Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Electrophilic Boron Carboxylate and Phosphinate Complexes

Diya Zhu, James H. W. LaFortune, Rebecca L. Melen and Douglas W. Stephan *

This PDF file includes:

1. Materials and Methods

1.1 General Remarks

All reactions and work-up procedures were performed under an inert atmosphere of dry, oxygen-free N_2 by means of standard Schlenk techniques or glovebox techniques (MBRAUN glovebox equipped with a -35 °C freezer) unless otherwise specified. All glassware was oven-dried and cooled under vacuum before use. Dichloromethane (DCM) were distilled over CaH_2. Pentane was collected from a Grubbs-type column system manufactured by Innovative Technology and degassed. Solvents were stored over activated 4 Å molecular sieves. Molecular sieves, type 4 Å (pellets, 3.2 mm diameter) purchased from Sigma Aldrich were activated prior to usage by iteratively heating under vacuum for 24 hours. $CDCl_3$ purchased from Cambridge Isotope Laboratories was vacuum distilled, further degassed, and stored over activated 4 Å molecular sieves in the glovebox for at least 8 hours prior to use. Unless otherwise mentioned, chemicals were purchased from Sigma Aldrich or TCI. Lancaster's reagent and Piers' borane were prepared using literature methods.[1,2] NMR spectra were recorded at room temperature (298 K) unless otherwise mentioned on a Bruker Avance III 400 MHz, an Agilent DD2 400, and an Agilent DD2 500. Spectra were referenced to the residual solvent signals ($CDCl_3$: ^{1}H= 7.26; ^{13}C = 77.2 ppm. Toluene-*d8*: ^{1}H= 7.09, 7.01, 6.97, and 2.08 ppm; ^{13}C = 137.48, 128.87, 127.96, 125.13, and 20.43 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are listed as absolute values in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), overlapping (ov), and broad (br). High-resolution mass spectra (HRMS) were obtained on a JMS-T100LC JOEL DART mass spectrometer. Elemental analyses for C, H, and N were performed by ANALEST (University of Toronto) employing a Perkin Elmer 2400 Series II CHNS Analyser.

1.2 X-ray Diffraction Studies

Single crystals were coated with paratone oil, mounted on a cryoloop and frozen under a stream of cold nitrogen. Data were collected on a Bruker Apex2 X-ray diffractometer at 150(2) K for all crystals using graphite monochromated Mo-Kα radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

(1) Fuller, A. -M.; Hughes, D. L.; Lancaster, S. J.; White, C. M. *Organometallics* 2010, **29**, 2194-2197.

(2) Longobardi, L. E.; Johnstone, T. C.; Falconer, R. L.; Russell, C. A.; Stephan, D. W. *Chem. Eur. J.* 2016, **22**, 12665-12669. Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* 1998, **17**, 5492–5503.

1. Synthesis and Characterisation

2.1 [TolC(O)OB(C_6F_5)]$_2$O (1)

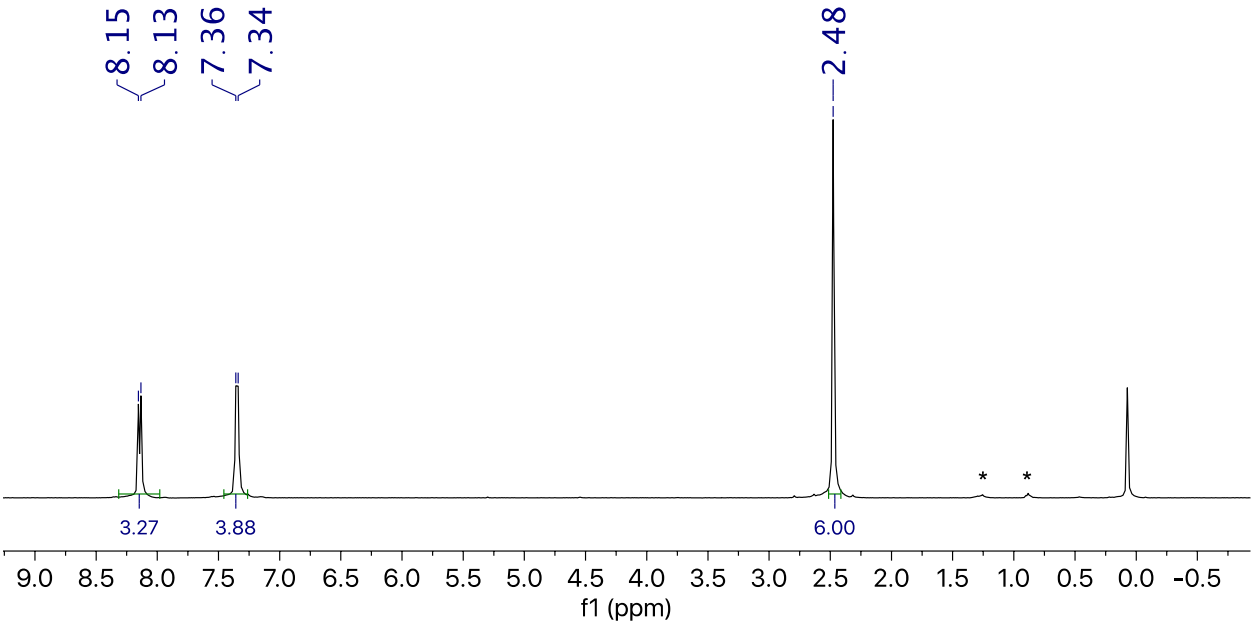


Figure S1. ^{1}H NMR spectrum of **1** ($CDCl_3$). Asterisks denote solvent impurities.

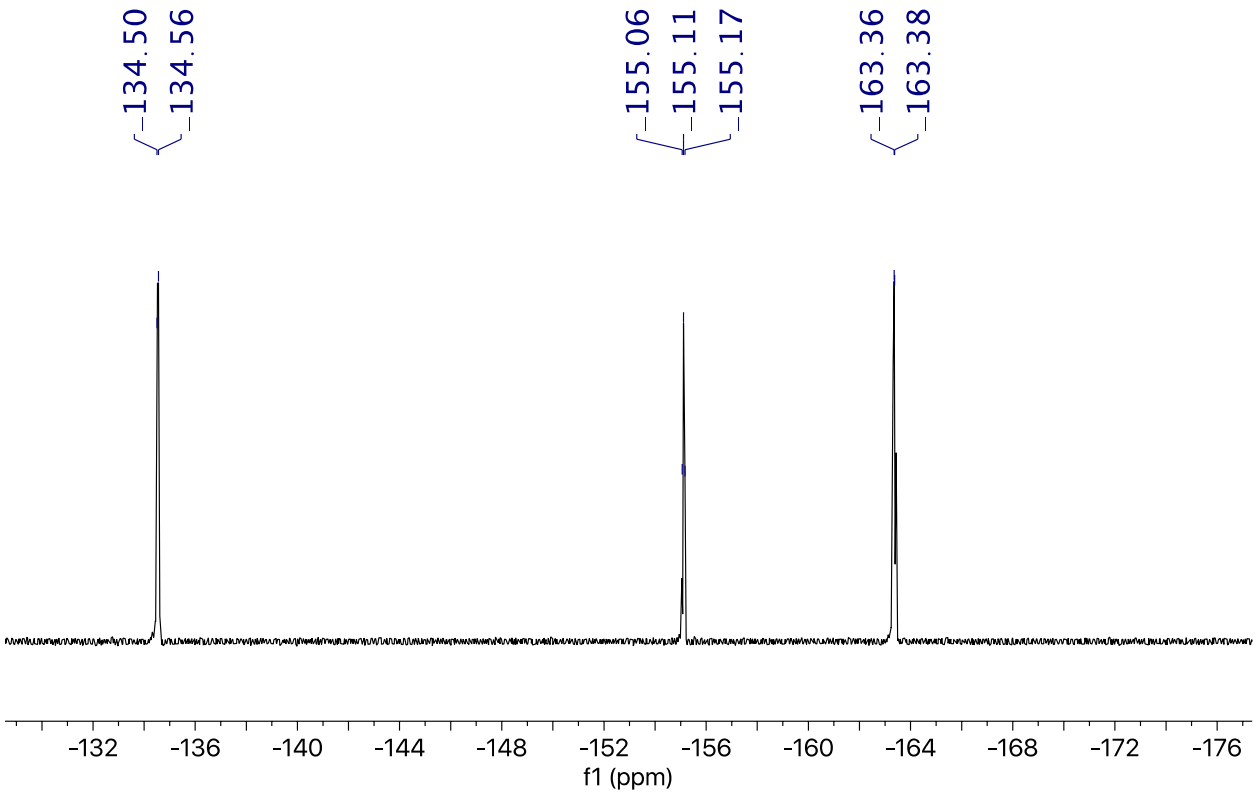


Figure S2. $^{19}F\{^{1}H\}$ NMR spectrum of **1** ($CDCl_3$).

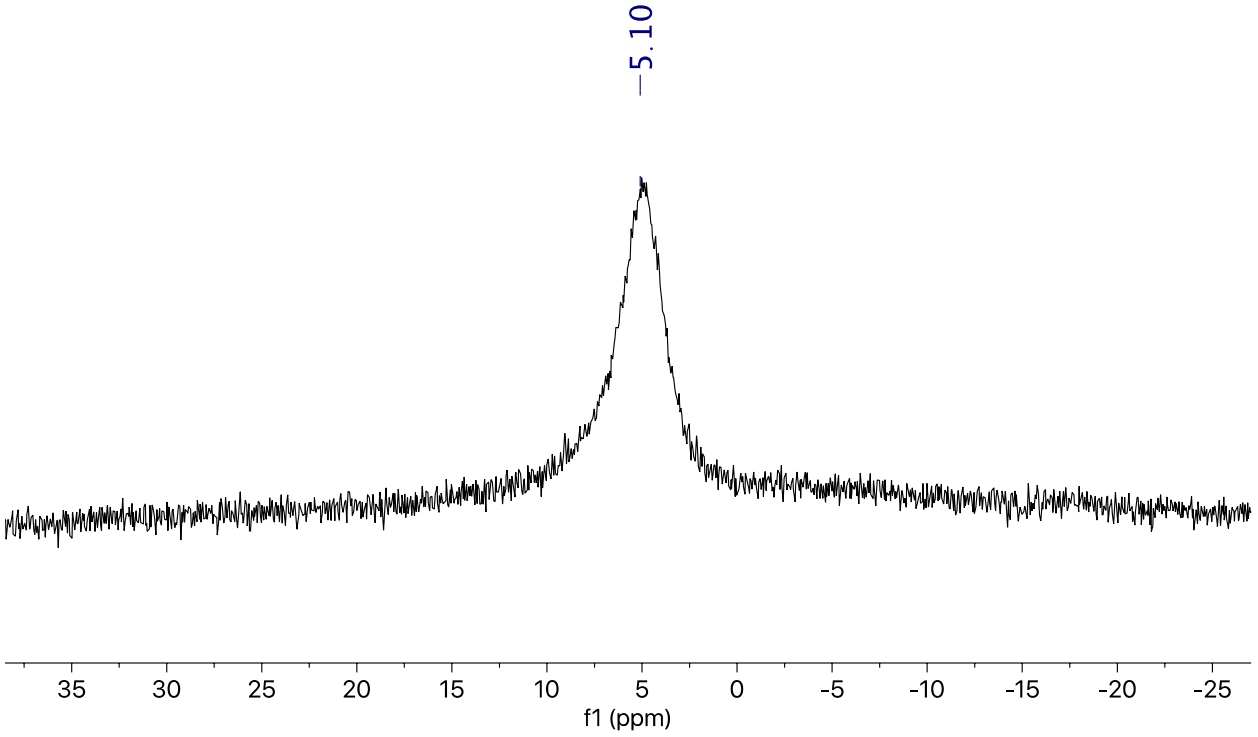


Figure S3. ^{11}B NMR spectrum of **1** ($CDCl_3$).

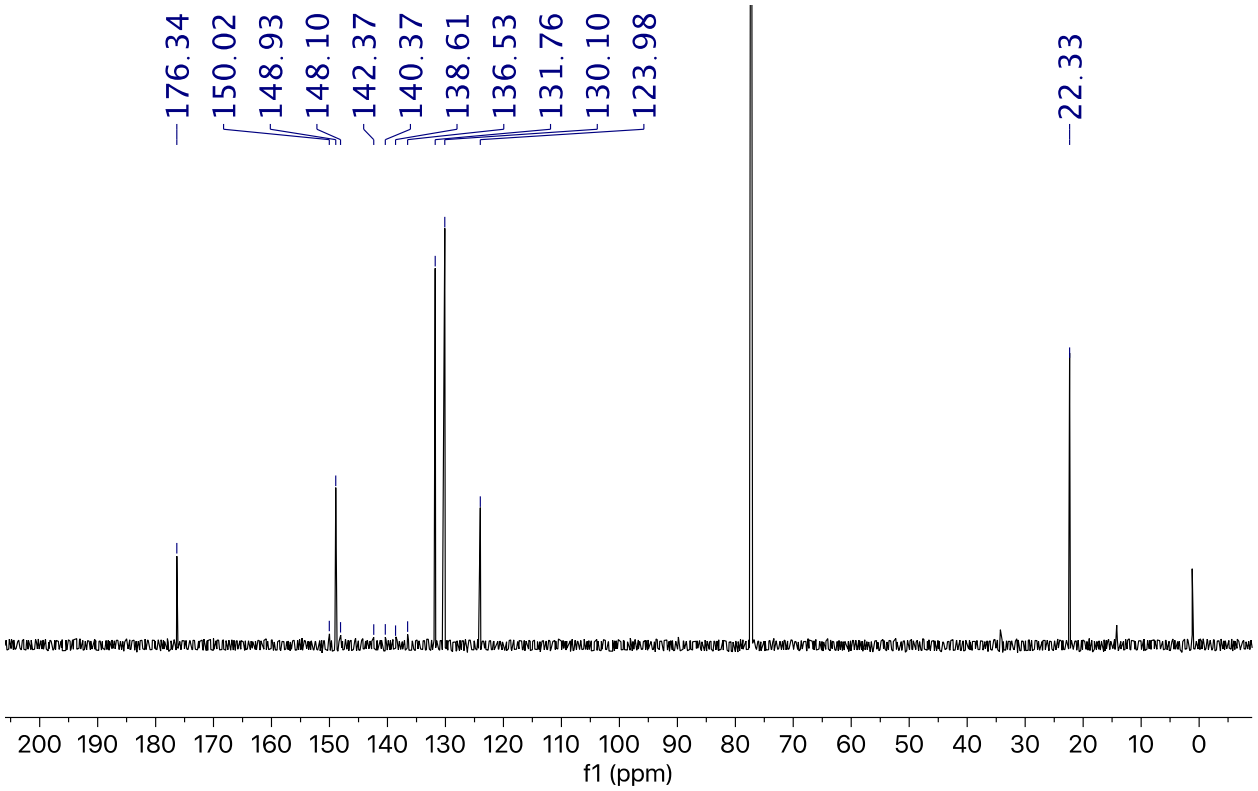


Figure S4. $^{13}C\{^1H\}$ NMR spectrum of **1** ($CDCl_3$).

2.2 [PhC(O)OB(C_6F_5)]$_2$O (2)

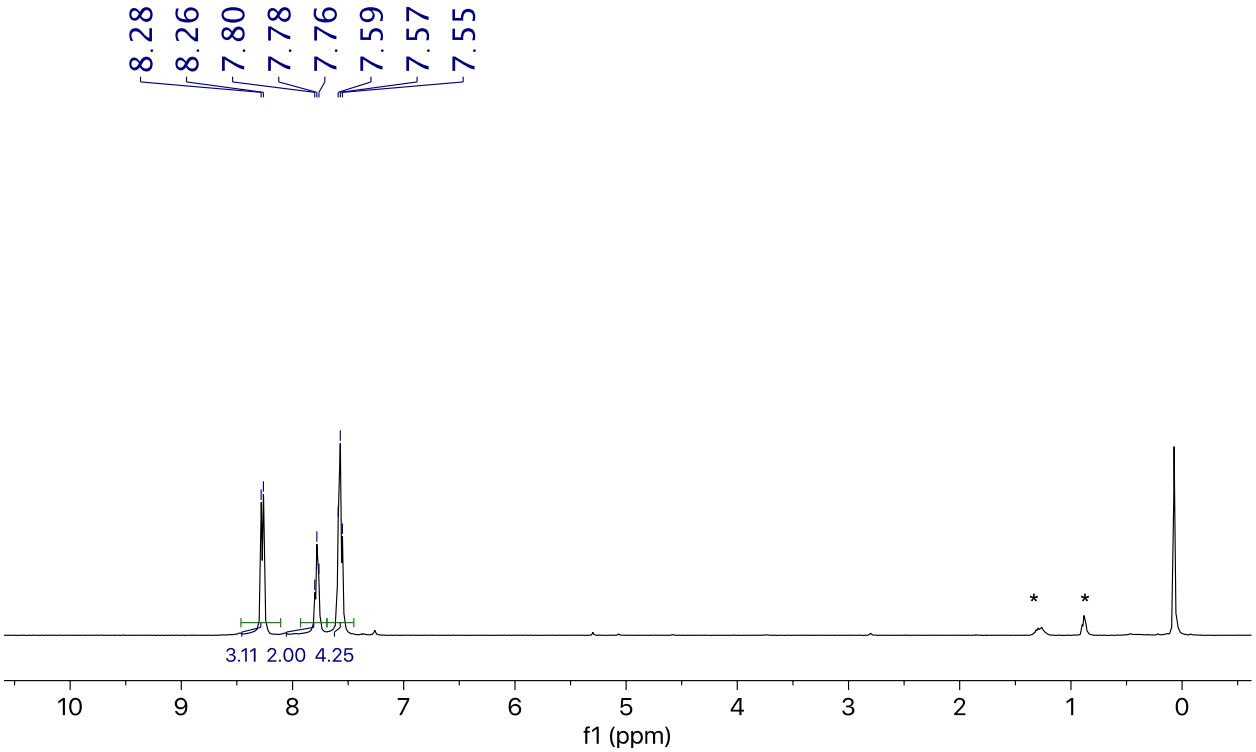


Figure S5. ^{1}H NMR spectrum of **2** ($CDCl_3$). Asterisks denote solvent impurities.

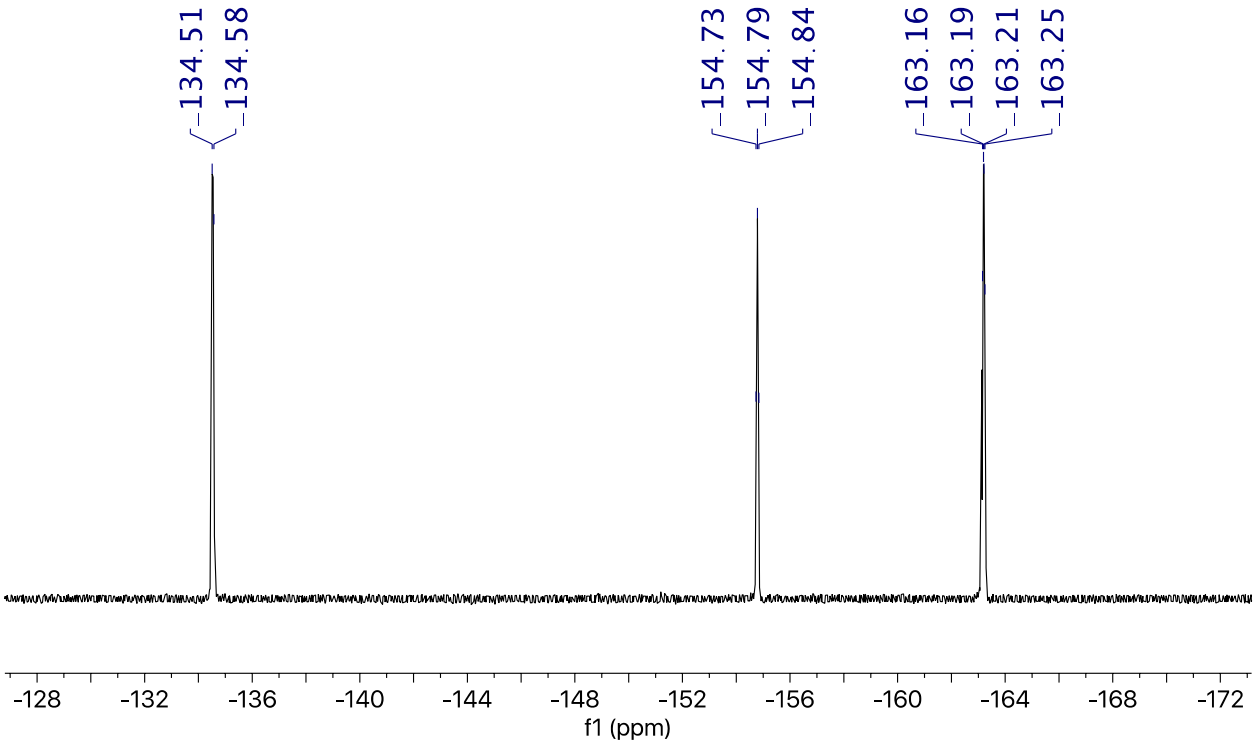


Figure S6. $^{19}F\{^{1}H\}$ NMR spectrum of **2** ($CDCl_3$).

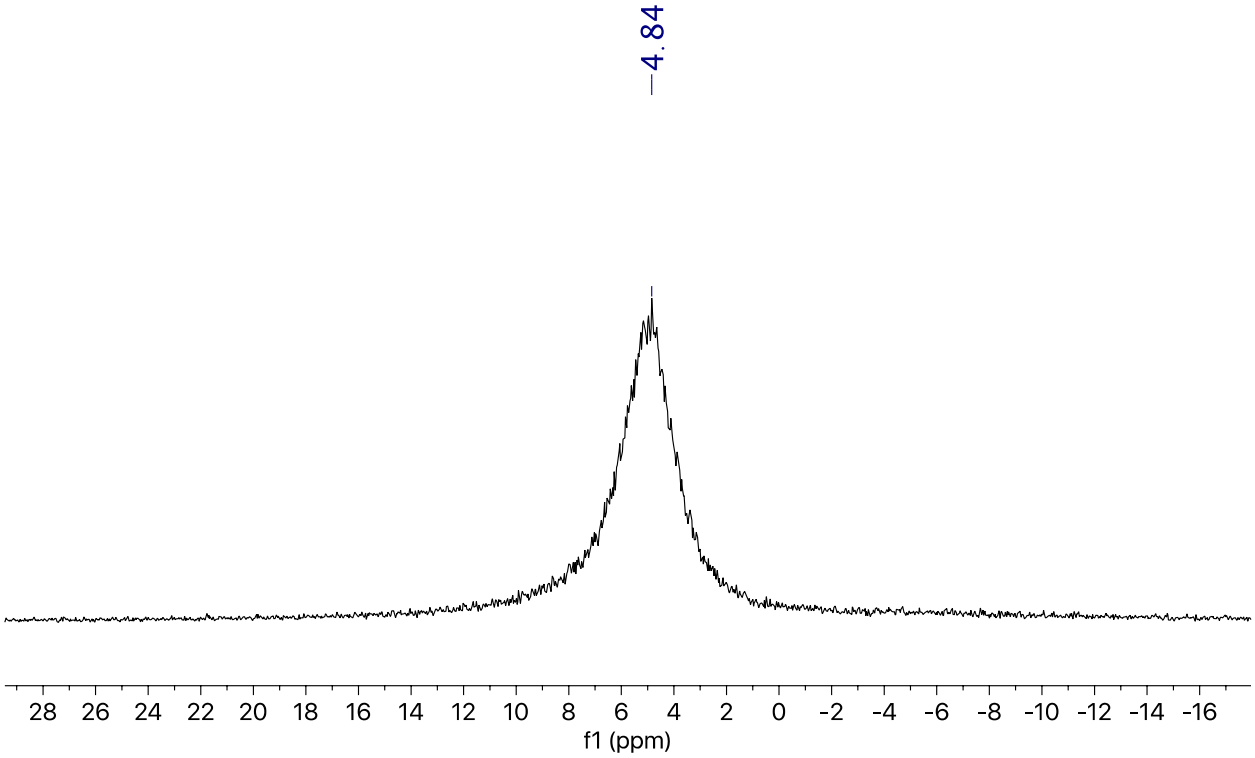


Figure S7. ^{11}B NMR spectrum of **2** ($CDCl_3$).

