Effective Donor Abilities of E-*t*-Bu and EPh (E = O, S, Se, Te) to a High Valent Transition Metal

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Example Files for NBO Overlap Calculations

Input File for NCr(NPr$^i{}_2$)$_2$OMe for G03

```
%chk=NCrOMeNBO.chk
%mem=3900MB
%nproc=4
# opt rb3pw91/lanl2dz pop=nboread geom=connectivity

Title Card Required

0 1
 Cr     -0.38478500   0.00008400   0.11229800
 N      -0.81275000  -1.50298200  -0.77547700
 H      -1.49423700  -2.18455900  -0.45678600
 H      -0.41713400  -1.72890600  -1.68723000
 N      -0.80539900   1.50562000  -0.77477500
 H      -0.41134100   1.72769500  -1.68815300
 H      -1.48145400   2.19196600  -0.45478000
 N      -1.26936500   0.00203400   1.34745900
 C       2.44102400  -0.00163300  -0.19719800
 H       3.33874900  -0.01110000   0.43084800
 H       2.45473800  -0.89368400  -0.84222700
 H       2.46238400   0.90135200  -0.82651700
 O       1.29369700  -0.00346100   0.67905400

 1 2 1.0 5 1.0 8 1.0 13 1.0
 2 3 1.0 4 1.0
 3
 4
 5 6 1.0 7 1.0
 6
 7
 8
 9 10 1.0 11 1.0 12 1.0 13 1.0
 10
 11
 12
 13

$NBO
$END
$CHOOSE
alpha
 lone 8 1 13 3 end
 bond d 1 2 d 1 5 t 1 8 s 2 3 s 2 4 s 5 6 s 5 7
      s 9 13 s 9 10 s 9 11 s 9 12 end
$END
```

Output file

Listed below are the interactions from the lone pairs on the ligand under investigation and Cr-based orbitals calculated in the second order perturbation theory analysis section. These were generated from NBO3 as implemented in G03 from the input file above.

```
Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis

    Threshold for printing:   0.50 kcal/mol
   (Intermolecular threshold: 0.05 kcal/mol)
                                                         E(2)  E(j)-E(i) F(i,j)
     Donor NBO (i)               Acceptor NBO (j)       kcal/mol   a.u.    a.u.
===============================================================================================

from unit  2 to unit  1
 26. LP (   1) O  13          / 67. BD*(   1)Cr   1 - N   2        7.17    1.06    0.082
 26. LP (   1) O  13          / 68. BD*(   2)Cr   1 - N   2       13.31    0.55    0.083
 26. LP (   1) O  13          / 69. BD*(   1)Cr   1 - N   5        7.21    1.06    0.082
 26. LP (   1) O  13          / 70. BD*(   2)Cr   1 - N   5       13.23    0.54    0.083
 26. LP (   1) O  13          / 71. BD*(   1)Cr   1 - N   8        0.24    0.86    0.013
 26. LP (   1) O  13          / 72. BD*(   2)Cr   1 - N   8        6.29    0.57    0.056
 26. LP (   1) O  13          / 73. BD*(   3)Cr   1 - N   8        0.11    0.57    0.007
 27. LP (   2) O  13          / 67. BD*(   1)Cr   1 - N   2        2.91    0.75    0.042
 27. LP (   2) O  13          / 68. BD*(   2)Cr   1 - N   2        6.97    0.24    0.037
 27. LP (   2) O  13          / 69. BD*(   1)Cr   1 - N   5        3.01    0.75    0.043
 27. LP (   2) O  13          / 70. BD*(   2)Cr   1 - N   5        7.22    0.24    0.038
 27. LP (   2) O  13          / 72. BD*(   2)Cr   1 - N   8        0.07    0.27    0.004
 27. LP (   2) O  13          / 73. BD*(   3)Cr   1 - N   8        3.27    0.26    0.027
 28. LP (   3) O  13          / 67. BD*(   1)Cr   1 - N   2       22.47    0.93    0.134
 28. LP (   3) O  13          / 68. BD*(   2)Cr   1 - N   2       57.36    0.42    0.138
 28. LP (   3) O  13          / 69. BD*(   1)Cr   1 - N   5       22.54    0.93    0.134
 28. LP (   3) O  13          / 70. BD*(   2)Cr   1 - N   5       56.67    0.42    0.137
 28. LP (   3) O  13          / 71. BD*(   1)Cr   1 - N   8        1.39    0.73    0.031
 28. LP (   3) O  13          / 72. BD*(   2)Cr   1 - N   8       74.18    0.45    0.171
 28. LP (   3) O  13          / 73. BD*(   3)Cr   1 - N   8        1.20    0.44    0.022
```

Table of LDP, Cr-E-C angle, BDE, and orbital overlap.

X =	**LDP (kcal/mol)**[a]	**Cr–E–C angle (°)**[b]	**BDE (kcal/mol)**	**Orbital overlap (A.U.)**
F	13.39 ± 0.27		93.7	1.608
Cl	15.05 ± 0.29		65.6	1.198
Br	15.45 ± 0.30		54.7	1.117
I	15.80 ± 0.30		44.8	1.027
OAd (**2b**) (OBu^t) (**2a**)	10.68 ± 0.24 (10.59)	137.1(7)[d]	59.3	 1.364
SBu^t (**3**)	12.81 ± 0.28	114.1(2)	41.2	1.125
SeBu^t (**4**)	13.13 ± 0.28	108.9(1)	38.4	1.088
TeBu^t (**5**)	13.76 ± 0.28	106.0(1)	32.0	1.002
OPh (**6**)	11.98 ± 0.26	135.0(2)[d]	53.5	1.463
SPh (**7**)	13.99 ± 0.27	108.4(1)[d]	35.9	1.199
SePh (**8**)	14.16 ± 0.27	106.8(1)	33.4	1.121
TePh (**9**)	14.20 ± 0.27	103.7(1)	28.1	1.041

