Supporting Information

Heterogenised N-Heterocyclic Carbene Complexes: Synthesis, Characterisation and Application for Hydroformylation and C–C Bond Formation Reactions

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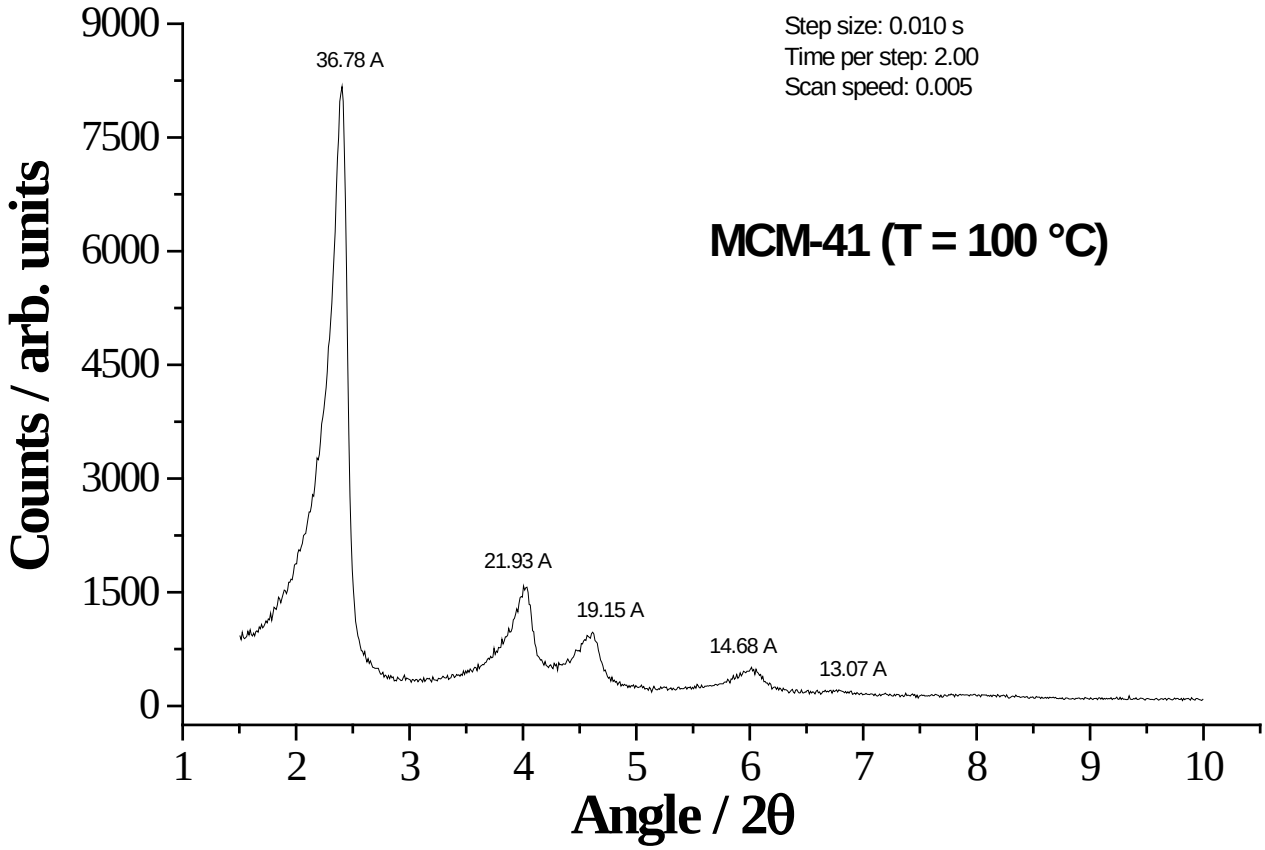


