Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

A (2-(Naphthalen-2-yl)phenyl)rhodium(I) Complex formed by a Proposed Intramolecular 1,4-*Ortho*-to-*Ortho'* Rh Metal-atom Migration and its Efficacy as an Initiator in the Stereospecific Polymerization of Phenylacetylene

Nicholas Sheng Loong Tan, Gareth L. Nealon, Jason M. Lynam, Alexandre N. Sobolev, Matthew R. Rowles, Mark I. Ogden, Massimiliano Massi, and Andrew B. Lowe

Computational Data

Collated energies, xyz coordinates and vibration spectra (first 50 lines)

III

SCF Energy (au) (RI)BP86/SV(P)		-2331.1847186240
SCF Energy (au) PBE0/def2-TZVPP		-2330.873811623
SCF Energy (au) PBE0/def2-TZVPP		-2330.8903011896 (CH_2Cl_2 correction)
Zero Point Energy (au)		0.5814117
Chemical potential (kJ mol^{-1})		1325.00
Dispersion correction (au) PBE0/def2-TZVPP		-0.13223627

xyz coordinates
77

Rh	0.80895	0.83402	0.52686
P	-0.45035	0.00267	-1.30070
C	-2.03189	-0.95567	-1.11866
C	-2.09403	-1.95977	-0.12520
H	-1.24533	-2.10880	0.56048
C	-3.23325	-2.76528	0.01630
H	-3.28970	-3.54487	0.79129
F	-5.42352	-3.32176	-0.70464
C	-4.32385	-2.55652	-0.83855
C	-4.29720	-1.56758	-1.83051
H	-5.17221	-1.43083	-2.48489
C	-3.14806	-0.77221	-1.96664
H	-3.13054	0.00088	-2.75090
C	-0.94811	1.40497	-2.41426
C	-1.96168	2.29842	-1.99040
H	-2.50181	2.11409	-1.04730
C	-2.30422	3.42096	-2.75791
H	-3.09789	4.11506	-2.44046
F	-1.93723	4.74084	-4.69412
C	-1.61445	3.66253	-3.95569
C	-0.59960	2.80571	-4.39752
H	-0.07761	3.02458	-5.34194
C	-0.27356	1.67793	-3.62386
H	0.52077	1.00201	-3.97758
C	0.50697	-1.10671	-2.45390
C	1.90991	-1.20858	-2.33121
H	2.42096	-0.66014	-1.52384
C	2.65837	-2.01422	-3.20516

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H          3.75249       -2.09948       -3.11594
F          2.69771       -3.50740       -5.04498
C          1.98896       -2.73111       -4.20526
C          0.59508       -2.66307       -4.34666
H          0.10058       -3.25084       -5.13581
C         -0.13788       -1.85060       -3.46914
H         -1.23363       -1.80654       -3.57581
C         -0.19843       -0.22830        2.00206
C          1.39036        2.34480        2.00058
H          0.69833        2.39196        2.85494
C          2.46522        1.44795        1.83517
H          2.77218        0.64949        2.52702
C          3.37147        2.05601        0.73663
H          4.39934        1.65240        0.67280
C          3.19470        3.57560        1.02894
H          3.61460        4.22578        0.22798
C          1.63970        3.49894        1.00121
H          1.06513        4.42909        1.17048
C          1.41040        2.78639       -0.35568
H          0.72667        3.15657       -1.13374
C          2.48916        1.90390       -0.52880
H          2.83385        1.47154       -1.47927
C         -1.57718       -1.49049        4.20512
C         -0.32817       -1.92589        3.80051
C          0.37405       -1.31052        2.70943
C         -1.48450        0.25952        2.45983
C         -2.18568       -0.37679        3.55623
H         -2.10750       -1.99102        5.03301
H          0.13858       -2.78765        4.30761
C          1.72632       -1.86035        2.39128
C         -2.10501        1.40818        1.87226
C         -3.45370        0.13077        3.97382
C          4.30196       -2.93827        1.82682
C          3.94234       -2.61348        3.14653
C          2.66908       -2.08860        3.42411
C          2.10560       -2.19618        1.07107
C          3.37360       -2.73281        0.79153
H          5.29787       -3.35815        1.60774
H          4.66071       -2.76778        3.96932
H          2.40229       -1.82761        4.46215
H          1.37438       -2.06969        0.25805
H          3.63157       -3.00706       -0.24535
C         -4.02463        1.23862        3.36224
H         -3.97231       -0.37363        4.80748
C         -3.33587        1.88950        2.30254
H         -1.54769        1.92169        1.06809
H         -3.77764        2.78218        1.82804
H         -5.00162        1.62027        3.70291
H          3.59733        3.88044        2.02184

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                        0.00         0.00000        -       -
```

2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	7.59	0.01209	YES	YES
8	a	15.51	0.10037	YES	YES
9	a	25.50	0.02614	YES	YES
10	a	27.27	0.02920	YES	YES
11	a	32.79	0.01369	YES	YES
12	a	34.87	0.03667	YES	YES
13	a	39.38	0.04786	YES	YES
14	a	41.58	0.10366	YES	YES
15	a	49.09	0.23461	YES	YES
16	a	52.80	0.43652	YES	YES
17	a	54.42	0.23562	YES	YES
18	a	58.23	0.02264	YES	YES
19	a	65.55	0.27902	YES	YES
20	a	68.82	0.49504	YES	YES
21	a	77.76	0.03226	YES	YES
22	a	80.37	0.28320	YES	YES
23	a	95.65	0.32940	YES	YES
24	a	121.11	0.61179	YES	YES
25	a	127.42	1.15150	YES	YES
26	a	137.91	0.36472	YES	YES
27	a	146.68	1.04575	YES	YES
28	a	158.80	1.18253	YES	YES
29	a	162.20	0.27064	YES	YES
30	a	173.68	0.03100	YES	YES
31	a	192.00	1.32467	YES	YES
32	a	200.21	0.21556	YES	YES
33	a	210.39	0.63678	YES	YES
34	a	224.13	1.73590	YES	YES
35	a	232.85	0.46567	YES	YES
36	a	250.17	0.03803	YES	YES
37	a	262.90	0.13928	YES	YES
38	a	278.20	3.80460	YES	YES
39	a	292.51	7.21763	YES	YES
40	a	305.31	1.58583	YES	YES
41	a	310.73	0.93240	YES	YES
42	a	324.63	0.01535	YES	YES
43	a	340.33	0.97565	YES	YES
44	a	366.42	0.51061	YES	YES
45	a	398.40	5.50234	YES	YES
46	a	399.73	1.33988	YES	YES
47	a	403.54	5.83863	YES	YES
48	a	406.06	0.53744	YES	YES
49	a	406.46	0.48951	YES	YES
50	a	411.91	0.35641	YES	YES

4

SCF Energy (au) (RI)BP86/SV(P)	-2331.1618713660
SCF Energy (au) PBE0/def2-TZVPP	-2330.846059185
SCF Energy (au) PBE0/def2-TZVPP	-2330.8647999965 (CH_2Cl_2 correction)
Zero Point Energy (au)	0.5800676
Chemical potential (kJ mol^{-1})	1332.56
Dispersion correction (au) PBE0/def2-TZVPP	-0.13690915

xyz coordinates
77

Rh	-0.30893	-0.07149	-1.64389
P	0.89611	-0.23609	0.59035
C	0.08310	1.91245	-1.92432
C	-0.90298	2.80660	-1.41223
C	-0.75299	4.19945	-1.60221
H	-1.51023	4.89716	-1.20697
C	0.34820	4.71397	-2.30583
H	0.45017	5.80234	-2.45109
C	1.30738	3.83515	-2.83594
H	2.16736	4.22778	-3.40525
C	1.16693	2.44384	-2.64858
H	1.92583	1.77815	-3.09698
C	0.30087	0.86054	1.97481
C	0.21922	2.24513	1.70231
H	0.43655	2.62475	0.69202
C	-0.12523	3.16070	2.70620
H	-0.19280	4.23923	2.49640
F	-0.72894	3.55934	4.96566
C	-0.39241	2.68592	3.99698
C	-0.30757	1.32252	4.30344
H	-0.51295	0.98211	5.33030
C	0.04475	0.41575	3.28994
H	0.12686	-0.65041	3.54972
C	0.83042	-1.94099	1.32476
C	-0.38308	-2.42225	1.87383
H	-1.26516	-1.76510	1.93615
C	-0.50087	-3.74431	2.32971
H	-1.44224	-4.11697	2.76258
F	0.49607	-5.87181	2.65900
C	0.60238	-4.60286	2.22330
C	1.81149	-4.16619	1.66735
H	2.65825	-4.86607	1.59122
C	1.91758	-2.83823	1.22084
H	2.87179	-2.50366	0.78457
C	2.70991	0.18551	0.72318
C	3.34113	0.92705	-0.29566
H	2.76814	1.22789	-1.18447
C	4.68134	1.33347	-0.17570
H	5.17662	1.91937	-0.96533
F	6.67723	1.36762	1.10342
C	5.39129	0.99054	0.98036
C	4.78791	0.27033	2.02305

H	5.37041	0.03454	2.92736
C	3.44788	-0.11867	1.89235
H	2.97082	-0.66278	2.72359
C	-2.02231	2.15345	-0.71658
C	-1.97909	0.74074	-0.66912
H	-1.34127	0.35343	-2.76567
C	-3.06701	0.04337	-0.03408
C	-3.14875	-1.38302	0.05007
H	-2.33593	-1.97676	-0.38440
C	-4.21418	-2.03378	0.66260
H	-4.23712	-3.13629	0.69555
C	-5.27480	-1.28639	1.24102
H	-6.11909	-1.80479	1.72527
C	-5.23881	0.10061	1.18755
H	-6.05536	0.69553	1.63229
C	-4.16132	0.79533	0.56061
C	-4.14265	2.21967	0.50084
H	-4.97447	2.78527	0.95379
C	-3.10029	2.87868	-0.12349
H	-3.10727	3.98025	-0.16727
C	0.64188	-0.68403	-3.58881
H	0.76395	0.19744	-4.23391
C	1.51924	-1.13673	-2.59487
H	2.47896	-0.69076	-2.30296
C	1.14058	-2.61776	-2.33959
H	1.88500	-3.22491	-1.79269
C	0.74743	-3.06194	-3.77933
H	0.26582	-4.06515	-3.81331
H	1.59695	-3.01933	-4.49735
C	-0.25992	-1.89006	-3.95487
H	-0.81709	-1.80486	-4.90657
C	-1.11486	-2.05828	-2.67905
H	-2.21294	-2.02539	-2.65707
C	-0.25703	-2.51440	-1.69215
H	-0.51589	-2.92048	-0.70682

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	10.55	0.04403	YES	YES
8	a	18.58	0.05320	YES	YES
9	a	30.45	0.01542	YES	YES
10	a	30.99	0.01683	YES	YES
11	a	38.03	0.00569	YES	YES
12	a	40.22	0.15903	YES	YES
13	a	49.51	0.40306	YES	YES
14	a	55.99	0.29201	YES	YES
15	a	63.07	0.17025	YES	YES

16	a	66.68	0.10446	YES	YES
17	a	78.02	0.79650	YES	YES
18	a	79.34	0.29531	YES	YES
19	a	84.45	0.07874	YES	YES
20	a	101.93	0.95669	YES	YES
21	a	106.30	0.51204	YES	YES
