Supporting Information

Achiral and chiral NNN-pincer nickel complexes with oxazolinyl backbone: application in transfer hydrogenation of ketones

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1. X-ray structure determination

X-ray intensity data measurement of compounds **4a**, **4d** and **4f** was carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source (MoK_α= 0.71073 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from three matrix sets of 36 frames (each matrix run consists of 12 frames). Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 10-20 sec depending on the diffraction power of the crystals keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016).[S1] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). Using the APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008)[S2] structure solution program, using direct methods. The model was refined with a version of ShelXL-2018/3 (Sheldrick, 2015)[S3] using Least Squares minimization. All the hydrogen atoms were placed in a geometrically idealized position and constrained to ride on its parent atoms. An *ORTEP* III[S4] view of the compounds was drawn with 50% probability displacement ellipsoids, and H atoms are shown as small spheres of arbitrary radii. Crystal data for the structures have been deposited in the Cambridge Crystallographic Data Center with numbers (compound numbers) CCDC-2074093 (**4a**), CCDC-2074094 (**4d**) and CCDC-2074095 (**4f**).

A single crystal of a compound **4a** with molecular formula $C_{15}H_{20}ClN_3NiO_2$, approximate crystal dimensions 0.041 mm x 0.138 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 41734 reflections to a maximum θ angle of 30.02° (0.71 Å resolution), of which 4658 were independent (average redundancy 8.960, completeness = 99.7%, R_{int} =3.29%, R_{sig} = 1.65%) and 4192 (90.00%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.793(3) Å, b = 9.9261(18) Å, c = 19.198(4) Å, volume = 3200.1(10) Å^3, are based upon the refinement of the XYZ-centroids of 1269 reflections above 20 $\sigma(I)$ with 4.851° < 2θ

< 58.65°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.908. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8190 and 0.9450. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pbca*, with Z = 8 for the formula unit, $C_{15}H_{20}ClN_3NiO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 201 variables converged at $R1$ = 2.31%, for the observed data and $wR2$ = 5.75% for all data. The goodness-of-fit (S) was 1.028. The largest peak in the final difference electron density synthesis was 0.456 $e^-/Å^3$ and the largest hole was -0.461 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was1.530 g/cm^3 and $F(000)$, 1536 e^-.

A single crystal of a compound **4d** with molecular formula $C_{22}H_{26}ClN_3NiO_2$, approximate crystal dimensions 0.030 mm x 0.150 mm x 0.210 mm, was used for the X-ray crystallographic analysis. The integration of the data using an orthorhombic unit cell yielded a total of 44424 reflections to a maximum θ angle of 34.63° (0.63 Å resolution), of which 8381 were independent (average redundancy 5.301, completeness = 95.2%, R_{int} = 3.62%, R_{sig} = 3.49%) and 7601 (90.69%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.9695(4) Å, b = 10.0137(3) Å, c =21.4431(7) Å, volume = 2140.70(13) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 $\sigma(I)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8090 and 0.9690. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{22}H_{26}ClN_3NiO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 264 variables converged at $R1$ = 2.64%, for the observed data and $wR2$ = 5.85% for all data. The goodness-of-fit (S) was 1.036. The largest peak in the final difference electron density synthesis was 0.254 $e^-/Å^3$ and the largest hole was -0.369 $e^-/Å^3$ with an RMS deviation of 0.052 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.423 g/cm^3 and $F(000)$, 960 e^-. The absolute configuration (Flack parameter, x = 0.008(4)) is established by the structure determination of **4d** containing a chiral reference fragment of known absolute configuration and confirmed by anomalous dispersion effects in diffraction measurements on the crystals.

A single crystal of a compound **4f** with molecular formula $C_{19}H_{28}ClN_3NiO_2$, approximate crystal dimensions 0.050 mm x 0.170 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The integration of the data using an orthorhombic unit cell yielded a total of 36549 reflections to a maximum θ angle of 30.52° (0.70 Å resolution), of which 6183 were independent (average redundancy 5.911, completeness = 99.9%, R_{int} = 2.40%, R_{sig} = 2.49%) and 6036 (97.62%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.7315(3) Å, b = 9.8437(3) Å, c =21.1840(7) Å, volume = 2029.30(11) Å^3, are based upon the refinement of the XYZ-centroids of reflections above $20\sigma(I)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8090 and 0.9470. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{19}H_{28}ClN_3NiO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 244 variables converged at $R1$ = 1.87%, for the observed data and $wR2$ = 4.83% for all data. The goodness-of-fit (S) was 1.031. The largest peak in the final difference electron density synthesis was 0.305 e$^-$/Å^3 and the largest hole was -0.296 e$^-$/Å^3 with an RMS deviation of 0.042 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.390 g/cm^3 and F(000), 896 e$^-$. The absolute configuration (Flack parameter, x = 0.023(8)) is established by the structure determination of **4f** containing a chiral reference fragment of known absolute configuration and confirmed by anomalous dispersion effects in diffraction measurements on the crystals.

Table S1. Crystal data of complexes **4a**, **4d** and **4f**.

	4a	**4d**	**4f**
Formula	$C_{15}H_{20}ClN_3NiO_2$	$C_{22}H_{26}ClN_3NiO_2$	$C_{19}H_{28}ClN_3NiO_2$
Molecular weight	368.50	458.62	424.60
Crystal Size, mm	0.158 × 0.138 × 0.041	0.21 × 0.15 × 0.03	0.20 × 0.17 × 0.05
Temp. (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal Syst.	orthorhombic	orthorhombic	orthorhombic
Space Group	*Pbca*	$P2_12_12_1$	$P2_12_12_1$
a/Å	16.793(3)	9.9695(4)	9.7315(3)
b/Å	9.9261(18)	10.0137(3)	9.8437(3)
c/Å	19.198(4)	21.4431(7)	21.1840(7)
V/Å^3	3200.2(10)	2140.70(13)	2029.30(11)
Z	8	4	4
D_{calc}/g cm^{-3}	1.530	1.423	1.390
μ/mm^{-1}	1.389	1.054	1.105
F(000)	1536	960	896
Ab. Correct.	multi-scan	multi-scan	multi-scan
T_{min}/ T_{max}	0.819/0.945	0.809/0.969	0.809/0.947
$2\theta_{max}$	60	69.26	62
Total reflns.	41734	44424	36549
Unique reflns.	4658	8381	6183
Obs. reflns.	4192	7601	6036
h, k, l (min, max)	(-23, 23), (-12, 13), (-25, 27)	(-14, 15), (-15, 15), (-34, 33)	(-13, 13), (-14, 14), (-30, 30)
R_{int} / R_{sig}	0.0329 / 0.0165	0.0362 / 0.0349	0.0240 / 0.0249
No. of parameters	201	264	245
R1 [$I > 2\sigma(I)$]	0.0231	0.0264	0.0187
wR2[$I > 2\sigma(I)$]	0.0552	0.0557	0.0481
R1 [all data]	0.0272	0.0338	0.0193
wR2 [all data]	0.0575	0.0585	0.0483
goodness-of-fit	1.028	1.036	1.030
$\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	+0.456, -0.461	+0.254, -0.369	+0.305, -0.295
CCDC No.	2074093	2074094	2074095

Table S2. Bond lengths (Å) for **4a**.

Ni1-N1	1.8780(10)	Ni1-N2	1.8806(10)
Ni1-N3	1.9514(10)	Ni1-Cl1	2.2025(4)
O1-C3	1.3434(13)	O1-C2	1.4733(14)
O2-C10	1.2323(14)	N1-C3	1.2890(14)
N1-C1	1.4811(14)	N2-C10	1.3630(14)
N2-C9	1.4064(14)	N3-C11	1.4880(14)
N3-C12	1.4984(15)	N3-C14	1.5091(15)
C1-C2	1.5283(16)	C1-H1A	0.99
C1-H1B	0.99	C2-H2A	0.99
C2-H2B	0.99	C3-C4	1.4570(15)
C4-C5	1.4033(15)	C4-C9	1.4145(15)
C5-C6	1.3854(17)	C5-H5	0.95
C6-C7	1.3959(17)	C6-H6	0.95
C7-C8	1.3889(16)	C7-H7	0.95
C8-C9	1.4107(16)	C8-H8	0.95
C10-C11	1.5101(16)	C11-H11A	0.99
C11-H11B	0.99	C12-C13	1.5209(18)
C12-H12A	0.99	C12-H12B	0.99
C13-H13A	0.98	C13-H13B	0.98
C13-H13C	0.98	C14-C15	1.5187(18)
C14-H14A	0.99	C14-H14B	0.99
C15-H15A	0.98	C15-H15B	0.98

Table S3. Bond angles (°) for **4a**.

N1-Ni1-N2	91.05(4)	N1-Ni1-N3	167.95(4)
N2-Ni1-N3	85.93(4)	N1-Ni1-Cl1	92.46(3)
N2-Ni1-Cl1	165.90(3)	N3-Ni1-Cl1	93.28(3)
C3-O1-C2	106.55(8)	C3-N1-C1	108.27(9)
C3-N1-Ni1	126.43(8)	C1-N1-Ni1	124.61(7)
C10-N2-C9	120.35(9)	C10-N2-Ni1	115.52(7)
C9-N2-Ni1	123.53(7)	C11-N3-C12	110.18(9)
C11-N3-C14	108.65(9)	C12-N3-C14	107.05(9)
C11-N3-Ni1	105.64(7)	C12-N3-Ni1	111.95(7)
C14-N3-Ni1	113.33(7)	N1-C1-C2	102.94(9)
N1-C1-H1A	111.2	C2-C1-H1A	111.2
N1-C1-H1B	111.2	C2-C1-H1B	111.2
H1A-C1-H1B	109.1	O1-C2-C1	103.99(9)
O1-C2-H2A	111.0	C1-C2-H2A	111.0
O1-C2-H2B	111.0	C1-C2-H2B	111.0
H2A-C2-H2B	109.0	N1-C3-O1	116.53(10)
N1-C3-C4	125.89(10)	O1-C3-C4	117.58(9)
C5-C4-C9	120.86(10)	C5-C4-C3	119.24(10)
C9-C4-C3	119.89(10)	C6-C5-C4	120.57(11)
C6-C5-H5	119.7	C4-C5-H5	119.7
C5-C6-C7	119.07(11)	C5-C6-H6	120.5
C7-C6-H6	120.5	C8-C7-C6	121.04(11)
C8-C7-H7	119.5	C6-C7-H7	119.5
C7-C8-C9	120.94(11)	C7-C8-H8	119.5
C9-C8-H8	119.5	N2-C9-C8	122.09(10)
N2-C9-C4	120.42(10)	C8-C9-C4	117.43(10)
O2-C10-N2	128.05(10)	O2-C10-C11	119.97(10)
N2-C10-C11	111.92(9)	N3-C11-C10	111.86(9)
N3-C11-H11A	109.2	C10-C11-H11A	109.2

N3-C11-H11B	109.2	C10-C11-H11B	109.2
H11A-C11-H11B	107.9	N3-C12-C13	115.14(10)
N3-C12-H12A	108.5	C13-C12-H12A	108.5
N3-C12-H12B	108.5	C13-C12-H12B	108.5
H12A-C12-H12B	107.5	C12-C13-H13A	109.5
C12-C13-H13B	109.5	H13A-C13-H13B	109.5
C12-C13-H13C	109.5	H13A-C13-H13C	109.5
H13B-C13-H13C	109.5	N3-C14-C15	113.91(10)
N3-C14-H14A	108.8	C15-C14-H14A	108.8
N3-C14-H14B	108.8	C15-C14-H14B	108.8
H14A-C14-H14B	107.7	C14-C15-H15A	109.5
C14-C15-H15B	109.5	H15A-C15-H15B	109.5
C14-C15-H15C	109.5	H15A-C15-H15C	109.5
H15B-C15-H15C	109.5		

Table S4. Torsion angles (°) for **4a**.

N2-Ni1-N1-C3	-21.00(10)	N3-Ni1-N1-C3	-96.3(2)
Cl1-Ni1-N1-C3	145.34(9)	N2-Ni1-N1-C1	148.34(9)
N3-Ni1-N1-C1	73.1(2)	Cl1-Ni1-N1-C1	-45.33(8)
N1-Ni1-N2-C10	-150.51(8)	N3-Ni1-N2-C10	17.82(8)
Cl1-Ni1-N2-C10	105.06(13)	N1-Ni1-N2-C9	38.35(9)
N3-Ni1-N2-C9	-153.33(9)	Cl1-Ni1-N2-C9	-66.08(16)
C3-N1-C1-C2	-11.31(11)	Ni1-N1-C1-C2	177.72(7)
C3-O1-C2-C1	-10.34(11)	N1-C1-C2-O1	12.76(11)
C1-N1-C3-O1	5.33(13)	Ni1-N1-C3-O1	176.10(7)
C1-N1-C3-C4	-173.85(10)	Ni1-N1-C3-C4	-3.08(16)
C2-O1-C3-N1	3.55(13)	C2-O1-C3-C4	-177.20(9)
N1-C3-C4-C5	-160.97(11)	O1-C3-C4-C5	19.85(15)
N1-C3-C4-C9	19.54(16)	O1-C3-C4-C9	-159.63(10)
C9-C4-C5-C6	-2.36(16)	C3-C4-C5-C6	178.16(10)

C4-C5-C6-C7	-0.17(17)	C5-C6-C7-C8	1.97(17)
C6-C7-C8-C9	-1.25(17)	C10-N2-C9-C8	-26.69(15)
Ni1-N2-C9-C8	144.04(9)	C10-N2-C9-C4	156.29(10)
Ni1-N2-C9-C4	-32.97(14)	C7-C8-C9-N2	-178.33(10)
C7-C8-C9-C4	-1.23(16)	C5-C4-C9-N2	-179.84(10)
C3-C4-C9-N2	-0.37(15)	C5-C4-C9-C8	3.01(15)
C3-C4-C9-C8	-177.51(10)	C9-N2-C10-O2	-14.88(17)
Ni1-N2-C10-O2	173.67(10)	C9-N2-C10-C11	167.90(9)
Ni1-N2-C10-C11	-3.55(12)	C12-N3-C11-C10	-90.45(11)
C14-N3-C11-C10	152.57(9)	Ni1-N3-C11-C10	30.65(10)
O2-C10-C11-N3	163.61(10)	N2-C10-C11-N3	-18.92(13)
C11-N3-C12-C13	60.69(13)	C14-N3-C12-C13	178.67(10)
Ni1-N3-C12-C13	-56.55(12)	C11-N3-C14-C15	-69.66(12)
C12-N3-C14-C15	171.38(10)	Ni1-N3-C14-C15	47.45(11)

Table S5. Bond lengths (Å) for **4d**.

Ni1-N2	1.8826(12)	Ni1-N1	1.8904(12)
Ni1-N3	1.9611(12)	Ni1-Cl1	2.1896(4)
O1-C3	1.3505(18)	O1-C2	1.455(2)
O2-C10	1.2306(19)	N1-C3	1.2862(19)
N1-C1	1.4953(19)	N2-C10	1.356(2)
N2-C9	1.4114(19)	N3-C11	1.486(2)
N3-C14	1.506(2)	N3-C12	1.509(2)
C1-C16	1.522(2)	C1-C2	1.527(2)
C1-H1	1.0	C2-H2A	0.99
C2-H2AB	0.99	C3-C4	1.446(2)
C4-C5	1.402(2)	C4-C9	1.408(2)
C5-C6	1.380(3)	C5-H5	0.95
C6-C7	1.384(3)	C6-H6	0.95

C7-C8	1.380(2)	C7-H7	0.95
C8-C9	1.405(2)	C8-H8	0.95
C10-C11	1.509(2)	C11-H11A	0.99
C11-H11B	0.99	C12-C13	1.513(2)
C12-H12A	0.99	C12-H12B	0.99
C13-H13A	0.98	C13-H13B	0.98
C13-H13C	0.98	C14-C15	1.515(3)
C14-H14A	0.99	C14-H14B	0.99
C15-H15A	0.98	C15-H15B	0.98
C15-H15C	0.98	C16-C17	1.514(2)
C16-H16A	0.99	C16-H16B	0.99
C17-C18	1.387(2)	C17-C22	1.388(2)
C18-C19	1.394(2)	C18-H18	0.95
C19-C20	1.382(3)	C19-H19	0.95
C20-C21	1.379(3)	C20-H20	0.95
C21-C22	1.388(2)	C21-H21	0.95
C22-H22	0.95		

Table S6. Bond angles (°) for **4d**.

