Supplementary Information for

A Long-Tethered (P-B-P)-Pincer Ligand: Synthesis, Complexation, and Application to Catalytic Dehydrogenation of Alkanes

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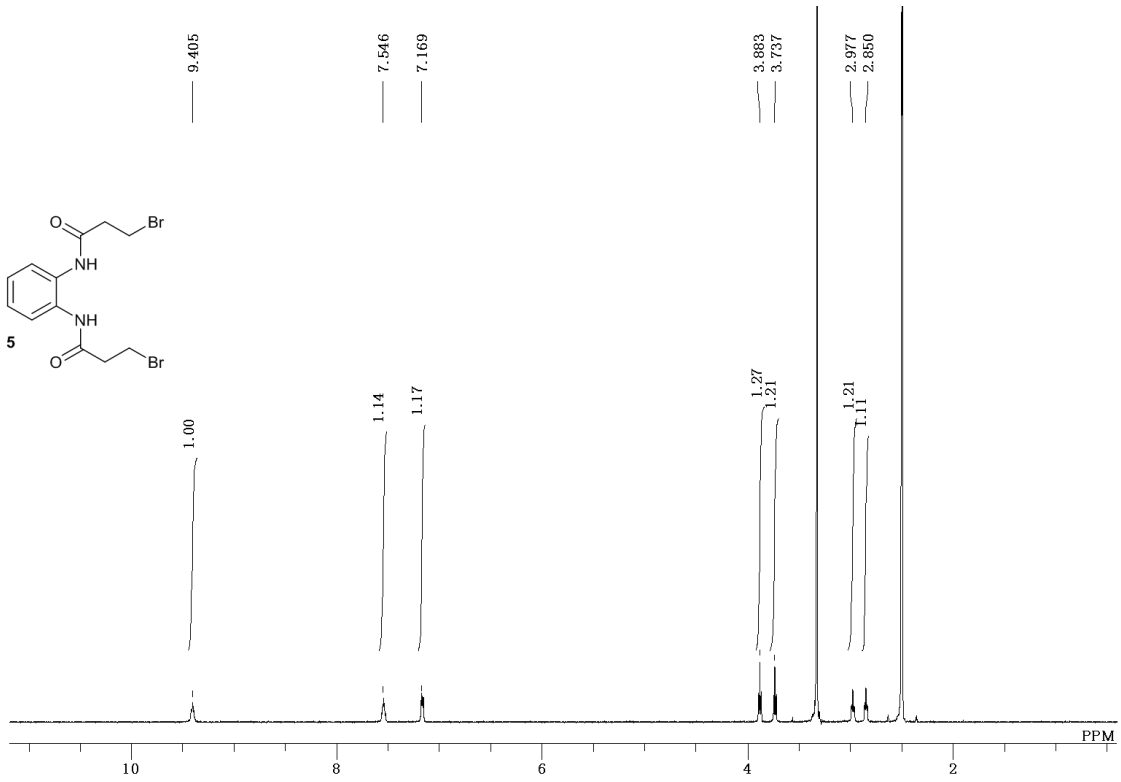

Figure S1. ^{1}H NMR spectrum of **5** (d_6-DMSO, 25 °C, 500 MHz)

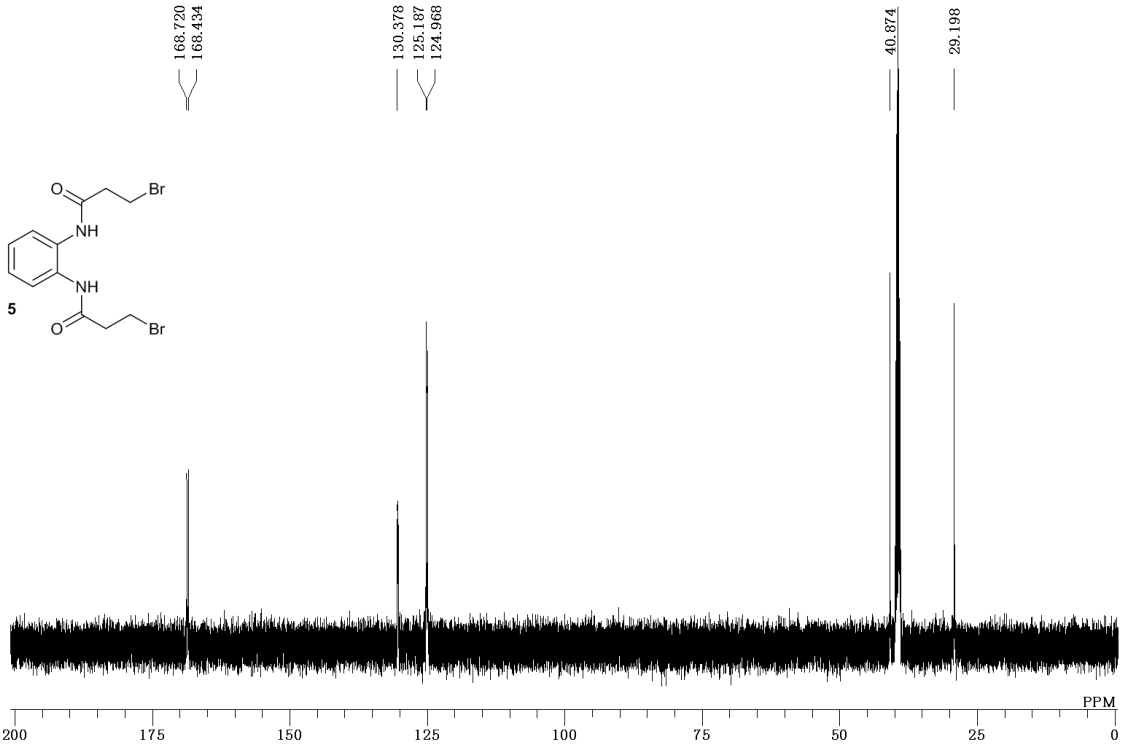

Figure S2. ^{13}C NMR spectrum of **5** (d_6-DMSO, 25 °C, 126 MHz)

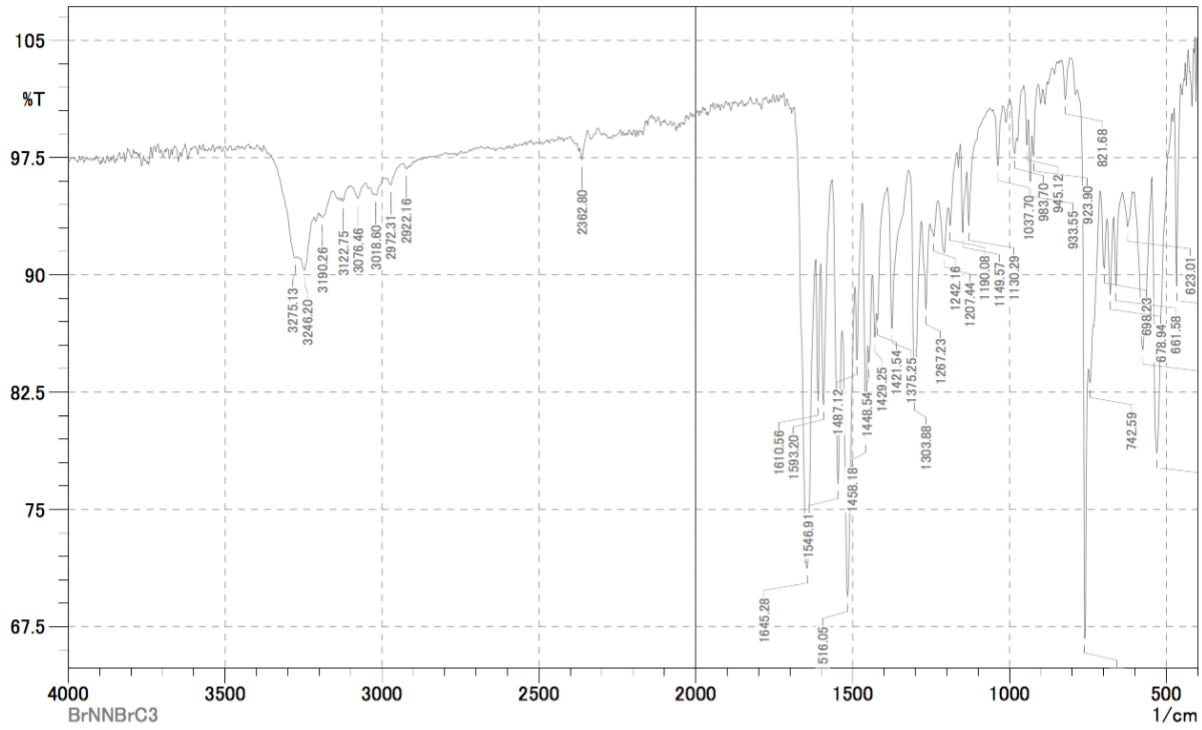

Figure S3. IR spectrum of **5**

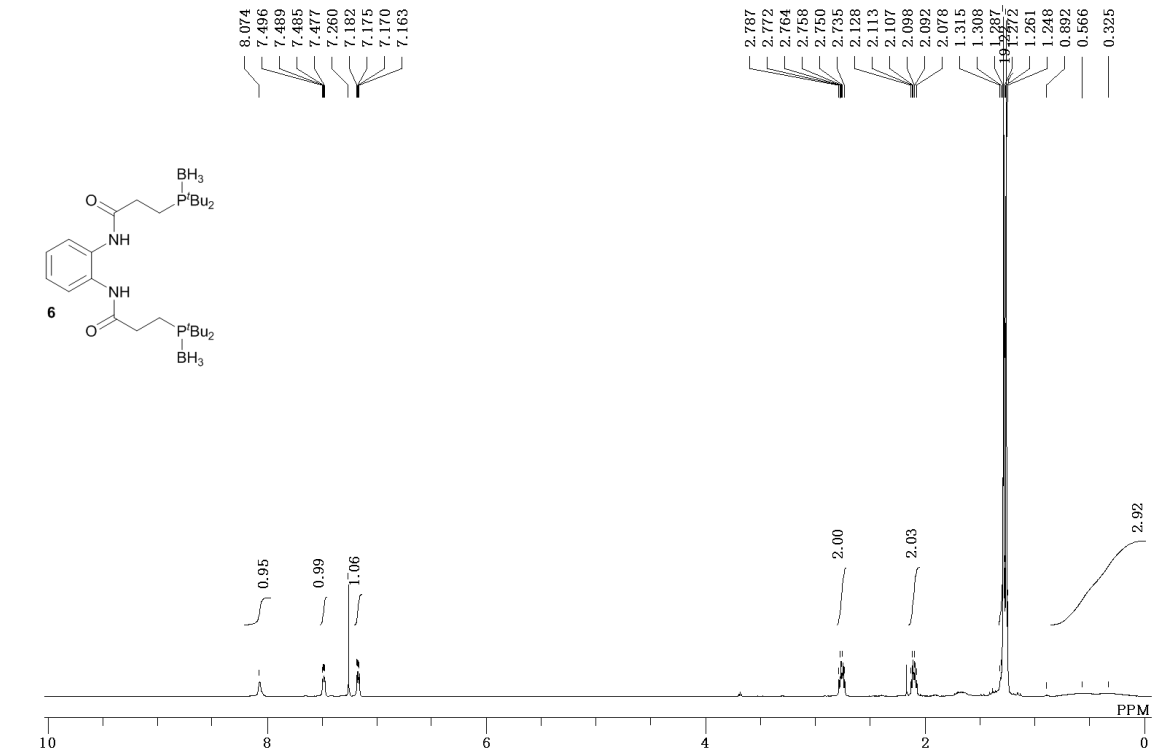

Figure S4. ^{1}H NMR spectrum of **6** ($CDCl_3$, 25 °C, 500 MHz)

