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Supporting Information for:

Isoquinolino[4,3,2-*de*]phenanthridine: synthesis and its use in 1,3-dipolar cycloadditions to form nitrogen-containing polyaromatic hydrocarbons

Shingo Ito*, Yuki Tokimaru and Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Experimental Section

General: All reactions were carried out in a glove box or using standard Schlenk techniques under argon atmosphere. Thin-layer chromatography (TLC) was performed using glass plates pre-coated with silica gel impregnated with a fluorescent indicator (Merck, #1.15685.0001). Silica gel column chromatography was performed as described by Still, et al.,(1) employing silica gel 60N (spherical, neutral) purchased from Kanto Chemical Co. Inc. (Kanto). Preparative TLC was performed with Merck PLC Silica gel 60 F_{254} (#1.13895.0001).

Instrumentation: NMR spectra were recorded on Bruker Ascend 500 (^{1}H: 500 MHz and ^{13}C: 126 MHz) and JEOL ECS400 (^{1}H: 400 MHz and ^{13}C: 101 MHz) NMR spectrometers. Chemical shift values for protons are referenced to the residual signal of chloroform-*d* (δ 7.26) or dichloromethane-d_2 (δ 5.33), and chemical shift values for carbons are referenced to the carbon resonance of chloroform-*d* (δ 77.7) or dichloromethane-d_2 (δ 54.2). Preparative HPLC separation for fullerene compound **9** was carried out with a JASCO LC-2000 system equipped with buckyprep columns (Nacalai, Co. Ltd.) and a photodiode array (PDA) detector by eluting with toluene at room temperature. High-resolution mass (HRMS) spectra were taken with the electron spray ionization (ESI) method on a JEOL JMS-T100LP mass spectrometer. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8400 spectrometer. Melting points and decomposition points were recorded on an OptiMelt MPA-100 apparatus. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, Graduate School of Science, The University of Tokyo.

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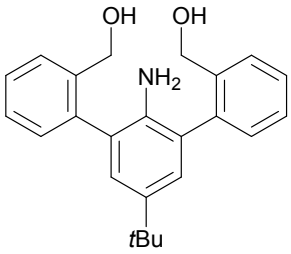
(1) W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.

Materials: Anhydrous dichloromethane, diethyl ether, and toluene were purchased from Kanto and purified by the method of Pangborn, *et al*.[2] Carbon tetrachloride was purchased from Kanto and purified by distillation from CaH_2. The following reagents were purchased and used as received: hexane (Kanto), anhydrous 1,2-dichloroethane (Aldrich), triethylamine (Wako), 1,3-dihydro-1-hydroxy-2,1-benzoxaborole (Tokyo Chemical Industry, Co. Ltd. (TCI)), sodium carbonate (Wako Pure Chmical Industries, Ltd. (Wako)), dry ethanol (Wako), hydrogen chloride in 1,4-dioxane (Aldrich), dimethyl acetylenedicarboxylate (DMAD) (TCI), 1,2-diphenylethyne (TCI), and fullerene C_{60} (Aldrich). The following compounds were prepared according to literature procedures: 2,6-dibromo-4-*t*-butylaniline,[3] and dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate.[4]

Compound Data:

4-*t*-Butyl-2,6-bis[(2'-hydroxymethyl)phenyl]aniline (3)



To a solution of 2,6-dibromo-4-*t*-butylaniline (307 mg, 1.0 mmol), 1,3-dihydro-1-hydroxy-2,1-benzoxaborole (400 mg, 2.8 mmol), and aqueous potassium carbonate (2.0 M, 4.0 mL, 8.0 mmol) in toluene (10 mL) and ethanol (2 mL) was added $Pd(PPh_3)_4$ (160 mg, 0.14 mmol) and the mixture was stirred for 13 h at 100 °C. After cooling to room temperature, the mixture was extracted with dichloromethane, and the extracts were evaporated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (1:1) to yield **3** as a colorless powder (220 mg, 0.61 mmol, 61 %); R_f = 0.40 (hexane/ethyl acetate (1:1)); mp 143–147 °C; IR (neat) cm^{-1} 3377 (br), 3063, 2952, 2864, 1614, 1452, 1360, 1240, 1040, 985, 885, 768, 773, 646; ^1H NMR (500 MHz, $CDCl_3$, 294 K) δ 7.62–7.51 (m, 2H), 7.47–7.39 (m, 4H), 7.36–7.29 (m, 2H), 7.12, 7.10 (7:3) (s, 2H), 4.54–4.42 (m, 4H), 3.6–2.8 (br, 4H), 1.31, 1.29 (7:3) (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 295 K) δ *major* isomer: 143.6 (4°), 140.7 (2C, 4°), 138.7 (2C, 4°), 138.4 (4°), 130.5 (2C, 3°), 130.3 (2C, 3°), 129.3 (2C, 3°), 129.1 (2C, 3°), 128.7 (2C, 4°), 127.2 (2C, 3°), 64.4 (2C, CH_2), 34.9 (CMe_3), 32.2 (3C, CH_3), *minor* isomer: 143.1 (4°), 140.2 (2C, 4°), 138.9 (2C, 4°), 138.3 (4°), 131.2 (2C, 3°), 130.2 (2C, 3°), 129.2 (2C, 3°), 129.1 (2C, 3°), 128.3 (2C, 4°), 127.3 (2C, 3°), 64.6 (2C), 34.8, 32.2 (3C) (Two isomers were observed in ca. 7:3 ratio because hydrogen bonds prevent free rotation of the aryl substituents); HRMS (ESI): *m/z* calcd for $C_{24}H_{28}NO_2$ $[M+H]^+$ 361.2120, found 361.2117; Anal. Calcd for $C_{24}H_{27}NO_2$, C, 79.74; H, 7.53; N, 3.87. found: C, 79.37; H, 7.47; N, 3.78.

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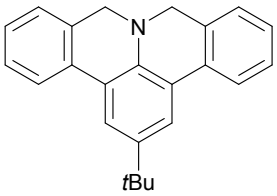
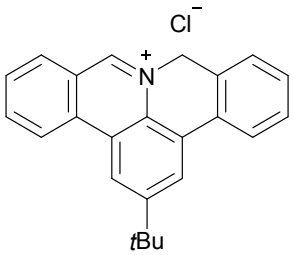
(2) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, **1996**, *15*, 1518.
(3) T. C. Bedard and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 10662.
(4) T. Gadzikwa, B.-S. Zeng, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2008, 3672.

2-*t*-Butyl-8,10-dihydroisoquinolino[4,3,2-*de*]phenanthridine (4)



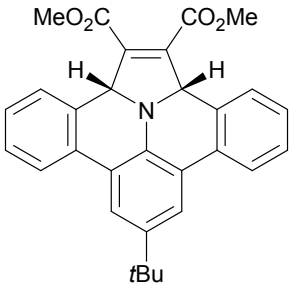
To a solution of **3** (1.21 g, 3.35 mmol) in 1,2-dichloroethane (30 mL) was added hydrogen chloride (4.0-M solution in 1,3-dioxane, 20 mL, 80 mmol) and the mixture was stirred for 15 h at 100 °C. After dilution with diethyl ether, the mixture was washed with saturated aqueous sodium bicarbonate. The mixture was extracted with dichloromethane, and evaporated. The crude product was purified by washing with methanol to yield **4** as a yellow powder (0.76 g, 2.34 mmol, 70 %); R_f = 0.64 (hexane/ethyl acetate (17:3)); mp 130–135 °C; IR (neat) cm^{-1} 3053, 2960, 2868, 1732, 1645, 1497, 1341, 1310, 1286, 1267, 1252, 1111, 1040, 874, 779, 736, 686, 636; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 7.71 (s, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.33 (td, *J* = 7.6, 1.2 Hz, 2H), 7.23 (td, *J* = 7.6, 1.2 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 4.21 (s, 4H), 1.41 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 293 K) δ 142.8 (4°), 142.3 (4°), 132.9 (2C, 4°), 132.0 (2C, 4°), 128.6 (2C, 3°), 127.8 (2C, 3°), 126.7 (2C, 3°), 123.1 (2C, 3°), 122.4 (2C, 4°), 120.9 (2C, 3°), 54.9 (2C, *C*H$_2$), 35.0 (*C*Me$_3$), 32.2 (3C, *C*H$_3$). HRMS (ESI) *m/z* calcd for $C_{24}H_{23}N$ [M−H]$^+$ 324.1752, found 324.1765, [M+H]$^+$ 326.1909, found 326.1904.

2-*t*-butyl-8-hydroisoquinolino[4,3,2-*de*]phenanthridin-9-ium chloride (5)



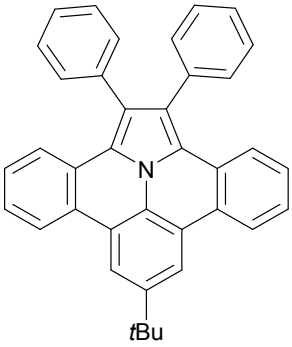
A solution of **4** (325 mg, 1.0 mmol) in carbon tetrachloride (80 mL) was stirred for 20 h at room temperature under irradiation of ambient light. To the solution was added hydrogen chloride (4.0 M solution in 1,4-dioxane, 7.0 mL, 28 mmol), and the mixture was stirred for 3.5 h at room temperature. After adding diethyl ether (200 mL), the form precipitates were collected by filtration. The crude product was purified by recrystallization from methanol/diethyl ether to yield **5** as a yellow powder (209 mg, 0.58 mmol, 58 %); dp ca. 140 °C; IR (neat) cm^{-1} 3061, 2959, 2868, 1626, 1603, 1531, 1504, 1420, 1354, 1242, 1055, 874, 785, 754; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 11.63 (s, 1H), 8.89 (d, *J* = 8.3 Hz, 1H), 8.73 (d, *J* = 8.6 Hz, 1H), 8.61 (s, 1H), 8.46 (s, 1H), 8.21 (t, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 6.52 (s, 2H), 1.54 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 293 K) δ 155.0 (4°), 154.5 (3°), 138.3 (3°), 134.9 (4°), 134.6 (3°), 130.9 (3°), 130.8 (3°), 130.0 (3°), 128.7 (4°), 128.4 (4°), 127.7 (3°), 127.7 (4°), 127.5 (4°), 126.9 (4°), 125.2 (4°), 124.0 (3°), 123.8 (3°), 122.9 (3°), 119.7 (3°), 57.8 (*C*H$_2$), 36.5 (*C*Me$_3$), 31.8 (3C, *C*H$_3$); HRMS (ESI) *m/z* calcd for $C_{24}H_{22}ClN$ [M−Cl]$^+$ 324.1752, found 324.1749.

meso-Dimethyl 8-_t_-butyl-2_a_,13_b_-dihydrobenzo[7,8]indolizino[6,5,4,3-_def_]phenanthridine-1,2-dicarbo-xylate (7a)



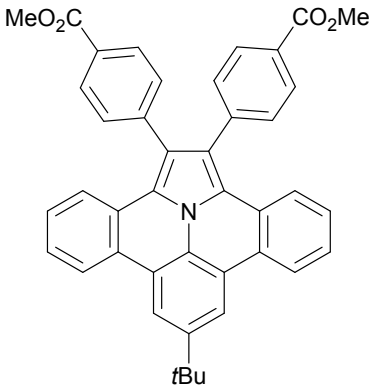
To a solution of **5** (72 mg, 0.20 mmol) and dimethyl acetylenedicarboxylate (57 mg, 0.40 mmol) in dichloromethane (12 mL) was added triethylamine (20 mg, 0.20 mmol) and the mixture was stirred for 6 h at room temperature (ca. 293K). After volatile matters were evaporated, the crude product was purified by silica gel column chromatography eluted with dichloromethane to yield **7a** as a yellow powder (57 mg, 0.12 mmol, 60 %); R_f = 0.23 (hexane/dichloromethane (2:3)); mp 205–208 °C; IR (neat) cm^{-1} 3063, 2959, 2868, 1710 (C=O), 1622, 1504, 1431, 1271, 1217, 1109, 1070, 959, 876, 787, 762, 744, 727, 638; ^1H NMR (500 MHz, $CDCl_3$, 296 K) δ 7.81 (d, J = 7.8 Hz, 2H), 7.69 (s, 2H), 7.42 (t, J = 7.4 Hz, 2H), 7.39 (d, J = ~7 Hz, 2H; overlapped), 7.30 (t, J = 7.4 Hz, 2H), 5.35 (s, 2H), 3.60 (s, 6H), 1.40 (s, 9H);$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 294 K) δ 165.0 (2C, *C*=O), 144.5 (4°), 141.8 (2C, 4°), 136.9 (4°), 132.1 (2C, 4°), 129.8 (4C, 3°), 128.5 (2C, 4°), 127.7 (2C, 3°), 123.0 (2C, 3°), 121.4 (2C, 3°), 68.7 (2C, O*C*H_3), 52.8 (2C, N*C*H), 35.1 (*C*Me_3), 32.1 (3C, C(*C*H_3)$_3$); HRMS (ESI) *m/z* calcd for $C_{30}H_{28}NO_4$ $[M+H]^+$ 466.2018, found 466.2005.

8-_t_-Butyl-1,2-diphenylbenzo[7,8]indolizino[6,5,4,3-_def_]phenanthridine (8b)



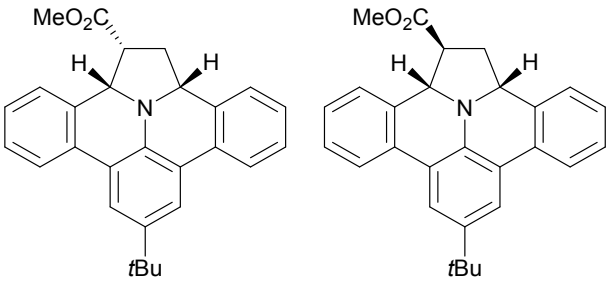
To a solution of **5** (36 mg, 0.10 mmol) and diphenylacetylene (36 mg, 0.20 mmol) in toluene (5.0 mL) was added triethylamine (10 mg, 0.10 mmol) and the mixture was stirred for 18 h at 100 °C. After dilution with dichloromethane, the mixture was washed with water. The crude product was evaporated and purified by preparative TLC eluted with toluene to yield **8b** as a yellow powder (15 mg, 0.030 mmol, 30 %); R_f = 0.85 (toluene); mp 273–275 °C; IR (neat) cm^{-1} 3070, 2953, 2920, 2851, 1604, 1570, 1454, 1433, 1418, 1390, 1247, 1028, 897, 783, 754, 714, 687, 640, 621; ^1H NMR (500 MHz, $CDCl_3$, 293 K): δ 8.39 (s, 2H), 8.37 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 7.3 Hz, 2H), 7.40–7.26 (m, 12H), 7.19 (t, J = 7.2 Hz, 2H), 1.58 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 293 K) δ 146.7 (4°), 137.0 (2C, 4°), 132.1 (4C, 3°), 129.0 (4C, 3°), 128.9 (4°), 128.5 (2C, 3°), 127.5 (2C, 3°), 127.4 (2C, 4°), 126.8 (2C, 4°), 126.5 (2C, 3°), 124.3 (2C, 3°), 123.6 (2C, 4°), 123.4 (2C, 3°), 122.9 (2C, 4°), 121.2 (2C, 4°), 118.1 (2C, 3°), 36.0 (*C*Me_3), 32.5 (3C, *C*H_3); HRMS (ESI) *m/z* calcd for $C_{38}H_{29}N$ $[M]^+$ 499.2300, found 499.2309.

