

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 $^t\text{BuNC}$ were purchased from commercial sources and used without further purification. $(\text{C}_2\text{B}_{10}\text{H}_{10})_2\text{BBr}$ (**1**)¹, MeI/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 (^1H 400.1 MHz; ^{11}B 128.5 MHz; ^{13}C 101 MHz; ^{31}P : 162. MHz) spectrometer at room temperature. ^{11}B NMR, $^{11}\text{B}\{^1\text{H}\}$ spectra were referenced relative to 15% $\text{BF}_3\cdot\text{OEt}_2$. $^{31}\text{P}\{^1\text{H}\}$ 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.

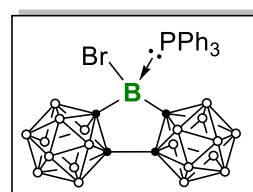
Synthesis and characterization

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.

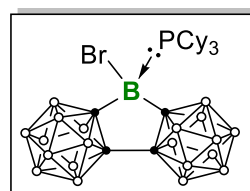
For **2a**:

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



For **2b**:

$^1\text{H NMR}$ (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, BH). $^1\text{H}\{^{11}\text{B}\}$ 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, BH), 2.72 to 2.80 (s, 1H, BH), 3.22 (s, 1H, BH), 3.61 (s, 1H, BH). $^{11}\text{B NMR}$ (128 MHz, C_6D_6): δ [ppm] = 0.50 (d, $J = 130.8$ Hz, $B_{\text{carborane}}$), -5.37 to -8.29 (m, $B_{\text{carborane}}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ [ppm] = 0.42 (s, $B_{\text{carborane}}$), -4.61 (s, C_{carbeneB}), -5.31 (s, $B_{\text{carborane}}$), -6.38 (s, $B_{\text{carborane}}$), -7.89 (s, $B_{\text{carborane}}$), -10.32 (s, $B_{\text{carborane}}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6): δ [ppm] = 8.8 (q, $J = 140.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ [ppm] = 25.6 (d, $J_{\text{P-C}} = 1.3$ Hz, C of Cy), 25.8 (d, $J_{\text{P-C}} = 1.3$ Hz, C of Cy), 26.9 (d, $J_{\text{P-C}} = 11.5$ Hz, C of Cy), 27.6 (d, $J_{\text{P-C}} = 10.5$ Hz, C of Cy), 27.9 (d, $J_{\text{P-C}} = 9.6$ Hz, C of Cy), 28.6 (d, $J_{\text{P-C}} = 2.1$ Hz, C of Cy),



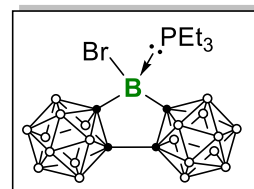
29.6 (d, $J_{P-C} = 5.6$ Hz. C of Cy), 29.7 (d, $J_{P-C} = 4.6$ Hz. C of Cy), 32.2 (d, $J_{P-C} = 23.1$ Hz. C of Cy), 35.1 (d, $J_{P-C} = 30.1$ Hz. C of Cy), 80.7 (s, $C_{\text{carborane}}$). **HRMS:** $[M-Br]^+$ calcd. for $C_{22}B_{21}H_{53}P$, 575.5984; found 575.5960. Yield: 86 % (180.1 mg, 0.27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

For **2c**:

1H 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, BH).

$^1H\{^{11}B\}$ 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, BH), 2.63 (s, 2H, BH), 2.74 (s, 4H, BH), 2.80 (s, 2H, BH), 2.89 (s, 2H, BH), 3.00 (s, 2H, BH), 3.06

(s, 4H, BH), 3.84 (s, 2H, BH). **^{11}B NMR** (128 MHz, C_6D_6): δ [ppm] = 0.49 (d. $J = 149.9$ Hz, $B_{\text{carborane}}$), -3.87 (d. $J = 149.7$ Hz, $B_{\text{carborane}}$), -5.35 to -10.99 (m, $B_{\text{carborane}}$). **$^{11}B\{^1H\}$ NMR** (128 MHz, C_6D_6): δ [ppm] = 0.30 (s, $B_{\text{carborane}}$), -4.03 (s, C_{carbeneB}), -5.97 (s, $B_{\text{carborane}}$), -7.61 (s, $B_{\text{carborane}}$), -10.50 (s, $B_{\text{carborane}}$). **$^{31}P\{^1H\}$ NMR** (162 MHz, C_6D_6): δ [ppm] = 1.5 (q. $J = 123.0$ Hz). **$^{13}C\{^1H\}$ NMR** (100 MHz, C_6D_6): δ [ppm] = 7.5 (d, $J_{P-C} = 6.6$ Hz. CH_2CH_3), 13.9 (d, $J_{P-C} = 38.3$ Hz. CH_2CH_3), 80.9 (s). **HRMS:** $[M-Br]^+$ calcd. for $C_{10}B_{21}H_{35}P$, 413.4576; found 413.4565. Yield: 81 % (127.6 mg, 0.26 mmol).

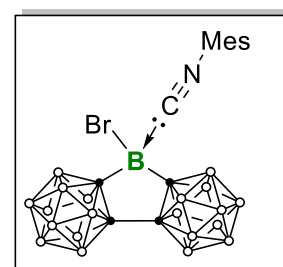


Synthetic protocols for **3**

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**:

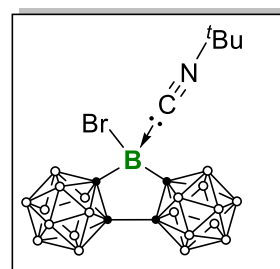
1H NMR (400 MHz, C_6D_6): δ [ppm] = 1.75 (s, 3H, CCH_3), 1.78 (s, 6H, CCH_3), 2.13 to 3.63 (br. m, 20H, BH), 6.10 (s, 2H, H of Ar). **$^1H\{^{11}B\}$ NMR** (400 MHz, C_6D_6): δ [ppm] = 1.75 (s, 3H, CCH_3), 1.79 (s, 6H, CCH_3), 2.49 (s, 2H, BH), 2.69 (s, 4H, BH), 2.87 (s, 2H, BH), 2.98 (s, 6H, BH), 3.06 (s, 2H, NCH_3), 3.39 (s, 2H, BH), 3.70 (s, 2H, BH). **^{11}B NMR** (128 MHz, C_6D_6): δ [ppm] = 0.11 (d. $J = 157.6$ Hz, $B_{\text{carborane}}$), -3.40 (d. $J = 158.0$ Hz, $B_{\text{carborane}}$), -6.18 to -11.62 (m, $B_{\text{carborane}}$), -12.84 (s, $C_{\text{isocyanideB}}$). **$^{11}B\{^1H\}$ NMR** (128 MHz,



C_6D_6): δ [ppm] = 0.08 (s, $B_{\text{carborane}}$), -3.43 (s, $C_{\text{isocyanideB}}$), -6.61 (s, $B_{\text{carborane}}$), -9.13 (s, $B_{\text{carborane}}$), -11.00 (s, $B_{\text{carborane}}$), -12.85 (s, $C_{\text{isocyanideB}}$). **$^{13}C\{^1H\}$ NMR** (100 MHz, C_6D_6): δ [ppm] = 17.5 (s, CCH_3), 20.7 (s, CCH_3), 80.7 (s, $C_{\text{carborane}}$), 129.1 (s, C of Ar), 137.4 (s, C of Ar), 144.1 (s, C of Ar). **HRMS (LIFDI):** calcd. for $C_{14}B_{21}H_{31}BrN$, 519.3739; found 519.3736. Yield: 76 % (125.8 mg, 0.24 mmol).

For **3b**:

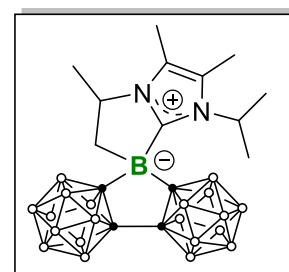
$^1\text{H NMR}$ (400 MHz, C_6D_6): δ [ppm] = 0.45 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.11 to 3.77 (br. m, 20H, BH). $^1\text{H}\{^{11}\text{B}\}$ NMR (400 MHz, C_6D_6): δ [ppm] = 0.46 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.35 (s, 2H, BH), 2.67 (s, 4H, BH), 2.86 (s, 2H, BH), 2.94 (s, 2H, BH), 3.05 (s, 6H, BH), 3.15 (s, 2H, NCH_3), 3.62 (s, 2H, BH). $^{11}\text{B NMR}$ (128 MHz, C_6D_6): δ [ppm] = 0.04 (d. $J = 146.6$ Hz, $B_{\text{carborane}}$), -3.44 (d. $J = 153.5$ Hz, $B_{\text{isocyanide}}$), -6.25 to -10.04 (m, $B_{\text{carborane}}$), -13.88 (s, $B_{\text{isocyanide}}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ [ppm] = -0.19 (s, $B_{\text{carborane}}$), -3.68 (s, $B_{\text{isocyanide}}$), -6.97 (s, $B_{\text{carborane}}$), -9.43 (s, $B_{\text{carborane}}$), -11.43 (s, $B_{\text{carborane}}$), -13.96 (s, $B_{\text{isocyanide}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ [ppm] = 27.2 (s, $\text{C}(\text{CH}_3)_3$), 62.1 (s, $\text{C}(\text{CH}_3)_3$), 80.7 (s, $C_{\text{carborane}}$). HRMS $[\text{M}-\text{Br}]^+$ calcd. for $\text{C}_9\text{B}_{21}\text{H}_{29}\text{N}$, 378.4399; found 378.4394. Yield: 87 % (127.3 mg, 0.28 mmol).



Synthesis of **4**

Path A: In an argon-filled glove box, $^{\text{Me}}\text{iPr}$ (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.

$^1\text{H NMR}$ (400 MHz, C_6D_6): δ [ppm] = 0.84 (d, $J = 6.4$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.99 (d, $J = 6.9$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, $J = 7.0$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.18 (s, 3H, CCH_3), 1.33 (dd, $J = 14.5, 7.8$ Hz, 1H, BCH_2CH), 1.42 (s, 3H, CCH_3), 1.89 (dd, $J = 14.8, 7.7$ Hz, 1H, BCH_2CH), 3.67 (sept, $J = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 4.98 (sept, $J = 6.8$ Hz, 1H, CHCH_3). $^1\text{H}\{^{11}\text{B}\}$ NMR (400 MHz, C_6D_6): δ [ppm] = 0.85 (d, $J = 6.4$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.00 (d, $J = 6.9$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, $J = 7.0$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.19 (s, 3H, CCH_3), 1.33 (dd, $J = 14.4, 6.7$ Hz, 1H, BCH_2CH), 1.42 (s, 3H, CCH_3), 1.89 (dd, $J = 14.3, 7.9$ Hz, 1H, BCH_2CH), 2.25 (s, 1H, BH), 2.45 (s, 1H, BH), 2.61 (s, 1H, BH), 2.84 to 3.09 (m, 14H, BH), 3.36 (s, 1H, BH), 3.50 (s, 2H, BH), 3.66 (sept, $J = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 4.98 (sept, $J = 6.8$ Hz, 1H, CHCH_3). $^{11}\text{B NMR}$ (128 MHz, C_6D_6): δ [ppm] = -0.96 (d. $J = 128.1$ Hz, $B_{\text{carborane}}$), -3.87 (d. $J = 171.3$ Hz, $B_{\text{carborane}}$), -6.11 to -7.04 (m, $B_{\text{carborane}}$), -8.03 (s, CH_2B), -9.57 (s, $B_{\text{carborane}}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ [ppm] = -1.26 (s, B_{carbene}), -4.19 (s, $B_{\text{carborane}}$), -7.31 (s, $B_{\text{carborane}}$), -8.11 (s, CH_2B), -9.40 (s, $B_{\text{carborane}}$). $^3\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ [ppm] = 7.9 (s, $\text{C}(\text{CH}_3)$), 9.9 (s, $\text{C}(\text{CH}_3)$), 21.0 (s, $\text{CH}(\text{CH}_3)$), 21.3 (s, $\text{C}(\text{CH}_3)$), 22.8 (s, $\text{C}(\text{CH}_3)$), 38.1 (br, s, BCH_2), 50.75 (s, $\text{CH}(\text{CH}_3)_2$), 54.2 (s, CHCH_3), 80.6 (s, $C_{\text{carborane}}$), 128.2 (s, CCH_3) HRMS (LIFDI): calc. for $\text{C}_{15}\text{B}_{21}\text{N}_2\text{H}_{39}$, 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 $^{Me}I/Pr$ (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 $^{Me}I/Pr$ (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.