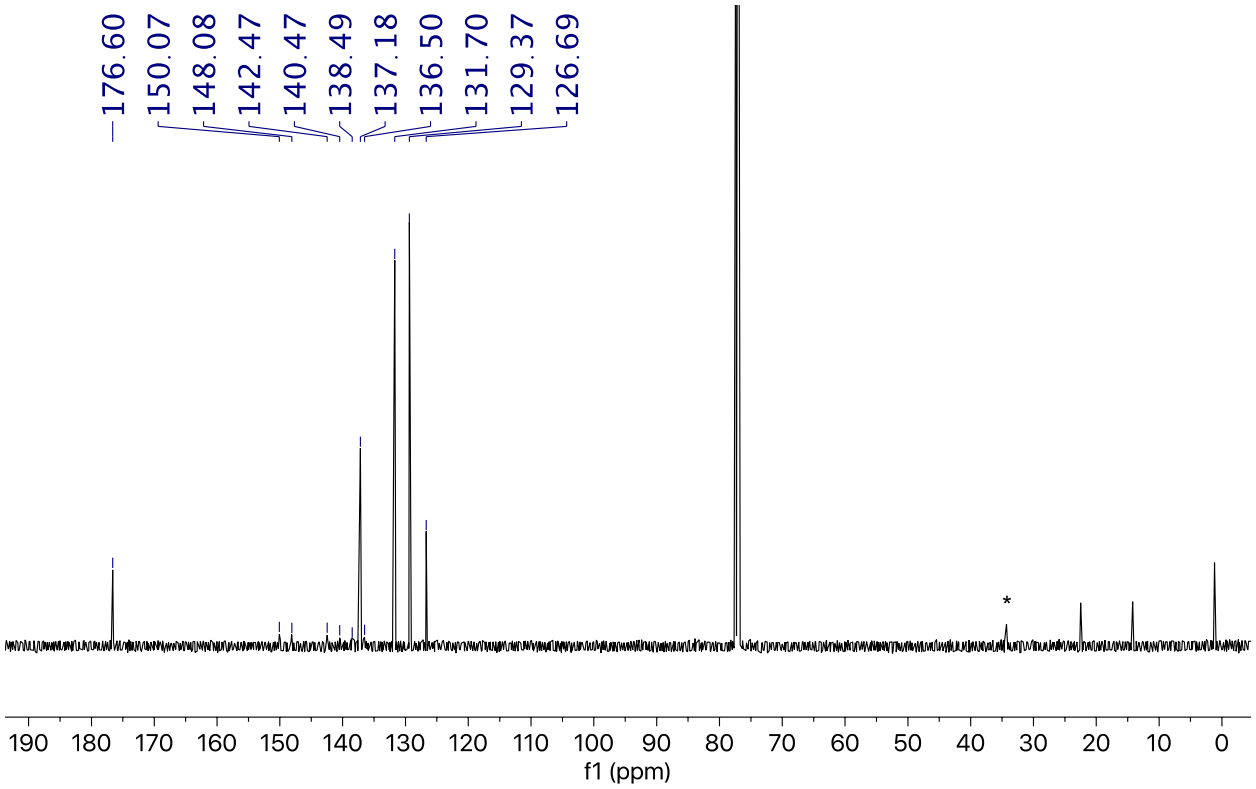


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **2** ($CDCl_3$). Asterisks denote solvent impurities.

2.3 [(C$_6$F$_5$)C(O)OB(C$_6$F$_5$)]$_2$O (3)

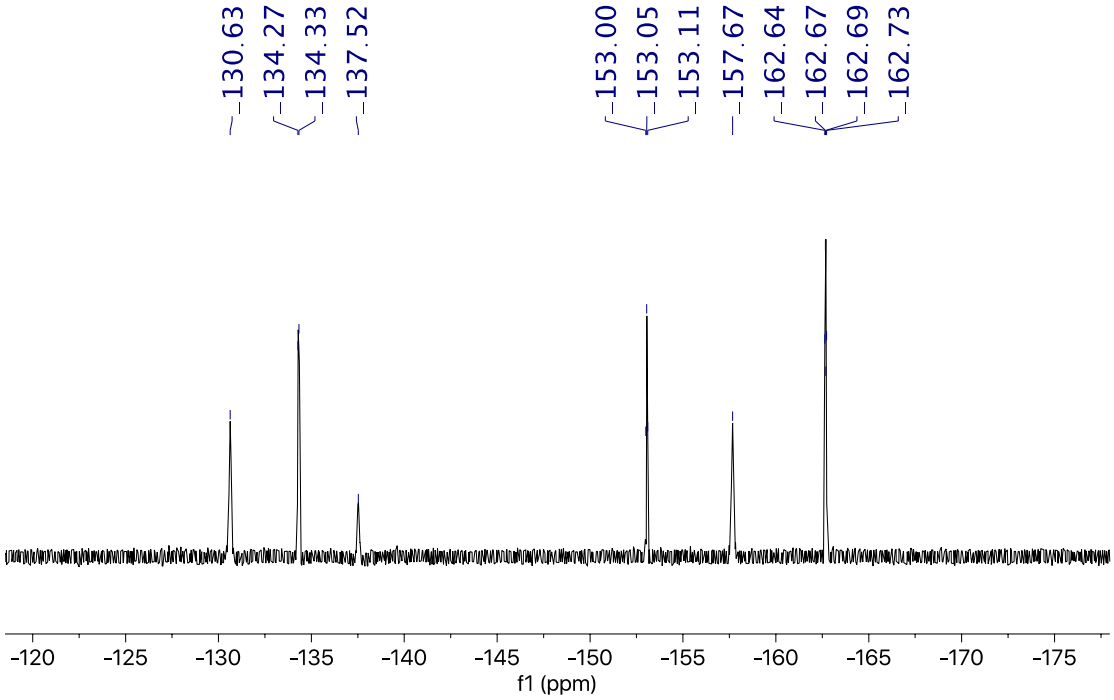


Figure S9. $^{19}F\{^{1}H\}$ NMR spectrum of **3** (toluene-*d8*).

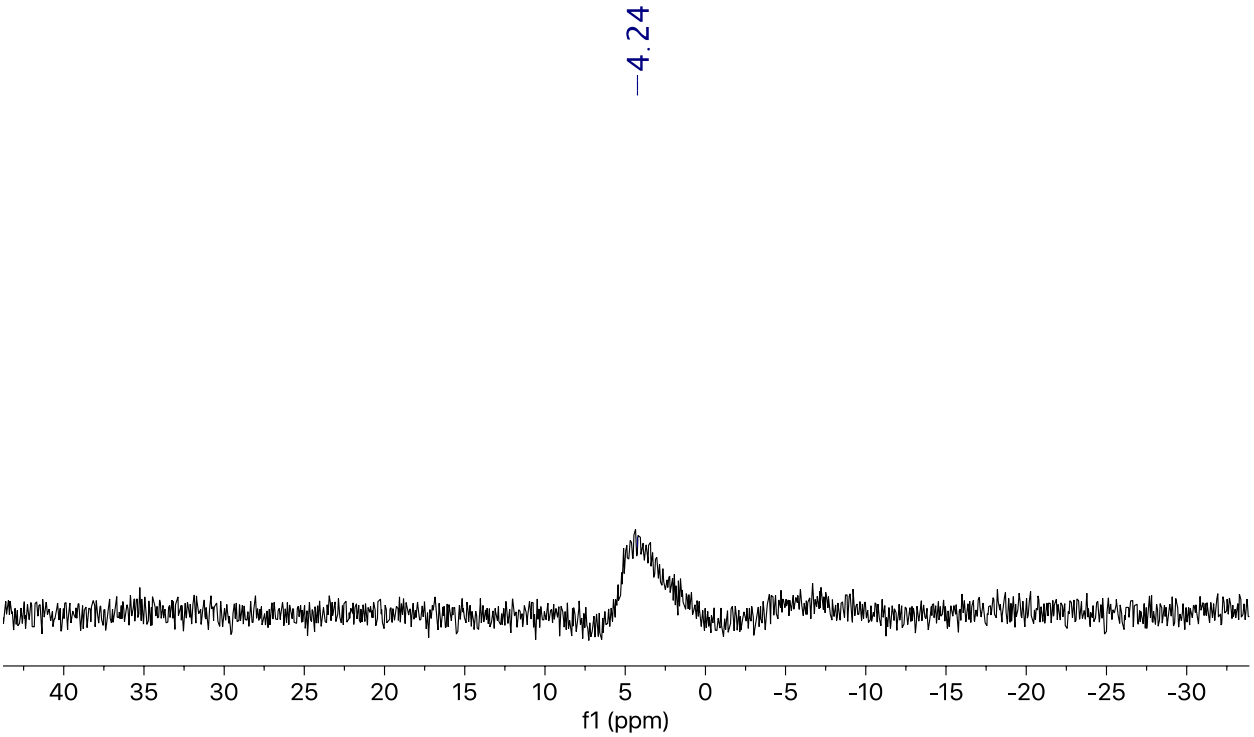


Figure S10. ^{11}B NMR spectrum of **3** (toluene-*d8*).

2.4 [(Me$_2$Br)C(O)OB(C$_6$F$_5$)]$_2$O (4)

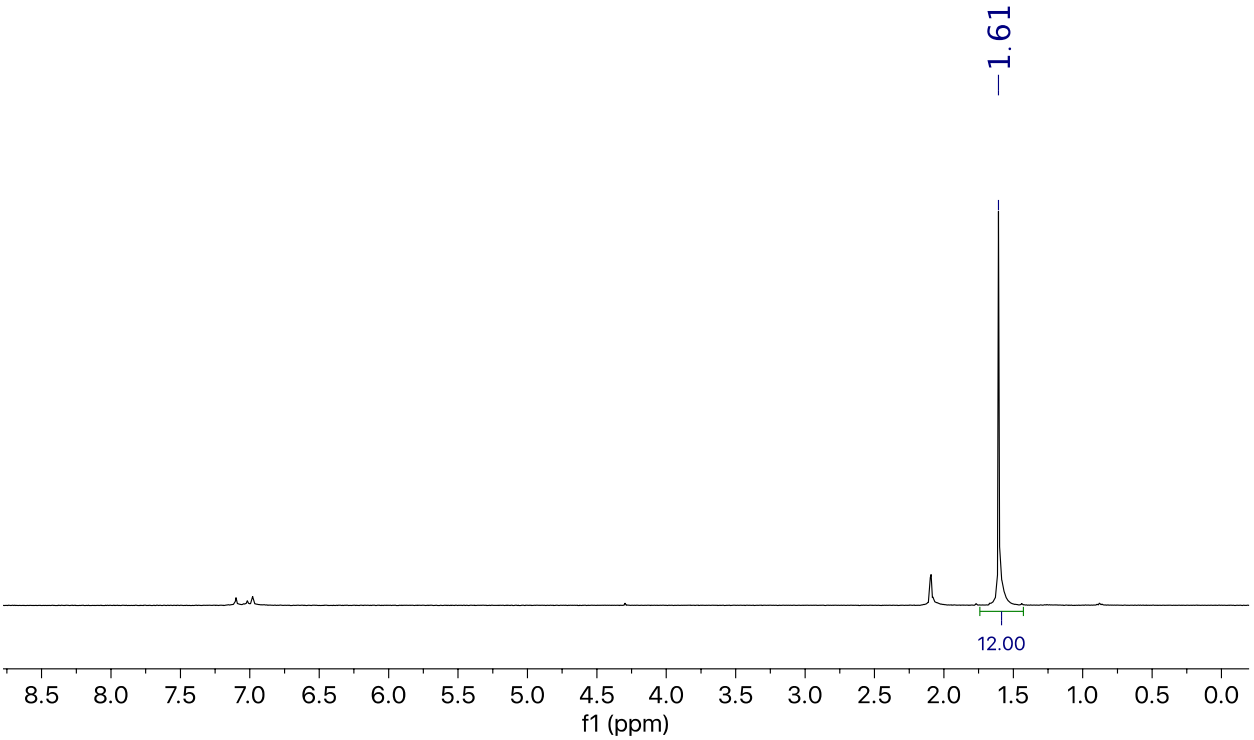


Figure S11. ^{1}H NMR spectrum of **4** (toluene-*d8*).

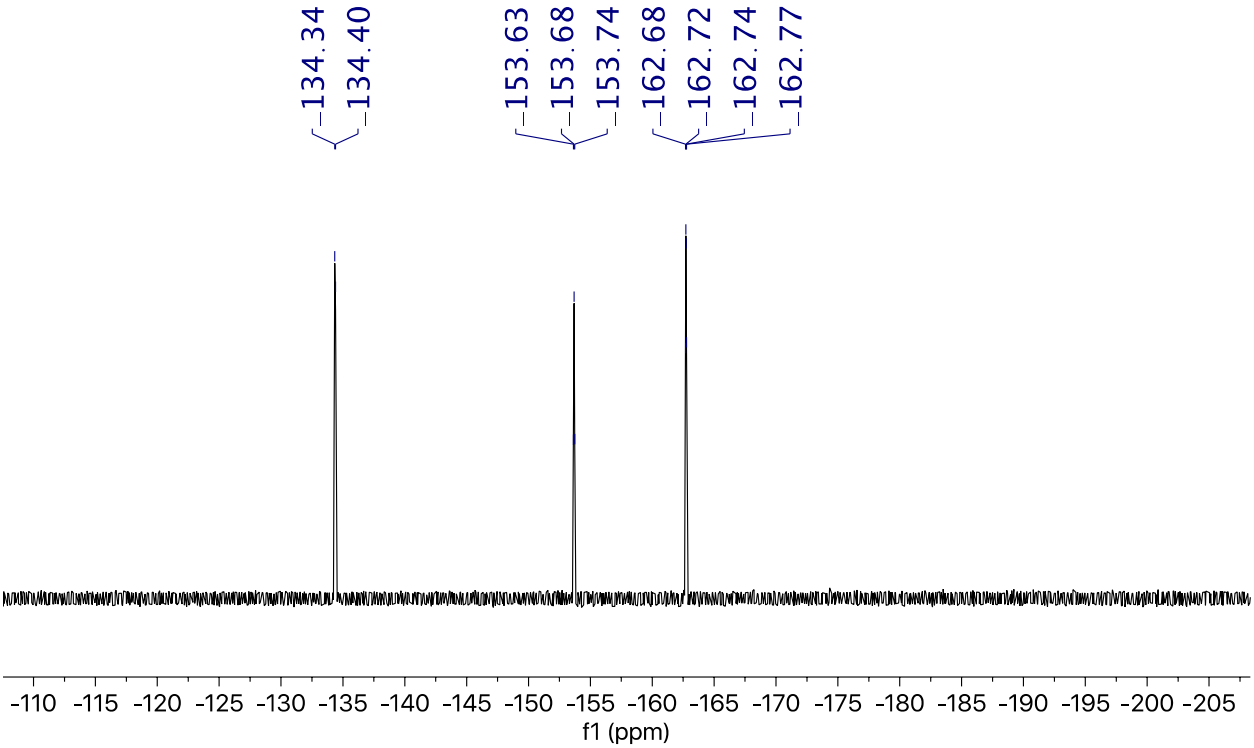


Figure S12. $^{19}F\{^{1}H\}$ NMR spectrum of **4** (toluene-*d8*).

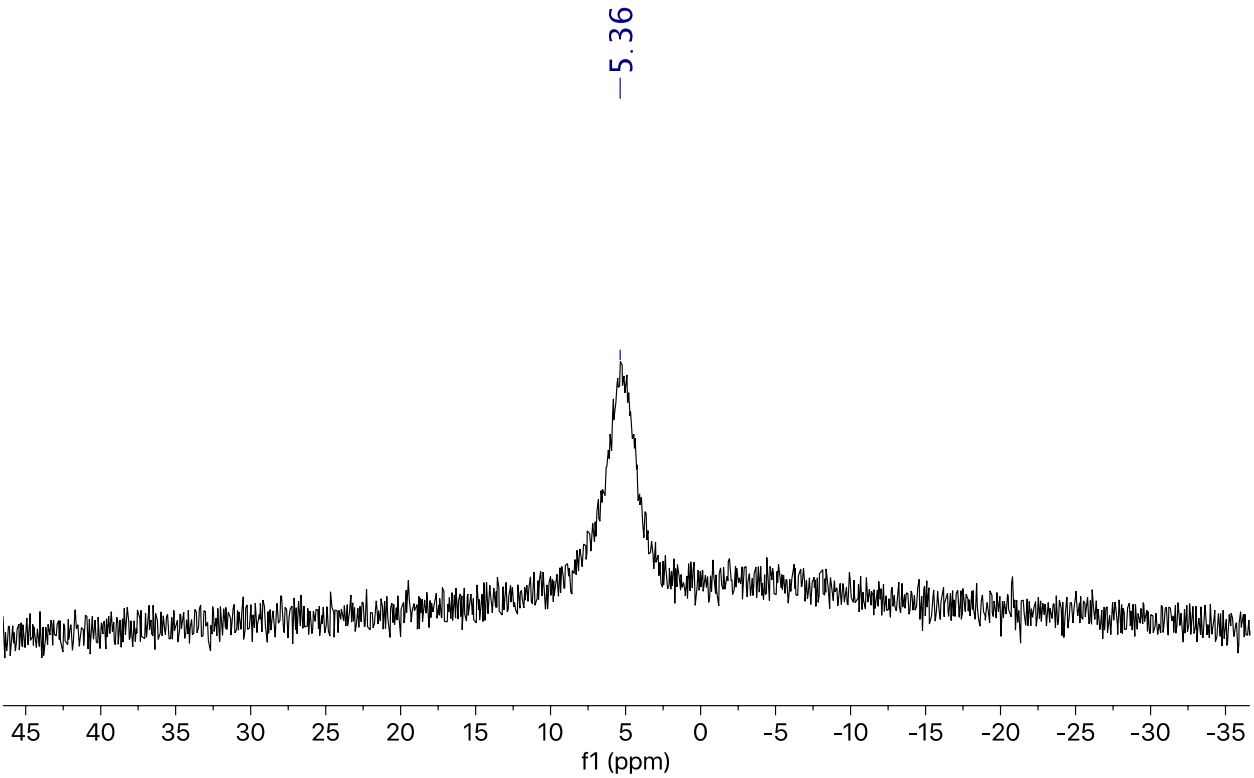


Figure S13. ^{11}B NMR spectrum of **4** (Toluene-*d8*).

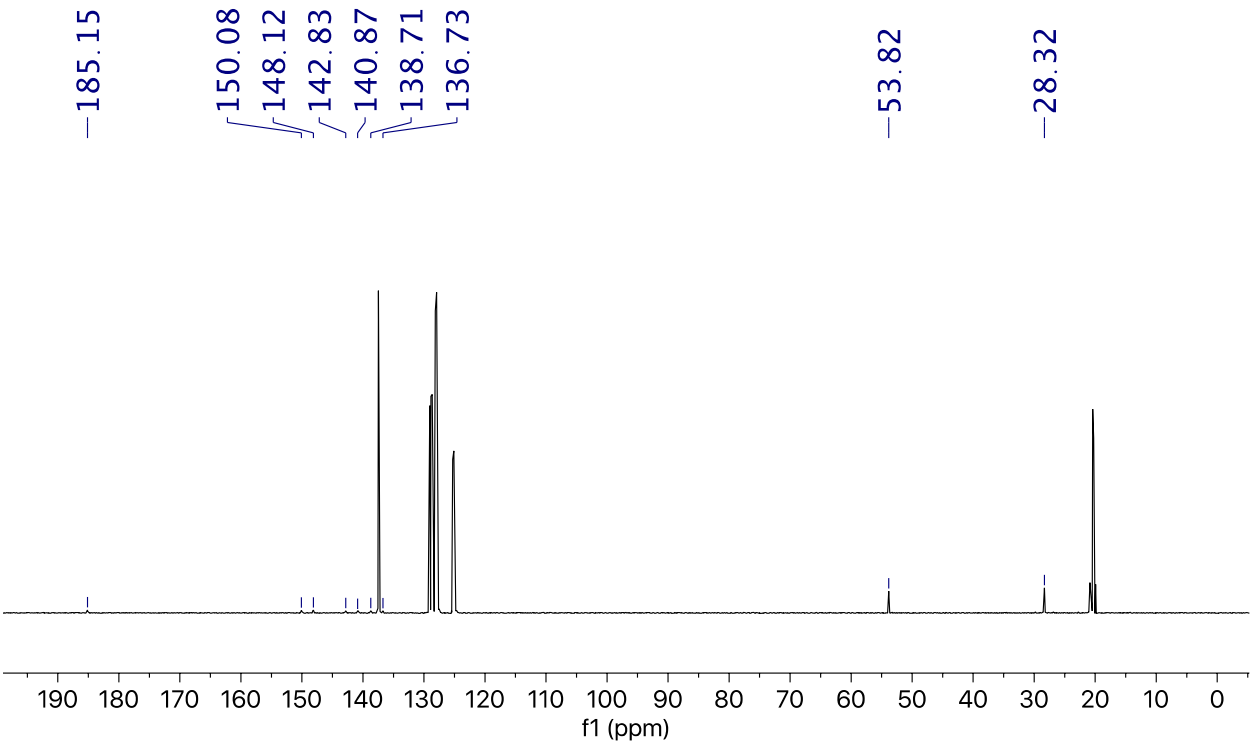


Figure S14. ^{13}C NMR spectrum of **4** (Toluene-*d8*).

