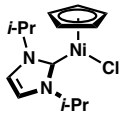
APPENDIX 2

X-Ray Crystallographic Reports Relevant to Chapter 1: Development of a Ni-Catalyzed N–N Cross-Coupling for the Synthesis of Hydrazides

A2.1 GENERAL EXPERIMENTAL

X-ray crystallographic analysis was obtained from the Caltech X-Ray Crystallography Facility using a Bruker D8 Venture Kappa Duo Photon 100 CMOS diffractometer.

A2.2 X-RAY CRYSTAL STRUCTURE ANALYSIS OF CATALYST 24



24

Ni catalyst **24** was recrystallized from a mixture of dichloromethane and hexanes at 23 °C to provide crystals suitable for X-ray analysis.

Figure A2.1 *X-ray crystal structure of Ni-catalyst* ***24***.

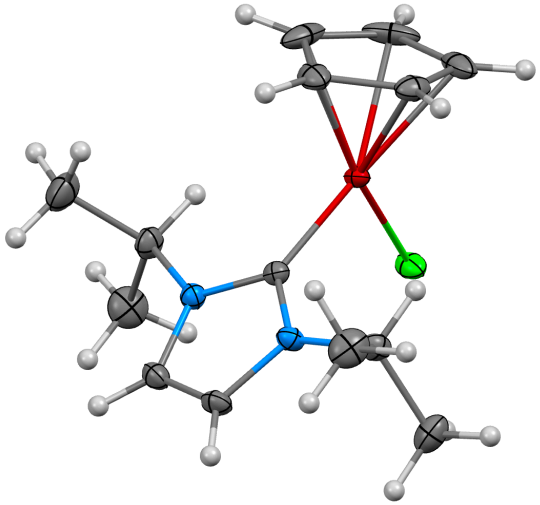


Table A2.1 *Crystal data and structure refinement for Ni-catalyst* ***24***.

Identification code	V22313.	
Empirical formula	C14 H21 Cl N2 Ni	
Formula weight	311.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 11.858(3) Å	a= 90°.
	b = 9.642(3) Å	b= 90°.
	c = 13.085(3) Å	g = 90°.
Volume	1496.1(7) Å3	
Z	4	
Density (calculated)	1.383 Mg/m3	
Absorption coefficient	1.460 mm-1	
F(000)	656	
Crystal size	0.300 x 0.200 x 0.150 mm3	
Theta range for data collection	2.624 to 36.319°.	
Index ranges	-17<=h<=19, -16<=k<=15, -21<=l<=21	
Reflections collected	26205	
Independent reflections	7121 [R(int) = 0.0409]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7471 and 0.6003
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	7121 / 1 / 167
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0201, wR2 = 0.0436
R indices (all data)	R1 = 0.0226, wR2 = 0.0442
Absolute structure parameter	0.025(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.343 and -0.248 e.Å-3

Table A2.2 *Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for* ***24****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
Cl(1)	5916(1)	5176(1)	5298(1)	20(1)
Ni(1)	4391(1)	6328(1)	5714(1)	12(1)
C(1)	3144(1)	7582(2)	6257(1)	22(1)
C(2)	4136(2)	8409(2)	6256(1)	30(1)
C(3)	4904(1)	7761(2)	6901(1)	34(1)
C(4)	4363(2)	6596(2)	7373(1)	28(1)
C(5)	3277(1)	6521(2)	7006(1)	21(1)
C(6)	3706(1)	5849(1)	4476(1)	13(1)
N(1)	2998(1)	4782(1)	4277(1)	15(1)
C(9)	2612(1)	3758(1)	5030(1)	18(1)
C(10)	3162(1)	2362(2)	4821(1)	26(1)
C(11)	1332(1)	3683(2)	5024(1)	28(1)
C(7)	2765(1)	4714(1)	3238(1)	18(1)
C(8)	3325(1)	5759(2)	2794(1)	18(1)
N(2)	3898(1)	6450(1)	3559(1)	15(1)
C(12)	4622(1)	7671(2)	3411(1)	19(1)
C(13)	5529(1)	7372(2)	2620(1)	30(1)
C(14)	3894(2)	8921(2)	3141(1)	32(1)

Table A2.3 *Bond lengths [Å] and angles [°] for* ***24****.*

Cl(1)-Ni(1)	2.1913(6)
Ni(1)-C(6)	1.8699(12)
Ni(1)-C(1)	2.0372(14)
Ni(1)-C(2)	2.1488(15)
Ni(1)-C(5)	2.1529(14)
Ni(1)-C(3)	2.1654(14)
Ni(1)-C(4)	2.1859(15)
C(1)-C(2)	1.421(2)
C(1)-C(5)	1.425(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.389(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.434(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.376(2)
C(4)-H(4)	0.9500
C(5)-H(5)	0.9500
C(6)-N(2)	1.3520(16)
C(6)-N(1)	1.3536(17)
N(1)-C(7)	1.3888(15)
N(1)-C(9)	1.4676(17)
C(9)-C(11)	1.519(2)

