Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Enantioselective reduction of *N*-alkyl ketimines with frustrated Lewis pair catalysis using chiral borenium ions

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Data files are openly available (DOI: 10.14469/hpc/5645).

Contents

1. General considerations

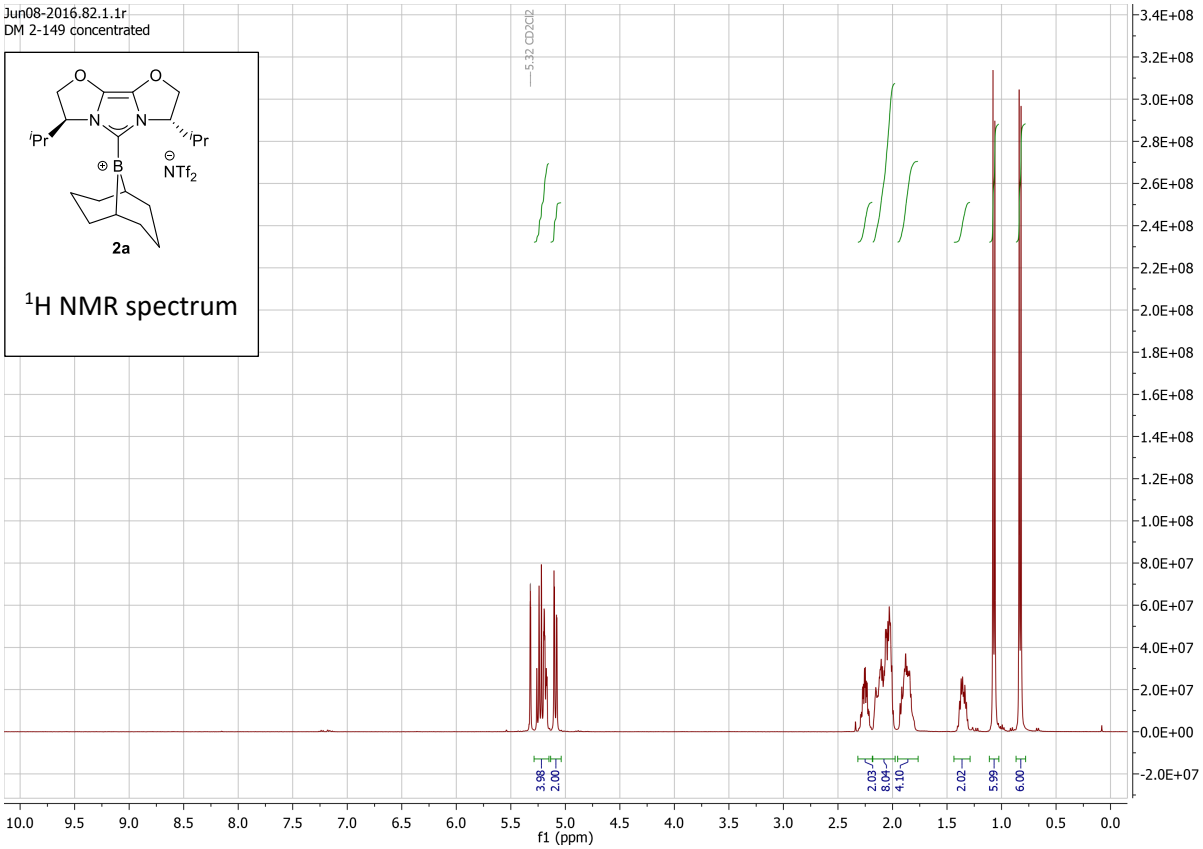
Glassware was oven-dried at temperatures >80 °C and allowed to cool under vacuum or in an inert atmosphere. Manipulations involving moisture or oxygen-sensitive materials were carried out either in an inert atmosphere glovebox or by using standard Schlenk line techniques. 1,2-difluorobenzene and dichloromethane were dried by distilling from calcium hydride and stored over activated 4Å molecular sieves and degassed. Toluene was stored over potassium mirrors. $PhMe_2SiH$ and Ph_2MeSiH were stored over activated 4Å molecular sieves. Yields refer to isolated

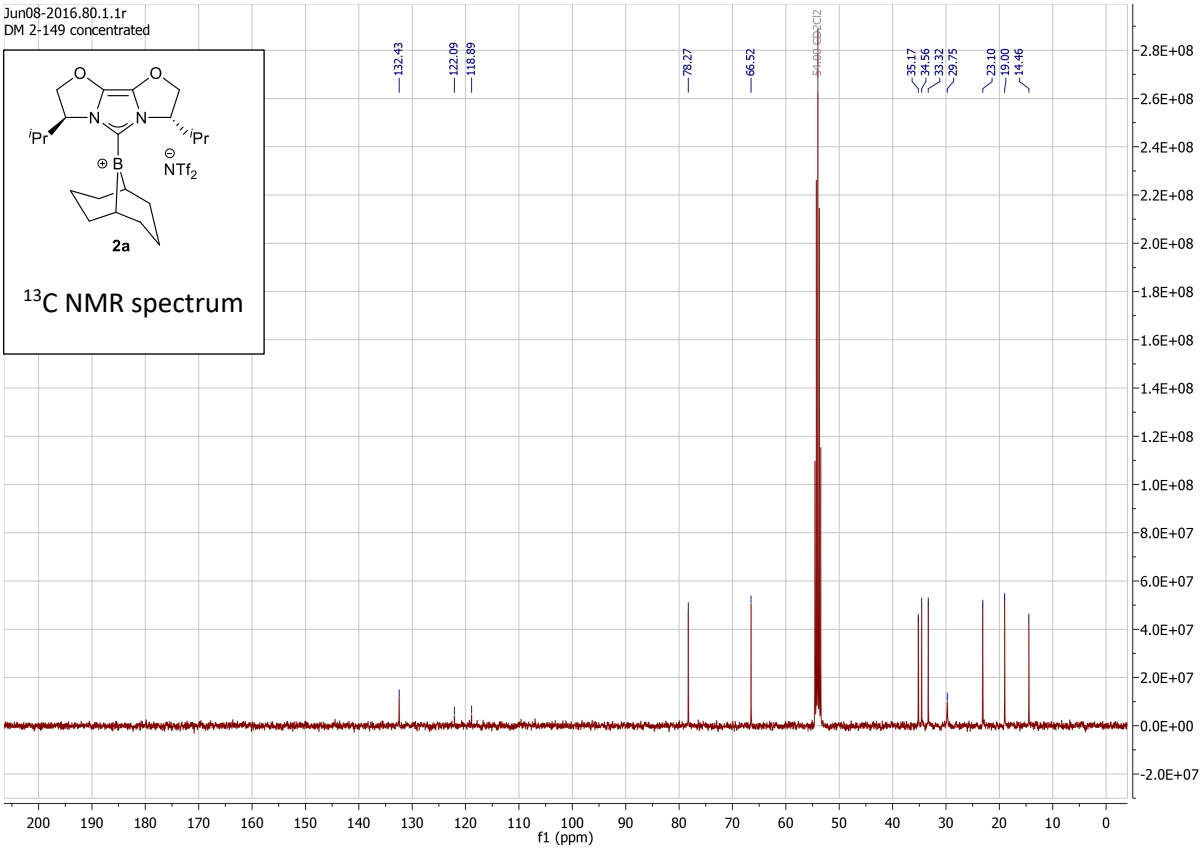
yields. Optical rotations were determined on a Bellingham+Stanley polarimeter model ADP440+, concentrations are reported in g/100 mL. IR data was collected using a Perkin Elmer Cary 630 FTIR instrument. NMR data was collected on Bruker AV-400MHz, AV-500MHZ and DRX-400MHz instruments. Enantiomeric ratios were determined using HPLC with a chiral stationary phase: Chiralcel OD-H; integrations are reported rounded to the nearest 0.5. HPLC method development was carried out using racemic authentic samples. Where necessary analysis was carried out on the *N*-acetyl derivatives. Elemental microanalysis was carried out by Stephen Boyer at London Metropolitan University. Melting points are uncorrected.

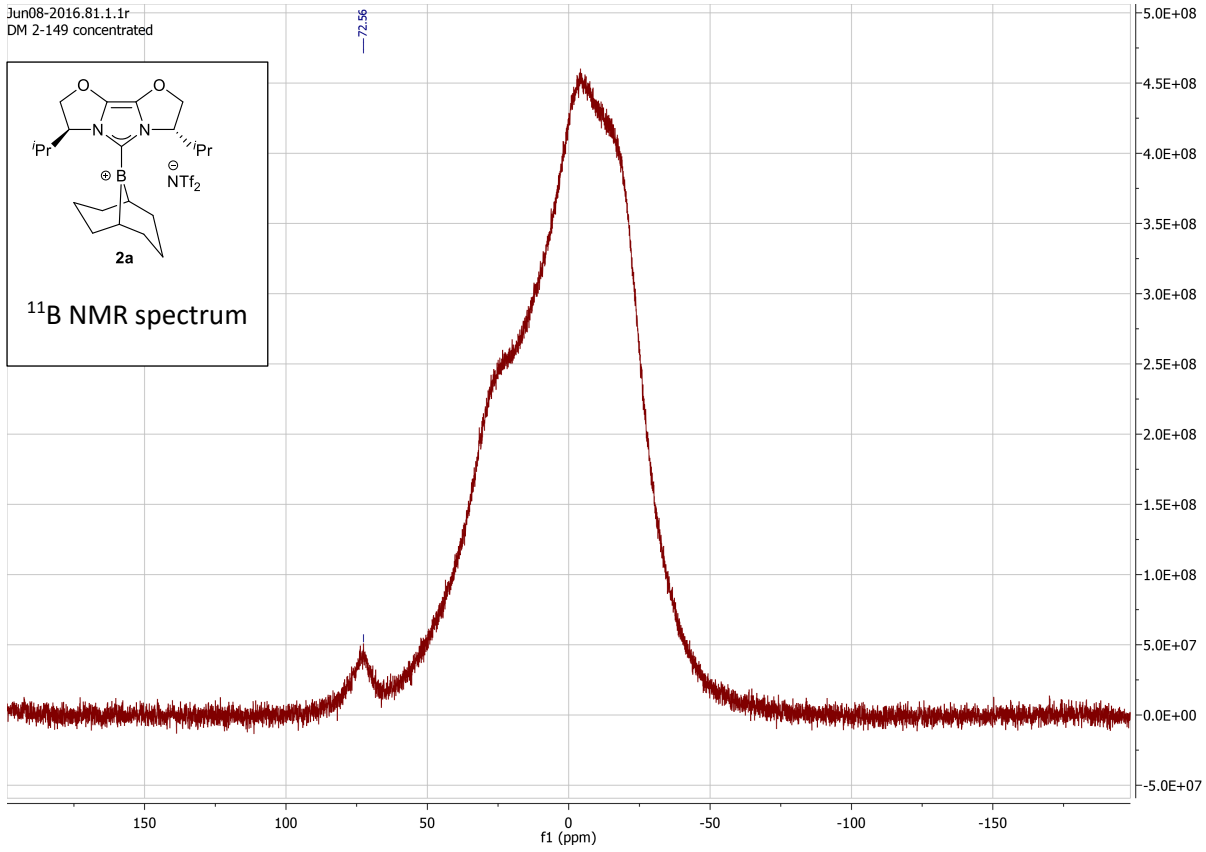
2. Catalyst synthesis and characterisation

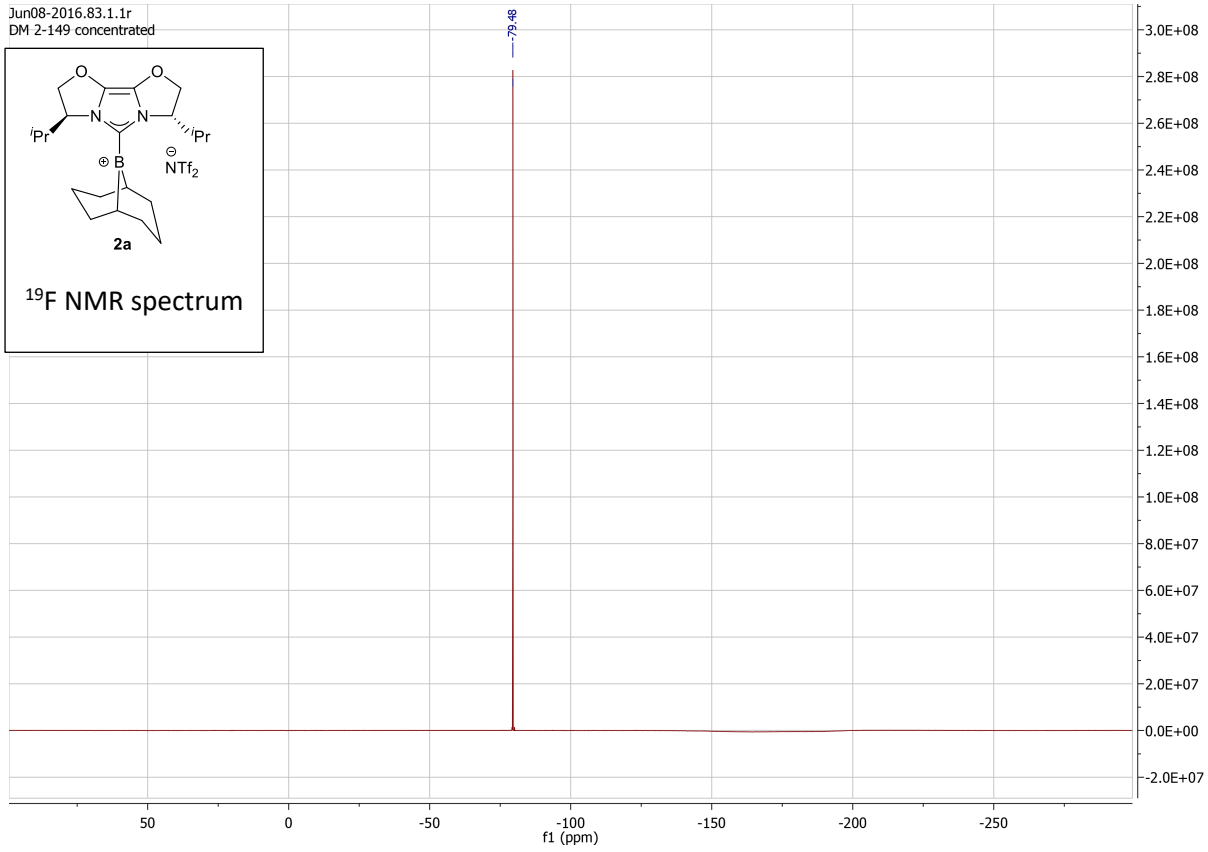
To a solution of hydride **3a** (890 mg, 2.49 mmol, 1 equiv.) in toluene (~100 mL) was added, with vigorous stirring, a solution of $HNTf_2$ (699 mg, 2.49 mmol, 1 equiv.) in toluene (~20 mL) dropwise over 1-2 min. Gas evolution and precipitate formation was observed. Stirring was continued for 1 h after which the yellow supernatant was removed. To the resulting solid was added toluene (~50 mL) then following stirring for 30 min the supernatant was removed. The resulting white solid was dried under high vacuum. Yield: 1.156g, 1.81 mmol, 73% yield; elemental microanalysis calculated for $C_{23}H_{34}BF_6N_3O_6S_2$ %C 43.34, %H 5.38, %N 6.59, found: %C 43.51, %H 5.31, %N 6.78.

^{1}H (400 MHz, CD_2Cl_2) 5.22 (m, 4H), 5.09 (m, 2H), 2.25 (m, 2H), 2.08 (m, 8H), 1.87 (m, 4H), 1.35 (m, 2H), 1.07 (d, *J* = 7 Hz, 6H), 0.83 (d, *J* = 6.9 Hz, 6H); ^{13}C (100 MHz, CD_2Cl_2) 132.4, 120.5 (q), 78.3, 66.5, 35.2, 34.6, 33.3, 29.8, 23.1, 19, 14.5; ^{19}F (376 MHz, CD_2Cl_2) −79.5; ^{11}B (128 MHz, CD_2Cl_2) 73 (FWHM 1160Hz);


Jun08-2016.82.1.1r
DM 2-149 concentrated
2a
1H NMR spectrum
f1 (ppm)


Jun08-2016.80.1.1r
DM 2-149 concentrated
2a
13C NMR spectrum
132.43
122.09
118.89
78.27
66.52
35.17
34.56
33.32
29.75
23.10
19.00
14.46
f1 (ppm)

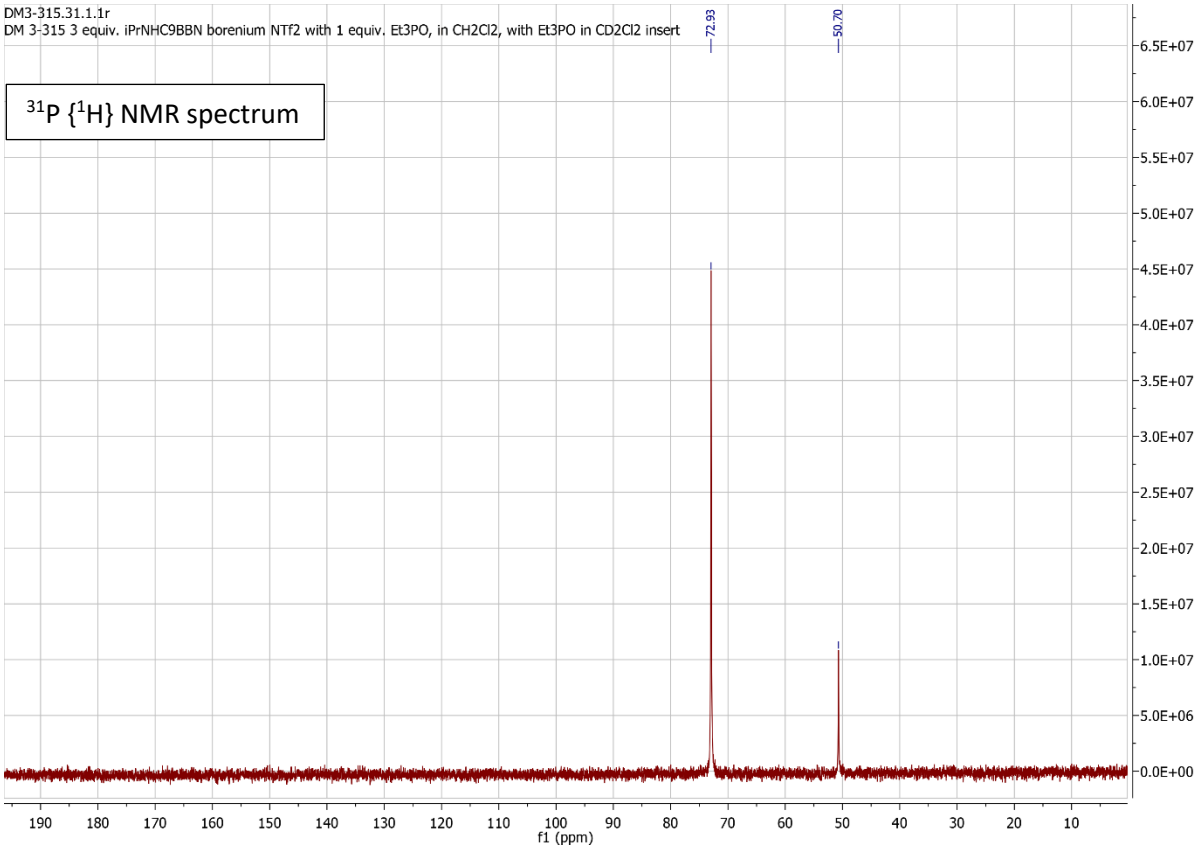

Jun08-2016.81.1.1r
DM 2-149 concentrated
72.56
2a
11B NMR spectrum
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
150
100
50
0
-50
-100
-150
f1 (ppm)


Jun08-2016.83.1.1r
DM 2-149 concentrated
-79.48
2a
19F NMR spectrum
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
50
0
-50
-100
-150
-200
-250
f1 (ppm)

2.1 Guttmann-Beckett Lewis acidity measurement for **2a**

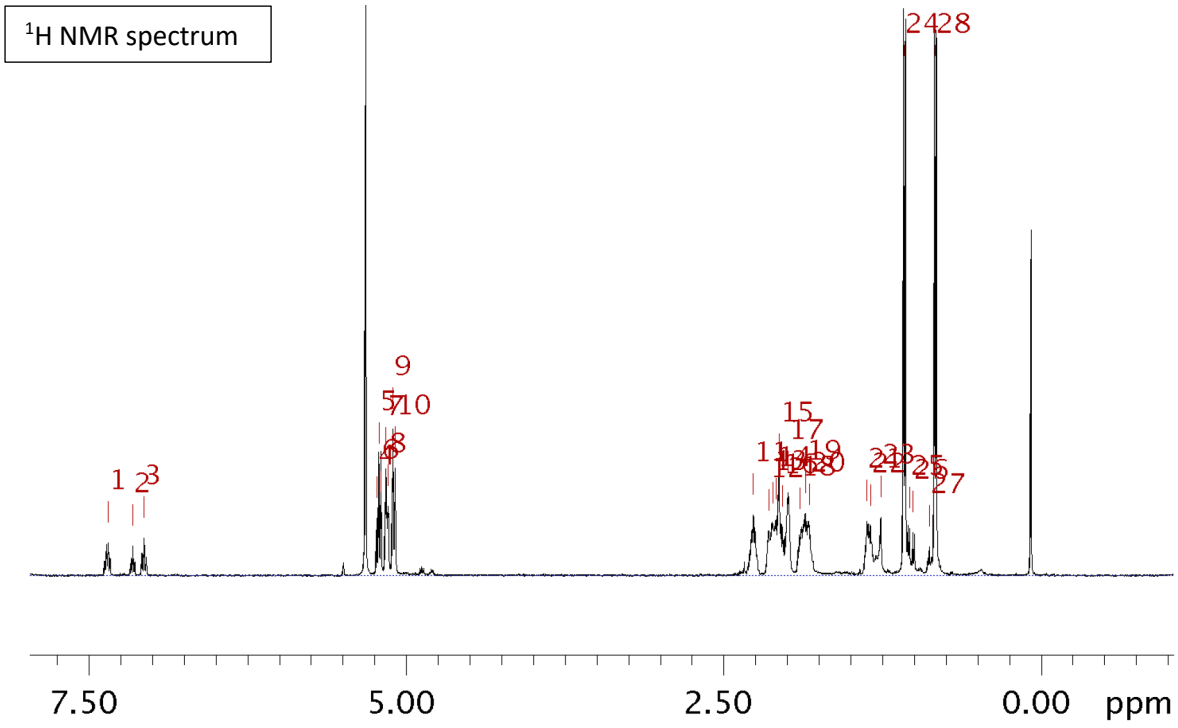
A solution containing Et_3PO (27mg, 0.02 mmol, 1 equiv.) and **2a** (38.2 mg, 0.06 mmol, 3 equiv.) was prepared in DCM (0.4 mL) and transferred to a Young's tap NMR tube. A capillary insert containing a solution of Et_3PO in CD_2Cl_2 was added.

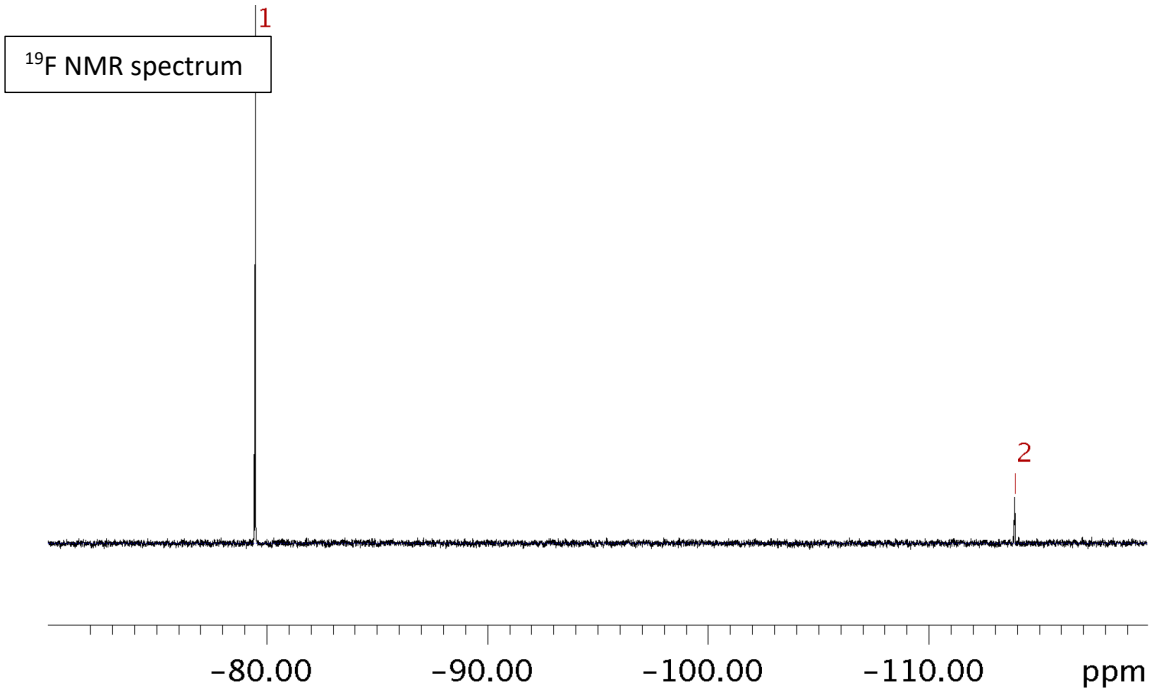
$$AN = 100(72.93 - 41)/(86.14 - 41) = 70.7$$



2.2 DOSY NMR studies for **2a**

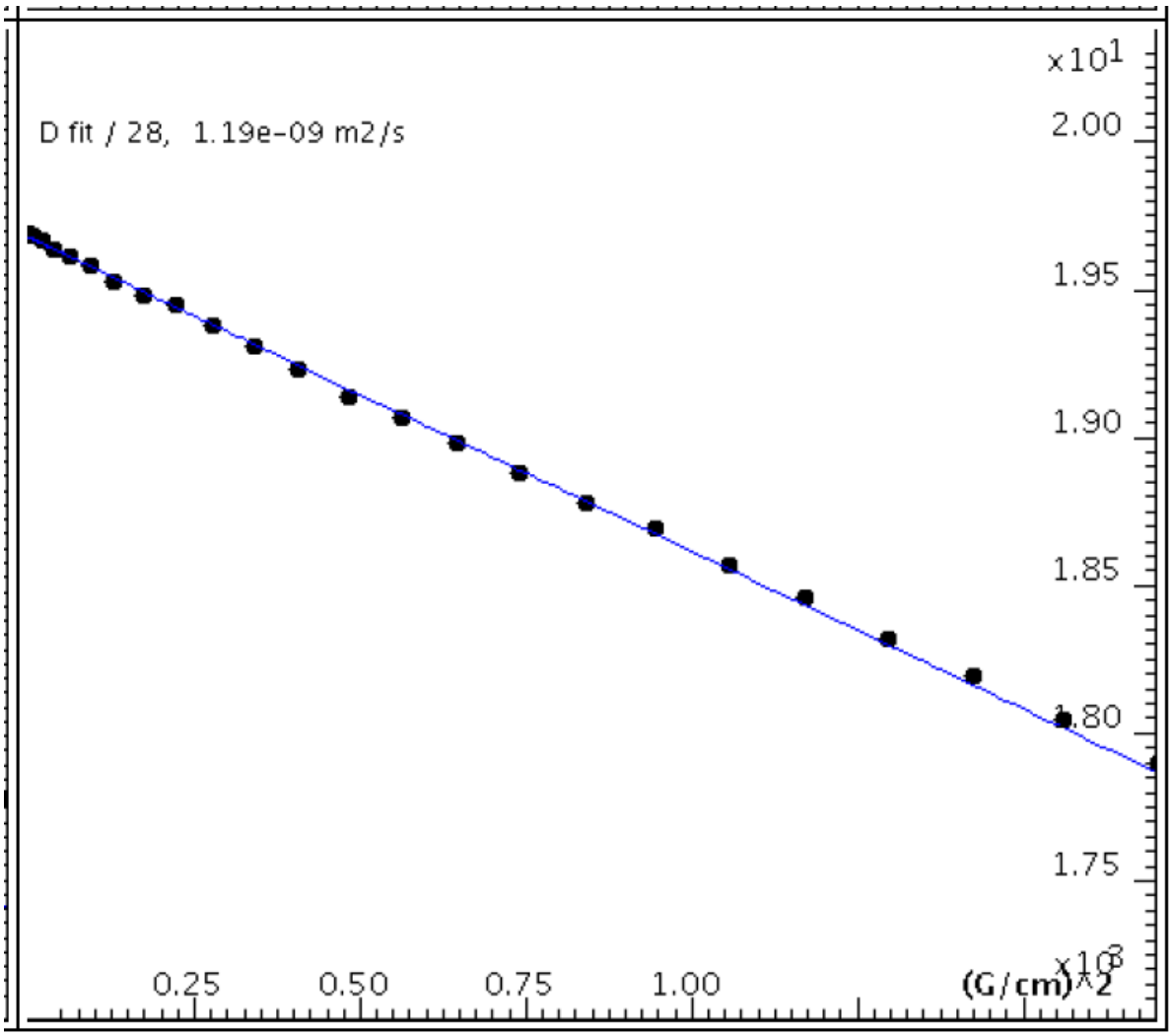
A solution containing **2a** (5.4 mg, 0.0084 mmol, 1 equiv.) and PhF (1.6 µL, 0.0168 mmol, 2 equiv.) was prepared in CD_2Cl_2 (0.6 mL). An aliquot was diluted tenfold and submitted for NMR analysis.





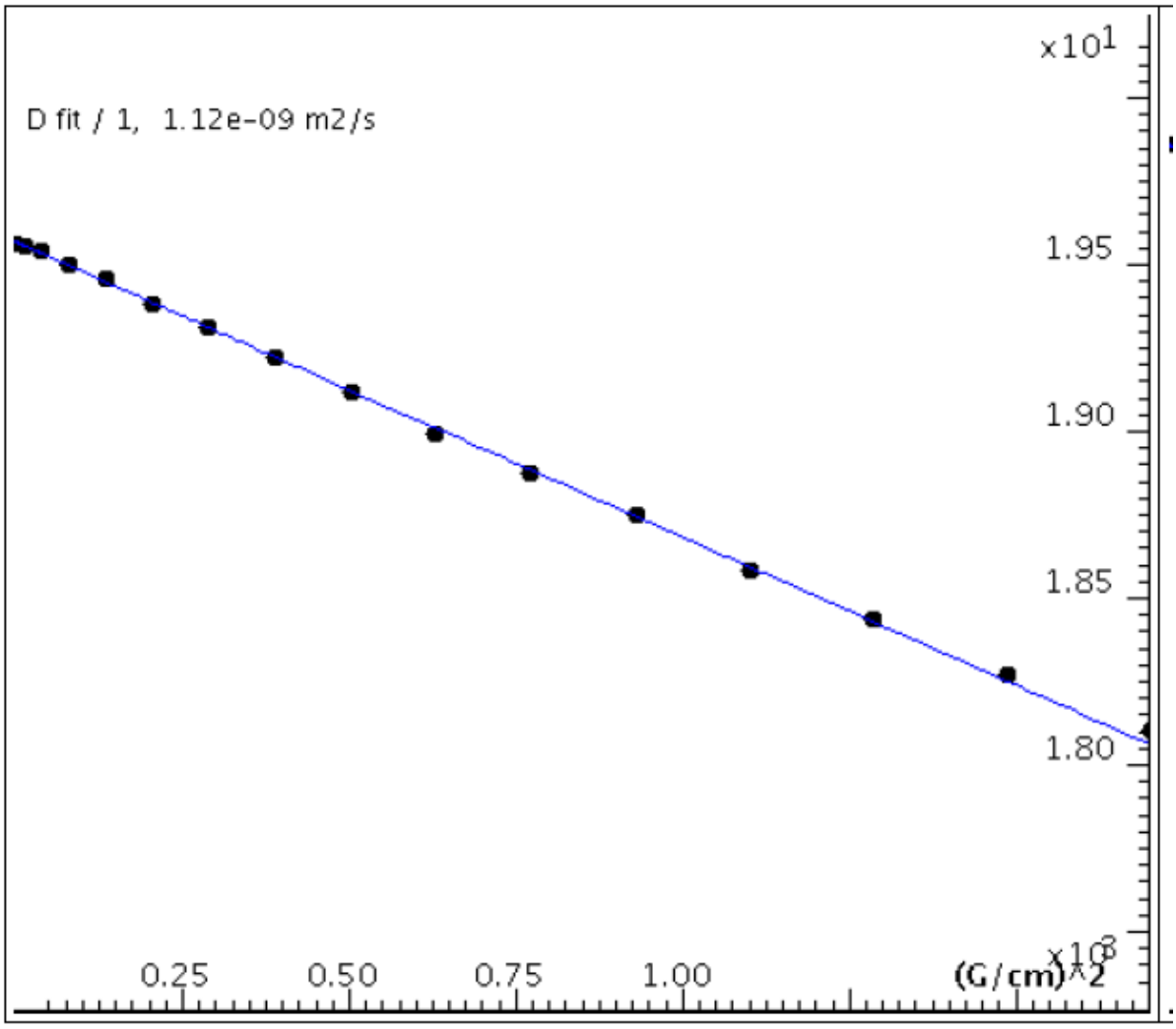
Fitted function:	f (x) = A * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0030000 s
used big delta:	0.014900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from Monte Carlo simulations
Confidence level:	95%
Used peaks:	peaks from /opt/topspin/data/mf/nmr/~TEMP/1/pdata/1/peaklist.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	D [m2/s]	error
1	7.349	3.16e-09	7.736e-11
2	7.154	3.22e-09	9.449e-11
3	7.066	3.17e-09	7.987e-11
4	5.234	1.18e-09	1.273e-10
5	5.217	1.17e-09	2.792e-10
6	5.199	1.19e-09	1.495e-10
7	5.162	1.17e-09	2.113e-10
8	5.147	1.19e-09	1.391e-10
9	5.107	1.19e-09	1.133e-10
10	5.089	1.19e-09	5.719e-11
11	2.269	1.17e-09	2.187e-10
12	2.149	1.16e-09	9.960e-11
13	2.118	1.17e-09	1.276e-10
14	2.090	1.17e-09	1.278e-10
15	2.066	1.16e-09	8.441e-12
16	2.037	1.18e-09	1.806e-10
17	1.993	1.17e-09	9.871e-11
18	1.903	1.16e-09	2.104e-11
19	1.859	1.20e-09	1.612e-10
20	1.827	1.21e-09	1.162e-10
21	1.373	1.16e-09	8.204e-11
22	1.345	1.18e-09	1.519e-10
23	1.263	1.24e-09	1.564e-11
24	1.084	1.20e-09	1.552e-12
25	1.037	1.24e-09	2.144e-11
26	1.011	1.24e-09	2.293e-11
27	0.880	1.58e-09	4.244e-11
28	0.839	1.19e-09	1.645e-12



Fitted function:	f (x) = A * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	25172 rad/(s*Gauss)
used little delta:	0.0030000 s
used big delta:	0.014900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from Monte Carlo simulations
Confidence level:	95%
Used peaks:	peaks from /opt/topspin/data/mf/nmr/~TEMP/1/pdata/1/peaklist.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	D [m2/s]	error
1	-79.492	1.12e-09	7.164e-12
2	-113.899	2.66e-09	2.129e-10


D fit / 1, 1.12e-09 m2/s
x10^1
1.95
1.90
1.85
1.80
x10^8
0.25
0.50
0.75
1.00
(G/cm)^2

2.3 X-Ray diffraction data for **2a**

Crystals of suitable quality for X-ray diffraction studies of **2a** were grown using vapour diffusion of pentane at room temperature into a solution of **2a** (2 mg in 0.5 mL 1,2-DFB). Single crystal X-ray diffraction data was collected with an Oxford Diffraction Xcalibur unit; crystals were mounted on a nylon MicroLoop™ using perfluoropolyether oil and measured in a stream of N_2 at 173 K. All structures were solved using the Superflip charge flipping package.[1] All data were subsequently refined with the ShelXL refinement package.[2] CCDC 1902956 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Elemental formula	$C_{23}H_{34}BF_6N_3O_6S_2$	
Formula weight	637.5	
Crystal system, Space group	Trigonal, P 32	
Unit cell dimensions	a = 10.6336(3) Å	α = 90°
	b = 10.6336(3) Å	β = 90°
	c = 22.5220(7) Å	γ = 120°
Volume, Z	2205.45(14) Å^3, 3	
Calculated density	1.440 Mg/m^3	
F(000)	996	
Absorption coefficient	0.261 mm^{-1}	
Temperature	173.05(10) K	
Wavelength	0.71073 Å	
Crystal colour / morphology	colourless block	
Crystal size	0.575 × 0.299 × 0.219 mm^3	
θ range for data collection	2.7 to 28.2°	
Index Ranges	-13<=h<=12, -14<=k<=9, -29<=l<=29	
Completeness to θ = 25.2°	99.7 %	
Absorption correction	Analytical	
Max. and min. transmission	0.957 and 0.915	
Reflections collected (not including absences)		8361
No. of unique reflections	5821 [R_{int} for equivalents = 0.020]	
No. of 'observed' reflections [I > 2σ(I)]	4911	
Structure determined by:	dual methods, in SIR-92	
Refinement method:	Full-matrix least-squares on F^2	

Data / restraints / parameters	5821 / 1 / 446
Goodness-of-fit on F^2	1.046
Final R indices ('observed' data)	R_1 = 0.055, wR_2 = 0.114
Final R indices (all data)	R_1 = 0.070, wR_2 = 0.124
Absolute structure parameter	0.01(4)
Largest diff. peak and hole	0.46 and -0.39 e $Å^{-3}$

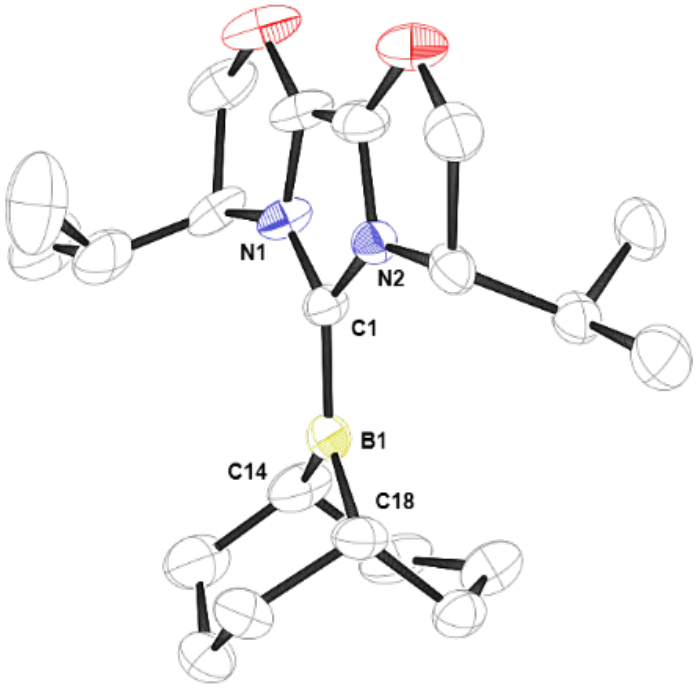
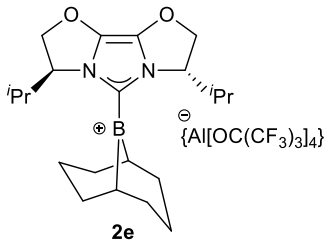


Figure S1. ORTEP diagram for structure **2a**. H atoms and $N(SO_2CF_3)_2$ counteranion omitted for clarity. Thermal ellipsoids shown at 50% probability level. O atoms red, C atoms white, N atoms blue, B atom yellow.