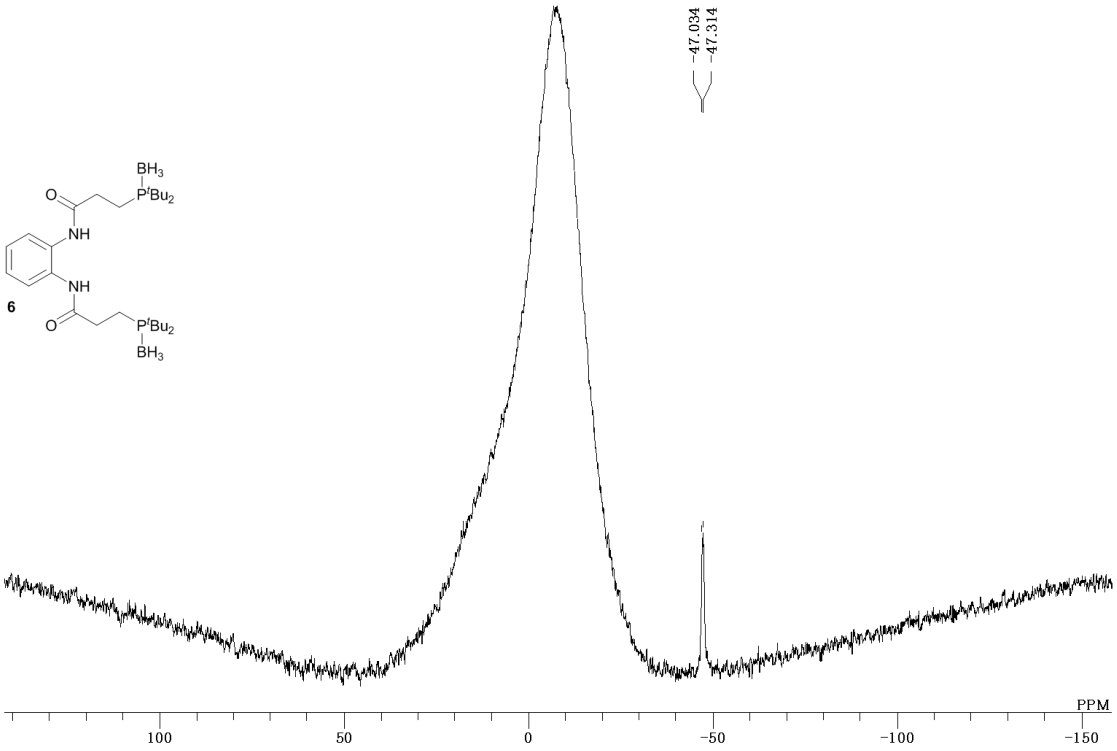

Figure S5. ^{11}B NMR spectrum of **6** ($CDCl_3$, 25 °C, 161 MHz)

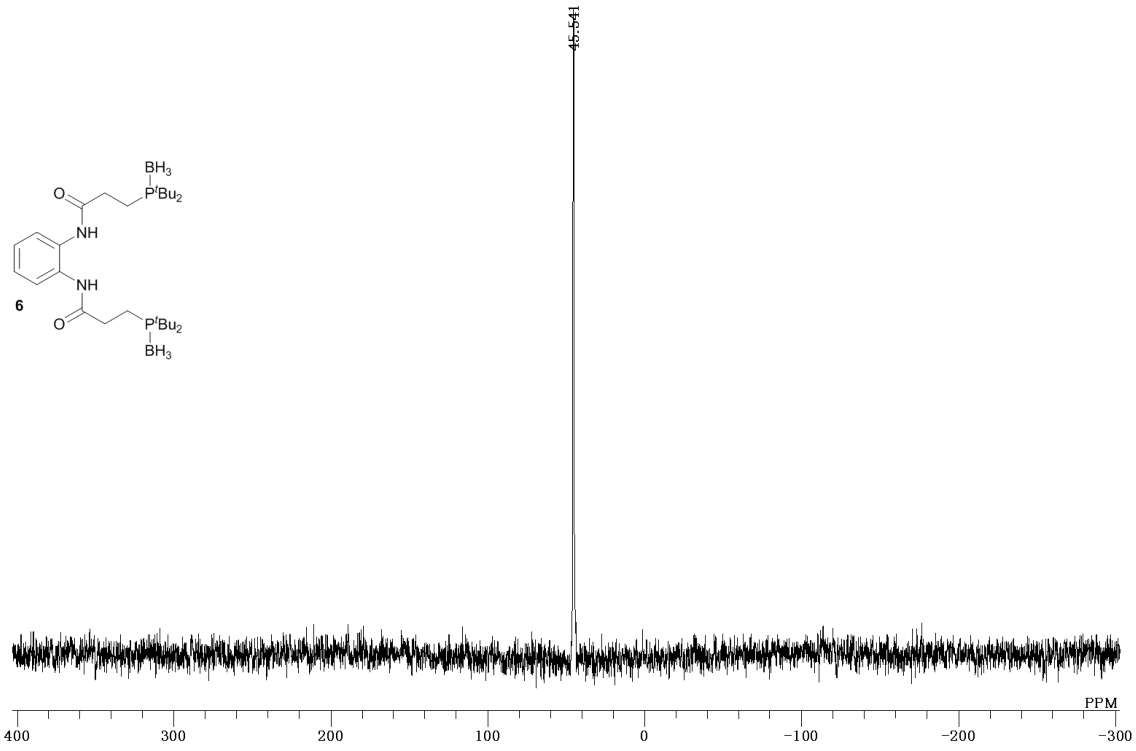

Figure S6. ^{31}P NMR spectrum of **6** ($CDCl_3$, 25 °C, 202 MHz)

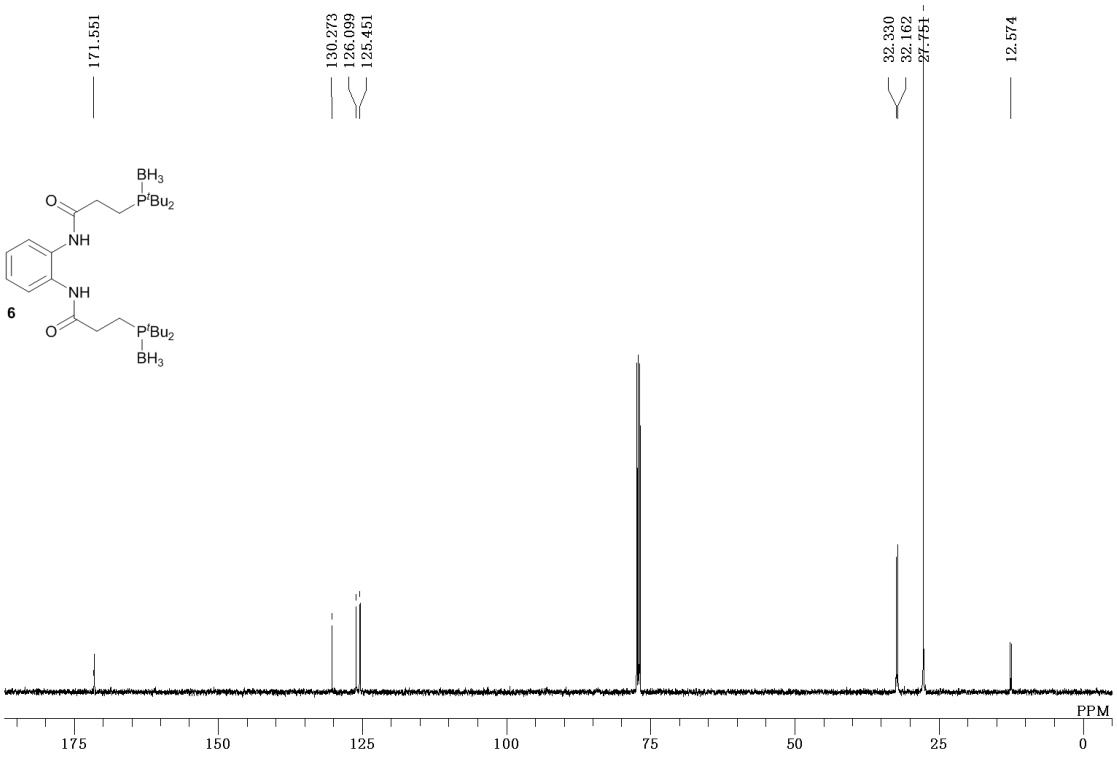

Figure S7. ^{13}C NMR spectrum of **6** ($CDCl_3$, 25 °C, 126 MHz)