Dimethyl 4,4'-(8-*t*-butylbenzo[7,8]indolizino[6,5,4,3-*def*]phenanthridine-1,2-diyl)dibenzoate (8c)



To a solution of **5** (36 mg, 0.10 mmol) and dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (59 mg, 0.20 mmol) in toluene (5.0 mL) was added triethylamine (10 mg, 0.10 mmol) and the mixture was stirred for 18 h at 100 °C. After dilution with dichloromethane, the mixture was washed with water. The crude product was purified by silica gel column chromatography eluted with hexane/dichloromethane (1:2) to yield **8c** as a yellow powder (12 mg, 0.02 mmol, 20 %); R_f = 0.38 (hexane/dichloromethane (1:2)); mp 271–273 °C; IR (neat) cm^{-1} 3067, 2949, 2920, 2851, 1715 (C=O), 1609, 1431, 1273, 1113, 1097, 1018, 872, 754, 739, 684; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.41 (s, 2H), 8.38 (d, *J* = 7.9 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 4H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.41 (t, *J* = ~8 Hz, 2H; overlapped), 7.40 (d, *J* = 8.4 Hz, 4H), 7.19 (t, *J* = 7.6 Hz, 2H), 3.94 (s, 6H), 1.58 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 296 K) δ 166.6 (2C, *C*=O), 146.5 (4°), 141.1 (2C, 4°), 131.3 (4C, 3°), 129.2 (4C, 3°), 128.7 (2C, 4°), 127.7 (2C, 3°), 127.6 (4°), 126.0 (2C, 4°), 126.0 (2C, 3°), 125.9 (2C, 4°), 123.3 (2C, 3°), 122.7 (2C, 3°), 121.9 (2C, 4°), 121.4 (2C, 4°), 120.6 (2C, 4°), 117.6 (2C, 3°), 51.7 (2C, O*C*H_3), 35.0 (*C*Me_3), 31.3 (3C, C(*C*H_3)$_3$); HRMS (ESI): *m/z* calcd for $C_{42}H_{33}NO_4$ $[M]^+$ 615.2410, found 615.2387.

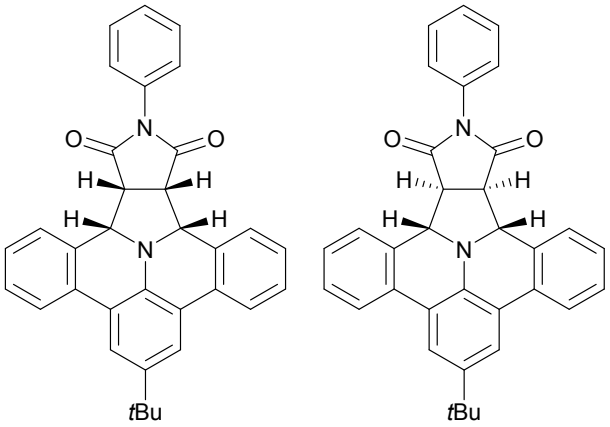
***rel*-methyl (1*R*,2a*S*,13b*R*)-8-(*tert*-butyl)-1,2,2a,13b-tetrahydrobenzo[7,8]indolizino[6,5,4,3-*def*]phenanthridine-1-carboxylate and *rel*-methyl (1*R*,2a*R*,13b*S*)-8-(*tert*-butyl)-1,2,2a,13b-tetrahydrobenzo[7,8]indolizino[6,5,4,3-*def*]phenanthridine-1-carboxylate (6d)**



To a solution of **5** (36 mg, 0.10 mmol) and methyl acrylate (18 μL, 0.20 mmol) in dichloromethane (5.0 mL) was added triethylamine (10 mg, 0.10 mmol) and the mixture was stirred for 18 h at ambient temperature. After dilution with dichloromethane, the mixture was washed with water. The crude product was purified by preparative TLC eluted with dichloromethane to obtain **6d** as a yellow powder (25 mg, 0.061 mmol, 61 %, *endo*: *exo* = 53:47). The mixture of *endo* and *exo* isomers could not be separated by preparative TLC; R_f = 0.74 (dichloromethane); dp 140–145 °C; IR (neat) cm^{-1} 3055, 2949, 2903, 2866, 1724 (C=O), 1429, 1194. 1159, 1095, 1042, 933, 872, 779, 738, 621; ^1H NMR (400 MHz, $CDCl_3$, 295 K) *major* isomer, δ 7.89–7.81 (m, 2H), 7.74 (s, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.43–7.33 (m, 2H), 7.32–7.15 (m, 4H), 4.84 (d, *J* = 8.8 Hz, 1H), 4.42 (dd, *J* = 10.6, 6.8 Hz, 1H), 3.30 (dd, *J* = 16.3, 8.7 Hz, 1H), 3.00 (s, 3H), 2.37–2.25 (m, 1H), 2.07 (dt, *J* = 13.3, 10.3 Hz, 1H), 1.41 (s, 9H); *minor* isomer, δ 7.89–7.81 (m, 2H), 7.74 (s, 2H), 7.43–7.33 (m, 2H), 7.32–

7.15 (m, 4H), 4.67 (d, J = 9.2 Hz, 1H), 4.62 (dd, J = 10.4, 7.3 Hz, 1H), 3.75 (s, 3H), 2.95–2.87 (m, 1H), 2.44–2.35 (m, 1H), 2.35–2.25 (m, 1H), 1.42 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 293 K) δ 175.4 (*C*=O), 173.4 (*C*=O), 142.6, 141.5, 136.8, 136.8, 133.6, 133.1, 132.3, 131.4, 130.6, 130.5, 130.4, 129.9, 128.4, 128.1, 128.1, 127.9, 127.8, 127.3, 127.2, 127.0, 126.8, 126.8, 126.7, 122.6 122.5, 122.4, 121.9, 121.1, 121.1, 120.9, 120.4, 120.3, 119.9, 119.5, 66.7 (O*C*H_3), 65.1 (O*C*H_3), 62.7, 62.5, 51.9, 51.1, 49.7, 49.1, 37.4, 36.2, 34.4 (*C*Me_3), 34.3 (*C*Me_3), 31.5 (C(*C*H_3)$_3$), 31.5 (C(*C*H_3)$_3$) (^{13}C NMR signals for major and minor isomers could not be distinguished); HRMS (ESI) *m/z* calcd for $C_{28}H_{27}NO_2$ $[M+H]^+$ 410.2120, found 410.2135.

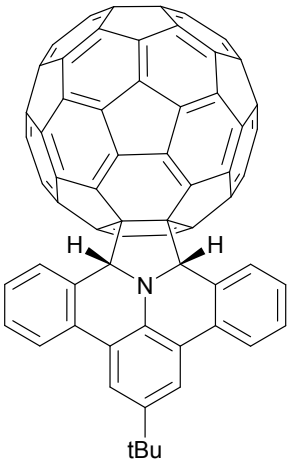
(3a*R*,3b*S*,14b*R*,14c*S*)-9-(*tert*-butyl)-2-phenyl-3a,3b,14b,14c-tetrahydro-1*H*-benzo[7,8]pyrrolo[3',4':1,2]indolizino[6,5,4,3-*def*]phenanthridine-1,3(2*H*)-dione (6e)



To a solution of **5** (36 mg, 0.10 mmol) and *N*-phenylmaleimide (34 mg, 0.20 mmol) in dichloromethane (5.0 mL) was added triethylamine (10 mg, 0.10 mmol) and the mixture was stirred for 18 h at ambient temperature. After dilution with dichloromethane, the mixture was washed with water. The crude product was purified by preparative TLC eluted with dichloromethane to obtain *endo* adduct **6e-*endo*** as a yellow powder (13 mg, 0.026 mmol, 26 %) and *exo* adduct **6e-*exo*** as a yellow powder (11 mg, 0.022 mmol, 22 %); For *endo* isomer, R_f = 0.77 (dichloromethane); dp 125–135 °C; IR (neat) cm^{-1} 3026, 2959, 2868, 1709 (C=O), 1499, 1371, 1175, 1072, 1047, 781, 743, 690, 621; ^1H NMR (500 MHz, $CDCl_3$, 294 K): δ 7.87 (d, J = 7.6 Hz, 2H), 7.79 (s, 2H), 7.58–7.34 (m, 11H), 4.67 (dd, J = 5.5, 2.2 Hz, 2H), 3.47 (dd, J = 5.5, 2.2 Hz, 2H), 1.43 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 293 K) δ 176.1 (2C, *C*=O), 144.4 (4°), 136.0 (4°), 132.2 (4°), 131.7 (2C, 4°), 130.9 (2C, 4°), 129.9 (2C, 3°), 128.6 (2C, 3°), 129.4 (3°), 128.7 (2C, 3°), 128.6 (2C, 3°), 127.1 (2C, 3°), 123.3 (2C, 3°), 121.9 (2C, 3°), 121.4 (2C, 4°), 66.5 (2C, *C*HC=O), 52.9 (2C, N*C*H), 35.2 (*C*Me_3), 32.2 (3C, C(*C*H_3)$_3$) HRMS (ESI) *m/z* calcd for $C_{34}H_{28}N_2O_2$ $[M-3H]^+$ 493.1916, found 493.1930, $[M+H]^+$ 497.2229, found 497.2233. For *exo* isomer, R_f = 0.32 (dichloromethane); dp 260–265 °C; IR (neat) cm^{-1} 3061, 2961, 1705 (C=O), 1499, 1431, 1379, 1163, 1041, 779, 743, 693; ^1H NMR (500 MHz, $CDCl_3$, 294 K) δ 7.85 (d, J = 7.9 Hz, 2H), 7.73 (s, 2H), 7.46–7.36 (m, 6H), 7.16–7.12 (m, 3H), 6.44–6.39 (m, 2H), 4.99 (d, J = 5.5 Hz, 2H), 3.65 (d, J = 5.5 Hz, 2H), 1.36 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_3, 293 K) δ 173.9 (2C, C=O), δ 174.6 (2C, *C*=O), 143.8 (4°), 136.5 (4°), 132.1 (2C, 4°), 131.7 (2C, 4°), 129.9 (4°), 129.7 (2C, 3°), 129.4 (2C, 4°), 129.3 (2C, 3°), 128.8 (3°), 128.4 (2C, 3°), 128.3 (2C, 3°), 126.9 (2C, 3°), 123.4 (2C, 3°), 121.4 (2C, 3°), 121.3 (4°), 66.0 (2C, *C*HC=O),

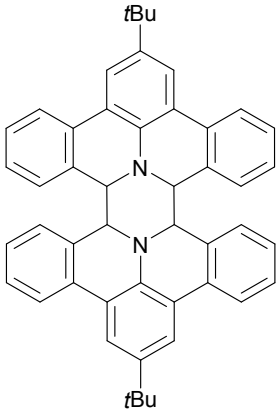
51.6 (2C, NCH), 35.2 (*C*Me$_3$), 32.2 (3C, C(*C*H$_3$)$_3$); HRMS (ESI): *m/z* calcd for $C_{34}H_{28}N_2O_2$ $[M-3H]^+$ 493.1916, found 493.1910, $[M+H]^+$ 497.2229, found 497.2232.

meso-8-_t_-Butyl-2_a_,13_b_-dihydrobenzo[7,8]indolizino[6,5,4,3-_def_]phenanthridino[1',2':1,9](C$_{60}$-I_h)-[5,6]fullerene (9)



To a solution of **5** (36 mg, 0.10 mmol) and C_{60} (108 mg, 0.15 mmol) in 1,2-dichlorobenzene (15 mL) was added triethylamine (11 mg, 1.0 mmol) at room temperature and the mixture was stirred for 18 h at 40 °C. The reaction mixture was reprecipitated by adding acetone (300 mL), and precipitates were collected by filtration. The crude product was purified by preparative HPLC using a buckyprep® column eluted with toluene to yield **9** as a brown powder (68 mg, 0.065 mmol, 65 %); Retention time (HPLC) 10.7 min (*cf.* C_{60}: 17.3 min); mp: Clear melting point was not observed until 400 °C; IR (neat) cm^{-1} 3065, 2920, 2851, 1732, 1651, 1495, 1462, 1427, 1259, 870, 777, 694, 524; ^{1}H NMR (500 MHz, CS_2/$CDCl_3$(1:1), 295 K) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.74 (s, 2H), 7.73 (d, *J* = ~8 Hz (overlapped), 2H), 7.52 (td, *J* = 7.6, 1.2 Hz, 2H), 7.40 (td, *J* = 7.5, 1.1 Hz, 2H), 6.26 (s, 2H), 1.46 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, CS_2/$CDCl_3$(1:1), 296 K) δ 153.4 (2C, 4°), 153.1 (2C, 4°), 147.2 (2C, 4°), 147.1 (2C, 4°), 146.8 (2C, 4°), 146.6 (2C, 4°), 146.3 (2C, 4°), 146.2 (2C, 4°), 146.0 (2C, 4°), 146.0 (4°), 145.9 (4°), 145.8 (2C, 4°), 145.6 (2C, 4°), 145.4 (2C, 4°), 145.2 (2C, 4°), 144.8 (2C, 4°), 144.6 (2C, 4°), 143.6 (4°), 143.6 (4°), 143.4 (4°), 143.0 (2C, 4°), 143.0 (2C, 4°), 142.6 (2C, 4°), 142.5 (2C, 4°), 142.4 (2C, 4°), 141.9 (2C, 4°), 141.5 (2C, 4°), 140.6 (2C, 4°), 139.8 (2C, 4°), 138.7 (4°), 136.5 (2C, 4°), 136.1 (2C, 4°), 135.9 (2C, 4°), 132.3 (2C, 4°), 130.6 (2C, 4°), 129.9 (2C, 3°), 128.7 (2C, 3°), 128.2 (2C, 3°), 124.1 (2C, 3°), 123.6 (2C, 4°), 121.1 (2C, 3°), 81.5 (2C, 4°), 76.5 (2C, *C*H), 35.1 (*C*Me$_3$), 32.2 (3C, *C*H$_3$).