C(9)-C(10)	1.520(2)
C(9)-H(9)	1.0000
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(7)-C(8)	1.339(2)
C(7)-H(7)	0.9500
C(8)-N(2)	1.3810(17)
C(8)-H(8)	0.9500
N(2)-C(12)	1.4697(18)
C(12)-C(13)	1.521(2)
C(12)-C(14)	1.524(2)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(6)-Ni(1)-C(1)	97.68(6)

C(6)-Ni(1)-C(2)	117.07(7)
C(1)-Ni(1)-C(2)	39.57(7)
C(6)-Ni(1)-C(5)	115.80(6)
C(1)-Ni(1)-C(5)	39.66(6)
C(2)-Ni(1)-C(5)	64.81(6)
C(6)-Ni(1)-C(3)	154.22(7)
C(1)-Ni(1)-C(3)	64.85(6)
C(2)-Ni(1)-C(3)	37.56(8)
C(5)-Ni(1)-C(3)	63.53(6)
C(6)-Ni(1)-C(4)	151.99(6)
C(1)-Ni(1)-C(4)	64.72(6)
C(2)-Ni(1)-C(4)	63.92(7)
C(5)-Ni(1)-C(4)	36.98(6)
C(3)-Ni(1)-C(4)	38.47(7)
C(6)-Ni(1)-Cl(1)	91.02(4)
C(1)-Ni(1)-Cl(1)	170.50(4)
C(2)-Ni(1)-Cl(1)	132.16(5)
C(5)-Ni(1)-Cl(1)	138.18(4)
C(3)-Ni(1)-Cl(1)	105.67(5)
C(4)-Ni(1)-Cl(1)	108.60(4)
C(2)-C(1)-C(5)	108.18(14)
C(2)-C(1)-Ni(1)	74.46(9)
C(5)-C(1)-Ni(1)	74.55(8)

C(2)-C(1)-H(1)	125.9
C(5)-C(1)-H(1)	125.9
Ni(1)-C(1)-H(1)	117.1
C(3)-C(2)-C(1)	106.82(14)
C(3)-C(2)-Ni(1)	71.87(9)
C(1)-C(2)-Ni(1)	65.98(8)
C(3)-C(2)-H(2)	126.6
C(1)-C(2)-H(2)	126.6
Ni(1)-C(2)-H(2)	127.1
C(2)-C(3)-C(4)	108.75(14)
C(2)-C(3)-Ni(1)	70.57(9)
C(4)-C(3)-Ni(1)	71.54(9)
C(2)-C(3)-H(3)	125.6
C(4)-C(3)-H(3)	125.6
Ni(1)-C(3)-H(3)	123.9
C(5)-C(4)-C(3)	107.98(15)
C(5)-C(4)-Ni(1)	70.20(8)
C(3)-C(4)-Ni(1)	69.99(9)
C(5)-C(4)-H(4)	126.0
C(3)-C(4)-H(4)	126.0
Ni(1)-C(4)-H(4)	125.4
C(4)-C(5)-C(1)	107.80(15)
C(4)-C(5)-Ni(1)	72.82(9)

C(1)-C(5)-Ni(1)	65.79(7)
C(4)-C(5)-H(5)	126.1
C(1)-C(5)-H(5)	126.1
Ni(1)-C(5)-H(5)	126.8
N(2)-C(6)-N(1)	105.02(10)
N(2)-C(6)-Ni(1)	126.20(10)
N(1)-C(6)-Ni(1)	128.58(9)
C(6)-N(1)-C(7)	110.34(11)
C(6)-N(1)-C(9)	125.17(10)
C(7)-N(1)-C(9)	124.27(11)
N(1)-C(9)-C(11)	109.90(12)
N(1)-C(9)-C(10)	109.92(11)
C(11)-C(9)-C(10)	112.69(12)
N(1)-C(9)-H(9)	108.1
C(11)-C(9)-H(9)	108.1
C(10)-C(9)-H(9)	108.1
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5

C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(7)-N(1)	106.91(11)
C(8)-C(7)-H(7)	126.5
N(1)-C(7)-H(7)	126.5
C(7)-C(8)-N(2)	106.98(11)
C(7)-C(8)-H(8)	126.5
N(2)-C(8)-H(8)	126.5
C(6)-N(2)-C(8)	110.75(11)
C(6)-N(2)-C(12)	123.90(11)
C(8)-N(2)-C(12)	125.35(11)
N(2)-C(12)-C(13)	110.56(12)
N(2)-C(12)-C(14)	109.47(14)
C(13)-C(12)-C(14)	113.10(13)
N(2)-C(12)-H(12)	107.8
C(13)-C(12)-H(12)	107.8
C(14)-C(12)-H(12)	107.8
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5

