Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Experimental and Theoretical Insights into trans influence of organo-sulfur and -selenium ligands in 5,6-Membered Palladium(II) Cationic Pincer Complexes Based on Iminophosphoranes

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New Journal of Chemistry

CONTENT OF SUPPORTING INFORMATION

Spectroscopy data for compound 3a

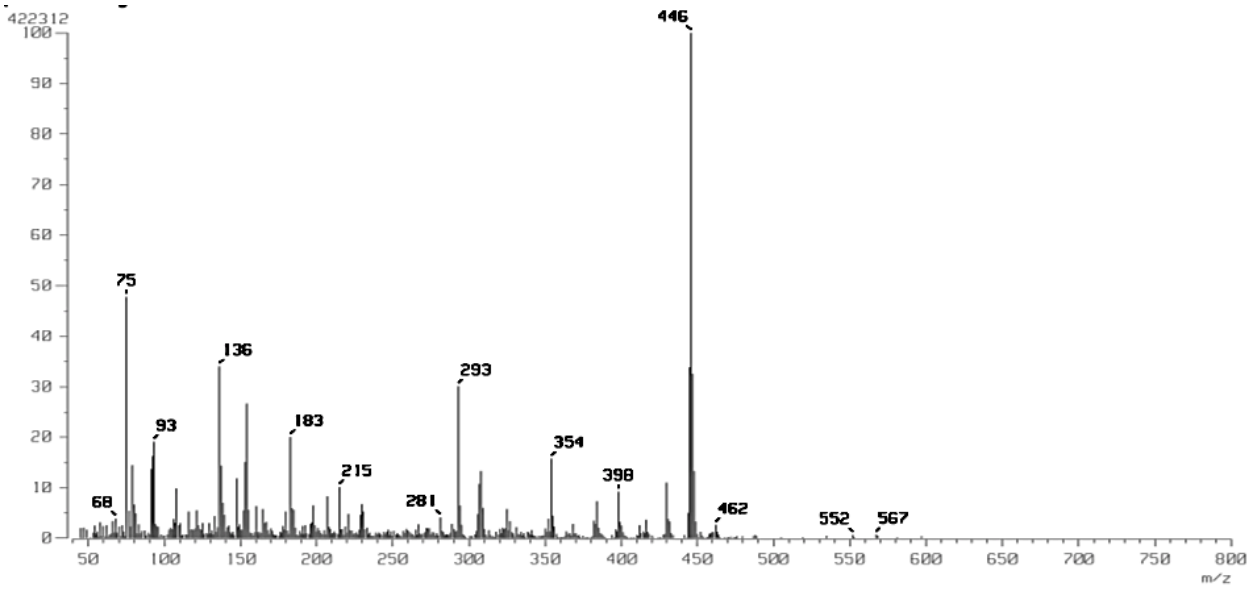

Figure S1. Mass Spectrum (FAB+) for compound 3a.

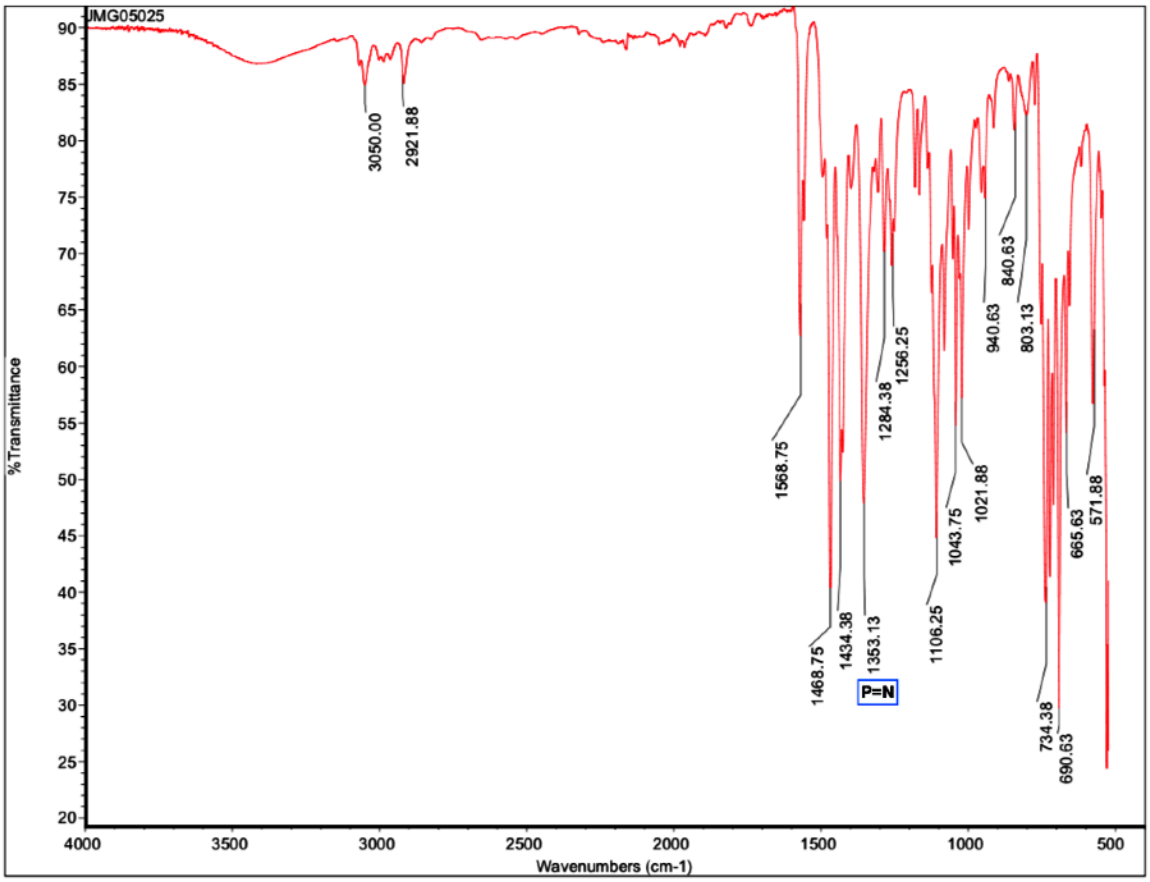

Figure S2. Infrared spectrum for compound **3a**.

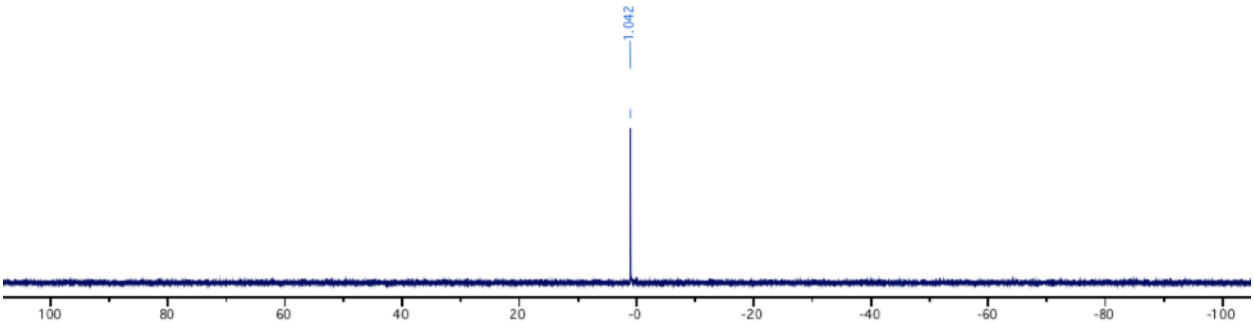

Figure S3. ^{31}P NMR spectrum for compound 3a in $CDCl_3$ (202 MHz).

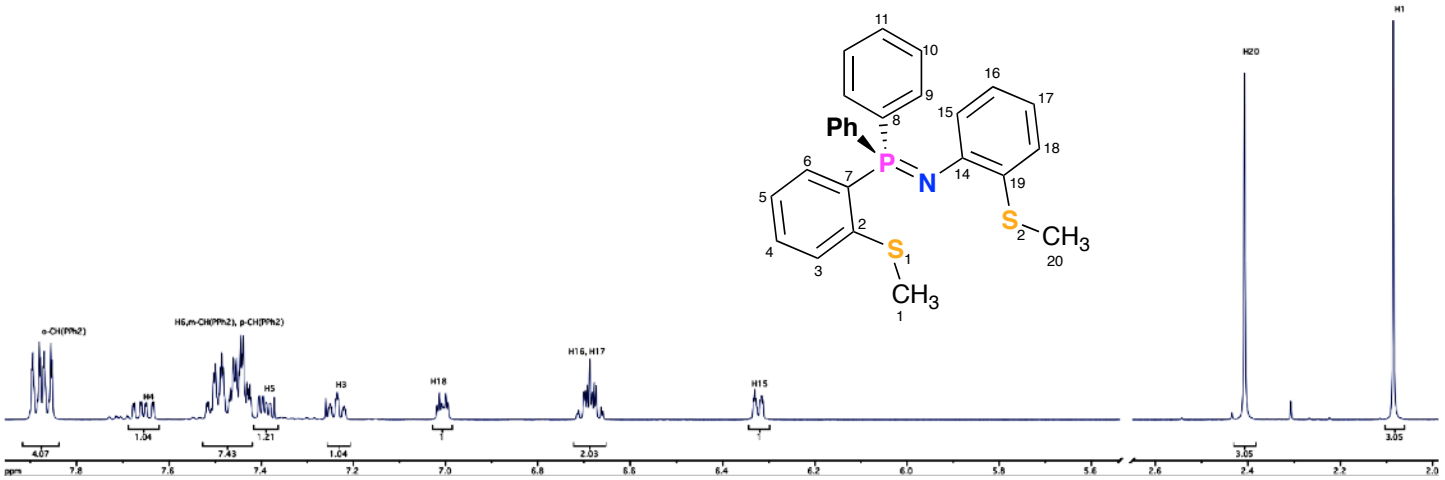

Figure S4. ^{1}H NMR spectrum for compound **3a** in $CDCl_3$ (500 MHz).

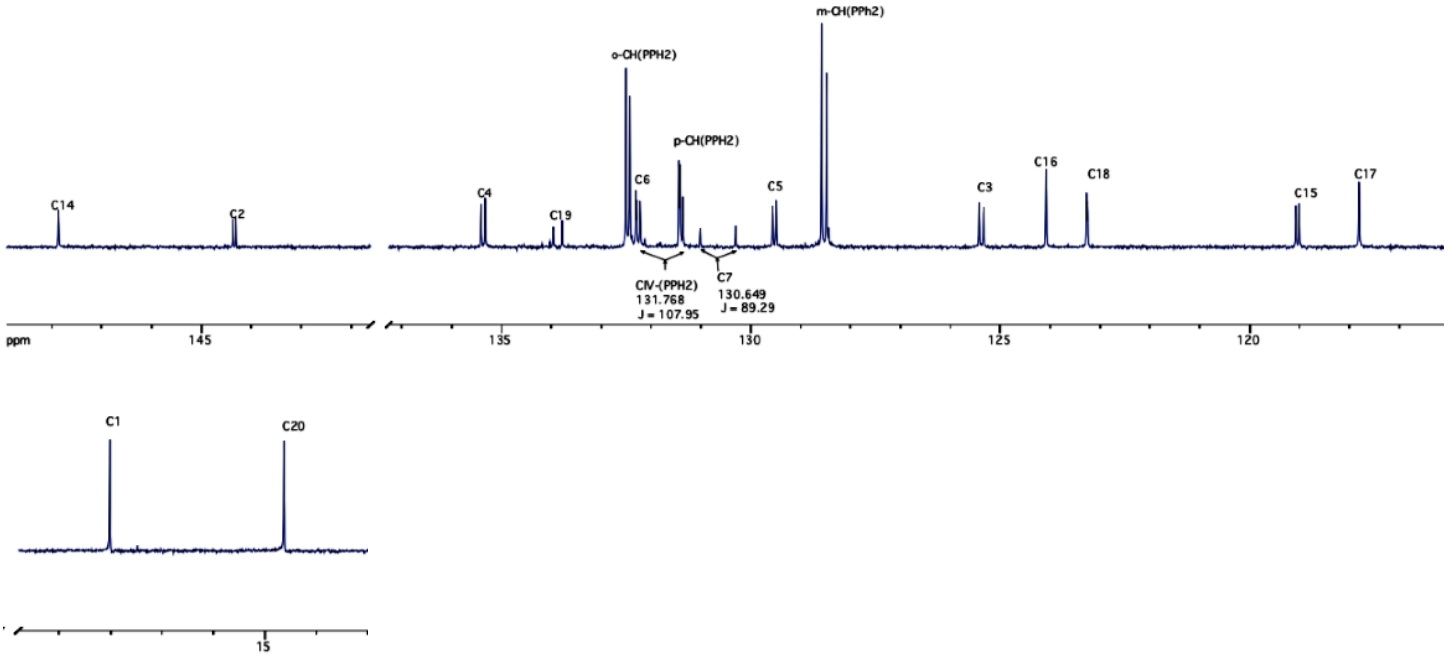

Figure S5. ^{13}C NMR spectrum for compound **3a** in $CDCl_3$ (125 MHz).

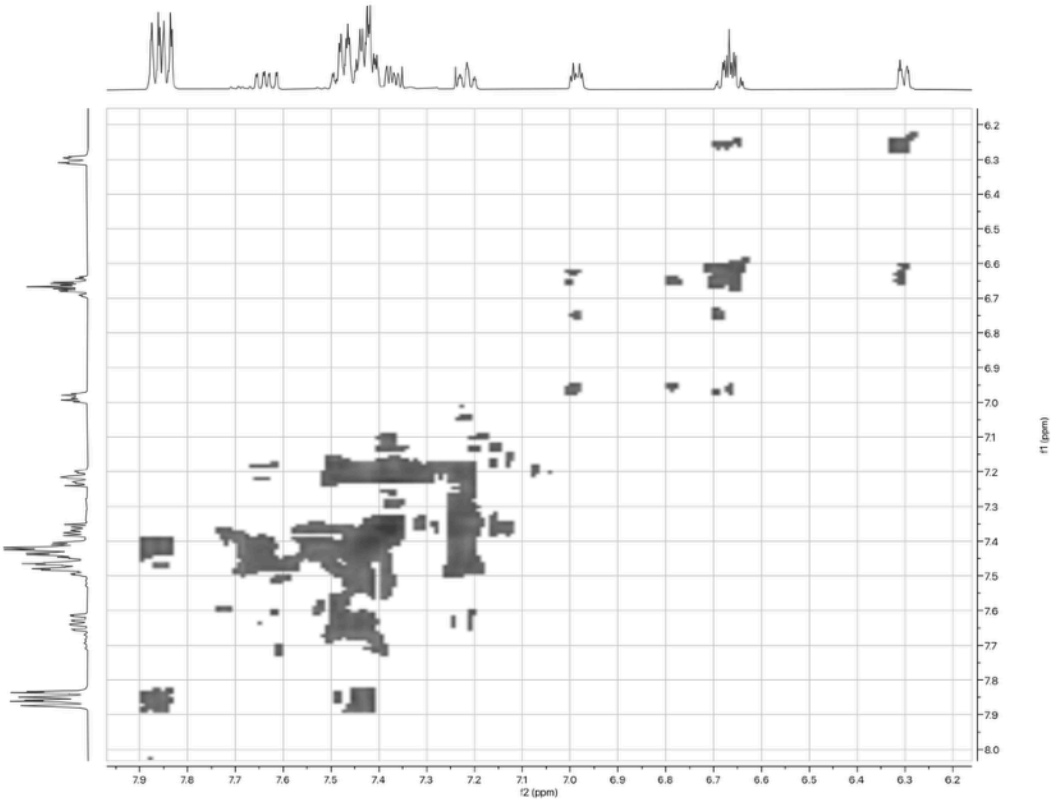

Figure S6. COSY NMR spectrum for compound **3a** in $CDCl_3$.

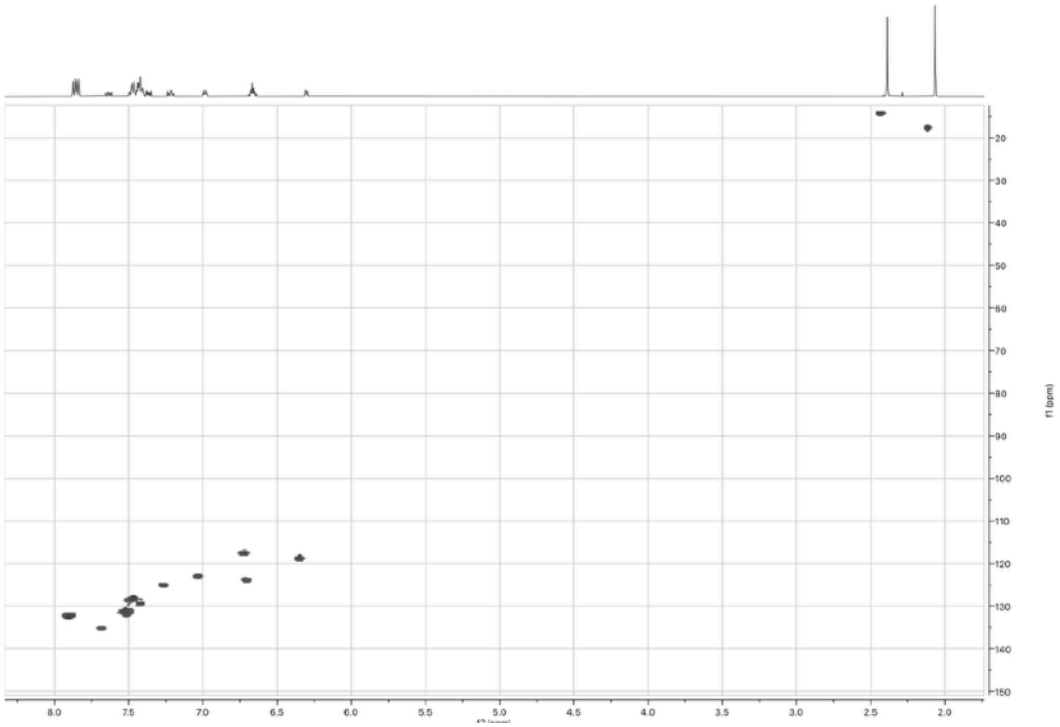

Figure S7. HSQC NMR spectrum for compound **3a** in $CDCl_3$.