Figure 1. Powder X-ray diffraction pattern for pure MCM-41

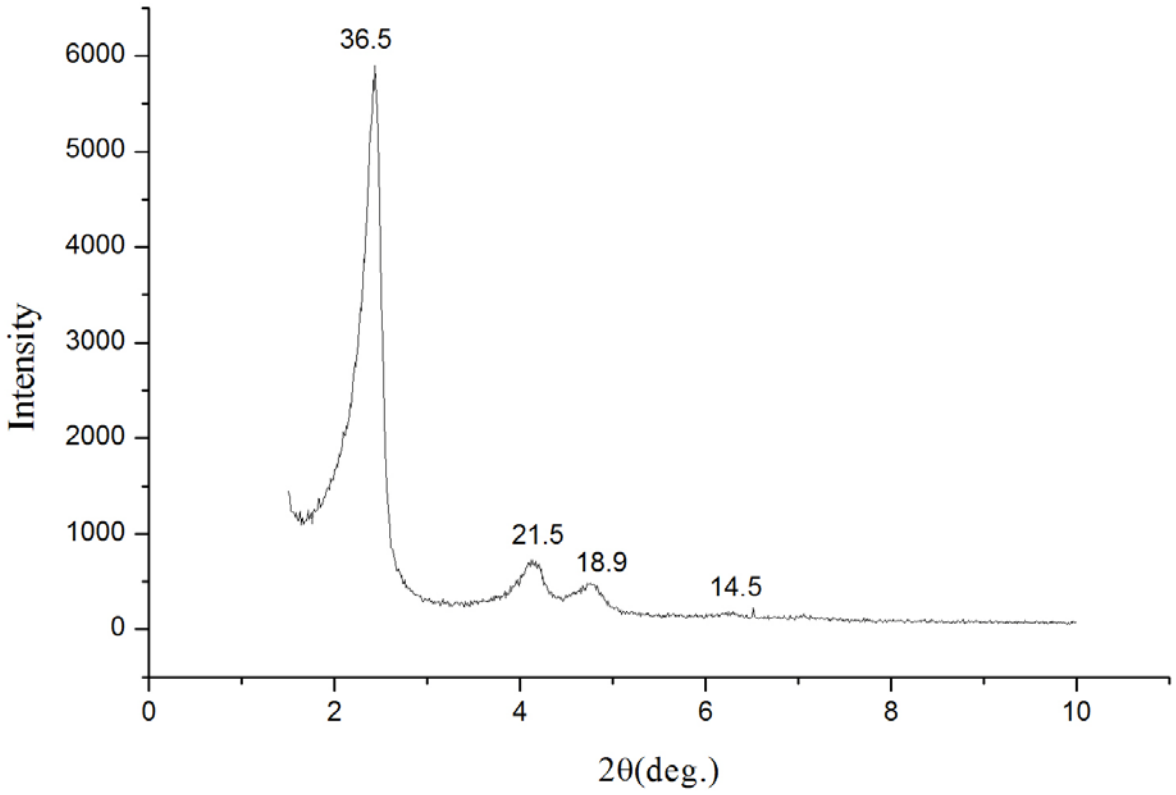


Figure 2. Powder X-ray diffraction pattern for Chemically modified MCM-41

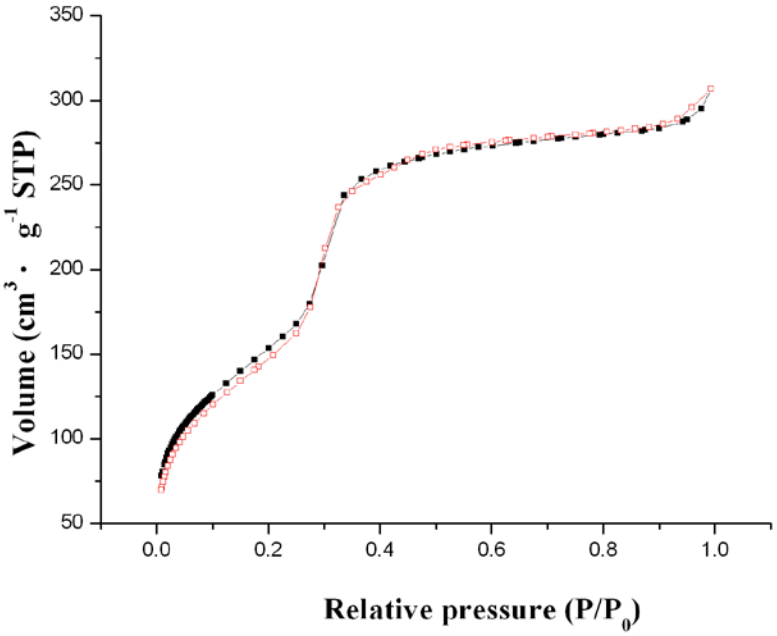


Figure 3.Nitrogen absorption-desorption isotherm of chemically modified MCM-41

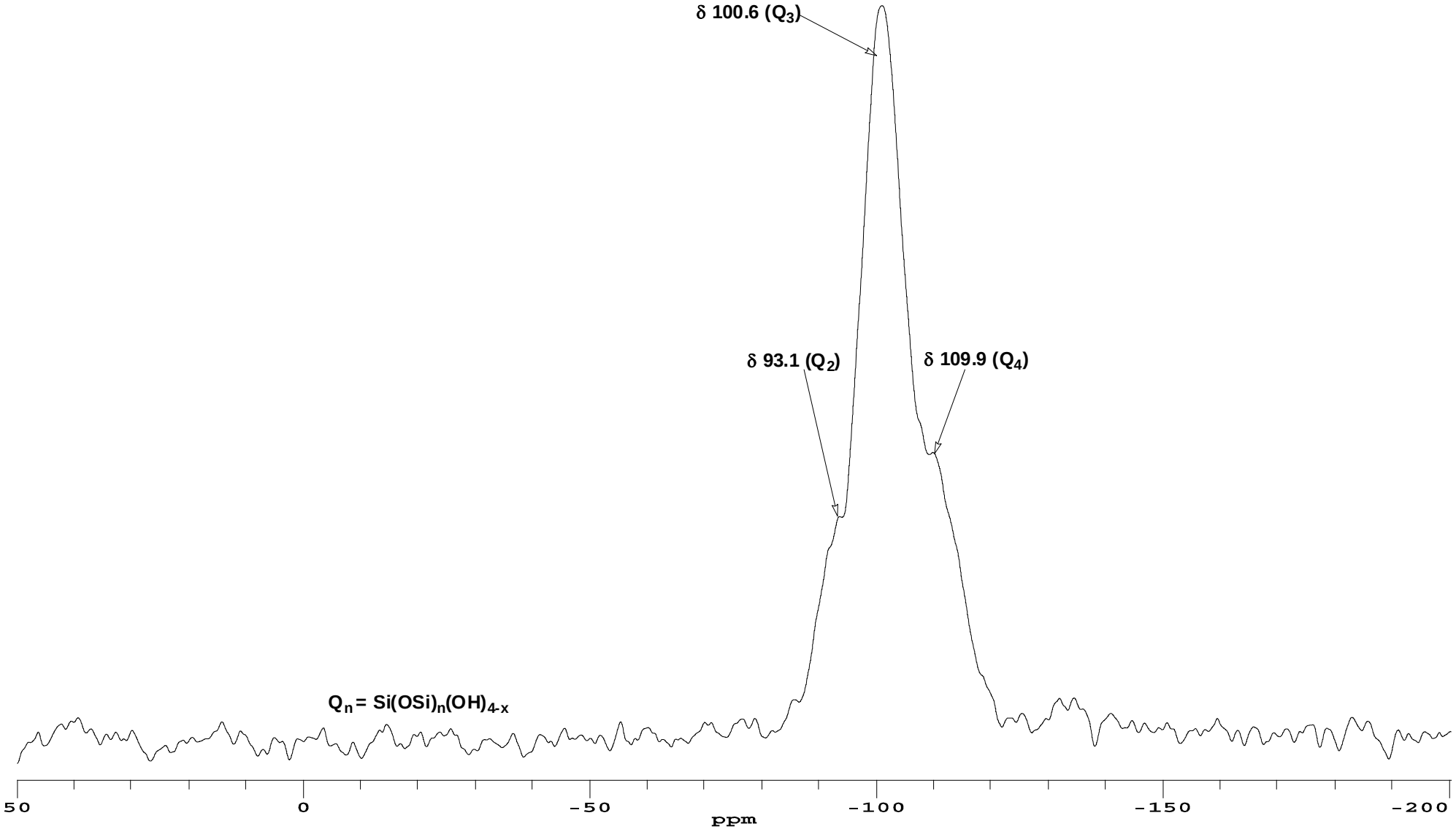


Figure 4. ^{29}Si CP/MAS NMR of MCM-41

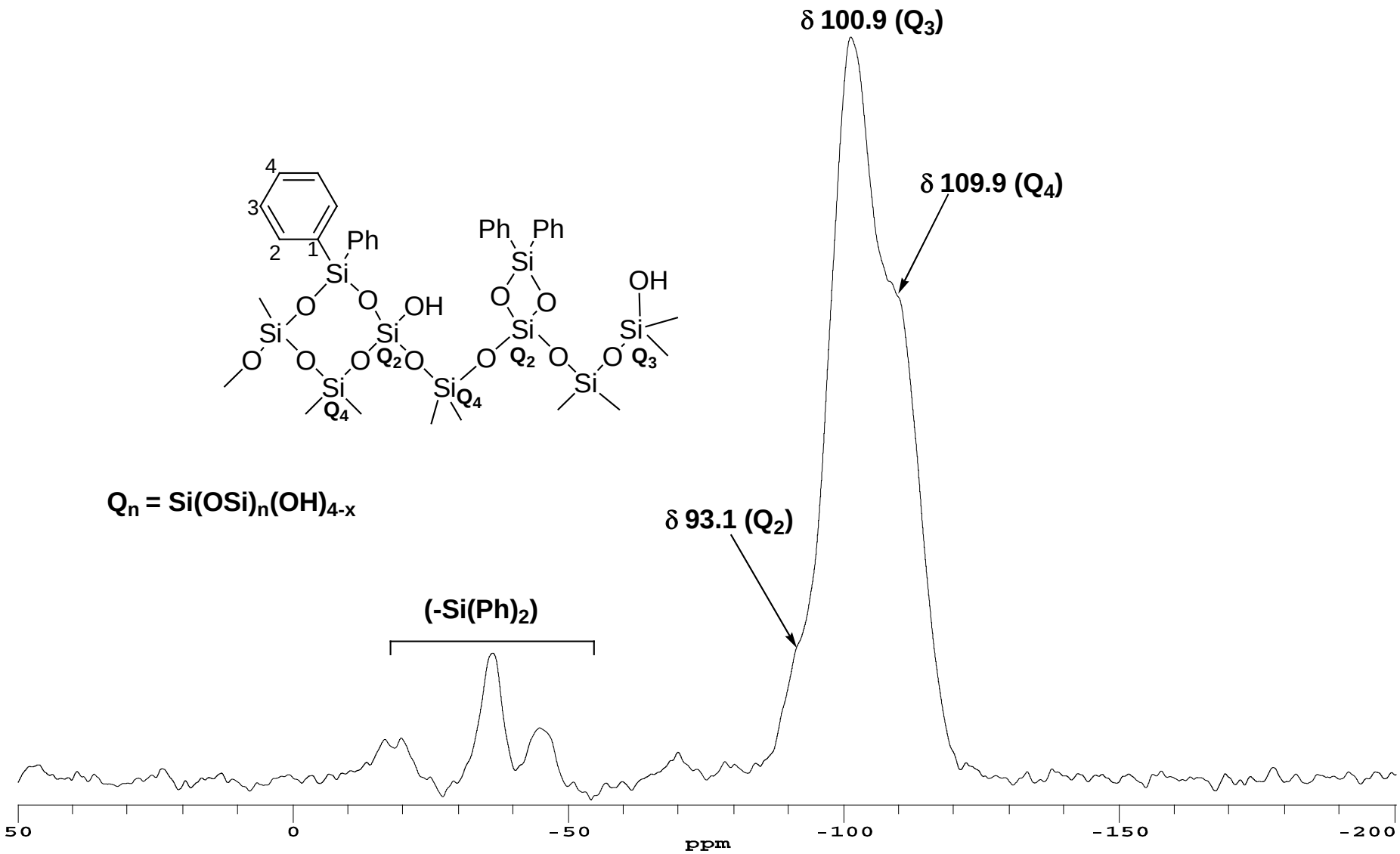