1H NMR (500 MHz, C_6D_6): δ [ppm] = 0.74 (d, J = 6.7 Hz, 12H, $CH(CH_3)_2$), 1.28 (s, 6H, CH_3), 3.27 (sept, J = 6.8 Hz, $CH(CH_3)_2$), 2.06 to 3.44 (br. m, BH).

^{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, $B_{carborane}$). $^{11}B\{^1H\}$ NMR (160 MHz,

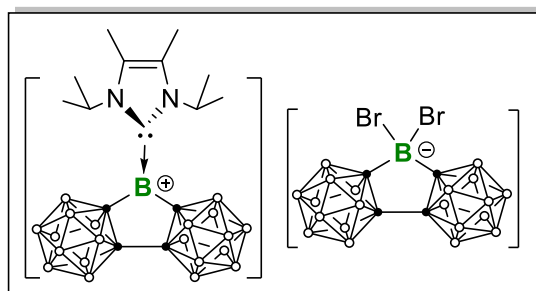
C_6D_6): δ [ppm] = -0.26 (s), -3.87 (s, $B_{carborane}$),

-7.30 (m, $B_{carborane}$). $^{13}C\{^1H\}$ NMR (125 MHz,

C_6D_6): δ [ppm] = 7.4 (s, CH_3), 21.6 (s, CH_3), 50.2

(s, $CHCH_3$), 80.4 (s, $C_{carborane}$), 128.0 (s, CCH_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

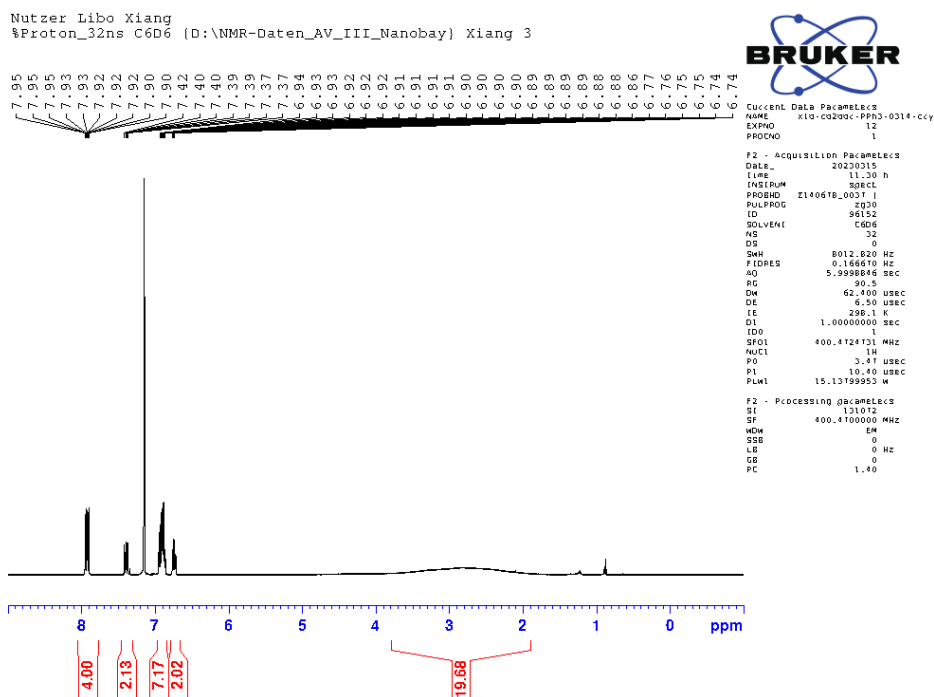


Figure S1. ^1H NMR spectra of **2a** in C_6D_6 at 298 K.

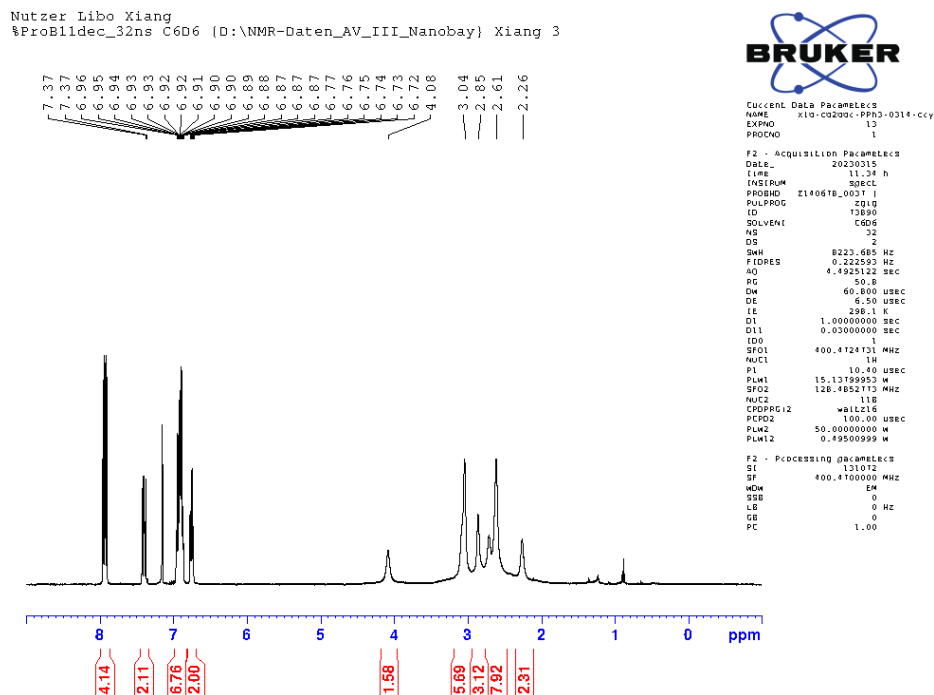
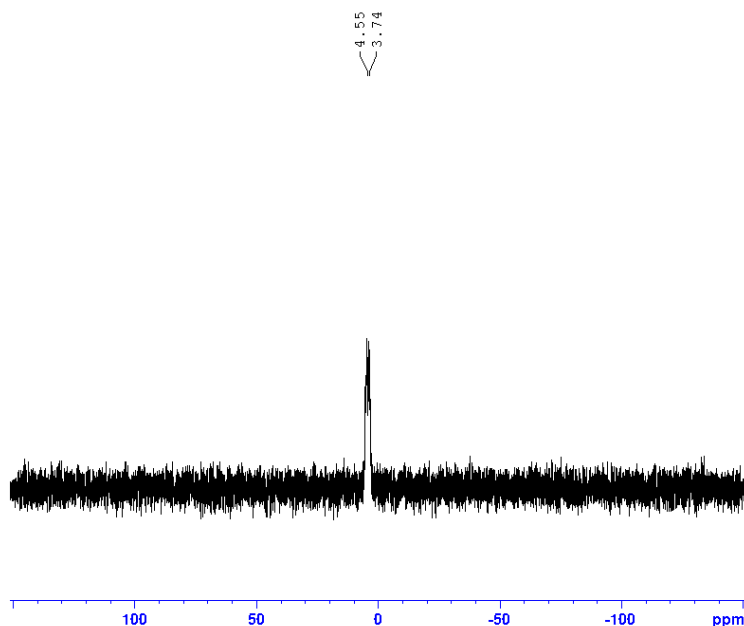


Figure S2. $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of **2a** in C_6D_6 at 298 K.

Nutzer Libo Xiang
 %P31_CPD_128ns C6D6 [D:\NMR-Daten_AV_III_Nanobay] Xiang 3



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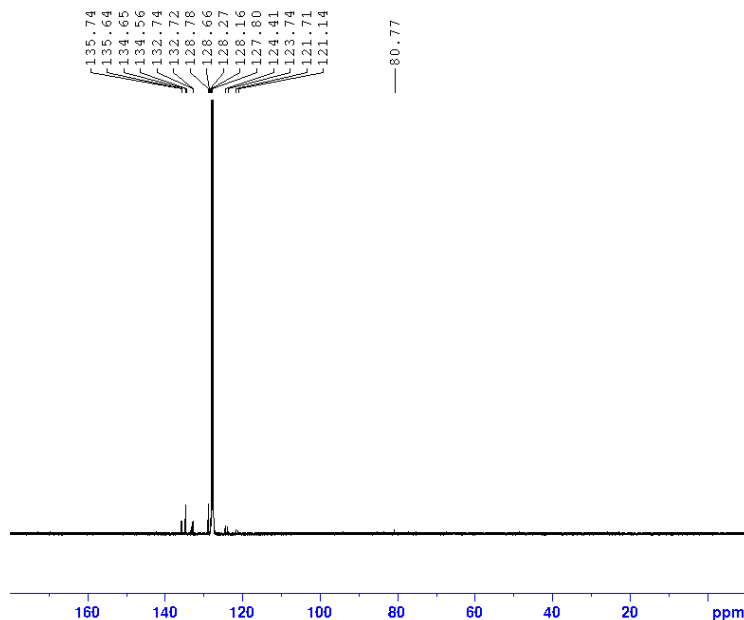
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Figure S5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2a** in C_6D_6 at 298 K.