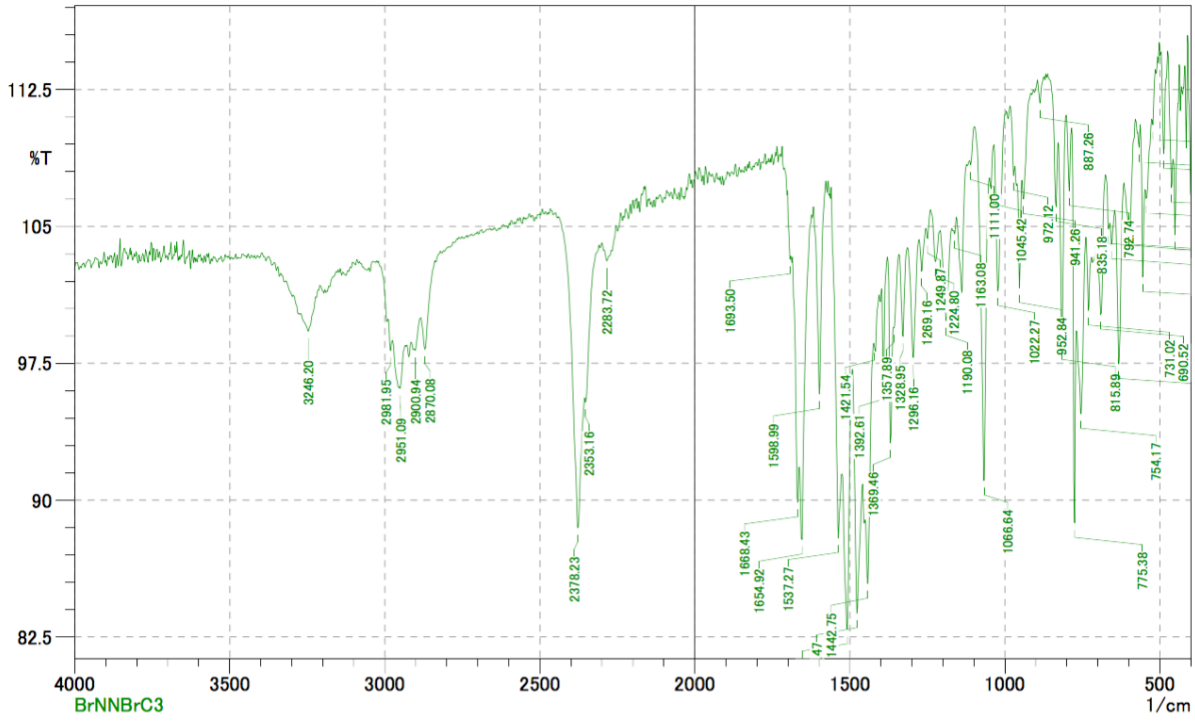

Figure S8. IR spectrum of **6**

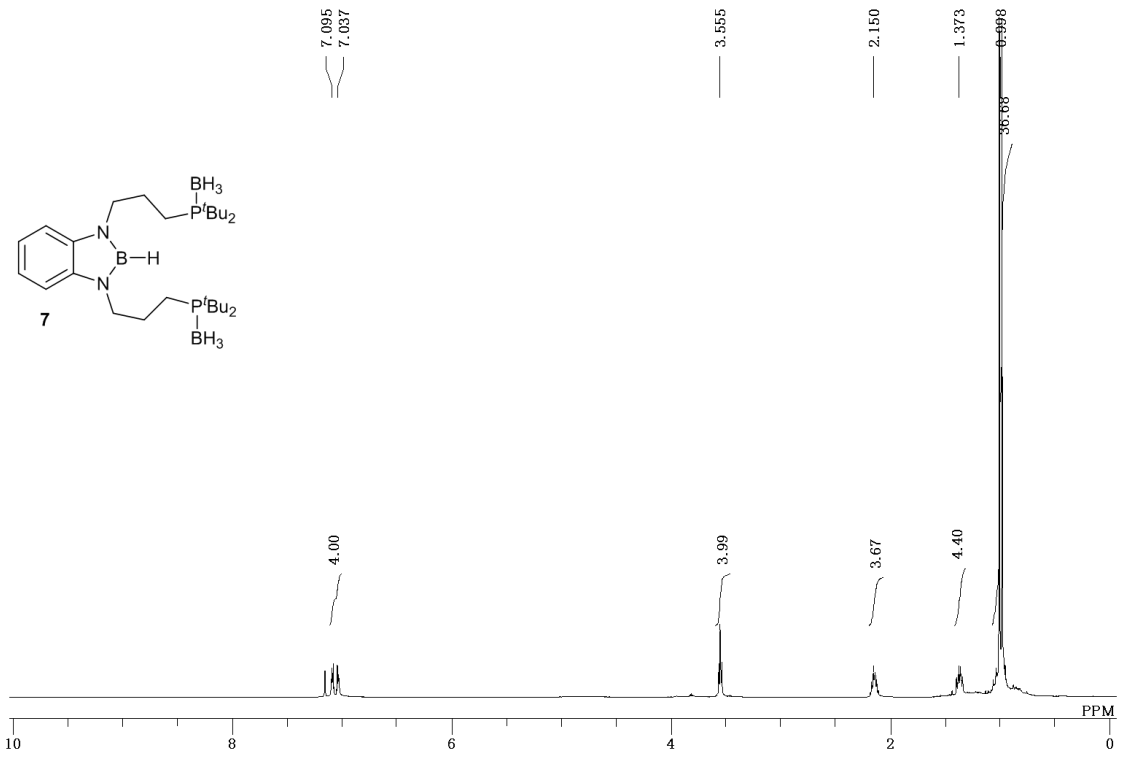

Figure S9. ^{1}H NMR spectrum of **7** (C_6D_6, 25 °C, 500 MHz)

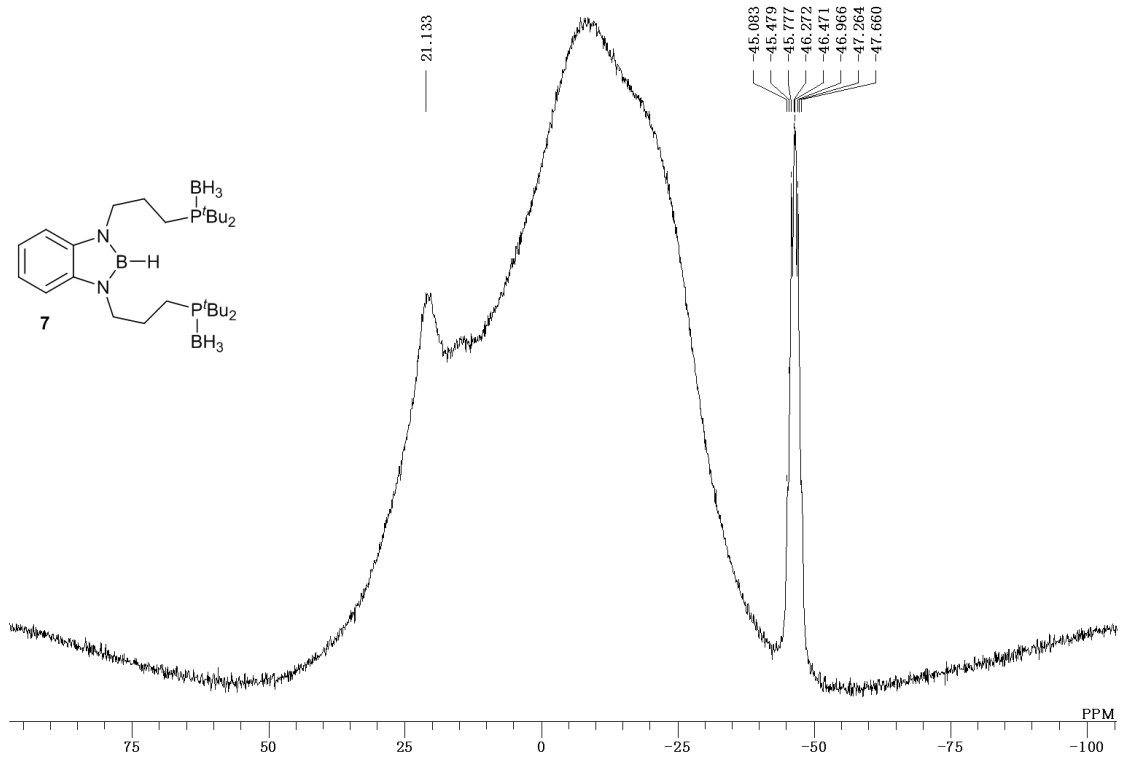

Figure S10. ^{11}B NMR spectrum of **7** (C_6D_6, 25 °C, 161 MHz)

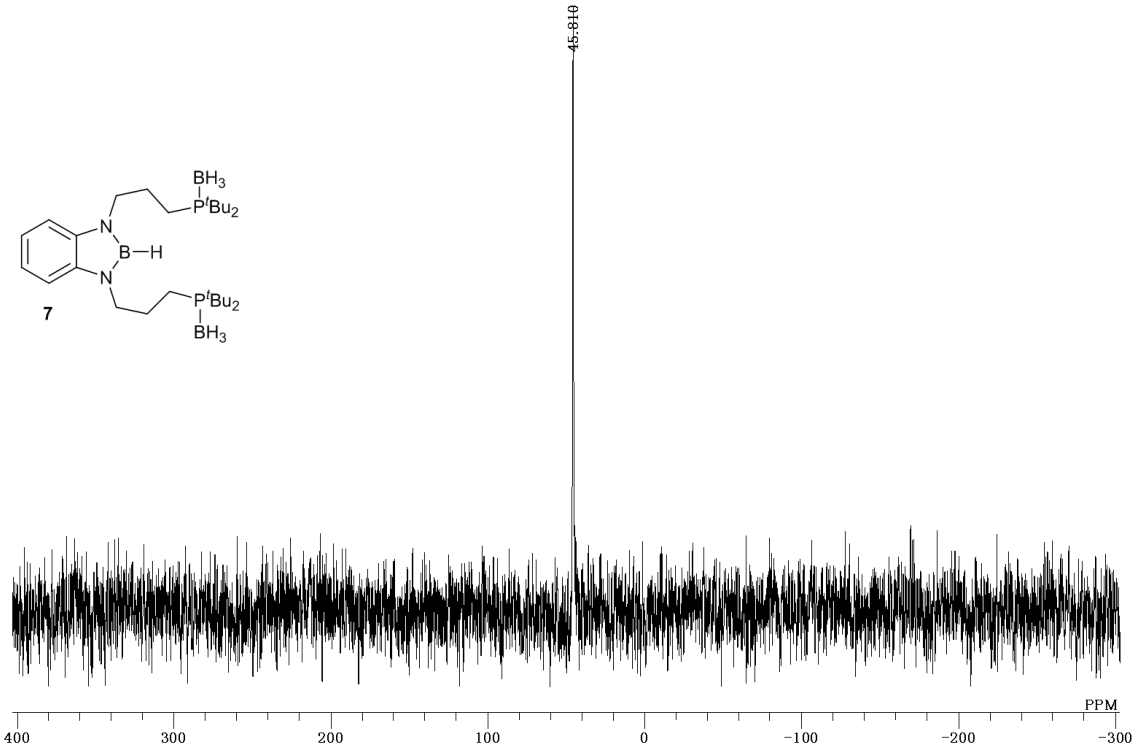

Figure S11. ^{31}P NMR spectrum of **7** (C_6D_6, 25 °C, 202 MHz)

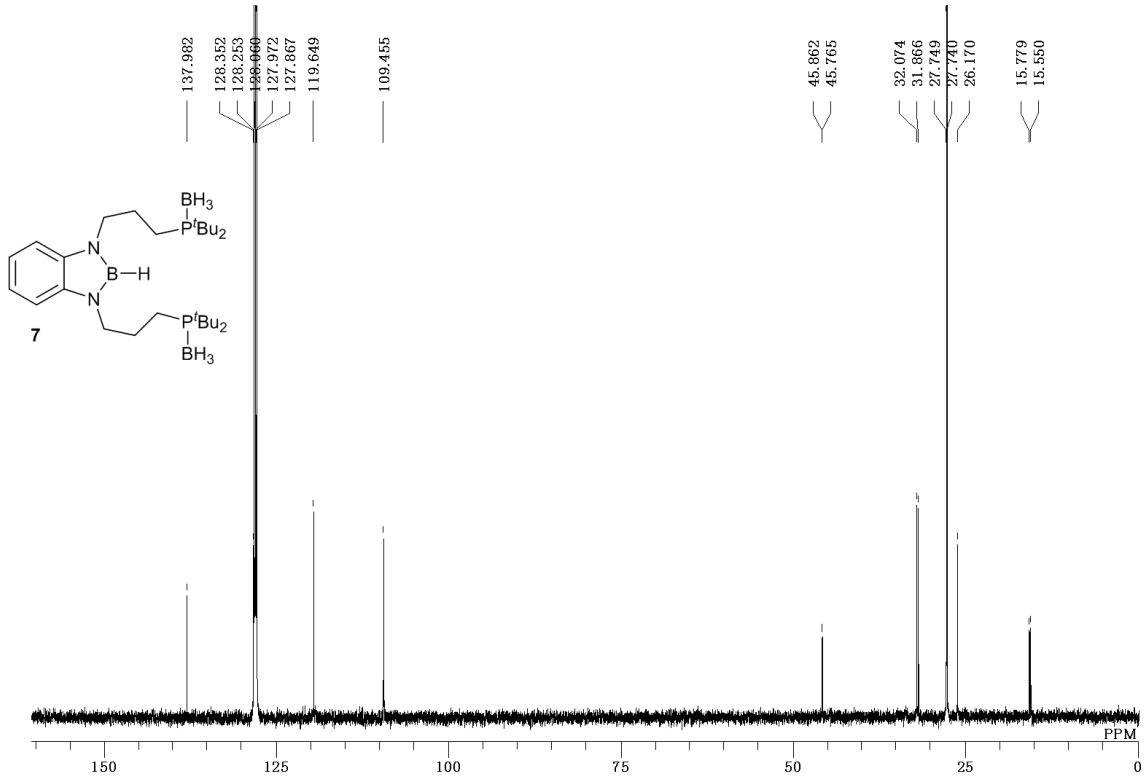

Figure S12. ^{13}C NMR spectrum of **7** (C_6D_6, 25 °C, 126 MHz)