22	a	122.15	1.65858	YES	YES
23	a	133.34	0.15592	YES	YES
24	a	135.19	0.12812	YES	YES
25	a	142.26	0.17421	YES	YES
26	a	156.79	0.24230	YES	YES
27	a	160.57	0.36840	YES	YES
28	a	165.02	0.16904	YES	YES
29	a	171.23	0.05847	YES	YES
30	a	192.90	0.26351	YES	YES
31	a	201.34	0.13707	YES	YES
32	a	210.94	0.26278	YES	YES
33	a	214.29	1.74860	YES	YES
34	a	218.13	4.38416	YES	YES
35	a	239.05	0.38190	YES	YES
36	a	239.45	0.61185	YES	YES
37	a	267.94	1.01674	YES	YES
38	a	285.86	0.84789	YES	YES
39	a	299.92	0.20019	YES	YES
40	a	316.53	0.04625	YES	YES
41	a	318.10	0.04192	YES	YES
42	a	319.28	1.05410	YES	YES
43	a	352.17	0.49971	YES	YES
44	a	368.18	1.95701	YES	YES
45	a	396.32	2.24848	YES	YES
46	a	397.94	2.59516	YES	YES
47	a	403.45	7.31311	YES	YES
48	a	407.32	3.78763	YES	YES
49	a	411.46	0.14305	YES	YES
50	a	417.33	3.23181	YES	YES

2a

SCF Energy (au) (RI)BP86/SV(P)	-2331.1924404700
SCF Energy (au) PBE0/def2-TZVPP	-2330.880845609
SCF Energy (au) PBE0/def2-TZVPP	-2330.8967247921 (CH_2Cl_2 correction)
Zero Point Energy (au)	0.5815712
Chemical potential (kJ mol^{-1})	1331.40
Dispersion correction (au) PBE0/def2-TZVPP	-0.13426295

xyz coordinates
77

Rh	1.30297	0.43913	0.89333
P	0.41265	-0.79658	-0.89504
C	0.51706	-0.87398	2.25772
C	-0.82204	-0.71610	2.74605
C	-1.31250	-1.58563	3.75457
H	-2.32723	-1.42678	4.15782
C	-0.53082	-2.62628	4.27115
H	-0.93316	-3.28386	5.05978
C	0.77004	-2.81540	3.77291
H	1.39774	-3.64005	4.15339
C	1.27646	-1.94513	2.79191
H	2.29804	-2.12783	2.41824
C	-1.26825	-1.58120	-0.80024
C	-1.45857	-2.62985	0.13151
H	-0.62083	-2.97243	0.75933
C	-2.70833	-3.24980	0.27084
H	-2.86455	-4.06610	0.99265
F	-4.98429	-3.39422	-0.38210
C	-3.77796	-2.80884	-0.52083
C	-3.62156	-1.77606	-1.45285
H	-4.48149	-1.45879	-2.06292
C	-2.36305	-1.16691	-1.58828
H	-2.24249	-0.35963	-2.32680
C	0.32003	0.21013	-2.45357
C	-0.33968	1.46129	-2.38713
H	-0.80407	1.78881	-1.44087
C	-0.41482	2.30123	-3.50838
H	-0.93397	3.27122	-3.46544
F	0.15095	2.70215	-5.77725
C	0.20115	1.89468	-4.70109
C	0.87479	0.67075	-4.79609
H	1.35139	0.38689	-5.74740
C	0.92637	-0.16894	-3.67072
H	1.45576	-1.13134	-3.74876
C	1.44803	-2.25853	-1.38425
C	2.76442	-2.36535	-0.88904
H	3.13337	-1.58490	-0.20192
C	3.58378	-3.45001	-1.24076
H	4.61131	-3.54767	-0.85707
F	3.84080	-5.48665	-2.42672
C	3.06795	-4.43734	-2.09068
C	1.76092	-4.36515	-2.59480

H	1.38952	-5.16564	-3.25356
C	0.95540	-3.27432	-2.23605
H	-0.07627	-3.22169	-2.62096
C	-1.72647	0.32386	2.18807
C	-1.24192	1.56245	1.74798
H	-0.17042	1.81131	1.91514
C	-2.09452	2.56081	1.18419
C	-1.60797	3.83636	0.76084
H	-0.53509	4.06118	0.88273
C	-2.46521	4.78689	0.21835
H	-2.07166	5.76705	-0.09873
C	-3.85302	4.50566	0.07815
H	-4.52561	5.26640	-0.35153
C	-4.36024	3.27951	0.49201
H	-5.43746	3.06061	0.39513
C	-3.50659	2.28499	1.05510
C	-3.99030	1.02118	1.51224
H	-5.06563	0.79573	1.41138
C	-3.13499	0.08048	2.06205
H	-3.53845	-0.89492	2.37602
C	2.46835	1.58464	2.33760
H	2.06852	1.60720	3.36276
C	3.27808	0.55636	1.78166
H	3.62015	-0.34850	2.30856
C	4.03597	1.20244	0.59640
H	4.92535	0.66001	0.22228
C	4.23367	2.65426	1.12103
H	4.59566	3.35570	0.33495
H	4.89187	2.70843	2.01776
C	2.72661	2.83935	1.46256
H	2.40682	3.81035	1.88645
C	2.07507	2.42561	0.11635
H	1.30665	3.00117	-0.42028
C	2.88212	1.41446	-0.41440
H	2.88572	1.05163	-1.45243

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	11.78	0.01182	YES	YES
8	a	19.57	0.01533	YES	YES
9	a	29.91	0.03569	YES	YES
10	a	30.37	0.16710	YES	YES
11	a	36.52	0.29347	YES	YES
12	a	40.07	0.00261	YES	YES
13	a	44.31	0.08638	YES	YES
14	a	48.63	0.24262	YES	YES
15	a	51.88	0.03614	YES	YES

16	a	54.30	0.14651	YES	YES
17	a	60.78	0.32739	YES	YES
18	a	62.05	0.05873	YES	YES
19	a	73.33	0.35399	YES	YES
20	a	77.00	0.00591	YES	YES
21	a	86.12	0.30008	YES	YES
22	a	88.44	1.31380	YES	YES
23	a	104.85	0.96340	YES	YES
24	a	123.56	0.97988	YES	YES
25	a	137.87	0.23305	YES	YES
26	a	151.64	0.17912	YES	YES
27	a	155.69	1.10374	YES	YES
28	a	160.84	0.46585	YES	YES
29	a	170.92	0.30726	YES	YES
30	a	186.84	0.78800	YES	YES
31	a	201.26	0.31674	YES	YES
32	a	203.43	1.21223	YES	YES
33	a	210.47	1.31349	YES	YES
34	a	211.43	0.05901	YES	YES
35	a	233.37	0.22769	YES	YES
36	a	261.44	3.07324	YES	YES
37	a	272.12	0.96851	YES	YES
38	a	282.51	3.81238	YES	YES
39	a	306.87	0.59142	YES	YES
40	a	310.59	0.09792	YES	YES
41	a	323.50	3.71623	YES	YES
42	a	330.05	0.16333	YES	YES
43	a	339.83	0.69971	YES	YES
44	a	350.33	0.71071	YES	YES
45	a	394.11	1.07059	YES	YES
46	a	398.21	2.14857	YES	YES
47	a	401.35	3.89191	YES	YES
48	a	406.62	0.69484	YES	YES
49	a	409.25	2.76926	YES	YES
50	a	410.22	0.20267	YES	YES

2a'

SCF Energy (au) (RI)BP86/SV(P)	-2331.1914399000
SCF Energy (au) PBE0/def2-TZVPP	-2330.879607762
SCF Energy (au) PBE0/def2-TZVPP	-2330.8959858261 (CH_2Cl_2 correction)
Zero Point Energy (au)	0.5810835
Chemical potential (kJ mol^{-1})	1327.23
Dispersion correction (au) PBE0/def2-TZVPP	-0.13294019

xyz coordinates
77

Rh	1.51317	0.60041	0.84408
P	0.62701	-0.63559	-0.94787
C	0.72450	-0.72614	2.19761
C	-0.60689	-0.55861	2.70390
C	-1.09105	-1.43063	3.71281
H	-2.09596	-1.25811	4.13438
C	-0.31638	-2.48938	4.20369
H	-0.71483	-3.14941	4.99215
C	0.97387	-2.69031	3.68354
H	1.59755	-3.52598	4.04582
C	1.47747	-1.81373	2.70614
H	2.49233	-2.00242	2.31699
C	-1.05503	-1.41931	-0.84276
C	-1.23783	-2.47531	0.08219
H	-0.39364	-2.82929	0.69464
C	-2.48988	-3.08684	0.23767
H	-2.64017	-3.90754	0.95588
F	-4.77845	-3.20977	-0.37706
C	-3.57011	-2.63095	-0.53073
C	-3.42184	-1.59018	-1.45496
H	-4.29049	-1.25804	-2.04415
C	-2.16096	-0.98957	-1.60667
H	-2.04953	-0.17538	-2.33913
C	0.53262	0.36665	-2.51143
C	-0.14007	1.61129	-2.45296
H	-0.61198	1.93317	-1.50834
C	-0.21920	2.44697	-3.57727
H	-0.74885	3.41181	-3.54345
F	0.34612	2.84572	-5.84639
C	0.40547	2.04348	-4.76654
C	1.09580	0.82823	-4.85261
H	1.58162	0.54729	-5.80010
C	1.15111	-0.00750	-3.72410
H	1.69304	-0.96341	-3.79669
C	1.66403	-2.09749	-1.43566
C	2.98301	-2.19911	-0.94614
H	3.35271	-1.41649	-0.26204
C	3.80568	-3.28069	-1.30002
H	4.83506	-3.37414	-0.92030
F	4.06844	-5.31598	-2.48748
C	3.29098	-4.27093	-2.14720

C	1.98069	-4.20476	-2.64407
H	1.60929	-5.00793	-3.29953
C	1.17192	-3.11651	-2.28363
H	0.13891	-3.06790	-2.66476
C	-1.51159	0.49288	2.16331
C	-2.89185	0.29244	2.04788
H	-3.33039	-0.67306	2.34866
C	-3.76368	1.28108	1.50686
C	-5.17169	1.06653	1.38264
H	-5.59185	0.10266	1.71664
C	-5.99989	2.04772	0.85394
H	-7.08440	1.86686	0.76847
C	-5.45676	3.29138	0.42167
H	-6.12451	4.06471	0.00684
C	-4.09193	3.52980	0.52184
H	-3.66786	4.49254	0.18800
C	-3.21337	2.54024	1.05786
C	-1.80573	2.73788	1.18012
H	-1.37387	3.70470	0.86817
C	-0.98877	1.75118	1.71679
H	0.09352	1.95838	1.87422
C	2.68535	1.72137	2.30480
H	2.29403	1.72327	3.33378
C	3.49231	0.70577	1.72241
H	3.83862	-0.20882	2.22907
C	4.24035	1.37679	0.54428
H	5.12806	0.84370	0.15368
C	4.43913	2.81847	1.09653
H	4.79383	3.53551	0.32138
H	5.10387	2.85704	1.98916
C	2.93425	2.99360	1.45230
H	2.61459	3.95535	1.89693
C	2.27494	2.60580	0.10211
H	1.49901	3.19165	-0.41269
C	3.08024	1.60802	-0.45520
H	3.07677	1.26489	-1.49989

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	10.43	0.00249	YES	YES
8	a	19.43	0.02394	YES	YES
9	a	23.18	0.09970	YES	YES
10	a	28.45	0.10250	YES	YES
11	a	33.45	0.03196	YES	YES
12	a	36.54	0.08041	YES	YES
13	a	42.05	0.50250	YES	YES
14	a	44.73	0.66980	YES	YES

15	a	50.42	0.19608	YES	YES
16	a	54.18	0.14253	YES	YES
17	a	58.54	0.17859	YES	YES
18	a	59.70	0.06530	YES	YES
19	a	65.01	0.42829	YES	YES
20	a	72.81	0.03556	YES	YES
21	a	82.61	0.47344	YES	YES
22	a	88.88	0.98953	YES	YES
23	a	103.07	0.91777	YES	YES
24	a	119.75	0.75562	YES	YES
25	a	135.46	0.26566	YES	YES
26	a	148.32	0.02437	YES	YES
27	a	150.56	0.60056	YES	YES
28	a	158.62	0.27074	YES	YES
29	a	171.38	0.84570	YES	YES
30	a	191.16	0.67494	YES	YES
31	a	196.83	0.69917	YES	YES
32	a	201.66	0.30481	YES	YES
33	a	208.50	0.91739	YES	YES
34	a	211.09	0.55877	YES	YES
35	a	233.27	0.20356	YES	YES
36	a	260.37	2.35036	YES	YES
37	a	269.22	1.06363	YES	YES
38	a	281.65	4.22651	YES	YES
39	a	307.00	1.20281	YES	YES
40	a	309.64	0.28756	YES	YES
41	a	322.43	3.32278	YES	YES
42	a	328.20	0.17722	YES	YES
43	a	338.08	0.90103	YES	YES
44	a	350.23	1.20900	YES	YES
45	a	392.44	0.09549	YES	YES
46	a	397.30	1.83315	YES	YES
47	a	400.97	4.10121	YES	YES
48	a	406.25	1.46646	YES	YES
49	a	407.50	2.42241	YES	YES
50	a	409.29	0.21562	YES	YES

5

SCF Energy (au) (RI)BP86/SV(P)	-2331.1698859460
SCF Energy (au) PBE0/def2-TZVPP	-2330.853715041
SCF Energy (au) PBE0/def2-TZVPP	-2330.8730013566 (CH_2Cl_2 correction)
Zero Point Energy (au)	0.5796976
