Supporting Information for

New Catalyst Systems for Iron-catalyzed Hydrosilane Reduction of Carboxamides

Hironori Tsutsumi, [a] Yusuke Sunada[a,b] and Hideo Nagashima*[a,b]

[a] *Graduate School of Engineering Sciences, Kyushu University , 6-1 Kasugakoen, Kasuga, Fukuoka, 816-8580, Japan*

[b] *Institute for Materials Chemistry and Engineering, Kyushu University , 6-1 Kasugakoen, Kasuga, Fukuoka, 816-8580, Japan*

Contents

S-1. General Information

Manipulation of air and moisture sensitive organometallic compounds was carried out under a dry argon atmosphere using standard Schlenk tube techniques associated with a high-vacuum line or in the glove box under dry nitrogen atmosphere. All solvents were distilled over Ph_2CO/Na prior to use. ^{1}H, ^{13}C, ^{29}Si, ^{195}Pt NMR spectra were recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature unless otherwise noted. ^{1}H, ^{13}C NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^{1}H, ^{13}C). Elemental analyses were performed by a Perkin Elmer 2400II/CHN analyzer. IR spectra were recorded on a JASCO FT/IR-550 spectrometer. Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F_{254}, layer thickness 0.25 and 0.2 mm, respectively). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid. 1,2-bis(dimethylsilyl)benzene[1], $(Me_2SiC_6H_4SiMe_2)Fe(CO)_4$ (**2**)[2], and all carboxamides[3] were synthesized by the method reported in the literature.

S-2. Synthesis of $[Fe_3(H)(CO)_{11}]_2\{Fe(DMF)_4\}$ (4).

In a glove box, $Fe(CO)_5$ (1050 μL, 8 mmol) was dissolved in toluene (4 mL), and dimethylformamide (6.4 mL, 80 mmol) was added to this solution at room temperature. The resulting mixture was stirred at 65 ^{o}C for 4 days during which time the color of the solution changed from yellow to red-violet. The solvent was removed under vacuum, and the residue was washed with cold ether (3 mL x 2) and pentane (5 mL) to afford **4** as red-violet powder (720 mg, 48 %). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from ether/pentane as dark red-violet crystals. For brief summary of X-ray crystallographic analysis, see **S-4.** UV (dioxane): λ_{max} = 499 nm, ε = 4960 $L{\cdot}mol^{-1}{\cdot}cm^{-1;}$ IR (KBr): $\nu_{C\equiv O}$ = 2070-1950 cm^{-1}, $\nu_{C=O}$ = 1592 cm^{-1}, $\nu_{C=O}$ = 1654 cm^{-1}; Anal calcd for $C_{34}H_{30}Fe_7N_4O_{26}$ C 31.38, H 2.32, N 4.30; found: C 31.91, H 1.97, N 4.52.

S-3. General Procedure for the Reduction of Carboxamides:

S-3-1. Reduction of carboxamides with BDSB catalyzed by 4 (0.5 mol% for Fe).

In a 20 mL Schlenk tube, **4** (0.9 mg, 6.9 x 10^{-4} mmol, 0.5 mol% for Fe) was dissolved in the mixture of toluene (0.5 mL) and carboxamide **1** (1 mmol), and 1,2-bis(dimethylsilyl)benzene (BDSB: 475 μL, 2.2 mmo) was added to this solution. The solution was stirred at 100 °C for 0.5 - 3 h. After complete consumption of **1** was confirmed by TLC analysis, the reaction mixture was passed through a Florisil® column with Celite putting on the head. After removal of the solvent, purification of the residue by alumina column chromatography gave the amine **2**.

S-3-2. A Procedure for Gram-Scale Production of Amine 2a.

In a 20 mL Schlenk tube, **4** (9.3 mg, 6.9 x 10^{-3} mmol, 0.5 mol% for Fe) was dissolved in the mixture of toluene (5 mL) and **1a** (1.79g, 10 mmol), and 1,2-bis(dimethylsilyl)benzene (BDSB: 4750 μL, 2.2 mmo) was added to this solution. This solution was heated at 100 ^{o}C for 50 min, then the resultant mixture was diluted

with Et_2O (20 mL). The solution was washed with HCl (1M, 20 mL), and the aqueous layers were treated with NaOH aq. The mixture was extracted two times with ether (30 mL in total). The combined extracts were dried over $MgSO_4$, and dried to afford the corresponding amine **2a** in 95 % yield (1.57 g, 9.5 mmol). ICP-mass analysis of this product revealed that the extracted amine contained approximately 0.7 ppm of iron species. In other words, over 99.6 % of the charged iron species was removed by this simple purification procedure.

S-4. X-ray data collection and reduction

Single crystals of **4** were grown from ether/pentane. X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71070A). The data were collected at 123(2) K using ω scan in the θ range of $3.0 \leq \theta \leq 27.5$ deg. The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer, and were corrected for Lorentz and polarization effects. The structure was solved by direct methods[4], and expanded using Fourier techniques.[5] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model except for the hydride atoms**.** The hydride atom in **4** was detected from the Fourier map, and refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 5,478 observed reflections and 340 variable parameters for **4**. Neutral atom scattering factors were taken from Cromer and Waber.[6] All calculations were performed using the CrystalStructure[7,8] crystallographic software package. Details of final refinement as well as the bond distances and angles are summarized in the table shown below, and the numbering scheme employed is also shown below, which was drawn with ORTEP at 50% probability ellipsoid.

S-4-1. ORTEP drawing of **4** with 50 % probability ellipsoid.