Nutzer Libo Xiang
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GB        0
PC        1.40
  
```

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

Nutzer Libo Xiang
 %Proton_32ns CDCl3 (D:\NMR-Daten_AV_III_Nanobay) Xiang 52

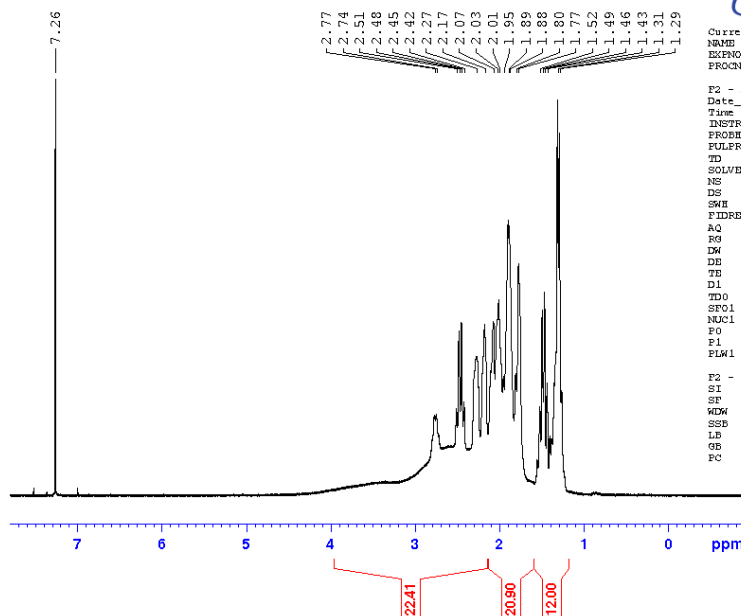


Figure S7. ¹H NMR spectra of **2b** in C₆D₆ at 298 K.

Nutzer Libo Xiang
 %ProB11dec_32ns CDCl3 (D:\NMR-Daten_AV_III_Nanobay) Xiang 52

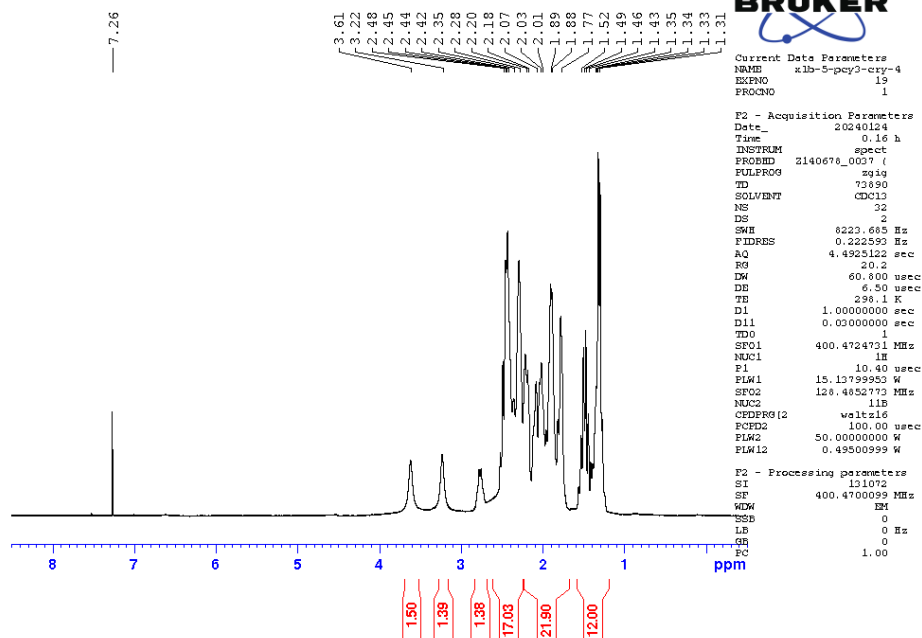
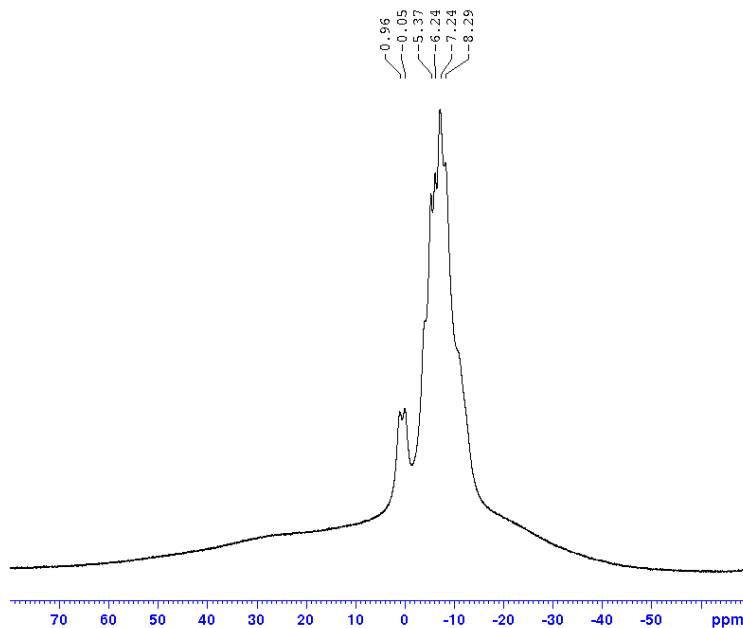


Figure S8. ¹H{¹³B} NMR spectra of **2b** in C₆D₆ at 298 K.

Nutzer Libo Xiang
 %B11_ZG_256ns CDC13 (D:\NMR-Daten_AV_III_Nanobay) Xiang 52



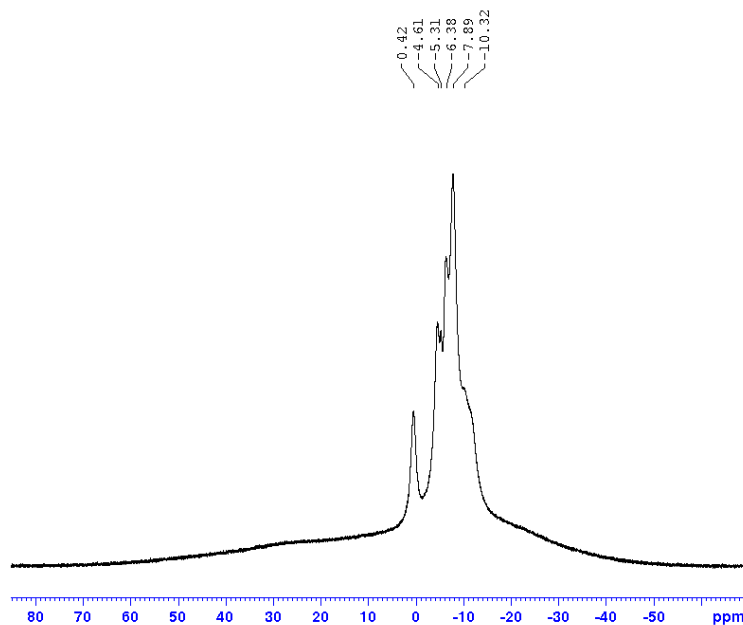
Current Data Parameters
 NAME xlb-5-pcy3-cry-4
 EXPNO 17
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240124
 Time 0.06 h
 INSTRUM spect
 PROBHD Z140678_0037 (4
 PULPROG zgpg
 TD 20190
 SOLVENT CDC13
 NS 256
 DS 0
 SWH 25510.203 Hz
 FIDRES 2.527014 Hz
 AQ 0.3957240 sec
 RG 200
 DW 19.600 usec
 DE 6.50 usec
 TE 298.1 K
 D1 1.00000000 sec
 TD0 1
 SF01 128.4905453 MHz
 NUC1 11B
 P1 9.95 usec
 PLW1 50.00000000 W

F2 - Processing parameters
 SI 32768
 SF 128.4866907 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

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

Nutzer Libo Xiang
 %B11_CPD_128ns CDC13 (D:\NMR-Daten_AV_III_Nanobay) Xiang 52



Current Data Parameters
 NAME xlb-5-pcy3-cry-4
 EXPNO 13
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240124
 Time 0 h
 INSTRUM spect
 PROBHD Z140678_0037 (4
 PULPROG zgpg
 TD 20190
 SOLVENT CDC13
 NS 128
 DS 0
 SWH 25510.203 Hz
 FIDRES 2.527014 Hz
 AQ 0.3957240 sec
 RG 200
 DW 19.600 usec
 DE 6.50 usec
 TE 298.1 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SF01 128.4905453 MHz
 NUC1 11B
 P1 9.95 usec
 PLW1 50.00000000 W
 SF02 400.4720024 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 15.13799953 W
 PLW12 0.20214000 W
 PLW13 0.10167000 W

F2 - Processing parameters
 SI 65536
 SF 128.4866907 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 3.00

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

Nutzer Libo Xiang
%P31_CPD_128ns CDCl3 (D:\NMR-Daten_AV_III_Nanobay) Xiang 52

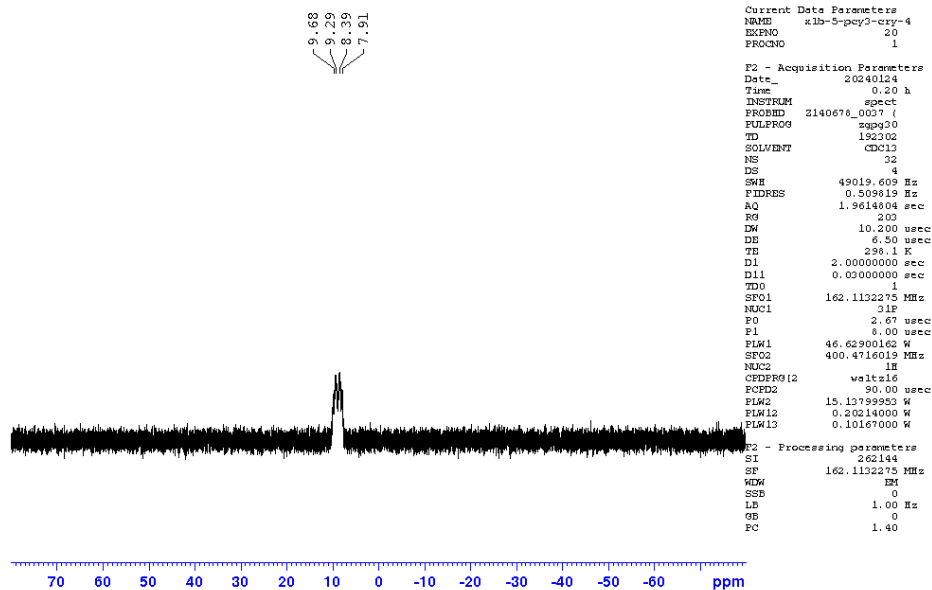


Figure S11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2b** in C_6D_6 at 298 K.

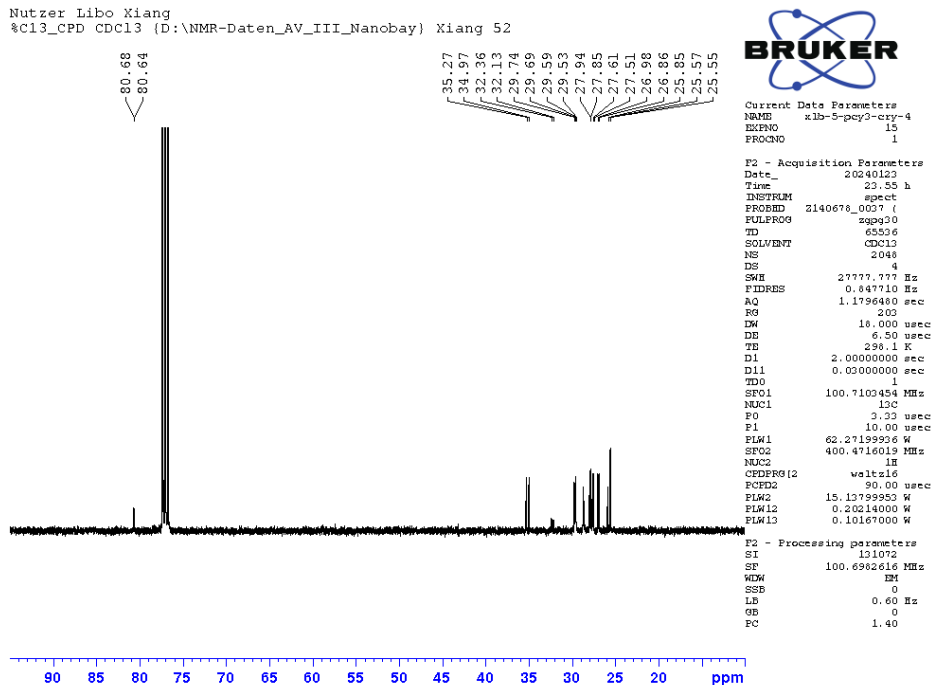


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2b** in C_6D_6 at 298 K.

Nutzer Libo Xiang
 %Proton_32ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 43

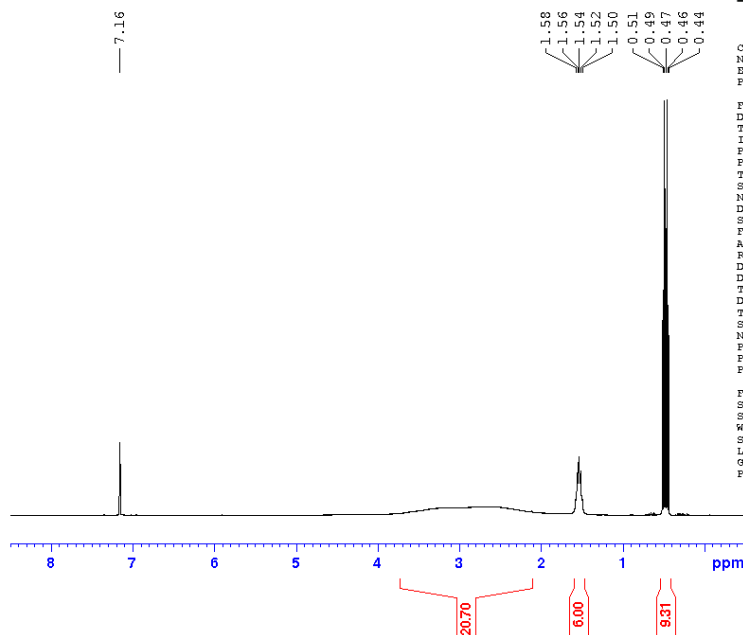


Figure S13. ^1H NMR spectra of **2c** in C_6D_6 at 298 K.

Nutzer Libo Xiang
 %ProB11dec_32ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 43

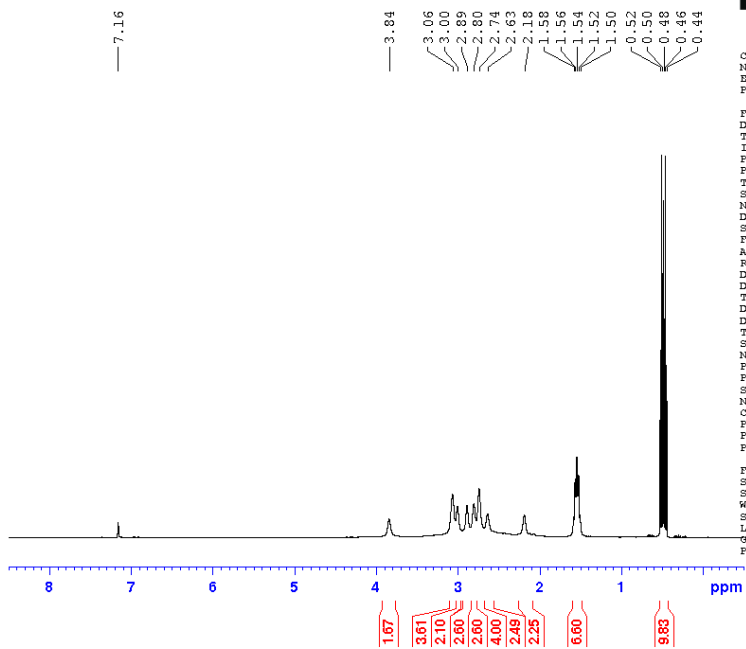
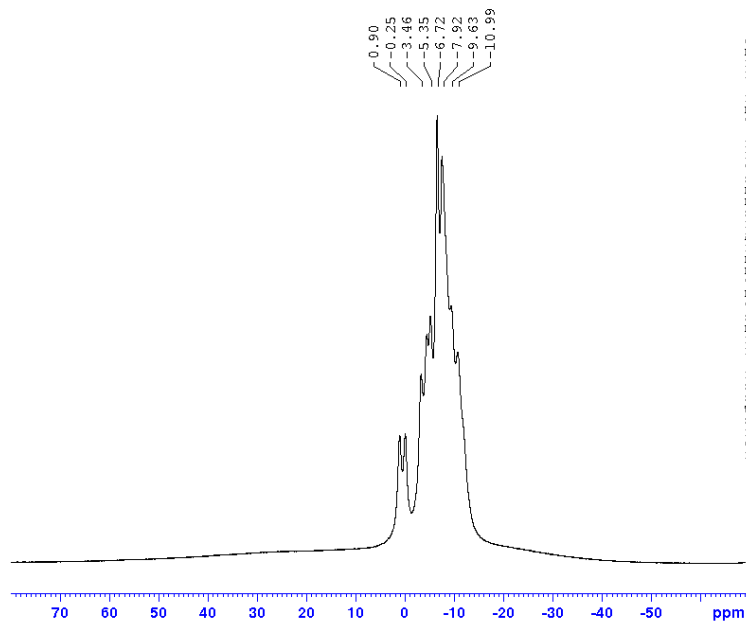


Figure S14. $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of **2c** in C_6D_6 at 298 K.

Nutzer Libo Xiang
%B11_ZG_256ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 43



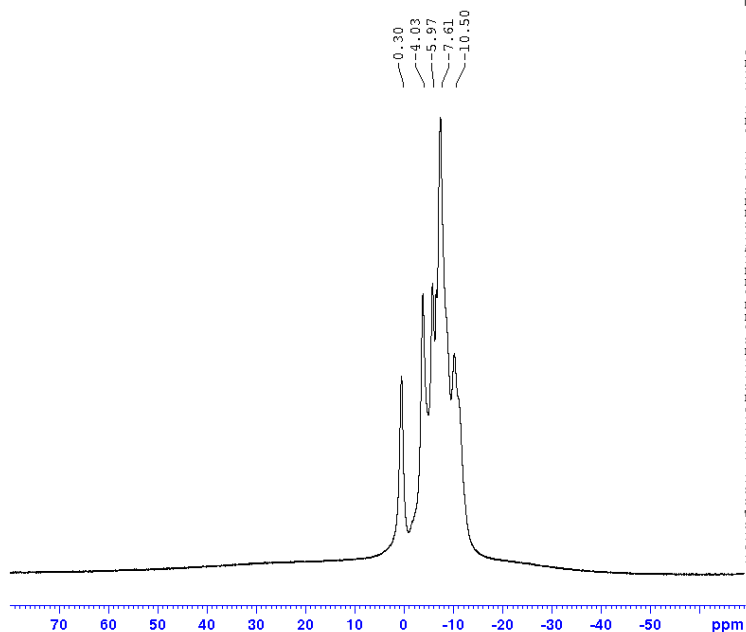
Current Data Parameters
NAME xlb-5-pet3-cry-2
EXFNO 27
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240123
Time 8.14 h
INSTRUM spect
PROBHD Z140678_0037 (4
PULPROG zgpg
TD 20190
SOLVENT C6D6
NS 256
DS 0
SWH 25510.200 Hz
FIDRES 2.527014 Hz
AQ 0.3957240 sec
RG 200
DM 19.600 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
SFO1 128.4905453 MHz
