Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

A Practical Method for the Generation of Organoarsenic Nucleophiles towards the Construction of a Versatile Arsenic Library

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Contents:

1. Materials

Phenylmagnesium chloride solution (2.0 M in THF), cyclohexylmagnesium chloride solution (1.0 M in 2-methyltetrahydrofuran), *cis*-1,2-dichloroethylene, and *cis*-bis(benzonitrile)dichloroplatinum(II) were purchased from Sigma Aldrich. Benzyl chloride, dichloromethane, 1,2-dichloroethane, chlorobenzene, bromobenzene and toluene were purchased from Nacalai Tesque, Inc. Tetrahydrofuran, distilled water, ethanol, and iodobenzene were purchased from Wako Pure Chemical Industry, Ltd. Phenyllithium solution (1.6 M in butyl ether) and *α*-*α*'-dichloro-*o*-xylene were purchased from Tokyo Chemical Industry Co., Ltd. Hexaphenylcyclohexaarsine (**1**) was prepared by following the literature.[1]

2. Measurement

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer. The samples were analyzed in $CDCl_3$ using Me_4Si as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, m: multiplet. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer.

3. X-ray crystallographic data for single crystalline products

The single crystal was mounted on a nylon loop. Intensity data were collected at room temperature on a Rigaku XtaLAB mini with graphite monochromated Mo Kα radiation. Readout was performed in the 0.073 mm pixel mode. The data were collected at room temperature to a maximum 2θ value of 55.0°. Data were processed by Crystal Clear.[2] An empirical absorption correction[3] was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct method[4] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on observed reflections and variable parameters. All calculations were performed using the CrystalStructure[4] crystallographic software package except for refinement, which was performed using SHELXL2013.[5] The crystal data has been treated by the PLATON SQUEEZE for the analysis of solvent-containing voids. Crystal data and more information on X-ray data collection are summarized in Tables S2 and S3.

4. Synthesis

Synthesis of benzyldiphenylarsine by using phenyllithium as a nucleophile (Table 1, run 1). A butyl ether solution of phenyllithium (1.6 M, 2.62 mL, 4.20 mmol) was added dropwise into a THF (20 mL) dispersion of **1** (0.638 g, 7.00×10^{-4} mol) at 0 °C, and the mixture was stirred at room temperature for 2 h. To this solution, benzyl chloride (0.60 mL, 5.2 mmol) was added dropwise into the mixture at 0 °C, and the mixture was stirred overnight at room temperature. H_2O (20 mL) was added to the reaction mixture, and extracted with dichloromethane. Collected organic layer was dried with Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was recrystallized from ethanol to obtain a colorless solid (1.12 g, 3.50 mmol, 83%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.46-7.44 (m, 4H), 7.37-7.34 (m, 6H), 7.16 (t, J = 3.0 Hz, 2H), 7.07 (t, J = 2.6 Hz, 3H), 3.47 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.14, 130.72, 129.19, 128.76, 128.49, 128.41, 128.26, 35.19 ppm. HR FAB-MS (m/z): calculated for $C_{19}H_{17}As$ $[M]^+$; 320.0546, found; 320.0545.

Synthesis of benzyldiphenylarsine by using phenylmagnesium chloride as a nucleophile (Table 1, run 2). A THF solution of phenylmagnesium chloride (2.0 M, 2.10 mL, 4.20 mmol) was added dropwise into a THF (20 mL) dispersion of **1** (0.638 g, 7.00×10^{-4} mol) at 0 °C, and the mixture was stirred at 60 °C for 3.5 h. To this solution, benzyl chloride (0.60 mL, 5.2 mmol) was added dropwise into the mixture, and the mixture was stirred at 60 °C overnight. H_2O (20 mL) was added to the reaction mixture, and extracted with dichloromethane. Collected organic layer was dried with Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was recrystallized from ethanol to obtain a colorless solid (0.874 g, 2.71 mmol, 65%). The results of ^{1}H and ^{13}C NMR spectroscopies and HR FAB-MS analysis were corresponding to these of Table 1, run 1.

Synthesis of cyclohexylphenyl(phenylmethyl)arsine by using cyclohexylmagnesium chloride as a nucleophile (Table 1, run 3). A THF solution of cyclohexylmagnesium chloride (1.0 M, 4.20 mL, 4.20 mmol) was added dropwise into a THF (30 mL) dispersion of **1** (0.638 g, 7.00×10^{-4} mol) at 0 °C, and the mixture was stirred at 60 °C for 3.5 h. To this solution, benzyl chloride (0.60 mL, 5.2 mmol) was added dropwise into the mixture, and the mixture was stirred at 60 °C overnight. H_2O (20 mL) was added to the reaction mixture, and extracted with dichloromethane. Organic layer was dried with Na_2SO_4, filtrated, and collected under reduced pressure. The residue was purified through silica column chromatography to afford title compound (0.480 g, 1.47

mmol, 35%) as a colorless solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51-7.46 (m, 3H), 7.36 (d, J = 3.7 Hz, 2H), 7.21-7.19 (m, 3H), 7.16-7.14 (m, 2H), 3.61 (s, 2H), 2.38 (s, 11H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.55, 132.39, 130.59, 129.84, 128.90, 128.66, 127.36, 40.80 ppm.