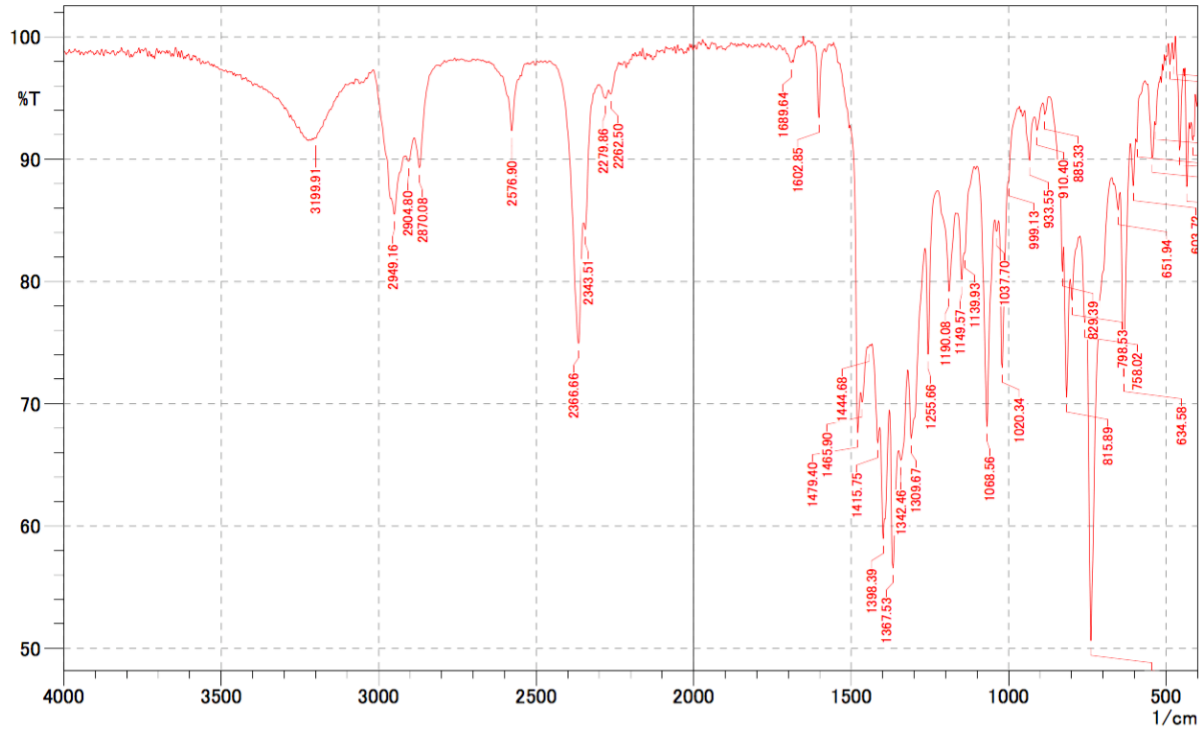

Figure S13. IR spectrum of **7**

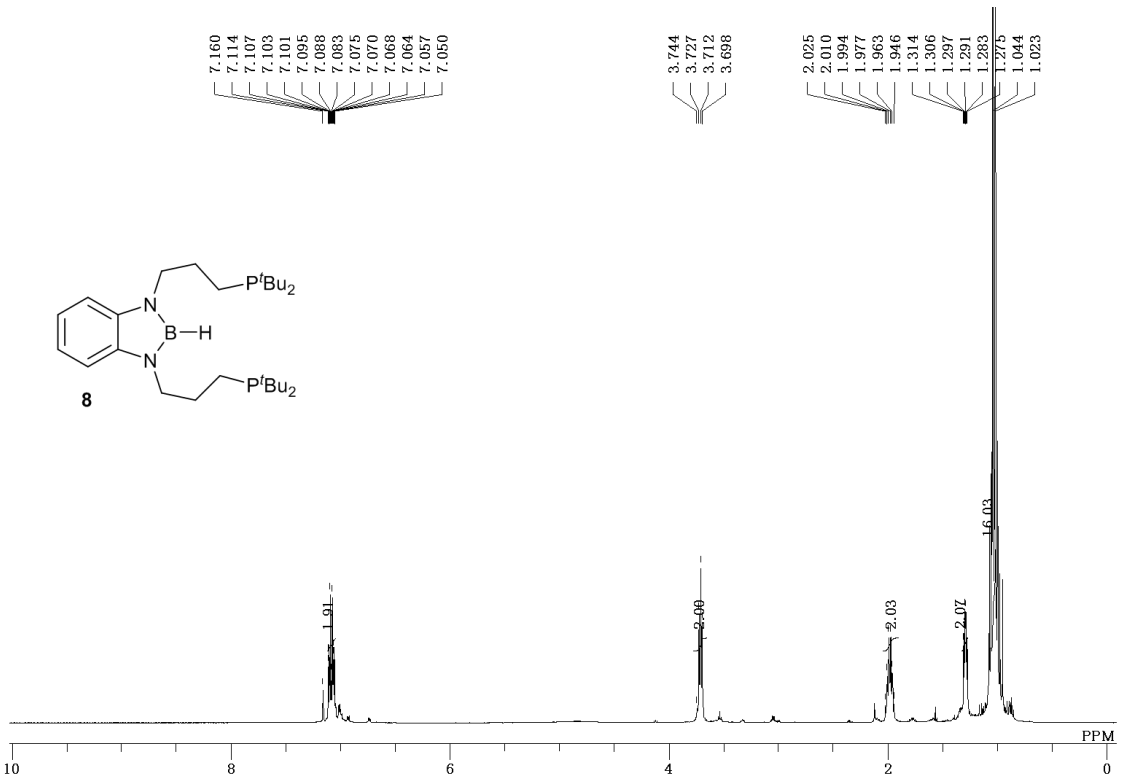

Figure S14. ^{1}H NMR spectrum of **8** (C_6D_6, 25 °C, 500 MHz)

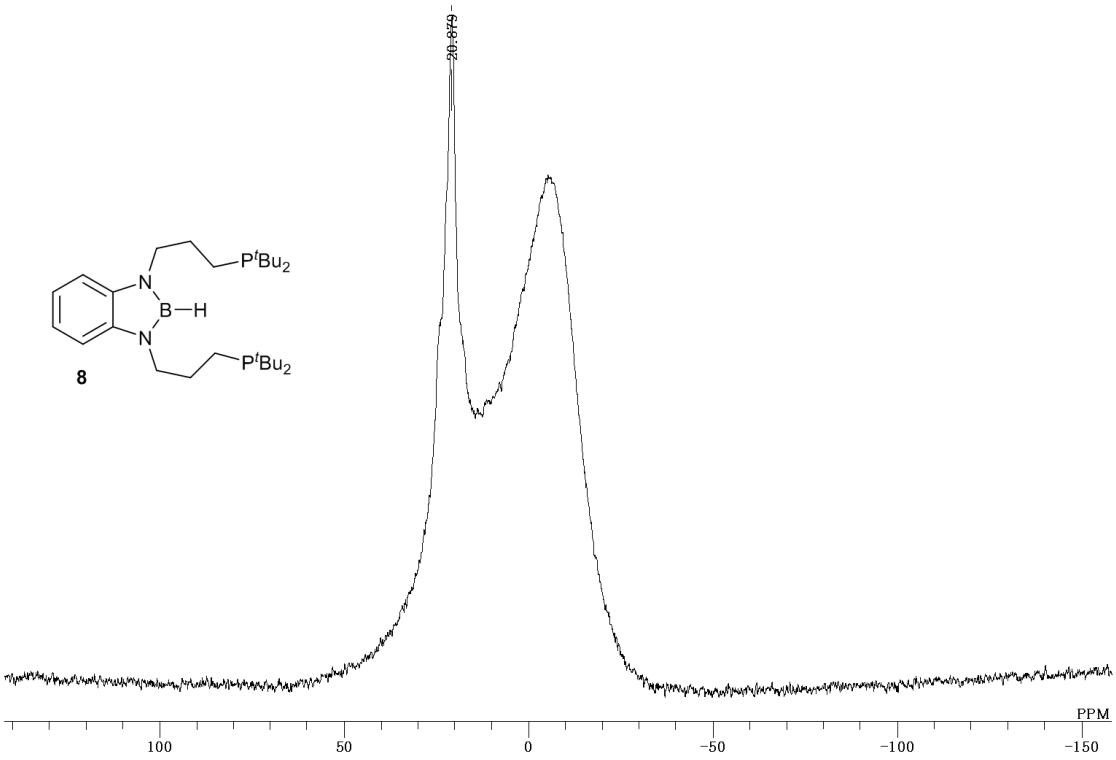

Figure S15. ^{11}B NMR spectrum of **8** (C_6D_6, 25 °C, 161 MHz)

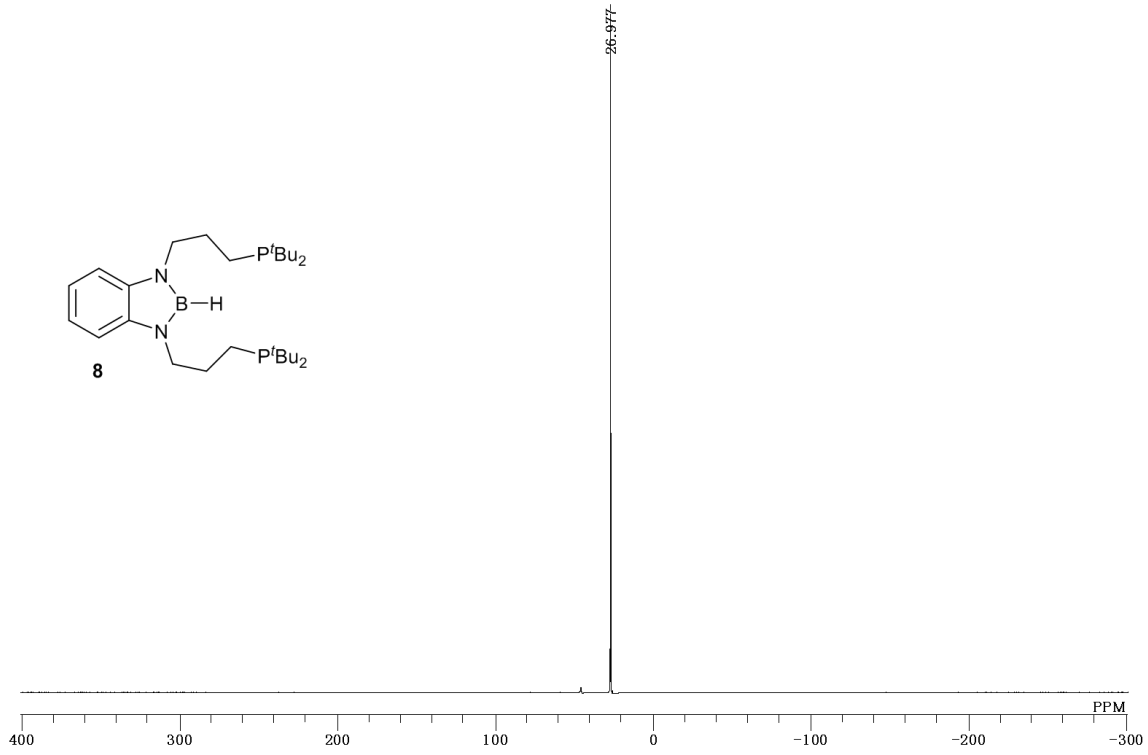

Figure S16. ^{31}P NMR spectrum of **8** (C_6D_6, 25 °C, 202 MHz)