Chemical potential (kJ mol^{-1})	1330.45
Dispersion correction (au) PBE0/def2-TZVPP	-0.13517272

xyz coordinates
77

Rh	-0.11225	-0.25936	-1.76763
P	1.05975	-0.39595	0.45553
C	0.23558	1.76623	-1.87019
C	-0.76350	2.58079	-1.25301
C	-0.64651	3.98834	-1.29114
H	-1.41679	4.61914	-0.81602
C	0.44005	4.59873	-1.93670
H	0.52027	5.69838	-1.96194
C	1.41531	3.80318	-2.56547
H	2.26337	4.27668	-3.08956
C	1.30253	2.39797	-2.53682
H	2.06665	1.79614	-3.06141
C	0.54790	0.86665	1.72874
C	0.88451	2.21379	1.45569
H	1.40392	2.47955	0.52234
C	0.57937	3.23443	2.36642
H	0.83806	4.28315	2.15460
F	-0.36845	3.88262	4.44217
C	-0.07018	2.90591	3.56354
C	-0.40360	1.58179	3.87083
H	-0.90284	1.35343	4.82520
C	-0.08986	0.56748	2.95109
H	-0.33921	-0.46959	3.21825
C	0.80801	-2.03143	1.29448
C	-0.49410	-2.39585	1.72009
H	-1.33010	-1.68651	1.60922
C	-0.75537	-3.66602	2.25640
H	-1.76400	-3.94729	2.59705
F	0.04723	-5.81434	2.86331
C	0.29093	-4.59463	2.34937
C	1.58159	-4.28043	1.90650
H	2.37916	-5.03633	1.97833
C	1.83209	-3.00160	1.38091
H	2.84916	-2.76750	1.03018
C	2.89925	-0.12200	0.59262
C	3.61374	0.45877	-0.47488
H	3.08656	0.71778	-1.40453
C	4.98153	0.76096	-0.35710
H	5.54255	1.22094	-1.18520
F	6.94576	0.75435	0.96953
C	5.63499	0.47694	0.84739

C	4.94935	-0.07852	1.93894
H	5.48980	-0.26734	2.87964
C	3.58339	-0.36340	1.80864
H	3.04116	-0.77118	2.67715
C	-1.86919	1.83476	-0.62858
C	-1.77155	0.39917	-0.77102
H	-1.03766	0.28425	-2.93472
C	-2.79264	-0.40345	-0.27860
C	-4.97848	-0.66138	0.92476
C	-3.92434	0.14872	0.40596
C	-4.00177	1.58225	0.57448
C	-5.12654	2.13429	1.26035
C	-2.95898	2.39342	0.03896
H	-3.03964	3.48741	0.16050
C	0.88539	-0.95685	-3.71889
H	1.09596	-0.08506	-4.35482
C	1.68598	-1.48069	-2.70567
H	2.66701	-1.11797	-2.37543
C	1.13312	-2.89373	-2.40085
H	1.79917	-3.56399	-1.82650
C	0.70021	-3.33661	-3.82966
H	0.09678	-4.27202	-3.83276
H	1.55380	-3.42760	-4.53855
C	-0.15318	-2.05695	-4.06013
H	-0.68550	-1.93912	-5.02260
C	-1.03964	-2.07679	-2.78939
H	-2.13367	-1.96729	-2.79547
C	-0.24888	-2.59969	-1.76738
H	-0.58687	-2.98388	-0.79684
H	-2.76218	-1.50063	-0.40928
H	-5.18297	3.22912	1.38801
C	-6.13474	1.31772	1.75840
H	-6.99621	1.76117	2.28503
C	-6.06061	-0.09293	1.58777
H	-6.86637	-0.73489	1.98176
H	-4.92256	-1.75563	0.78858

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	9.63	0.01233	YES	YES
8	a	19.68	0.05651	YES	YES
9	a	24.56	0.06716	YES	YES
10	a	32.85	0.02256	YES	YES
11	a	36.84	0.00171	YES	YES
12	a	39.35	0.07561	YES	YES
13	a	48.83	0.44338	YES	YES
14	a	56.99	0.36500	YES	YES

15	a	58.93	0.11007	YES	YES
16	a	66.18	0.10898	YES	YES
17	a	68.28	0.18551	YES	YES
18	a	79.55	1.12346	YES	YES
19	a	84.59	0.10159	YES	YES
20	a	101.32	1.31266	YES	YES
21	a	105.25	0.23827	YES	YES
22	a	113.40	0.40164	YES	YES
23	a	126.68	1.11594	YES	YES
24	a	133.31	0.07679	YES	YES
25	a	145.54	0.00828	YES	YES
26	a	146.03	0.03471	YES	YES
27	a	162.82	0.05936	YES	YES
28	a	166.86	0.02432	YES	YES
29	a	183.21	2.60054	YES	YES
30	a	193.48	0.22309	YES	YES
31	a	202.08	0.77681	YES	YES
32	a	207.99	0.84235	YES	YES
33	a	210.30	0.35967	YES	YES
34	a	235.82	0.88302	YES	YES
35	a	241.63	1.02069	YES	YES
36	a	260.28	0.86673	YES	YES
37	a	274.50	0.47981	YES	YES
38	a	286.64	2.06632	YES	YES
39	a	304.33	0.37570	YES	YES
40	a	310.51	1.71434	YES	YES
41	a	313.47	0.06436	YES	YES
42	a	316.48	0.14101	YES	YES
43	a	349.41	1.04936	YES	YES
44	a	365.27	1.99751	YES	YES
45	a	395.91	2.24213	YES	YES
46	a	398.31	1.98421	YES	YES
47	a	403.96	7.64162	YES	YES
48	a	406.62	0.72886	YES	YES
49	a	409.91	0.63984	YES	YES
50	a	412.42	0.61978	YES	YES

2b

SCF Energy (au) (RI)BP86/SV(P)	-2331.1878343110
SCF Energy (au) PBE0/def2-TZVPP	-2330.874749807
SCF Energy (au) PBE0/def2-TZVPP	-2330.8925768748 (CH_2Cl_2 correction)
Zero Point Energy (au)	0.5809053
Chemical potential (kJ mol^{-1})	1323.46
Dispersion correction (au) PBE0/def2-TZVPP	-0.13063846

xyz coordinates
77

Rh	1.10131	0.20044	1.12945
P	0.64201	-0.49175	-1.08511
C	-1.00736	-0.12985	-1.86265
C	-2.13556	-0.82596	-1.36999
H	-2.01850	-1.56919	-0.56422
C	-3.41380	-0.59334	-1.89530
H	-4.29702	-1.13182	-1.51828
F	-4.79378	0.58368	-3.42417
C	-3.56686	0.35473	-2.91698
C	-2.47152	1.06334	-3.42387
H	-2.62585	1.79944	-4.22814
C	-1.19393	0.81483	-2.89354
H	-0.33513	1.36915	-3.30263
C	1.82269	0.35036	-2.25469
C	1.99862	1.74768	-2.11502
H	1.44361	2.28539	-1.32869
C	2.87282	2.45683	-2.95165
H	3.00857	3.54539	-2.85516
F	4.45118	2.42521	-4.72211
C	3.59957	1.75340	-3.92406
C	3.46287	0.36843	-4.07700
H	4.05426	-0.15338	-4.84559
C	2.56823	-0.32593	-3.24367
H	2.46070	-1.41449	-3.37091
C	0.83633	-2.29019	-1.52469
C	1.51541	-3.14148	-0.62788
H	1.89089	-2.72952	0.32232
C	1.69942	-4.50342	-0.91536
H	2.22336	-5.17614	-0.21888
F	1.34956	-6.32074	-2.39673
C	1.18511	-5.01481	-2.11378
C	0.49414	-4.20025	-3.02324
H	0.09487	-4.64098	-3.95016
C	0.32234	-2.84070	-2.72223
H	-0.22923	-2.20127	-3.43059
C	-1.04759	2.34897	1.01048
C	2.19722	1.96544	1.66233
H	1.74717	2.92792	1.37244
C	1.90472	1.23978	2.85764
H	1.18439	1.54352	3.63265
C	3.15381	0.35835	3.11947

H	3.24772	-0.07746	4.13237
C	4.29154	1.29341	2.61700
H	5.27991	0.78484	2.54052
C	3.61931	1.52914	1.23279
H	4.13700	2.18083	0.50447
C	3.36533	0.06903	0.78433
H	3.63271	-0.33440	-0.20252
C	3.07385	-0.64847	1.94463
H	3.04659	-1.74265	2.06242
C	-3.09062	0.81560	2.14173
C	-1.84256	0.22788	1.90189
C	-0.76325	1.02106	1.33769
C	-2.32103	2.95905	1.22458
C	-3.37116	2.17230	1.82274
H	-3.89067	0.22137	2.61625
C	-1.64950	-1.21537	2.21397
C	-2.59386	4.31944	0.88509
C	-4.64174	2.77804	2.06661
C	-4.87501	4.10445	1.72718
H	-5.43989	2.17119	2.52819
C	-3.84091	4.88091	1.12993
H	-1.79212	4.92279	0.42491
H	-4.03423	5.93363	0.86321
H	-5.86080	4.56029	1.91814
H	4.38471	2.22445	3.22068
H	-0.26919	2.98608	0.55522
C	-1.24866	-3.98740	2.77070
C	-0.19091	-3.07454	2.91292
C	-0.39318	-1.71048	2.64220
C	-2.70285	-2.15532	2.07787
C	-2.50729	-3.51759	2.35311
H	-1.09644	-5.05791	2.98626
H	0.79688	-3.42252	3.25948
H	0.42626	-0.98125	2.84130
H	-3.68908	-1.81410	1.72265
H	-3.34589	-4.22338	2.22968

$vibrational spectrum

# mode	symmetry	wave number	IR intensity	selection rules	
# mode	symmetry	wave number	IR intensity	selection rules	
#		cm**(-1)	km/mol	IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	9.35	0.03384	YES	YES
8	a	15.28	0.00541	YES	YES
9	a	19.14	0.00738	YES	YES
10	a	25.13	0.03623	YES	YES
11	a	28.79	0.05525	YES	YES
12	a	37.51	0.40454	YES	YES
13	a	40.34	0.06657	YES	YES

14	a	42.16	0.11193	YES	YES
15	a	46.79	0.07237	YES	YES
16	a	49.76	0.20946	YES	YES
17	a	55.71	0.40205	YES	YES
18	a	59.34	0.15987	YES	YES
19	a	66.00	0.01671	YES	YES
20	a	68.74	0.00236	YES	YES
21	a	80.75	1.09143	YES	YES
22	a	86.61	0.56239	YES	YES
23	a	95.60	0.62816	YES	YES
24	a	110.92	0.63345	YES	YES
25	a	135.01	0.04213	YES	YES
26	a	147.85	0.51042	YES	YES
27	a	150.30	0.55652	YES	YES
28	a	155.46	0.62738	YES	YES
29	a	164.51	0.99330	YES	YES
30	a	174.27	0.34819	YES	YES
31	a	191.64	1.27952	YES	YES
32	a	202.90	0.38861	YES	YES
33	a	210.12	0.65366	YES	YES
34	a	230.78	0.21578	YES	YES
35	a	248.40	1.47328	YES	YES
36	a	253.32	1.28608	YES	YES
37	a	265.55	0.93491	YES	YES
38	a	277.78	0.09210	YES	YES
39	a	286.94	0.80683	YES	YES
40	a	308.62	0.33682	YES	YES
41	a	320.88	6.11374	YES	YES
42	a	330.94	0.26704	YES	YES
43	a	336.58	0.80929	YES	YES
44	a	340.54	1.72588	YES	YES
45	a	398.52	2.11121	YES	YES
46	a	400.09	5.57822	YES	YES
47	a	404.74	1.97036	YES	YES
48	a	405.89	1.47468	YES	YES
49	a	406.86	0.50428	YES	YES
50	a	408.48	0.03587	YES	YES

ts_{III-4}

SCF Energy (au) (RI)BP86/SV(P)	-2331.1545169800
SCF Energy (au) PBE0/def2-TZVPP	-2330.838941383
SCF Energy (au) PBE0/def2-TZVPP	-2330.8567051285 (CH_2Cl_2 correction)
Zero Point Energy (au)	0.5783580
Chemical potential (kJ mol^{-1})	1327.83
Dispersion correction (au) PBE0/def2-TZVPP	-0.13774722

xyz coordinates
77

Rh	-0.27446	-0.34769	-1.59953
P	0.91057	-0.19259	0.57947
C	0.06548	1.64552	-2.19152
C	-0.83956	2.58321	-1.61062
C	-0.63453	3.96785	-1.81672
H	-1.31708	4.70295	-1.35964
C	0.43065	4.42783	-2.60485
H	0.57338	5.51022	-2.75977
C	1.30595	3.50453	-3.20619
H	2.13840	3.85781	-3.83818
C	1.11620	2.12561	-3.00413
H	1.81111	1.42222	-3.49503
C	0.26942	1.07020	1.79005
C	0.45990	2.42762	1.43845
H	0.96359	2.69081	0.49516
C	0.02788	3.46119	2.28023
H	0.17586	4.51797	2.01005
F	-1.02549	4.12361	4.30036
C	-0.60658	3.13473	3.48631
C	-0.80414	1.80278	3.86694
H	-1.29662	1.57825	4.82590
C	-0.36380	0.77536	3.01523
H	-0.50956	-0.26574	3.33808
C	0.95836	-1.78032	1.54279
C	-0.25381	-2.33541	2.02281