NUC1 11B
P1 9.95 usec
PLW1 50.00000000 W

F2 - Processing parameters
SI 32768
SF 128.4866907 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

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

Nutzer Libo Xiang
%B11_CPD_128ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 43



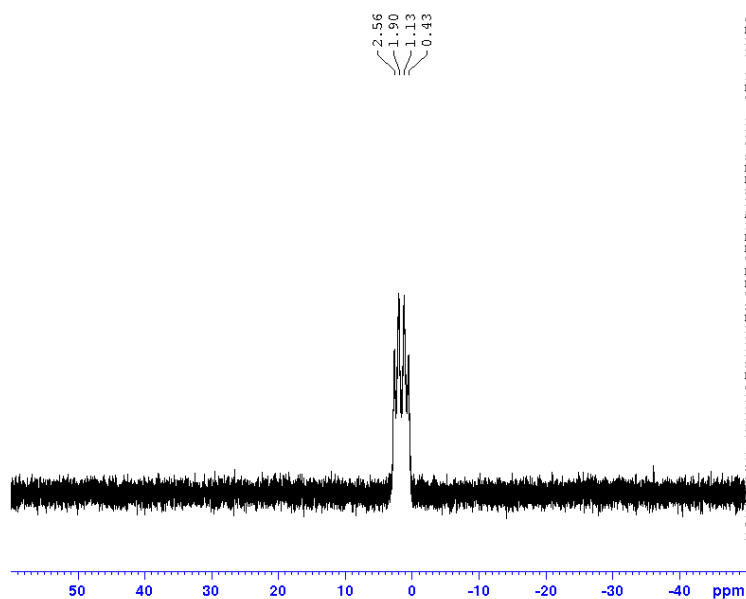
Current Data Parameters
NAME xlb-5-pet3-cry-2
EXFNO 26
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240123
Time 8.07 h
INSTRUM spect
PROBHD Z140678_0037 (4
PULPROG zgpg
TD 20190
SOLVENT C6D6
NS 128
DS 0
SWH 25510.200 Hz
FIDRES 2.527014 Hz
AQ 0.3957240 sec
RG 200
DM 19.600 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 128.4905453 MHz
NUC1 11B
P1 9.95 usec
PLW1 50.00000000 W
SFO2 400.4720024 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 15.13799953 W
PLW12 0.20214000 W
PLW13 0.10167000 W

F2 - Processing parameters
SI 65536
SF 128.4866907 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 3.00

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

Nutzer Libo Xiang
%P31_CPD_128ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 43



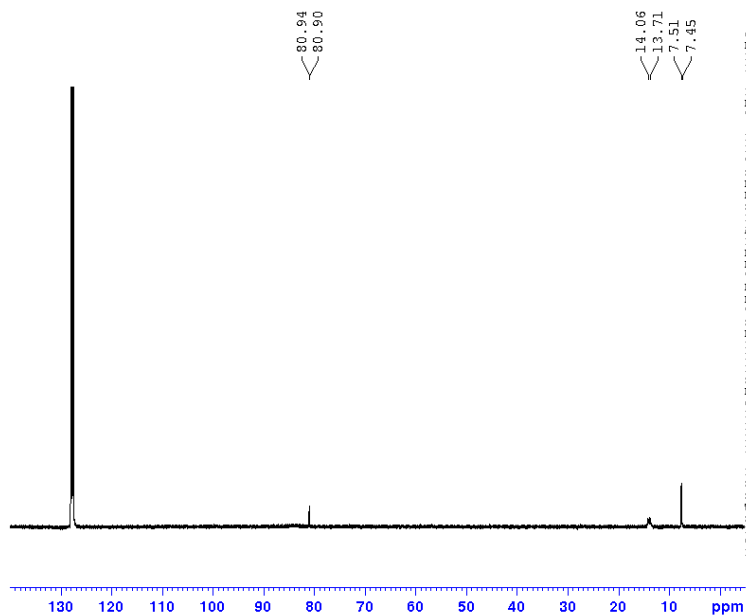
Current Data Parameters
NAME xlb-5-pet3-cry-2
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240123
Time 8.28 h
INSTRUM spect
PROBHD Z140678_0037 (
FULPROG zgpg30
TD 152302
SOLVENT C6D6
NS 32
DS 4
SWH 49019.609 Hz
FIDRES 0.509819 Hz
AQ 1.9614804 sec
RG 203
DW 10.200 usec
DE 6.50 usec
TE 298.1 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 162.1132275 MHz
NUC1 31P
P0 2.67 usec
P1 8.00 usec
PLW1 46.62900162 W
SFO2 400.4716019 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 15.12799953 W
PLW12 0.20214000 W
PLW13 0.10167000 W

F2 - Processing parameters
SI 262144
SF 162.1132275 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

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

Nutzer Libo Xiang
%C13_CPD C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 43



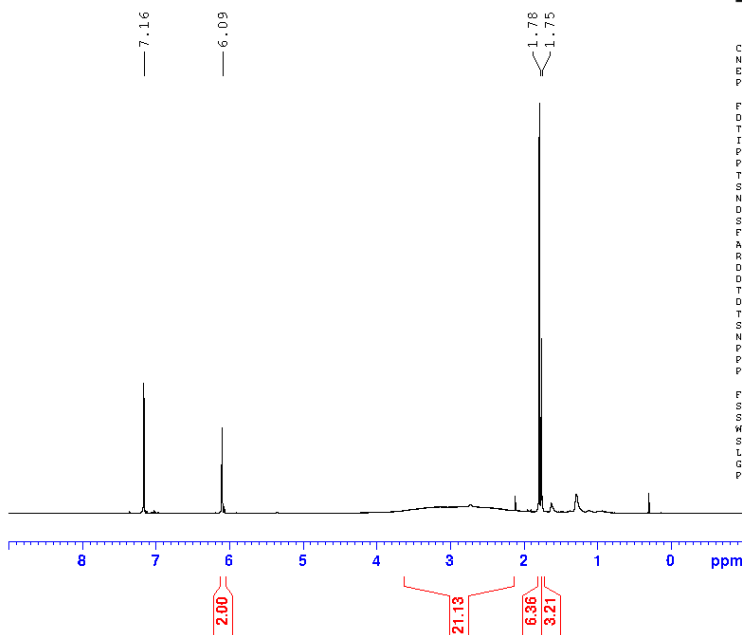
Current Data Parameters
NAME xlb-5-pet3-cry-2
EXPNO 31
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240123
Time 21.56 h
INSTRUM spect
PROBHD Z140678_0037 (
FULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 2048
DS 4
SWH 27777.777 Hz
FIDRES 0.847710 Hz
AQ 1.1796480 sec
RG 203
DW 18.000 usec
DE 6.50 usec
TE 298.1 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 100.7102454 MHz
NUC1 13C
P0 2.23 usec
P1 10.00 usec
PLW1 62.27199956 W
SFO2 400.4716019 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 15.12799953 W
PLW12 0.20214000 W
PLW13 0.10167000 W

F2 - Processing parameters
SI 131072
SF 100.6982616 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
PC 1.40

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

Nutzer Libo Xiang
 %Proton_32ns C6D6 [D:\NMR-Daten_AV_III_Nanobay] Xiang 41



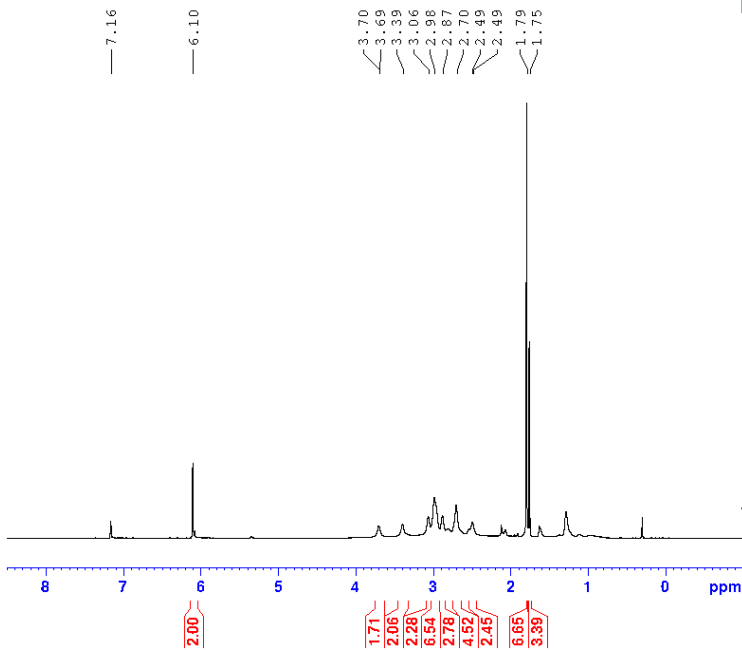
Current Data Parameters
 NAME x1b-5-MeCN-cry
 EXPNO 29
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20231126
 Time 7.30 h
 INSTRUM spect
 PROBHD Z140678_0037_1
 PULPROG zg30
 TD 96152
 SOLVENT C6D6
 NS 32
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.166670 Hz
 AQ 5.9998846 sec
 RG 71.8
 DW 62.400 usec
 DE 6.50 usec
 TE 298.1 K
 D1 1.00000000 sec
 TD0 1
 SF01 400.4724731 MHz
 NUC1 1H
 P0 3.47 usec
 P1 10.40 usec
 PLW1 15.13799953 W

F2 - Processing parameters
 SI 131072