2.5 [MeC(O)OB(C$_6$F$_5$)]$_2$O (5)

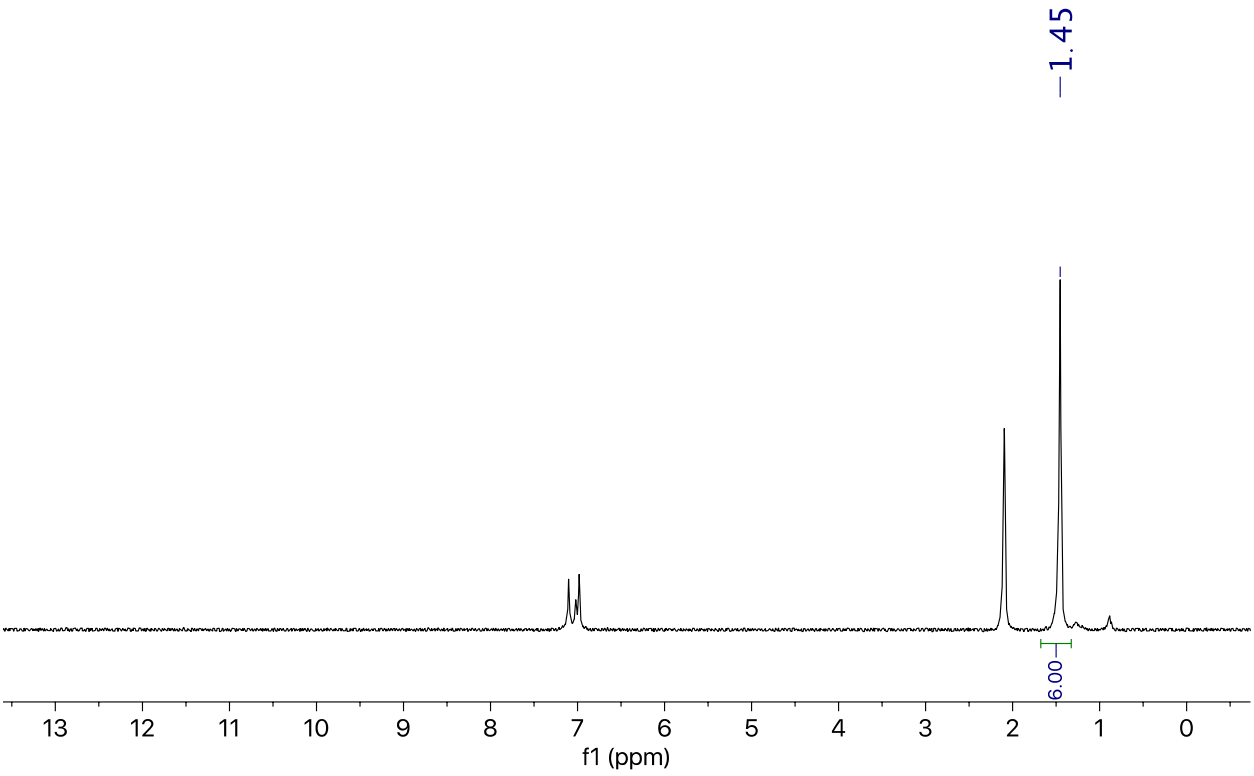


Figure S15. ^{1}H NMR spectrum of **5** (toluene-*d8*).

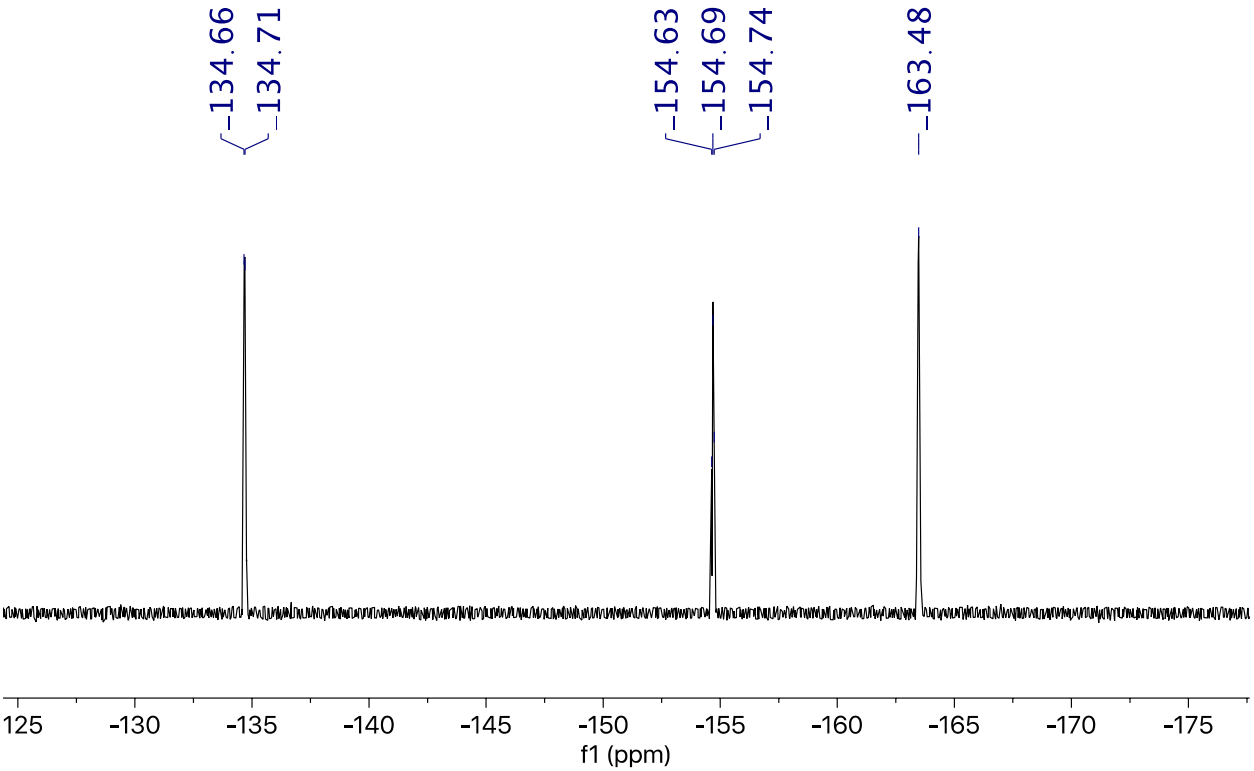


Figure S16. ^{19}F NMR spectrum of **5** (toluene-*d8*).

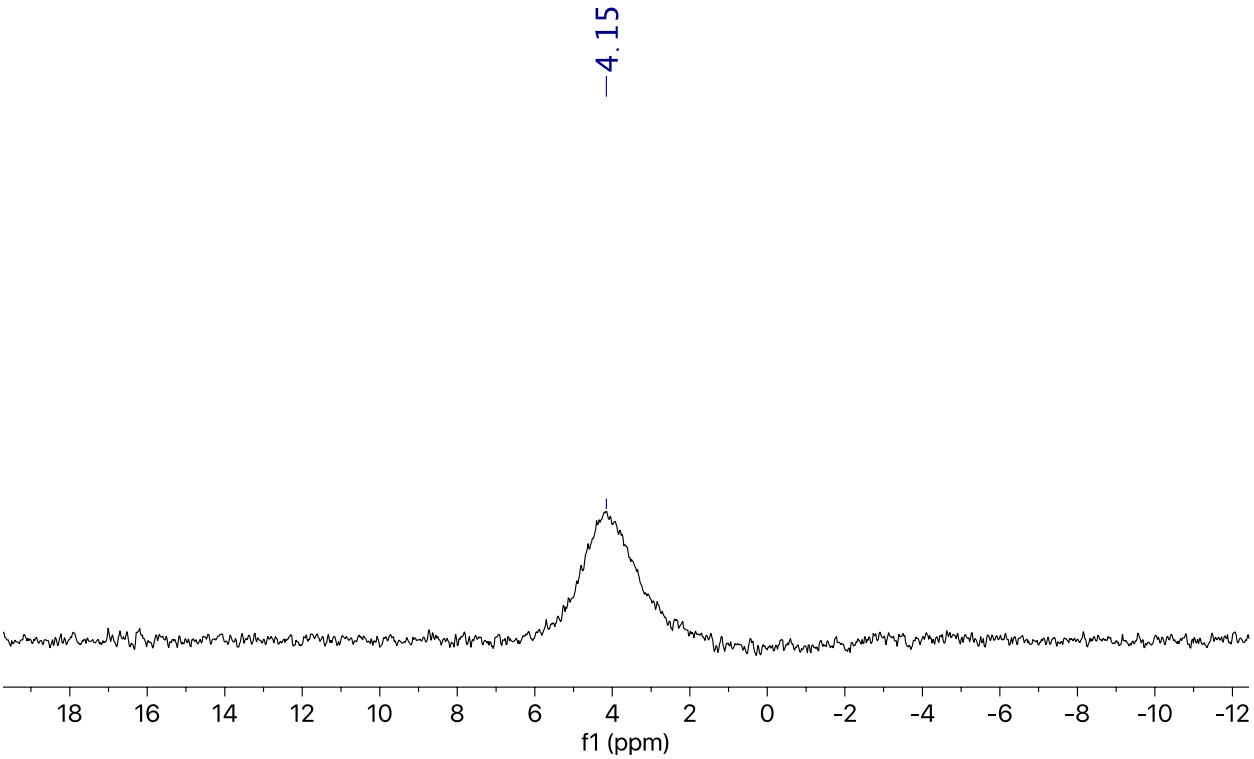


Figure S17. ^{11}B NMR spectrum of **5** (toluene-*d8*).

2.6 [TolC(O)OB(C_6F_5)$_2$]$_2$ (6)

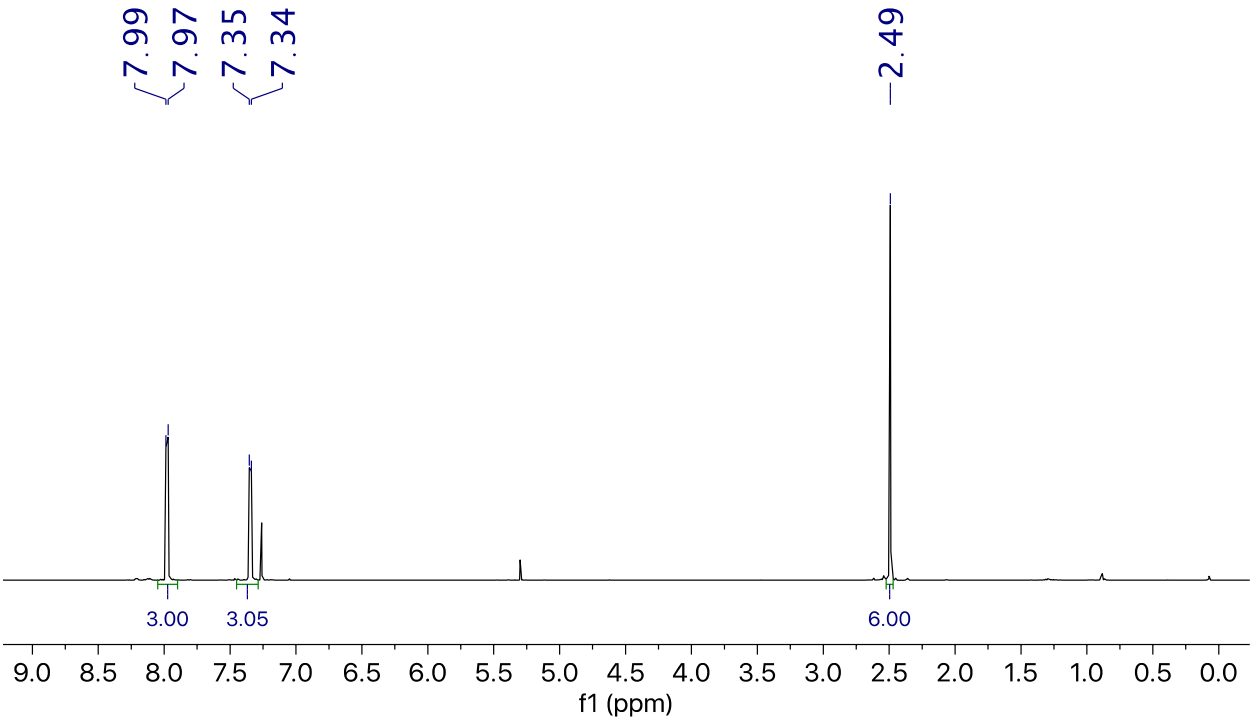


Figure S18. ^{1}H NMR of **6** in $CDCl_3$.

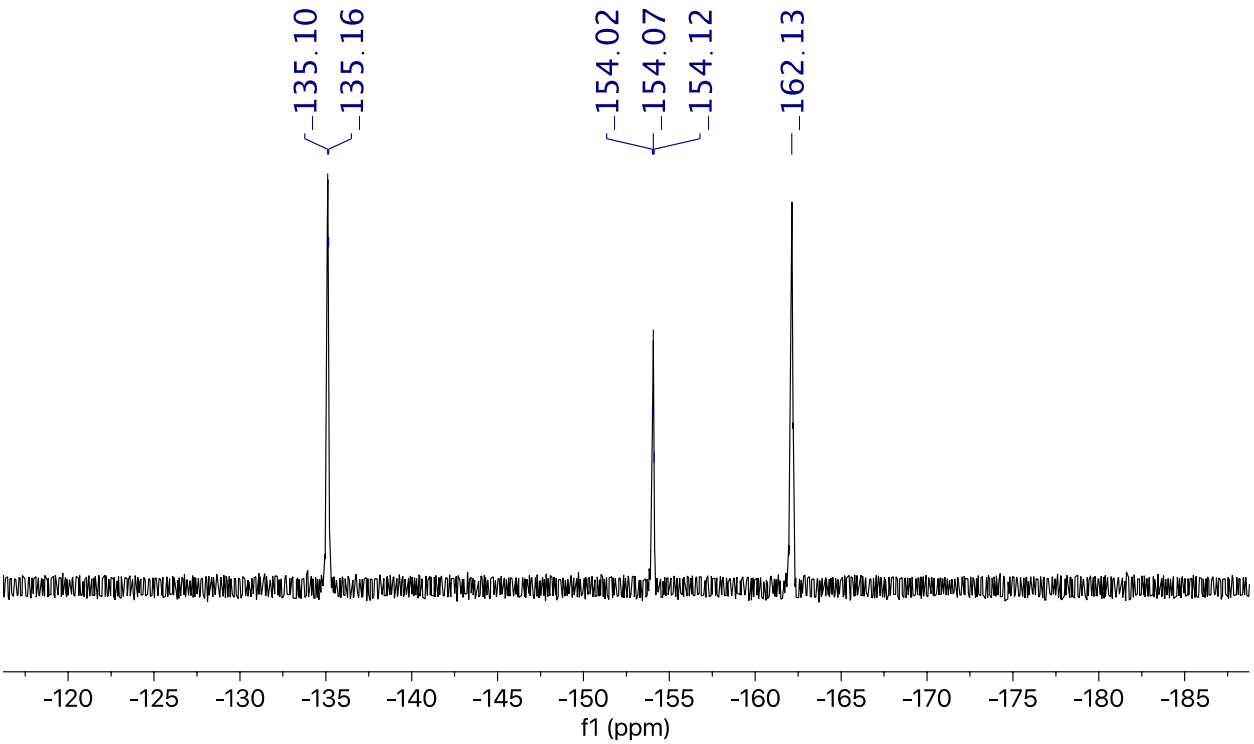


Figure S19. ^{19}F NMR of **6** in $CDCl_3$.

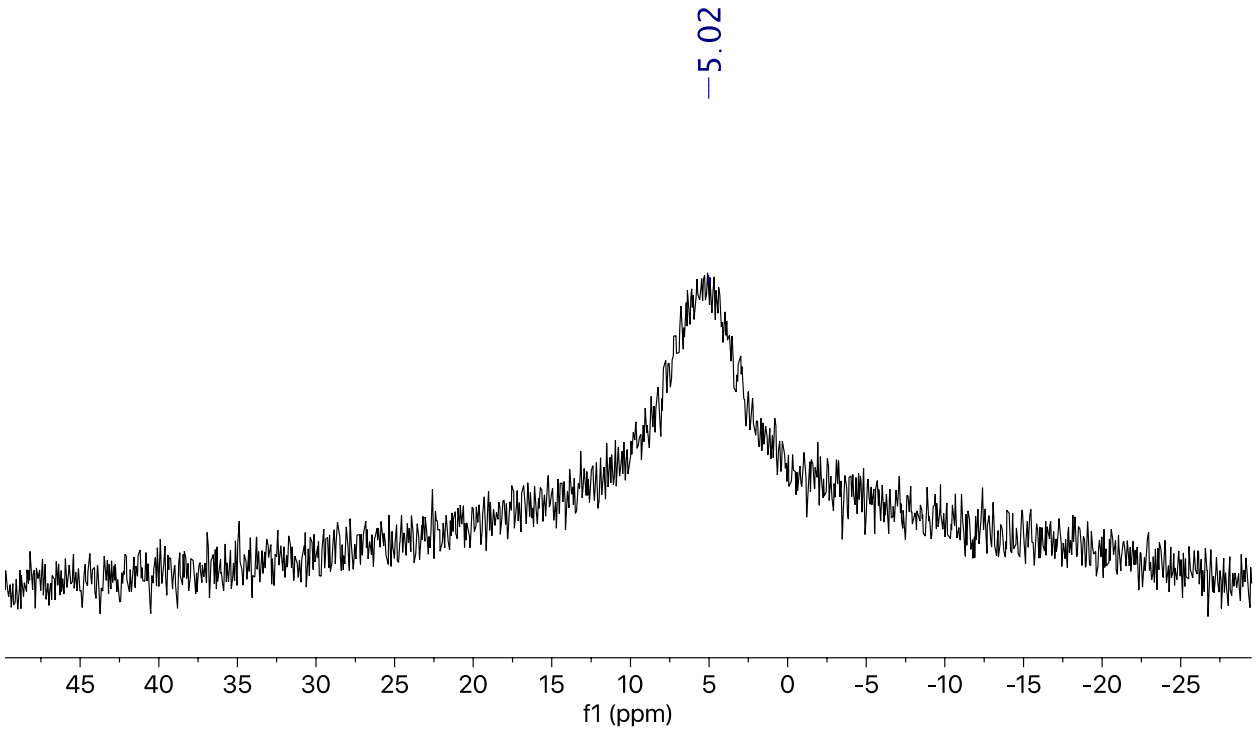


Figure S20. ^{11}B NMR of **6** in $CDCl_3$.

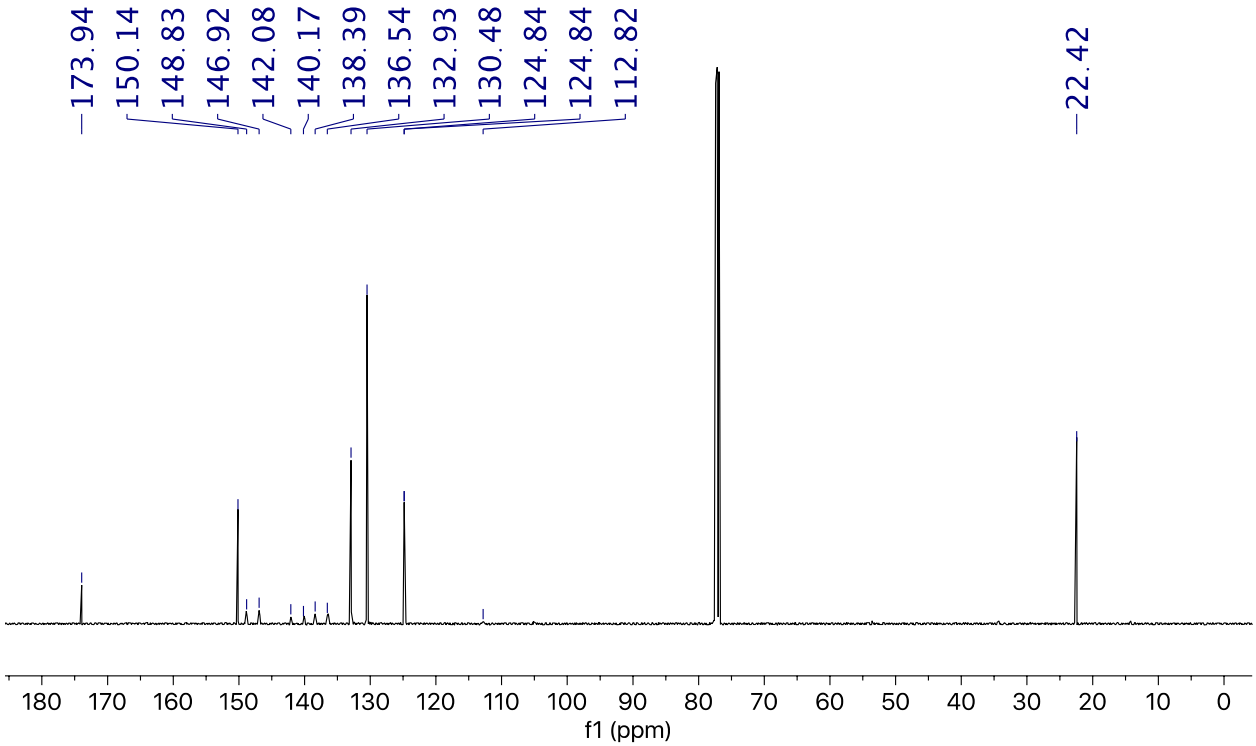


Figure S21. ^{13}C NMR of **6** in $CDCl_3$.

2.7 [(C$_6$F$_5$)C(O)OB(C$_6$F$_5$)$_2$]$_2$ (7)

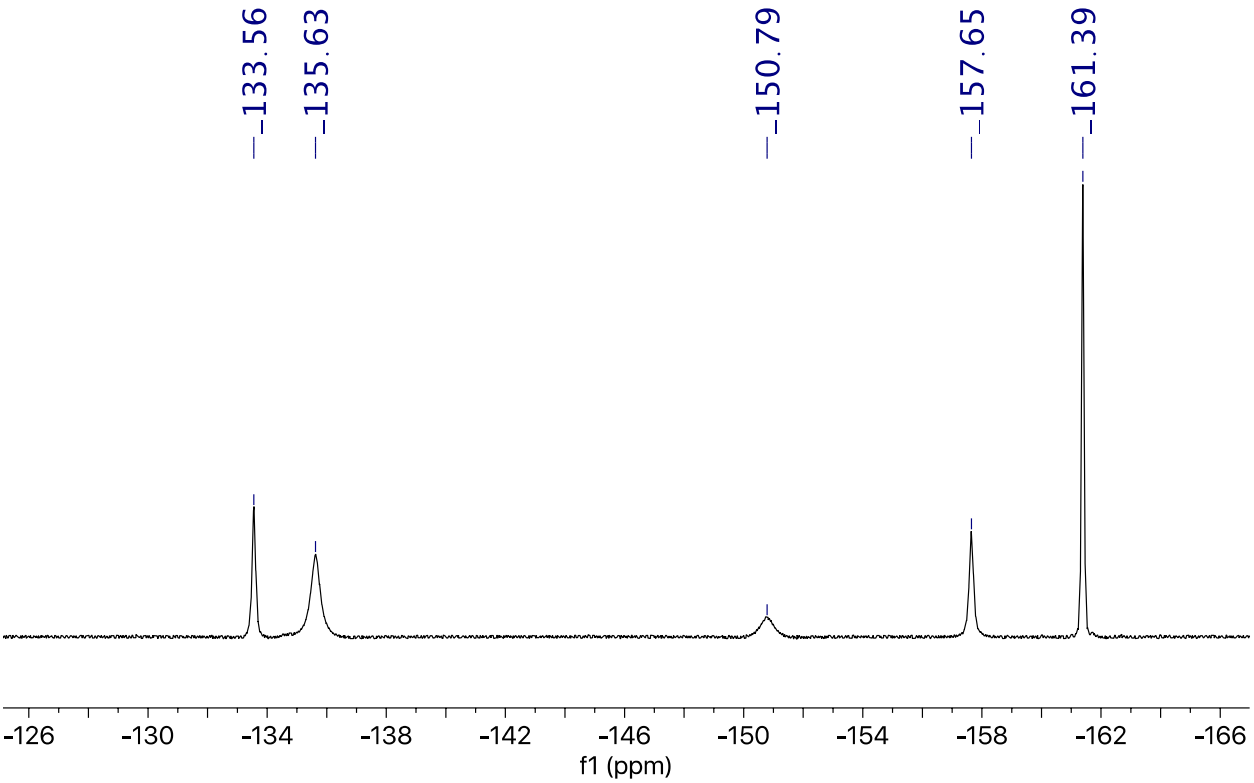


Figure S22. ^{19}F NMR of **7** in toluene-*d8*.

