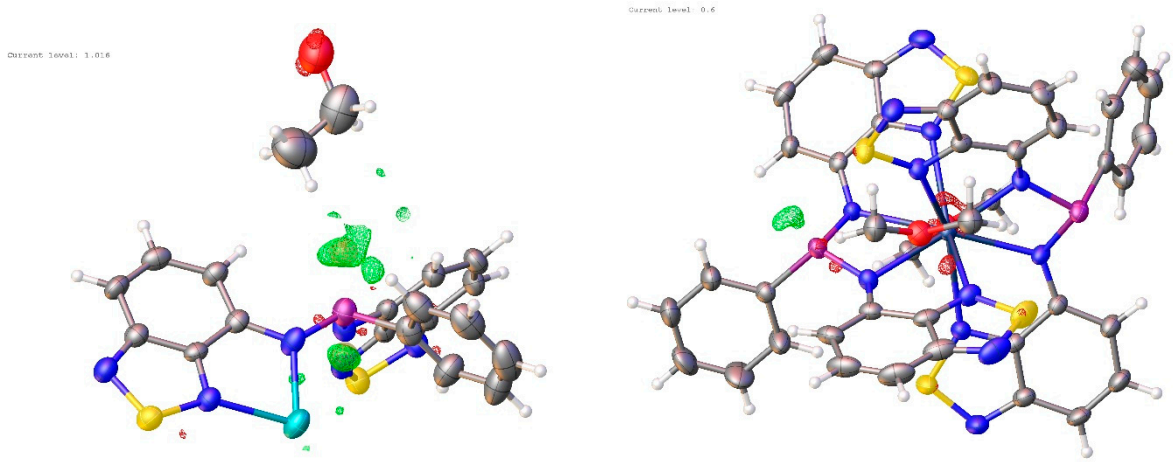
Yttrium and lithium complexes with diamidophosphane ligand bearing 2,1,3-benzothiazolyl substituent: Polydentate complexation and reversible NH–PH tautomery

by Radmir M. Khisamov, Taisiya S. Sukhikh, Sergey N. Konchenko, Nikolay A. Pushkarevsky



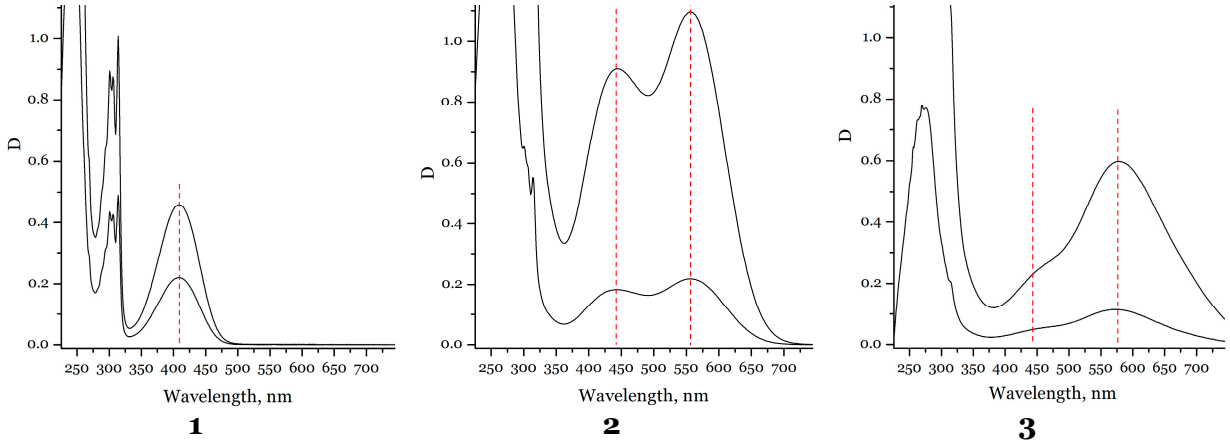
(a) (b)

Figure S1. Residual electron density map for compounds **2**$_2$·Et$_2$O (a) and [**5**$_2$(μ-dioxane)]·dioxane (b) in the absence of the hydrogen at the P atom. Green area indicate the excess of the electron density, red area indicate the lack of the electron density.

Table S1. M–N (M = Li, Y) and P–N bonds (Å) in the compounds. For disordered units, only the major components are listed.

2$_2$·Et$_2$O			**4**$_2$·Et$_2$O			**5**$_2$·(μ-dioxane)·dioxane			**6**·hexane			**6**·1.5thf		
N2	Li1	2.253(8)	Y1	N2	2.545(3)	Y1	N1	2.496(2)	Y1	N2	2.582(4)	Y1	N2	2.543(5)
N3	Li1	2.030(9)	Y1	N3	2.333(3)	Y1	N2	2.631(2)	Y1	N2^3	2.582(4)	Y1	N3	2.384(5)
N5	Li1^1	2.111(8)	Y1	N5	2.580(3)	Y1	N3	2.674(2)	Y1	N3^3	2.371(4)	Y1	N5	2.557(6)
N6	Li1^1	2.065(8)	Y1	N6	2.320(3)	Y1	N4	2.388(2)	Y1	N3	2.371(4)	Y1	N6	2.374(5)
			Y1	N7	2.221(4)	Y1	N5	2.611(2)	Y1	N5	2.544(4)	Y1	N8	2.582(5)
			Y2	N9	2.534(3)	Y1	N6	2.372(2)	Y1	N5^3	2.544(4)	Y1	N9	2.371(5)
			Y2	N10	2.377(3)	Y1	N7	2.450(2)	Y1	N6^3	2.389(4)	Y1	N11	2.523(6)
			Y2	N12	2.536(3)	Y1	N8	2.540(2)	Y1	N6	2.388(4)	Y1	N12	2.371(5)
			Y2	N13	2.491(3)									
			Y2	N14	2.265(3)									
P1	N3	1.598(4)	P1	N3	1.645(4)	P1	N1	1.599(2)	P1	N3	1.685(4)	P1	N3	1.702(5)
P1	N6	1.598(4)	P1	N6	1.660(4)	P1	N7	1.602(2)	P1	N6	1.691(4)	P1	N6	1.695(5)
			P3	N10	1.677(5)	P2	N4	1.691(2)				P2	N9	1.692(5)
			P3	N13	1.701(4)	P2	N6	1.697(2)				P2	N12	1.701(5)

^{1}1-*x*, *y*, 1/2-*z*; ^{2}1-*x*, -1-*y*, 4-*z*; ^{3}1-*x*, *y*, 3/2-*z*.



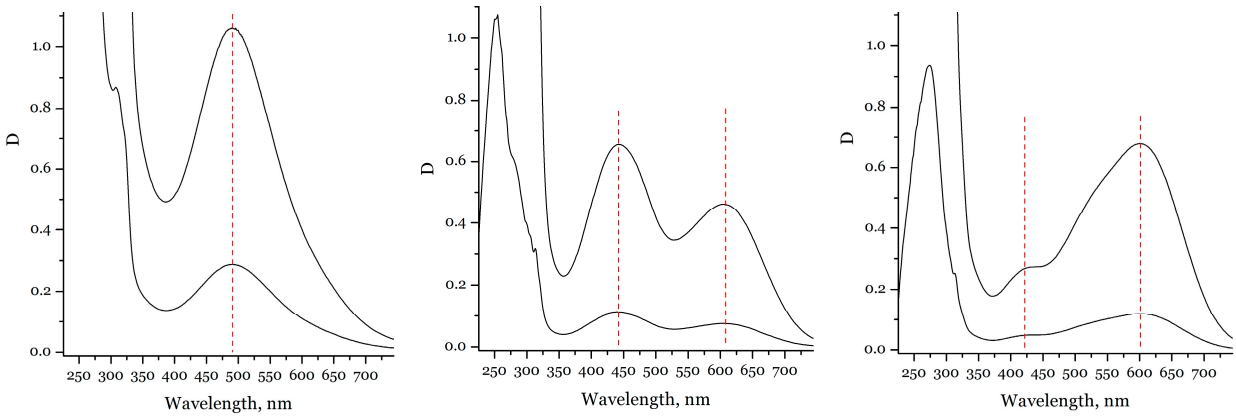


Figure S2. UV-Vis spectra of concentrated (top spectra; 8.9·10−5 – 7.8·10−4 M) and diluted (bottom spectra; 1.7·10−5 – 1.2·10−4 M) solutions of the compounds. Vertical dashed lines indicate the positions of the long wavelength bands.

