

Reactivity of triphosphinoboranes towards $H_3B \cdot SMe_2$: Access to derivatives of boraphosphacycloalkanes with diversified substituents

Anna Ordyszewska*, Jarosław Chojnacki, Rafał Grubba*

Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, G.
Narutowicza St. 11/12. PL-80-233, Gdansk, Poland

1. Experimental Details
2. Crystallographic Details
3. NMR Spectroscopic Details
4. References

1. Experimental details

Materials and methods

All experiments were carried out under argon atmosphere using Schlenk technique. All manipulations were performed using standard vacuum, Schlenk, and glove box techniques. All solvents were purified and dried using commonly known methods. Solvents for NMR spectroscopy (C_6D_6) were purified with metallic sodium/potassium. Triphosphenoboranes¹ were synthesized following the literature methods. $BH_3 \cdot SMe_2$ was purchased from commercial sources and used without further purification. $BH_3 \cdot SMe_2$ solution in toluene was freshly prepared prior to use. The reported yields are referring to obtained crystalline products. NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer at ambient temperature (external standard TMS for 1H , ^{13}C ; 85% H_3PO_4 for ^{31}P , $BF_3 \cdot Et_2O$ for ^{11}B). The crystal structure analyses were performed on a STOE IPDS II diffractometer using MoK_{α} or CuK_{α} radiation ($\lambda = 0.71073 \text{ \AA}$ or $\lambda = 1.54186 \text{ \AA}$). Elemental analysis was performed at the University of Gdańsk using a Vario El Cube CHNS apparatus.

Synthesis of 1a

The solution 2.0 mL (1.5 mmol, $C = 0.749 \text{ M}$) $BH_3 \cdot SMe_2$ in toluene was added to the solution of 0.223 g (0.5 mmol) **1** in 4 mL of toluene at $-40^\circ C$. The reacting mixture was warmed up to room temperature and stirred for 24 h. Then the solvent was evaporated under reduced pressure and solid residue was redissolved in petroleum ether and the solute was concentrated to the volume of 1.5 mL. Colorless crystals of **1a** (0.042 g, 0.132 mmol, 26.6% yield) were obtained at $-20^\circ C$.

1a: 1H NMR (C_6D_6 , 400 MHz, δ): 1.32 (pseudo t, $N = 6 \text{ Hz}$ 36H, $C(CH_3)_3$), 2.58 (b quartet, $^1J_{BH} = 100 \text{ Hz}$, 4H, BH_2);

^{11}B NMR (C_6D_6 , 128 MHz, δ): -27.2 (bm, $^1J_{PB} = 60 \text{ Hz}$, BH_2)

$^{31}P\{^1H\}$ NMR (C_6D_6 , 162 MHz, δ): 8.7 (b septet, $^1J_{PB} = 60 \text{ Hz}$, tBu_2P);

$^{13}C\{^1H\}$ NMR (C_6D_6 , 100 MHz, δ): 30.5 (bs, $C(CH_3)_3$), 32.5 (pseudo t, $N = 14 \text{ Hz}$, $C(CH_3)_3$);

1b: ^{11}B NMR (C_6D_6 , 128 MHz, δ): -17.5 (bm, $^1J_{PB} = 105 \text{ Hz}$, BH_2), -39.7 (bm, $^1J_{PB} = 56 \text{ Hz}$, BH_3)

$^{31}P\{^1H\}$ NMR (C_6D_6 , 162 MHz, δ): 19.0 (bs, BH_2PBH_3)

Elemental analysis: calculated for $C_{16}H_{40}B_2P_2$, $M = 316.06 \text{ g/mol}$): %C = 60.80%, %H = 12.76%, found: %C = 60.62%, %H = 12.63%;

Synthesis of 2a

The solution of 0.82 mL (0.4 mmol, $C = 0.8 \text{ M}$) $BH_3 \cdot SMe_2$ in toluene was added to the solution of 0.097 g (0.2 mmol) **2** in 4 mL of toluene at $-40^\circ C$. The reacting mixture was warmed up to room temperature and stirred for 18 h. Then the solvent was evaporated under reduced pressure and solid residue was washed with petroleum ether and then redissolved in toluene, the solute was concentrated to the volume of 1 mL. Colorless crystals of **2a** (0.067 g, 0.13 mmol, 63.7 % yield) were obtained at $-20^\circ C$.

1H NMR (C_6D_6 , 400 MHz, δ): 0.98-1.34 (bm, overlapped, 11H (8H+3H) CH_2 (Cy), BH_3), 1.40 (d, $^3J_{PH} = 12 \text{ Hz}$, 9H, $C(CH_3)_3$), 1.40 (d, $^3J_{PH} = 12 \text{ Hz}$, 9H, $C(CH_3)_3$), 1.41 (d, overlapped, $^3J_{PH} = 13 \text{ Hz}$, 9H, $C(CH_3)_3$), 1.45 (d, $^3J_{PH} = 13 \text{ Hz}$, 9H, $C(CH_3)_3$), 1.54-1.85 (bm, overlapped, 10H (8H+2H), CH_2 (Cy), BH_2), 2.14 bm, 2H, CH_2 (Cy)), 2.42 (bs, 2H, CH_2 (Cy)), 3.44 (bd, 1H, BH);

^{11}B NMR (C_6D_6 , 128 MHz, δ): -25.6 (bs, BH), -35.7 (bs, overlapped, BH_2 , BH_3);

$^{31}P\{^1H\}$ NMR (C_6D_6 , 162 MHz, δ): 38.3 (bs, tBu_2P), 30.2 (bs, tBu_2P), -3.4 (bs, Cy_2P);

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz, δ): 25.9 (s, CH_2 , (Cy)), 26.1 (s, CH_2 , (Cy)), 26.6 (d, $J_{\text{CP}} = 9$ Hz, CH_2 , (Cy)), 26.8 (d, $J_{\text{CP}} = 12$ Hz, CH_2 (Cy)), 27.4 (m, overlapped, CH_2 (Cy)), 28.3 (d, $J_{\text{CP}} = 11$ Hz, CH_2 (Cy)), 28.9 (d, $J_{\text{CP}} = 5$ Hz, CH_2 (Cy)), 29.4 (d, $J_{\text{CP}} = 3$ Hz, CH_2 (Cy)), 29.8 (d, $^2J_{\text{PC}} = 2$ Hz, $\text{C}(\text{CH}_3)_3$), 30.1 (bs, overlapped, $\text{C}(\text{CH}_3)_3$), 30.6 (d, $^2J_{\text{PC}} = 2$ Hz, $\text{C}(\text{CH}_3)_3$), 32.0 (bd, $J = 3$ Hz, CH_2 (Cy)), 32.2 (bd, $J_{\text{CP}} = 4$ Hz, PCH (Cy)), 32.1 (dd, $^1J_{\text{PC}} = 22$ Hz, $^2J_{\text{PC}} = 3$ Hz, $\text{C}(\text{CH}_3)_3$), 32.4 (dd, $^1J_{\text{PC}} = 14$ Hz, $^2J_{\text{PC}} = 3$ Hz, $\text{C}(\text{CH}_3)_3$), 32.5 (dd, $^1J_{\text{PC}} = 23$ Hz, $^2J_{\text{PC}} = 4$ Hz, $\text{C}(\text{CH}_3)_3$), 33.1 (dd, $^1J_{\text{PC}} = 22$ Hz, $^2J_{\text{PC}} = 20$ Hz, PCH (Cy)), 35.8 (dd, $^1J_{\text{PC}} = 23$ Hz, $^2J_{\text{PC}} = 13$ Hz, $\text{C}(\text{CH}_3)_3$);

Elemental analysis: calculated for $\text{C}_{28}\text{H}_{64}\text{B}_3\text{P}_3$, $M = 526.16$ g/mol): %C = 63.92%, %H = 12.26%, found: %C = 63.77%, %H = 12.15%;

Reaction of **4** with BMS

The solution of 0.82 mL (0.4 mmol, $C = 0.8$ M) $\text{BH}_3\cdot\text{SMe}_2$ in toluene was added to the solution of 0.093 g (0.2 mmol) **4** in 4 mL of toluene at -40°C . The reacting mixture was warmed up to room temperature and stirred for 24 h. Then the solvent was evaporated under reduced pressure and solid residue was partially redissolved in petroleum ether, the solute was concentrated to the volume of 1 mL. Mix of colorless crystals of **1a**, **4a**, **4b** along with **1b** and other unidentified compounds were obtained at -20°C in molar ratio 0.5:1:1:1.

^{11}B NMR (C_6D_6 , 128 MHz, δ):

4a (δ): -14.4 (bs, BH_2), -20.9 (bs, BH_2);

4b (δ): -18.3 (bt, BH_2), -34.2 (bm, BH_3);

^{31}P NMR (C_6D_6 , 162 MHz, δ):

4a (δ): 13.7 (bs, $t\text{Bu}_2\text{PB}$), -4.6 (bs, $t\text{BuPhPB}$);

4b (δ): -1.0 (bs);

Synthesis of **5a**

The solution of 0.52 mL (0.4 mmol, $C = 0.8$ M) $\text{BH}_3\cdot\text{SMe}_2$ in toluene was added to the solution of 0.097 g (0.2 mmol) **5** in 2 mL of toluene at -40°C . The reacting mixture was warmed up to room temperature and stirred for 1 h. Then the solvent was evaporated under reduced pressure and solid residue was redissolved in petroleum ether and the solute was concentrated to the volume of 1.5 mL. Big colorless crystals of **5a** (0.054 g, 0.105 mmol, 52.5% yield) were obtained at -20°C .