N2-Ni1-N1	91.69(5)	N2-Ni1-N3	85.96(5)
N1-Ni1-N3	172.85(6)	N2-Ni1-Cl1	171.32(4)
N1-Ni1-Cl1	91.73(4)	N3-Ni1-Cl1	91.55(4)
C3-O1-C2	106.20(13)	C3-N1-C1	107.70(11)
C3-N1-Ni1	126.58(10)	C1-N1-Ni1	124.64(10)
C10-N2-C9	119.11(13)	C10-N2-Ni1	115.07(10)
C9-N2-Ni1	125.74(11)	C11-N3-C14	108.05(13)
C11-N3-C12	110.45(13)	C14-N3-C12	105.85(12)
C11-N3-Ni1	106.44(9)	C14-N3-Ni1	116.01(10)
C12-N3-Ni1	110.02(10)	N1-C1-C16	108.30(13)

N1-C1-C2	102.02(13)	C16-C1-C2	114.04(14)
N1-C1-H1	110.7	C16-C1-H1	110.7
C2-C1-H1	110.7	O1-C2-C1	104.43(13)
O1-C2-H2A	110.9	C1-C2-H2A	110.9
O1-C2-H2AB	110.9	C1-C2-H2AB	110.9
H2A-C2-H2AB	108.9	N1-C3-O1	116.56(14)
N1-C3-C4	127.03(13)	O1-C3-C4	116.40(13)
C5-C4-C9	120.55(15)	C5-C4-C3	119.03(15)
C9-C4-C3	120.41(14)	C6-C5-C4	120.82(17)
C6-C5-H5	119.6	C4-C5-H5	119.6
C5-C6-C7	118.83(16)	C5-C6-H6	120.6
C7-C6-H6	120.6	C8-C7-C6	121.34(17)
C8-C7-H7	119.3	C6-C7-H7	119.3
C7-C8-C9	121.07(16)	C7-C8-H8	119.5
C9-C8-H8	119.5	C8-C9-C4	117.35(14)
C8-C9-N2	121.96(14)	C4-C9-N2	120.63(13)
O2-C10-N2	128.00(15)	O2-C10-C11	118.85(15)
N2-C10-C11	113.12(14)	N3-C11-C10	112.33(13)
N3-C11-H11A	109.1	C10-C11-H11A	109.1
N3-C11-H11B	109.1	C10-C11-H11B	109.1
H11A-C11-H11B	107.9	N3-C12-C13	115.16(13)
N3-C12-H12A	108.5	C13-C12-H12A	108.5
N3-C12-H12B	108.5	C13-C12-H12B	108.5
H12A-C12-H12B	107.5	C12-C13-H13A	109.5
C12-C13-H13B	109.5	H13A-C13-H13B	109.5
C12-C13-H13C	109.5	H13A-C13-H13C	109.5
H13B-C13-H13C	109.5	N3-C14-C15	114.59(14)
N3-C14-H14A	108.6	C15-C14-H14A	108.6
N3-C14-H14B	108.6	C15-C14-H14B	108.6

H14A-C14-H14B	107.6	C14-C15-H15A	109.5
C14-C15-H15B	109.5	H15A-C15-H15B	109.5
C14-C15-H15C	109.5	H15A-C15-H15C	109.5
H15B-C15-H15C	109.5	C17-C16-C1	113.98(13)
C17-C16-H16A	108.8	C1-C16-H16A	108.8
C17-C16-H16B	108.8	C1-C16-H16B	108.8
H16A-C16-H16B	107.7	C18-C17-C22	118.57(14)
C18-C17-C16	122.13(14)	C22-C17-C16	119.30(14)
C17-C18-C19	120.99(16)	C17-C18-H18	119.5
C19-C18-H18	119.5	C20-C19-C18	119.47(17)
C20-C19-H19	120.3	C18-C19-H19	120.3
C21-C20-C19	120.12(16)	C21-C20-H20	119.9
C19-C20-H20	119.9	C20-C21-C22	120.06(16)
C20-C21-H21	120.0	C22-C21-H21	120.0
C17-C22-C21	120.71(15)	C17-C22-H22	119.6
C21-C22-H22	119.6		

Table S7. Torsion angles (°) for **4d**.

N2-Ni1-N1-C3	12.98(14)	Cl1-Ni1-N1-C3	-159.04(14)
N2-Ni1-N1-C1	-153.65(12)	Cl1-Ni1-N1-C1	34.34(12)
N1-Ni1-N2-C10	153.65(12)	N3-Ni1-N2-C10	-19.58(12)
N1-Ni1-N2-C9	-29.69(13)	N3-Ni1-N2-C9	157.07(13)
C3-N1-C1-C16	-106.75(15)	Ni1-N1-C1-C16	62.01(15)
C3-N1-C1-C2	13.86(17)	Ni1-N1-C1-C2	-177.39(12)
C3-O1-C2-C1	15.0(2)	N1-C1-C2-O1	-17.14(18)
C16-C1-C2-O1	99.38(16)	C1-N1-C3-O1	-5.07(19)
Ni1-N1-C3-O1	-173.55(11)	C1-N1-C3-C4	175.61(17)
Ni1-N1-C3-C4	7.1(3)	C2-O1-C3-N1	-6.8(2)
C2-O1-C3-C4	172.62(16)	N1-C3-C4-C5	161.32(18)

O1-C3-C4-C5	-18.0(2)	N1-C3-C4-C9	-17.5(3)
O1-C3-C4-C9	163.20(15)	C9-C4-C5-C6	1.1(3)
C3-C4-C5-C6	-177.69(18)	C4-C5-C6-C7	0.7(3)
C5-C6-C7-C8	-1.4(3)	C6-C7-C8-C9	0.2(3)
C7-C8-C9-C4	1.5(3)	C7-C8-C9-N2	178.76(17)
C5-C4-C9-C8	-2.2(2)	C3-C4-C9-C8	176.60(16)
C5-C4-C9-N2	-179.45(16)	C3-C4-C9-N2	-0.7(2)
C10-N2-C9-C8	26.8(2)	Ni1-N2-C9-C8	-149.69(14)
C10-N2-C9-C4	-156.03(15)	Ni1-N2-C9-C4	27.4(2)
C9-N2-C10-O2	14.3(3)	Ni1-N2-C10-O2	-168.77(15)
C9-N2-C10-C11	-167.65(14)	Ni1-N2-C10-C11	9.24(18)
C14-N3-C11-C10	-149.88(13)	C12-N3-C11-C10	94.77(16)
Ni1-N3-C11-C10	-24.63(16)	O2-C10-C11-N3	-170.54(15)
N2-C10-C11-N3	11.3(2)	C11-N3-C12-C13	-57.84(19)
C14-N3-C12-C13	-174.56(15)	Ni1-N3-C12-C13	59.38(17)
C11-N3-C14-C15	69.60(18)	C12-N3-C14-C15	-172.06(16)
Ni1-N3-C14-C15	-49.75(19)	N1-C1-C16-C17	174.16(12)
C2-C1-C16-C17	61.35(18)	C1-C16-C17-C18	48.5(2)
C1-C16-C17-C22	-132.29(15)	C22-C17-C18-C19	-2.0(3)
C16-C17-C18-C19	177.22(17)	C17-C18-C19-C20	-0.7(3)
C18-C19-C20-C21	2.5(3)	C19-C20-C21-C22	-1.6(3)
C18-C17-C22-C21	2.8(2)	C16-C17-C22-C21	-176.36(15)
C20-C21-C22-C17	-1.1(3)		

Table S8. Bond lengths (Å) for **4f**.

Ni1-N2	1.8860(12)	Ni1-N1	1.8887(12)
Ni1-N3	1.9569(13)	Ni1-Cl1	2.1952(4)
O1-C3	1.3509(18)	O1-C2	1.452(2)
O2-C10	1.2275(19)	N1-C3	1.2899(19)

N1-C1	1.4890(18)	N2-C10	1.3668(19)
N2-C9	1.4078(18)	N3-C11	1.486(2)
N3-C12	1.504(2)	N3-C14	1.510(2)
C1-C16	1.524(2)	C1-C2	1.533(2)
C1-H1	1.0	C2-H2A	0.99
C2-H2AB	0.99	C3-C4	1.447(2)
C4-C5	1.404(2)	C4-C9	1.408(2)
C5-C6	1.380(2)	C5-H5	0.95
C6-C7	1.394(3)	C6-H6	0.95
C7-C8	1.387(2)	C7-H7	0.95
C8-C9	1.409(2)	C8-H8	0.95
C10-C11	1.507(2)	C11-H11A	0.99
C11-H11B	0.99	C12-C13	1.518(2)
C12-H12A	0.99	C12-H12B	0.99
C13-H13A	0.98	C13-H13B	0.98
C13-H13C	0.98	C14-C15	1.507(3)
C14-H14A	0.99	C14-H14B	0.99
C15-H15A	0.98	C15-H15B	0.98
C15-H15C	0.98	C16-C17	1.538(2)
C16-H16A	0.99	C16-H16B	0.99
C17-C19A	1.409(6)	C17-C18	1.494(3)
C17-C19B	1.593(4)	C17-H17	1.0
C18-H18A	0.98	C18-H18B	0.98
C18-H18C	0.98	C19A-H19A	0.98
C19A-H19B	0.98	C19A-H19C	0.98
C19B-H19C	0.98	C19B-H19D	0.98
C19B-H19E	0.98		

Table S9. Bond angles (°) for **4f**.

N2-Ni1-N1	92.04(5)	N2-Ni1-N3	85.95(5)
N1-Ni1-N3	173.47(6)	N2-Ni1-Cl1	169.78(4)
N1-Ni1-Cl1	91.43(4)	N3-Ni1-Cl1	91.60(4)
C3-O1-C2	106.28(12)	C3-N1-C1	108.02(12)
C3-N1-Ni1	126.06(10)	C1-N1-Ni1	125.55(10)
C10-N2-C9	119.50(13)	C10-N2-Ni1	114.88(10)
C9-N2-Ni1	125.46(10)	C11-N3-C12	110.19(13)
C11-N3-C14	107.96(13)	C12-N3-C14	106.47(13)
C11-N3-Ni1	107.07(10)	C12-N3-Ni1	109.88(9)
C14-N3-Ni1	115.23(11)	N1-C1-C16	110.56(12)
N1-C1-C2	101.68(12)	C16-C1-C2	113.31(13)
N1-C1-H1	110.3	C16-C1-H1	110.3
C2-C1-H1	110.3	O1-C2-C1	104.18(12)
O1-C2-H2A	110.9	C1-C2-H2A	110.9
O1-C2-H2AB	110.9	C1-C2-H2AB	110.9
H2A-C2-H2AB	108.9	N1-C3-O1	116.06(13)
N1-C3-C4	127.12(13)	O1-C3-C4	116.80(13)
C5-C4-C9	120.92(14)	C5-C4-C3	118.26(14)
C9-C4-C3	120.81(13)	C6-C5-C4	120.76(15)
C6-C5-H5	119.6	C4-C5-H5	119.6
C5-C6-C7	118.90(15)	C5-C6-H6	120.5
C7-C6-H6	120.5	C8-C7-C6	121.03(15)
C8-C7-H7	119.5	C6-C7-H7	119.5
C7-C8-C9	121.11(15)	C7-C8-H8	119.4
C9-C8-H8	119.4	C4-C9-N2	120.73(13)
C4-C9-C8	117.26(14)	N2-C9-C8	121.98(13)
O2-C10-N2	127.84(16)	O2-C10-C11	118.99(14)
N2-C10-C11	113.15(13)	N3-C11-C10	112.20(12)

N3-C11-H11A	109.2	C10-C11-H11A	109.2
N3-C11-H11B	109.2	C10-C11-H11B	109.2
H11A-C11-H11B	107.9	N3-C12-C13	114.72(13)
N3-C12-H12A	108.6	C13-C12-H12A	108.6
N3-C12-H12B	108.6	C13-C12-H12B	108.6
H12A-C12-H12B	107.6	C12-C13-H13A	109.5
C12-C13-H13B	109.5	H13A-C13-H13B	109.5
C12-C13-H13C	109.5	H13A-C13-H13C	109.5
H13B-C13-H13C	109.5	C15-C14-N3	114.95(17)
C15-C14-H14A	108.5	N3-C14-H14A	108.5
C15-C14-H14B	108.5	N3-C14-H14B	108.5
H14A-C14-H14B	107.5	C14-C15-H15A	109.5
C14-C15-H15B	109.5	H15A-C15-H15B	109.5
C14-C15-H15C	109.5	H15A-C15-H15C	109.5
H15B-C15-H15C	109.5	C1-C16-C17	112.70(13)
C1-C16-H16A	109.1	C17-C16-H16A	109.1
C1-C16-H16B	109.1	C17-C16-H16B	109.1
H16A-C16-H16B	107.8	C19A-C17-C18	120.4(3)
C19A-C17-C16	117.5(3)	C18-C17-C16	111.51(16)
C18-C17-C19B	104.3(2)	C16-C17-C19B	108.50(17)
C19A-C17-H17	100.9	C18-C17-H17	100.9
C16-C17-H17	100.9	C17-C18-H18A	109.5
C17-C18-H18B	109.5	H18A-C18-H18B	109.5
C17-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	C17-C19A-H19A	109.5
C17-C19A-H19B	109.5	H19A-C19A-H19B	109.5
C17-C19A-H19C	109.5	H19A-C19A-H19C	109.5
H19B-C19A-H19C	109.5	C17-C19B-H19C	109.5
C17-C19B-H19D	109.5	H19C-C19B-H19D	109.5

C17-C19B-H19E	109.5	H19C-C19B-H19E	109.5
H19D-C19B-H19E	109.5		

Table S10. Torsion angles (°) for **4f**.

N2-Ni1-N1-C3	15.65(13)	Cl1-Ni1-N1-C3	-154.74(12)
N2-Ni1-N1-C1	-156.46(12)	Cl1-Ni1-N1-C1	33.15(11)
N1-Ni1-N2-C10	154.58(11)	N3-Ni1-N2-C10	-19.20(11)
Cl1-Ni1-N2-C10	-95.6(2)	N1-Ni1-N2-C9	-30.14(12)
N3-Ni1-N2-C9	156.08(12)	Cl1-Ni1-N2-C9	79.7(3)
C3-N1-C1-C16	-105.69(14)	Ni1-N1-C1-C16	67.62(15)
C3-N1-C1-C2	14.91(15)	Ni1-N1-C1-C2	-171.78(10)
C3-O1-C2-C1	16.96(16)	N1-C1-C2-O1	-18.91(15)
C16-C1-C2-O1	99.74(14)	C1-N1-C3-O1	-4.95(18)
Ni1-N1-C3-O1	-178.21(10)	C1-N1-C3-C4	176.66(14)
Ni1-N1-C3-C4	3.4(2)	C2-O1-C3-N1	-8.20(18)
C2-O1-C3-C4	170.37(13)	N1-C3-C4-C5	163.55(15)
O1-C3-C4-C5	-14.8(2)	N1-C3-C4-C9	-15.8(2)
O1-C3-C4-C9	165.85(13)	C9-C4-C5-C6	1.0(2)
C3-C4-C5-C6	-178.31(15)	C4-C5-C6-C7	0.2(3)
C5-C6-C7-C8	-0.8(3)	C6-C7-C8-C9	0.2(2)
C5-C4-C9-N2	-179.29(14)	C3-C4-C9-N2	0.0(2)
C5-C4-C9-C8	-1.5(2)	C3-C4-C9-C8	177.78(14)
C10-N2-C9-C4	-158.53(14)	Ni1-N2-C9-C4	26.39(19)
C10-N2-C9-C8	23.8(2)	Ni1-N2-C9-C8	-151.27(12)
C7-C8-C9-C4	0.9(2)	C7-C8-C9-N2	178.65(14)
C9-N2-C10-O2	15.0(2)	Ni1-N2-C10-O2	-169.38(14)
C9-N2-C10-C11	-166.37(13)	Ni1-N2-C10-C11	9.21(17)
C12-N3-C11-C10	95.44(15)	C14-N3-C11-C10	-148.66(15)
Ni1-N3-C11-C10	-24.03(16)	O2-C10-C11-N3	-170.56(15)

N2-C10-C11-N3	10.7(2)	C11-N3-C12-C13	-57.95(17)
C14-N3-C12-C13	-174.78(14)	Ni1-N3-C12-C13	59.80(15)
C11-N3-C14-C15	69.87(19)	C12-N3-C14-C15	-171.83(15)
Ni1-N3-C14-C15	-49.73(19)	N1-C1-C16-C17	-172.40(13)
C2-C1-C16-C17	74.21(16)	C1-C16-C17-C19A	52.5(4)
C1-C16-C17-C18	-162.43(17)	C1-C16-C17-C19B	83.3(2)

2. References

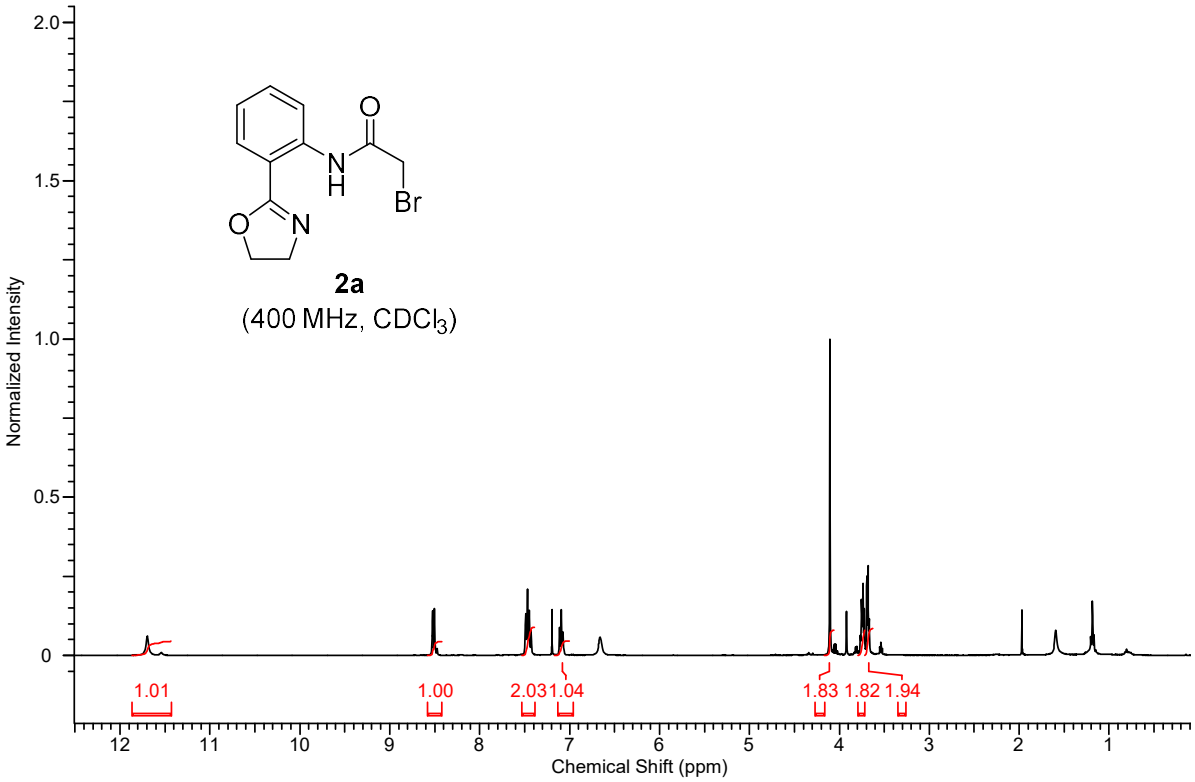
S1. Bruker (2016). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.

