Supplementary Information

Optimizing dirhodium(II) tetrakiscarboxylates as chiral NMR auxiliaries

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Scheme 3 Structures of the dirhodium tetracarboxylate complexes and the ligands investigated.

Experimental Complete spectral data sets of the dirhodium complexes (for their structures see Scheme 1).

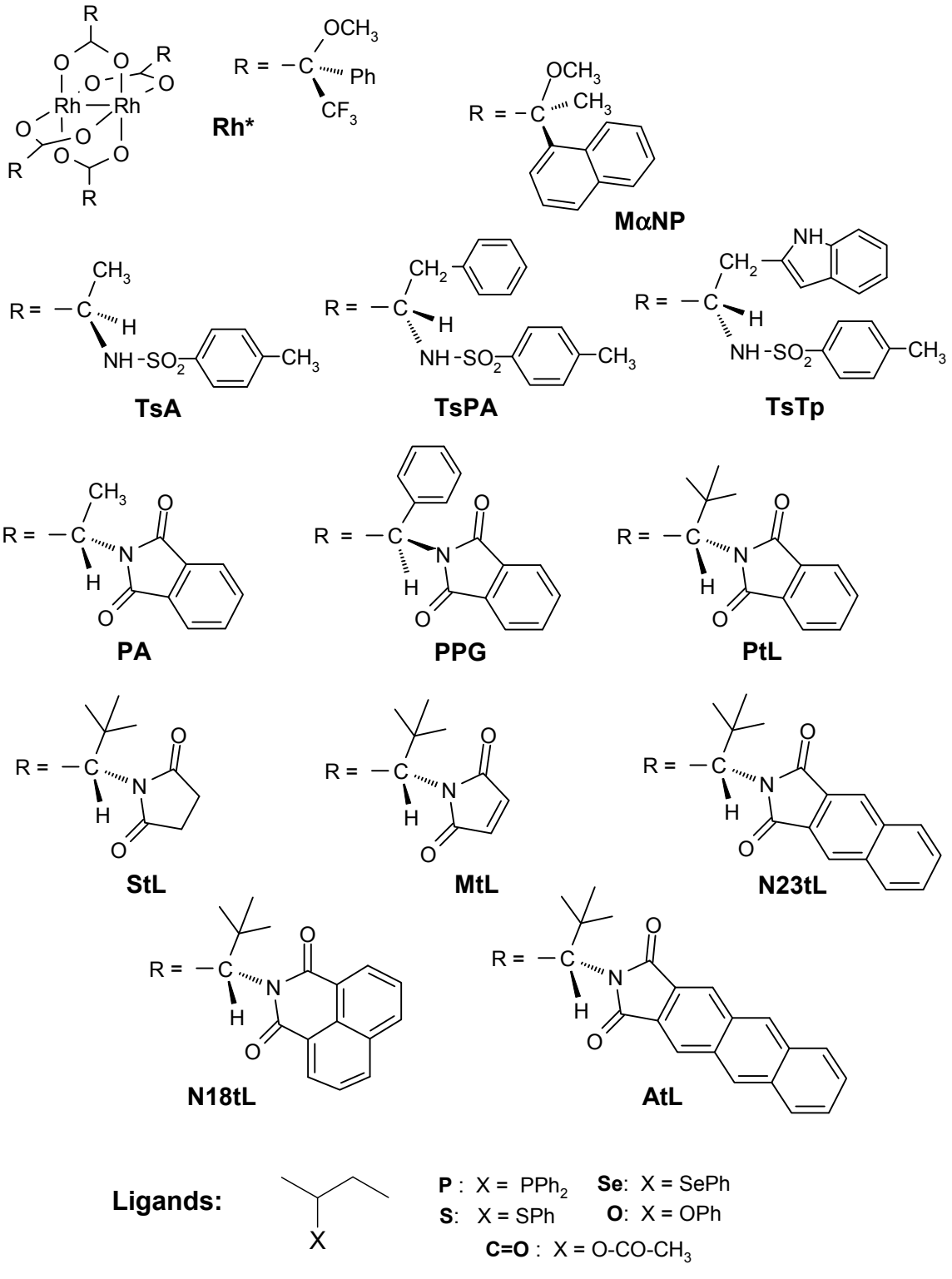
Table S1 Spectral data of the ligands.

Tables S2a – S2e NMR spectral data of the dirhodium complexe – ligand adducts (for their structures see Scheme 1).

Table S3 X-ray data and ORTEP plot of the bis(methanol) adduct of **N2tL**.

NMR Spectra Eleven ^{1}H and eleven ^{13}C NMR spectra of 1:1-adducts and ligands.

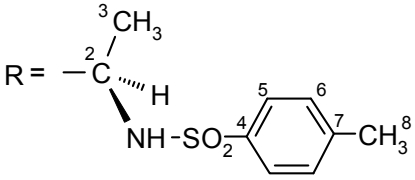
Scheme 3 Structures of the dirhodium tetracarboxylate complexes and the ligands investigated.



Experimental

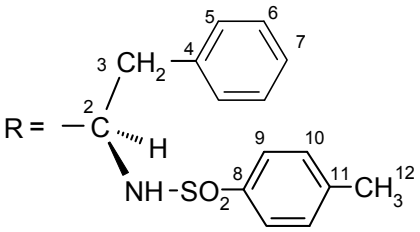
For details on NMR measurements see original manuscript. IR spectra were recorded on a Bruker Vector 22 spectrometer without solvent. Specific rotations $[\alpha]_D^{20}$ at 589 nm were measured in methanol or chloroform at room temperature; concentrations (in g/ml) are given in parentheses. Mass spectrometry of the dirhodium complexes using a Micromass LCT (ESI mode) was not successful. Complete spectral data sets are given in the following for those dirhodium complexes unreported hitherto (see structures in Scheme 3):

Dirhodium(II) tetrakis[*N*-p-toluenesulfonyl-(R)-alaninate] (TsA)



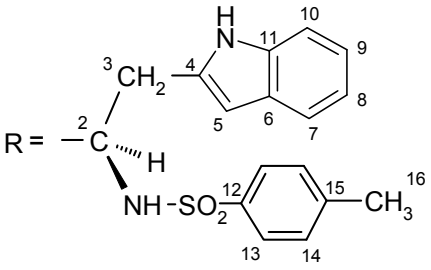
Yield: 35 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 1.27 (d, 12H, H-3, $^3J_{HH}$ = 7.3 Hz); 2.36 (s, 12H, H-8); 3.71 (q, 4H, H-2, $^3J_{HH}$ = 7.3 Hz); 7.34 (dd, 8H, H-6/6´), 7.73 (m, 8H, H-5/5´). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 20.2 (CH_3, C-3); 21.5 (CH_3, C-8); 53.7 (CH, C-2); 128.3 (CH, C-5/5´); 130.7 (CH, C-6/6´); 139.3 (C, C-4); 143.7 (C, C-7); 192.8 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 3035, 2978, 1741, 1705, 1621, 1378, 1154, 1075, 717, 696. $[\alpha]_D^{20}$ = -16.7 (MeOH, c = 0.004).

Dirhodium(II) tetrakis[*N*-*p*-toluenesulfonyl-(*S*)-phenylalaninate] (TsPA)



Yield: 51 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 2.32 (s, 12H, H-12); 2.70 (ddd, 8H, H-3, $^2J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 4.5 Hz); 3.73 (dd, 4H, H-2, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 4.5 Hz); 6.98 (m, 8H, H-10/10‘), 7.09 (m, 20H, H-5/5´/6/6´/7); 7.26 (m, 8H, H-9/9´). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 21.6 (CH_3, C-12); 40.4 (CH_2, C-3); 59.7 (CH, C-2); 127.5 (CH, C-7); 127.8 (CH, C-9/9´); 129.3 (CH, C-5/5´); 130.5 (CH, C-6/6´); 130.6 (CH, C-10/10´); 138.6 (C, C-8); 139.3 (C, C-4); 144.2 (C, C-11); 191.8 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 3050, 2925, 2362, 2348, 1585, 1403, 1324, 1155, 1091, 812, 699, 665. $[\alpha]_D^{20}$ = -44.61 (MeOH, c = 0.0023).

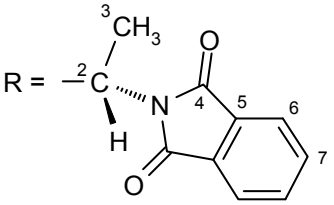
Dirhodium(II) tetrakis[3-(*N*-*p*-toluenesulfonyl)-(*S*)-tryptophanate] (TsTp)



Yield: 24 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 2.27 (s, 12H, H-16); 3.10 (ddd, 8H, H-3, $^2J_{HH}$ = 14.6 Hz, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.4 Hz); 3.88 (dd, 4H, H-2, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.4 Hz); 6.89 (m 4H, H-9); 6.96 (dd, 8H, H-14/14´); 6.98 (s 4H, H-5); 7.03 (m, 4H, H-8), 7.24 (m, 4H, H-7); 7.34 (dd, 8H, H-13/13´), 7.44 (m, 4H, H-

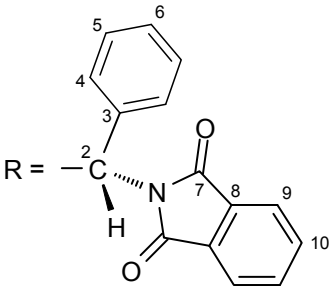
10). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 21.6 (CH_3, C-16); 30.3 (CH_2, C-3); 59.8 (CH, C-2); 111.5 (C, C-4); 112.2 (CH, C-7); 119.6 (CH, C-9); 119.7 (CH, C-10); 122.1 (CH, C-8); 124.8 (CH, C-5); 127.8 (CH, C-13/13′); 128.9 (CH, C-11); 130.2 (C, C-14/14′); 138.0 (C, C-6); 138.5 (C, C-12); 144.1 (C, C-15); 188.7 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 3054, 2915, 2358, 2343, 1601, 1399, 1322, 1153, 1090, 812, 741, 664. $[\alpha]_D^{20}$ = -95.6 ($CHCl_3$, c = 0.0046).

Dirhodium(II) tetrakis[*N*-phthaloyl-(*S*)-alaninate] (PA)



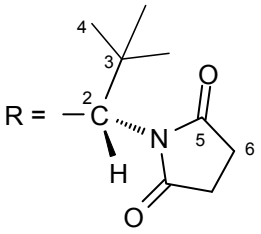
Yield: 59 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 1.54 (s, 12H, H-3, $^3J_{HH}$ = 7.2 Hz); 5.09 (q, 4H, H-2, $^3J_{HH}$ = 7.2 Hz); 7.62 (m, 8H, H-7/7′); 7.77 (m, 8H, H-6/6′). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 15.9 (CH_3, C-3); 48.6 (CH, C-2); 123.3 (CH, C-6/6′); 131.9 (CH, C-7/7′); 133.7 (C, C-5/5′); 167.2 (C=O, C-4/4′); 188.5 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 3102, 2933, 2357, 1777, 1708, 1604, 1385, 1344, 1082, 883, 717. $[\alpha]_D^{20}$ = +48.9 (MeOH, c = 0.006).

Dirhodium(II) tetrakis[*N*-phthaloyl-(*R*)-phenylglycinate] (PPG)



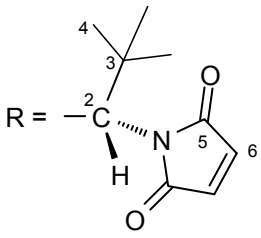
Yield: 48 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 5.55 (s, 4H, H-2); 7.14 (m, 8H, H-4/4′); 7.22 (m, 8H, H-5/5′), 7.46 (m, 4H, H-6); 7.62 (m, 8H, H-10/10′); 7.77 (m, 8H, H-9/9′). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 56.7 (CH, C-2); 123.4 (CH, C-9/9′); 127.9 (C, C-6); 128.2 (CH, C-4/4′); 129.8 (CH, C-5/5′); 131.9 (CH, C-10/10′); 133.9 (C, C-8/8′); 135.9 (C, C-3); 166.9 (C=O, C-7/7′); 186.7 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 3012, 2919, 1770, 1713, 1610, 1378, 1110, 1075, 717, 696. $[\alpha]_D^{20}$ = +672.7 ($CHCl_3$, c = 0.0073).

Dirhodium(II) tetrakis[*N*-succinyl-(*S*)-*tert*-leucinate] (StL)



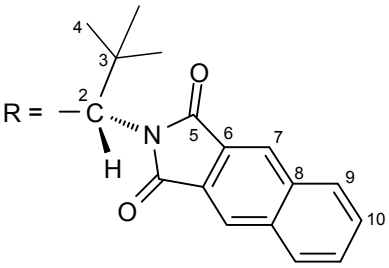
Yield: 94 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 0.98 (s, 36H, H-4); 2.82 (s, 16H, H-6/6′); 4.49 (s, 4H, H-2). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 28.4 (CH_3, C-4); 31.9 (CH_2, C-6/6′); 35.9 (C, C-3); 61.6 (CH, C-2); 177.2 (C=O, C-5/5′); 186.4 (CO_2, C-1). IR (solid, $\tilde{\nu}$ in cm^{-1}): 2961, 2363, 1703, 1610, 1379, 1346, 1172, 769, 657. $[\alpha]_D^{20}$ = +116.1 (MeOH, c = 0.0031).

Dirhodium(II) tetrakis[*N*-maleinyl-(*S*)-*tert*-leucinate] (MtL)



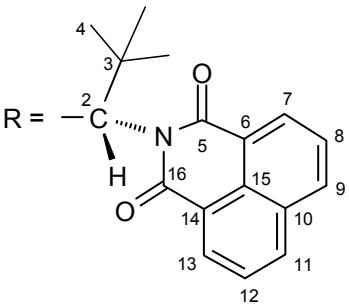
Yield: 78 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 0.99 (s, 36H, H-4); 4.54 (s, 4H, H-2), 7.37 (s, 8H, H-6/6´). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 27.8 (CH_3, C-4); 35.3 (C, C-3); 61.3 (CH, C-2); 133.3 (CH, C-6/6´); 170.4 (C=O, C-5/5´); 187.3 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 2959, 2360, 1712, 1689, 1607, 1398, 1155, 830, 698. $[\alpha]_D^{20}$ = -129.0 (MeOH, c = 0.0031).

Dirhodium(II) tetrakis[(*S*)-*N*-naphthalene-2,3-dicarboxyl-*tert.*-leucinate] (N23tL)



Yield: 79 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 1.20 (s, 36H, H-4); 5.04 (s, 4H, H-2), 7.61 (m, 8H, H-10/10´); 7.97 (s, 8H, H-9/9´); 8.26 (s, 8H, H-7/7´). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 28.0 (CH_3, C-4); 35.8 (C, C-3); 61.7 (CH, C-2); 124.6 (CH, C-10/10´); 127.8 (CH, C-9/9´); 128.7 (CH, C-7/7´); 130.2 (CH, C-6/6´); 135.5 (C, C-8/8´); 173.5 (C=O, C-5/5´); 187.2 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 3112, 2978, 2334, 1710, 1606, 1365, 1341, 773, 659. $[\alpha]_D^{20}$ = -221.6 (MeOH, c = 0.0037).

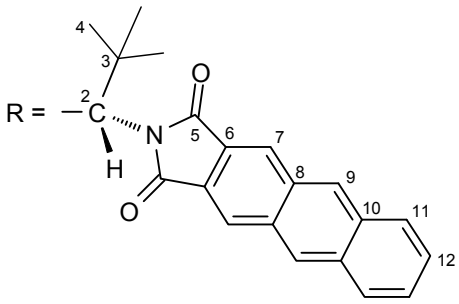
Dirhodium(II) tetrakis[(*S*)-*N*-naphthalene-1,8-dicarboxyl-*tert.*-leucinate] (N18tL)



Yield: 75 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 1.29 (s, 36H, H-4); 5.83 (s, 4H, H-2), 7.58 (t, 4H, H-9); 7.84 (t, 4H, H-11); 8.04 (dd, 8H, H-8/12); 8.45 (d, 4H, H-13); 8.73 (d, 4H, H-7). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 28.9 (CH_3, C-4); 36.2 (C, C-3); 61.9 (CH, C-2); 122.8 (C, C-6/14); 126.3 (C, C-15); 127.3 (CH, C-12); 127.9 (CH, C-8); 130.8 (CH, C-11); 130.8 (C, C-10); 131.2 (CH, C-9); 133.2 (CH, C-13); 133.5 (CH, C-7); 163.0 (C=O, C-16); 164.7 (C=O, C-5); 187.2 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 3010, 2920, 1705, 1663, 1604, 1588, 1397, 1375, 1338, 1237, 787, 777. $[\alpha]_D^{20}$ = +92.5 ($CHCl_3$, c = 0.004).

