Palladium(II) Pincer Complexes of a *C,C,C*-NHC, Diphosphonium Bis(Ylide) Ligand

Rachid Taakili, Christine Lepetit, Carine Duhayon, Dmitry A. Valyaev, Noël Lugan,

Yves Canac*

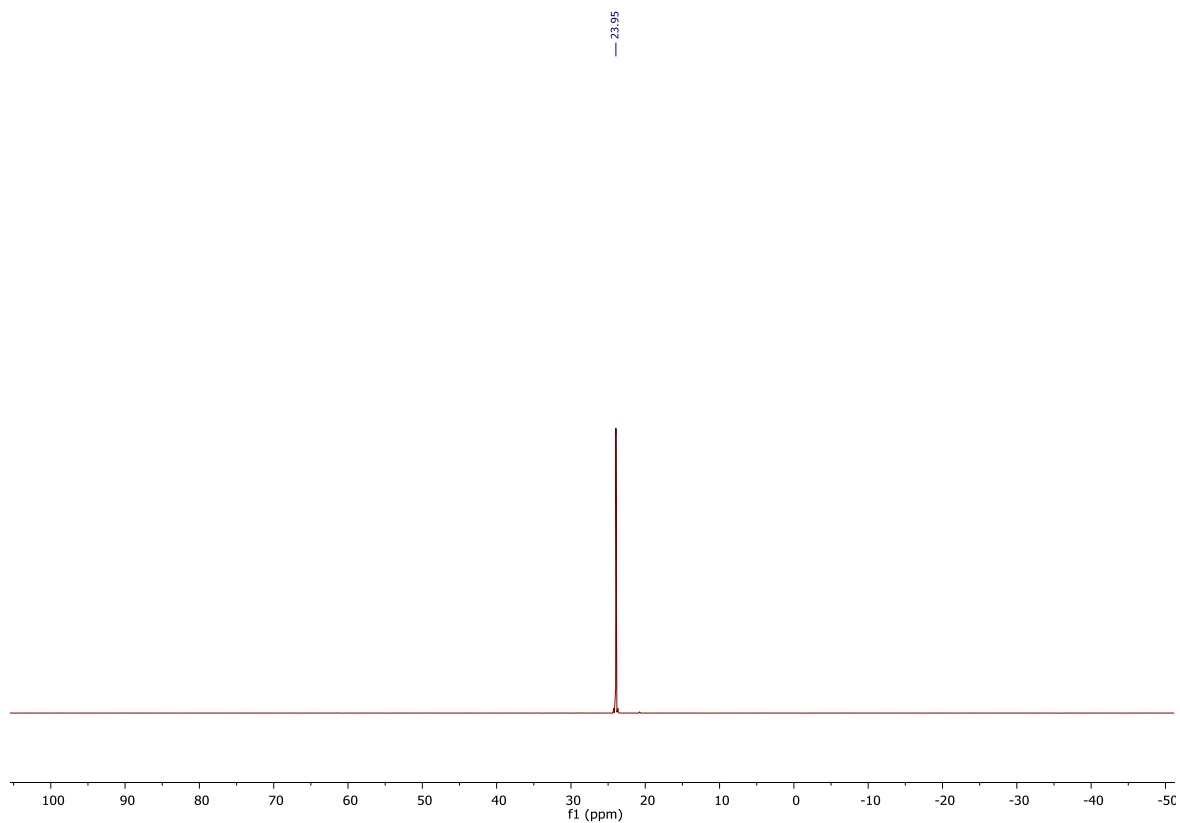LCC–CNRS, Université de Toulouse, CNRS, Toulouse, France

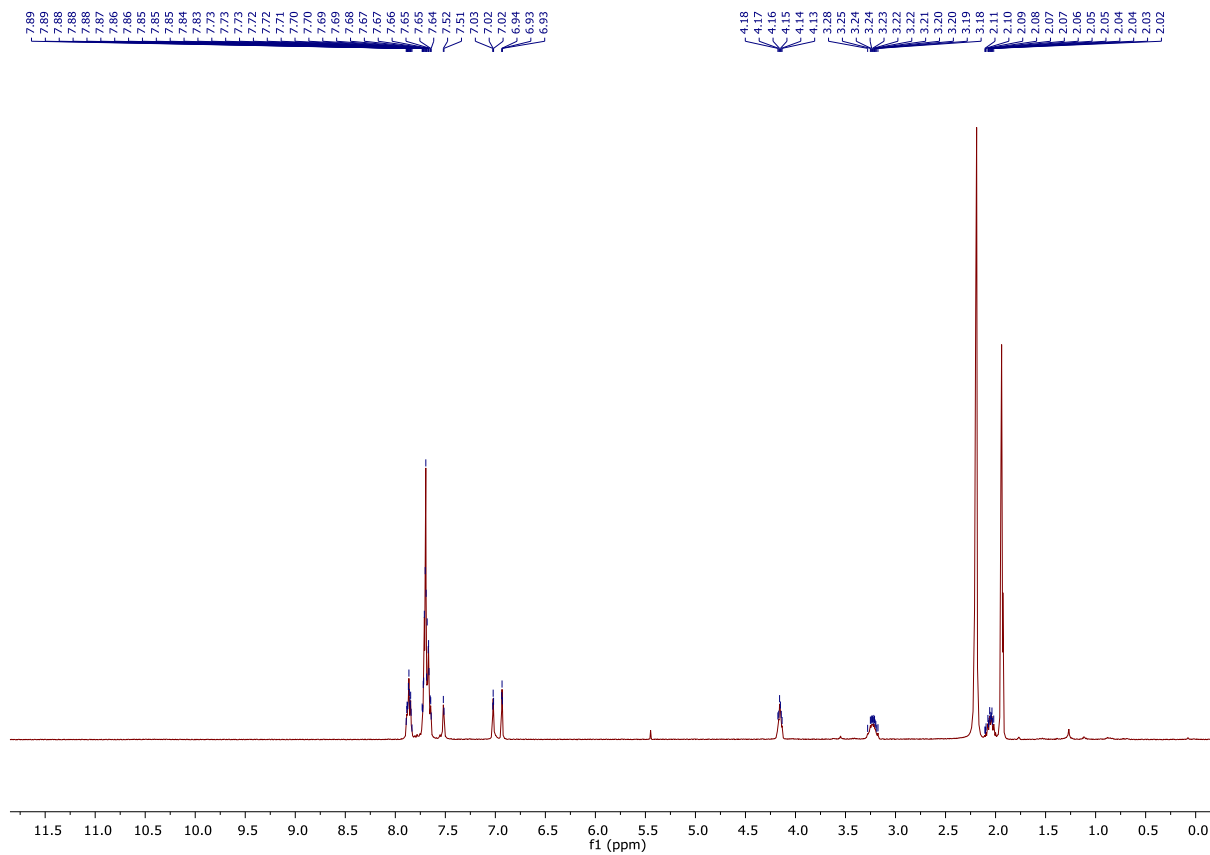E-mail: yves.canac@lcc-toulouse.fr

Supporting Information

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^{31}P{^{1}H} NMR spectrum of [2]Br (in CDCl$_3$)

— 23.95

^{1}H NMR spectrum of [2]Br (in CDCl$_3$)

^{13}C{^{1}H} NMR spectrum of [2]Br (in CDCl$_3$)

137.08
134.81
134.78
134.65
133.03
132.93
130.15
130.10
130.02
129.97
128.87
121.12
118.79
117.41
116.55
77.48
77.16
76.84
45.49
45.29
24.42
24.39
19.57
19.04

^{31}P{^{1}H} NMR spectrum of [3]Br$_3$ (in CDCl$_3$)

24.72

3
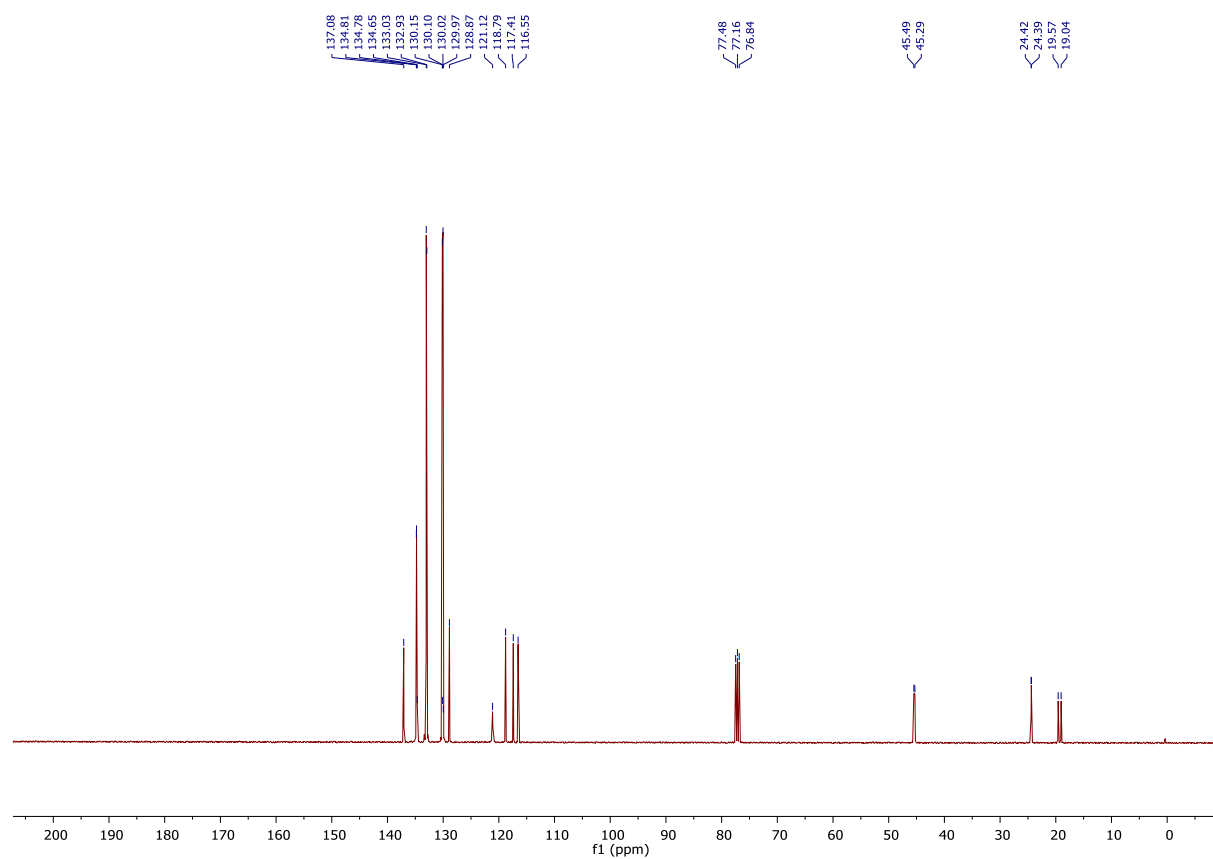
¹H NMR spectrum of [3]Br₃ (in CDCl₃)

¹H NMR spectrum of [3]Br₃ (in CDCl₃)

10.14
7.99
7.96
7.92
7.88
7.87
7.86
7.85
7.83
7.83
7.81
7.80
7.78
7.78
7.76
7.76
7.75
7.74
7.71
7.69
7.68
7.67
7.66
7.65
7.64
7.29 CDCl3

4.92
4.90
4.89
4.12
4.11
4.09
4.08
4.06
4.05

2.94 DMF
2.85 DMF

2.36
2.34
2.32
1.99

11.5	11.0	10.5	10.0	9.5	9.0	8.5	8.0	7.5	7.0	6.5	6.0	5.5	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5	0.0	-0.5				

f1 (ppm)

¹³C{¹H} NMR spectrum of [3]Br₃ (in CDCl₃)

¹³C{¹H} NMR spectrum of [3]Br₃ (in CDCl₃)

162.86

136.68
135.58
135.48
135.45
134.41
134.30
134.21
134.11
131.09
130.91
130.86
123.55

118.38
117.52

77.80
77.48
77.16

49.32
49.11

36.85

31.78

24.36
24.34
20.65
20.12

200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

f1 (ppm)

$^{31}P\{^1H\}$ NMR spectrum of [3](OTf)$_3$ (in CD$_3$CN)

