Supporting Information

Regio- and Stereo-selective Intermolecular [2+2] Cycloaddition of Allenol Esters with C\textsubscript{60} Leading to Alkylidenecyclobutane-annulated Fullerenes

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1. General information

$^1$H NMR spectra were recorded using JEOL ECP-500 (500 MHz) or JEOL ECS-400 (400 MHz) spectrometers in CDCl$_3$ and are referenced at 7.26 ppm for CHCl$_3$. $^{13}$C NMR spectra were recorded using JEOL ECP-500 (125 MHz) or JEOL ECS-400 (100 MHz) spectrometers in CDCl$_3$ and are referenced at 77.16 ppm for CHCl$_3$. Chemical shifts are reported in parts per million (δ). Splitting patterns are indicated as follows: br = broad, s = singlet, d = doublet, t = triplet, m = multiplet. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. High-resolution mass spectra (HRMS) were recorded with a Thermo Fisher Scientific LTQ Orbitrap XL and a JEOL MS-700 spectrometer. The products were purified by flash column chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 mm)). HPLC analysis have been carried out on HITACHI Elite LaChrom L-2000 HPLC system equipped with a YMC-Pack ODS-AM column (150 x 4.6 mm I.D.(s-5µm,12 nm)) with detection at 290 nm. A mixture of toluene/MeOH (gradient 0 min 30% toluene, 15 min 40% toluene, 30 min 63% toluene) was used as eluent at 0.8 mL/min flow rate. All reagents were purchased and used without further purification.

2. General method for preparation of propargyl pivalate 1

**Typical Procedure for Preparation of Propargyl Alcohol**

To a solution of alkyne (39 mmol) in anhydrous THF (50 mL) at −78 °C under N$_2$ atmosphere was added n-BuLi (1.6 M solution in hexanes, 20.6 mL, 33 mmol). The reaction was stirred at this temperature for 20 min, and then at room temperature for 1 h. After cooling to −78 °C, aldehyde (30 mmol) was added to the mixture. The reaction mixture was warmed up to room temperature gradually, and was stirred for an additional hour before quenched with aqueous NH$_4$Cl. The mixture was extracted with EtOAc (3 x 20 mL), and the combined organic phases were washed with water and brine, dried over anhydrous MgSO$_4$. After filtration of MgSO$_4$, the filtrate was concentrated under reduced pressure. Then, the residue was purified by column chromatography on SiO$_2$ (hexane/EtOAc) to give the desired propargyl alcohol as oil in quantitative yield.

**Typical Procedure for Preparation of Propargyl Pivalate 1**

To a solution of a propargyl alcohol (1 equiv), Et$_3$N (10 equiv) and DMAP (0.05 equiv) in anhydrous CH$_2$Cl$_2$ (0.5 M) was added trimethylacetyl chloride (1.2 equiv) at 0 °C. The mixture was stirred at room temperature for 2 h. After the propargyl alcohol was consumed, the mixture was quenched with methanol (1 mL/1 mmol), and the resulting solution was stirred at room temperature for 1 h. The reaction mixture was diluted with diethyl ether (50 mL) and washed with water (2 x 50 mL), 1 M aqueous HCl (2 x 50 mL), 1 M aqueous NaOH (20 mL) and water (50 mL). The combined organic phase was dried over anhydrous MgSO$_4$ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on SiO$_2$ (hexane/EtOAc) to give propargyl pivalate 1. Compound 1a, 1c, 1e, 1g, and 4 are known in literature.
H NMR (400 MHz, CDCl$_3$) δ 0.90 (t, $J = 7.6$ Hz, 3H), 1.20 (s, 9H), 1.36-1.45 (m, 2H), 1.48-1.55 (m, 2H), 2.25 (dt, $J = 2.4$, 6.8 Hz, 2H), 6.43 (s, 1H), 7.33-7.38 (m, 3H), 7.48-7.50 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.7, 18.6, 22.0, 27.1, 30.6, 38.8, 65.9, 76.8, 88.0, 127.4, 128.5, 128.6, 138.1, 177.4.