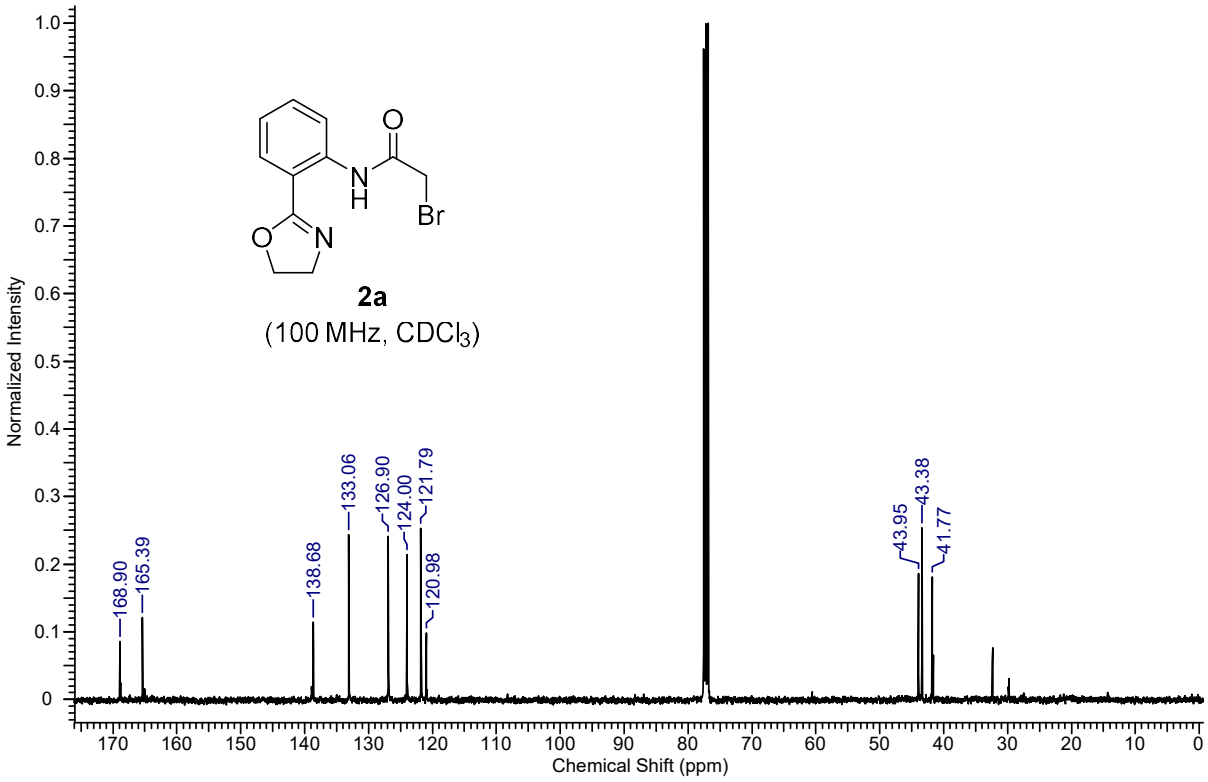
S2. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

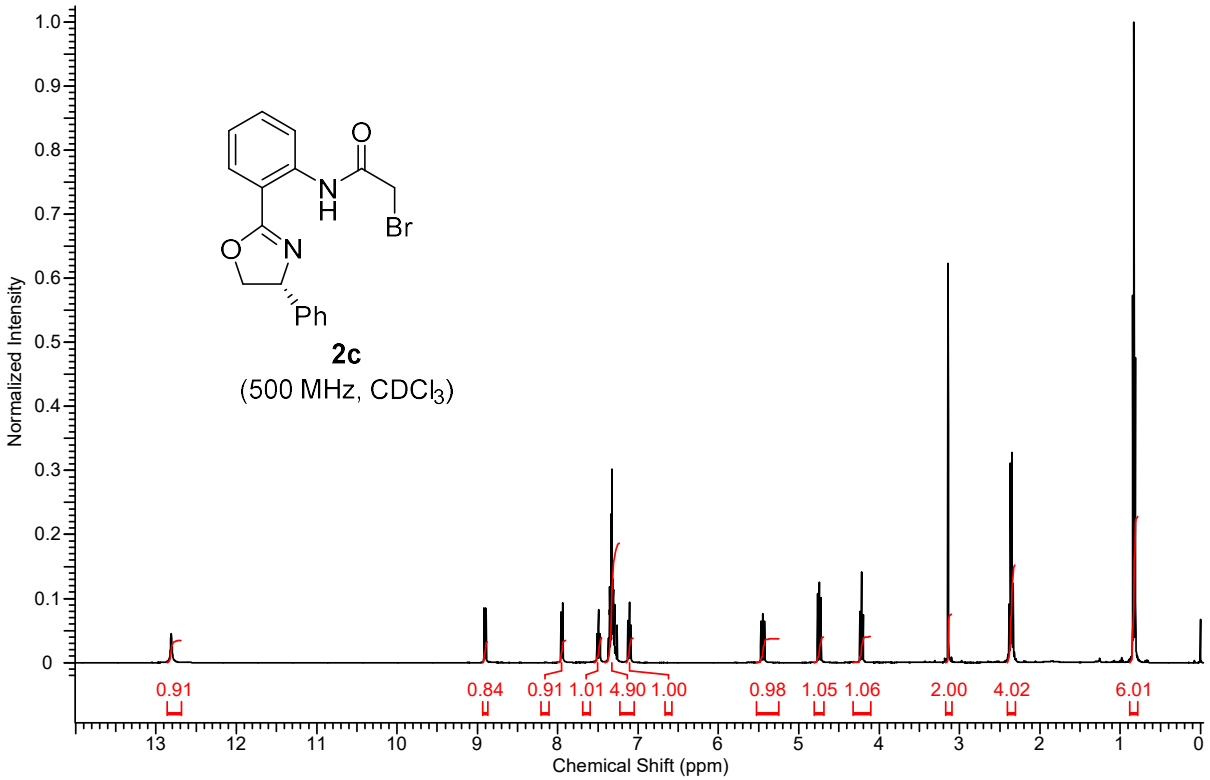
S3. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3–8.

S4. L. J. Farrugia, *J. Appl. Crystallogr.* 2012, **45**, 849–854.

