Electronic Supporting Information for

COORDINATION CHEMISTRY OF 2,2'-BIPHENYLENEDITHIOPHOSPHINATE AND DIPHENYLDITHIOPHOSPHINATE WITH U, NP, and Pu

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Table of Contents

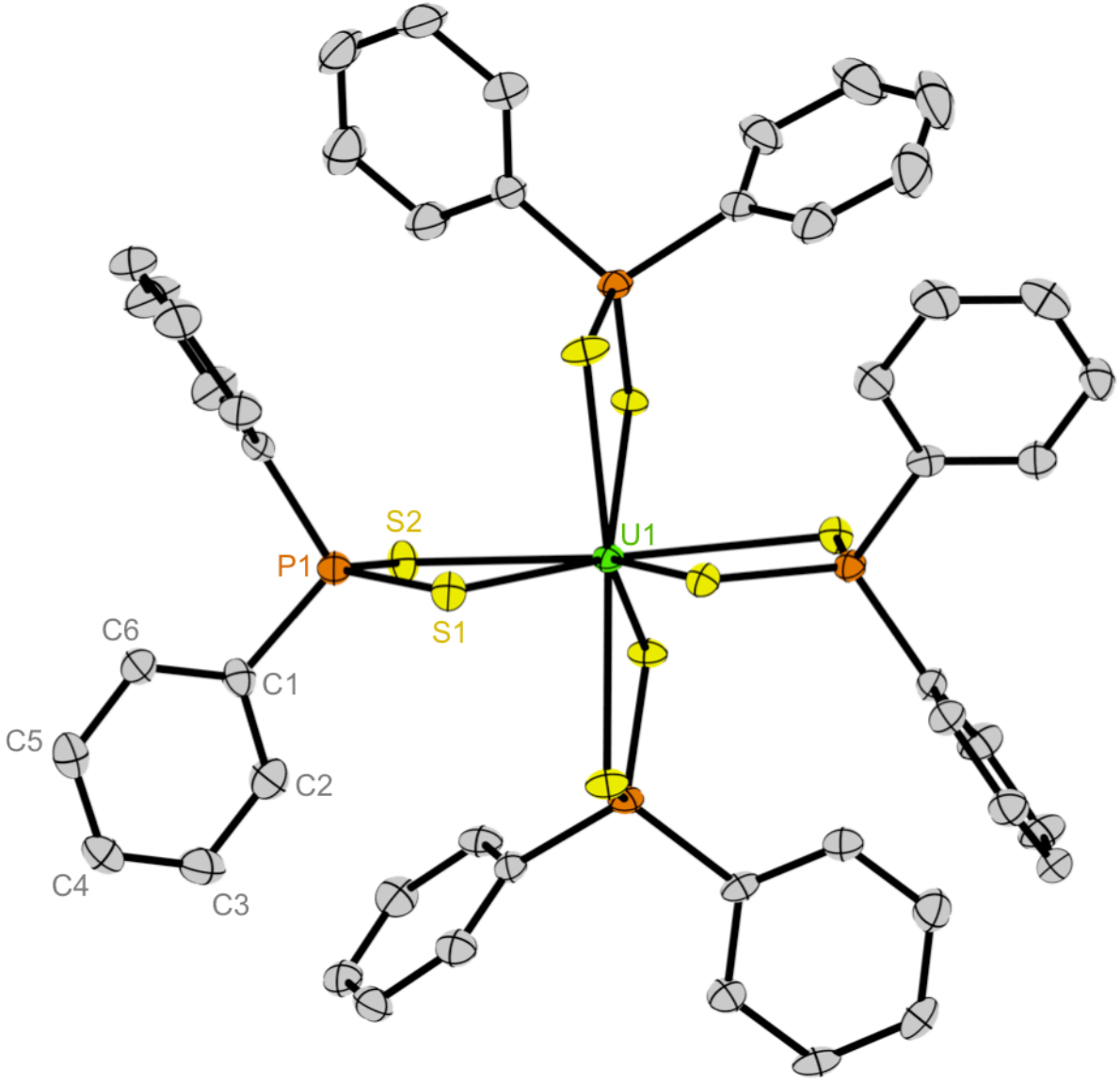


Figure S1: Molecular structure of $U[S_2P(C_6H_5)_2]_4$. Thermal ellipsoids show the 50% probability density surfaces. The PPh_4^{1+} countercation and hydrogen atoms have been omitted.

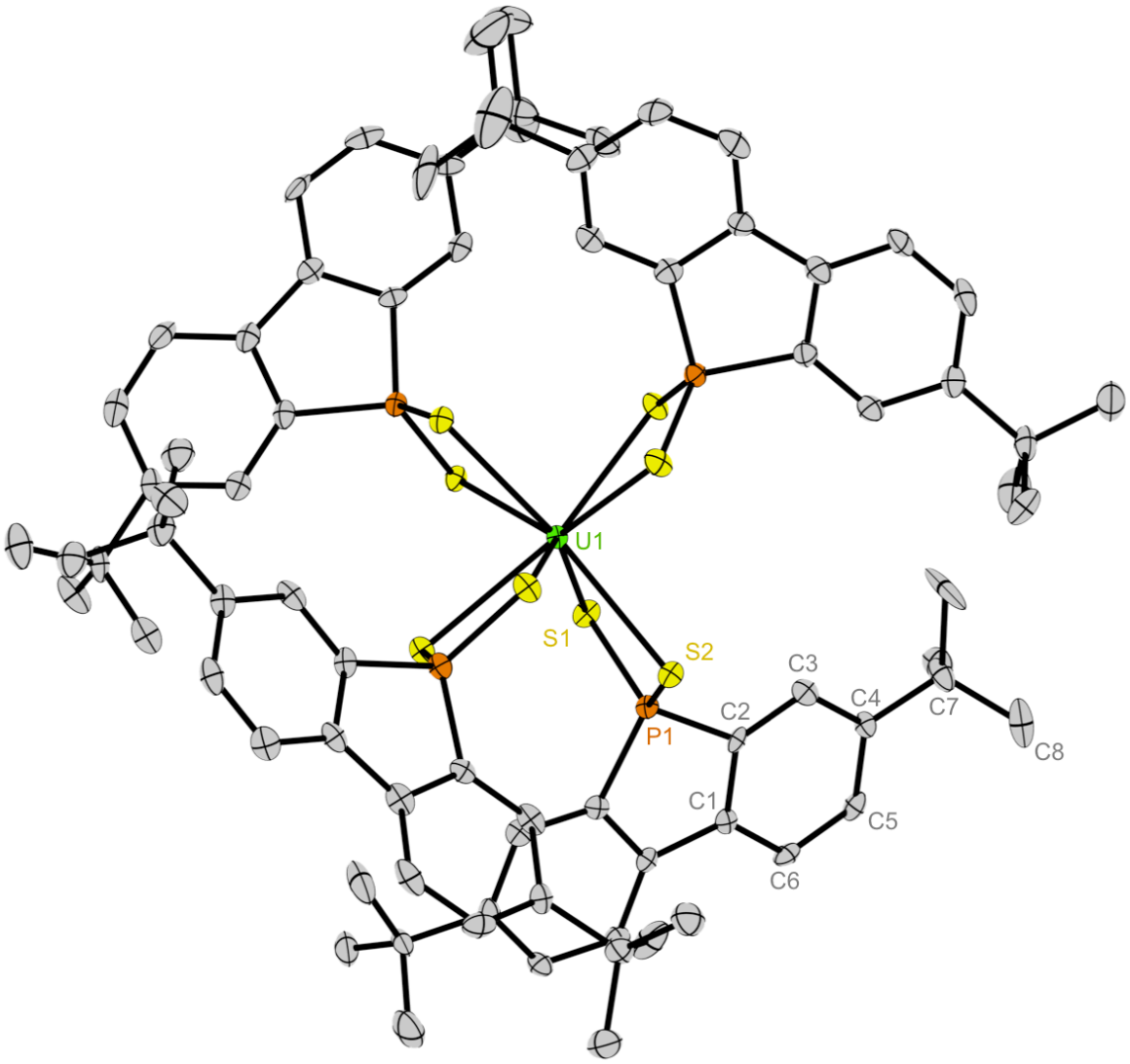


Figure S2: Molecular structure of $U[S_2P(^tBu_2C_{12}H_6)]_4$. Thermal ellipsoids show the 50% probability density surfaces. The PPh_4^{1+} countercation and hydrogen atoms have been omitted.