Dimer 10



A solution of **5** (72 mg, 0.20 mmol) in acetonitrile (12 mL) was added triethylamine (22 mg, 0.22 mmol) at room temperature, and the mixture was stirred for 53 h at 80 °C. After cooling to room temperature, the mixture was extracted by dichloromethane. The crude product was purified by silica gel column chromatography eluted with hexane/dichloromethane (4:1) to yield **10** as a yellow powder (4.5 mg, 0.007 mmol, 3.5 %); ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 7.82 (s, 4H), 7.66 (d, J = 8.0 Hz, 4H), 7.24 (t, J = ~8 Hz, 4H; overlapped with the solvent residue), 6.81 (t, J = 7.2 Hz, 4H), 6.08 (d, J = 7.4 Hz, 4H), 5.18 (s, 4H), 1.49 (s, 18H).

^{1}H and ^{13}C NMR Spectra

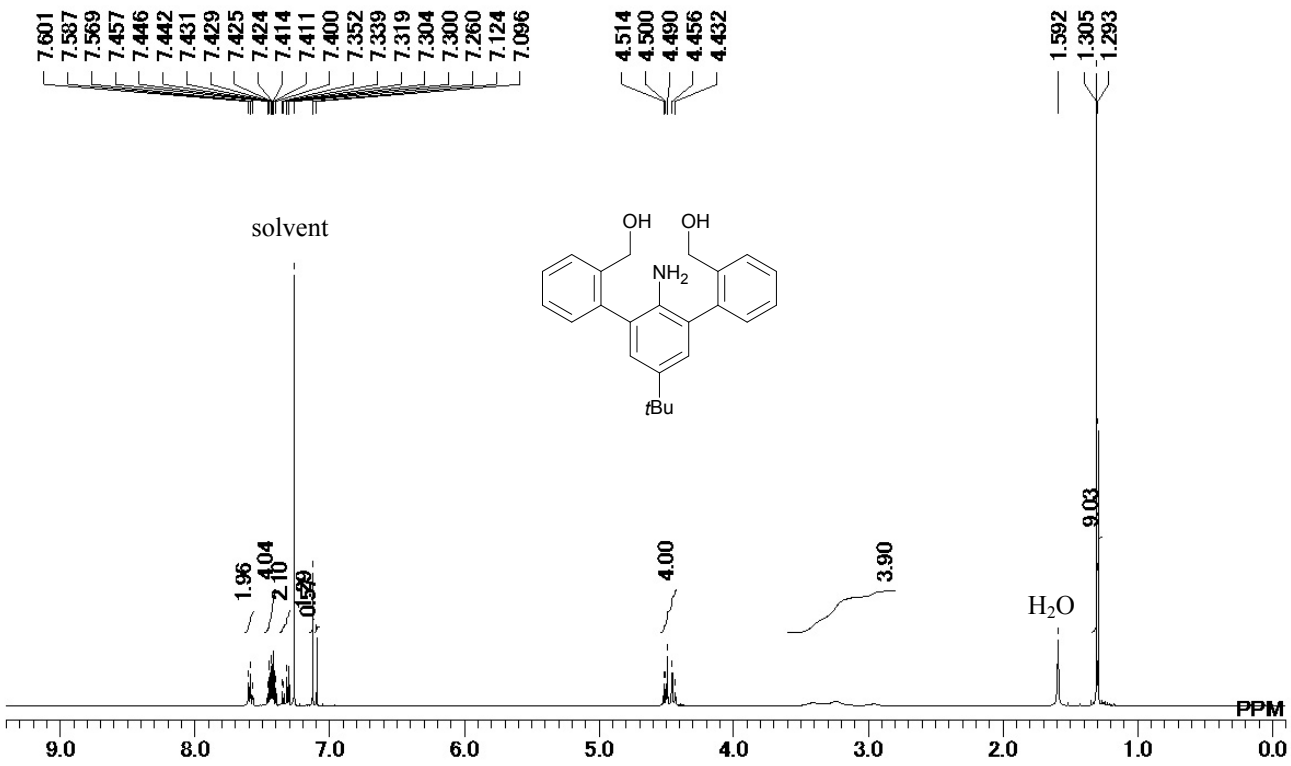


Figure S1. ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$).

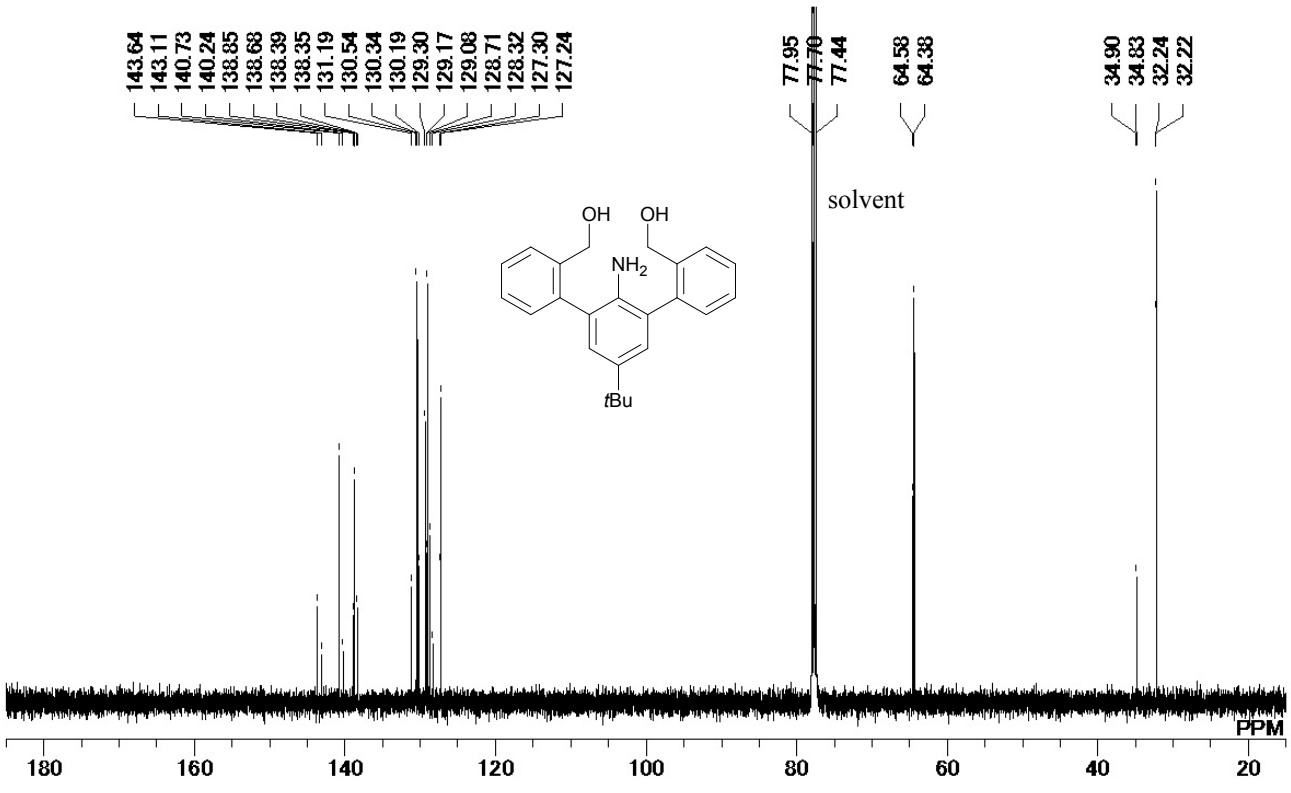


Figure S2. ^{13}C NMR spectrum of **3** (126 MHz, $CDCl_3$).

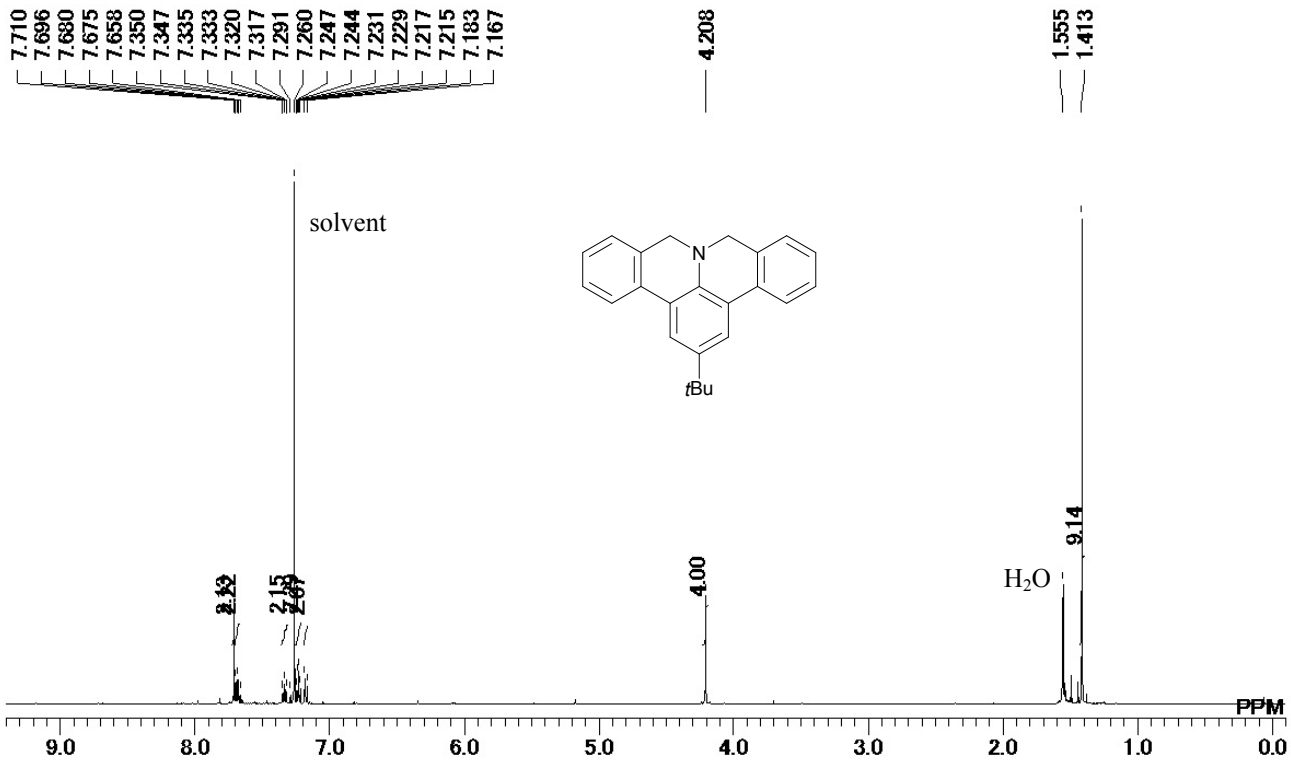


Figure S3. ^{1}H NMR spectrum of **4** (500 MHz, $CDCl_3$).

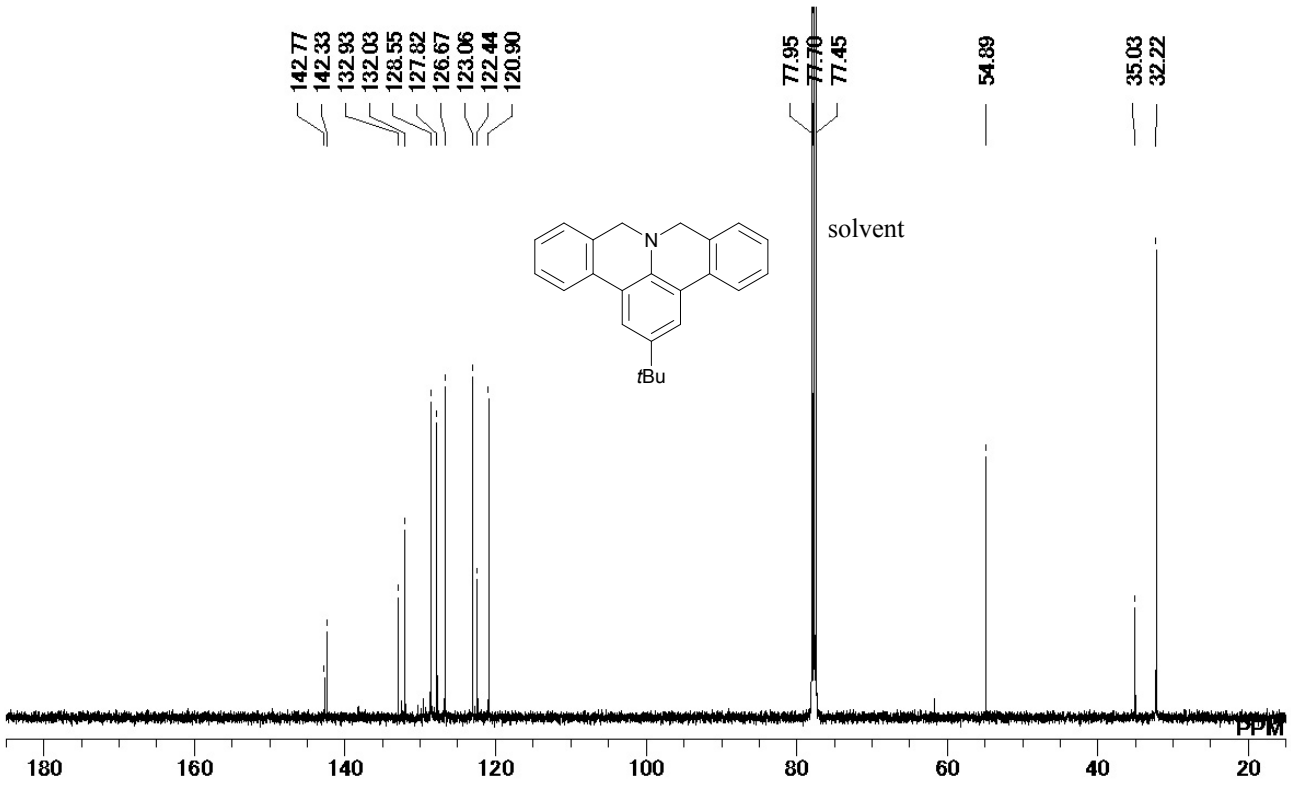


Figure S4. ^{13}C NMR spectrum of **4** (126 MHz, $CDCl_3$).

