

Supporting Information
for
A Dual-Phase Luminescent Phosgene Sensor Based
on an AIE-Active Ruthenium(II) Polypyridine
Complex

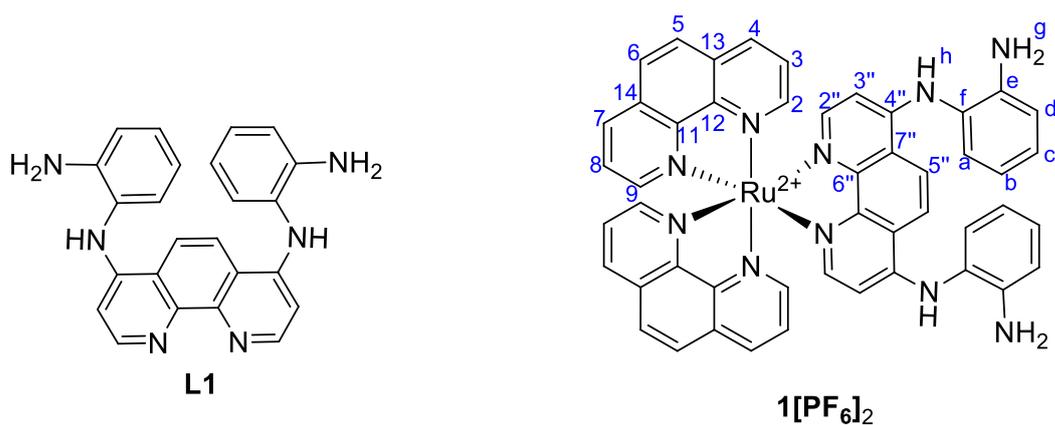
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Table of Contents	Page no
1. Compound used in this study	S2
2. NMR spectra of L1	S3
3. ESI-MS spectrum of L1	S4
4. NMR spectra of 1[PF₆]₂	S4-S6
5. ESI-MS spectrum of 1[PF₆]₂	S7
6. UV-vis selectivity and titration study	S7
7. NMR spectra of 2[PF₆]₂	S8-S9
8. ESI-MS spectrum of 2[PF₆]₂	S9
9. IR spectra of 1[PF₆]₂ and 2[PF₆]₂	S10
10. HRMS spectra of 1[PF₆]₂ in the absence and presence of phosgene in acetonitrile.	S11
11. Previously reported luminescent probes for phosgene.	S11-S13
12. Optimized structures of 1[PF₆]₂ and 2[PF₆]₂	S14
13. Bond length, and bond angles of optimized 1[PF₆]₂ and 2[PF₆]₂	S15
14. Singlet state TDDFT calculations of 1[PF₆]₂ and 2[PF₆]₂	S16-S17
15. Cartesian coordinates of 1[PF₆]₂ and 2[PF₆]₂	S18-S20

Chart S1: Compound used in this study.



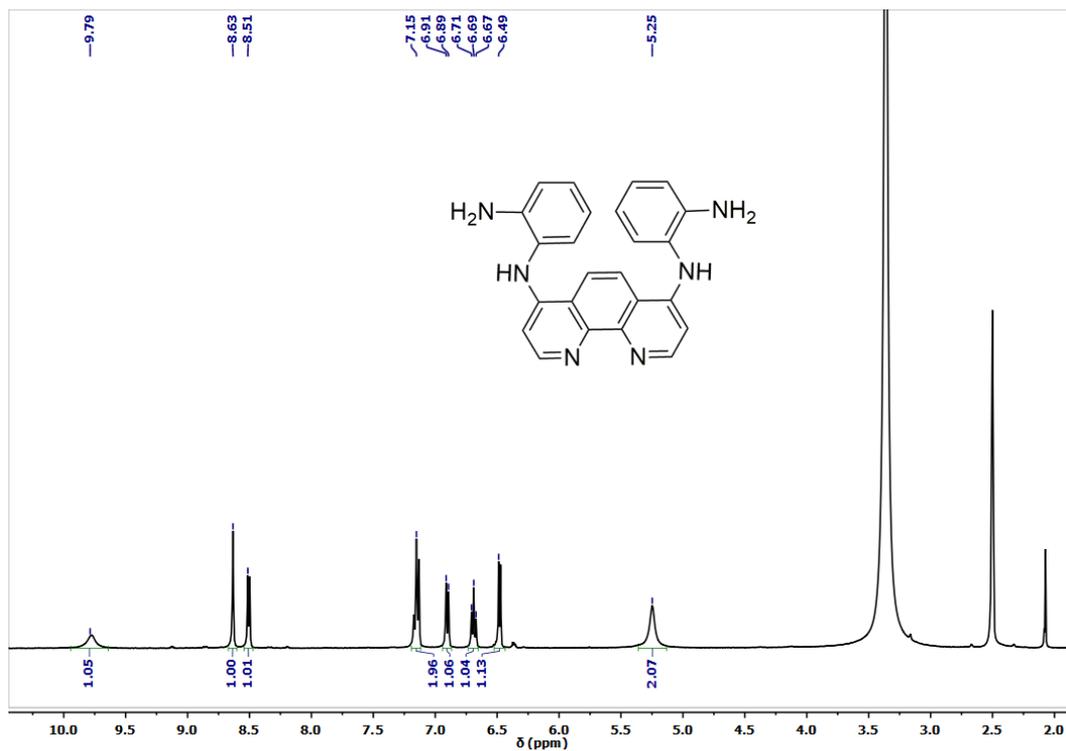


Fig. S1. ^1H NMR spectrum of L1 in $\text{DMSO-}d_6$.

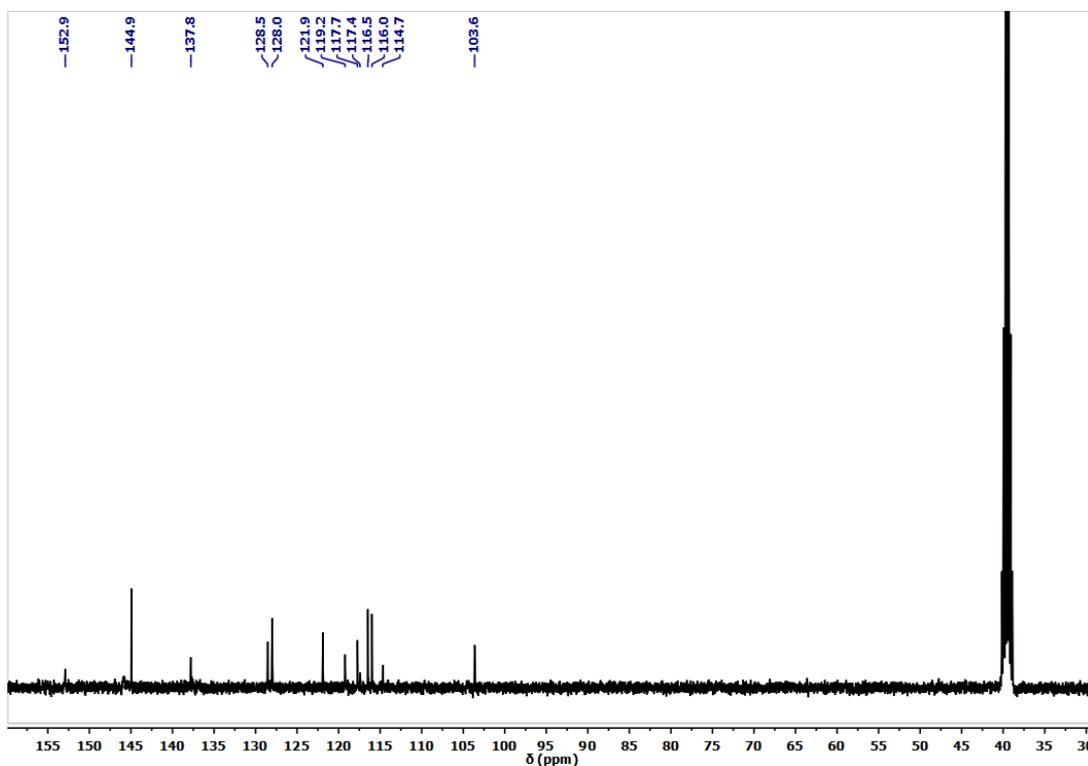


Fig. S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of L1 in $\text{DMSO-}d_6$.

