Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Dialkylboron Guanidinates: Syntheses, Structures and Carbodiimide De-insertion Reactions

Antonio Antiñolo,*[a] Fernando Carrillo-Hermosilla,[a] Rafael Fernández-Galán,[a] María Pilar Montero-Rama,[a] Alberto Ramos,*[b] Elena Villaseñor,[a] Rene S. Rojas[c] and Antonio Rodríguez-Diéguez[d]

[a] Centro de Innovación en Química Avanzada (ORFEO-CINQA), Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Campus Universitario, E-13071 Ciudad Real, Spain.

[b] Centro de Innovación en Química Avanzada (ORFEO-CINQA), Departamento de Química Inorgánica, Orgánica y Bioquímica, Instituto Regional de Investigación Científica Aplicada, Universidad de Castilla-La Mancha, Campus Universitario, E-13071 Ciudad Real, Spain.

[c] Pontificia Universidad Católica de Chile. Facultad de Química, Vicuña Makenna 4860, Casilla 306, Correo 22, Santiago de Chile.

[d] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Avenida de la Fuente Nueva S/N, 18071 Granada, Spain.

Table S1. Equilibrium constants (K_{eq}) for the carbodiimide de-insertion reaction of compound **1** at different temperatures in toluene-d_8. ($K_{eq} = \frac{[10][DIC]}{[1]}$; $[\mathbf{1}]_0 = 5.70 \cdot 10^{-2}$ M).

T (ºC)	[**1**] (M)	[**10**] = [DIC] (M)	K_{eq} (M)
25	$3.31 \cdot 10^{-2}$	$2.39 \cdot 10^{-2}$	$1.73 \cdot 10^{-2}$
50	$1.97 \cdot 10^{-2}$	$3.73 \cdot 10^{-2}$	$7.06 \cdot 10^{-2}$
60	$8.84 \cdot 10^{-3}$	$4.82 \cdot 10^{-2}$	$2.63 \cdot 10^{-1}$
70	$6.50 \cdot 10^{-3}$	$5.05 \cdot 10^{-2}$	$3.93 \cdot 10^{-1}$
80	$3.39 \cdot 10^{-3}$	$5.36 \cdot 10^{-2}$	$8.49 \cdot 10^{-1}$

Table S2. Rate constants (k_1) for the carbodiimide de-insertion reaction of compound **1** at different temperatures in toluene-d_8.

T (ºC)	k_1 (s^{-1})
25	$1.83(2) \cdot 10^{-6}$
50	$2.51(3) \cdot 10^{-5}$
60	$1.31(3) \cdot 10^{-4}$
70	$3.8(1) \cdot 10^{-4}$
80	$9.0(4) \cdot 10^{-4}$

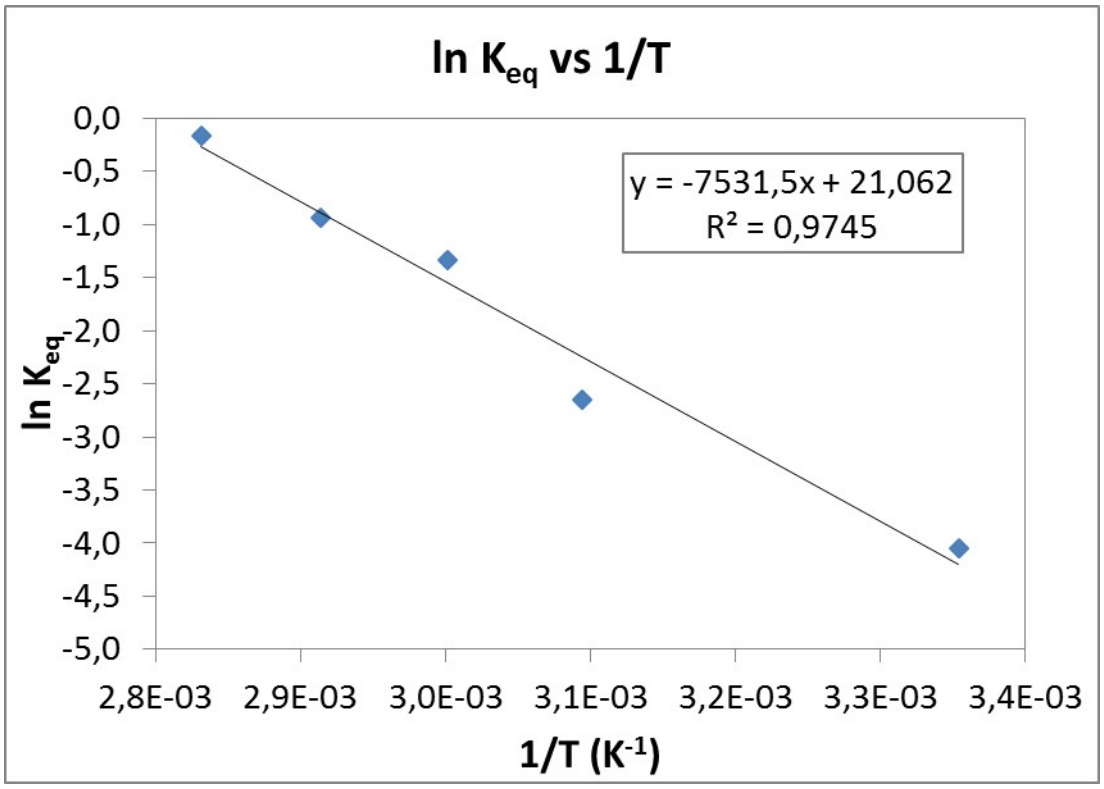
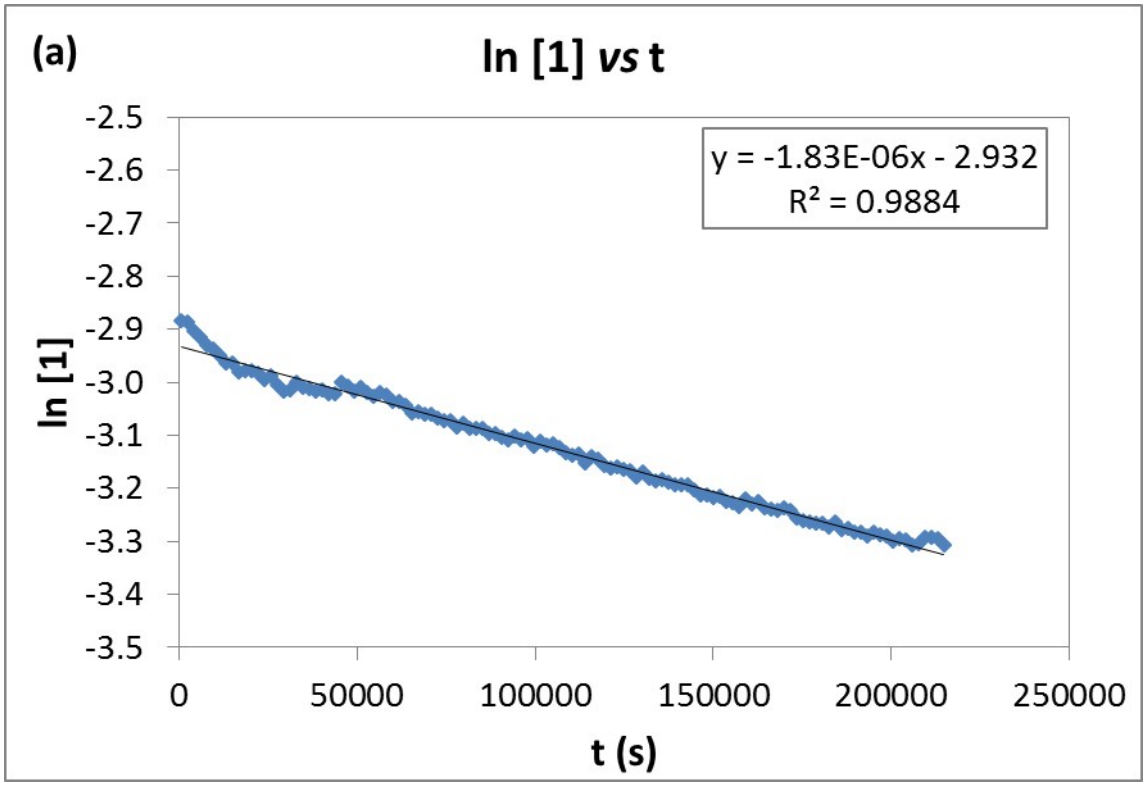
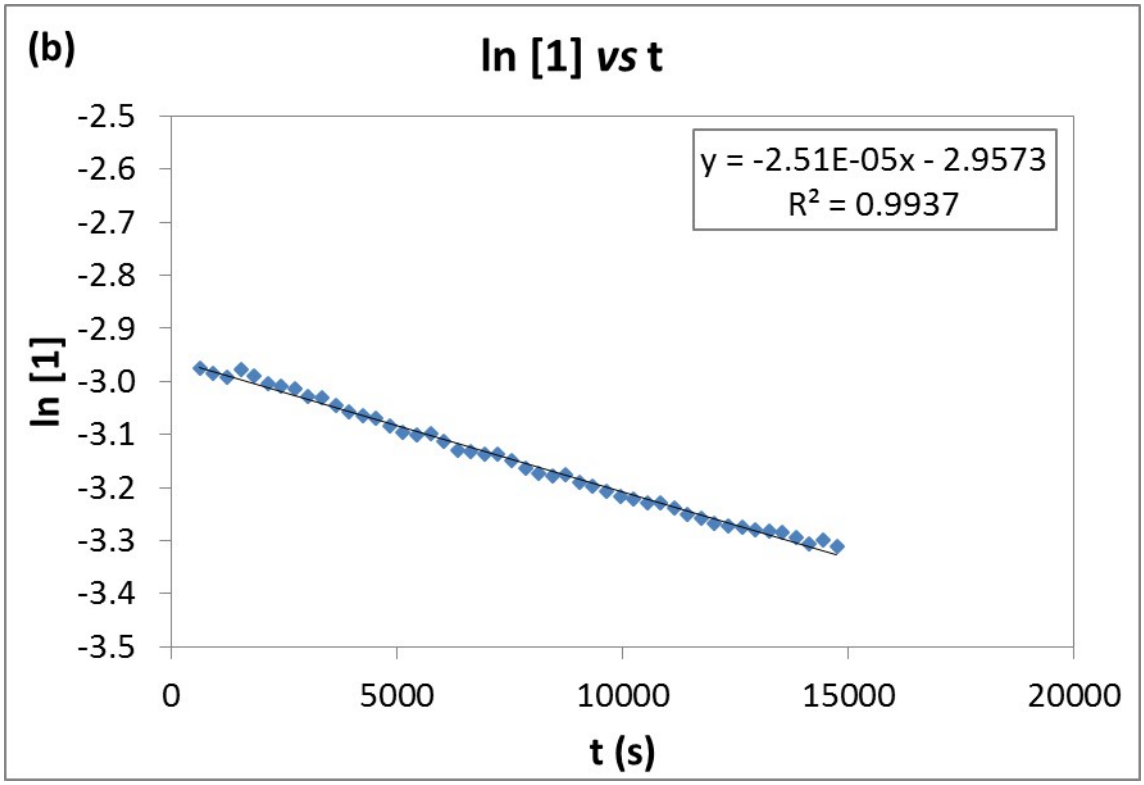
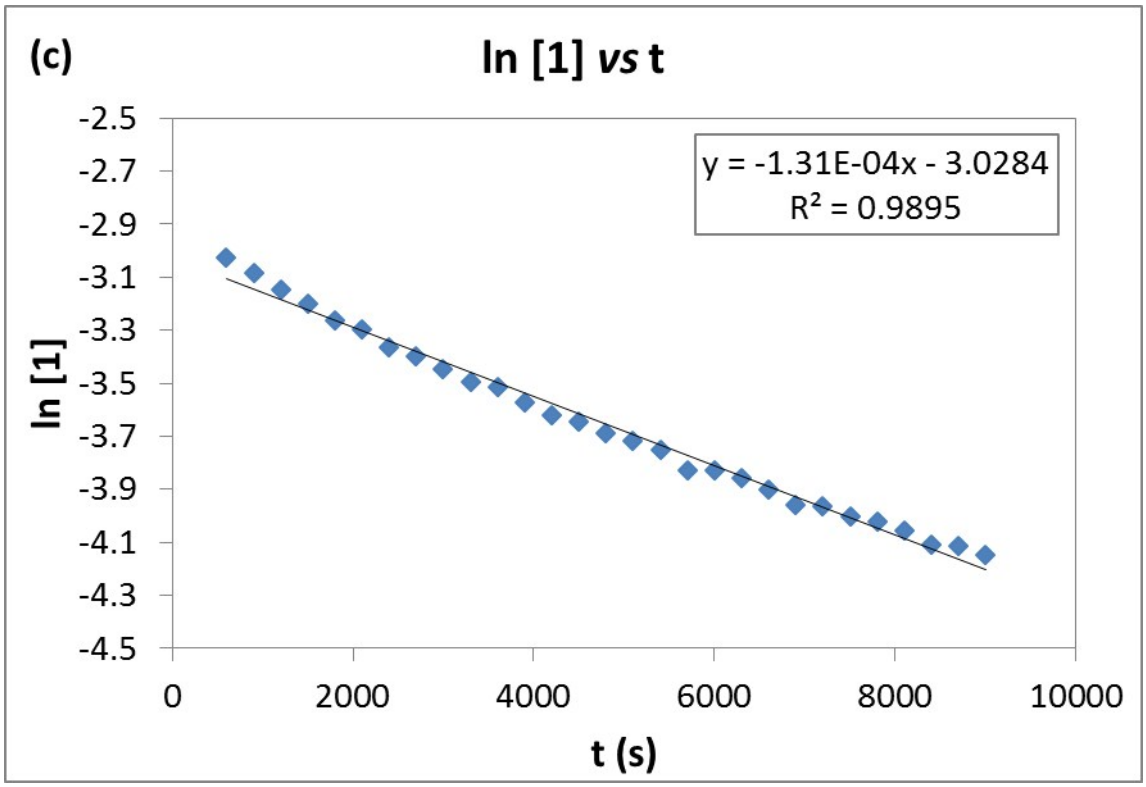


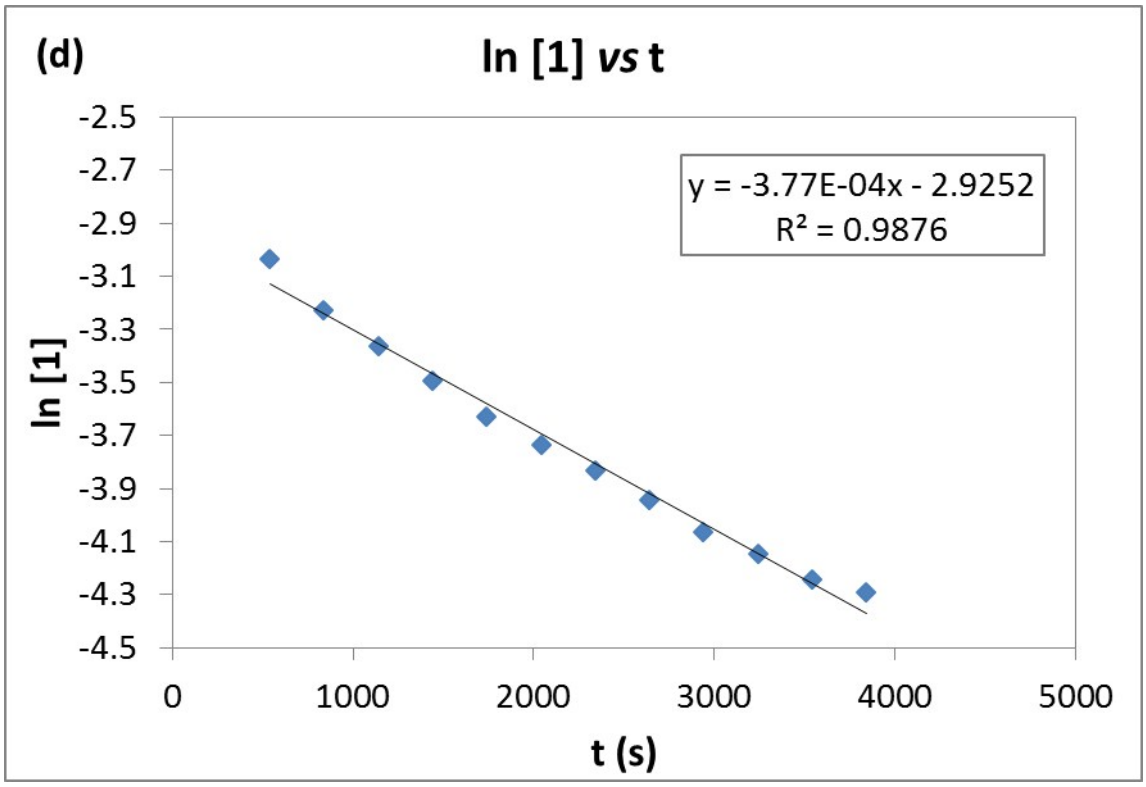
Figure S1. Van't Hoff plot (ln K_{eq} *vs* 1/T) for the carbodiimide de-insertion reaction of compound **1** ($\Delta H°$ = 63(6) KJ mol^{-1}, $\Delta S°$ = 175(18) J mol^{-1} K^{-1}).

