

## Supporting Information

### **Structure-Constraint Induced Increase in Lewis Acidity of Tris(ortho-carboranyl)borane and Selective Complexation with Bestmann Ylides**

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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.  $C_6D_6$  was distilled from Na/K and stored under an argon atmosphere before use.  $CDCl_3$  was dried and stored over 4 molecular sieves before use.  $Ph_3PCCO$  was purchased from commercial sources and used without further purification.  $Cy_3PCCO$ <sup>1</sup>,  $LiC_2B_{10}H_{11}$ <sup>2</sup>,  $(C_2B_{10}H_{10})_2BBr$ <sup>3a</sup> and  $^{Me}iPr$ <sup>3b</sup> were synthesized according to the literature. Other reagents were used as received without further purification.

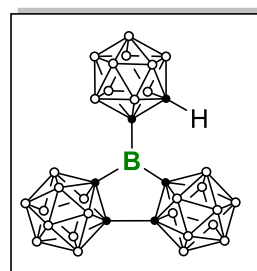
The nuclear magnetic resonance spectroscopy was recorded on a Bruker Avance-400 ( $^1H$  400.1 MHz;  $^{11}B$  128.5 MHz;  $^{13}C$  101 MHz;  $^{31}P$ : 162. MHz) spectrometer at room temperature.  $^{11}B$  NMR,  $^{11}B\{^1H\}$  spectra were referenced relative to 15%  $BF_3 \cdot OEt_2$ .  $^{31}P\{^1H\}$  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. IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox.

## Synthesis and Spectral Data

### Synthesis of **1**

The 5 mL toluene solution of  $(C_2B_{10}H_{10})_2BBr$  (375.1 mg, 1 mmol) was slowly added to a toluene (50 mL) suspension of  $LiC_2B_{10}H_{11}$  (150.2 mg, 1 mmol) at  $-78\text{ }^\circ\text{C}$  and warmed to room temperature gradually. The reaction mixture was stirred for 12 hours at room temperature. The suspension was filtrated to separate the lithium salt and all volatiles of the filtrate were removed under reduced pressure to obtain the product as a pale-yellow solid. The analytically pure product was crystallized from concentrated toluene solution at  $-30\text{ }^\circ\text{C}$  for 12 h to yield **1** as a colorless crystalline solid.

$^1\text{H NMR}$  (400 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 3.68–1.42 (br. m, 30H, BH), 3.70 (s, 1H,  $C_{\text{carborane}}H$ ).  $^1\text{H}\{^{11}\text{B}\}$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 2.11 (s, 3H, BH), 2.28 (s, 5H, BH), 2.33 (s, 3H, BH), 2.45 (s, 3H, BH), 2.67 (s, 4H, BH), 2.76 (s, 4H, BH), 2.87 (s, 4H, BH), 2.98 (s, 1H, BH), 3.09 (s, 2H, BH), 3.20 (s, 1H, BH), 3.70 (s, 1H,  $C_{\text{carborane}}H$ ).  $^{11}\text{B NMR}$  (128 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 65.22 (br, s,  $B\text{-}o\text{-carborane}$ ), 5.64 (d.  $J = 153.3\text{ Hz}$ ,  $B_{\text{carborane}}$ ),  $-2.40$  (d.  $J = 163.4\text{ Hz}$ ,  $B_{\text{carborane}}$ ),  $-5.51$  (d.  $J = 153.3\text{ Hz}$ ,  $B_{\text{carborane}}$ ),  $-11.60$  (d.  $J = 147.9\text{ Hz}$ ,  $B_{\text{carborane}}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 64.94 (br, s,  $B\text{-}o\text{-carborane}$ ), 5.63 (s,  $B_{\text{carborane}}$ ),  $-0.64$  (s,  $C_{\text{carborane}}B$ ),  $-2.43$  (s,  $B_{\text{carborane}}$ ),  $-5.42$  (s,  $B_{\text{carborane}}$ ),  $-7.33$  (s,  $B_{\text{carborane}}$ ),  $-11.54$  (s,  $B_{\text{carborane}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 59.7 (s,  $C_{\text{carborane}}$ ), 79.7 (s,  $C_{\text{carborane}}$ ), **Elemental analysis:** calcd. for  $C_6H_{31}B_{31}$ , C, 16.44; H, 7.13; found C, 16.20; H, 6.22. **HRMS (LIFDI):** calcd. for  $C_6H_{31}B_{31}$  438.5528; found: 438.5519. Yield: 64 % (279.9 mg, 0.64 mmol).

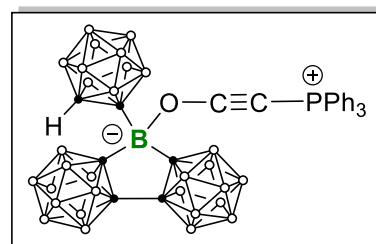


### Synthetic protocols for **3**

The 1 mL toluene solution of Bestmann's ylide  $R_3PCCO$  (0.32 mmol) was slowly added to a solution of **1** (106 mg, 0.32 mmol) in 5 mL toluene at room temperature. The reaction mixture was stirred for 4 h. The precipitate was collected through filtration and 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  $-30\text{ }^\circ\text{C}$  for 12 h to yield **2** as a colorless crystalline solid.

For **3a**:

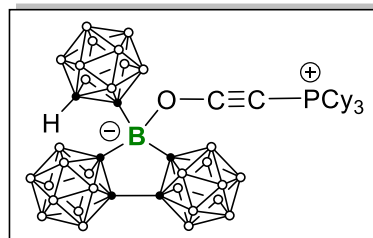
**<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 2.02–3.98 (br. m, 30H, BH), 4.12 (s, 1H, C<sub>carborane</sub>H), 6.88–6.92 (m, 6H, H of Ph), 6.94–6.97 (m, 3H, H of Ph), 7.17 to 7.23 (m, 6H, H of Ph). **<sup>1</sup>H{<sup>11</sup>B}** **NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 2.51 (s, 2H, BH), 2.62 (s, 2H, BH), 2.67 (s, 2H, BH), 2.73 (s, 4H, BH), 2.80 (s, 4H, BH), 2.90 (s, 8H, BH), 3.10 (s, 3H, BH), 3.19 (s, 1H, BH), 3.25 (s, 2H, BH), 3.66



(s, 2H, BH), 4.12 (s, 1H, C<sub>carborane</sub>H), 6.88–6.92 (m, 6H, H of Ph), 6.95–6.97 (m, 3H, H of Ph), 7.18–7.23 (m, 6H, H of Ph). **<sup>11</sup>B NMR** (128 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 0.65 (br, s, B<sub>carborane</sub>), -3.64 (d, J = 153.7 Hz, B<sub>carborane</sub>), -7.71 (br, s, B<sub>carborane</sub>), -11.88 (br, s, B<sub>carborane</sub>). **<sup>11</sup>B{<sup>1</sup>H}** **NMR** (128 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 0.80 (s, B<sub>carborane</sub>), -3.53 (s, C<sub>carborane</sub>B), -7.53 (s, B<sub>carborane</sub>), -12.00 (s, B<sub>carborane</sub>). **<sup>31</sup>P{<sup>1</sup>H}** **NMR** (162 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 5.17. **<sup>13</sup>C{<sup>1</sup>H}** **NMR** (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 13.30 (d, J<sub>P-C</sub> = 133 Hz, P=C), 60.6 (s, C<sub>carborane</sub>), 78.5 (s, C<sub>carborane</sub>), 121.3 (d, J<sub>P-C</sub> = 100.6 Hz, C of Ph), 128.6 (d, J<sub>P-C</sub> = 76.9 Hz, CO), 129.6 (d, J<sub>P-C</sub> = 13.8 Hz, C of Ph), 132.4 (d, J<sub>P-C</sub> = 12.3 Hz, C of Ph), 134.2 (d, J<sub>P-C</sub> = 3.2 Hz, C of Ph). **HRMS**: calcd. for [C<sub>26</sub>H<sub>46</sub>B<sub>31</sub>OP]<sup>+</sup>, 740.6389; found: 740.6497. Yield: 75 % (177.8 mg, 0.24 mmol). **IR**: 2198, 1603, 1439, 1112 cm<sup>-1</sup>.

For **3b**:

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ [ppm] = 1.32–1.38 (m, 10H, H of Cy), 1.54–1.57 (m, 6H, H of Cy), 3.30–3.67 (m, 47H, Cy and carborane overlapped), 3.96 (s, 1H, C<sub>carborane</sub>H). **<sup>1</sup>H{<sup>11</sup>B}** **NMR** (400 MHz, CDCl<sub>3</sub>): δ [ppm] = 1.33–1.39 (m, 10H, H of Cy), 1.54 to 1.57 (m, 6H, H of Cy), 1.85 (br, s, 3H, H of Cy), 1.98–2.02 (m, 14H, H of Cy), 2.12–2.24 (s, 15H, BH), 2.36 (s, 4H, BH), 2.40



(s, 4H, BH), 2.54 (s, 2H, BH), 2.62 (s, 2H, BH), 3.17 (s, 1H, BH), 3.29 (s, 2H, C<sub>carborane</sub>H), 3.97 (s, 1H, C<sub>carborane</sub>H). **<sup>11</sup>B NMR** (128 MHz, CDCl<sub>3</sub>): δ [ppm] = -0.36 (s, B<sub>carborane</sub>), -4.30 (d, J = 148.8 Hz, B<sub>carborane</sub>), -8.08 (br, s, B<sub>carborane</sub>), -12.26 (br, s, B<sub>carborane</sub>). **<sup>11</sup>B{<sup>1</sup>H}** **NMR** (128 MHz, CDCl<sub>3</sub>): δ [ppm] = -0.29 (s, B<sub>carborane</sub>), -4.17 (s, B<sub>carborane</sub>), -8.16 (s, B<sub>carborane</sub>), -12.52 (s, B<sub>carborane</sub>). **<sup>31</sup>P{<sup>1</sup>H}** **NMR** (162 MHz, CDCl<sub>3</sub>): δ [ppm] = 23.3. **<sup>13</sup>C{<sup>1</sup>H}** **NMR** (100 MHz, CDCl<sub>3</sub>): δ [ppm] = 25.3 (d, J<sub>P-C</sub> = 1.6 Hz, C of Cy), 26.5 (d, J<sub>P-C</sub> = 13.2 Hz, C of Cy), 27.0 (d, J<sub>P-C</sub> = 3.5 Hz, C of Cy), 32.7 (d, J<sub>P-C</sub> = 51.6 Hz, C of Cy), 60.2 (s, C<sub>carborane</sub>), 77.2 (s, C<sub>carborane</sub>), 128.6 (d, J<sub>P-C</sub> = 81.9 Hz, CO). **HRMS**: calcd. for [C<sub>26</sub>B<sub>31</sub>H<sub>63</sub>OP]<sup>-</sup>, 757.7719; found: 757.7708. Yield: 82 % (197.0 mg, 0.26 mmol). **IR**: 2199, 1640, 1447, 1078 cm<sup>-1</sup>.

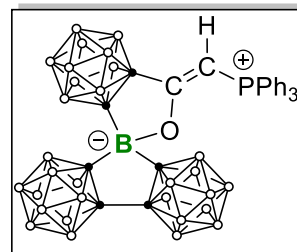
### Synthetic protocols for **4a**

Me<sub>2</sub>iPr (5 mg, 0.027 mmol) was added to a toluene (1 mL) solution of **3a** (200 mg, 0.27 mmol) and

stirred at room temperature for 10 min. All volatiles were removed under reduced pressure to obtain a colorless solid. Colorless crystals were obtained by storing the saturated toluene solution of **4a** under  $-30\text{ }^{\circ}\text{C}$  overnight.