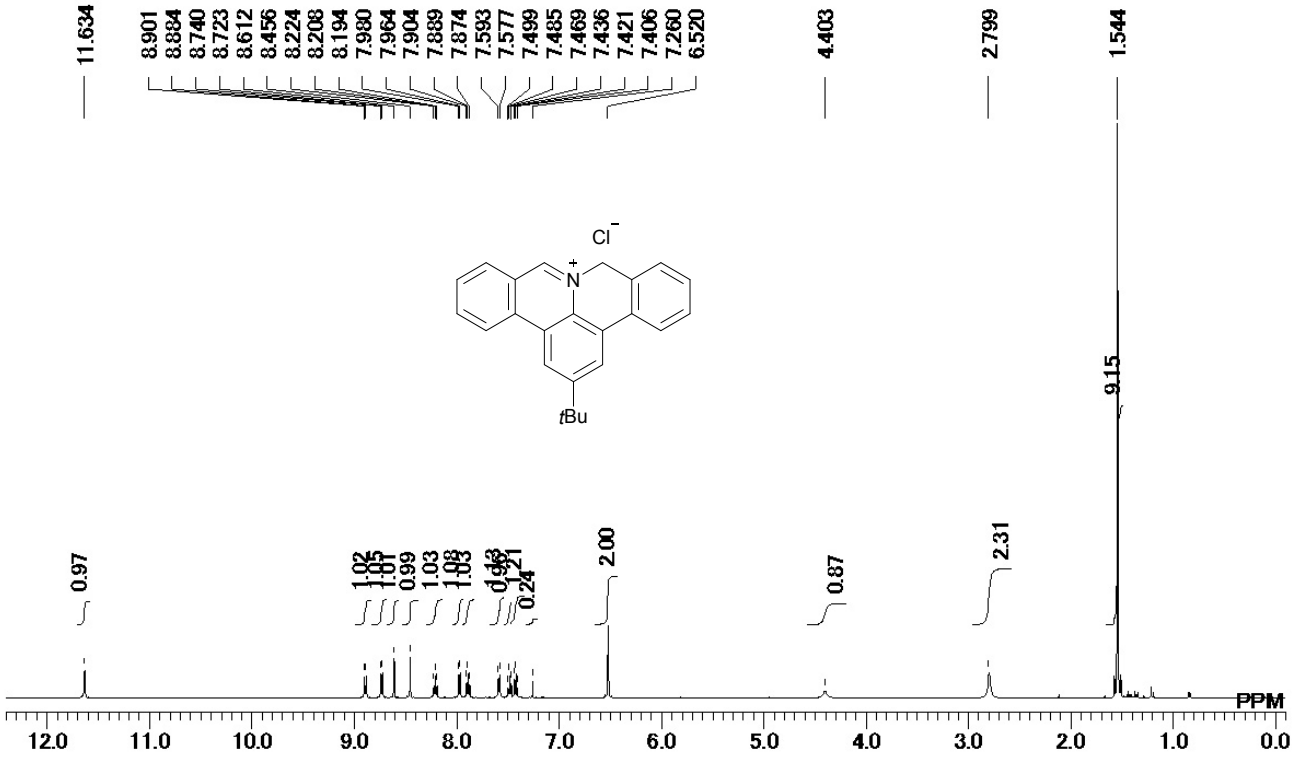


Figure S5. ^{1}H NMR spectrum of **5** (500 MHz, $CDCl_3$).

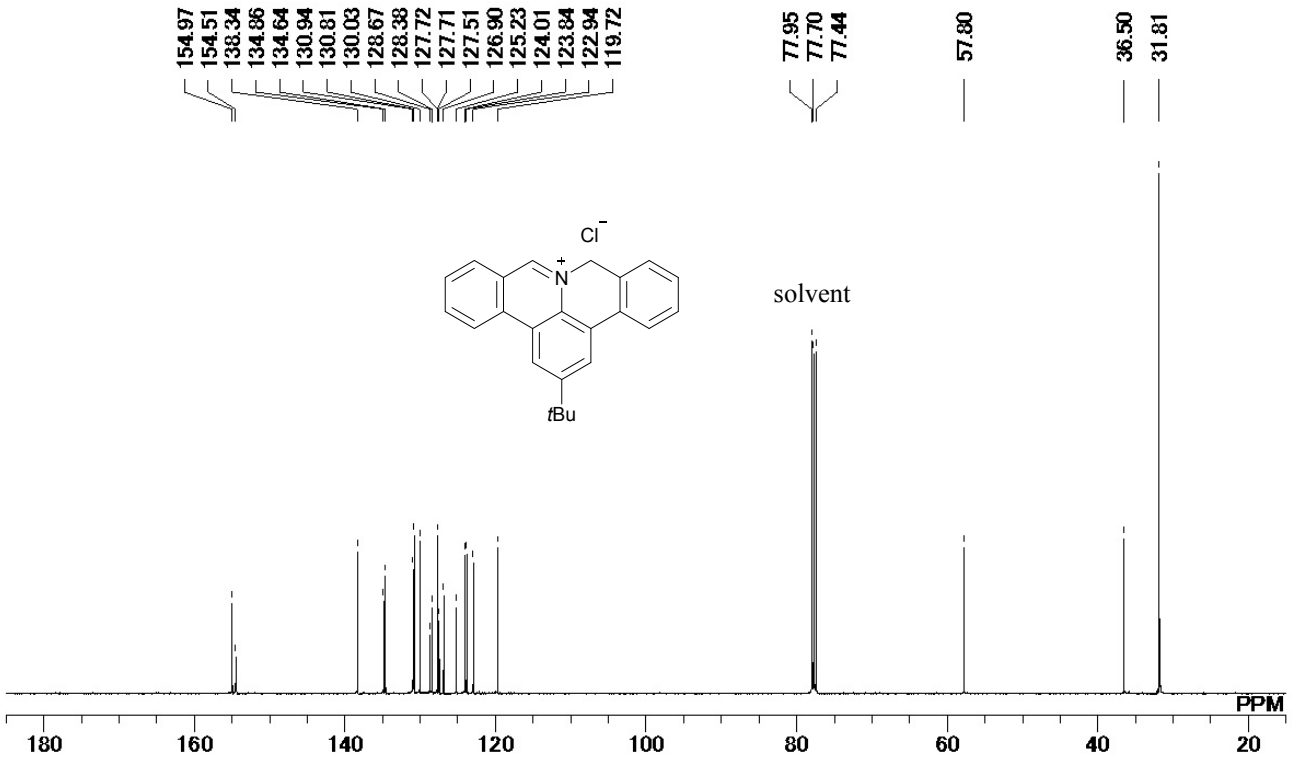


Figure S6. ^{13}C NMR spectrum of **5** (126 MHz, $CDCl_3$).

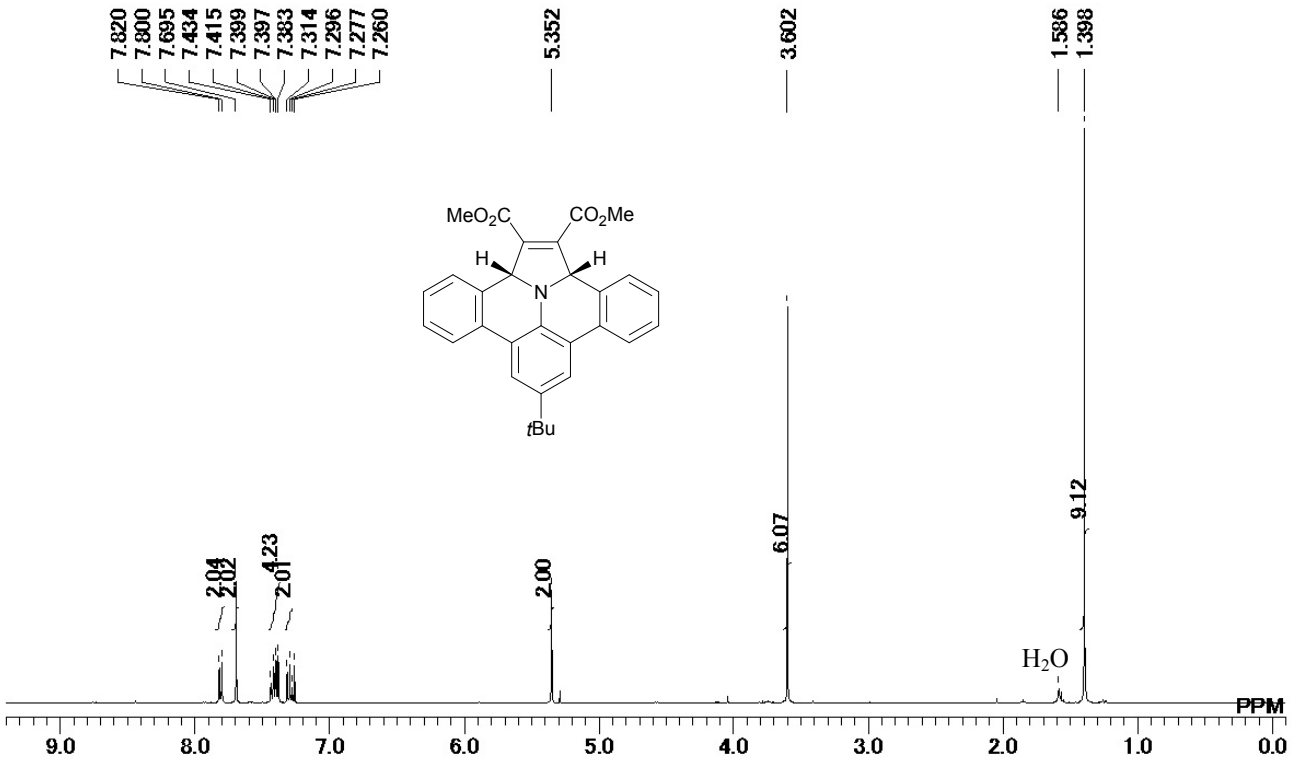


Figure S7. ^{1}H NMR spectrum of **7a** (500 MHz, $CDCl_3$).

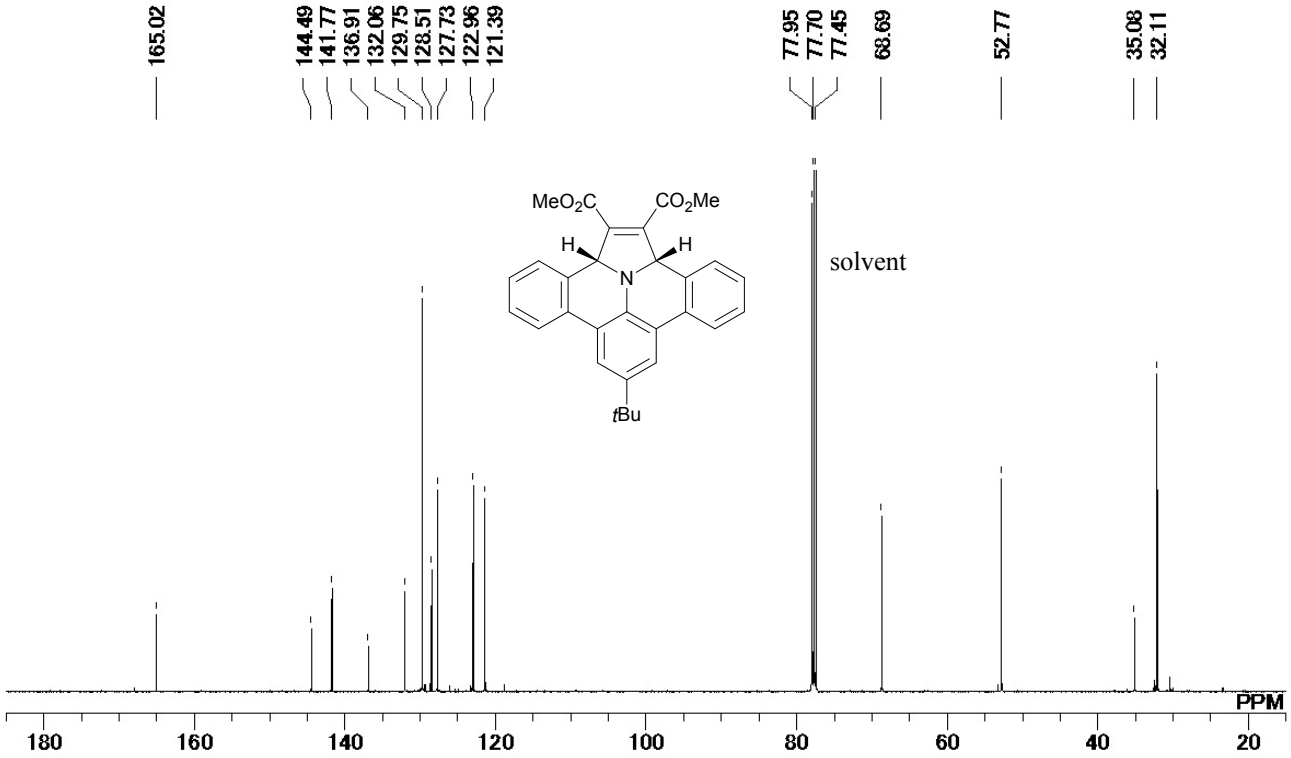


Figure S8. ^{13}C NMR spectrum of **7a** (126 MHz, $CDCl_3$).