 SF 400.4699968 MHz
 WDW EM
 SSB 0
 LB 0 Hz
 GB 0
 PC 1.40

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

Nutzer Libo Xiang
 %ProB11dec_32ns C6D6 [D:\NMR-Daten_AV_III_Nanobay] Xiang 41



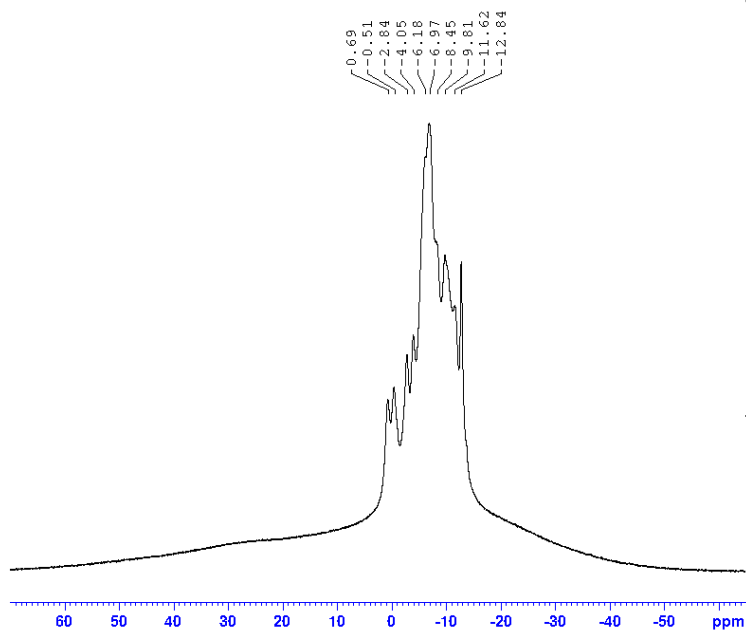
Current Data Parameters
 NAME x1b-5-MeCN-cry
 EXPNO 31
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20231126
 Time 7.35 h
 INSTRUM spect
 PROBHD Z140678_0037_1
 PULPROG zg30
 TD 73890
 SOLVENT C6D6
 NS 32
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.222593 Hz
 AQ 4.4925122 sec
 RG 22.6
 DW 60.800 usec
 DE 6.50 usec
 TE 298.1 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SF01 400.4724731 MHz
 NUC1 1H
 P1 10.40 usec
 PLW1 15.13799953 W
 SF02 128.4852773 MHz
 NUC2 11B
 CPOPRG2 waltz16
 PCPD2 100.00 usec
 PLW2 50.00000000 W
 PLW12 0.49500999 W

F2 - Processing parameters
 SI 131072
 SF 400.4699968 MHz
 WDW EM
 SSB 0
 LB 0 Hz
 GB 0
 PC 1.00

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

Nutzer Libo Xiang
%B11_ZG_256ns C6D6 [D:\NMR-Daten_AV_III_Nanobay] Xiang 41



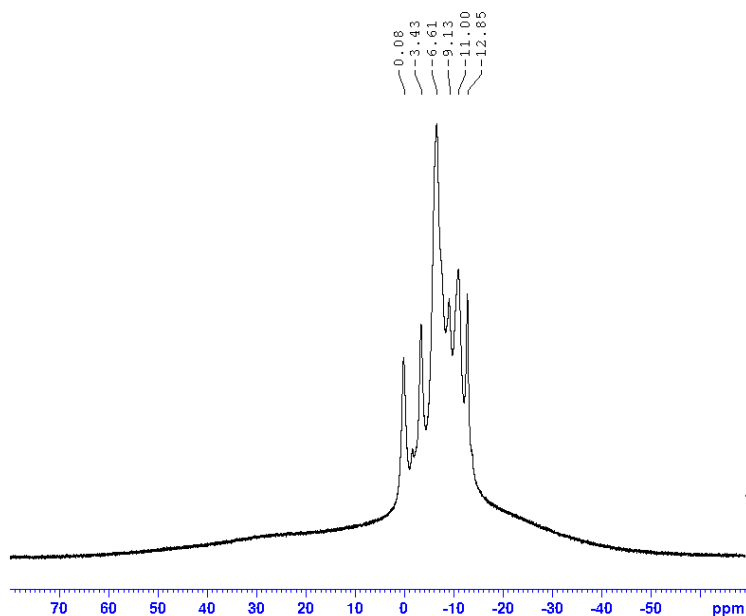
Current Data Parameters
NAME xlb-5-MeNC-cry
EXPNO 28
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231126
Time 7.25 h
INSTRUM spect
PROBHD Z140678_0037 1
PULPROG zg
TD 20190
SOLVENT C6D6
NS 256
DS 0
SWH 25510.203 Hz
FIDRES 2.527014 Hz
AQ 0.3957240 sec
RG 203
DW 19.600 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
SF01 128.4905453 MHz
NUC1 11B
P1 9.95 usec
PLW1 50.00000000 W

F2 - Processing parameters
SI 32768
SF 128.4866907 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

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

Nutzer Libo Xiang
%B11_CPD_128ns C6D6 [D:\NMR-Daten_AV_III_Nanobay] Xiang 41



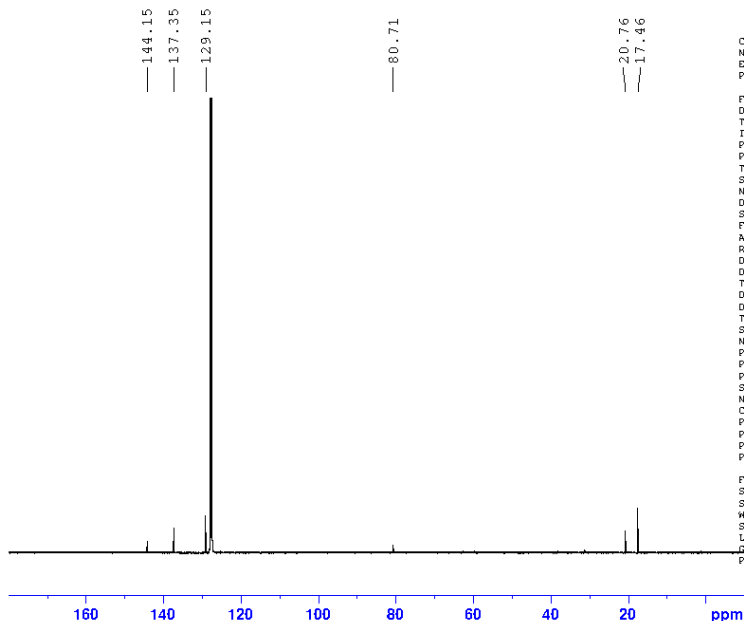
Current Data Parameters
NAME xlb-5-MeNC-cry
EXPNO 27
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231126
Time 7.19 h
INSTRUM spect
PROBHD Z140678_0037 1
PULPROG zpgg
TD 20190
SOLVENT C6D6
NS 128
DS 0
SWH 25510.203 Hz
FIDRES 2.527014 Hz
AQ 0.3957240 sec
RG 203
DW 19.600 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SF01 128.4905453 MHz
NUC1 11B
P1 9.95 usec
PLW1 50.00000000 W
SF02 400.4720024 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 15.13799953 W
PLW12 0.20214000 W
PLW13 0.10157000 W

F2 - Processing parameters
SI 65536
SF 128.4866907 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 3.00

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

Nutzer Libo Xiang
%c13_CPD C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 41



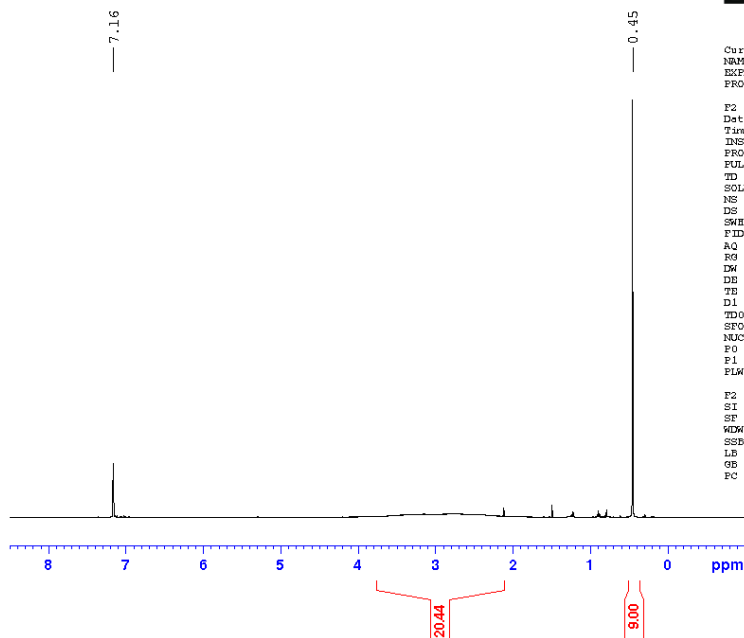
Current Data Parameters
NAME x1b-5-Me6NC-cry
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231125
Time 12.07 h
INSTRUM spect
PROBHD Z140678_0037 J
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 5000
DS 4
SWH 27777.777 Hz
FIDRES 0.847710 Hz
AQ 1.1796480 sec
RG 203
DW 18.000 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SF01 100.7103454 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 62.27199936 W
SF02 400.4716019 MHz
NUC2 1H
PCPD2[2] walcz16
PCPD2 90.00 usec
PLW2 15.13799953 W
PLW12 0.20214000 W
PLW13 0.10167000 W

F2 - Processing parameters
SI 131072
SF 100.6982616 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
PC 1.40

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

Nutzer Libo Xiang
%Proton_32ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 53



