Electronic Supplementary Material (ESI) for RSC Advances.

Reactivity of azido terpyridine Pd(II) and Pt(II) complexes towards 4,4,4-trifluoro-2-butynoic acid: Structural insight into the triazolato coordination mode

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Supporting information

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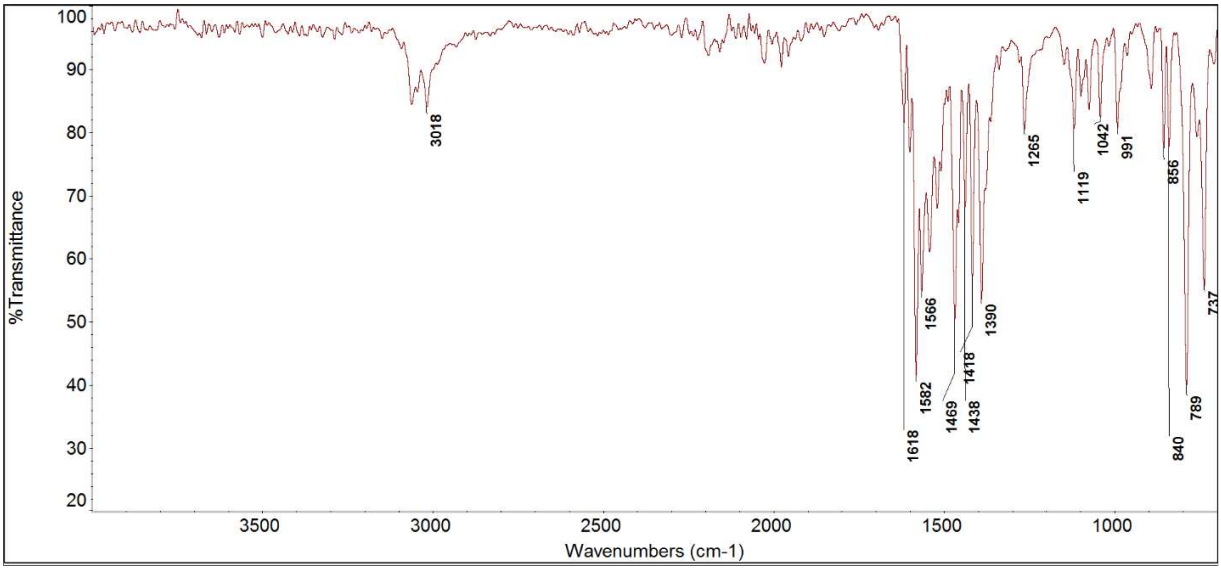


Fig. S1 ATR IR spectrum of the free terpyridine ligand.

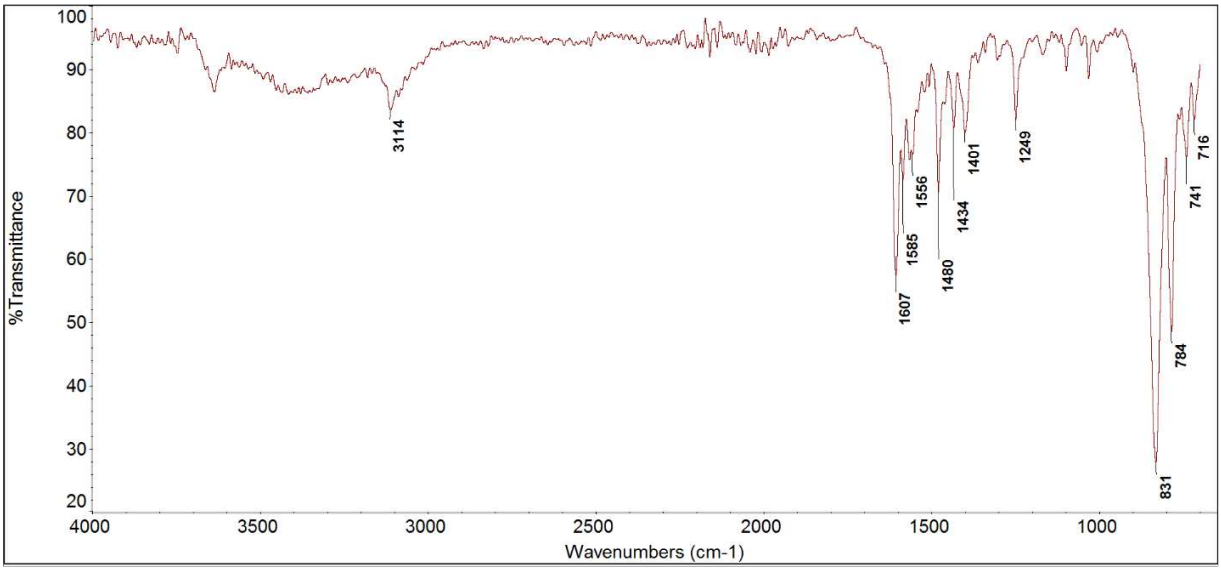


Fig. S2 ATR IR spectrum of **1**.

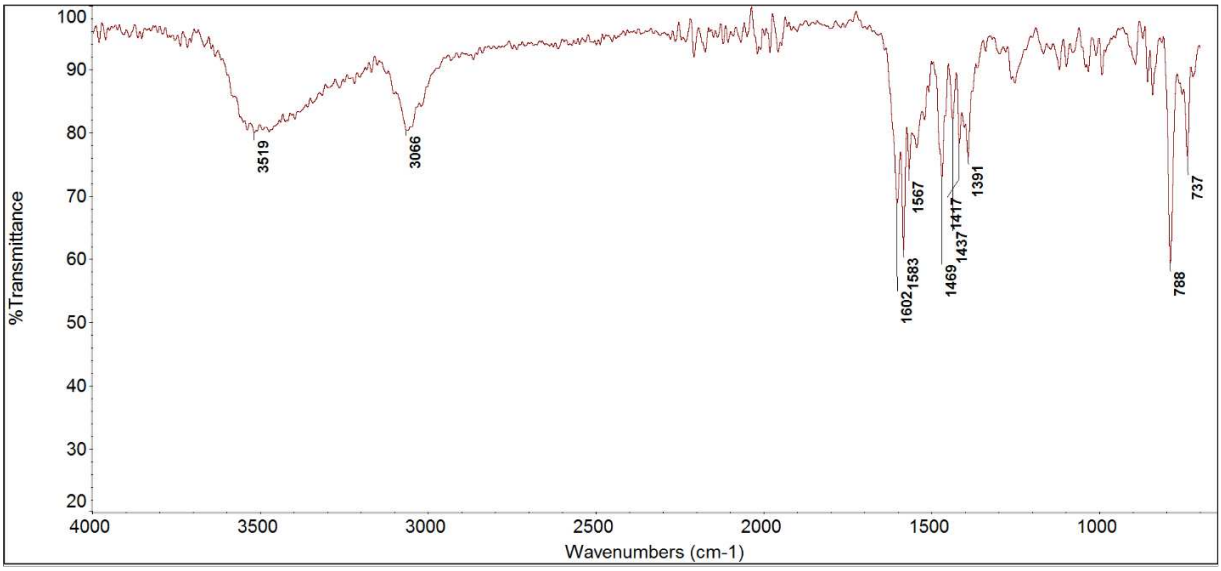


Fig. S3 ATR IR spectrum of **2**.

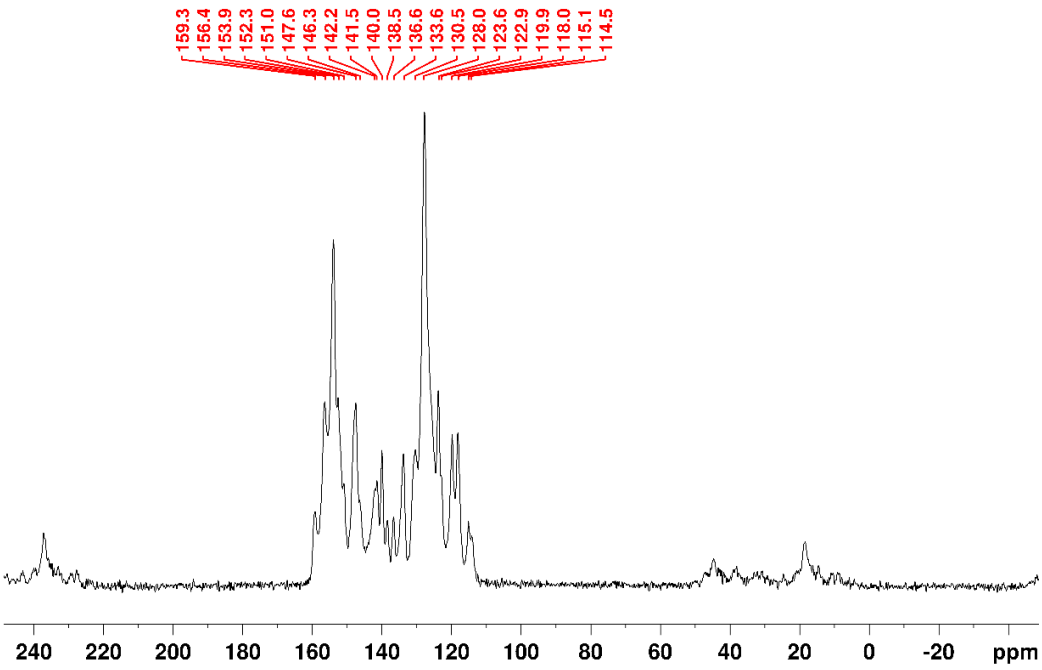


Fig. S4 Solid-state ^{13}C NMR spectrum of **1**.

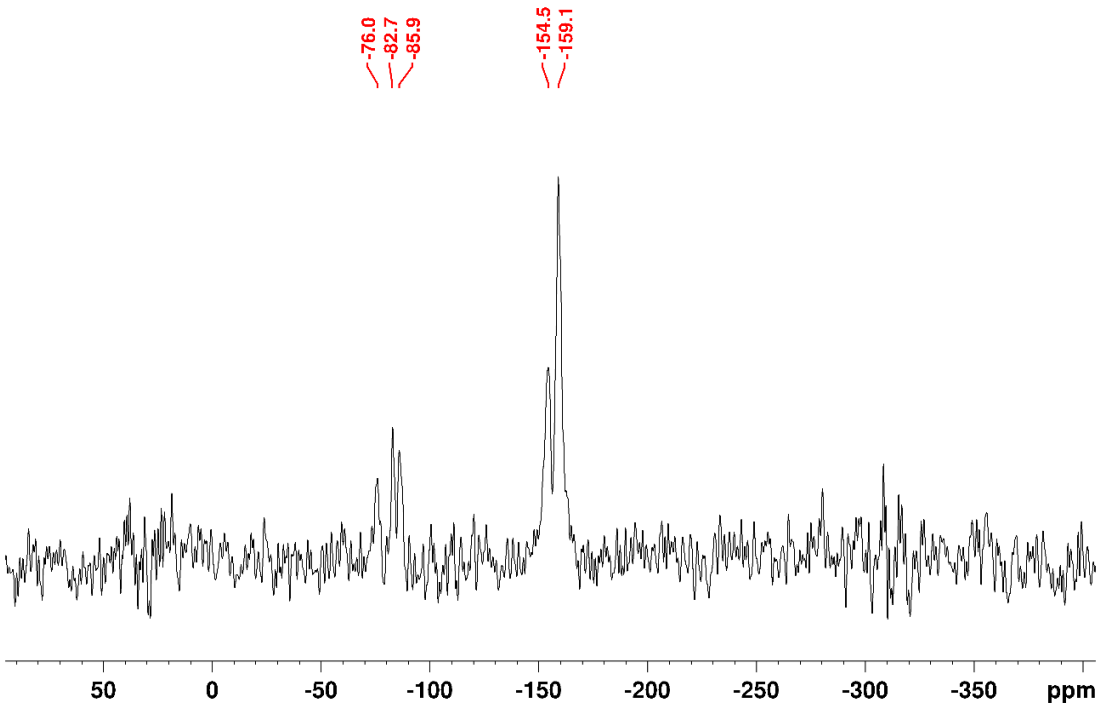


Fig. S5 Solid-state ^{15}N NMR spectrum of **1**.

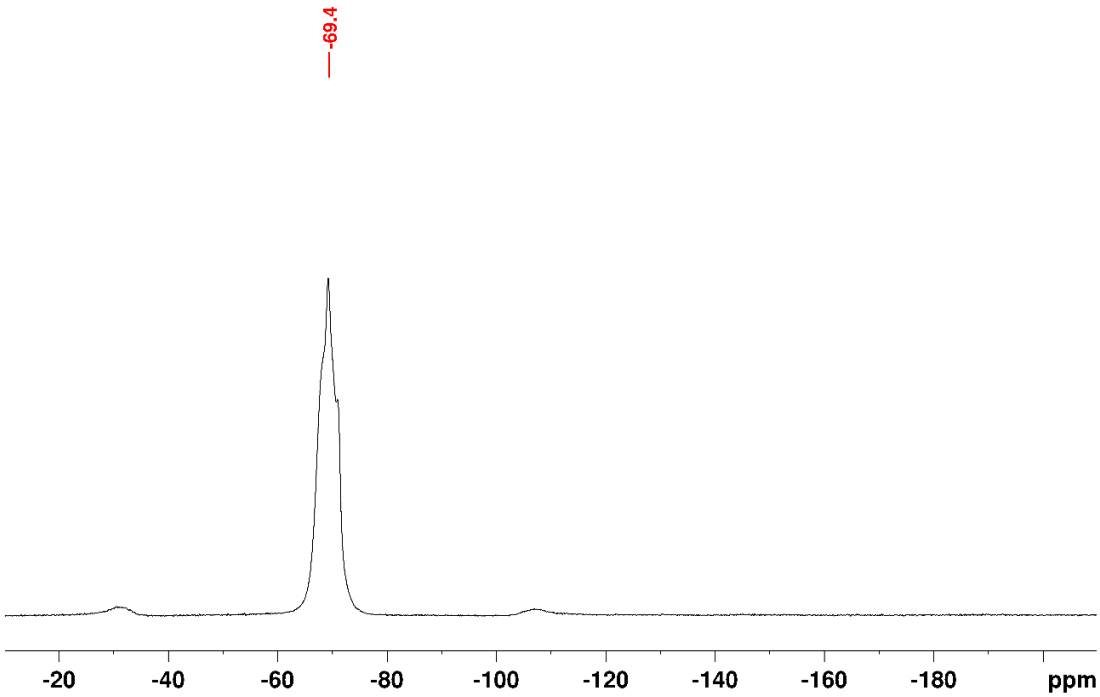


Fig. S6 Solid-state ^{19}F NMR spectrum of **1**.