The solid-state structure of **2a** shows the boron atom to be in a distorted trigonal planar geometry (∡ (C1-B1-C14) = 123.8(5) °, (C1-B1-C18) = 124.0(5) °, (C14-B1-C18) = 112.2(5) °). The NTf_2 anion is non-coordinating with no close contacts to B, supporting an ionic assignment of the salt. The B-C_{NHC} distance for **2a** (1.540(7) Å) is comparable to the value of 1.580(3) Å reported in the literature for $[(I^iPr_2)(BC_8H_{14})][B(C_6F_5)_4]$.[3]

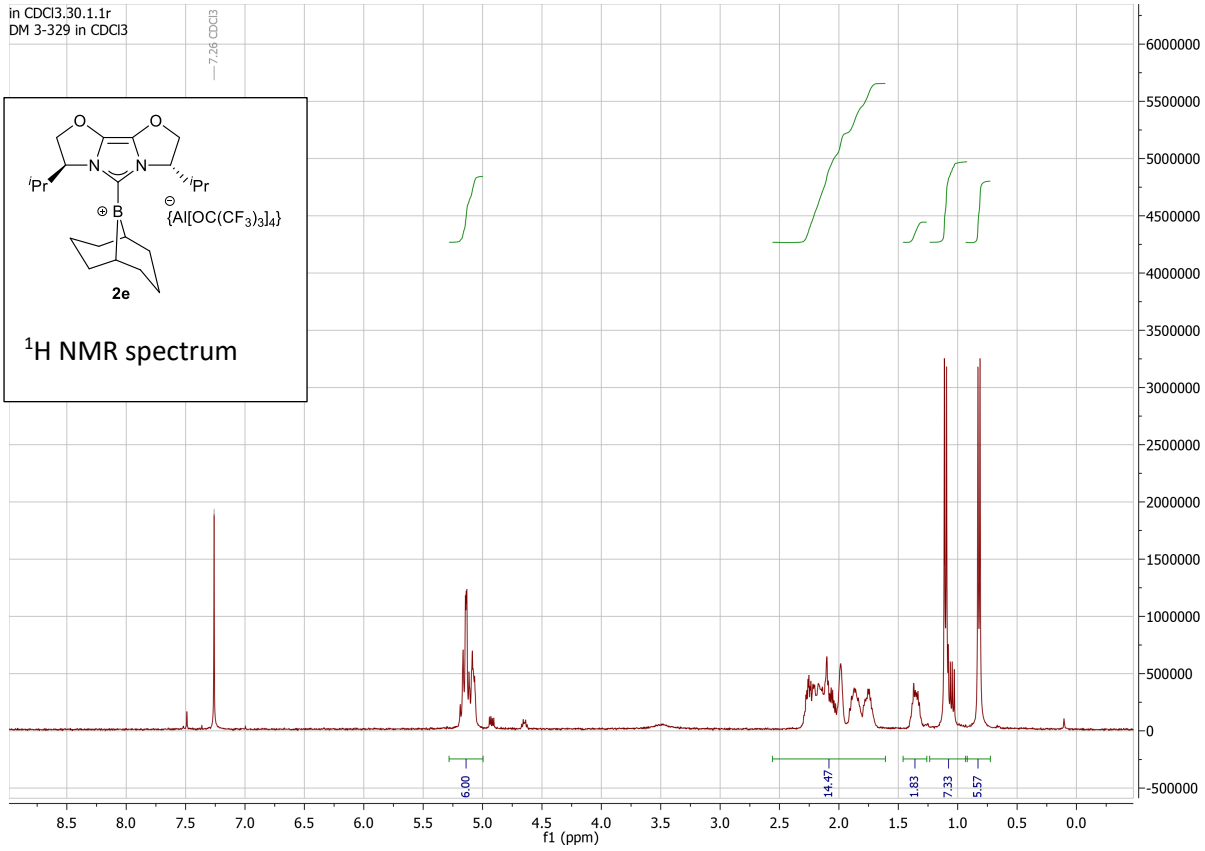
2.4 Preparation of catalyst **2e** *via* counterion exchange

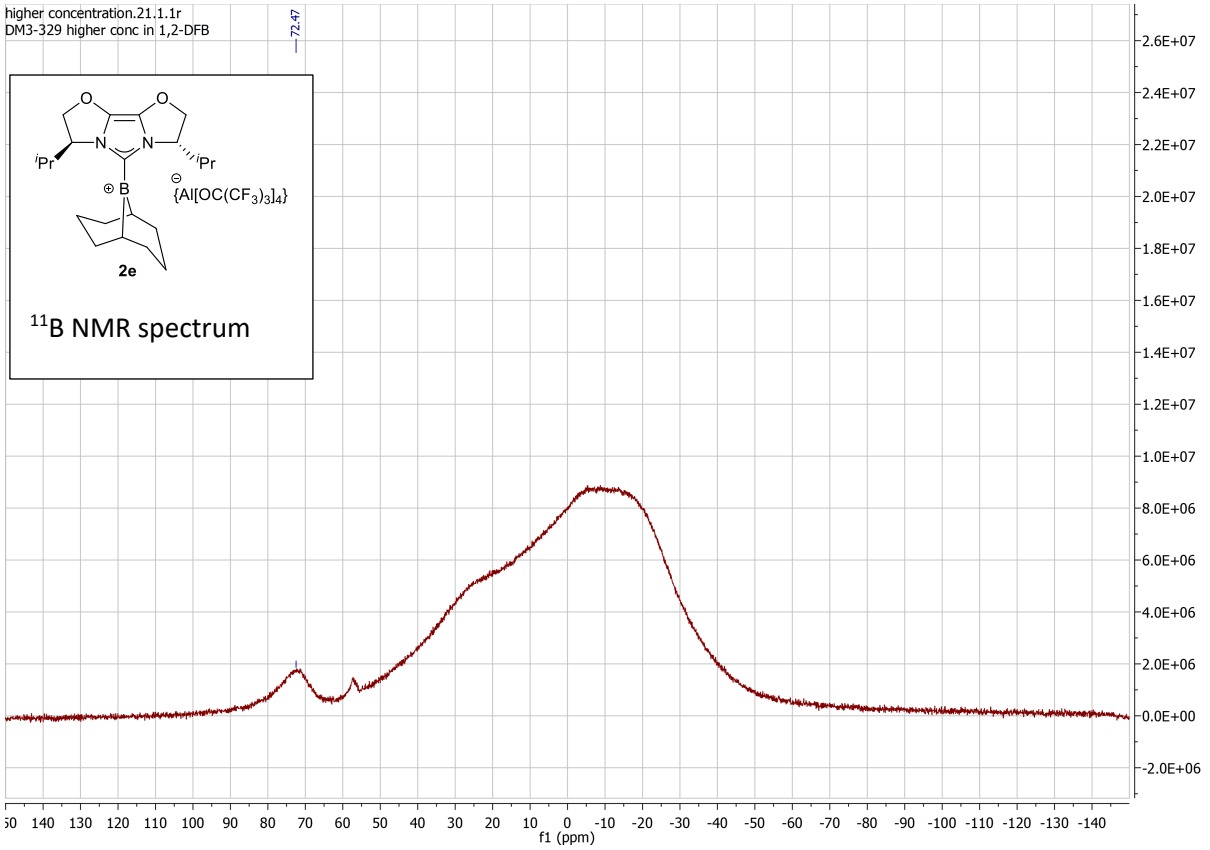


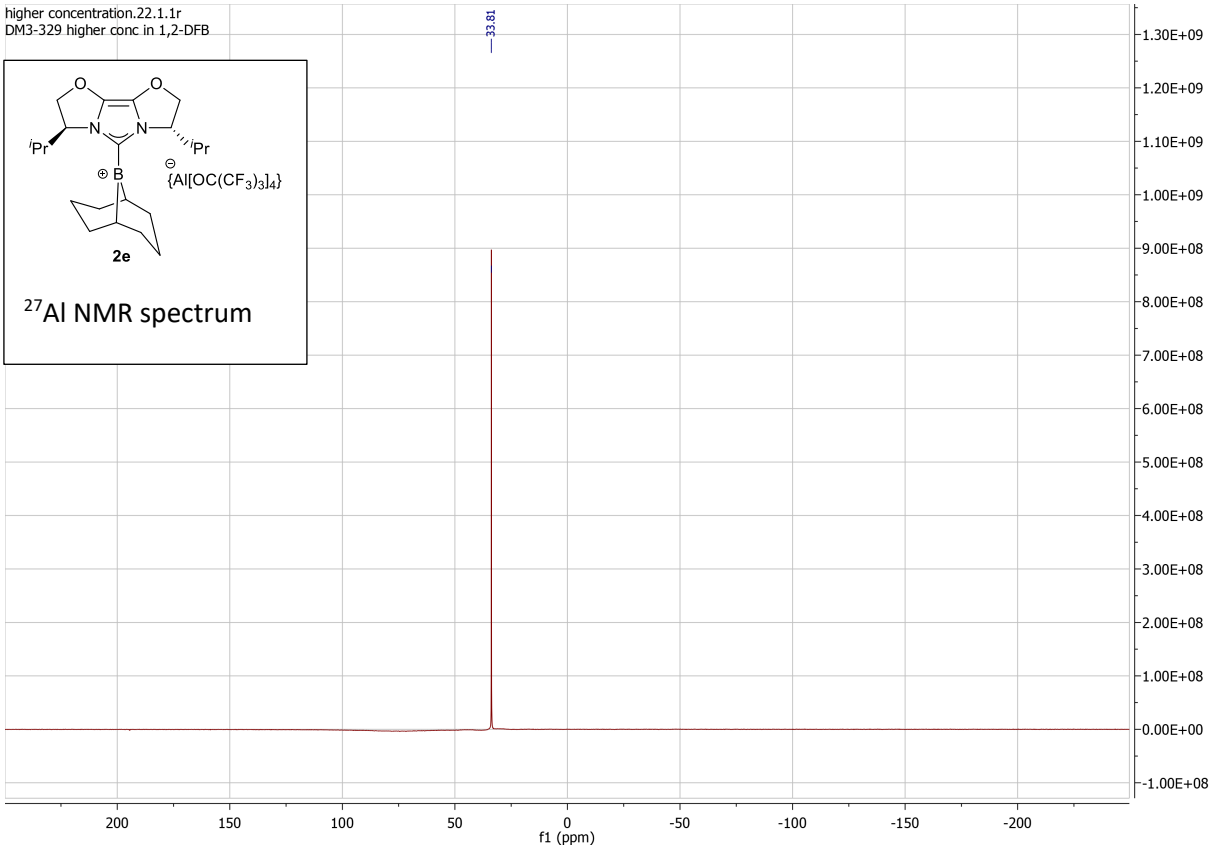
2e

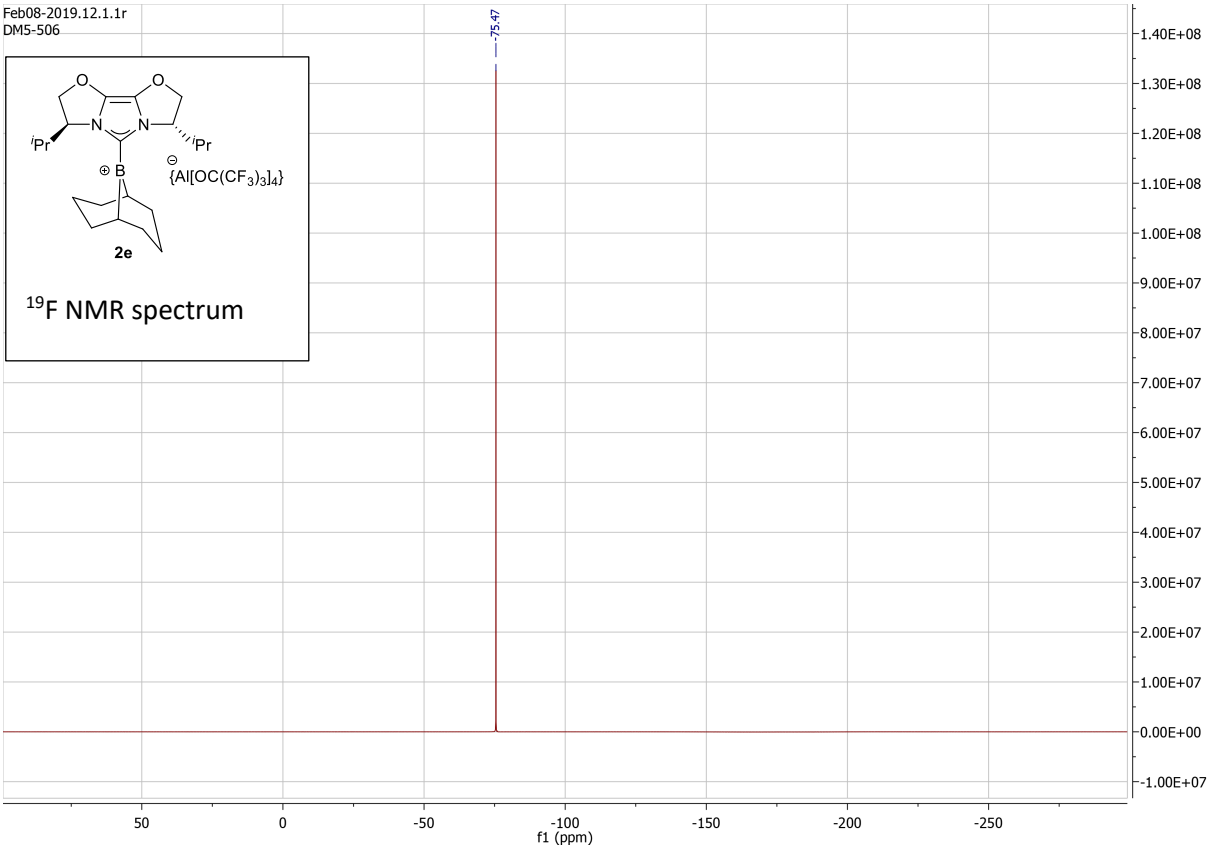
Exchange of NTf_2 anion for $\{Al[OC(CF_3)_3]_4\}$ anion was performed using either the Li or K $\{Al[OC(CF_3)_3]_4\}$ salts. In a vial were mixed **2a** (159.3 mg, 0.25 mmol, 1 equiv.) and $Li\{Al[OC(CF_3)_3]_4\}$ (243.5 mg, 0.25 mmol, 1 equiv.) and DCM (3 mL) was added. The mixture was stirred vigorously for 48 h after which it was filtered. The resulting solution was dried under high vacuum to give **2e** (240 mg, 0.18 mmol, 73% yield) as a white solid.

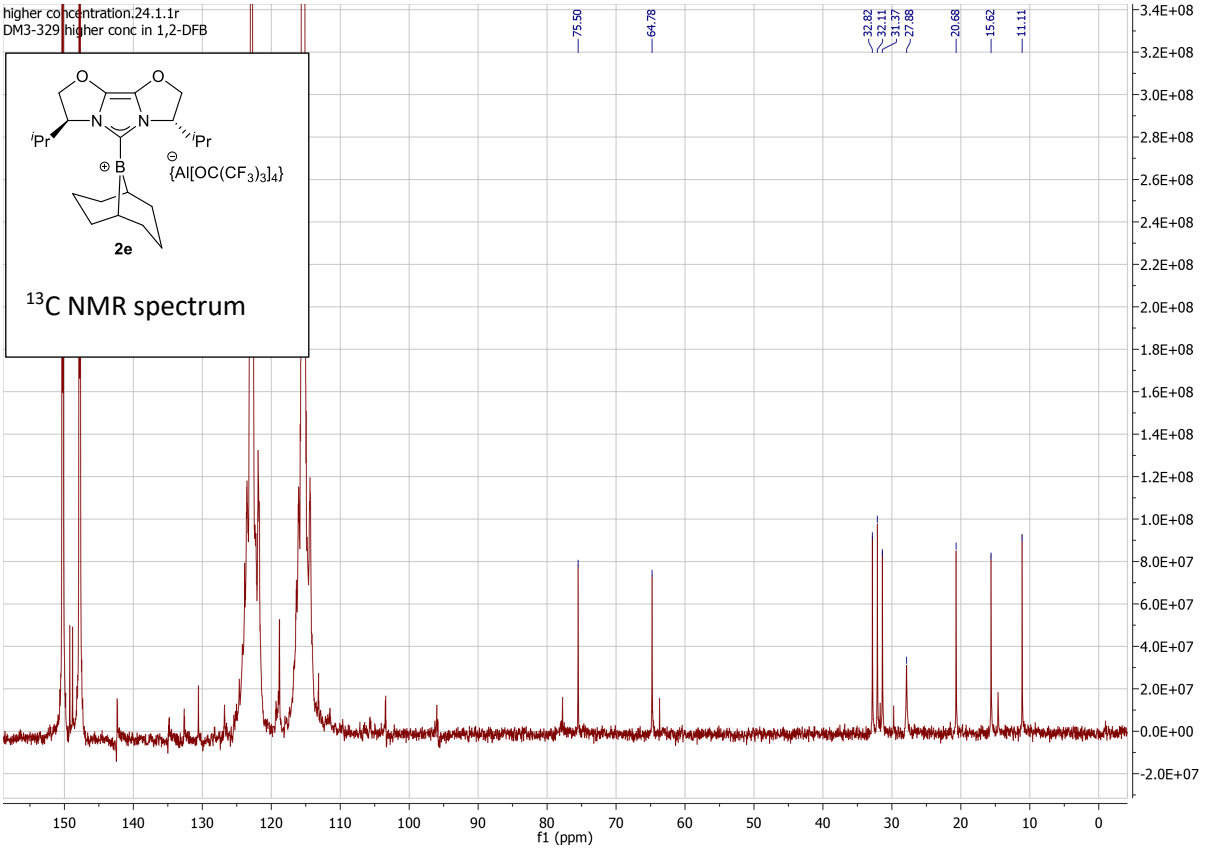
^{1}H (400 MHz, $CDCl_3$) 5.11 (m, 6H), 2.31-1.66 (m, 14H), 1.35 (m, 2H), 1.1 (d, *J* = 6.7 Hz, 6H), 0.82 (d, *J* = 6.9 Hz, 6H); ^{13}C (100 MHz, 1,2-DFB) 75.5, 64.9, 32.9, 32.1, 31.4, 27.9, 20.7, 15.6, 11.1; ^{19}F (376 MHz, $CDCl_3$) −75.5 ; ^{11}B (128 MHz, 1,2-DFB) 72.5 (br, FWHM 1432 Hz); ^{27}Al (104 MHz, 1,2-DFB) 33.8.



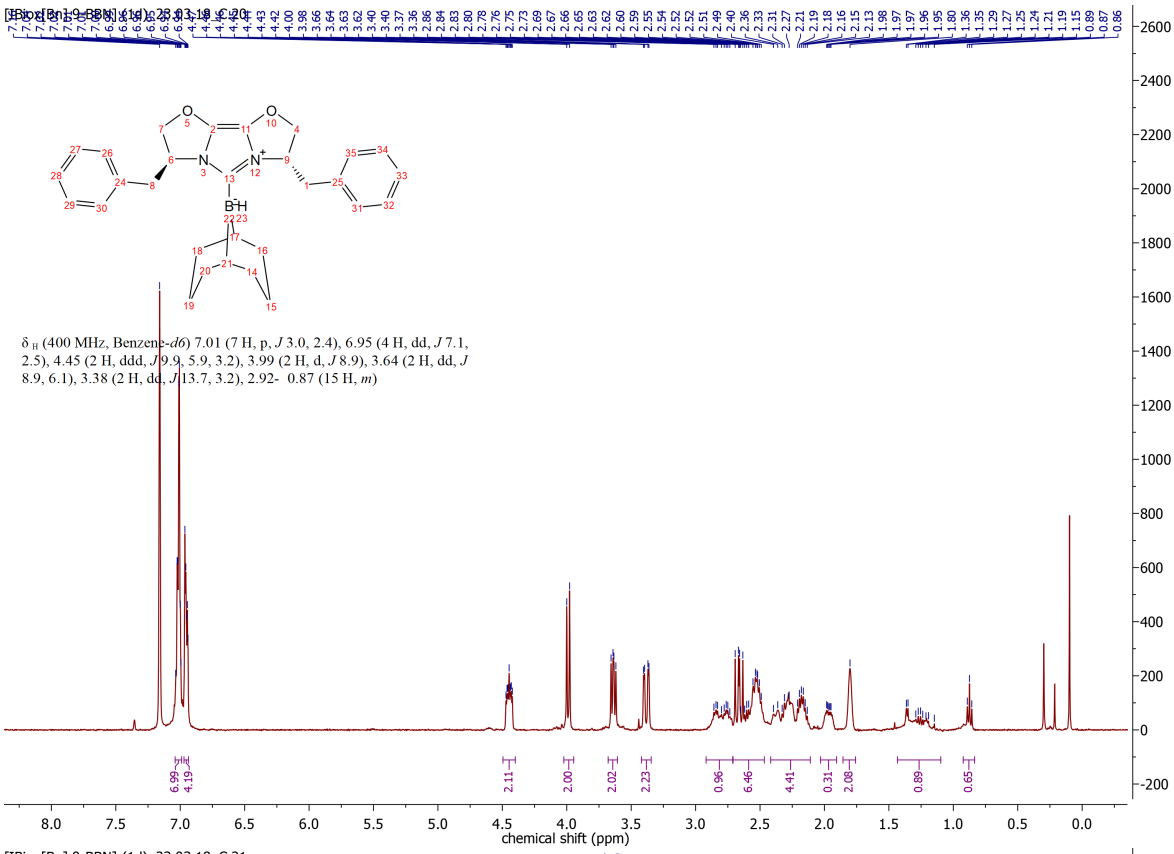

higher concentration.21.1.1r
DM3-329 higher conc in 1,2-DFB
72.47
2e
11B NMR spectrum
f1 (ppm)

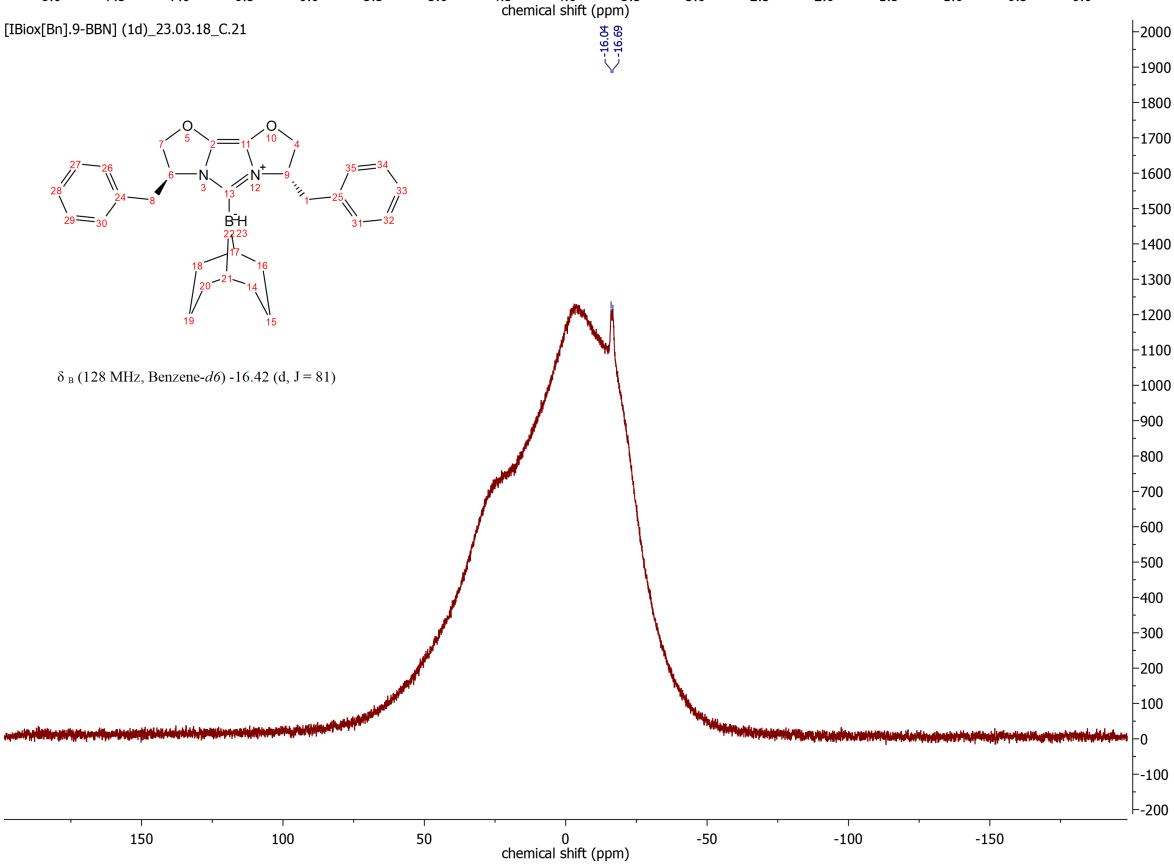

higher concentration.22.1.1r
DM3-329 higher conc in 1,2-DFB
33.81
2e
27Al NMR spectrum
f1 (ppm)


Feb08-2019.12.1.1r
DM5-506
-75.47
2e
{Al[OC(CF3)3]4}
19F NMR spectrum
f1 (ppm)

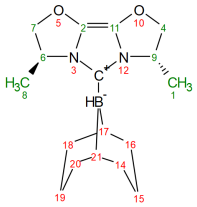

higher concentration.24.1.1r
DM3-329 higher conc in 1,2-DFB
75.50
64.78
32.82
32.11
31.37
27.88
20.68
15.62
11.11
2e
{Al[OC(CF3)3]4}
13C NMR spectrum
f1 (ppm)

2.5 IBiox borohydride precursors **3b** and **3c**



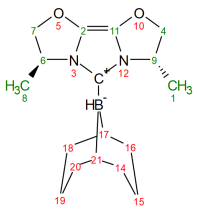


[IBiox[Me].9-BBN] (1c)_30.1.18_C.122

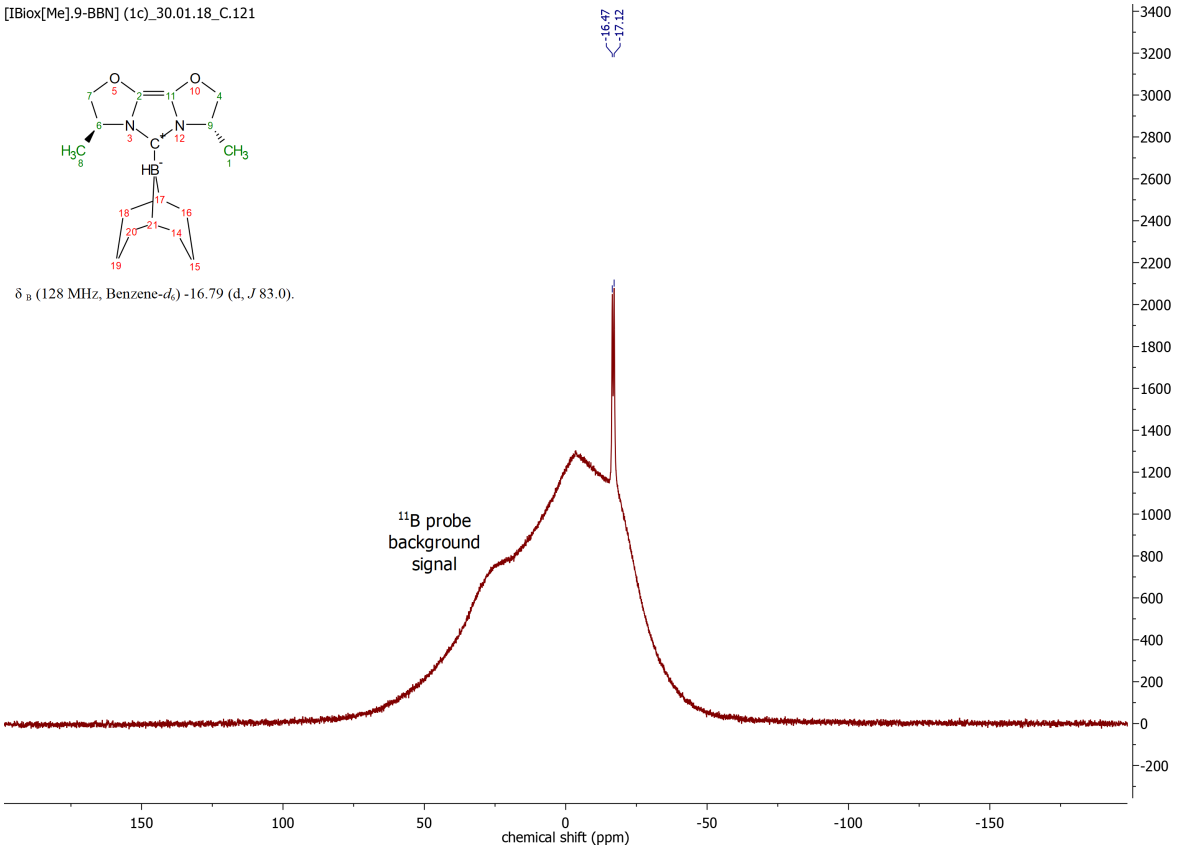


δ H (400 MHz, Benzene-d_6) 3.95 (2 H, p, *J* 6.4), 3.64 (2 H, dd, *J* 8.4, 6.4), 3.39 (2 H, d, *J* 8.4), 2.78 – 1.88 (13 H, m), 1.40 (2 H, s), 1.03 (6 H, d, *J* 6.4).

[IBiox[Me].9-BBN] (1c)_30.01.18_C.122

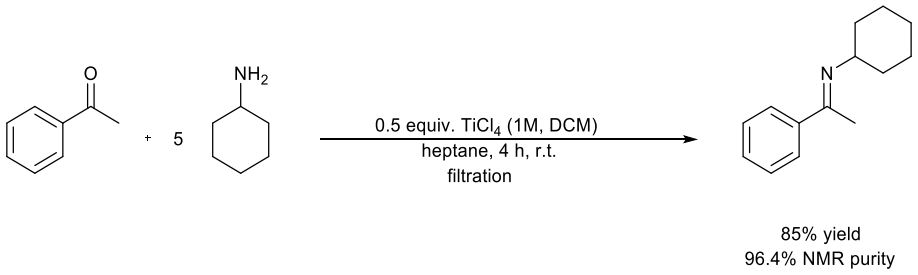


δ C (101 MHz, Benzene-d_6) 123.3, 82.1, 53.5, 36.7, 36.4, 33.7, 33.6, 26.6, 26.3, 19.3.


[IBiox[Me].9-BBN] (1c)_30.01.18_C.121
δ B (128 MHz, Benzene-d6) -16.79 (d, J 83.0).
-16.47
-17.12
11B probe background signal
chemical shift (ppm)

3. Substrate preparation and copies of NMR spectra

Example (modified literature procedure):[4–6]



Scheme S2. *N*-alkyl ketimine synthesis

General procedure: To a stirred solution of acetophenone (3.5 mL, 30 mmol, 1 equiv.) in pentane (500 mL) was added the amine component (150 mmol, 5 equiv., opalescence develops) followed by $TiCl_4$ (1.65 mL, 15 mmol, 0.5 equiv.). A coloured voluminous precipitate develops. Stirring was continued at room temperature, during which time the colour of the precipitate changes to white. Aliquots were collected for NMR analysis. The reaction was filtered and the volatiles removed under low or high vacuum. The resulting oils were stored over activated 3 or 4Å MS.

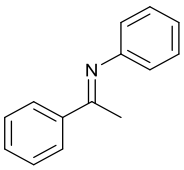
For substrates **4b** and **4h**, reaction was performed with auxiliary base Et_3N (4 equiv.) and the resulting products were dried under high vacuum, with heating if required.

For reaction development substrates **4a, 4c, 4d** were distilled, **4b** was distilled and recrystallised from pentane. We observed similar reactivity for purified and un-purified materials and therefore other substrates were used as prepared for carrying out substrate scope investigation.

Substrate **4a** was prepared according to a literature procedure.[7]

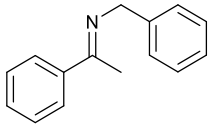
Ketimine	Time	Yield	Appearance
4b	27 h	67%	Orange solid
4c	1.5 h	86%	Pale yellow clear oil
4d	3 h	97%	Colourless clear oil
4e	5 h	87%	Pale yellow clear oil
4f	6 h	87%	White crystalline solid
4g	1.5 h	93%	Pale yellow clear oil
4h	72 h	70%	Orange solid
4i	4 h	79%	Colourless viscous clear oil

Table S3. Ketimine preparation



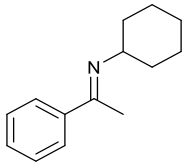
4a

^{1}H NMR (400 MHz, CD_2Cl_2) 8.01 (m, 2H), 7.48 (m, 3H), 7.39 (m, 2H), 7.11 (m, 1H), 6.81 (m, 2H), 2.24 (s, 3H), in agreement with literature data;[8] ^{13}C NMR (100 MHz, CD_2Cl_2) 165.7, 152.5, 140.1, 131, 129.5, 128.8, 127.7, 123.6, 119.8, 17.6.



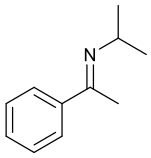
4b

b.p. 160-170 °C, 0.016 mbar; white crystalline solid; E/Z ratio = 20:1 ^{1}H NMR (400 MHz, $CDCl_3$) 7.92 (m, 2H), 7.51-7.19 (m, 8H), 4.79 (s, 2H), 2.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.1, 141.2, 140.7, 129.7, 128.5, 128.3, 127.8, 126.9, 126.7, 55.8, 16. In agreement with literature data.[9] HRMS (ES+) calculated for $C_{15}H_{16}N$ ($[M+H]^+$) 210.1283, found 210.1290; IR (powder, cm^{-1}) 3081, 3056, 3022, 2856, 1629, 1491, 1446, 1375, 1348, 1300, 1282, 1267, 1044, 1025, 756, 724, 693, 686, 570.



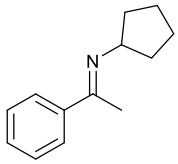
4c

b.p. 130 °C, <5 mbar; E/Z ratio = 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) 7.75 (m, 2H), 7.36 (m, 3H), 3.48 (m, 1H), 2.24 (s, 3H), 1.83 (m, 2H), 1.69 (m, 3H), 1.56 (m, 3H), 1.35 (m, 3H); minor isomer 7.39 (m), 7.1 (m, 2H), 3.05 (m, 1H), 2.26 (s) 1.12 (m); ^{13}C NMR (100 MHz, $CDCl_3$) major isomer 162.5, 142.1, 129.2, 128.3, 126.8, 60, 33.7, 25.9, 25, 15.4; minor isomer 166.3, 139.8, 128.5, 127.9, 125.8, 60.9, 34.1, 29.5, 25.7, 24.7. HRMS (ES+) calculated for $C_{14}H_{20}N$ ($[M+H]^+$) 202.1596, found 202.1591; IR (neat, cm^{-1}) 2923, 2851, 1631, 1444, 1279, 1025, 759, 691, 573.



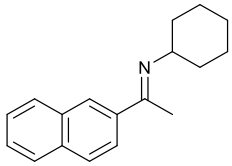
4d

b.p. 65 °C, <5 mbar, E/Z ratio = 7.7: 1; ^{1}H NMR (400 MHz, $CDCl_3$) major isomer 7.74 (m, 2H), 7.35 (m, 3H), 3.84 (septet, *J* = 6.1 Hz, 1H), 2.23 (s, 3H), 1.22 (d, *J* = 6.1 Hz, 6H) minor isomer 7. 39 (m) 7.1 (m, 2H), 3.41 (septet, *J* = 6.2 Hz, 1H), 2.25 (s), 1.07 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) major isomer 162.42, 142.1, 129.2, 128.3, 126.8, 51.3, 23.7, 15.3; minor isomer 166.2, 139.9, 128.6, 128, 125.9, 52.3, 29.5, 24. HRMS (ES+) calculated for $C_{11}H_{16}N$ ($[M+H]^+$) 162.1283, found 162.1278; IR (neat, cm^{-1}) 2964, 2927, 2866, 1631, 1376, 1444, 1359, 1276, 1025, 759, 691, 574.



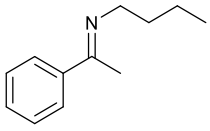
4e

E/Z ratio = 16.7: 1; ^{1}H NMR (400 MHz, $CDCl_3$) 7.77 (m, 2H), 7.37 (m, 3H), 4.04 (m, 1H), 2.26 (s, 3H), 1.91 (m, 4H), 1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) major isomer 163, 141.9, 129.2, 128.3, 126.7, 61.9, 34.3, 24.9, 15.9; HRMS (ES+) calculated for $C_{13}H_{18}N$ ($[M+H]^+$) 188.1439, found 188.1444; IR (neat, cm^{-1}) 2950, 2865, 1629, 1444, 1275, 1026, 759, 691, 571.



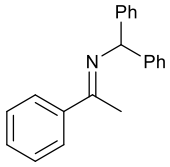
4f

white crystalline solid, m.p. (pentane) 80.5-82.5 °C; E/Z ratio = 12.5: 1; ^{1}H NMR (400 MHz, $CDCl_3$) 8.16 (m, 1H), 8.06 (m, 1H), 7.87 (m, 3H), 7.5 (2H, m), 3.58 (m, 1H), 2.37 (s, 3H), 1.94-1.29 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) major isomer 162.2, 139.3, 134, 133.2, 128.8, 127.8, 127.7, 126.5, 126.4, 126.1, 124.5, 60.2, 33.8, 26, 25, 15.3; minor isomer 166.4, 137.3, 132.8, 128.3, 128.2, 126.6, 124.8, 124.1, 61.1, 34.1, 29.7, 25.6, 24.7; IR (powder) 3053, 2915, 2850, 1619, 1446, 1359, 1286, 1127, 952, 892, 861, 836; HRMS (ES+) calculated for $C_{18}H_{22}N$ ($[M+H]^+$) 252.1752, found 252.1763.



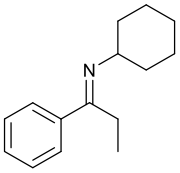
4g

E/Z ratio = 18.2:1, ^{1}H NMR (400 MHz, $CDCl_3$) 7.77 (m, 2H), 7.38 (m, 3H), 3.49 (t, *J* = 7.1 Hz, 2H), 2.24 (s, 3H), 1.75 (m, 2H), 1.48 (m, 2H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 164.8, 141.6, 129.3, 128.3, 126.6, 52.1, 33.2, 20.9, 15.5, 14.2; In agreement with literature data.[4] HRMS (ES+) calculated for $C_{12}H_{18}N$ ($[M+H]^+$) 176.1439, found 176.1432; IR (neat, cm^{-1}) 2926, 2954, 2869, 1362, 1444, 1280, 1027, 759, 691, 571.