Table of SST Measurement Temperature, Rate Constant, and ***ΔG‡****.*

X=	**SST Measurement Temperature (°C)**	**Rate Constant (s^{-1})**	**ΔG‡ (kcal/mol)**
F	1.8	1.424	15.86
Cl	28.1	0.489	17.68
Br	28.5	0.429	18.16
I	28.6	0.231	18.51
OBu^t (**2a**)	-39.0	6.870	12.70
OAd (**2b**)	-39.3	6.701	12.72
SBu^t (**3**)	2.1	4.160	15.30
SeBu^t (**4**)	2.0	2.282	15.62
TeBu^t (**5**)	2.1	0.729	16.24
OPh (**6**)	-18.5	3.028	14.27
SPh (**7**)	-4.0	0.265	16.41
SePh (**8**)	-3.0	0.360	16.56
TePh (**9**)	2.0	0.324	16.63

Crystallographic Data with Selected Bond Distances and Angles for New NCr(NPr$^i_2$)$_2$X Complexes

X =	SBu^t (**3**)	SeBu^t (**4**)	TeBu^t (**5**)	SePh (**8**)	TePh (**9**)
Molecular Formula	$C_{16}H_{37}CrN_3S$	$C_{16}H_{37}CrN_3Se$	$C_{16}H_{37}CrN_3Te$	$C_{18}H_{33}CrN_3Se$	$C_{18}H_{33}CrN_3Te$
Molecular Weight (g/mol)	355.21	403.15	453.15	423.12	473.12
a (Å)	9.9625(8)	13.0772(9)	13.1606(12)	7.6213(6)	8.3363(10)
b (Å)	10.7349(9)	9.4776(7)	9.5014(8)	14.7207(11)	12.2722(15)
c (Å)	19.7412(16)	17.8289(13)	18.0100(16)	18.6479(14)	21.057(3)
α	90	90	90	90	90
β	90	105.233(1)	103.494(1)	90.9310(10)	96.7990(10)
γ	90	90	90	90	90
Volume (Å^3)	2111.25	2132.08	2189.88	2091.85	2139.1
Z	4	4	4	4	4
Space Group	P 2_1 2_1 2_1	P 2_1/n	P 2_1/n	P 2_1/c	P 2_1/c
Temperature (K)	173	173	173	173	173
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calcd}	1.1185	1.2537	1.3681	1.2537	1.463
R	0.0334	0.0342	0.0342	0.0354	0.0242
R_w	0.0858	0.0763	0.0719	0.0797	0.0603
Cr-E (Å)	2.444(2)	2.3814(1)	2.584(1)	2.395(1)	2.614(1)
Cr-E-C (°)	114.1(2)	108.9(1)	106.0(1)	106.8(1)	103.7(1)
Cr-N(nitrido) (Å)	1.547(1)	1.537(1)	1.540(1)	1.539(3)	1.542(2)
Avg. Cr-N(amido) (Å)	1.816(1)	1.815(1)	1.817(1)	1.812(1)	1.817(2)

Linear and 2nd order polynomial fits for Overlap and BDE vs LDP

Figure 4: Linear and 2nd order polynomial ($y = M0 + M1 \bullet x + M2 \bullet x^2$) fits for Calc. Overlap

