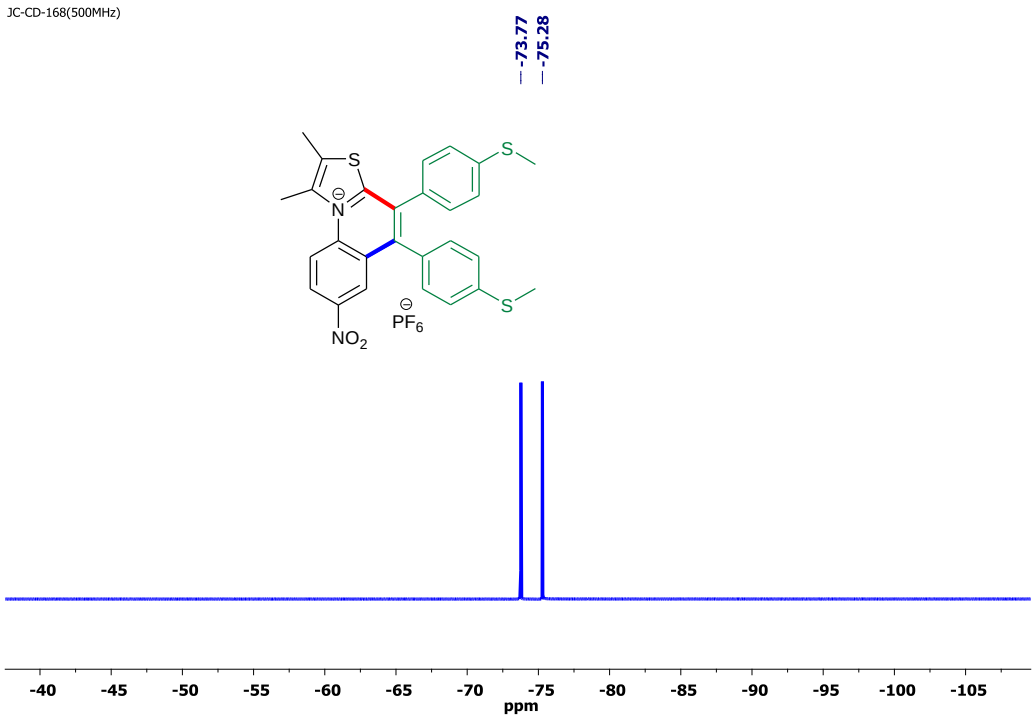
ESI-HRMS (positive ion mode) spectrum of **3q**



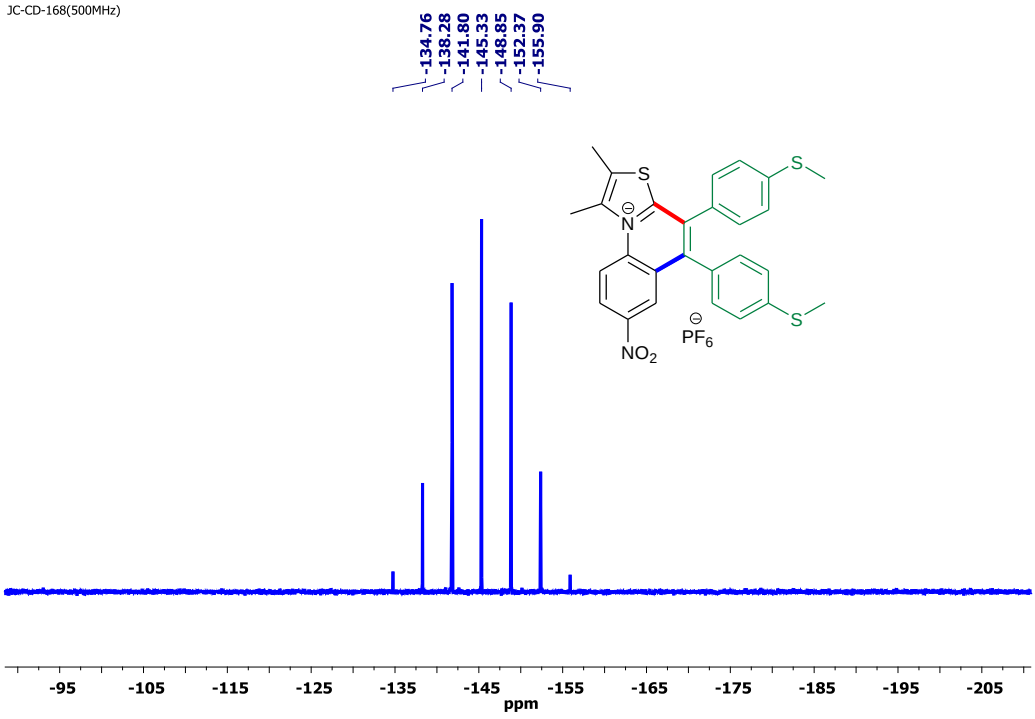
^{1}H NMR spectrum of **3r** (500 MHz, $CDCl_3$).



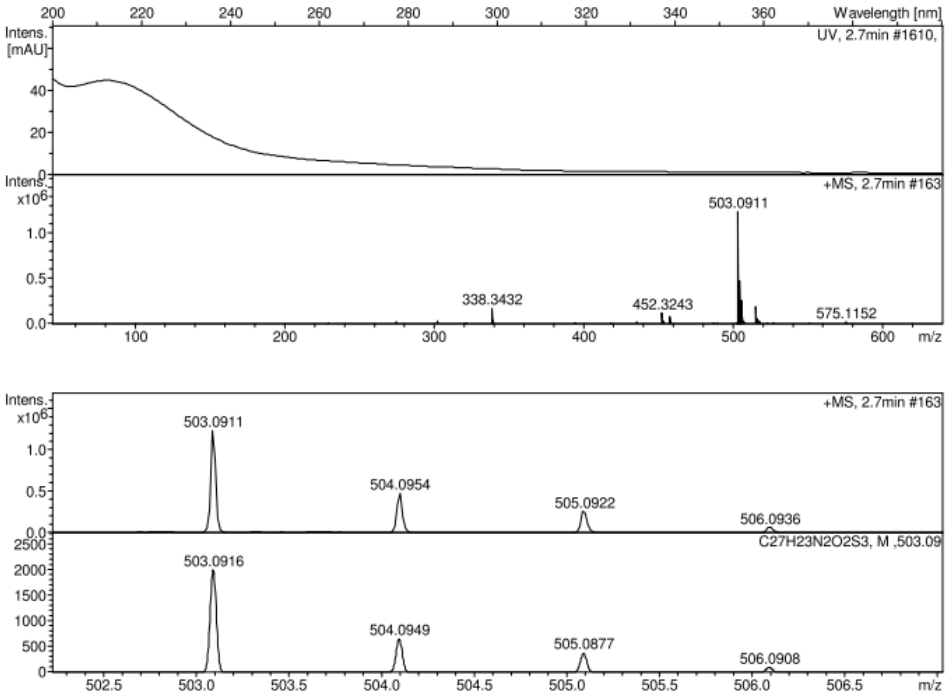
^{13}C{^{1}H} NMR spectrum of **3r** (125 MHz, $CDCl_3$).



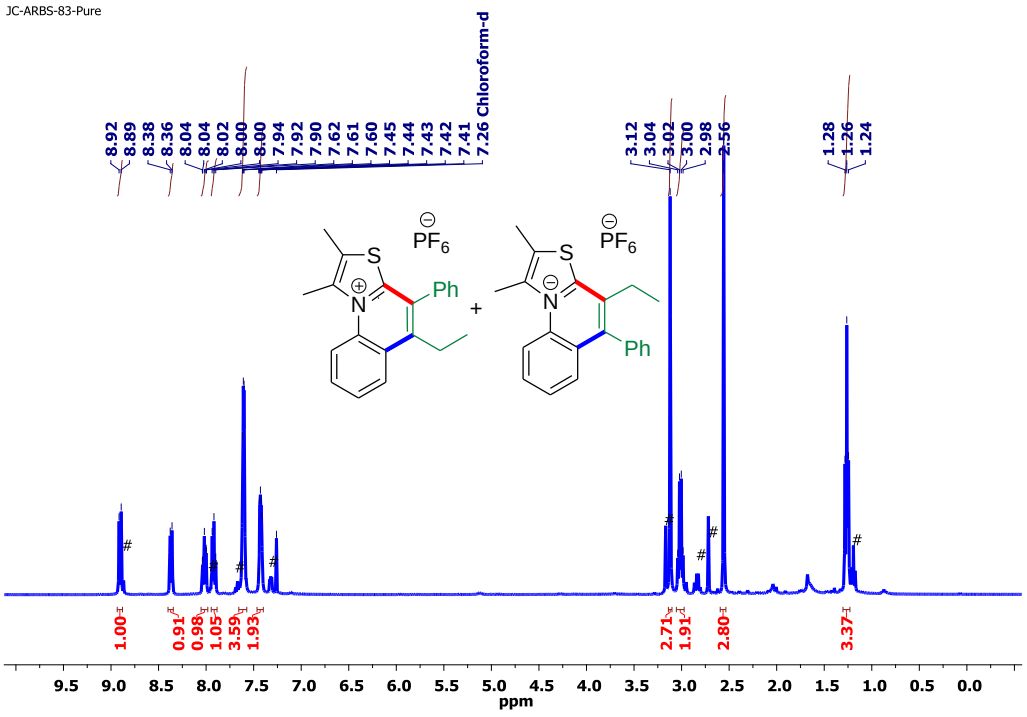
^{19}F NMR spectrum of **3r** (471 MHz, CD_3CN)



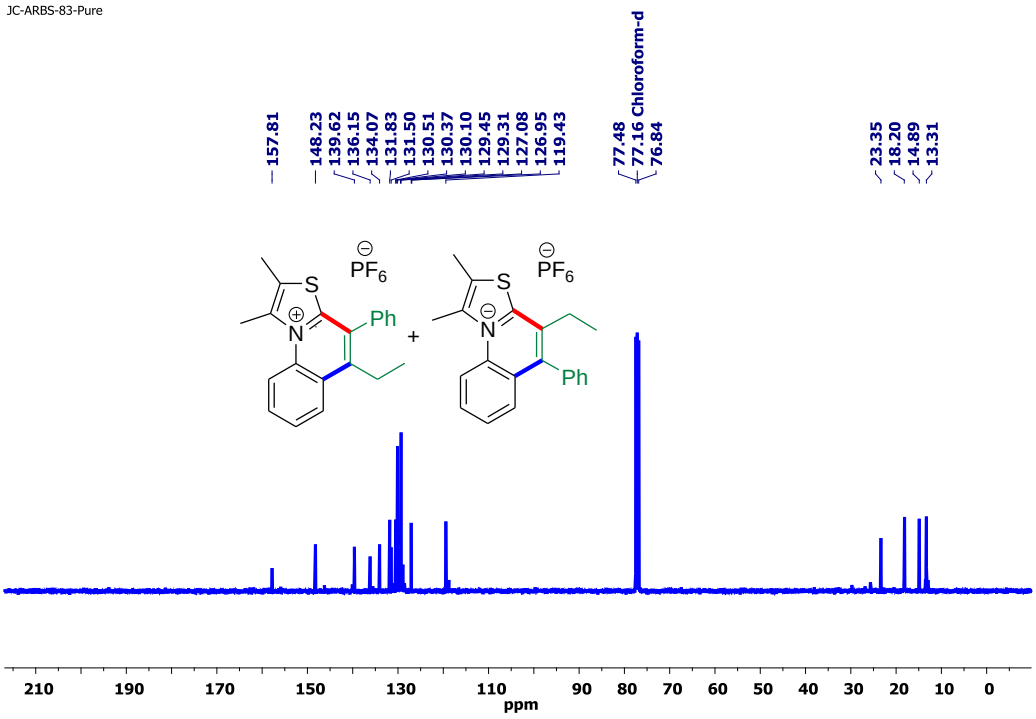
^{31}P NMR spectrum of **3r** (202 MHz, CD_3CN)



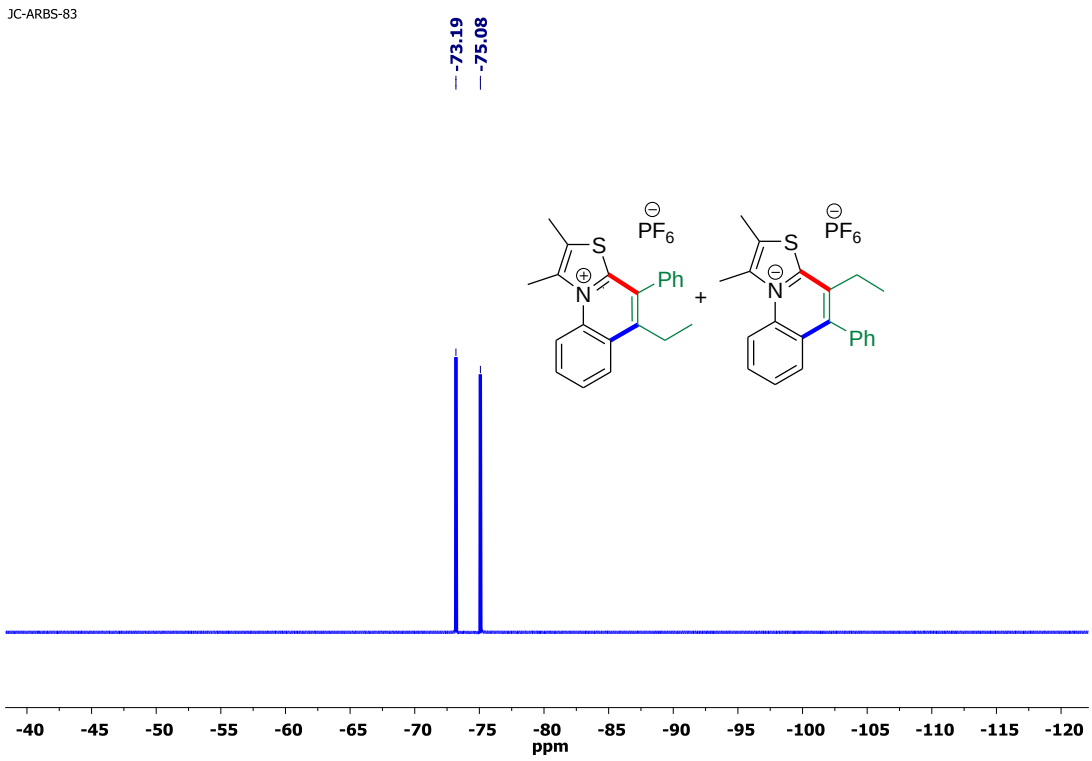
ESI-HRMS (positive ion mode) spectrum of **3r**



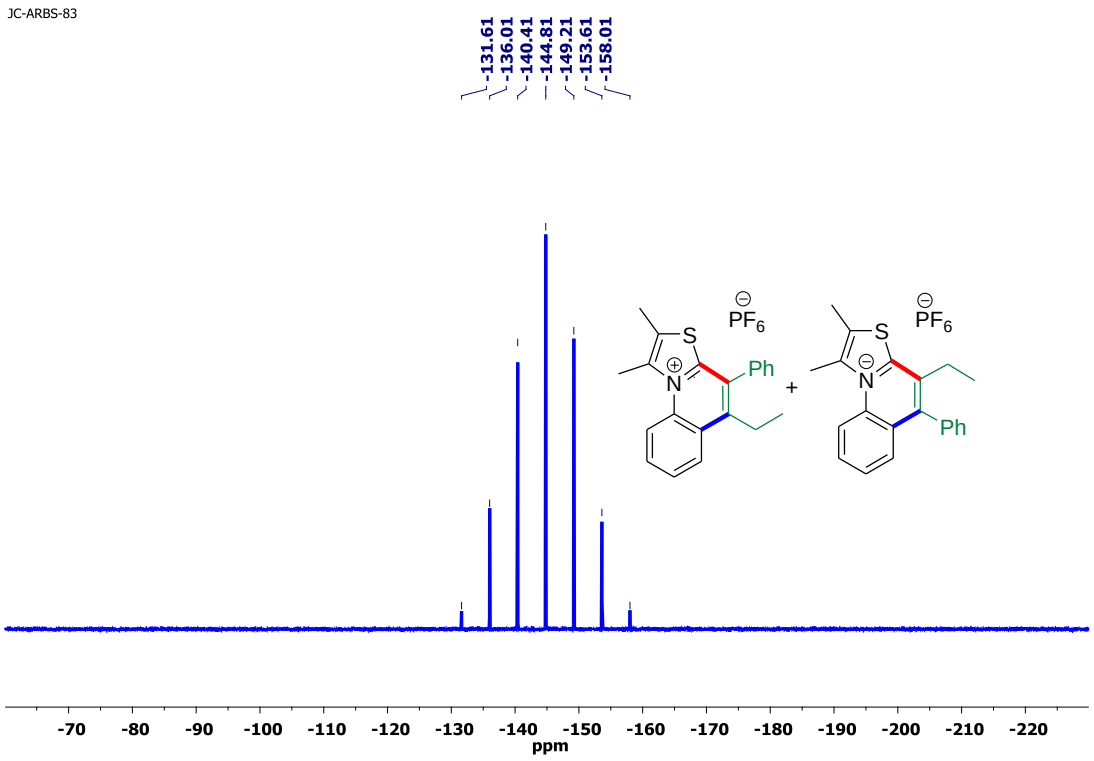
^{1}H NMR spectrum of **3s** + **3s'** (400 MHz, $CDCl_3$). (# marked are for protons of **3s'**)



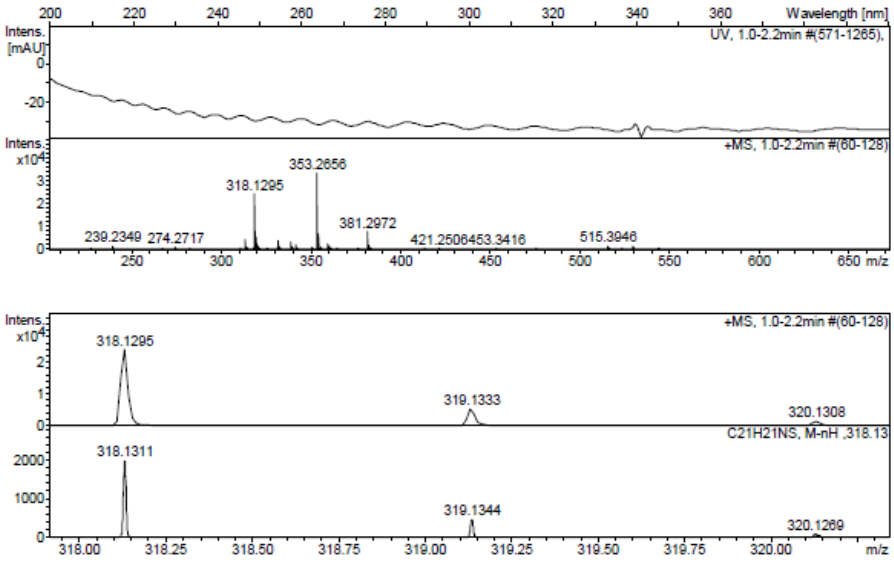
$^{13}C\{^{1}H\}$ NMR spectrum of **3s+ 3s'** (101 MHz, $CDCl_3$)



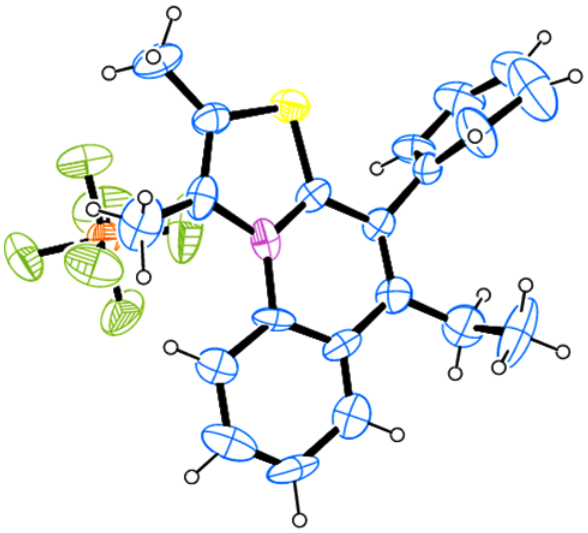
^{19} F NMR spectrum of **3s+ 3s'** (376 MHz, $CDCl_3$).