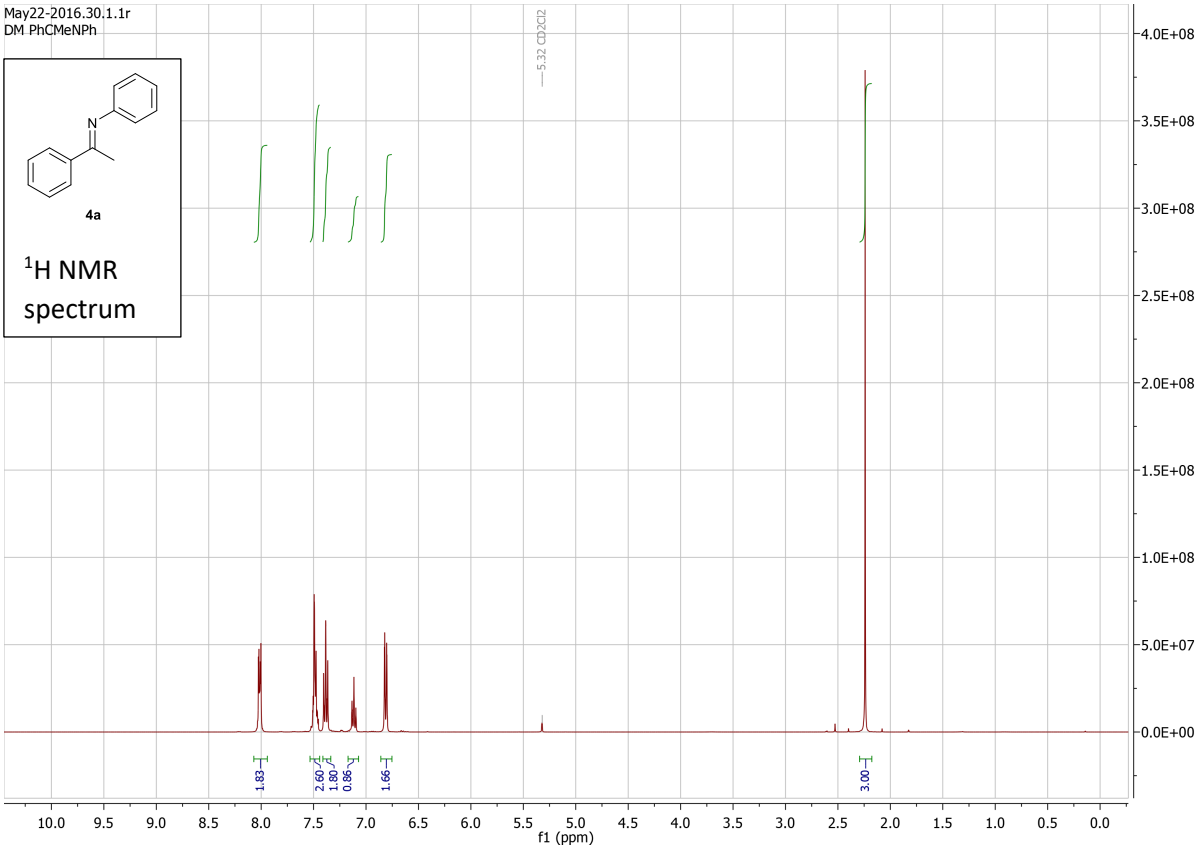
4h

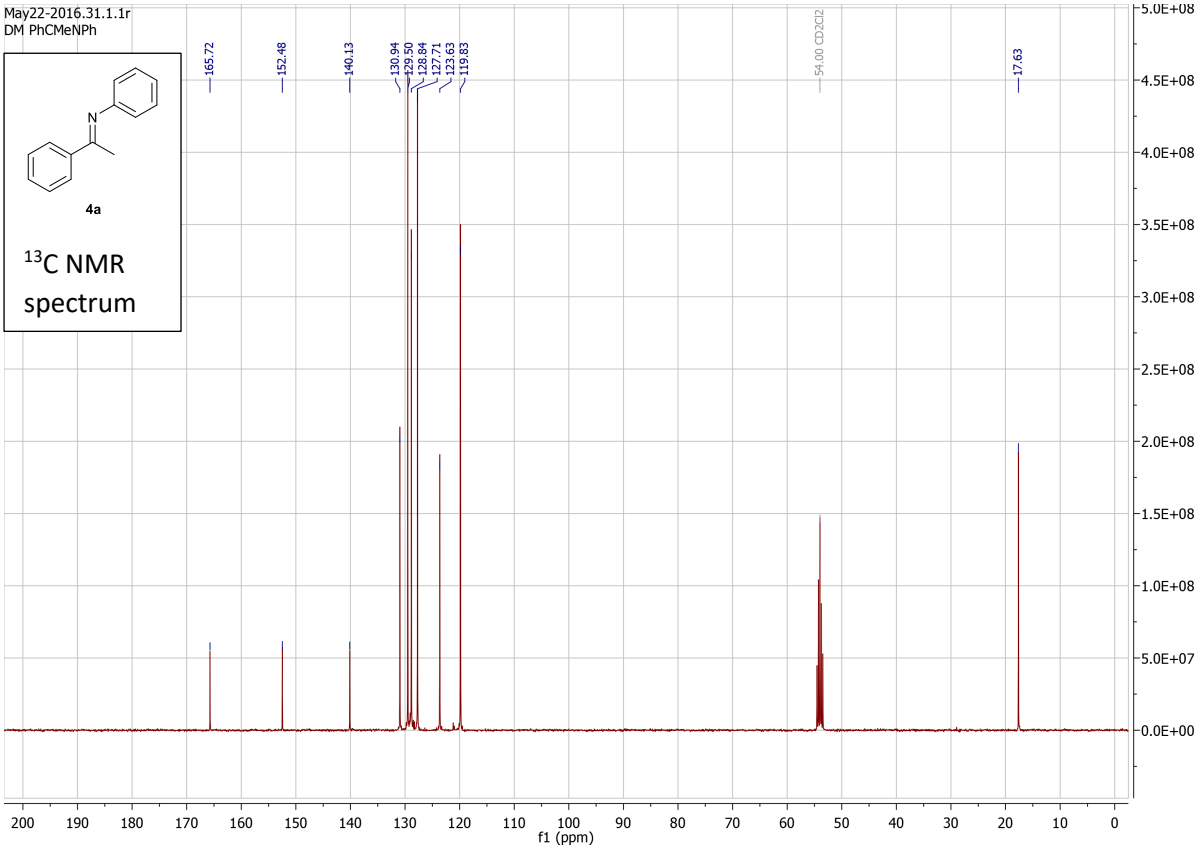
E/Z ratio = 12.5:1; ^{1}H NMR (400 MHz, $CDCl_3$) 7.95 (m, 2H), 7.47 (m, 4H), 7.39 (m, 3H), 7.3 (m, 4H), 7.21 (m, 3H), 5.87 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 164.5, 145, 141.3, 129.8, 128.5, 128.3, 127.7, 127.1, 126.8, 68.5, 16.1. HRMS (ES+) calculated for $C_{21}H_{20}N$ ($[M+H]^+$) 286.1596, found 286.1594; IR (powder, cm^{-1}) 3081, 3055, 3023, 2872, 1635, 1597, 1577, 1489, 1445, 1368, 1283, 1265, 1047, 1021, 760, 738, 690, 613, 575, 561.

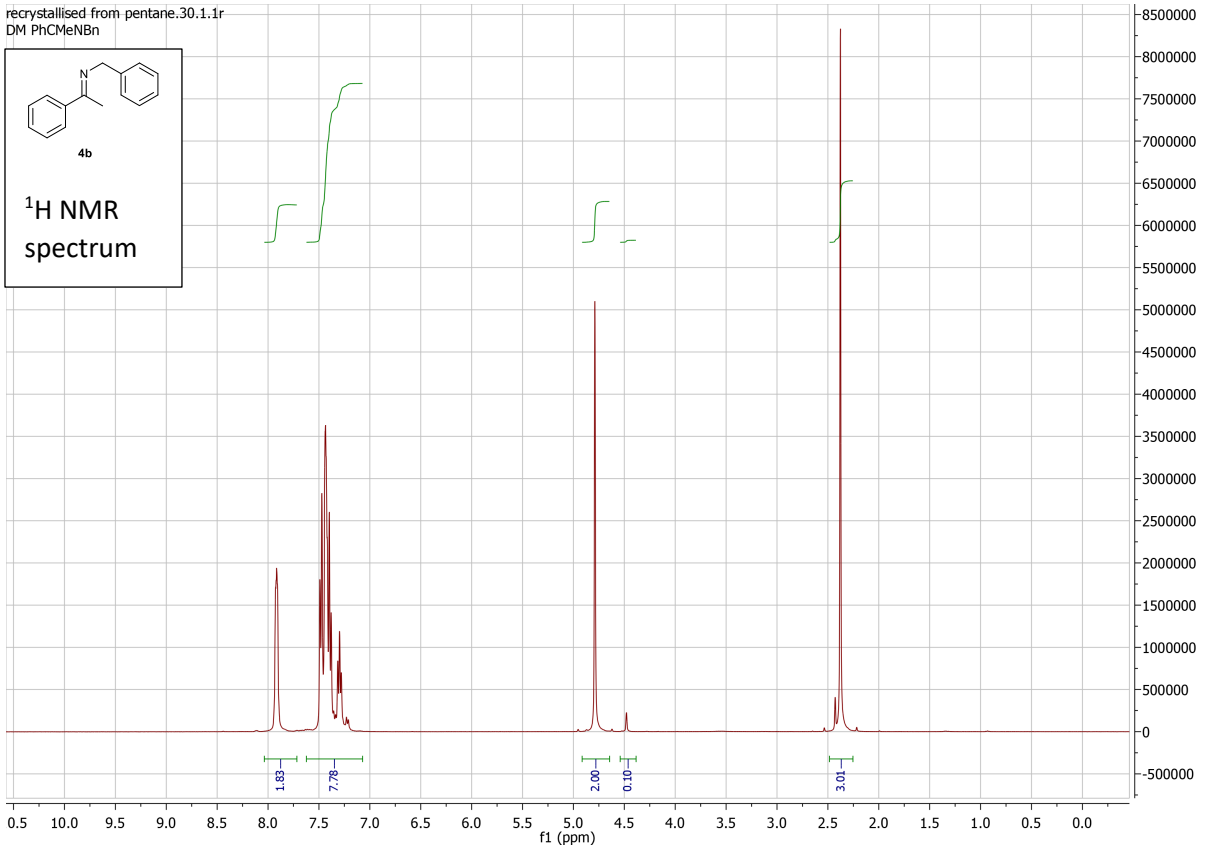


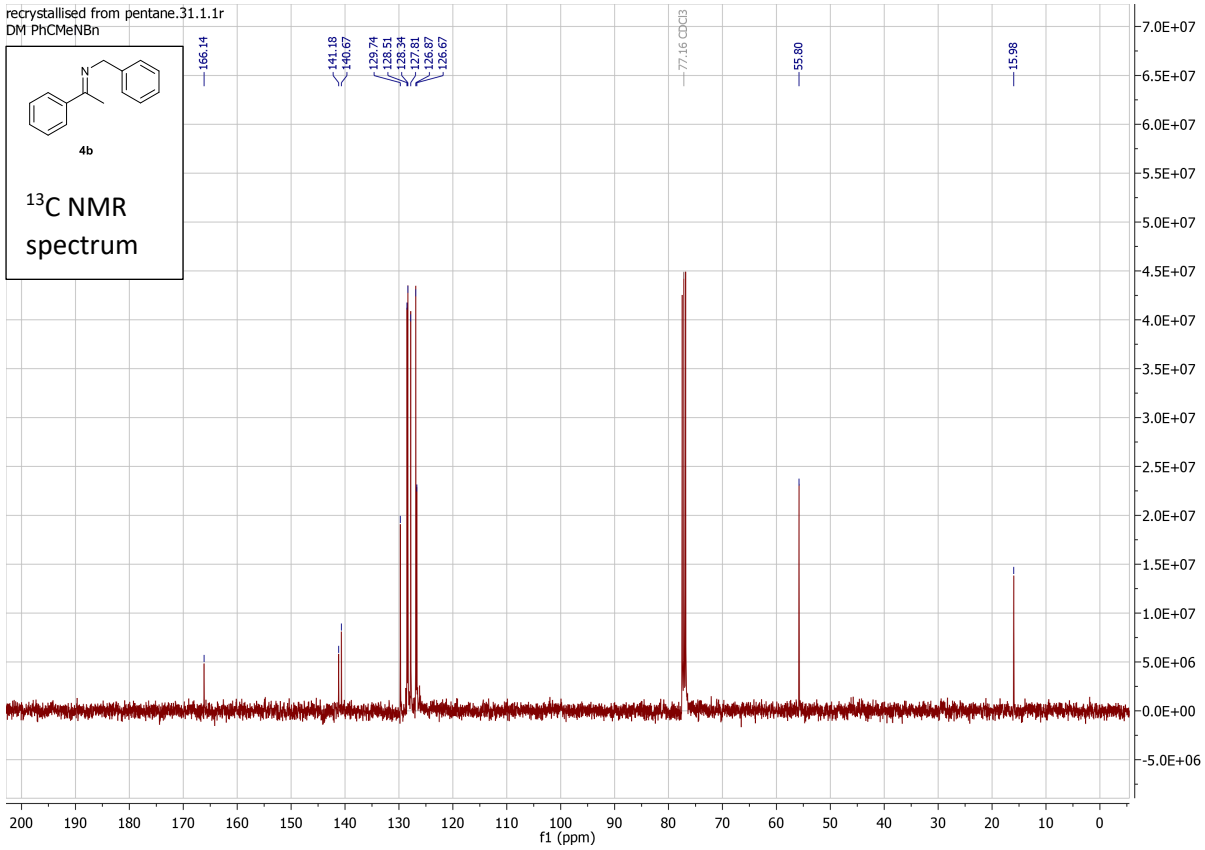
4i

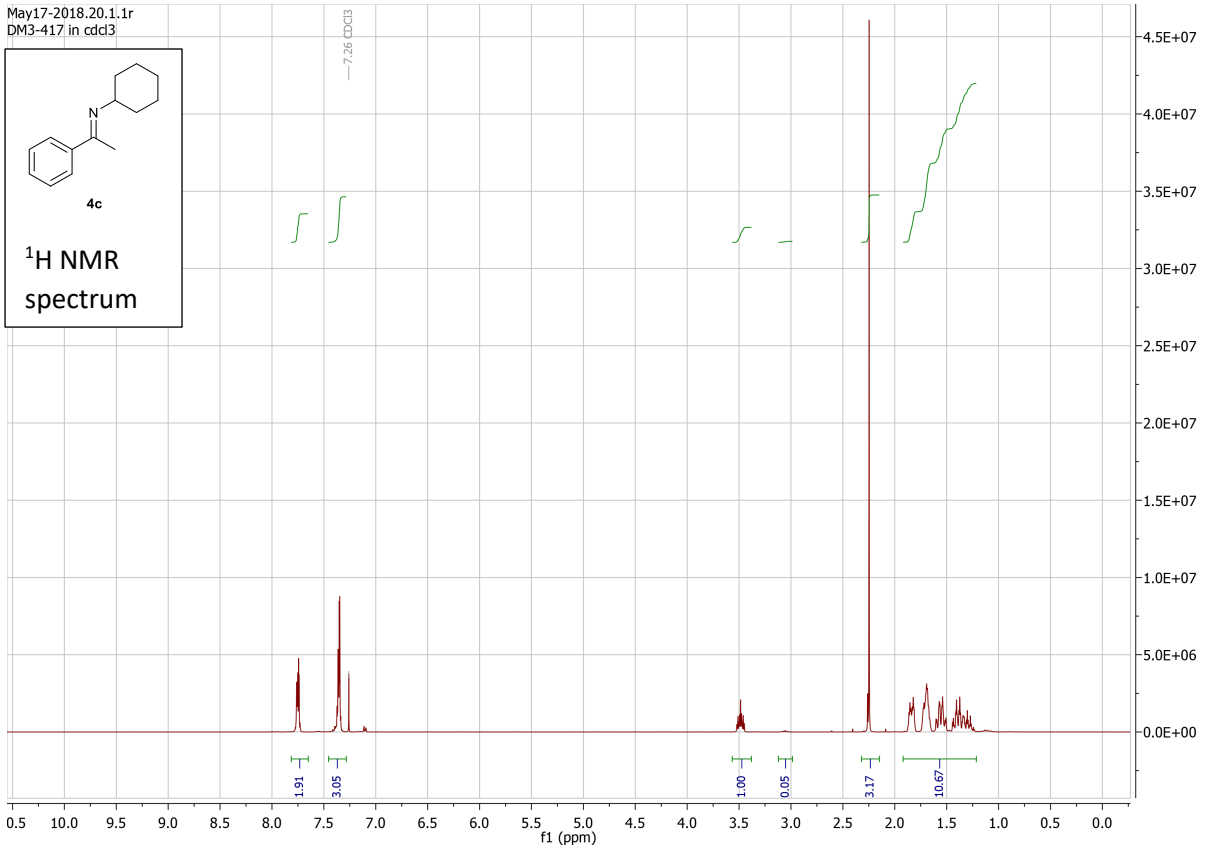
E/Z ratio = 1.8:1; ~88% purity; ^{1}H NMR (400 MHz, $CDCl_3$) major 7.72 (m, 2H), 7.36 (m), 3.53 (m, 1H), 2.7 (q, *J* = 7.7 Hz, 2H), 1.87-1.28 (m), 1.09 (t, *J* = 7.6 Hz, 3H); minor 7.36 (m), 7.06 (m), 3.02 (m), 2.51 (q, *J* = 7.6 Hz), 1.87-1.28 (m), 1.04 (t, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 170.9, 167.8, 140.8, 139.1, 129.1, 128.4, 128.3, 127.1, 126.4, 60.7, 59.6, 34.22, 34.1, 25.9, 25.7, 25, 24.7, 22.1, 12.7, 11.4; HRMS (ES+) calculated for $C_{15}H_{22}N$ ($[M+H]^+$) 216.1752, found 216.1753; IR (neat, cm^{-1}) 2924, 2851, 1689, 1628, 1444, 1219, 962, 889, 770, 744, 692.

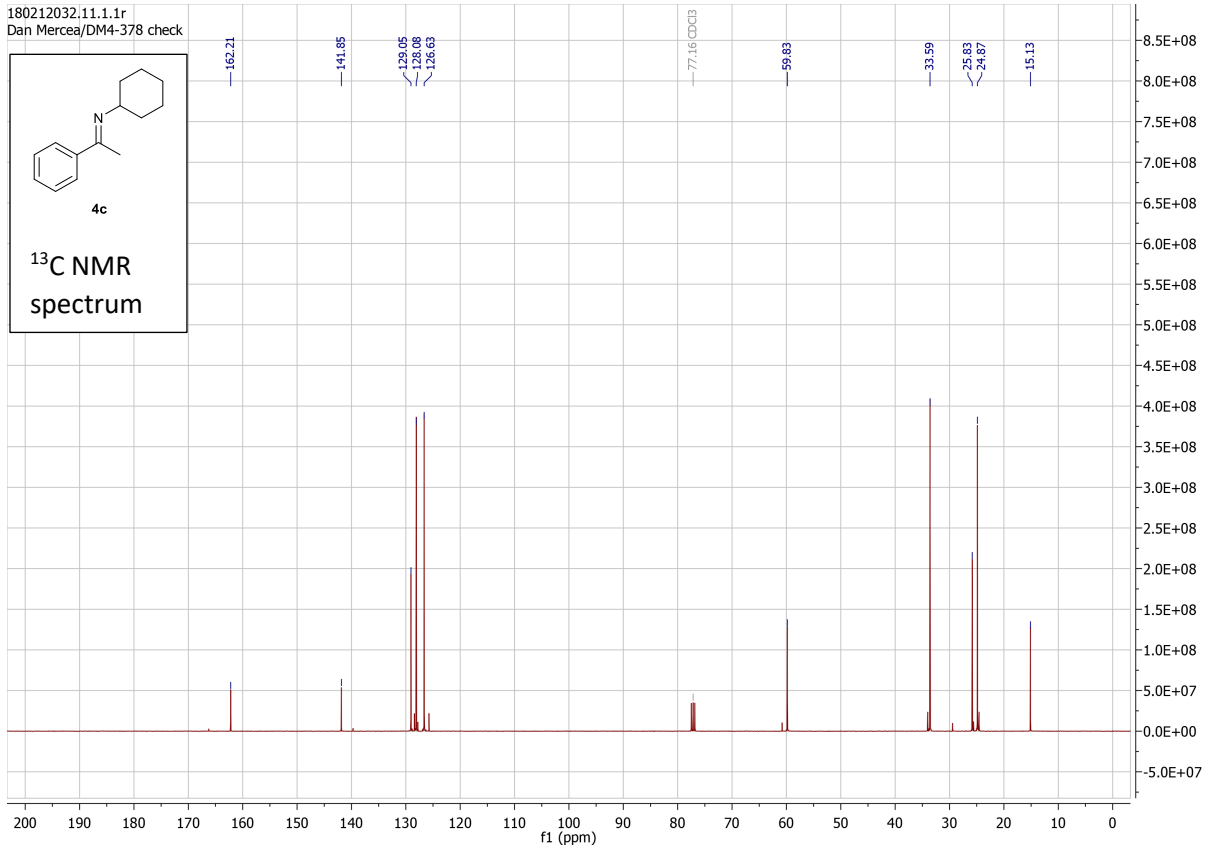

May22-2016.30.1.1r
DM PhCMeNPh
4a
1H NMR
spectrum
5.32 CD2Cl2
1.83
2.60
1.80
0.86
1.66
3.00
f1 (ppm)

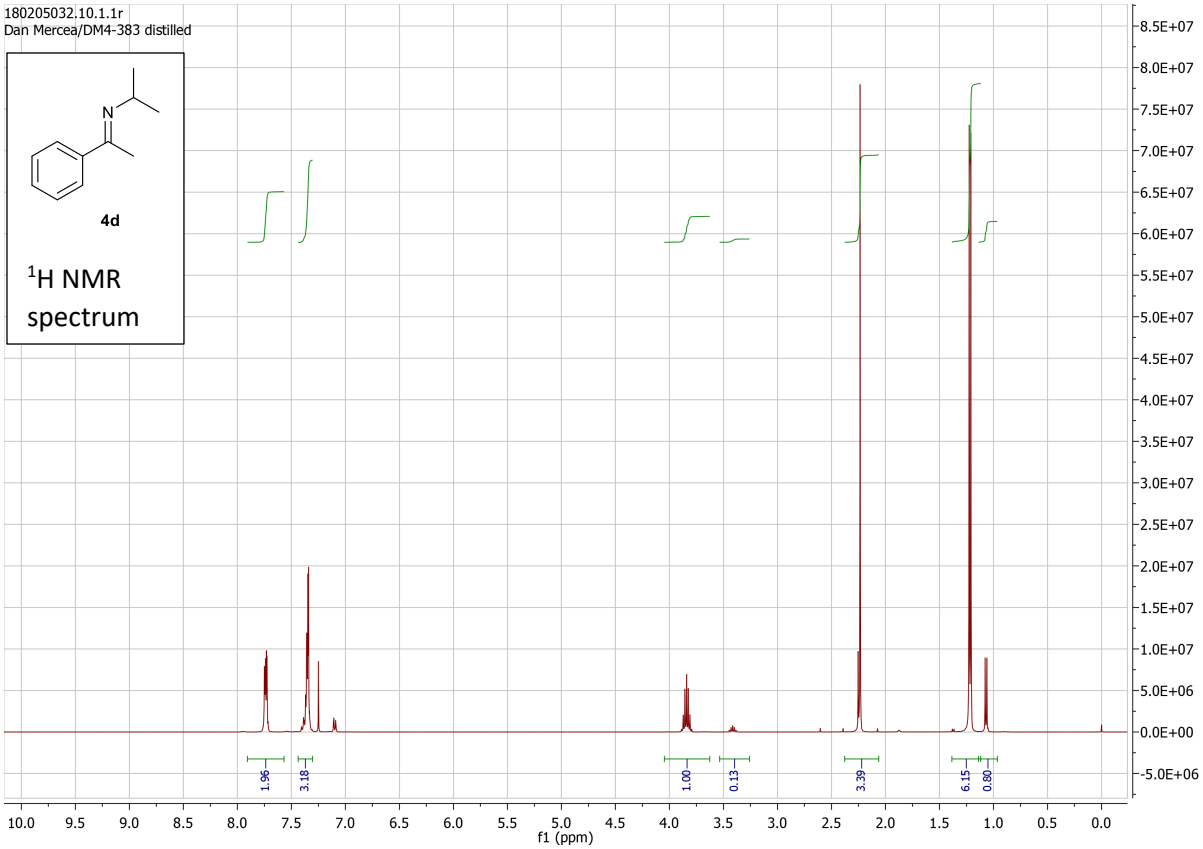

May22-2016.31.1.1r
DM PhCMeNPh
4a
13C NMR
spectrum
165.72
152.48
140.13
130.94
129.50
128.84
127.71
123.63
119.83
54.00 CD2Cl2
17.63
f1 (ppm)

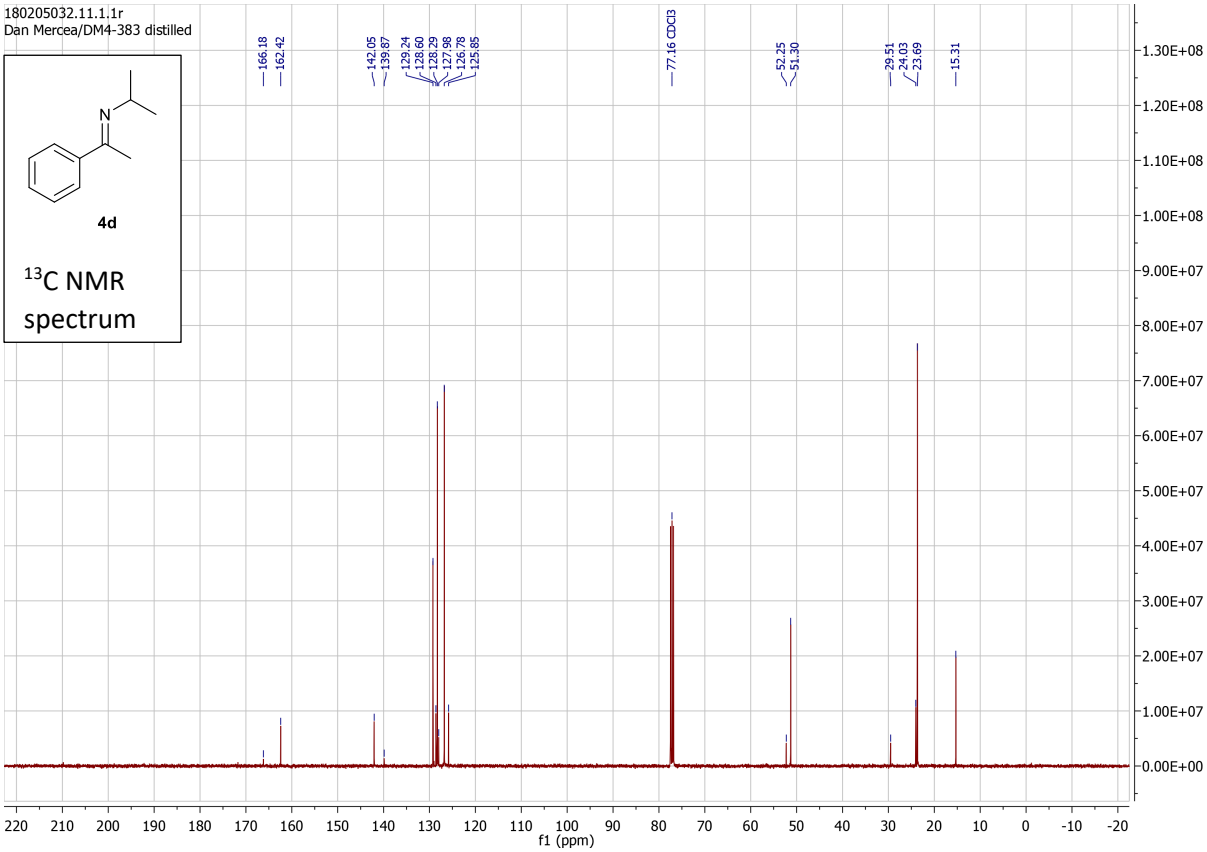

recrystallised from pentane.30.1.1r
DM PhCMeNBn
4b
1H NMR spectrum
1.83
7.78
2.00
0.10
3.01
f1 (ppm)

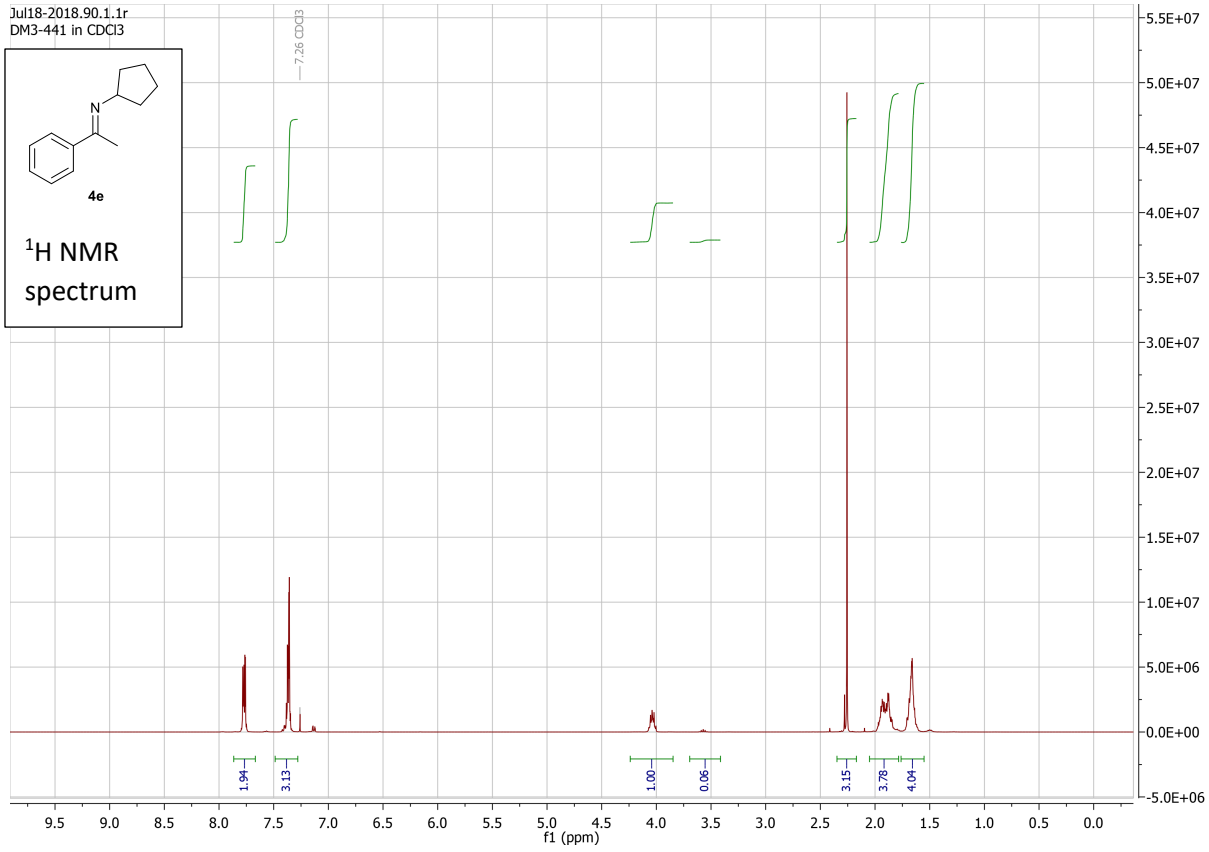

recrystallised from pentane.31.1.1r
DM PhCMeNBn
4b
13C NMR spectrum
166.14
141.18
140.67
129.74
128.51
128.34
127.81
126.87
126.67
77.16 CDCl3
55.80
15.98
f1 (ppm)

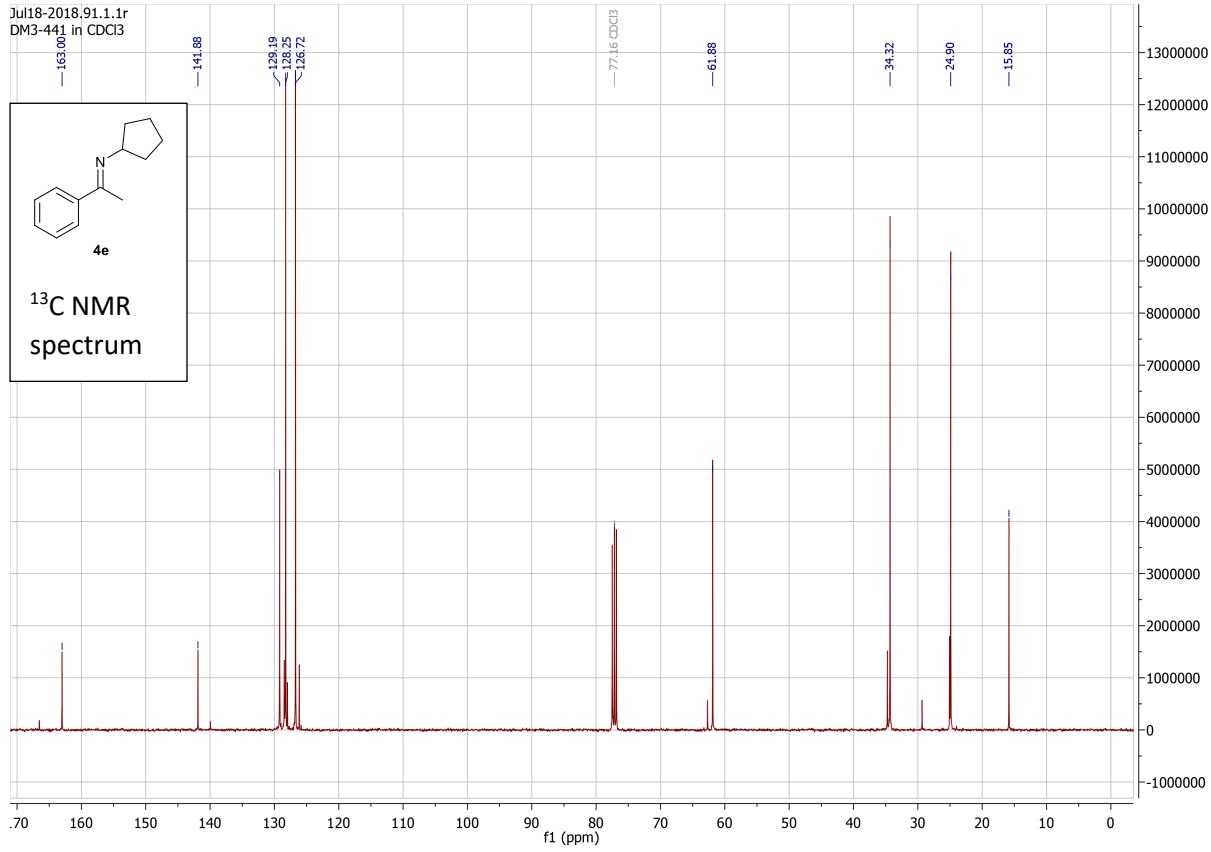

May17-2018.20.1.1r
DM3-417 in cdcl3
4c
^{1}H NMR spectrum
7.26 CDCl3
1.91
3.05
1.00
0.05
3.17
10.67
f1 (ppm)

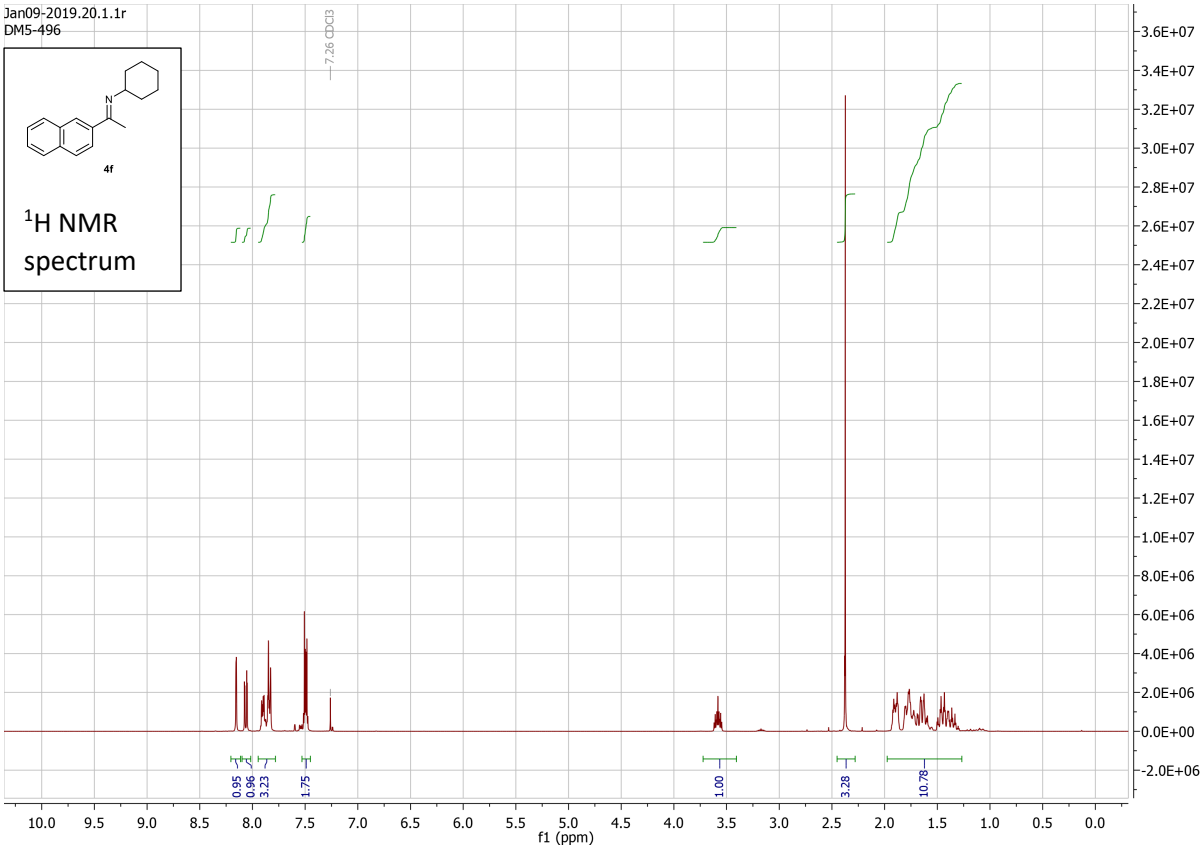

180212032.11.1.1r
Dan Mercea/DM4-378 check
4c
^{13}C NMR spectrum
162.21
141.85
129.05
128.08
126.63
77.16 CDCl3
59.83
33.59
25.83
24.87
15.13
f1 (ppm)