Synthesis of triphenylarsine (Table 2, run 1-6). A butyl ether solution of phenyllithium (1.6 M, 2.62 mL, 4.20 mmol) was added dropwise into a THF (20 mL) dispersion of **1** (0.638 g, 7.00×10^{-4} mol) at 0 °C, and the mixture was stirred at room temperature for 2 h. To this solution, chloro-, bromo-, or iodobenzene (5.2 mmol) was added dropwise into the mixture at 0 °C or -78 °C, and the mixture was stirred overnight at room temperature. H_2O (20 mL) was added to the reaction mixture, and extracted with dichloromethane. Collected organic layer was dried with Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was recrystallized from methanol to obtain a colorless solid. Table 2 in the main text shows the reaction conditions and isolated yields of triphenylarsine. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49-7.45 (m, 9H), 7.45-7.40 (m, 6H) ppm.[6]

*Synthesis of 1,2-bis(diphenylarsino)ethane (**2**).* A butyl ether solution of phenyllithium (1.6 M, 2.62 mL, 4.20 mmol) was added dropwise into a THF (20 mL) dispersion of **1** (0.638 g, 7.00×10^{-4} mol) at 0 °C, and the mixture was stirred at room temperature for 2 h. To this solution, 1,2-dichloroethane (0.165 mL, 2.1 mmol) was added dropwise into the mixture at -78 °C, and the mixture was stirred overnight at room temperature. H_2O (20 mL) was added to the reaction mixture, and extracted with dichloromethane. Collected organic layer was dried with Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified through silica column chromatography to afford title compound (0.878 g, 1.79 mmol, 85%) as a colorless solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.28 (m, 20H), 2.11 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.12, 132.96, 128.54, 128.30, 23.96 ppm. HR FAB-MS (m/z): calculated for $C_{26}H_{24}As_2$ $[M]^+$; 486.0310, found; 486.0310.

*Synthesis of cis-1,2-vinylenebis(diphenylarsine) (**3**).* A butyl ether solution of phenyllithium (1.6 M, 2.62 mL, 4.20 mmol) was added dropwise into a THF (20 mL) dispersion of **1** (0.638 g, 7.00×10^{-4} mol) at 0 °C, and the mixture was stirred at room temperature for 2 h. To this solution, *cis*-1,2-dichloroethylene (0.159 mL, 2.1 mmol) was added dropwise into the mixture at -78 °C, and the mixture was stirred overnight at room temperature. H_2O (20 mL) was added to the reaction mixture, and extracted with

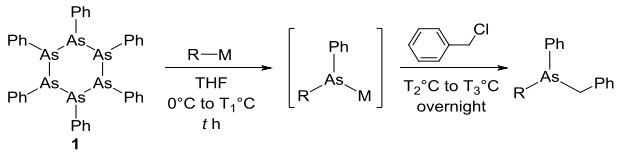
dichloromethane. Collected organic layer was dried with Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified through silica column chromatography to afford title compound (0.79 g, 1.64 mmol, 78%) as a colorless solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (s, 2H), 7.40-7.37 (m, 8H), 7.29-7.26 (m, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.97, 140.85, 133.09, 128.61, 128.26 ppm. HR FAB-MS (m/z): calculated for $C_{26}H_{22}As_2$ $[M]^+$; 484.0153, found; 484.0154.

*Synthesis of 1,2-bis((diphenylarsino)methyl)benzene (**4**).* A butyl ether solution of phenyllithium (1.6 M, 2.62 mL, 4.20 mmol) was added dropwise into a THF (20 mL) dispersion of **1** (0.638 g, 7.00×10^{-4} mol) at 0 °C, and the mixture was stirred at room temperature for 2 h. To this solution, a THF solution of *α*,*α*'-dichloro-*o*-xylene (0.367 g, 2.1 mmol) was added dropwise into the mixture at 0 °C, and the mixture was stirred overnight at room temperature. H_2O (20 mL) was added to the reaction mixture, and extracted with dichloromethane. Collected organic layer was dried with Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was recrystallized from ethanol to obtain a colorless solid (0.770 g, 1.37 mmol, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.28 (m, 20H), 3.22 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.42, 136.27, 133.21, 129.97, 128.48, 128.39, 125.68, 32.99 ppm. HR FAB-MS (m/z): calculated for $C_{32}H_{28}As_2$ $[M]^+$; 562.0623, found; 562.0620.

*Synthesis of **4**–$PtCl_2$.* A toluene (10 ml) solution of **4** (58 mg, 0.103 mmol) and *cis*-$PtCl_2(PhCN)_2$ (48.6 mg, 1.03 mmol) was stirred at 85 °C under N_2. The solvent was removed, and the title compound was obtained as a colorless solid (81.1 mg, 9.79×10^{-5} mol, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 5.4 Hz, 8H) , 7.52-7.43 (m, 12H), 6.93-6.91 (m, 2H), 6.31 (m, 2H), 3.89 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.51, 131.67, 130.86, 130.57, 128.85, 127.38, 34.15 ppm.

5. Optimization of reaction conditions in Table 1

Table S1. Investigation of the reaction condition described in Table 1



run	R	M	conditions				yield[a] (%)
			T_1 (°C)	T_2 (°C)	T_3 (°C)	*t* (h)	
1	Ph	Li	r.t.	0	r.t.	2	83
2	Ph	MgCl	r.t.	0	r.t.	2	< 1
3	Ph	MgCl	40	40	40	0.5	3
4	Ph	MgCl	40	40	40	3.5	20
5	Ph	MgCl	60	60	60	3.5	65
6	Cy	MgCl	40	40	40	0.5	< 1[b]
7	Cy	MgCl	40	40	40	3.5	5[b]
8	Cy	MgCl	60	60	60	3.5	37[b]

[a]Isolated yield. [b]Obtained as racemic mixture.