^1H NMR (C_6D_6 , 400 MHz, δ): 1.14 (d, $^3J_{\text{PH}} = 12$ Hz, 9H, $(\text{CH}_3)_3\text{C}$), 1.30 (bs, overlapped, 9H, $(\text{CH}_3)_3\text{C}$), 1.34 (bd, overlapped, $^3J_{\text{PH}} = 12$ Hz, 9H, $(\text{CH}_3)_3\text{C}$), 1.41 (d, $^3J_{\text{PH}} = 13$ Hz, 9H, $(\text{CH}_3)_3\text{C}$), 1.77 (bs, 3H, BH_3), 2.53 (bs, 2H, BH_2), 3.71 (bd, 1H, BH), 7.00 (m, overlapped, 4H, C- H_{para} and C- H_{meta}), 7.12 (m, 2H, C- H_{meta}), 7.58 (m, 2H, C- H_{ortho}), 8.33 (m, 2H, C- H_{ortho});

^{11}B NMR (C_6D_6 , 128 MHz, δ): -18.3 (bs, BH), -25.7 (bs, BH_2), -36.8 (bs, BH_3);

$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, δ): 30.3 (bs, $t\text{Bu}_2\text{P}$), 17.1 (bs, $t\text{Bu}_2\text{P}$), -7.8 (bs, Ph_2P);

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz, δ): 29.9 (d, $^2J_{\text{PC}} = 14$ Hz, overlapped, $\text{C}(\text{CH}_3)_3$), 30.2 (m, overlapped, $\text{C}(\text{CH}_3)_3$), 32.8 (m, overlapped, $\text{C}(\text{CH}_3)_3$), 35.4 (dd, $^1J_{\text{PC}} = 27$ Hz, $^3J_{\text{PC}} = 13$ Hz, $\text{C}(\text{CH}_3)_3$), 128.0 (s, C_p), 128.1 (s, C_p), 129.2 (d, $^3J_{\text{CP}} = 4$ Hz, C_m), 130.1 (d, $^3J_{\text{CP}} = 2$ Hz, C_m), 130.2 (dd, $^1J_{\text{CP}} = 42$ Hz, $^3J_{\text{CP}} = 3$ Hz, C_i), 132.8 (d, $^2J_{\text{CP}} = 8$ Hz, C_o), 136.4 (dd, $^1J_{\text{CP}} = 40$ Hz, $^3J_{\text{CP}} = 29$ Hz, C_i), 136.6 (d, $^2J_{\text{CP}} = 9$ Hz, C_o);

Elemental analysis: calculated for $\text{C}_{28}\text{H}_{52}\text{B}_3\text{P}_3$, $M = 514.07$ g/mol): %C = 65.42%, %H = 10.19%, found: %C = 65.50%, %H = 10.22%;

Synthesis of **6a**

The solution of 0.61 mL (0.5 mmol, $C = 0.817$ M) $\text{BH}_3\cdot\text{SMe}_2$ in toluene was added to the solution of 0.190 g (0.5 mmol) **6** in 5 mL of toluene at -40°C . The reacting mixture was warmed up to room

temperature and stirred for 1 h. Then the solvent was evaporated under reduced pressure and solid residue was redissolved in petroleum ether and the solute was concentrated to the volume of 3 mL. Colorless crystals of **6a** (0.163 g, 0.41 mmol, 82.5% yield) were obtained at -20°C.

^1H NMR (C_6D_6 , 400 MHz, δ): 1.25 (pseudo t, $N = 6$ Hz 18H, $\text{C}(\text{CH}_3)_3$), 1.41 (pseudo t, $N = 6$ Hz 18H, $\text{C}(\text{CH}_3)_3$), 2.32 (b quartet, $^1J_{\text{BH}} = 107$ Hz, 2H, BH_2), 3.93 (b quartet, $^1J_{\text{BH}} = 117$ Hz, 1H, BBrH);

^{11}B NMR (C_6D_6 , 128 MHz, δ): -17.8 (bm, BBrH), -31.1 (bm, BH_2),

$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, δ): 10.1 (bs, $t\text{Bu}_2\text{P}$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz, δ): 30.3 (bs, $\text{C}(\text{CH}_3)_3$), 30.7 (bs, $\text{C}(\text{CH}_3)_3$), 34.1 (pseudo t, $N = 14$ Hz, $\text{C}(\text{CH}_3)_3$), 35.5 (pseudo t, $N = 14$ Hz, $\text{C}(\text{CH}_3)_3$);

Elemental analysis: calculated for $\text{C}_{16}\text{H}_{39}\text{B}_2\text{BrP}_2$, $M = 394.95$ g/mol): %C = 48.66%, %H = 9.95%, found: %C = 48.52%, %H = 9.93%;

2. Crystallographic Details

Diffraction intensity data for all crystals were collected on an IPDS 2T dual beam diffractometer (STOE & Cie GmbH, Darmstadt, Germany) at 120.0(2) K with MoK_α or CuK_α radiation of a microfocus X-ray source (GeniX 3D Mo High Flux, Xenocs, Sassenage, 50 kV, 1.0 mA, and $\lambda = 0.71069$ or $\lambda = 1.54186$ Å). Investigated crystals were thermostated under a nitrogen stream at 120 K using the CryoStream-800 device (Oxford CryoSystem, UK) during the entire experiment.

Data collection and data reduction were controlled by using the X-Area 1.75 program (STOE, 2015). Absorption correction was performed only for data with absorption coefficient > 0.5 mm^{-1} . The structures were solved using intrinsic phasing implemented in SHELXT and refined anisotropically using the program packages Olex2² and SHELX-2015^{3,4}.

Hydrogen atoms of the C-H type were positioned geometrically and refined with the usual constraints using the riding model. All B-H hydrogen atoms were found in the Fourier electron density map and refined without constraints.

Structure **1a** contained half of the molecule in the asymmetric unit $Z=2$ in space group $P2_1/c$. Structure **2a** was refined without special treatments. Compound **4a** did not form larger crystals, so for the tiny specimens available we decided to use copper radiation to enhance their scattering power. The smallest R_1 index, which could have been achieved, is still rather high. Nevertheless the structure looks sensible and even B-H hydrogen atoms could have been found. Structures **4b** and **5a** were refined with no special treatment. Structure **6a** is refined in the non-centrosymmetric space group $P2_1$ as a racemic twin with practically equal populations for both enantiomer-pure domains.

Crystallographic data for all structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 2192413-2192418. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S1. Crystal data and structure refinement for **1a**, **2a**, and **4a**.

	1a	2a	4a
CCDC no.	2192413	2192414	2192415
Chemical formula	$\text{C}_{16}\text{H}_{40}\text{B}_2\text{P}_2$	$\text{C}_{28}\text{H}_{64}\text{B}_3\text{P}_3$	$\text{C}_{26}\text{H}_{56}\text{B}_3\text{P}_3$
M_r (g/mol)	316.04	526.13	494.04

Temperature (K)	120	120	120
Radiation type	Mo K α	Mo K α	Cu K α
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	8.1530(17)	11.0382(2)	19.778(4)
b (Å)	15.095(3)	19.0404(3)	8.6662(10)
c (Å)	8.1050(17)	15.9387(3)	20.415(4)
α (°)	90	90	90
β (°)	95.505(17)	106.256(2)	118.914(13)
γ (°)	90	90	90
V (Å ³)	992.9(4)	3215.94(10)	3063.0(10)
Z	2	4	4
D _x (g/cm ³)	1.057	1.087	1.071
Crystal size (mm)	0.24x0.13x0.11	0.21x0.16x0.12	0.12x0.03x0.02
θ Range (°)	29.16-2.70	29.25-2.27	59.99-4.33
Reflections collected/unique	6678/2665	45312/8660	10114/4509
Completeness to θ max (%)	99.4	98.8	99.3
Data/restraints/parameters	2665/105/0	8660/343/0	4509/323/0
Goodness-of-fit on F ²	1.078	1.079	1.019
Final R indexes [$I > 2\sigma(I)$]	R ₁ = 0.0229 R ₂ = 0.0410	R ₁ = 0.0388 R ₂ = 0.0523	R ₁ = 0.1179 R ₂ = 0.2738
R indexes (all data)	wR ₁ = 0.0875 wR ₂ = 0.0900	wR ₁ = 0.0969 wR ₂ = 0.1027	wR ₁ = 0.2506 wR ₂ = 0.3517
Largest diff. peak and hole (e Å ⁻³)	0.353, -0.225	1.166, -0.313	0.461, -0.454

Table S2. Crystal data and structure refinement for **4b**, **5a**, and **6a**.

