# Supporting Information

## Reactivity study of Lewis superacidic carborane-based analogue of 9-bromo-9-borafluorene towards Lewis bases

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# Experimental procedures

**General remarks**

Unless otherwise noted, the following conditions apply.

All the manipulations were carried out using standard schlenk lines or glovebox under an argon atmosphere. All the solvents were dried following standard techniques. Deuterated benzene was distilled from Na/K and stored under an argon atmosphere before use. $Ph_3P$, $Cy_3P$, $Et_3P$ and $^t$BuNC were purchased form commercial sources and used without further purification. $(C_2B_{10}H_{10})_2BBr$ (**1**)[1], $^{Me}I$*i*Pr[2], and MesNC[3] were synthesized according to the literature. Other reagents were used as received without further purification.

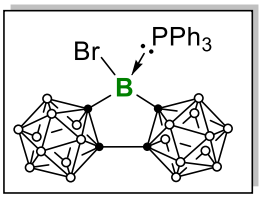
The nuclear magnetic resonance spectroscopy was recorded on a Bruker Avance-400 ($^1$H 400.1 MHz; $^{11}$B 128.5 MHz; $^{13}$C 101 MHz; $^{31}$P: 162. MHz) spectrometer at room temperature. $^{11}$B NMR, $^{11}B\{^1H\}$ spectra were referenced relative to 15% $BF_3{\cdot}OEt_2$. $^{31}P\{^1H\}$ NMR chemical shifts are relative to 85% $H_3PO_4$. High-resolution mass spectrometry (HRMS) was performed with a Thermo Fisher Scientific Q-Exactive MS System. Elemental analysis (C, H, N) was performed on a vario micro cube CHNS analyzer.

# Synthesis and characterization

### Synthetic protocols for 2

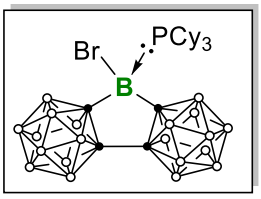
The 1 mL toluene solution of phosphines ligands (0.32 mmol) was slowly added to a solution of **1** (106 mg, 0.32 mmol) in 5 mL hexane at −78 °C. The reaction mixture was allowed to gradually warm to room temperature for a period of 4 h. The precipitate was collected through filtration and washed with hexane (3*2 mL). The remaining solid was dried under high vacuum to give the crude product as a white solid. The analytically pure product was crystallized from concentrated toluene solution at −30 °C for 12 h to yield **2** as a colorless crystalline solid.

For **2a:**




**$^{1}$H NMR** (400 MHz, $C_6D_6$): δ [ppm] = 1.88 to 3.78 (m, 20H, B*H*), 6.72 to 6.77 (m, 2H, *H* of Ph), 6.86 to 6.96 (m, 7H, *H* of Ph), 7.36 to 7.42 (m, 2H, *H* of Ph), 7.90 to 7.95 (m, 4H, *H* of Ph). **$^{1}$H{$^{11}$B} NMR** (400 MHz, $C_6D_6$): δ [ppm] = 2.26 (s, 2H, B*H*), 2.61 (s, 8H, B*H*), 2.85 (s, 3H, B*H*), 3.04 (s, 5H, B*H*), 4.08 (s, 2H, B*H*), 6.72 to 6.78 (m, 2H, *H* of Ph), 6.87 to 6.96 (m, 7H, *H* of Ph), 7.37 to 7.42 (m, 2H, *H* of Ph), 7.90 to 7.95 (m, 4H, *H* of Ph). **$^{11}$B NMR** (128 MHz, $C_6D_6$): δ [ppm] = 1.09 (d. *J* = 145.3 Hz, $B_{carborane}$), −3.87 (d. *J* = 156.4 Hz, $B_{carborane}$), −7.00 to −10.70 (m, $B_{carborane}$). **$^{11}$B{$^{1}$H} NMR** (128 MHz, $C_6D_6$): δ [ppm] = 1.06 (s, $B_{carborane}$), -3.85 (s, $C_{carbene}$B), −6.15 (s, $B_{carborane}$), −7.39 (s, $B_{carborane}$), −10.18 (s, $B_{carborane}$). **$^{31}$P{$^{1}$H} NMR** (162 MHz, $C_6D_6$): δ [ppm] = 4.14 (q. *J* = 125.8 Hz). **$^{13}$C{$^{1}$H} NMR** (100 MHz, $C_6D_6$): δ [ppm] = 80.8 (s, $C_{carborane}$), 121.4 (d, $J_{P\text{-}C}$ = 57.6 Hz. *C* of Ph), 124.1 (d, $J_{P\text{-}C}$ = 68.3 Hz. *C* of Ph), 128.2 (d, $J_{P\text{-}C}$ = 10.9 Hz. *C* of Ph), 128.7 (d, $J_{P\text{-}C}$ = 11.2 Hz. *C* of Ph), 132.7 (d, $J_{P\text{-}C}$ = 2.9 Hz. *C* of Ph), 133.2 (d, $J_{P\text{-}C}$ = 3.0 Hz. *C* of Ph), 134.7 (d, $J_{P\text{-}C}$ = 8.6 Hz. *C* of Ph), 135.7 (d, $J_{P\text{-}C}$ = 9.3 Hz. *C* of Ph). **Elemental analysis**: calcd. for $C_{22}H_{35}B_{21}BrP$, C, 41.46; H, 5.53; found C, 41.59; H, 5.84. Yield: 78 % (150.9 mg, 0.25 mmol).

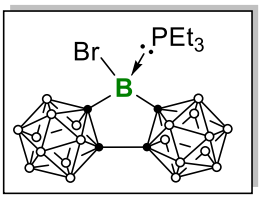
For **2b:**




**$^{1}$H NMR** (400 MHz, $C_6D_6$): δ [ppm] = 1.29 to 1.52 (m, 12H, *H* of Cy), 1.78 to 2.07 (m, 22H, *H* of Cy), 2.18 to 3.96 (m, 20H, B*H*). **$^{1}$H{$^{11}$B} NMR** (400 MHz, $C_6D_6$): δ [ppm] = 1.26 to 1.52 (m, 12H, *H* of Cy), 1.78 to 1.20 (m, 21H, *H* of Cy), 2.28 to 2.48 (s, 17H, B*H*), 2.72 to 2.80 (s, 1H, B*H*), 3.22 (s, 1H, B*H*), 3.61 (s, 1H, B*H*). **$^{11}$B NMR** (128 MHz, $C_6D_6$): δ [ppm] = 0.50 (d. *J* = 130.8 Hz, $B_{carborane}$), −5.37 to −8.29 (m, $B_{carborane}$). **$^{11}$B{$^{1}$H} NMR** (128 MHz, $C_6D_6$): δ [ppm] = 0.42 (s, $B_{carborane}$), -4.61 (s, ***C*$_{carbene}$B**), −5.31 (s, $B_{carborane}$), −6.38 (s, $B_{carborane}$), −7.89 (s, $B_{carborane}$), −10.32 (s, $B_{carborane}$). **$^{31}$P{$^{1}$H} NMR** (162 MHz, $C_6D_6$): δ [ppm] = 8.8 (q. *J* = 140.3 Hz). **$^{13}$C{$^{1}$H} NMR** (100 MHz, $C_6D_6$): δ [ppm] = 25.6 (d, $J_{P\text{-}C}$ = 1.3 Hz. *C* of Cy), 25.8 (d, $J_{P\text{-}C}$ = 1.3 Hz. *C* of Cy), 26.9 (d, $J_{P\text{-}C}$ = 11.5 Hz. *C* of Cy), 27.6 (d, $J_{P\text{-}C}$ = 10.5 Hz. *C* of Cy), 27.9 (d, $J_{P\text{-}C}$ = 9.6 Hz. *C* of Cy), 28.6 (d, $J_{P\text{-}C}$ = 2.1 Hz. *C* of Cy),

29.6 (d, $J_{P\text{-}C}$ = 5.6 Hz. *C* of Cy), 29.7 (d, $J_{P\text{-}C}$ = 4.6 Hz. *C* of Cy), 32.2 (d, $J_{P\text{-}C}$ = 23.1 Hz. *C* of Cy), 35.1 (d, $J_{P\text{-}C}$ = 30.1 Hz. *C* of Cy), 80.7 (s, $C_{carborane}$). **HRMS**: $[M\text{-}Br]^+$ calcd. for $C_{22}B_{21}H_{53}P$, 575.5984; found 575.5960. Yield: 86 % (180.1 mg, 0.27 mmol).

For **2c:**

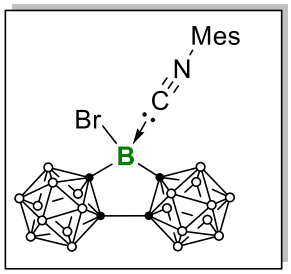



**$^1$H NMR** (400 MHz, $C_6D_6$): δ [ppm] = 0.44 to 0.51 (m, 9H, *H* of $CH_2CH_3$), 1.54 (quintet, *J* = 8.5 Hz, 6H, $CH_2CH_3$), 2.11 to 3.77 (br. m, 20H, B*H*). **$^1$H{$^{11}$B} NMR** (400 MHz, $C_6D_6$): δ [ppm] = 0.44 to 0.52 (m, 9H, $CH_2CH_3$), 1.54 (quintet, *J* = 8.4 Hz, 6H, $CH_2CH_3$), 2.18 (s, 2H, B*H*), 2.63 (s, 2H, B*H*), 2.74 (s, 4H, B*H*), 2.80 (s, 2H, B*H*), 2.89 (s, 2H, B*H*), 3.00 (s, 2H, B*H*), 3.06 (s, 4H, B*H*), 3.84 (s, 2H, B*H*). **$^{11}$B NMR** (128 MHz, $C_6D_6$): δ [ppm] = 0.49 (d. *J* = 149.9 Hz, $B_{carborane}$), −3.87 (d. *J* = 149.7 Hz, $B_{carborane}$), −5.35 to −10.99 (m, $B_{carborane}$). **$^{11}$B{$^1$H} NMR** (128 MHz, $C_6D_6$): δ [ppm] = 0.30 (s, $B_{carborane}$), -4.03 (s, $C_{carbene}$B), −5.97 (s, $B_{carborane}$), −7.61 (s, $B_{carborane}$), −10.50 (s, $B_{carborane}$). **$^{31}$P{$^1$H} NMR** (162 MHz, $C_6D_6$): δ [ppm] = 1.5 (q. *J* = 123.0 Hz). **$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$): δ [ppm] = 7.5 (d, $J_{P\text{-}C}$ = 6.6 Hz. $CH_2CH_3$), 13.9 (d, $J_{P\text{-}C}$ = 38.3 Hz. $CH_2CH_3$), 80.9 (s). **HRMS**: $[M\text{-}Br]^+$ calcd. for $C_{10}B_{21}H_{35}P$, 413.4576; found 413.4565. Yield: 81 % (127.6 mg, 0.26 mmol).

**Synthetic protocols for 3**

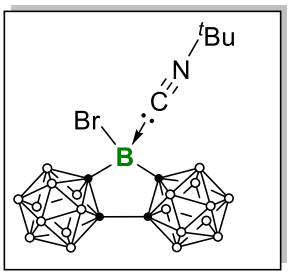
The 1 mL toluene solution of isocyanide (0.32 mmol) was slowly added to a solution of **1** (106 mg, 0.32 mmol) in 5 mL hexane at −78 °C. The reaction mixture was allowed to gradually warm to room temperature for a period of 4 h. The precipitate was collected through filtration and washed with hexane (3*2 mL). The remaining solid was dried under high vacuum to give the crude product as a white solid. The analytically pure product was crystallized from concentrated toluene solution at −30 °C for 12 h to yield crystalline solids.

For **3a:**




**$^1$H NMR** (400 MHz, $C_6D_6$): δ [ppm] = 1.75 (s, 3H, $CCH_3$), 1.78 (s, 6H, $CCH_3$), 2.13 to 3.63 (br. m, 20H, B*H*), 6.10 (s, 2H, *H* of Ar). **$^1$H{$^{11}$B} NMR** (400 MHz, $C_6D_6$): δ [ppm] = 1.75 (s, 3H, $CCH_3$), 1.79 (s, 6H, $CCH_3$), 2.49 (s, 2H, B*H*), 2.69 (s, 4H, B*H*), 2.87 (s, 2H, B*H*), 2.98 (s, 6H, B*H*), 3.06 (s, 2H, $NCH_3$), 3.39 (s, 2H, B*H*), 3.70 (s, 2H, B*H*). **$^{11}$B NMR** (128 MHz, $C_6D_6$): δ [ppm] = 0.11 (d. *J* = 157.6 Hz, $B_{carborane}$), −3.40 (d. *J* = 158.0 Hz, $B_{carborane}$), −6.18 to −11.62 (m, $B_{carborane}$), −12.84 (s, $C_{isocyanide}B$). **$^{11}$B{$^1$H} NMR** (128 MHz, $C_6D_6$): δ [ppm] = 0.08 (s, $B_{carborane}$), −3.43 (s, $C_{isocyanide}B$), −6.61 (s, $B_{carborane}$), −9.13 (s, $B_{carborane}$), −11.00 (s, $B_{carborane}$), −12.85 (s, $C_{isocyanide}B$). **$^{13}$C{$^1$H} NMR** (100 MHz, $C_6D_6$): δ [ppm] = 17.5 (s, $CCH_3$), 20.7 (s, $CCH_3$), 80.7 (s, $C_{carborane}$), 129.1 (s, *C* of Ar), 137.4 (s, *C* of Ar), 144.1 (s, *C* of Ar). **HRMS (LIFDI)**: calc. for $C_{14}B_{21}H_{31}BrN$, 519.3739; found 519.3736. Yield: 76 % (125.8 mg, 0.24 mmol).