Table S4-1. Crystal data and structure refinement for **4**

Empirical Formula	$C_{34}H_{30}Fe_7N_4O_{26}$
Formula Weight	1301.55
Crystal Color, Habit	purple red, block
Temperature	-160.0 °C
Radiation	MoKα (λ = 0.71070 Å)
	graphite monochromated
Crystal System	triclinic
Space Group	P-1 (#2)
Lattice Parameters	a = 9.979(5) Å
	b = 11.850(3) Å
	c = 11.906(5) Å
	α = 76.2(2) °
	β = 73.60(12) °
	γ = 66.89(8) °
Volume	1229.2(13) Å^3
Z value	1
D_{calc}	1.758 g/cm^3
F_{000}	652.00
Crystal Dimensions	0.100 X 0.100 X 0.080 mm
Theta range for data collection	3.2 to 27.5 °
No. Observations (All reflections)	5478
No. Variables	340
Refinement	Full-matrix least-squares on F^2
Goodness of fit on F^2	1.002
Residuals: R_1 (I>2.00σ(I))	R_1 = 0.0247
Residuals: R (All reflections)	R = 0.0255
R indices (All data)	wR_2 = 0.0989
Largest diff. peak and hole	0.92 e/Å^3 and -0.42 e/Å^3

Table S4-2. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
Fe1	0.5000	1.0000	0.0000	1.224(6)	1/2
Fe2	0.59425(2)	0.81770(2)	0.39791(2)	1.383(6)	1
Fe3	0.63645(2)	0.63533(2)	0.29237(2)	1.467(6)	1
Fe4	0.87379(2)	0.68252(2)	0.30672(2)	1.477(6)	1
O1	0.55747(12)	0.88217(11)	0.15463(9)	2.25(3)	1
O2	0.67425(13)	1.03943(10)	0.30166(11)	2.44(3)	1
O3	0.27295(13)	0.95051(12)	0.44755(11)	2.78(3)	1
O4	0.6488(2)	0.7678(2)	0.64010(11)	3.57(3)	1
O5	0.8101(2)	0.57588(13)	0.05833(11)	3.35(3)	1
O6	0.3511(2)	0.6620(2)	0.24882(13)	3.58(3)	1
O7	0.6878(2)	0.37841(11)	0.41905(12)	3.11(3)	1
O8	0.8830(2)	0.86234(13)	0.08674(11)	3.21(3)	1
O9	1.15016(13)	0.50075(11)	0.19714(11)	2.69(3)	1
O10	1.0068(2)	0.78739(12)	0.42726(13)	3.20(3)	1
O11	0.8305(2)	0.51114(11)	0.52555(10)	2.60(3)	1
O12	0.60035(12)	1.11775(10)	0.01690(9)	1.85(2)	1
O13	0.30241(11)	1.10657(9)	0.10222(9)	1.72(2)	1
N1	0.6194(2)	1.27594(12)	0.07715(12)	2.05(3)	1
N2	0.0829(2)	1.13871(11)	0.23425(11)	1.82(3)	1
C1	0.5884(2)	0.80959(13)	0.24093(12)	1.48(3)	1
C2	0.6453(2)	0.9514(2)	0.34268(13)	1.84(3)	1
C3	0.3993(2)	0.8975(2)	0.43129(12)	1.89(3)	1
C4	0.6281(2)	0.7830(2)	0.54788(13)	2.19(3)	1
C5	0.7449(2)	0.5994(2)	0.1508(2)	2.17(3)	1
C6	0.4619(2)	0.6503(2)	0.2677(2)	2.23(3)	1
C7	0.6716(2)	0.4781(2)	0.3741(2)	2.13(3)	1
C8	0.8725(2)	0.7942(2)	0.1720(2)	2.10(3)	1
C9	1.0400(2)	0.5689(2)	0.24000(13)	1.97(3)	1
C10	0.9547(2)	0.74876(13)	0.3790(2)	2.05(3)	1
C11	0.8371(2)	0.5781(2)	0.4383(2)	1.99(3)	1
C12	0.5431(2)	1.2108(2)	0.06758(13)	1.82(3)	1
C13	0.7784(2)	1.2392(2)	0.0291(2)	3.07(4)	1
C14	0.5501(3)	1.3810(2)	0.1422(3)	4.01(5)	1
C15	0.2062(2)	1.06837(13)	0.17193(13)	1.83(3)	1
C16	0.0531(2)	1.2698(2)	0.2260(2)	3.03(4)	1
C17	-0.0220(2)	1.0885(2)	0.3217(2)	3.15(4)	1

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S4-3. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}	occ
H1	0.575(3)	0.684(2)	0.424(2)	2.6(4)	1