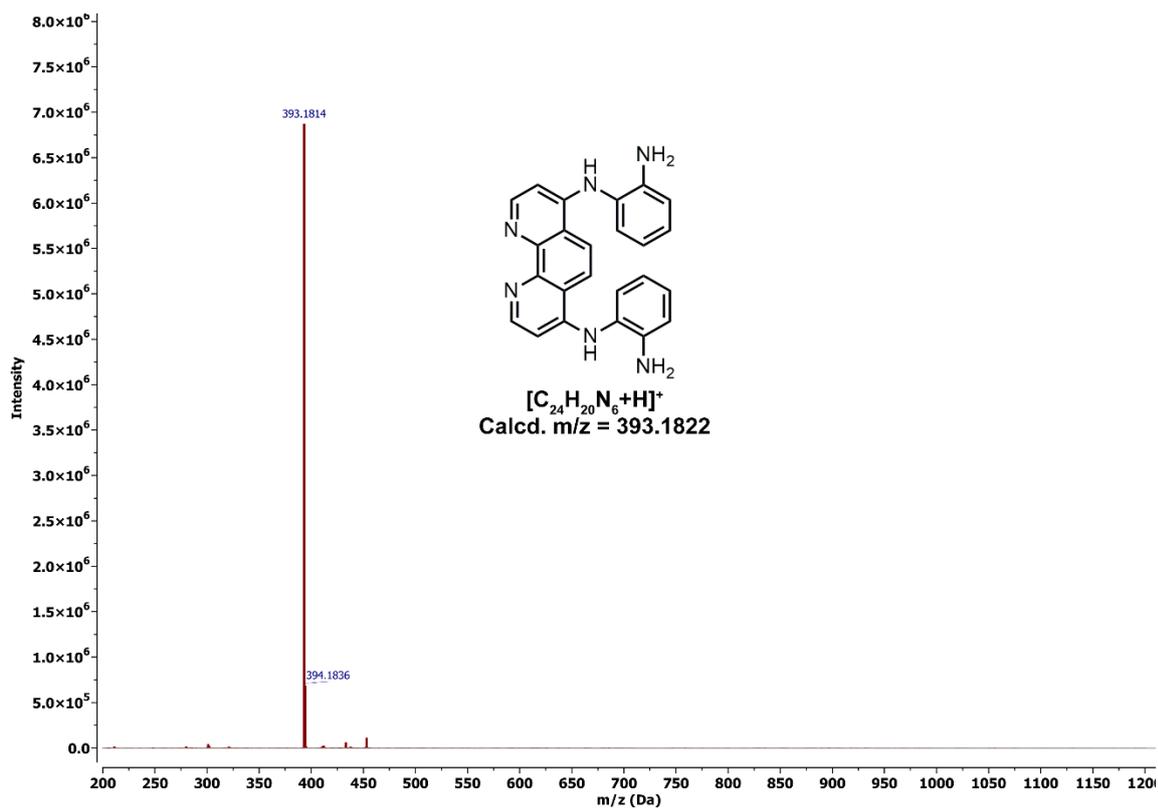


Fig. S3. ESI-MS spectrum of L1 in CH₃OH

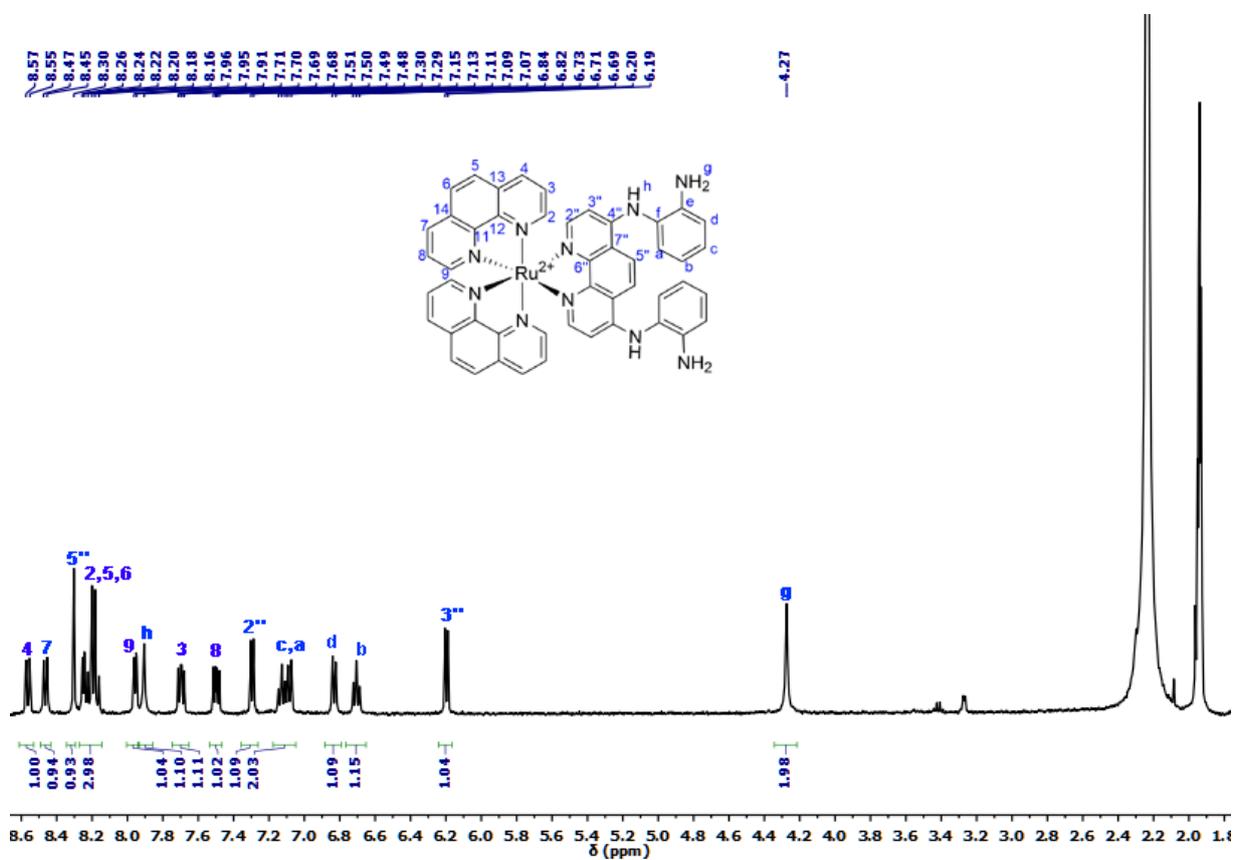


Fig. S4. ¹H NMR spectrum of 1[PF₆]₂ in CD₃CN.

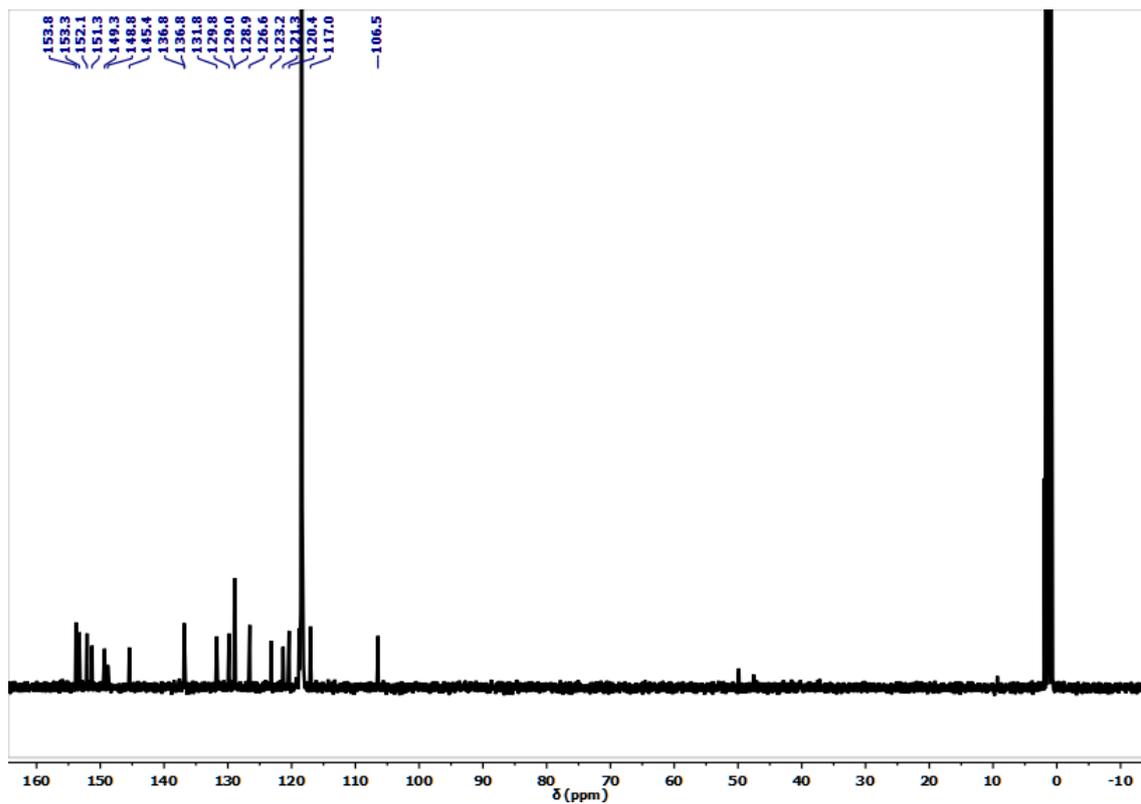


Fig. S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $1[\text{PF}_6]_2$ in CD_3CN .

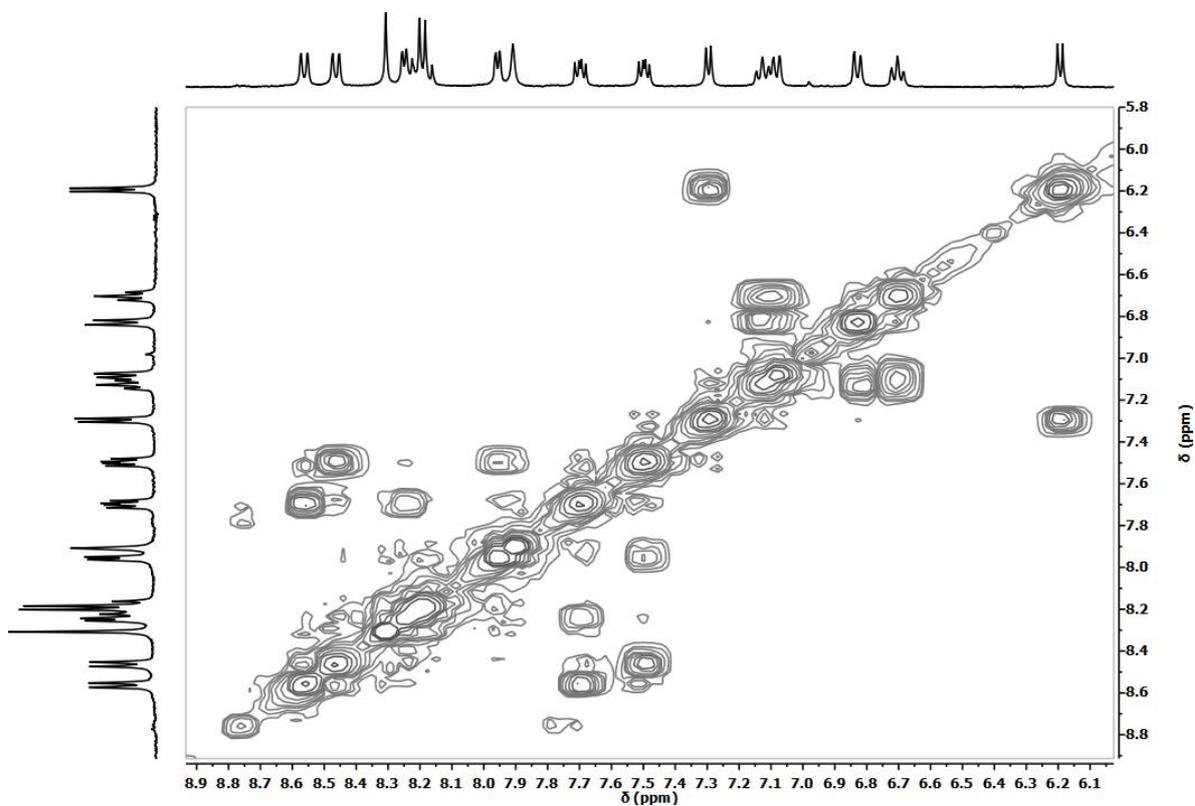


Fig. S6. $^1\text{H}\text{-}^1\text{H}$ COSY NMR spectrum of $1[\text{PF}_6]_2$ in CD_3CN .