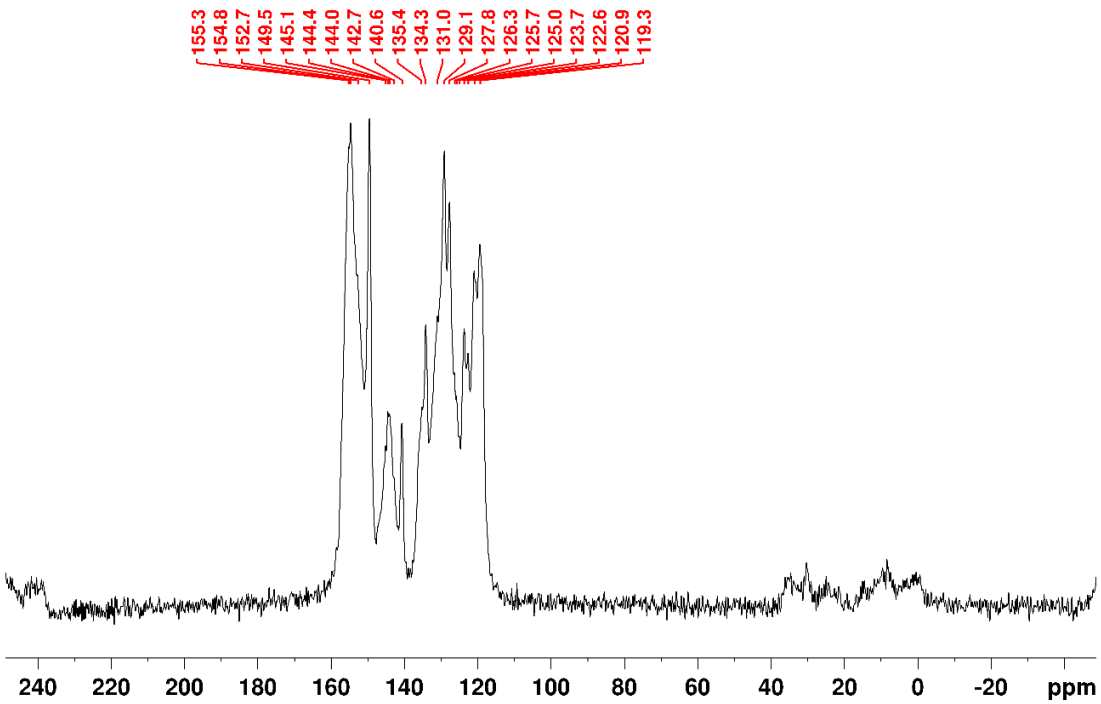


Fig. S7 Solid-state ^{13}C NMR spectrum of **2**.

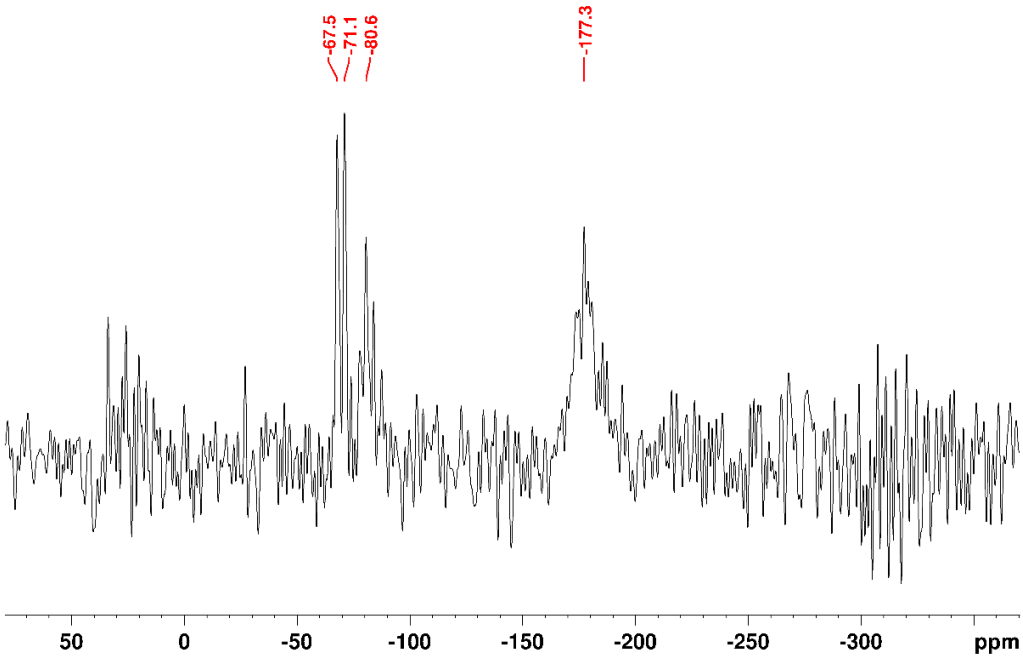
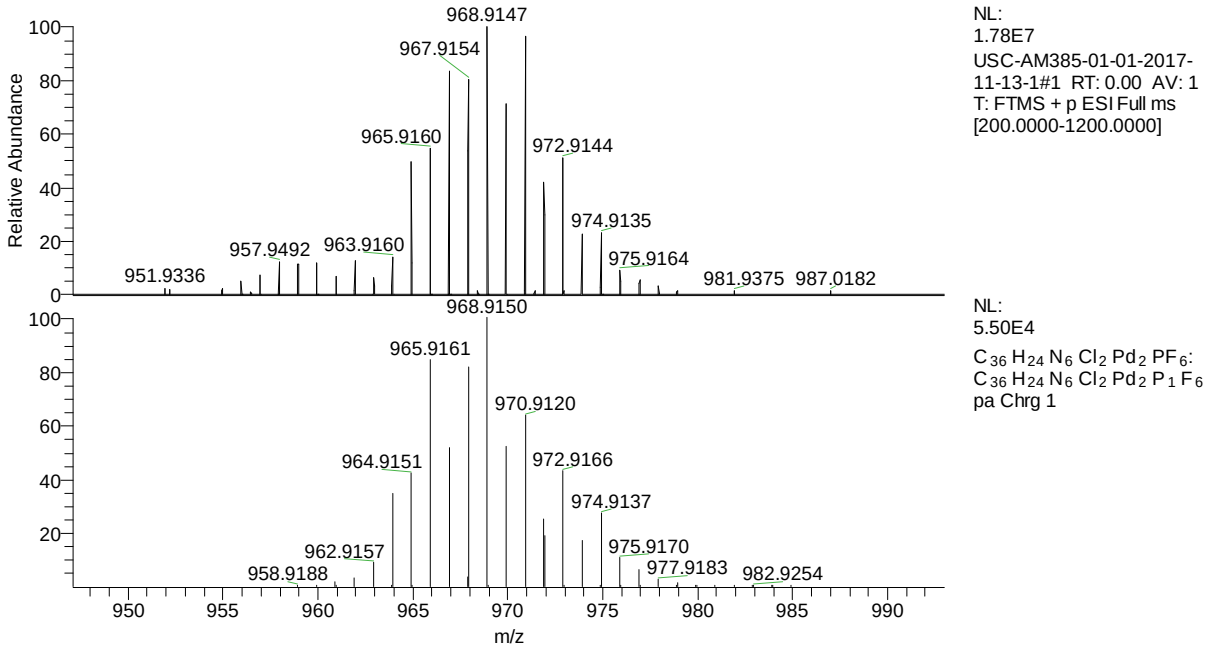
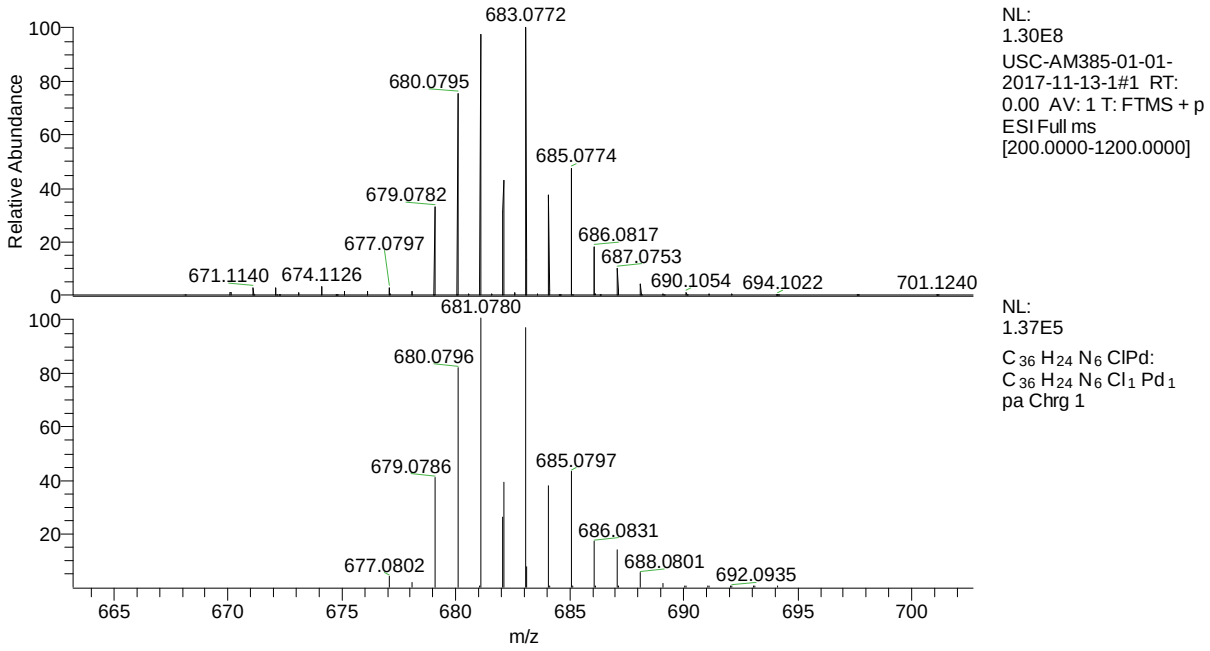


Fig. S8 Solid-state ^{15}N NMR spectrum of **2**.



a)



b)

Fig. S9 ASAP mass spectra: Experimental (Up) and theoretical (down) ISOTOPIC pattern for **1** of **a)** m/z = 968.9147 and **b)** m/z = 683.0772.

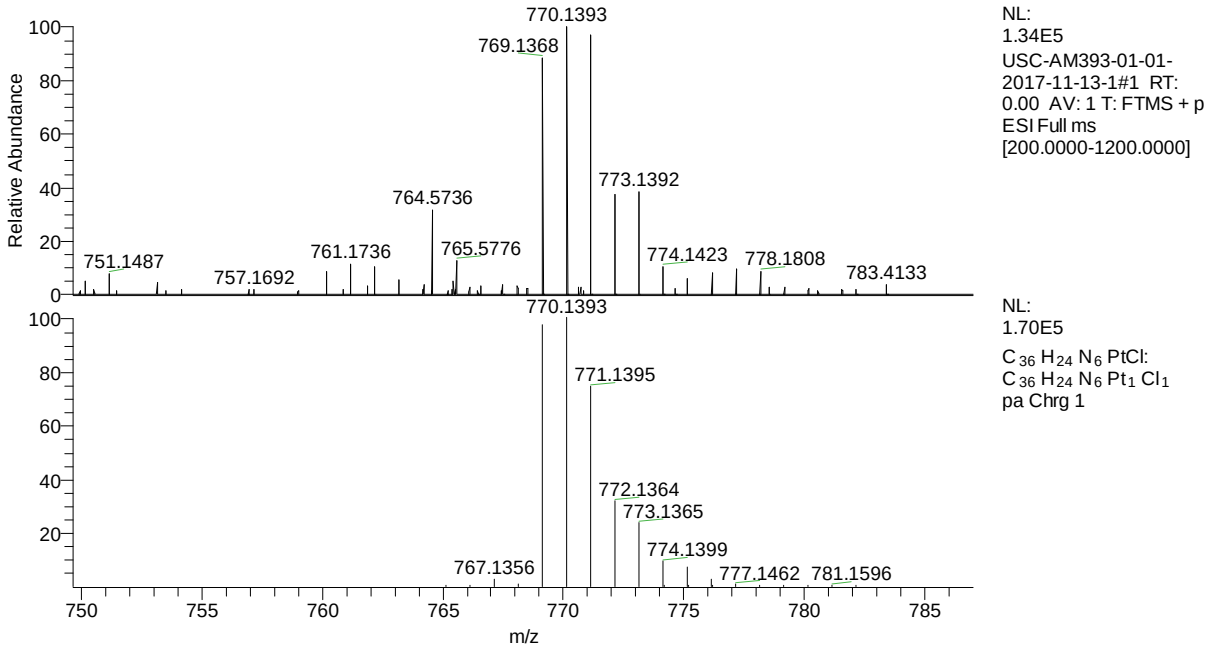


Fig. S10 ASAP mass spectra: Experimental (Up) and theoretical (down) ISOTOPIC pattern for **2**.

