Supplementary Information for

Structure and electrochemical properties of (μ-O)$_2$Mn$_2$(III,III) and (μ-O)$_2$Mn$_2$(III,IV) complexes supported by pyridine-, quinoline-, isoquinoline- and quinoxaline-based tetranitrogen ligands

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Table S1. Crystallographic data for **L12**·$HClO_4$ and [Mn(**L4**)$(CH_3CN)_3$]$(ClO_4)_2$

	L12·$HClO_4$	[Mn(**L4**)$(CH_3CN)_3$]-$(ClO_4)_2$
Formula	$C_{28}H_{33}ClN_4O_4$	$C_{36}H_{33}Cl_2MnN_7O_8$
FW	525.05	817.54
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a, Å	9.2827(8)	12.156(5)
b, Å	11.7724(15)	12.543(5)
c, Å	12.7181(13)	14.590(6)
α, deg	107.289(5)	104.912(3)
β, deg	100.460(2)	109.608(4)
γ, deg	93.730(4)	106.407(2)
V, Å^3	1294.5(2)	1851.3(14)
Z	2	2
D_{calc}, g cm^{-3}	1.347	1.466
μ, mm^{-1}	0.1896	0.5622
$2\theta_{max}$, deg	55	55
temp, K	173	153
no. reflns collected	10067	14482
no. reflns used	5627	8079
no. of params	466	490
R_{int}	0.0144	0.0243
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0481	0.0626
*wR*2 (all data)[b]	0.1346	0.1741
GOF	1.040	1.070

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2. Crystallographic data for **4**·3CH_3CN and **5**·2CH_3CN

	4·3CH_3CN	**5**·2CH_3CN
Formula	$C_{66}H_{57}Cl_3Mn_2N_{11}O_{14}$	$C_{52}H_{58}Cl_3Mn_2N_{10}O_{14}$
FW	1444.48	1263.32
Crystal system	monoclinic	monoclinic
Space group	*Cc*	$P2_1/n$
a, Å	23.2584(13)	12.3782(19)
b, Å	20.6984(9)	17.197(3)
c, Å	13.4561(9)	25.590(4)
β, deg	98.163(3)	93.913(3)
V, Å^3	6412.3(6)	5434.8(14)
Z	4	4
D_{calc}, g cm^{-3}	1.496	1.544
μ, mm^{-1}	0.5947	0.6884
$2\theta_{max}$, deg	55	55
temp, K	153	123
no. reflns collected	24976	42026
no. reflns used	10690	12400
no. of params	868	736
R_{int}	0.0328	0.0436
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0471	0.0485
*wR*2 (all data)[b]	0.1180	0.1243
GOF	1.081	1.092

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S3. Crystallographic data for **6**·4CH_3CN·H_2O and **7**·4CH_3CN·H_2O

	6·4CH_3CN·H_2O	**7**·4CH_3CN·H_2O
Formula	$C_{64}H_{78}Cl_3Mn_2N_{12}O_{15}$	$C_{68}H_{62}Cl_3Mn_2N_{12}O_{15}$
FW	1471.63	1503.54
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*Cc*
a, Å	25.494(2)	14.7283(10)
b, Å	19.1689(11)	22.1188(14)
c, Å	19.1973(17)	21.6214(14)
β, deg	132.362(2)	101.584(3)
V, Å^3	6932.1(10)	6900.2(8)
Z	4	4
D_{calc}, g cm^{-3}	1.410	1.447
μ, mm^{-1}	0.5525	0.5572
$2\theta_{max}$, deg	55	55
temp, K	153	153
no. reflns collected	33734	33906
no. reflns used	7928	14719
no. of params	471	932
R_{int}	0.0418	0.0286
Final *R*1 ($I > 2\sigma(I)$)[a]	0.0789	0.0741
*wR*2 (all data)[b]	0.2376	0.2129
GOF	1.085	1.096

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S4. Crystallographic data for **8**·4CH_3CN and **9**·3CH_3CN·2.5H_2O

	8·4CH_3CN	**9**·3CH_3CN·2.5H_2O
Formula	$C_{56}H_{64}Cl_3Mn_2N_{12}O_{14}$	$C_{62}H_{78}Cl_3Mn_2N_{11}O_{16.5}$
FW	1345.43	1457.6
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a, Å	18.4506(18)	11.2594(3)
b, Å	13.8386(12)	14.51210(10)
c, Å	24.104(3)	22.1759(5)
α, deg	90	75.873(7)
β, deg	99.862(4)	84.419(7)
γ, deg	90	74.520(5)
V, Å^3	6932.1(10)	3384.43(17)
Z	4	2
D_{calc}, g cm^{-3}	1.474	1.430
μ, mm^{-1}	0.6229	0.5662
$2\theta_{max}$, deg	55	55
temp, K	153	153
no. reflns collected	58369	33529
no. reflns used	13847	15261
no. of params	818	916
R_{int}	0.0479	0.0266
Final $R1$ ($I > 2\sigma(I)$)[a]	0.0809	0.0655
$wR2$ (all data)[b]	0.2149	0.1973
GOF	1.144	1.053

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S5. Crystallographic data for **12**·CH_3OH and [Mn(**L15**)$(CH_3O)_2$]ClO_4·CH_3CN