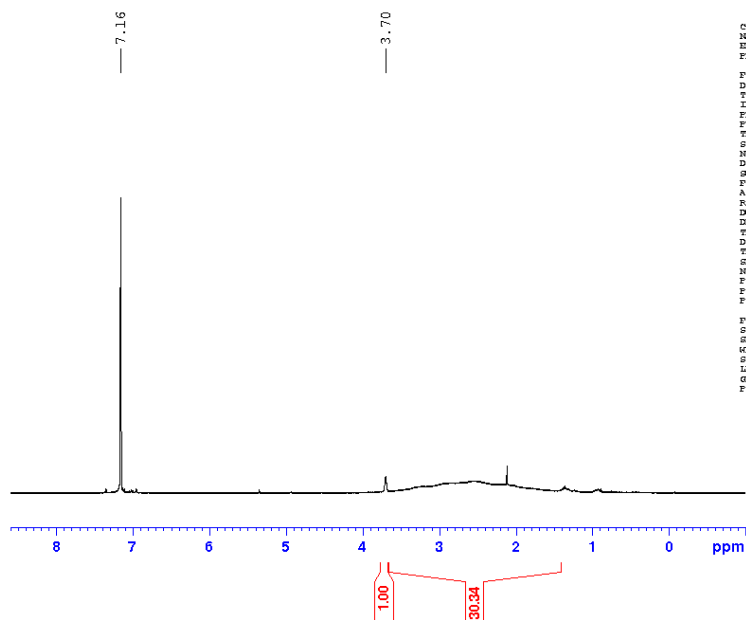
For **4a**:

$^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 2.01–3.76 (br. m, 30H, BH), 4.65 (d, 1H,  $J_{\text{P-C}} = 12.9$  Hz. CH), 6.92–6.94 (m, 6H, H of Ph), 6.95–6.99 (m, 6H, H of Ph), 7.03 to 7.08 (m, 3H, H of Ph).  $^1\text{H}\{^{11}\text{B}\}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 1.88 (s, 2H, BH), 2.55 (s, 4H, BH), 2.63 (s, 2H, BH), 2.72 (s, 4H, BH), 2.80 (s, 2H, BH), 2.87 (s, 2H, BH), 2.96 (s, 2H, BH), 3.05 (s, 8H, BH), 3.20 (s, 2H, BH), 3.46 (s, 2H, BH), 4.65 (d, 1H,  $J_{\text{P-C}} = 13.0$  Hz. CH), 6.88–6.92 (m, 6H, H of Ph), 6.95–6.97 (m, 3H, H of Ph), 7.18–7.23 (m, 6H, H of Ph).  $^{11}\text{B NMR}$  (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 2.69 (br, s,  $B_{\text{carborane}}$ ), 0.49 (br, s,  $B_{\text{carborane}}$ ),  $-3.74$  (br, s,  $B_{\text{carborane}}$ ),  $-7.52$  (br, s,  $B_{\text{carborane}}$ ),  $-10.85$  (br, s,  $B_{\text{carborane}}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 2.76 (s,  $B_{\text{carborane}}$ ), 0.01 (s,  $C_{\text{carboraneB}}$ ),  $-4.50$  (s,  $B_{\text{carborane}}$ ),  $-6.98$  (s,  $B_{\text{carborane}}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 12.64.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 67.5 (s,  $C_{\text{carborane}}$ ), 77.9 (s,  $C_{\text{carborane}}$ ), 119.9 (d,  $J_{\text{P-C}} = 95.6$  Hz. C of Ph), 128.6 (d,  $J_{\text{P-C}} = 75.4$  Hz. CO), 129.9 (d,  $J_{\text{P-C}} = 13.2$  Hz. C of Ph), 132.8 (d,  $J_{\text{P-C}} = 12.3$  Hz. C of Ph), 134.3 (d,  $J_{\text{P-C}} = 3.1$  Hz. C of Ph). HRMS: calcd. for  $[\text{C}_{26}\text{H}_{46}\text{B}_{31}\text{OP}]^+$ , 740.6389; found: 740.6496. Yield: 82 % (163.1 mg, 0.22 mmol); IR: 2923, 1615, 1436, 1112  $\text{cm}^{-1}$ .



# NMR Spectroscopy

Nutzer Libo Xiang  
 %Proton\_32ns C6D6 {D:\NMR-Daten\_AV\_III\_Nanobay} Xiang 1



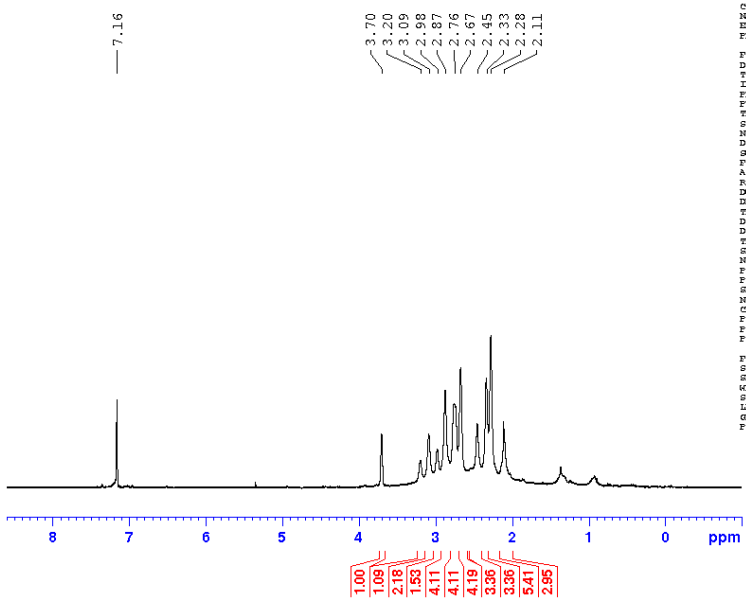
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FIDRES   0.166670 Hz
AQ        3.9998948 sec
RG        101
EM        62.400 usec
DE        6.50 usec
TE        298.1 K
D1        1.00000000 sec
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NUC1      1H
FO        3.47 usec
FI        10.40 usec
FID1     13.13799933 W

F2 - Processing parameters
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SOLV      EM
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Figure S1.  $^1\text{H}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
 %ProB11dec\_32ns C6D6 {D:\NMR-Daten\_AV\_III\_Nanobay} Xiang 1



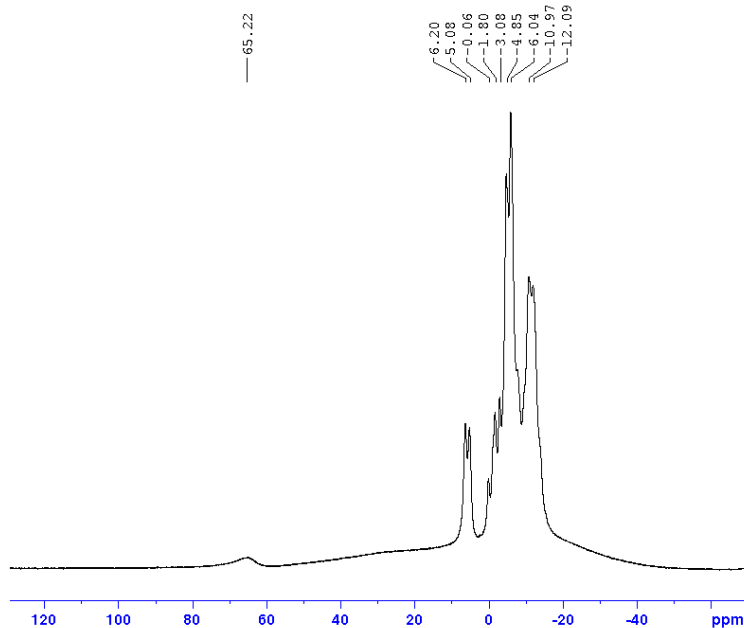
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AQ        4.4923182 sec
RG        50.8
EM        60.908 usec
DE        6.50 usec
TE        298.1 K
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D11      0.03000000 sec
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NUC1      1H
FO        10.40 usec
FID1     13.13799933 W
SFO2     126.4832772 MHz
NUC2      11B
CDEPRG12 waltz16
SFO2C    100.00 usec
FID2     30.00000000 W
FID2C    0.493009999 W