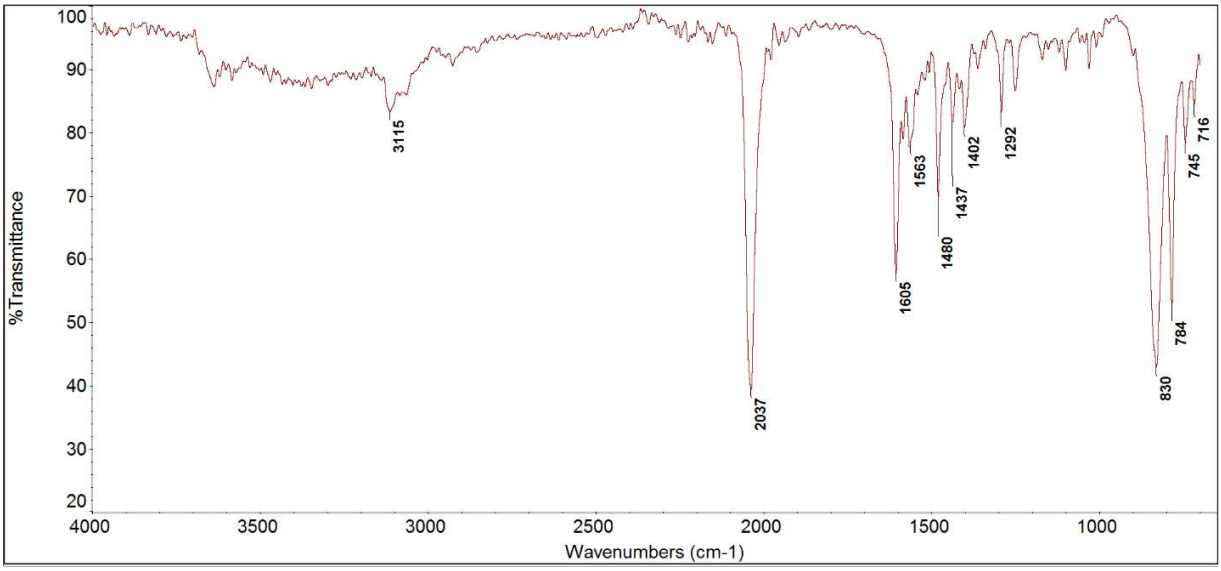


Fig. S11 ATR IR spectrum of **3**.

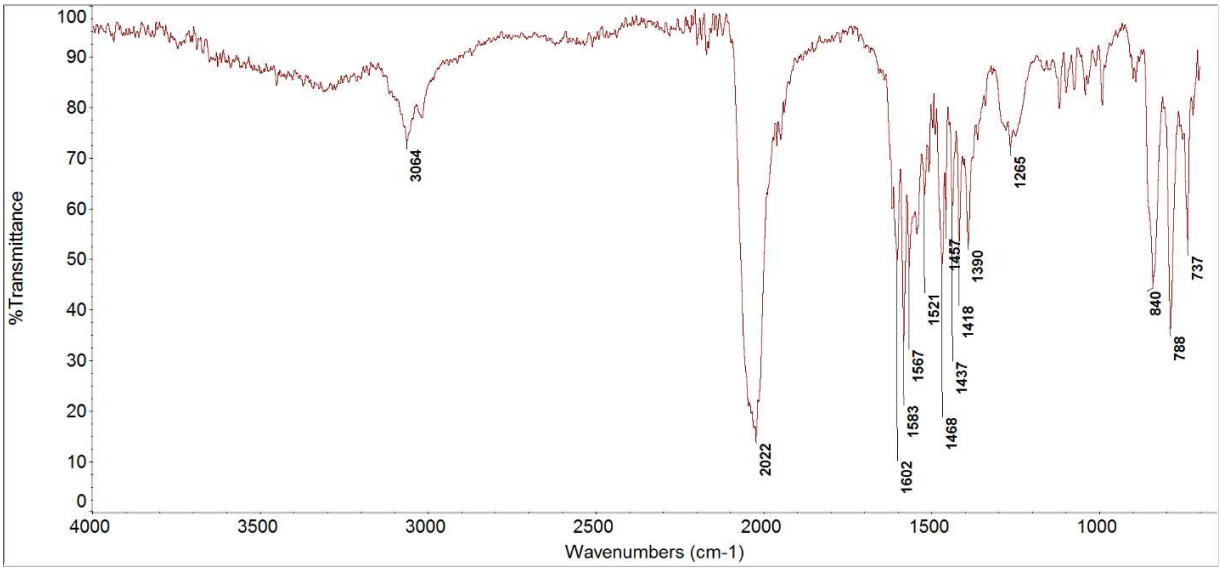


Fig. S12 ATR IR spectrum of **4**.

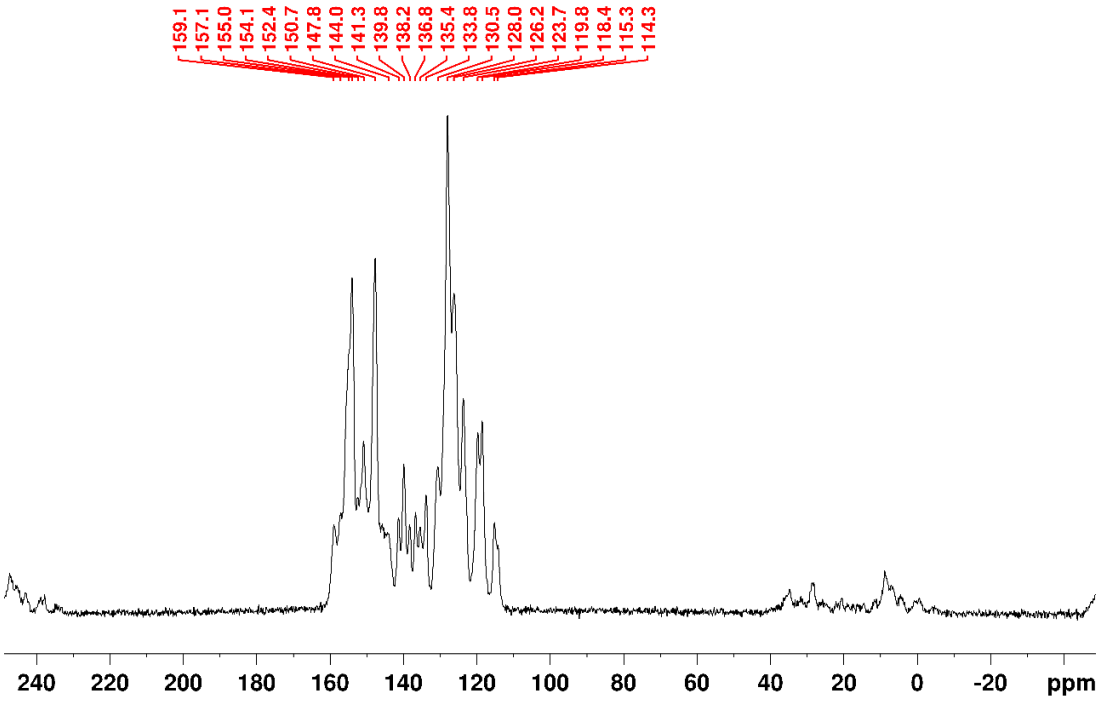


Fig. S13 Solid-state ^{13}C NMR spectrum of **3**.

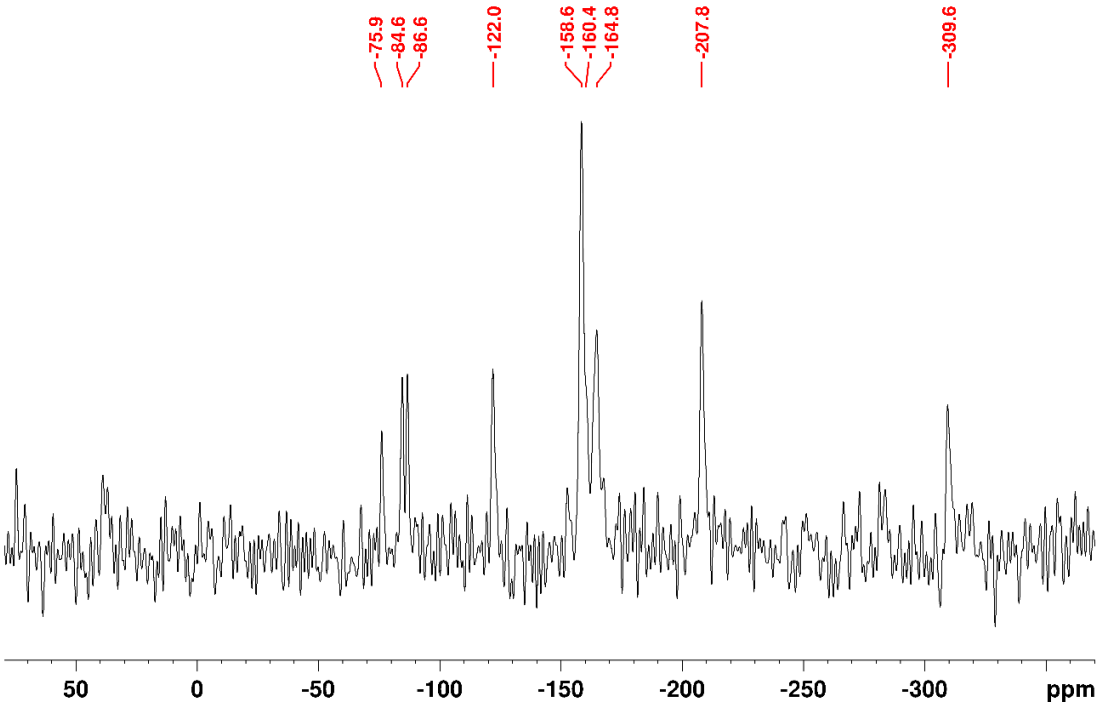


Fig. S14 Solid-state ^{15}N NMR spectrum of **3**.

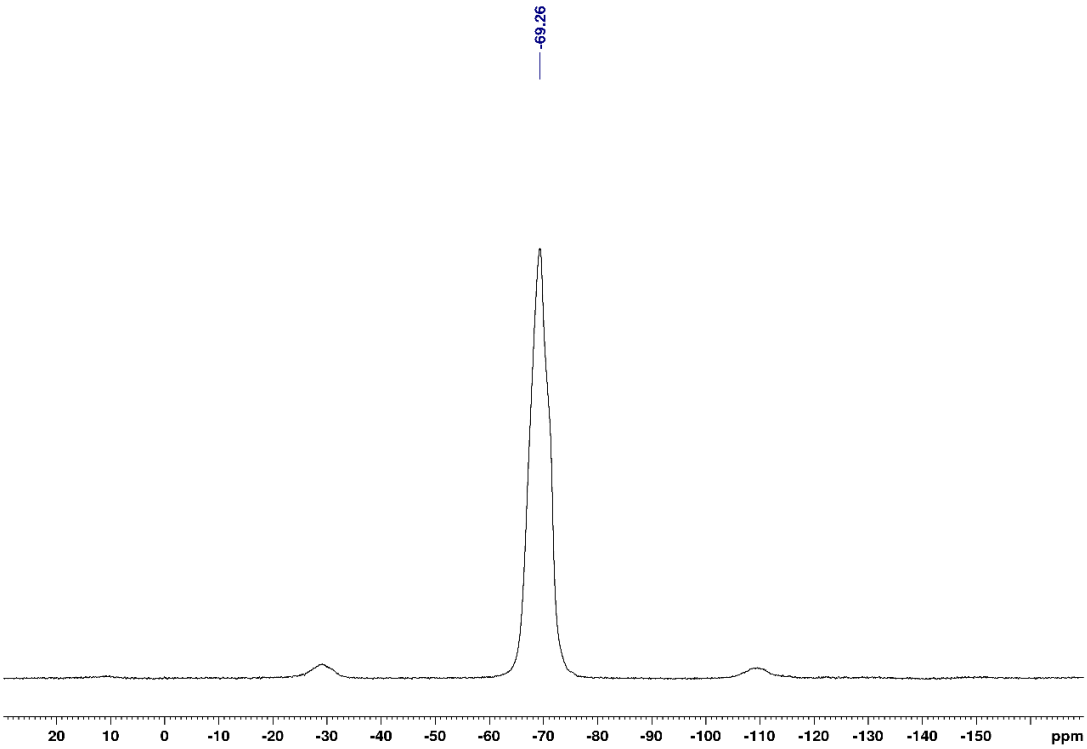


Fig. S15 Solid-state ^{19}F NMR spectrum of **3**.

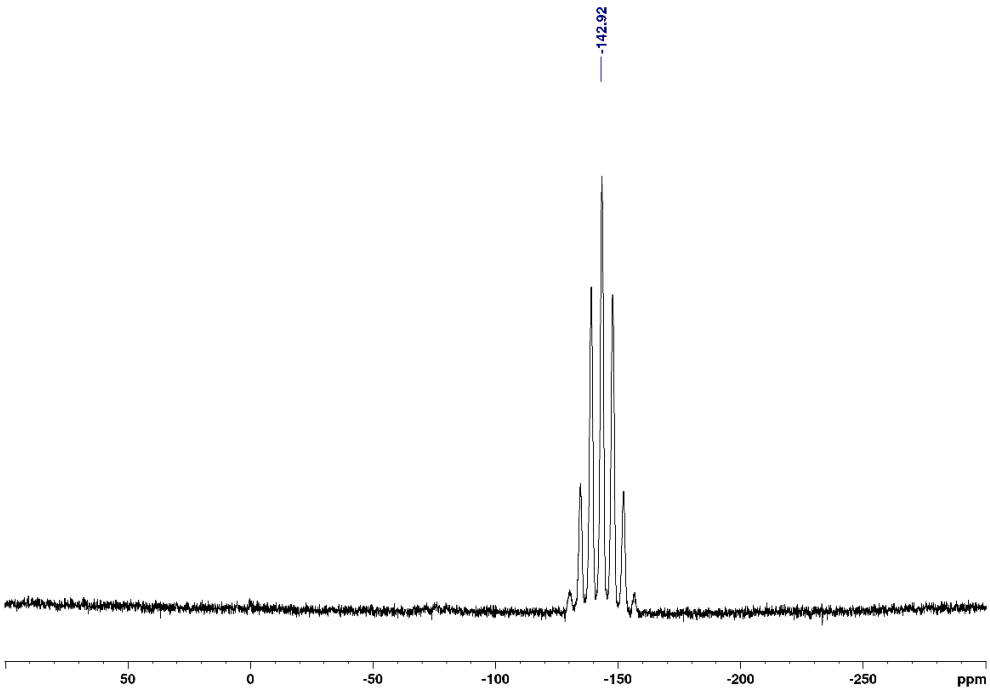


Fig. S16 Solid-state ^{31}P NMR spectrum of **3**.

