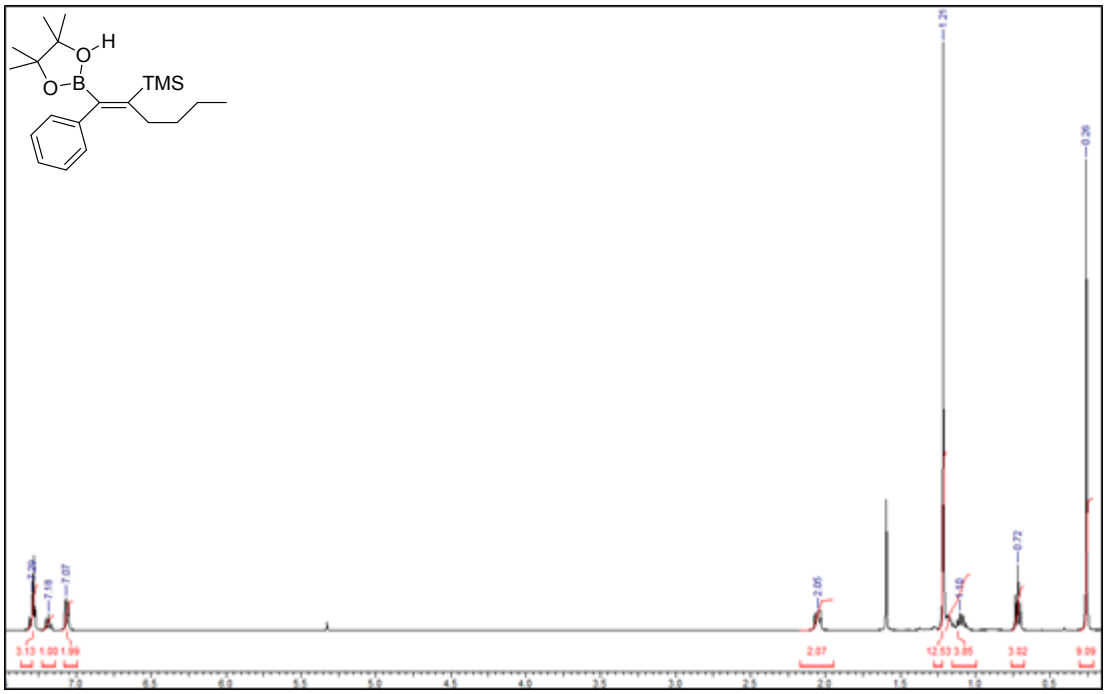
Supporting Information

NMR Spectra: ^{1}H NMR spectra for all isolated compounds are shown below as an indicator of purity.

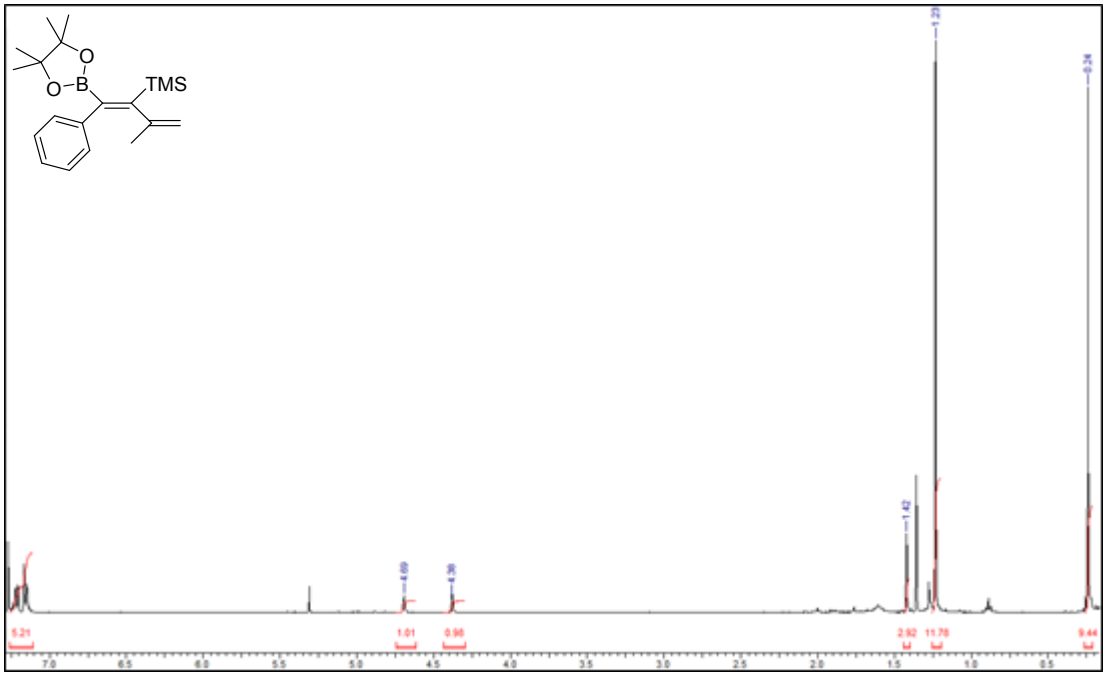
For compounds **2x** the ^{1}H NMR spectra are shown synthesized via route 2 and without column chromatography to show the relative purity at this stage. If necessary the compounds can be further purified by chromatography. Resonances for residual solvents, water and minor pinacol containing by-products are observed in some spectra, especially pre-column (i.e. **2x**). Unless otherwise stated all spectra are recorded in $CDCl_3$ at 293 K.

2a

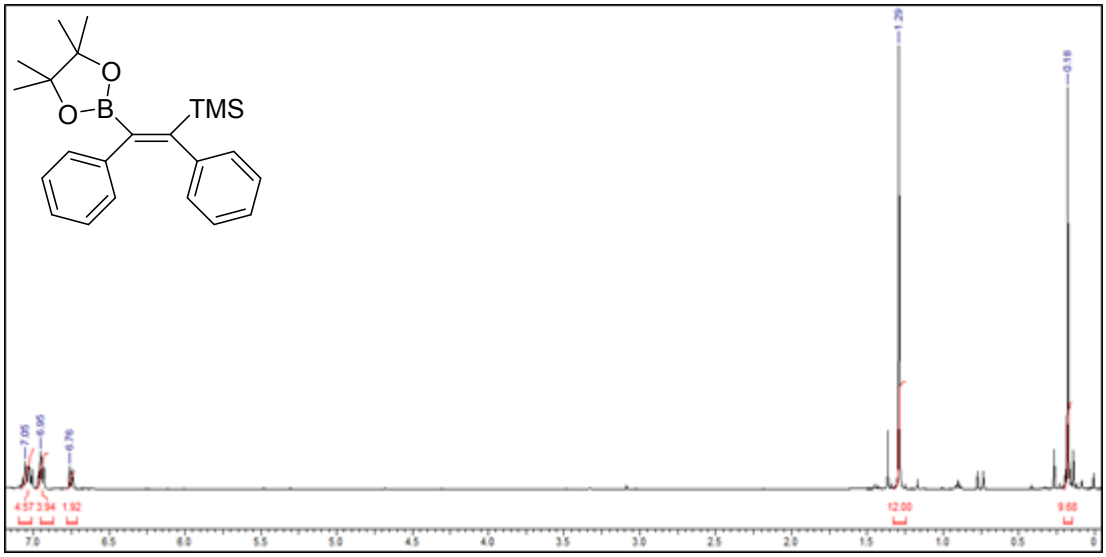
2b



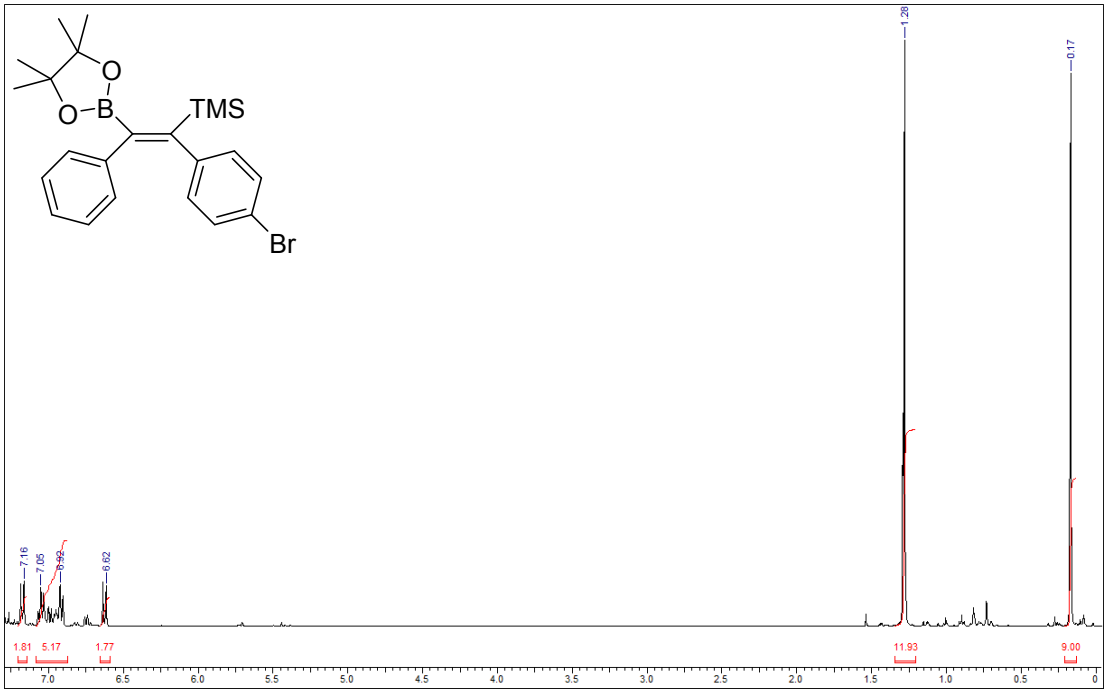
2c (resonance at 5.32 is residual DCM and not any other vinyl containing species)