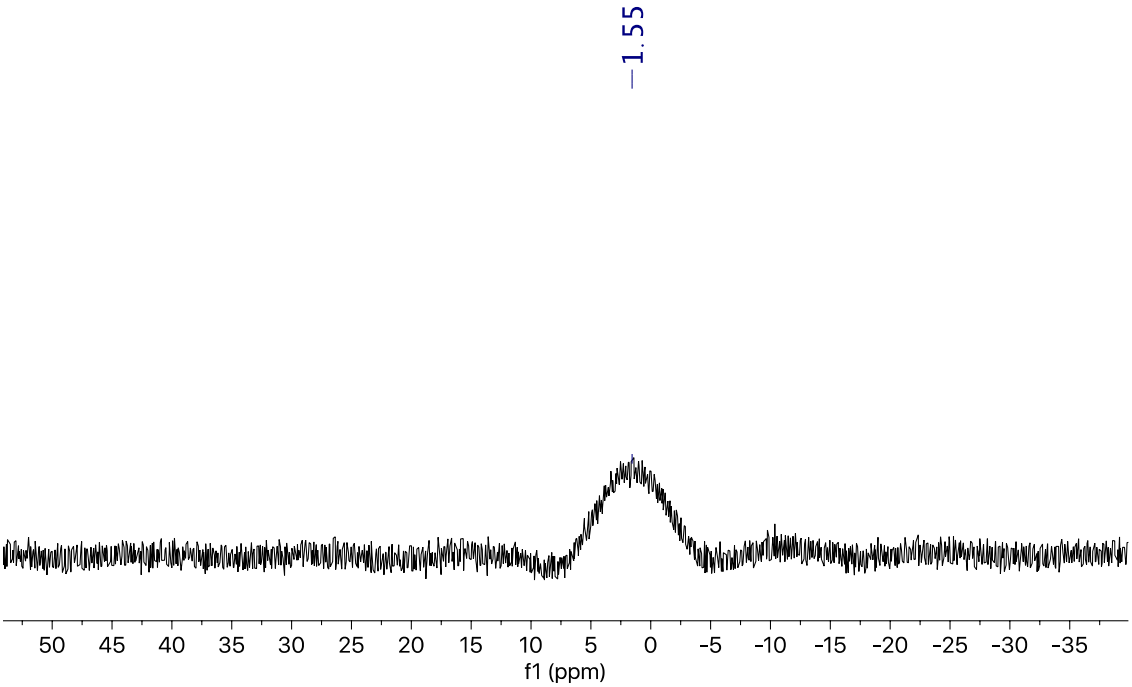


Figure S23. ^{11}B NMR of **7** in toluene-*d8*.

2.8 [$Ph_2PO_2BH(C_6F_5)]_2$ (8)

Recrystallized compound **8** (checked by unit cell) in $CDCl_3$ shows two ^{31}P signals and two sets of pentafluorophenyl resonances in ^{19}F NMR spectrum representing two four-coordinate boron environments. The $^{1}H\{^{11}B\}$ NMR spectrum shows there are two B-H environments. These data point to a reversible dynamic process that complex **6** dissociates into monomer.

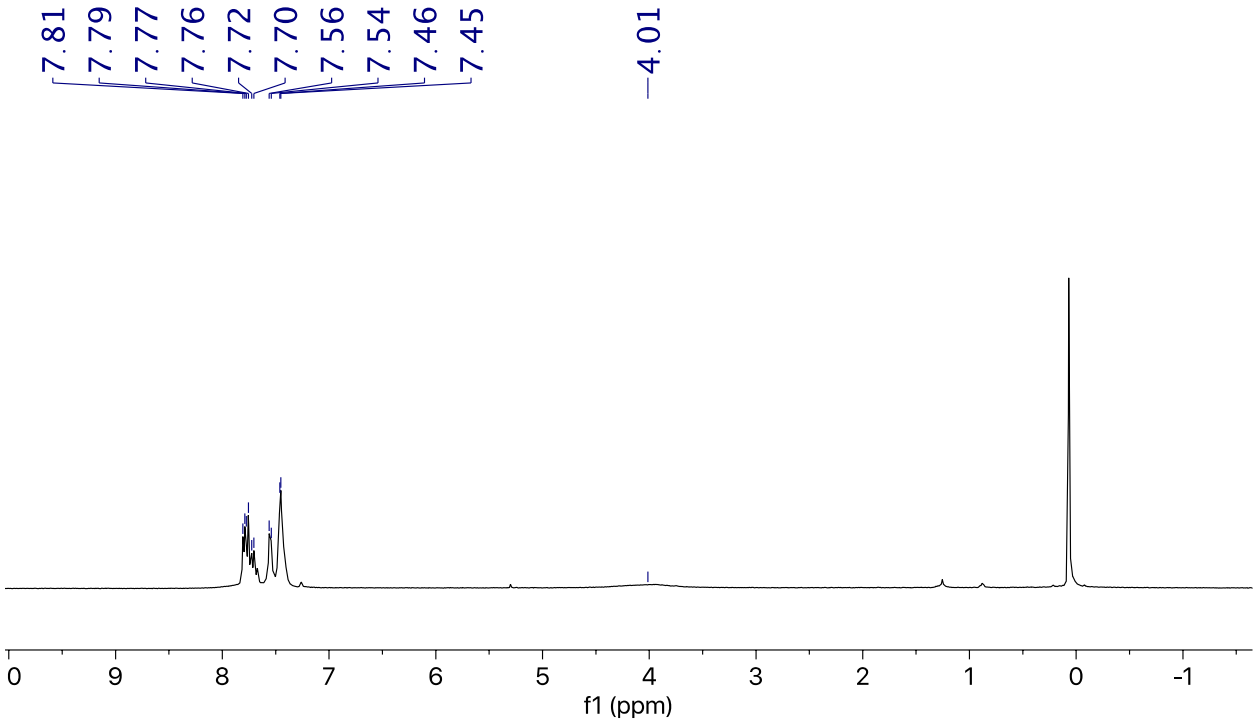


Figure S24. ^{1}H NMR spectrum of **8** ($CDCl_3$).

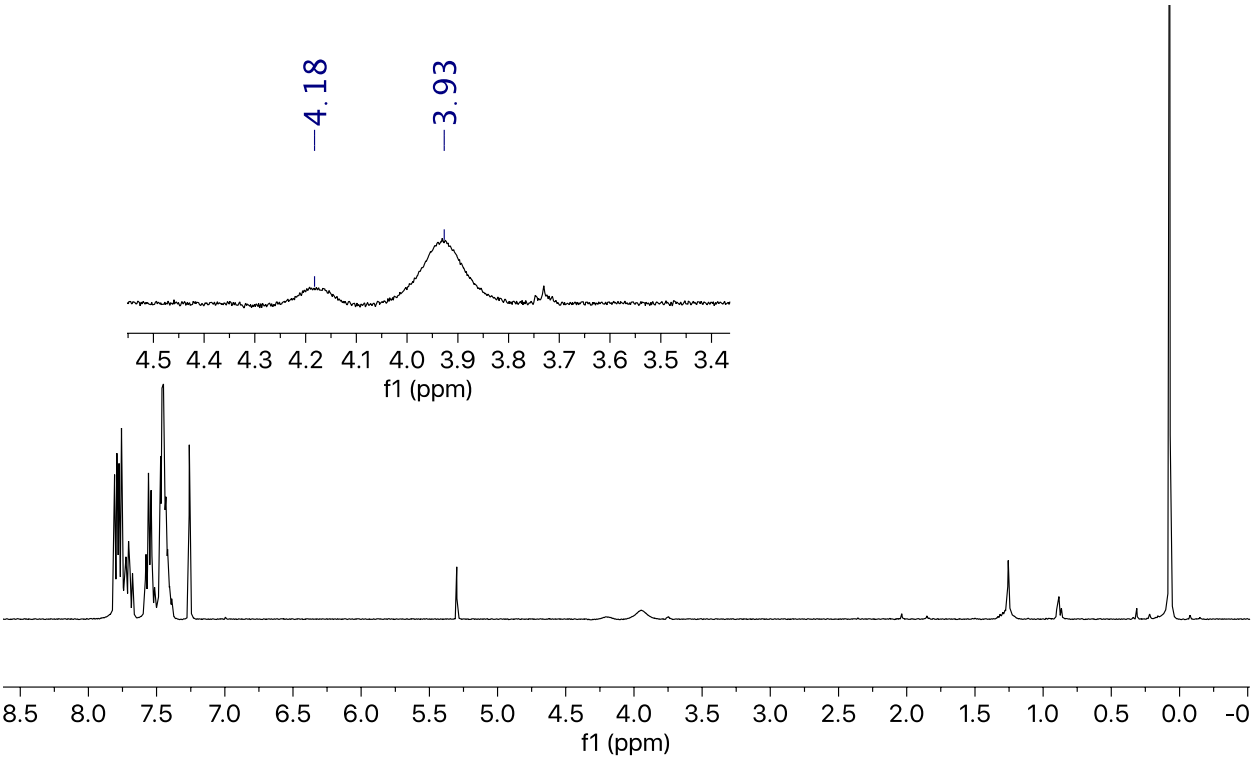


Figure S25. $^{1}H\{^{11}B\}$ NMR spectrum of **8** ($CDCl_3$). Small resonances at 3.75-0.00 ppm are solvent impurities.

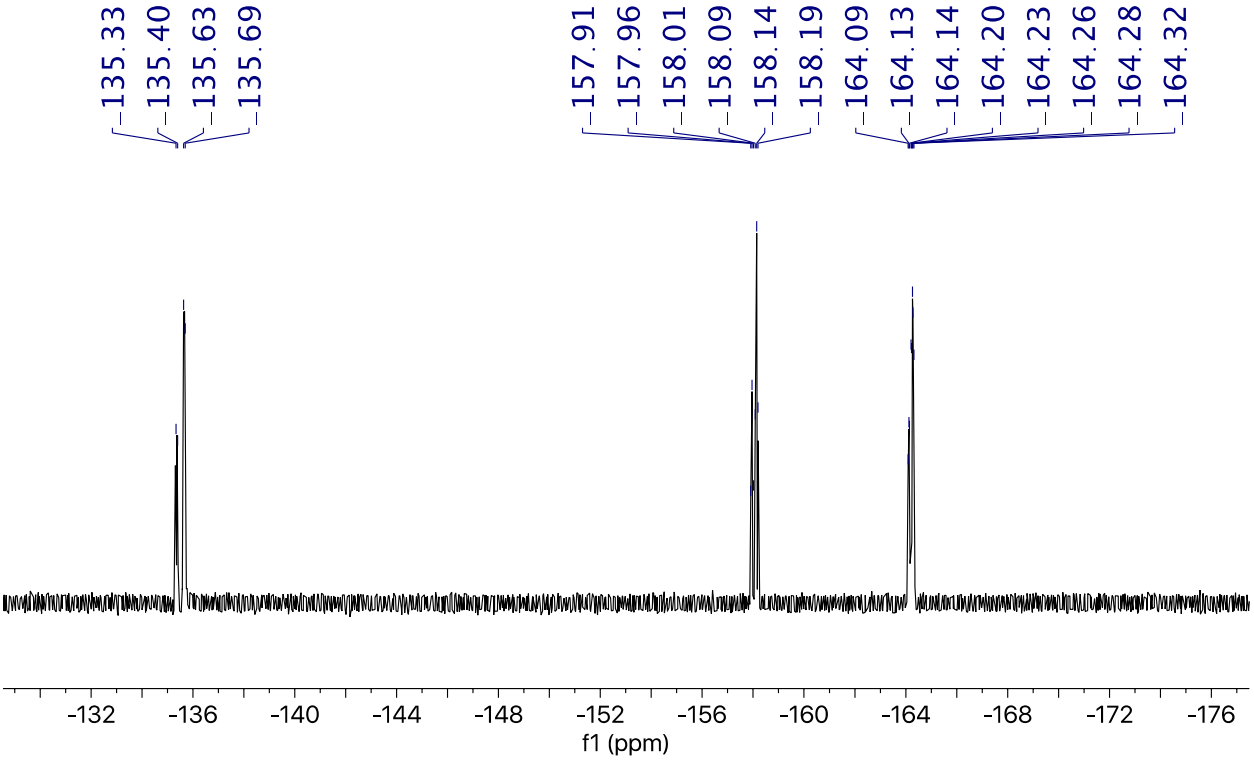


Figure S26. ^{19}F NMR spectrum of **8** ($CDCl_3$).

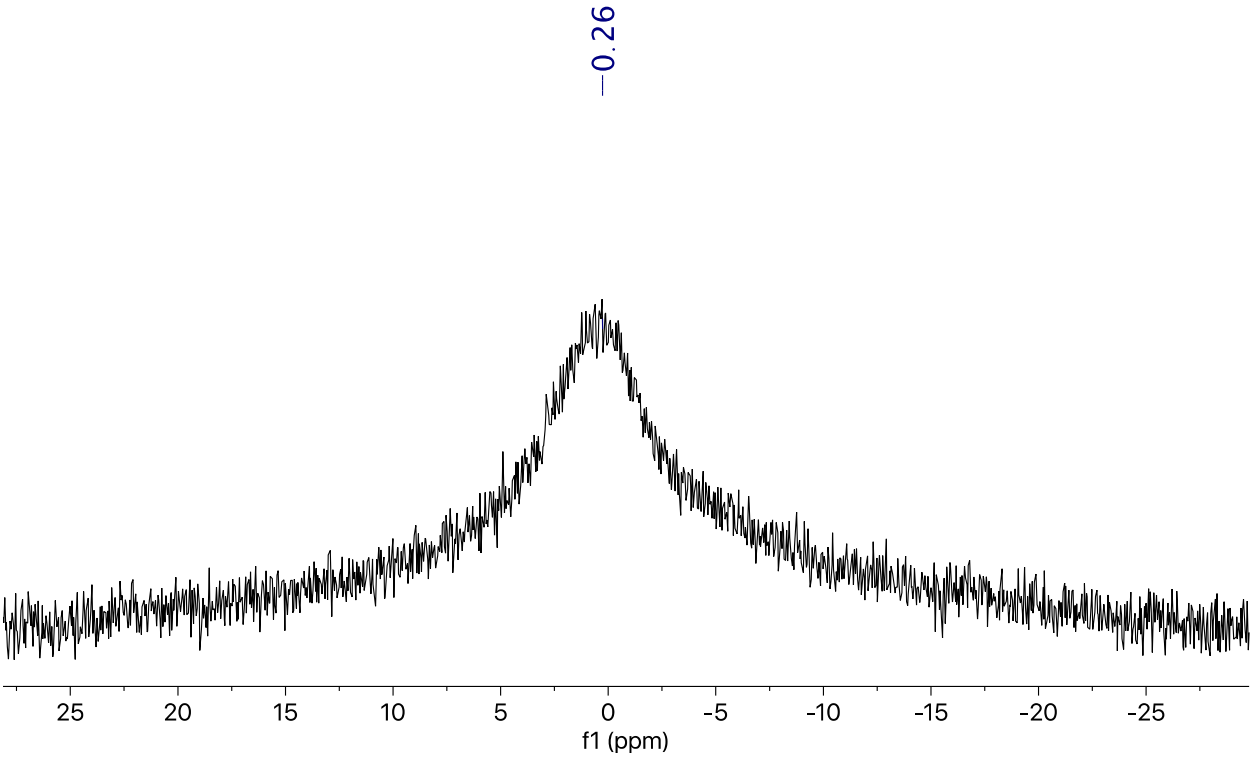


Figure S27. ^{11}B NMR spectrum of **8** ($CDCl_3$).

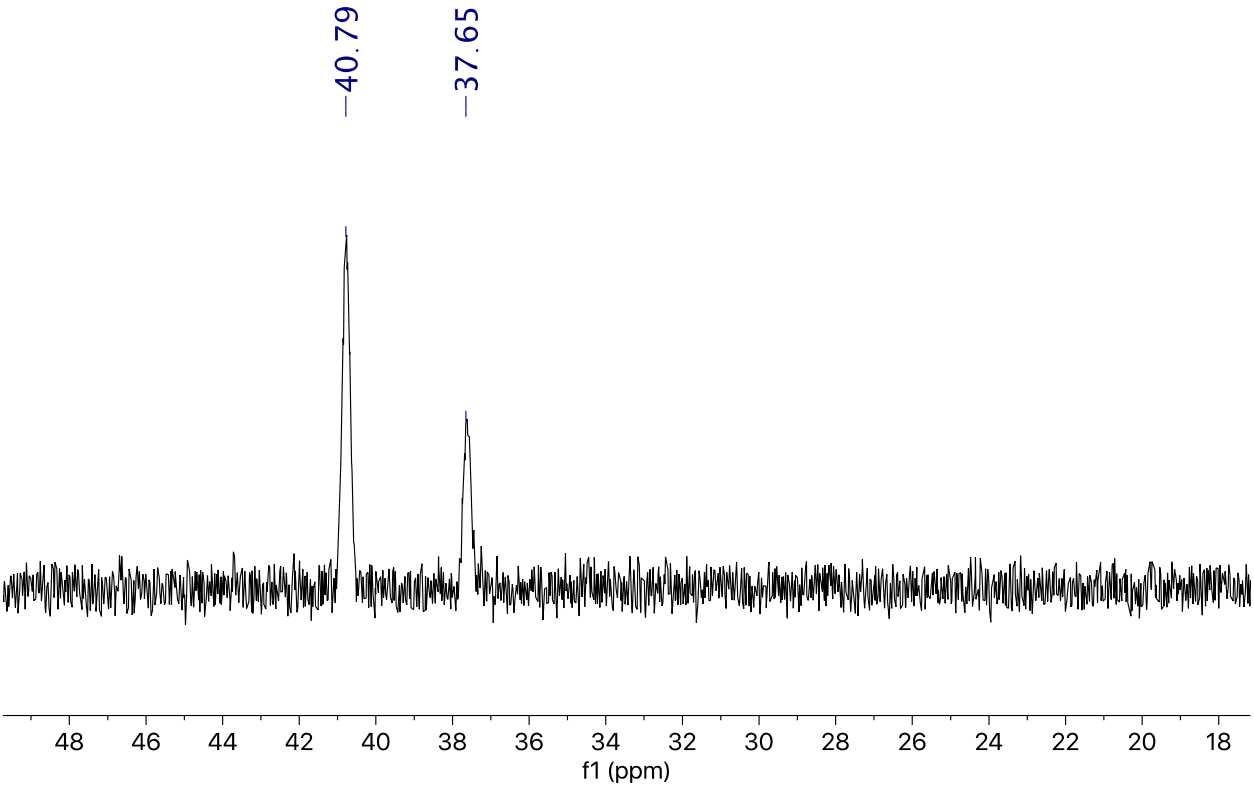


Figure S28. ^{31}P NMR spectrum of **8** ($CDCl_3$).

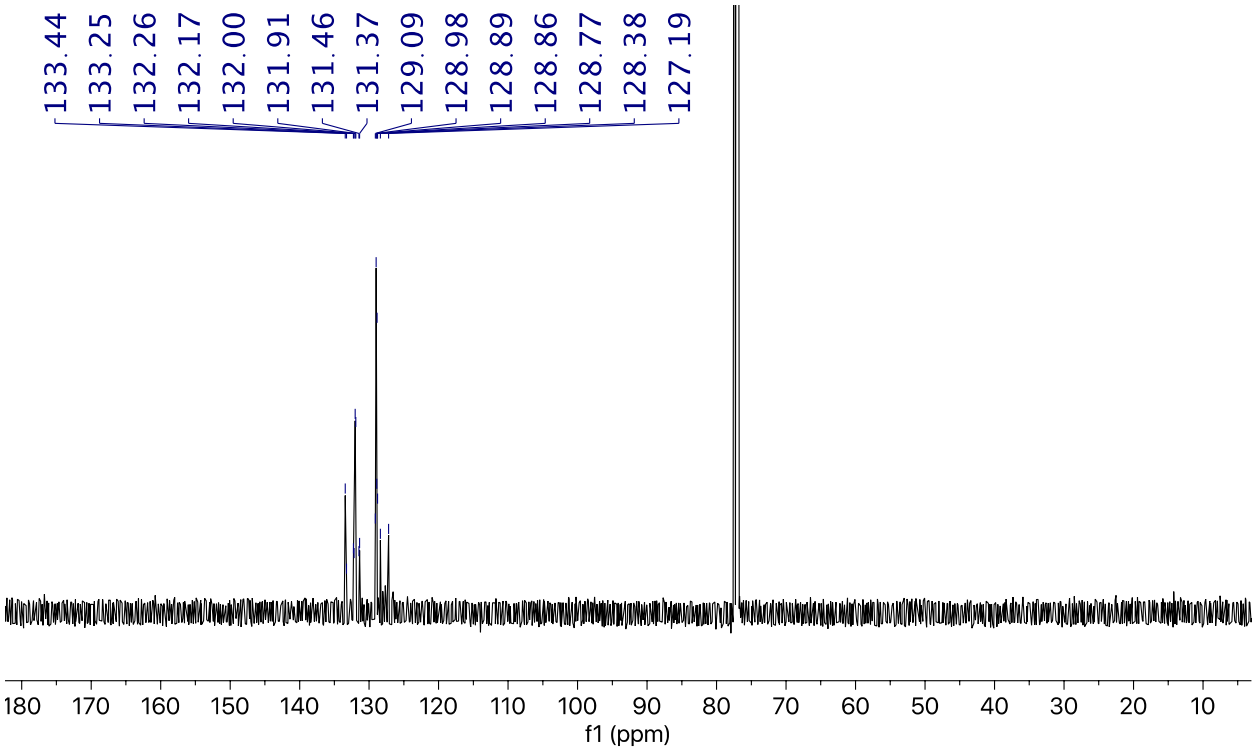


Figure S29. ^{13}C NMR spectrum of **8** ($CDCl_3$).

2.9 [TolC(O)OB(C_6F_5)$_2$][$NC_5H_4N(CH_3)_2$] (9)

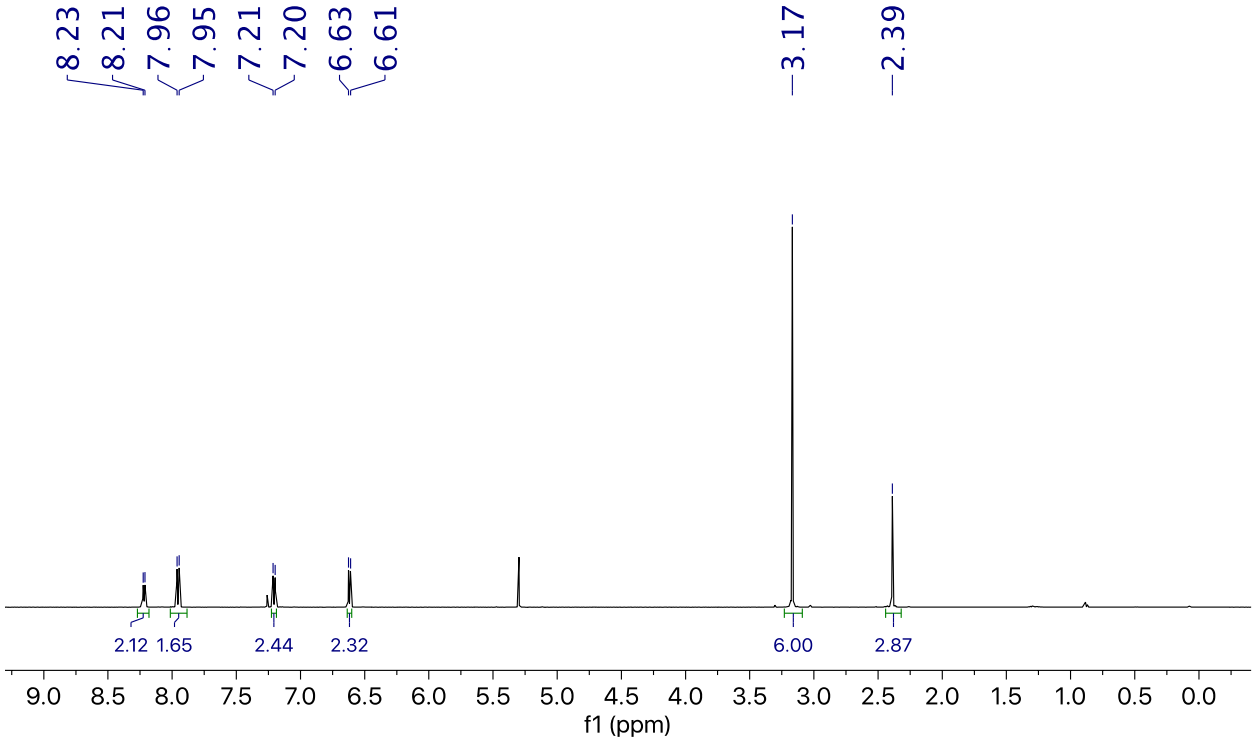


Figure S30. ^{1}H NMR of **9** in $CDCl_3$.

