Hydroboration of nitriles and imines by highly active zinc dihydride catalysts

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Supporting Information

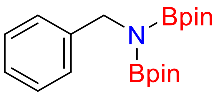
General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. The assignments of NMR data were supported by 1D and 2D NMR experiments. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. Melting points were determined using an Electrotherman IA9000.

Materials: Zinc hydride complexes **2a**[1], **2b**[1] and **L**^{NNP}ZnH[2] were synthesized by following the literature procedures. $LiAlD_4$, $NaBD_4$ and HBpin were purchased from Adamas. $PhSiD_3$[3] and DBpin[4] were synthesized via the known literature procedures. All the nitriles were bought from Sigma-Aldrich and all the imines were synthesized using literature procedures[5]. All the solid substrates used in catalysis reaction were dried under vacuum for 12 h. All the liquid substrates used in catalysis reaction were distilled and stored over activated 4 Å molecular sieves.

General procedure for hydroboration of nitrile and imine

In a nitrogen filled glove box, zinc dihydride (0.0015 mmol), nitrile (0.30 mmol) and HBpin (0.63 mmol) [or imine (0.30 mmol) and HBpin (0.33 mmol)] were mixed. The reaction mixture was allowed to stand at room temperature or heated in a pre-heated oil bath at 80 ^{o}C till the solid product precipitated out or the entire reaction mixture solidified. Then, the reaction mixture was diluted with 0.5 mL of undried C_6D_6 and monitored by NMR spectra. Conversion was determined by ^{1}H NMR spectroscopy through integration of residual nitrile (or imine) *vs* hydroboration product. The C_6D_6 was then removed in vacuum and hexane (5 mL*3) was added to extract the residue. The upper clear solution was combined and concentrated to *ca.* 1 mL, which was placed in a refrigerator (-30 °C) to eventually give pure product.

Characterizations of borylamines obtained from nitrile and imine hydroboration



5a[6] (white solid, 97 mg, 90% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.59 (d, 2H, *J* = 7.7 Hz, *phenyl*), 7.26 (m, 2H, *phenyl*), 7.12 (m, 1H, *phenyl*), 4.62 (s, 2H, CH_2), 1.03 (s, 24H, C(CH_3)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 143.8 (*phenyl*), 128.4 (*phenyl*), 128.1 (*phenyl*), 126.7 (*phenyl*), 82.6 (*C*(CH_3)$_2$), 47.9 (*C*H_2), 24.7 (C(*C*H_3)$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298K): δ = 26.3.

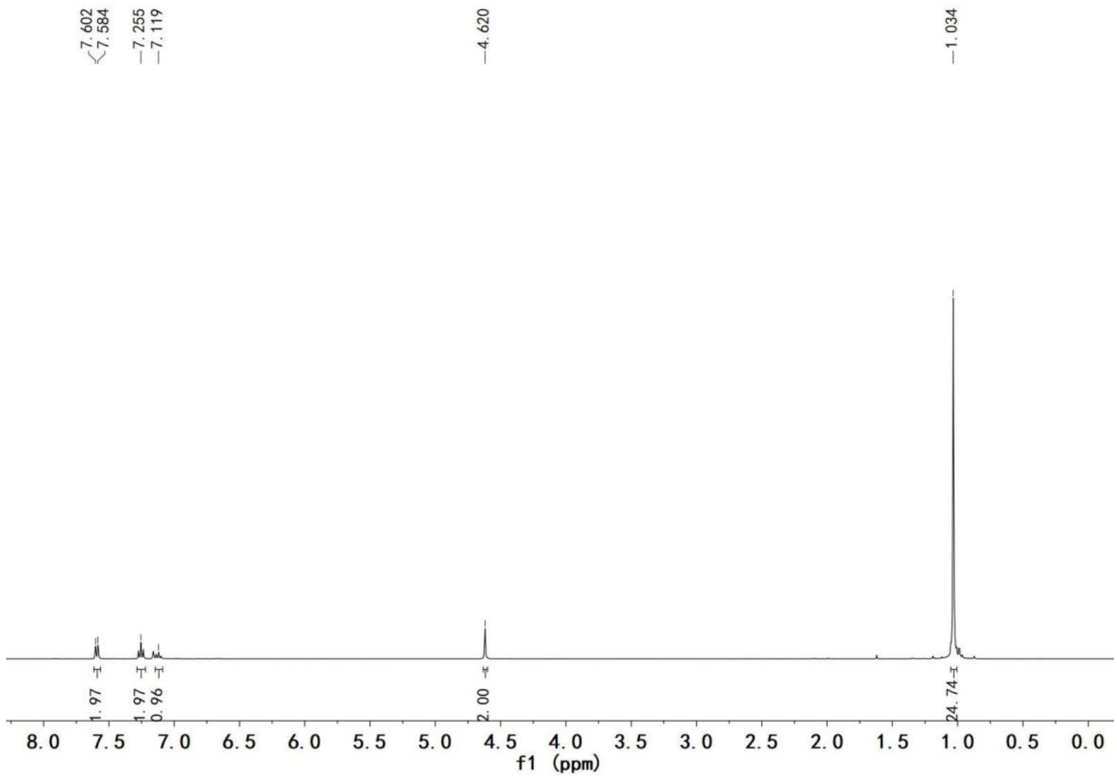


Figure S1. [1]H NMR spectrum of **5a** (400 MHz, C_6D_6, 298 K).

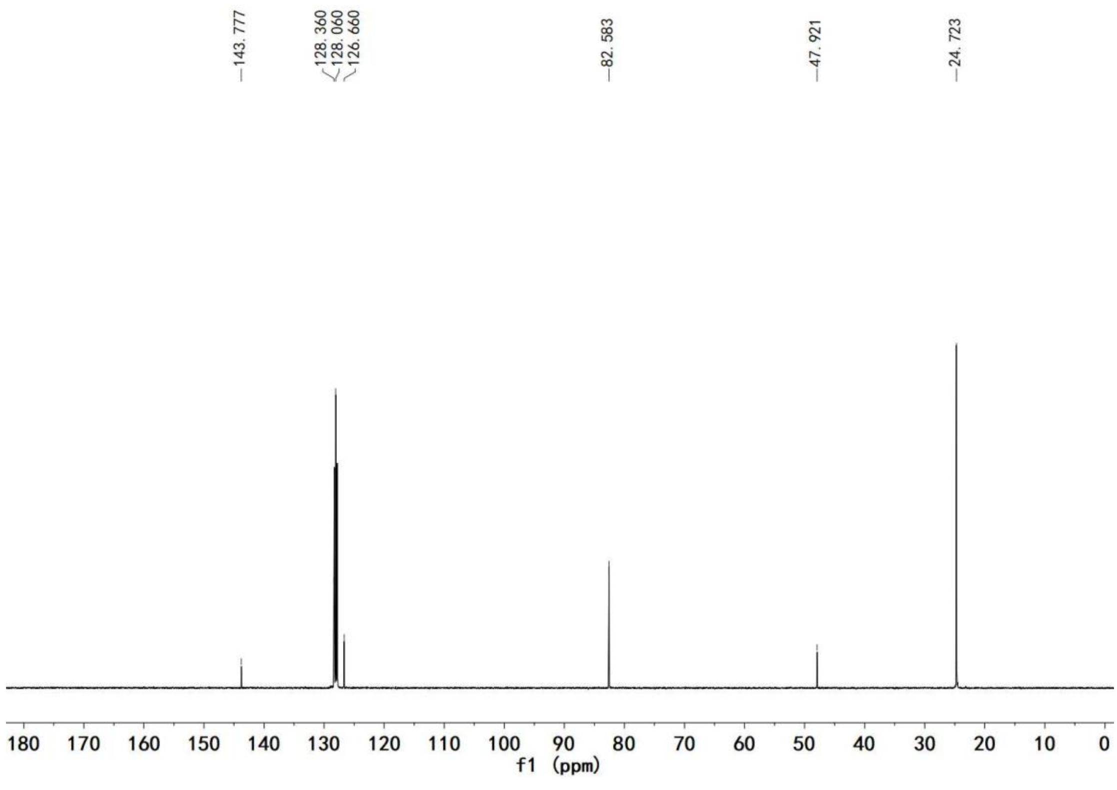


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **5a** (101 MHz, C_6D_6, 298 K).

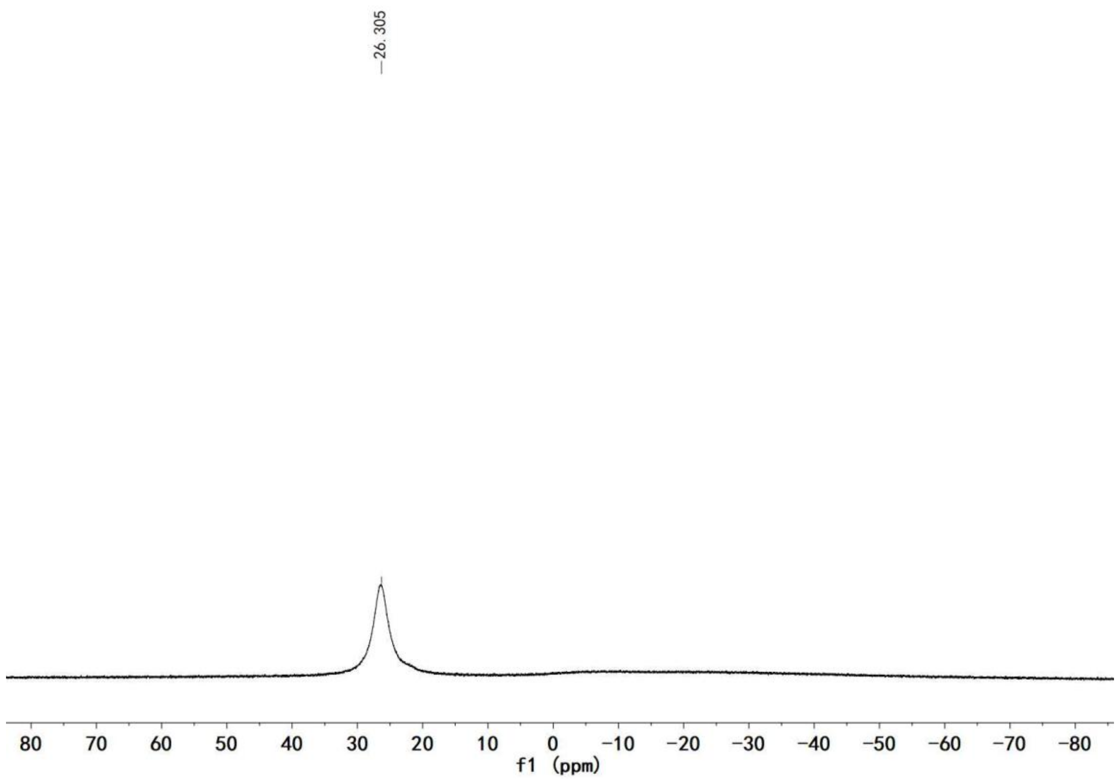
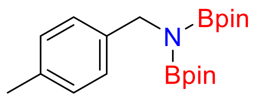


Figure S3. ^{11}B NMR spectrum of **5a** (128 MHz, C_6D_6, 298 K).



5b[6] (white solid, 104 mg, 93% yield)

^1H NMR (400 MHz, C_6D_6, 298 K): δ = 7.54 (d, 2H, J = 8.0 Hz, *phenyl*), 7.08 (d, 2H, J = 7.8 Hz, *phenyl*), 4.62 (s, 2H, C*H*$_2$), 2.16 (s, 3H, C*H*$_3$), 1.05 (s, 24H, C(C*H*$_3$)$_2$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ = 140.9 (*phenyl*), 135.8 (*phenyl*), 129.1 (*phenyl*), 128.1 (*phenyl*), 82.6 (*C*(CH$_3$)$_2$), 47.6 (*C*H$_2$), 24.8 (C(*C*H$_3$)$_2$), 21.2 (*C*H$_3$).

^{11}B NMR (128 MHz, C_6D_6, 298K): δ = 26.6.

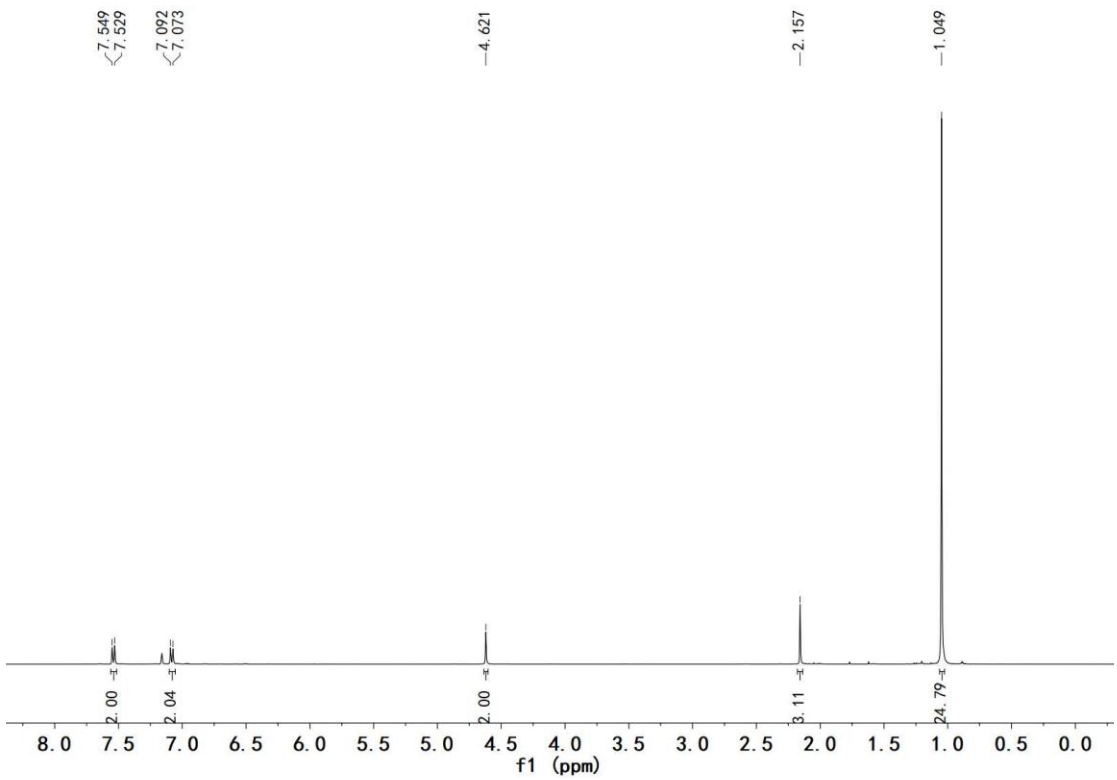


Figure S4. ^{1}H NMR spectrum of **5b** (400 MHz, C_6D_6, 298 K).

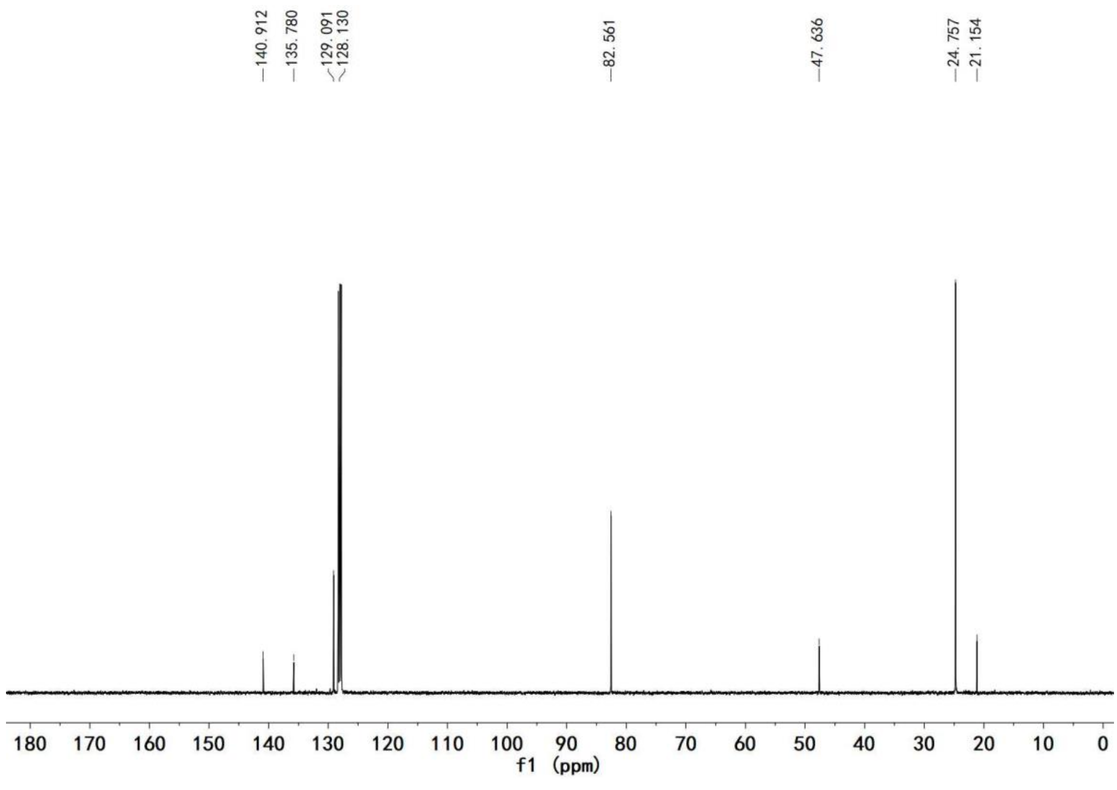


Figure S5. $^{13}C\{^{1}H\}$ spectrum of **5b** (101 MHz, C_6D_6, 298 K).

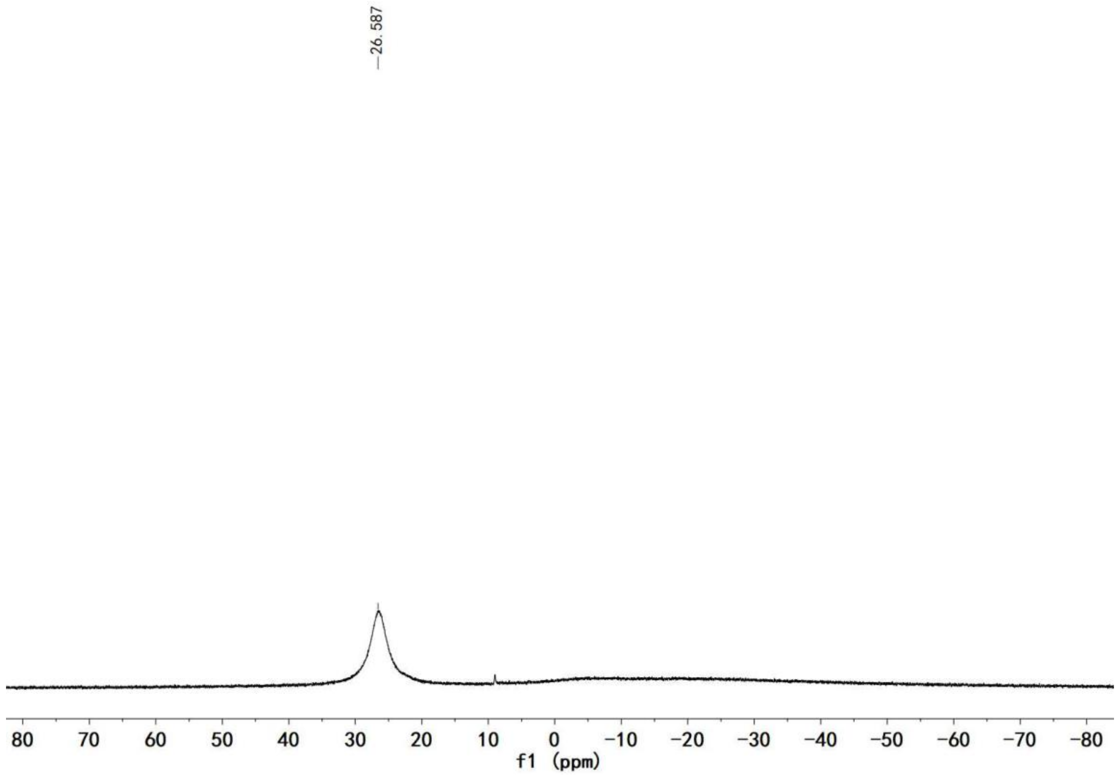
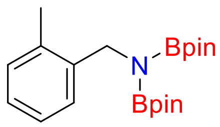


Figure S6. ^{11}B NMR spectrum of **5b** (128 MHz, C_6D_6, 298 K).



5c[6] (white solid, 96 mg, 86% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.67 (m, 1H, *phenyl*), 7.26 (m, 1H, *phenyl*), 7.09 (m, 1H, *phenyl*), 7.00 (m, 1H, *phenyl*), 4.63 (s, 2H, C*H*$_2$), 2.14 (s, 3H, C*H*$_3$), 1.04 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 140.8 (*phenyl*), 135.0 (*phenyl*), 129.8 (*phenyl*), 125.8 (*phenyl*), 125.6 (*phenyl*), 125.3 (*phenyl*), 82.2 (*C*(CH$_3$)$_2$), 45.1 (*C*H$_2$), 24.3 (C(*C*H$_3$)$_2$), 18.7 (*C*H$_3$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = 26.5.

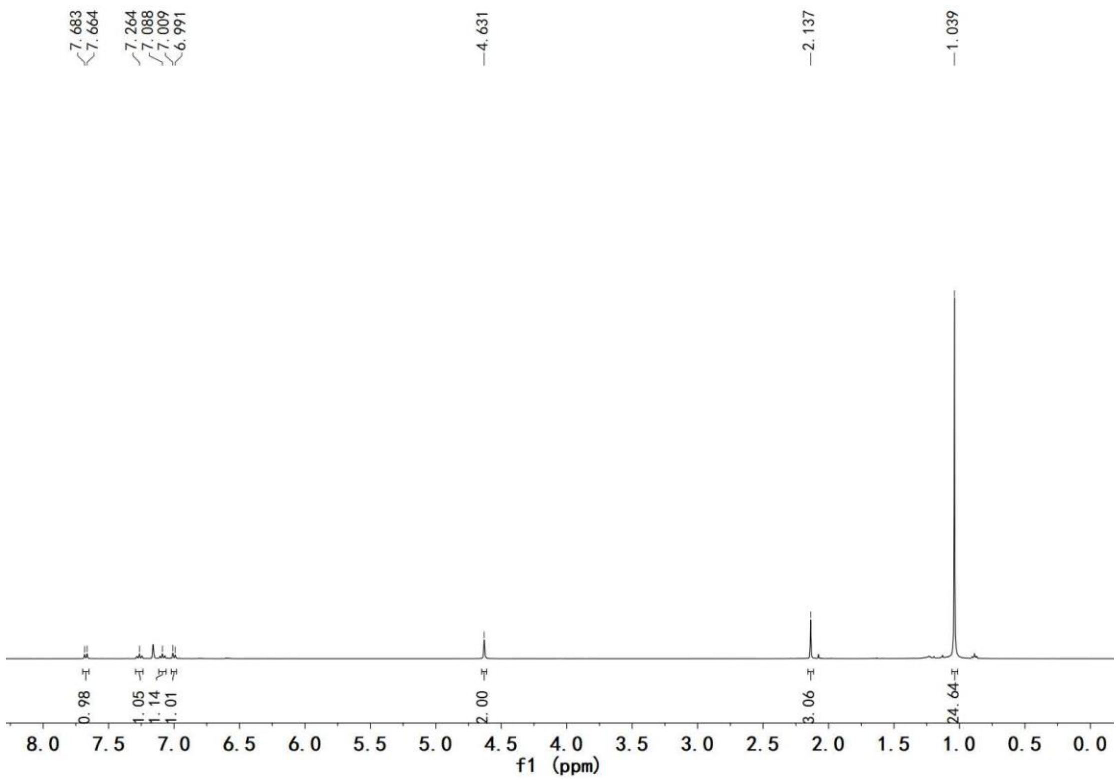


Figure S7. [1]H NMR spectrum of **5c** (400 MHz, C_6D_6, 298 K).

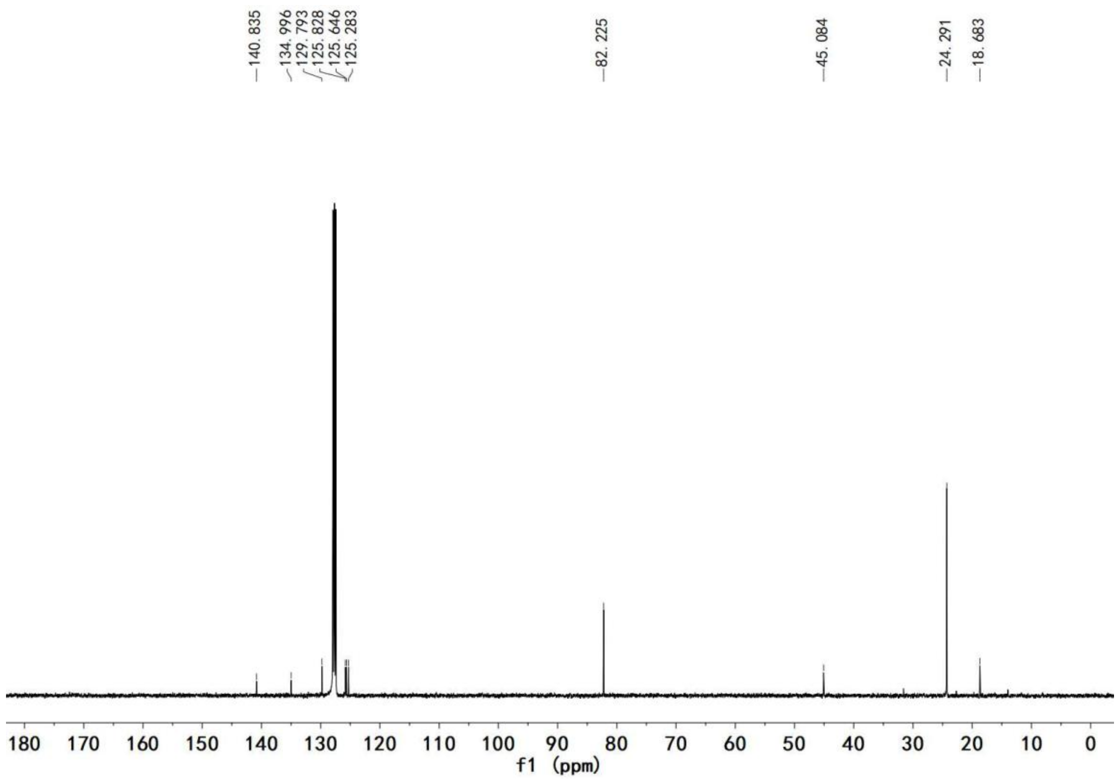


Figure S8. $^{13}C\{^1H\}$ NMR spectrum of **5c** (101 MHz, C_6D_6, 298 K).

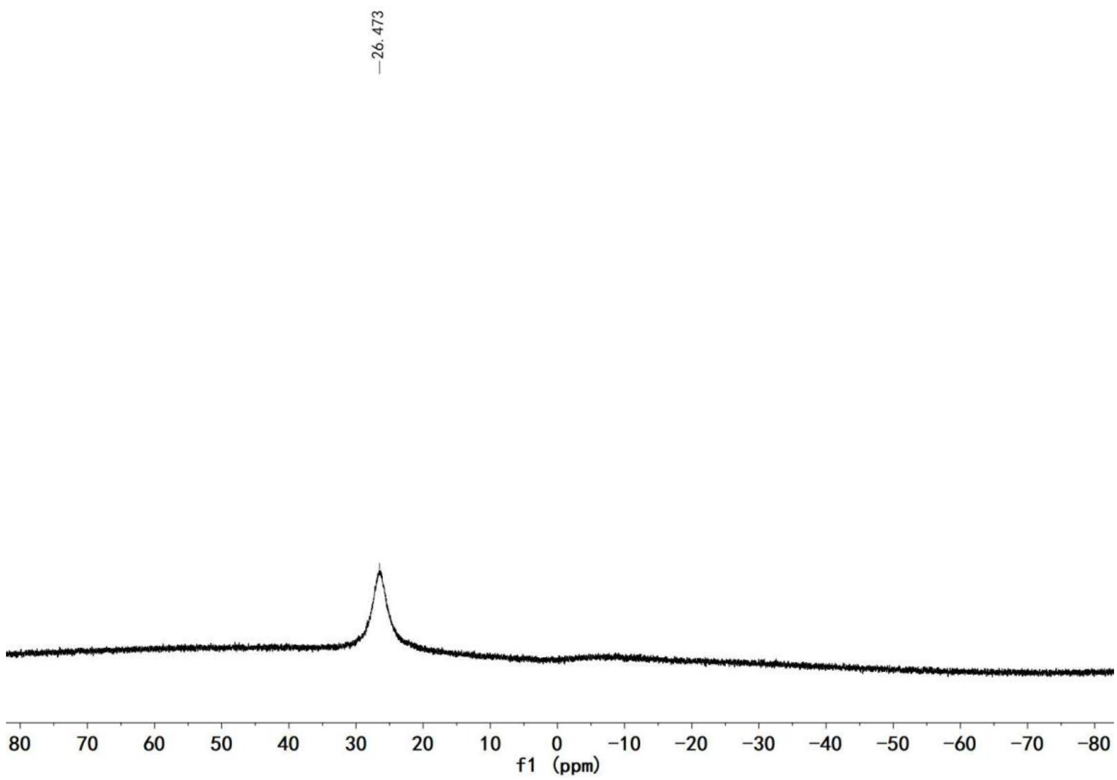
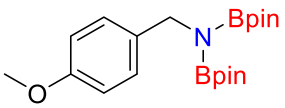


Figure S9. ^{11}B NMR spectrum of **5c** (128 MHz, C_6D_6, 298 K).



5d[6] (white solid, 107 mg, 92% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.52 (d, 1H, J = 8.6 Hz, *phenyl*), 6.84 (d, 1H, J = 8.7 Hz, *phenyl*), 4.52 (s, 2H, CH_2), 3.36 (s, 3H, OCH_3), 1.04 (s, 24H, C(CH_3)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 159.0 (*phenyl*), 136.1 (*phenyl*), 129.5 (*phenyl*), 113.9 (*phenyl*), 82.6 (*C*(CH_3)$_2$), 54.8 (O*C*H_3), 47.3 (*C*H_2), 24.8 (C(*C*H_3)$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = 26.4.

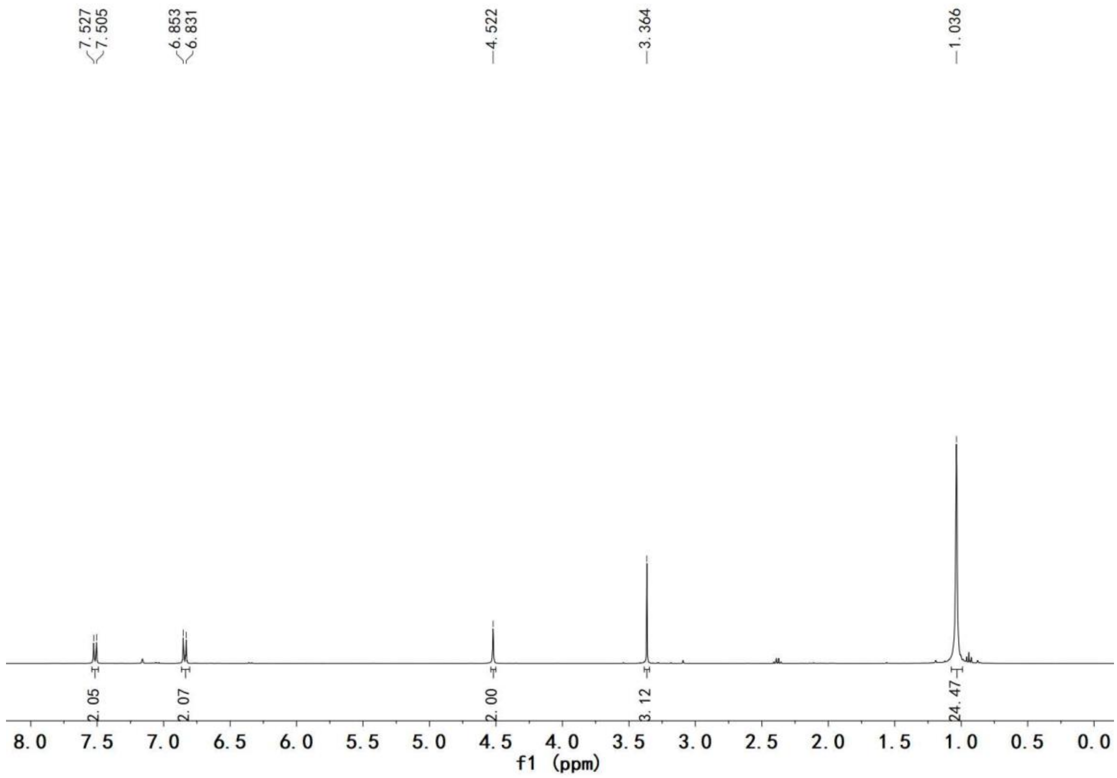


Figure S10. [1]H NMR spectrum of **5d** (400 MHz, C_6D_6, 298 K).

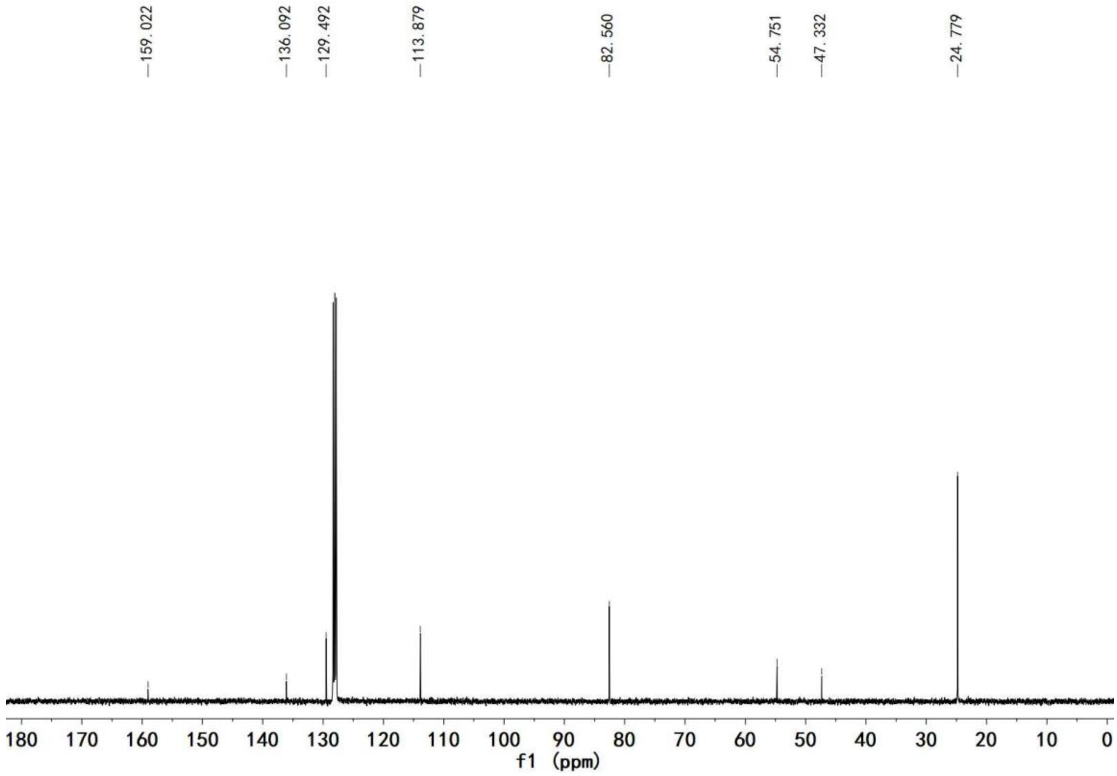


Figure S11. [13]C{[1]H} NMR spectrum of **5d** (101 MHz, C_6D_6, 298 K).

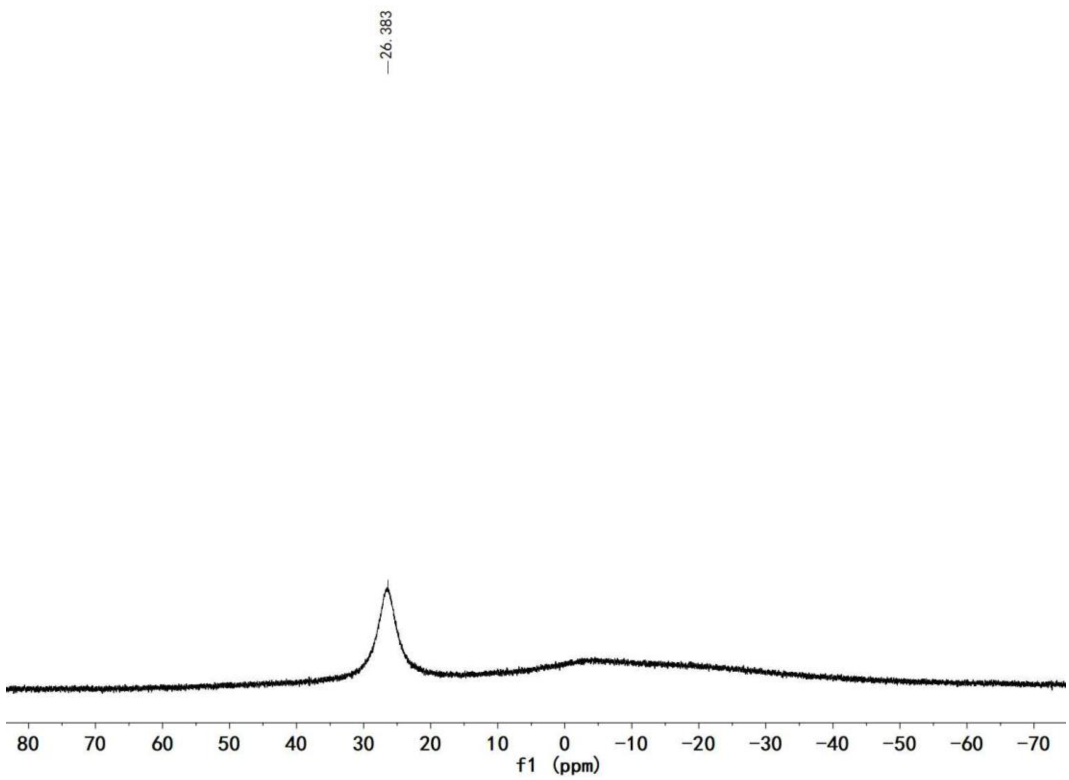
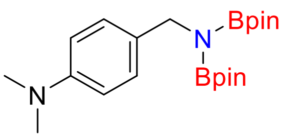


Figure S12. ^{11}B NMR spectrum of **5d** (128 MHz, C_6D_6, 298 K).



5e[6] (white solid, 104 mg, 86% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.61 (m, 2H, *phenyl*), 6.71 (m, 2H, *phenyl*), 4.61(s, 2H, C*H*$_2$), 2.57 (s, 6H, NC*H*$_3$), 1.07 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 149.9 (*phenyl*), 132.3 (*phenyl*), 129.3 (*phenyl*), 113.0 (*phenyl*), 82.4 (*C*(CH$_3$)$_2$), 47.4 (*C*H$_2$), 40.6 (N*C*H$_3$), 24.8 (C(*C*H$_3$)$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298K): δ = 26.4.

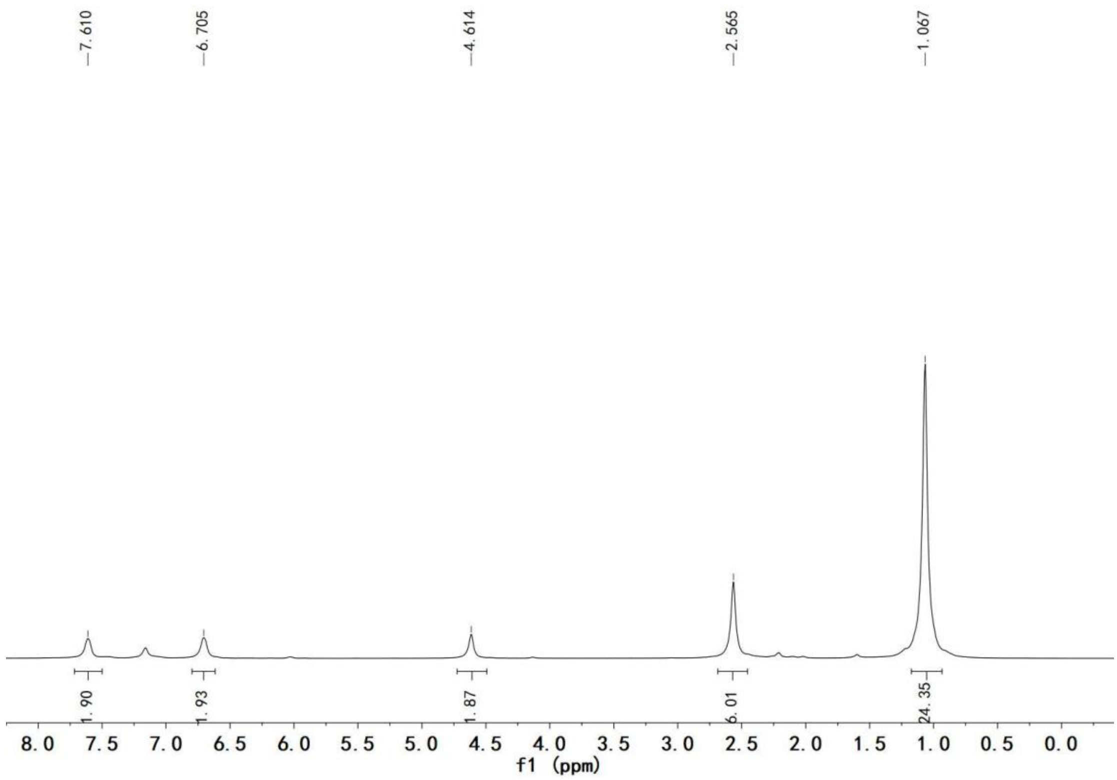


Figure S13. ^{1}H NMR spectrum of **5e** (400 MHz, C_6D_6, 298 K).

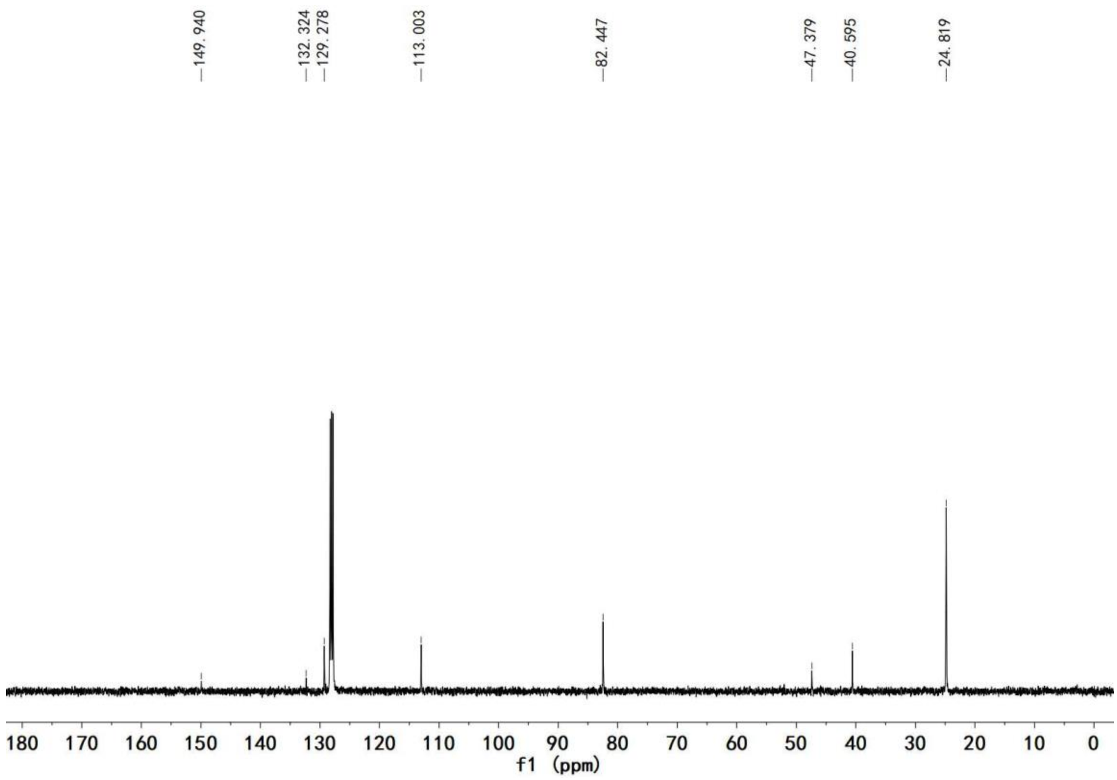


Figure S14. ^{13}C{^{1}H} NMR spectrum of **5e** (101 MHz, C_6D_6, 298 K).