Figure 5. ^{29}**Si CP/MAS NMR of Chemically Modified MCM-41**

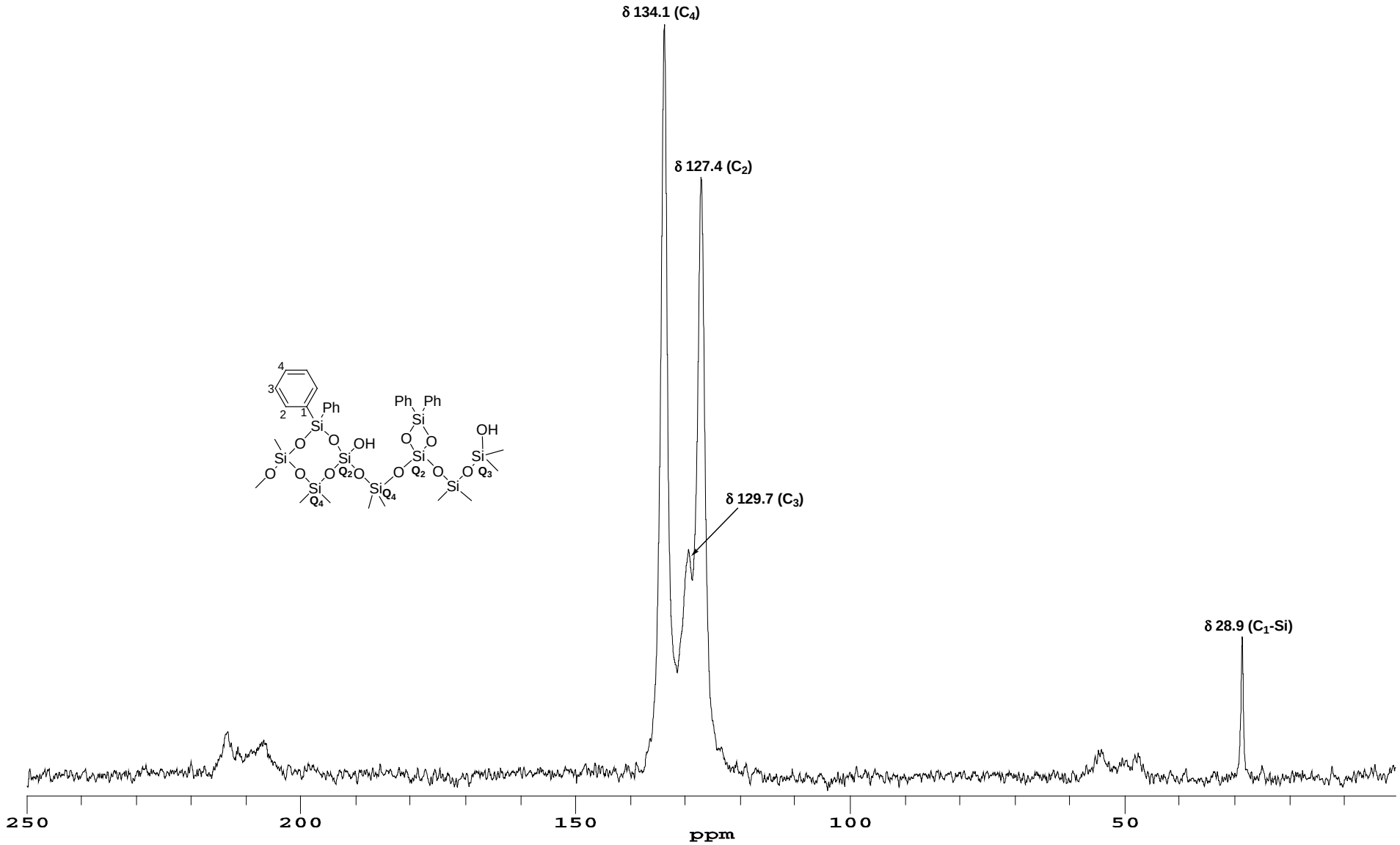
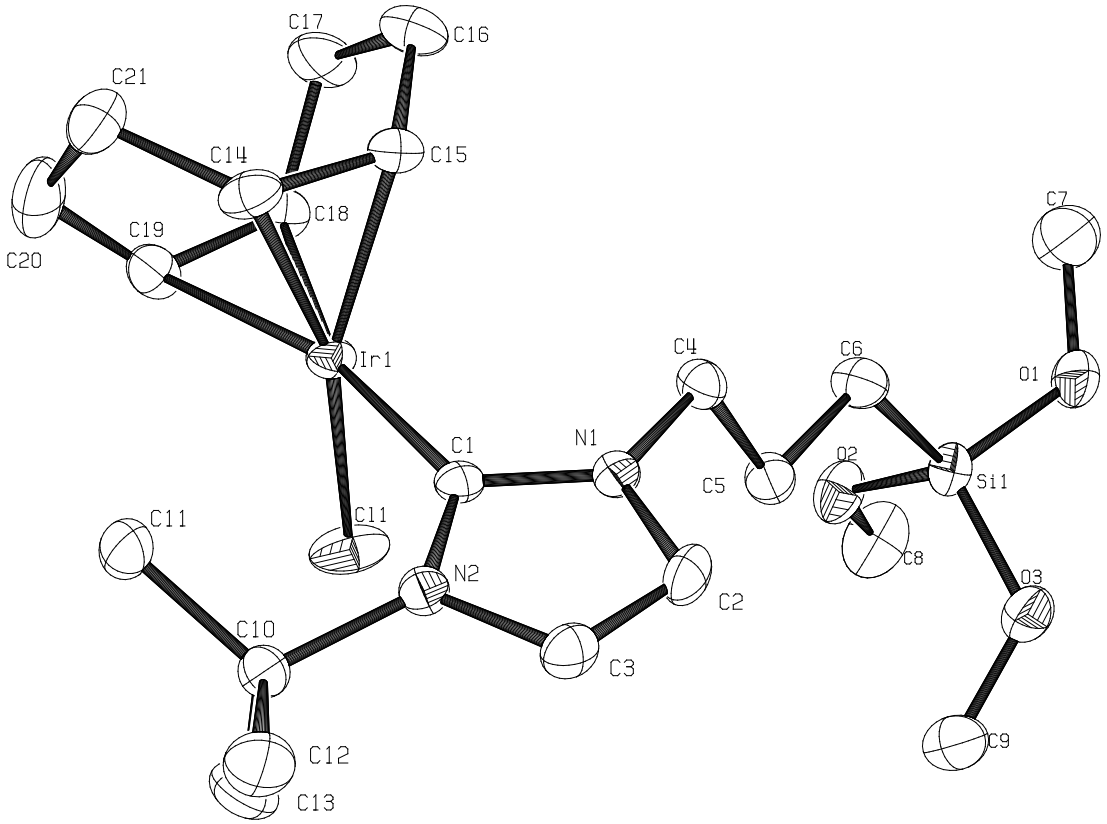


Figure 6. $^{13}C\{^{1}H\}$ CP/MAS NMR of Chemically Modified MCM-41

Inorganic Chemistry Crystallography Service

Department of Chemistry, University of Oxford
Chemistry Research Laboratory
Mansfield Road
Oxford, OX1 3TA



H atoms not shown

Crystals of Iridium complex 7b were grown from slow evaporation of concentrated benzene solution under constant flow of nitrogen.. A single crystal having dimensions approximately 0.08 x 0.08 x 0.22 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package[1].

The structure was solved in the space group $P\ \bar{1}$ using the direct-methods program SIR92[2], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite[3]. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The hydrogen atoms of the coordinated alkene groups were located in a difference Fourier map and their coordinates and a common isotropic thermal parameter subsequently refined. Other hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0311, wR = 0.0341.

Attached is a thermal ellipsoid plot (ORTEP-3[4]) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

2 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.