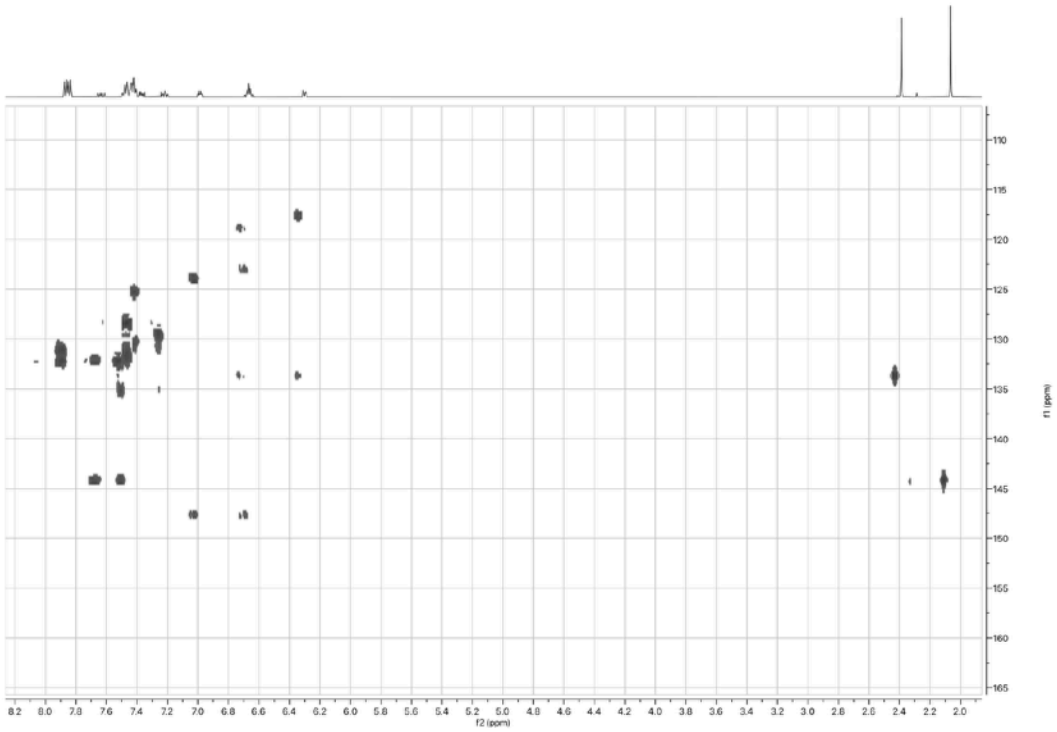

Figure S8. HMBC NMR spectrum for compound **3a** in $CDCl_3$.

Spectroscopy data for compound 3b

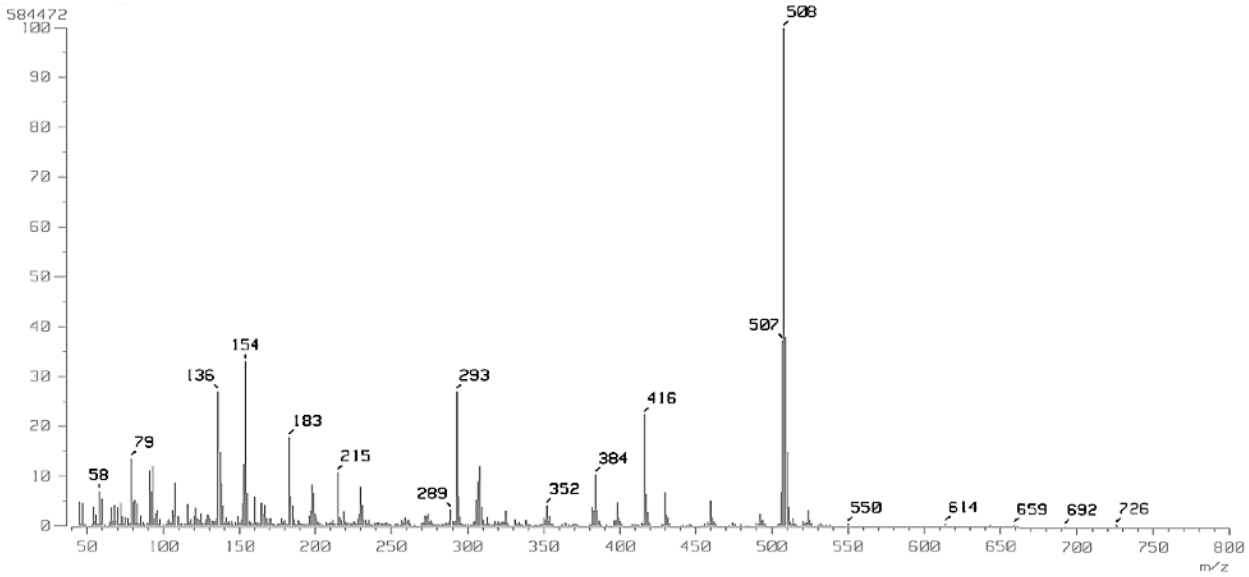

Figure S9. Mass Spectrum (FAB+) for compound **3b.**

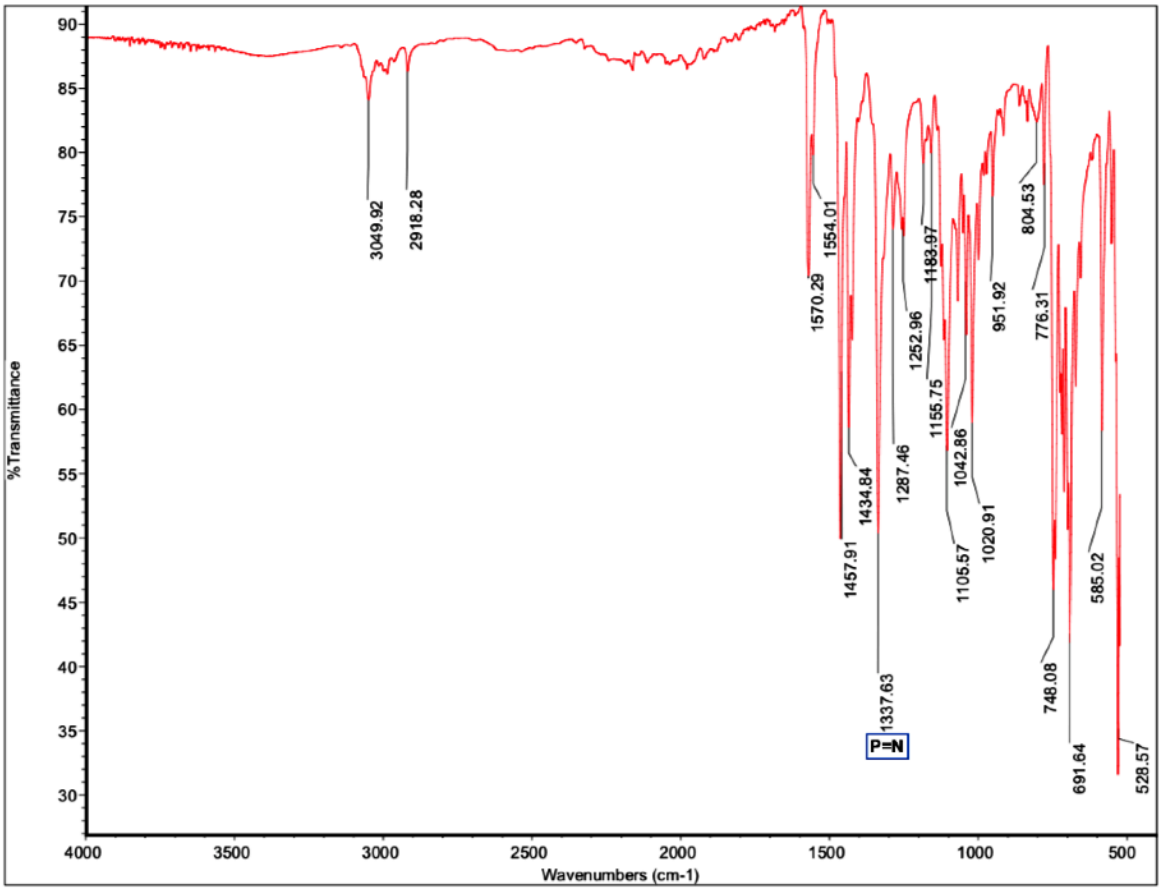

Figure S10. Infrared spectrum for compound **3b.**

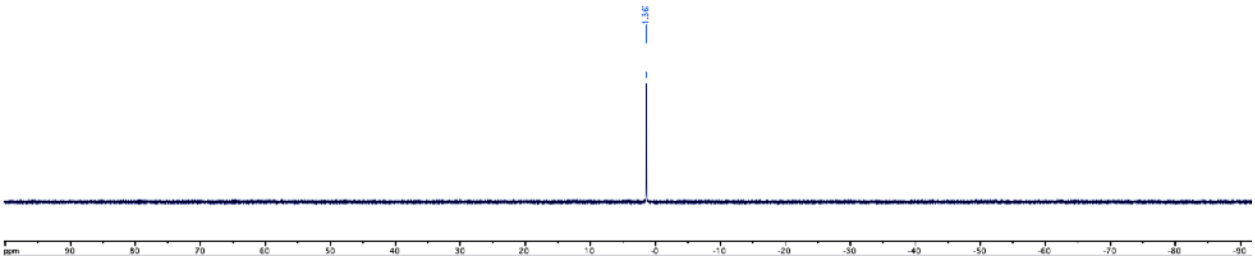

Figure S11. ^{31}P NMR spectrum for compound **3b** in $CDCl_3$ (202 MHz).

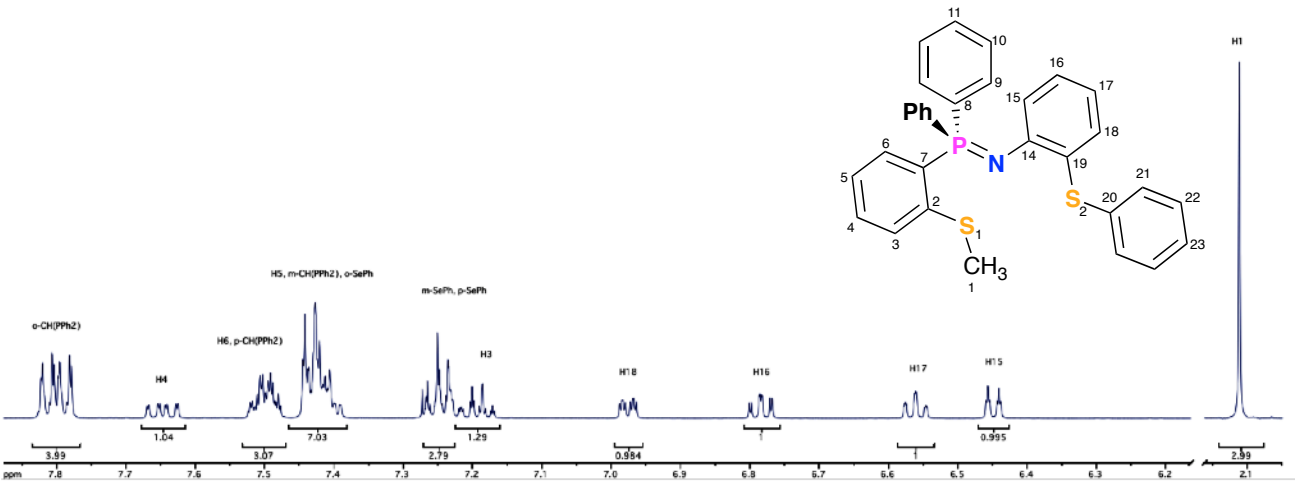

Figure S12. ^{1}H NMR spectrum for compound **3b** in $CDCl_3$ (500 MHz).

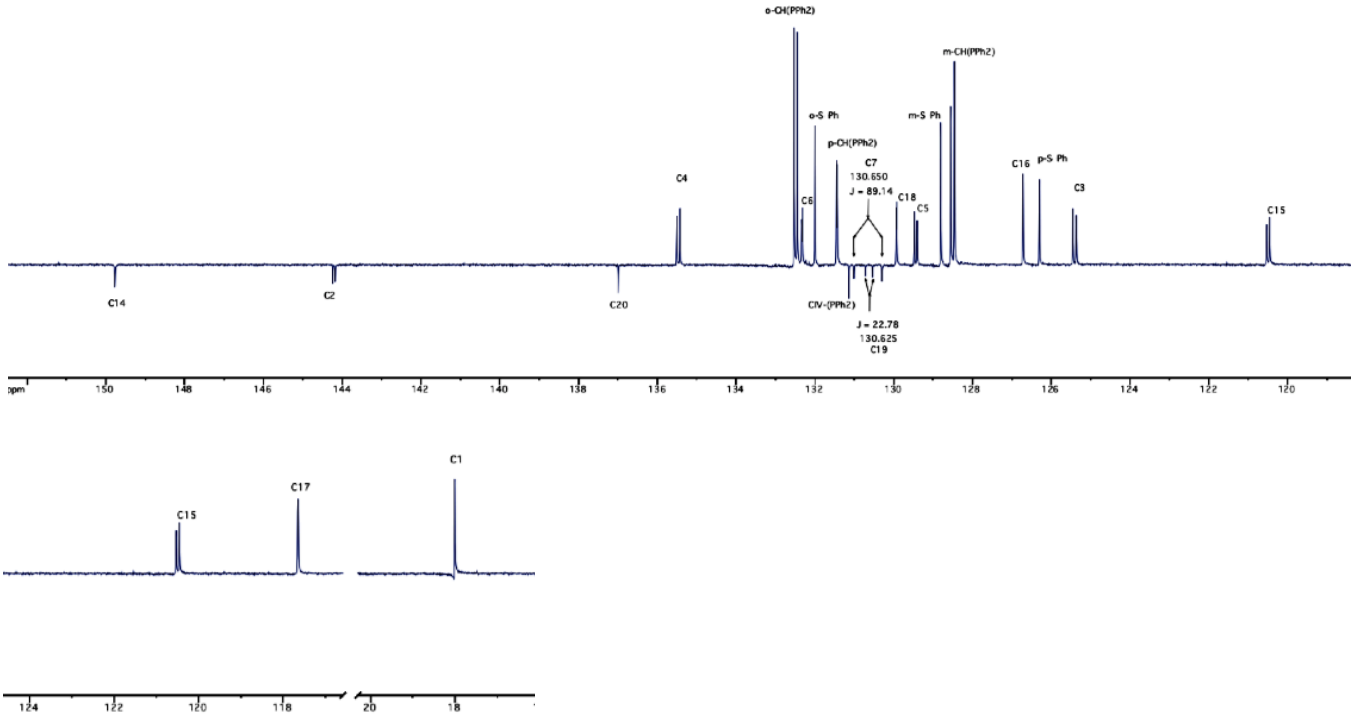

Figure S13. ^{13}C NMR spectrum for compound **3b** in $CDCl_3$ (125 MHz).

Spectroscopy data for compound 3c

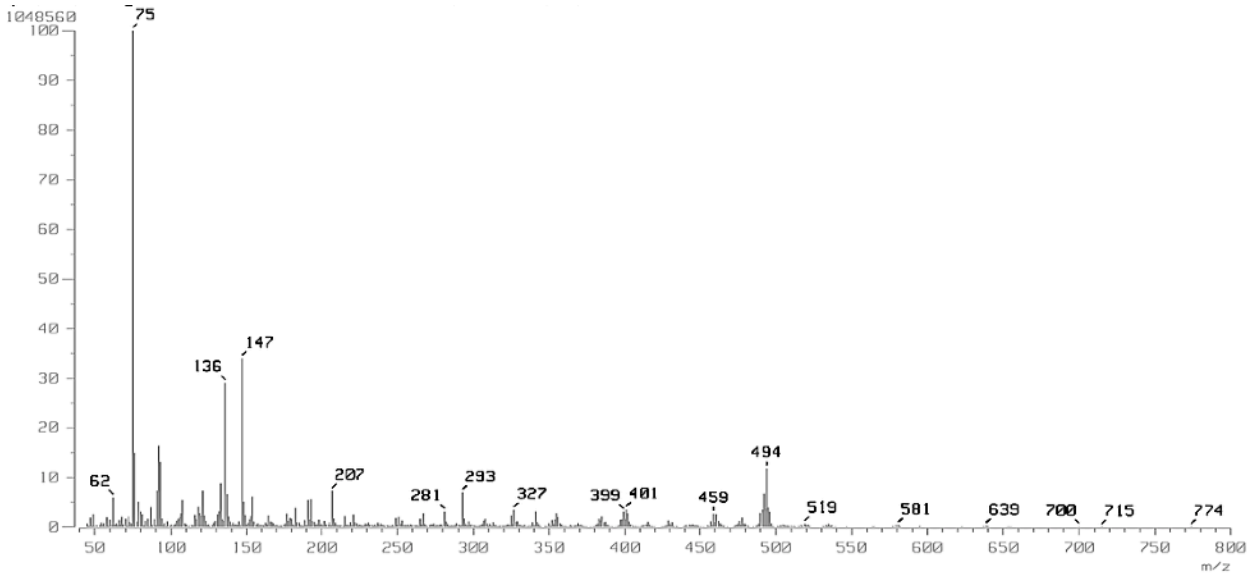

Figure S14. Mass Spectrum (FAB+) for compound **3c**.

