Supporting Information

Facile Fullerene Modification: $FeCl_3$-mediated Quantitative Conversion of C_{60} to Polyarylated Fullerenes Containing Pentaaryl(chloro)[60]fullerenes

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1. General methods and materials

All reactions were carried out under argon or nitrogen atmosphere. Analytical gradient reversed-phase HPLC was performed on an Agilent 1200 series instrument equipped with an ODS column (YMC-Pack ODS-AM, 5 micron, 4.6 x 150 mm). All runs used linear gradients of methanol (solvent A) and toluene (solvent B). The gradient ran from 25% B up to 55% B over 25 min. Flow rate was 1.0 mL/min and routine UV detection was performed at 290 nm. All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 400 NMR spectrometer system. NMR spectra are reported in part per million from internal tetramethylsilane (δ 0.00 ppm) for ^{1}H NMR and from $CDCl_3$ (δ 77.00 ppm) for ^{13}C NMR. Mass spectra were measured with Agilent1100LC/MS (APPI, Negative mode) equipped on an ODS column (YMC-Pack ODS-AM). Preparative HPLC was performed on a Buckyprep column (Nacalai Tesque Inc., 20 mm x 250 mm) using toluene/methanol (7/3) as eluent (flow rate: 10 mL/min, detected at 290 nm with an UV spectrometer, Shimadzu SPD-6AV).

Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Sigma-Aldrich Co., Wako Pure Chemical Industries, or other commercial suppliers and used after appropriate purification. [60]Fullerene (99.5%) was purchased from Frontier Carbon Corporation. Iron(III)chloride was purchased from Wako Pure Chemical Industries and used as received.

2. Synthesis of 1

To a mixture of C_{60} (501 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added chlorobenzene (25 mL) at room temperature. After stirred for 2 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta-adduct **1** mainly, and small amounts of polyarylated products as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S1. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave the title compound $C_{60}(C_6H_4\text{-Cl-4})_5Cl$ as orange powder (228 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02-7.08 (m, 4H, C_6H_4), 7.23 (d, J = 8.8 Hz, 4H, C_6H_4), 7.30 (d, J = 8.8 Hz, 4H, C_6H_4), 7.40-7.49 (m, 4H, C_6H_4), 7.61-7.80 (m, 4H, C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 57.28 (2C, sp^3-C_{60}), 59.96 (2C, sp^3-C_{60}), 62.65 (1C, sp^3-C_{60}), 75.85(1C, C(sp^3-C_{60})-Cl), 128.06 (1C, C_6H_4Cl), 128.94 (4C, C_6H_4Cl), 129.00 (4C, C_6H_4Cl), 129.36 (4C, C_6H_4Cl), 129.49 (4C, C_6H_4Cl), 130.85 (2C, C_6H_4Cl), 133.90 (2C, C_6H_4Cl), 134.33 (2C, C_6H_4Cl), 134.36 (2C, C_6H_4Cl), 134.99 (2C, C_6H_4Cl), 136.50 (2C, C_6H_4Cl), 141.13 (2C), 142.58 (2C), 142.62 (2C), 142.86 (1C, C_6H_4Cl), 143.01 (2C), 143.34 (2C), 143.36 (2C), 144.12 (2C), 144.18 (2C), 144.28 (2C), 144.44 (2C), 144.56 (2C), 144.71 (2C), 145.75 (2C), 146.95 (2C+1C), 147.09 (2C), 148.00 (1C), 148.07 (2C), 148.43 (2C), 148.53 (2C), 148.54 (6C), 148.57 (2C), 149.41 (2C), 150.26 (2C), 153.19 (2C), 155.81 (2C); APPI-MS (-): calcd for $C_{90}H_{20}Cl_5$ [M-Cl]-), 1278.4; found, 1279.0; Anal. Calcd for $C_{90}H_{20}Cl_6$, C 82.28; H, 1.53. Found: C 81.90; H, 1.66.