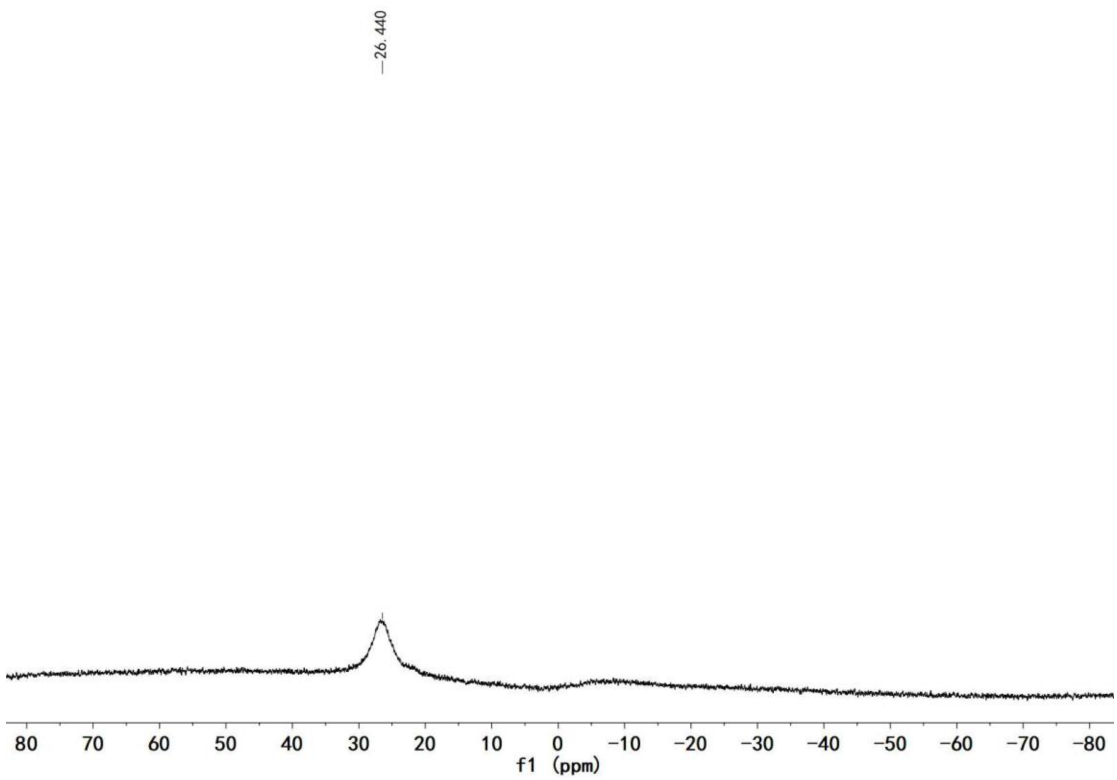
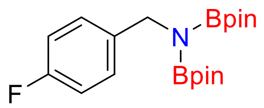


Figure S15. ^{11}B NMR spectrum of **5e** (128 MHz, C_6D_6, 298 K).



5f[6] (white solid, 96 mg, 85% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.42 (m, 2H, *phenyl*), 6.84 (m, 2H, *phenyl*), 4.47 (s, 2H, C*H*$_2$), 1.02 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 162.2 (d, *J* = 243.3 Hz, *phenyl*), 139.6 (d, *J* = 3.2 Hz, *phenyl*), 129.8 (d, *J* = 7.8 Hz, *phenyl*), 115.0 (d, *J* = 21.1 Hz, *phenyl*), 82.6 (*C*(CH$_3$)$_2$), 47.1 (*C*H$_2$), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298K): δ = 26.1.

^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 298K): δ = -116.9.

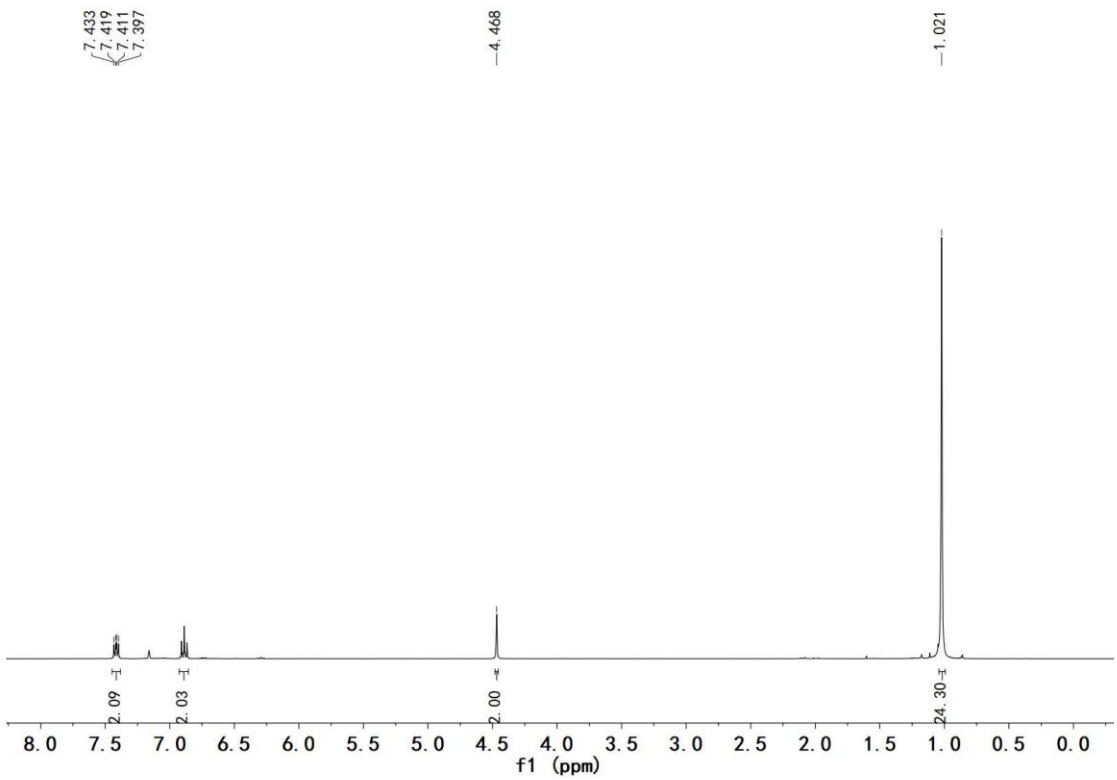


Figure S16. ^{1}H NMR spectrum of **5f** (400 MHz, C_6D_6, 298 K).

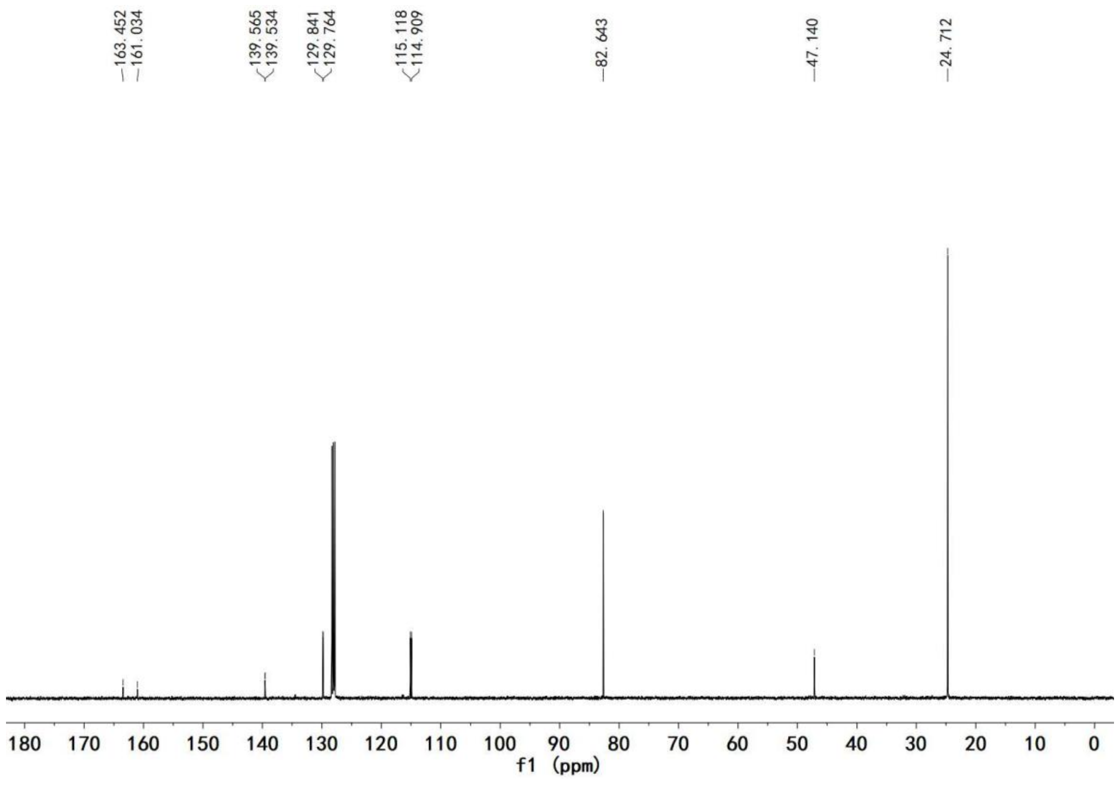


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **5f** (101 MHz, C_6D_6, 298 K).

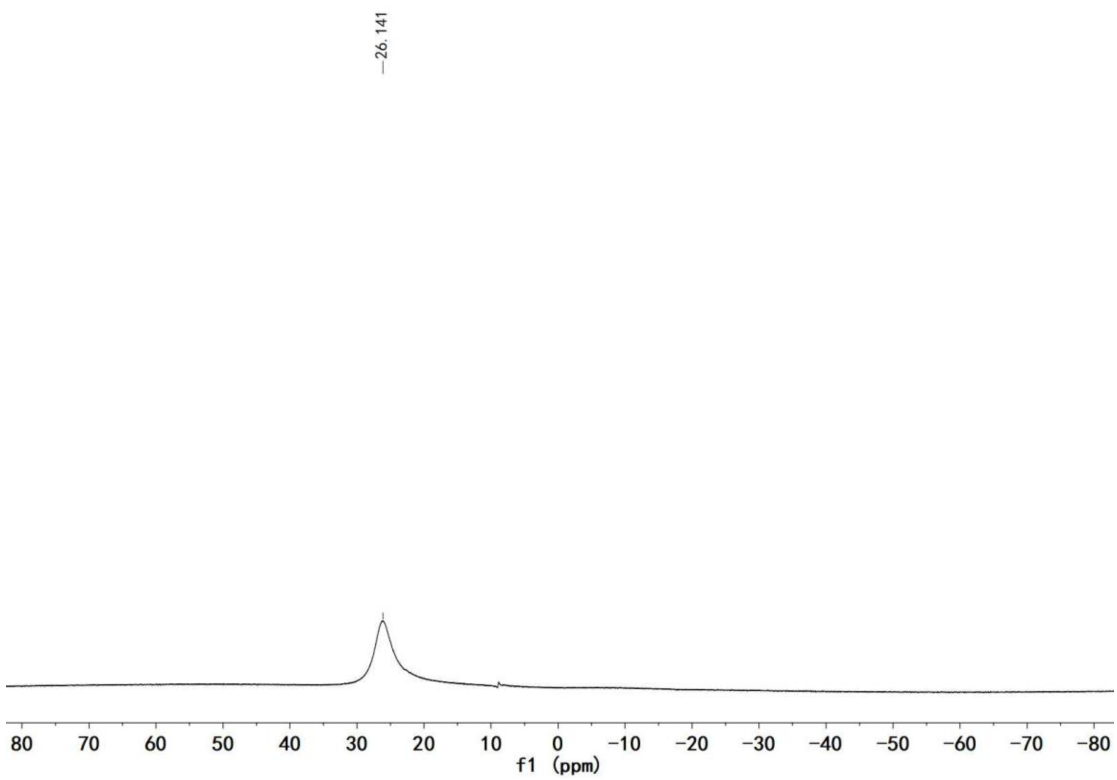


Figure S18. ^{11}B NMR spectrum of **5f** (128 MHz, C_6D_6, 298 K).

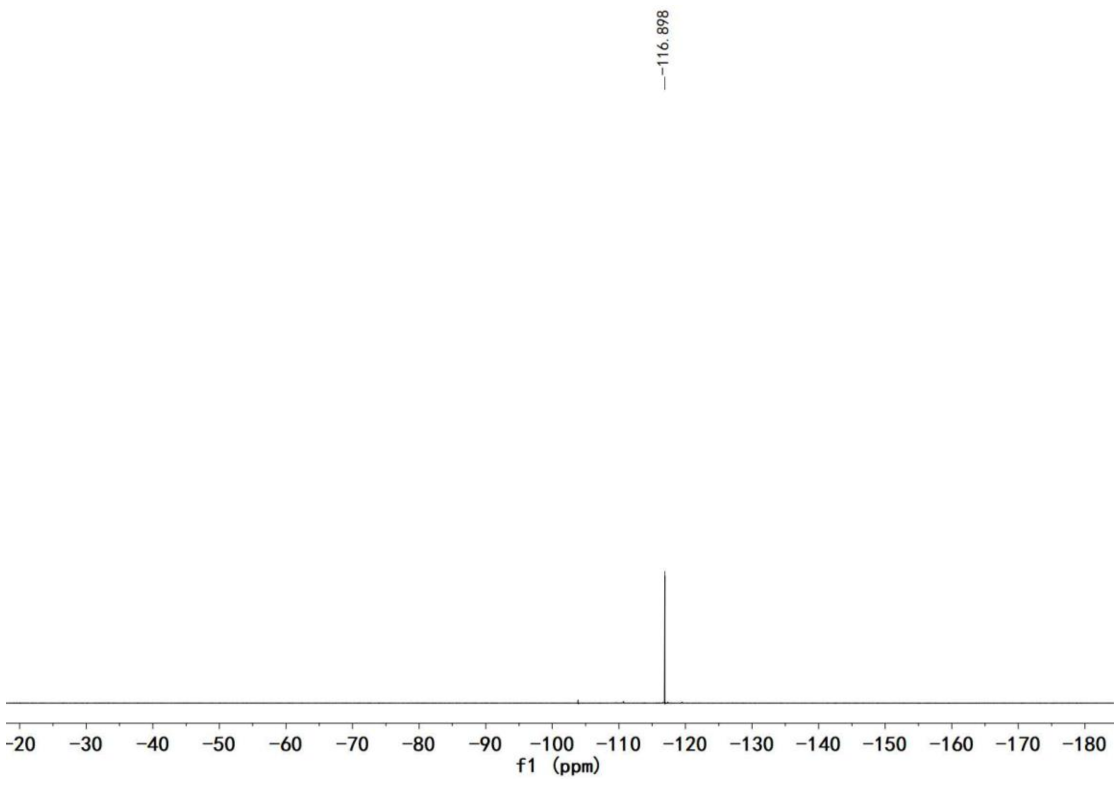
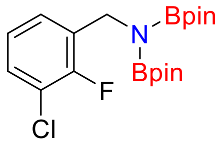


Figure S19. ^{19}F{^{1}H} NMR spectrum of **5f** (376 MHz, C_6D_6, 298 K).



5g (white solid, 110 mg, 89% yield)

Melting Point: 91-92 ºC

Elemental Analysis: calcd. for $C_{19}H_{29}B_2ClFNO_4$: C, 55.46; H, 7.10; N, 3.40. Found: C, 55.59; H, 7.03; N, 3.43.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.35 (m, 1H, *phenyl*), 6.95 (m, 1H, *phenyl*), 6.68 (m, 1H, *phenyl*), 4.70 (s, 2H, C*H*$_2$), 1.01 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 156.5 (d, *J* = 248.6 Hz, *phenyl*), 132.4 (d, *J* = 14.5 Hz, *phenyl*), 128.6 (*phenyl*), 127.0 (d, *J* = 4.3 Hz, *phenyl*), 124.2 (d, *J* = 4.6 Hz, *phenyl*), 121.1 (d, *J* = 18.1 Hz, *phenyl*), 82.8 (*C*(CH$_3$)$_2$), 41.8 (*C*H$_2$), 24.6 (C(*C*H$_3$)$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = 26.1.

^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 298 K): δ = -120.1.

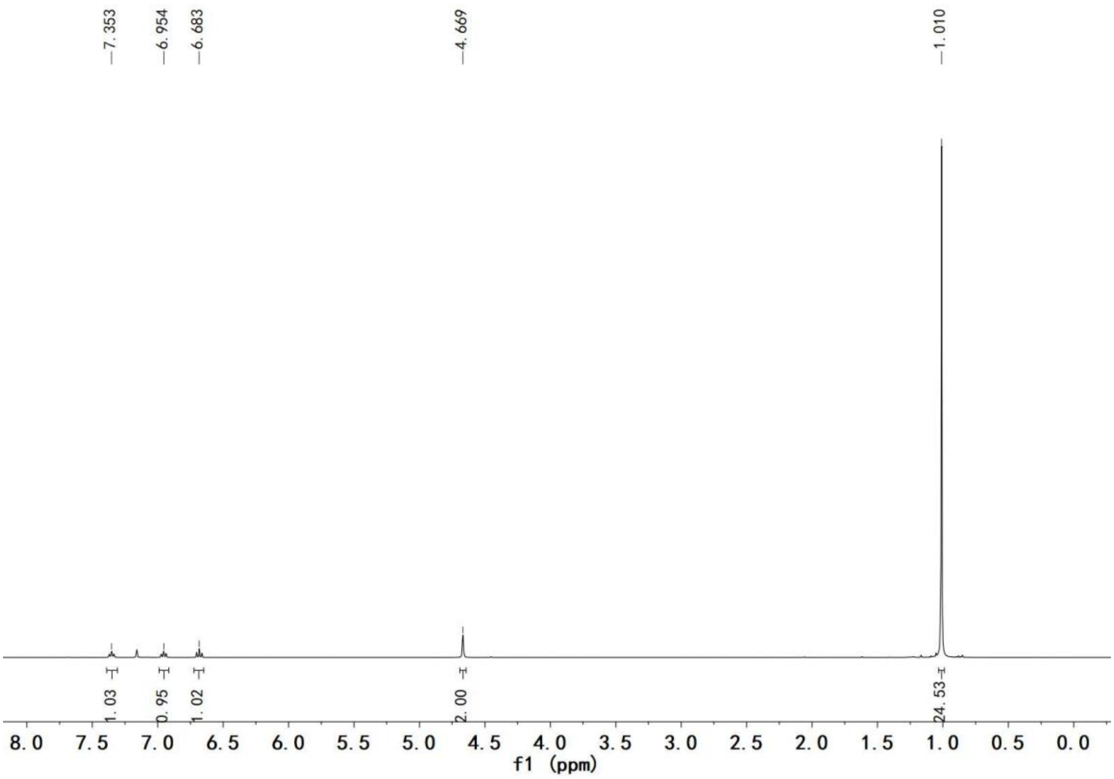


Figure S20. ^{1}H NMR spectrum of **5g** (400 MHz, C_6D_6, 298 K).

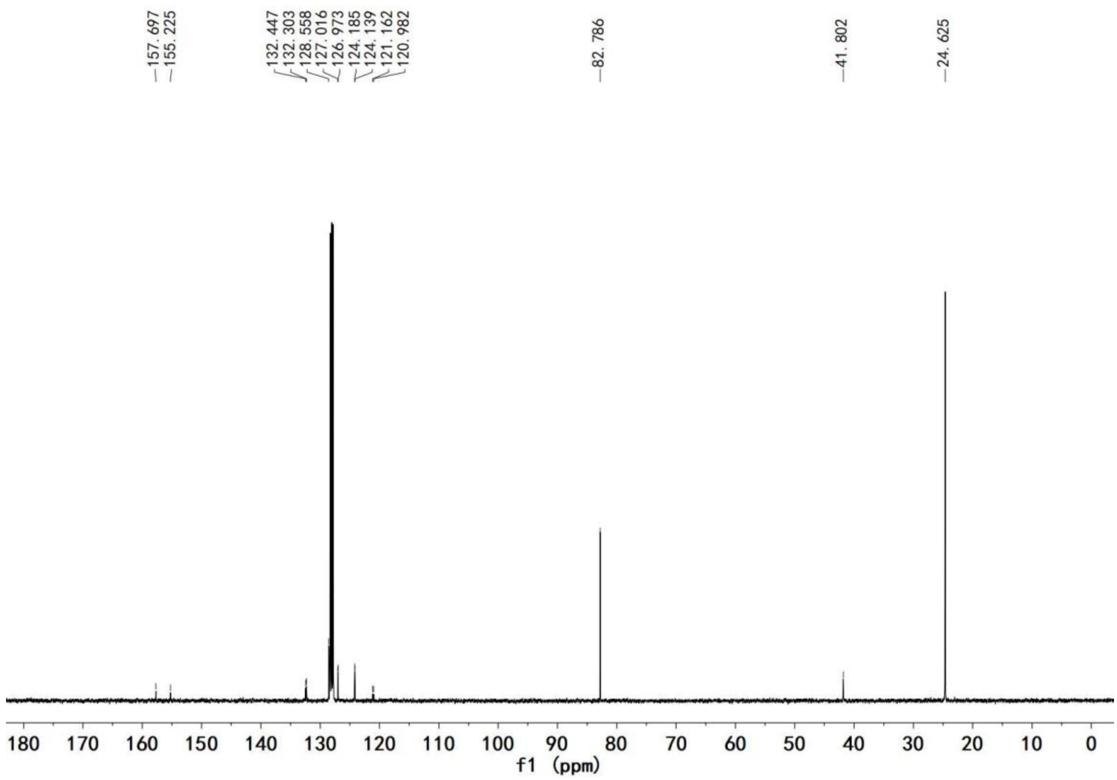


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **5g** (101 MHz, C_6D_6, 298 K).

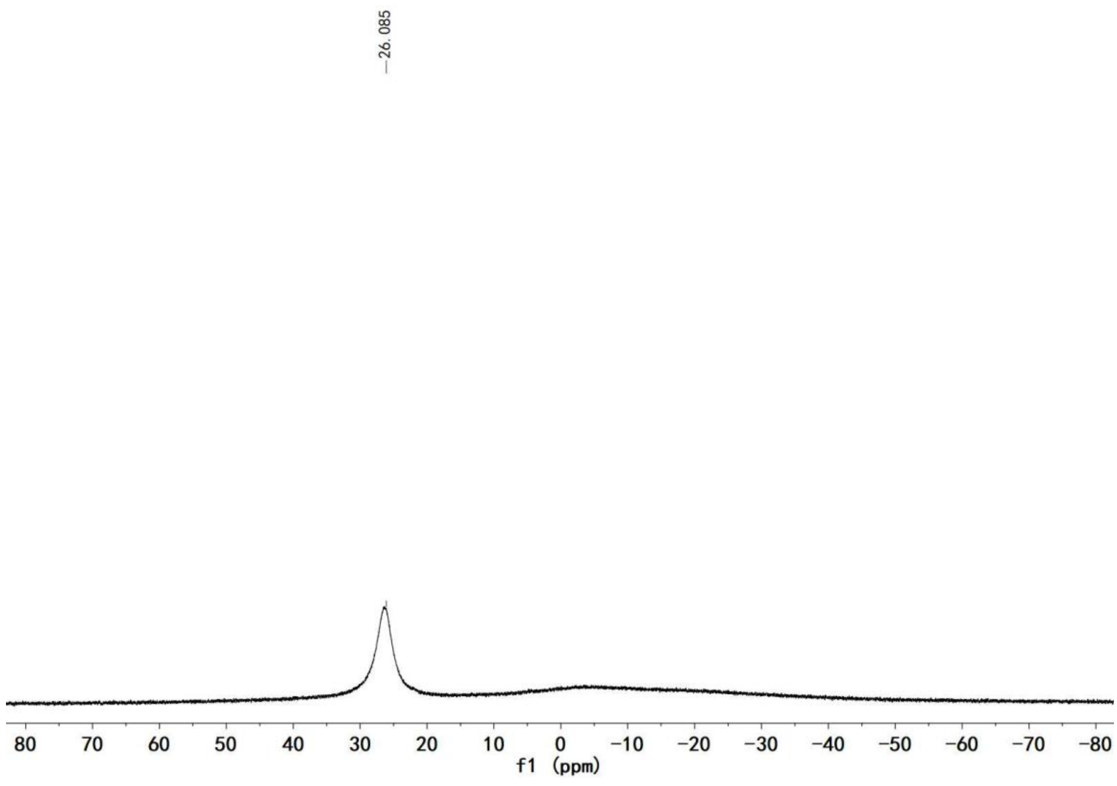


Figure S22. ^{11}B NMR spectrum of **5g** (128 MHz, C_6D_6, 298 K).

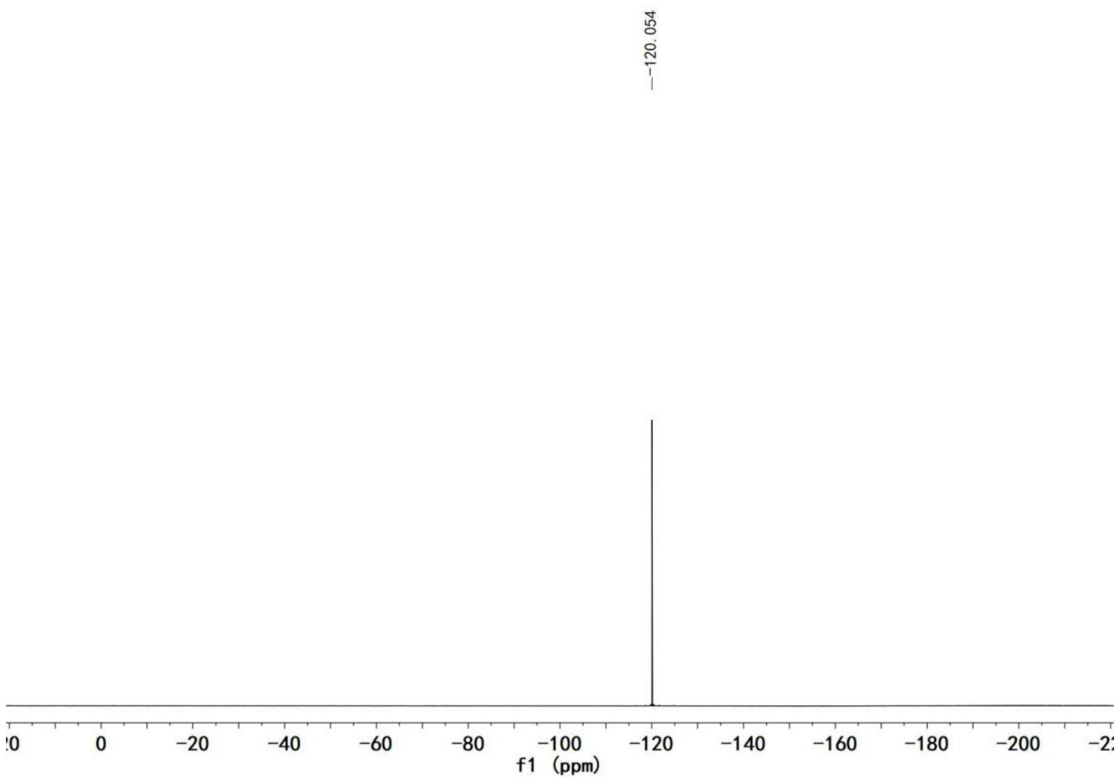
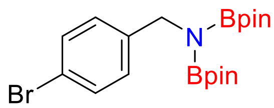


Figure S23. $^{19}F\{^{1}H\}$ NMR spectrum of **5g** (376 MHz, C_6D_6, 298 K).



5h[6] (white solid, 121 mg, 92% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.31 (m, 2H, *phenyl*), 7.26 (m, 2H, *phenyl*), 4.39 (s, 2H, C*H*$_2$), 1.00 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 142.7 (*phenyl*), 131.5 (*phenyl*), 129.9 (*phenyl*), 120.6 (*phenyl*), 82.7 (*C*(CH$_3$)$_2$), 47.2 (*C*H$_2$), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = 26.3.

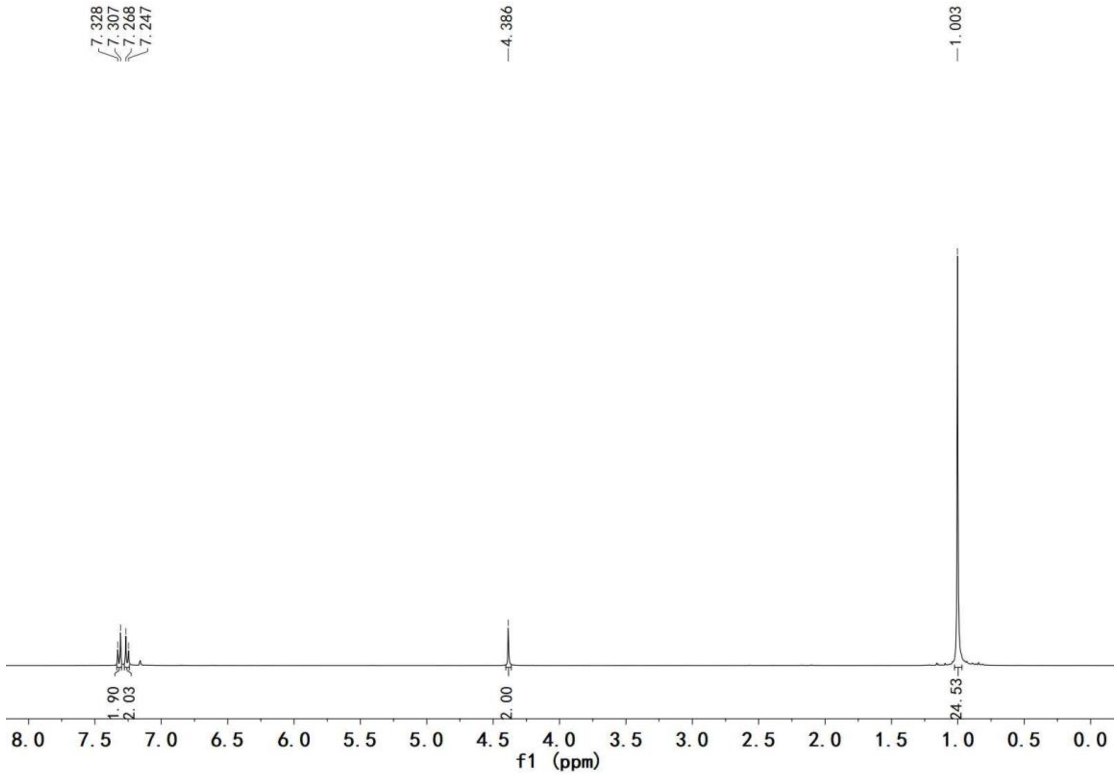


Figure S24. ^{1}H NMR spectrum of **5h** (400 MHz, C_6D_6, 298 K).

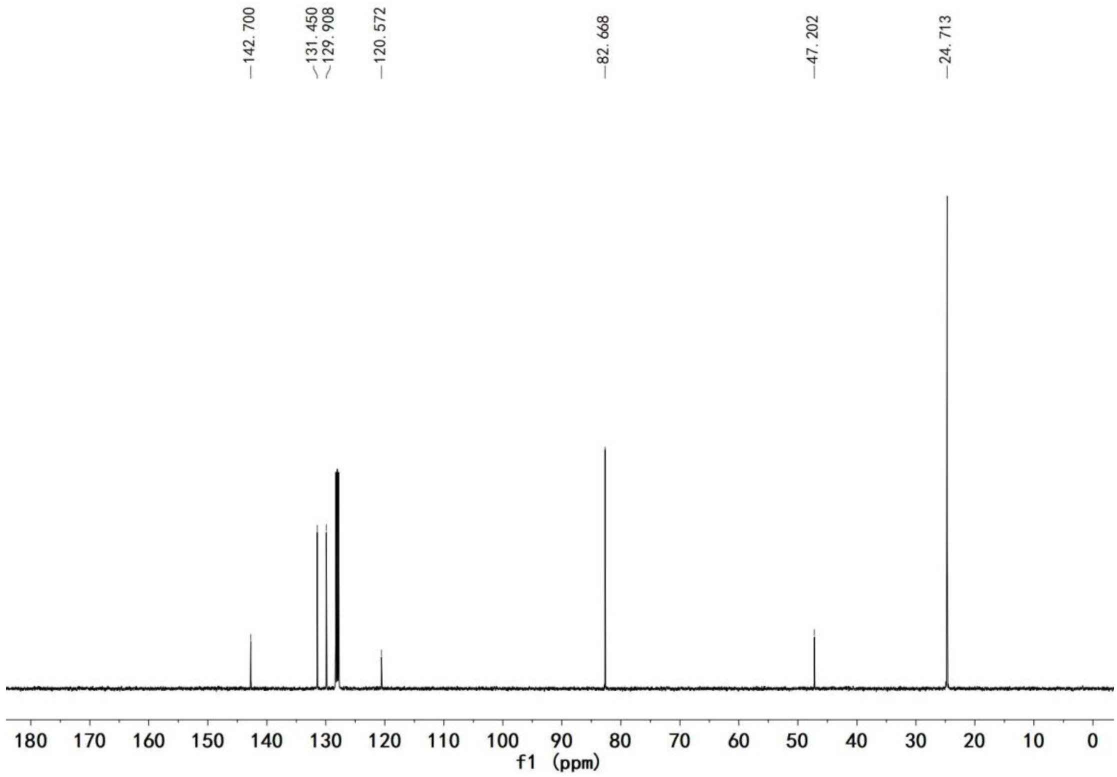


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **5h** (101 MHz, C_6D_6, 298 K).

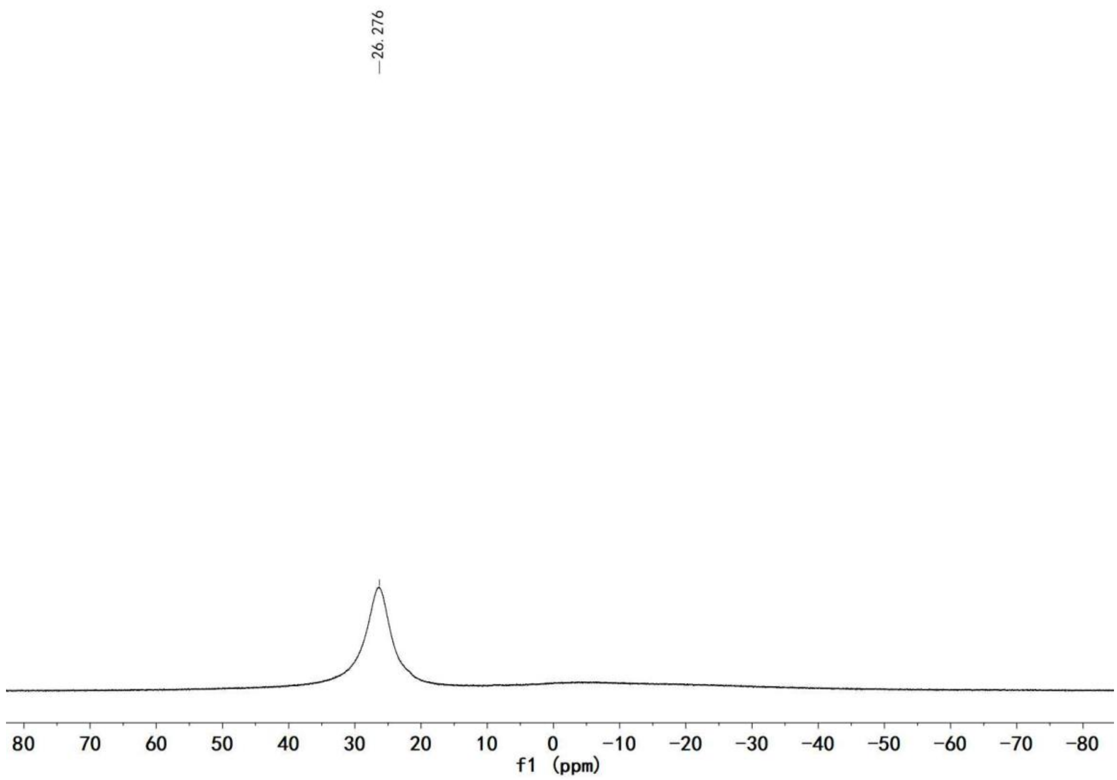
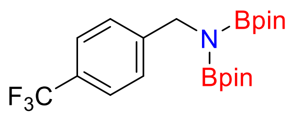


Figure S26. ^{11}B NMR spectrum of **5h** (128 MHz, C_6D_6, 298 K).



5i[6] (white solid, 110 mg, 86% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.41 (m, 4H, *phenyl*), 4.47 (s, 2H, CH_2), 1.01 (s, 24H, C(CH_3)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 147.7 (q, *J* = 1.2 Hz, *phenyl*), 128.8 (q, *J* = 32.0 Hz, *phenyl*), 128.1 (*phenyl*), 124.9 (q, *J* = 271.7 Hz, *C*F_3), 124.8 (q, *J* = 3.8 Hz, *phenyl*), 82.8 (*C*(CH_3)$_2$), 47.5 (*C*H_2), 24.7 (C(*C*H_3)$_2$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = 26.3.

^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 298 K): δ = -61.9.

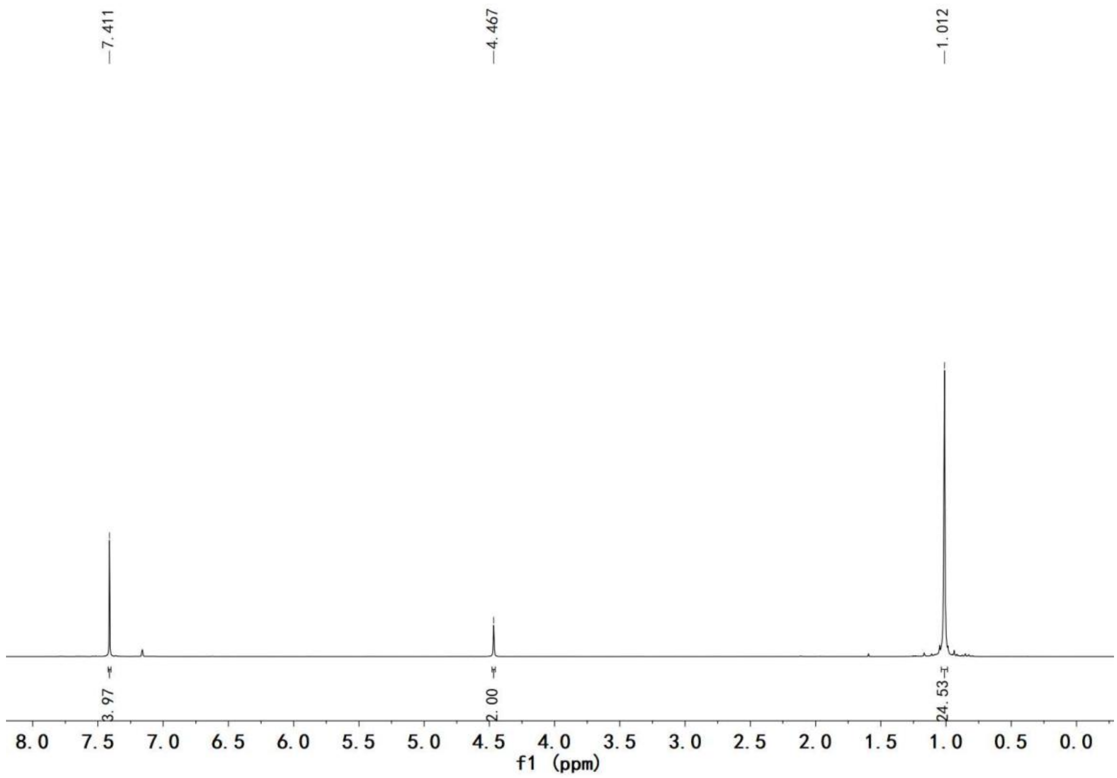


Figure S27. ^{1}H NMR spectrum of **5i** (400 MHz, C_6D_6, 298 K).

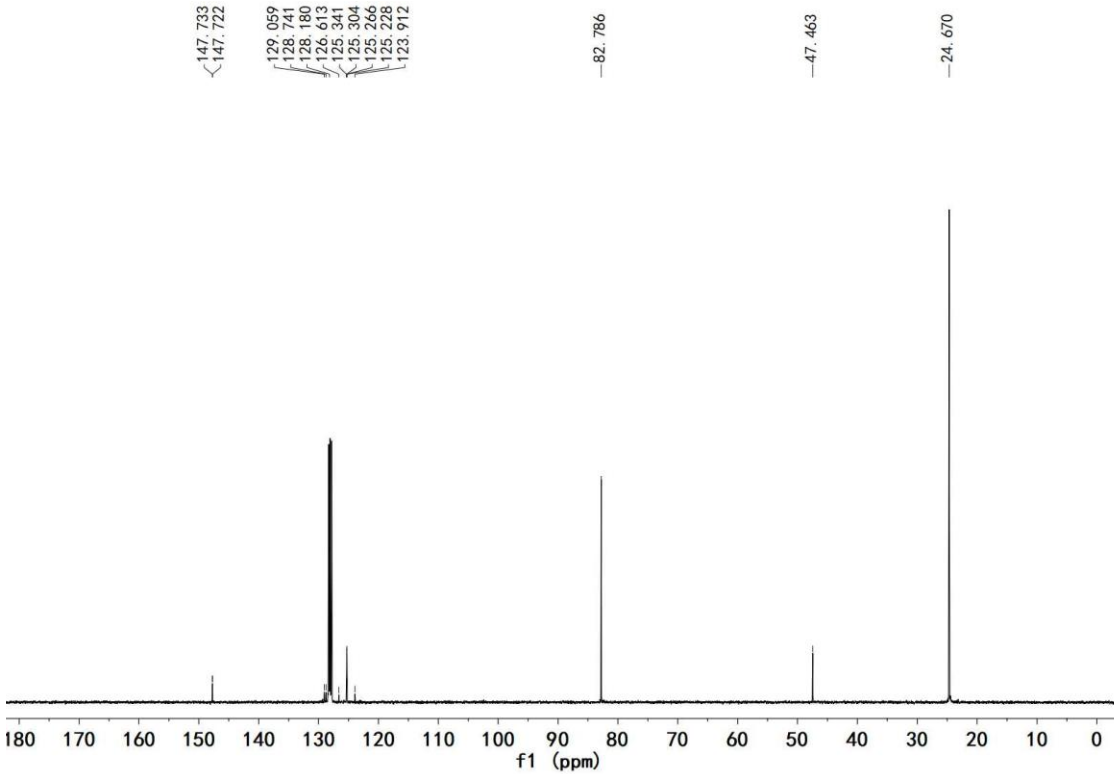


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **5i** (101 MHz, C_6D_6, 298 K).

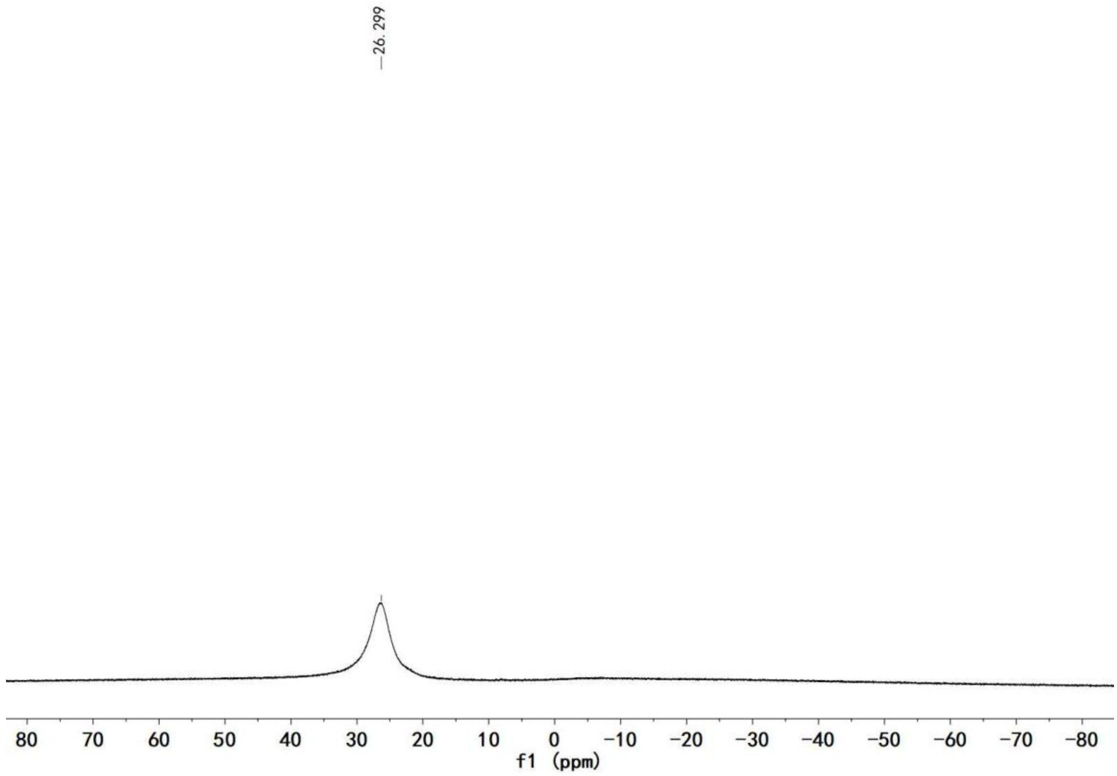


Figure S29. ^{11}B NMR spectrum of **5i** (128 MHz, C_6D_6, 298 K).

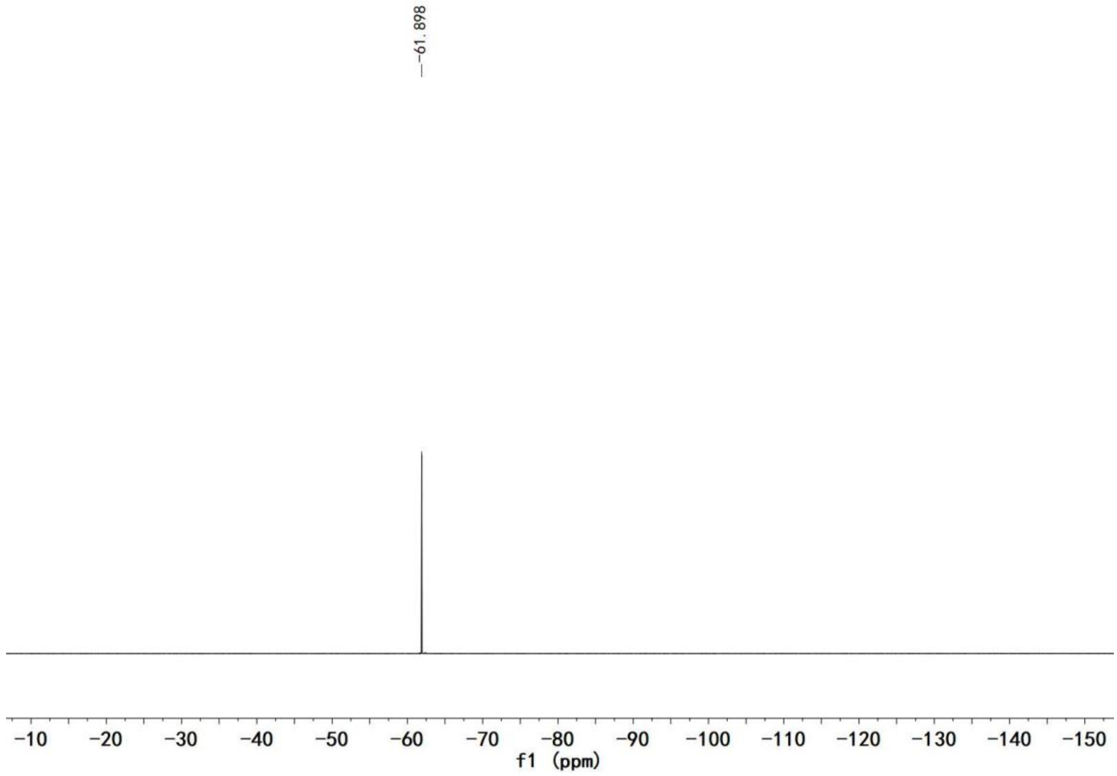
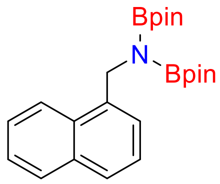


Figure S30. $^{19}F\{^1H\}$ NMR spectrum of **5i** (376 MHz, C_6D_6, 298 K).