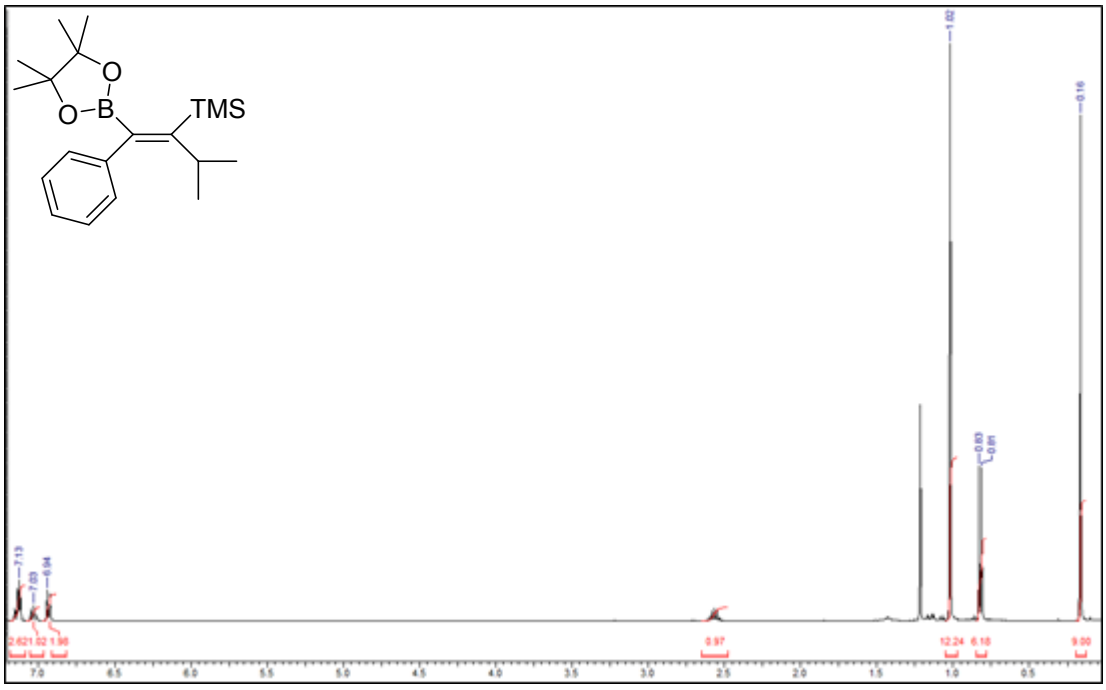
2d



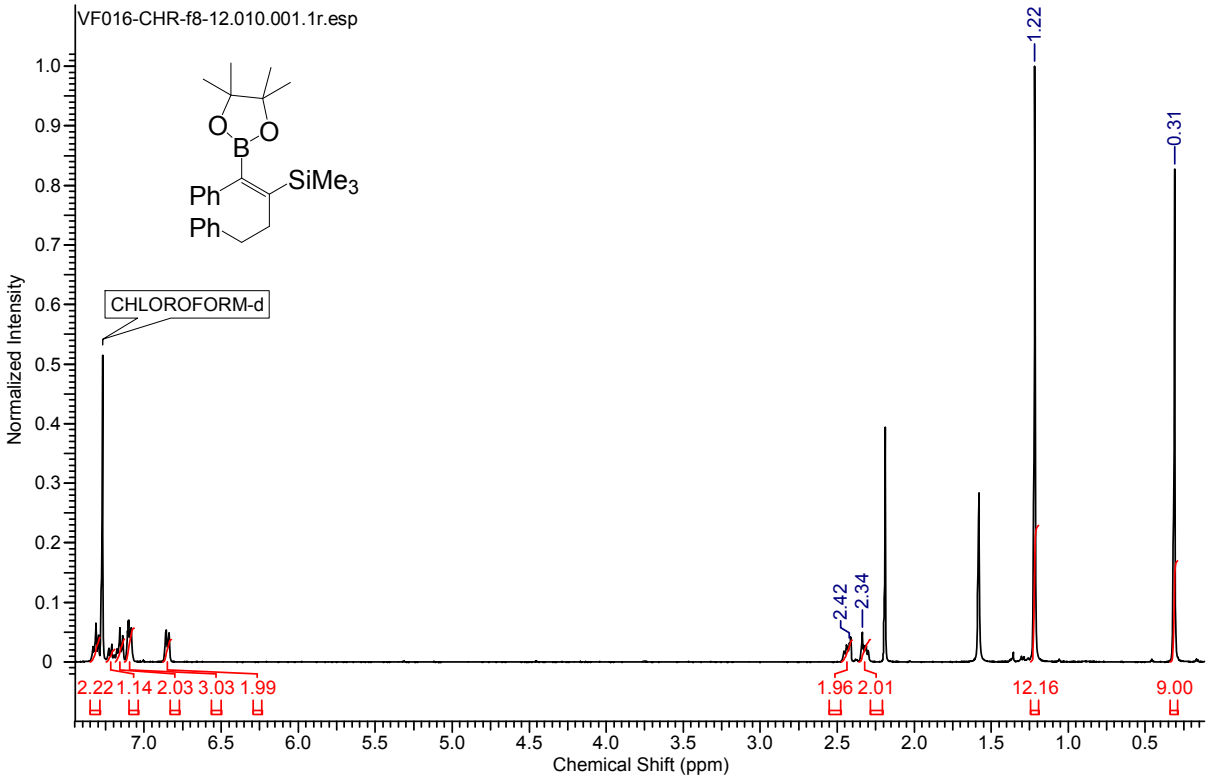
2e


O
O
B
TMS
Br
1.28
0.17
7.16
7.05
6.92
6.62
1.81
5.17
1.77
11.93
9.00

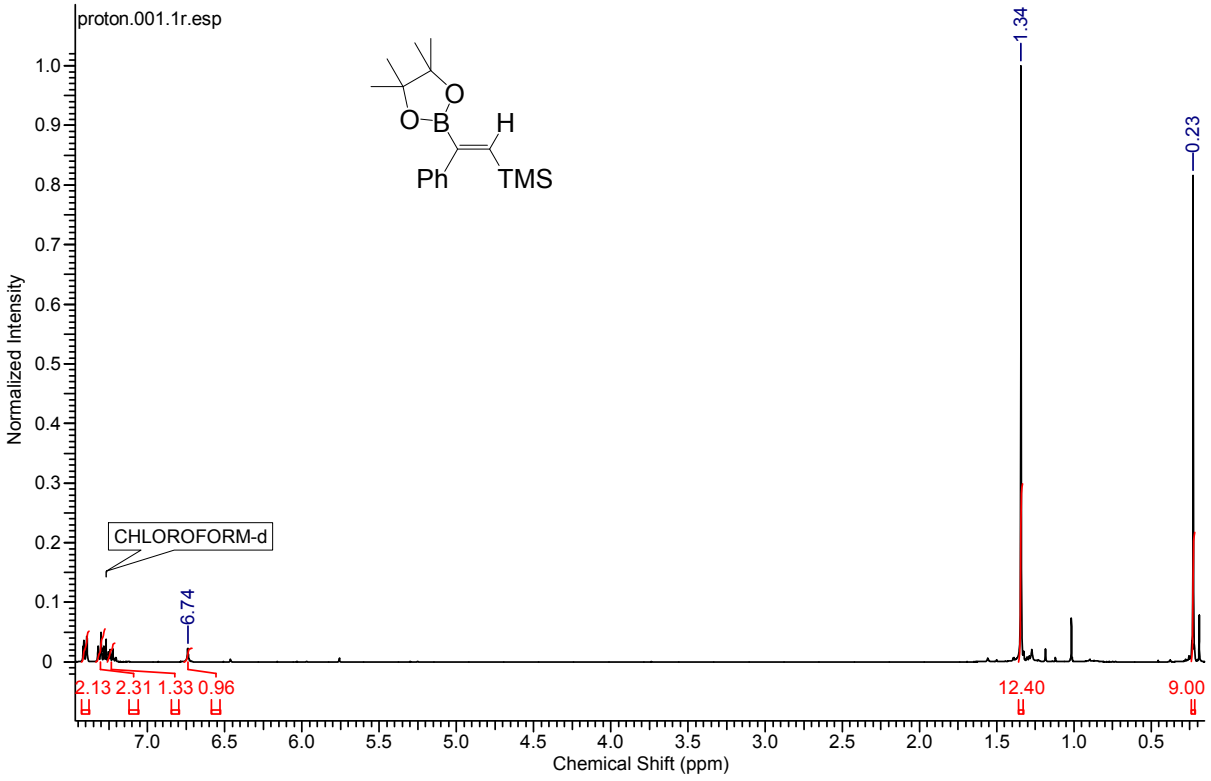
2f


O
O
B
TMS
1.02
0.16
0.83
0.81
7.13
7.03
6.94
2.62
1.02
1.38
0.97
12.24
6.10
9.00

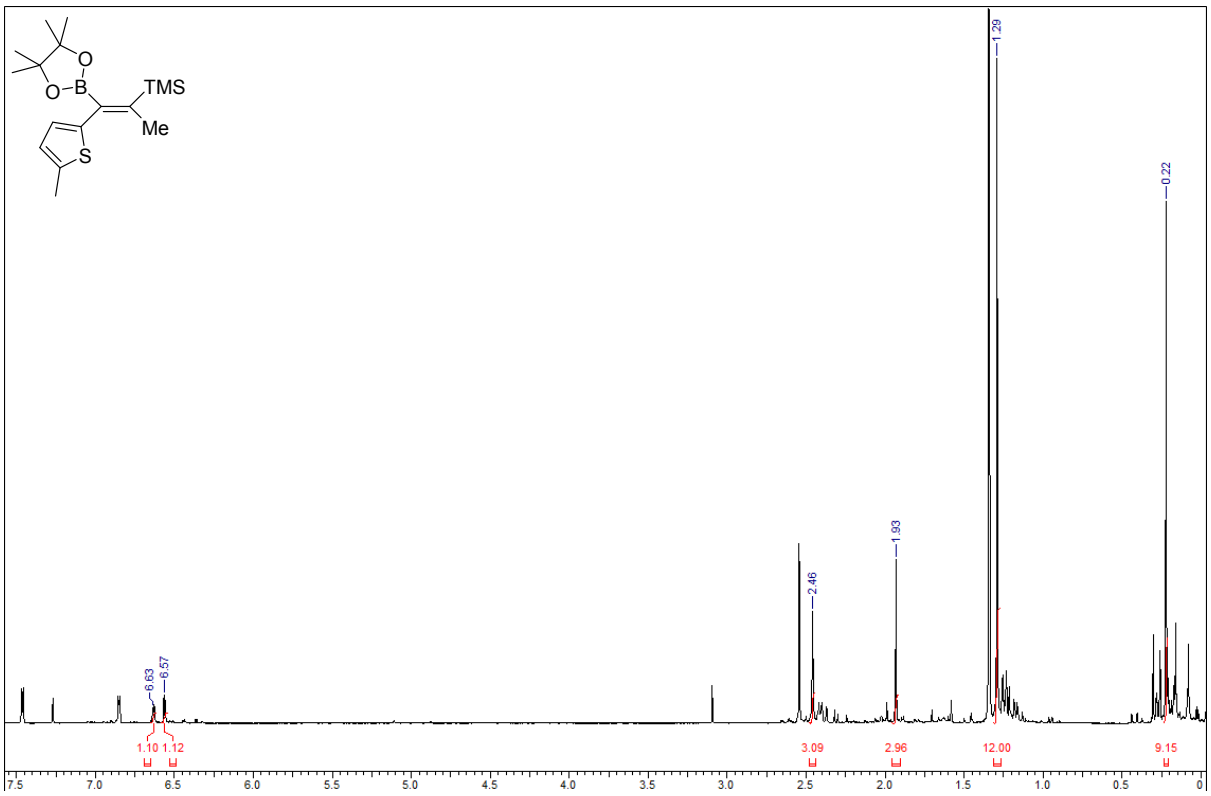
2g


VF016-CHR-f8-12.010.001.1r.esp
O
O
B
Ph
Ph
SiMe3
CHLOROFORM-d
1.22
0.31
2.42
2.34
2.22 1.14 2.03 3.03 1.99
1.96 2.01
12.16
9.00