	4b	5a	6a
CCDC no.	2192416	2192417	2192418
Chemical formula	C ₁₂ H ₂₅ B ₂ P ₂ S	C ₂₈ H ₅₂ B ₃ P ₃	C ₁₆ H ₃₉ B ₂ BrP ₂
M _r (g/mol)	253.97	514.03	394.94
Temperature (K)	120	120	120
Radiation type	Mo K α	Mo K α	Mo K α
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1$
a (Å)	7.7997(13)	12.990(5)	8.5887(9)
b (Å)	10.8175(17)	18.828(6)	13.8357(16)
c (Å)	18.377(4)	12.969(5)	9.1332(11)
α (°)	90	90	90
β (°)	90	100.24(3)	98.207(9)
γ (°)	90	90	90
V (Å ³)	1550.5(5)	3121(2)	1074.2(2)
Z	4	4	2

D_x (g/cm ³)	1.088	1.094	1.221
Crystal size (mm)	0.12x0.07x0.06	0.22x0.17x0.11	0.08x0.06x0.04
θ Range (°)	29.25-2.84	29.26-2.31	29.22-2.25
Reflections collected/unique	23835/4207	42411/8402	12967/5715
Completeness to θ max (%)	99.6	98.8	99.1
Data/restraints/parameters	4207/170/0	8402/343/0	5715/211/1
Goodness-of-fit on F^2	1.062	1.122	1.025
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0529$ $R_2 = 0.0630$	$R_1 = 0.0626$ $R_2 = 0.0718$	$R_1 = 0.0343$ $R_2 = 0.0450$
R indexes (all data)	$wR_1 = 0.1372$ $wR_2 = 0.1426$	$wR_1 = 0.1792$ $wR_2 = 0.1903$	$wR_1 = 0.0746$ $wR_2 = 0.0790$
Largest diff. peak and hole (e Å ⁻³)	0.561, -0.418	0.676, -0.795	0.408, -0.261

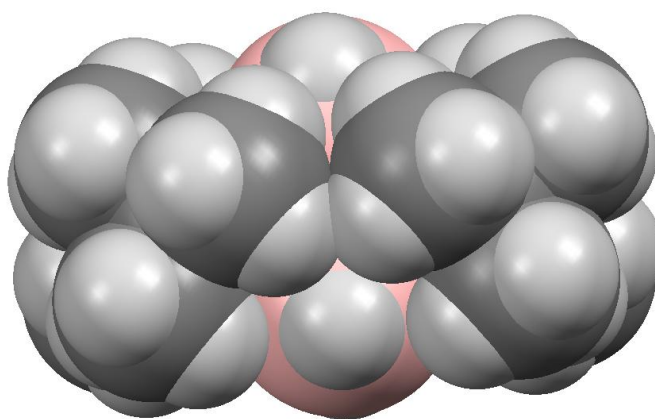


Figure S1. Space-filling model for **1a**.

3. NMR Spectroscopic Details

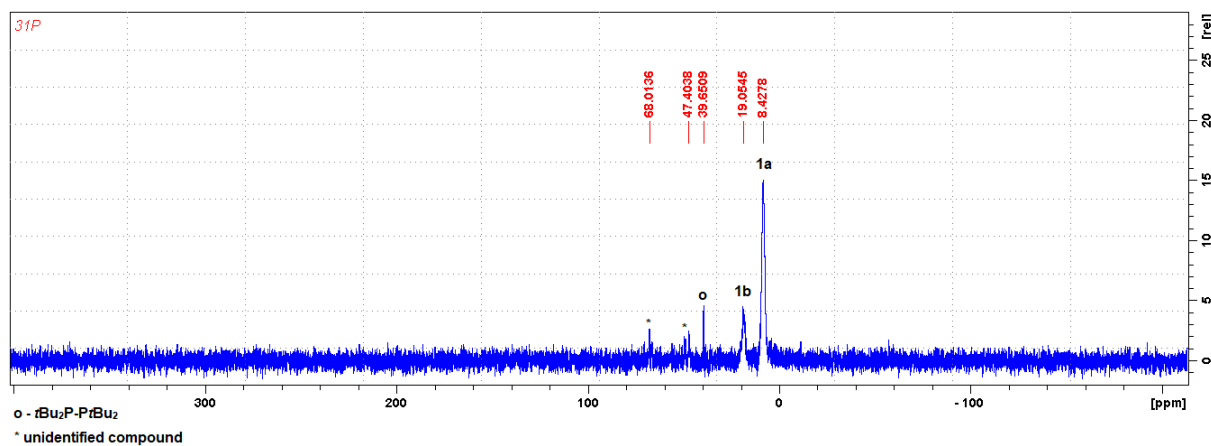


Figure S2. ³¹P NMR (C₆D₆, 162 MHz) spectrum of reacting mixture of **1a**.

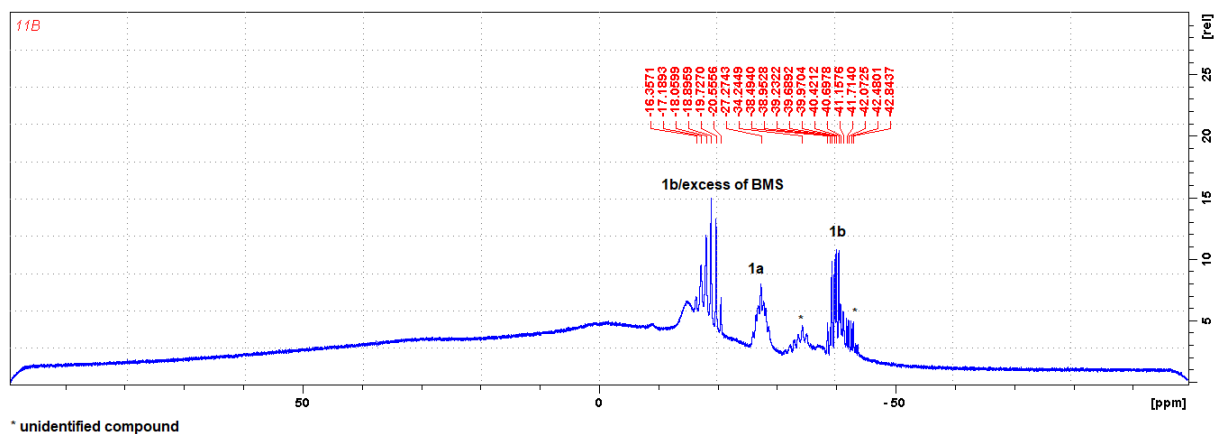


Figure S3. ^{11}B NMR (C_6D_6 , 128 MHz) spectrum of reacting mixture of **1a**.

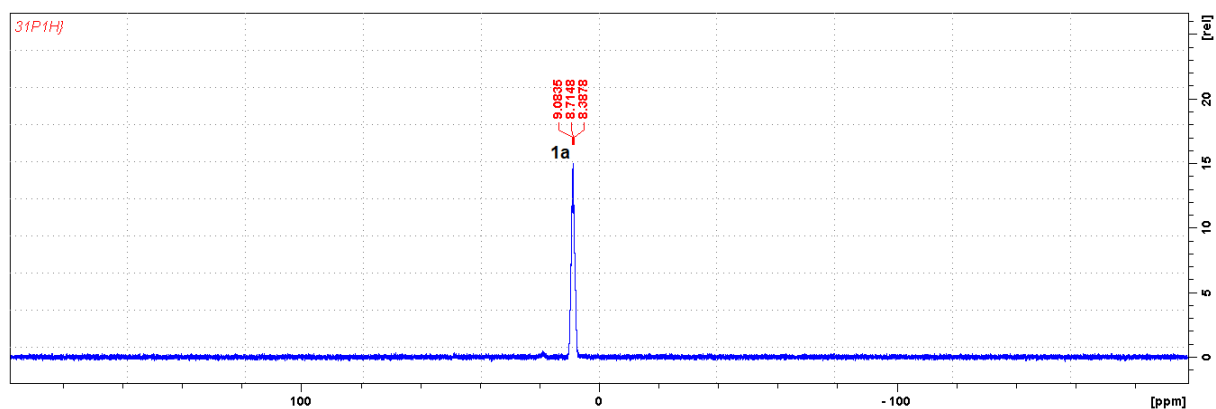


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz) spectrum of **1a**.

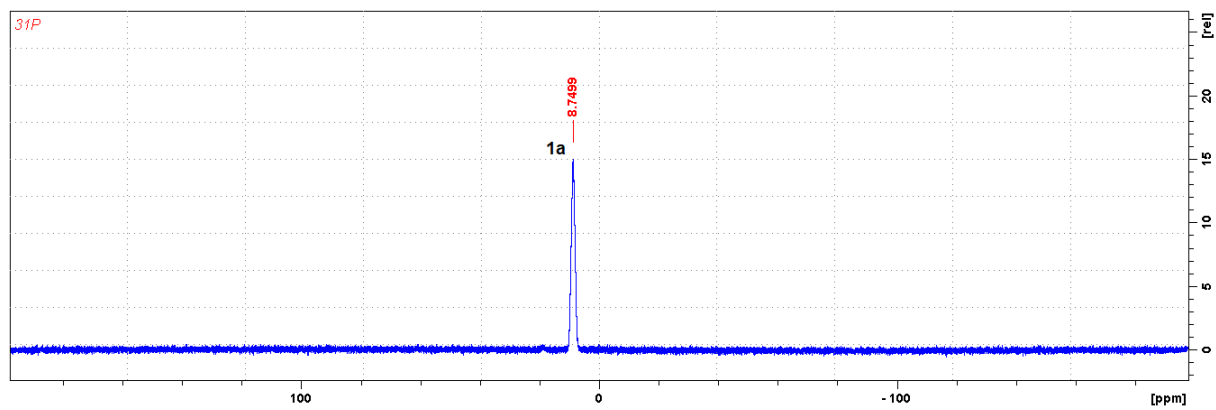


Figure S5. ^{31}P NMR (C_6D_6 , 162 MHz) spectrum of **1a**.