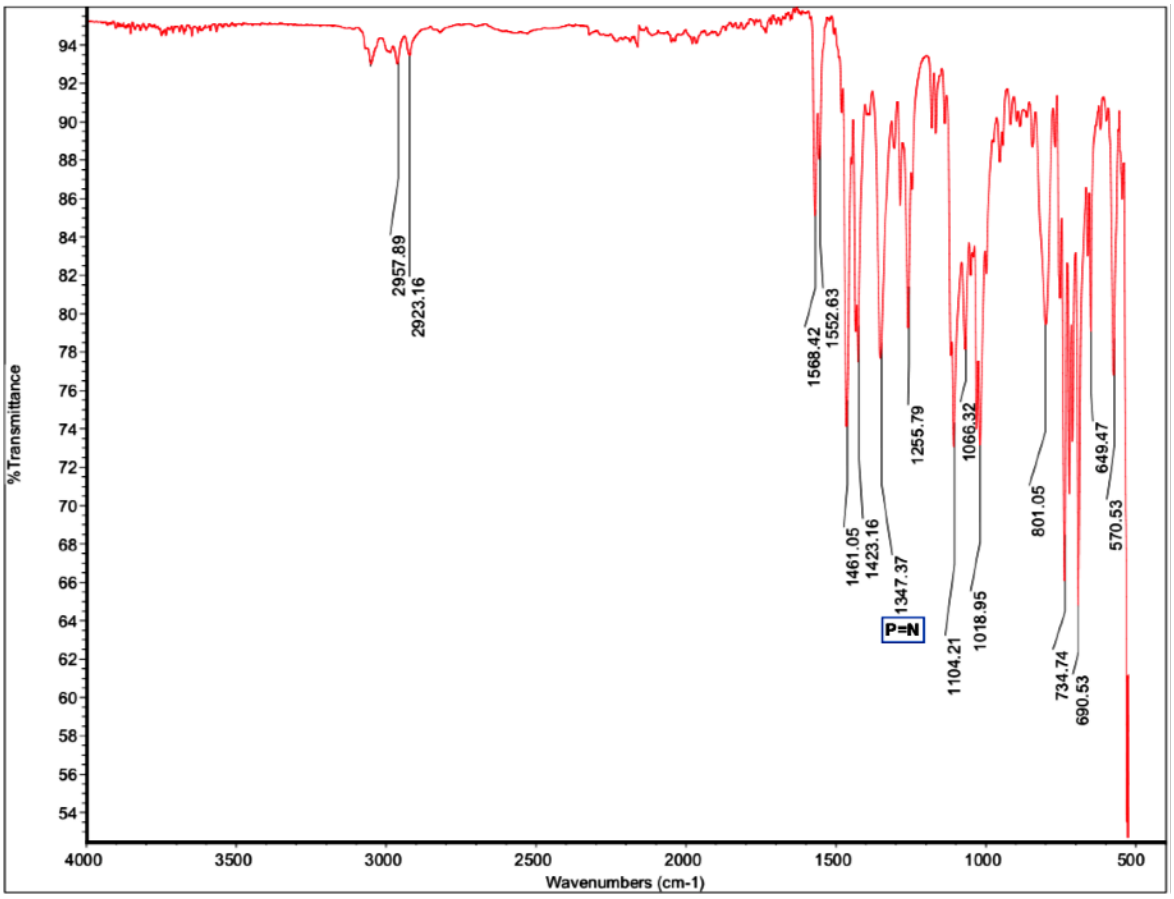

Figure S15. Infrared spectrum for compound **3c**.

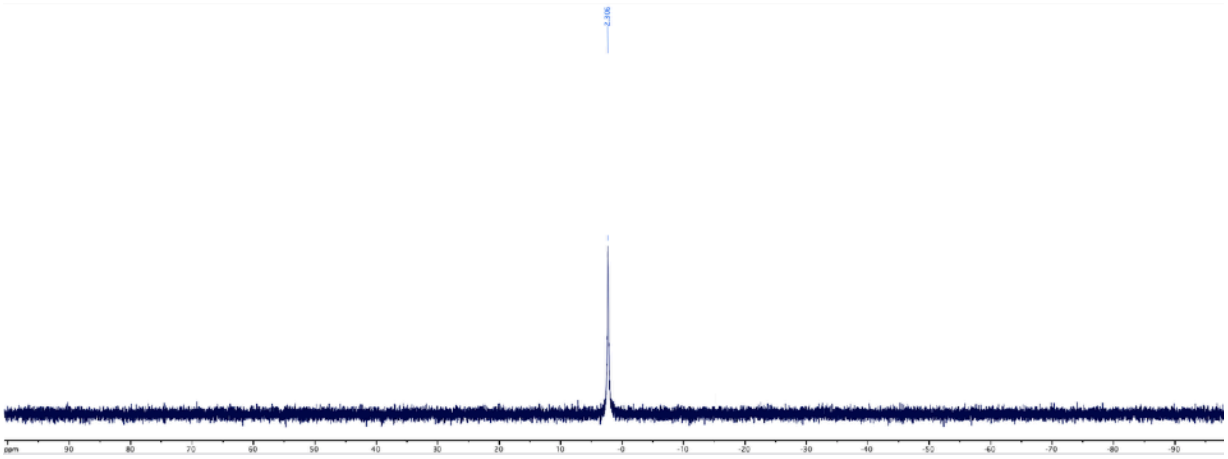

Figure S16. ^{31}P NMR spectrum for compound **3b** in $CDCl_3$ (202 MHz).

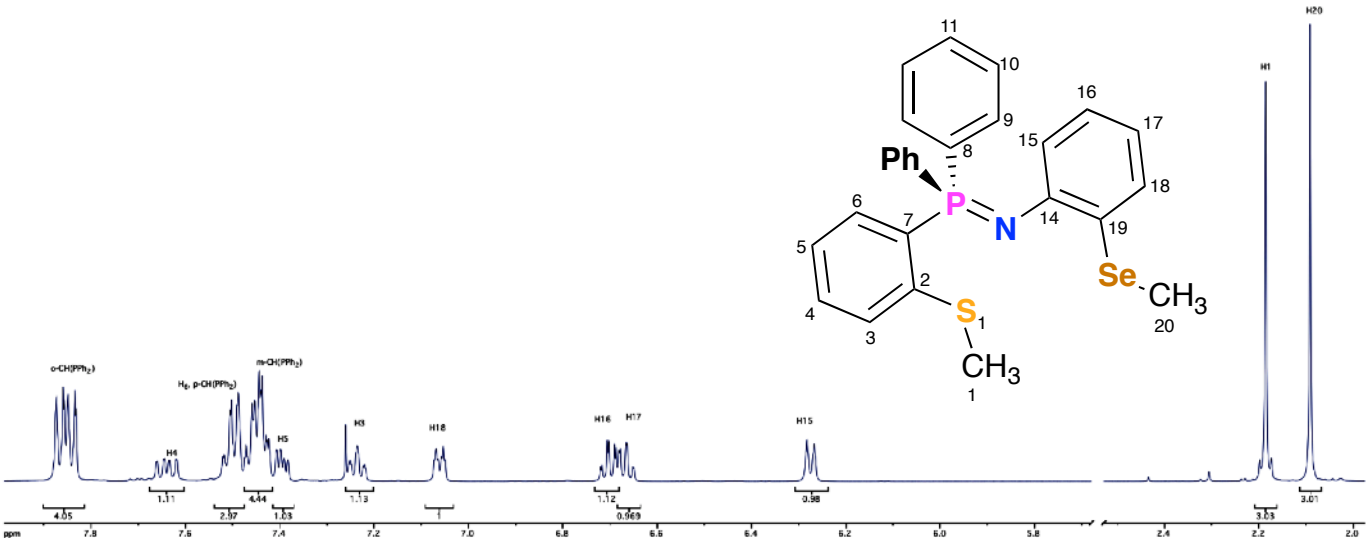

Figure S17. ^{1}H NMR spectrum for compound **3c** in $CDCl_3$ (500 MHz).

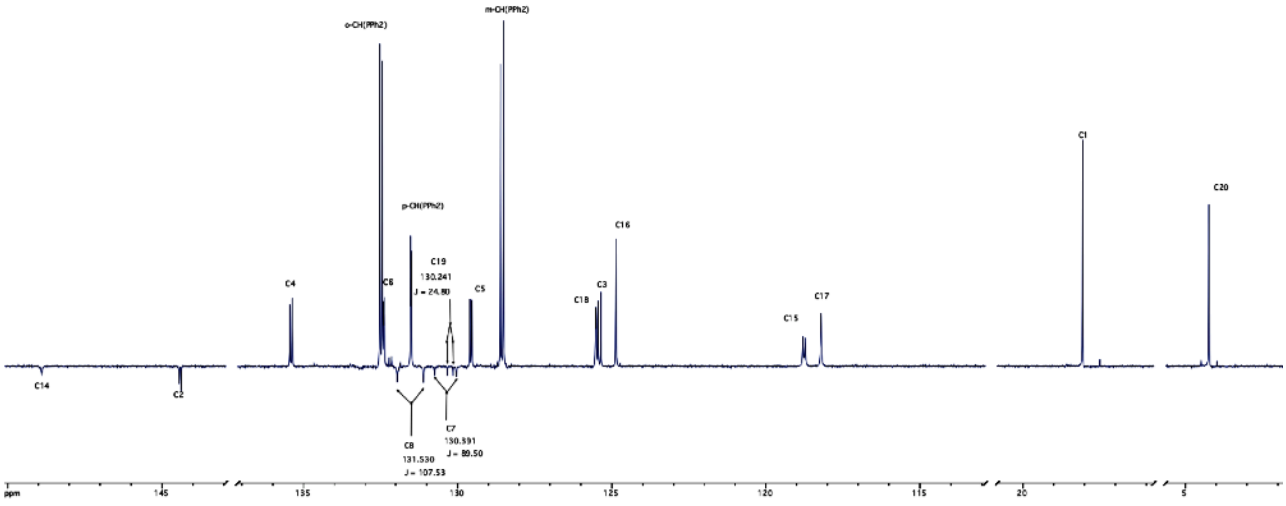

Figure S18. ^{13}C NMR (DEPTQ) spectrum for compound **3c** in $CDCl_3$ (125 MHz).

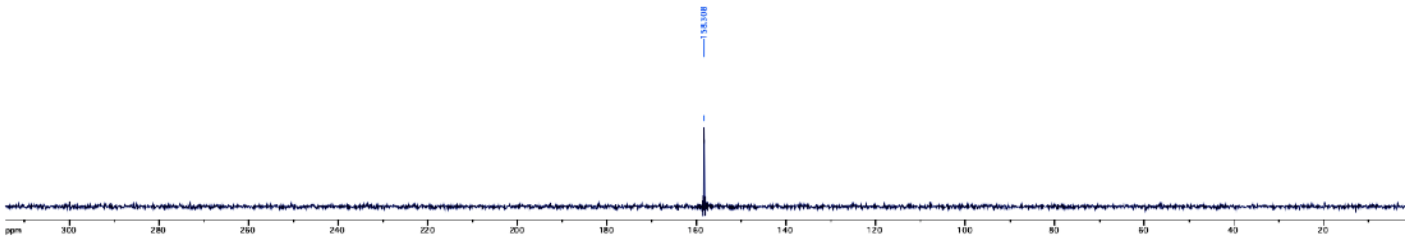

Figure S19. ^{77}Se NMR spectrum for compound **3c** in $CDCl_3$ (95 MHz).

Spectroscopy data for compound 3d

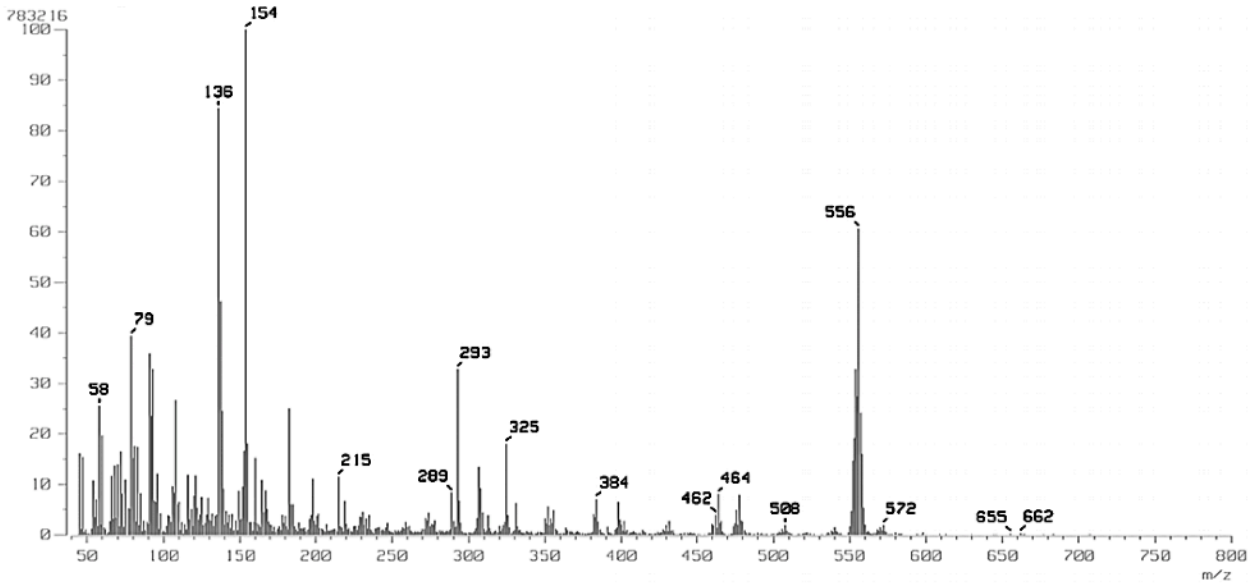

Figure S20. Mass Spectrum (FAB+) for compound **3d**.

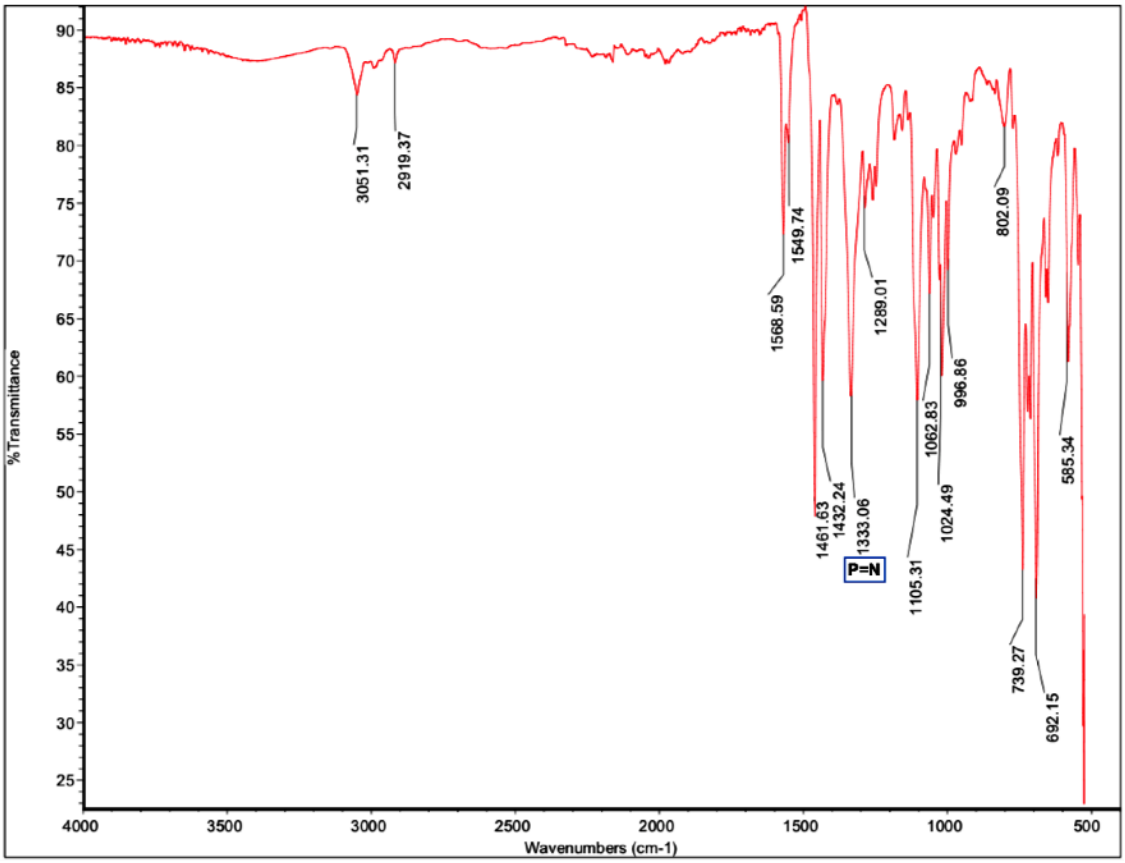

Figure S21. Infrared spectrum for compound **3d**.

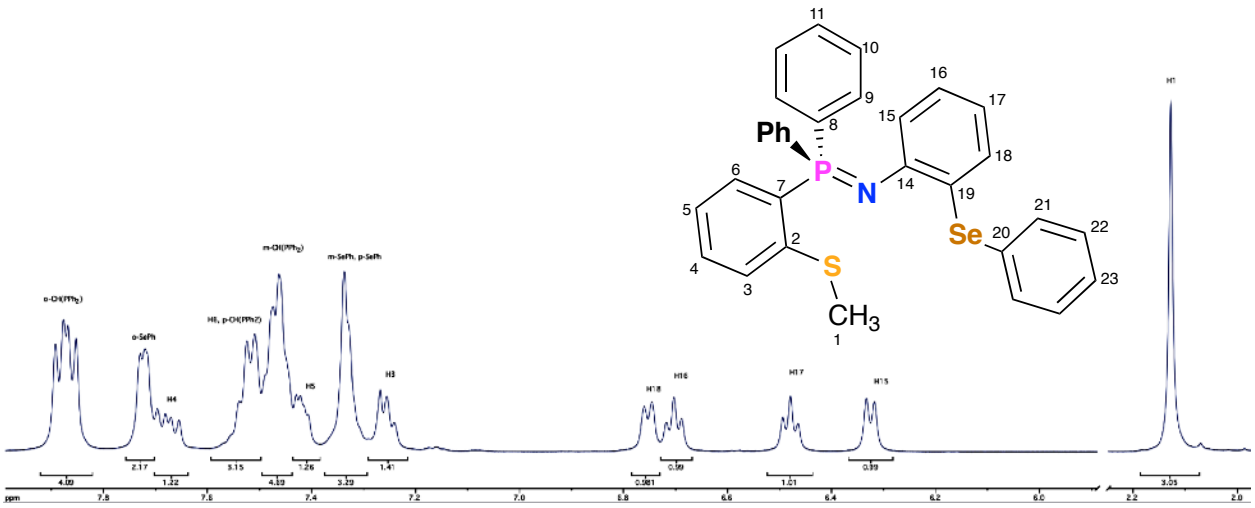

Figure S22. ^{1}H NMR spectrum for compound **3d** in $CDCl_3$ (500 MHz).