Normalized Intensity
Chemical Shift (ppm)

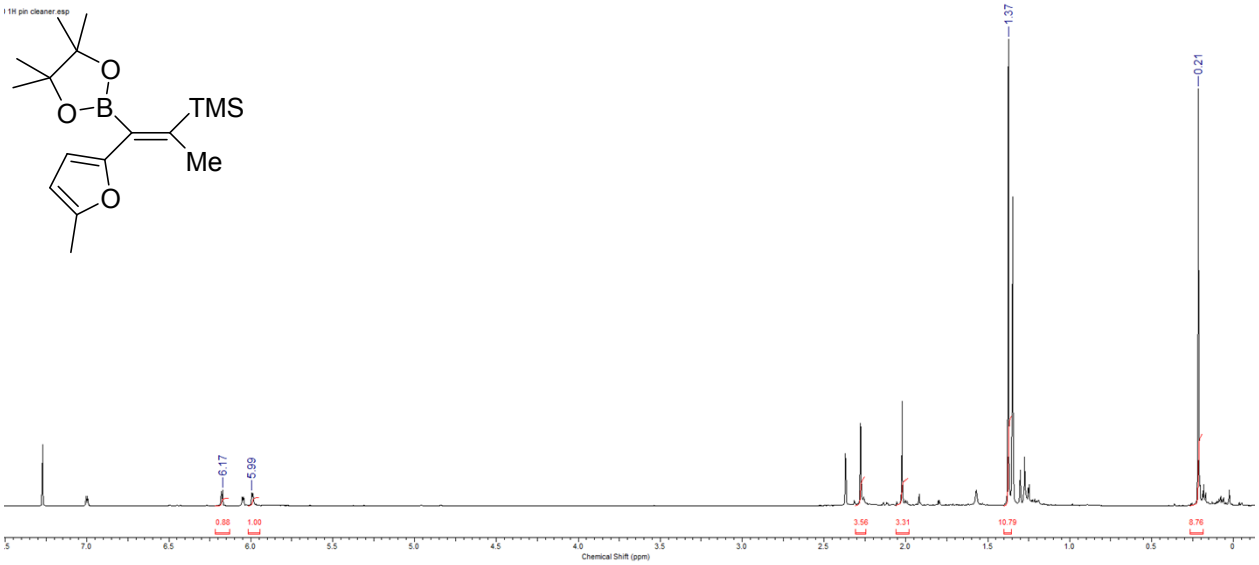
2h


proton.001.1r.esp
O
O
B
H
Ph
TMS
CHLOROFORM-d
1.34
0.23
6.74
2.13 2.31 1.33 0.96
12.40
9.00
Normalized Intensity
Chemical Shift (ppm)

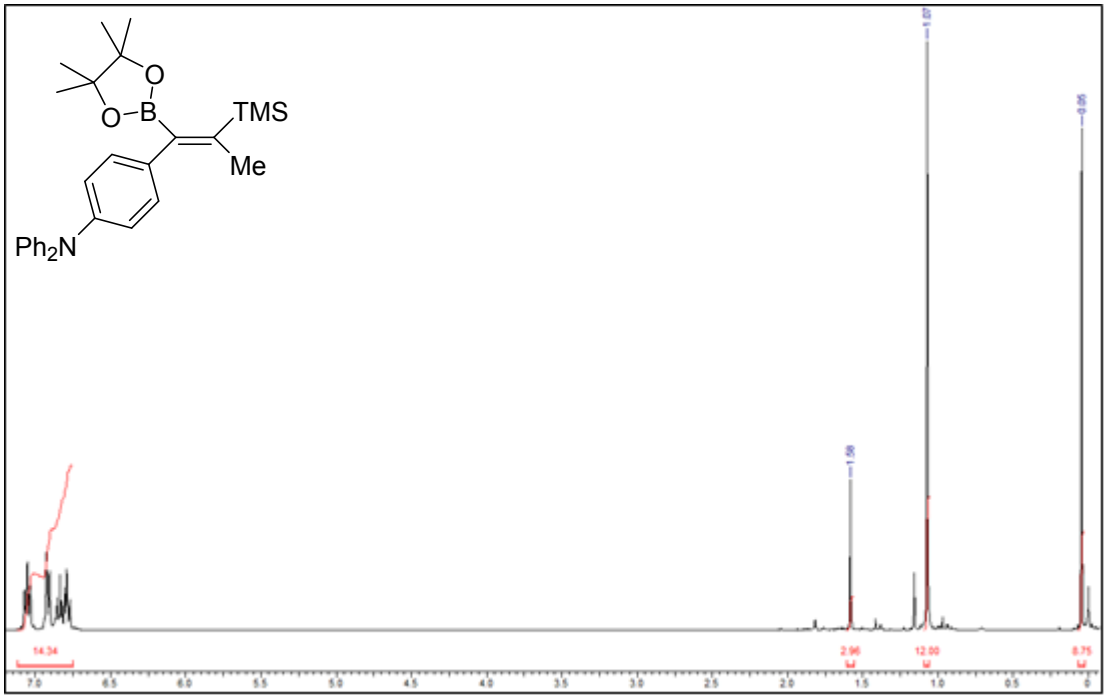
2i After filtration through a one inch plug of silica **2i** is the major product (resonances integrated in the spectrum below) with the only significant by-product observed being 2-methyl-5-BPin-thiophene.