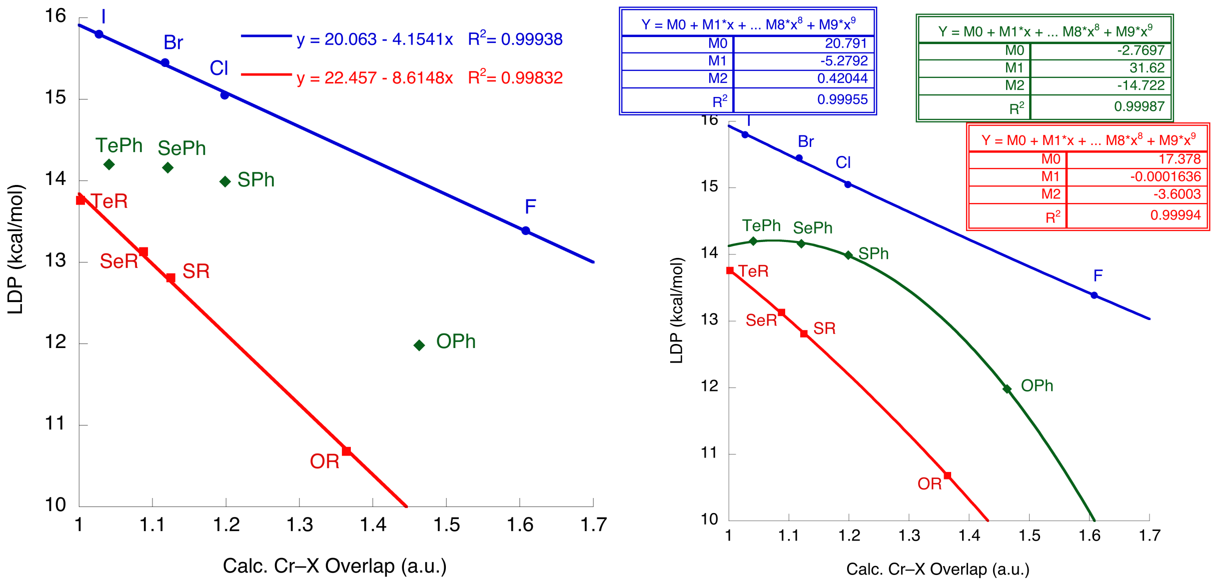
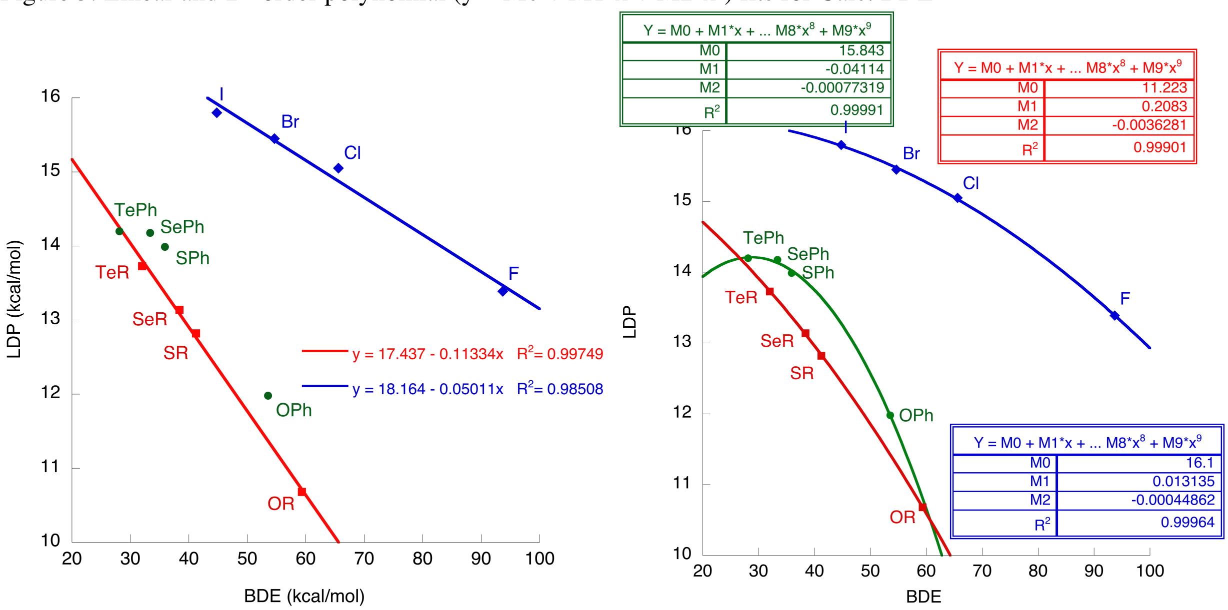
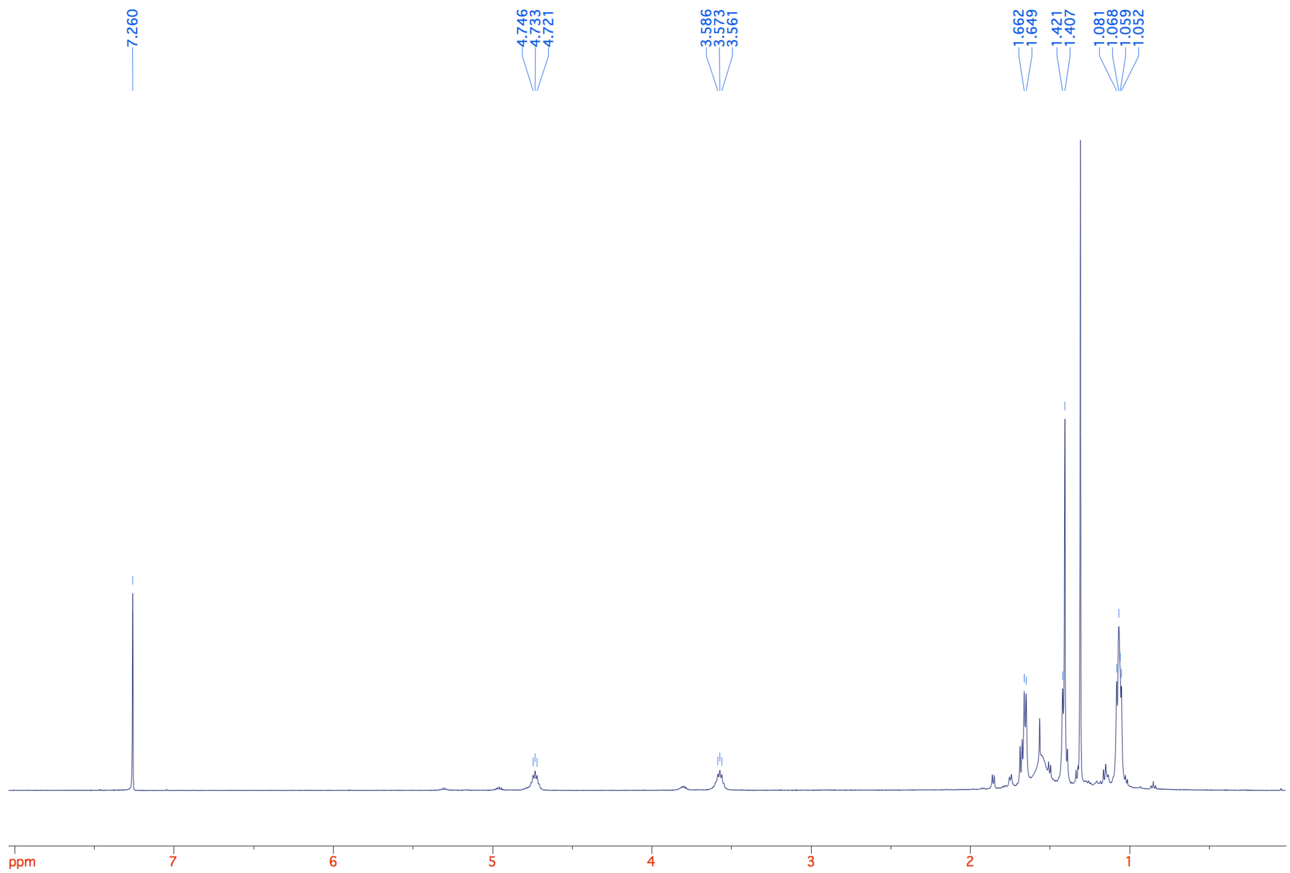