5. NMR spectra

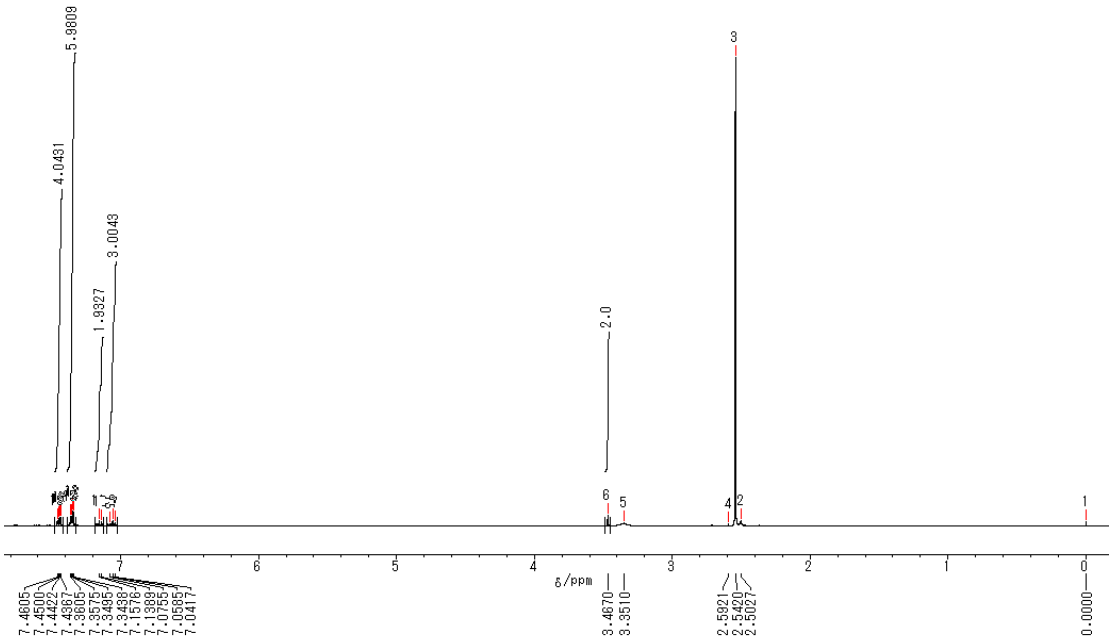


Figure S1. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of benzyldiphenylarsine.

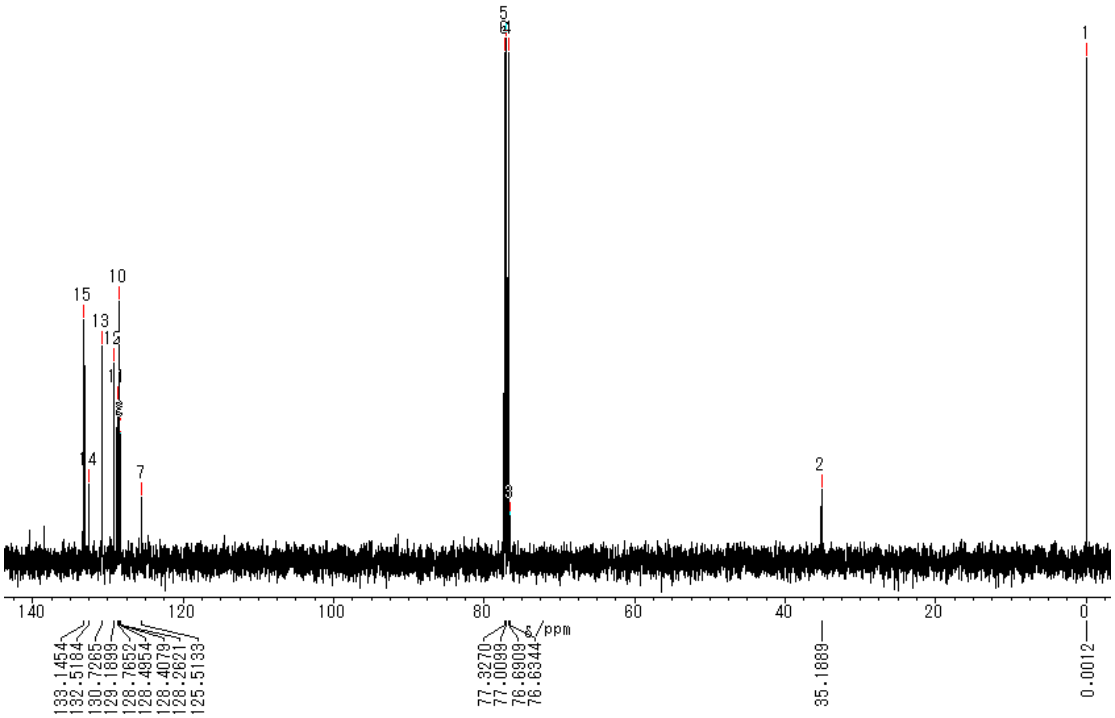


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of benzyldiphenylarsine.