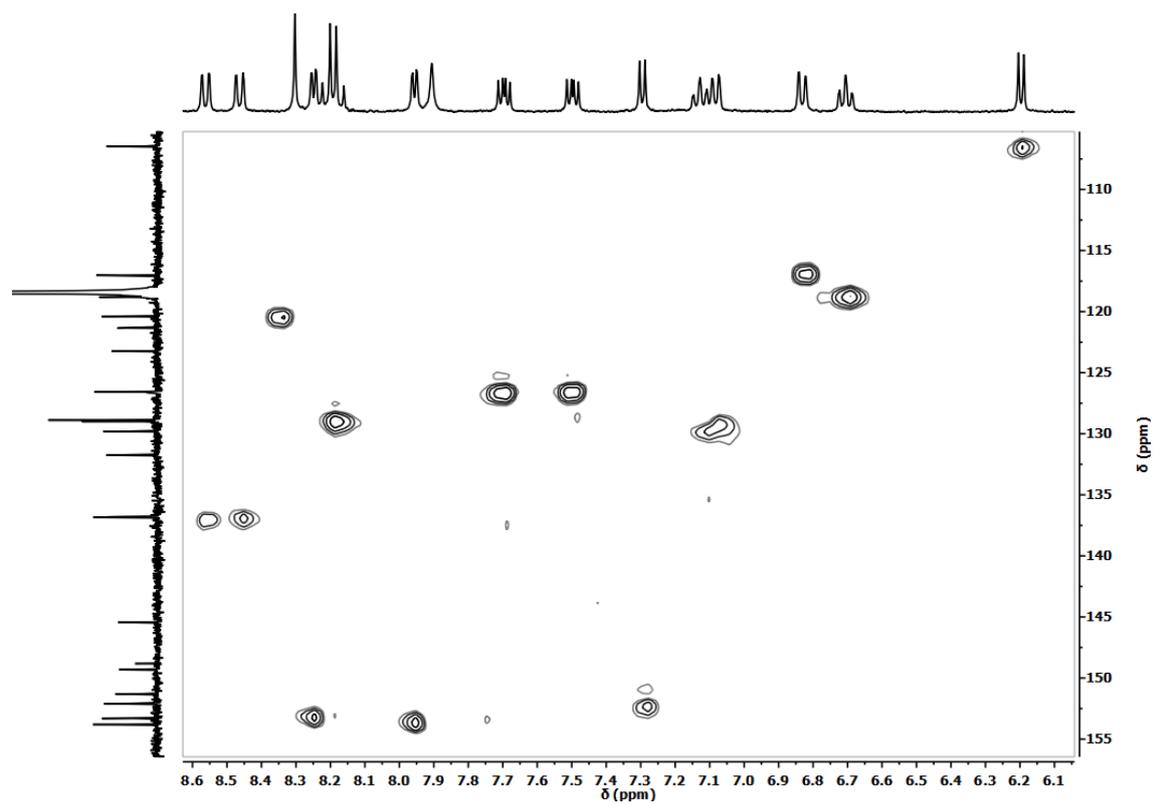


Fig. S7. ^1H - ^{13}C HSQC NMR spectrum of $1[\text{PF}_6]_2$ in CD_3CN .

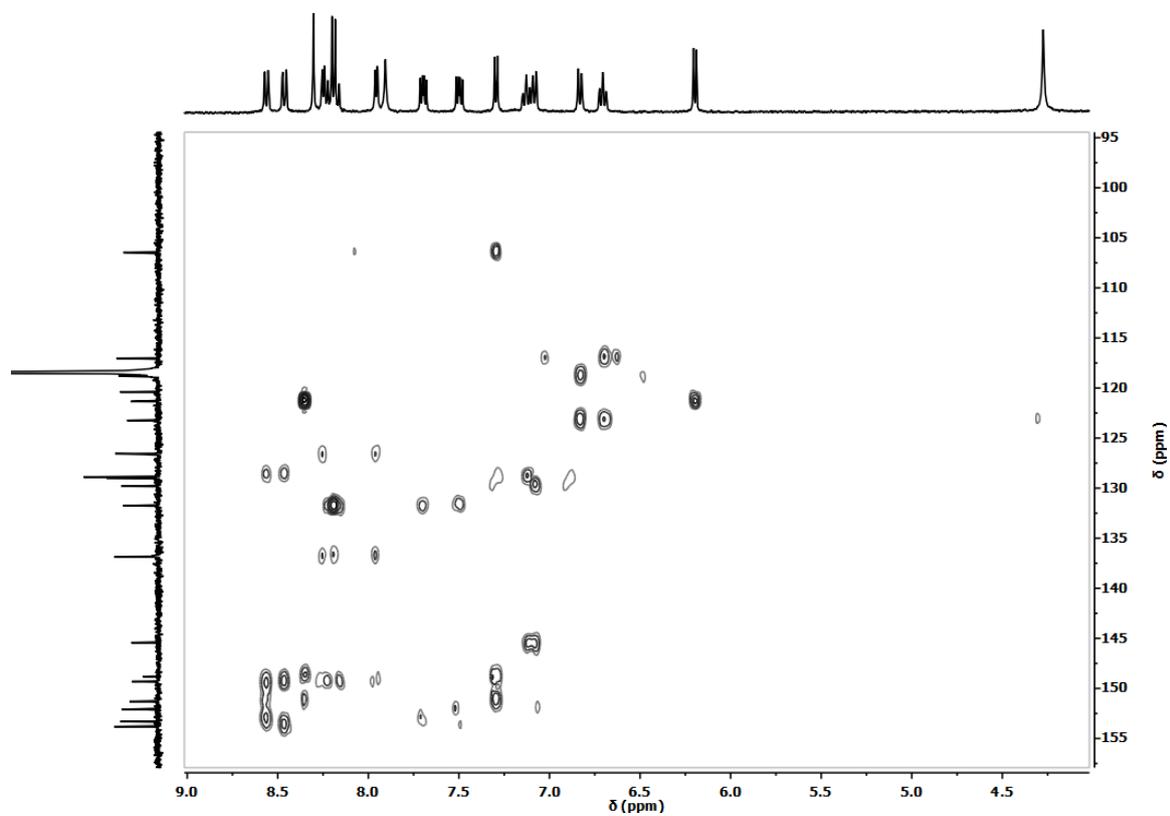


Fig. S8. Partial ^1H - ^{13}C HMBC NMR spectrum of $1[\text{PF}_6]_2$ in CD_3CN .