Van't Hoff equation: $\ln K_{eq} = \frac{-\Delta H°}{R}\left(\frac{1}{T}\right) + \frac{\Delta S°}{R}$


(a)
ln [1] vs t
y = -1.83E-06x - 2.932
R² = 0.9884
ln [1]
t (s)
-2.5
-2.6
-2.7
-2.8
-2.9
-3.0
-3.1
-3.2
-3.3
-3.4
-3.5
0
50000
100000
150000
200000
250000


(b)
ln [1] vs t
y = -2.51E-05x - 2.9573
R² = 0.9937
ln [1]
t (s)
-2.5
-2.6
-2.7
-2.8
-2.9
-3.0
-3.1
-3.2
-3.3
-3.4
-3.5
0
5000
10000
15000
20000


(c)
ln [1] vs t
y = -1.31E-04x - 3.0284
R² = 0.9895
ln [1]
-2.5
-2.7
-2.9
-3.1
-3.3
-3.5
-3.7
-3.9
-4.1
-4.3
-4.5
0
2000
4000
6000
8000
10000
t (s)


(d)
ln [1] vs t
y = -3.77E-04x - 2.9252
R² = 0.9876
ln [1]
-2.5
-2.7
-2.9
-3.1
-3.3
-3.5
-3.7
-3.9
-4.1
-4.3
-4.5
0
1000
2000
3000
4000
5000
t (s)

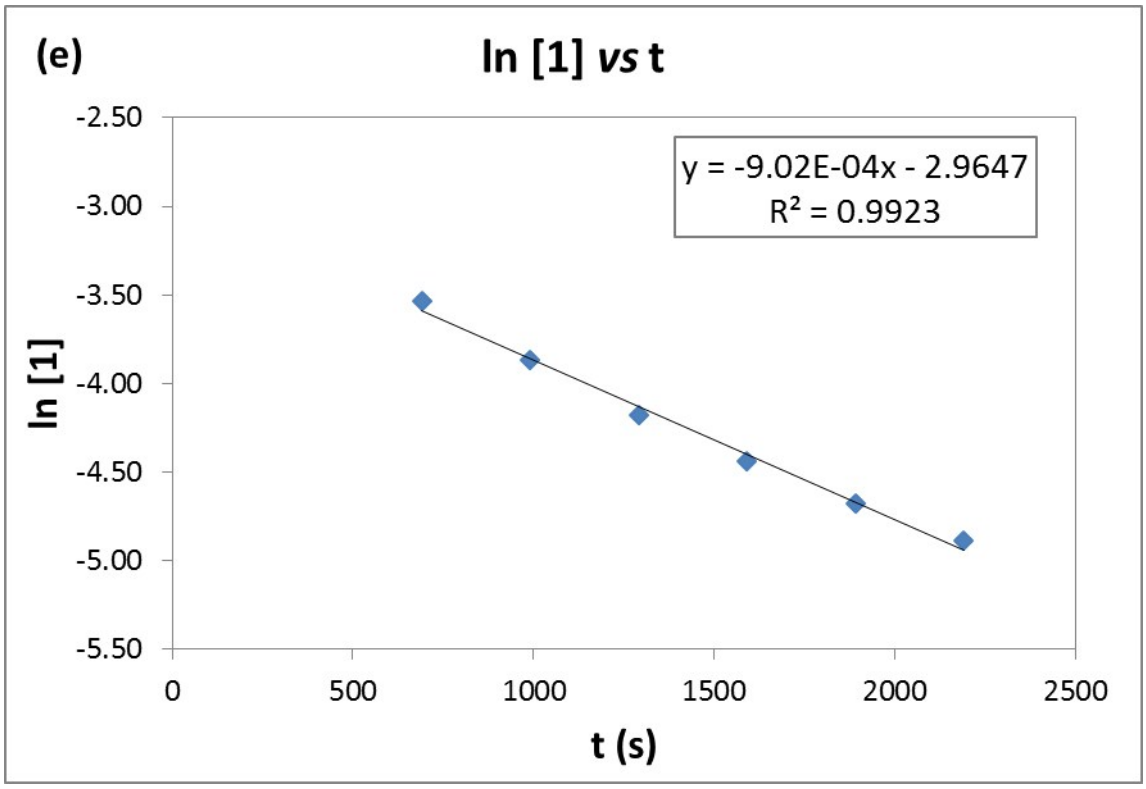
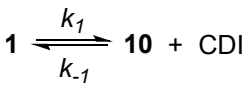


Figure S2. First order rate plot (ln [**1**] vs t) for the carbodiimide de-insertion reaction of compound **1** at (a) 25 ºC, (b) 50 ºC, (c) 60 ºC, (d) 70 ºC, (e) 80 ºC.



Assuming: k_{-1}[**10**][CDI] << k_1[**1**],

$\ln [\mathbf{1}] = \ln [\mathbf{1}]_0 - k_1 t$

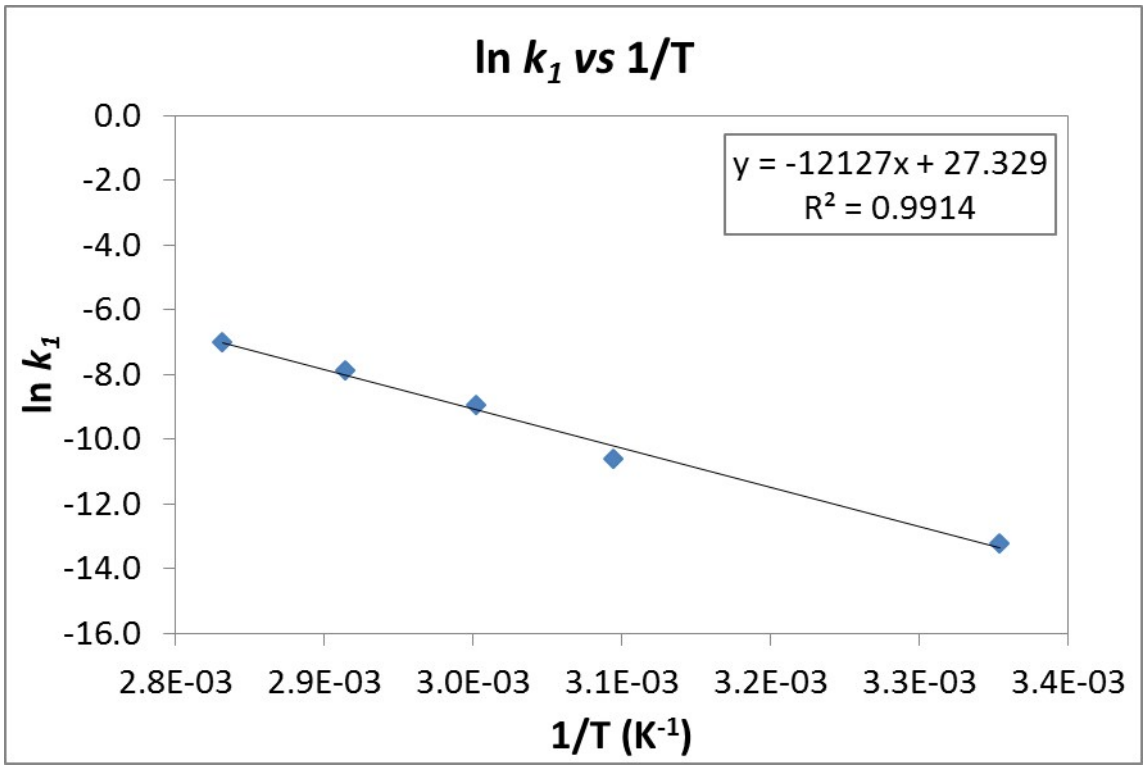


Figure S3. Arrhenius plot (ln k_1 *vs* 1/T) for the carbodiimide de-insertion reaction of compound **1** (E_a = 101(5) KJ mol^{-1}).

Arrhenius equation: $$\ln k_1 = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

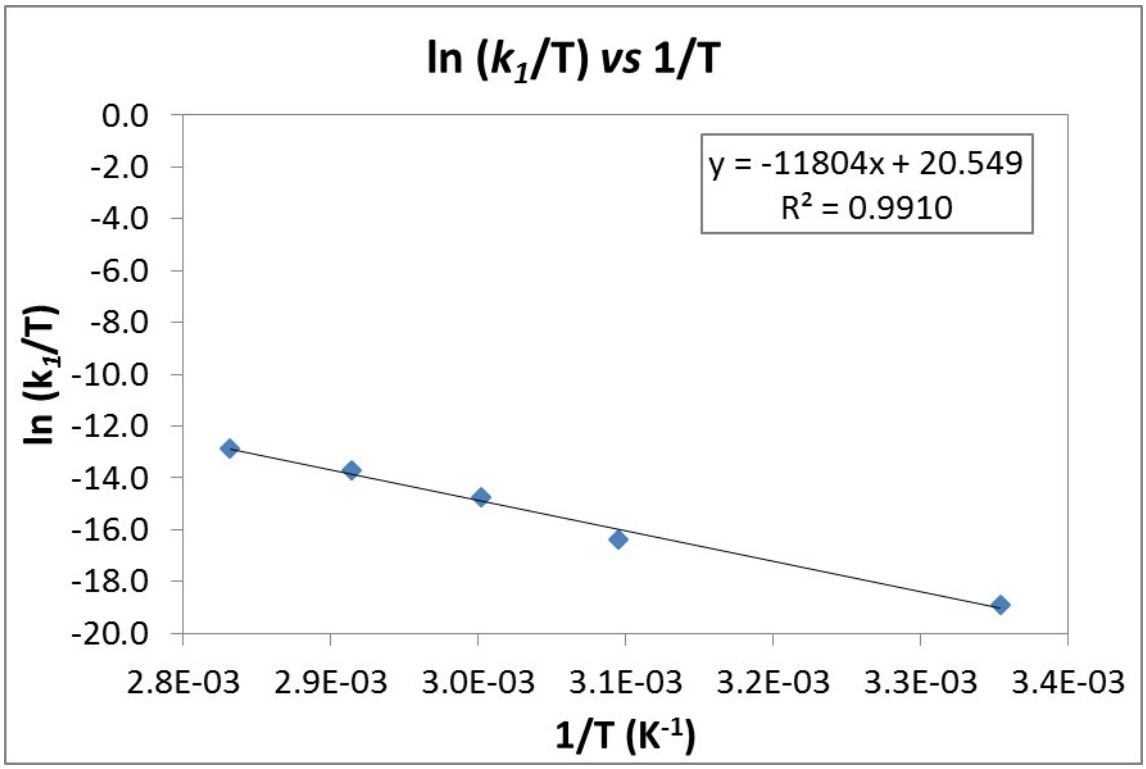
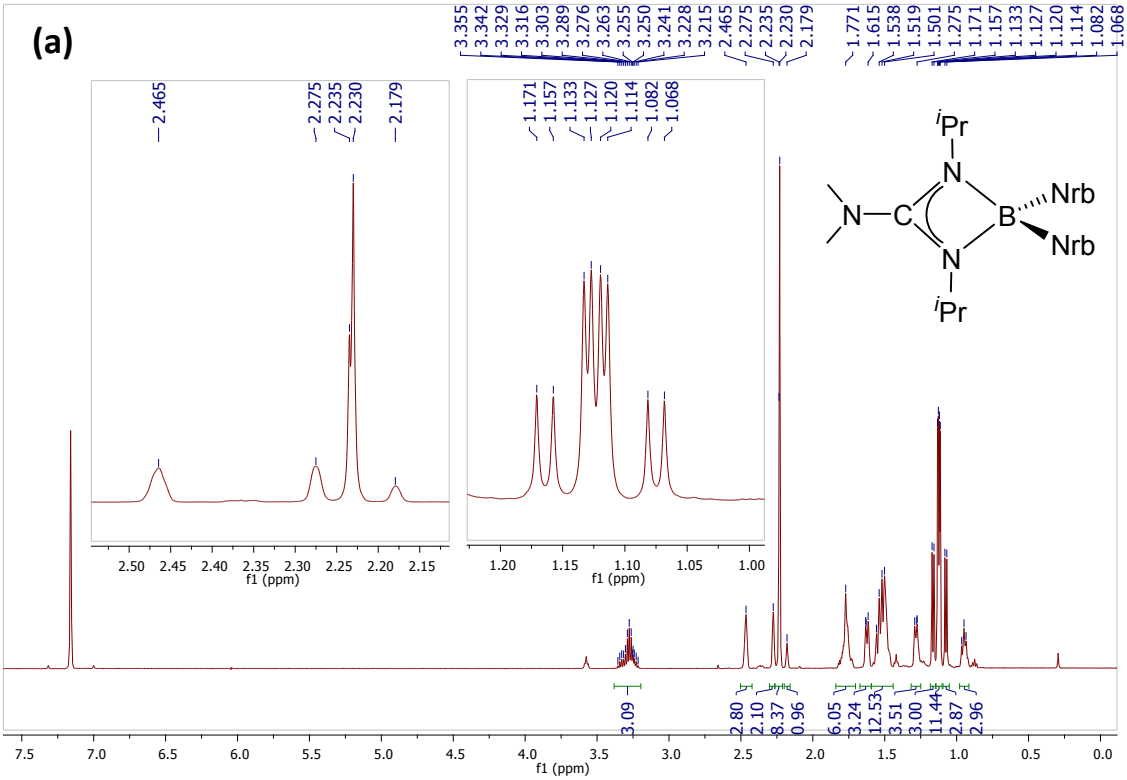
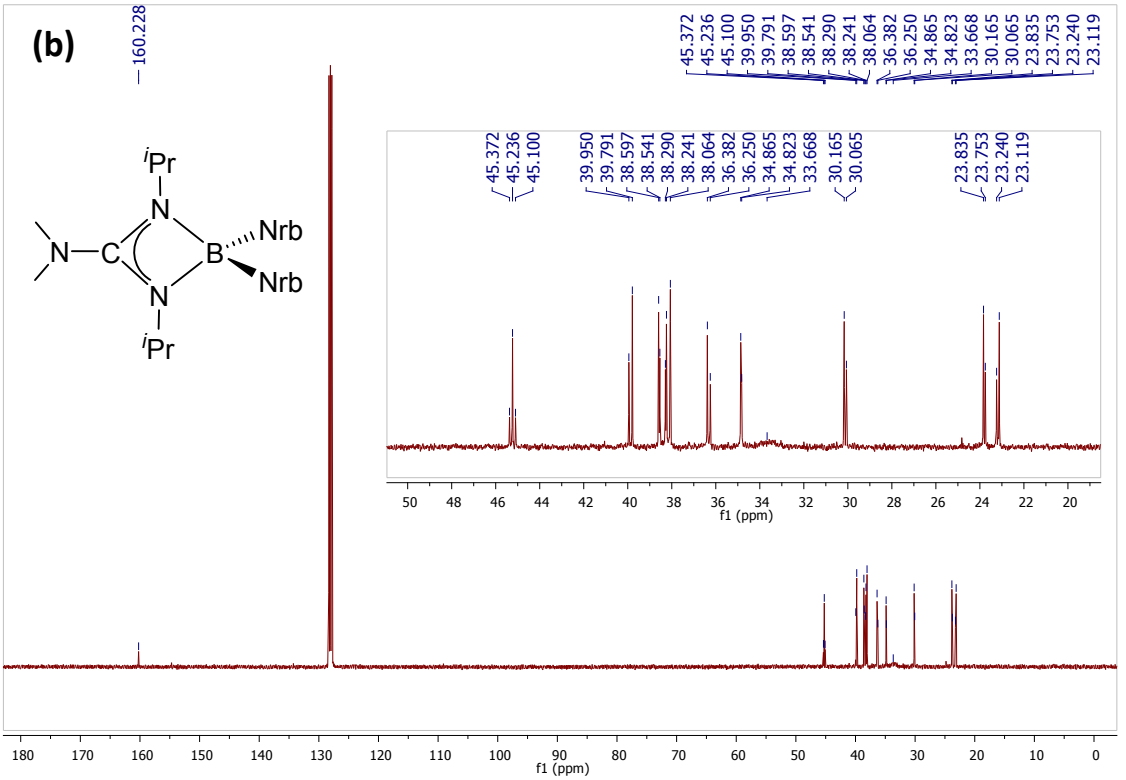


Figure S4. Eyring plot (ln k_1/T *vs* 1/T) for the carbodiimide de-insertion reaction of compound **1** ($\Delta H^{\ddagger}$ = 98(5) KJ mol^{-1}, $\Delta S^{\ddagger}$ = –27(16) J mol^{-1} K^{-1}).