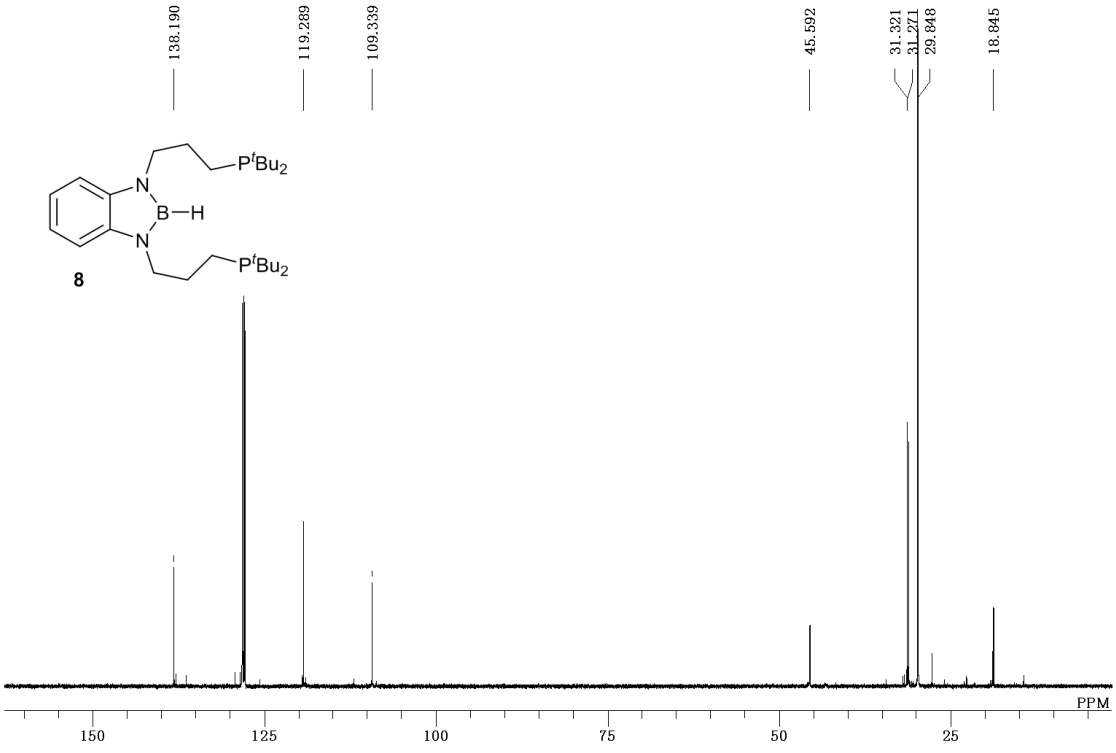

Figure S17. ^{13}C NMR spectrum of **8** (C_6D_6, 25 °C, 126 MHz)

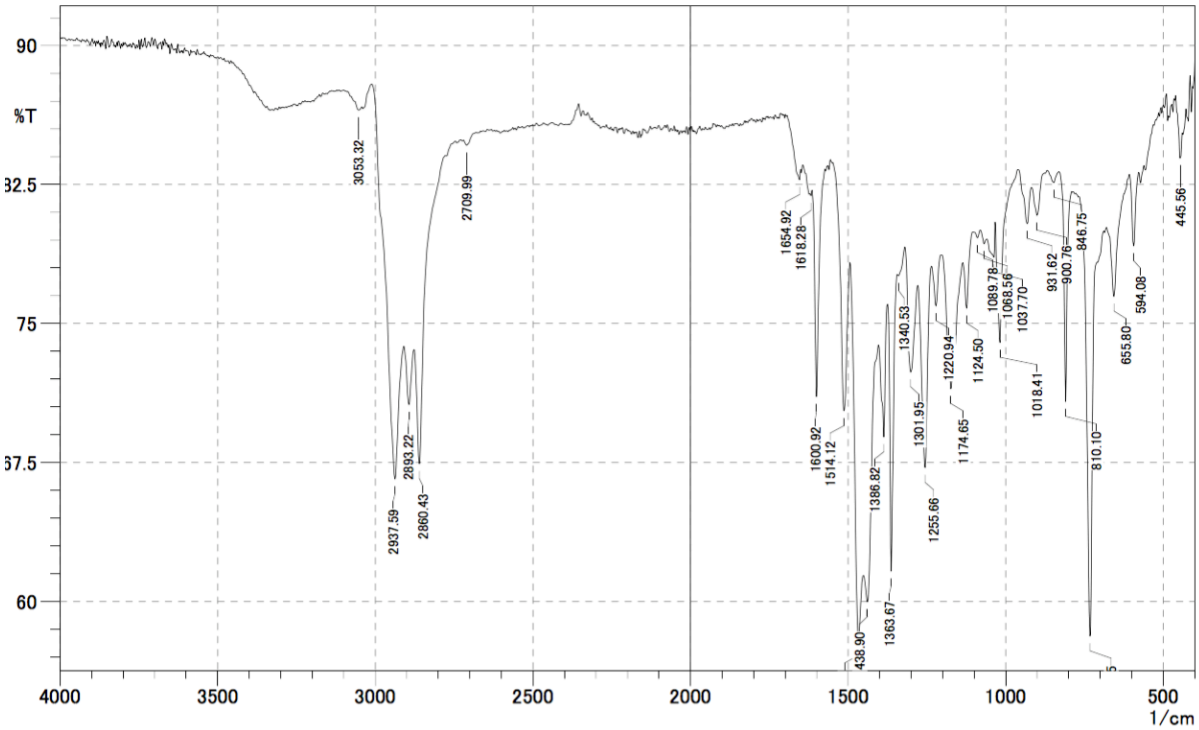

Figure S18. IR spectrum of **8**

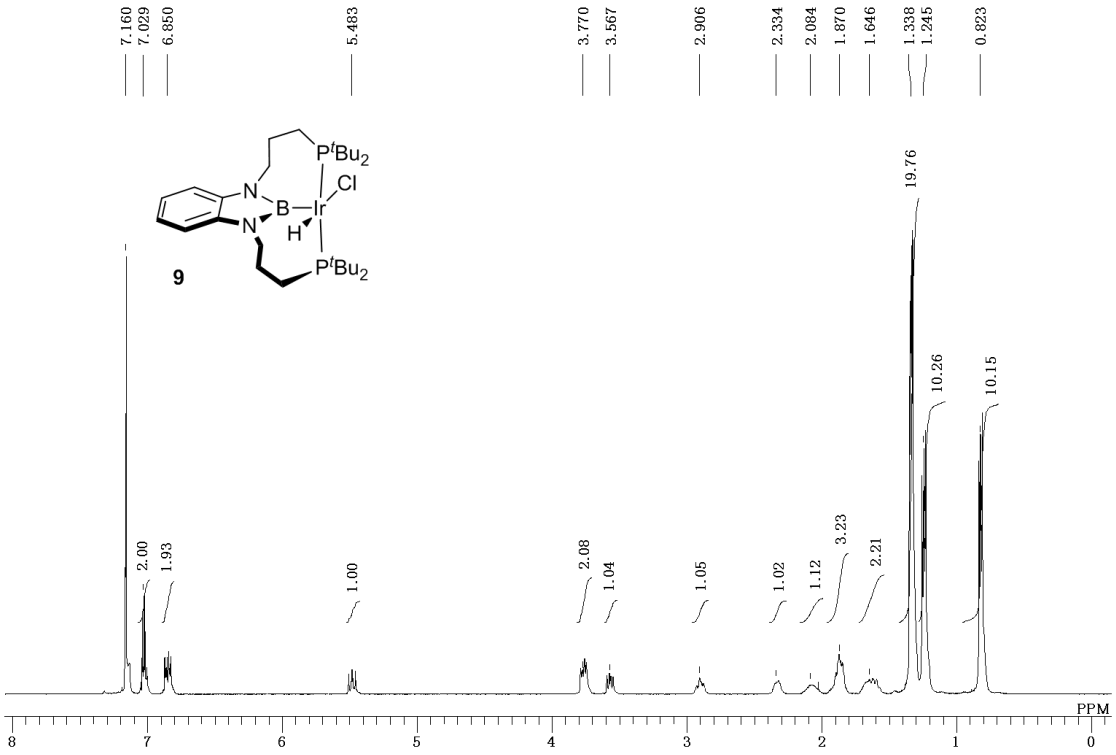

Figure S19. ^{1}H NMR spectrum of **9** (C_6D_6, 25 °C, 500 MHz)

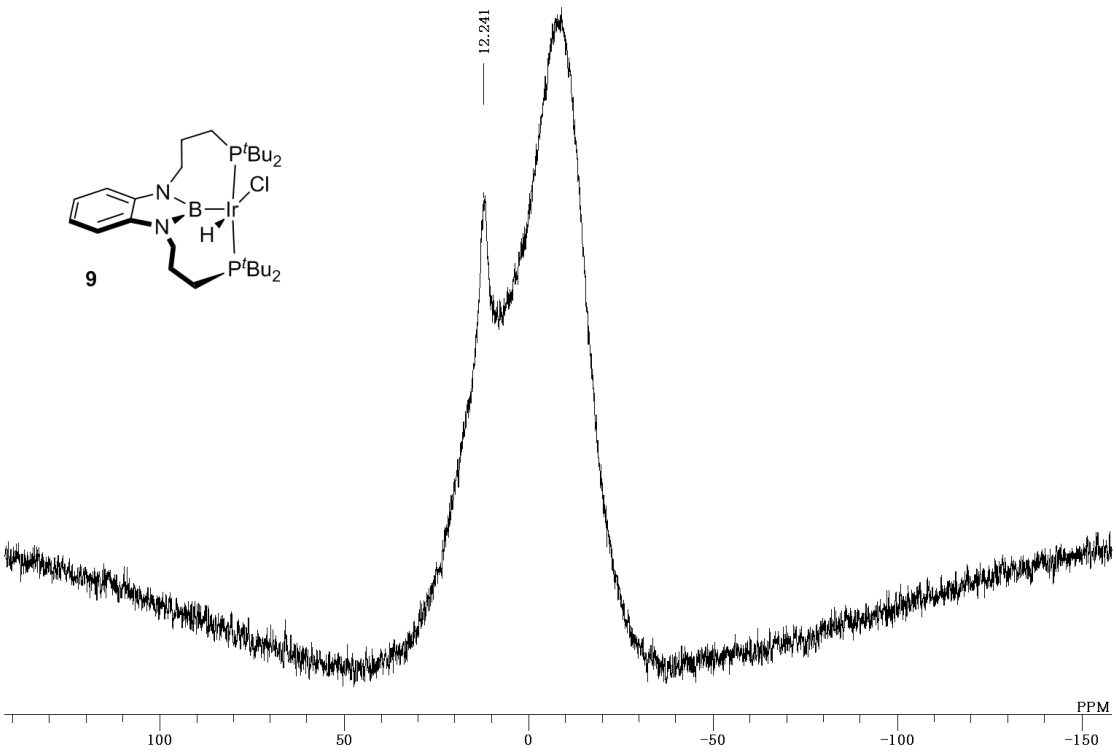

Figure S20. ^{11}B NMR spectrum of **9** (C_6D_6, 25 °C, 161 MHz)

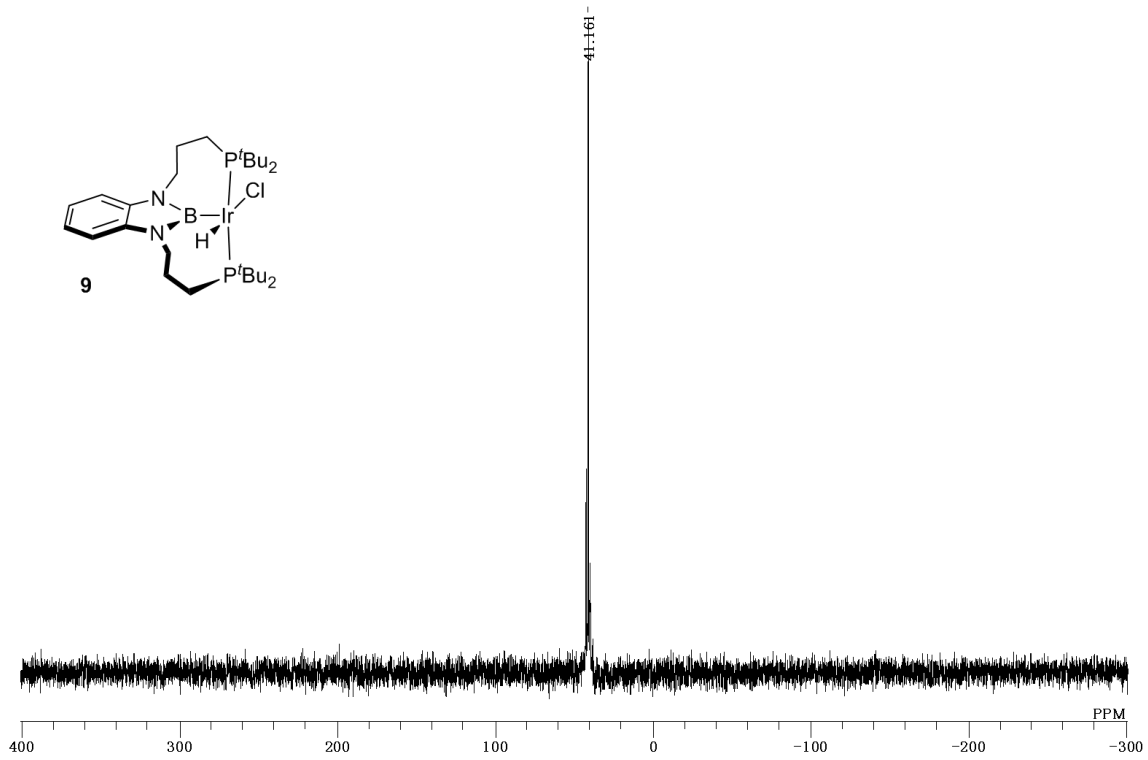

Figure S21. ^{31}P NMR spectrum of **9** (C_6D_6, 25 °C, 202 MHz)