F2 - Processing parameters
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SF        400.4699966 MHz
SOLV      EM
SGB       0
LB        0 Hz
GB        0
FC        1.00
```

Figure S2.  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
%B11\_ZG\_256ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 32



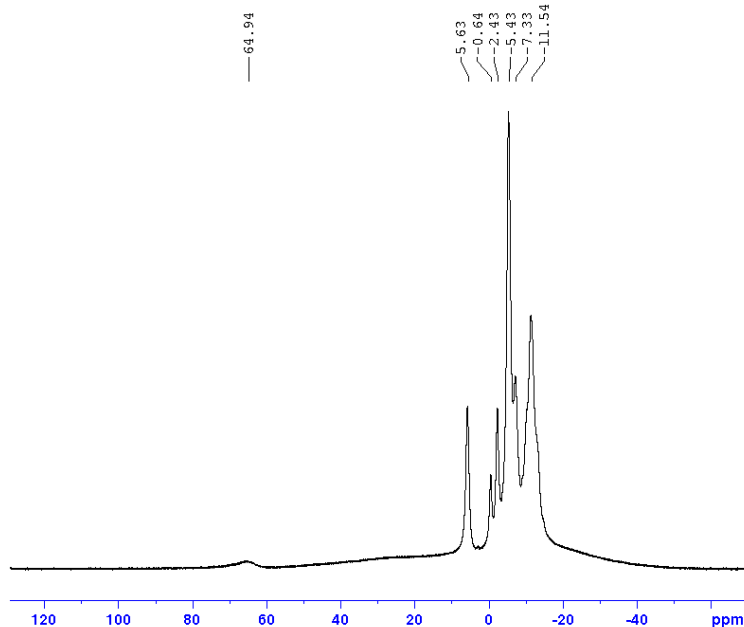
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SOLVENT C6D6  
NS 256  
DS 0  
SWH 25510.203 Hz  
FIDRES 2.527014 Hz  
AQ 0.3957240 sec  
RG 200  
DM 19.600 usec  
DE 6.50 usec  
TE 298.1 K  
D1 1.00000000 sec  
TD0 1  
SFO1 128.4905453 MHz  
NUC1 11B  
P1 9.95 usec  
PLW1 50.00000000 W

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

Figure S3.  $^{11}\text{B}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
%B11\_CPD\_128ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 32



Current Data Parameters  
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PROCNO 1

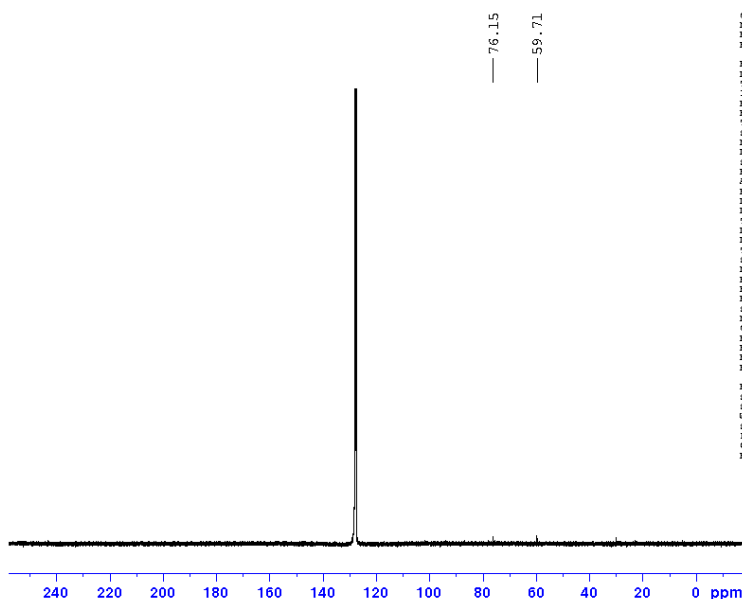
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SOLVENT C6D6  
NS 128  
DS 0  
SWH 25510.203 Hz  
FIDRES 2.527014 Hz  
AQ 0.3957240 sec  
RG 200  
DM 19.600 usec  
DE 6.50 usec  
TE 298.1 K  
D1 1.00000000 sec  
D11 0.03000000 sec  
TD0 1  
SFO1 128.4905453 MHz  
NUC1 11B  
P1 9.95 usec  
PLW1 50.00000000 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  
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WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 3.00

Figure S4.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.



Nutzer Libo Xiang  
 %c13\_CPD C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 44



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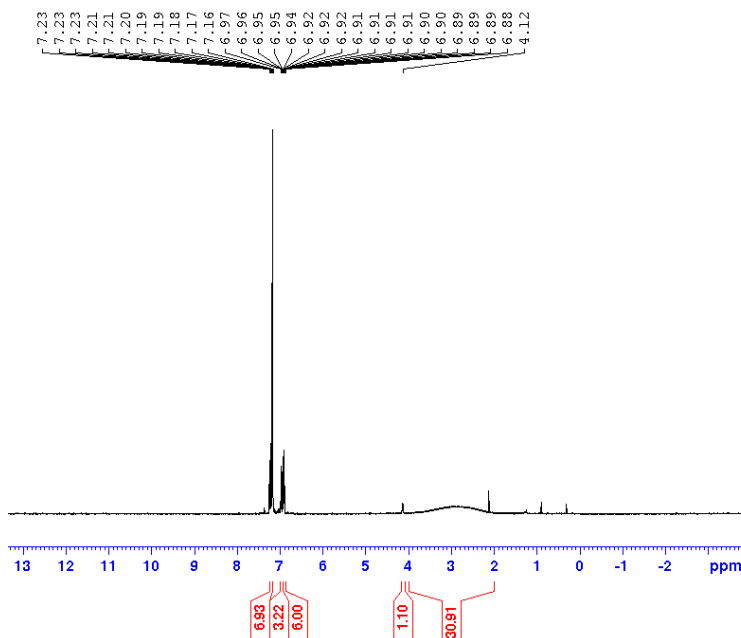
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FIDRES  0.847710 Hz
AQ  1.1749880 sec
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EM  18.000 usec
DE  6.50 usec
TE  298.1 K
D1  2.00000000 sec
D11  0.03000000 sec
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NUC1  13C
FO  3.33 usec
F1  10.00 usec
FIM1  62.27199956 W
SFO2  400.4710151 MHz
NUC2  1H
CEPRG2  waltz16
PCPD2  50.00 usec
FIM2  15.13799953 W
FIM12  0.2014000 W
FIM13  0.1017000 W

F2 - Processing parameters
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SSB  0
GB  0
PC  1.40
  
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Figure S5.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
 %Proton\_32ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 2



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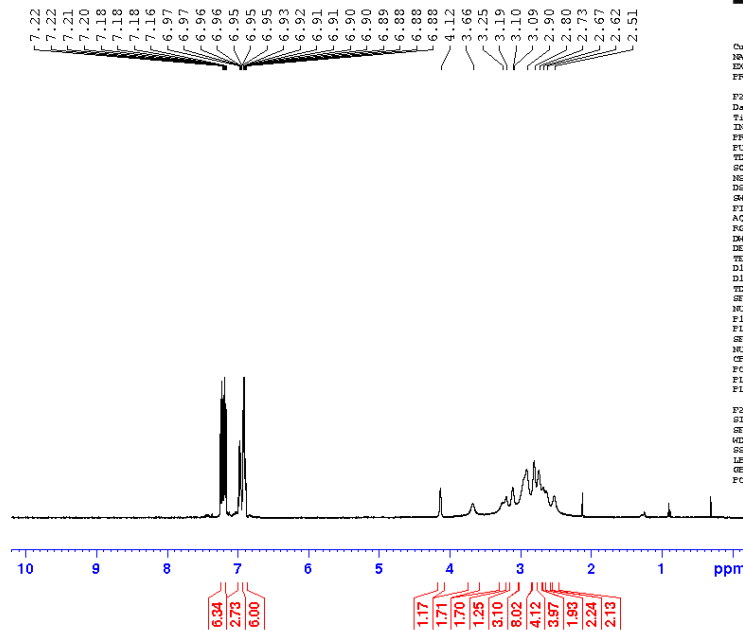
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NS  32
DS  0
SWH  8012.520 Hz
FIDRES  0.166670 Hz
AQ  3.9999996 sec
RG  101
EM  62.800 usec
DE  6.50 usec
TE  298.1 K
D1  1.00000000 sec
D11  0
SFO1  400.4724711 MHz
NUC1  1H
FO  3.87 usec
F1  10.80 usec
FIM1  15.13799953 W

F2 - Processing parameters
SI  131072
SF  400.4599967 MHz
WDW  EM
SSB  0
GB  0
PC  1.40
  
```

Figure S6.  $^1\text{H}$  NMR spectrum of **3a** in  $\text{C}_6\text{D}_6$  at 298 K.

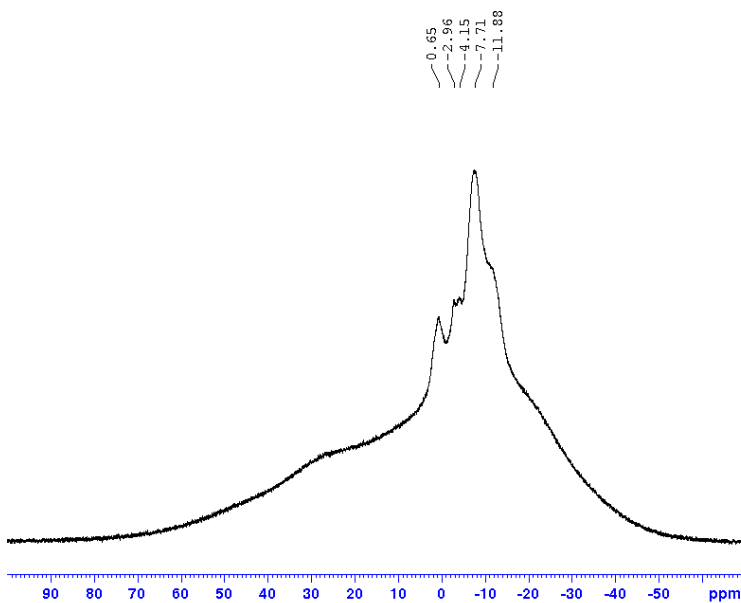
Nutzer Libo Xiang  
%Probl1dec\_32ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 2



Current Data Parameters  
NAME x1b-c63-phocco-1006-CRY  
EXPNO 1  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20230613  
Time 20.30 h  
INSTRUM spect  
PROBHD 2140678\_0037 ( )  
PULPROG zgpg  
TD 75850  
SOLVENT C6D6  
NS 32  
DS 2  
SFO 822.563 Hz  
FIDRES 0.222593 Hz  
AQ 4.4922122 sec  
RG 64  
RM 60.800 usec  
DE 6.50 usec  
TE 298.15 K  
D1 1.0000000 sec  
D11 0.0000000 sec  
TDO  
SFO1 400.4724731 MHz  
NUC1 1H  
F1 10.40 usec  
P1M1 15.1779953 W  
SFO2 125.4630933 MHz  
NUC2 11B  
GDEPRG2 waltz16  
PCPD2 100.00 usec  
P1M2 30.0000000 W  
P1M12 0.49300993 W  
F2 - Processing parameters  
SI 313074  
SF 400.4659968 MHz  
WDW EM  
SSB 0  
LB 0 Hz  
GB 0  
PC 1.00

Figure S7.  ${}^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **3a** in  $\text{C}_6\text{D}_6$  at 298 K.

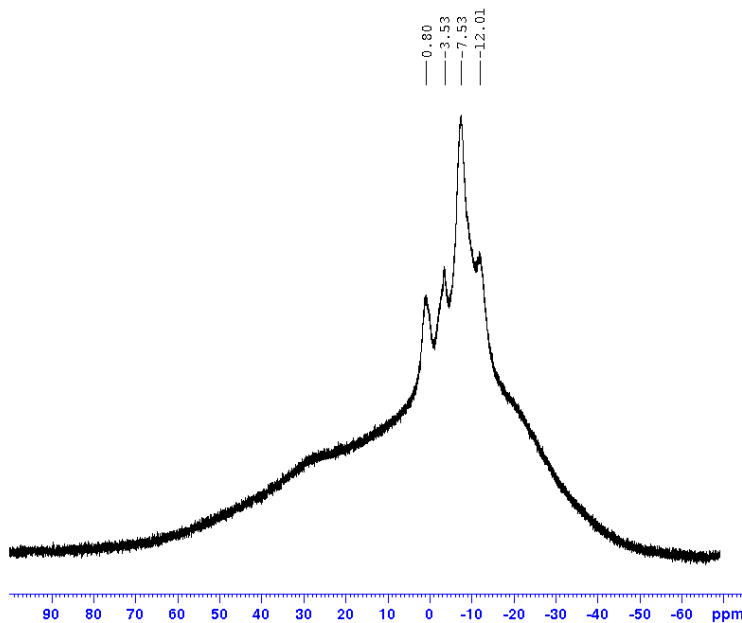
Nutzer Libo Xiang  
%B11\_2G\_256ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 2



Current Data Parameters  
NAME x1b-c63-phocco-1006-CRY  
EXPNO 1  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20230613  
Time 20.31 h  
INSTRUM spect  
PROBHD 2140678\_0037 ( )  
PULPROG zgpg  
TD 20190  
SOLVENT C6D6  
NS 256  
DS 0  
SFO 251.000 MHz  
FIDRES 2.527014 Hz  
AQ 0.2837580 sec  
RG 203  
RM 19.600 usec  
DE 6.50 usec  
TE 298.15 K  
D1 1.0000000 sec  
D11 0.0000000 sec  
TDO  
SFO1 125.4630933 MHz  
NUC1 11B  
SFO2 50.933 MHz  
P1M1 30.0000000 W  
F2 - Processing parameters  
SI 32766  
SF 125.4660947 MHz  
WDW EM  
SSB 0  
LB 3.00 Hz  
GB 0  
PC 1.90