— 23.71
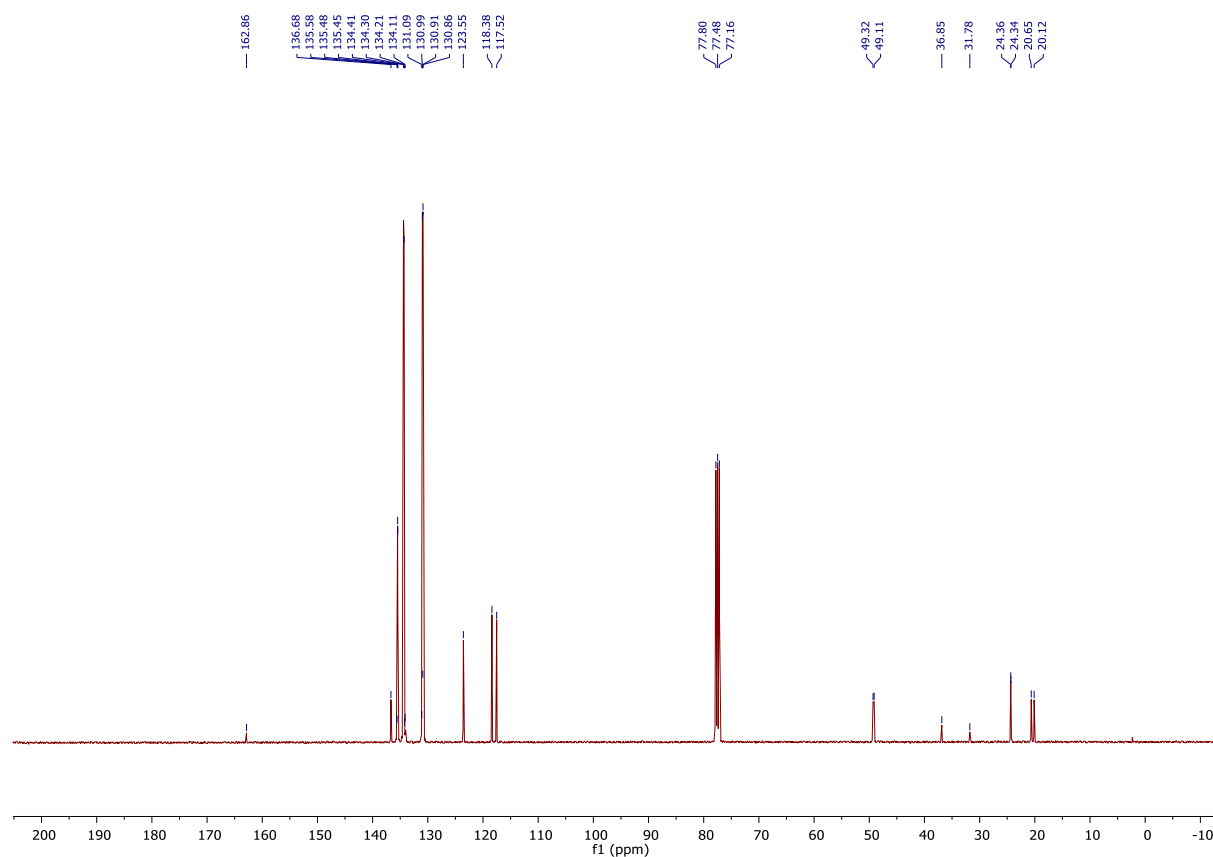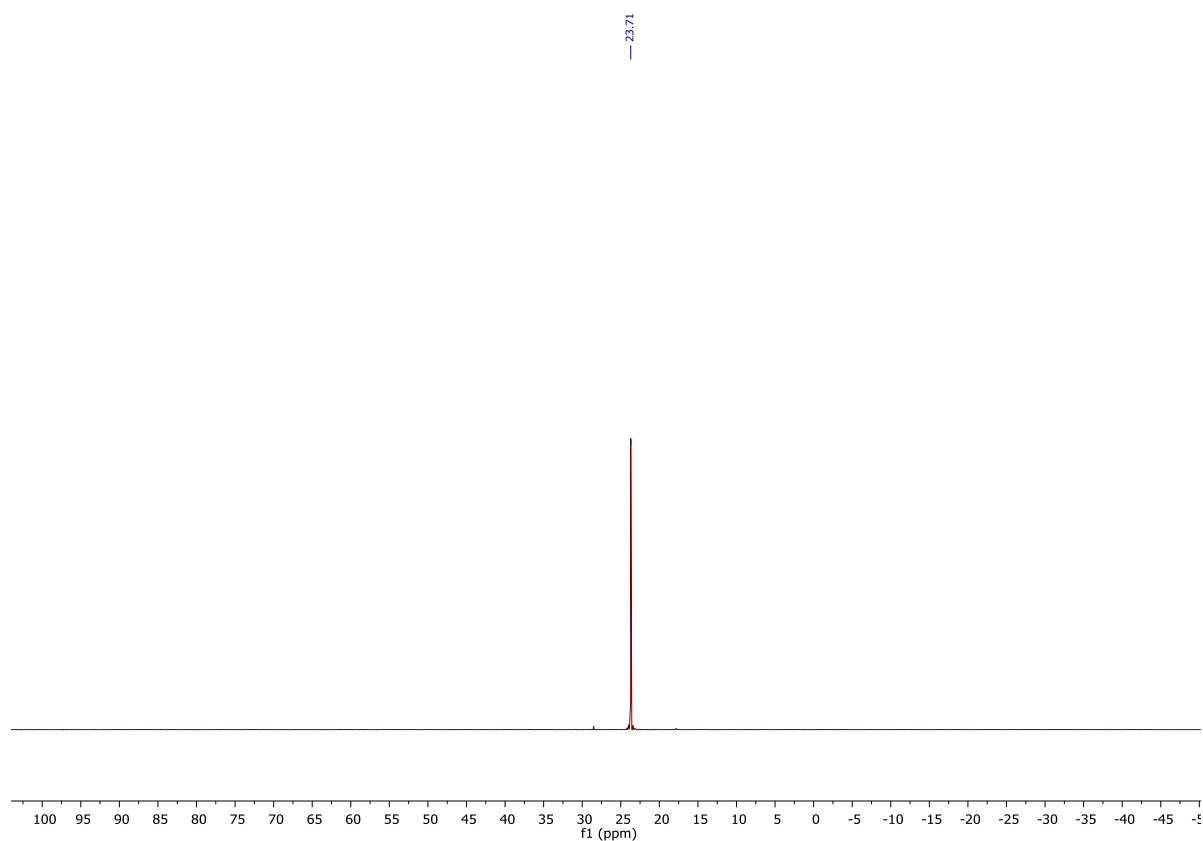
^1H NMR spectrum of [3](OTf)$_3$ (in CD$_3$CN)

$^{13}C\{^1H\}$ NMR spectrum of [3](OTf)$_3$ (in CD$_3$CN)

137.42
136.25
136.22
136.19
136.16
136.10
135.00
134.90
134.82
134.80
134.72
134.66
134.62
134.61
134.55
134.51
131.50
131.39
131.35
131.27
131.22
131.16
131.14
131.08
123.72
119.08
118.39
118.36
118.21
50.04
49.83
23.95
23.93
20.15
19.61
1.73
1.53
1.32
1.12

$^{31}P\{^1H\}$ NMR spectrum of [4](OTf)$_2$ (in CD$_3$CN)