Table S2. Frank-Condon (vertical) S_0–S_n (n = 1–20) transitions of $[YL_2]^-$ (TD-PBE0/def2-TZVPD level, geometry was optimized at PBE0-D3BJ/def2-SVPD)

State	Energy, cm-1	Wavelength, nm	Oscilator strength	Transitions	Contributions
1	15520.6	644.3	0.044986123	H → L	0.018984
				H → L	0.017465
				H → L	0.932314
2	16038.6	623.5	0.041626802	H → L	0.229340
				H → L + 1	0.017775
				H → L	0.722730
3	16648.3	600.7	0.003842003	H → L	0.718426
				H → L	0.207879
				H → L + 1	0.022366
				H → L	0.011839
				H → L + 2	0.011562
4	17347.3	576.5	0.003218488	H → L	0.251520
				H → L + 2	0.031013
				H → L + 1	0.013007
				H → L + 2	0.047606
				H → L + 1	0.614870
5	17783.9	562.3	0.005445304	H → L	0.105198
				H → L + 2	0.017390
				H → L + 1	0.190591
				H → L + 2	0.025342
				H → L + 1	0.092014
				H → L + 2	0.495518
				H → L + 3	0.046746
6	18042.6	554.2	0.049178960	H → L	0.028943
				H → L + 2	0.023139
				H → L + 1	0.077855
				H → L + 2	0.010271
				H → L	0.012692
				H → L + 1	0.544772
				H → L + 2	0.081674
				H → L + 3	0.011223
				H → L + 1	0.012063
				H → L + 2	0.117123
				H → L + 3	0.053808
7	18173.6	550.2	0.028270641	H → L	0.187940
				H → L + 1	0.124410
				H → L + 2	0.291867
				H → L + 1	0.151075
				H → L + 2	0.208086
8	18453.4	541.9	0.014236485	H → L	0.256124
				H → L + 1	0.039091
				H → L + 2	0.011734
				H → L	0.010935
				H → L + 1	0.197988
				H → L + 2	0.012246
				H → L + 1	0.018948
				H → L + 2	0.224811
				H → L + 3	0.055913
				H → L + 1	0.045473
				H → L + 2	0.052362
				H → L + 3	0.043429
9	18489.7	540.8	0.026823814	H → L	0.089968
				H → L + 1	0.044508
				H → L + 2	0.015364
				H → L + 3	0.011141
				H → L	0.012226
				H → L + 1	0.188527
				H → L + 2	0.051192

				H → L + 1	0.128720
				H → L + 2	0.138009
				H → L + 3	0.270938
10	18725.0	534.0	0.063804064	H → L	0.034775
				H → L + 1	0.016343
				H → L + 1	0.022710
				H → L + 2	0.519294
				H → L + 3	0.126768
				H → L + 1	0.036755
				H → L + 2	0.072986
				H → L + 3	0.105058
				H → L + 1	0.039390
11	19122.7	522.9	0.001105243	H → L + 2	0.051794
				H → L + 1	0.338771
				H → L + 2	0.035389
				H → L + 1	0.018183
				H → L + 2	0.034706
				H → L + 3	0.018228
				H → L + 2	0.072640
				H → L + 3	0.408394
12	19497.6	512.9	0.000310298	H → L + 1	0.256764
				H → L + 2	0.015854
				H → L + 2	0.257007
				H → L + 2	0.032789
				H → L + 3	0.391007
				H → L + 2	0.012686
13	19958.0	501.1	0.000375698	H → L + 1	0.457062
				H → L + 2	0.017188
				H → L + 2	0.042523
				H → L + 3	0.267295
				H → L + 2	0.031819
				H → L + 3	0.118037
				H → L + 3	0.028099
14	20272.4	493.3	0.005964629	H - 1 → L	0.010106
				H → L + 2	0.796792
				H → L + 3	0.078616
				H → L + 3	0.080250
15	20283.1	493.0	0.005352692	H → L + 1	0.131875
				H → L + 2	0.024436
				H → L + 3	0.580905
				H → L + 3	0.195826
				H → L + 3	0.031800
16	21541.0	464.2	0.006780555	H → L + 3	0.940740
17	23422.5	426.9	0.001838889	H - 1 → L	0.966630
18	24834.2	402.7	0.000495399	H - 2 → L	0.970025
19	25191.4	397.0	0.000949699	H - 2 → L + 2	0.015592
				H - 1 → L + 1	0.934567
				H - 1 → L + 2	0.016065
				H → L + 3	0.010893
20	25537.9	391.6	0.000008970	H - 2 → L + 1	0.042204
				H - 1 → L + 1	0.014264
				H - 1 → L + 2	0.908005

Table S3. Frank-Condon (vertical) S_0–S_n (n = 1–20) transitions of [{Y(HL)L}$_2$(dioxane)] (TD-PBE0/def2-TZVPD level; geometry was optimized at PBE0-D3BJ/def2-SVP)

State	Energy, cm-1	Wavelength, nm	Oscilator strength	Transitions	Contributions
1	14184.4	705.0	0.008511733	H → L	0.033468
				H → L	0.900561
				H → L + 1	0.044827
2	14655.3	682.3	0.007147318	H - 1 → L + 1	0.059865
				H - 1 → L	0.076881
				H - 1 → L + 1	0.766837
				H - 1 → L + 3	0.049444
3	14723.0	679.2	0.008175342	H - 1 → L + 1	0.112016
				H - 1 → L + 3	0.839225
4	14778.8	676.6	0.017375322	H - 1 → L + 2	0.030718
				H - 1 → L + 1	0.023297
				H - 1 → L + 2	0.909011
5	15375.8	650.4	0.002860398	H - 1 → L + 3	0.033845
				H → L	0.022418
				H → L + 1	0.259737
				H → L + 2	0.011880
				H → L + 3	0.600086
				H → L + 1	0.011487
				H → L + 3	0.024211
6	15525.6	644.1	0.001015699	H - 1 → L + 1	0.060207
				H - 1 → L + 2	0.811866
				H → L + 2	0.067618
				H → L + 2	0.034089
				H → L + 4	0.011250
7	15774.6	633.9	0.001637870	H → L	0.726301
				H → L + 1	0.018564
				H → L + 3	0.093279
				H → L	0.044157
				H → L	0.050165
				H → L + 1	0.045863
8	15887.0	629.4	0.000316019	H - 1 → L	0.016180
				H → L	0.107184
				H → L + 1	0.378548
				H → L + 3	0.194458
				H → L	0.052670
				H → L + 1	0.178742
				H → L + 3	0.028798
9	15964.4	626.4	0.000289192	H - 1 → L	0.507417
				H → L	0.053429
				H → L + 1	0.029694
				H → L	0.373070
				H → L + 1	0.014727
10	16246.1	615.5	0.002337747	H - 1 → L	0.017567
				H - 1 → L + 1	0.753828
				H - 1 → L + 2	0.048725
				H - 1 → L + 3	0.046890
				H - 1 → L + 1	0.091786
11	16946.5	590.1	0.003753251	H - 1 → L + 1	0.012448
				H → L	0.014420
				H → L + 1	0.226627
				H → L + 3	0.033056
				H → L	0.040936
				H → L + 1	0.553227
				H → L + 3	0.054249
				H → L + 5	0.022349
12	17220.9	580.7	0.001252318	H - 1 → L	0.436720
				H - 1 → L + 1	0.042839
				H → L	0.031117
				H → L	0.433525
				H → L + 1	0.034179
13	17618.3	567.6	0.029373532	H - 1 → L + 4	0.434232
				H - 1 → L + 5	0.014555
				H → L + 4	0.010956
				H → L + 5	0.083180

				H → L + 6	0.367087
				H → L + 7	0.045691
14	17670.8	565.9	0.128829624	H - 1 → L + 4	0.024739
				H - 1 → L + 5	0.033827
				H → L + 1	0.010974
				H → L + 4	0.053125
				H → L + 5	0.312605
				H → L + 4	0.030301
				H → L + 6	0.058986
				H → L + 5	0.065681
				H → L + 7	0.365759
15	17772.4	562.7	0.015949152	H - 1 → L + 4	0.044885
				H - 1 → L + 6	0.082589
				H - 1 → L + 4	0.743149
				H - 1 → L + 5	0.042672
				H - 1 → L + 5	0.018509
				H - 1 → L + 7	0.013521
16	17883.1	559.2	0.022105128	H - 1 → L + 5	0.016319
				H → L + 4	0.021491
				H → L + 5	0.152167
				H → L + 7	0.075622
				H → L + 1	0.016365
				H → L + 2	0.060364
				H → L + 4	0.067064
				H → L + 5	0.544939
17	17948.1	557.2	0.001298013	H → L + 2	0.020263
				H → L + 1	0.012547
				H → L + 2	0.871473
				H → L + 5	0.057164
18	18225.6	548.7	0.000200790	H - 1 → L + 3	0.023876
				H - 1 → L + 1	0.045612
				H - 1 → L + 3	0.895951
				H - 1 → L + 5	0.014838
19	18543.2	539.3	0.000021501	H - 1 → L + 2	0.063368
				H → L + 1	0.023435
				H → L + 2	0.873779
				H → L + 2	0.024787
20	18841.9	530.7	0.002907557	H → L + 4	0.022496
				H → L + 5	0.204172
				H → L + 7	0.045070
				H → L + 4	0.024846
				H → L + 5	0.148243
				H → L + 7	0.507117

Table S4. Frank-Condon (vertical) S_0–S_n (n = 1–20) transitions of $[Li(H^pL)]_2$ (TD-PBE0/def2-TZVPD level; geometry was optimized at PBE0-D3BJ/def2-SVPD)