Figure S8.  $^{11}\text{B}$  NMR spectrum of **3a** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
 %B11\_CPD\_128ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 2



```

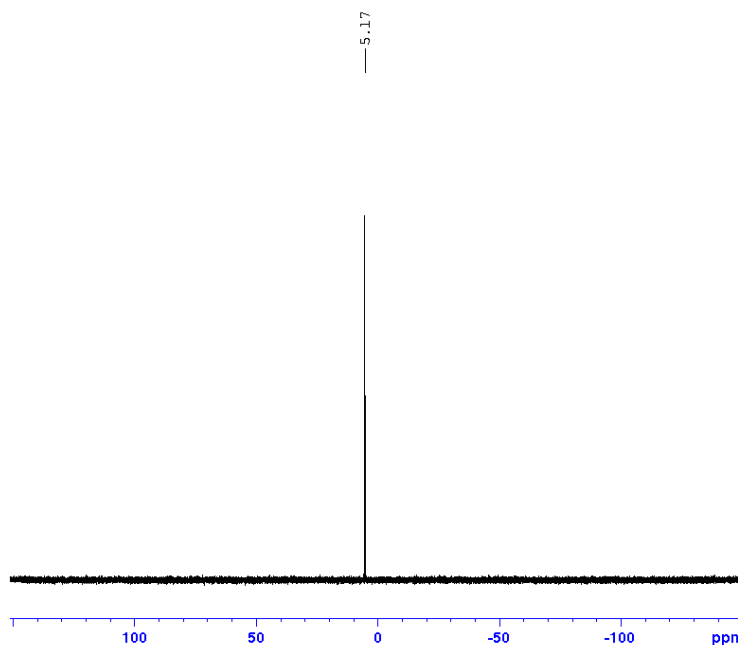
Current Data Parameters
NAME  xmr-dm0-c6d6-1000-1000-GH
EXPNO  10
PROCNO  1

F2 - Acquisition Parameters
Date_  20230513
Time  20.18 h
INSTRUM  spect
PROBHD  BBOGVT_0037 (
PULPROG  zgpg
TD  65536
SOLVENT  c6d6
NS  120
DS  0
SWH  25510.000 Hz
FIDRES  2.527014 Hz
AQ  0.2877880 sec
RG  203
RW  19.000 usec
RE  6.30 usec
TE  298.1 K
D1  1.00000000 sec
d11  0.02000000 sec
TEO  1
SFO1  128.460443 MHz
SFO2  128
SF1  5.93 usec
P1  50.00000000 W
SFO3  900.472024 MHz
MPC2  in
CPDPRG2  waltz16
PCPD2  90.00 usec
P2  15.1279823 W
P3  0.25218000 W
P4  0.10167000 W

F2 - Processing parameters
SI  65536
SF  128.4606607 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  3.00
  
```

Figure S9.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **3a** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
 %P31\_CPD\_128ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 2



```

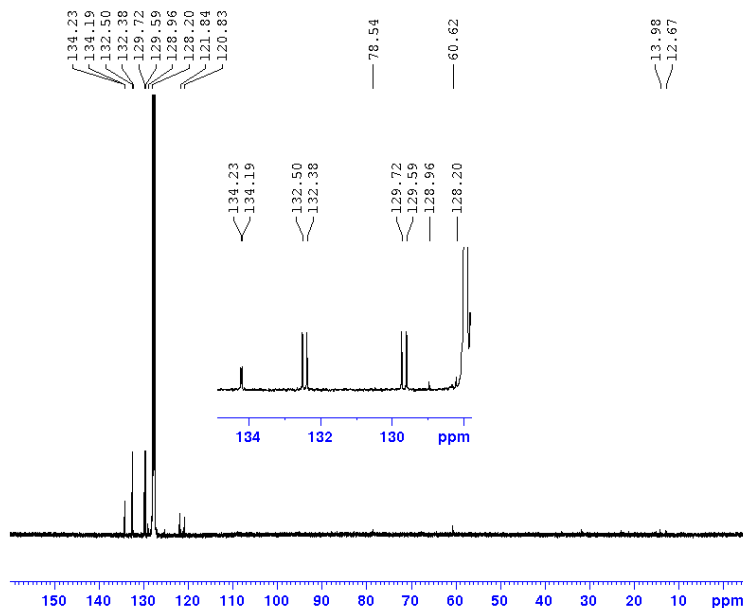
Current Data Parameters
NAME  xmr-dm0-c6d6-1000-1000-GH
EXPNO  14
PROCNO  1

F2 - Acquisition Parameters
Date_  20230513
Time  20.36 h
INSTRUM  spect
PROBHD  BBOGVT_0037 (
PULPROG  zgpg
TD  65536
SOLVENT  c6d6
NS  64
DS  4
SWH  49019.000 Hz
FIDRES  0.509819 Hz
AQ  1.9018684 sec
RG  203
RW  10.000 usec
RE  6.30 usec
TE  298.1 K
D1  2.00000000 sec
d11  0.02000000 sec
TEO  1
SFO1  162.113273 MHz
SFO2  162
SF1  2.67 usec
P1  50.00000000 W
SFO3  900.4716019 MHz
MPC2  in
CPDPRG2  waltz16
PCPD2  90.00 usec
P2  15.1279823 W
P3  0.25218000 W
P4  0.10167000 W

F2 - Processing parameters
SI  65536
SF  162.113273 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.90
  
```

Figure S10.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3a** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
%c13\_CPD C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 45

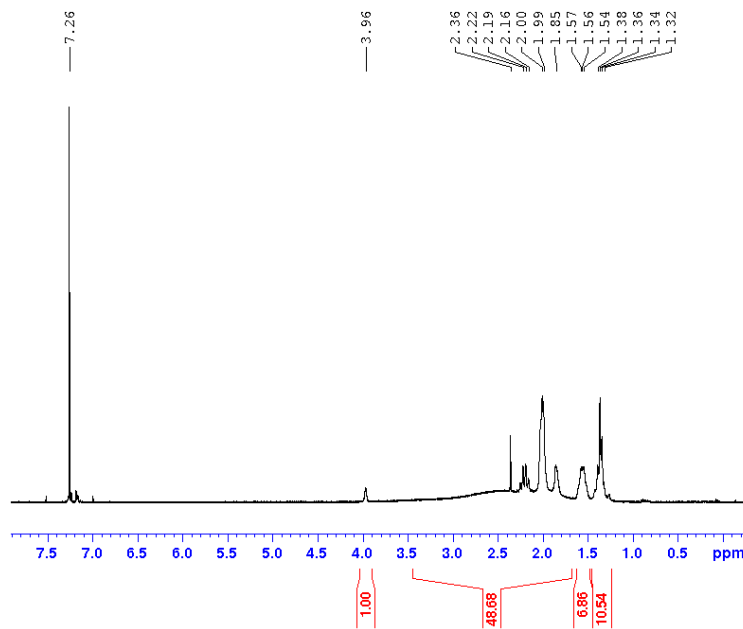


```
Current Data Parameters
NAME xlb-cb3-cypcco-cdcl3
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240215
Time 21.57 h
INSTRUM spect
PROBHD 2140678_0037 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 27777.777 Hz
FIDRES 0.59710 Hz
AQ 1.179680 sec
RG 403
EQ 114
DE 62.400 usec
TE 298.1 K
D1 1.00000000 sec
D11 0.02000000 sec
D12 0.02000000 sec
D13 0.02000000 sec
D14 0.02000000 sec
SFO1 400.4724731 MHz
NUC1 13C
NUC2 1H
PC 1.40
```

Figure S11.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3a** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
%Proton\_32ns CDCl3 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 5

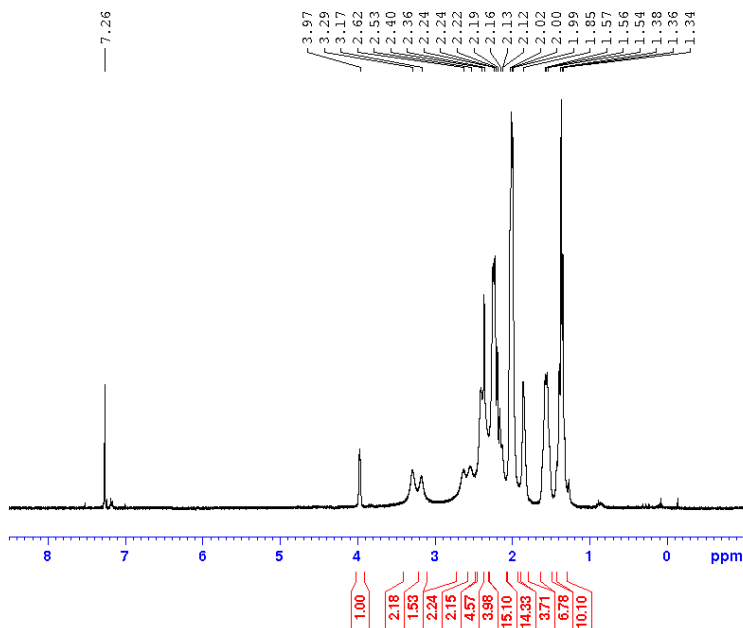


```
Current Data Parameters
NAME xlb-cb3-cypcco-cdcl3
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240215
Time 22.10 h
INSTRUM spect
PROBHD 2140678_0037 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.166670 Hz
AQ 5.9998846 sec
RG 114
EQ 114
DE 62.400 usec
TE 298.1 K
D1 1.00000000 sec
D11 0.02000000 sec
D12 0.02000000 sec
D13 0.02000000 sec
D14 0.02000000 sec
SFO1 400.4724731 MHz
NUC1 1H
NUC2 13C
PC 1.40
```

Figure S12.  $^1\text{H}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  at 298 K.

Nutzer Libo Xiang  
 %Probl1dec\_32ns CDCl3 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 5



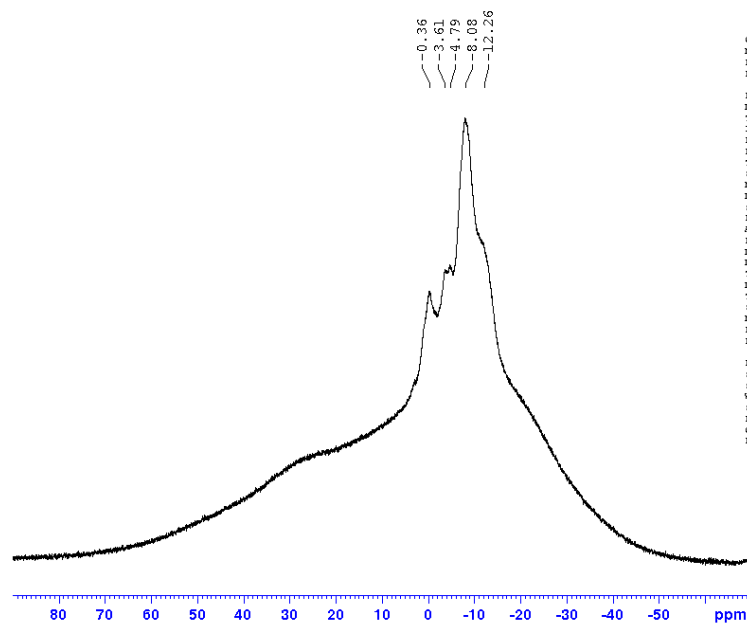
Current Data Parameters  
 NAME k1b-cb3-cypcco-cdcl3  
 EXPRNO 13  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20240215  
 Time 22.14 h  
 INSTRUM spect  
 FPROBHD 2140678\_0037 ( )  
 PULPROG zgpg  
 TD 73890  
 SOLVENT CDCl3  
 NS 32  
 DS 2  
 SWH 8223.665 Hz  
 FIDRES 0.222593 Hz  
 AQ 4.4925122 sec  
 RG 64  
 DW 60.800 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 1.00000000 sec  
 D11 0.03000000 sec  
 TDO 1  
 SF01 400.4724731 MHz  
 NUC1 1H  
 F1 10.40 usec  
 FLW1 15.13793953 W  
 SF02 128.4852773 MHz  
 NUC2 11B  
 CPDPRG2 waltz16  
 FCID2 100.00 usec  
 FLW2 50.00000000 W  
 FLW12 0.49500399 W

F2 - Processing parameters  
 SI 131072  
 SF 400.4700039 MHz  
 WDW EM  
 SSB 0  
 LB 0 Hz  
 GB 0  
 FC 1.00

Figure S13.  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  at 298 K.