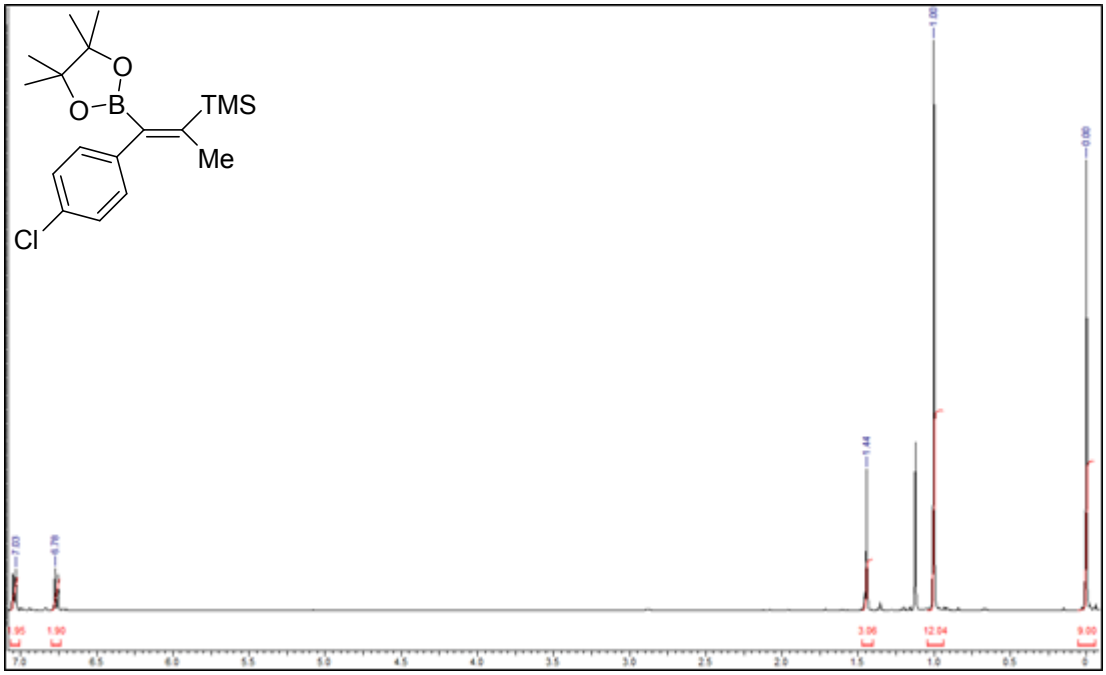
2j After filtration through a one inch plug of silica **2j** is the major product (resonances integrated in the spectrum below) with the only significant by-product being 2-methyl-5-BPin-furan.



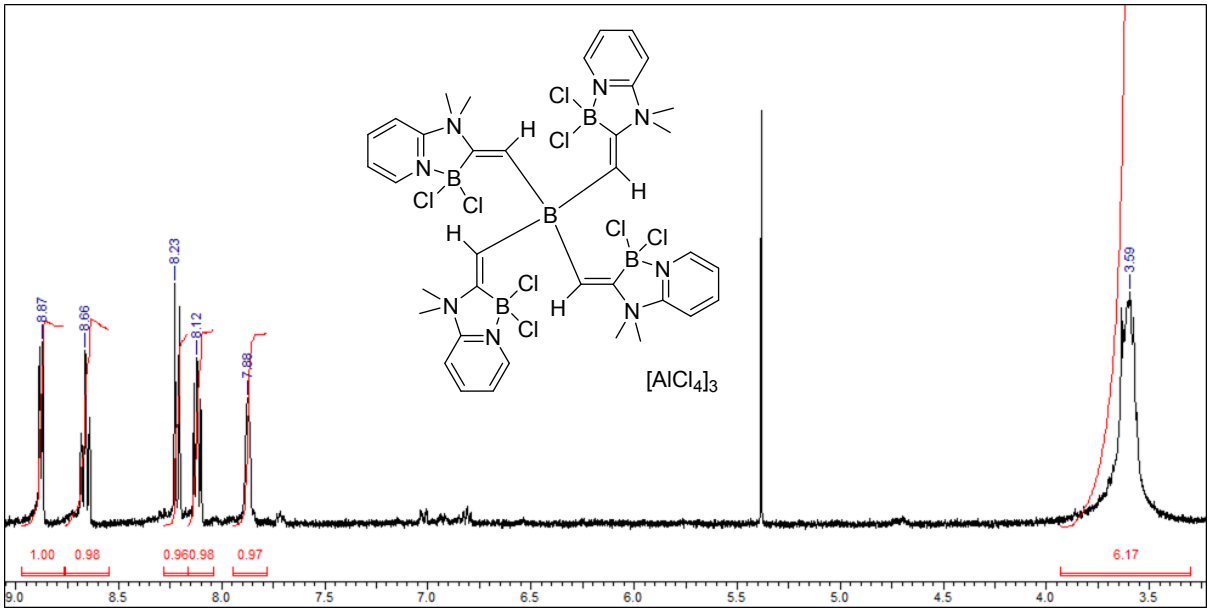
2k



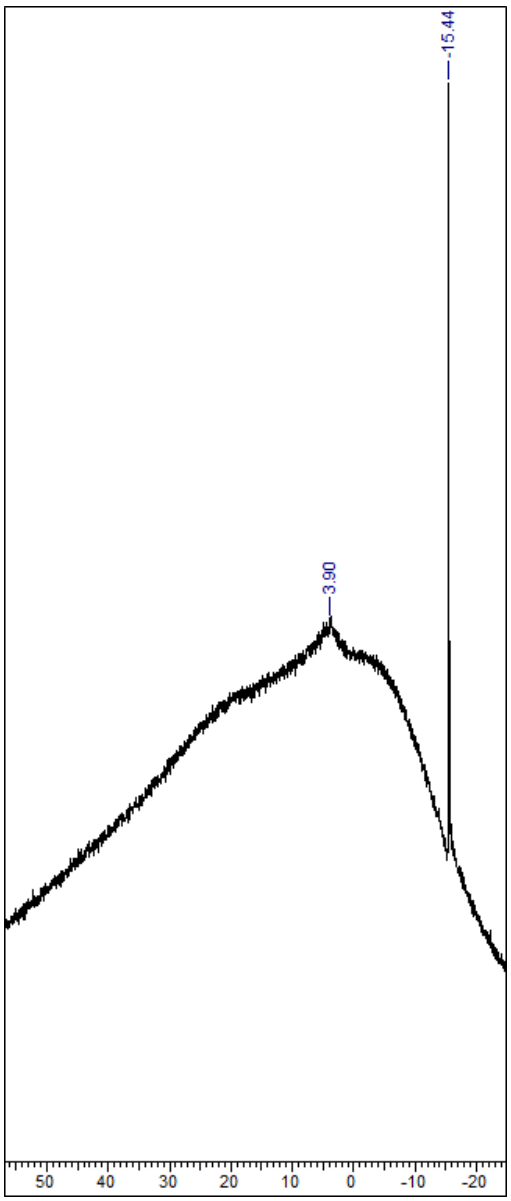
2l



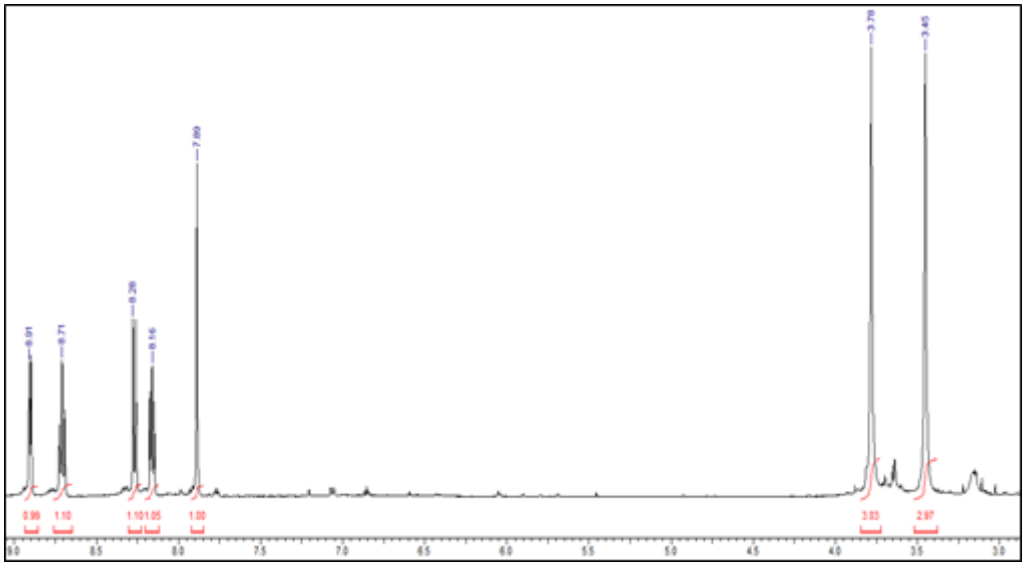
Compound 4 ^{1}H NMR (d_3-MeCN) resonance at 5.4 due to residual DCM)