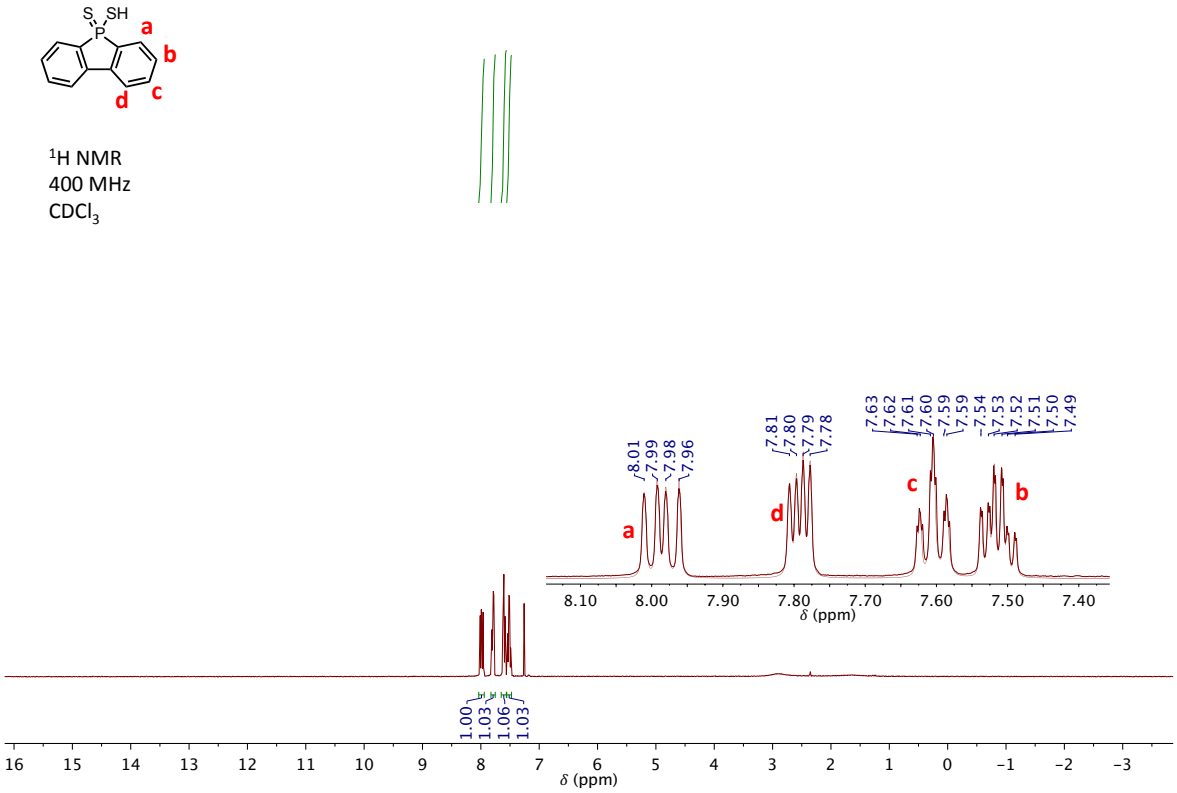
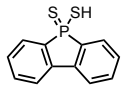


Figure S3: ^{1}H NMR spectrum of $HS_2P(C_{12}H_8)$.



^{31}P NMR
162 MHz
$CDCl_3$

Figure S4: ^{31}P NMR spectrum of $HS_2P(C_{12}H_8)$.

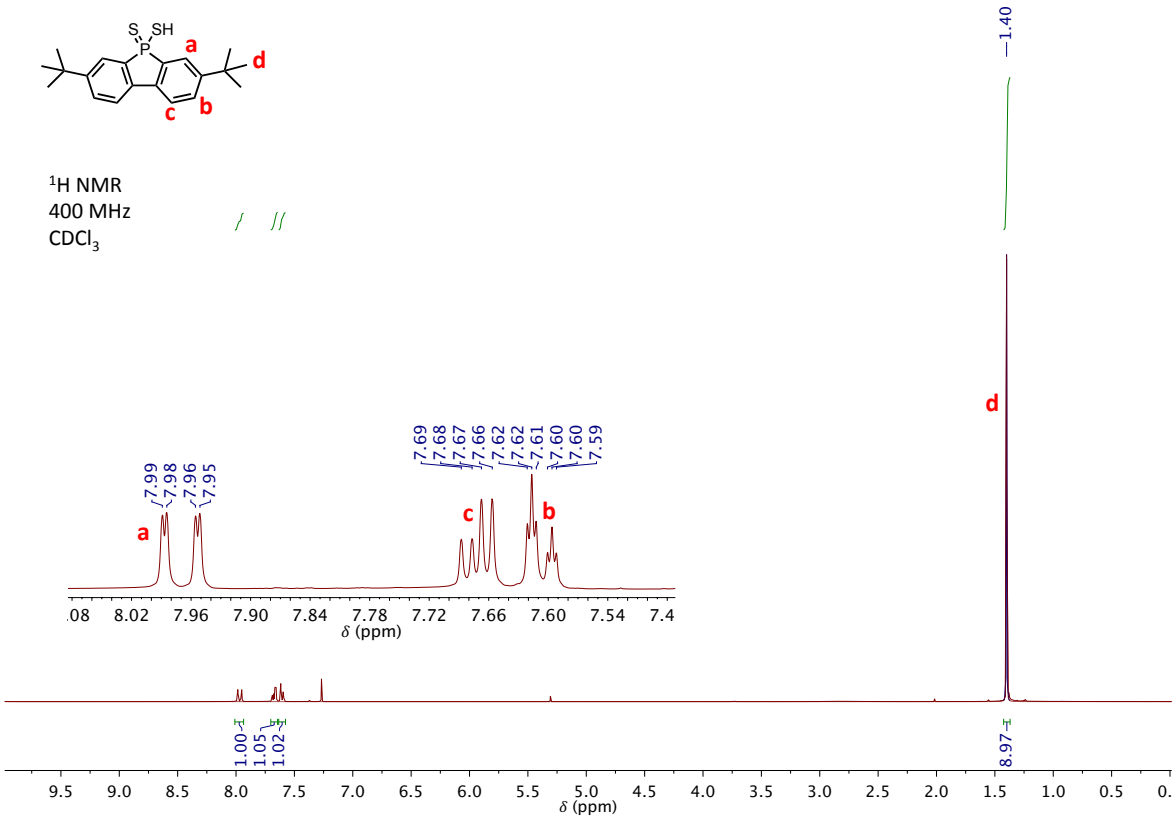
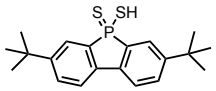


Figure S5: ^{1}H NMR spectrum of $HS_2P(^{t}Bu_2C_{12}H_6)$.



46.43

^{31}P NMR
162 MHz
$CDCl_3$

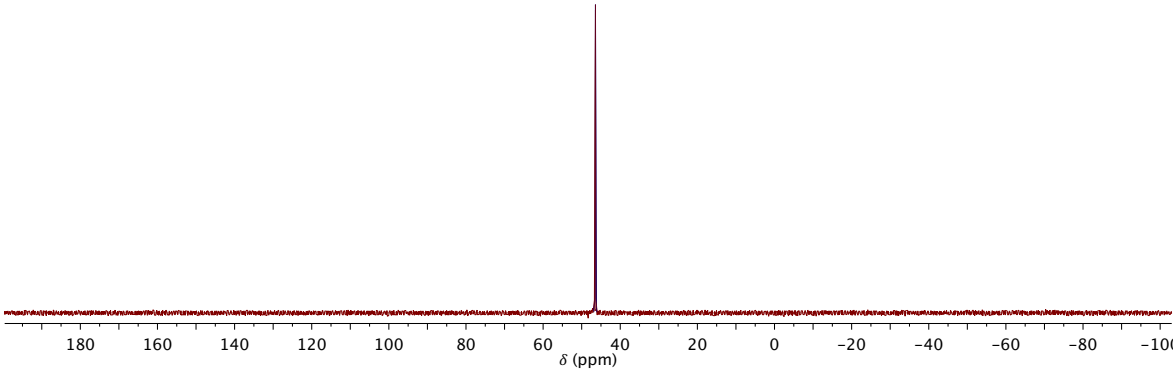


Figure S6: ^{31}P NMR spectrum of $HS_2P(^tBu_2C_{12}H_6)$.