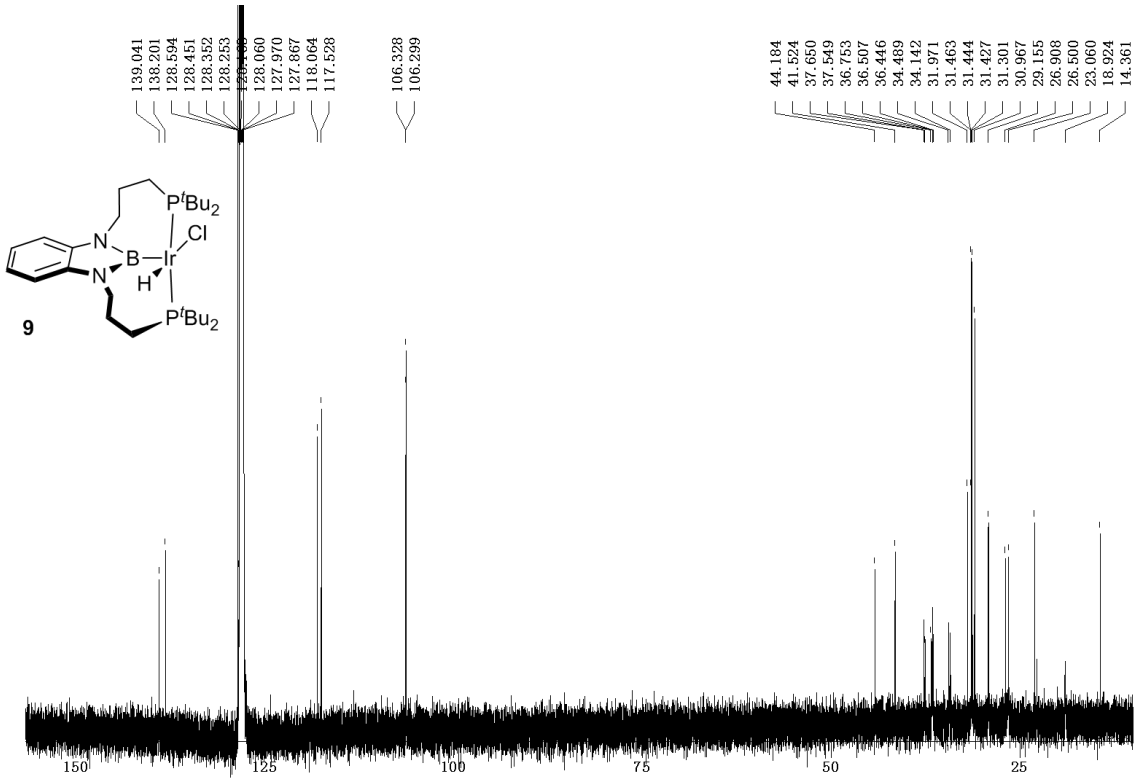

Figure S22. ^{13}C NMR spectrum of **9** (C_6D_6, 25 °C, 126 MHz)

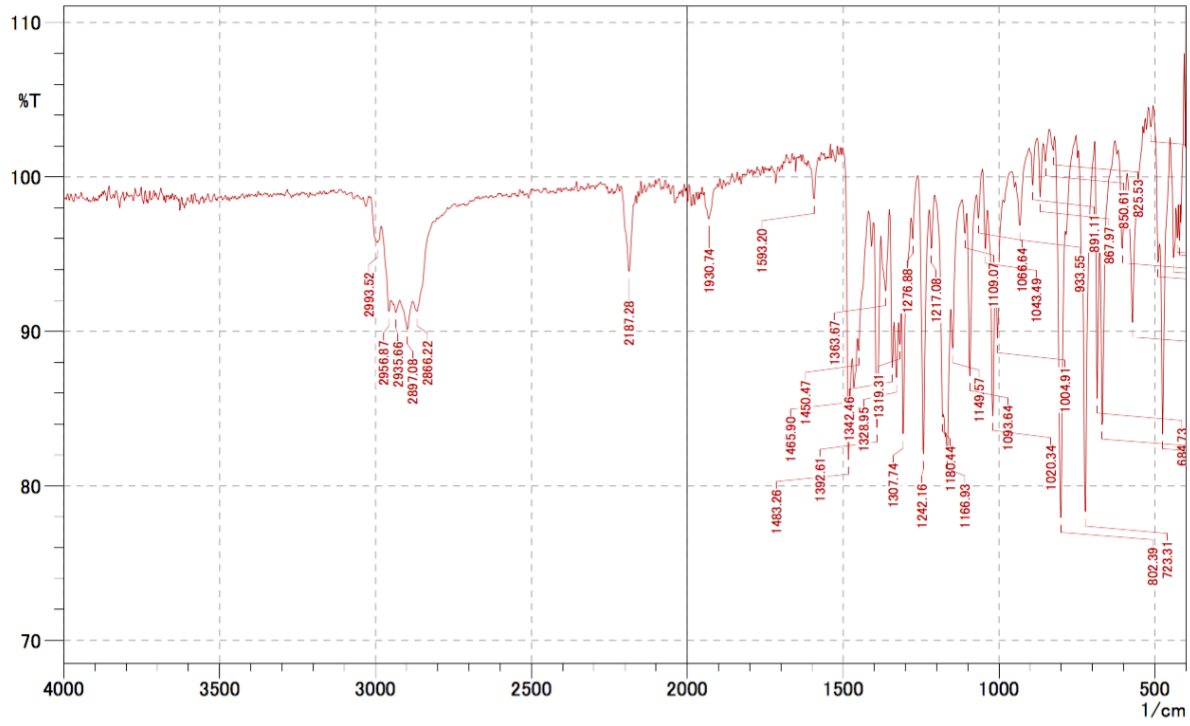

Figure S23. IR spectrum of **9**

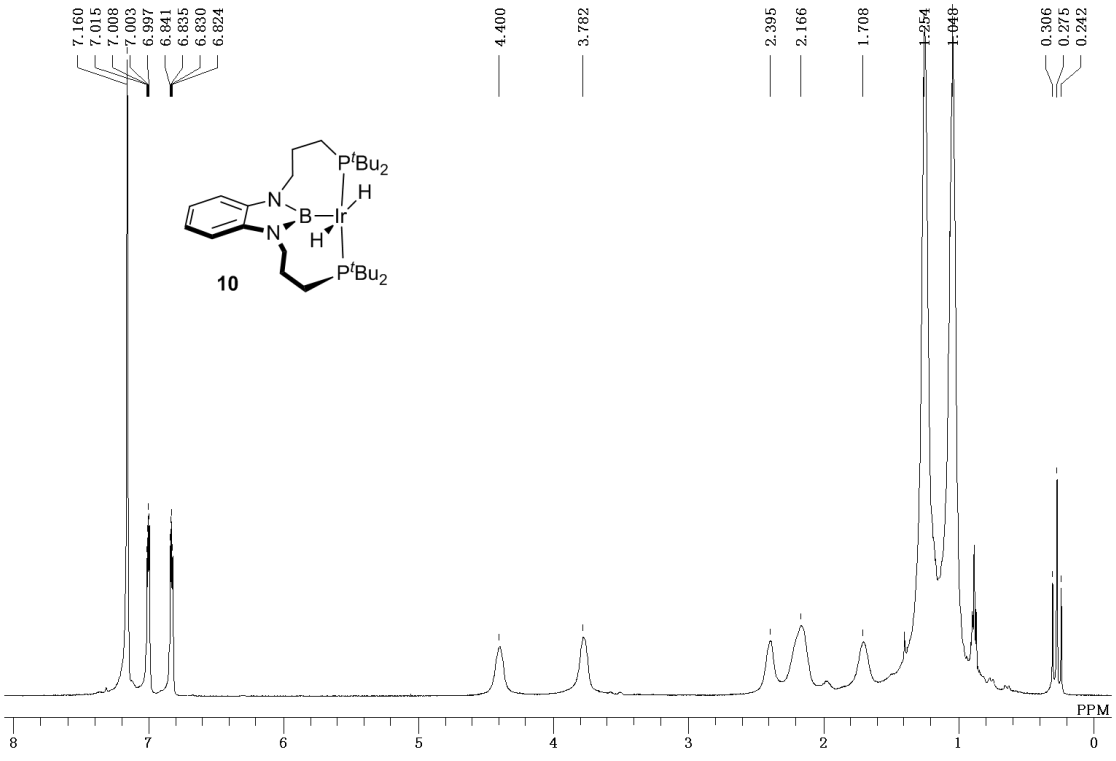

Figure S24. $^{1}H\{^{11}B\}$ NMR spectrum of **10** (C_6D_6, 25 °C, 500 MHz)

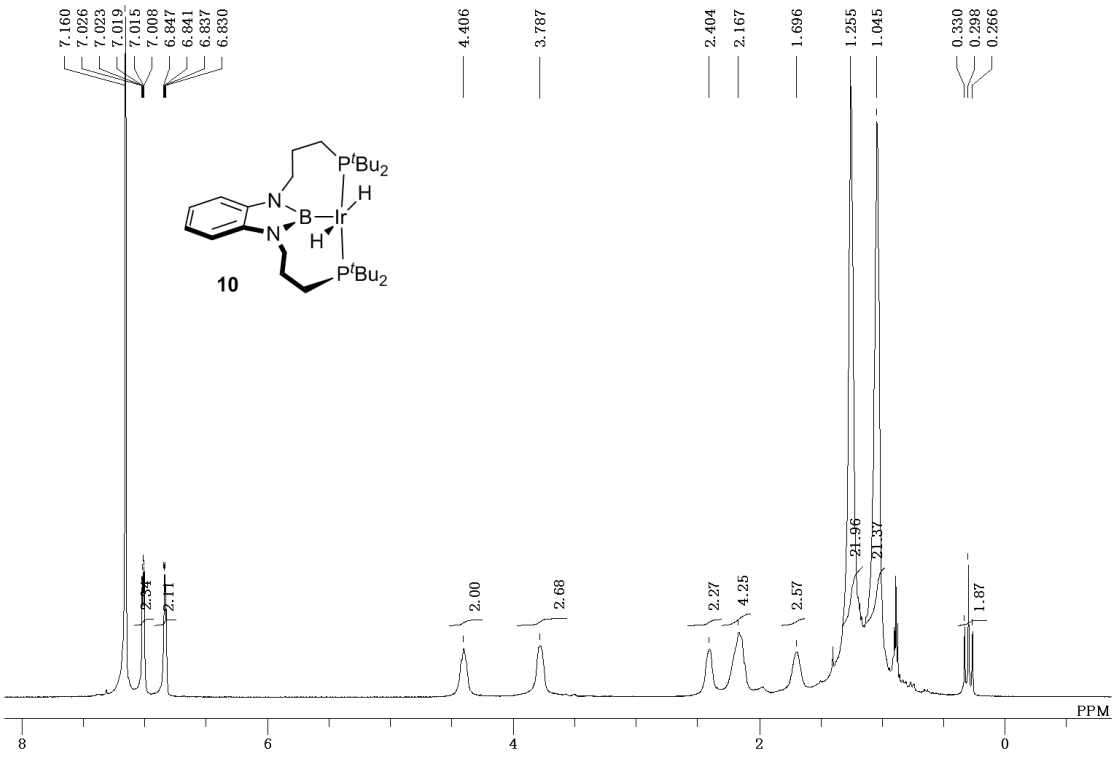

Figure S25. ^{1}H NMR spectrum of **10** (C_6D_6, 25 °C, 500 MHz)