3. ^{1}H and ^{13}C NMR Spectra of 2a-2f



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Ph
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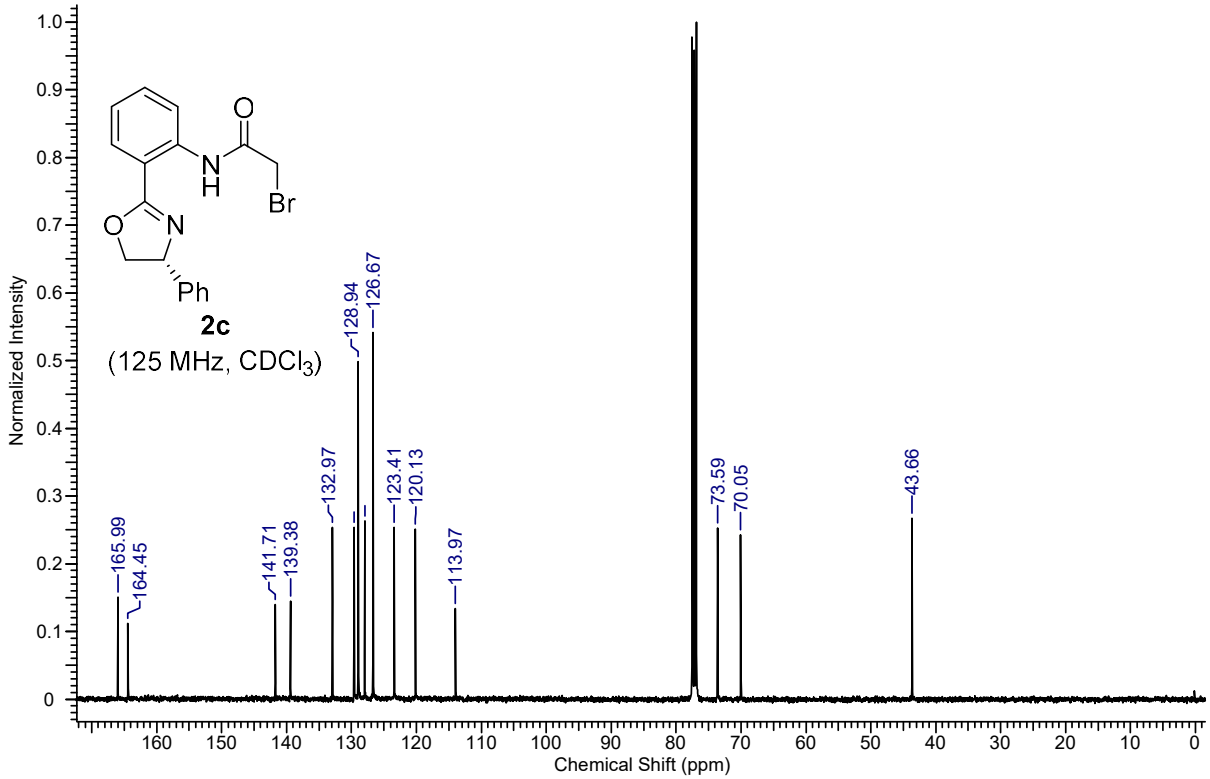
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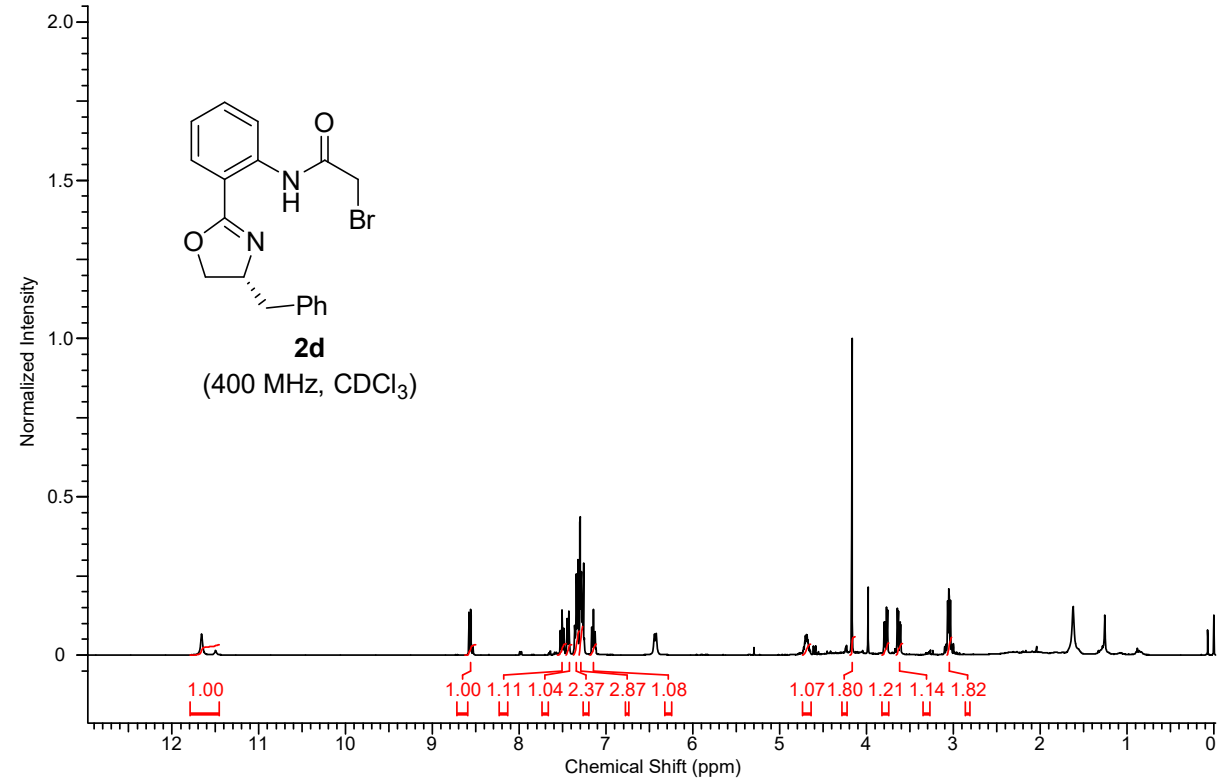
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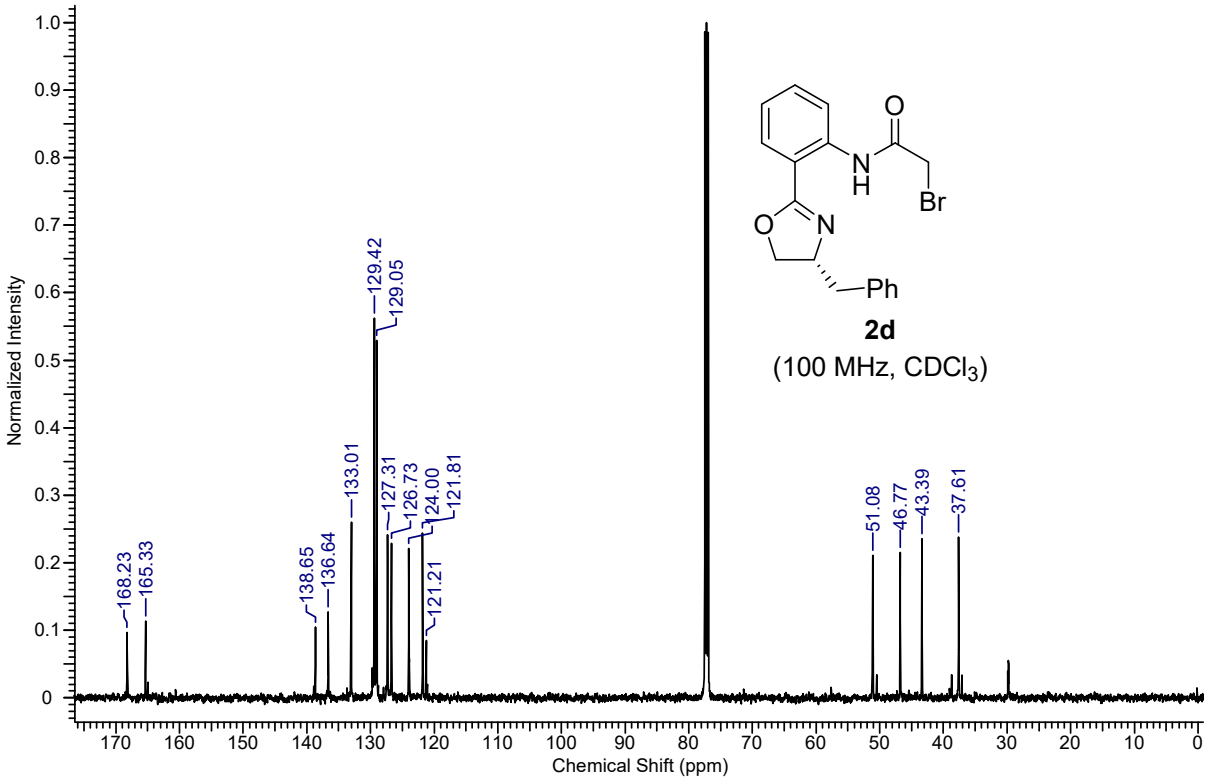
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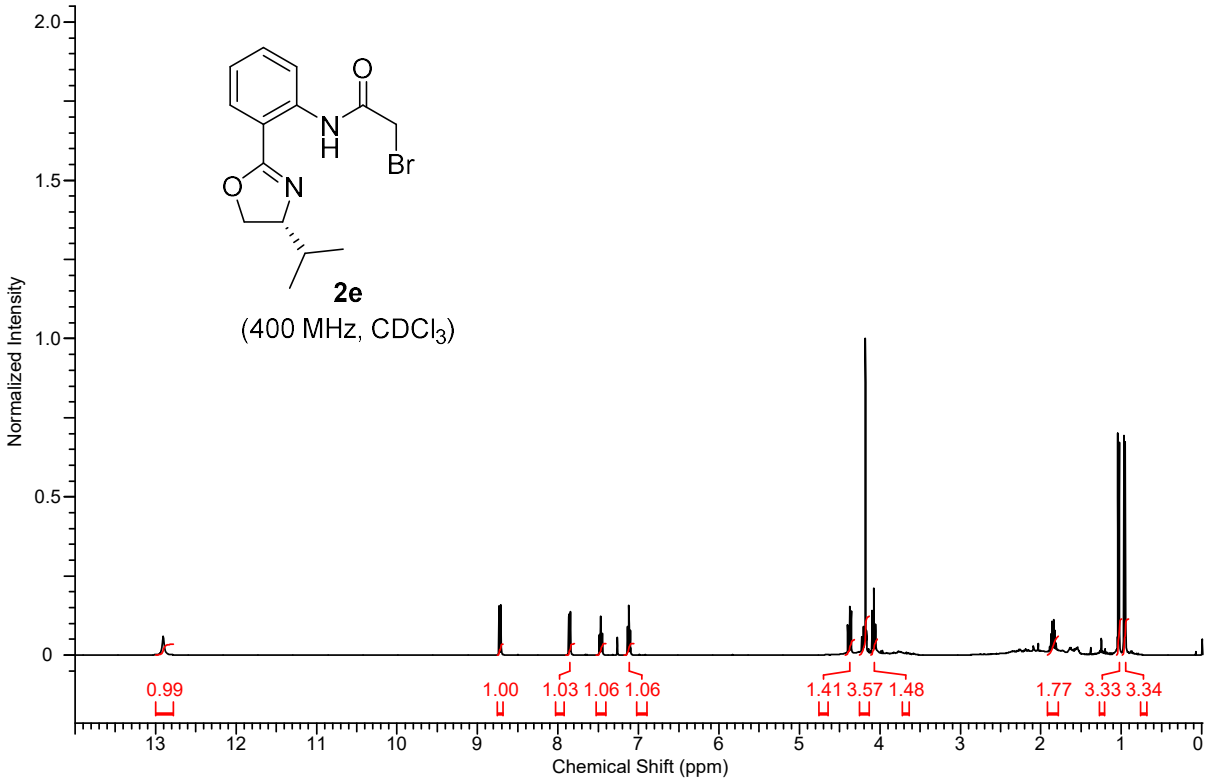
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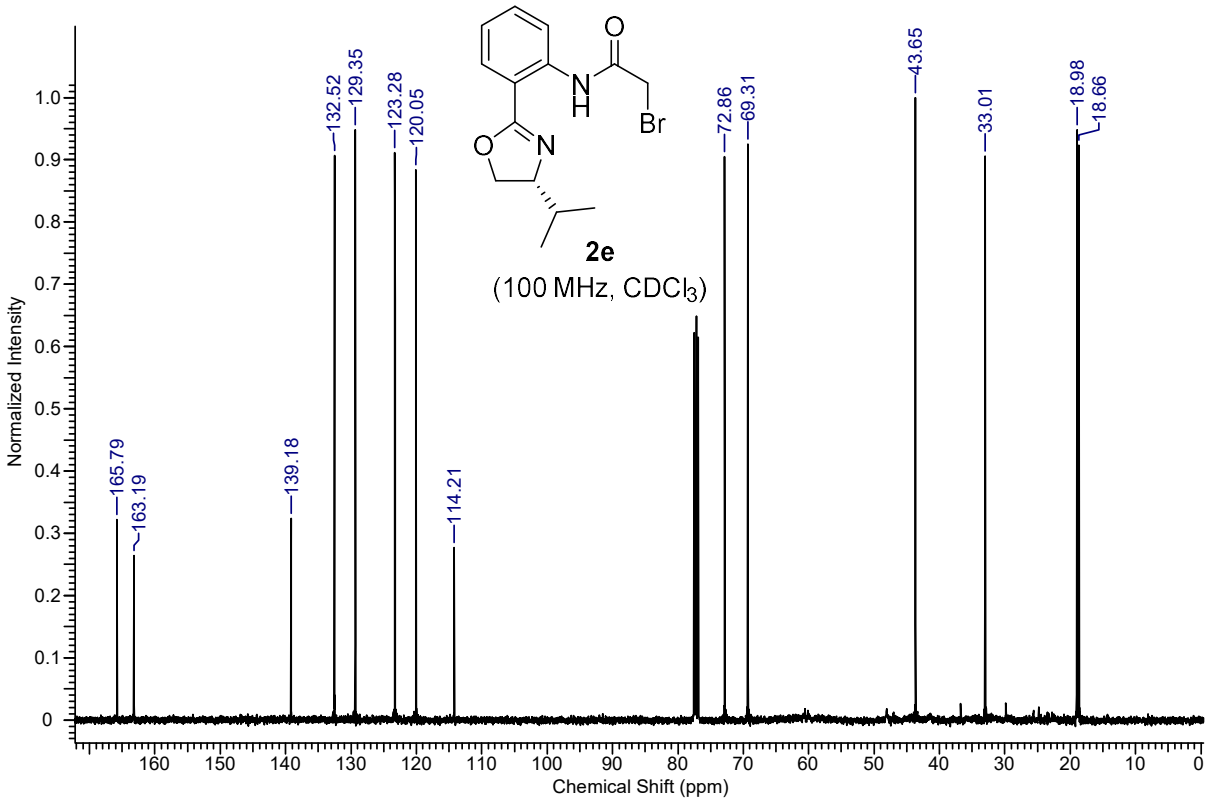
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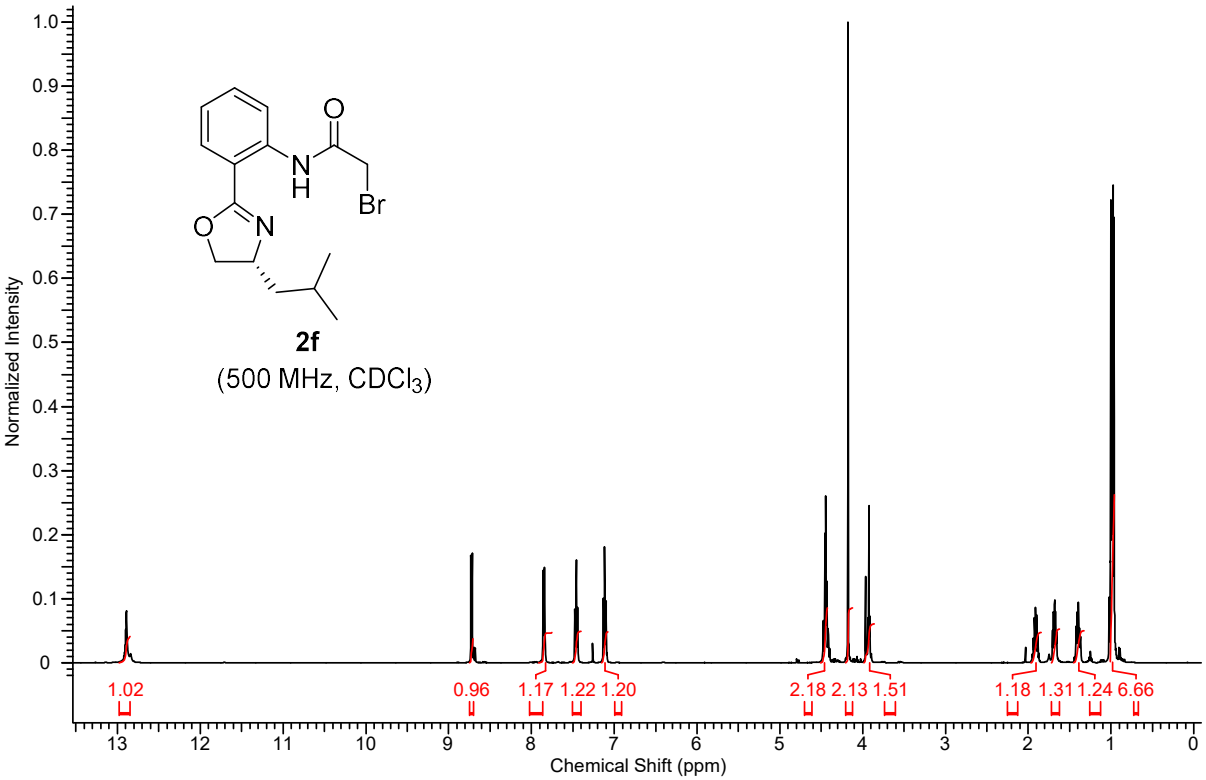
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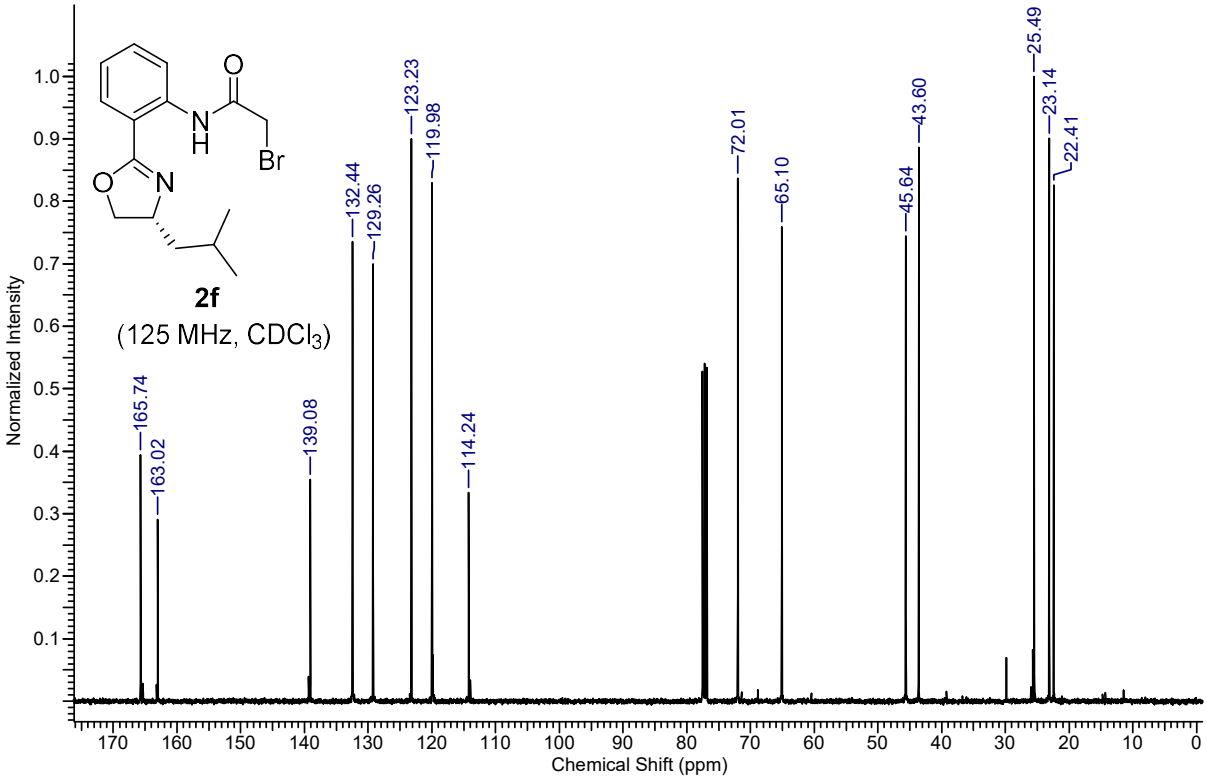
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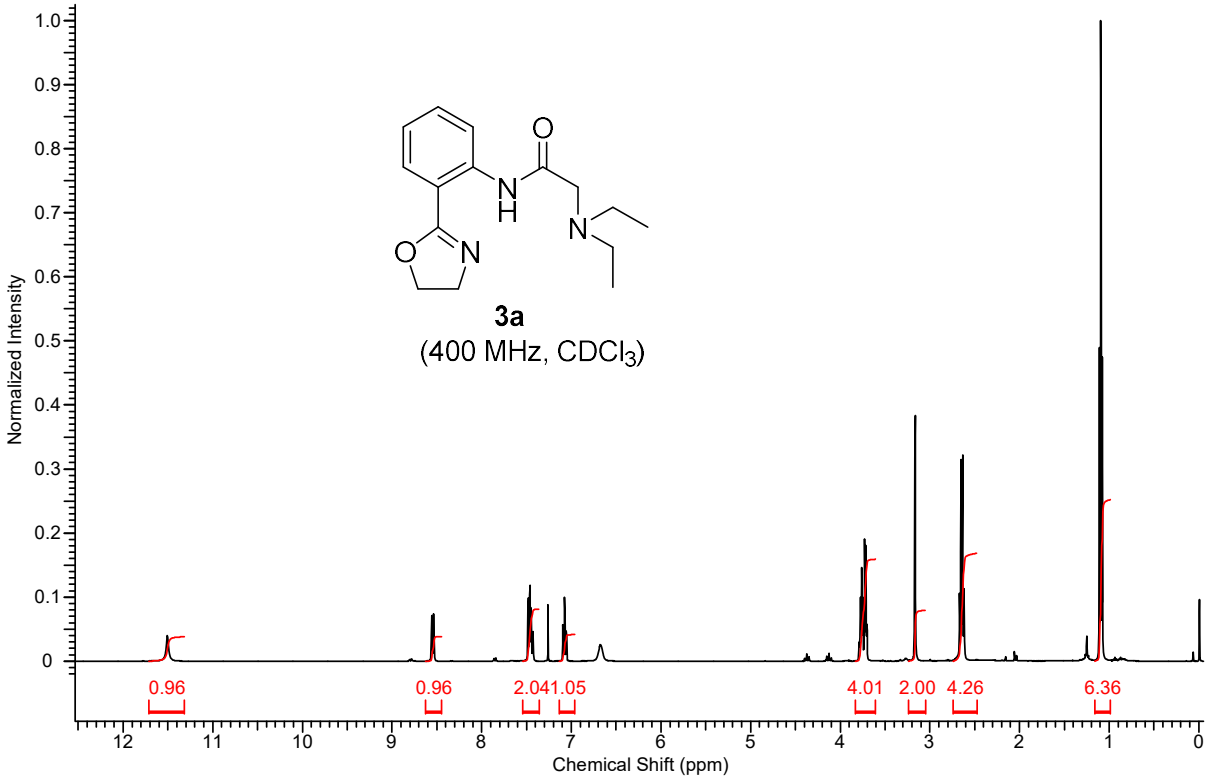
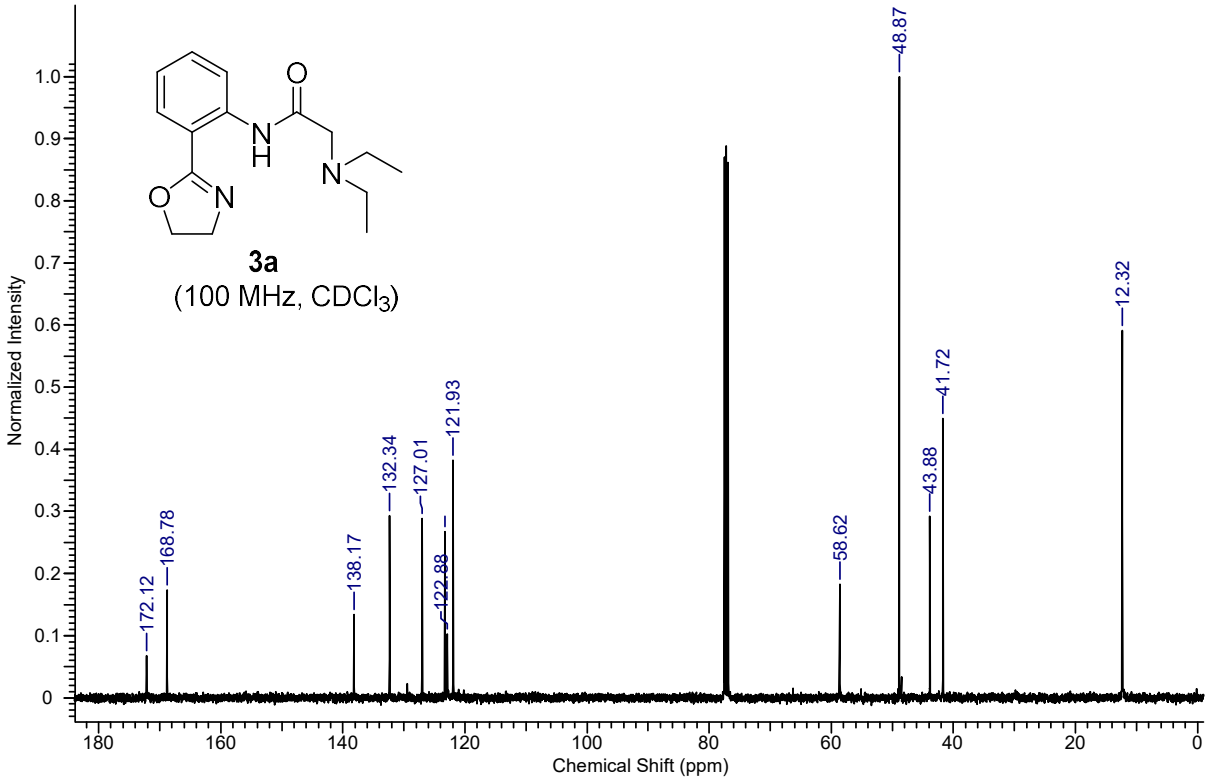
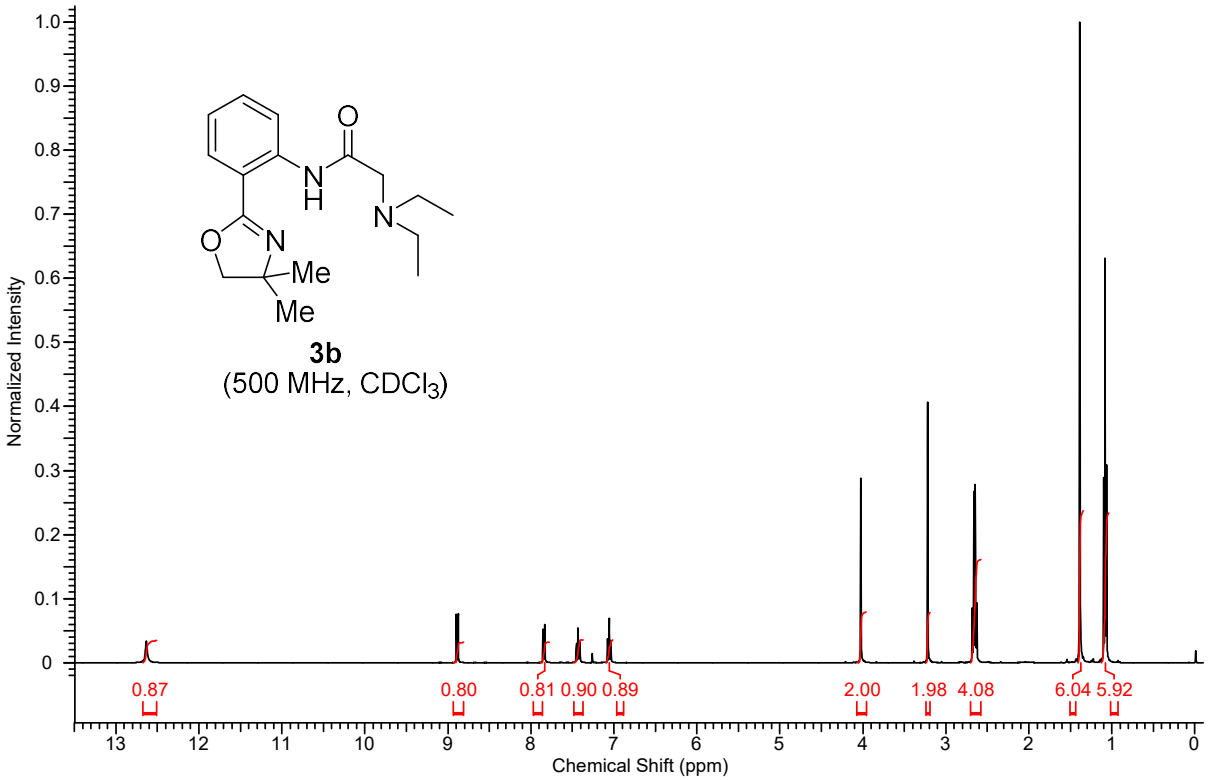
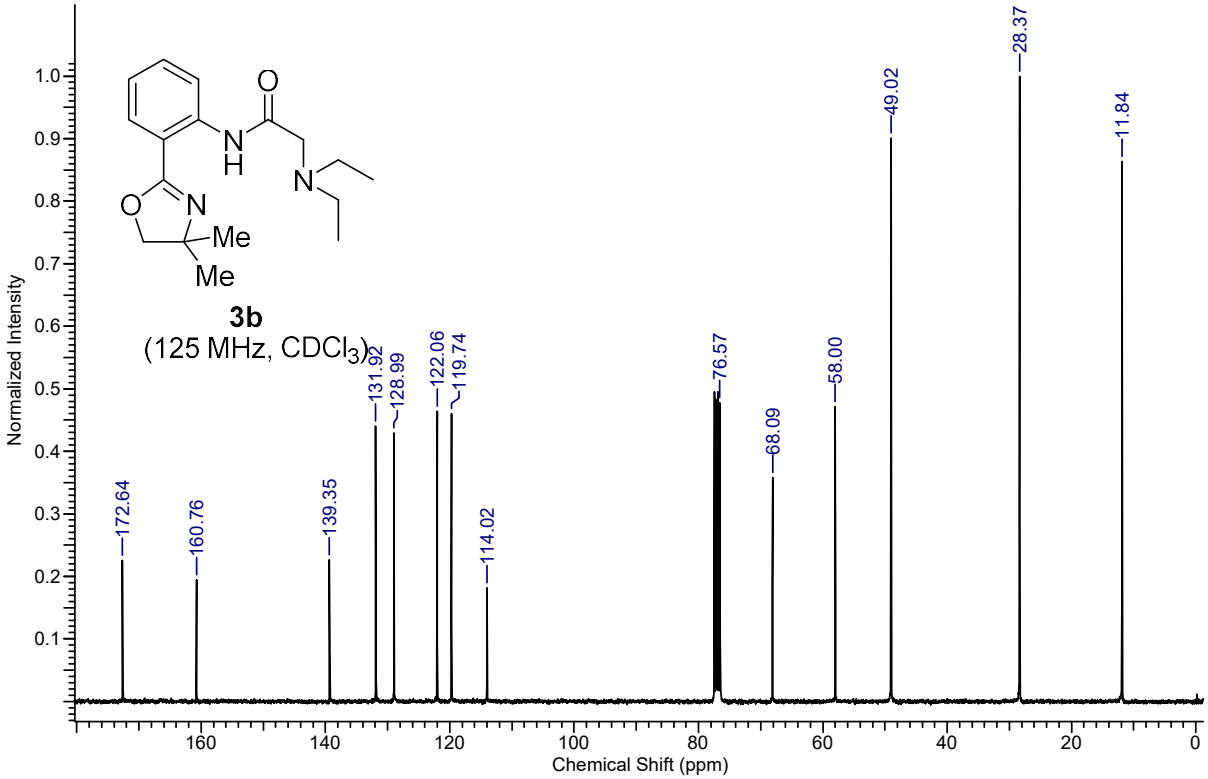
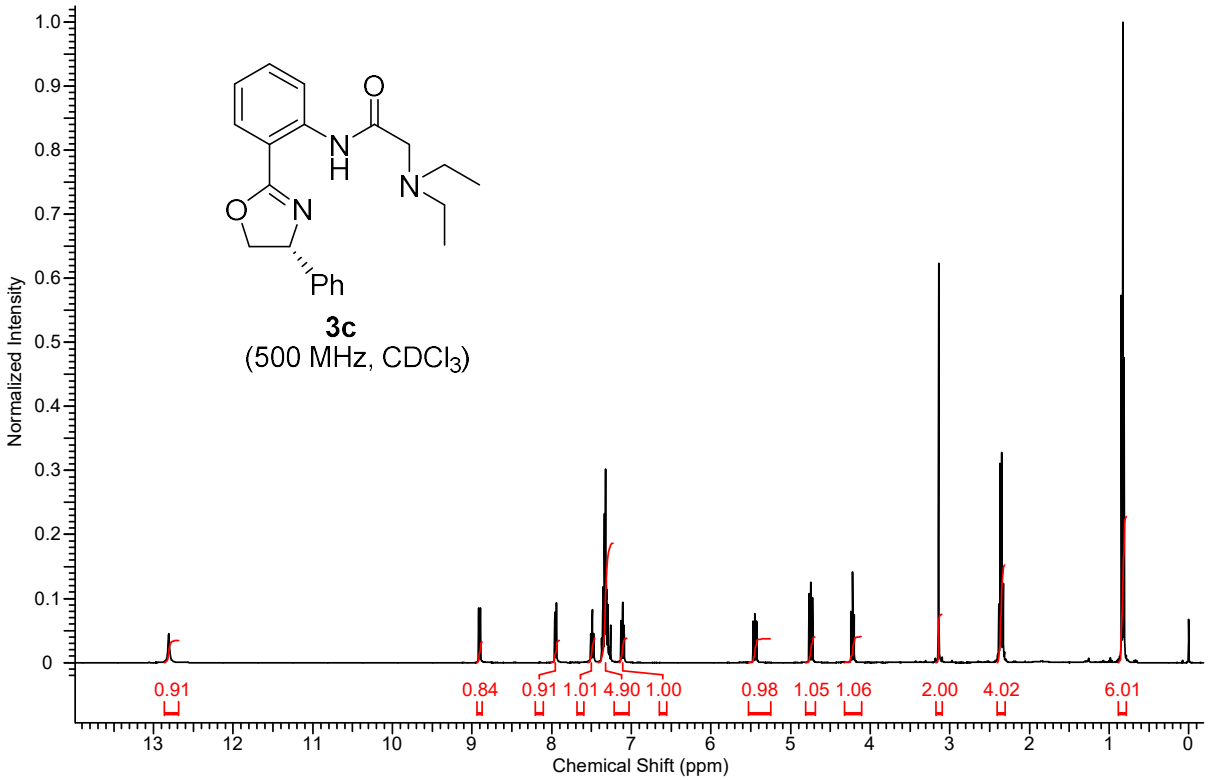
4. ^{1}H and ^{13}C NMR Spectra of Ligands