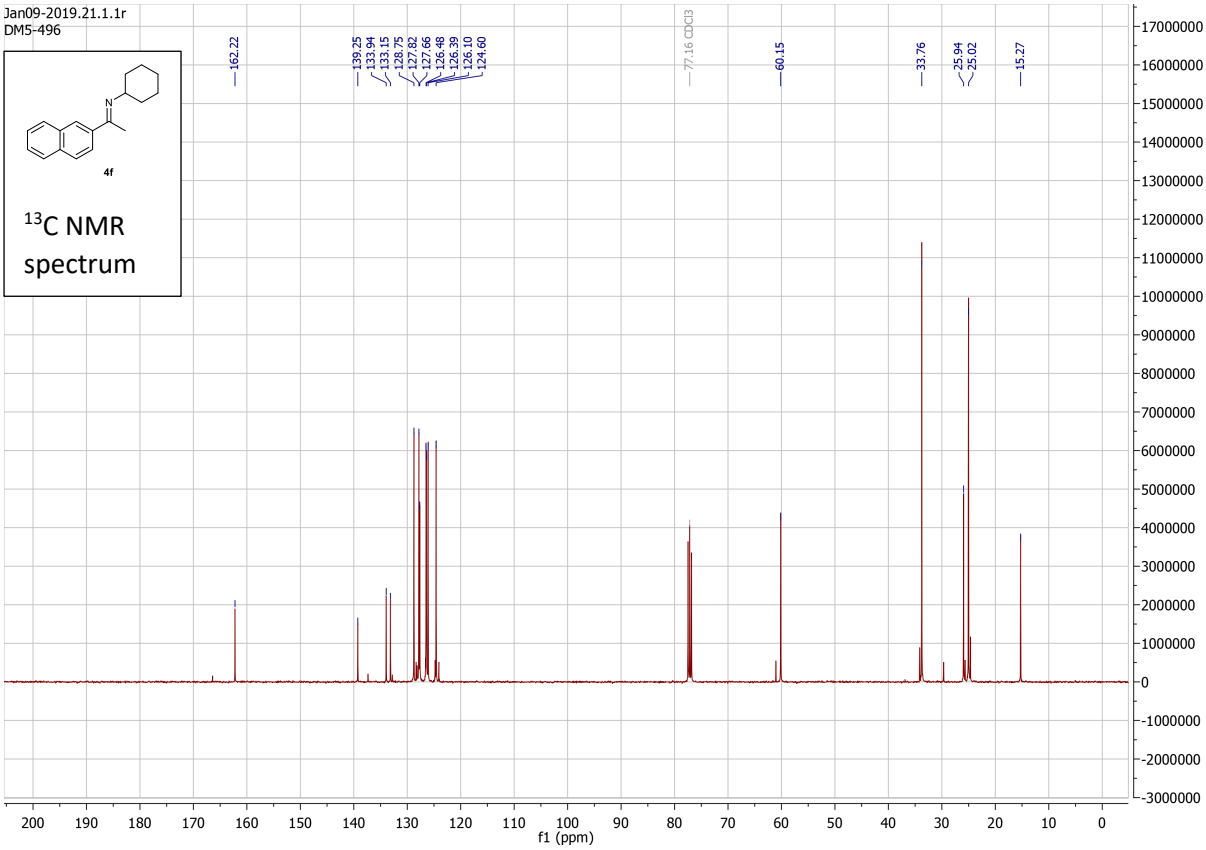

180205032.10.1.1r
Dan Mercea/DM4-383 distilled
4d
1H NMR spectrum
1.96
3.18
1.00
0.13
3.39
6.15
0.80
f1 (ppm)

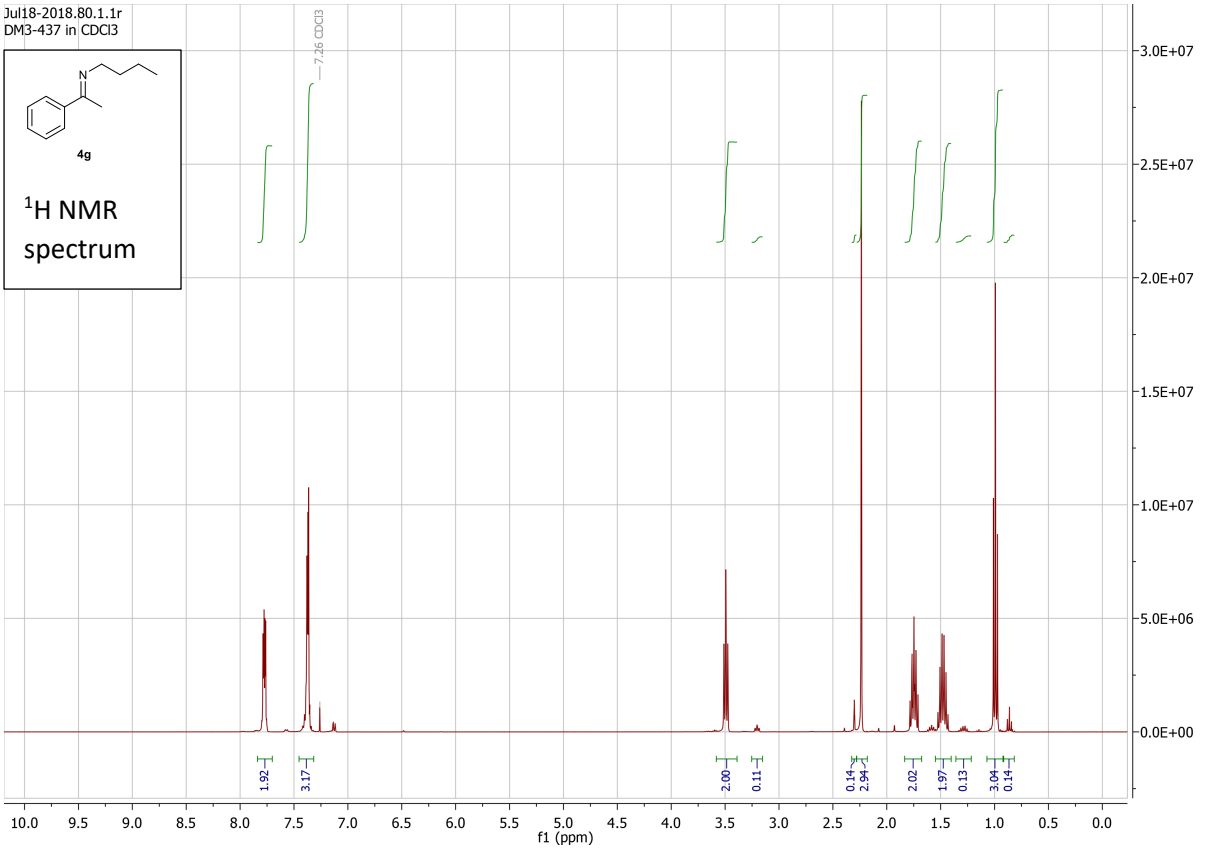

180205032.11.1.1r
Dan Mercea/DM4-383 distilled
4d
13C NMR spectrum
166.18
162.42
142.05
139.87
129.24
128.60
128.29
127.98
126.78
125.85
77.16 CDCl3
52.25
51.30
29.51
24.03
23.69
15.31
f1 (ppm)

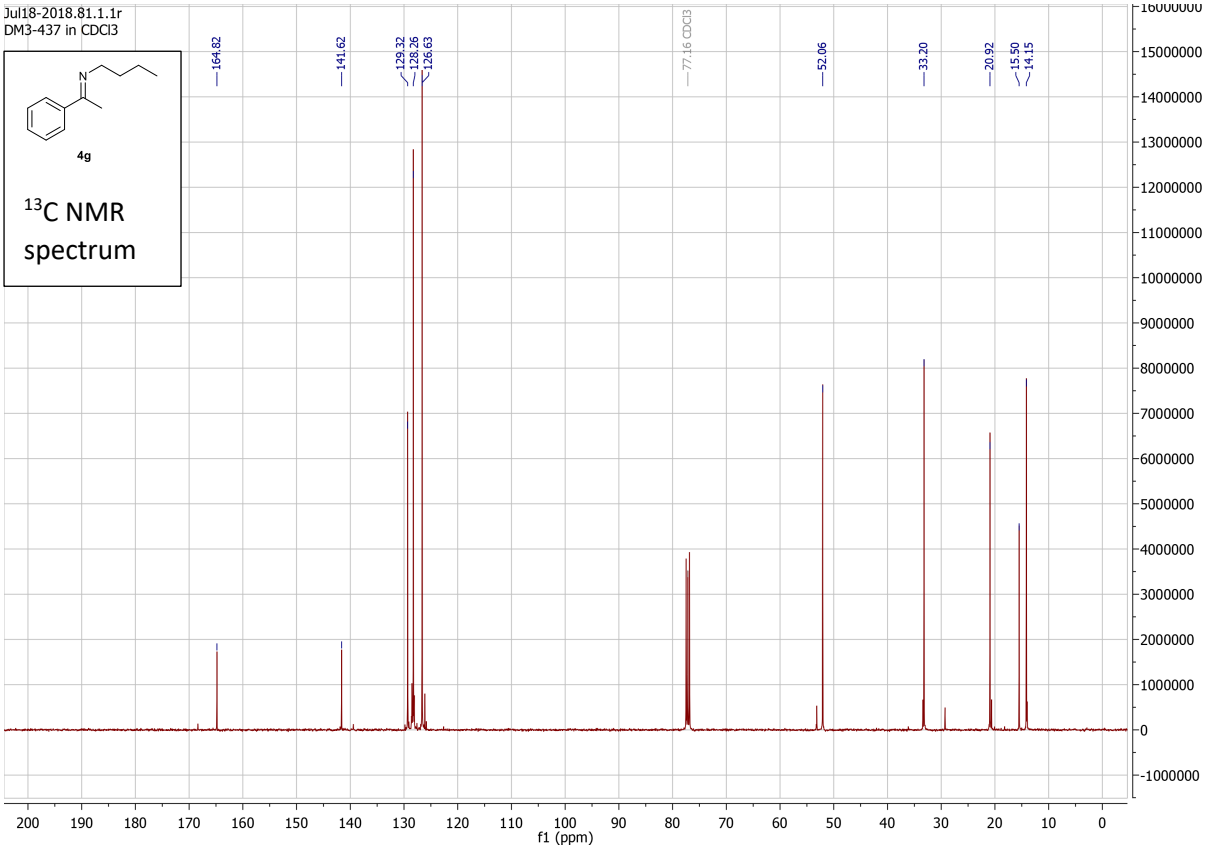

Jul18-2018.90.1.1r
DM3-441 in CDCl3
4e
^{1}H NMR spectrum
7.26 CDCl3
1.94
3.13
1.00
0.06
3.15
3.78
4.04
f1 (ppm)

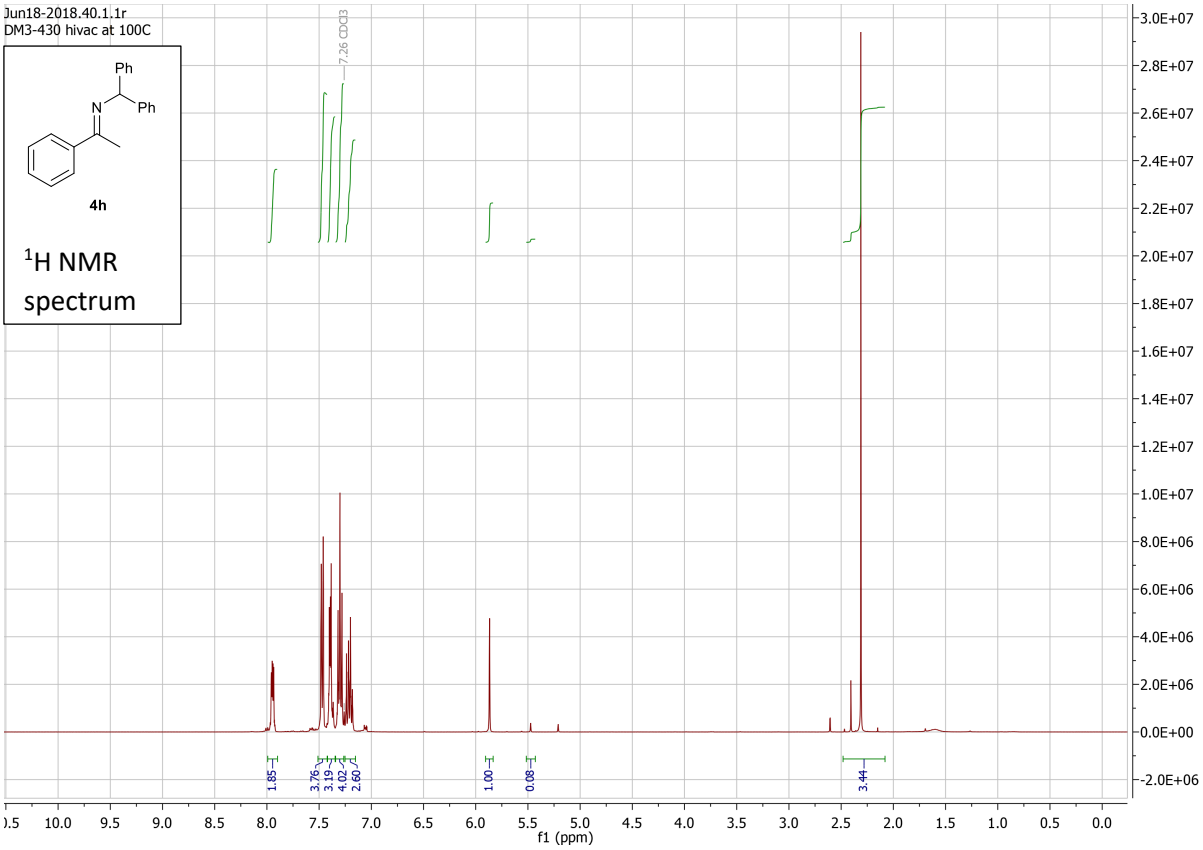

Jul18-2018.91.1.1r
DM3-441 in CDCl3
4e
^{13}C NMR spectrum
163.00
141.88
129.19
128.25
126.72
77.16 CDCl3
61.88
34.32
24.90
15.85
f1 (ppm)

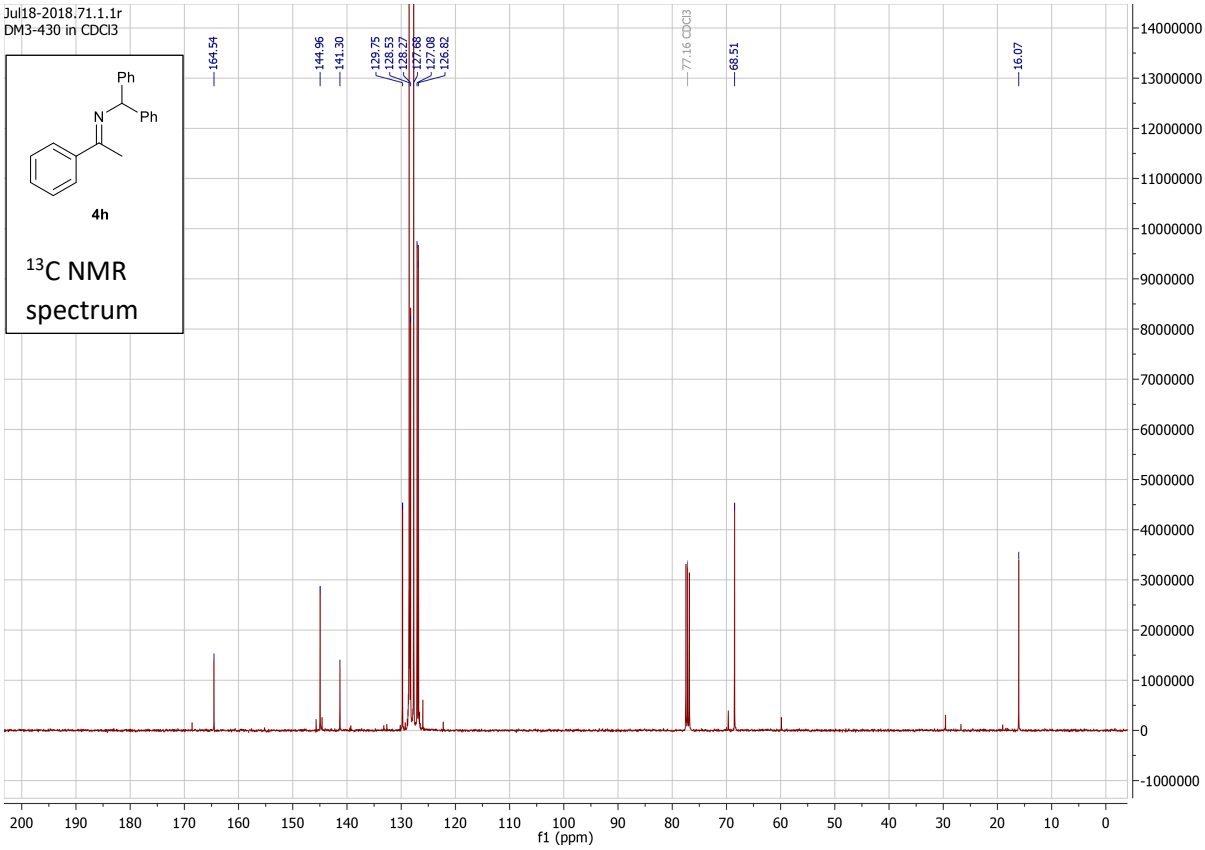

Jan09-2019.20.1.1r
DM5-496
4f
^{1}H NMR spectrum
7.26 CDCl3
0.95
0.96
3.23
1.75
1.00
3.28
10.78
f1 (ppm)

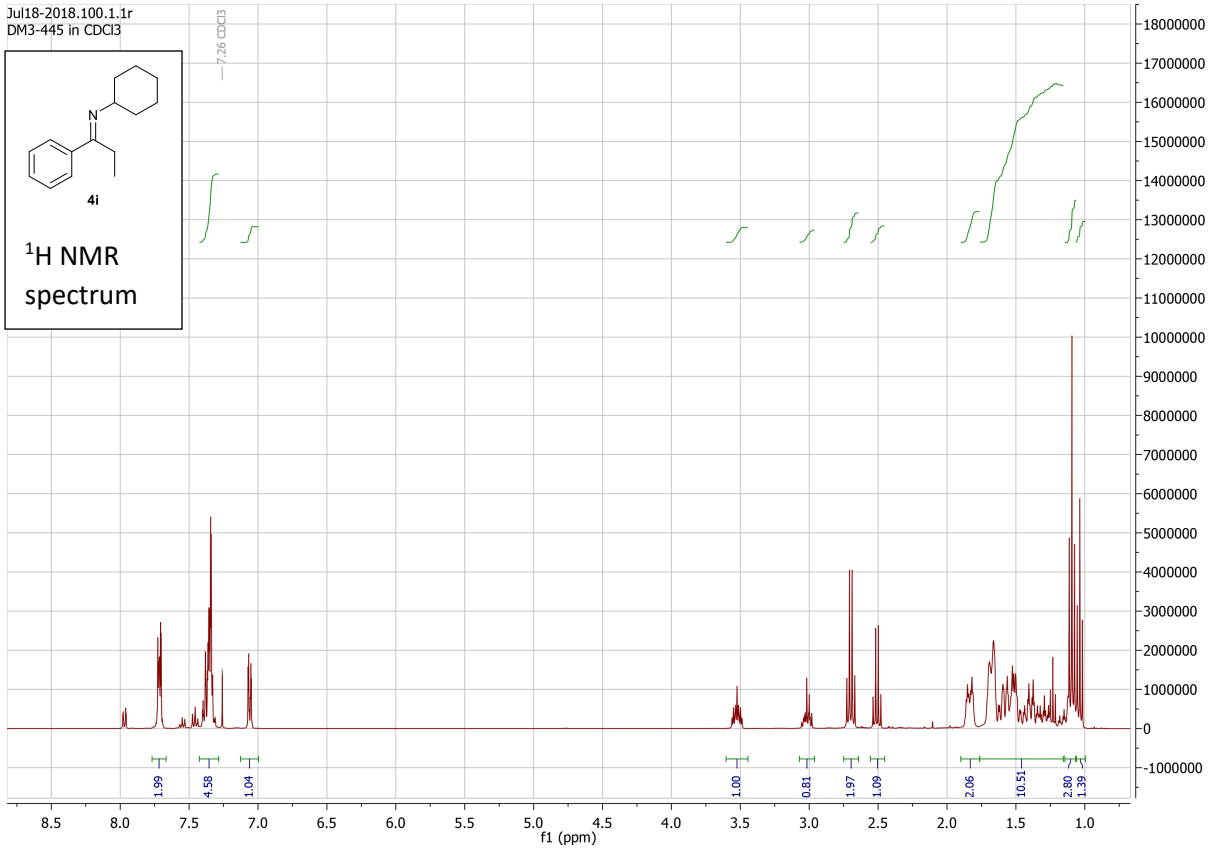

Jan09-2019.21.1.1r
DM5-496
4f
^{13}C NMR spectrum
162.22
139.25
133.94
133.15
128.75
127.82
127.66
126.48
126.39
126.10
124.60
77.16 CDCl3
60.15
33.76
25.94
25.02
15.27
f1 (ppm)

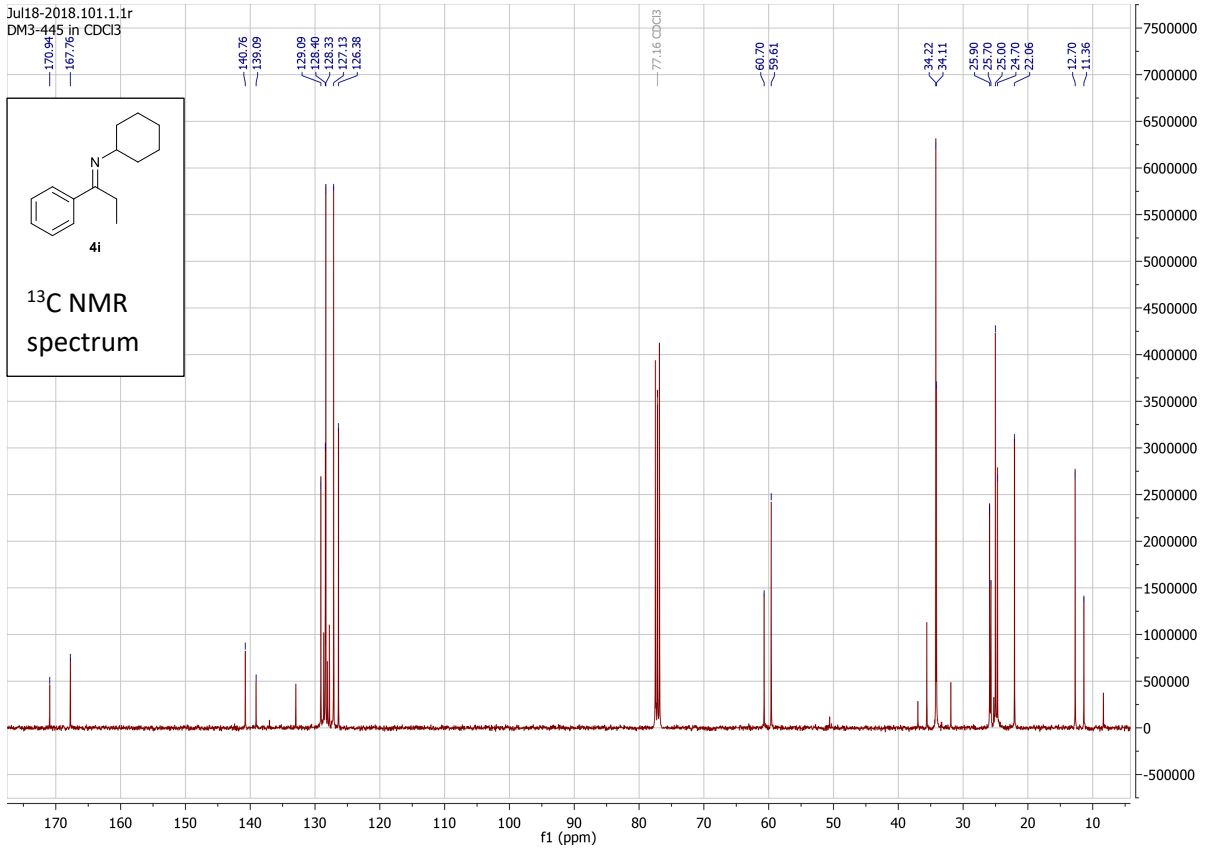

Jul18-2018.80.1.1r
DM3-437 in CDCl3
4g
^{1}H NMR spectrum
7.26 CDCl3
1.92
3.17
2.00
0.11
0.14
2.94
2.02
1.97
0.13
3.04
0.14
f1 (ppm)


Jul18-2018.81.1.1r
DM3-437 in CDCl3
4g
^{13}C NMR spectrum
164.82
141.62
129.32
128.26
126.63
77.16 CDCl3
52.06
33.20
20.92
15.50
14.15
f1 (ppm)


Jun18-2018.40.1.1r
DM3-430 hivac at 100C
Ph
N
Ph
4h
1H NMR spectrum
7.26 CDCl3
1.85
3.76
3.19
4.02
2.60
1.00
0.08
3.44
f1 (ppm)


Jul18-2018.71.1.1r
DM3-430 in CDCl3
Ph
N
Ph
4h
13C NMR spectrum
164.54
144.96
141.30
129.75
128.53
128.27
127.68
127.08
126.82
77.16 CDCl3
68.51
16.07
f1 (ppm)


Jul18-2018.100.1.1r
DM3-445 in CDCl3
7.26 CDCl3
4i
1H NMR
spectrum
1.99
4.58
1.04
1.00
0.81
1.97
1.09
2.06
10.51
2.80
1.39
f1 (ppm)


Jul18-2018.101.1.1r
DM3-445 in CDCl3
170.94
167.76
140.76
139.09
129.09
128.40
128.33
127.13
126.38
77.16 CDCl3
60.70
59.61
34.22
34.11
25.90
25.70
25.00
24.70
22.06
12.70
11.36
4i
13C NMR
spectrum
f1 (ppm)

4. Hydrosilylation catalysis

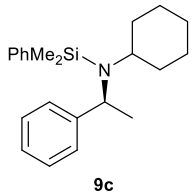
Reactions were carried out either in NMR tubes equipped with Young's valves (method A) or in glass vials (method B). Workup with methanol was carried out to generate the free amines **5** from the *N*-silylamines **9**.

Method A: A sealed glass capillary insert (0.1M 1,3,5-trimethoxybenzene/C_6D_6, calibrated against a solution of 1,4-dinitrobenzene) was included and the reaction initiated by the addition of hydrosilane using a microsyringe, sealing and mixing. The reaction was allowed to proceed at room temperature and analysed by NMR at the specified time points. Results are reported as percentage composition. Mass balance was approximately constant throughout the reaction and in the 90-110% range based on theoretical (for $PhMe_2SiH$ the concentration adjusted for hydrosilane volume is 0.57M). Workup with methanol was carried out as soon as possible following the last reported time point.

Method B: Reactions were set up in an analogous fashion but allowed to proceed in the glovebox before being worked up with methanol. NMR analysis was carried out in $CDCl_3$ on the crude reaction mixtures; a sealed glass capillary insert (0.1M 1,3,5-trimethoxybenzene/C_6D_6) was optionally included.

For both methods purification was carried out through preparative TLC (20x20cm, 0.2mm thickness) or flash column chromatography (10-15 g silicagel).

4.1 NMR characterisation for *N*-silylamine **9c**



9c

All volatiles were removed under high vacuum. The resulting residue was extracted with C_6D_6. NMR analysis was carried out on the resulting solution following filtration.

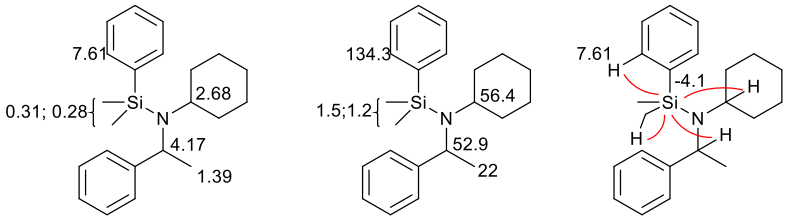
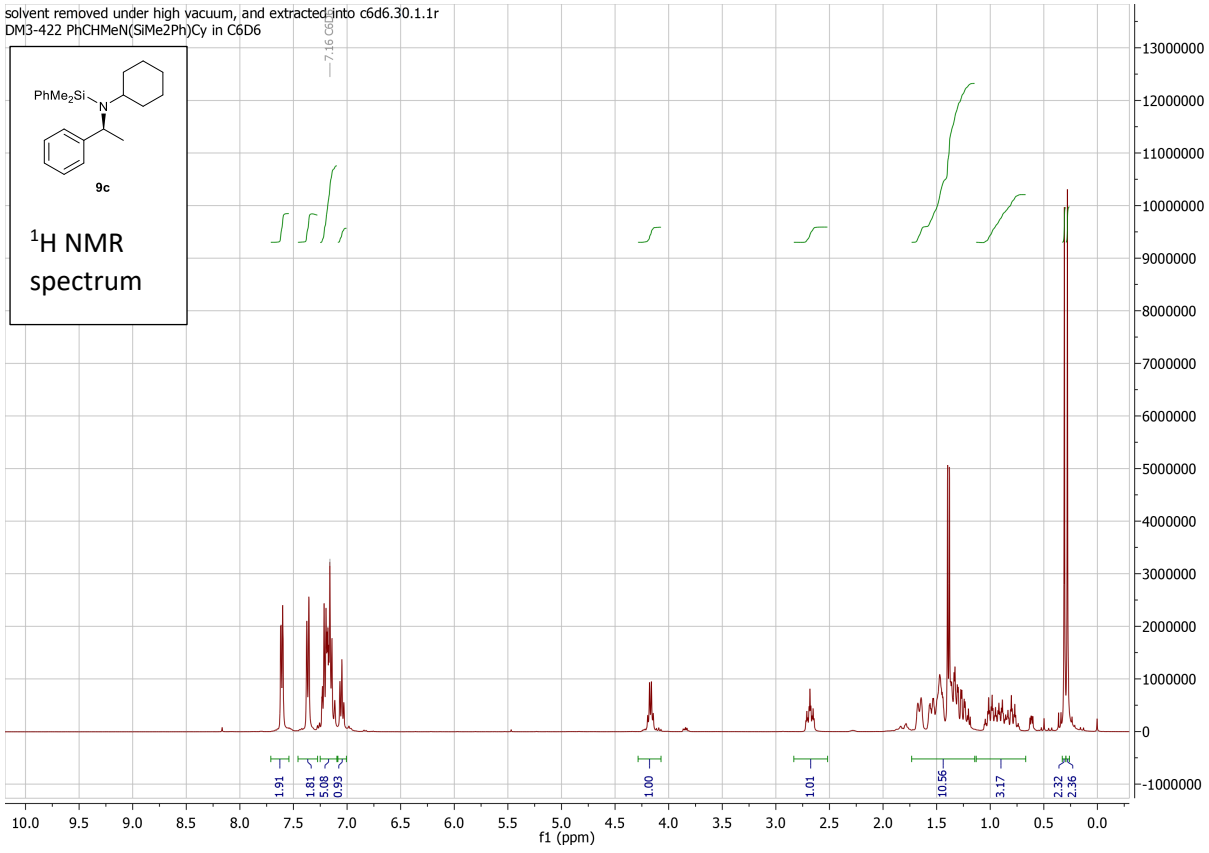
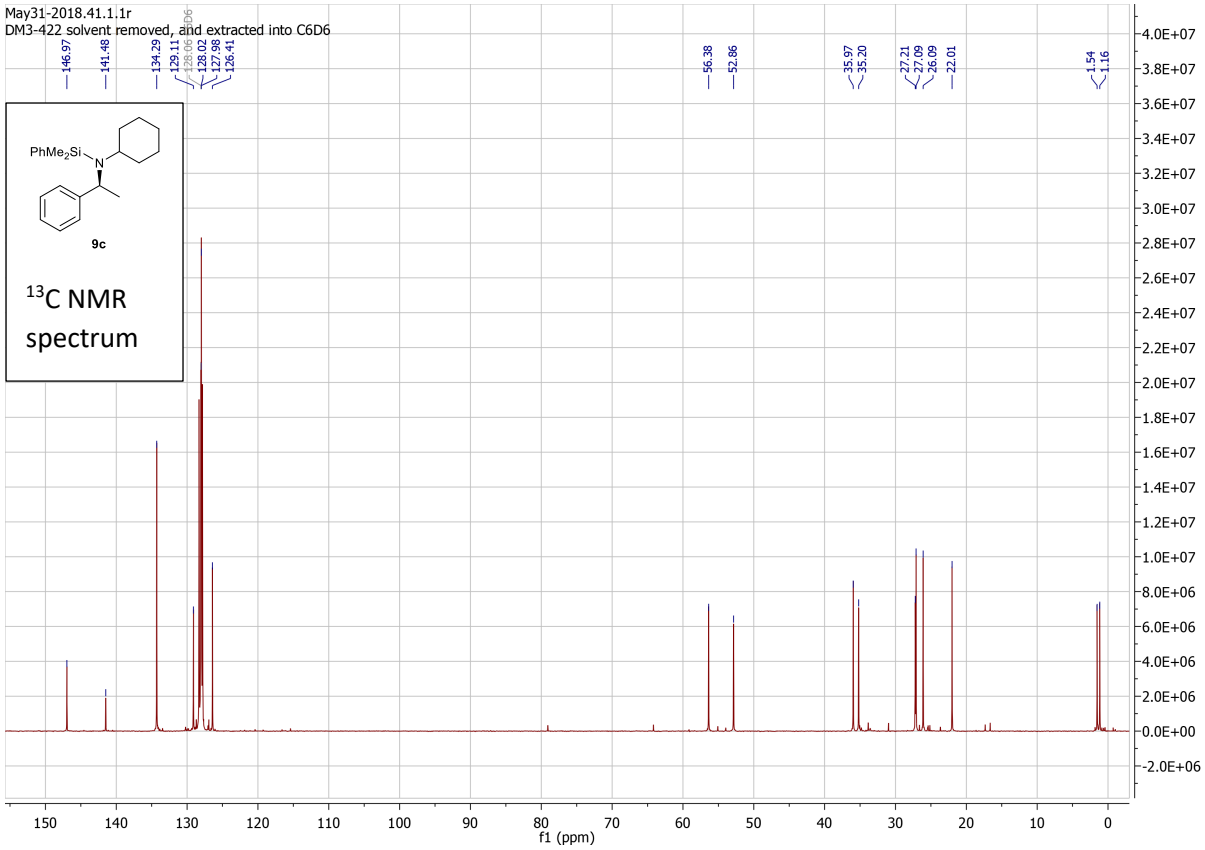
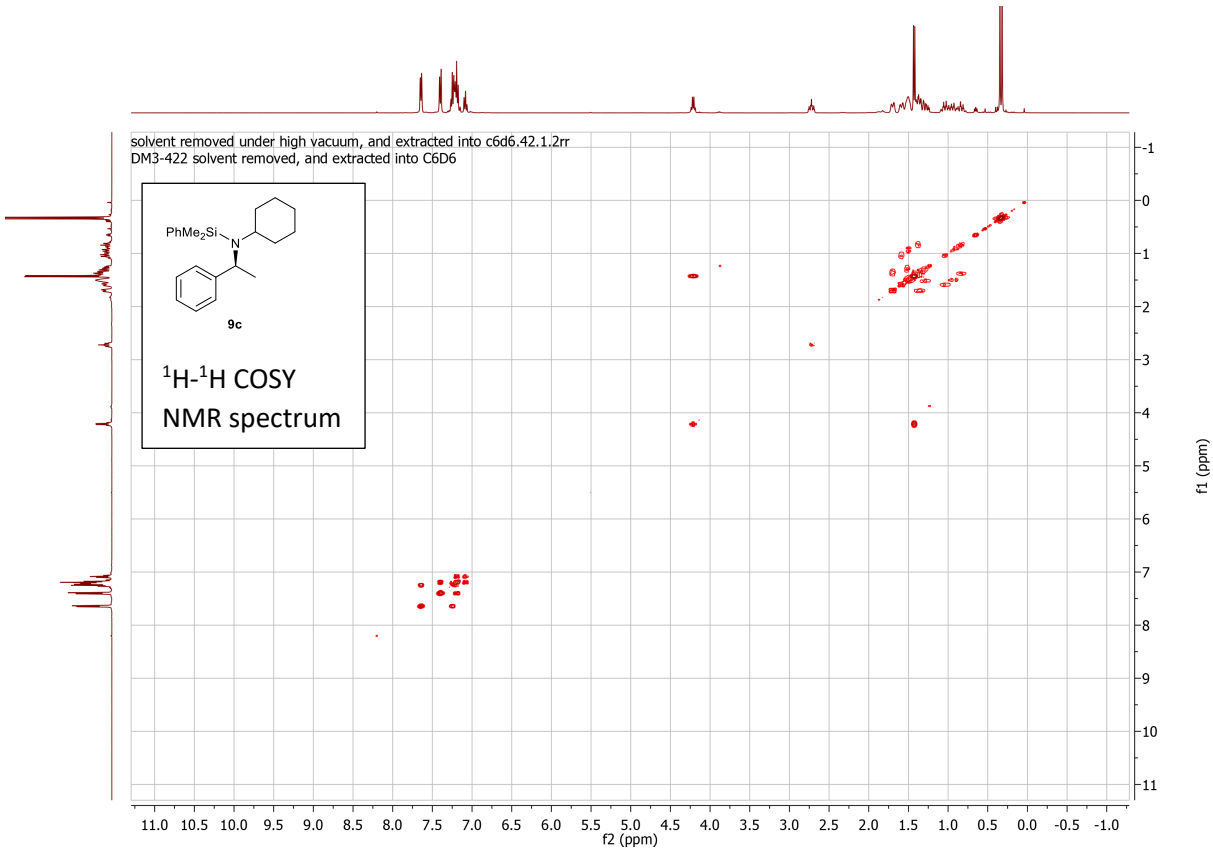


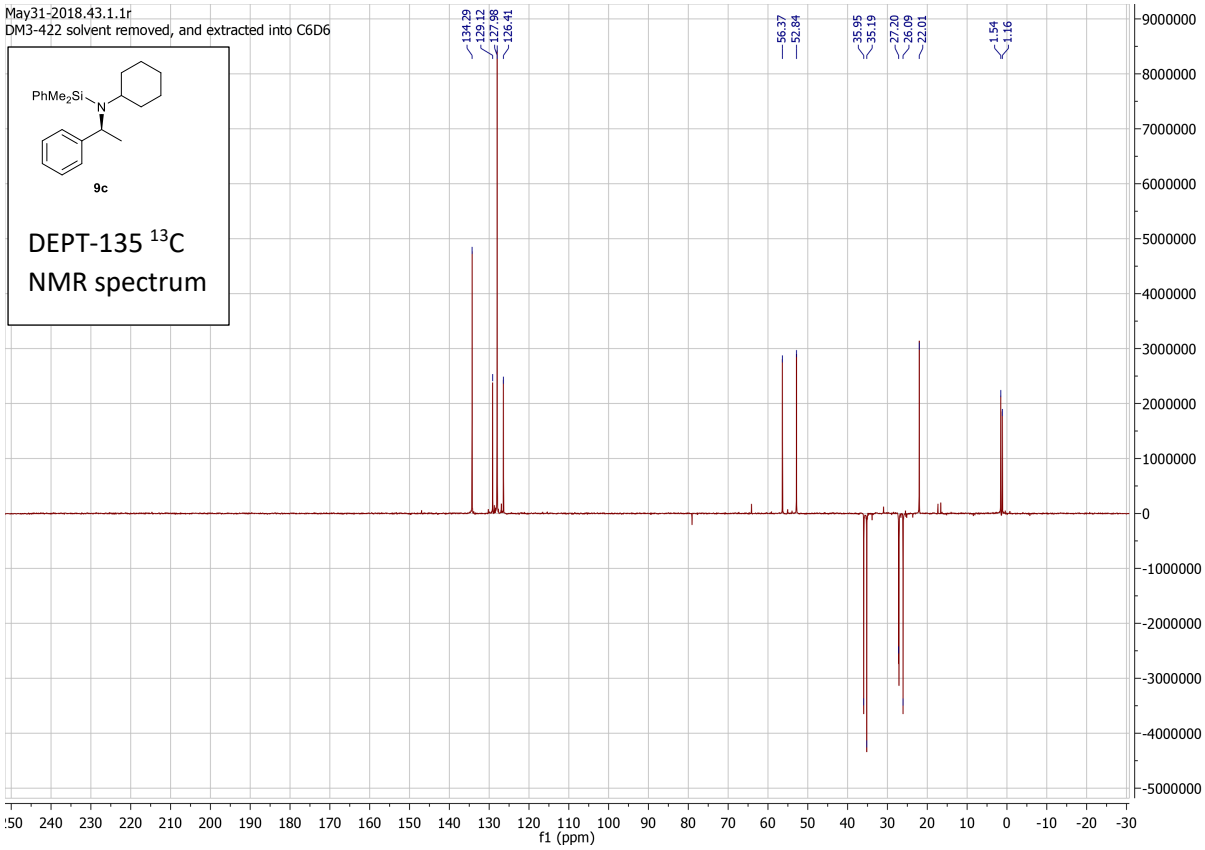
Figure S4. NMR assignment for compound **9c**

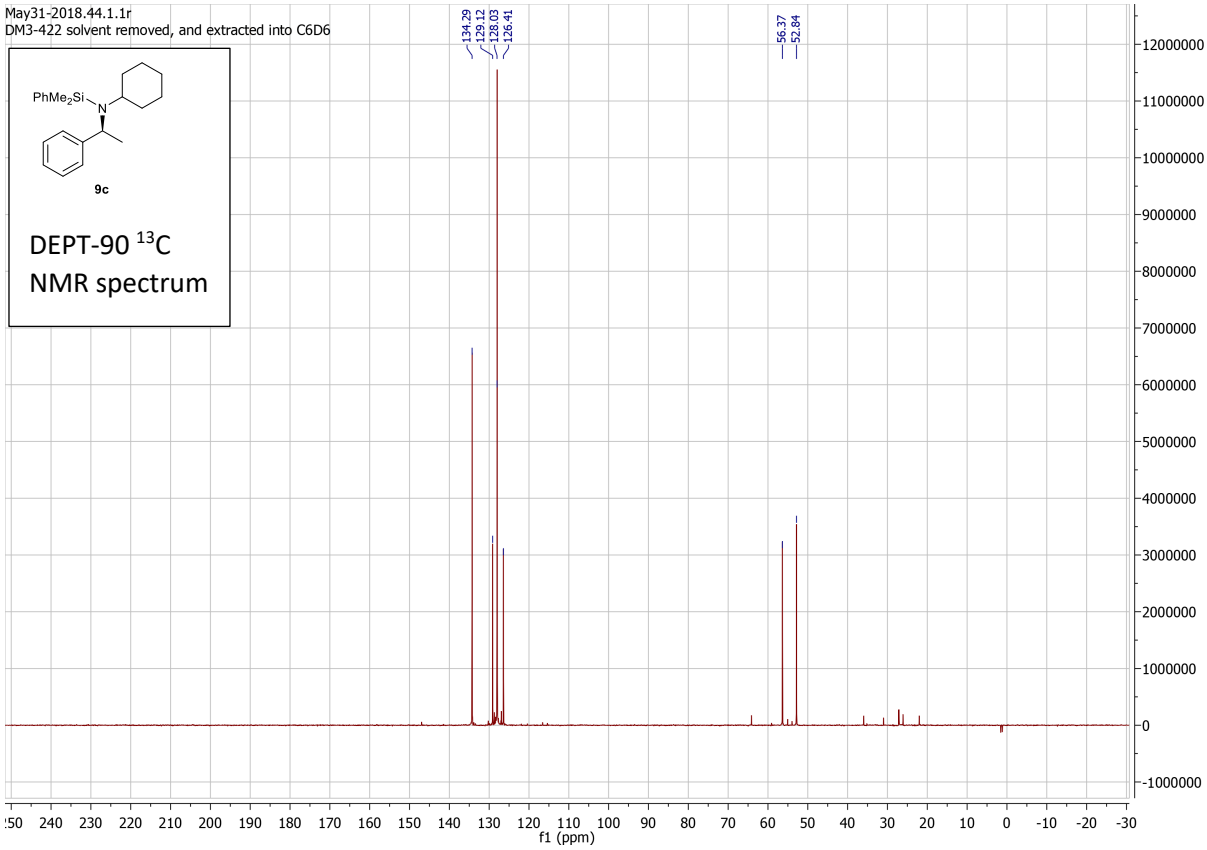
^{1}H NMR (400 MHz, C_6D_6): 7.61 (m, 2H), 7.37 (m, 2H), 7.18 (m, 5H), 7.05 (m, 1H), 4.17 (q, *J* = 7 Hz, 1H), 2.68 (m, 1H), 1.59-1.17 (m, 10H): 1.39 (d, *J* = 6.9 Hz), 1.07-0.72 (m, 3H), 0.31 (s, 3H), 0.28 (s, 3H); ^{13}C (100 MHz, C_6D_6): 147, 141.5, 134.3, 129.1, 128 (2), 126.4, 56.4, 52.9, 36, 35.2, 27.2, 27.1, 26.1, 22, 1.5, 1.2; ^{29}Si NMR (80 MHz, C_6D_6) -4.1 (s).