3 CRYSTALS Issue 12, P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487

4 ORTEP-3 v. 1.0.2, C. K. Johnson and M. K. Burnett, 1998.

Table 1: Crystal data and refinement details

Crystal identification	**(η^4-1,5-COD)(tmp^{t}Bu)IrCl, 7b**
Chemical formula	$C_{21H38}ClIrN_2O_3Si$
Formula weight	622.30
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\ \bar{1}$
a (Å)	7.3574(2)
b (Å)	9.8123(3)
c (Å)	17.6344(5)
α (°)	97.7864(10)
β (°)	99.9008(11)
γ (°)	100.0573(13)
Cell volume (Å^3)	1216.74(6)
Z	2
Calculated density (Mg/m^3)	1.698
Absorption coefficient (mm^{-1})	5.669
F_{000}	620
Crystal size (mm)	0.08 x 0.08 x 0.22 mm
Description of crystal	Yellow prism
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.27, 0.64
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-9 \leq h \leq 9$, $-12 \leq k \leq 12$, $0 \leq l \leq 22$
Reflections measured	14106
Unique reflections	5525
R_{int}	0.044
Observed reflections ($I > 3\sigma(I)$)	4674
Refinement method	Full-matrix least-squares on *F*
Parameters refined	275
Weighting scheme	Chebychev 3-term polynomial

Goodness of fit	1.0899
R	0.0311
wR	0.0341
Residual electron density (min,max) ($eÅ^{-3}$)	-1.33, 1.30

Table 2: Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}
Ir(1)	0.53509(3)	0.296987(18)	0.308514(11)	0.0227
Cl(1)	0.6960(2)	0.26680(14)	0.20472(9)	0.0456
C(1)	0.5169(6)	0.4950(5)	0.2869(3)	0.0209
N(1)	0.3701(5)	0.5193(4)	0.2361(2)	0.0235
C(2)	0.3896(7)	0.6598(5)	0.2308(3)	0.0299
C(3)	0.5490(7)	0.7262(5)	0.2787(3)	0.0285
N(2)	0.6300(5)	0.6251(4)	0.3142(2)	0.0231
C(4)	0.2140(7)	0.4102(5)	0.1886(3)	0.0279
C(5)	0.2252(7)	0.3842(5)	0.1030(3)	0.0301
C(6)	0.0463(8)	0.2798(6)	0.0564(3)	0.0349
Si(1)	0.0215(2)	0.23857(15)	-0.05049(8)	0.0307
O(1)	-0.1978(6)	0.1832(5)	-0.0934(2)	0.0461
C(7)	-0.3263(11)	0.0847(9)	-0.0653(5)	0.0694
O(2)	0.1471(6)	0.1217(4)	-0.0677(2)	0.0425
C(8)	0.1466(13)	0.0577(8)	-0.1449(4)	0.0609
O(3)	0.0822(6)	0.3730(4)	-0.0923(2)	0.0408
C(9)	0.2744(9)	0.4370(7)	-0.0899(4)	0.0469
C(10)	0.8278(6)	0.6593(5)	0.3603(3)	0.0256
C(11)	0.8494(8)	0.5758(6)	0.4268(3)	0.0394
C(12)	0.8803(8)	0.8161(6)	0.3959(4)	0.0403
C(13)	0.9572(8)	0.6259(7)	0.3047(4)	0.0439
C(14)	0.4666(8)	0.3327(5)	0.4200(3)	0.0308
C(15)	0.3002(7)	0.2877(5)	0.3622(3)	0.0265
C(16)	0.1771(8)	0.1415(6)	0.3476(3)	0.0373
C(17)	0.2838(8)	0.0257(6)	0.3323(4)	0.0454
C(18)	0.4627(8)	0.0706(5)	0.3028(3)	0.0329
C(19)	0.6338(7)	0.1241(5)	0.3531(4)	0.0362
C(20)	0.6705(10)	0.1493(7)	0.4393(4)	0.0533
C(21)	0.5457(9)	0.2379(7)	0.4746(4)	0.0480

Table 3: Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(1)	0.493(8)	0.428(7)	0.438(3)	0.031(7)
H(2)	0.258(8)	0.362(6)	0.351(3)	0.031(7)
H(3)	0.482(8)	0.034(6)	0.249(4)	0.031(7)
H(4)	0.743(9)	0.117(6)	0.335(3)	0.031(7)
H(21)	0.3004	0.7035	0.1971	0.0381
H(31)	0.6021	0.8294	0.2879	0.0354
H(41)	0.0926	0.4402	0.1931	0.0327
H(42)	0.2165	0.3206	0.2094	0.0327
H(51)	0.2348	0.4749	0.0826	0.0364
H(52)	0.3388	0.3439	0.0970	0.0364
H(61)	-0.0648	0.3197	0.0669	0.0407
H(62)	0.0434	0.1895	0.0770	0.0407
H(71)	-0.4531	0.0656	-0.1006	0.0766
H(72)	-0.3364	0.1246	-0.0113	0.0766
H(73)	-0.2793	-0.0048	-0.0644	0.0766
H(81)	0.2324	-0.0109	-0.1431	0.0750
H(82)	0.1912	0.1315	-0.1752	0.0750
H(83)	0.0157	0.0074	-0.1707	0.0750
H(91)	0.2779	0.5174	-0.1194	0.0558
H(92)	0.3403	0.4723	-0.0344	0.0558
H(93)	0.3390	0.3661	-0.1143	0.0558
H(111)	0.9828	0.6010	0.4564	0.0441
H(112)	0.7634	0.5985	0.4627	0.0441
H(113)	0.8165	0.4731	0.4050	0.0441
H(121)	1.0124	0.8390	0.4267	0.0460
H(122)	0.7923	0.8382	0.4311	0.0460
H(123)	0.8703	0.8734	0.3531	0.0460
H(131)	1.0906	0.6479	0.3341	0.0538
H(132)	0.9447	0.6839	0.2624	0.0538
H(133)	0.9213	0.5240	0.2811	0.0538
H(161)	0.1211	0.1289	0.3946	0.0431
H(162)	0.0741	0.1337	0.3012	0.0431
H(171)	0.3179	-0.0102	0.3822	0.0537
H(172)	0.1990	-0.0516	0.2923	0.0537
H(201)	0.8048	0.1985	0.4590	0.0621
H(202)	0.6499	0.0563	0.4571	0.0621
H(211)	0.6216	0.2987	0.5238	0.0572
H(212)	0.4376	0.1735	0.4869	0.0572