C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table A2.4 *Anisotropic displacement parameters ($Å^2$ x 10^3) for* ***24****. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11}+...+2hka^*b^*U^{12}]$.*

	U11	U22	U33	U23	U13	U12
Cl(1)	18(1)	24(1)	17(1)	-5(1)	-2(1)	8(1)
Ni(1)	12(1)	12(1)	12(1)	-3(1)	-1(1)	0(1)
C(1)	22(1)	25(1)	19(1)	-6(1)	-1(1)	10(1)
C(2)	45(1)	13(1)	33(1)	-7(1)	21(1)	-3(1)
C(3)	19(1)	43(1)	38(1)	-31(1)	5(1)	-8(1)
C(4)	33(1)	35(1)	18(1)	-12(1)	-7(1)	17(1)
C(5)	24(1)	18(1)	20(1)	-4(1)	8(1)	-2(1)
C(6)	13(1)	12(1)	14(1)	-2(1)	0(1)	0(1)
N(1)	15(1)	15(1)	14(1)	-2(1)	-1(1)	-2(1)
C(9)	19(1)	17(1)	18(1)	-1(1)	1(1)	-6(1)
C(10)	23(1)	18(1)	36(1)	5(1)	1(1)	1(1)
C(11)	20(1)	28(1)	37(1)	1(1)	9(1)	-3(1)
C(7)	18(1)	19(1)	16(1)	-5(1)	-4(1)	-1(1)
C(8)	18(1)	21(1)	13(1)	-2(1)	-2(1)	1(1)
N(2)	15(1)	14(1)	14(1)	1(1)	-1(1)	-1(1)
C(12)	21(1)	16(1)	21(1)	4(1)	0(1)	-4(1)
C(13)	23(1)	34(1)	33(1)	3(1)	6(1)	-6(1)
C(14)	39(1)	19(1)	37(1)	7(1)	1(1)	2(1)

Table A2.5 *Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3) for* ***24****.*

	x	y	z	U(eq)
H(1)	2504	7714	5832	26
H(2)	4252	9244	5885	36
H(3)	5661	8044	7010	40
H(4)	4696	5983	7855	34
H(5)	2716	5878	7214	25
H(9)	2857	4077	5722	22
H(10A)	2912	2013	4155	39
H(10B)	2946	1703	5356	39
H(10C)	3984	2471	4817	39
H(11A)	1020	4601	5178	42
H(11B)	1079	3017	5541	42
H(11C)	1072	3383	4348	42
H(7)	2297	4054	2906	21
H(8)	3328	5982	2087	21
H(12)	5006	7871	4076	23
H(13A)	6021	6628	2869	45
H(13B)	5977	8211	2503	45
H(13C)	5174	7084	1978	45
H(14A)	3517	8757	2486	48

H(14B)	4371	9748	3089	48
H(14C)	3327	9062	3676	48

Table A2.6 *Torsion angles [°] for* ***24****.*

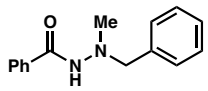
C(5)-C(1)-C(2)-C(3)	6.91(15)
Ni(1)-C(1)-C(2)-C(3)	-60.61(10)
C(5)-C(1)-C(2)-Ni(1)	67.52(9)
C(1)-C(2)-C(3)-C(4)	-4.82(16)
Ni(1)-C(2)-C(3)-C(4)	-61.68(10)
C(1)-C(2)-C(3)-Ni(1)	56.87(10)
C(2)-C(3)-C(4)-C(5)	0.89(17)
Ni(1)-C(3)-C(4)-C(5)	-60.19(10)
C(2)-C(3)-C(4)-Ni(1)	61.08(10)
C(3)-C(4)-C(5)-C(1)	3.42(16)
Ni(1)-C(4)-C(5)-C(1)	-56.63(9)
C(3)-C(4)-C(5)-Ni(1)	60.05(10)
C(2)-C(1)-C(5)-C(4)	-6.44(16)
Ni(1)-C(1)-C(5)-C(4)	61.02(10)
C(2)-C(1)-C(5)-Ni(1)	-67.46(10)
C(1)-Ni(1)-C(6)-N(2)	97.07(12)
C(2)-Ni(1)-C(6)-N(2)	60.65(13)
C(5)-Ni(1)-C(6)-N(2)	134.16(11)
C(3)-Ni(1)-C(6)-N(2)	52.1(2)
C(4)-Ni(1)-C(6)-N(2)	145.46(13)
Cl(1)-Ni(1)-C(6)-N(2)	-79.08(11)
C(1)-Ni(1)-C(6)-N(1)	-88.92(13)

