Square planar-tetrahedral interconversion without spin flip in (β-diiminate)Rh(1,3-diene) complexes

Rebecca S. Sherbo,[†] Gurmeet Singh Bindra, Peter H.M. Budzelaar*

Department of Chemistry, University of Manitoba, Winnipeg, MB R3T 2N2, Canada

[†] Present address: Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, BC V6H 1Z1, Canada

Supporting Information

Contents

Crystal structures

Table S1. Details of crystal structure determinations.

Complex	**(^{Et}BDI)Li(THF)**	**(^{Et}BDI)Rh(COD)**	**(^{Et}BDI)Rh (Me_3SiO-CHD)**	**(^{Et}BDI)Rh(PD)**	**(^{Me}BDI)Rh(BD)**	**(^{Me}BDI)Ir(BD)**
Formula	$C_{29}H_{38}LiN_2O$	$C_{33}H_{45}N_2Rh$	$C_{34}H_{49}N_2ORhSi$	C30 H41 N2 Rh	C25 H31 N2 Rh	C25 H31 N2 Ir
Mol wt	437.55	572.62	632.75	532.56	462.43	551.72
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	123(2)
Crystal system	Monoclinic	Tetragonal	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P4_32_12$	P-1	$P2_1/c$	$P2_1/n$	$P2_1/n$
a / Å	13.952(8)	9.780(3)	9.744(5)	13.858(4)	13.477(3)	13.5679(2)
b / Å	14.900(8)	9.780(3)	11.613(5)	9.515(4)	13.562(3)	13.3427(2)
c / Å	14.031(10)	30.773(9)	15.834(7)	20.971(7)	13.754(4)	13.5761(2)
α/ deg	90	90	93.135(5)	90	90	90
β/ deg	101.583(6)	90	101.617(15)	98.383(8)	114.866(17)	115.5604(5)
γ/ deg	90	90	104.610(9)	90	90	90
V / Å^3	2857(3)	2943.3(12)	1687.6(14)	2735.7(17)	2280.9(10)	2217.18(6)
Z	4	4	2	4	4	4
D_c / g cm^{-3}	1.017	1.292	1.245	1.293	1.347	1.653
abs coef / mm^{-1}	0.06	0.603	0.568	0.643	0.760	6.04
F_{000}	948	1208	668	1120	960	1088
index ranges	-16 < *h* < 16 -18 < *k* < 18 -16 < *l* < 16	-11 < *h* < 11 -11 < *k* < 11 -37 < *l* <37	-11 < *h* < 11 -14 < *k* < 14 -19 < *l* < 19	-16 < *h* < 16 -11 < *k* < 11 -25 < *l* < 25	-16 < *h* < 16 -16 < *k* < 16 -16 < *l* < 16	-16 < *h* < 16 -16 < *k* < 16 -16 < *l* < 16
$2\theta_{max}$ / deg	51.0	51.0	51.0	51.0	51.0	51.0
# rflctns	10397	21811	12540	19731	16595	56313
# unique	2663	2741	6275	5102	4250	4126
# > 2σ	1960	2725	6013	4816	3892	3698
GOF	1.192	0.885	1.064	1.059	1.111	1.364
# parameters	152	167	361	293	259	259
R (*F*o > 4 σ(*F*))	0.0779	0.0245	0.031	0.0745	0.0250	0.0201
R (all data)	0.0944	0.0246	0.0322	0.0763	0.0280	0.0271
*wR*2 (all data)	0.2777	0.0681	0.0877	0.1966	0.1966	0.0725
largest peak, hole / *e* Å^{-3}	0.442, -0.303	0.282, -0.553	0.751, -0.518	4.159, -0.826	0.652 -0.427	1.549 -1.000

(^{Et}BDI)Li(THF)

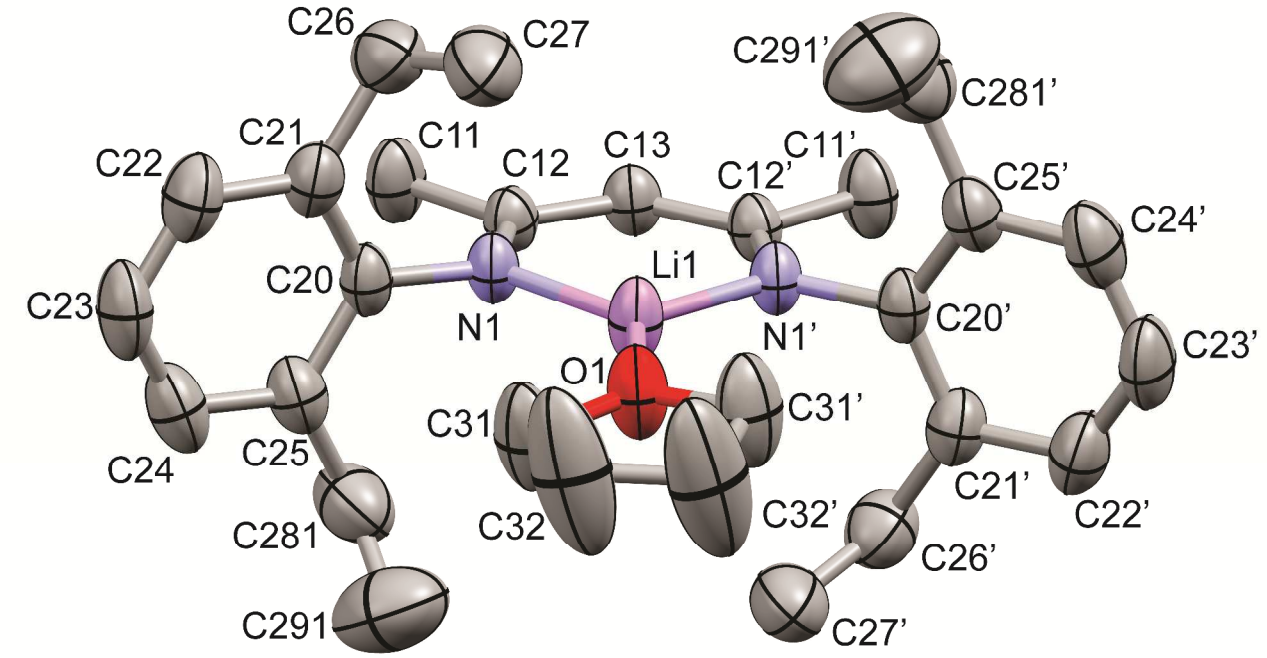


Figure S1. Crystal structure of (^{Et}BDI)Li(THF) (35% probability ellipsoids). Hydrogen atoms omitted for clarity. Only one of the two orientations of the disordered C28-C29 Et group is shown. The molecule is located on a twofold rotation axis.

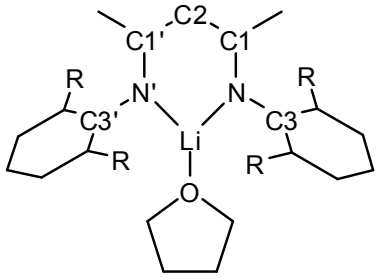


Table S2. Comparison of bond lengths (Å) in (^{R}BDI)Li(THF) complexes.

	(^{Me}BDI)Li(THF)[a]	(^{Et}BDI)Li(THF)[b]	(^{iPr}BDI)Li(THF)[c]	(^{iPr}BDI)Li(THF)[d]
Li-O	1.862(7)	1.887(6)	1.790(7)	1.889
Li-N	1.912(7), 1.905(9)	1.908(4)	1.957(5)	1.892
N-C1	1.323(5), 1.315(5)	1.318(3)	1.325(3)	1.326(3)
C1-C2	1.405(6), 1.413(5)	1.403(3)	1.410(2)	1.399
N-Li-N'	101.1(3)	100.7(3)	95.5(3)	99.9
Li-N-C3	120.5(3) 120.7(3)	119.4(2)	119.8(2)	118.3
C1-N-C3	119.2(3), 120.7(3)	119.7(2)	119.8(2)	119.5

[a] Yao, Y.; Zhang, Z.; Shen, Q.; Sun, J., *Chem. Res. Appln.* **2003,** *15*, 859 (CCDC code KODQAW). Crystallographically independent bond lengths listed separately. [b] this work. [c] Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P., *J. Chem. Soc., Dalton Trans.* **2001**, 3465-3469 (CCDC code CACKIB). [d] Monillas, W.H.; Theopold, K.H.; Yap, G.P.A., *Private Communication to CCDC*, **2007** (CCDC code CACKIB01).

(^{Et}BDI)Rh(COD)

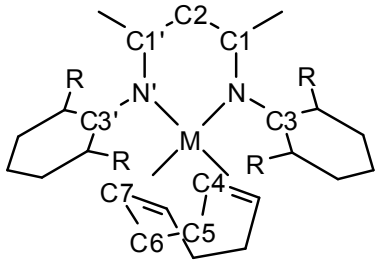


Table S3. Comparison of bond lengths (Å) in (^{R}BDI)(Rh/Ir)(COD) complexes.

	(^{Me}BDI)Rh(COD)[a]	(^{Et}BDI)Rh(COD)[b]	(^{iPr}BDI)Ir(COD)[c]
M-(C=C)	2.043	2.045	2.009 2.021
M-N	2.095(2)	2.101(2)	2.096(2) 2.088(2)
N-C1	1.333(2)	1.331(3)	1.352(3) 1.339(3)
C1-C2	1.388	1.384(3)	1.384(5) 1.392(5)
N-M-N'	89.21	89.2(1)	90.1(1)
M-N-C3	119.8	119.3(2)	120.2(2) 120.2(2)
C1-N-C3	114.2	114.9(2)	114.2(2) 114.0(3)
C4-C5-C6-C7	32.0(3)	33.6(4)	28.5(4) 33.0(4)

[a] Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gall, A. W., *Eur. J. Inorg. Chem.* **2000**, 753-769 (CCDC code FOPWEM). [b] this work. [c] Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J., *Organometallics* **2005**, *24*, 6250-6259 (CCDC code DEBCAP). Crystallographically independent bond lengths listed separately.

(^{Et}BDI)Rh(PD)

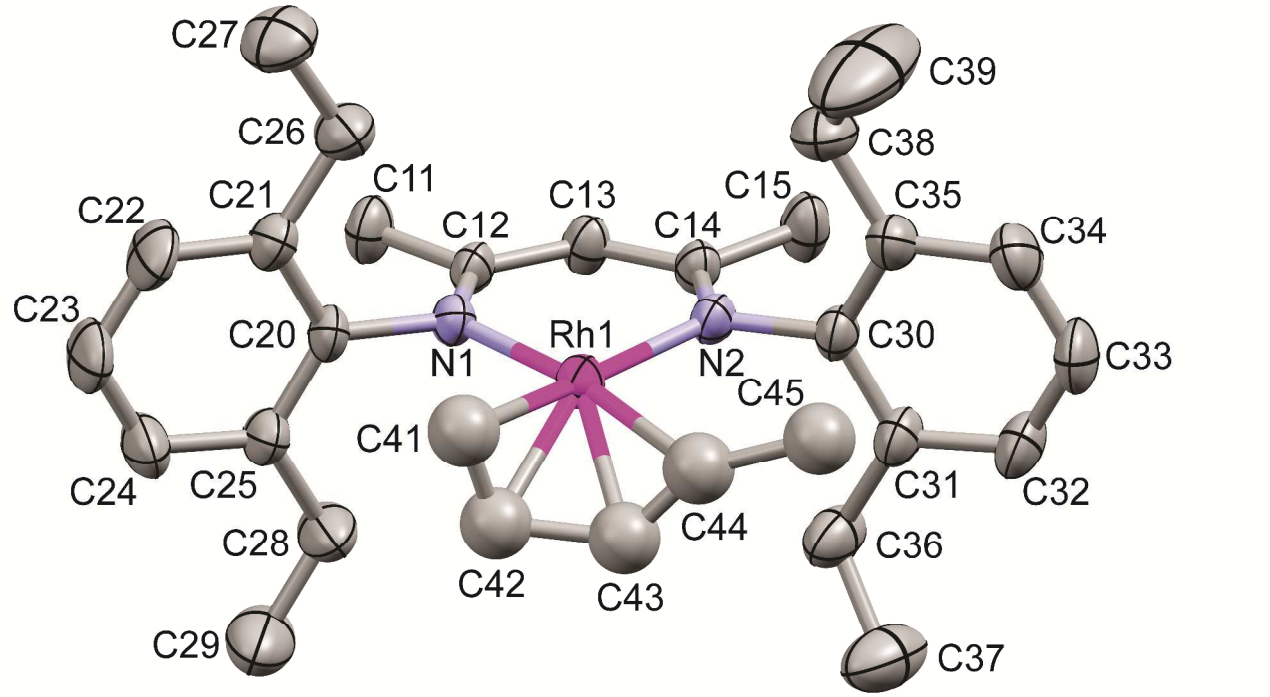


Figure S2. Crystal structure of (^{Et}BDI)Rh(PD) (35% probability ellipsoids). Hydrogen atoms omitted for clarity. Only one of the two orientations of the disordered PD fragment group (refined isotropically) is shown.

(^{Me}BDI)Ir(BD)

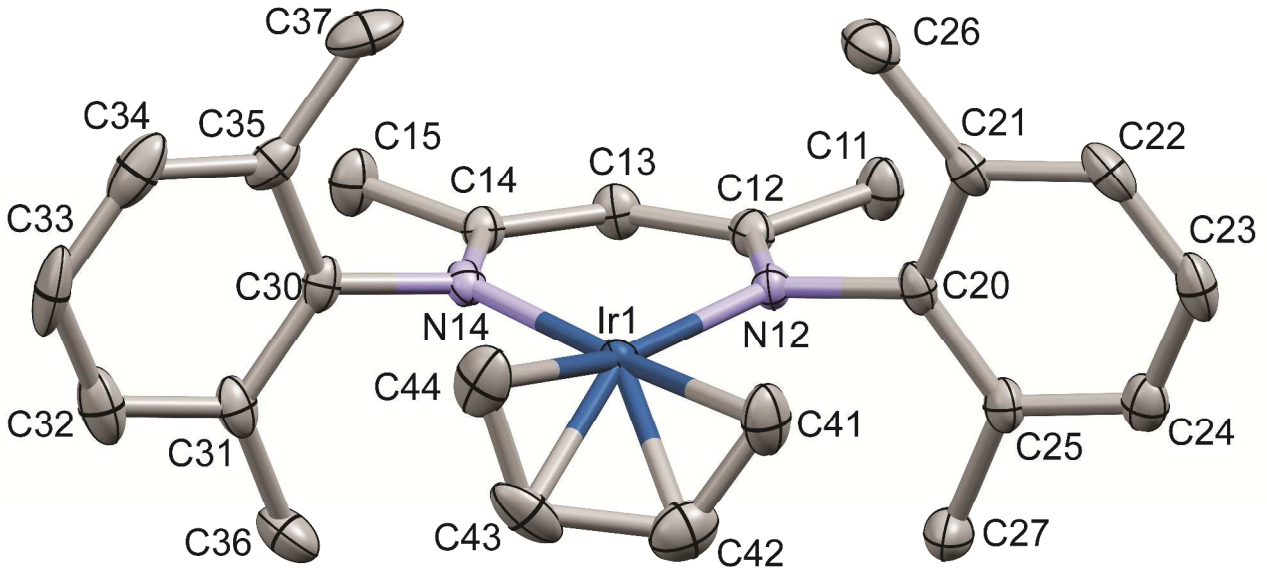


Figure S3. Crystal structure of (^{Me}BDI)Ir(BD) (45% probability ellipsoids). Hydrogen atoms omitted for clarity.

Singlet and triplet geometries

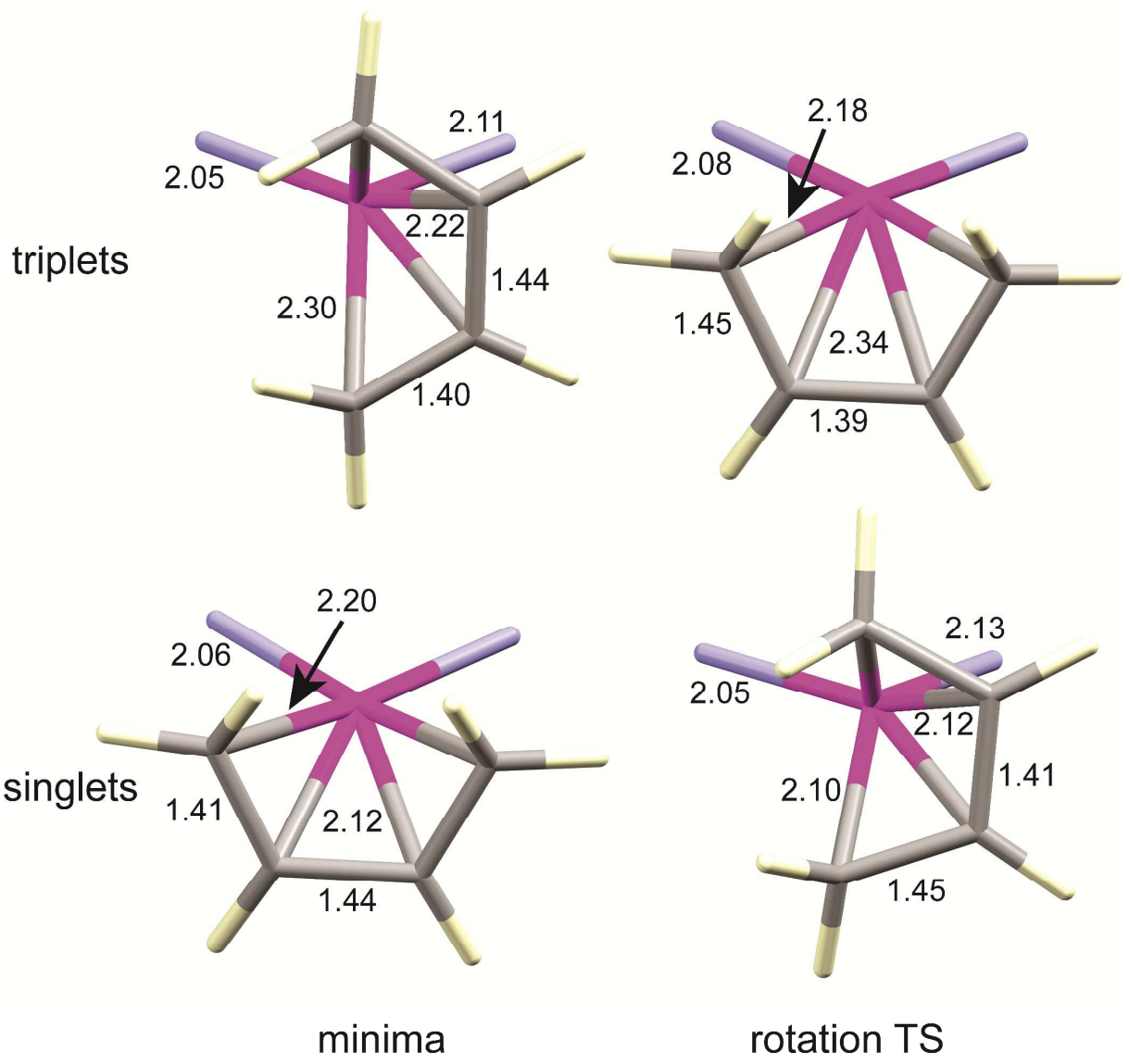
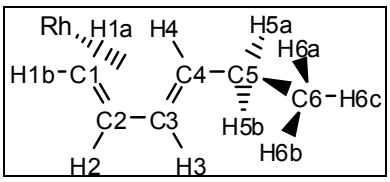


Figure S4. Comparison of optimized core geometries (at TPSSh/TZVP level) of (^{Me}BDI)Rh(BD) in singlet and triplet states during diene rotation. Most of the ^{Me}BDI ligand omitted for clarity. Bond lengths in Å.

Comparison of calculated and observed NMR parameters

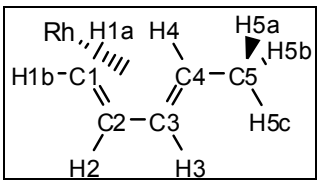
Chemical shifts (δ) in ppm relative to Me_4Si calculated at the same level. Coupling constants (J) in Hz.

Complex 1



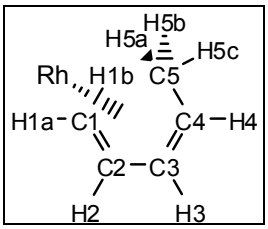
Shift	B3LYP	TPSSh	Observed	Coupling	B3LYP	TPSSh	Observed
C1	64.857	62.906	50.6	H1b-H1a	-1.1	0.4	~0
C2	79.329	76.312	76.5	H1b-H2	7.0	7.0	7.0
C3	99.225	95.209	87.5	H1a-H2	9.0	10.7	11.0
C4	79.144	75.273	70.5	H2-H3	4.7	4.5	4.5
C5	27.213	26.760	22.0	H3-H4	9.3	11.2	10.5
C6	20.023	19.891	15.3	H4-H5a	3.6	3.3	4
H1b	0.667	0.872	0.81	H4-H5b	10.3	11.9	11
H1a	1.220	1.429	0.55	H5a-H5b	-12.9	-13.1	13.0
H2	2.918	2.988	4.08	H5a-H6	7.1	7.6	7.5
H3	5.070	5.025	4.60	H5b-H6	6.9	7.4	7.5
H4	1.241	1.436	1.44				
H5a	-0.978	-0.887	-0.23				
H5b	0.153	0.224	-0.11				
H6	0.389	0.403	0.48				

Complex 2a



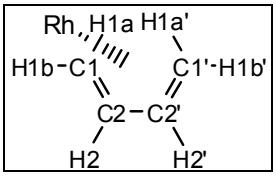
Shift	B3LYP	TPSSh	Observed	Coupling	B3LYP	TPSSh	Observed
C1	64.743	62.795	50.5	H1b-H1a	-1.2	0.3	~0
C2	79.055	76.045	76.2	H1b-H2	7.0	7.0	7.0
C3	99.467	95.457	88.3	H1a-H2	9.1	10.7	10.5
C4	72.153	69.132	63.8	H2-H3	4.7	4.5	4.5
C5	15.734	16.305	13.5	H3-H4	9.3	11.2	11.5
H1b	0.626	0.832	0.77	H4-H5	6.4	6.7	6.0
H1a	1.176	1.388	0.53				
H2	2.944	3.014	4.10				
H3	5.043	4.994	4.57				
H4	1.293	1.494	1.52				
H5	-0.216	-0.166	-0.43				

Complex 2b



Shift	B3LYP	TPSSh	Observed	Coupling	B3LYP	TPSSh	Observed
C1	67.200	64.741	52.8	H1b-H1a	-1.7	-0.3	~0
C2	89.243	85.379	83.1	H1b-H2	7.9	8.1	8.0
C3	89.138	85.739	77.7	H1a-H2	10.0	11.8	11.5
C4	80.867	77.557	n.o.	H2-H3	4.6	4.4	4.5
C5	19.594	20.095	14.3	H3-H4	8.4	8.6	7.5
H1b	0.131	0.327	0.82	H4-H5	7.0	7.4	7.0
H1a	2.028	2.175	1.54				
H2	4.107	4.117	4.62				
H3	4.457	4.492	3.88				
H4	0.553	0.744	1.63				
H5	0.780	0.816	0.42				

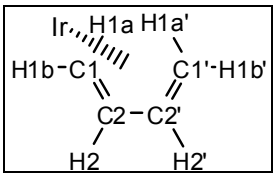
Complex 3 [a]



Shift	B3LYP	TPSSh	Observed	Coupling	B3LYP	TPSSh	Observed
C1	62.263	59.991	50.7	H1b-H1a	-1.6	-0.2	~0
C2	87.852	85.379	81.3	H1b-H2	7.1	7.2	6.5
H1b	0.056	0.245	0.68	H1a-H2	9.4	11.2	10.0
H1a	1.253	1.419	0.85	H2-H2'	4.3	4.1	
H2	4.328	4.326	4.36				

[a] Symmetry-related values averaged.

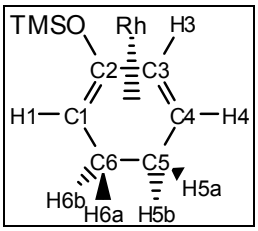
Complex 4 [a]



Shift	B3LYP	TPSSh	Observed	Coupling	B3LYP	TPSSh	Observed
C1	52.759	51.231	36.8	H1b-H1a	-2.2	-0.8	~0
C2	77.825	74.956	69.5	H1b-H2	6.7	6.8	~7
H1b	0.158	0.158	0.89	H1a-H2	8.3	9.8	~9
H1a	-0.030	1.020	-0.13	H2-H2'	3.7	3.4	
H2	3.907	3.950	4.19				

[a] Symmetry-related values averaged.