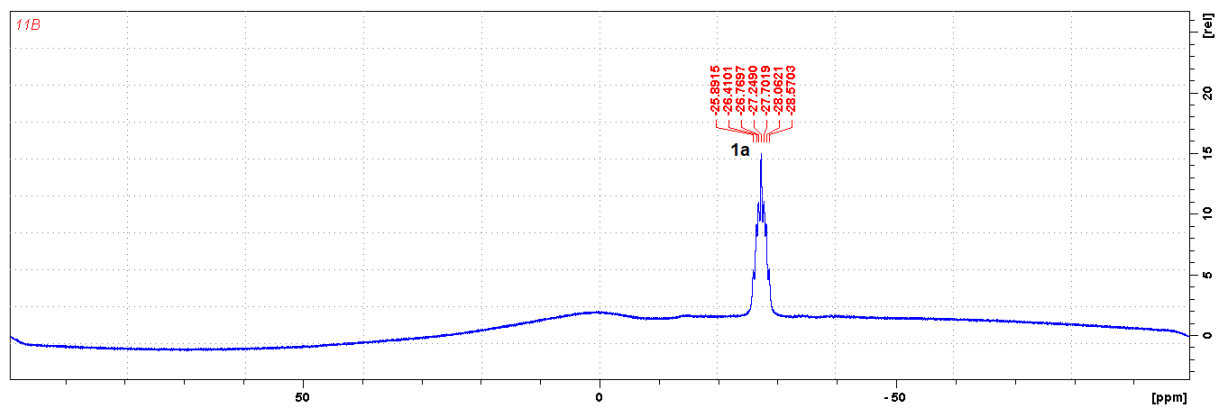


Figure S6. ^{11}B NMR (C_6D_6 , 128 MHz) spectrum of **1a**.

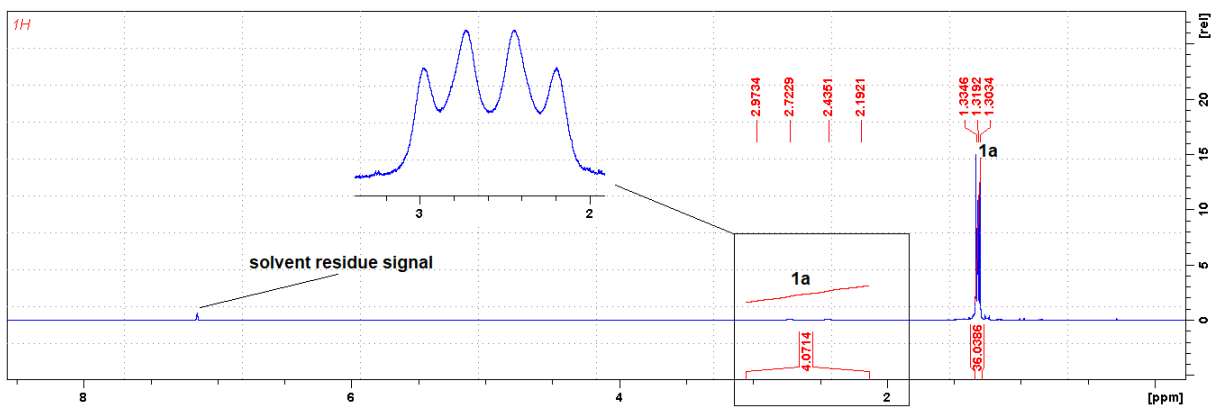


Figure S7. ^1H NMR (C_6D_6 , 400 MHz) spectrum of **1a**.

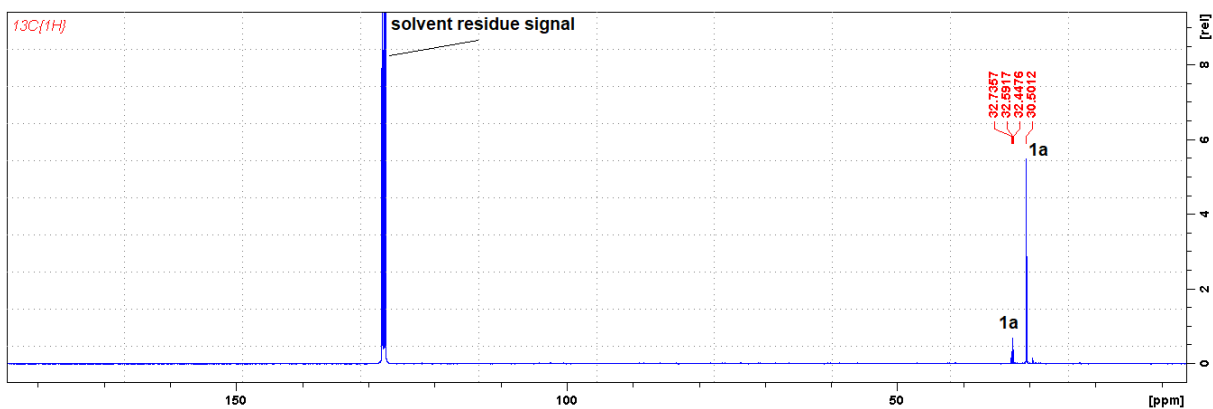


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) spectrum of **1a**.

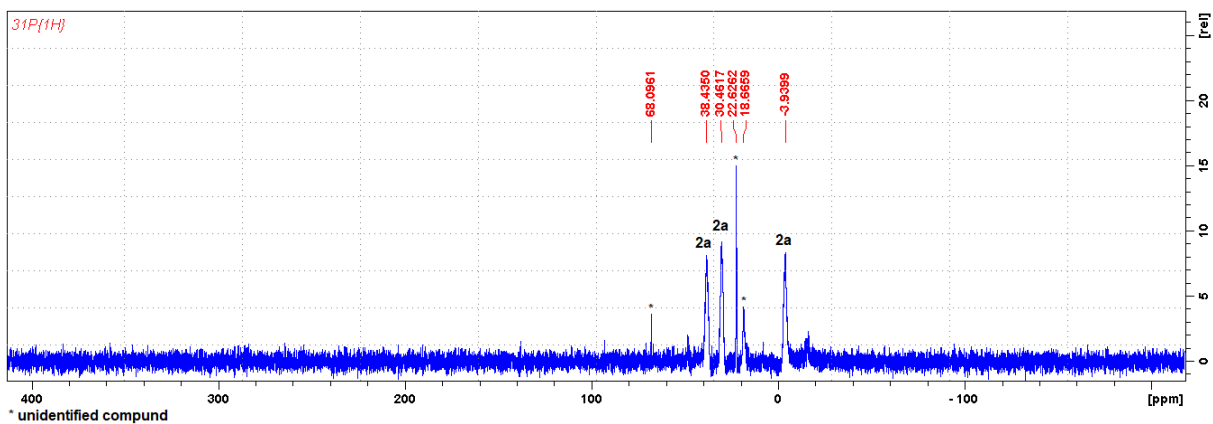


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz) spectrum of reacting mixture of **2a**.

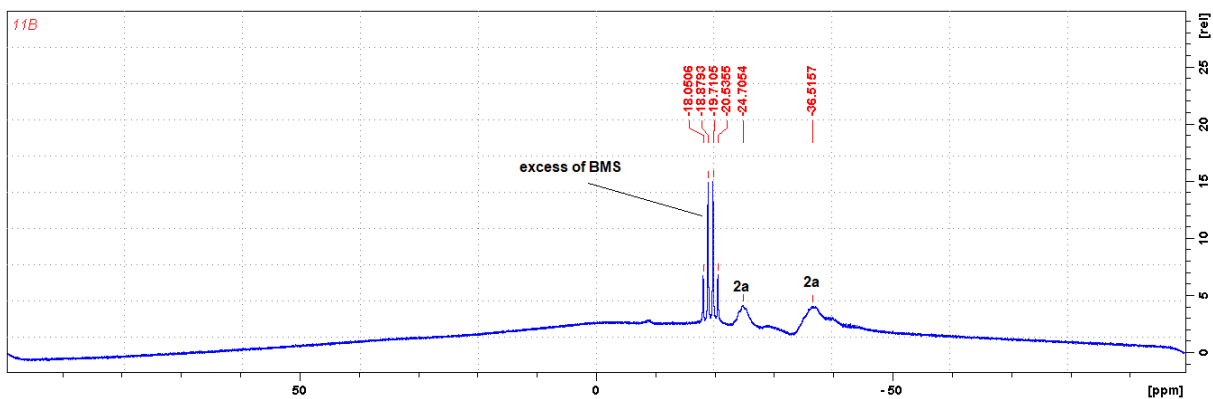


Figure S10. ^{11}B NMR (C_6D_6 , 128 MHz) spectrum of reacting mixture of **2a**.

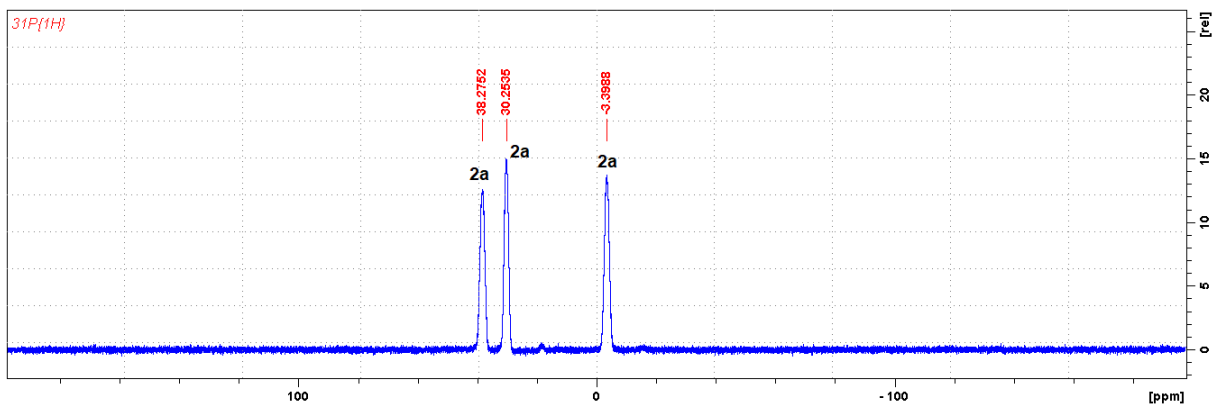


Figure S11. ³¹P{¹H} NMR (C₆D₆, 162 MHz) spectrum of 2a.