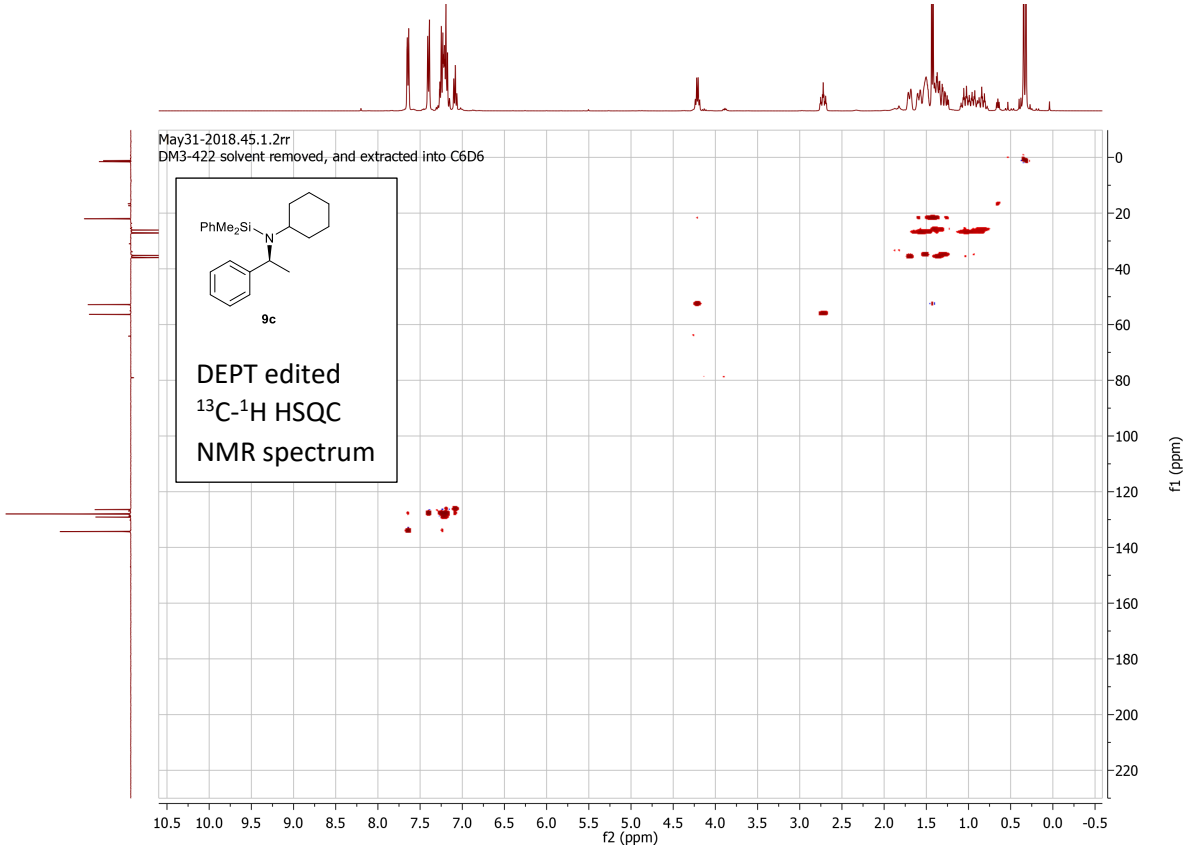


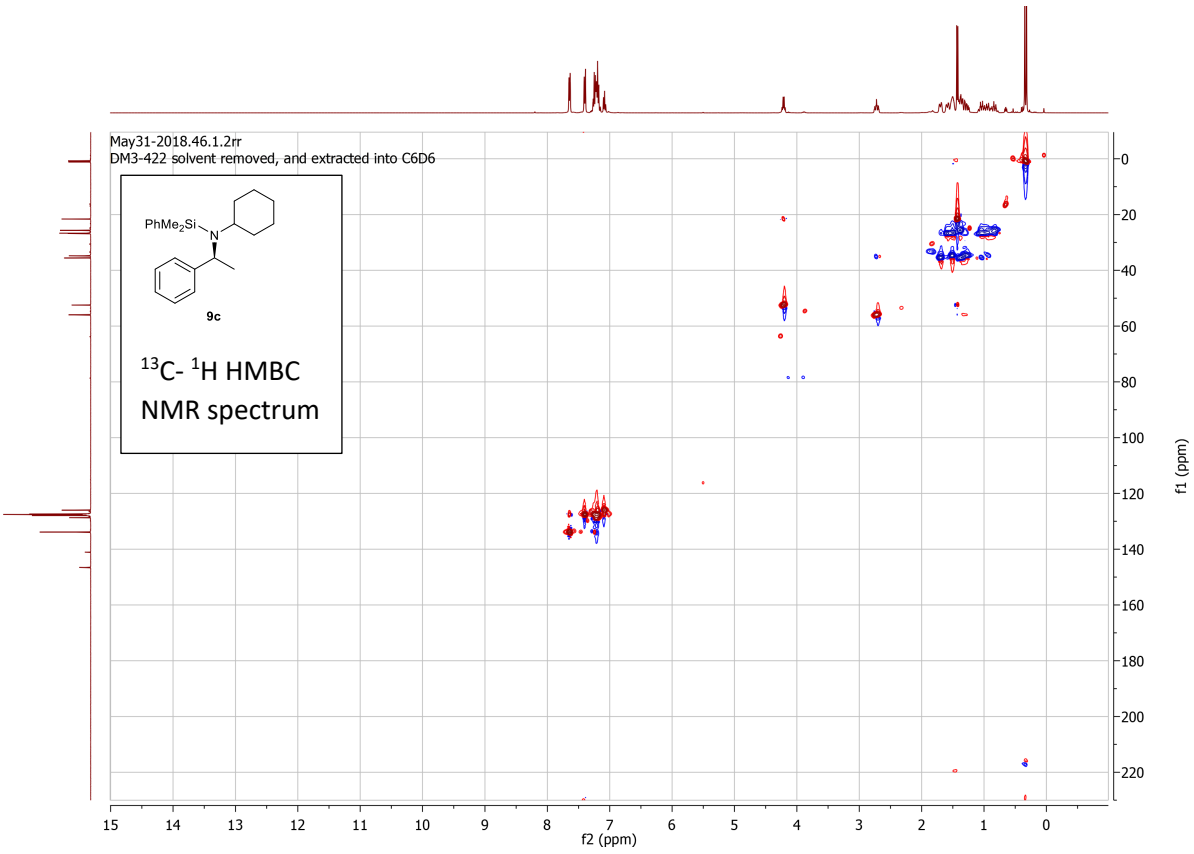

May31-2018.41.1.1r
DM3-422 solvent removed, and extracted into C6D6
146.97
141.48
134.29
129.11
128.02
127.98
126.41
56.38
52.86
35.97
35.20
27.21
27.09
26.09
22.01
1.54
1.16
PhMe2Si
N
9c
13C NMR spectrum
f1 (ppm)

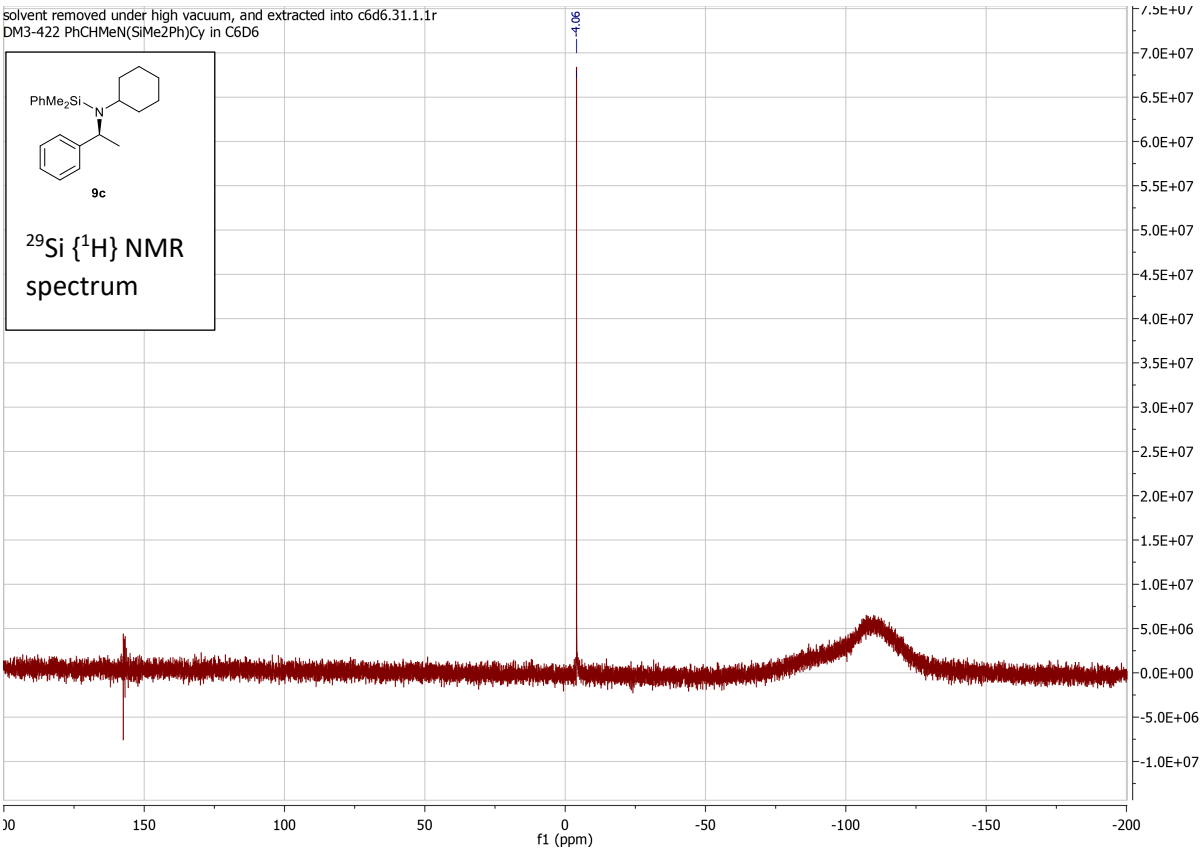

solvent removed under high vacuum, and extracted into c6d6.42.1.2rr
DM3-422 solvent removed, and extracted into C6D6
PhMe2Si
N
9c
1H-1H COSY NMR spectrum
f2 (ppm)
f1 (ppm)

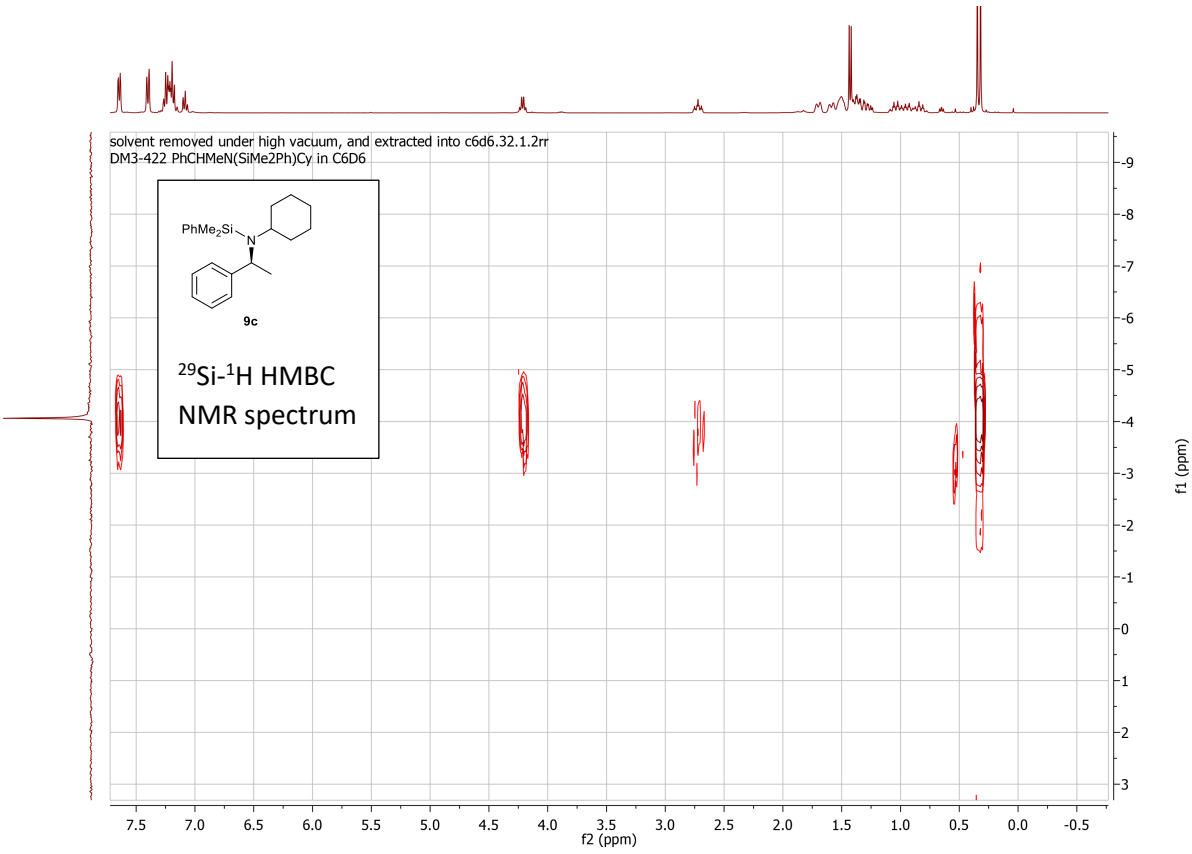

May31-2018.43.1.1r
DM3-422 solvent removed, and extracted into C6D6
PhMe2Si
N
9c
DEPT-135 13C
NMR spectrum
134.29
129.12
127.98
126.41
56.37
52.84
35.95
35.19
27.20
26.09
22.01
1.54
1.16
f1 (ppm)


May31-2018.44.1.1r
DM3-422 solvent removed, and extracted into C6D6
PhMe2Si
N
9c
DEPT-90 13C
NMR spectrum
134.29
129.12
128.03
126.41
56.37
52.84
f1 (ppm)


May31-2018.45.1.2rr
DM3-422 solvent removed, and extracted into C6D6
PhMe2Si
N
9c
DEPT edited
13C-1H HSQC
NMR spectrum
f2 (ppm)
f1 (ppm)


May31-2018.46.1.2rr
DM3-422 solvent removed, and extracted into C6D6
PhMe2Si
N
9c
13C- 1H HMBC
NMR spectrum
f2 (ppm)
f1 (ppm)


solvent removed under high vacuum, and extracted into c6d6.31.1.1r
DM3-422 PhCHMeN(SiMe2Ph)Cy in C6D6
PhMe2Si
N
9c
29Si {1H} NMR spectrum
-4.06
f1 (ppm)


solvent removed under high vacuum, and extracted into c6d6.32.1.2rr
DM3-422 PhCHMeN(SiMe2Ph)Cy in C6D6
PhMe2Si
N
9c
29Si-1H HMBC NMR spectrum
f2 (ppm)
f1 (ppm)

4.2 NMR monitoring and mechanistic interpretation

The hydrosilylation of *N*-aryl ketimine **4a** is characterised by the profile in **Figure S5**: starting material is present throughout the reaction. The hydrosilylation of *N*-alkyl ketimine **4c** is characterised by the profile in **Figure S6**: starting material is consumed rapidly to generate reaction intermediates **5c** and **8c**. The intermediates are then slowly converted to final product **9c**. When the hydrosilylation of substrate **4c** was carried out in 1,2-DFB to 34% conversion the product amine could be isolated with an *e.r.* value of 90.5:9.5. The rate of hydrosilylation depends on the nature of the hydrosilane reducing agent: **Figure S7**. These observations are summarised in **Figure S8**.

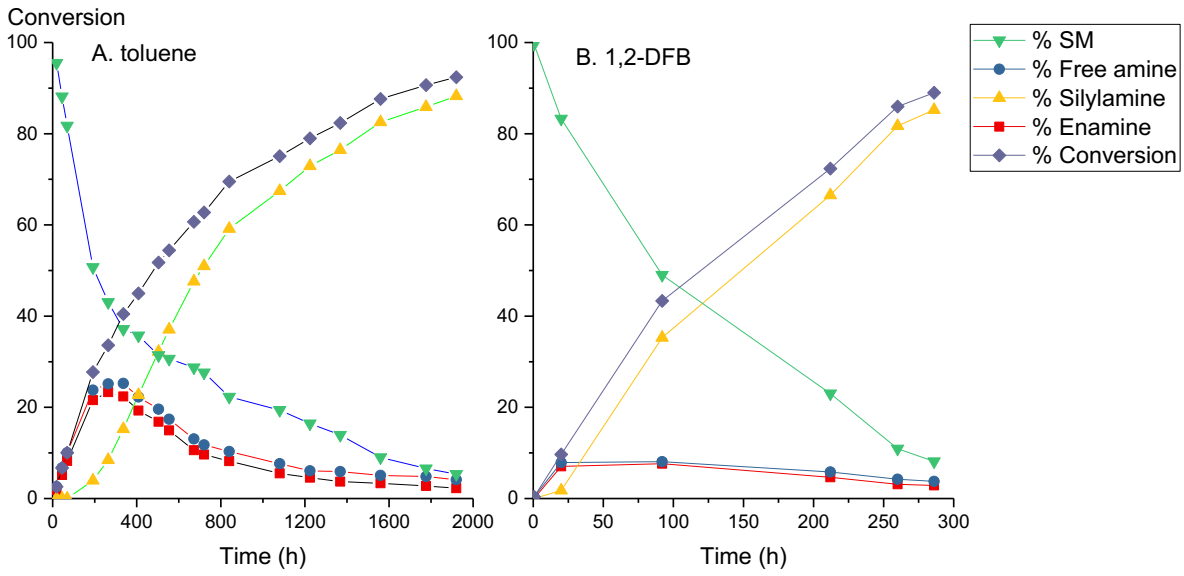


Figure S5. Solvent effect in the hydrosilylation of substrate **4a**, 4 mol% **2a**, 1.1 equiv. Ph_2MeSiH

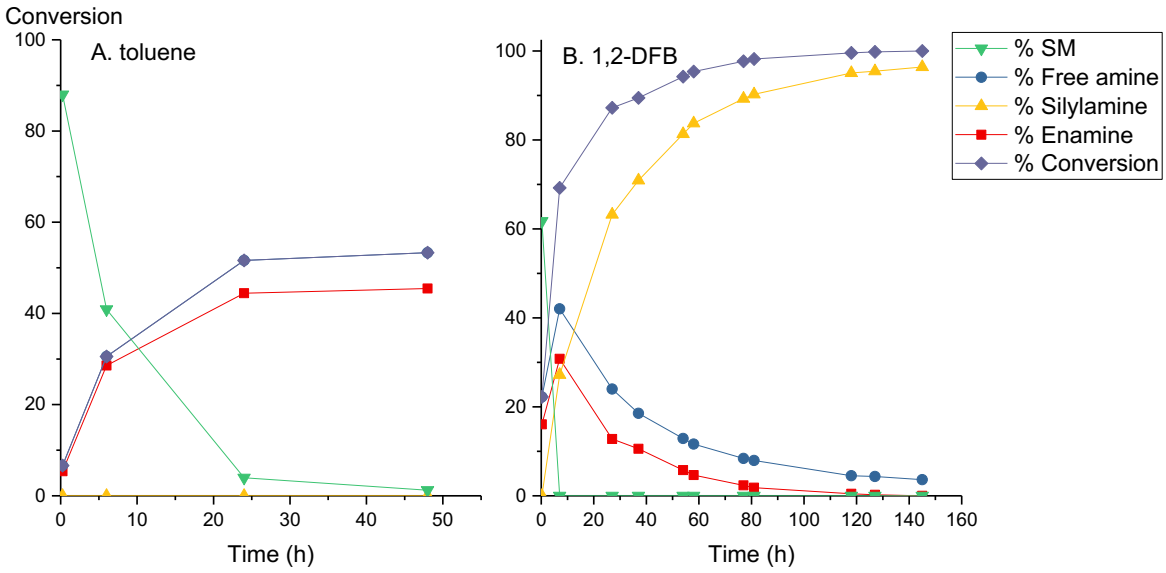


Figure S6. Solvent effect in the hydrosilylation of substrate **4c**, 4 mol% **2a**, 1.1 equiv. $PhMe_2SiH$

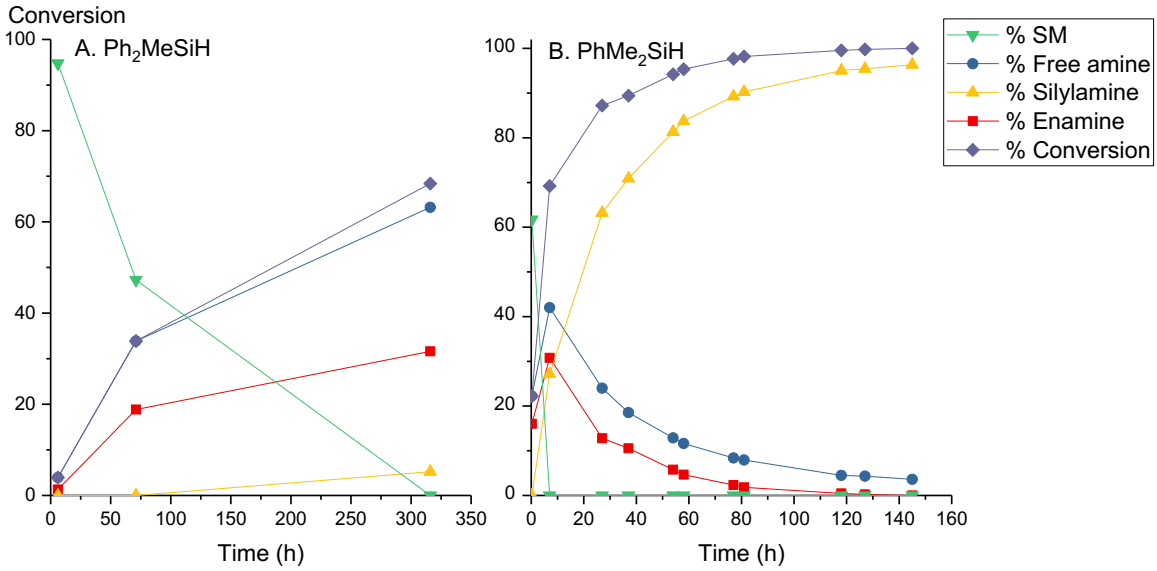


Figure S7. Reagent effect in the hydrosilylation of substrate **4c**, 4 mol% **2a**, 1.2-DFB

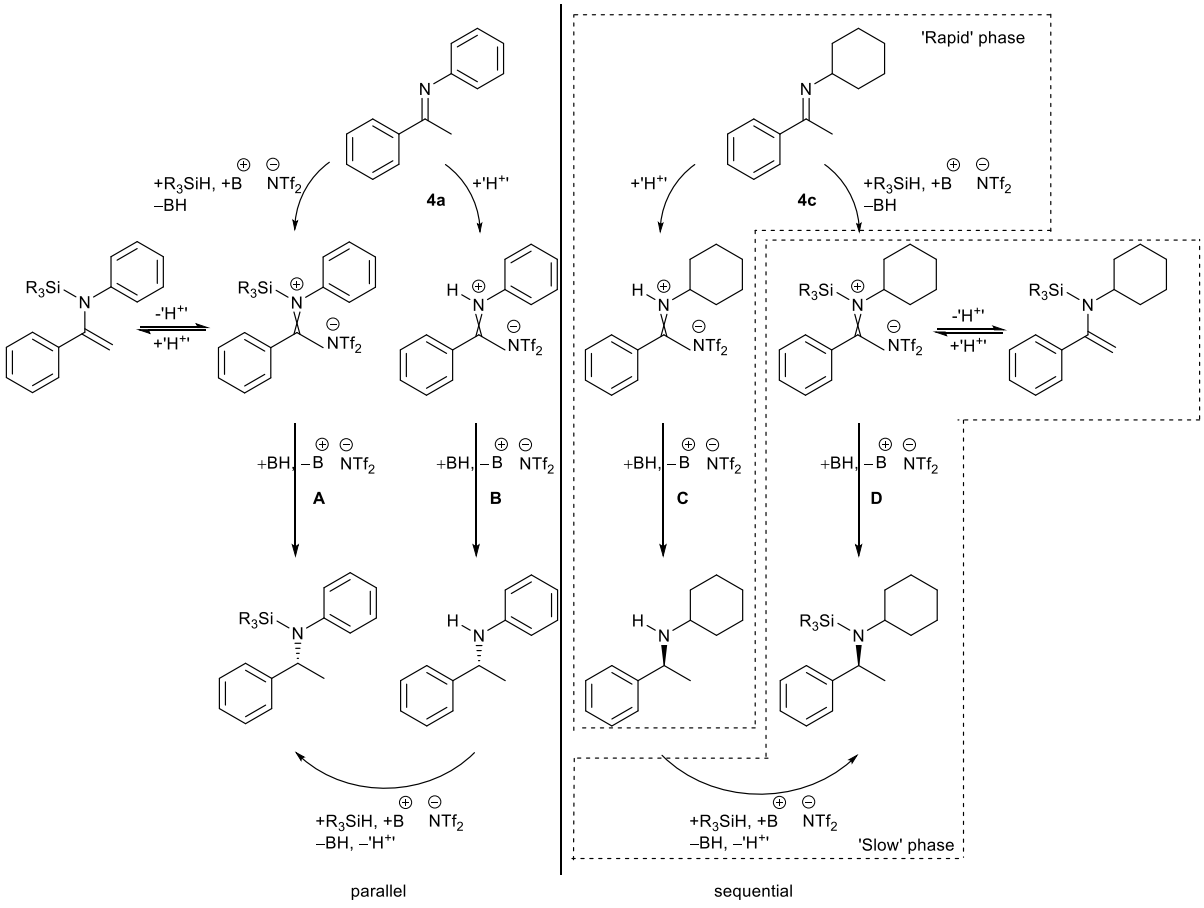


Figure S8. Mechanistic interpretation of reactivity difference between substrates **4a** and **4c**; ±'⁺H' denotes proton exchange with any competent species.

4.3 Copies of reaction NMR spectra for **4a-c**

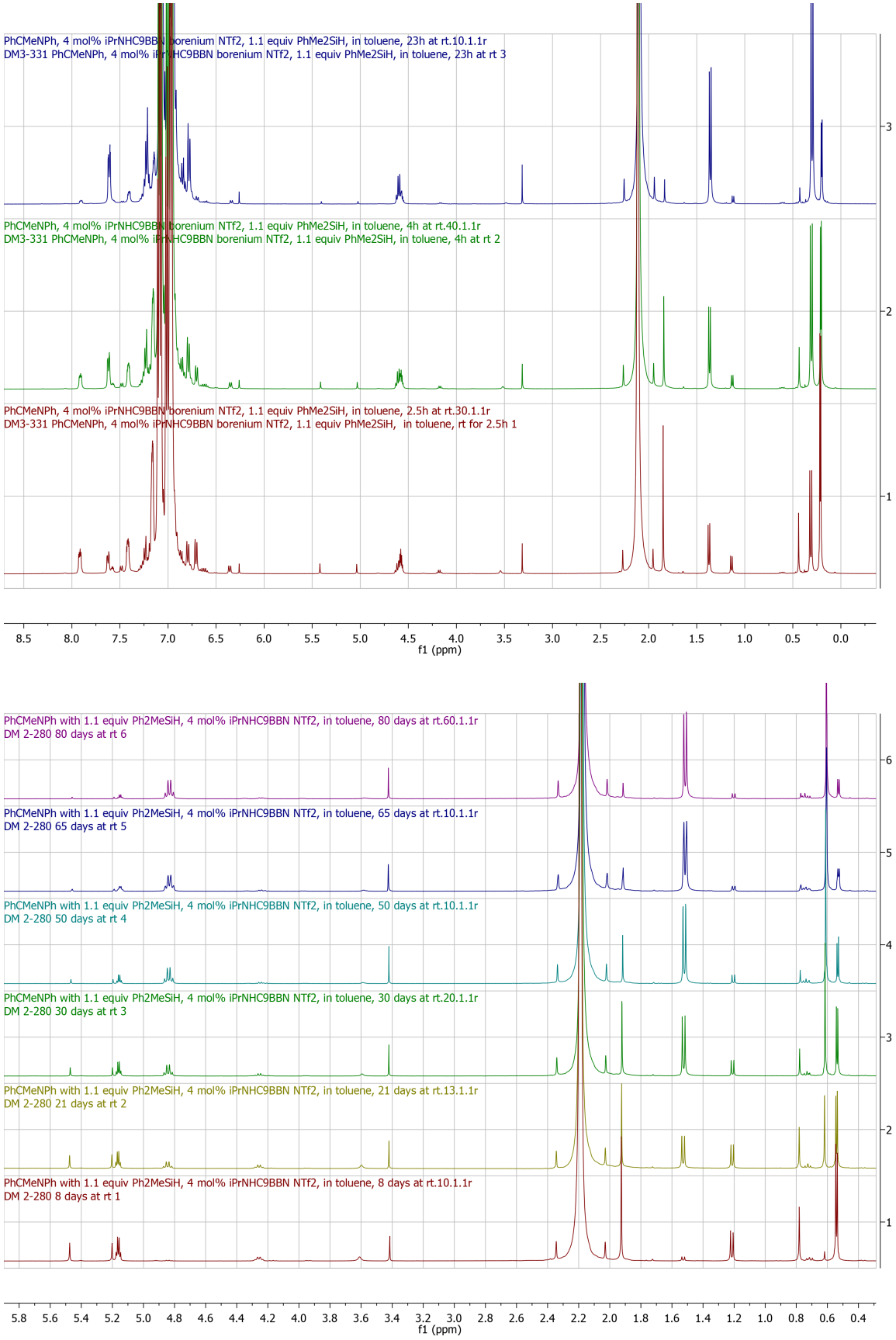


Figure S9. ^{1}H reaction NMR spectra: substrate **4a**, 4 mol% **2a**, 1.1 equiv. $PhMe_2SiH$ or Ph_2MeSiH, toluene

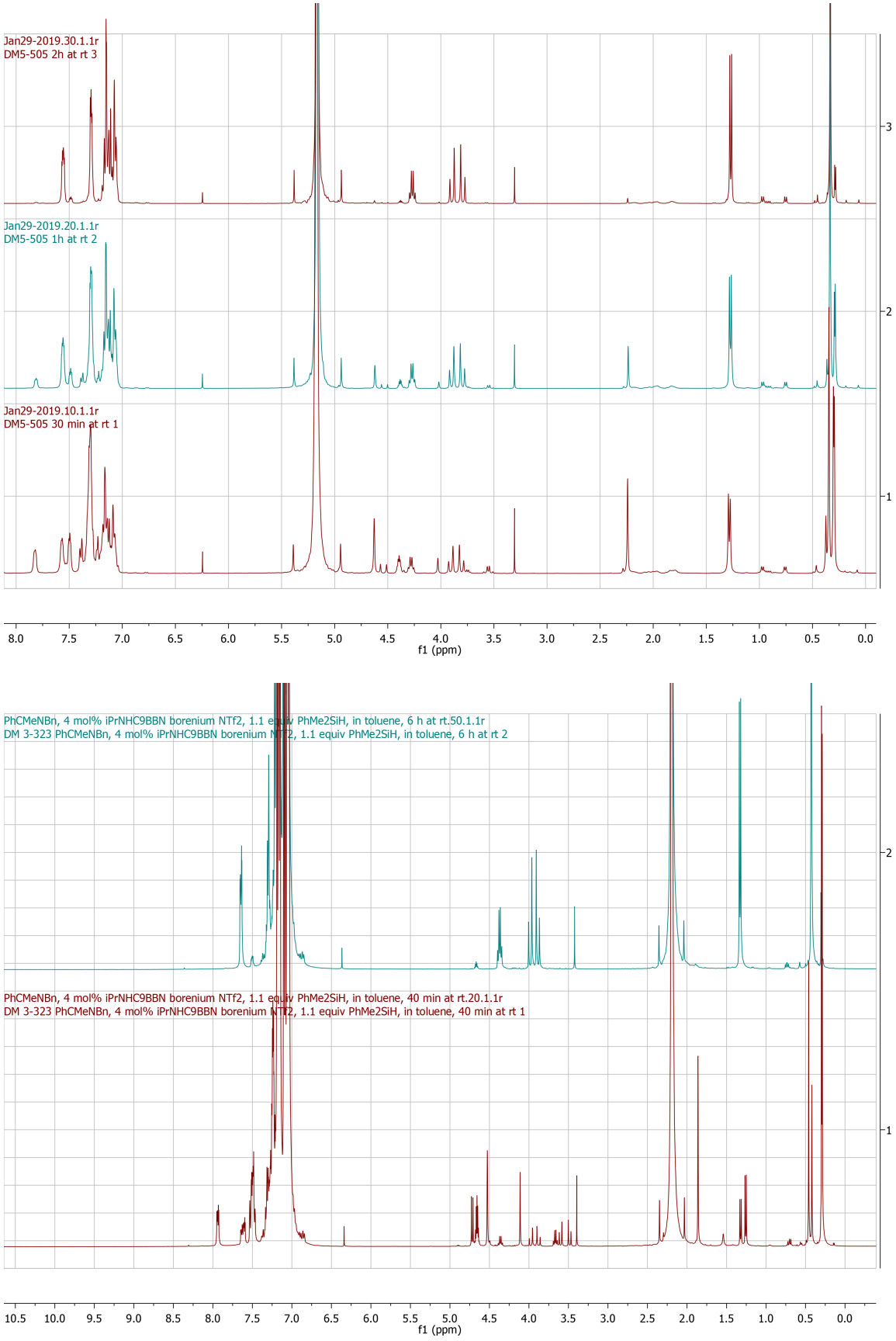


Figure S10. ^{1}H reaction NMR spectra for substrate **4b**, 4 mol% **2a**, 1.1 equiv. $PhMe_2SiH$, in DCM and toluene, respectively

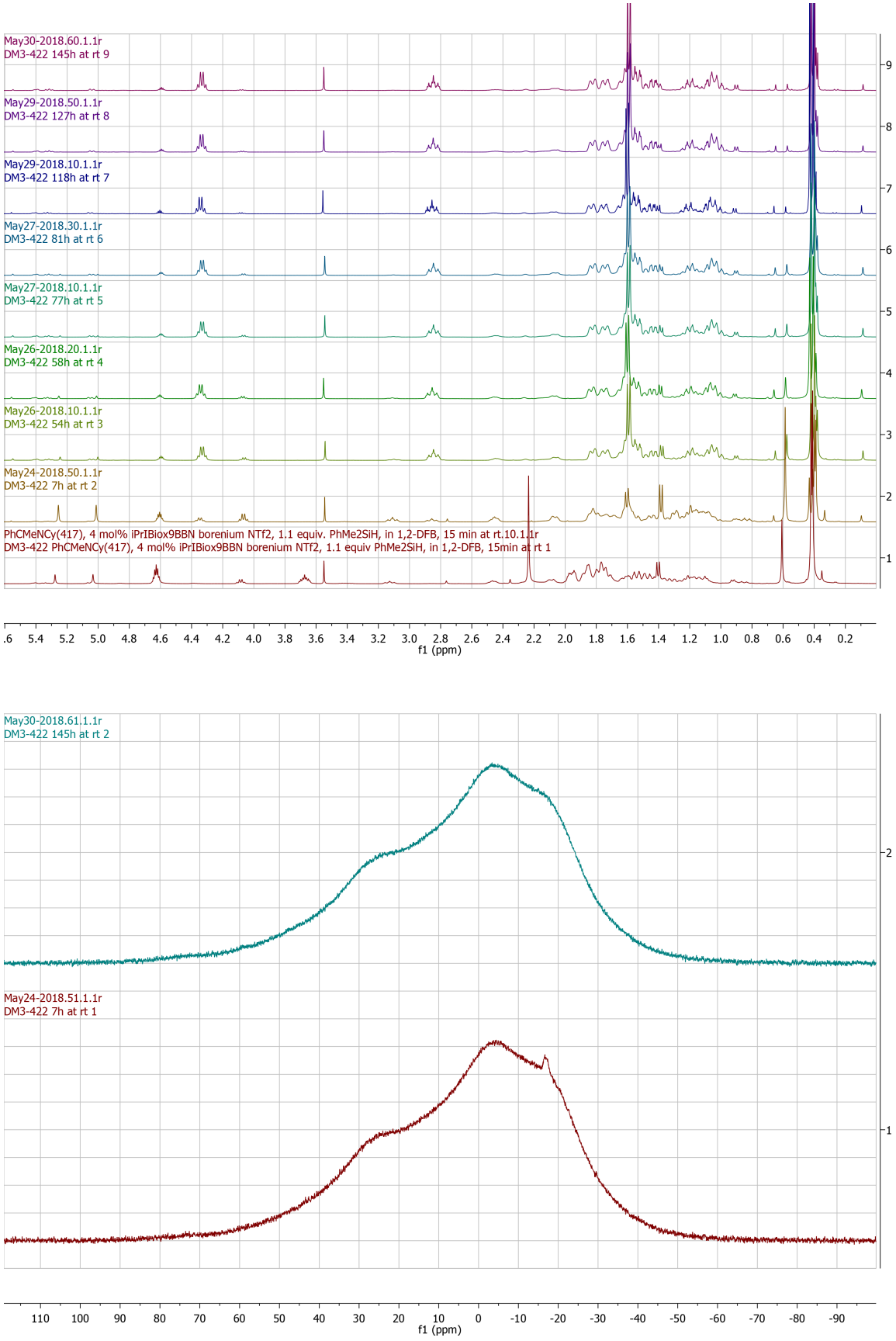
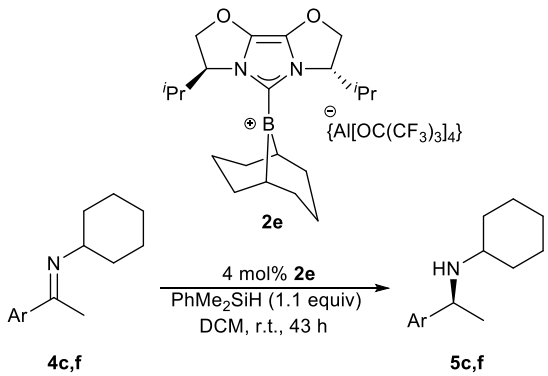


Figure S11. ^{1}H and ^{11}B reaction NMR spectra for substrate **4c**, 4 mol% **2a**, 1. 1 equiv. $PhMe_2SiH$, 1,2-DFB

4.4 Catalyst **2e** assessment



Ar	Conversion	Yield	*e.r* (*S*:*R*)
Ph	70%	60%	95:5
2-Naphthyl	78%	60%	96:4

Table S12. Hydrosilylation in the presence of a very weakly coordinating counterion.