Nutzer Libo Xiang  
 %B11\_2G\_256ns CDCl3 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 5



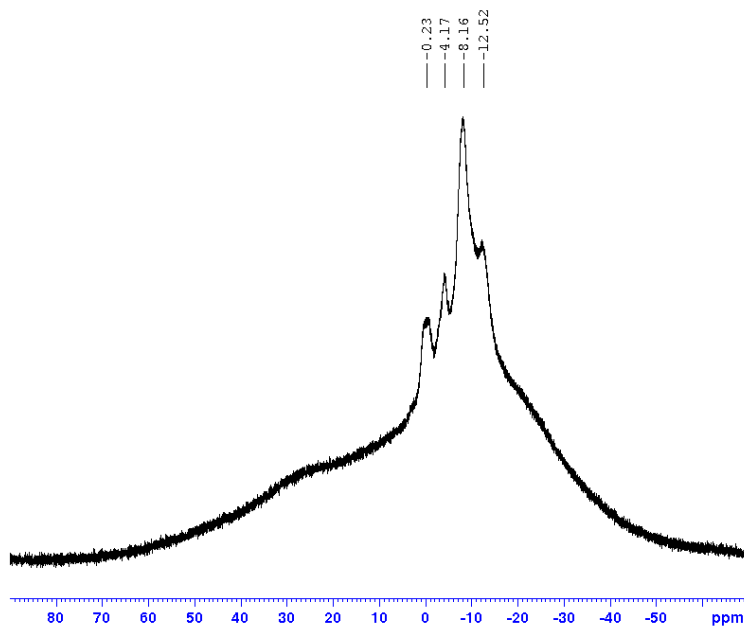
Current Data Parameters  
 NAME k1b-cb3-cypcco-cdcl3  
 EXPRNO 11  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20240215  
 Time 22.05 h  
 INSTRUM spect  
 FPROBHD 2140678\_0037 ( )  
 PULPROG zgpg  
 TD 20190  
 SOLVENT CDCl3  
 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  
 TDO 1  
 SF01 128.4905453 MHz  
 NUC1 11B  
 F1 3.95 usec  
 FLW1 50.00000000 W

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

Figure S14.  $^{11}\text{B}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  at 298 K.

Nutzer Libo Xiang  
 %B11\_CPD\_128ns CDCl3 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 5



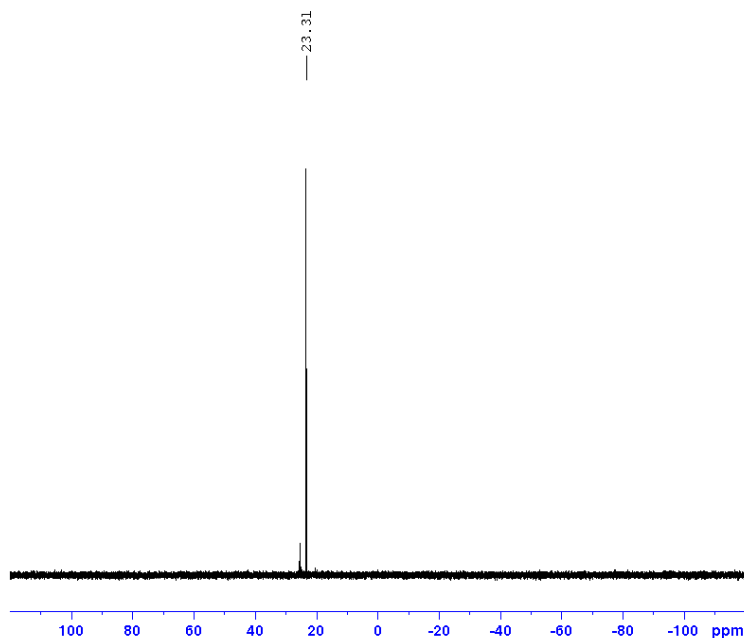
Current Data Parameters  
 NAME xlb-cb3-cyppco-cdcl3  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20240215  
 Time 21.58 h  
 INSTRUM spect  
 PROBRD 2140678\_0007 ( )  
 PULPROG zgpg  
 TD 20190  
 SOLVENT CDCl3  
 NS 128  
 DS 0  
 SWH 25510.203 Hz  
 FIDRES 2.527014 Hz  
 AQ 0.3957240 sec  
 RG 203  
 DW 19.400 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 1.00000000 sec  
 D11 0.03000000 sec  
 TDO 1  
 SFO1 128.4905453 MHz  
 NUC1 11B  
 P1 9.95 usec  
 PL1 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 45536  
 SF 128.486907 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 3.00

Figure S15.  $^1\text{H}\{^1\text{H}\}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  at 298 K.

Nutzer Libo Xiang  
 %P31\_CPD\_128ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 3



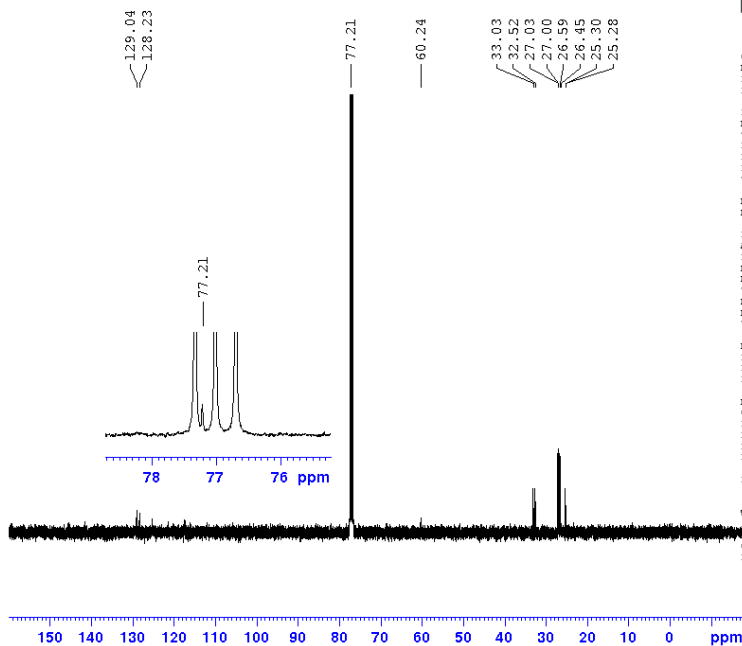
Current Data Parameters  
 NAME xlb-cb3-cyppco-cy-1402  
 EXPNO 20  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20240215  
 Time 2.19 h  
 INSTRUM spect  
 PROBRD 2140678\_0007 ( )  
 PULPROG zgpg30  
 TD 192302  
 SOLVENT C6D6  
 NS 128  
 DS 4  
 SWH 49019.609 Hz  
 FIDRES 0.309819 Hz  
 AQ 1.9614908 sec  
 RG 203  
 DM 10.200 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TDO 1  
 SFO1 162.1132275 MHz  
 NUC1 31P  
 P1 2.67 usec  
 PL 6.00 usec  
 PLW1 46.62900162 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 262144  
 SF 162.1132275 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S16.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  at 298 K.

Nutzer Libo Xiang  
 %c13\_CPD CDCl3 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 5



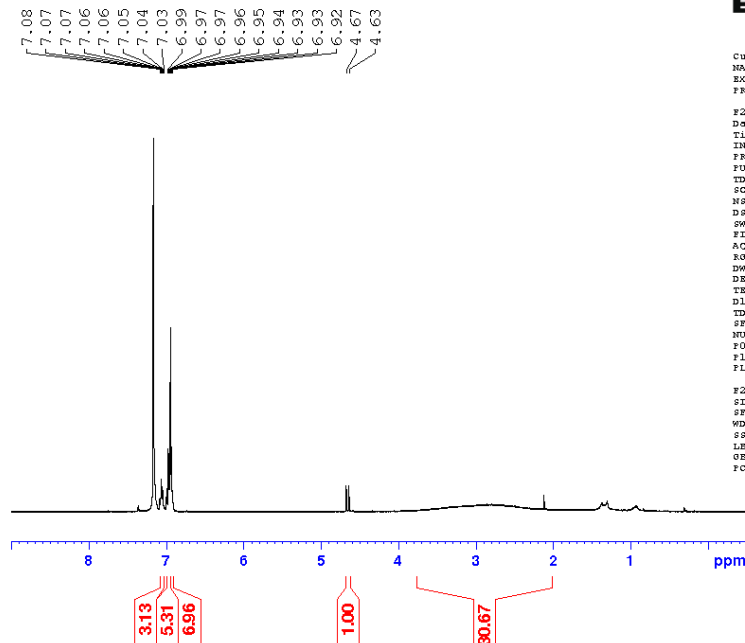
Current Data Parameters  
 NAME k1b-cb3-cypccc-cdcl3  
 EXPNO 15  
 FREQNO 1

F2 - Acquisition Parameters  
 Date\_ 20240318  
 Time 1.36 h  
 INSTRUM spect  
 PROBRD 2140678\_0037 ( )  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 3500  
 DS 4  
 SWE 27777.777 Hz  
 FIDRES 0.847710 Hz  
 AQ 1.1796480 sec  
 RG 203  
 SW 18.000 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TDO 1  
 SF01 100.7103454 MHz  
 NUC1 13C  
 F0 3.33 usec  
 F1 10.00 usec  
 FLW1 62.27199936 W  
 SF02 400.4716019 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 FCPD2 90.00 usec  
 FLW2 15.13799953 W  
 FHM2 0.20214000 W  
 FLW3 0.10167000 W

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

Figure S17.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  at 298 K.