23.76

6
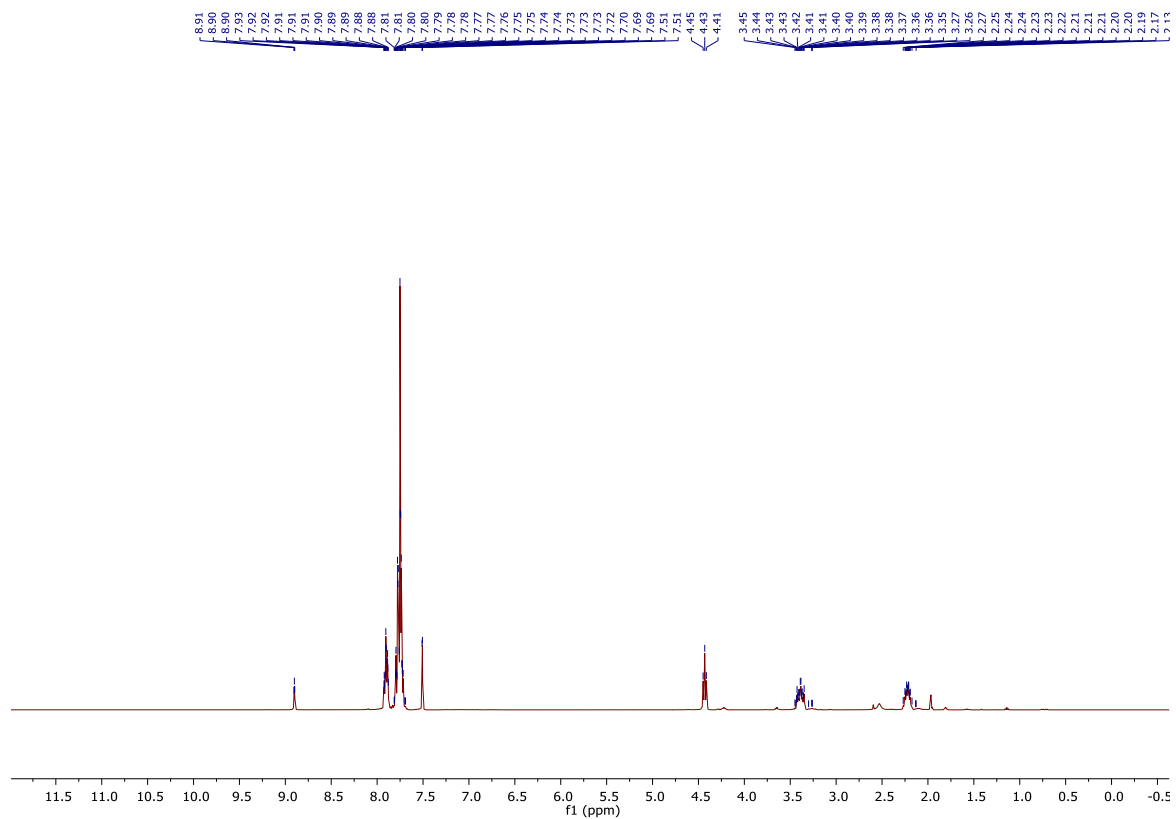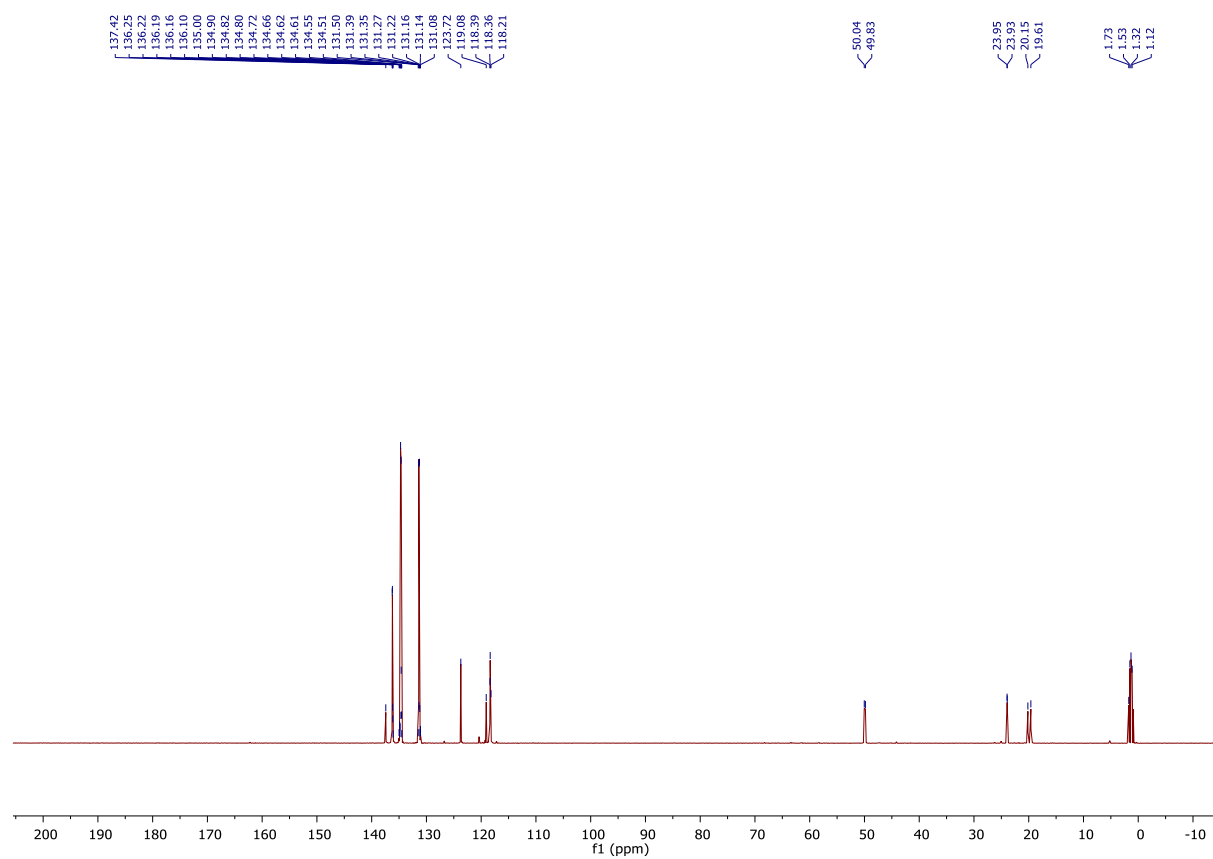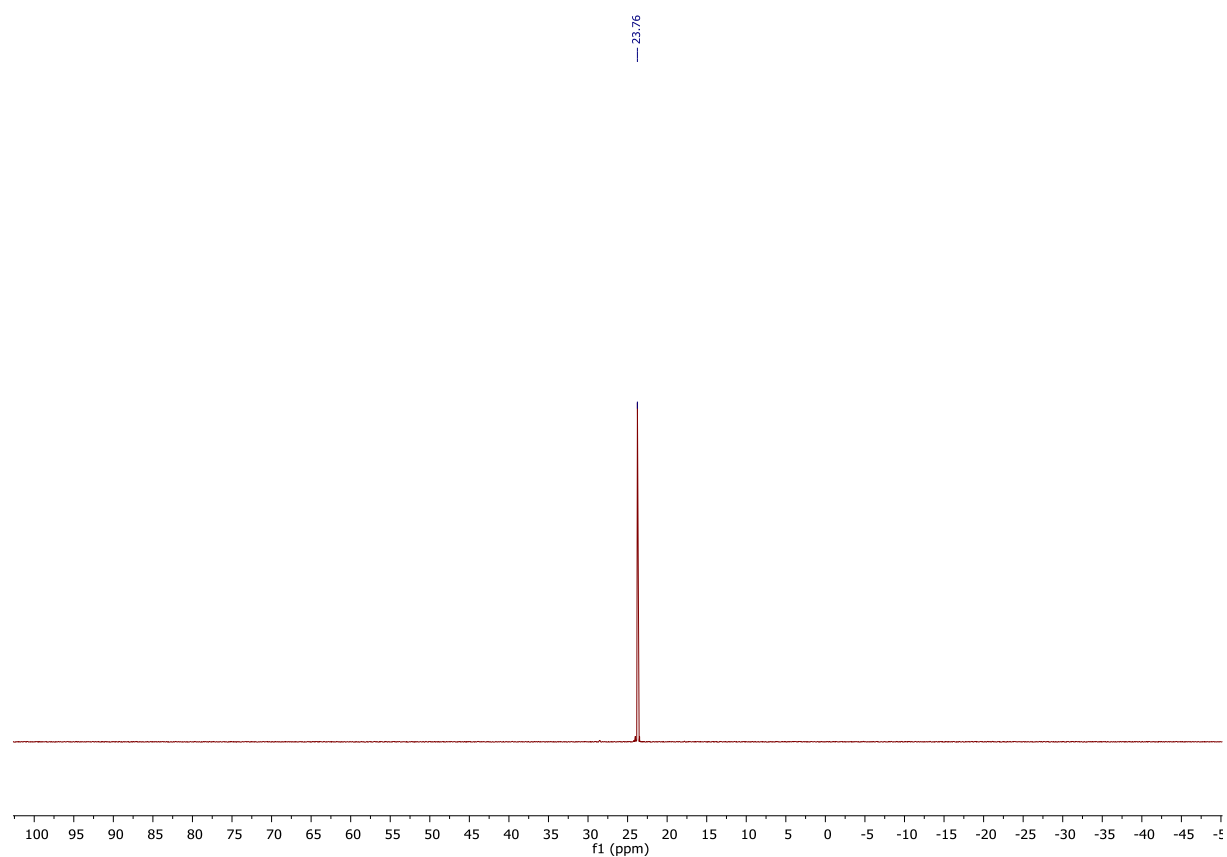
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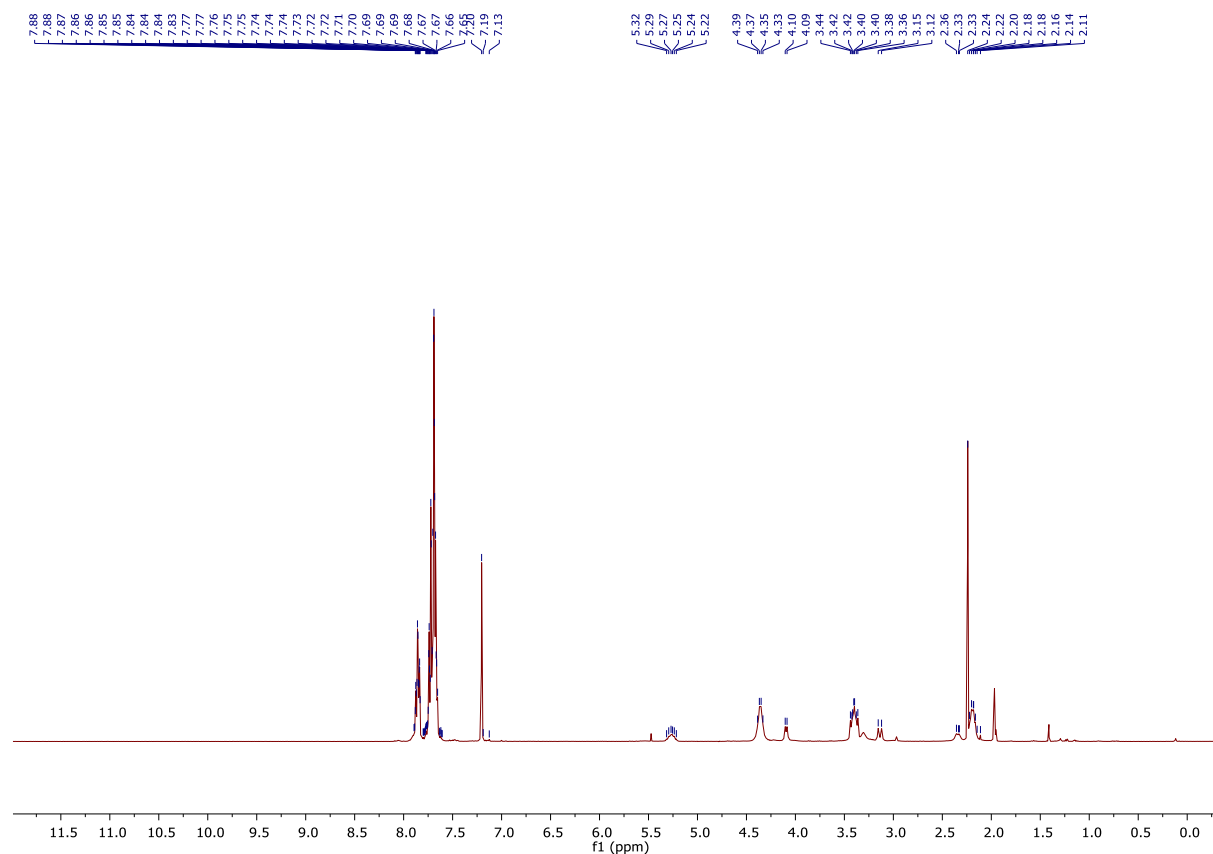
^{13}C{^{1}H} NMR spectrum of [4](OTf)$_2$ (in CD$_3$CN)
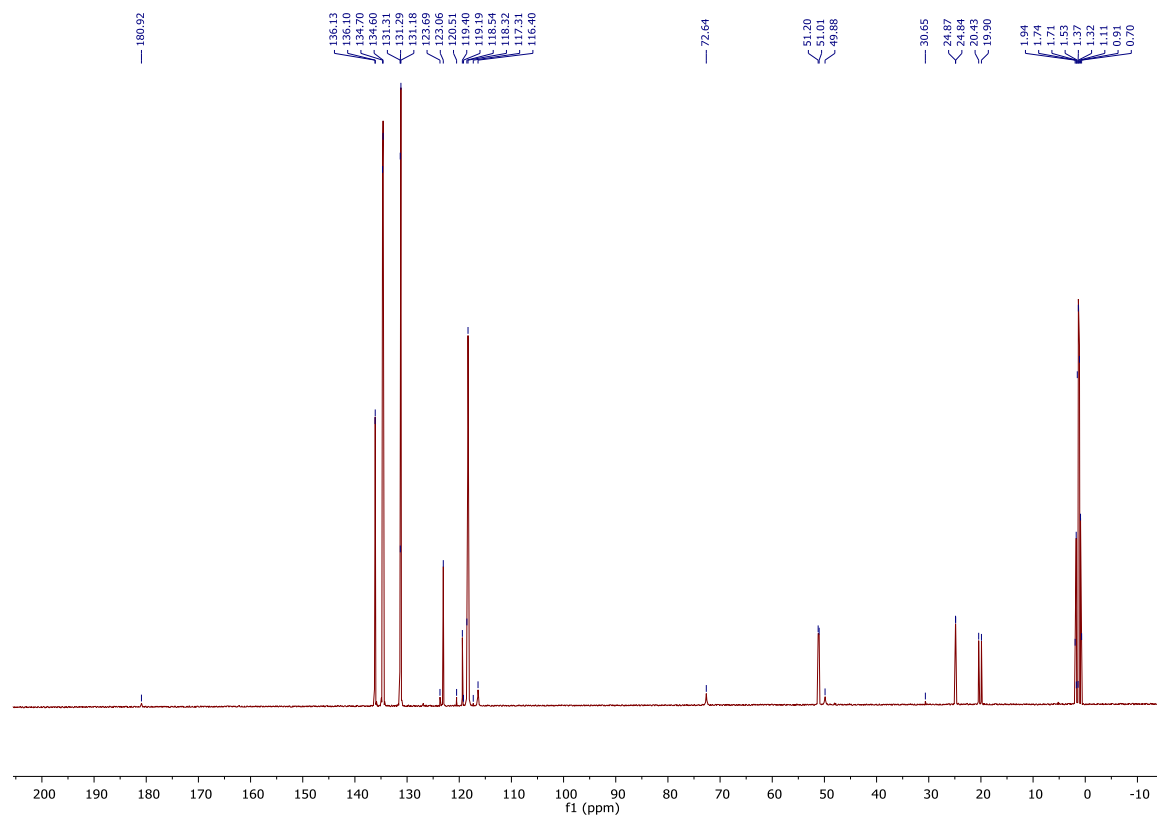
$^{31}P\{^1H\}$ NMR spectrum of [5](OTf)$_2$ (in CD$_3$CN)

— 23.74

.05 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -5
f1 (ppm)

^1H NMR spectrum of [5](OTf)$_2$ (in CD$_3$CN)

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
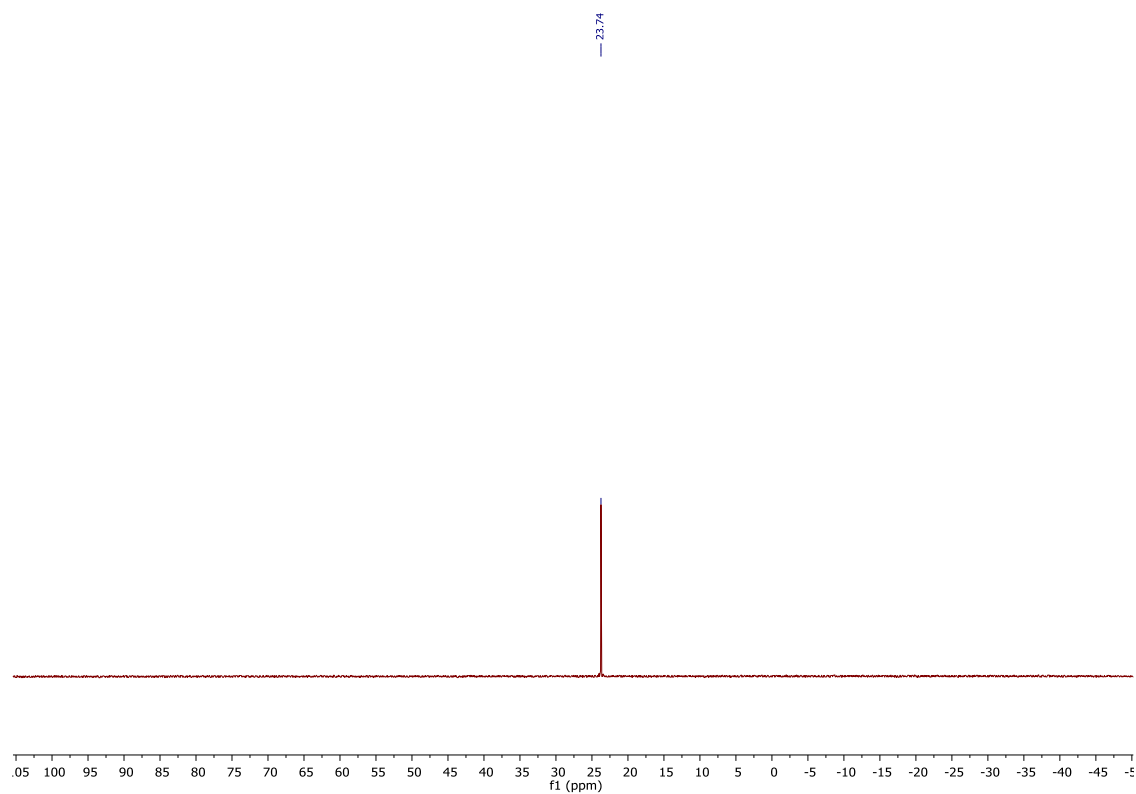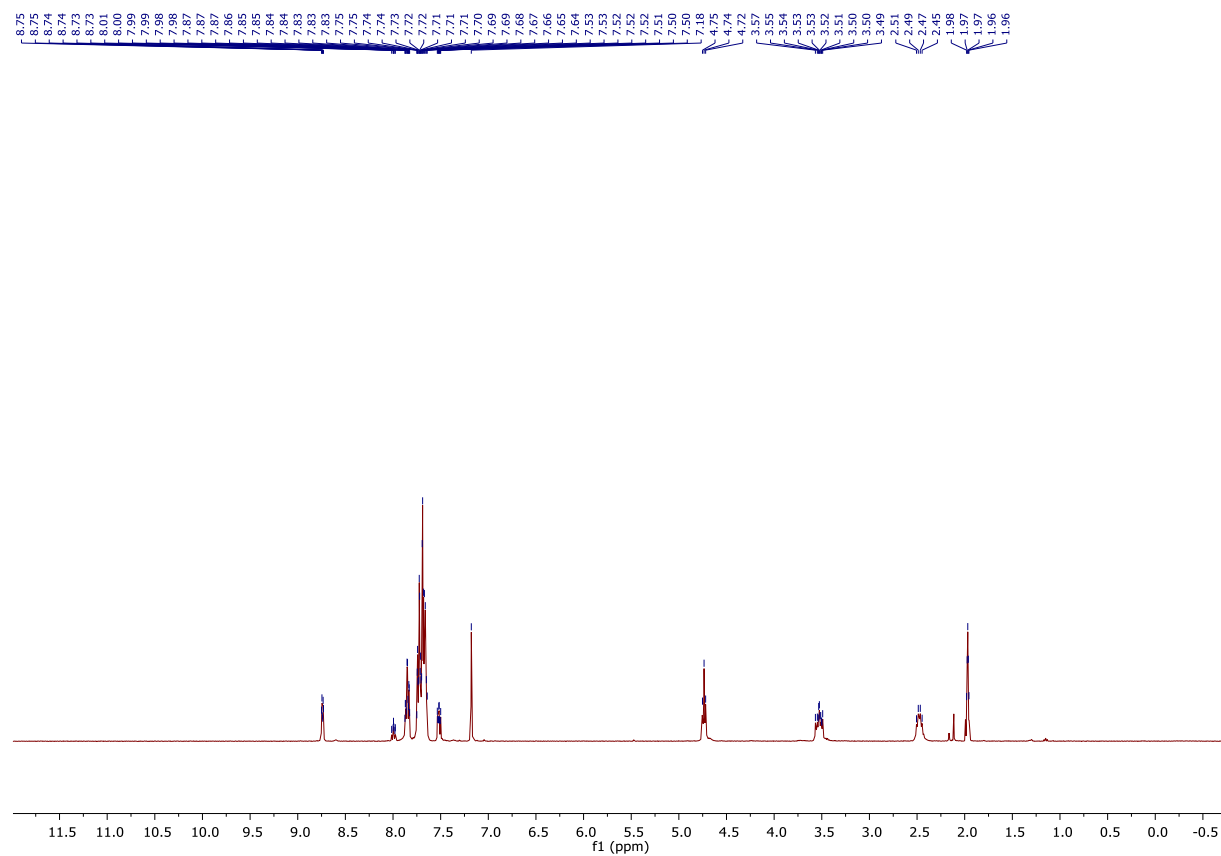
$^{13}C\{^1H\}$ NMR spectrum of [5](OTf)$_2$ (in CD$_3$CN)