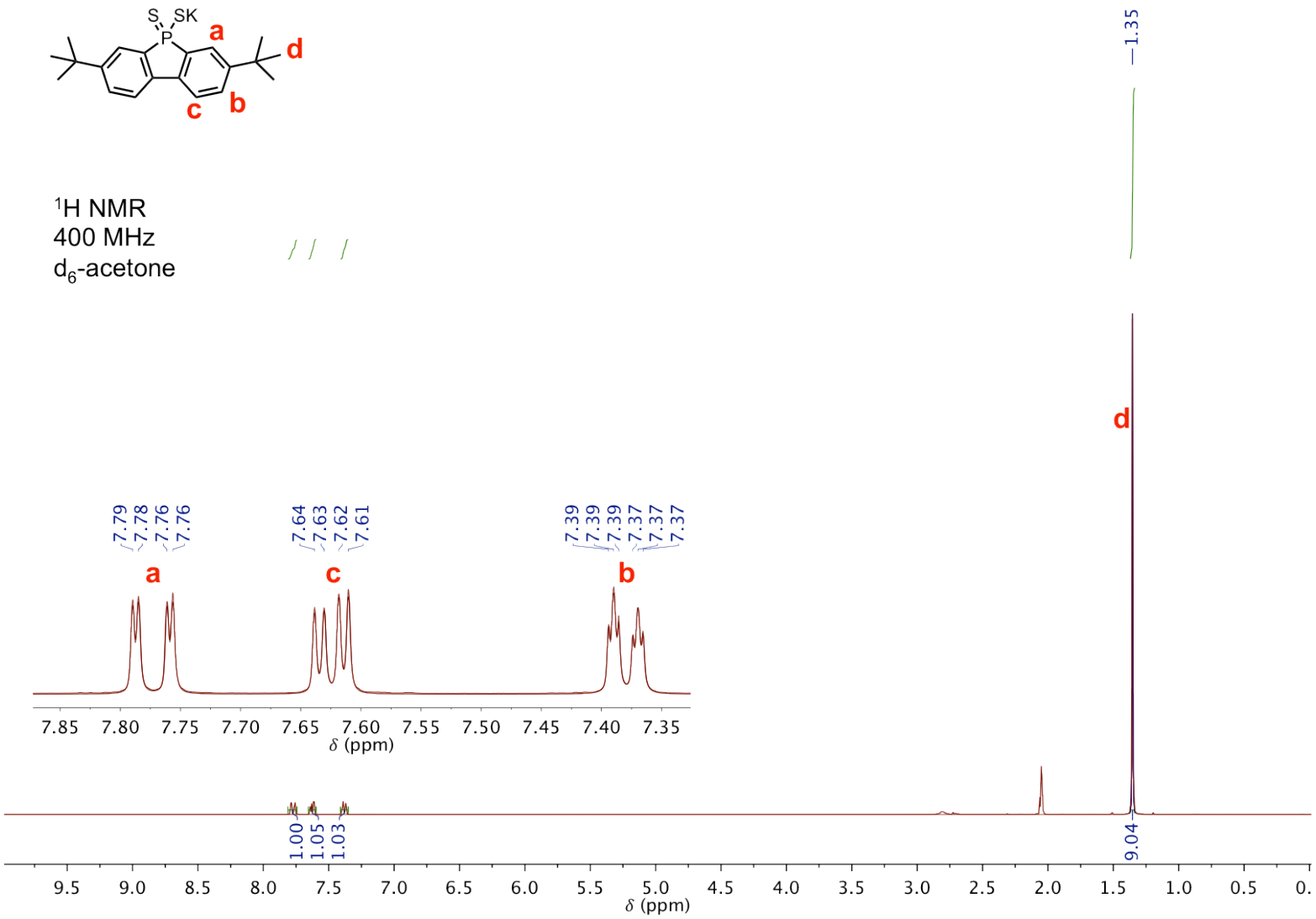


Figure S3: ^{1}H NMR spectrum of K[$S_2P(^tBu_2C_{12}H_6)$].

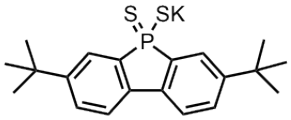


Figure S4: ^{31}P NMR spectrum of K[$S_2P(^tBu_2C_{12}H_6)$].

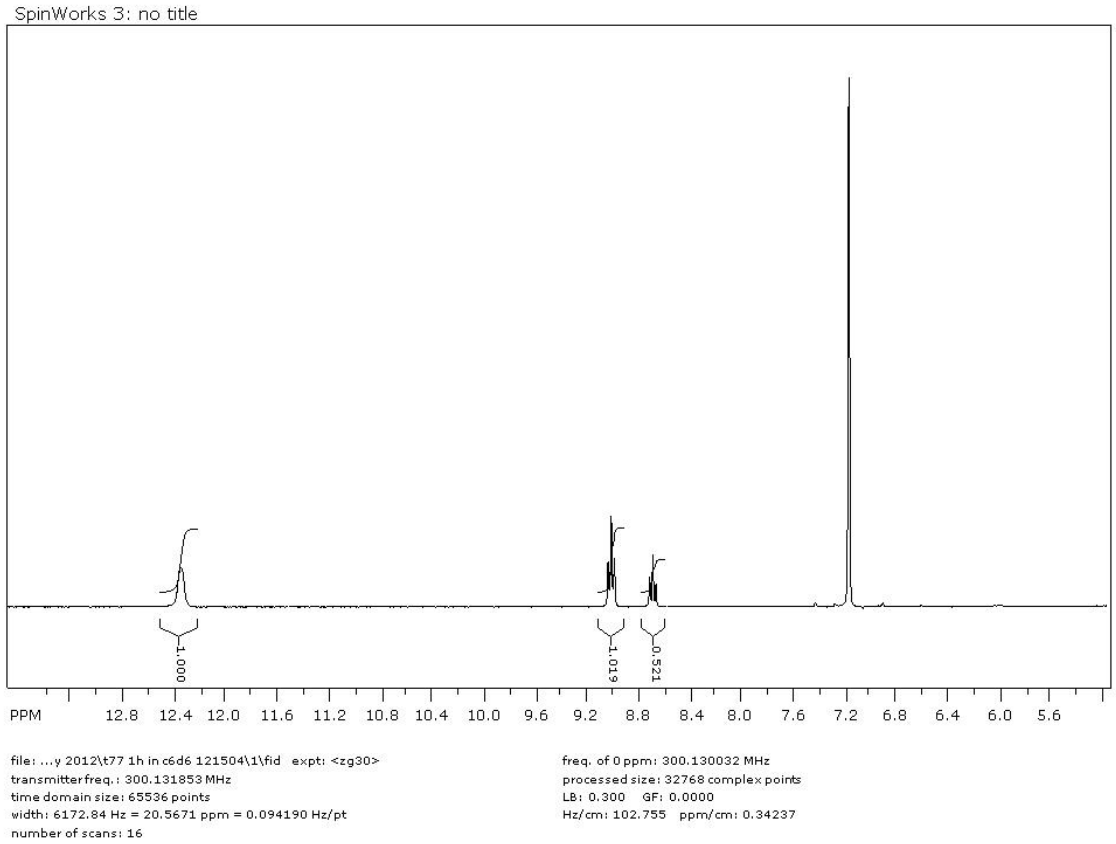


Figure S11. ^{1}H NMR spectrum of $U[S_2P(C_6H_5)_2]_4$, dissolved in C_6D_6 solvent.

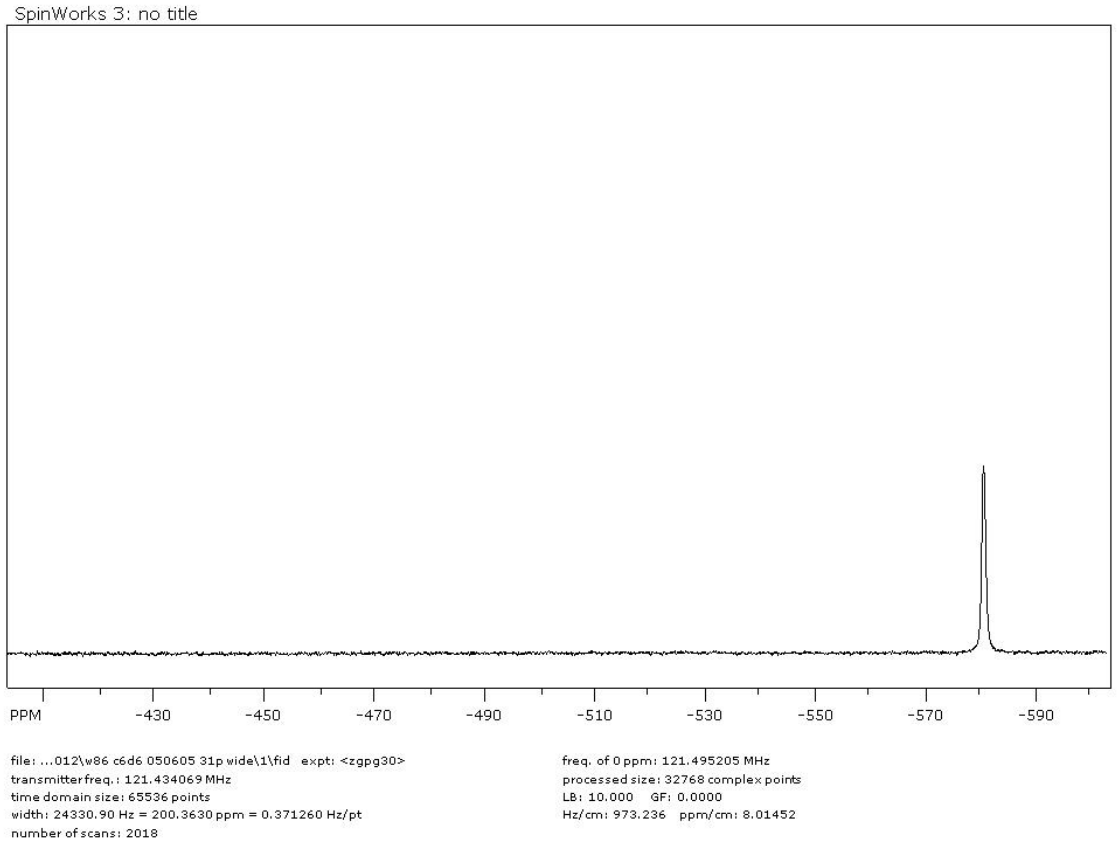


Figure S12. ^{31}P NMR spectrum of $U[S_2P(C_6H_5)_2]_4$, dissolved in C_6D_6 solvent.