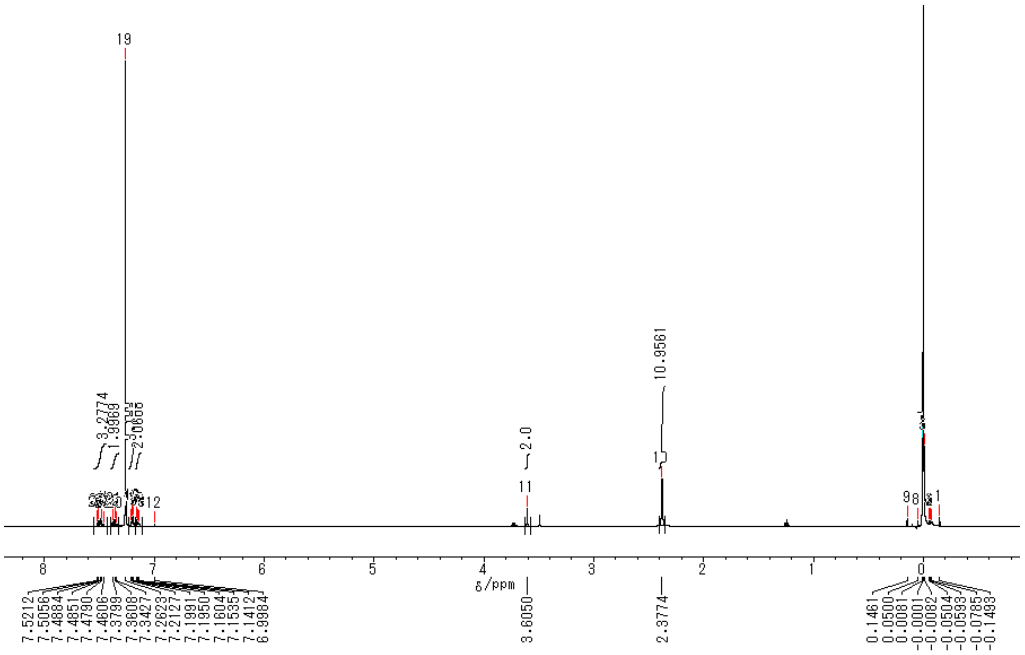


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of cyclohexylphenyl(phenylmethyl)arsine.

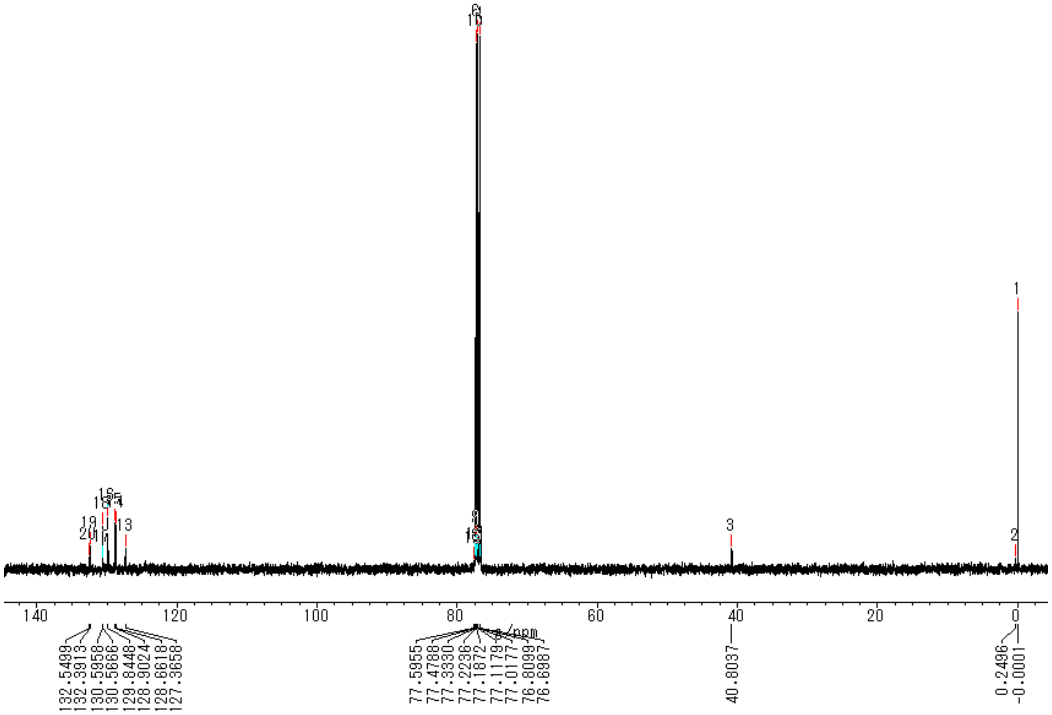


Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of cyclohexylphenyl(phenylmethyl)arsine.

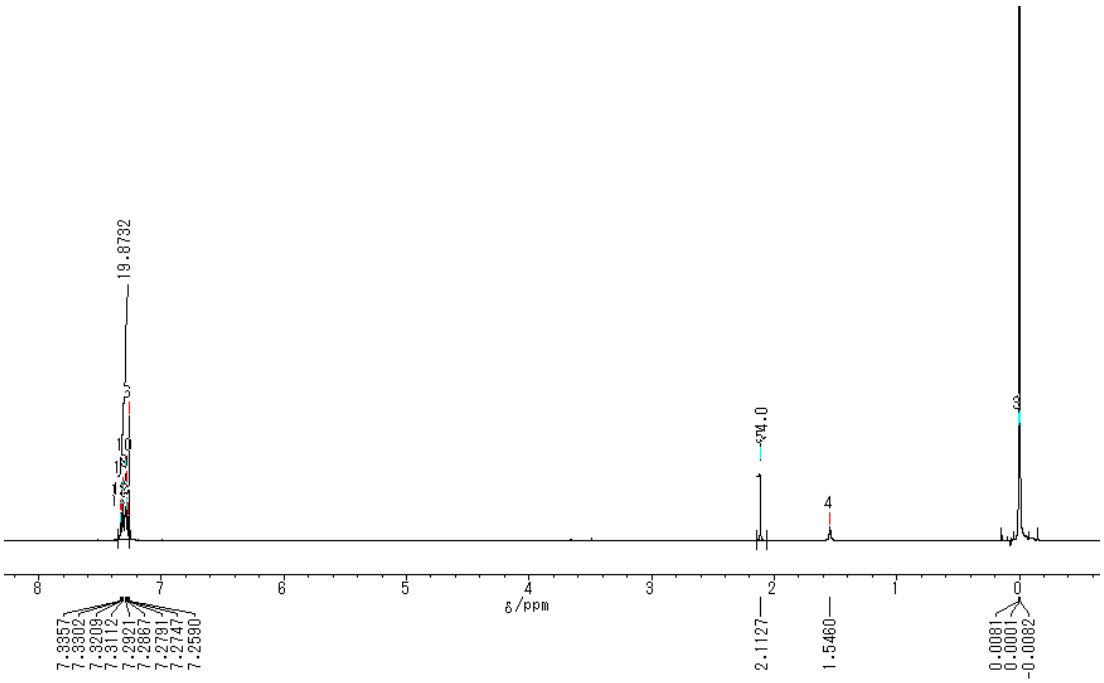


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**.