$^{31}P\{^1H\}$ NMR spectrum of [6](OTf)$_2$ (in CD$_3$CN)

9
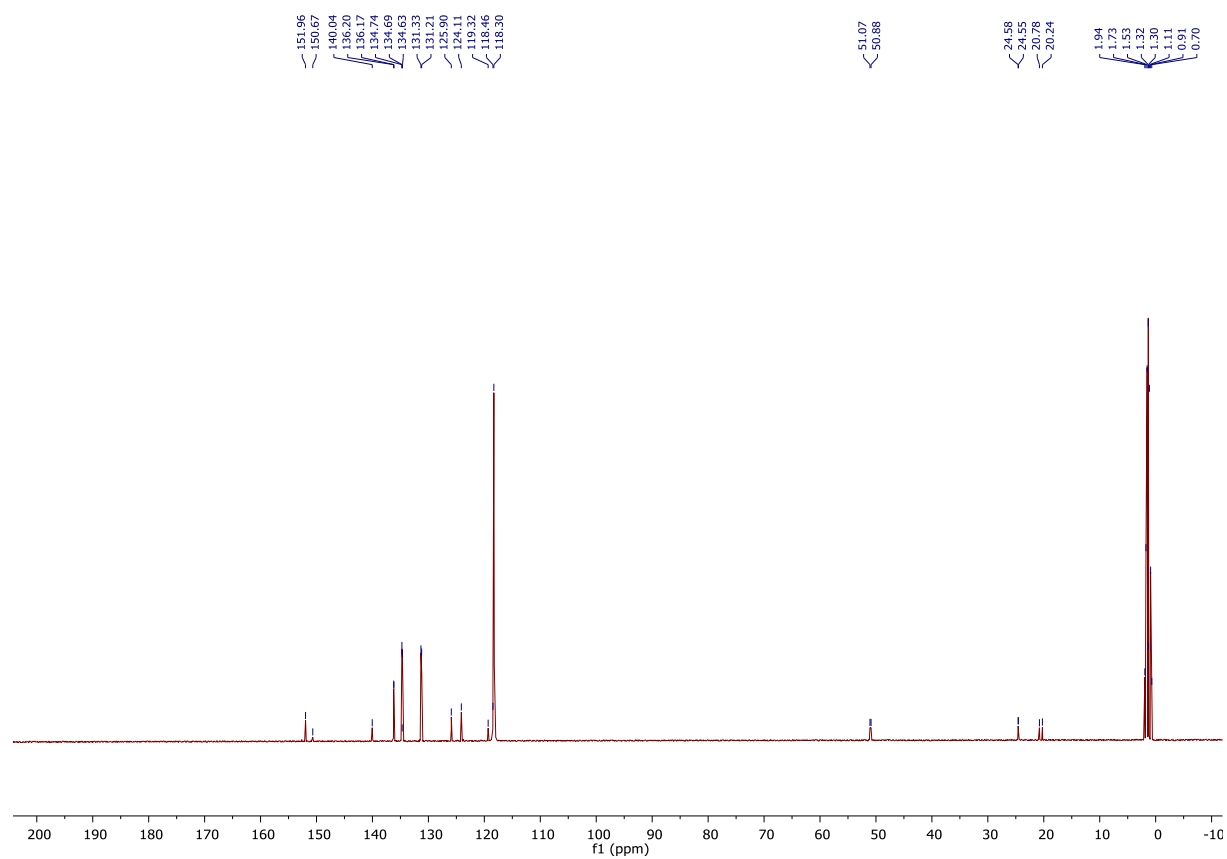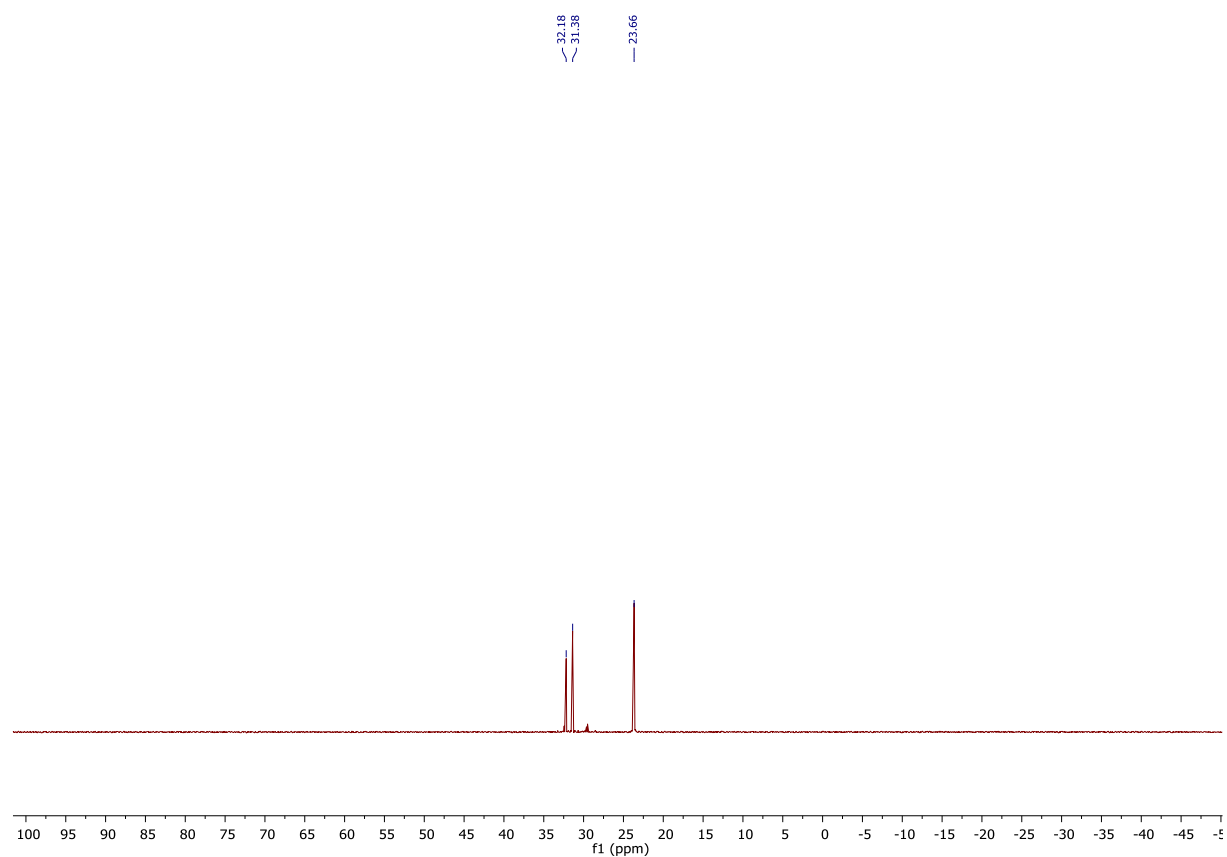
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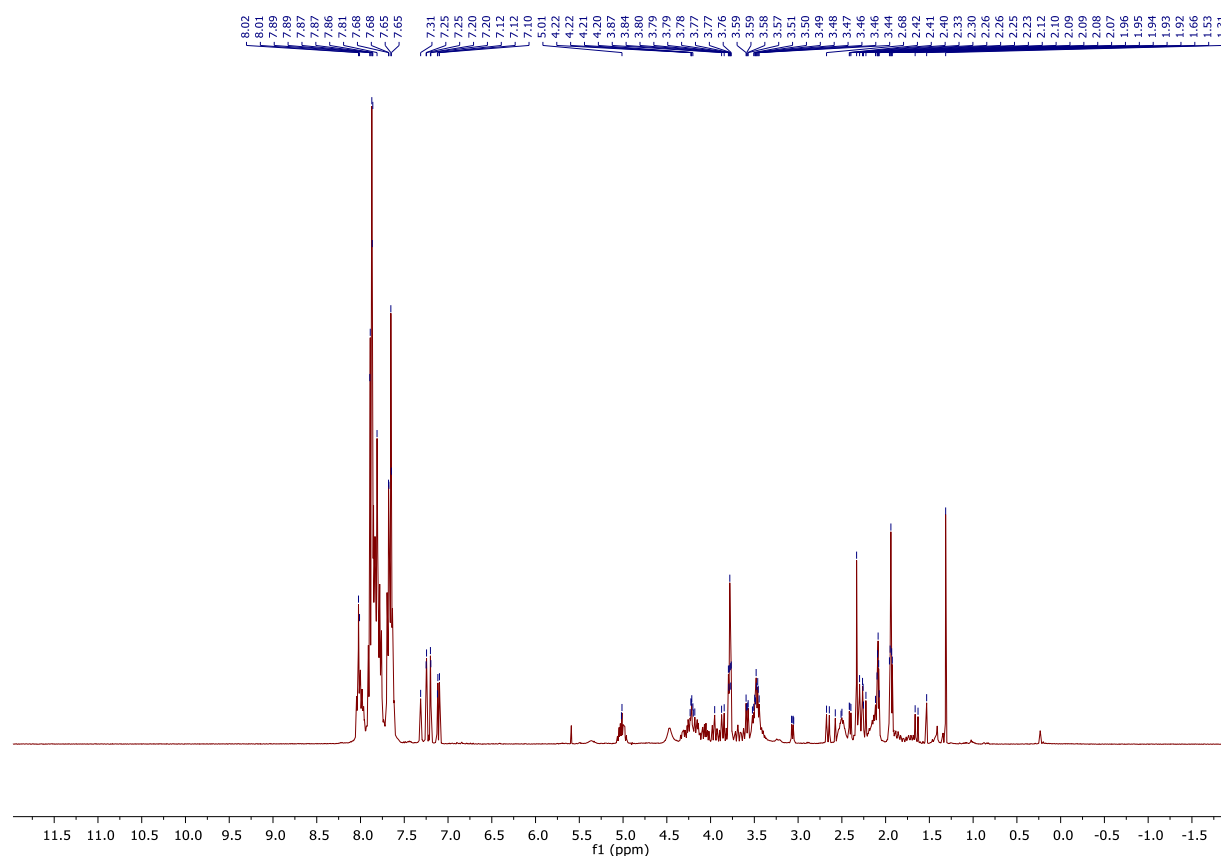
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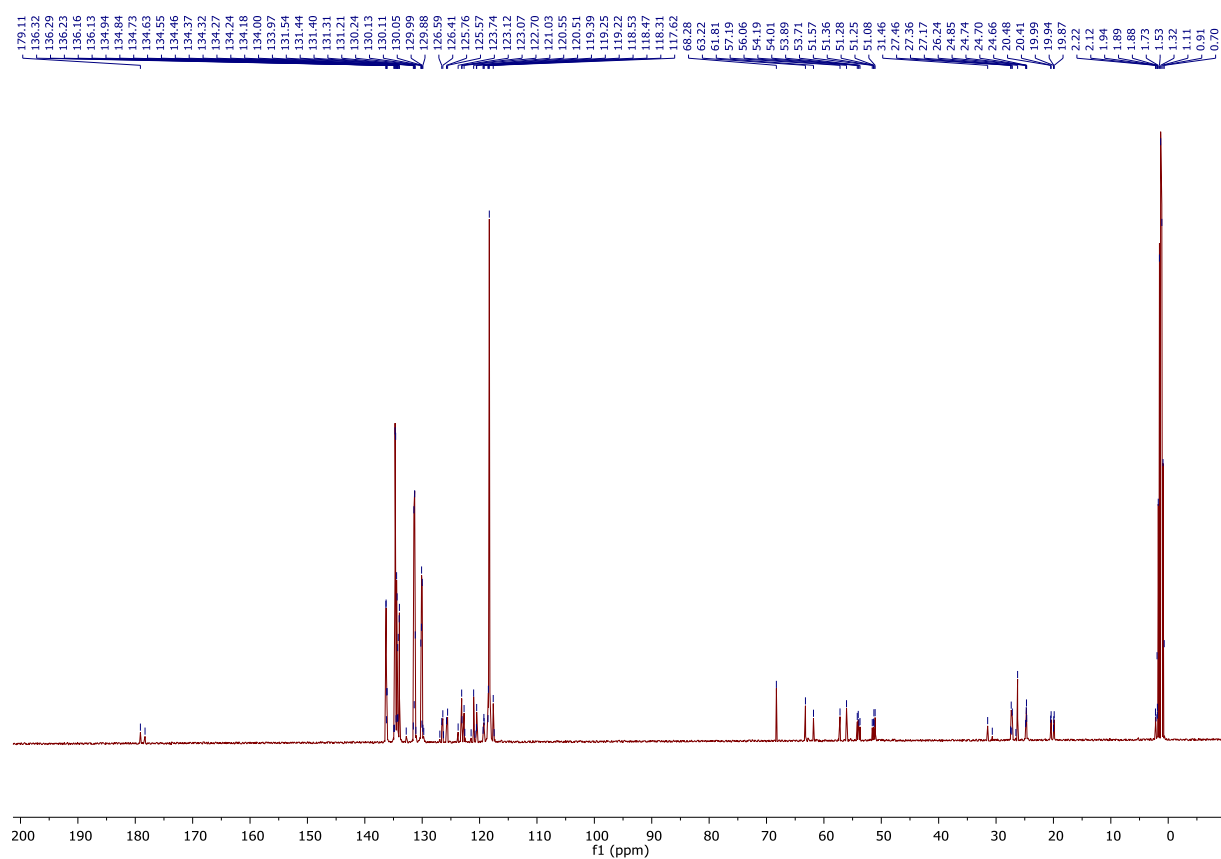
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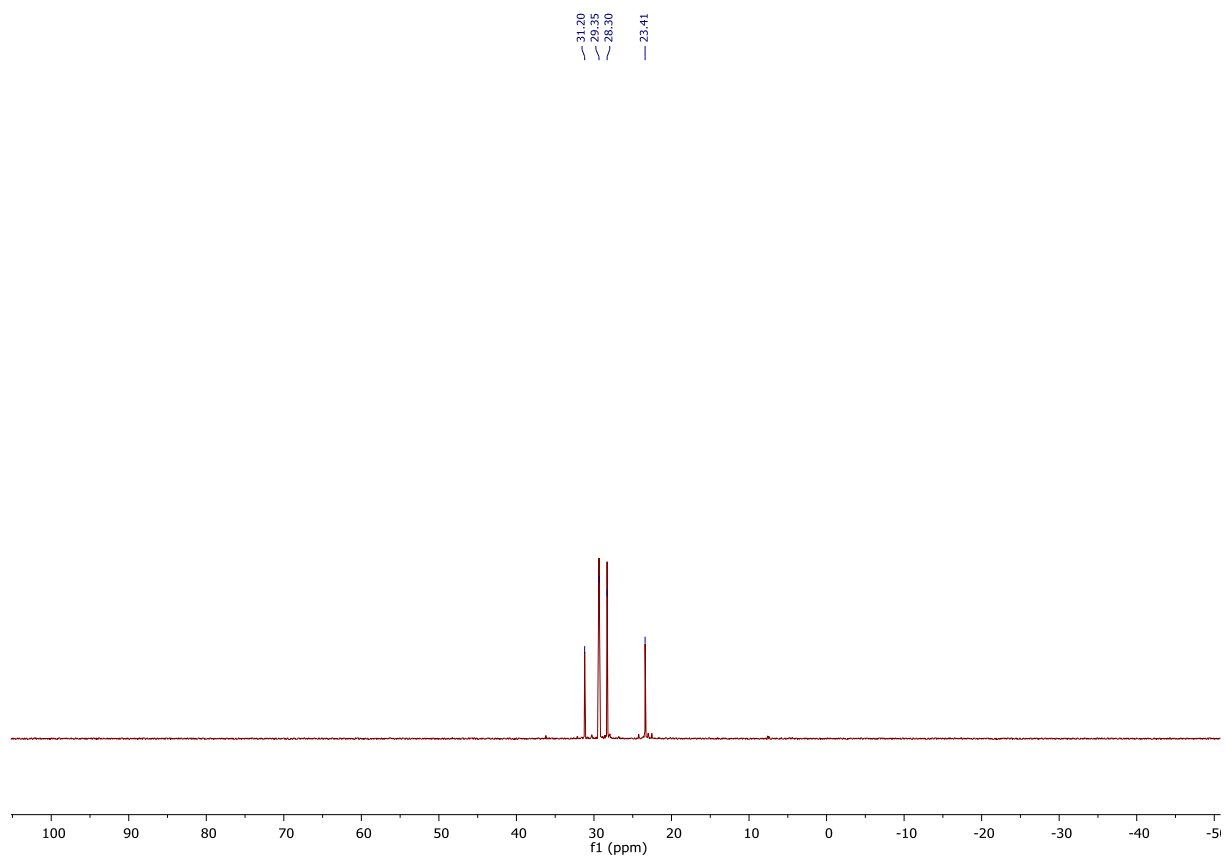