Table S4-4. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.0172(2)	0.0148(2)	0.0140(2)	-0.00444(11)	-0.00343(11)	-0.00284(11)
Fe2	0.01606(13)	0.01801(13)	0.01697(13)	-0.00374(9)	-0.00405(9)	-0.00297(9)
Fe3	0.01809(13)	0.0206(2)	0.01779(13)	-0.00778(10)	-0.00242(9)	-0.00398(9)
Fe4	0.01528(13)	0.01810(13)	0.02108(13)	-0.00431(9)	-0.00466(9)	-0.00150(9)
O1	0.0256(6)	0.0352(6)	0.0213(5)	-0.0105(5)	-0.0098(5)	0.0078(5)
O2	0.0317(6)	0.0260(6)	0.0379(6)	-0.0128(5)	-0.0063(5)	-0.0065(5)
O3	0.0187(6)	0.0434(7)	0.0362(7)	-0.0034(5)	-0.0036(5)	-0.0082(6)
O4	0.0487(8)	0.0524(8)	0.0271(6)	-0.0012(7)	-0.0170(6)	-0.0104(6)
O5	0.0493(8)	0.0502(8)	0.0272(6)	-0.0183(7)	0.0040(6)	-0.0172(6)
O6	0.0307(7)	0.0582(9)	0.0571(9)	-0.0213(7)	-0.0161(6)	-0.0084(7)
O7	0.0433(8)	0.0247(6)	0.0465(8)	-0.0157(6)	-0.0047(6)	0.0019(6)
O8	0.0254(6)	0.0475(7)	0.0359(7)	-0.0112(6)	-0.0060(5)	0.0147(6)
O9	0.0262(6)	0.0296(6)	0.0410(7)	-0.0030(5)	-0.0013(5)	-0.0138(5)
O10	0.0477(8)	0.0303(7)	0.0534(8)	-0.0125(6)	-0.0258(7)	-0.0077(6)
O11	0.0294(6)	0.0317(6)	0.0333(6)	-0.0103(5)	-0.0138(5)	0.0114(5)
O12	0.0245(6)	0.0241(5)	0.0255(5)	-0.0108(5)	-0.0040(4)	-0.0078(5)
O13	0.0184(5)	0.0210(5)	0.0231(5)	-0.0052(4)	0.0002(4)	-0.0062(4)
N1	0.0244(7)	0.0277(7)	0.0297(7)	-0.0127(6)	-0.0024(5)	-0.0088(6)
N2	0.0197(6)	0.0244(6)	0.0236(6)	-0.0095(5)	0.0001(5)	-0.0034(5)
C1	0.0152(6)	0.0224(7)	0.0176(6)	-0.0061(5)	-0.0025(5)	-0.0027(5)
C2	0.0189(7)	0.0250(7)	0.0262(7)	-0.0039(6)	-0.0069(6)	-0.0081(6)
C3	0.0236(7)	0.0267(7)	0.0205(7)	-0.0079(6)	-0.0036(6)	-0.0042(6)
C4	0.0259(8)	0.0285(8)	0.0245(7)	-0.0019(6)	-0.0080(6)	-0.0060(6)
C5	0.0285(8)	0.0291(8)	0.0259(8)	-0.0109(7)	-0.0035(6)	-0.0073(6)
C6	0.0292(8)	0.0296(8)	0.0286(8)	-0.0123(7)	-0.0053(6)	-0.0065(6)
C7	0.0233(7)	0.0283(8)	0.0290(8)	-0.0093(6)	-0.0006(6)	-0.0091(7)
C8	0.0147(7)	0.0309(8)	0.0295(8)	-0.0042(6)	-0.0043(6)	-0.0025(6)
C9	0.0248(8)	0.0234(7)	0.0287(8)	-0.0098(6)	-0.0065(6)	-0.0040(6)
C10	0.0249(7)	0.0190(7)	0.0321(8)	-0.0038(6)	-0.0100(6)	-0.0020(6)
C11	0.0182(7)	0.0235(7)	0.0322(8)	-0.0043(6)	-0.0076(6)	-0.0036(6)
C12	0.0212(7)	0.0251(7)	0.0242(7)	-0.0100(6)	-0.0034(6)	-0.0045(6)
C13	0.0247(8)	0.0497(11)	0.0494(11)	-0.0201(8)	-0.0013(8)	-0.0159(9)
C14	0.0451(12)	0.0482(12)	0.071(2)	-0.0240(10)	0.0055(10)	-0.0389(12)
C15	0.0242(7)	0.0192(7)	0.0257(7)	-0.0075(6)	-0.0049(6)	-0.0029(6)
C16	0.0330(9)	0.0280(8)	0.0474(10)	-0.0111(7)	0.0090(8)	-0.0136(8)
C17	0.0284(9)	0.0460(10)	0.0419(10)	-0.0204(8)	0.0063(8)	-0.0039(8)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S4-5. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Fe1	O1	2.100(4)	Fe1	O1[1]	2.100(4)
Fe1	O12	2.0820(18)	Fe1	O12[1]	2.0820(18)
Fe1	O13	2.094(4)	Fe1	O13[1]	2.094(4)
Fe2	Fe4	2.671(4)	Fe2	C1	1.9125(18)
Fe2	C4	1.831(3)	Fe3	Fe4	2.6954(13)
Fe3	C1	1.912(3)	Fe3	C7	1.832(3)
Fe4	C8	1.820(3)	O1	C1	1.200(3)
O2	C2	1.151(3)	O3	C3	1.149(2)
O4	C4	1.133(3)	O5	C5	1.145(3)
O6	C6	1.139(3)	O7	C7	1.143(3)
O8	C8	1.144(3)	O9	C9	1.142(3)
O10	C10	1.136(3)	O11	C11	1.150(3)
O12	C12	1.238(3)	O13	C15	1.236(3)
N1	C12	1.320(3)	N1	C13	1.448(3)
N1	C14	1.453(4)	N2	C15	1.316(3)
N2	C16	1.447(3)	N2	C17	1.454(3)

Symmetry Operators:

(1) -X+1,-Y+2,-Z

Table S4-6. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
Fe2	H1	1.61(3)	Fe3	H1	1.67(2)

Table S4-7. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	Fe1	O1[1]	180.0(2)	O1	Fe1	O12	91.84(10)
O1	Fe1	O12[1]	88.16(10)	O1	Fe1	O13	89.57(11)
O1	Fe1	O13[1]	90.43(11)	O1[1]	Fe1	O12	88.16(10)
O1[1]	Fe1	O12[1]	91.84(10)	O1[1]	Fe1	O13	90.43(11)
O1[1]	Fe1	O13[1]	89.57(11)	O12	Fe1	O12[1]	180.00(6)
O12	Fe1	O13	88.09(9)	O12	Fe1	O13[1]	91.91(9)
O12[1]	Fe1	O13	91.91(9)	O12[1]	Fe1	O13[1]	88.09(9)
O13	Fe1	O13[1]	180.00(7)	Fe4	Fe2	C1	76.01(14)
Fe4	Fe2	C4	93.18(14)	C1	Fe2	C4	165.23(7)
Fe4	Fe3	C1	75.41(10)	Fe4	Fe3	C7	101.43(11)
C1	Fe3	C7	167.39(8)	Fe2	Fe4	Fe3	57.70(5)
Fe2	Fe4	C8	90.63(13)	Fe3	Fe4	C8	95.02(12)
Fe1	O1	C1	176.06(15)	Fe1	O12	C12	128.31(13)
Fe1	O13	C15	126.30(12)	C12	N1	C13	120.45(17)
C12	N1	C14	121.66(17)	C13	N1	C14	117.8(3)
C15	N2	C16	120.50(17)	C15	N2	C17	122.57(16)
C16	N2	C17	116.69(17)	Fe2	C1	Fe3	85.24(15)
Fe2	C1	O1	136.61(15)	Fe3	C1	O1	137.93(17)
Fe2	C4	O4	176.35(18)	Fe3	C7	O7	174.35(19)
Fe4	C8	O8	174.75(15)	O12	C12	N1	123.11(16)
O13	C15	N2	124.42(17)				

Symmetry Operators:

(1) -X+1,-Y+2,-Z

Table S4-8. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
Fe4	Fe2	H1	81.4(7)	C1	Fe2	H1	82.2(8)
C4	Fe2	H1	86.3(8)	Fe4	Fe3	H1	79.8(9)
C1	Fe3	H1	80.9(7)	C7	Fe3	H1	86.5(7)
Fe2	H1	Fe3	104.2(11)				