Nutzer Libo Xiang  
 %Proton\_32ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 15



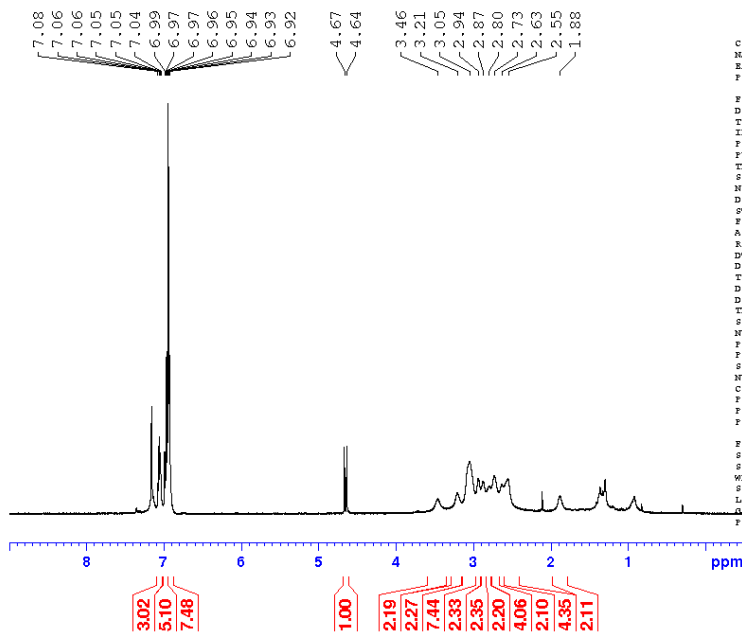
Current Data Parameters  
 NAME k1b-4-H-transfer-cy  
 EXPNO 12  
 FREQNO 1

F2 - Acquisition Parameters  
 Date\_ 20240901  
 Time 13.20 h  
 INSTRUM spect  
 PROBRD 2140678\_0037 ( )  
 PULPROG zg30  
 TD 96152  
 SOLVENT C6D6  
 NS 32  
 DS 0  
 SWE 8012.820 Hz  
 FIDRES 0.166670 Hz  
 AQ 5.9998846 sec  
 RG 101  
 SW 62.400 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 1.00000000 sec  
 TDO 1  
 SF01 400.4724731 MHz  
 NUC1 1H  
 F0 3.47 usec  
 F1 10.40 usec  
 FLW1 15.13799953 W

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

Figure S18.  $^1\text{H}$  NMR spectrum of **4a** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
 %Probl1dec\_32ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 15



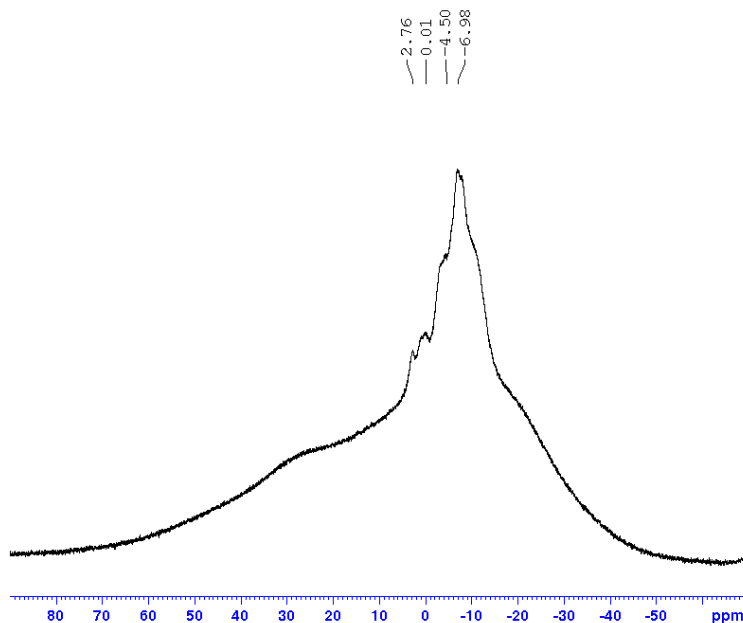
Current Data Parameters  
 NAME k1b-4-R-transfer-cry  
 EXPRNO 13  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20240901  
 Time 19.24 h  
 INSTRUM spect  
 PROBRD 2140678\_0037 ( )  
 FULPROG zgpg  
 TD 73890  
 SOLVENT C6D6  
 NS 32  
 DS 2  
 SWH 8223.665 Hz  
 FIDRES 0.222593 Hz  
 AQ 4.4925122 sec  
 RG 64  
 DW 60.800 usec  
 DE 6.50 usec  
 TE 298.2 K  
 D1 1.00000000 sec  
 D11 0.03000000 sec  
 TDO 1  
 SFO1 400.4724731 MHz  
 NUC1 1H  
 P1 10.40 usec  
 PL1 15.13793953 W  
 SFO2 128.4852773 MHz  
 NUC2 11B  
 CPDPRG2 waltz16  
 TC1D2 100.00 usec  
 PLW2 50.00000000 W  
 PLW12 0.49500999 W

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

Figure S19.  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of **4a** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
 %B11\_2G\_256ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 15



Current Data Parameters  
 NAME k1b-4-R-transfer-cry  
 EXPRNO 11  
 PROCNO 1

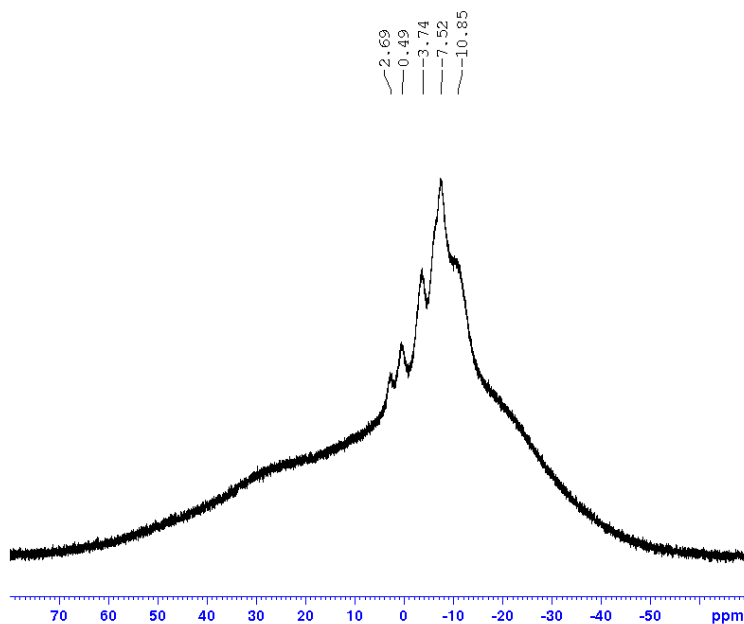
F2 - Acquisition Parameters  
 Date\_ 20240901  
 Time 19.15 h  
 INSTRUM spect  
 PROBRD 2140678\_0037 ( )  
 FULPROG zgpg  
 TD 20190  
 SOLVENT C6D6  
 NS 256  
 DS 0  
 SWH 25510.203 Hz  
 FIDRES 2.527014 Hz  
 AQ 0.3957240 sec  
 RG 203  
 DW 19.600 usec  
 DE 6.50 usec  
 TE 298.1 K  
 D1 1.00000000 sec  
 TDO 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  
 FC 1.40

Figure S20.  $^{11}\text{B}$  NMR spectrum of **4a** in  $\text{C}_6\text{D}_6$  at 298 K.



Nutzer Libo Xiang  
%B11\_CPD\_128ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 15



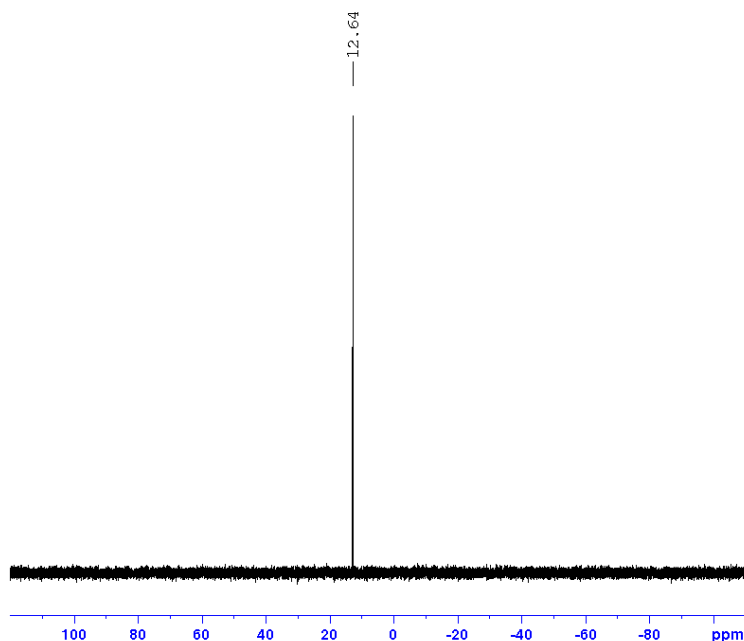
```
Current Data Parameters
NAME      xlb-4-R-transfer-cry
EXPNO    10
PROCNO    1

F2 - Acquisition Parameters
Date_     20240301
Time      19.08 h
INSTRUM   spect
PROBRD    2140678_0037 (
PULPROG   zgpg
TD         20190
SOLVENT   CDCl3
NS         128
DS         0
SWH        25510.203 Hz
FIDRES     2.527014 Hz
AQ         0.3957240 sec
RG         203
DW         19.400 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
PL1        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 S21.  $^1\text{H}\{^1\text{H}\}$  NMR spectrum of **4a** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
%P31\_CPD\_128ns C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 15



```
Current Data Parameters
NAME      xlb-4-R-transfer-cry
EXPNO    14
PROCNO    1

F2 - Acquisition Parameters
Date_     20240301
Time      19.29 h
INSTRUM   spect
PROBRD    2140678_0037 (
PULPROG   zgpg30
TD         192302
SOLVENT   CDCl3
NS         32
DS         4
SWH        49013.609 Hz
FIDRES     0.509819 Hz
AQ         1.9614804 sec
RG         203
DW         10.200 usec
DE         6.50 usec
TE         298.1 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1
SFO1       162.1132275 MHz
NUC1       31P
P1         2.67 usec
PL1        46.62900162 W
SFO2       400.4716019 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         262144
SF         162.1132275 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```

Figure S22.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4a** in  $\text{C}_6\text{D}_6$  at 298 K.

Nutzer Libo Xiang  
 %C13\_CPD C6D6 (D:\NMR-Daten\_AV\_III\_Nanobay) Xiang 15

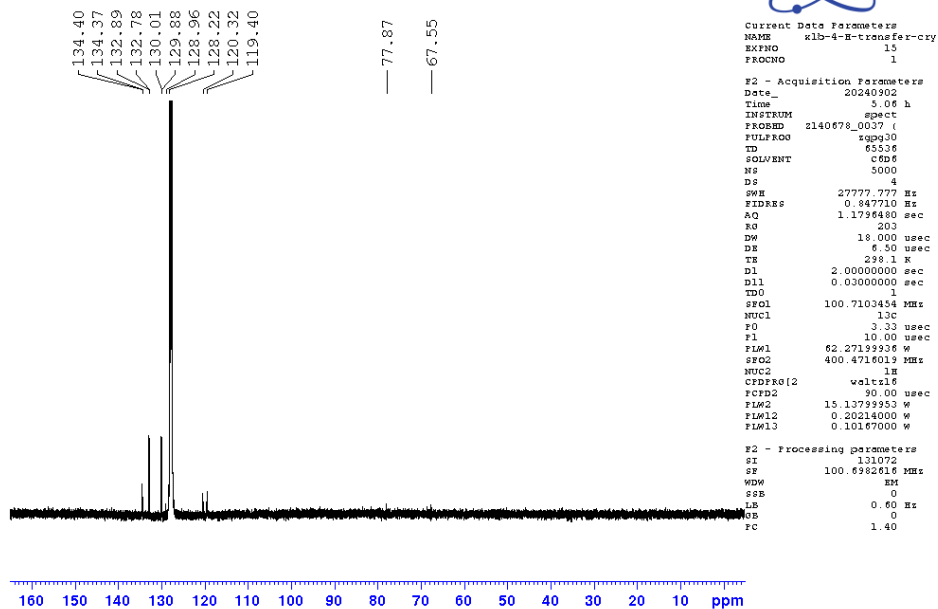


Figure S23.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4a** in  $\text{C}_6\text{D}_6$  at 298 K.