^1H NMR spectrum of [7](OTf) (in CD$_3$CN)
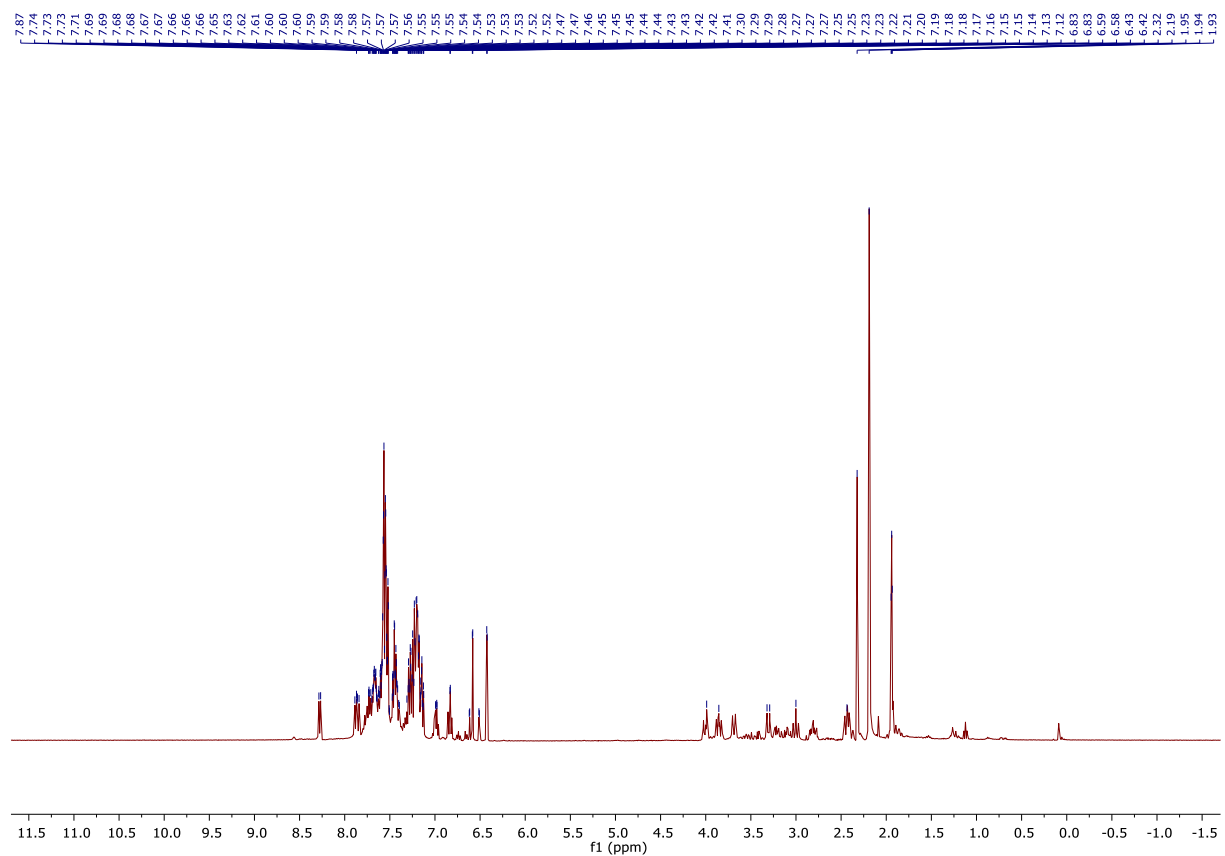
$^{13}C\{^1H\}$ NMR spectrum of [7](OTf) (in CD$_3$CN)
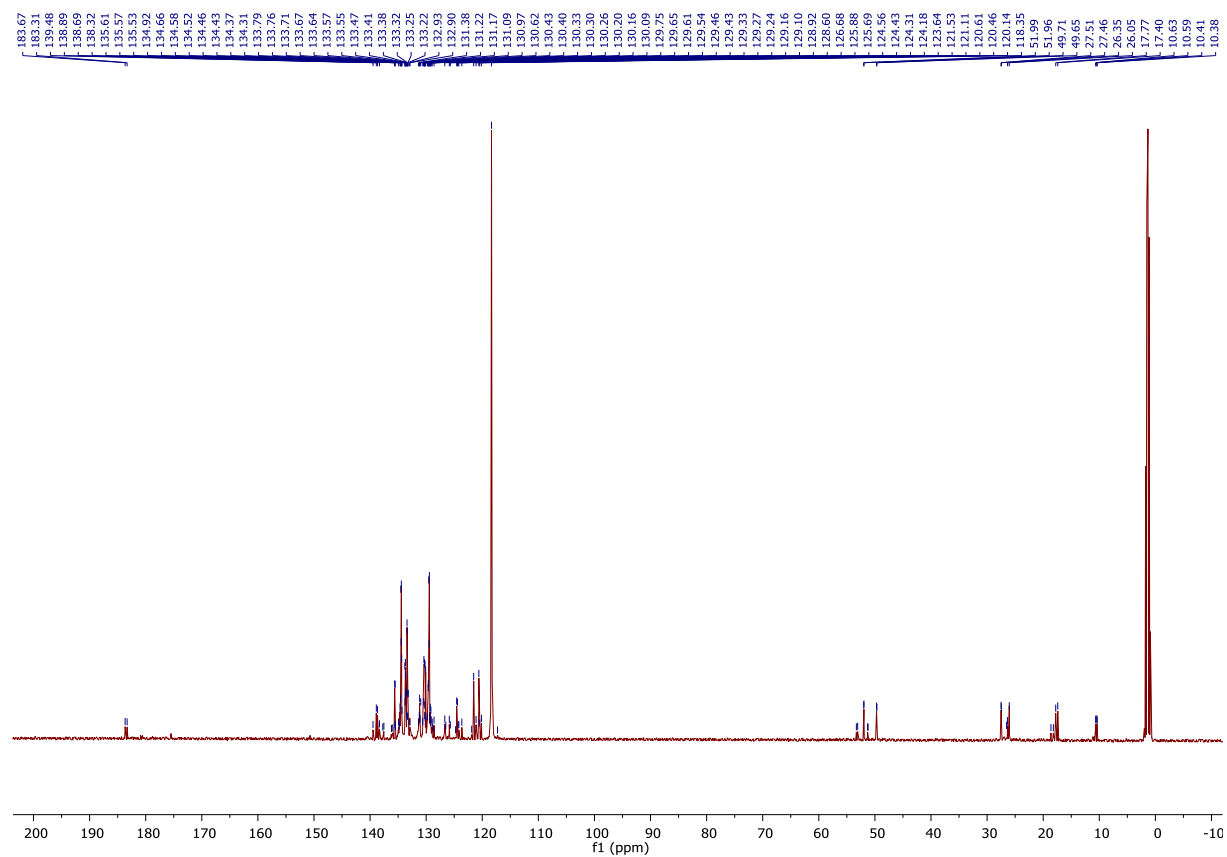
$^{31}P\{^1H\}$ NMR spectrum of [8](OTf)$_2$ (in CD$_3$CN)
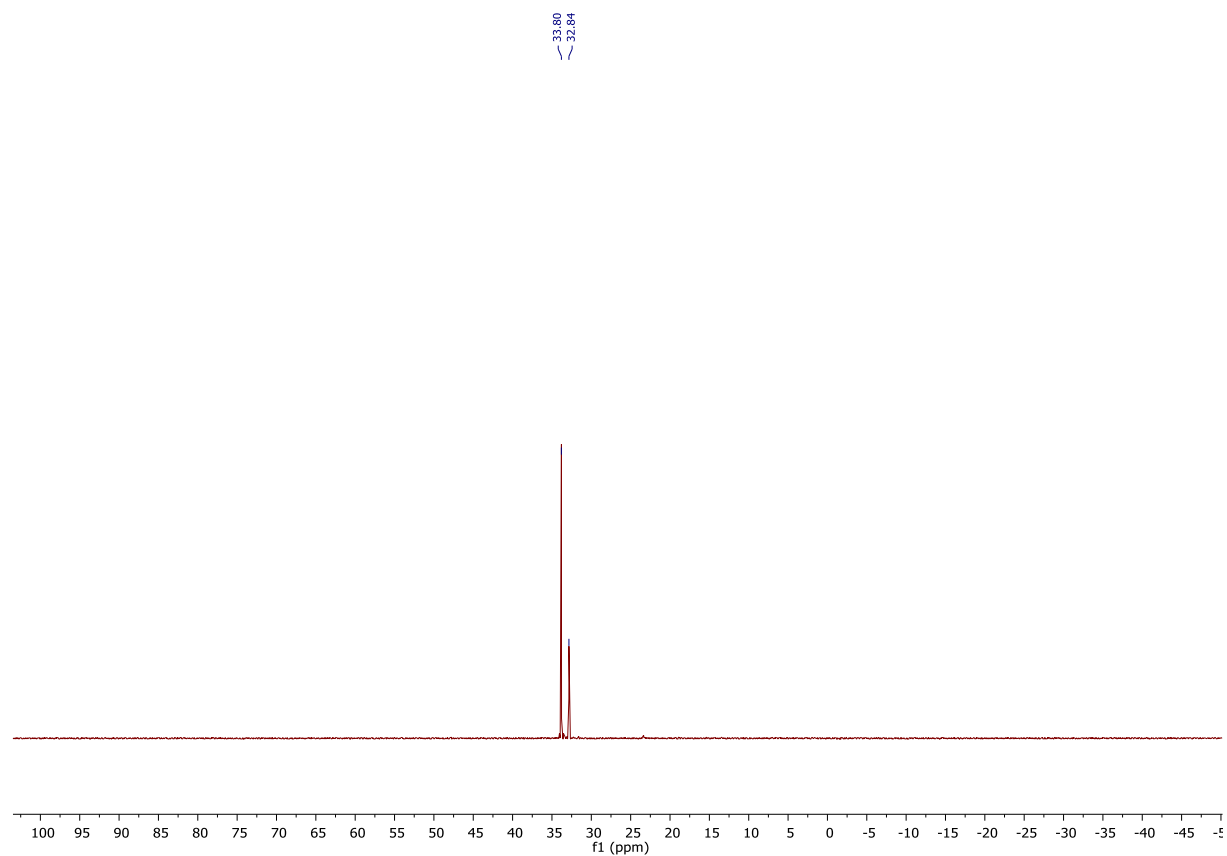
^{1}H NMR spectrum of [8](OTf)$_2$ (in CD$_3$CN)
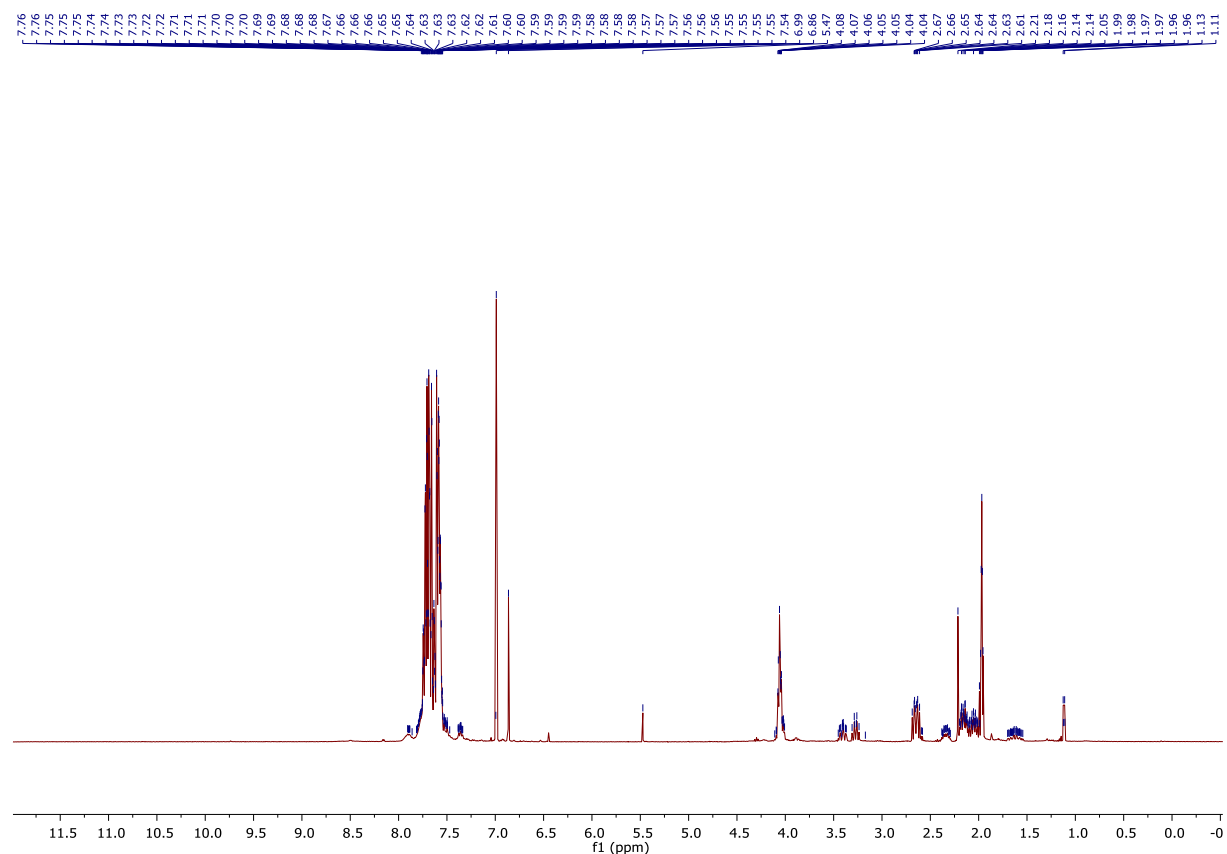
^{13}C{^{1}H} NMR spectrum of [8](OTf)$_2$ (in CD$_3$CN)