Table S4-9. Torsion Angles(°)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O1	Fe1	O12	C12	-91.68(14)	O1	Fe1	O12[1]	C12[1]	-88.32(14)
O1	Fe1	O13	C15	-55.56(14)	O1	Fe1	O13[1]	C15[1]	-124.44(14)
O1[1]	Fe1	O12	C12	88.32(14)	O1[1]	Fe1	O12[1]	C12[1]	91.68(14)
O1[1]	Fe1	O13	C15	124.44(14)	O1[1]	Fe1	O13[1]	C15[1]	55.56(14)
O12	Fe1	O13	C15	-147.42(11)	O13	Fe1	O12	C12	-2.17(9)
O12	Fe1	O13[1]	C15[1]	-32.58(11)	O13[1]	Fe1	O12	C12	177.83(9)
O12[1]	Fe1	O13	C15	32.58(11)	O13	Fe1	O12[1]	C12[1]	-177.83(9)
O12[1]	Fe1	O13[1]	C15[1]	147.42(11)	O13[1]	Fe1	O12[1]	C12[1]	2.17(9)
Fe4	Fe2	C1	Fe3	64.11(9)	Fe4	Fe2	C1	O1	-120.81(18)
C1	Fe2	Fe4	Fe3	-48.79(10)	C1	Fe2	Fe4	C8	46.74(8)
C4	Fe2	Fe4	Fe3	121.00(11)	C4	Fe2	Fe4	C8	-143.46(9)
Fe4	Fe3	C1	Fe2	-63.38(12)	Fe4	Fe3	C1	O1	121.66(19)
C1	Fe3	Fe4	Fe2	48.99(8)	C1	Fe3	Fe4	C8	-38.58(11)
C7	Fe3	Fe4	Fe2	-118.47(8)	C7	Fe3	Fe4	C8	153.96(9)
Fe1	O12	C12	N1	177.01(8)	Fe1	O13	C15	N2	-179.66(10)
C13	N1	C12	O12	-1.0(3)	C14	N1	C12	O12	-176.92(15)
C16	N2	C15	O13	-1.2(3)	C17	N2	C15	O13	-175.34(17)

Symmetry Operators:

(1) -X+1,-Y+2,-Z

S-5. Spectral Data of Amines

N,*N*-Dimethyl-(*p*-methoxybenzyl)amine (2a)

IR (neat): ν = 2941, 2813, 2768, 1613, 1511, 1456, 1300, 1177, 1038, 854, 810 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 6H), 3.34 (s, 2H), 3.80 (s, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.0, 55.1, 63.6, 113.5, 130.1, 130.7, 158.6.

N,*N*-Dimethylbenzylamine (2b)

IR (neat) ν 2964, 2925, 1260, 1093, 1021 800 cm^{-1}; , ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.18 (s, 6H), 3.38 (s, 2H), 7.17-7.34 (m, 3H), 7.42-7.45 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 45.4, 64.4, 127.0, 128.2, 129.1, 138.9.

N,*N*-Dimethyl-(*p*-chlorobenzyl)amine (2c)

IR (neat): ν = 2973, 2945, 2854, 2815, 2769, 1499, 1460, 1369, 1262, 1093, 1030, 861, 811 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 6H), 3.38 (s, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.2, 63.5, 128.3, 130.3, 132.7, 137.3.

N,*N*-Dimethyl-(*p*-bromobenzyl)amine (2d)

IR (neat): ν = 2941, 2815, 1487, 1361, 1259, 1173, 1070, 1011, 856, 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 6H), 3.36 (s, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.4, 63.7, 120.9, 130.7, 131.4, 138.1.

N,*N*-Dimethyl-(*p*-methoxycarbonyl)amine (2e)

IR (neat): ν = 2948, 2816, 2769, 1726, 1611, 1435, 1414, 1361, 1280, 1173, 1146, 1110, 1019, 968, 865, 757, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 6H), 3.46 (s, 2H), 3.91 (s, 3H), 7.38 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.4, 51.9, 63.9, 128.8, 128.9, 129.5, 144.3, 166.9.

N,*N*-Dimethyl-3-phenylpropylamine (2f)

IR (neat): ν = 3062, 3026, 2942, 2764, 1603, 1496, 1454, 1265, 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.80 (tt, *J* = 8.2, 7.7 Hz, 2H), 2.23 (s, 6H), 2.30 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 8.2 Hz, 2H), 7.15–7.23 (m, 3H), 7.25–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.5, 33.6, 45.5, 59.3, 125.7, 128.3, 128.4, 142.3.

N,*N*-Dimethyl-cyclohexylmethylamine (2g)

IR (neat): ν = 2922, 2851, 2761, 1455, 1264, 1032, 852, 832 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (m, 2H), 1.10–1.31 (m, 3H), 1.43 (m, 1H), 1.60–1.84 (m, 5H), 2.04 (d, *J* = 7.2 Hz, 2H), 2.18 (d, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.1, 26.8, 31.8, 35.8, 46.0, 67.2.

1-Benzylazepane (2h)

IR (neat): ν = 2925, 2852, 1453, 1354, 1153, 1071, 961, 745, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ =

1.53–1.73 (m, 8H), 2.51–2.68 (m, 4H), 3.64 (s, 2H), 7.19–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.1, 28.3, 55.7, 62.8, 126.7, 128.1, 128.88, 140.2.

4-[[4-(chloromethyl)phenyl]methyl]-morpholine (2i)

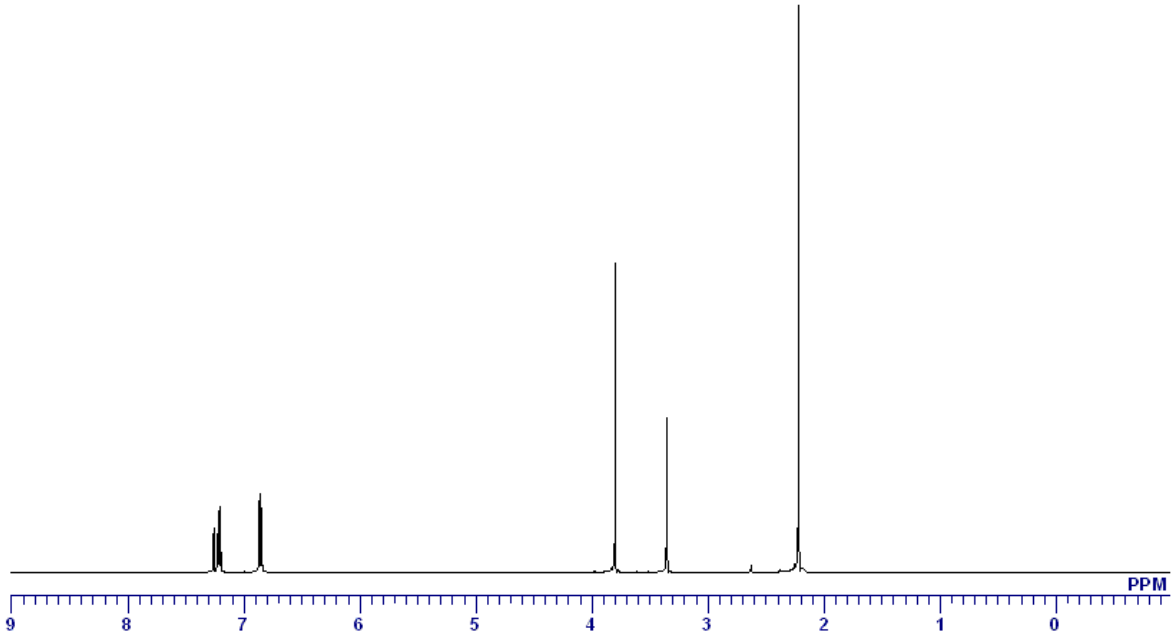
IR (neat): ν = 2959, 2854, 2806, 1454, 1349, 1266, 1117, 1008, 867, 729, 676, 517 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (t, *J* = 4.3 Hz, 4H), 3.50 (s, 2H), 3.71 (t, *J* = 4.3 Hz, 4H), 4.58 (s, 2H), 7.28-7.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.5, 54.1, 63.5, 67.4, 129.0, 130.0, 136.9, 138.6. HRMS (EI) calcd for $C_{12}H_{16}ClNO$ 225.0920, found 225.0926