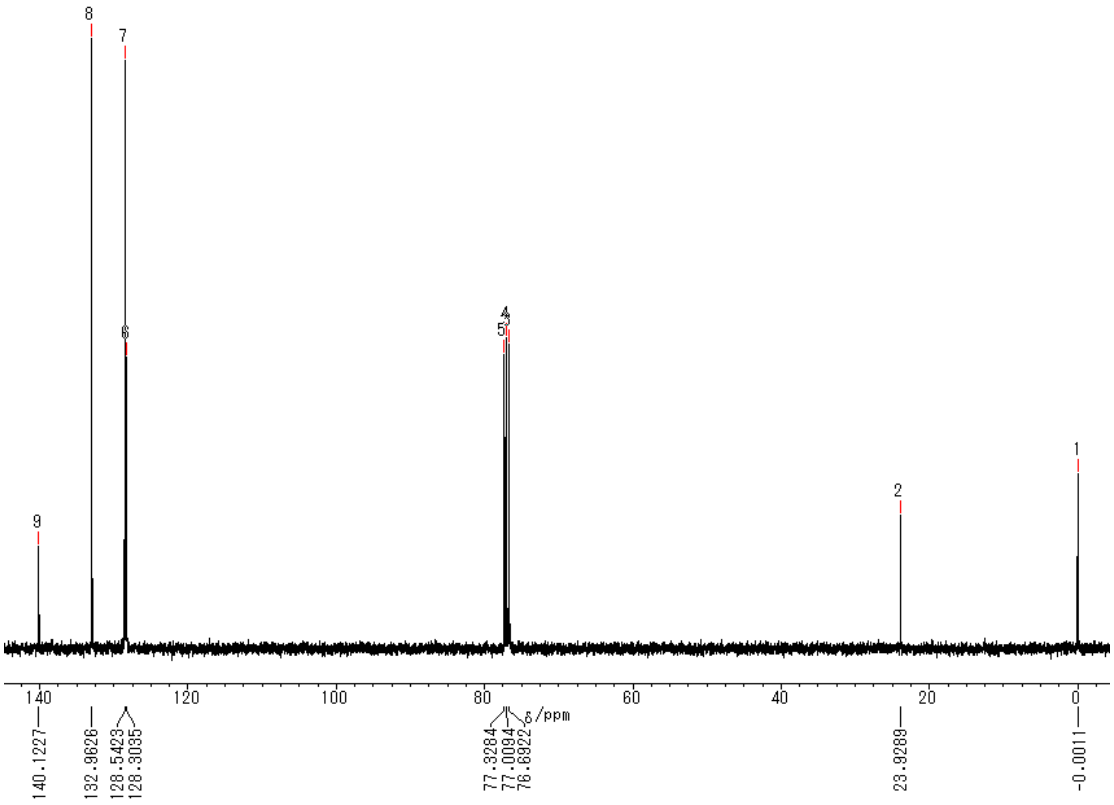


Figure S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2**.