Note: in contrast to all other complexes, diastereotopic nuclei in the naphthyl residue are not isochronous pairwise. Here, local symmetry is no longer dominant for the chemical shifts of ^{1}H and ^{13}C.

Dirhodium(II) tetrakis[*N*-2,3-anthracenedicarboxyl-(*S*)-*tert*-leucinate] (AtL)



Yield: 73 %. ^{1}H NMR recorded in $CDCl_3$ (ppm): δ = 1.27 (s, 36H, H-4); 4.88 (s, 4H, H-2), 7.21 (m, 8H, H-12/12´); 7.63 (s, 8H, H-11/11´); 8.05 (m, 8H, H-9/9´); 8.50 (m, 8H, H-7/7´). ^{13}C NMR recorded in $CDCl_3$ (ppm): δ = 28.4 (CH_3, C-4); 36.1 (C, C-3); 60.6 (CH, C-2); 125.3 (CH, C-12/12´); 125.8 (CH, C-9/9´); 126.3 (CH, C-7/7´); 127.3 (CH, C-11/11´); 128.3 (CH, C-6/6´); 129.1 (CH, C-8/8´); 133.0 (CH, C-10/10´); 178.4 (C=O, C-5/5´); δ = 188.1 (CO_2, C-1). IR (solid, cm^{-1}): $\tilde{\nu}$ = 3010, 2925, 1769, 1709, 1609,1365, 1337, 1133, 917, 741. $[\alpha]_D^{20}$ = -1011.5 ($CHCl_3$, c = 0.0026).

Table S1 ^{1}H / ^{13}C chemical shifts of the ligands 2-butyldiphenylphosphane (**P**), 2-butylphenylselenide (**Se**), 2-butylphenylsulfide (**S**), 2-butylphenylether (**O**) and 2-butyl acetate (**C=O**); in $CDCl_3$.

Atom #	1	2	3[a]	4	*ipso*	*ortho*	*meta*	*para*
P[b]	1.03/15.6	2.23/31.8	1.24, 1.57/26.0	0.98/12.1	– /137.4	7.48/133.4	7.31/128.2	7.31/128.5
Se	1.40/21.6	3.24/41.5	1.61, 1.71/30.4	1.00/12.3	– /127.2	7.54/134.8	7.26/128.8	7.26/129.5
S	1.27/20.5	3.15/44.8	1.53, 1.66/29.4	1.00/11.4	–/135.5	7.39/128.7	7.27/131.8	7.20/126.5
O	1.29/19.3	4.29/74.9	1.60, 1.75/29.2	0.98/9.8	–/158.2	7.26/115.9	6.90/129.4	6.90/120.4

	1	2	3	4	CH_3	C=O
C=O	1.20/19.4	4.83/72.2	1.57/28.8	0.90/9.7	2.03/21.3	170.8

[a] Diastereotopic protons; no stereochemical assignment.

[b] Separate consistent data sets for each diastereotopic phenyl group but no stereochemical assignment.

Table S2a ^{1}H and ^{13}C complexations shifts $\Delta\delta$ / diastereomeric dispersion effects $\Delta\nu$ (integers in Hz) of 2-butyldiphenylphosphane (**P**) in the presence of an equimolar amount of dirhodium tetra-carboxylate complexes, in $CDCl_3$, recorded at 9.4 Tesla (400.1 MHz ^{1}H, 100.6 MHz ^{13}C).[a]

Atom #		1	2	3[b]	4	*ipso*	*ortho*	*meta*	*para*
Rh*	^{1}H	0.26 / 7	0.79 / 0	0.07 / 0 0.66 / 0	-0.03 / 6	-	0.21 / 44	n.d.[c] / n.d.[c]	0.04 / 0
	^{13}C	-2.2 / 0	-1.0 / 3	-2.1 / 0	0.2 / 10	-8.8 / 0 -8.8 / 0	0.5 / 9 0.5 / 9	n.d.[c] n.d.[c]	1.4 / 13 1.5 / 9
MαNP	^{1}H	———	———	———	coal[d]	———	———	———	
	^{13}C	———	———	———	coal	———	———	———	
PtL	^{1}H	———	———	———	coal	———	———	———	
PtL	^{13}C	———	———	———	coal	———	———	———	
TsA	^{1}H	0.12 / 17	0.83 / 0	0.07 / 0 -0.11 / 0	0.03 / 37	-	0.31 / 0	0.15 / 0	0.21 / 0
	^{13}C	-2.3 / 0	-1.3 / 7	-2.1 / 0	0.6 / 6	-3.6 / 0 -3.5 / 3	-3.3 / 2 -3.6 / 2	0.2 / 3 0.4 / 3	2.6 / 0 2.4 / 0
TsPA	^{1}H	———	———	———	coal	———	———	———	
	^{13}C	———	———	———	coal	———	———	———	
TsTp	^{1}H	———	———	———	coal	———	———	———	
	^{13}C	———	———	———	coal	———	———	———	
PA	^{1}H	-0.53 / 35	-0.10 / 13	-0.54 / 11 -0.04 / 0	-0.64 / 36	-	-0.38 / 0	-0.51 / 0	-0.21 / 0
	^{13}C	-3.4 / 0	-1.2 / 0	-3.0 / 0	-0.1 / 6	-3.9 / 0 -3.9 / 0	-0.9 / 8 -1.2 / 8	0.5 / 0 0.3 / 0	0.6 / 2 0.7 / 0
PPG	^{1}H	———	———	———	coal	———	———	———	
	^{13}C	———	———	———	coal	———	———	———	
StL	^{1}H	———	———	———	coal	———	———	———	
	^{13}C	———	———	———	coal	———	———	———	
MtL	^{1}H	-0.28 / 3	0.06 / 0	-0.20 / 0 -0.03 / 0	-0.16 / 0	-	-0.16 / 0	-0.15 / 0	-0.10 / 0
	^{13}C	-2.4 / 0	0.2 / 4	-2.9 / 0	0.8 / 0	-3.8 / 0 -3.8 / 0	-1.0 / 0 -1.0 / 0	-0.1 / 0 0 / 0	0.5 / 0 0.5 / 0
N23tL	^{1}H	-1.06 / 86	-0.85 / 0	-0.84 / 135 -0.74 / 0	-1.46 / 117	-	-0.88 / 65	-1.10 / 9	-0.81 / 0
	^{13}C	-3.4 / 0	-0.7 / 14	-3.3 / 0	-0.8 / 31	-4.7 / 0 -4.8 / 0	-1.7 / 0 -2.5 / 0	-1.4 / 39 -1.9 / 39	-0.2 / 3 -0.7 / 2
N18tL	^{1}H	-1.40 / 82	-1.09 / 0	-1.40 / 47 -1.06 / 117	-1.94 / 56	-	-1.13 / 18	-0.63 / 46	-2.06 / 197
	^{13}C	-3.7 / 41	-1.3 / 120	-0.5 / 3	-1.6 / 10	n.d.[c] n.d.[c]	-2.4 / 6 -2.2 / 6	-2.6 / 17 -2.8 / 17	1.5 / 0 1.6 / 0
AtL	^{1}H	———	———	———	coal	———	———	———	
	^{13}C	———	———	———	coal	———	———	———	

[a] Separate data sets for the diastereotopic phenyl groups; no stereochemical assignment.

[b] Diastereotopic protons; no stereochemical assignment.

[c] Not detectable, n.d., due to signal complexity or overlap.

[d] Not detectable at room temperature due to signal broadening by coalescence (coal).

Table S2b Complexations shifts $\Delta\delta$ / diastereomeric dispersion effects $\Delta\nu$ (integers in Hz) of 2-butylphenylselenide (**Se**) in the presence of an equimolar amount of dirhodium tetracarboxylate complexes, in $CDCl_3$, recorded at 9.4 Tesla (400 MHz ^{1}H, 100.6 MHz ^{13}C).

Atom #		1	2	3[a]	4	*ipso*	*ortho*	*meta*	*para*
Rh*	^{1}H	0.10 / 2	0.63 / 2	0.24 / 0 0.27 / 1	-0.02 / 4	-	0.26 / 1	-0.09 / 0	0.05 / 0
	^{13}C	-2.9 / 8	4.5 / 0	-1.9 / 2	-0.6 / 3	-1.1 / 0	0 / 0	0.2 / 0	-0.1 / 0
MαNP	^{1}H	-0.44 / 11	-0.16 / 0	0 / 0 0 / 0	-0.26 / 15	-	-0.56 / 0	-0.19 / 0	-0.19 / 0
	^{13}C	-3.3 / 10	3.2 / 8	-2.1 / 11	-0.6 / 13	n.d.[b]	0.1 / 6	-0.8 /3	n.d.[b]
PtL	^{1}H	-1.17 / 49	-0.91 / 45	-0.68 / 0 -0.91 / 40	-0.95 / 22	-	-0.66 / 0	-0.72 / 14	-0.52 / 7
	^{13}C	-3.1 / 18	4.2 / 53	1.2 / 0	-0.5 / 14	n.d.[b]	-0.8 / 0	-1.0 / 5	-1.7 / 5
TsA	^{1}H	0.20 / 7	0.72 / 0	0.11 / 0 0.13 / 0	0.13 / 2	-	0.32 / 0	0.18 / 0	0.18 / 0
	^{13}C	-2.7 / 5	4.0 / 10	-1.7 / 7	-0.4 / 13	-0.7 / 0	-0.1 / 3	0.4 / 0	-2.2 / 6
TsPA	^{1}H	0.21 / 27	0.84 / 0	0.24 / 0 0.42 / 0	0.12 / 9	-	0.33 / 0	-0.56 / 0	-0.56 / 0
	^{13}C	-2.5 / 6	3.4 / 13	-1.6 / 8	-0.5 / 18	1.4 / 0	0.2 / 0	0.8 / 0	n.d[b] / n.d[b]
TsTp	^{1}H	———	———	———	coal[c]	———	———	———	———
	^{13}C	———	———	———	coal[c]	———	———	———	———
PA	^{1}H	-0.60 / 13	-0.15 / 0	-0.31 / 0 -0.51 / 0	-0.20 / 16	-	-0.05 / 11	-0.26 / 0	-0.26 / 0
	^{13}C	-3.1 / 6	3.7 / 0	-2.0 / 33	-0.4 / 6	-0.4 / 18	0.2 / 21	-0.6 / 6	-1.4 / 6
PPG	^{1}H	———	———	———	coal[c]	———	———	———	———
	^{13}C	———	———	———	coal[c]	———	———	———	———
StL	^{1}H	-0.08 / 34	0.10 / 24	-0.04 / 18 0.08 / 0	0.03 / 0	-	0.22 / 0	0.08 / 0	0.14 / 0
	^{13}C	-2.1 / 25	4.3 / 51	-1.4 / 25	0.4 / 17	-0.5 / 31	1.0 / 10	0.1 / 3	-0.5 / 8
MtL	^{1}H	-0.08 / 32	0.15 / 13	-0.05 / 10 0 / 0	-0.01 / 14	-	0.22 / 0	0.03 / 0	0.03 / 0
	^{13}C	-1.5 / 2	3.4 / 17	-1.1 / 25	0.5 / 7	-0.3 / 13	-1.2 / 0	0 / 3	-1.1 / 5
N23tL	^{1}H	-1.07 / 36	-0.85 / 59	-0.80 / 43 n.d[b]	-1.09 / 15	-	-0.44 / 0	-0.81 / 0	-0.28 / 0
	^{13}C	-2.5 / 0	3.3 / 17	-1.9 / 0	-0.6 / 32	0.1 / 3	0 / 6	-1.2 / 10	-1.6 / 0
N18tL	^{1}H	———	———	———	coal[c]	———	———	———	———
	^{13}C	———	———	———	coal[c]	———	———	———	———
AtL	^{1}H	———	———	———	coal[c]	———	———	———	———
	^{13}C	———	———	———	coal[c]	———	———	———	———

[a] Diastereotopic protons; no stereochemical assignment.

[b] Not detectable, n.d., due to signal complexity or overlap.

[c] Not detectable at room temperature due to signal broadening by coalescence (coal).

Table S2c Complexations shifts $\Delta\delta$/ diastereomeric dispersion effects $\Delta\nu$ (integers in Hz) of 2-butylphenylsulfide (**S**) in the presence of an equimolar amount of dirhodium tetracarboxylate complexes, in $CDCl_3$, recorded at 9.4 Tesla (400 MHz ^{1}H, 100.6 MHz ^{13}C).

Atom #		1	2	3[a]	4	*ipso*	*ortho*	*meta*	*para*
Rh*	^{1}H	0.18 / 5	0.61 / 0	0.13 / 0 0.44 / 0	0.01 / 4	-	0.39 / 0	n.d.[b]	0.10 / 0
	^{13}C	-2.5 / 11	3.4 / 7	-1.8 / 4	-0.3 / 11	-6.1 / 0	0.1 / 1	2.3 / 3	2.6 / 0
MαNP	^{1}H	-0.52 / 6	-1.69 / 7	-0.67 / 0 -0.47 / 0	-0.33 / 23	-	n.d.	-0.06 / 0	0.28 / 0
	^{13}C	-3.5 / 6	2.1 / 0	-2.4 / 5	-0.7 / 9	-6.5 / 0	-0.7 / 12	1.3 / 25	4.1 / 0
PtL	^{1}H	-1.09 / 39	-0.93 / 32	-0.93 / 0 -1.22 / 43	-0.94 / 17	-	-0.59 / 0	-0.82 / 0	-0.59 / 31
	^{13}C	-2.9 / 21	3.4 / 55	-2.3 / 52	-1.0 / 25	-2.2 / 0	-0.9 / 8	-4.5 / 6	2.7 / 0
TsA	^{1}H	0.24 / 6	0.70 / 0	0.21 / 3 0.39 / 4	0.13 / 2	-	0.05 / 0	0.05 / 0	0.01 / 0
	^{13}C	-2.3 / 0	2.2 / 13	-1.6 / 0	-0.3 / 15	-2.3 / 7	0.1 / 3	-2.1 / 0	0 / 0
TsPA	^{1}H	0.21 / 20	0.71 / 0	0.20 / 0 0.34 / 0	0.10 / 7	-	0.35 / 0	0.06 / 0	0.13 / 0
	^{13}C	-1.9 / 7	1.5 / 13	-1.2 / 0	-0.3 / 14	-2.2 / 0	0.1 / 0	-3.7 / 0	-0.1 / 0
TsTp	^{1}H	———	———	———	coal[c]	———	———	———	———
	^{13}C	———	———	———	coal[c]	———	———	———	———
PA	^{1}H	-0.57 / 29	-0.19 / 0	-0.52 / 1 -0.30 / 1	-0.49 / 12	-	-0.04 / 0	-0.38 / 0	-0.24 / 0
	^{13}C	-3.1 / 7	3.1 / 17	-2.1 / 27	-0.4 / 14	-1.6 / 0	-0.9 / 0	-1.7 / 0	1.4 / 8
PPG	^{1}H	-1.27 / 0	-0.31 / 0	-0.66 / 0 -0.74 / 0	-0.53 / 0	-	0.11 / 0	0.03 / 0	0.10 / 0
	^{13}C	-2.8 / 0	2.4 / 0	-2.0 / 0	-0.3 / 0	0.4 / 2	0.3 / 4	0.3 / 3	-0.3 / 0
StL	^{1}H	0.03 / 19	0.15 / 14	0.03 / 13 0.17 / 11	0.08 / 3	-	0.40 / 0	0.11 / 0	0.18 / 0
	^{13}C	-1.3 / 11	4.0 / 35	-1.1 / 18	0.8 / 14	-0.3 / 21	-0.1 / 2	-0.8 / 5	2.3 / 5
MtL	^{1}H	-0.08 / 22	-0.01 / 9	0.07 / 12 0.08 / 11	-0.01 / 6	-	0.26 / 0	0.08 / 0	0.15 / 0
	^{13}C	-1.2 / 6	3.3 / 9	-1.0 / 23	0.7 / 8	-0.5 / 0	-0.1 / 2	1.8 / 0	1.9 / 0
N23tL	^{1}H	-0.96 / 38	-0.82 / 54	-0.74 / 65 n.d.[b]	-1.05 / 25	-	n.d.[b]	0.05 / 0	0.12 / 0
	^{13}C	-2.2 / 0	3.0 / 37	-2.1 / 53	-0.5 / 23	-1.5 / 4	-1.4 / 0	-4.4 / 0	1.5 / 0
N18tL	^{1}H	———	———	———	coal[c]	———	———	———	———
	^{13}C	———	———	———	coal[c]	———	———	———	———
AtL	^{1}H	-0.66 / 46	-0.87 / 99	-0.47 / 0 -0.12 / 0	-0.82 / 27	-	0.28 / 0	-0.09 / 0	-0.09 / 0
	^{13}C	-1.6 / 4	2.6 / 29	-1.6 / 48	-0.2 / 21	-1.3 / 0	-1.2 / 5	-4.2 / 0	1.2 / 0

[a] Diastereotopic protons; no stereochemical assignment.