***N*-Methylbenzylamine (2j)**

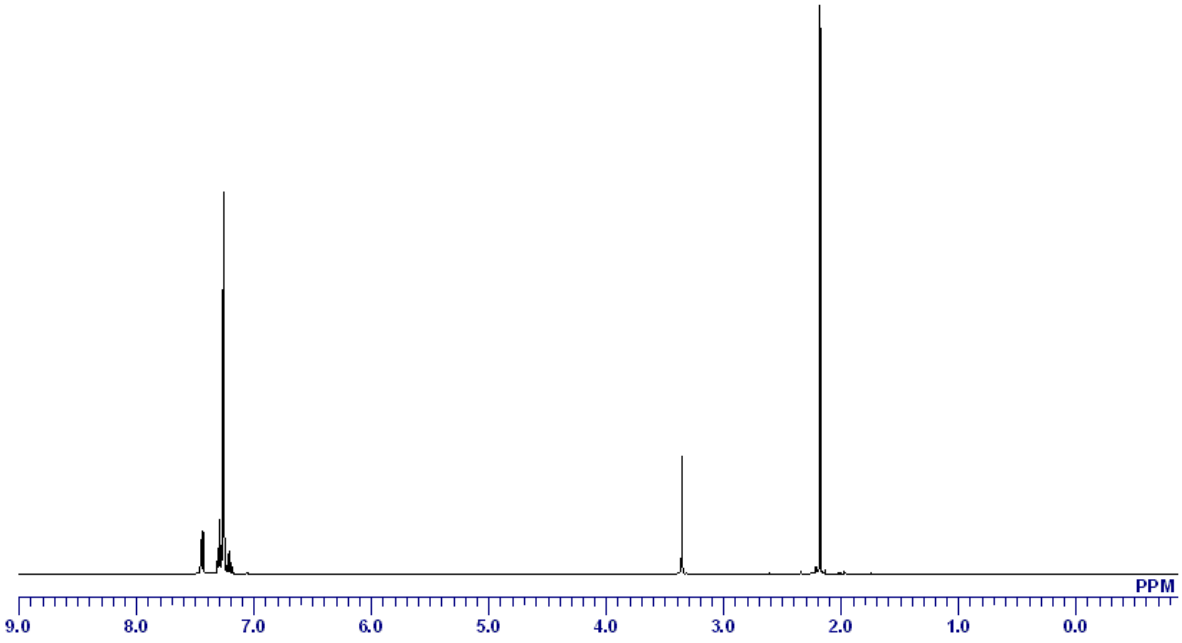
IR (neat): ν = 3321, 3284, 3084, 3062, 2968, 2932, 2843, 2788, 1603, 1494, 1473, 1453, 1356, 1128, 1104, 1073, 1028, 824, 735, 698 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 3.70 (s, 2H), 7.16-7.34 (m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 36.5, 61.0, 127.4, 128.7, 128.9, 140.5.

S-6. Copies of the actual NMR spectrum

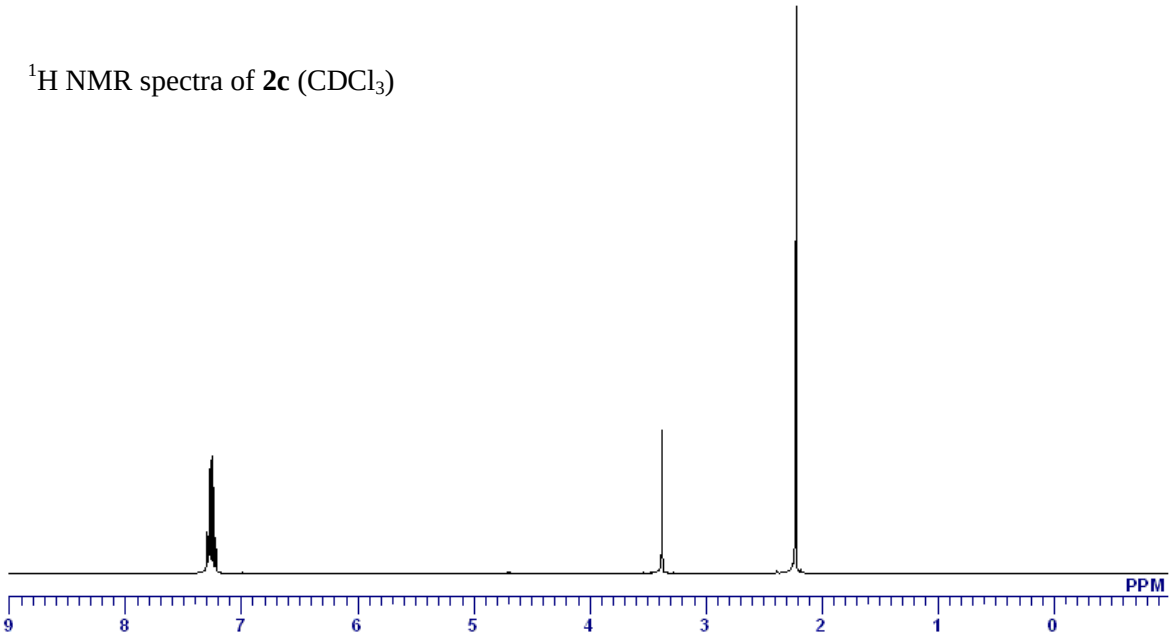
^{1}H NMR spectra of **2a** ($CDCl_3$)