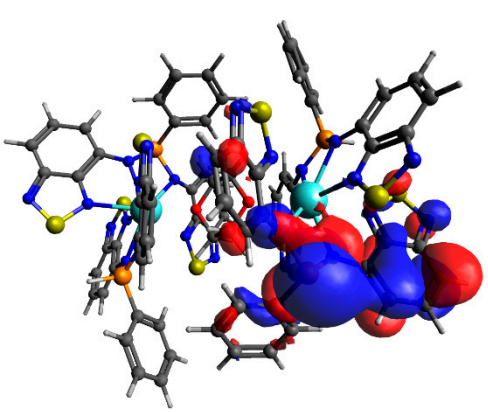
State	Energy, cm-1	Wavelength, nm	Oscilator strength	Transitions	Contributions
1	21083.5	474.3	0.030773129	H → L	0.022681
				H → L + 1	0.025985
				H → L + 1	0.024421
				H → L + 1	0.043930
				H → L + 1	0.018343
				H → L	0.039818
				H → L + 1	0.156588
				H → L + 2	0.093900
				H → L	0.229205
				H → L + 1	0.227898
				H → L + 2	0.091275
2	21286.8	469.8	0.031325643	H → L	0.024967
				H → L + 1	0.042769
				H → L + 1	0.686780
				H → L + 1	0.012785
				H → L	0.123102
				H → L + 1	0.042934
				H → L + 2	0.030600
3	21445.9	466.3	0.057683514	H → L + 2	0.042149
				H → L	0.027390
				H → L	0.076149
				H → L	0.048384
				H → L + 2	0.011726
				H → L + 2	0.060410
				H → L	0.110645
				H → L + 1	0.018059
				H → L + 2	0.169538
				H → L + 2	0.118443
				H → L	0.163133
				H → L + 1	0.015616
				H → L + 2	0.122342
4	21494.3	465.2	0.085704878	H → L + 2	0.038186
				H → L	0.043881
				H → L	0.226692
				H → L	0.239218
				H → L	0.012870
				H → L + 2	0.016720
				H → L + 2	0.018174
				H → L	0.099503
				H → L + 1	0.276916
5	21713.7	460.5	0.003070963	H → L + 1	0.010481
				H → L + 2	0.026379
				H → L + 2	0.032432
				H → L + 2	0.044472
				H → L + 2	0.011559
				H → L + 2	0.049401
				H → L + 1	0.269930
				H → L + 2	0.524016
6	22033.4	453.9	0.065837967	H → L + 2	0.063834
				H → L + 2	0.552637
				H → L + 2	0.122672
				H → L + 1	0.067490
				H → L + 2	0.159615
7	22217.5	450.1	0.003341159	H → L + 2	0.016661
				H → L + 2	0.218861
				H → L + 2	0.039496
				H → L + 2	0.597845
				H → L	0.070243
				H → L + 1	0.029007
8	22487.6	444.7	0.000035694	H → L + 1	0.010031
				H → L + 1	0.036442
				H → L	0.727782
				H → L + 1	0.028887
				H → L + 2	0.018912

				H → L + 2	0.010553
				H → L	0.151157
9	23077.7	433.3	0.004482217	H → L	0.044117
				H → L	0.452756
				H → L	0.365743
				H → L	0.030696
				H → L	0.057507
				H → L	0.018447
10	23562.8	424.4	0.004329880	H → L	0.026924
				H → L	0.214540
				H → L	0.010027
				H → L	0.549384
				H → L	0.040374
				H → L	0.132952
11	24489.8	408.3	0.000309616	H → L	0.012939
				H → L	0.026265
				H → L + 2	0.011029
				H → L	0.052201
				H → L + 1	0.701037
				H → L + 2	0.104774
				H → L + 1	0.065635
12	24724.6	404.5	0.001001486	H → L + 1	0.794521
				H → L + 1	0.117699
				H → L	0.042475
				H → L + 1	0.019704
13	24824.7	402.8	0.002204527	H → L	0.528649
				H → L	0.027572
				H → L	0.211760
				H → L + 1	0.107831
				H → L + 2	0.065891
14	24908.8	401.5	0.000128782	H → L	0.092351
				H → L + 1	0.100380
				H → L + 2	0.017018
				H → L	0.041764
				H → L + 1	0.028260
				H → L + 2	0.631424
				H → L + 2	0.054745
15	25522.8	391.8	0.006278843	H → L + 1	0.793026
				H → L + 2	0.066671
				H → L + 2	0.065459
				H → L + 1	0.035385
16	25818.6	387.3	0.000076609	H → L + 1	0.040574
				H → L + 2	0.840448
				H → L + 1	0.029517
				H → L + 2	0.039288
				H → L + 2	0.037576
17	29883.7	334.6	0.000740007	H → L + 3	0.014223
				H → L + 3	0.171428
				H → L + 3	0.758512
				H → L + 4	0.027502
18	30533.6	327.5	0.018248756	H → L + 3	0.016820
				H → L + 4	0.027864
				H → L + 3	0.124763
				H → L + 4	0.623507
				H → L + 3	0.028904
				H → L + 4	0.149244
19	31401.3	318.5	0.013405933	H → L + 3	0.565301
				H → L + 3	0.165951
				H → L + 4	0.020210
				H → L + 3	0.048549
				H → L + 4	0.181587
20	31481.4	317.6	0.004412492	H → L + 4	0.021587
				H → L + 3	0.030369
				H → L + 4	0.207387
				H → L + 3	0.023545
				H → L + 4	0.169687
				H → L + 3	0.074259
				H → L + 4	0.466540

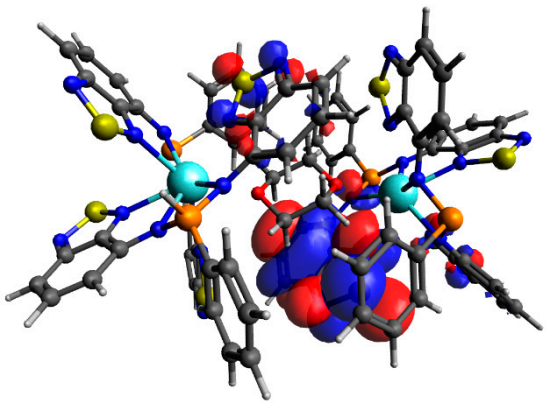
Table S5. Frank-Condon (vertical) S_0–S_n (n = 1–20) transitions of [Li(H^NL)(thf)$_2$] (TD-PBE0/def2-TZVPD level; geometry was optimized at PBE0-D3BJ/def2-SVPD)

State	Energy, cm-1	Wavelength, nm	Oscilator strength	Transitions	Contributions
1	17559.4	569.5	0.084958137	H → L	0.069454
				H → L + 1	0.914984
2	18408.1	543.2	0.004022390	H - 1 → L	0.011584
				H → L	0.918922
				H → L + 1	0.066421
3	21033.5	475.4	0.088083944	H - 2 → L	0.011969
				H - 1 → L	0.958975
4	22977.2	435.2	0.000672731	H - 2 → L + 1	0.056324
				H - 1 → L + 1	0.928511
5	26488.5	377.5	0.002904644	H - 2 → L	0.971147
				H - 1 → L	0.012185
6	28135.4	355.4	0.001331102	H - 2 → L + 1	0.918142
				H - 1 → L + 1	0.059644
7	29215.8	342.3	0.002369214	H - 1 → L + 2	0.016174
				H → L + 2	0.963139
8	31186.2	320.7	0.001786021	H - 1 → L + 3	0.025770
				H → L + 3	0.953882
9	32657.0	306.2	0.001509184	H → L + 4	0.777959
				H → L + 5	0.106117
				H → L + 6	0.020777
				H → L + 7	0.028210
				H → L + 9	0.028811
				H → L + 10	0.010768
10	33772.4	296.1	0.042114531	H - 1 → L + 2	0.951557
				H → L + 2	0.017738
11	34885.7	286.7	0.011577244	H - 3 → L	0.014302
				H - 3 → L + 1	0.254314
				H - 1 → L + 3	0.047114
				H → L + 4	0.027101
				H → L + 5	0.084337
				H → L + 6	0.015499
				H → L + 7	0.127628
				H → L + 10	0.021329
				H → L + 11	0.261699
				H → L + 13	0.102503
12	34930.4	286.3	0.004731419	H - 3 → L + 1	0.063411
				H → L + 4	0.092204
				H → L + 5	0.110396
				H → L + 6	0.104243
				H → L + 7	0.275315
				H → L + 8	0.221513
				H → L + 10	0.014525
				H → L + 11	0.035083
				H → L + 13	0.028961
13	35329.6	283.0	0.029141603	H - 3 → L + 1	0.020133
				H - 1 → L + 3	0.844963
				H → L + 3	0.026002
				H → L + 5	0.013676
				H → L + 11	0.010242
14	35667.0	280.4	0.001639452	H - 3 → L + 1	0.024797
				H - 1 → L + 3	0.011467
				H → L + 4	0.067410
				H → L + 5	0.475726
				H → L + 7	0.089103
				H → L + 8	0.123380
				H → L + 9	0.066813
				H → L + 10	0.039074
				H → L + 12	0.026859
				H → L + 14	0.013069
				H → L + 15	0.016860
15	36279.1	275.6	0.053588994	H - 6 → L	0.225627
				H - 5 → L	0.184655
				H - 4 → L	0.176234
				H - 3 → L + 1	0.014082