	12·CH_3OH	[Mn(**L15**)$(OCH_3)_2$]-ClO_4·CH_3CN
Formula	$C_{57}H_{68}Cl_2Mn_2N_8O_{11}$	$C_{30}H_{39}ClMnN_7O_6$
FW	1221.99	684.07
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/c$
a, Å	9.302(3)	8.601(4)
b, Å	12.216(3)	35.692(18)
c, Å	24.174(7)	10.382(5)
β, deg	99.794(3)	96.789(4)
V, Å^3	2706.8(13)	3165(3)
Z	2	4
D_{calc}, g cm^{-3}	1.499	1.436
μ, mm^{-1}	0.6357	0.5558
$2\theta_{max}$, deg	55	55
temp, K	173	153
no. reflns collected	27040	30798
no. reflns used	1184	7244
no. of params	735	420
R_{int}	0.0263	0.0350
Final $R1$ ($I > 2\sigma(I)$)[a]	0.0423	0.0511
$wR2$ (all data)[b]	0.1103	0.1321
GOF	1.077	1.077

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

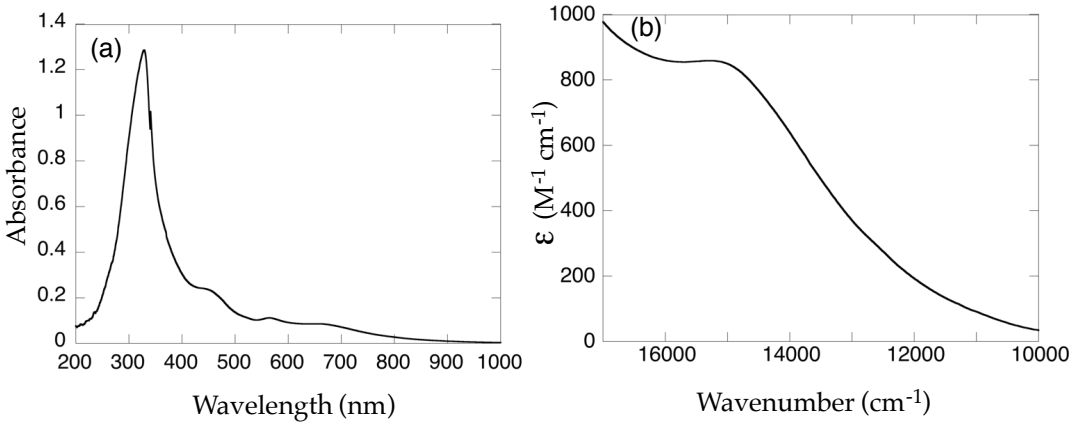

Fig. S1. UV-vis spectrum of **4** in acetonitrile in 1.0 x 10^{-5} M concentration. (a) Whole spectrum. (b) Expansion of 10000-17000 cm^{-1} region.

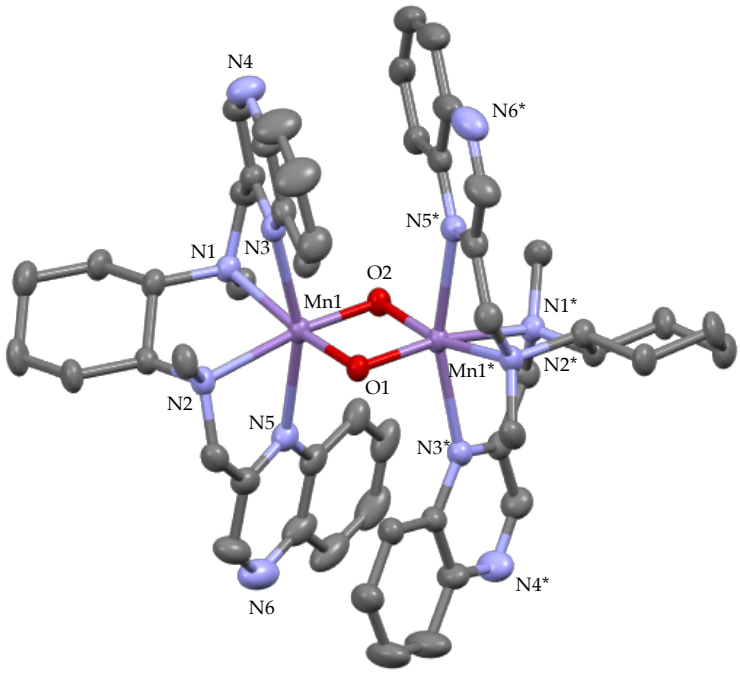

Fig. S2. Perspective view of cationic portion of **15** from preliminary X-ray crystallography.