C(2)-Ni(1)-C(6)-N(1)	-125.34(12)
C(5)-Ni(1)-C(6)-N(1)	-51.83(14)
C(3)-Ni(1)-C(6)-N(1)	-133.93(14)
C(4)-Ni(1)-C(6)-N(1)	-40.5(2)
Cl(1)-Ni(1)-C(6)-N(1)	94.94(12)
N(2)-C(6)-N(1)-C(7)	0.68(15)
Ni(1)-C(6)-N(1)-C(7)	-174.32(10)
N(2)-C(6)-N(1)-C(9)	175.41(12)
Ni(1)-C(6)-N(1)-C(9)	0.41(19)
C(6)-N(1)-C(9)-C(11)	126.81(14)
C(7)-N(1)-C(9)-C(11)	-59.17(17)
C(6)-N(1)-C(9)-C(10)	-108.62(14)
C(7)-N(1)-C(9)-C(10)	65.40(17)
C(6)-N(1)-C(7)-C(8)	-0.59(16)
C(9)-N(1)-C(7)-C(8)	-175.38(13)
N(1)-C(7)-C(8)-N(2)	0.25(16)
N(1)-C(6)-N(2)-C(8)	-0.52(15)
Ni(1)-C(6)-N(2)-C(8)	174.64(10)
N(1)-C(6)-N(2)-C(12)	179.55(12)
Ni(1)-C(6)-N(2)-C(12)	-5.29(19)
C(7)-C(8)-N(2)-C(6)	0.17(16)
C(7)-C(8)-N(2)-C(12)	-179.90(13)
C(6)-N(2)-C(12)-C(13)	125.09(14)

C(8)-N(2)-C(12)-C(13)	-54.83(19)
C(6)-N(2)-C(12)-C(14)	-109.67(15)
C(8)-N(2)-C(12)-C(14)	70.42(17)

Symmetry transformations used to generate equivalent atoms:

A2.3 X-RAY CRYSTAL STRUCTURE ANALYSIS OF N–N PRODUCT 27



27

Compound **27** was crystallized from a mixture of dichloromethane and hexanes at 23 °C to provide crystals suitable for X-ray analysis.

Figure A2.2 *X-ray crystal structure of N–N product* ***27***.

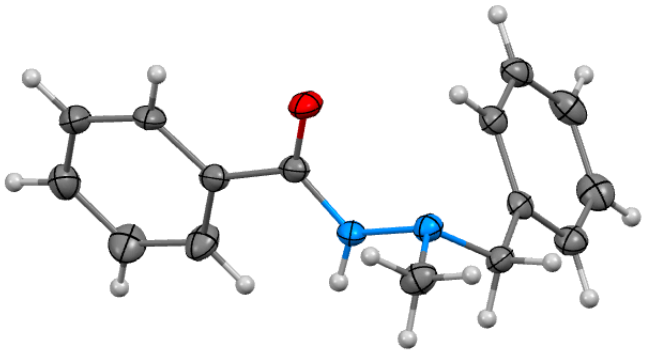


Table A2.7 *Crystal data and structure refinement for N–N product* ***27***.

Empirical formula	$C_{15}H_{16}N_2O$
Formula weight	240.30
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	Pbcn
Unit cell dimensions	a = 15.570(2) Å a= 90°.
	b = 9.7681(14) Å b= 90°.
	c = 17.1374(19) Å g = 90°.
Volume	2606.4(6) Å3
Z	8
Density (calculated)	1.225 Mg/m^3
Absorption coefficient	0.617 mm^{-1}
F(000)	1024
Crystal size	0.400 x 0.050 x 0.030 mm3
Theta range for data collection	5.162 to 74.603°.
Index ranges	-19<=h<=19, -11<=k<=12, -21<=l<=21
Reflections collected	30984
Independent reflections	2675 [R(int) = 0.1106]
Completeness to theta =	67.679° 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.5363

Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	2675 / 1 / 167
Goodness-of-fit on F2	1.067
Final R indices	[I>2sigma(I)] R1 = 0.0458, wR2 = 0.1156
R indices (all data)	R1 = 0.0615, wR2 = 0.1218
Extinction coefficient	n/a
Largest diff. peak and hole	0.300 and -0.203 e.Å-3

Table A2.8 *Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for* ***27****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
O(1)	2972(1)	5181(1)	1190(1)	28(1)
C(1)	3078(1)	3941(1)	1271(1)	22(1)
C(2)	3967(1)	3334(1)	1260(1)	23(1)
C(3)	4637(1)	4196(2)	1050(1)	28(1)
C(4)	5477(1)	3729(2)	1049(1)	33(1)
C(5)	5659(1)	2393(2)	1264(1)	32(1)
C(6)	4994(1)	1517(2)	1454(1)	36(1)
C(7)	4147(1)	1978(2)	1453(1)	32(1)
N(1)	2426(1)	3063(1)	1382(1)	22(1)
N(2)	1575(1)	3578(1)	1401(1)	22(1)
C(8)	1093(1)	2874(1)	2012(1)	23(1)
C(9)	1413(1)	3151(1)	2828(1)	21(1)
C(10)	1924(1)	4272(2)	3017(1)	24(1)
C(11)	2170(1)	4496(2)	3787(1)	28(1)
C(12)	1904(1)	3623(2)	4378(1)	31(1)
C(13)	1389(1)	2512(2)	4192(1)	33(1)
C(14)	1155(1)	2271(2)	3425(1)	27(1)
C(15)	1172(1)	3377(2)	635(1)	30(1)