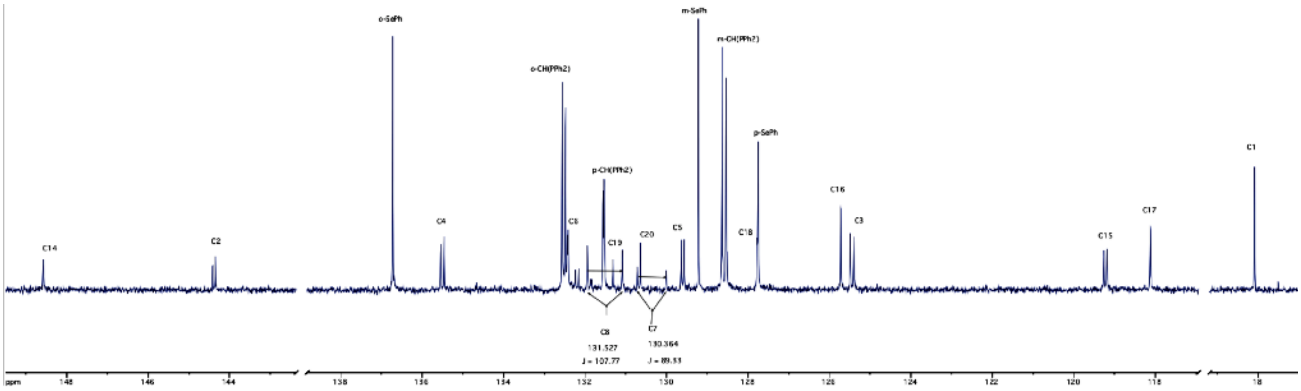

Figure S23. ^{13}C NMR spectrum for compound **3d** in $CDCl_3$ (125 MHz).

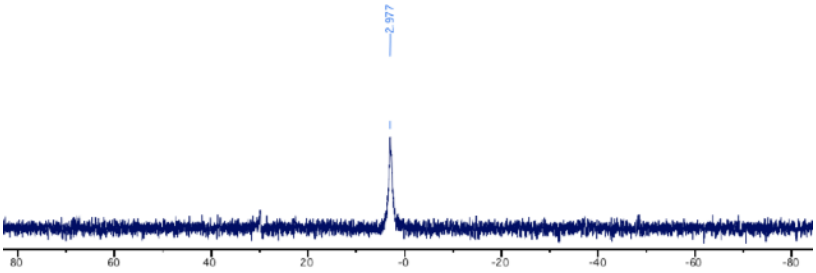

Figure S24. ^{31}P NMR spectrum for compound **3d** in $CDCl_3$ (202 MHz).

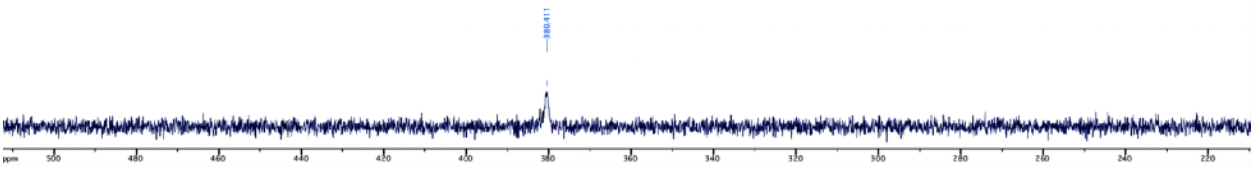

Figure S25. ^{77}Se NMR spectrum for compound **3d** in $CDCl_3$ (95 MHz).

Spectroscopy data for compound 4a

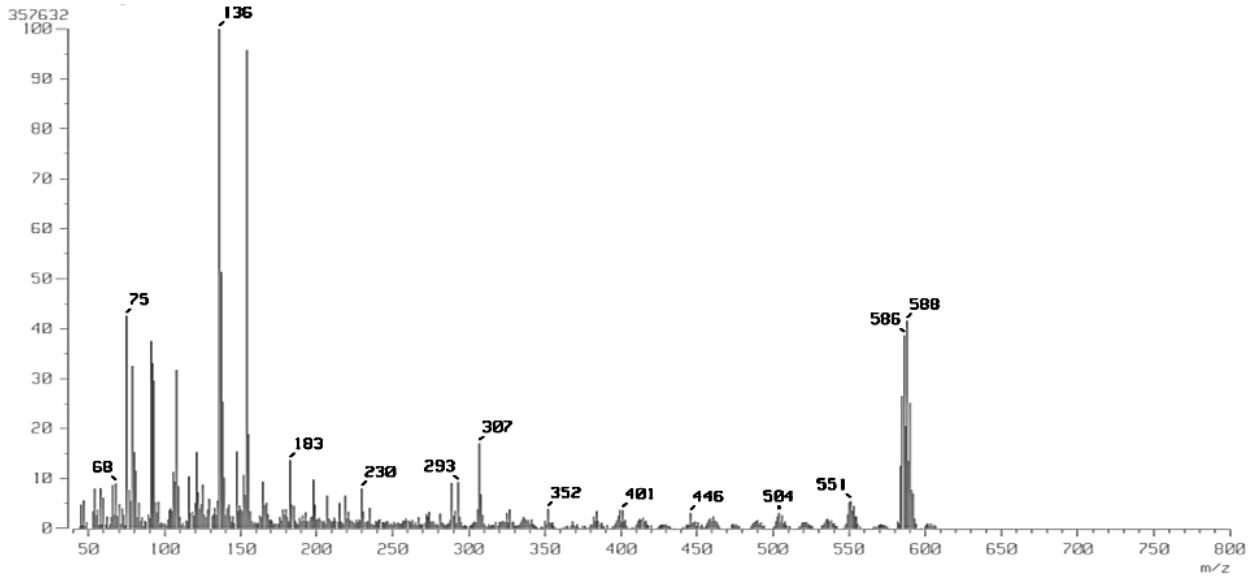

Figure 26. Mass Spectrum (FAB+) for compound **4a**.

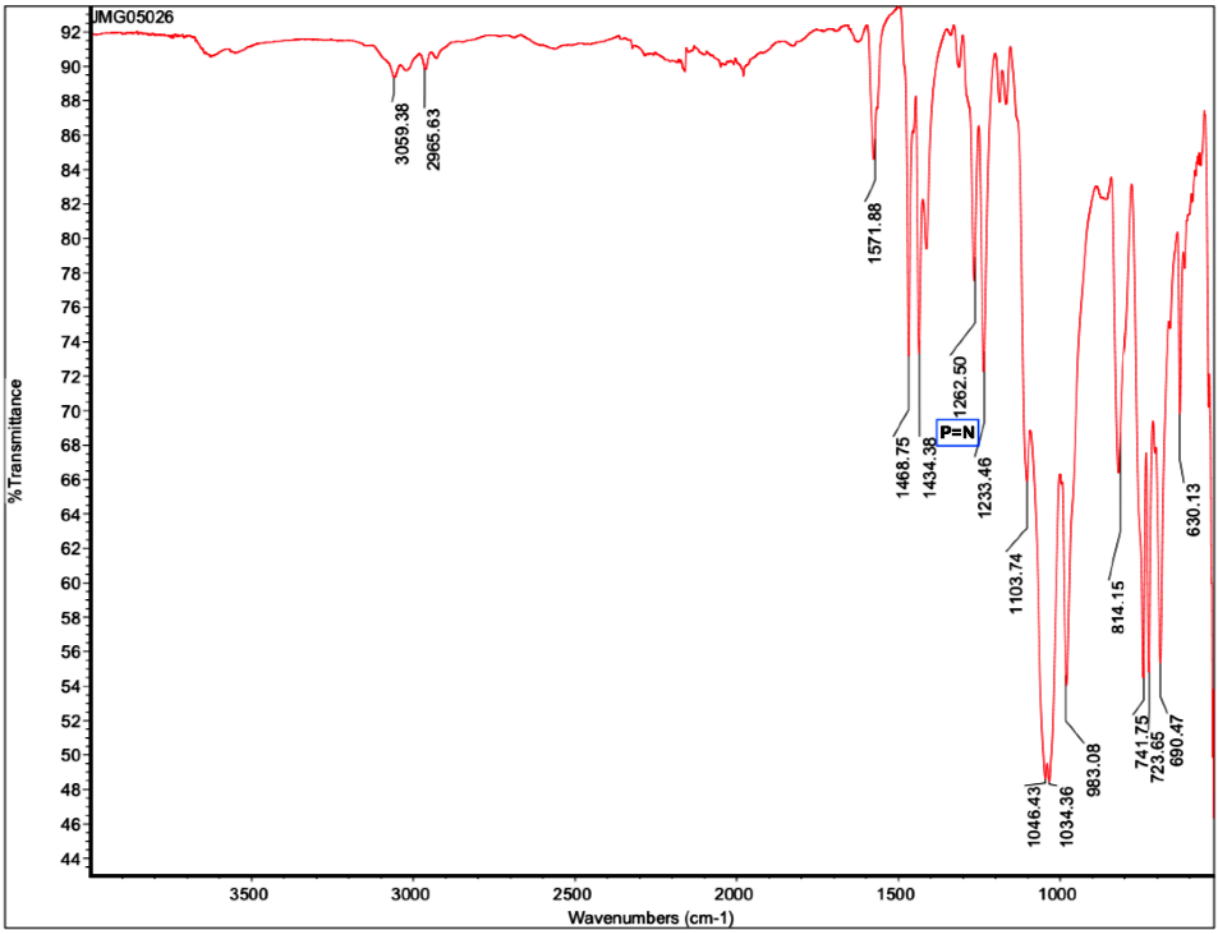

Figure 27. Infrared spectrum for compound **4a**.

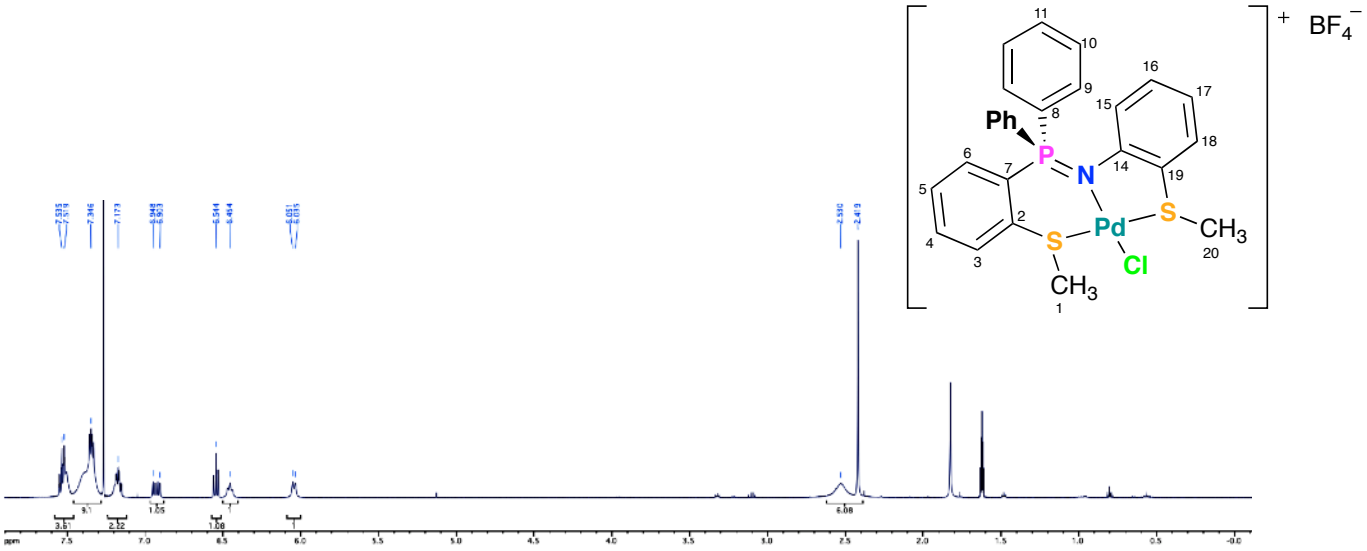

Figure 28. ^{1}H NMR spectrum for compound 4**a** in $CDCl_3$ (500 MHz).

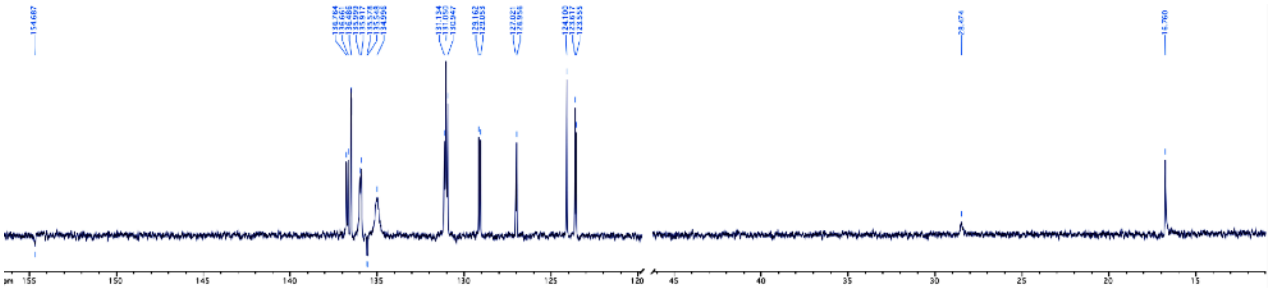

Figure 29. ^{13}C NMR (DEPTQ) spectrum for compound 4**a** in $CDCl_3$ (126 MHz).

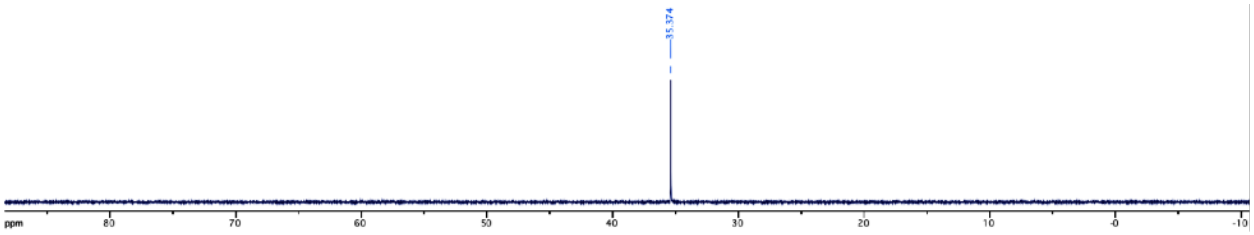

Figure 30. ^{31}P NMR spectrum for compound 4**a** in $CDCl_3$ (202 MHz).

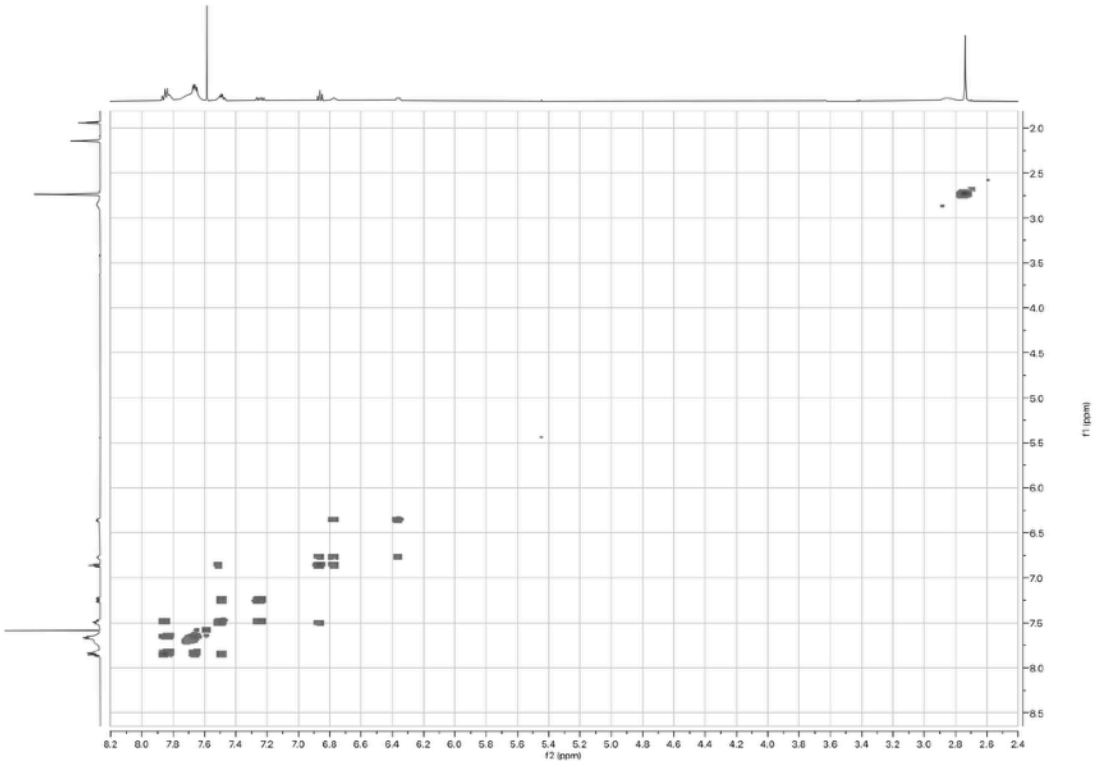

Figure 31. COSY NMR spectrum for compound **4a** in $CDCl_3$.