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$^{31}P\{^1H\}$ NMR spectrum of [9](OTf)$_2$ (in CD$_2$Cl$_2$)

34.62
33.61
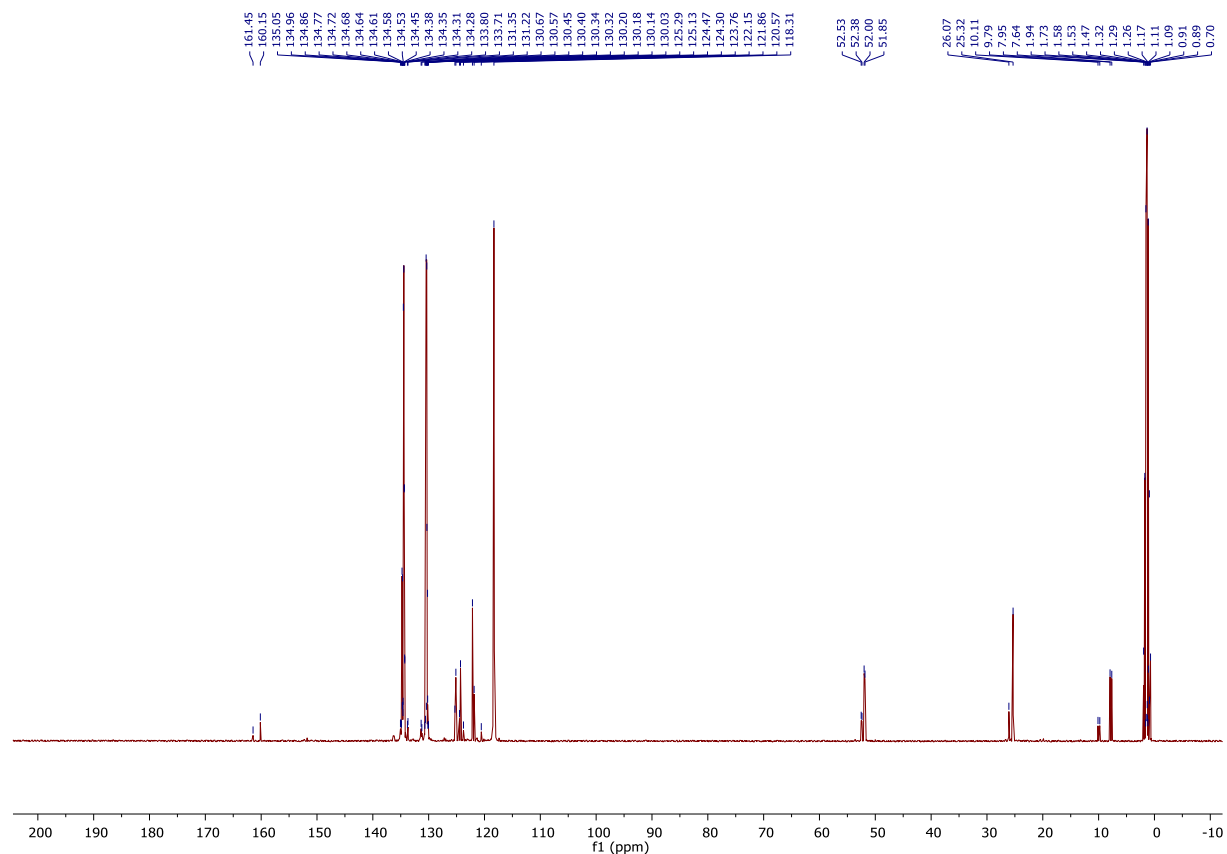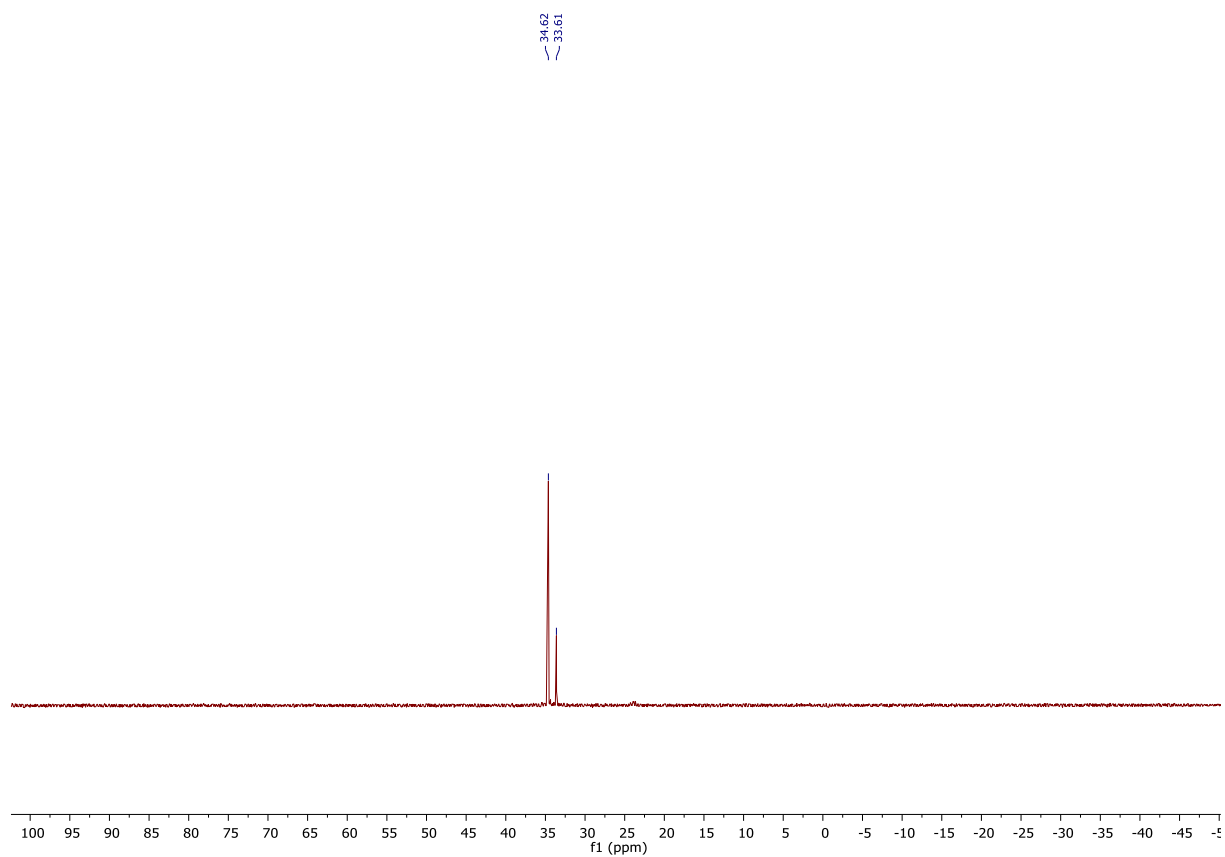
^{1}H NMR spectrum of [9](OTf)$_2$ (in CD$_2$Cl$_2$)