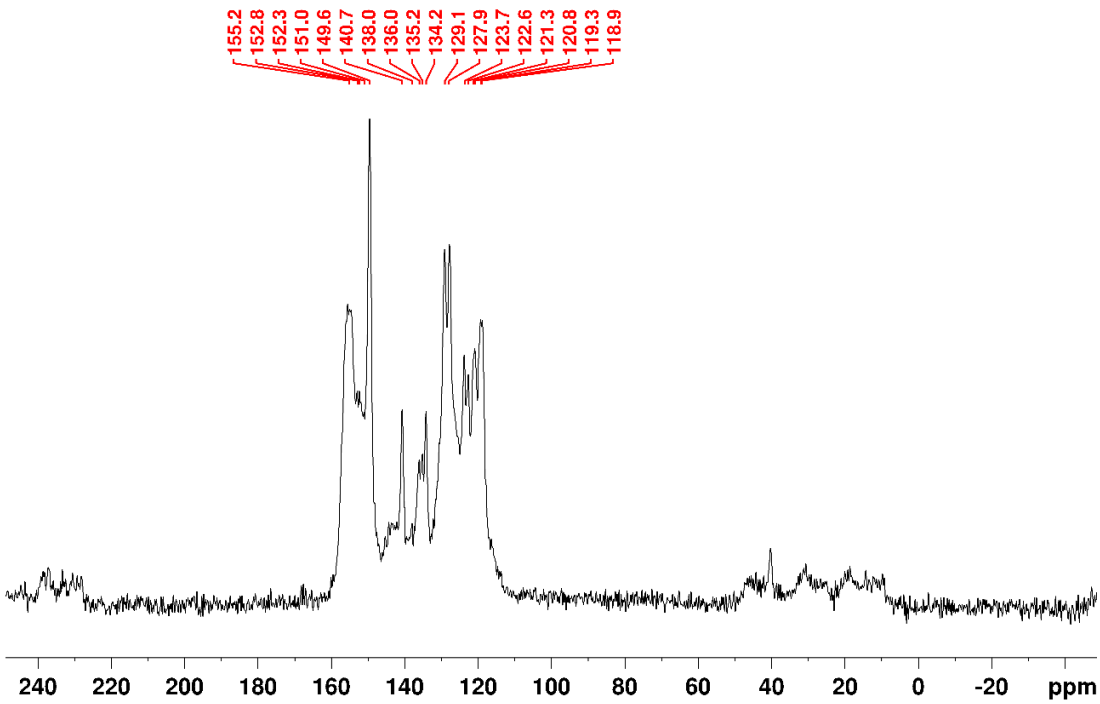


Fig. S17 Solid-state ^{13}C NMR spectrum of **4**.

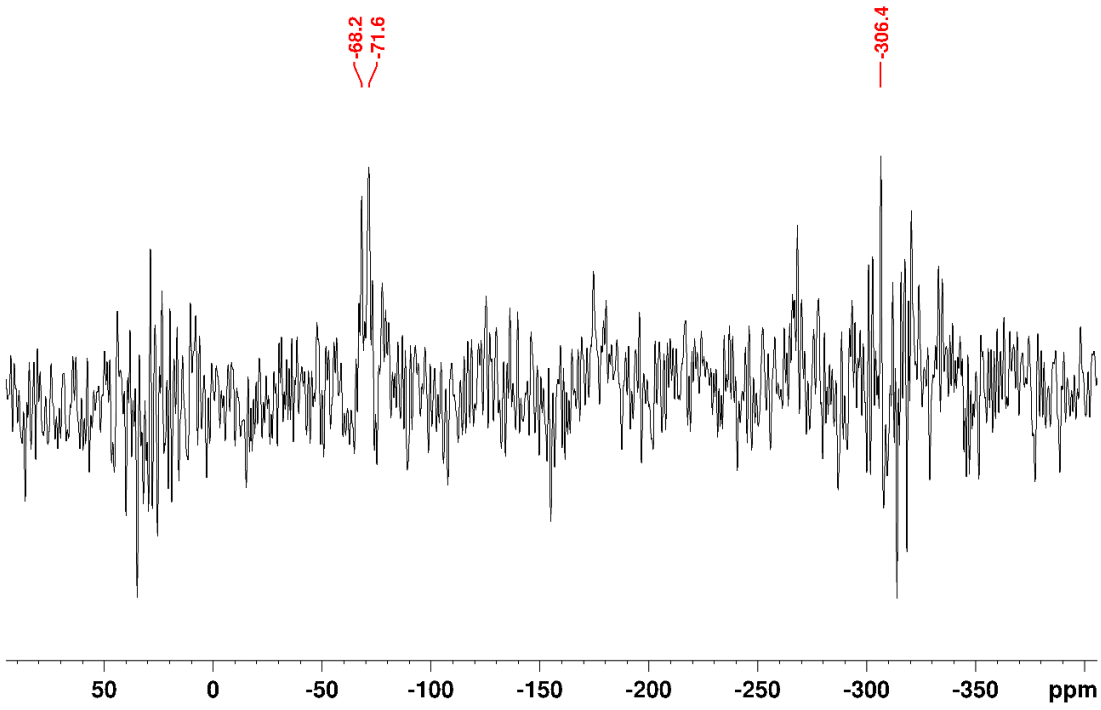


Fig. S18 Solid-state ^{15}N NMR spectrum of **4**.

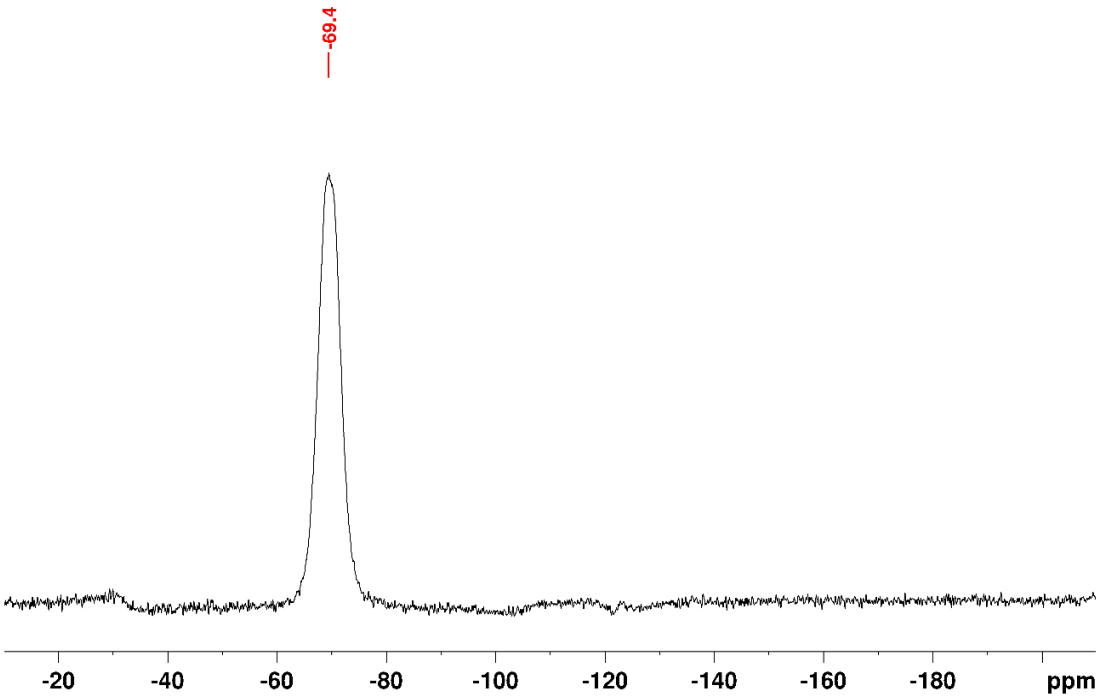
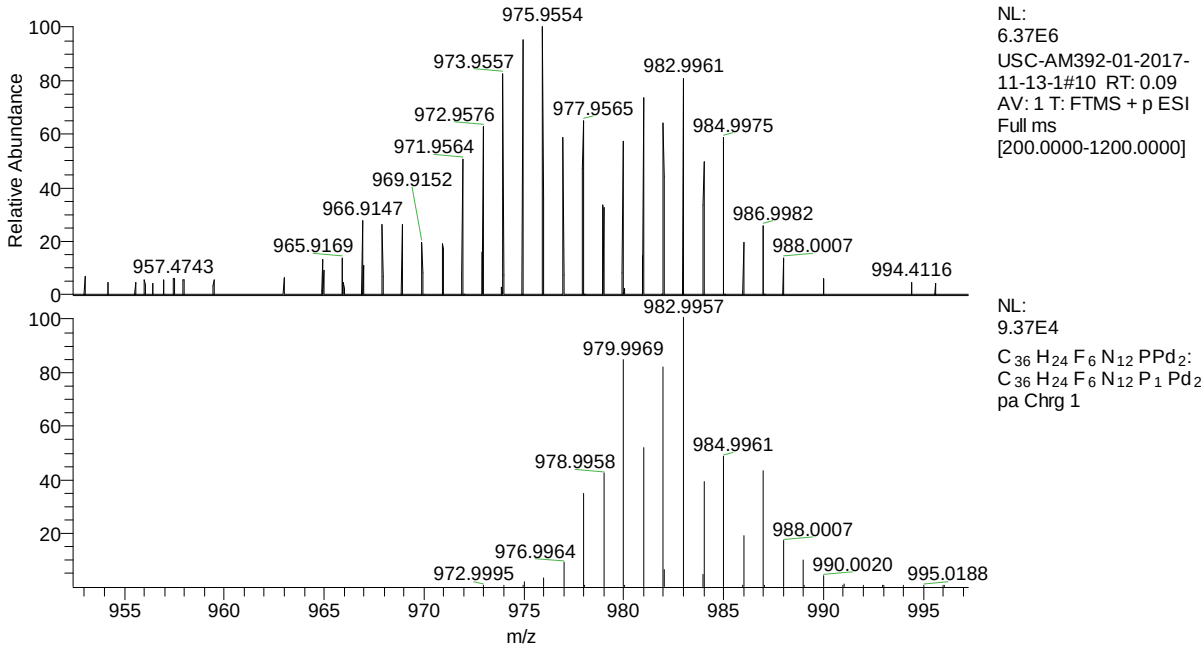
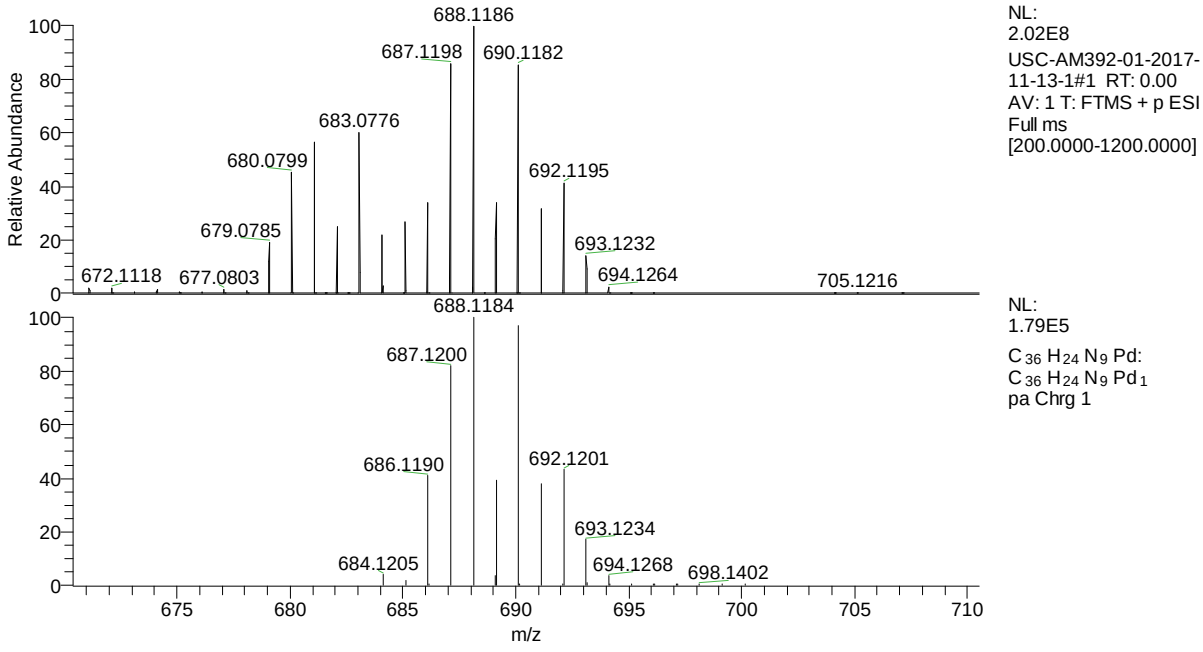


Fig. S19 Solid-state ^{19}F NMR spectrum of **4**.



a)



b)

Fig. S20 ASAP mass spectra: Experimental (Up) and theoretical (down) ISOTOPIC pattern for complex **3** of **a)** m/z = 975.9554 and **b)** m/z = 688.1186.