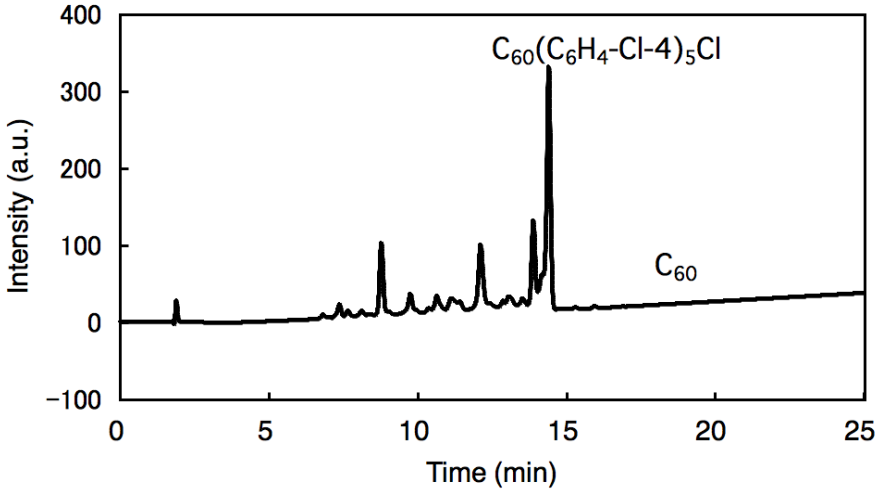

Figure S1. HPLC chart for the synthesis of **1**

<Alternative Synthetic Method using Solvent>

To a mixture of C_{60} (500mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by chlorobenzene (470 mg, 4.18 mmol) at room temperature. After stirred for 4 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired-penta adduct **1** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S2. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **1** as orange powder (265 mg, 29%).

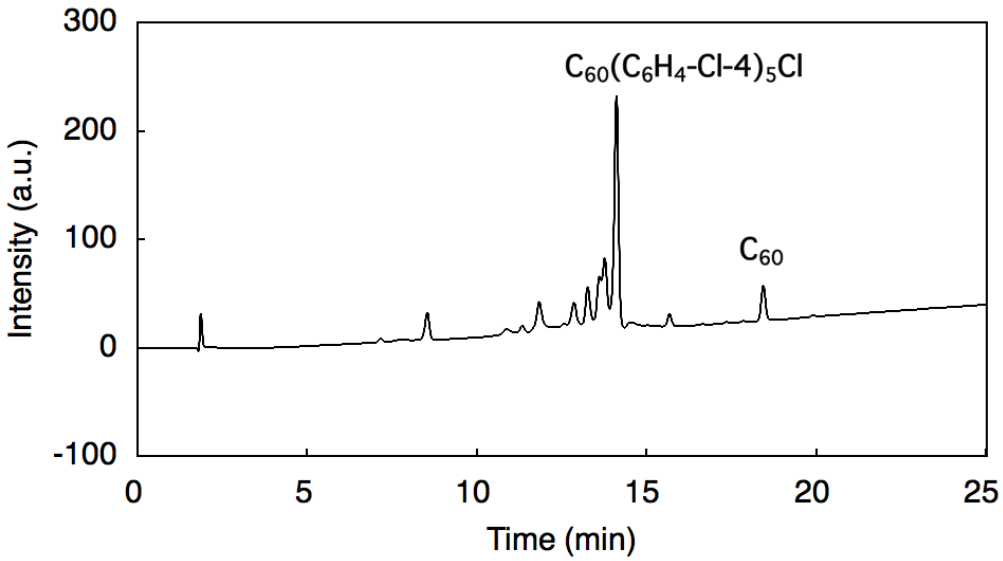

Figure S2. HPLC chart for the synthesis of **1** in 1,1,2,2-tetrachloroethane

3. Synthesis of 2

To a mixture of C_{60} (500mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by bromobenzene (650 mg, 4.14 mmol) at room temperature. After stirred for 6 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta adduct **2** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S3. Purification with HPLC (Buckyprep column, Nacalai

Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **2** as orange powder (245 mg, 23%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, J = 8.8 Hz, 2H, C_6H_4), 7.22 (d, J = 8.8 Hz, 2H, C_6H_4), 7.39 (s, 8H, C_6H_4), 7.44 (d, J = 8.4 Hz, 4H, C_6H_4), 7.70 (d, J = 8.4 Hz, 4H, C_6H_4); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 57.53 (2C, sp^3-C_{60}), 60.18 (2C, sp^3-C_{60}), 62.88 (1C, sp^3-C_{60}), 75.78 (1C, C(sp^3-C_{60})-Cl), 129.83 (4C, C_6H_4Br), 129.92 (4C, C_6H_4Br), 130.74 (2C, C_6H_4Br), 131.19 (2C, C_6H_4Br), 131.29 (2C, C_6H_4Br), 132.04 (4C, C_6H_4Br), 132.10 (4C, C_6H_4Br), 134.14 (4C, C_6H_4Br), 135.54 (2C, C_6H_4Br), 137.32 (2C, C_6H_4Br), 142.65 (2C), 142.75 (2C), 142.93 (2C), 143.45 (2C), 143.48 (2C), 144.20 (2C), 144.26 (2C), 144.40 (2C), 144.52 (2C), 144.73 (2C), 144.84 (2C), 145.86 (2C), 147.10 (2C+1C), 147.23 (2C), 148.14 (1C), 148.33 (2C), 148.39 (2C), 148.57 (2C), 148.67 (6C), 148.71 (2C), 149.23 (2C), 150.40 (2C), 153.07 (2C), 155.90 (2C); APPI-MS (-): calcd for $C_{90}H_{20}Br_5$ [M-Cl]-), 1500.6; found, 1500.6; Anal. Calcd for $C_{90}H_{20}Br_5Cl$, C 70.37; H, 1.31. Found: C 70.36; H, 1.36.