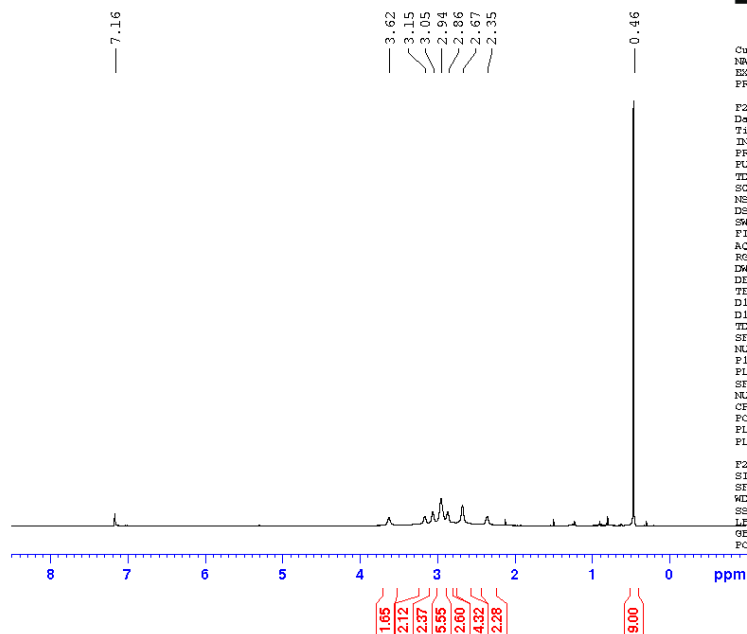
Current Data Parameters
NAME x1b-5-tBunc-cry-1
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240124
Time 0.43 h
INSTRUM spect
PROBHD Z140678_0037 J
PULPROG zg20
TD 96152
SOLVENT C6D6
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 5.9998846 sec
RG 11.8
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
SF01 400.4724721 MHz
NUC1 1H
P0 3.47 usec
P1 10.40 usec
PLW1 15.13799953 W

F2 - Processing parameters
SI 131072
SF 400.4699967 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.40

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

Nutzer Libo Xiang
 %Probl1dec_32ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 53



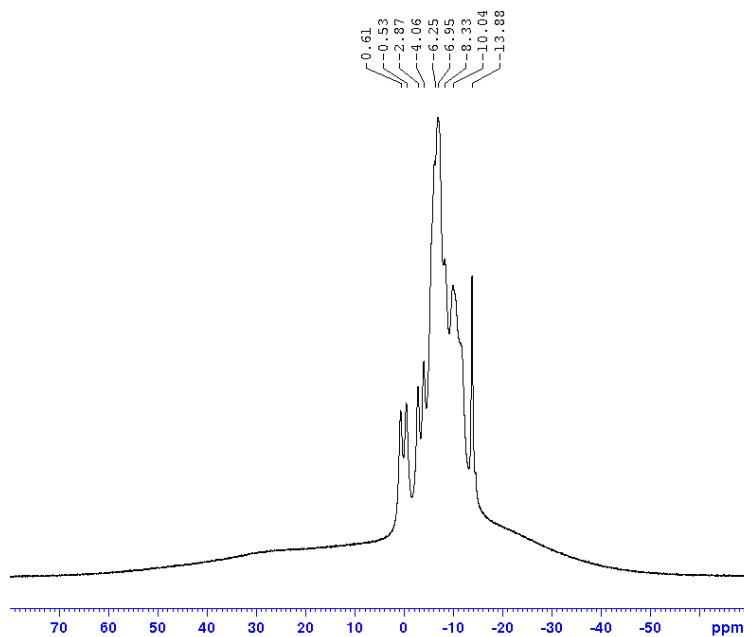
Current Data Parameters
 NAME xlb-5-tBunc-cxy-1
 EXPNO 13
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240124
 Time 0.47 h
 INSTRUM spect
 PROBHD Z140678_0037 ()
 PULPROG zgpg
 TD 73690
 SOLVENT C6D6
 NS 32
 DS 2
 SWH 6223.665 Hz
 FIDRES 0.222593 Hz
 AQ 4.4925122 sec
 RG 22.6
 DW 60.800 usec
 DE 6.50 usec
 TE 298.1 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SFO1 400.4724731 MHz
 NUC1 1H
 P1 10.40 usec
 PL1 15.13799883 W
 SFO2 126.4652773 MHz
 NUC2 11B
 CDEPRG12 waltz16
 PCPD2 100.00 usec
 PLW2 50.00000000 W
 PLW12 0.49500999 W

F2 - Processing parameters
 SI 131072
 SF 400.4699967 MHz
 WDM EM
 SSB 0
 LB 0 Hz
 GB 0
 PC 1.00

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

Nutzer Libo Xiang
 %B11_2G_256ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 53



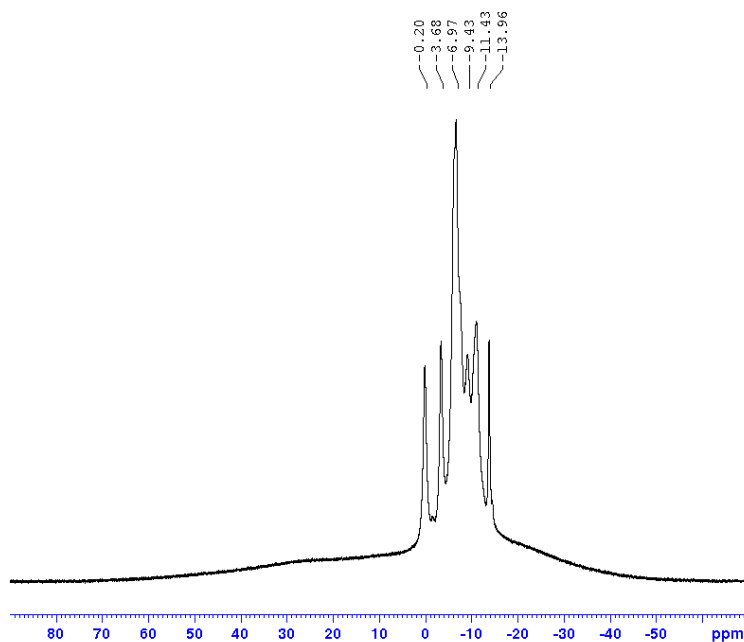
Current Data Parameters
 NAME xlb-5-tBunc-cxy-1
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240124
 Time 0.28 h
 INSTRUM spect
 PROBHD Z140678_0037 ()
 PULPROG zg
 TD 20190
 SOLVENT C6D6
 NS 256
 DS 0
 SWH 25510.203 Hz
 FIDRES 2.527014 Hz
 AQ 0.3957240 sec
 RG 203
 DW 19.600 usec
 DE 6.50 usec
 TE 298.1 K
 D1 1.00000000 sec
 TD0 1
 SFO1 126.4905453 MHz
 NUC1 11B
 P1 9.95 usec
 PLW1 50.00000000 W

F2 - Processing parameters
 SI 52768
 SF 126.4666907 MHz
 WDM EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

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

Nutzer Libo Xiang
 %B11_CPD_128ns C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 53



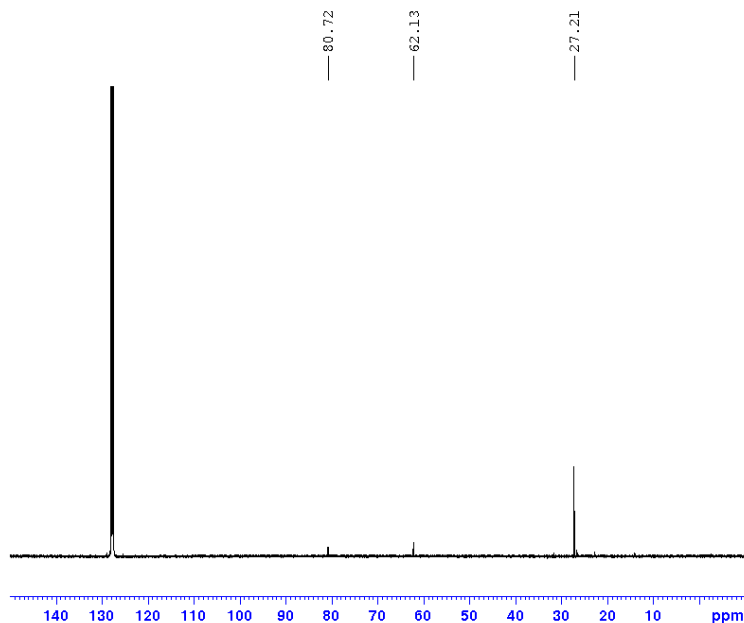
Current Data Parameters
 NAME x1b-5-tBunc-cxy-1
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240124
 Time 0.21 h
 INSTRUM spect
 PROBHD Z140678_0037 ()
 PULPROG zgpg
 TD 20190
 SOLVENT C6D6
 NS 128
 DS 0
 SWH 25510.200 Hz
 FIDRES 2.527014 Hz
 AQ 0.3957240 sec
 RG 200
 DW 19.600 usec
 DE 6.50 usec
 TE 298.1 K
 D1 1.0000000 sec
 D11 0.0300000 sec
 TD0 1
 SFO1 128.4905453 MHz
 NUC1 11B
 P1 9.95 usec
 PL11 50.0000000 W
 SFO2 400.4720024 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 15.1379953 W
 PLW12 0.20214000 W
 PLW13 0.10167000 W

F2 - Processing parameters
 SI 65536
 SF 128.4866907 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 3.00

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

Nutzer Libo Xiang
 %C13_CPD C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 53



Current Data Parameters
 NAME x1b-5-tBunc-cxy-1
 EXPNO 14
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240124
 Time 5.40 h
 INSTRUM spect
 PROBHD Z140678_0037 ()
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 NS 2048
 DS 4
 SWH 27777.777 Hz