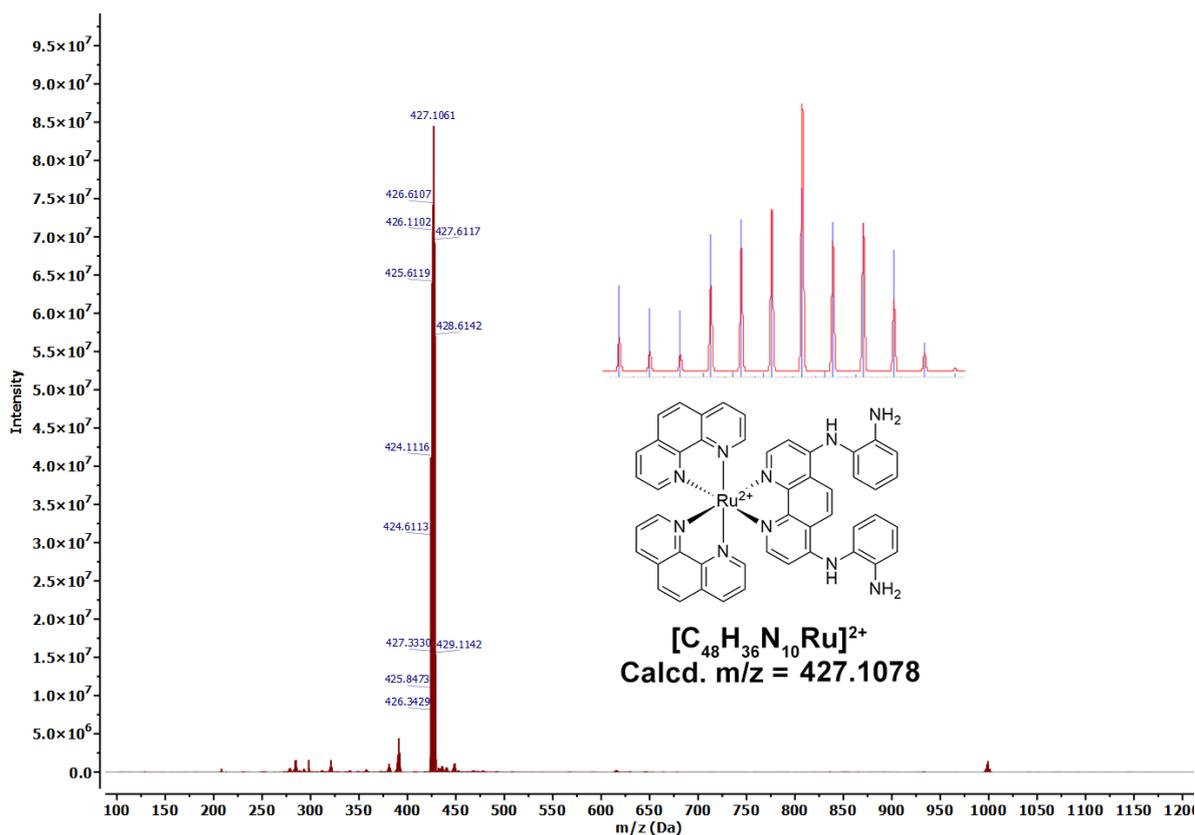


Fig. S9. ESI-HRMS spectrum of **1**[PF₆]₂ in CH₃CN

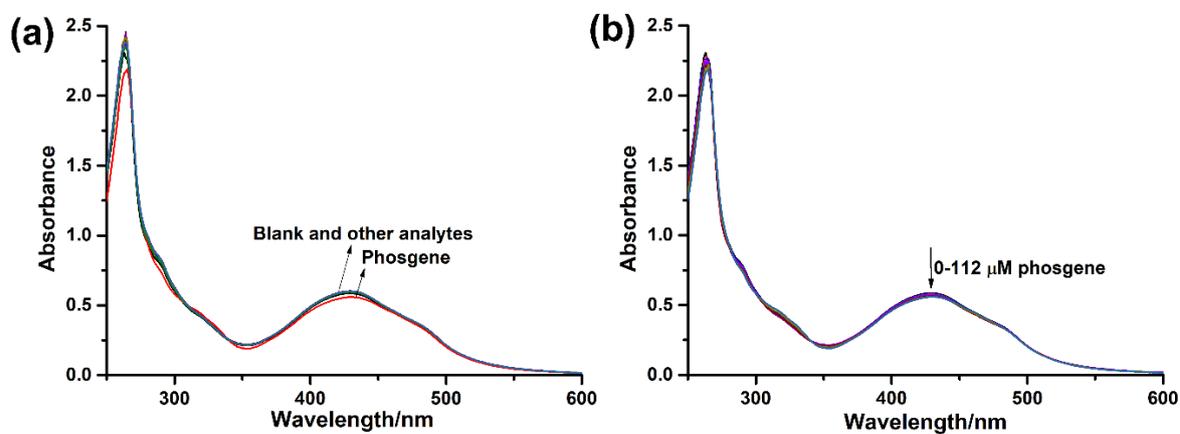


Fig. S10. (a) Selectivity study of **1**[PF₆]₂ with phosgene and other analytes using UV-vis spectroscopy. (b) Titration of **1**[PF₆]₂ with increasing amounts of phosgene.

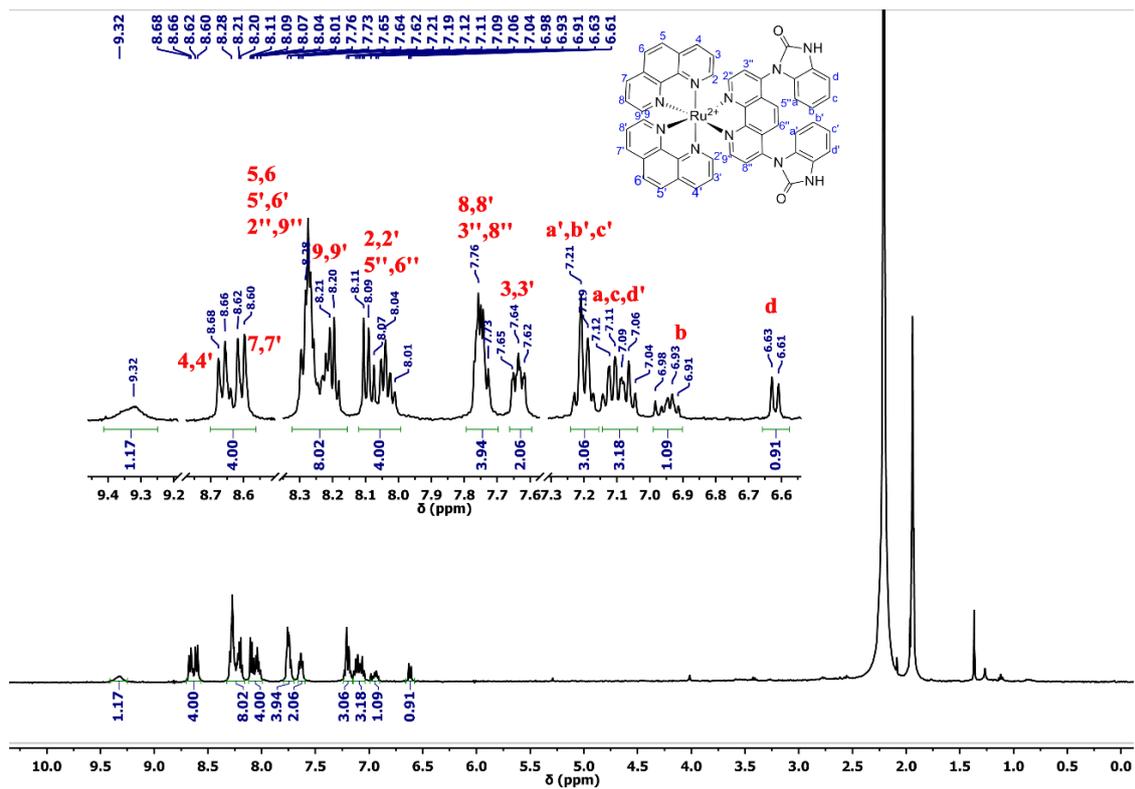


Fig. S11. 1H NMR spectrum of $2[PF_6]_2$ in CD_3CN .

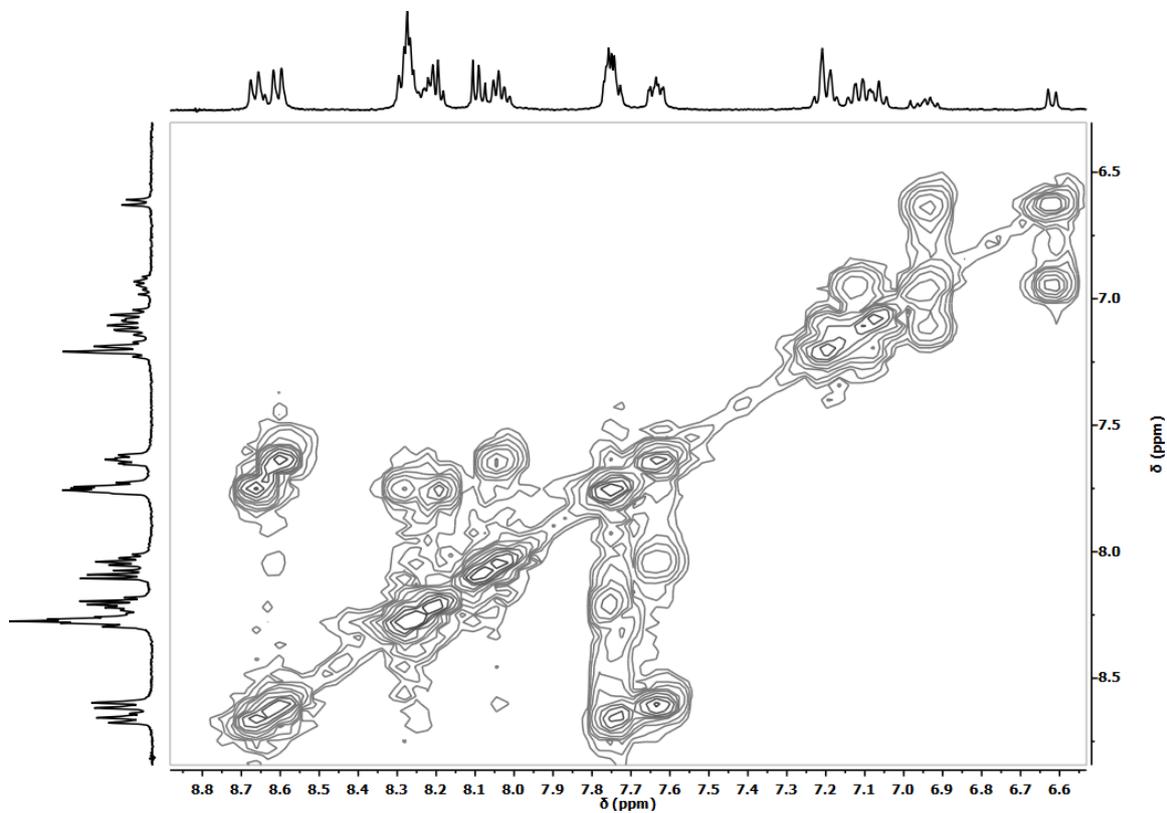


Fig. S12. Partial 1H - 1H COSY NMR spectrum of $2[PF_6]_2$ in CD_3CN .

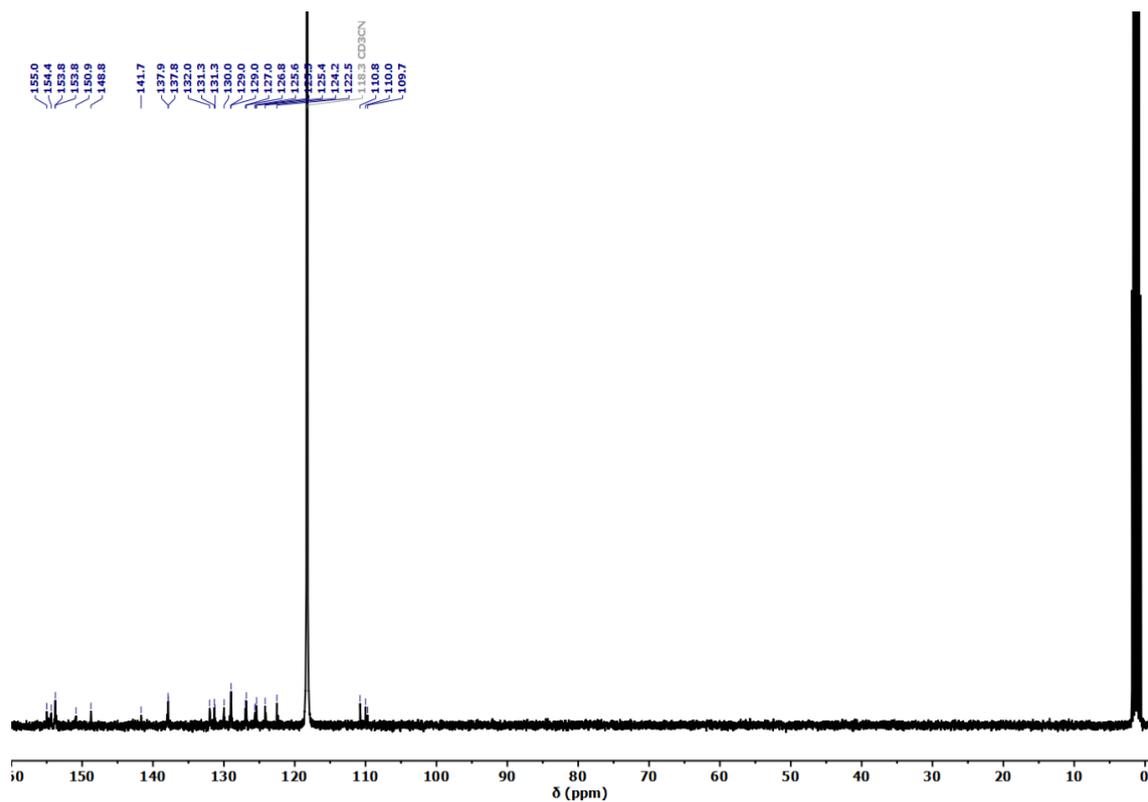


Fig. S13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $2[\text{PF}_6]_2$ in CD_3CN .