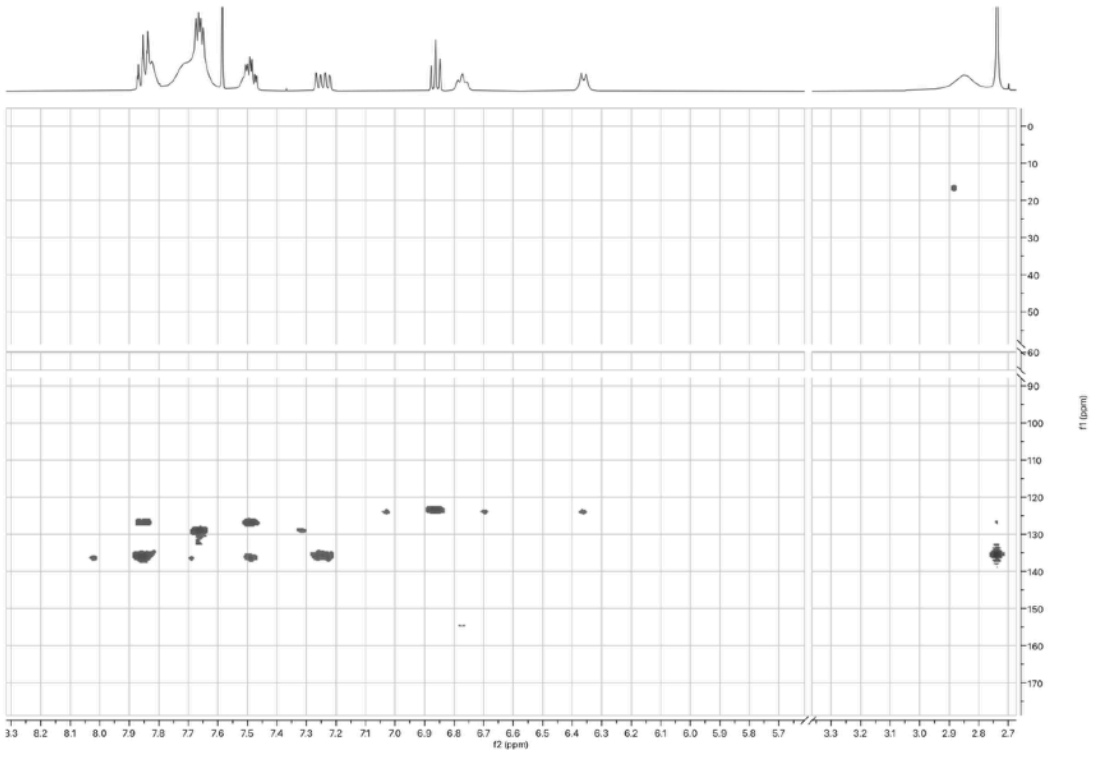

Figure 32. HMBC NMR spectrum for compound **4a** in $CDCl_3$.

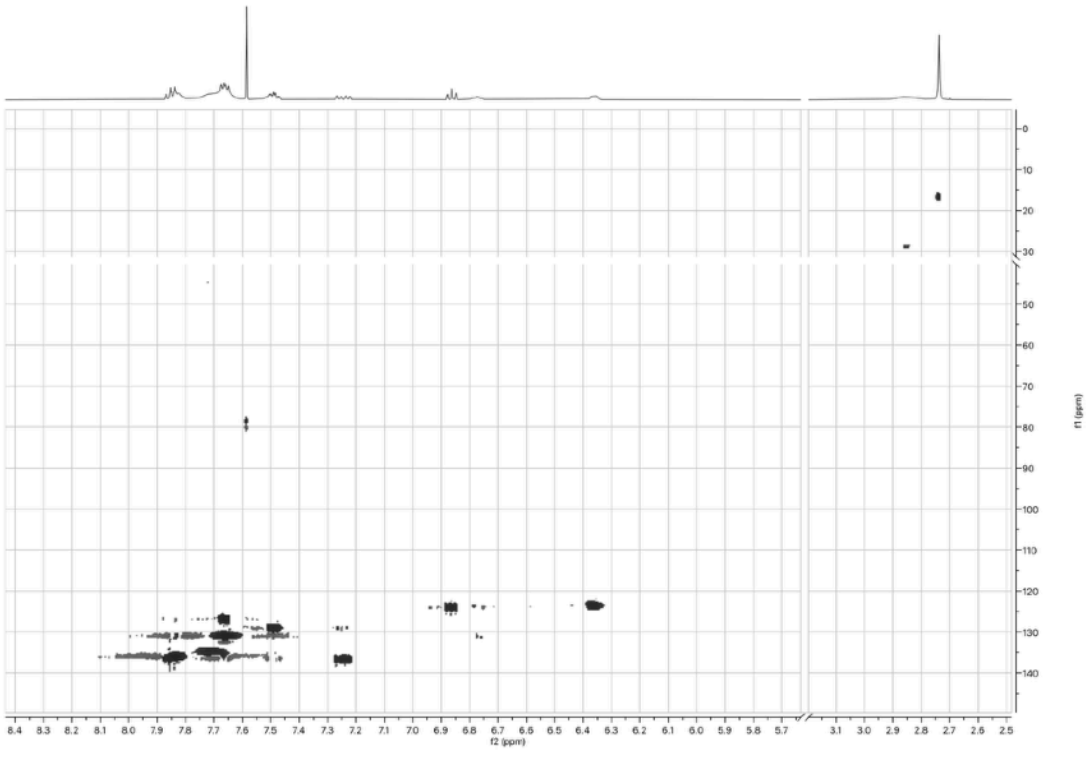

Figure 33. HSQC NMR spectrum for compound 4**a** in $CDCl_3$.

Spectroscopy data for compound 4b

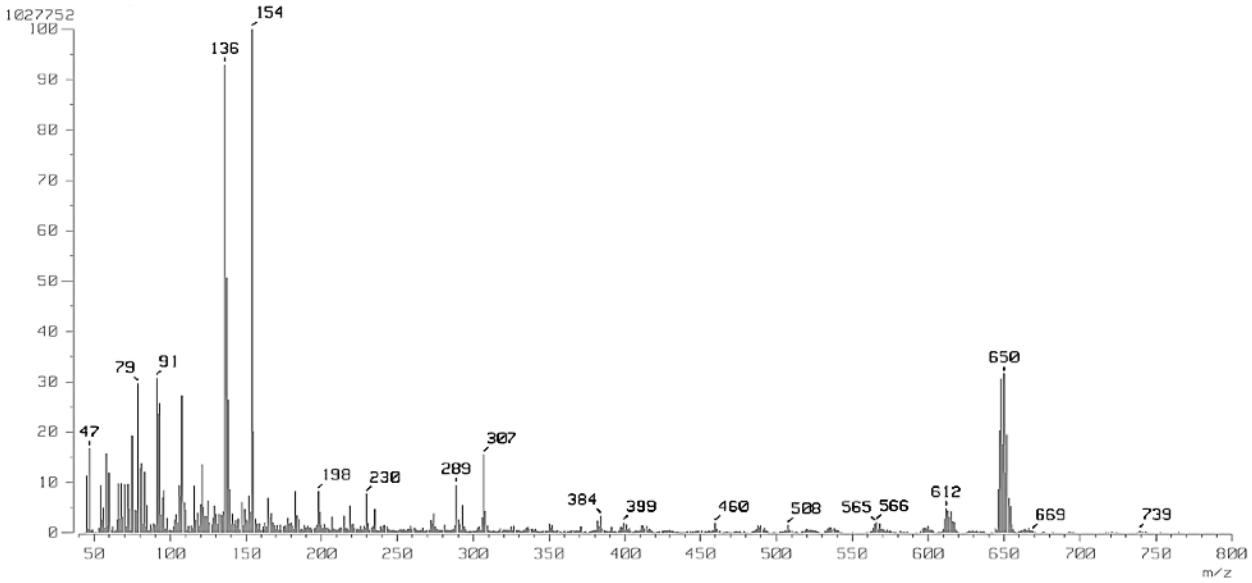

Figure 34. Mass Spectrum (FAB+) for compound **4b.**

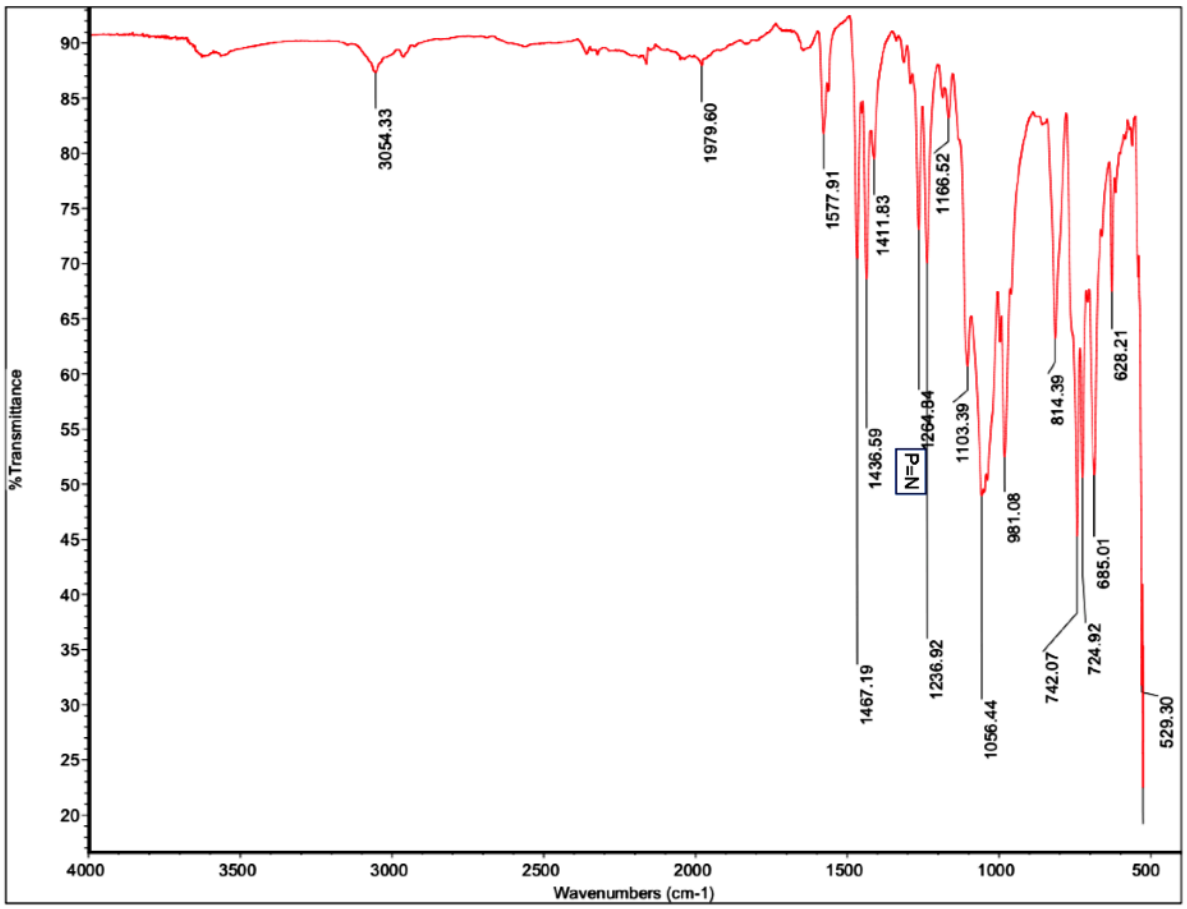

Figure 35. Infrared spectrum for compound **4b**.

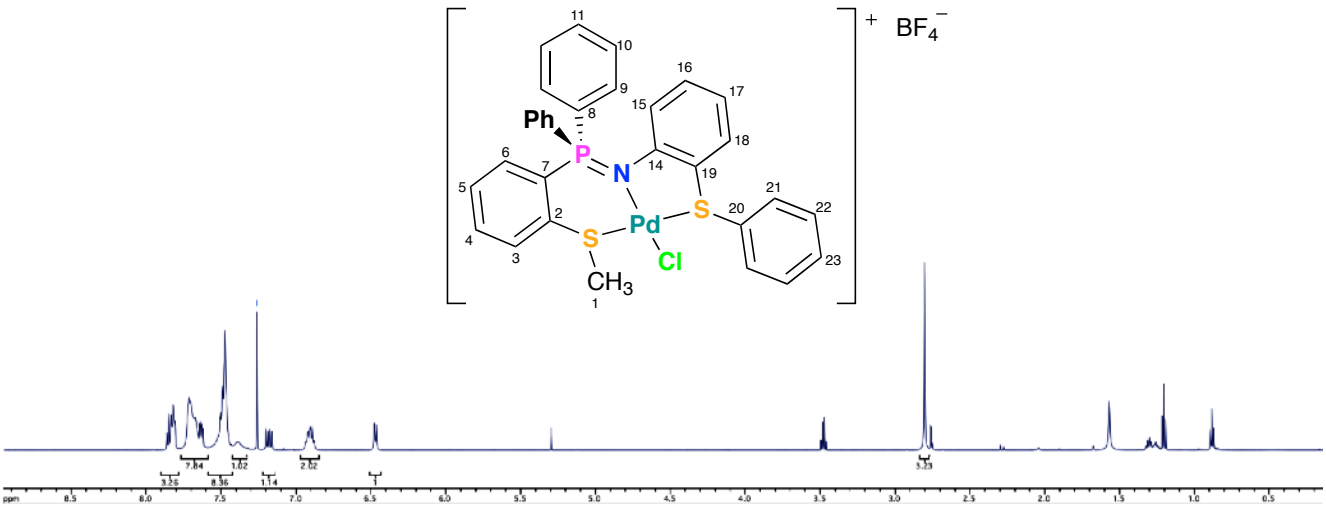

Figure S36. ^{1}H NMR spectrum for compound 4**b** in $CDCl_3$ (500 MHz).

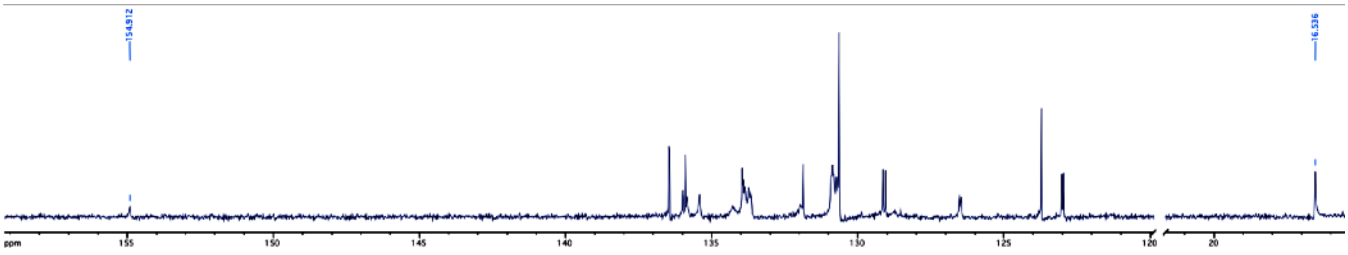

Figure S37. ^{13}C NMR (DEPTQ) spectrum for compound 4**b** in $CDCl_3$ (126 MHz).

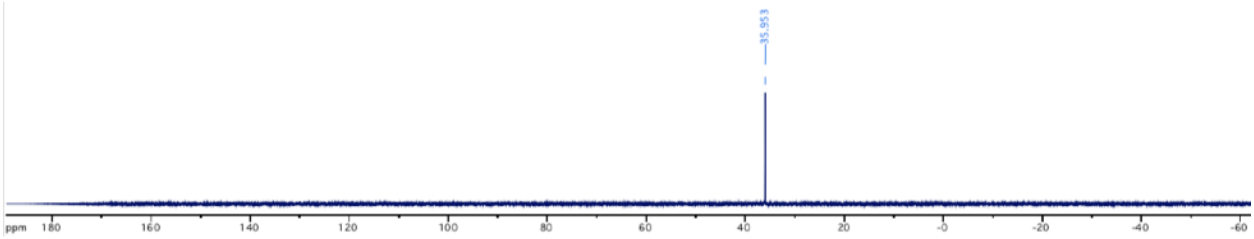

Figure S38. ^{31}P NMR spectrum for compound **4b** in $CDCl_3$ (202 MHz).

Spectroscopy data for compound 4c

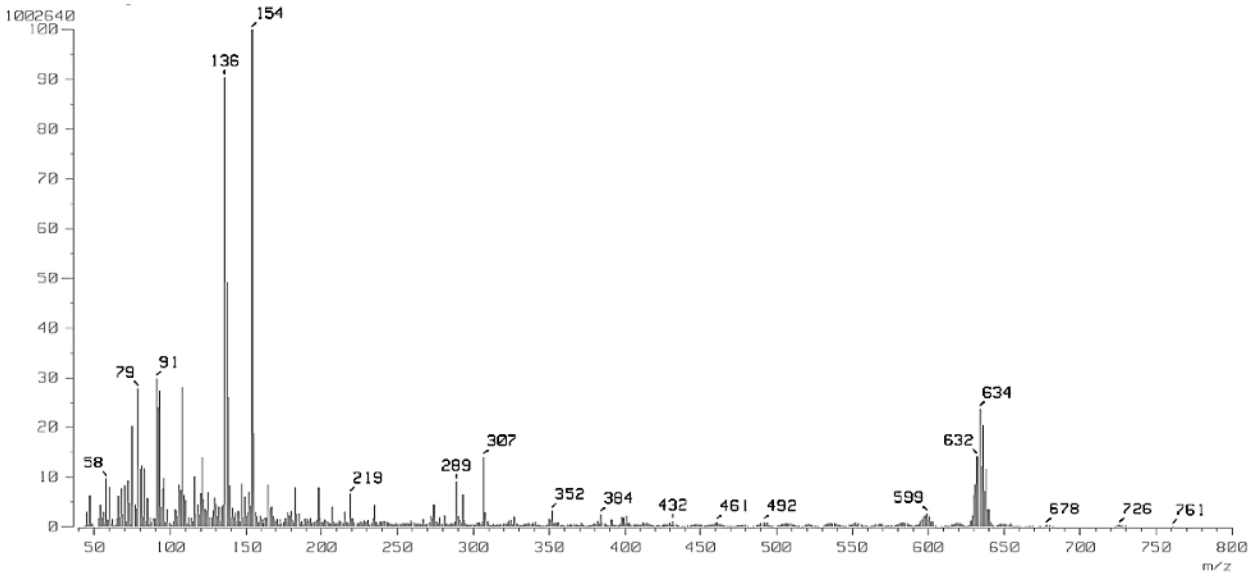

Figure S39. Mass Spectrum (FAB+) for compound **4c.**

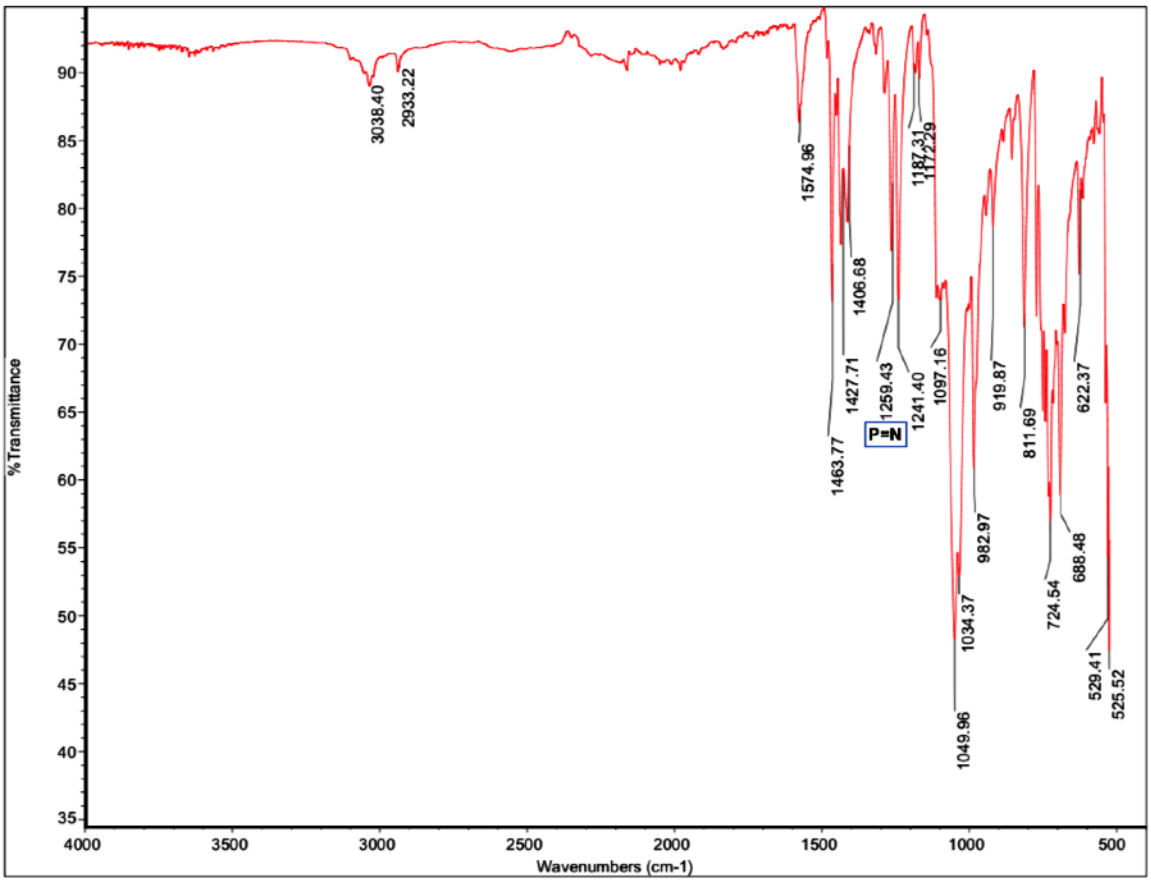

Figure S40. Infrared spectrum for compound **4c**.