 FIDRES 0.647710 Hz
 AQ 1.1796480 sec
 RG 200
 DW 18.000 usec
 DE 6.50 usec
 TE 298.1 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1
 SFO1 100.7103454 MHz
 NUC1 13C
 P0 3.23 usec
 PL1 10.00 usec
 PLW1 62.27199926 W
 SFO2 400.4716019 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 15.1379953 W
 PLW12 0.20214000 W
 PLW13 0.10167000 W

F2 - Processing parameters
 SI 131072
 SF 100.6982616 MHz
 WDW EM
 SSB 0
 LB 0.60 Hz
 GB 0
 PC 1.40

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

Nutzer Libo Xiang
 %Proton_32ns C6D6 {D:\NMR-Daten_AV_III_Nanobay} Xiang 23

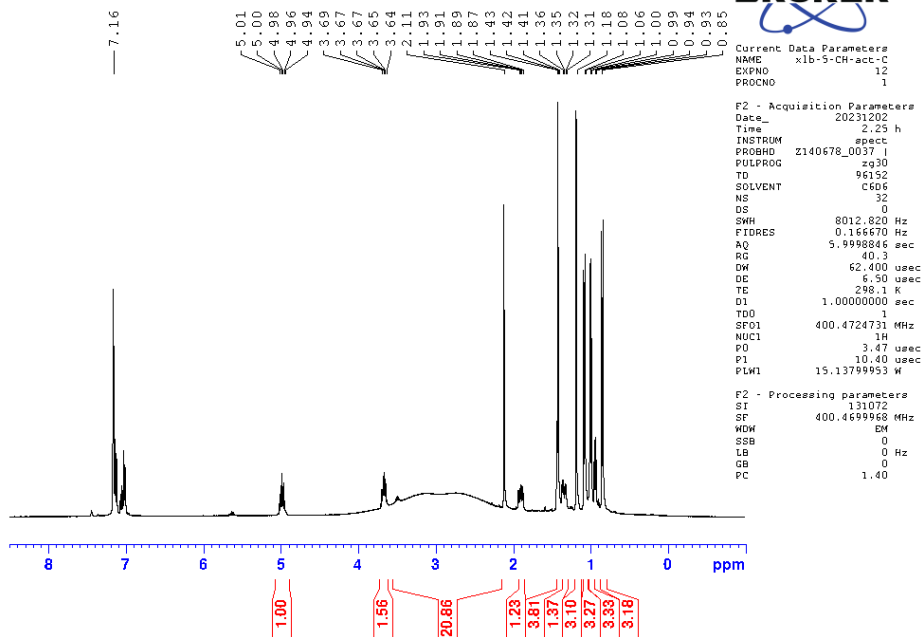


Figure S29. ^1H NMR spectra of 4 in C_6D_6 at 298 K.

Nutzer Libo Xiang
 %ProB11dec_32ns C6D6 {D:\NMR-Daten_AV_III_Nanobay} Xiang 23

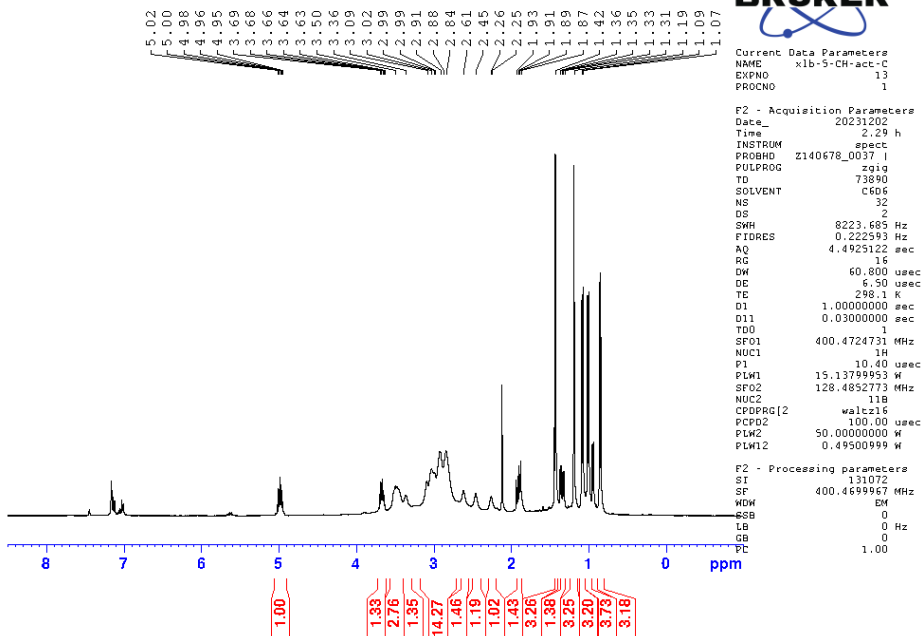
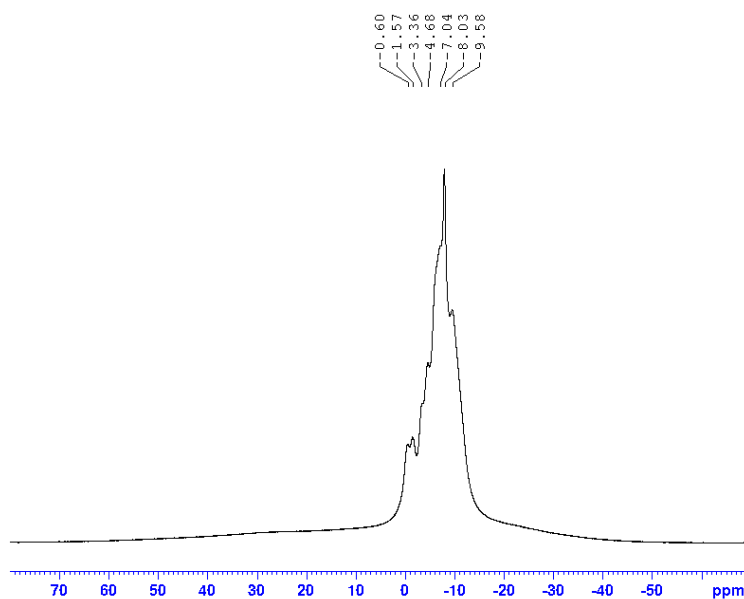


Figure S30. $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of 4 in C_6D_6 at 298 K.

Nutzer Libo Xiang
%B11_ZG_256ns C6D6 [D:\NMR-Daten_AV_III_Nanobay] Xiang 23



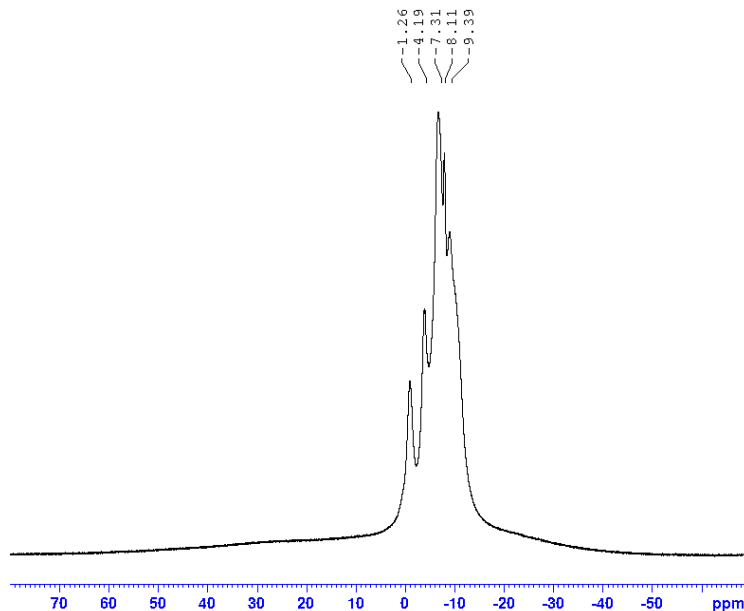
Current Data Parameters
NAME xlb-5-CH-act-C
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231202
Time 2.20 h
INSTRUM spect
PROBHD Z140678_0037 1
PULPROG zg
TD 20190
SOLVENT C6D6
NS 256
DS 0
SWH 25510.203 Hz
FIDRES 2.527014 Hz
AQ 0.3957240 sec
RG 203
DW 19.600 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
SF01 128.4905453 MHz
NUC1 11B
P1 9.95 usec
PLW1 50.00000000 W

F2 - Processing parameters
SI 32768
SF 128.4866907 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

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

Nutzer Libo Xiang
%B11_CPD_128ns C6D6 [D:\NMR-Daten_AV_III_Nanobay] Xiang 23



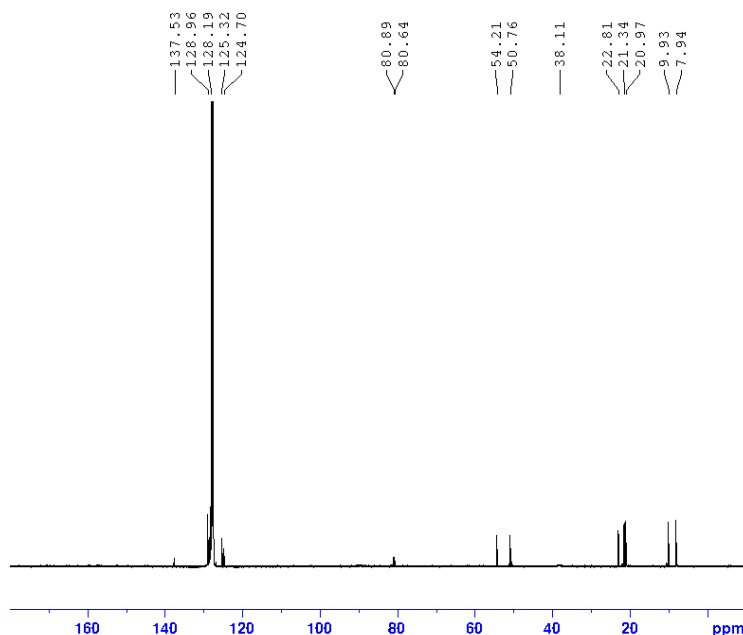
Current Data Parameters
NAME xlb-5-CH-act-C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231202
Time 2.13 h
INSTRUM spect
PROBHD Z140678_0037 1
PULPROG zpgg
TD 20190
SOLVENT C6D6
NS 128
DS 0
SWH 25510.203 Hz
FIDRES 2.527014 Hz
AQ 0.3957240 sec
RG 203
DW 19.600 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SF01 128.4905453 MHz
NUC1 11B
P1 9.95 usec
PLW1 50.00000000 W
SF02 400.4720024 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 15.13799953 W
PLW12 0.20214000 W
PLW13 0.10157000 W

F2 - Processing parameters
SI 65536
SF 128.4866907 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 3.00

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

Nutzer Libo Xiang
 %C13_CPD C6D6 (D:\NMR-Daten_AV_III_Nanobay) Xiang 23



Current Data Parameters
 NAME xlb-5-CH-act-C
 EXPNO 14
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20231202
 Time 7.02 h
 INSTRUM spect
 PROBHD Z140678_0037 J
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 NS 5000
 DS 4
 SWH 27777.777 Hz
 FIDRES 0.847710 Hz
 AQ 1.1796480 sec
 RG 203
 DW 18.000 usec
 DE 6.50 usec
 TE 298.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDD 1
 SFO1 100.7103454 MHz
 NUC1 13C
 P0 3.33 usec
 P1 10.00 usec
 PLW1 62.27199936 W
 SFO2 400.4716019 MHz
 NUC2 1H
 SFOPRG[2] walcz16
 PCPD2 90.00 usec
 PLW2 15.13799953 W
 PLW12 0.20214000 W
 PLW13 0.10167000 W

F2 - Processing parameters
 SI 131072
 SF 100.6982616 MHz
 WDW EM
 SSB 0
 LB 0.60 Hz
 GB 0
 PC 1.40

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

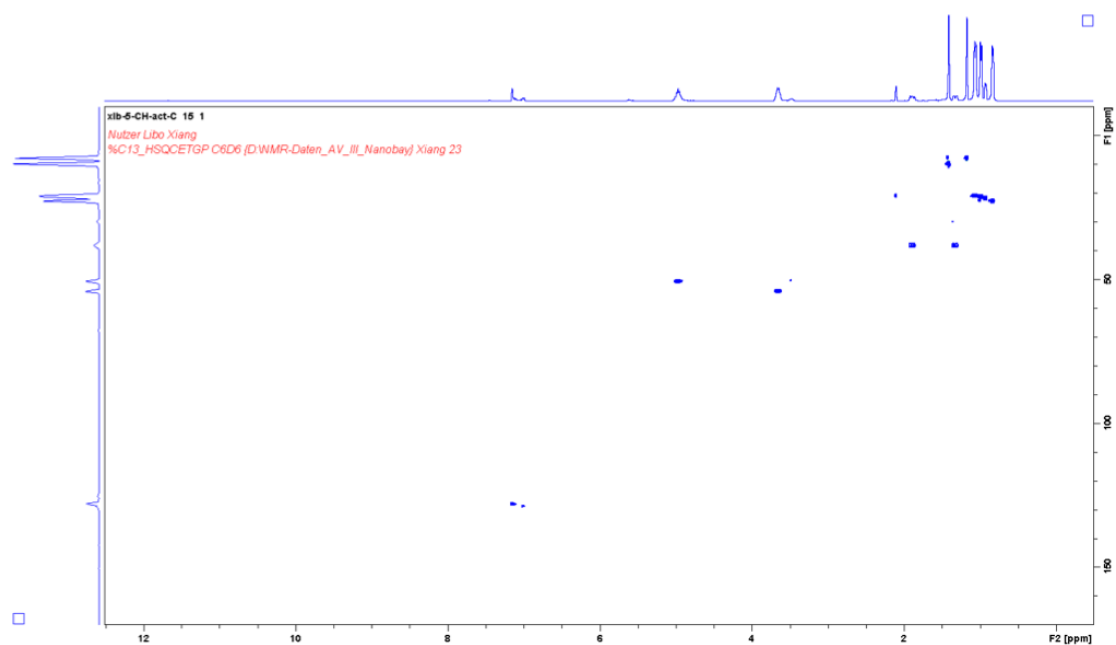


Figure S34. HSQC spectra of **4** in C_6D_6 at 298 K.

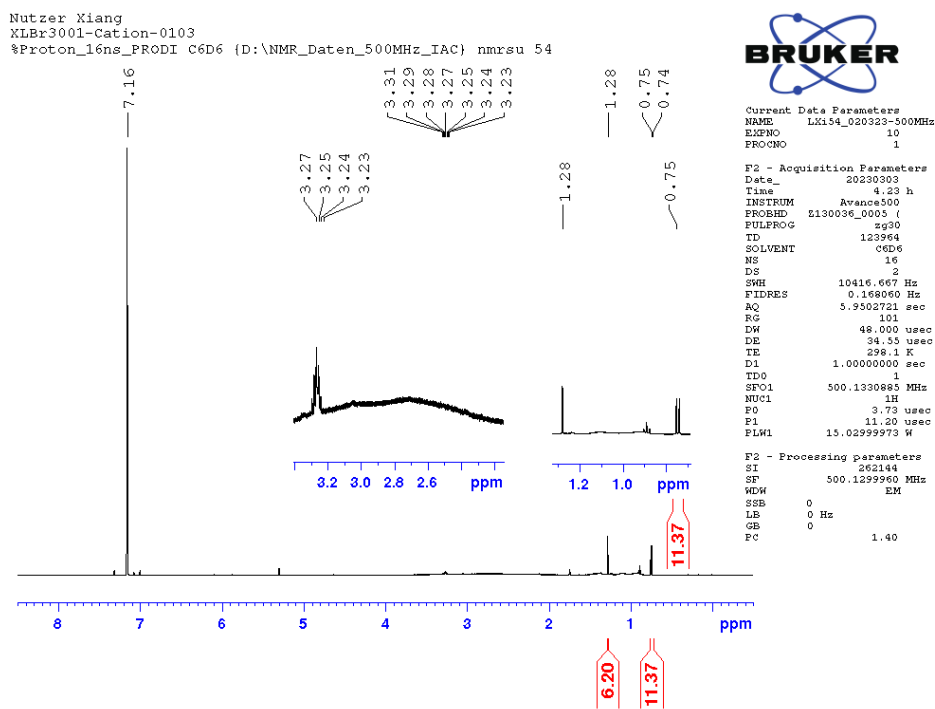