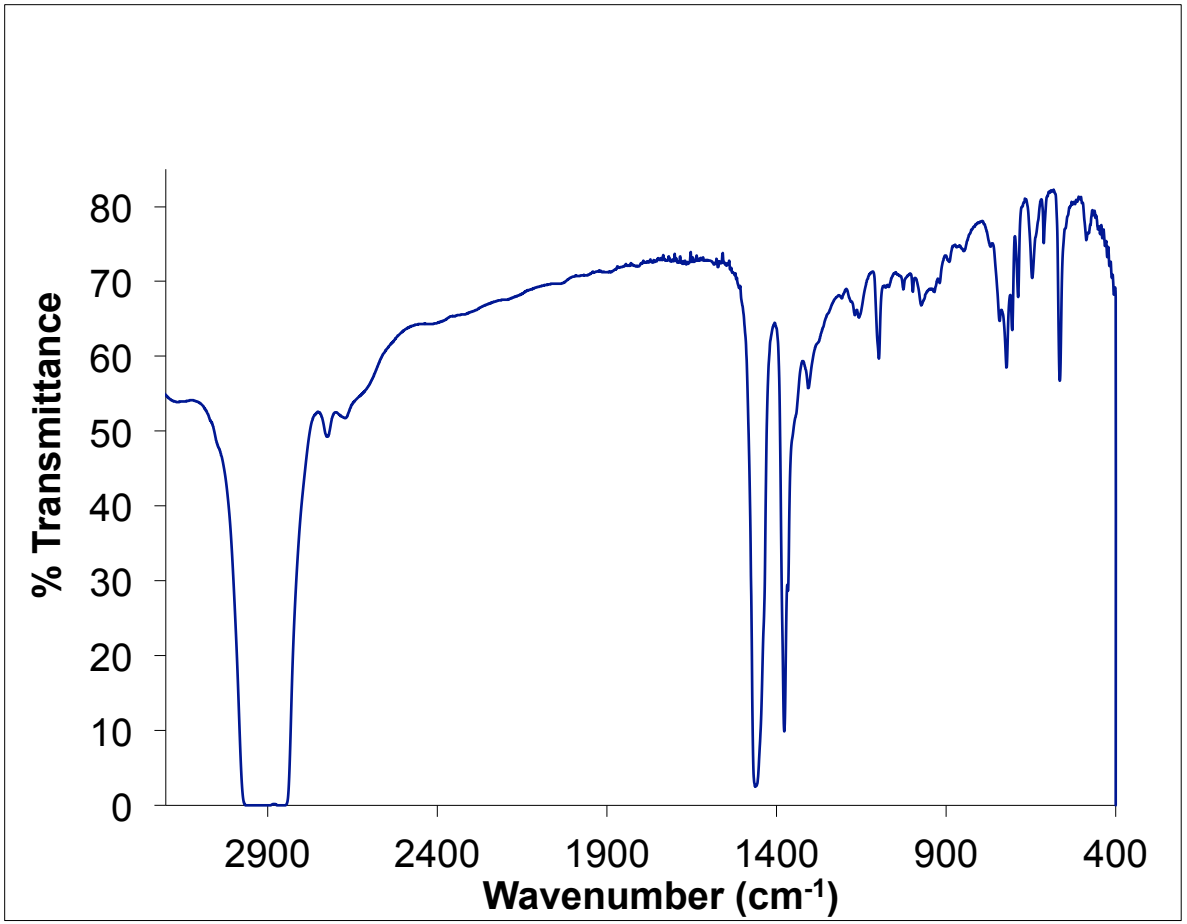


Figure S9. IR spectrum of $U[S_2P(C_6H_5)_2]_4$, recorded as a Nujol mull suspension.

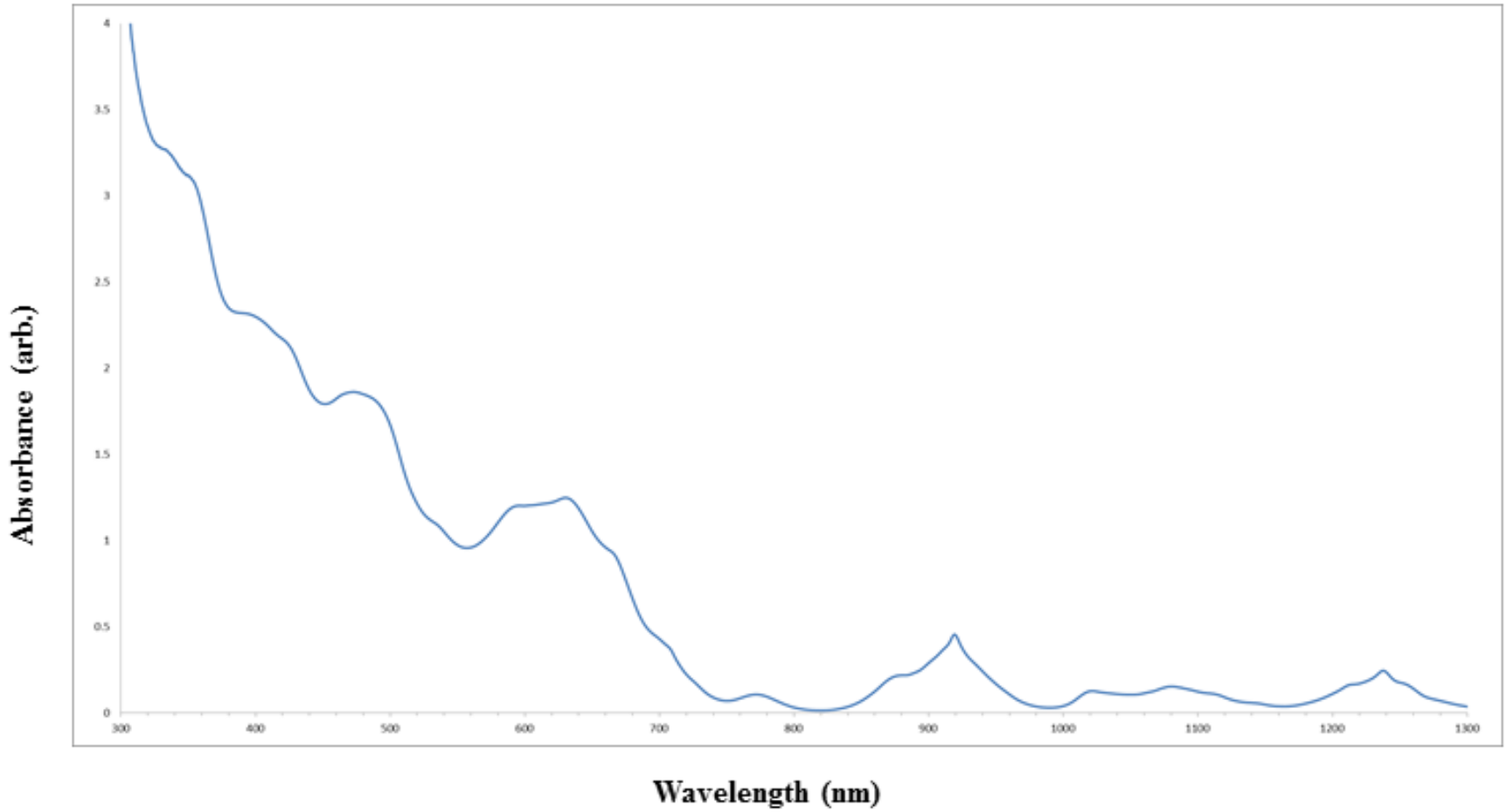


Figure S10. Electronic absorption spectrum of $U[S_2P(C_6H_5)_2]_4$, dissolved in THF solvent.