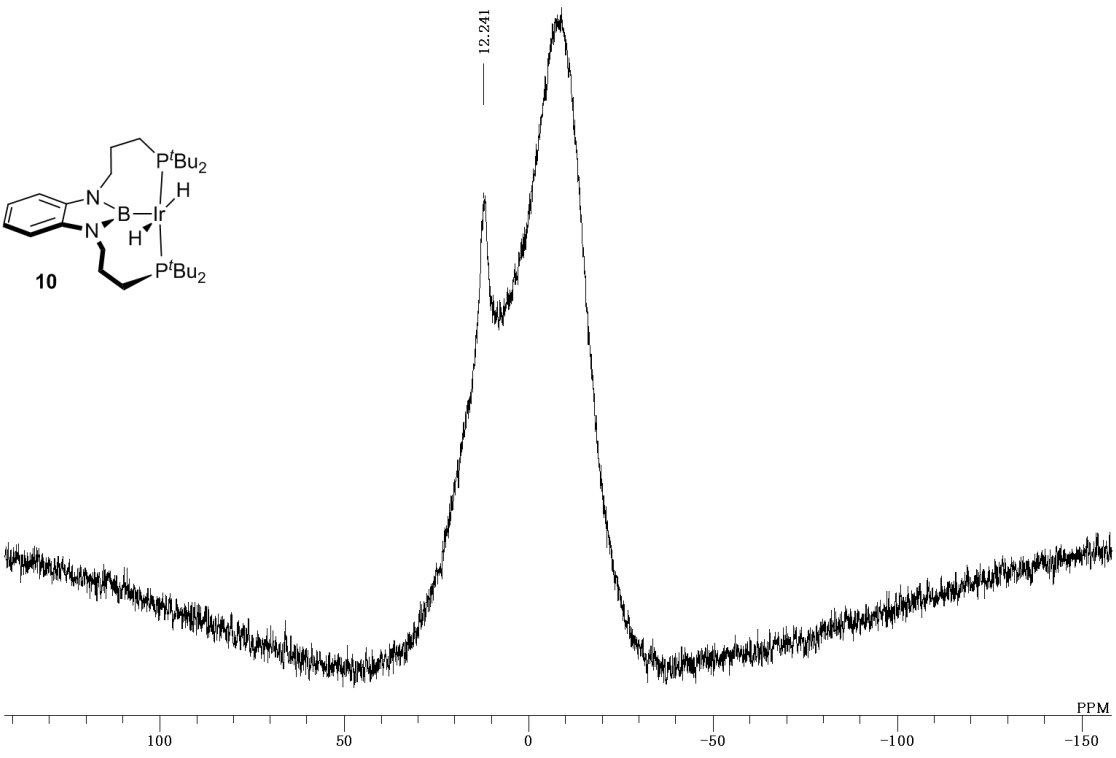

Figure S26. ^{11}B NMR spectrum of **10** (C_6D_6, 25 °C, 161 MHz)

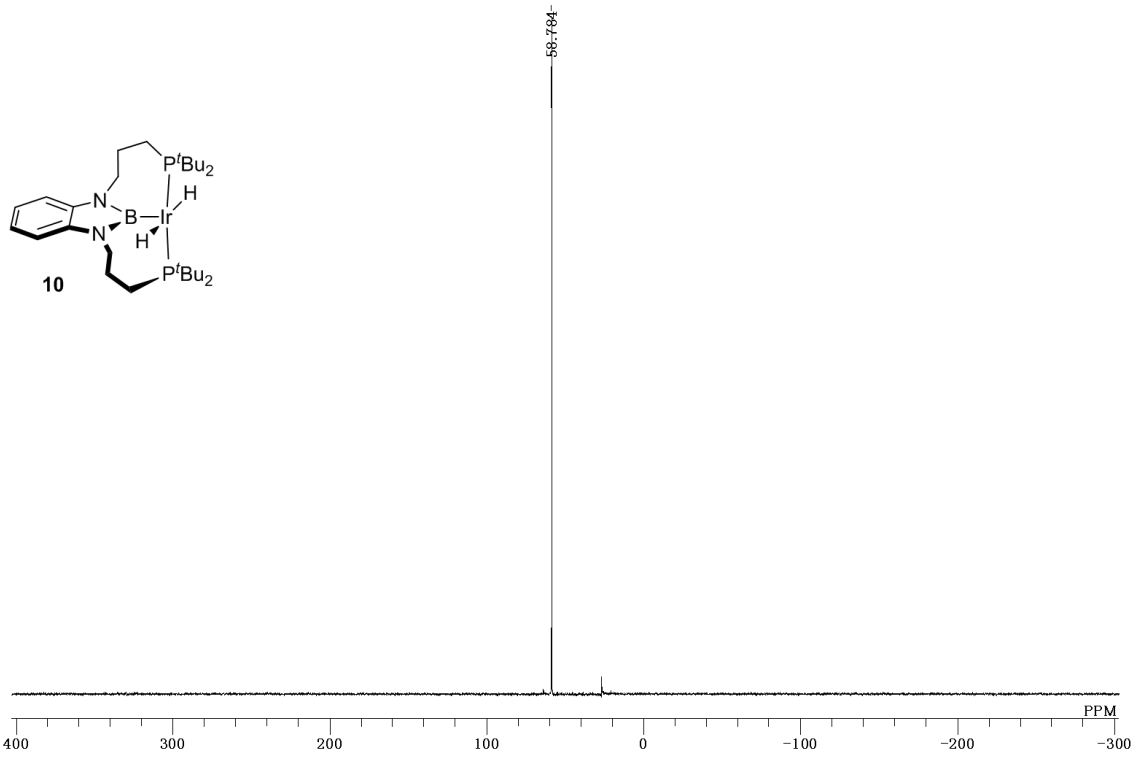

Figure S27. ^{31}P NMR spectrum of **10** (C_6D_6, 25 °C, 202 MHz)

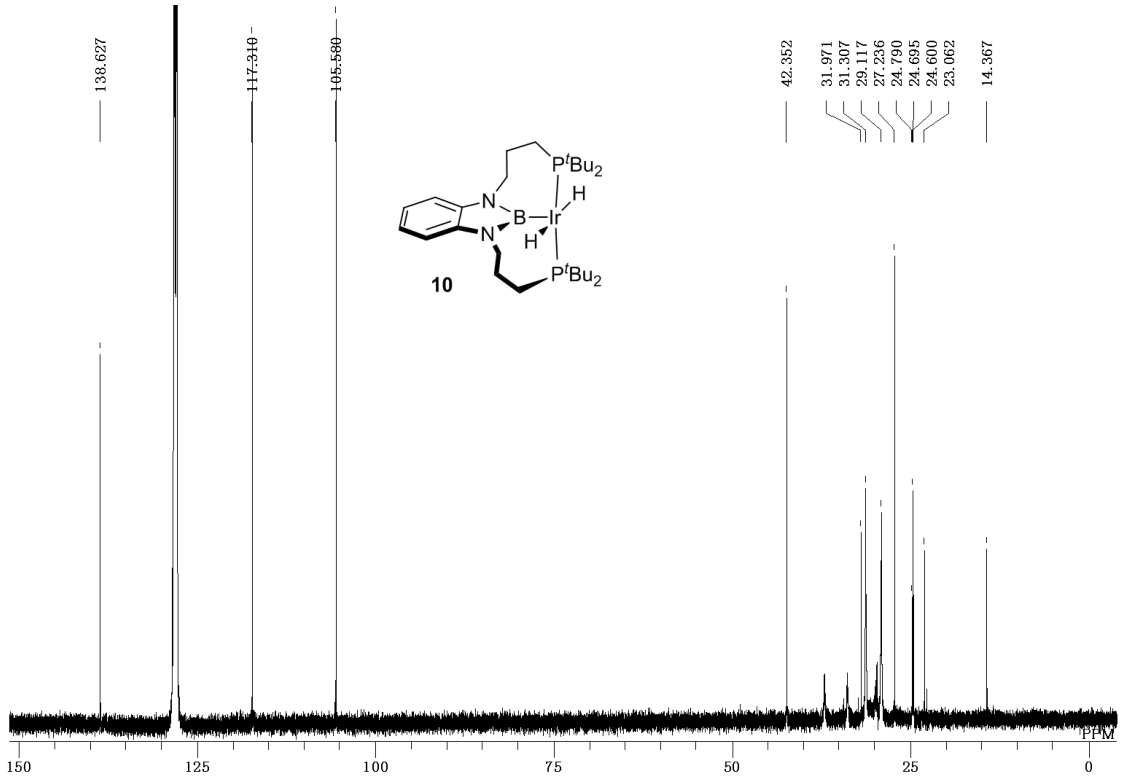

Figure S28. ^{13}C NMR spectrum of **10** (C_6D_6, 25 °C, 126 MHz)