Figure 5: Linear and 2nd order polynomial ($y = M0 + M1 \bullet x + M2 \bullet x^2$) fits for Calc. BDE

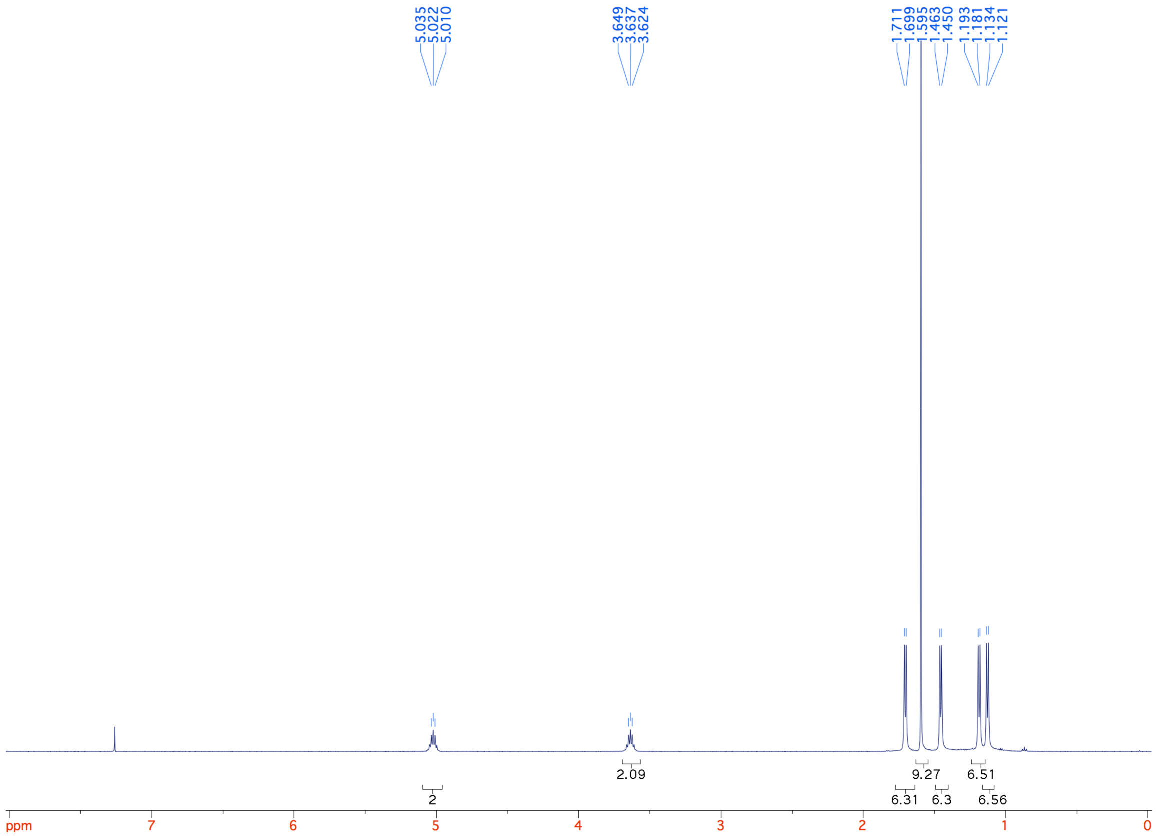


NMR spectra

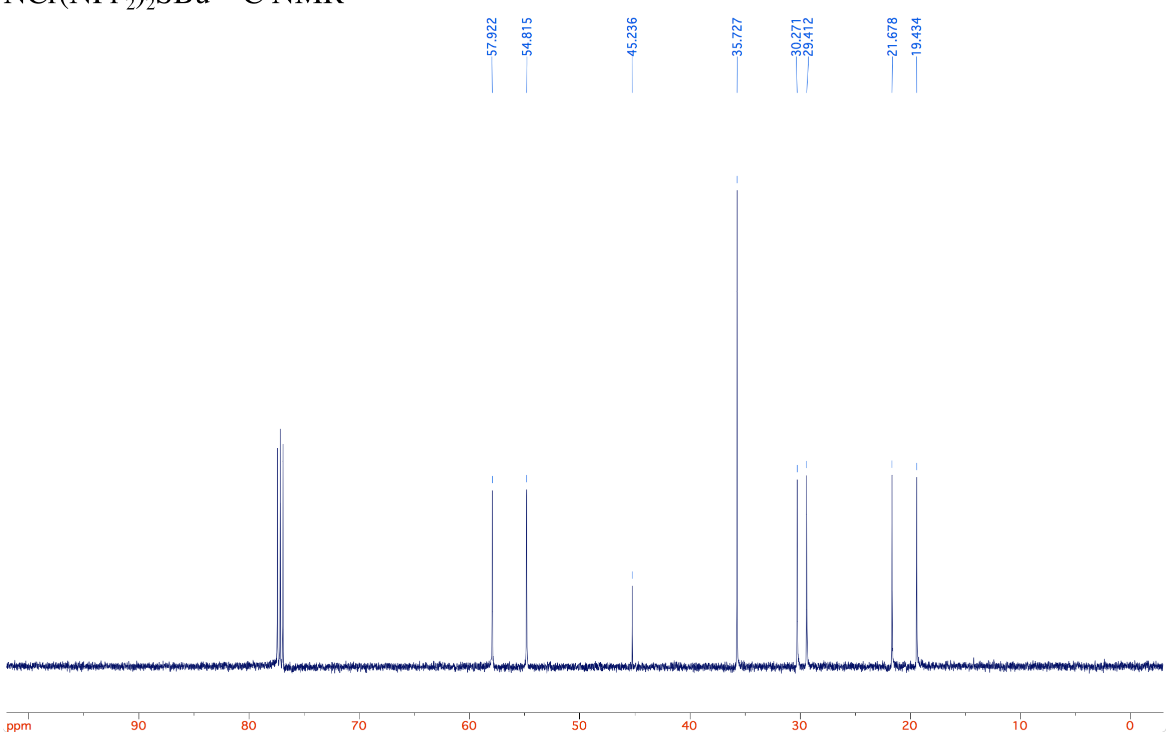
NCr(NPr$^{i}{}_2$)$_2$OBu^t (**2a**) ^{1}H NMR