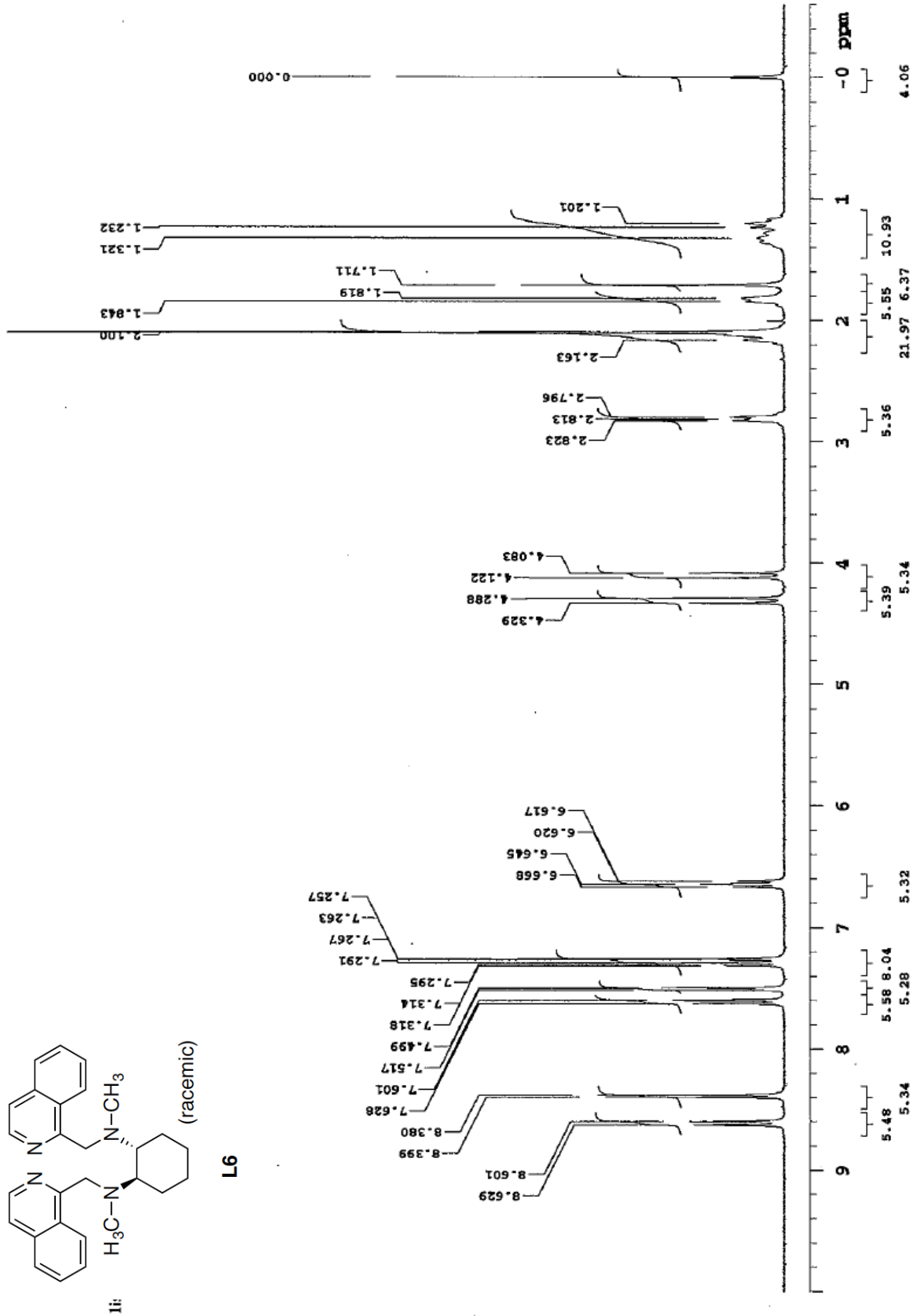

Figure S3. ^{1}H NMR spectrum of **L6** in $CDCl_3$.