[b] Not detectable, n.d., due to signal complexity or overlap.

[c] Not detectable at room temperature due to signal broadening by coalescence (coal).

Table S2d Complexations shifts $\Delta\delta$ / diastereomeric dispersion effects $\Delta\nu$ (integers in Hz) of 2-butylphenylether (**O**) in the presence of an equimolar amount of dirhodium tetracarboxylate complexes, in $CDCl_3$, recorded at 9.4 Tesla (400 MHz ^{1}H, 100.6 MHz ^{13}C).

Atom #		1	2	3[a]	4	*ipso*	*ortho*	*meta*	*para*
Rh*	^{1}H	0.01 / 0	0.02 / 0	0.02 / 0 0.02 / 0	-0.01 / 0	-	n.d.[b]	0.02 / 0	0.02 / 0
	^{13}C	0 / 0	0.6 / 4	0 / 1	0 / 1	0 / 1	0.4 / 0	0.1 / 2	0 / 1
MαNP	^{1}H	0 / 0	0.01 / 0	0.01 / 0 0 / 0	0 / 0	-	n.d.	0 / 3	0 / 3
	^{13}C	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 1	0 / 0
PtL	^{1}H	-0.02 / 3	-0.01 / 4	-0.02 / 0 -0.02 / 0	-0.03 / 4	-	-0.37 / 0	0.33 / 0	-0.01 / 0
	^{13}C	0 / 1	0.3 / 15	-0.1 / 1	0 / 1	0 / 3	0.2 / 5	0 / 2	0 / 2
TsA	^{1}H	0 / 0	0.01 / 0	0.02 / 0 0 / 0	0 / 0	-	0.01 / 0	0 / 0	0.03 / 0
	^{13}C	0 / 0	0 / 0	0 / 0	0 / 2	0 / 1	0 / 0	0 / 0	0 / 0
TsPA	^{1}H	0 / 0	0.01 / 0	0.01 / 0 0 / 0	0 / 0	-	0.01 / 0	0 / 0	0 / 0
	^{13}C	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0
TsTp	^{1}H	0 / 0	0 / 0	0 / 0 0 / 0	0 / 0	-	0 / 0	0 / 0	0 / 0
	^{13}C	-0.1 / 0	-0.1 / 0	-0.1 / 0	-0.1 / 0	0 / 0	-0.1 / 0	-0.1 / 0	-0.1 / 0
PA	^{1}H	0 / 1	0 / 0	0.06 / 0 0 / 0	-0.01 / 0	-	0.01 / 0	0 / 0	0 / 0
	^{13}C	0 / 0	0.1 / 3	0 / 0	0 / 0	0 / 1	0 / 1	0 / 0	0 / 1
PPG	^{1}H	-0.01 / 0	-0.01 / 0	0.01 / 0 -0.01 / 0	-0.01 / 0	-	-0.12 / 0	-0.02 / 0	-0.02 / 0
	^{13}C	0 / 0	0.1 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0
StL	^{1}H	0.13 / 0	0.13 / 0	0.09 / 0 0.14 / 0	0.14 / 0	-	0.14 / 0	0.12 / 0	0.12 / 0
	^{13}C	0 / 0	-0.1 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0
MtL	^{1}H	0 / 0	0.01 / 0	0.02 / 0 0 / 0	0 / 0	-	0 / 0	0 / 0	0 / 0
	^{13}C	0 / 0	0 / 0	0 / 0	0 / 1	0 / 1	0 / 1	0 / 0	0 / 0
N23tL	^{1}H	-0.02 / 6	-0.01 / 4	-0.01 / 6 -0.02 / 1	-0.03 / 3	-	0.05 / 5	-0.03 / 2	0.02 / 3
	^{13}C	0 / 0	0.2 / 9	-0.1 / 1	0 / 1	0 / 2	0.1 / 3	0 / 1	0 / 1
N18tL	^{1}H	-0.02 / 3	-0.01 / 4	-0.01 / 2 -0.01 / 5	-0.02 / 4	-	0.01 / 0	0 / 0	0 / 0
	^{13}C	0 / 0	0.1 / 7	0 / 0	0 / 0	0 / 1	0 / 2	0 / 1	-0.1 / 0
AtL	^{1}H	0 / 0	0.01 / 0	0.01 / 0 -0.01 / 0	0 / 0	-	0 / 0	-0.01 / 0	0.02 / 0
	^{13}C	0 / 0	0 / 0	0 / 0	0 / 1	0 / 1	0 / 1	0 / 2	0 / 0

[a] Diastereotopic protons; no stereochemical assignment.

[b] Not detectable, n.d., due to signal complexity or overlap.

Table S2e Complexations shifts $\Delta\delta$ / diastereomeric dispersion effects $\Delta\nu$ (integers in Hz) of 2-butylacetate (**C=O**) in the presence of an equimolar amount of dirhodium tetracarboxylate complexes, in $CDCl_3$, recorded at 9.4 Tesla (400 MHz ^{1}H, 100.6 MHz ^{13}C).

Atom #		1	2	3[a]	4	CH_3	C=O
Rh*	^{1}H	0.05 / 2	0.18 / 6	0.05 / 1	0.01 / 1	0.13 / 1	-
	^{13}C	-0.1 / 1	1.1 / 1	0 / 0	0 / 0	0 / 0	2.7 / 0
MαNP	^{1}H	0 / 0	0 / 0	-0.01 / 0	0 / 0	0 / 0	-
	^{13}C	0 / 1	0.1 / 0	0 / 0	0 / 1	0 /0	0.2 / 1
PtL	^{1}H	-0.04 / 6	-0.35 / 2	-0.05 / 2	-0.04 / 4	-0.01 / 2	-
	^{13}C	-0.1 / 3	0.4 / 2	-0.1 / 1	0 / 1	0 / 1	1.0 / 2
TsA	^{1}H	0 / 0	0.01 / 0	-0.01 / 0	0.30 / 0	0.01 / 0	-
	^{13}C	0 / 0	0.1 / 0	0 / 0	0 / 0	0.1 / 0	0.2 / 0
TsPA	^{1}H	0 / 0	0.01 / 0	-0.01 / 0	0 / 0	0.01 / 0	-
	^{13}C	0 / 0	0.1 / 0	0 / 0	0 / 0	0 / 0	n.d.[b]
TsTp	^{1}H	0 / 0	0.01 / 0	-0.01 / 0	0 / 0	2.81 / 0	-
	^{13}C	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0.1 /0
PA	^{1}H	-0.54 / 31	-1.92 / 0	0.10 / 0	-0.40 / 4	-0.15 / 0	-
	^{13}C	-2.2 / 7	n.d.[b]	-1.5 / 36	-1.3 / 14	-0.3 / 0	0.6 / 0
PPG	^{1}H	-0.05 / 0	0.02 / 0	-0.03 / 0	-0.03 / 0	-0.05 / 0	-
	^{13}C	-0.1 / 0	0.4 / 0	-0.1 / 1	-0.1 / 1	-0.1 / 0	1.2 / 0
StL	^{1}H	0 / 0	0 / 0	-0.01 / 0	-0.01 / 0	0.01 / 0	-
	^{13}C	0 / 0	0.1 / 0	0 / 0	0 / 1	0 / 1	0.1 / 0
MtL	^{1}H	0.02 / 0	0.02 / 0	0.01 / 0	0 / 0	0.02 / 0	-
	^{13}C	0 / 0	0.1 / 0	0 / 0	0 / 0	0.1 / 0	-0.4 / 0
N23tL	^{1}H	-0.13 / 6	-0.07 / 0	-0.14 / 0	-0.13 / 7	-0.06 / 3	-
	^{13}C	-0.2 / 5	0.4 / 2	-0.2 / 2	-0.1 / 2	-0.1 / 0	1.1 / 2
N18tL	^{1}H	-0.05 / 2	-0.04 / 0	-0.13 / 0	-0.05 / 2	-0.01 / 0	-
	^{13}C	-0.1 / 1	0.1 / 0	-0.1 / 0	0 / 1	0 / 0	0.4 / 0
AtL	^{1}H	-0.01 / 0	0.04 / 0	-0.02 / 0	-0.01 / 0	0 / 0	-
	^{13}C	0 / 1	0 / 0	-0.5 / 0	0 / 1	0 / 1	0.1 / 1

[a] Diastereotopic protons; no stereochemical assignment.

[b] Not detectable, n.d., due to signal complexity or overlap.

Table S3 X-ray data and ORTEP plot of the bis(methanol) adduct of **N2tL**.

checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: d_14ag1x

Bond precision: C-C = 0.0063 A Wavelength=0.71067

Cell: a=28.965(14) b=36.811(18) c=15.395(16)
alpha=90 beta=90 gamma=90

Temperature: 100 K

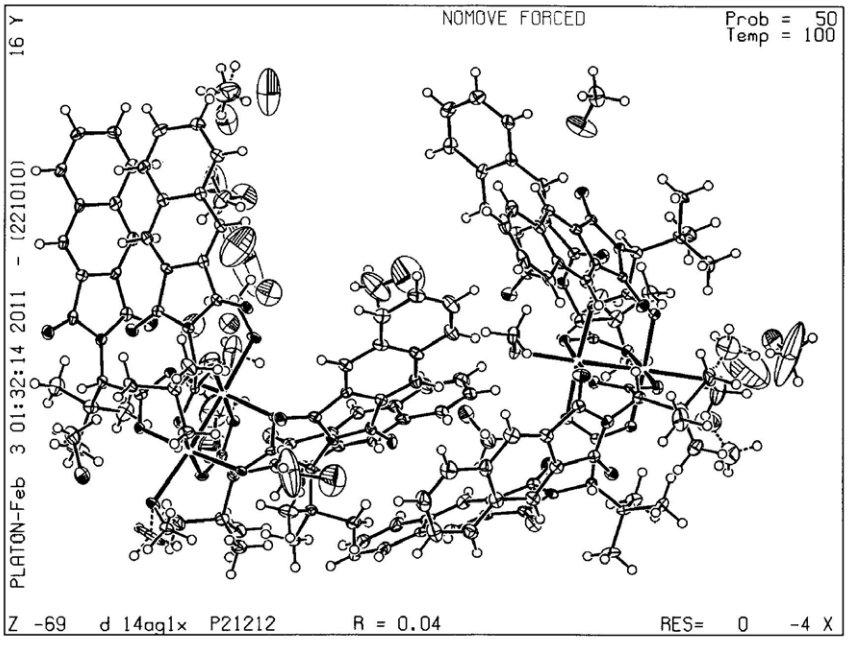
	Calculated	Reported
Volume	16415(20)	16415(20)
Space group	P 21 21 2	P21212
Hall group	P 2 2ab	P 2 2ab
Moiety formula	4(C74 H70 N4 O18 Rh2), 16(C H3 O), 4(C H3), 13(O)	2(C74 H72 N4 O18 Rh2), 4.5(H2 O), 10(C1 H4 O1)
Sum formula	C316 H340 N16 O101 Rh8	C159 H215 N8 O50.5 Rh4
Mr	6801.34	3458.04
Dx,g cm-3	1.376	1.399
Z	2	4
Mu (mm-1)	0.473	0.481
F000	7032.0	7236.0
F000'	7017.96	
h,k,lmax	36,46,19	36,44,18
Nref	18907[35221]	33748
Tmin,Tmax		
Tmin'		

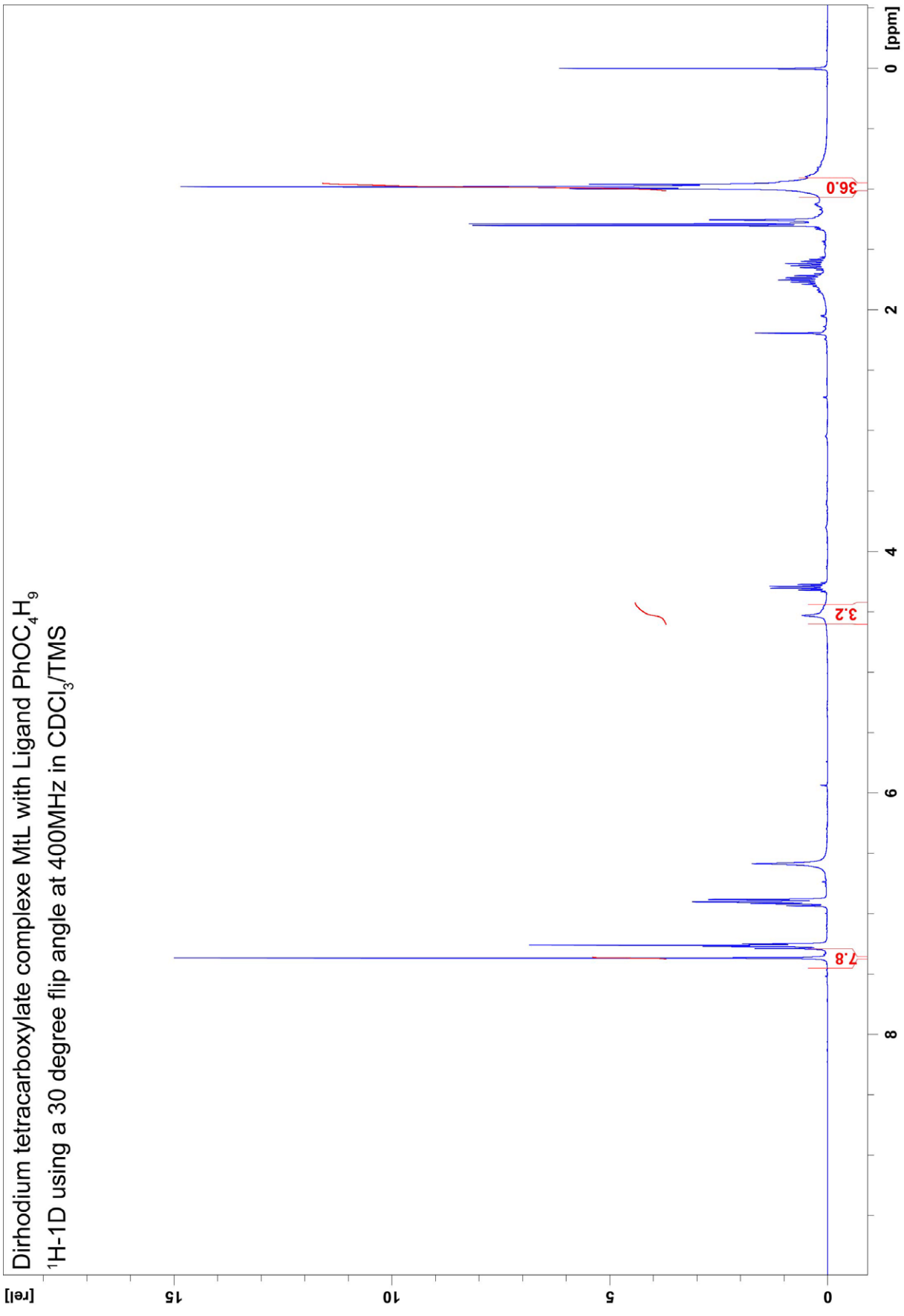
Correction method= Not given

Data completeness= 1.78/0.96 Theta(max)= 26.820

R(reflections)= 0.0418(31041) wR2(reflections)= 0.1054(33748)