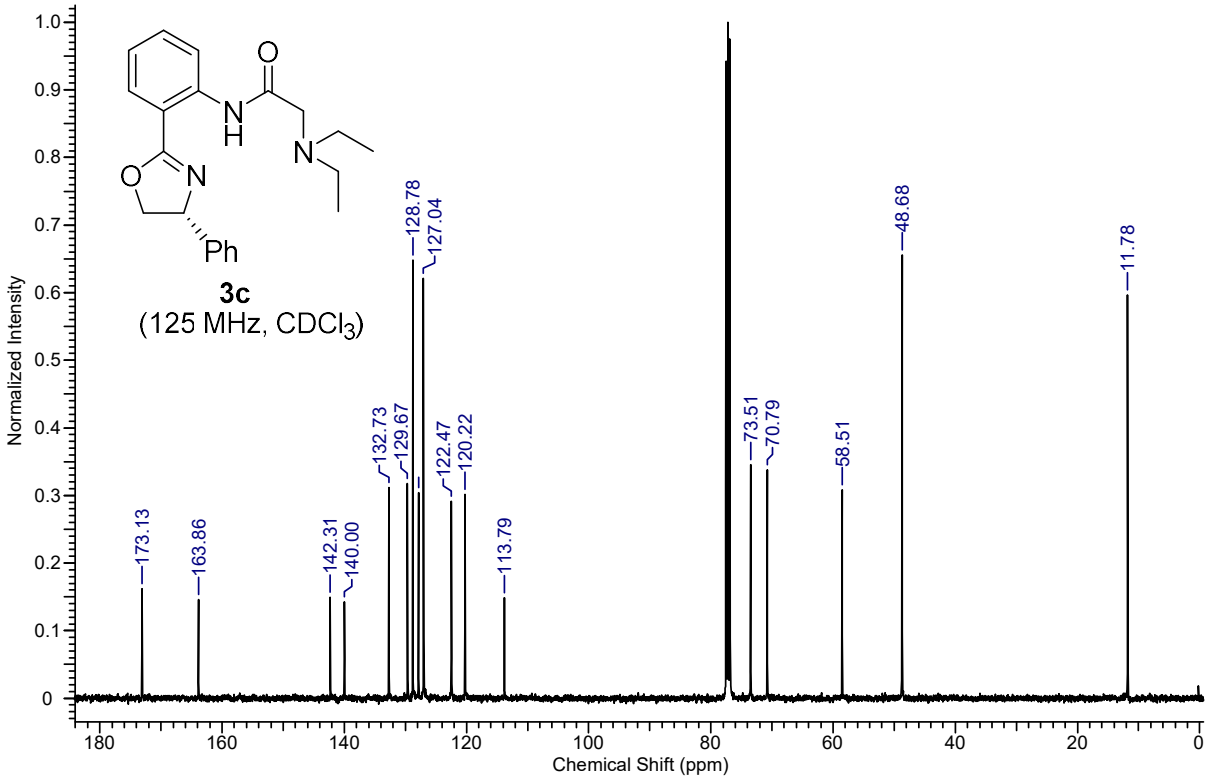


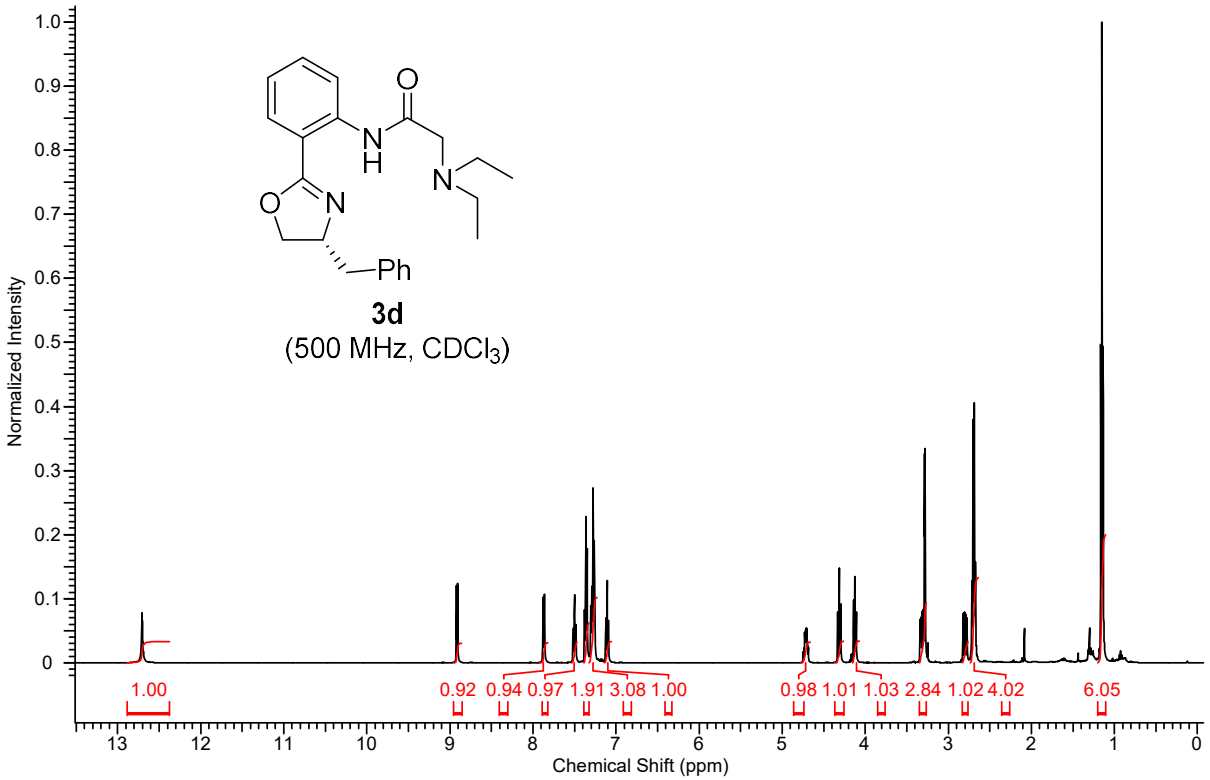


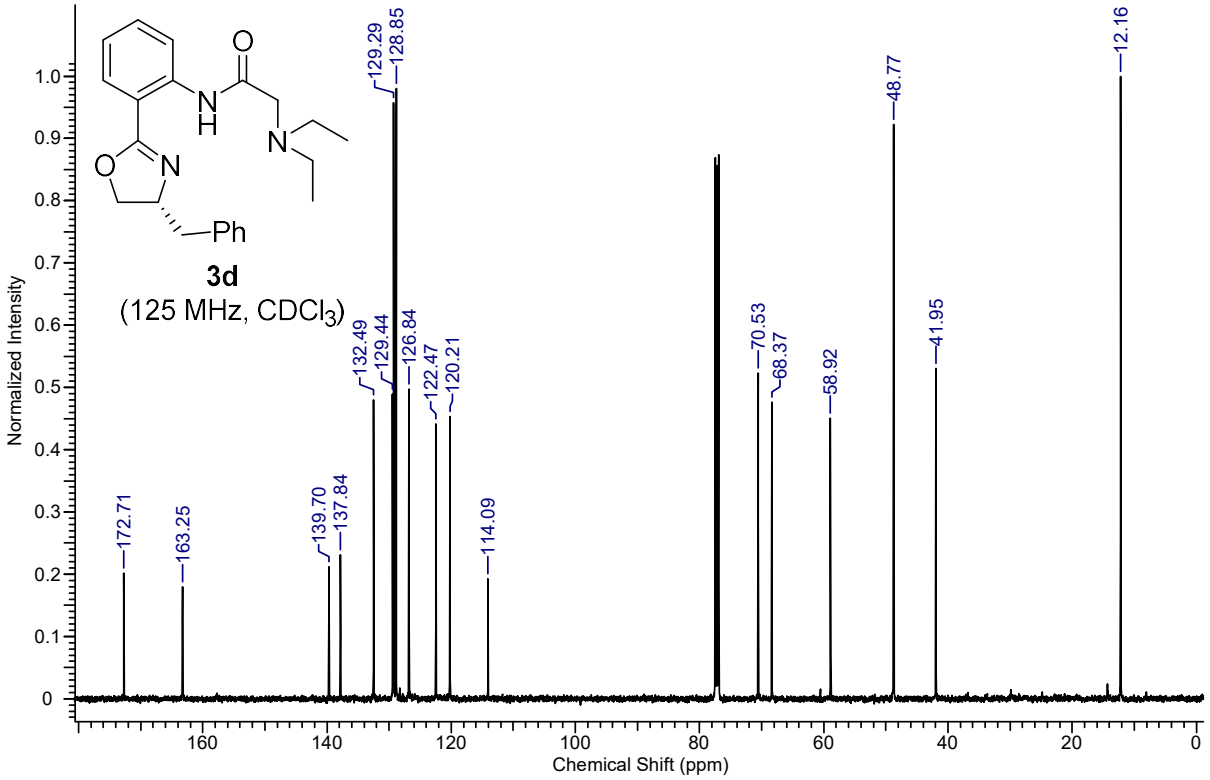

3b
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
0.87
0.80
0.81
0.90
0.89
2.00
1.98
4.08
6.04
5.92