5j[6] (white solid, 110 mg, 90% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 8.14 (m, 1H, *naphthyl*), 7.82 (m, 1H, *naphthyl*), 7.66 (m, 1H, *naphthyl*), 7.60 (m, 1H, *naphthyl*), 7.42 (m, 1H, *naphthyl*), 7.24 (m, 2H, *naphthyl*), 5.16 (s, 2H, CH_2), 1.04 (s, 24H, $C(CH_3)_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 138.4 (*naphthyl*), 134.3 (*naphthyl*), 131.9 (*naphthyl*), 128.9 (*naphthyl*), 128.3 (*naphthyl*), 127.2 (*naphthyl*), 125.8 (*naphthyl*), 125.6 (*naphthyl*), 123.8 (*naphthyl*), 123.4 (*naphthyl*), 82.7 ($C(CH_3)_2$), 45.4 (CH_2), 24.7 ($C(CH_3)_2$).

^{11}B NMR (128 MHz, C_6D_6, 298 K): δ = 26.5.

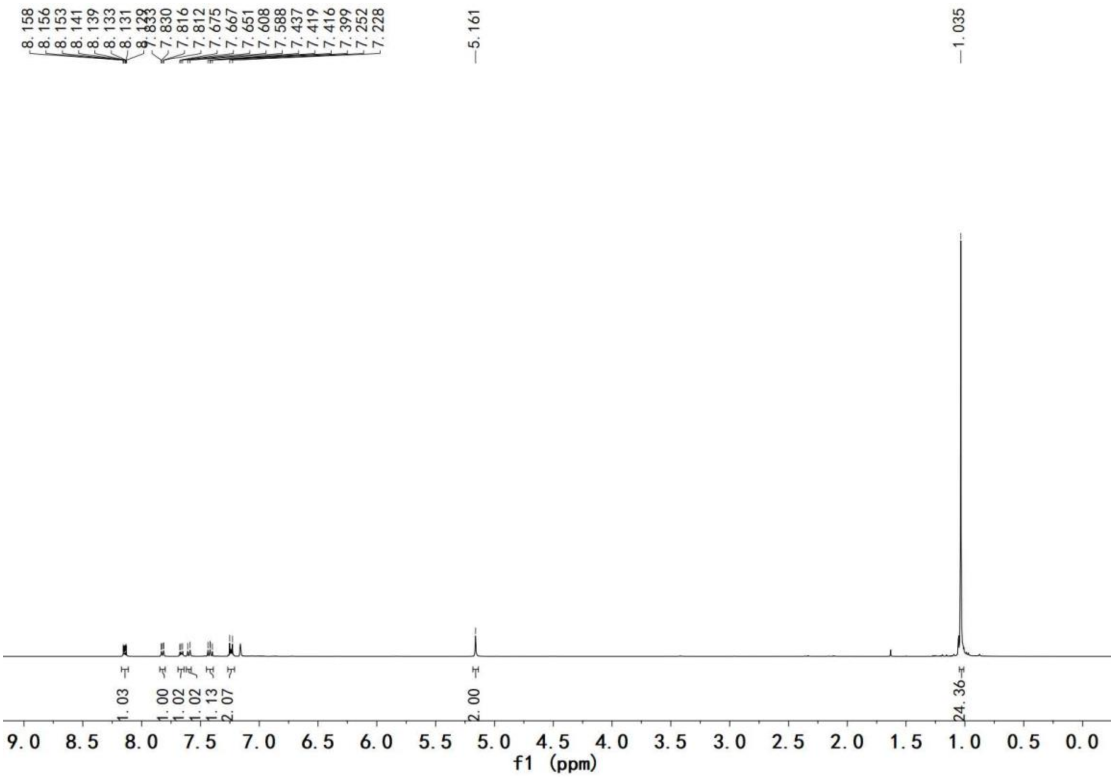


Figure S31. ^{1}H NMR spectrum of **5j** (400 MHz, C_6D_6, 298 K).

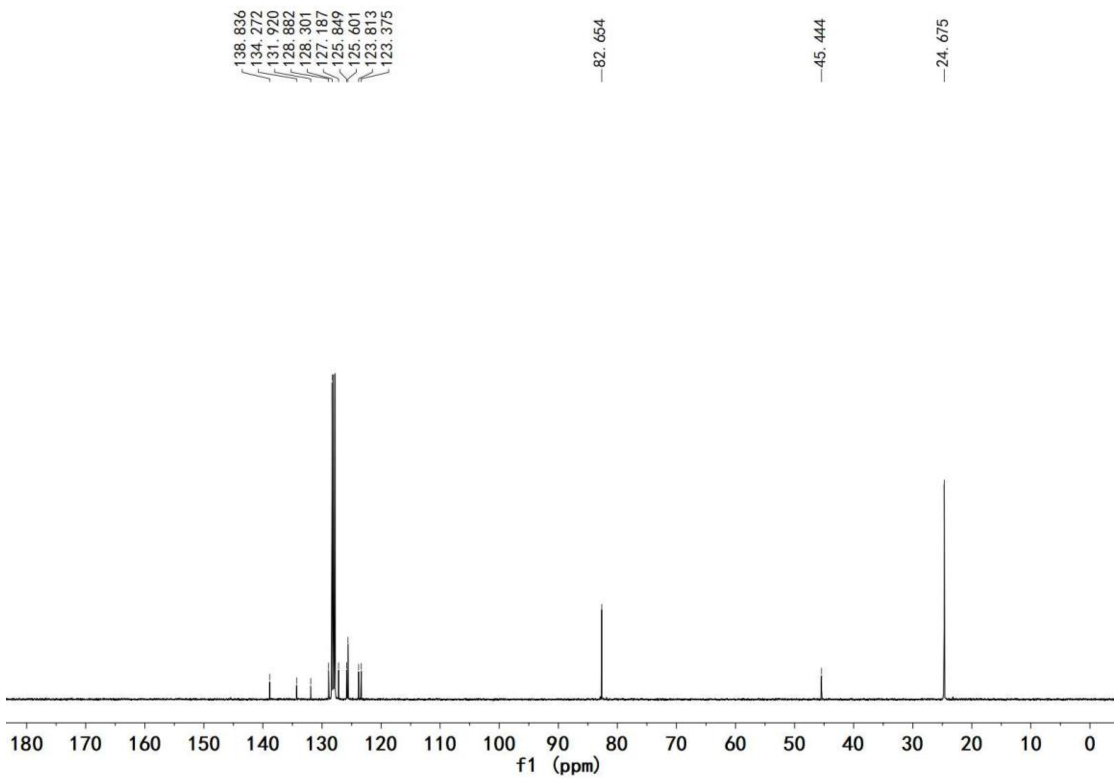


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **5j** (101 MHz, C_6D_6, 298 K).

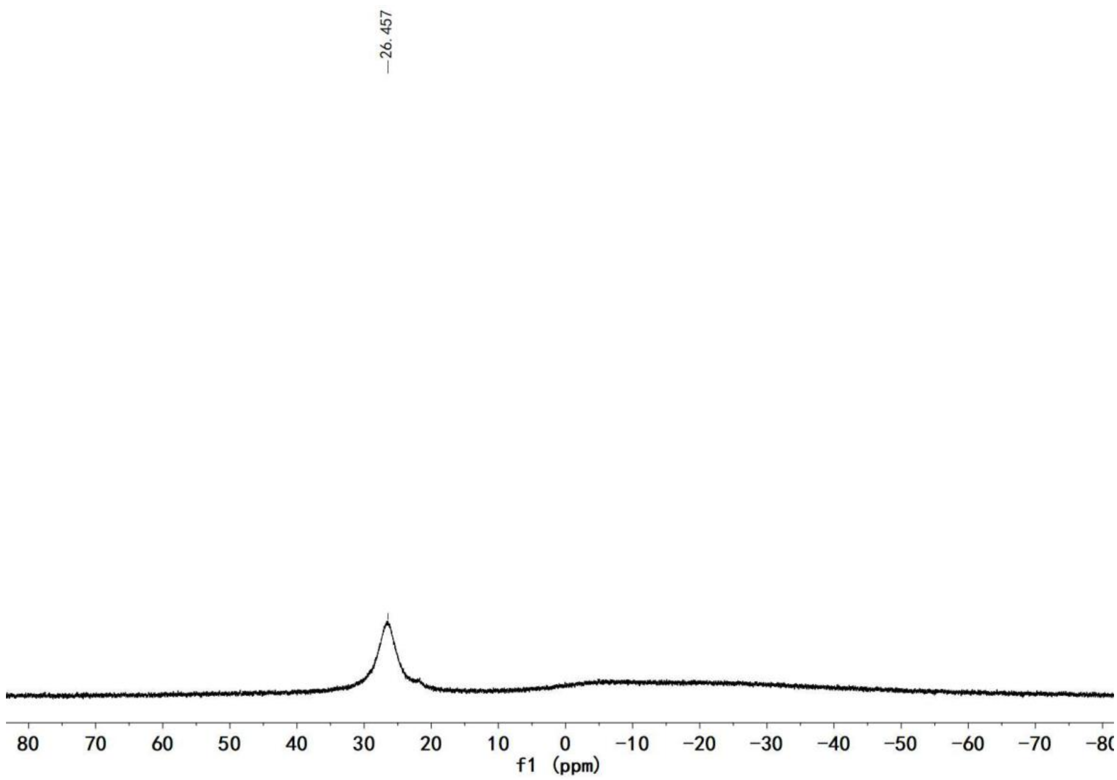
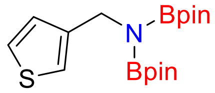


Figure S33 ^{11}B NMR spectrum of **5j** (128 MHz, C_6D_6, 298 K).



5k[6] (white solid, 96 mg, 88% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.24 (m, 1H, *thio*), 7.23 (m, 1H, *thio*), 6.97 (m, 1H, *thio*), 4.53 (s, 2H, C*H*$_2$), 1.02 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 144.8 (*thio*), 128.4 (*thio*), 125.2 (*thio*), 121.7 (*thio*), 82.6 (*C*(CH$_3$)$_2$), 43.0 (*C*H$_2$), 24.8 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 26.0.

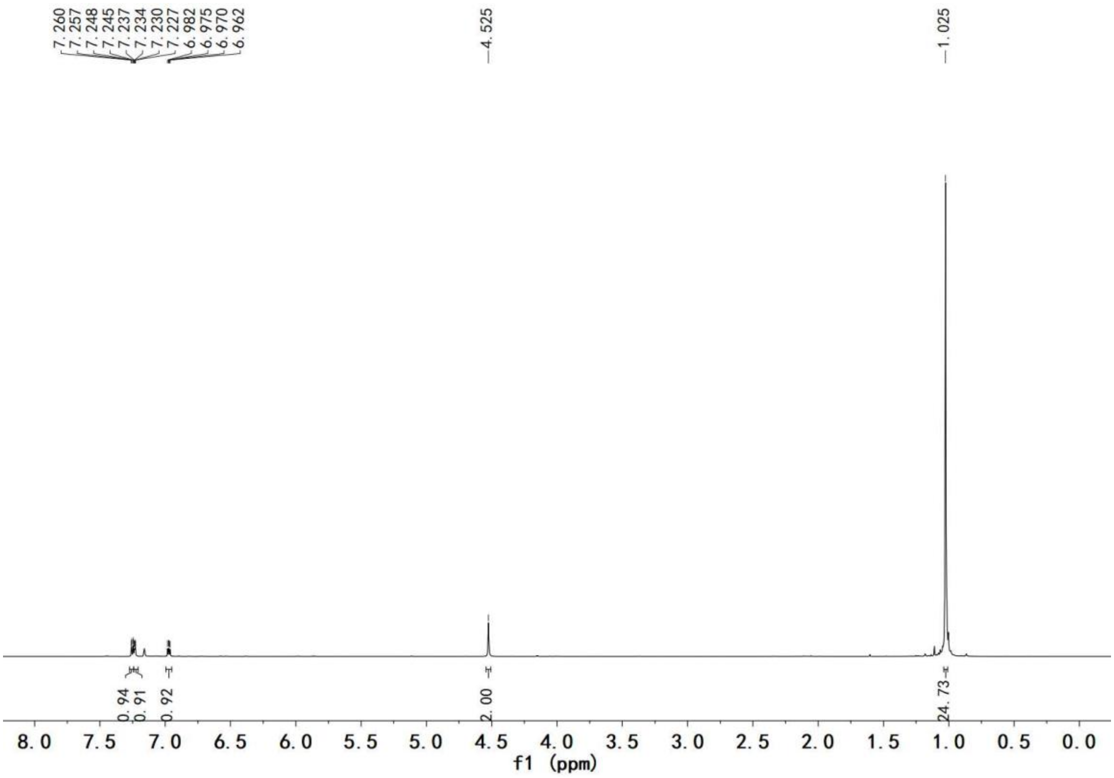


Figure S34. ^{1}H NMR spectrum of **5k** (400 MHz, C_6D_6, 298 K).

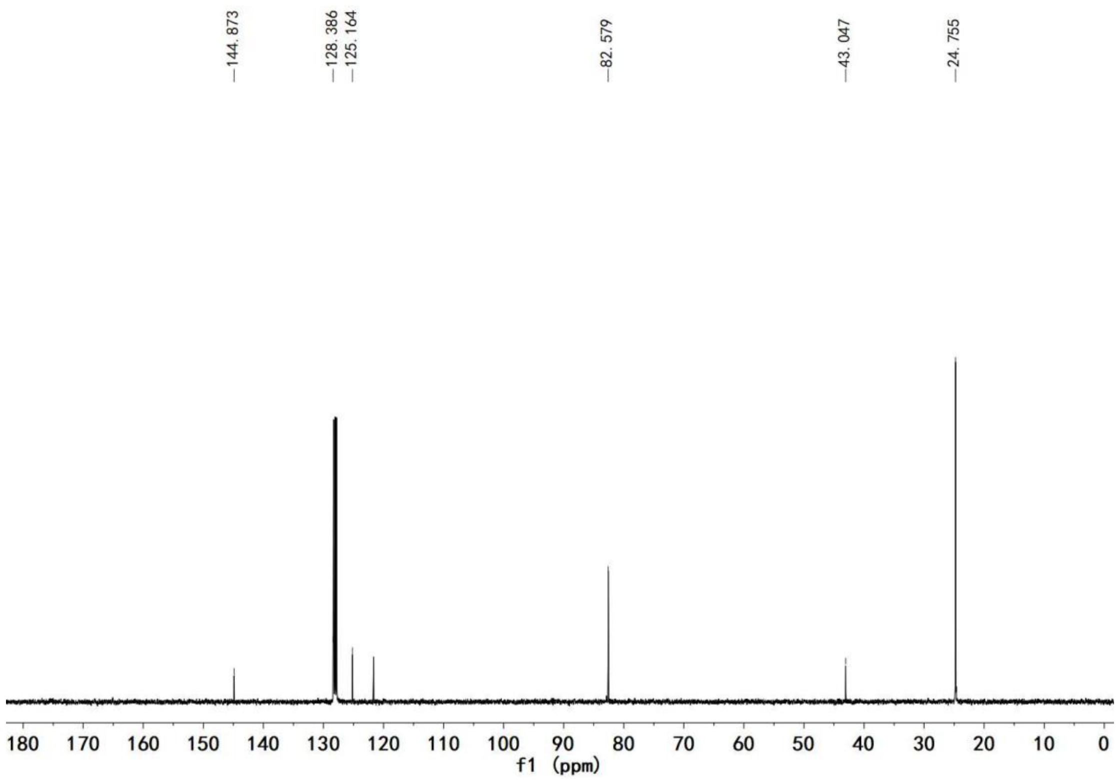


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **5k** (101 MHz, C_6D_6, 298 K).

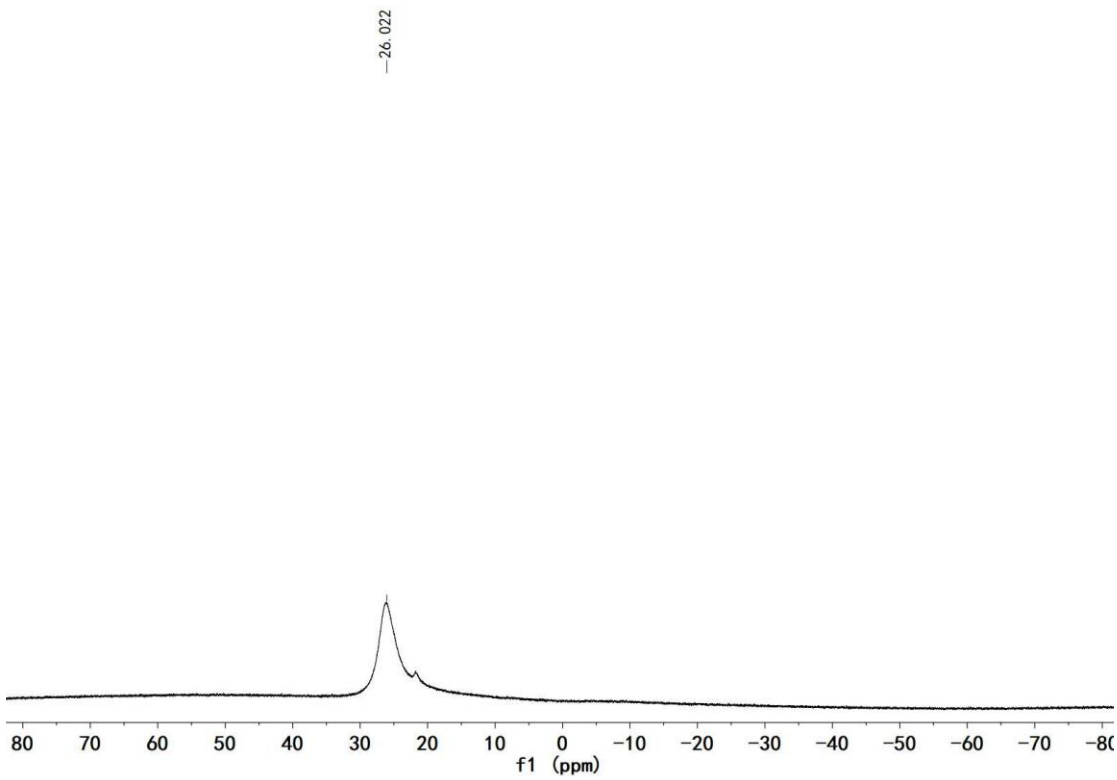
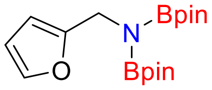


Figure S36. ^{11}B NMR spectrum of **5k** (128 MHz, C_6D_6, 298 K).



5l[6] (white solid, 94 mg, 90% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.13 (m, 1H, *furan*), 6.27 (m, 1H, *furan*), 6.15 (m, 1H, *furan*), 4.57 (s, 2H, C*H*$_2$), 1.04 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 157.3 (*furan*), 141.3 (*furan*), 110.4 (*furan*), 105.8 (*furan*), 82.6 (*C*(CH$_3$)$_2$), 41.3 (*C*H$_2$), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 26.0.

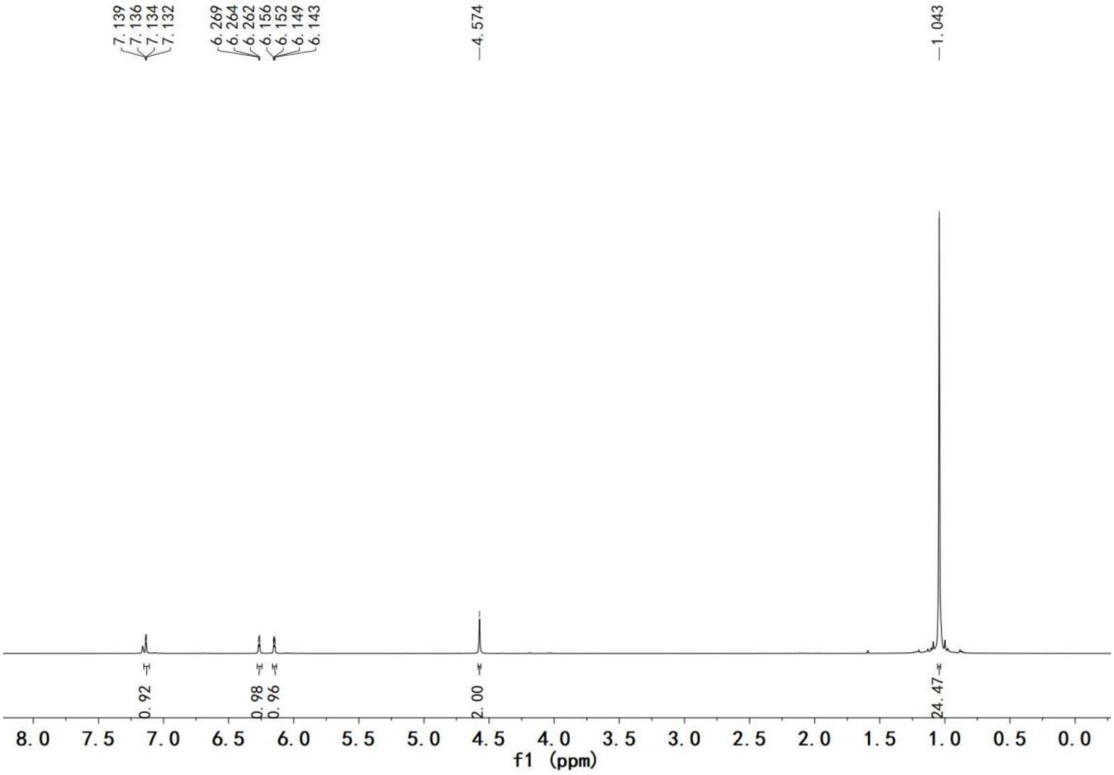


Figure S37. ^{1}H NMR spectrum of **5l** (400 MHz, C_6D_6, 298 K).

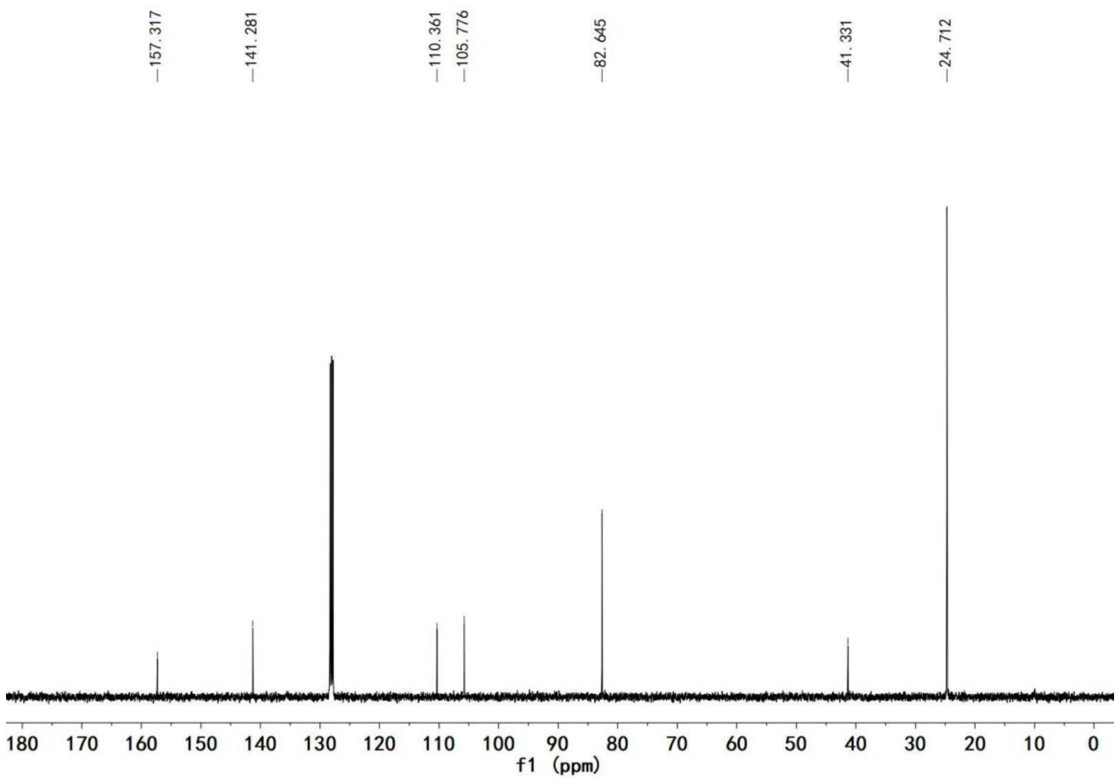


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **5l** (101 MHz, C_6D_6, 298 K).

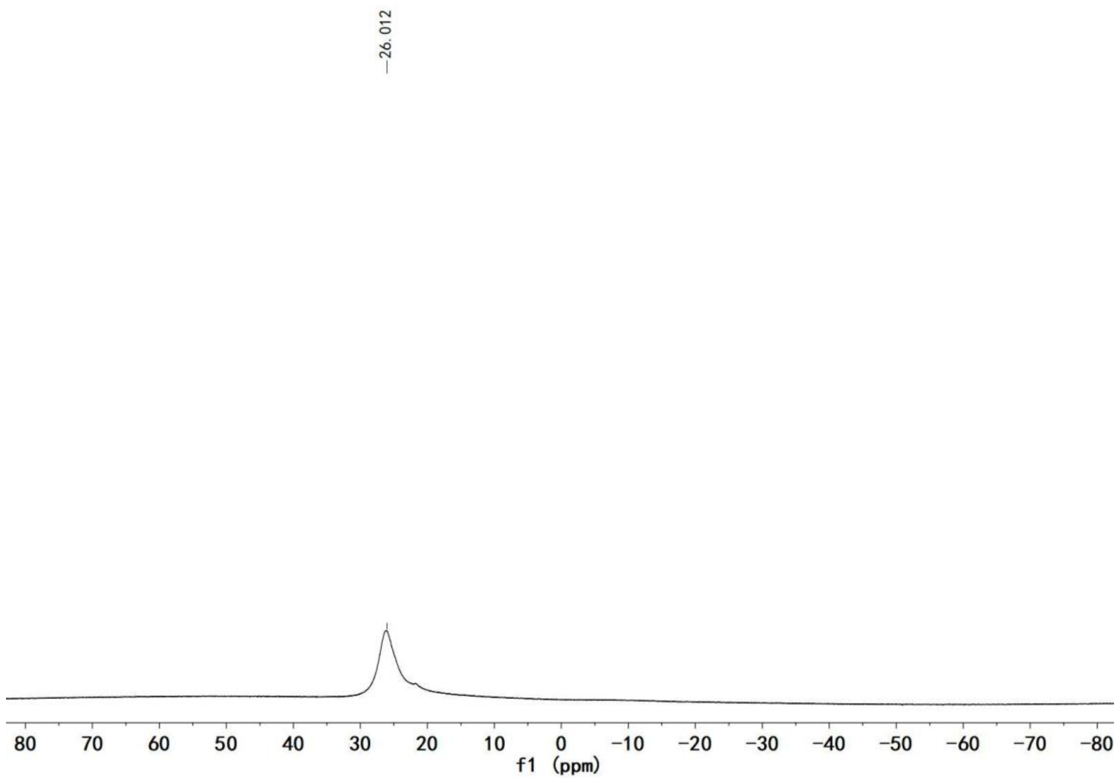
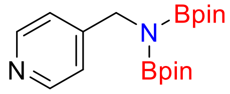


Figure S39. ^{11}B NMR spectrum of **5l** (128 MHz, C_6D_6, 298 K).



5m[6] (white solid, 86 mg, 80% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 8.62 (m, 2H, *pyridyl*), 7.19 (m, 2H, *pyridyl*), 4.43 (s, 2H, C*H*$_2$), 1.01 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 151.8 (*pyridyl*), 150.2 (*pyridyl*), 122.5 (*pyridyl*), 82.8 (*C*(CH$_3$)$_2$), 47.0 (*C*H$_2$), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 26.3.

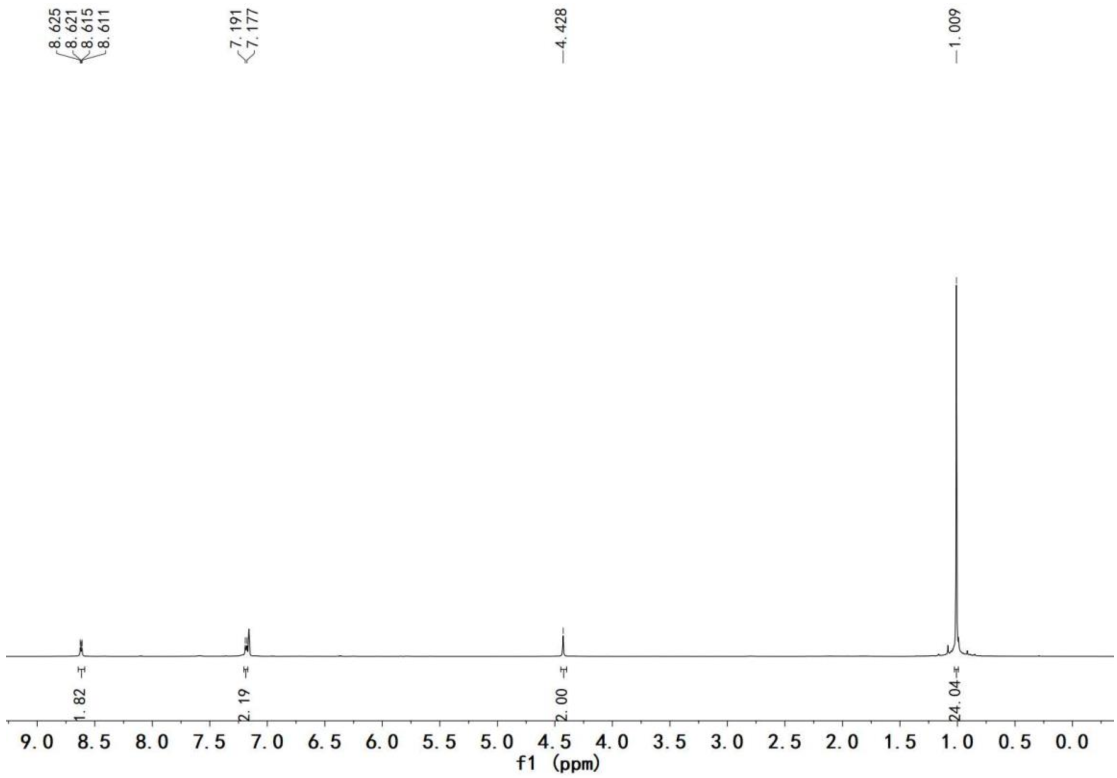


Figure S40. ^{1}H NMR spectrum of **5m** (400 MHz, C_6D_6, 298 K).

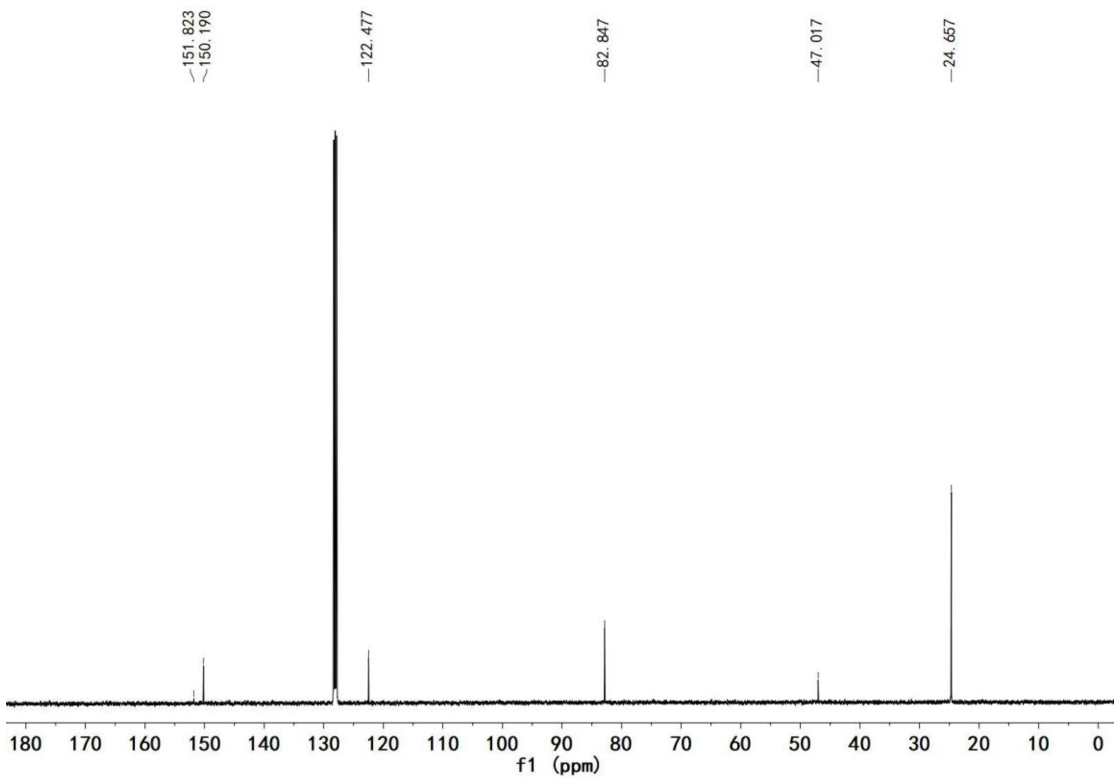


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of **5m** (101 MHz, C_6D_6, 298 K).

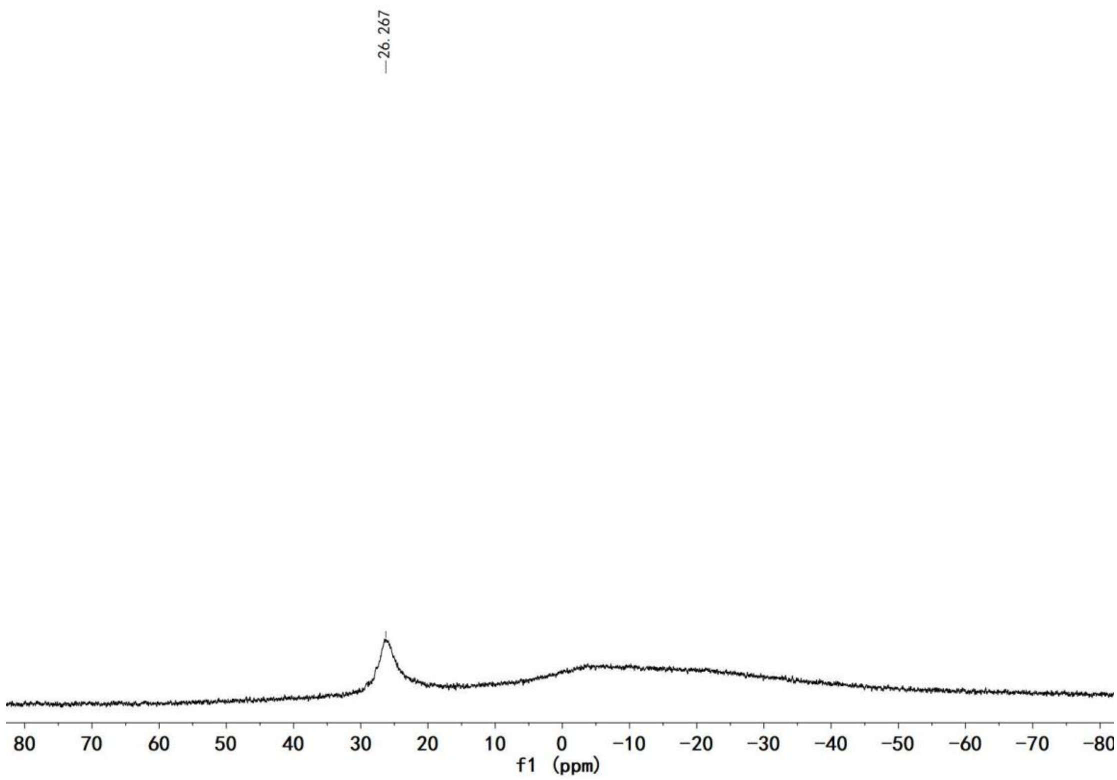
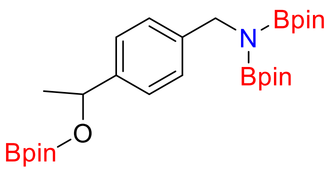


Figure S42. ^{11}B NMR spectrum of **5m** (128 MHz, C_6D_6, 298 K).



5n[6] (white solid, 130 mg, 82% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.57 (m, 2H, *phenyl*), 7.43 (m, 2H, *phenyl*), 5.46 (q, *J* = 6.4 Hz, 1H, ArC*H*CH_3), 4.60 (s, 2H, CH_2), 1.50 (d, *J* = 6.4 Hz, 3H, ArCHCH_3), 1.04 (s, 30H, C(CH_3)$_2$), 1.02 (s, 6H, C(CH_3)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 143.4 (*phenyl*), 142.6 (*phenyl*), 128.1 (*phenyl*), 125.5 (*phenyl*), 82.6 (*C*(CH_3)$_2$), 82.5 (*C*(CH_3)$_2$), 73.0 (Ar*C*HCH_3), 47.7 (*C*H_2), 25.7 (ArCH*C*H_3), 24.7 (C(*C*H_3)$_2$), 24.5 (C(*C*H_3)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 26.0 (N*B*pin), 22.4 (O*B*pin).

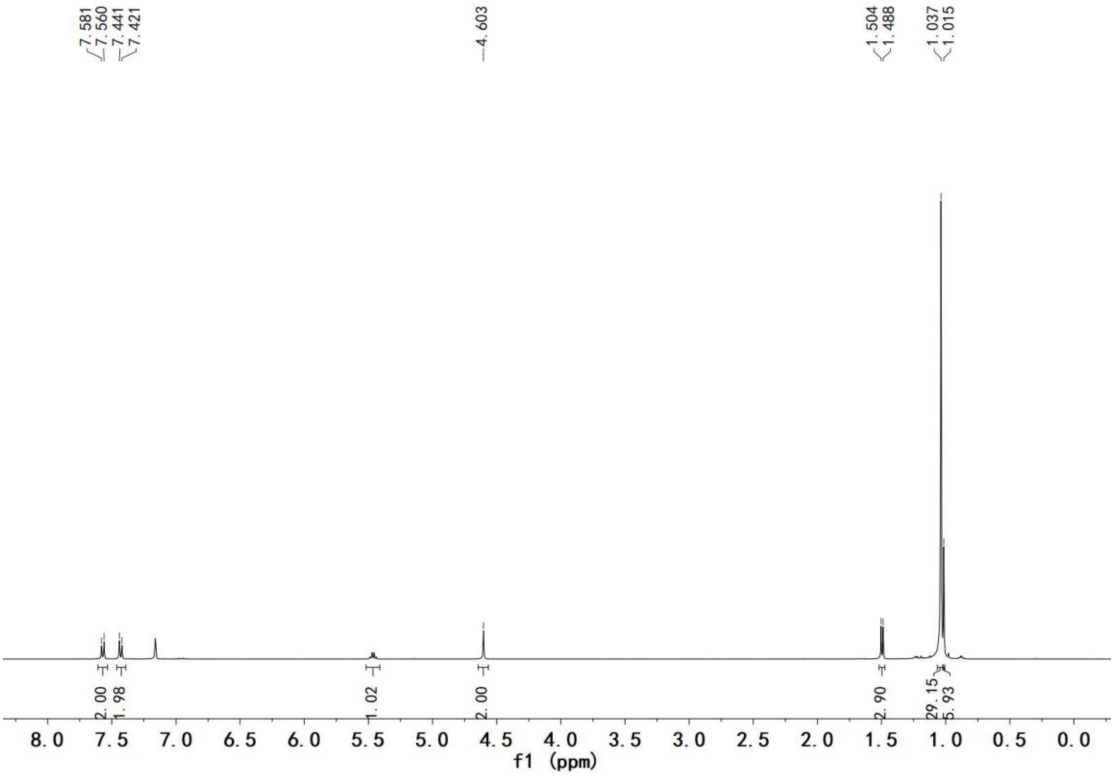


Figure S43. ^{1}H NMR spectrum of **5n** (400 MHz, C_6D_6, 298 K).

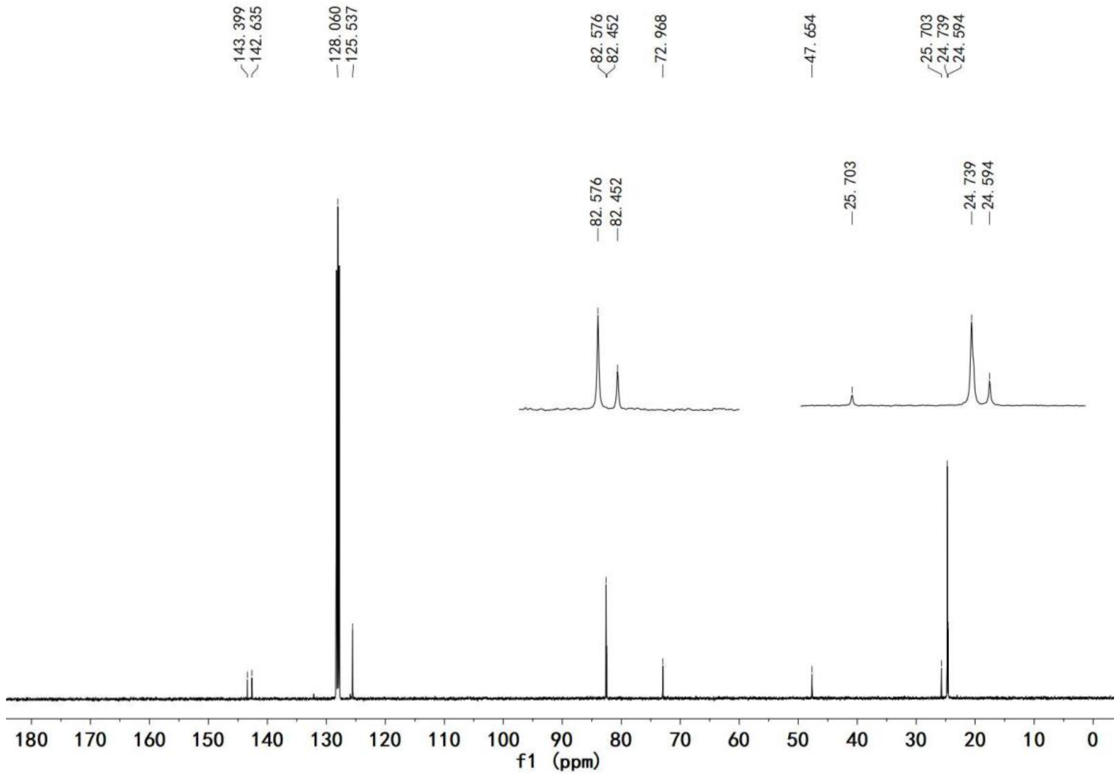


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of **5n** (101 MHz, C_6D_6, 298 K).

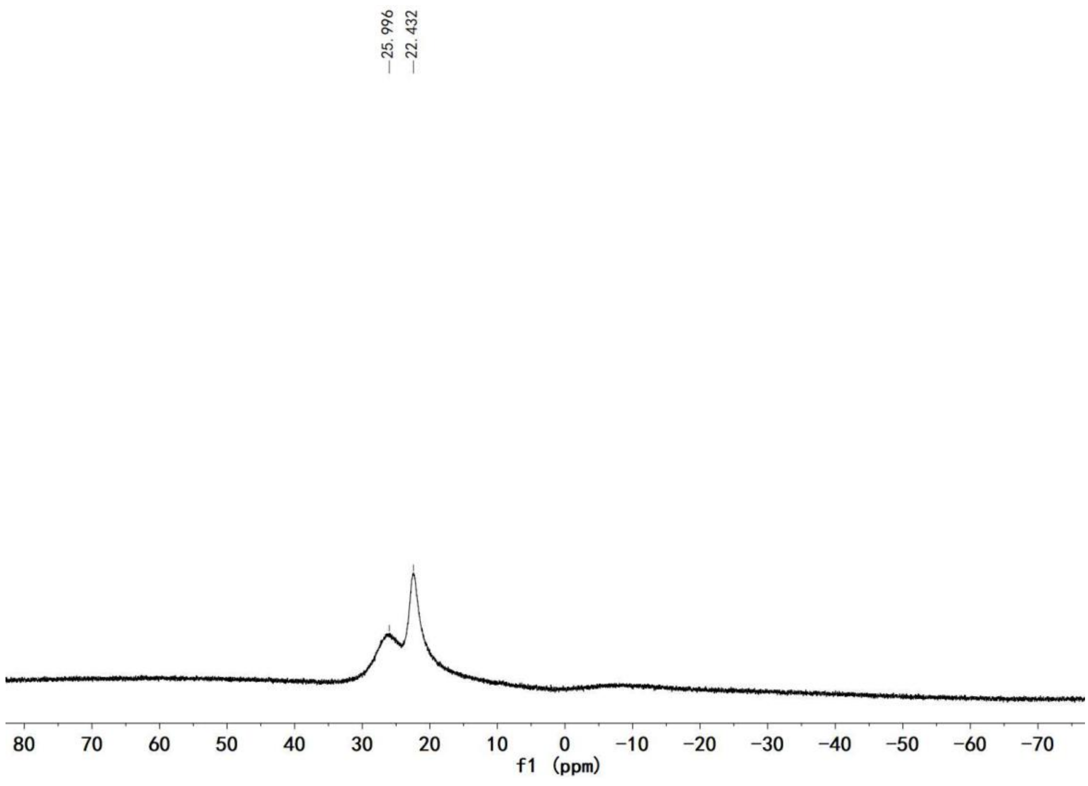
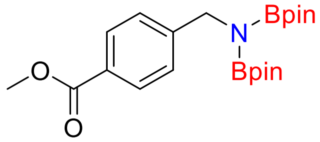


Figure S45. ^{11}B NMR spectrum of **5n** (128 MHz, C_6D_6, 298 K).