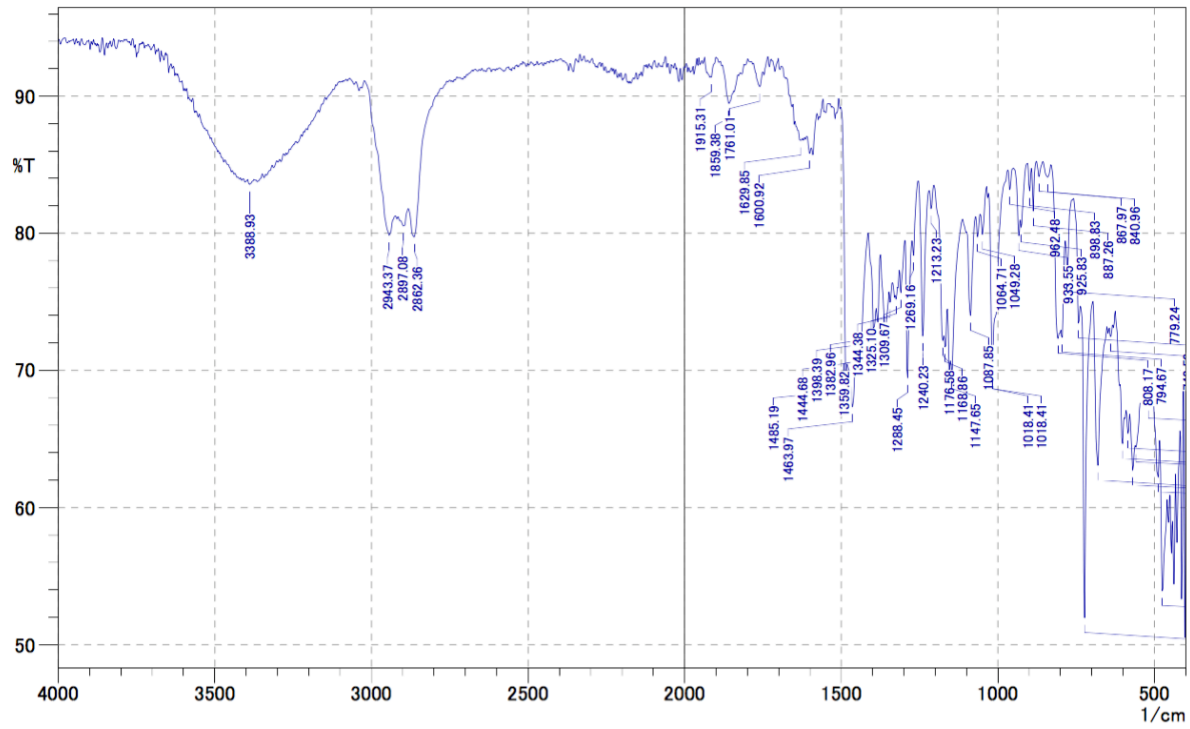

Figure S29. IR spectrum of **10**

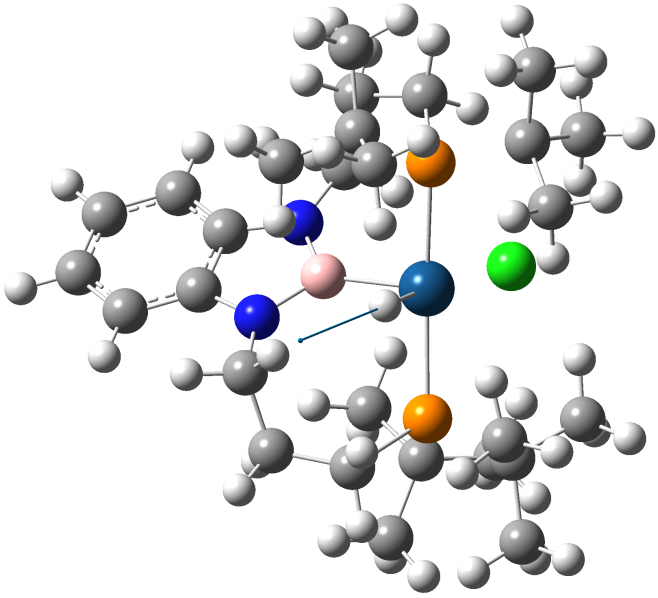

Figure S30. Calculated displacement vector at 2156 cm^{-1} (scaled with 0.977)[1] for **9** (gray: carbon, pale orange: boron, orange: phosphorus, white: hydrogen, blue-green: iridium, blue: nitrogen, light green: chlorine)

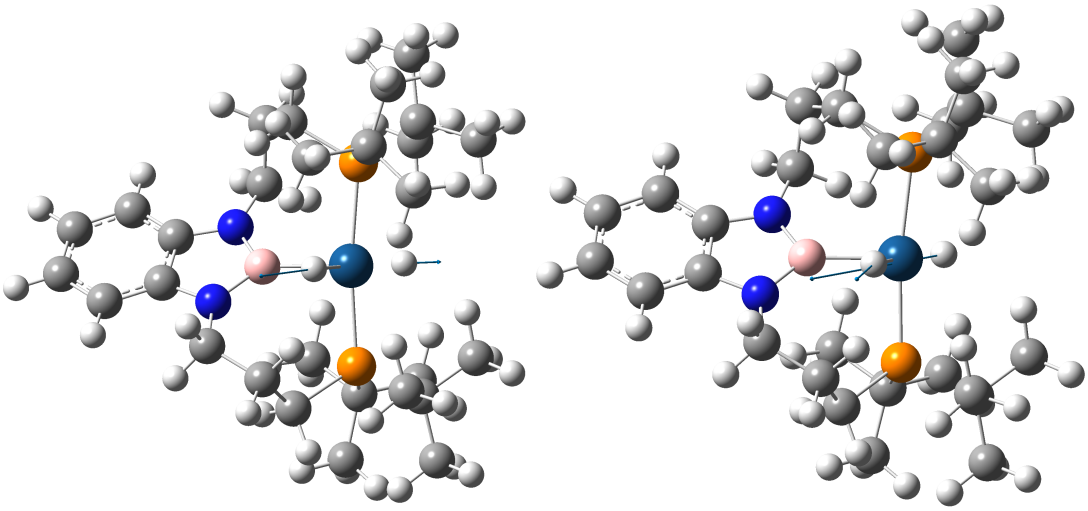

Figure S31. Calculated displacement vectors at 1768 and 2077 cm^{-1} (scaled with 0.977)[1] for **10** (gray: carbon, pale orange: boron, orange: phosphorus, white: hydrogen, blue-green: iridium, blue: nitrogen)

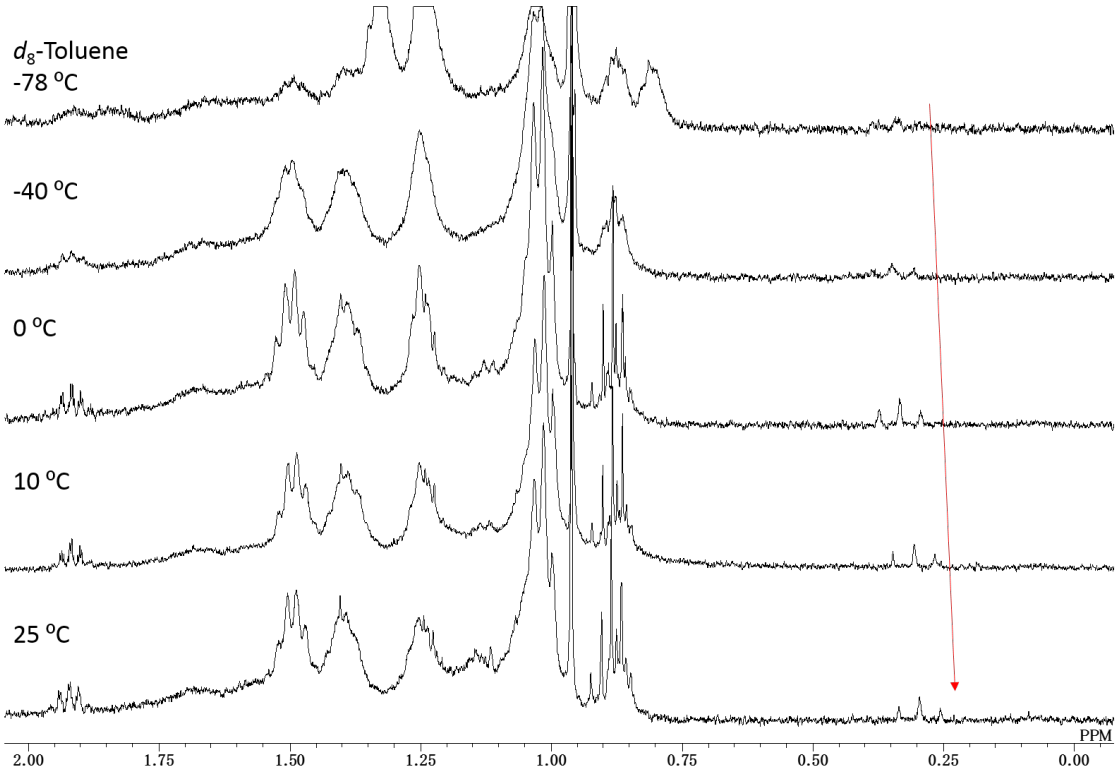

Figure S32. Reaction of **9** with ^{n}BuLi at low temperature as monitored by ^{1}H NMR spectroscopy. Signal assignable to the dihydride ligands was detected upon addition even at -78 °C.

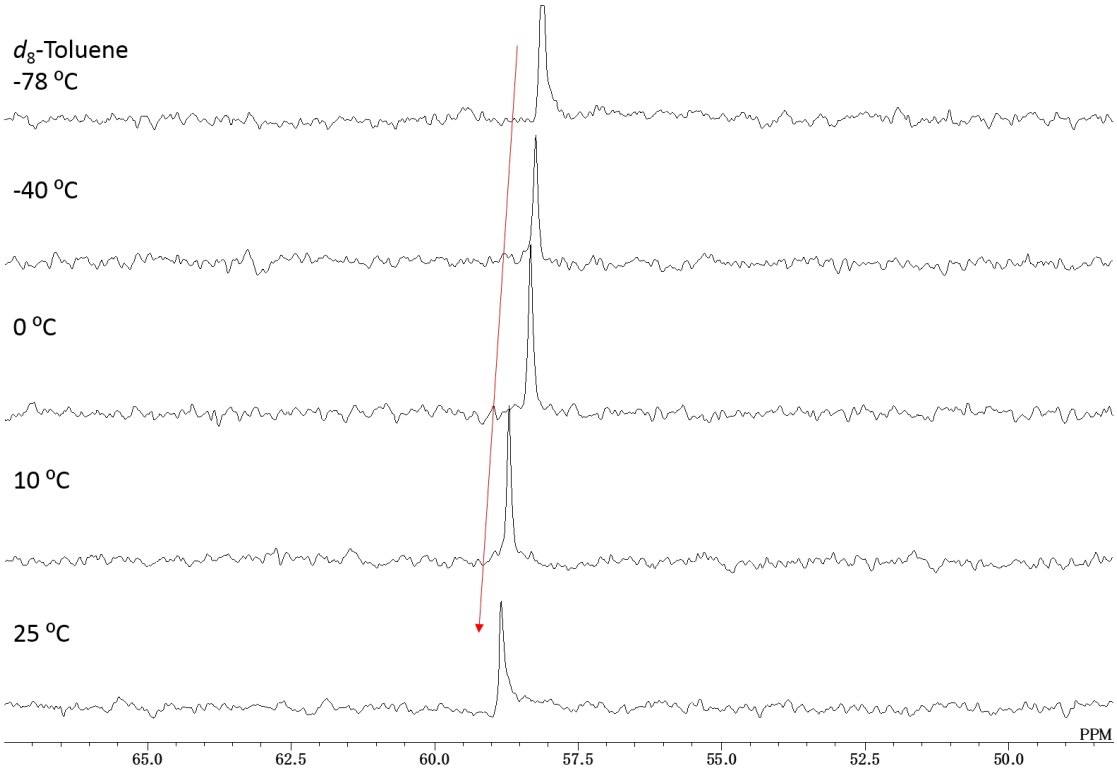

Figure S33. Reaction of **9** with ^{n}BuLi at low temperature as monitored by ^{31}P NMR spectroscopy.

Table S1. Crystallographic data and structure refinement details for **9** and **10**

	4(**9**)·3(C_6H_6)	**10**
CCDC deposit #	1481611	1481612
formula	$C_{130}H_{230}B_4Cl_4Ir_4N_8P_8$	$C_{28}H_{54}BIrN_2P_2$
fw	3106.81	683.68
T (K)	93(2)	93(2)
crystal system	orthorhombic	monoclinic
space group	*Pbca*	*C2/c*
a, (Å)	9.369(3)	33.074(11)
b, (Å)	21.885(6)	8.348(3)
c, (Å)	33.532(9)	24.590(9)
α, (°)	90	90
β, (°)	90	119.367(4)
γ, (°)	90	90
V, (Å^3)	6876(3)	5917(4)
Z	2	8
D_{calc}, (g/cm^3)	1.501	1.535
μ (mm^{-1})	4.079	4.641
F(000)	3164	2784
crystal size (mm)	0.07 x 0.06 x 0.04	0.160 x 0.080 x 0.040
2θ range , (°)	3.061-27.470	3.062-27.520
reflns collected	67732	23516
indep reflns/R_{int}	7855/0.0853	6773/0.0587
params	400	325
GOF on F^2	1.184	1.133
R_1, wR_2 [$I>2\sigma(I)$]	0.0501, 0.0889	0.0500, 0.0941
R_1, wR_2 (all data)	0.0611, 0.0928	0.0588, 0.0985

Calculated SCF GIAO Magnetic shielding tensor (ppm)

$SiMe_4$

3 H Isotropic = 31.7839
4 H Isotropic = 31.7806
5 H Isotropic = 31.7820
7 H Isotropic = 31.7839
8 H Isotropic = 31.7793
9 H Isotropic = 31.7819
11 H Isotropic = 31.7839
12 H Isotropic = 31.7804
13 H Isotropic = 31.7817
15 H Isotropic = 31.7819
16 H Isotropic = 31.7836
17 H Isotropic = 31.7833

Complex 10

2 H Isotropic = 30.4190 (close to boron atom)
3 H Isotropic = 37.1463 (far from boron atom)

Reference

1. I. M. Alecu, J. Zheng, Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput*., 2010, **6**, 2872.