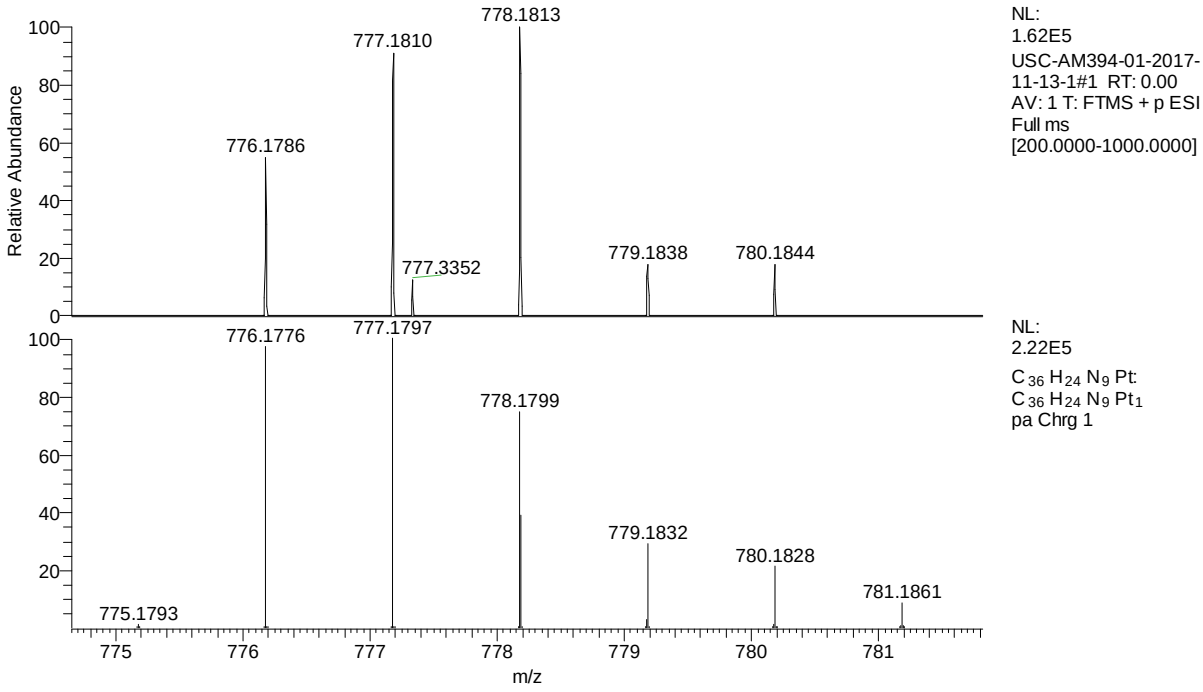


Fig. S21 Electrospray ionization mass spectra: Experimental (Up) and theoretical (down) ISOTOPIC pattern for **4**.

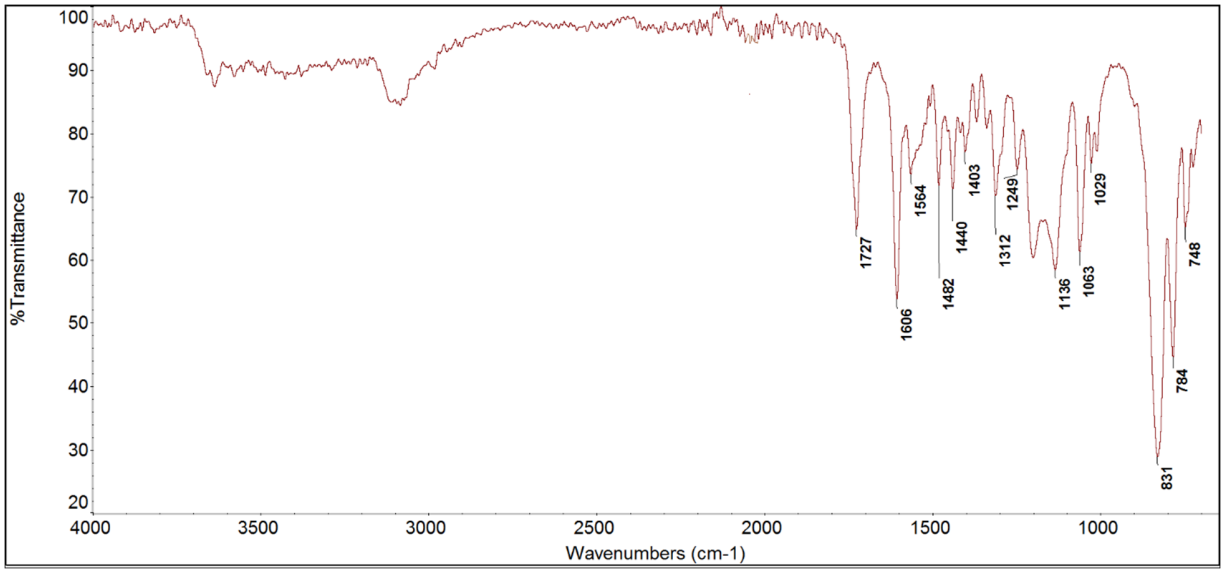


Fig. S22 ATR IR spectrum of **5**.

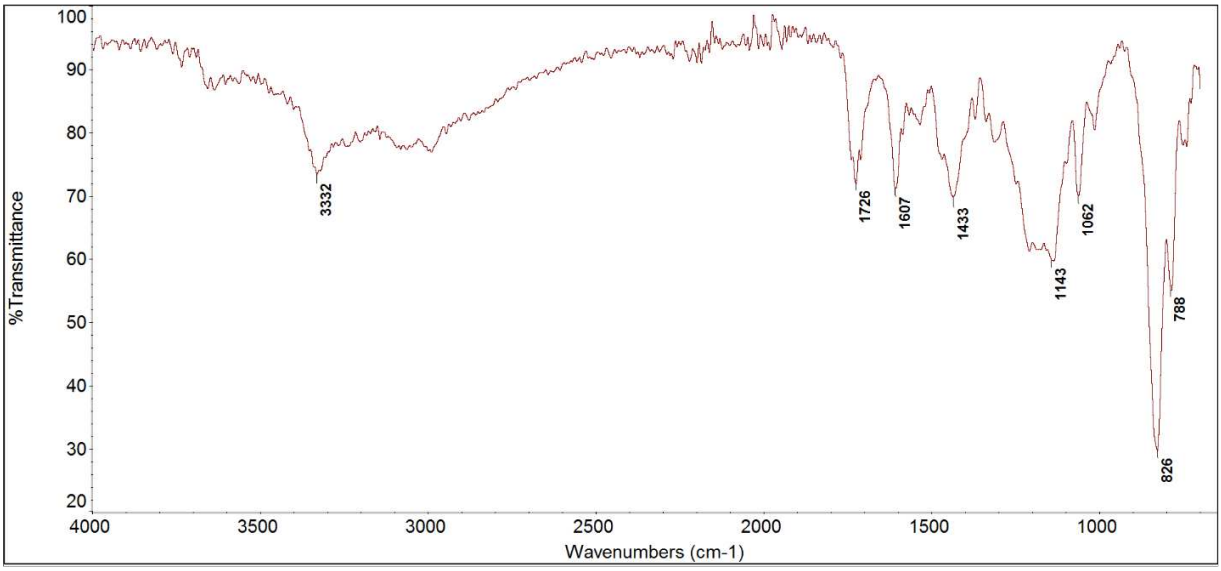
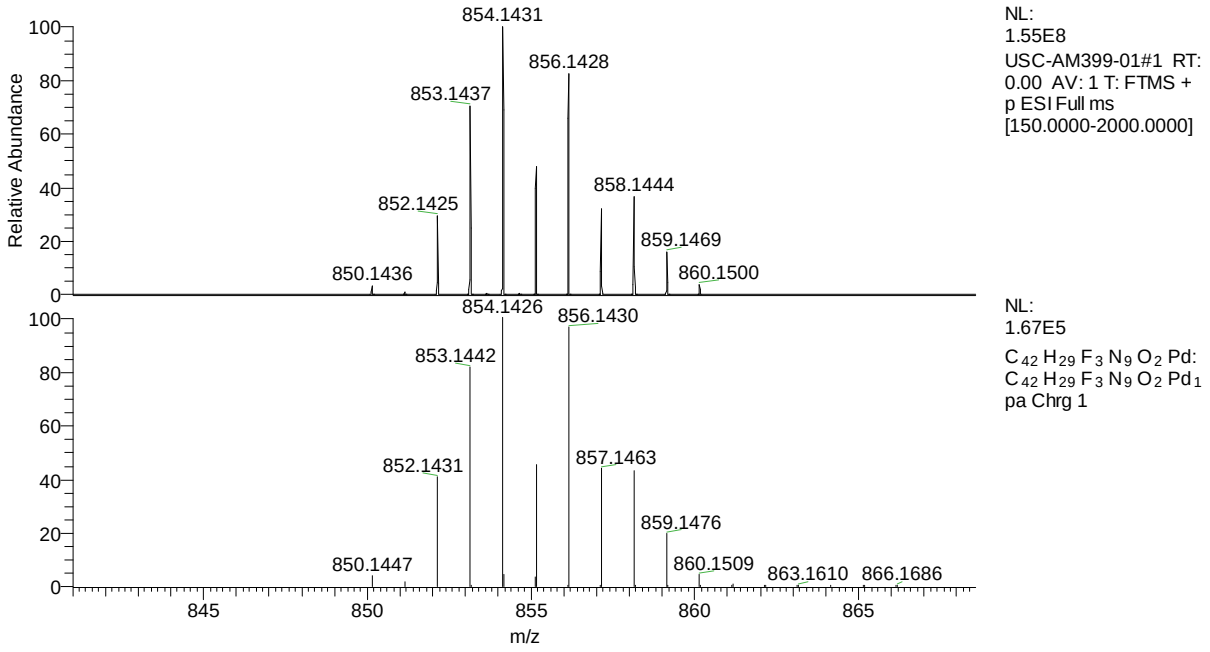
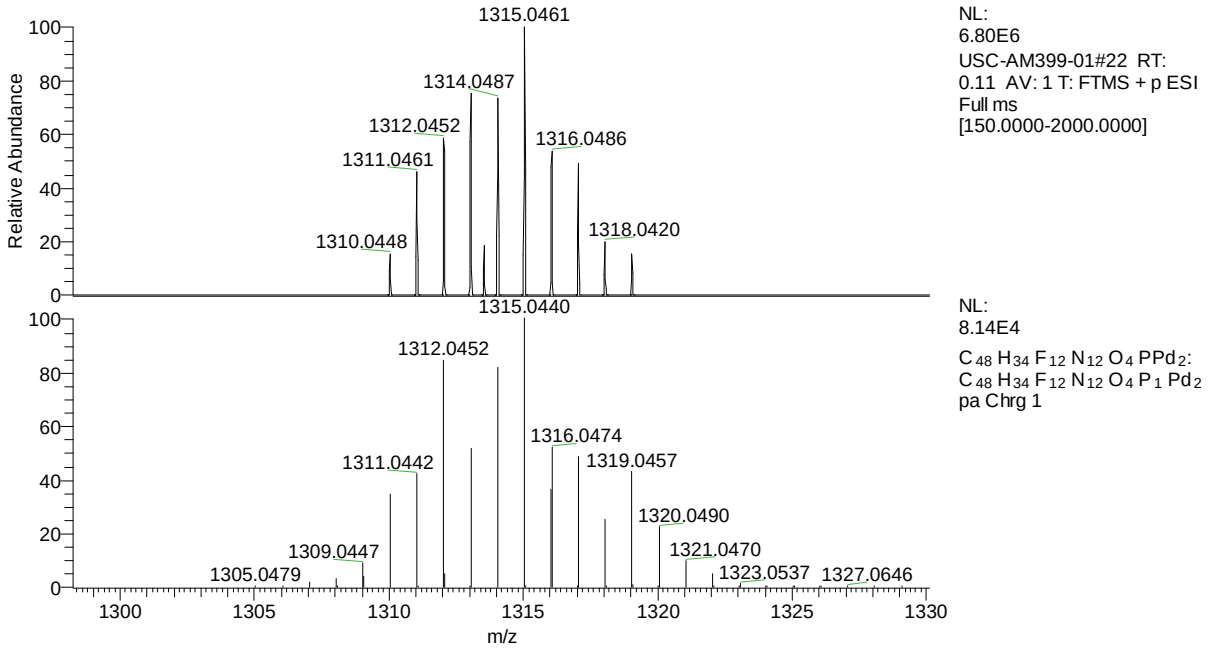


Fig. S23 ATR IR spectrum of **6**.



a)



b)

Fig. S24 Electrospray ionization mass spectra: Experimental (Up) and theoretical (down) ISOTOPIC pattern for complex **5** of **a)** m/z = 854.1431 and **b)** m/z = 1315.0461.