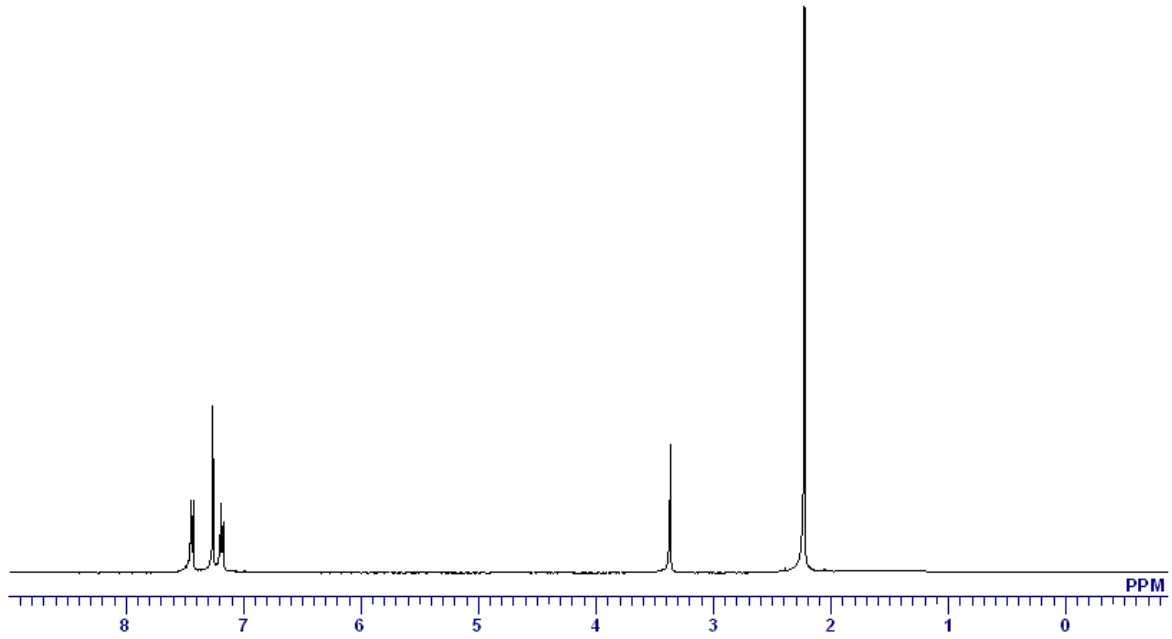
^{1}H NMR spectra of **2b** ($CDCl_3$)



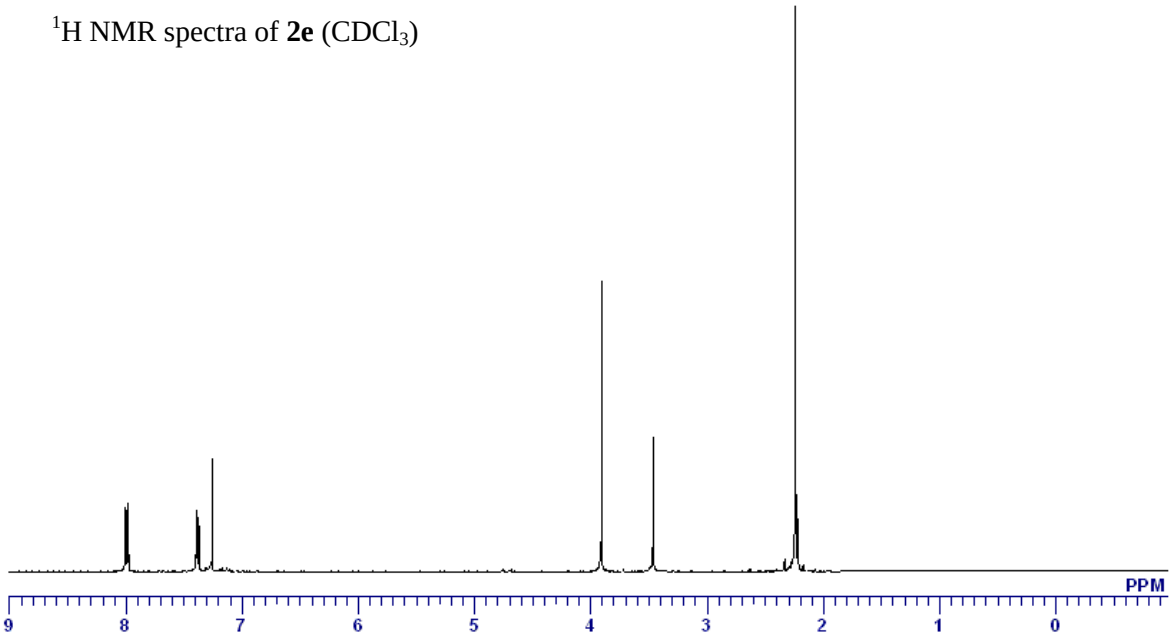
^{1}H NMR spectra of **2c** ($CDCl_3$)



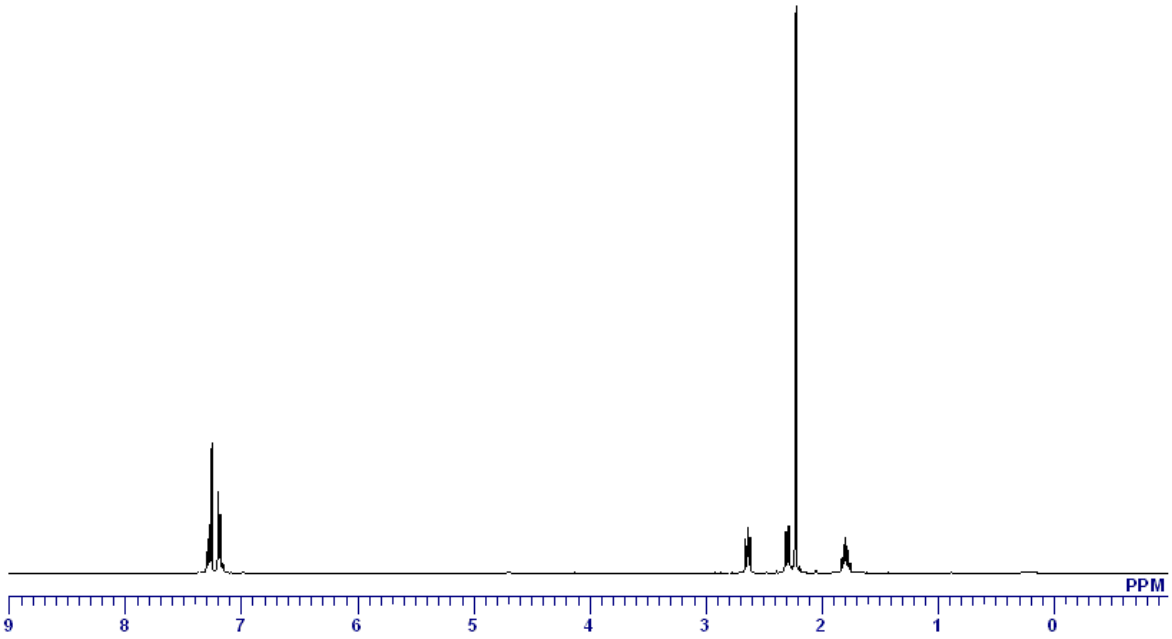
^{1}H NMR spectra of **2d** ($CDCl_3$)