Eyring equation: $$\ln\left(\frac{k_1}{T}\right) = \frac{-\Delta H^{\ddagger}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right)$$


(a)
3.355 3.342 3.329 3.316 3.303 3.289 3.276 3.263 3.255 3.250 3.241 3.228 3.215 2.465 2.275 2.235 2.230 2.179 1.771 1.615 1.538 1.519 1.501 1.275 1.171 1.157 1.133 1.127 1.120 1.114 1.082 1.068
2.465 2.275 2.235 2.230 2.179
1.171 1.157 1.133 1.127 1.120 1.114 1.082 1.068
iPr N C N B Nrb Nrb iPr
3.09 2.80 2.10 8.37 0.96 6.05 3.24 12.53 3.51 3.00 11.44 2.87 2.96
f1 (ppm)


(b)
160.228
45.372 45.236 45.100 39.950 39.791 38.597 38.541 38.290 38.241 38.064 36.382 36.250 34.865 34.823 33.668 30.165 30.065 23.835 23.753 23.240 23.119
iPr N C N B Nrb Nrb iPr
f1 (ppm)

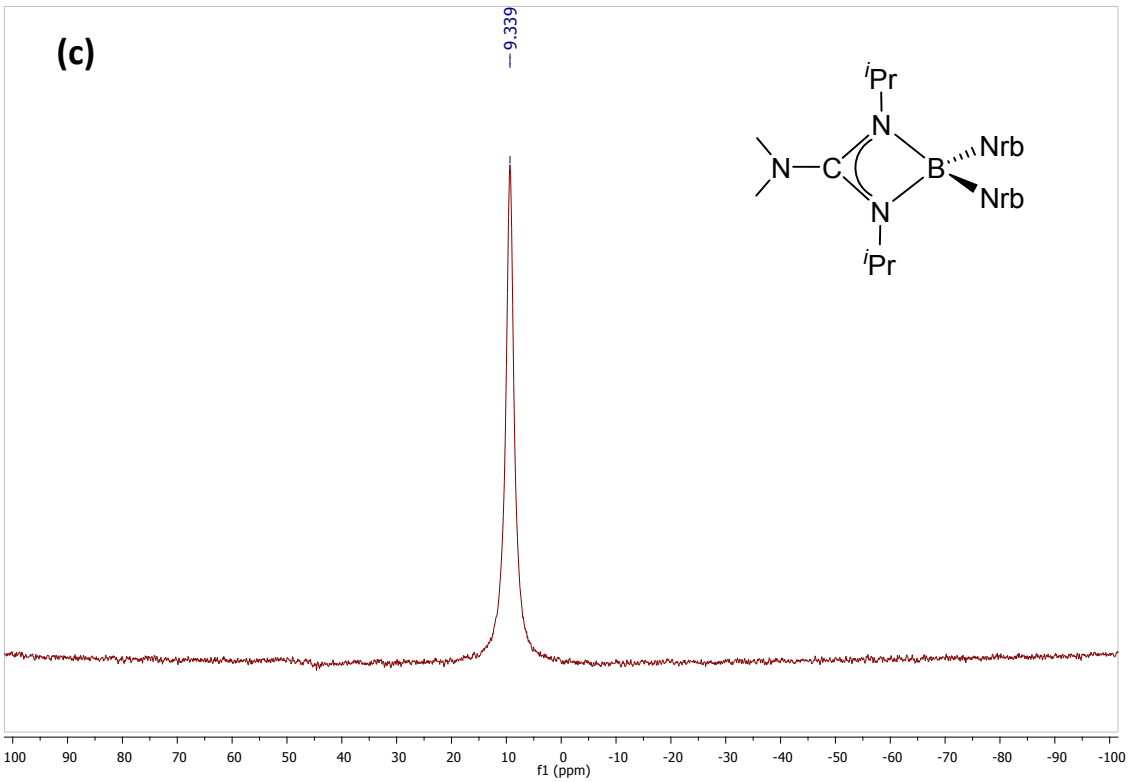
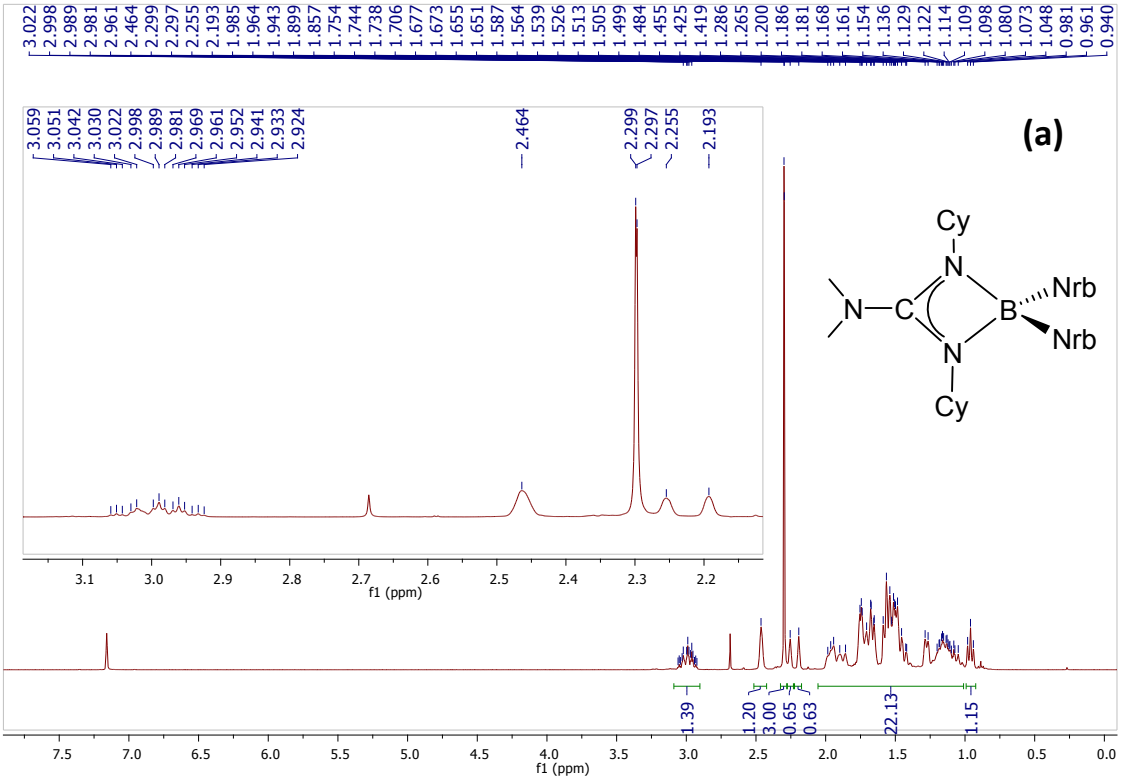
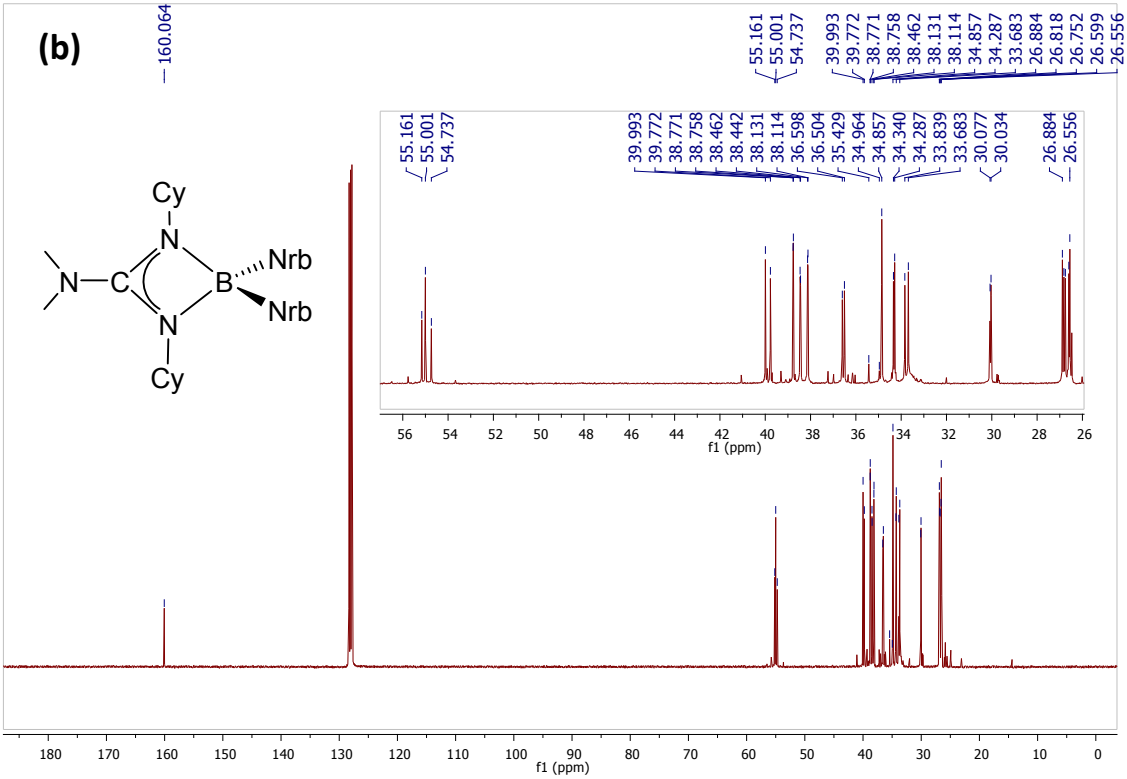


Figure S5. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **1** (diastereomer mixture).


(a)
Cy
N
N
C
B
Nrb
Nrb
N
Cy
f1 (ppm)


(b)
160.064
Cy
N
N
C
B
Nrb
Nrb
N
Cy
f1 (ppm)

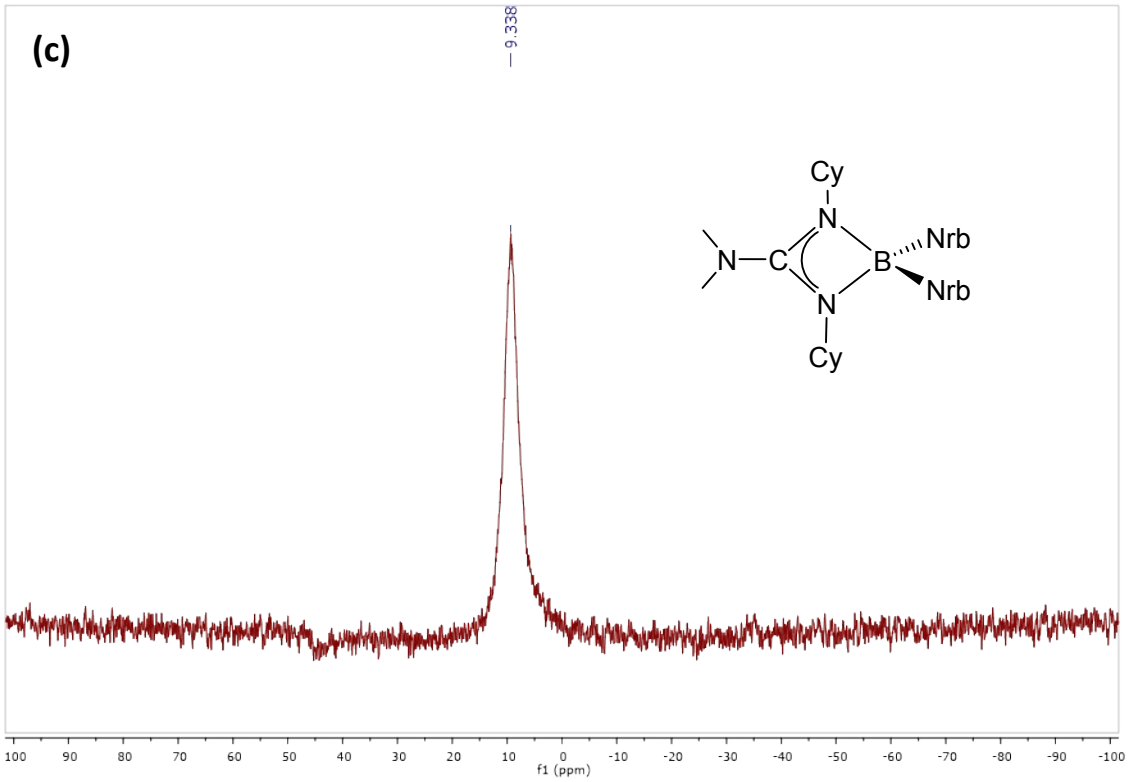
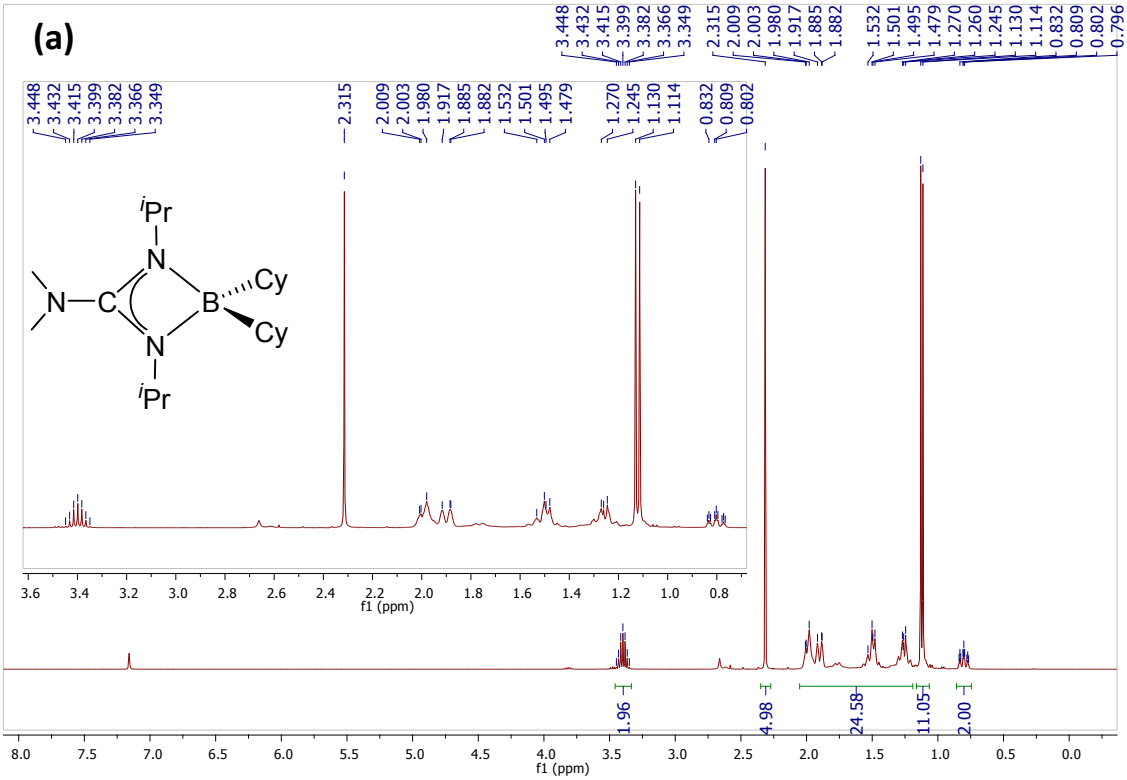
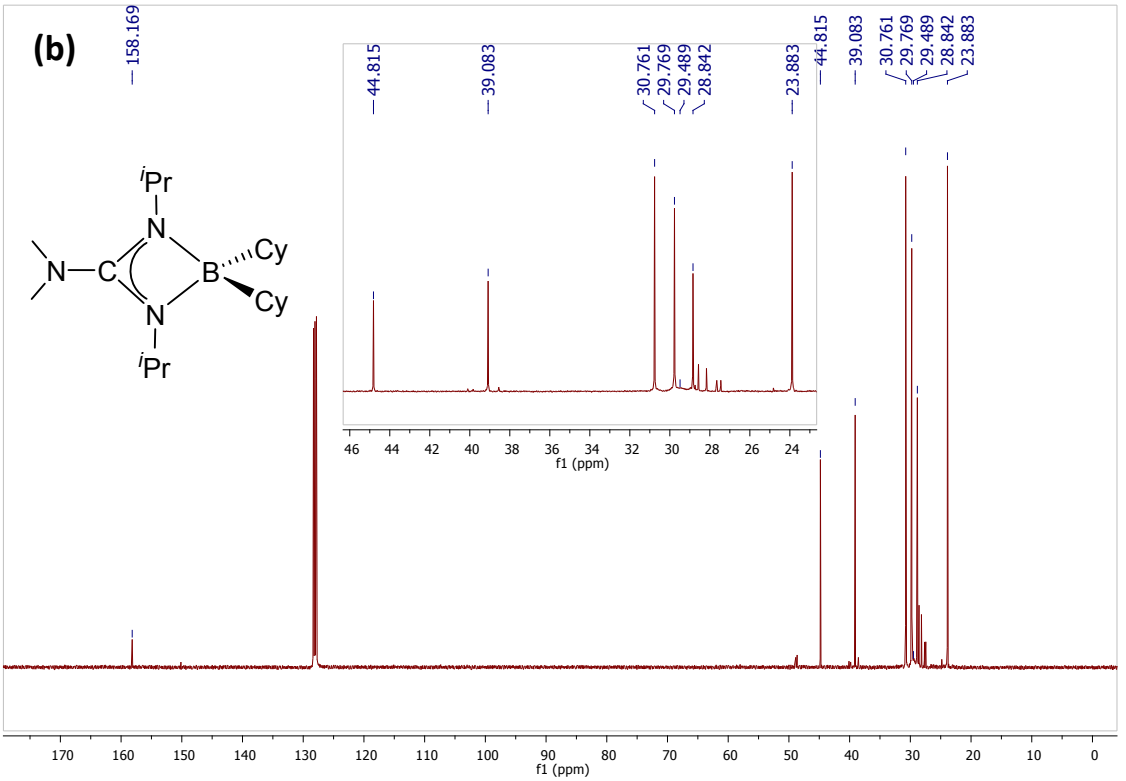