S = 1.079 Npar= 2058




Dirhodium tetracarboxylate complexe MtL with Ligand PhOC4H9
1H-1D using a 30 degree flip angle at 400MHz in CDCl3/TMS
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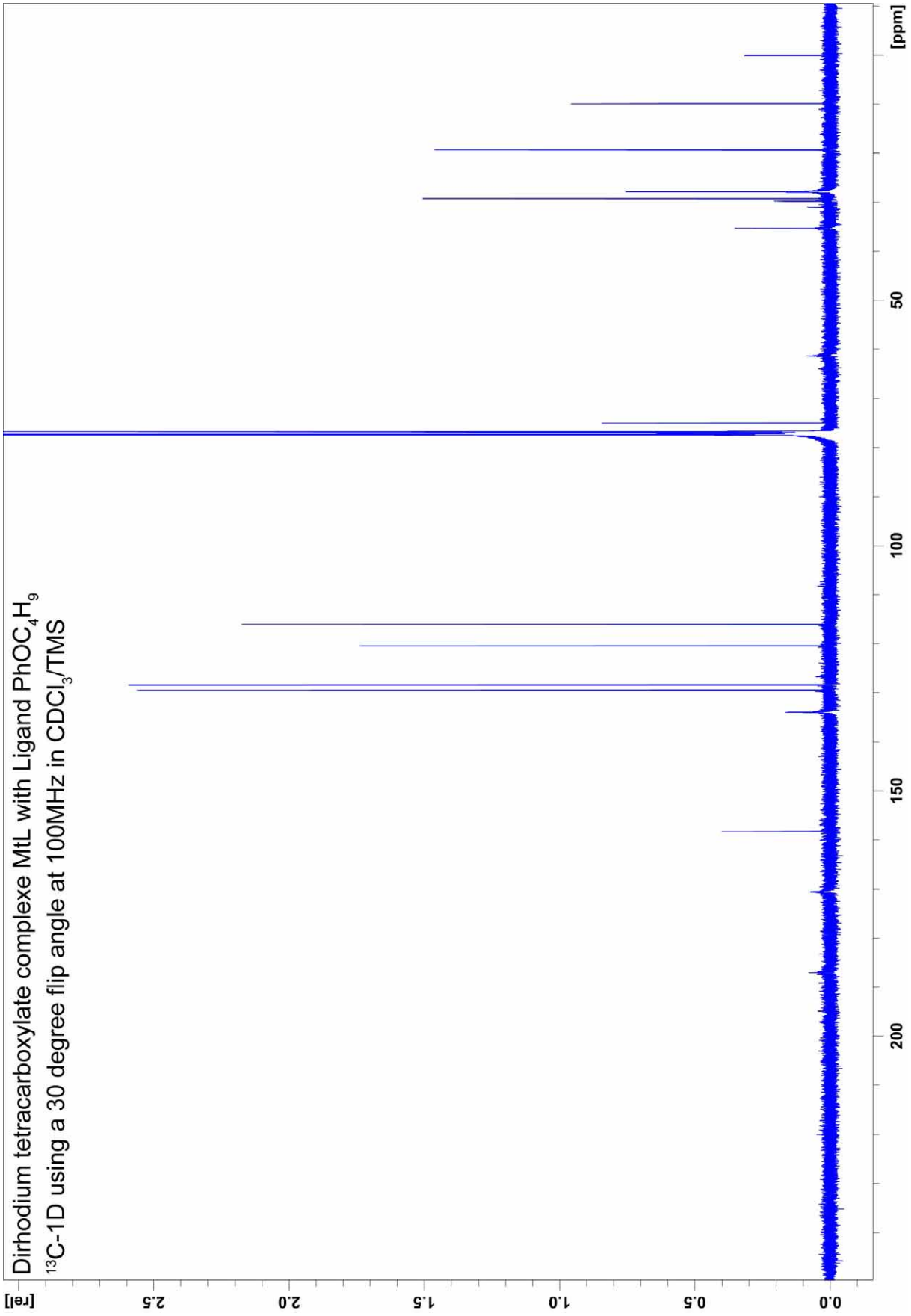
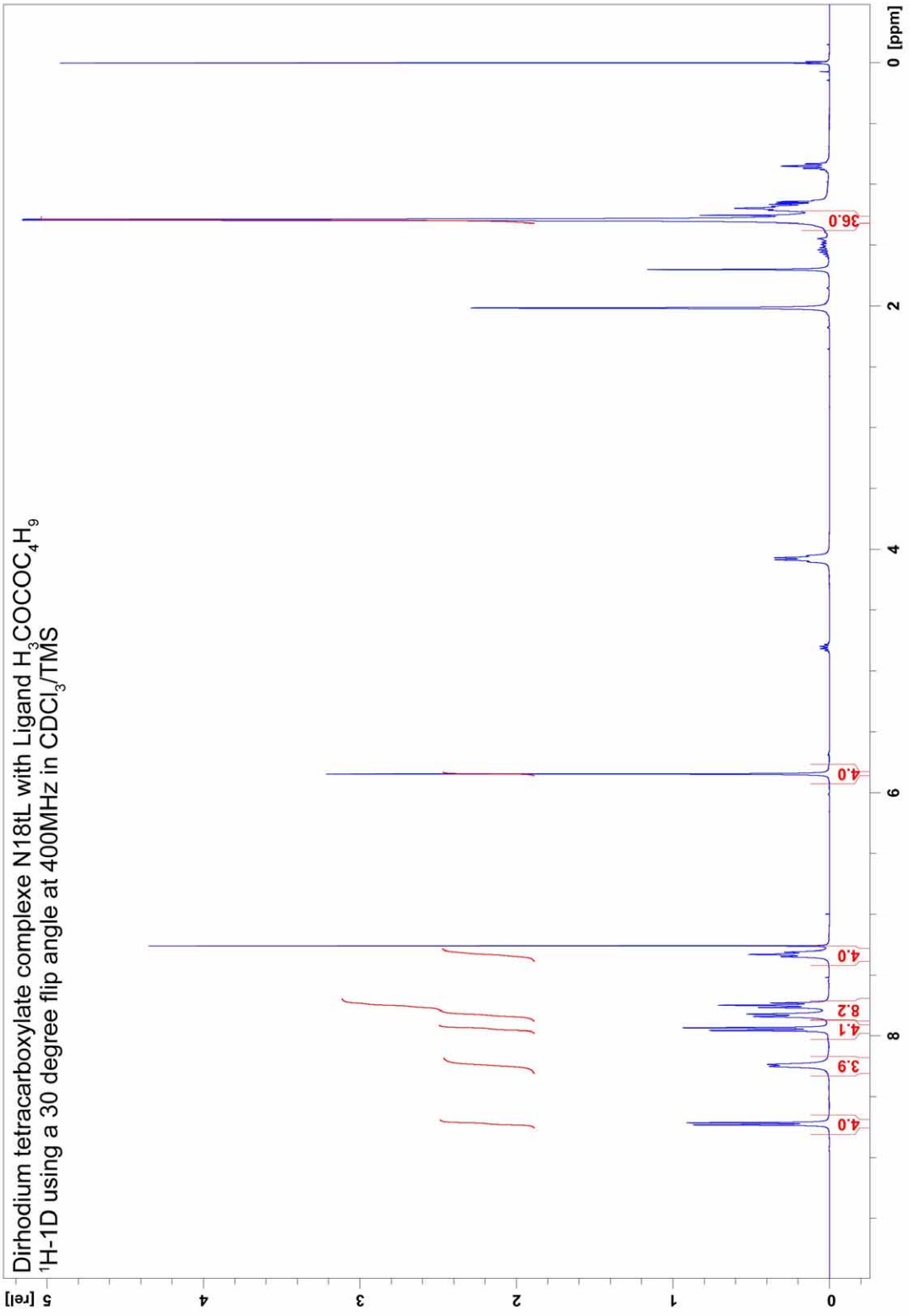
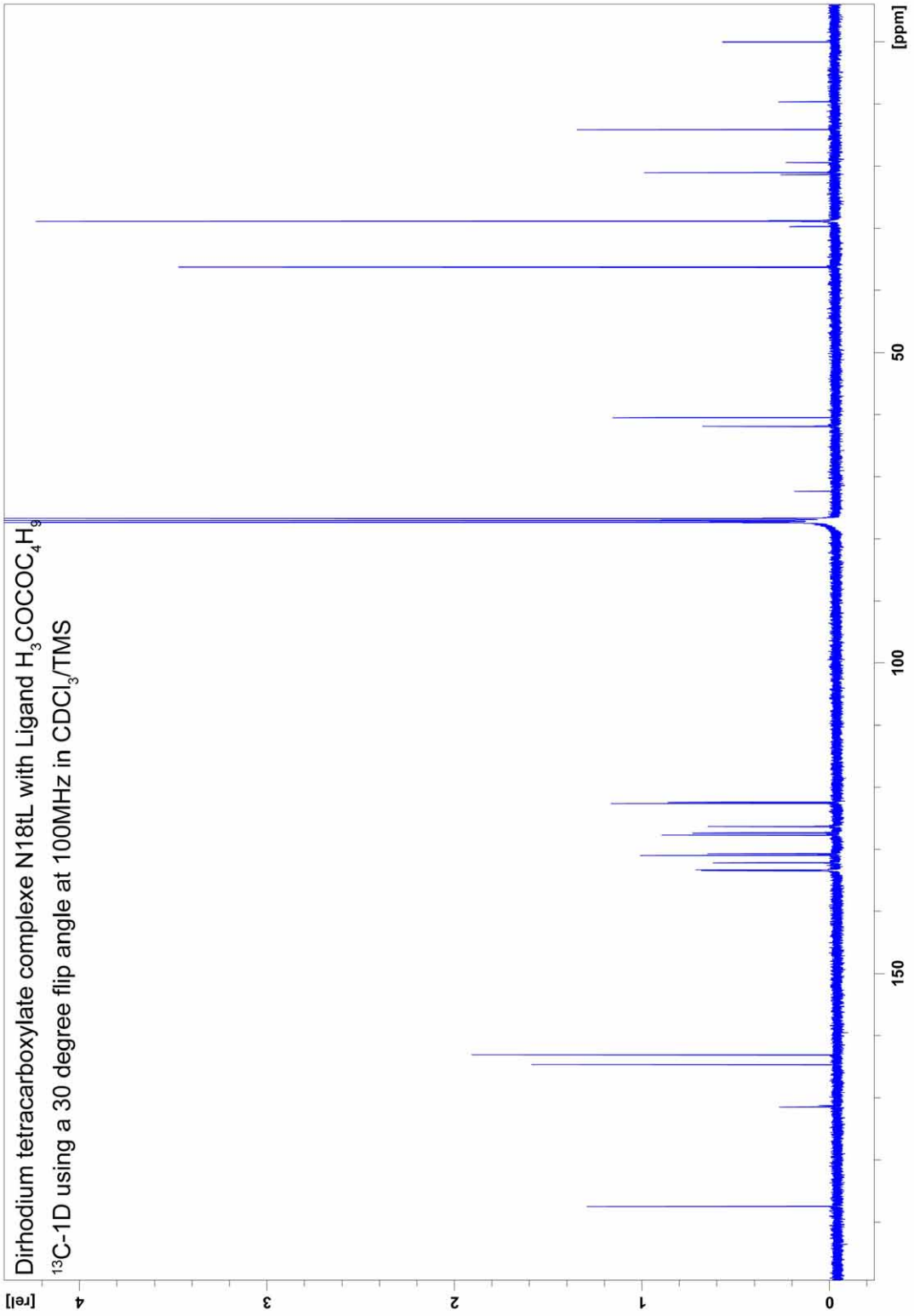
15
10
5
0
0 [ppm]
2
4
6
8
36.0
3.2
7.8