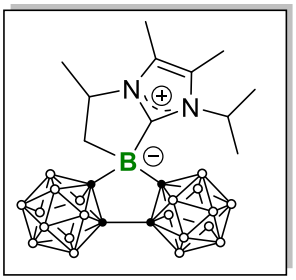
For **3b:**




**$^{1}$H NMR** (400 MHz, $C_6D_6$): δ [ppm] = 0.45 (s, 9H, C($CH_3$)$_3$), 2.11 to 3.77 (br. m, 20H, B*H*). **$^{1}$H{$^{11}$B} NMR** (400 MHz, $C_6D_6$): δ [ppm] = 0.46 (s, 9H, C($CH_3$)$_3$), 2.35 (s, 2H, B*H*), 2.67 (s, 4H, B*H*), 2.86 (s, 2H, B*H*), 2.94 (s, 2H, B*H*), 3.05 (s, 6H, B*H*), 3.15 (s, 2H, NC$H_3$), 3.62 (s, 2H, B*H*). **$^{11}$B NMR** (128 MHz, $C_6D_6$): δ [ppm] = 0.04 (d. *J* = 146.6 Hz, $B_{carborane}$), −3.44 (d. *J* = 153.5 Hz, $C_{isocyanide}B$), −6.25 to −10.04 (m, $B_{carborane}$), −13.88 (s, $C_{isocyanide}B$). **$^{11}$B{$^{1}$H} NMR** (128 MHz, $C_6D_6$): δ [ppm] = −0.19 (s, $B_{carborane}$), −3.68 (s, $C_{isocyanide}B$), −6.97 (s, $B_{carborane}$), −9.43 (s, $B_{carborane}$), −11.43 (s, $B_{carborane}$), −13.96 (s, $C_{isocyanide}B$). **$^{13}$C{$^{1}$H} NMR** (100 MHz, $C_6D_6$): δ [ppm] = 27.2 (s, C($CH_3$)$_3$), 62.1 (s, $C$($CH_3$)$_3$), 80.7 (s, $C_{carborane}$). **HRMS** [M-Br]$^+$ calcd. for $C_9B_{21}H_{29}N$, 378.4399; found 378.4394. Yield: 87 % (127.3 mg, 0.28 mmol).

**Synthesis of 4**

Path A: In an argon-filled glove box, $^{Me}$I*i*Pr (60 mg, 0.32 mmol) was added to a solution of **1** (106 mg, 0.32 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature, leading to an immediate color change to orange. The orange suspension was further stirred at room temperature for 12 h, then all volatiles were removed under high vacuum. The obtained solid was washed with hexane (3*2 mL). The remaining solid was extracted with 2 mL toluene. The toluene solution was concentrated and stored at −30 °C for 12 h to yield **4** an orange crystalline solid.

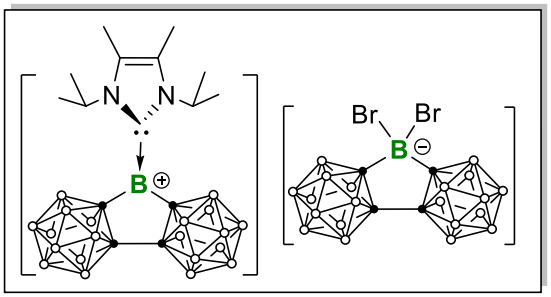



**$^{1}$H NMR** (400 MHz, $C_6D_6$): δ [ppm] = 0.84 (d, *J* = 6.4 Hz, 3H, CH(C$H_3$)$_2$), 0.99 (d, *J* = 6.9 Hz, 3H, CH(C$H_3$)$_2$), 1.07 (d, *J* = 7.0 Hz, 3H, CH(C$H_3$)$_2$), 1.18 (s, 3H, CC$H_3$), 1.33 (dd, *J* = 14.5, 7.8 Hz, 1H, BC$H_2$CH), 1.42 (s, 3H, CC$H_3$), 1.89 (dd, *J* = 14.8, 7.7 Hz, 1H, BC$H_2$CH), 3.67 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.98 (sept, J = 6.8 Hz, 1H, C*H*CH$_3$). **$^{1}$H{$^{11}$B} NMR** (400 MHz, $C_6D_6$): δ [ppm] = 0.85 (d, *J* = 6.4 Hz, 3H, CH(C$H_3$)$_2$), 1.00 (d, *J* = 6.9 Hz, 3H, CH(C$H_3$)$_2$), 1.08 (d, *J* = 7.0 Hz, 3H, CH(C$H_3$)$_2$), 1.19 (s, 3H, CC$H_3$), 1.33 (dd, *J* = 14.4, 6.7 Hz, 1H, BC$H_2$CH), 1.42 (s, 3H, CC$H_3$), 1.89 (dd, J = 14.3, 7.9 Hz, 1H, BC$H_2$CH), 2.25 (s, 1H, B*H*), 2.45 (s, 1H, B*H*), 2.61 (s, 1H, B*H*), 2.84 to 3.09 (m, 14H, B*H*), 3.36 (s, 1H, B*H*), 3.50 (s, 2H, B*H*), 3.66 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 4.98 (sept, *J* = 6.8 Hz, 1H, C*H*CH$_3$). **$^{11}$B NMR** (128 MHz, $C_6D_6$): δ [ppm] = −0.96 (d. *J* = 128.1 Hz, $B_{carborane}$), −3.87 (d. *J* = 171.3 Hz, $B_{carborane}$), −6.11 to −7.04 (m, $B_{carborane}$), −8.03 (s, $CH_2B$), −9.57(s, $B_{carborane}$). **$^{11}$B{$^{1}$H} NMR** (128 MHz, $C_6D_6$): δ [ppm] = −1.26 (s, $C_{carbene}B$), −4.19 (s, $B_{carborane}$), −7.31 (s, $B_{carborane}$), −8.11 (s, $CH_2B$), −9.40 (s, $B_{carborane}$). **$^{3}$C{$^{1}$H} NMR** (100 MHz, $C_6D_6$): δ [ppm] = 7.9 (s, C($CH_3$)), 9.9 (s, C($CH_3$)), 21.0 (s, CH($CH_3$)), 21.3 (s, C($CH_3$)), 22.8 (s, C($CH_3$)), 38.1 (br, s, B$CH_2$), 50.75 (s, *C*H(CH$_3$)$_2$), 54.2 (s, *C*HCH$_3$), 80.6 (s, $C_{carborane}$), 128.2 (s, *C*CH$_3$) **HRMS** (LIFDI): calc. for $C_{15}B_{21}N_2H_{39}$, 474.5213; found 474.5207. Yield: 34 % (51.6 mg, 0.11 mmol).

Path B: In an argon-filled glove box, a 1 mL benzene solution of $^{Me}I$*i*Pr (30 mg, 0.16 mmol) was dropwise added to a 3 mL benzene solution of **1** (106 mg, 0.32 mmol). The reaction mixture was stirred for 10 min to afford a yellowish-green solid **5**. Then added $^{Me}I$*i*Pr (30 mg, 0.16 mmol) dropwise to it and stir overnight as the color of the solution changes to orange. The **5** was obtained after the removal of all volatiles under high vacuum.

Note: **5** decomposes in $CDCl_3$ and $CD_2Cl_2$. Therefore, NMR spectra of **5** were acquired in $C_6D_6$ despite its poor solubility in $C_6D_6$. As a consequence, the NMR signals are weak and some of the signals were not observed.

**$^1$H NMR** (500 MHz, $C_6D_6$): δ [ppm] = 0.74 (d, *J* = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.28 (s, 6H, C*H*$_3$), 3.27 (sept, J = 6.8 Hz, C*H*(CH$_3$)$_2$), 2.06 to 3.44 (br. m, B*H*).




**$^{11}$B NMR** (160 MHz, $C_6D_6$): δ [ppm] = –0.25 (s), –3.71 (d, *J* = 142.5 Hz, *B*$_{carborane}$), –5.33 to –8.15 (m, *B*$_{carborane}$). **$^{11}$B{$^1$H} NMR** (160 MHz, $C_6D_6$): δ [ppm] = –0.26 (s), –3.87 (s, *B*$_{carborane}$), –7.30 (m, *B*$_{carborane}$). **$^{13}$C{$^1$H} NMR** (125 MHz, $C_6D_6$): δ [ppm] = 7.4 (s, *C*H$_3$), 21.6 (s, *C*H$_3$), 50.2 (s, *C*HCH$_3$), 80.4 (s, *C*$_{carborane}$), 128.0 (s, *C*CH$_3$) HRMS (m/z): [M]+ calcd. for $C_{15}H_{40}B_{21}N_2$, 479.5146; found 479.5140. Yield: 69 % (112.4 mg, 0.12 mmol).