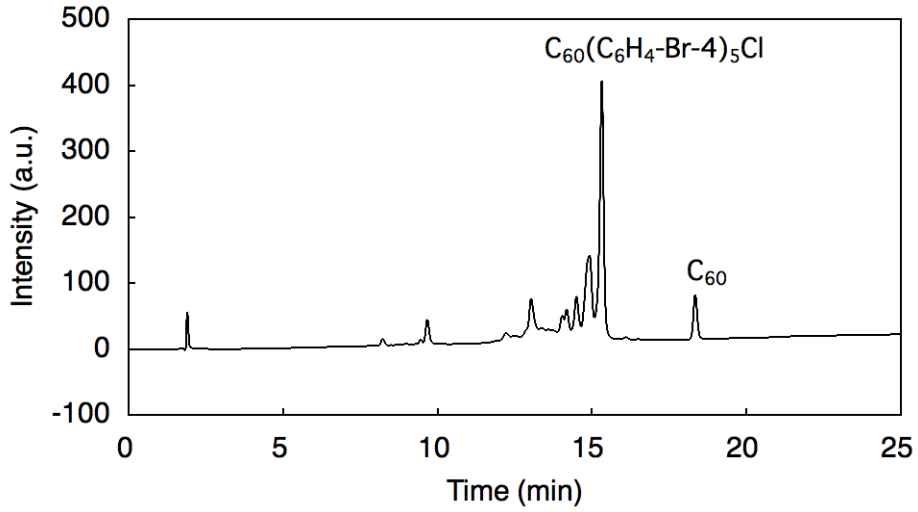

Figure S3. HPLC chart for the synthesis of **2** in 1,1,2,2-tetrachloroethane

4. Synthesis of 3

To a mixture of C_{60} (501 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by iodobenzene (850 mg, 4.17 mmol) at room temperature. After stirred for 4 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta adduct **3** mainly, and small amounts of polyarylated

products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S4. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **3** as orange powder (221 mg, 18%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (d, J = 8.8 Hz, 2H, C_6H_4), 7.26 (d, J = 8.8 Hz, 4H, C_6H_4), 7.42 (d, J = 8.8 Hz, 4H, C_6H_4) , 7.54-7.60 (m, 8H, C_6H_4), 7.64 (d, J = 8.8 Hz, 4H, C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 57.63 (2C, sp^3-C_{60}), 60.27 (2C, sp^3-C_{60}), 62.99 (1C, sp^3-C_{60}), 75.67(1C, C(sp^3-C_{60})-Cl), 130.01 (4C, C_6H_4I), 130.10 (4C, C_6H_4I), 131.52 (2C, C_6H_4I), 136.56 (2C, C_6H_4I), 137.11 (2C, C_6H_4I), 137.98 (4C, C_6H_4I), 138.04 (4C, C_6H_4I), 142.62 (2C), 142.67 (2C), 142.74 (2C), 142.92 (8C, C_6H_4I), 143.14 (2C), 143.42 (2C), 144.17 (2C), 144.25 (2C), 144.37 (2C), 144.51 (2C), 144.72 (2C), 144.83 (2C), 145.82 (2C), 147.10 (2C+1C), 147.23 (2C), 147.73 (1C), 148.20 (2C), 148.38 (2C), 148.55 (2C), 148.66 (6C), 148.70 (2C), 149.44 (2C), 150.37 (2C), 153.39 (2C), 155.85 (2C); APPI-MS (-): calcd for $C_{90}H_{20}I_5$ [M-Cl]-), 1735.6; found, 1734.6; Anal. Calcd for $C_{90}H_{20}I_5Cl$, C 61.03; H, 1.14. Found: C 61.02; H, 0.65.