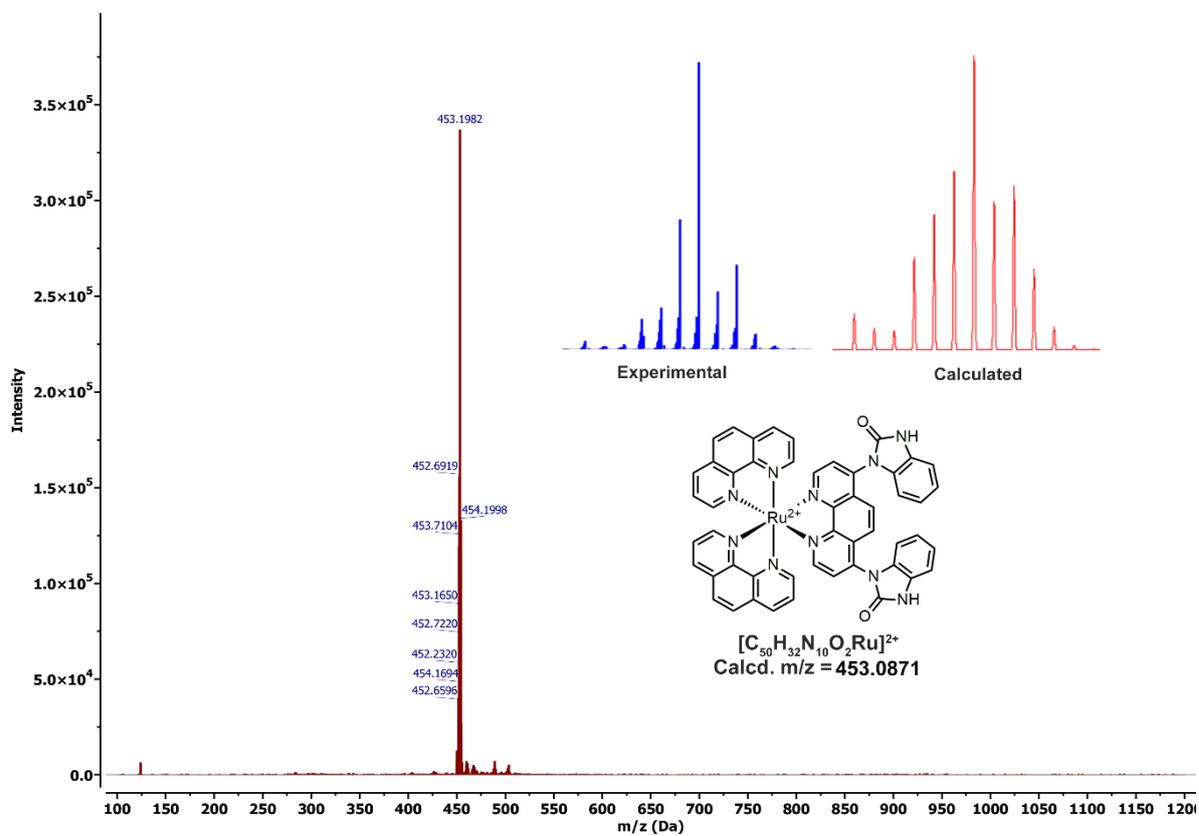
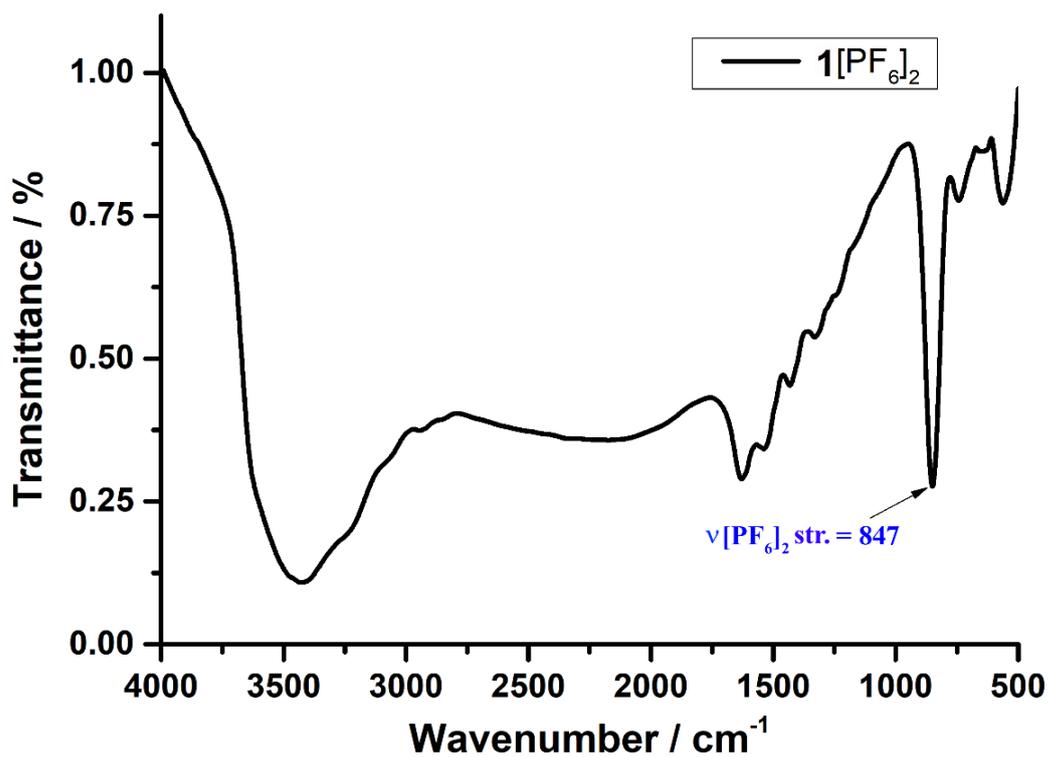
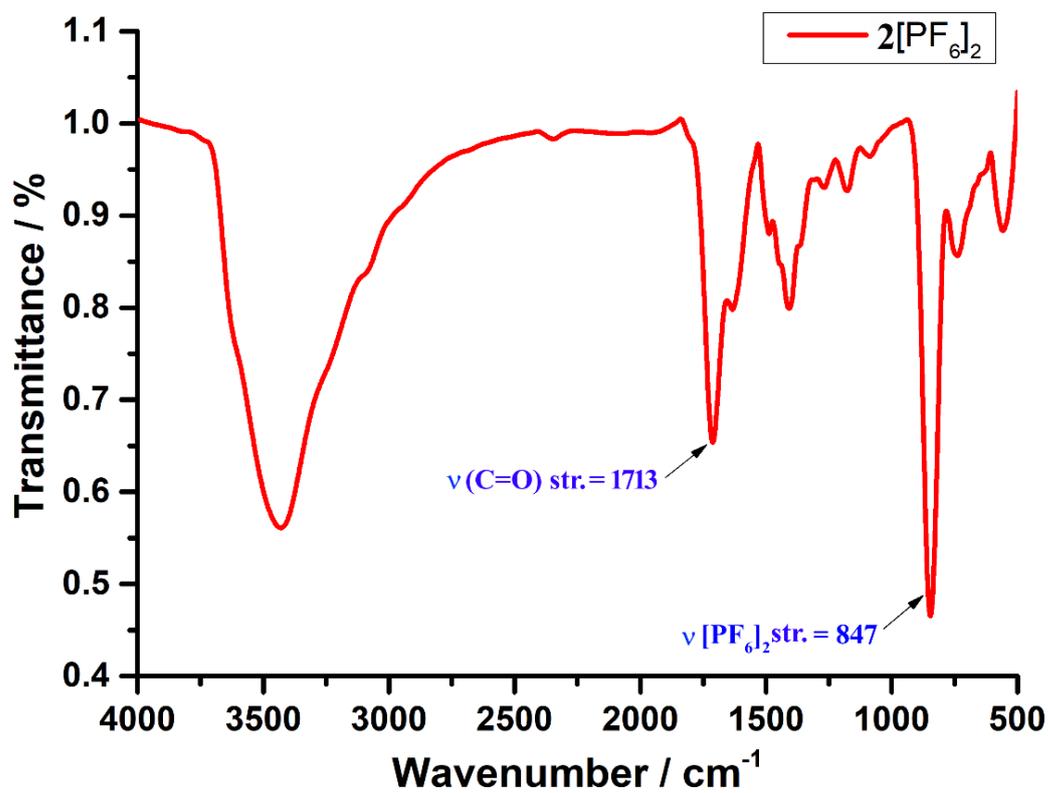


Fig. S14. ESI-HRMS spectrum of $2[\text{PF}_6]_2$ in CH_3CN .