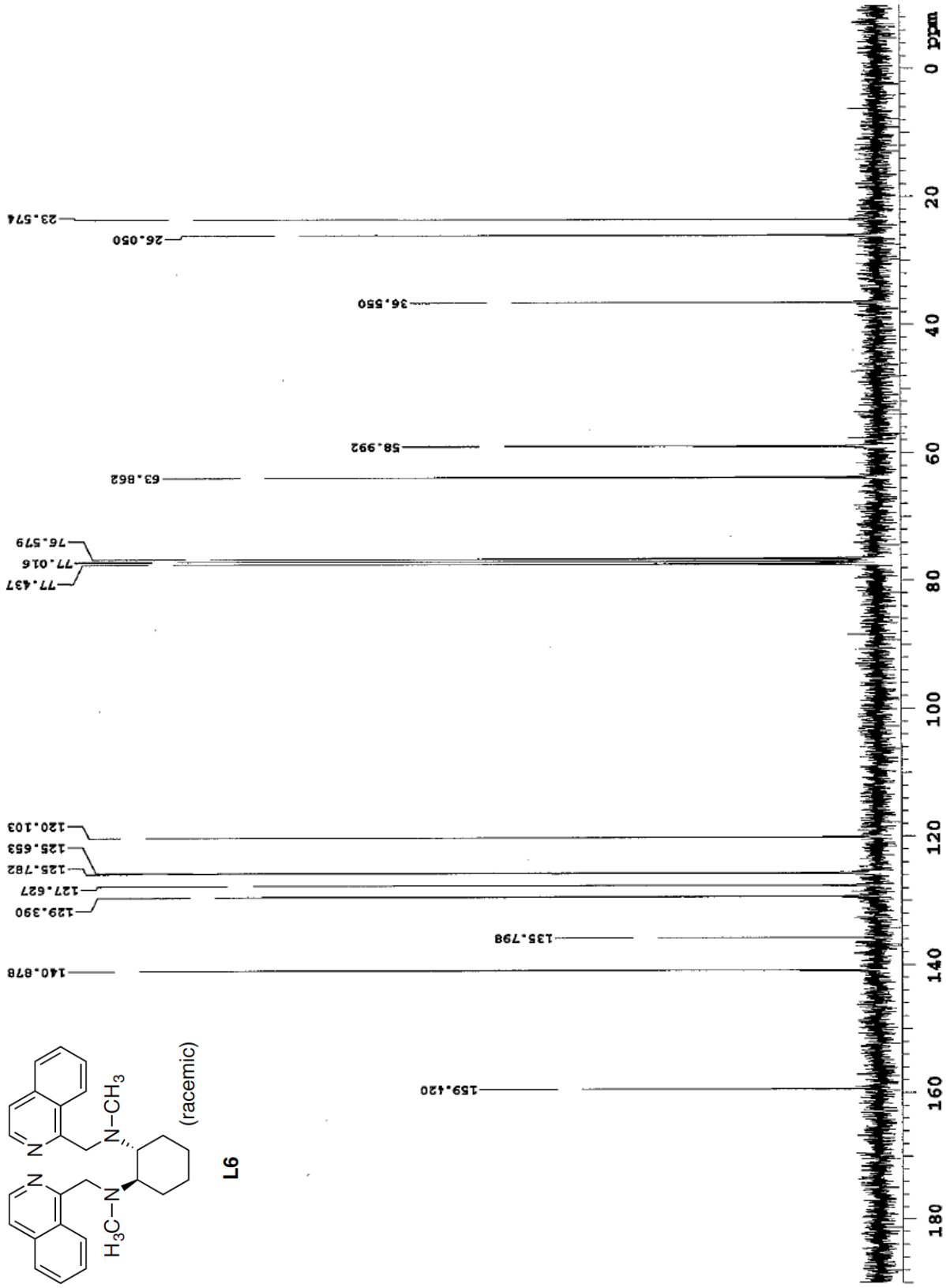

Figure S4. ^{13}C NMR spectrum of **L6** in $CDCl_3$.