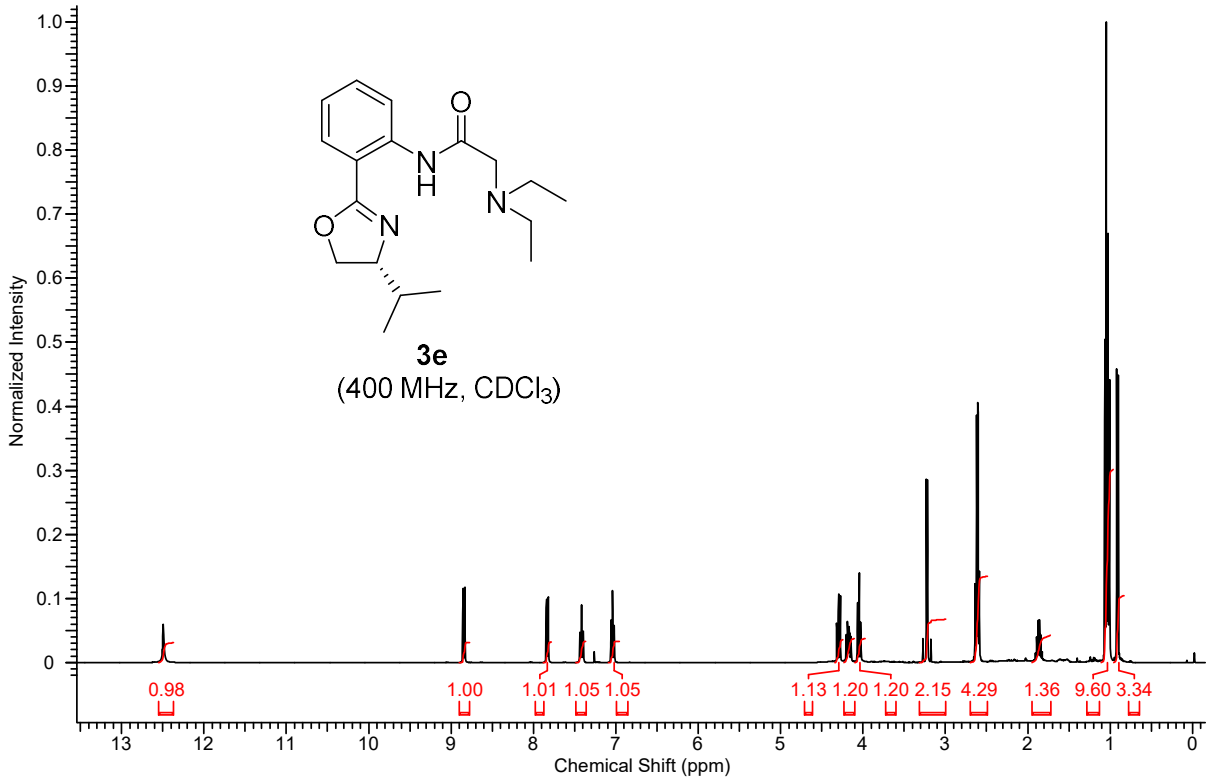

3b
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
172.64
160.76
139.35
131.92
128.99
122.06
119.74
114.02
76.57
68.09
58.00
49.02
28.37
11.84

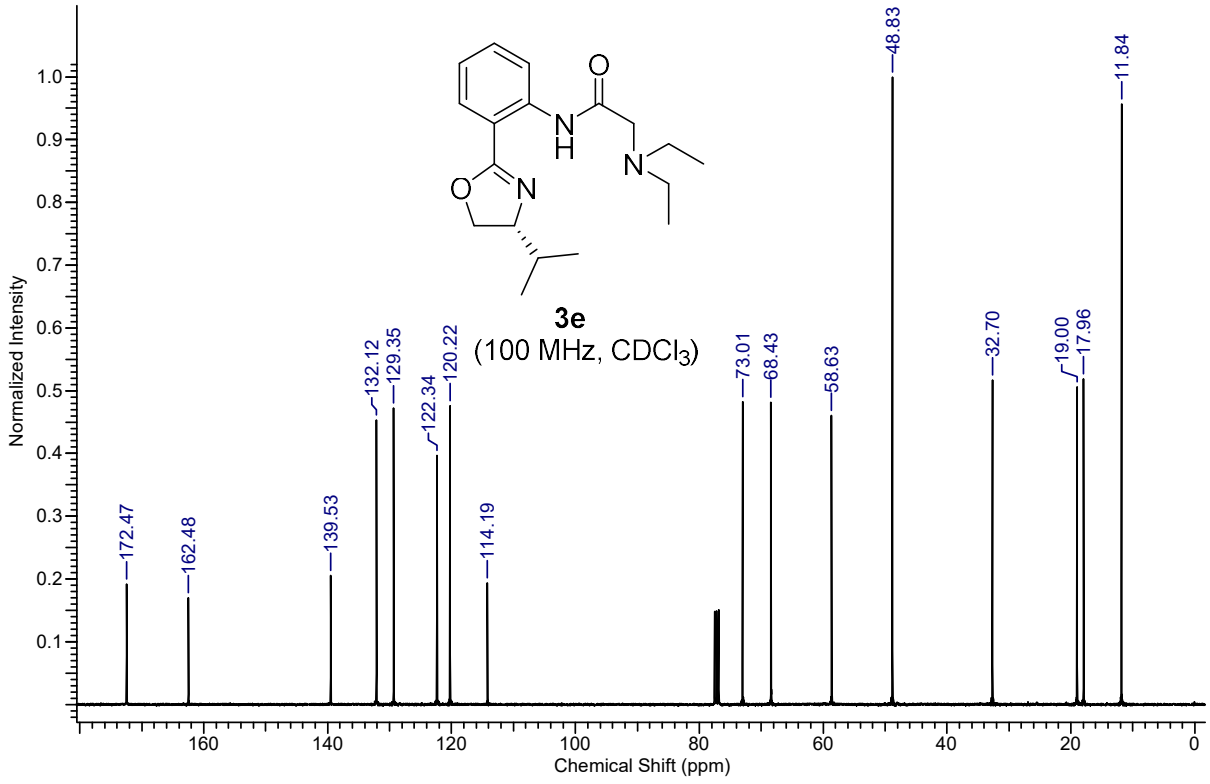

3c
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
0.91
0.84
0.91
1.01
4.90
1.00
0.98
1.05
1.06
2.00
4.02
6.01

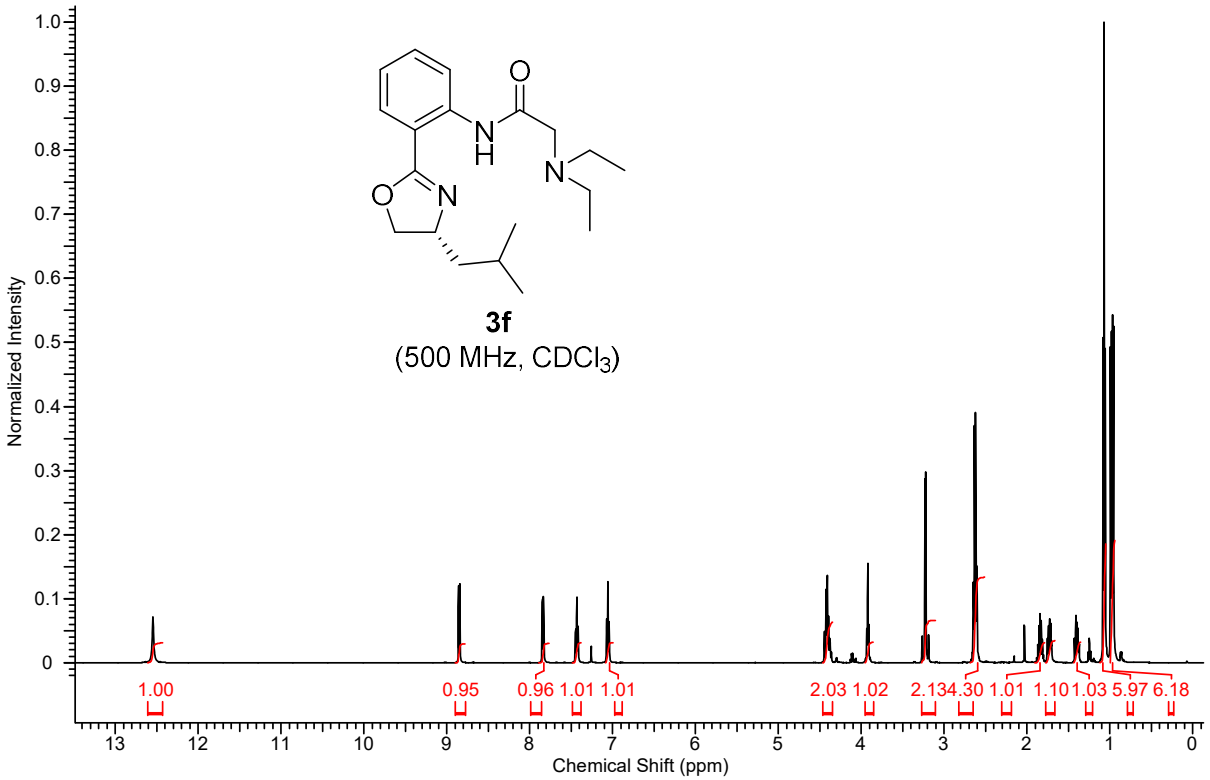

3c
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
173.13
163.86
142.31
140.00
132.73
129.67
128.78
127.04
122.47
120.22
113.79
73.51
70.79
58.51
48.68
11.78

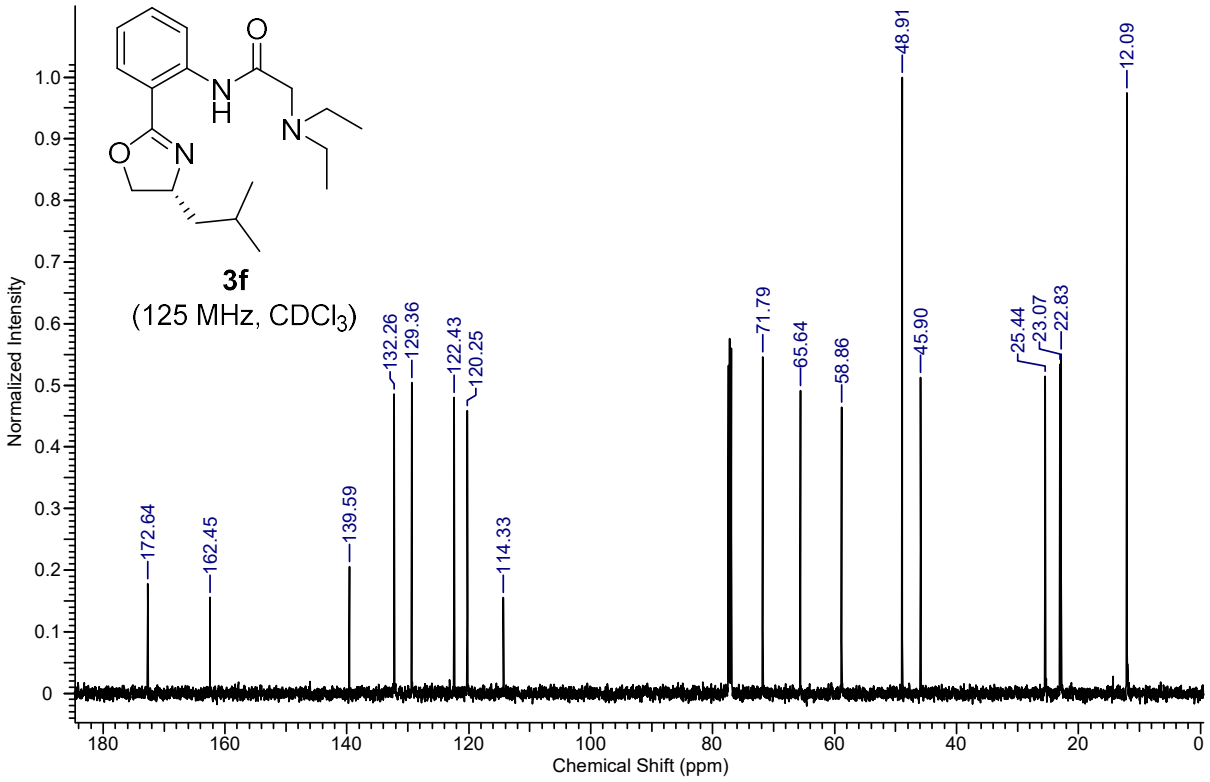

3d
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.00
0.92 0.94 0.97 1.91 3.08 1.00
0.98 1.01 1.03 2.84 1.02 4.02
6.05


3d
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
172.71
163.25
139.70
137.84
132.49
129.44
129.29
128.85
126.84
122.47
120.21
114.09
70.53
68.37
58.92
48.77
41.95
12.16

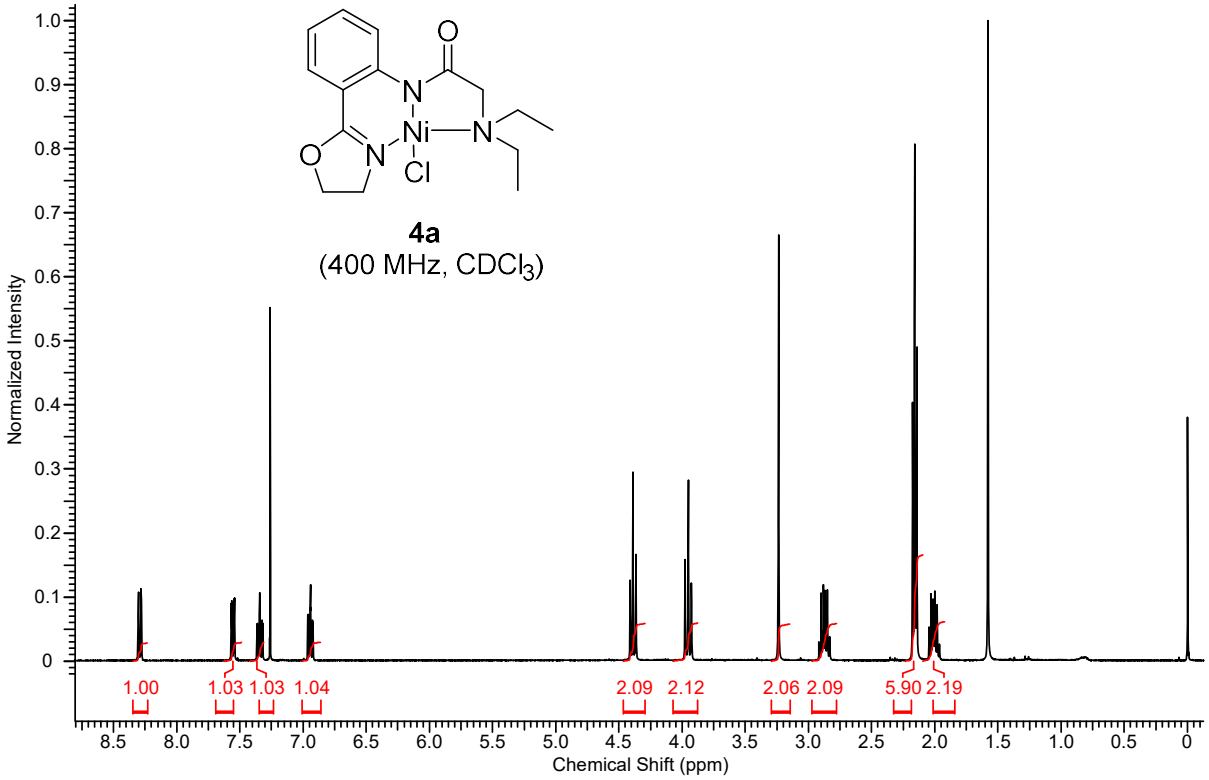

3e
(400 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
0.98
1.00
1.01
1.05
1.05
1.13
1.20
1.20
2.15
4.29
1.36
9.60
3.34