# NMR Spectroscopy

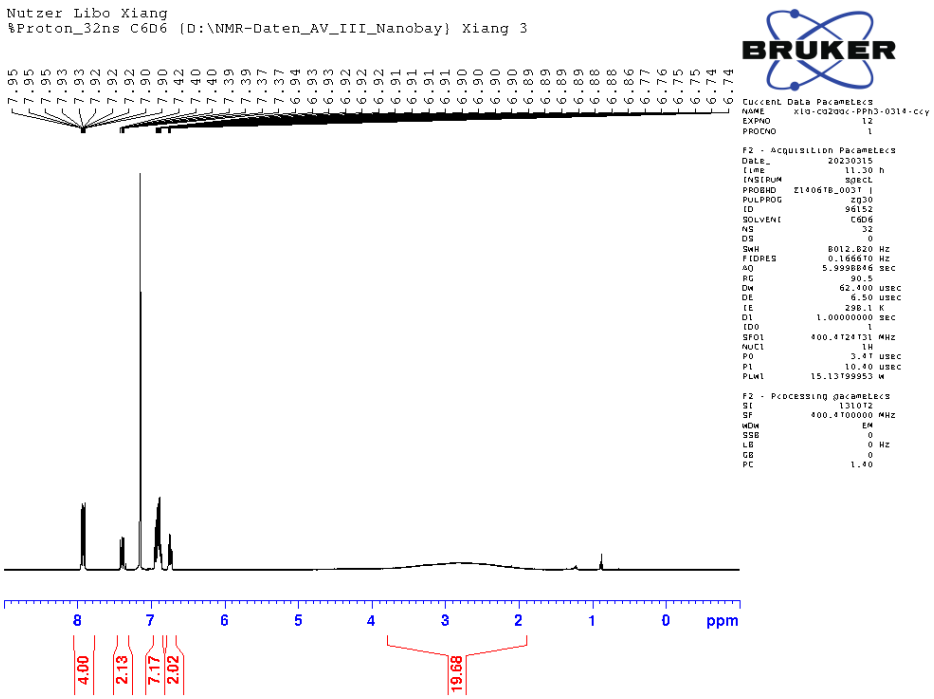



**Figure S1**. $^{1}H$ NMR spectra of **2a** in $C_6D_6$ at 298 K.

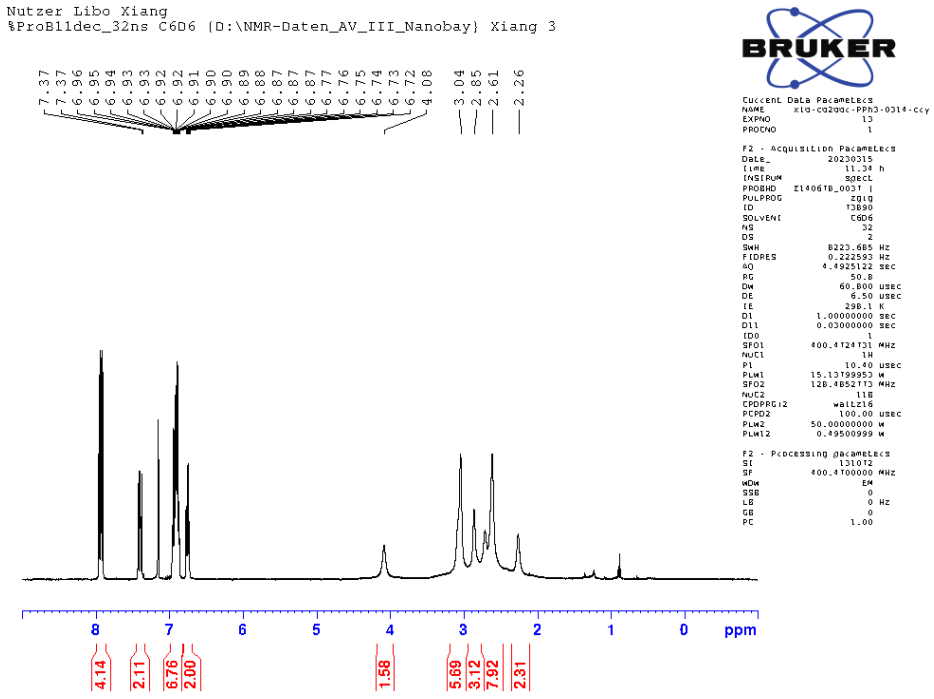



**Figure S2**. $^{1}H\{^{11}B\}$ NMR spectra of **2a** in $C_6D_6$ at 298 K.

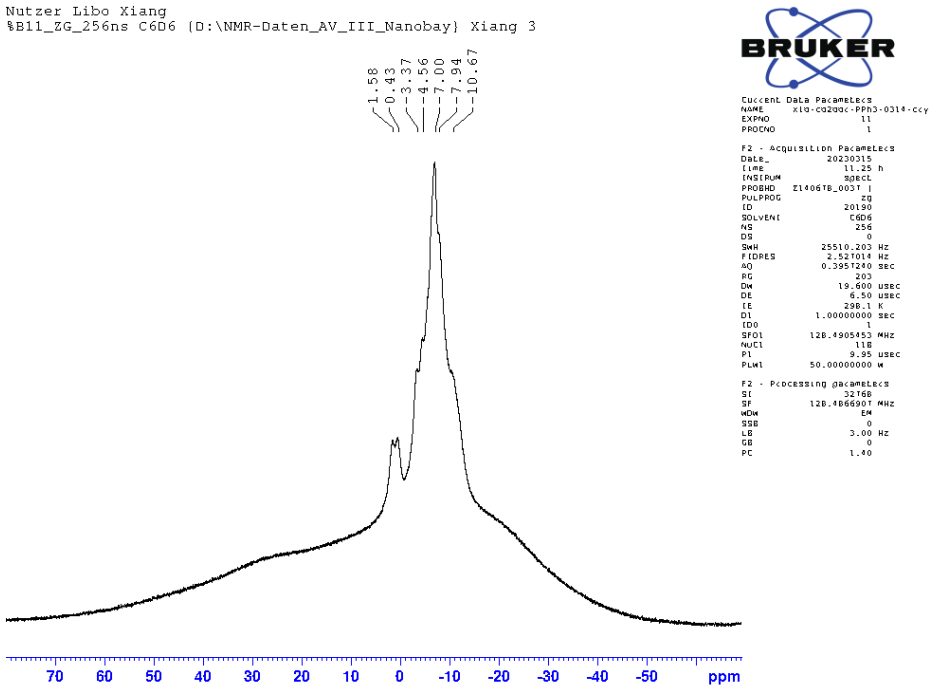



**Figure S3**. $^{11}B$ NMR spectra of **2a** in $C_6D_6$ at 298 K.

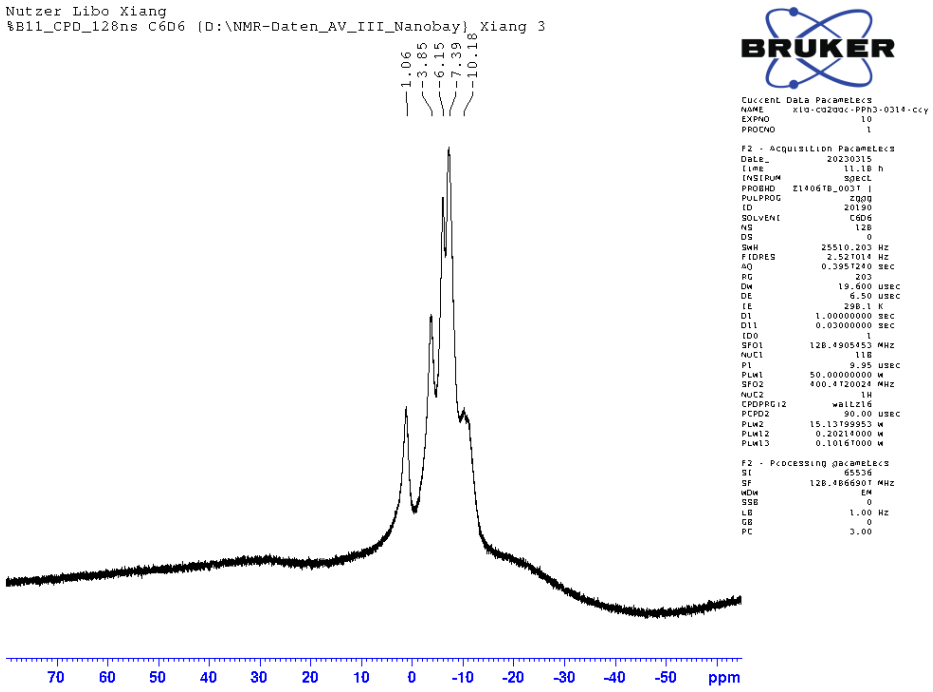



**Figure S4**. $^{11}B\{^1H\}$ NMR spectra of **2a** in $C_6D_6$ at 298 K.

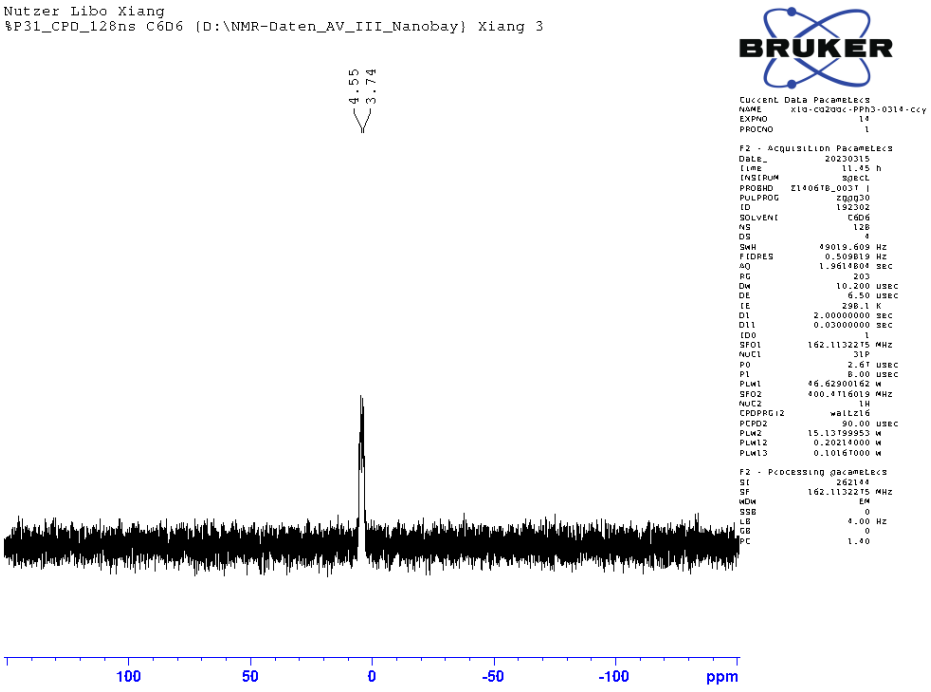



**Figure S5.** $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in $C_6D_6$ at 298 K.

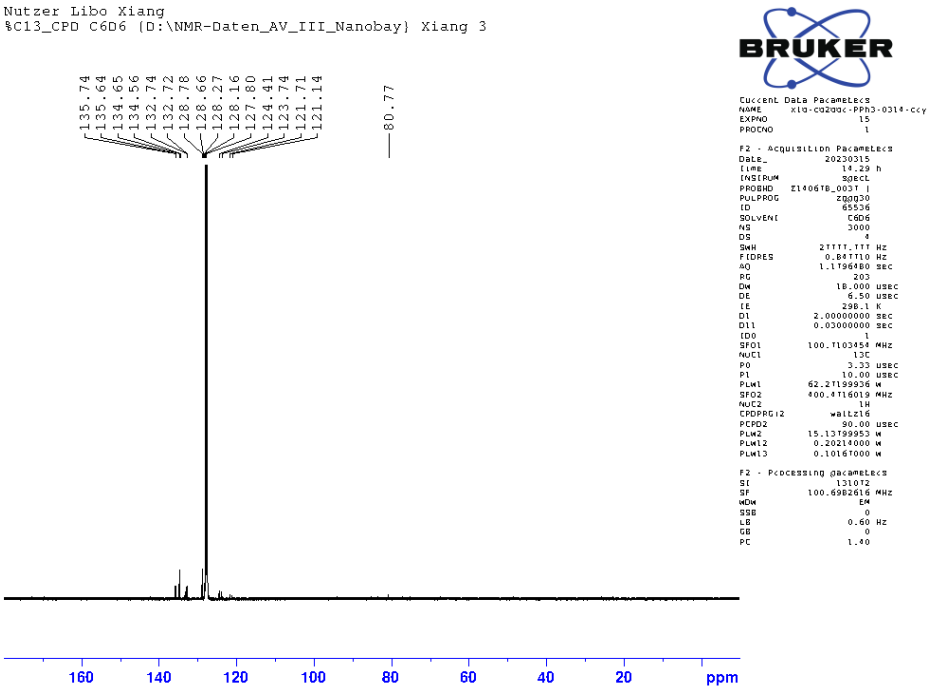



**Figure S6**. $^{13}C\{^{1}H\}$ NMR spectra of **2a** in $C_6D_6$ at 298 K.

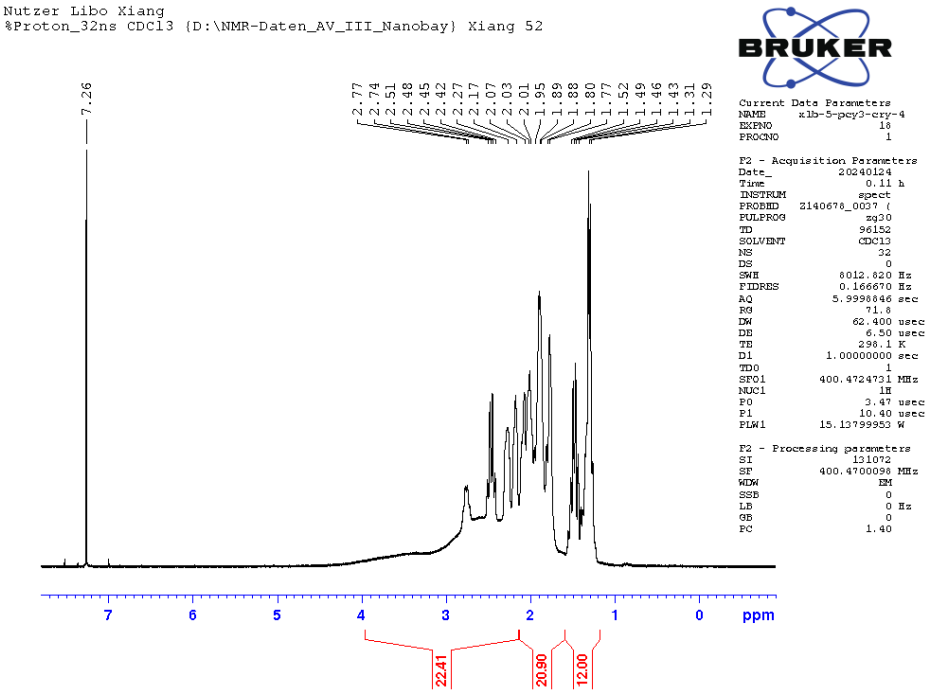



**Figure S7**. $^{1}H$ NMR spectra of **2b** in $C_6D_6$ at 298 K.

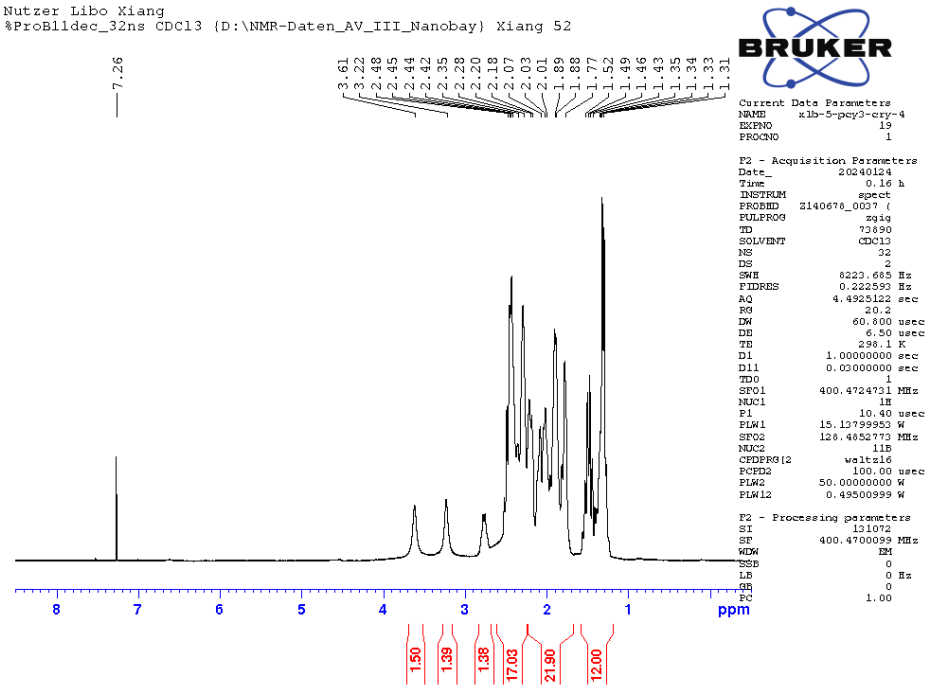



**Figure S8**. $^{1}H\{^{11}B\}$ NMR spectra of **2b** in $C_6D_6$ at 298 K.

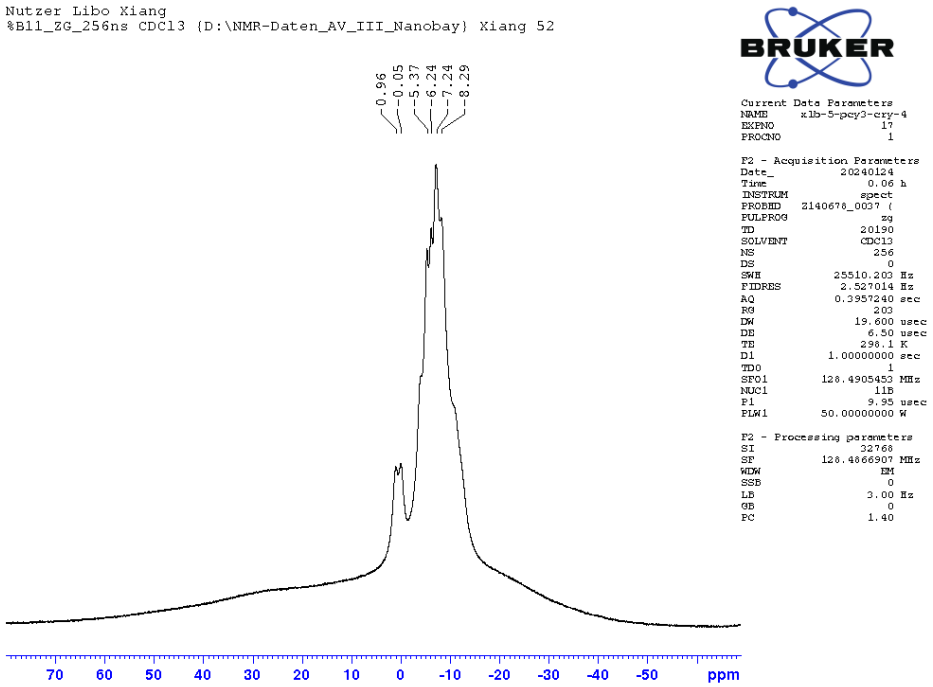



**Figure S9**. $^{11}B$ NMR spectra of **2b** in $C_6D_6$ at 298 K.

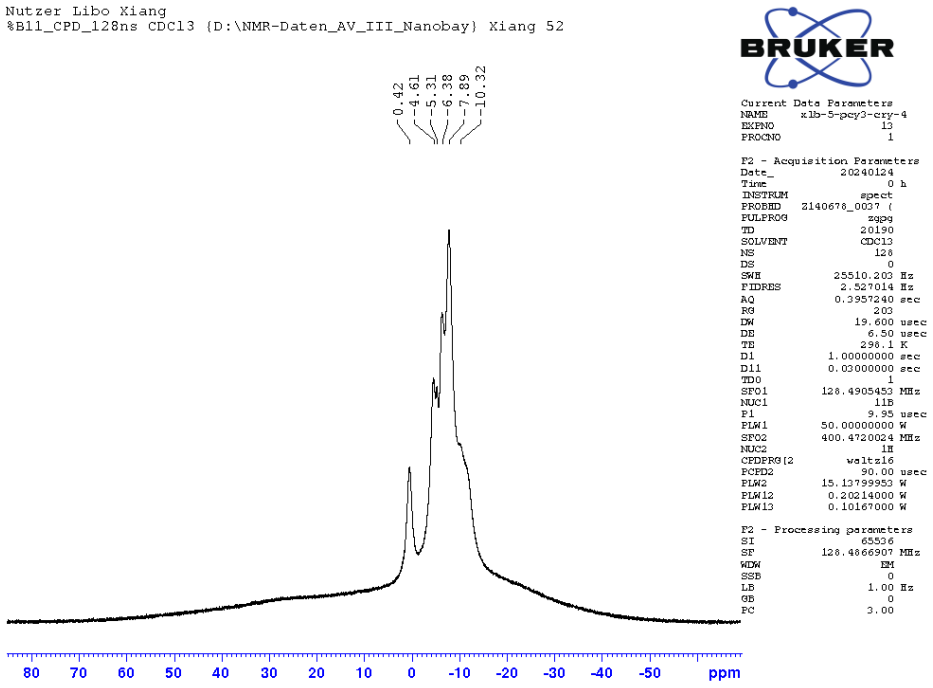



**Figure S10**. $^{11}B\{^1H\}$ NMR spectra of **2b** in $C_6D_6$ at 298 K.

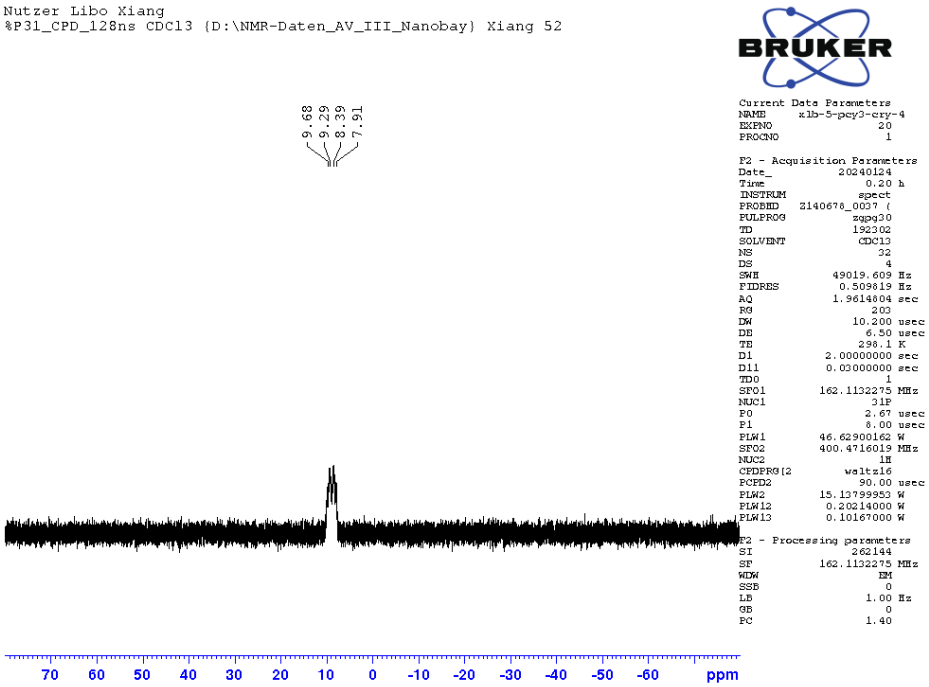



**Figure S11.** $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in $C_6D_6$ at 298 K.

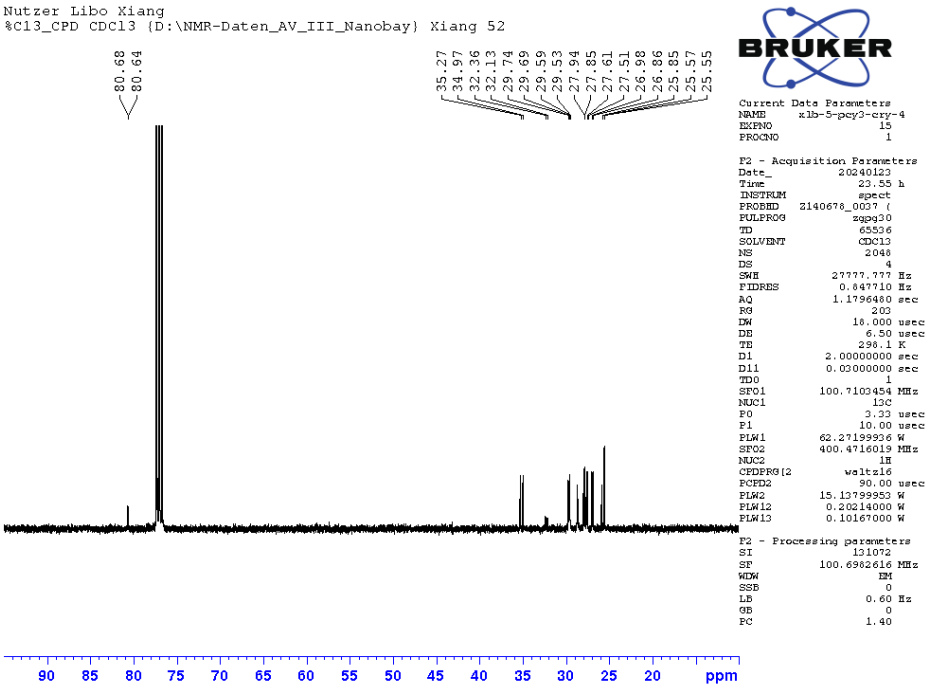



**Figure S12**. $^{13}C\{^{1}H\}$ NMR spectra of **2b** in $C_6D_6$ at 298 K.

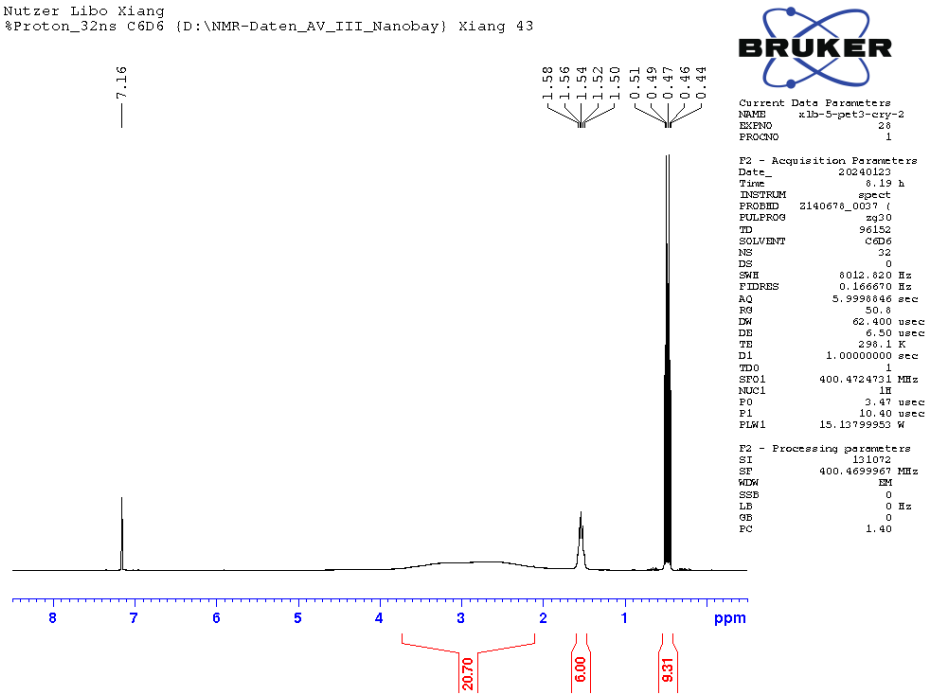



**Figure S13**. $^{1}H$ NMR spectra of **2c** in $C_6D_6$ at 298 K.

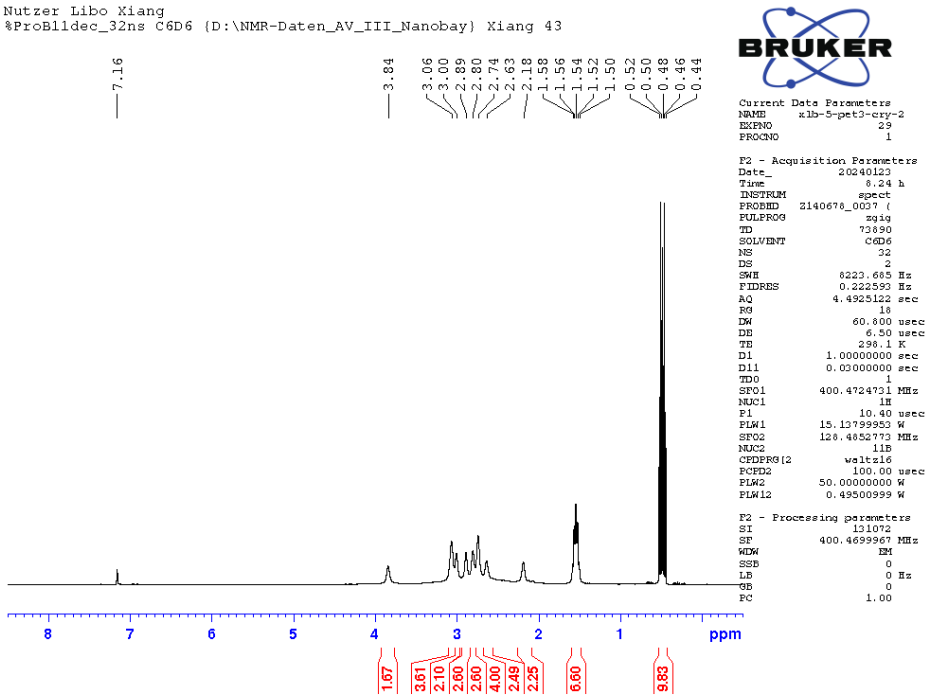