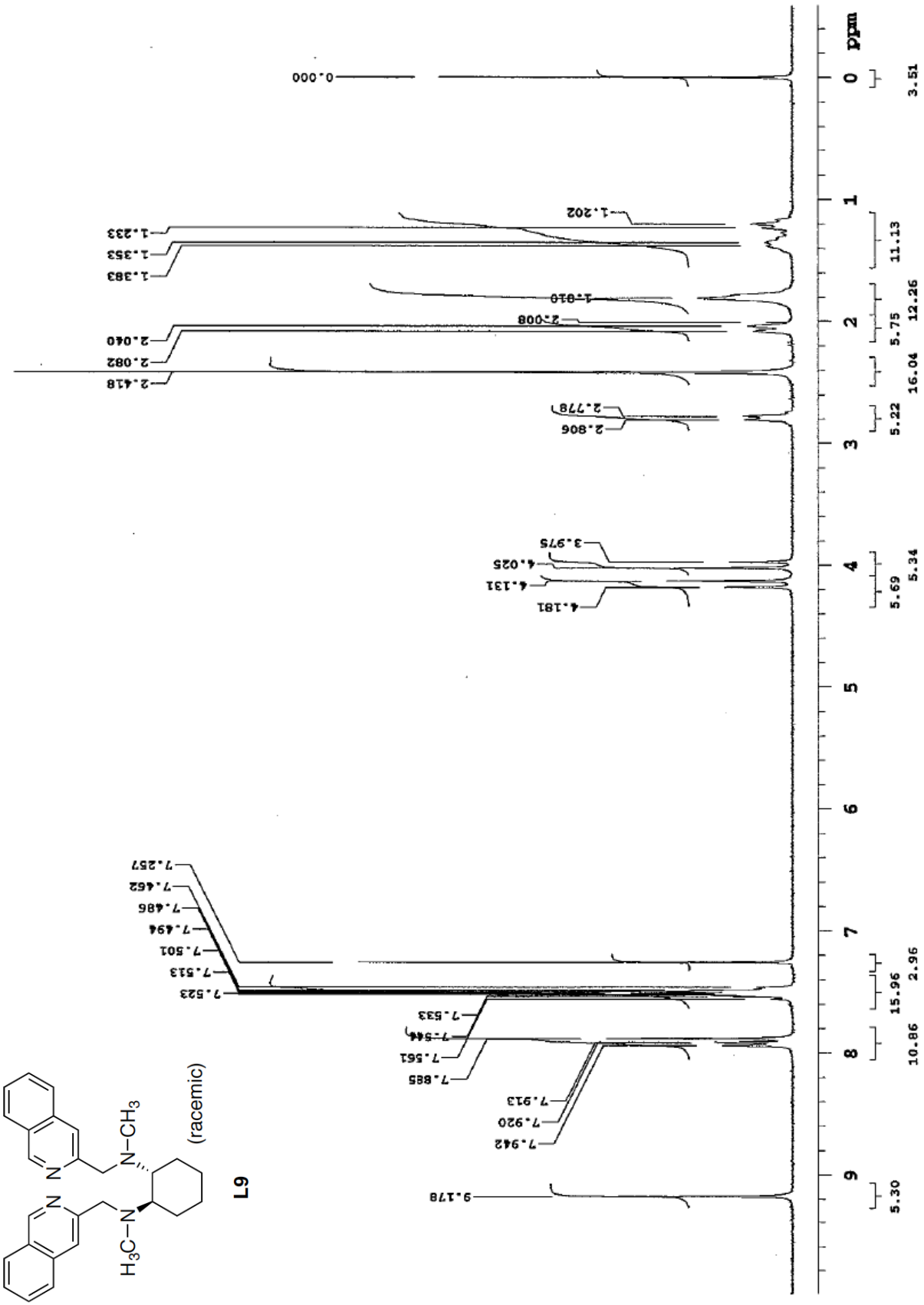

Figure S5. ^{1}H NMR spectrum of **L9** in $CDCl_3$.

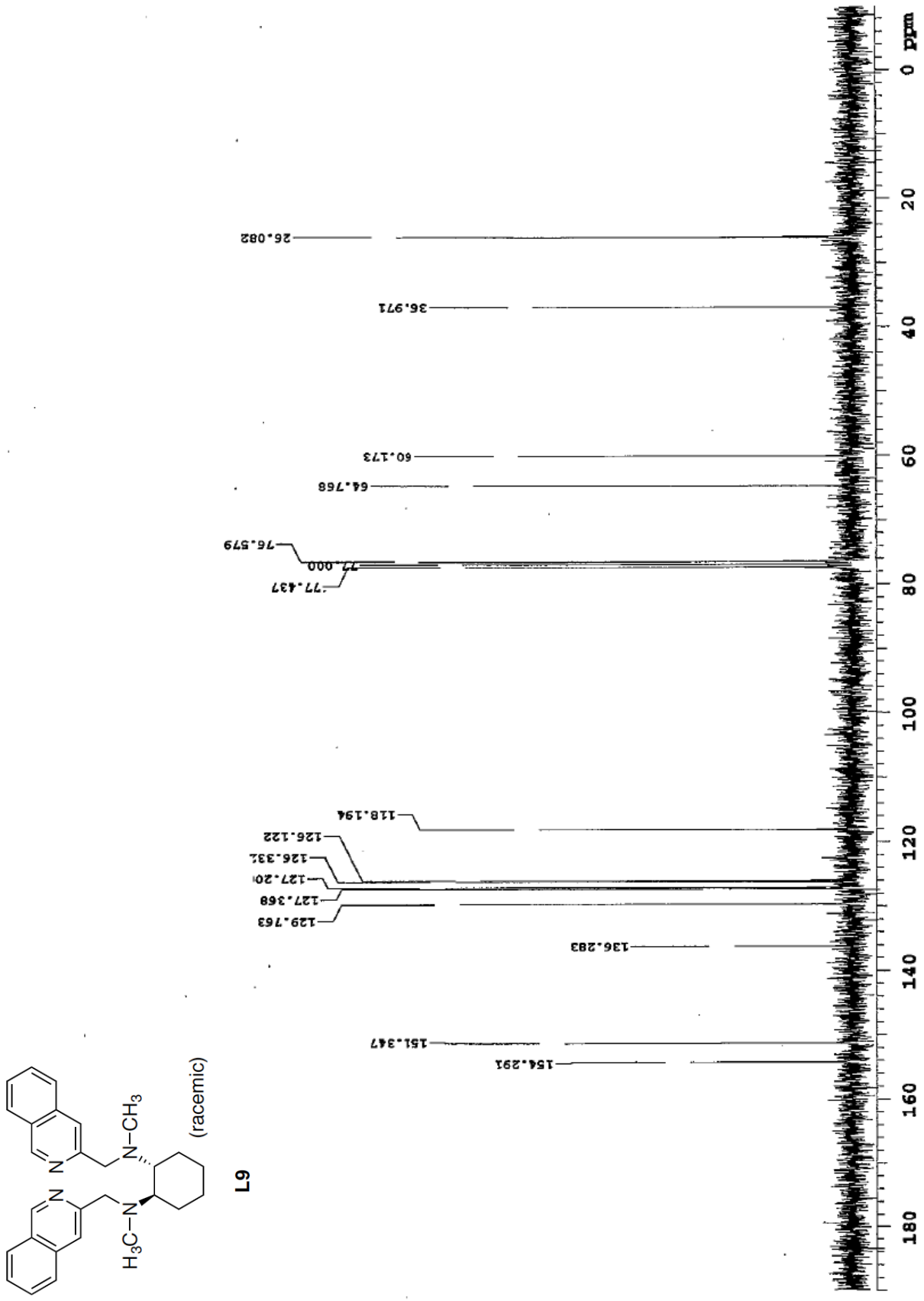

Figure S6. ^{13}C NMR spectrum of **L9** in $CDCl_3$.