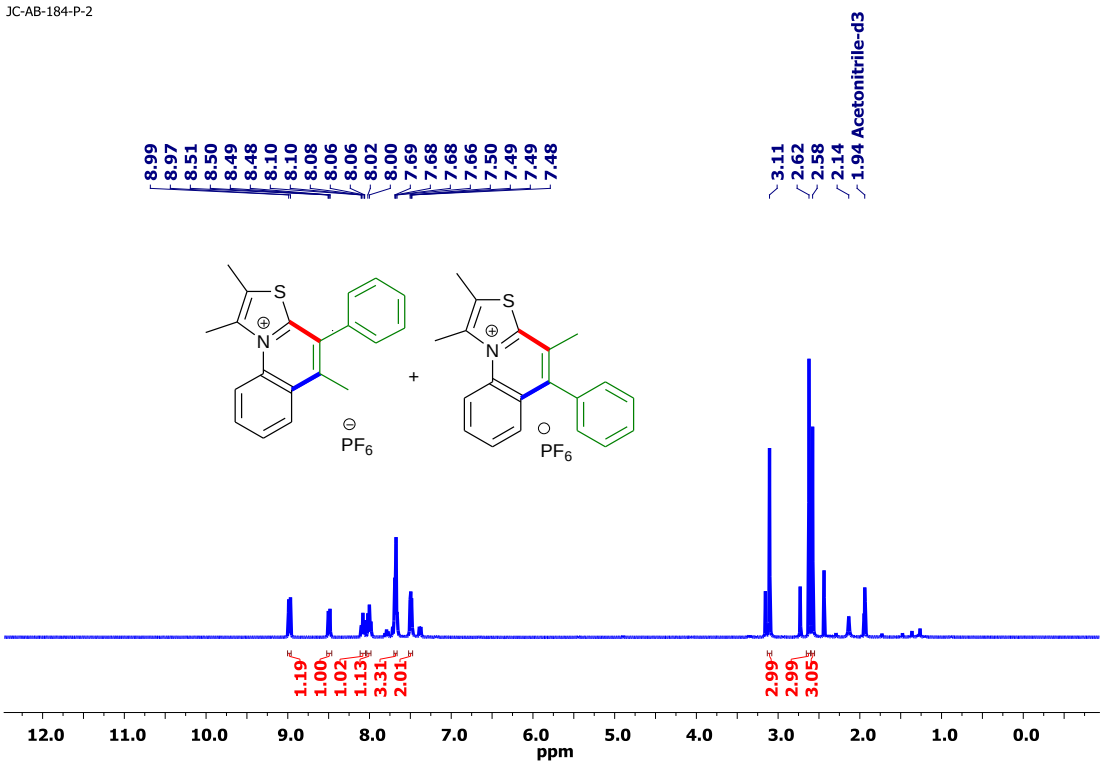
^{31}P NMR spectrum of **3s+ 3s'** (162 MHz, $CDCl_3$)



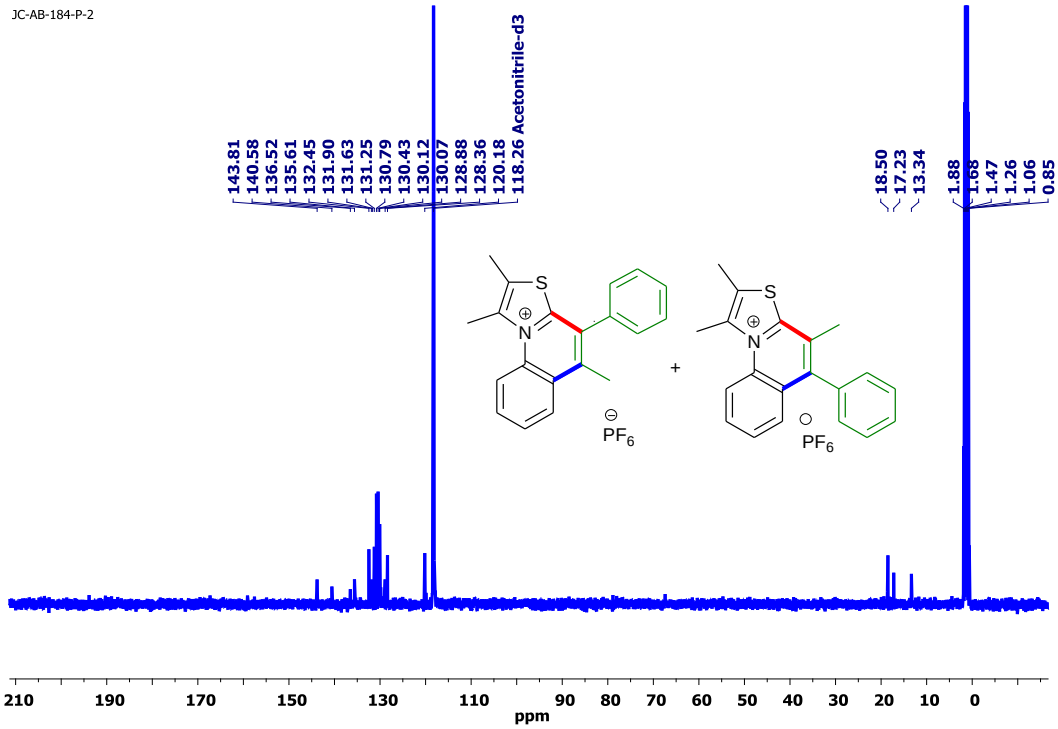
ESI-HRMS (positive ion mode) spectrum of **3s+ 3s'**



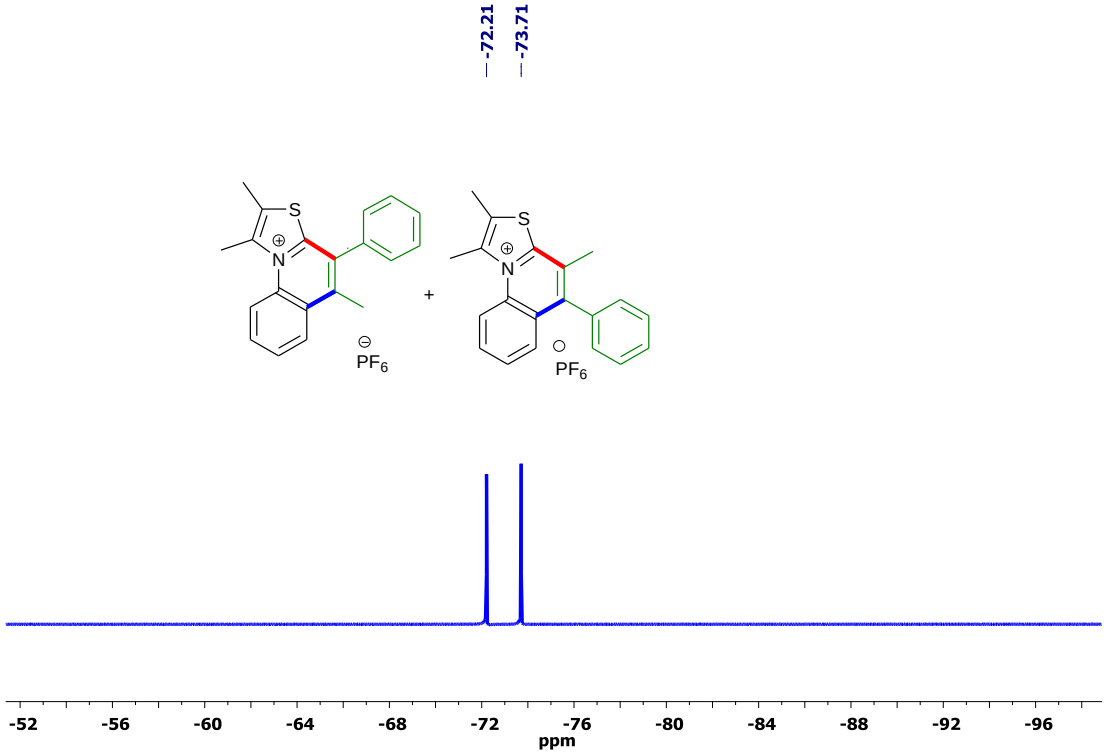
Single crystal XRD structure of **3s (30% probability ellipsoid)**



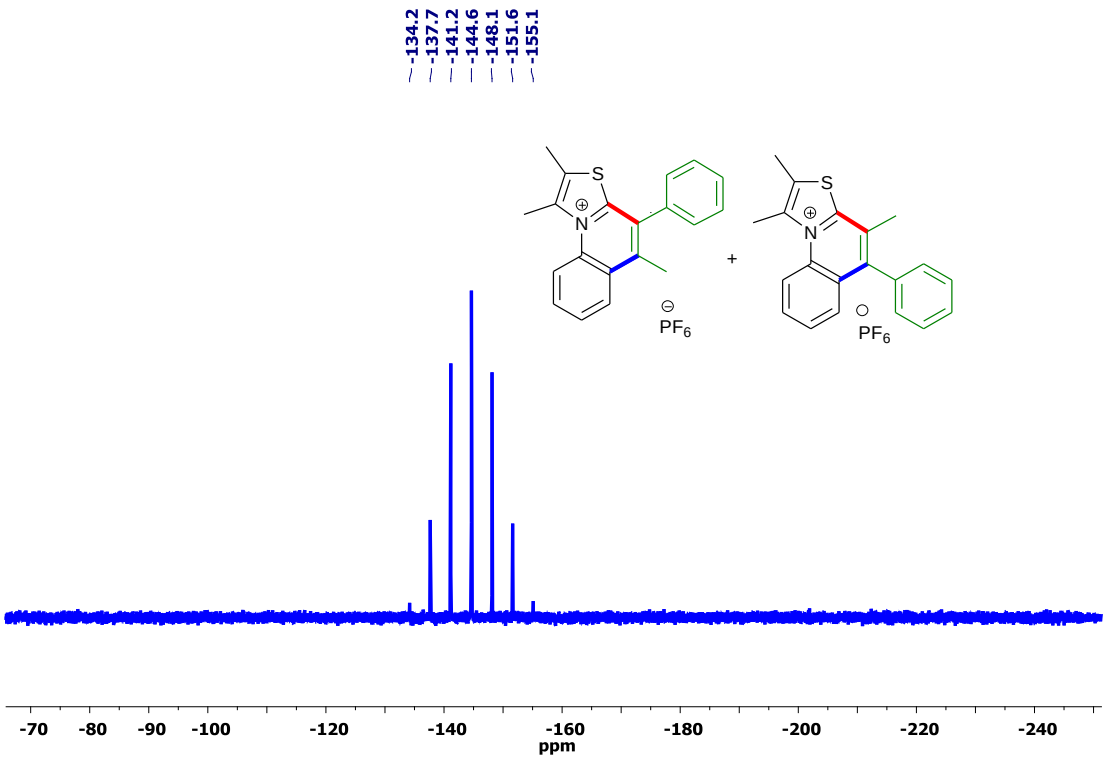
^{1}H NMR spectrum of **3t+ 3t'** (400 MHz, CD_3CN)



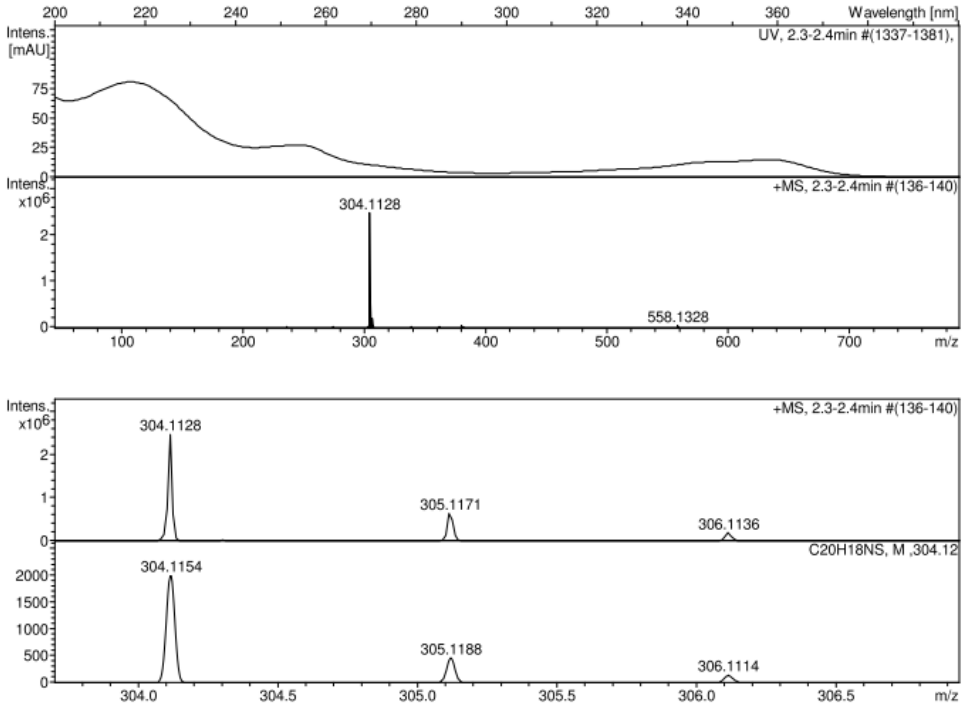
$^{13}C\{^{1}H\}$ NMR spectrum of **3t+3t'** (100 MHz, CD_3CN)



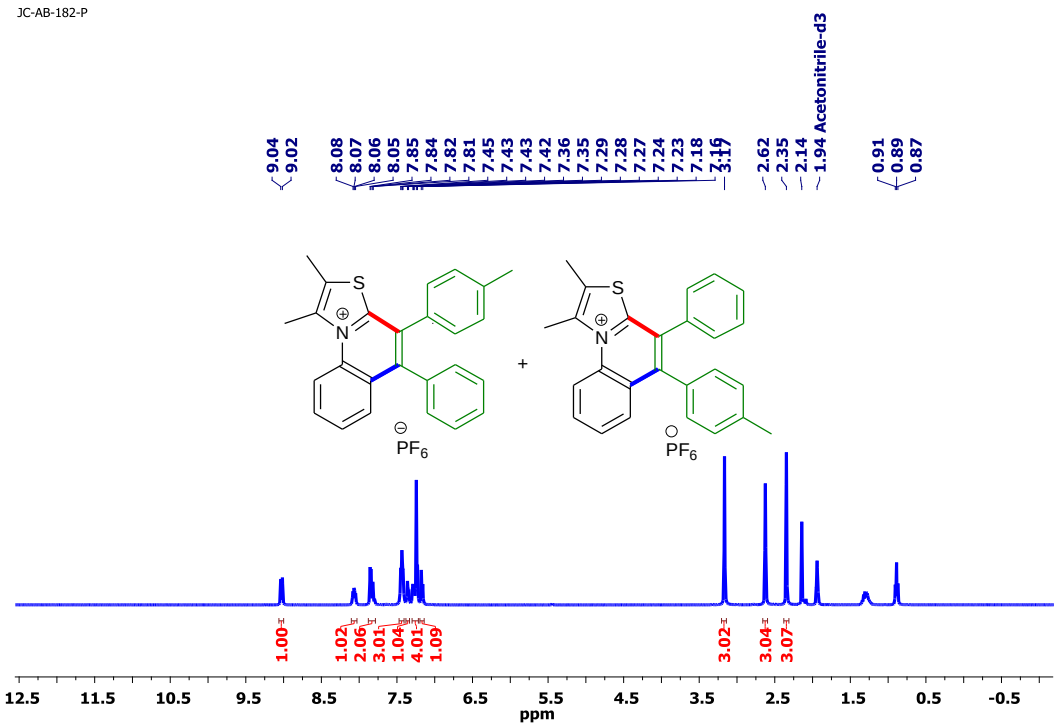
^{19}F NMR spectrum of **3t+3t'** (471 MHz, CD_3CN)



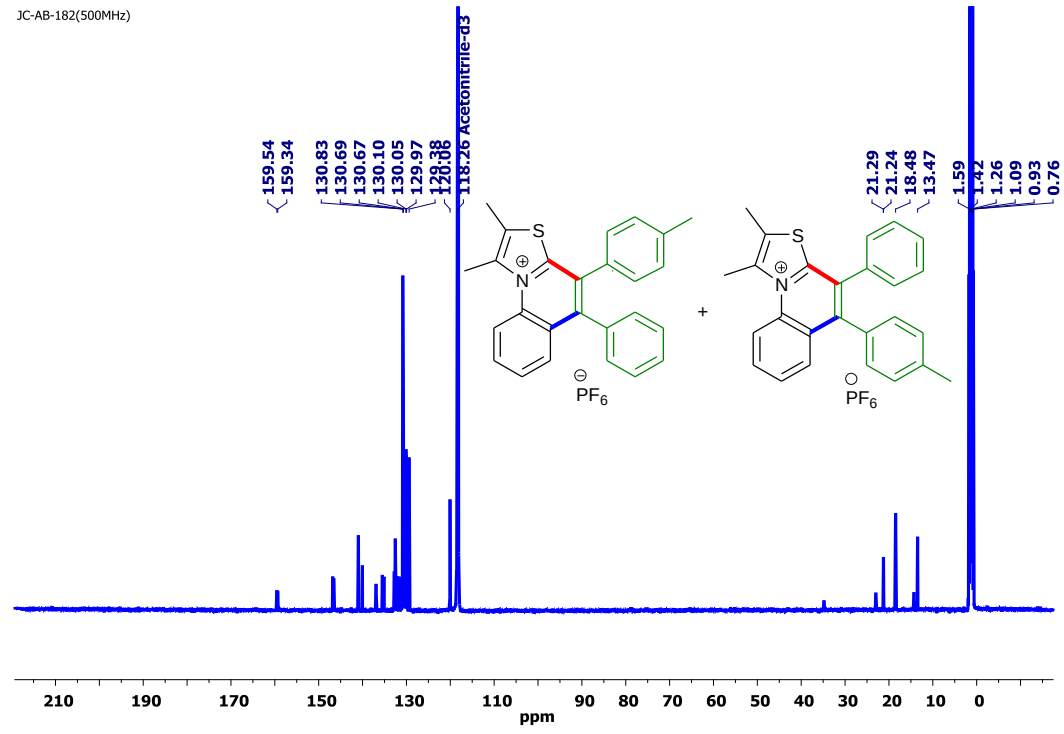
$^{31}P\{^{1}H\}$ NMR spectrum of **3t+3t'** (202 MHz, CD_3CN)



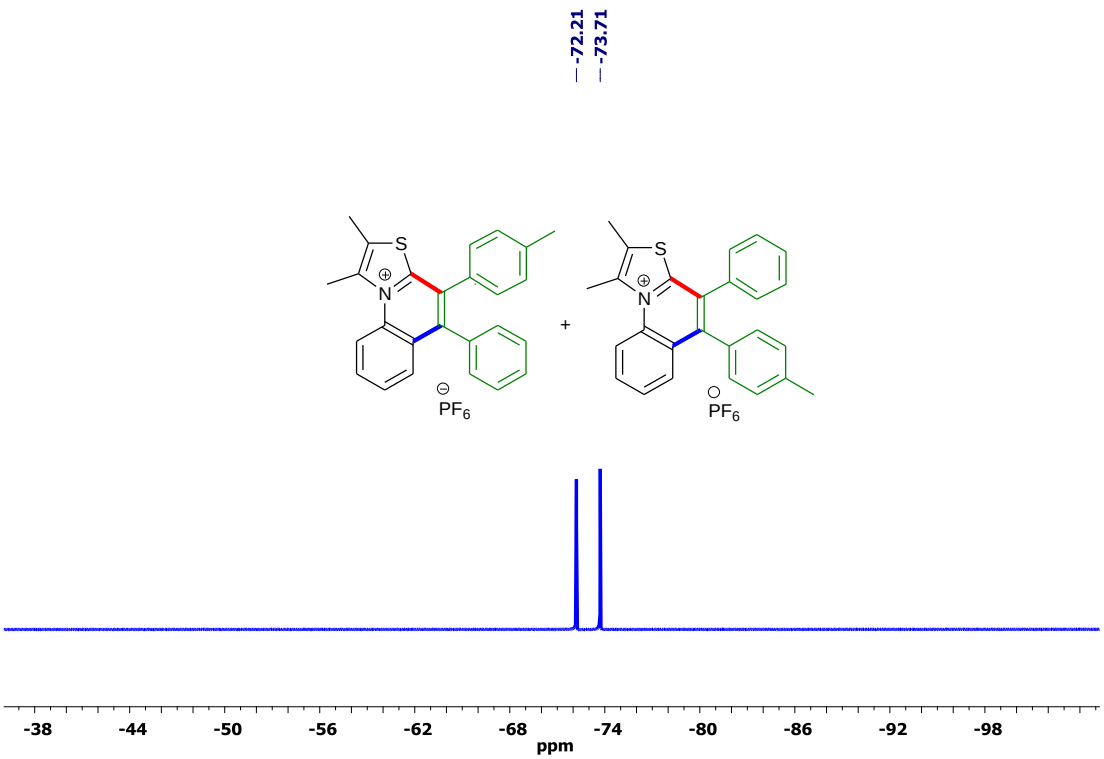
ESI-HRMS (positive ion mode) spectrum of **3t+ 3t'**