**Figure S14**. $^{1}H\{^{11}B\}$ NMR spectra of **2c** in $C_6D_6$ at 298 K.

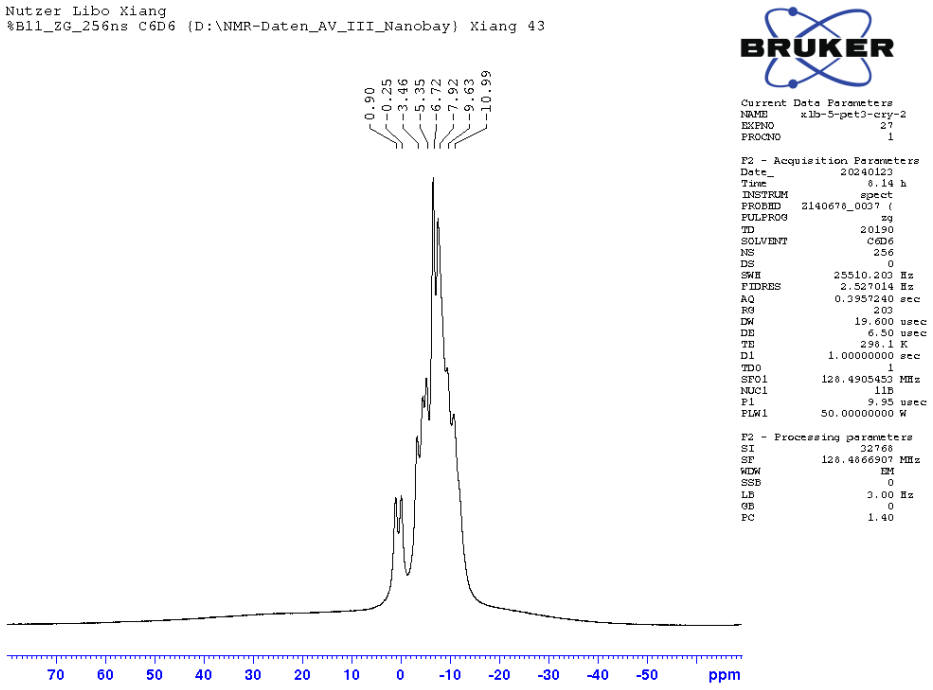



**Figure S15**. $^{11}B$ NMR spectra of **2c** in $C_6D_6$ at 298 K.

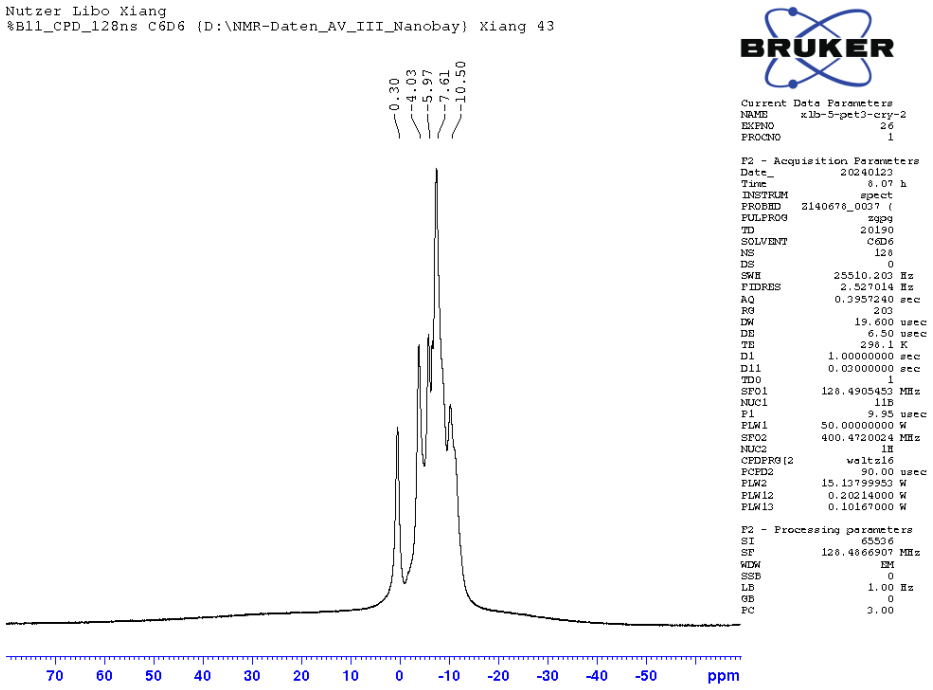



**Figure S16**. $^{11}B\{^1H\}$ NMR spectra of **2c** in $C_6D_6$ at 298 K.

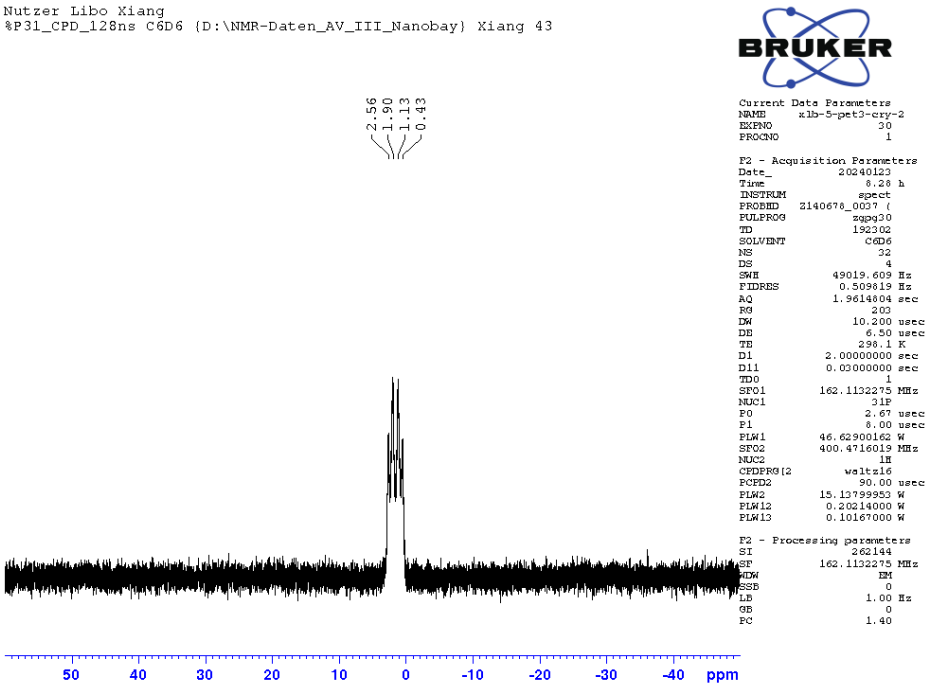



**Figure S17.** $^{31}P\{^{1}H\}$ NMR spectrum of **2c** in $C_6D_6$ at 298 K.

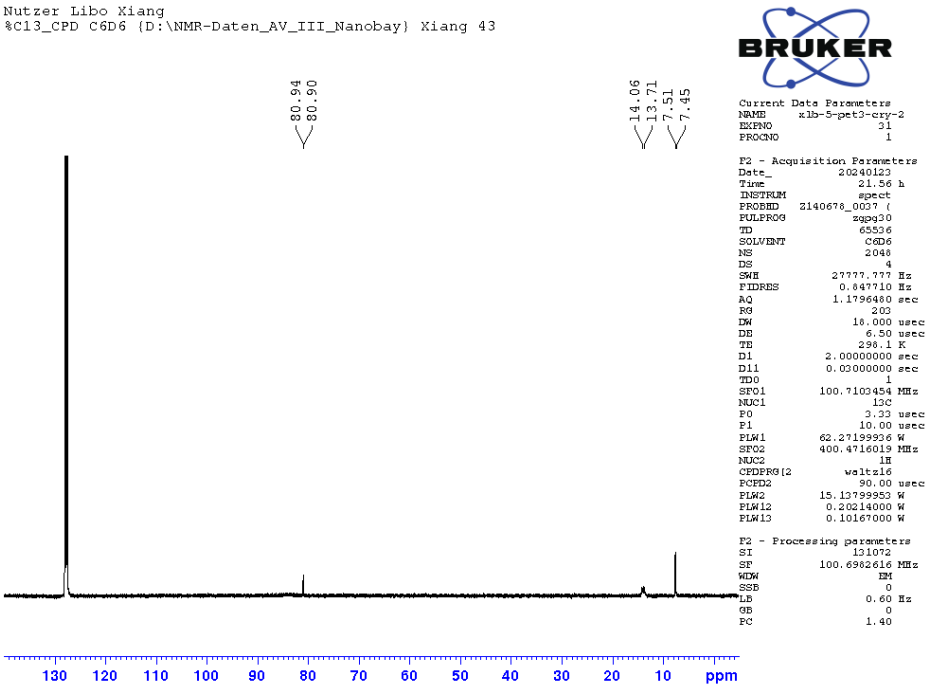



**Figure S18**. $^{13}C\{^{1}H\}$ NMR spectra of **2c** in $C_6D_6$ at 298 K.

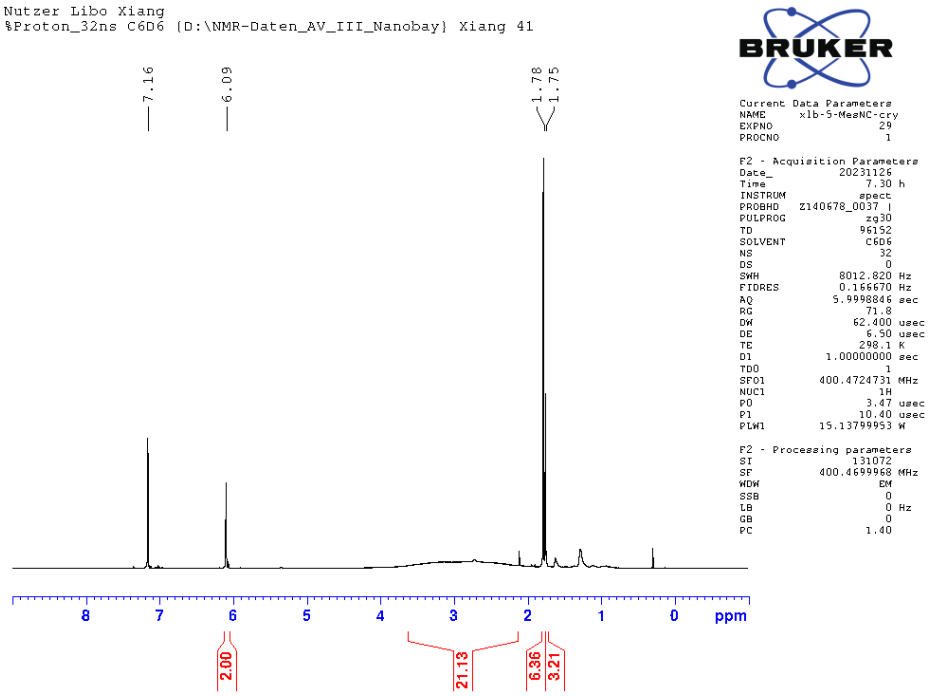



**Figure S19**. $^{1}H$ NMR spectra of **3a** in $C_6D_6$ at 298 K.

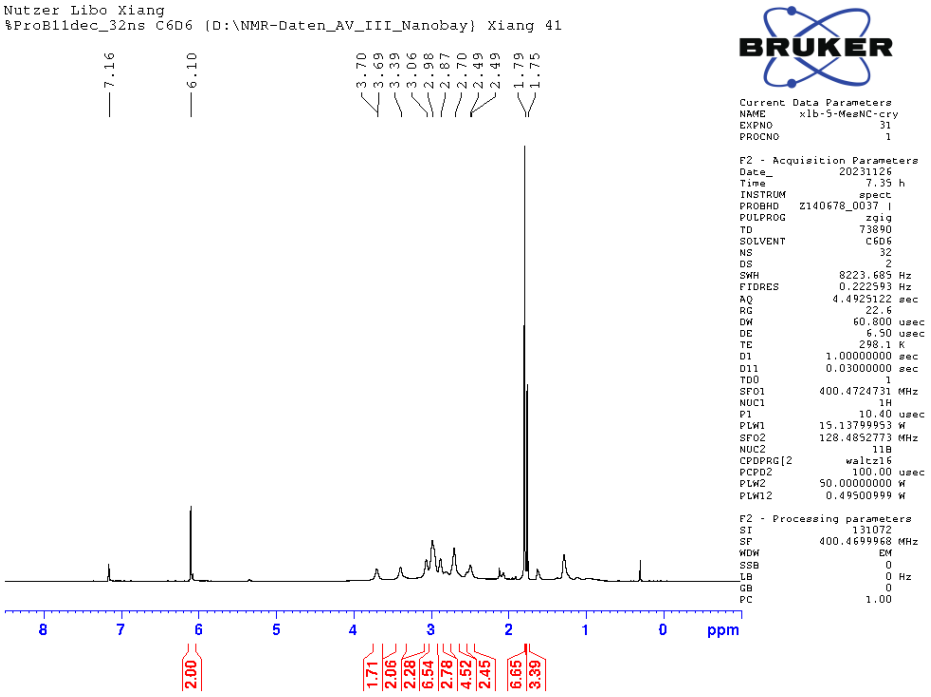



**Figure S20**. $^{1}H\{^{11}B\}$ NMR spectra of **3a** in $C_6D_6$ at 298 K.

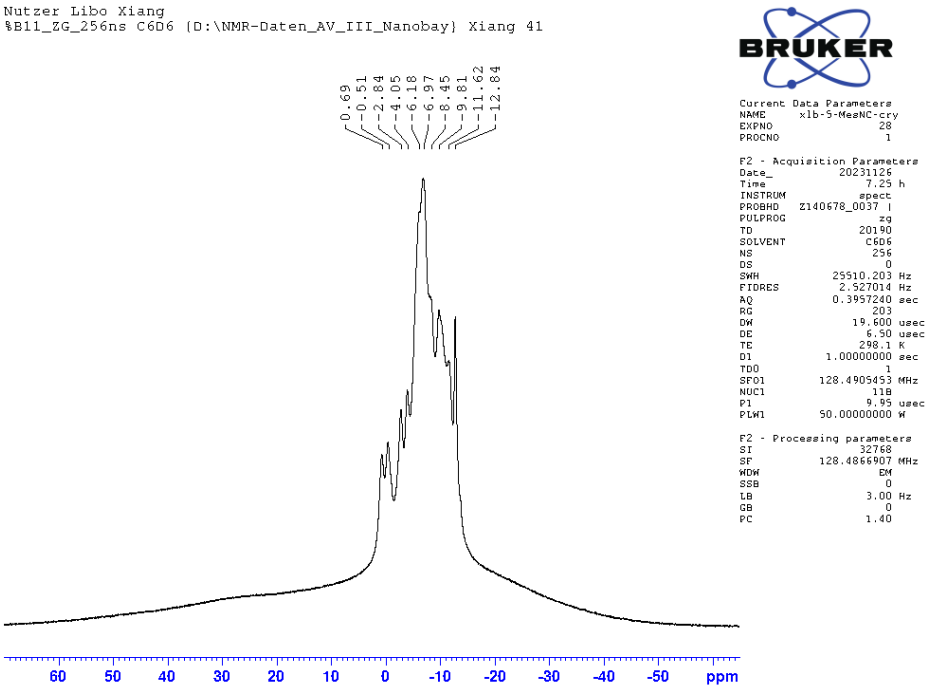



**Figure S21**. $^{11}B$ NMR spectra of **3a** in $C_6D_6$ at 298 K.

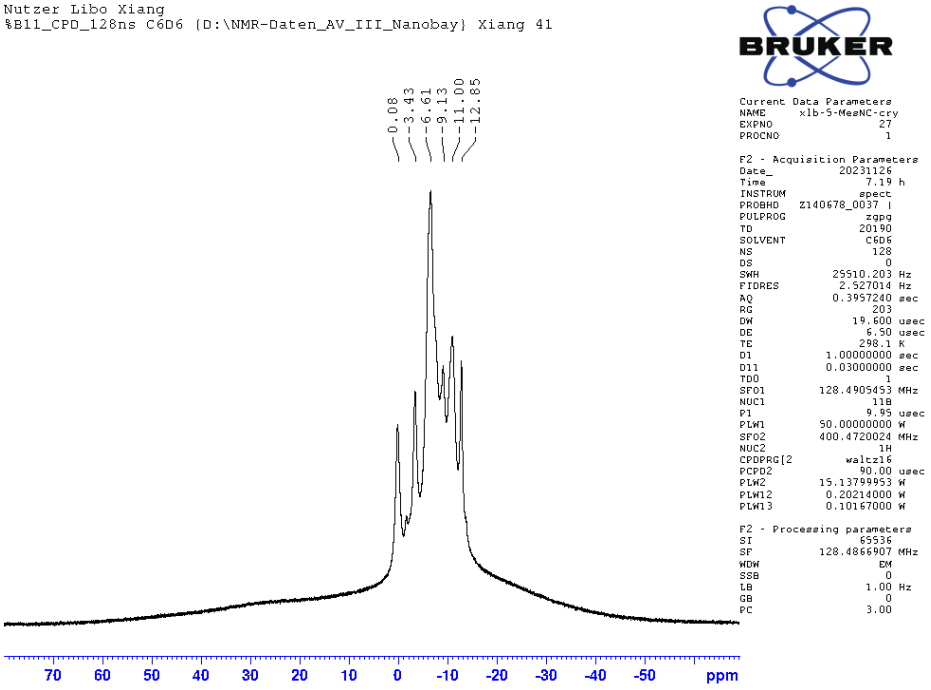



**Figure S22**. $^{11}B\{^1H\}$ NMR spectra of **3a** in $C_6D_6$ at 298 K.

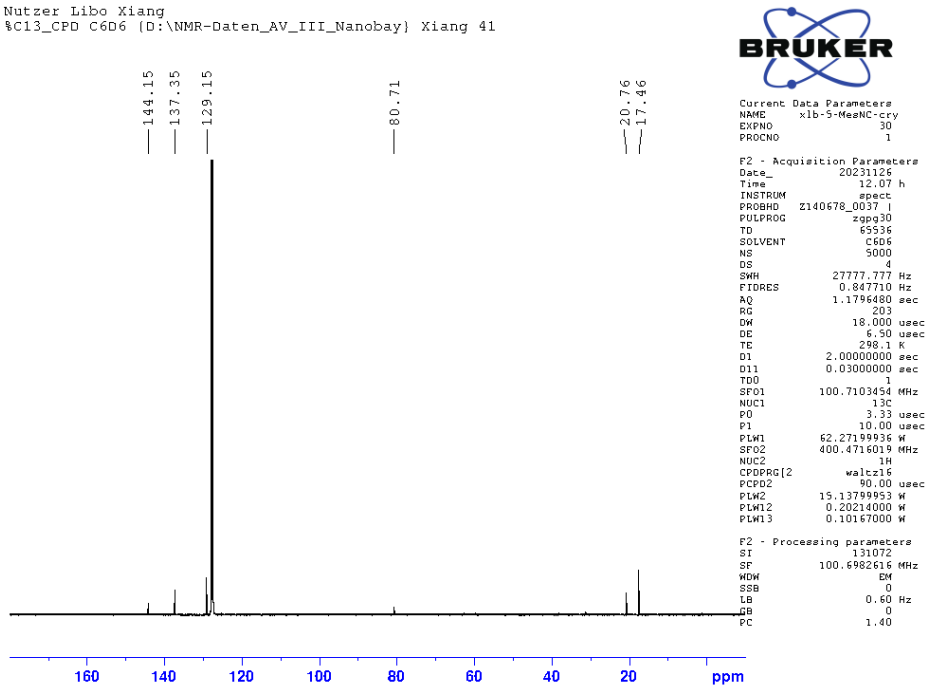



**Figure S23**. $^{13}C\{^{1}H\}$ NMR spectra of **3a** in $C_6D_6$ at 298 K.

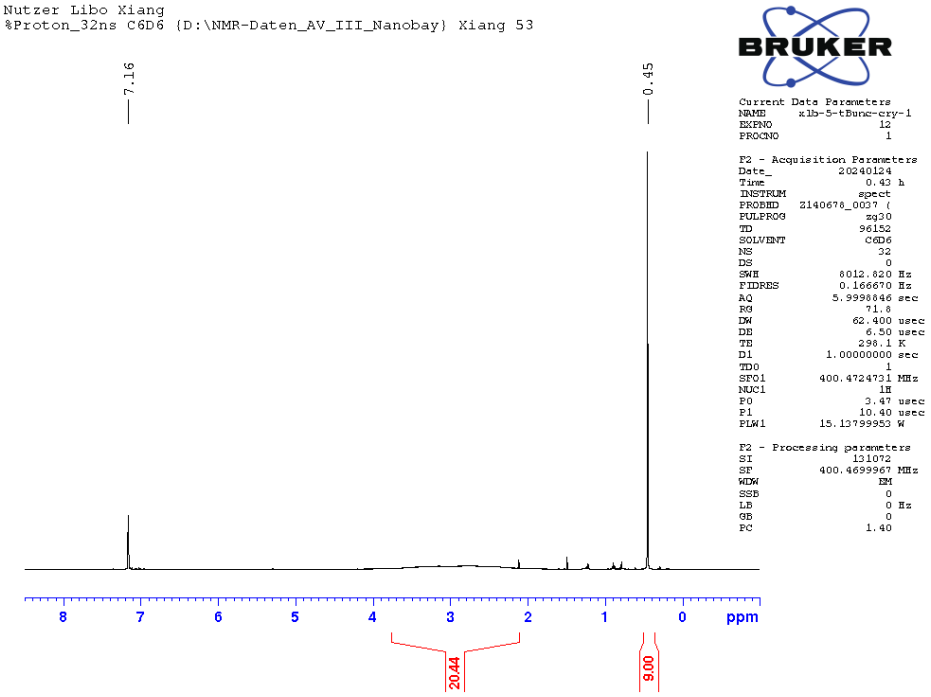



**Figure S24**. $^{1}H$ NMR spectra of **3b** in $C_6D_6$ at 298 K.

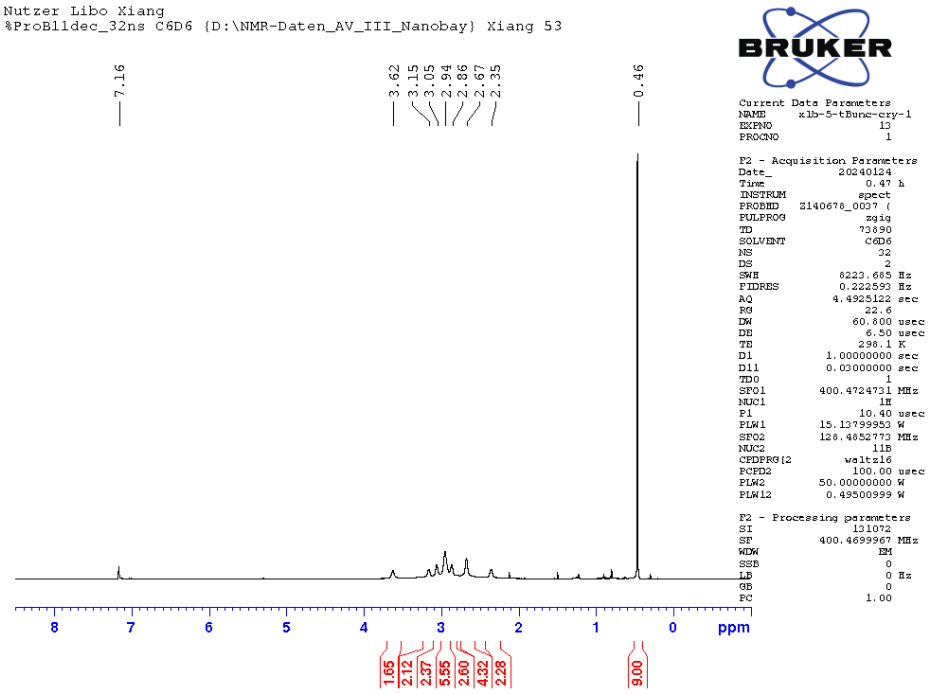



**Figure S25**. $^{1}H\{^{11}B\}$ NMR spectra of **3a** in $C_6D_6$ at 298 K.

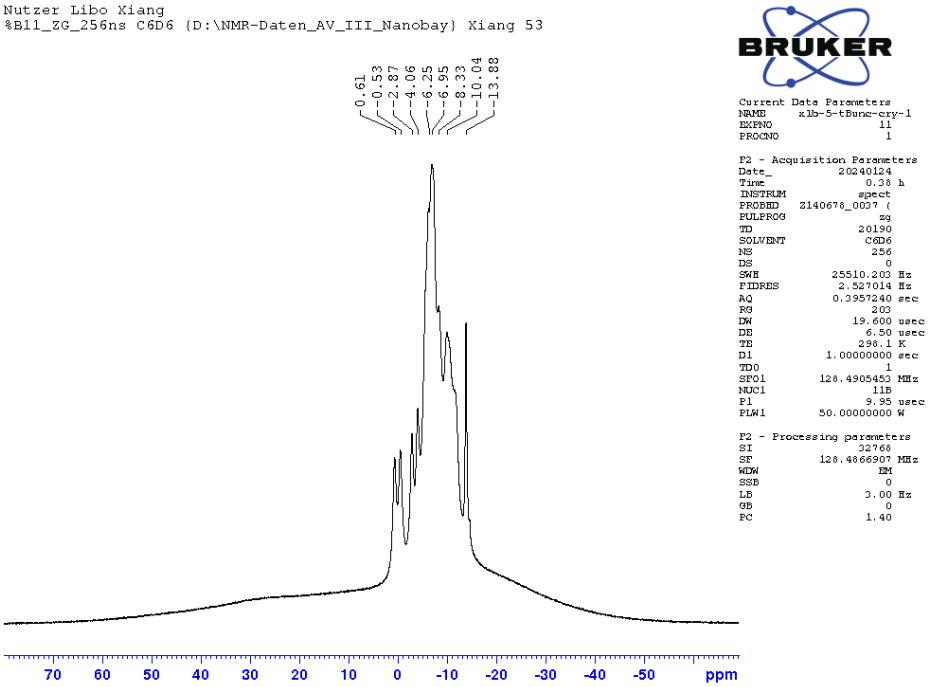



**Figure S26**. $^{11}B$ NMR spectra of **3b** in $C_6D_6$ at 298 K.

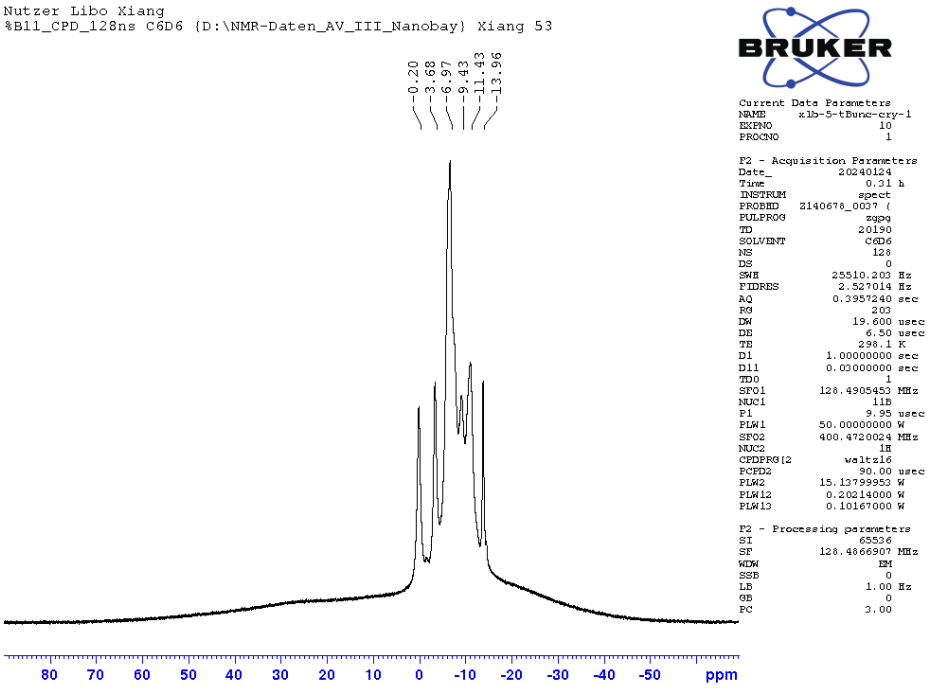



**Figure S27**. $^{11}B\{^{1}H\}$ NMR spectra of **3b** in $C_6D_6$ at 298 K.

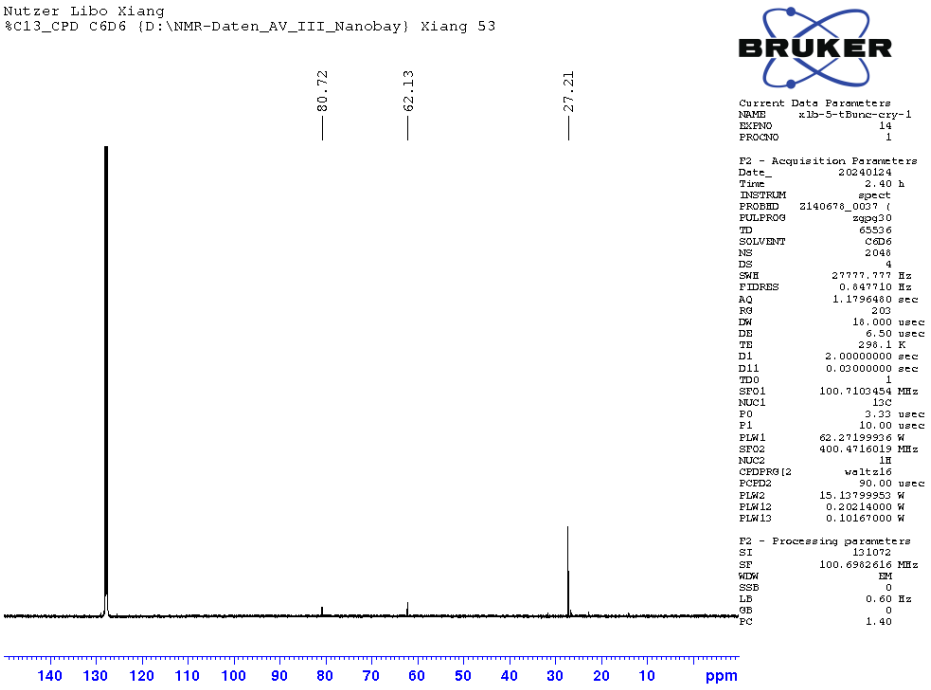