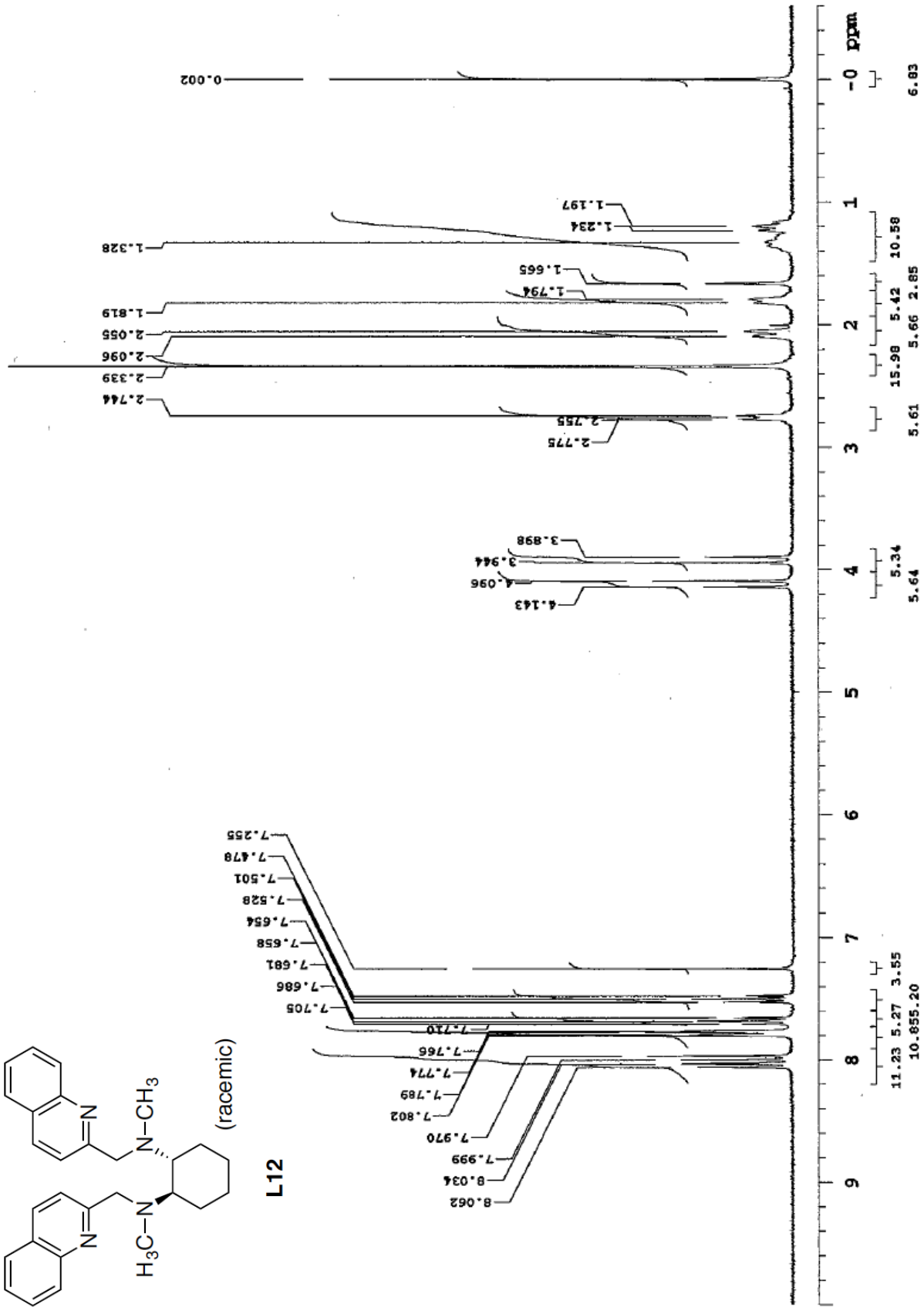

Figure S7. ^{1}H NMR spectrum of **L12** in $CDCl_3$.