Table A2.9 *Bond lengths [Å] and angles [°] for* ***27****.*

O(1)-C(1)	1.2301(18)
C(1)-N(1)	1.3419(19)
C(1)-C(2)	1.505(2)
C(2)-C(3)	1.389(2)
C(2)-C(7)	1.394(2)
C(3)-C(4)	1.384(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.385(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.382(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.393(2)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
N(1)-N(2)	1.4177(17)
N(1)-H(1N)	0.865(15)
N(2)-C(8)	1.4608(19)
N(2)-C(15)	1.468(2)
C(8)-C(9)	1.509(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.392(2)

C(9)-C(14)	1.395(2)
C(10)-C(11)	1.392(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.386(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.387(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.384(2)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
O(1)-C(1)-N(1)	122.94(13)
O(1)-C(1)-C(2)	120.61(13)
N(1)-C(1)-C(2)	116.44(12)
C(3)-C(2)-C(7)	119.07(14)
C(3)-C(2)-C(1)	117.12(13)
C(7)-C(2)-C(1)	123.80(13)
C(4)-C(3)-C(2)	120.70(14)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	120.22(15)

C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	119.50(15)
C(6)-C(5)-H(5)	120.2
C(4)-C(5)-H(5)	120.2
C(5)-C(6)-C(7)	120.56(15)
C(5)-C(6)-H(6)	119.7
C(7)-C(6)-H(6)	119.7
C(6)-C(7)-C(2)	119.90(15)
C(6)-C(7)-H(7)	120.1
C(2)-C(7)-H(7)	120.1
C(1)-N(1)-N(2)	118.91(12)
C(1)-N(1)-H(1N)	121.7(13)
N(2)-N(1)-H(1N)	118.1(13)
N(1)-N(2)-C(8)	109.28(11)
N(1)-N(2)-C(15)	109.39(12)
C(8)-N(2)-C(15)	110.99(11)
N(2)-C(8)-C(9)	114.23(11)
N(2)-C(8)-H(8A)	108.7
C(9)-C(8)-H(8A)	108.7
N(2)-C(8)-H(8B)	108.7
C(9)-C(8)-H(8B)	108.7
H(8A)-C(8)-H(8B)	107.6

C(10)-C(9)-C(14)	118.66(14)
C(10)-C(9)-C(8)	123.04(13)
C(14)-C(9)-C(8)	118.25(13)
C(11)-C(10)-C(9)	120.07(14)
C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	120.88(15)
C(12)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
C(11)-C(12)-C(13)	119.13(15)
C(11)-C(12)-H(12)	120.4
C(13)-C(12)-H(12)	120.4
C(14)-C(13)-C(12)	120.23(15)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(9)	121.01(15)
C(13)-C(14)-H(14)	119.5
C(9)-C(14)-H(14)	119.5
N(2)-C(15)-H(15A)	109.5
N(2)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
N(2)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C) 109.5

Symmetry transformations used to generate equivalent atoms:

Table A2.10 *Anisotropic displacement parameters ($Å^2$ x 10^3) for* ***27****. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.*

	U11	U22	U33	U23	U13	U12
O(1)	25(1)	16(1)	44(1)	2(1)	1(1)	-1(1)
C(1)	26(1)	18(1)	22(1)	-2(1)	1(1)	-2(1)
C(2)	26(1)	20(1)	22(1)	-2(1)	1(1)	-2(1)
C(3)	29(1)	14(1)	42(1)	-5(1)	4(1)	-1(1)
C(4)	26(1)	24(1)	50(1)	-9(1)	7(1)	-5(1)
C(5)	25(1)	32(1)	38(1)	-4(1)	1(1)	4(1)
C(6)	34(1)	26(1)	48(1)	12(1)	2(1)	6(1)
C(7)	29(1)	26(1)	42(1)	11(1)	4(1)	-2(1)
N(1)	22(1)	15(1)	28(1)	-1(1)	3(1)	0(1)
N(2)	21(1)	19(1)	27(1)	1(1)	0(1)	0(1)
C(8)	20(1)	20(1)	29(1)	0(1)	1(1)	-2(1)
C(9)	18(1)	17(1)	29(1)	0(1)	1(1)	5(1)
C(10)	22(1)	21(1)	30(1)	-1(1)	2(1)	2(1)
C(11)	25(1)	23(1)	37(1)	-8(1)	-3(1)	4(1)
C(12)	36(1)	31(1)	27(1)	-4(1)	-4(1)	11(1)
C(13)	41(1)	27(1)	31(1)	7(1)	2(1)	7(1)
C(14)	27(1)	20(1)	33(1)	2(1)	1(1)	1(1)
C(15)	33(1)	28(1)	28(1)	4(1)	-2(1)	-5(1)