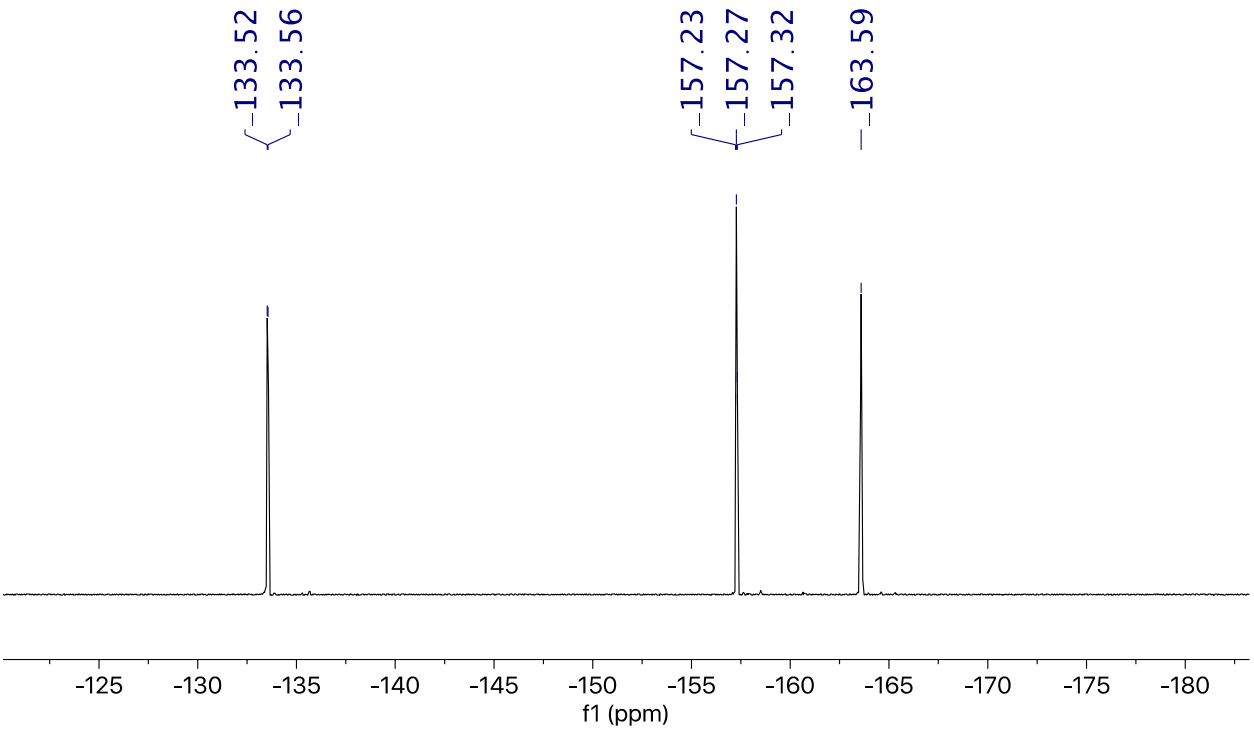


Figure S31. ^{19}F NMR of **9** in $CDCl_3$.

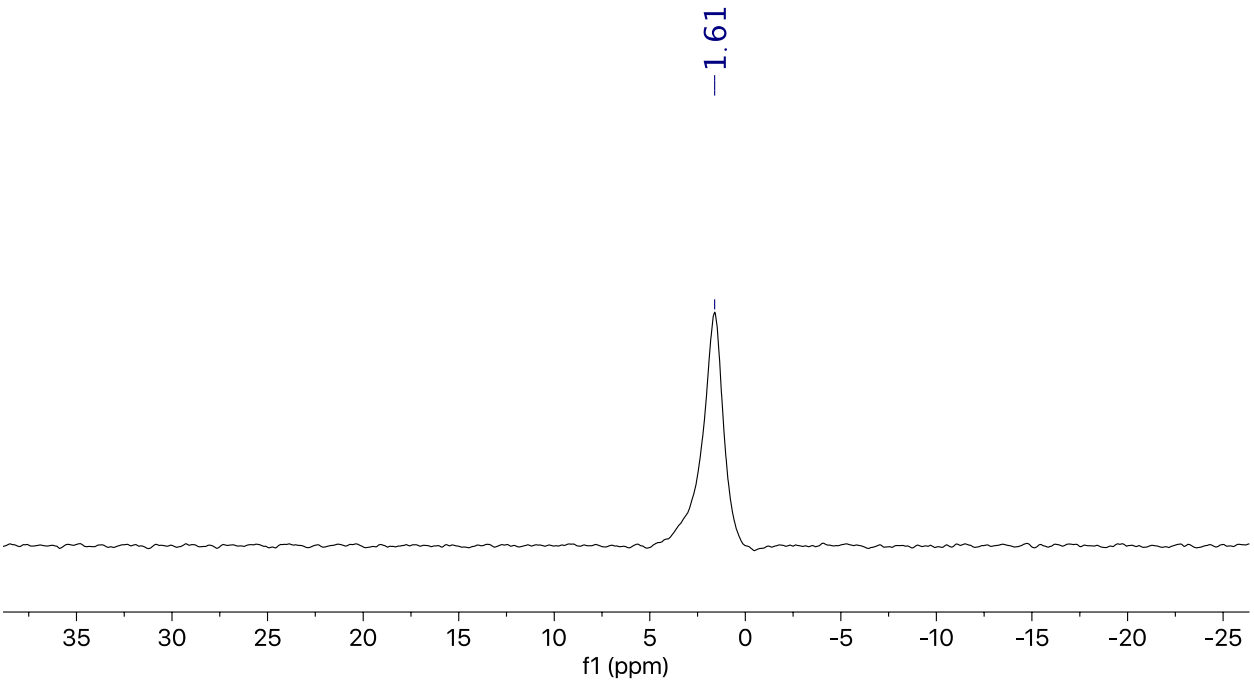


Figure S32. ^{11}B NMR of **9** in $CDCl_3$.

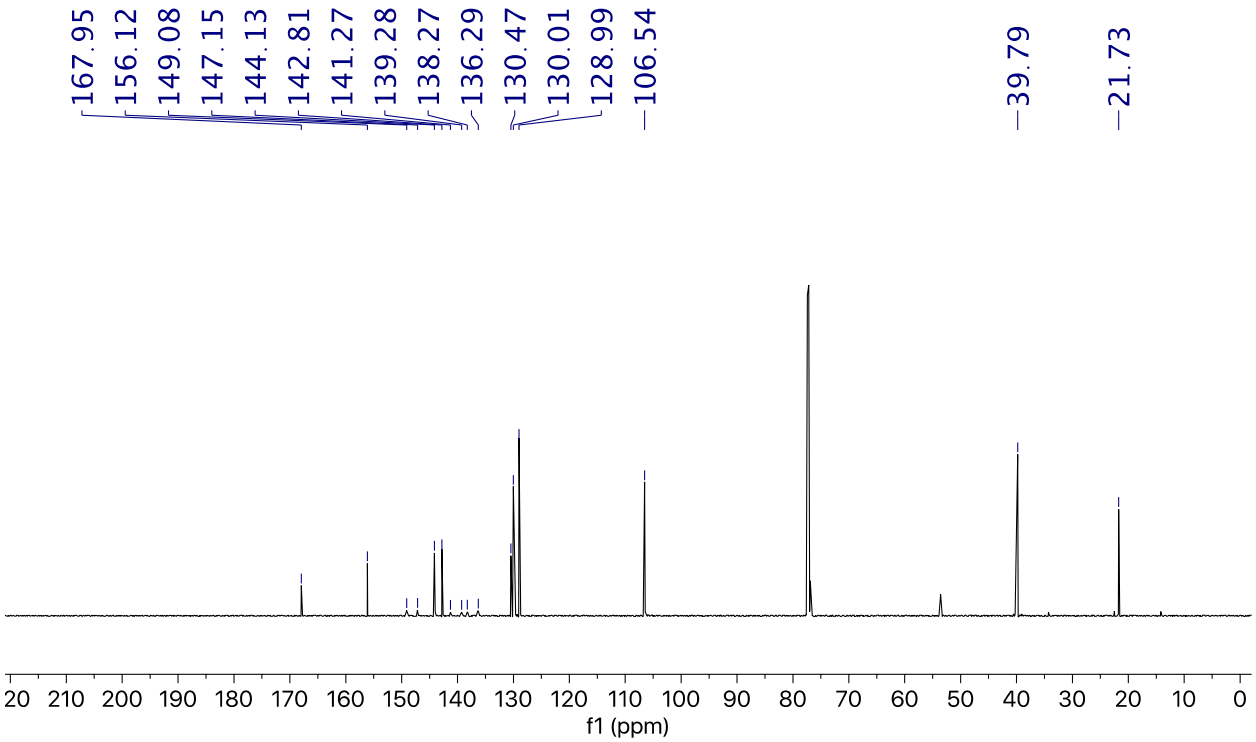


Figure S33. ^{13}C NMR of **9** in $CDCl_3$.

2.10 $[Ph_2PO_2BH(C_6F_5)][NC_5H_4N(CH_3)_2]$ (10)

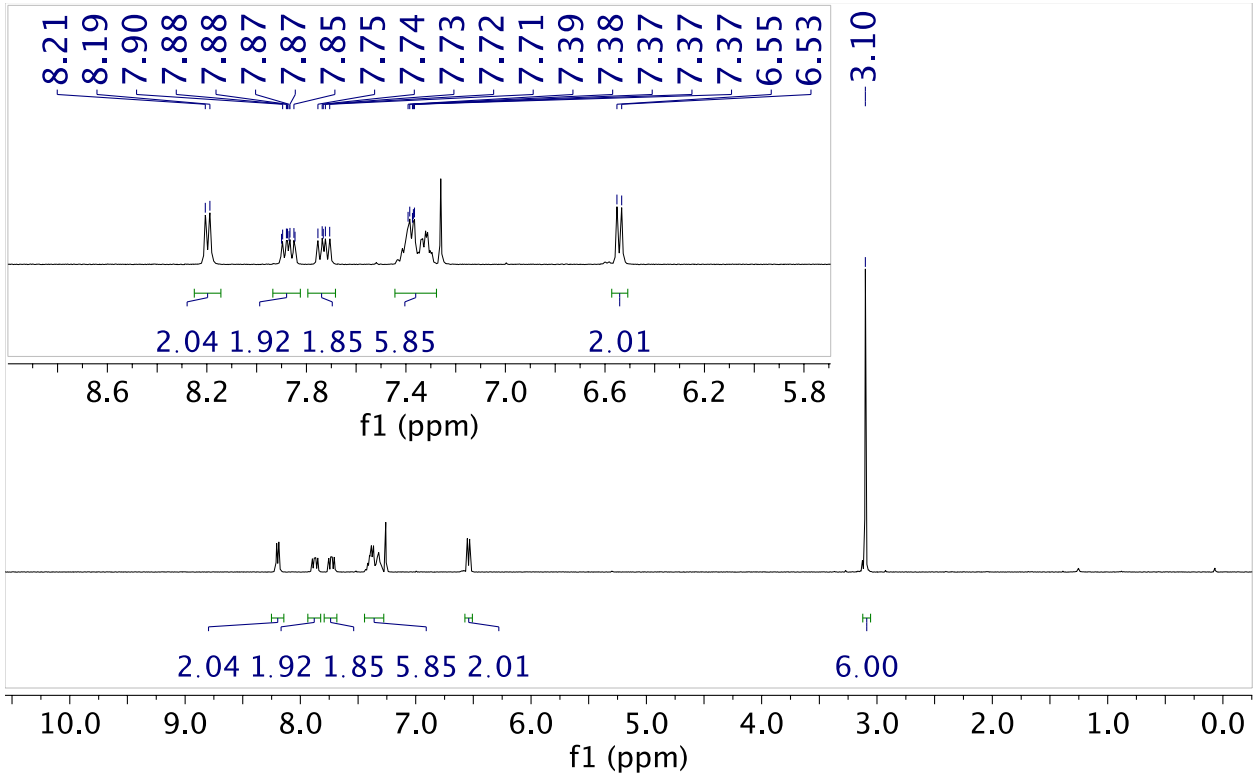


Figure S34. ^{1}H NMR spectrum of **10** ($CDCl_3$).

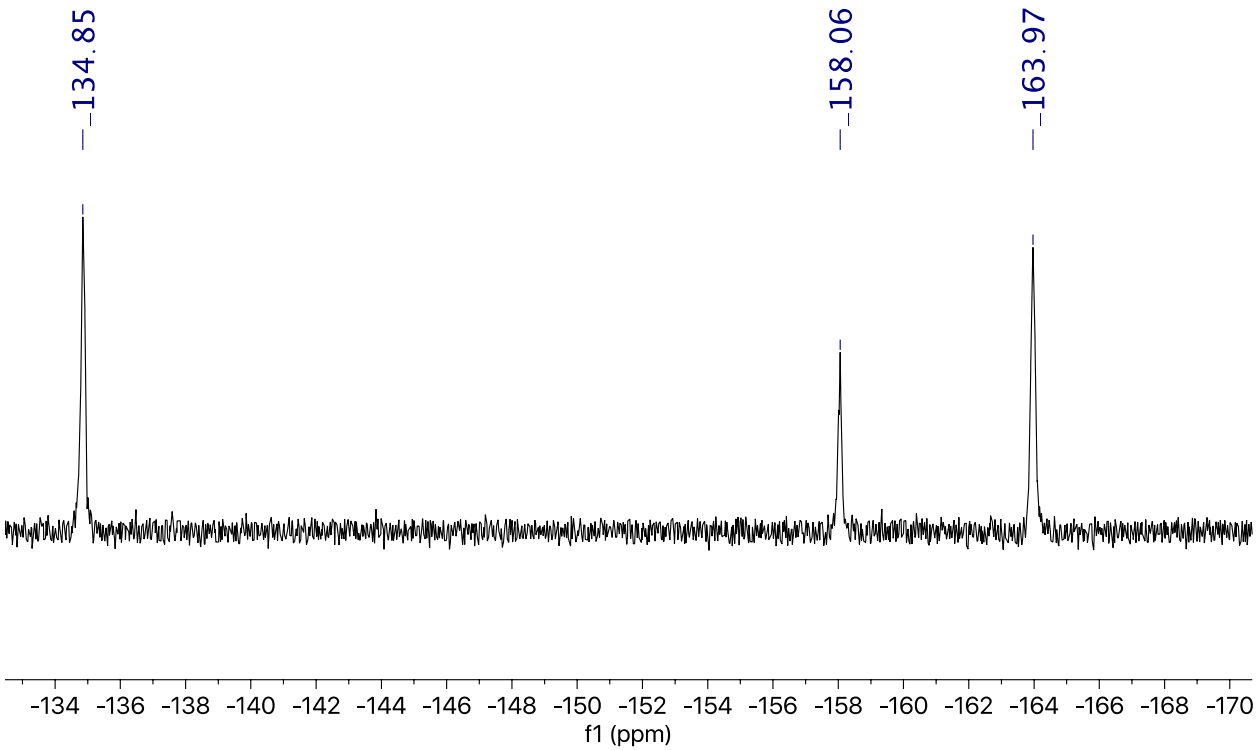


Figure S35. ^{19}F NMR spectrum of **10** ($CDCl_3$).

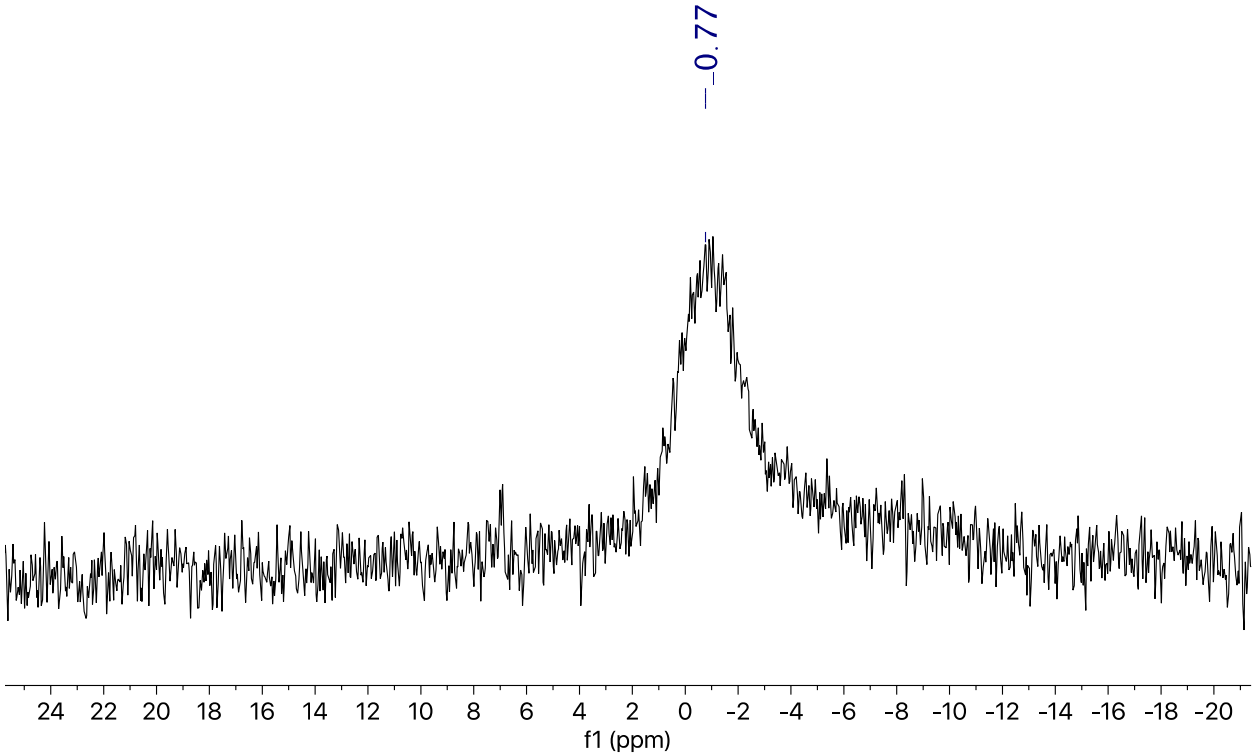


Figure S36. ^{11}B NMR spectrum of **10** ($CDCl_3$).

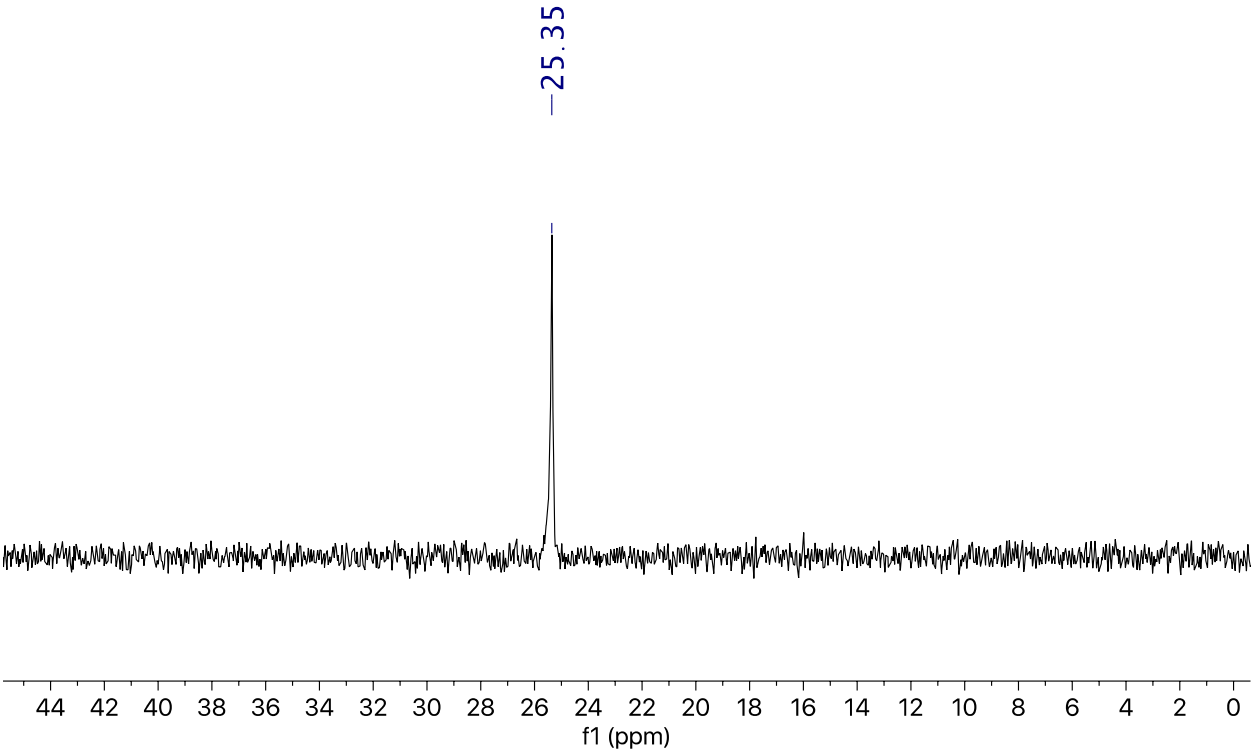


Figure S37. ^{31}P NMR spectrum of **10** ($CDCl_3$).