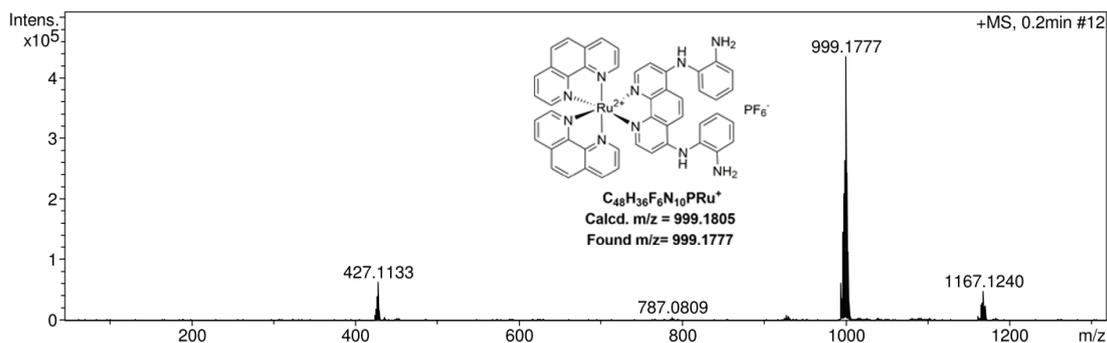


(a)



(b)

Fig. S15. FTIR spectra of (a) $1[PF_6]_2$, and (b) $2[PF_6]_2$.



1[PF₆]₂ + Et₃N + Triphosgene

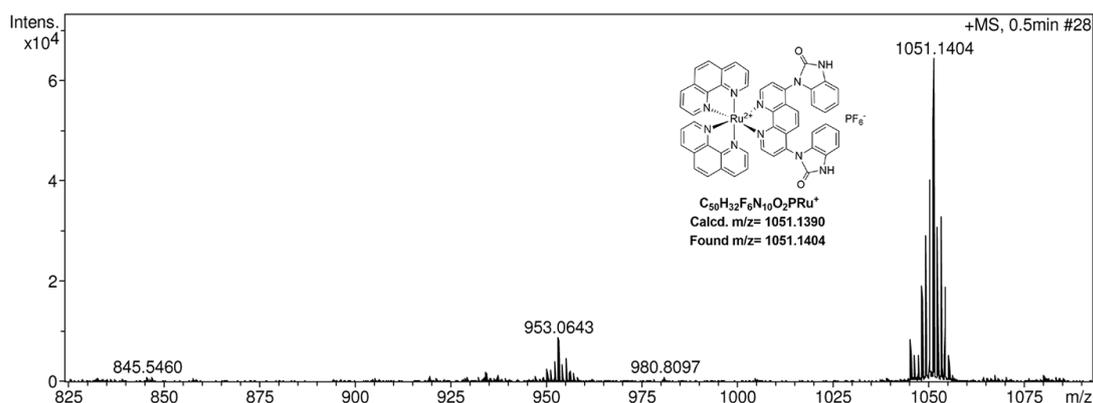
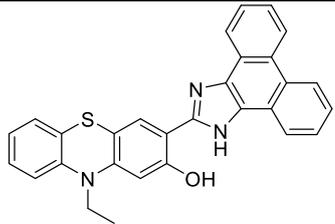
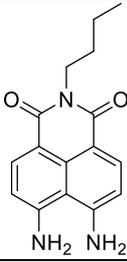
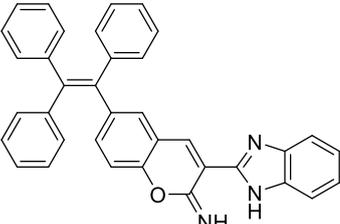
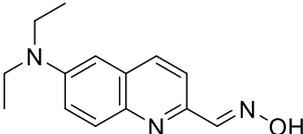
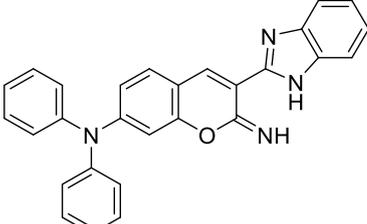
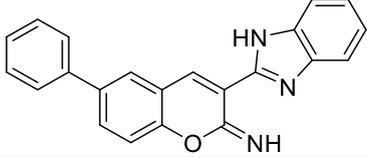
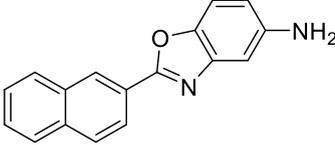
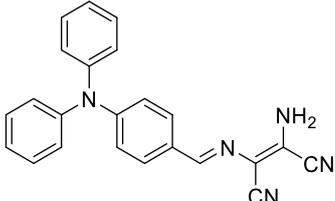
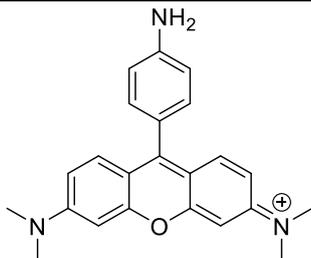
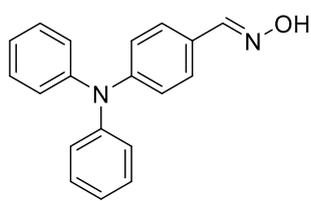
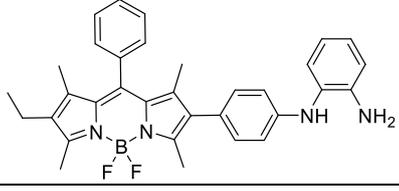
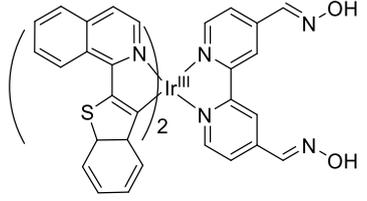
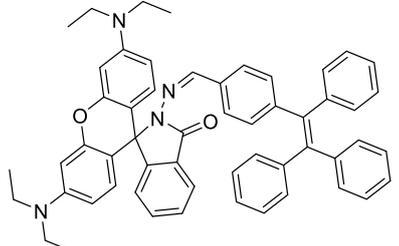
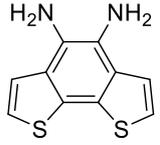
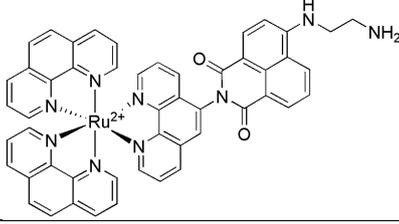


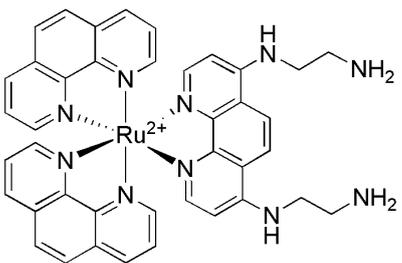
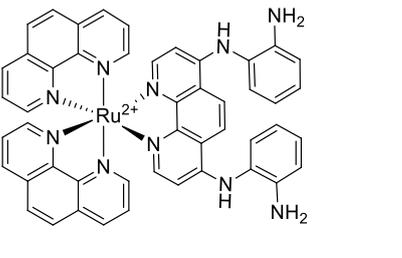
Fig. S16. HRMS spectra of **1**[PF₆]₂ in the absence (top) and presence of phosgene (bottom) in acetonitrile.

Table S1. Summary of previously reported luminescent probes for phosgene.

Sl. No.	Probe	Detection Limit	Response time	Reference
1.		179 nM	<10 s	<i>Chem. Eur. J.</i> 2018 , <i>24</i> , 3136–3140.
2.		0.4 μM	<1 min	<i>New J. Chem.</i> , 2019 , <i>43</i> , 11743–11748.
3.		0.12 μM	1 min	<i>New J. Chem.</i> 2020 , <i>44</i> , 5784–5791.

4.		84.2 nM	2 min	<i>Dyes Pigm.</i> 2020 , <i>173</i> , 107933.
5.		2.25 μM	20 min	<i>J. Chin. Chem. Soc.</i> 2020 , <i>67</i> , 1213–1218.
6.		0.36 μM	6 s	<i>Dyes Pigm.</i> 2020 , <i>176</i> , 108229.
7.		5.55 μM	1 min	<i>Microchem. J.</i> 2021 , <i>168</i> , 106334.
8.		0.27 μM	2 min	<i>Spectrochim. Acta, Part A</i> , 2021 , <i>253</i> , 119589.
9.		0.1 μM	4 min	<i>New J. Chem.</i> 2023 , <i>47</i> , 17154–17162.
10.		60 nM	20 s	<i>Chem. Res. Toxicol.</i> 2023 , <i>36</i> , 2010–2018.
11.		4.3 μM	80 s	<i>New J. Chem.</i> 2024 , <i>48</i> , 13776–13782.

12.		50 nM	68 s	<i>New J. Chem.</i> 2024 , <i>48</i> , 14813–14818.
13.		21.53 μ M	30 s	<i>New J. Chem.</i> 2024 , <i>48</i> , 9103–9109.
14.		126 nM	<10 s	<i>J. Mater. Chem. B</i> , 2024 , <i>12</i> , 12282–12290.
15.		0.18 μ M	5 s	<i>New J. Chem.</i> 2025 , <i>49</i> , 8939–8946.
16.		0.1 μ M	<30 s	<i>Chem. Commun.</i> , 2025 , <i>61</i> , 11041–11044.
17.		0.16 μ M	30 s	<i>Sensors</i> , 2025 , <i>25</i> , 407.
18.		126 nM	<10 s	<i>Inorg. Chem. Front.</i> , 2026 , https://doi.org/10.1039/D5QI01770J .