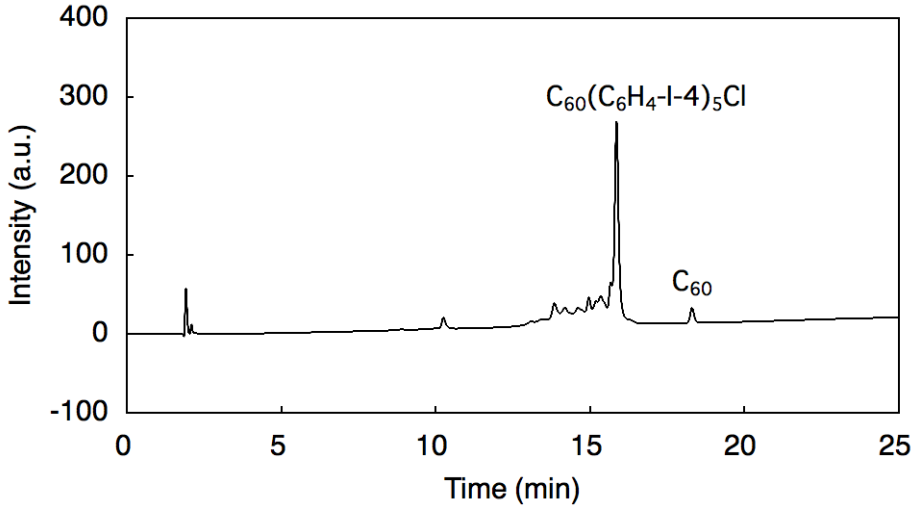

Figure S4. HPLC chart for the synthesis of **3** in 1,1,2,2-tetrachloroethane

5. Synthesis of 4

To a mixture of C_{60} (502 mg, 0.70 mmol) and iron(III) chloride (1.14 g, 7.03 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by fluorobenzene (402 mg, 4.18 mmol) at room temperature. After stirred for 4 hours, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude

product contained the desired penta adduct **4** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S4. Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **4** as orange powder (103 mg, 12%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80-6.85 (m, 2H, C_6H_4), 6.99-7.09 (m, 8H, C_6H_4), 7.13-7.17 (m, 2H, C_6H_4), 7.56-7.59 (m, 4H, C_6H_4), 7.87-7.90 (m, 4H, C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 57.39 (2C, sp^3-C_{60}), 60.06 (2C, sp^3-C_{60}), 62.78 (1C, sp^3-C_{60}), 77.17(1C, C(sp^3-C_{60})-Cl), 115.04 (2C, C_6H_4F), 115.72 (4C, C_6H_4F), 115.95 (4C, C_6H_4F), 129.93 (4C, C_6H_4F), 130.05 (4C, C_6H_4F), 130.09 (4C, C_6H_4F), 131.40 (2C, C_6H_4F), 131.48 (2C, C_6H_4F), 132.64 (2C, C_6H_4F), 134.22 (2C, C_6H_4F), 142.91 (4C), 143.28 (2C), 143.62 (2C), 143.70 (2C), 144.20 (2C), 144.26 (2C), 144.41 (2C), 144.51 (2C), 144.82 (2C), 144.95 (2C), 146.16 (2C), 147.15 (2C), 147.28 (2C+1C), 147.76 (2C), 148.15 (1C), 148.23 (2C), 148.40 (2C), 148.61 (2C), 148.69 (6C), 148.72 (2C), 149.87 (2C), 150.68 (2C), 153.42 (2C), 156.28 (2C); APPI-MS (-): calcd for $C_{90}H_{20}F_5$ [M-Cl]-), 1196.1; found, 1196.1; Anal. Calcd for $C_{90}H_{20}F_5Cl$, C 87.77; H, 1.64. Found: C 88.07; H, 1.17.