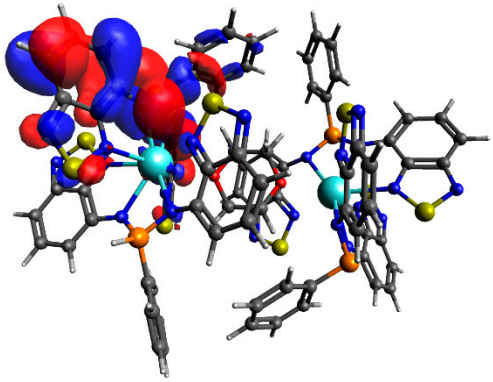
				H - 2 → L + 10	0.016712
				H - 1 → L + 3	0.010156
				H - 1 → L + 9	0.039020
				H - 1 → L + 10	0.142046
				H → L + 6	0.095199
				H → L + 7	0.017313
16	36396.6	274.8	0.043785282	H - 6 → L	0.028974
				H - 5 → L	0.049203
				H - 4 → L	0.027303
				H - 3 → L	0.019616
				H - 3 → L + 1	0.048869
				H - 1 → L + 10	0.016171
				H → L + 5	0.015848
				H → L + 6	0.616843
				H → L + 7	0.070518
				H → L + 13	0.032202
17	36970.5	270.5	0.001065059	H - 5 → L	0.072172
				H - 4 → L	0.034076
				H - 3 → L	0.717392
				H → L + 5	0.029251
				H → L + 6	0.015296
				H → L + 9	0.022026
				H → L + 10	0.053321
				H → L + 11	0.012516
18	37090.1	269.6	0.003882443	H - 4 → L	0.014740
				H - 3 → L	0.089700
				H - 3 → L + 1	0.024181
				H - 1 → L + 5	0.019788
				H → L + 4	0.012581
				H → L + 5	0.115545
				H → L + 7	0.060653
				H → L + 8	0.010336
				H → L + 9	0.347430
				H → L + 10	0.181526
				H → L + 12	0.061844
				H → L + 14	0.013170
				H → L + 15	0.010016
19	37307.4	268.0	0.001095629	H - 6 → L	0.166476
				H - 5 → L	0.034942
				H - 4 → L	0.692565
				H - 4 → L + 1	0.010065
				H - 3 → L	0.049010
				H - 1 → L + 10	0.010459
20	37363.7	267.6	0.002666824	H - 2 → L + 5	0.019229
				H - 1 → L + 4	0.604129
				H - 1 → L + 5	0.267175
				H - 1 → L + 9	0.023392
				H → L + 5	0.024868
				H → L + 10	0.010486



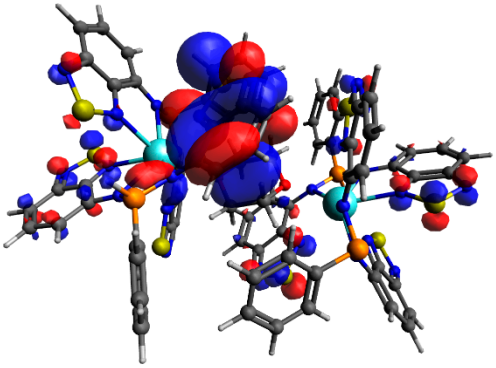
HOMO



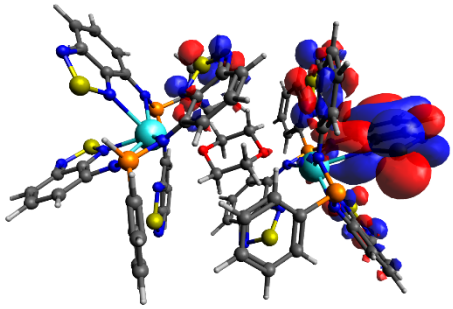
LUMO



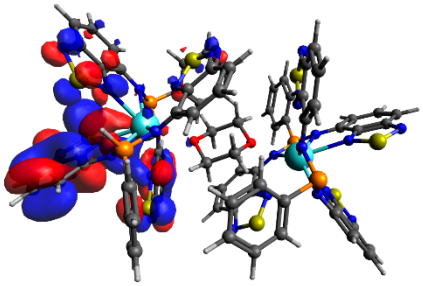
HOMO–1



LUMO+1



LUMO+3



LUMO+2

Figure S3. Frontier molecular orbitals for the complexes [{Y(HL)L}$_2$(dioxane)] at TD-PBE0/def2-TZVPD level (isovalue = 0.03). HOMO is localized at P and one of N-Btd units of the L^{2-} ligand, LUMO – at one of N-Btd units of the LH^- ligand binded to the same Y. HOMO–1 is centrosymmetric with HOMO, LUMO–1 is centrosymmetric with LUMO. LUMO+2 and LUMO+3 are centrosymmetric with each other and are located on N-Btds of the LH^- ligands.

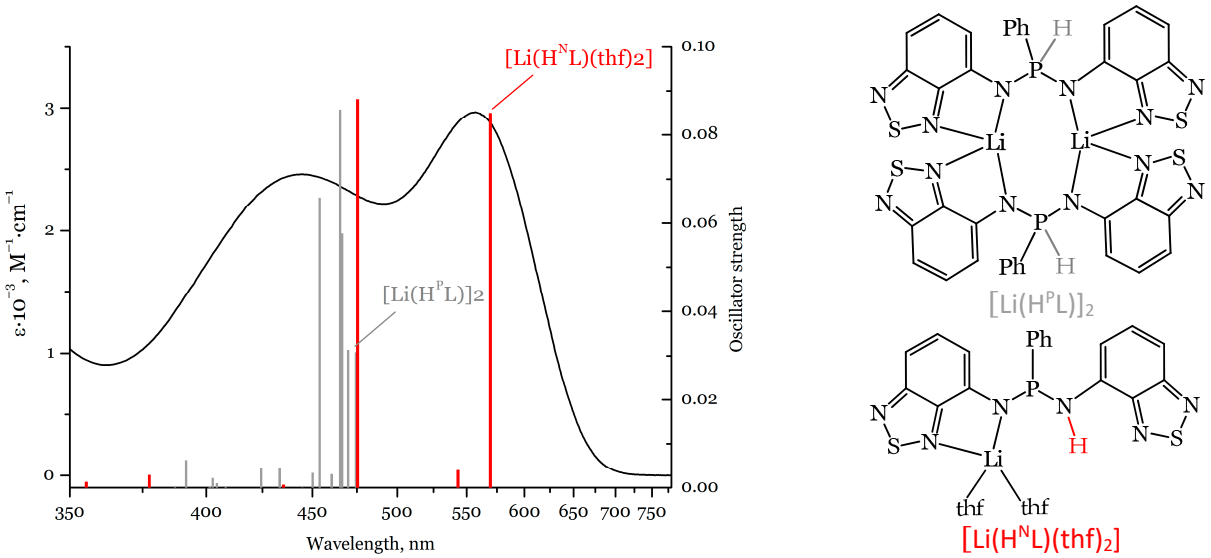
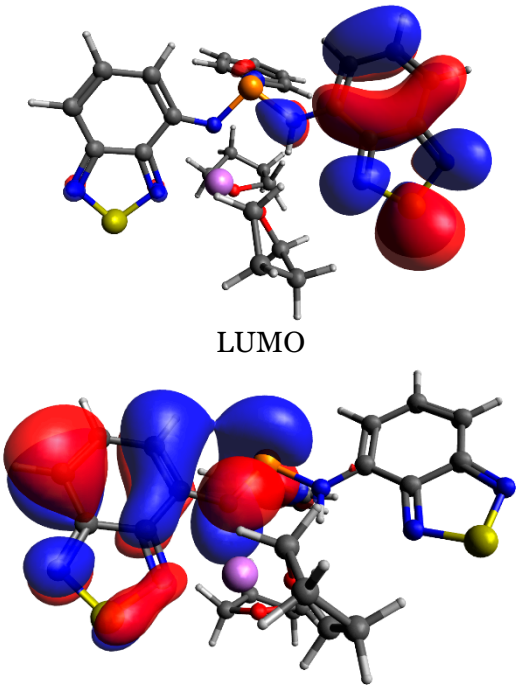


Figure S4. Comparison of the computed electronic transitions for the models $[Li(H^PL)]_2$ (gray bars) and $[Li(H^NL)(thf)_2]$ (red bars) with different positions of the proton. The data for $[Li(H^NL)(thf)_2]$ give a better agreement with the experimental spectrum of solution **2** in thf (black curve).



LUMO

HOMO

Figure S5. Frontier molecular orbitals for $[Li(H^NL)(thf)_2]$ at TD-PBE0/def2-TZVPD level (isovalue = 0.03).

Table S6. Crystal data and structure refinement for the compounds.