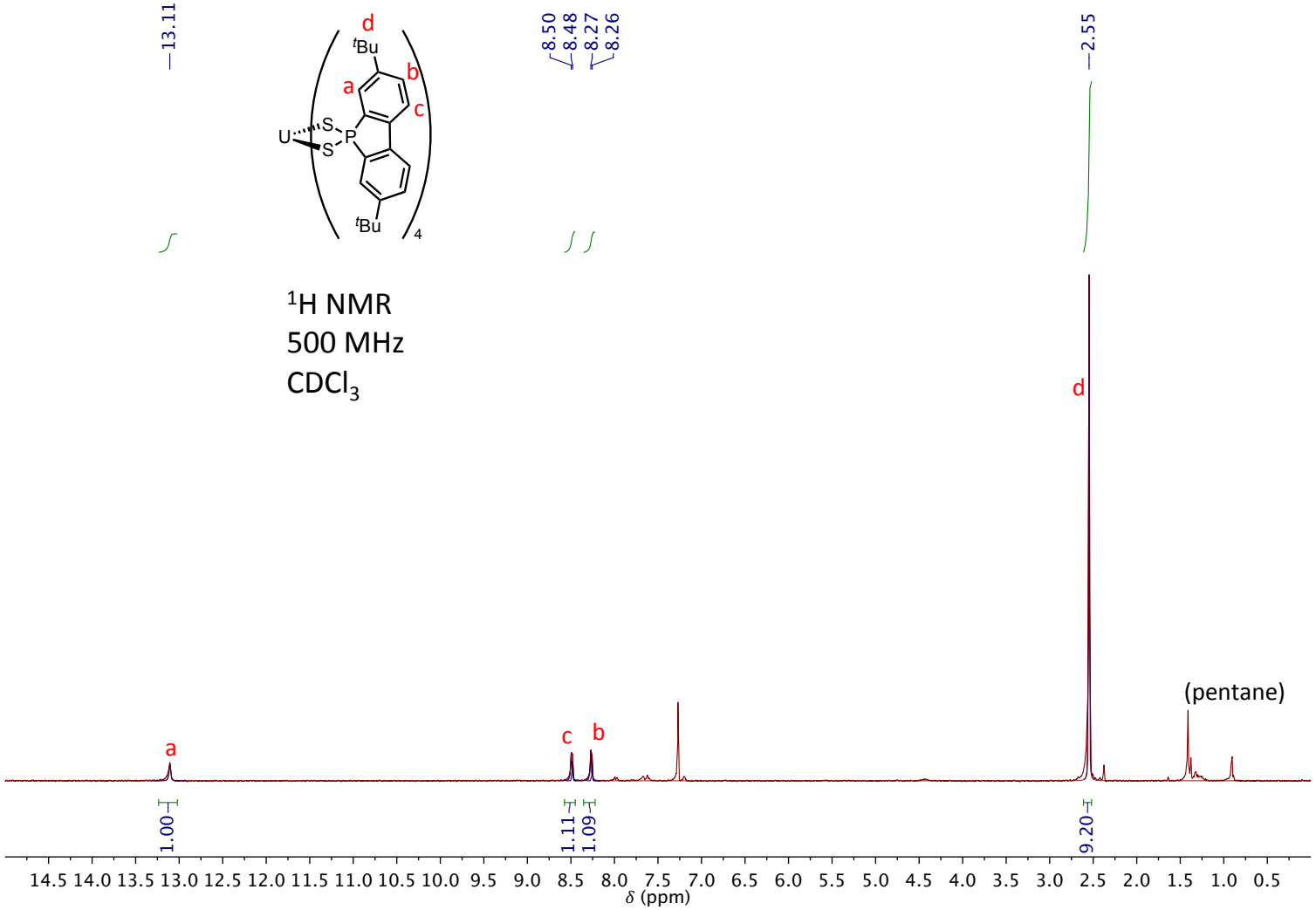
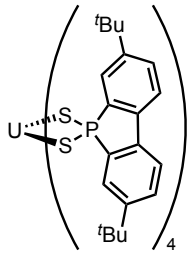


Figure S9: ^{1}H NMR spectrum of U[$S_2P(^{t}Bu_2C_{12}H_6)$]$_4$.



$^{31}P\{^{1}H\}$ NMR
202 MHz
$CDCl_3$

Figure S10: ^{31}P NMR spectrum of $U[S_2P(^{t}Bu_2C_{12}H_6)]_4$.

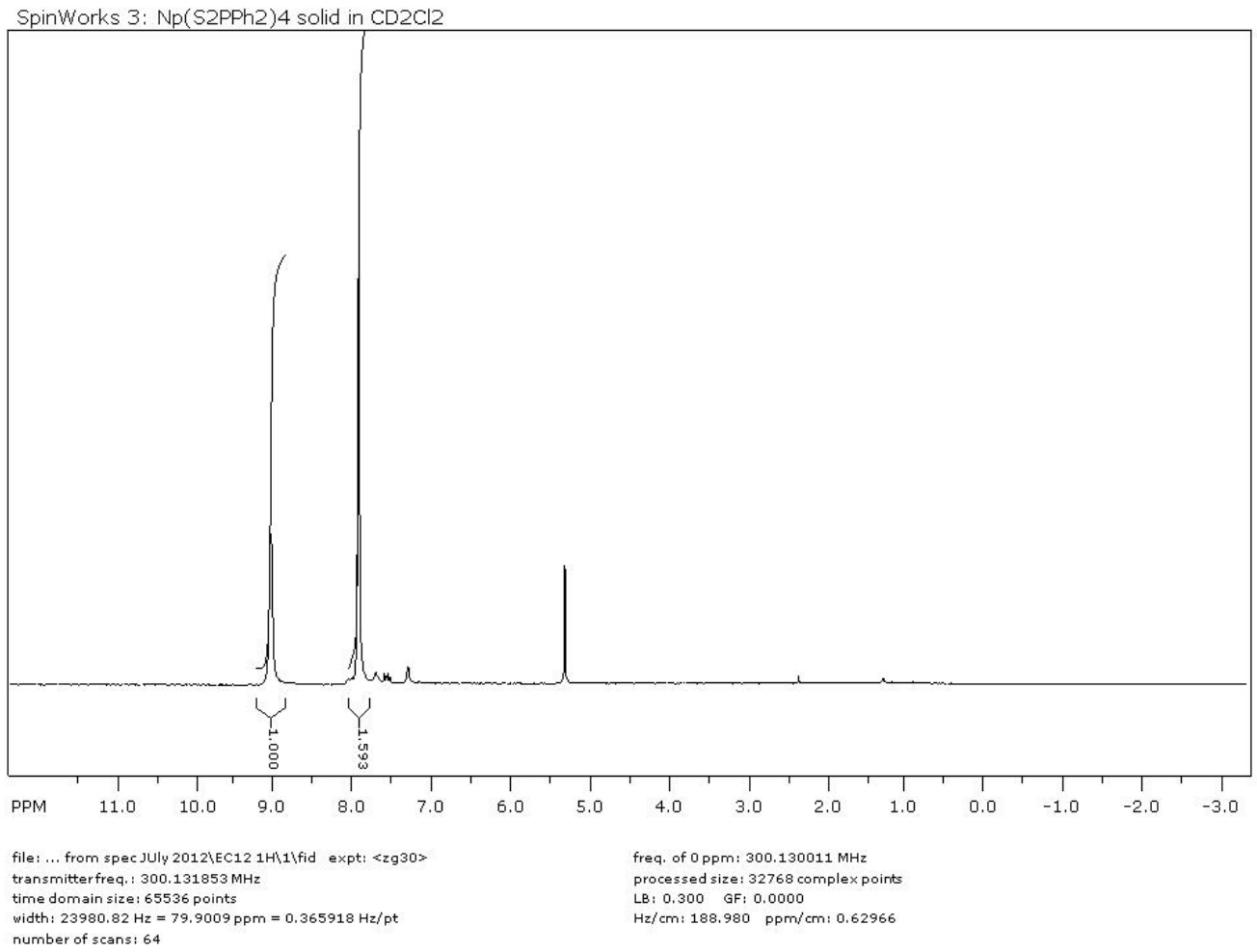


Figure S7. ^{1}H NMR spectrum of $Np[S_2P(C_6H_5)_2]_4$, dissolved in CD_2Cl_2 solvent.