H	-1.20905	-1.80753	1.86595
C	-0.27741	-3.57414	2.68136
H	-1.21803	-4.00024	3.06368
F	0.90513	-5.47451	3.46799
C	0.92124	-4.28340	2.84079
C	2.13233	-3.78108	2.34951
H	3.05550	-4.36750	2.47828
C	2.14399	-2.53267	1.70462
H	3.10177	-2.14716	1.32264
C	2.69498	0.34686	0.59804
C	3.33249	0.77445	-0.58316
H	2.77245	0.78123	-1.52892
C	4.65854	1.24140	-0.56654
H	5.15869	1.58586	-1.48462
F	6.61790	1.71809	0.67927
C	5.34652	1.27815	0.65128
C	4.73605	0.87802	1.85038

H	5.30160	0.93845	2.79331
C	3.41082	0.42417	1.81759
H	2.92433	0.13202	2.76249
C	-1.93928	1.98619	-0.84107
C	-1.94477	0.57329	-0.71217
H	-0.87623	0.50756	-2.83693
C	-3.05206	-0.03268	-0.00525
C	-3.21618	-1.44430	0.16698
H	-2.46920	-2.11534	-0.26457
C	-4.29334	-2.00038	0.84957
H	-4.37228	-3.09683	0.94210
C	-5.29338	-1.16814	1.41583
H	-6.14667	-1.61027	1.95646
C	-5.18571	0.20804	1.27186
H	-5.95516	0.87424	1.69911
C	-4.09404	0.80441	0.57269
C	-4.01855	2.22013	0.42827
H	-4.81056	2.84773	0.87048
C	-2.97204	2.79025	-0.26595
H	-2.93552	3.88569	-0.38031
C	0.73647	-1.24100	-3.45084
H	0.97975	-0.43990	-4.16286
C	1.50691	-1.68435	-2.37451
H	2.49290	-1.31788	-2.06200
C	0.90262	-3.04388	-1.95754
H	1.52925	-3.67846	-1.30417
C	0.47340	-3.61043	-3.34194
H	-0.16652	-4.51779	-3.26300
H	1.33350	-3.80547	-4.02234
C	-0.32650	-2.33175	-3.71645
H	-0.83081	-2.28875	-4.69998
C	-1.23339	-2.16760	-2.47341
H	-2.32584	-2.05783	-2.52458
C	-0.46637	-2.61902	-1.38069
H	-0.82134	-2.96447	-0.40236

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-695.83	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	10.09	0.09818	YES	YES
9	a	14.26	0.00291	YES	YES
10	a	28.22	0.02214	YES	YES
11	a	32.07	0.01790	YES	YES
12	a	35.99	0.02517	YES	YES
13	a	40.26	0.17285	YES	YES
14	a	47.79	0.43904	YES	YES
15	a	54.33	0.22265	YES	YES

16	a	61.68	0.19353	YES	YES
17	a	67.01	0.15668	YES	YES
18	a	73.26	0.30707	YES	YES
19	a	78.30	0.91726	YES	YES
20	a	95.73	0.03827	YES	YES
21	a	101.02	0.37458	YES	YES
22	a	112.93	0.93461	YES	YES
23	a	122.71	0.86179	YES	YES
24	a	129.87	1.04130	YES	YES
25	a	143.13	0.05277	YES	YES
26	a	148.15	0.14987	YES	YES
27	a	159.64	0.28202	YES	YES
28	a	161.97	0.22876	YES	YES
29	a	167.69	0.18471	YES	YES
30	a	187.66	1.53417	YES	YES
31	a	197.36	0.20492	YES	YES
32	a	200.08	0.43982	YES	YES
33	a	208.89	0.16919	YES	YES
34	a	216.53	0.85112	YES	YES
35	a	218.97	2.00330	YES	YES
36	a	236.97	0.36180	YES	YES
37	a	262.54	1.54934	YES	YES
38	a	277.75	1.99952	YES	YES
39	a	293.88	1.76643	YES	YES
40	a	306.16	0.46975	YES	YES
41	a	311.39	0.18122	YES	YES
42	a	317.86	0.17347	YES	YES
43	a	321.45	0.52518	YES	YES
44	a	345.48	1.30008	YES	YES
45	a	367.31	2.39107	YES	YES
46	a	395.39	2.88920	YES	YES
47	a	398.91	2.63613	YES	YES
48	a	403.41	6.91119	YES	YES
49	a	406.47	1.23050	YES	YES
50	a	409.83	0.11391	YES	YES

$ts_{4\text{-}2a}$

SCF Energy (au) (RI)BP86/SV(P)	-2331.1581837150
SCF Energy (au) PBE0/def2-TZVPP	-2330.841951061
SCF Energy (au) PBE0/def2-TZVPP	-2330.8595897220 (CH_2Cl_2 correction)
Zero Point Energy (au)	0.5783433
Chemical potential (kJ mol^{-1})	1328.22
Dispersion correction (au) PBE0/def2-TZVPP	-0.13636541

xyz coordinates
77

Rh	-0.29787	-0.07354	-1.60336
P	0.93365	-0.26288	0.58837
C	0.07489	1.91018	-1.88802
C	-0.90373	2.81075	-1.36604
C	-0.75146	4.20437	-1.55837
H	-1.50287	4.90305	-1.15385
C	0.34182	4.71637	-2.27267
H	0.44485	5.80425	-2.42011
C	1.29324	3.83308	-2.81218
H	2.14575	4.22292	-3.39458
C	1.15467	2.44399	-2.62009
H	1.90709	1.77800	-3.07797
C	0.35062	0.81044	1.99525
C	0.26002	2.19828	1.74201
H	0.47018	2.59169	0.73531
C	-0.08242	3.09866	2.76060
H	-0.15513	4.17987	2.56676
F	-0.67624	3.46323	5.02854
C	-0.34106	2.60475	4.04582
C	-0.24999	1.23730	4.33273
H	-0.44901	0.88211	5.35587
C	0.10107	0.34622	3.30513
H	0.18825	-0.72355	3.54859
C	0.86626	-1.97981	1.29185
C	-0.34767	-2.46846	1.83366
H	-1.22652	-1.80861	1.91316
C	-0.46935	-3.79969	2.26074
H	-1.41037	-4.17848	2.68909
F	0.51930	-5.93860	2.53790
C	0.62989	-4.66038	2.13057
C	1.83851	-4.21658	1.57936
H	2.68144	-4.91859	1.48294
C	1.94906	-2.87924	1.16294
H	2.90207	-2.53893	0.72848
C	2.75051	0.14505	0.71064
C	3.38203	0.87478	-0.31611
H	2.80503	1.17457	-1.20227
C	4.72750	1.26683	-0.20777
H	5.22395	1.84346	-1.00347
F	6.73307	1.28405	1.05659
C	5.44209	0.92030	0.94434
C	4.83926	0.20956	1.99394

H	5.42653	-0.03021	2.89412
C	3.49411	-0.16503	1.87466
H	3.01739	-0.70300	2.71018
C	-2.02330	2.17486	-0.65865
C	-2.02347	0.75927	-0.65728
H	-1.69505	0.37097	-2.26845
C	-3.10044	0.06398	0.00095
C	-3.18881	-1.36118	0.07067
H	-2.38584	-1.95584	-0.38405
C	-4.24425	-2.00718	0.70651
H	-4.27683	-3.10952	0.73216
C	-5.27900	-1.25444	1.32279
H	-6.11548	-1.76937	1.82381
C	-5.22561	0.13328	1.29268
H	-6.01852	0.73081	1.77482
C	-4.15697	0.82301	0.64640
C	-4.10487	2.24912	0.62397
H	-4.90904	2.82040	1.11768
C	-3.06277	2.90421	-0.00537
H	-3.03948	4.00622	-0.00564
C	0.42422	-0.54093	-3.62209
H	0.46560	0.35735	-4.25487
C	1.41853	-0.98730	-2.71646
H	2.40221	-0.52889	-2.54700
C	1.15175	-2.50402	-2.52220
H	1.97170	-3.08991	-2.06669
C	0.67450	-2.89949	-3.95035
H	0.25547	-3.93009	-4.00496
H	1.46076	-2.76362	-4.72644
C	-0.41438	-1.78980	-3.98812
H	-1.05132	-1.70118	-4.88809
C	-1.14690	-2.06687	-2.66153
H	-2.23980	-2.07014	-2.54794
C	-0.19397	-2.51592	-1.76444
H	-0.35903	-2.96034	-0.77511

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-634.77	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	10.77	0.02186	YES	YES
9	a	18.34	0.05803	YES	YES
10	a	30.20	0.02758	YES	YES
11	a	30.88	0.01001	YES	YES
12	a	37.54	0.01443	YES	YES
13	a	39.71	0.11381	YES	YES
14	a	48.81	0.44764	YES	YES
15	a	54.87	0.23706	YES	YES

16	a	62.75	0.33951	YES	YES
17	a	65.87	0.12546	YES	YES
18	a	77.05	0.47183	YES	YES
19	a	80.55	0.18337	YES	YES
20	a	82.21	0.43556	YES	YES
21	a	99.31	0.50223	YES	YES
22	a	107.88	0.73926	YES	YES
23	a	121.67	1.68362	YES	YES
24	a	132.96	0.04523	YES	YES
25	a	138.33	0.12199	YES	YES
26	a	140.59	0.07035	YES	YES
27	a	157.63	0.18796	YES	YES
28	a	163.74	0.05465	YES	YES
29	a	165.78	0.10638	YES	YES
30	a	170.34	0.25647	YES	YES
31	a	192.88	0.35581	YES	YES
32	a	202.56	0.71123	YES	YES
33	a	210.78	0.40136	YES	YES
34	a	217.92	2.28285	YES	YES
35	a	231.88	1.06918	YES	YES
36	a	237.32	0.82055	YES	YES
37	a	240.44	0.37318	YES	YES
38	a	282.23	3.24009	YES	YES
39	a	299.85	0.47002	YES	YES
40	a	305.63	2.57719	YES	YES
41	a	316.36	0.02722	YES	YES
42	a	318.27	0.77266	YES	YES
43	a	323.35	1.57569	YES	YES
44	a	351.10	0.46432	YES	YES
45	a	369.91	1.68024	YES	YES
46	a	395.93	2.98136	YES	YES
47	a	397.94	2.48237	YES	YES
48	a	403.42	7.13537	YES	YES
49	a	407.30	4.45040	YES	YES
50	a	411.21	0.15294	YES	YES

$ts_{2a'-5}$

SCF Energy (au) (RI)BP86/SV(P)	-2331.1635465730
SCF Energy (au) PBE0/def2-TZVPP	-2330.846999193
SCF Energy (au) PBE0/def2-TZVPP	-2330.8647426048(CH_2Cl_2 correction)
Zero Point Energy (au)	0.5780973
Chemical potential (kJ mol^{-1})	1619.93
Dispersion correction (au) PBE0/def2-TZVPP	-0.13304516

xyz coordinates
77

Rh	-0.29895	-0.30758	-1.62590
P	1.11631	-0.45617	0.46879
C	0.09949	1.67865	-1.84151
C	-0.81522	2.57545	-1.20766
C	-0.60913	3.97072	-1.30460
H	-1.31289	4.66697	-0.81794
C	0.47769	4.48642	-2.02626
H	0.62265	5.57718	-2.10001
C	1.36938	3.60694	-2.66942
H	2.21771	4.00638	-3.25167
C	1.17582	2.21403	-2.57754
H	1.89237	1.54489	-3.08484
C	0.52330	-1.67290	1.74586
C	-0.87237	-1.81364	1.91355
H	-1.55685	-1.24261	1.26563
C	-1.40489	-2.64902	2.90775
H	-2.49256	-2.75161	3.04802
F	-1.02703	-4.17113	4.68687
C	-0.52700	-3.36001	3.73657
C	0.86312	-3.24041	3.60118
H	1.52351	-3.80669	4.27590
C	1.38182	-2.38917	2.61217
H	2.47450	-2.28002	2.52856
C	2.88483	-0.99145	0.20491
C	3.18531	-2.35888	-0.00298
H	2.39018	-3.11657	0.07613
C	4.49114	-2.78718	-0.28607
H	4.72665	-3.85258	-0.43531
F	6.76926	-2.23607	-0.65203
C	5.51405	-1.83325	-0.37747
C	5.25387	-0.47165	-0.18141
H	6.07885	0.25449	-0.24959
C	3.94302	-0.06020	0.11144
H	3.75618	1.01080	0.28241
C	1.33063	1.07070	1.51996
C	1.71449	2.29558	0.92363
H	1.83957	2.37080	-0.16648
C	1.93571	3.44343	1.70078
H	2.23394	4.39502	1.23506
F	1.96408	4.47141	3.83826
C	1.75504	3.37309	3.08714

C	1.35673	2.18292	3.70858
H	1.21616	2.15972	4.80045
C	1.14728	1.03978	2.92206
H	0.83707	0.11093	3.42277
C	-1.95464	1.93723	-0.52697
C	-2.01822	0.49935	-0.68956
H	-1.68345	0.20030	-2.26996
C	-3.13194	-0.18540	-0.20671
C	-6.20415	1.85719	1.94395
H	-6.99711	2.38320	2.50115
C	-6.30776	0.45472	1.72400
H	-7.18083	-0.09690	2.11109
C	-5.31430	-0.21802	1.02249
H	-5.39491	-1.30516	0.84804
C	-4.17583	0.47613	0.51214
C	-4.07287	1.90166	0.72975
C	-5.11057	2.56211	1.45600