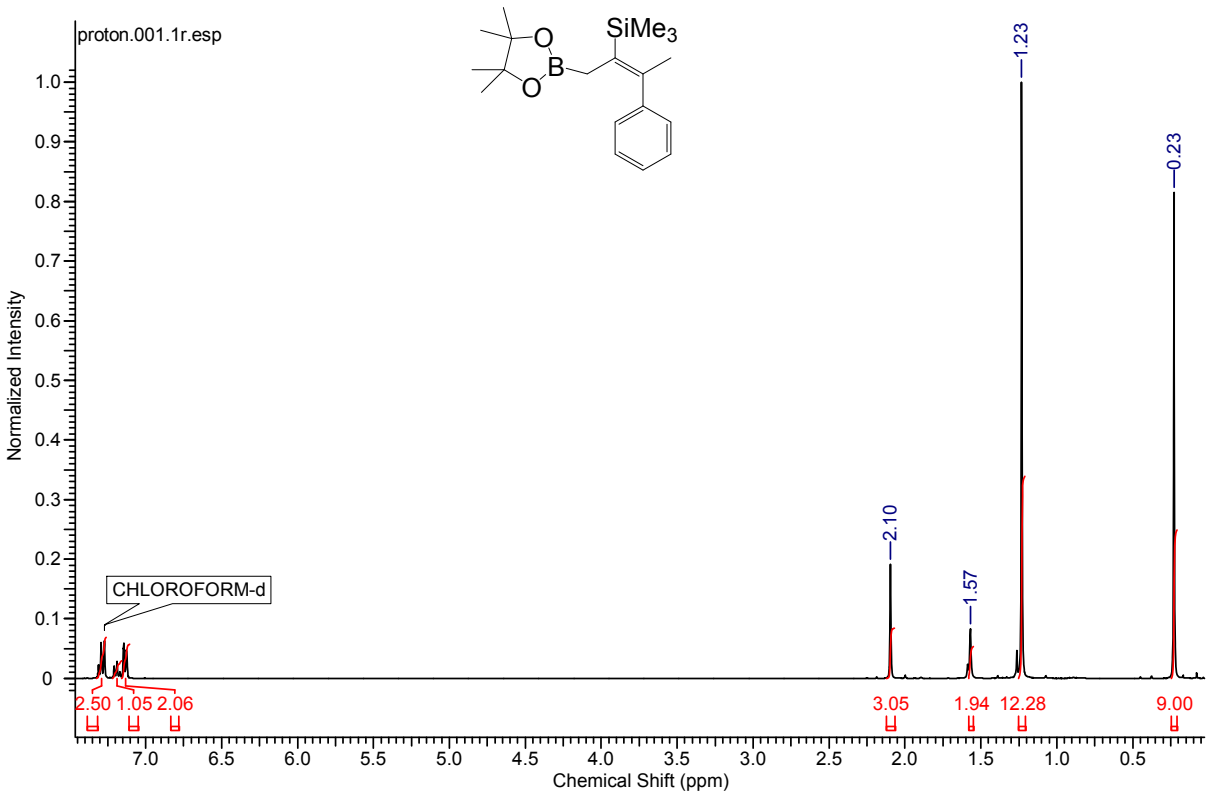
Compound 4 ^{11}B NMR (d_3-MeCN)



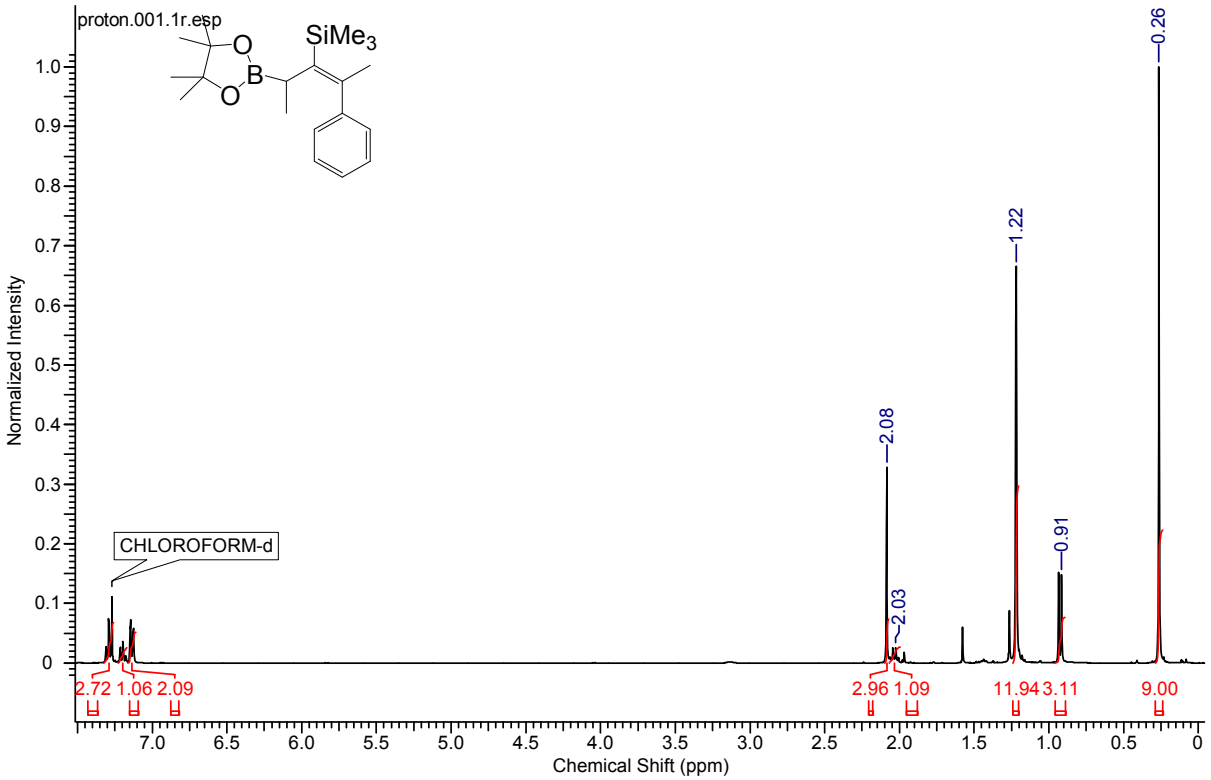
Compound 4 (d_3-MeCN, -40°C)



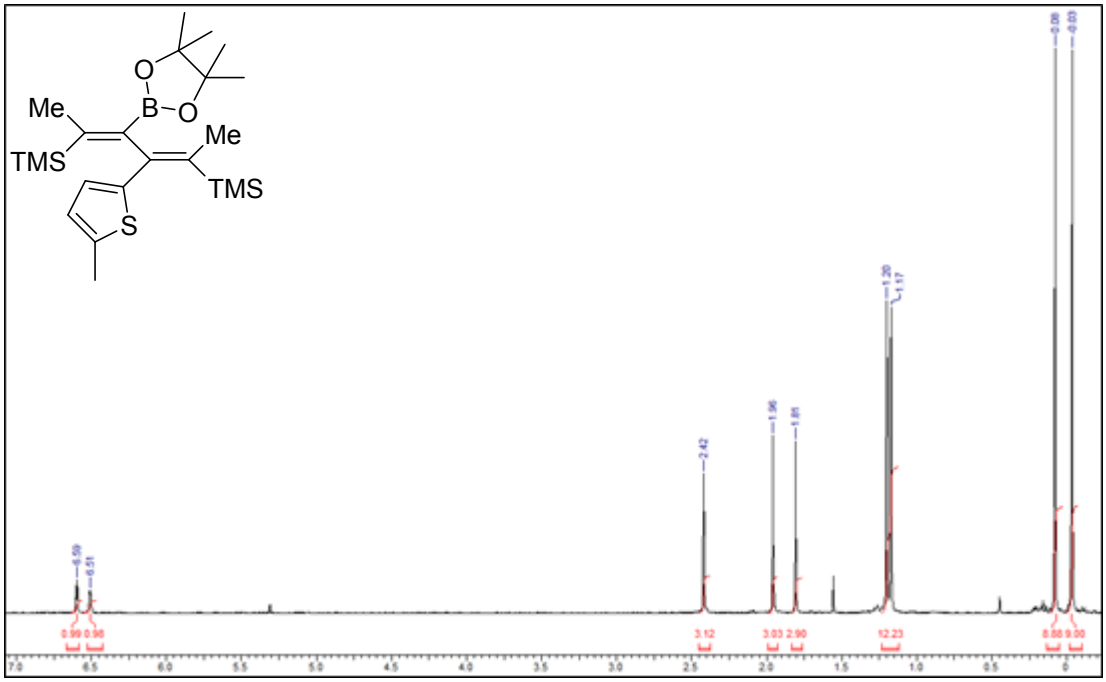
9a


proton.001.1r.esp
SiMe3
O
B
O
1.23
0.23
2.10
1.57
CHLOROFORM-d
2.50 1.05 2.06
3.05 1.94 12.28 9.00
Normalized Intensity
Chemical Shift (ppm)