## IR Spectroscopy

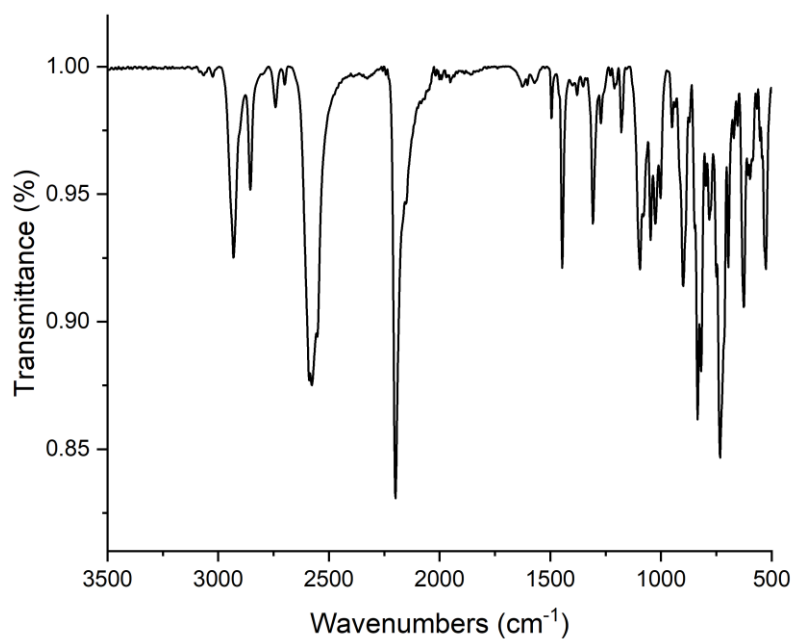


Figure S24. IR spectrum of 3a.

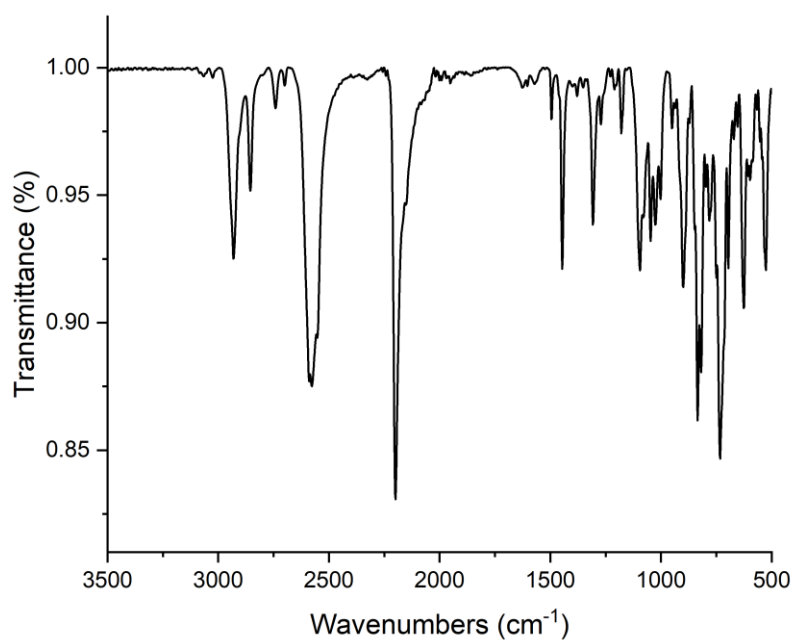


Figure S25. IR spectrum of 3b.

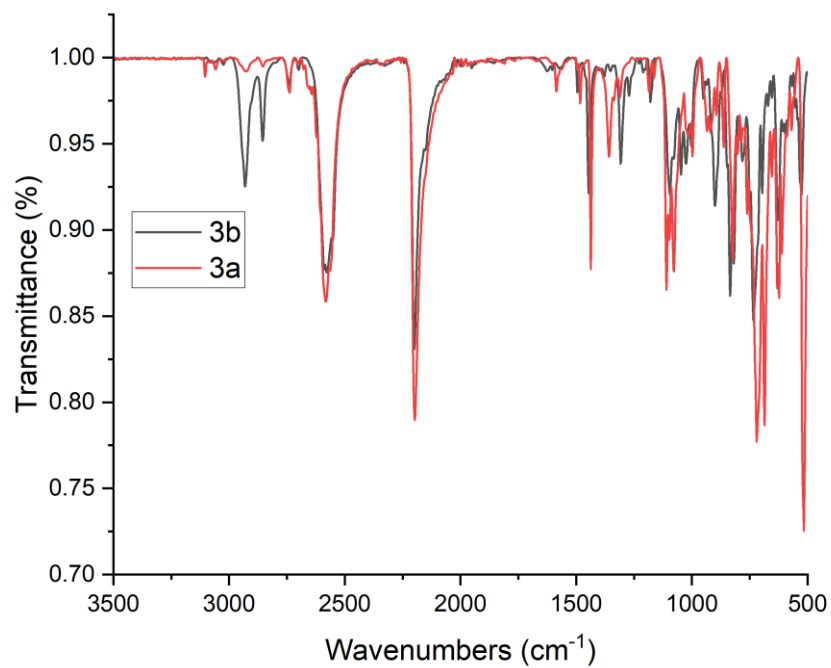


Figure S26. IR spectrum of 3a and 3b

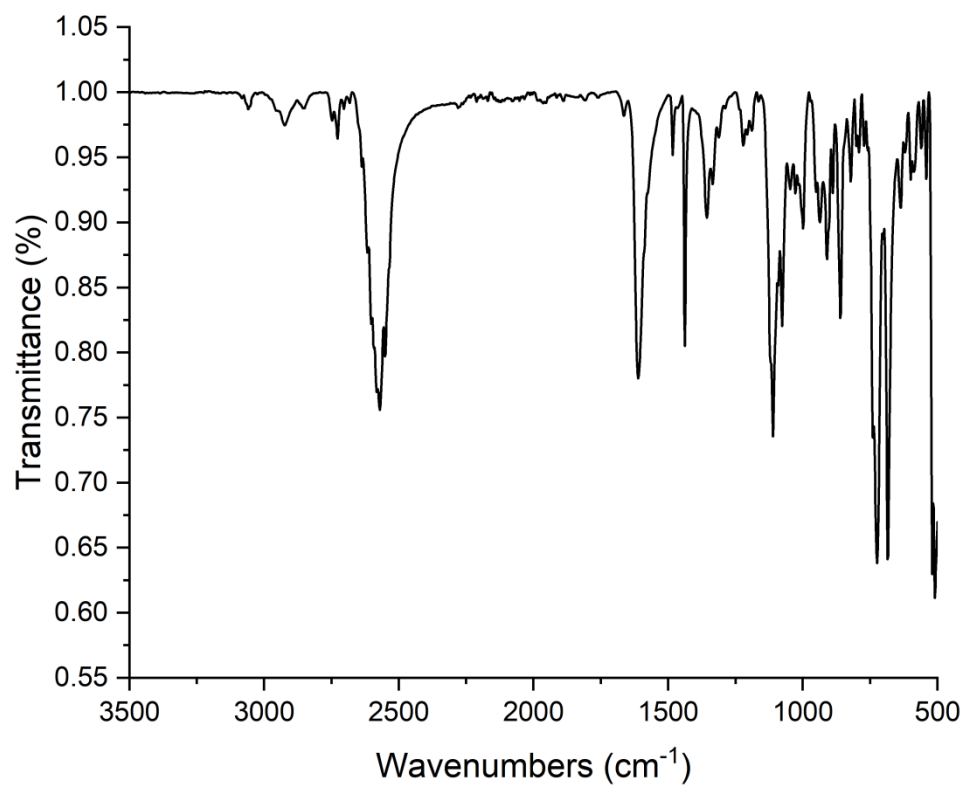


Figure S27. IR spectrum of 4a.

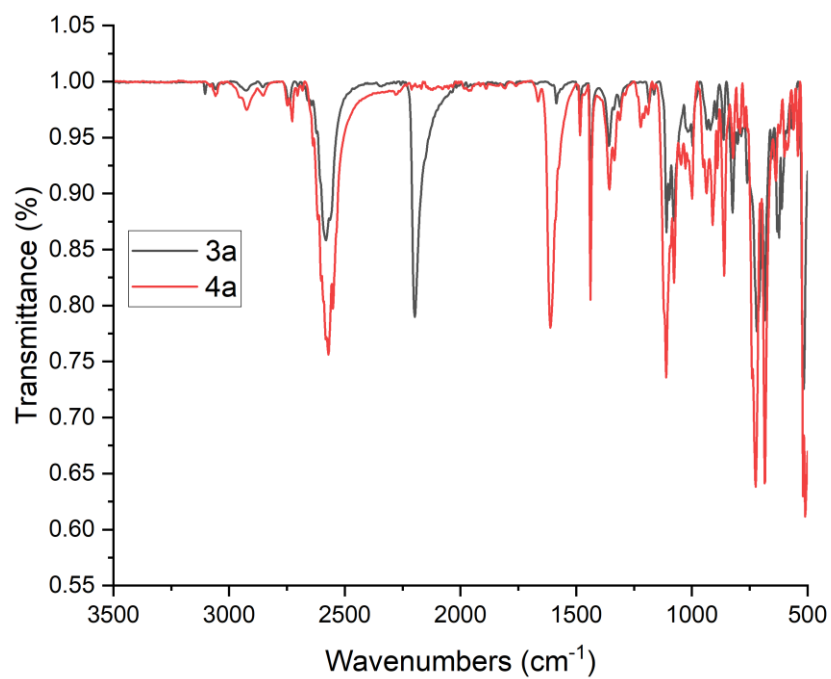


Figure S28. IR spectrum of 3a and 4a.

## Characterizations of Lewis acidity

### Gutmann–Beckett methods

Equimolar amount of Et<sub>3</sub>PO was added to the C<sub>6</sub>D<sub>6</sub> solution of **1**.

**Table S1.** Gutmann–Beckett method of **1**

Entry (in C <sub>6</sub> D <sub>6</sub> )	<sup>31</sup> P NMR ( $\delta$ )	$\Delta\delta$ ( $\delta_{\text{sample}} - \delta_{\text{TEPO}}$ )	Acceptor Numbers
Et <sub>3</sub> PO	45.60		
<b>1</b> -Et <sub>3</sub> PO	80.52	34.92	76.8

### DFT calculation

All calculations were performed with the Gaussian 09 program.<sup>4</sup> All ground-state geometries were optimized using the B3LYP hybrid functional<sup>5</sup> in combination with def2-TZVP basis set.<sup>6</sup> Frequency calculations were performed to confirm that a local minimum has no imaginary frequency. For the FIA and HIA calculations, geometries and final electronic energies were obtained at the BP86-D3/def2-SVP level of theory.<sup>7</sup> The FIA reaction enthalpies were calculated according to the scheme proposed by Krossing using the given G3 anchor points and isodesmic reactions.<sup>8</sup> %V<sub>Bur</sub> of values for the selected Lewis acids, obtained from the geometry of FIA adducts, were calculated using the SambVca 2.1 web application: <https://www.molnac.unisa.it/OMtools/sambvca2.1/index.html>.<sup>9</sup>

**Table S2.** FIA calculational data.

	E/Hartree	corr. Entha/ Hartree	E(H)/kJ mol <sup>-1</sup>	FIA/kJ mol <sup>-1</sup>	FIA/kJ mol <sup>-1</sup> (ref. to SbF <sub>5</sub> )
<b>1</b>	-1017.39	0.493927	-2669825.803	621.42	146.53
<b>1-F<sup>-</sup></b>	-1117.38	0.497998	-2932332.526		
<b>A</b>	-719.32	0.286094	-1887798.876	354.35	-120.53
<b>A-F<sup>-</sup></b>	-819.21	0.287503	-2150038.529		
<b>B</b>	-718.13	0.263823	-1884715.974	366.27	-108.62
<b>B-F<sup>-</sup></b>	-818.01	0.265238	-2146967.544		
<b>C</b>	-2206.67	0.180139	-5793060.606	452.68	-22.21
<b>C-F<sup>-</sup></b>	-2306.60	0.182442	-6055398.583		
<b>D</b>	-2007.17	0.172461	-5269288.298	456.67	-18.22
<b>D-F<sup>-</sup></b>	-2107.09	0.174809	-5531630.269		
<b>E</b>	-1018.59	0.516750	-2672918.865	581.53	106.64
<b>E-F<sup>-</sup></b>	-1118.57	0.520052	-2935385.692		