C	-2.95220	2.59795	0.19054
H	-2.89818	3.68934	0.34453
C	0.28023	-0.81968	-3.68160
H	0.27995	0.06641	-4.33344
C	1.33675	-1.26530	-2.85643
H	2.32753	-0.80412	-2.73989
C	1.04353	-2.76414	-2.57814
H	1.89074	-3.36626	-2.20578
C	0.39975	-3.19624	-3.92632
H	-0.06049	-4.20976	-3.88753
H	1.10446	-3.12685	-4.78507
C	-0.64292	-2.04667	-3.90069
H	-1.36936	-1.96865	-4.73139
C	-1.24316	-2.23832	-2.48627
H	-2.31994	-2.24355	-2.26381
C	-0.20961	-2.69076	-1.67218
H	-0.29904	-3.11393	-0.66176
H	-3.23511	-1.27375	-0.36705
H	-5.03117	3.65035	1.62112

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-612.68	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	8.91	0.02639	YES	YES
9	a	19.38	0.00422	YES	YES
10	a	25.78	0.05931	YES	YES
11	a	31.11	0.01667	YES	YES
12	a	34.72	0.18660	YES	YES
13	a	43.54	0.06645	YES	YES
14	a	47.17	0.10706	YES	YES

15	a	56.40	0.51061	YES	YES
16	a	66.58	0.25673	YES	YES
17	a	71.41	0.03306	YES	YES
18	a	72.34	0.07960	YES	YES
19	a	77.17	0.54784	YES	YES
20	a	80.24	0.03362	YES	YES
21	a	92.49	1.27581	YES	YES
22	a	96.28	0.97087	YES	YES
23	a	114.22	0.74942	YES	YES
24	a	119.16	0.84956	YES	YES
25	a	139.62	0.12276	YES	YES
26	a	149.47	0.23380	YES	YES
27	a	152.60	0.29838	YES	YES
28	a	155.27	0.34878	YES	YES
29	a	170.61	0.02609	YES	YES
30	a	191.16	1.35705	YES	YES
31	a	198.42	0.19021	YES	YES
32	a	211.90	0.31573	YES	YES
33	a	213.62	0.52945	YES	YES
34	a	219.57	0.16674	YES	YES
35	a	229.92	0.55462	YES	YES
36	a	243.29	0.43457	YES	YES
37	a	259.78	0.29119	YES	YES
38	a	285.51	4.05137	YES	YES
39	a	298.61	1.01476	YES	YES
40	a	307.86	0.24314	YES	YES
41	a	318.56	1.98280	YES	YES
42	a	327.15	3.75179	YES	YES
43	a	327.66	0.03416	YES	YES
44	a	339.74	0.94075	YES	YES
45	a	369.03	1.36396	YES	YES
46	a	395.74	3.83141	YES	YES
47	a	399.67	3.72874	YES	YES
48	a	402.45	4.36197	YES	YES
49	a	407.21	0.65460	YES	YES
50	a	411.58	0.76384	YES	YES

ts_{5-2b}

SCF Energy (au) (RI)BP86/SV(P)	-2331.1653858650
SCF Energy (au) PBE0/def2-TZVPP	-2330.848815209
SCF Energy (au) PBE0/def2-TZVPP	-2330.8671897882 (CH_2Cl_2 correction)
Zero Point Energy (au)	0.577859
Chemical potential (kJ mol^{-1})	1326.17
Dispersion correction (au) PBE0/def2-TZVPP	-0.13489117

xyz coordinates
77

Rh	-0.11379	-0.51271	-1.65539
P	1.09055	-0.34963	0.50276
C	0.18048	1.52735	-2.15783
C	-0.78277	2.40595	-1.56871
C	-0.64670	3.80329	-1.73099
H	-1.37971	4.48488	-1.26792
C	0.41252	4.33910	-2.47818
H	0.50528	5.43133	-2.59862
C	1.34641	3.47784	-3.08536
H	2.17350	3.89219	-3.68679
C	1.21958	2.08487	-2.93308
H	1.94872	1.42697	-3.43806
C	0.54544	1.00545	1.65699
C	0.82104	2.33177	1.24763
H	1.33656	2.52277	0.29376
C	0.45970	3.42500	2.04675
H	0.67265	4.45784	1.73123
F	-0.54023	4.23665	4.03879
C	-0.18862	3.19020	3.26647
C	-0.46808	1.89036	3.70426
H	-0.96982	1.73854	4.67243
C	-0.09794	0.80294	2.89589
H	-0.30681	-0.21286	3.26214
C	0.99937	-1.89398	1.52589
C	-0.26734	-2.32902	1.99001
H	-1.16643	-1.72456	1.78524
C	-0.40968	-3.53359	2.69493
H	-1.39046	-3.86857	3.06714
F	0.59299	-5.48892	3.58897
C	0.72320	-4.32980	2.91670
C	1.98422	-3.94704	2.44369
H	2.85244	-4.60032	2.62338
C	2.11540	-2.73060	1.75214
H	3.11116	-2.43864	1.38403
C	2.90913	0.04967	0.48570
C	3.55548	0.38215	-0.72190
H	2.98007	0.38700	-1.65926
C	4.91215	0.74966	-0.74365
H	5.42161	1.01800	-1.68199
F	6.92236	1.12826	0.45335
C	5.62180	0.78351	0.46223

C	5.00464	0.47784	1.68556
H	5.58959	0.53410	2.61686
C	3.64909	0.12232	1.69068
H	3.15821	-0.09343	2.65380
C	-1.86875	1.73680	-0.83386
C	-1.76682	0.29480	-0.77311
H	-0.68647	0.32617	-2.90709
C	-2.78385	-0.42765	-0.15876
C	-6.11901	1.55997	1.63002
H	-6.97877	2.07162	2.09378
C	-6.04211	0.13879	1.65996
H	-6.84403	-0.44196	2.14600
C	-4.96289	-0.51640	1.07851
H	-4.90487	-1.61871	1.09930
C	-3.91254	0.21391	0.44467
C	-3.99338	1.65647	0.40922
C	-2.95637	2.38239	-0.24244
H	-3.03880	3.48229	-0.27784
C	0.92605	-1.55261	-3.46406
H	1.28203	-0.78783	-4.16952
C	1.58703	-2.04900	-2.34551
H	2.58054	-1.76707	-1.97361
C	0.80975	-3.30922	-1.90445
H	1.33703	-3.98911	-1.21004
C	0.37008	-3.86890	-3.28865
H	-0.37867	-4.68847	-3.20779
H	1.22518	-4.19156	-3.92542
C	-0.25368	-2.51769	-3.73816
H	-0.71143	-2.45315	-4.74319
C	-1.18715	-2.21206	-2.53928
H	-2.26267	-2.00382	-2.63884
C	-0.52431	-2.70779	-1.39322
H	-0.98301	-2.98310	-0.43422
H	-2.75563	-1.53163	-0.12859
C	-5.11577	2.29930	1.01640
H	-5.17366	3.40109	0.98814

$vibrational spectrum

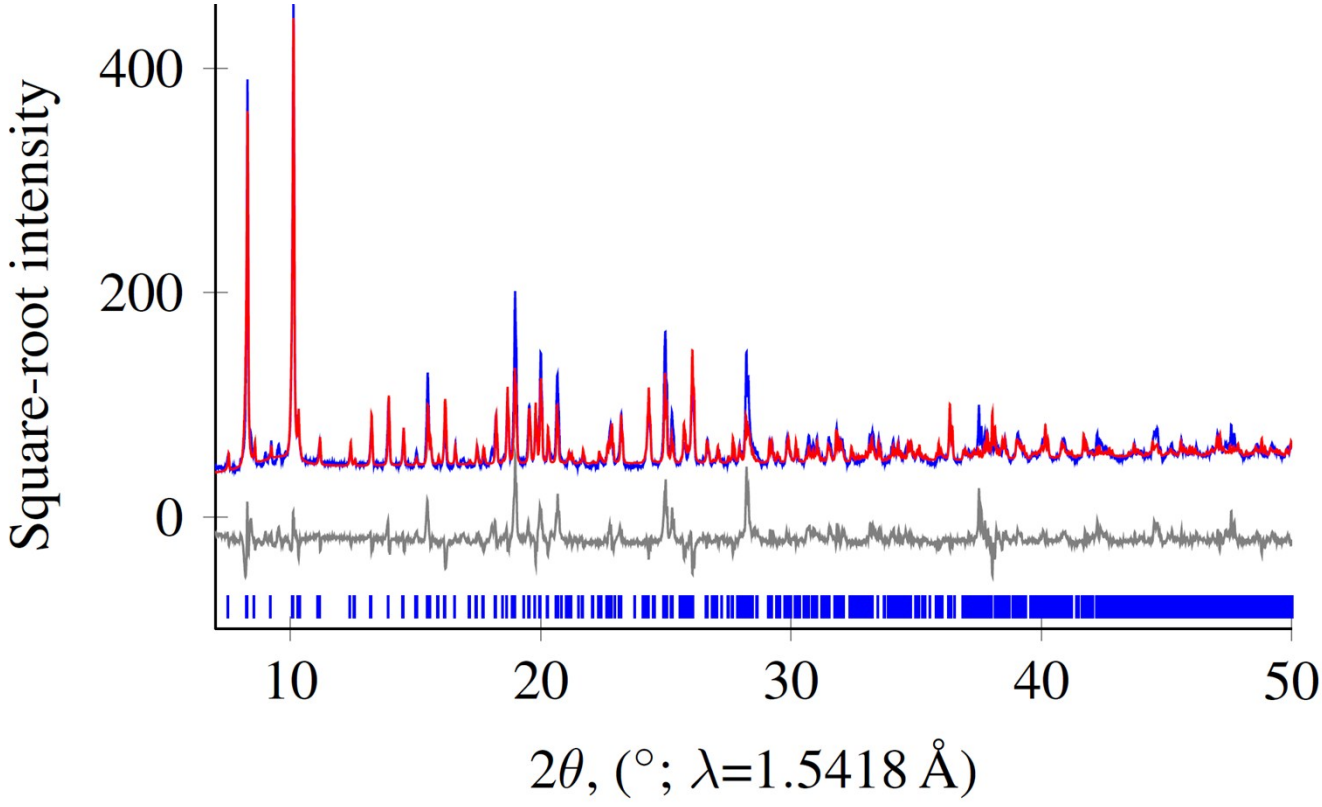
# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-619.77	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	12.07	0.01379	YES	YES
9	a	16.56	0.05870	YES	YES
10	a	23.84	0.03377	YES	YES
11	a	32.42	0.01279	YES	YES
12	a	36.13	0.00222	YES	YES
13	a	40.54	0.10194	YES	YES
14	a	48.62	0.52121	YES	YES

15	a	56.26	0.12798	YES	YES
16	a	64.21	0.20062	YES	YES
17	a	65.76	0.21918	YES	YES
18	a	72.75	0.58934	YES	YES
19	a	78.25	1.00405	YES	YES
20	a	81.39	0.32223	YES	YES
21	a	98.41	0.38187	YES	YES
22	a	102.44	0.16395	YES	YES
23	a	110.01	0.49564	YES	YES
24	a	128.19	1.25497	YES	YES
25	a	133.94	0.15156	YES	YES
26	a	145.27	0.20335	YES	YES
27	a	152.06	0.24543	YES	YES
28	a	159.19	0.19157	YES	YES
29	a	164.88	0.04016	YES	YES
30	a	191.94	1.52609	YES	YES
31	a	197.21	0.12679	YES	YES
32	a	207.92	0.55336	YES	YES
33	a	208.96	1.24726	YES	YES
34	a	217.30	0.10188	YES	YES
35	a	236.21	0.35112	YES	YES
36	a	245.26	0.61247	YES	YES
37	a	259.78	1.02795	YES	YES
38	a	292.39	2.79822	YES	YES
39	a	302.93	0.74289	YES	YES
40	a	305.57	0.00158	YES	YES
41	a	306.72	2.33179	YES	YES
42	a	317.57	0.71154	YES	YES
43	a	319.47	1.33576	YES	YES
44	a	344.26	1.09970	YES	YES
45	a	363.94	1.72764	YES	YES
46	a	396.50	2.31213	YES	YES
47	a	398.72	2.81459	YES	YES
48	a	403.88	7.99887	YES	YES
49	a	406.74	0.56741	YES	YES
50	a	409.99	0.35852	YES	YES

X-ray powder diffraction

Powder diffraction data was collected with a Bruker D8 diffractometer using copper Kα radiation at room temperature over the range 5 – 80° 2θ with a step size of 0.01° 2θ. Approximately 30 mg of as-crystallised sample was placed on a silicon low-background holder and spun at 1 Hz during data collection. The data was modelled by the Rietveld[1,2] method with TOPAS,[3,4] using the current single-crystal structure. Unit cell parameters were refined with atomic coordinates remaining fixed. A preferred orientation correction[5] was applied to correct model intensities.

Figure S1. X-ray powder diffraction spectra of Rh(nbd)(P(4-$FC_6H_4)_3$)(2-NapthPh) (**2**). In red is shown the predicted spectra based on the obtained single-crystal structure and in blue is the experimentally obtained spectra of a bulk sample of Rh(nbd)(P(4-$FC_6H_4)_3$)(2-NapthPh)



NMR spectra

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum, in $CDCl_3$, of $P(4\text{-}FC_6H_4)_3$. Phosphine oxide is seen at ca. 27 ppm.

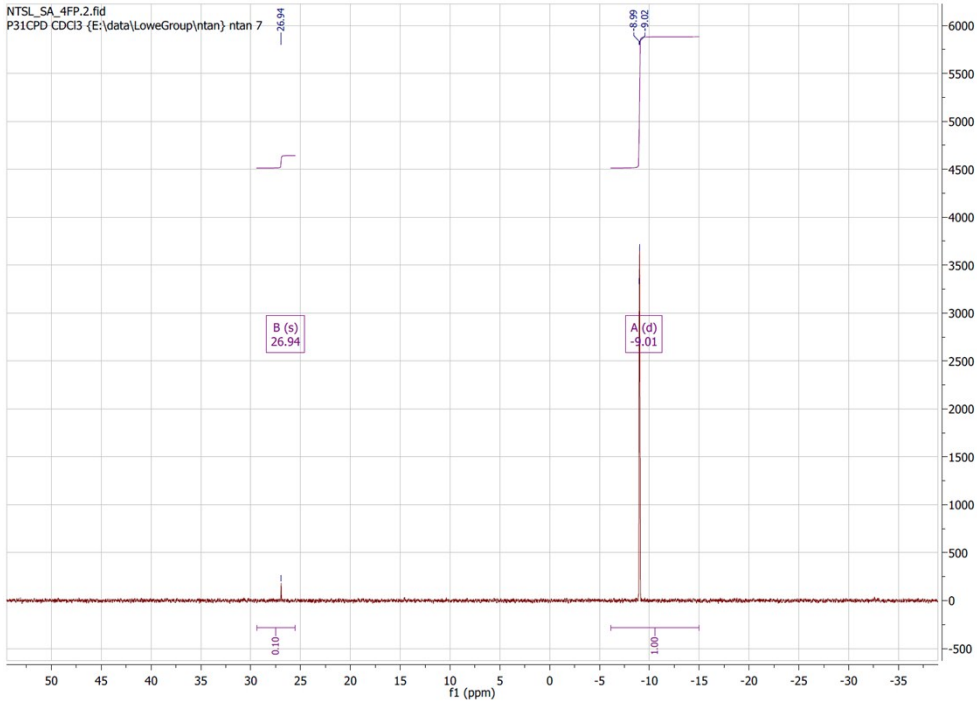


Figure S3. ^{1}H NMR spectra, aromatic region expanded

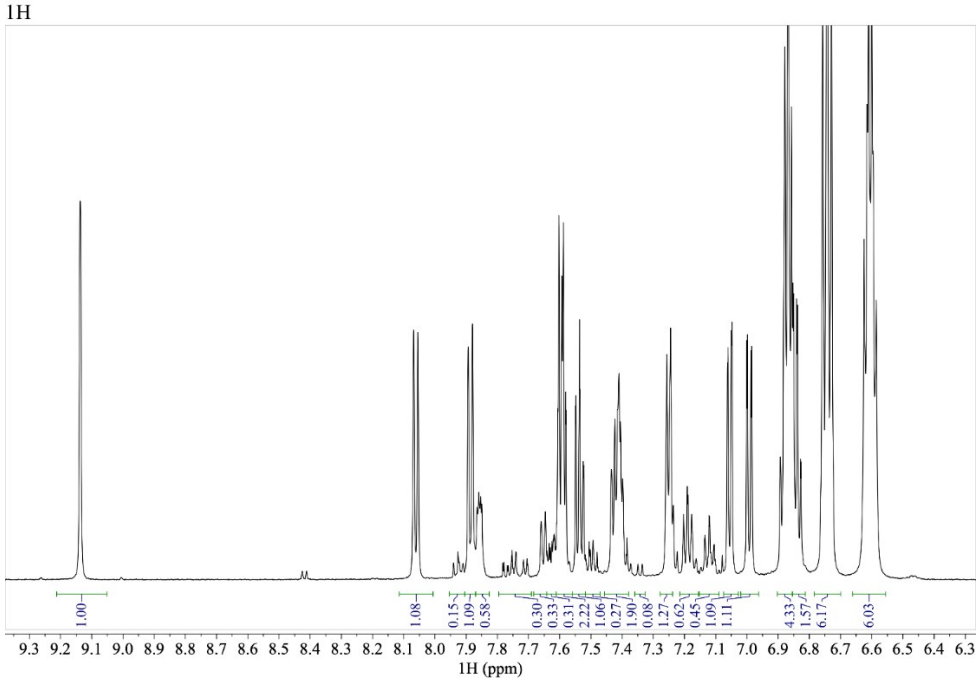


Figure S4. $^{13}C\{^{1}H\}$ full

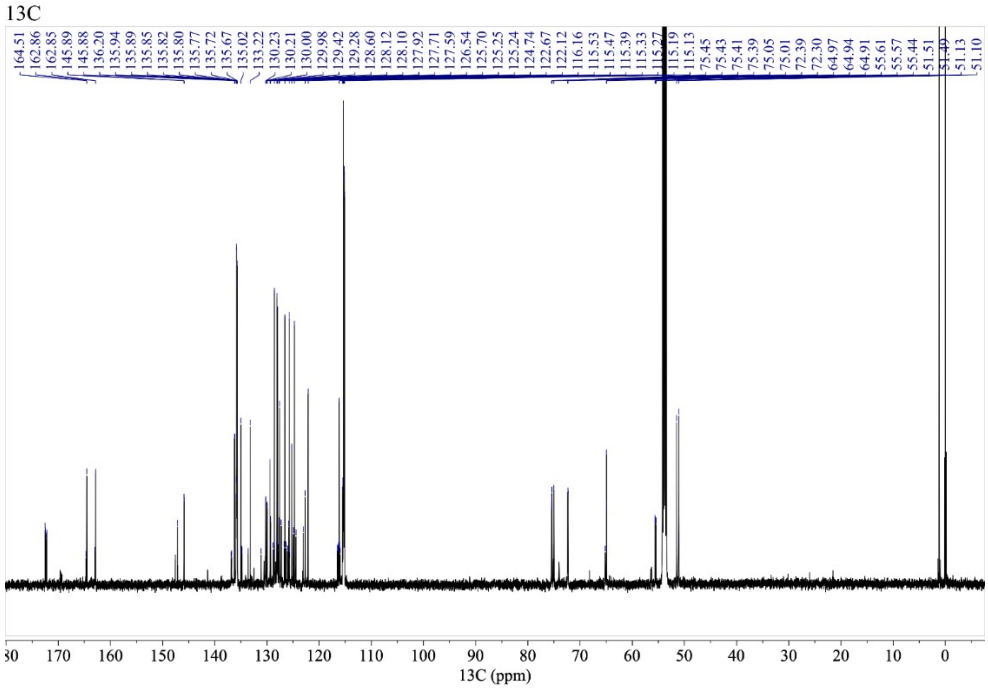


Figure S5. $^{13}C\{^{1}H\}$ aromatic region

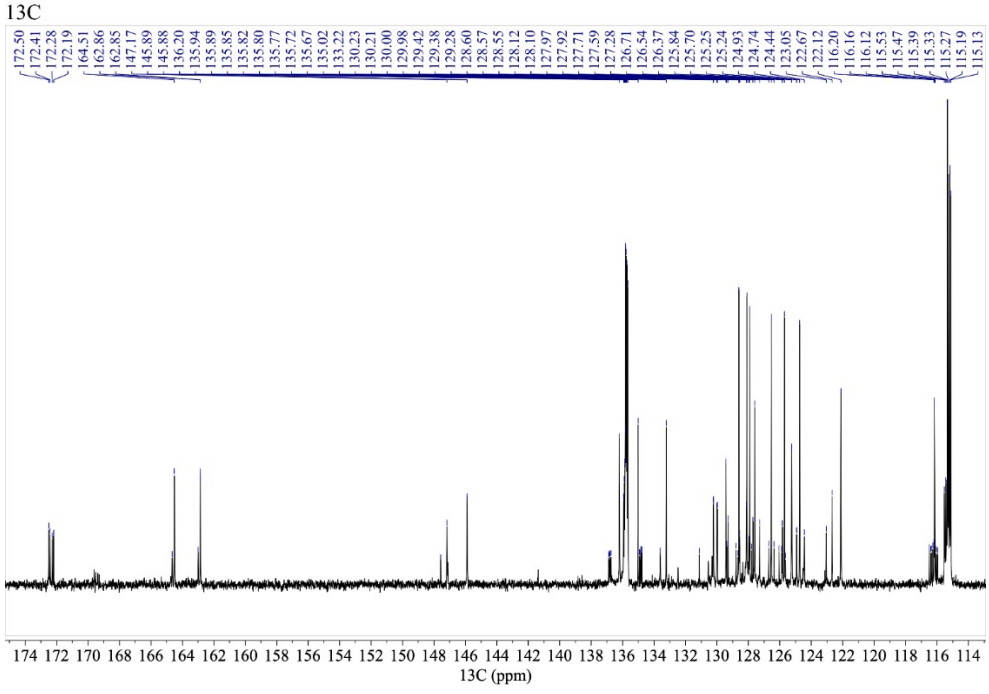


Figure S6. $^{13}C\{^{1}H\}$ expanded

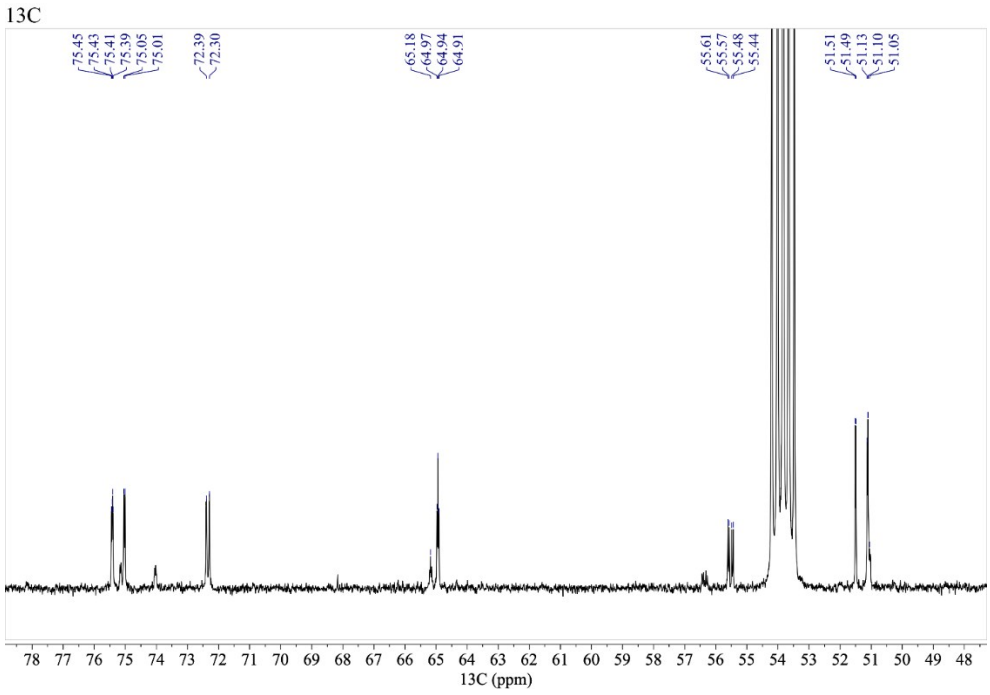


Figure S7. $^{19}F\{^{1}H\}$ NMR spectrum

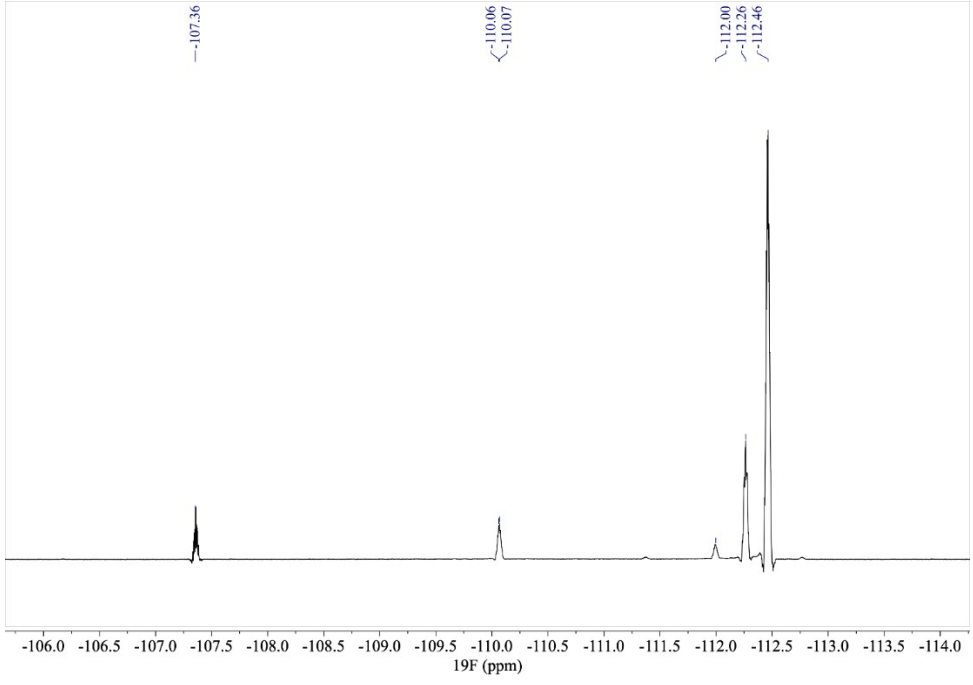


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of the isolated complex

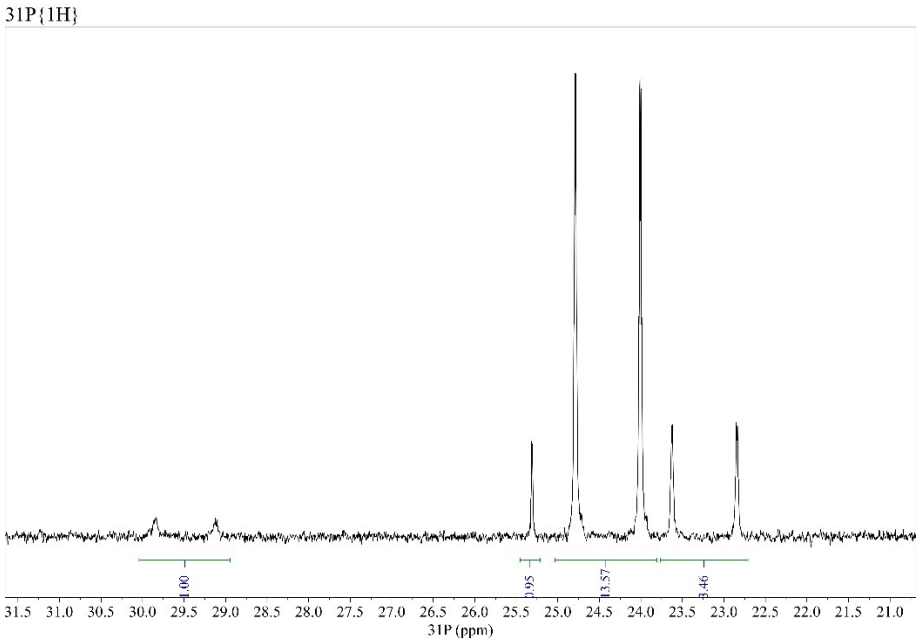


Figure S9. Full ^{31}P-$^{103}Rh\{^{1}H, ^{103}Rh\}$ HMQC spectrum

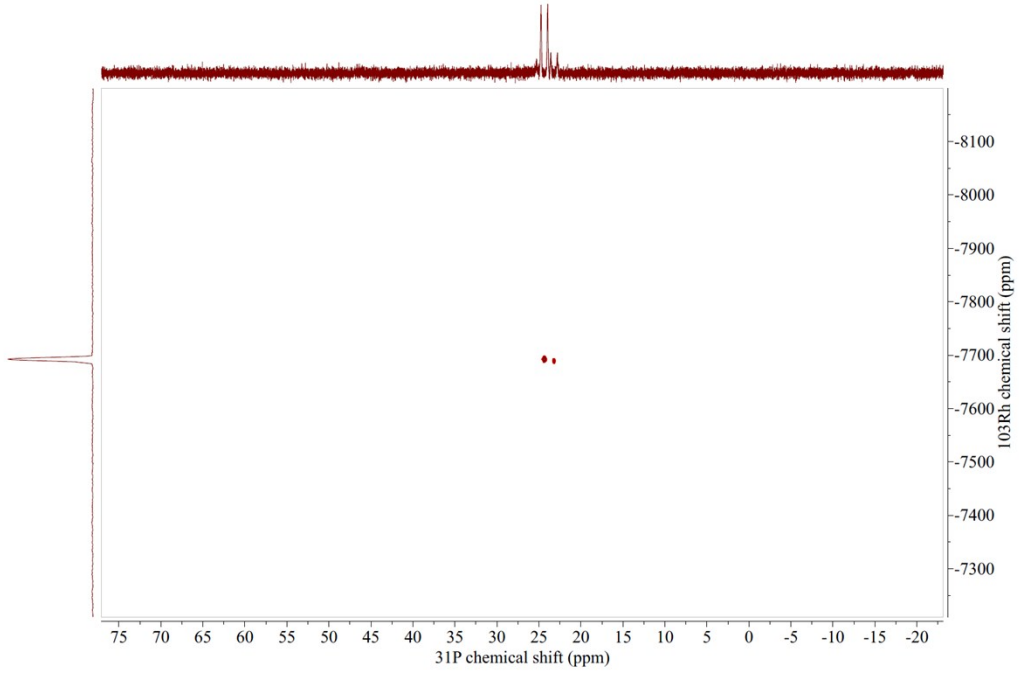


Figure S10. COSY NMR spectrum

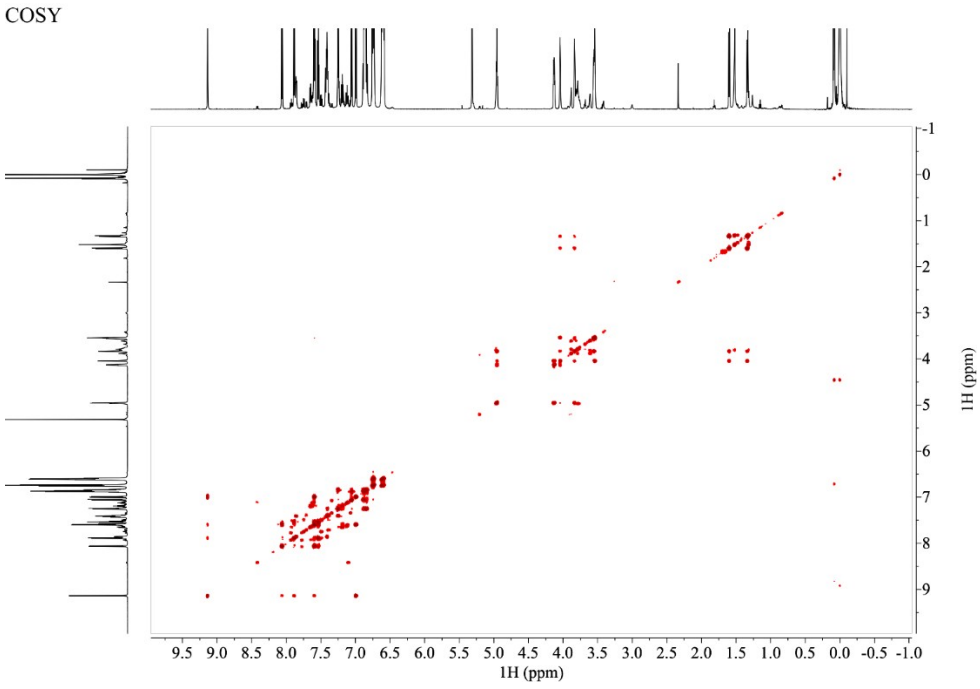


Figure S11. COSY aromatic region

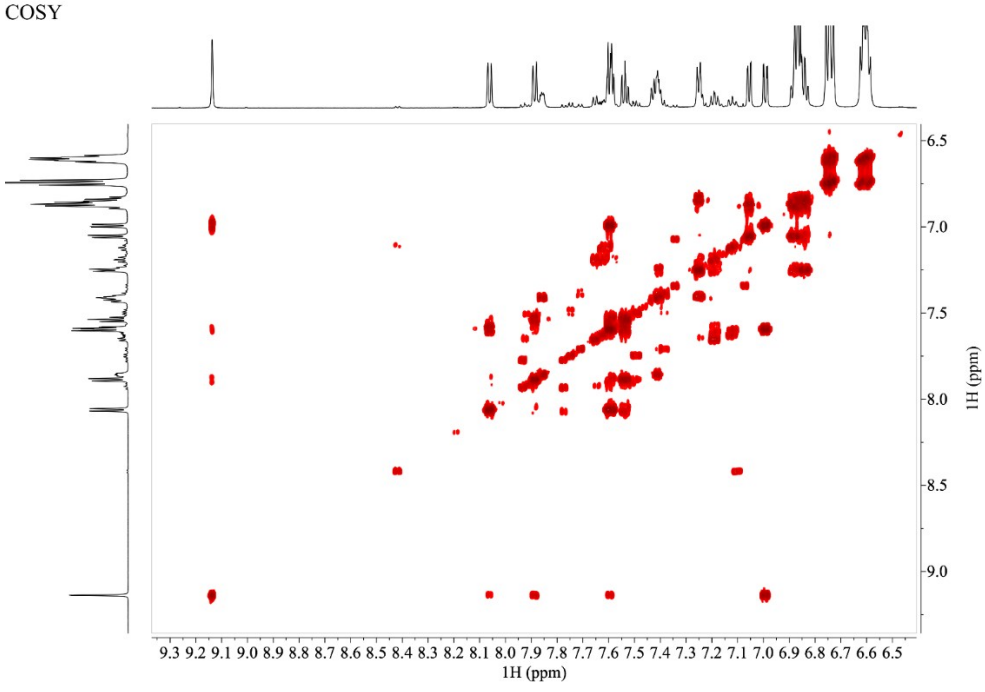


Figure S12. H2BC NMR

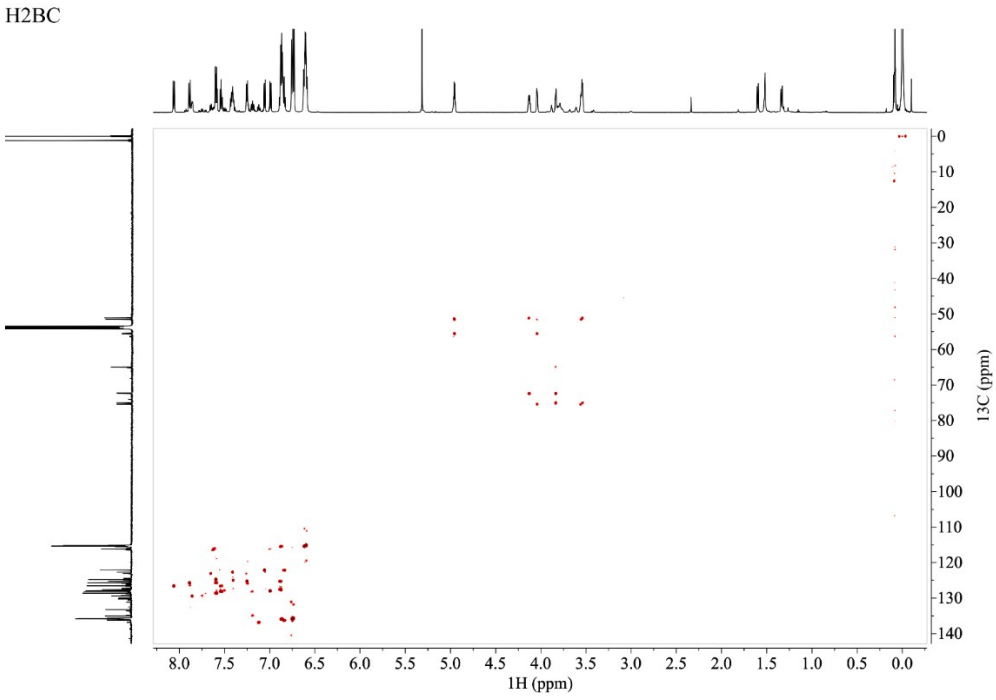


Figure S13. Band selective HMBC

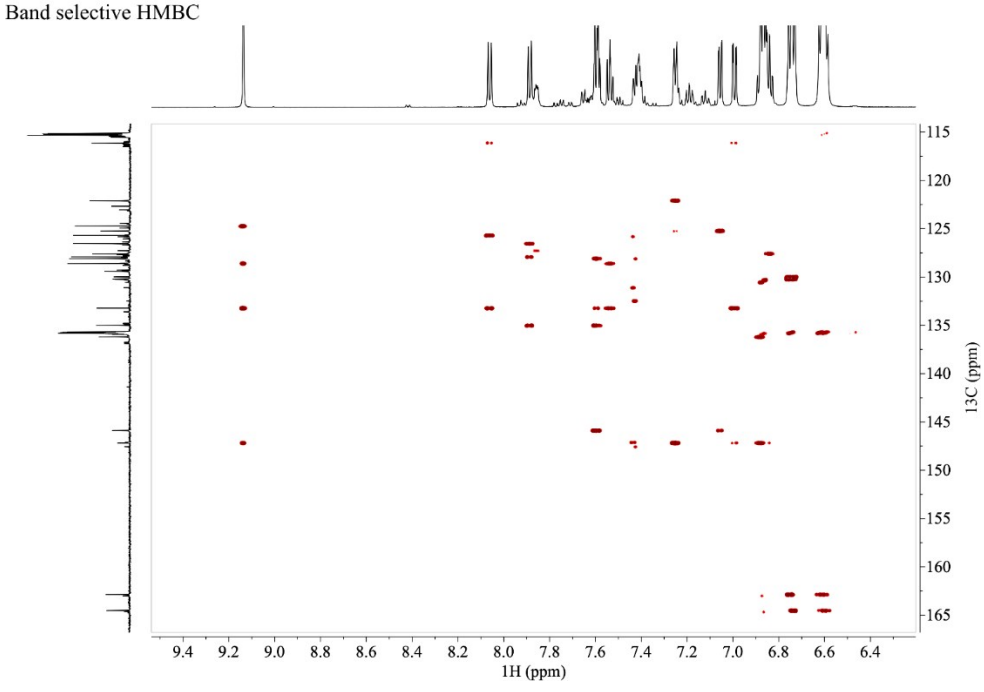


Figure S14. HMBC NMR

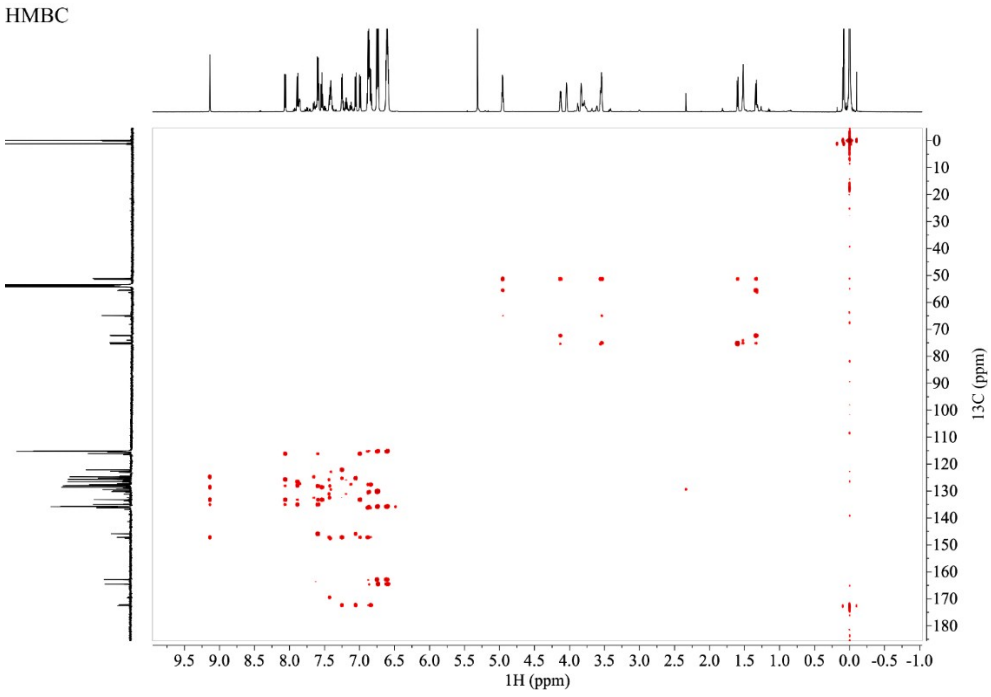


Figure S15. HSQC NMR

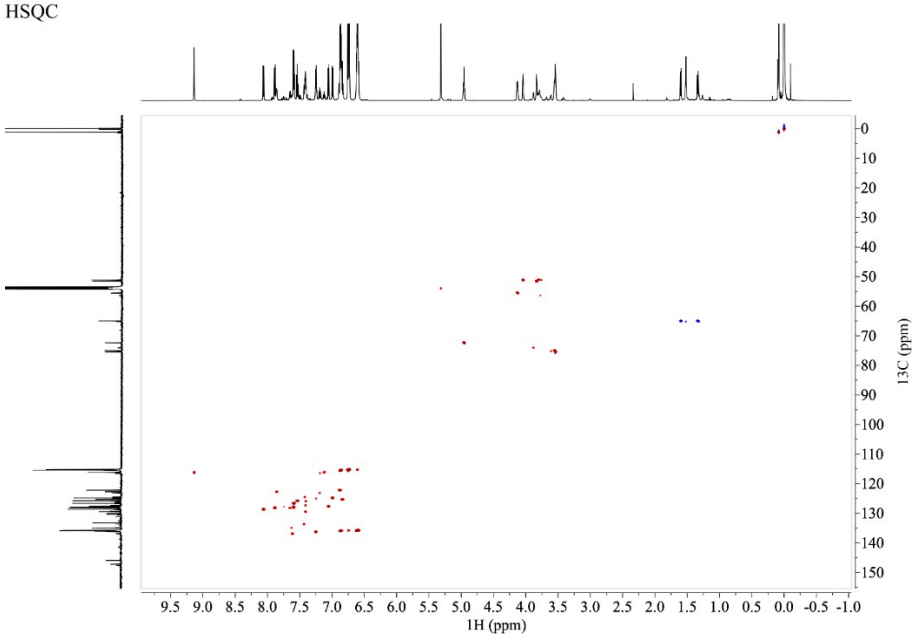


Figure S16. HSQC aromatic

HSQC

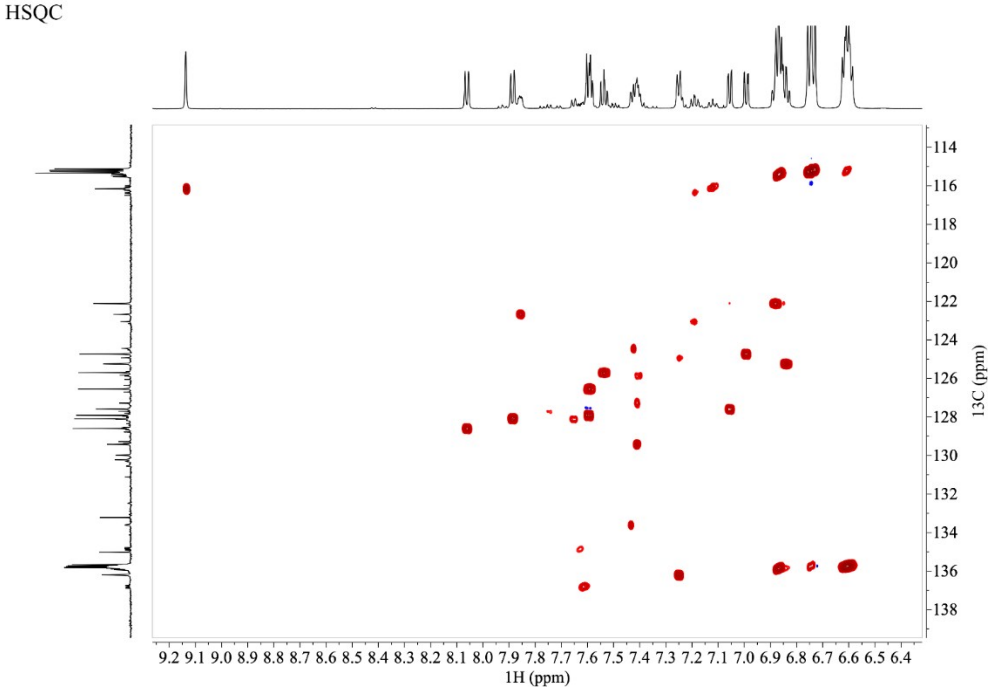


Figure S17. NOESY NMR

NOESY

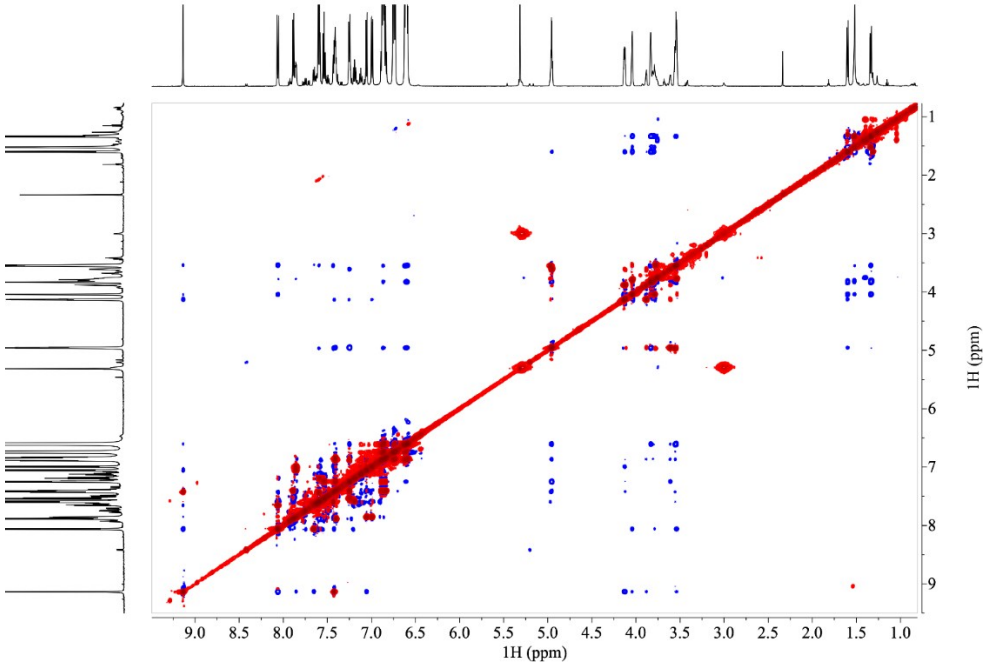
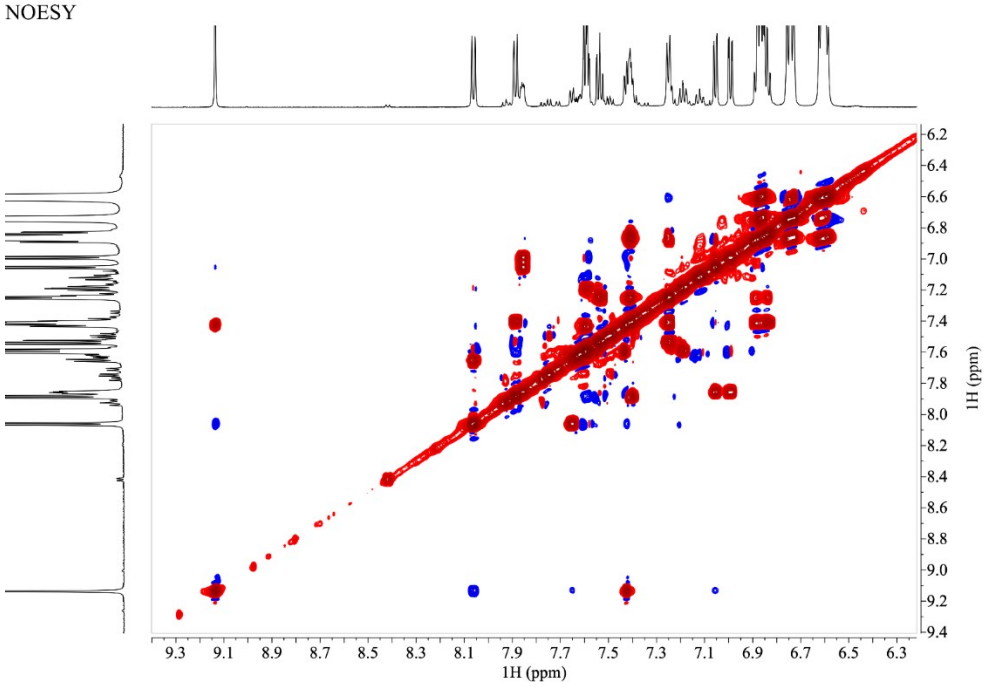


Figure S18. NOESY NMR aromatic region



Crystallographic data

Experimental details

Data collection: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); program(s) used to solve structure: *SHELXT2015*/1 (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2018*/3 (Sheldrick, 2015); molecular graphics: *X-SEED* v. 4.0 (Barbour, 2001); software used to prepare material for publication: *SHELXL2018*/3 (Sheldrick, 2015).