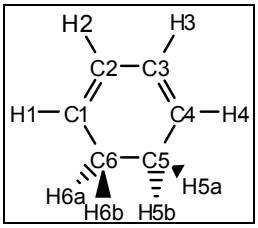
Complex 5



Shift	B3LYP	TPSSh	Observed	Coupling	B3LYP	TPSSh	Observed
C1	67.315	64.968	57.3	H1-H6b	5.0	5.0	4
C2	139.155	134.623	127.6	H1-H6a	2.1	1.9	2
C3	78.951	75.728	72.7	H3-H4	6.6	6.7	6.5
C4	82.102	79.177	68.4	H4-H5a	3.0	2.8	2.5
C5	30.279	30.058	24.5	H4-H5b	4.3	4.1	4

C6	24.183	24.376	21.2	H5a-H5b	-16.2	-16.5	25.5
H1	0.545	0.755	1.23	H5a-H6b	2.1	2.2	4
H3	3.058	3.146	3.46	H5a-H6a	9.2	9.4	9
H4	1.590	1.786	1.76	H5b-H6b	11.6	12.3	11.5
H5a	1.463	1.492	0.34	H5b-H6a	5.1	5.6	5
H5b	1.856	1.864	1.31	H6b-H6a	-13.9	-13.9	14
H6b	1.148	1.194	1.01				
H6a	1.068	1.099	0.52				

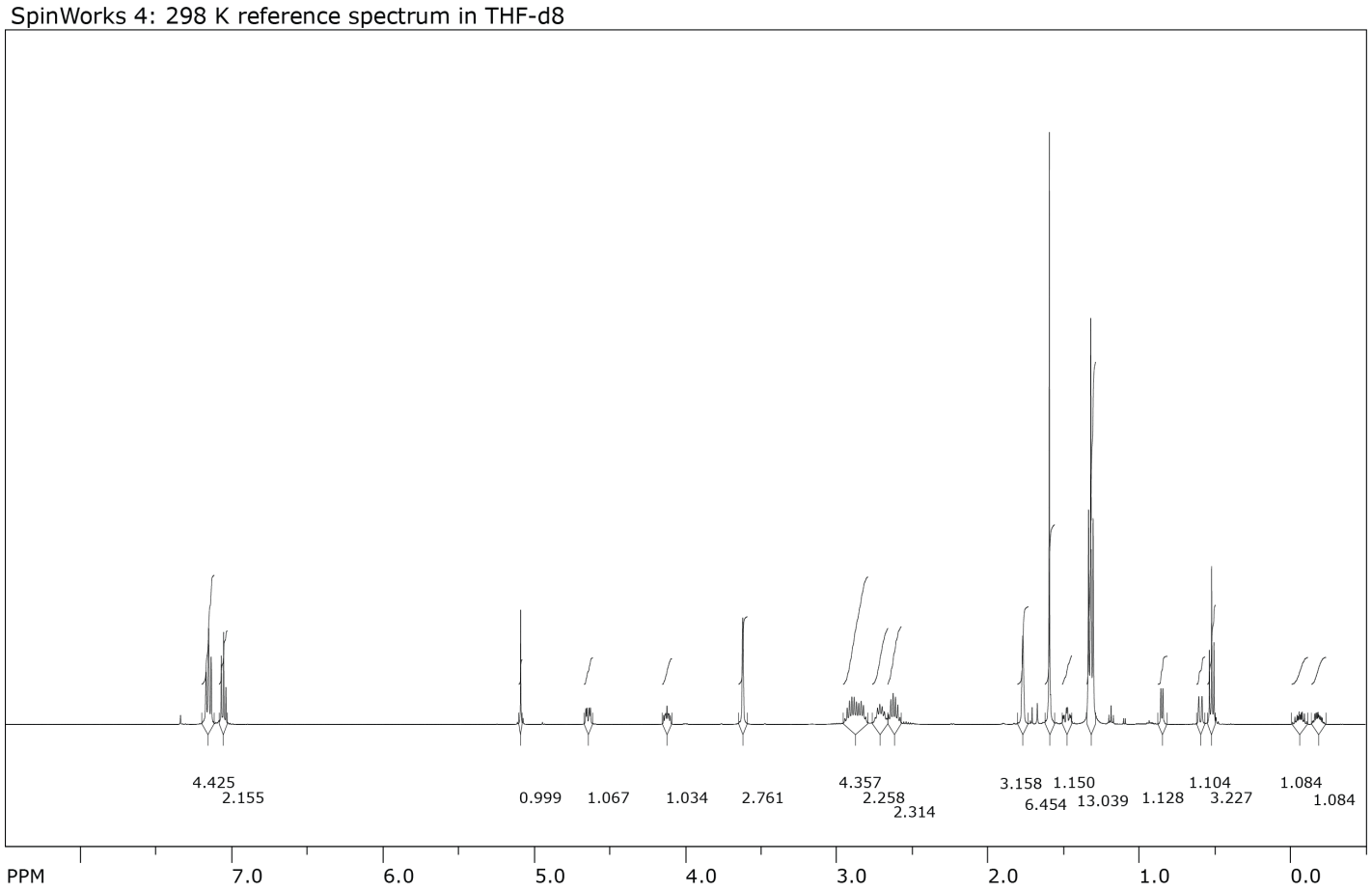
(EtBDI)Rh(1,3-CHD) [d]



Shift	B3LYP	TPSSh	Observed[a]	Coupling	B3LYP	TPSSh	*Observed*[c]
C1	83.414	80.131	72.4	H1-H2	6.8	6.9	
C2	85.121	81.740	79.5	H1-H6a	4.7	4.6	
C5	26.977	26.887	24.5	H1-H6b	2.7	2.4	
H1	0.917	1.122	0.54[a]	H2-H3	4.0	3.8	
H2	4.091	4.135	4.26	H5b-H6a	11.0	11.5	
H5a	1.298	1.317	1.37[b]	H5b-H6b	3.8	4.1	
H5b	1.597	1.607	1.64[b]	H6a-H6b	-15.6	-15.8	

[a] Observed data for (^{Me}BDI)Rh(1,3-CHD) from: Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gall, A. W., *Eur. J. Inorg. Chem.* **2000**, 753-769; Calculated data for (^{Et}BDI)Rh(1,3-CHD). [b] Assignment switched from original publication. [c] Couplings were not reported. [d] The CHD ring is slightly twisted and therefore has no symmetry, but inversion is fast. All listed values are averages between the two twisted conformations of the CHD ring.

NMR spectra for (^{Et}BDI)Rh(trans-1,3-HD)



file: ..._data\rss-1-14_lt EtBDIRhHxD\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

Figure S5. ^{1}H NMR spectrum of (^{Et}BDI)Rh(*trans*-1,3-HD) (THF-d_8, 298K), overview.

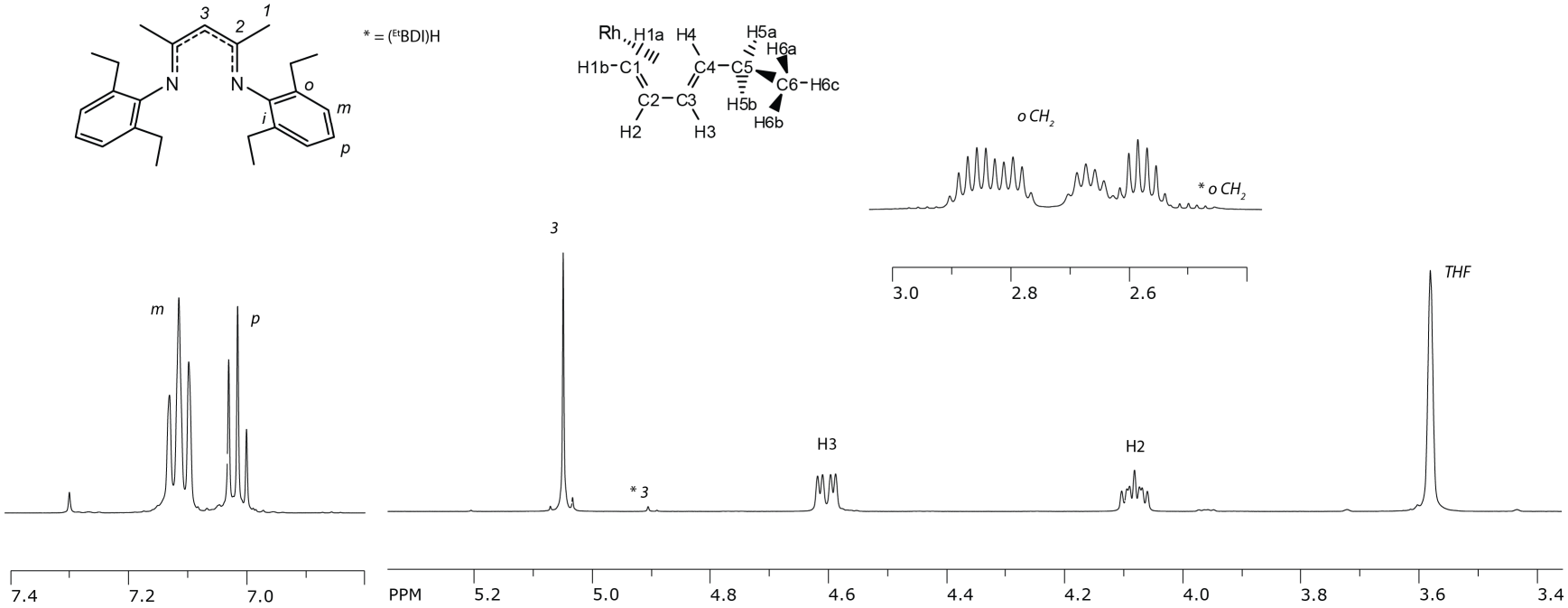


Figure S6. ^{1}H NMR spectrum of (^{Et}BDI)Rh(*trans*-1,3-HD) (THF-d_8, 298K), assignments (part 1).

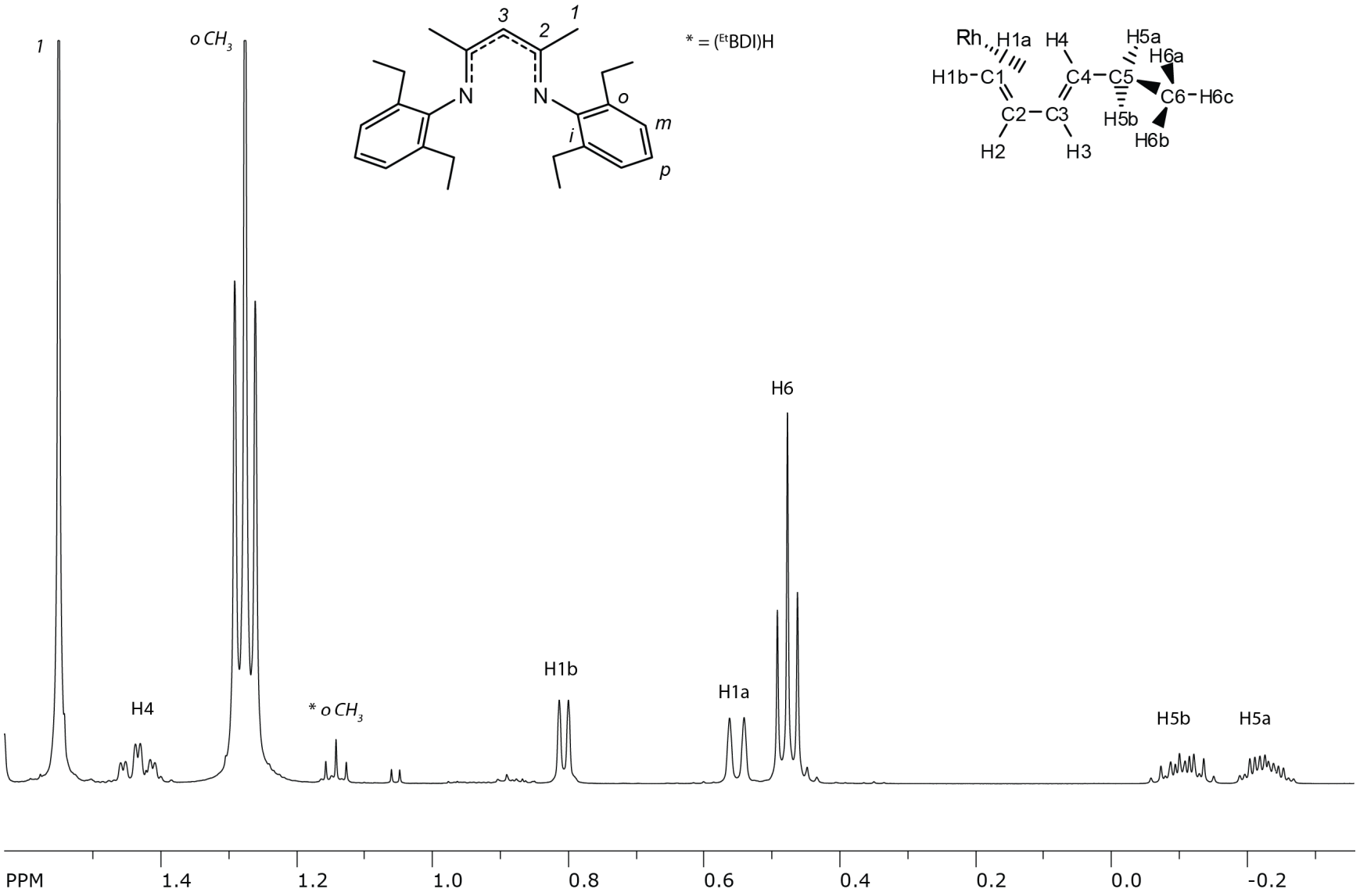


Figure S7. ^{1}H NMR spectrum of (^{Et}BDI)Rh(*trans*-1,3-HD) (THF-d_8, 298K), assignments (part 2).

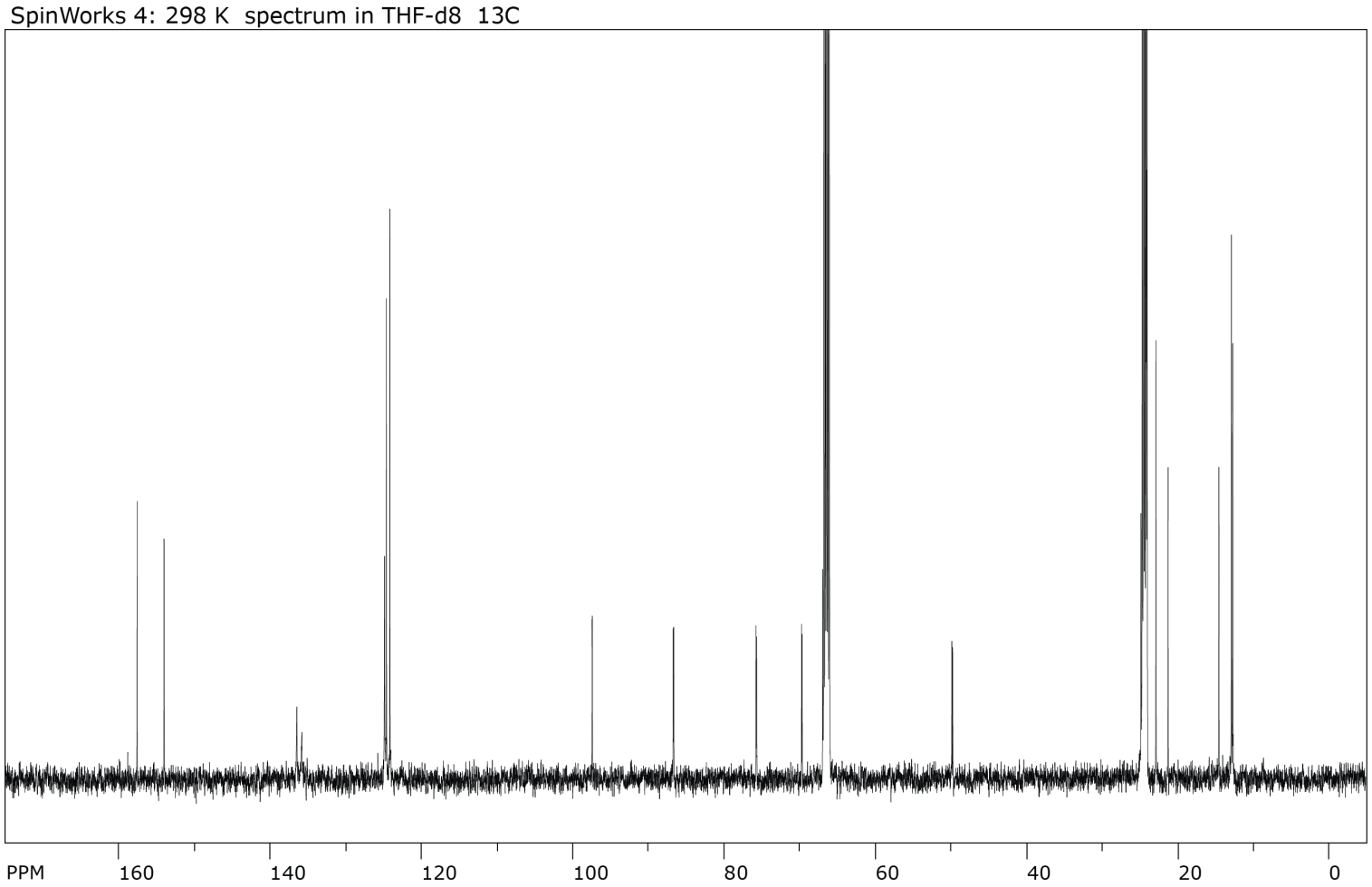


Figure S8. ^{13}C NMR spectrum of (^{Et}BDI)Rh(*trans*-1,3-HD) (THF-d_8, 298K), overview.

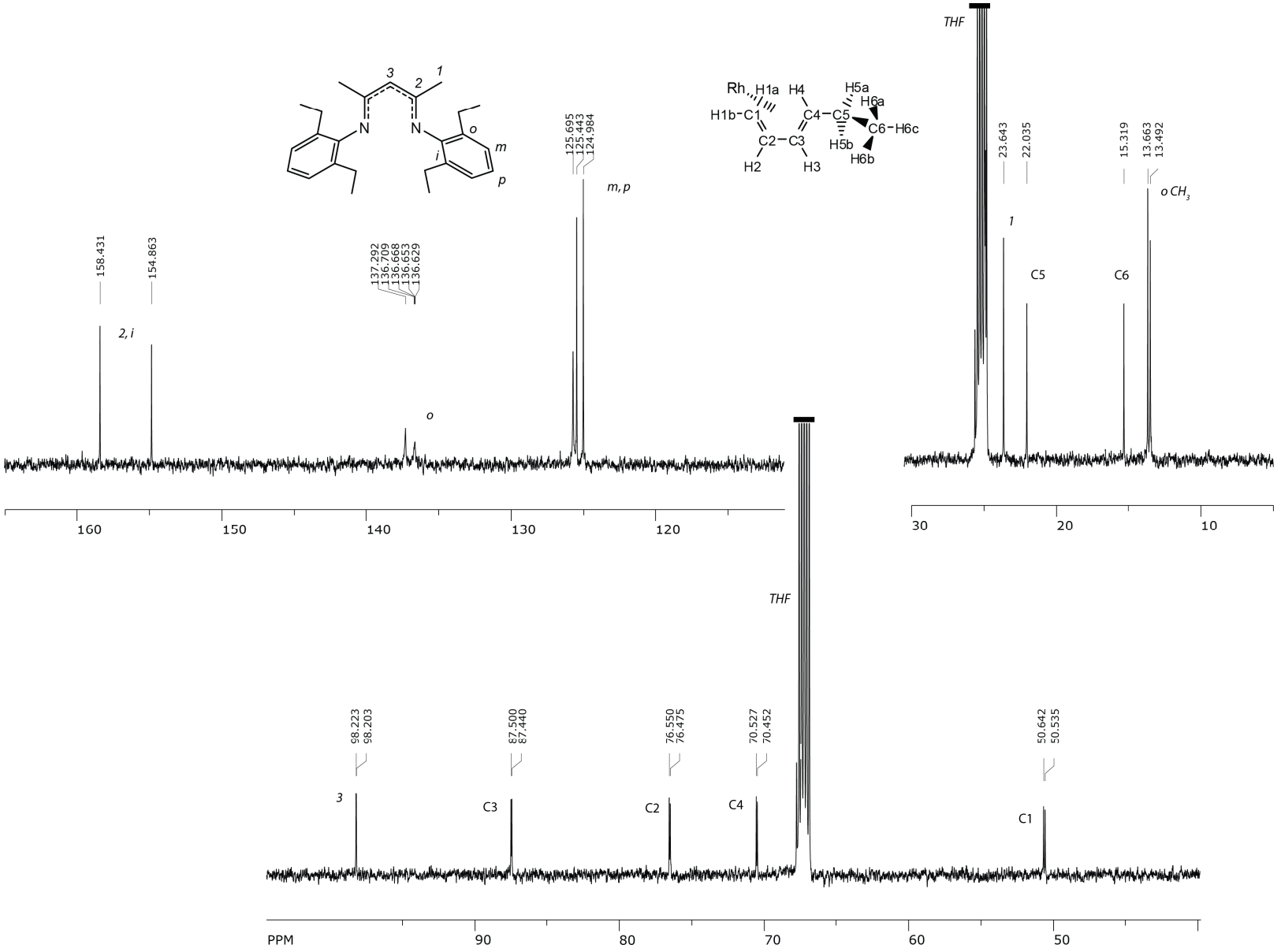


Figure S9. ^{13}C NMR spectrum of (^{Et}BDI)Rh(trans-1,3-HD) (THF-d_8, 298K), assignments.

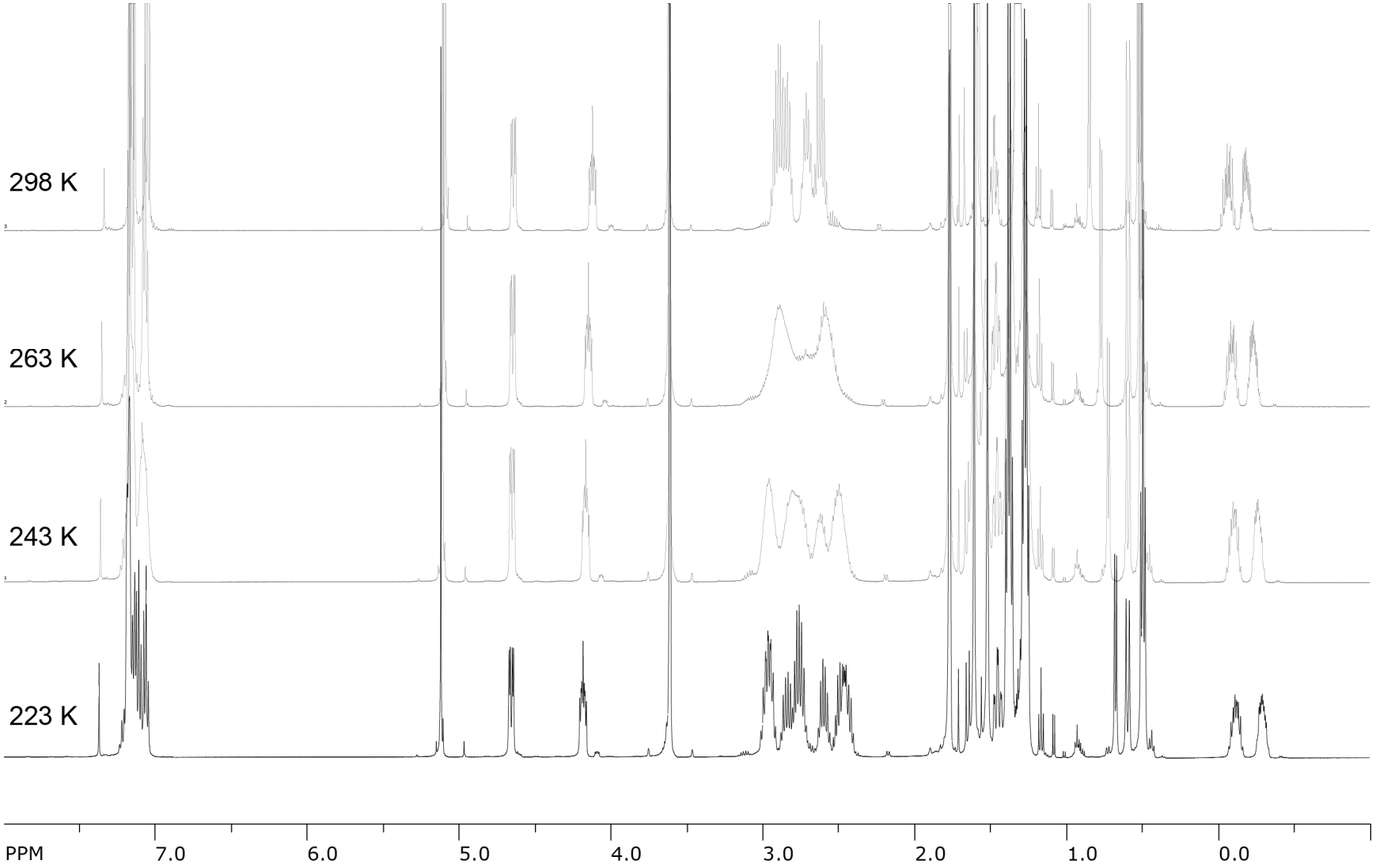


Figure S10. Selected ^{1}H VT-NMR spectra for (^{Et}BDI)Rh(trans-1,3-HD) (THF-d_8).