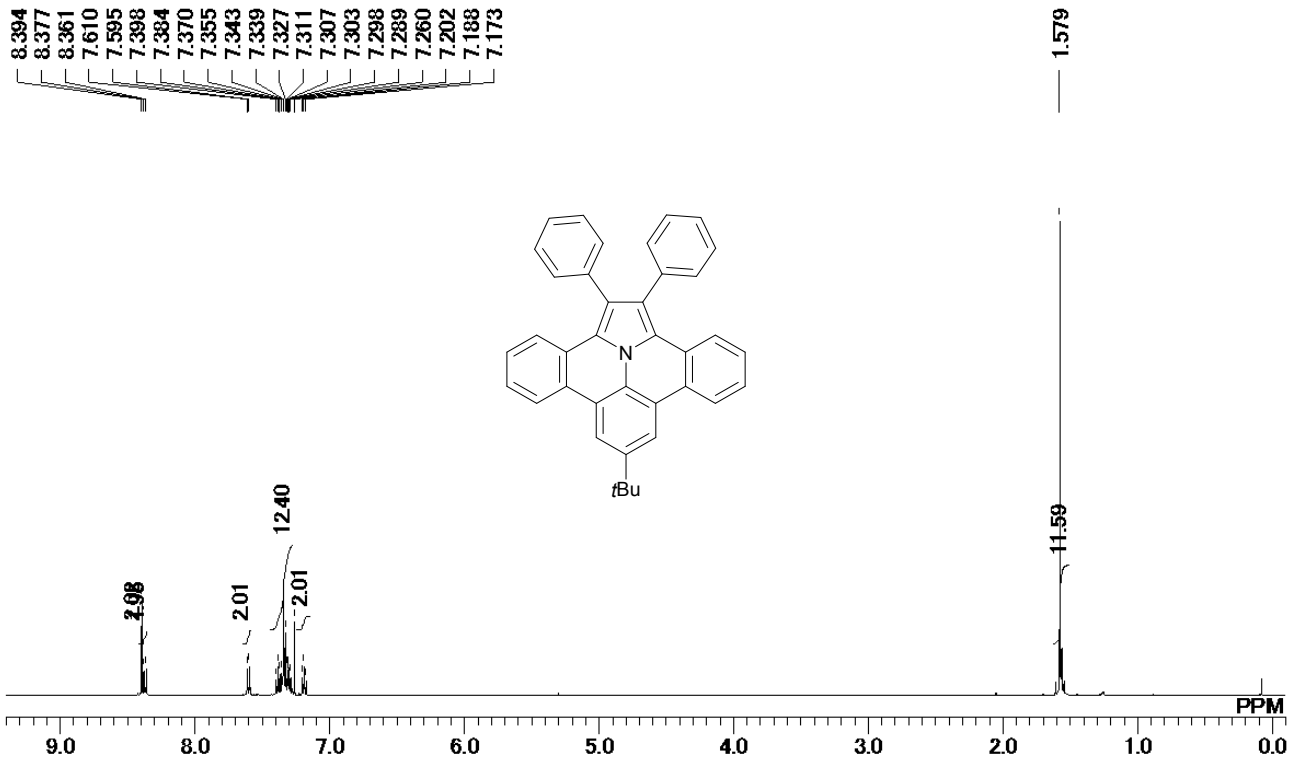


Figure S9. ^{1}H NMR spectrum of **8b** (500 MHz, $CDCl_3$).

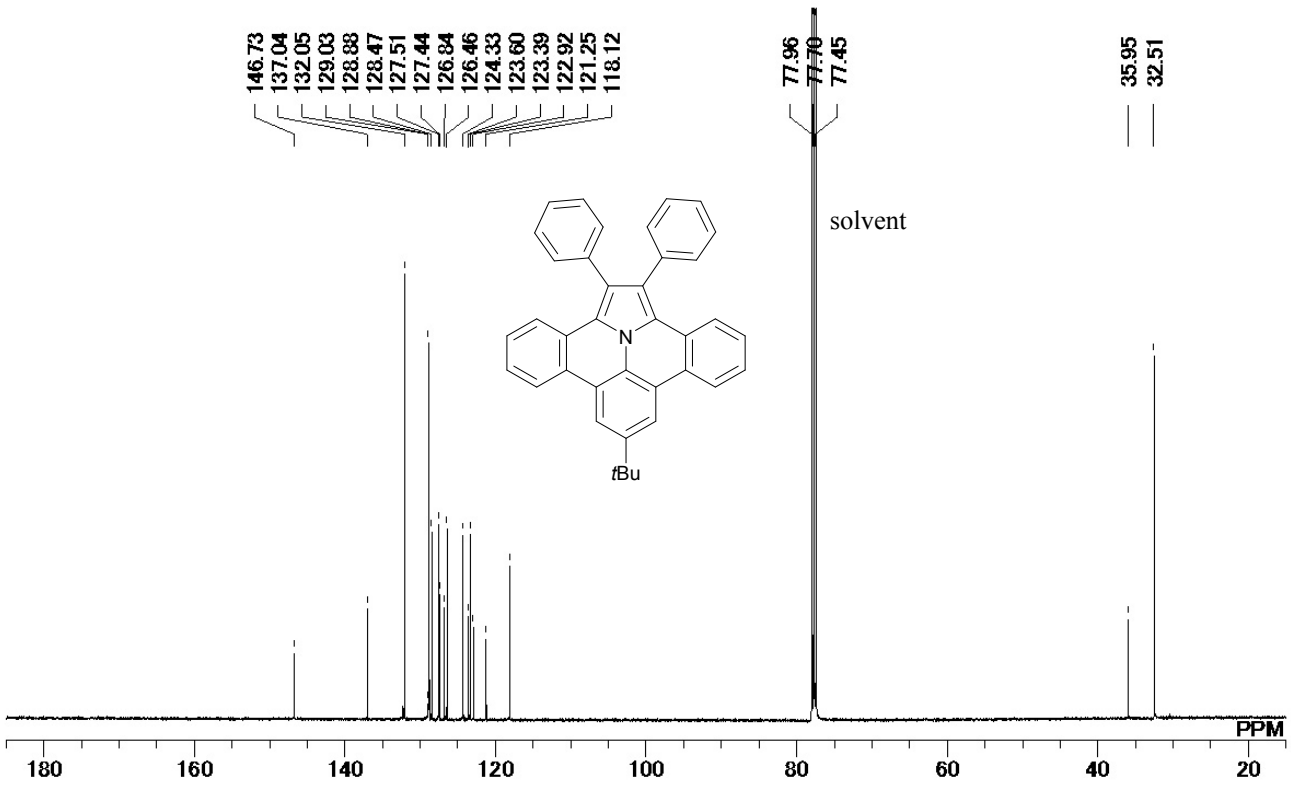


Figure S10. ^{13}C NMR spectrum of **8b** (126 MHz, $CDCl_3$).

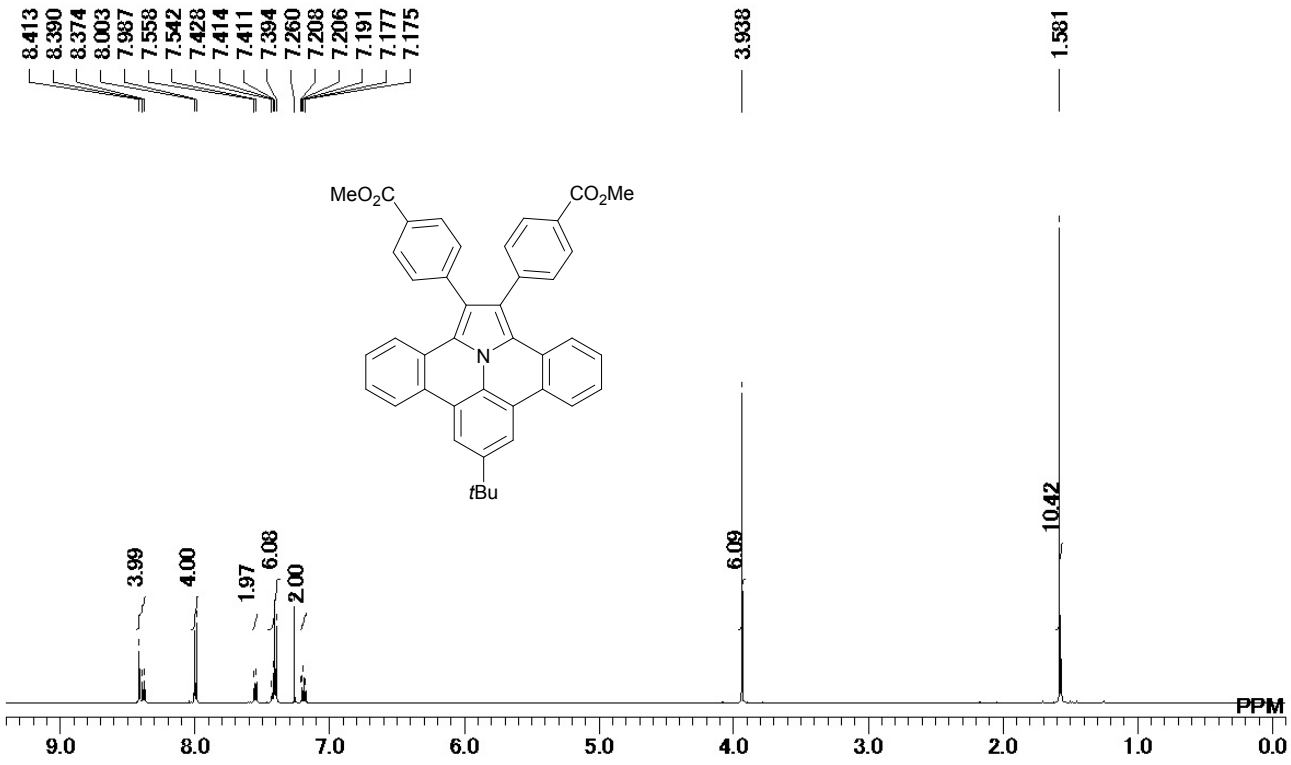


Figure S11. ^{1}H NMR spectrum of **8c** (500 MHz, $CDCl_3$).

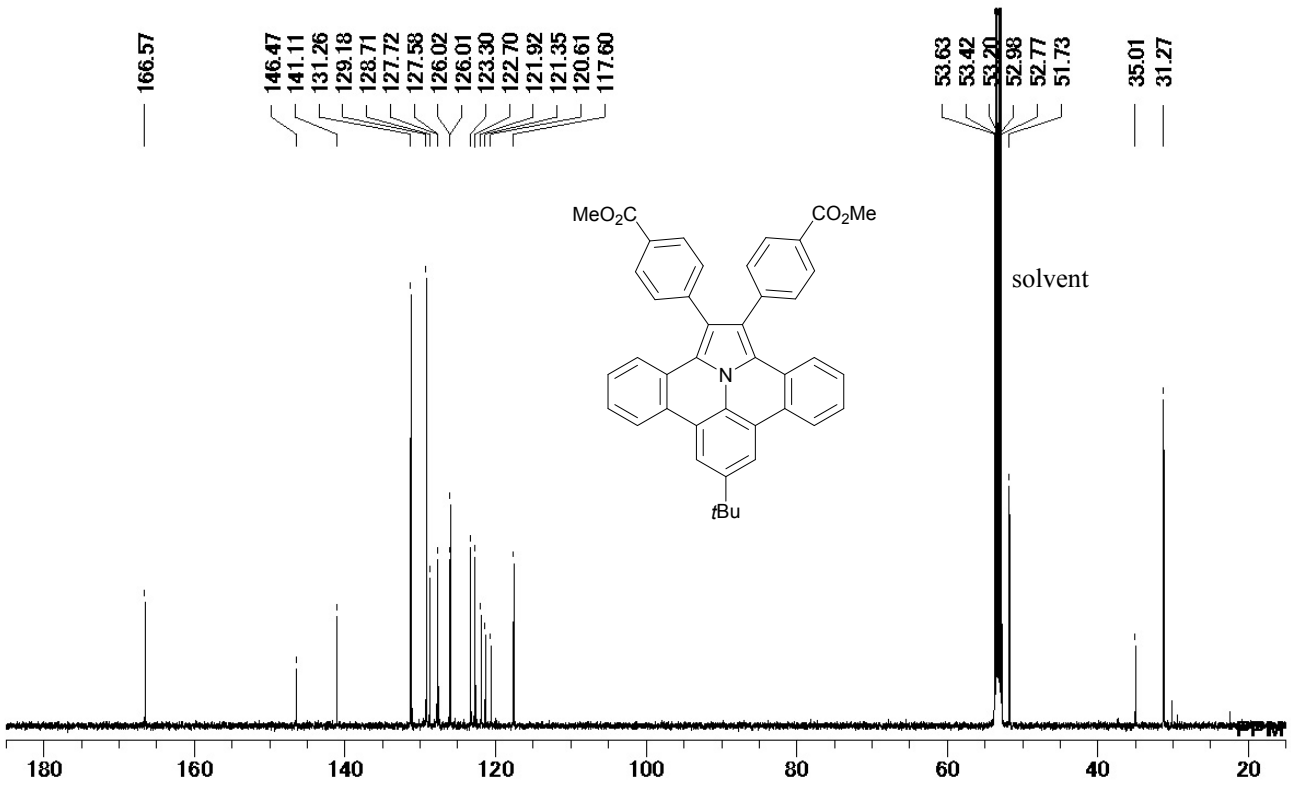


Figure S12. ^{13}C NMR spectrum of **8c** (126 MHz, CD_2Cl_2).

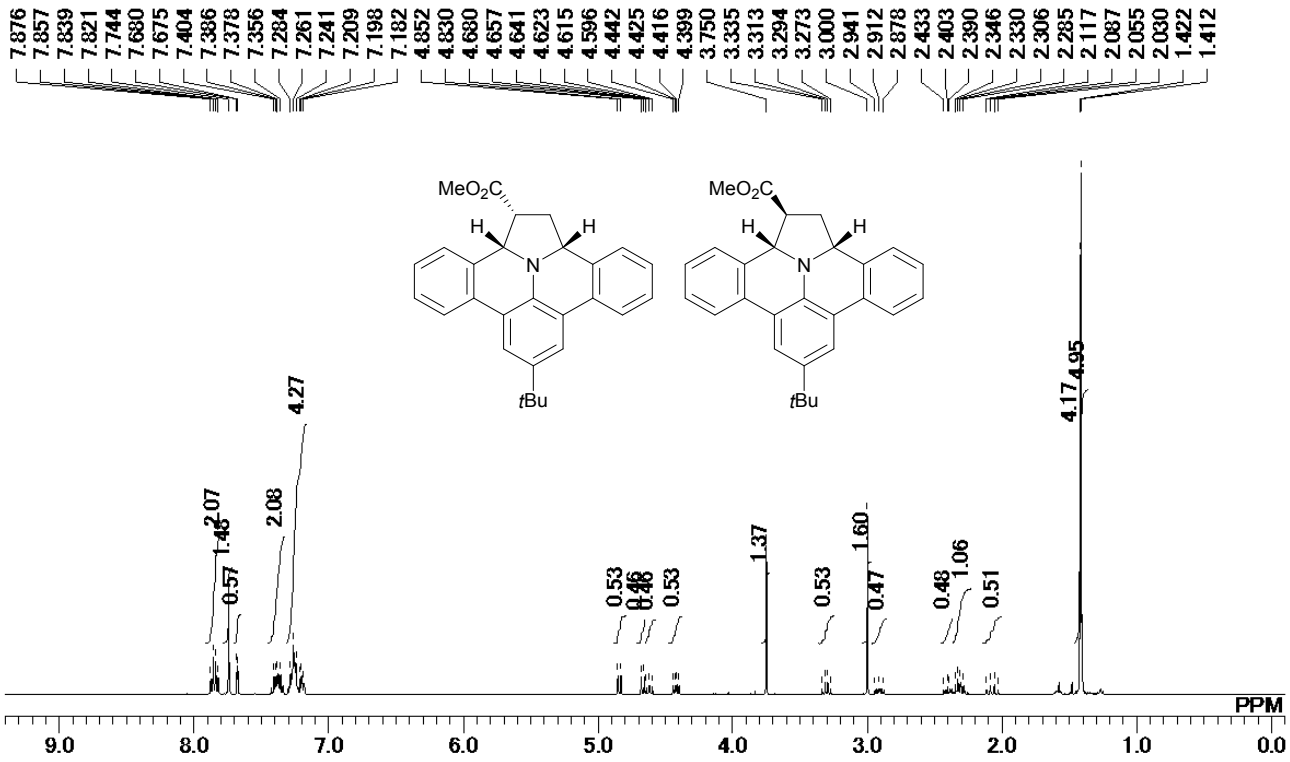


Figure S13. ^{1}H NMR spectrum of **6d** (400 MHz, $CDCl_3$).