Dirhodium tetracarboxylate complexe N18tL with Ligand $H_3COCOC_4H_9$
^{13}C-1D using a 30 degree flip angle at 100MHz in $CDCl_3$/TMS
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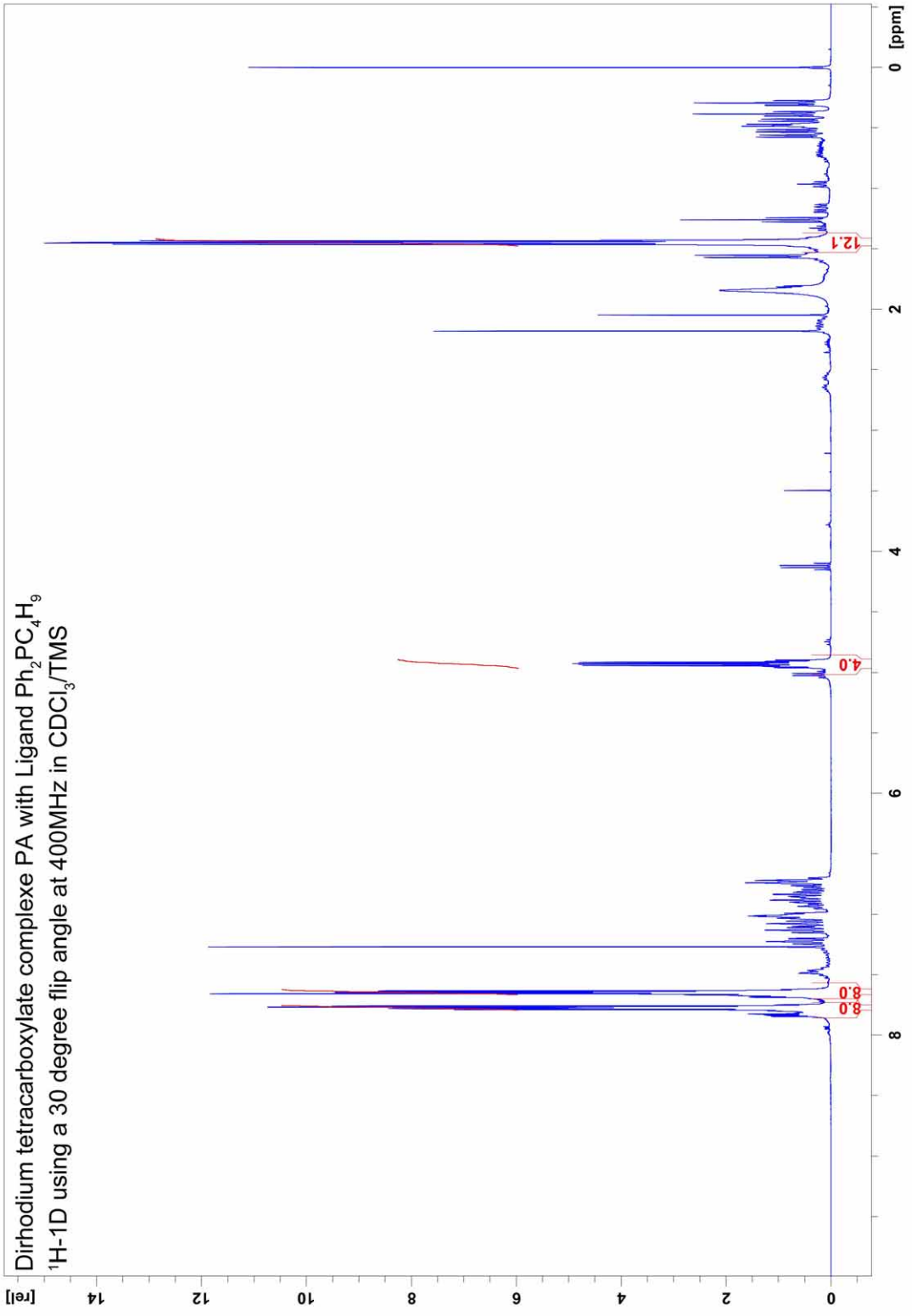
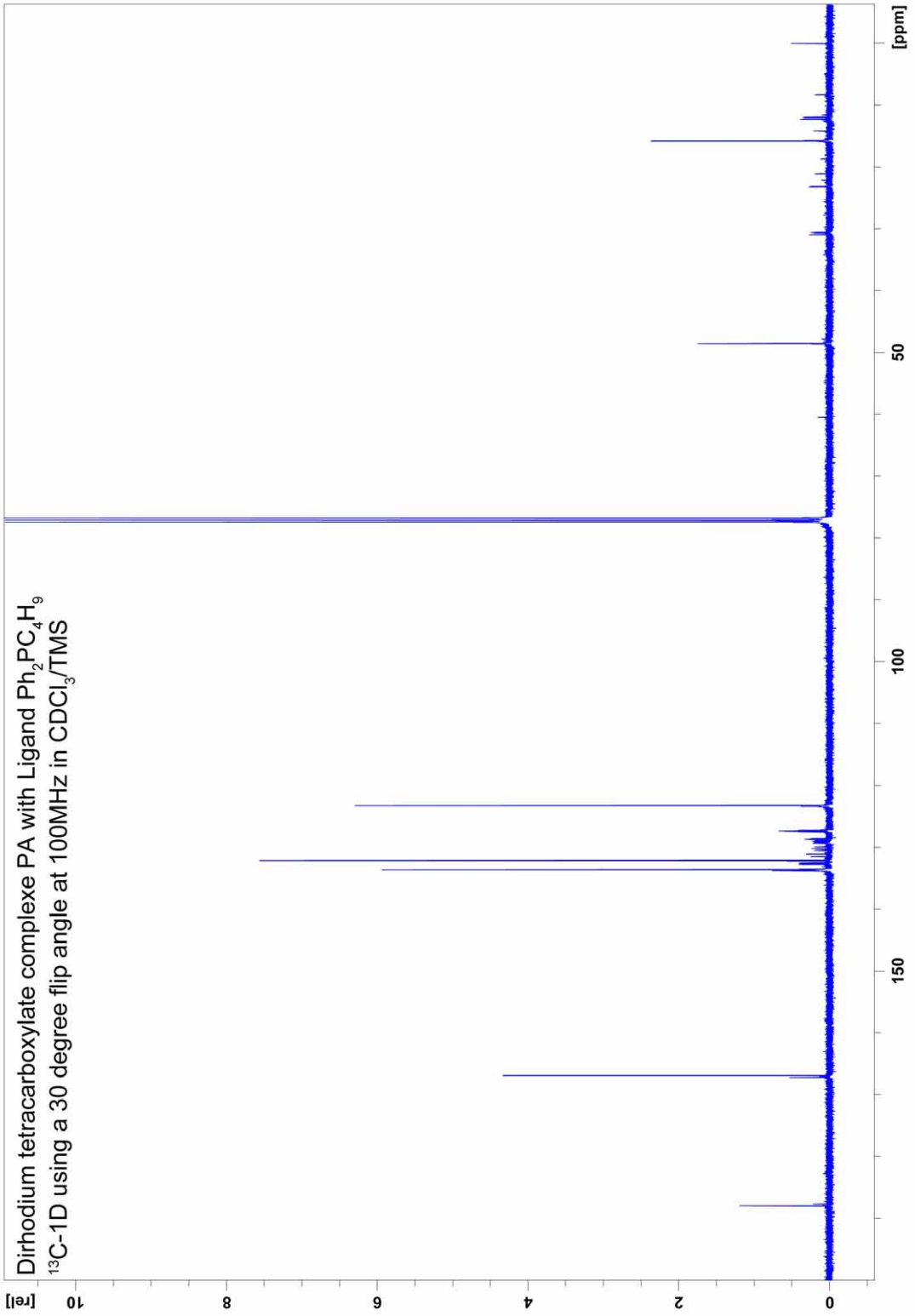
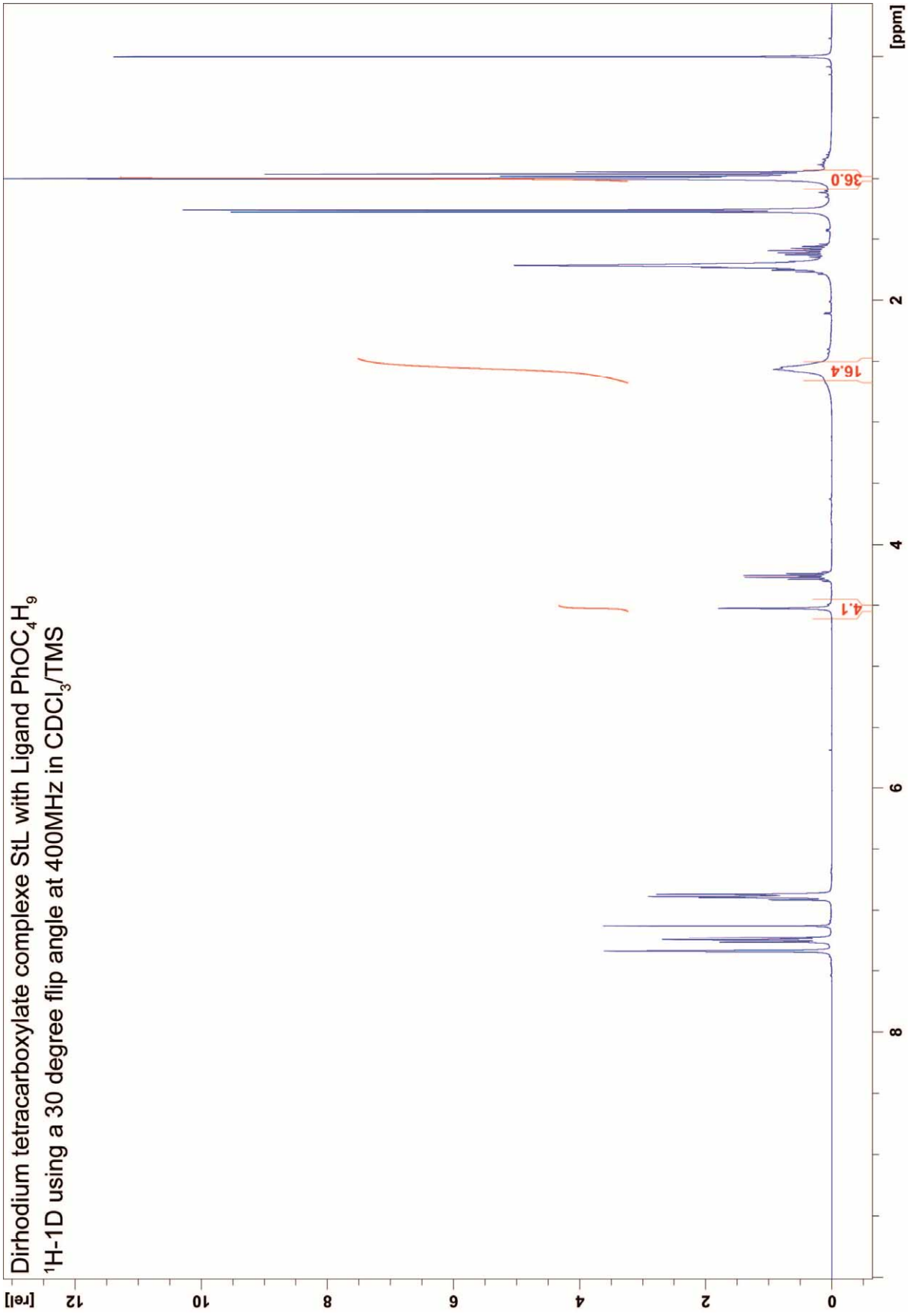
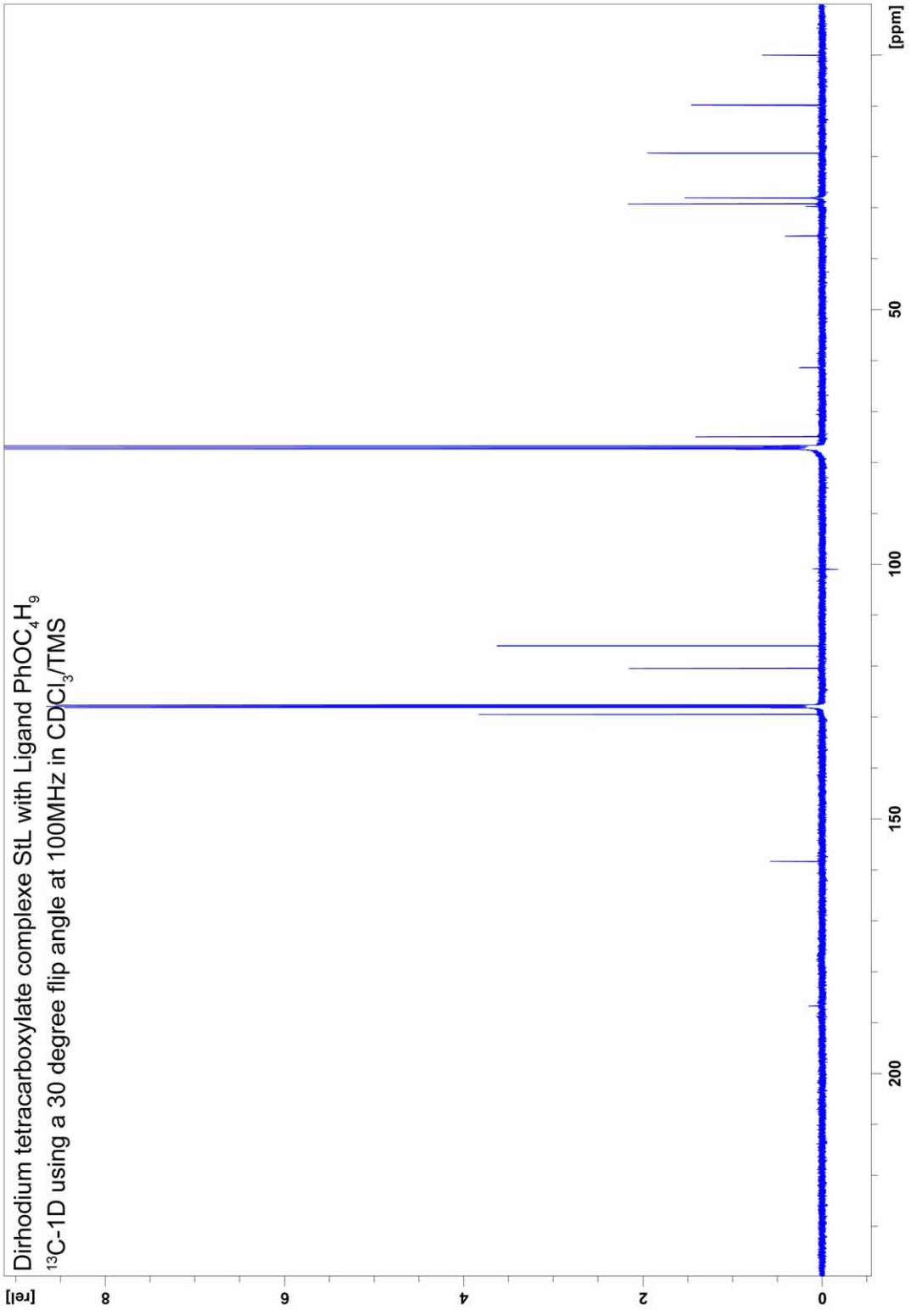
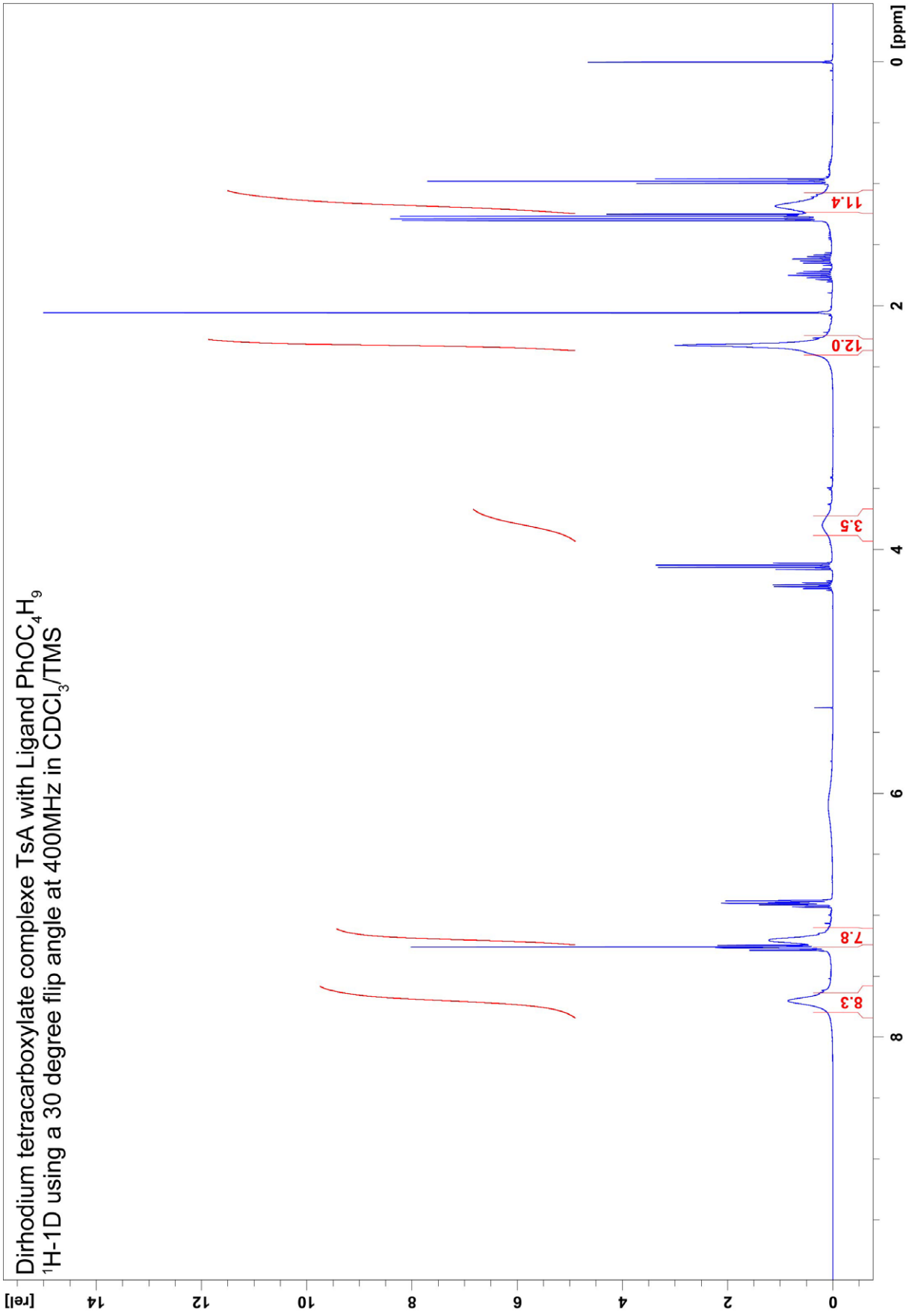
0
1
2
3
4
[ppm]
50
100
150


Dirhodium tetracarboxylate complexe PA with Ligand $Ph_2PC_4H_9$
^{1}H-1D using a 30 degree flip angle at 400MHz in $CDCl_3$/TMS
12.1
4.0
8.0
8.0
8.0
[rel]
[ppm]




Dirhodium tetracarboxylate complexe StL with Ligand PhOC4H9
1H-1D using a 30 degree flip angle at 400MHz in CDCl3/TMS
36.0
16.4
4.1
[ppm]
[rel]
0
2
4
6
8
10
12