**Figure S28**. $^{13}C\{^{1}H\}$ NMR spectra of **3b** in $C_6D_6$ at 298 K.

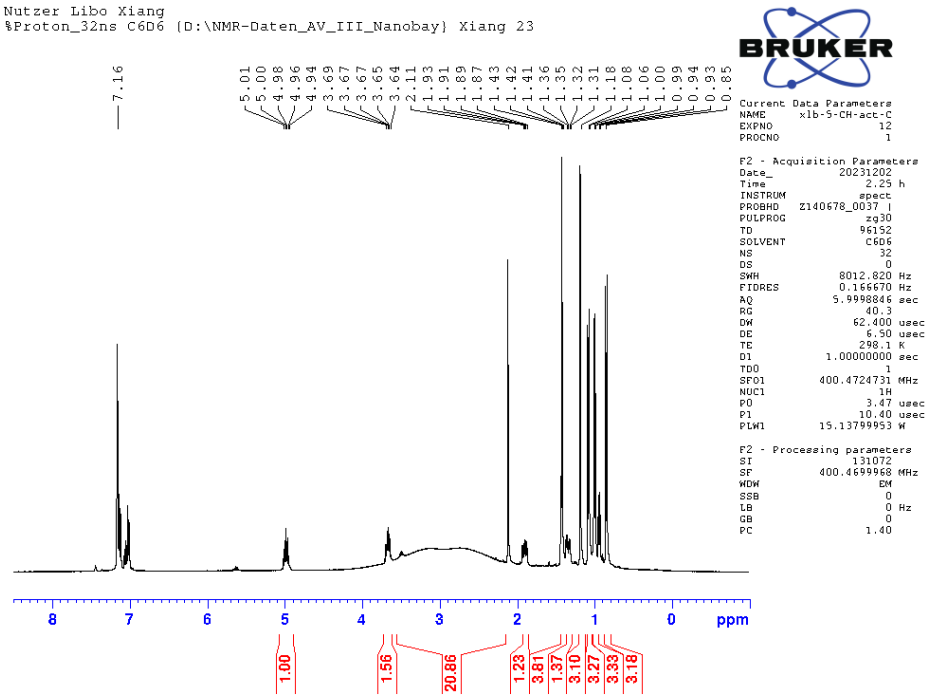



**Figure S29**. $^{1}H$ NMR spectra of **4** in $C_6D_6$ at 298 K.

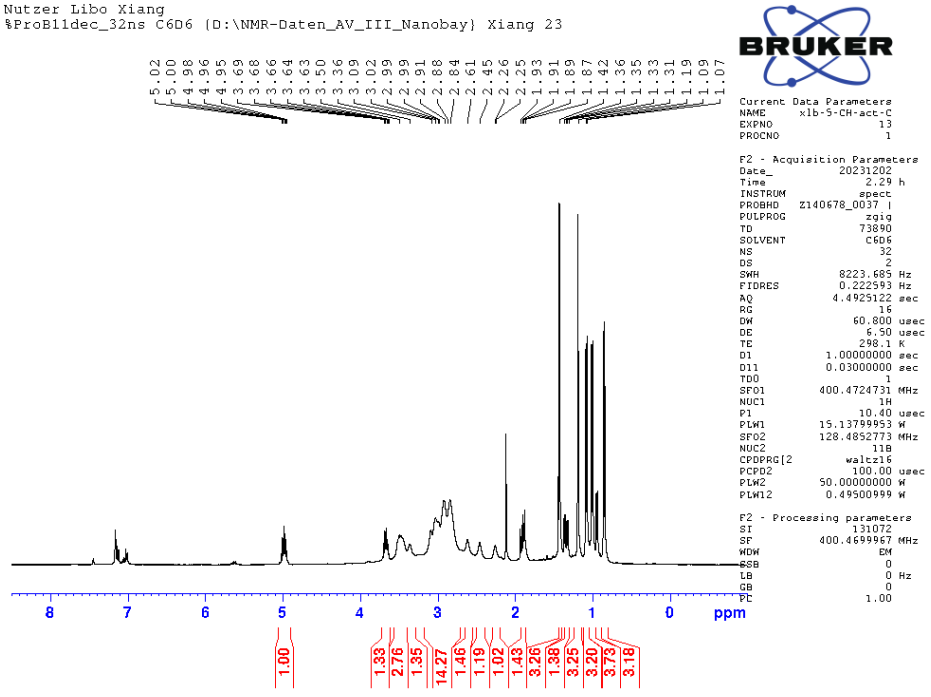



**Figure S30**. $^{1}H\{^{11}B\}$ NMR spectra of **4** in $C_6D_6$ at 298 K.

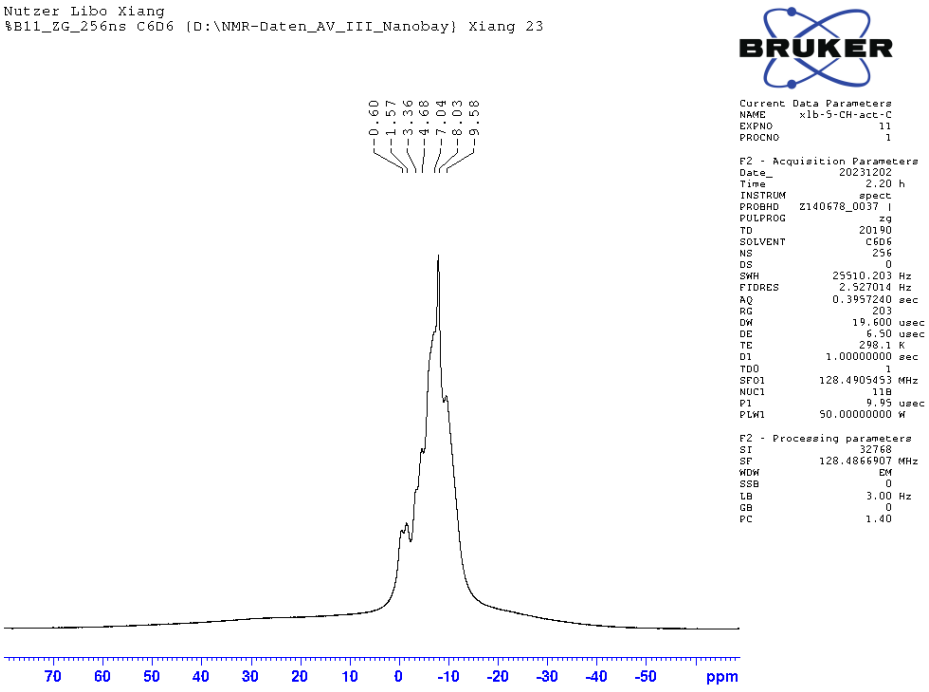



**Figure S31**. $^{11}B$ NMR spectra of **4** in $C_6D_6$ at 298 K.

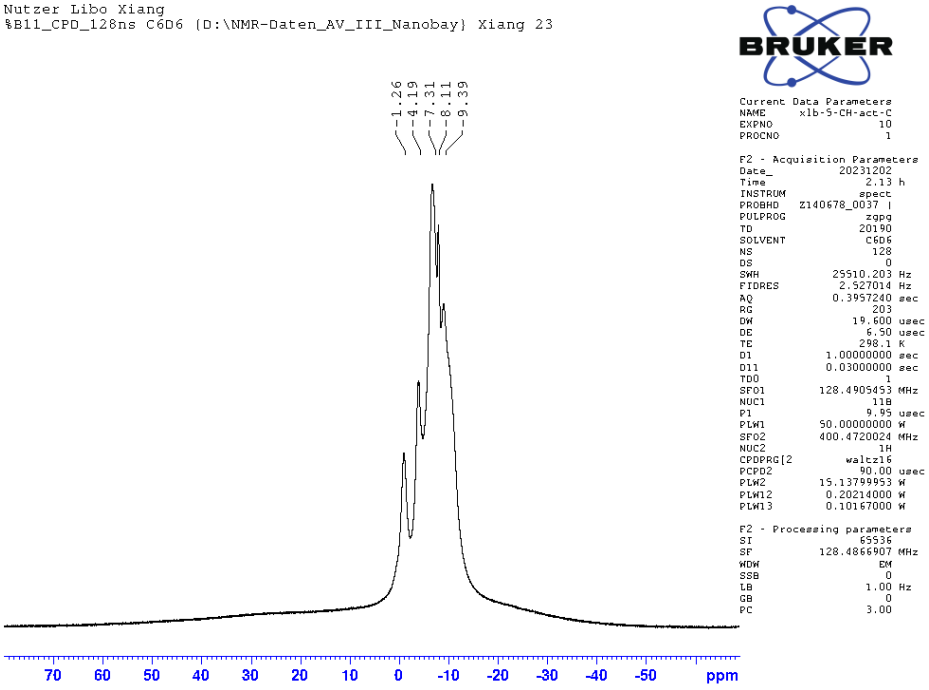



**Figure S32**. $^{11}B\{^1H\}$ NMR spectra of **4** in $C_6D_6$ at 298 K.

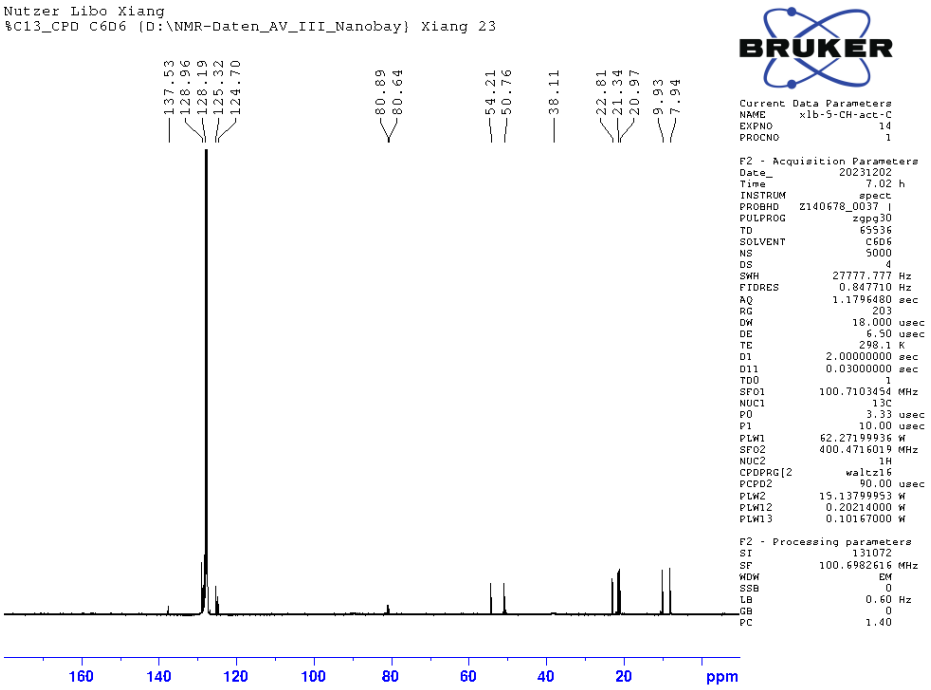



**Figure S33**. $^{13}C\{^{1}H\}$ NMR spectra of **4** in $C_6D_6$ at 298 K.

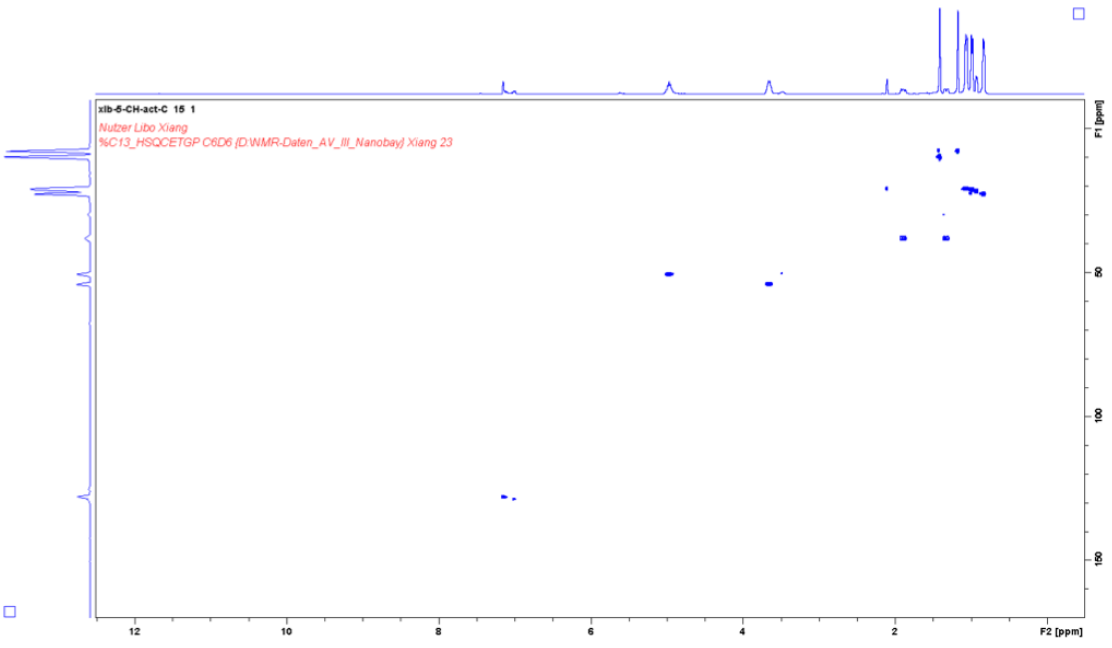



**Figure S34**. HSQC spectra of **4** in $C_6D_6$ at 298 K.

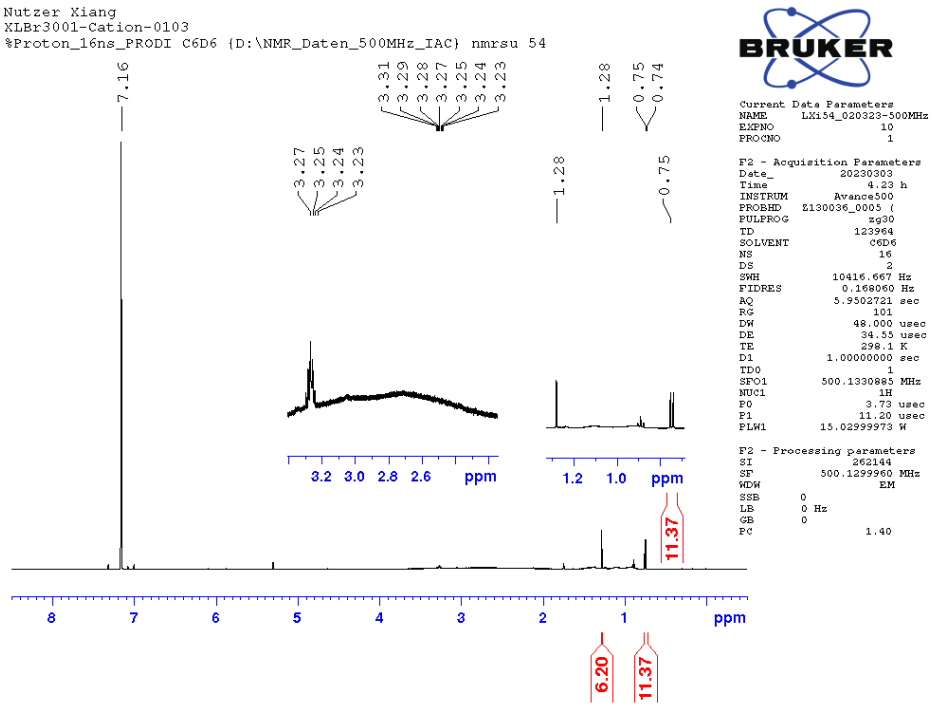



**Figure S35**. $^{1}$H NMR spectra of **5** in $C_6D_6$ at 298 K.

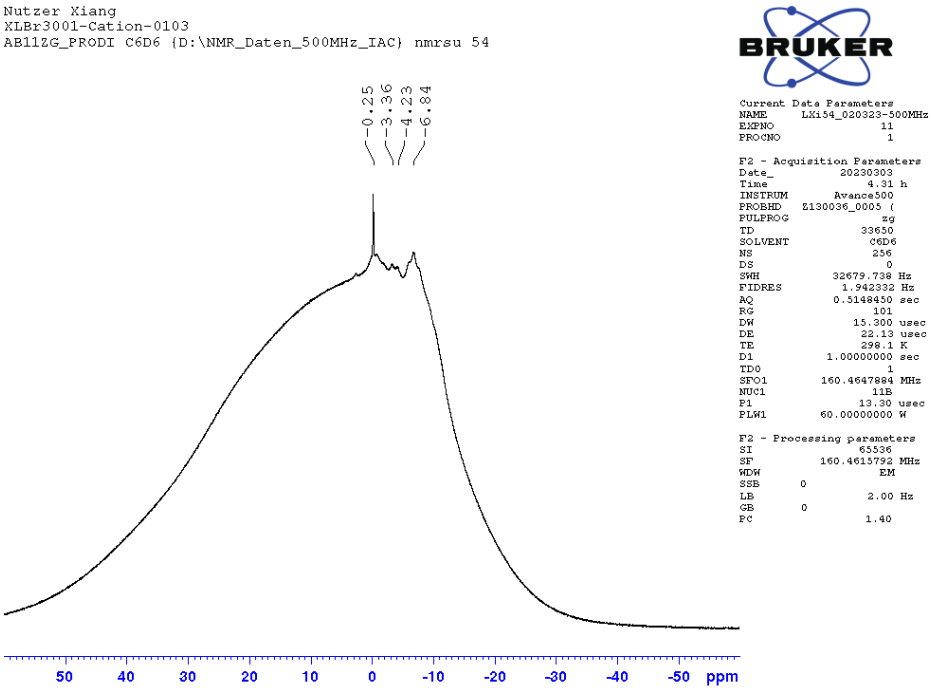



**Figure S36**. $^{11}$B NMR spectra of **5** in $C_6D_6$ at 298 K.

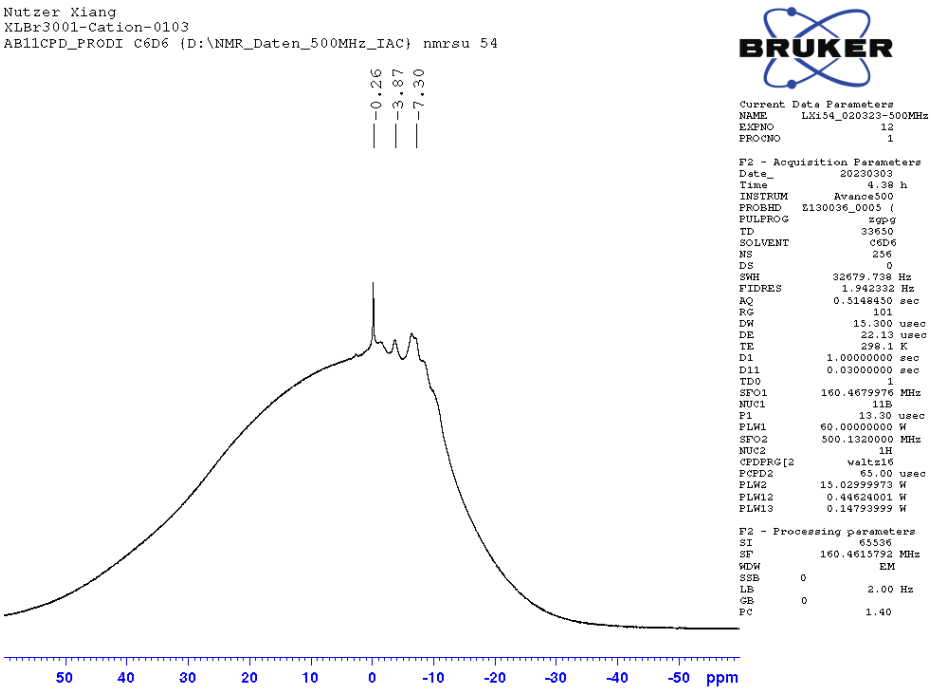



**Figure S37**. $^{11}B\{^{1}H\}$ NMR spectra of **5** in $C_6D_6$ at 298 K.

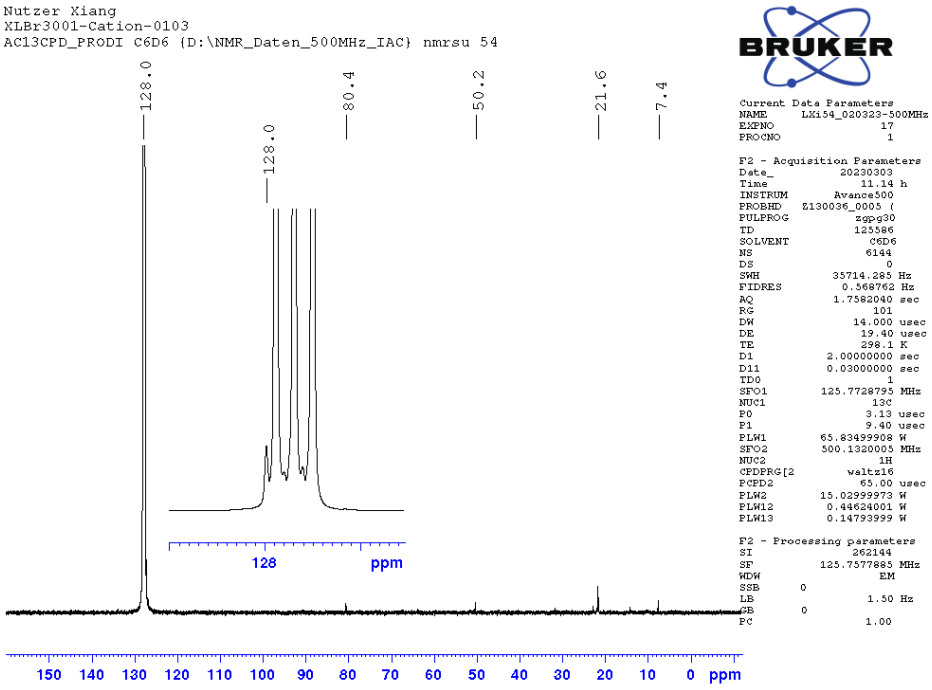



**Figure S38**. $^{13}C\{^{1}H\}$ NMR spectra of **5** in $C_6D_6$ at 298 K.

# Crystallographic Details

The crystal data of **4** and **5** was collected on a Bruker D8 VENTURE diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.38A, 2013). The structure was solved with the XT structure solution program using the Intrinsic Phasing solution method[4] and by using Olex2[5] as the graphical interface. The model was refined with the ShelXL program[6] using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