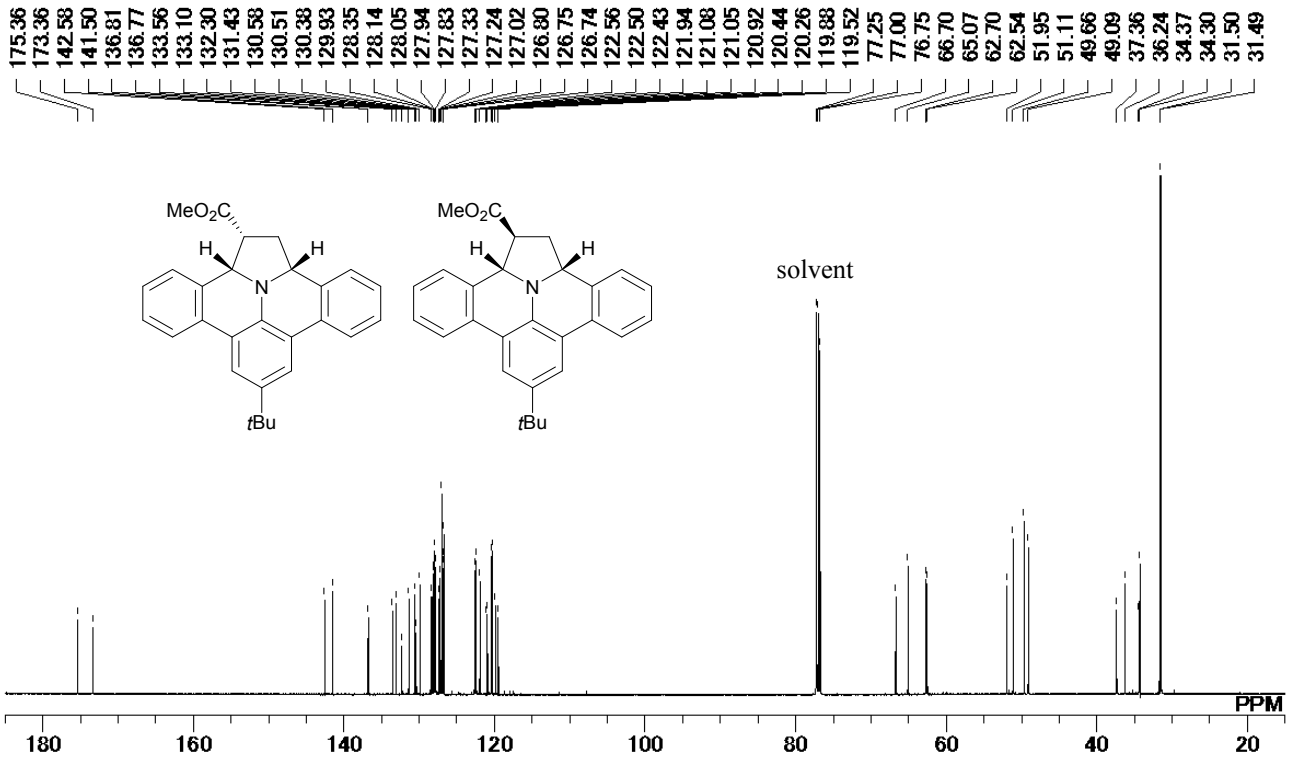


Figure S14. ^{13}C NMR spectrum of **6d** (126 MHz, $CDCl_3$).

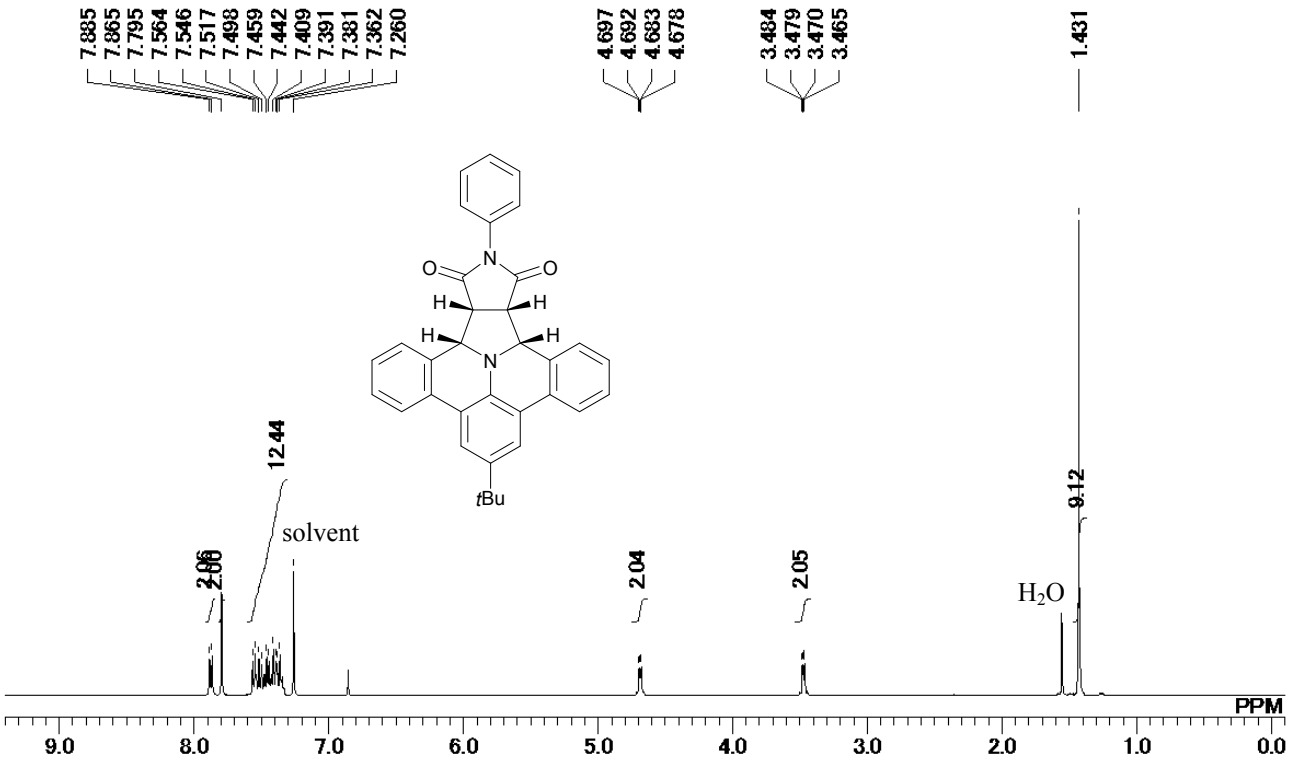


Figure S15. ^{1}H NMR spectrum of **6e-*endo*** (500 MHz, $CDCl_3$).

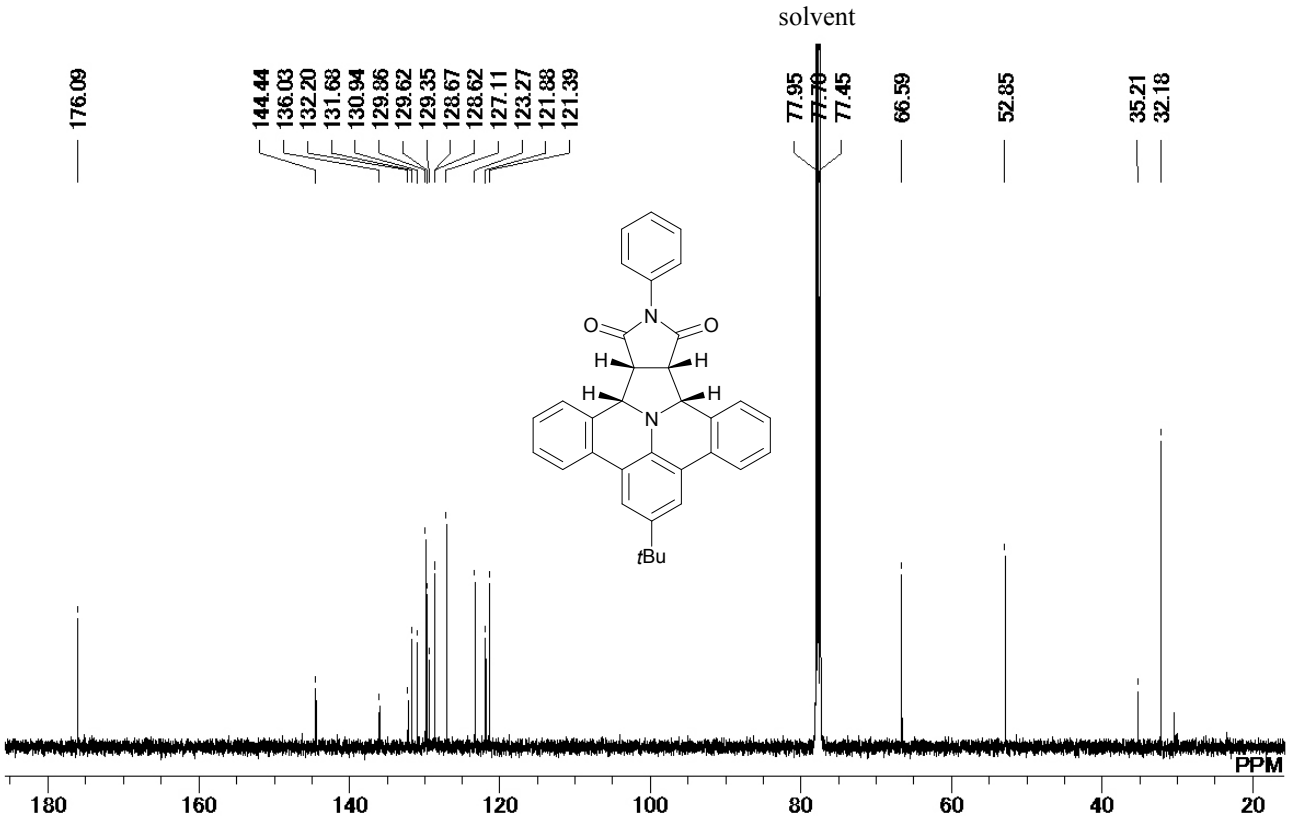


Figure S16. ^{13}C NMR spectrum of **6e-*endo*** (126 MHz, $CDCl_3$).

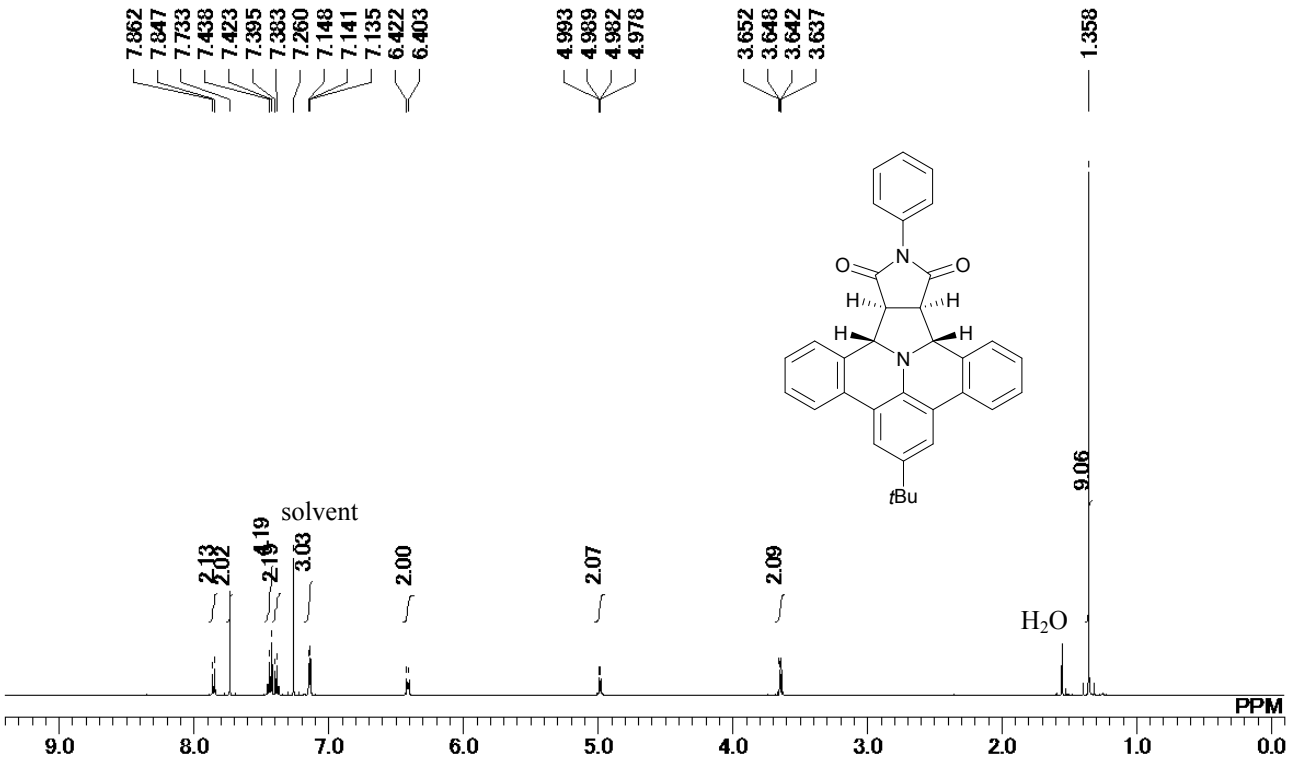


Figure S17. ^{1}H NMR spectrum of **6e-*exo*** (500 MHz, $CDCl_3$).