Figure S6. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **2** (diastereomer mixture).


(a)
3.448
3.432
3.415
3.399
3.382
3.366
3.349
2.315
2.009
2.003
1.980
1.917
1.885
1.882
1.532
1.501
1.495
1.479
1.270
1.245
1.130
1.114
0.832
0.809
0.802
0.796
iPr
N
C
N
B
Cy
Cy
iPr
f1 (ppm)
1.96
4.98
24.58
11.05
2.00


(b)
158.169
44.815
39.083
30.761
29.769
29.489
28.842
23.883
iPr
N
C
N
B
Cy
Cy
iPr
f1 (ppm)

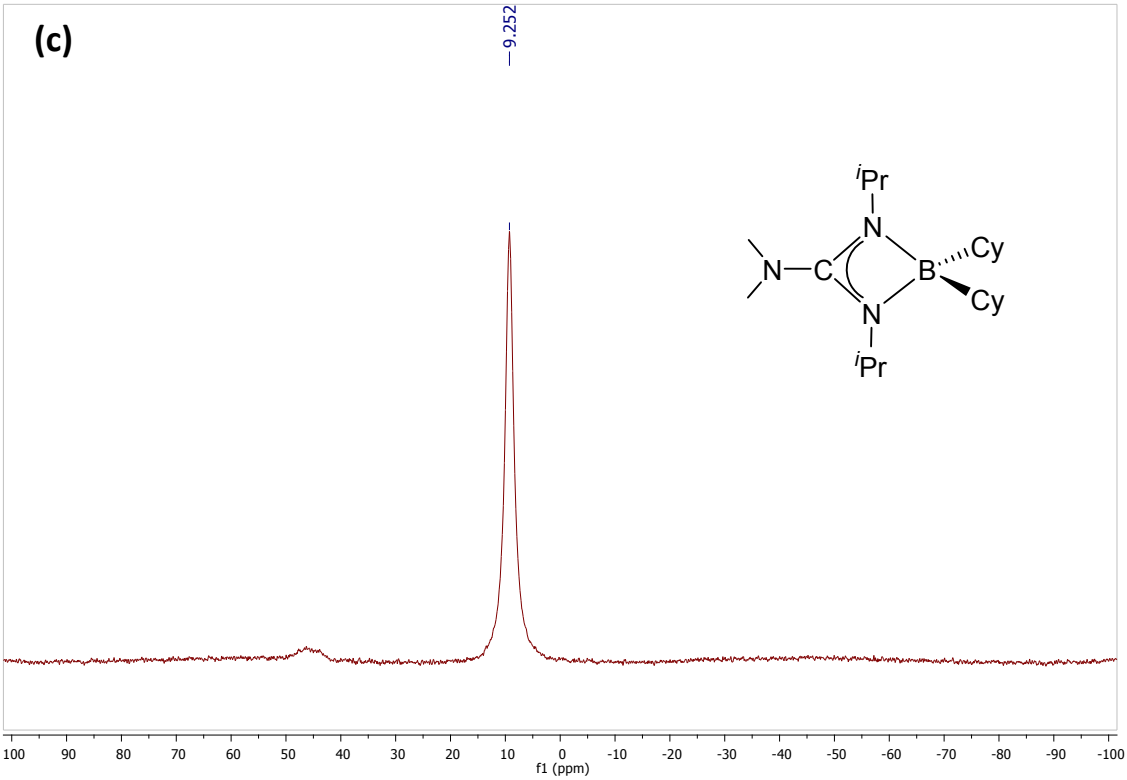
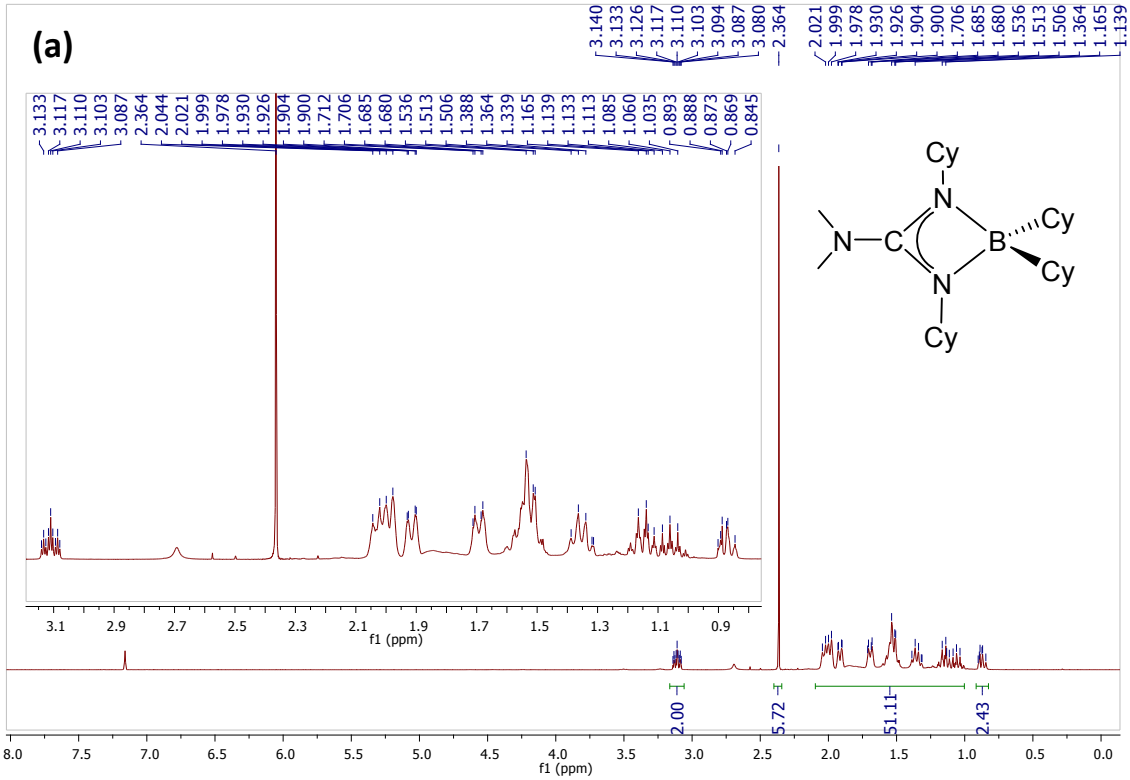
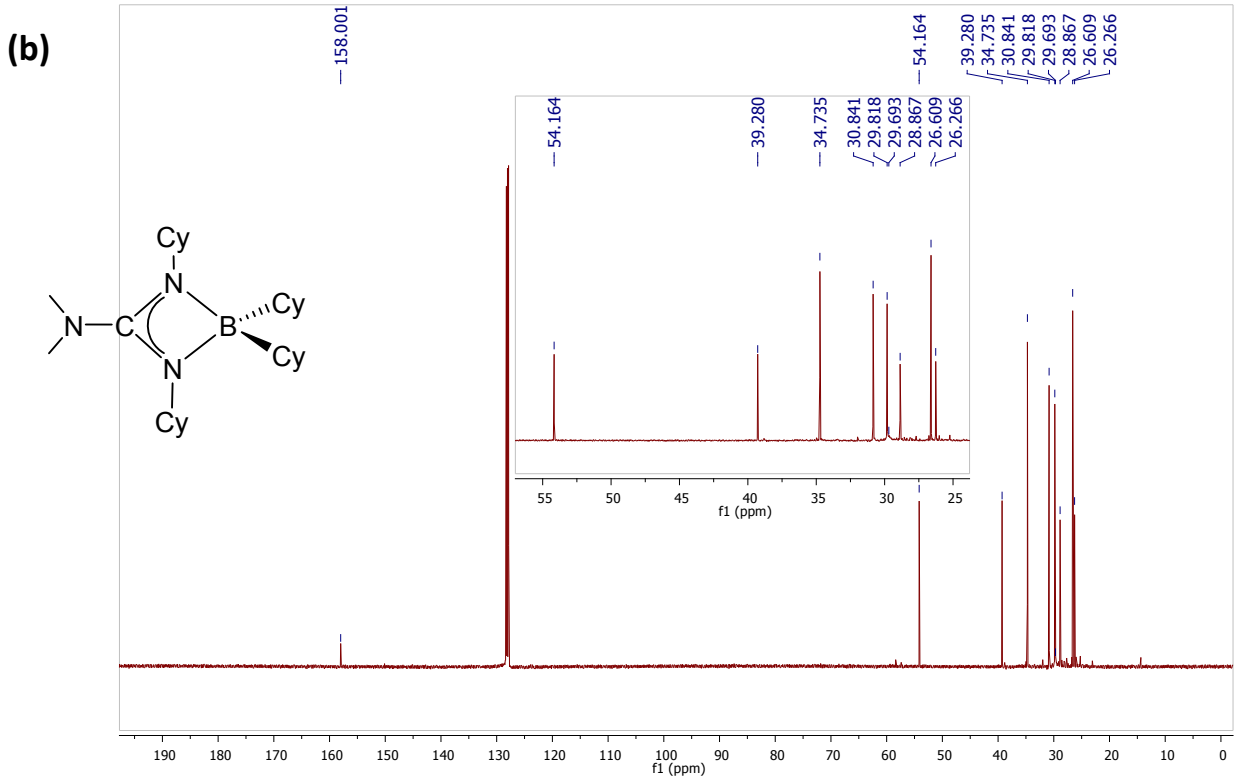


Figure S7. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **3**.


(a)
Cy
N
N
C
B
Cy
Cy
Cy
f1 (ppm)
2.00
5.72
51.11
2.43


(b)
158.001
54.164
39.280
34.735
30.841
29.818
29.693
28.867
26.609
26.266
Cy
N
N
C
B
Cy
Cy
Cy
f1 (ppm)