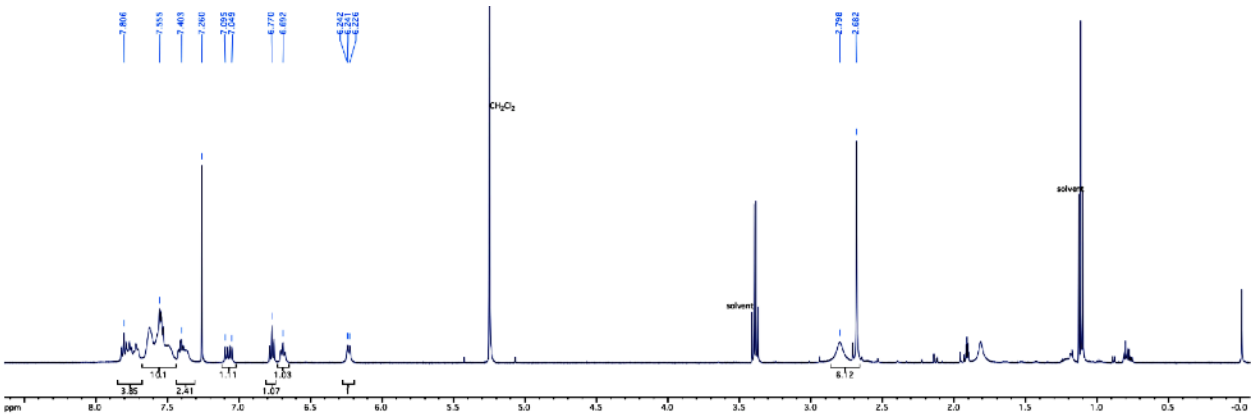

Figure S41. ^{1}H NMR spectrum for compound **4c** in $CDCl_3$ (500 MHz).

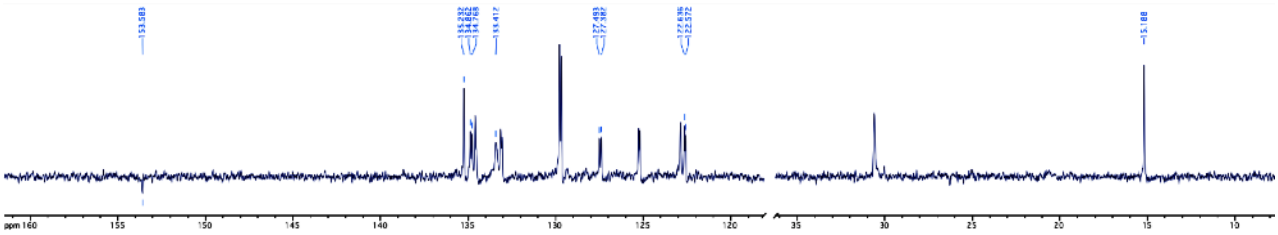

Figure S42. ^{13}C NMR (DEPTQ) spectrum for compound 4**c** in $CDCl_3$ (126 MHz).

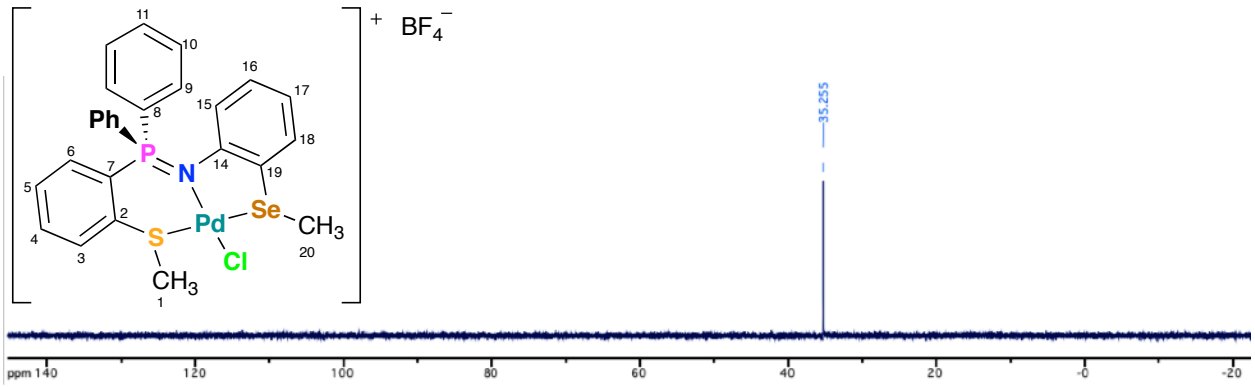

Figure S43. ^{31}P NMR spectrum for compound **4c** in $CDCl_3$ (202 MHz).

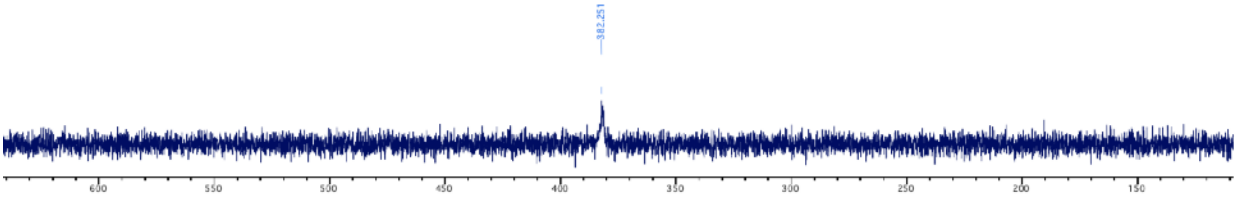

Figure S44. ^{77}Se NMR spectrum for compound **4c** in $CDCl_3$ (95 MHz).

Spectroscopy data for compound 4d

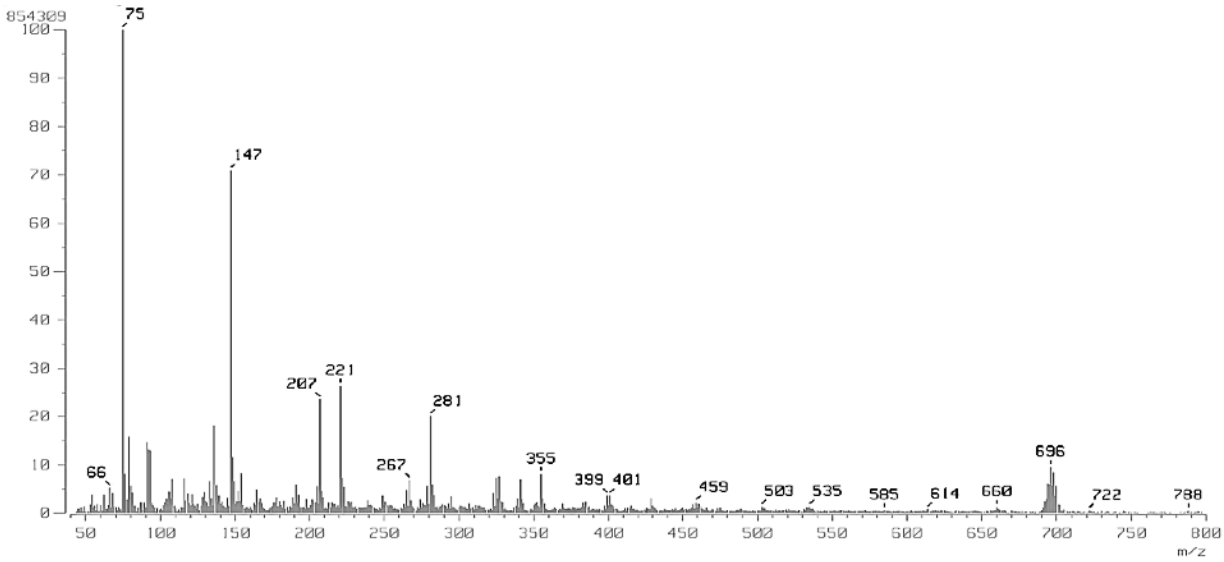

Figure S45. Mass Spectrum (FAB+) for compound **4d.**

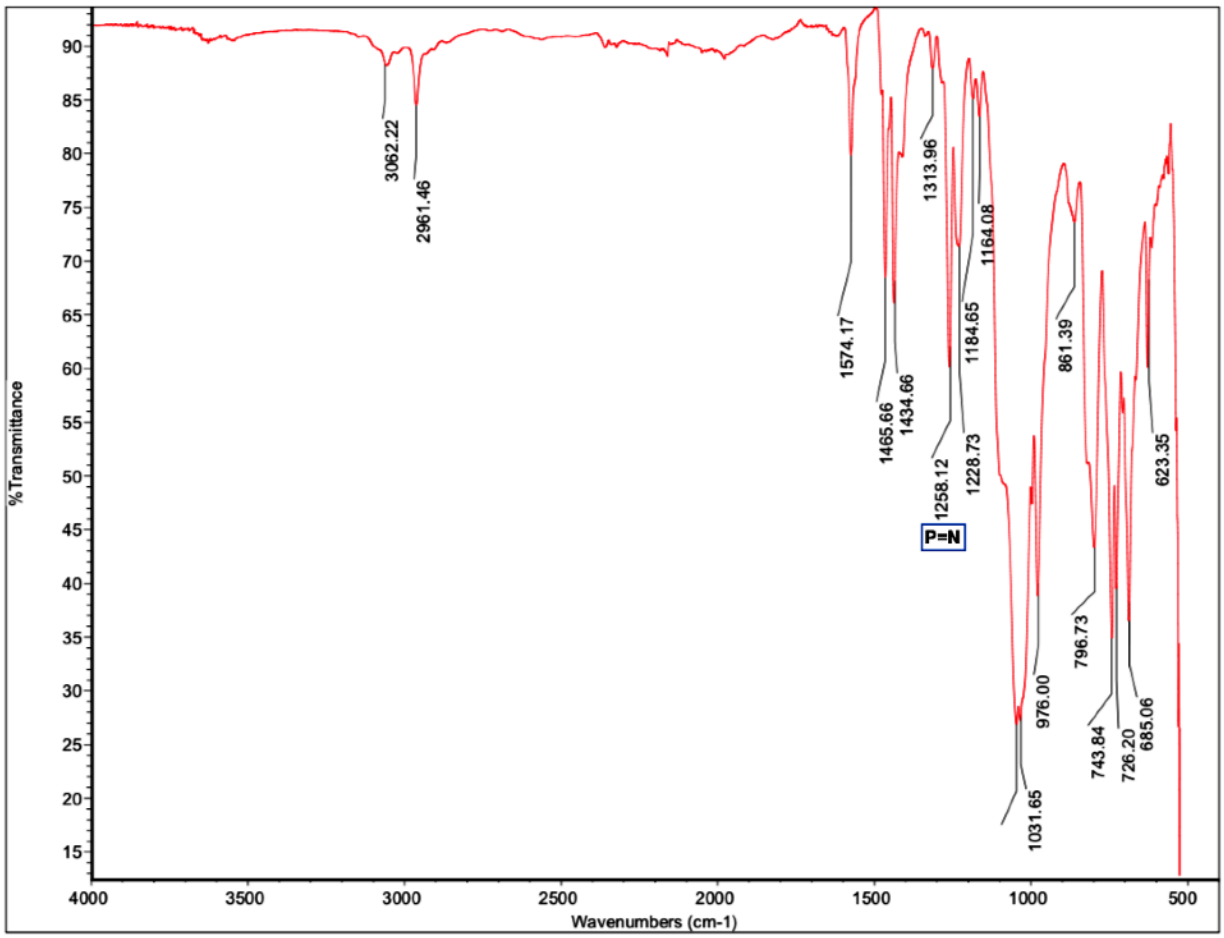

Figure S46. Infrared spectrum for compound **4d**.

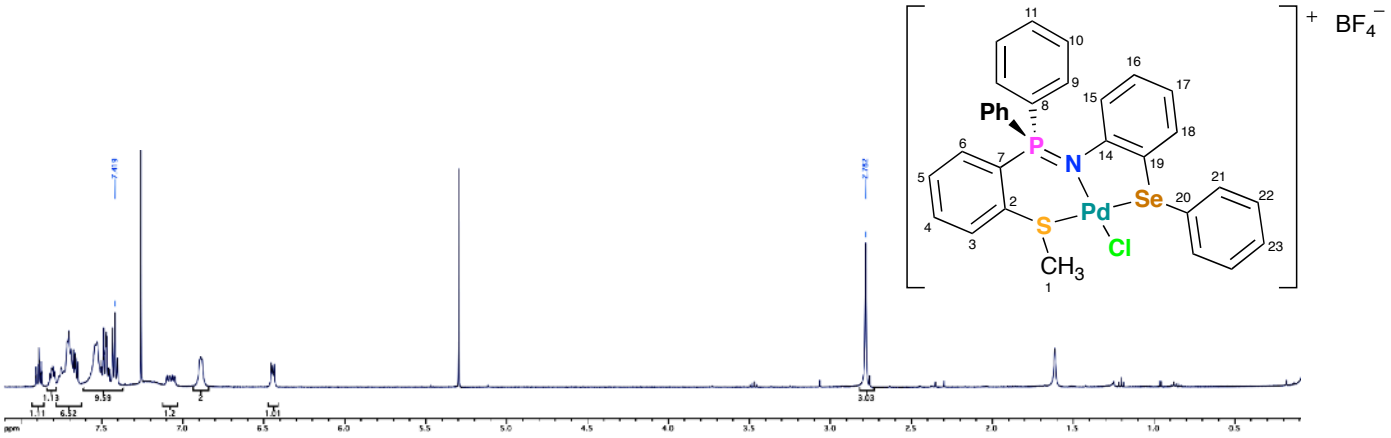

Figure S47. ^{1}H NMR spectrum for compound 4**c** in $CDCl_3$ (500MHz).

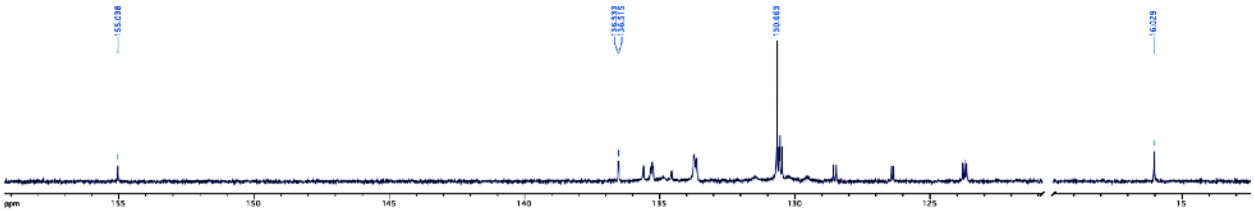

Figure S48. ^{13}C NMR (DEPTQ) spectrum for compound 4**c** in $CDCl_3$ (126 MHz).

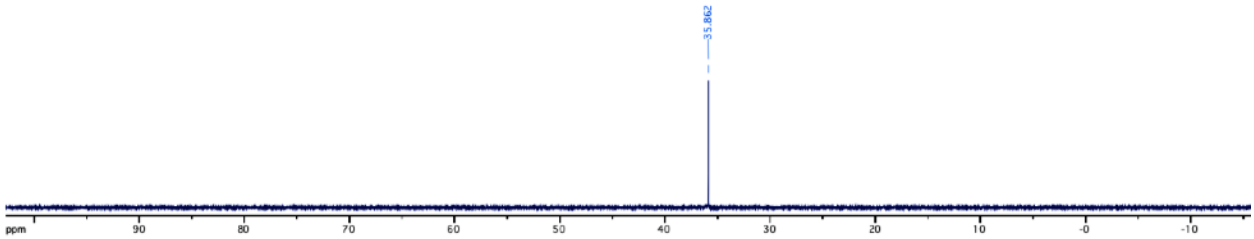

Figure S49. ^{31}P NMR spectrum for compound 4**c** in $CDCl_3$ (202 MHz).