Table 4: Anisotropic thermal parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir(1)	0.02356(9)	0.01796(9)	0.02918(10)	0.00628(6)	0.00943(6)	0.00497(6)
Cl(1)	0.0630(9)	0.0315(6)	0.0585(9)	0.0133(6)	0.0432(8)	0.0181(6)
C(1)	0.022(2)	0.022(2)	0.021(2)	0.0041(16)	0.0094(17)	0.0052(16)
N(1)	0.0229(18)	0.0223(18)	0.0261(19)	0.0065(15)	0.0050(15)	0.0044(14)
C(2)	0.036(3)	0.029(2)	0.031(2)	0.0119(19)	0.006(2)	0.016(2)
C(3)	0.033(2)	0.022(2)	0.033(2)	0.0075(18)	0.010(2)	0.0090(18)
N(2)	0.0237(18)	0.0197(17)	0.0256(19)	0.0041(14)	0.0043(15)	0.0037(14)
C(4)	0.024(2)	0.036(3)	0.022(2)	0.0030(19)	0.0035(18)	0.0036(19)
C(5)	0.029(2)	0.035(3)	0.027(2)	0.0052(19)	0.0062(19)	0.008(2)
C(6)	0.034(3)	0.039(3)	0.029(3)	0.002(2)	0.007(2)	0.001(2)
Si(1)	0.0331(7)	0.0312(7)	0.0274(7)	0.0058(5)	0.0014(5)	0.0094(6)
O(1)	0.038(2)	0.057(3)	0.040(2)	0.0199(19)	-0.0059(17)	0.0041(19)
C(7)	0.051(4)	0.076(5)	0.064(5)	0.025(4)	-0.013(4)	-0.018(4)
O(2)	0.055(2)	0.041(2)	0.036(2)	0.0079(17)	0.0092(18)	0.0228(19)
C(8)	0.093(6)	0.050(4)	0.044(4)	-0.003(3)	0.017(4)	0.033(4)
O(3)	0.045(2)	0.037(2)	0.044(2)	0.0161(17)	0.0093(18)	0.0134(17)
C(9)	0.052(4)	0.045(3)	0.043(3)	0.011(3)	0.011(3)	0.002(3)
C(10)	0.026(2)	0.024(2)	0.023(2)	0.0016(17)	0.0002(18)	-0.0008(17)
C(11)	0.035(3)	0.036(3)	0.039(3)	0.015(2)	-0.008(2)	-0.006(2)
C(12)	0.043(3)	0.028(3)	0.045(3)	0.007(2)	0.003(2)	-0.003(2)
C(13)	0.025(2)	0.051(3)	0.058(4)	0.012(3)	0.015(2)	0.007(2)
C(14)	0.041(3)	0.027(2)	0.022(2)	0.0020(18)	0.010(2)	-0.002(2)
C(15)	0.026(2)	0.026(2)	0.029(2)	0.0055(18)	0.0107(19)	0.0036(18)
C(16)	0.031(3)	0.037(3)	0.040(3)	-0.001(2)	0.013(2)	-0.004(2)
C(17)	0.037(3)	0.027(3)	0.070(4)	0.013(3)	0.012(3)	-0.004(2)
C(18)	0.039(3)	0.018(2)	0.042(3)	0.004(2)	0.011(2)	0.0050(19)
C(19)	0.028(2)	0.022(2)	0.062(4)	0.018(2)	0.007(2)	0.0088(19)
C(20)	0.059(4)	0.042(3)	0.054(4)	0.018(3)	-0.011(3)	0.012(3)
C(21)	0.050(3)	0.059(4)	0.035(3)	0.019(3)	0.002(3)	0.005(3)

Table 5: Bond lengths (Å)