5o[6] (white solid, 110 mg, 88% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 8.21 (m, 2H, *phenyl*), 7.53 (m, 2H, *phenyl*), 4.56 (s, 2H, C*H*$_2$), 3.50 (s, 3H, OC*H*$_3$), 1.02 (s, 24H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 166.8 (Ar*C*OOCH$_3$), 148.9 (*phenyl*), 132.1 (*phenyl*), 129.0 (*phenyl*), 126.8 (*phenyl*), 82.7 (*C*(CH$_3$)$_2$), 51.4 (ArCOO*C*H$_3$), 47.6 (*C*H$_2$), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 26.1.

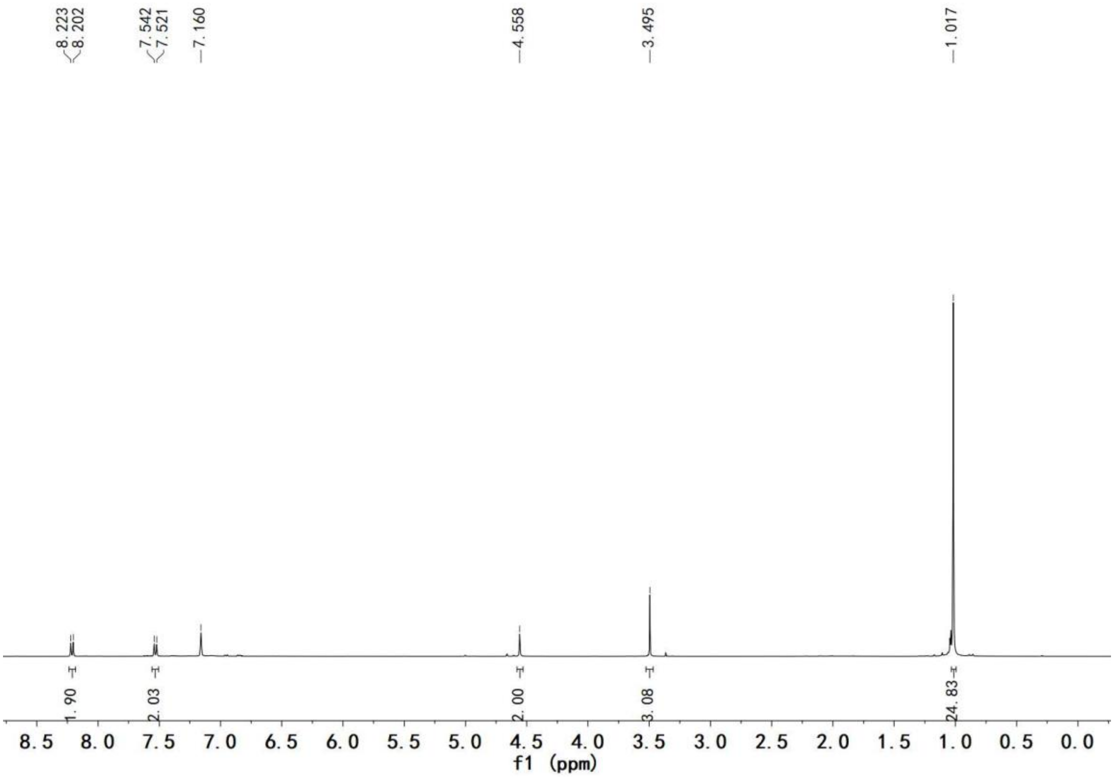


Figure S46. ^{1}H NMR spectrum of **5o** (400 MHz, C_6D_6, 298 K).

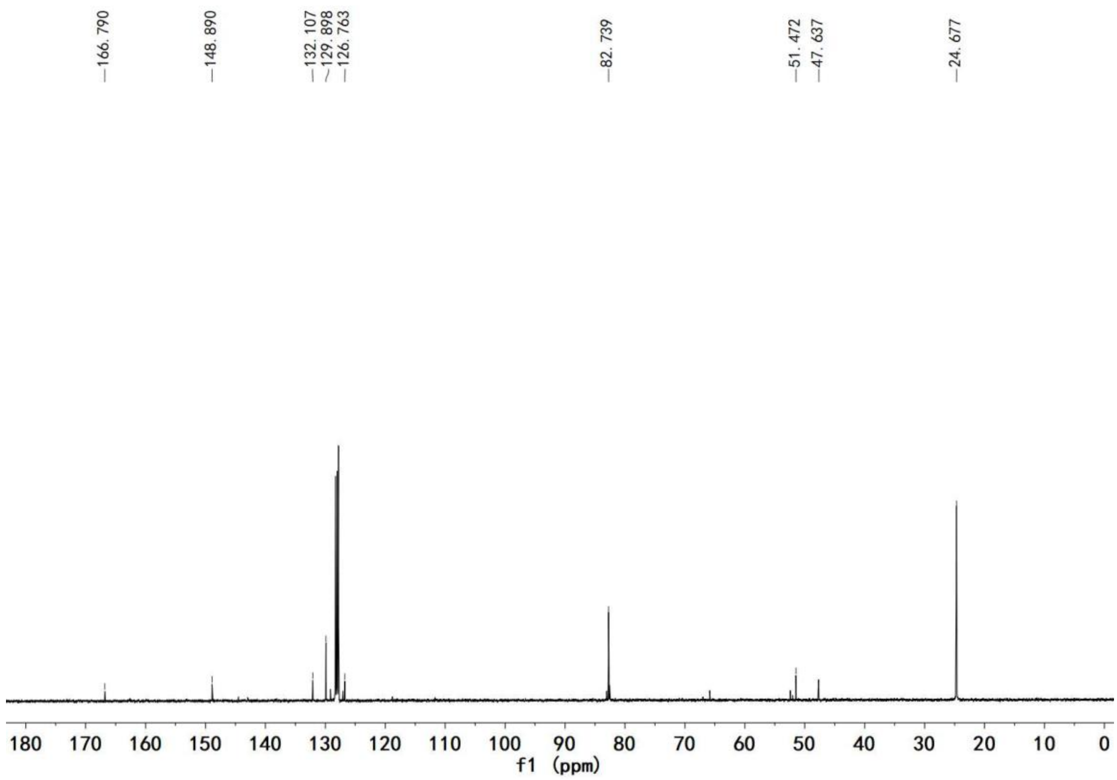


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of **5o** (101 MHz, C_6D_6, 298 K).

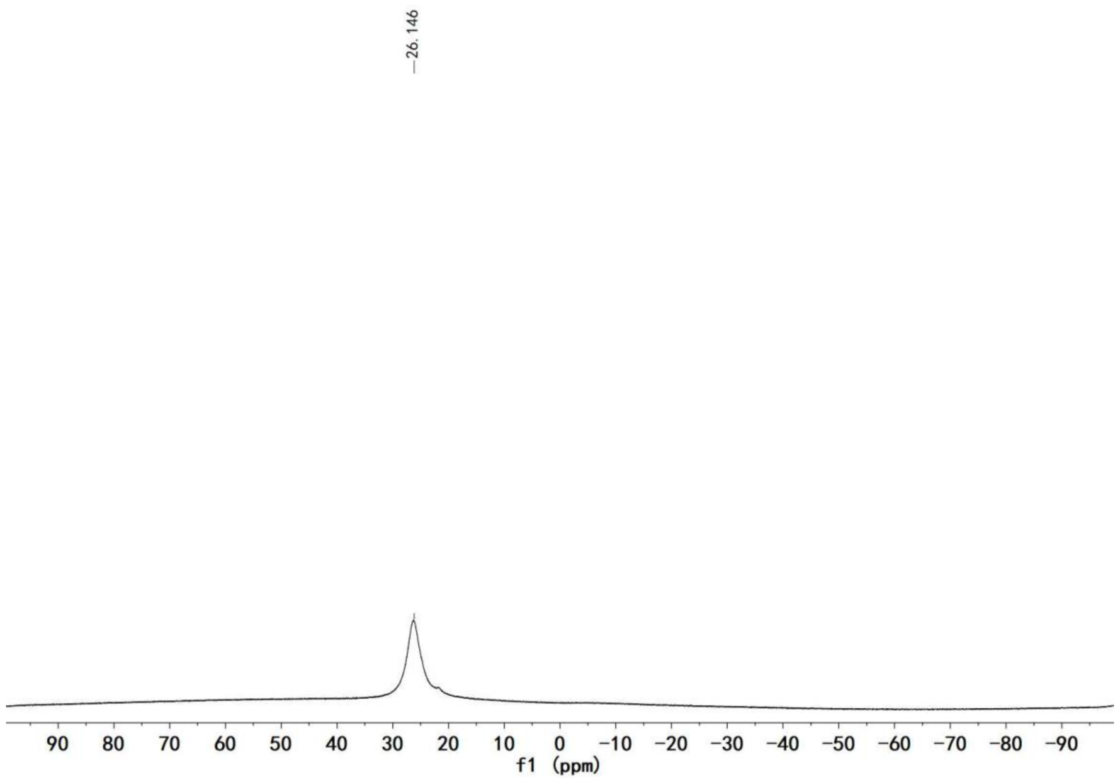
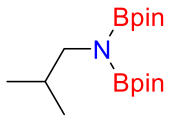


Figure S48. ^{11}B NMR spectrum of **5o** (128 MHz, C_6D_6, 298 K).



5p[6] (white solid, 88 mg, 90% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 3.19 (d, 2H, *J* = 7.2 Hz, C*H*$_2$), 1.97 (sep, 1H, *J* = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.04 (s, 24H, C(C*H*$_3$)$_2$), 0.95 (d, 6H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 82.2 (*C*(CH$_3$)$_2$), 51.7 (*C*H$_2$), 31.2 (*C*H(CH$_3$)$_2$), 24.7 (C(*C*H$_3$)$_2$), 20.4 (CH(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 26.1.

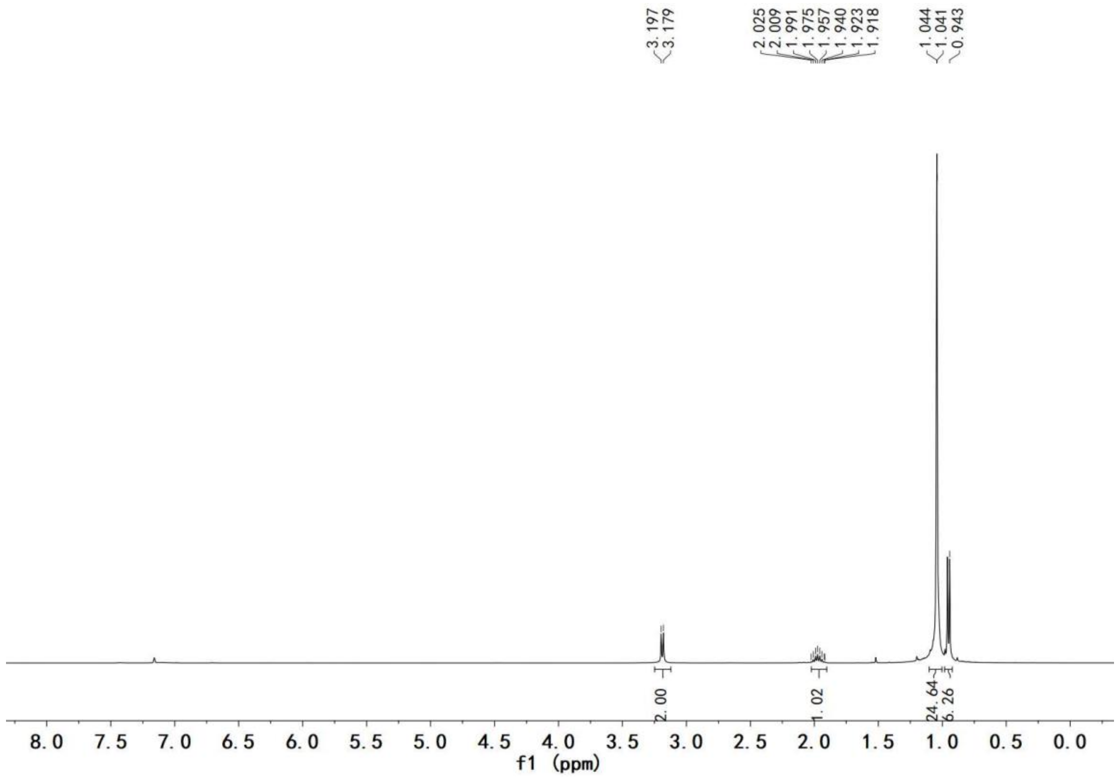


Figure S49. ^{1}H NMR spectrum of **5p** (400 MHz, C_6D_6, 298 K).

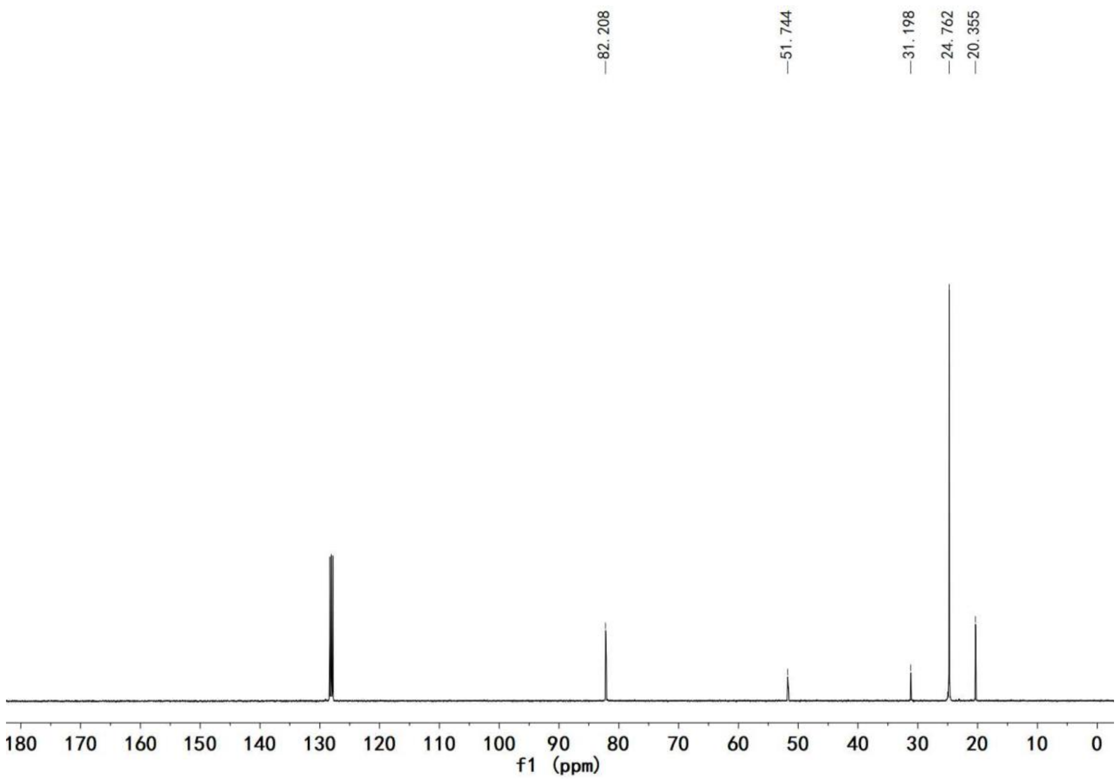


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of **5p** (101 MHz, C_6D_6, 298 K).

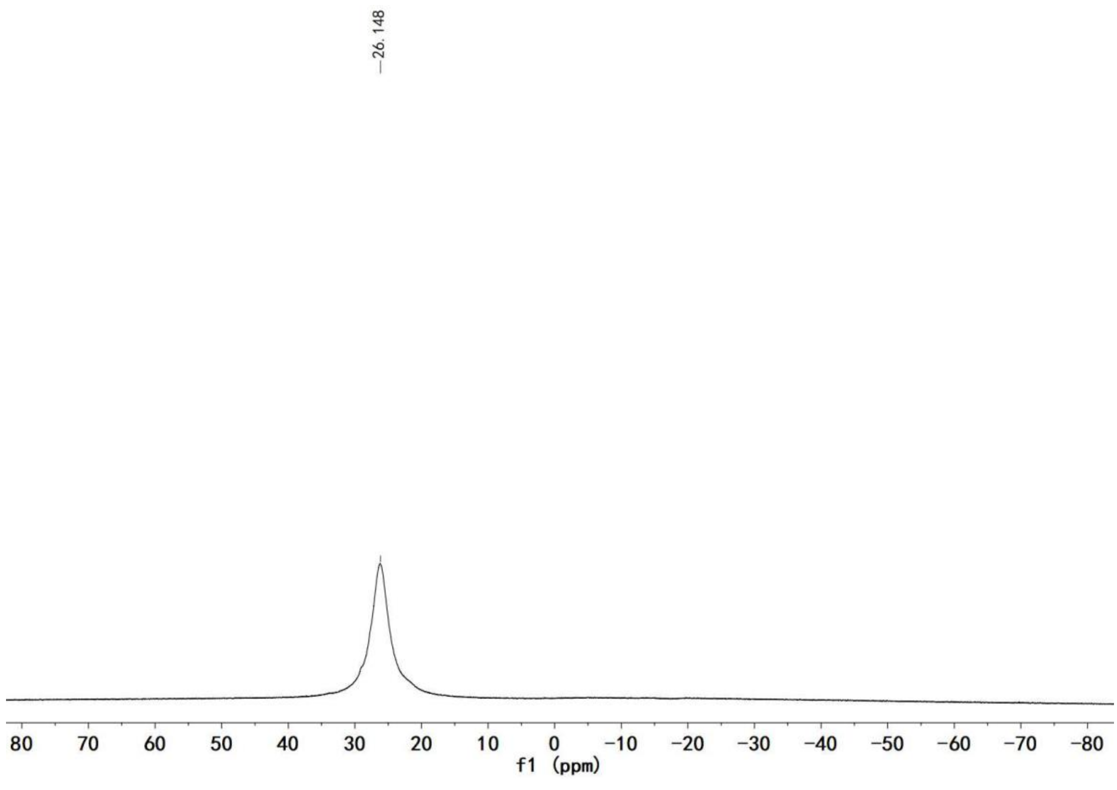
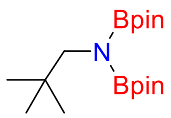


Figure S51. ^{11}B NMR spectrum of **5n** (128 MHz, C_6D_6, 298 K).



5q[6] (white solid, 90 mg, 88% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 3.27 (s, 2H, CH_2), 1.07 (s, 24H, C(CH_3)$_2$), 1.00 (s, 9H, C(CH_3)$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 82.2 (*C*(CH$_3$)$_2$), 55.0 (*C*H$_2$), 33.6 (*C*(CH$_3$)$_3$), 28.0 (C(*C*H$_3$)$_3$), 24.8 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 26.1.

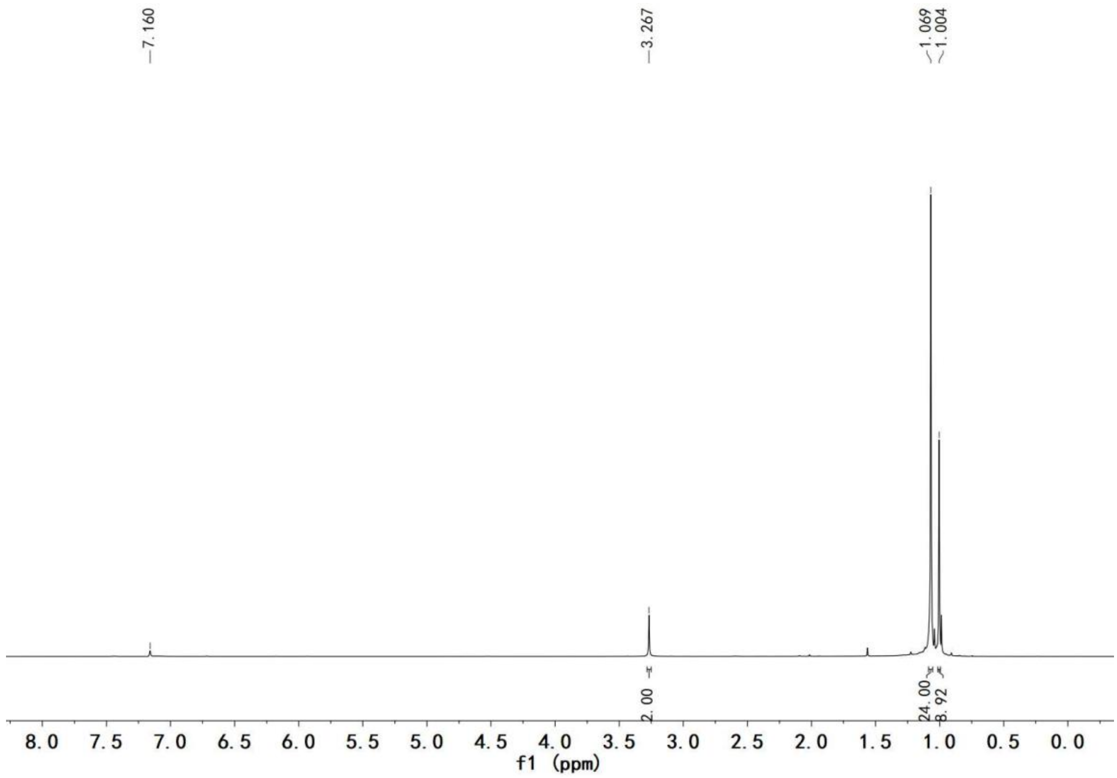


Figure S52. ^{1}H NMR spectrum of **5q** (400 MHz, C_6D_6, 298 K).

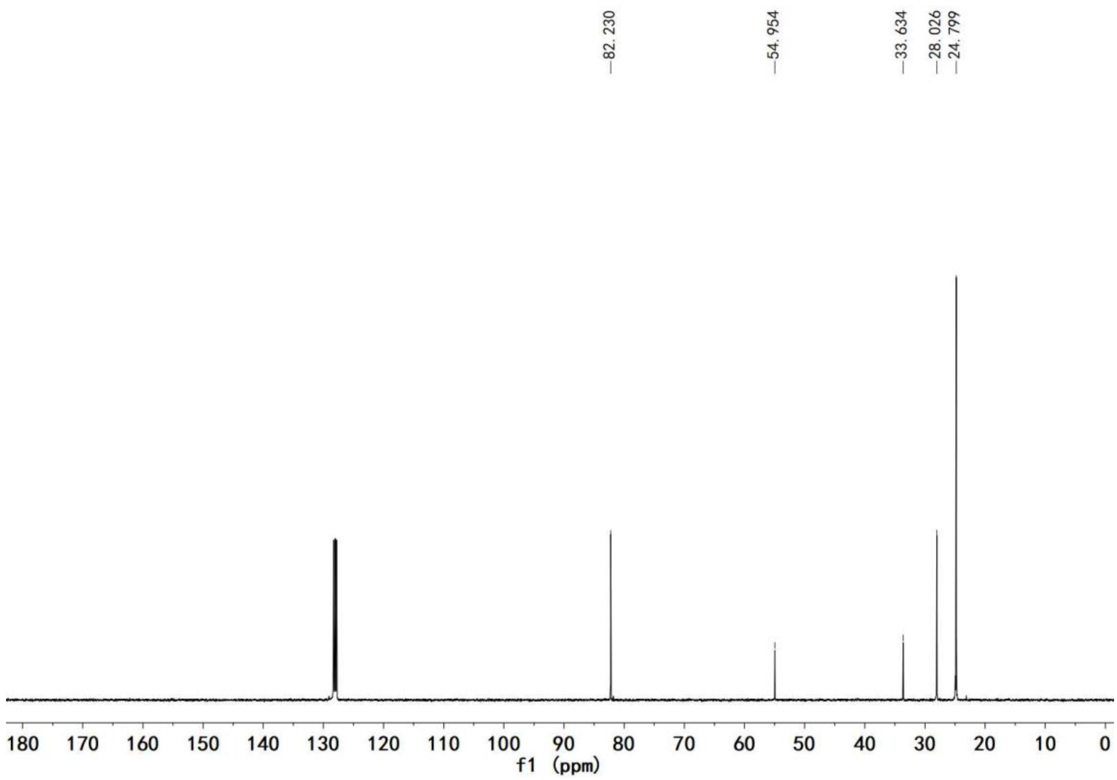


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **5q** (101 MHz, C_6D_6, 298 K).

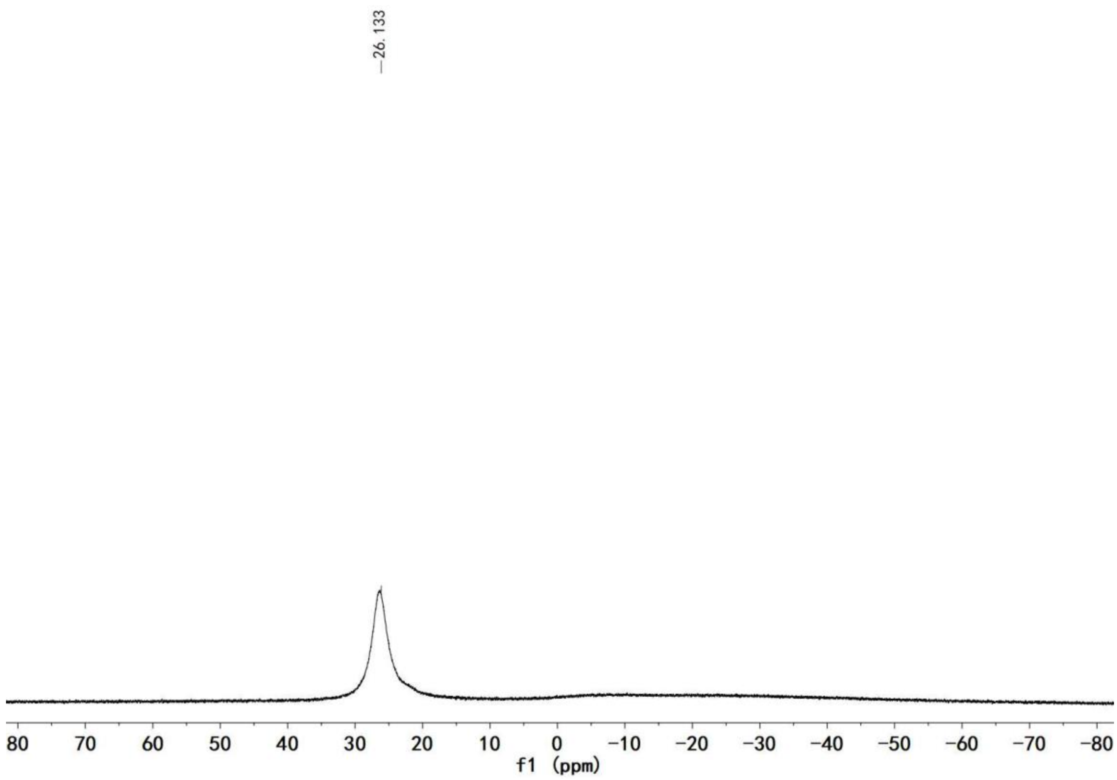
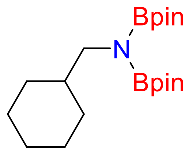


Figure S54. ^{11}B NMR spectrum of **5q** (128 MHz, C_6D_6, 298 K).



5r[6] (white solid, 95 mg, 87% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 3.28 (d, 2H, *J* = 8.1 Hz, CH_2), 1.89-1.86 (m, 2H, *Cy*), 1.70-1.60 (m, 4H, *Cy*), 1.30-1.12 (m, 5H, *Cy*), 1.06 (s, 24H, C(CH_3)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 82.2 (*C*(CH$_3$)$_2$), 50.5 (*C*H$_2$), 40.9 (*Cy*), 31.2 (*Cy*), 27.3 (*Cy*), 26.7 (*Cy*), 24.8 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 26.3.

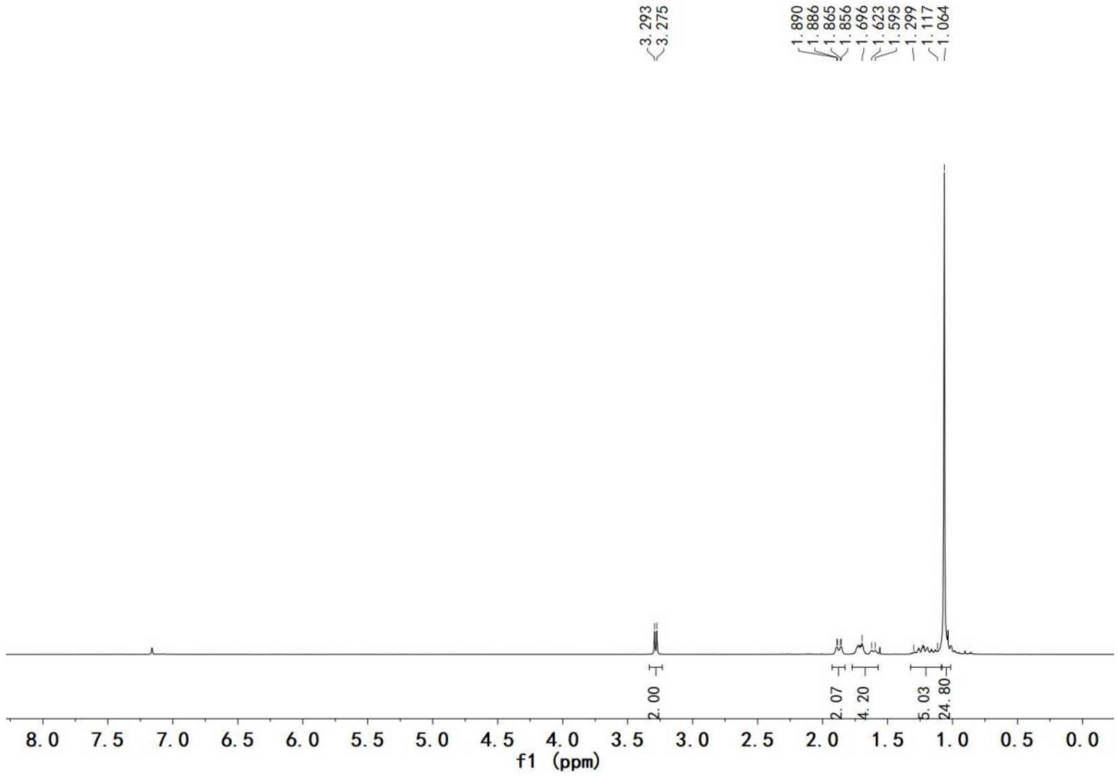


Figure S55. ^{1}H NMR spectrum of **5r** (400 MHz, C_6D_6, 298 K).

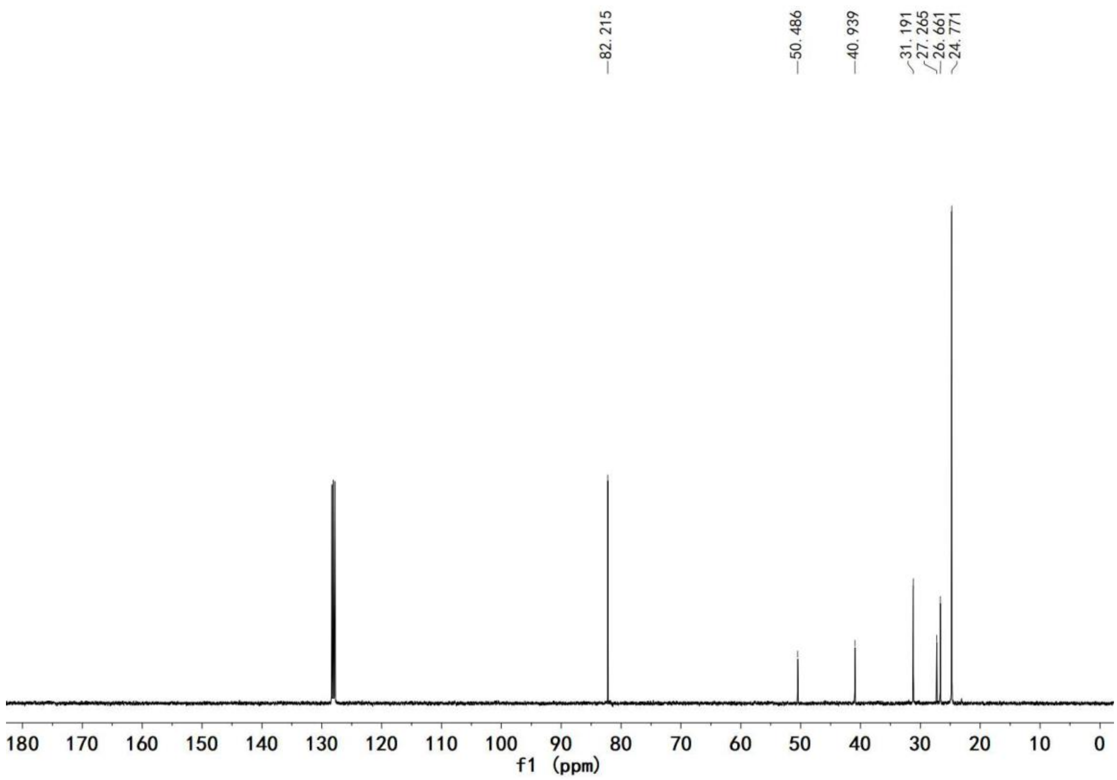


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **5r** (101 MHz, C_6D_6, 298 K).

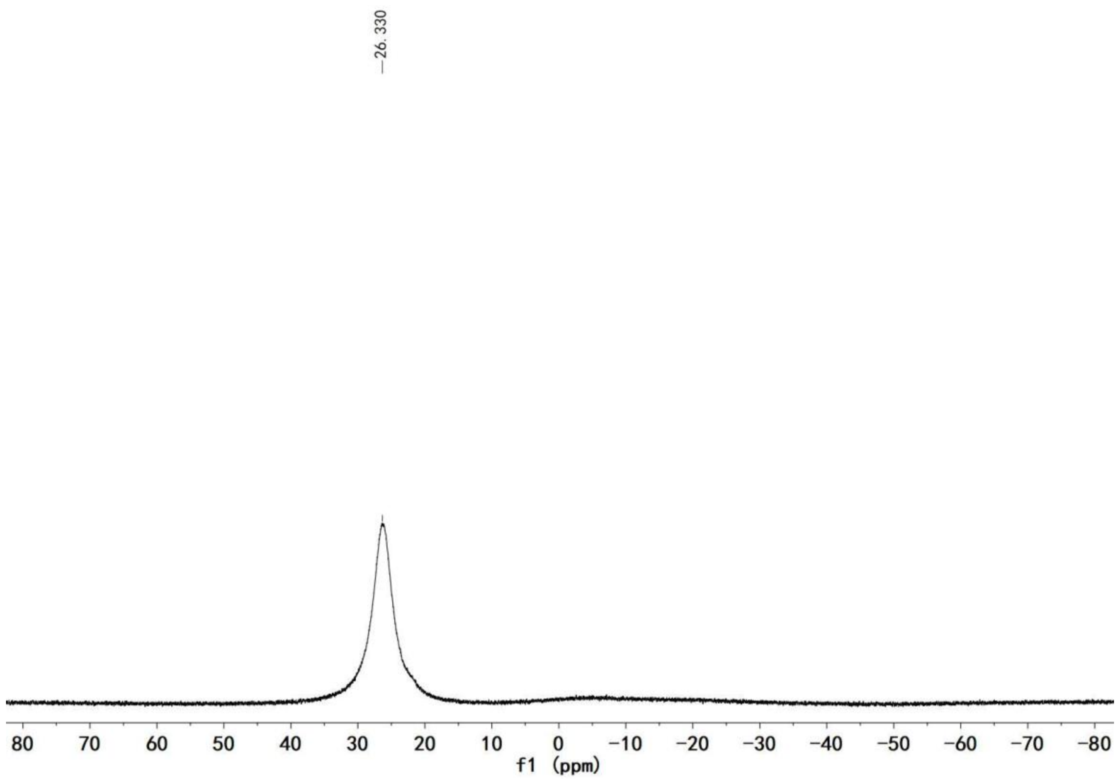
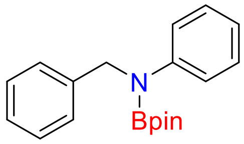


Figure S57. ^{11}B NMR spectrum of **5r** (128 MHz, C_6D_6, 298 K).



7a[7] (white solid, 85 mg, 92% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.50-7.48 (m, 2H, *phenyl*), 7.25-7.23 (m, 2H, *phenyl*), 7.14-7.09 (m, 4H, *phenyl*), 7.02 (m, 1H, *phenyl*), 6.81 (m, 1H, *phenyl*), 4.78 (s, 2H, C*H*$_2$), 1.08 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 146.8 (*phenyl*), 141.0 (*phenyl*), 128.9 (*phenyl*), 128.7 (*phenyl*), 126.8 (*phenyl*), 126.7 (*phenyl*), 121.8 (*phenyl*), 121.0 (*phenyl*), 83.0 (*C*(CH$_3$)$_2$), 51.5 (*C*H$_2$), 24.6 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.1.

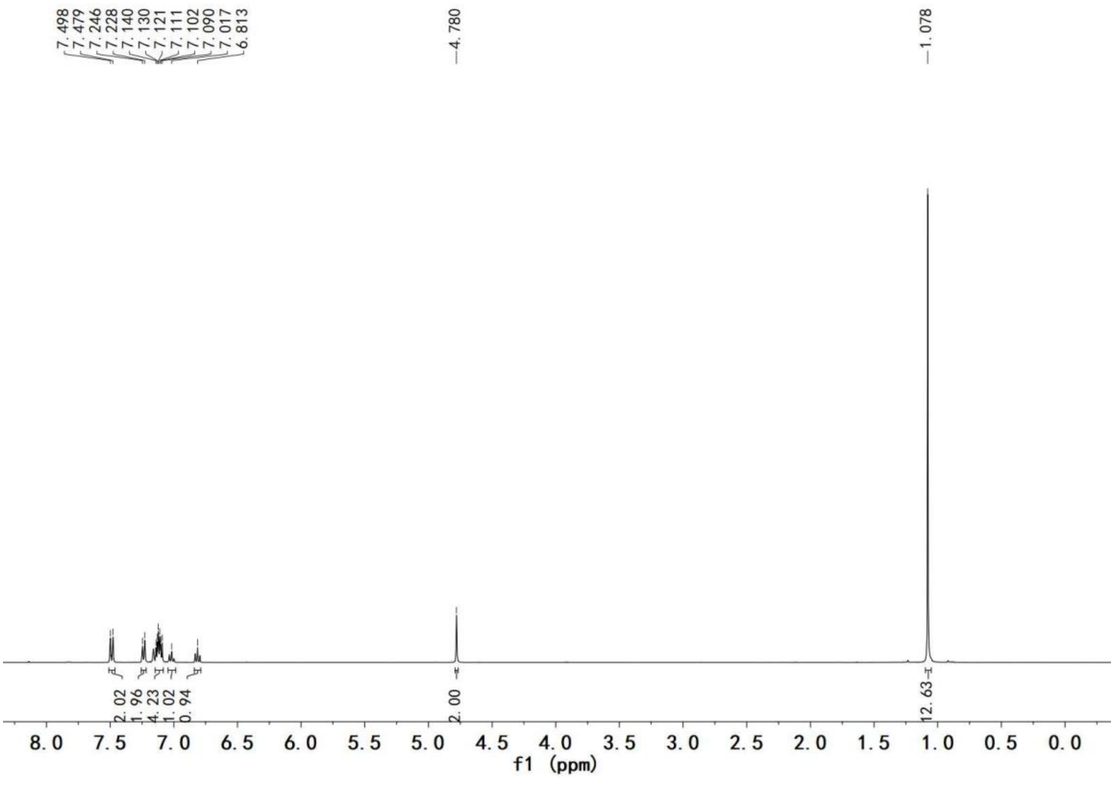


Figure S58. ^{1}H NMR spectrum of **7a** (400 MHz, C_6D_6, 298 K).

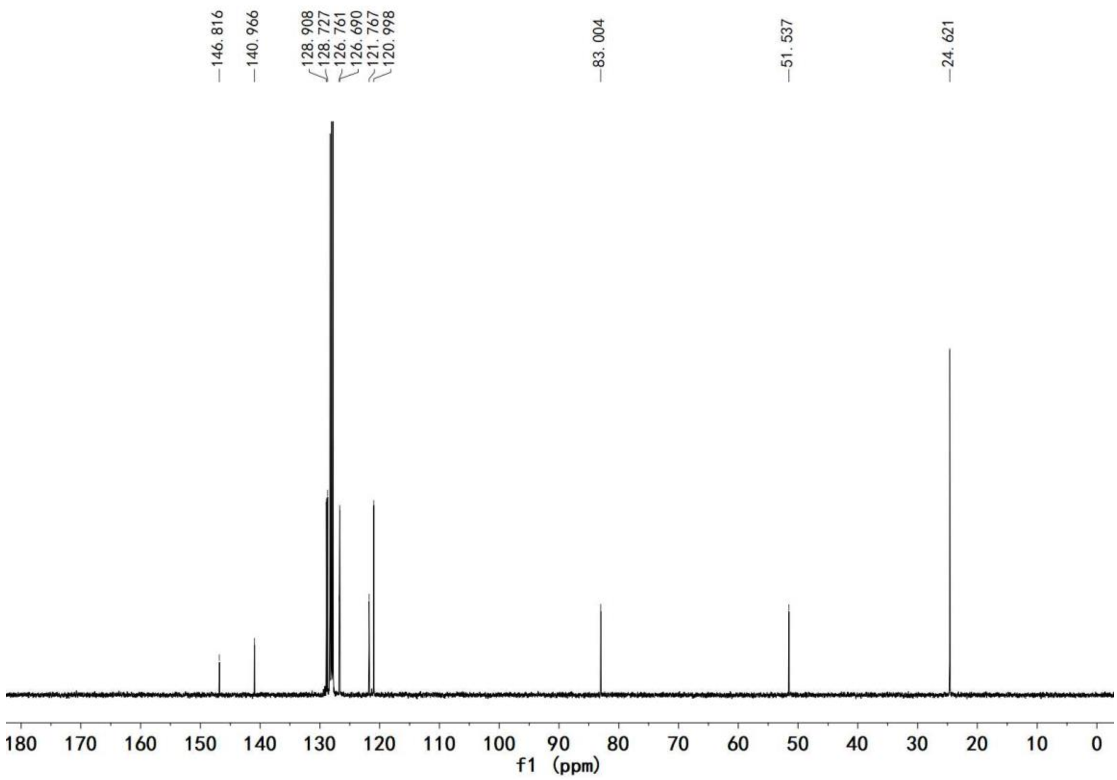


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** (101 MHz, C_6D_6, 298 K).

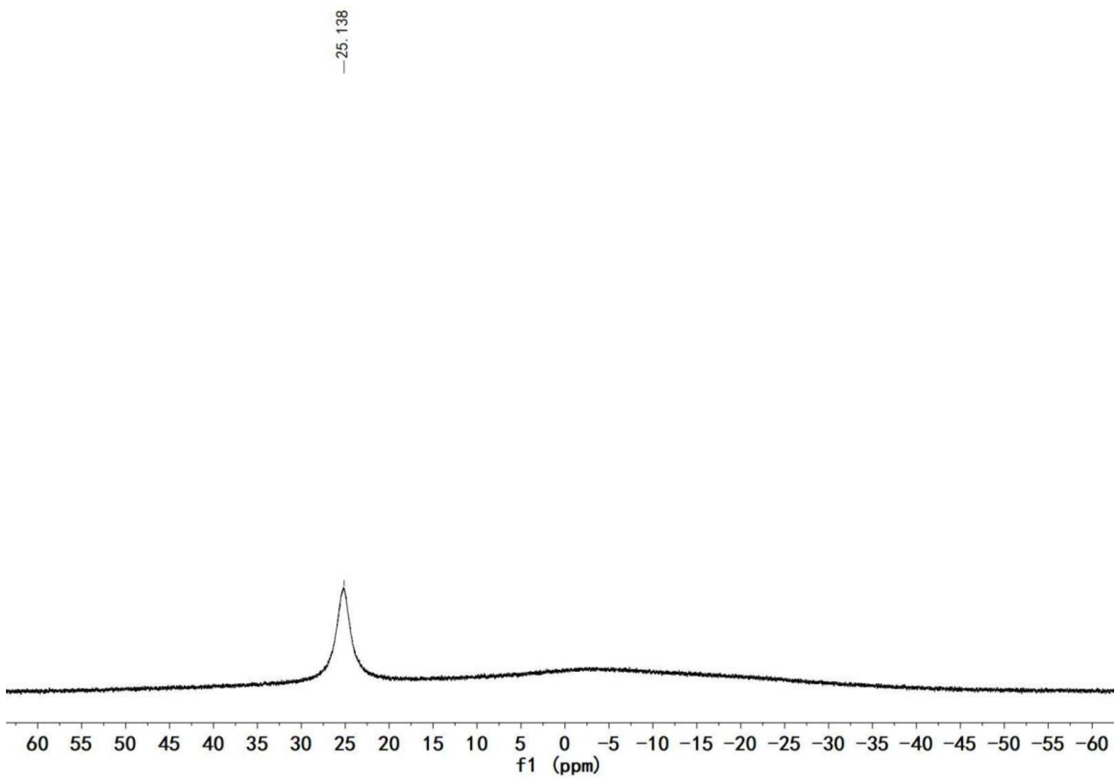
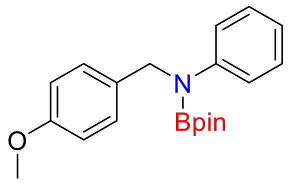


Figure S60. ^{11}B NMR spectrum of **7a** (128 MHz, C_6D_6, 298 K).