**Table S3.** HIA calculational data.

	E/Hartree	corr. Entha/ Hartree	E(H)/kJ mol <sup>-1</sup>	FIA/kJ mol <sup>-1</sup>	FIA/kJ mol <sup>-1</sup> (ref. to B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> )
<b>1</b>	-1017.39	0.493927	-2669825.803	631.89	147.41
<b>1-H<sup>-</sup></b>	-1018.15	0.503462	-2671796.654		
<b>A</b>	-719.32	0.286094	-1887798.876	359.70	-124.78
<b>A-H<sup>-</sup></b>	-719.97	0.291212	-1889497.538		
<b>B</b>	-718.12	0.263823	-1884715.974	382.43	-102.04
<b>B-H<sup>-</sup></b>	-718.79	0.269972	-1886437.37		
<b>C</b>	-2206.67	0.180139	-5793060.606	484.47	0
<b>C-H<sup>-</sup></b>	-2207.38	0.18806	-5794884.043		
<b>D</b>	-2007.17	0.172461	-5269288.298	490.81	6.34
<b>D-H<sup>-</sup></b>	-2007.87	0.180164	-5271118.076		
<b>E</b>	-1018.59	0.516750	-2672918.865	602.45	117.98
<b>E-H<sup>-</sup></b>	-1019.34	0.525671	-2674860.28		

**Table S4.** Global Electrophilicity Index (GEI)<sup>10</sup> of compound **1** and **A** to **E**.

Compound	LUMO/eV	HOMO/eV	GEI/eV
<b>1</b>	-3.947	-8.865	4.17
<b>A</b>	-2.019	-6.883	2.04
<b>B</b>	-2.519	-6.098	2.59
<b>C</b>	-3.523	-7.651	3.78
<b>D</b>	-3.782	-7.236	4.39
<b>E</b>	-3.979	-8.986	4.20

**Table S5.** %V<sub>Bur</sub> and pyramidization energy of compound **1** and **E**.

Compound	Anion	%V <sub>Bur</sub>	d(LA-F)/Å	Pyramidization energy/kJ•mol <sup>-1</sup>	Steric Map
<b>1</b>	<b>1-F<sup>-</sup></b>	67.7	1.423	122.0	
<b>E</b>	<b>E-F<sup>-</sup></b>	73.3	1.426	130.1	



## Crystallographic Details

The crystal data of **1** and **3a** was collected on a Bruker D8 VENTURE diffractometer with graphite monochromated Mo<sub>Kα</sub> 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 method<sup>11</sup> and by using Olex2<sup>12</sup> as the graphical interface. The model was refined with the ShelXL program<sup>13</sup> 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 **3b** and **4a** were collected on a Rigaku XtaLAB Synergy-R diffractometer with a HPA area detector and multi-layer mirror monochromated Cu<sub>Kα</sub> radiation. The structure was solved using intrinsic phasing method<sup>5</sup>, refined with the ShelXL program<sup>13</sup> and expanded using Fourier techniques.

Crystallographic data have been deposited with the Cambridge Crystallographic Data as supplementary publication nos. CCDC-2355581 (**1**), 2355582 (**3a**), 2355583 (**3b**), 2382930(**4a**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via Data <https://www.ccdc.cam.ac.uk>

Details of the data collection and refinement for complexes **1–4a** are given in Table S6-S9.

<b>Table S6. Crystal data and structure refinement for 1.</b>	
Identification code	1
Empirical formula	C <sub>6</sub> H <sub>31</sub> B <sub>31</sub>
Formula weight	438.42
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	<i>Pnma</i>
<i>a</i> /Å	21.639(4)
<i>b</i> /Å	16.953(2)
<i>c</i> /Å	6.7994(12)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
Volume/Å <sup>3</sup>	2494.3(7)
<i>Z</i>	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.167
$\mu$ /mm <sup>-1</sup>	0.047
F(000)	888.0
Crystal size/mm <sup>3</sup>	0.444 × 0.32 × 0.251
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	3.764 to 52.728
Index ranges	-27 ≤ <i>h</i> ≤ 24, -18 ≤ <i>k</i> ≤ 21, -8 ≤ <i>l</i> ≤ 8
Reflections collected	27425
Independent reflections	2643 [ <i>R</i> <sub>int</sub> = 0.0574, <i>R</i> <sub>sigma</sub> = 0.0280]
Data/restraints/parameters	2643/0/175
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.111
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0615, <i>wR</i> <sub>2</sub> = 0.1808
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0678, <i>wR</i> <sub>2</sub> = 0.1869
Largest diff. peak/hole / e Å <sup>-3</sup>	0.38/-0.57

<b>Table S7. Crystal data and structure refinement for 3a.</b>	
Identification code	3a
Empirical formula	C <sub>26</sub> H <sub>46</sub> B <sub>31</sub> OP
Formula weight	740.71
Temperature/K	100(2)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	12.196(3)
<i>b</i> /Å	12.565(3)
<i>c</i> /Å	15.872(4)
$\alpha$ /°	91.154(8)
$\beta$ /°	106.328(9)
$\gamma$ /°	117.784(7)
Volume/Å <sup>3</sup>	2032.1(9)
<i>Z</i>	2
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.211
$\mu$ /mm <sup>-1</sup>	0.096
<i>F</i> (000)	760.0
Crystal size/mm <sup>3</sup>	0.34 × 0.236 × 0.116
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	3.724 to 53.462
Index ranges	-15 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 15, -20 ≤ <i>l</i> ≤ 20
Reflections collected	68538
Independent reflections	8626 [ <i>R</i> <sub>int</sub> = 0.0623, <i>R</i> <sub>sigma</sub> = 0.0340]
Data/restraints/parameters	8626/0/535
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.075
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0498, <i>wR</i> <sub>2</sub> = 0.1258
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0562, <i>wR</i> <sub>2</sub> = 0.1300
Largest diff. peak/hole / e Å <sup>-3</sup>	0.82/-0.26

<b>Table S8. Crystal data and structure refinement for 3b.</b>	
Identification code	3b
Empirical formula	C <sub>27</sub> H <sub>64</sub> B <sub>31</sub> OP·C <sub>7</sub> H <sub>8</sub>
Formula weight	850.277
Temperature/K	100.15
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	10.9967(1)
<i>b</i> /Å	15.5241(2)
<i>c</i> /Å	15.9285(3)
$\alpha$ /°	69.719(1)
$\beta$ /°	81.164(1)
$\gamma$ /°	78.446(1)
Volume/Å <sup>3</sup>	2488.44(6)
<i>Z</i>	2
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.135
$\mu$ /mm <sup>-1</sup>	0.678
<i>F</i> (000)	896.6
Crystal size/mm <sup>3</sup>	0.14 × 0.11 × 0.09
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54184)
2 $\theta$ range for data collection/°	5.94 to 150.28
Index ranges	-13 ≤ <i>h</i> ≤ 13, -19 ≤ <i>k</i> ≤ 17, -19 ≤ <i>l</i> ≤ 19
Reflections collected	45284
Independent reflections	9641 [ <i>R</i> <sub>int</sub> = 0.0300, <i>R</i> <sub>sigma</sub> = 0.0170]
Data/restraints/parameters	9641/0/596
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.024
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0703, <i>wR</i> <sub>2</sub> = 0.1808
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0722, <i>wR</i> <sub>2</sub> = 0.1814
Largest diff. peak/hole / e Å <sup>-3</sup>	0.83/-0.44

<b>Table S9. Crystal data and structure refinement for 4a.</b>	
Identification code	4a
Empirical formula	C <sub>26</sub> H <sub>46</sub> B <sub>31</sub> OP
Formula weight	740.71
Temperature/K	100(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	13.9904(2)
<i>b</i> /Å	17.1121(2)
<i>c</i> /Å	19.3321(2)
$\alpha$ /°	90
$\beta$ /°	109.8020(10)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	4354.53(10)
<i>Z</i>	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.130
$\mu$ /mm <sup>-1</sup>	0.720
<i>F</i> (000)	1520.0
Crystal size/mm <sup>3</sup>	0.3 × 0.25 × 0.12
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54184)
2 $\theta$ range for data collection/°	6.826 to 146.206
Index ranges	-17 ≤ <i>h</i> ≤ 17, -19 ≤ <i>k</i> ≤ 21, -23 ≤ <i>l</i> ≤ 21
Reflections collected	42906
Independent reflections	8374 [Rint = 0.0204, Rsigma = 0.0168]
Data/restraints/parameters	8374/0/532
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.036
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0381, <i>wR</i> <sub>2</sub> = 0.1018
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0401, <i>wR</i> <sub>2</sub> = 0.1032
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.29

## Reference

- 1 A. Brar, D. K. Unruh, A. J. Aquino, C. Krempner, *Chem. Commun.* **2019**, *55*, 3513-3516.
- 2 F. A. Gomez, M. F. Hawthorne, *J. Org. Chem.* **1992**, *57*, 1384-1390.
- 3 (a) C. Zhang, J. Wang, Z. Lin, Q. Ye, *Inorg. Chem.* **2022**, *61*, 18275–18284; (b) Ryan, S. J.; Schimler, S. D.; Bland, D. C.; Sanford, M. S. *Org. Lett.* **2015**, *17*, 1866-1869.
- 4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford CT, **2013**.
- 5 A. D. J. Becke, *Chem. Phys.* **1993**, *98*, 5648–5652.
- 6 P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. J. Frisch, *Phys. Chem.* **1994**, *98*, 11623–11627.
- 7 a) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; c) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465; d) E. R. Johnson, A. D. Becke, *J. Chem. Phys.* **2005**, *123*, 24101; e) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; f) A. D. Becke, E. R. Johnson, *J. Chem. Phys.* **2005**, *122*, 154104.
- 8 a) H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* **2015**, *44*, 7489–7499; b) L. Greb, *Chem. Eur. J.* **2018**, *24*, 17881–17896; c) L. O. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quiñones, V. Brecht, I. Krossing, *Angew. Chem. Int. Ed.* **2008**, *47*, 7659–7663.
- 9 a) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, S. P. Nolan, *Organometallics*, **2003**, *22*, 4322-4326; b) A. Poater, F. Ragone, S. Giudice, C. Costabile, R. Dorta, S. P. Nolan, L. Cavallo, *Organometallics*, **2008**, *27*, 2679-2681; (d) S. Díez-González and S. P. Nolan, *Coord. Chem. Rev.*, **2007**, *251*, 874-883; (e) A. Gómez-Suárez, D. J. Nelson and S. P. Nolan, *Chem. Commun.*, **2017**, *53*, 2650-2660.
- 10 a) P. Pérez, L. R. Domingo, A. Aizman, R. Contreras, *Theor. Comput. Chem.* **2007**, *19*, 139-201; b) A. R. Jupp, T. C. Johnstone, D. W. Stephan, *Inorg. Chem.* **2018**, *57*, 14764–14771.
- 11 G. M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst. A* **2015**, *71*, 3-8.
- 12 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.

13 G. M. Sheldrick, A short history of SHELX. *Acta Cryst. A* **2008**, *64*, 112-122.