Table A2.11 *Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for* ***27****.*

	x	y	z	U(eq)
H(3)	4519	5115	904	34
H(4)	5930	4327	901	40
H(5)	6236	2081	1281	38
H(6)	5115	593	1587	44
H(7)	3693	1369	1583	39
H(1N)	2497(13)	2187(16)	1346(11)	26
H(8A)	1119	1877	1914	27
H(8B)	483	3156	1979	27
H(10)	2106	4885	2619	29
H(11)	2525	5258	3911	34
H(12)	2073	3784	4902	37
H(13)	1196	1914	4592	39
H(14)	813	1495	3303	32
H(15A)	504	3863	236	45
H(15B)	584	3736	647	45
H(15C)	1158	2398	512	45

Table A2.12. *Torsion angles [°] for* ***27****.*

O(1)-C(1)-C(2)-C(3)	-8.6(2)
N(1)-C(1)-C(2)-C(3)	172.17(14)
O(1)-C(1)-C(2)-C(7)	170.86(15)
N(1)-C(1)-C(2)-C(7)	-8.3(2)
C(7)-C(2)-C(3)-C(4)	-1.6(2)
C(1)-C(2)-C(3)-C(4)	177.89(15)
C(2)-C(3)-C(4)-C(5)	-0.4(3)
C(3)-C(4)-C(5)-C(6)	2.1(3)
C(4)-C(5)-C(6)-C(7)	-1.9(3)
C(5)-C(6)-C(7)-C(2)	-0.1(3)
C(3)-C(2)-C(7)-C(6)	1.9(3)
C(1)-C(2)-C(7)-C(6)	-177.62(16)
O(1)-C(1)-N(1)-N(2)	0.6(2)
C(2)-C(1)-N(1)-N(2)	179.75(12)
C(1)-N(1)-N(2)-C(8)	-139.83(13)
C(1)-N(1)-N(2)-C(15)	98.48(14)
N(1)-N(2)-C(8)-C(9)	65.32(15)
C(15)-N(2)-C(8)-C(9)	-173.95(12)
N(2)-C(8)-C(9)-C(10)	19.30(19)
N(2)-C(8)-C(9)-C(14)	-163.31(12)
C(14)-C(9)-C(10)-C(11)	0.1(2)
C(8)-C(9)-C(10)-C(11)	177.50(13)

C(9)-C(10)-C(11)-C(12)	-0.7(2)
C(10)-C(11)-C(12)-C(13)	0.2(2)
C(11)-C(12)-C(13)-C(14)	0.9(2)
C(12)-C(13)-C(14)-C(9)	-1.5(2)
C(10)-C(9)-C(14)-C(13)	1.0(2)
C(8)-C(9)-C(14)-C(13)	-176.55(14)

Symmetry transformations used to generate equivalent atoms:

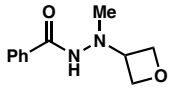
Table A2.13 *Hydrogen bonds for* ***27*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.865(15)	2.108(17)	2.9018(16)	152.2(18)
C(8)-H(8A)...O(1)#1	0.99	2.51	3.3207(18)	139.2

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,z

A2.3 X-RAY CRYSTAL STRUCTURE ANALYSIS OF N–N PRODUCT 70



70

Compound **70** was crystallized from a mixture of dichloromethane and hexanes at 23 °C to provide crystals suitable for X-ray analysis.

Figure A2.3 *X-ray crystal structure of N–N product* ***70***.