7b[7] (white solid, 86 mg, 85% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.52 (m, 2H, *phenyl*), 7.15 (m, 4H, *phenyl*), 6.83 (m, 1H, *phenyl*), 6.74 (m, 2H, *phenyl*), 4.77 (s, 2H, C*H*$_2$), 3.26 (s, 3H, OC*H*$_3$), 1.01 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 159.0 (*phenyl*), 146.8 (*phenyl*), 132.8 (*phenyl*), 128.9 (*phenyl*), 127.9 (*phenyl*), 121.8 (*phenyl*), 121.3 (*phenyl*), 114.3 (*phenyl*), 83.0 (*C*(CH$_3$)$_2$), 54.7 (O*C*H$_3$), 51.0 (*C*H$_2$), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.1.

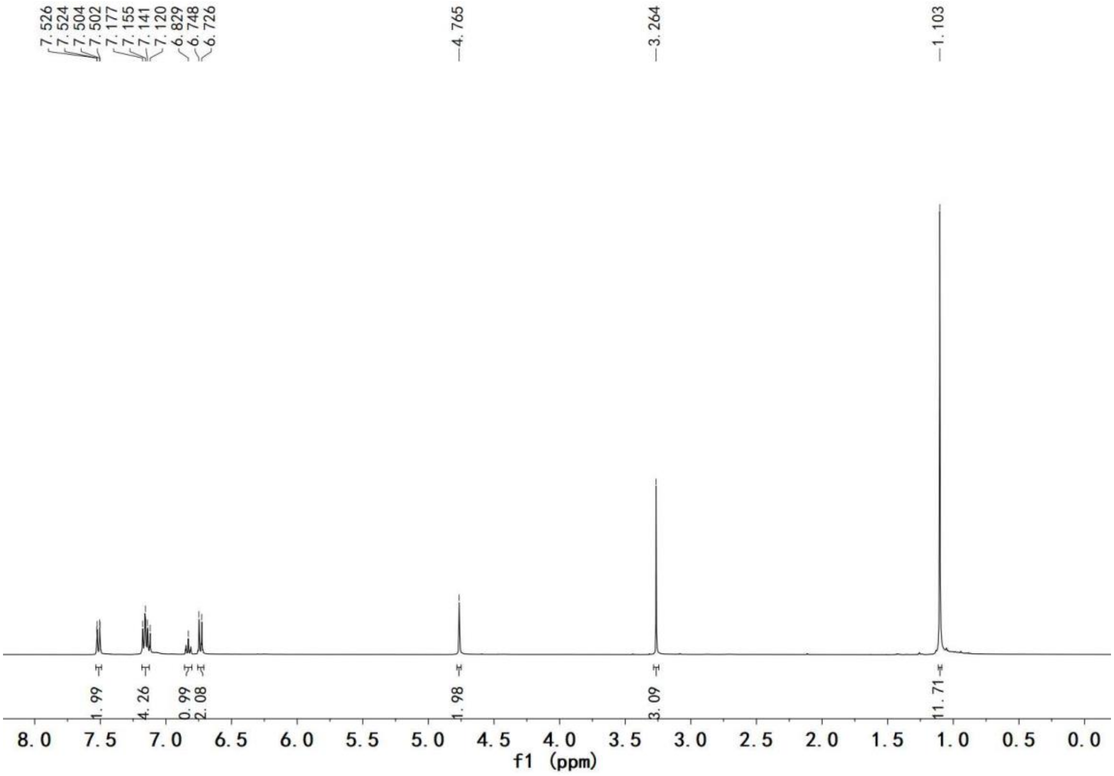


Figure S61. ^{1}H NMR spectrum of **7b** (400 MHz, C_6D_6, 298 K).

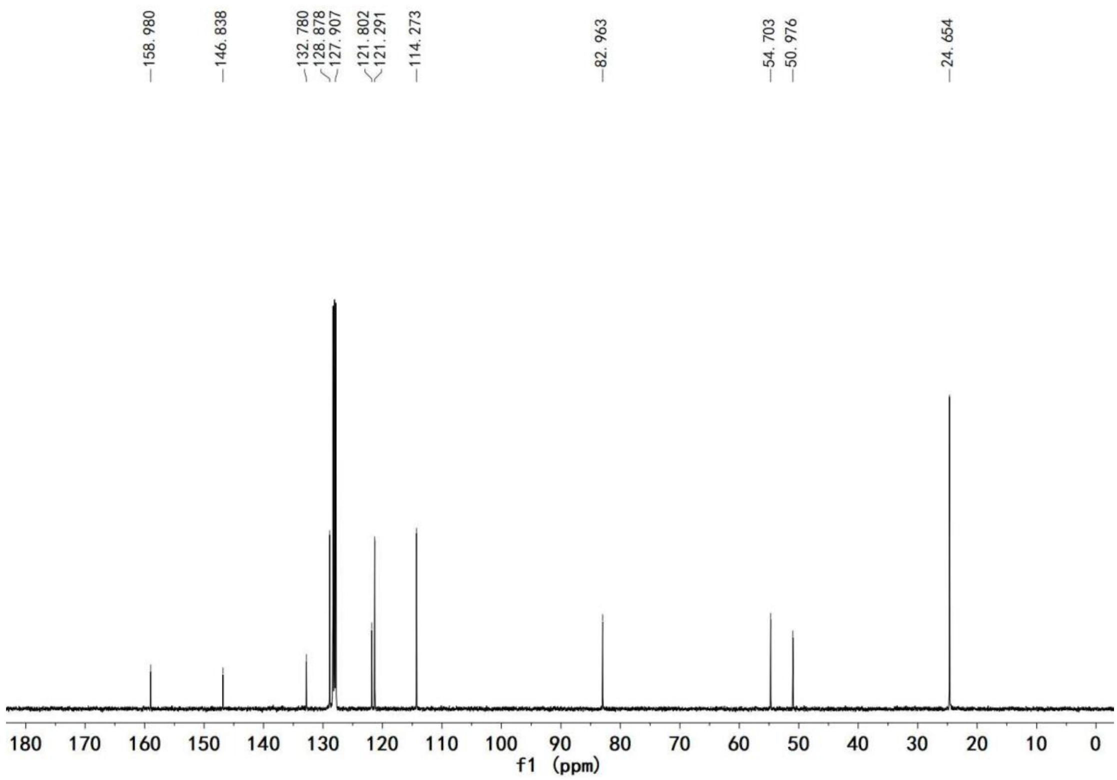


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of **7b** (101 MHz, C_6D_6, 298 K).

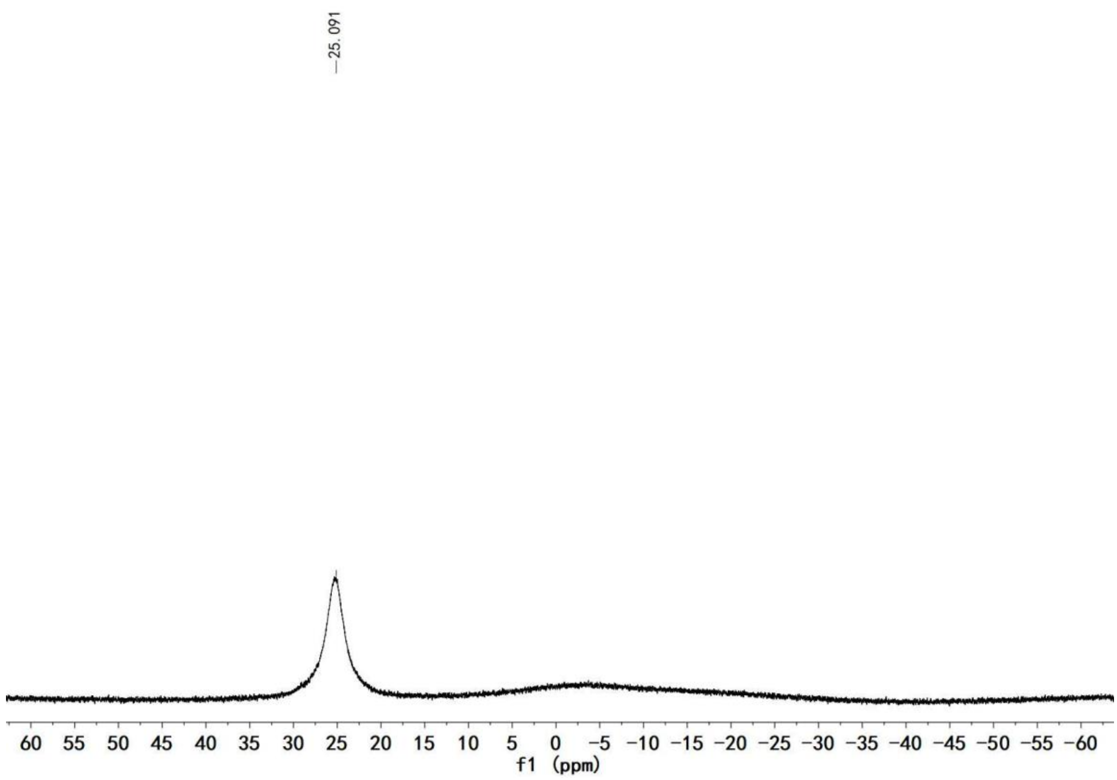
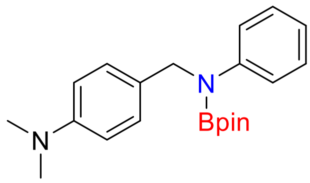


Figure S63. ^{11}B NMR spectrum of **7b** (128 MHz, C_6D_6, 298 K).



7c (white solid, 92 mg, 87% yield)

Melting Point: 80-81 °C

Elemental Analysis: calcd. for $C_{21}H_{29}BN_2O_2$: C, 71.60; H, 8.30; N, 7.95. Found: C, 71.06; H, 8.31; N, 7.73.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.58 (m, 2H, *phenyl*), 7.25 (m, 2H, *phenyl*), 7.14 (m, 2H, *phenyl*), 6.83 (m, 1H, *phenyl*), 6.58 (m, 2H, *phenyl*), 4.84 (s, 2H, C*H*$_2$), 2.48 (s, 6H, NC*H*$_3$), 1.12 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 149.9 (*phenyl*), 147.1 (*phenyl*), 128.8 (*phenyl*), 127.7 (*phenyl*), 121.7 (*phenyl*), 121.4 (*phenyl*), 113.3 (*phenyl*), 82.9 (*C*(CH$_3$)$_2$), 51.1 (*C*H$_2$), 40.4 (N*C*H$_3$), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.2.

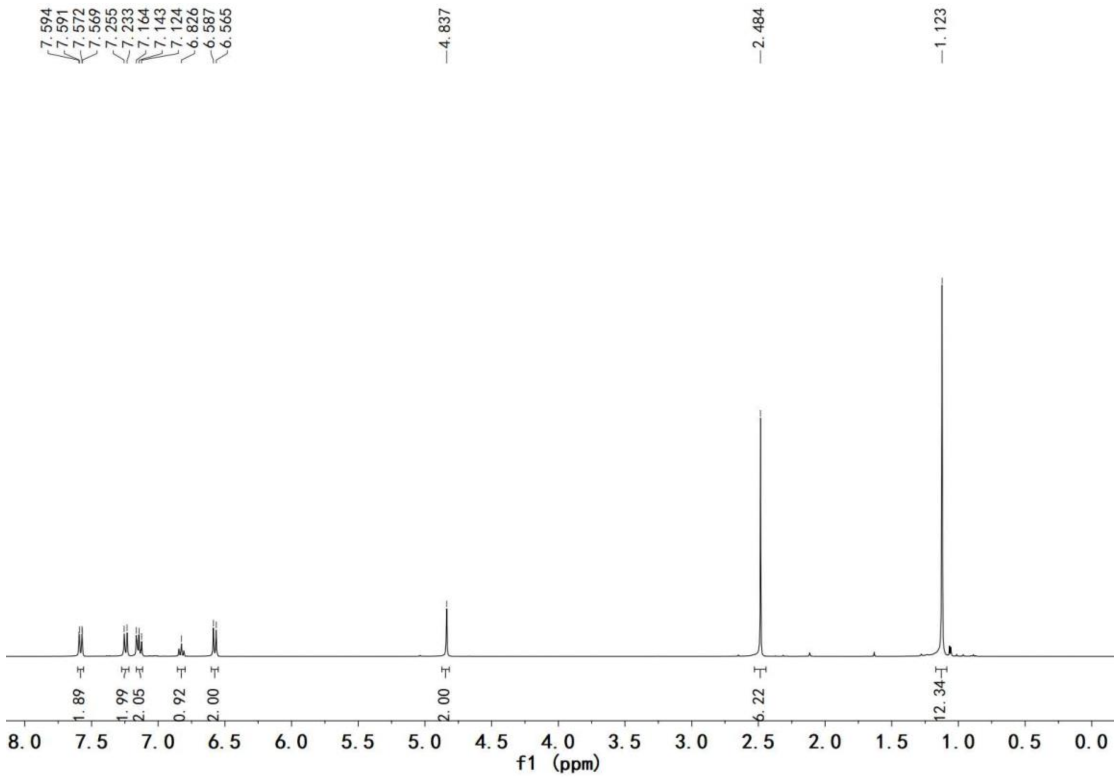


Figure S64. ^{1}H NMR spectrum of **7c** (400 MHz, C_6D_6, 298 K).

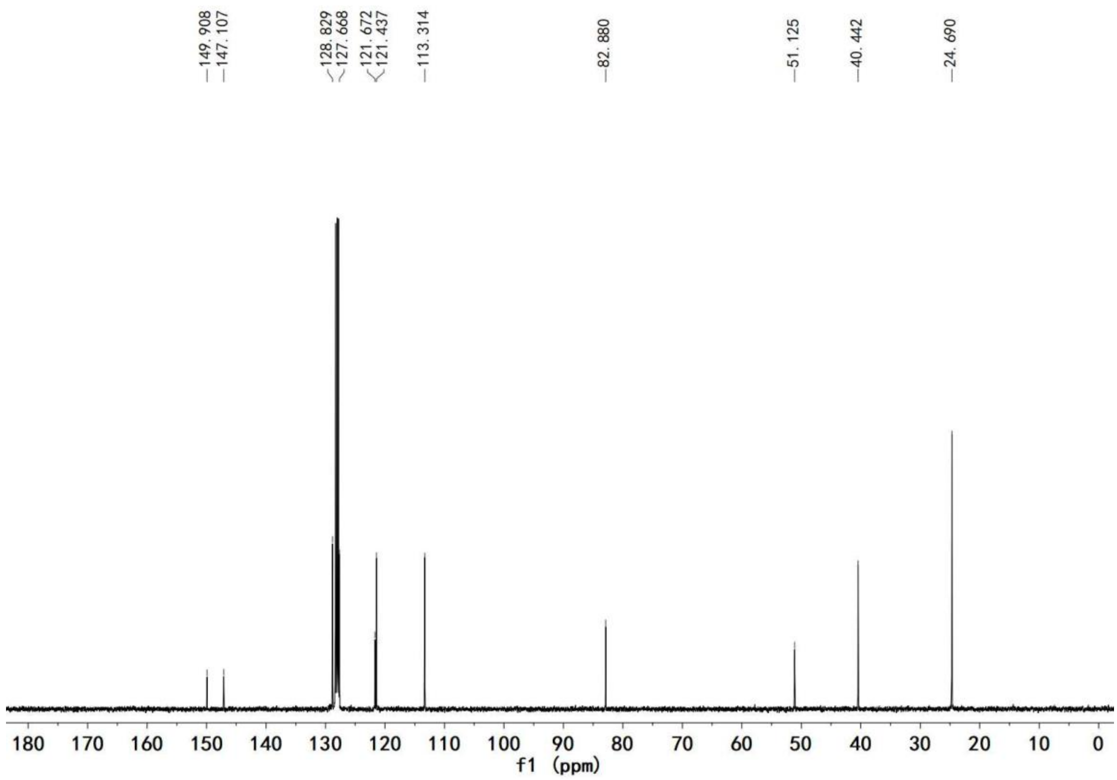


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of **7c** (101 MHz, C_6D_6, 298 K).

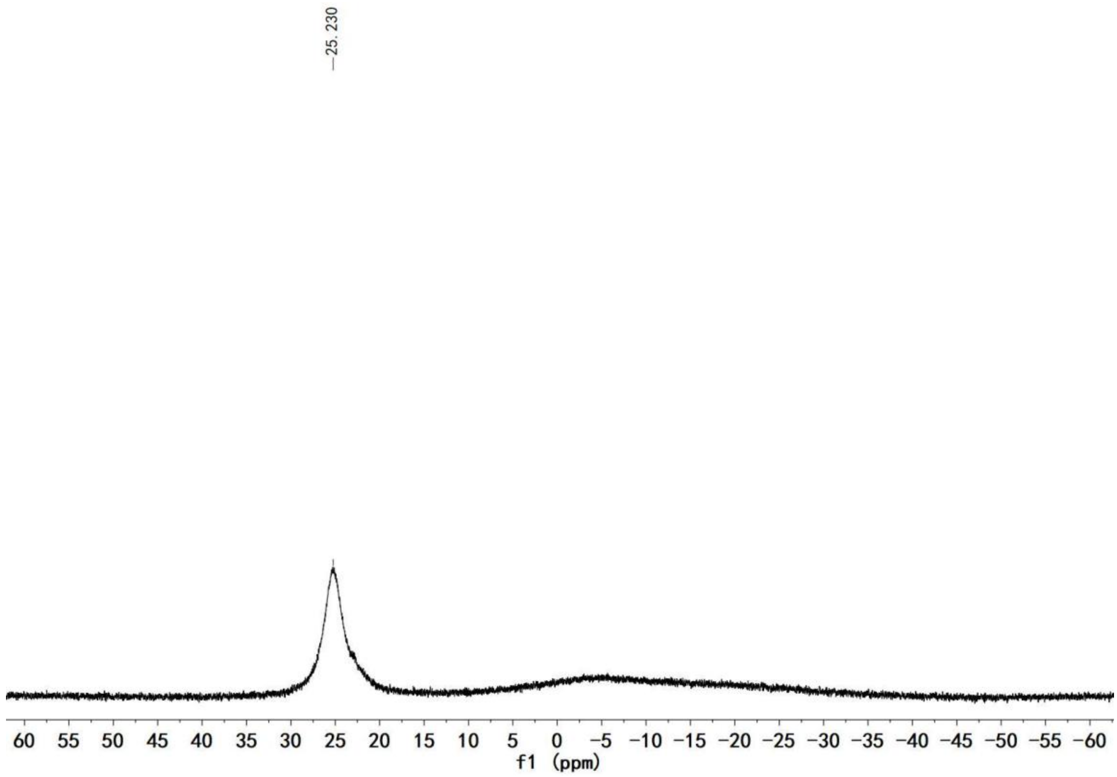
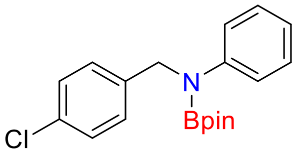


Figure S66. ^{11}B NMR spectrum of **7c** (128 MHz, C_6D_6, 298 K).



7d[7] (white solid, 97 mg, 94% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.38 (m, 2H, *phenyl*), 7.12 (m, 2H, *phenyl*), 7.04 (m, 2H, *phenyl*), 6.93 (m, 2H, *phenyl*), 6.82 (m, 1H, *phenyl*), 4.60 (s, 2H, CH_2), 1.07 (s, 12H, C(CH_3)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 146.4 (*phenyl*), 139.4 (*phenyl*), 132.5 (*phenyl*), 129.0 (*phenyl*), 128.8 (*phenyl*), 128.1 (*phenyl*), 122.0 (*phenyl*), 120.9 (*phenyl*), 83.1 (*C*(CH_3)$_2$), 50.8 (*C*H_2), 24.6 (C(*C*H_3)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.0.

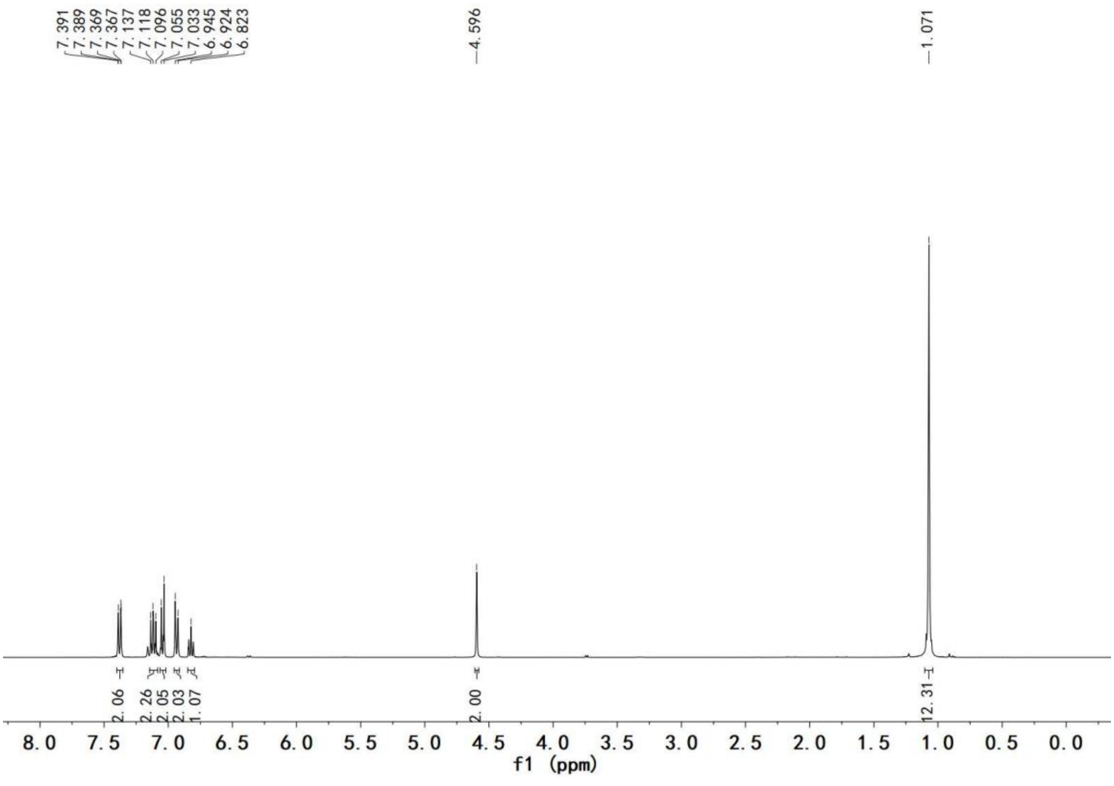


Figure S67. ^{1}H NMR spectrum of **7d** (400 MHz, C_6D_6, 298 K).

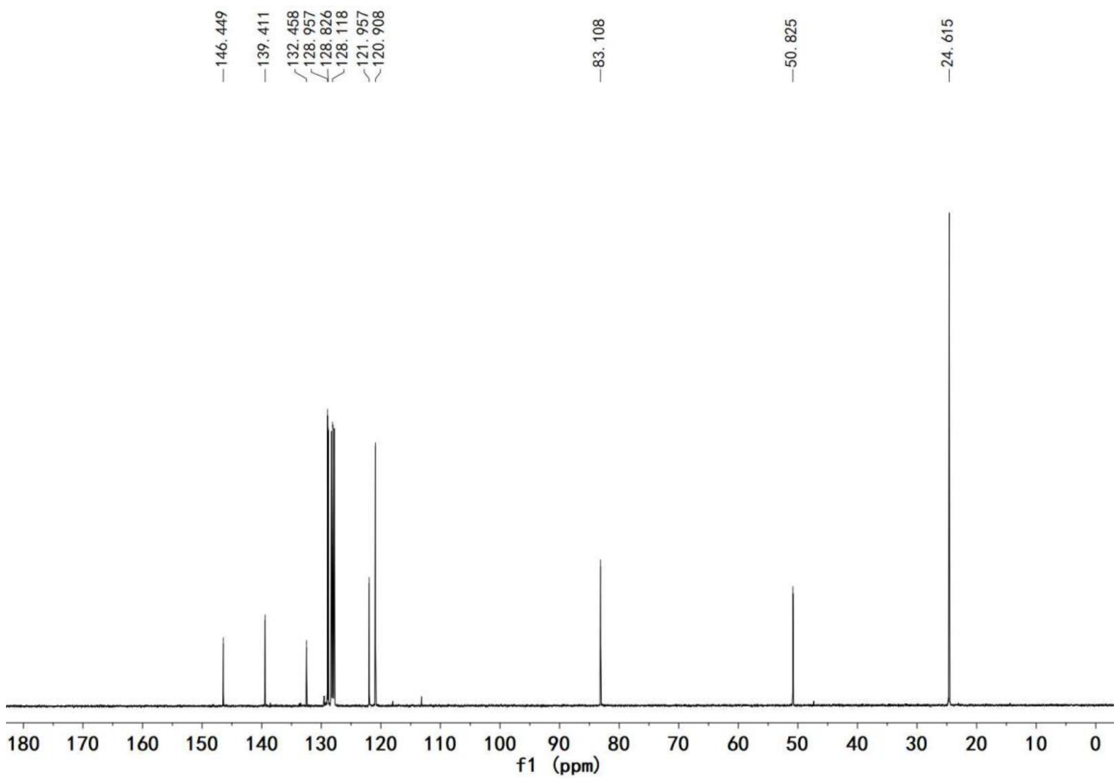


Figure S68. $^{13}C\{^1H\}$ NMR spectrum of **7d** (101 MHz, C_6D_6, 298 K).

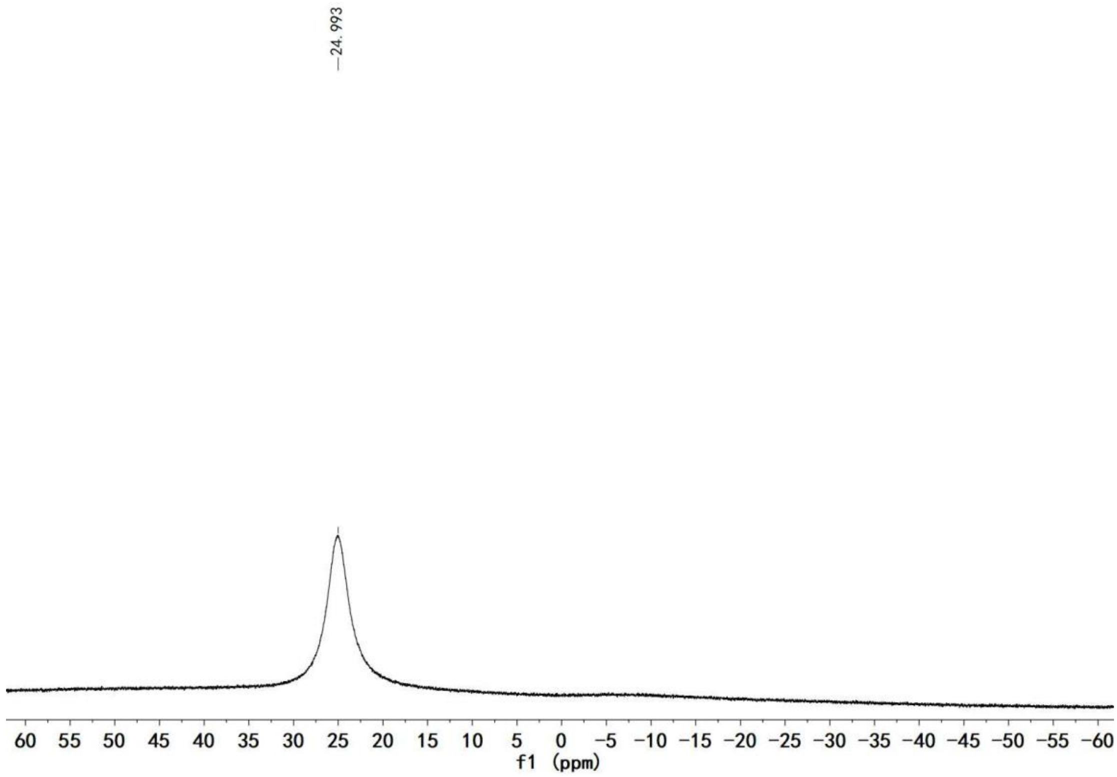
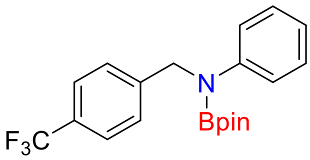


Figure S69. ^{11}B NMR spectrum of **7d** (128 MHz, C_6D_6, 298 K).



7e[7] (white solid, 96 mg, 85% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.36 (m, 2H, *phenyl*), 7.28 (m, 2H, *phenyl*), 7.11 (m, 2H, *phenyl*), 7.04 (m, 2H, *phenyl*), 6.82 (m, 1H, *phenyl*), 4.63 (s, 2H, C*H*$_2$), 1.08 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 146.3 (*phenyl*), 145.2 (q, *J* = 1.5 Hz, *phenyl*), 129.0 (*phenyl*), 128.9 (q, *J* = 32.0 Hz, *phenyl*), 126.9 (*phenyl*), 125.6 (q, *J* = 3.8 Hz, *phenyl*), 125.1 (q, *J* = 271.6 Hz, *C*F$_3$), 122.0 (*phenyl*), 120.7 (*phenyl*), 83.2 (*C*(CH$_3$)$_2$), 51.0 (*C*H$_2$), 24.6 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.1.

^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 298K): δ = -62.0.

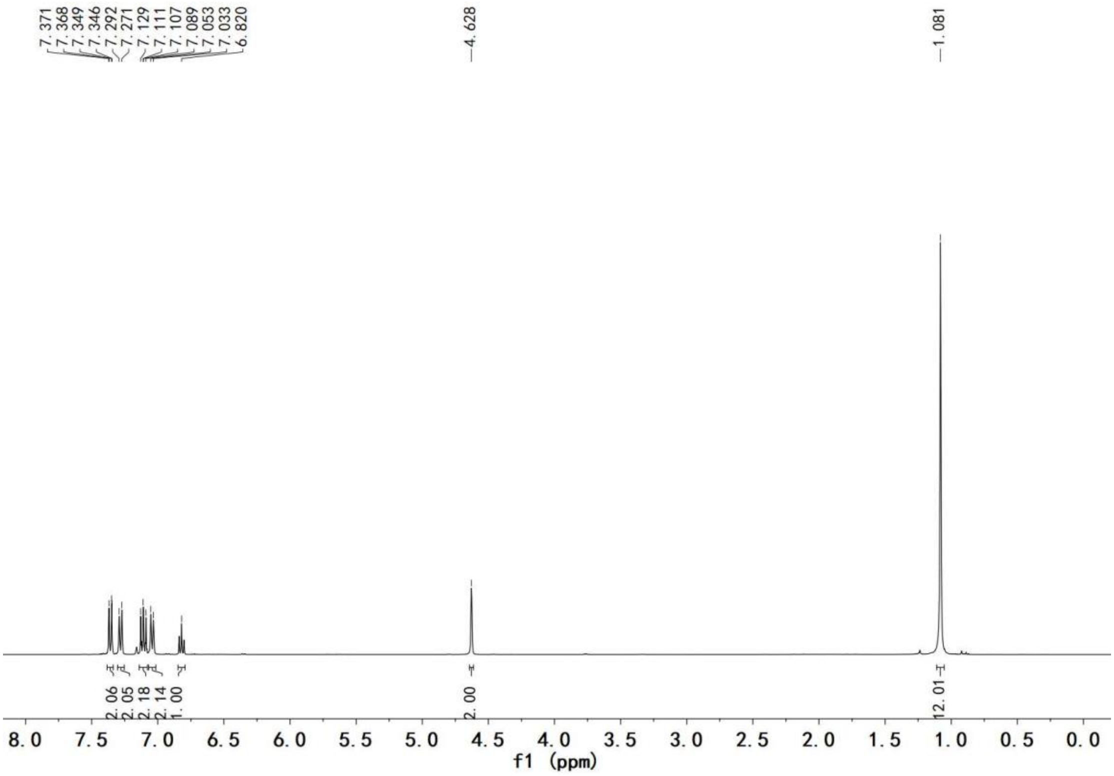


Figure S70. ^{1}H NMR spectrum of **7e** (400 MHz, C_6D_6, 298 K).

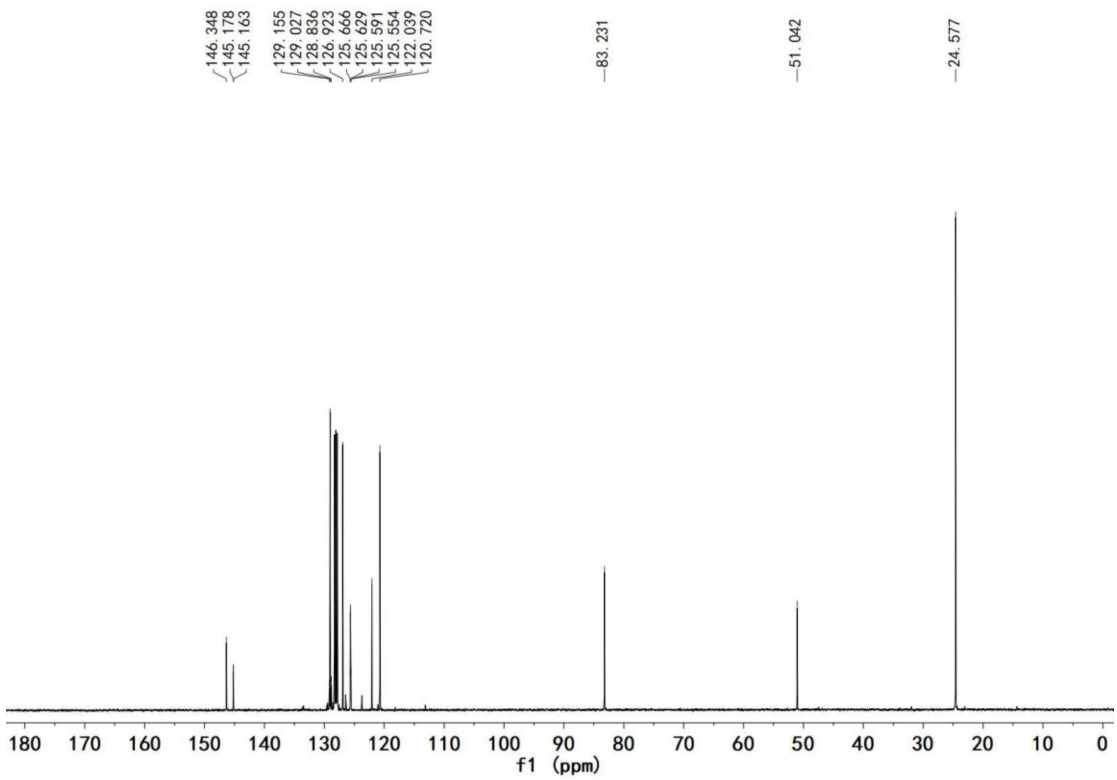


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of **7e** (101 MHz, C_6D_6, 298 K).

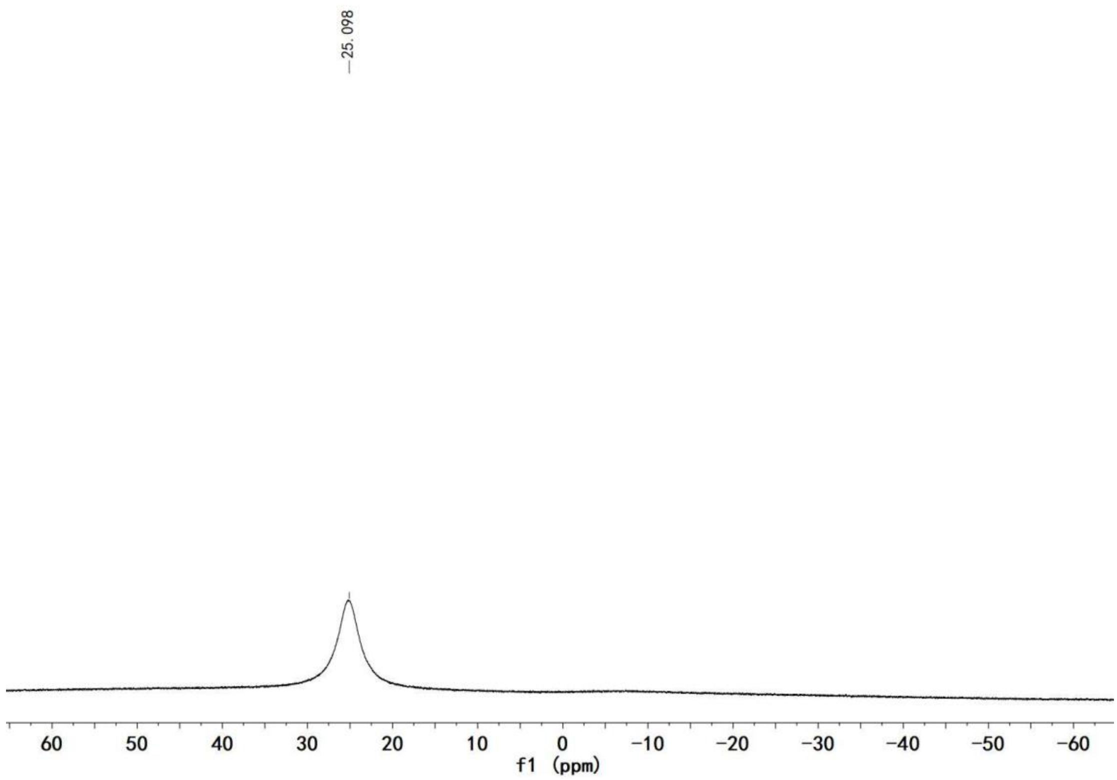


Figure S72. ^{11}B NMR spectrum of **7e** (128 MHz, C_6D_6, 298 K).

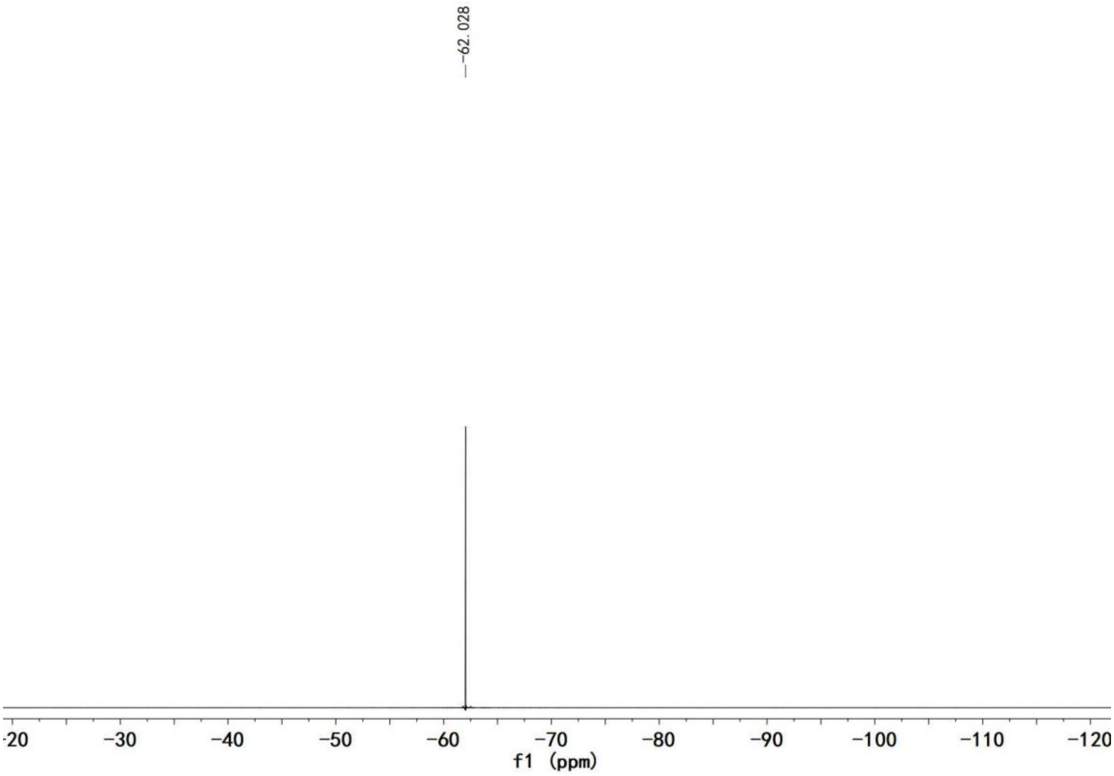
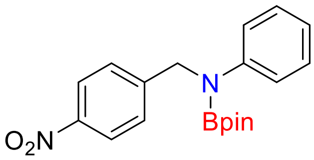


Figure S73. $^{19}F\{^{1}H\}$ NMR spectrum of **7e** (376 MHz, C_6D_6, 298 K).



7f[7] (white solid, 87 mg, 82% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.75 (m, 2H, *phenyl*), 7.31 (m, 2H, *phenyl*), 7.13 (m, 2H, *phenyl*), 6.85 (m, 3H, *phenyl*), 4.54 (s, 2H, CH_2), 1.07 (s, 12H, $C(CH_3)_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 147.9 (*phenyl*), 147.2 (*phenyl*), 146.0 (*phenyl*), 129.1 (*phenyl*), 127.0 (*phenyl*), 123.8 (*phenyl*), 122.2 (*phenyl*), 120.7 (*phenyl*), 83.3 ($C(CH_3)_2$), 50.9 (CH_2), 24.6 ($C(CH_3)_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.2.

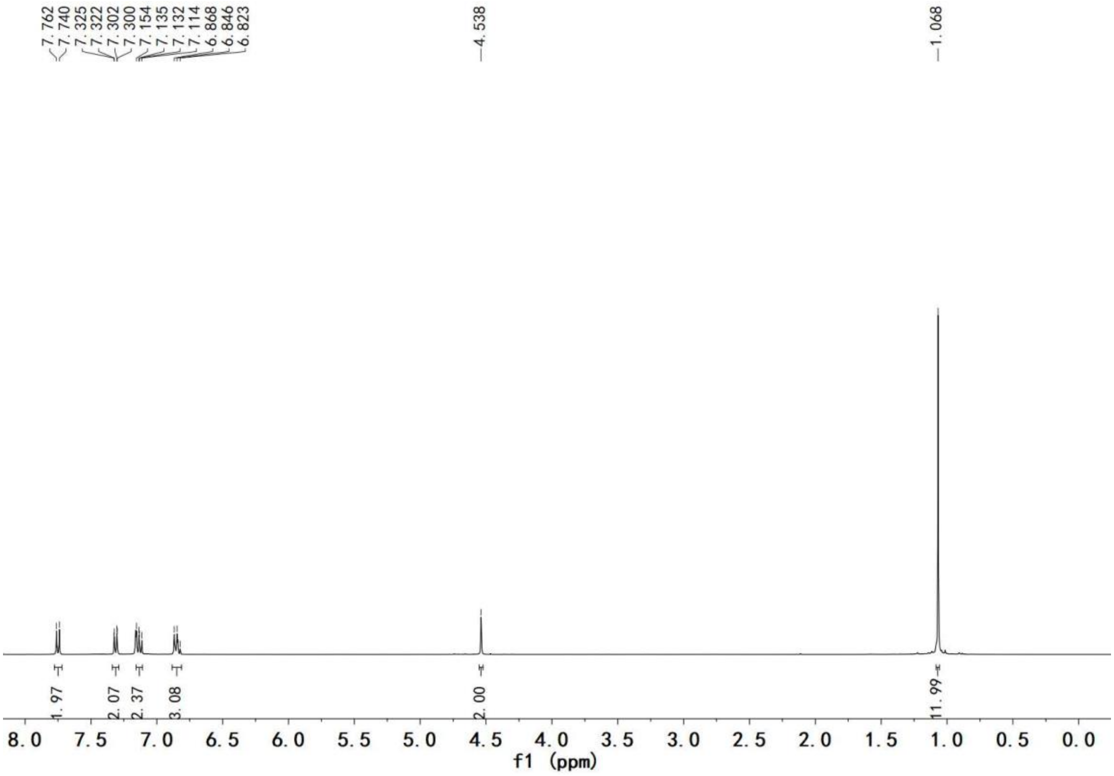


Figure S74. ^{1}H NMR spectrum of **7f** (400 MHz, C_6D_6, 298 K).

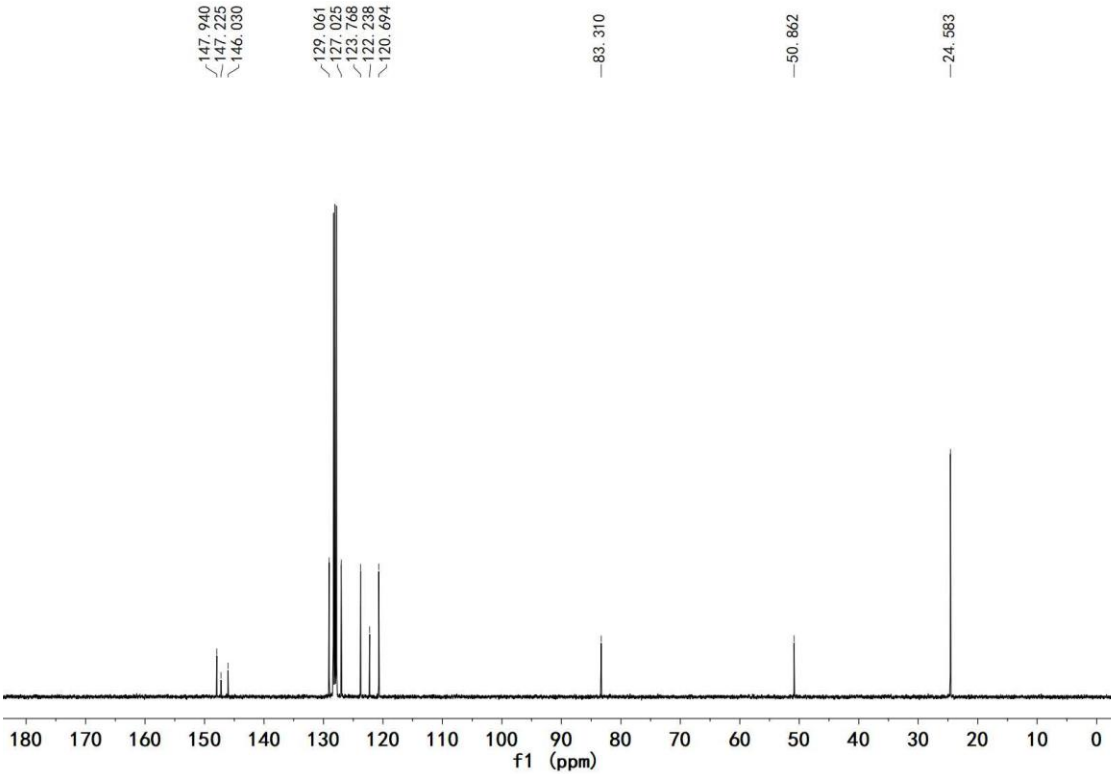


Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum of **7f** (101 MHz, C_6D_6, 298 K).