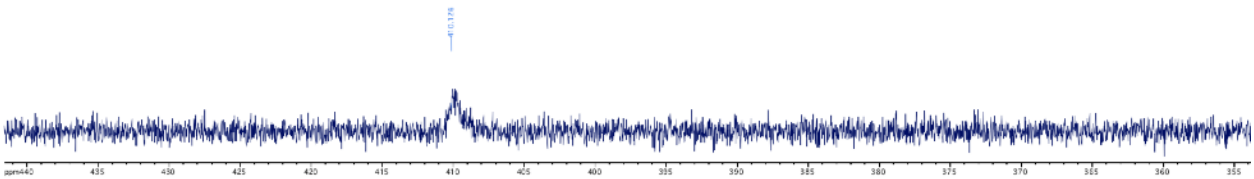

Figure S50. ^{77}Se NMR spectrum for compound **4c** in $CDCl_3$ (95 MHz).

Crystallography data for 3d, 4a, 4b, 4c and 4b

Table S1. Crystal data and structure refinement for 3d.

Identification code	2132462
Empirical formula	$C_{31}H_{26}NPSSe$
Formula weight	554.52
Temperature/K	101(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.3859(4)
b/Å	12.4127(5)
c/Å	12.8167(6)
α/°	62.093(5)
β/°	74.683(4)
γ/°	87.704(4)
Volume/Å^3	1266.55(11)
Z	2
ϱ_{calc}g/cm^3	1.454
μ/mm^{-1}	3.526
F(000)	568.0
Crystal size/mm^3	0.1 × 0.07 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.1 to 146.056
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	18864
Independent reflections	4957 [R_{int} = 0.0524, R_{sigma} = 0.0383]
Data/restraints/parameters	4957/0/317
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1412
Final R indexes [all data]	R_1 = 0.0560, wR_2 = 0.1446
Largest diff. peak/hole / e Å^{-3}	1.57/-1.00

Table S2. Crystal data and structure refinement for 4a

Identification code	2132186
Empirical formula	$C_{27}H_{26}BCl_3F_4NPPdS_2$
Formula weight	759.14
Temperature/K	100.0(4)
Crystal system	triclinic
Space group	P-1
a/Å	10.3604(4)
b/Å	12.8764(5)
c/Å	12.9364(7)
α/°	65.103(5)
β/°	73.145(4)
γ/°	74.459(4)
Volume/Å^3	1476.84(13)
Z	2
ϱ_{calc}g/cm^3	1.707
μ/mm^{-1}	1.141
F(000)	760.0
Crystal size/mm^3	0.18 × 0.14 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.868 to 58.468
Index ranges	-13 ≤ h ≤ 8, -17 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	12349
Independent reflections	6823 [R_{int} = 0.0434, R_{sigma} = 0.0791]
Data/restraints/parameters	6823/98/437
Goodness-of-fit on F^2	0.999
Final R indexes [I>=2σ (I)]	R1 = 0.0389, wR2 = 0.0687
Final R indexes [all data]	R1 = 0.0521, wR2 = 0.0748
Largest diff. peak/hole / e Å^{-3}	0.68/-0.85

Table S3. Crystal data and structure refinement for 4b

Identification code	2132185
Empirical formula	$C_{32}H_{30}BCl_3F_4NOPPdS_2$
Formula weight	839.22
Temperature/K	100.0(4)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.5136(7)
b/Å	15.1765(5)
c/Å	19.8095(6)
α/°	90
β/°	92.705(3)
γ/°	90
Volume/Å^3	6760.9(3)
Z	8
ϱ_{calc}g/cm^3	1.649
μ/mm^{-1}	1.008
F(000)	3376.0
Crystal size/mm^3	0.34 × 0.25 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.17 to 58.314
Index ranges	-29 ≤ h ≤ 30, -20 ≤ k ≤ 19, -26 ≤ l ≤ 16
Reflections collected	29675
Independent reflections	8127 [R_{int} = 0.0460, R_{sigma} = 0.0456]
Data/restraints/parameters	8127/0/407
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.0837
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.0894
Largest diff. peak/hole / e Å^{-3}	1.88/-0.99

Table S4. Crystal data and structure refinement for 4c

Identification code	2132447
Empirical formula	$C_{27}H_{26}BCl_3F_4NPPdSSe$
Formula weight	805.03
Temperature/K	99.9(4)
Crystal system	triclinic
Space group	P-1
a/Å	10.3865(5)
b/Å	12.8750(7)
c/Å	12.9927(7)
α/°	65.113(5)
β/°	72.940(4)
γ/°	74.721(5)
Volume/Å^3	1486.99(15)
Z	2
ϱ_{calc}g/cm^3	1.798
μ/mm^{-1}	2.287
F(000)	794.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.856 to 58.426
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 16, -17 ≤ l ≤ 12
Reflections collected	12602
Independent reflections	6826 [R_{int} = 0.0524, R_{sigma} = 0.0800]
Data/restraints/parameters	6826/98/437
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0425, wR2 = 0.0844
Final R indexes [all data]	R1 = 0.0589, wR2 = 0.0940
Largest diff. peak/hole / e Å^{-3}	0.91/-0.95

Table S5. Crystal data and structure refinement for 4d

Identification code	2132458
Empirical formula	$C_{32}H_{27}Cl_7NPPd_2SSe$
Formula weight	1028.48
Temperature/K	99.9(3)
Crystal system	trigonal
Space group	P3221
a/Å	15.9613(6)
b/Å	15.9613(6)
c/Å	25.1755(10)
α/°	90
β/°	90
γ/°	120
Volume/Å3	5554.5(5)
Z	6
ϱ_{calc}g/cm^3	1.845
μ/mm−1	2.584
F(000)	3012.0
Crystal size/mm3	0.25 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.354 to 58.208
Index ranges	-16 ≤ h ≤ 20, -21 ≤ k ≤ 18, -33 ≤ l ≤ 25
Reflections collected	28648
Independent reflections	8831 [Rint = 0.0431, Rsigma = 0.0537]
Data/restraints/parameters	8831/48/444
Goodness-of-fit on F2	1.032
Final R indexes [I>=2σ (I)]	R1 = 0.0380, wR2 = 0.0692
Final R indexes [all data]	R1 = 0.0512, wR2 = 0.0743
Largest diff. peak/hole / e Å-3	0.78/-0.67
Flack parameter	0.000(6)

Table S6. Cartesian coordinates for optimized geometry **4a** (PBE0/SDD/6-31+G(d)).

Pd	-1.5049270000	0.2551210000	-0.9942370000
Cl	-3.3543620000	-0.0857390000	-2.3219150000
S	-1.2486900000	-1.9706530000	-0.3647480000
S	-1.7639640000	2.5181840000	-1.2186060000
P	1.4870640000	-0.3968800000	0.0677080000
F	-2.1643390000	0.7941660000	1.7861060000
F	-4.2918890000	0.4559350000	2.6089220000
F	-3.1826390000	-1.2536800000	1.5330640000
F	-2.4818160000	-0.5568210000	3.6129730000
N	0.3119630000	0.7283210000	-0.1082370000
C	3.2974040000	1.2075950000	-1.2671260000
C	4.5261400000	1.8207240000	-1.4859330000
C	5.5848020000	1.5965920000	-0.6047690000
C	5.4112480000	0.7626340000	0.4974930000
C	4.1819130000	0.1450240000	0.7217730000
C	3.1227600000	0.3605680000	-0.1642570000
C	2.2878780000	-2.3755730000	1.8746780000
C	2.2127960000	-3.0525680000	3.0857680000
C	1.2873900000	-2.6500740000	4.0534190000
C	0.4300120000	-1.5812860000	3.8093290000
C	0.5061150000	-0.8848600000	2.6030580000
C	1.4456390000	-1.2754570000	1.6438070000
C	1.3206410000	-1.6656970000	-1.2350930000
C	2.4343740000	-1.9913150000	-2.0147130000
C	2.3668670000	-2.9984250000	-2.9759490000
C	1.1769880000	-3.6920940000	-3.1613870000
C	0.0570460000	-3.3876990000	-2.3897050000
C	0.1178800000	-2.3838920000	-1.4253970000
C	-2.6153630000	-2.9873720000	-0.9385590000
C	-1.1080880000	2.9667770000	-2.8528420000
C	-0.4547330000	3.0175410000	-0.1151210000
C	-0.3911250000	4.3427830000	0.3057110000
C	0.5506620000	4.7312100000	1.2532100000
C	1.3891120000	3.7632570000	1.8017890000
C	1.3132140000	2.4354600000	1.3957580000
C	0.4085310000	2.0314290000	0.4009860000
B	-3.0583010000	-0.1324140000	2.4029040000

H	-0.1075620000	2.5557570000	-2.9980860000
H	-1.7993460000	2.5394940000	-3.5844390000
H	-1.0929160000	4.0561800000	-2.9452740000
H	2.4680120000	1.3906590000	-1.9462320000
H	4.6559590000	2.4796580000	-2.3401330000
H	6.5434800000	2.0795720000	-0.7748550000
H	6.2310890000	0.5954460000	1.1908610000
H	4.0465530000	-0.4888630000	1.5935300000
H	2.9831780000	-2.7138770000	1.1084630000
H	2.8623330000	-3.9045520000	3.2696660000
H	1.2201100000	-3.1937420000	4.9924420000
H	-0.3351650000	-1.2957780000	4.5241540000
H	-0.2033710000	-0.0846440000	2.4013140000
H	3.3666740000	-1.4528060000	-1.8756240000
H	3.2422530000	-3.2323430000	-3.5748300000
H	1.1102550000	-4.4757040000	-3.9114180000
H	-0.8671140000	-3.9328860000	-2.5491220000
H	-2.3856090000	-4.0377170000	-0.7404030000
H	-2.8445110000	-2.7929040000	-1.9875430000
H	-3.4510790000	-2.6626390000	-0.3135620000
H	-1.1049370000	5.0624790000	-0.0882220000
H	0.5957180000	5.7621630000	1.5908810000
H	2.0973210000	4.0355310000	2.5801440000
H	1.9492360000	1.7019660000	1.8817750000

Table S7. Cartesian coordinates for optimized geometry **4b** (PBE0/SDD/6-31+G(d)).

Pd	0.2801970000	-1.5662490000	0.3961270000
Cl	0.7528240000	-3.5505230000	1.4629280000
S	-1.6781770000	-1.1398100000	1.5729550000
S	2.0257390000	-1.8573210000	-1.0863610000
P	-0.5999170000	1.5615620000	0.2514780000
F	-1.5736780000	-1.9095990000	-1.8615860000
F	-2.6617210000	-3.8892670000	-2.3262710000
F	-2.9163250000	-2.8827540000	-0.2687500000
F	-3.8505530000	-1.9233480000	-2.1413080000
N	0.1090720000	0.2938980000	-0.5007440000
C	1.7309090000	3.0171970000	0.0868730000
C	2.5115490000	4.1368390000	-0.1796580000
C	1.9139440000	5.3147230000	-0.6301660000
C	0.5347500000	5.3708450000	-0.8189360000
C	-0.2542860000	4.2531550000	-0.5519200000
C	0.3413960000	3.0759690000	-0.0908110000
C	-3.0985540000	2.8027300000	0.4703460000
C	-4.4485220000	2.9322040000	0.1676170000
C	-5.0456570000	2.0581620000	-0.7459060000
C	-4.2998390000	1.0501830000	-1.3500590000
C	-2.9403750000	0.9202530000	-1.0653150000
C	-2.3398530000	1.8060050000	-0.1650710000
C	-0.5396650000	1.2991030000	2.0552930000
C	-0.0669470000	2.3296430000	2.8724220000
C	-0.0670060000	2.2010780000	4.2601770000
C	-0.5456940000	1.0329200000	4.8408660000
C	-1.0267010000	-0.0042310000	4.0435740000
C	-1.0325750000	0.1179830000	2.6557720000
C	-2.1415260000	-2.4980720000	2.6549390000
C	4.0167560000	-1.8995340000	0.7755450000
C	5.1809600000	-1.4527100000	1.3932210000
C	5.8241810000	-0.2993680000	0.9425690000
C	5.2937970000	0.4117280000	-0.1313090000
C	4.1244970000	-0.0201870000	-0.7579530000
C	3.4927570000	-1.1743350000	-0.2981630000
C	1.5311070000	-0.5891500000	-2.2344950000
C	2.0401650000	-0.6064130000	-3.5297350000

C	1.6161730000	0.3426880000	-4.4550760000
C	0.6596410000	1.2790150000	-4.0683100000
C	0.1348400000	1.2812330000	-2.7801320000
C	0.5672410000	0.3510960000	-1.8222840000
B	-2.7611530000	-2.6777170000	-1.6688850000
H	2.1989880000	2.0943340000	0.4230370000
H	3.5882310000	4.0876610000	-0.0404260000
H	2.5264280000	6.1873980000	-0.8415980000
H	0.0693820000	6.2834430000	-1.1815150000
H	-1.3270330000	4.2963800000	-0.7179620000
H	-2.6451370000	3.4599500000	1.2101220000
H	-5.0400100000	3.7028140000	0.6553830000
H	-6.1058580000	2.1533230000	-0.9669690000
H	-4.7578640000	0.3280890000	-2.0188610000
H	-2.3764570000	0.1012280000	-1.5082230000
H	0.3123910000	3.2427110000	2.4236030000
H	0.3104220000	3.0110810000	4.8774610000
H	-0.5454970000	0.9176160000	5.9214680000
H	-1.3905990000	-0.9129810000	4.5108190000
H	-2.9729740000	-2.1776140000	3.2884820000
H	-1.2877210000	-2.8632700000	3.2276010000
H	-2.4788210000	-3.2709060000	1.9598060000
H	3.5029810000	-2.7885170000	1.1343610000
H	5.5863510000	-2.0126770000	2.2318360000
H	6.7368470000	0.0403600000	1.4250050000
H	5.7934670000	1.3067990000	-0.4943790000
H	3.7154070000	0.5335110000	-1.5983550000
H	2.7555730000	-1.3751670000	-3.8110660000
H	2.0004450000	0.3275070000	-5.4704030000
H	0.2891400000	2.0046900000	-4.7878190000
H	-0.6494110000	1.9907700000	-2.5333100000

Table S8. Cartesian coordinates for optimized geometry **4c** (PBE0/SDD/6-31+G(d)).

Pd	2.305240	-0.957124	-0.128313
Se	3.738414	0.784042	-0.923434
Cl	3.977922	-2.496300	-0.525665
S	0.819861	-2.542265	0.749877
P	-0.697458	0.273697	0.210234
N	0.938193	0.557900	0.202944
C	-2.858449	3.661745	-1.987192
C	-1.555109	1.635642	-0.601286
C	2.730919	2.173574	-0.078074
C	-2.617772	-0.483937	2.086663
C	-1.318265	0.003033	1.886985
C	-2.547825	-2.306453	-2.335029
C	-0.455269	-2.472820	-0.495842
C	0.754079	2.878358	1.069895
C	-0.989826	2.150706	-1.778634
C	5.213977	0.657370	0.354748
C	3.262869	3.455890	0.022891
C	1.290882	4.154873	1.187875
C	1.488841	-4.208593	0.609073
C	-0.860854	-3.603674	-1.194072
C	-3.422770	3.140501	-0.828071
C	-3.075665	-0.680082	3.387718
C	-2.132614	-1.166420	-1.648114
C	2.544087	4.461231	0.660623
C	-0.946854	0.053073	4.271915
C	-0.478677	0.261109	2.978259
C	-2.770429	2.129773	-0.124666
C	-1.078463	-1.229634	-0.734021
C	-1.907652	-3.515478	-2.114917
C	1.449836	1.849430	0.406338
C	-1.641408	3.167204	-2.463577
C	-2.246802	-0.411252	4.475746
B	-5.474728	-0.221943	-0.529119
H	-3.375299	4.444275	-2.536585
H	-3.281534	-0.717797	1.253871
H	-3.392778	-2.231514	-3.011846
H	-0.221185	2.682433	1.504197

H	-0.047074	1.758153	-2.152154
H	4.812654	0.664634	1.368130
H	5.886570	1.501655	0.190846
H	5.716700	-0.288841	0.146166
H	4.245249	3.667481	-0.393056
H	0.716000	4.918545	1.705011
H	1.829213	-4.419270	-0.405809
H	0.731739	-4.919695	0.949350
H	2.351031	-4.236683	1.278232
H	-0.382086	-4.561964	-1.026987
H	-4.390577	3.484074	-0.476755
H	-4.087932	-1.044351	3.538428
H	-2.681233	-0.243764	-1.806731
H	2.958313	5.460797	0.750893
H	-0.296128	0.250863	5.119725
H	0.538407	0.607689	2.814494
H	-3.246514	1.713718	0.756653
H	-2.225525	-4.410844	-2.642156
H	-1.205991	3.568705	-3.374727
H	-2.611959	-0.569302	5.487499
F	-5.434523	0.787987	0.459227
F	-4.858836	0.264514	-1.708795
F	-6.775458	-0.619761	-0.783338
F	-4.702984	-1.324677	-0.058117

Table S9. Cartesian coordinates for optimized geometry **4d** (PBE0/SDD/6-31+G(d)).