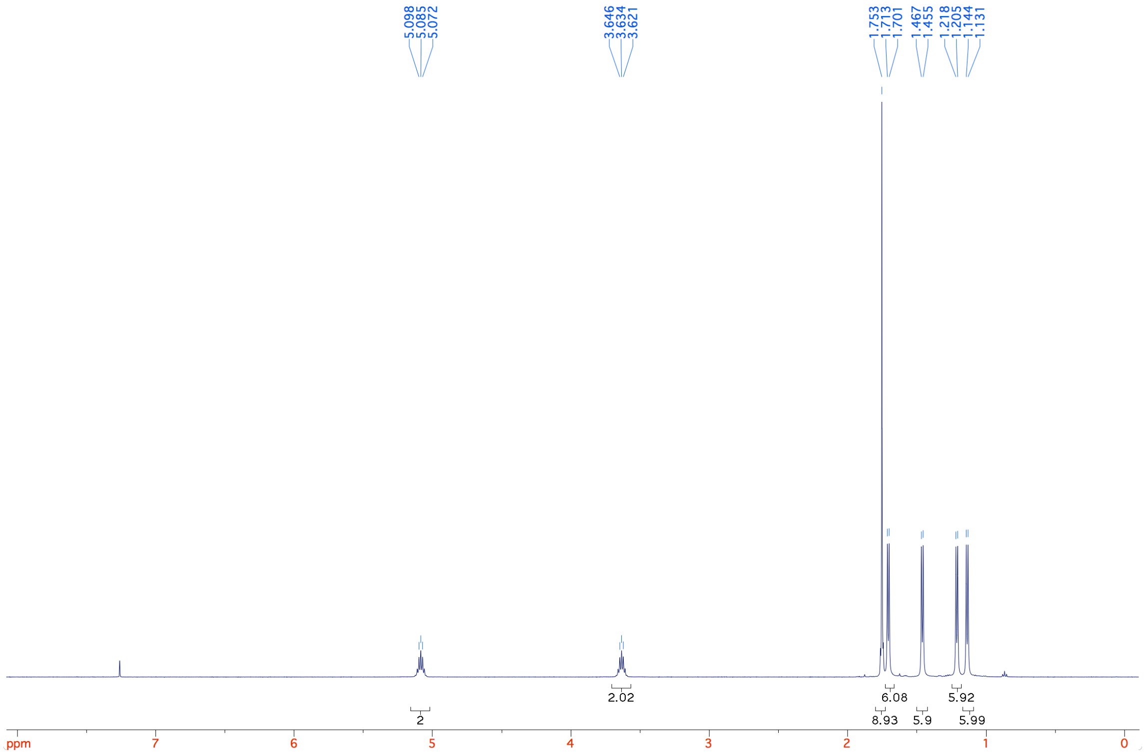
NCr(NPr$^{i}{}_{2}$)$_2$SBu^t (**3**) ^{1}H NMR



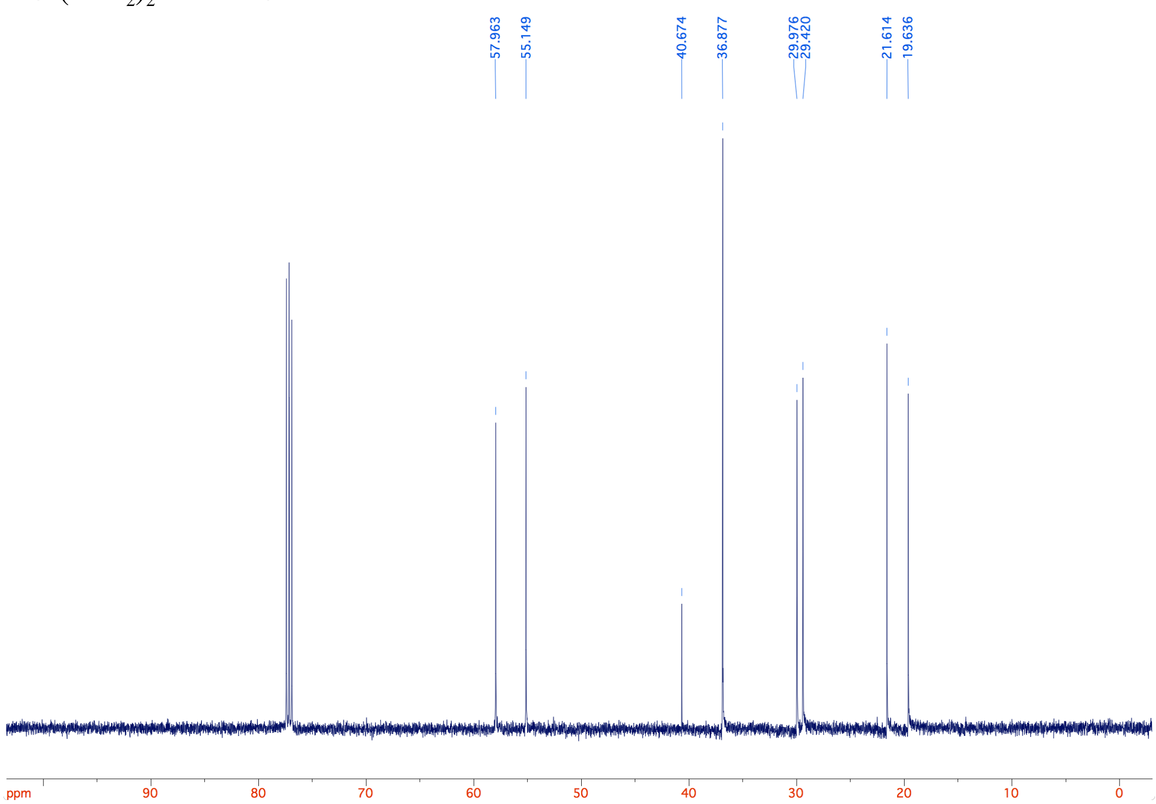
NCr(NPr$^{i}{}_{2}$)$_2$SBu^t ^{13}C NMR