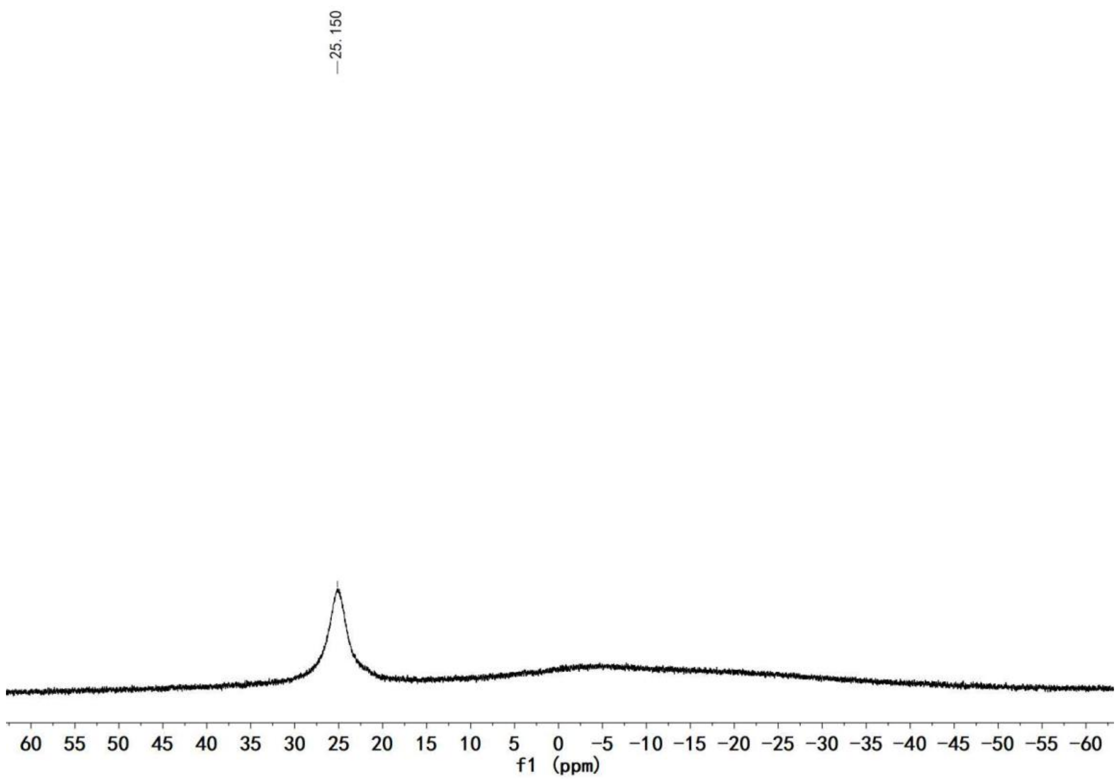
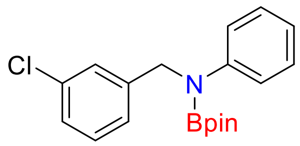


Figure S76. ^{11}B NMR spectrum of **7f** (128 MHz, C_6D_6, 298 K).



7g[7] (white solid, 95 mg, 92% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.38 (m, 2H, *phenyl*), 7.29 (m, 1H, *phenyl*), 7.09 (m, 2H, *phenyl*), 6.96 (m, 2H, *phenyl*), 6.80 (m, 2H, *phenyl*), 4.59 (s, 2H, CH_2), 1.07 (s, 12H, $C(CH_3)_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 146.4 (*phenyl*), 143.6 (*phenyl*), 134.8 (*phenyl*), 130.0 (*phenyl*), 129.0 (*phenyl*), 127.1 (*phenyl*), 127.0 (*phenyl*), 124.7 (*phenyl*), 122.0 (*phenyl*), 121.0 (*phenyl*), 83.2 ($C(CH_3)_2$), 51.1 (CH_2), 24.6 ($C(CH_3)_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.1.

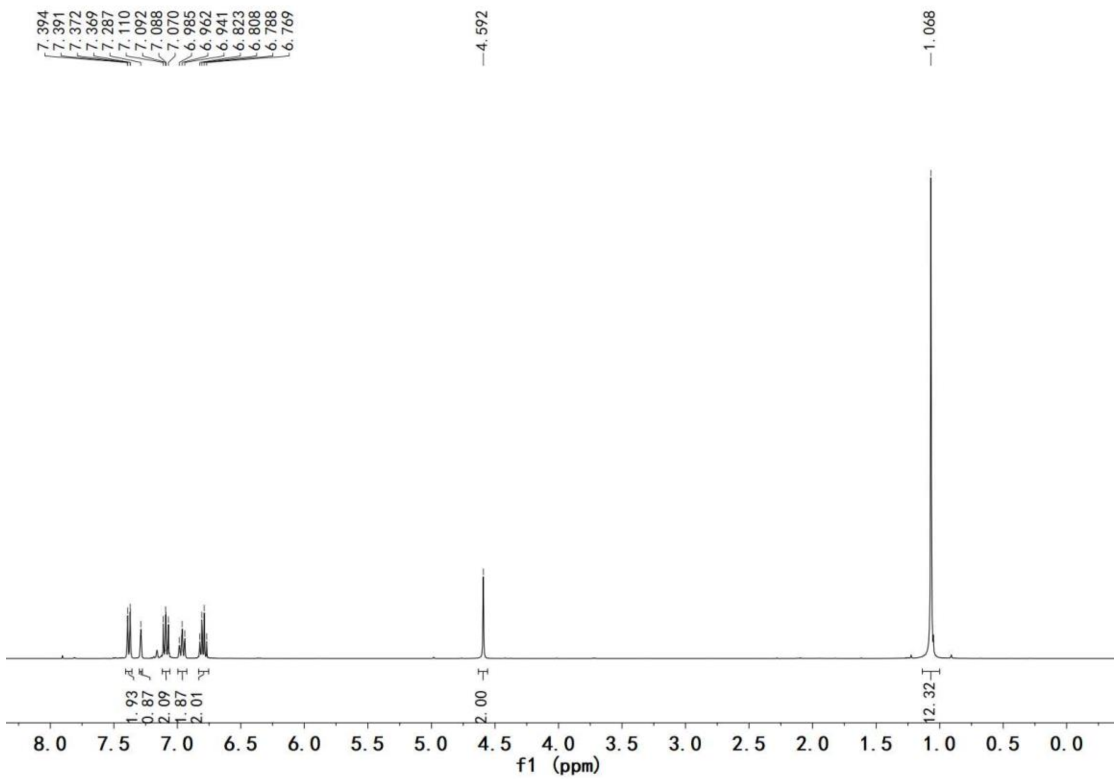


Figure S77. [1]H NMR spectrum of **7g** (400 MHz, C_6D_6, 298 K).

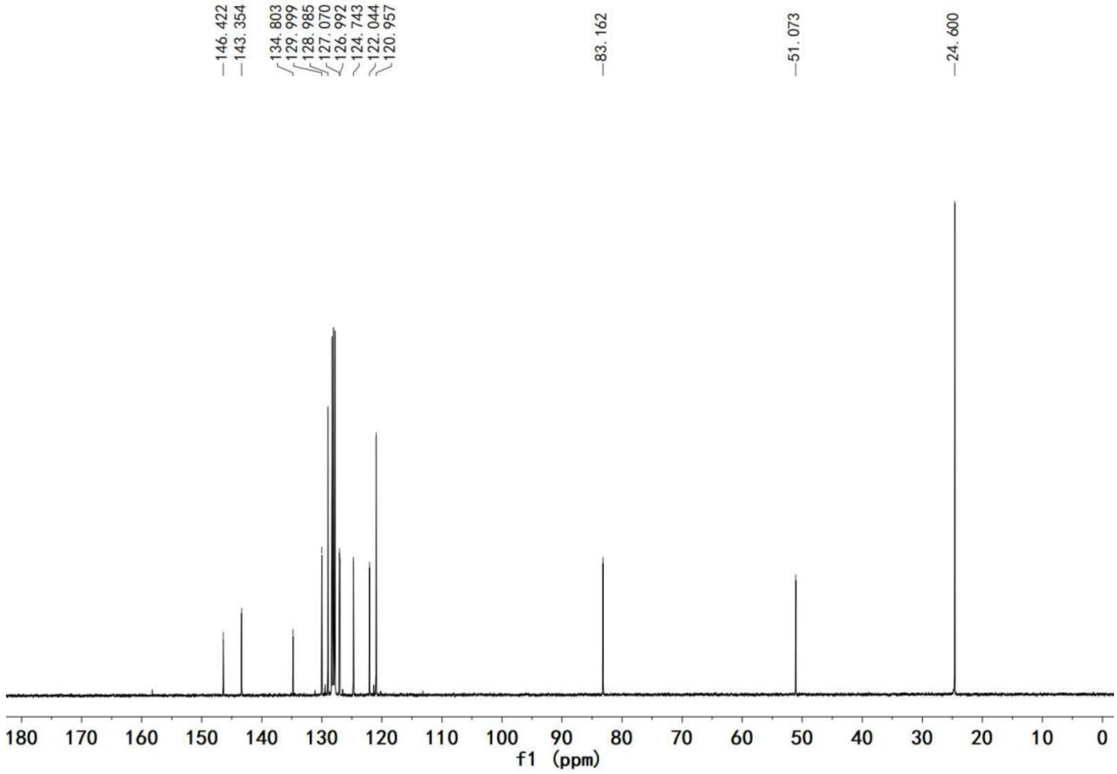


Figure S78. [13]C{[1]H} NMR spectrum of **7g** (101 MHz, C_6D_6, 298 K).

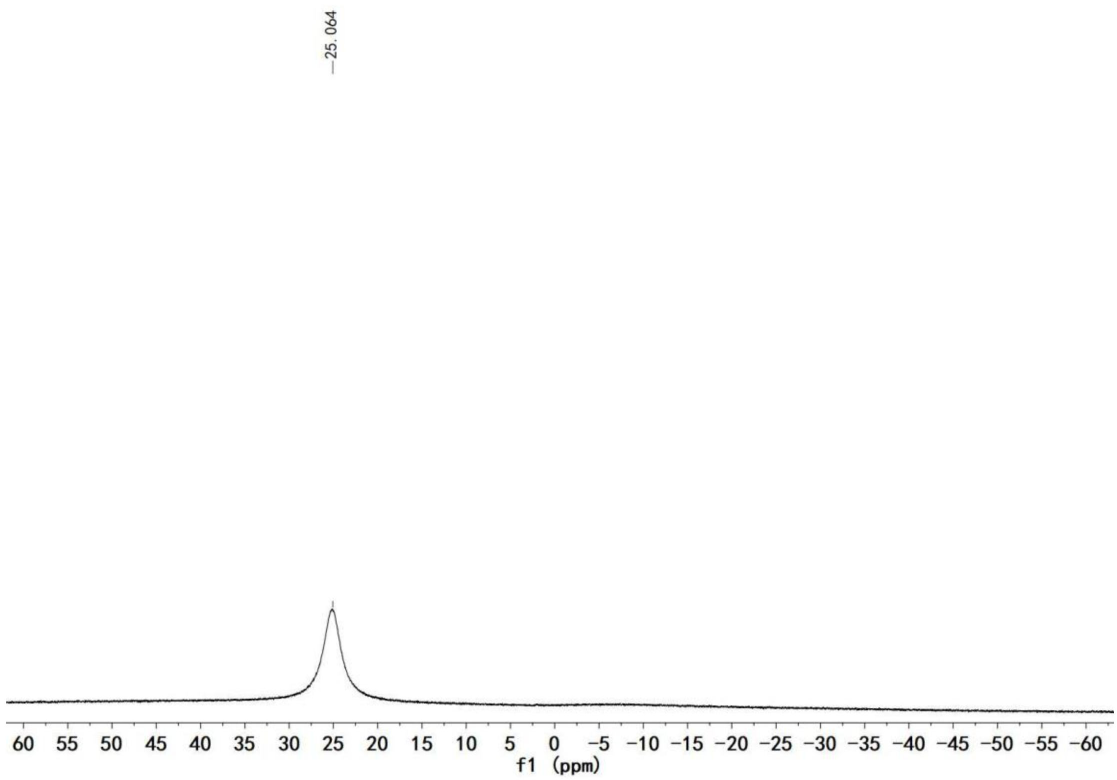
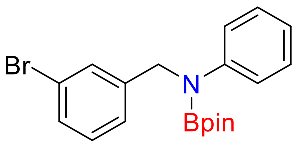


Figure S79. ^{11}B NMR spectrum of **7g** (128 MHz, C_6D_6, 298 K).



7h[7] (white solid, 102 mg, 88% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.45 (m, 1H, *phenyl*), 7.38 (m, 2H, *phenyl*), 7.10 (m, 3H, *phenyl*), 6.99 (m, 1H, *phenyl*), 6.81 (m, 1H, *phenyl*), 6.71 (m, 1H, *phenyl*), 4.58 (s, 2H, C*H*$_2$), 1.07 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 146.4 (*phenyl*), 143.6 (*phenyl*), 130.3 (*phenyl*), 130.0 (*phenyl*), 129.9 (*phenyl*), 129.0 (*phenyl*), 125.1 (*phenyl*), 123.1 (*phenyl*), 122.1 (*phenyl*), 121.0 (*phenyl*), 83.2 (*C*(CH$_3$)$_2$), 51.1 (*C*H$_2$), 24.6 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.1.

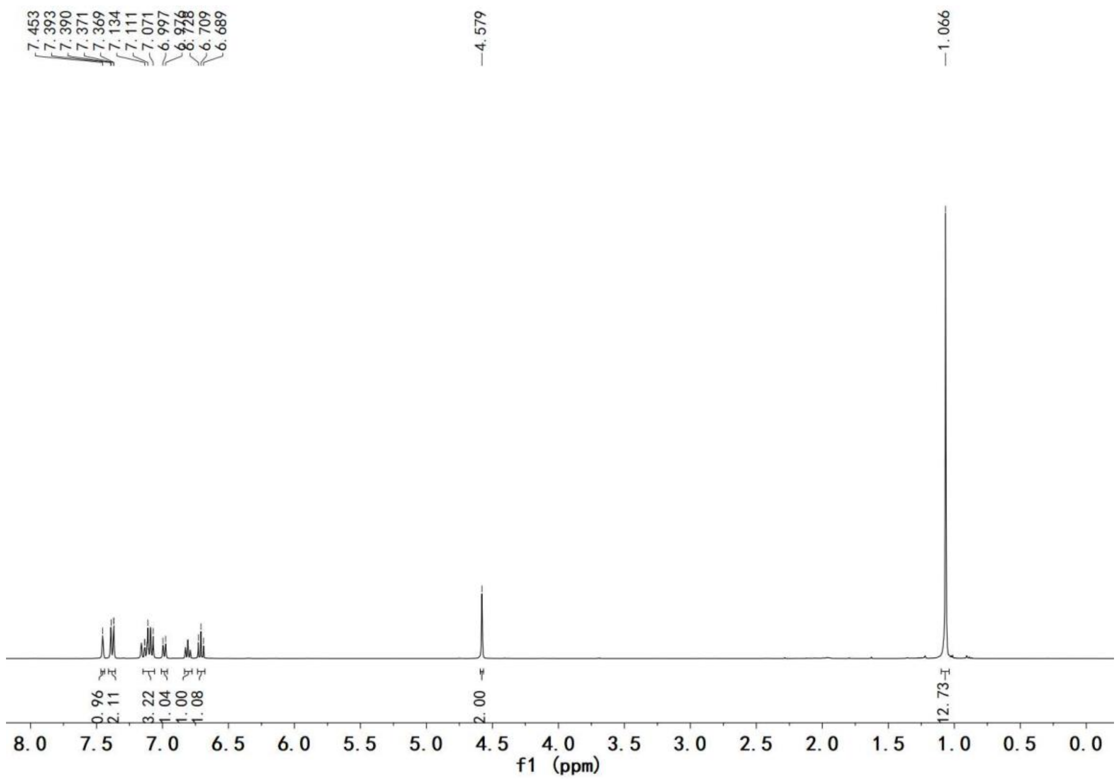


Figure S80. ^{1}H NMR spectrum of **7h** (400 MHz, C_6D_6, 298 K).

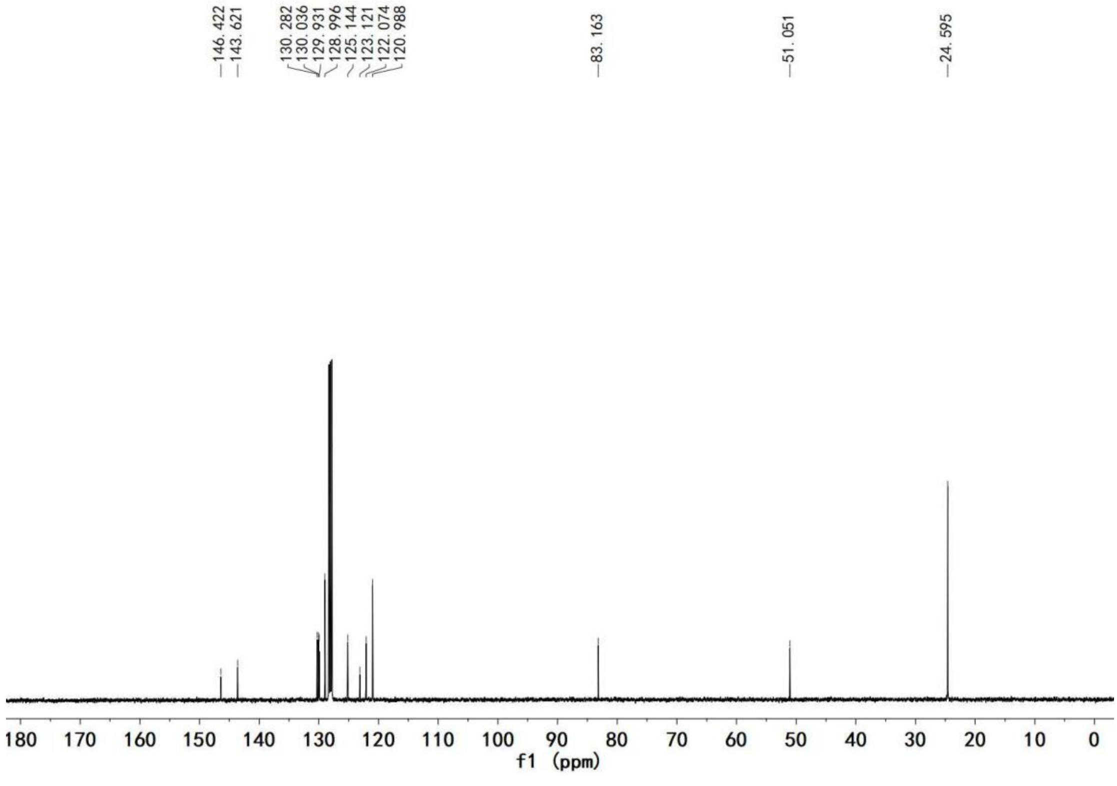


Figure S81. ^{13}C{^{1}H} NMR spectrum of **7h** (101 MHz, C_6D_6, 298 K).

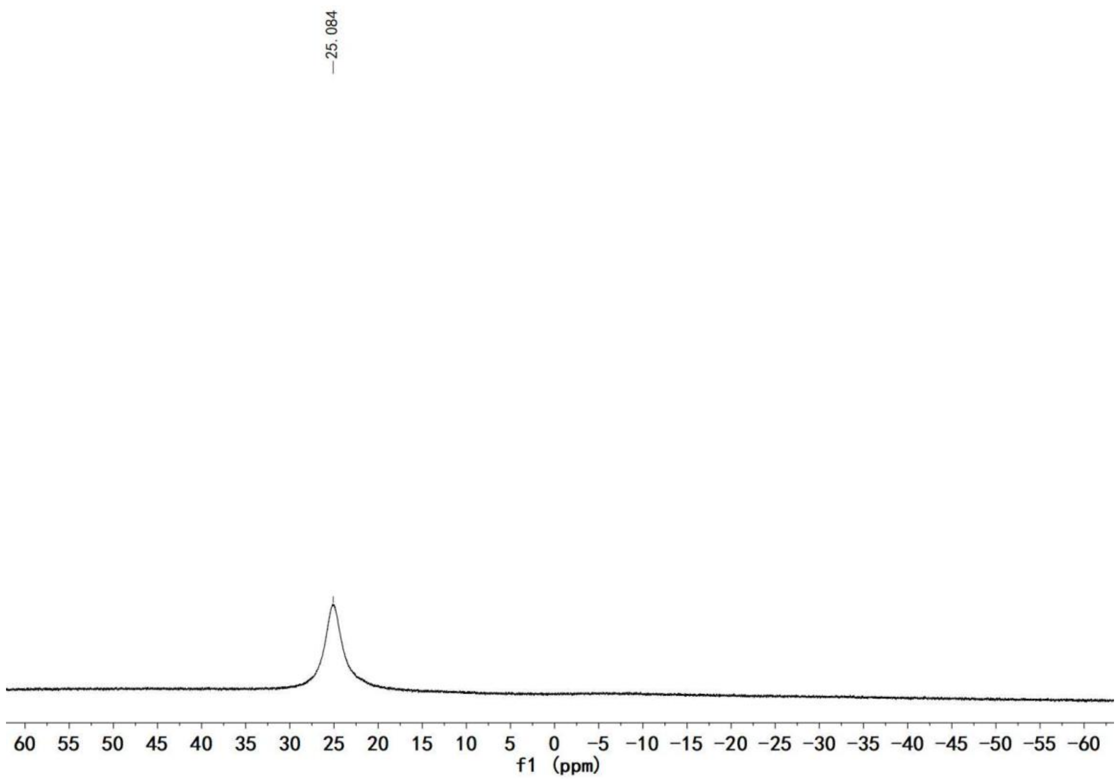
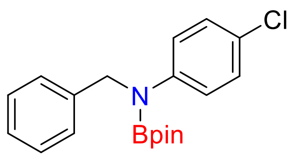


Figure S82. ^{11}B NMR spectrum of **7h** (128 MHz, C_6D_6, 298 K).



7i[7] (white solid, 92 mg, 89% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.24 (m, 2H, *phenyl*), 7.13 (m, 4H, *phenyl*), 7.02 (m, 3H, *phenyl*), 4.64 (s, 2H, CH_2), 1.05 (s, 12H, C(CH_3)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 145.3 (*phenyl*), 140.3 (*phenyl*), 128.8 (*phenyl*), 128.7 (*phenyl*), 126.9 (*phenyl*), 126.7 (*phenyl*), 126.6 (*phenyl*), 122.1 (*phenyl*), 83.2 (*C*(CH$_3$)$_2$), 51.3 (*C*H$_2$), 24.6 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.1.

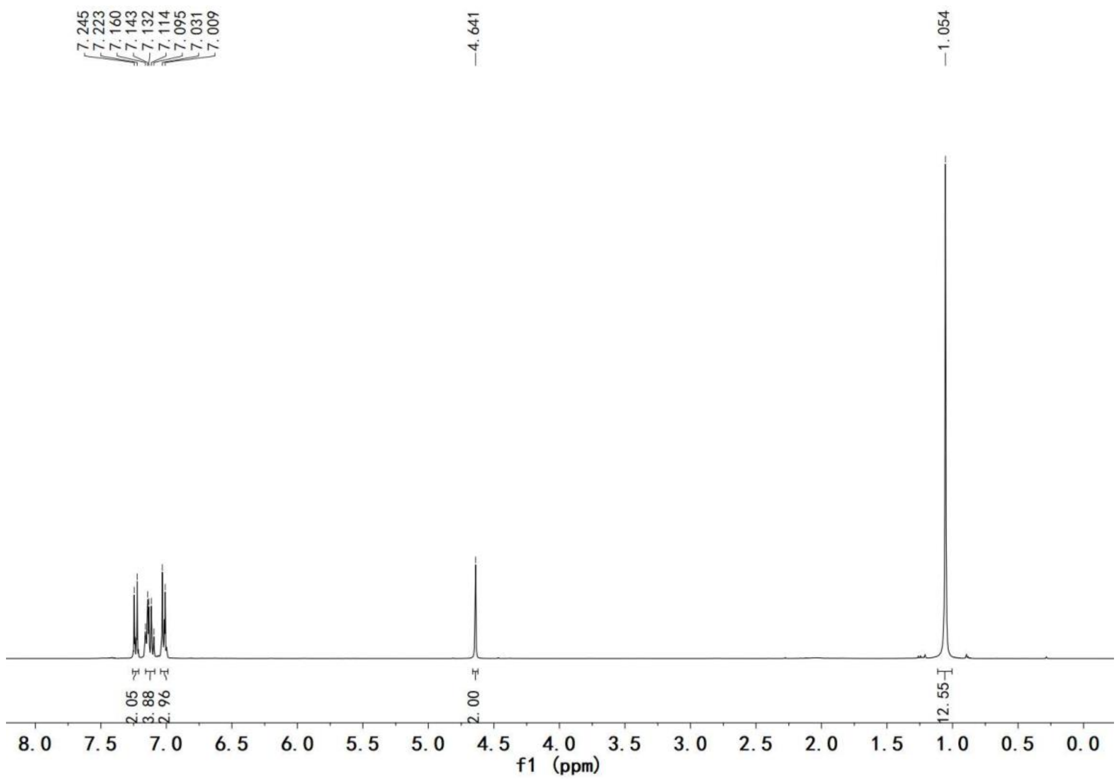


Figure S83. ^{1}H NMR spectrum of **7i** (400 MHz, C_6D_6, 298 K).

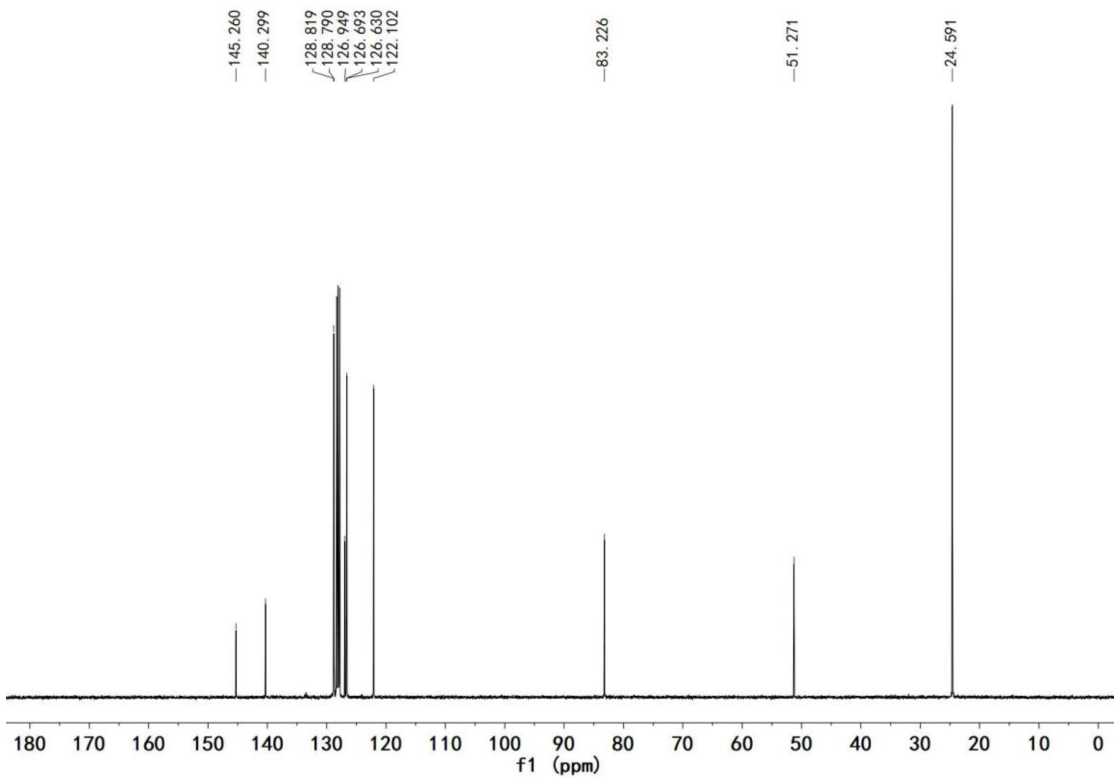


Figure S84. $^{13}C\{^{1}H\}$ NMR spectrum of **7i** (101 MHz, C_6D_6, 298 K).

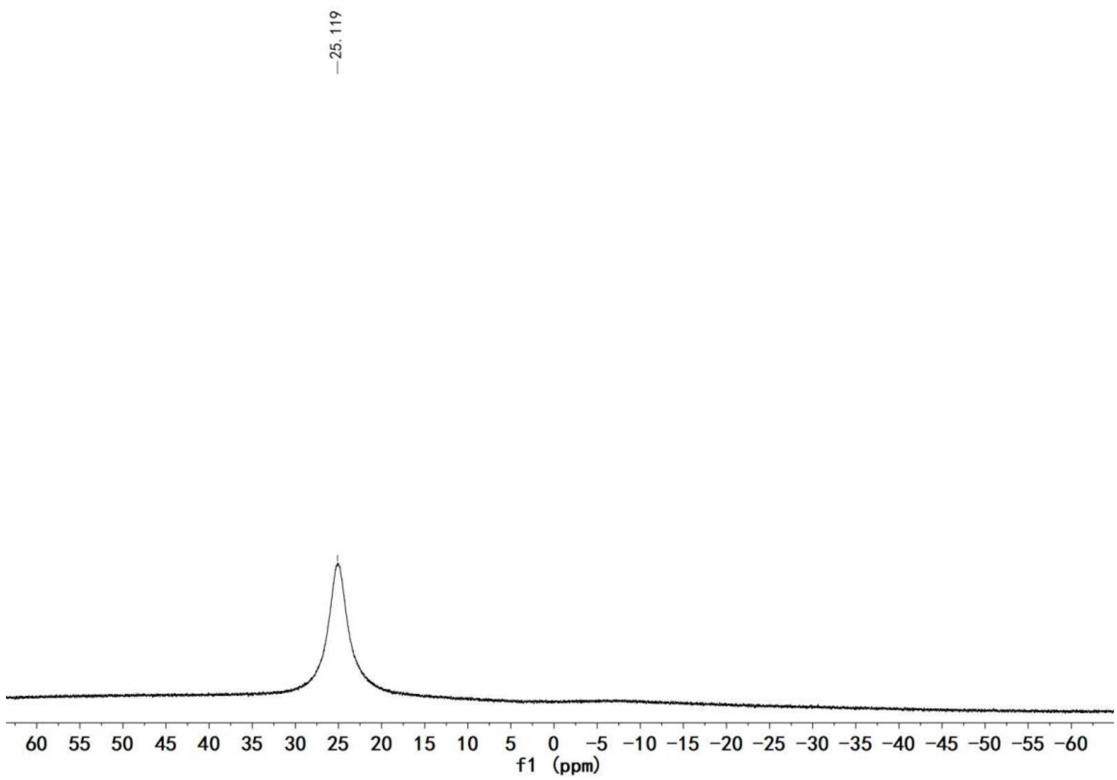
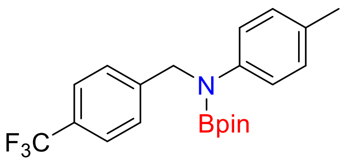


Figure S85. ^{11}B NMR spectrum of **7i** (128 MHz, C_6D_6, 298 K).



7j (white solid, 106 mg, 90% yield)

Melting Point: 74-75 ^{o}C

Elemental Analysis: calcd. for $C_{21}H_{25}BF_3O_2$: C, 64.47; H, 6.44; N, 3.58. Found: C, 64.33; H, 6.33; N, 3.50.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.31 (m, 2H, *phenyl*), 7.20 (m, 2H, *phenyl*), 7.10 (m, 2H, *phenyl*), 6.70 (m, 2H, *phenyl*), 4.61 (s, 2H, CH_2), 3.28 (s, 3H, ArCH_3), 1.11 (s, 12H, C(CH_3)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 155.7 (*phenyl*), 145.5 (*phenyl*), 139.3 (*phenyl*), 129.0 (q, J = 32.1 Hz, *phenyl*), 127.3 (*phenyl*), 125.6 (q, J = 3.8 Hz, *phenyl*), 125.0 (q, J = 272.6 Hz, *C*F_3), 123.1 (*phenyl*), 114.4 (*phenyl*), 83.1 (*C*(CH$_3$)$_2$), 54.9 (Ar*C*H$_3$), 51.9 (*C*H$_2$), 24.6 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 24.8.

^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 298K): δ = -62.0.

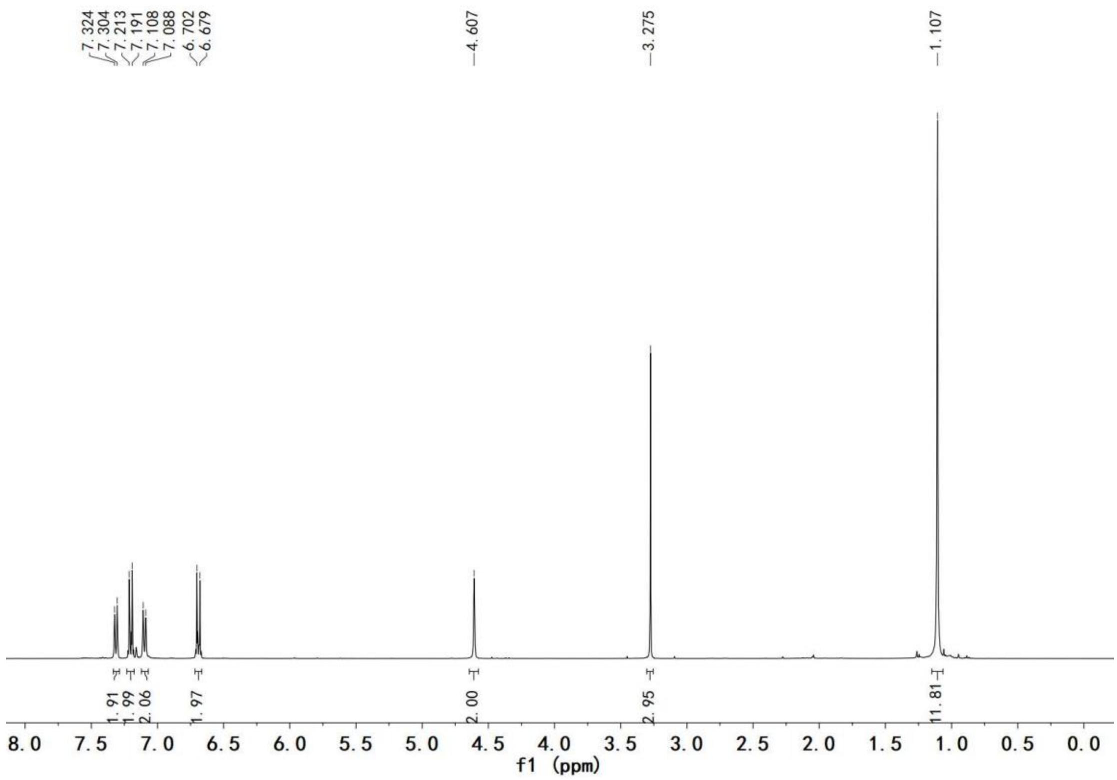


Figure S86. ^{1}H NMR spectrum of **7j** (400 MHz, C_6D_6, 298 K).

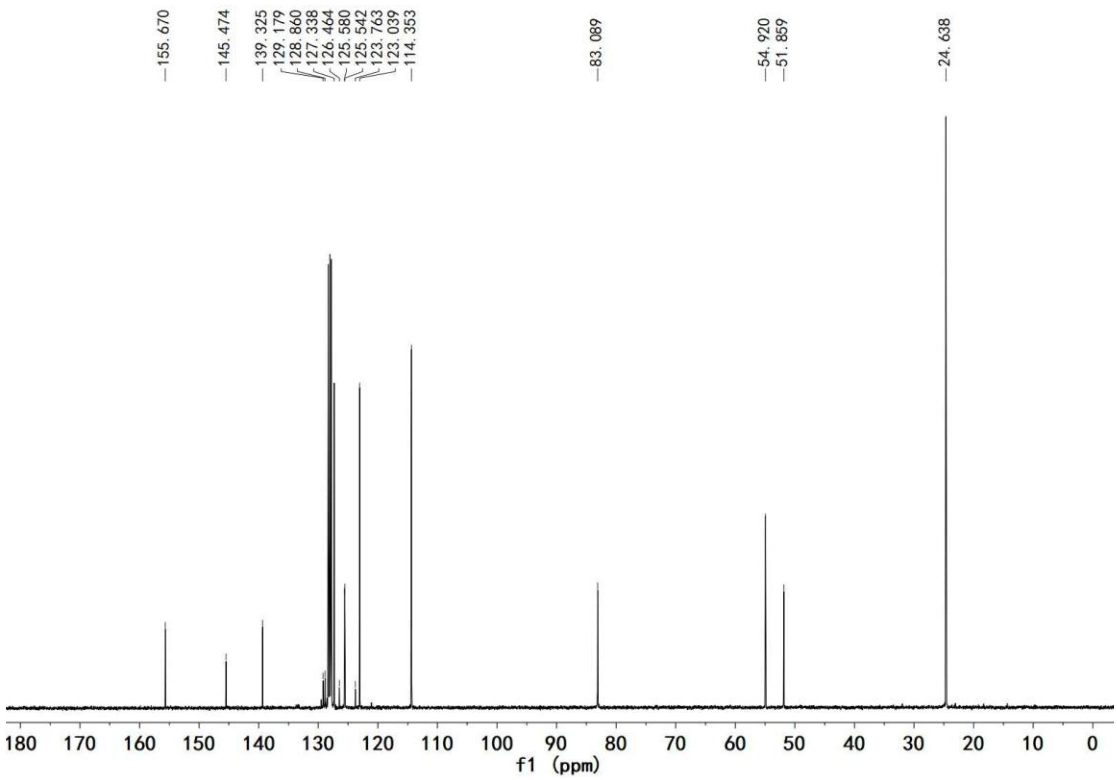


Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum of **7j** (101 MHz, C_6D_6, 298 K).

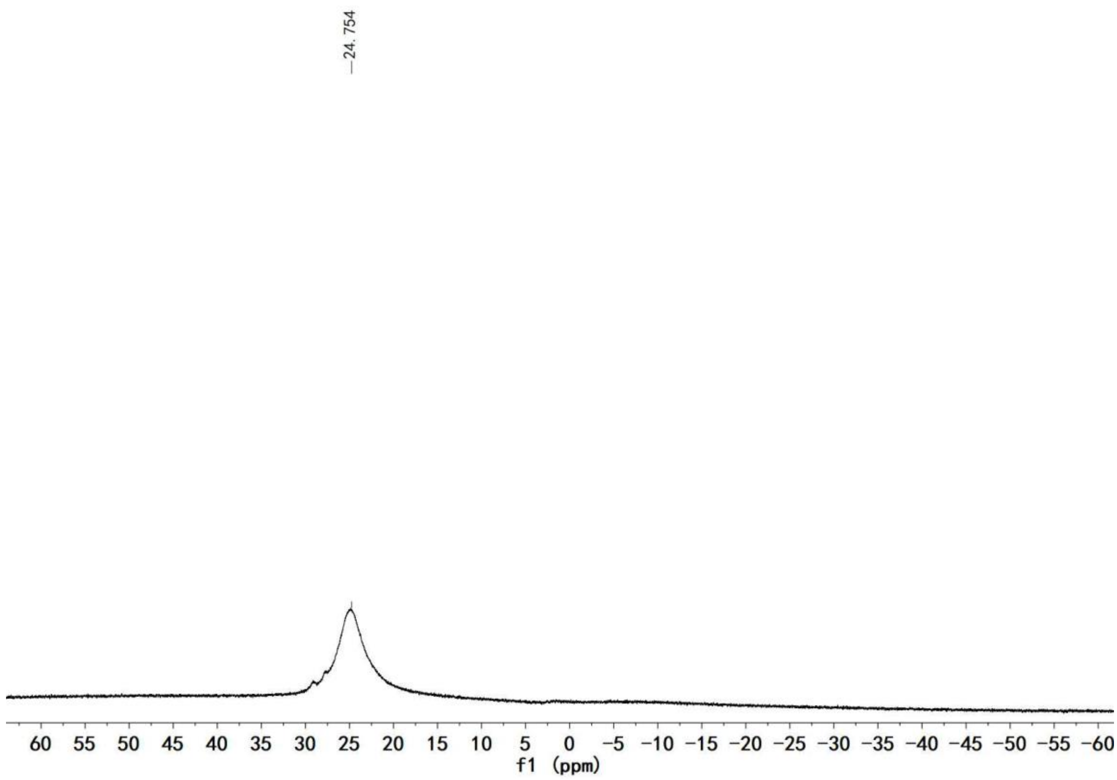


Figure S88. ^{11}B NMR spectrum of **7j** (128 MHz, C_6D_6, 298 K).

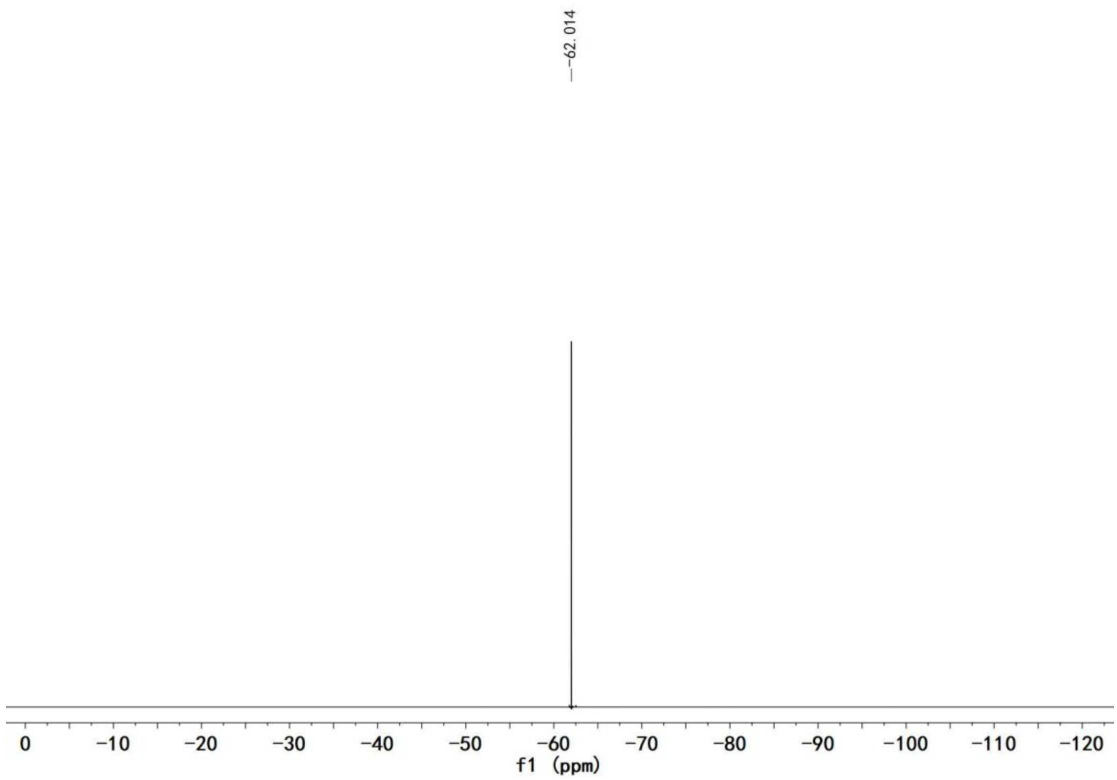
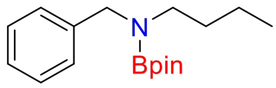


Figure S89. $^{19}F\{^1H\}$ NMR spectrum of **7j** (376 MHz, C_6D_6, 298 K).



7k[7] (colorless oil liquid, 73 mg, 84% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.30 (m, 2H, *phenyl*), 7.20 (m, 2H, *phenyl*), 7.09 (m, 1H, *phenyl*), 4.22 (s, 2H, ArC*H*$_2$), 2.98 (t, 2H, *J* = 7.2 Hz, ^{n}*Bu*), 1.40 (m, 2H, ^{n}*Bu*), 1.22 (m, 2H, ^{n}*Bu*), 1.15 (s, 12H, C(C*H*$_3$)$_2$), 0.85 (t, 3H, *J* = 7.2 Hz, ^{n}*Bu*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 141.4 (*phenyl*), 128.6 (*phenyl*), 128.1 (*phenyl*), 127.0 (*phenyl*), 82.3 (*C*(CH$_3$)$_2$), 49.6 (Ar*C*H$_2$), 44.8 (^{n}*Bu*), 31.2 (^{n}*Bu*), 24.8 (C(*C*H$_3$)$_2$), 20.1 (^{n}*Bu*), 14.2 (^{n}*Bu*).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 24.8.