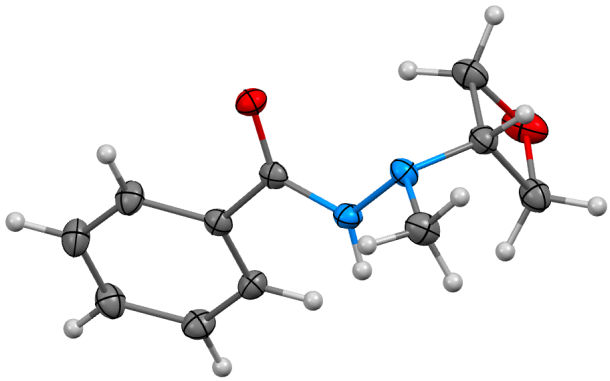


Figure A2.14 *Crystal data and structure refinement for N–N product* ***70****.*

Empirical formula	$C_{11}H_{14}N_2O_2$	
Formula weight	206.24	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Tetragonal	
Space group	$I4_1/a$	
Unit cell dimensions	a = 18.1243(9) Å	a= 90°.
	b = 18.1243(9) Å	b= 90°.
	c = 12.9625(14) Å	g = 90°.
Volume	4258.1(6) $Å^3$	
Z	16	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.734 mm^{-1}	
F(000)	1760	
Crystal size	0.050 x 0.050 x 0.050 mm^3	
Theta range for data collection	4.193 to 74.554°.	
Index ranges	-22<=h<=22, -20<=k<=22, -16<=l<=16	
Reflections collected	27679	
Independent reflections	2186 [R(int) = 0.0683]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6823	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2186 / 1 / 140
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0874
R indices (all data)	R1 = 0.0503, wR2 = 0.0983
Extinction coefficient	n/a
Largest diff. peak and hole	0.232 and -0.186 e.$Å^{-3}$

Table A2.15 *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for* ***70****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
O(1)	1333(1)	5983(1)	2099(1)	21(1)
C(1)	1354(1)	5592(1)	2881(1)	17(1)
C(2)	1169(1)	5909(1)	3918(1)	18(1)
C(3)	1221(1)	6672(1)	4038(1)	23(1)
C(4)	1040(1)	6999(1)	4975(1)	27(1)
C(5)	795(1)	6565(1)	5790(1)	25(1)
C(6)	728(1)	5807(1)	5671(1)	23(1)
C(7)	913(1)	5479(1)	4736(1)	20(1)
N(1)	1530(1)	4871(1)	2853(1)	19(1)
N(2)	1680(1)	4541(1)	1886(1)	19(1)
C(11)	2394(1)	4169(1)	1901(1)	26(1)
C(8)	1080(1)	4064(1)	1554(1)	22(1)
C(9)	322(1)	4426(1)	1440(1)	28(1)
O(2)	-19(1)	3873(1)	2086(1)	34(1)
C(10)	688(1)	3530(1)	2307(1)	26(1)

Table A2.16 *Bond lengths [Å] and angles [°] for* ***70****.*

O(1)-C(1)	1.2381(17)
C(1)-N(1)	1.3451(18)
C(1)-C(2)	1.5001(19)
C(2)-C(7)	1.3942(19)
C(2)-C(3)	1.3948(19)
C(3)-C(4)	1.391(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.391(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.387(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.391(2)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
N(1)-N(2)	1.4161(16)
N(1)-H(1N)	0.884(14)
N(2)-C(8)	1.4537(18)
N(2)-C(11)	1.4598(18)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(8)-C(9)	1.530(2)

C(8)-C(10)	1.548(2)
C(8)-H(8)	1.0000
C(9)-O(2)	1.4452(19)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
O(2)-C(10)	1.4525(19)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
O(1)-C(1)-N(1)	122.79(12)
O(1)-C(1)-C(2)	120.54(12)
N(1)-C(1)-C(2)	116.66(12)
C(7)-C(2)-C(3)	119.48(13)
C(7)-C(2)-C(1)	122.82(12)
C(3)-C(2)-C(1)	117.61(12)
C(4)-C(3)-C(2)	120.23(13)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	119.83(13)
C(5)-C(4)-H(4)	120.1
C(3)-C(4)-H(4)	120.1
C(6)-C(5)-C(4)	120.25(14)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9

C(5)-C(6)-C(7)	119.94(13)
C(5)-C(6)-H(6)	120.0
C(7)-C(6)-H(6)	120.0
C(6)-C(7)-C(2)	120.24(13)
C(6)-C(7)-H(7)	119.9
C(2)-C(7)-H(7)	119.9
C(1)-N(1)-N(2)	118.68(11)
C(1)-N(1)-H(1N)	123.8(11)
N(2)-N(1)-H(1N)	117.3(11)
N(1)-N(2)-C(8)	111.75(11)
N(1)-N(2)-C(11)	110.71(11)
C(8)-N(2)-C(11)	113.10(11)
N(2)-C(11)-H(11A)	109.5
N(2)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
N(2)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(2)-C(8)-C(9)	116.40(12)
N(2)-C(8)-C(10)	121.88(12)
C(9)-C(8)-C(10)	85.18(11)
N(2)-C(8)-H(8)	110.3
C(9)-C(8)-H(8)	110.3

C(10)-C(8)-H(8)	110.3
O(2)-C(9)-C(8)	91.79(11)
O(2)-C(9)-H(9A)	113.3
C(8)-C(9)-H(9A)	113.3
O(2)-C(9)-H(9B)	113.3
C(8)-C(9)-H(9B)	113.3
H(9A)-C(9)-H(9B)	110.7
C(9)-O(2)-C(10)	91.91(10)
O(2)-C(10)-C(8)	90.77(11)
O(2)-C(10)-H(10A)	113.5
C(8)-C(10)-H(10A)	113.5
O(2)-C(10)-H(10B)	113.5
C(8)-C(10)-H(10B)	113.5
H(10A)-C(10)-H(10B)	110.8