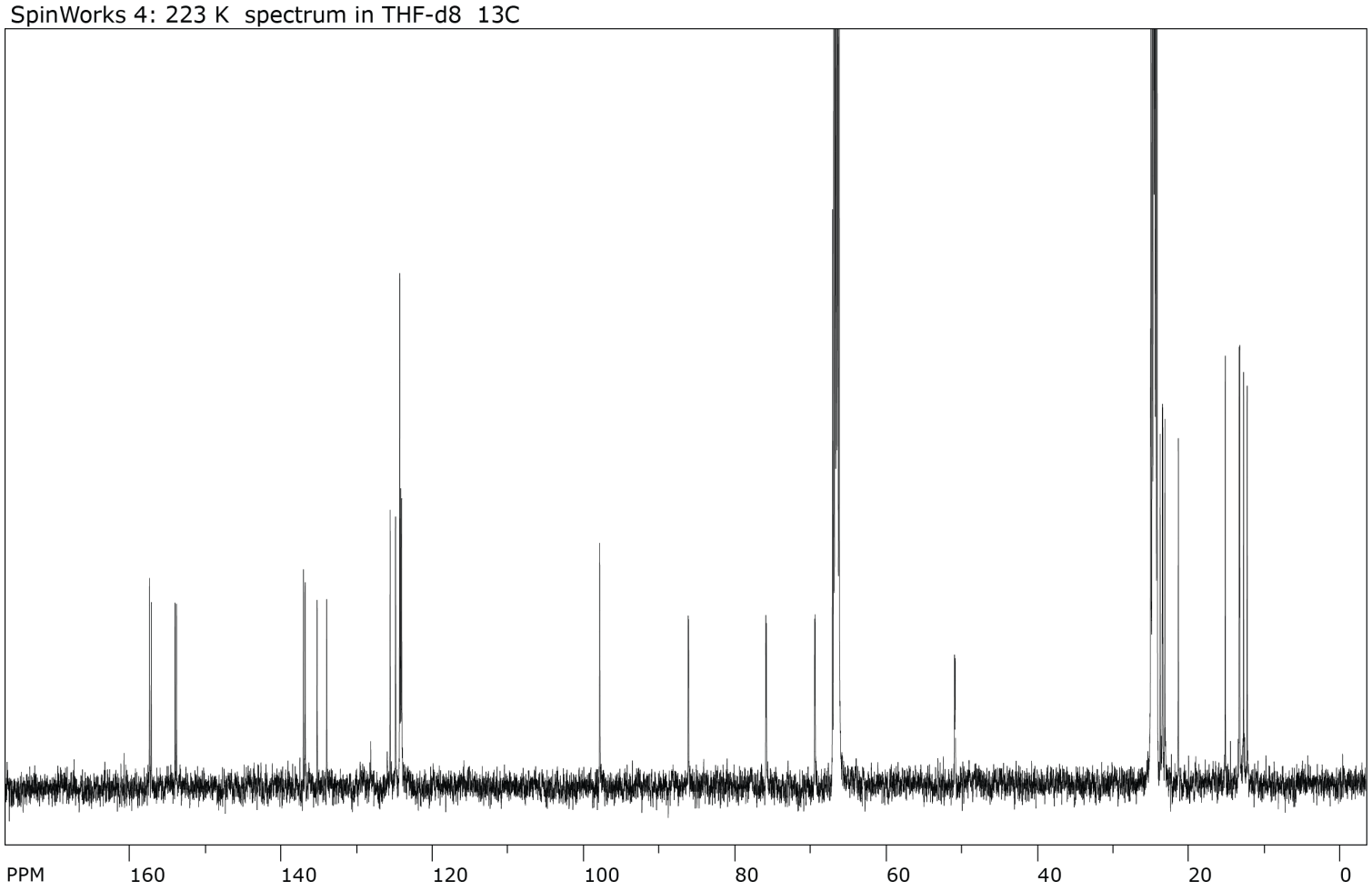


Figure S11. ^{13}C NMR spectrum of (^{Et}BDI)Rh(*trans*-1,3-HD) (THF-d_8, 223K), overview.

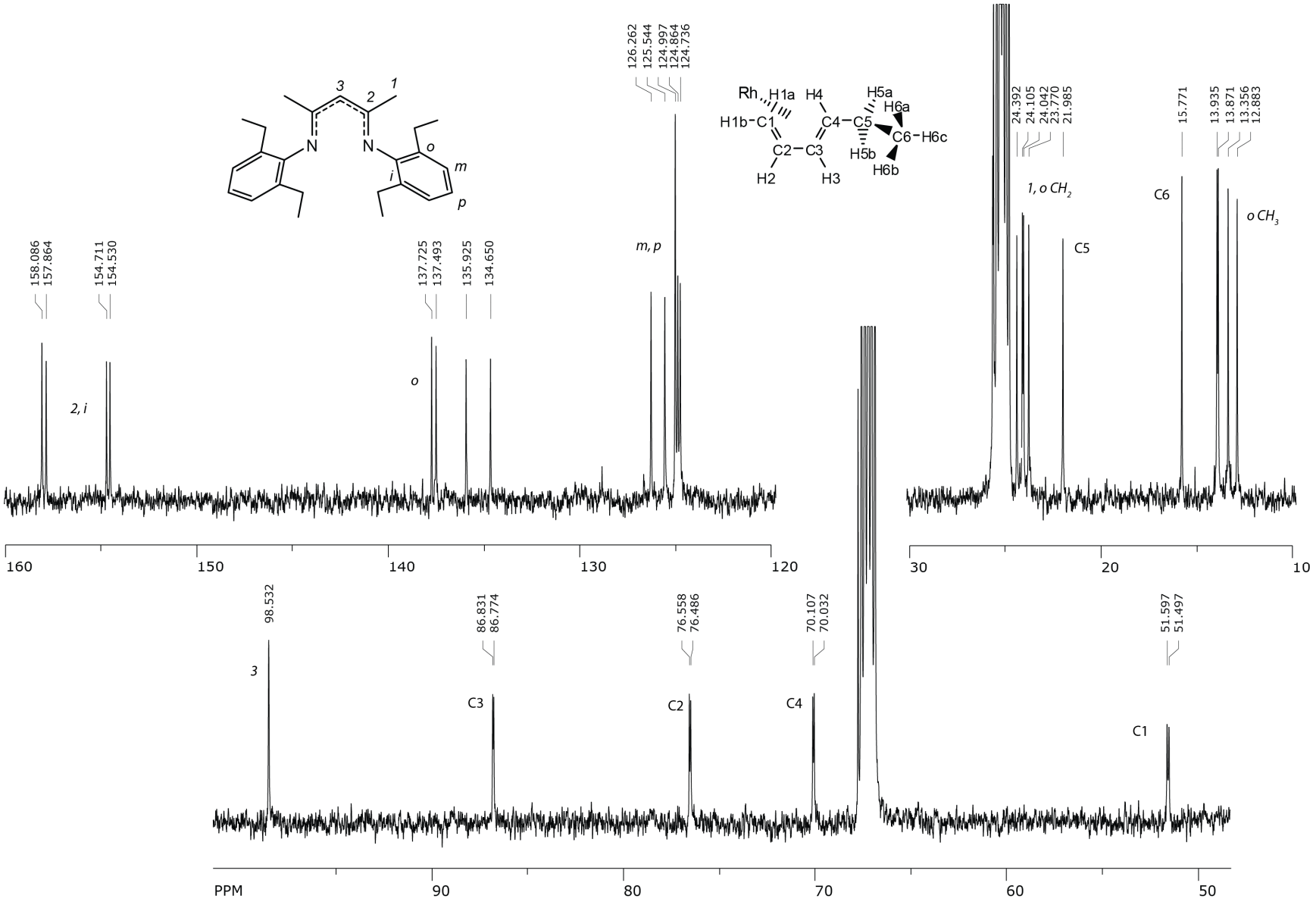
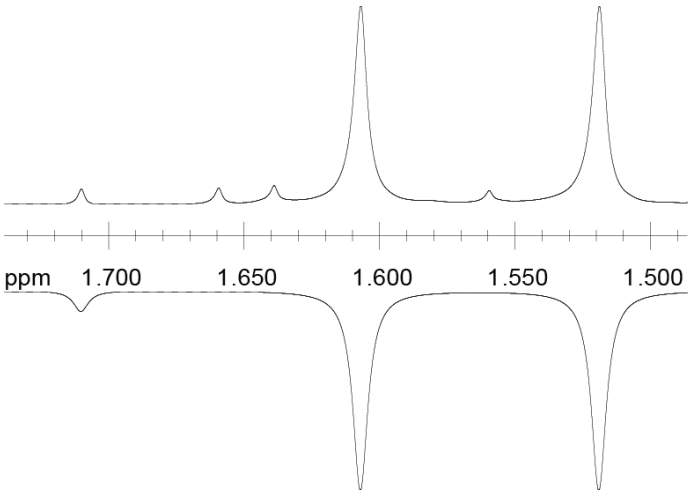
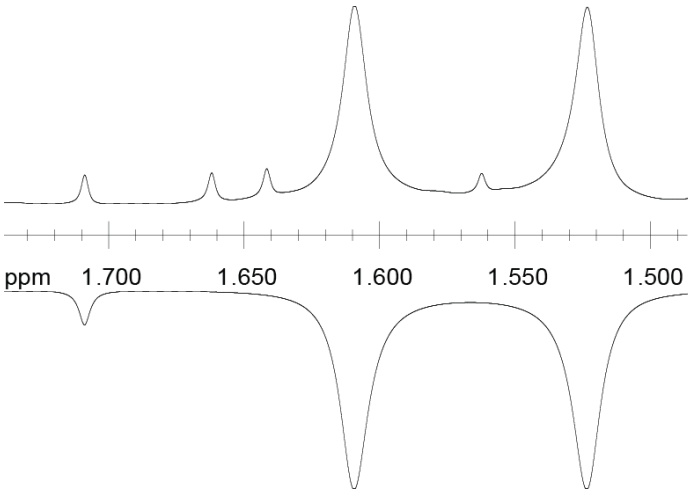
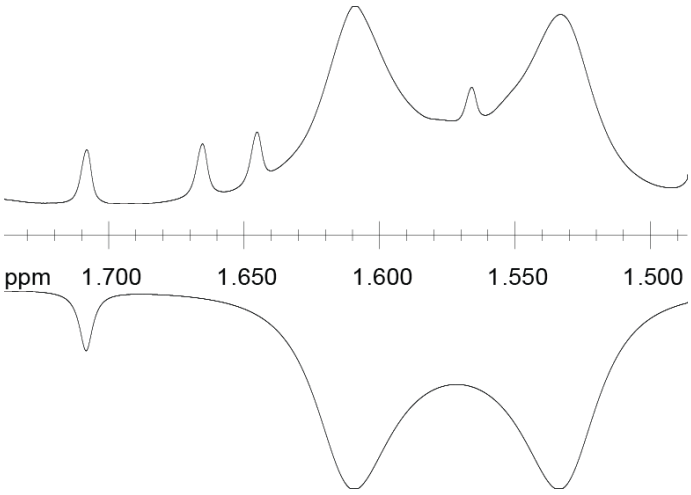
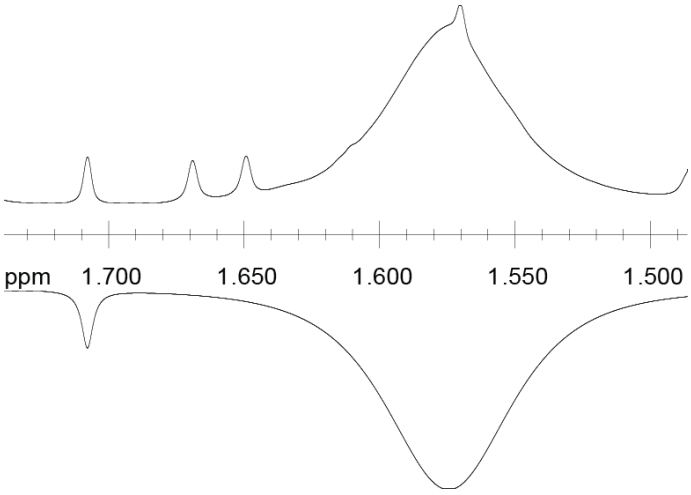
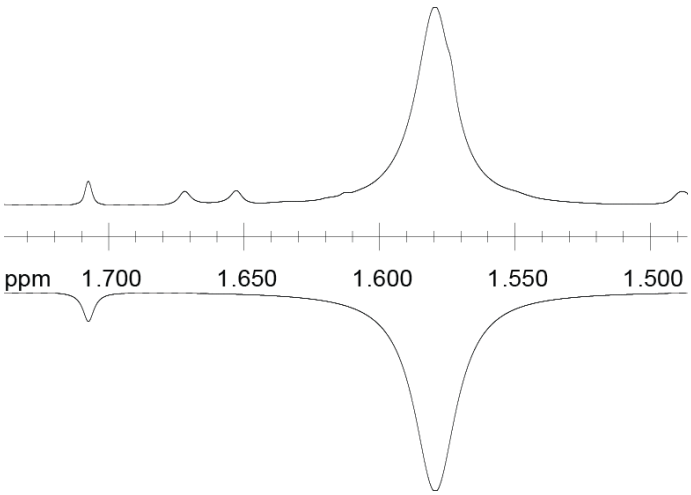


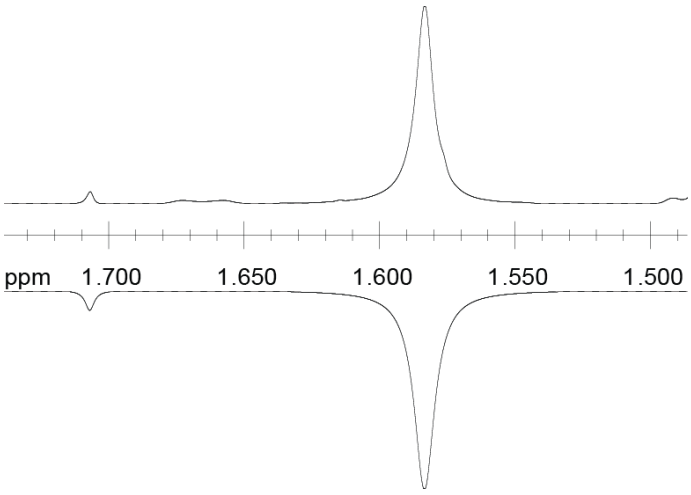
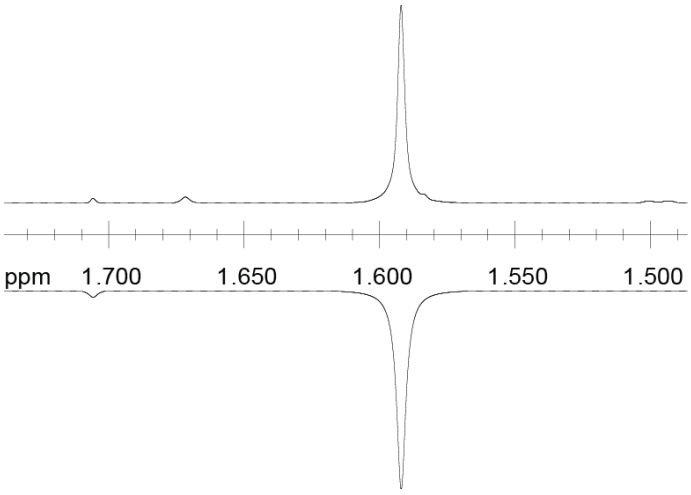
Figure S12. ^{13}C NMR spectrum of (^{Et}BDI)Rh(trans-1,3-HD) (THF-d_8, 223K), assignments.

Simulation of VT-NMR spectra, (^{Et}BDI)Rh(trans-1,3-HD), imine methyl region.

Table S4. Chemical shifts of imine methyl groups, fitted rate constants, and fitted spectrum traces for VT-NMR spectra of (^{Et}BDI)Rh(trans-1,3-HD).

T (K)	δ_1 (ppm)	δ_2 (ppm)	*k* (mol L^{-1})	Fitted spectrum[b]
223	1.519	1.607	~0	
233	1.523	1.610	11.7	

243	1.528	1.615	44.8	
253	1.534	*1.615*[a]	131	
263	1.544	*1.615*[a]	300	

273	1.552	*1.615*[a]	626	
298	1.569	*1.615*[a]	~inf	

[a] δ_2 fixed in these lineshape fits. [b] Peak near 1.71 ppm is free (^{Et}BDI)H, fitted concentration about 4 mol%; peaks near 1.65 and 1.67 ppm at low temperature are traces of a second isomer, likely (^{Et}BDI)Rh(*cis*-1,3-HD), not included in the lineshape fit.

Eyring plot

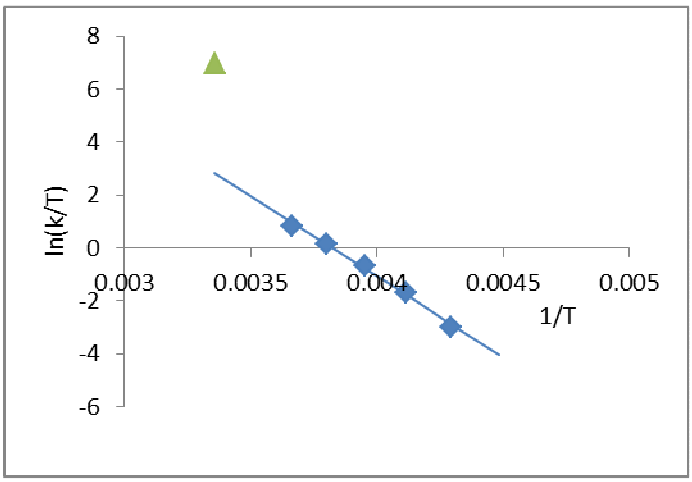
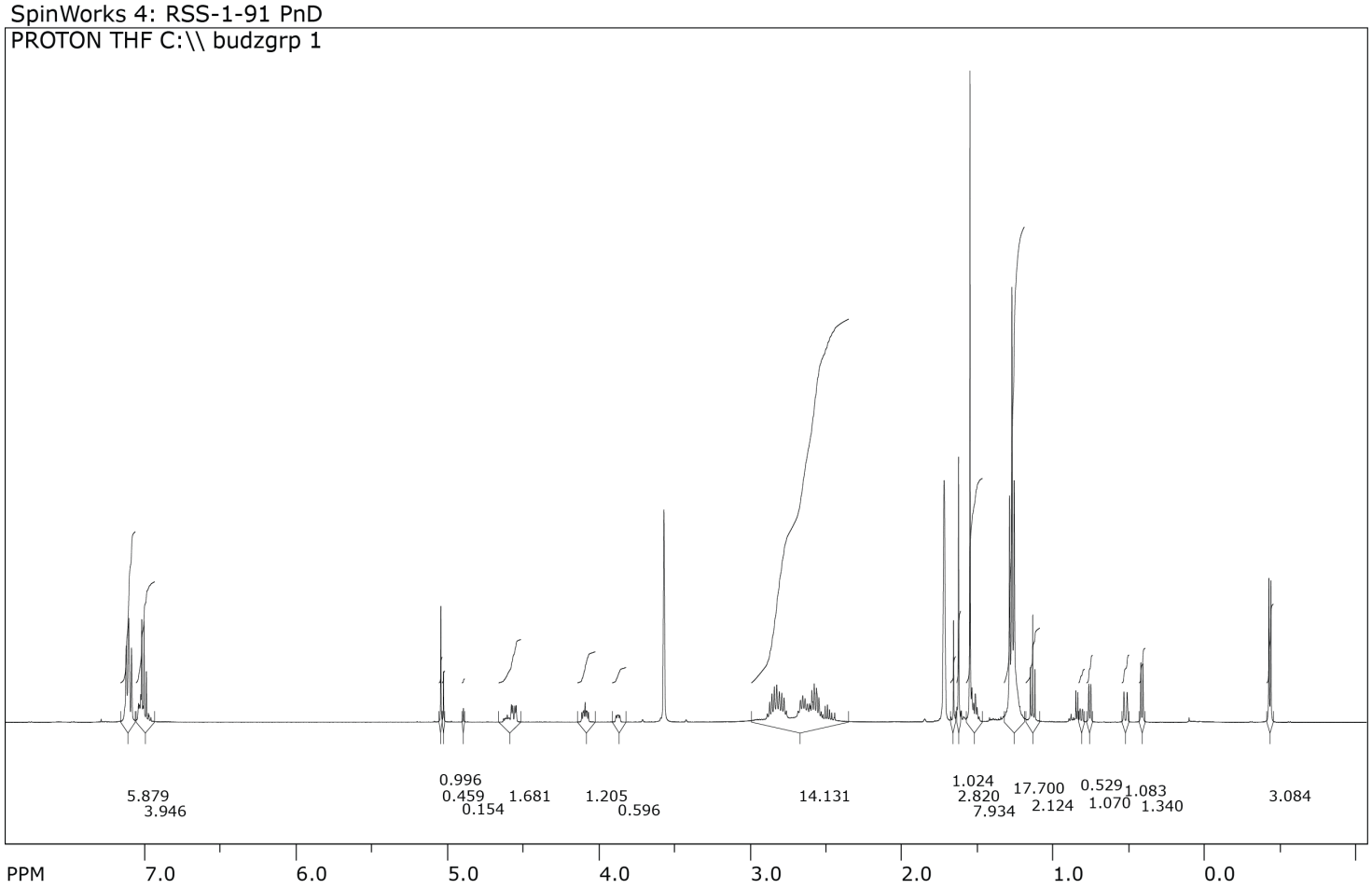


Figure S13. Eyring plot (ln k/T vs $1/T$) for (^{Et}BDI)Rh(trans-1,3-HD) over the range 233-273 K.

Fit results:

$\Delta H^{\ddagger}$ =	50.3±2.4	kJ mol^{-1}	12.0±0.6	kcal mol^{-1}
$\Delta S^{\ddagger}$ =	-5.4±9.7	J mol^{-1} K^{-1}	-1.3±2.3	cal mol^{-1} K^{-1}

NMR spectra for (^{Et}BDI)Rh(trans/cis-1,3-PD)



file: ...nal_data\RSS-1-91 EtBDIRhPnD\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.129096 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

Figure S14. ^{1}H NMR spectrum of (^{Et}BDI)Rh(*trans/cis*-1,3-PD) (THF-d_8, 298K), overview.