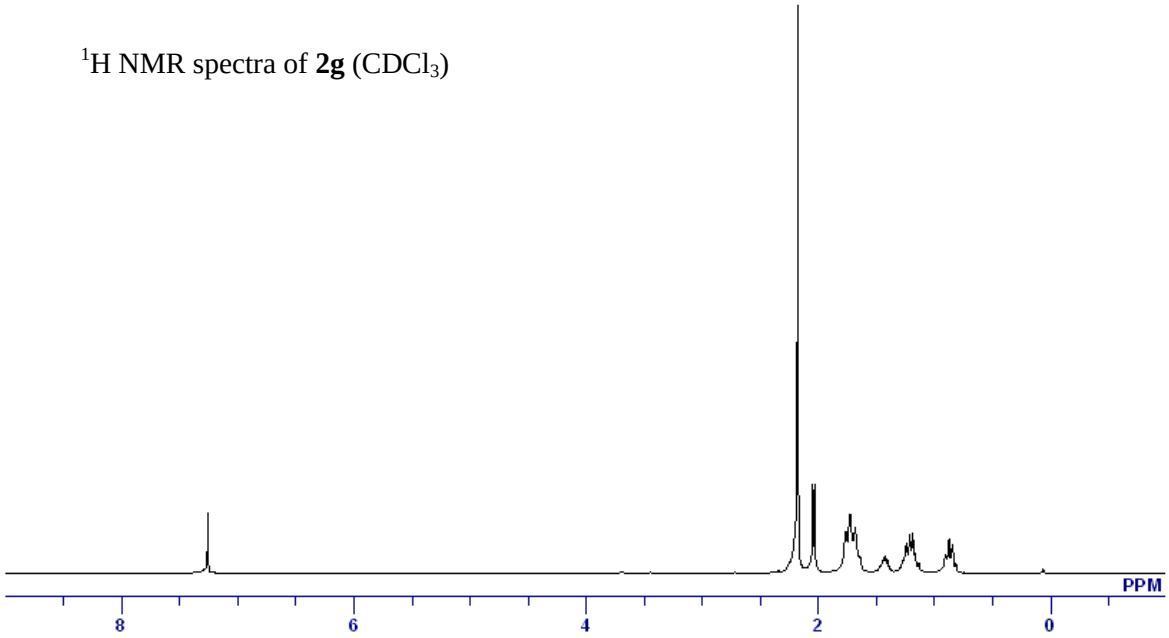
^{1}H NMR spectra of **2e** ($CDCl_3$)



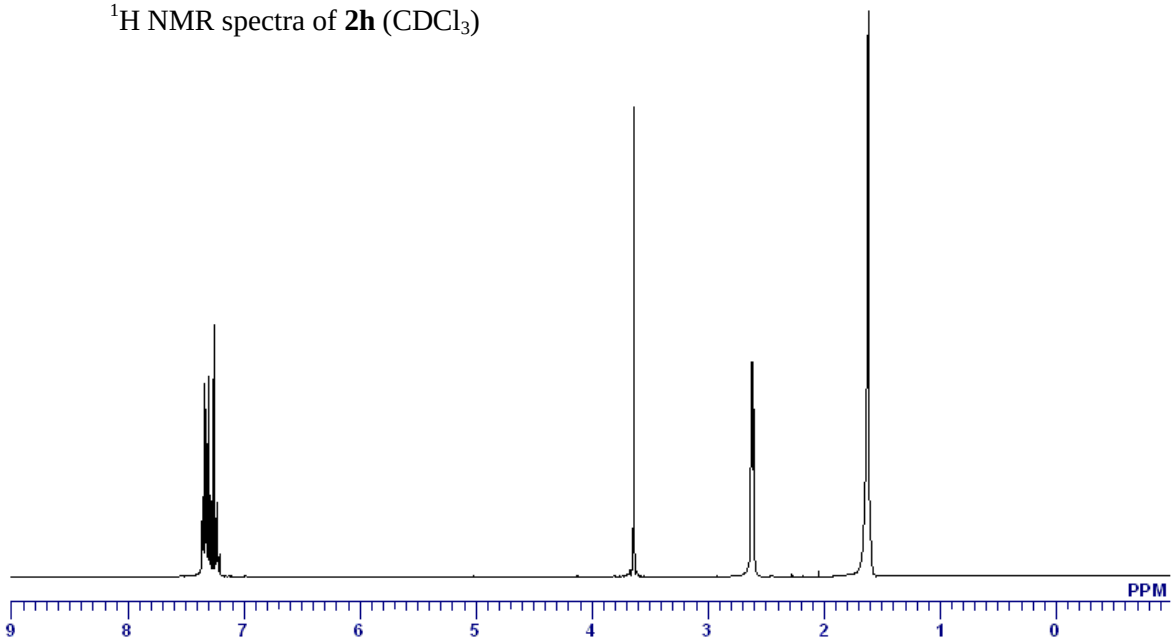
^{1}H NMR spectra of **2f** ($CDCl_3$)