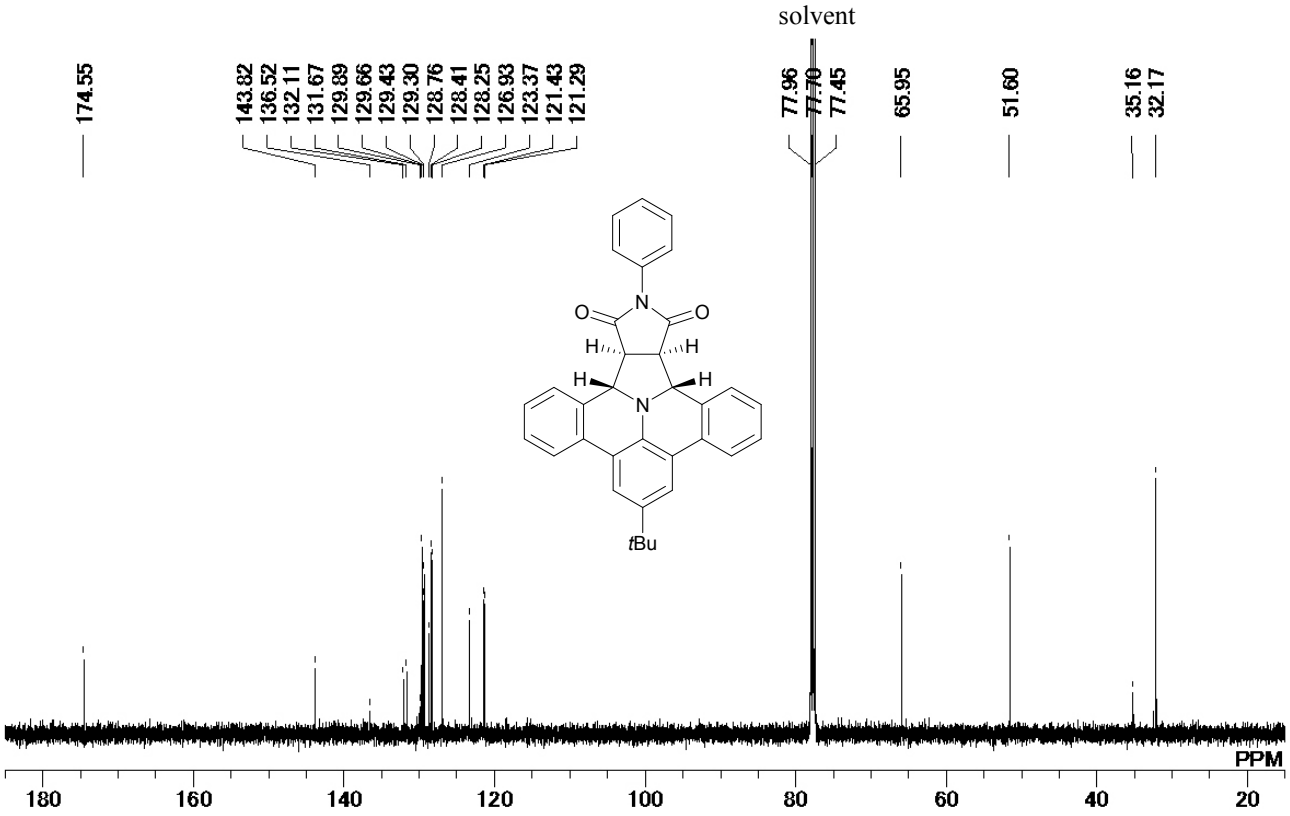


Figure S18. ^{13}C NMR spectrum of **6e-*exo*** (126 MHz, $CDCl_3$).

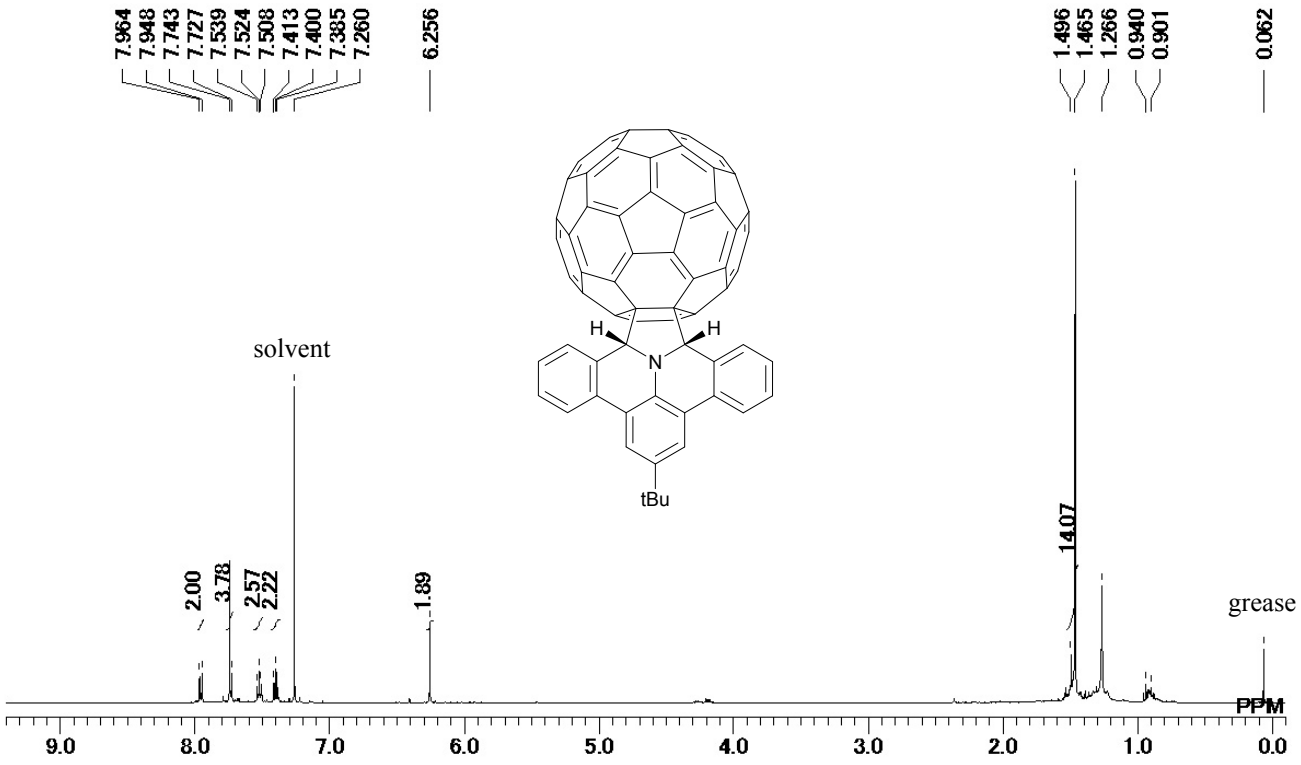


Figure S19. ^{1}H NMR spectrum of **9** (500 MHz, $CDCl_3$).

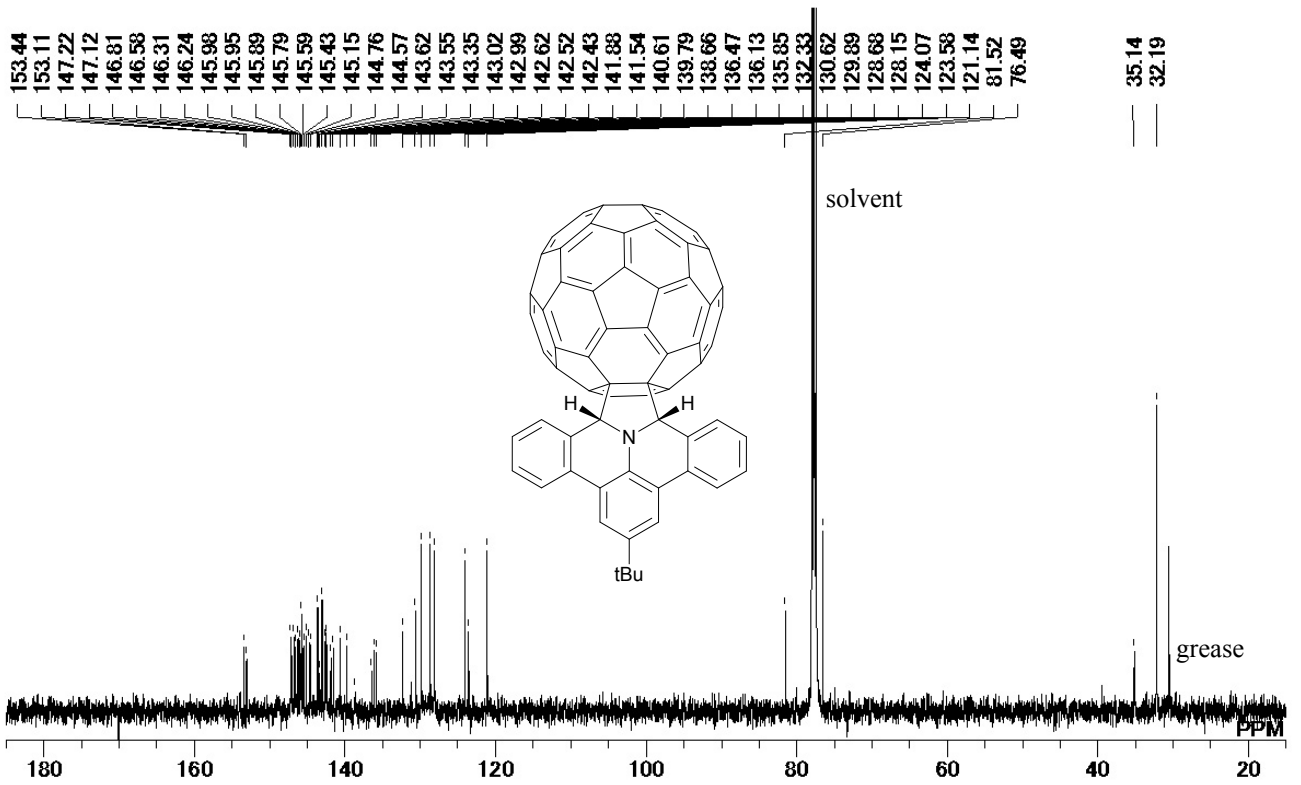


Figure S20. ^{13}C NMR spectrum of **9** (126 MHz, $CDCl_3$).

HRMS Spectra

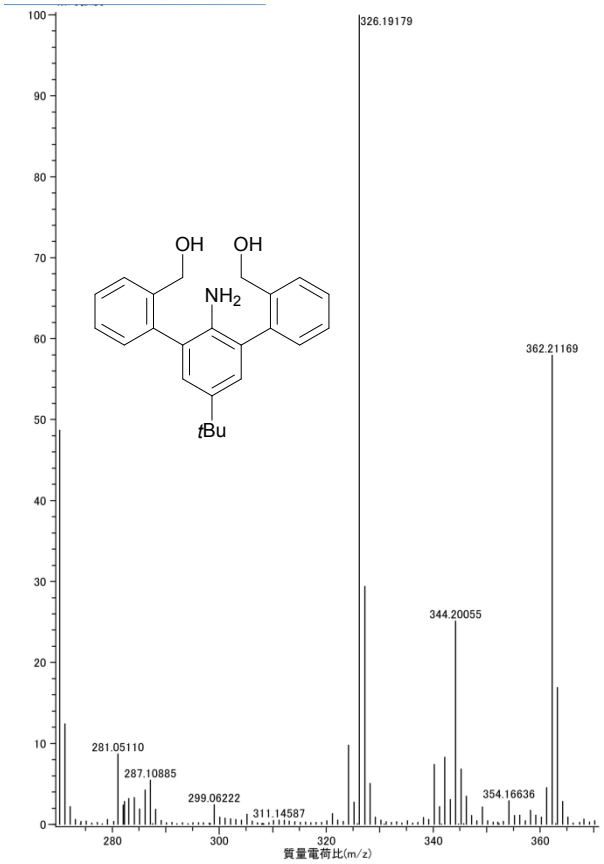


Figure S21. HRMS spectrum of **3**.

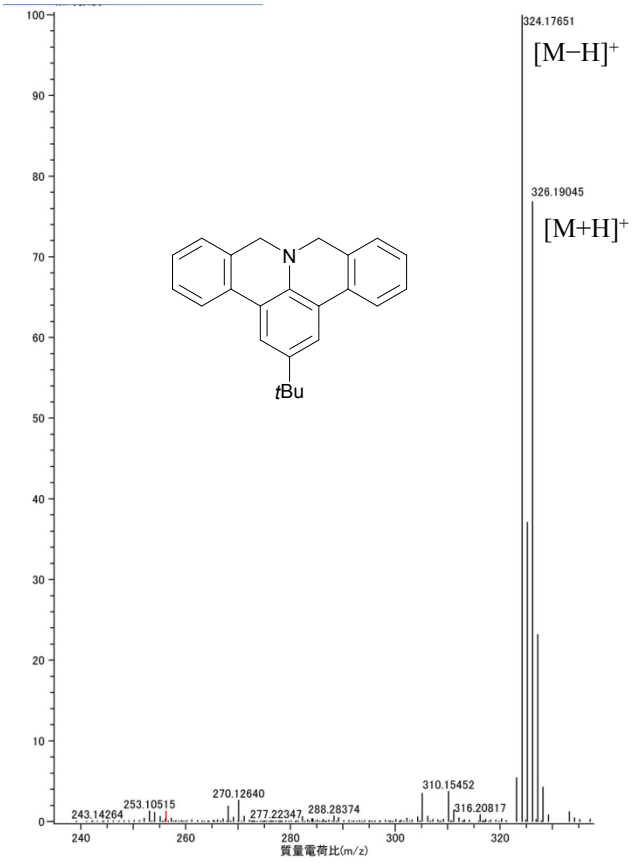


Figure S22. HRMS spectrum of **4**.