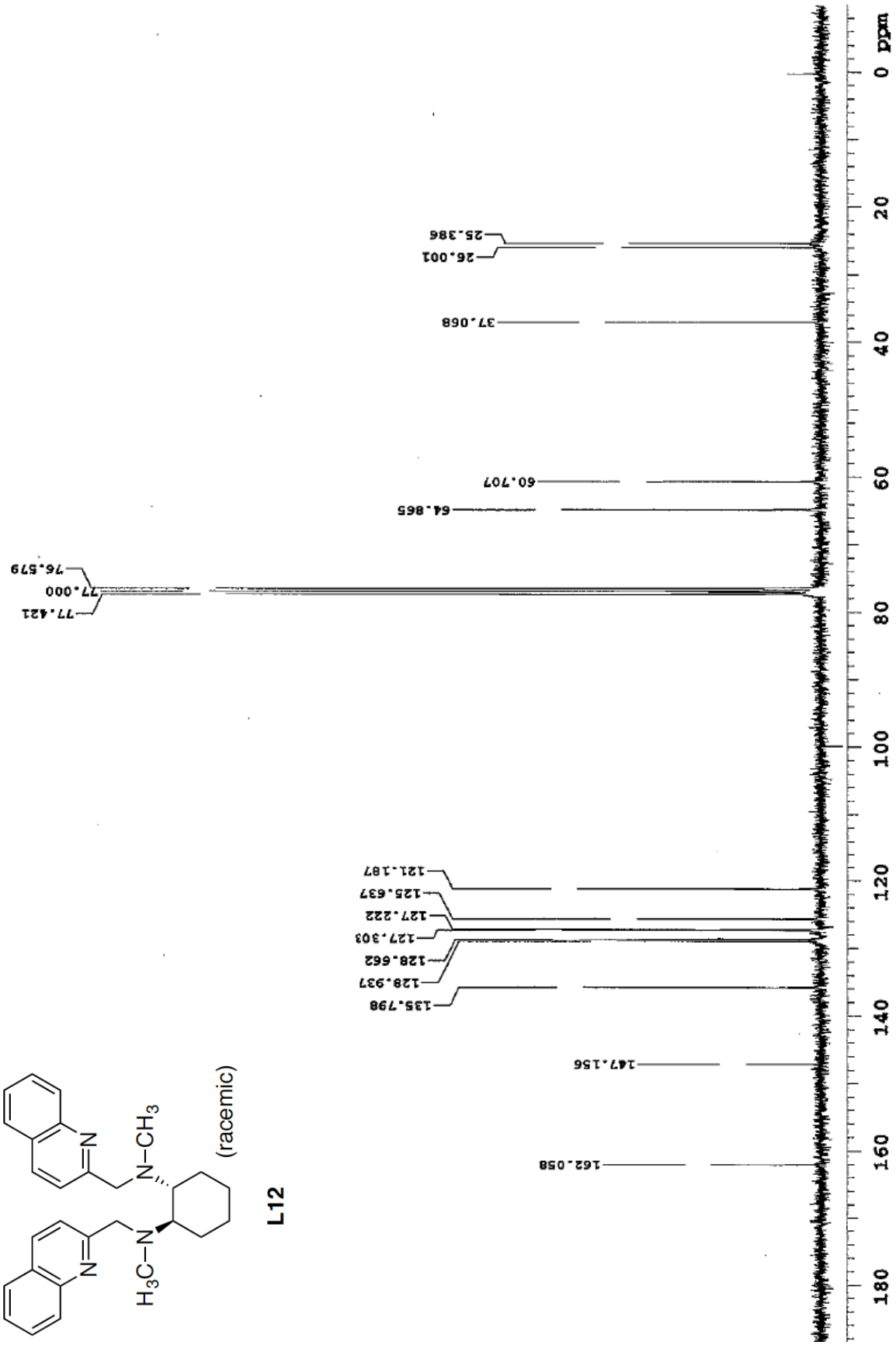

Figure S8. ^{13}C NMR spectrum of **L12** in $CDCl_3$

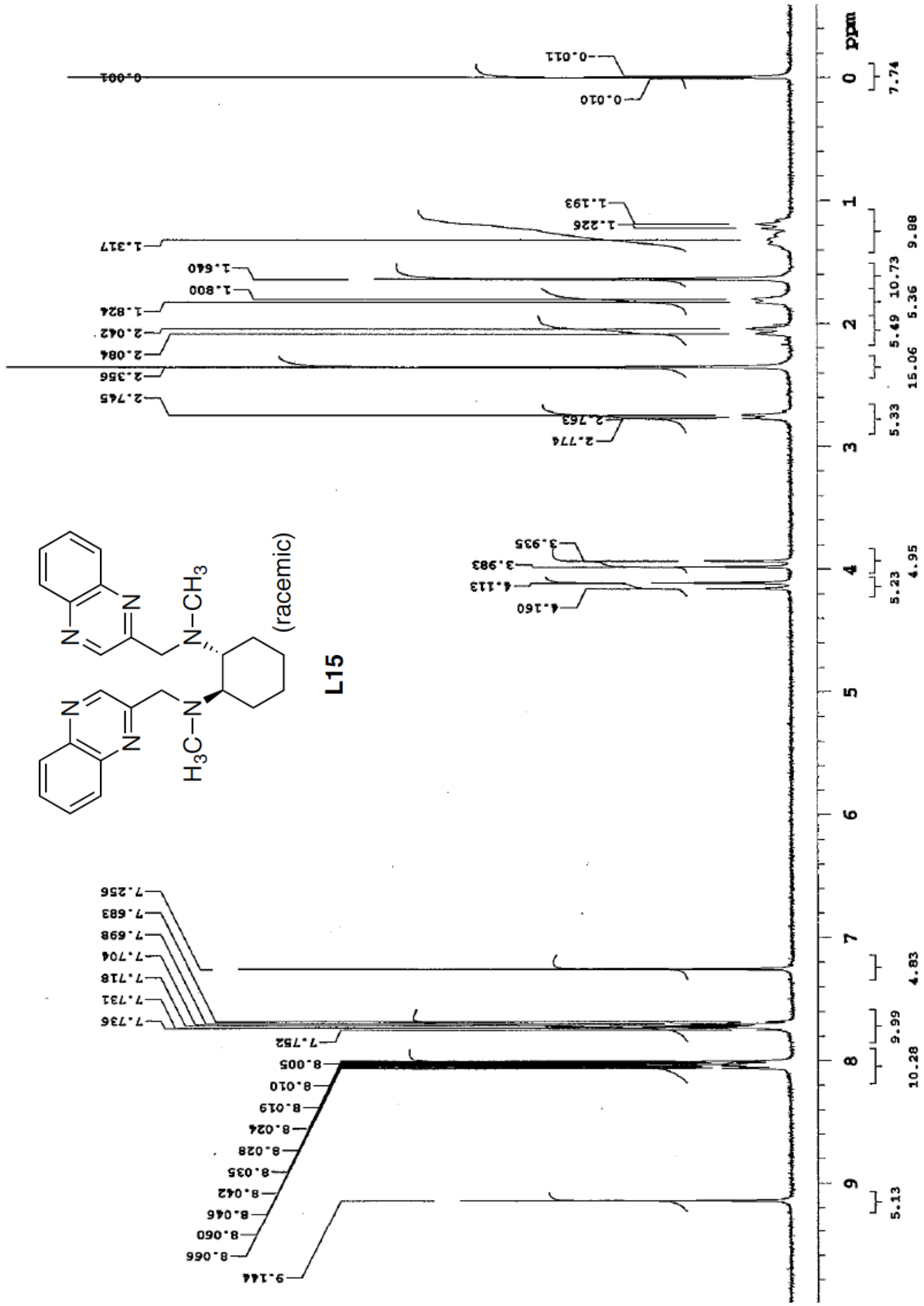