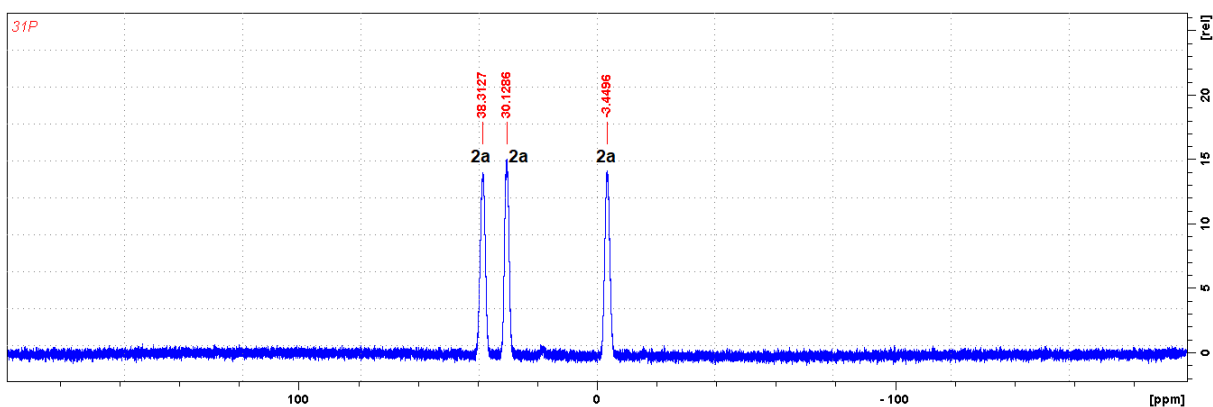


Figure S12. ³¹P NMR (C₆D₆, 162 MHz) spectrum of 2a.

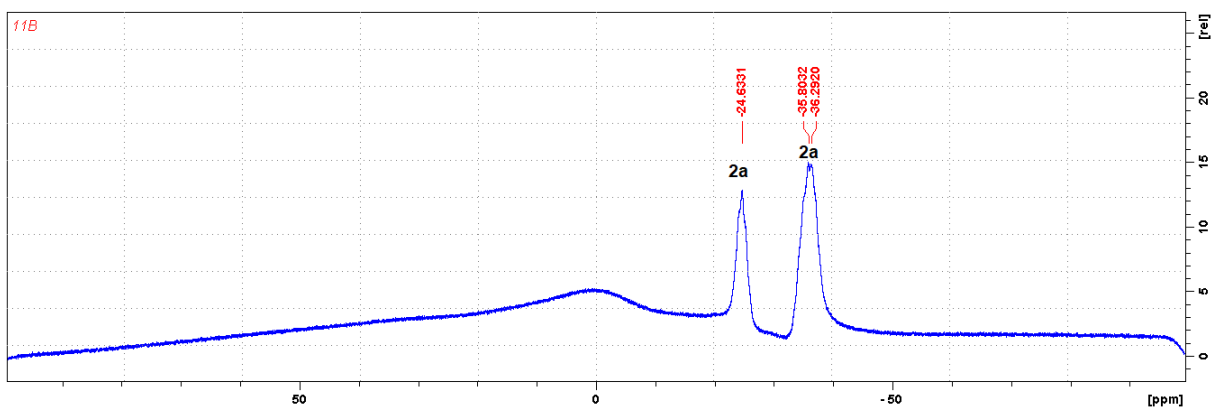


Figure S13. ¹¹B NMR (C₆D₆, 128 MHz) spectrum of 2a.

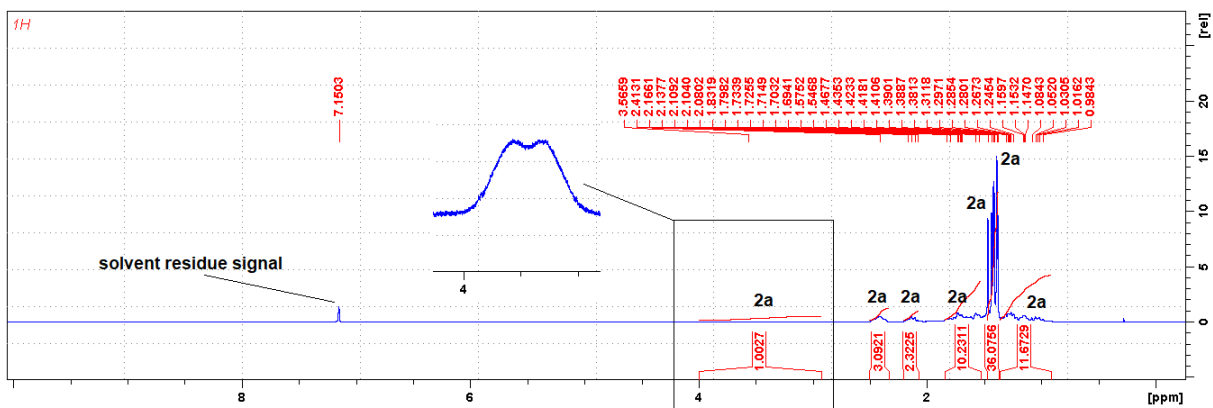


Figure S14. ¹H NMR (C₆D₆, 400 MHz) spectrum of 2a.

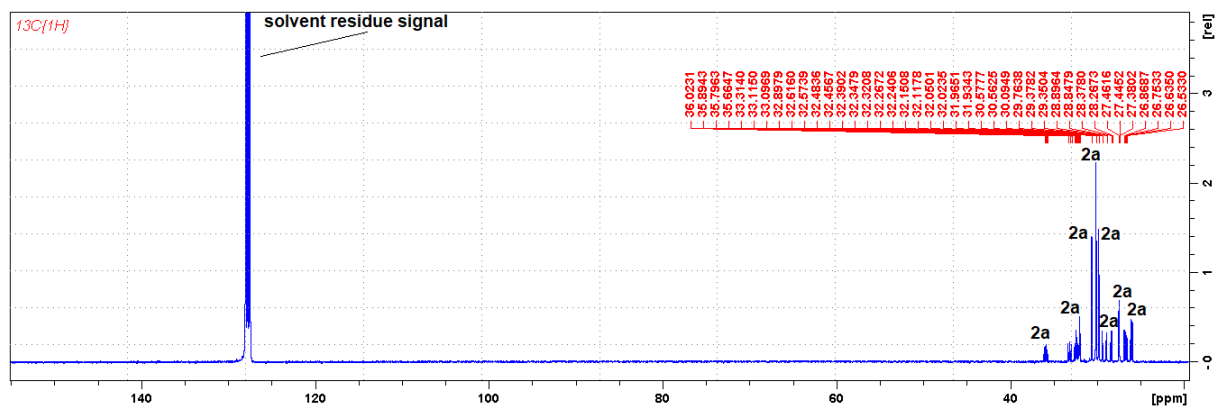
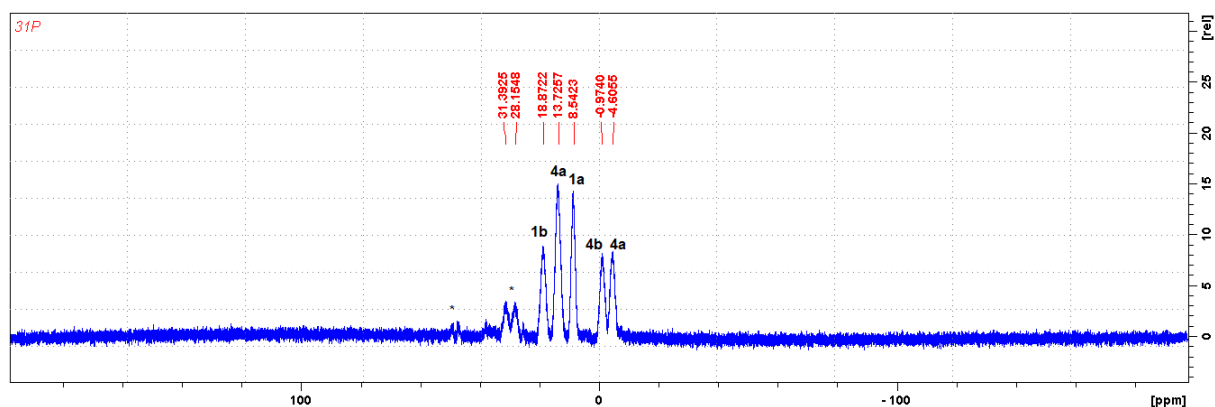
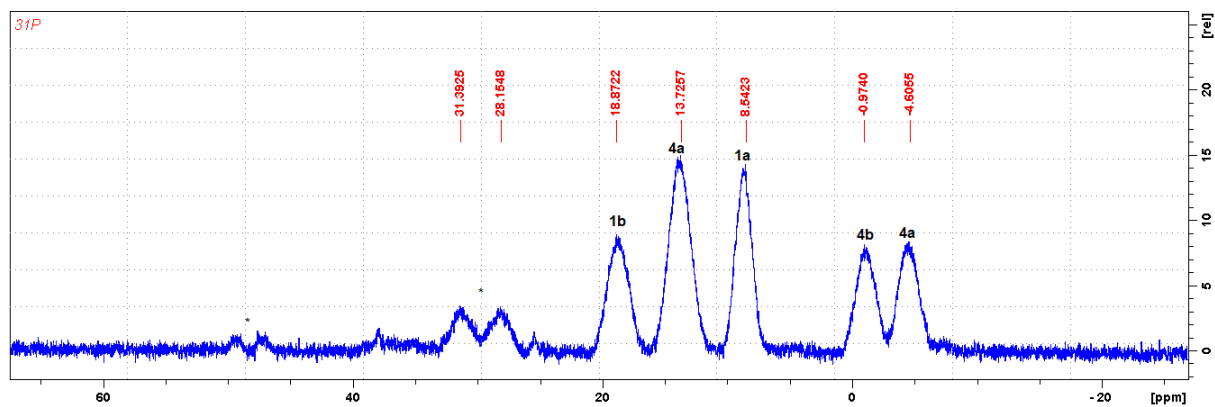


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz) spectrum of **2a**.