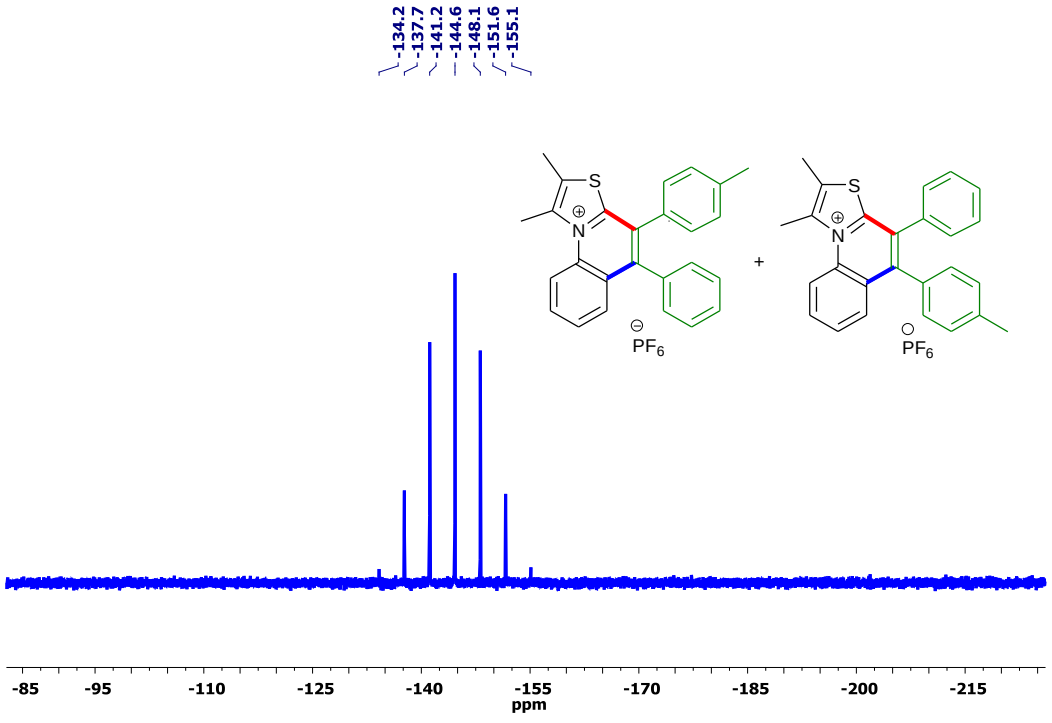
^{1}H NMR spectrum of **3u** + **3u'** (400 MHz, CD_3CN)



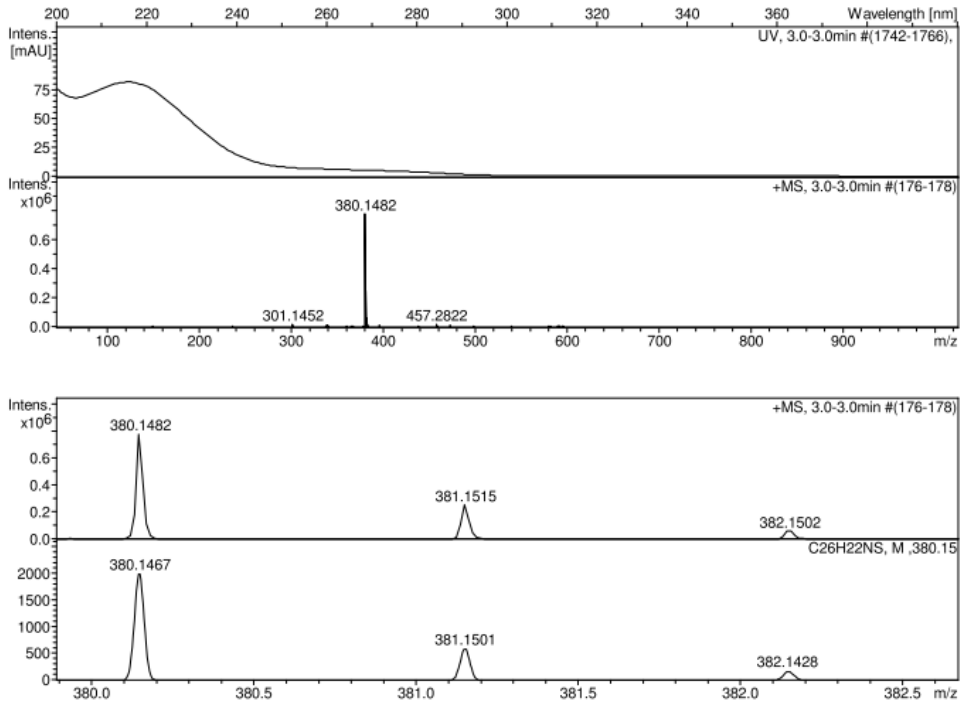
^{13}C{^{1}H} NMR spectrum of **3u** + **3u'** (126 MHz, CD_3CN)



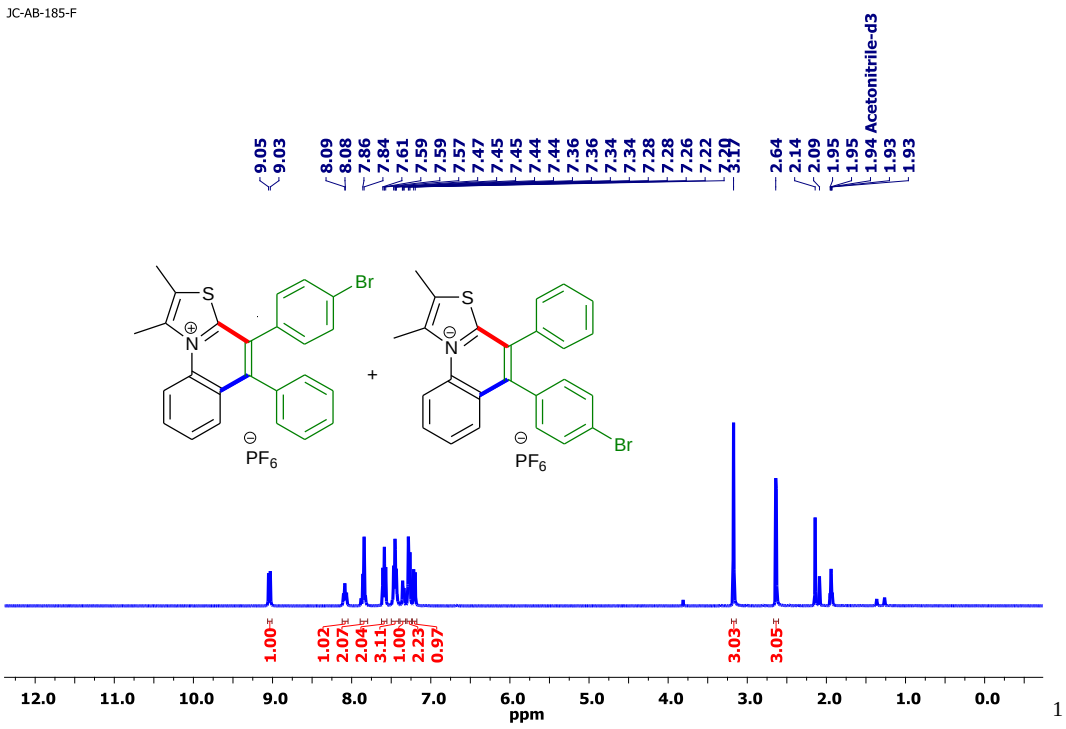
^{19}F NMR spectrum of **3u**+**3u'** (471 MHz, CD_3CN)



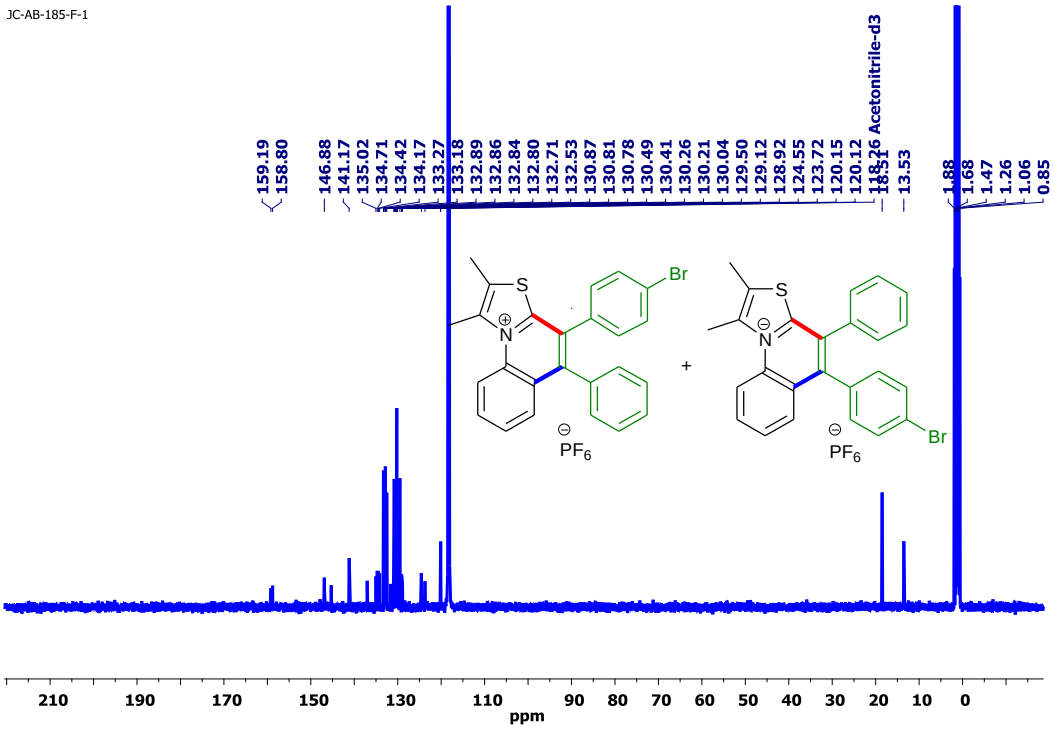
^{31}P NMR spectrum of **3u**+**3u'** (202 MHz, CD_3CN)



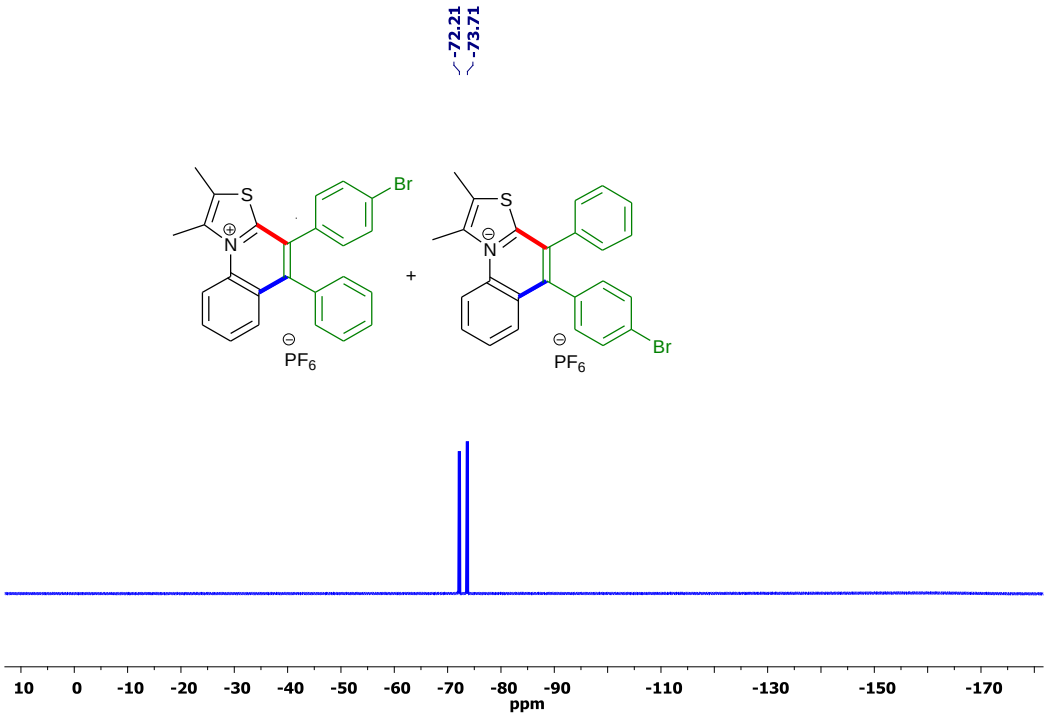
ESI-HRMS (positive ion mode) spectrum of **3u**+ **3u'**



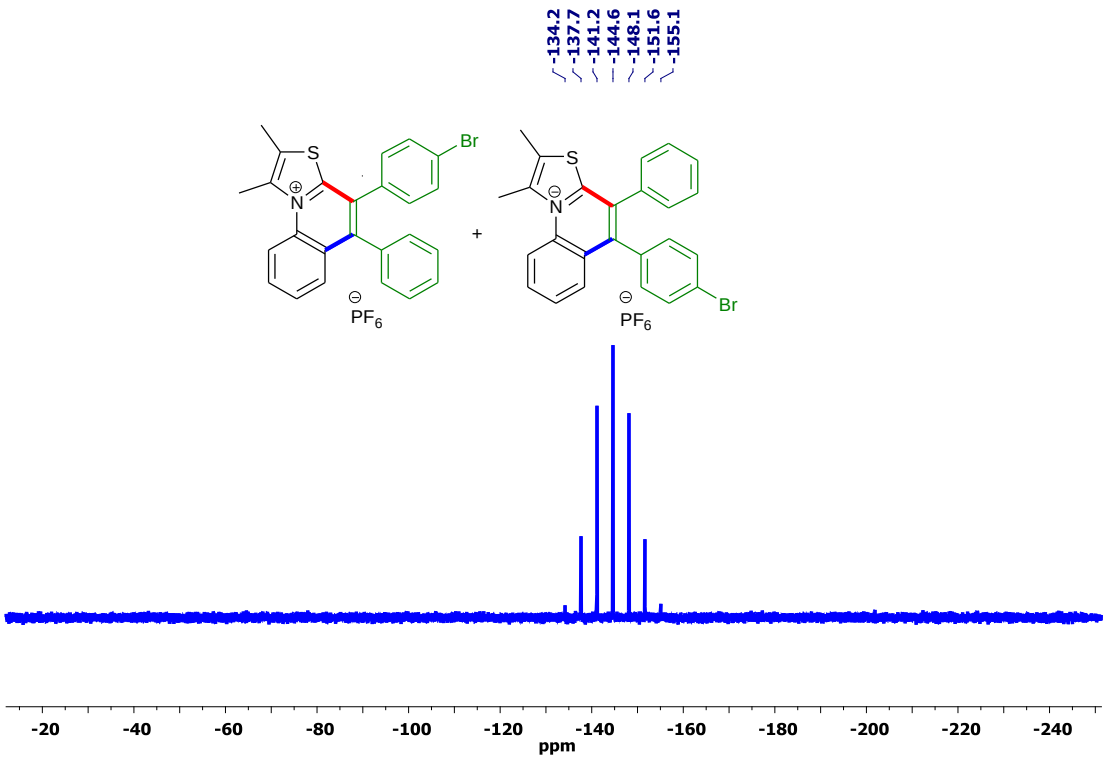
^{1}H NMR spectrum of **3v**+ **3v'** (400 MHz, CD_3CN)



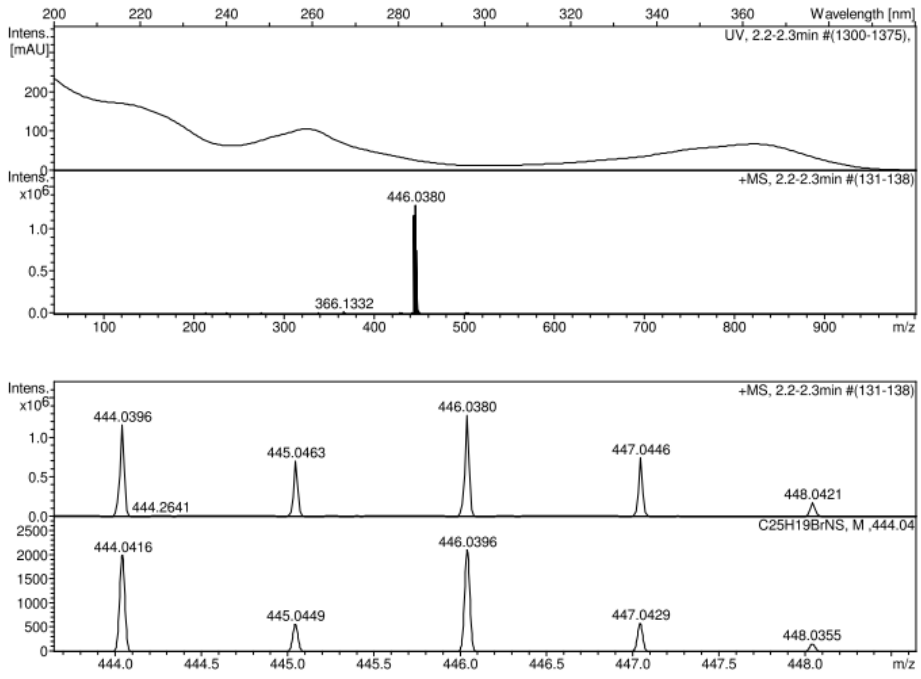
$^{13}C\{^{1}H\}$ NMR spectrum of **3v** + **3v'** (400 MHz, CD_3CN)



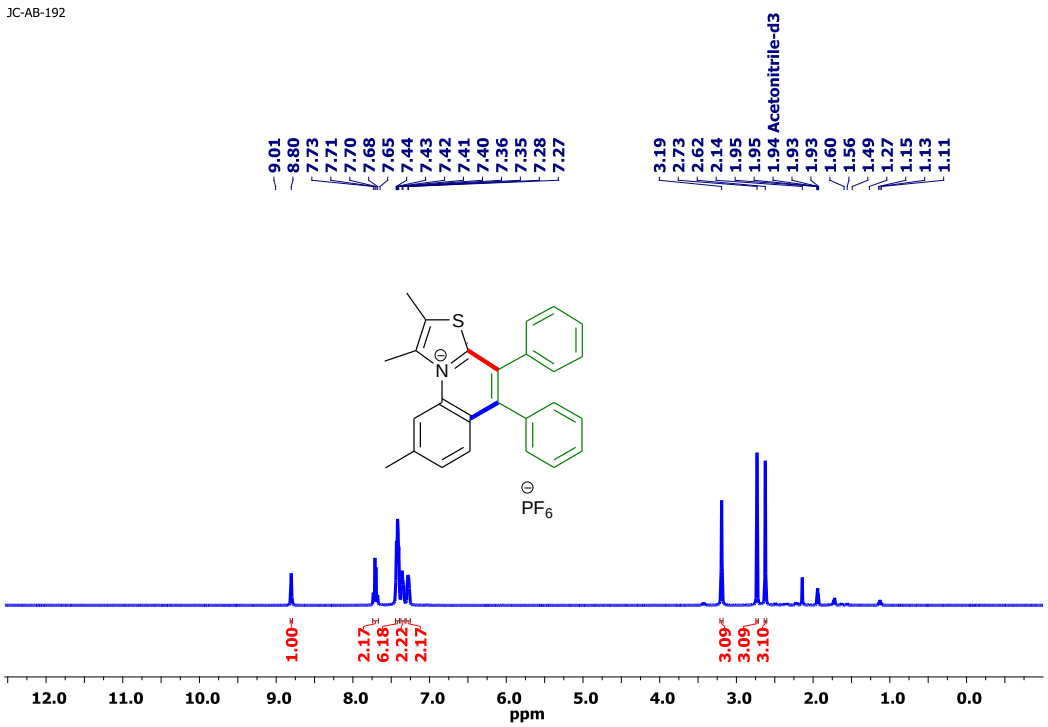
^{19}F NMR spectrum of **3v+ 3v'** (471 MHz, CD_3CN)



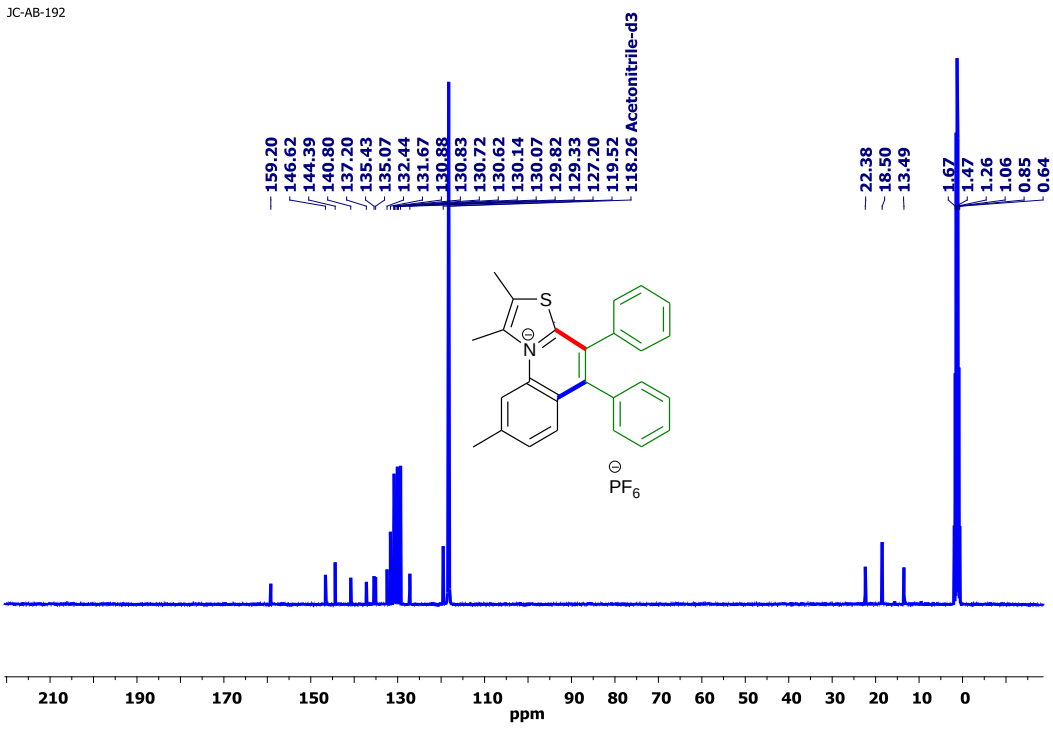
^{31}P NMR spectrum of **3v+ 3v'** (202 MHz, CD_3CN)