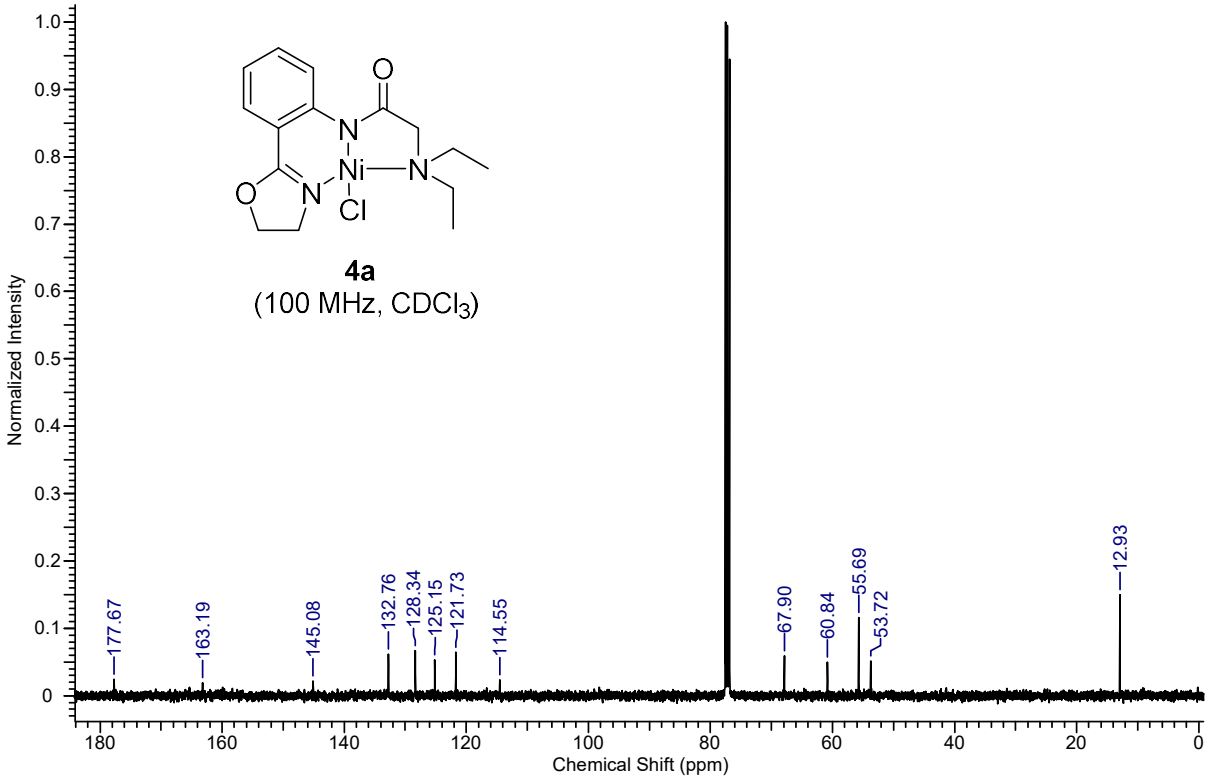

3e
(100 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
172.47
162.48
139.53
132.12
129.35
122.34
120.22
114.19
73.01
68.43
58.63
48.83
32.70
19.00
17.96
11.84

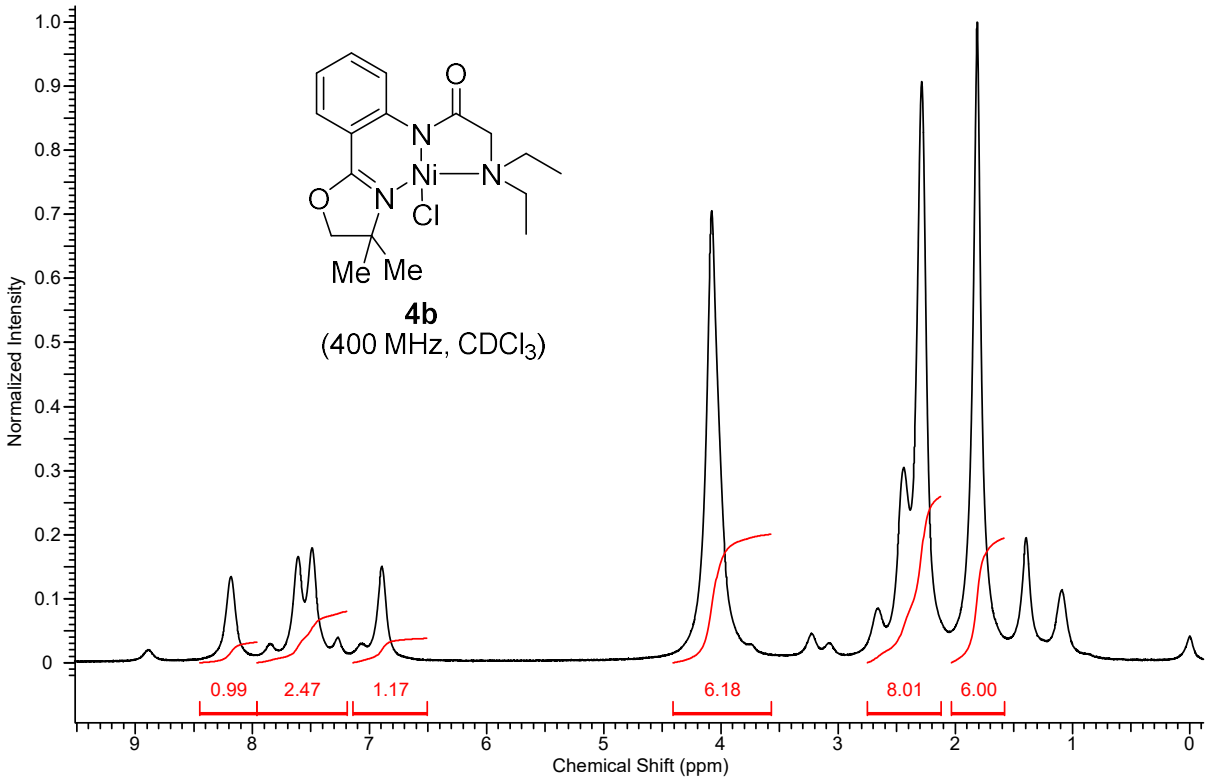

3f
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.00
0.95
0.96
1.01
1.01
2.03
1.02
2.13
4.30
1.01
1.10
1.03
5.97
6.18

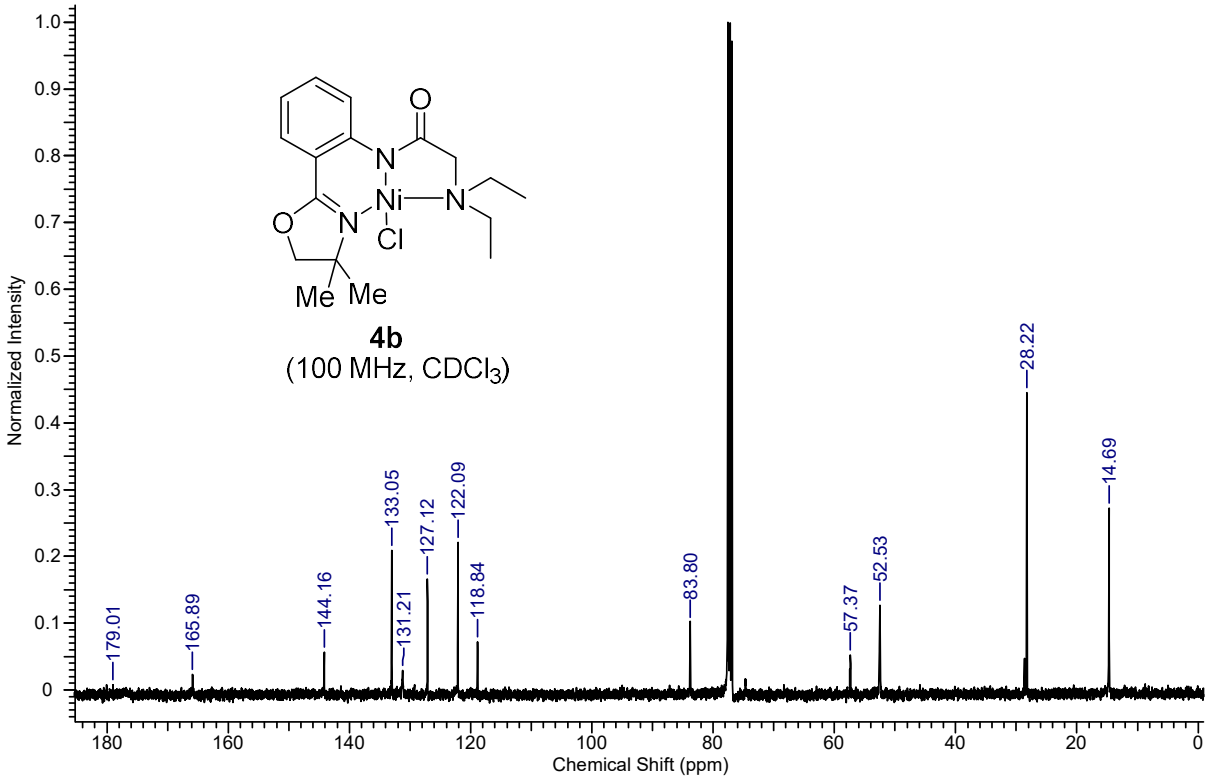

3f
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
172.64
162.45
139.59
132.26
129.36
122.43
120.25
114.33
71.79
65.64
58.86
48.91
45.90
25.44
23.07
22.83
12.09

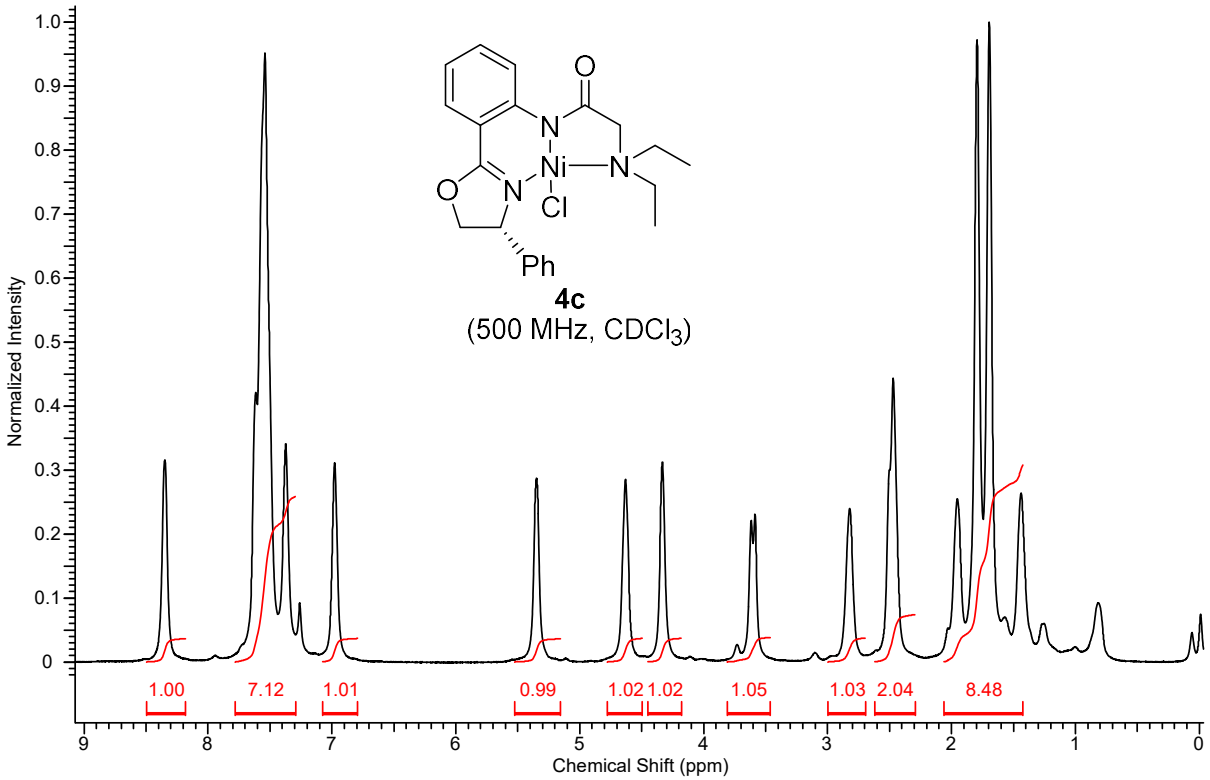
5. ^{1}H and ^{13}C NMR Spectra of Nickel Complexes