Identification code	**2**$_2$·Et_2O	**5**$_2$(dioxane)·dioxane	**4**$_2$·Et_2O	**6**·hexane	**6**·1.5thf
Empirical formula	$C_{40}H_{34}Li_2N_{12}OP_2S_4$	$C_{80}H_{62}N_{24}O_4P_4S_8Y_2$	$C_{52}H_{66}N_{14}O_{1.35}P_2S_4Si_4Y_2$	$C_{58}H_{68}LiN_{12}O_{4.44}P_2S_4Y$	$C_{58}H_{66}LiN_{12}O_{5.5}P_2S_4Y$
Formula weight	902.85	1981.71	1389.06	1290.27	1305.25
Temperature/K	150(2)	150(2)	150(2)	120(2)	150(2)
Space group	*C*2/*c*	*P*–1	*P*–1	$C222_1$	*C*2
a/Å	16.2210(16)	12.7016(5)	11.3563(15)	17.1047(13)	20.4710(6)
b/Å	16.2345(16)	13.4532(6)	14.0602(17)	21.2579(18)	17.6930(4)
c/Å	16.4504(17)	15.2339(6)	20.387(3)	17.3786(11)	17.2725(5)
α/°	90	95.2940(10)	86.742(4)	90	90
β/°	106.737(3)	110.9220(10)	77.207(4)	90	97.1100(10)
γ/°	90	117.9530(10)	89.549(4)	90	90
Volume/Å^3	4148.5(7)	2038.69(15)	3169.2(7)	6319.0(8)	6207.9(3)
Z	4	1	2	4	4
ρ_{calc}g/cm^3	1.446	1.614	1.456	1.356	1.397
μ/mm^{-1}	0.357	1.769	2.130	1.161	1.184
F(000)	1864.0	1008.0	1430.0	2686.0	2712.0
Crystal size/mm^3	0.08 × 0.06 × 0.06	0.15 × 0.06 × 0.04	0.2 × 0.12 × 0.08	0.23 × 0.15 × 0.06	0.2 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.874 to 48.83	5.218 to 52.836	2.902 to 48.814	4.492 to 48.81	4.908 to 51.364
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -19 ≤ l ≤ 15	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23	-19 ≤ h ≤ 17, -24 ≤ k ≤ 24, -19 ≤ l ≤ 20	-24 ≤ h ≤ 24, 0 ≤ k ≤ 21, 0 ≤ l ≤ 21
Reflections collected	9525	33857	30088	28004	6021
Independent reflections	3409 [R_{int} = 0.0620, R_{sigma} = 0.0763]	8331 [R_{int} = 0.0455, R_{sigma} = 0.0446]	10375 [R_{int} = 0.0541, R_{sigma} = 0.0755]	5203 [R_{int} = 0.0615, R_{sigma} = 0.0541]	6021 [R_{int} = 0.0811, R_{sigma} = 0.0624]
Data/restraints/parameters	3409/0/280	8331/0/553	10375/38/742	5203/59/384	6021/53/726
Goodness-of-fit on F^2	1.023	1.013	1.032	1.024	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0587, wR_2 = 0.1445	R_1 = 0.0355, wR_2 = 0.0774	R_1 = 0.0443, wR_2 = 0.0859	R_1 = 0.0347, wR_2 = 0.0843	R_1 = 0.0491, wR_2 = 0.1225
Final R indexes [all data]	R_1 = 0.1038, wR_2 = 0.1683	R_1 = 0.0549, wR_2 = 0.0842	R_1 = 0.0815, wR_2 = 0.0965	R_1 = 0.0422, wR_2 = 0.0878	R_1 = 0.0606, wR_2 = 0.1278
Largest diff. peak/hole / e Å^{-3}	0.68/-0.40	0.34/-0.56	0.67/-0.44	0.48/-0.26	0.67/-0.45
Flack parameter				0.166(7)	0.448(14)

^{1}H and ^{31}P NMR spectra of the compounds

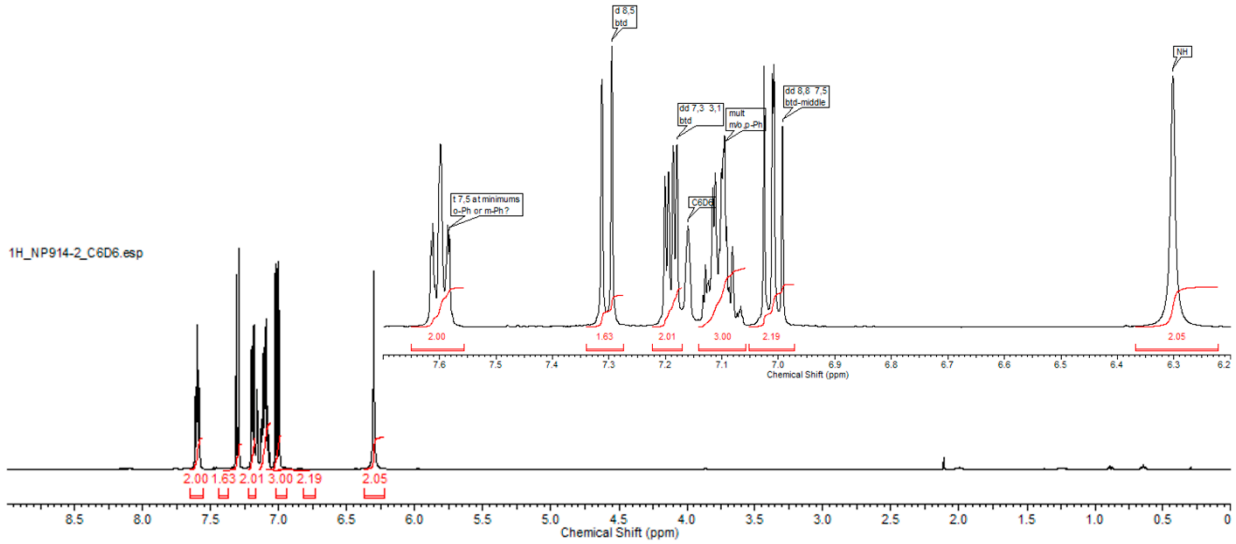


Figure S6. ^{1}H NMR spectrum of H_2L, solution in C_6D_6. The inset shows low-field part of the spectrum.

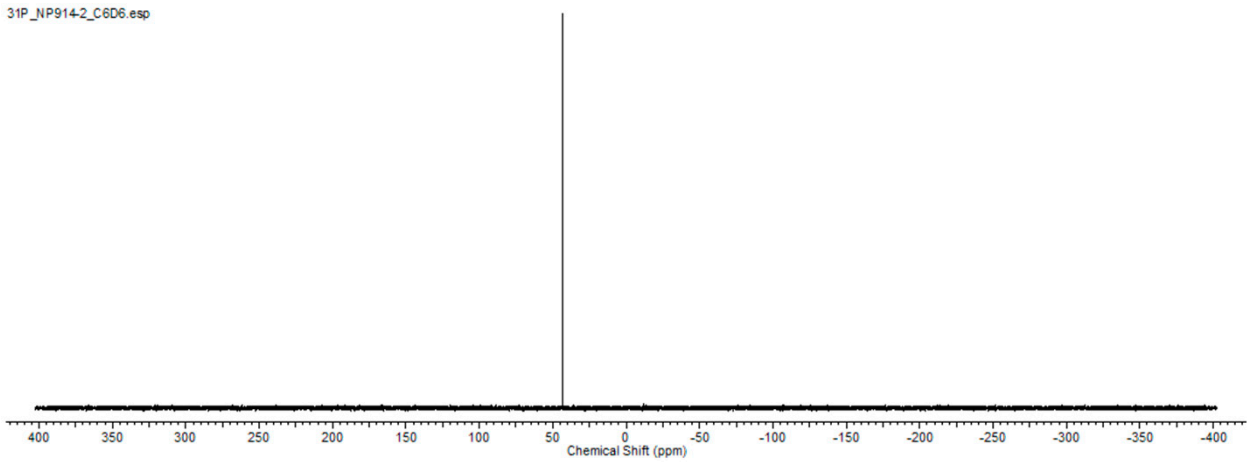


Figure S7. ^{31}P NMR spectrum of H_2L, solution in C_6D_6.

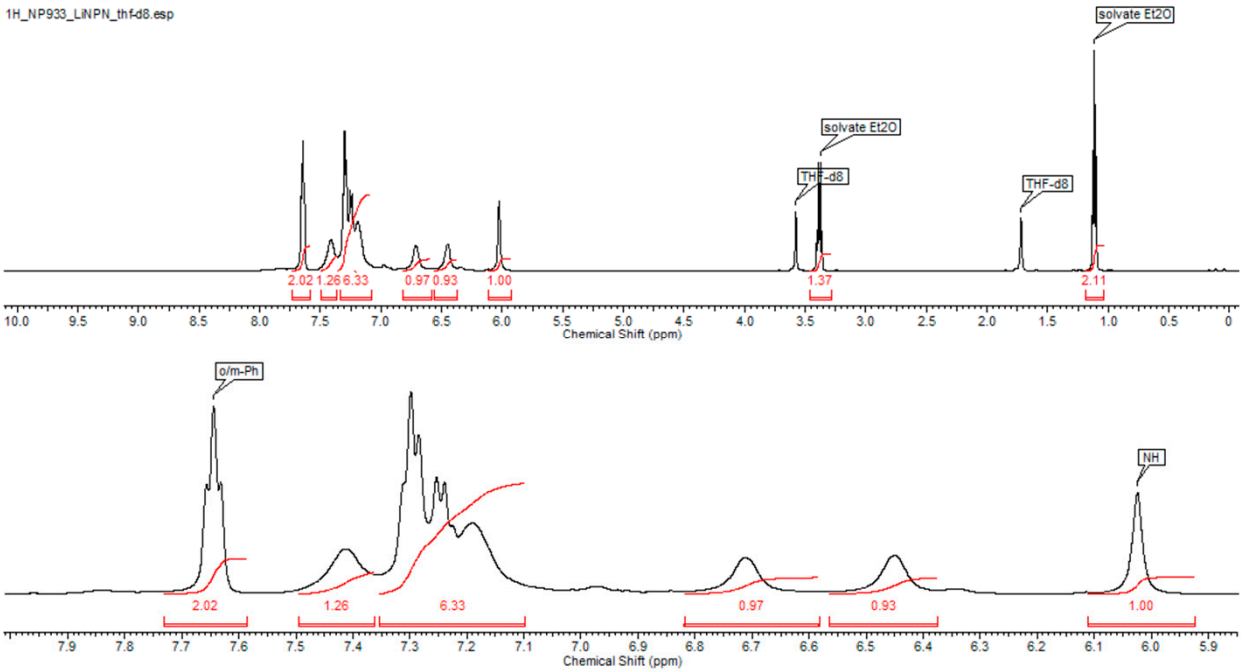


Figure S8. (top) ^{1}H NMR spectrum of [Li(HL)]$_2$ (**2**$_2$), solution in thf-d8; (bottom) low-field part of the spectrum.