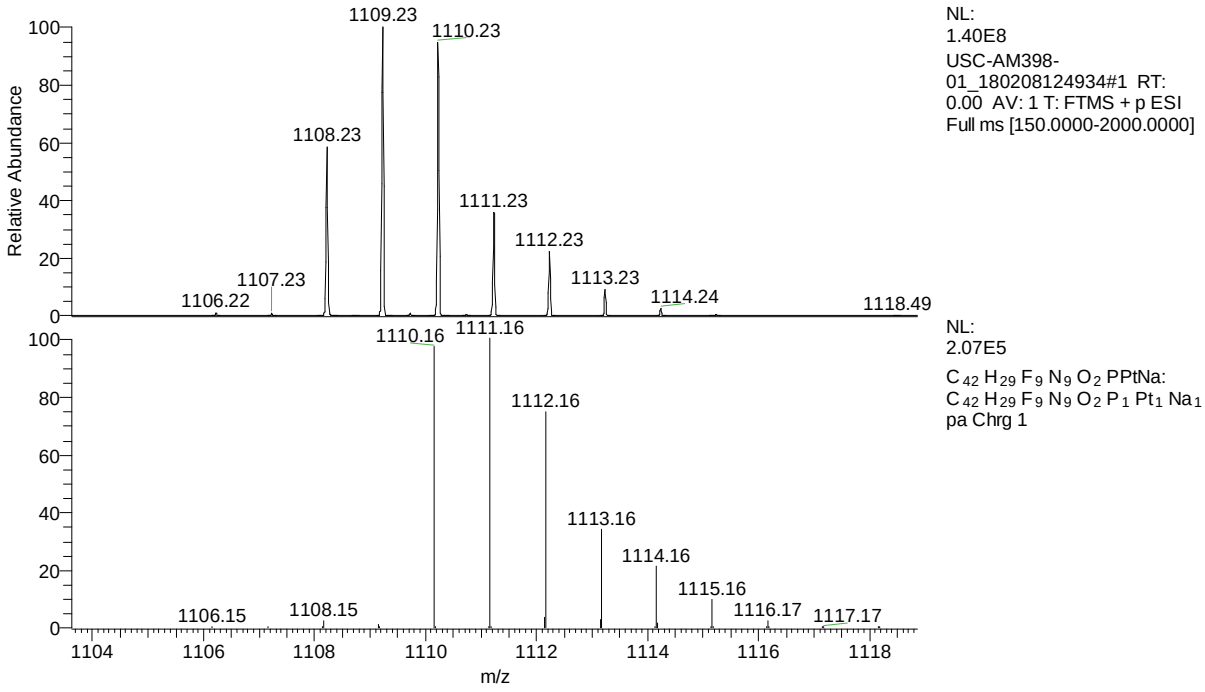


Fig. S25 Electrospray ionization mass spectra: Experimental (Up) and theoretical (down) ISOTOPIC pattern for complex **6**.

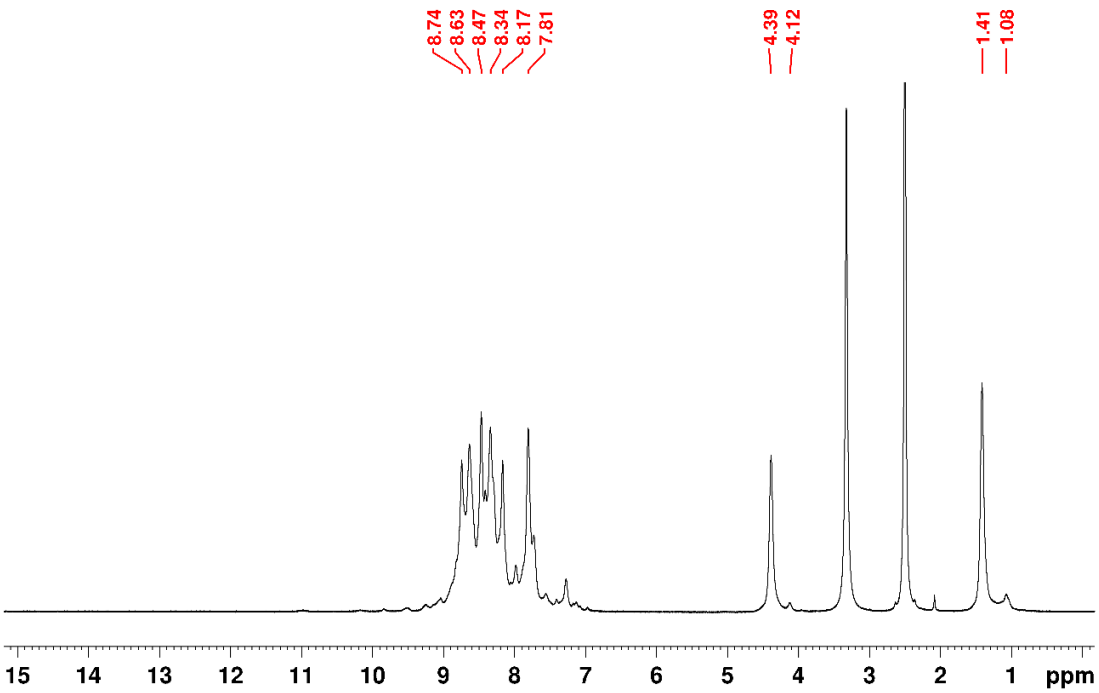


Fig. S26 ^{1}H NMR spectrum of **5**.

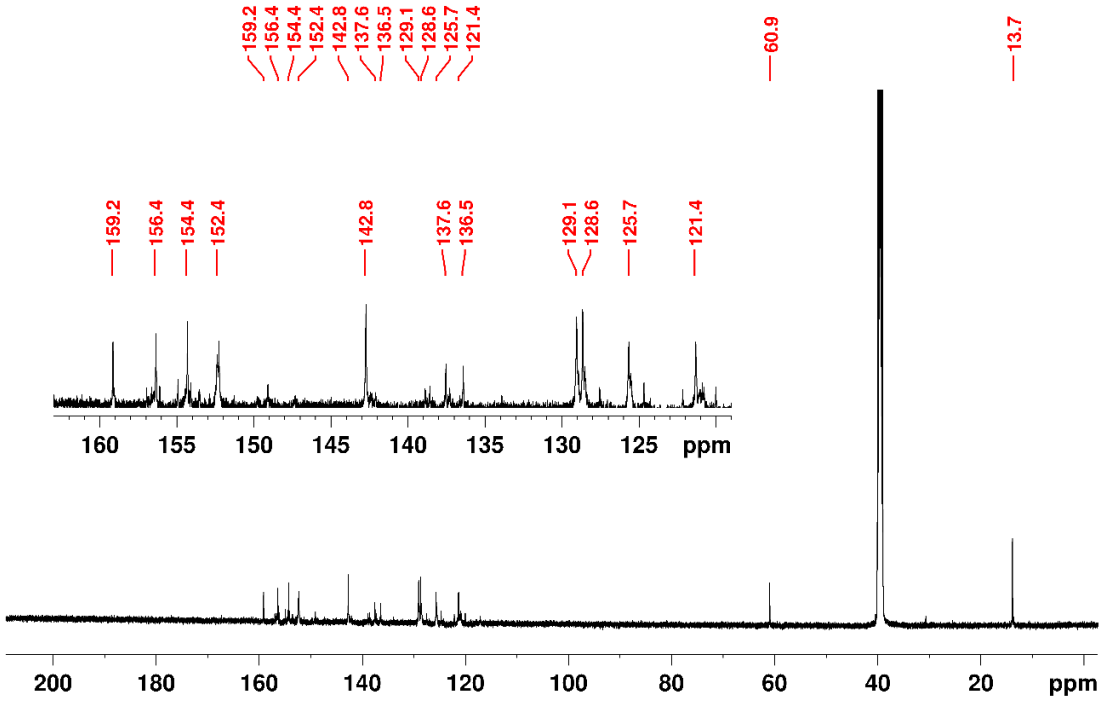


Fig. S27 ^{13}C NMR spectrum of **5**.

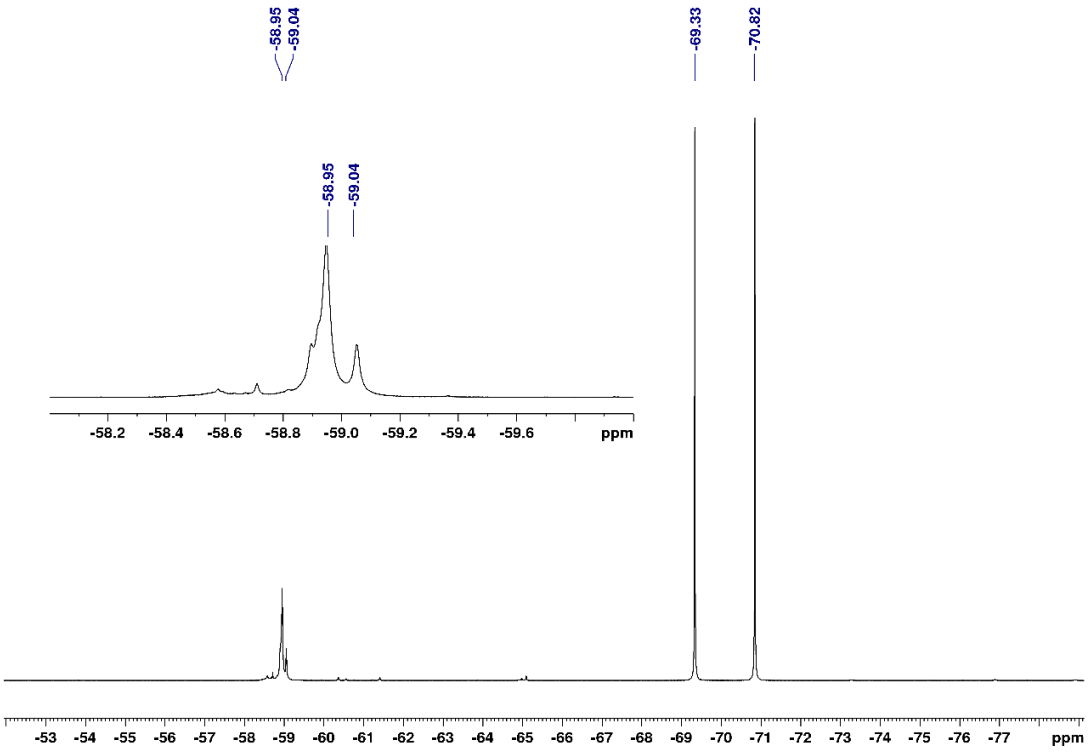


Fig. S28 ^{19}F NMR spectrum of **5**.

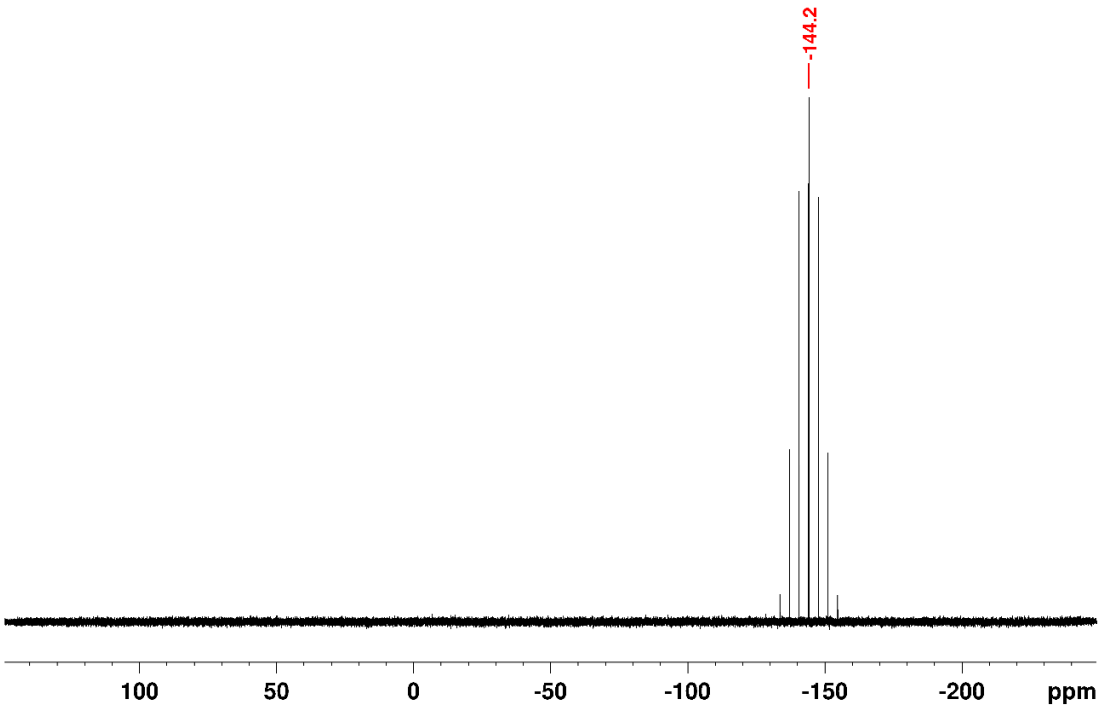


Fig. S29 ^{31}P NMR spectrum of **5**.

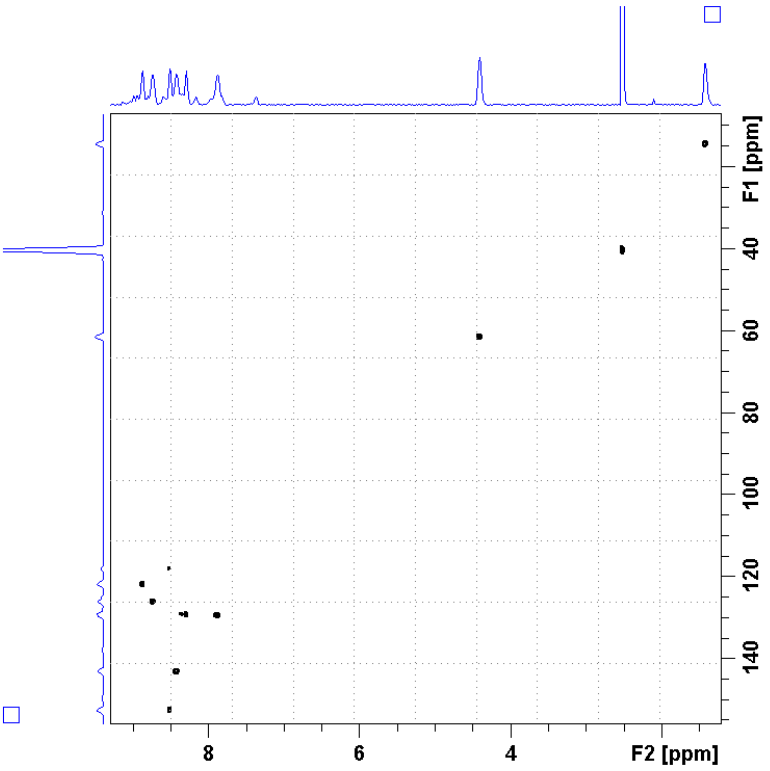


Fig. S30 HSQC {^{1}H, ^{13}C} NMR spectrum of **5**.