$^{13}C\{^1H\}$ NMR spectrum of [9](OTf)$_2$ (in CD$_2$Cl$_2$)

167.98, 166.59, 135.73, 134.43, 134.36, 134.33, 134.25, 134.17, 134.03, 134.00, 131.06, 130.96, 130.92, 130.39, 130.28, 130.23, 130.12, 129.70, 124.60, 124.40, 123.77, 123.57, 123.21, 121.94, 120.94, 120.02

66.19, 58.47, 54.54, 54.47, 54.40, 54.27, 54.00, 53.93, 53.73, 53.46, 52.06, 51.92, 51.52, 51.38, 29.81, 29.40, 29.07, 26.51, 25.40, 22.87, 15.64, 14.36, 7.17, 6.85, 6.69, 6.36
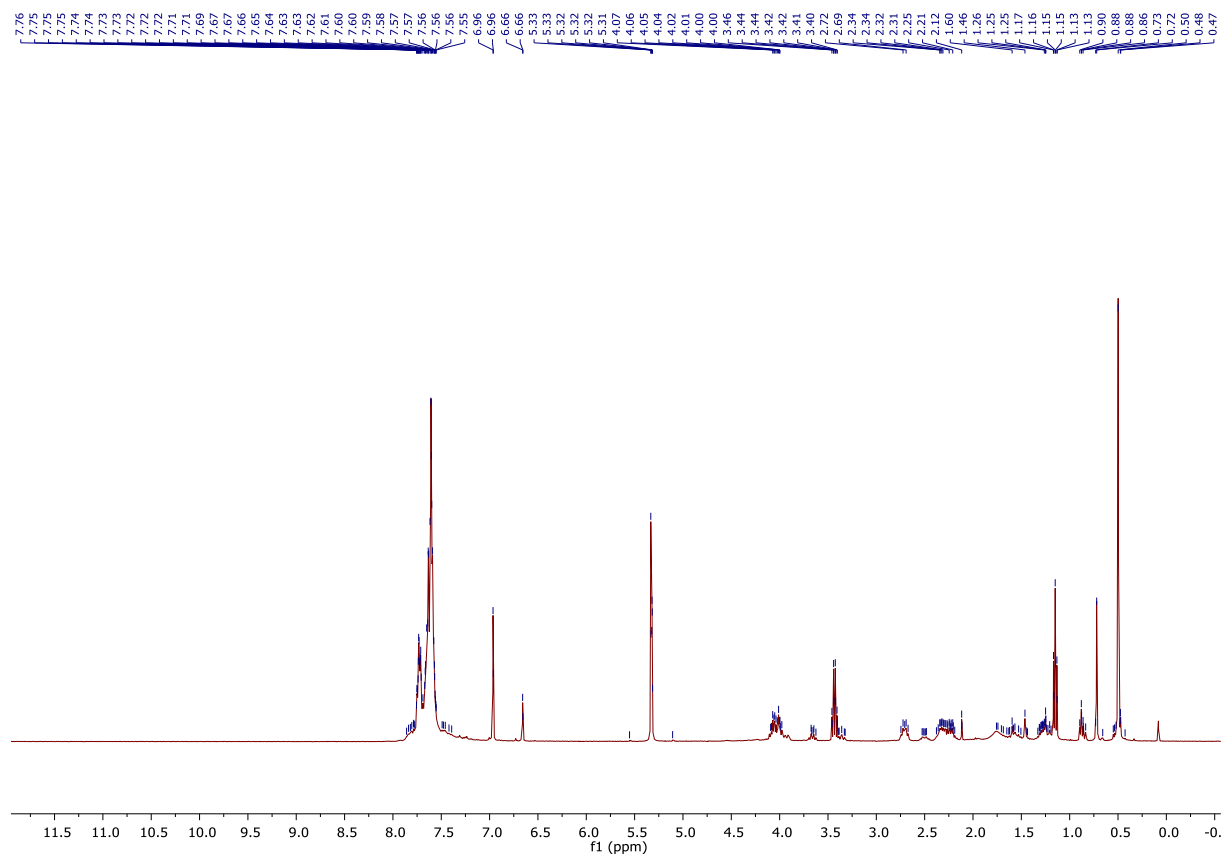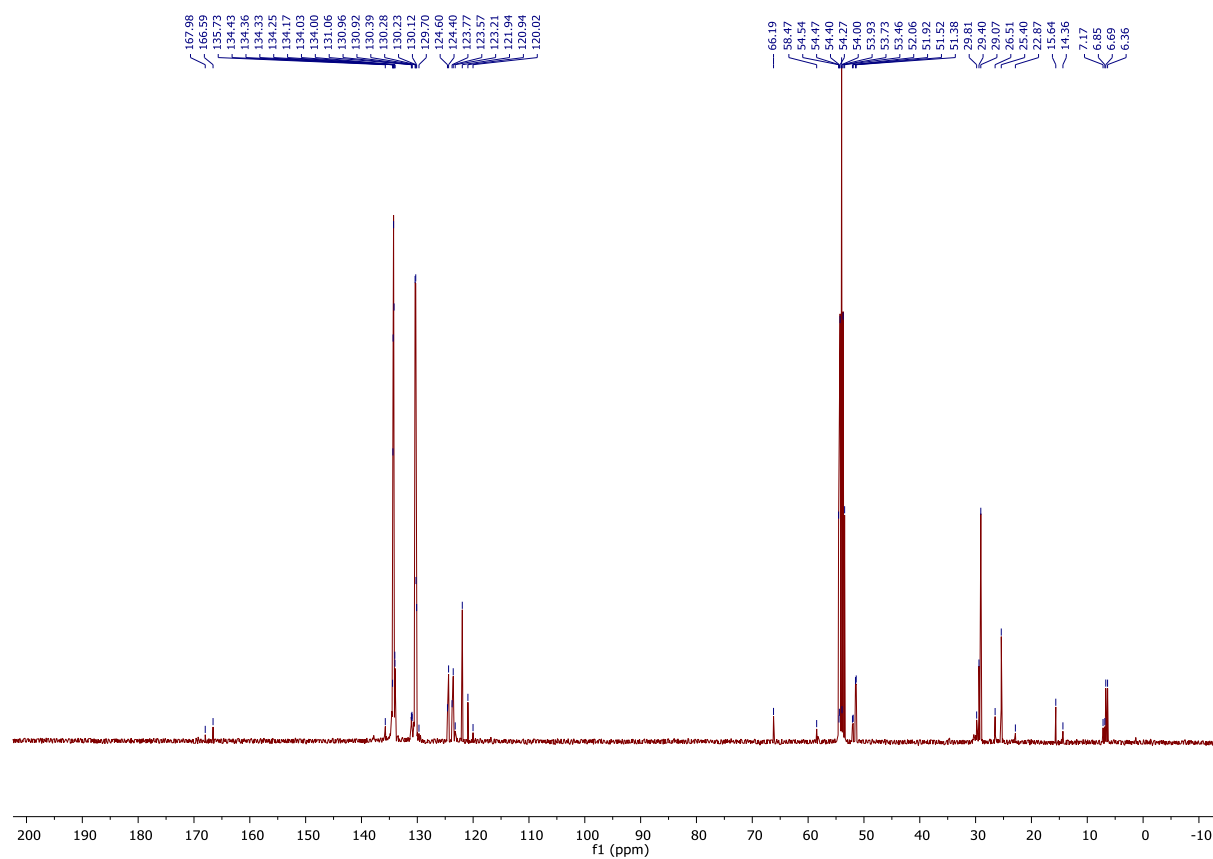
IR spectrum of [9](OTf)$_2$ (in CH$_2$Cl$_2$)

2322,09cm-1; 0,05A
2301,96cm-1; 0,25A
2197,39cm-1; 0,69A
2139,35cm-1; 0,11A
2092,21cm-1; 0,08A
2003,55cm-1; 0,05A
1751,59cm-1; 0,19A
1633,77cm-1; 0,03A
1588,65cm-1; 0,01A
1537,39cm-1; 0,00A