* unidentified compound

Figure S16. ^{31}P NMR (C_6D_6 , 162 MHz) spectrum of obtained crystal mixture after reaction of **4** with BMS.



* unidentified compound

Figure S17. Selected region of ^{31}P NMR (C_6D_6 , 162 MHz) spectrum of obtained crystal mixture after reaction of **4** with BMS.

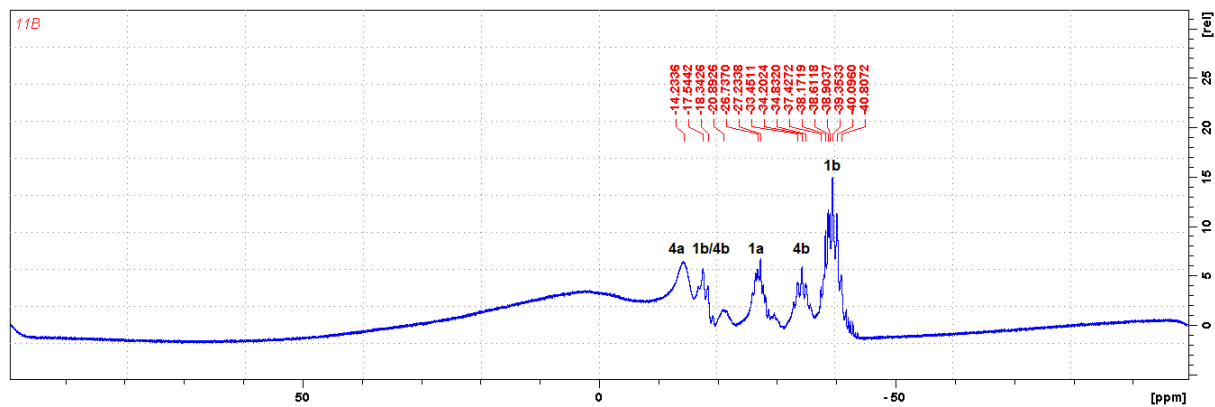


Figure S18. ^{11}B NMR (C_6D_6 , 128 MHz) spectrum of obtained crystal mixture after reaction of **4** with BMS.

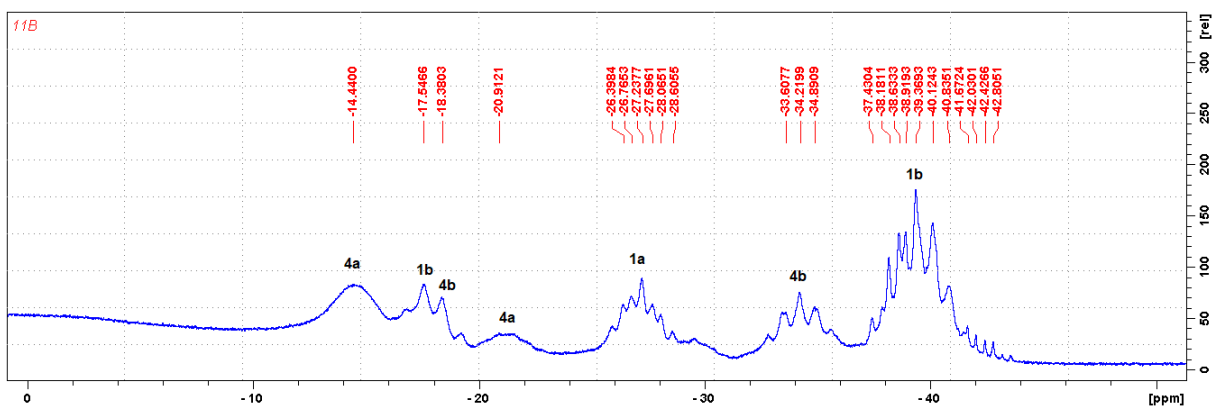


Figure S19. Selected region of ^{11}B NMR (C_6D_6 , 128 MHz) spectrum of obtained crystal mixture after reaction of 4 with BMS.

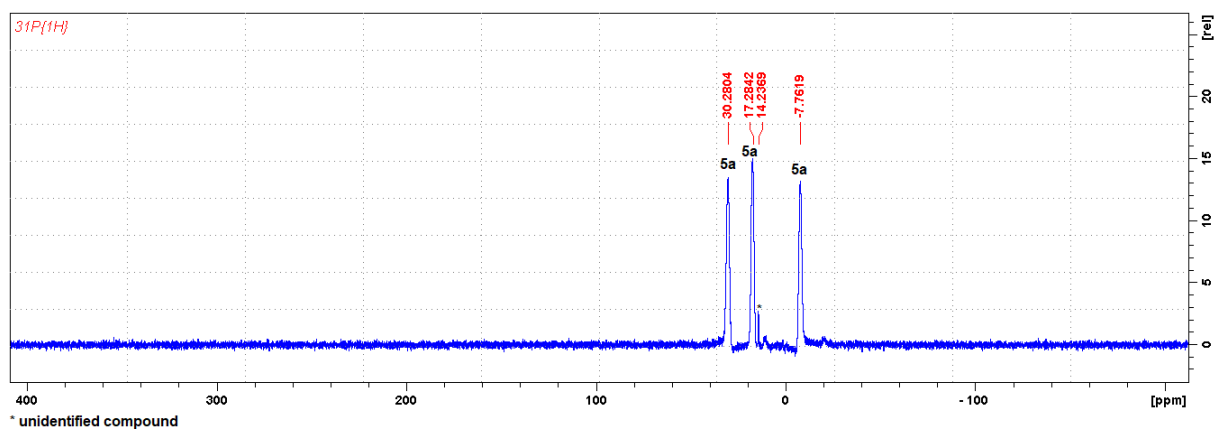


Figure S20. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz) spectrum of reacting mixture of 5a.

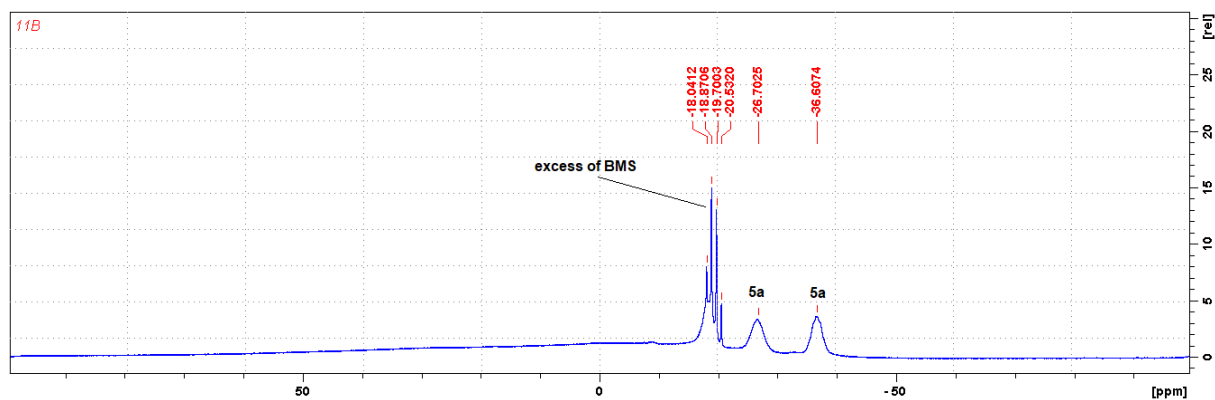


Figure S21. ^{11}B NMR (C_6D_6 , 128 MHz) spectrum of reacting mixture 5a.