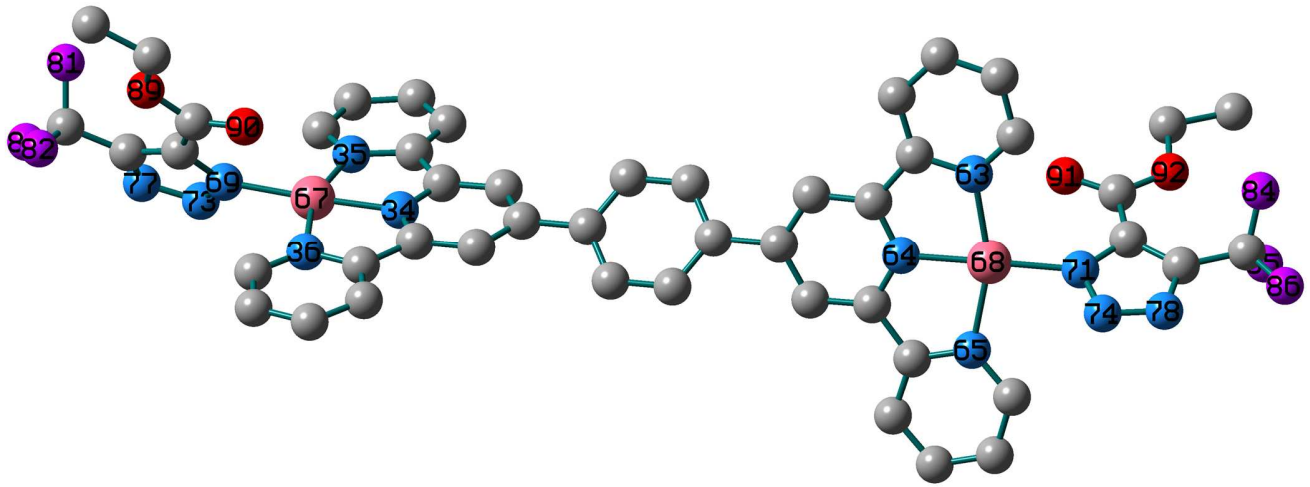
Table S1 Corrected energies values of Pd(II) and Pt(II) triazolate bound isomers (**5** and **6**).

	N1	N2	N3
• **5**			
Electronic Energy (EE)	–2679.336996	–2679.196433	-2679.330052
Zero-point Energy Correction	0.643316	0.638885	0.643157
Thermal Correction to Energy	0.690310	0.679139	0.690140
Thermal Correction to Enthalpy	0.691254	0.680083	0.691084
Thermal Correction to Free Energy	0.553438	0.563539	0.553476
EE + Zero-point Energy	–2678.693680	–2678.557548	-2678.686896
EE + Thermal Energy Correction	–2678.646686	–2678.517294	-2678.639913
EE + Thermal Enthalpy Correction	–2678.645742	–2678.516350	-2678.638969
EE + Thermal Free Energy Correction	–2678.783558	–2678.632894	-2678.776576
Imaginary frequencies	0	10	0
• **6**			
Electronic Energy (EE)	–3659.266939	–3659.272574	-3659.241110
Zero-point Energy Correction	0.769904	0.771597	0.769330
Thermal Correction to Energy	0.832047	0.833372	0.831495
Thermal Correction to Enthalpy	0.832992	0.834316	0.832439
Thermal Correction to Free Energy	0.661075	0.663870	0.660585
EE + Zero-point Energy	–3658.497035	–3658.500978	-3658.471780
EE + Thermal Energy Correction	–3658.434891	–3658.439203	-3658.409615
EE + Thermal Enthalpy Correction	–3658.433947	–3658.438258	-3658.408671
EE + Thermal Free Energy Correction	–3658.605864	–3658.608705	-3658.580525
Imaginary frequencies	0	0	0

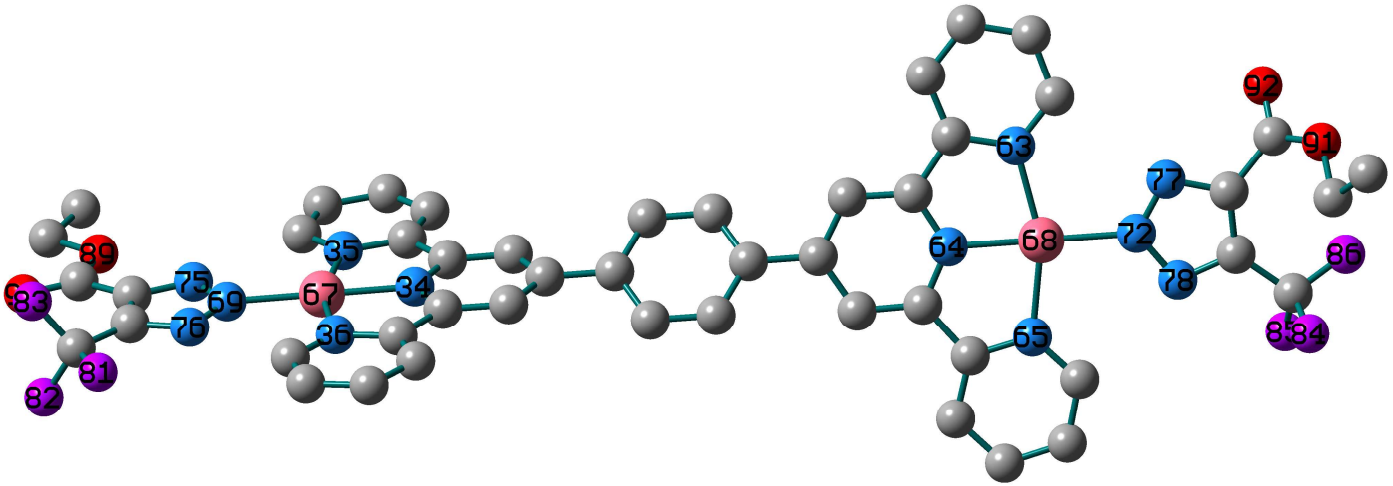
Table S2 calculated bond lengths of the Pd(II) triazolate isomers (N1, N2 and N3).

5		
N1	**N2**	**N3**
Pd–N34 = 1.97462	Pd–N34 = 1.98458	Pd–N34 = 1.97570
Pd–N35 = 2.06841	Pd–N35 = 2.09047	Pd–N35 = 2.07218
Pd–N36 = 2.07493	Pd–N36 = 2.09454	Pd–N36 = 2.07551
Pd–N69 = 2.02709	Pd–N69 = 2.02863	Pd–N69 = 2.03211
Pd–N63 = 2.07532	Pd–N63 = 2.09568	Pd–N63 = 2.06878
Pd–N64 = 1.97436	Pd–N64 = 1.98393	Pd–N64 = 1.97459
Pd–N65 = 2.06805	Pd–N65 = 2.08859	Pd–N65 = 2.07743
Pd–N71 = 2.02641	Pd–N72 = 2.03216	Pd–N71 = 2.03473
N69–N73 = 1.37872	N69–N75 = 1.35856	N69–N73 = 1.38611
N73–N77 = 1.35490	N69–N76 = 1.35956	N73–N77 = 1.34699
C20…N73 = 3.23423	C20…N75 = 2.94835	C20…N73 = 3.15394
N34–Pd–N35 = 80.4	N34–Pd–N35 = 79.9	N34–Pd–N35 = 80.3
N34–Pd–N36 = 80.2	N34–Pd–N36 = 79.8	N34–Pd–N36 = 80.3
N34–Pd–N69 = 177.6	N34–Pd–N69 = 179.8	N34–Pd–N69 = 177.0
N35–Pd–N36 = 160.2	N35–Pd–N36 = 159.6	N35–Pd–N36 = 160.3
N35–Pd–N69 = 98.2	N35–Pd–N69 = 100.0	N35–Pd–N69 = 98.3
N36–Pd–N69 = 101.2	N36–Pd–N69 = 100.3	N36–Pd–N69 = 101.1
N63–Pd–N64 = 80.2	N63–Pd–N64 = 79.8	N63–Pd–N64 = 80.4
N64–Pd–N65 = 80.4	N64–Pd–N65 = 79.9	N64–Pd–N65 = 80.3
N64–Pd–N71 = 177.4	N64–Pd–N71 = 179.8	N64–Pd–N71 = 176.2
N63–Pd–N65 = 160.2	N63–Pd–N65 = 159.6	N63–Pd–N65 = 160.3
N63–Pd–N71 = 101.2	N63–Pd–N72 = 100.2	N63–Pd–N71 = 98.7
N65–Pd–N71 = 98.3	N65–Pd–N72 = 100.1	N65–Pd–N71 = 100.8

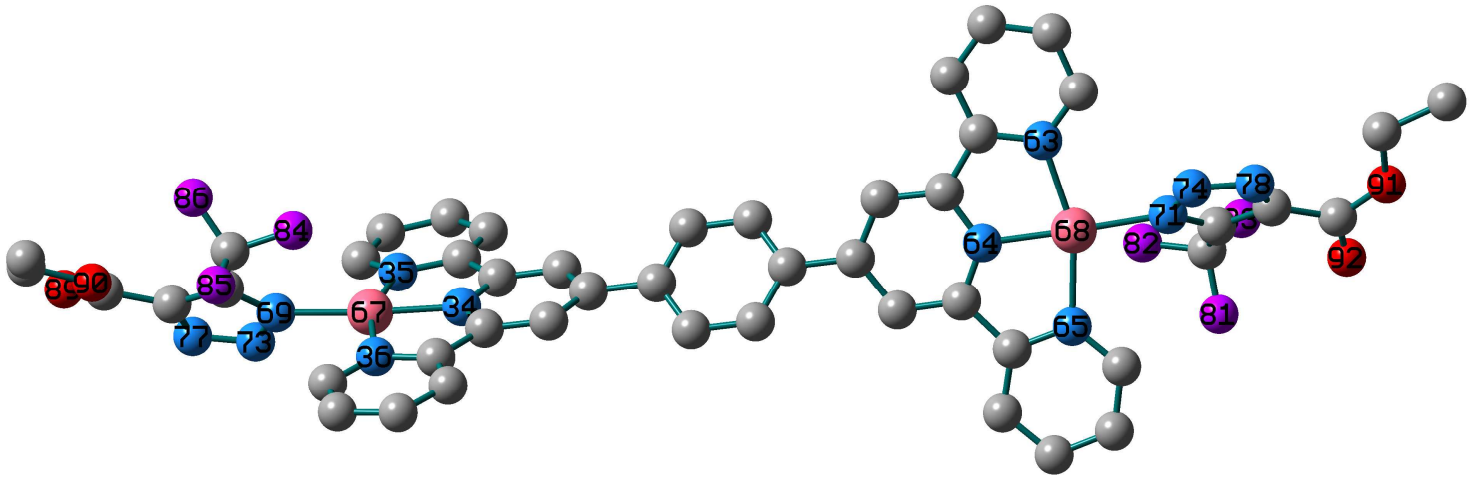
For numbering, please see the figures below.



N1-isomer



N2-isomer

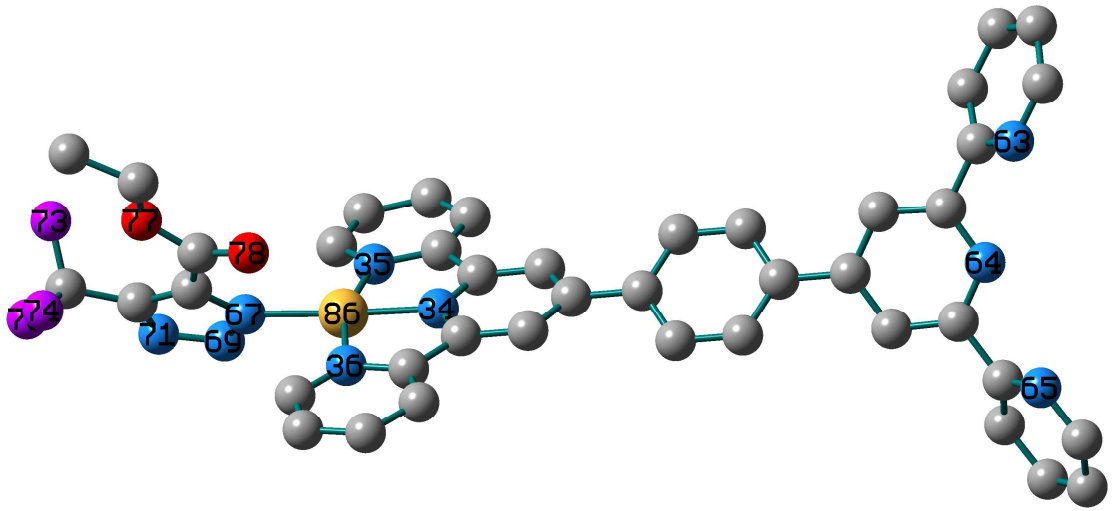


N3-isomer

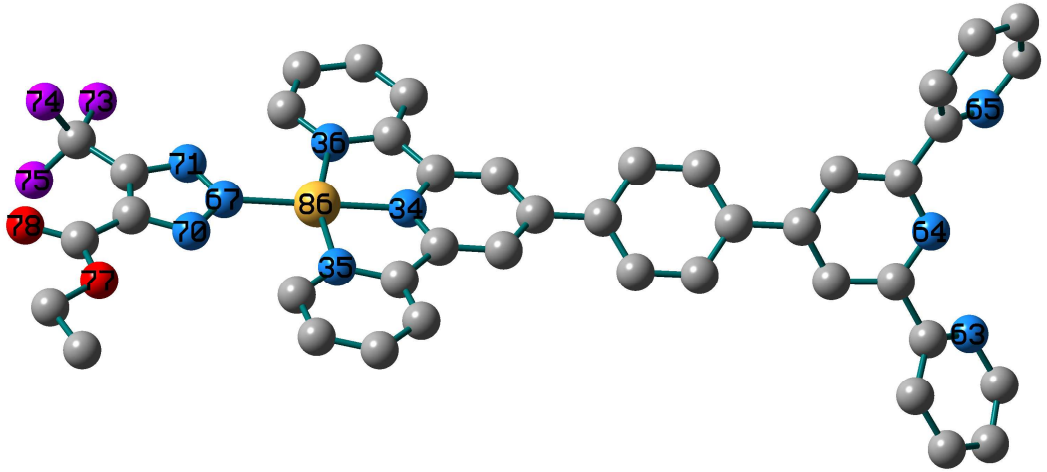
Table S3 calculated bond lengths of the Pt(II) triazolate isomers (N1, N2 and N3).