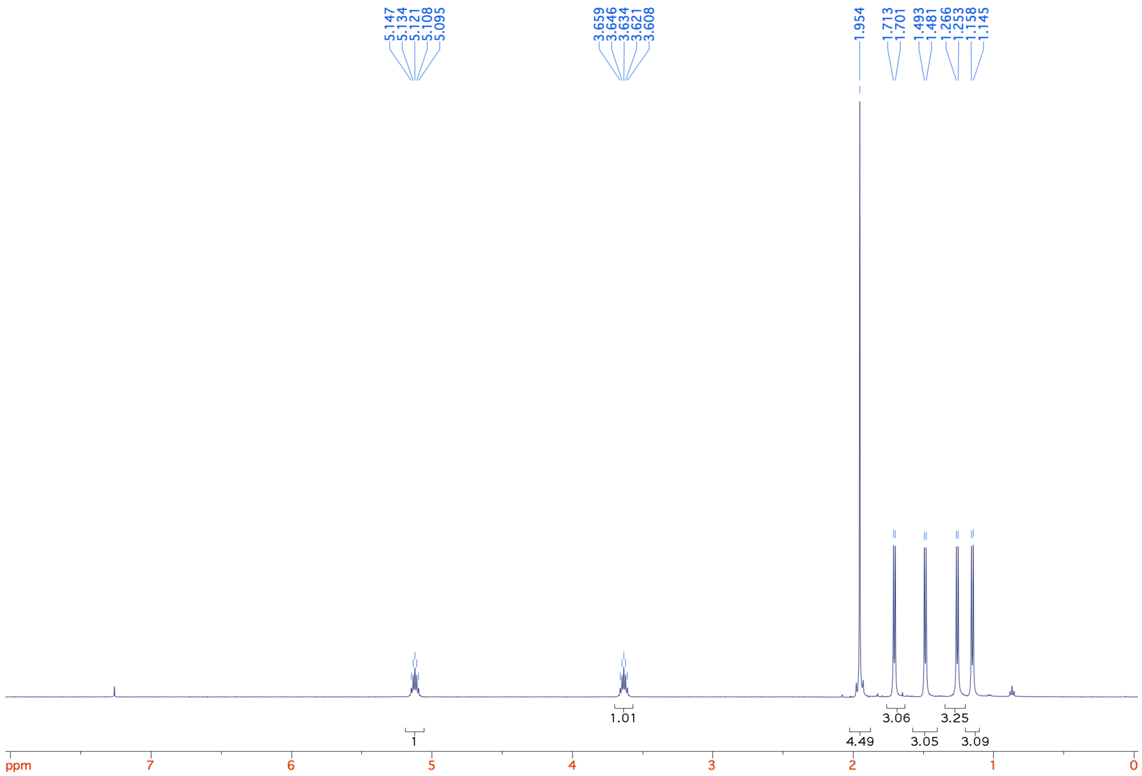
NCr(NPr$^i_2$)$_2$SeBu^t (**4**) ^{1}H NMR