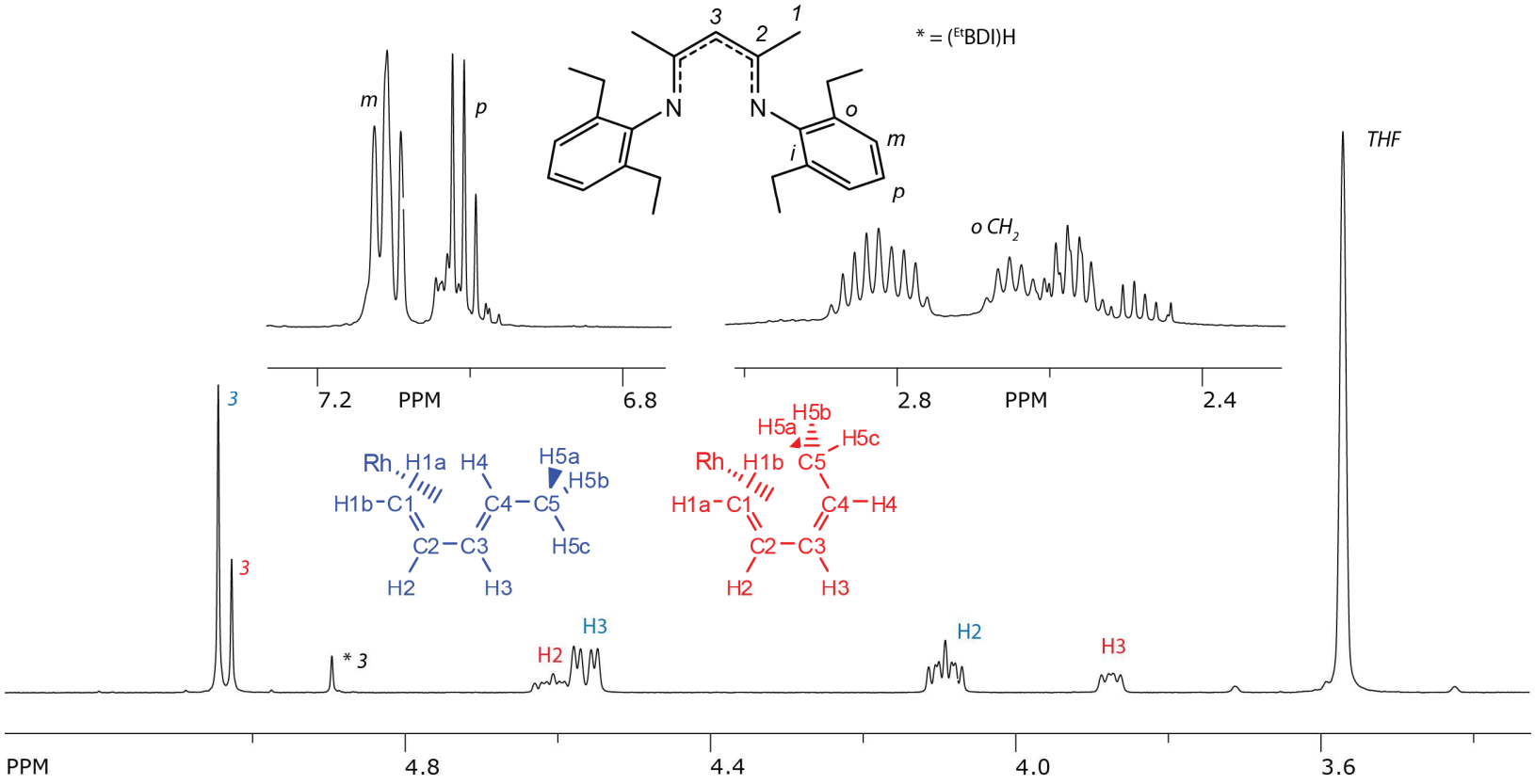


Figure S15. ^{1}H NMR spectrum of (^{Et}BDI)Rh(*trans/cis*-1,3-PD) (THF-d_8, 298K), assignments (part 1).

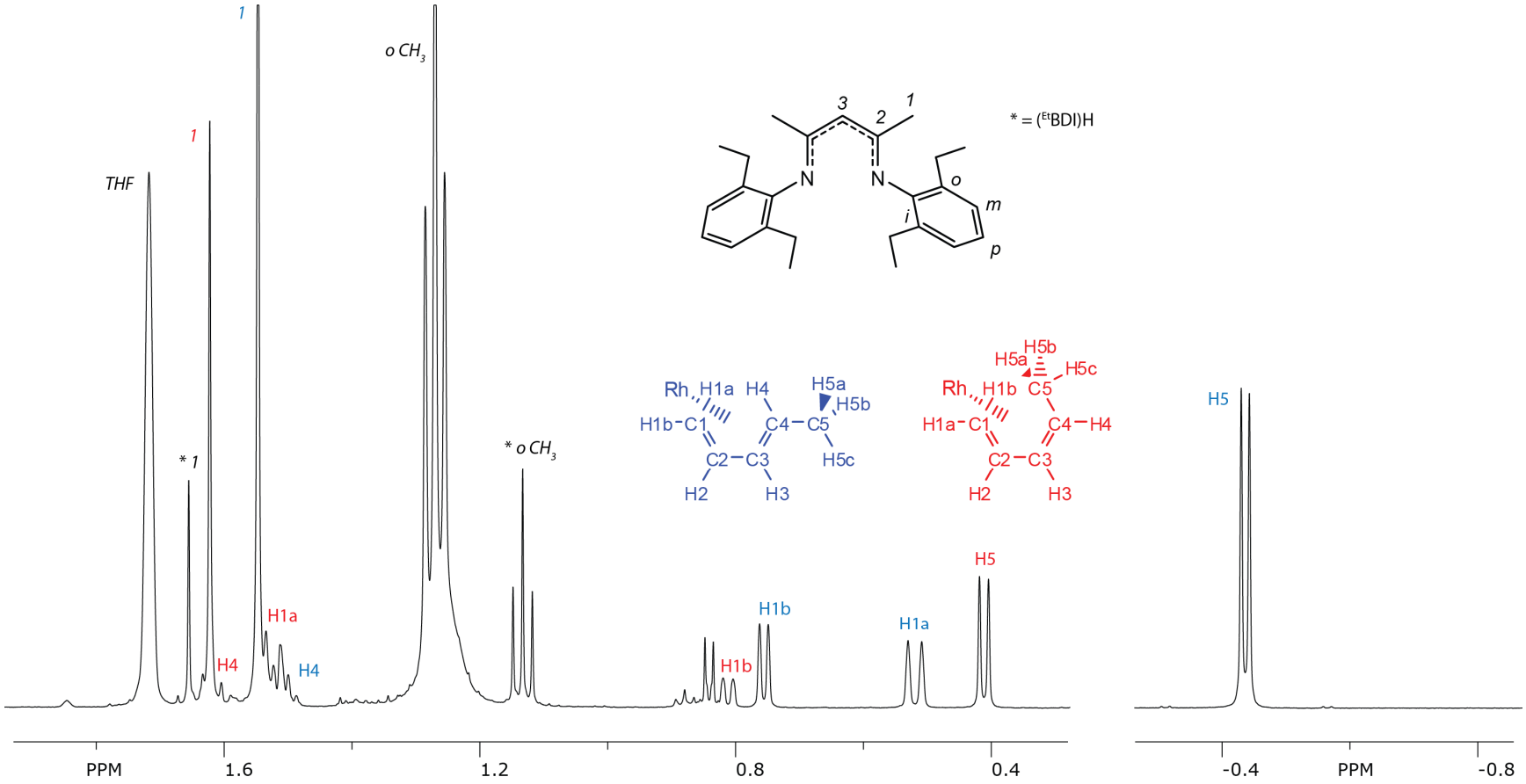
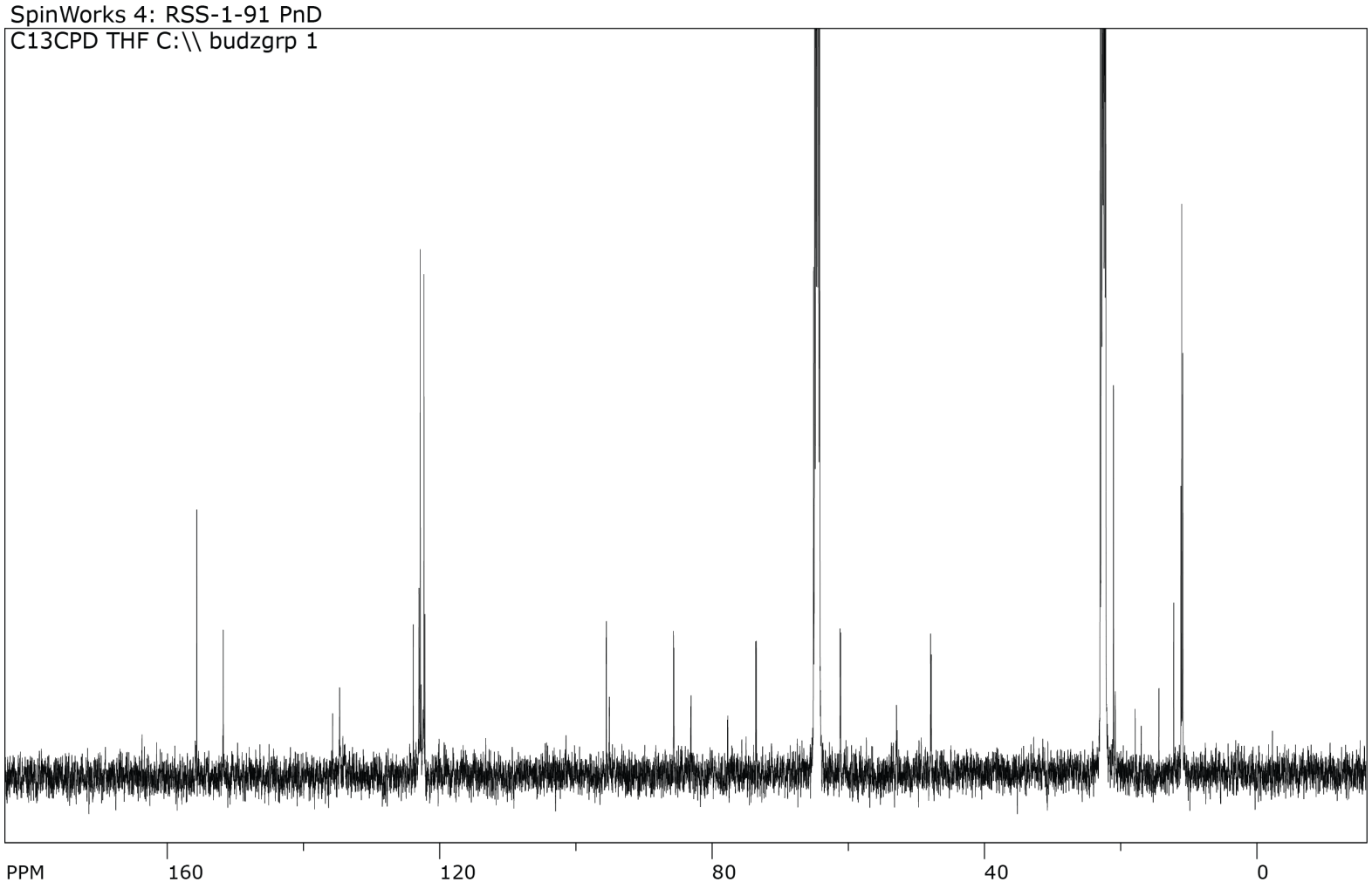


Figure S16. ^{1}H NMR spectrum of (^{Et}BDI)Rh(*trans/cis*-1,3-PD) (THF-d_8, 298K), assignments (part 2).



file: ...nal_data\RSS-1-91 EtBDIRhPnD\2\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.91 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 1024

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000

Figure S17. ^{13}C NMR spectrum of (^{Et}BDI)Rh(*trans/cis*-1,3-PD) (THF-d_8, 298K), overview.

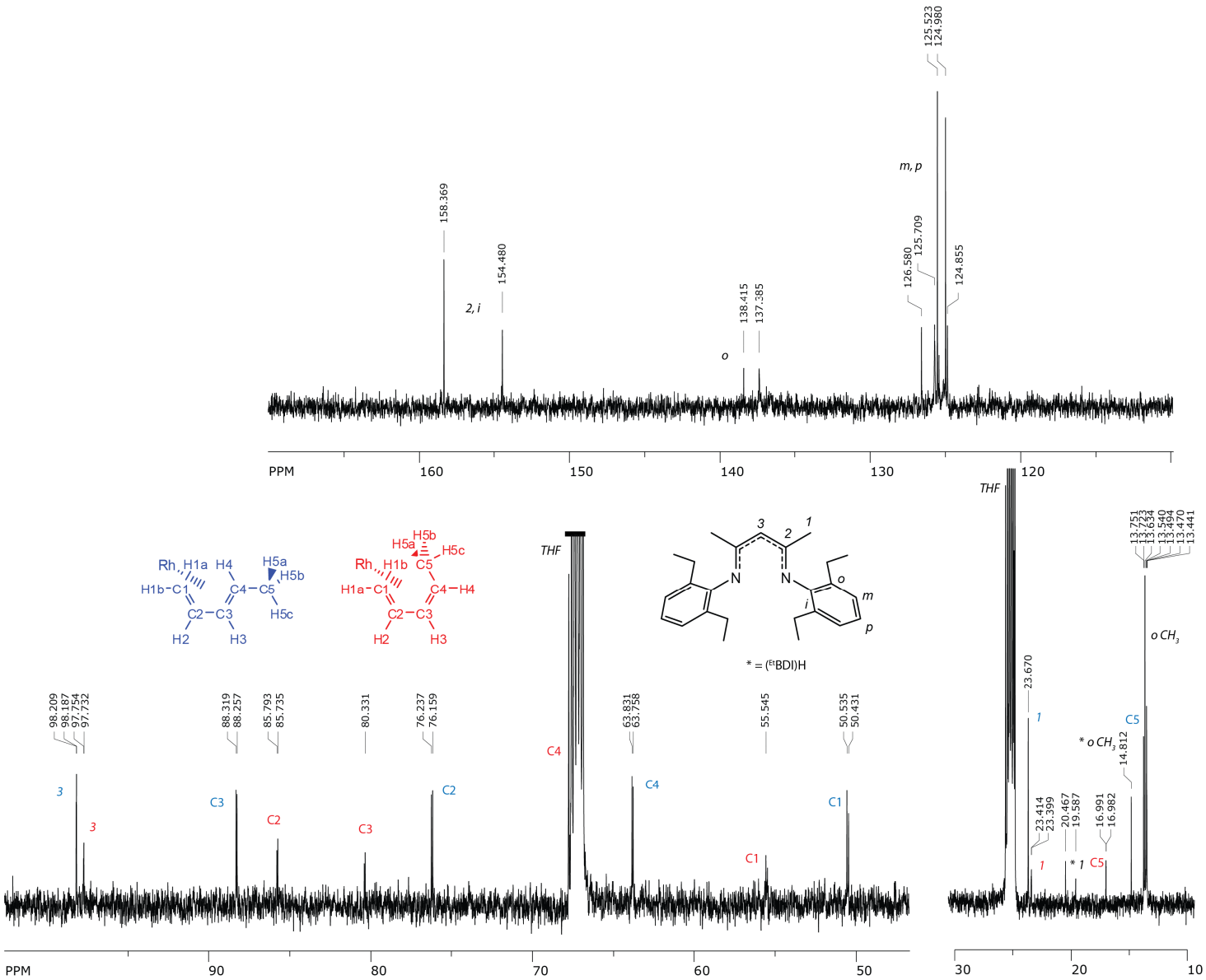


Figure S18. ^{13}C NMR spectrum of (^{Et}BDI)Rh(*trans/cis*-1,3-PD) (THF-d_8, 298K), assignments.

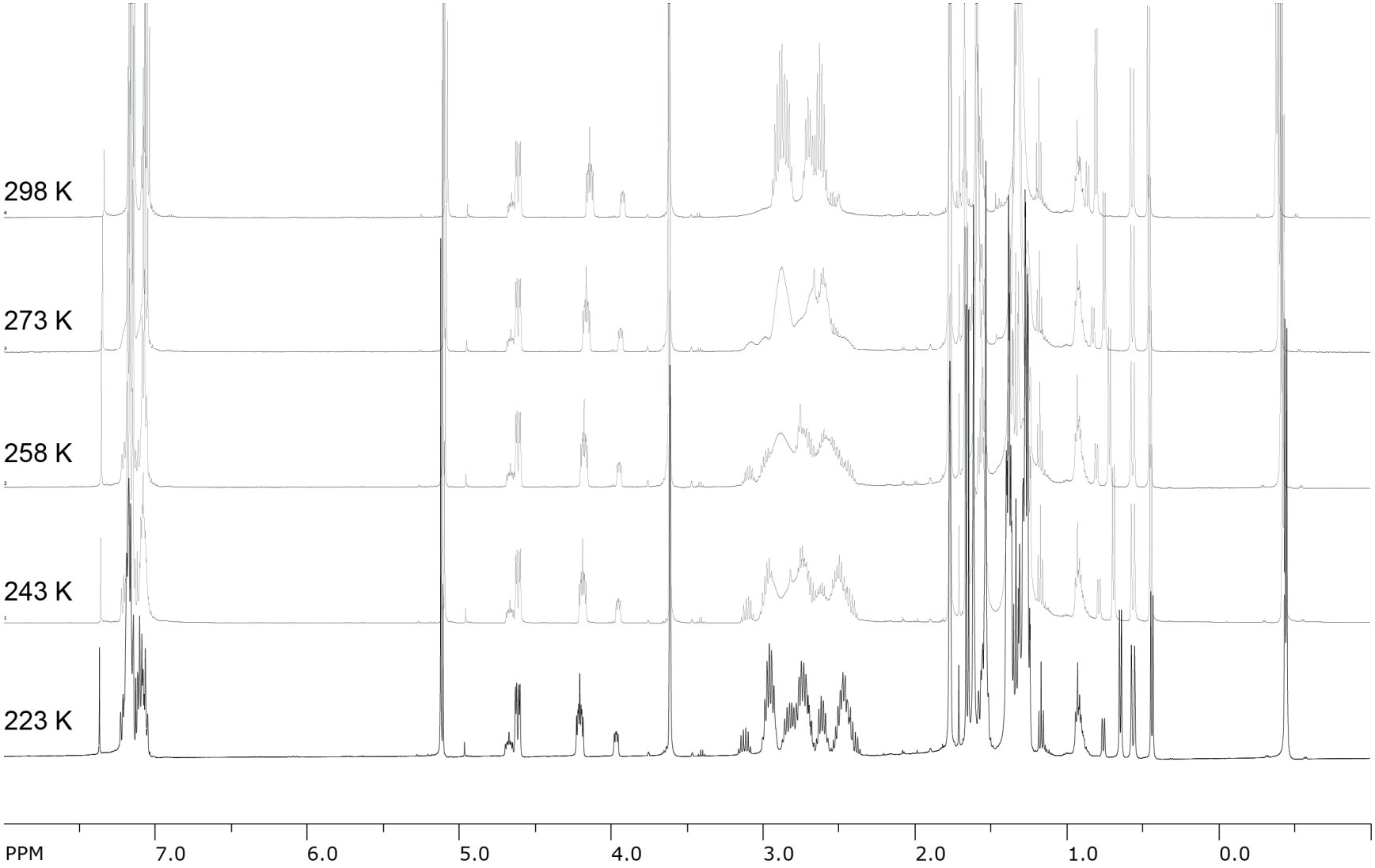
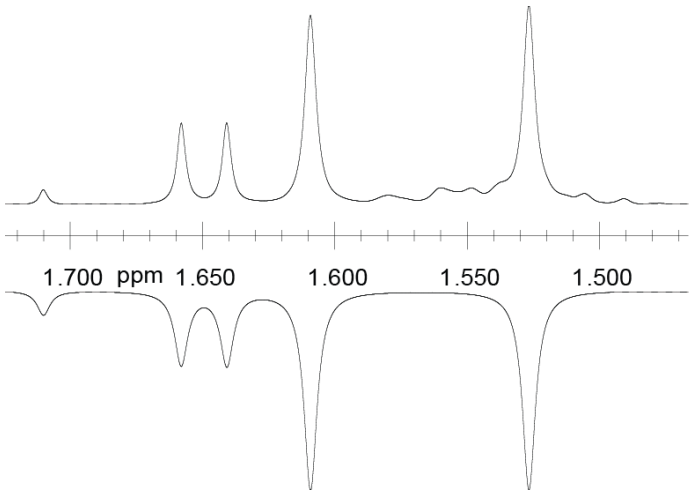
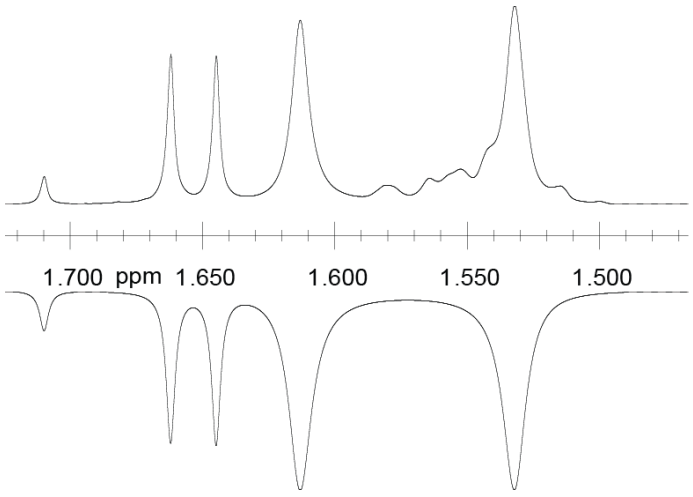
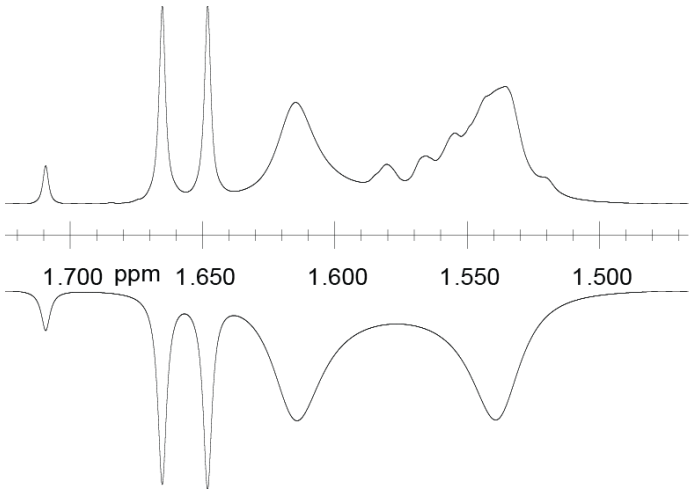
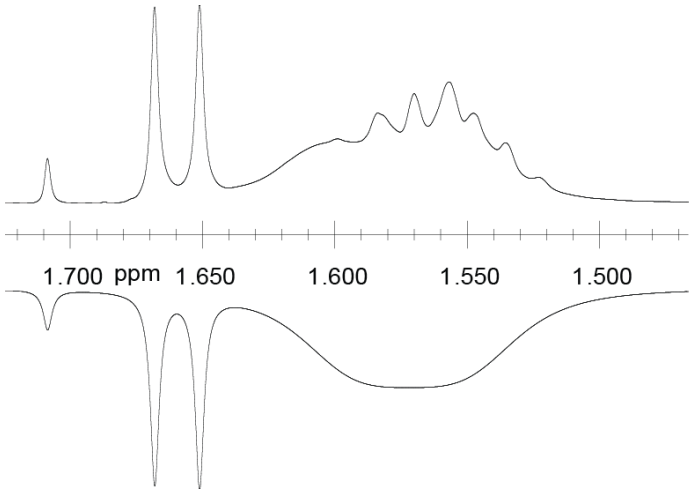
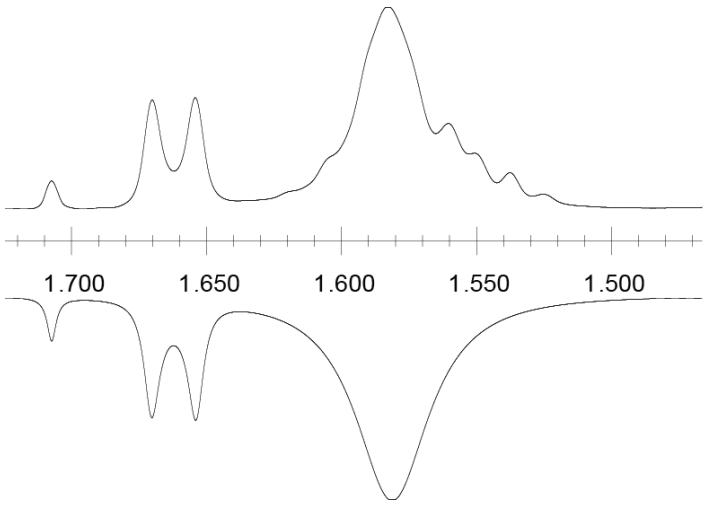


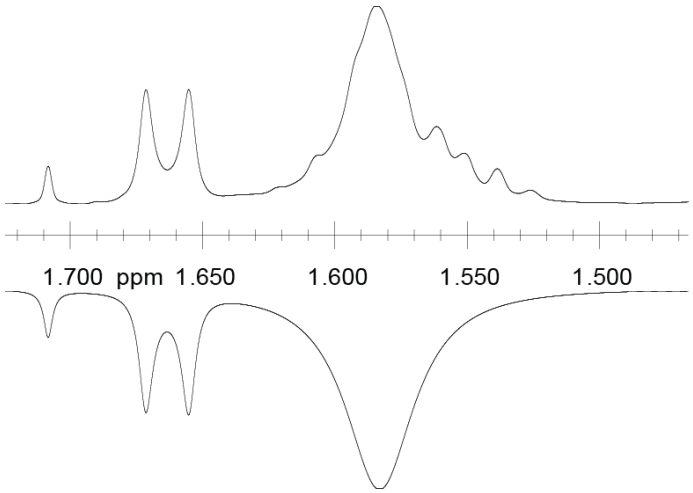
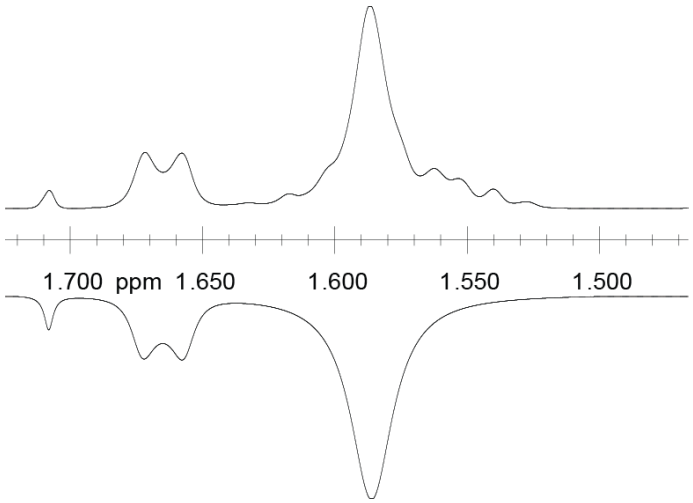
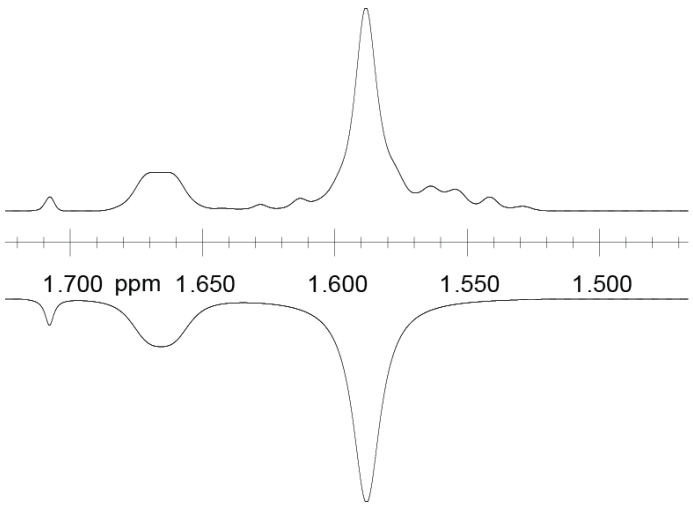
Figure S19. Selected ^{1}H VT-NMR spectra for (^{Et}BDI)Rh(*trans/cis*-1,3-PD) (THF-d_8).