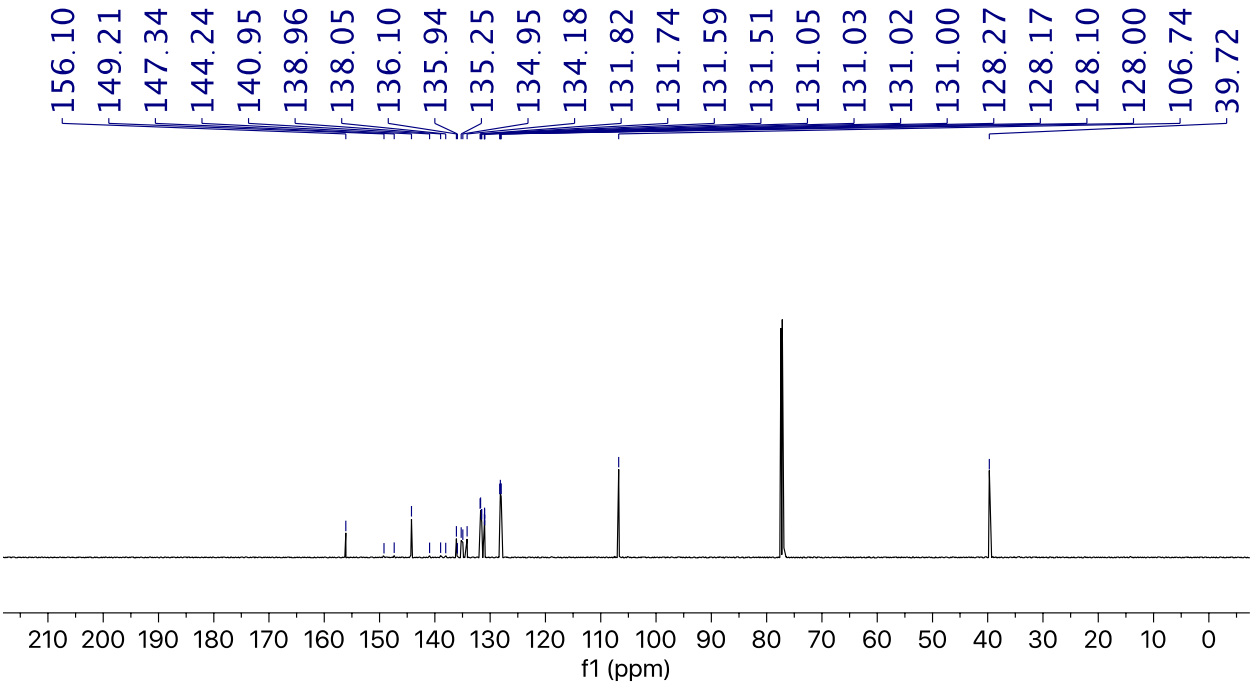
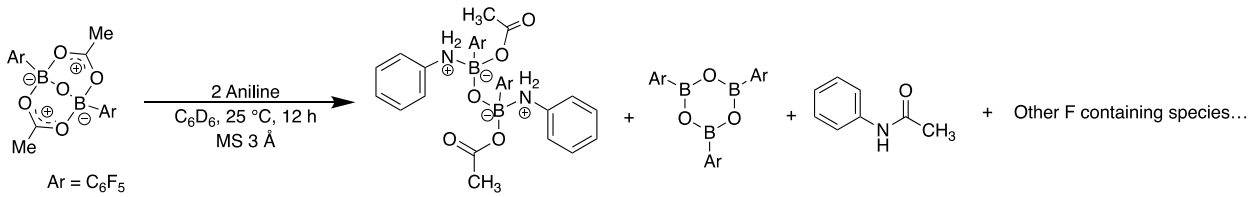


Figure S38. ^{13}C NMR spectrum of **10** ($CDCl_3$).

2. Stoichiometric Reaction with Aniline



To a solution of **5** (20 mg, 0.04 mmol) in dichloromethane was added aniline (7.6 mg, 0.08 mmol). The reaction was monitor by ^{11}B NMR spectroscopy over 12 h.

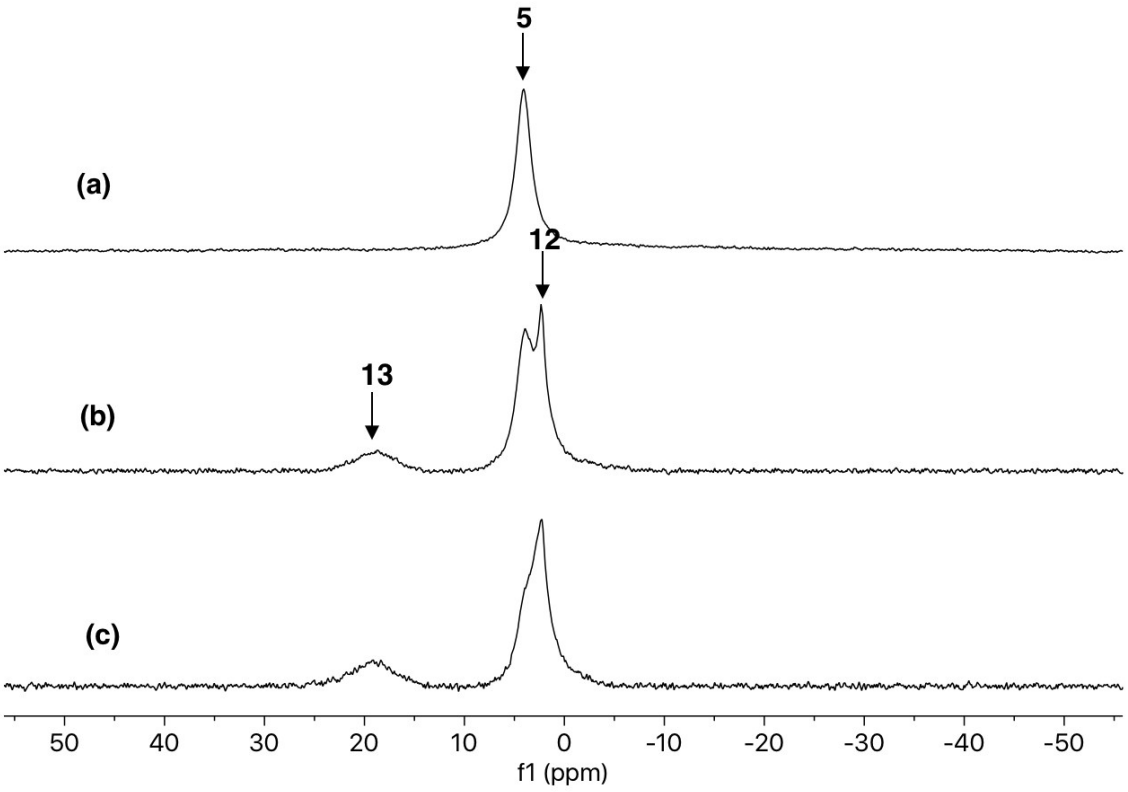


Figure S39. The ^{11}B NMR spectra of (a) complex **5**, (b) 20 min after addition of aniline to **5**, and (c) 12 h after addition of aniline to **5**.

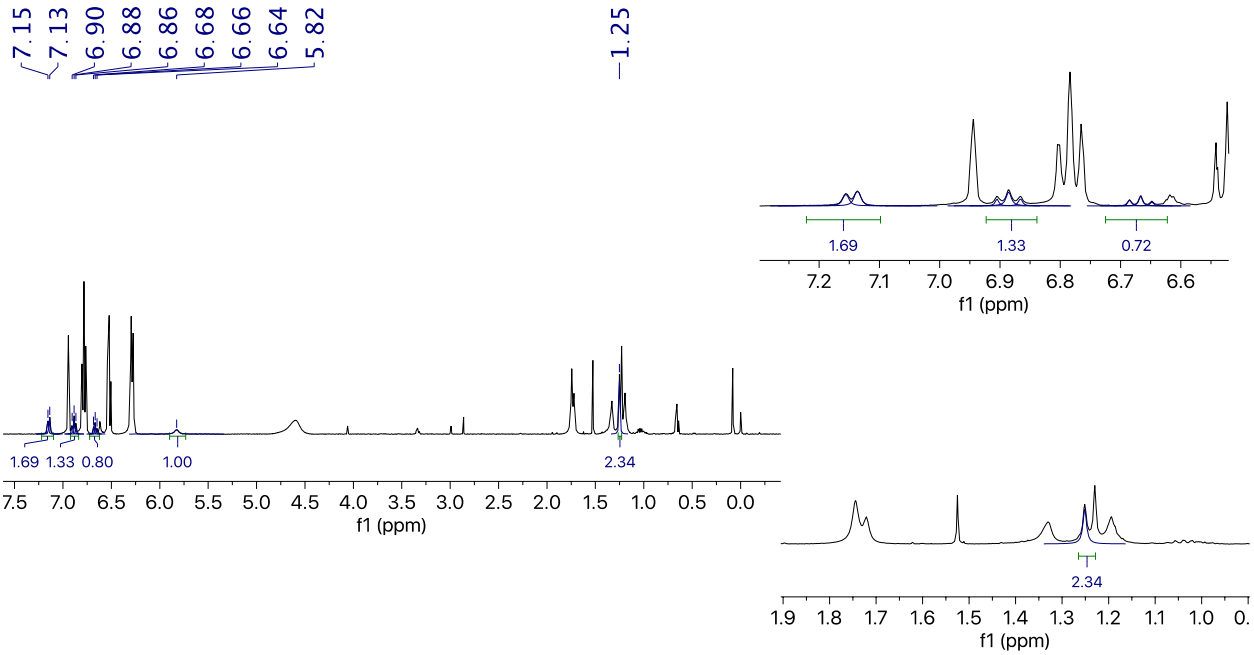


Figure S40. ^{1}H NMR spectrum of stoichiometric reaction of **5** and aniline.

3. VT Experimental of 8

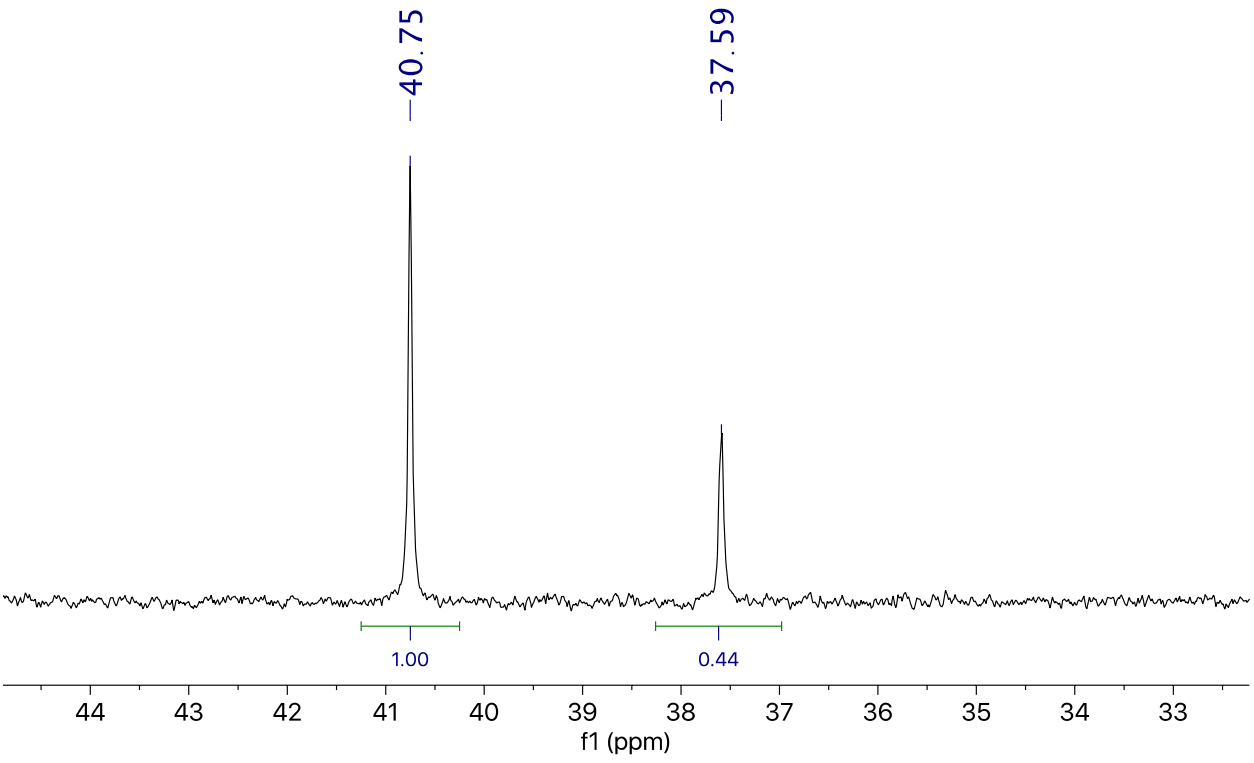


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum of **8** at 298 K in $CDCl_3$.

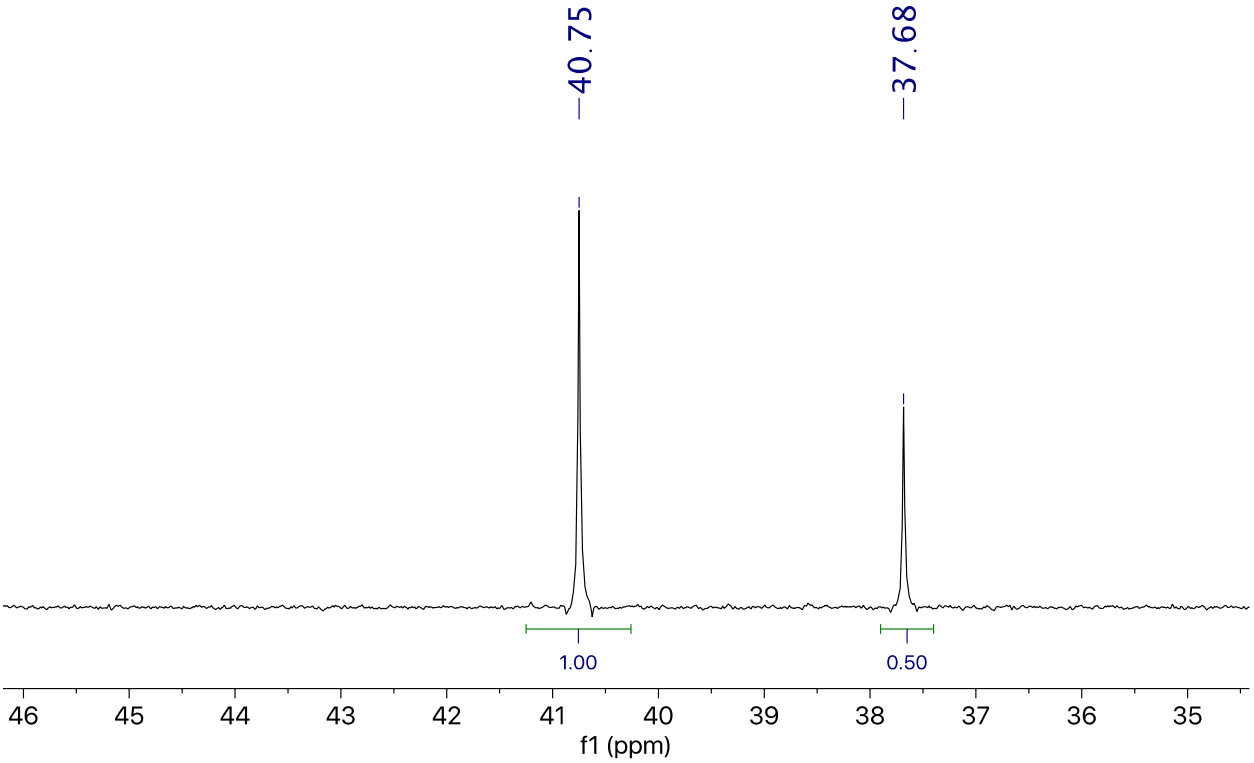


Figure S42. $^{31}P\{^{1}H\}$ NMR spectrum of **8** at 283 K in $CDCl_3$.

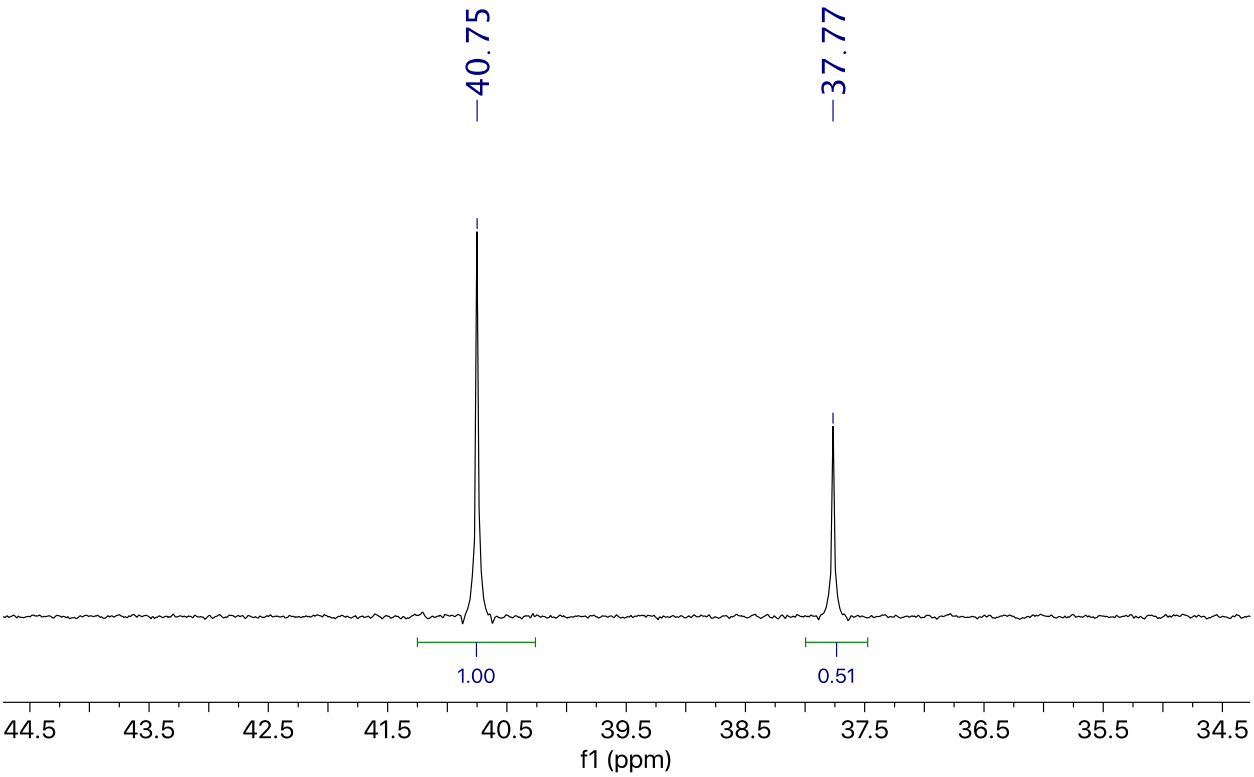


Figure S43. $^{31}P\{^{1}H\}$ NMR spectrum of **8** at 273 K in $CDCl_3$.

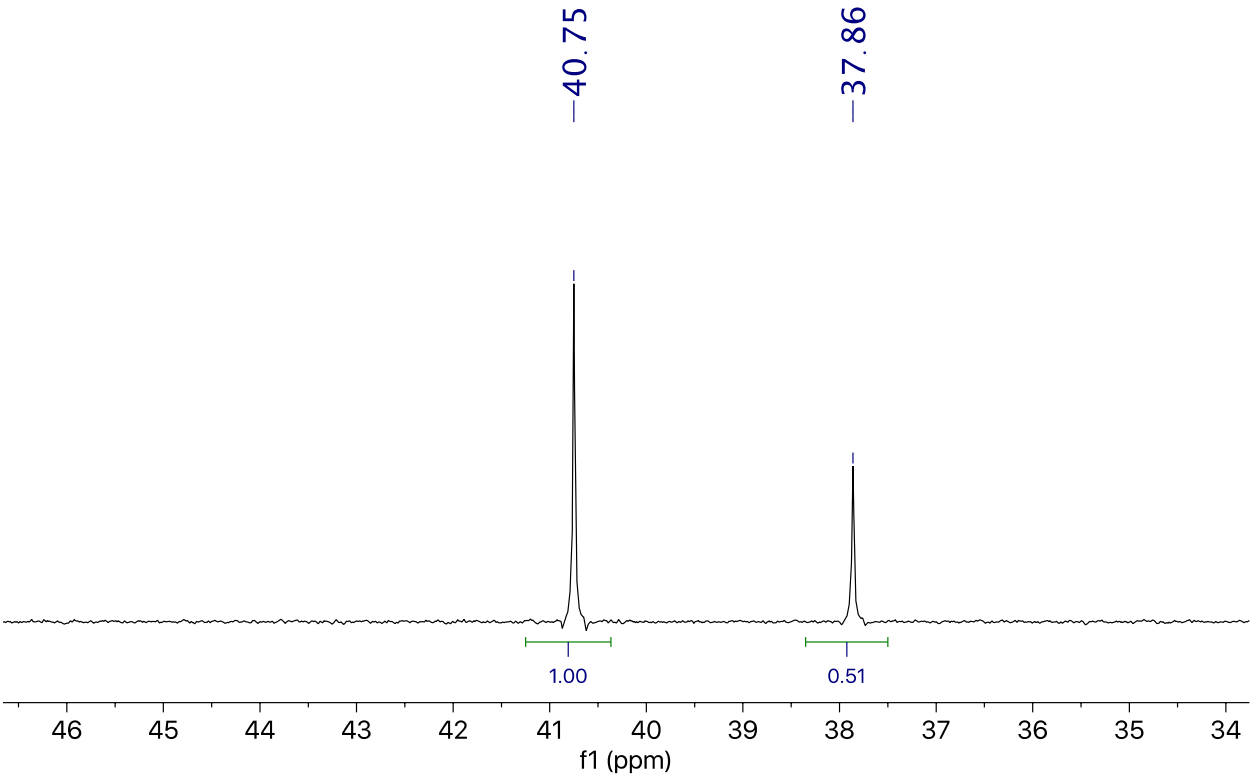


Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum of **8** at 263 K in $CDCl_3$.

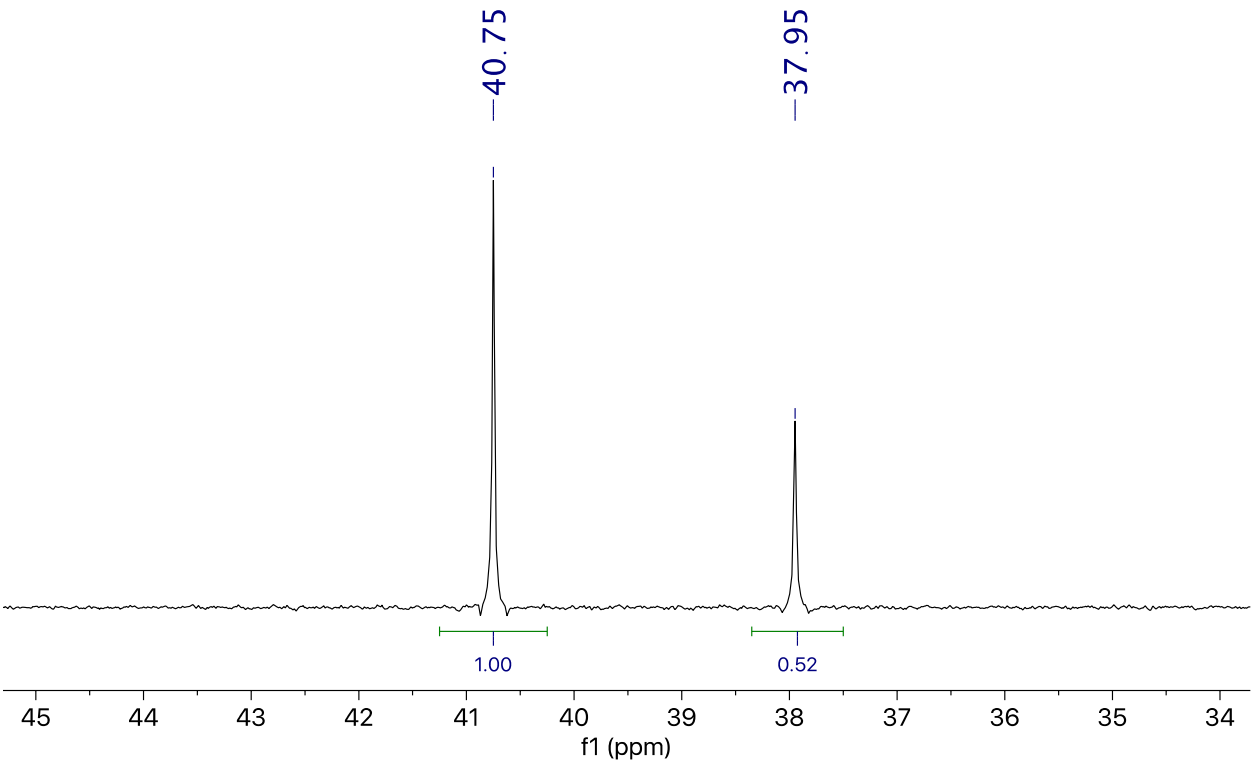


Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum of **8** at 253 K in $CDCl_3$.