Compound 1a is known in literature.$^1$

H NMR (400 MHz, CDCl$_3$) δ 0.91 (t, $J = 7.2$ Hz, 3H), 1.19 (s, 9H), 1.36-1.45 (m, 2H), 1.48-1.55 (m, 2H), 2.25 (dt, $J = 2.0$, 6.8 Hz, 2H), 3.80 (s, 3H), 6.38 (s, 1H), 6.88 (d, $J = 8.8$ Hz, 2H), 7.42 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.7, 14.3, 18.6, 22.0, 27.1, 30.6, 38.8, 55.4, 65.6, 87.8, 113.9, 129.0, 130.4, 159.8, 177.4; HRMS (EI) m/z Calcd for C$_{19}$H$_{26}$O$_3$ [M$^+$]: 302.1882, found: 302.1880.

Compound 1c is known in literature.$^2$

H NMR (500 MHz, CDCl$_3$) δ 0.90 (t, $J = 7.5$ Hz, 3H), 1.20 (s, 9H), 1.38-1.42 (m, 2H), 1.48-1.52 (m, 2H), 2.25 (dt, $J = 2.0$, 7.5 Hz, 2H), 6.39 (t, $J = 2.0$ Hz, 1H), 7.32 (d, $J = 6.8$ Hz, 2H), 7.43 (d, $J = 7.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 13.6, 18.5, 22.0, 27.0, 30.5, 38.8, 65.2, 76.6, 88.4, 128.7, 128.8, 134.4, 136.7, 177.2.

H NMR (400 MHz, CDCl$_3$) δ 0.91 (t, $J = 6.8$ Hz, 3H), 1.20 (s, 9H), 1.40-1.46 (m, 2H), 1.49-1.55 (m, 2H), 2.27 (dt, $J = 2.0$, 7.2 Hz, 2H), 6.65 (s, 1H), 6.95 (t, $J = 3.6$ Hz, 1H), 7.18 (d, $J = 3.6$ Hz, 1H), 7.28 (d, $J = 5.2$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.7, 18.5, 22.0, 27.0, 30.5, 38.8, 61.3, 76.50, 87.61, 126.5, 126.6, 126.9, 141.3, 177.2; HRMS (EI) m/z Calcd for C$_{18}$H$_{22}$O$_2$S [M$^+$]: 278.1341, found: 278.1344.

H NMR (400 MHz, CDCl$_3$) δ 1.22 (s, 9H), 2.61 (d, $J = 2.0$ Hz, 1H), 6.42 (d, $J = 2.4$ Hz, 1H),
7.34-7.38 (m, 3 H), 7.50-7.52 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 27.1, 38.8, 65.1, 75.2, 80.5, 127.4, 128.7, 128.9, 136.9, 177.2.

**Compound 1e** is known in literature.$^3$

![Image of compound 1f]

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.93 (t, $J = 7.6$ Hz, 3H), 1.23 (s, 9H), 1.39-1.42 (m, 2H), 1.45-1.52 (m, 2H), 1.83-1.88 (m, 2H), 5.57 (t, $J = 6.4$ Hz), 7.27-7.32 (m, 3H), 7.42-7.47 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.1, 22.4, 27.2, 34.7, 38.9, 64.4, 77.4, 84.9, 87.1, 122.7, 128.3, 128.5, 132.0, 177.6; HRMS (El) m/z Calcd for C$_{18}$H$_{24}$O$_2$ [M$^+$]: 272.1776, found: 272.1767.

![Image of compound 1g]

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.24 (s, 9H), 6.68 (s, 1H), 7.30-7.31 (m, 3H), 7.33-7.42 (m, 3H), 7.45-7.47 (m, 2H), 7.56-7.58 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 27.1, 39.0, 65.9, 85.9, 86.9, 122.4, 127.5, 128.4, 128.7, 128.8, 128.83, 132.0, 137.6, 177.3.