(mxm379nt)

Crystal data

$C_{41}H_{31}F_3PRh\cdot CH_2Cl_2$

$M_r = 799.46$

Monoclinic, $P2_1/n$
$a = 11.7509\ (1)$ Å
$b = 21.0929\ (2)$ Å
$c = 13.9381\ (1)$ Å
$\beta = 96.153\ (1)°$
$V = 3434.80\ (5)$ Å^3
$Z = 4$

$F(000) = 1624$
$D_x = 1.546$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 26188 reflections
$\theta = 2.4–31.6°$
$\mu = 0.75$ mm^{-1}

$T = 99$ K

Needle, yellow

0.21 ×

0.12 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur-S diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.0009 pixels mm^{-1}
ω scans

Absorption correction: multi-scan *CrysAlis PRO* 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{min} = 0.938$, $T_{max} = 1.0$

71355 measured reflections
11686 independent reflections
9483 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$

$\theta_{max} = 32.4°$, $\theta_{min} = 2.4°$

$h = -17 \rightarrow 17$
$k = -30 \rightarrow 31$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.101$

$S = 1.00$

11686 reflections
442 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 4.430P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 1.02$ e Å^{-3}

$\Delta\rho_{min} = -1.11$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Rh1	0.65374 (2)	0.31281 (2)	0.41630 (2)	0.01530 (5)
P1	0.56078 (4)	0.25624 (2)	0.29092 (4)	0.01635 (10)
C1	0.59995 (17)	0.24929 (10)	0.51269 (14)	0.0176 (4)
C2	0.49018 (17)	0.25691 (10)	0.54489 (14)	0.0180 (4)
C3	0.4505 (2)	0.21494 (11)	0.61217 (16)	0.0237 (4)
H3	0.377268	0.221331	0.633597	0.028*
C4	0.5178 (2)	0.16408 (11)	0.64759 (17)	0.0264 (4)
H4	0.490868	0.135895	0.693305	0.032*
C5	0.6245 (2)	0.15478 (11)	0.61569 (16)	0.0249 (4)
H5	0.670246	0.119715	0.638751	0.030*
C6	0.66441 (19)	0.19675 (10)	0.55003 (16)	0.0209 (4)
H6	0.737930	0.189753	0.529535	0.025*
C11	0.42379 (17)	0.21655 (10)	0.29999 (14)	0.0191 (4)
C12	0.42076 (19)	0.16586 (11)	0.36510 (16)	0.0226 (4)
H12	0.488787	0.153372	0.403445	0.027*
C13	0.3189 (2)	0.13383 (11)	0.37384 (17)	0.0252 (4)
H13	0.316116	0.099556	0.417753	0.030*
F14	0.12261 (12)	0.12110 (8)	0.32434 (11)	0.0333 (3)
C14	0.22198 (19)	0.15335 (12)	0.31679 (16)	0.0251 (4)
C15	0.22037 (19)	0.20321 (12)	0.25334 (16)	0.0268 (5)
H15	0.151592	0.215807	0.216167	0.032*
C16	0.32304 (18)	0.23462 (12)	0.24540 (16)	0.0238 (4)
H16	0.324325	0.269152	0.201767	0.029*
C21	0.52980 (17)	0.30492 (10)	0.18252 (15)	0.0187 (4)
C22	0.4793 (2)	0.36421 (11)	0.19387 (16)	0.0247 (4)
H22	0.462318	0.376992	0.256137	0.030*
C23	0.4534 (2)	0.40475 (11)	0.11597 (17)	0.0270 (5)
H23	0.418920	0.444858	0.124120	0.032*
F24	0.45430 (16)	0.42402 (8)	−0.04989 (11)	0.0406 (4)
C24	0.4792 (2)	0.38500 (12)	0.02639 (16)	0.0274 (5)
C25	0.5291 (2)	0.32696 (11)	0.01170 (16)	0.0261 (4)
H25	0.545565	0.314549	−0.050855	0.031*
C26	0.55445 (19)	0.28721 (11)	0.09048 (15)	0.0217 (4)
H26	0.589182	0.247269	0.081596	0.026*
C31	0.64638 (18)	0.19081 (9)	0.25076 (15)	0.0182 (4)
C32	0.76368 (18)	0.18922 (10)	0.28100 (16)	0.0216 (4)
H32	0.796295	0.220748	0.324221	0.026*
C33	0.83358 (19)	0.14209 (11)	0.24874 (17)	0.0249 (4)
H33	0.913446	0.141357	0.268727	0.030*
F34	0.85091 (13)	0.05081 (7)	0.15551 (11)	0.0320 (3)
C34	0.7836 (2)	0.09668 (10)	0.18716 (16)	0.0232 (4)
C35	0.6677 (2)	0.09558 (11)	0.15647 (16)	0.0250 (4)
H35	0.635823	0.063162	0.114544	0.030*

C36	0.59913 (19)	0.14299 (10)	0.18843 (15)	0.0218 (4)
H36	0.519372	0.143150	0.167968	0.026*
C40	0.41412 (17)	0.30762 (10)	0.50151 (14)	0.0178 (4)
C41	0.45623 (17)	0.36581 (10)	0.47682 (14)	0.0181 (4)
H41	0.534607	0.375361	0.494874	0.022*
C42	0.38579 (17)	0.41177 (10)	0.42526 (14)	0.0183 (4)
C43	0.42964 (19)	0.47041 (10)	0.39604 (15)	0.0216 (4)
H43	0.507703	0.480634	0.414274	0.026*
C44	0.3612 (2)	0.51270 (11)	0.34182 (16)	0.0256 (4)
H44	0.392218	0.551707	0.322586	0.031*
C45	0.2446 (2)	0.49842 (12)	0.31445 (17)	0.0278 (5)
H45	0.197649	0.527627	0.276372	0.033*
C46	0.1994 (2)	0.44258 (11)	0.34281 (16)	0.0253 (4)
H46	0.120752	0.433665	0.324750	0.030*
C47	0.26779 (18)	0.39764 (10)	0.39878 (15)	0.0201 (4)
C48	0.22515 (18)	0.33861 (11)	0.42745 (16)	0.0224 (4)
H48	0.146385	0.328948	0.411815	0.027*
C49	0.29500 (18)	0.29521 (10)	0.47719 (16)	0.0215 (4)
H49	0.263770	0.256137	0.495892	0.026*
C51	0.77167 (18)	0.36657 (10)	0.51706 (15)	0.0201 (4)
H51	0.732766	0.364820	0.573338	0.024*
C52	0.82996 (18)	0.31702 (10)	0.47667 (16)	0.0218 (4)
H52	0.837093	0.274575	0.499306	0.026*
C53	0.88016 (18)	0.34501 (11)	0.38829 (16)	0.0233 (4)
H53	0.943886	0.321003	0.362842	0.028*
C54	0.90601 (19)	0.41388 (11)	0.42278 (17)	0.0257 (4)
H54A	0.924924	0.442340	0.370283	0.031*
H54B	0.965862	0.416354	0.478324	0.031*
C55	0.78355 (19)	0.42454 (10)	0.45155 (15)	0.0217 (4)
H55	0.766654	0.467029	0.478513	0.026*
C56	0.71247 (18)	0.40466 (10)	0.35701 (15)	0.0207 (4)
H56	0.641805	0.422477	0.330380	0.025*
C57	0.77140 (18)	0.35598 (10)	0.31859 (15)	0.0212 (4)
H57	0.749180	0.333594	0.260447	0.025*
C10	0.8416 (3)	0.52931 (14)	0.0912 (2)	0.0428 (7)
H10A	0.814706	0.566029	0.126900	0.051*
H10B	0.845179	0.542344	0.023410	0.051*
Cl11	0.74482 (8)	0.46634 (5)	0.09516 (8)	0.0637 (2)
Cl12	0.97959 (8)	0.50650 (4)	0.14318 (9)	0.0673 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rh1	0.01395 (7)	0.01707 (7)	0.01485 (7)	0.00018 (5)	0.00145 (5)	0.00007 (5)
P1	0.0145 (2)	0.0183 (2)	0.0161 (2)	0.00174 (18)	0.00104 (17)	−0.00112 (18)
C1	0.0163 (9)	0.0187 (9)	0.0177 (9)	−0.0012 (7)	0.0009 (7)	−0.0013 (7)
C2	0.0177 (9)	0.0182 (9)	0.0181 (9)	−0.0008 (7)	0.0014 (7)	−0.0008 (7)
C3	0.0244 (10)	0.0252 (10)	0.0221 (10)	−0.0029 (8)	0.0055 (8)	0.0015 (8)
C4	0.0318 (12)	0.0244 (10)	0.0234 (10)	−0.0023 (9)	0.0042 (9)	0.0064 (8)
C5	0.0281 (11)	0.0210 (10)	0.0246 (10)	0.0016 (8)	−0.0012 (9)	0.0042 (8)
C6	0.0193 (9)	0.0208 (9)	0.0220 (9)	0.0003 (7)	−0.0011 (7)	0.0009 (7)
C11	0.0171 (9)	0.0223 (9)	0.0179 (9)	0.0000 (7)	0.0021 (7)	−0.0055 (7)

C12	0.0195 (9)	0.0236 (10)	0.0244 (10)	−0.0012 (8)	0.0011 (8)	−0.0038 (8)
C13	0.0253 (11)	0.0235 (10)	0.0273 (11)	−0.0041 (8)	0.0048 (9)	−0.0044 (8)
F14	0.0217 (7)	0.0420 (8)	0.0375 (8)	−0.0126 (6)	0.0081 (6)	−0.0133 (7)
C14	0.0175 (9)	0.0333 (12)	0.0252 (10)	−0.0064 (8)	0.0058 (8)	−0.0121 (9)
C15	0.0177 (10)	0.0412 (13)	0.0209 (10)	0.0007 (9)	−0.0005 (8)	−0.0071 (9)
C16	0.0191 (10)	0.0334 (11)	0.0186 (9)	0.0012 (8)	0.0006 (7)	−0.0021 (8)
C21	0.0166 (9)	0.0223 (9)	0.0172 (9)	−0.0001 (7)	0.0013 (7)	−0.0003 (7)
C22	0.0277 (11)	0.0253 (10)	0.0203 (10)	0.0063 (9)	−0.0004 (8)	−0.0021 (8)
C23	0.0305 (12)	0.0241 (10)	0.0258 (11)	0.0072 (9)	−0.0001 (9)	0.0004 (8)
F24	0.0590 (11)	0.0361 (8)	0.0263 (7)	0.0130 (8)	0.0032 (7)	0.0121 (6)
C24	0.0302 (12)	0.0297 (11)	0.0219 (10)	0.0032 (9)	0.0001 (9)	0.0073 (9)
C25	0.0318 (12)	0.0286 (11)	0.0187 (10)	0.0017 (9)	0.0061 (8)	0.0027 (8)
C26	0.0213 (10)	0.0231 (10)	0.0212 (9)	0.0008 (8)	0.0041 (8)	−0.0003 (8)
C31	0.0187 (9)	0.0172 (9)	0.0189 (9)	0.0011 (7)	0.0032 (7)	0.0004 (7)
C32	0.0197 (9)	0.0219 (9)	0.0231 (10)	0.0013 (8)	0.0018 (8)	−0.0026 (8)
C33	0.0202 (10)	0.0241 (10)	0.0306 (11)	0.0050 (8)	0.0039 (8)	0.0011 (9)
F34	0.0322 (7)	0.0244 (7)	0.0412 (8)	0.0101 (6)	0.0118 (6)	−0.0054 (6)
C34	0.0259 (10)	0.0202 (9)	0.0249 (10)	0.0074 (8)	0.0087 (8)	−0.0003 (8)
C35	0.0309 (11)	0.0194 (10)	0.0248 (10)	0.0018 (8)	0.0040 (9)	−0.0038 (8)
C36	0.0201 (9)	0.0226 (10)	0.0221 (10)	0.0005 (8)	0.0000 (8)	−0.0017 (8)
C40	0.0160 (8)	0.0206 (9)	0.0172 (8)	0.0005 (7)	0.0038 (7)	−0.0021 (7)
C41	0.0156 (8)	0.0206 (9)	0.0183 (9)	0.0003 (7)	0.0029 (7)	−0.0014 (7)
C42	0.0174 (9)	0.0206 (9)	0.0174 (9)	0.0021 (7)	0.0030 (7)	−0.0020 (7)
C43	0.0213 (10)	0.0215 (10)	0.0225 (10)	0.0017 (8)	0.0053 (8)	0.0001 (8)
C44	0.0307 (11)	0.0226 (10)	0.0245 (10)	0.0028 (9)	0.0067 (9)	0.0018 (8)
C45	0.0309 (12)	0.0283 (11)	0.0232 (10)	0.0093 (9)	−0.0014 (9)	0.0007 (9)
C46	0.0214 (10)	0.0284 (11)	0.0251 (10)	0.0042 (8)	−0.0024 (8)	−0.0040 (9)
C47	0.0174 (9)	0.0226 (10)	0.0202 (9)	0.0027 (7)	0.0015 (7)	−0.0033 (7)
C48	0.0148 (9)	0.0247 (10)	0.0278 (10)	−0.0015 (8)	0.0028 (8)	−0.0052 (8)
C49	0.0184 (9)	0.0201 (9)	0.0267 (10)	−0.0022 (7)	0.0058 (8)	−0.0035 (8)
C51	0.0171 (9)	0.0227 (9)	0.0199 (9)	−0.0039 (7)	−0.0003 (7)	−0.0002 (7)
C52	0.0174 (9)	0.0228 (10)	0.0248 (10)	−0.0012 (8)	0.0003 (8)	0.0023 (8)
C53	0.0163 (9)	0.0264 (10)	0.0278 (11)	0.0003 (8)	0.0048 (8)	0.0002 (8)
C54	0.0200 (10)	0.0286 (11)	0.0287 (11)	−0.0049 (8)	0.0031 (8)	0.0013 (9)
C55	0.0217 (10)	0.0217 (10)	0.0221 (10)	−0.0023 (8)	0.0036 (8)	−0.0001 (8)