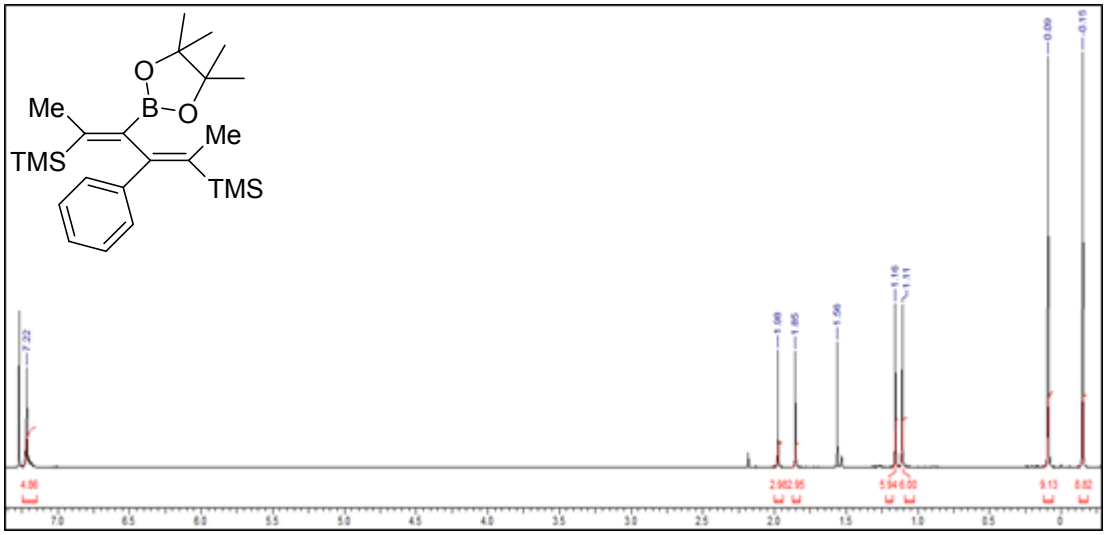
9b


proton.001.1r.esp
SiMe3
O
B
O
0.26
1.22
2.08
0.91
2.03
CHLOROFORM-d
2.72 1.06 2.09
2.96 1.09 11.94 3.11 9.00
Normalized Intensity
Chemical Shift (ppm)