19.		13.9 nM	300 s	<i>Previous Work</i> <i>Inorg. Chem.</i> 2021, 60, 19175–19188
20.		72 nM	~120 s	<i>Present work</i>

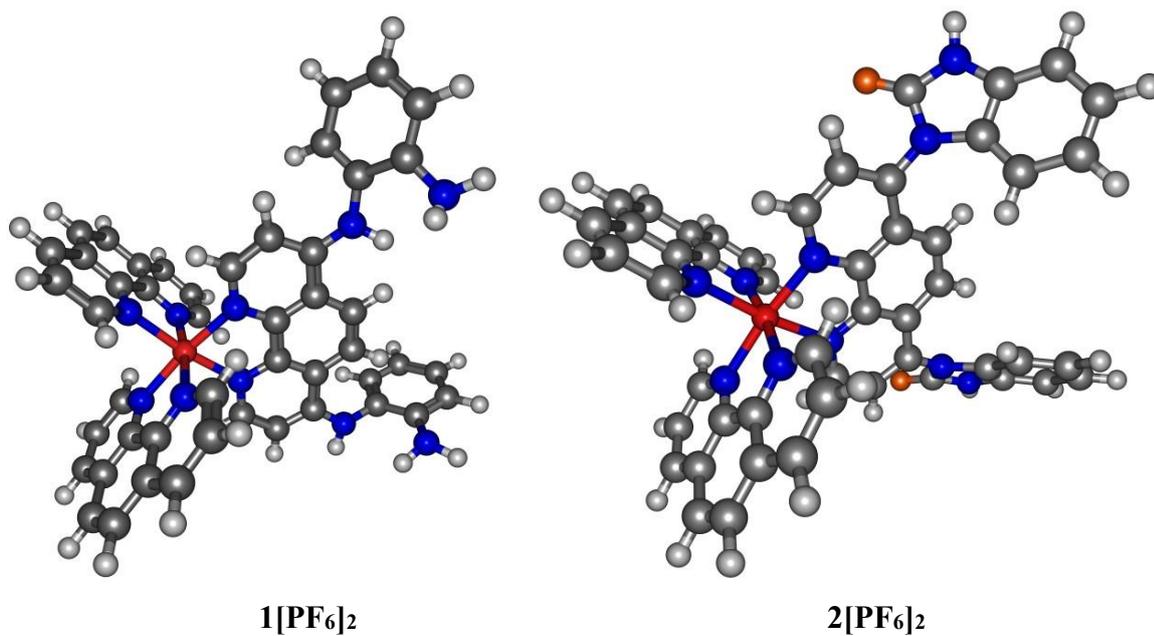


Fig. S17. Optimized structures of **1[PF₆]₂** and **2[PF₆]₂** obtained from DFT optimization at B3LYP/6-31G (d) // LANL2DZ level.

Table S2. Selected bond lengths (Å) and angles (°) around the Ir(III) center in **1[PF₆]₂**.

Bond length(Å)			
N(48)-Ru(59)	2.1170	N(34)-Ru(59)	2.1181
N(55)-Ru(59)	2.1286	N(4)-Ru(59)	2.1147
N(41)-Ru(59)	2.1265	N(11)-Ru(59)	2.1177

Bond angles (°)			
N(48)-Ru(59)-N(55)	78.5	N(34)-Ru(59)-N(4)	89.1
N(55)-Ru(59)-N(41)	88.8	N(4)-Ru(59)-N(11)	77.6
N(41)-Ru(59)-N(34)	78.56	N(11)-Ru(59)-N(48)	89.3

Table S3: Selected bond lengths (Å) and angles (°) around the Ir(III) center in **2[PF₆]**.

Bond length(Å)			
N(53)-Ru(57)	2.1208	N(32)-Ru(57)	2.1240
N(46)-Ru(57)	2.1261	C(4)-Ru(57)	2.1165
N(39)-Ru(57)	2.1267	C(11)-Ru(57)	2.1144

Bond angles (°)			
N(53)-Ru(57)-N(46)	78.6	N(32)-Ru(57)-N(4)	89.9
N(46)-Ru(57)-N(39)	89.05	N(4)-Ru(57)-N(11)	77.9
N(39)-Ru(57)-N(32)	78.57	N(11)-Ru(57)-N(53)	88.5

Table S4. Selected transitions obtained from ground state TD-DFT calculation at B3LYP/6-31G(d,p) // LANL2DZ level responsible for experimental ¹MLCT transitions for **1**[PF₆]₂ and **2**[PF₆]₂ in CH₃CN.

Compound	Wavelength(nm/eV)		Transition	Oscillator strength (f)
	Experimentally observed	Theoretically obtained		
1 [PF ₆] ₂ .	425 nm(2.91 eV)	423.56 nm (2.92 eV)	HOMO-1→LUMO+3 HOMO-2→LUMO+3 HOMO-3→LUMO+1 HOMO-3→LUMO	0.069
		417.40 nm (2.97 eV)	HOMO→LUMO+4 HOMO-3 →LUMO+3 HOMO-3→LUMO+2	0.3472
2 [PF ₆] ₂ .	429 nm(2.89 eV)	426.48 nm (2.90 eV)	HOMO-2→LUMO HOMO→LUMO+1	0.0895
		442.25nm (2.91 eV)	HOMO→LUMO+2 HOMO-1 →LUMO+1 HOMO-4→LUMO+2	0.0787
		422.25 nm (2.93 eV)	HOMO-4 →LUMO+3 HOMO →LUMO+3	0.033

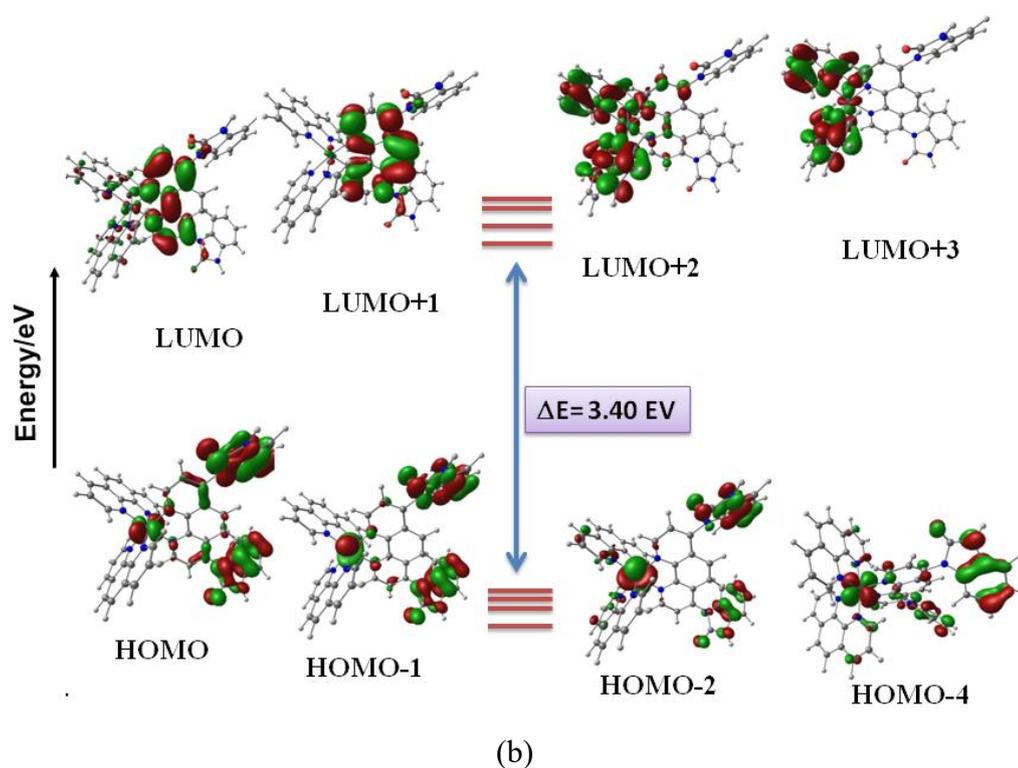
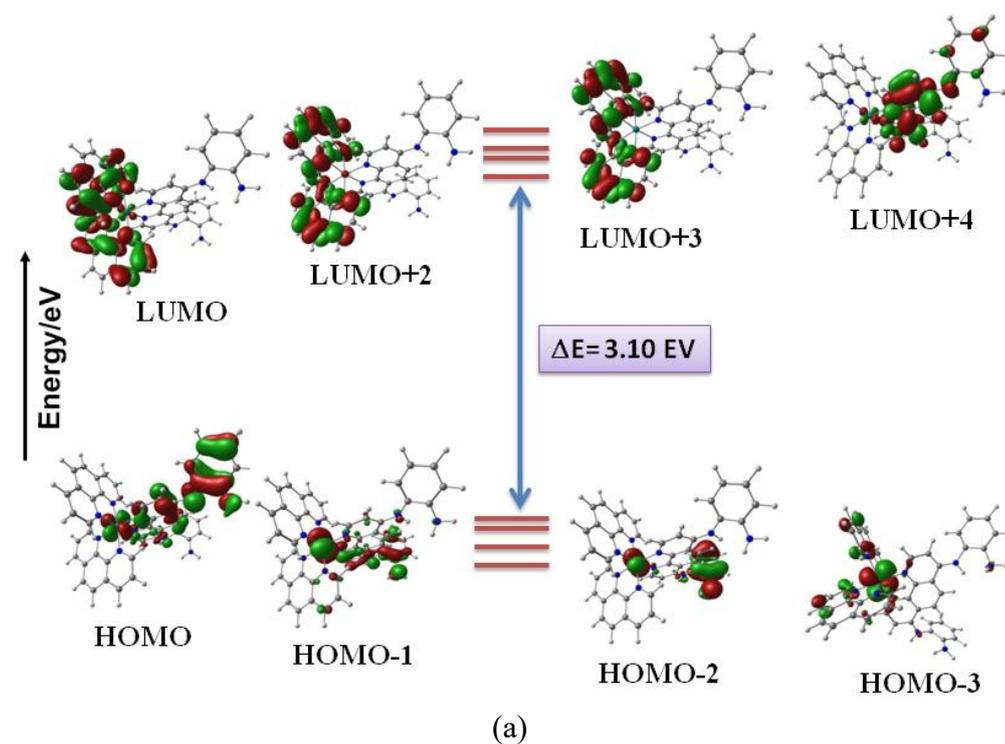


Fig. S18. Energy level diagram of selected molecular orbitals of (a) **1[PF₆]₂** and (b) **2[PF₆]₂**, obtained from singlet state TD-DFT (B3LYP/6-31G+(d) // LANL2DZ) calculation in CH₃CN at the optimized ground-state geometry (isovalue = 0.03).

Table S5. The x,y,z Cartesian coordinates of the complex **1[PF₆]₂** and **2[PF₆]₂** obtained from DFT optimization at B3LYP/6-31G (d) // LANL2DZ level.