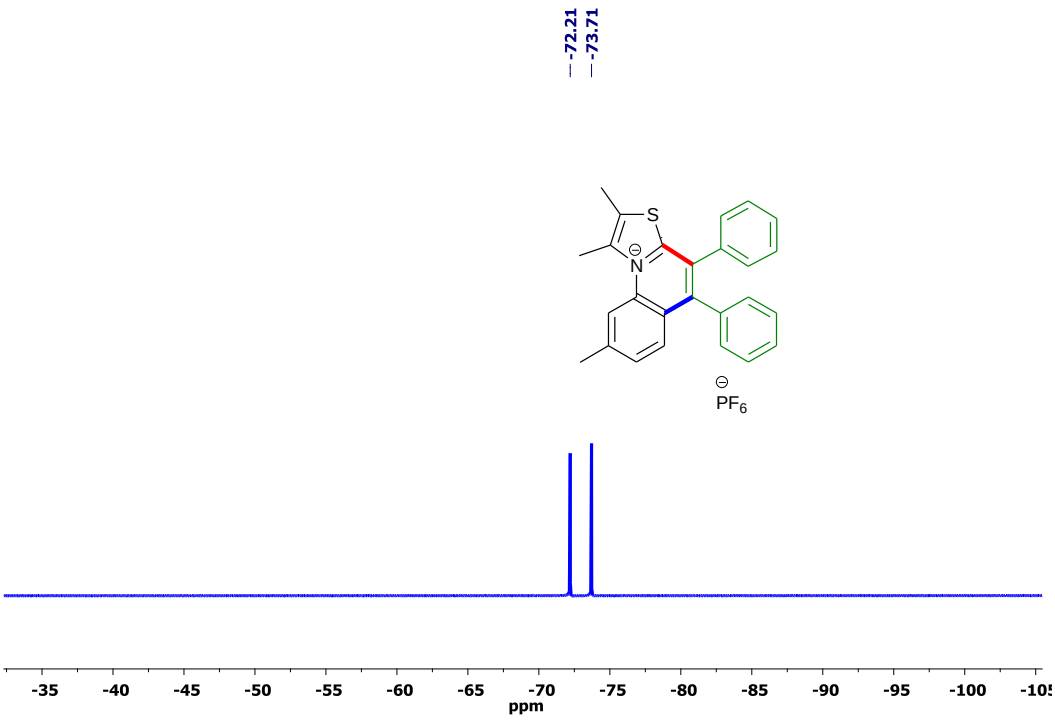
ESI-HRMS (positive ion mode) spectrum of **3v+ 3v'**



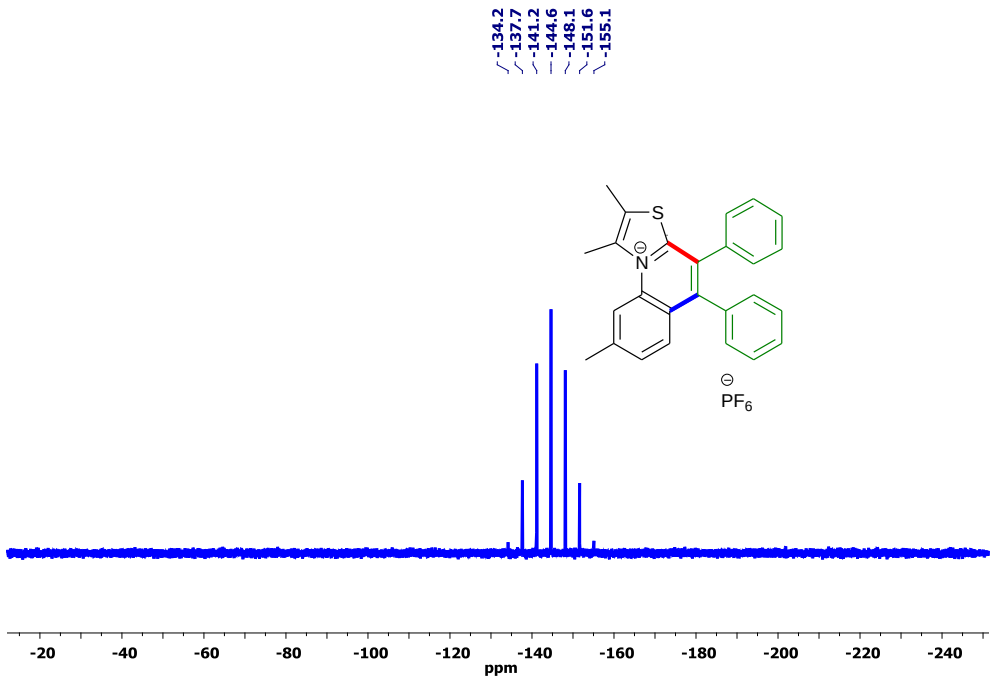
^{1}H NMR spectrum of **3w** (400 MHz, CD_3CN)



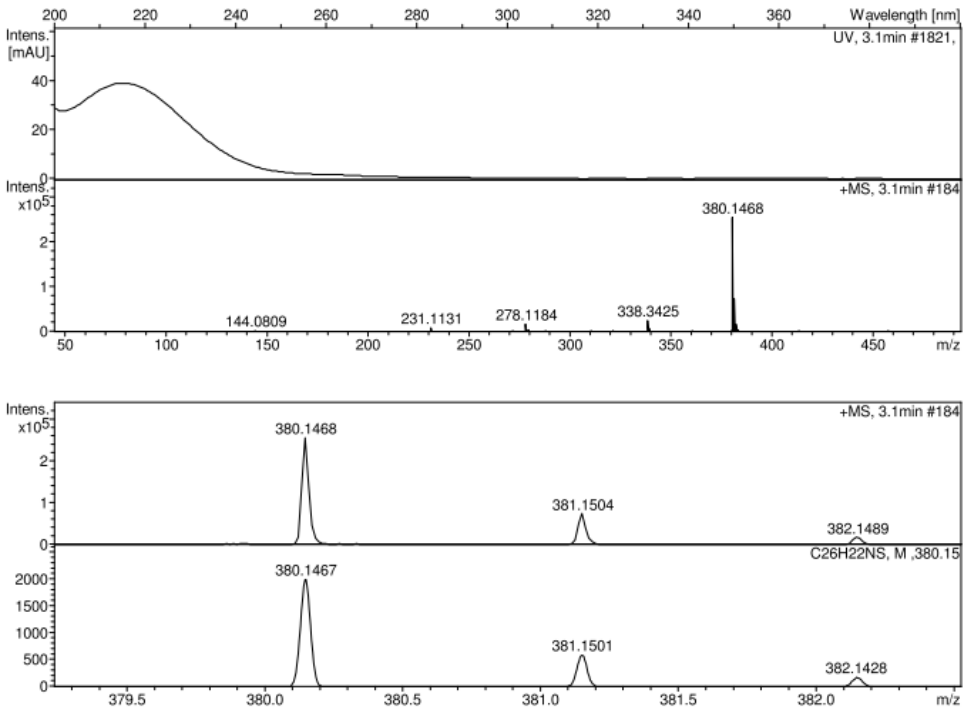
^{1}H{^{13}C} NMR spectrum of **3w** (100 MHz, CD_3CN)



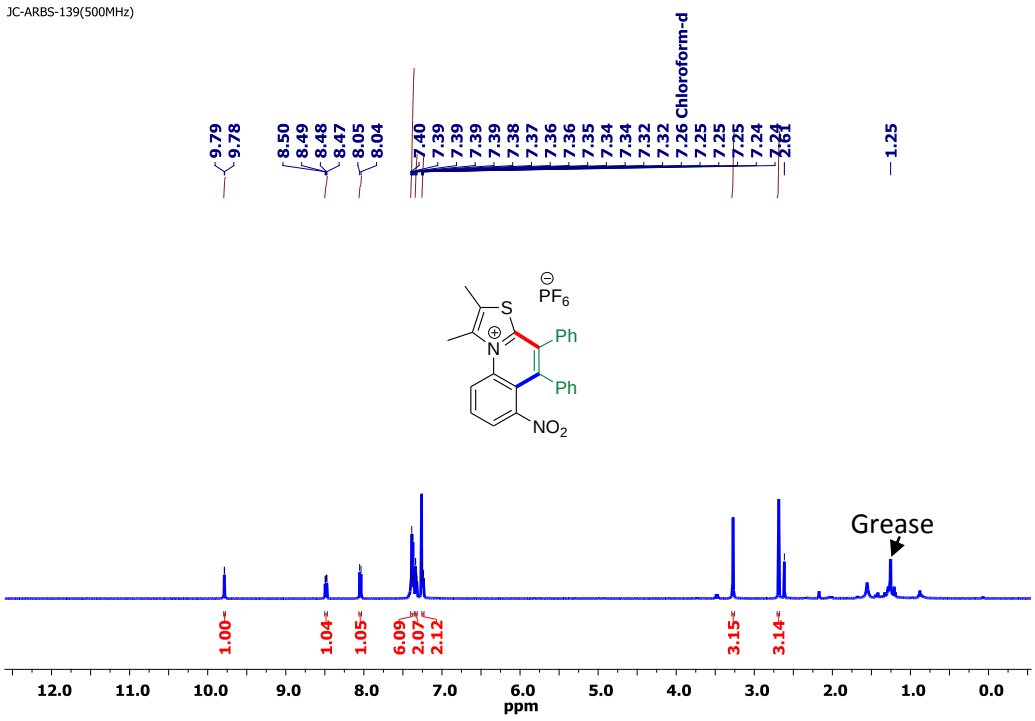
^{19}F NMR spectrum of **3w** (376 MHz, CD_3CN)



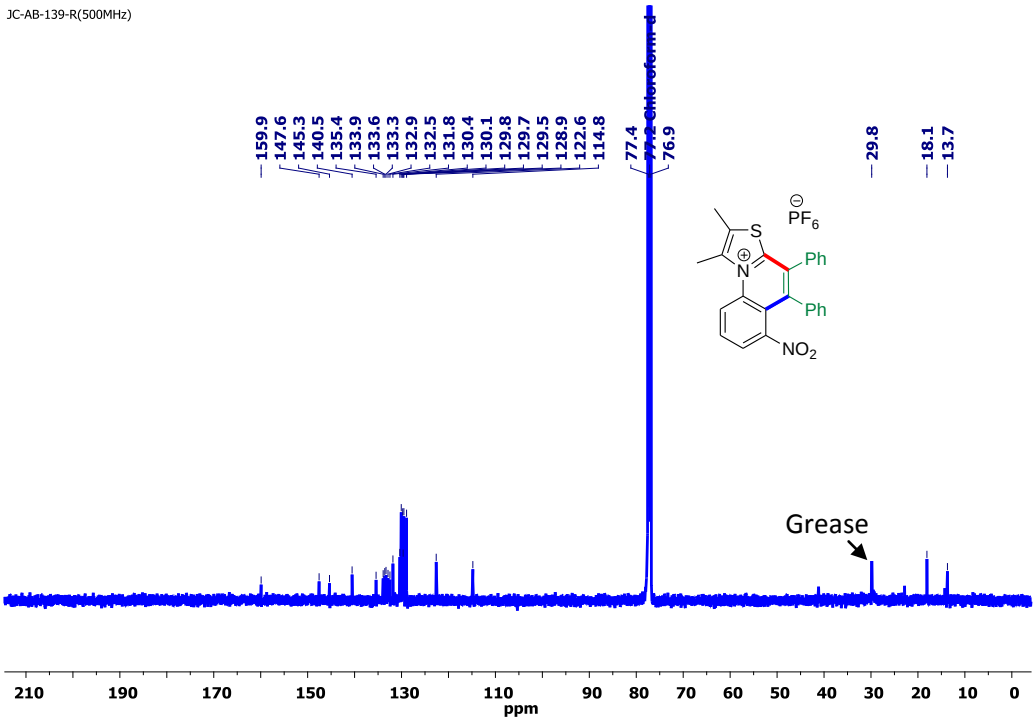
^{19}F NMR spectrum of **3w** (162 MHz, CD_3CN)



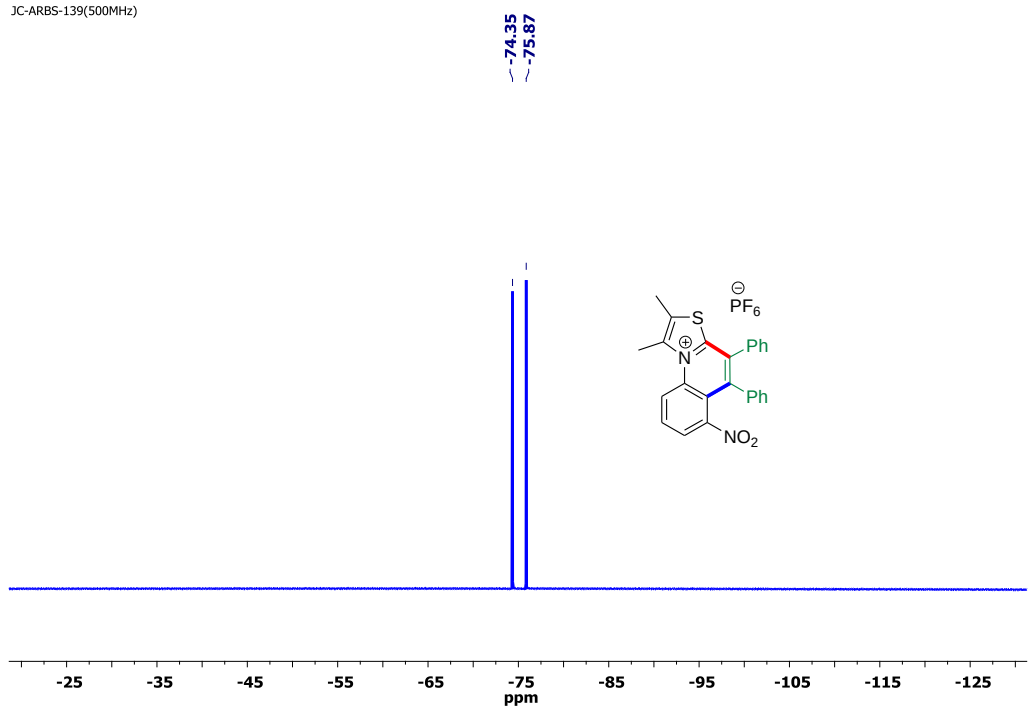
ESI-HRMS (positive ion mode) spectrum of **3w**



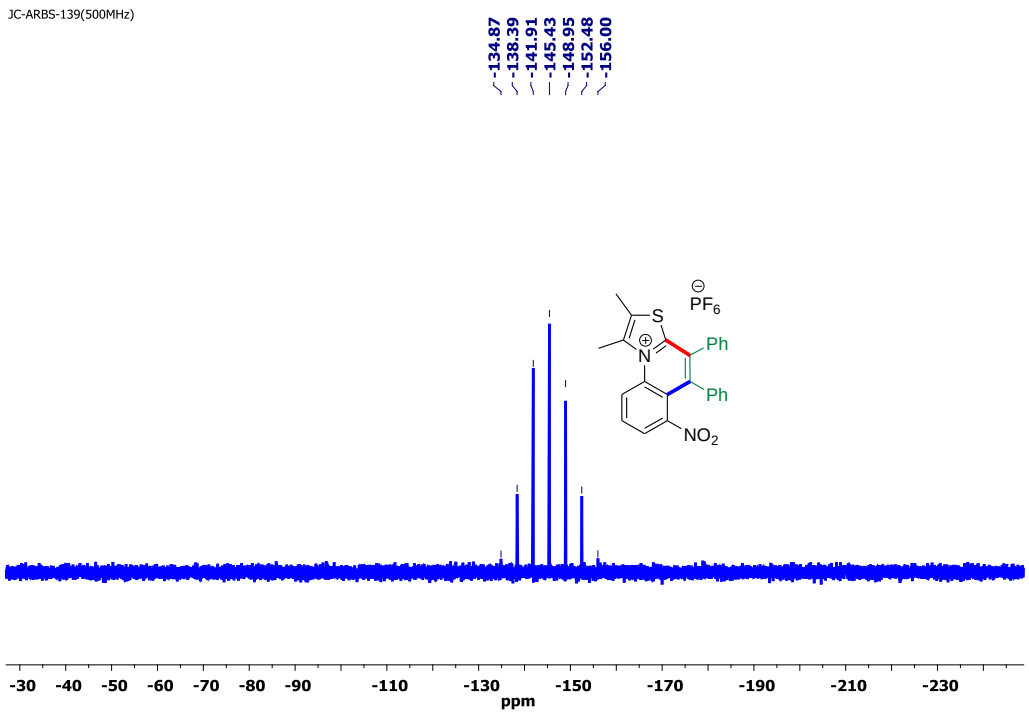
^{1}H NMR spectrum of **3x** (500 MHz, $CDCl_3$).



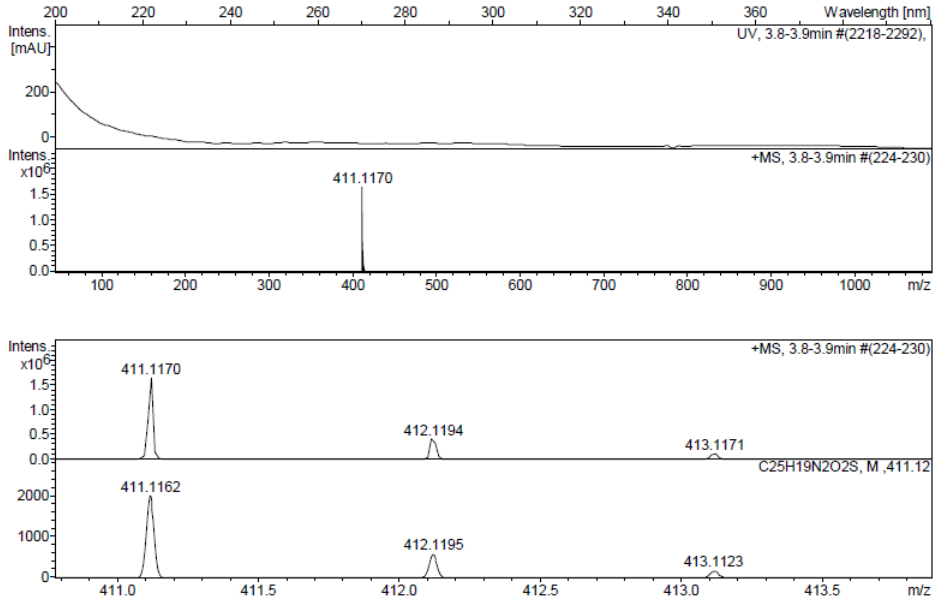
$^{13}C\{^{1}H\}$ NMR spectrum of **3x** (125 MHz, $CDCl_3$).



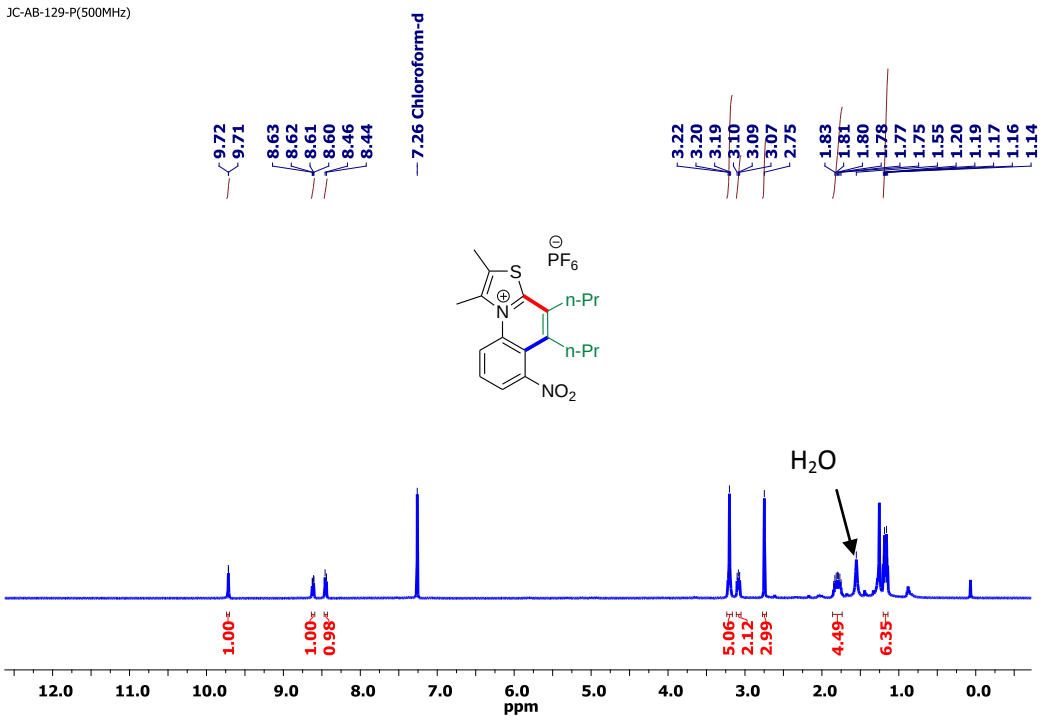
^{19} F NMR spectrum of **3x** (471 MHz, $CDCl_3$).