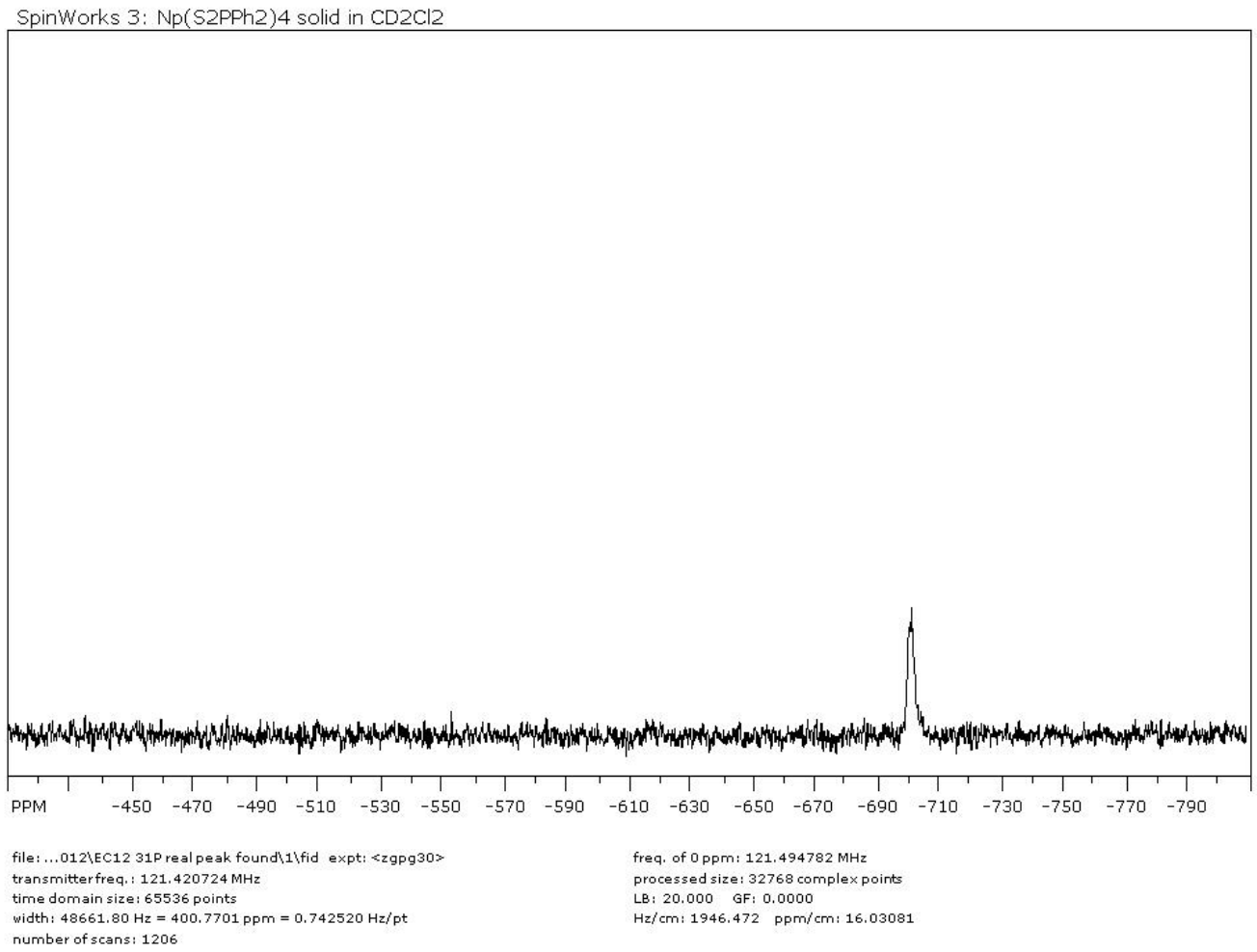


Figure S8. ^{31}P NMR spectrum of $Np[S_2P(C_6H_5)_2]_4$, dissolved in CD_2Cl_2 solvent.

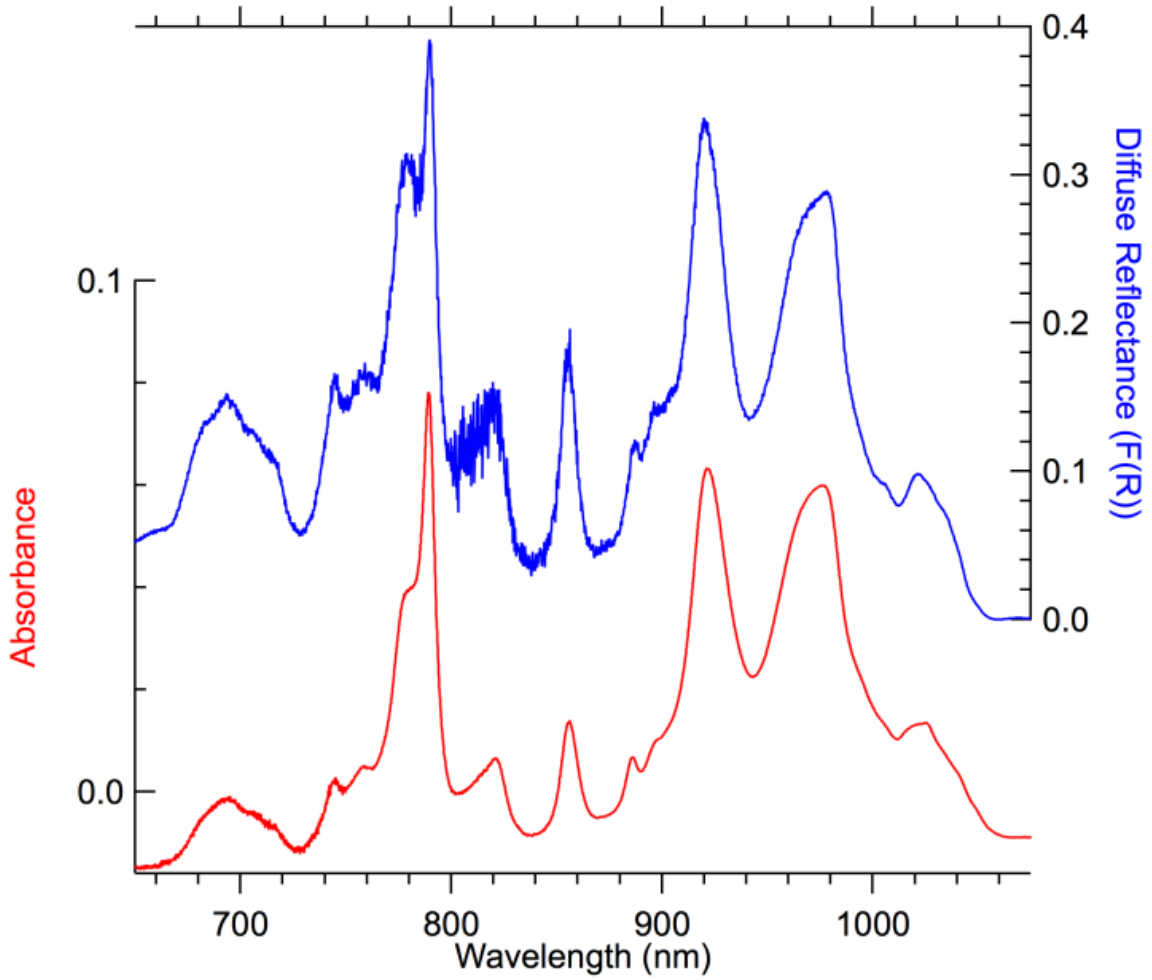


Fig S5. Vis/NIR diffuse reflectance solid-state spectrum of crystalline $Np[S_2P(C_6H_5)_2]_4$ (blue line, top), and solution phase spectrum of $Np[S_2P(C_6H_5)_2]_4$ dissolved in THF solvent (red line, bottom).

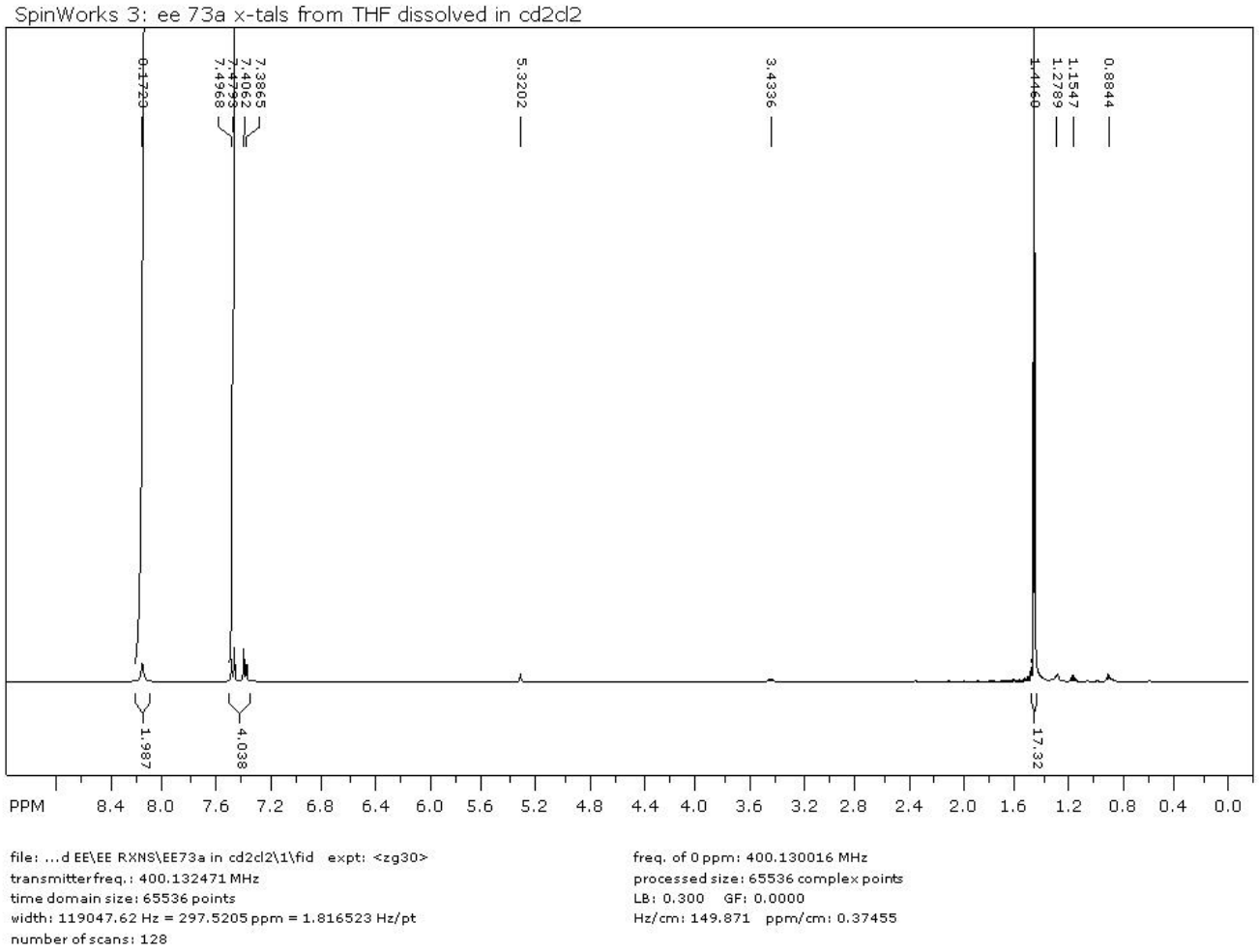


Figure S13. ^{1}H NMR spectrum of $Np[S_2P(^{t}Bu_2C_6H_6)_2]_4$, dissolved in CD_2Cl_2 solvent.