C56	0.0200 (9)	0.0232 (10)	0.0194 (9)	0.0002 (8)	0.0040 (7)	0.0043 (7)
C57	0.0199 (9)	0.0241 (10)	0.0204 (9)	−0.0030 (8)	0.0054 (7)	0.0005 (8)
C10	0.0494 (17)	0.0337 (14)	0.0451 (16)	0.0062 (12)	0.0044 (13)	0.0017 (12)
Cl11	0.0407 (4)	0.0554 (5)	0.0948 (7)	−0.0023 (4)	0.0052 (4)	−0.0001 (5)
Cl12	0.0463 (5)	0.0349 (4)	0.1167 (9)	−0.0010 (3)	−0.0102 (5)	−0.0025 (5)

Geometric parameters (Å, º)

Rh1—C1	2.045 (2)	C33—C34	1.375 (3)
Rh1—C52	2.152 (2)	C33—H33	0.9500
Rh1—C51	2.182 (2)	F34—C34	1.354 (2)
Rh1—C57	2.236 (2)	C34—C35	1.383 (3)
Rh1—C56	2.244 (2)	C35—C36	1.387 (3)
Rh1—P1	2.2938 (5)	C35—H35	0.9500
P1—C31	1.830 (2)	C36—H36	0.9500
P1—C11	1.831 (2)	C40—C41	1.381 (3)
P1—C21	1.831 (2)	C40—C49	1.429 (3)

C1—C6	1.410 (3)	C41—C42	1.419 (3)
C1—C2	1.419 (3)	C41—H41	0.9500
C2—C3	1.405 (3)	C42—C43	1.417 (3)
C2—C40	1.481 (3)	C42—C47	1.428 (3)
C3—C4	1.392 (3)	C43—C44	1.373 (3)
C3—H3	0.9500	C43—H43	0.9500
C4—C5	1.389 (3)	C44—C45	1.415 (3)
C4—H4	0.9500	C44—H44	0.9500
C5—C6	1.391 (3)	C45—C46	1.368 (3)
C5—H5	0.9500	C45—H45	0.9500
C6—H6	0.9500	C46—C47	1.421 (3)
C11—C16	1.390 (3)	C46—H46	0.9500
C11—C12	1.405 (3)	C47—C48	1.415 (3)
C12—C13	1.391 (3)	C48—C49	1.368 (3)
C12—H12	0.9500	C48—H48	0.9500
C13—C14	1.380 (3)	C49—H49	0.9500
C13—H13	0.9500	C51—C52	1.400 (3)
F14—C14	1.365 (3)	C51—C55	1.541 (3)
C14—C15	1.373 (4)	C51—H51	0.9500
C15—C16	1.391 (3)	C52—C53	1.539 (3)
C15—H15	0.9500	C52—H52	0.9500
C16—H16	0.9500	C53—C57	1.538 (3)
C21—C26	1.396 (3)	C53—C54	1.550 (3)
C21—C22	1.401 (3)	C53—H53	1.0000
C22—C23	1.390 (3)	C54—C55	1.551 (3)
C22—H22	0.9500	C54—H54A	0.9900
C23—C24	1.381 (3)	C54—H54B	0.9900
C23—H23	0.9500	C55—C56	1.541 (3)
F24—C24	1.352 (3)	C55—H55	1.0000
C24—C25	1.382 (3)	C56—C57	1.378 (3)
C25—C26	1.388 (3)	C56—H56	0.9500
C25—H25	0.9500	C57—H57	0.9500
C26—H26	0.9500	C10—Cl11	1.753 (3)
C31—C32	1.398 (3)	C10—Cl12	1.770 (3)
C31—C36	1.406 (3)	C10—H10A	0.9900
C32—C33	1.394 (3)	C10—H10B	0.9900
C32—H32	0.9500		

C1—Rh1—C52	97.03 (8)	C33—C34—C35	123.1 (2)
C1—Rh1—C51	97.89 (8)	C34—C35—C36	118.4 (2)
C52—Rh1—C51	37.70 (8)	C34—C35—H35	120.8
C1—Rh1—C57	157.20 (8)	C36—C35—H35	120.8
C52—Rh1—C57	65.76 (8)	C35—C36—C31	120.7 (2)
C51—Rh1—C57	77.81 (8)	C35—C36—H36	119.6
C1—Rh1—C56	159.49 (8)	C31—C36—H36	119.6
C52—Rh1—C56	77.72 (8)	C41—C40—C49	118.16 (19)
C51—Rh1—C56	65.74 (8)	C41—C40—C2	121.82 (18)
C57—Rh1—C56	35.84 (8)	C49—C40—C2	119.85 (18)
C1—Rh1—P1	90.24 (6)	C40—C41—C42	121.90 (19)
C52—Rh1—P1	132.78 (6)	C40—C41—H41	119.1
C51—Rh1—P1	168.06 (6)	C42—C41—H41	119.1
C57—Rh1—P1	91.31 (6)	C43—C42—C41	122.12 (19)

C56—Rh1—P1	107.98 (6)	C43—C42—C47	118.76 (19)
C31—P1—C11	101.09 (9)	C41—C42—C47	119.08 (19)
C31—P1—C21	103.75 (9)	C44—C43—C42	121.1 (2)
C11—P1—C21	102.41 (10)	C44—C43—H43	119.5
C31—P1—Rh1	113.13 (7)	C42—C43—H43	119.5
C11—P1—Rh1	122.39 (7)	C43—C44—C45	120.2 (2)
C21—P1—Rh1	111.92 (7)	C43—C44—H44	119.9
C6—C1—C2	116.28 (18)	C45—C44—H44	119.9
C6—C1—Rh1	124.45 (15)	C46—C45—C44	120.0 (2)
C2—C1—Rh1	119.26 (15)	C46—C45—H45	120.0
C3—C2—C1	121.17 (19)	C44—C45—H45	120.0
C3—C2—C40	119.90 (19)	C45—C46—C47	121.3 (2)
C1—C2—C40	118.81 (18)	C45—C46—H46	119.4
C4—C3—C2	120.4 (2)	C47—C46—H46	119.4
C4—C3—H3	119.8	C48—C47—C46	123.0 (2)
C2—C3—H3	119.8	C48—C47—C42	118.29 (19)
C5—C4—C3	119.6 (2)	C46—C47—C42	118.6 (2)
C5—C4—H4	120.2	C49—C48—C47	121.4 (2)
C3—C4—H4	120.2	C49—C48—H48	119.3
C4—C5—C6	120.1 (2)	C47—C48—H48	119.3
C4—C5—H5	120.0	C48—C49—C40	121.1 (2)
C6—C5—H5	120.0	C48—C49—H49	119.4
C5—C6—C1	122.5 (2)	C40—C49—H49	119.4
C5—C6—H6	118.7	C52—C51—C55	105.94 (18)
C1—C6—H6	118.7	C52—C51—Rh1	69.98 (12)
C16—C11—C12	118.9 (2)	C55—C51—Rh1	97.04 (13)
C16—C11—P1	122.70 (17)	C52—C51—H51	127.0
C12—C11—P1	118.42 (16)	C55—C51—H51	127.0
C13—C12—C11	120.5 (2)	Rh1—C51—H51	100.5
C13—C12—H12	119.7	C51—C52—C53	106.34 (18)
C11—C12—H12	119.7	C51—C52—Rh1	72.33 (12)
C14—C13—C12	118.0 (2)	C53—C52—Rh1	97.94 (13)
C14—C13—H13	121.0	C51—C52—H52	126.8
C12—C13—H13	121.0	C53—C52—H52	126.8
F14—C14—C15	118.6 (2)	Rh1—C52—H52	97.9
F14—C14—C13	117.8 (2)	C57—C53—C52	101.50 (16)
C15—C14—C13	123.6 (2)	C57—C53—C54	100.19 (18)
C14—C15—C16	117.6 (2)	C52—C53—C54	100.98 (18)
C14—C15—H15	121.2	C57—C53—H53	117.1
C16—C15—H15	121.2	C52—C53—H53	117.1
C11—C16—C15	121.4 (2)	C54—C53—H53	117.1
C11—C16—H16	119.3	C53—C54—C55	93.42 (16)
C15—C16—H16	119.3	C53—C54—H54A	113.0
C26—C21—C22	118.36 (19)	C55—C54—H54A	113.0
C26—C21—P1	124.46 (16)	C53—C54—H54B	113.0
C22—C21—P1	117.18 (16)	C55—C54—H54B	113.0
C23—C22—C21	121.4 (2)	H54A—C54—H54B	110.4
C23—C22—H22	119.3	C56—C55—C51	102.45 (17)
C21—C22—H22	119.3	C56—C55—C54	99.92 (17)
C24—C23—C22	118.0 (2)	C51—C55—C54	100.58 (17)
C24—C23—H23	121.0	C56—C55—H55	117.0
C22—C23—H23	121.0	C51—C55—H55	117.0

F24—C24—C23	118.5 (2)	C54—C55—H55	117.0
F24—C24—C25	118.8 (2)	C57—C56—C55	106.63 (18)
C23—C24—C25	122.6 (2)	C57—C56—Rh1	71.77 (12)
C24—C25—C26	118.4 (2)	C55—C56—Rh1	94.58 (12)
C24—C25—H25	120.8	C57—C56—H56	126.7
C26—C25—H25	120.8	C55—C56—H56	126.7
C25—C26—C21	121.1 (2)	Rh1—C56—H56	101.2
C25—C26—H26	119.4	C56—C57—C53	106.54 (19)
C21—C26—H26	119.4	C56—C57—Rh1	72.39 (12)
C32—C31—C36	118.71 (19)	C53—C57—Rh1	94.60 (13)
C32—C31—P1	118.84 (16)	C56—C57—H57	126.7
C36—C31—P1	122.43 (16)	C53—C57—H57	126.7
C33—C32—C31	121.0 (2)	Rh1—C57—H57	100.7
C33—C32—H32	119.5	Cl11—C10—Cl12	110.50 (17)
C31—C32—H32	119.5	Cl11—C10—H10A	109.5
C34—C33—C32	118.1 (2)	Cl12—C10—H10A	109.5
C34—C33—H33	121.0	Cl11—C10—H10B	109.5
C32—C33—H33	121.0	Cl12—C10—H10B	109.5
F34—C34—C33	118.4 (2)	H10A—C10—H10B	108.1
F34—C34—C35	118.5 (2)		

C6—C1—C2—C3	1.6 (3)	C33—C34—C35—C36	0.8 (4)
Rh1—C1—C2—C3	−179.04 (16)	C34—C35—C36—C31	−0.2 (3)
C6—C1—C2—C40	−174.40 (18)	C32—C31—C36—C35	−0.8 (3)
Rh1—C1—C2—C40	5.0 (2)	P1—C31—C36—C35	177.37 (17)
C1—C2—C3—C4	−1.1 (3)	C3—C2—C40—C41	146.9 (2)
C40—C2—C3—C4	174.9 (2)	C1—C2—C40—C41	−37.1 (3)
C2—C3—C4—C5	−0.3 (4)	C3—C2—C40—C49	−38.0 (3)
C3—C4—C5—C6	1.1 (4)	C1—C2—C40—C49	138.0 (2)
C4—C5—C6—C1	−0.5 (3)	C49—C40—C41—C42	−2.5 (3)
C2—C1—C6—C5	−0.8 (3)	C2—C40—C41—C42	172.60 (19)
Rh1—C1—C6—C5	179.87 (17)	C40—C41—C42—C43	−177.15 (19)
C31—P1—C11—C16	−118.90 (18)	C40—C41—C42—C47	0.5 (3)
C21—P1—C11—C16	−12.0 (2)	C41—C42—C43—C44	176.5 (2)
Rh1—P1—C11—C16	114.34 (17)	C47—C42—C43—C44	−1.1 (3)
C31—P1—C11—C12	61.27 (18)	C42—C43—C44—C45	0.3 (3)
C21—P1—C11—C12	168.20 (16)	C43—C44—C45—C46	0.6 (3)
Rh1—P1—C11—C12	−65.48 (18)	C44—C45—C46—C47	−0.8 (3)
C16—C11—C12—C13	0.8 (3)	C45—C46—C47—C48	−178.3 (2)
P1—C11—C12—C13	−179.37 (17)	C45—C46—C47—C42	0.0 (3)
C11—C12—C13—C14	0.1 (3)	C43—C42—C47—C48	179.32 (19)
C12—C13—C14—F14	178.89 (19)	C41—C42—C47—C48	1.6 (3)
C12—C13—C14—C15	−1.2 (3)	C43—C42—C47—C46	1.0 (3)
F14—C14—C15—C16	−178.77 (19)	C41—C42—C47—C46	−176.75 (19)
C13—C14—C15—C16	1.3 (3)	C46—C47—C48—C49	176.7 (2)
C12—C11—C16—C15	−0.7 (3)	C42—C47—C48—C49	−1.6 (3)
P1—C11—C16—C15	179.49 (17)	C47—C48—C49—C40	−0.5 (3)
C14—C15—C16—C11	−0.3 (3)	C41—C40—C49—C48	2.6 (3)
C31—P1—C21—C26	8.5 (2)	C2—C40—C49—C48	−172.7 (2)
C11—P1—C21—C26	−96.41 (19)	C55—C51—C52—C53	1.5 (2)
Rh1—P1—C21—C26	130.75 (17)	Rh1—C51—C52—C53	93.31 (15)
C31—P1—C21—C22	−170.69 (17)	C55—C51—C52—Rh1	−91.81 (14)

C11—P1—C21—C22	84.44 (18)	C51—C52—C53—C57	−69.9 (2)
Rh1—P1—C21—C22	−48.40 (18)	Rh1—C52—C53—C57	3.95 (17)
C26—C21—C22—C23	0.3 (3)	C51—C52—C53—C54	33.0 (2)
P1—C21—C22—C23	179.48 (19)	Rh1—C52—C53—C54	106.86 (15)
C21—C22—C23—C24	−0.2 (4)	C57—C53—C54—C55	52.34 (18)
C22—C23—C24—F24	179.9 (2)	C52—C53—C54—C55	−51.62 (19)
C22—C23—C24—C25	0.2 (4)	C52—C51—C55—C56	67.3 (2)
F24—C24—C25—C26	180.0 (2)	Rh1—C51—C55—C56	−3.84 (16)
C23—C24—C25—C26	−0.3 (4)	C52—C51—C55—C54	−35.5 (2)
C24—C25—C26—C21	0.4 (4)	Rh1—C51—C55—C54	−106.59 (14)
C22—C21—C26—C25	−0.4 (3)	C53—C54—C55—C56	−52.33 (19)
P1—C21—C26—C25	−179.55 (18)	C53—C54—C55—C51	52.46 (18)
C11—P1—C31—C32	−147.03 (17)	C51—C55—C56—C57	−68.6 (2)
C21—P1—C31—C32	107.10 (18)	C54—C55—C56—C57	34.7 (2)
Rh1—P1—C31—C32	−14.40 (19)	C51—C55—C56—Rh1	3.71 (16)
C11—P1—C31—C36	34.8 (2)	C54—C55—C56—Rh1	106.98 (14)
C21—P1—C31—C36	−71.11 (19)	C55—C56—C57—C53	−0.2 (2)
Rh1—P1—C31—C36	167.40 (15)	Rh1—C56—C57—C53	−89.63 (14)
C36—C31—C32—C33	1.4 (3)	C55—C56—C57—Rh1	89.39 (14)
P1—C31—C32—C33	−176.92 (17)	C52—C53—C57—C56	69.2 (2)
C31—C32—C33—C34	−0.8 (3)	C54—C53—C57—C56	−34.3 (2)
C32—C33—C34—F34	180.0 (2)	C52—C53—C57—Rh1	−3.78 (16)
C32—C33—C34—C35	−0.3 (3)	C54—C53—C57—Rh1	−107.32 (14)
F34—C34—C35—C36	−179.5 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25···F14^{i}	0.95	2.45	3.137 (3)	129
C33—H33···F14^{ii}	0.95	2.53	3.475 (3)	171

Symmetry codes: (i) $x+1/2, -y+1/2, z-1/2$; (ii) $x+1, y, z$.