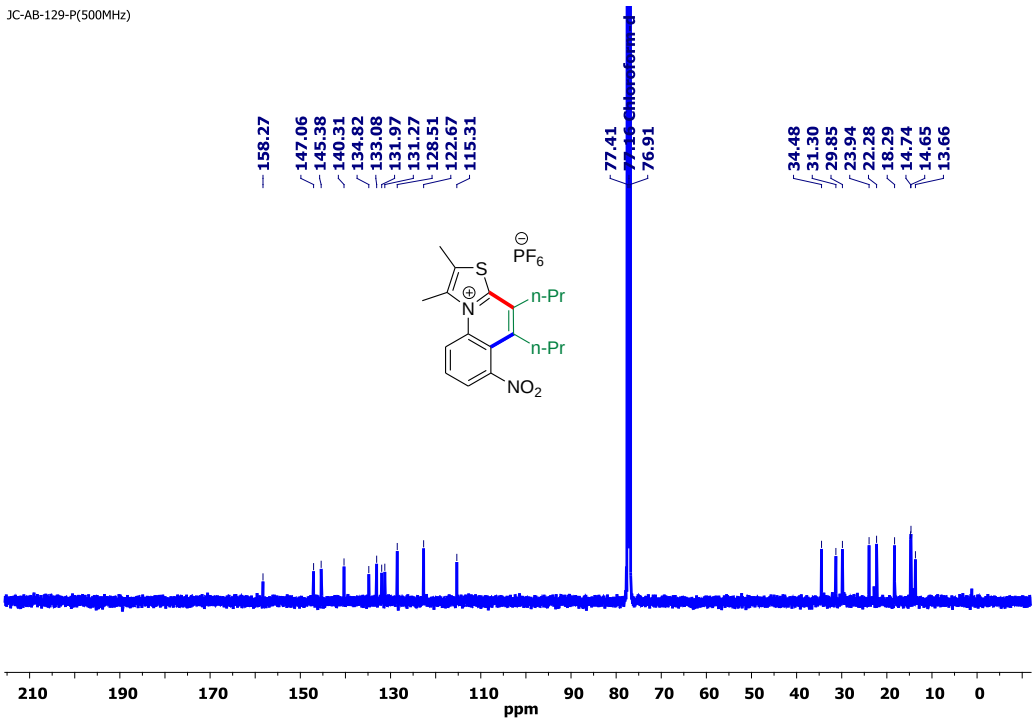
^{31}P NMR spectrum of **3x** (202 MHz, $CDCl_3$)



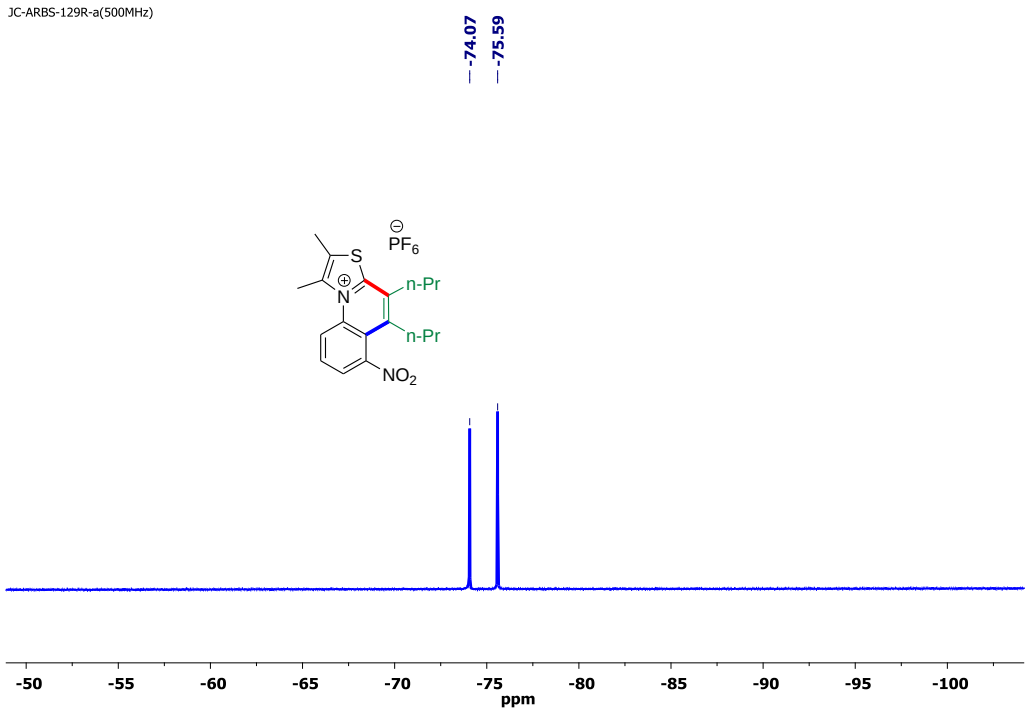
ESI-HRMS (positive ion mode) spectrum of **3x**



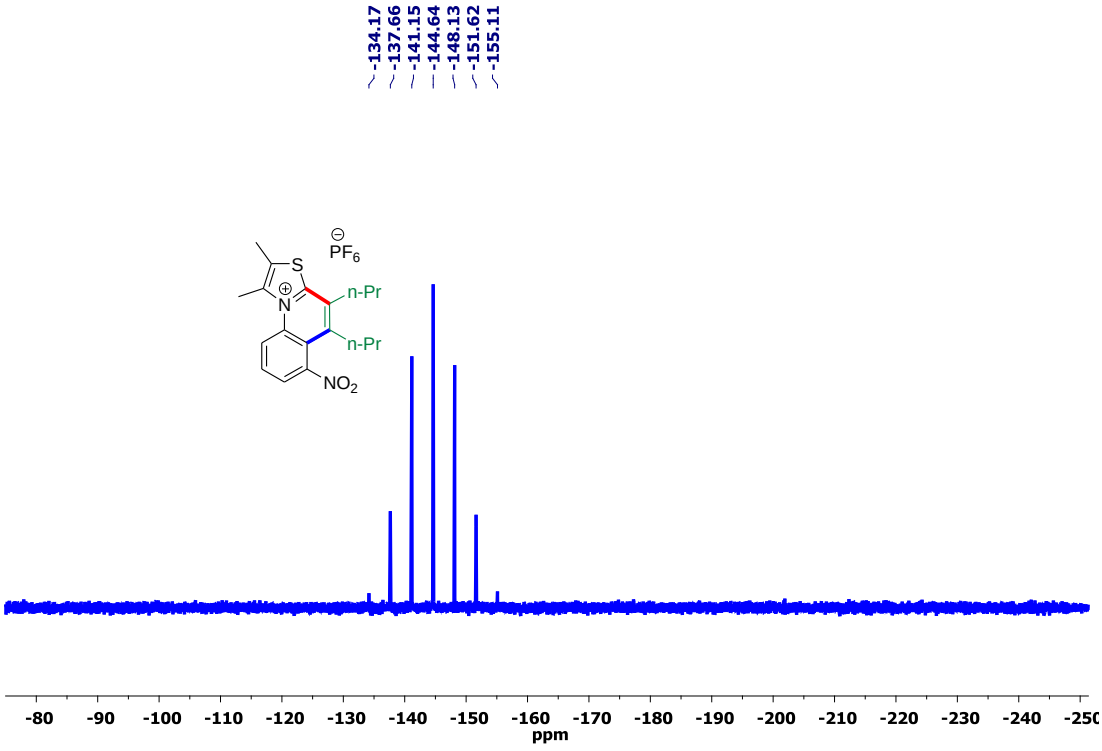
^{1}H NMR spectrum of **3y** (500 MHz, $CDCl_3$).



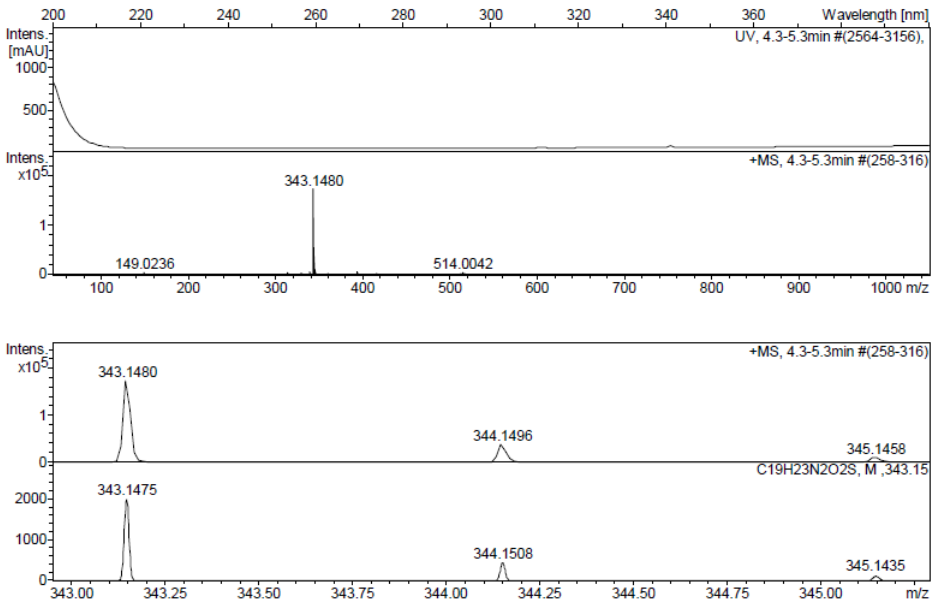
^{13}C{^{1}H} NMR spectrum of **3y** (125 MHz, $CDCl_3$).



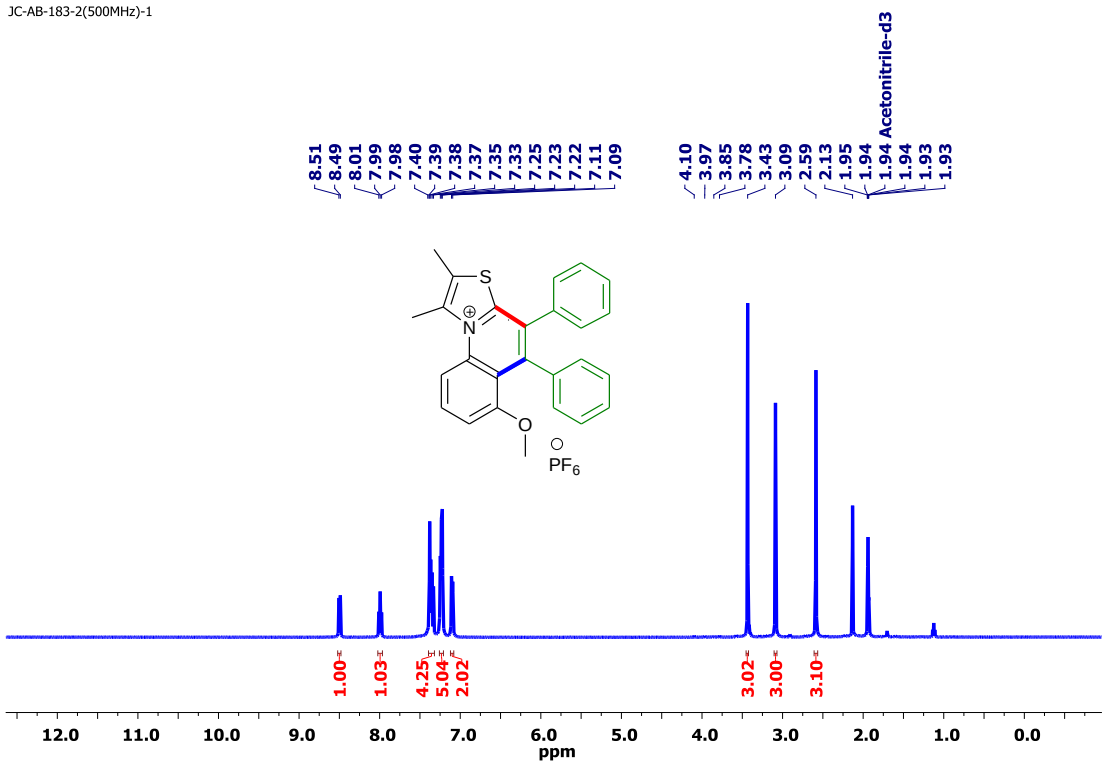
^{19}F NMR spectrum of **3y** (471 MHz, $CDCl_3$).



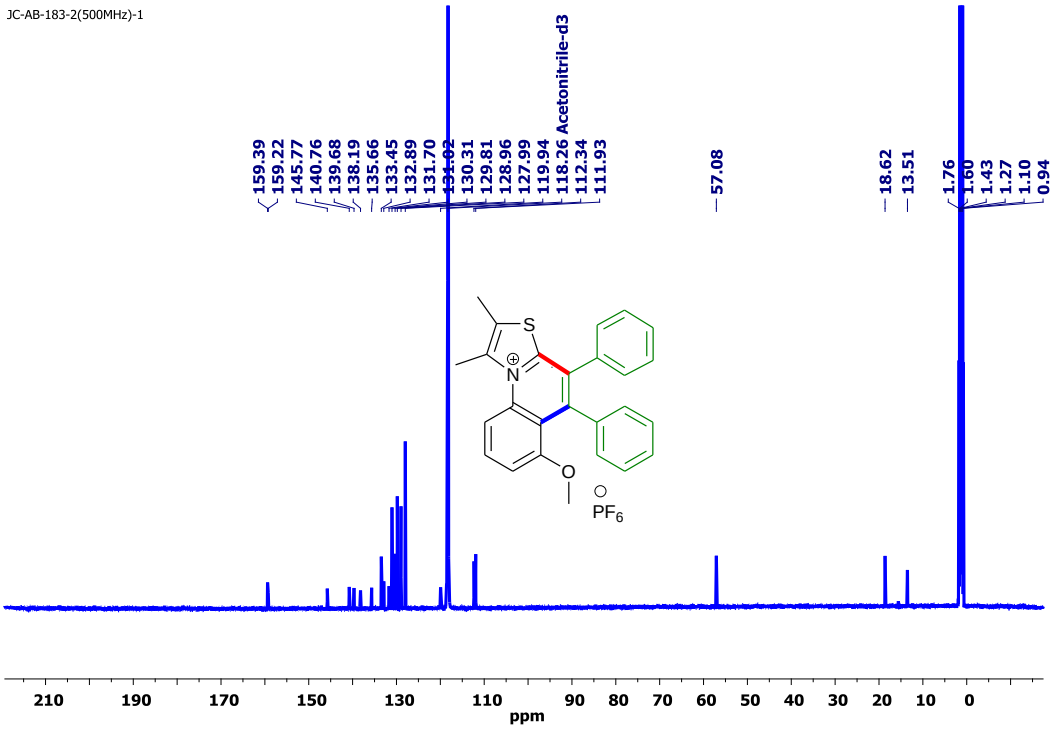
^{31}P NMR spectrum of **3y** (202 MHz, $CDCl_3$)



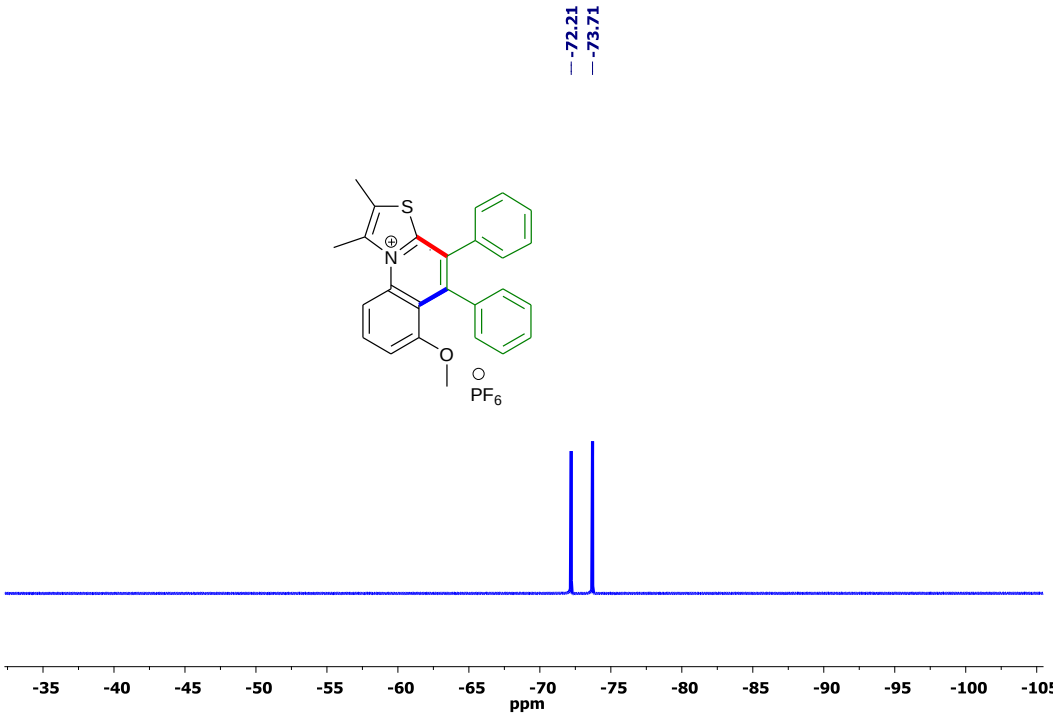
ESI-HRMS (positive ion mode) spectrum of **3y**



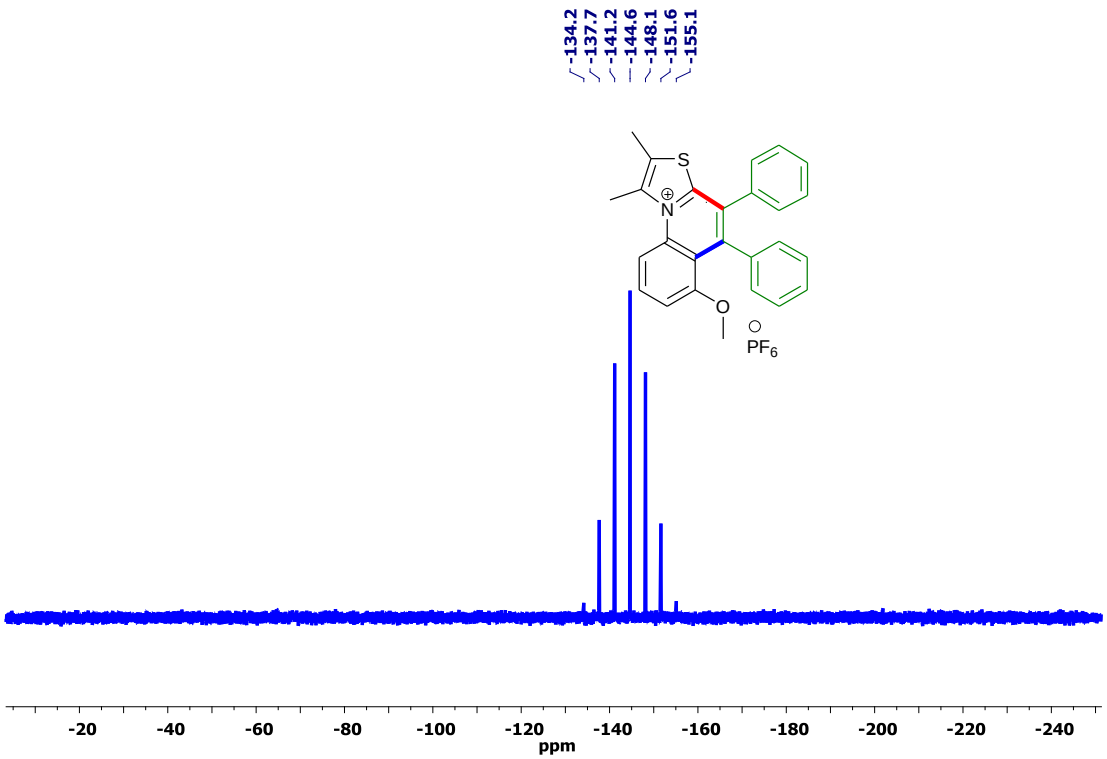
^{1}H NMR spectrum of **3z** (500 MHz, CD_3CN)