15
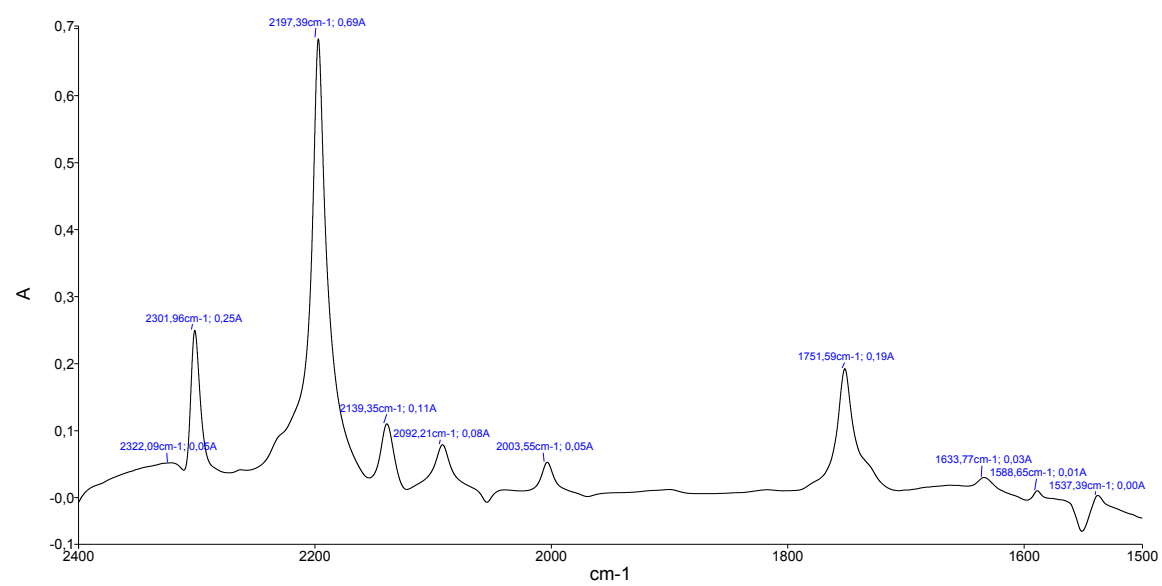
^{31}P{^{1}H} NMR spectrum of [10](OTf)$_2$ (in CD$_2$Cl$_2$): 90% conversion.
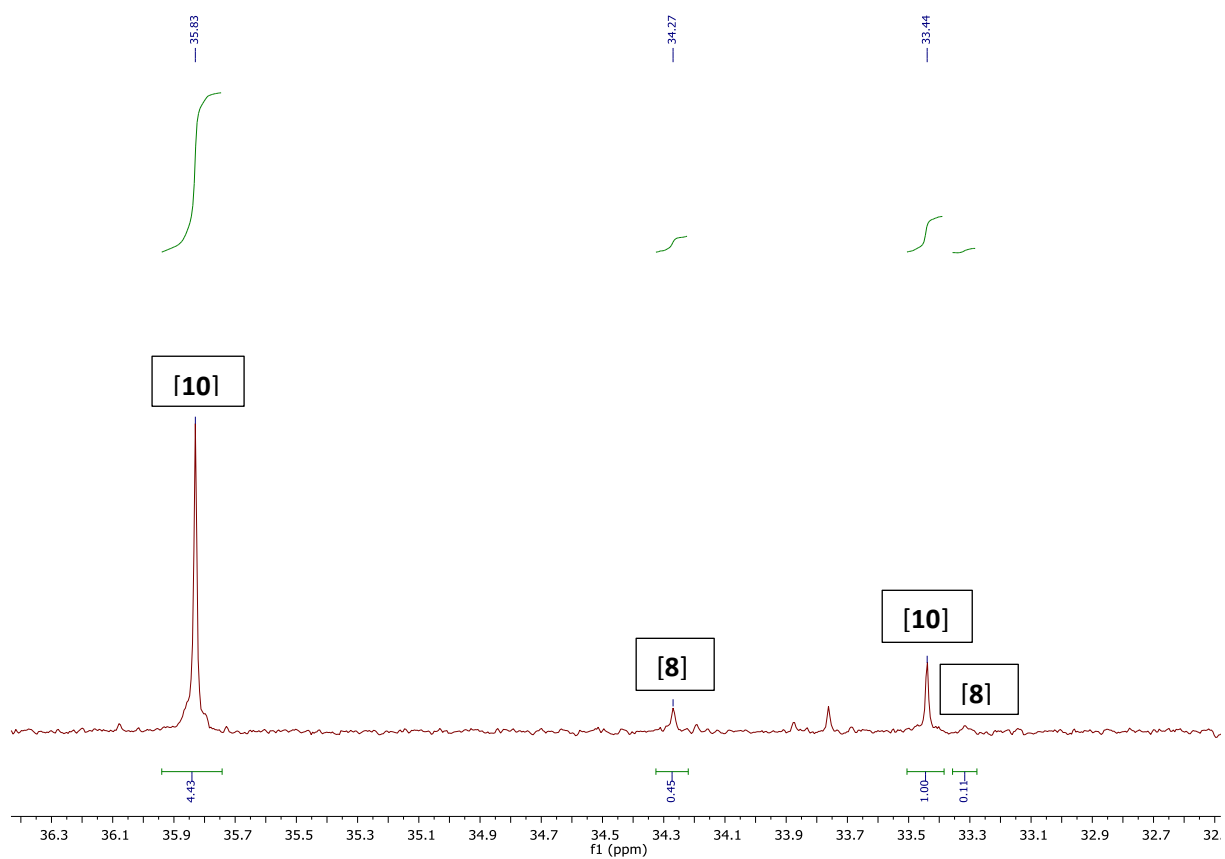
IR spectrum of [10](OTf)$_2$ (in CH$_2$Cl$_2$)
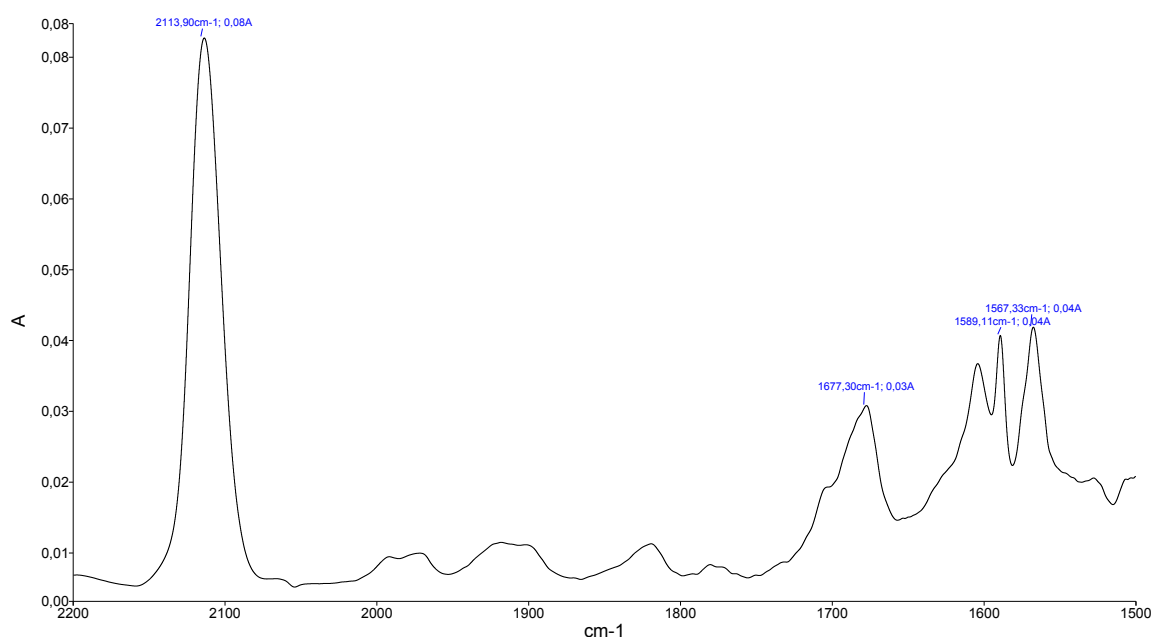
Crystallographic table for [2](Br), [3](OTf)$_3$, [4](OTf)$_2$, [5](OTf)$_2$, *meso*-[9](OTf)$_2$, and *dl*-[9](OTf)$_2$

|	[2]Br	[3](OTf)$_3$	[4](OTf)$_2$	[5](OTf)$_2$	*meso*-[9](OTf)$_2$	*dl*-[9](OTf)$_2$
Empirical formula	C$_{24}$H$_{24}$BrN$_2$P	C$_{48}$H$_{45}$F$_9$N$_2$O$_9$P$_2$S$_3$	C$_{54}$H$_{54.45}$ClF$_6$N$_4$O$_6$P$_2$PdS$_2$	C$_{52}$H$_{47}$Cl$_2$F$_6$N$_3$O$_6$P$_2$PdS$_2$	C$_{52}$H$_{51}$F$_6$N$_3$O$_6$P$_2$PdS$_2$	C$_{52}$H$_{52.2}$F$_6$N$_3$O$_{6.60}$P$_2$PdS$_2$
Formula moiety	C$_{24}$H$_{24}$N$_2$P, Br	C$_{45}$H$_{45}$N$_2$P$_2$,3(CF$_3$O$_3$S)	C$_{48}$H$_{48.45}$Cl N$_2$ P$_2$ Pd, 2(CF$_3$O$_3$S), 2(C$_2$H$_3$N)	C$_{50}$H$_{47}$Cl$_2$N$_3$P$_2$Pd, 2(CF$_3$O$_3$S)	C$_{50}$H$_{51}$N$_3$P$_2$Pd, 2(CF$_3$O$_3$S)	C$_{50}$H$_{51}$N$_3$P$_2$ Pd, 2(CF$_3$O$_3$S), 0.6(H$_2$O)
Formula mass	451.35	1122.98	1237.42	1227.29	1160.46	1171.27
Crystal system	orthorhombic	triclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	P b c a	P -1	P -1	C 2/c	P -1	P 2$_1$/n
T [K]	100	100	100	173	100	100
a [Å]	15.3294(6)	10.000(7)	12.9726(6)	25.8085(10)	12.7979(6)	13.6658(9)
b [Å]	15.1363(6)	13.831(10)	14.7721(7)	13.8014(6)	13.2777(6)	17.1283(10)
c [Å]	18.3583(7)	21.778(14)	16.7001(8)	18.8584(14)	16.1350(9)	21.6507(13)
a [°]	90	85.044(17)	88.0820(10)	90	84.604(2)	90
b [°]	90	79.313(18)	73.5710(10)	126.5450(10)	77.121(2)	91.366(2)
g [°]	90	89.59(2)	65.1440(10)	90	70.633(2)	90
V [Å^3]	4259.7(3)	2949(3)	2771.8(2)	5396.6(5)	2520.9(2)	5066.4(5)
D_c	1.407	1.265	1.483	1.511	1.529	1.538
Z	8	2	2	4	2	4
μ [mm^{-1}]	2.017	0.257	0.589	0.652	0.590	0.589
Refl. measured	79348	169010	74501	15653	72138	103825
Refl. unique/R_{int}	4053/0.043	12063/0.050	11316/0.042	5491/0.028	9939/0.069	9276/0.170
Refl. with $I > n$s(I)	3399, n=3	11276, n=2	10685, n=2	5045, n=2	7672, n=3	5636, n=2.2
Nb parameters	253	728	712	336	649	556
R with $I > n$s(I)	0.0239	0.0625	0.0323	0.0325	0.0385	0.0808
R_w with $I > n$s(I)	0.0243	0.1433	0.089	0.0792	0.0403	0.0857
GooF	1.09	1.151	1.031	1.058	1.12	1.105
Dr$_{max}$/Dr$_{min}$ [e.Å^{-3}]	0.44/-0.38	0.69/-0.57	1.82/-0.60	0.83/-0.56	0.74/-0.52	1.94/-1.73

Computational details

Geometries were fully optimized at the PBE-D3/6-31G**/LANL2DZ* (Pd) level of calculation using Gaussian 09.[1] Vibrational analysis was performed at the same level as the geometry optimization in order to check the obtention of a minimum on the potential energy surface. Gibbs free energies were calculated at 298.15 K. Solvent effects of acetonitrile (ε = 35.688) were included using the polarizable continuum model (PCM) implemented in Gaussian 09.

Optimized geometry of complex 7$^+$ at the PBE-D3/6-31G/LANL2DZ* (Pd) level of calculation:** *cis*-**isomer** *(left)* **and** *trans*-**isomer** *(right)*
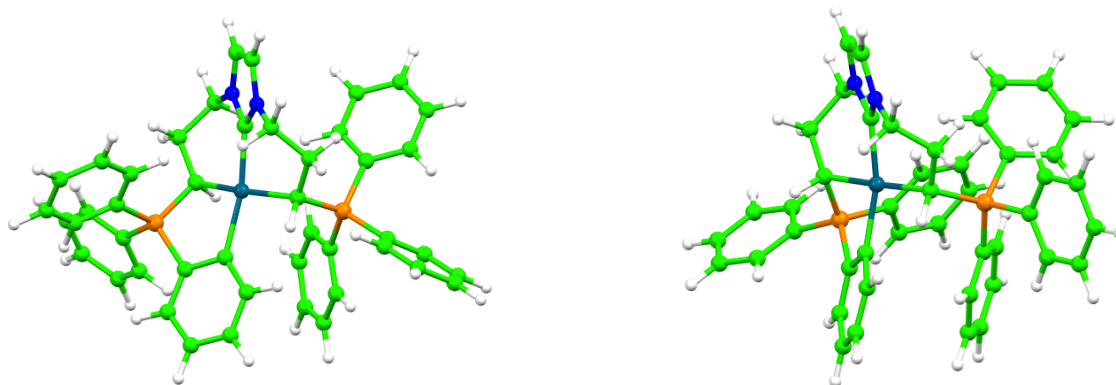
Optimized geometry of complex 8^{2+} at the PBE-D3/6-31G/LANL2DZ* (Pd) level of calculation:** *cis*-**isomer** *(left)* **and** *trans*-**isomer** *(right)*
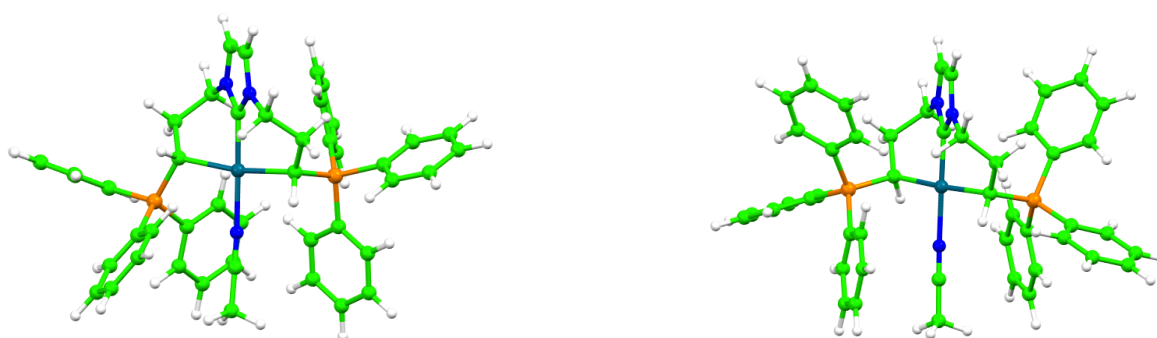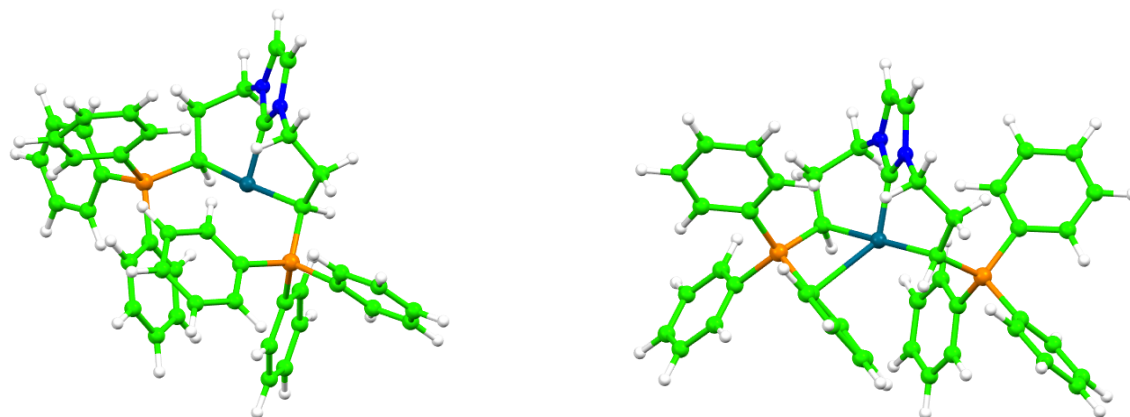
Optimized geometry of complex 8'²⁺ at the PBE-D3/6-31G**/LANL2DZ* (Pd) level of calculation: *cis*-isomer *(left)* and *trans*-isomer *(right)*

1 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. 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. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, 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, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.