**Compound 1g** is known in literature.$^4$

### 3. General method for preparation of propargylic carbonate 4

![Image of reaction scheme]

To a solution of corresponding propargyl alcohol (15 mmol) in anhydrous THF (50 mL) was added $n$-BuLi (1.6 M solution in hexanes, 6.5 mL, 10 mmol) at −78 °C, and the resulting solution was stirred at the same temperature for 15 min. To this mixture was added the solution of Boc$_2$O (9 mmol) in THF (25 mL), and the reaction mixture was stirred for 2 h at room temperature. Aqueous NH$_4$Cl was added to quench the reaction. The mixture was extracted with diethyl ether (3 × 30 mL). The combined organic phase was washed with water (60 mL) and brine (60 mL), and dried over anhydrous MgSO$_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on SiO$_2$ (hexane/EtOAc) to give tert-butyl(1-phenylhept-2-yn-1-yl) carbonate (4).
$^1$H NMR (400 MHz, CDCl$_3$) δ 0.90 (t, $J$ = 7.6 Hz, 3H), 1.39-1.43 (m, 2H), 1.48 (s, 9H), 1.49-1.55 (m, 2H), 2.26 (dt, $J$ = 2.4 Hz, 7.2 Hz, 2H), 6.24 (s, 1H), 7.32-7.38 (m, 3H), 7.52-7.55 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.6, 18.6, 22.0, 27.8, 30.5, 69.1, 76.6, 82.7, 89.0, 127.8, 128.6, 128.9, 137.5, 152.7.

Compound 4 is known in literature.

4. General procedure of intermolecular [2+2] cycloaddition of in-situ generated allenol ester with C$_{60}$

To a 50 mL screw capped test tube, C$_{60}$ (108.1 mg, 0.15 mmol), PtCl$_2$ (4.0 mg, 0.015 mmol), ODCB (7.5 mL), and propargyl ester 1a-1e (1.5 mmol, 10 equiv) were added. The reaction mixture was bubbled with argon for 10 min. Then, this test tube was purged with argon and sealed. The reaction mixture was stirred at 80 °C. The reaction was monitored by analytical HPLC. After 18 h, MeOH was added to the reaction mixture, and the sediment was filtered and washed with MeOH to removed propargyl ester and allenol ester. The residue was purified by flash column chromatography on SiO$_2$ (hexane/toluene) to give the desired alkylidene cyclobutane annulated fullerene derivatives 2a-2e as a solid.

Brown solid; $R_f$ = 0.55 (hexane/toluene = 1/1); $^1$H NMR (400 MHz, CDCl$_3$) δ 0.91 (t, $J$ = 7.2 Hz, 3H), 1.22 (s, 9H), 1.32-1.64 (m, 4H), 2.39-2.42 (m, 2H), 6.17 (s, 1H), 7.39-7.43 (m, 1H), 7.54-7.58 (m, 2H), 8.06-8.08 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.06, 22.51, 27.54, 28.24, 30.30, 39.59, 56.98, 71.48, 72.84, 126.86, 127.84, 128.17, 128.46, 129.00, 129.40, 130.67, 132.68, 137.44, 137.64, 138.15, 138.65, 138.98, 140.30, 140.39, 140.67, 141.80, 142.10, 142.14, 142.18, 142.23, 142.49, 142.52, 142.56, 142.60, 142.64, 142.78, 142.82, 142.87, 143.04, 143.07, 144.51, 144.60, 144.62, 145.24, 145.30, 145.36, 145.44, 145.55, 145.59, 145.61, 146.04, 146.07, 146.13, 146.48, 146.68, 146.76, 147.06, 147.10, 150.80, 151.13, 151.34, 152.39, 153.88, 176.78; DEPT-135 (100 MHz, CDCl$_3$) δ 22.47, 28.20, 30.26, negative; δ 14.03, 27.51, 56.95, 127.81, 128.14, 128.96, 129.36, 130.63, positive; HRMS (ESI) m/z Calcd for C$_{78}$H$_{24}$O$_2$ [M$^+$]: 992.1771, found: 992.1784; The E/Z configuration of 2a was determined by NOESY analysis.