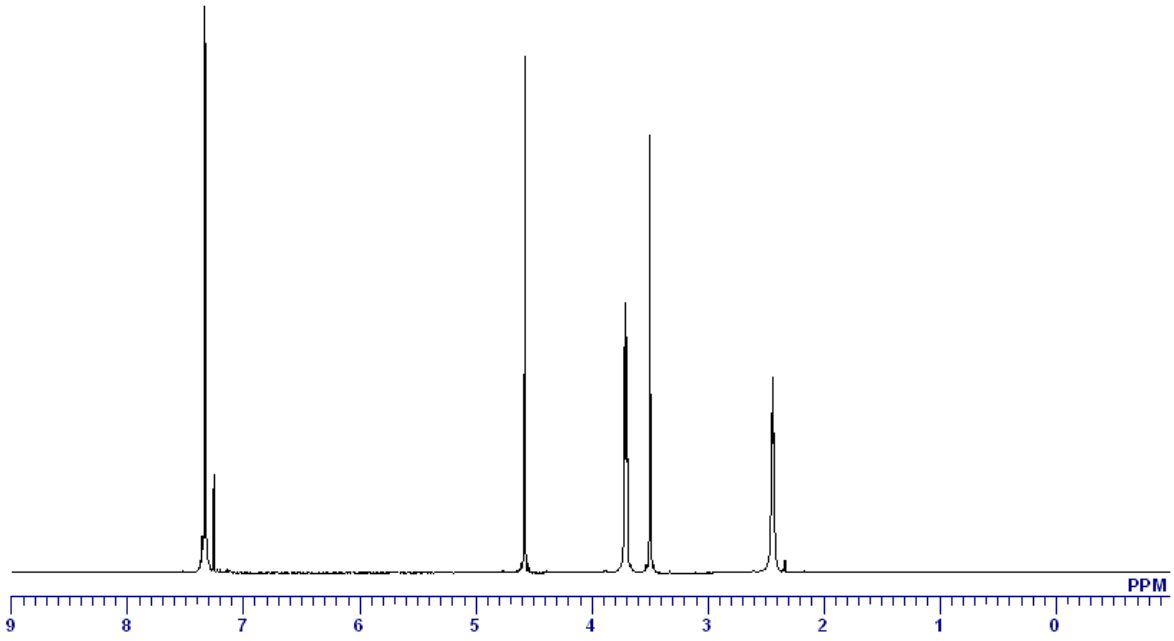
^{1}H NMR spectra of **2g** ($CDCl_3$)



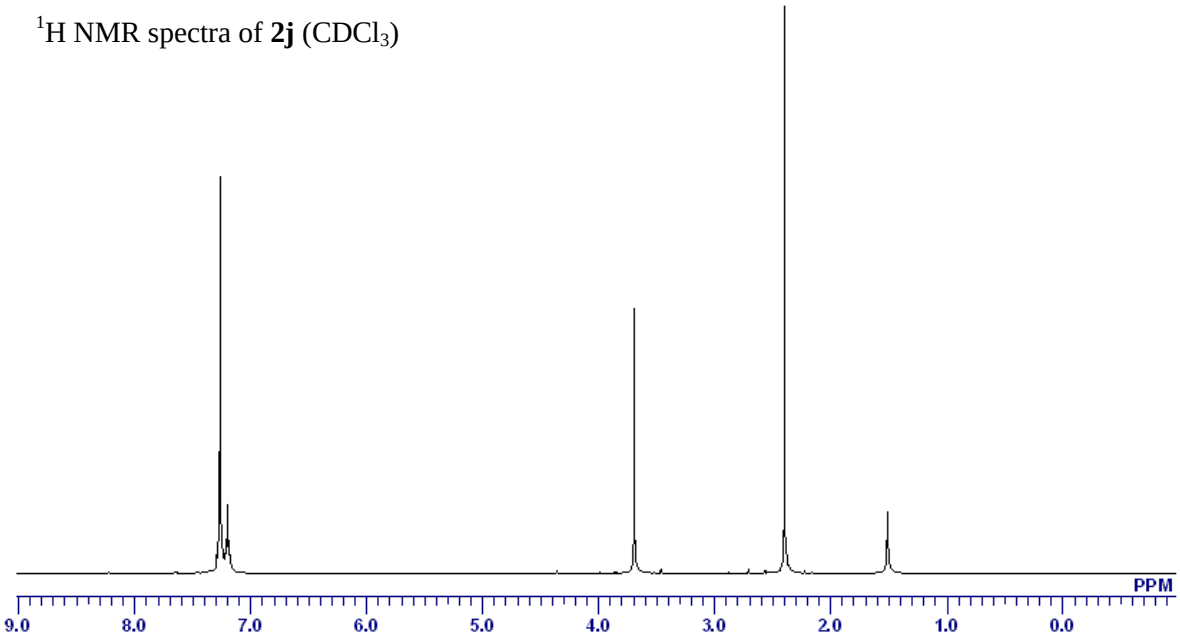
^{1}H NMR spectra of **2h** ($CDCl_3$)



^{1}H NMR spectra of **2i** ($CDCl_3$)



^{1}H NMR spectra of **2j** ($CDCl_3$)



S-7. References

1. H. Nagashima, K. Tatebe, I. Ishibashi, A. Nakaoka, J. Sakakibara, K. Itoh, *Organometallics* **1995**, *14*, 2868.

2. (a) W. Fink, *Helv. Chem. Acta.* **1975**, 58, 1464. (b) W. Fink, *Helv. Chem. Acta.* **1976**, 59, 606.

3. (a) Y. Sunada, H. Kawakami, T. Imaoka, T, Y. Motoyama, H. Nagashima, *Angew. Chem. Int. Ed*., **2009**, 48, 9511. (b) S. Hanada, Y. Motoyama, H. Nagashima, *Tetrahedron Lett.* **2006**, *47*, 6173. (c) S. Hanada, E. Tsutsumi, Y. Motoyama, H. Nagashima, *J. Am. Chem. Soc*. **2009**, 131, 15032.

4. (a) SHELX97: Sheldrick, G. M. **1997**. (b) SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. **1999**.

5. DIRDIF99: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. The DIRDIF-99 program system; *Technical Report of the Crystallography Laboratory*; University of Nijmegen, Nijmegen, The Netherlands, **1999**.

6. Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., **1974** *Vol. 4*.

7. CrystalStructure 3.8.0: Crystal Structure Analysis Package; Package, Rigaku and Rigaku/MSC. 9009 New Trails Dr. The Woodlands TX 77381 USA. **2000-2006**.

8. CRYSTALS Issue 11: Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W.; Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. *Chemical Crystallography Laboratory*; Oxford, U.K., **1999**.