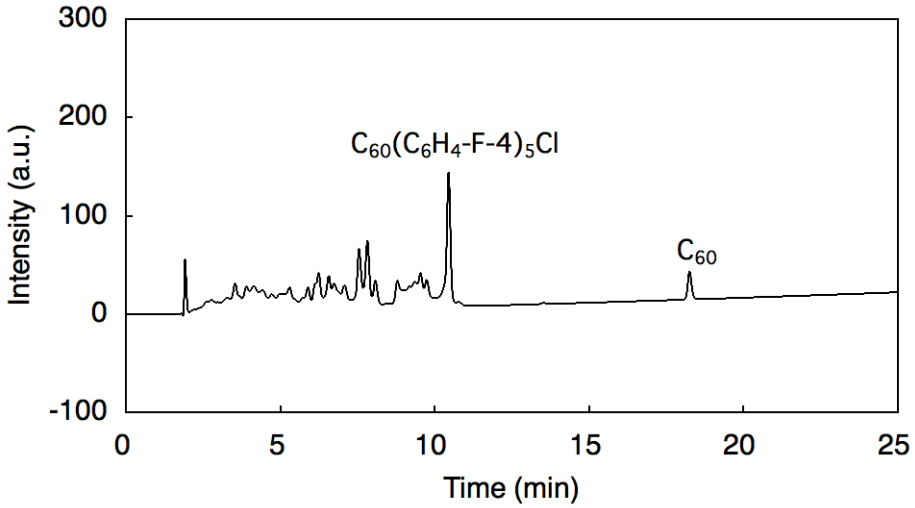

Figure S5. HPLC chart for the synthesis of **4** in 1,1,2,2-tetrachloroethane

6. The use of non-halogenated arene (toluene)

To a mixture of C_{60} (503 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added toluene (25 mL) at room temperature. After stirred for 8 hours, the reaction mixture was analyzed by HPLC (YMC-Pack ODS-AM). As shown in Figure S6, a complex mixture containing C60 (ca. 30%) was obtained.

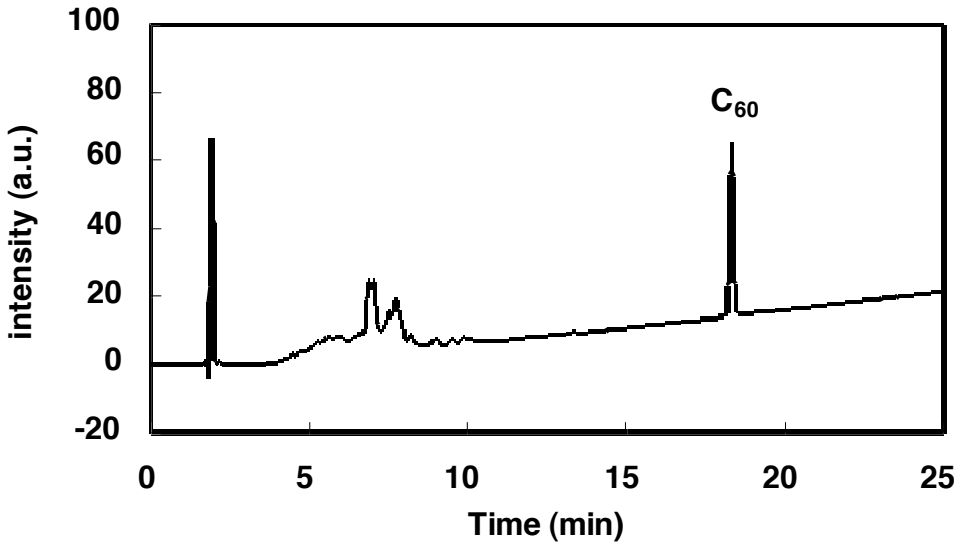

Figure S6. HPLC chart for the reaction with toluene

Table 1. Crystal and refinement data for **1**.

Empirical formula	$C_{60}(C_6H_4Cl)_5Cl \cdot C_7H_8$
Formula weight	1405.89
Temperature	293(2) K
Radiation	Mo$K\alpha$ (λ = 0.71073 Å)
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 14.5009(18) Å
	b = 16.212(2) Å
	c = 14.5134(18) Å
	α = 97.198(2) °
	β = 99.991(2) °
	γ = 86.541(2) °
V (Å^3)	3331.0(7)
Z	2
Density ρ calc (g·cm^{-3})	1.402
Absorption coefficient (mm^{-1})	0.312
F(000)	1424
Crystal dimensions (mm^3)	0.3 · 0.25 · 0.2
range for data collection	4.08 ≤ θ ≤ 26.37°
Index ranges	-13 ≤ h ≤ 18
	-17 ≤ k ≤ 20
	-18 ≤ l ≤ 15
Reflections collected / unique	19536 / 13280 (R_{int} = 0.0356)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6183 / 0 / 288
Goodness-of-fit on F^2	1.102
Final R indices [I>2σ(I)][a), b)]	R1 = 0.1051, wR2 = 0.2953
R indices (all data)[a), b)]	R1 = 0.1994, wR2 = 0.3703
Largest diff. peak and hole (e·Å^3)	1.099 / -0.548

[a)] $\Sigma(||Fo| - |Fc||)/\Sigma|Fo|$

[b)] $wR2 = [\Sigma\omega(|Fo^2| - |Fc^2|)^2 / \Sigma(\omega Fo^4)]^{1/2}$