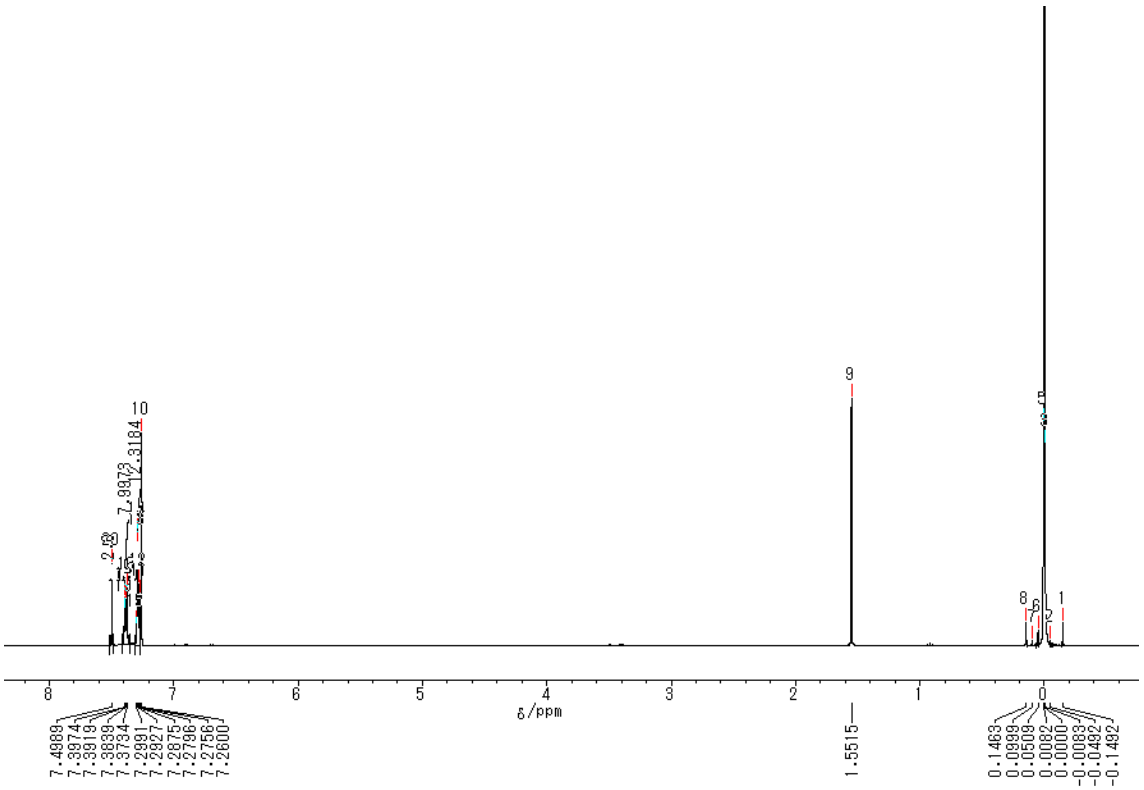


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

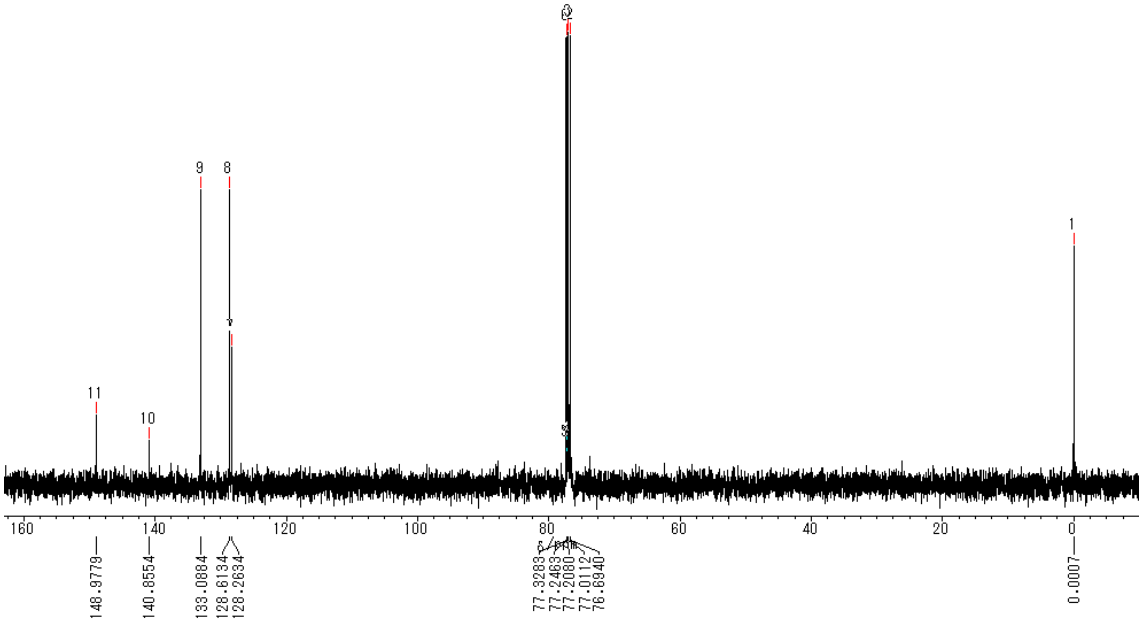


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3**.

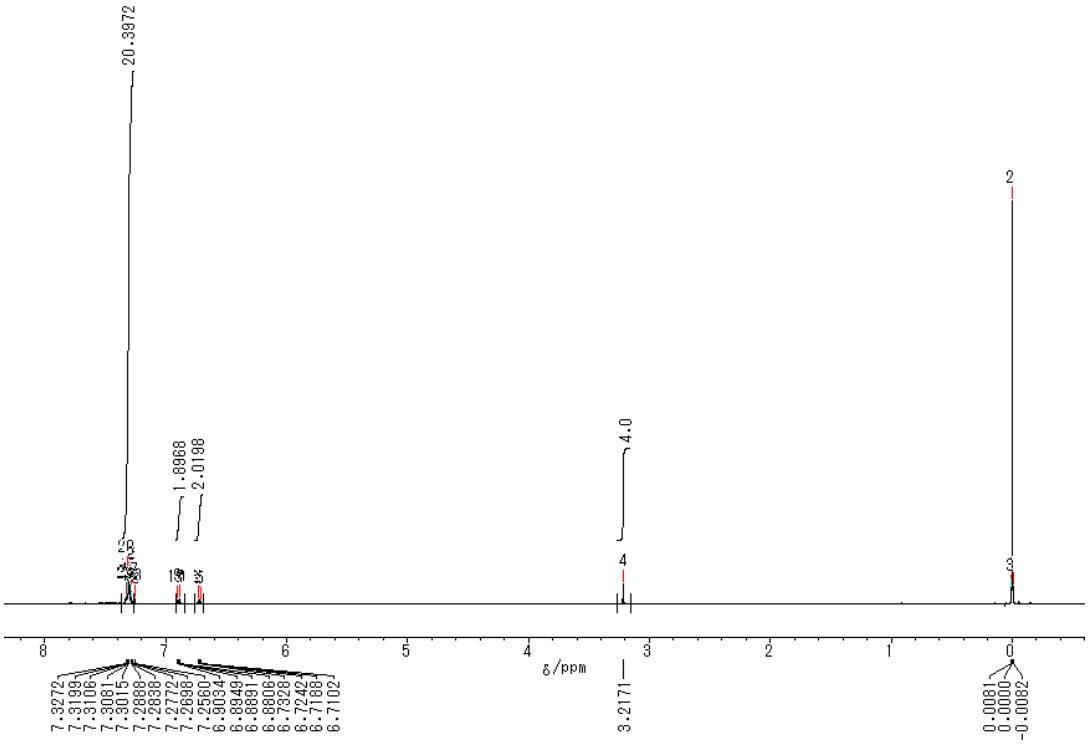


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**.