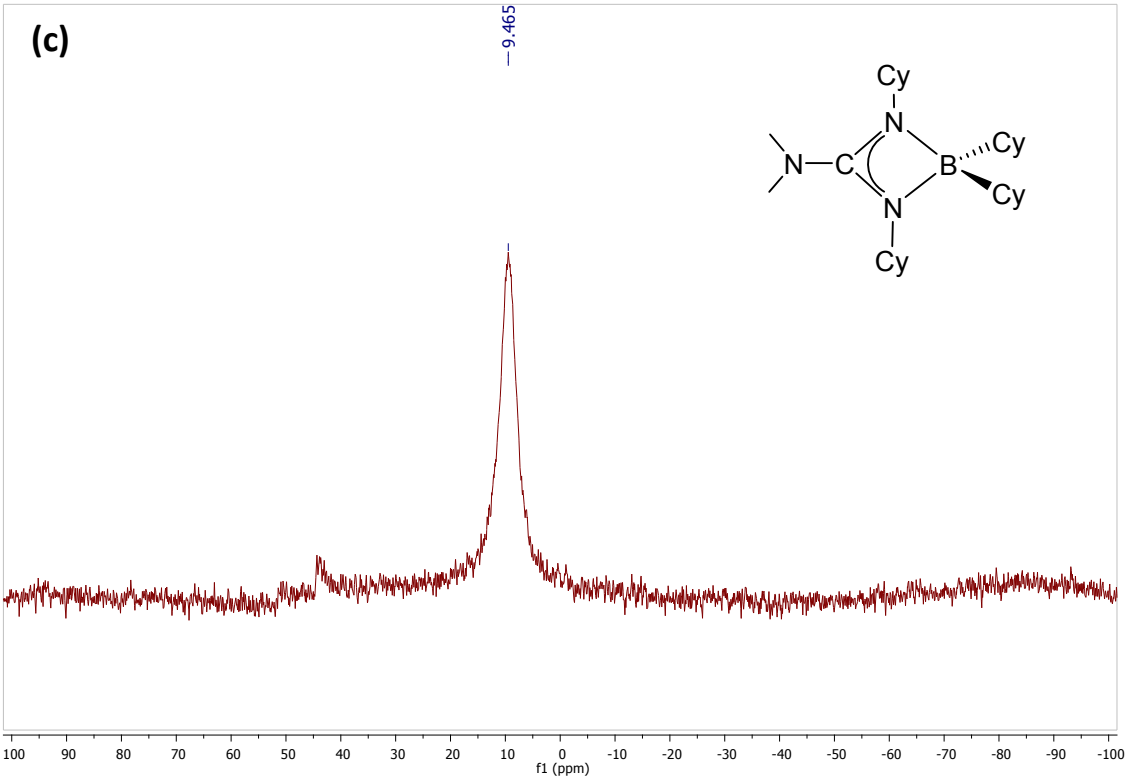
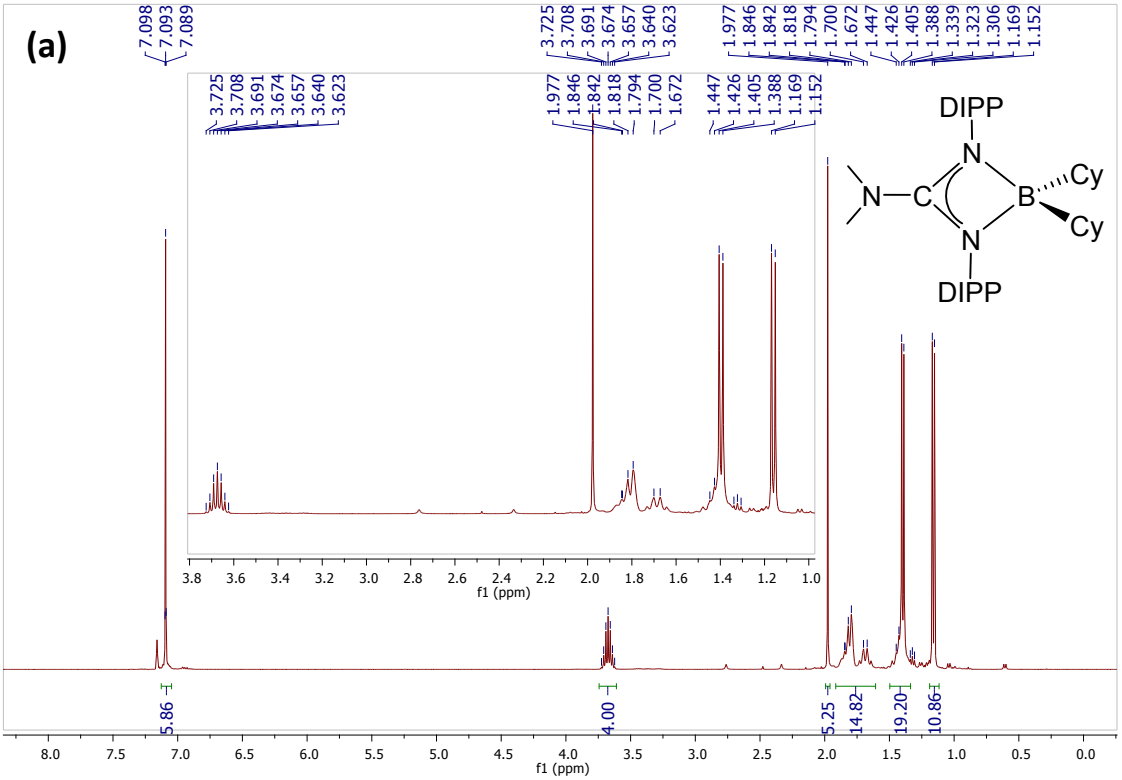
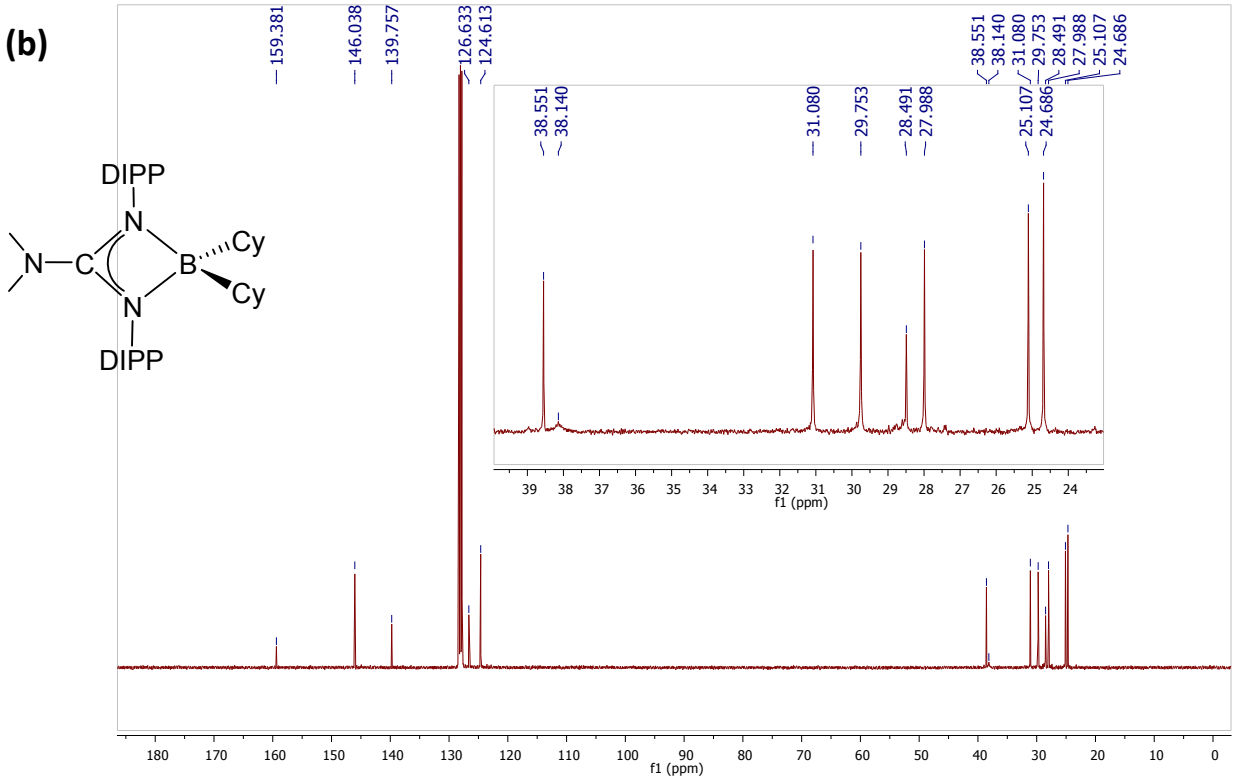


Figure S8. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **4**.


(a)
DIPP
N
N—C
B
Cy
Cy
N
DIPP
f1 (ppm)


(b)
DIPP
N
N—C
B
Cy
Cy
N
DIPP
f1 (ppm)

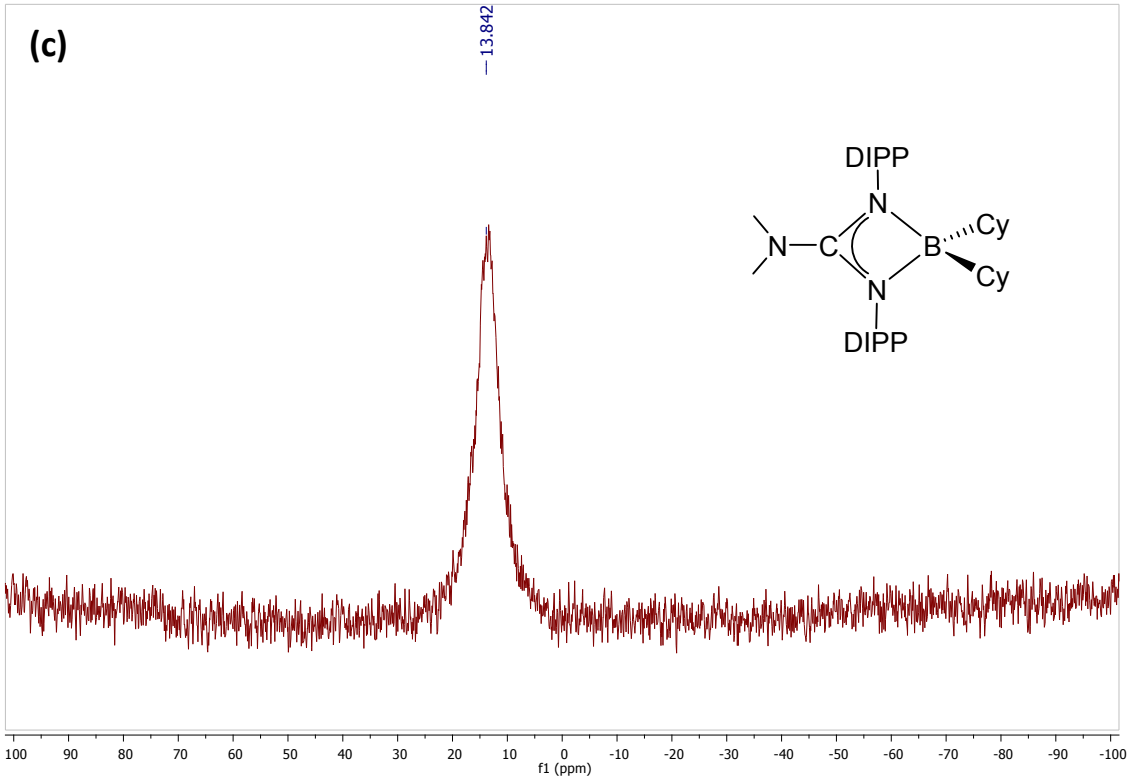
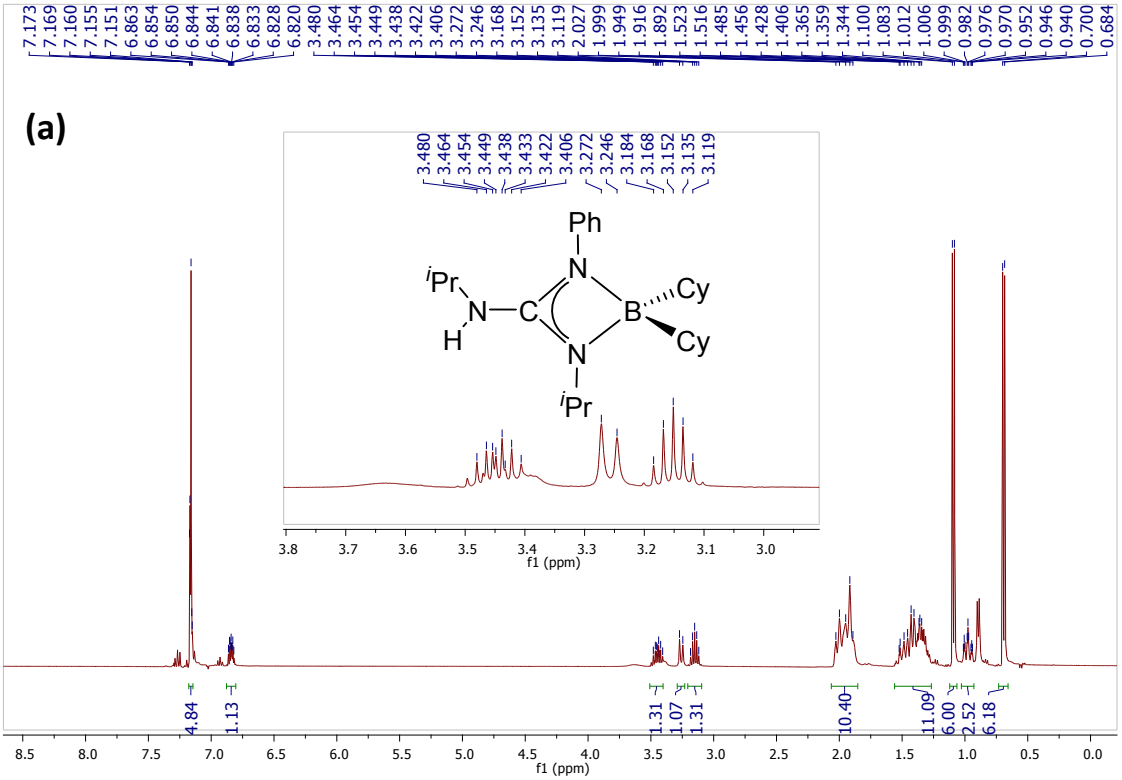
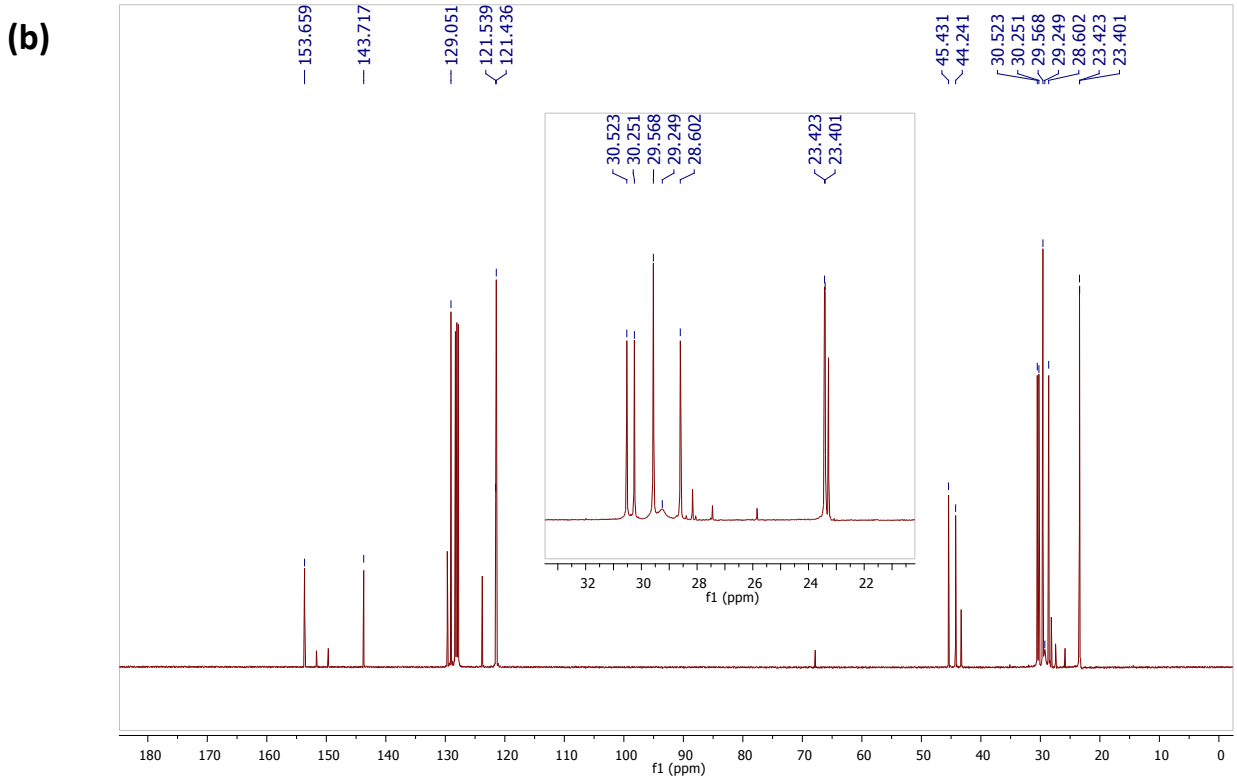
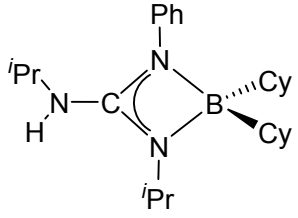


Figure S9. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **5**.