Dirhodium tetracarboxylate complexe TsA with Ligand PhOC4H9
1H-1D using a 30 degree flip angle at 400MHz in CDCl3/TMS
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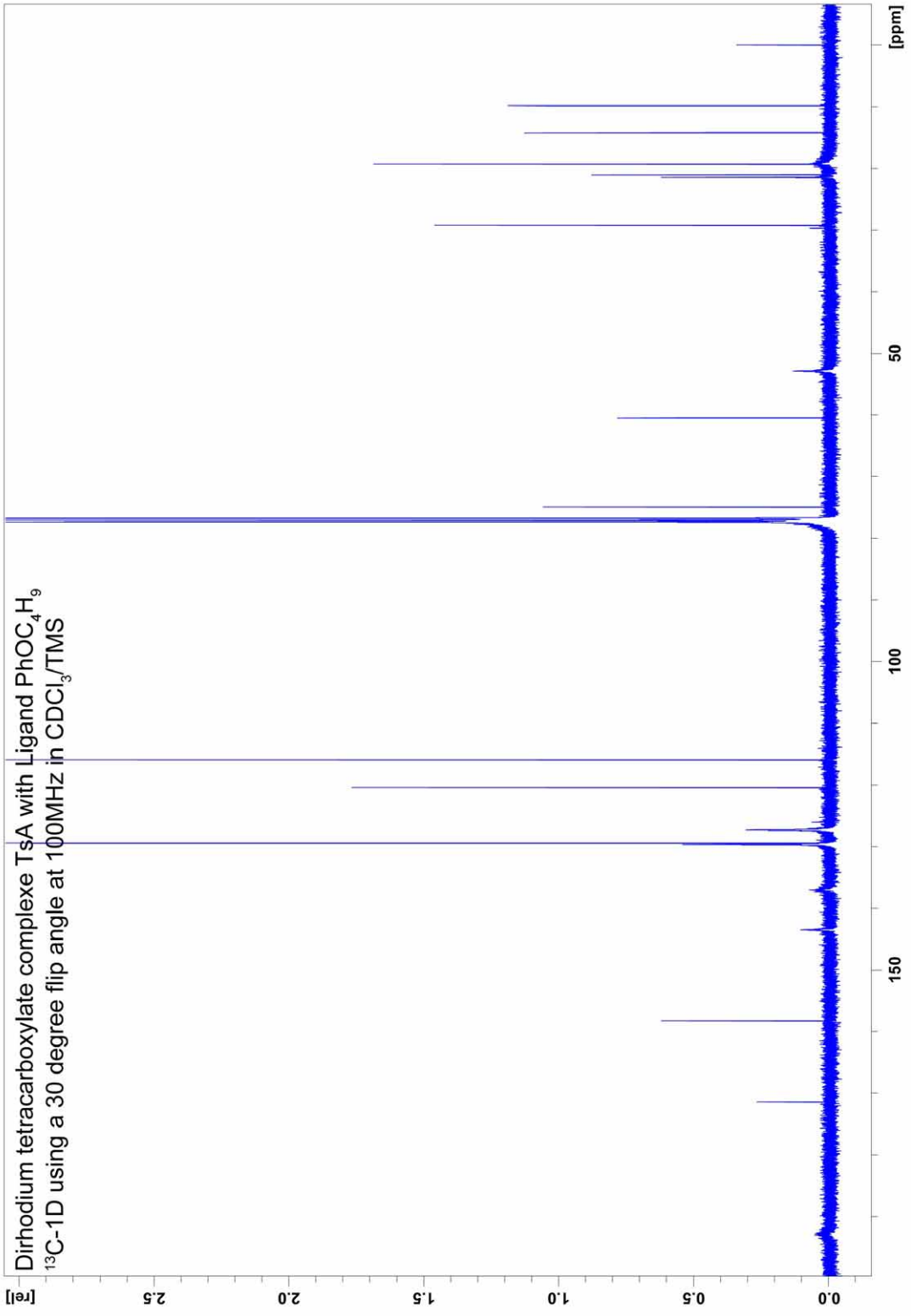
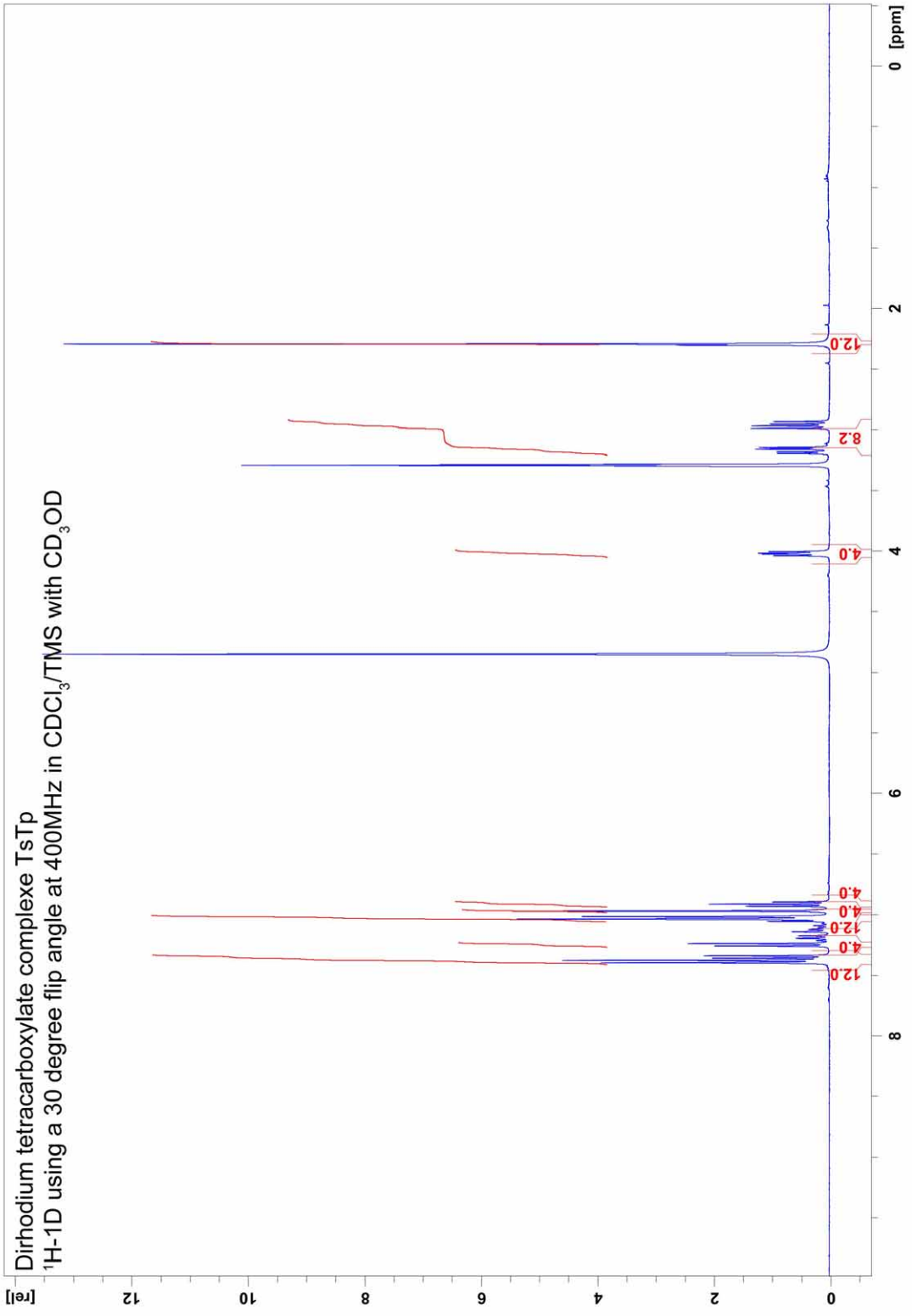
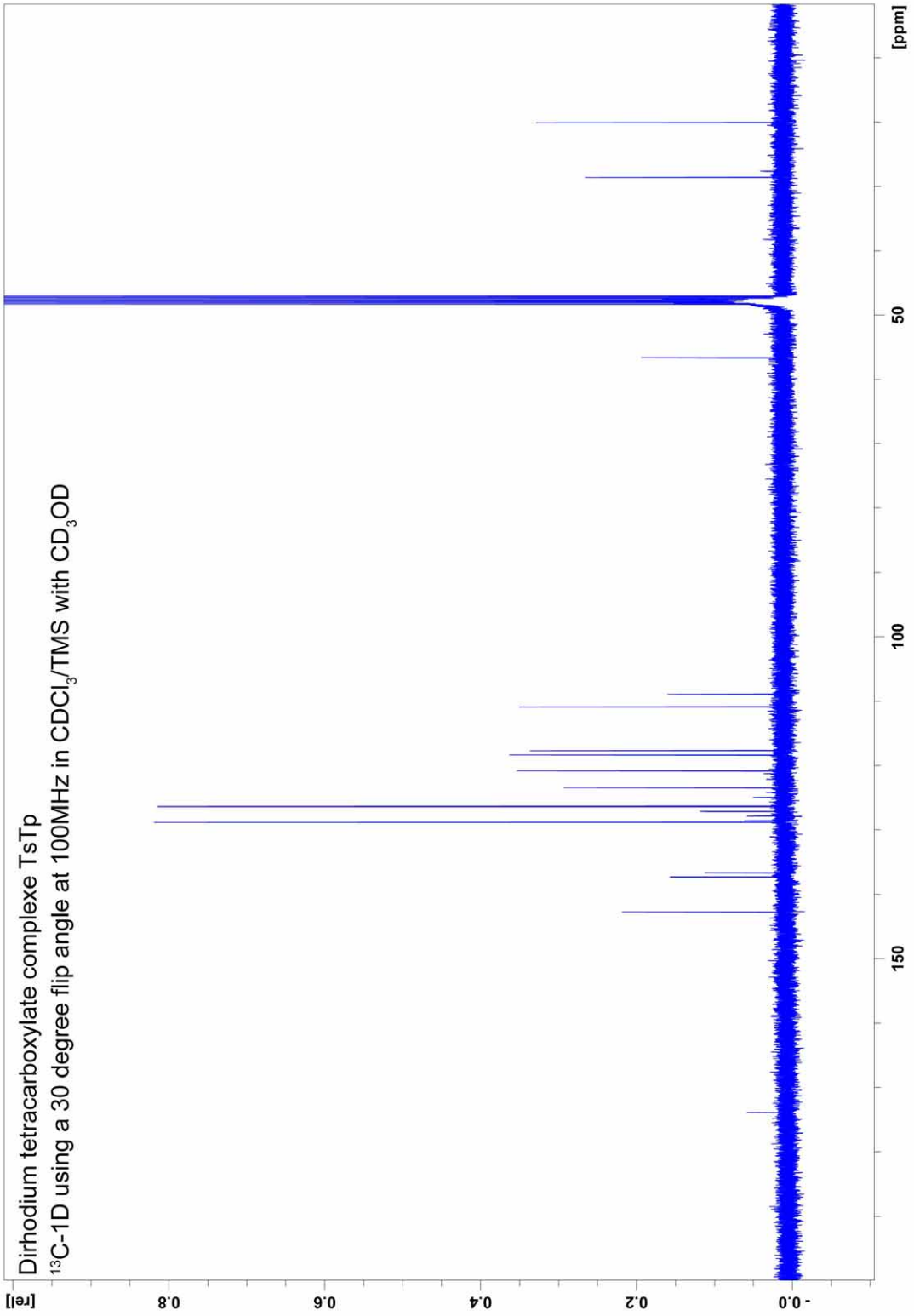
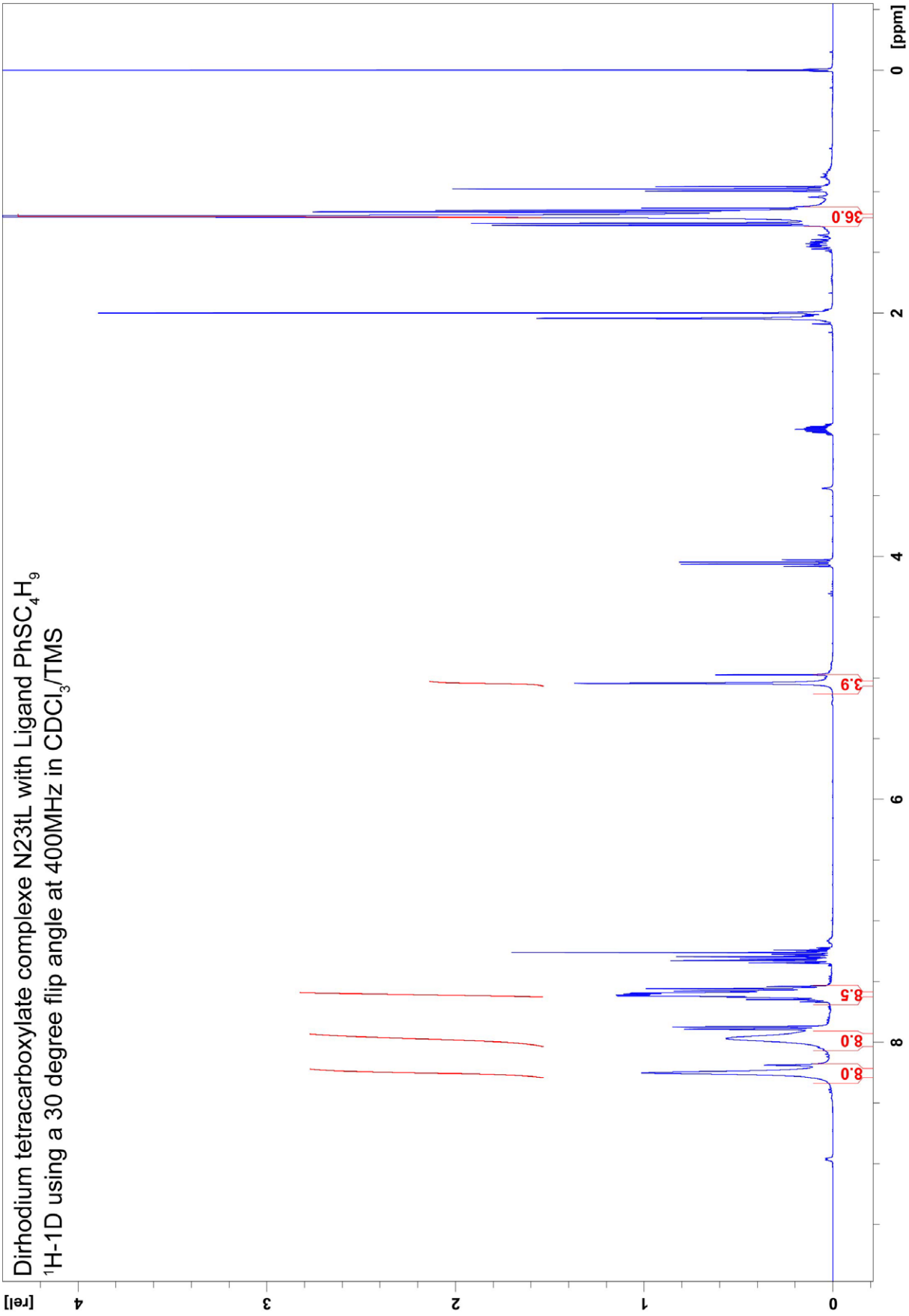
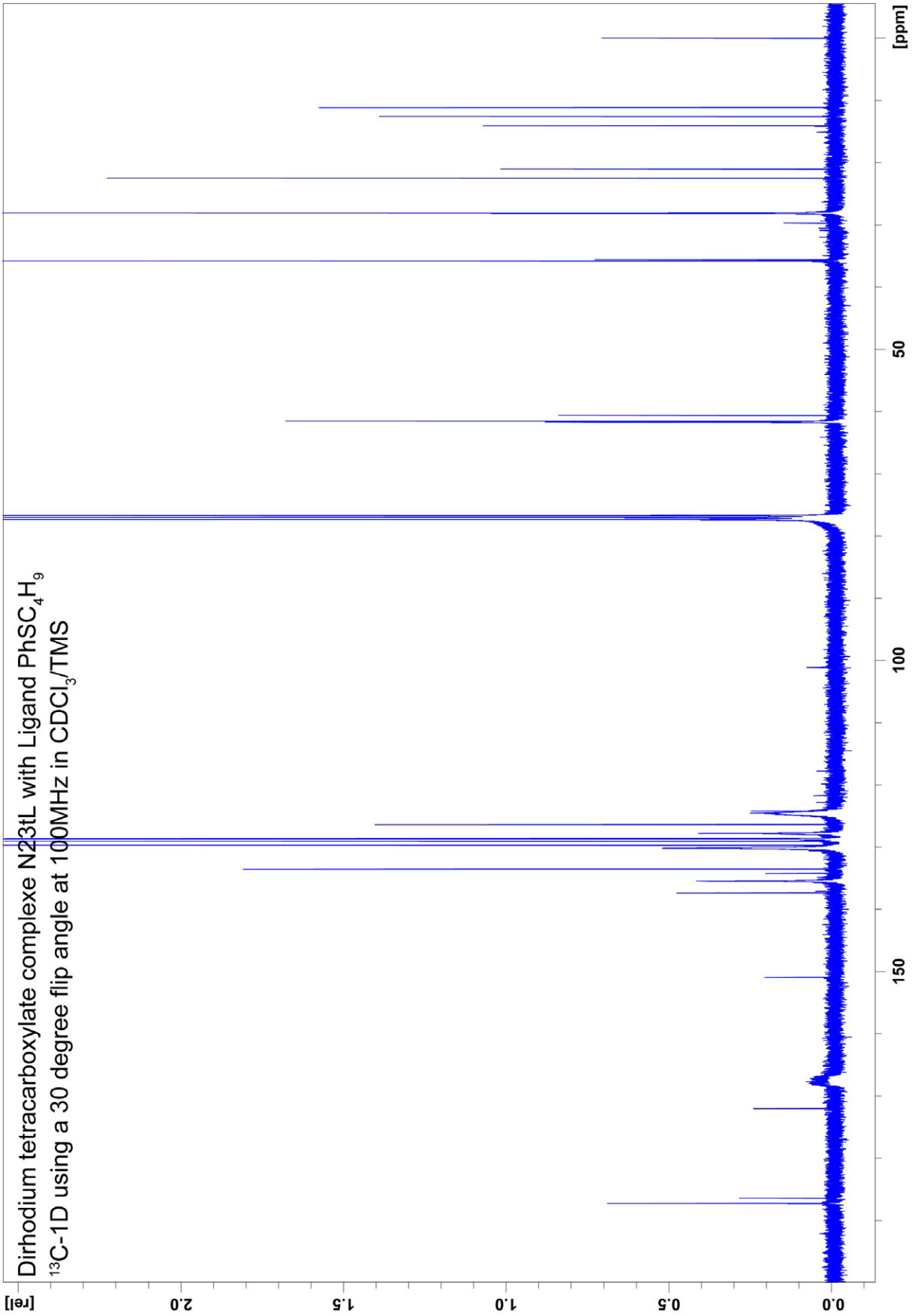
0 [ppm]
11.4
12.0
3.5
7.8
8.3