6		
N1	**N2**	**N3**
Pt–N34 = 1.96947	Pt–N34 = 1.97758	Pt–N34 = 1.96990
Pt–N35 = 2.05598	Pt–N35 = 2.07729	Pt–N35 = 2.05829
Pt–N36 = 2.05472	Pt–N36 = 2.07918	Pt–N36 = 2.05763
Pt–N67 = 2.03856	Pt–N67 = 2.03320	Pt–N67 = 2.04240
N67–N69 = 1.38645	N67–N70 = 1.36070	N67–N69 = 1.39375
N69–N71 = 1.35034	N67–N71 = 1.36270	N69–N71 = 1.34447
C20…N69 = 3.19623	C20…N70 = 2.94163	C20…N69 = 3.30979
N34–Pt–N35 = 80.6	N34–Pt–N35 = 80.0	N34–Pt–N35 = 80.5
N34–Pt–N36 = 80.4	N34–Pt–N36 = 80.0	N34–Pt–N36 = 80.5
N35–Pt–N67 = 98.0	N35–Pt–N67 = 99.8	N35–Pt–N67 = 98.4
N36–Pt–N67 = 101.0	N36–Pt–N67 = 100.1	N36–Pt–N67 = 100.7
N34–Pt–N67 = 177.6	N34–Pt–N67 = 179.8	N34–Pt–N67 = 176.8
N35–Pt–N36 = 160.8	N35–Pt–N36 = 160.0	N35–Pt–N36 = 160.7

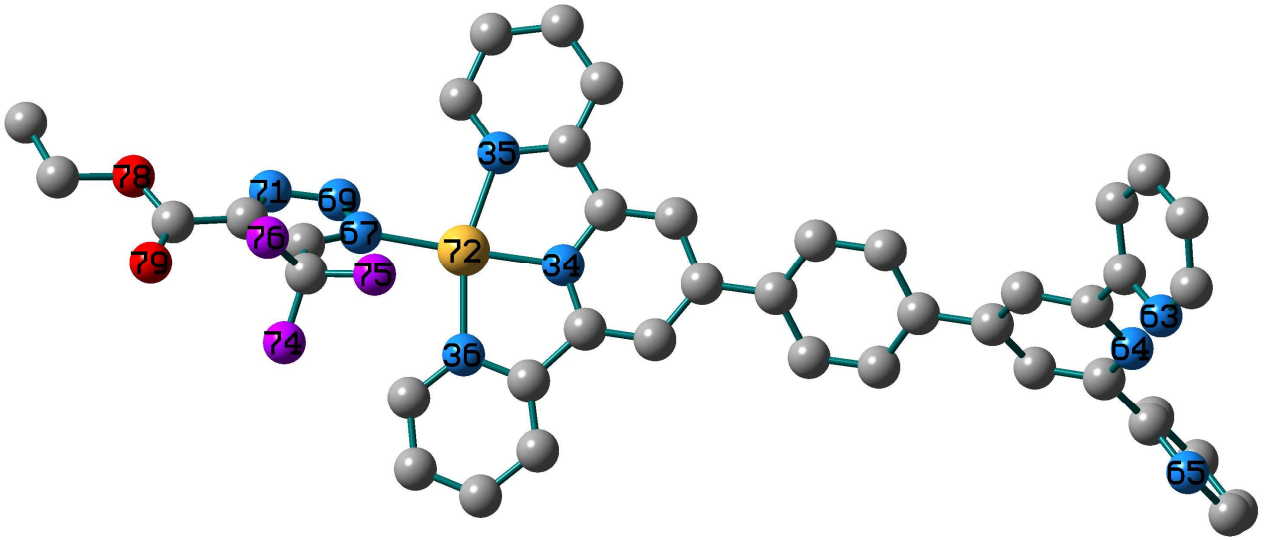
For numbering, please see the figures below.



N1-isomer



N2-isomer



N3-isomer

Table S4: The electronic configuration of the metal center (Pd or Pt) of the triazolate isomers (N1, N2 and N3) , its 4d (or 5d) electronic distribution and the natural atomic charge

	Occupancies of 4d or 5d orbitals					natural charge of metal center	electronic arrangement of metal center (Pd or Pt)
	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}		
• **5**							
N1	1.94494	1.95223	1.90568	1.64607	1.34579	0.68498	$[Kr]5s^{0.31}4d^{8.79}5p^{0.22}5d^{0.01}$
	1.96439	1.93930	1.80233	1.18047	1.90757	0.68575	$[Kr]5s^{0.31}4d^{8.79}5p^{0.22}5d^{0.01}$
N2	1.97206	1.94229	1.85229	1.10805	1.92903	0.68069	$[Kr]5s^{0.32}4d^{8.80}5p^{0.20}5d^{0.01}$
	1.95252	1.96486	1.74671	1.47997	1.65949	0.68299	$[Kr]5s^{0.32}4d^{8.80}5p^{0.20}5d^{0.01}$
N3	1.93959	1.94465	1.79695	1.20524	1.90079	0.69165	$[Kr]5s^{0.30}4d^{8.79}5p^{0.22}5d^{0.01}$
	1.95916	1.95146	1.73449	1.39017	1.75174	0.69155	$[Kr]5s^{0.30}4d^{8.79}5p^{0.22}5d^{0.01}$
• **6**							
N1	1.91865	1.93822	1.66505	1.41819	1.65163	0.71638	$[Xe]6s^{0.47}5d^{8.59}6p^{0.22}6d^{0.02}$
N2	1.94685	1.89800	1.80598	1.05430	1.88533	0.73683	$[Xe]6s^{0.47}5d^{8.59}6p^{0.20}6d^{0.01}$
N3	1.93263	1.92642	1.68693	1.21879	1.83169	0.70854	$[Xe]6s^{0.47}5d^{8.60}6p^{0.22}6d^{0.02}$

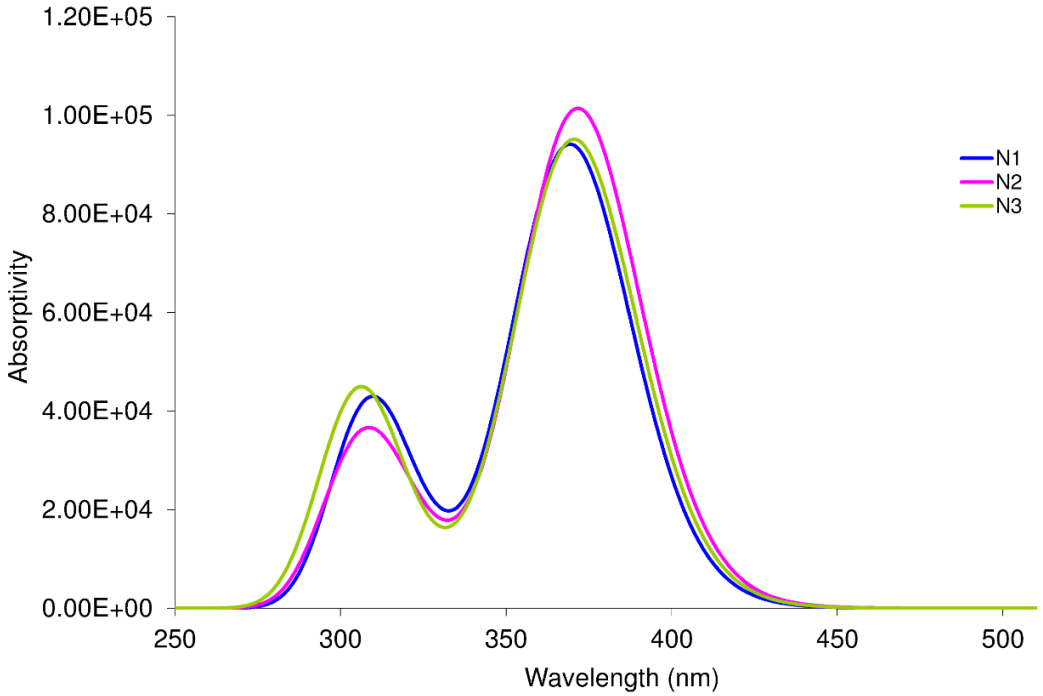


Fig. S31 TDDFT spectrum of the triazolate isomers of **5** calculated at B3LYP/LANL2DZ level of theory using PCM solvation model.

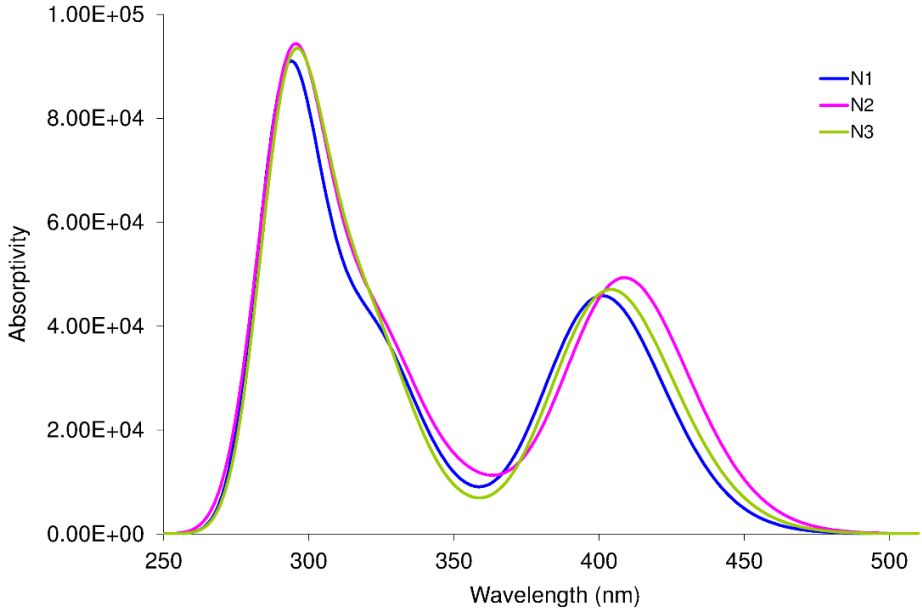


Fig. S32 TDDFT spectrum of the triazolate isomers of **6** calculated at B3LYP/LANL2DZ level of theory using PCM solvation model.

Table S5 Computed excitation energies (eV), electronic transition configurations and oscillator strengths (*f*) of rhenium(I) compounds (selected, *f* > 0.001) (Selected)			
Energy (cm^{-1})	Wavelength (nm)	*f*	Major contributions
• Pd(II) triazolate isomers			
✓ **N1**			
27040	369	1.2152	HOMO→LUMO (94%)
32137	311	0.1118	HOMO–3→LUMO (23%)
32656	306	0.1615	HOMO–4→LUMO+1 (58%)
✓ **N2**			
26835	372	1.2845	HOMO→LUMO (92%)
28163	355	0.0816	HOMO–2→LUMO (68%)
31914	313	0.0342	HOMO–1→LUMO (29%), HOMO–1→LUMO+1 (37%)
32327	309	0.1331	HOMO–8→LUMO (37%), HOMO–1→LUMO+1 (32%)
✓ **N3**			
26991	370	1.0199	HOMO→LUMO (74%)
28223	354	0.0645	HOMO–3→LUMO (40%)
32690	305	0.2082	HOMO–9→LUMO (21%), HOMO–3→LUMO+1 (33%)
• Pt(II) triazolate isomers			
✓ **N1**			
24954	400	0.6288	HOMO→LUMO (93%)
28638	349	0.0272	HOMO–9→LUMO (36%), HOMO–4→LUMO (39%)
30813	324	0.2778	HOMO–10→LUMO (78%)
32694	305	0.0663	HOMO–9→L+1 (49%), HOMO–4→LUMO+1 (22%)
34117	293	0.8383	HOMO→LUMO+3 (69%)
✓ **N2**			
24479	408	0.673	HOMO→LUMO (92%)
27990	357	0.0905	HOMO–7→LUMO (57%)
30378	329	0.0626	HOMO–9→LUMO (72%)
30617	326	0.2639	HOMO–10→LUMO (70%),
31576	316	0.1009	HOMO–8→LUMO (49%), HOMO–4→LUMO+7 (23%)
31900	313	0.0541	HOMO–7→LUMO+1 (61%)
32522	307	0.1003	HOMO–6→LUMO+1 (47%), HOMO–4→LUMO+7 (35%)
33897	295	0.6919	HOMO→LUMO+2 (52%)
✓ **N3**			

24795	403	0.6226	HOMO→LUMO (88%)
25860	386	0.0014	HOMO−6→LUMO (92%)
26776	373	0.0048	HOMO−1→LUMO (98%)
28385	352	0.0076	HOMO−9→LUMO (22%), HOMO−3→LUMO (60%)
28753	347	0.022	HOMO−9→LUMO (22%), HOMO−4→LUMO+1 (30%)
29311	341	0.0135	HOMO−5→LUMO (61%)
30883	323	0.2503	HOMO−10→LUMO (72%)
33907	294	0.9382	HOMO→LUMO+2 (84%)