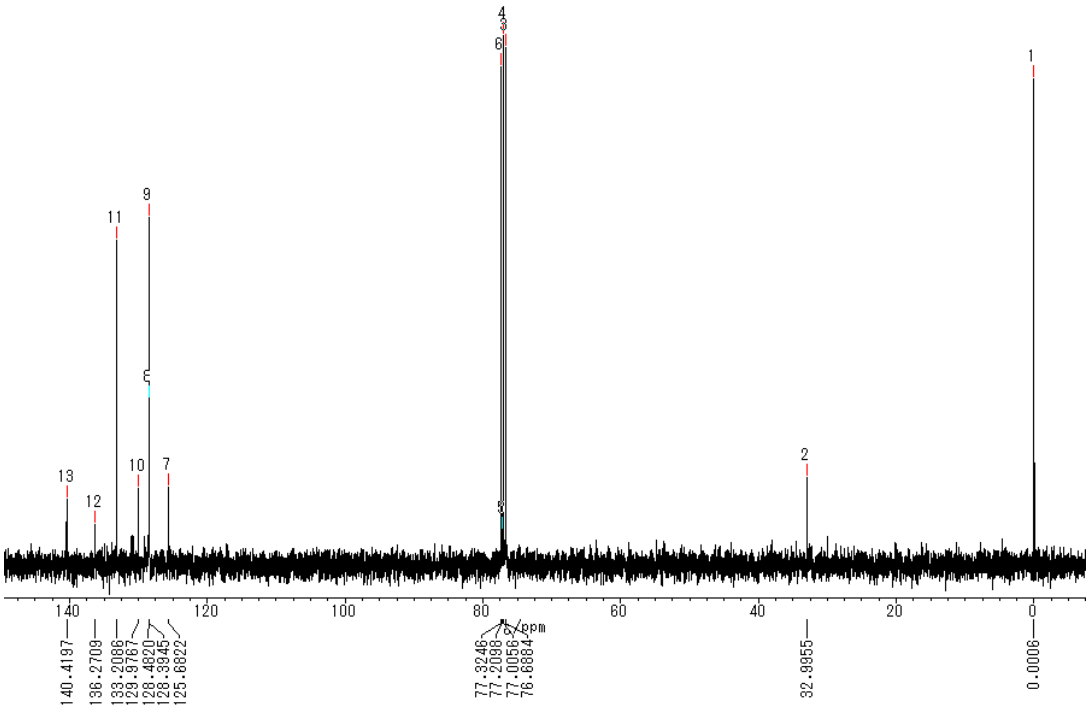


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4**.

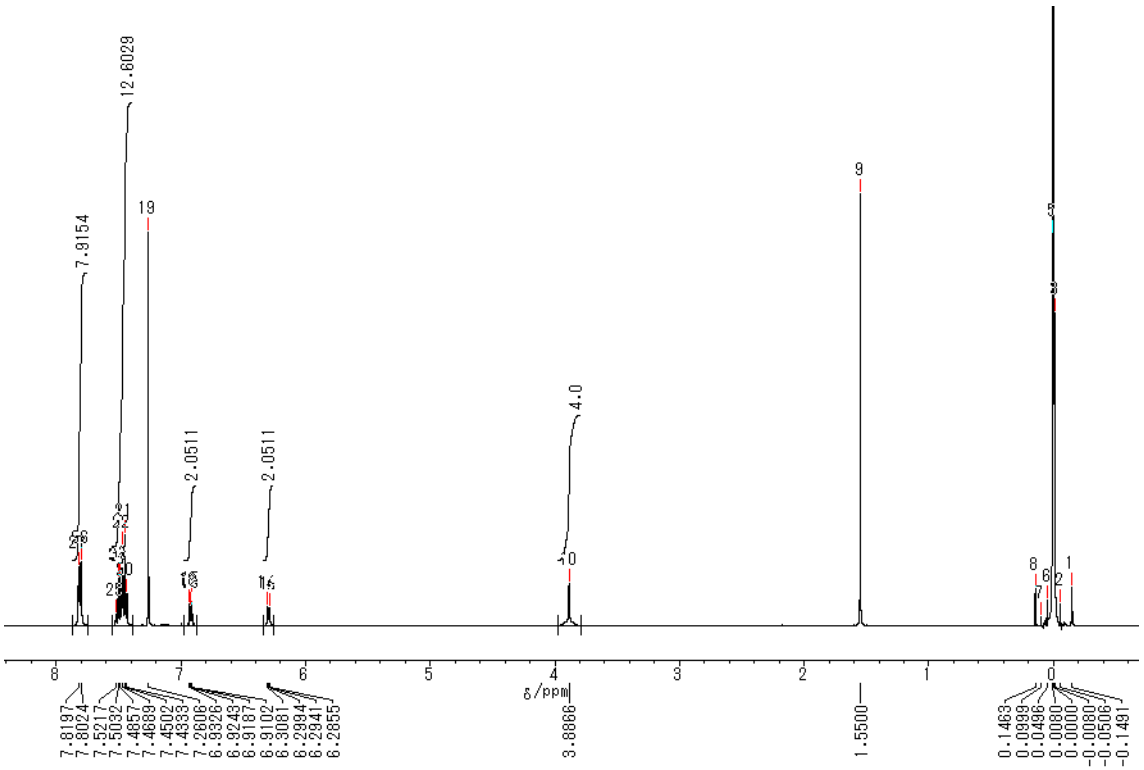


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**−$PtCl_2$.