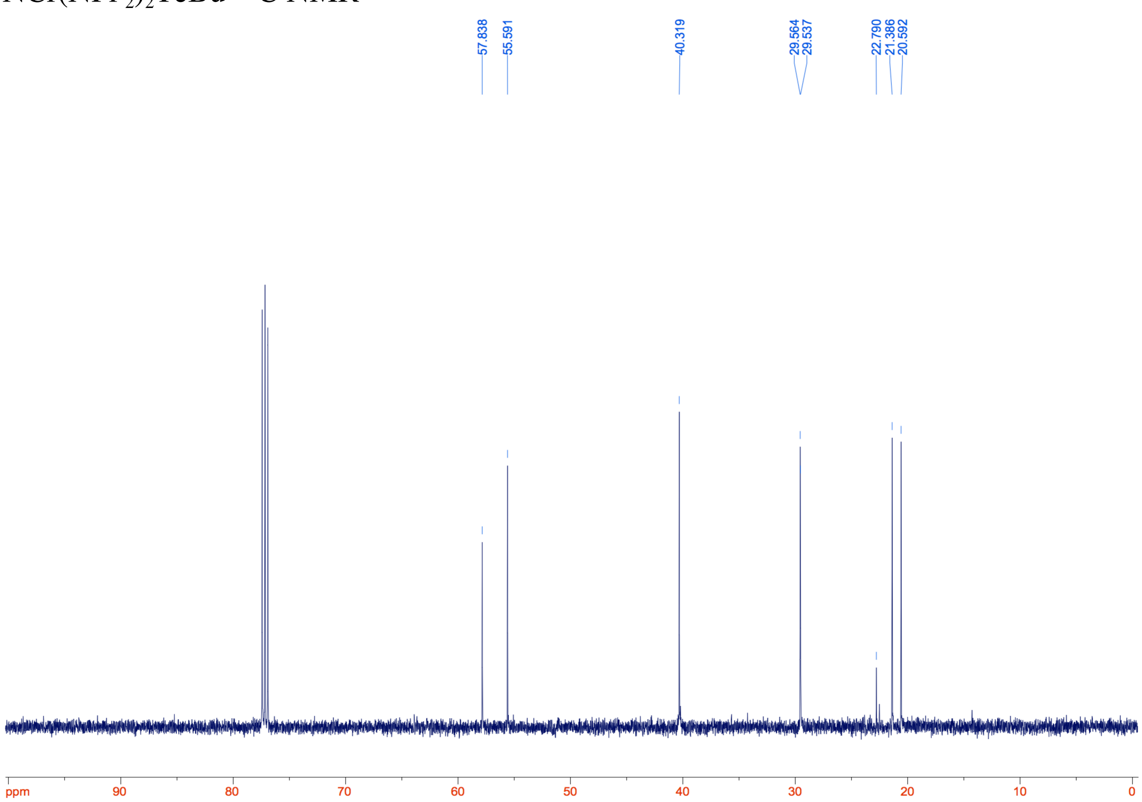
NCr(NPr$^i_2$)$_2$SeBu^t ^{13}C NMR



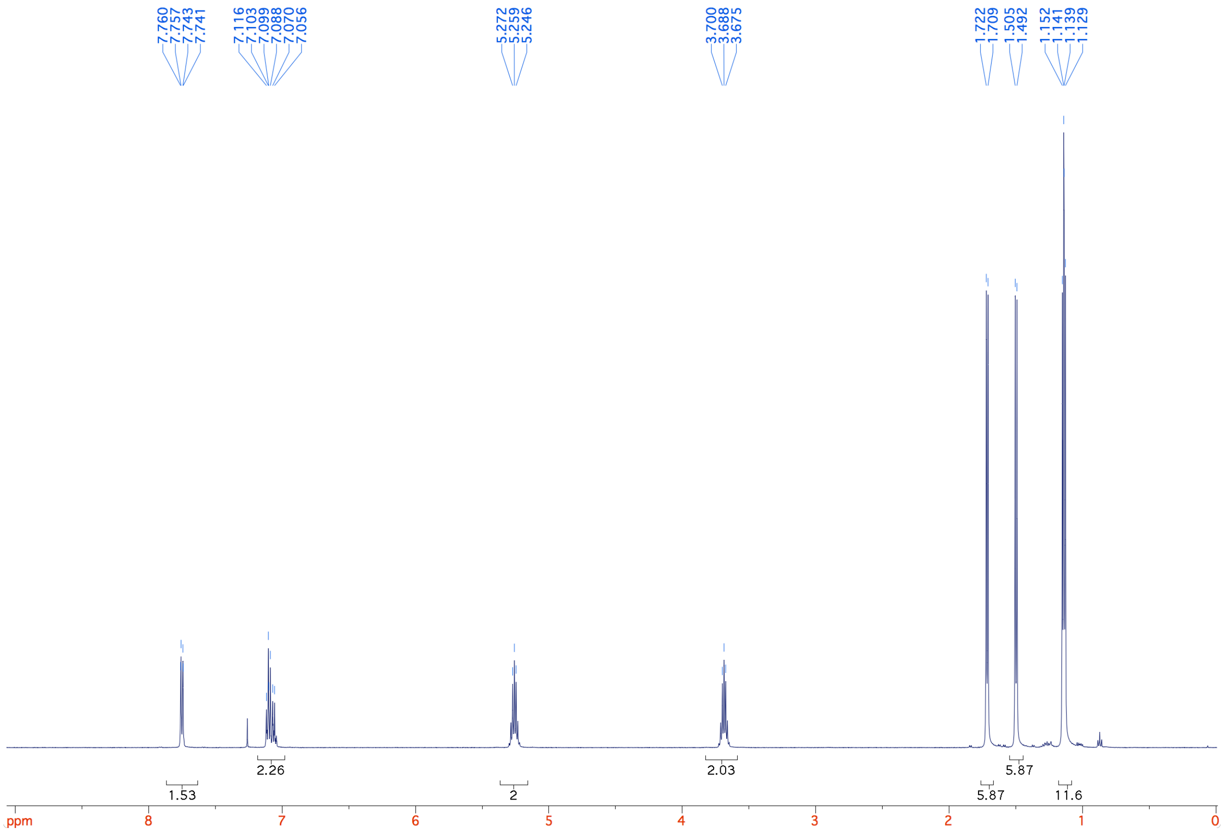
NCr(NPr$^{i}_{2}$)$_2$TeBu^{t} (**5**) ^{1}H NMR