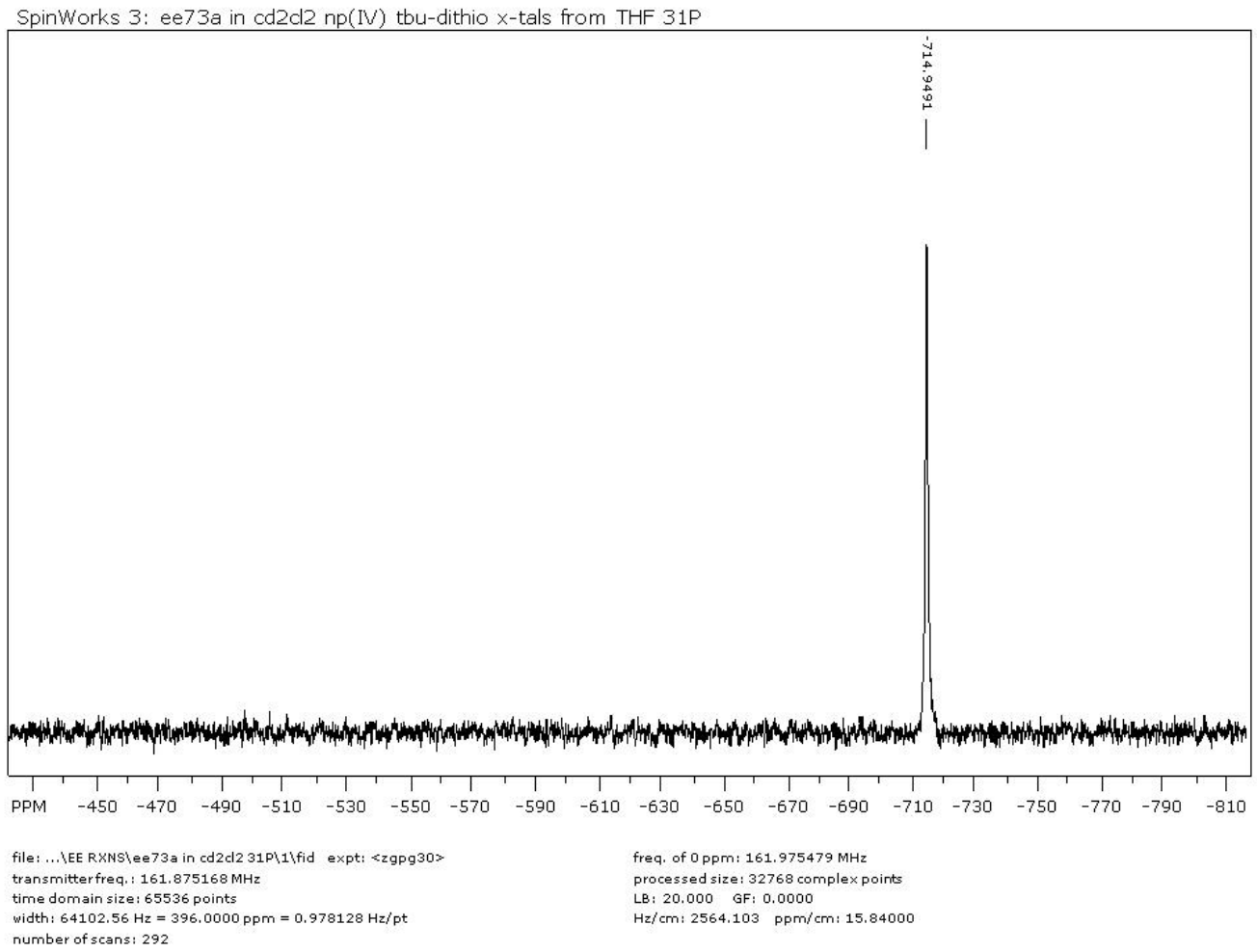


Figure S14. ^{31}P NMR spectrum of Np[$S_2P(^tBu_2C_{12}H_8)]_4$, dissolved in CD_2Cl_2 solvent.

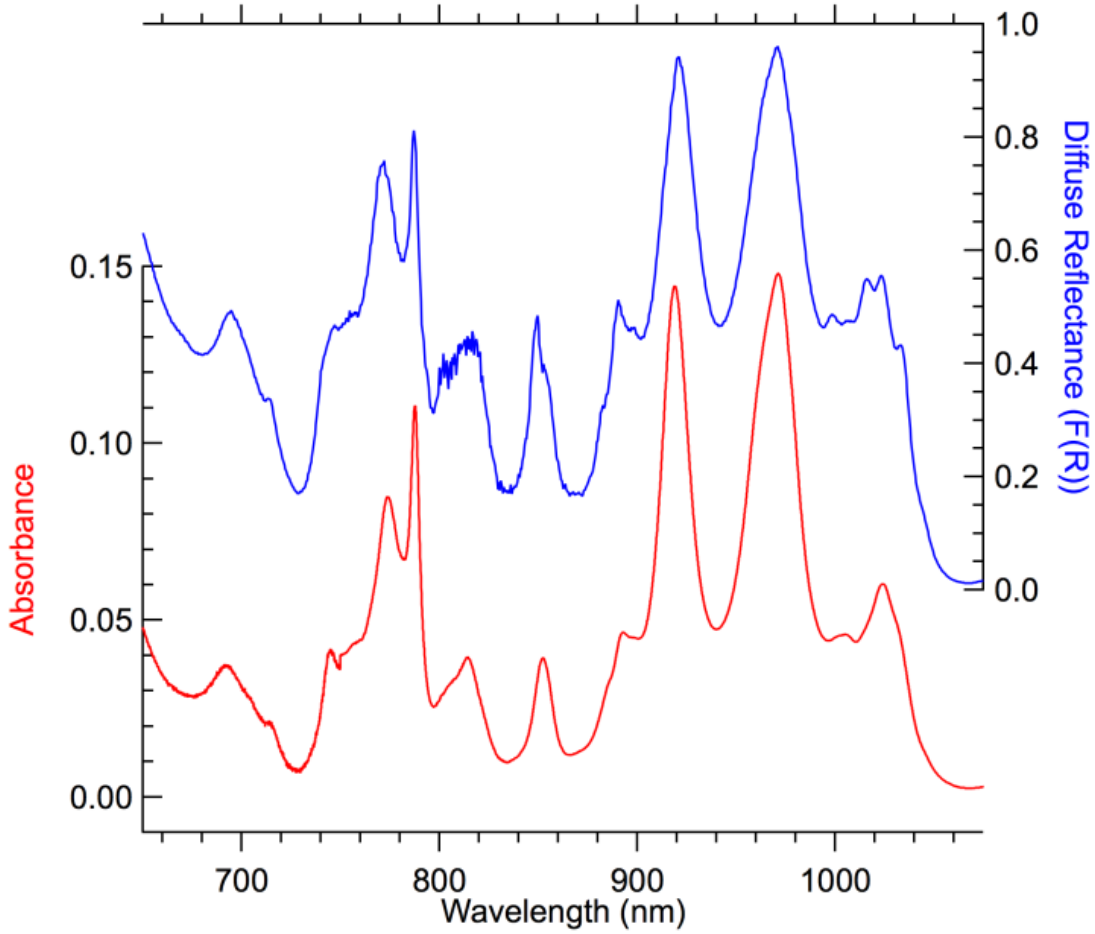


Figure S6. Vis/NIR diffuse reflectance solid-state spectrum of crystalline $Np[S_2P(^tBuC_{12}H_8)]_4$ (blue line, top), and solution phase spectrum of $Np[S_2P(^tBuC_{12}H_8)]_4$ dissolved in THF solvent (red line, bottom).