Ir(1) - Cl(1)	2.3582(13)	Si(1) - O(2)	1.623(4)
Ir(1) - C(1)	2.052(4)	Si(1) - O(3)	1.629(4)
Ir(1) - C(14)	2.112(5)	O(1) - C(7)	1.430(8)
Ir(1) - C(15)	2.103(5)	O(2) - C(8)	1.419(8)
Ir(1) - C(18)	2.176(5)	O(3) - C(9)	1.435(7)
Ir(1) - C(19)	2.150(5)	C(10) - C(11)	1.521(7)
C(1) - N(1)	1.357(6)	C(10) - C(12)	1.536(7)
C(1) - N(2)	1.371(6)	C(10) - C(13)	1.523(7)
N(1) - C(2)	1.379(6)	C(14) - C(15)	1.412(7)
N(1) - C(4)	1.471(6)	C(14) - C(21)	1.539(8)
C(2) - C(3)	1.326(7)	C(15) - C(16)	1.519(7)
C(3) - N(2)	1.406(6)	C(16) - C(17)	1.511(8)
N(2) - C(10)	1.497(6)	C(17) - C(18)	1.514(8)
C(4) - C(5)	1.516(7)	C(18) - C(19)	1.380(8)
C(5) - C(6)	1.544(7)	C(19) - C(20)	1.476(9)
C(6) - Si(1)	1.844(5)	C(20) - C(21)	1.521(10)
Si(1) - O(1)	1.623(4)		

Note – H atoms have been excluded

Table 6: Bond angles (°)

Cl(1) - Ir(1) - C(1)	89.32(12)	C(6) - Si(1) - O(2)	107.0(2)
Cl(1) - Ir(1) - C(14)	164.20(15)	O(1) - Si(1) - O(2)	111.8(2)
C(1) - Ir(1) - C(14)	94.11(18)	C(6) - Si(1) - O(3)	114.9(2)
Cl(1) - Ir(1) - C(15)	156.40(14)	O(1) - Si(1) - O(3)	101.6(2)
C(1) - Ir(1) - C(15)	90.91(18)	O(2) - Si(1) - O(3)	110.4(2)
C(14) - Ir(1) - C(15)	39.1(2)	Si(1) - O(1) - C(7)	123.0(4)
Cl(1) - Ir(1) - C(18)	90.67(15)	Si(1) - O(2) - C(8)	121.6(4)
C(1) - Ir(1) - C(18)	160.23(19)	Si(1) - O(3) - C(9)	123.4(4)
C(14) - Ir(1) - C(18)	91.3(2)	N(2) - C(10) - C(11)	111.4(4)
C(15) - Ir(1) - C(18)	81.3(2)	N(2) - C(10) - C(12)	109.5(4)
Cl(1) - Ir(1) - C(19)	90.10(17)	C(11) - C(10) - C(12)	108.0(4)
C(1) - Ir(1) - C(19)	162.56(19)	N(2) - C(10) - C(13)	107.9(4)
C(14) - Ir(1) - C(19)	82.0(2)	C(11) - C(10) - C(13)	110.4(5)
C(15) - Ir(1) - C(19)	96.5(2)	C(12) - C(10) - C(13)	109.8(4)
C(18) - Ir(1) - C(19)	37.2(2)	Ir(1) - C(14) - C(15)	70.1(3)
Ir(1) - C(1) - N(1)	122.1(3)	Ir(1) - C(14) - C(21)	112.5(4)
Ir(1) - C(1) - N(2)	133.6(3)	C(15) - C(14) - C(21)	123.6(5)
N(1) - C(1) - N(2)	104.4(4)	Ir(1) - C(15) - C(14)	70.8(3)
C(1) - N(1) - C(2)	111.6(4)	Ir(1) - C(15) - C(16)	113.2(3)
C(1) - N(1) - C(4)	125.0(4)	C(14) - C(15) - C(16)	124.0(5)
C(2) - N(1) - C(4)	123.3(4)	C(15) - C(16) - C(17)	113.3(4)
N(1) - C(2) - C(3)	107.1(4)	C(16) - C(17) - C(18)	114.3(4)
C(2) - C(3) - N(2)	107.6(4)	Ir(1) - C(18) - C(17)	112.3(4)
C(1) - N(2) - C(3)	109.4(4)	Ir(1) - C(18) - C(19)	70.4(3)
C(1) - N(2) - C(10)	127.8(4)	C(17) - C(18) - C(19)	122.0(5)
C(3) - N(2) - C(10)	121.6(4)	Ir(1) - C(19) - C(18)	72.4(3)
N(1) - C(4) - C(5)	113.1(4)	Ir(1) - C(19) - C(20)	110.6(4)
C(4) - C(5) - C(6)	109.5(4)	C(18) - C(19) - C(20)	127.1(6)
C(5) - C(6) - Si(1)	117.6(4)	C(19) - C(20) - C(21)	114.3(5)
C(6) - Si(1) - O(1)	111.2(2)	C(14) - C(21) - C(20)	113.4(5)

Note – H atoms have been excluded