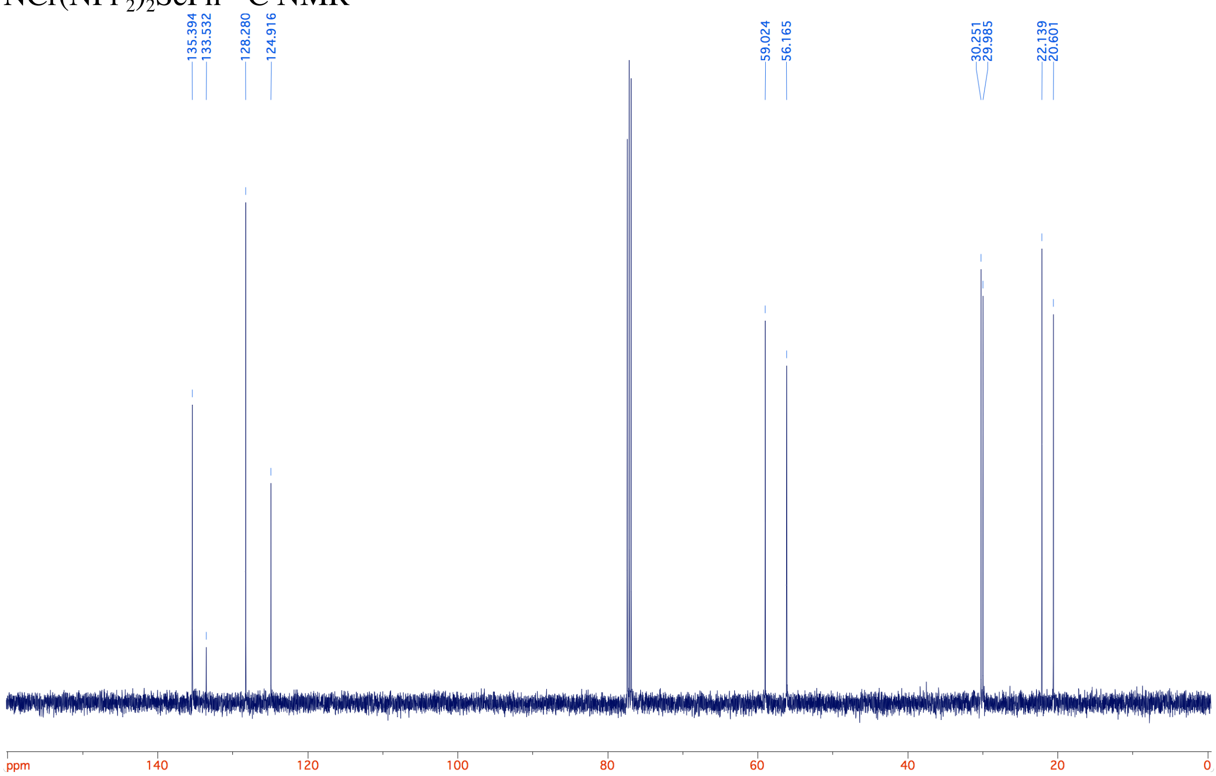
NCr(NPr$^{i}_{2}$)$_2$TeBu^{t} ^{13}C NMR



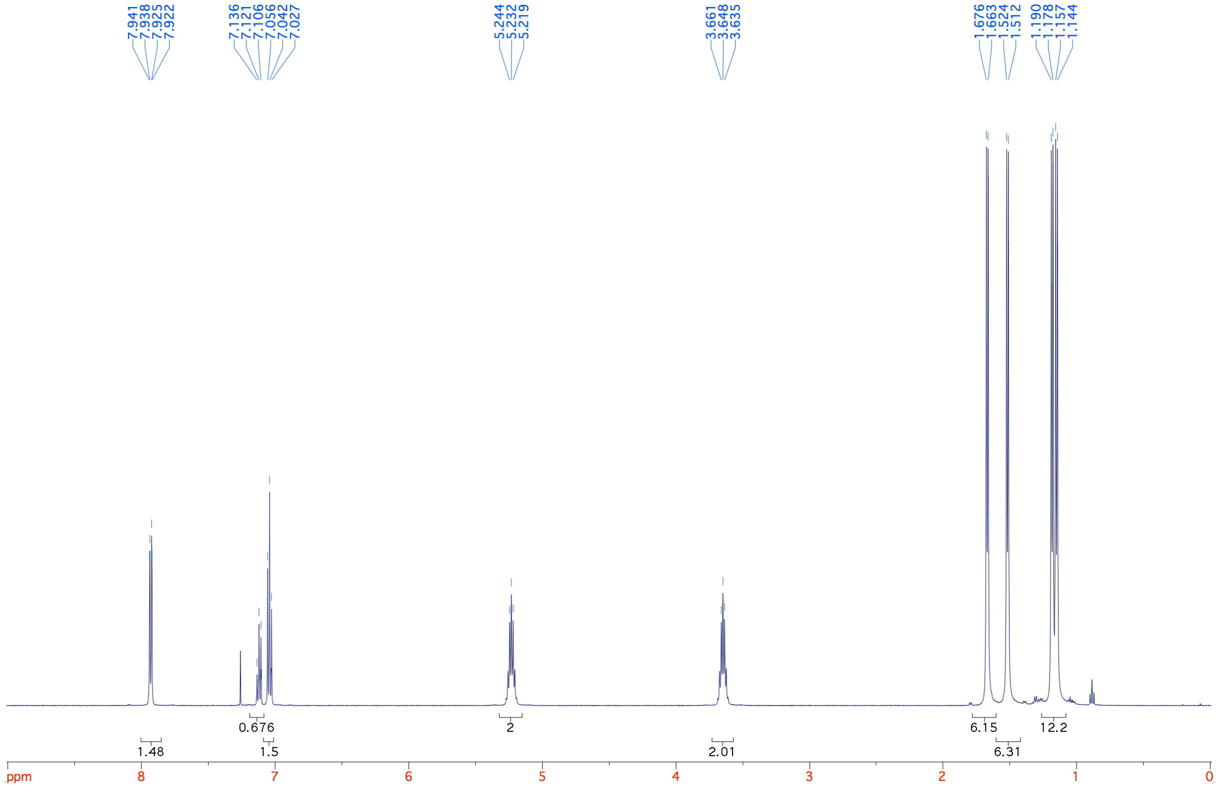
NCr(NPr$^i_2$)$_2$SePh (**8**) ^{1}H NMR



NCr(NPr$^i_2$)$_2$SePh ^{13}C NMR



NCr(NPr$^{i}_{2}$)$_2$TePh (**9**) ^{1}H NMR



NCr(NPr$^{i}_{2}$)$_2$TePh ^{13}C NMR