The crystal data of **2a** and **3a** were collected on a Rigaku XtaLAB Synergy-R diffractometer with a HPA area detector and multi-layer mirror monochromated $Cu_{Ka}$ radiation. The structure was solved using intrinsic phasing method[4], refined with the ShelXL program[6] and expanded using Fourier techniques.

The X-ray crystal structures have been deposited in the Cambridge Crystallographic Data Centre (CCDC) CODE. The data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif). Details of the data collection and refinement for complexes **2**–**5** are given in Table S1-S5.

| **Table S1.** Crystal data and structure refinement for **2a.** | |
|---|---|
| Identification code | 2359952 |
| Empirical formula | $C_{44}H_{70}B_{42}P_2Br_2$ |
| Formula weight | 1274.78 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 22.582(5) |
| b/Å | 18.782(3) |
| c/Å | 16.656(6) |
| α/° | 90 |
| β/° | 117.637(12) |
| γ/° | 90 |
| Volume/Å$^3$ | 6258(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.353 |
| μ/mm$^{-1}$ | 1.384 |
| F(000) | 2576.0 |
| Crystal size/mm$^3$ | 0.358 × 0.238 × 0.171 |
| Radiation | $Mo_{K\alpha}$ (λ = 0.71073) |
| 2Θ range for data collection/° | 4.656 to 52.742 |
| Index ranges | -28 ≤ h ≤ 24, 0 ≤ k ≤ 23, 0 ≤ l ≤ 20 |
| Reflections collected | 6413 |
| Independent reflections | 6413 |
| Data/restraints/parameters | 6413/0/407 |
| Goodness-of-fit on F$^2$ | 1.055 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0288, $wR_2$ = 0.0728 |
| Final R indexes [all data] | $R_1$ = 0.0319, $wR_2$ = 0.0750 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.34/-0.34 |

| **Table S2.** Crystal data and structure refinement for **3a.** | |
|---|---|