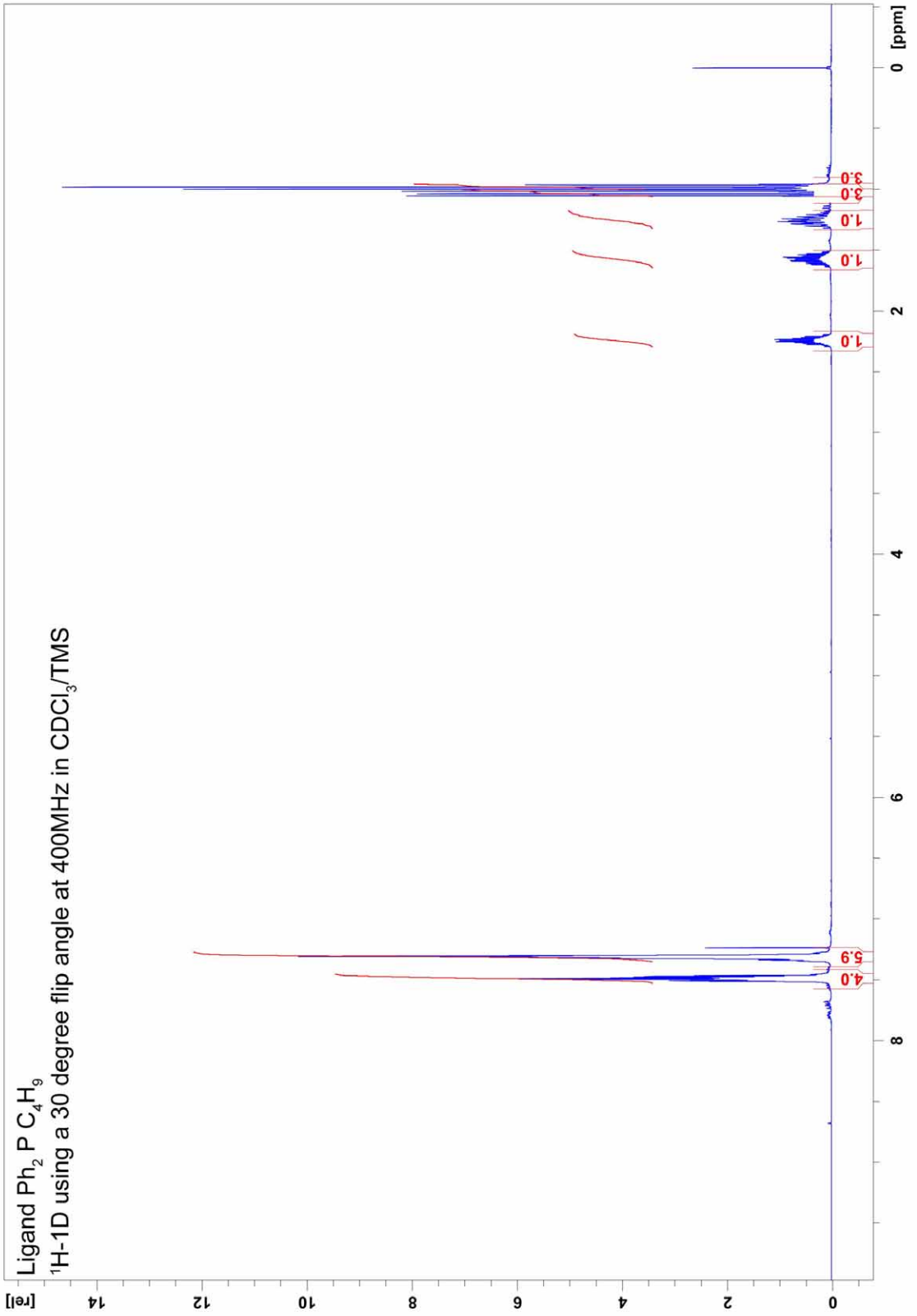


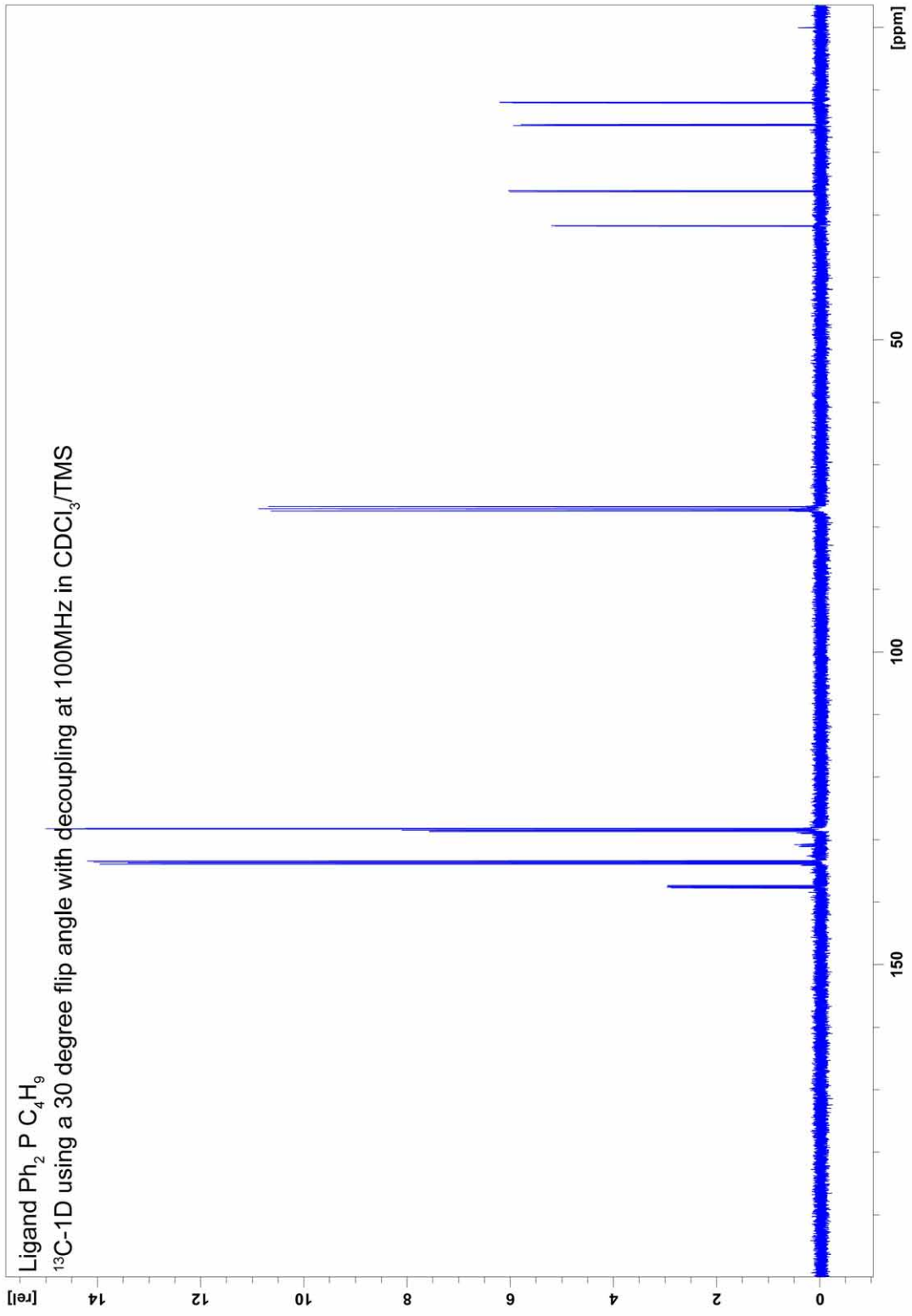


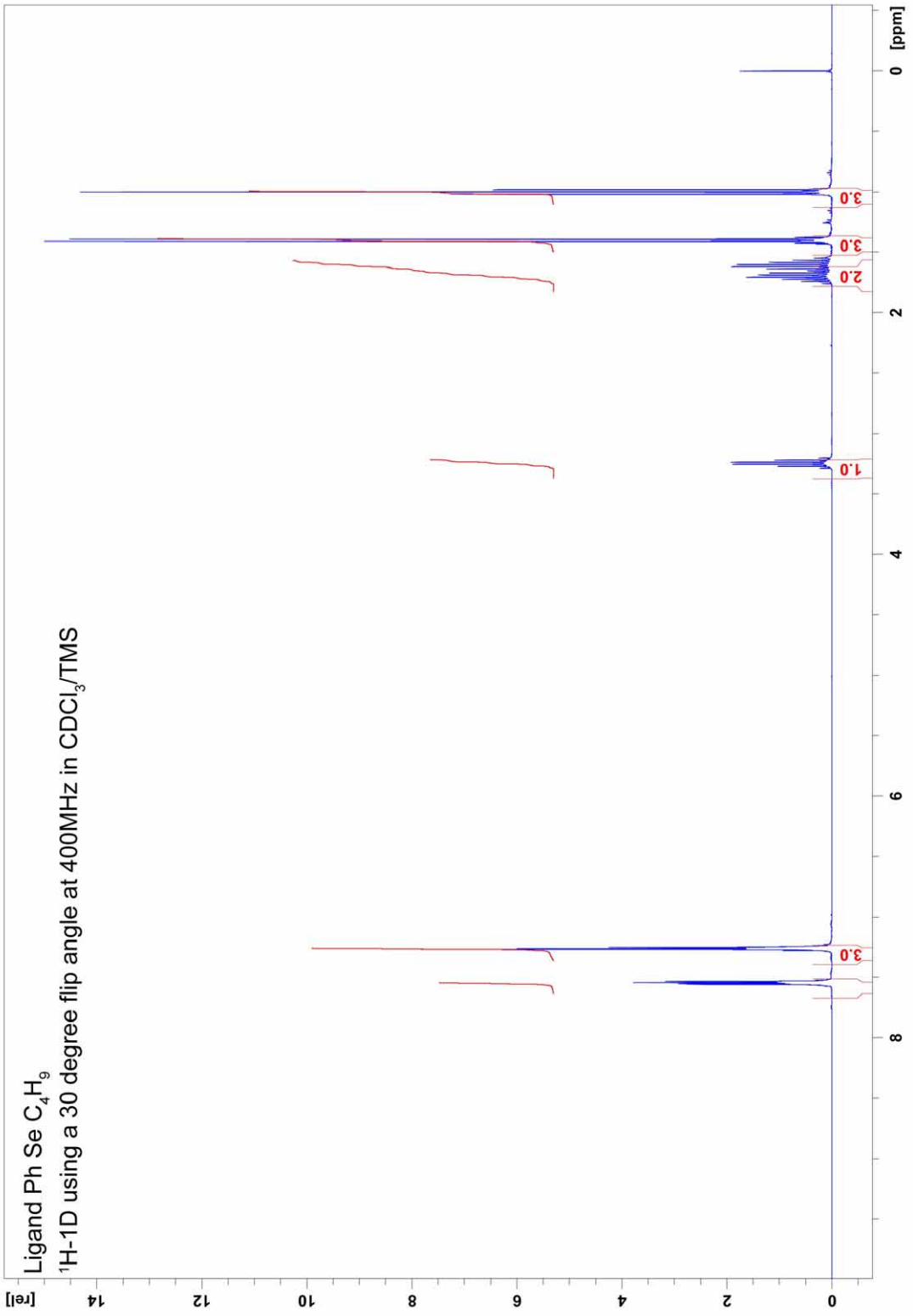









Ligand Ph_2 P C_4H_9
^{13}C-1D using a 30 degree flip angle with decoupling at 100MHz in $CDCl_3$/TMS
[rel]
14
12
10
8
6
4
2
0
[ppm]
50
100
150