5. Hydrogenation catalysis

Monitoring was performed by carrying out reactions in NMR tubes equipped with Young's valves (4 bar, achieved by admitting hydrogen gas to degassed samples at liquid nitrogen temperature) or in Wilmad high pressure NMR tubes fitted with a PV-ANV PTFE valve (up to 10 bar, room temperature). Reactions were set up in an inert atmosphere glovebox, sealed and then pressurised on a dual manifold system; hydrogen gas (BOC Research Grade) was purified using a Matheson Tri-Gas Weldassure^{TM} column. Temperature was room temperature unless otherwise stated. Purification was carried out through flash column chromatography (column I.D. ~2.5cm, ~10-15g silicagel) or by preparative TLC (20x20cm, 0.2mm thickness).

Screening was performed on a Symyx SPR system using a 48-well plate. Reactions were carried out in HPLC vials and were set up in an inert atmosphere glovebox. Lines were flushed with nitrogen prior to connection then the assembly was flushed with hydrogen gas (4x60 psi). The temperature was adjusted (30 °C) before the assembly was pressurised and sealed. Agitation was carried out with a circular motion (500 rpm) for the duration of the reaction. NMR analysis was carried out in $CDCl_3$.

In both cases NMR conversions were determined by relative integration of relevant species. Where necessary polymerisation/hydrolysis of SM was taken into account.

5.1 Reaction development

Details of preliminary development involving counterion (OTf, OMs, OTs) (**Figure S13**) and substrate/solvent screening are included (**Table S14**).

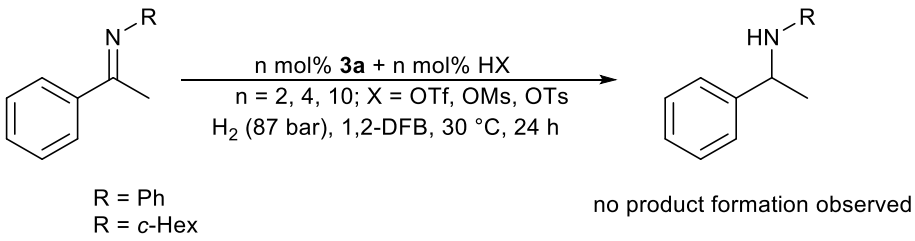
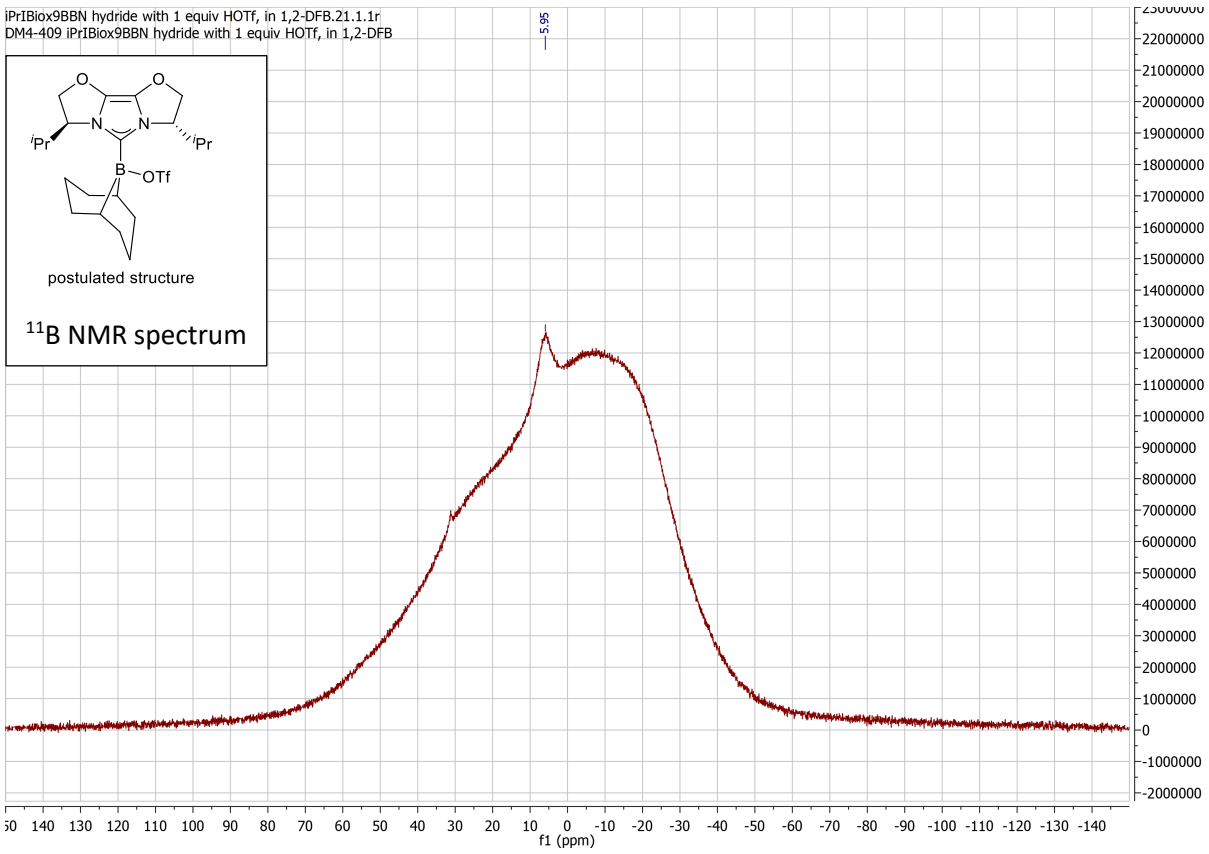
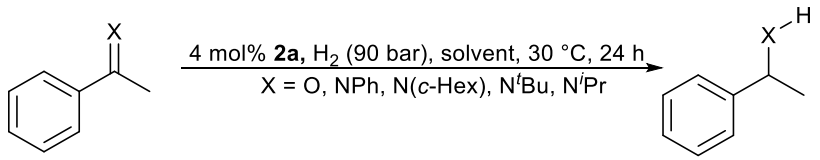


Figure S13. Counterion screening at various catalyst loadings

^{11}B NMR data indicates that counterion coordination to the boron atom limits reactivity. Treatment of borohydride **3a** with HOTf generated a species (characterised *in situ*) displaying a chemical shift of 6.0 ppm (1,2-DFB), which is indicative of four-coordinate boron, through coordination of the smaller and more basic OTf counterion.





for X = NPh see table **S14**
for all other substrates no product formation was observed

solvent = toluene, o-xylene, diethyl ether, THF, 1,4-dioxane, TBME, sulfolane, 1,2-DFB, acetonitrile

Solvent (ε_r)	Conversion	*e.r.* (R:S)
Acetonitrile (37.5)	0%	-
Tetrahydrofuran (7.6)	3%	55.5:44.5
o-xylene (2.57)	8%	64:36
Toluene (2.38)	10%	64:36
Methyl tert-butyl ether (4.5)	29%	54:46
Diethyl ether (4.3)	37%	53:47
1,4-Dioxane (2.21)	42%	58:42
Sulfolane (44)/toluene 1:1	53%	58:42
1,2-DFB (13.8)	100%	59:41

Table S14. Substrate/solvent screen at 4 mol% catalyst loading

6. General procedure for the synthesis of racemic amines and acetamides

Ketimine **4** (100 mg, x mmol) and sodium borohydride (y mg, 2x mmol) were weighed and to the resulting mixture MeOH (generally 1 mL) was added (hydrogen evolution). The solution was stirred at room temperature for the specified amount of time. The MeOH was removed and the resulting residue extracted with DCM (or pentane/heptane) with filtration. The resulting crude product was purified by flash column chromatography (10-15g silica).

Product	Reaction time	Purification	Yield	Appearance
(±)-5a	5 h	100:1 P: EA	83%	Yellow oil
(±)-5b	19 h	10:1 P: EA, 1% Et_3N	71%	Yellow oil
(±)-5c	18 h	3:1 P: EA, 1% Et_3N	71%	Colourless oil
(±)-5d	24 h	4:1 P: EA, 1% Et_3N	71%	Yellow oil
(±)-5e	19 h	4:1 P: EA, 1% Et_3N	76%	Colourless oil
(±)-5f	21 h	4:1 P: EA, 1% Et_3N	82%	Pale yellow oil
(±)-5g	20 h	4:1 P: EA, 1% Et_3N	65%	Colourless oil
(±)-5i	22 h	10:1 P: EA, 1% Et_3N	40%	Colourless oil

Table S15. Racemic amine preparation

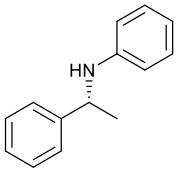
To a solution of amine **(±)-5** (<30 mg) in DCM (0.5 or 1 mL DCM) was added triethylamine (2 equiv, approx. volume) and then acetic anhydride (4 equiv, approx. volume). The resulting solution was allowed to react at room temperature with or without stirring for the indicated period of time. Sometimes an extra batch of reagents was added. The volatiles were removed and the resulting residue purified by flash column chromatography (~1-2g silica).

Product	Reaction time	Purification	Yield	Appearance
(±)-10c	27 h	4:1 P: EA	79%	Colourless oil
(±)-10d	4 h	4:1 P: EA	28%	Colourless oil
(±)-10e	16 h	4:1 P: EA	84%	White solid
(±)-10f	21 h	4:1 P: EA	75%	White solid
(±)-10g	15 h	1:1 P: EA	92%	Pale yellow oil
(±)-10i	24 h	4:1 P: EA	81%	White solid

Table S16. Racemic acetamide preparation

7. Characterisation data

7.1 Characterisation data for chiral enantioenriched amines **5** and copies of NMR spectra

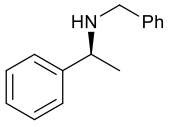


5a

$[\alpha]_D^{26}$ = −4.6 ° (c 7.47, MeOH, 65:35 *e.r.*); literature value: $[\alpha]_{578}^{25}$ = −19.5 ° (MeOH, R enantiomer)[10]

98% purity, 97% yield (elution performed with 0.5% EtOAc, 0.5 % Et_3N in pentane)

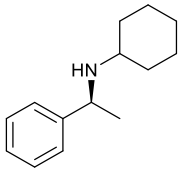
^{1}H NMR (400 MHz, $CDCl_3$) 7.38 (m, 4H), 7.27 (m, 2H), 7.13 (m, 2H), 6.68 (m, 1H), 6.55 (m, 2H), 4.53 (q, *J* = 6.8 Hz, 1H), 4.06 (br.s, 1H), 1.56 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 147.3, 145.3, 129.2, 128.8, 127, 126, 117.5, 113.5, 53.7, 25.1. IR (neat, cm^{-1}) 3051, 3407, 3020, 2964, 2922, 2865, 1597, 1500, 1447, 1314, 1255, 746, 690; HRMS (ES+) calculated for $C_{14}H_{16}N$ ([M+H]$^+$) 198.1283, found 198.1290.



5b

$[\alpha]_D^{26}$= − 30.2° (c 7.03, cyclopentane, 82:18 *e.r.*); Literature value: $[\alpha]_D^{20}$ − 49.2° (cyclopentane, S enantiomer)[11]

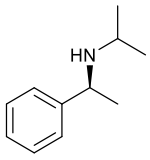
^{1}H NMR (400 MHz, $CDCl_3$) 7.32 (m, 10H), 3.83 (q, *J* = 6.8 Hz, 1H), 3.64 (m, 2H), 1.65 (br. s, 1H), 1.38 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.6, 140.7, 128.5, 128.4, 128.2, 127, 126.9, 126.7, 57.5, 51.7, 24.5; HRMS (ES+) calculated for $C_{15}H_{18}N$ ([M+H]$^+$) 212.1439, found 212.1446; IR (neat, cm^{-1}) 3024, 2960, 2922, 2834, 1491, 1450, 1117, 1027, 759, 732, 695.



5c

$[\alpha]_D^{25}$= − 49.8° (c 2.77, $CHCl_3$, 89:11 *e.r.*); Literature value: $[\alpha]_D^{25}$ + 67.7° ($CHCl_3$, R enantiomer)[12]

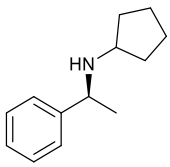
^{1}H NMR (400 MHz, $CDCl_3$) 7.35-7.2 (m, 5H); 3.95 (q, *J* = 6.5 Hz, 1H), 2.27 (m, 1H), 1.98 (m, 1H), 1.73-1.45 (m, 5H), 1.32 (d, *J* = 6.5 Hz, 3H), 1.24-0.95 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.5, 128.5, 126.8, 126.6, 54.5, 53.7, 34.7, 33.3, 26.3, 25.4, 25.2, 25.1. HRMS (ES+) calculated for $C_{14}H_{22}N$ ($[M+H]^+$) 204.1752, found 204.1760; IR (neat, cm^{-1}) 2921, 2850, 1491, 1448, 1366, 1127, 760, 699.



5d

$[\alpha]_D^{22}$ = −43.2 ° (c 0.97, CH_2Cl_2, 90:10 *e.r.*), literature value $[\alpha]_D^{25}$ = −29.2 ° (neat, S enantiomer)[13]

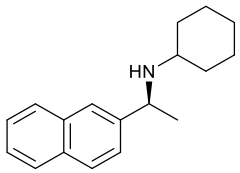
^{1}H NMR (400 MHz, $CDCl_3$) 7.31 (m, 5H), 3.92 (q, *J* = 6.6 Hz, 1H), 2.65 (septet, *J* = 6.3 Hz), 1.49 (br. s, 1H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.04 (dd, *J* = 6.1, 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.3, 128.5, 126.9, 126.6, 55.2, 45.6, 25, 24, 22.3; HRMS (ES+) calculated for $C_{11}H_{18}N$ ($[M+H]^+$) 164.1439, found 164.1450; IR (neat, cm^{-1}) 2959, 2924, 2864, 1472, 1465, 1450, 1378, 1366, 1169, 1126, 1102, 1021, 759, 698, 585, 554, 517.



5e

$[\alpha]_D^{25}$ = −52 ° (c 3.38, CH_2Cl_2, 90:10 *e.r.*); literature value: $[\alpha]_D^{20}$ +63.8 ° ($CHCl_3$, R enantiomer)[14]

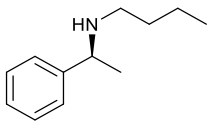
^{1}H NMR (400 MHz, $CDCl_3$) 7.32 (m, 4H), 7.24 (m, 1H), 3.83 (q, *J* = 6.5 Hz, 1H), 2.89 (p, *J* = 7 Hz, 1H), 1.88-1.57 (m, 5H), 1.45 (m, 2H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.37-1.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.1, 128.5, 127, 126.8, 57.3, 56.8, 33.9, 33, 24.7, 24.1, 24; HRMS ES+ calculated for $C_{13}H_{20}N$ ($[M+H]^+$) 190.1596, found 190.1601; IR (neat, cm^{-1}) 2952, 2864, 1491, 1464, 1449, 1130, 760, 699.



5f

$[\alpha]_D^{25}$ = −52.4 ° (c 5.15, $CHCl_3$, 96:4 *e.r.*), literature value: $[\alpha]_D^{23}$ = −56.5 ° ($CHCl_3$, S enantiomer)[15]

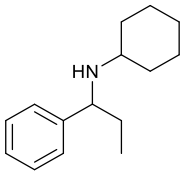
^{1}H NMR (400 MHz, $CDCl_3$) 7.82 (m, 3H), 7.72 (m, 1H), 7.46 (m, 3H), 4.14 (q, *J* = 6.8 Hz, 1H), 2.29 (m, 1H), 2.03 (m, 1H), 1.67 (m, 3H), 1.54 (m, 1H), 1.4 (d, *J* = 6.6 Hz, 3H), 1.36-1.22 (m, 1H), 1.18-0.97 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) 144, 133.6, 132.9, 128.3, 127.9, 127.8, 126, 125.5, 125.2, 125, 54.8, 53.9, 34.8, 26.3, 25.4, 25.2, 25.1. HRMS (ES+) calculated for $C_{18}H_{24}N$ ($[M+H]^+$) 254.1909, found 254.1910; IR (neat, cm^{-1}) 3051, 2920, 2849, 1506, 1457, 1446, 1365, 1314, 1268, 1128, 887, 854, 816, 744.



5g

$[\alpha]_D^{25}$= −28.8 ° (c 3.4, CH_2Cl_2, 79:21 *e.r.*); Literature value: $[\alpha]_D^{25}$ −84 ° (neat, S enantiomer)[13]

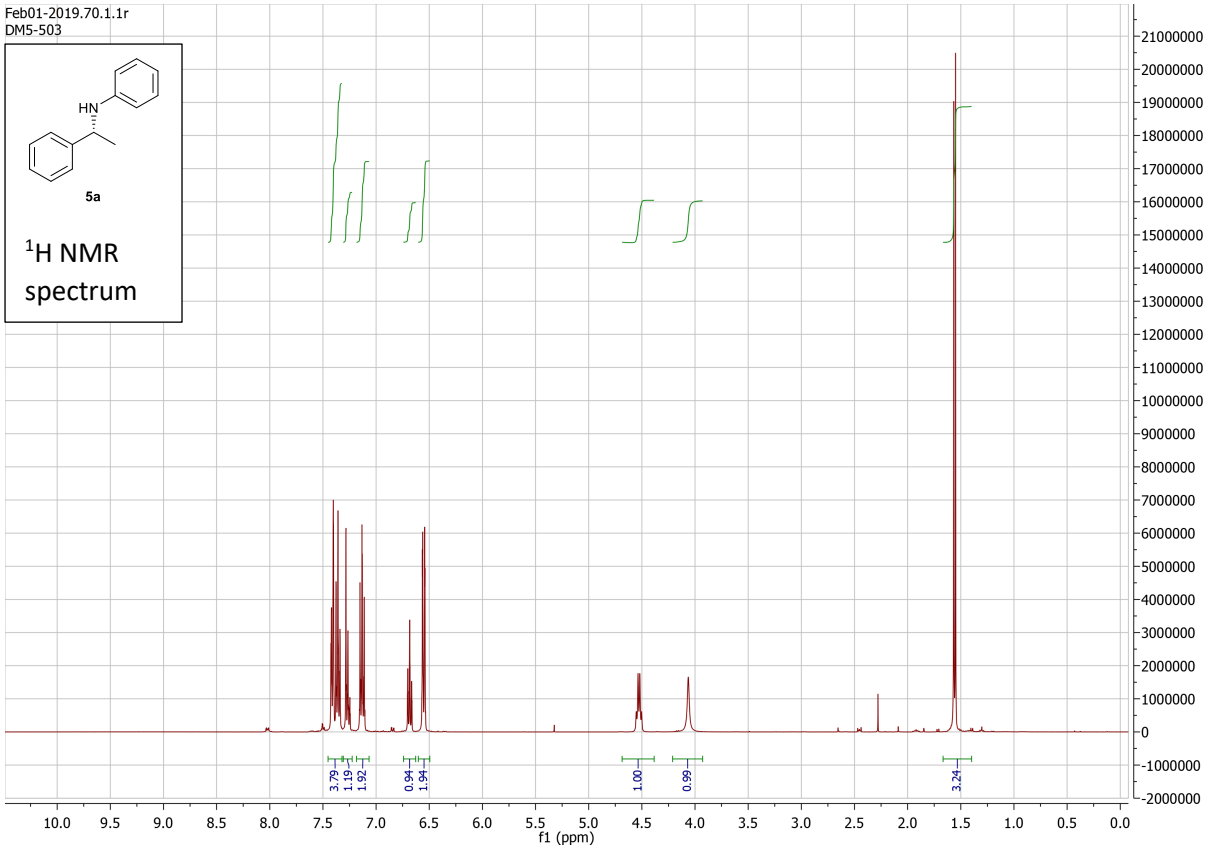
^{1}H NMR (400 MHz, $CDCl_3$) 7.32 (m, 4H), 7.24 (m, 1H), 3.75 (q, *J* = 6.7 Hz, 1H), 2.46 (m , 2H), 1.44 (m, 2H), 1.35 (d, *J* = 6.7 Hz, 3H), 1.29 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.2, 128.5, 126.9, 126.7, 58.6, 47.7, 32.6, 24.5, 20.6, 14.1; IR (neat, cm^{-1}) 2956, 2924, 2870, 1491, 1464, 1450, 1367, 1129, 759, 698; HRMS ES+ calculated for $C_{12}H_{20}N$ ($[M+H]^+$) 178.1596, found 178.1595.

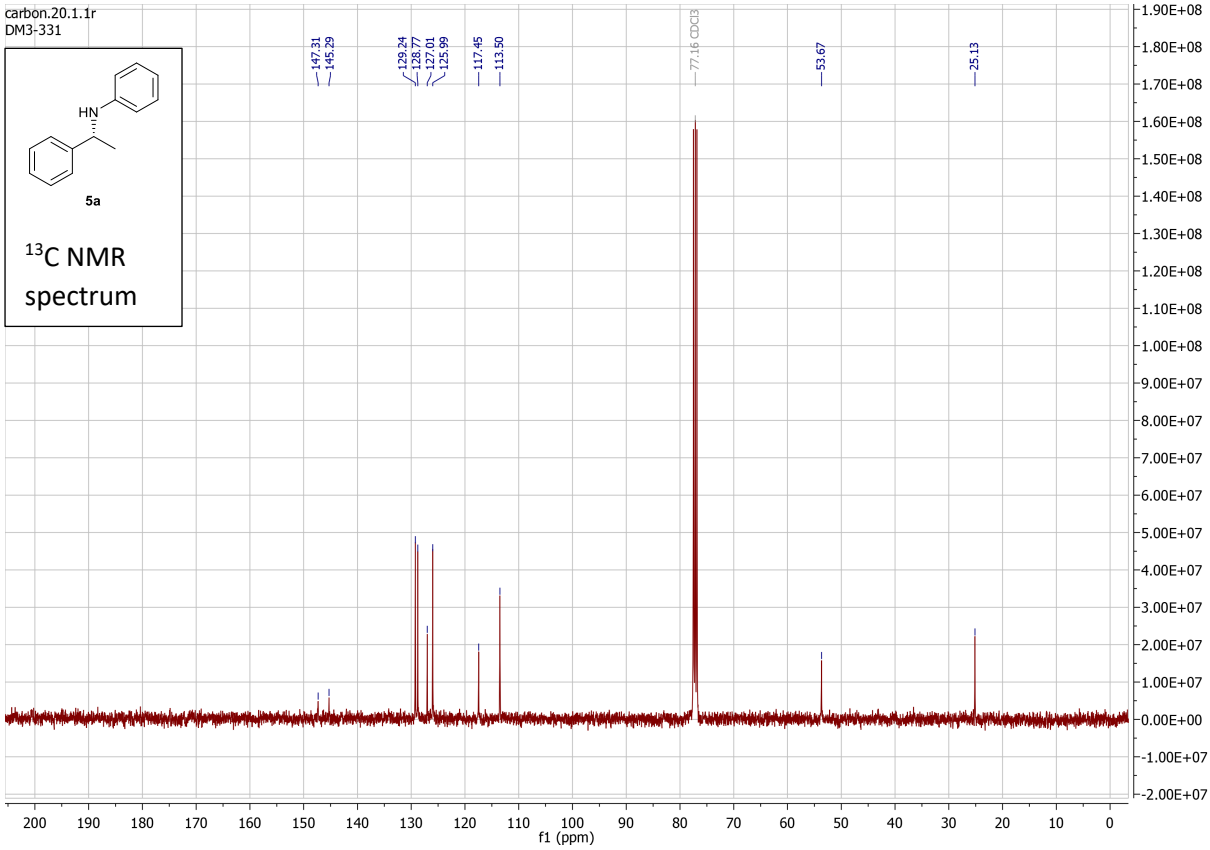


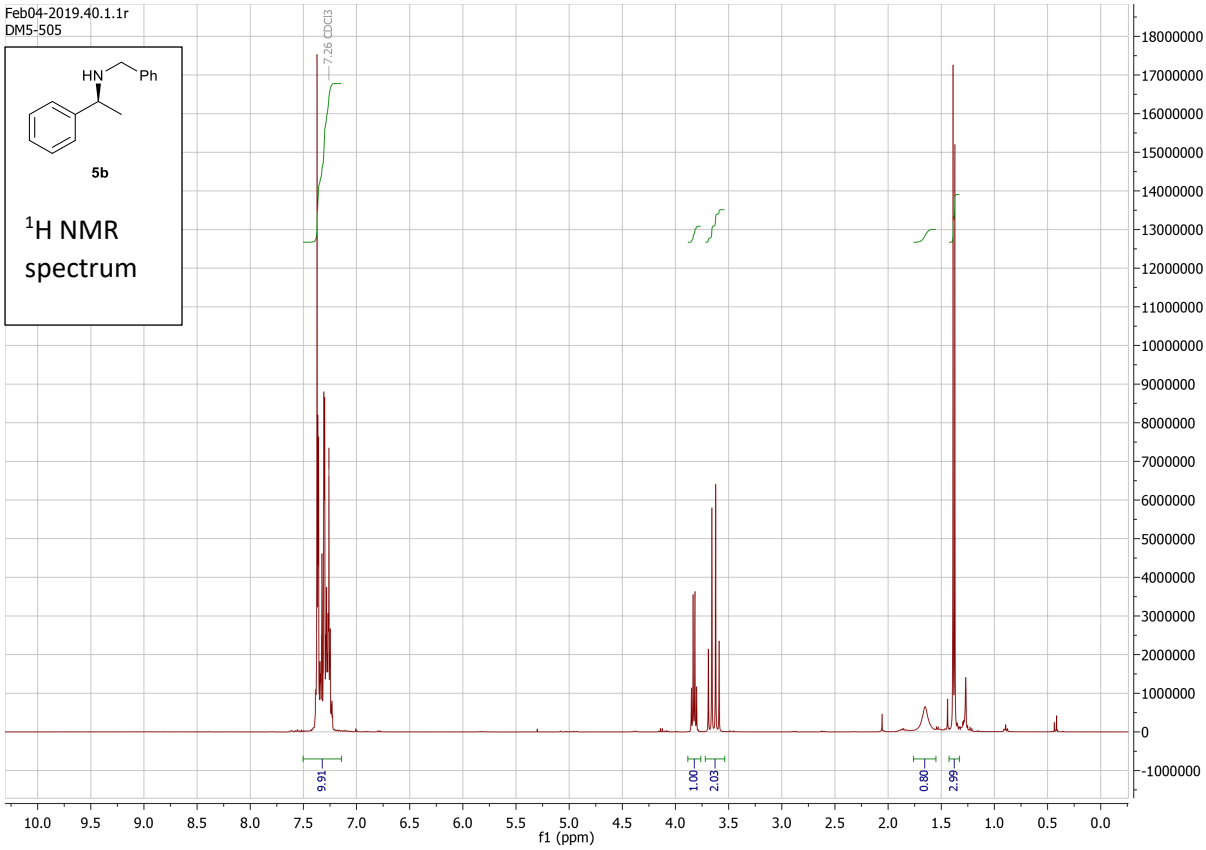
5i

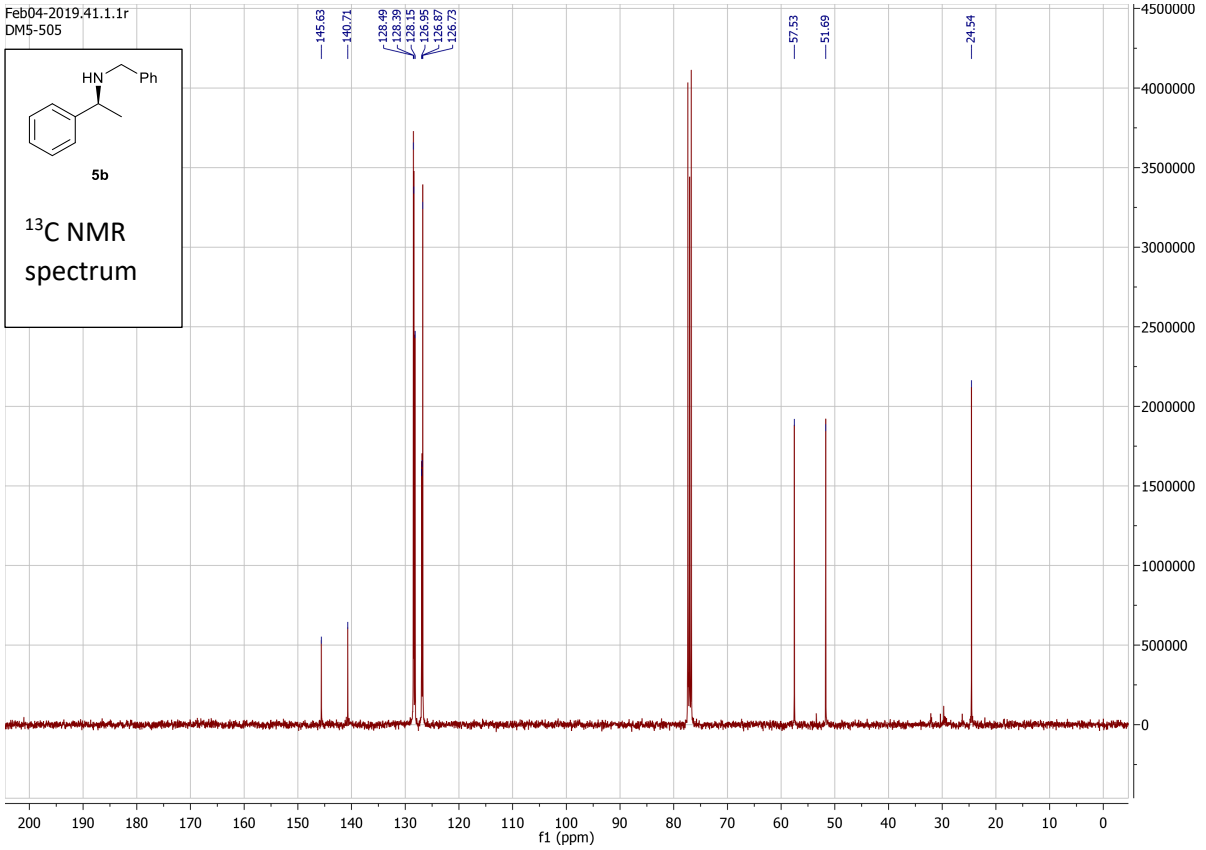
$[\alpha]_D^{25}$ = −17.4° (c 3.23, CH_2Cl_2, 64:36 *e.r.*)

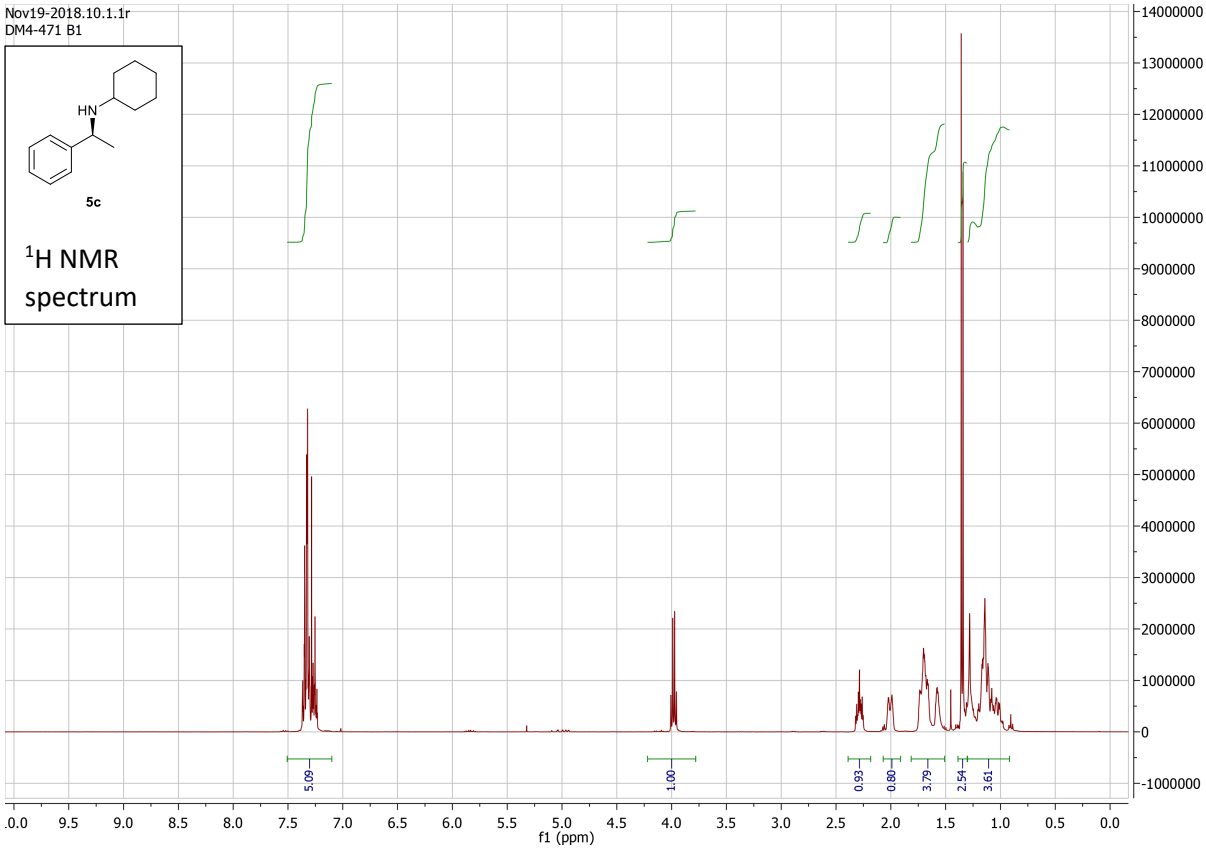
^{1}H NMR (400 MHz, $CDCl_3$) 7.28 (m, 5H), 3.64 (dd, *J* = 5.9 Hz, 7.8 Hz, 1H), 2.23 (m, 1H), 1.97 (m, 1H, NH), 1.62 (m, 6H), 1.06 (m, 6H), 0.78 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.2, 128.3, 127.4, 126.8, 61.5, 53.7, 34.9, 33.3, 31.7, 26.4, 25.4, 25, 11.1; HRMS (ES+) calculated for $C_{15}H_{24}N$ ($[M+H]^+$) 218.1909, found 218.1909. IR (neat, cm^{-1}) 2921, 2850, 1448, 1125, 752, 699.