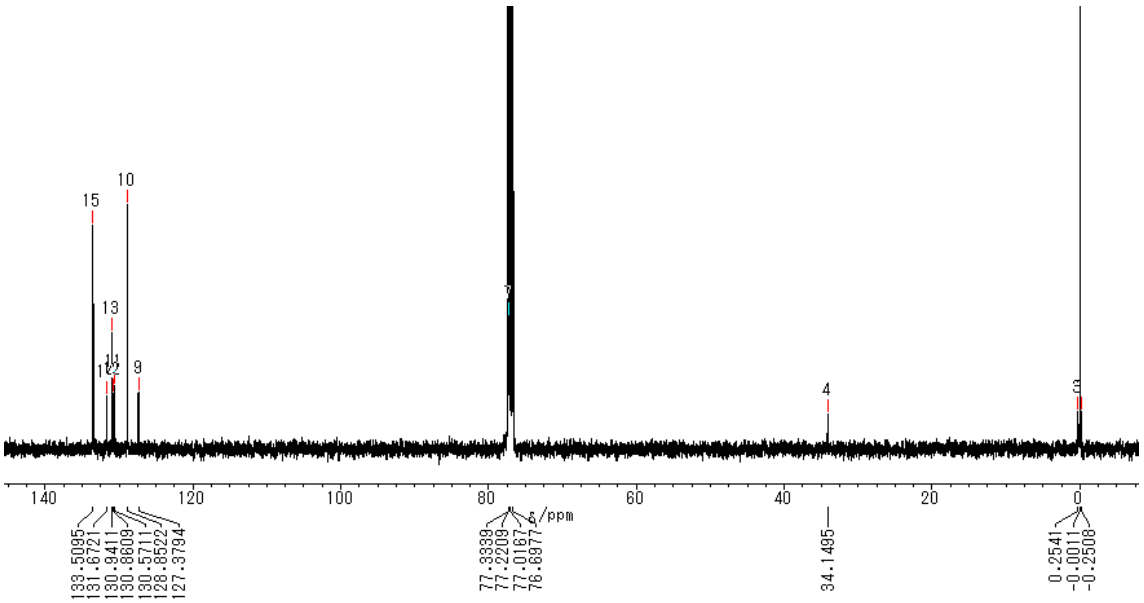


Figure S12. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4**−$PtCl_2$.

6. Crystallographic data

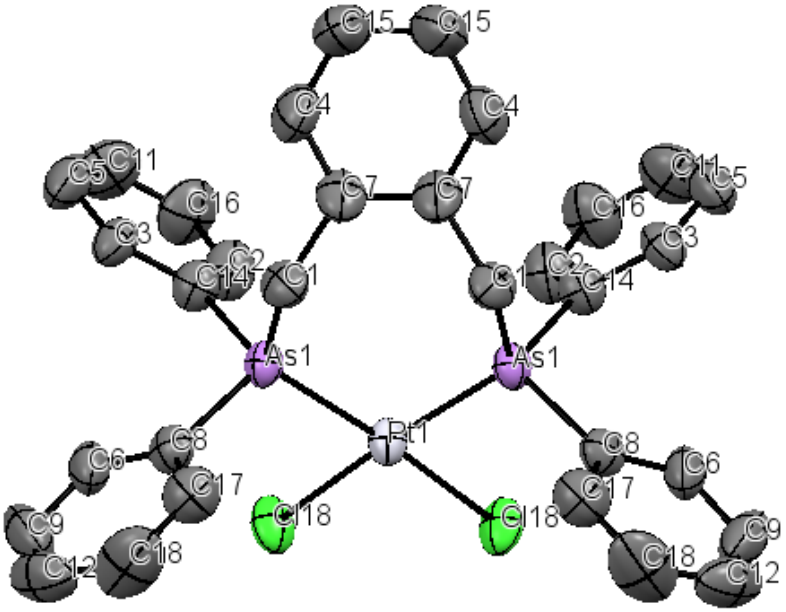
Table S2. Crystallographic Data of **4**−$PtCl_2$

	4−$PtCl_2$
Crystal data	
Empirical Formula	C32H28As2Cl2Pt
Formula Weight	828.41
Crystal Dimension, mm^3	0.200 × 0.200 × 0.200
Crystal System	orthorhombic
Space Group	Cmc21 (#36)
a, Å	19.081(12)
b, Å	22.404(14)
c, Å	8.210(5)
α, deg	
β, deg	
γ, deg	
Volume, $Å^3$	3510(4)
D_{calcd}, g cm^{-3}	1.568
Z	4
F(000)	1592.00
Data Collection	
Temperature, deg	0.0
2θmax, deg	54.5
Tmin/Tmax	0.184 – 0.300
Refinement	
No. of Observed Data	3946
No. of Parameters	169
R1[a], wR2[b]	0.0547, 0.1430
Goodness of Fit Indictor	1.093

[a] $R1 = \Sigma \mid |Fo| - |Fc| \mid / \Sigma |Fo|$ [b] $wR2 = [\ \Sigma\ w ((Fo^2-Fc^2)^2 / \Sigma\ w (Fo^2)^2\ ]^{1/2}$ $w = [\ \sigma^2(Fo^2)\ ]^{-1}$

CCDC # 1453192 (**4**−$PtCl_2$)

Table S3. Selected angles (deg) and distance (Å) of **4**−$PtCl_2$.



distances (Å)	
Pt(1)-Cl(18)	2.331(4)
Pt(1)-As(1)	2.3477(18)
As(1)-C(14)	1.924(17)
As(1)-C(8)	1.946(16)
As(1)-C(1)	1.940(16)
C(1)-C(7)	1.53(3)

angles (°)	
Cl(18)-Pt(1)-Cl(18)	89.96(15)
Cl(18)-Pt(1)-As(1)	85.31(11)
	175.27(11)
As(1)-Pt(1)-As(1)	99.42(7)
Pt(1)-As(1)-C(1)	120.9(5)
As(1)-C(1)-C(7)	115.4(11)
C(1)-C(7)-C(7)	121.5(17)

The crystallographic data shows that the structure of **4**−$PtCl_2$ contains large solvent-accessible voids. Actually, some solvent molecules were observed in the course of analysis, but their structures could not be determined completely owing to their strong disorder. Thus the crystal data has been treated by the PLATON SQUEEZE for the analysis of solvent-containing voids. The result is given for the discussion because the data was converged well and final R1 value has been lowered sufficiently.[7]

7. References

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