| Identification code | 2359953 |
| Empirical formula | $C_{14}H_{31}B_{21}BrN$ |
| Formula weight | 520.32 |
| Temperature/K | 100(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 7.324(2) |
| b/Å | 12.901(4) |
| c/Å | 14.453(3) |
| α/° | 76.495(14) |
| β/° | 85.066(14) |
| γ/° | 89.27(2) |
| Volume/Å$^3$ | 1323.0(6) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.306 |
| μ/mm$^{-1}$ | 1.563 |
| F(000) | 524.0 |
| Crystal size/mm$^3$ | 0.24 × 0.23 × 0.12 |
| Radiation | $Mo_{K\alpha}$ (λ = 0.71073) |
| 2Θ range for data collection/° | 4.84 to 54.206 |
| Index ranges | -9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18 |
| Reflections collected | 17106 |
| Independent reflections | 5809 [$R_{int}$ = 0.0471, $R_{sigma}$ = 0.0507] |
| Data/restraints/parameters | 5809/0/337 |
| Goodness-of-fit on F$^2$ | 1.029 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0342, $wR_2$ = 0.0819 |
| Final R indexes [all data] | $R_1$ = 0.0416, $wR_2$ = 0.0859 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.37/-0.32 |

| **Table S3.** Crystal data and structure refinement for **4**•($C_7H_8$)**.** | |
|---|---|
| Identification code | 2359954 |
| Empirical formula | $C_{37}H_{86}B_{42}N_4$ |
| Formula weight | 1041.740 |
| Temperature/K | 100.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.4445(3) |
| b/Å | 11.4808(4) |
| c/Å | 14.0816(5) |
| α/° | 67.709(3) |
| β/° | 86.457(3) |
| γ/° | 76.241(3) |
| Volume/Å$^3$ | 1516.76(10) |
| Z | 1 |
| $\rho_{calc}$g/cm$^3$ | 1.140 |
| μ/mm$^{-1}$ | 0.384 |
| F(000) | 547.2 |
| Crystal size/mm$^3$ | 0.142 × 0.121 × 0.089 |
| Radiation | Cu $_{K\alpha}$ (λ = 1.54184) |