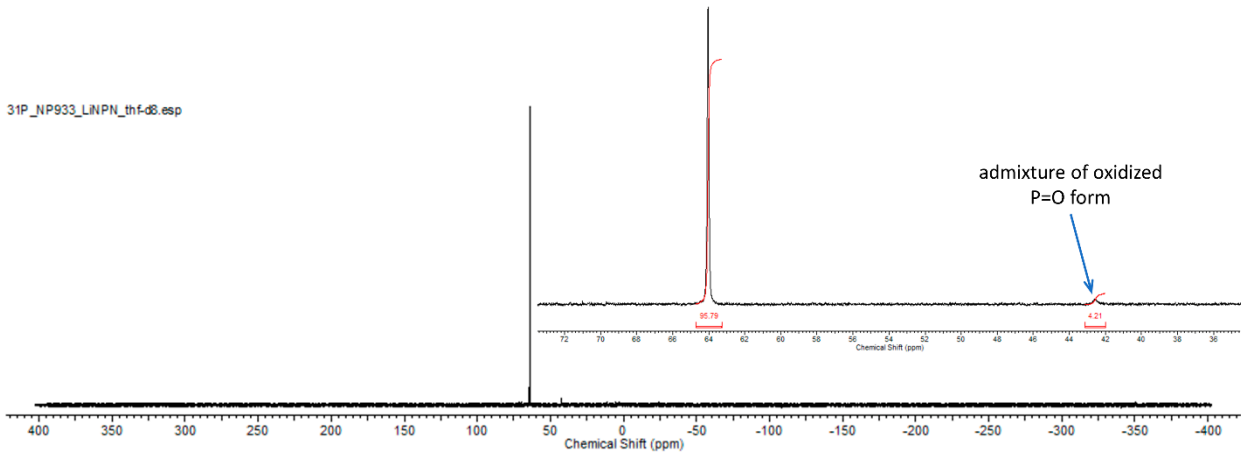


Figure S9. ^{31}P NMR spectrum of [Li(HL)]$_2$ (**2**$_2$), solution in thf-d8; the inset shows enlarged central part of the spectrum.

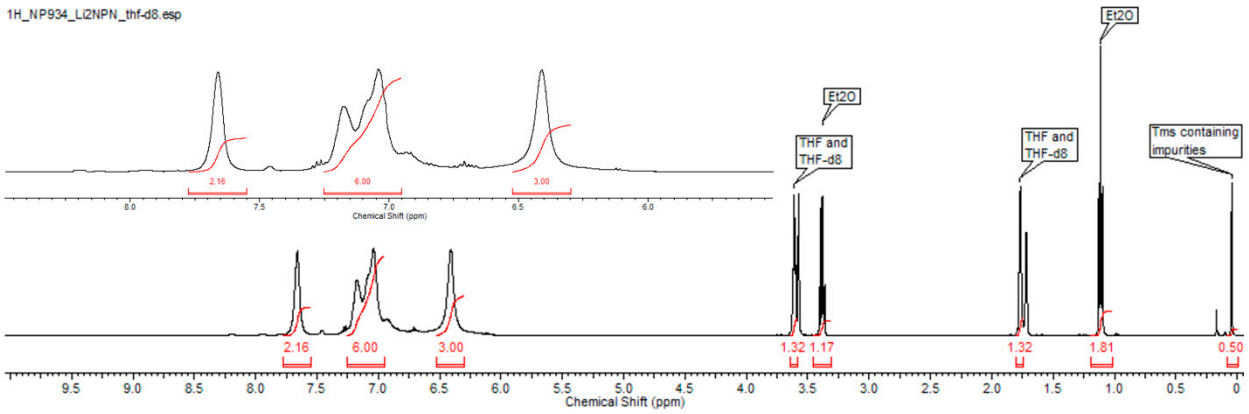


Figure S10. ^{1}H NMR spectrum of Li_2L (**3**), solution in thf-d8; the inset shows enlarged low-field part of the spectrum.

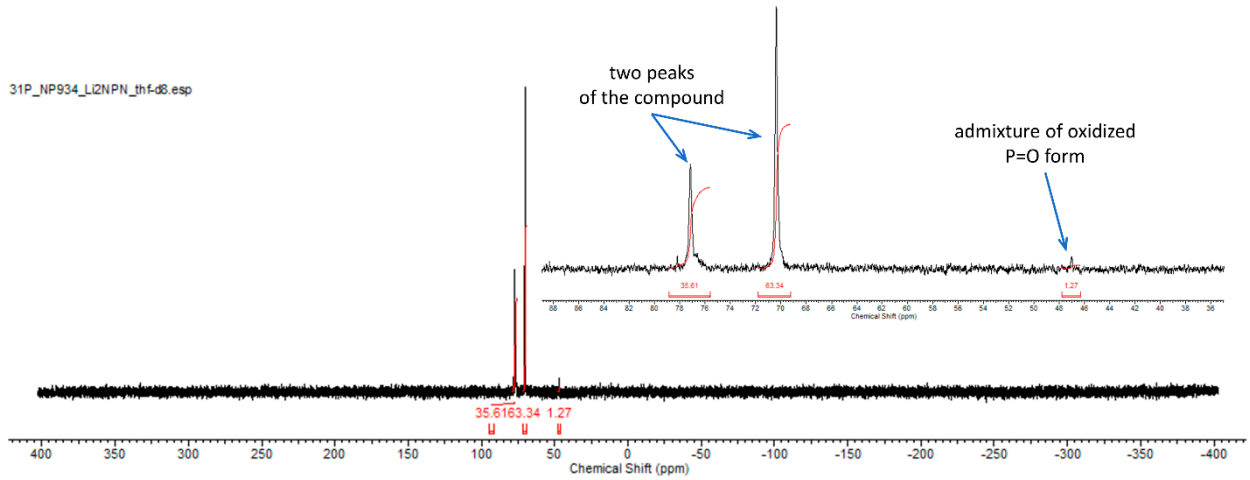


Figure S11. ^{31}P NMR spectrum of Li_2L (**3**), solution in thf-d8; the inset shows enlarged central part of the spectrum.

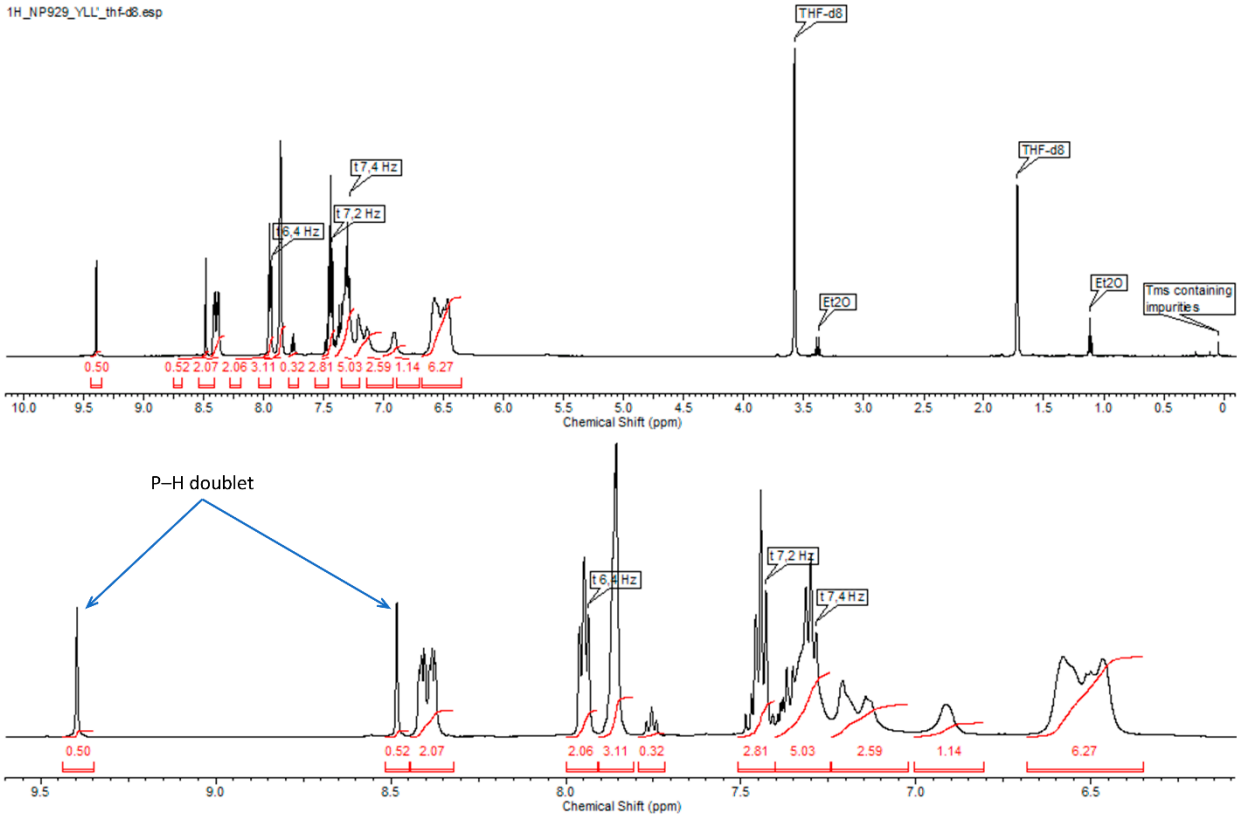


Figure S12. (top) ^{1}H NMR spectrum of [Y(L)(HL)] (**5**), solution in thf-d8; (bottom) enlarged low-field part of the spectrum.