(a)
Ph
N
iPr
N
C
B
Cy
Cy
H
N
iPr
f1 (ppm)


(b)
153.659
143.717
129.051
121.539
121.436
45.431
44.241
30.523
30.251
29.568
29.249
28.602
23.423
23.401
f1 (ppm)


Ph
N
iPr
N
C
B
Cy
Cy
H
N
iPr

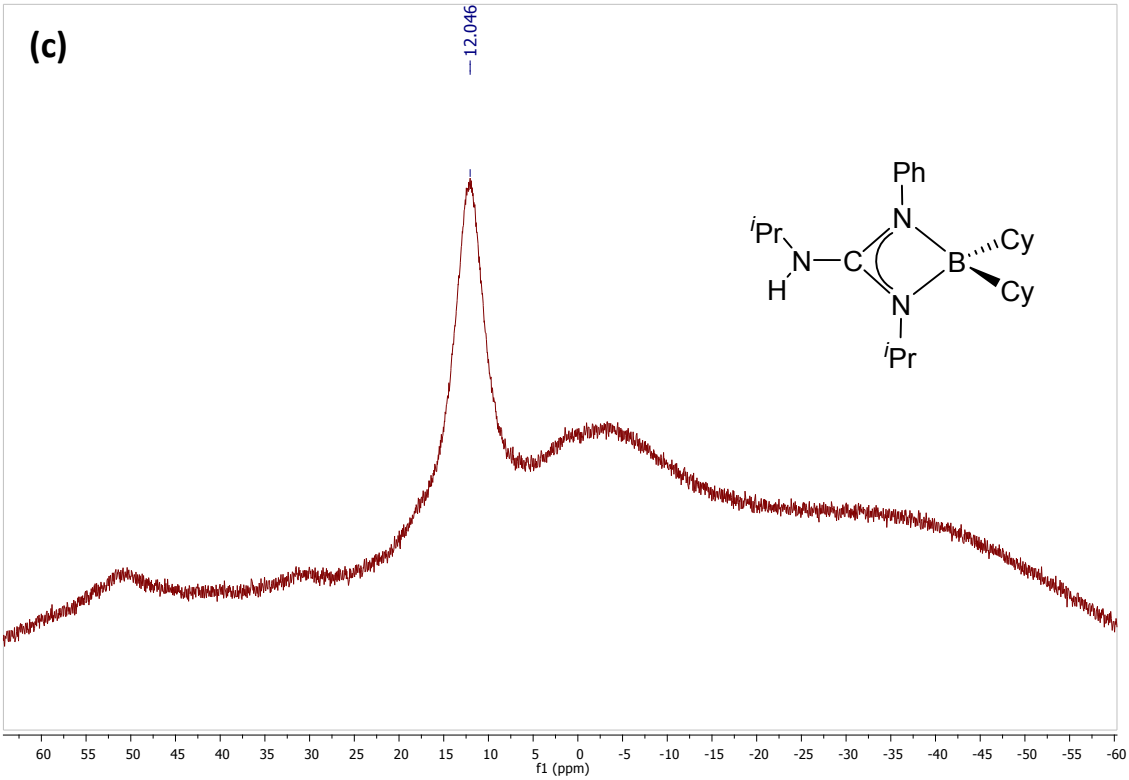
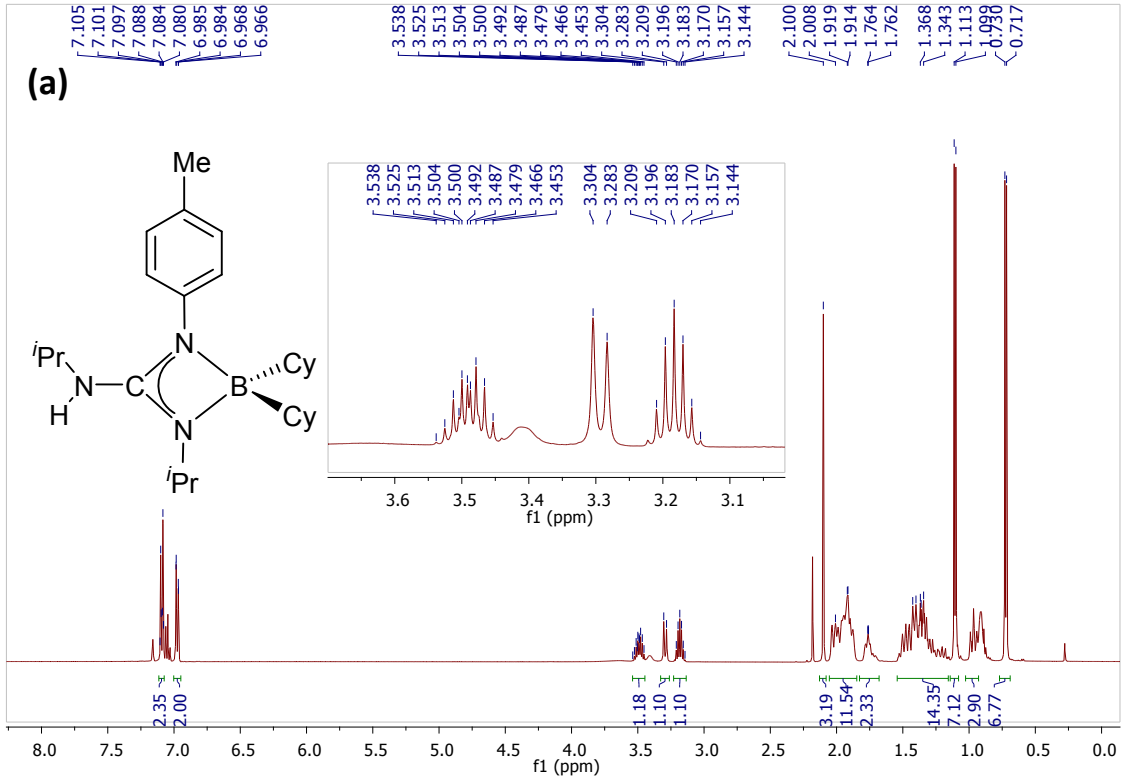
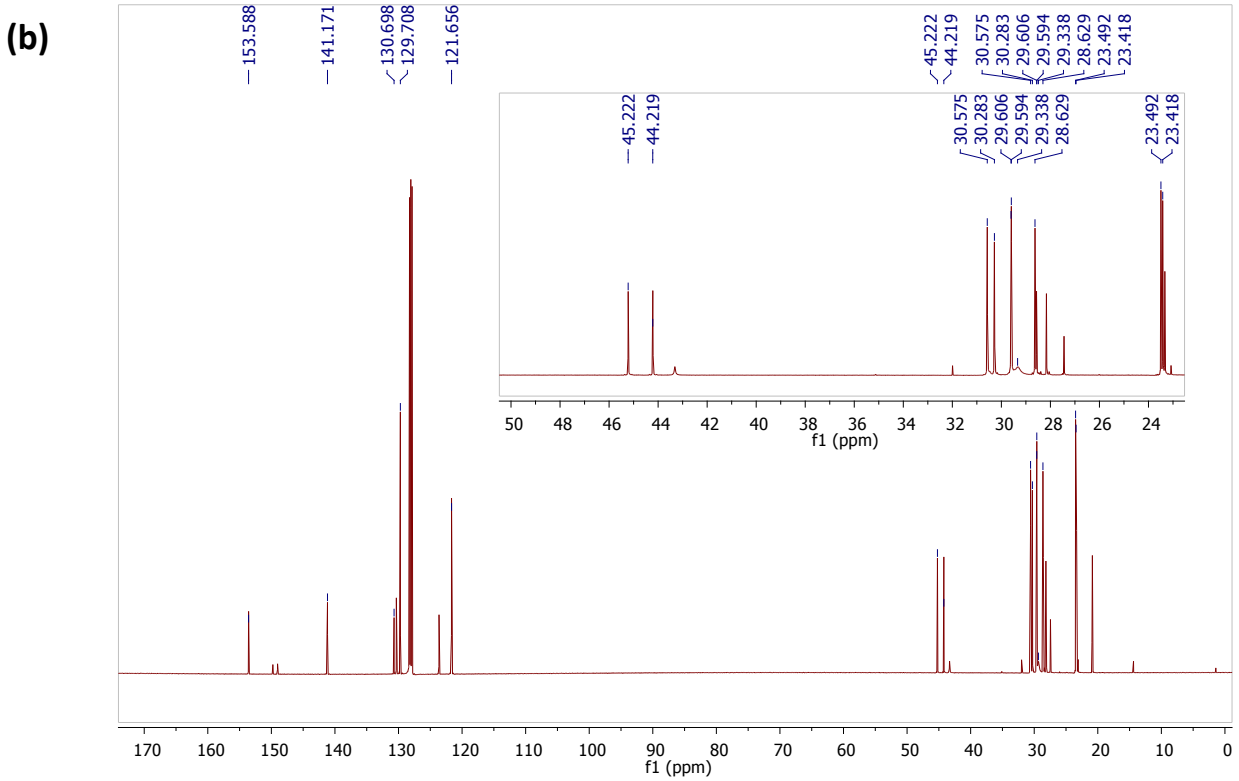
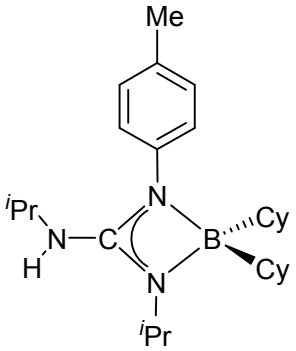


Figure S10. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **6**.


(a)
Me
iPr
N
C
H
N
B
Cy
Cy
N
iPr
f1 (ppm)


(b)
f1 (ppm)


Me
iPr
N
C
H
N
B
Cy
Cy
N
iPr

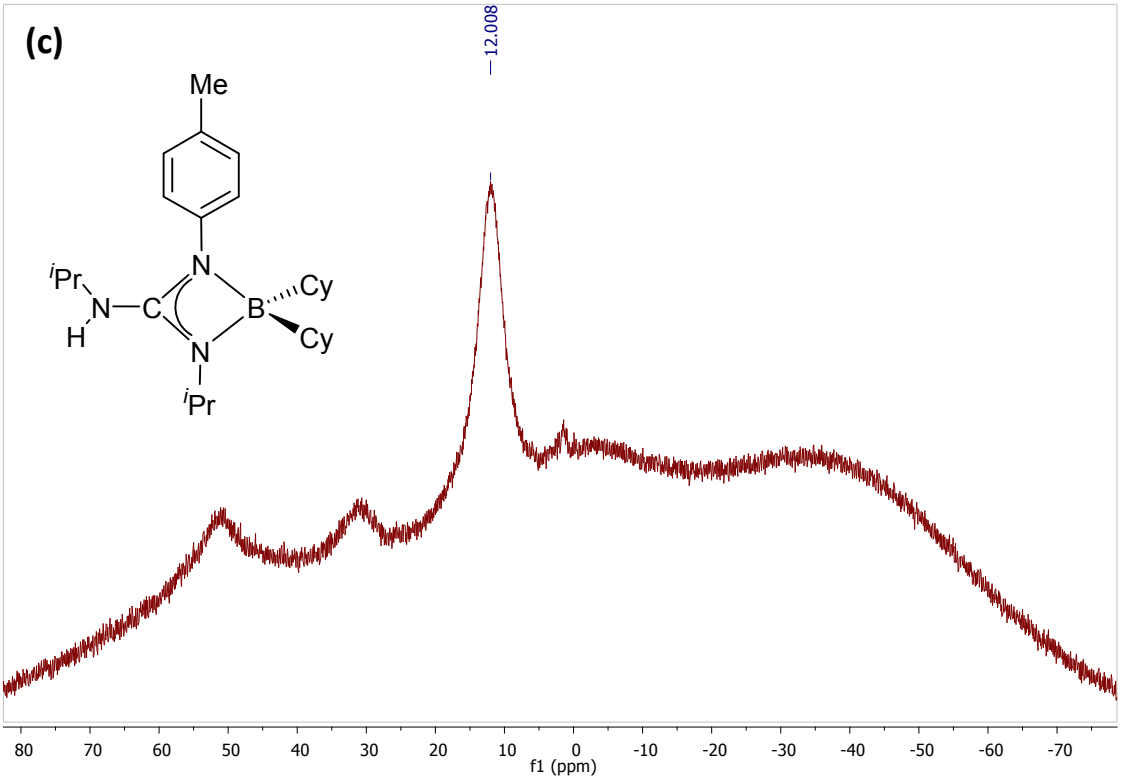
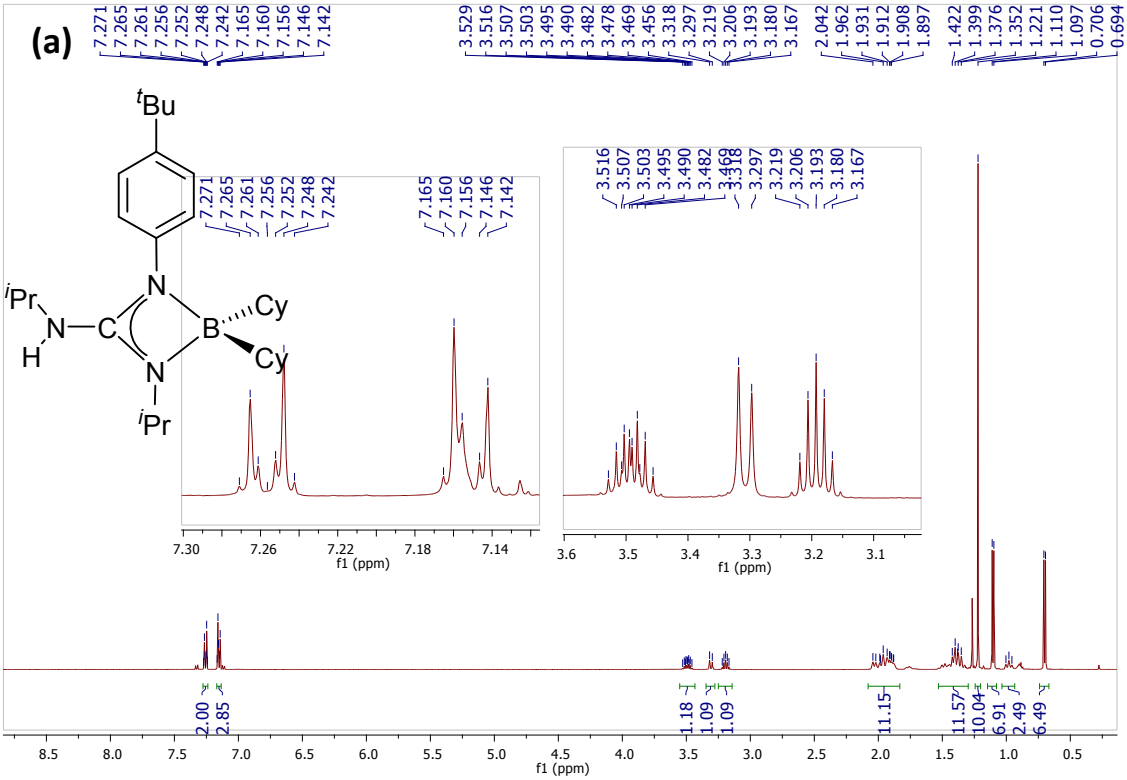
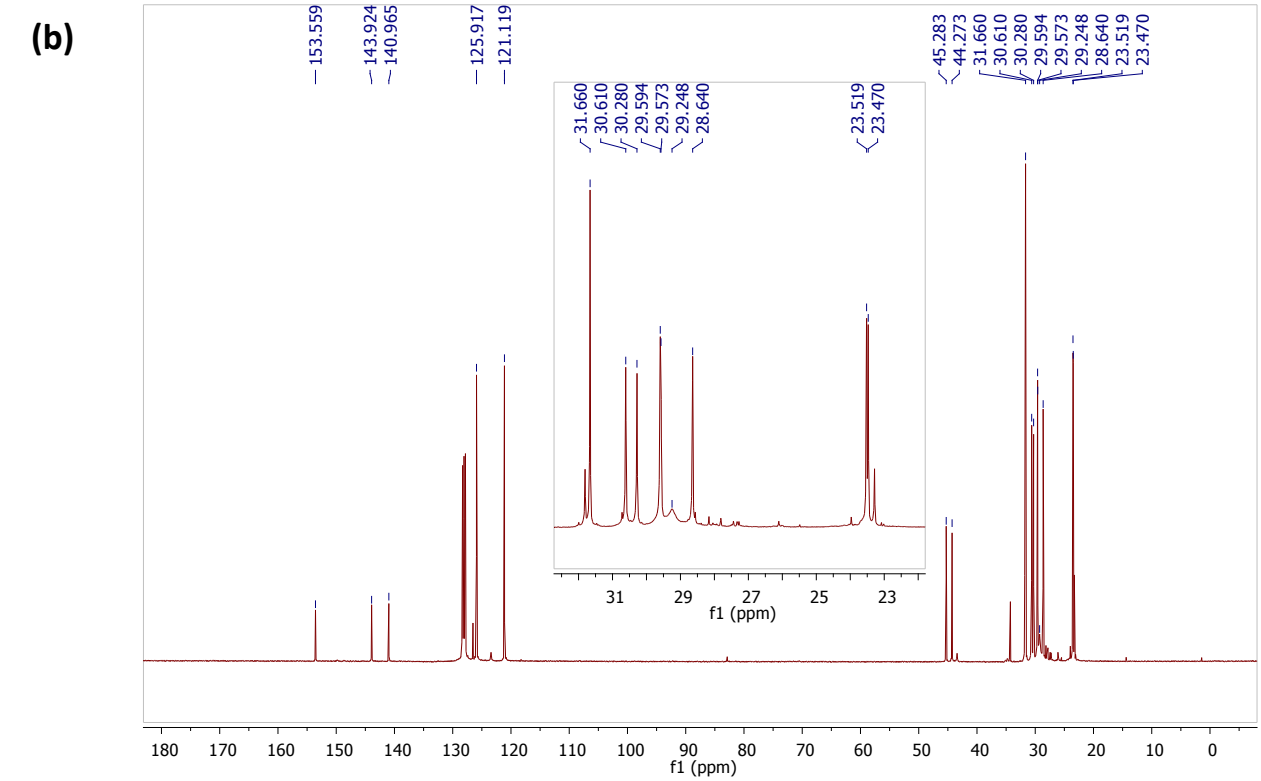
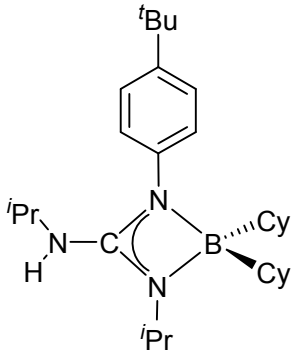


Figure S11. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **7**.