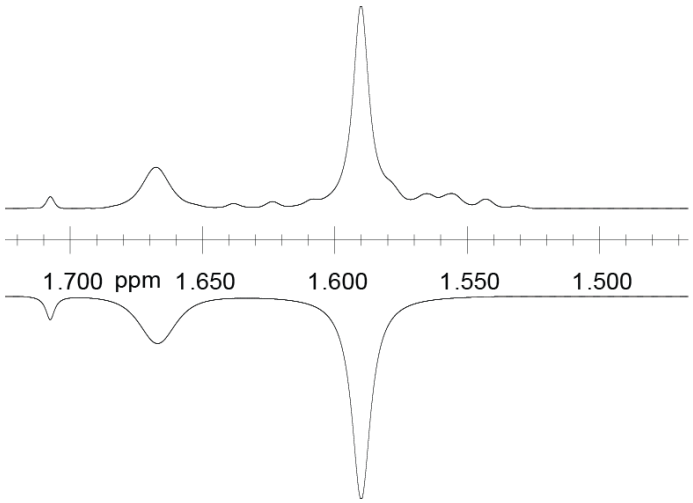
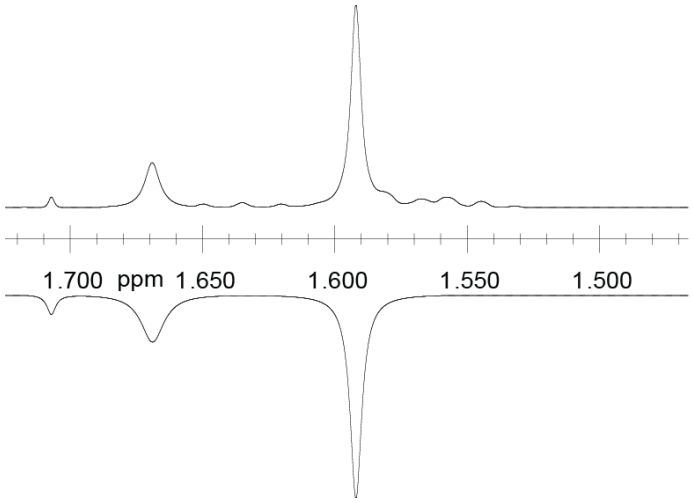
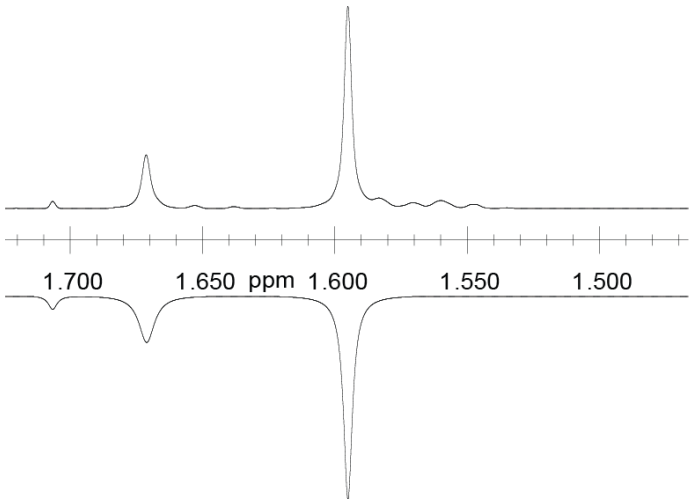
Simulation of VT-NMR spectra, (^{Et}BDI)Rh(trans/cis-1,3-PD), imine methyl region.

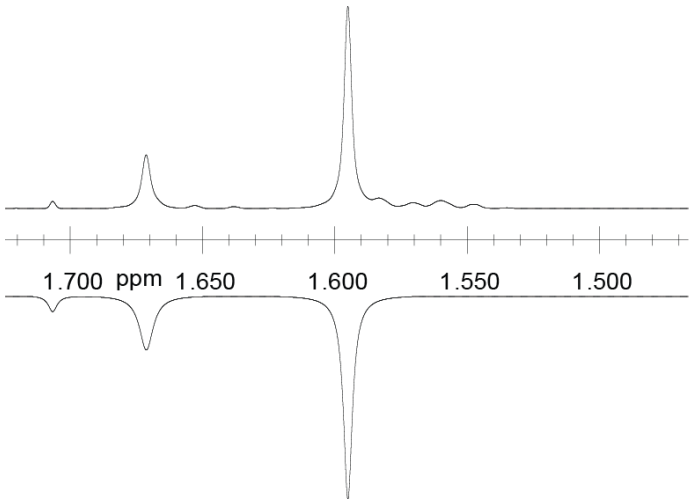
Table S5. Chemical shifts of imine methyl groups, fitted rate constants, and fitted spectrum traces for VT-NMR spectra of (^{Et}BDI)Rh(trans/cis-1,3-PD).

T **(K)**	δ_1 **(ppm):** ***trans*** ***cis***	δ_2 **(ppm):** ***trans*** ***cis***	***k*** **(mol L^{-1})**	**Fitted spectrum[b]**
213	1.527 1.641	1.609 1.658	~0 ~0	
223	1.532 1.645	1.613 1.662	9.94 ~0	

233	1.537 1.648	1.617 1.665	29.5 ~0	
243	1.532 1.651	1.612 1.668	89.1 ~0	
253	1.546 1.654	*1.616*[a] 1.671	153 1.23	

258	1.549 1.655	*1.617*[a] 1.672	152 0.94	
263	1.555 1.656	*1.617*[b] 1.674	209 3.10	
268	1.558 1.656	*1.618*[a] *1.676*[a]	337 7.27	

273	1.561 1.657	*1.619*[a] *1.677*[a]	589 11.6	
278	1.565 1.659	*1.619*[a] *1.679*[a]	1760 23.1	
288	1.569 1.660	*1.621*[a] *1.682*[a]	~inf 49.6	

298	1.568 1.657	*1.622*[a] *1.685*[a]	~inf 111	

[a] δ_2 extrapolated from lower-temperature spectra for these lineshape fits. [b] Peak near 1.71 ppm is free (^{Et}BDI)H, fitted concentrations 70 mol% *trans*, 26 mol% *cis*, 4 mol% (^{Et}BDI)H; broader peaks in the range of 1.48-1.58 ppm are due to the diene ligand, not included in the lineshape fit.

Eyring plot for *trans* isomer

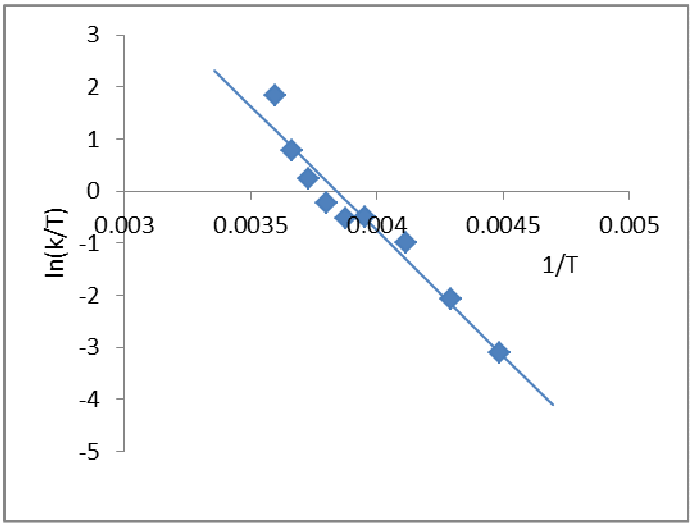


Figure S20. Eyring plot (ln *k*/*T* vs 1/*T*) for (^{Et}BDI)Rh(trans-1,3-PD) over the range 223-278 K.

Fit results:

$\Delta H^{\ddagger}$ =	39.8±3.7	kJ mol^{-1}	9.5±0.9	kcal mol^{-1}
$\Delta S^{\ddagger}$ =	-44.9±14.5	J mol^{-1} K^{-1}	-10.7±3.5	cal mol^{-1} K^{-1}

Eyring plot for *cis* isomer

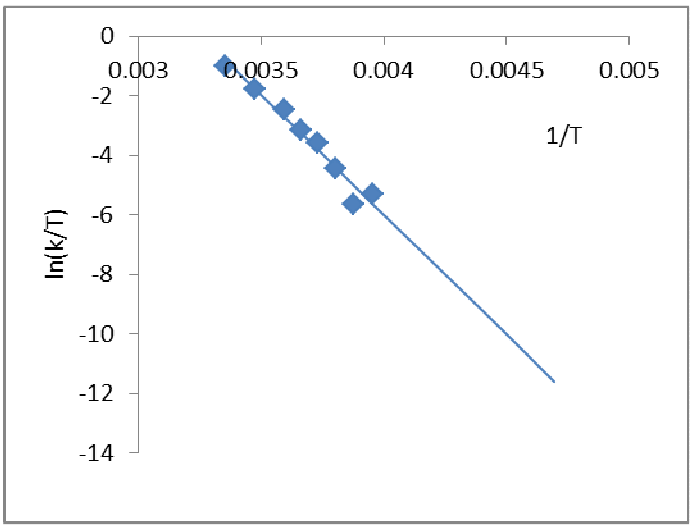


Figure S21. Eyring plot (ln k/T vs $1/T$) for (^{Et}BDI)Rh(cis-1,3-PD) over the range 253-298 K.

Fit results:

$\Delta H^{\ddagger}$ =	67.1±5.2	kJ mol^{-1}	16.0±1.2	kcal mol^{-1}
$\Delta S^{\ddagger}$ =	21.0±19.2	J mol^{-1} K^{-1}	5.0±4.6	cal mol^{-1} K^{-1}

NMR spectra for ([Me]BDI)Rh(BD)

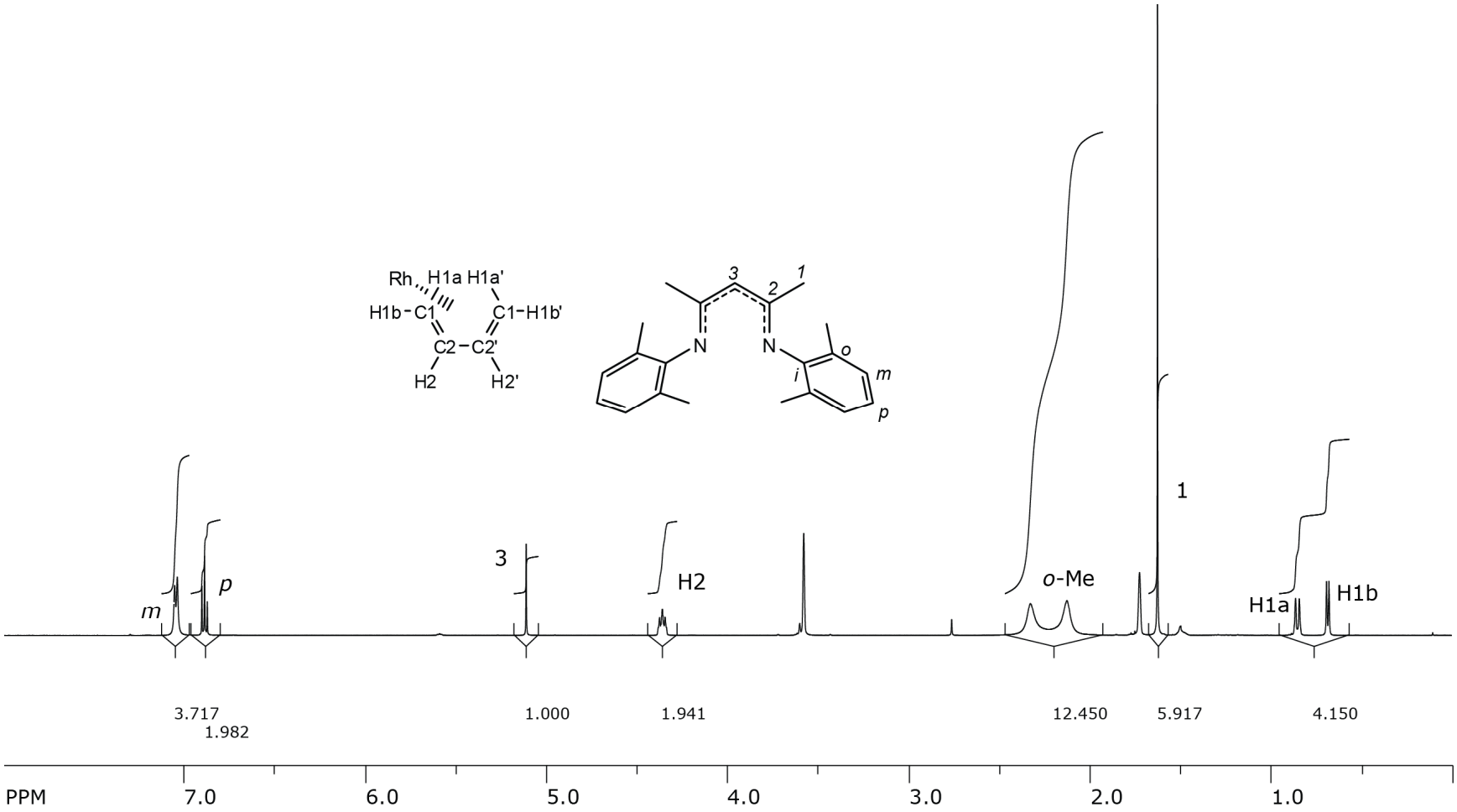


Figure S22. ^{1}H NMR spectrum of ([Me]BDI)Rh(BD) (THF-d_8, 298K).

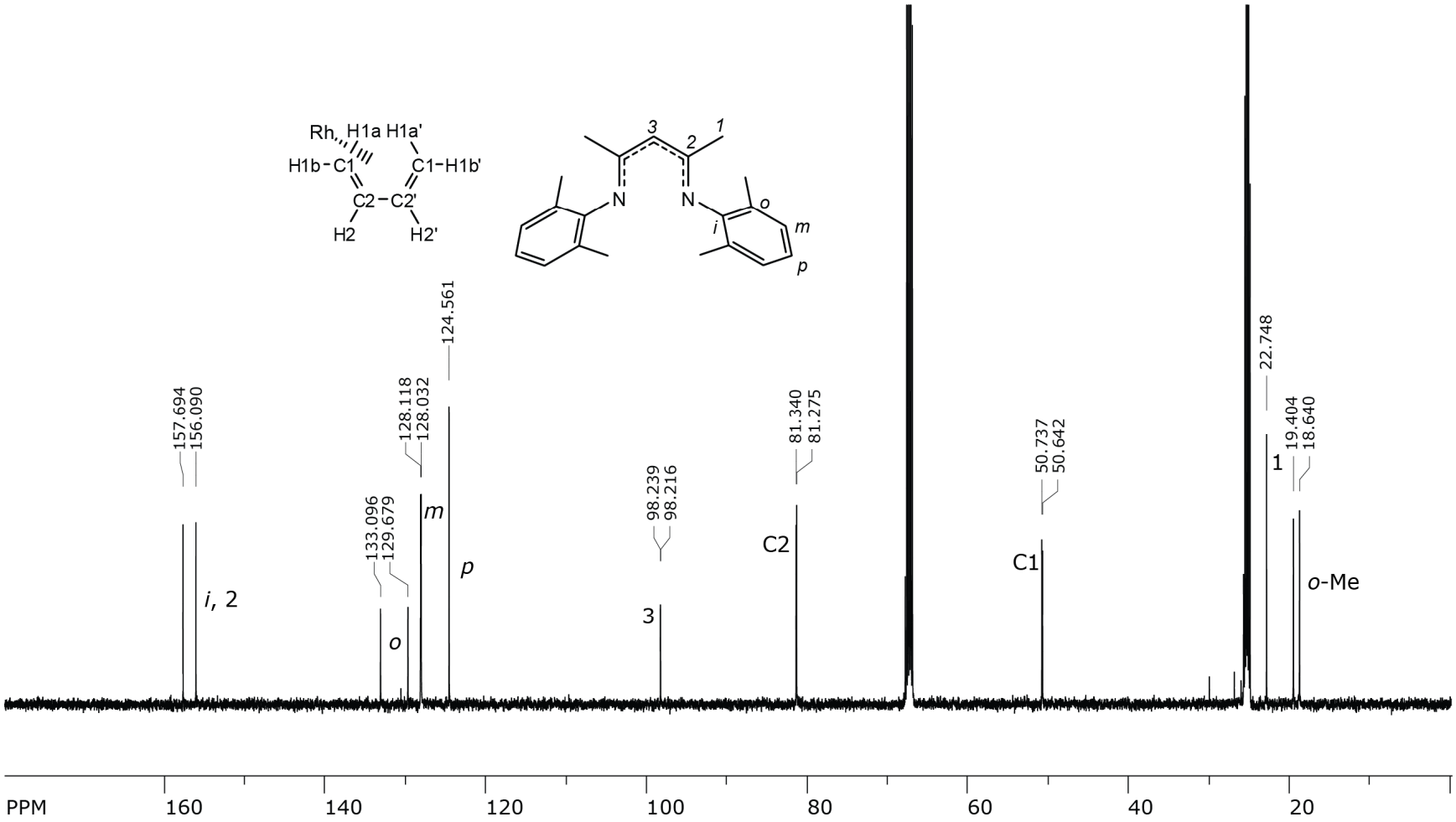


Figure S23. ^{13}C NMR spectrum of (^{Me}BDI)Rh(BD) (THF-d_8, 268K).

Simulation of VT-NMR spectra, (^{Me}BDI)Rh(BD), aryl methyl region.

Table S6. Fitted rate constants for VT-NMR spectra of (^{Me}BDI)Rh(BD).

T (K)	*k* (mol L^{-1})	1/*T*	ln(*k*/*T*)	pred ln(*k*/*T*)
273	*~0*	*0.00366*		*-4.174*
278	*3.77*	*0.00360*	*-4.301*	*-3.628*
283	10.7	0.00353	-3.275	-3.101
288	20.8	0.00347	-2.628	-2.592
293	37.8	0.00341	-2.048	-2.101
298	63.4	0.00336	-1.548	-1.627
303	106	0.00330	-1.050	-1.168
308	163	0.00325	-0.636	-0.723
313	244	0.00319	-0.249	-0.294
318	358	0.00314	0.118	0.123
323	534	0.00310	0.503	0.526
328	781	0.00305	0.868	0.918
333	1110	0.00300	1.204	1.297

Eyring plot

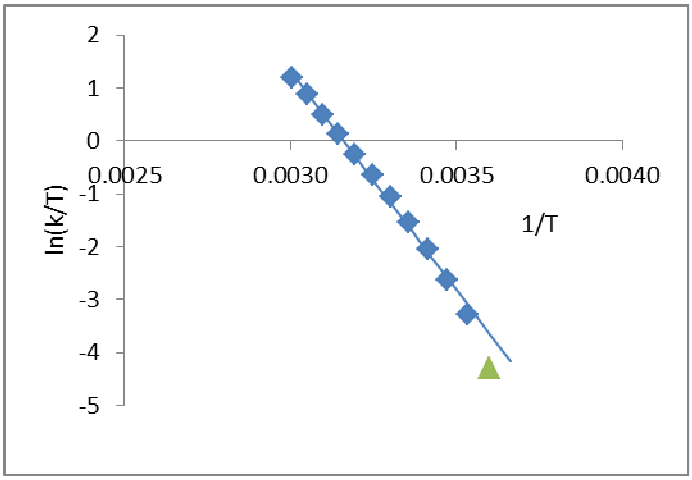


Figure S24. Eyring plot (ln *k*/*T* vs 1/*T*) for (^{Me}BDI)Rh(BD) over the range 273-333 K.

Fit results:

$\Delta H^{\ddagger}$ =	68.9±1.4	kJ mol^{-1}	16.5±0.3	kcal mol^{-1}
$\Delta S^{\ddagger}$ =	20.2±4.5	J mol^{-1} K^{-1}	4.8±1.1	cal mol^{-1} K^{-1}

NMR spectra for (^{Me}BDI)Ir(BD)

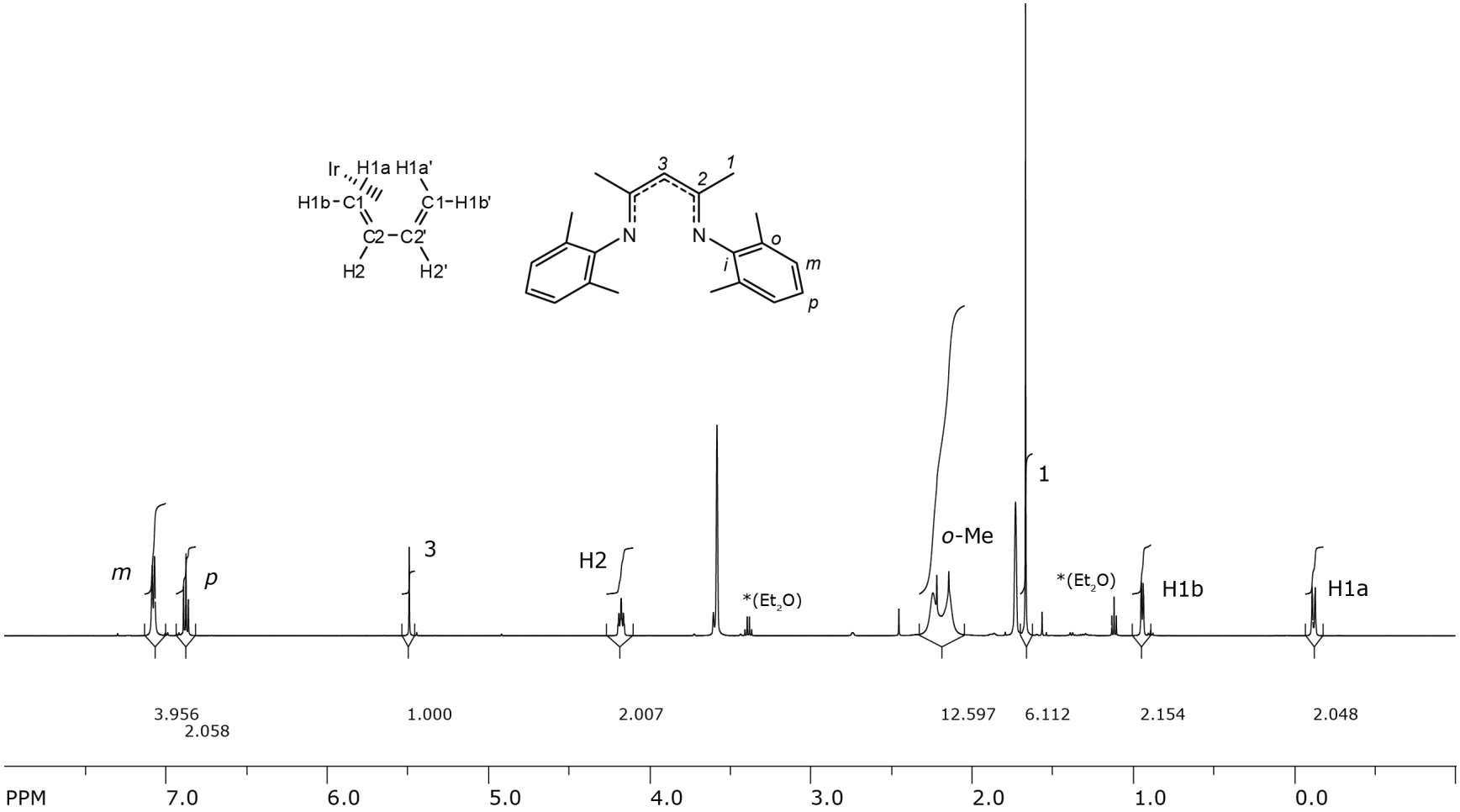


Figure S25. ^{1}H NMR spectrum of (^{Me}BDI)Ir(BD) (THF-d_8, 298K).