Figure S35. ^1H NMR spectra of **5** in C_6D_6 at 298 K.

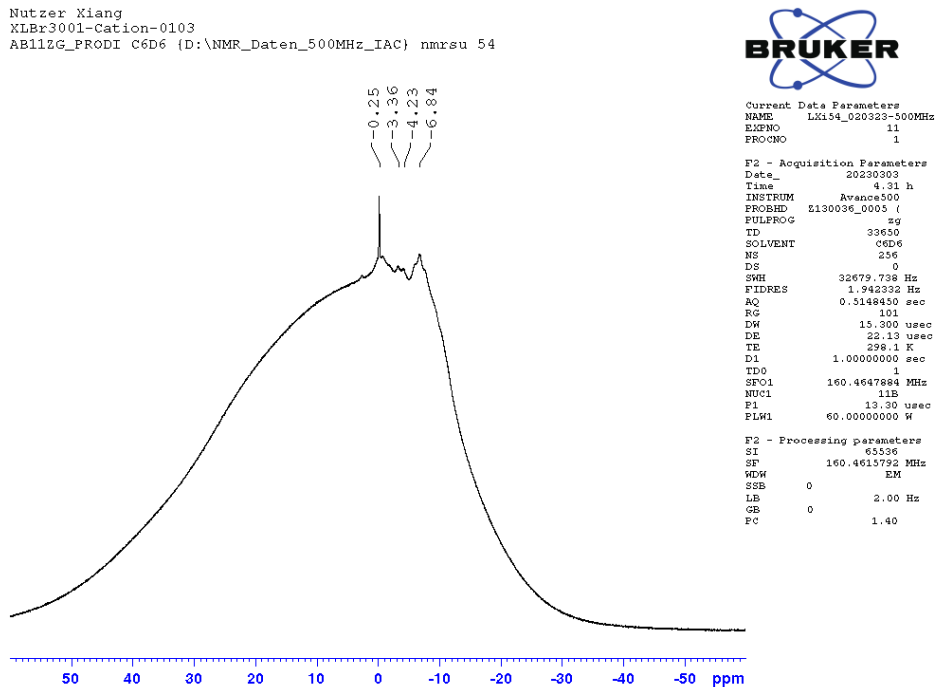


Figure S36. ^{11}B NMR spectra of **5** in C_6D_6 at 298 K.

Nutzer Xiang
 XLBr3001-Cation-0103
 AB11CPD_PRODI C6D6 {D:\NMR_Daten_500MHz_IAC} nmrsu 54



Current Data Parameters
 NAME LK154_020323-500MHz
 EXPNO 12
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20230303
 Time 4.38 h
 INSTRUM Avance500
 PROBHD E130036_0005 (zggg
 PULPROG zgpg30
 TD 33630
 SOLVENT C6D6
 NS 256
 DS 0
 SWH 32679.738 Hz
 FIDRES 1.942332 Hz
 AQ 0.5148450 sec
 RG 101
 DW 15.300 usec
 DE 22.13 usec
 TE 298.1 K
 D1 1.0000000 sec
 D11 0.0300000 sec
 TD0 1
 SFO1 160.4679976 MHz
 NUC1 11B
 P1 13.30 usec
 PLW1 60.0000000 W
 SFO2 500.1320000 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 65.00 usec
 PLW2 15.02999973 W
 PLW12 0.44624001 W
 PLW13 0.14793999 W

F2 - Processing parameters
 SI 63536
 SF 160.4615752 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.40

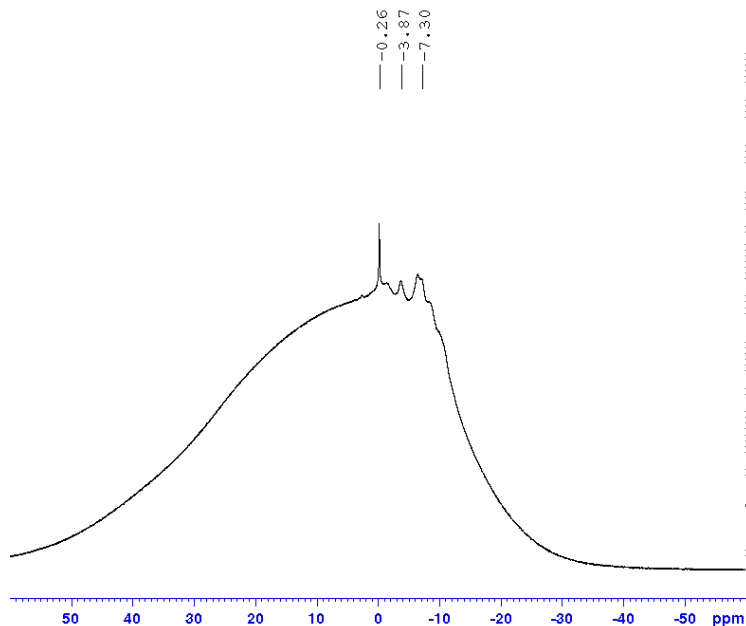


Figure S37. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of **5** in C_6D_6 at 298 K.

Nutzer Xiang
 XLBr3001-Cation-0103
 AC13CPD_PRODI C6D6 {D:\NMR_Daten_500MHz_IAC} nmrsu 54



Current Data Parameters
 NAME LK154_020323-500MHz
 EXPNO 17
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20230303
 Time 11.14 h
 INSTRUM Avance500
 PROBHD E130036_0005 (zggg30
 PULPROG zgpg30
 TD 123586
 SOLVENT C6D6
 NS 6144
 DS 0
 SWH 35714.285 Hz
 FIDRES 0.568762 Hz
 AQ 1.7582040 sec
 RG 101
 DW 14.000 usec
 DE 19.40 usec
 TE 298.1 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1
 SFO1 125.7728795 MHz
 NUC1 13C
 P1 3.13 usec
 PLW1 9.40 usec
 PLW1 65.83499908 W
 SFO2 500.1320000 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 65.00 usec
 PLW2 15.02999973 W
 PLW12 0.44624001 W
 PLW13 0.14793999 W

F2 - Processing parameters
 SI 262144
 SF 125.7577885 MHz
 WDW EM
 SSB 0
 LB 1.50 Hz
 GB 0
 PC 1.00

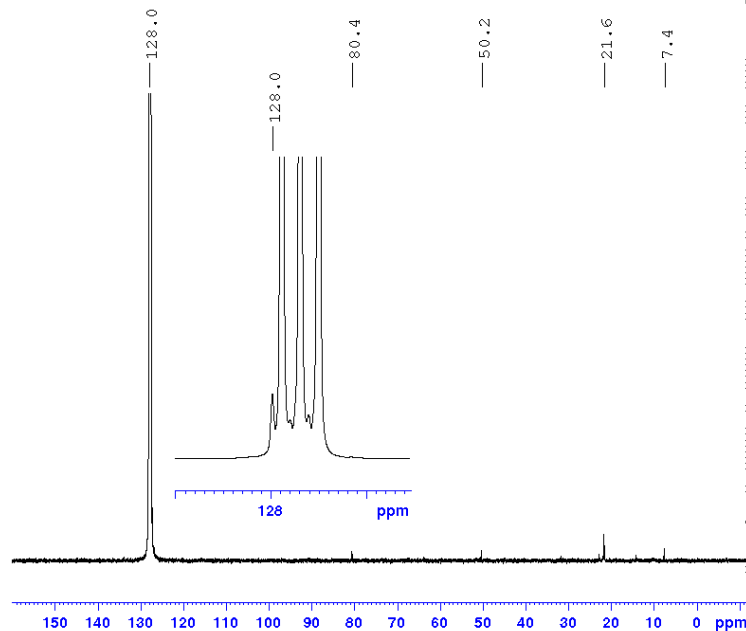


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5** in C_6D_6 at 298 K.

Crystallographic Details

The crystal data of **4** and **5** was collected on a Bruker D8 VENTURE diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). 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 method⁴ and by using Olex2⁵ as the graphical interface. The model was refined with the ShelXL program⁶ 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 $\text{CuK}\alpha$ radiation. The structure was solved using intrinsic phasing method⁴, refined with the ShelXL program⁶ 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 ₂ Br 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
ρ _{calc} /cm ³	1.353
μ/mm ⁻¹	1.384
F(000)	2576.0
Crystal size/mm ³	0.358 × 0.238 × 0.171
Radiation	MoKα (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
ρ _{calc} /cm ³	1.306
μ/mm ⁻¹	1.563
F(000)	524.0
Crystal size/mm ³	0.24 × 0.23 × 0.12
Radiation	MoKα (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•(C₇H₈) .	
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
ρ _{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 Kα (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
ρ _{calc} /cm ³	1.230
μ/mm ⁻¹	1.183
F(000)	1780.0
Crystal size/mm ³	0.2 × 0.2 × 0.1
Radiation	MoKα (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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