	$[PPh_4][S_2P(C_{12}H_8)]$	$[AsPh_4][S_2P(^tBu_2C_{12}H_6)]$•0.5acetone
P–S (Å)	1.9751	1.9797
	1.9781	1.9792
avg	**1.9766**	**1.97945**
STDEV	**0.00212132**	**0.000353553**
STDEV(%)	**0.107321681**	**0.017861193**
P–C (Å)	1.8197	1.8177
	1.8224	1.8218
AVG	**1.82105**	**1.81975**
STDEV	**0.001909188**	**0.002899138**
STDEV(%)	**0.104839972**	**0.15931517**
S–P–S (°)	118.53	119.22
C–P–C (°)	90.65	90.74
$C–C_{tether}$ (Å)	1.4684	1.476
$C–C_{arene}$ (Å)	1.3836	1.382
	1.402	1.4
	1.3887	1.399
	1.3914	1.4
	1.3777	1.382
	1.3909	1.392
	1.3882	1.389
	1.3976	1.402
	1.3789	1.381
	1.3848	1.407
	1.3789	1.398
	1.383	1.386

	$U(S_2PPh_2)_4$•THF	$Np(S_2PPh_2)_4$•THF	$Pu(S_2PPh_2)_3(py)_2$•toluene
P–S (Å)	2.011	2.016	1.998
	2.025	2.0094	1.99
	2.015	2.0089	1.998
	2.009	2.0072	1.996
	2.018	2.0065	2.006
	2.006	2.0101	1.991
	2.014	2.0052	
	2.013	2.0106	
avg	**2.013875**	**2.0092375**	**1.9965**
STDEV	**0.005817154**	**0.003304083**	**0.005787918**
STDEV(%)	**0.288853798**	**0.16444462**	**0.289903253**
P–C (Å)	1.819	1.8042	1.822
	1.81	1.81	1.823
	1.809	1.81	1.816
	1.816	1.8092	1.809
	1.808	1.8114	1.809
	1.821	1.8046	1.818
	1.818	1.8081	
	1.81	1.8126	
AVG	**1.813875**	**1.8087625**	**1.816166667**
STDEV	**0.005166859**	**0.003012326**	**0.006112828**
STDEV(%)	**0.28485197**	**0.166540708**	**0.336578584**
M–S (Å)	2.872	2.8004	2.937
	2.819	2.8493	2.934
	2.805	2.7863	2.923
	2.878	2.8587	2.932
	2.845	2.8523	2.957
	2.8557	2.7853	2.9
	2.808	2.8334	
	2.8742	2.8245	
avg	**2.8446125**	**2.823775**	**2.9305**
STDEV	**0.030305419**	**0.029783061**	**0.018684218**
STDEV(%)	**1.065361927**	**1.054725**	**0.637577817**

	$U(S_2PPh_2)_4$•THF	$Np(S_2PPh_2)_4$•THF	$Pu(S_2PPh_2)_3(py)_2$•toluene
M–N (Å)			2.624
			2.607
AVG			**2.6155**
STDEV			**0.012020815**
STDEV(%)			**0.459599131**
S–P–S (º)	109.23	108.82	111.66
	109.46	109.11	112.52
	109.47	108.89	111.26
	109.33	109.06	
AVG	**109.3725**	**108.97**	**111.8133333**
STDEV	**0.114418821**	**0.137355985**	**0.643842631**
STDEV(%)	**0.104613885**	**0.126049358**	**0.575819191**
C–P–C (º)	105.6	105.53	105.1
	106.3	106.05	103.5
	102.8	106.08	103.8
	106.2	103.17	
AVG	**105.225**	**105.2075**	**104.1333333**
STDEV	**1.645954637**	**1.381602331**	**0.850490055**
STDEV(%)	**1.564223936**	**1.313216577**	**0.816731807**
S–M–S (º)	70.64	70.81	68.39
	70.63	70.83	69.12
	70.4	70.84	68.56
	70.63	70.63	
AVG	**70.575**	**70.7775**	**68.69**
STDEV	**0.116761866**	**0.099121138**	**0.381968585**
STDEV(%)	**0.165443664**	**0.140046114**	**0.556075972**
$C–C_{arene}$ (Å)	1.391	1.3962	1.38
	1.391	1.3869	1.36
	1.384	1.3852	1.397
	1.386	1.3828	1.34
	1.39	1.3858	1.34
	1.399	1.3831	1.401
	1.385	1.39	1.385
	1.399	1.3868	1.382
	1.394	1.3851	1.378
	1.39	1.3767	1.37

	$U(S_2PPh_2)_4$•THF	$Np(S_2PPh_2)_4$•THF	$Pu(S_2PPh_2)_3(py)_2$•toluene
$C–C_{arene}$ (Å)	1.392	1.3856	1.39
	1.389	1.3875	1.375
	1.393	1.3783	1.388
	1.379	1.3798	1.39
	1.376	1.375	1.378
	1.37	1.3695	1.368
	1.398	1.389	1.383
	1.391	1.3902	1.403
	1.401	1.389	1.384
	1.393	1.3865	1.387
	1.369	1.3737	1.38
	1.386	1.3722	1.372
	1.392	1.3899	1.395
	1.395	1.3898	1.387
	1.391	1.386	1.382
	1.381	1.3772	1.367
	1.379	1.3743	1.377
	1.388	1.373	1.373
	1.386	1.3837	1.38
	1.385	1.3913	1.384
	1.383	1.3845	1.379
	1.391	1.3901	1.392
	1.381	1.3721	1.36
	1.37	1.3706	1.375
	1.399	1.386	1.392
	1.392	1.3883	
	1.395	1.387	
	1.377	1.3935	
	1.386	1.3736	
	1.378	1.3809	
	1.395	1.3835	
	1.393	1.3897	
	1.389	1.3843	
	1.386	1.3863	
	1.39	1.377	
	1.37	1.374	
	1.386	1.389	
AVG	**1.3874375**	**1.383066667**	**1.379444444**
STDEV	**0.008052768**	**0.00679115**	**0.013966172**
STDEV(%)	**0.580405829**	**0.49102115**	**1.012449058**

	$U[S_2P(^tBu_2C_{12}H_6)]_4$•toluene	$Np[S_2P(^tBu_2C_{12}H_6)]_4$•4toluene
P–S (Å)	2.0019	2.002
	1.9931	2.007
	1.9943	1.9952
	2.0083	2.009
	2.0072	
	1.9916	
	1.9986	
	2.009	
avg	**2.0005**	**2.0033**
STDEV	**0.007131019**	**0.006150339**
STDEV(%)	**0.356461823**	**0.30701037**
P–C (Å)	1.8048	1.793
	1.8019	1.793
	1.7892	1.798
	1.7992	1.793
	1.794	
	1.7985	
	1.7991	
	1.814	
AVG	**1.8000875**	**1.79425**
STDEV	**0.007357491**	**0.0025**
STDEV(%)	**0.408729649**	**0.139333984**
M–S (Å)	2.8522	2.8328
	2.8243	2.8253
	2.8524	2.8364
	2.817	2.8162
	2.8307	
	2.8589	
	2.8634	
	2.8722	
avg	**2.8463875**	**2.827675**
STDEV	**0.019927686**	**0.00893882**
STDEV(%)	**0.700104474**	**0.316119067**

	$U[S_2P(^tBu_2C_{12}H_6)]_4$•toluene	$Np[S_2P(^tBu_2C_{12}H_6)]_4$•4toluene
S–P–S (º)	108.19	109.78
	110.07	109.73
	110.35	
	108.82	
AVG	**109.3575**	**109.755**
STDEV	**1.023828599**	**0.035355339**
STDEV(%)	**0.936221657**	**0.032212964**
C–P–C (º)	92.3	92.7
	92.65	92.3
	92.58	
	92.17	
AVG	**92.425**	**92.5**
STDEV	**0.227522893**	**0.282842712**
STDEV(%)	**0.246170292**	**0.305775905**
S–M–S (º)	69.51	70.85
	70.7	70.8
	70.47	
	69.25	
AVG	**69.9825**	**70.825**
STDEV	**0.709994131**	**0.035355339**
STDEV(%)	**1.014530963**	**0.049919293**
$C–C_{tether}$ (Å)	1.4741	1.479
	1.4833	1.475
	1.4723	
	1.4773	
AVG	**1.47675**	**1.477**
STDEV	**0.004831494**	**0.002828427**
STDEV(%)	**0.32717074**	**0.191498113**
$C–C_{arene}$ (Å)	1.377	1.3864
	1.3925	1.402
	1.4042	1.396
	1.3923	1.404
	1.3787	1.39
	1.3911	1.399
	1.3735	1.39
	1.402	1.401

	$U[S_2P(^tBu_2C_{12}H_6)]_4$•toluene	$Np[S_2P(^tBu_2C_{12}H_6)]_4$•4toluene
$C–C_{arene}$ (Å)	1.3999	1.393
	1.386	1.402
	1.3898	1.39
	1.3814	1.397
	1.4006	1.397
	1.3795	1.403
	1.3971	1.406
	1.3799	1.383
	1.3969	1.404
	1.3822	1.394
	1.4003	1.398
	1.3812	1.397
	1.393	1.404
	1.4067	1.389
	1.3852	1.391
	1.3885	
	1.392	
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	1.3896	
	1.3836	
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	1.3993	
	1.3718	
	1.3825	
	1.3934	
	1.3989	
	1.3956	
	1.3746	
	1.3892	
	1.3852	
	1.4027	
	1.3852	
	1.3965	
	1.3961	
	1.3731	
AVG	**1.389591667**	**1.3971**
STDEV	**0.009361234**	**0.007238544**
STDEV(%)	**0.673667945**	**0.518112102**