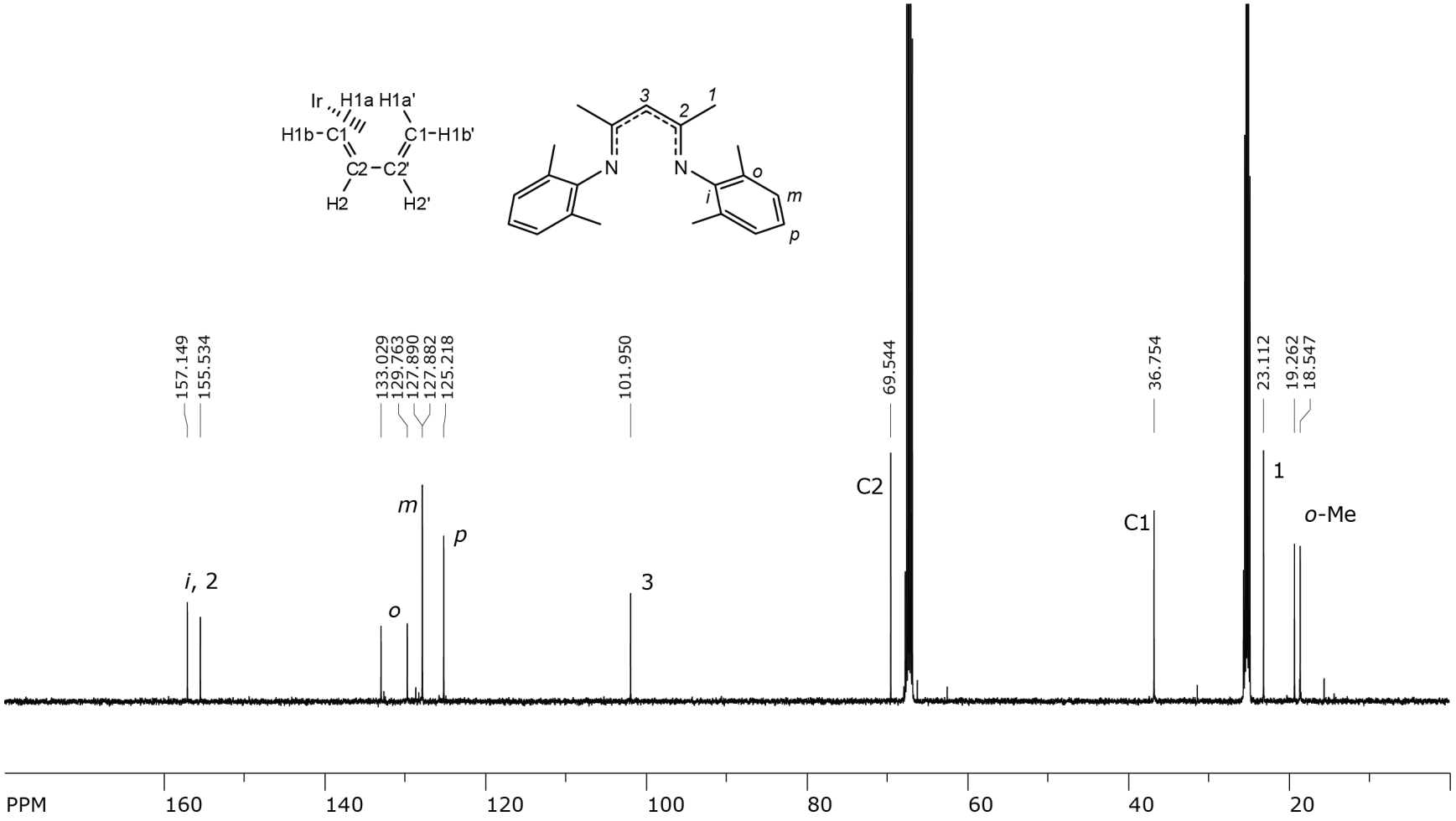


Figure S26. ^{13}C NMR spectrum of (^{Me}BDI)Ir(BD) (THF-d_8, 268K).

Simulation of VT-NMR spectra, (^{Me}BDI)Ir(BD), aryl methyl region.

Table S7. Fitted rate constants for VT-NMR spectra of (^{Me}BDI)Rh(BD).

T (K)	*k* (mol L^{-1})	1/*T*	ln(*k*/*T*)	pred ln(*k*/*T*)
263	*~0*	*0.00380*		*-5.460*
268	*~0*	*0.00373*		*-4.858*
273	*1.7*	*0.00366*	*-5.079*	*-4.278*
278	5.1	0.00360	-3.998	-3.719
283	11.3	0.00353	-3.221	-3.180
288	20.1	0.00347	-2.662	-2.660
293	37.8	0.00341	-2.048	-2.157
298	61.7	0.00336	-1.575	-1.671
303	112	0.00330	-0.995	-1.202
308	175	0.00325	-0.565	-0.747
313	277	0.00319	-0.122	-0.307
318	340	0.00314	0.067	0.119
323	486	0.00310	0.409	0.532
328	628	0.00305	0.650	0.932

Eyring plot

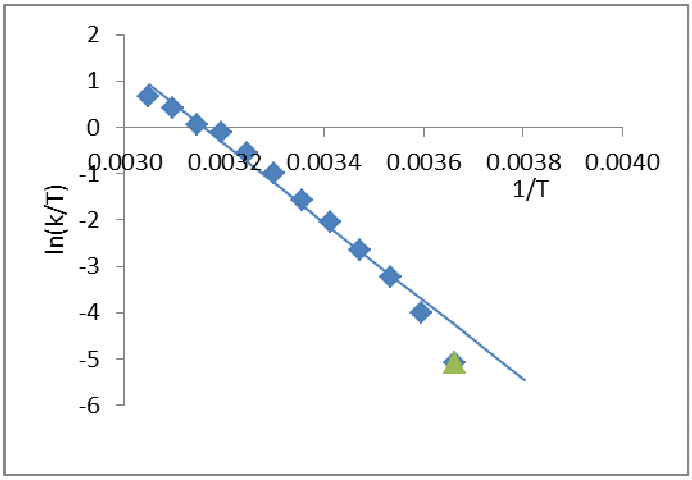


Figure S27. Eyring plot (ln *k*/*T* vs 1/*T*) for (^{Me}BDI)Ir(BD) over the range 263-328 K.

Fit results:

$\Delta H^{\ddagger}$ =	70.5±2.7	kJ mol^{-1}	16.8±0.6	kcal mol^{-1}
$\Delta S^{\ddagger}$ =	25.2±8.9	J mol^{-1} K^{-1}	6.0±2.1	cal mol^{-1} K^{-1}

NMR spectra for (^{Et}BDI)Rh(2-TMSO-1,3-CHD)

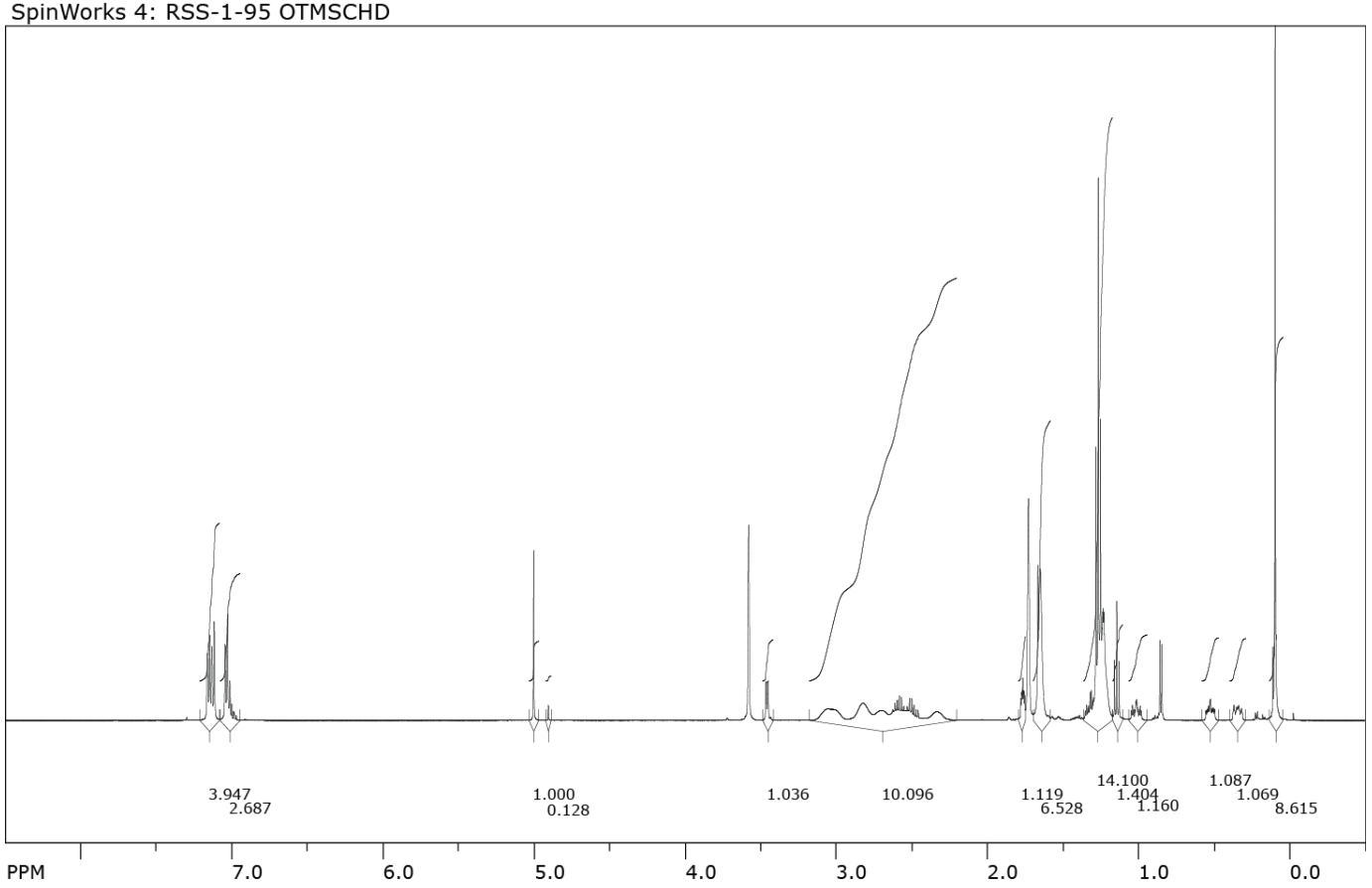


Figure S28. ^{1}H NMR spectrum of (^{Et}BDI)Rh(2-TMSO-1,3-CHD) (THF-d_8, 298K), overview.

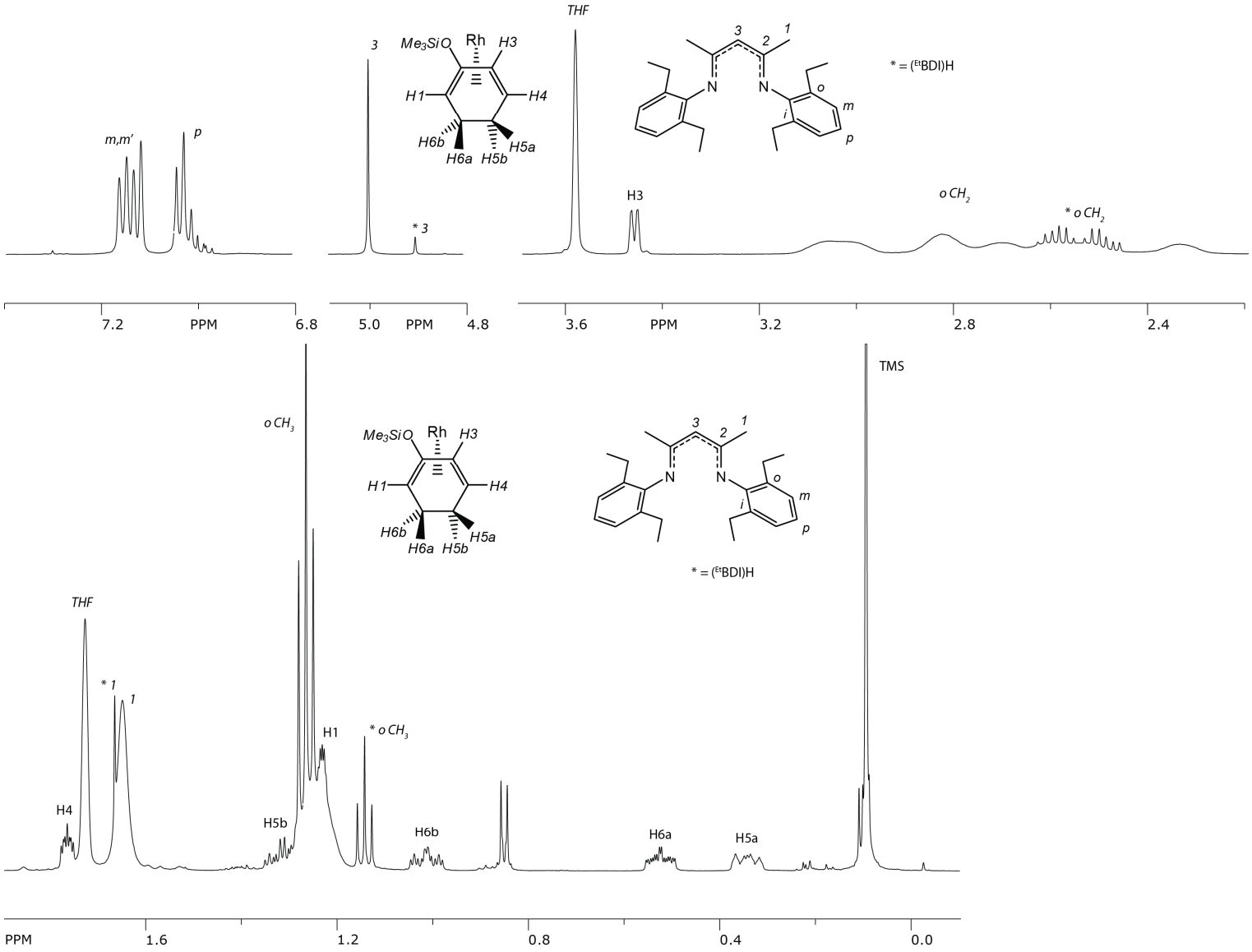


Figure S29. ^{1}H NMR spectrum of (^{Et}BDI)Rh(2-TMSO-1,3-CHD) (THF-d_8, 298K), assignments.

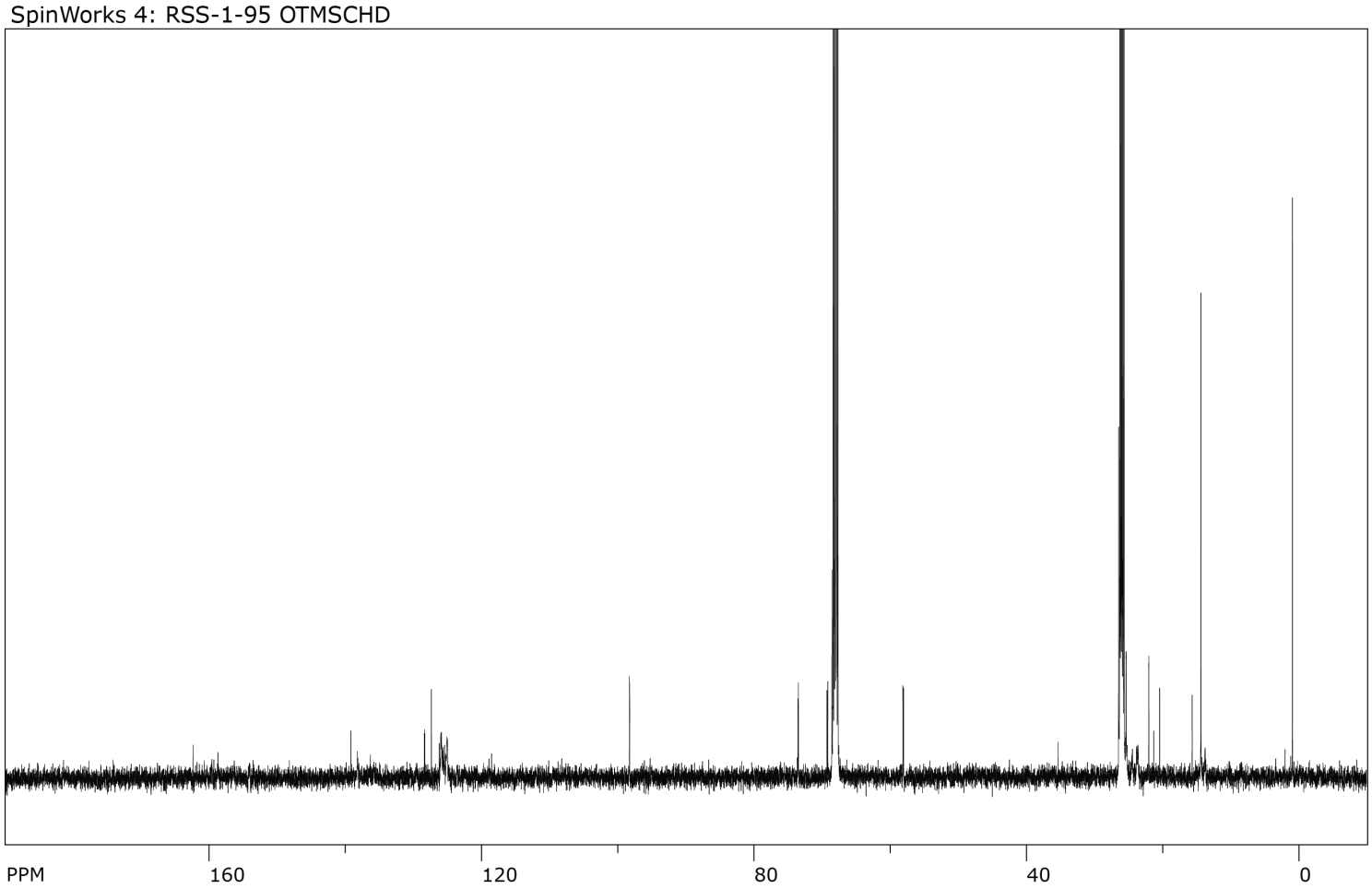


Figure S30. ^{13}C NMR spectrum of (^{Et}BDI)Rh(2-TMSO-1,3-CHD) (THF-d_8, 298K), overview.

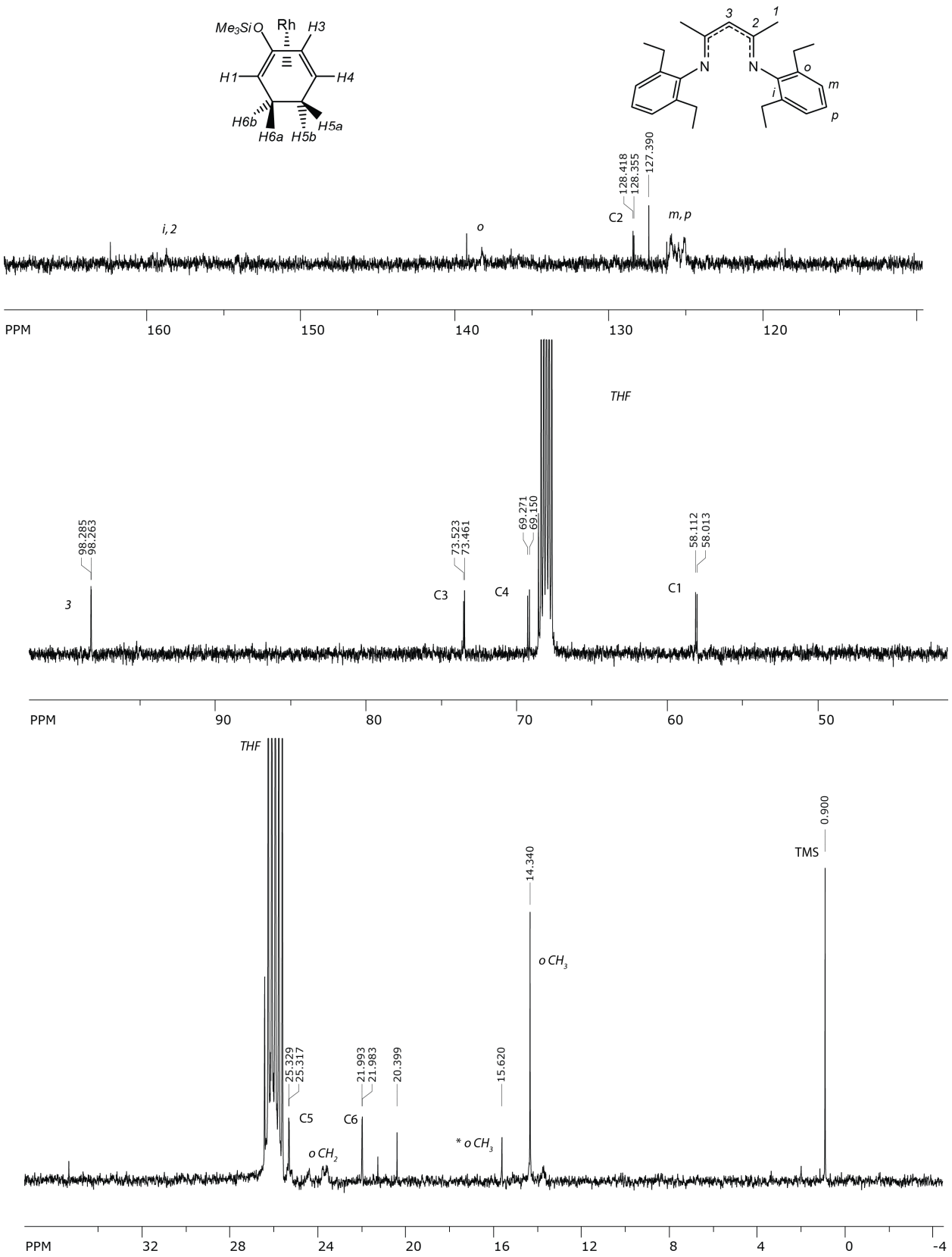


Figure S31. ^{13}C NMR spectrum of (^{Et}BDI)Rh(2-TMSO-1,3-CHD) (THF-d_8, 298K), assignments.