Brown solid; $R_f$ = 0.30 (hexane/toluene = 1/1); $^1$H NMR (400 MHz, CDCl$_3$) δ 0.92 (t, $J$ = 7.2 Hz, 3H), 1.21 (s, 9H), 1.37-1.59 (m, 4H), 2.38-2.43 (m, 2H), 3.88 (s, 3H), 6.12 (s, 1H), 7.07-7.10 (m, 2H), 7.98-8.00 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.09, 22.52, 27.54, 28.28, 30.29, 39.59, 55.44, 56.44, 71.41, 73.24, 114.67, 127.4, 128.46, 130.14, 130.93, 137.37, 137.69, 138.15, 139.01, 140.27, 140.39, 140.43, 140.66, 141.85, 142.10, 142.13, 142.18,
Brown solid; $R_f = 0.65$ (hexane/toluene = 1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.93(m, 3H), 1.21(s, 9H), 1.34-1.53(m, 2H), 1.56-1.70(m, 2H), 2.36-2.40(m, 2H), 6.13(s, 1H), 7.52-7.55(m, 2H), 8.00-8.02(m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.07, 22.53, 27.52, 28.24, 30.34, 39.61, 56.26, 71.42, 72.63, 126.66, 128.47, 128.97, 129.65, 130.30, 133.99, 137.25, 137.57, 139.00, 140.44, 141.76, 142.44, 142.56, 142.84, 142.90, 143.08, 144.21, 145.61, 145.75, 146.12, 146.78, 147.06, 147.09, 150.68, 159.38, 176.80; HRMS (ESI) m/z Calcd for C\(_{79}\)H\(_{26}\)O\(_3\) [M\(^+\)]: 1022.1876, found: 1022.1885.

Brown solid; $R_f = 0.55$ (hexane/toluene = 1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.95(t, J = 7.2 Hz, 3H), 1.21(s, 9H), 1.44-1.52(m, 2H), 1.59-1.71(m, 2H), 2.50-2.56(m, 2H), 6.33(s, 1H), 7.18-7.20(m, 1H), 7.39-7.41(m, 1H), 7.74-7.75(m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.10, 22.58, 27.54, 28.28, 30.46, 39.62, 51.66, 71.25, 73.36, 124.82, 126.01, 127.12, 127.78, 127.92, 128.47, 128.86, 129.71, 133.05, 137.59, 138.23, 139.20, 140.29, 140.39, 141.48, 141.77, 141.93, 142.12, 142.25, 142.39, 142.52, 142.59, 142.65, 142.85, 142.91, 143.03, 144.50, 144.65, 145.25, 145.37, 145.58, 145.69, 145.78, 146.12, 146.21, 146.44, 146.67, 146.83, 147.09, 147.13, 150.53, 151.36, 151.47, 152.15, 153.02, 176.66; HRMS (ESI) m/z Calcd for C\(_{76}\)H\(_{22}\)O\(_2\)S [M\(^+\)]: 998.1335, found: 998.1346.