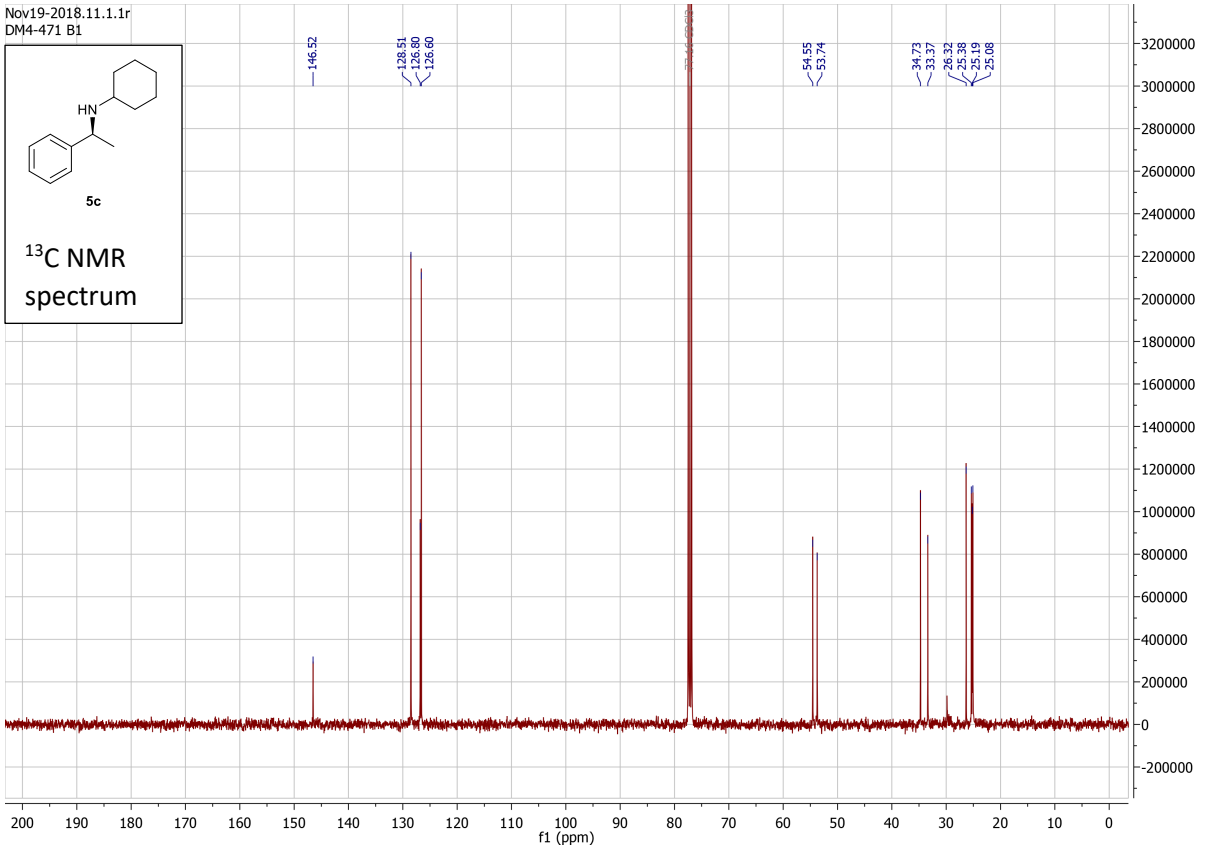

Feb01-2019.70.1.1r
DM5-503
HN
5a
^{1}H NMR spectrum
3.79
1.19
1.92
0.94
1.94
1.00
0.99
3.24
f1 (ppm)

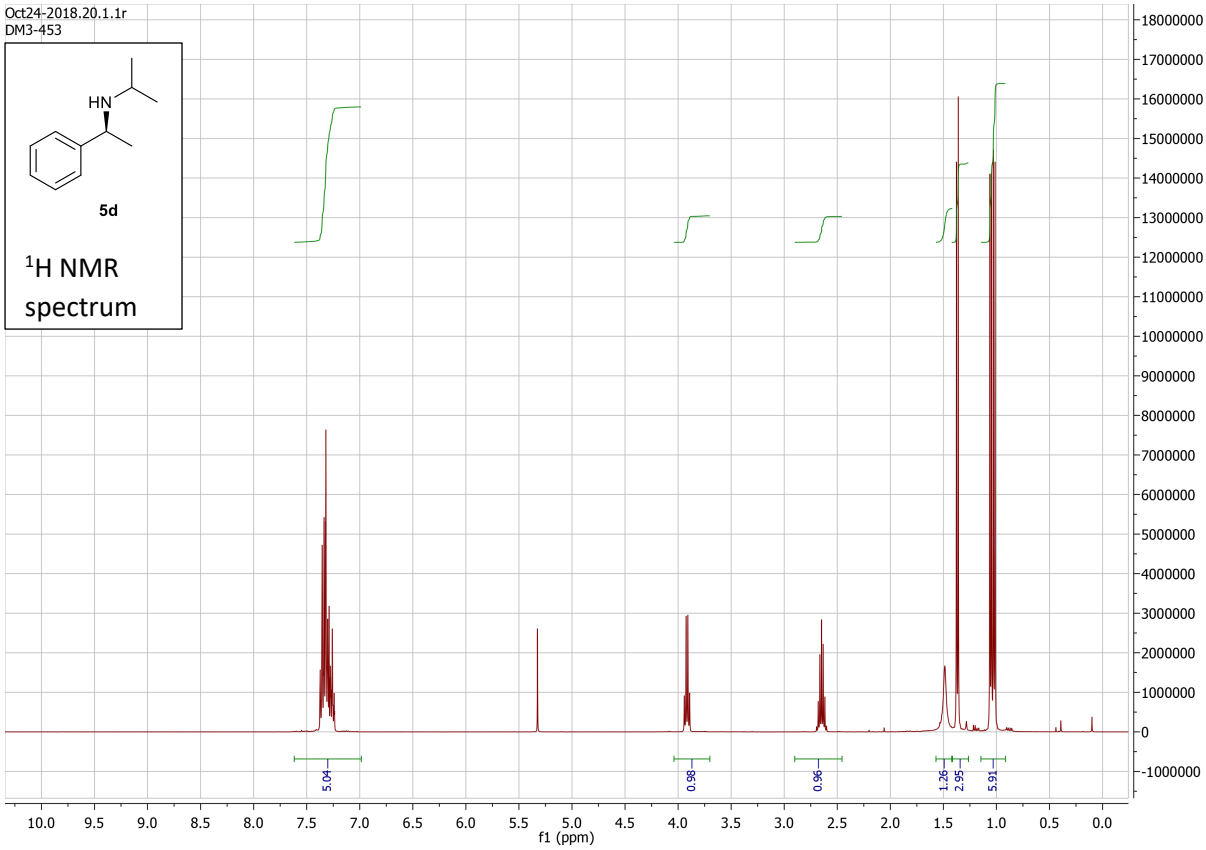

carbon.20.1.1r
DM3-331
HN
5a
^{13}C NMR spectrum
147.31
145.29
129.24
128.77
127.01
125.99
117.45
113.50
77.16 CDCl3
53.67
25.13
f1 (ppm)

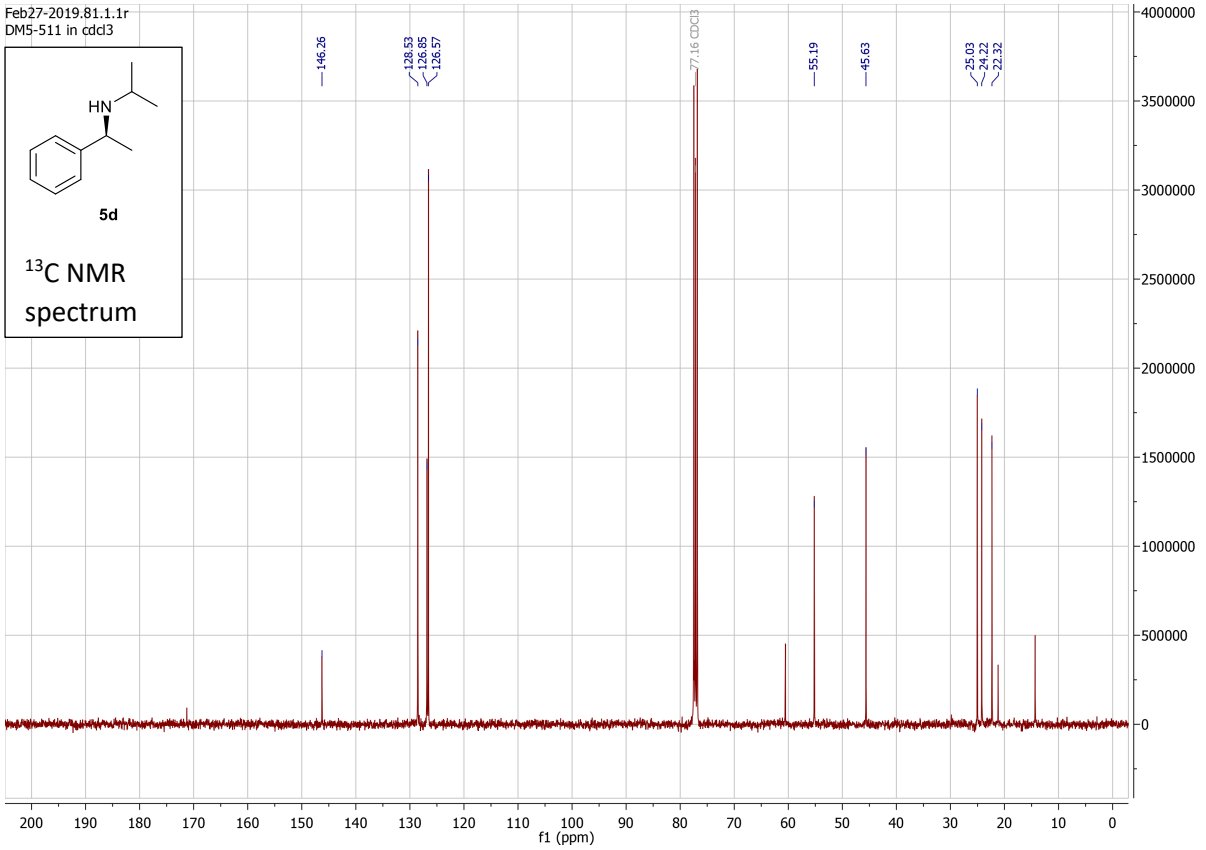

Feb04-2019.40.1.1r
DM5-505
HN
Ph
5b
1H NMR
spectrum
7.26 CDCl3
9.91
1.00
2.03
0.80
2.99
f1 (ppm)

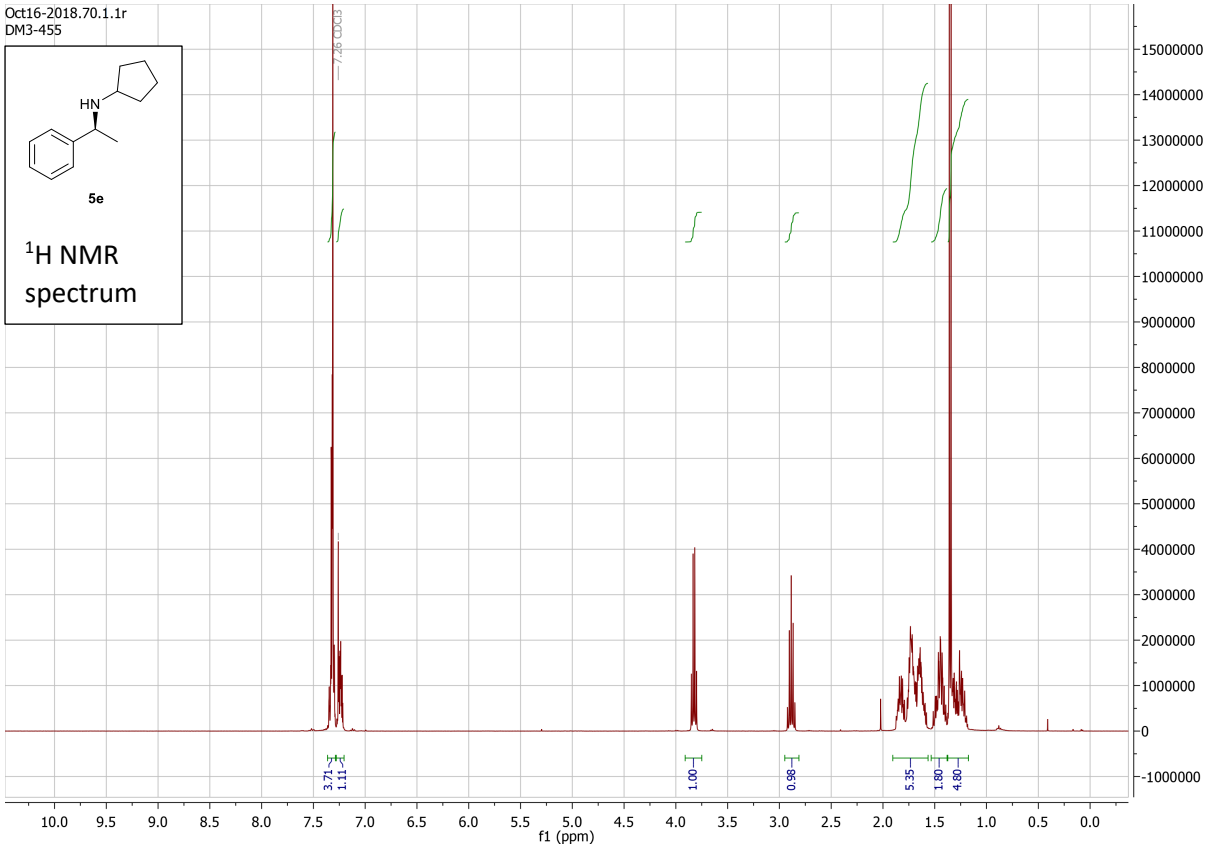

Feb04-2019.41.1.1r
DM5-505
HN
Ph
5b
13C NMR
spectrum
145.63
140.71
128.49
128.39
128.15
126.95
126.87
126.73
57.53
51.69
24.54
f1 (ppm)

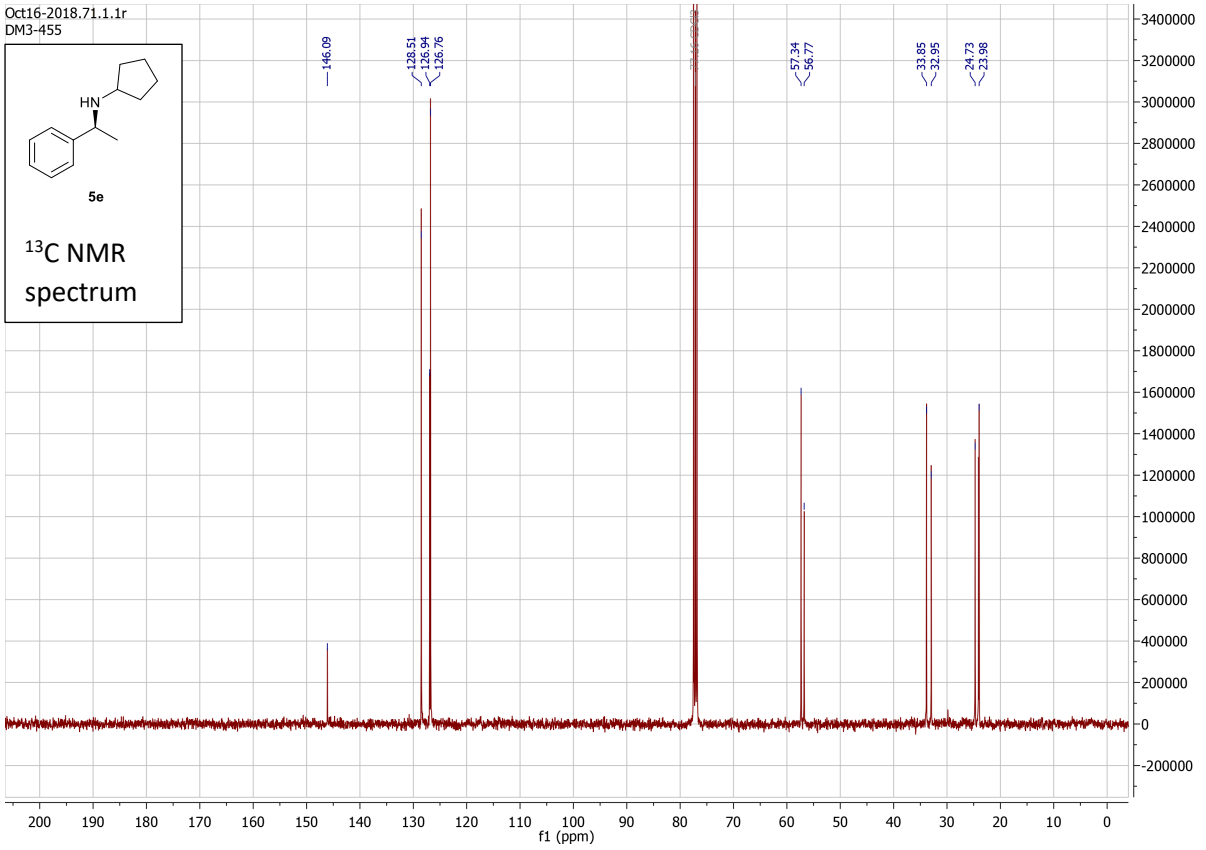

Nov19-2018.10.1.1r
DM4-471 B1
HN
5c
1H NMR
spectrum
5.09
1.00
0.93
0.80
3.79
2.54
3.61
f1 (ppm)

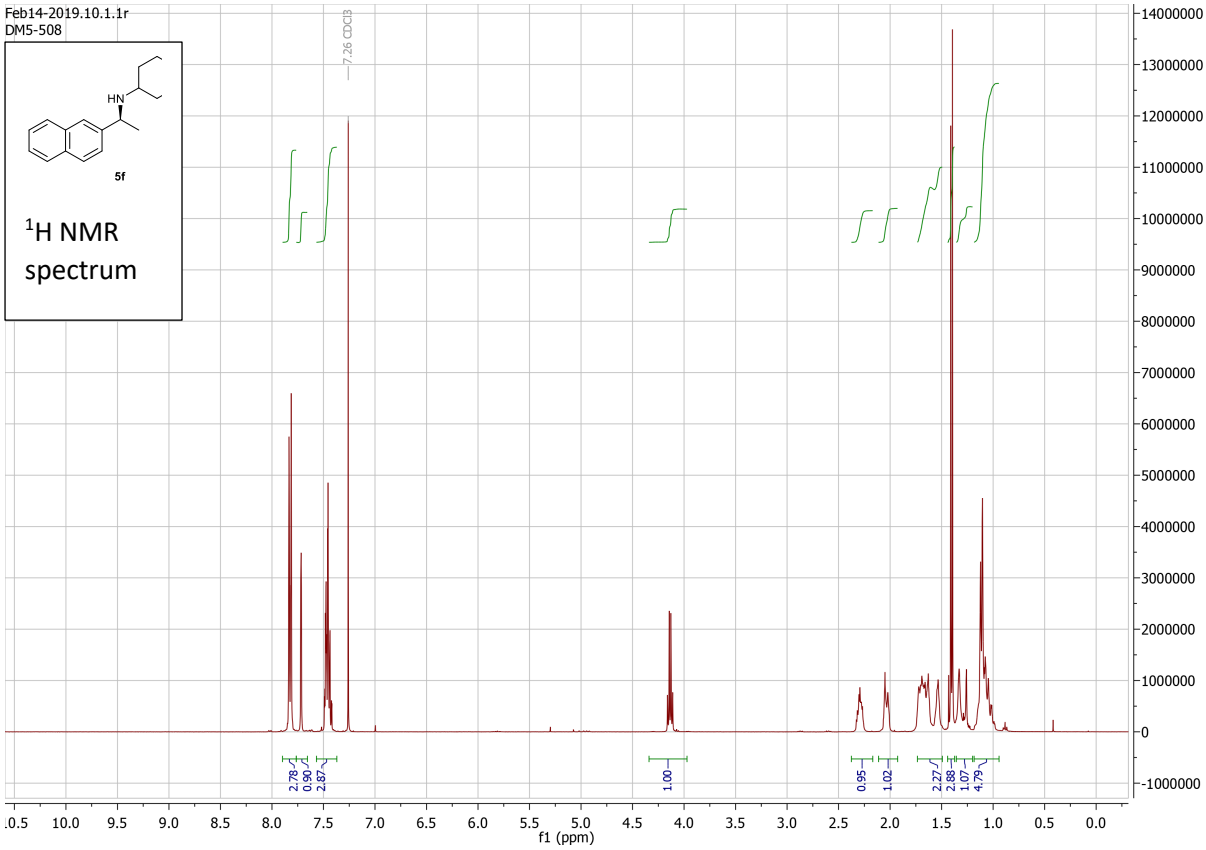

Nov19-2018.11.1.1r
DM4-471 B1
HN
5c
13C NMR
spectrum
146.52
128.51
126.80
126.60
77.16
54.55
53.74
34.73
33.37
26.32
25.38
25.19
25.08
f1 (ppm)

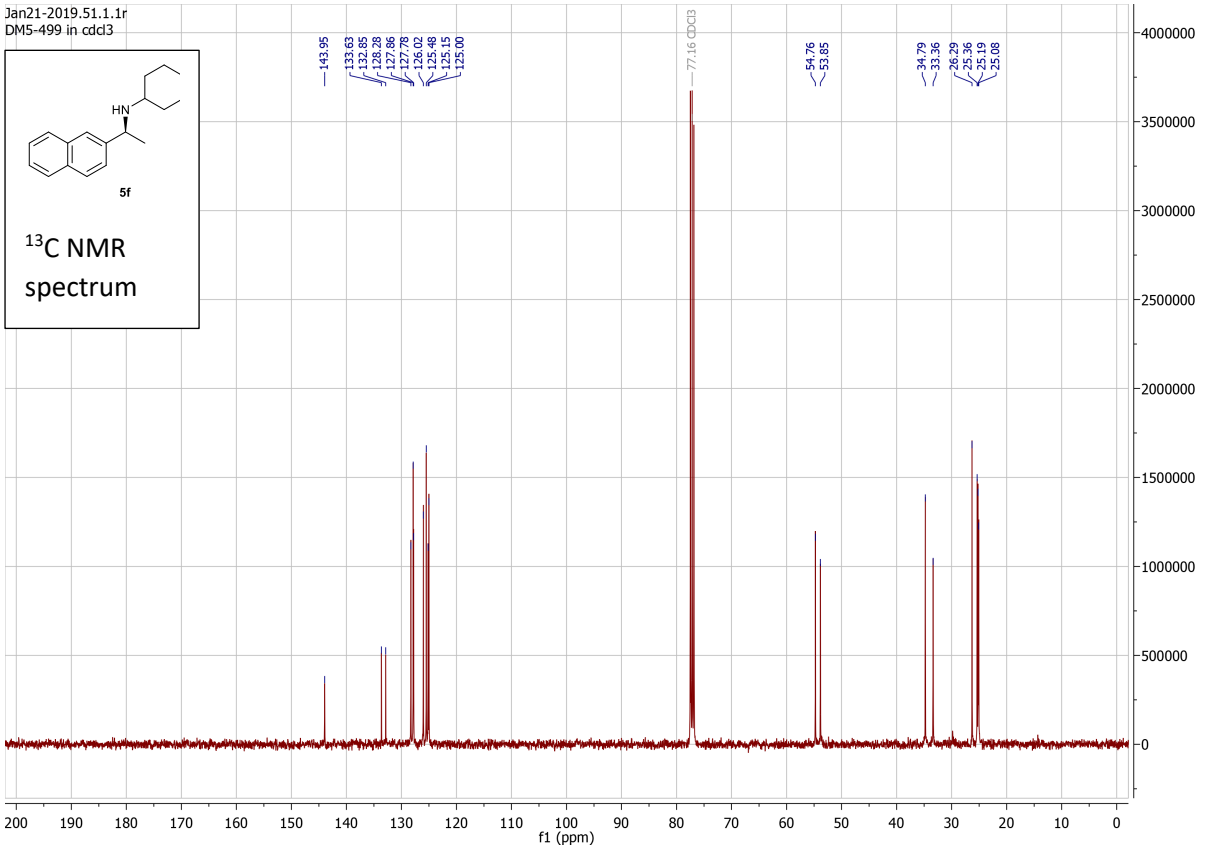

Oct24-2018.20.1.1r
DM3-453
HN
5d
1H NMR
spectrum
5.04
0.98
0.96
1.26
2.95
5.91
f1 (ppm)

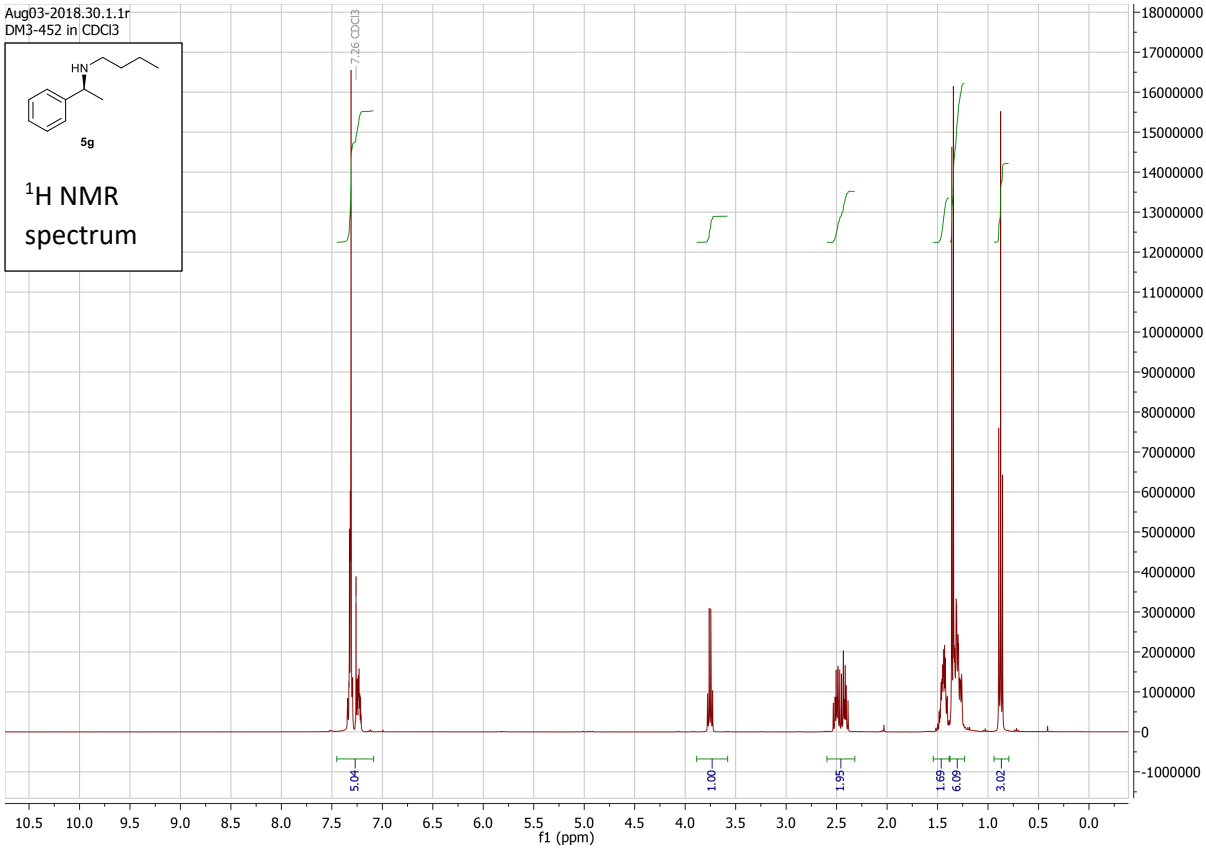

Feb27-2019.81.1.1r
DM5-511 in cdcl3
HN
5d
13C NMR
spectrum
146.26
128.53
126.85
126.57
77.16 CDCl3
55.19
45.63
25.03
24.22
22.32
f1 (ppm)

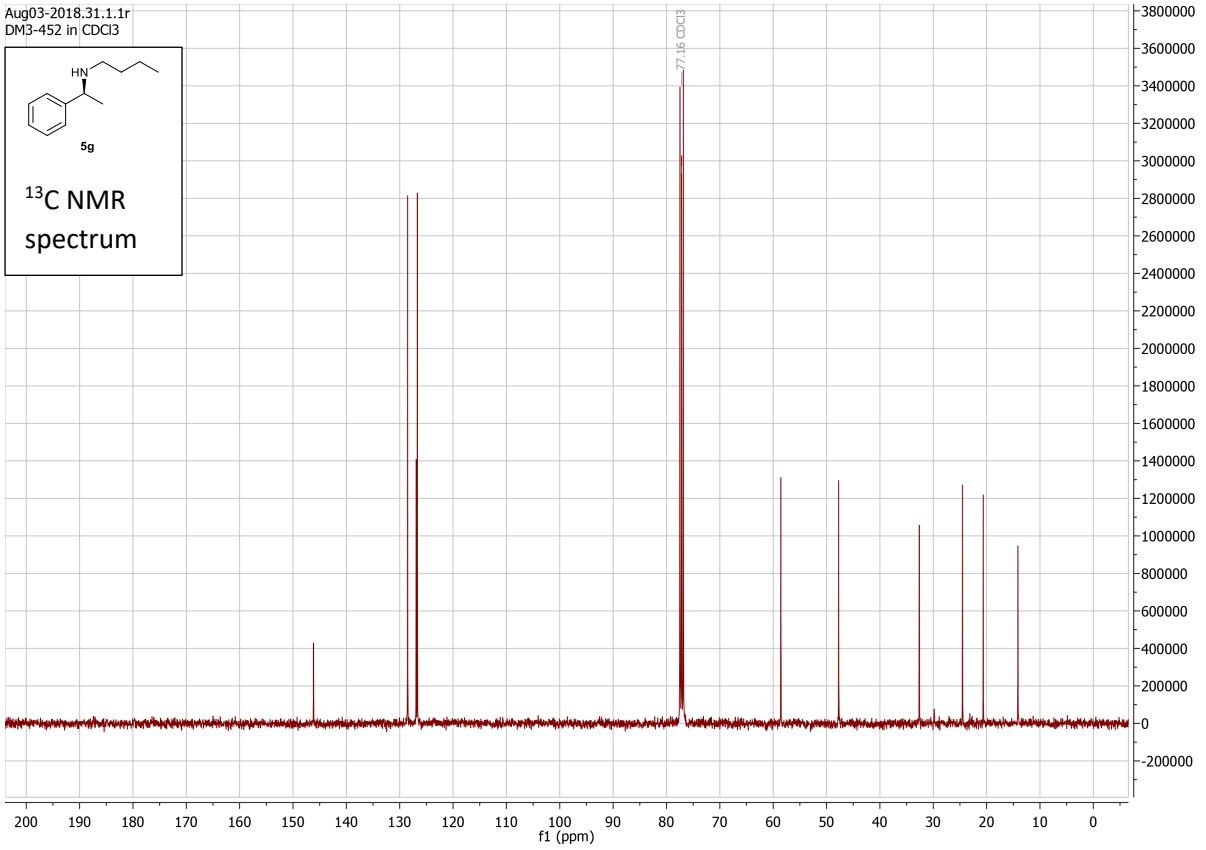

Oct16-2018.70.1.1r
DM3-455
HN
5e
^{1}H NMR
spectrum
7.26 CDCl3
3.71
1.11
1.00
0.98
5.35
1.80
4.80
f1 (ppm)

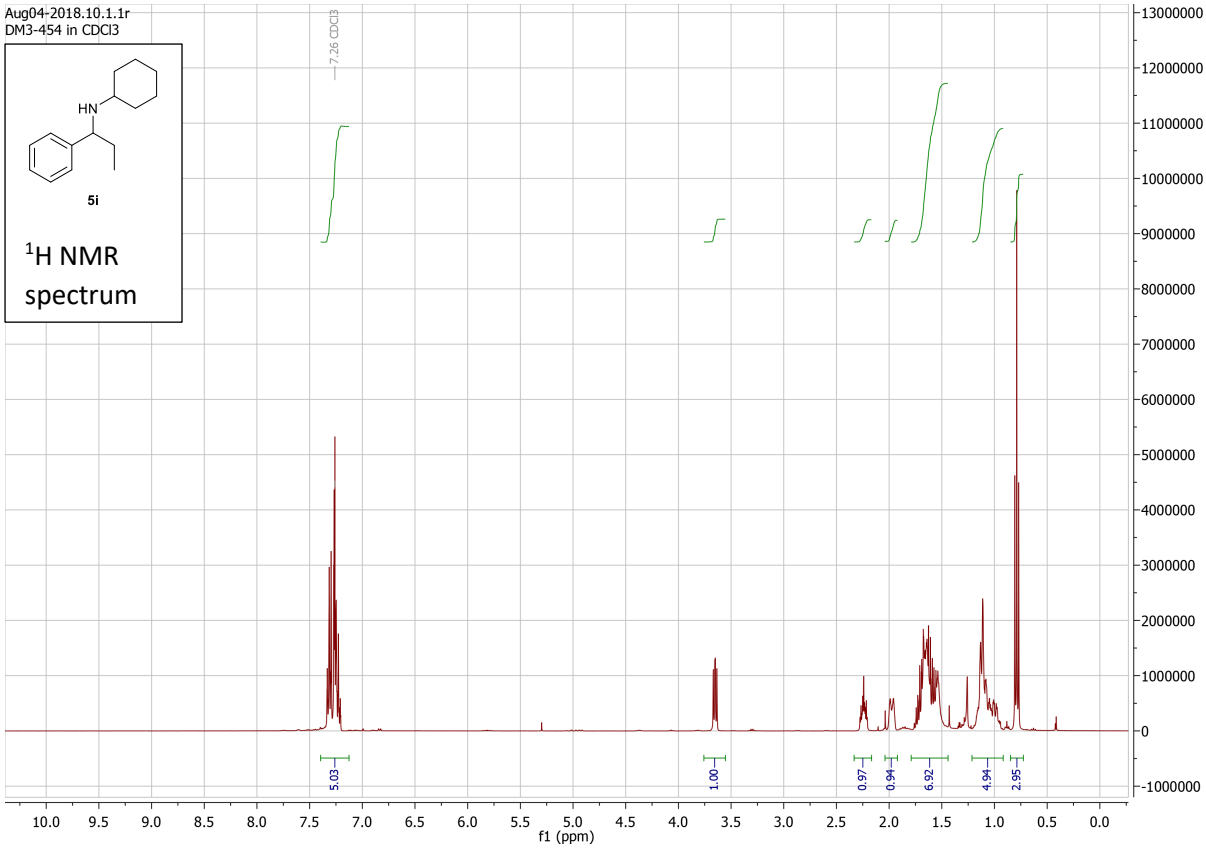

Oct16-2018.71.1r
DM3-455
HN
5e
^{13}C NMR
spectrum
146.09
128.51
126.94
126.76
77.16 CDCl3
57.34
56.77
33.85
32.95
24.73
23.98
f1 (ppm)

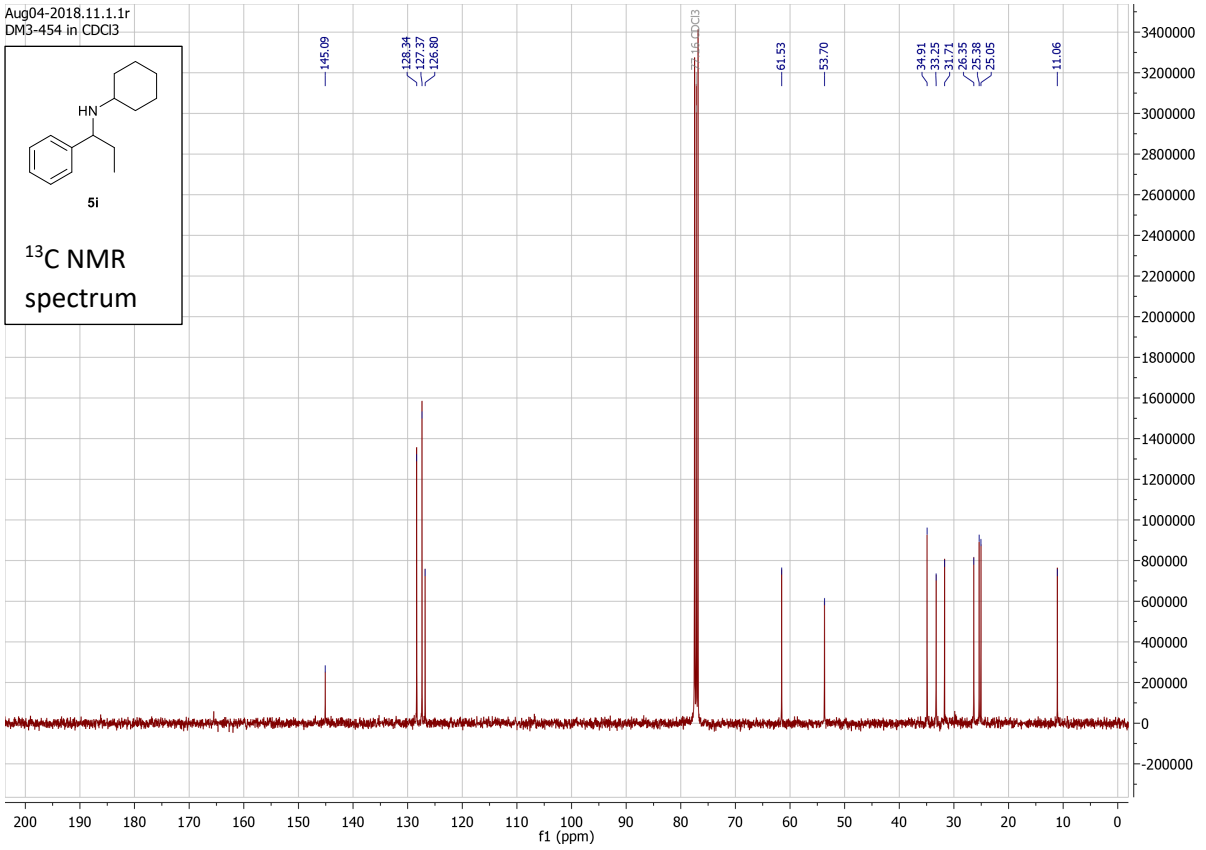

Feb14-2019.10.1.1r
DM5-508
HN
5f
^{1}H NMR spectrum
7.26 CDCl3
2.78
0.90
2.87
1.00
0.95
1.02
2.27
2.88
1.07
4.79
f1 (ppm)


Jan21-2019.51.1.1r
DM5-499 in cdcl3
HN
5f
^{13}C NMR spectrum
143.95
133.63
132.85
128.28
127.86
127.78
126.02
125.48
125.15
125.00
77.16 CDCl3
54.76
53.85
34.79
33.36
26.29
25.36
25.19
25.08
f1 (ppm)


Aug03-2018.30.1.1r
DM3-452 in CDCl3
HN
5g
^{1}H NMR spectrum
7.26 CDCl3
5.04
1.00
1.95
1.69
6.09
3.02
f1 (ppm)

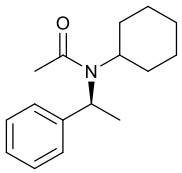

Aug03-2018.31.1.1r
DM3-452 in CDCl3
HN
5g
^{13}C NMR spectrum
77.16 CDCl3
f1 (ppm)


Aug04-2018.10.1.1r
DM3-454 in CDCl3
HN
5i
^{1}H NMR spectrum
7.26 CDCl3
5.03
1.00
0.97
0.94
6.92
4.94
2.95
f1 (ppm)


Aug04-2018.11.1.1r
DM3-454 in CDCl3
HN
5i
^{13}C NMR spectrum
145.09
128.34
127.37
126.80
77.16 CDCl3
61.53
53.70
34.91
33.25
31.71
26.35
25.38
25.05
11.06
f1 (ppm)

7.2 Characterisation data for acetamides **10**

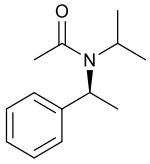
Acetamides were prepared and purified as described in section 6.