Shape analysis

Geometrical parameters for relevant examples of $Rh(L)(ndb)PR_3$ complexes were calculated. The analysis was carried out considering the degree of distortion with respect to square planar and tetrahedral geometries using software developed by Alvarez et al.[6] that allows a mathematical calculation of continuous shape measures (CShM)[7] relative to the ideal geometries. The centroids of the double bonds of nbd were used in this calculation, along with the coordinated P and C atoms.

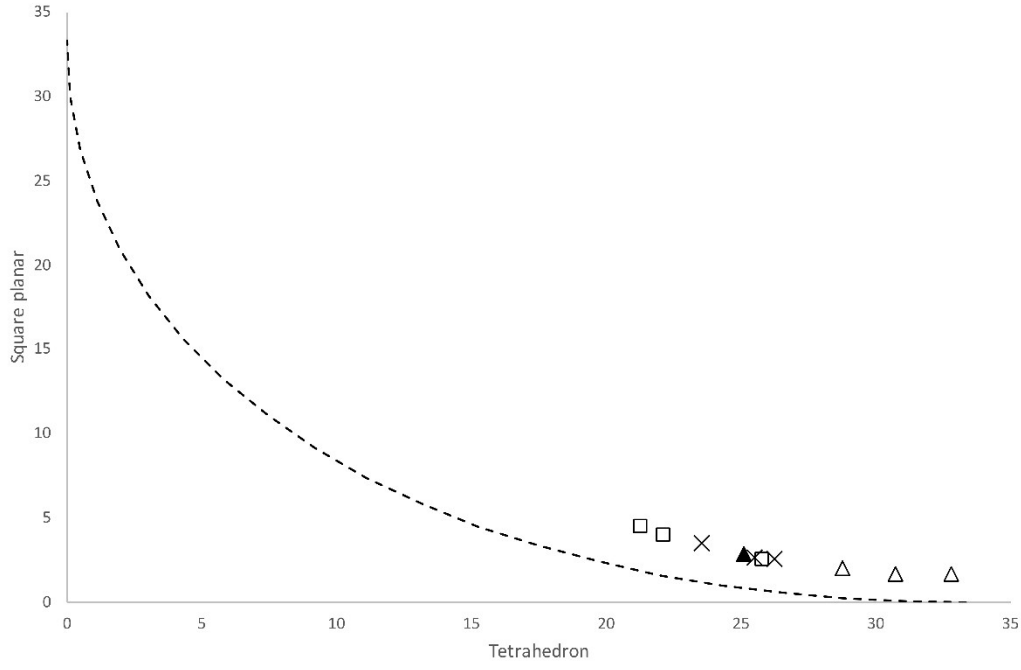


Figure S19. Plot of the geometrical parameters for the coordination sphere of the $Rh(L)(nbd)PR_3$ complexes, where L is a phenyl derivative (triangles, solid triangle is (**2**)), triphenylvinyl (squares), or α-phenylvinylfluorenyl (crosses), with respect to the ideal square planar and tetrahedral geometries.

Table 2.- CShM values of Rh(L)(nbd)PR_3 complexes against the reference tetrahedral and square planar geometries.

Complex	CSD Refcode	Reference	Tetrahedral	Square Planar
L = Phenyl derivative				
(**2**)	_	This work	25.047	2.952
[Rh(2-Me-1-Napth)(nbd)PPh_3]	LEDSIX	10.1021/om0509692	30.697	1.723
[Rh(*m*-Xylene) (nbd)PPh_3]	QEMTEH	10.1021/om0005809	32.761	1.744
[Rh(C_6F_5) (nbd)PCy_3]	RUPYAE	10.1039/C5DT01981H	28.736	2.091
L = α-phenylvinylfluorenyl				
II - [Rh(L)(nbd)P(4-$FC_6H_4)_3$]	XITVAA	10.1002/ejic.201801411	26.231	2.555
[Rh(L)(nbd)P(4-(CF_3)$C_6H_4)_3$]	XITVEE	10.1002/ejic.201801411	25.518	2.664
[Rh(L)(nbd)P(3,5-(CF_3)$C_6H_3)_3$]	XITTUS	10.1002/ejic.201801411	23.556	3.527
L = triphenylvinyl				
[[Rh(CPh=CPh_2)(nbd-$(CH_2)_4PPh_2$)]	HEZBAR	10.1021/om301147n	25.763	2.552
[Rh(CPh=CPh_2)(nbd)PPh_3]	QIDCEN	10.1021/om300642b	22.125	4.015
[Rh(CPh=CPh_2)(nbd)P(4-$ClC_6H_4)_3$]	PERHEC	10.1021/ma000497x	21.23	4.519

Figure S20. DFT Calculations at the D3-(RI)-pbe0/def2-TZVPP//bp86/sv(p) level with COSMO solvent correction in CH_2Cl_2. Energies are Free Energies at 298 K in kJ mol^{-1}.

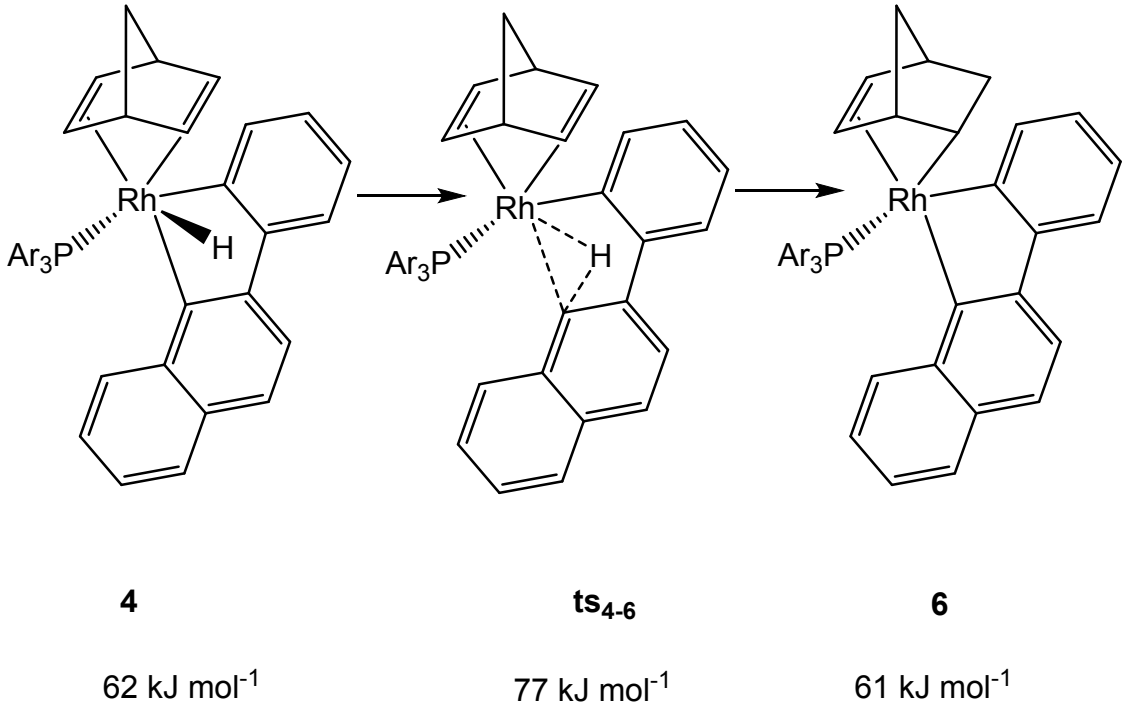


Figure S21. Kinetic data for the homopolymerization of PA with (**2**) for a target MW of 5k at [P]/[Rh] 10 and 20.

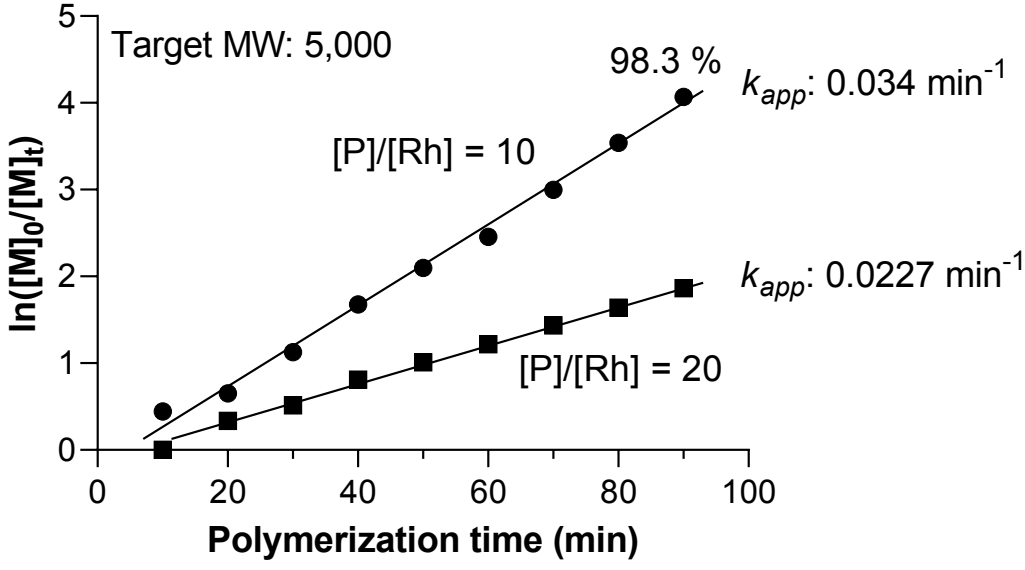
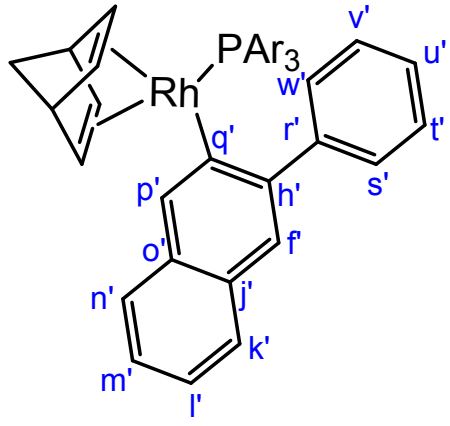


Figure S22. Chemical structure and NMR assignments for (3-phenylnaphthalen-1-yl)rhodium(I)(2,5-norbornadiene)(*tris*-*para*-fluorophenylphosphine)



^{1}H NMR (600 MHz, DCM-d_2) δ 7.84 – 7.87 (m, 2H, $H_{w'+s'}$), 7.65 (d, J = 8.0 Hz, 1H, $H_{k'}$), 7.43 (s, 1H, $H_{p'}$), 7.42 (s, 1H, $H_{i'}$), 7.42 – 7.39 (m, 4H, $H_{v'+t'}$, $H_{u'}$, $H_{n'}$), 7.24- 7.23 (m, 1H, $H_{m'}$), 7.19 (dd, J = 8.7, 6.8 Hz, 1H, $H_{l'}$), 6.90 - 6.85 (m, 12H, $H_{x'}$, $H_{y'}$), 4.97 (m, 1H, $H_{a'}$), 3.88 (dd, J = 4.2, 3.4 Hz, $H_{f'}$), 3.82 – 3.74 (m, 3H, $H_{e'}$, $H_{b'}$, $H_{d'}$), 3.61 (dd, J = 8.3, 4.2 Hz, $H_{g'}$), 1.52 (m, 1H, $H_{c'}$), 1.32 (m, 1H, $H_{c''}$).

^{13}C NMR (151 MHz, DCM-d_2) δ 169.4 (dd, J = 33.7, 13.1 Hz, $C_{q'}$), 163.8 (dd, J= 250.1, 1.6 Hz, C-F), 147.6 (d, J=1.6 Hz, $C_{r'}$), 147.1($C_{h'}$), 135.9, (dd, J=14.3, 7.9 Hz, $C_{x'}$), 133.6 (m, $C_{p'}$), 132.5 ($C_{o'}$), 131.1 ($C_{j'}$), 130.4 (d, J = 35.8 Hz, C-P), 129.4 ($C_{v'+t'}$), 128.1 ($C_{k'}$), 127.3 ($C_{u'}$), 125.8 ($C_{n'}$), 124.9 ($C_{m'}$), 124.4 ($C_{i'}$), 123.1 ($C_{l'}$), 122.7 ($C_{w'+s'}$), 115.4 (dd, J= 21.2, 10.2 Hz, $C_{y'}$), 75.2 (m, $C_{g'}$), 74.0 (m, $C_{f'}$), 72.3 (m, $C_{a'}$), 65.2 (t, J= 4.6 Hz, $C_{c'}$), 56.4 (dd, J= 19.6, 7.4 Hz, $C_{e'}$), 51.1 (m, $C_{b'}$), 51.0 (d, J=4.0 Hz, $C_{d'}$).

^{19}F NMR (565 MHz, CD_2Cl_2) δ -112.21 (m).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2) δ 23.23 (dq, $J_{P\text{-}Rh}$ = 189.8, $J_{P\text{-}F}$ = 2.9 Hz).

^{103}Rh NMR (19 MHz, d_8-toluene) δ -7682. (544 ppm for Rh metal)

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