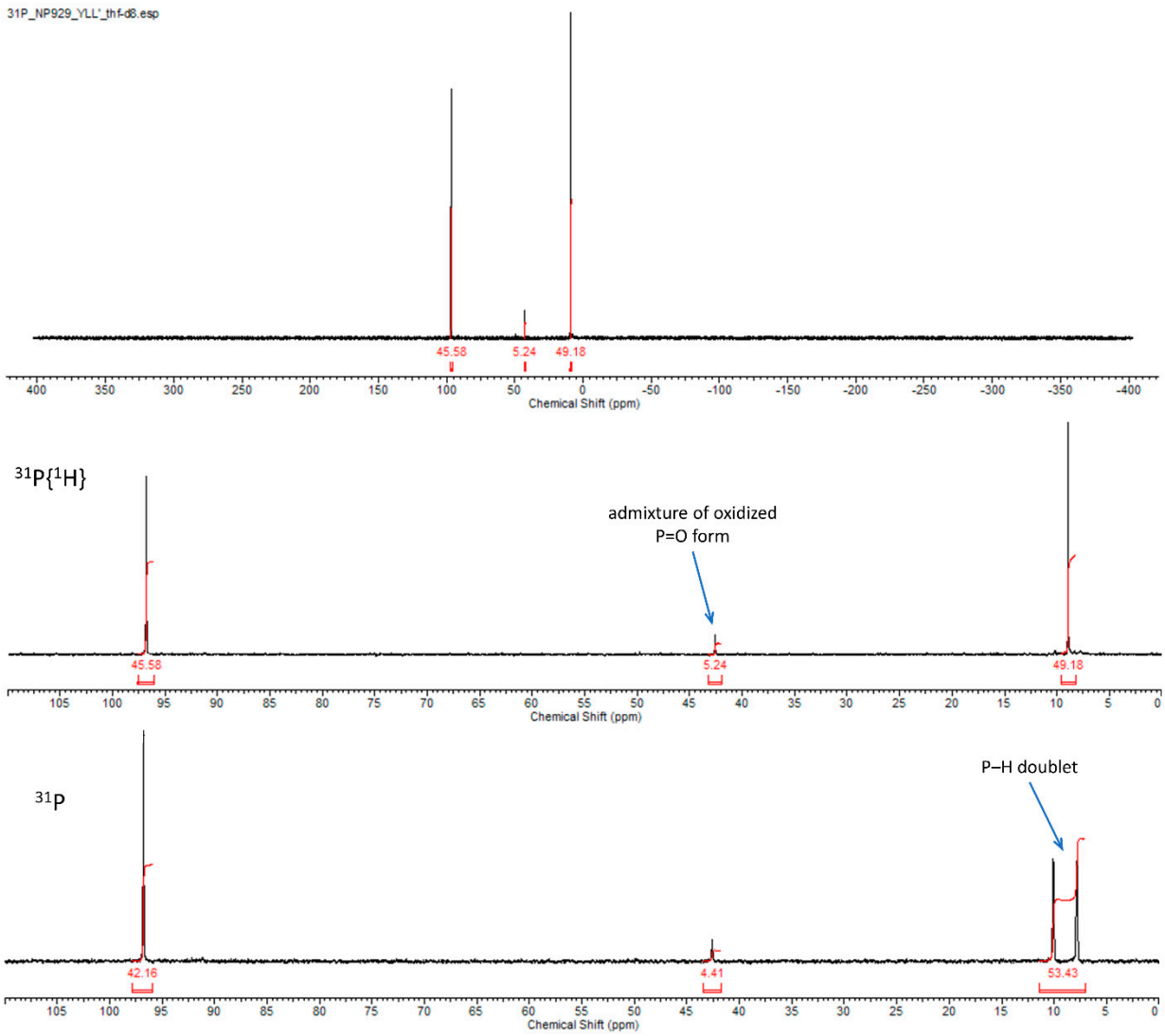


Figure S13. (top) $^{31}P\{^{1}H\}$ NMR spectrum of [Y(L)(HL)] (**5**), solution in thf-d8; (bottom) comparison of peaks in ^{31}P and $^{31}P\{^{1}H\}$ spectra.

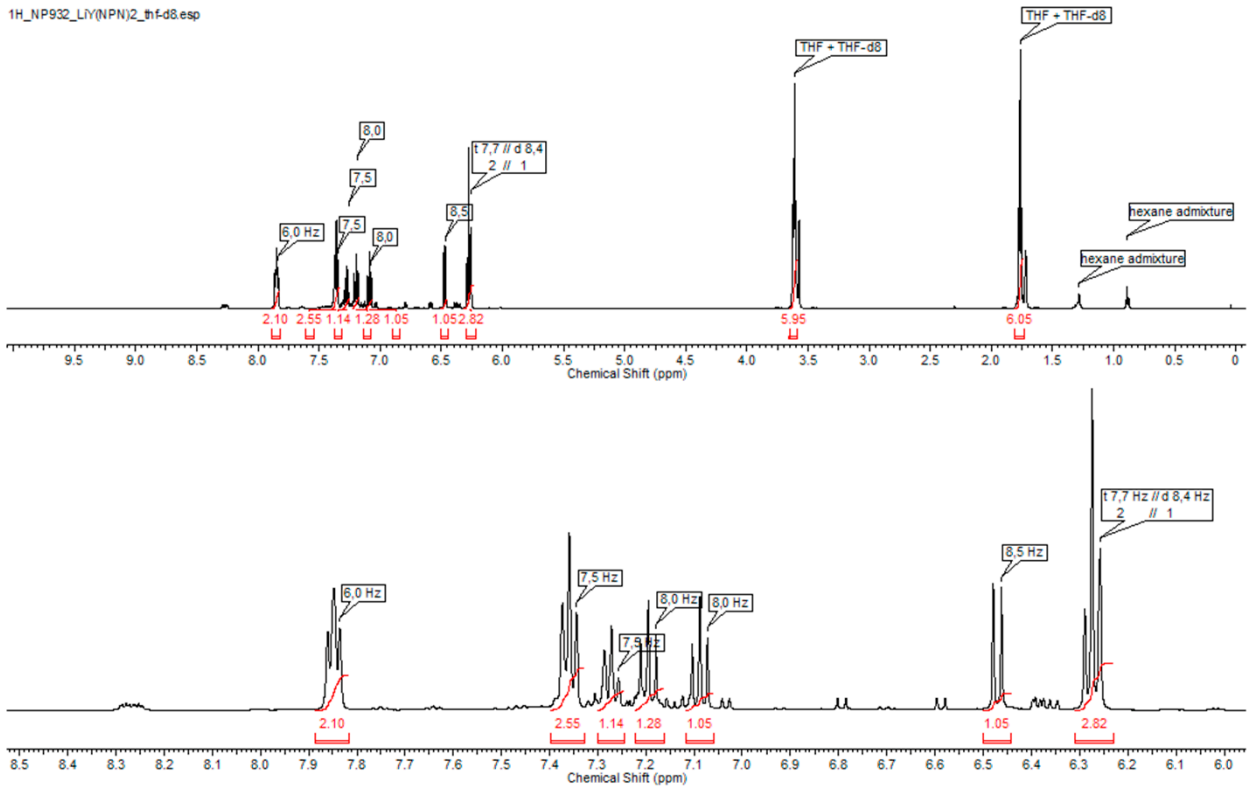


Figure S14. (top) ^{1}H NMR spectrum of [Li(thf)$_4$][YL$_2$] (**6**), solution in thf-d8; (bottom) enlarged view of the low-field part of the spectrum.