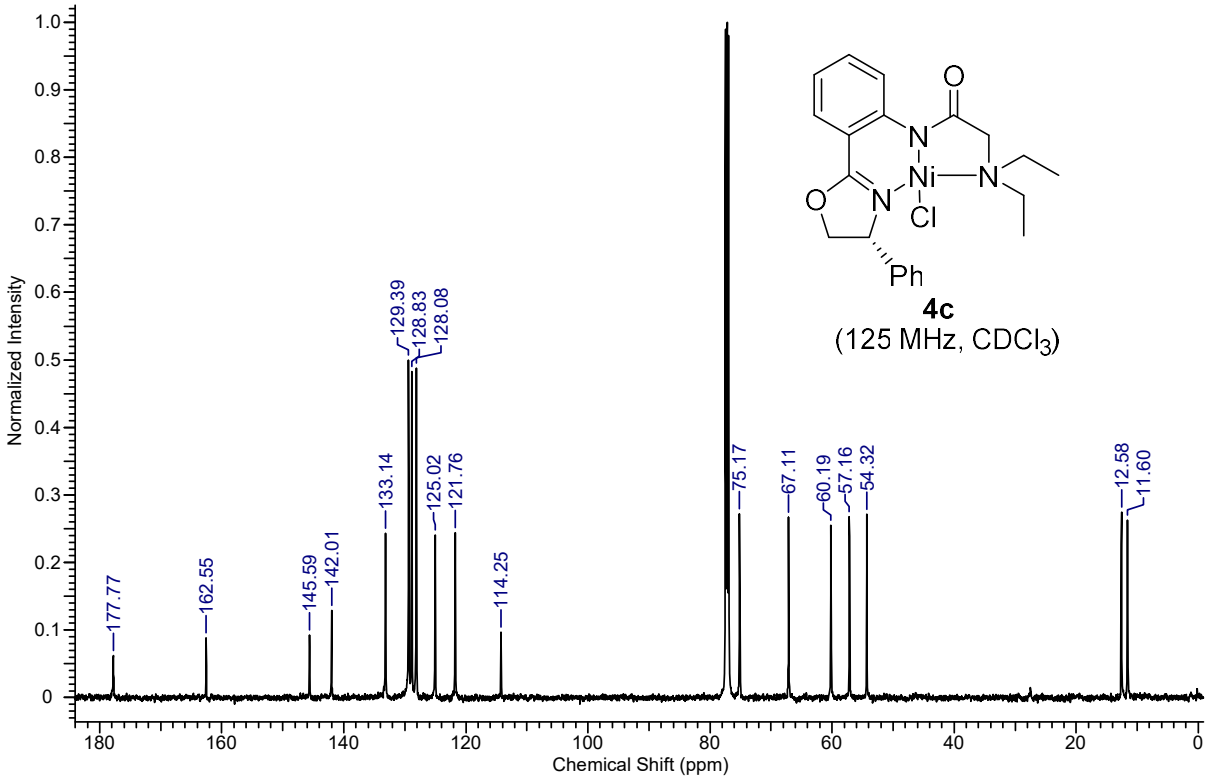


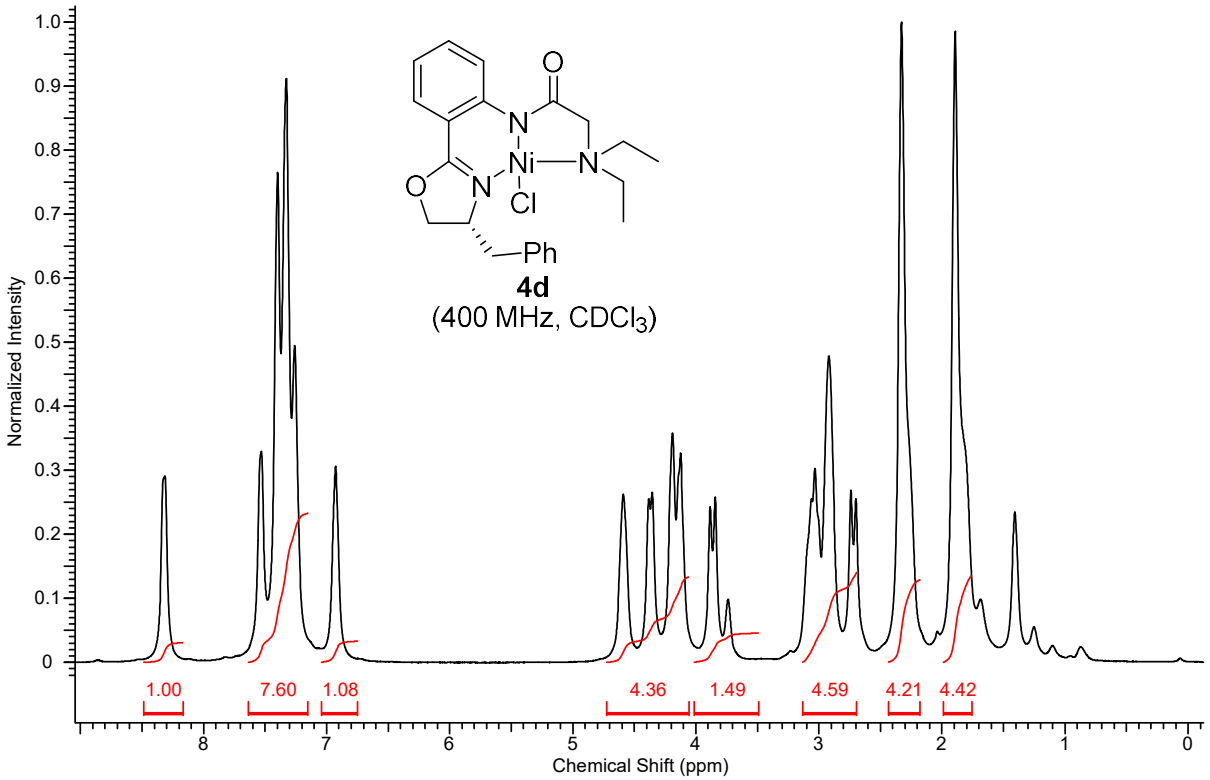


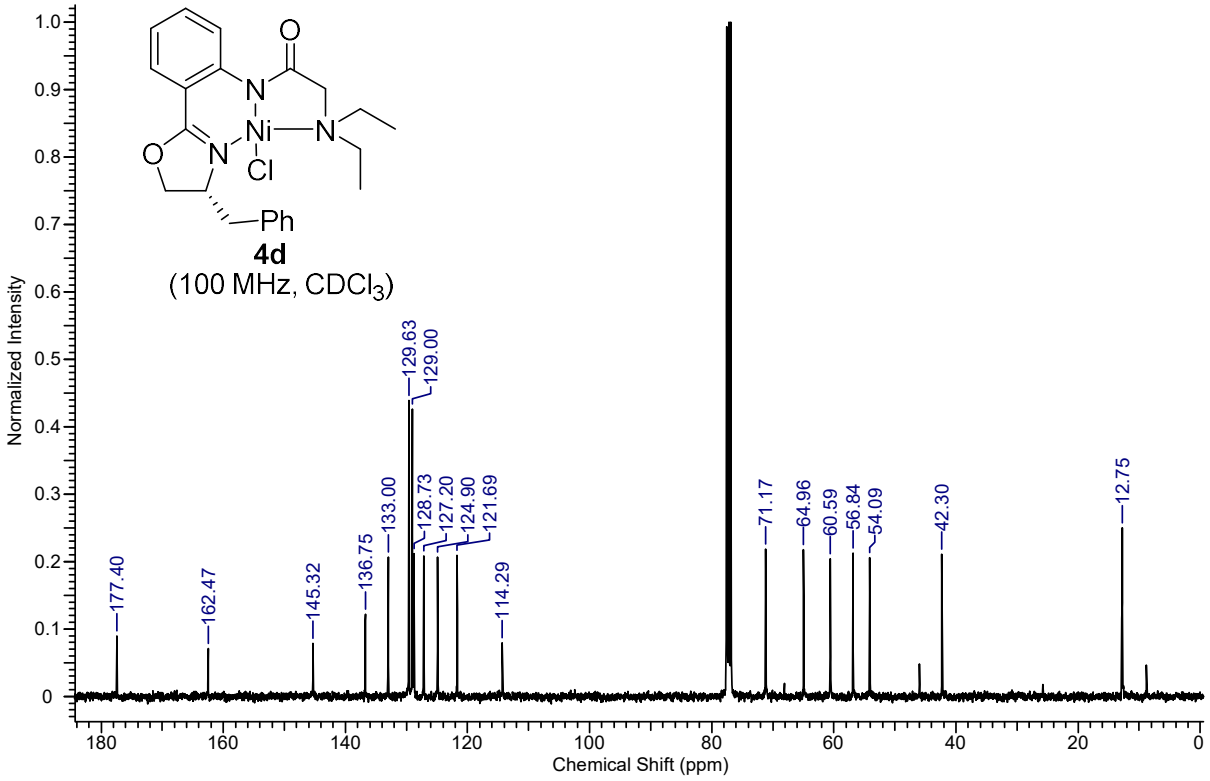

Normalized Intensity
Chemical Shift (ppm)
0.99
2.47
1.17
6.18
8.01
6.00
Me Me
4b
(400 MHz, CDCl3)

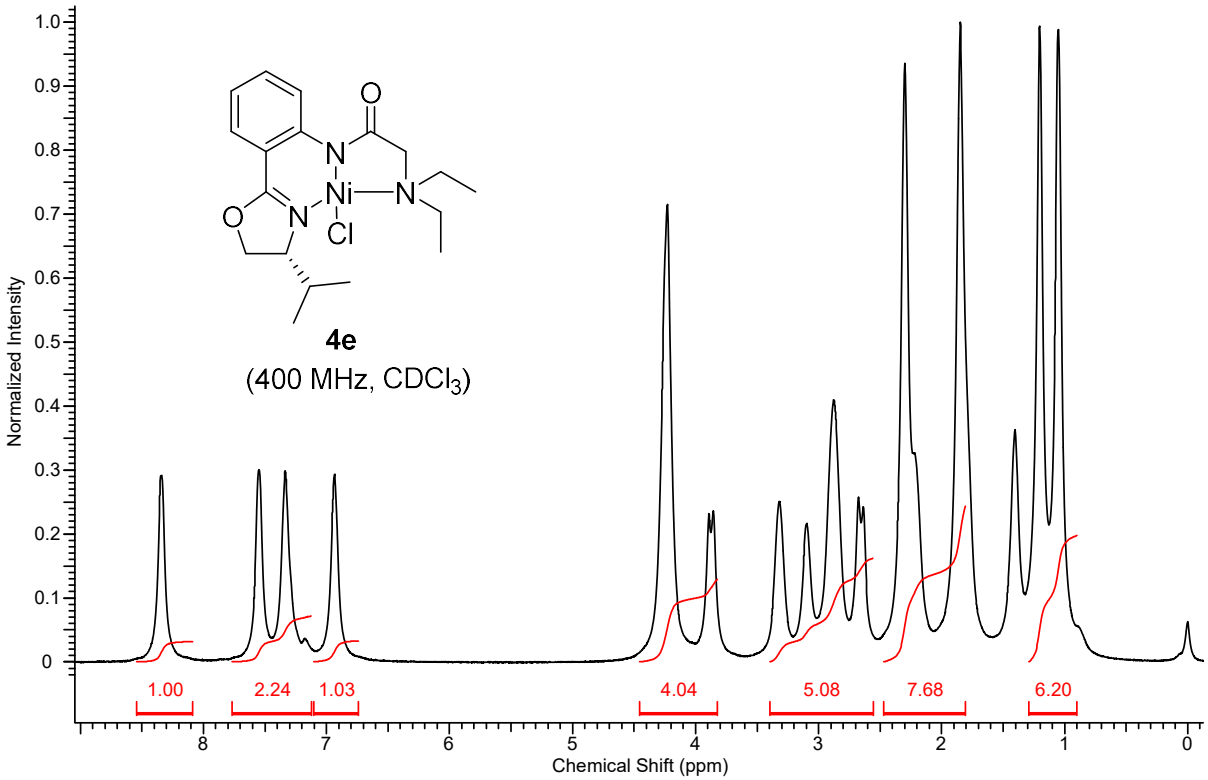

Normalized Intensity
Chemical Shift (ppm)
179.01
165.89
144.16
133.05
131.21
127.12
122.09
118.84
83.80
57.37
52.53
28.22
14.69
Me Me
4b
(100 MHz, CDCl3)

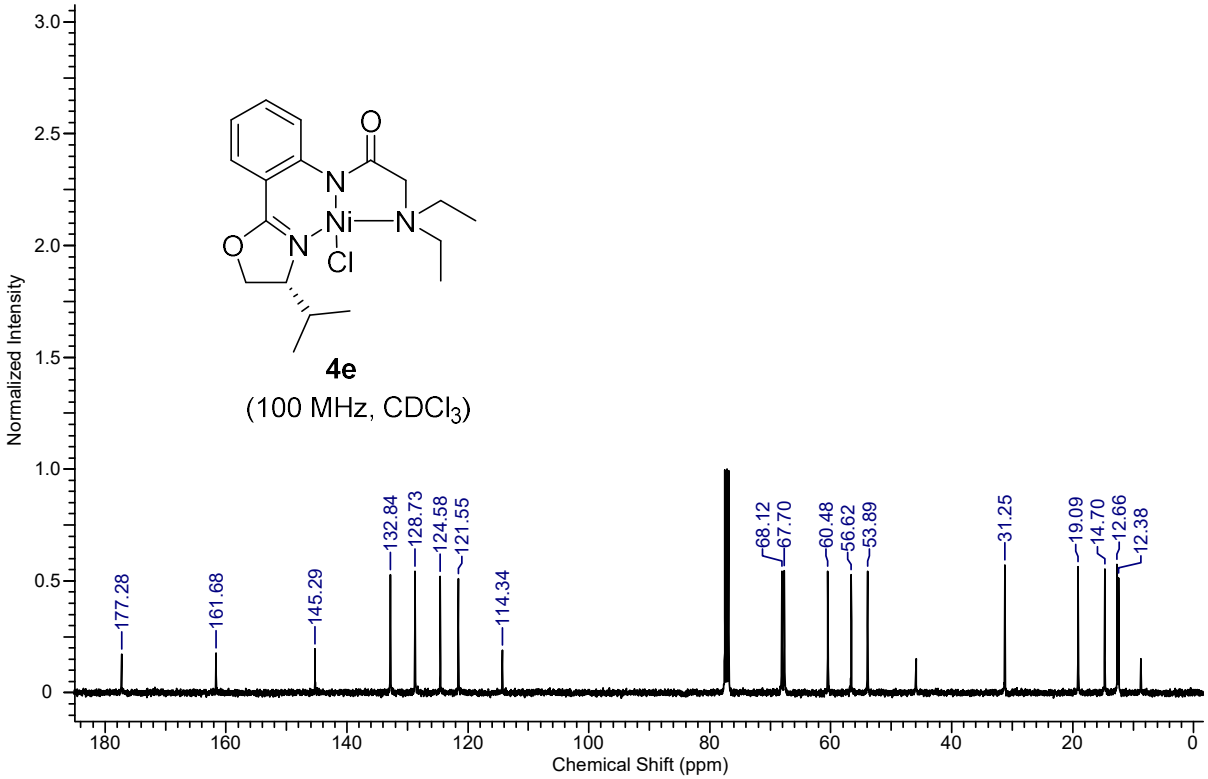

Normalized Intensity
Chemical Shift (ppm)
1.00
7.12
1.01
0.99
1.02
1.02
1.05
1.03
2.04
8.48
Ph
4c
(500 MHz, CDCl3)

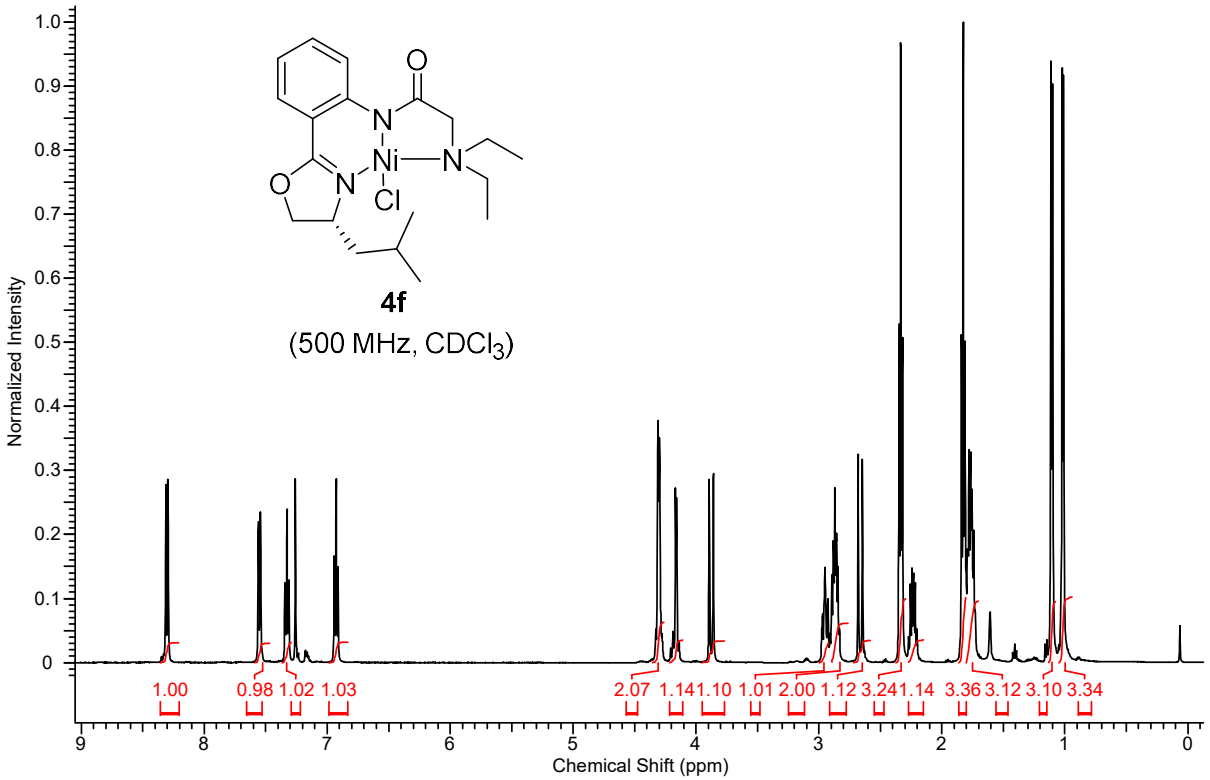

Normalized Intensity
Chemical Shift (ppm)
177.77
162.55
145.59
142.01
133.14
129.39
128.83
128.08
125.02
121.76
114.25
75.17
67.11
60.19
57.16
54.32
12.58
11.60
Ph
4c
(125 MHz, CDCl3)

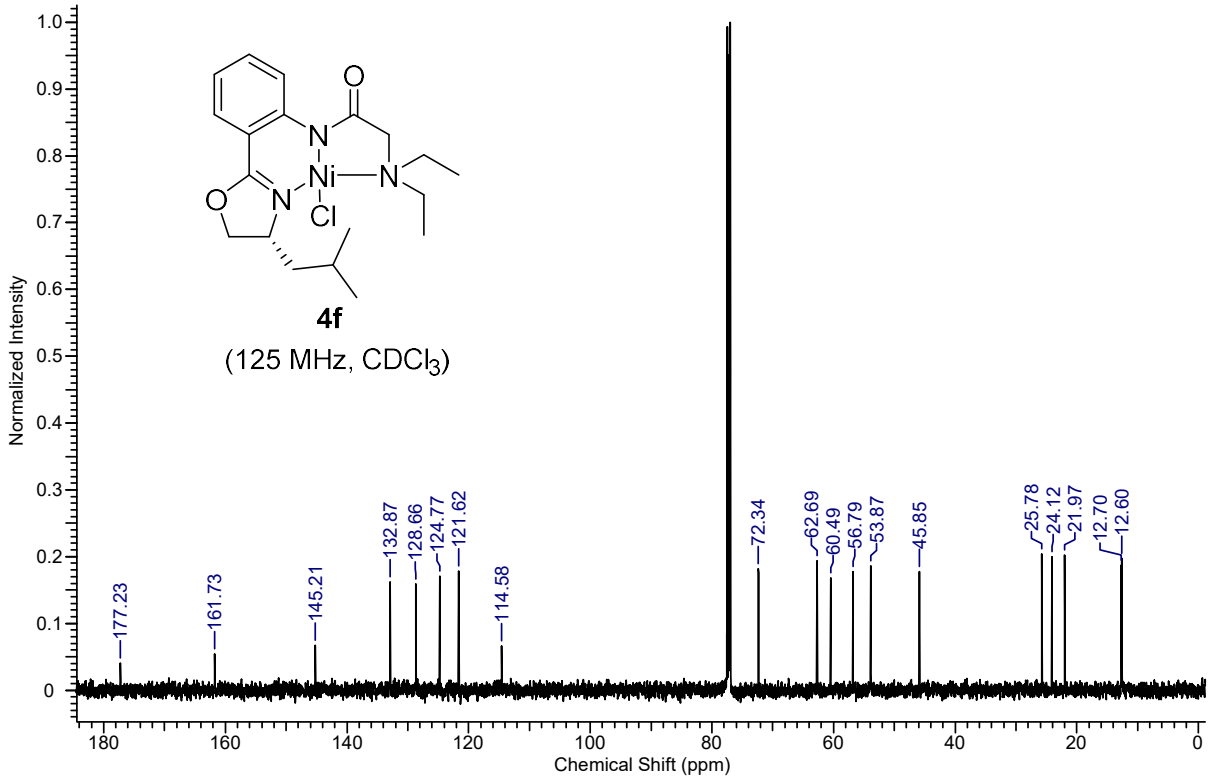

Normalized Intensity
Chemical Shift (ppm)
1.00
7.60
1.08
4.36
1.49
4.59
4.21
4.42
Ph
4d
(400 MHz, CDCl3)


Normalized Intensity
Chemical Shift (ppm)
177.40
162.47
145.32
136.75
133.00
129.63
129.00
128.73
127.20
124.90
121.69
114.29
71.17
64.96
60.59
56.84
54.09
42.30
12.75
Ph
4d
(100 MHz, CDCl3)


4e
(400 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.00
2.24
1.03
4.04
5.08
7.68
6.20


4e
(100 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
177.28
161.68
145.29
132.84
128.73
124.58
121.55
114.34
68.12
67.70
60.48
56.62
53.89
31.25
19.09
14.70
12.66
12.38


4f
(500 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.00
0.98
1.02
1.03
2.07
1.14
1.10
1.01
2.00
1.12
3.24
1.14
3.36
3.12
3.10
3.34


4f
(125 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
177.23
161.73
145.21
132.87
128.66
124.77
121.62
114.58
72.34
62.69
60.49
56.79
53.87
45.85
25.78
24.12
21.97
12.70
12.60

6. ^{1}H and ^{13}C NMR Spectra of 6a