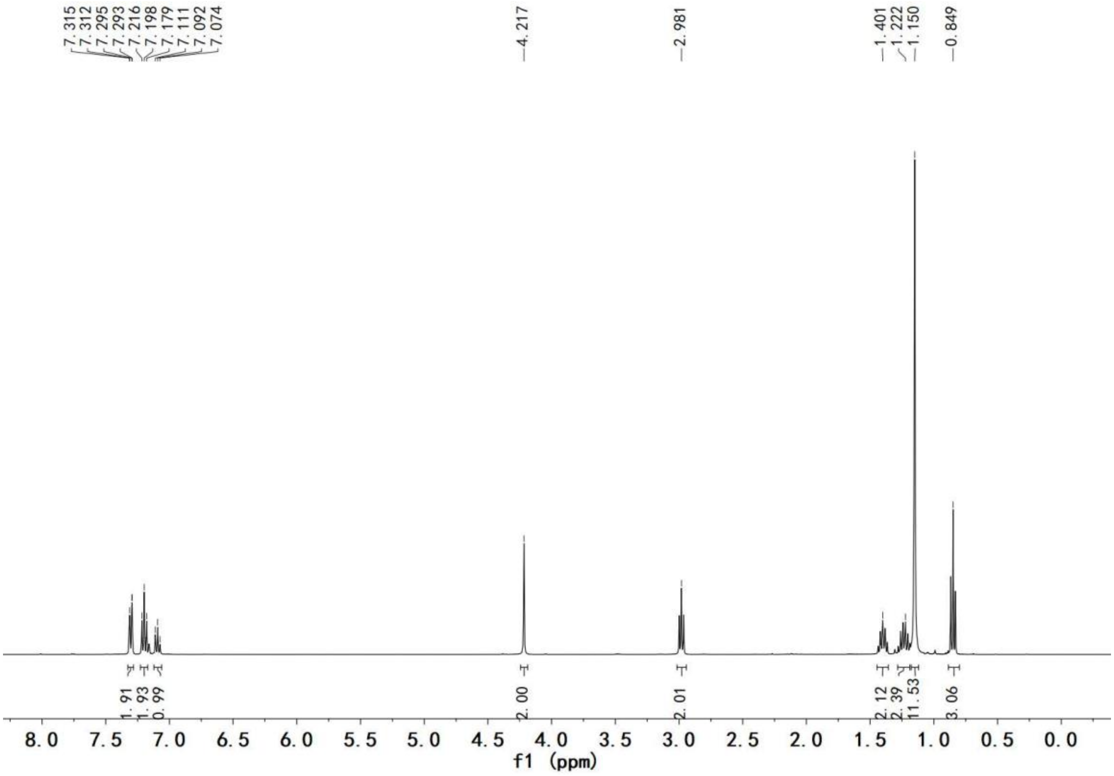


Figure S90. ^{1}H NMR spectrum of **7k** (400 MHz, C_6D_6, 298 K).

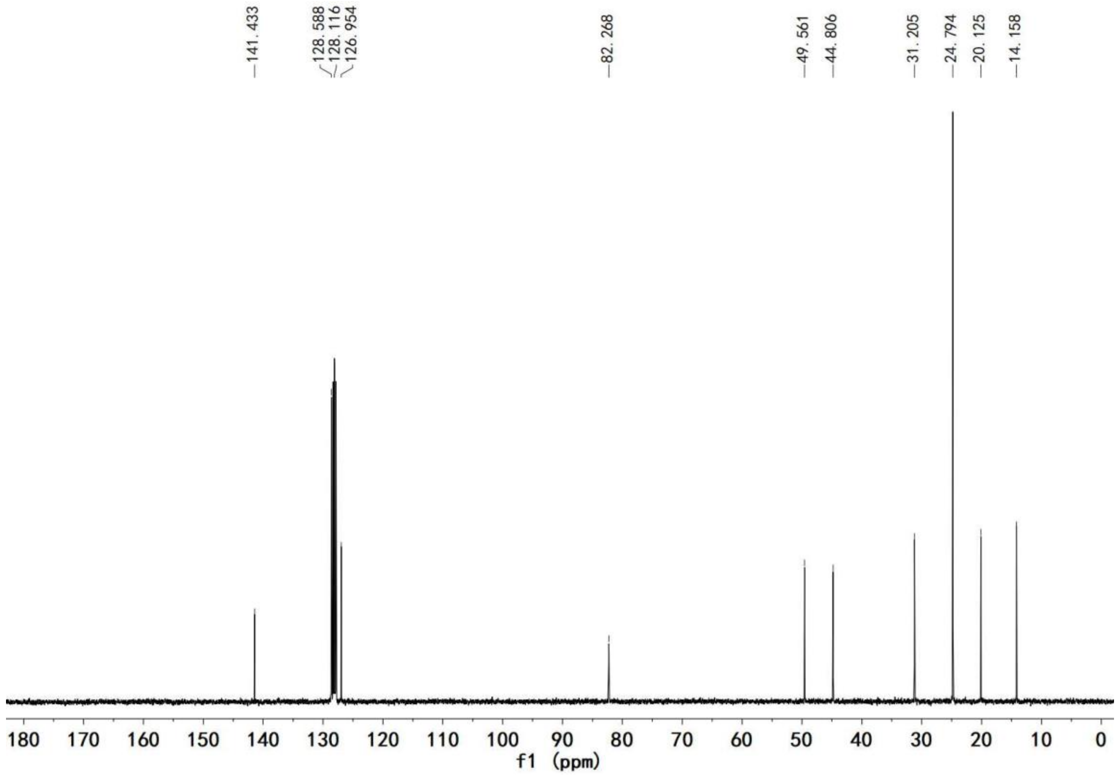


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of **7k** (101 MHz, C_6D_6, 298 K).

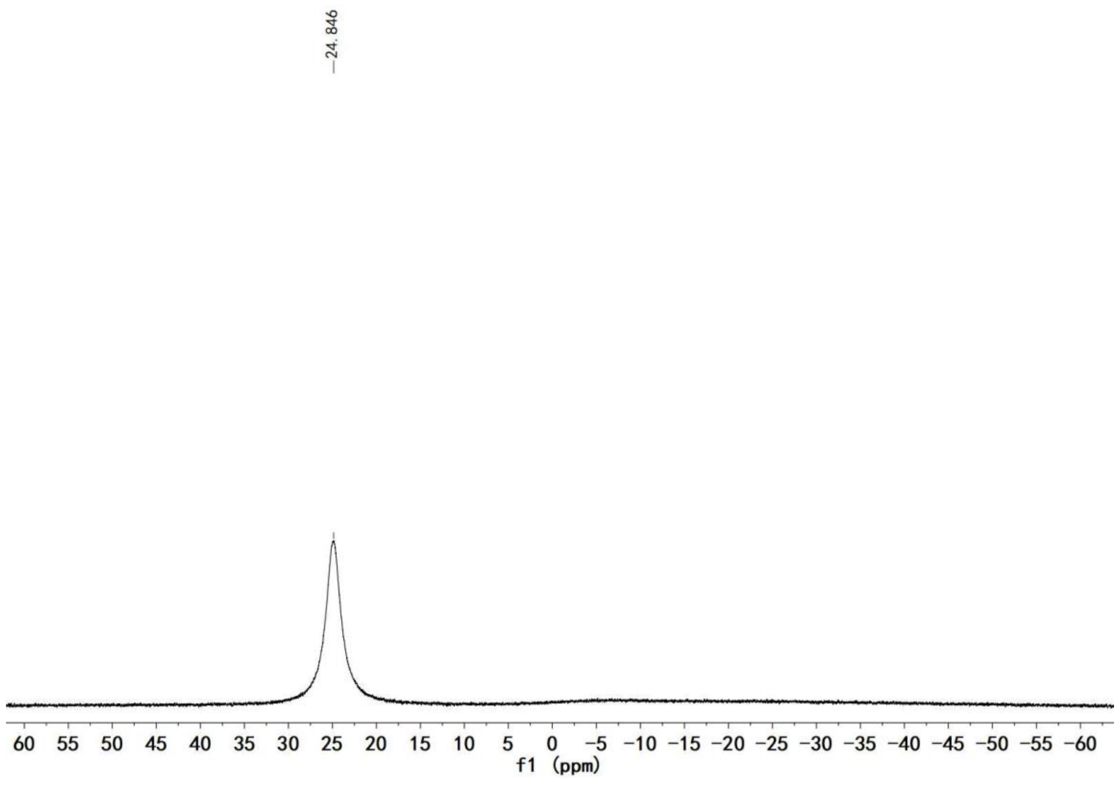
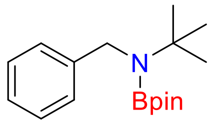


Figure S92. ^{11}B NMR spectrum of **7k** (128 MHz, C_6D_6, 298 K).



7l[7] (colorless oil liquid, 76 mg, 88% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.32 (m, 2H, *phenyl*), 7.22 (m, 2H, *phenyl*), 7.08 (m, 1H, *phenyl*), 4.37 (s, 2H, C*H*$_2$), 1.30 (s, 9H, ^{t}*Bu*), 1.12 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 144.6 (*phenyl*), 128.4 (*phenyl*), 127.1 (*phenyl*), 126.3 (*phenyl*), 81.7 (*C*(CH$_3$)$_2$), 53.4 (^{t}*Bu*), 48.8 (*C*H$_2$), 31.0 (^{t}*Bu*), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.0.

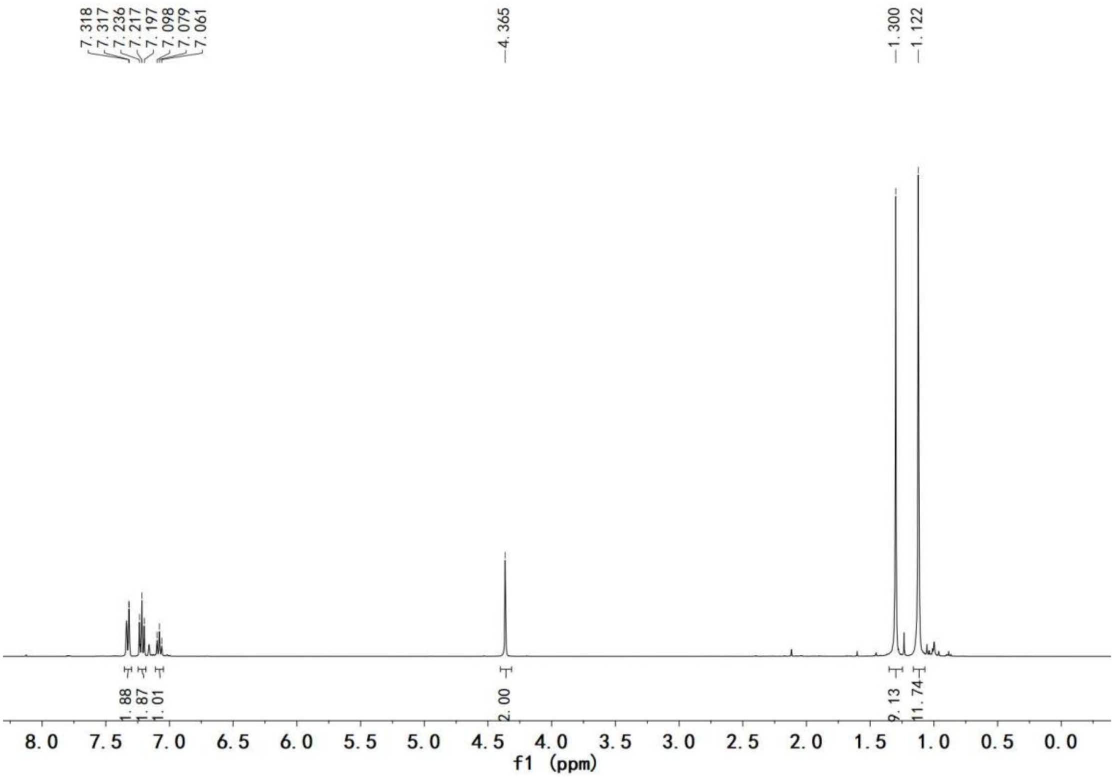


Figure S93. ^{1}H NMR spectrum of **7l** (400 MHz, C_6D_6, 298 K).

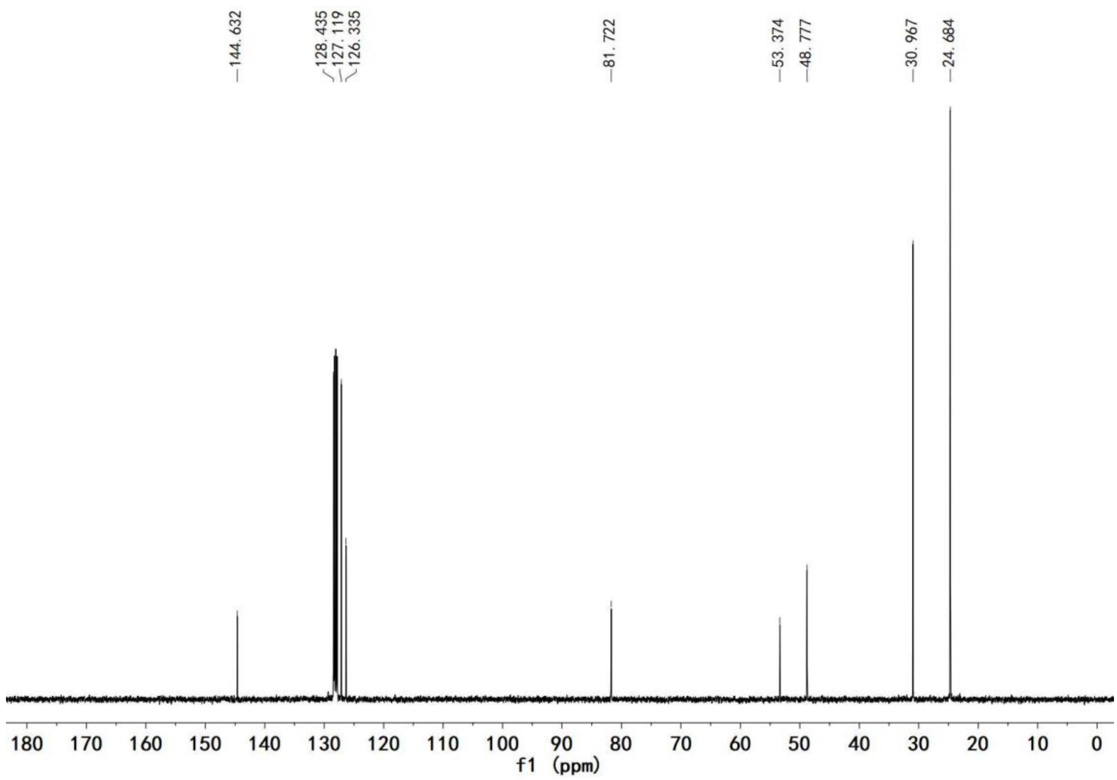


Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum of **7l** (101 MHz, C_6D_6, 298 K).

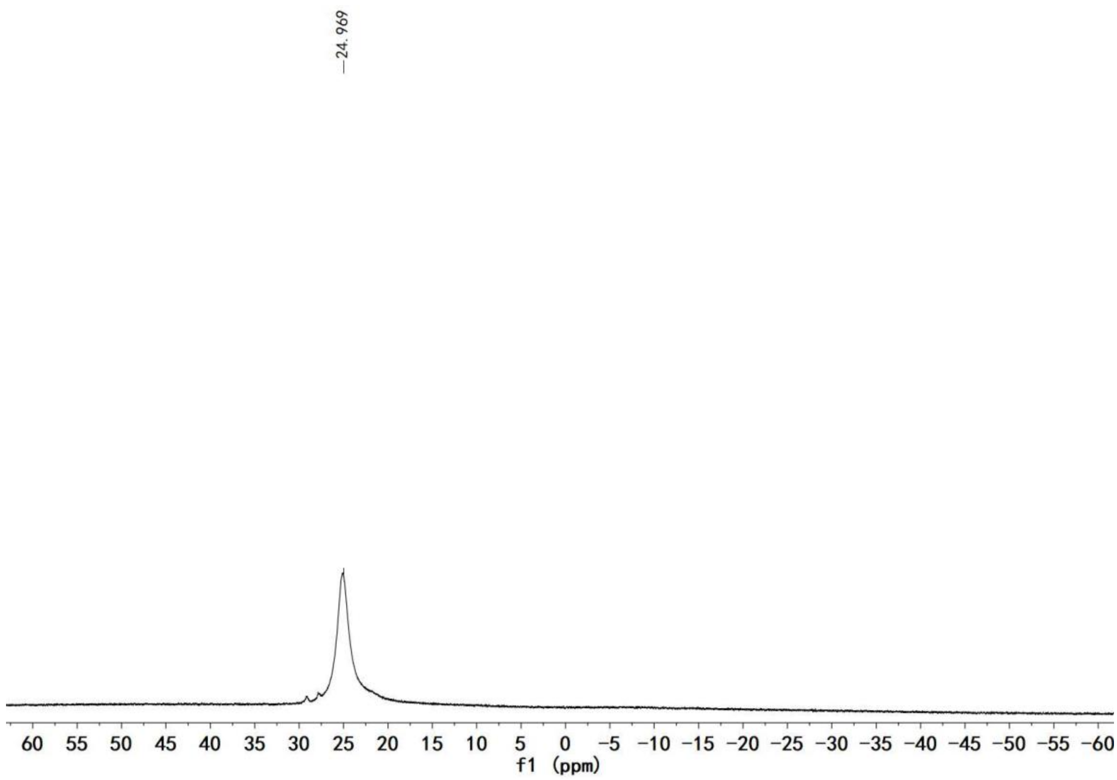
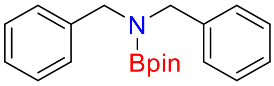


Figure S95. ^{11}B NMR spectrum of **7l** (128 MHz, C_6D_6, 298 K).



7m[7] (white solid, 92 mg, 89% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.26 (m, 4H, *phenyl*), 7.21-7.18 (m, 4H, *phenyl*), 7.12-7.08 (m, 2H, *phenyl*), 4.13 (s, 4H, C*H*$_2$), 1.18 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 140.6 (*phenyl*), 128.7 (*phenyl*), 128.4 (*phenyl*), 127.1 (*phenyl*), 82.7 (*C*(CH$_3$)$_2$), 48.8 (*C*H$_2$), 24.8 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 24.8.

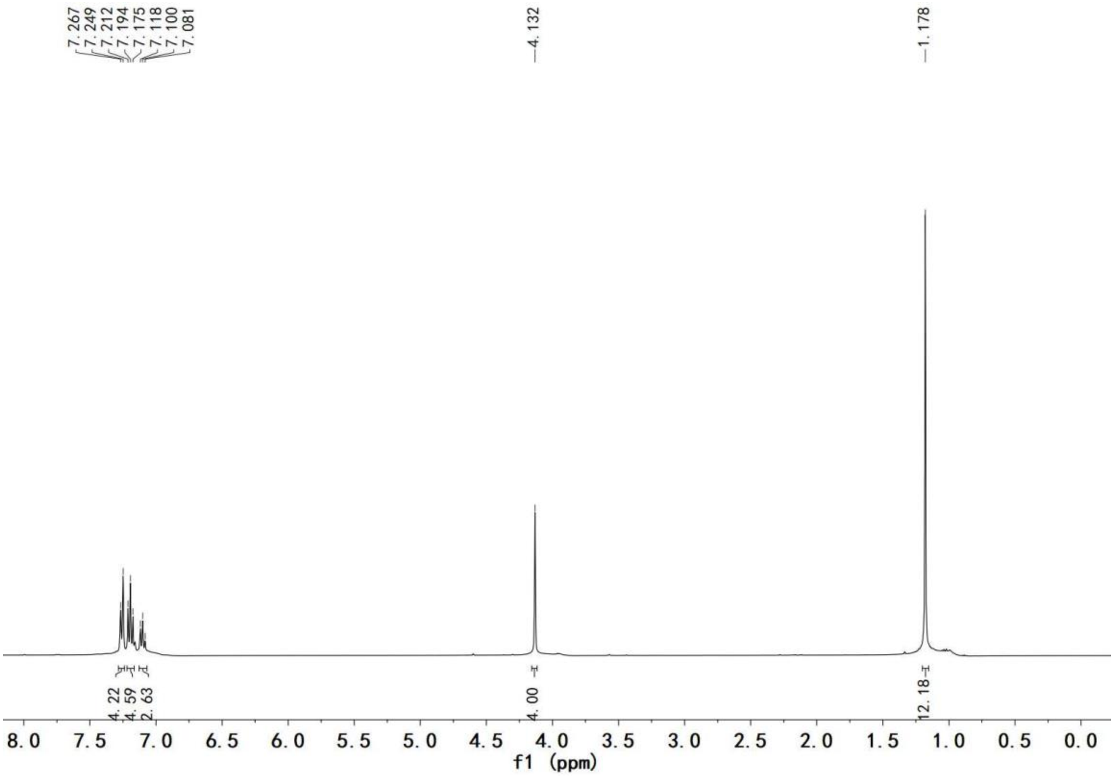


Figure S96. ^{1}H NMR spectrum of **7m** (400 MHz, C_6D_6, 298 K).

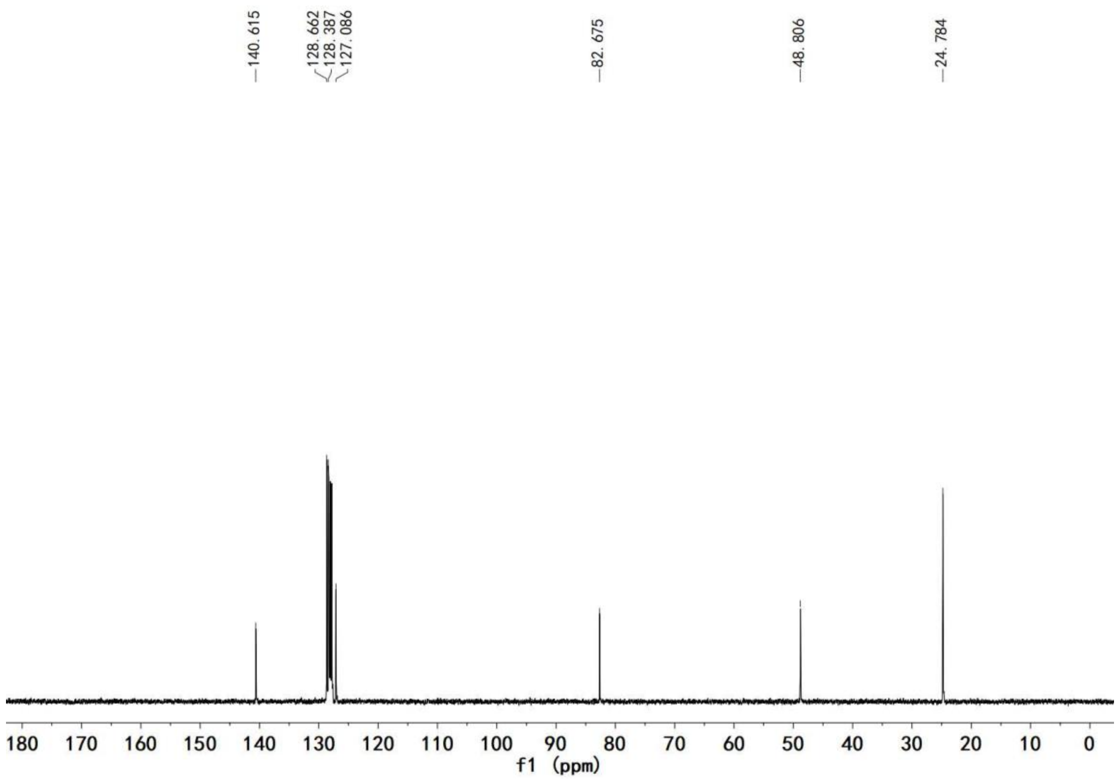


Figure S97. $^{13}C\{^{1}H\}$ NMR spectrum of **7m** (101 MHz, C_6D_6, 298 K).

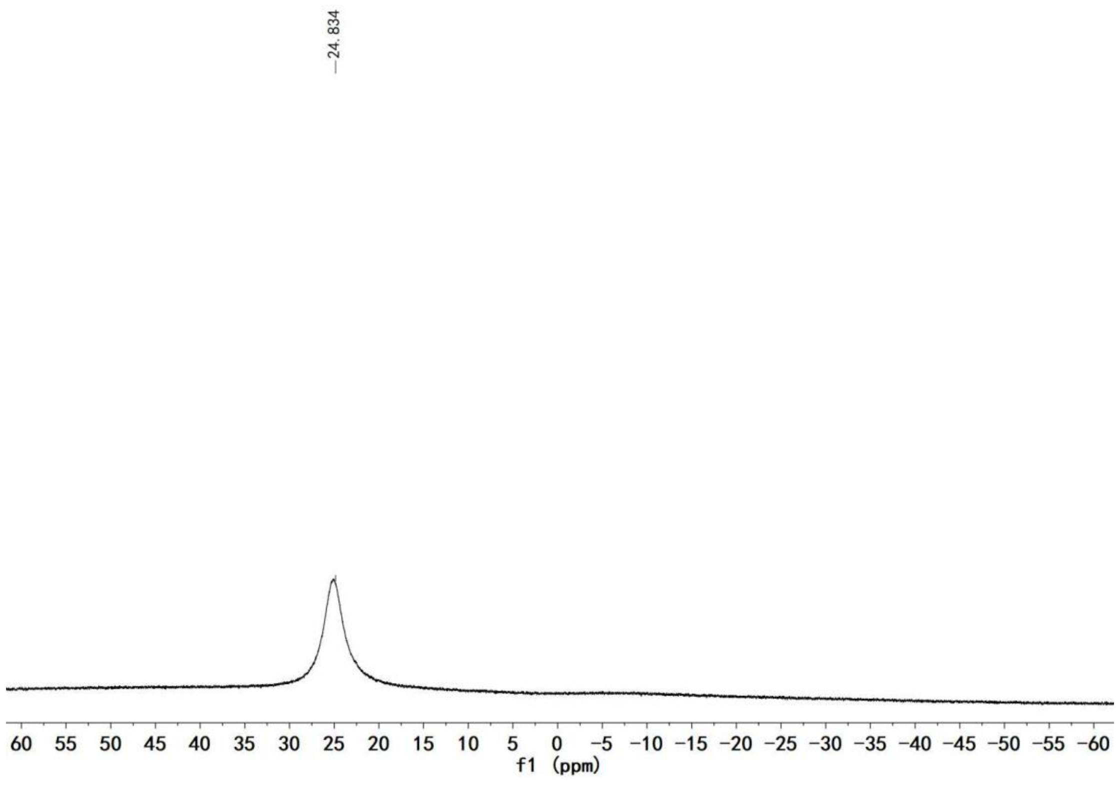
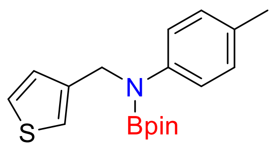


Figure S98. ^{11}B NMR spectrum of **7m** (128 MHz, C_6D_6, 298 K).



7n (white solid, 84 mg, 85% yield)

Melting Point: 62-63 °C

Elemental Analysis: calcd. for $C_{18}H_{24}BNO_2S$: C, 65.66; H, 7.35; N, 4.25. Found: C, 65.81; H, 7.09; N, 4.09.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.27 (m, 2H, *phenyl*), 6.95 (m, 1H, *thio*), 6.90 (m, 1H, *thio*), 6.83 (m, 1H, *thio*), 6.70 (m, 2H, *phenyl*), 4.65 (s, 2H, C*H*$_2$), 3.23 (s, 3H, ArC*H*$_3$), 1.10 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 155.6 (*Ar*), 142.7 (*Ar*), 139.8 (*Ar*), 127.3 (*Ar*), 125.8 (*Ar*), 123.6 (*Ar*), 121.0 (*Ar*), 114.2 (*Ar*), 82.8 (*C*(CH$_3$)$_2$), 54.9 (Ar*C*H$_3$), 48.3 (*C*H$_2$), 24.7 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 24.7.

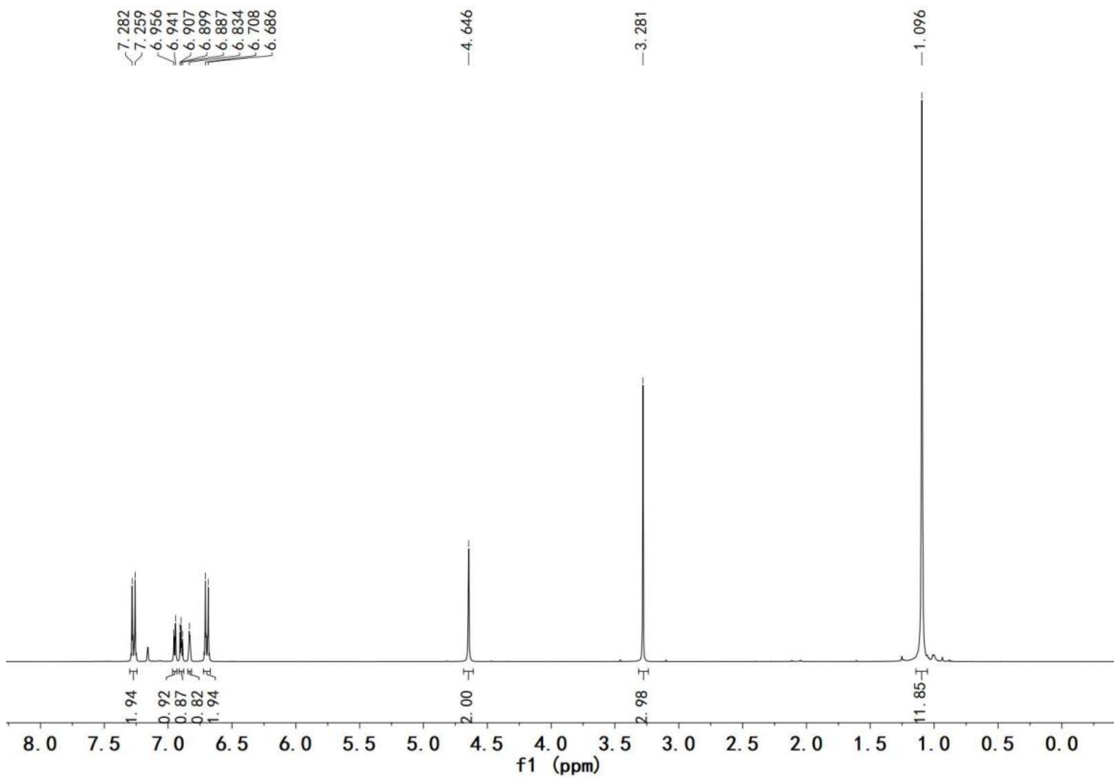


Figure S99. ^{1}H NMR spectrum of **7n** (400 MHz, C_6D_6, 298 K).

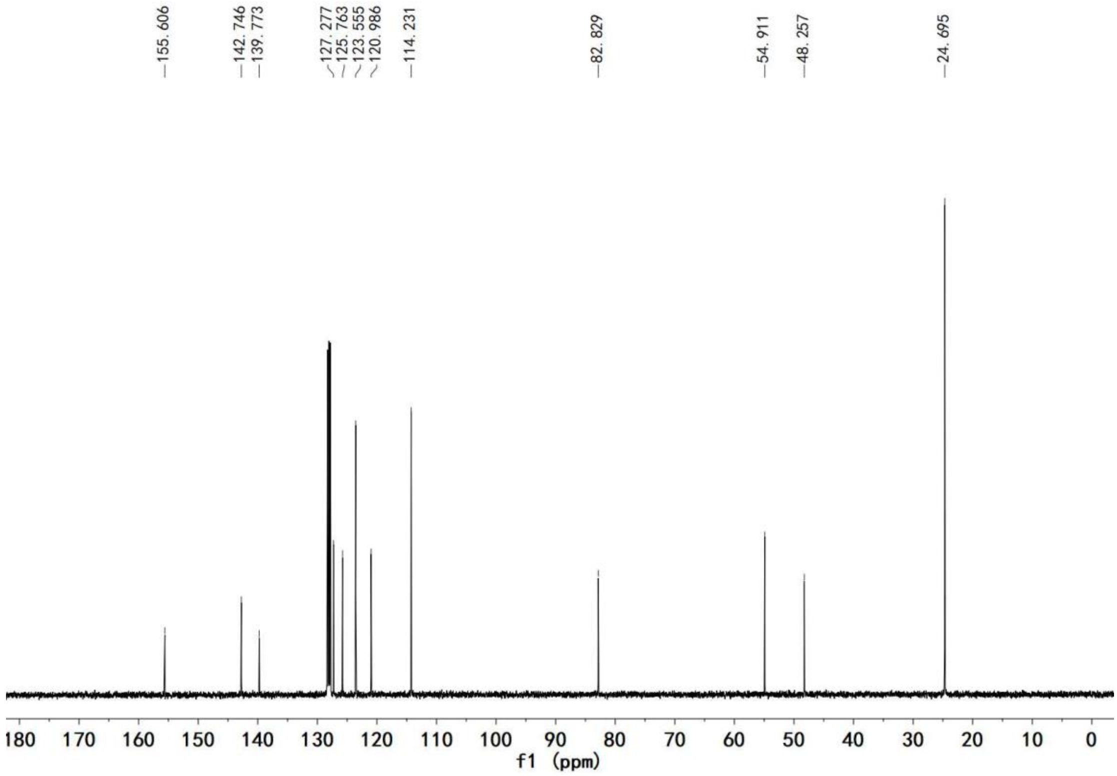


Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum of **7n** (101 MHz, C_6D_6, 298 K).

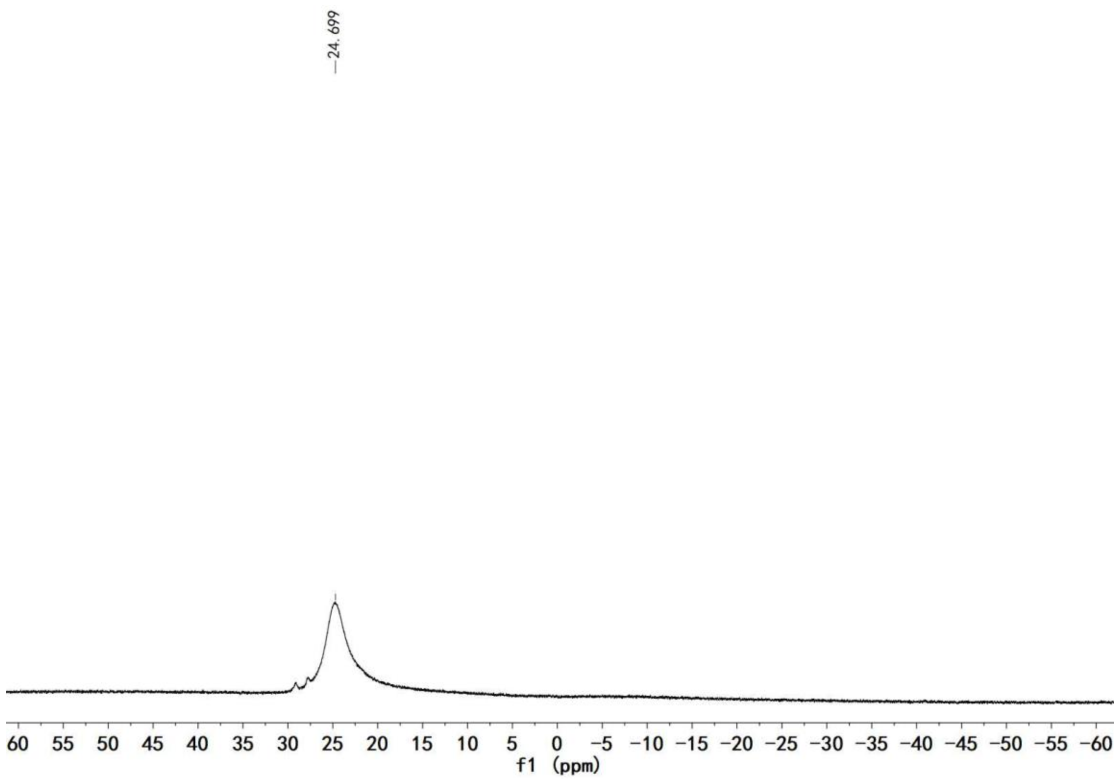
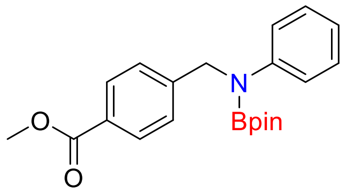


Figure S101. ^{11}B NMR spectrum of **7n** (128 MHz, C_6D_6, 298 K).



7o[7] (colorless solid, 90 mg, 82% yield)

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 8.03-8.00 (m, 2H, *phenyl*), 7.38-7.36 (m, 2H, *phenyl*), 7.16-7.14 (m, 2H, *phenyl*), 7.10 (m, 2H, *phenyl*), 6.81 (m, 1H, *phenyl*), 4.67 (s, 2H, C*H*$_2$), 3.47 (s, 3H, COOC*H*$_3$), 1.06 (s, 12H, C(C*H*$_3$)$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 166.6 (*C*OOCH$_3$), 146.5 (*phenyl*), 146.3 (*phenyl*), 130.2 (*phenyl*), 129.3 (*phenyl*), 129.0 (*phenyl*), 126.6 (*phenyl*), 121.9 (*phenyl*), 120.8 (*phenyl*), 83.2 (*C*(CH$_3$)$_2$), 51.5 (*C*H$_2$), 51.4 (COO*C*H$_3$), 24.6 (C(*C*H$_3$)$_2$).

^{11}B NMR (162 MHz, C_6D_6, 298 K): δ = 25.2.

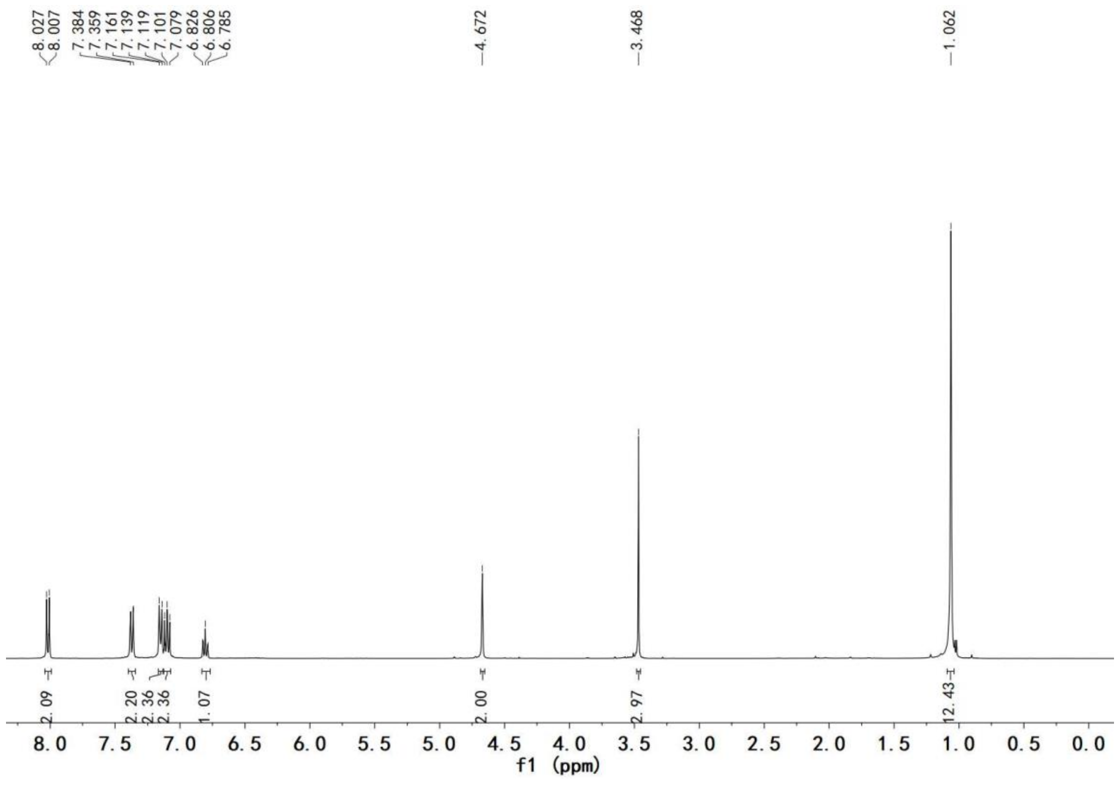


Figure S102. ^{1}H NMR spectrum of **7o** (400 MHz, C_6D_6, 298 K).

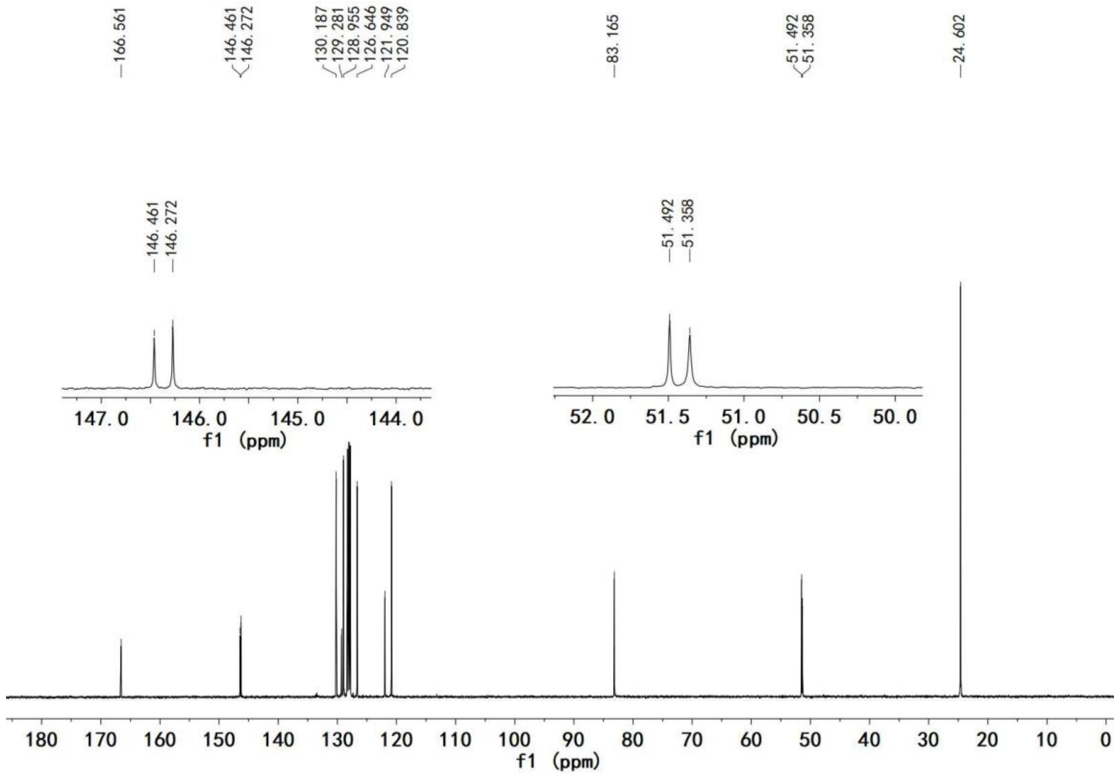


Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum of **7o** (101 MHz, C_6D_6, 298 K).

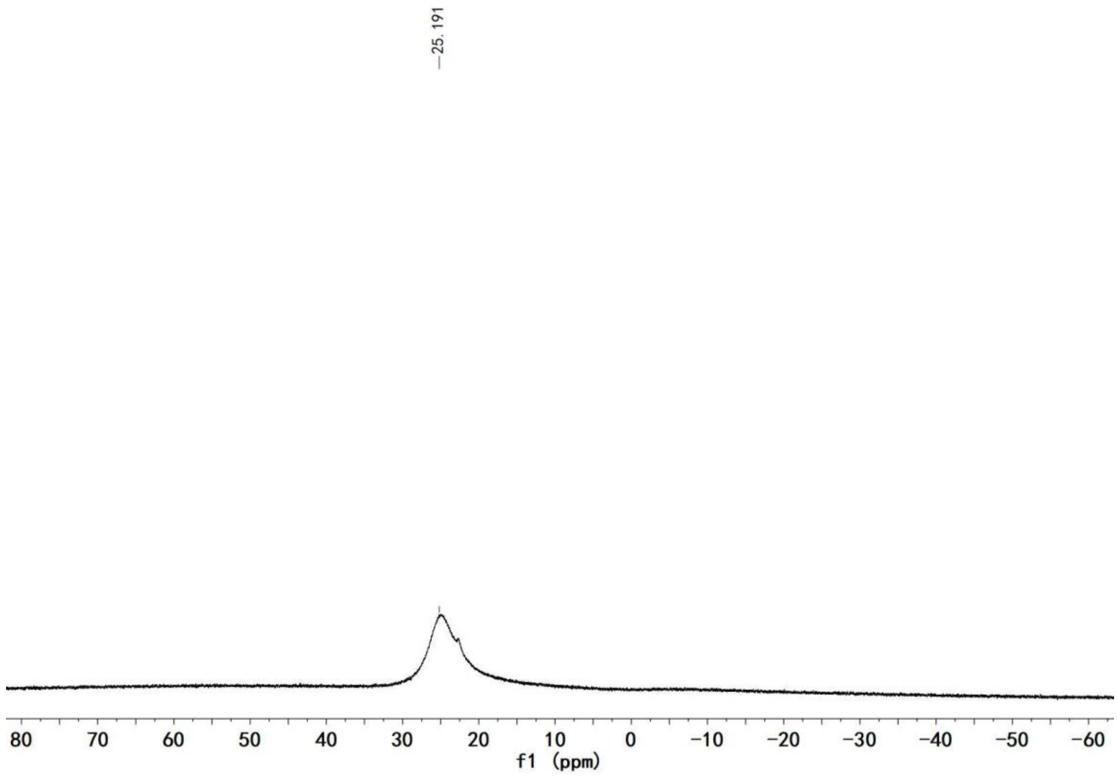
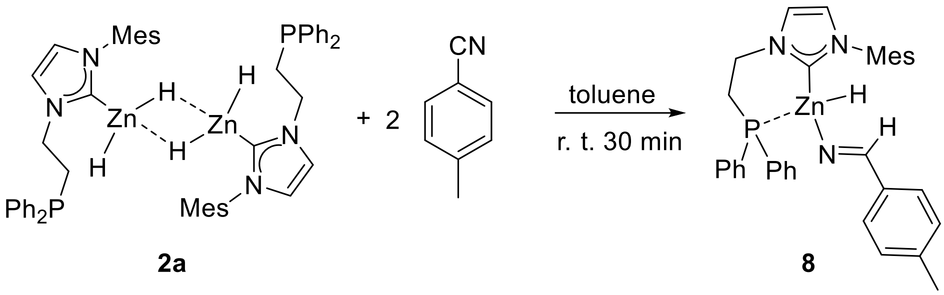


Figure S104. ^{11}B NMR spectrum of **7o** (128 MHz, C_6D_6, 298 K).