Brown solid; $R_f = 0.60$ (hexane/toluene = 1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.10(s, 9H), 6.26-6.27(m, 1H), 7.40-7.45(m, 1H), 7.50-7.58(m, 2H), 7.94(d, J = 6.8 Hz, 2H), 8.26(d, J = 2.8 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.89, 39.02, 57.33, 73.92, 78.13, 127.30, 128.02, 128.85, 129.02, 129.11, 133.80, 134.80, 135.47, 137.41, 137.78, 138.09, 138.94, 139.12, 140.44, 140.65, 140.82, 141.89, 142.10, 142.17, 142.24, 142.43, 142.65, 142.69, 142.75, 142.84, 142.90, 142.99, 143.05, 144.56, 144.59, 144.65, 144.72, 145.25, 145.28, 145.33, 145.37, 145.40, 145.48, 145.55, 145.64, 145.66, 145.84, 145.90, 146.06, 146.10, 146.14, 146.27, 146.36, 146.75, 147.11, 147.14, 150.91, 152.40, 152.57, 154.20, 174.93; HRMS (ESI) m/z Calcd for C\(_{74}\)H\(_{16}\)O\(_2\) [M\(^+\)]: 936.1145, found: 936.1149. The E/Z configuration of \(\textbf{2e}\) was determined by NOESY analysis.
Brown solid; $R_f = 0.60$ (hexane/toluene = 1/1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.96(t, J = 9.5 Hz, 3H), 1.45(s, 9H), 1.47-1.60(m, 4H), 2.44-2.63(m, 2H), 6.82(t, J = 9.5 Hz, 1H), 7.43(t, J = 9.0 Hz, 1H), 7.56(t, J = 9.0 Hz, 2H), 8.08(d, J = 9.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.28, 22.77, 27.58, 29.83, 31.61, 39.97, 72.13, 79.79, 92.00, 126.62, 128.84, 129.08, 136.16, 137.35, 138.15, 138.98, 139.21, 140.06, 140.94, 140.29, 140.76, 141.57, 141.60, 142.11, 142.49, 142.56, 142.58, 142.65, 142.80, 142.95, 143.22, 144.47, 144.63, 144.80, 145.04, 145.24, 145.28, 145.35, 145.37, 145.52, 145.94, 146.00, 146.07, 146.58, 146.86, 146.93, 147.05, 147.17, 150.45, 151.75, 153.14, 153.70, 176.23; HRMS (ESI) m/z Calcd for C$_{78}$H$_{24}$O$_2$ [M$^+$]: 992.1771, found: 992.1781.

Brown solid; $R_f = 0.55$ (hexane/toluene = 1/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.36(s, 9H), 7.28-7.31(m, 3H), 7.42-7.45(m, 1H), 7.49-7.56(m, 4H), 7.71(s, 1H), 8.25(d, J = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 27.67, 39.87, 72.09, 80.83, 91.86, 127.31, 128.55, 128.66, 129.31, 129.36, 129.63, 131.91, 134.51, 137.59, 138.07, 138.53, 139.30, 139.97, 140.15, 140.31, 140.76, 141.02, 141.39, 142.18, 142.26, 142.46, 142.73, 142.77, 142.89, 142.95, 143.23, 144.47, 144.56, 144.60, 145.04, 145.24, 145.28, 145.33, 145.55, 145.70, 145.93, 146.02, 146.12, 146.77, 147.00, 147.06, 147.19, 147.50, 148.98, 152.50, 152.69, 153.26, 176.47; HRMS (ESI) m/z Calcd for C$_{80}$H$_{20}$O$_2$ [M$^+$]: 1012.1458, found: 1012.1458.

**5. Procedure of hydrolysis of alkylidenecyclobutane-annulated fullerene 5**

To a solution of fullerene derivative 3h (63.5 mg, 0.07 mmol) in toluene (10 mL) was added TsOH $\cdot$ H$_2$O (39.9 mg, 0.21 mmol). The mixture was refluxed for 6 h. After removal of solvent, the residue was purified by column chromatography on SiO$_2$ (hexane/toluene) to give 6 (35.6 mg, 56%) as brown solid.
Brown solid; \( R_f = 0.475 \) (hexane/toluene = 1/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 0.94 (t, \( J = 7.2 \) Hz, 3H), 1.35-1.46 (m, 2H), 1.77-1.85 (m, 2H), 2.91-3.05 (m, 2H), 5.61 (d, \( J = 9.2 \) Hz, 1H), 6.13 (d, \( J = 9.2 \) Hz, 1H), 7.43 (t, \( J = 7.2 \) Hz, 1H), 7.56 (t, \( J = 7.6 \) Hz, 2H), 7.97 (d, \( J = 7.2 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 14.13, 22.59, 25.90, 43.50, 50.02, 59.88, 67.06, 71.64, 125.44, 128.16, 128.37, 128.61, 129.18, 129.32, 136.92, 137.40, 138.79, 139.15, 139.48, 140.51, 140.55, 140.87, 140.92, 141.73, 142.06, 142.09, 142.24, 142.30, 142.34, 142.60, 142.62, 142.66, 142.80, 142.86, 142.94, 142.96, 143.12, 143.14, 144.52, 144.58, 144.63, 144.86, 145.86, 145.09, 145.23, 145.31, 145.38, 145.47, 145.51, 145.53, 145.65, 145.87, 146.04, 146.14, 146.17, 146.21, 146.30, 146.34, 146.74, 147.17, 147.26, 149.76, 151.15, 154.00, 154.47, 206.29; DEPT-135 (100 MHz, CDCl\(_3\)) \( \delta \): 22.59, 25.90, 43.52, negative; \( \delta \) 14.13, 50.03, 59.89, 125.46, 128.16, 128.36, 128.61, 129.18, 129.31, positive; HRMS (ESI) m/z Calcd for C\(_{73}\)H\(_{60}\) [M\(^+\)]: 908.1196, found: 908.1204. The cis/trans configuration of 6 was determined by the coupling constant.\(^6\)