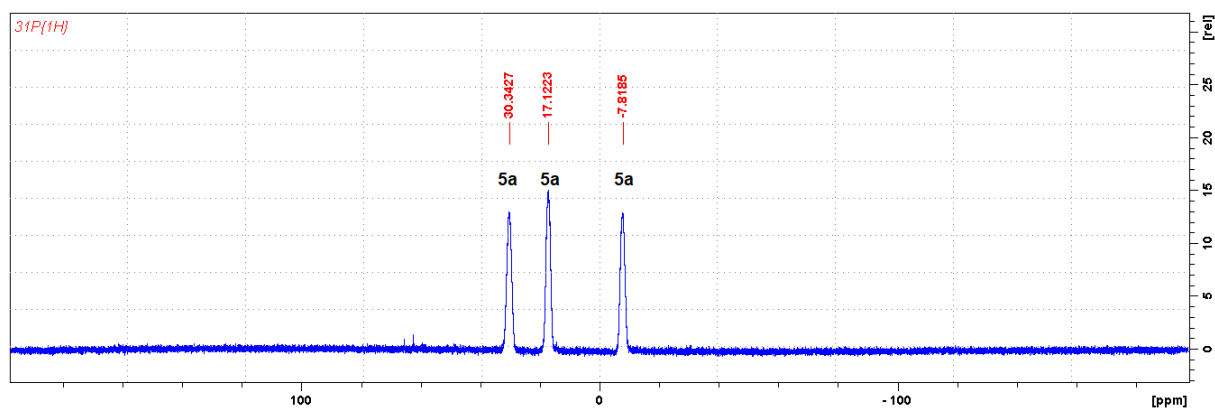
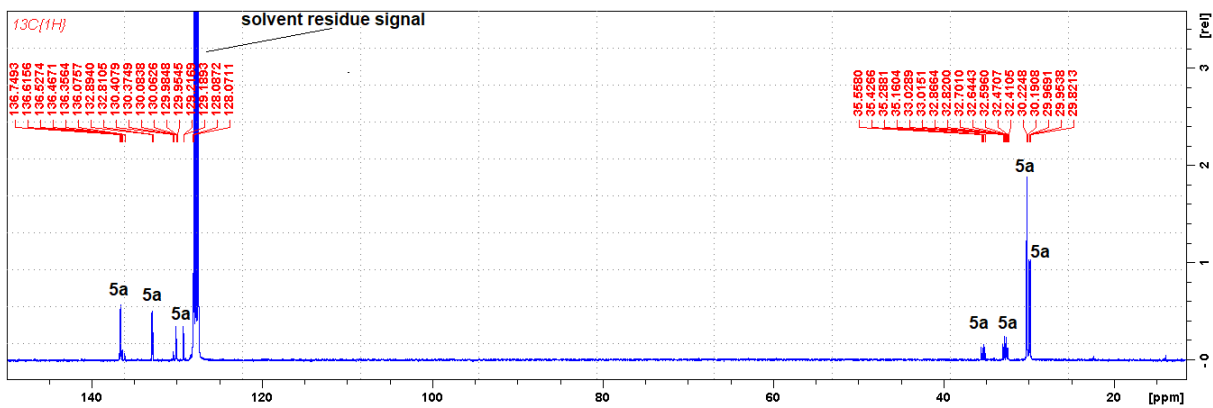
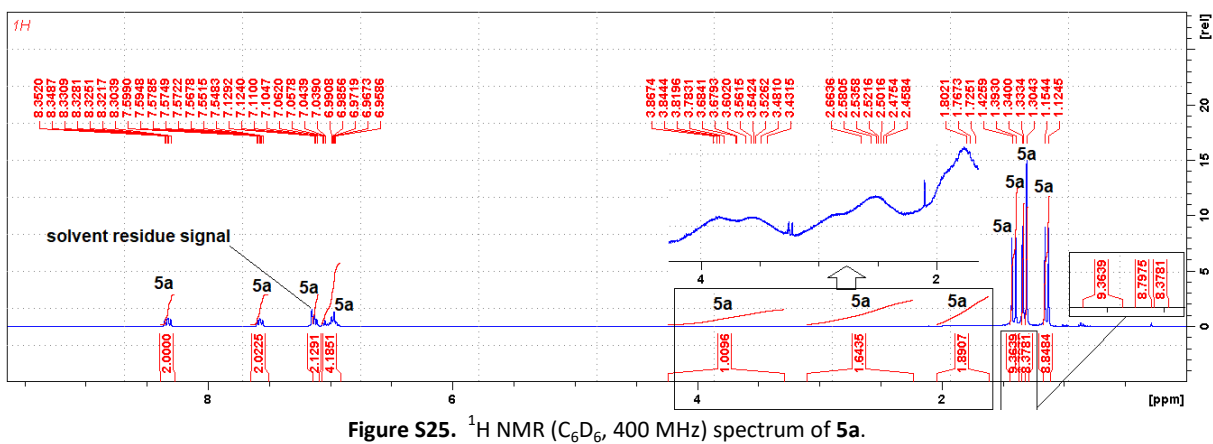
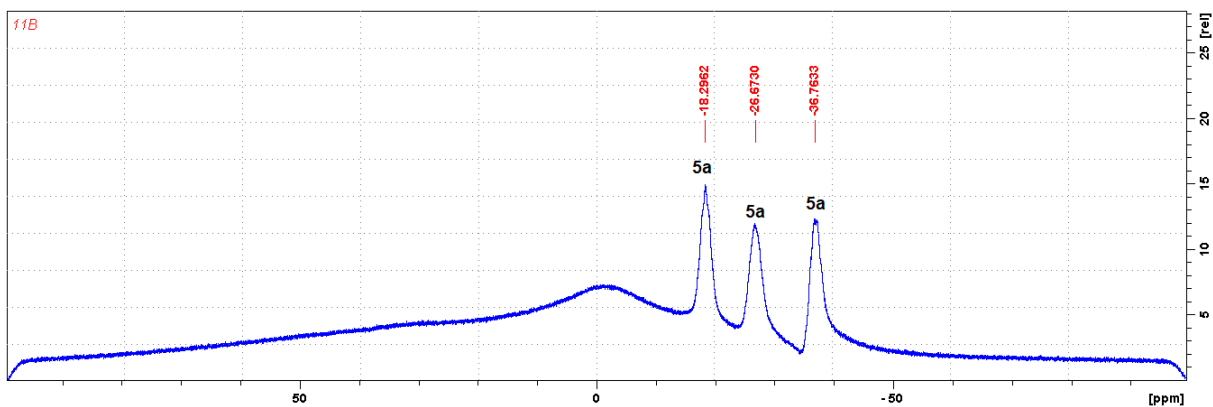
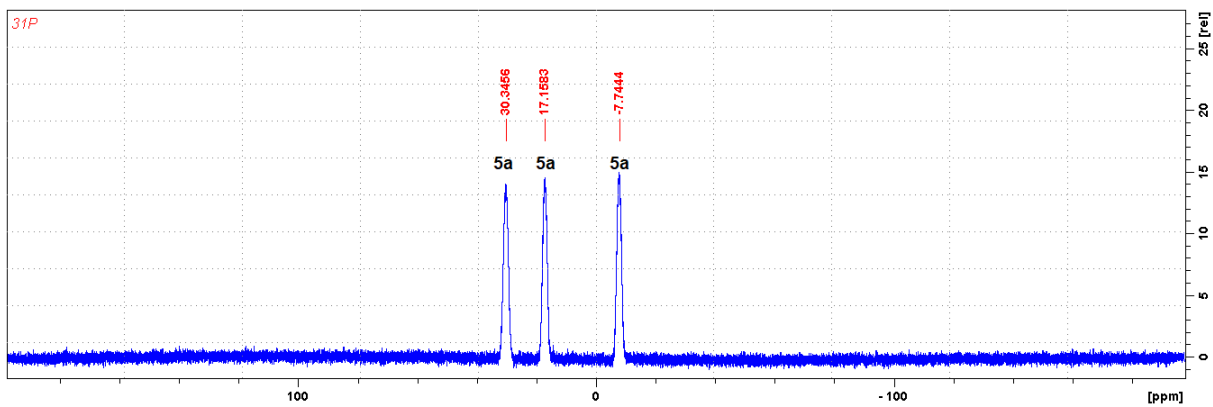


Figure S22. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz) spectrum of 5a.



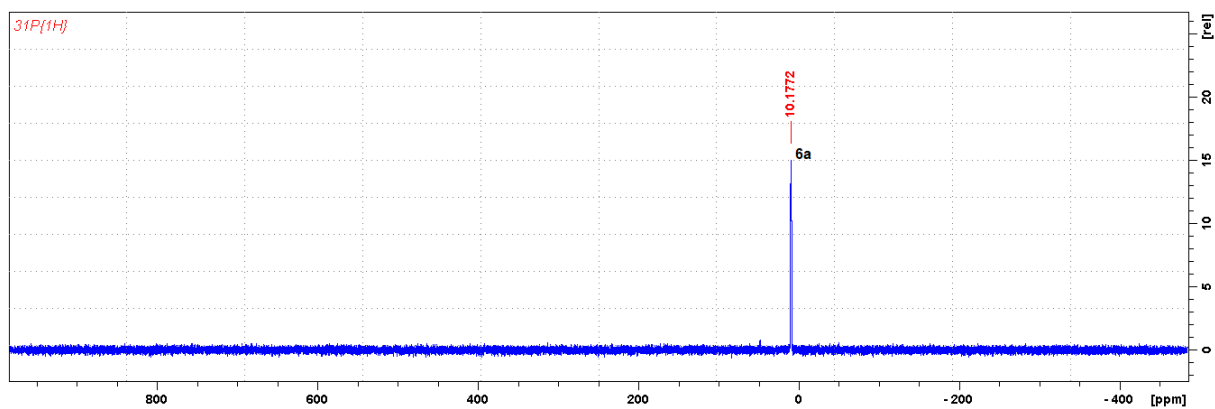


Figure S27. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz) spectrum of reacting mixture of **6a**.

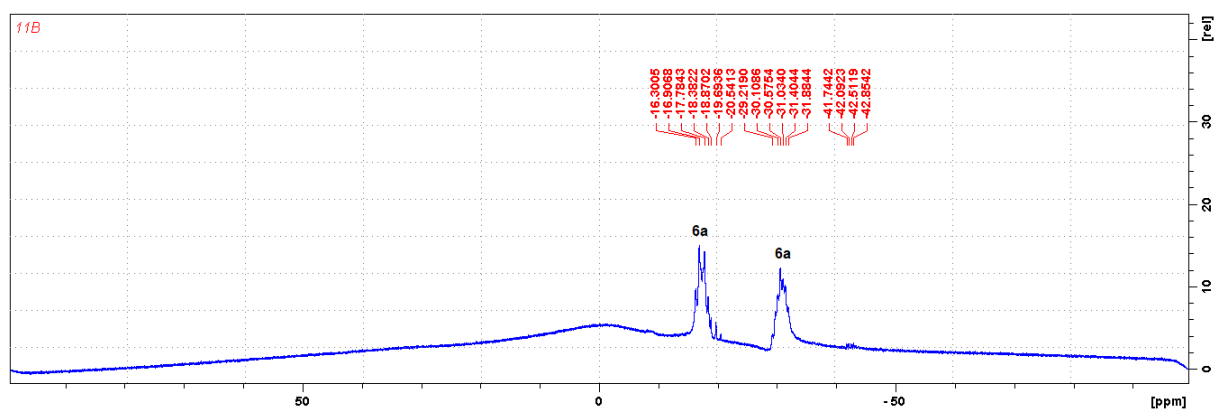


Figure S28. ^{11}B NMR (C_6D_6 , 128 MHz) spectrum of reacting mixture of **6a**.