Preparation of complex 8



p-Tolunitrile (33 mg, 0.28 mmol) was added to a solution of **2a** (131 mg, 0.14 mmol) in toluene (3 mL). The reaction mixture was stirred at room temperature for 30 min. The volatiles were removed under vacuum, and then the residue was washed with hexane (3 * 2 mL) to eventually give **8** as a yellow solid (150 mg, 92% yield).

Elemental Analysis: calcd. for $C_{34}H_{35}N_3PZn$: C, 70.04; H, 6.22; N, 7.21. Found: C, 70.53; H, 6.48; N, 6.98.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 9.39 (s, 1H, Zn-N=C*H*Ar), 7.98 (m, 2H, *phenyl*), 7.33 (m, 4H, *phenyl*), 7.10 (m, 3H, *phenyl*), 7.04 (m, 7H, *phenyl*), 6.17 (m, 1H, NHC), 5.89 (m, 1H, NHC), 4.81 (s, 1H, Zn*H*), 4.30 (m, 2H, NCH_2), 2.65 (m, 2H, PCH_2), 2.19-2.01 (m, 12H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 185.6 (N*C*N), 161.6 (Zn-N=*C*HAr), 139.9 (*phenyl*), 139.3 (d, *J* = 14.1 Hz, *phenyl*), 138.0 (*phenyl*), 137.6 (*phenyl*), 136.6 (*phenyl*), 135.5 (*phenyl*), 133.4 (d, *J* = 18.9 Hz, *phenyl*), 129.3 (*phenyl*), 129.0 (*phenyl*), 128.7 (d, *J* = 6.5 Hz, *phenyl*), 128.6 (*phenyl*), 128.5 (*phenyl*), 121.02 (NHC), 120.98 (NHC), 47.8 (d, *J* = 19.8 Hz, N*C*H_2), 31.8 (d, *J* = 15.3 Hz, P*C*H_2), 21.5 (*C*H_3), 21.4 (*C*H_3), 18.4 (*C*H_3).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -20.4.

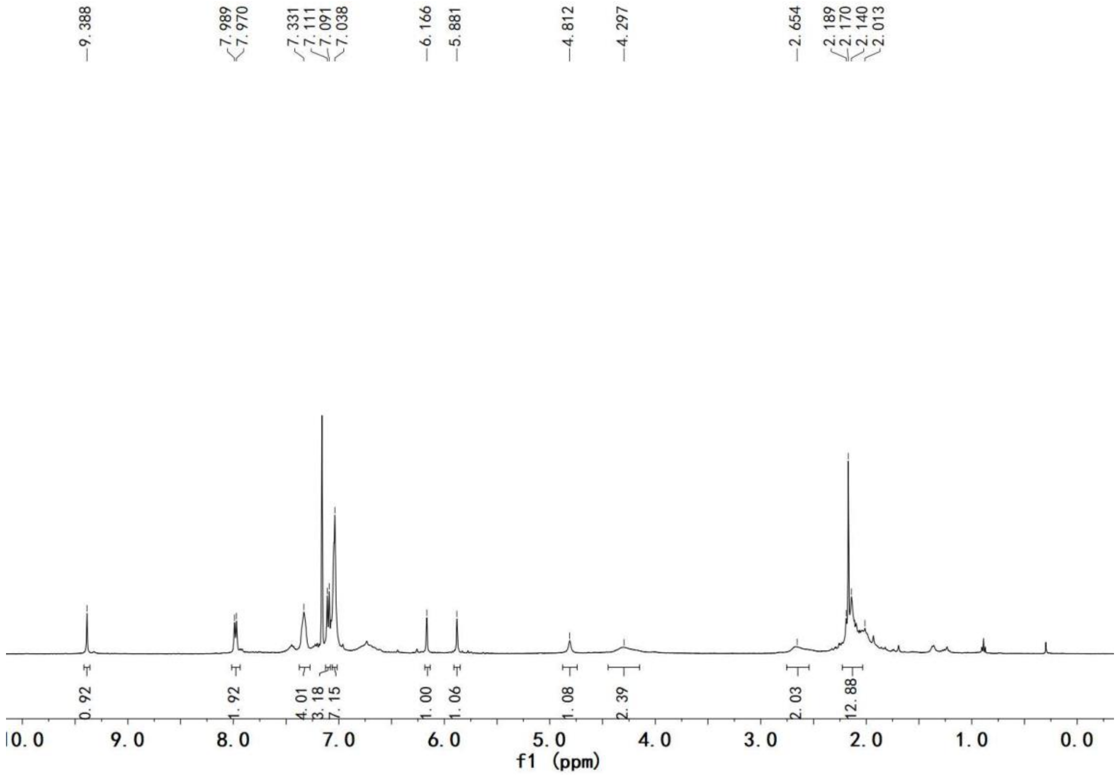


Figure S105. ^{1}H NMR spectrum of **8** (400 MHz, C_6D_6, 298 K).

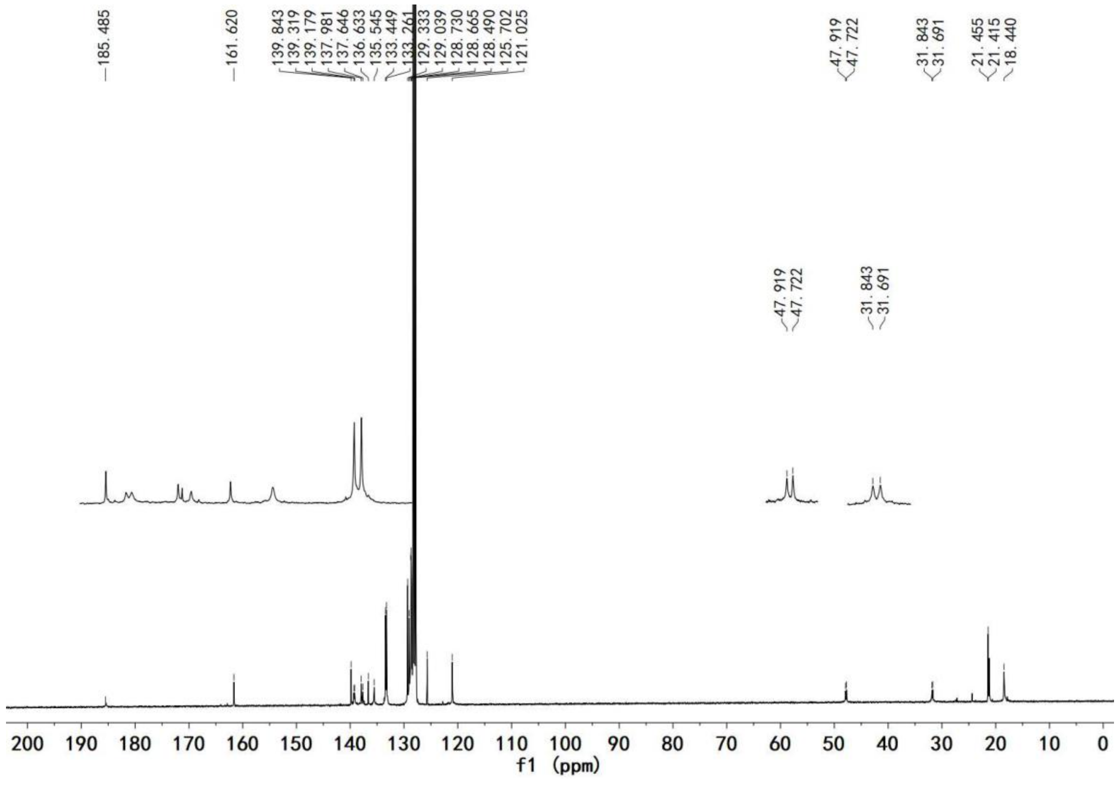


Figure S106. $^{13}C\{^{1}H\}$ NMR spectrum of **8** (101 MHz, C_6D_6, 298 K).

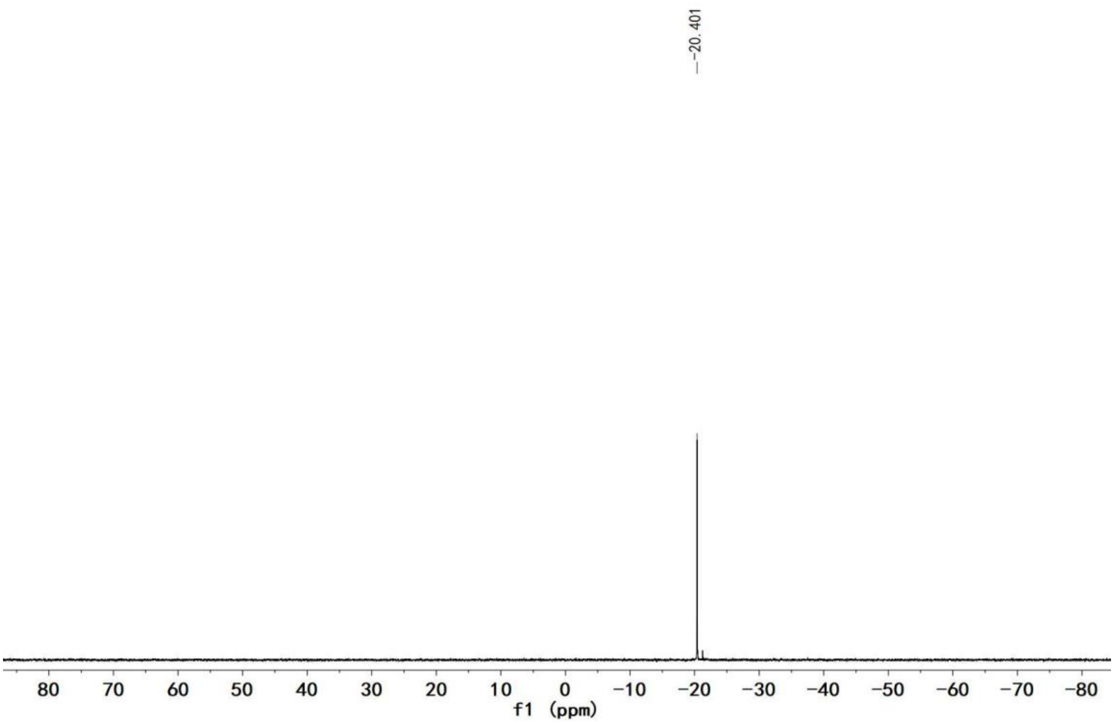
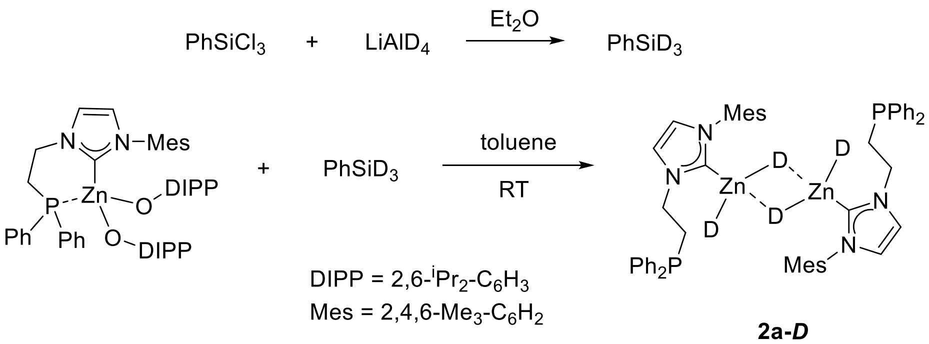


Figure S107. $^{31}P\{^1H\}$ NMR spectrum of **8** (162 MHz, C_6D_6, 298 K).

Preparation of complex 2a-*D*



2a-*D*

$PhSiD_3$ was prepared according to a slightly modified literature procedure.[3] $PhSiCl_3$ (1.3 mL, 8.1 mmol) was added to a cooled (0 °C) suspension of lithium aluminum deuteride (341 mg, 8.1 mmol) in diethyl ether. The reaction mixture was diluted with additional 8 mL of diethyl ether and stirred at 45 °C for two hours. The volatiles were vacuum transferred into a Schlenk tube and the remaining ether was removed by applying an oil pump vacuum at -30 °C. Yield: 580 mg, 64%.

$PhSiD_3$ (129 mg, 1.16 mmol) was added to a solution of zinc diaryloxide (499 mg, 0.58 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under vacuum, and then the residue was washed with hexane (3*2 mL) to eventually give **2a-*D*** as a colorless solid (235 mg, 87%

yield).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.50 (m, 8H, *phenyl*), 7.13-7.02 (m, 12H, *phenyl*), 6.73 (s, 4H, *phenyl*), 6.18 (m, 2H, ArNCH=C*H*), 5.95 (m, 2H, ArNC*H*), 4.33 (m, 4H, NCH_2), 2.82 (m, 4H, PCH_2), 2.09 (s, 18H, CH_3).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -20.0.

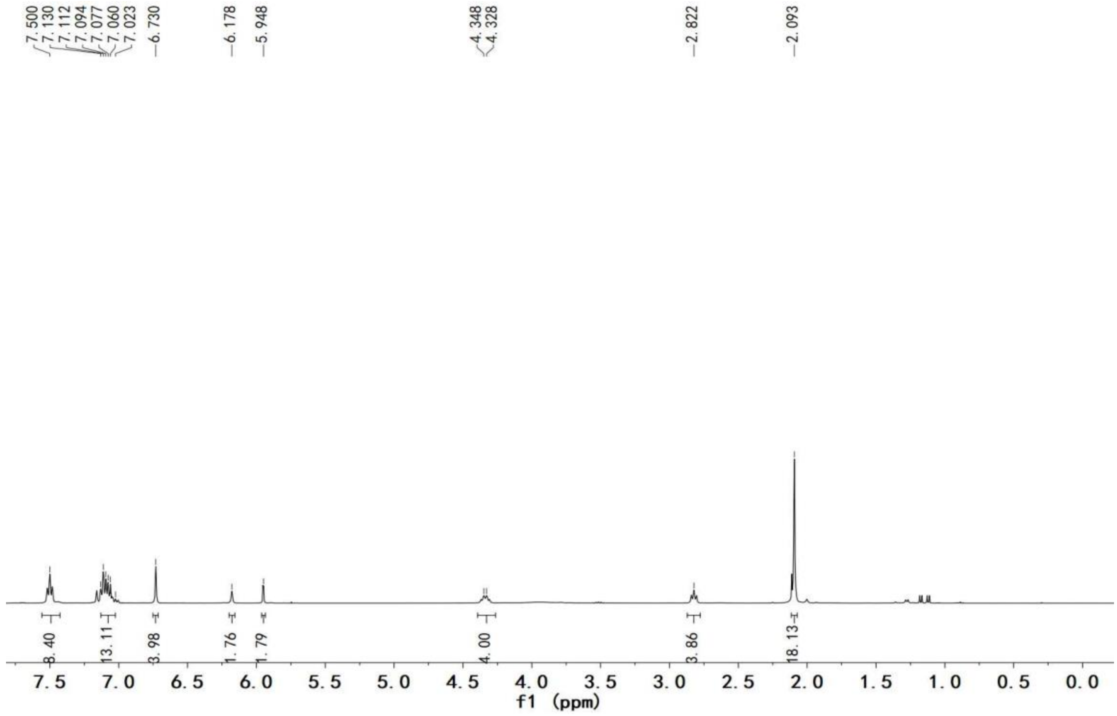


Figure S108. ^{1}H NMR spectrum of **2a-*D*** (400 MHz, C_6D_6, 298 K).

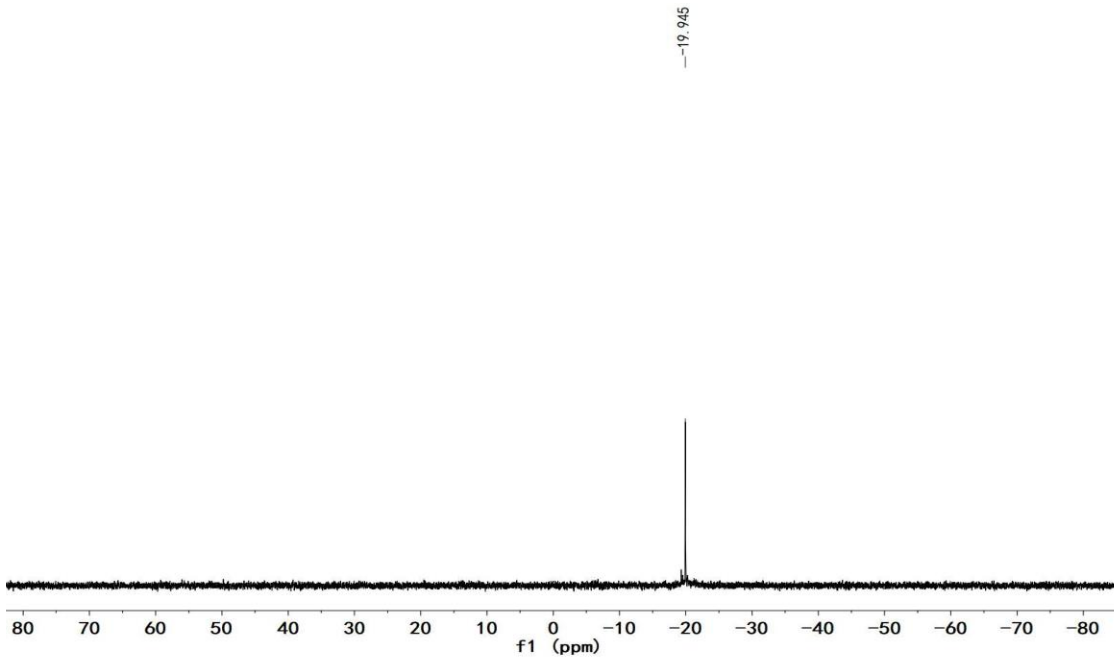


Figure S109. ^{31}P{^{1}H} NMR spectrum of **2a-*D*** (400 MHz, C_6D_6, 298 K).

Stoichiometric reaction of 2a-*D* with *p*-MePhCN

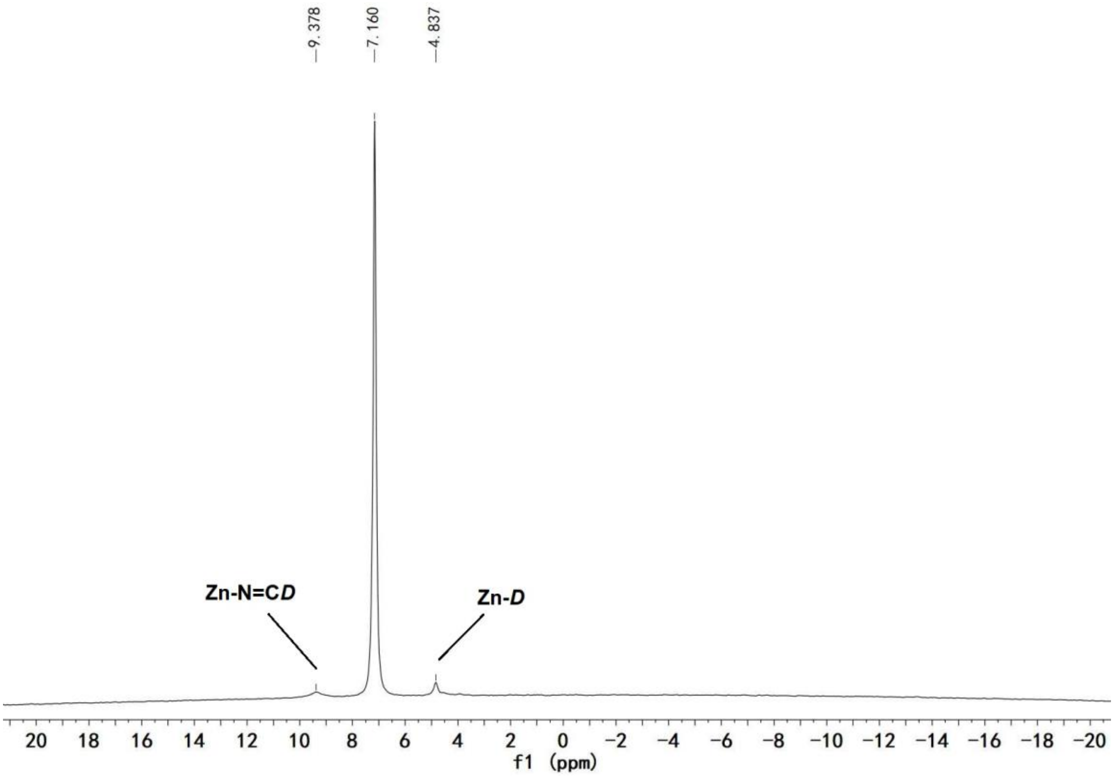


Figure S110. ^{2}H NMR spectrum of **2a-*D*** with p-MePhCN (1 : 2)

(400 MHz, 3.0 mg C_6D_6 + 0.5 mL C_6H_6, 298 K).

Kinetic studies

Hydroboration of the nitrile

In a glovebox, *p*-MePhCN (0.40 mmol), HBpin (0.84 mmol) and zinc catalyst (0.0146-0.0232 mmol, based on zinc) were mixed in C_6D_6 (1.0 mL) and transferred to an oven-dried J-Young NMR tube. The tube was sealed and removed from the glovebox, immediately frozen with liquid nitrogen and thawed just prior to loading into the NMR spectrometer. ^{1}H NMR spectra were recorded at regular intervals.

Catalyst loading of 0.0146 M:

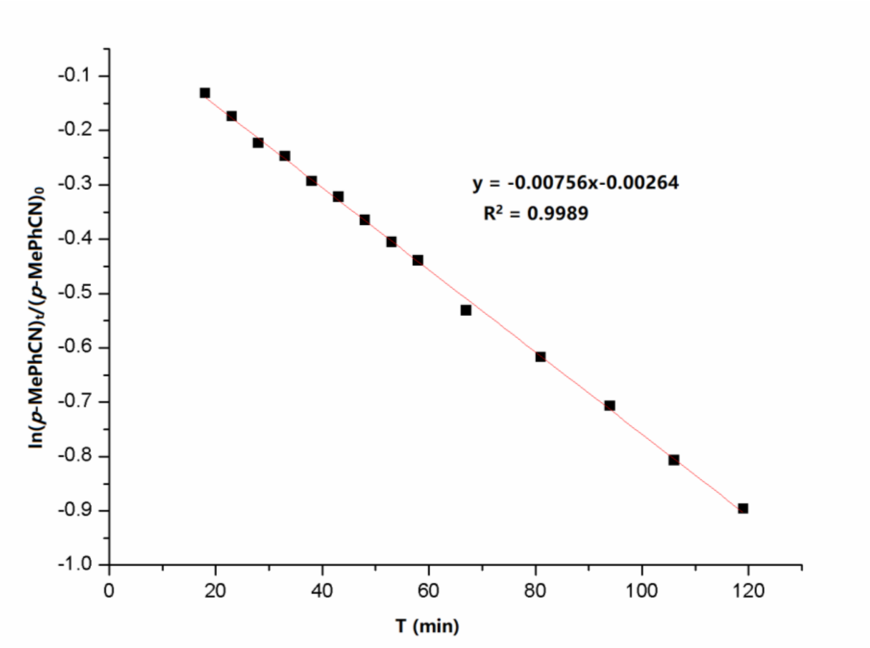


Figure S111. Plot of In(*p*-MePhCN)$_t$/(*p*-MePhCN)$_0$ versus time (min) for the reaction of *p*-tolunitrile (**3b**) and HBpin (**4**) catalyzed by complex **2a**. Conditions: *p*-tolunitrile (0.40 M), HBpin (0.84 M), complex **2a** (0.0146 M).

Catalyst loading of 0.0180 M:

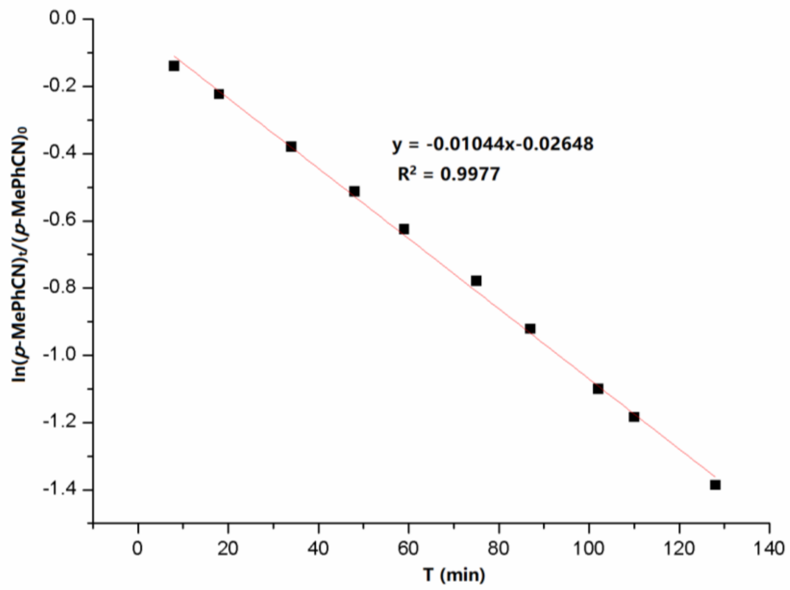


Figure S112. Plot of In(p-MePhCN)$_t$/(p-MePhCN)$_0$ versus time (min) for the reaction of *p*-tolunitrile (**3b**) and HBpin (**4**) catalyzed by complex **2a**. Conditions: *p*-tolunitrile (0.40 M), HBpin (0.84 M), complex **2a** (0.0180 M).

Catalyst loading of 0.0206 M:

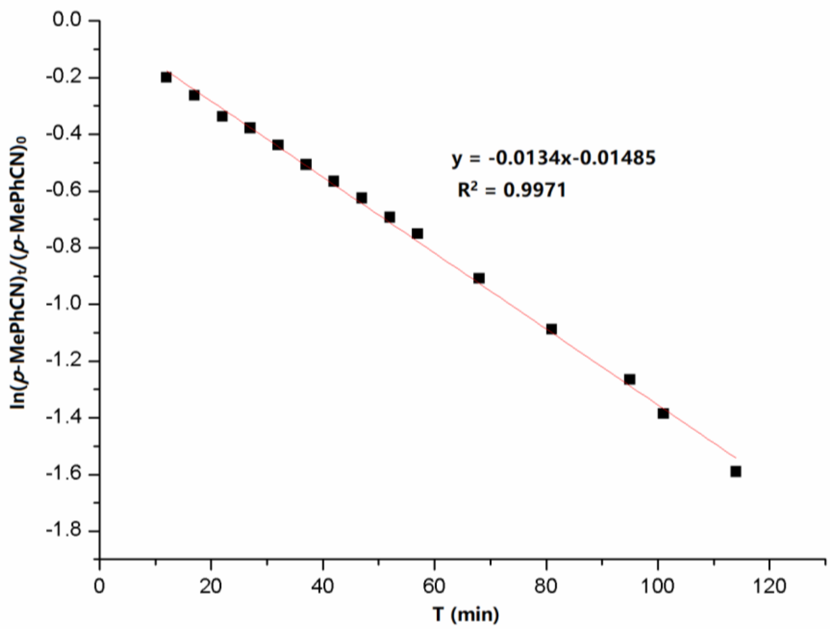


Figure S113. Plot of In(p-MePhCN)$_t$/(p-MePhCN)$_0$ versus time (min) for the reaction of *p*-tolunitrile (**3b**) and HBpin (**4**) catalyzed by complex **2a**. Conditions: *p*-tolunitrile (0.40 M), HBpin (0.84 M), complex **2a** (0.0206 M).

Catalyst loading of 0.0232 M:

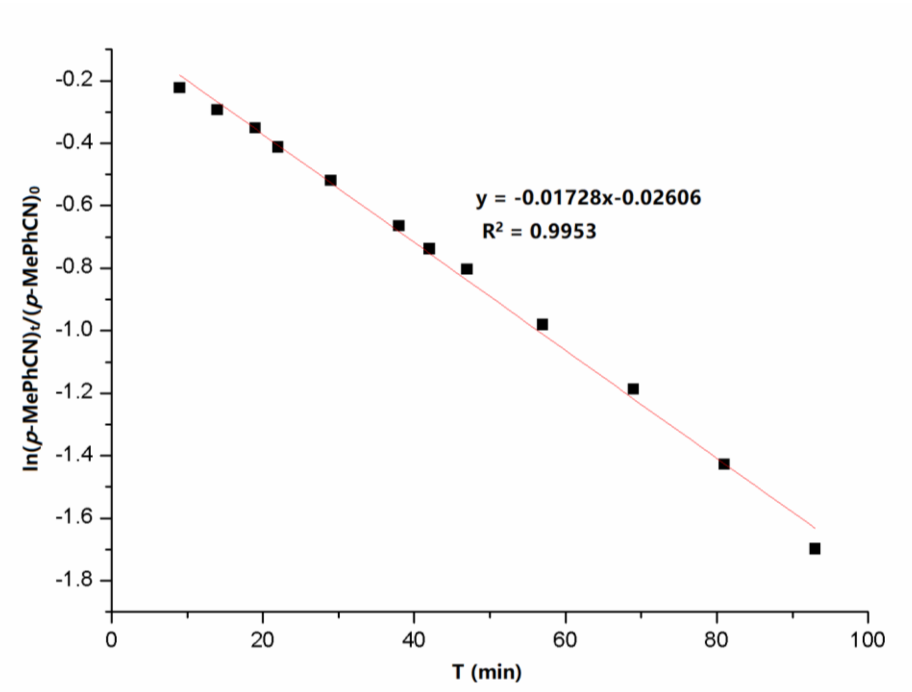


Figure S114. Plot of In(p-MePhCN)$_t$/(p-MePhCN)$_0$ versus time (min) for the reaction of p-tolunitrile (**3b**) and HBpin (**4**) catalyzed by complex **2a**. Conditions: p-tolunitrile (0.40 M), HBpin (0.84 M), complex **2a** (0.0232 M).

***p*-MePhCN loading of 2.0 M (5 equiv)**:

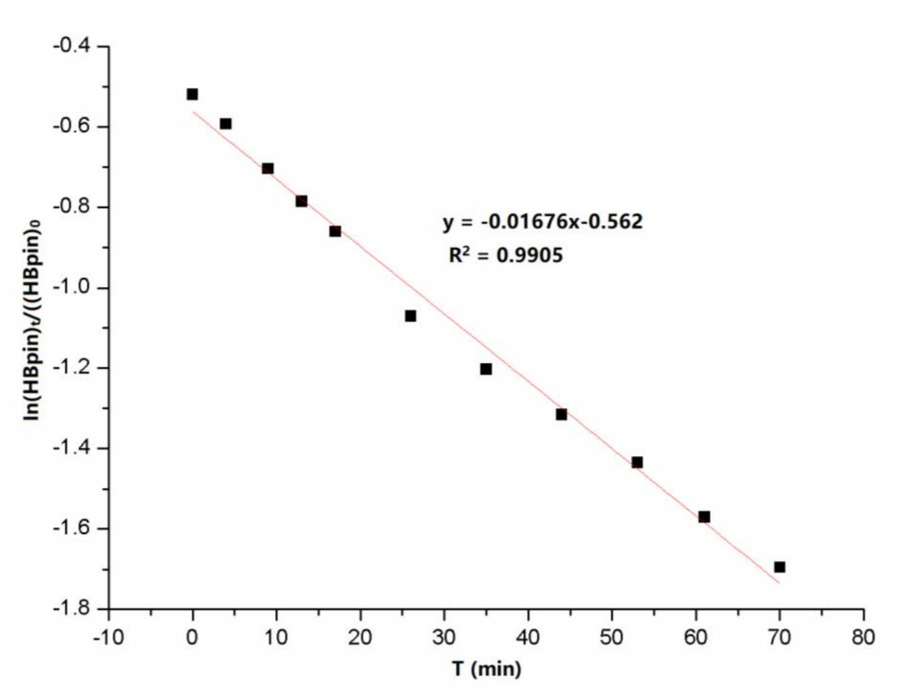
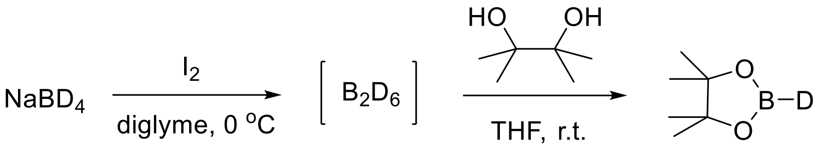


Figure S115. Plot of In(HBpin)$_t$/(HBpin)$_0$ *versus* time (min) for the reaction of p-tolunitrile (**3b**) and HBpin (**4**) catalyzed by complex **2a**. Conditions: p-tolunitrile (2.0 M), HBpin (0.84 M), complex **2a** (0.0232 M).

Preparation of DBpin[4]



A solution of iodine (5.08 g, 20 mmol) in diglyme (20 mL) was added dropwise at rt over 3 h to a solution of $NaBD_4$ (1.67 g , 40 mmol) in diglyme (20 mL). The resulting gas was vented, through a plastic cannula, into a solution of pinacol (2.36 g, 20 mmol) in THF (10 mL). After completion of addition of the iodine solution, a stream of N_2 was applied to the diglyme solution for 2 h. Distillation of the reaction mixture in vacuo (50 mbar, 40 °C) afforded *d*1-pinacolborane in 45% yield.

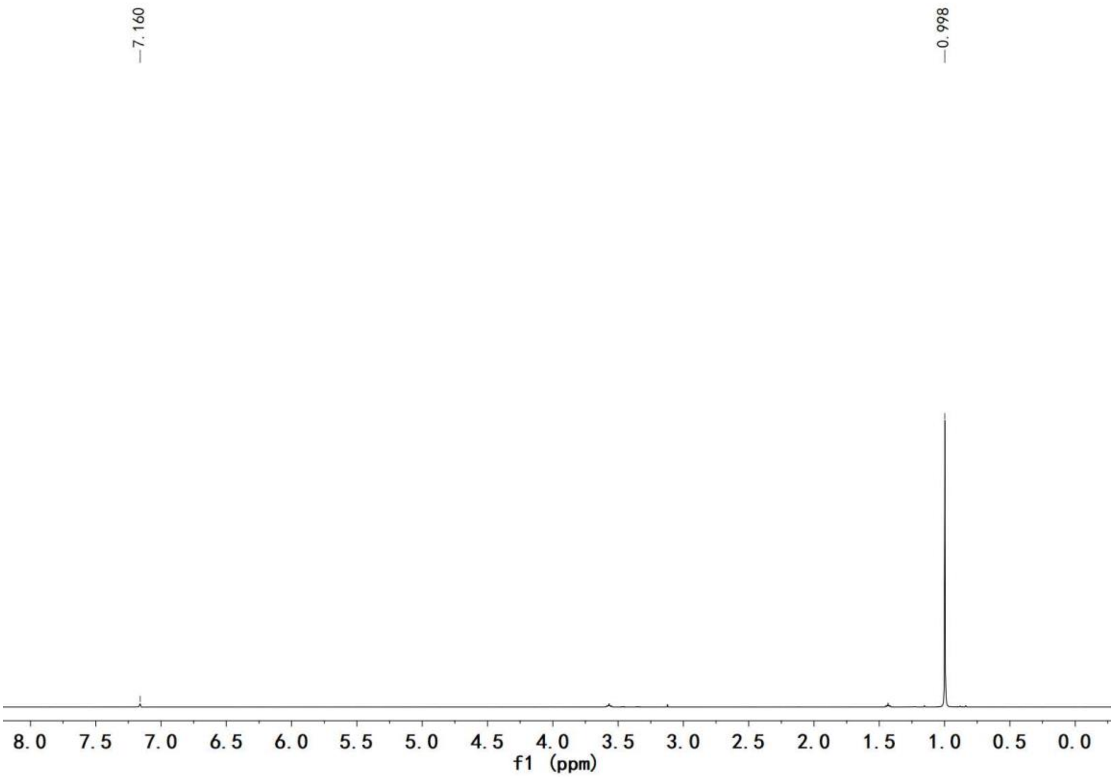


Figure S116. ^{1}H NMR spectrum of **DBpin** (400 MHz, C_6D_6, 298 K).

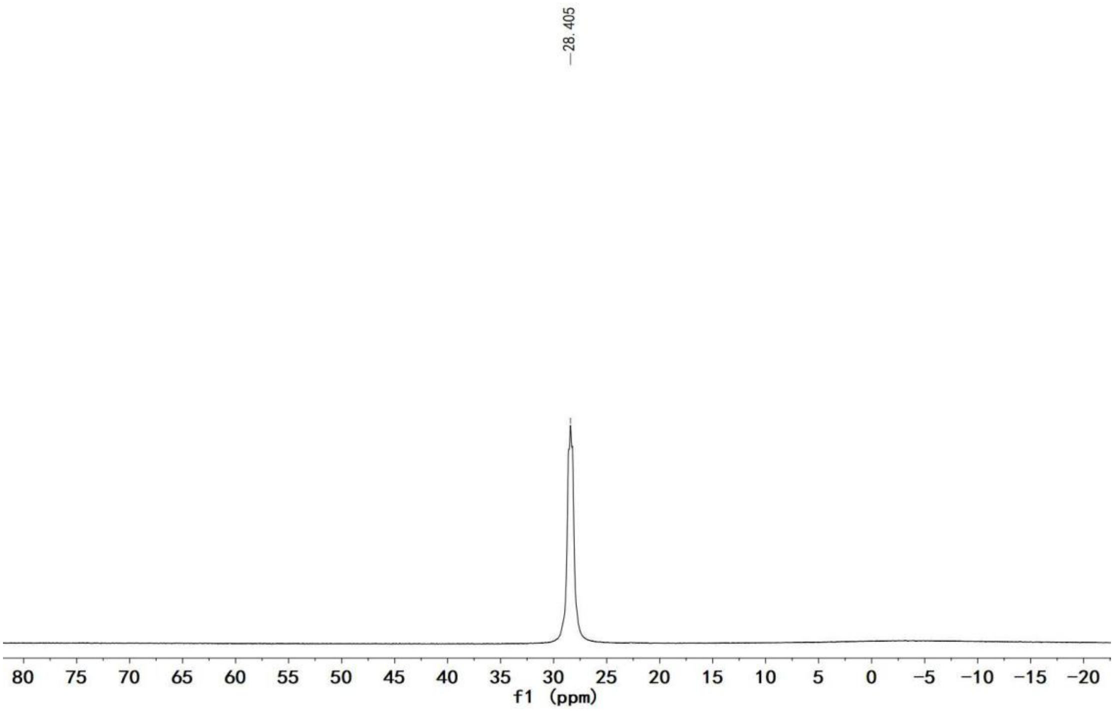


Figure S117. ^{11}B NMR spectrum of **DBpin** (128 MHz, C_6D_6, 298 K).

Deuterium labeling experiment:

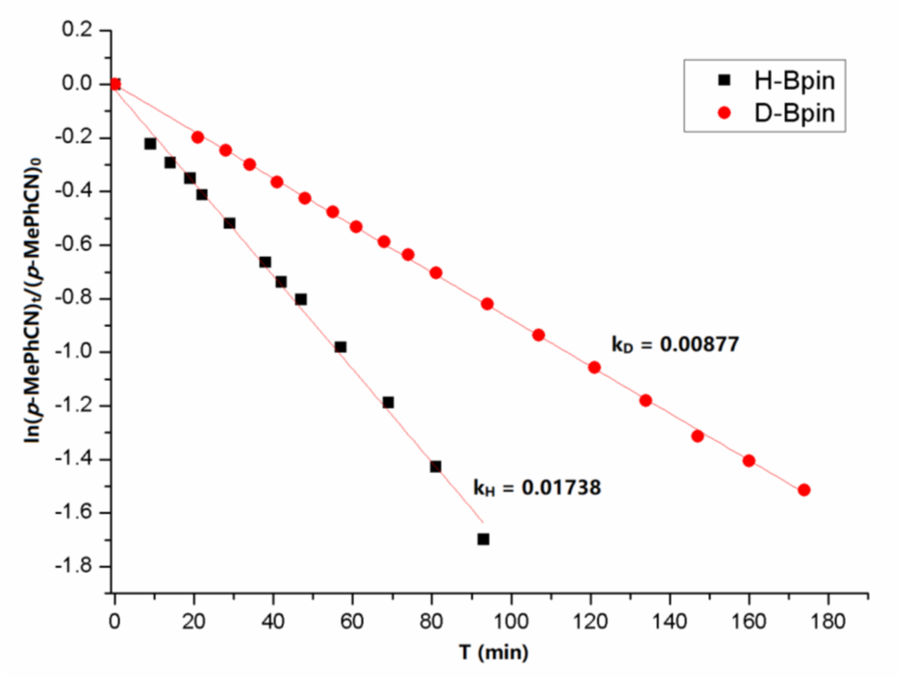
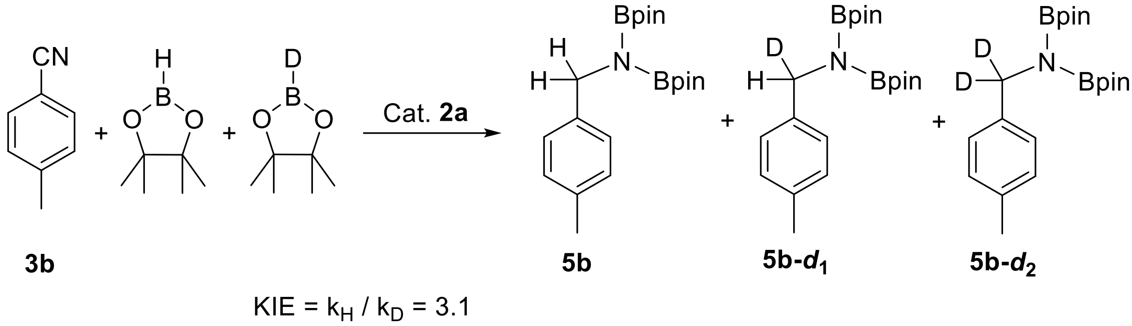


Figure S118. Plots of ln(p-MePhCN)$_t$/(p-MePhCN)$_0$ versus time for the reaction of p-tolunitrile (**3b**), DBpin and HBpin catalyzed by complex **2a**. Conditions: p-tolunitrile (0.40 M), HBpin (0.84 M), DBpin (0.84 mmol), complex **2a** (0.0232 M).

Intermolecular competition experiments:



In a nitrogen filled glove box, zinc catalyst (0.0232 mmol, based on Zn), *p*-tolunitrile (0.30 mmol), DBpin (0.63 mmol), HBpin (0.63 mmol) were mixed in C_6D_6 and transferred to an oven-dried J-Young NMR tube. The reaction mixture was allowed to stand at room temperature for 120 min till the *p*-tolunitrile was converted completely. The product was analyzed by ^{1}H NMR and a KIE value of 3.1 was determined using the integration values of ArCH_2N(Bpin)$_2$ (s, 4.59).

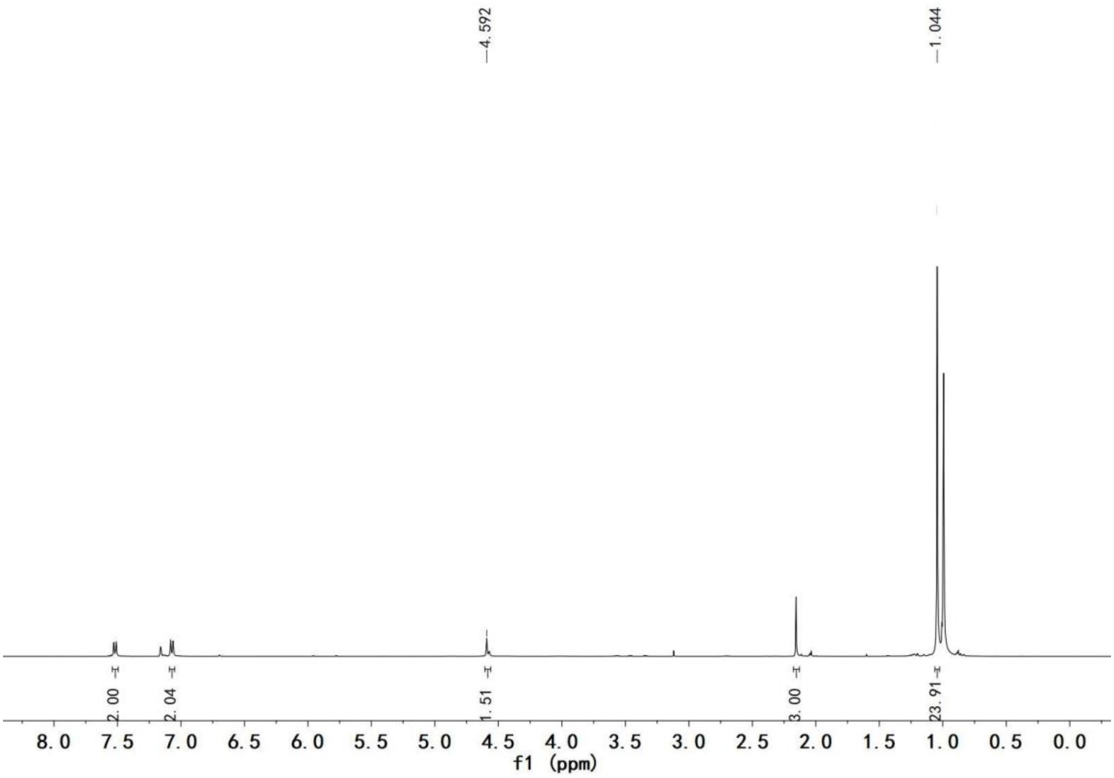


Figure S119. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K).

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