(a)
7.271 7.265 7.261 7.256 7.252 7.248 7.242 7.165 7.160 7.156 7.146 7.142
3.529 3.516 3.507 3.503 3.495 3.490 3.482 3.478 3.469 3.456 3.318 3.297 3.219 3.206 3.193 3.180 3.167
2.042 1.962 1.931 1.912 1.908 1.897 1.422 1.399 1.376 1.352 1.221 1.110 1.097 0.706 0.694
tBu
iPr
N
C
H
B
Cy
Cy
N
iPr
2.00 2.85 1.18 1.09 1.09 11.15 11.57 10.04 6.91 2.49 6.49
f1 (ppm)


(b)
153.559 143.924 140.965 125.917 121.119
45.283 44.273 31.660 30.610 30.280 29.594 29.573 29.248 28.640 23.519 23.470
f1 (ppm)


tBu
iPr
N
C
H
B
Cy
Cy
N
iPr

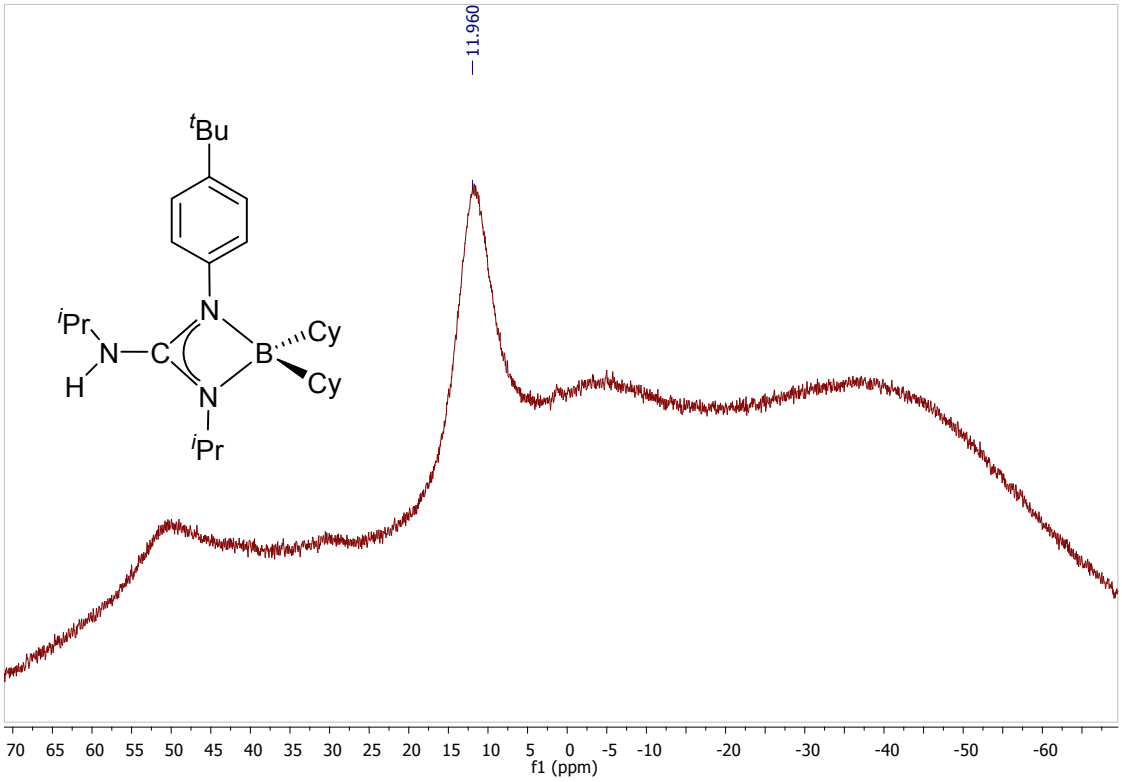
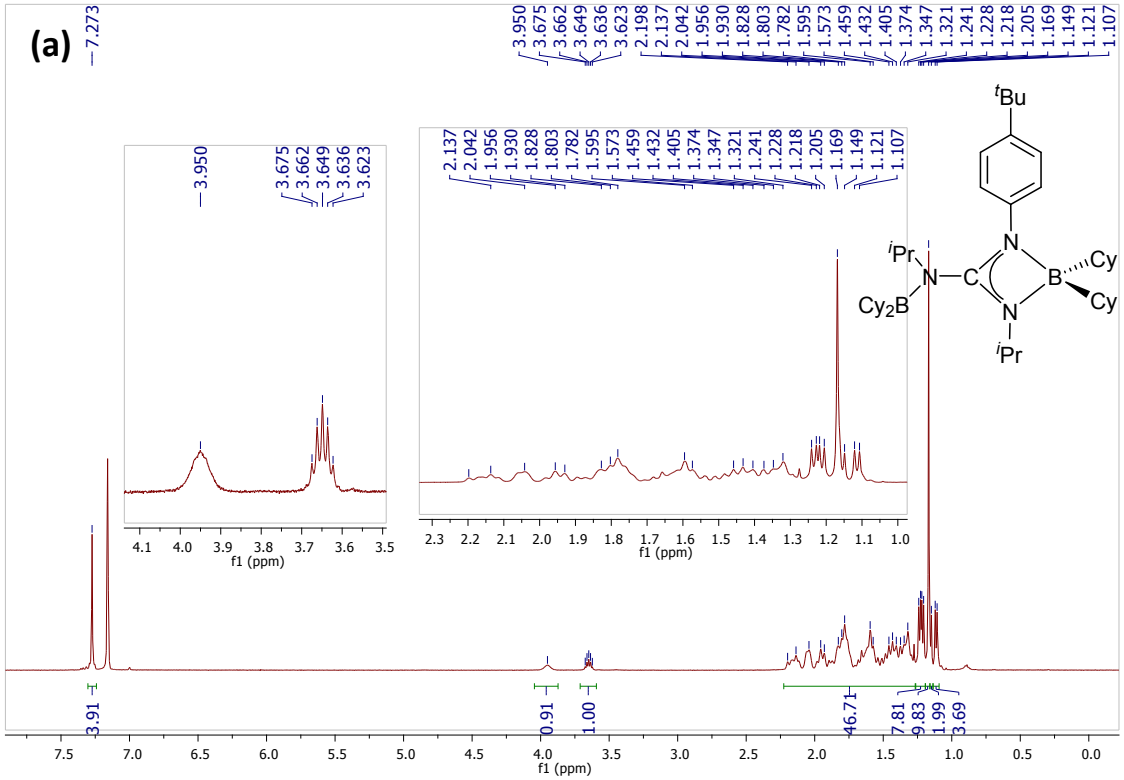
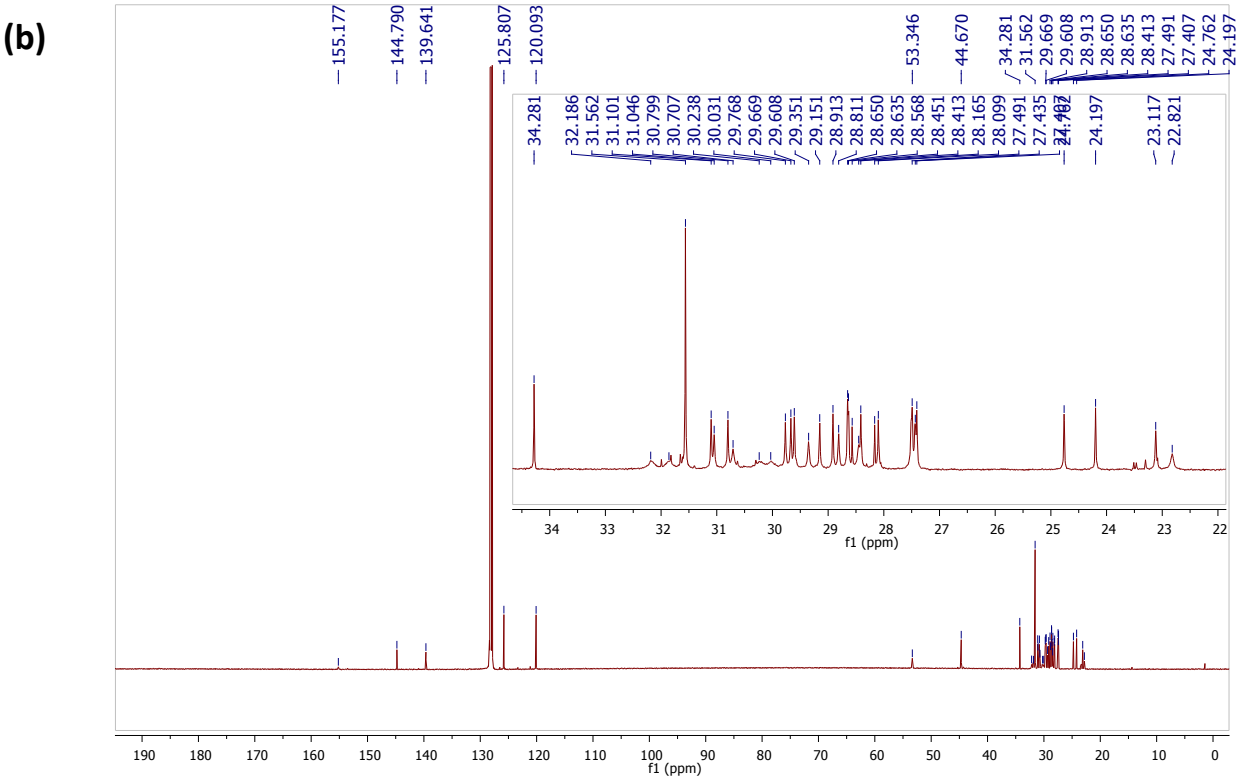
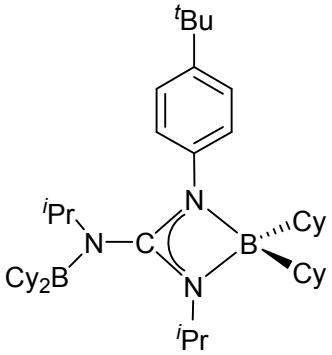


Figure S12. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **8**.


(a)
7.273
3.950
3.675
3.662
3.649
3.636
3.623
2.198
2.137
2.042
1.956
1.930
1.828
1.803
1.782
1.595
1.573
1.459
1.432
1.405
1.374
1.347
1.321
1.241
1.228
1.218
1.205
1.169
1.149
1.121
1.107
tBu
iPr
N
C
B
Cy
Cy2B
f1 (ppm)
3.91
0.91
1.00
46.71
7.81
9.83
1.99
3.69


(b)
155.177
144.790
139.641
125.807
120.093
53.346
44.670
34.281
31.562
29.669
29.608
28.913
28.650
28.635
28.413
27.491
27.407
24.762
24.197
32.186
31.101
31.046
30.799
30.707
30.238
30.031
29.768
29.351
29.151
28.811
28.568
28.451
28.165
28.099
27.435
23.117
22.821
f1 (ppm)