Ligand Ph Se C_4H_9
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[ppm]
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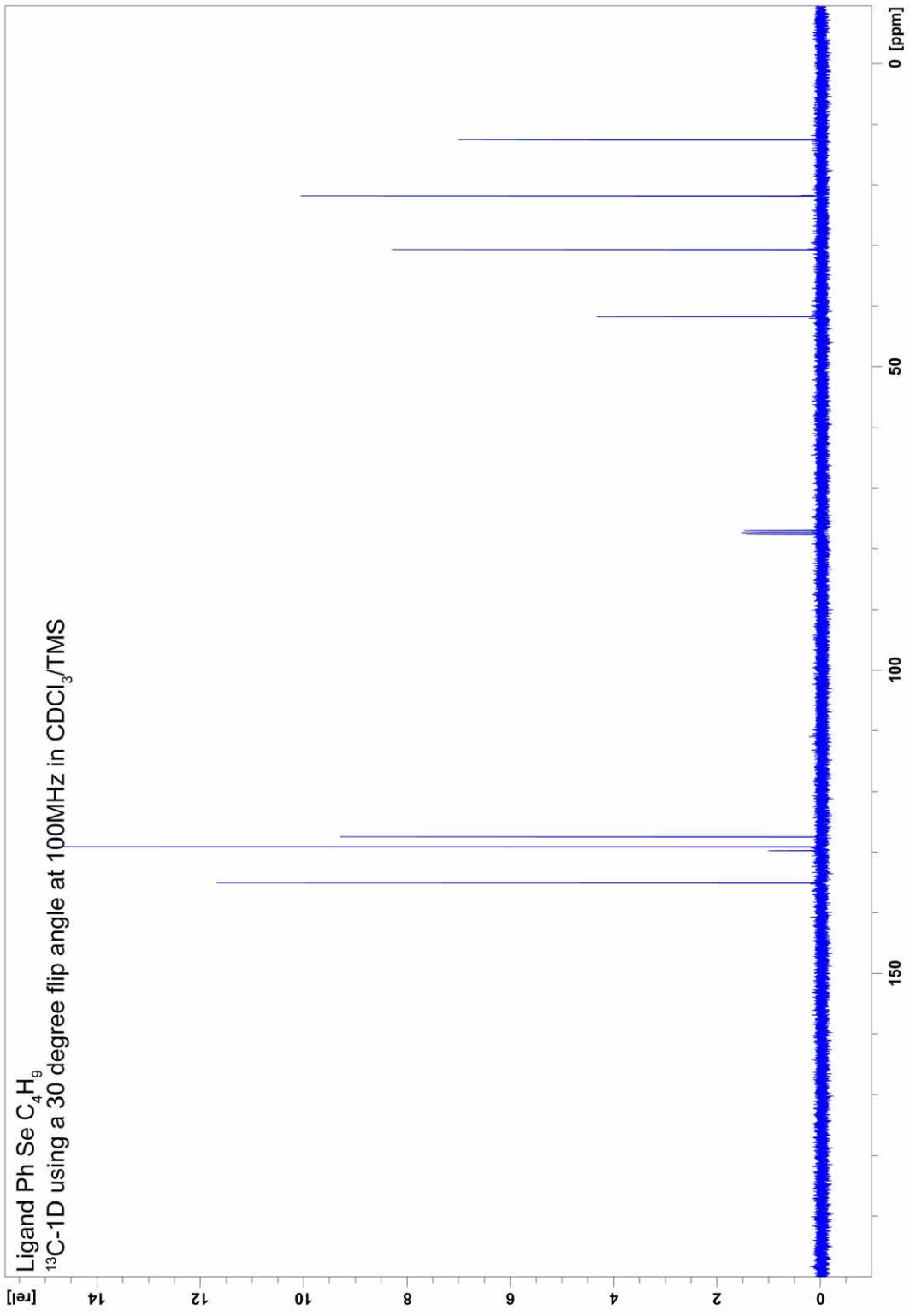
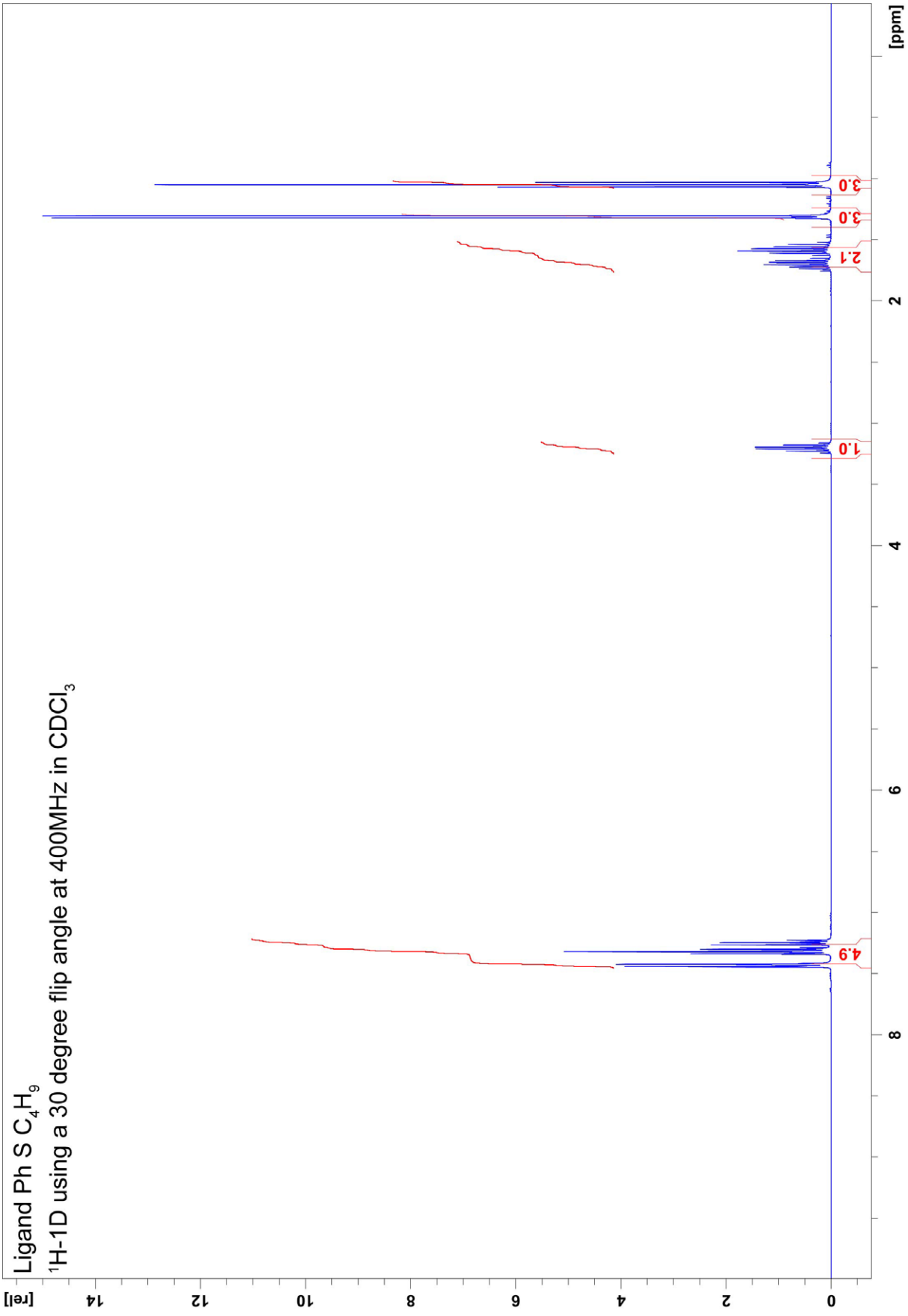
3.0
2.0
1.0
3.0




Ligand Ph S C_4H_9
^{1}H-1D using a 30 degree flip angle at 400MHz in $CDCl_3$
[rel]
[ppm]
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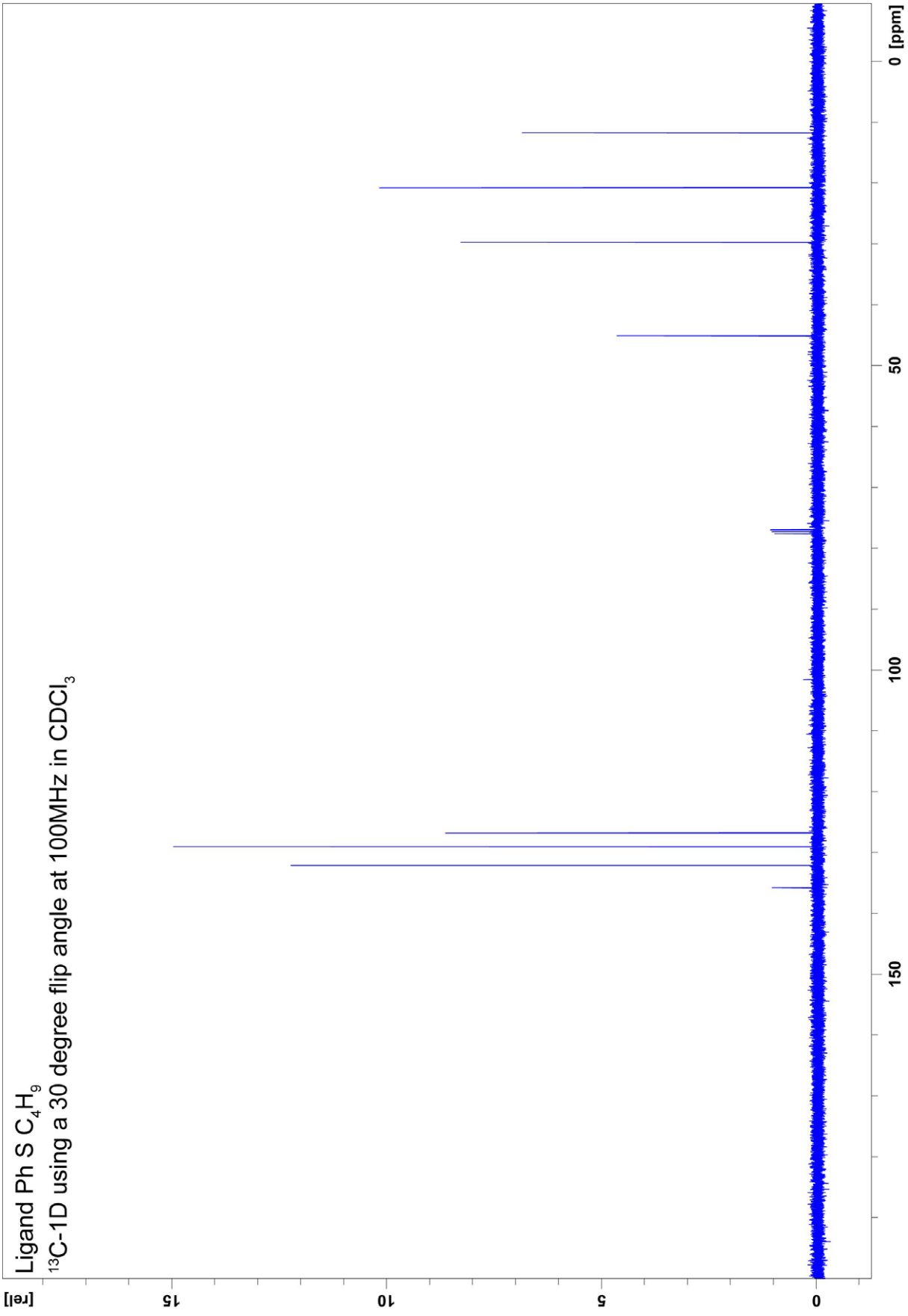
4
6
8
10
12
14
1.0
4.9
2.1
3.0
3.0


Ligand Ph S C_4H_9
^{13}C-1D using a 30 degree flip angle at 100MHz in $CDCl_3$
[rel]
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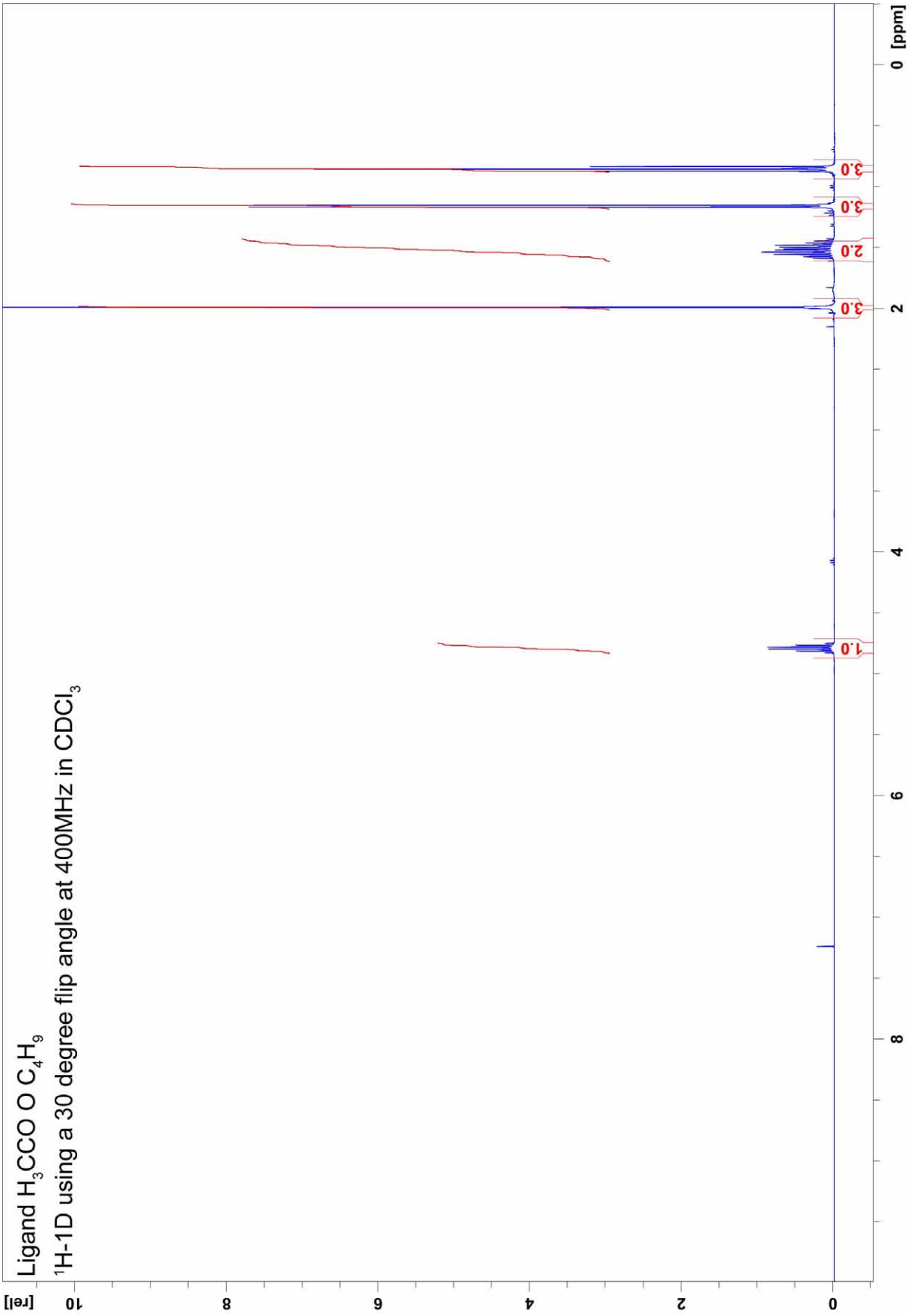
10
5
0
0 [ppm]
50
100
150


Ligand $H_3CCO\ O\ C_4H_9$
^{1}H-1D using a 30 degree flip angle at 400MHz in $CDCl_3$
[rel]
10
8
6
4
2
0
[ppm]
0
2
4
6
8
3.0
3.0
2.0
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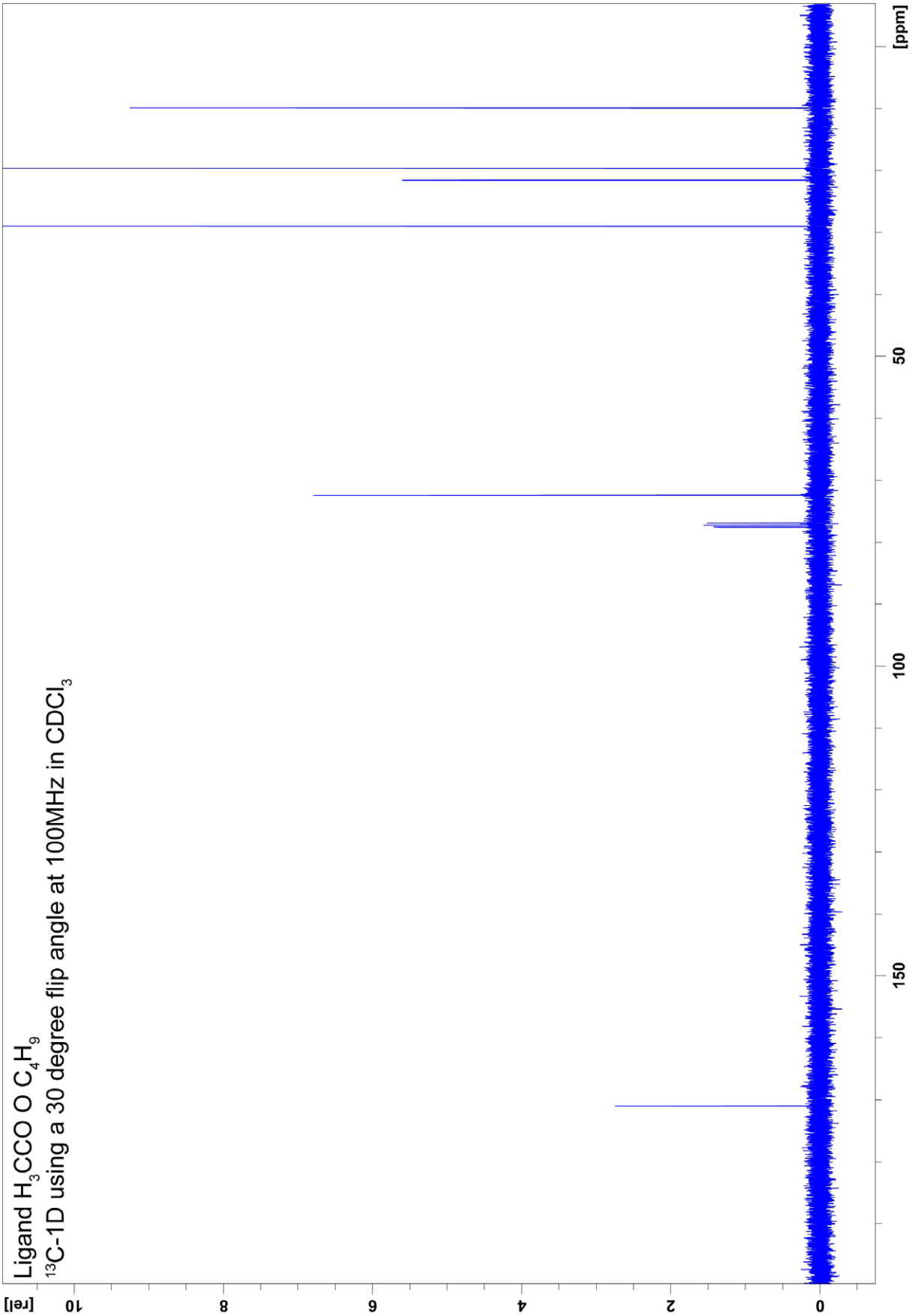
1.0


Ligand $H_3CCO\ O\ C_4H_9$
^{13}C-1D using a 30 degree flip angle at 100MHz in $CDCl_3$
[rel]
10
8
6
4
2
0
[ppm]
50
100
150