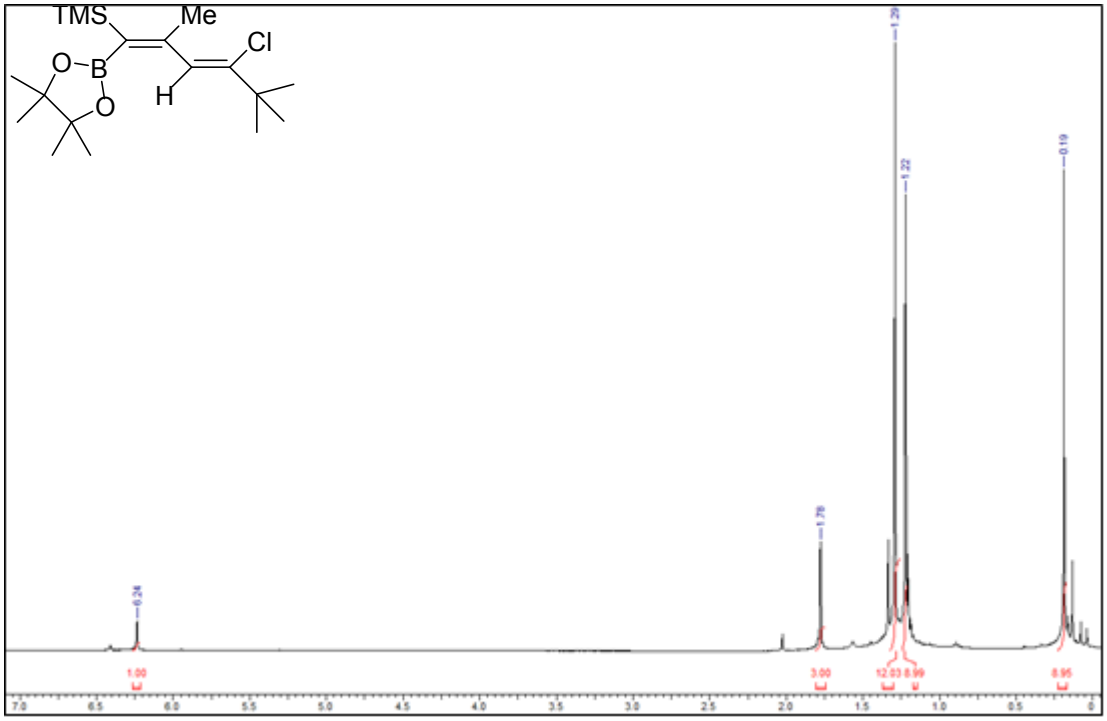
11a



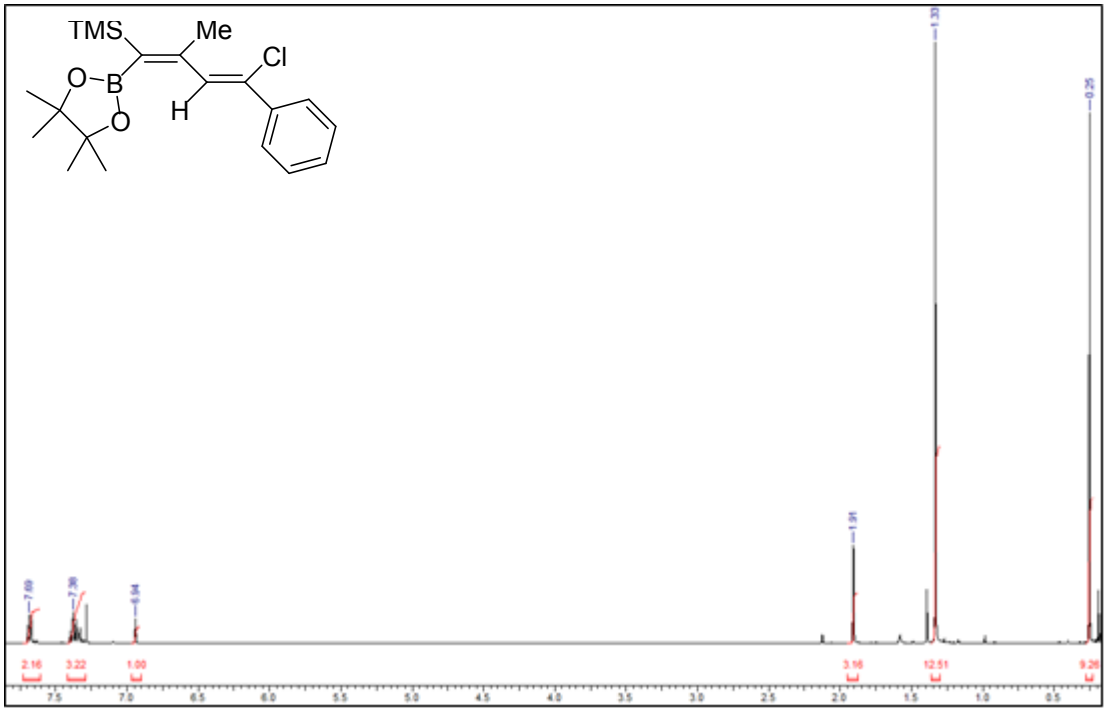
11b



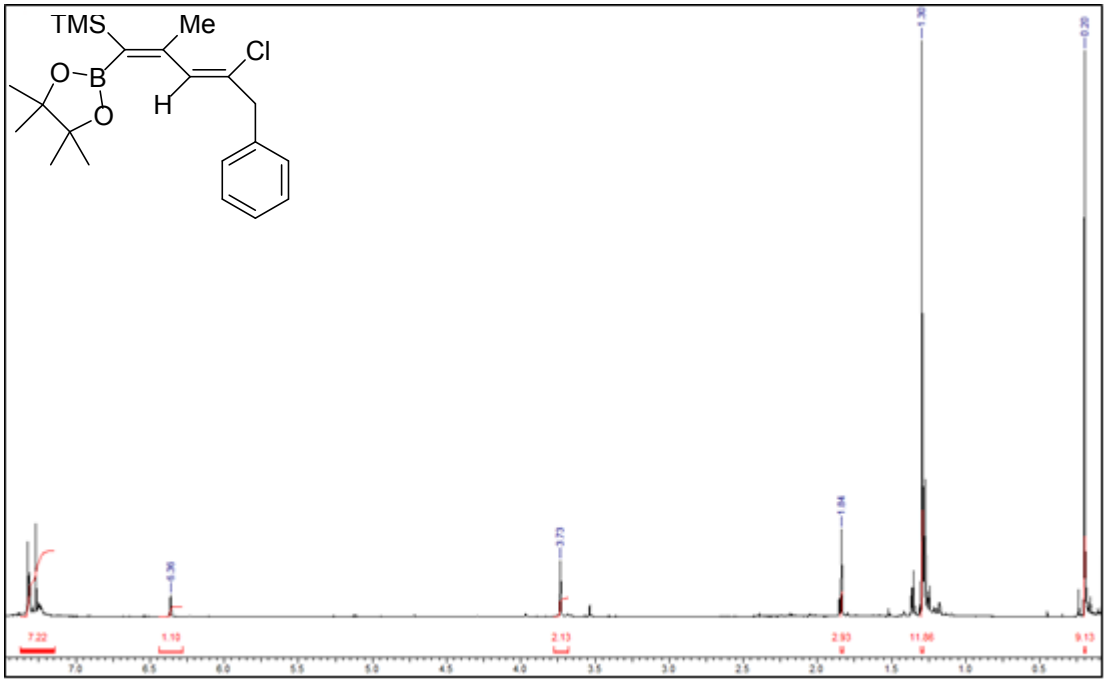
13a



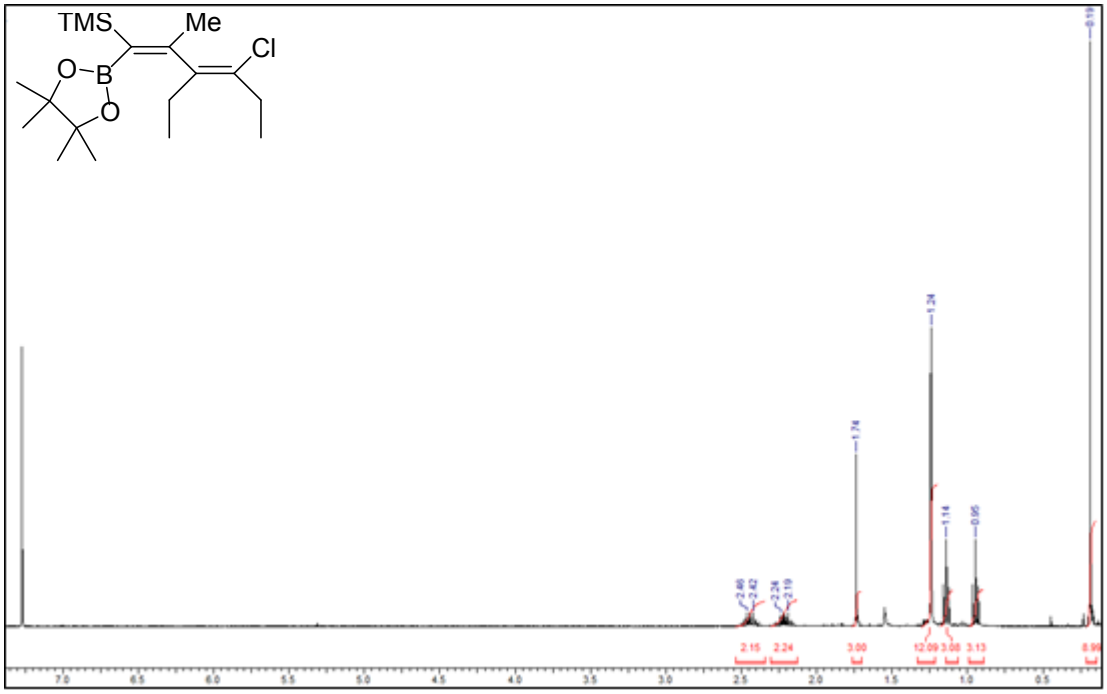
13b



13c



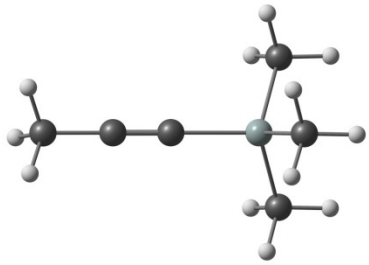
13f



Computational Details

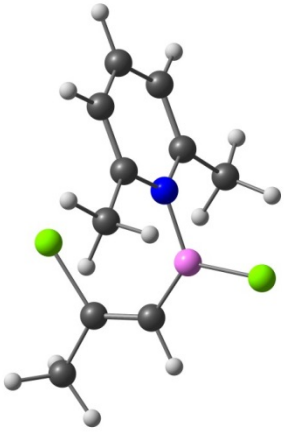
Calculations were performed using the Gaussian09 suite of programmes.[1] Geometries were optimised with the DFT method using M06-2X functional[2] and 6-311G(d,p) as a basis set. All stationary geometry optimizations were full, with no restrictions. All stationary points were characterised as a minima by vibrational analysis. Solvent effects of the dichloromethane were introduced using the self consistent field approach, by means of the integral equation formalism polarisable continuum model (IEFPCM).[3]

Full Cartesian coordinates and energies of the optimised structures are provided below.



1-(Trimethylsilyl)propyne
E(RM062X) = -525.280661847

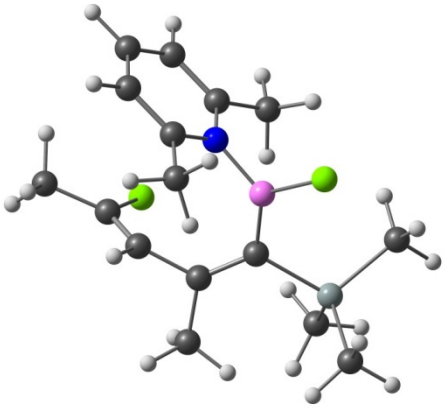
C	-0.761991000	-4.056777000	-1.734559000
H	-0.028775000	-3.318183000	-2.066309000
H	-0.263966000	-5.028358000	-1.675737000
H	-1.546655000	-4.122611000	-2.491777000
C	-0.121808000	-3.489411000	1.223316000
H	-0.525104000	-3.182878000	2.191103000
H	0.360134000	-4.462829000	1.347974000
H	0.642103000	-2.766556000	0.927884000
C	-2.780832000	-4.837556000	0.452796000
H	-3.226904000	-4.560054000	1.410553000
H	-3.579366000	-4.900054000	-0.289928000
H	-2.336884000	-5.831027000	0.559233000
Si	-1.477894000	-3.594754000	-0.065640000
C	-2.277296000	-1.936725000	-0.207364000
C	-2.802141000	-0.848573000	-0.293715000
C	-3.434323000	0.463833000	-0.396234000
H	-3.767359000	0.807202000	0.584609000
H	-2.732692000	1.197641000	-0.796427000
H	-4.301653000	0.422479000	-1.057226000



12Me

E(RM062X) = -1388.70470370

C	-0.022819000	-1.864594000	-0.330877000
C	-1.119141000	-1.087038000	-0.242737000
B	-1.228905000	0.418741000	-0.114293000
Cl	-2.789096000	1.202982000	-0.053674000
N	-0.031875000	1.354396000	-0.031211000
C	0.517962000	1.602057000	1.188553000
C	0.477144000	1.864265000	-1.185212000
C	1.631607000	2.416619000	1.266722000
C	1.591770000	2.678891000	-1.120928000
C	2.172411000	2.956869000	0.108264000
H	2.069462000	2.611979000	2.235716000
H	1.997565000	3.082950000	-2.037760000
H	3.048674000	3.590789000	0.161970000
C	-0.100275000	0.952401000	2.386145000
H	0.427715000	1.258915000	3.285778000
H	-1.150798000	1.234157000	2.489924000
H	-0.040170000	-0.136888000	2.304821000
C	-0.195311000	1.506507000	-2.473061000
H	-1.190418000	1.955315000	-2.526921000
H	0.393420000	1.872333000	-3.310987000
H	-0.300133000	0.422253000	-2.572792000
H	-2.057598000	-1.633532000	-0.279221000
Cl	1.591137000	-1.203436000	-0.298804000
C	-0.034564000	-3.346983000	-0.466970000
H	0.475403000	-3.635864000	-1.389021000
H	0.511212000	-3.798317000	0.364755000
H	-1.056791000	-3.719555000	-0.480478000

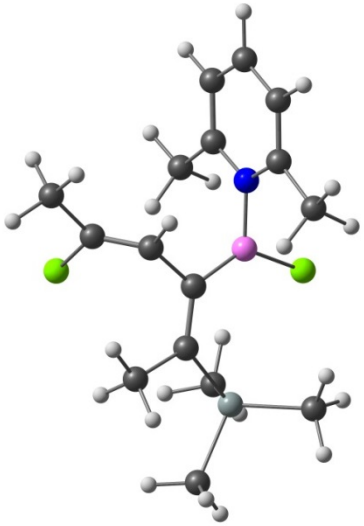


A

E(RM062X) = -1914.02754830

C	1.115425000	-1.068277000	-1.053410000
H	1.331386000	-0.756376000	-2.074109000
C	2.119361000	-1.020907000	-0.186034000
C	-0.222185000	-1.673587000	-0.784104000
C	-1.315096000	-1.002477000	-0.322206000
Si	-2.899017000	-1.961623000	0.201142000
C	-3.937296000	-0.925441000	1.378754000
H	-4.649204000	-1.599257000	1.864169000
H	-3.339530000	-0.463643000	2.169337000
H	-4.508348000	-0.144361000	0.877783000
C	-2.367493000	-3.477572000	1.187883000
H	-2.127739000	-4.344774000	0.572179000
H	-1.493935000	-3.249501000	1.806244000
H	-3.183275000	-3.761652000	1.857572000
C	-3.920859000	-2.406828000	-1.307832000
H	-4.817357000	-2.954482000	-1.005176000
H	-4.238471000	-1.500231000	-1.829282000
H	-3.367091000	-3.027717000	-2.015218000
C	-0.206666000	-3.138953000	-1.130908000
H	-1.197898000	-3.566638000	-1.256916000
H	0.359047000	-3.287590000	-2.053262000
H	0.323257000	-3.684971000	-0.341796000
B	-1.307332000	0.519515000	-0.246056000
Cl	1.874552000	-1.611790000	1.455564000
C	3.504350000	-0.532139000	-0.454056000
H	3.565229000	-0.127548000	-1.464895000
H	3.780275000	0.246553000	0.259960000
H	4.220170000	-1.350459000	-0.350605000
Cl	-2.741235000	1.499885000	-0.513880000
N	-0.069486000	1.365747000	0.052706000
C	0.354197000	1.441435000	1.342508000
C	0.593845000	1.962082000	-0.973279000
C	1.523472000	2.125063000	1.624904000
C	1.761648000	2.652246000	-0.706023000
C	2.233530000	2.728575000	0.596963000
H	1.863839000	2.177895000	2.649839000
H	2.292785000	3.119490000	-1.524062000