| 2Θ range for data collection/° | 6.78 to 149.72 |
| Index ranges | -13 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 13 |
| Reflections collected | 29929 |
| Independent reflections | 5998 [$R_{int}$ = 0.0663, $R_{sigma}$ = 0.0396] |
| Data/restraints/parameters | 5998/0/361 |
| Goodness-of-fit on F$^2$ | 1.003 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0751, $wR_2$ = 0.2109 |
| Final R indexes [all data] | $R_1$ = 0.0883, $wR_2$ = 0.2273 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.59/-0.40 |

| **Table S4.** Crystal data and structure refinement for **5.** | |
|---|---|
| Identification code | 2359955 |
| Empirical formula | $C_{19}H_{60}B_{42}Br_{1.34}N_2$ |
| Formula weight | 878.19 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | P21/c |
| a/Å | 12.3887(13) |
| b/Å | 12.963(2) |
| c/Å | 29.552(3) |
| α/° | 90 |
| β/° | 92.692(5) |
| γ/° | 90 |
| Volume/Å$^3$ | 4740.5(10) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.230 |
| μ/mm$^{-1}$ | 1.183 |
| F(000) | 1780.0 |
| Crystal size/mm$^3$ | 0.2 × 0.2 × 0.1 |
| Radiation | $Mo_{K\alpha}$ (λ = 0.71073) |
| 2Θ range for data collection/° | 4.182 to 52.896 |
| Index ranges | -15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -37 ≤ l ≤ 36 |
| Reflections collected | 129764 |
| Independent reflections | 9751 [Rint = 0.0943, Rsigma = 0.0403] |
| Data/restraints/parameters | 9751/0/594 |
| Goodness-of-fit on F$^2$ | 1.043 |
| Final R indexes [I>=2σ (I)] | *R1* = 0.0371, *wR2* = 0.0954 |
| Final R indexes [all data] | *R1* = 0.0517, *wR2* = 0.1043 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.39/-0.26 |

# Reference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