Pd	0.3511060000	-1.4271590000	0.5441280000
Se	2.2485270000	-1.6123450000	-0.9006840000
Cl	1.0690740000	-3.2393950000	1.7740490000
S	-1.7051750000	-1.2064330000	1.6349420000
P	-0.9384020000	1.5211480000	0.1791590000
F	-1.1889910000	-2.2037470000	-1.8007990000
F	-2.0229920000	-4.3242700000	-2.1535280000
F	-2.4894520000	-3.2092640000	-0.1911640000
F	-3.4338670000	-2.5013990000	-2.1673940000
N	-0.0291880000	0.3358400000	-0.4901130000
C	1.1537030000	3.2972220000	-0.0501910000
C	1.7607580000	4.5089600000	-0.3622160000
C	0.9974100000	5.5662570000	-0.8587630000
C	-0.3740550000	5.4096140000	-1.0480740000
C	-0.9895810000	4.1985340000	-0.7363160000
C	-0.2280020000	3.1419390000	-0.2296920000
C	-3.6094390000	2.3552490000	0.2859830000
C	-4.9533220000	2.2556940000	-0.0537930000
C	-5.3762530000	1.2650210000	-0.9449590000
C	-4.4611210000	0.3687820000	-1.4900580000
C	-3.1080720000	0.4686730000	-1.1669270000
C	-2.6826670000	1.4707830000	-0.2890250000
C	-0.8990290000	1.3764720000	1.9975110000
C	-0.5780410000	2.5020680000	2.7612350000
C	-0.6058730000	2.4543530000	4.1538970000
C	-0.9612250000	1.2727500000	4.7932320000
C	-1.2901080000	0.1406640000	4.0496650000
C	-1.2657310000	0.1810630000	2.6573100000
C	-2.0094790000	-2.5581330000	2.7794560000
C	4.0527430000	-0.9771650000	1.2186140000
C	5.0658520000	-0.2700610000	1.8614850000
C	5.6146680000	0.8697780000	1.2734700000
C	5.1447860000	1.3050590000	0.0358510000
C	4.1294600000	0.6065270000	-0.6184480000
C	3.5891560000	-0.5285960000	-0.0191550000
C	1.5575640000	-0.3673130000	-2.1758890000
C	2.0941610000	-0.3345850000	-3.4584200000

C	1.5517080000	0.5154720000	-4.4184550000
C	0.4517080000	1.2973230000	-4.0752050000
C	-0.0971020000	1.2448410000	-2.7980100000
C	0.4508160000	0.4181120000	-1.8041450000
B	-2.2896990000	-3.0879840000	-1.5956550000
H	1.7519970000	2.4680610000	0.3216250000
H	2.8322990000	4.6250100000	-0.2231350000
H	1.4747100000	6.5109530000	-1.1060270000
H	-0.9678970000	6.2278770000	-1.4464410000
H	-2.0557910000	4.0750300000	-0.9043900000
H	-3.2891420000	3.1032110000	1.0090120000
H	-5.6741740000	2.9387620000	0.3882820000
H	-6.4309130000	1.1809150000	-1.1950540000
H	-4.7774380000	-0.4401690000	-2.1412940000
H	-2.4094220000	-0.2644650000	-1.5648000000
H	-0.2971550000	3.4270210000	2.2669780000
H	-0.3465880000	3.3381340000	4.7295270000
H	-0.9817550000	1.2214560000	5.8786000000
H	-1.5573820000	-0.7771890000	4.5623080000
H	-2.8961660000	-2.3287670000	3.3765370000
H	-1.1301840000	-2.7691130000	3.3902320000
H	-2.2117230000	-3.4060780000	2.1201430000
H	3.6115310000	-1.8565860000	1.6829870000
H	5.4251000000	-0.6138180000	2.8280290000
H	6.4086530000	1.4147260000	1.7774200000
H	5.5728300000	2.1886470000	-0.4318520000
H	3.7647720000	0.9464270000	-1.5840950000
H	2.9252080000	-0.9891460000	-3.7096130000
H	1.9597940000	0.5391230000	-5.4243430000
H	-0.0113110000	1.9401470000	-4.8194870000
H	-0.9879230000	1.8293220000	-2.5878640000

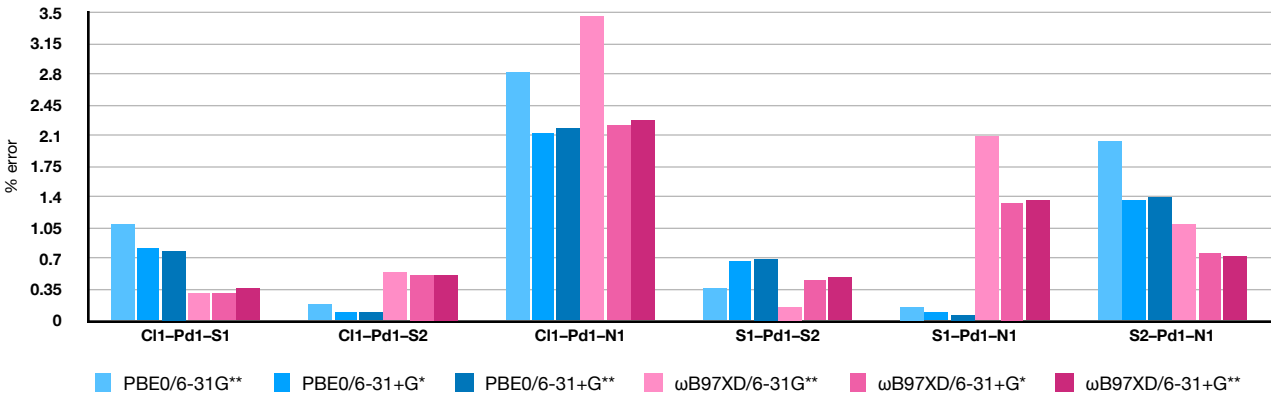

Figure S51:The average percent errors between calculated and experimental bond angles of **4b**.

Table S10. bond distances (Å) of PBE0/SDD/6-31+G(d) optimized geometries (E= S(2), Se).

comp.	Pd–S(1)	Pd–S(2)/Se	Pd–N	Pd–Cl
4a	2.3272	2.2889	2.0761	2.302
4b	2.3242	2.3086	2.0722	2.3019
4c	2.3431	2.3912	2.0673	2.3076
4d	2.3381	2.3921	2.0791	2.3049

Table S11. Bond angles (degree) of PBE0/SDD/6-31+G(d) optimized geometries (E= S(2), Se).

comp.	S(1)–Pd–E	S(1)–Pd–N	E–Pd–N	Cl–Pd–N	Cl–Pd–S(1)	Cl–Pd–E
4a	169.93	90.36	85.15	169.42	95.9	89.94
4b	170.19	89.13	84.13	172.46	95.54	91.93
4c	175.7	90.95	85.18	174.71	94.18	89.65
4d	170.64	89.49	84.85	171.56	95.69	90.82

Table S12. Experimental bond angles for 4a-d (X-ray) (E= S(2), Se).

comp.	S(1)–Pd–E	S(1)–Pd–N	E–Pd–N	Cl–Pd–N	Cl–Pd–S(1)	Cl–Pd–E
4a	175.04	93.64	85.21	173.46	92.9	88.28
4b	171.35	87.92	84.06	176.23	95.44	92.68
4c	176.2	93.79	85.84	172.72	93.49	86.92
4d	172.71	87.46	85.40	174.79	96.43	90.79

Table S13. % error on bond angles calculated (PBE0/SDD/6-31+G(d)) (E= S(2), Se).

comp.	S(1)–Pd–E	S(1)–Pd–N	E–Pd–N	Cl–Pd–N	Cl–Pd–S(1)	Cl–Pd–E	T.% Error
4a	2.9193	3.5028	0.0704	2.3291	3.2293	1.8804	2.3219
4b	0.6770	1.3763	0.0833	2.1392	0.1048	0.8092	0.8650
4c	0.2894	3.0074	0.7573	1.1522	0.7165	3.1408	1.5106
4d	1.1985	2.3211	0.6440	1.8479	0.7674	0.0330	1.1353

Table S14. Experimental and calculated bond lengths and the percent error.

comp.	bonds	exp (Å)	calc. (Å)	% error
4a	Pd–Cl	2.2814	2.30203	0.90427
	Pd–S (1)	2.3323	2.32723	0.21738
	Pd–S(2)	2.2728	2.28886	0.70662
	Pd–N	2.059	2.07605	0.82807
4b	Pd–Cl	2.2919	2.3019	0.43632
	Pd–S (1)	2.2989	2.3242	1.10053
	Pd–S(2)	2.3040	2.3086	0.19965
	Pd–N	2.042	2.0722	1.47894
4c	Pd–Cl	2.2828	2.3076	1.08639
	Pd–S (1)	2.3440	2.3431	0.03712
	Pd–Se	2.3673	2.3912	1.00959
	Pd–N	2.064	2.0673	0.16134
4d	Pd–Cl	2.2938	2.3049	0.48391
	Pd–S (1)	2.3183	2.3381	0.85407
	Pd–Se	2.3921	2.3880	0.17140
	Pd–N	2.034	2.0761	2.06981

Table S15. Distance (Å) from L to the bond critical points in Pd–L bonds (E= S(2), Se).

comp.	E–BCP	S(1)–BCP	N–BCP	Cl–BCP
4a	1.18342	1.20906	1.01341	1.18985
4b	1.19459	1.20463	1.01265	1.1912
4c	1.125502	1.21706	1.00885	1.19561
4d	1.125562	1.2137	1.01573	1.19263

Table S16. Distance (Å) from Pd to the bond critical points (PBE0/SDD/6-31+G(d)) (E= S(2), Se).

comp.	Pd–E	Pd–S(1)	Pd–N	Pd–Cl
4a	1.10561	1.11827	1.06294	1.11204
4b	1.11418	1.11933	1.05957	1.11152
4c	1.13601	1.12576	1.05848	1.11218
4d	1.13715	1.12434	1.06331	1.1121

Table S17. Topological values of the electron density in the bond critical point (a.u.) (PBE0/SDD/6-31+G(d)).

comp	bond	$\rho(r)$	$\nabla^2\rho(r)$	G (r)	V (r)	H (r)	|V (r)|/ G(r)	ε	H/rho
4a	Pd–S(1)	0.08752	0.22389	0.07987	-0.10377	-0.02390	1.29923	0.09774	-0.27308
	Pd–Cl	0.08661	0.23637	0.08039	-0.10169	-0.02130	1.26493	0.07566	-0.24592
	Pd–S(2)	0.09651	0.22681	0.08596	-0.11523	-0.02926	1.34041	0.05773	-0.30323
	Pd-N	0.09562	0.40853	0.12027	-0.13841	-0.01814	1.15082	0.06185	-0.18970
4b	Pd–S(1)	0.08832	0.22084	0.07962	-0.10402	-0.02441	1.30656	0.08657	-0.27634
	Pd–Cl	0.08656	0.23703	0.08055	-0.10185	-0.02130	1.26439	0.07908	-0.24605
	Pd–S(2)	0.09201	0.22008	0.08168	-0.10834	-0.02666	1.32640	0.06546	-0.28975
	Pd-N	0.09640	0.41110	0.12135	-0.13993	-0.01858	1.15310	0.06565	-0.19273
4c	Pd–S(1)	0.08556	0.21445	0.07654	-0.09946	-0.02293	1.29954	0.08273	-0.26795
	Pd–Cl	0.08535	0.23772	0.08012	-0.10080	-0.02069	1.25819	0.06587	-0.24237
	Pd–Se	0.09045	0.16013	0.07006	-0.10009	-0.03003	1.42861	0.02503	-0.33199
	Pd-N	0.09859	0.40538	0.12120	-0.14106	-0.01986	1.16383	0.05202	-0.20139
4d	Pd–S(1)	0.08571	0.21949	0.07778	-0.10069	-0.02291	1.29453	0.09615	-0.26726
	Pd–Cl	0.08593	0.23643	0.08007	-0.10103	-0.02096	1.26182	0.07452	-0.24395
	Pd–Se	0.08926	0.16528	0.07051	-0.09971	-0.02920	1.41405	0.04629	-0.32710
	Pd-N	0.09477	0.40543	0.11899	-0.13662	-0.01763	-1.14818	0.06761	-0.18605

Table S18. Atomic Charge (QTAIM) (PBE0/SDD/6-31+G(d)) (E= S(2), Se).

AIM charge	4a	4b	4c	4d
Pd	0.549	0.570	0.476	0.541
Cl	-0.530	-0.534	-0.547	-0.538
S	0.245	0.223	0.127	0.221
E	0.209	0.205	0.428	0.505
N	-1.562	-1.618	-1.591	-1.616
P	2.782	2.955	2.934	2.946

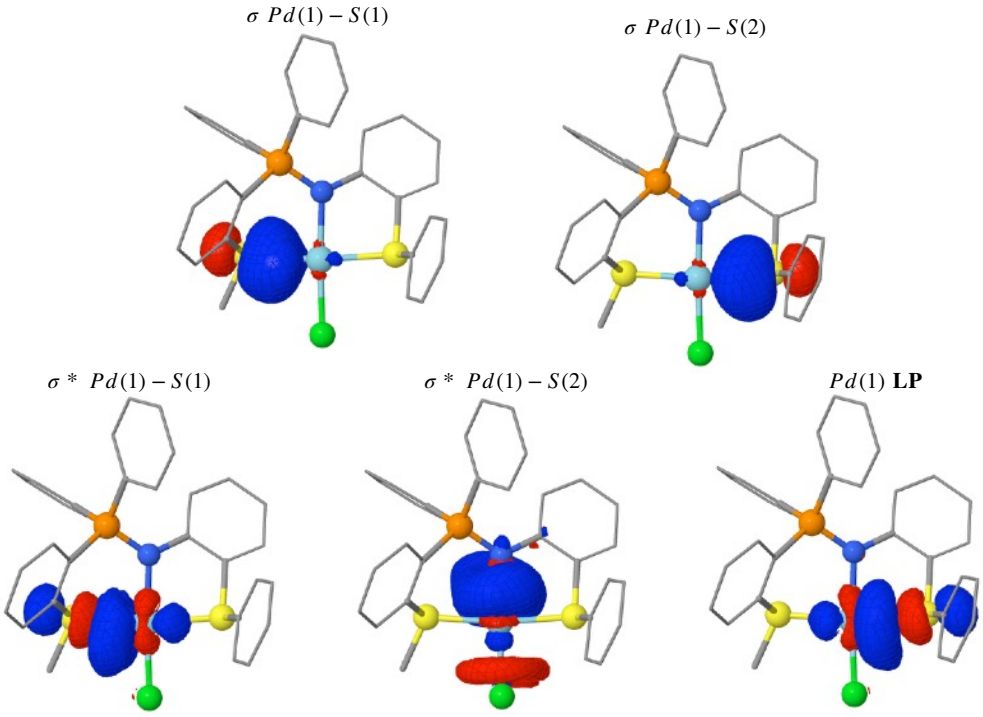

Figure S52. Relevant NBOs of complex **4b.**

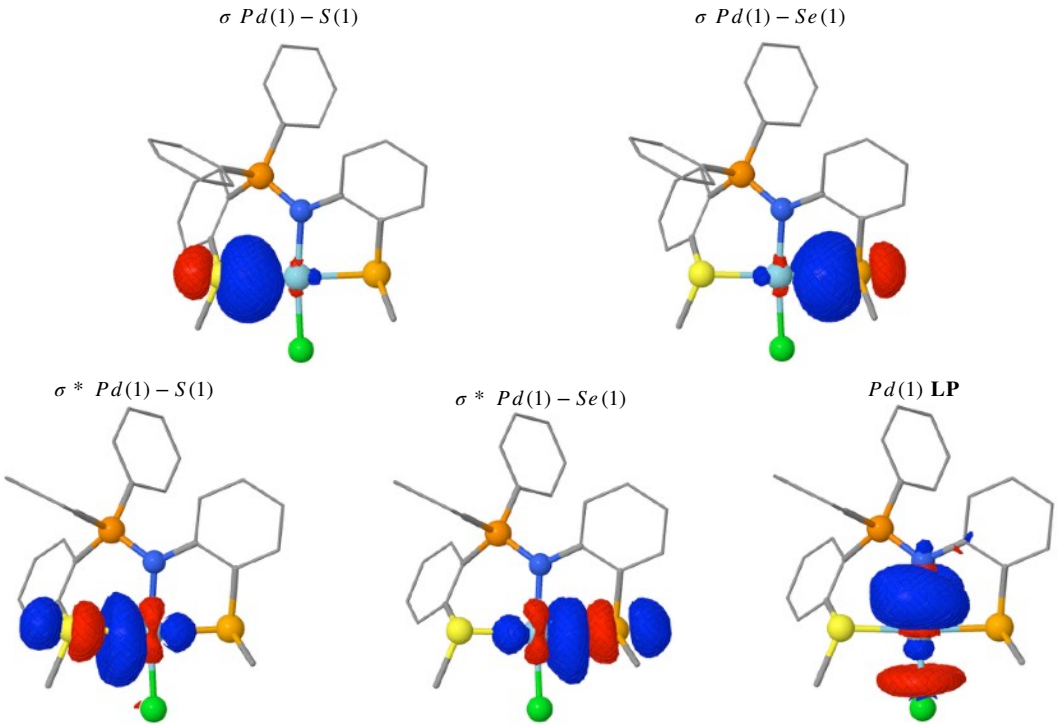

Figure S53. Relevant NBOs of complex **4c.**

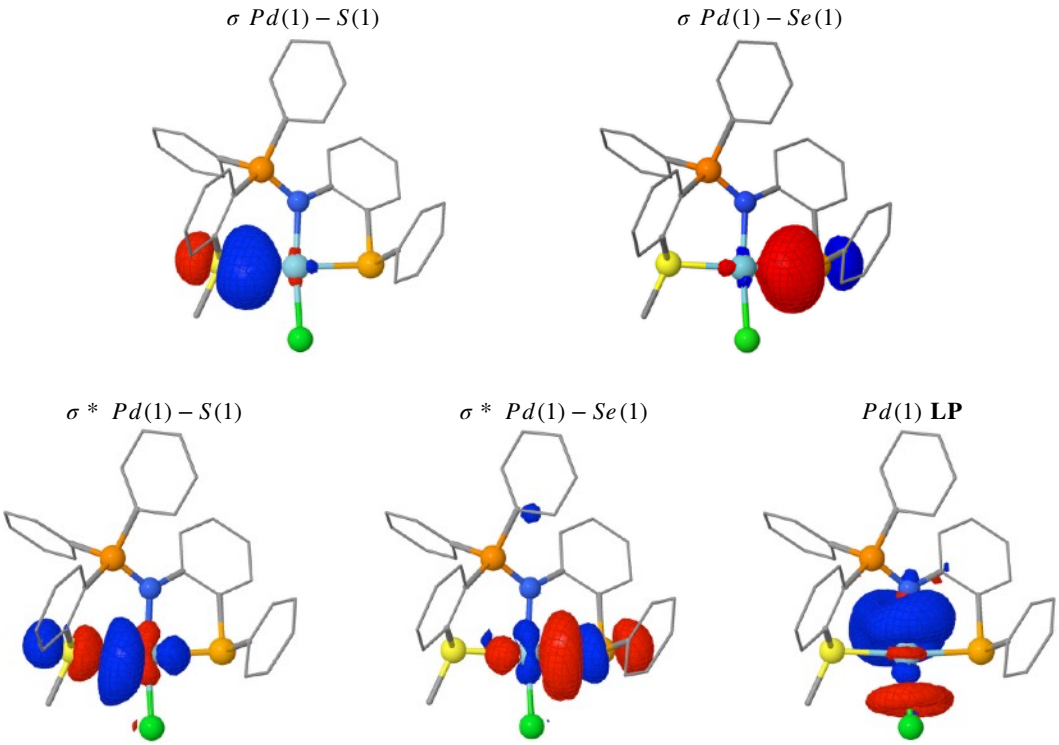

Figure S54. Relevant NBOs of complex **4d.**