Figure S9. ^{1}H NMR spectrum of **L15** in $CDCl_3$.

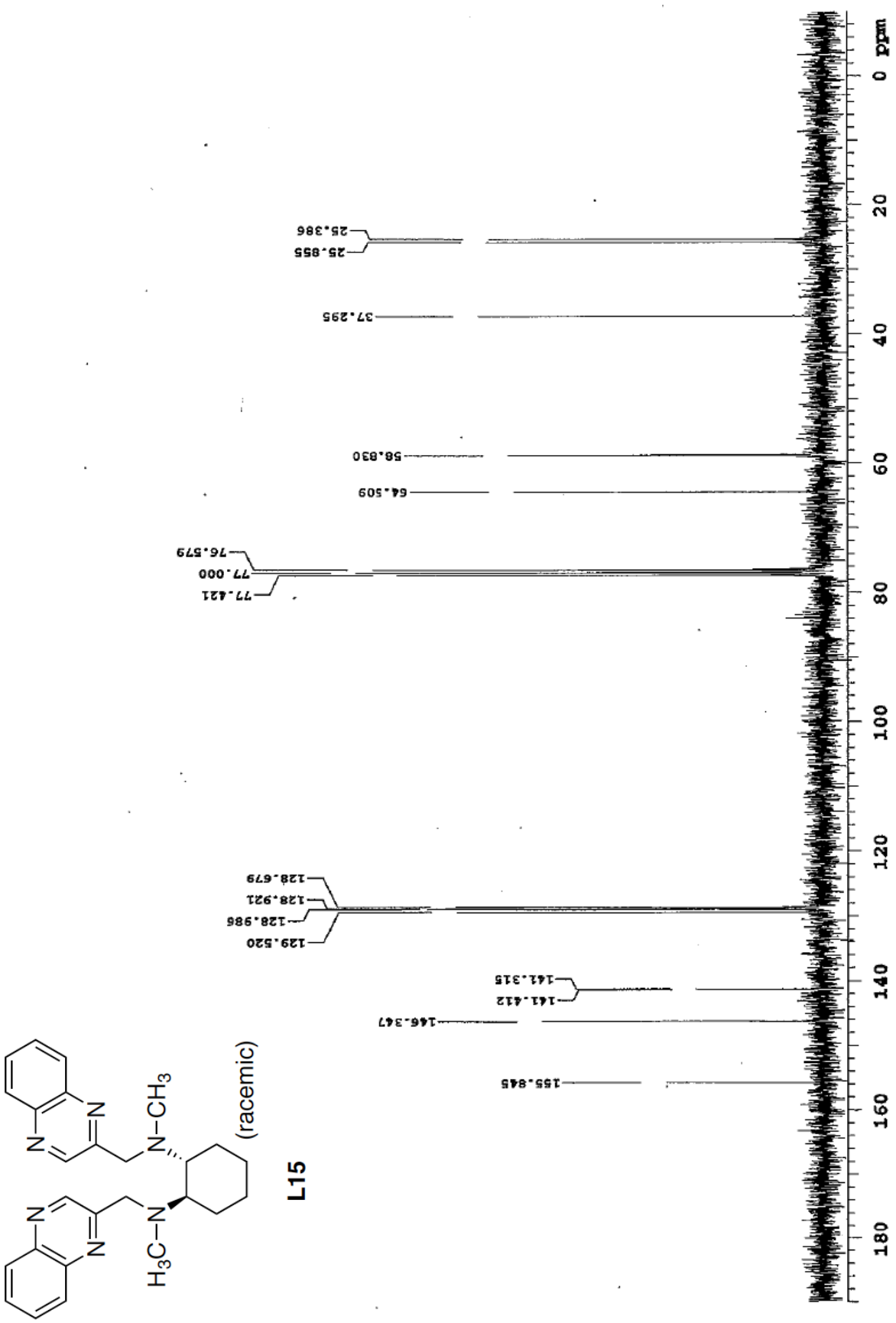

Figure S10. ^{13}C NMR spectrum of **L15** in $CDCl_3$.