H	3.152242000	3.260642000	0.811487000
C	-0.490705000	0.805828000	2.402086000
H	-0.017228000	0.925257000	3.373920000
H	-1.474895000	1.282509000	2.436503000
H	-0.623160000	-0.261732000	2.209968000
C	0.029399000	1.856905000	-2.356983000
H	-0.732385000	2.626219000	-2.505623000
H	0.820783000	2.008639000	-3.088546000
H	-0.435056000	0.885966000	-2.545151000

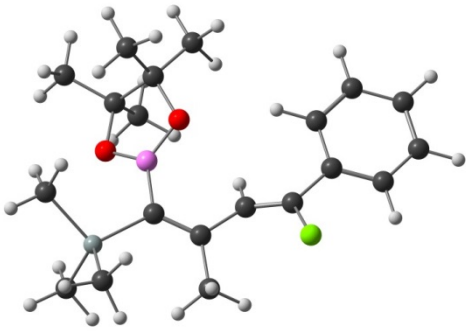


B

E(RM062X) = -1914.01946760

C	-1.615045000	3.390308000	-0.101528000
C	-0.522897000	2.812641000	-0.595220000
H	-0.697360000	2.140729000	-1.434407000
C	0.872822000	2.920109000	-0.068657000
C	1.567828000	4.099769000	-0.114430000
C	0.950875000	5.309672000	-0.760589000
H	0.714717000	6.049844000	0.013520000
H	1.671736000	5.789406000	-1.426794000
H	0.038142000	5.089053000	-1.310770000
C	-3.008584000	3.222713000	-0.611617000
H	-3.658552000	2.836090000	0.176149000
H	-3.412549000	4.184030000	-0.936217000
H	-3.015529000	2.530924000	-1.453829000
Cl	-1.497889000	4.475616000	1.277738000
B	1.389357000	1.589537000	0.471088000
Si	3.297510000	4.499774000	0.660955000
C	4.677413000	3.463609000	-0.099931000
H	5.364926000	4.127633000	-0.628868000
H	5.243575000	2.931183000	0.666665000
H	4.304552000	2.727598000	-0.814544000
C	3.686496000	6.296810000	0.275397000
H	2.922441000	6.987036000	0.638666000
H	4.625044000	6.545961000	0.780193000

H	3.835089000	6.471827000	-0.792474000
C	3.115503000	4.381510000	2.527546000
H	2.447055000	5.179023000	2.863967000
H	2.715668000	3.432184000	2.882648000
H	4.088008000	4.542484000	3.001517000
Cl	2.899527000	1.191897000	1.254796000
N	0.464410000	0.371144000	0.327075000
C	0.543877000	-0.387521000	-0.798075000
C	-0.442045000	0.132656000	1.311304000
C	-0.331778000	-1.446287000	-0.955784000
C	-1.326694000	-0.920651000	1.166386000
C	-1.273291000	-1.712749000	0.028750000
H	-0.271434000	-2.047474000	-1.852378000
H	-2.050812000	-1.106711000	1.947201000
H	-1.966606000	-2.535696000	-0.091709000
C	-0.423614000	1.018728000	2.516969000
H	0.479495000	0.836289000	3.105757000
H	-0.444426000	2.075292000	2.235676000
H	-1.289879000	0.812223000	3.141355000
C	1.583195000	-0.030485000	-1.815121000
H	1.517540000	1.024678000	-2.096544000
H	2.585193000	-0.214905000	-1.419086000
H	1.448841000	-0.633425000	-2.709877000



13b

E(RM062X) = -1705.14265648

C	1.062356000	-0.911482000	-0.546496000
H	0.928454000	0.075582000	-0.976799000
C	2.310065000	-1.156855000	-0.139765000
C	-0.163452000	-1.730837000	-0.423011000
C	-1.336393000	-1.120199000	-0.127545000
Si	-2.978836000	-2.039158000	0.109456000
C	-4.077885000	-0.997828000	1.228914000
H	-5.005970000	-1.535648000	1.441065000
H	-3.581850000	-0.801501000	2.184372000
H	-4.325783000	-0.039581000	0.770474000
C	-2.764877000	-3.703713000	0.969684000
H	-2.393406000	-4.487060000	0.307753000
H	-2.081042000	-3.622284000	1.819007000

H	-3.737144000	-4.024593000	1.354824000
C	-3.820678000	-2.281285000	-1.556558000
H	-4.788911000	-2.773540000	-1.429076000
H	-3.988957000	-1.317022000	-2.042481000
H	-3.212805000	-2.896557000	-2.225036000
C	-0.044216000	-3.214581000	-0.705288000
H	-0.930110000	-3.570108000	-1.232774000
H	0.827460000	-3.426903000	-1.324003000
H	0.055166000	-3.791621000	0.217237000
B	-1.417980000	0.429679000	0.015379000
O	-2.497913000	1.138818000	-0.454041000
O	-0.476890000	1.250383000	0.592503000
C	-1.069301000	2.567218000	0.728403000
C	-2.168163000	2.547156000	-0.381769000
C	-1.631854000	2.946551000	-1.753043000
H	-2.388358000	2.718112000	-2.505426000
H	-1.409144000	4.014473000	-1.795162000
H	-0.724535000	2.388193000	-1.996326000
C	-3.423090000	3.333357000	-0.046880000
H	-3.178635000	4.385713000	0.118025000
H	-4.125470000	3.270438000	-0.879847000
H	-3.908521000	2.940210000	0.845887000
C	0.011870000	3.616381000	0.536930000
H	-0.425130000	4.618012000	0.546118000
H	0.732226000	3.550296000	1.355177000
H	0.542405000	3.473941000	-0.404801000
C	-1.651798000	2.643249000	2.136238000
H	-0.854391000	2.455508000	2.856939000
H	-2.078464000	3.628285000	2.335197000
H	-2.429044000	1.887890000	2.276655000
Cl	2.756514000	-2.673624000	0.631651000
C	3.396735000	-0.154848000	-0.219729000
C	4.709190000	-0.515120000	-0.534651000
C	3.094528000	1.190940000	0.017664000
C	5.695392000	0.458113000	-0.639907000
H	4.953587000	-1.556889000	-0.705677000
C	4.085066000	2.159889000	-0.084929000
H	2.084634000	1.464217000	0.305570000
C	5.386813000	1.797325000	-0.418418000
H	6.707914000	0.169536000	-0.895641000
H	3.841271000	3.198097000	0.109044000
H	6.159415000	2.552756000	-0.497344000

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Crystallography

Data Collection. X-ray data for compounds **2e** and **4** was collected at a temperature of 150 K using a using Mo-K_α radiation on an Agilent Supernova, equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. Data were measured using CrysAlisPro suite of programs.

Crystal structure determinations and refinements. X-ray data were processed and reduced using CrysAlisPro suite of programs. Absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.[1] The crystal structure was solved and refined against all F^2 values using the SHELXTL suite of programs.[2] Atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. X-ray data was trimmed for compound **4** due absence of diffraction beyond 1.1 Å. The C-C distances of the disordered ligands in compound **2** were restrained to be the same using SADI and DFIX commands. The atomic displacement parameters (adp) of the disordered ligands have been restrained using RIGU and SIMU commands.

CCDC 1416375-1416376 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic information for **2e** and **4**

	2e	**4**
Crystal colour	colourless	brown
Crystal size (mm)	0.1 × 0.06 × 0.03	0.4 × 0.1 × 0.1
Crystal system	Monoclinic	Monoclinic
Space group, *Z*	$P2_1/c$, *4*	I2/a, *4*
a (Å)	11.5585(7)	22.085(4)
b (Å)	18.4820(8)	13.066(2)
c (Å)	12.0048(9)	23.157(6)
β (°)	115.161(8)	96.49(2)
V (Å^3)	2321.2(3)	6640(2)
Density (Mg.m^{-3})	1.309	1.518
Wavelength (Å)	0.71073	0.71073
Temperature (K)	150	150
μ(Mo-Kα) (mm^{-1})	1.838	0.979
2Θ range (°)	6.82 to 57.958	6.16 to 37.692
Reflns collected	8379	5396
Independent reflns (R_{int})	5079 (0.0291)	2585 (0.0697)
L.S. parameters, *p*	326	317
No. of restraints, *r*	135	174
*R*1 (*F*)[a] *I* > 2.0σ*(I)*	0.0555	0.0922
*wR*2(F^2),[a] all data	0.1343	0.2559
S(F^2),[a] all data	1.046	1.071

[a] $R1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; [b] $wR^2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{½}$; [c] $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{½}$

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