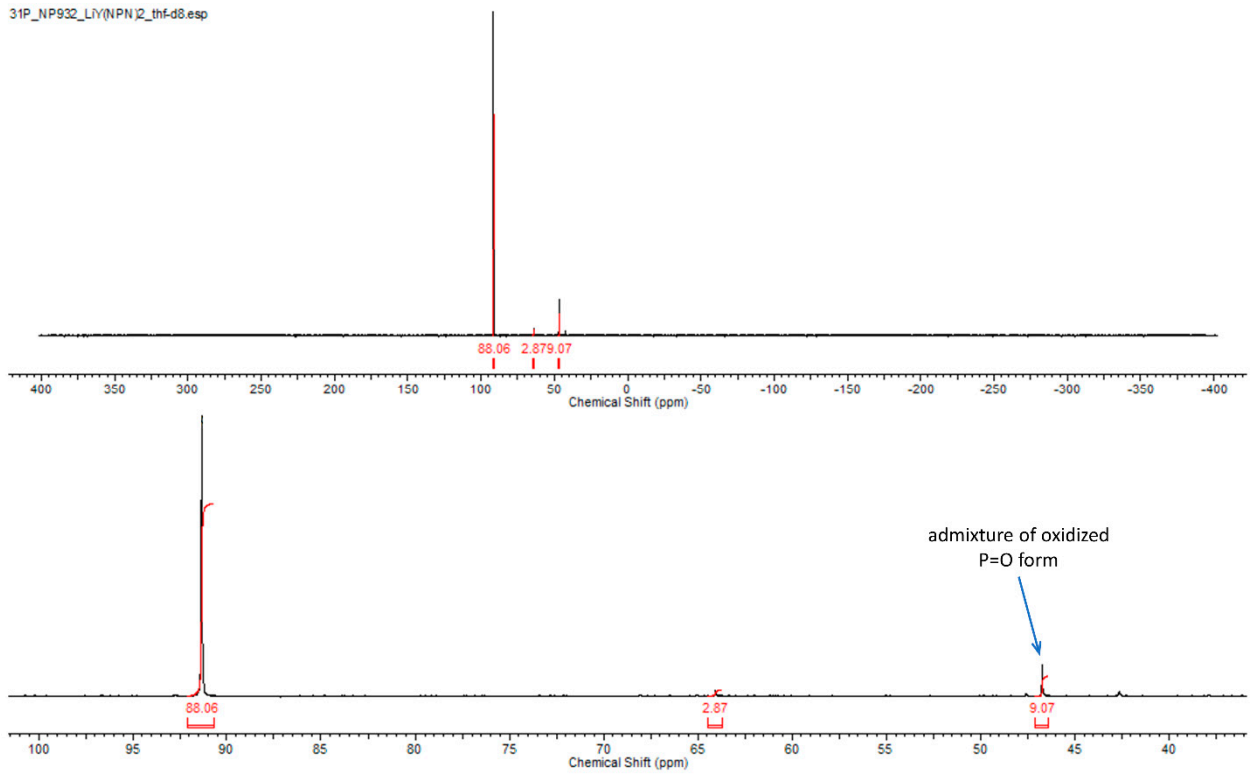


Figure S15. (top) ^{31}P NMR spectrum of [Li(thf)$_4$][YL$_2$] (**6**), solution in thf-d8; (bottom) enlarged view of the central part of the spectrum.

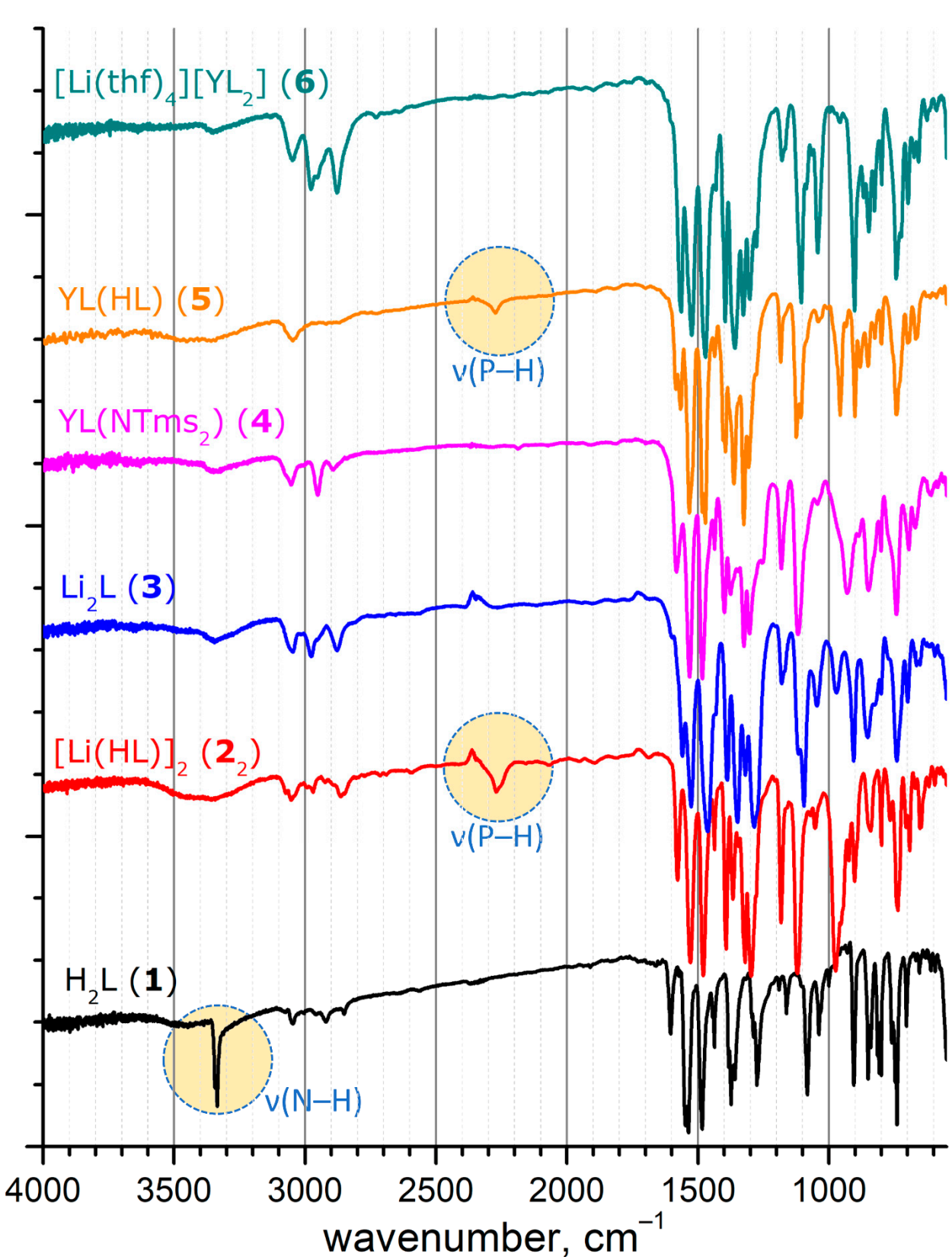


Figure S16. IR spectra of the compounds under study (4000–550 cm⁻¹), in KBr pellets. Characteristic NH and PH peaks are highlighted.

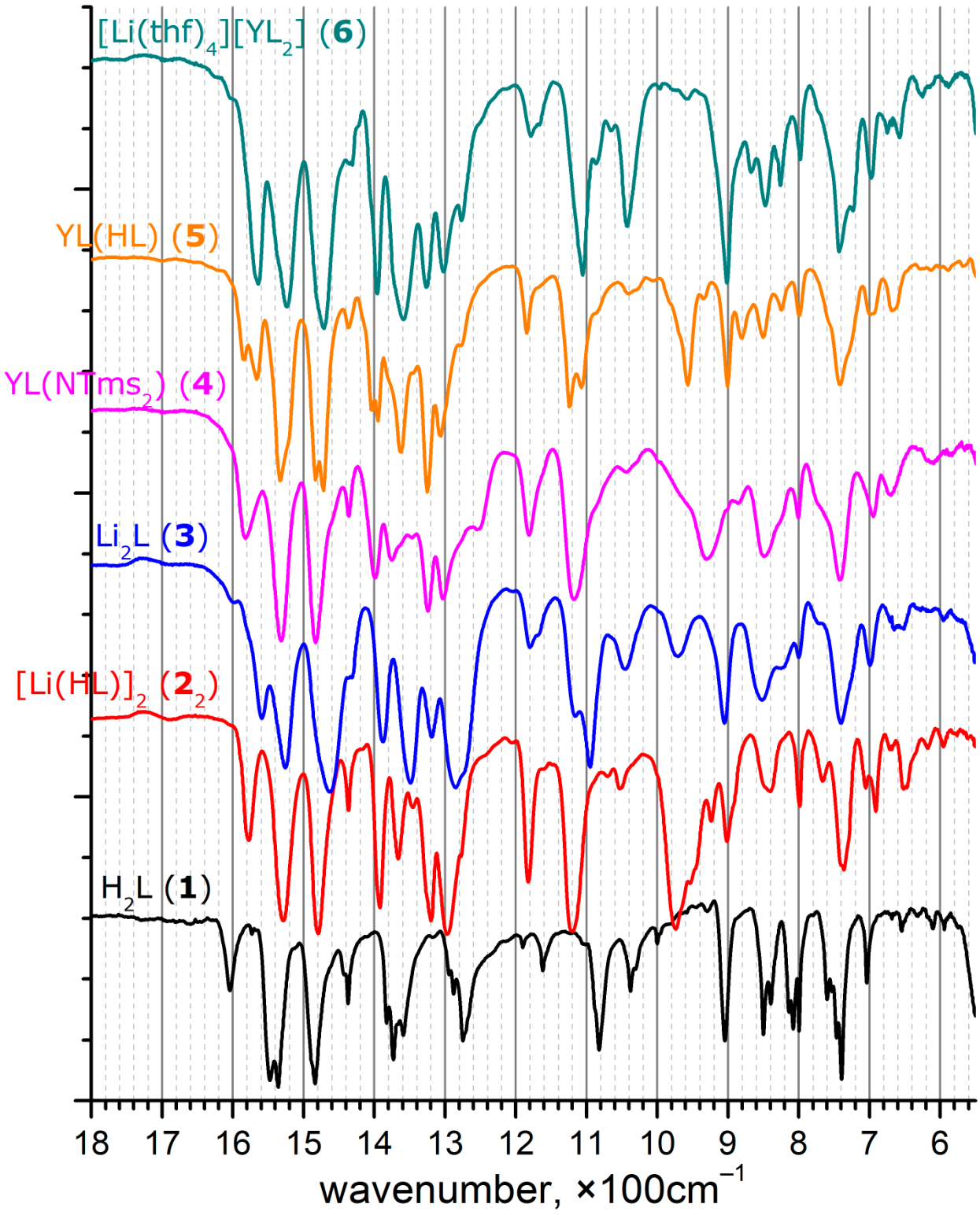


Figure S17. Fingerprint region of the IR spectra above (1800–550 cm^{-1}), in KBr pellets.