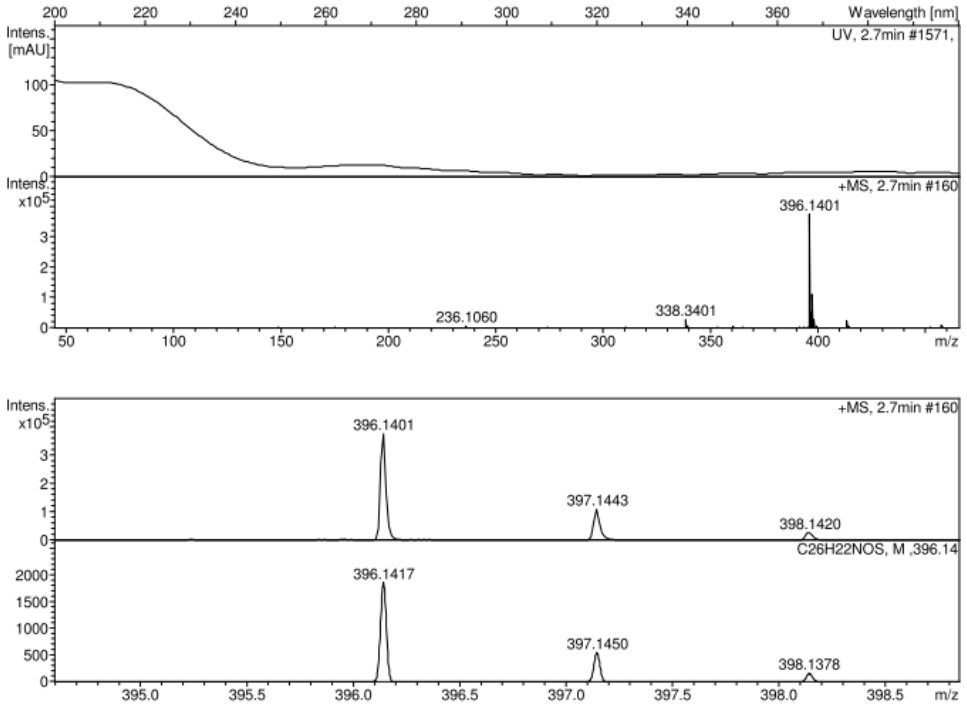
$^{13}C\{^{1}H\}$ NMR spectrum of **3z** (126 MHz, CD_3CN)



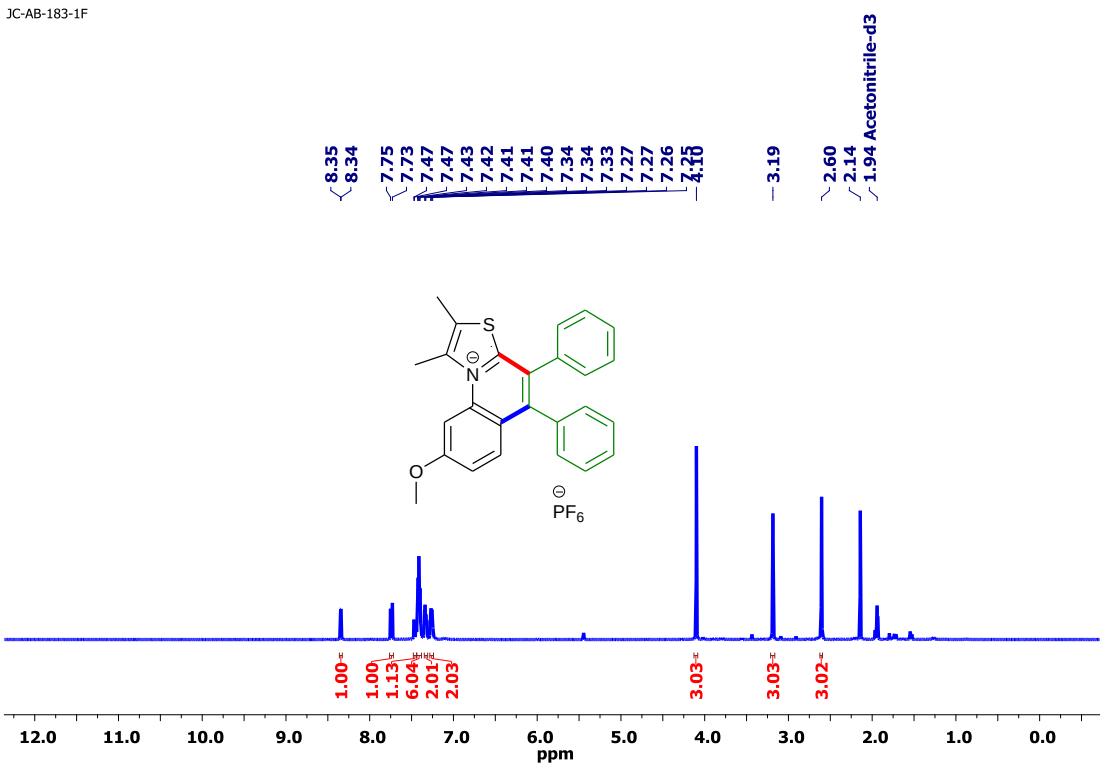
^{19}F NMR spectrum of **3z** (471 MHz, CD_3CN)



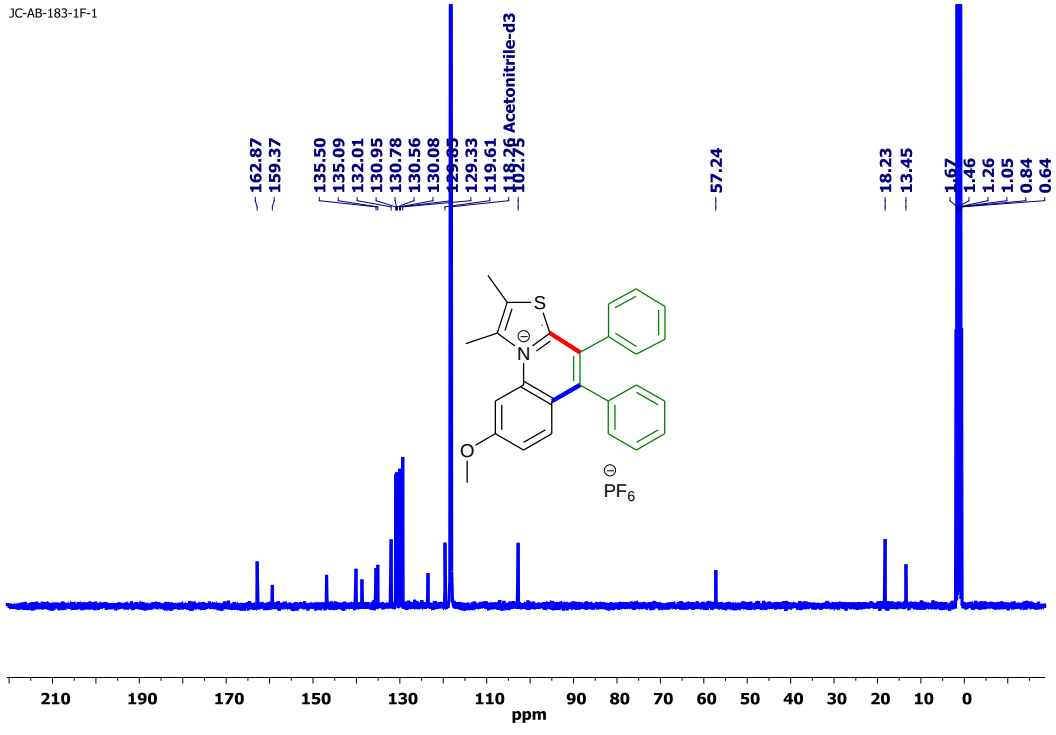
^{19}F NMR spectrum of **3z** (202 MHz, CD_3CN)



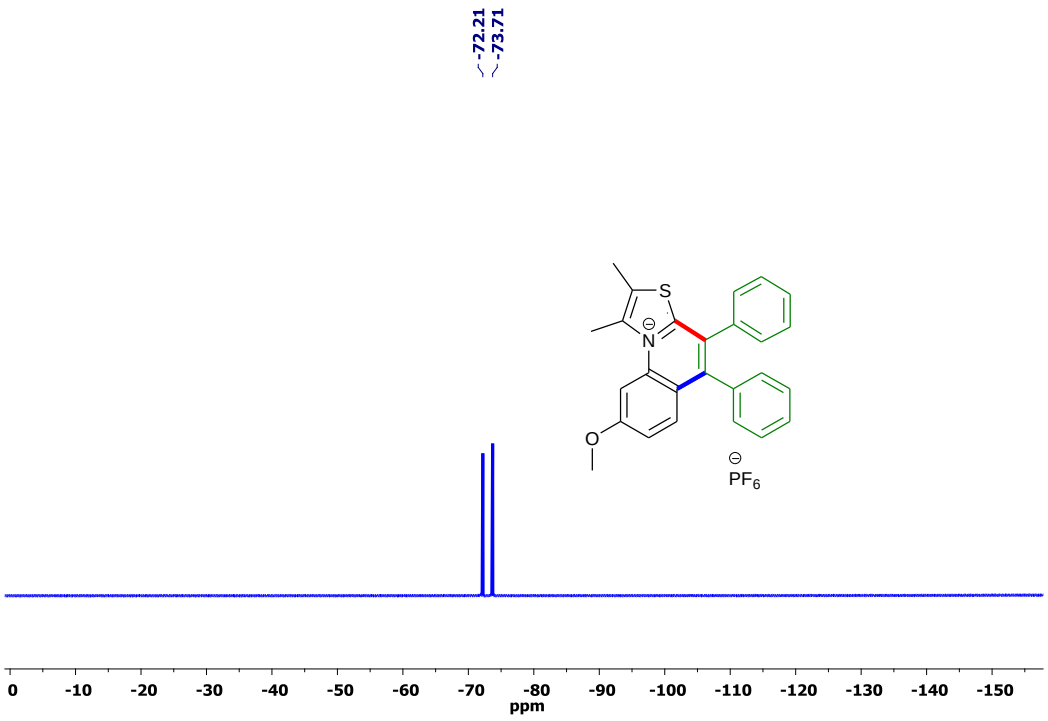
ESI-HRMS (positive ion mode) spectrum of **3z**



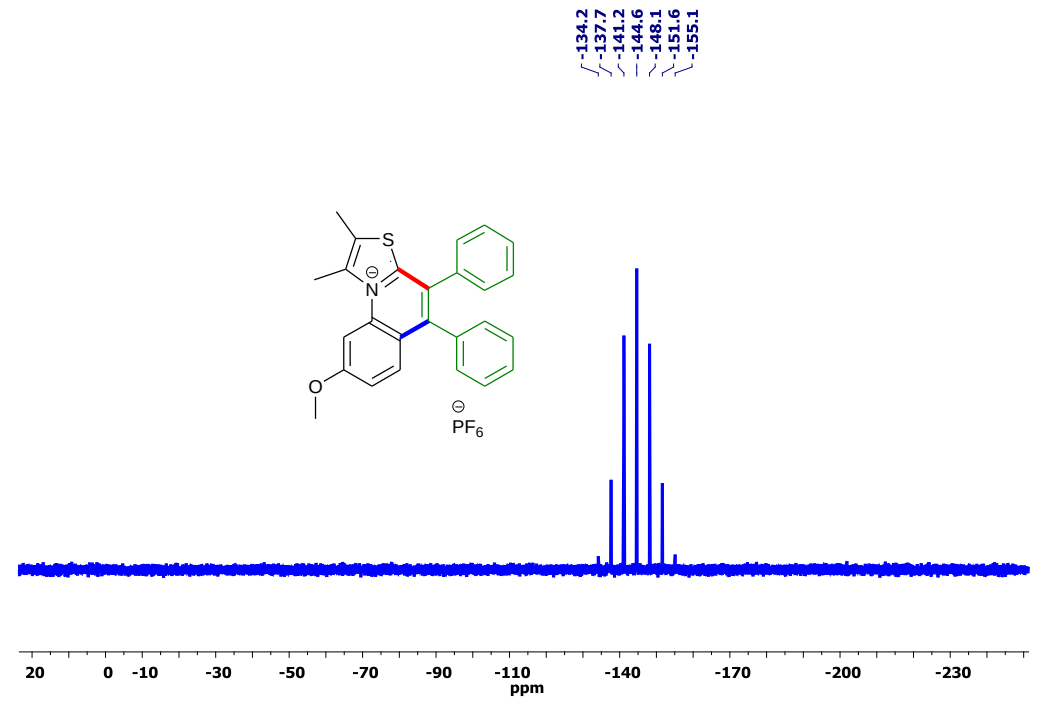
^{1}H NMR spectrum of **3z'** (500 MHz, CD_3CN)



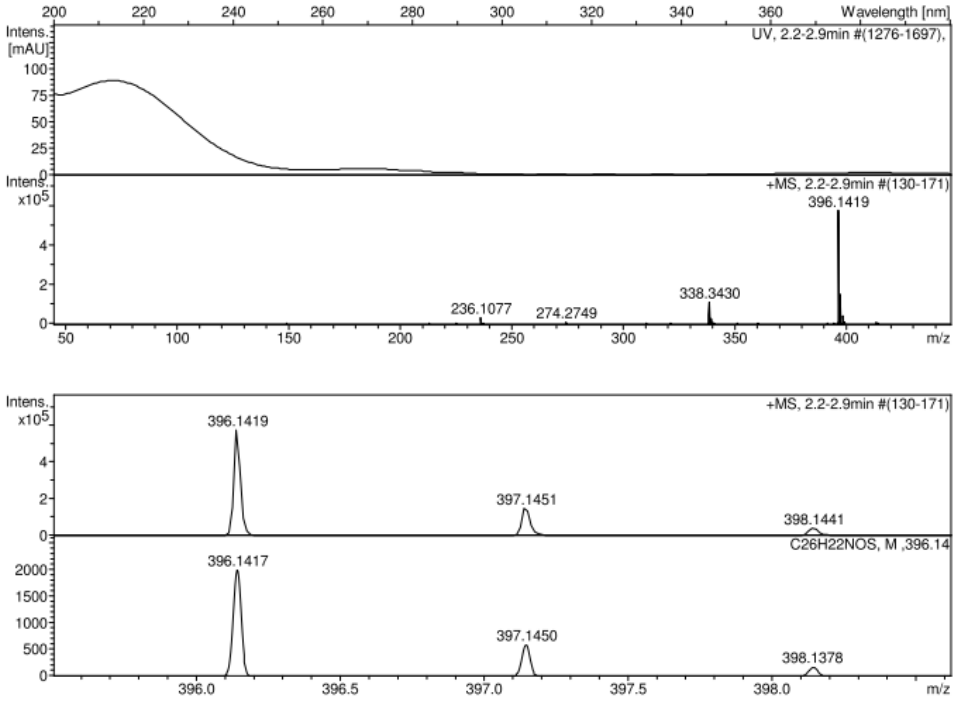
^{13}C{^{1}H} NMR spectrum of **3z'** (126 MHz, CD_3CN)



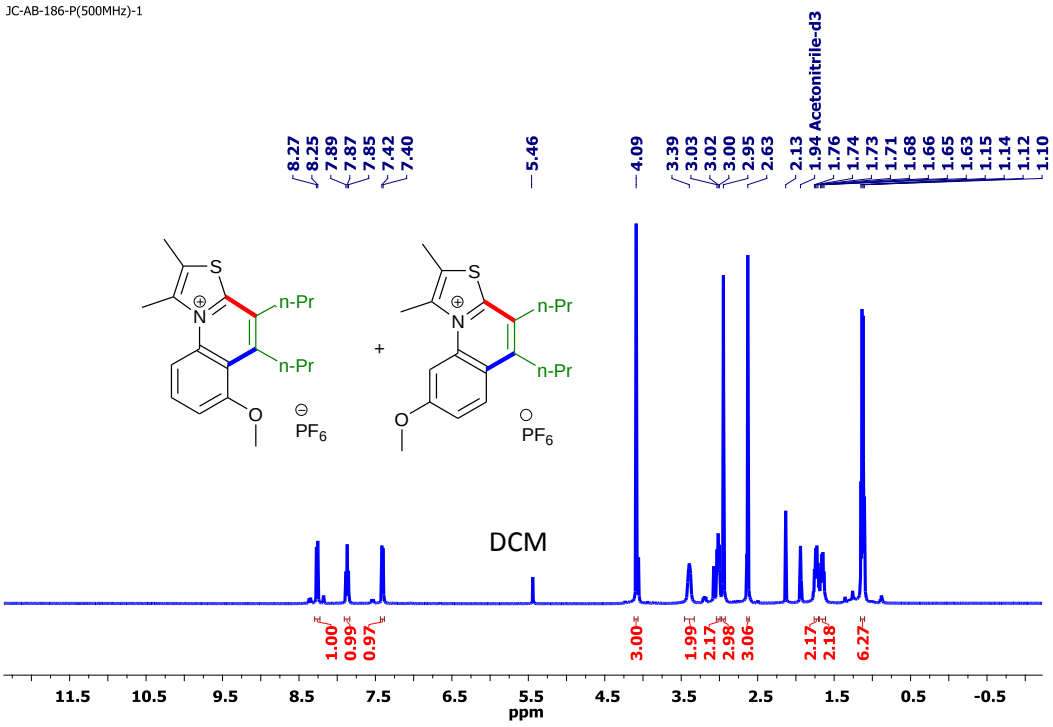
^{19}F NMR spectrum of **3z'** (471 MHz, CD_3CN)



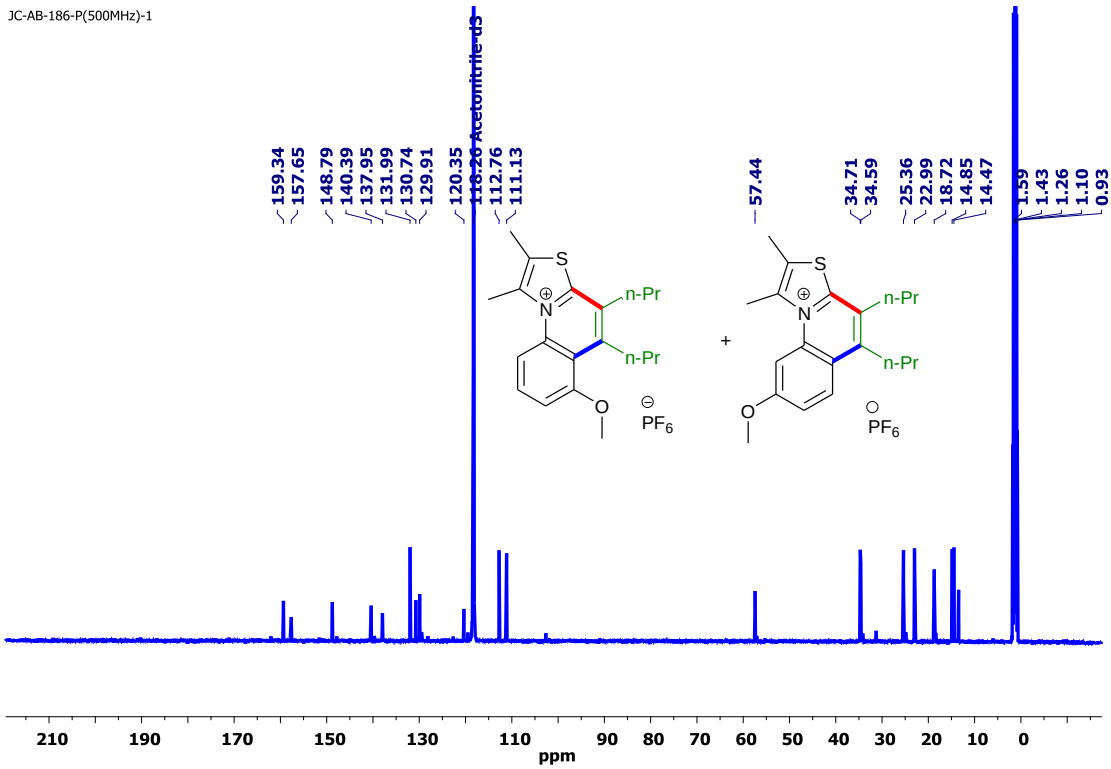
^{31}P NMR spectrum of **3z'** (202 MHz, CD_3CN)



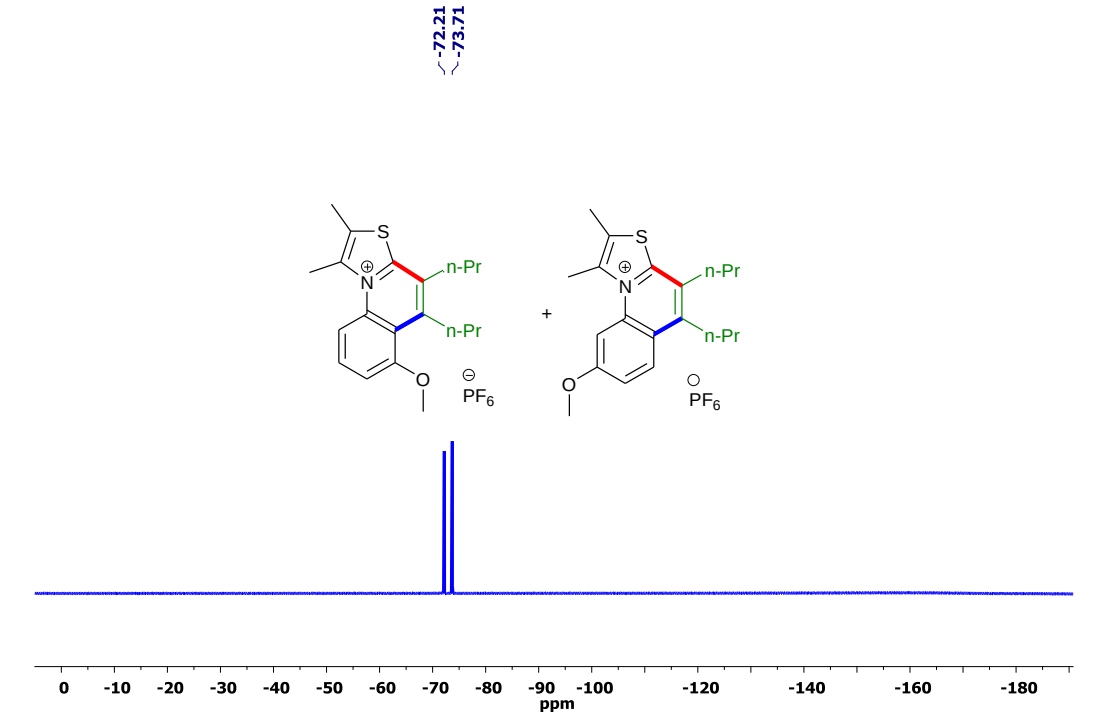
ESI-HRMS (positive ion mode) spectrum of **3z'**