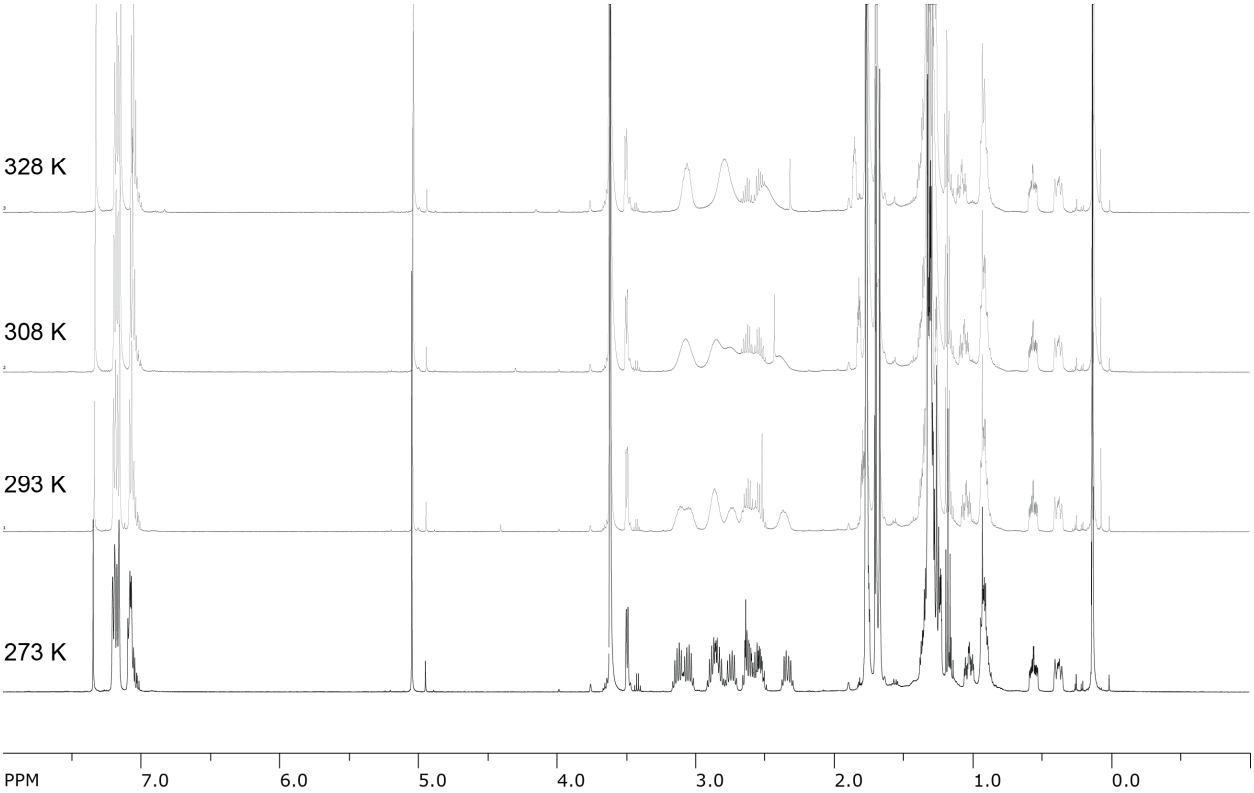
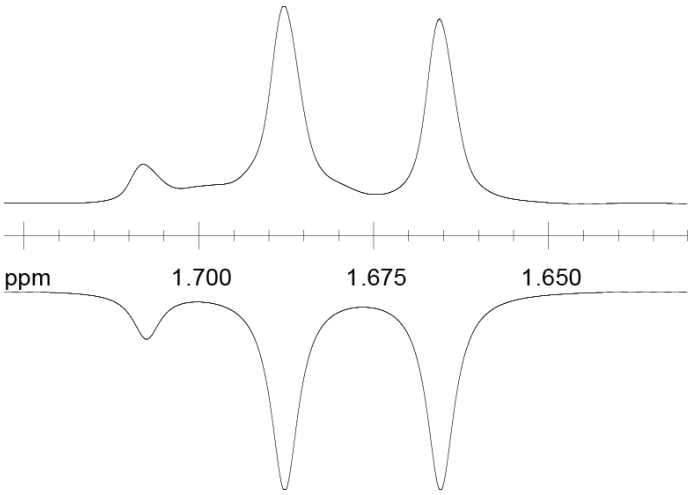
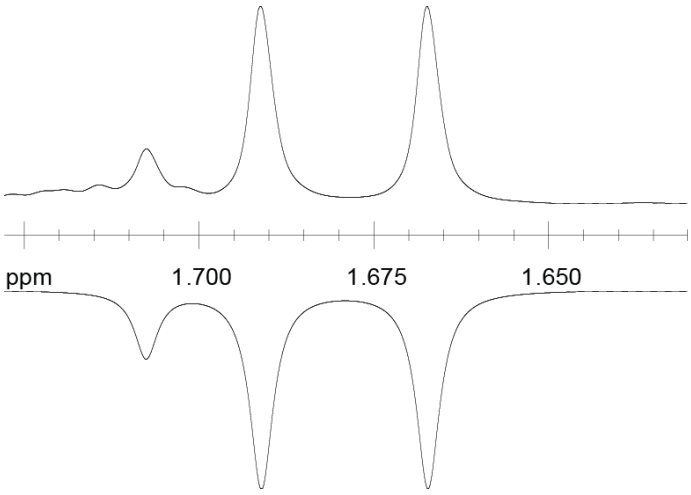
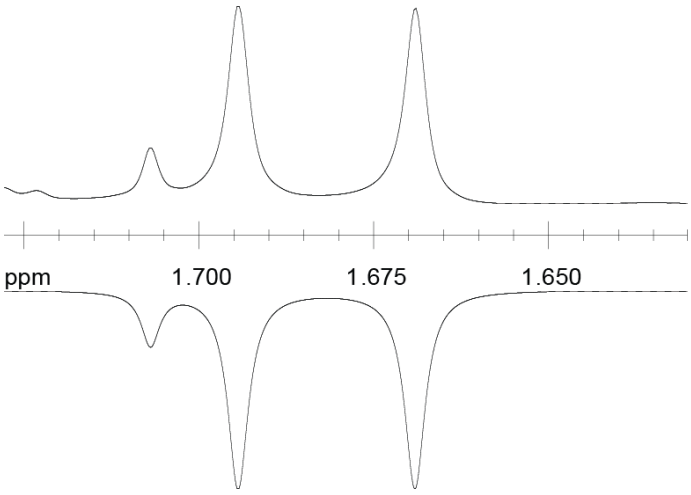
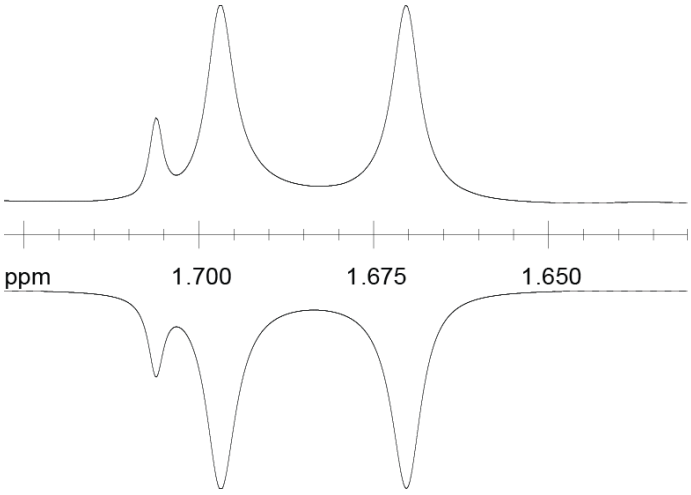
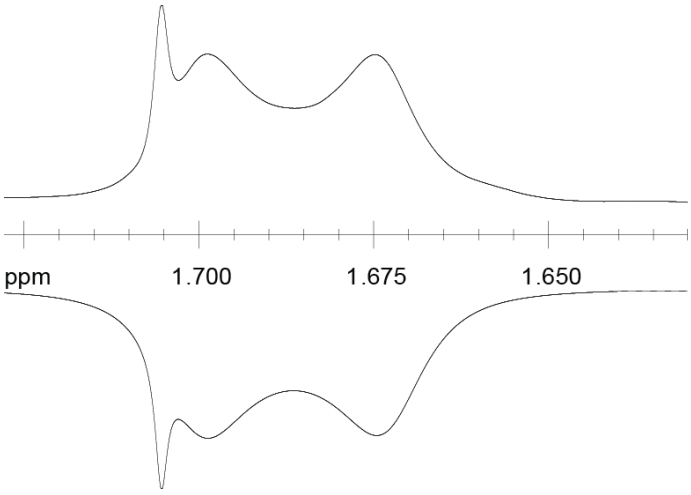


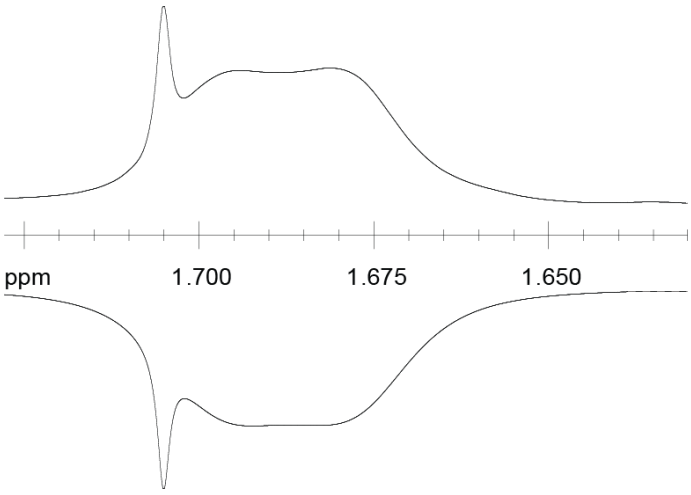
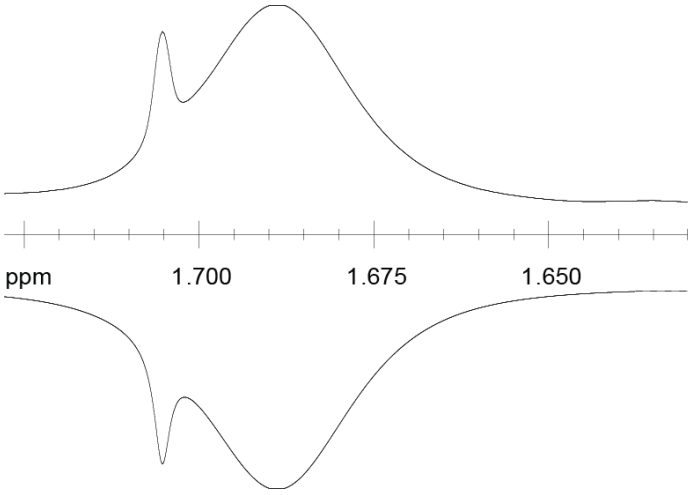
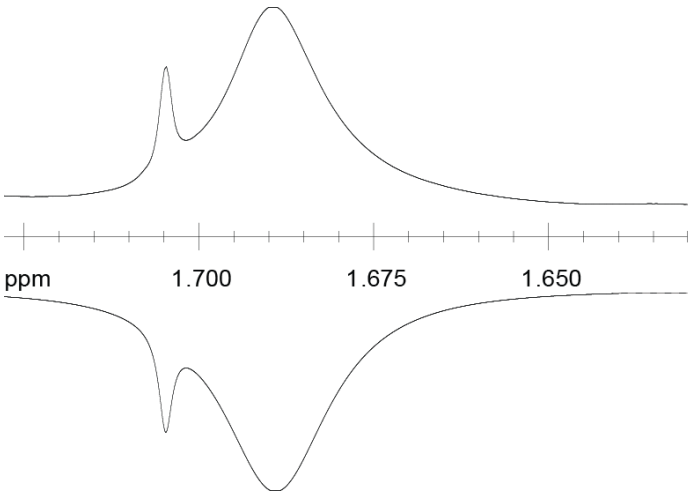
Figure S32. Selected ^{1}H VT-NMR spectra for (^{Et}BDI)Rh(2-TMSO-1,3-CHD) (THF-d_8).

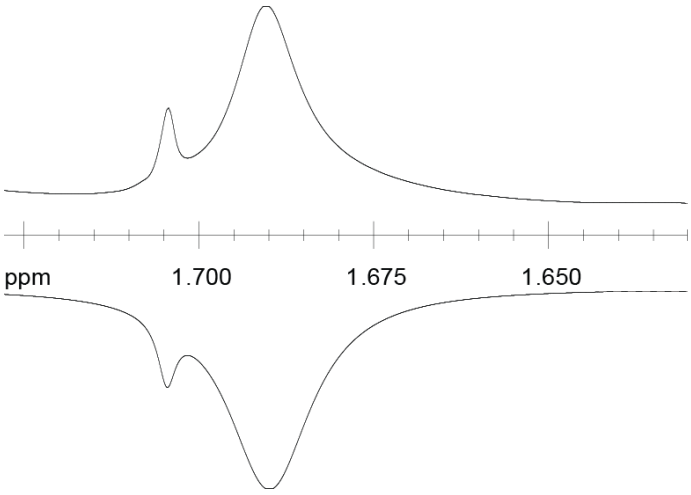
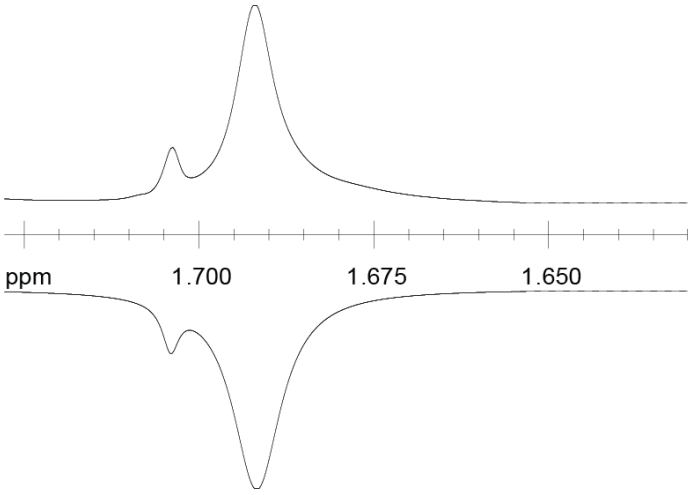
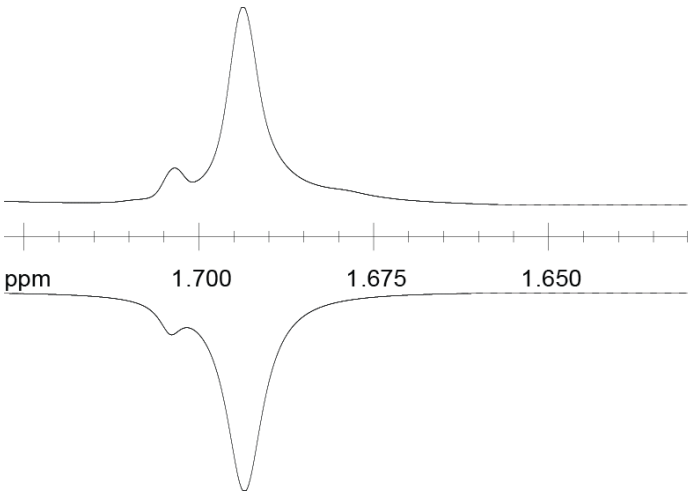
Simulation of VT-NMR spectra, (^{Et}BDI)Rh(2-TMSO-1,3-CHD), imine methyl region.

Table S8. Chemical shifts of imine methyl groups, fitted rate constants, and fitted spectrum traces for VT-NMR spectra of (^{Et}BDI)Rh(2-TMSO-1,3-CHD).

T (K)	δ_1 (ppm)	δ_2 (ppm)	*k* (mol L^{-1})	Fitted spectrum[b]
243	1.665	1.688	~0	
253	1.667	1.691	~0	

263	1.669	1.694	0.524	
273	1.670	1.697	3.94	
288	1.671	1.702	21.3	

293	1.671	1.704	34.1	
298	*1.671*[a]	1.707	57.0	
303	*1.671*[a]	1.707	75.6	

308	*1.671*[a]	1.709	108	
318	*1.671*[a]	1.713	254	
328	*1.671*[a]	1.716	632	

[a] δ_2 fixed at lower-temperature value for these lineshape fits. [b] Peak near 1.71 ppm is free (^{Et}BDI)H, fitted concentrations 5 mol%.

Eyring plot

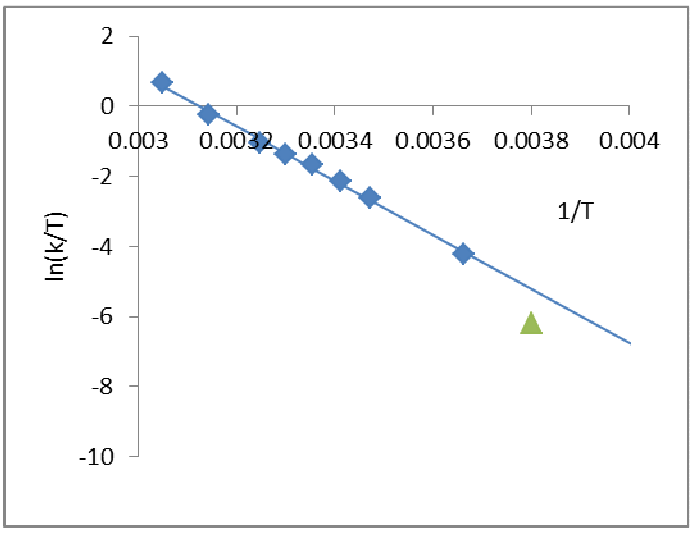


Figure S33. Eyring plot (ln *k*/*T* vs 1/*T*) for (^{Et}BDI)Rh(2-TMSO-1,3-CHD) over the range 273-328 K.

Fit results:

$\Delta H^{\ddagger}$ =	64.3±1.6	kJ mol^{-1}	15.4±0.4	kcal mol^{-1}
$\Delta S^{\ddagger}$ =	3.5±5.3	J mol^{-1} K^{-1}	0.8±1.3	cal mol^{-1} K^{-1}

Calculated b-p energies

Table S9. Calculated b-p energies, thermal and dispersion corrections, and rotation activation parameters.[a]

		b-p/tzvp		b-p/tzvpp							
	H_{corr}	TS_{corr}	Dispersion	E_{elec}	$<S^2>$	H	S	G	H_{rel}	S_{rel}	G_{rel}
Name	**a.u.**	**a.u.**	**a.u.**	**a.u.**		**a.u.**	**a.u./K**	**a.u.**	**kcal/mol**	**cal/mol.K**	**kcal/mol**
MeBDI_Rh_Bd (**3**)	0.51376	0.09208	-0.09416	-1192.03157		-1191.61197	0.000309	-1191.70404	0.00	0.00	0.00
MeBDI_Rh_Bd_rotTS	0.51173	0.09008	-0.09148	-1192.01114		-1191.59089	0.000302	-1191.68098	13.23	-4.19	14.48
MeBDI_Rh_Bd_triplet [b]	0.51204	0.09419	-0.09204	-1191.98668	2.01	-1191.56667	0.000316	-1191.66086	28.42	4.45	27.10
MeBDI_Rh_Bd_rotTS_triplet [b]	0.51053	0.09049	-0.09332	-1191.96078	2.01	-1191.54358	0.000304	-1191.63407	42.92	-3.34	43.91

[a] Thermal corrections calculated from vibrational analysis at b-p/TZVP optimized geometries, 298 K, 1 bar, gas phase. Total electronic energies and DFT-D3 dispersion corrections calculated using b-p/TZVPP at TZVP geometries. $H = E_{elec}+Dispersion+H_{corr}$; $G = E_{elec}+Dispersion+H_{corr}-S_{corr}$. [b] The preferred BD orientations for singlet and triplet are opposite, so the geometry of the singlet rotation TS resembles the triplet minimum and vice versa.

Calculated TPSSh energies

Table S10. Calculated TPSSh energies, thermal and dispersion corrections, and rotation activation parameters.[a]

	TPSSh/tzvp			TPSSh/tzvpp						
	H_{corr}	TS_{corr}	Dispersion	E_{elec}	$<S^2>$	H	S	G	H_{rel}	S_{rel}	G_{rel}
Name	**a.u.**	**a.u.**	**a.u.**	**a.u.**		**a.u.**	**a.u./K**	**a.u.**	**kcal/mol**	**cal/mol.K**	**kcal/mol**
Me4Si	0.15745	0.04056	-0.00690	-449.29789		-449.14733	0.000136	-449.18789			
CO	0.00828	0.02242	0.00000	-113.35952		-113.35124	0.000075	-113.37366			
Eth	0.05491	0.02484	-0.00066	-78.62564		-78.57139	0.000083	-78.59623			
Prn_	0.08447	0.03004	-0.00211	-117.96242		-117.88006	0.000101	-117.91011			
COD_cis	0.18799	0.03936	-0.01273	-312.16891		-311.99365	0.000132	-312.03301	(0)	(0)	(0)
COD_trans	0.18767	0.03996	-0.01307	-312.16456		-311.98996	0.000134	-312.02992	2.31	1.27	1.94
Bd	0.09043	0.03141	-0.00286	-156.06401		-155.97645	0.000105	-156.00786			
14PnD	0.11998	0.03561	-0.00494	-195.38718		-195.27213	0.000119	-195.30774	8.28	-0.65	8.48
13PnDcis	0.12012	0.03611	-0.00471	-195.39864		-195.28323	0.000121	-195.31934	1.32	0.41	1.20
13PnDtrans	0.11989	0.03592	-0.00445	-195.40077		-195.28533	0.000121	-195.32125	(0)	(0)	(0)
15HxD	0.14967	0.04003	-0.00717	-234.71832		-234.57581	0.000134	-234.61584	11.28	1.85	10.72
14HxDcis	0.14966	0.04042	-0.00694	-234.72123		-234.57851	0.000136	-234.61892	9.59	2.67	8.79
14HxDtrans	0.14947	0.04006	-0.00656	-234.72326		-234.58034	0.000134	-234.62041	8.44	1.93	7.86
13HxDcis	0.14999	0.03982	-0.00693	-234.72913		-234.58608	0.000134	-234.62590	4.84	1.42	4.41
13HxDtrans	0.14975	0.03962	-0.00659	-234.73138		-234.58822	0.000133	-234.62784	3.49	1.00	3.20
24HxDcis	0.14982	0.03969	-0.00660	-234.73301		-234.58979	0.000133	-234.62948	2.51	1.14	2.17
24HxDcistrans	0.14959	0.03999	-0.00634	-234.73514		-234.59189	0.000134	-234.63188	1.19	1.78	0.66
24HxDtrans	0.14935	0.03915	-0.00605	-234.73709		-234.59379	0.000131	-234.63293	(0)	(0)	(0)
14CyHxD	0.12784	0.03350	-0.00576	-233.52316		-233.40108	0.000112	-233.43458	0.25	-0.56	0.42
13CyHxD	0.12794	0.03376	-0.00610	-233.52332		-233.40149	0.000113	-233.43525	(0)	(0)	(0)
1_MeO_14CyHxD	0.16275	0.04129	-0.00962	-348.09406		-347.94093	0.000139	-347.98222	1.21	0.08	1.19
3_MeO_14CyHxD	0.16265	0.04161	-0.00951	-348.08798		-347.93484	0.000140	-347.97645	5.03	0.74	4.81
1_MeO_13CyHxD	0.16298	0.04126	-0.00984	-348.09599		-347.94286	0.000138	-347.98411	(0)	(0)	(0)

	TPSSh/tzvp			TPSSh/tzvpp						
	H_{corr}	TS_{corr}	Dispersion	E_{elec}	$<S^2>$	H	S	G	H_{rel}	S_{rel}	G_{rel}
Name	**a.u.**	**a.u.**	**a.u.**	**a.u.**		**a.u.**	**a.u./K**	**a.u.**	**kcal/mol**	**cal/mol.K**	**kcal/mol**
2_MeO_13CyHxD	0.16269	0.04131	-0.00969	-348.09314		-347.94013	0.000139	-347.98144	1.71	0.11	1.68
5_MeO_13CyHxD	0.16271	0.04113	-0.00999	-348.08916		-347.93644	0.000138	-347.97757	4.03	-0.26	4.10
1_TMSO_14CyHxD	0.24219	0.05674	-0.01639	-717.57955		-717.35374	0.000190	-717.41048	1.24	0.48	1.10
3_TMSO_14CyHxD	0.24214	0.05760	-0.01663	-717.56951		-717.34399	0.000193	-717.40160	7.36	2.30	6.68
1_TMSO_13CyHxD	0.24234	0.05651	-0.01668	-717.58139		-717.35573	0.000190	-717.41224	(0)	(0)	(0)
2_TMSO_13CyHxD	0.24222	0.05661	-0.01656	-717.57790		-717.35224	0.000190	-717.40885	2.19	0.21	2.12
5_TMSO_13CyHxD	0.24228	0.05708	-0.01713	-717.57088		-717.34574	0.000192	-717.40282	6.27	1.19	5.91
Acac_Rh	0.12238	0.04486	-0.00843	-455.86951		-455.75555	0.000151	-455.80041			
Acac_Rh_CO2	0.14414	0.05609	-0.01242	-682.76640		-682.63469	0.000188	-682.69078			
Acac_Rh_CO2_rotTS	0.14207	0.05654	-0.01213	-682.71067		-682.58072	0.000190	-682.63727	33.86	0.96	33.58
Acac_Rh_Eth2	0.23722	0.05747	-0.01886	-613.25576		-613.03739	0.000193	-613.09486			
Acac_Rh_Eth2_rotTS	0.23522	0.05727	-0.01827	-613.21383		-612.99688	0.000192	-613.05415	25.43	-0.41	25.55
Acac_Rh_COD	0.31237	0.06152	-0.02897	-768.17490		-767.89150	0.000206	-767.95302			
Acac_Rh_COD_rotTS	0.31025	0.06153	-0.02858	-768.13163		-767.84996	0.000206	-767.91149	26.07	0.02	26.06
Acac_Rh_Bd	0.21503	0.05546	-0.01556	-612.04817		-611.84870	0.000186	-611.90416			
Acac_Rh_Bd_rotTS	0.21346	0.05389	-0.01510	-612.02199		-611.82363	0.000181	-611.87752	15.73	-3.32	16.72
minxBDI_Rh	0.14732	0.04656	-0.00982	-416.12142		-415.98392	0.000156	-416.03048			
minxBDI_Rh_CO2	0.17015	0.05932	-0.01442	-643.01738		-642.86166	0.000199	-642.92097			
minxBDI_Rh_CO2_rotTS	0.16813	0.05636	-0.01399	-642.96227		-642.80813	0.000189	-642.86449	33.59	-6.22	35.44
minxBDI_Rh_Eth2	0.26254	0.06030	-0.02113	-573.50192		-573.26052	0.000202	-573.32082			
minxBDI_Rh_Eth2_rotTS	0.26085	0.05767	-0.02028	-573.46049		-573.21992	0.000194	-573.27758	25.48	-5.55	27.13
minxBDI_Rh_COD	0.33675	0.06189	-0.03154	-728.42005		-728.11485	0.000208	-728.17674			
minxBDI_Rh_COD_rotTS	0.33572	0.06119	-0.03081	-728.37513		-728.07022	0.000205	-728.13141	28.01	-1.48	28.45
minxBDI_Rh_Bd	0.24065	0.05686	-0.01792	-572.29947		-572.07673	0.000191	-572.13359			
minxBDI_Rh_Bd_rotTS	0.23915	0.05400	-0.01741	-572.27180		-572.05007	0.000181	-572.10407	16.73	-6.01	18.52
minBDI_Rh	0.20540	0.05150	-0.01556	-494.76783		-494.57799	0.000173	-494.62949			
minBDI_Rh_CO2	0.22838	0.06230	-0.02213	-721.64325		-721.43700	0.000209	-721.49930			
minBDI_Rh_CO2_rotTS	0.22604	0.06114	-0.02107	-721.59886		-721.39389	0.000205	-721.45504	27.05	-2.43	27.77