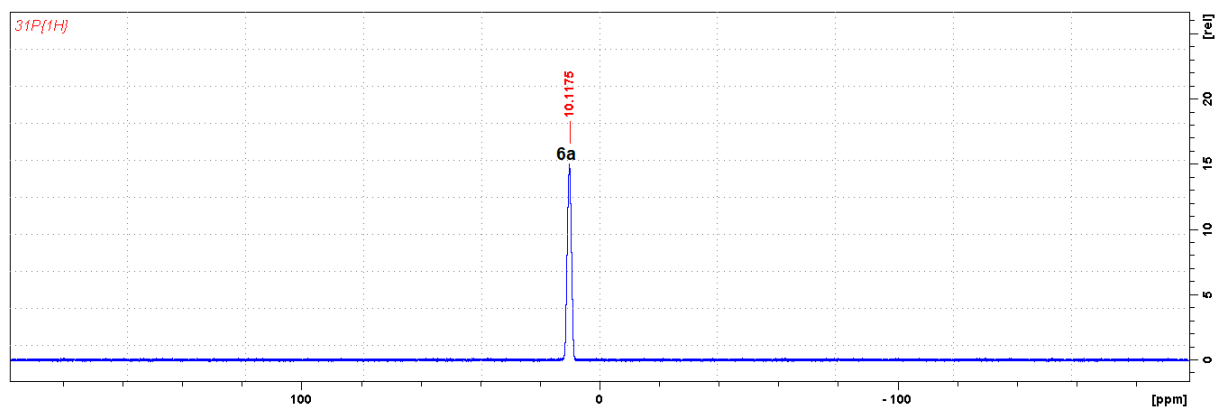
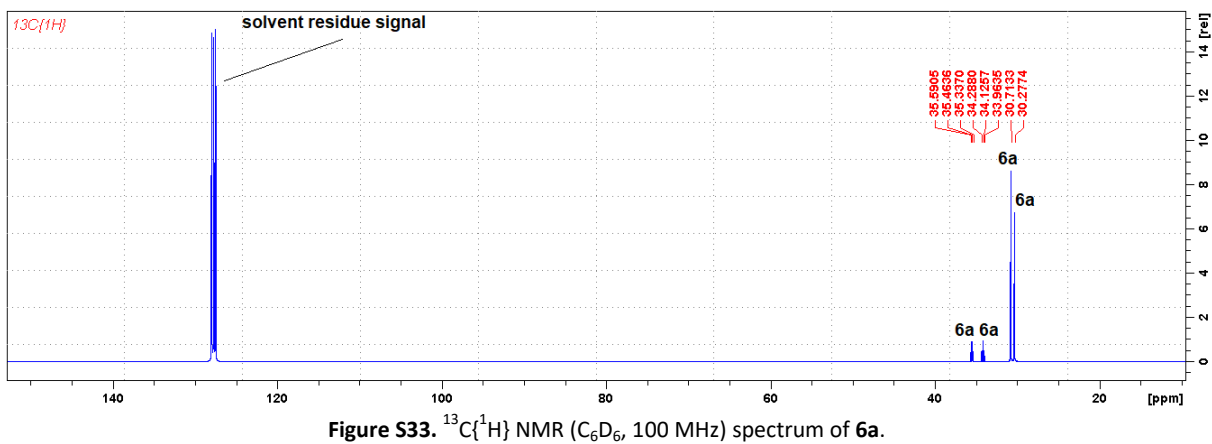
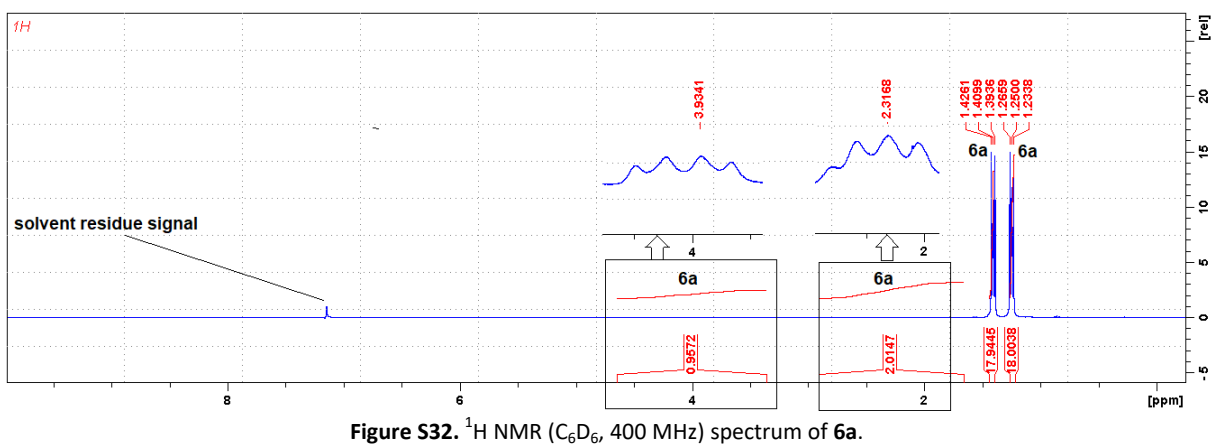
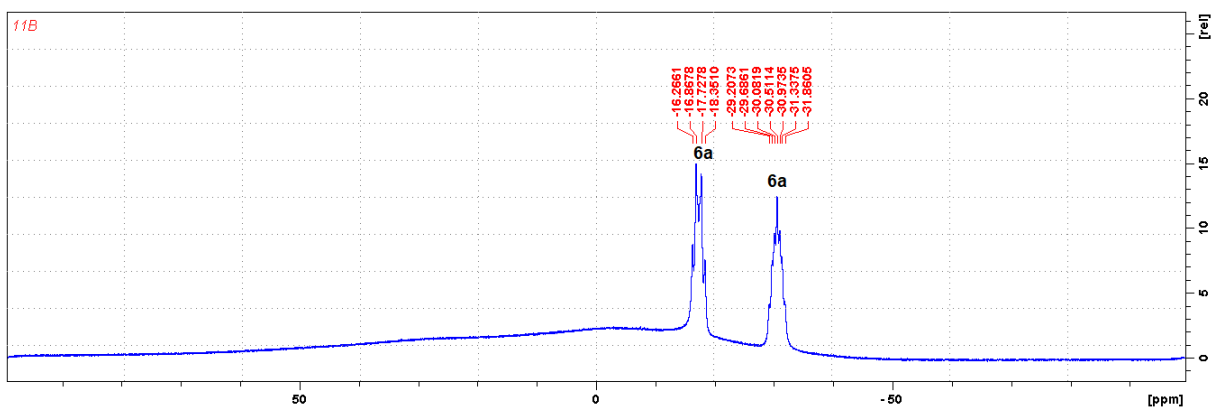
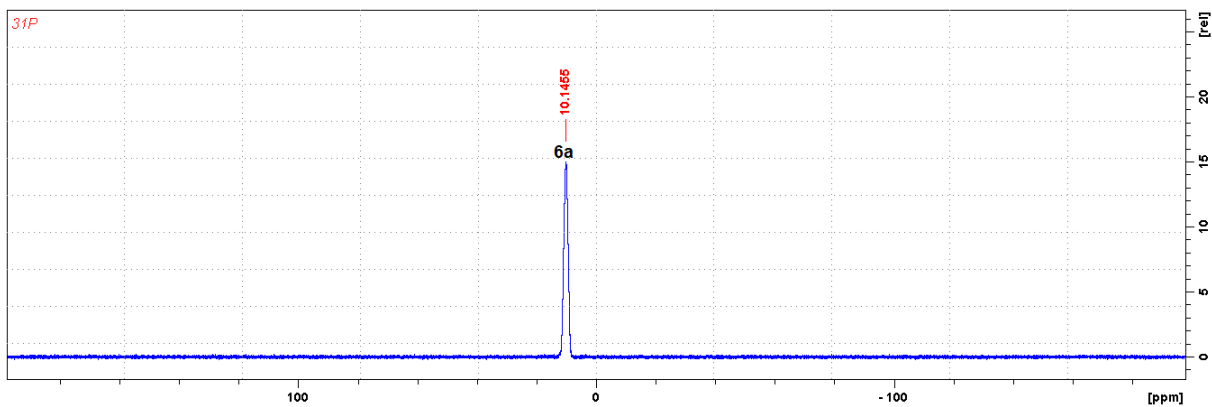


Figure S29. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz) spectrum of **6a**.



4. References

- (1) Ordyszewska, A.; Szykiewicz, N.; Chojnacki, J.; Grubba, R. *Inorg. Chem.* **2022**, *61* (10), 4361–4370.
- (2) Dolomanov, O. V; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- (3) Sheldrick, G. M. *Acta Cryst. A* **2015**, *71* (1), 3–8.
- (4) Sheldrick, G. M. *Acta Cryst. C* **2015**, *71*, 3–8.