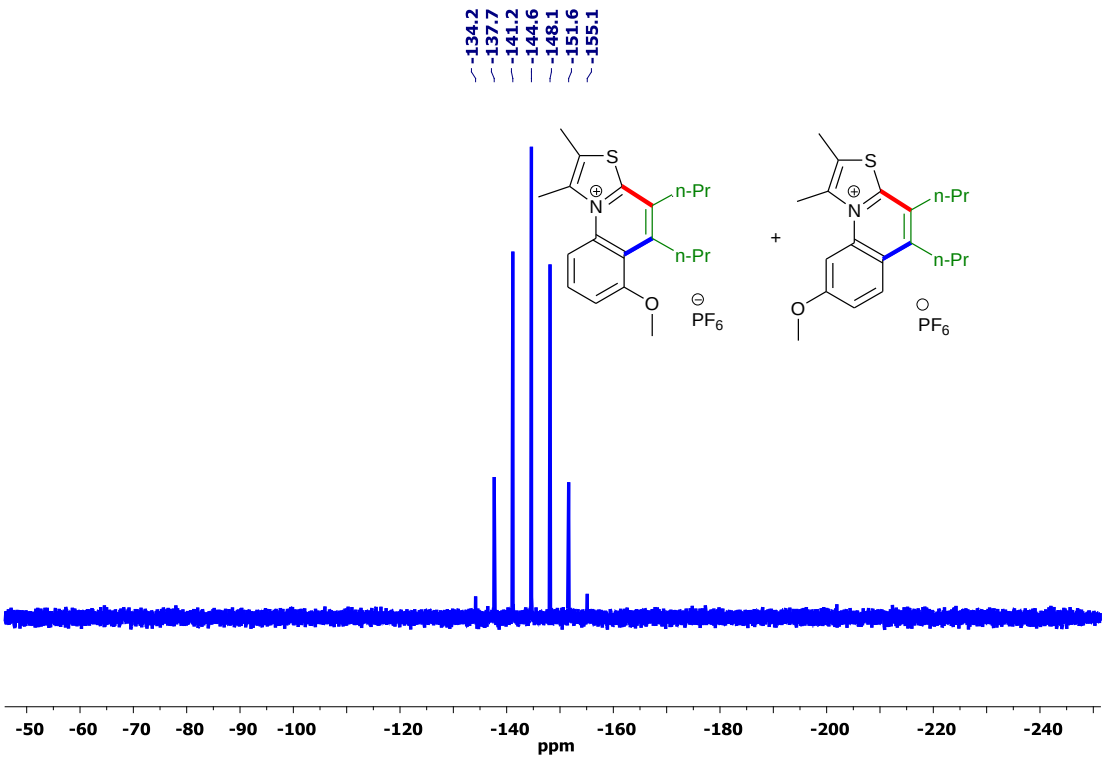
^{1}H NMR spectrum of **3aa+3aa'** (500 MHz, CD_3CN)



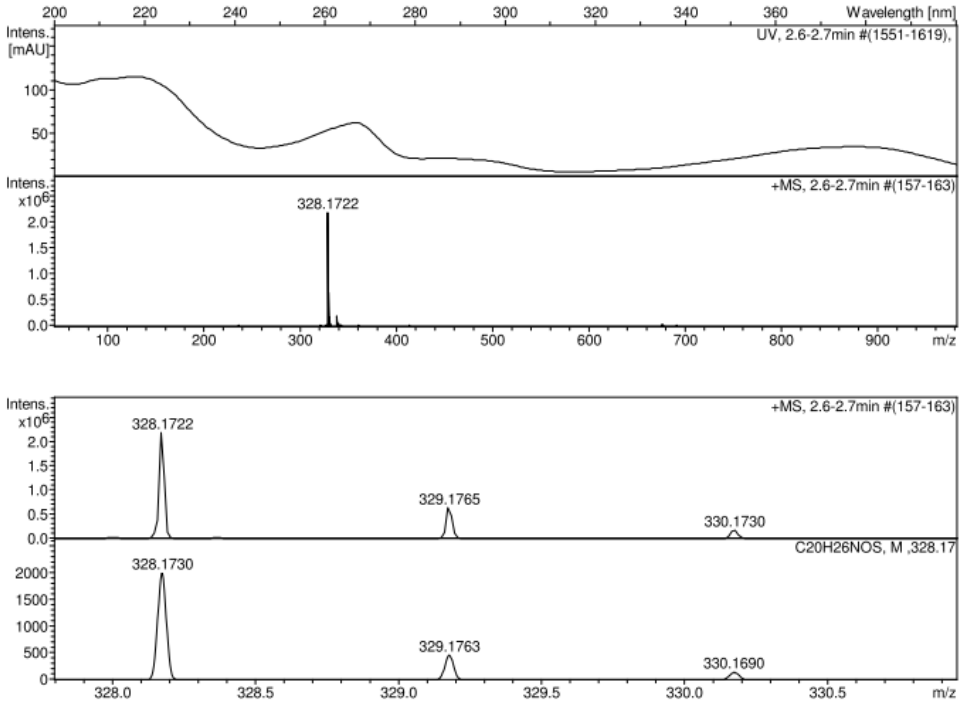
$^{13}C\{^{1}H\}$ NMR spectrum of **3aa + 3aa'** (126 MHz, CD_3CN)



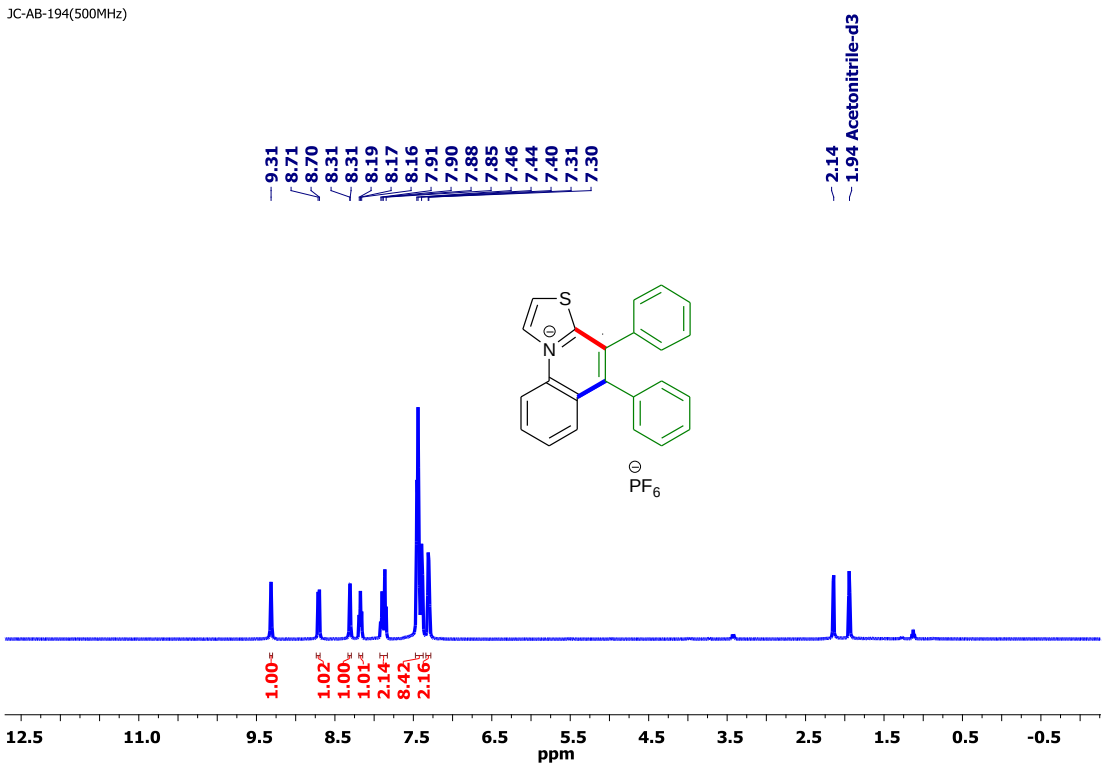
^{19}F NMR spectrum of **3aa+ 3aa'** (471 MHz, CD_3CN)



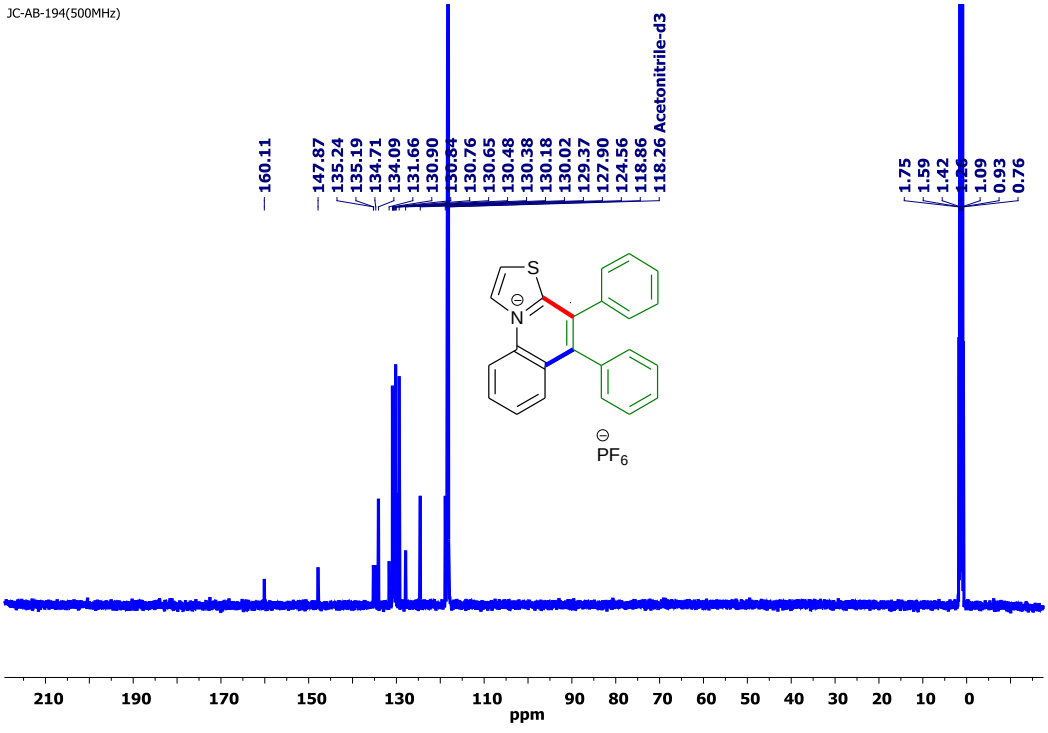
^{31}P NMR spectrum of **3aa+ 3aa'** (202 MHz, CD_3CN)



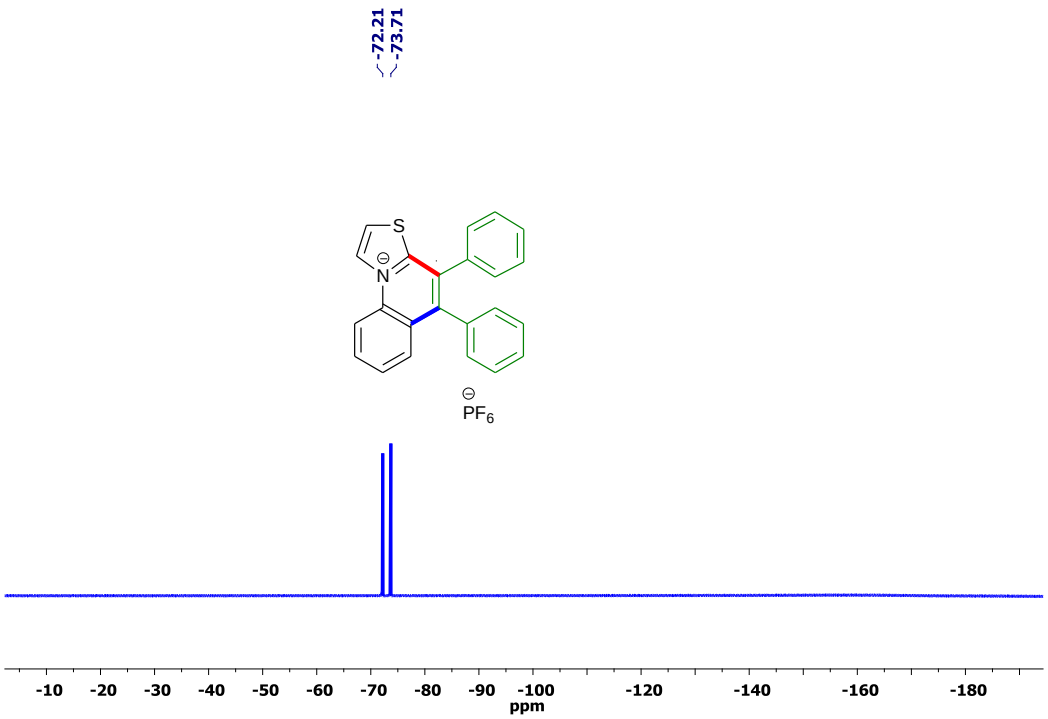
ESI-HRMS (positive ion mode) spectrum of **3aa+ 3aa'**



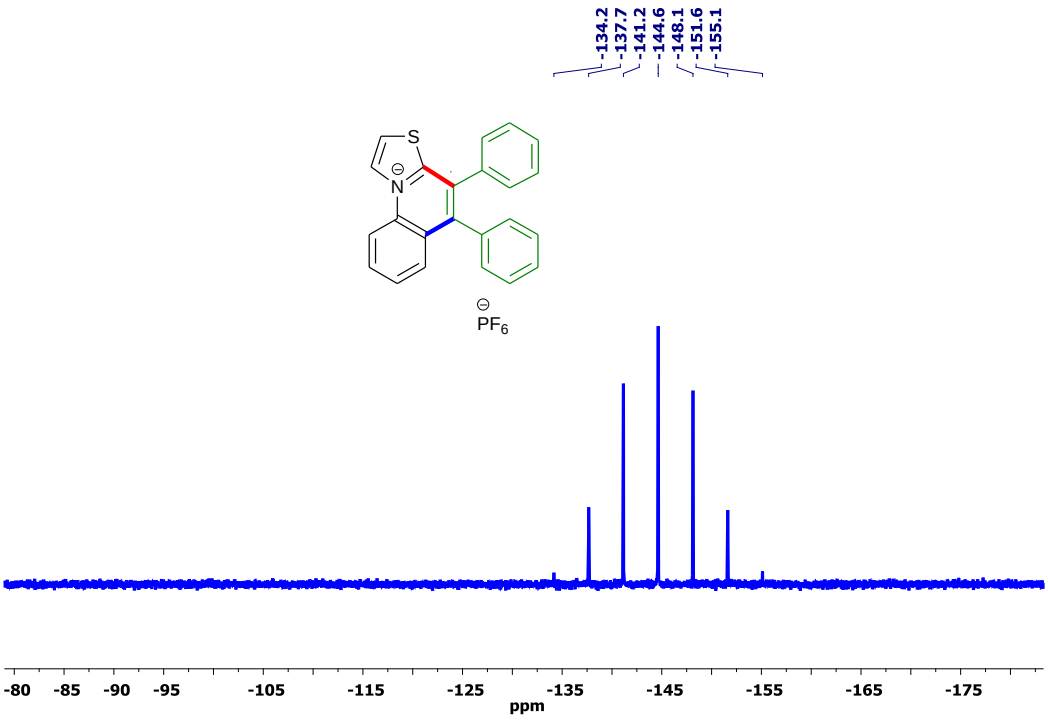
^{1}H NMR spectrum of **3ab** (500 MHz, CD_3CN)



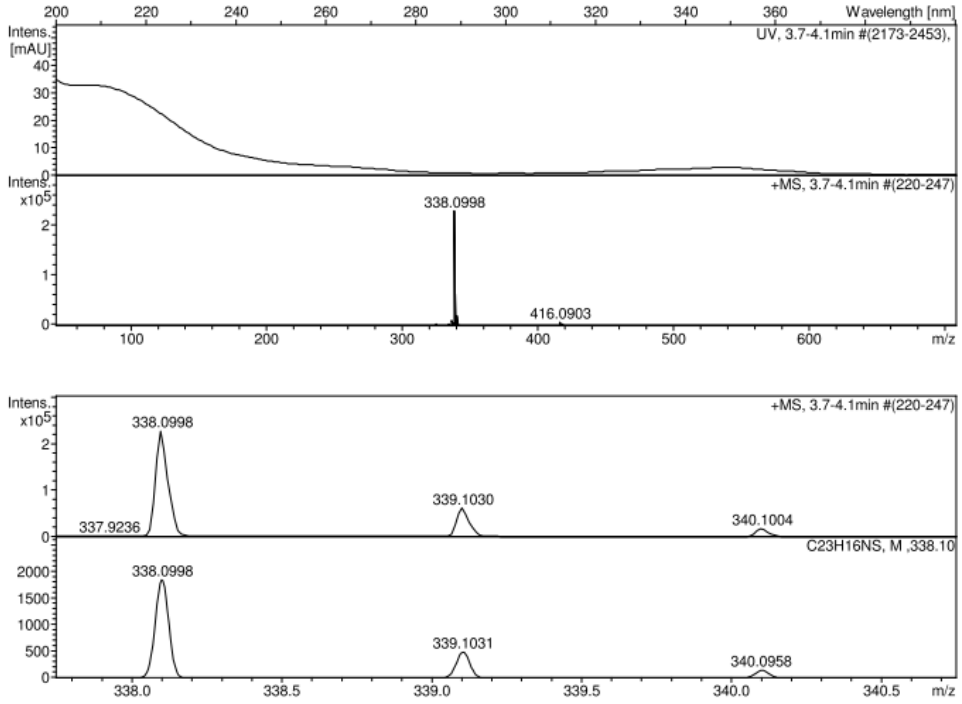
^{13}C{^{1}H} NMR spectrum of **3ab** (126 MHz, CD_3CN)



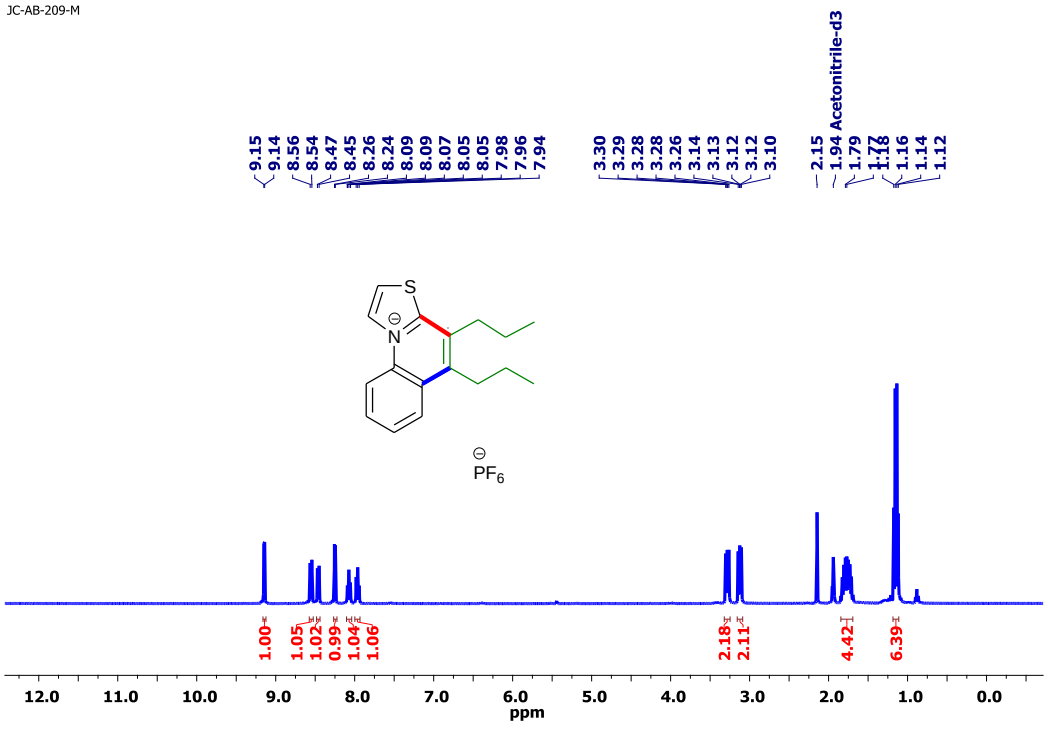
^{19}F NMR spectrum of **3ab** (476 MHz, CD_3CN)