1[PF₆]₂

	x	y	z		x	y	z
C	-2.69261700	2.10156900	-0.62326900	C	3.08061400	-1.40528300	-2.21051700
C	-1.52077200	2.87561700	-0.71033800	C	3.43183500	-1.89758700	-3.49094300
C	-0.27804100	2.28435400	-0.53440900	C	3.87287700	-1.75222200	-1.06826000
N	-0.09282400	0.98303000	-0.27096400	C	5.01074800	-2.58122000	-1.22218600
C	-1.21330300	0.19684600	-0.16448800	C	5.34659400	-3.06462500	-2.53231200
C	-2.52435500	0.69492100	-0.32924400	C	4.58921400	-2.73845600	-3.61887300
C	-0.99599100	-1.19685100	0.12240900	N	3.47745800	-1.25447500	0.14399500
C	-2.09722900	-2.08335000	0.25894000	C	4.20691100	-1.56289500	1.21966200
C	-3.41020300	-1.54463400	0.08400600	C	5.35152800	-2.37564700	1.15653600
C	-3.61023100	-0.21995700	-0.19154400	C	5.75640500	-2.88796000	-0.06196300
N	0.31342600	-1.58696600	0.24150300	Ru	1.73726900	-0.03444500	0.02507800
C	0.55033600	-2.88432800	0.47001300	H	-1.57373200	3.92933100	-0.94995500
C	-0.45191600	-3.82925300	0.62190000	H	0.62112800	2.88467400	-0.62261900
C	-1.81009500	-3.47015000	0.54524400	H	-4.26778000	-2.19369500	0.17639700
N	-2.74365600	-4.45713500	0.70327500	H	-4.63363300	0.12766000	-0.28418900
N	-3.93279400	2.60948400	-0.82403300	H	1.59160900	-3.17626400	0.55173500
C	-4.12394800	-4.34395500	1.10985800	H	-0.17427100	-4.85938300	0.82471800
C	-4.35899700	3.95866900	-0.92192600	H	-2.33131900	-5.36551800	0.89435600
C	-5.13837600	-4.62597800	0.16949800	H	-4.69546700	1.96007100	-0.99346100
C	-6.47456600	-4.57362100	0.61178800	H	-7.27234600	-4.78420200	-0.09580600
C	-6.77873600	-4.25841300	1.93104100	H	-7.81886400	-4.23210800	2.24248800
C	-5.76505400	-3.98590800	2.85748200	H	-6.00606500	-3.75036400	3.88871000
C	-4.43949900	-4.03819700	2.43841000	H	-3.62966100	-3.84830800	3.13801900
C	-3.83692400	4.99510600	-0.14064900	H	-3.02915100	4.79515800	0.55552200
C	-4.39385000	6.27119500	-0.21422500	H	-3.98664900	7.07119800	0.39586000
C	-5.49111200	6.50682100	-1.04497000	H	-5.93488400	7.49615100	-1.09609300
C	-6.02063700	5.47306200	-1.81689900	H	-6.87154000	5.65828300	-2.46752300
C	-5.46040000	4.19296300	-1.77467200	H	-6.87729700	3.31279700	-2.93712700
N	-5.99850100	3.08778400	-2.47999200	H	-5.35922900	2.70824000	-3.17538900
N	-4.83286400	-4.86426900	-1.16334600	H	-3.89747600	-5.20199300	-1.34812400
C	1.83746700	1.63674700	4.65101000	H	-5.54033800	-5.35584600	-1.69466500
C	1.08372500	0.50975200	4.38152300	H	1.88866600	2.04685100	5.65544400
C	1.03955600	0.00205400	3.07192800	H	0.52436700	0.00814100	5.16384500
N	1.70167200	0.56336400	2.05675000	H	0.45733900	-0.88063400	2.83328900
C	2.44548800	1.68401600	2.31065300	H	4.63918700	4.87503900	2.87172900
C	2.54792000	2.25942600	3.60045600	H	3.43368900	3.86570200	4.76884300
C	3.14148600	2.27433800	1.20635600	H	3.50359800	1.71809800	-2.01338900
C	3.93740400	3.42835400	1.40735000	H	4.95023200	3.73964700	-1.83103000
C	4.02680600	3.99015600	2.72614800	H	5.22453200	4.84977200	0.39460200
C	3.35969200	3.43117400	3.77639400	H	2.84758800	-1.88083600	-5.57923000
N	2.99508800	1.67964100	-0.01775100	H	0.86993600	-0.40444600	-5.16874500
C	3.64045100	2.21321700	-1.05846900	H	0.39574400	0.38074500	-2.84714100

C	4.45287800	3.35432300	-0.94745700	H	6.22071700	-3.69957400	-2.64176900
C	4.60325500	3.96586100	0.28317700	H	4.85243400	-3.11093600	-4.60438400
C	2.61296500	-1.52477500	-4.58028500	H	3.86742600	-1.15162900	2.16383600
C	1.52013200	-0.70853100	-4.35552700	H	5.90122500	-2.58978200	2.06677700
C	1.24458300	-0.26167100	-3.05195200	H	6.63691600	-3.51949200	-0.13667700
N	2.00005700	-0.59151300	-2.00096800				

2[PF₆]₂

	x	y	z		x	y	z
C	1.98800300	2.88718600	0.33429300	C	-2.83614200	-1.74532900	2.34284700
C	0.72502700	3.42679400	0.56923800	C	-2.97987800	-2.34801400	3.61621600
C	-0.40406500	2.60880400	0.52642800	C	-3.93795600	-3.40524100	3.78103300
N	-0.35065100	1.29745900	0.27050400	C	-4.70436000	-3.83018600	2.73566900
C	0.87518700	0.74650300	0.01280700	N	-1.95236300	-0.72828300	2.10136700
C	2.07664900	1.49826100	0.00826600	C	-1.19367500	-0.29672200	3.11244100
C	0.89518700	-0.65458900	-0.31008200	C	-1.27119500	-0.83954500	4.40629100
C	2.11656100	-1.29600900	-0.63506300	C	-2.16278500	-1.86446300	4.66271800
C	3.30087600	-0.49058200	-0.71123600	Ru	-1.97145400	-0.05187700	0.09140500
C	3.28154900	0.83955900	-0.40597000	N	4.33538600	5.53110900	-0.06851900
N	-0.31462300	-1.29369800	-0.33702500	C	3.08315100	5.00590700	-0.28905300
C	-0.33068600	-2.58750900	-0.67416700	N	4.47645100	-4.80887700	-2.48792900
C	0.82071300	-3.31091700	-0.98555900	C	3.21088700	-4.27065500	-2.45639400
C	2.06661900	-2.68823900	-0.95410100	O	2.14977400	5.47943700	-0.90490900
N	3.20579300	-3.42065100	-1.29978400	O	2.28601500	-4.43633400	-3.22619900
N	3.10616200	3.72534700	0.36036800	H	0.61294900	4.48160800	0.78034700
C	4.44923500	-3.52945200	-0.63069700	H	-1.38720400	3.02267400	0.71906500
C	4.35008700	3.55361500	1.01585300	H	4.22550000	-0.94830800	-1.03928800
C	4.91077300	-3.01322300	0.57529800	H	4.19101200	1.41971900	-0.49664100
C	6.20457300	-3.36494300	0.97903200	H	-1.30159900	-3.06908700	-0.69110800
C	6.99959600	-4.21600000	0.20408700	H	0.73901100	-4.35466600	-1.25719600
C	6.52412600	-4.75768900	-0.99493600	H	4.29419000	-2.36708200	1.19084600
C	5.24085500	-4.40661000	-1.39352600	H	6.59118900	-2.97361700	1.91460100
C	5.11531800	4.69933400	0.73339000	H	7.99900200	-4.47173700	0.54085800
C	6.39132500	4.86640600	1.25574300	H	7.13160500	-5.43563200	-1.58584400
C	6.88681300	3.85679800	2.08774100	H	6.97811100	5.75244700	1.03570000
C	6.11760600	2.72915600	2.39349200	H	7.88117700	3.95928600	2.51006500
C	4.83116900	2.56359200	1.86593000	H	6.51880500	1.96953100	3.05675000
C	-2.81150400	1.75994200	-4.40945100	H	4.23530300	1.69414300	2.12181100
C	-1.84590100	0.78043300	-4.27381300	H	-3.02945900	2.19743900	-5.37936300
C	-1.58704300	0.23457100	-3.00497000	H	-1.28209000	0.42354000	-5.12887200
N	-2.23938000	0.62125500	-1.90522100	H	-0.83577500	-0.53606200	-2.87472500
C	-3.19568100	1.59299200	-2.02720000	H	-5.97425900	4.34221700	-2.21237100
C	-3.52104400	2.19432300	-3.26720400	H	-4.78611200	3.65823400	-4.25996700
C	-3.88210500	1.99496800	-0.83556800	H	-3.83836300	1.24459800	2.36595800
C	-4.89000900	2.98777900	-0.90113600	H	-5.64012300	2.96580500	2.42315200
C	-5.20152500	3.58046100	-2.17159200	H	-6.31481300	4.09953800	0.29736100
C	-4.54407500	3.20155300	-3.30502200	H	-6.07423800	-4.43348000	0.41814500

N	-3.51769900	1.38771300	0.33589500	H	-5.71746500	-3.28787200	-1.77725600
C	-4.15064900	1.74537900	1.45639200	H	-4.01801000	-1.47205400	-1.94136600
C	-5.16448400	2.71803100	1.48037800	H	-4.04191200	-3.86214900	4.76059700
C	-5.53588000	3.34264500	0.30449100	H	-5.42642100	-4.62958600	2.87243100
C	-5.34279400	-3.63717600	0.31539300	H	-0.50512400	0.50932300	2.88501600
C	-5.14738000	-3.00580900	-0.89869400	H	-0.62980500	-0.44451700	5.18671800
C	-4.19192200	-1.98020000	-0.99950400	H	-2.24183800	-2.29948600	5.65478500
N	-3.45008500	-1.57867200	0.03618400	H	4.58658900	6.44773200	-0.41086400
C	-3.63872700	-2.19385600	1.24423100	H	4.74873400	-5.46601000	-3.20524400
C	-4.57772900	-3.23664600	1.43391500				