6. A survey of catalyst and solvent in the reaction of 1a with C\(_{60}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>1a (equiv)</th>
<th>Catalyst (y equiv)</th>
<th>Solvent (mL)</th>
<th>Time (h)</th>
<th>Yield of 2a (%)(^b)/Recovered C(_{60}) (%)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>AuCl(PPh(_3)) (0.5)</td>
<td>ODCB (1)</td>
<td>6</td>
<td>0/100(^b)</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>AuCl(PPh(_3))/AgOTf (0.5)</td>
<td>ODCB (1)</td>
<td>6</td>
<td>0/100(^b)</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>AgSbF(_6) (0.5)</td>
<td>ODCB (1)</td>
<td>6</td>
<td>1/99(^b)</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>AgCl (0.5)</td>
<td>ODCB (1)</td>
<td>6</td>
<td>0/100(^c)</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>AgOAc (0.5)</td>
<td>ODCB (1)</td>
<td>6</td>
<td>0/100(^c)</td>
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<tr>
<td>6</td>
<td>10</td>
<td>AgOTf (0.5)</td>
<td>ODCB (1)</td>
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<td>10/88</td>
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<td>7</td>
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<td>AgBF(_4) (0.5)</td>
<td>ODCB (1)</td>
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<td>13/85</td>
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<td>8</td>
<td>10</td>
<td>PtCl(_2) (0.5)</td>
<td>ODCB (1)</td>
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<td>21/73</td>
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<td>9</td>
<td>10</td>
<td>PtCl(_2) (0.5)</td>
<td>ODCB (1)</td>
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<td>47/32</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>PtCl(_2) (0.1)</td>
<td>ODCB (1)</td>
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<td>45/33</td>
</tr>
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<td>11</td>
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<td>PtCl(_2) (0.05)</td>
<td>ODCB (1)</td>
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<td>37/54</td>
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<tr>
<td>12</td>
<td>10</td>
<td>PtCl(_2) (0.1)</td>
<td>toluene (5)</td>
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<td>21/71</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>PtCl(_2) (0.1)</td>
<td>1,2,4-trimethylbenzene (1)</td>
<td>18</td>
<td>32/55</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>PtCl(_2) (0.1)</td>
<td>ODCB (1)</td>
<td>18</td>
<td>34/55</td>
</tr>
<tr>
<td>15</td>
<td>2</td>
<td>PtCl(_2) (0.1)</td>
<td>ODCB (1)</td>
<td>18</td>
<td>18/78</td>
</tr>
</tbody>
</table>
7. UV-visible spectra
UV-vis absorption spectra were recorded on a JASCO V-670 spectrometer. The concentrations are \(10^{-5}\) M in \(\text{CH}_2\text{Cl}_2\) solution.