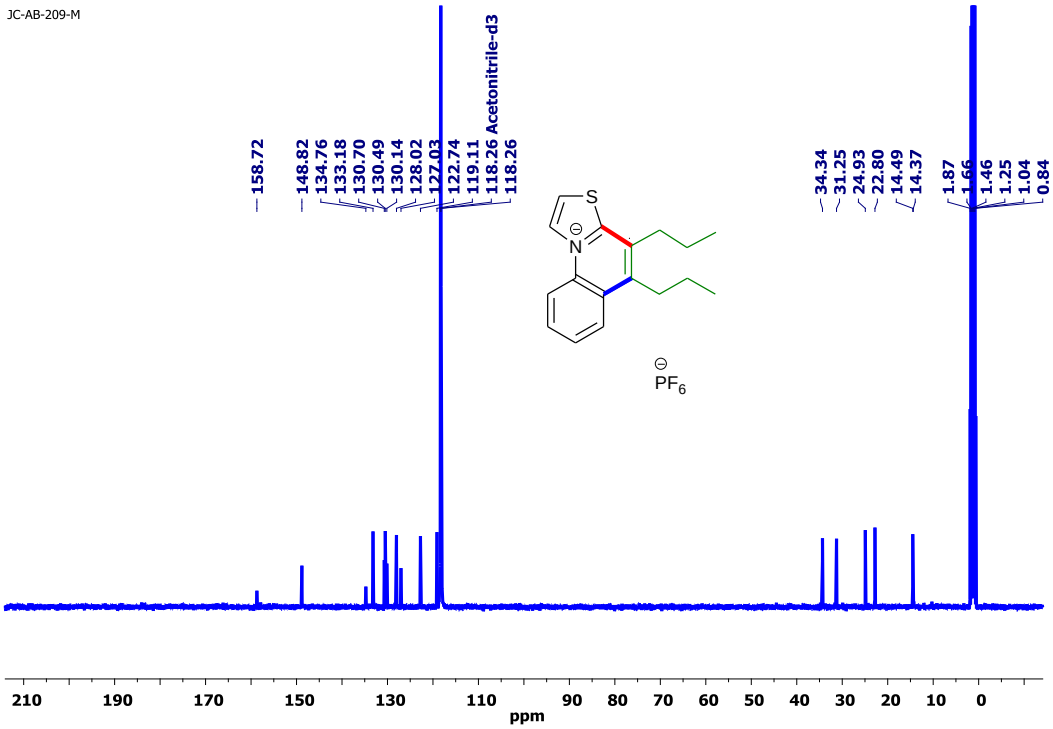
^{31}P NMR spectrum of **3ab** (202 MHz, CD_3CN)



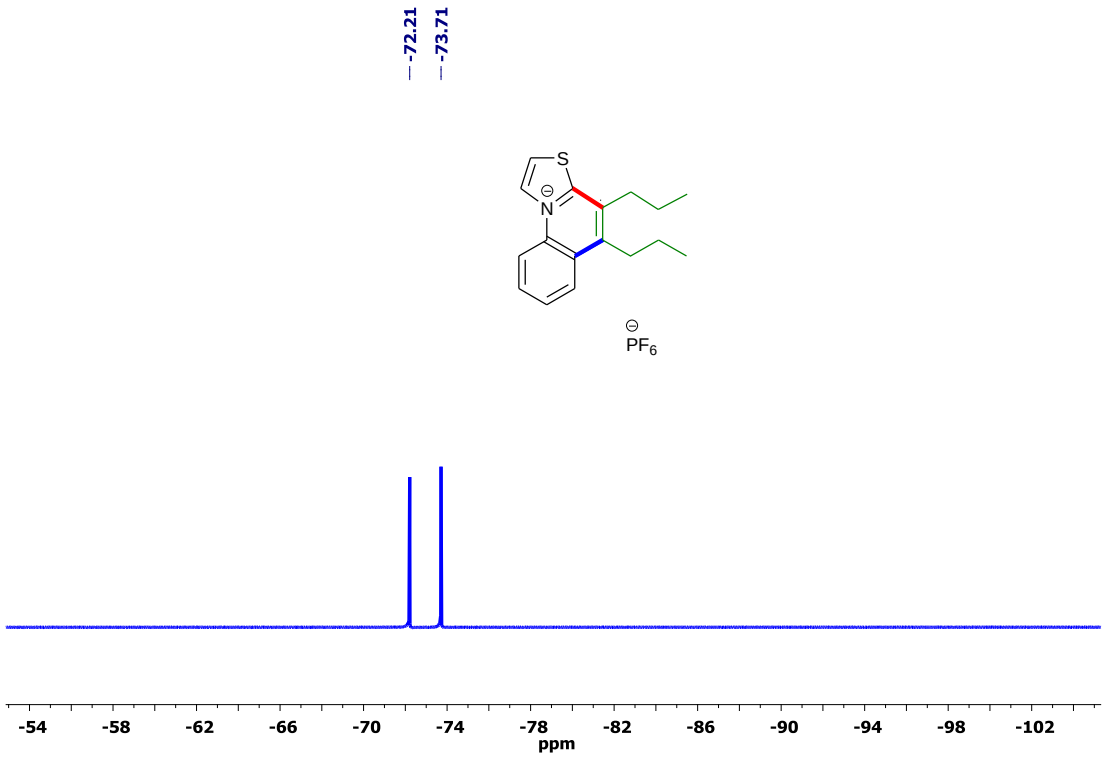
ESI-HRMS (positive ion mode) spectrum of **3ab**



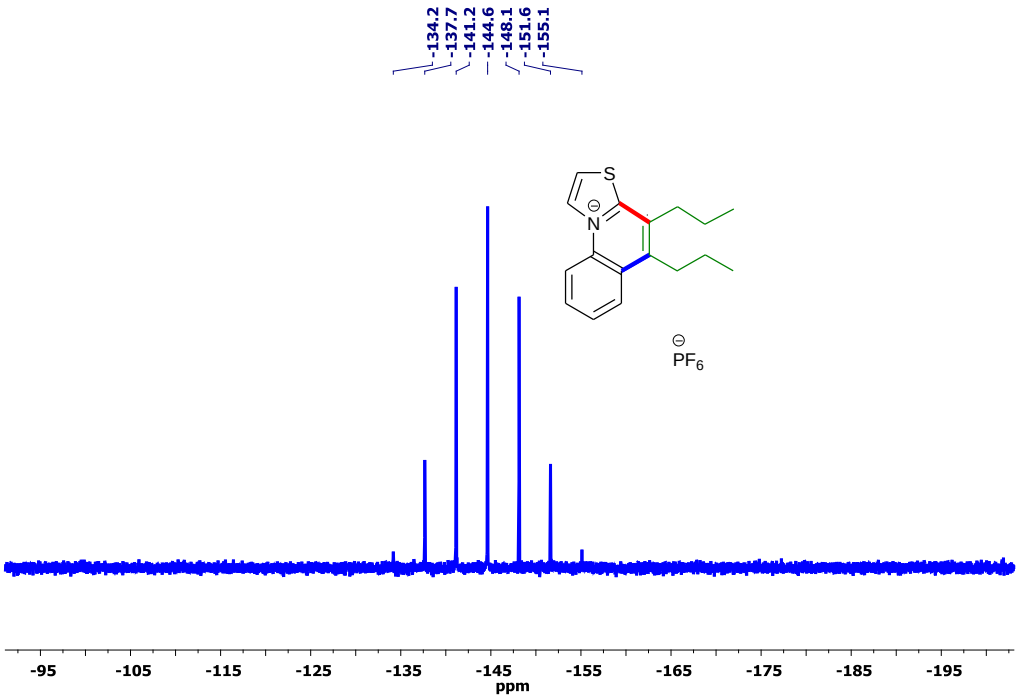
^{1}H NMR spectrum of **3ac** (400 MHz, CD_3CN)



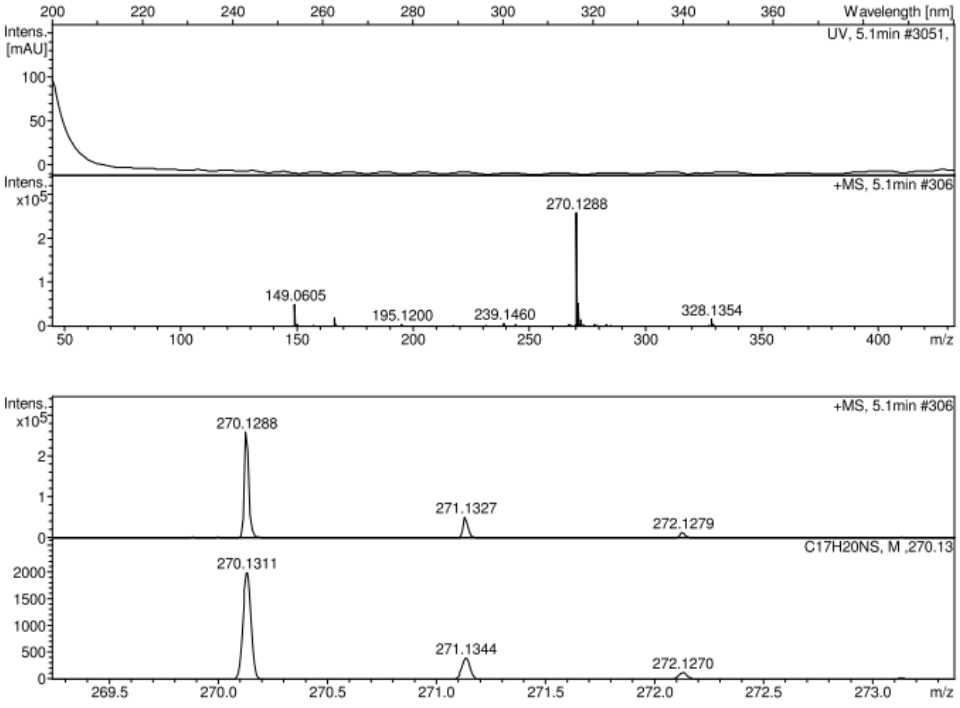
$^{13}C\{^{1}H\}$ NMR spectrum of **3ac** (100 MHz, CD_3CN)



^{19}F NMR spectrum of **3ac** (476 MHz, CD_3CN)



^{31}P NMR spectrum of **3ac** (202 MHz, CD_3CN)

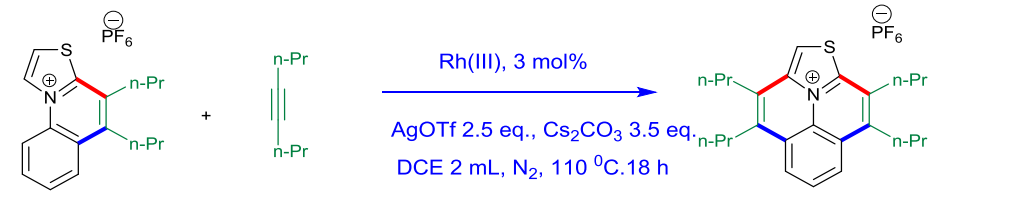


ESI-HRMS (positive ion mode) spectrum of **3ac**

13. Attempts for double annulation:

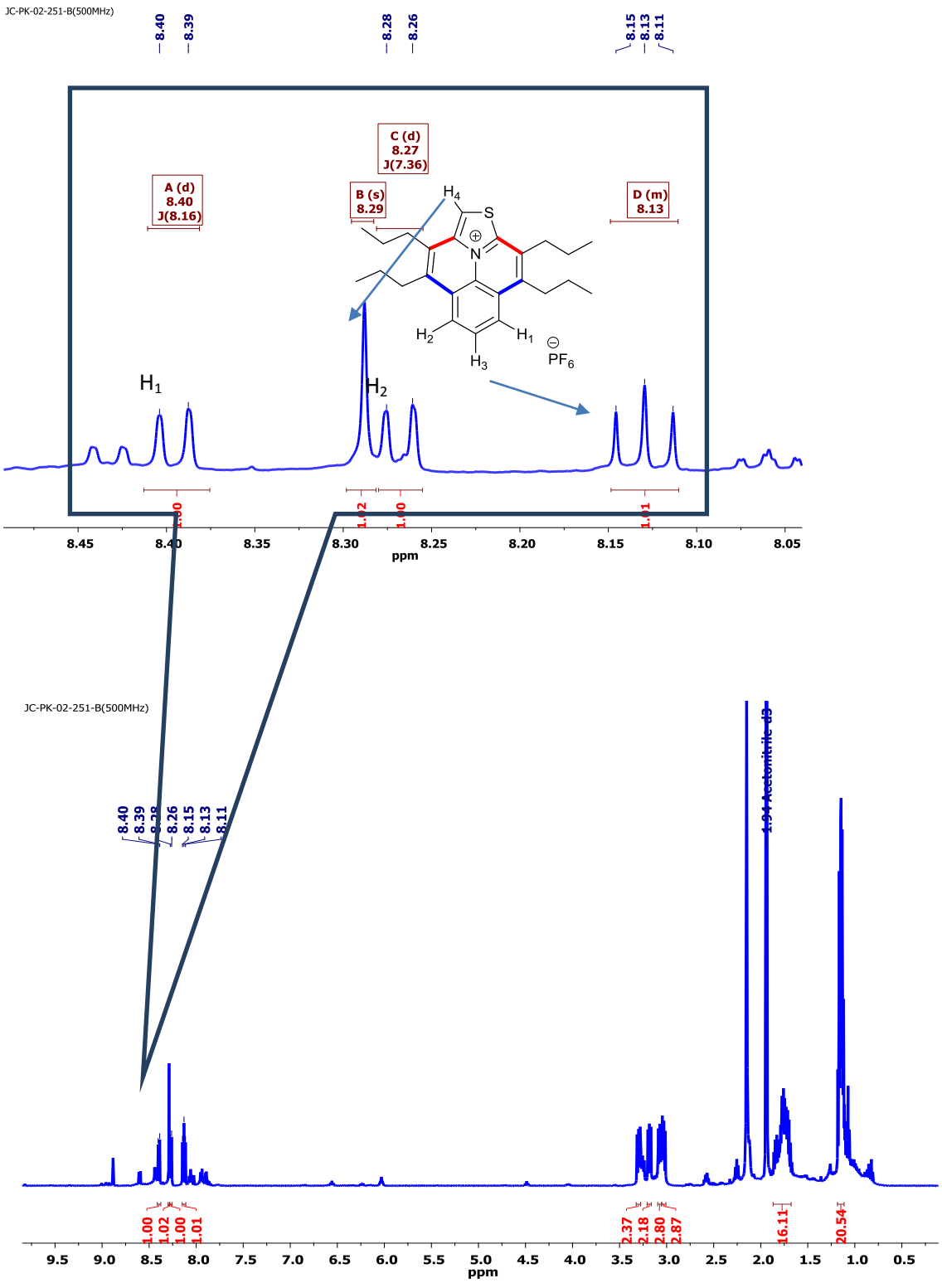
The present protocol failed to provide double annulation of unsubstituted thiazolium substrate with 2.0 equivalents of alkynes, even at higher temperature or using Cs_2CO_3 as base. However, following annulation on monoannulated product yielded trace amount (~10%) of double annulated product. The formation was only confirmed by ^{1}H NMR spectroscopic analysis. Further optimization shall be required in future to get enhanced yield.

Attempt 1: Bis-annulation from monoannulated product



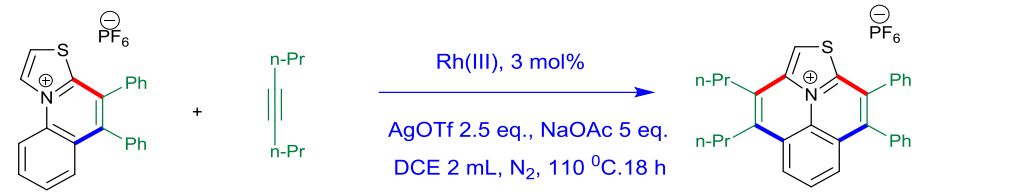
3ac, 0.05 mmol **2g, 1.5 eq.** **~ 12 % + 3ac (unreacted)**

3,4,8,9-tetrapropylbenzo[ij]thiazolo[2,3,4-de]quinolizin-10-iumhexafluorophosphate: Yield :~ 12 % , ^{1}H NMR (500 MHz, CD_3CN) δ 8.40 (d, *J* = 8.2 Hz, 1H), 8.29 (s, 1H), 8.27 (d, *J* = 7.4 Hz, 1H), 8.15 – 8.11 (m, 1H), 3.32 – 3.28 (m, 2H), 3.21 – 3.16 (m, 2H), 3.09 – 3.05 (m, 2H), 3.05 – 3.01 (m, 2H), 1.87 – 1.67 (m, 16H), 1.19 – 1.11 (m, 20H (*excess*)).

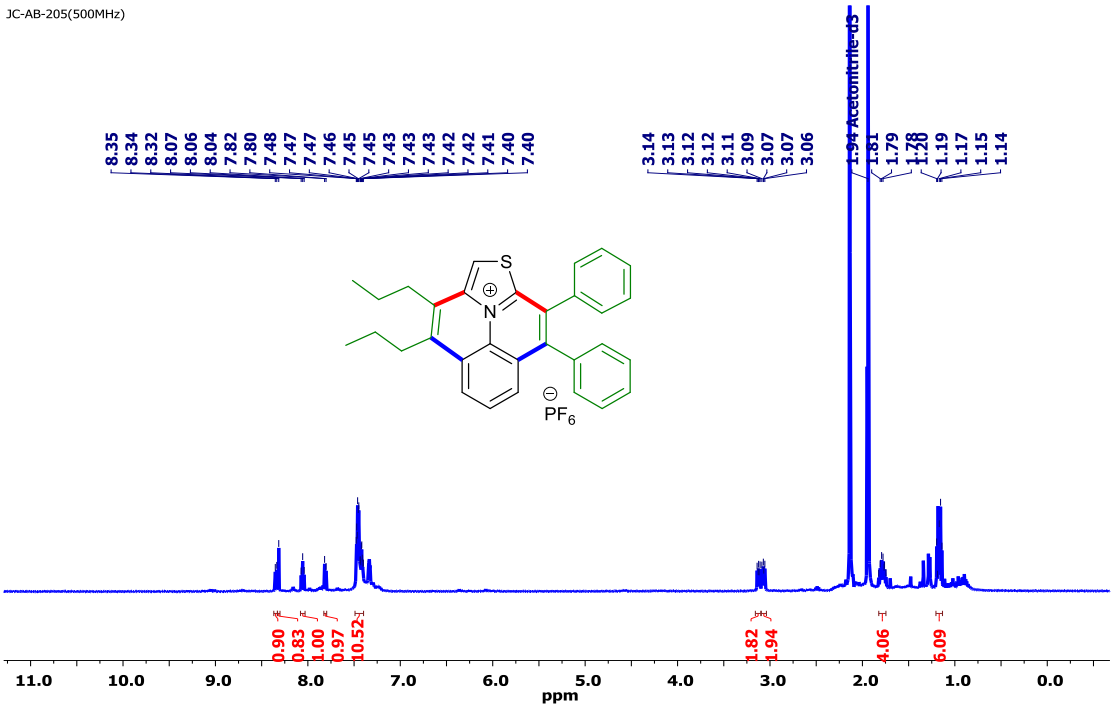


^{1}H NMR spectrum of the isolated double-annulated product

Attempt 2: Double annuation from monannulated product:



3ab, 0.05 mmol **2g, 1.5 eq.** **10 %, + 3ab (unreacted)**



^{1}H NMR spectrum of the isolated double-annulated product

8,9-diphenyl-3,4-dipropylbenzo[ij]thiazolo[2,3,4-de]quinolizin-10-iumhexafluorophosphate: Yield : 10%, ^{1}H NMR (500 MHz, CD_3CN) δ 8.34 (d, *J* = 7.9 Hz, 1H), 8.32 (s, 1H from thiazolium backbone), 8.06 (t, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.48-7.40 (m, 10H), 3.14 – 3.10 (m, 2H), 3.07 (dd, *J* = 9.1, 7.0 Hz, 2H), 1.83 – 1.74 (m, 4H), 1.20 – 1.12 (m, 6H). (N.B.: The distinct and characteristic singlet proton at 8.32 ppm indicates formation of double annulated product).

14. References

1. Y. Du, T. K. Hyster and T. Rovis, *Chem. Commun.*, 2011, **47**, 12074.

2. H. Leopold, A. Tronnier, G.Wagenblast, I. Münster and T. Strassner, *Organometallics*, 2016, **35**, 959.

3. H. Leopold and T. Strassner, *Dalton Trans*., 2017, **46**, 7800.

4. Gaussian 09 (Revision A.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennu H_2O A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, A. J., J. E. Peralta, F. Ogliaro, M.Bearpark, J. J.Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, azyev, A. Austin, R. Cammi, C. Pomelli, Chterski, R. L. Martin, K. Morokuma, G. Akrzewski, G. A. Oth, P. Salvador, Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. Cioslowski and D. J. Fox, Gaussian 09, Inc. Gaussian, CT. Wallingford, 2009.

5. (a) A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648. (b) C. Lee, W. T. Yang and R. G. Parr, *Phys. Rev.*, 1988, **B37**, 785.