10c

$[\alpha]_D^{23}$= −30 ° (c 0.69, CH_2Cl_2, 95:5 *e.r.*)

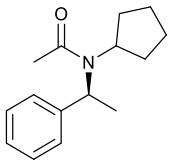
^{1}H NMR (400 MHz, $CDCl_3$, 298K) unresolved 7.4-7.15 (m, 9H); 4.91 (q, *J* = 7 Hz, 1H), 3.45 (m, 1H), 2.16 (br. s, 1H), 2.01 (br.s, 3H), 1.66 (d, J =7.4 Hz, 3H), 1.93-0.95 (m, 12 H); ^{1}H NMR (500 MHz, DMSO-d6, 403K) resolved 7.37-7.29 (m, 4H), 7.22 (m, 1H), 4.97 (q, *J* = 7.4 Hz, 1H), 3.39 (m, 1H), 2.02 (s, 3H), 1.92 (m, 1H), 1.77 (m, 2H), 1.67 (m, 2H), 1.62 (d, *J* = 7.4 Hz, 3H), 1.55 (m, 1H), 1.32 (m, 2H), 1.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.6, 141.4, 128.6, 128.1, 127.4, 127, 126.9, 126.6, 55.6, 52.3, 32.6, 32.3, 31, 30, 26.5, 26.4, 25.5, 24.5, 24.1, 18.8; HRMS (ES+) calculated for $C_{16}H_{24}NO$ ($[M+H]^+$) 246.1858, found 246.1860; IR (neat, cm^{-1}) 2926, 2851, 1635, 1427, 1379, 1362, 1306, 1247, 1178, 1025, 697, 609.



10d

$[\alpha]_D^{22}$= −44.5° (c 0.85, CH_2Cl_2, 90:10 *e.r.*)

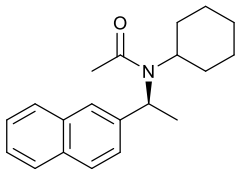
^{1}H NMR (400 MHz, $CDCl_3$) unresolved 7.32 (m, 8H), 5.3 (br), 4.94 (q, *J* = 6.9 Hz, 1H), 3.68 (m, 2H), 2.14 (m, 5H), 1.65 (d, *J* = 6.9 Hz, 5H), 1.32 (m, 5H), 1.09 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.3, 142.1, 140.9, 128.6, 128.2, 127.6, 127.1, 126.8, 55.1, 51.7, 48.1, 47.2, 24.3, 24.2, 22.5, 21.9, 21.1, 20.1, 18.2, 17.9; HRMS (ES+) calculated for $C_{13}H_{20}NO$ ($[M+H]^+$) 206.1545, found 206.1554; IR (neat, cm^{-1}) 2968, 2931, 2875, 1635, 1195, 1437, 1429, 1378, 1370, 1310, 1204, 1132, 1025, 758, 699, 640.



10e

$[\alpha]_D^{25}$ = −27.5 ° (c 0.73, CH_2Cl_2, 90:10 *e.r.*); m.p. ($CHCl_3$) 66-67 °C

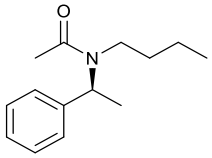
^{1}H NMR (400 MHz, $CDCl_3$) unresolved 7.32 (m, 7H), 5.32 (m), 4.96 (q, *J* = 6.9Hz, 1H), 3.8 (m), 3.43 (m, 1H), 2.15 (s, 4H), 2.1-1.2 (m, 14H), 1.64 (d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 170, 141.2, 128.7, 128.3, 127.4, 126.9, 56.7, 55.8, 30.2, 26, 25.6, 25.3, 24.2, 18.5; HRMS ES+ calculated for $C_{15}H_{22}NO$ ($[M+H]^+$) 232.1701, found 232.1694; IR (neat, cm^{-1}) 2969, 2943, 2865, 1635, 1428, 1445, 1376, 1302, 1157, 1025, 753, 697.



10f

$[\alpha]_D^{24}$= −51.5° (c 0.43, CH_2Cl_2, 96:4 *e.r.*); m.p. 114.5-116 °C

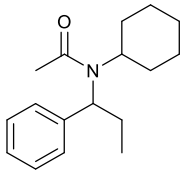
^{1}H NMR (400 MHz, $CDCl_3$) unresolved 7.79 (m, 7H), 7.47 (m, 5H), 5.05 (q, *J* = 6.3 Hz, 1H), 3.46 (m, 1H), 2.25-2.01 (m, 5H), 1.94-1.46 (m, 11H), 1.77 (d, *J* = 6.9 Hz), 1.43-0.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.9, 170.3, 140, 138.9, 133.3, 132.6, 132.5, 128.3, 128.1, 127.7, 127.6, 126.5, 126.3, 126, 125.7, 125.5, 125.2, 55.7, 52.4, 32.7, 32.3, 31, 30, 26.5, 26.4, 25.5, 24.6, 24.2, 18.8; HRMS (ES+) calculated for $C_{20}H_{26}NO$ ($[M+H]^+$) 296.2014, found 296.2023; IR (neat, cm^{-1}) 3055, 2926, 2851, 1636, 1437, 1427, 1183, 1377, 1362, 1307, 819, 751.



10g

$[\alpha]_D^{25}$ = −66.3° (c 0.75, CH_2Cl_2, 79:21 *e.r.*)

^{1}H NMR (400 MHz, $CDCl_3$) mixture of conformers, partially resolved, ~5:3 ratio 7.29 (m, 8H), 6.01 (q, *J* = 7.1 Hz, 1H), 5.04 (q, *J* = 6.7 Hz, 0.6H), 3.28 (m, 0.6H), 2.93 (m, 3H), 2.19 (s, 1.5H), 2.14 (s, 3H), 1.62 (d, *J* = 7.1 Hz, 1.7H), 1.51 (d, *J* = 7.1 Hz, 3H), 1.39 (m, 2H), 1.14 (m, 4H), 0.8 (2 x t, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.7, 170.4, 141.4, 141.1, 128.8, 128.5, 127.7, 127.6, 127.4, 126.8, 56.4, 51, 44.7, 43.3, 33, 31.3, 22.5, 22, 20.7, 20.5, 18.7, 17, 13.9, 13.7. IR (neat, cm^{-1}) 2958, 2931, 2872, 1635, 1448, 1413, 1375, 1293, 1206, 1029, 697; HRMS ES+ calculated for $C_{14}H_{22}NO$ ($[M+H]^+$) 220.1701, found 220.1694.



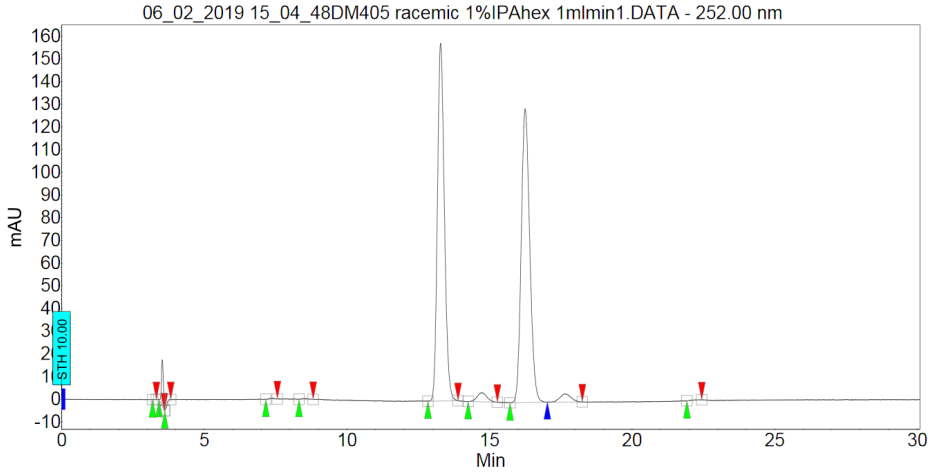
10i

$[\alpha]_D^{25}$ = −16.5° (c 0.36, CH_2Cl_2, 64:36 *e.r.*); m.p. 87-89 °C

^{1}H NMR (400 MHz, $CDCl_3$) unresolved 7.46-7.15 (m, 9H); 4.7 (m, br, 1H); 3.28 (br. s, 0.5H); 2.88 (br. s, 1H); 2.44-0.68 (31H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.7, 170.4, 128.5, 128.3, 128.1, 127.8, 126.9, 62.7, 59.8, 56.5, 32.5, 30.3, 29.5, 26.8, 26.6, 25.5, 24.5, 24.4, 24.3, 12.1, 11.8; HRMS (ES+) calculated for $C_{17}H_{26}NO$ ($[M+H]^+$) 260.2014, found 260.2021; IR (neat, cm^{-1}) 2963, 2917, 2930, 2872, 2849, 1632, 1437, 1425, 1381, 1373, 1313, 1261, 1026, 1004, 889, 756, 697.

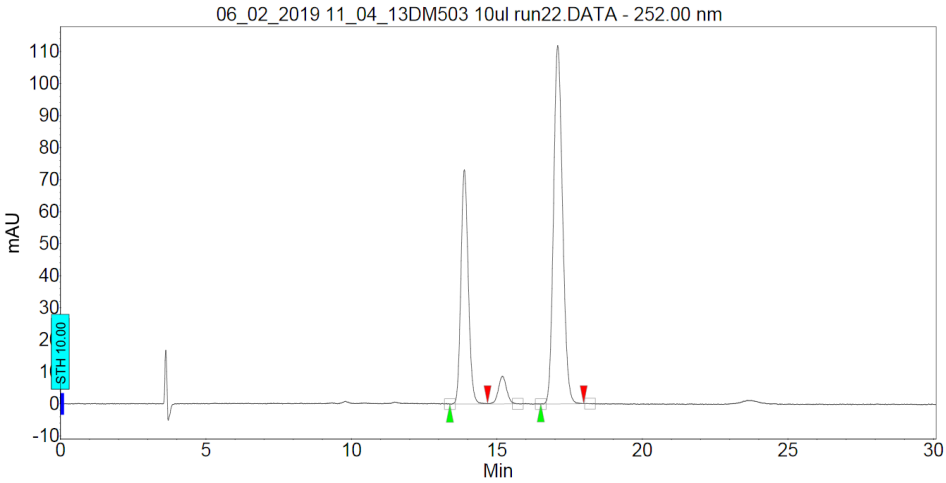
7.3 HPLC data for amines **5a,b** and acetamides **10**

Compound **5a**: Chiralcel OD-H, IPA/hexane 1:99, 1 ml/min, 252 nm detection, t = 13.9 min, t = 17.1 min.



Peak results :

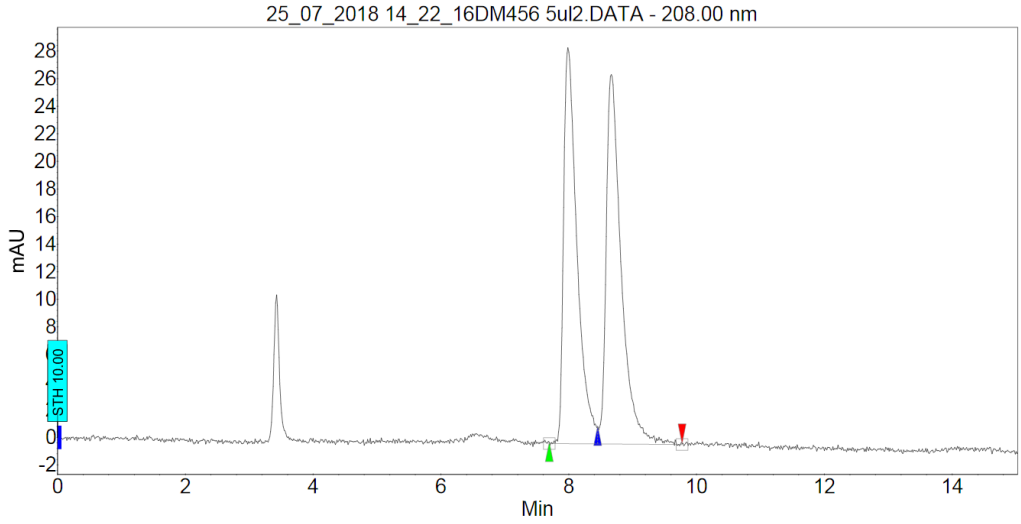
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.253	0.01	0.0	0.0	0.010
2	UNKNOWN	3.520	1.69	20.3	1.6	1.690
3	UNKNOWN	3.733	0.21	1.7	0.2	0.210
4	UNKNOWN	7.386	0.07	0.4	0.1	0.066
5	UNKNOWN	8.533	0.07	0.3	0.1	0.071
6	UNKNOWN	13.279	47.08	157.6	44.5	47.080
7	UNKNOWN	14.732	1.66	3.9	1.6	1.665
8	UNKNOWN	16.252	47.40	129.4	44.8	47.397
9	UNKNOWN	17.652	1.76	3.7	1.7	1.765
10	UNKNOWN	22.212	0.05	0.2	0.0	0.046
Total			100.00	317.3	94.5	100.000



Peak results :

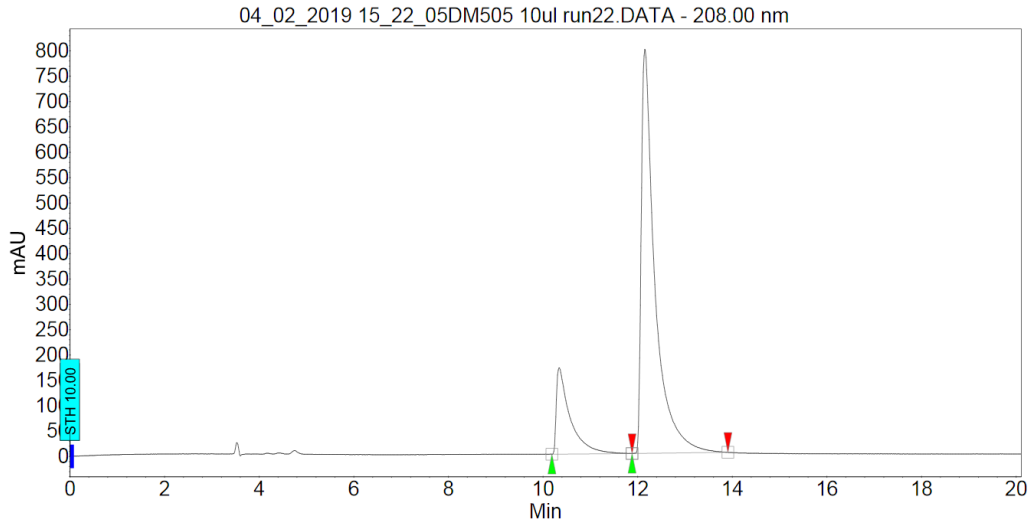
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.879	34.61	73.1	21.3	34.614
2	UNKNOWN	17.092	65.39	111.9	40.3	65.386
Total			100.00	184.9	61.6	100.000

Compound **5b:** Chiralcel OD-H, IPA/hexane 0.5:99.5, 1 ml/min, 208 nm detection, t = 10.3 min, t = 12.1 min.



Peak results :

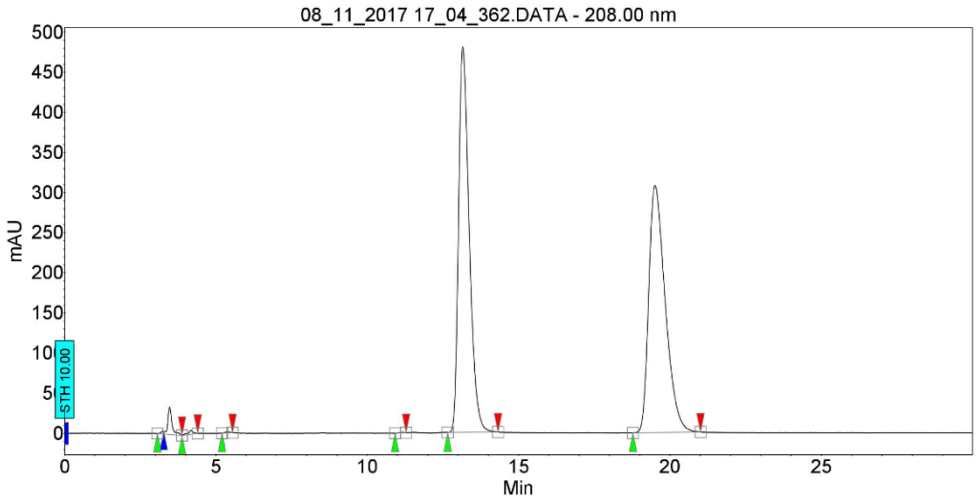
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.987	48.75	28.7	7.0	48.754
2	UNKNOWN	8.667	51.25	26.8	7.3	51.246
Total			100.00	55.5	14.3	100.000



Peak results :

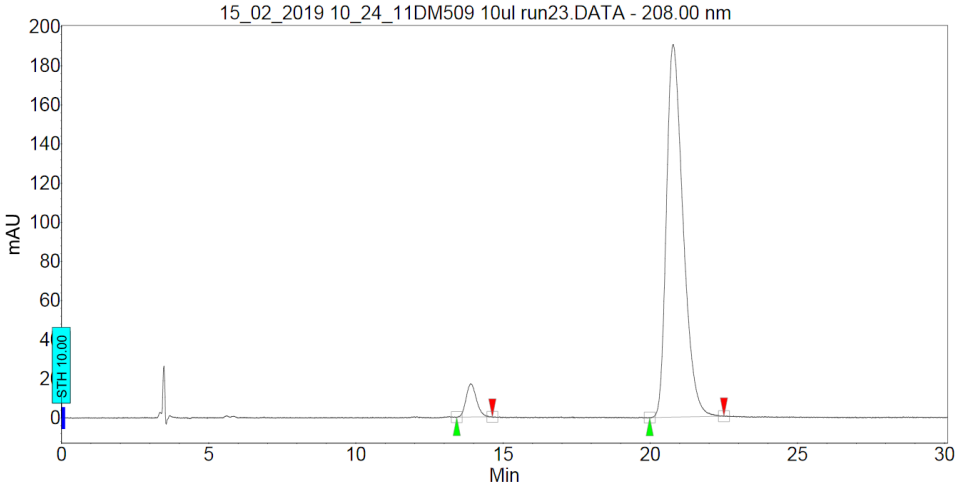
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.333	17.70	170.4	57.2	17.703
2	UNKNOWN	12.146	82.30	797.2	265.8	82.297
Total			100.00	967.7	323.0	100.000

Compound **10c**: Chiralcel OD-H, IPA/hexane 5:95, 1 ml/min, 208 nm detection, t_R = 13.9 min, t_S = 20.8 min.



Peak results :

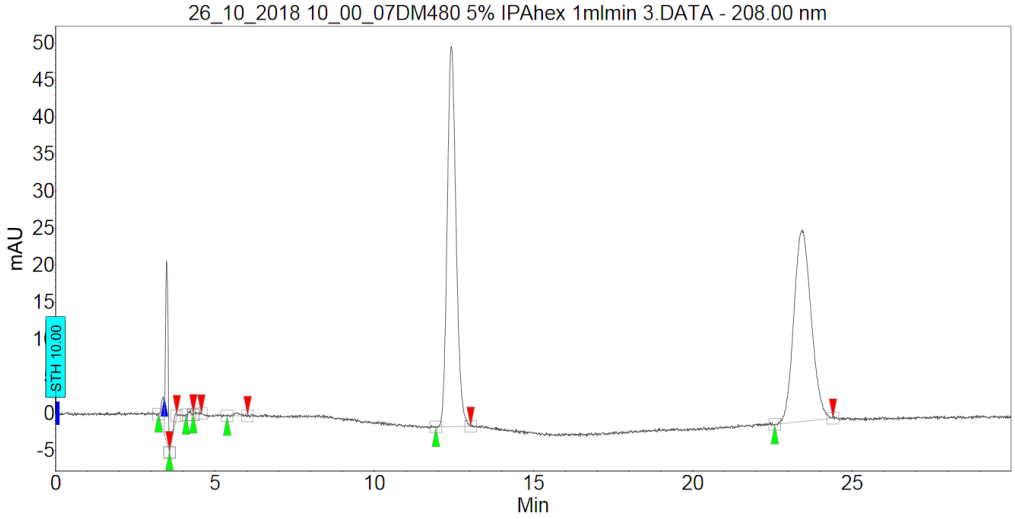
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.226	0.07	2.7	0.3	0.074
2	UNKNOWN	3.466	1.34	33.9	5.3	1.343
3	UNKNOWN	4.173	0.23	4.7	0.9	0.226
4	UNKNOWN	5.373	0.05	1.3	0.2	0.053
5	UNKNOWN	11.119	0.02	0.4	0.1	0.023
6	UNKNOWN	13.159	49.30	480.1	195.9	49.299
7	UNKNOWN	19.505	48.98	308.0	194.7	48.982
Total			100.00	831.2	397.5	100.000



Peak results :

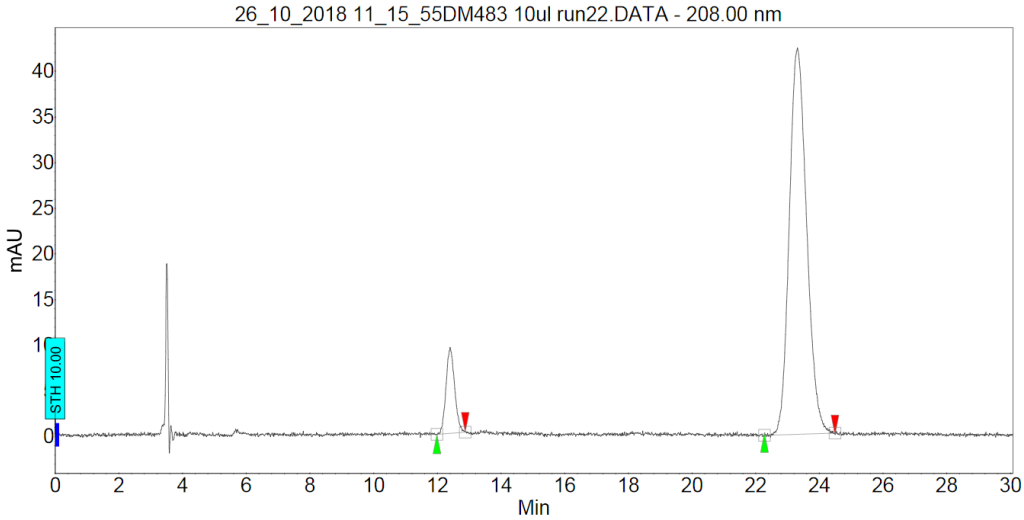
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.906	5.29	16.8	7.0	5.288
2	UNKNOWN	20.785	94.71	190.4	124.7	94.712
Total			100.00	207.2	131.7	100.000

Compound **10d**: Chiralcel OD-H, IPA/hexane 5:95, 1 ml/min, 208 nm detection, t = 12.4 min, t = 23.3 min.



Peak results :

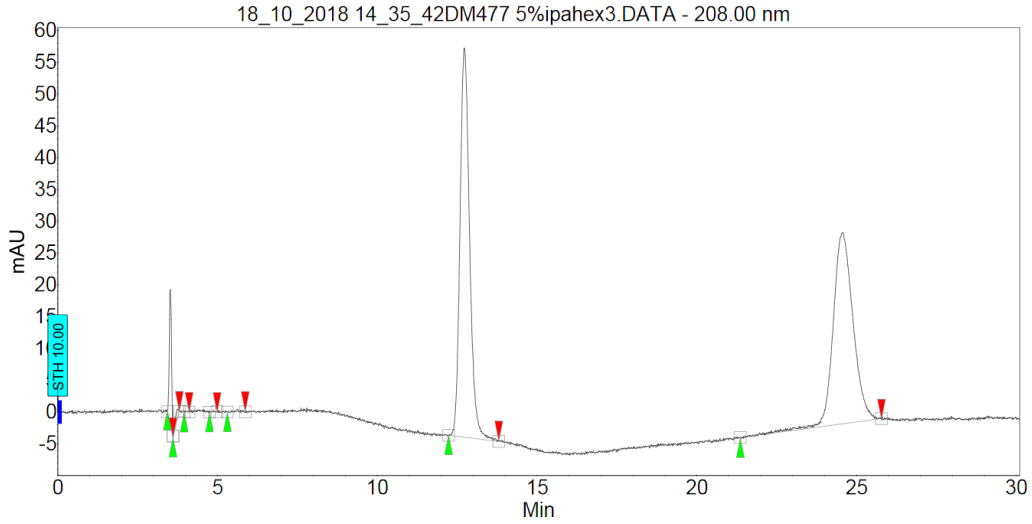
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.413	1.37	5.0	0.5	1.373
2	UNKNOWN	3.480	6.18	24.4	2.2	6.177
3	UNKNOWN	3.746	0.53	1.3	0.2	0.531
4	UNKNOWN	4.200	0.12	0.3	0.0	0.117
5	UNKNOWN	4.426	0.07	0.1	0.0	0.069
6	UNKNOWN	5.706	0.22	0.3	0.1	0.219
7	UNKNOWN	12.412	45.94	51.3	16.4	45.938
8	UNKNOWN	23.425	45.58	25.9	16.3	45.577
Total			100.00	108.7	35.7	100.000



Peak results :

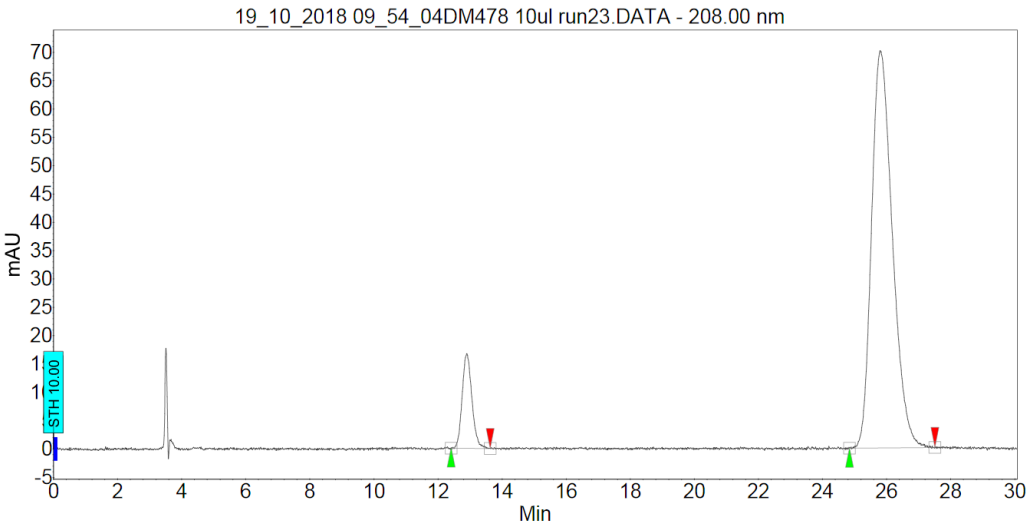
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12.399	9.88	9.4	2.9	9.885
2	UNKNOWN	23.305	90.12	42.3	26.7	90.115
Total			100.00	51.7	29.6	100.000

Compound **10e**: Chiralcel OD-H, IPA/hexane 5:95, 1 ml/min, 208 nm detection, t = 12.9 min, t = 25.8 min.



Peak results :

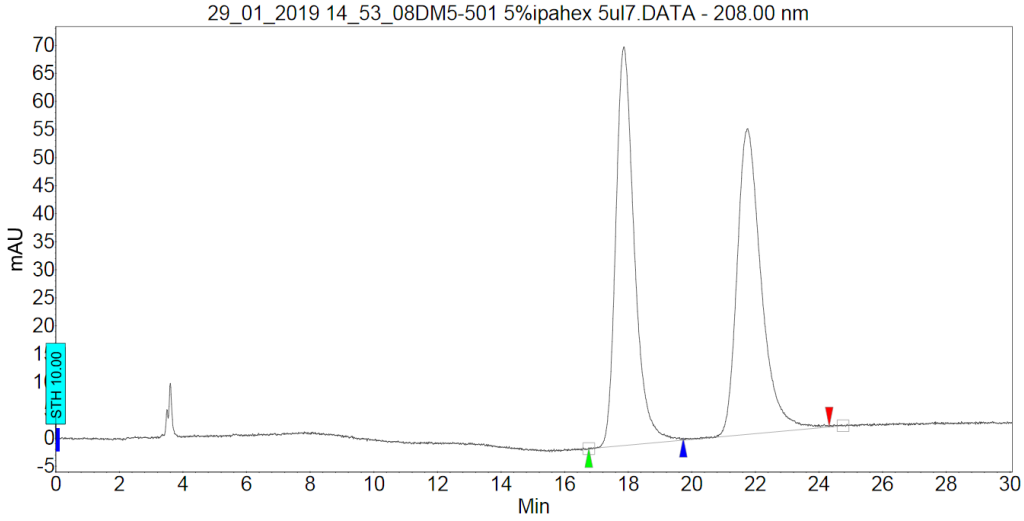
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	3.520	3.91	21.3	1.8	3.907
2	UNKNOWN	3.720	0.45	1.7	0.2	0.455
3	UNKNOWN	3.960	0.02	0.1	0.0	0.019
4	UNKNOWN	4.853	0.03	0.1	0.0	0.027
5	UNKNOWN	5.586	0.12	0.2	0.1	0.115
6	UNKNOWN	12.719	47.25	61.2	21.2	47.248
7	UNKNOWN	24.545	48.23	30.1	21.7	48.228
Total			100.00	114.9	44.9	100.000



Peak results :

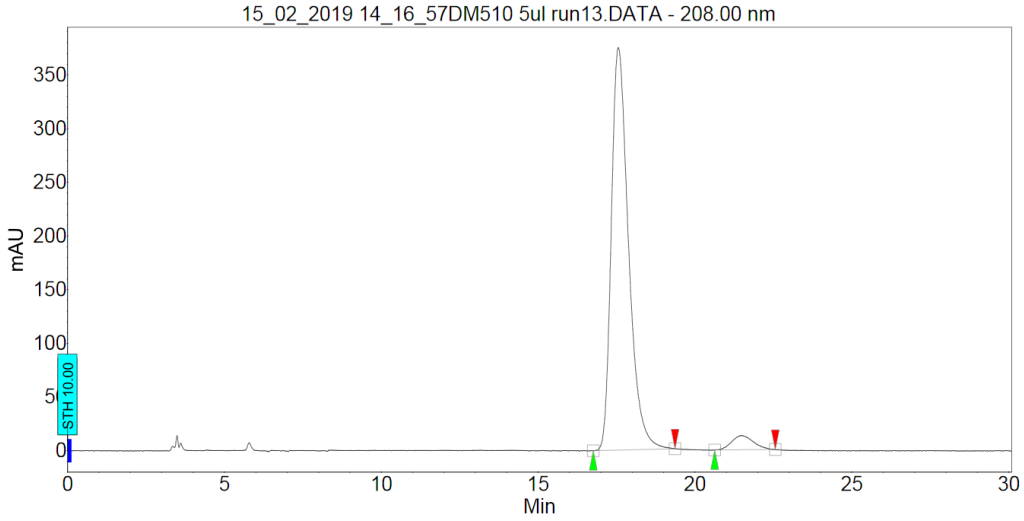
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12.892	10.03	16.7	5.9	10.030
2	UNKNOWN	25.811	89.97	69.9	52.7	89.970
Total			100.00	86.6	58.6	100.000

Compound **10f**: Chiralcel OD-H, IPA/hexane 5:95, 1 ml/min, 208 nm detection, t = 17.5 min, t = 21.5 min.



Peak results :

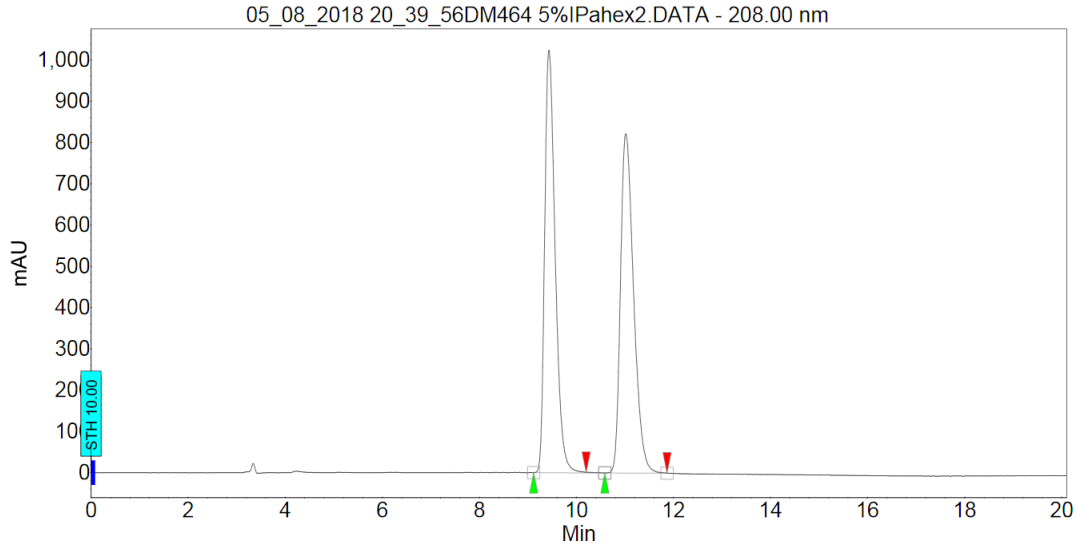
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.852	49.90	71.0	47.9	49.901
2	UNKNOWN	21.745	50.10	54.4	48.1	50.099
Total			100.00	125.4	95.9	100.000



Peak results :

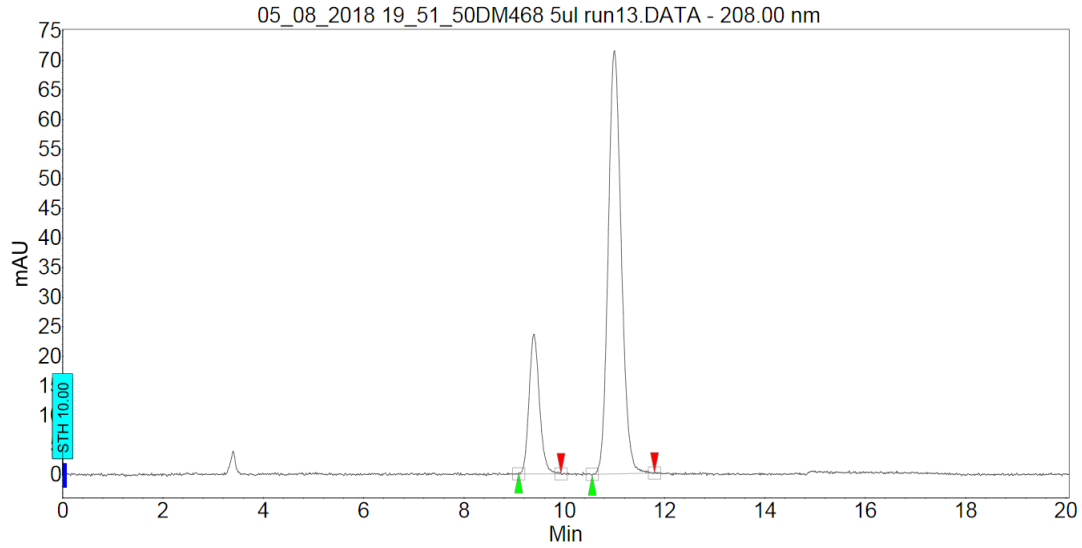
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.545	95.69	375.2	238.4	95.692
2	UNKNOWN	21.478	4.31	13.3	10.7	4.308
Total			100.00	388.5	249.1	100.000

Compound **10g**: Chiralcel OD-H, IPA/hexane 5:95, 1 ml/min, 208 nm detection, t = 9.4 min, t = 11 min.



Peak results :

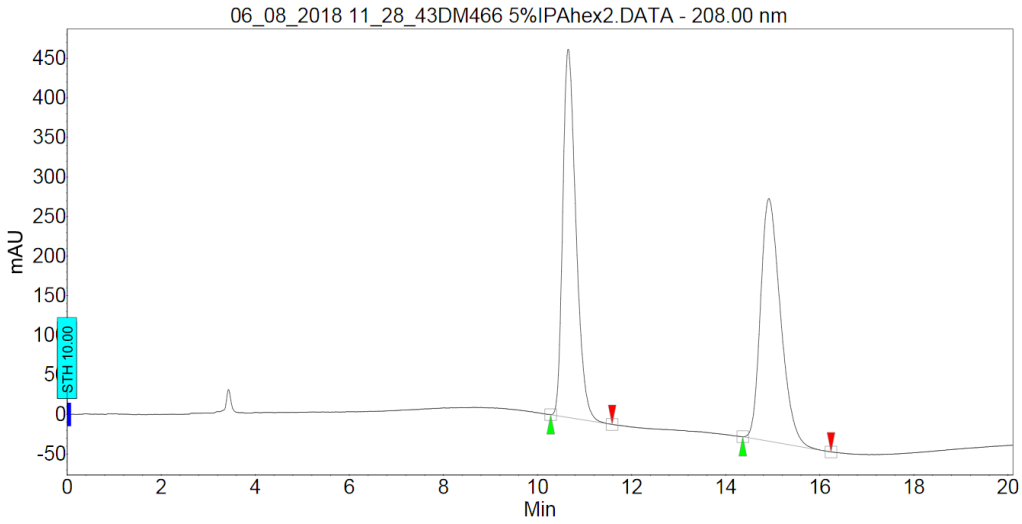
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.439	49.90	1023.6	256.5	49.903
2	UNKNOWN	11.013	50.10	821.2	257.5	50.097
Total			100.00	1844.9	514.1	100.000



Peak results :

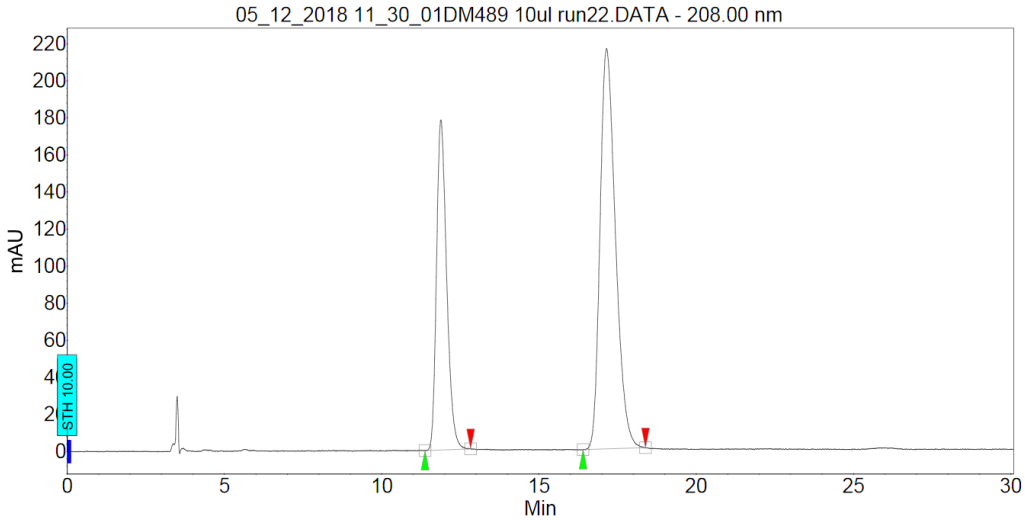
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.399	20.79	23.6	5.7	20.787
2	UNKNOWN	10.999	79.21	71.6	21.6	79.213
Total			100.00	95.1	27.2	100.000

Compound **10i**: Chiralcel OD-H, IPA/hexane 5:95, 1 ml/min, 208 nm detection, t = 11.9 min, t = 17.1 min.



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.653	50.12	465.3	151.5	50.124
2	UNKNOWN	14.919	49.88	306.7	150.7	49.876
Total			100.00	772.0	302.2	100.000



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.879	35.10	178.2	66.5	35.098
2	UNKNOWN	17.145	64.90	216.1	122.9	64.902
Total			100.00	394.3	189.4	100.000

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