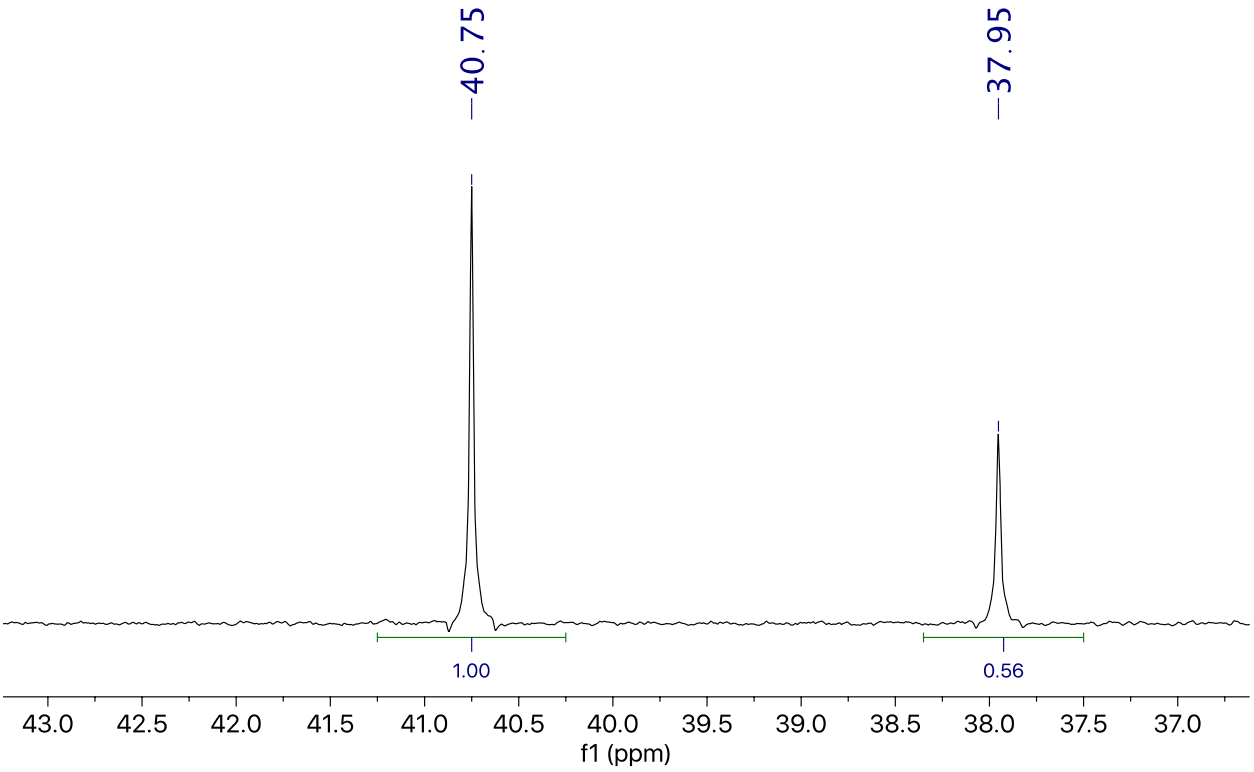


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum of **8** at 243 K in $CDCl_3$.

4. DART-MS Result & ^{1}H NMR Spectrum of Compound 1 Reaction Crude

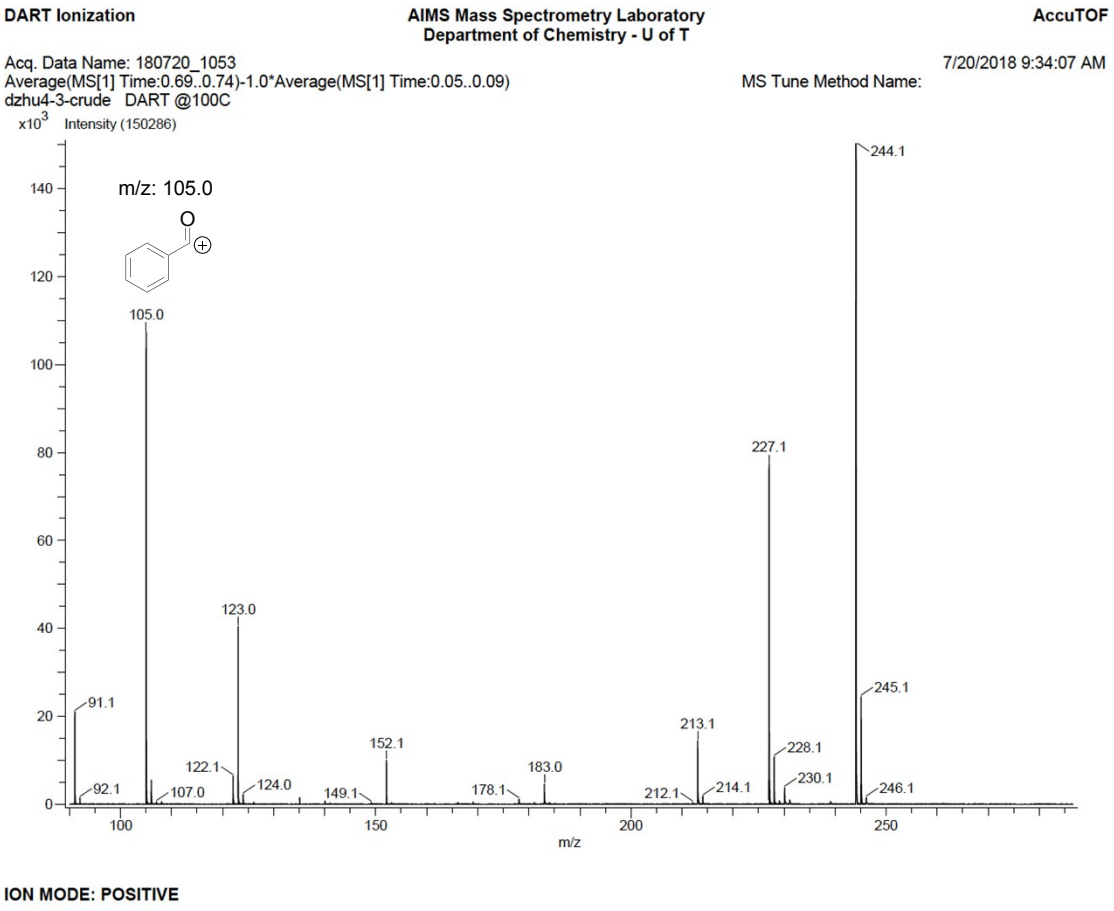


Figure S47. DART-MS result of compound **1** reaction mixture.

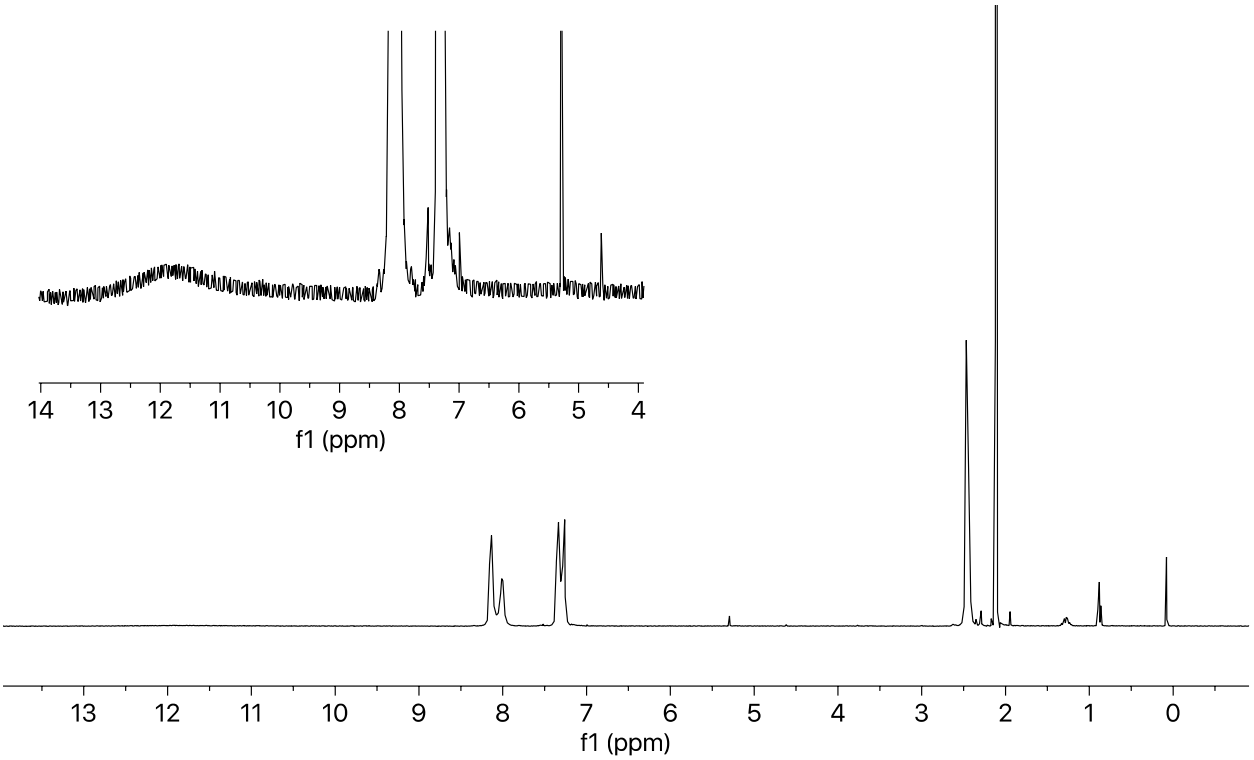


Figure S48. ^{1}H NMR spectrum of compound **1** reaction mixture in $CDCl_3$.

5. Computation Study

Electronic structure calculations were performed using *Gaussian 16*.[i] Geometry optimizations, frequency calculations, and energy determinations were performed using the M062X[ii] functional and the def2-TZVPP[iii] basis set with the D3 version of Grimme's dispersion (GD3)[iv] and dichloromethane solvation effect calculated using polarizable continuum model (PCM). The absence of any imaginary frequency with an absolute magnitude greater than 10 cm^{-1} confirmed that each optimized structure was indeed located at a minimum on its potential energy hypersurface. The Gibbs energy corrections from frequency calculations were added to the single-point energies to obtain the Gibbs free energies in solution. Natural bond orbital and natural population analyses were performed on optimized structures using the M062X functional and def2-TZVP[iii] basis set using NBO 6.0.[v] This work was made possible by the facilities of the Shared Hierarchical Academic Research Computing Network (SHARCNET: www.sharcnet.ca) and Compute Canada.

Table S1. Energies (ΔG) of various compounds

Compound	**NRG (kcal/mol)**	**NRG (relative, rounded, kcal/mol)**
Int1-eqeq	-1472736.436	0
Int1-eqax	-1472736.223	0.21
Int1-axax	-1472738.336	-1.90
Int1-axax-cis	-1472740.125	-3.69
8	-2144031.095	0
8-cis	-2144030.966	0.13

Table S2. NBO derived energies of HOMO and first instance of B-H in HOMO (above 5%)

Compound	**Orbital**	**NRG (rounded, kcal/mol)**	**NRG (relative, rounded, kcal/mol)**	**B-H incorporation into HOMO (%)**
Int1-eqeq	HOMO	-194.4	0	----
	HOMO-8	-239.7	-45.3	20.3 17.1
Int1-eqax	HOMO	-189.1	0	----
	HOMO-8	-229.0	-39.8	16.6 16.6
Int1-axax	HOMO	-192.7	0	----
	HOMO-2	-196.2	-3.5	6.0
	HOMO-8	-228.9	-36.2	22.5 18.5
Int1-axax-cis	HOMO	-195.2	0	----
	HOMO-8	-224.7	-29.4	25.6 25.5
8	HOMO	-190.5	0	----
	HOMO-12	-218.9	-28.4	17.1 17.1
8-cis	HOMO	-190.7	0	----
	HOMO-12	-218.7	-28.0	21.4 20.4

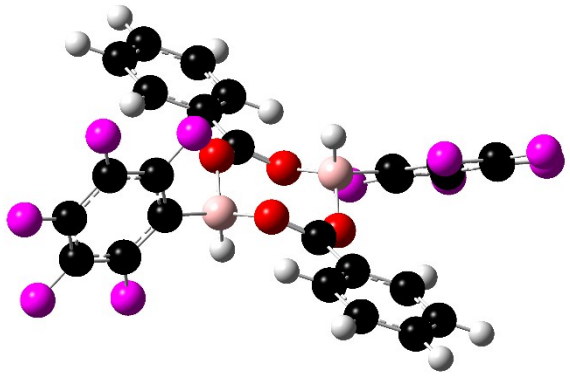


Figure S49. Optimized structure of **Int1**-eqeq.

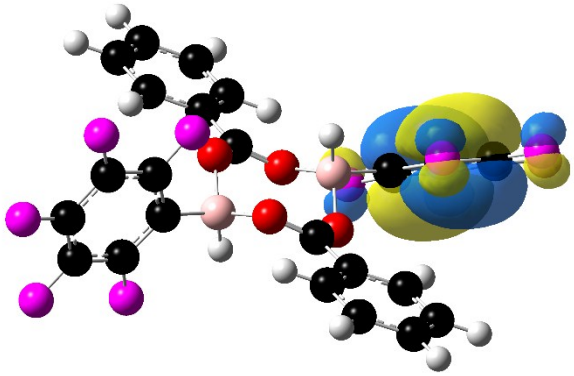


Figure S50. Surface contour plot (isovalue 0.03) of the HOMO of **Int1**-eqeq.

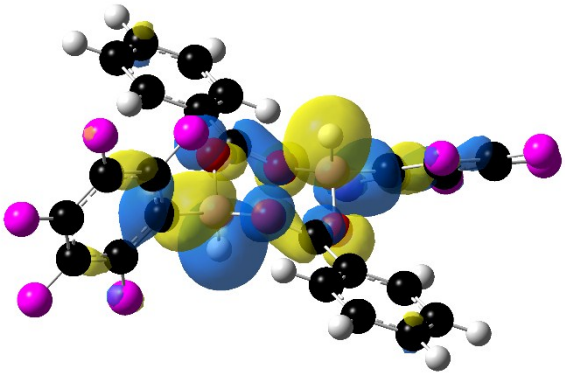


Figure S51. Surface contour plot (isovalue 0.03) of the HOMO-8 of **Int1**-eqeq.

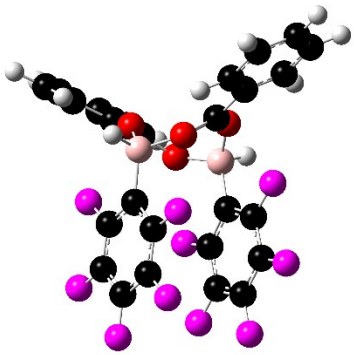


Figure S52. Optimized structure of **Int1**-eqax.

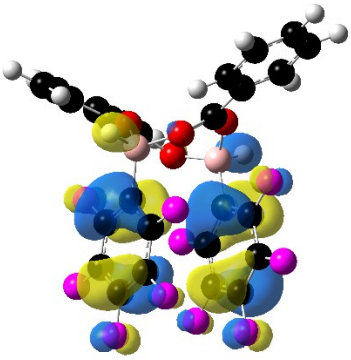


Figure S53. Surface contour plot (isovalue 0.03) of the HOMO of **Int1**-eqax.

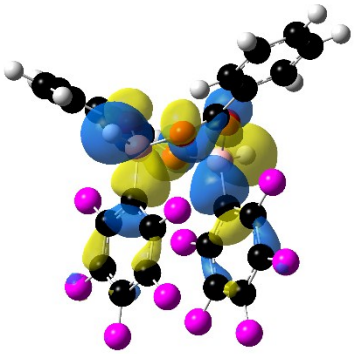


Figure S54. Surface contour plot (isovalue 0.03) of the HOMO-8 of **Int1**-eqax.

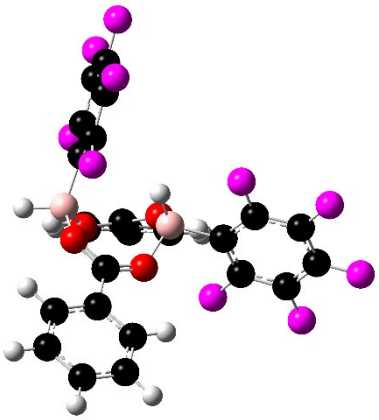


Figure S56. Optimized structure of **Int1**-axax.

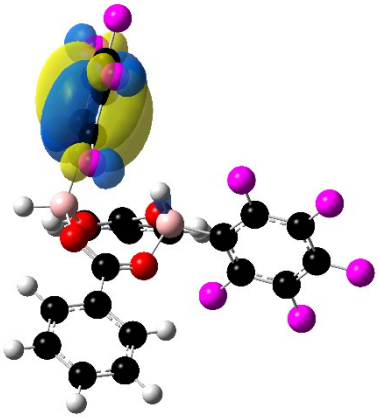


Figure S57. Surface contour plot (isovalue 0.03) of the HOMO of **Int1**-axax.

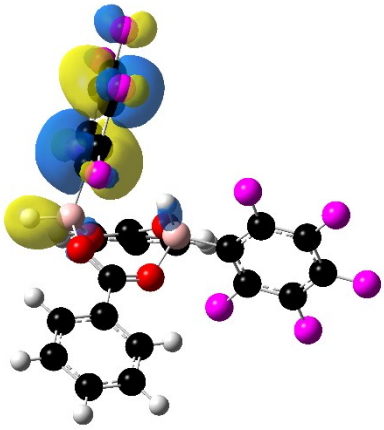


Figure S58. Surface contour plot (isovalue 0.03) of the HOMO-2 of **Int1**-axax.

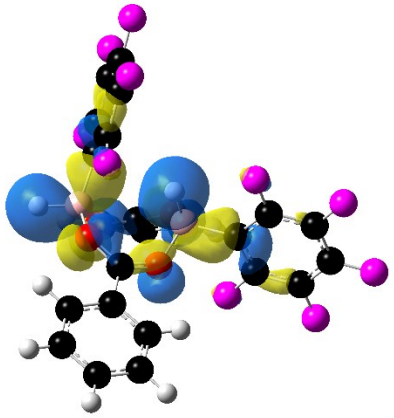


Figure S59. Surface contour plot (isovalue 0.03) of the HOMO-8 of **Int1**-axax.

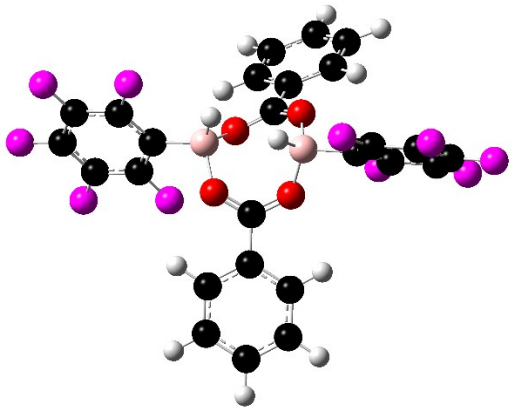


Figure S61. Optimized structure of **Int1**-axax-cis.

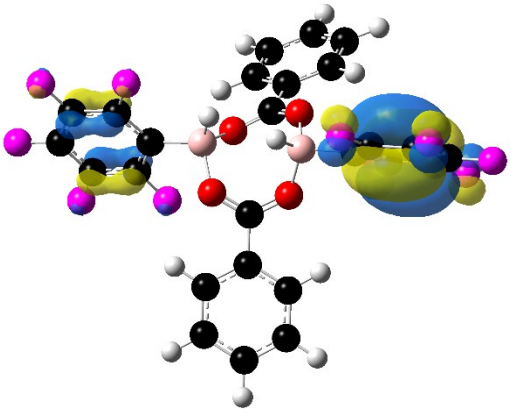


Figure S62. Surface contour plot (isovalue 0.03) of the HOMO of **Int1**-axax-cis.

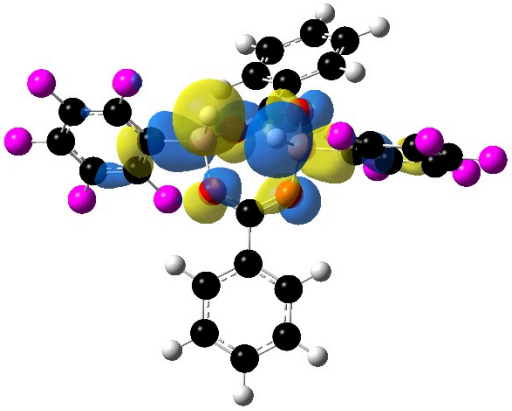


Figure S63. Surface contour plot (isovalue 0.03) of the HOMO-8 of **Int1**-axax-cis.

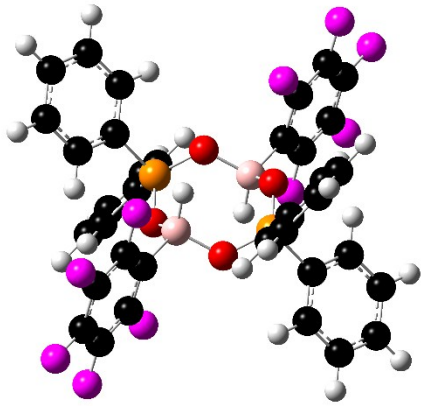


Figure S64. Optimized structure of **8.**

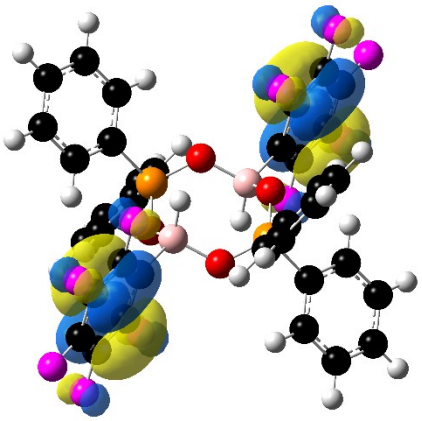


Figure S65. Surface contour plot (isovalue 0.03) of the HOMO of **8.**

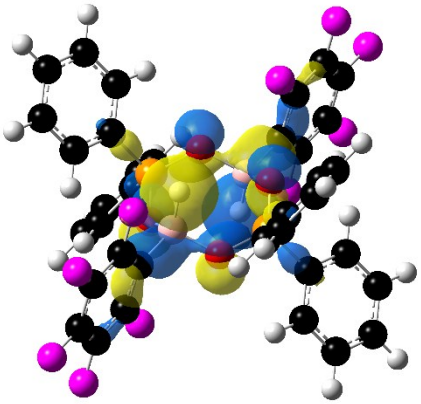


Figure S66. Surface contour plot (isovalue 0.03) of the HOMO-12 of **8**.

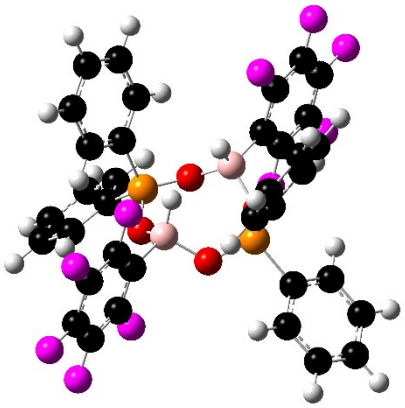


Figure S67. Optimized structure of **8**-cis.