	TPSSh/tzvp			TPSSh/tzvpp							
	H_{corr}	TS_{corr}	Dispersion	E_{elec}	$<S^2>$	H	S	G	H_{rel}	S_{rel}	G_{rel}
Name	**a.u.**	**a.u.**	**a.u.**	**a.u.**		**a.u.**	**a.u./K**	**a.u.**	**kcal/mol**	**cal/mol.K**	**kcal/mol**
minBDI_Rh_Eth2	0.32220	0.06093	-0.02907	-652.11867		-651.82554	0.000204	-651.88647			
minBDI_Rh_Eth2_rotTS	0.31883	0.06122	-0.02937	-652.09707		-651.80762	0.000205	-651.86884	11.25	0.62	11.07
minBDI_Rh_COD	0.39730	0.06515	-0.04000	-807.03849		-806.68119	0.000219	-806.74633			
minBDI_Rh_COD_rotTS	0.39376	0.06525	-0.04106	-807.01014		-806.65743	0.000219	-806.72268	14.91	0.22	14.84
minBDI_Rh_Bd	0.29935	0.06015	-0.02638	-650.92359		-650.65061	0.000202	-650.71077			
minBDI_Rh_Bd_rotTS	0.29705	0.05877	-0.02599	-650.90806		-650.63699	0.000197	-650.69576	8.55	-2.92	9.42
minBDI_Rh_Bd_flipSOSP	0.29411	0.05764	-0.02605	-650.82671		-650.55865	0.000193	-650.61629	57.71	-5.30	59.29
minBDI_Rh_Bd_flipSOSP2	0.29352	0.06168	-0.02508	-650.85394		-650.58549	0.000207	-650.64717	40.86	3.21	39.90
HBDI_Rh	0.31497	0.06785	-0.02943	-878.42722		-878.14167	0.000228	-878.20953			
HBDI_Rh_CO2	0.33860	0.07885	-0.04090	-1105.29072		-1104.99303	0.000265	-1105.07188			
HBDI_Rh_CO2_rotTS	0.33630	0.07951	-0.03844	-1105.24276		-1104.94490	0.000267	-1105.02441	30.20	1.39	29.79
HBDI_Rh_Eth2	0.43202	0.07717	-0.05019	-1035.76574		-1035.38390	0.000259	-1035.46107			
HBDI_Rh_Eth2_rotTS	0.42939	0.07865	-0.04882	-1035.74083		-1035.36026	0.000264	-1035.43891	14.84	3.12	13.91
HBDI_Rh_COD	0.50725	0.08202	-0.06166	-1190.68669		-1190.24110	0.000275	-1190.32312			
HBDI_Rh_COD_rotTS	0.50433	0.08187	-0.06308	-1190.65763		-1190.21639	0.000275	-1190.29826	15.51	-0.30	15.60
HBDI_Rh_Bd	0.40968	0.07750	-0.04670	-1034.57381		-1034.21082	0.000260	-1034.28833			
HBDI_Rh_Bd_rotTS	0.40747	0.07777	-0.04495	-1034.55441		-1034.19189	0.000261	-1034.26965	11.88	0.55	11.72
MeBDI_Rh	0.43254	0.08425	-0.04982	-1035.75410		-1035.37137	0.000283	-1035.45562			
MeBDI_Rh_CO2	0.45485	0.09242	-0.06147	-1262.62754		-1262.23417	0.000310	-1262.32659			
MeBDI_Rh_CO2_rotTS	0.45271	0.09172	-0.05938	-1262.57745		-1262.18412	0.000308	-1262.27584	31.40	-1.48	31.85
MeBDI_Rh_Eth2	0.54867	0.08979	-0.07228	-1193.09958		-1192.62319	0.000301	-1192.71298			
MeBDI_Rh_Eth2_rotTS	0.54625	0.09080	-0.07056	-1193.06739		-1192.59171	0.000305	-1192.68251	19.76	2.13	19.12
MeBDI_Rh_COD	0.62394	0.09372	-0.08513	-1348.02150		-1347.48268	0.000314	-1347.57640			
MeBDI_Rh_COD_rotTS	0.62113	0.09499	-0.08554	-1347.98529		-1347.44970	0.000319	-1347.54469	20.70	2.68	19.90
MeBDI_Rh_Bd **(3)**	0.52598	0.09122	-0.06860	-1191.90999		-1191.45261	0.000306	-1191.54383			
MeBDI_Rh_Bd_rotTS	0.52401	0.08872	-0.06688	-1191.88827		-1191.43115	0.000298	-1191.51987	13.47	-5.26	15.04
MeBDI_Rh_Bd_triplet[b]	0.52423	0.09271	-0.06700	-1191.86492	2.01	-1191.40769	0.000311	-1191.50040	28.19	3.14	27.25
MeBDI_Rh_Bd_rotTS_triplet[b]	0.52280	0.08951	-0.06804	-1191.83921	2.01	-1191.38444	0.000300	-1191.47395	42.78	-3.58	43.85

	TPSSh/tzvp			TPSSh/tzvpp							
	H_{corr}	TS_{corr}	Dispersion	E_{elec}	$<S^2>$	H	S	G	H_{rel}	S_{rel}	G_{rel}
Name	**a.u.**	**a.u.**	**a.u.**	**a.u.**		**a.u.**	**a.u./K**	**a.u.**	**kcal/mol**	**cal/mol.K**	**kcal/mol**
MeBDI_Ir_Bd **(4)**	0.52632	0.09036	-0.07118	-1185.71990		-1185.26476	0.000303	-1185.35512			
MeBDI_Ir_Bd_rotTS	0.52436	0.08882	-0.06955	-1185.69693		-1185.24212	0.000298	-1185.33094	14.20	-3.25	15.17
EtBDI_Rh	0.55184	0.09623	-0.06241	-1193.06972		-1192.58028	0.000323	-1192.67651			
EtBDI_Rh_CO2	0.57428	0.10373	-0.07471	-1419.94308		-1419.44351	0.000348	-1419.54724			
EtBDI_Rh_CO2_rotTS	0.57210	0.10444	-0.07268	-1419.89268		-1419.39326	0.000350	-1419.49770	31.53	1.49	31.09
EtBDI_Rh_Eth2	0.66806	0.10301	-0.08640	-1350.41443		-1349.83277	0.000346	-1349.93578			
EtBDI_Rh_Eth2_rotTS	0.66588	0.10259	-0.08524	-1350.38143		-1349.80079	0.000344	-1349.90338	20.07	-0.90	20.34
EtBDI_Rh_Eth	0.60907	0.10102	-0.07353	-1271.75481		-1271.21926	0.000339	-1271.32029			
EtBDI_Rh_Eth_tTS	0.60717	0.10023	-0.07202	-1271.74444		-1271.20930	0.000336	-1271.30952			
EtBDI_Rh_Eth_tTS2	0.60795	0.09804	-0.07619	-1271.73936		-1271.20760	0.000329	-1271.30565			
EtBDI_Rh_PrnEndo	0.63850	0.10466	-0.07791	-1311.08837		-1310.52778	0.000351	-1310.63244			
EtBDI_Rh_PrnExo	0.63840	0.10371	-0.07867	-1311.08384		-1310.52411	0.000348	-1310.62782			
EtBDI_Rh_Prn_tTS	0.63677	0.10416	-0.07734	-1311.07586		-1310.51643	0.000350	-1310.62059			
EtBDI_Rh_Prn_tTS2b	0.63744	0.10331	-0.08028	-1311.07017		-1310.51301	0.000347	-1310.61632			
EtBDI_Rh_Prn_tTS2d	0.63729	0.10442	-0.08076	-1311.06297		-1310.50643	0.000350	-1310.61085			
EtBDI_Rh_COD	0.74353	0.10688	-0.09978	-1505.33654		-1504.69279	0.000359	-1504.79967			
EtBDI_Rh_COD_rotTS	0.74065	0.10749	-0.10075	-1505.29951		-1504.65961	0.000361	-1504.76710	20.82	1.28	20.44
EtBDI_Rh_Bd	0.64534	0.10388	-0.08232	-1349.22525		-1348.66223	0.000349	-1348.76611			
EtBDI_Rh_Bd_rotTS	0.64340	0.10139	-0.08083	-1349.20335		-1348.64078	0.000340	-1348.74217	13.46	-5.25	15.02
EtBDI_Rh_Bdh2TS	0.64318	0.10565	-0.07889	-1349.17841		-1348.61412	0.000355	-1348.71977	30.19	3.72	29.08
EtBDI_Rh_Bdtrans	0.64474	0.10281	-0.08198	-1349.20273		-1348.63997	0.000345	-1348.74278	13.96	-2.26	14.64
EtBDI_Rh_Bdtrans_rotTS	0.64205	0.10261	-0.08048	-1349.15892		-1348.59735	0.000344	-1348.69996			
EtBDI_Rh_ADI	0.62334	0.10218	-0.07755	-1381.35465		-1380.80886	0.000343	-1380.91104			
EtBDI_Rh_ADI_rotTS	0.62080	0.10255	-0.07495	-1381.30581		-1380.75996	0.000344	-1380.86251	30.68	0.78	30.45
EtBDI_Rh_14PnD	0.67559	0.10234	-0.08830	-1388.54578		-1387.95848	0.000343	-1388.06083	1.57	-9.84	4.50
EtBDI_Rh_14PnD_rotTS	0.67289	0.10316	-0.08650	-1388.50971		-1387.92332	0.000346	-1388.02648	23.64	-8.12	26.06
EtBDI_Rh_14PnDh1	0.67395	0.11077	-0.08185	-1388.51321		-1387.92111	0.000372	-1388.03189	25.02	7.91	22.67
EtBDI_Rh_14PnDtrans	0.67455	0.10378	-0.08710	-1388.53148		-1387.94403	0.000348	-1388.04781	10.64	-6.82	12.67

	TPSSh/tzvp			TPSSh/tzvpp						
	H_{corr}	TS_{corr}	Dispersion	E_{elec}	$<S^2>$	H	S	G	H_{rel}	S_{rel}	G_{rel}
Name	**a.u.**	**a.u.**	**a.u.**	**a.u.**		**a.u.**	**a.u./K**	**a.u.**	**kcal/mol**	**cal/mol.K**	**kcal/mol**
EtBDI_Rh_13PnDcis **(2b)**	0.67514	0.10702	-0.08721	-1388.54892		-1387.96099	0.000359	-1388.06801	(0)	(0)	(0)
EtBDI_Rh_13PnDcis_rotTS	0.67299	0.10430	-0.08636	-1388.52892		-1387.94229	0.000350	-1388.04660	11.73	-5.71	13.43
EtBDI_Rh_13PnDtrans **(2a)**	0.67501	0.10472	-0.08812	-1388.55012		-1387.96322	0.000351	-1388.06794	-1.40	-4.83	0.04
EtBDI_Rh_13PnDtrans_rotTS	0.67301	0.10363	-0.08616	-1388.53339		-1387.94654	0.000348	-1388.05018	9.07	-7.12	11.19
EtBDI_Rh_15HxD	0.70586	0.10383	-0.09289	-1427.87928		-1427.26631	0.000348	-1427.37014	0.58	-9.61	3.45
EtBDI_Rh_15HxD_rotTS	0.70308	0.10413	-0.09278	-1427.84369		-1427.23339	0.000349	-1427.33751	21.25	-8.98	23.92
EtBDI_Rh_15HxDh1	0.70369	0.11470	-0.08420	-1427.84511		-1427.22562	0.000385	-1427.34032	26.12	13.28	22.16
EtBDI_Rh_15HxDtrans	0.70501	0.10575	-0.09277	-1427.87005		-1427.25782	0.000355	-1427.36357	5.91	-5.56	7.57
EtBDI_Rh_14HxDcis	0.70527	0.10547	-0.09292	-1427.87052		-1427.25817	0.000354	-1427.36364	5.69	-6.14	7.53
EtBDI_Rh_14HxDcis_rotTS	0.70239	0.10684	-0.09252	-1427.83658		-1427.22671	0.000359	-1427.33355	25.43	-3.27	26.41
EtBDI_Rh_14HxDtrans	0.70509	0.10623	-0.09433	-1427.86314		-1427.25237	0.000356	-1427.35860	9.33	-4.56	10.69
EtBDI_Rh_14HxDtrans_rotTS	0.70260	0.10457	-0.09285	-1427.83724		-1427.22748	0.000351	-1427.33205	24.95	-8.05	27.35
EtBDI_Rh_13HxDcis	0.70481	0.10969	-0.09113	-1427.87945		-1427.26576	0.000368	-1427.37545	0.93	2.73	0.12
EtBDI_Rh_13HxDcis_rotTS	0.70278	0.10760	-0.08974	-1427.85960		-1427.24656	0.000361	-1427.35416	12.98	-1.67	13.48
EtBDI_Rh_13HxDtrans	0.70491	0.10726	-0.09265	-1427.87659		-1427.26433	0.000360	-1427.37159	1.83	-2.38	2.54
EtBDI_Rh_13HxDtrans2 **(1)**	0.70482	0.10839	-0.09129	-1427.88078		-1427.26724	0.000364	-1427.37564	(0)	(0)	(0)
EtBDI_Rh_13HxDtrans_rotTS	0.70286	0.10706	-0.08936	-1427.86385		-1427.25035	0.000359	-1427.35741	10.60	-2.80	11.44
EtBDI_Rh_24HxDcis	0.70478	0.10880	-0.09325	-1427.86583		-1427.25430	0.000365	-1427.36311	8.12	0.87	7.86
EtBDI_Rh_24HxDcis_rotTS	0.70251	0.10770	-0.09263	-1427.84723		-1427.23735	0.000361	-1427.34504	18.76	-1.46	19.20
EtBDI_Rh_24HxDcistrans	0.70472	0.10835	-0.09303	-1427.87433		-1427.26264	0.000364	-1427.37099	2.89	-0.09	2.92
EtBDI_Rh_24HxDcistrans_rotTS	0.70253	0.10660	-0.09167	-1427.85852		-1427.24766	0.000358	-1427.35426	12.29	-3.78	13.42
EtBDI_Rh_24HxDtrans	0.70444	0.10702	-0.09413	-1427.87277		-1427.26247	0.000359	-1427.36949	3.00	-2.89	3.86
EtBDI_Rh_24HxDtrans_rotTS	0.70262	0.10610	-0.09147	-1427.86175		-1427.25061	0.000356	-1427.35670	10.44	-4.83	11.88
EtBDI_Rh_14CyHxD	0.68238	0.10285	-0.09019	-1426.68196		-1426.08978	0.000345	-1426.19263	2.11	-7.79	4.43
EtBDI_Rh_14CyHxD_rotTS	0.68003	0.10306	-0.08893	-1426.63716		-1426.04606	0.000346	-1426.14912	29.55	-7.34	31.73
EtBDI_Rh_13CyHxD	0.68283	0.10655	-0.08919	-1426.68678		-1426.09314	0.000358	-1426.19969	(0)	(0)	(0)
EtBDI_Rh_13CyHxD_rotTS	0.68102	0.10325	-0.08877	-1426.66528		-1426.07302	0.000346	-1426.17627	12.62	-6.95	14.69
EtBDI_Rh_1_MeO_14CyHxD	0.71746	0.10899	-0.09907	-1541.24625		-1540.62786	0.000366	-1540.73685	6.23	-2.71	7.03

	TPSSh/tzvp			TPSSh/tzvpp						
	H_{corr}	TS_{corr}	Dispersion	E_{elec}	$<S^2>$	H	S	G	H_{rel}	S_{rel}	G_{rel}
Name	**a.u.**	**a.u.**	**a.u.**	**a.u.**		**a.u.**	**a.u./K**	**a.u.**	**kcal/mol**	**cal/mol.K**	**kcal/mol**
EtBDI_Rh_1_MeO_14CyHxD_rotTS	0.71517	0.10818	-0.09746	-1541.20331		-1540.58559	0.000363	-1540.69378	32.75	-4.41	34.06
EtBDI_Rh_3_MeO_14CyHxD	0.71747	0.10961	-0.09515	-1541.25219		-1540.62987	0.000368	-1540.73948	4.96	-1.41	5.38
EtBDI_Rh_3_MeO_14CyHxD_rotTS	0.71534	0.10944	-0.09430	-1541.21014		-1540.58911	0.000367	-1540.69855	30.54	-1.75	31.06
EtBDI_Rh_1_MeO_13CyHxD	0.71771	0.11210	-0.09778	-1541.24594		-1540.62601	0.000376	-1540.73811	7.39	3.84	6.24
EtBDI_Rh_1_MeO_13CyHxD_rotTS	0.71558	0.10983	-0.09585	-1541.23420		-1540.61446	0.000369	-1540.72429	14.63	-0.95	14.91
EtBDI_Rh_2_MeO_13CyHxD	0.71778	0.11028	-0.09699	-1541.25857		-1540.63778	0.000370	-1540.74805	(0)	(0)	(0)
EtBDI_Rh_2_MeO_13CyHxD_rotTS	0.71578	0.10842	-0.09660	-1541.23335		-1540.61417	0.000364	-1540.72259	14.81	-3.92	15.98
EtBDI_Rh_5_MeO_13CyHxD	0.71754	0.11262	-0.09394	-1541.25464		-1540.63103	0.000378	-1540.74365	4.23	4.93	2.77
EtBDI_Rh_5_MeO_13CyHxD_rotTS	0.71583	0.10966	-0.09384	-1541.23327		-1540.61128	0.000368	-1540.72094	16.63	-1.31	17.02
EtBDI_Rh_1_TMSO_14CyHxD	0.79664	0.12357	-0.10940	-1910.72553		-1910.03828	0.000415	-1910.16186	6.62	-4.80	8.05
EtBDI_Rh_1_TMSO_14CyHxD_rotTS	0.79450	0.12367	-0.10664	-1910.68415		-1909.99628	0.000415	-1910.11995	32.97	-4.61	34.35
EtBDI_Rh_3_TMSO_14CyHxD	0.79691	0.12524	-0.10309	-1910.73309		-1910.03927	0.000420	-1910.16451	6.00	-1.29	6.38
EtBDI_Rh_3_TMSO_14CyHxD_rotTS	0.79475	0.12515	-0.10285	-1910.69182		-1909.99992	0.000420	-1910.12507	30.69	-1.49	31.13
EtBDI_Rh_1_TMSO_13CyHxD	0.79682	0.12598	-0.10828	-1910.72767		-1910.03913	0.000423	-1910.16511	6.08	0.26	6.01
EtBDI_Rh_1_TMSO_13CyHxD_rotTS	0.79514	0.12309	-0.10708	-1910.71705		-1910.02899	0.000413	-1910.15209	12.45	-5.81	14.18
EtBDI_Rh_2_TMSO_13CyHxD **(5)**	0.79679	0.12586	-0.10584	-1910.73978		-1910.04883	0.000422	-1910.17468	(0)	(0)	(0)
EtBDI_Rh_2_TMSO_13CyHxD_rotTS	0.79502	0.12418	-0.10638	-1910.71507		-1910.02643	0.000417	-1910.15061	14.05	-3.54	15.11
EtBDI_Rh_5_TMSO_13CyHxD	0.79721	0.12706	-0.10242	-1910.73527		-1910.04047	0.000426	-1910.16753	5.24	2.54	4.49
EtBDI_Rh_5_TMSO_13CyHxD_rotTS	0.79541	0.12555	-0.10295	-1910.71411		-1910.02165	0.000421	-1910.14719	17.06	-0.65	17.25
iPrBDI_Rh	0.66932	0.11069	-0.08423	-1350.38866		-1349.80357	0.000371	-1349.91425			
iPrBDI_Rh_CO2	0.69177	0.11699	-0.09692	-1577.25702		-1576.66217	0.000393	-1576.77916			
iPrBDI_Rh_CO2_rotTS	0.68987	0.11748	-0.09349	-1577.20444		-1576.60805	0.000394	-1576.72553	33.96	1.04	33.65
iPrBDI_Rh_Eth2	0.78556	0.11298	-0.10862	-1507.72147		-1507.04454	0.000379	-1507.15752			
iPrBDI_Rh_Eth2_rotTS	0.78305	0.11332	-0.10698	-1507.68924		-1507.01317	0.000380	-1507.12649	19.68	0.71	19.47
iPrBDI_Rh_COD	0.86117	0.11872	-0.12262	-1662.64228		-1661.90374	0.000398	-1662.02246			
iPrBDI_Rh_COD_rotTS	0.85718	0.11388	-0.12157	-1662.60631		-1661.87070	0.000382	-1661.98459	20.73	-10.19	23.77
iPrBDI_Rh_Bd	0.76325	0.11291	-0.10533	-1506.53592		-1505.87801	0.000379	-1505.99092			
iPrBDI_Rh_Bd_rotTS	0.76115	0.11204	-0.10264	-1506.51244		-1505.85393	0.000376	-1505.96598	15.11	-1.83	15.65

	TPSSh/tzvp			TPSSh/tzvpp						
	H_{corr}	TS_{corr}	Dispersion	E_{elec}	$<S^2>$	H	S	G	H_{rel}	S_{rel}	G_{rel}
Name	**a.u.**	**a.u.**	**a.u.**	**a.u.**		**a.u.**	**a.u./K**	**a.u.**	**kcal/mol**	**cal/mol.K**	**kcal/mol**
EtBDI_Ir	0.55206	0.09661	-0.06464	-1186.84986		-1186.36244	0.000324	-1186.45905			
EtBDI_Ir_CO2	0.57473	0.10380	-0.07678	-1413.76916		-1413.27120	0.000348	-1413.37500			
EtBDI_Ir_CO2_rotTS	0.57252	0.10413	-0.07499	-1413.71159		-1413.21405	0.000349	-1413.31818	35.86	0.69	35.65
EtBDI_Ir_Eth2	0.66878	0.10246	-0.08912	-1344.23037		-1343.65071	0.000344	-1343.75317			
EtBDI_Ir_Eth2_rotTS	0.66634	0.10141	-0.08787	-1344.19445		-1343.61599	0.000340	-1343.71739	21.79	-2.22	22.45
EtBDI_Ir_COD	0.74384	0.10645	-0.10297	-1499.15145		-1498.51059	0.000357	-1498.61704			
EtBDI_Ir_COD_rotTS	0.74096	0.10739	-0.10342	-1499.11100		-1498.47347	0.000360	-1498.58086	23.29	1.98	22.70
EtBDI_Ir_Bd	0.64562	0.10270	-0.08502	-1343.03510		-1342.47450	0.000345	-1342.57720			
EtBDI_Ir_Bd_rotTS	0.64376	0.10101	-0.08354	-1343.01202		-1342.45180	0.000339	-1342.55282	14.24	-3.56	15.30

[a] Thermal corrections calculated from vibrational analysis at TPSSh/TZVP optimized geometries, 298 K, 1 bar, gas phase. Total electronic energies and DFT-D3 dispersion corrections calculated using TPSSh/TZVPP at TZVP geometries. $H = E_{elec}+Dispersion+H_{corr}$; $G = E_{elec}+Dispersion+H_{corr}-S_{corr}$. [b] The preferred BD orientations for singlet and triplet are opposite, so the geometry of the singlet rotation TS resembles the triplet minimum and vice versa.