Symmetry transformations used to generate equivalent atoms:

Table A2.17 *Anisotropic displacement parameters ($Å^2$ x 10^3) for* ***70****. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2\ a^{*2}U^{11}+...+2\ h\ k\ a^*\ b^*\ U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	22(1)	21(1)	19(1)	4(1)	2(1)	0(1)
C(1)	13(1)	21(1)	18(1)	1(1)	0(1)	-2(1)
C(2)	14(1)	21(1)	20(1)	0(1)	-1(1)	0(1)
C(3)	25(1)	20(1)	24(1)	1(1)	5(1)	-4(1)
C(4)	31(1)	20(1)	29(1)	-4(1)	5(1)	-4(1)
C(5)	27(1)	27(1)	21(1)	-5(1)	4(1)	-2(1)
C(6)	25(1)	25(1)	21(1)	3(1)	4(1)	0(1)
C(7)	21(1)	18(1)	21(1)	1(1)	1(1)	1(1)
N(1)	22(1)	20(1)	14(1)	1(1)	0(1)	1(1)
N(2)	19(1)	22(1)	16(1)	-3(1)	1(1)	0(1)
C(11)	23(1)	31(1)	23(1)	-3(1)	1(1)	5(1)
C(8)	24(1)	23(1)	19(1)	-1(1)	-1(1)	-1(1)
C(9)	23(1)	34(1)	27(1)	0(1)	-4(1)	-2(1)
O(2)	22(1)	56(1)	25(1)	5(1)	1(1)	-4(1)
C(10)	26(1)	28(1)	24(1)	-1(1)	1(1)	-4(1)

Table A2.18 *Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for* ***70****.*

	x	y	z	U(eq)
H(3)	1382	6969	3477	28
H(4)	1082	7518	5057	32
H(5)	674	6788	6431	30
H(6)	555	5513	6227	28
H(7)	865	4961	4654	24
H(1N)	1591(9)	4596(9)	3409(12)	23
H(11A)	2781	4526	2076	39
H(11B)	2495	3958	1219	39
H(11C)	2387	3775	2417	39
H(8)	1218	3800	904	26
H(9A)	299	4929	1736	33
H(9B)	136	4424	722	33
H(10A)	715	3007	2093	31
H(10B)	847	3589	3033	31

Table A2.19 *Torsion angles [°] for* ***70****.*

O(1)-C(1)-C(2)-C(7)	155.11(13)
N(1)-C(1)-C(2)-C(7)	-23.97(18)
O(1)-C(1)-C(2)-C(3)	-21.46(19)
N(1)-C(1)-C(2)-C(3)	159.47(12)
C(7)-C(2)-C(3)-C(4)	1.8(2)
C(1)-C(2)-C(3)-C(4)	178.47(13)
C(2)-C(3)-C(4)-C(5)	-0.9(2)
C(3)-C(4)-C(5)-C(6)	-0.4(2)
C(4)-C(5)-C(6)-C(7)	0.7(2)
C(5)-C(6)-C(7)-C(2)	0.2(2)
C(3)-C(2)-C(7)-C(6)	-1.4(2)
C(1)-C(2)-C(7)-C(6)	-177.95(12)
O(1)-C(1)-N(1)-N(2)	-1.58(19)
C(2)-C(1)-N(1)-N(2)	177.47(11)
C(1)-N(1)-N(2)-C(8)	-106.43(13)
C(1)-N(1)-N(2)-C(11)	126.53(13)
N(1)-N(2)-C(8)-C(9)	58.61(16)
C(11)-N(2)-C(8)-C(9)	-175.65(12)
N(1)-N(2)-C(8)-C(10)	-42.83(17)
C(11)-N(2)-C(8)-C(10)	82.91(16)
N(2)-C(8)-C(9)-O(2)	-127.65(13)
C(10)-C(8)-C(9)-O(2)	-4.30(11)

C(8)-C(9)-O(2)-C(10)	4.57(11)
C(9)-O(2)-C(10)-C(8)	-4.51(11)
N(2)-C(8)-C(10)-O(2)	122.50(13)
C(9)-C(8)-C(10)-O(2)	4.27(11)

Symmetry transformations used to generate equivalent atoms:

Table A2.20 *Hydrogen bonds for* ***70*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.884(14)	2.075(14)	2.9435(15)	167.0(16)
C(8)-H(8)...O(2)#2	1.00	2.42	3.2099(18)	135.0
C(10)-H(10A)...O(2)#2	0.99	2.63	3.3047(19)	125.2
C(10)-H(10B)...O(1)#1	0.99	2.41	3.3735(18)	165.6

Symmetry transformations used to generate equivalent atoms:

#1 -y+3/4,x+1/4,z+1/4 #2 y-1/4,-x+1/4,-z+1/4