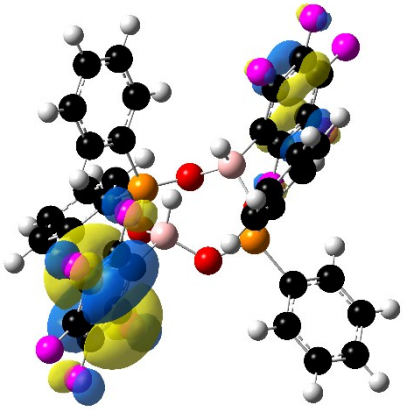


Figure S68. Surface contour plot (isovalue 0.03) of the HOMO of **8** –cis.

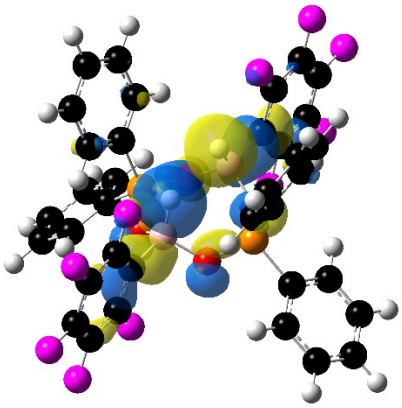


Figure S69. Surface contour plot (isovalue 0.03) of the HOMO-12 of **8**-cis.

Table S3. Cartesian coordinates (Å) of **Int1**-eqeq.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.964941	5.938529	2.769038
2	1	0	-2.541766	6.177893	-0.909429
3	8	0	-3.872497	5.591235	0.761441
4	8	0	-2.014261	4.426385	1.155944
5	8	0	-0.641720	6.549611	1.120047
6	8	0	-2.498663	7.707754	0.690794
7	6	0	-1.247281	7.642226	0.888779
8	6	0	-3.273450	4.498556	1.002606
9	6	0	-0.465488	8.879014	0.849206
10	6	0	-1.079718	10.071294	0.464442
11	6	0	0.885887	8.852225	1.195264
12	6	0	-0.337547	11.238259	0.428285
13	1	0	-2.127184	10.070981	0.197901
14	6	0	1.620989	10.023883	1.155304
15	1	0	1.343115	7.917725	1.487979
16	6	0	1.009505	11.212969	0.773274
17	1	0	-0.804545	12.166463	0.131065
18	1	0	2.668363	10.013457	1.421597
19	1	0	1.587283	12.126915	0.743501
20	6	0	-4.066649	3.272652	1.105552
21	6	0	-3.456031	2.089492	1.522339
22	6	0	-5.425309	3.299557	0.788941
23	6	0	-4.209009	0.932976	1.621805
24	1	0	-2.403176	2.088866	1.766140
25	6	0	-6.171200	2.138797	0.890820
26	1	0	-5.880458	4.225383	0.466742
27	6	0	-5.563090	0.959172	1.306512
28	1	0	-3.744630	0.012411	1.945624
29	1	0	-7.223948	2.149960	0.646728
30	1	0	-6.149156	0.053480	1.385640
31	5	0	-3.282055	6.682742	-0.118331
32	5	0	-1.219529	5.446231	1.969509
33	6	0	-4.529485	7.472974	-0.754068
34	6	0	-4.743351	7.563843	-2.118271
35	6	0	-5.463699	8.111987	0.046579
36	6	0	-5.817506	8.246059	-2.667144
37	6	0	-6.548667	8.802805	-0.458969
38	6	0	-6.724086	8.868347	-1.830501
39	6	0	-0.017557	4.610479	2.645005
40	6	0	-0.345738	3.745688	3.679694
41	6	0	1.326928	4.652837	2.314083
42	6	0	0.580234	2.978970	4.360859
43	6	0	2.289154	3.904408	2.974370
44	6	0	1.913929	3.063032	4.003239
45	9	0	1.771832	5.426150	1.317107
46	9	0	3.569479	3.982059	2.620009
47	9	0	2.823840	2.336798	4.640146
48	9	0	0.208162	2.166926	5.346567
49	9	0	-1.625808	3.625182	4.056646
50	9	0	-5.330133	8.072409	1.377191
51	9	0	-7.420756	9.401335	0.348084
52	9	0	-7.758588	9.526172	-2.338476
53	9	0	-5.985071	8.308666	-3.985703
54	9	0	-3.901196	6.982945	-2.978929

Sum of electronic and zero-point Energies= -2346.884275
Sum of electronic and thermal Energies= -2346.849188
Sum of electronic and thermal Enthalpies= -2346.848243
Sum of electronic and thermal Free Energies= -2346.956674

Table S4. Cartesian coordinates (Å) of **Int1**-eqax.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.547580	7.294805	-1.719450
2	8	0	-3.129651	5.520824	-0.556771
3	8	0	-3.185946	4.865531	1.587288
4	8	0	-1.347369	6.502457	1.558344
5	8	0	-2.321415	7.780780	-0.005676
6	6	0	-1.337522	7.450919	0.709647
7	6	0	-3.242109	4.634319	0.349604
8	6	0	-0.086640	8.203601	0.547725
9	6	0	0.024202	9.143123	-0.476252
10	6	0	0.975141	7.976866	1.422285
11	6	0	1.202363	9.854451	-0.624446

12	1	0	-0.809323	9.306864	-1.144093
13	6	0	2.149707	8.692427	1.268196
14	1	0	0.869490	7.249681	2.214417
15	6	0	2.262239	9.628636	0.246338
16	1	0	1.296076	10.583894	-1.416432
17	1	0	2.976462	8.524092	1.943652
18	1	0	3.181356	10.186700	0.128921
19	6	0	-3.440350	3.244146	-0.081094
20	6	0	-3.404608	2.219363	0.863387
21	6	0	-3.669569	2.962511	-1.427073
22	6	0	-3.596954	0.910291	0.456911
23	1	0	-3.226681	2.456131	1.902552
24	6	0	-3.862154	1.651253	-1.825704
25	1	0	-3.700774	3.769819	-2.144527
26	6	0	-3.825246	0.628014	-0.884983
27	1	0	-3.569531	0.110348	1.183155
28	1	0	-4.043534	1.425116	-2.866884
29	1	0	-3.976457	-0.395724	-1.199747
30	5	0	-3.492049	6.983055	-0.564823
31	5	0	-2.462620	5.933884	2.395883
32	6	0	-4.883302	7.329555	0.190790
33	6	0	-5.929697	6.435459	0.347200
34	6	0	-5.154189	8.624237	0.615858
35	6	0	-7.149525	6.772039	0.911840
36	6	0	-6.358025	9.004964	1.178083
37	6	0	-7.366404	8.069624	1.331155
38	9	0	-4.226123	9.581189	0.498888
39	9	0	-6.547280	10.253186	1.596981
40	9	0	-8.519746	8.414456	1.886333
41	9	0	-8.105383	5.860374	1.053525
42	9	0	-5.801750	5.160291	-0.051497
43	1	0	-1.926555	5.332853	3.281819
44	6	0	-3.482534	7.044143	2.989976
45	6	0	-3.145369	8.366625	3.226702
46	6	0	-4.748608	6.677347	3.428872
47	6	0	-3.998869	9.281859	3.821706
48	6	0	-5.629184	7.555081	4.032563
49	6	0	-5.252969	8.872160	4.229236
50	9	0	-1.937872	8.835391	2.874951
51	9	0	-3.622379	10.543321	4.000060
52	9	0	-6.092939	9.730832	4.790031
53	9	0	-6.841892	7.153185	4.402905
54	9	0	-5.179011	5.419941	3.273050

Sum of electronic and zero-point Energies= -2346.887894
Sum of electronic and thermal Energies= -2346.853254
Sum of electronic and thermal Enthalpies= -2346.852310
Sum of electronic and thermal Free Energies= -2346.956336

Table S5. Cartesian coordinates (Å) of **Int1**-axax.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.624587	6.183464	-0.515448
2	8	0	-2.938957	4.997894	1.259799
3	8	0	-1.916301	7.211827	1.585575
4	8	0	-1.648154	7.649956	-0.596906
5	6	0	-1.629427	7.987317	0.618845
6	6	0	-3.814731	5.340829	0.416745
7	6	0	-1.264041	9.372714	0.943456
8	6	0	-1.110308	9.749396	2.277265
9	6	0	-1.068740	10.296396	-0.082709
10	6	0	-0.760111	11.053420	2.581589
11	1	0	-1.263974	9.020240	3.060041
12	6	0	-0.718731	11.598381	0.229649
13	1	0	-1.193369	9.987794	-1.110645
14	6	0	-0.565000	11.975028	1.559255
15	1	0	-0.637824	11.352451	3.612946
16	1	0	-0.566299	12.320250	-0.560111
17	1	0	-0.291388	12.993436	1.799988
18	6	0	-5.148033	4.737317	0.532819
19	6	0	-5.471486	3.992240	1.666202
20	6	0	-6.076109	4.912628	-0.492583
21	6	0	-6.728909	3.423854	1.771668
22	1	0	-4.740943	3.872242	2.453561
23	6	0	-7.329902	4.337219	-0.381742
24	1	0	-5.803890	5.487409	-1.366166
25	6	0	-7.654679	3.595624	0.748677
26	1	0	-6.989274	2.848448	2.648689
27	1	0	-8.053580	4.463446	-1.174491
28	1	0	-8.635870	3.148246	0.832848
29	5	0	-2.375603	6.524722	-1.306279
30	5	0	-1.658954	5.718023	1.654841

31	1	0	-0.752842	5.419981	0.946206
32	6	0	-1.422610	5.364308	3.207390
33	6	0	-2.399164	5.610948	4.160016
34	6	0	-0.249073	4.803575	3.679905
35	6	0	-2.239187	5.323589	5.502147
36	6	0	-0.046451	4.500223	5.016978
37	6	0	-1.048767	4.762417	5.931196
38	9	0	-3.565199	6.155237	3.787525
39	9	0	-3.205445	5.577230	6.380803
40	9	0	-0.871967	4.478325	7.215190
41	9	0	1.097721	3.960800	5.428955
42	9	0	0.756640	4.526202	2.844577
43	1	0	-2.774936	7.006421	-2.326931
44	6	0	-1.448716	5.231587	-1.596465
45	6	0	-2.024763	4.037845	-2.001293
46	6	0	-0.061824	5.237333	-1.576705
47	6	0	-1.297608	2.911114	-2.341825
48	6	0	0.704596	4.136031	-1.914093
49	6	0	0.082227	2.962235	-2.297308
50	9	0	-3.361137	3.933495	-2.076044
51	9	0	-1.909434	1.790359	-2.713349
52	9	0	0.803542	1.896952	-2.621560
53	9	0	2.032637	4.193476	-1.869608
54	9	0	0.609700	6.334092	-1.208703

Sum of electronic and zero-point Energies= -2346.887203
Sum of electronic and thermal Energies= -2346.852182
Sum of electronic and thermal Enthalpies= -2346.851237
Sum of electronic and thermal Free Energies= -2346.959702

Table S6. Cartesian coordinates (Å) of **Int1**-axax-cis.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.729261	6.266354	-0.503041
2	8	0	-2.993791	5.026966	1.213545
3	8	0	-1.929386	7.206443	1.592313
4	8	0	-1.756921	7.726886	-0.580832
5	6	0	-1.718707	8.027410	0.645093
6	6	0	-3.900787	5.415285	0.425349
7	6	0	-1.427395	9.422141	1.002553
8	6	0	-1.228692	9.764941	2.339333
9	6	0	-1.355837	10.390514	0.001803
10	6	0	-0.954442	11.080146	2.672169
11	1	0	-1.288903	9.001370	3.101857
12	6	0	-1.082472	11.703674	0.342803
13	1	0	-1.520064	10.107790	-1.028266
14	6	0	-0.881579	12.046407	1.675223
15	1	0	-0.797136	11.353521	3.705899
16	1	0	-1.027336	12.460599	-0.426674
17	1	0	-0.667982	13.073613	1.938301
18	6	0	-5.249025	4.859417	0.601673
19	6	0	-5.526081	4.061474	1.711156
20	6	0	-6.239652	5.138091	-0.339030
21	6	0	-6.797878	3.541125	1.875658
22	1	0	-4.747872	3.862869	2.434205
23	6	0	-7.508638	4.612337	-0.168486
24	1	0	-6.007319	5.759248	-1.192460
25	6	0	-7.785916	3.815891	0.936880
26	1	0	-7.021374	2.923974	2.734288
27	1	0	-8.281450	4.821632	-0.894459
28	1	0	-8.778875	3.407578	1.068279
29	5	0	-2.438309	6.543242	-1.258350
30	5	0	-1.677153	5.706571	1.571251
31	1	0	-0.812933	5.435357	0.801958
32	6	0	-1.369426	5.279683	3.093429
33	6	0	-2.295933	5.488293	4.103843
34	6	0	-0.179193	4.690500	3.482381
35	6	0	-2.073324	5.137368	5.421774
36	6	0	0.085642	4.323664	4.792416
37	6	0	-0.868548	4.548887	5.765812
38	9	0	-3.473892	6.057441	3.816134
39	9	0	-2.993480	5.356141	6.357585
40	9	0	-0.632212	4.203614	7.025065
41	9	0	1.244130	3.758463	5.122190
42	9	0	0.783537	4.446475	2.588001
43	1	0	-1.743783	5.579015	-1.273502
44	6	0	-2.872477	7.072132	-2.716258
45	6	0	-2.502154	6.435025	-3.887642
46	6	0	-3.651015	8.209308	-2.869869
47	6	0	-2.874613	6.891326	-5.142205
48	6	0	-4.043927	8.699125	-4.100887
49	6	0	-3.649619	8.030277	-5.246907

50	9	0	-1.752616	5.328967	-3.853032
51	9	0	-2.495405	6.247632	-6.243166
52	9	0	-4.015246	8.481637	-6.439977
53	9	0	-4.790625	9.795979	-4.199244
54	9	0	-4.056782	8.886209	-1.787627

Sum of electronic and zero-point Energies= -2346.890753
Sum of electronic and thermal Energies= -2346.855701
Sum of electronic and thermal Enthalpies= -2346.854756
Sum of electronic and thermal Free Energies= -2346.962553

Table S7. Cartesian coordinates (Å) of **8**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	2.453402	-1.269056	6.393760
2	8	0	4.261725	-2.377987	3.638281
3	9	0	2.861528	2.295982	-0.503785
4	9	0	5.064165	0.378251	3.137857
5	8	0	3.122757	-0.830382	5.081135
6	9	0	5.004602	2.168885	1.150949
7	9	0	0.772679	0.605891	-0.146304
8	9	0	0.810748	-1.185241	1.825118
9	6	0	3.234470	-0.320435	7.683587
10	6	0	3.423301	-0.897369	8.937707
11	1	0	3.122395	-1.922480	9.114700
12	6	0	4.407397	1.153071	9.713915
13	1	0	4.869009	1.727790	10.505350
14	6	0	4.012770	-0.156828	9.951832
15	1	0	4.168544	-0.603918	10.923758
16	6	0	4.218593	1.728172	8.462537
17	1	0	4.534137	2.745891	8.279644
18	6	0	3.632005	0.994046	7.443995
19	1	0	3.494354	1.432462	6.464087
20	6	0	2.944763	-0.486681	2.569459
21	6	0	3.986283	0.401510	2.345859
22	6	0	3.980258	1.336826	1.327412
23	6	0	2.887864	1.405113	0.480634
24	6	0	1.825585	0.541806	0.666239
25	6	0	1.872714	-0.380893	1.699437
26	5	0	2.991824	-1.569508	3.768179
27	6	0	0.707061	-0.929230	6.301399
28	6	0	-0.179878	-1.587112	7.152212
29	1	0	0.186939	-2.328001	7.850813
30	6	0	-1.533784	-1.299235	7.084792
31	1	0	-2.226059	-1.811005	7.738719
32	6	0	-2.000046	-0.360024	6.172223
33	1	0	-3.057868	-0.140868	6.119685
34	6	0	-1.116614	0.293214	5.323019
35	1	0	-1.483234	1.016758	4.608250
36	6	0	0.240288	0.011942	5.386402
37	1	0	0.933099	0.511413	4.720514
38	1	0	2.029535	-2.293178	3.784305
39	15	0	4.382544	-3.874057	3.969848
40	8	0	2.574221	-2.765125	6.725327
41	9	0	3.974418	-7.439094	10.867394
42	9	0	1.771781	-5.521362	7.225752
43	8	0	3.713189	-4.312730	5.282473
44	9	0	1.831343	-7.311996	9.212659
45	9	0	6.063267	-5.749003	10.509912
46	9	0	6.025199	-3.957871	8.538490
47	6	0	3.601475	-4.822677	2.680022
48	6	0	3.412644	-4.245743	1.425902
49	1	0	3.713550	-3.220631	1.248909
50	6	0	2.428549	-6.296183	0.649694
51	1	0	1.966936	-6.870902	-0.141741
52	6	0	2.823175	-4.986284	0.411776
53	1	0	2.667401	-4.539194	-0.560150
54	6	0	2.617353	-6.871284	1.901071
55	1	0	2.301809	-7.889003	2.083964
56	6	0	3.203940	-6.137158	2.919613
57	1	0	3.341592	-6.575574	3.899521
58	6	0	3.891183	-4.656431	7.794149
59	6	0	2.849663	-5.544621	8.017750
60	6	0	2.855688	-6.479938	9.036197
61	6	0	3.948082	-6.548225	9.882975
62	6	0	5.010361	-5.684918	9.697369
63	6	0	4.963232	-4.762219	8.664171
64	5	0	3.844122	-3.573604	6.595429
65	6	0	6.128885	-4.213882	4.062209
66	6	0	7.015824	-3.556001	3.211395
67	1	0	6.649007	-2.815112	2.512794
68	6	0	8.369730	-3.843877	3.278815

69	1	0	9.062005	-3.332108	2.624888
70	6	0	8.835992	-4.783088	4.191384
71	1	0	9.893814	-5.002244	4.243922
72	6	0	7.952560	-5.436326	5.040589
73	1	0	8.319180	-6.159870	5.755358
74	6	0	6.595658	-5.155054	4.977206
75	1	0	5.902847	-5.654525	5.643094
76	1	0	4.806411	-2.849934	6.579303

Sum of electronic and zero-point Energies= -3416.644878
Sum of electronic and thermal Energies= -3416.598000
Sum of electronic and thermal Enthalpies= -3416.597056
Sum of electronic and thermal Free Energies= -3416.733616

Table S8. Cartesian coordinates (Å) of **8**-cis.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	2.328877	-1.340317	6.315524
2	8	0	3.779579	-2.546482	3.439375
3	9	0	4.610118	2.826034	0.082597
4	9	0	6.181521	0.697169	3.923782
5	8	0	2.651908	-0.949040	4.864389
6	9	0	6.468608	2.557407	2.037870
7	9	0	2.444431	1.196823	0.040150
8	9	0	2.134588	-0.676425	1.924953
9	6	0	3.459134	-0.495969	7.411449
10	6	0	3.719629	-1.026554	8.673631
11	1	0	3.271362	-1.966887	8.971238
12	6	0	5.155372	0.841201	9.146889
13	1	0	5.821739	1.360423	9.822278
14	6	0	4.569063	-0.355866	9.539556
15	1	0	4.779190	-0.769952	10.515892
16	6	0	4.896552	1.370655	7.888871
17	1	0	5.361387	2.297518	7.582786
18	6	0	4.047423	0.704017	7.018473
19	1	0	3.854205	1.106264	6.031630
20	6	0	4.142162	-0.076221	3.007417
21	6	0	5.229954	0.780033	2.985688
22	6	0	5.405049	1.756414	2.017413
23	6	0	4.460544	1.896588	1.019240
24	6	0	3.356106	1.062799	1.001196
25	6	0	3.220313	0.102461	1.986714
26	6	0	0.654553	-0.821832	6.614525
27	6	0	-0.133975	-1.520664	7.526308
28	1	0	0.256354	-2.403927	8.014536
29	6	0	-1.424590	-1.086454	7.788636
30	1	0	-2.042601	-1.629748	8.489801
31	6	0	-1.922275	0.040147	7.146339
32	1	0	-2.930069	0.375029	7.351402
33	6	0	-1.134757	0.736491	6.237681
34	1	0	-1.527910	1.608953	5.734692
35	6	0	0.156401	0.308987	5.969674
36	1	0	0.770647	0.841692	5.255484
37	15	0	4.237241	-3.925895	3.936896
38	8	0	2.373264	-2.846373	6.617780
39	9	0	3.071264	-7.741019	10.674695
40	9	0	1.369385	-5.594205	6.895099
41	8	0	3.547365	-4.428610	5.215935
42	9	0	1.128315	-7.449702	8.807617
43	9	0	5.264799	-6.149517	10.606165
44	9	0	5.526490	-4.296177	8.710853
45	6	0	3.817759	-5.082913	2.653824
46	6	0	3.774397	-4.657538	1.327540
47	1	0	3.947577	-3.616898	1.086372
48	6	0	3.256710	-6.903383	0.644936
49	1	0	3.034436	-7.613976	-0.139574
50	6	0	3.491758	-5.572178	0.324524
51	1	0	3.450150	-5.245539	-0.705198
52	6	0	3.300016	-7.326144	1.967700
53	1	0	3.109580	-8.361526	2.213650
54	6	0	3.582152	-6.417997	2.976592
55	1	0	3.607588	-6.738903	4.009731
56	6	0	3.455658	-4.861644	7.715387
57	6	0	2.353947	-5.700321	7.794475
58	6	0	2.204700	-6.666865	8.772014
59	6	0	3.194551	-6.818754	9.727196
60	6	0	4.310664	-6.005896	9.688471
61	6	0	4.420179	-5.049697	8.690927
62	5	0	3.592555	-3.739019	6.560545
63	6	0	6.002810	-3.891016	4.206340
64	6	0	6.800844	-3.026438	3.459811
65	1	0	6.348310	-2.346874	2.747753

66	6	0	8.174713	-3.026505	3.645546
67	1	0	8.795190	-2.350563	3.073776
68	6	0	8.749124	-3.887920	4.572227
69	1	0	9.820701	-3.882883	4.718813
70	6	0	7.954168	-4.750264	5.316830
71	1	0	8.403256	-5.413181	6.043255
72	6	0	6.579582	-4.754442	5.135334
73	1	0	5.954608	-5.415215	5.723488
74	1	0	4.595119	-3.085837	6.663591
75	1	0	4.865686	-1.262961	4.913776
76	5	0	3.950767	-1.216168	4.137667

Sum of electronic and zero-point Energies= -3416.645042
Sum of electronic and thermal Energies= -3416.598261
Sum of electronic and thermal Enthalpies= -3416.597317
Sum of electronic and thermal Free Energies= -3416.733411

References

[i] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, M. C. X. Li, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas and J. B. Foresman and D. J. Fox, Gaussian 09, Revision E.01, Wallingford, CT, 2016.

[ii] Y. Zhao and D. G. Truhlar, "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals," Theor. Chem. Acc., 120 (2008) 215-41. DOI: 10.1007/s00214-007-0310-x.

[iii] (a) F. Weigend and R. Ahlrichs, "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy," Phys. Chem. Chem. Phys., 7 (2005) 3297-305. DOI: 10.1039/B508541A. (b) F. Weigend, "Accurate Coulomb-fitting basis sets for H to Rn," Phys. Chem. Chem. Phys., 8 (2006) 1057-65. DOI: 10.1039/B515623H.

[iv] S. Grimme, J. Antony, S. Ehrlich and H. Kreig, "A consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu," *J. Chem. Phys.,* 132 (2010) 154105. DOI: 10.1063/1.3382344.

[v] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, NBO 6.0, Madison, WI, 2013.