![Figure S1. UV-vis absorption spectra of 2a](image1)

![Figure S2. UV-vis absorption spectra of 6](image2)

8. Electrochemical properties
All CV and DPV measurements were carried out in a one-compartment cell under argon gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag\(^+\) reference electrode. The supporting electrolyte was a 0.1 mol L\(^{-1}\) dichloromethane solution of
tetrabutylammonium hexafluorophosphate (TBAPF₆).

Figure S3. DPV measurements. X points are 2a and circles are 6

Figure S4. CV measurements. dashed line, 2a and solid line, 6

9. Device fabrication

Device section
Current–voltage ($J$–$V$) characteristics were measured using a source meter (Keithley 2400) under 1 sun AM 1.5G simulated sunlight irradiation (100 mW/cm$^2$) from a solar simulator (EMS-35AAA, Ushio Spax Inc.), which was calibrated using a silicon diode (BS-520BK, Bunkoukeiki).

The patterned ITO substrates were cleaned by sonicating in surfactant water, pure water, acetone, and isopropyl alcohol; each cycle lasted 15 min. The substrates were then dried using a N$_2$ gun and subjected to 15 min UV/O$_3$ treatment. Next, a PEDOT:PSS (Clevios PVP Al4083) solution was deposited on the substrate via spin-coating (3000 rpm for 30 sec) followed by thermal annealing in air for 10 min at 120 °C. These devices were carried to the glovebox and the active layer was deposited in the N$_2$ atmosphere.

P3HT:6 active layers: A solution of P3HT:6 (5:4 w/w ratio, 30 mg/mL vs mixture) in an ODCB solution was prepared and left stirring at 65 °C for 2 h. Next, the solution was filtered through a PTFE membrane (pore size = 0.2 µm). The solution was then deposited onto the ITO/PEDOT:PSS substrate and spin-coated at 700 rpm for 60 sec. Films were slowly evaporation in a petro dish and then thermally annealed at 120 °C for 10 min.

PTB7:6 active layers: 6 was blended with PTB7 using a 1:1 w/w ratio in ODCB. The total concentration of the solution was 20 mg/mL. The solution was left stirring at 65 °C overnight. The solution was then filtered and deposited onto the ITO/PEDOT:PSS substrates. For this system, spin-coating was also 700 rpm for 60 sec. No thermal annealing was applied to PTB7:6 pre- and post-fabrication.

Finally, the substrates were transferred into an evaporator chamber. All devices were deposited Ca (20 nm) and then Al (80 nm). The active area (0.04 cm$^2$) was defined by the geometric overlap between Al and ITO.

10. SCLC measurement

Electron mobility measurements based on space-charge limited current

The structure of the electron-only device was Al(100 nm)/active layer/LiF(0.6 nm)/Al(100 nm). The electron mobility of the P3HT:6 and PTB7:6 devices was obtained through space charge limited current (SCLC) method which was expressed by $J = \frac{9}{8\varepsilon_0\varepsilon_r}\mu V^2/L^3$, where $\varepsilon_0$ is relative permittivity, $\varepsilon_r$ is vacuum permittivity, $\mu$ is charge carrier mobility, $V$ is voltage applied, and $L$ is thickness. The mobility was determined by fitting the dark current to a model of a single-carrier SCLC, which is described by the equation: Then, the LiF/Al electrode (LiF = 0.6 nm; Al = 100 nm) was evaporated onto the active layer. The experimental dark current density $J$ of both P3HT:6 and PTB7:6 was measured under an applied voltage swept from 0 to −5 V.
Figure S5. $J-V$ characteristics of the electron-only device of P3HT:6.

Figure S6. $J-V$ characteristics of the electron-only device of PTB7:6.

11. AFM images
Figure S7. 1 mm square AFM height (a, b, c) and 3D (d, e, f) images of thin films of P3HT:6 annealed at 120 °C (a, d), P3HT:6 annealed at 150 °C (b, e), and PTB7:6 (c, f). Root-mean-square roughness values ($R_q$) were 8.20 nm, 10.2 nm, and 1.82 nm, respectively.

12. References
X: parts per Million: Proton
X: parts per Million: Proton
X : parts per Million : Proton