tBu
iPr
N
C
B
Cy
Cy2B
iPr

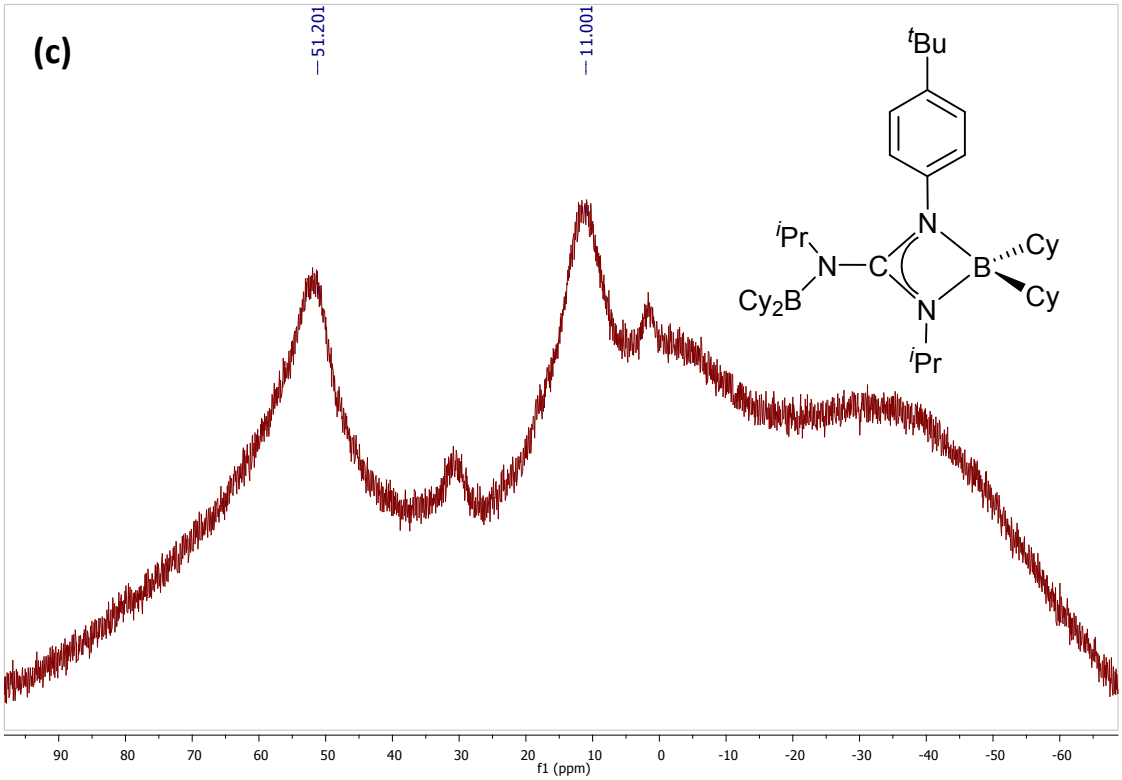
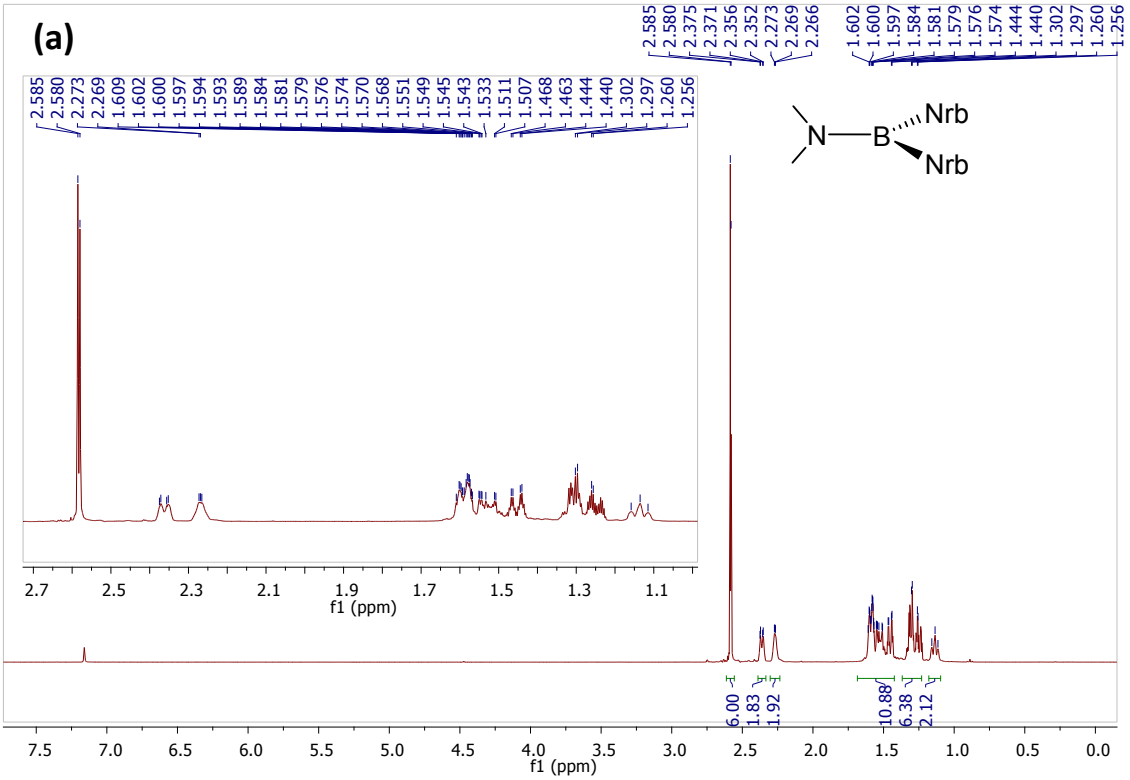
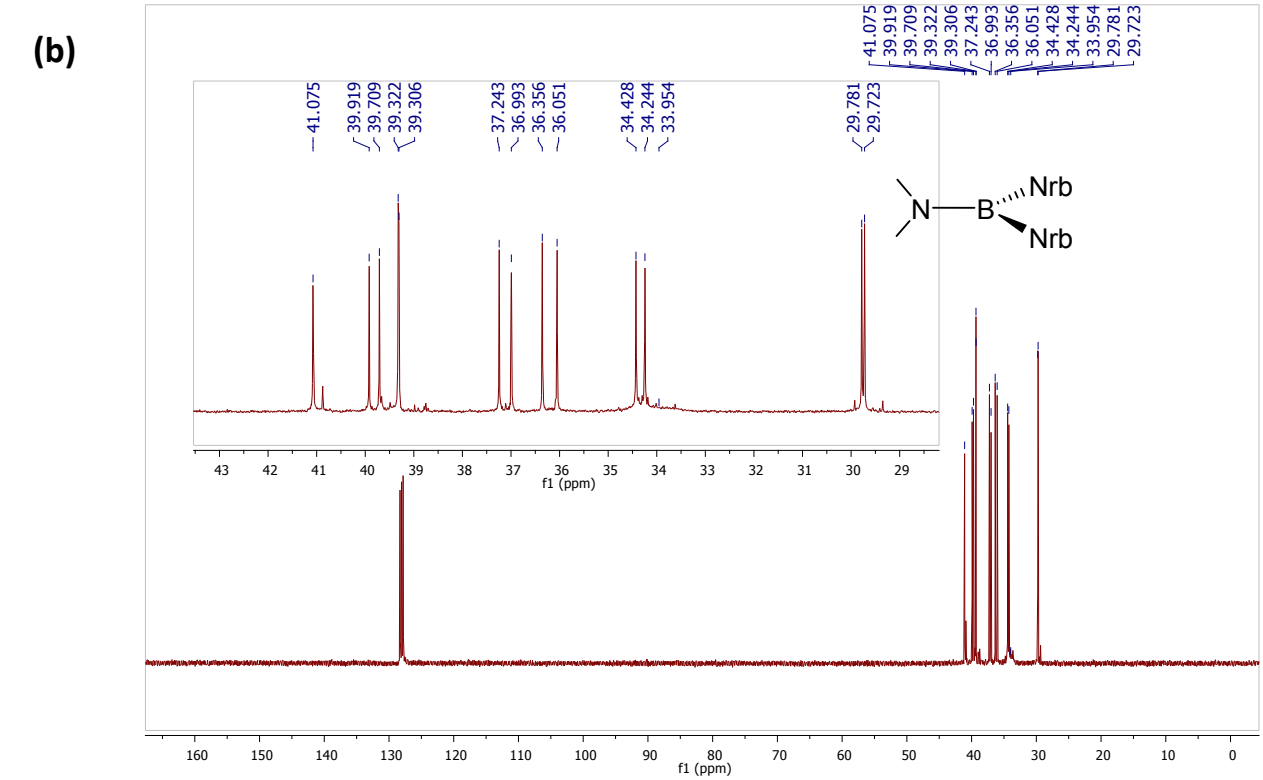


Figure S13. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **9**.


(a)
N
B
Nrb
Nrb
f1 (ppm)


(b)
N
B
Nrb
Nrb
f1 (ppm)

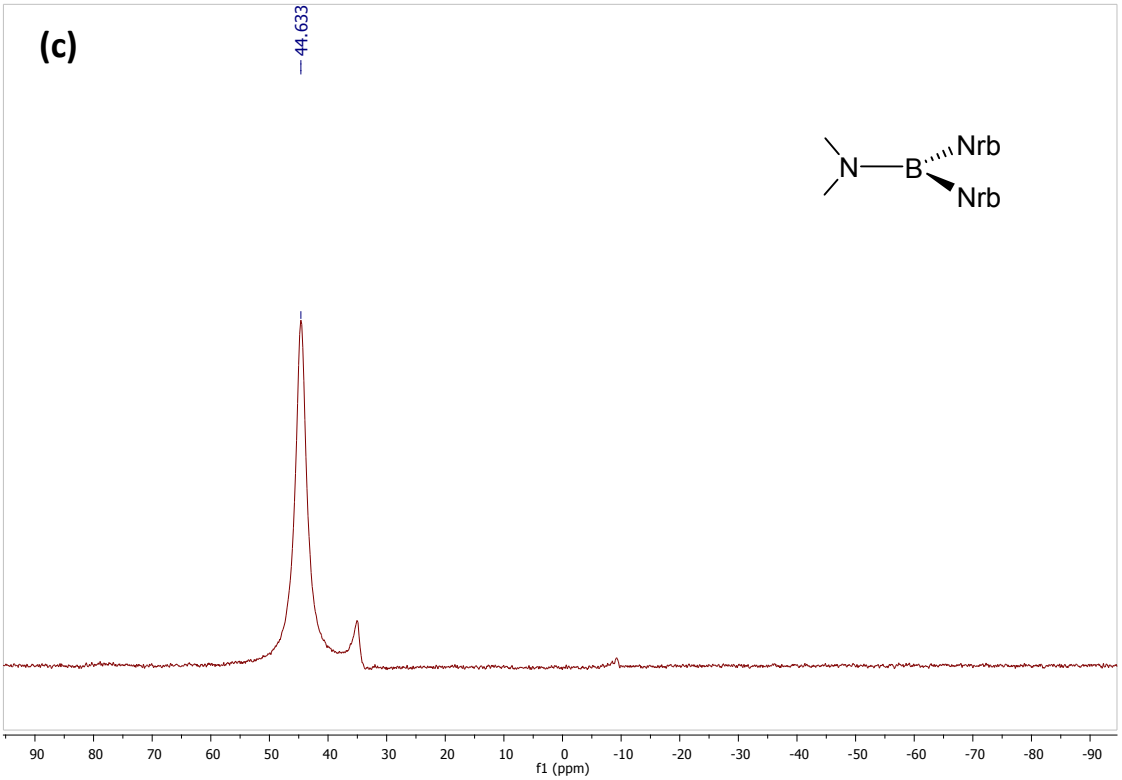
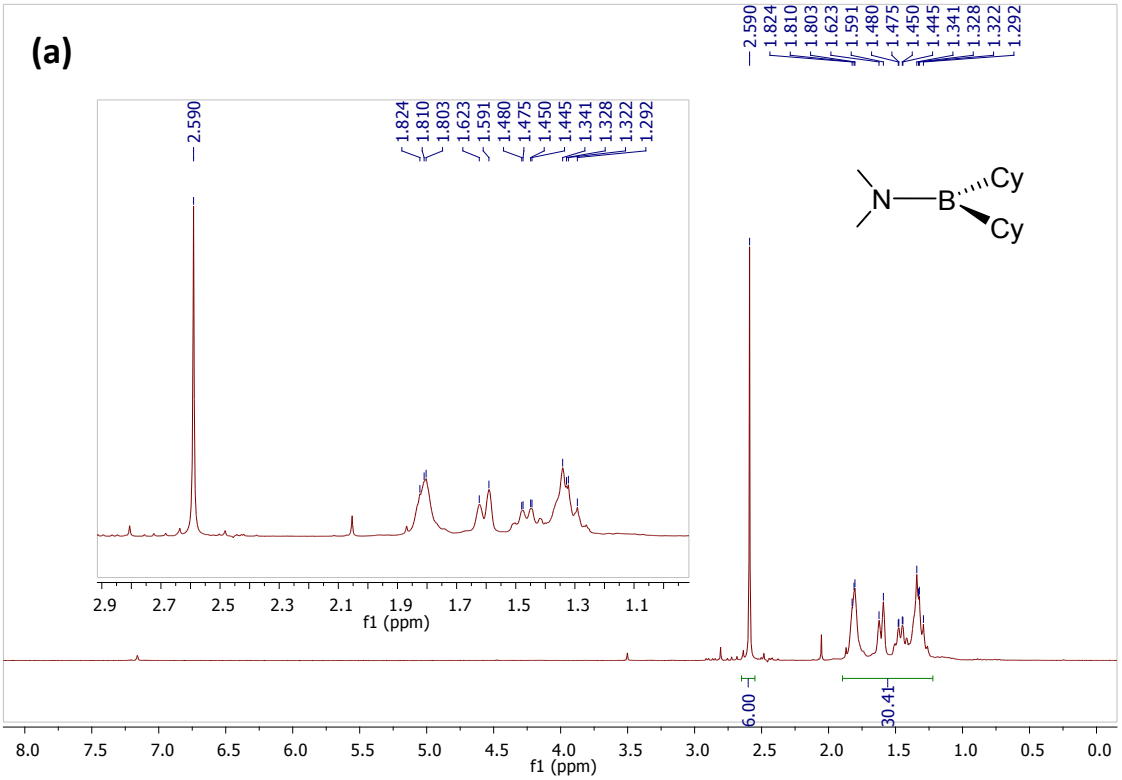
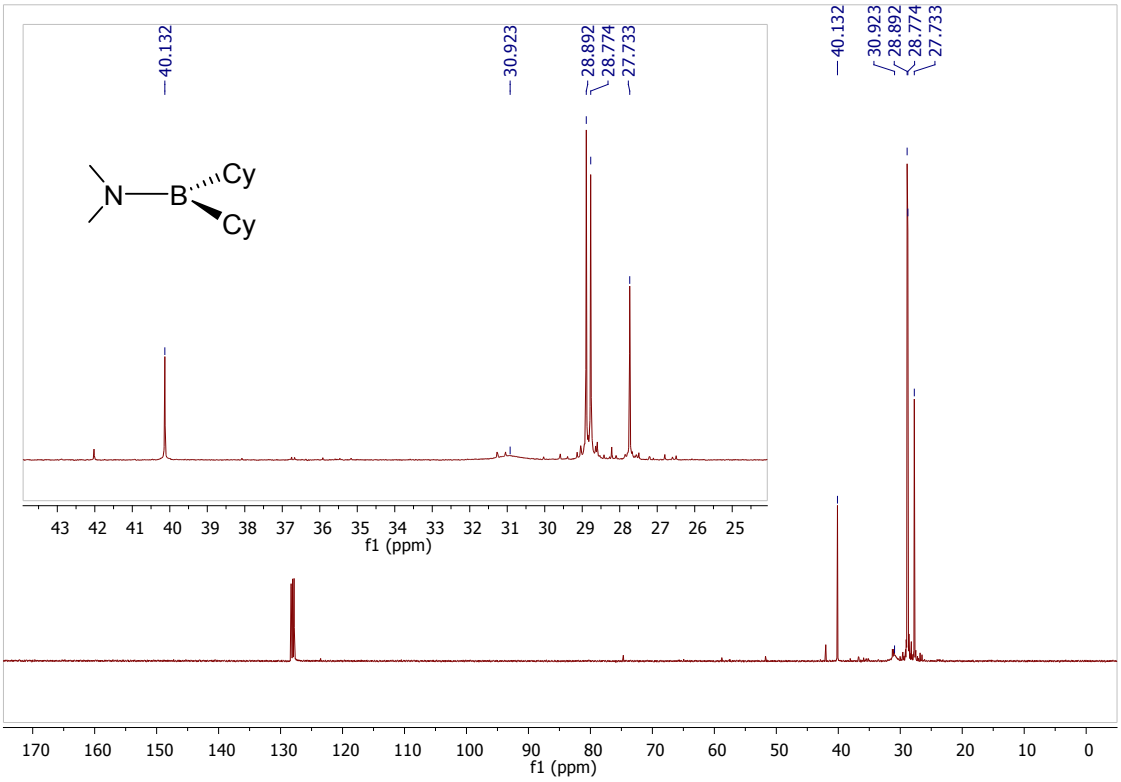


Figure S14. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **10** (diastereomer mixture).

(a)


2.590
1.824
1.810
1.803
1.623
1.591
1.480
1.475
1.450
1.445
1.341
1.328
1.322
1.292
N
B
Cy
Cy
6.00
30.41
f1 (ppm)

(b)


40.132
30.923
28.892
28.774
27.733
N
B
Cy
Cy
f1 (ppm)

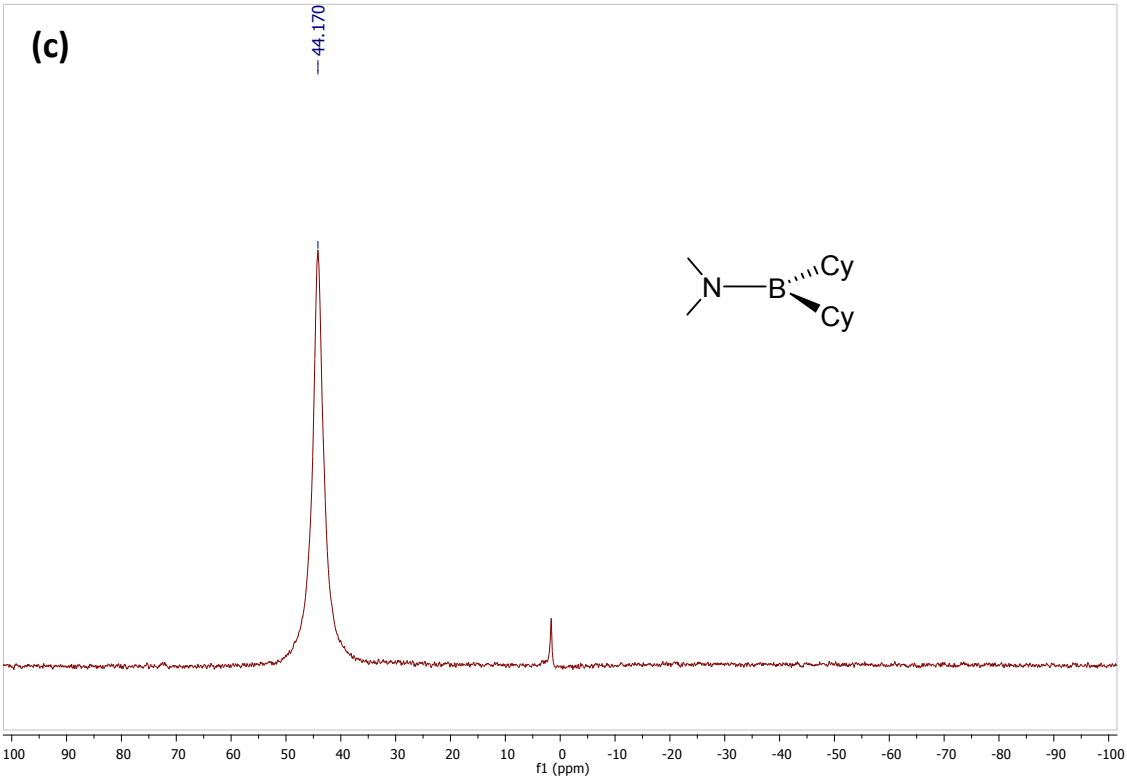


Figure S15. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and ^{11}B (c) NMR spectra for compound **11**.