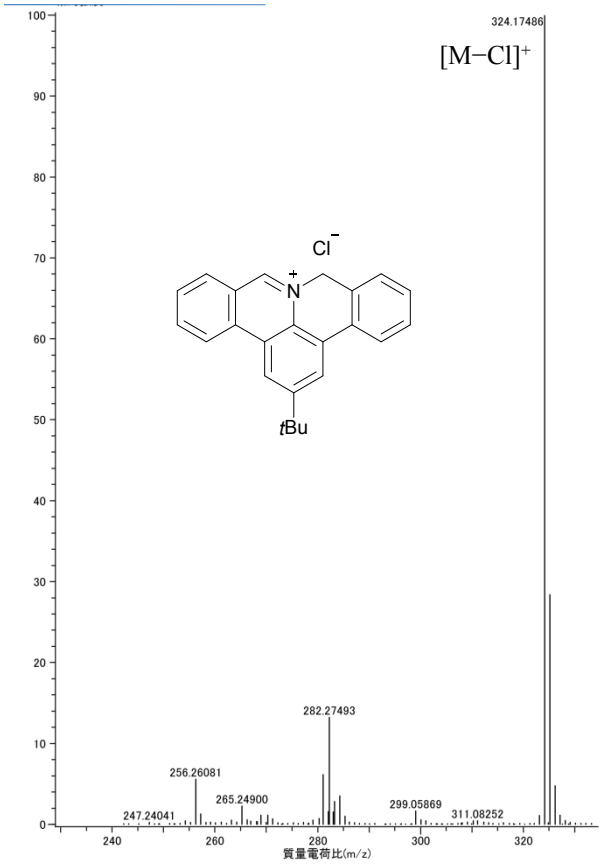


Figure S23. HRMS spectrum of **5**.

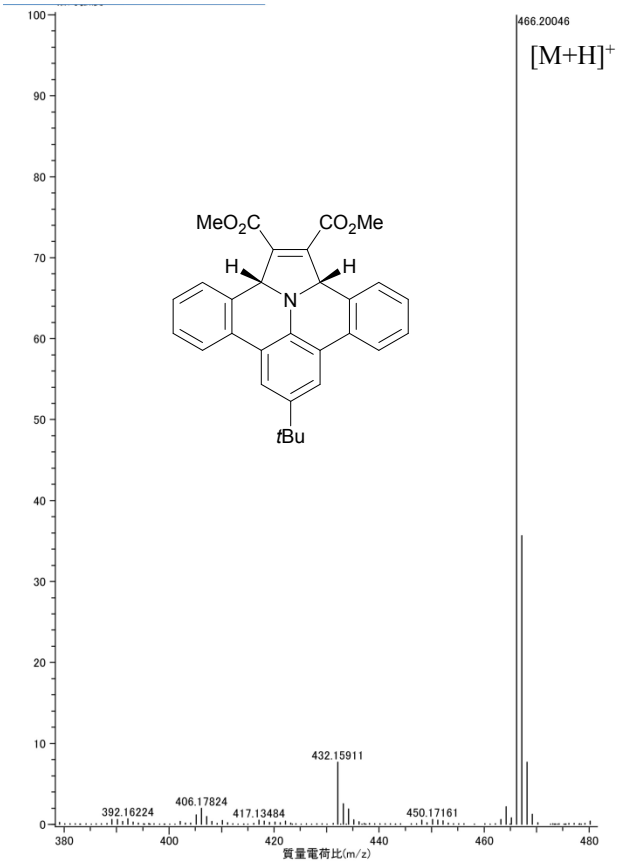


Figure S24. HRMS spectrum of **7a**.

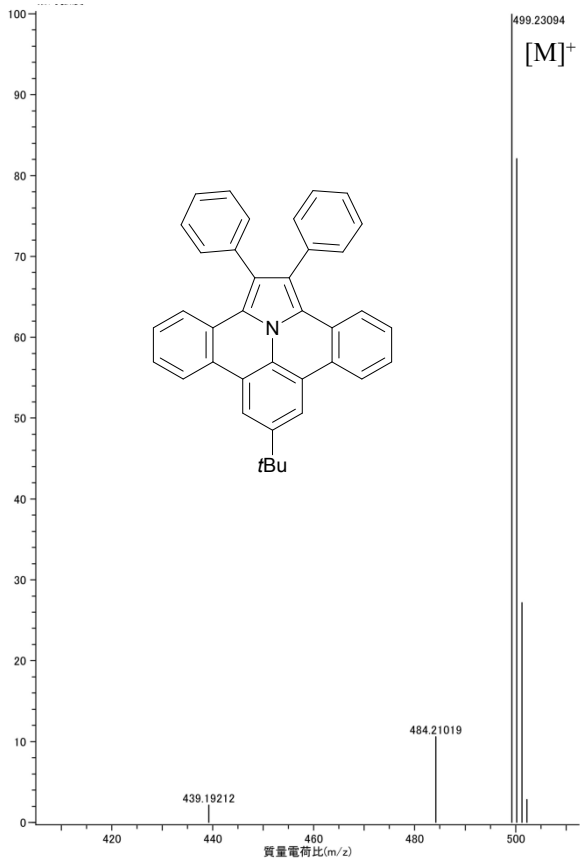


Figure S25. HRMS spectrum of **8b**.

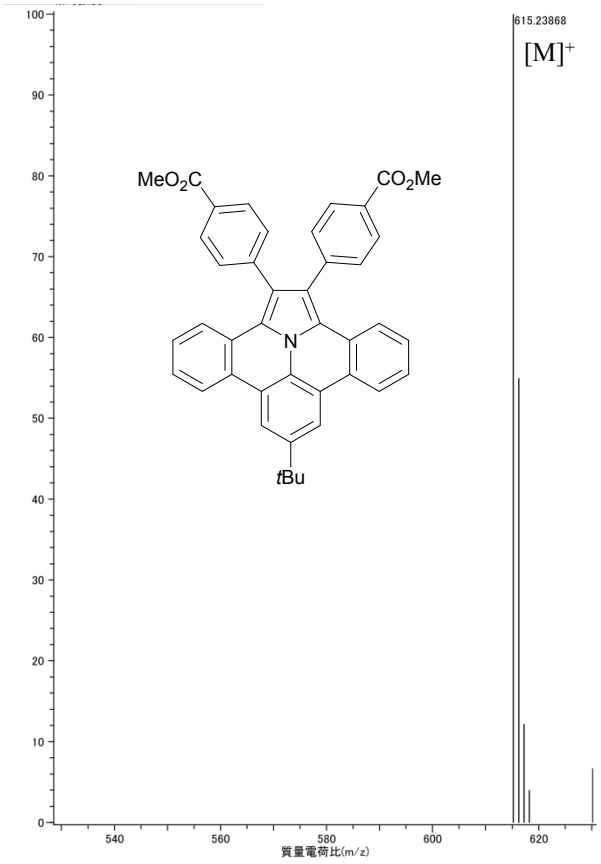


Figure S26. HRMS spectrum of **8c**.

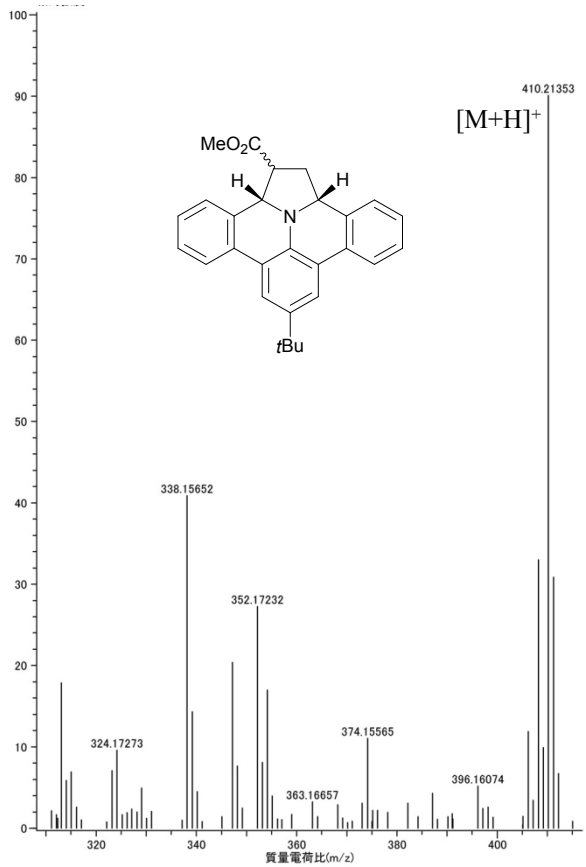


Figure S27. HRMS spectrum of **6d**.

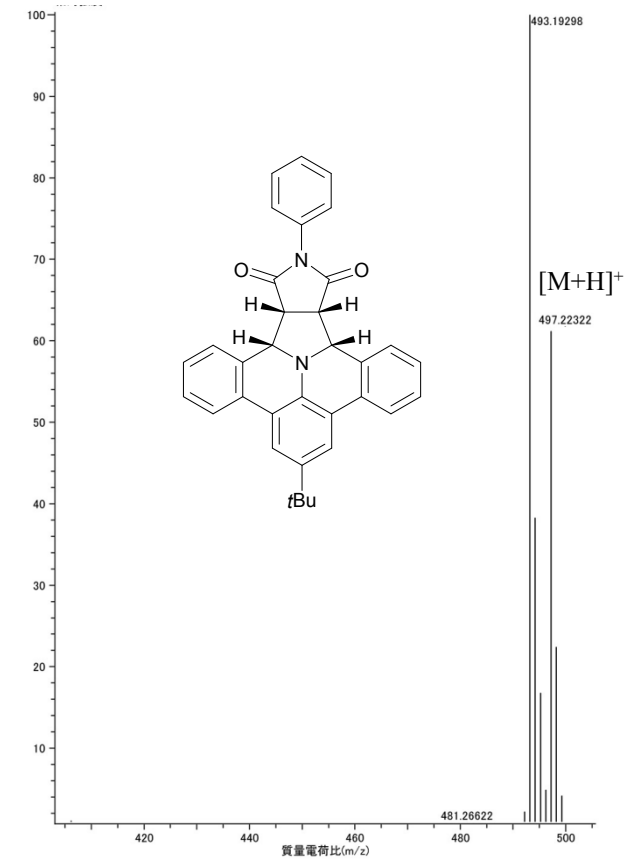


Figure S28. HRMS spectrum of **6e-*endo***.

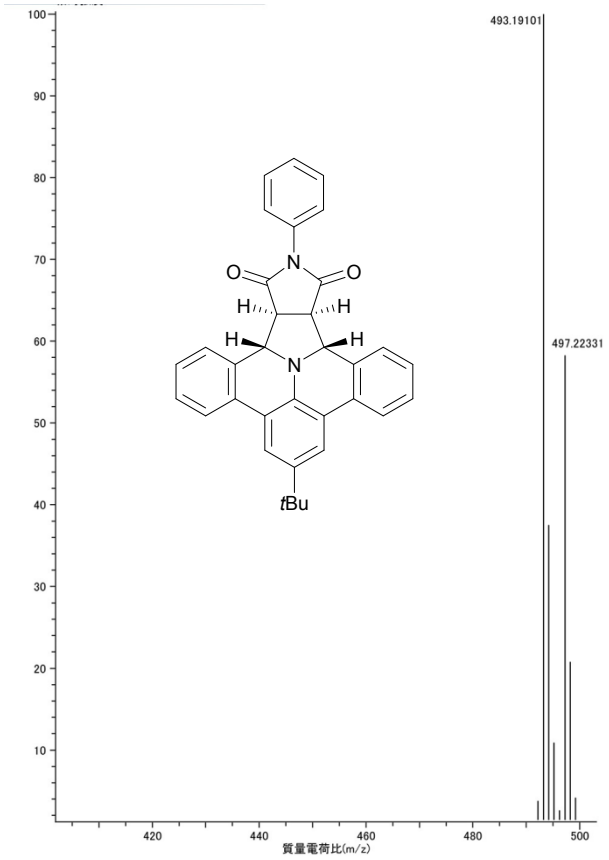


Figure S29. HRMS spectrum of **6e-*exo***.

X-Ray Crystallographic Data

Table S1. Crystal data and structure refinement for **7a**, **8b**, and **8c**.

Compound		**7a**	**8b**	**8c**
CCDC number		1019909	1019910	1019911
Molecular formula		$C_{30}H_{27}NO_4$	$C_{38}H_{29}N$	$C_{42}H_{33}NO_4$
Formula weight		465.53	499.62	615.69
Temperature (K)		93(2)	93(2)	93(2)
Wavelength (Å)		0.71075	0.71075	0.71075
Crystal system		Monoclinic	Orthorhombic	Orthorhombic
Space group		$P2_1/c$	*P*bca	*P*bca
Unit cell dimensions	a (Å)	16.322(6)	8.874(2)	9.666(3)
	b (Å)	9.073(3)	20.520(5)	22.449(6)
	c (Å)	16.857(6)	29.114(7)	29.445(8)
	α (°)	90	90	90
	β (°)	114.032(4)	90	90
	γ (°)	90	90	90
Volume (Å^3)		2280.0(14)	5248(2)	6389(3)
Z		4	8	8
Density (calculated) (Mg·m^{-3})		1.356	1.265	1.280
Absorption coefficient (mm^{-1})		0.090	0.072	0.082
F(000)		984	2112	2592
Crystal size (mm^3)		0.30×0.15×0.10	0.20×0.15×0.10	0.30×0.15×0.10
Theta range (°)		2.93–25.00	2.71–25.00	2.68–25.00
Index ranges		−19<=h<=19	−9<=h<=10	−11<=h<=11
		−10<=k<=10	−24<=h<=24	−23<=k<=26
		−20<=l<=20	−32<=l<=34	−34<=k<=35
Reflections collected		14803	32588	39918
Independent reflections		4011	4631	5622
R(int)		0.0586	0.0671	0.0851
Max. and min. transmission		0.9736, 0.9911	0.9857, 0.9928	0.9759, 0. 9919
Data / restraints / parameters		4011 / 0 / 321	4631 / 0 / 355	5622 / 0 / 429
Goodness-of-fit on F^2		1.167	1.143	1.301
Final *R* indices [$I > 2\sigma(I)$]		$R_1 = 0.0676$	$R_1 = 0.0592$	$R_1 = 0.0799$
		w$R_2 = 0.1240$	w$R_2 = 0.1202$	w$R_2 = 0.1425$
R indices (all data) [$I > 2\sigma(I)$]		$R_1 = 0.0820$	$R_1 = 0.0723$	$R_1 = 0.0865$
		w$R_2 = 0.1310$	w$R_2 = 0.1272$	w$R_2 = 0.1455$
Absolute structure parameter		---	---	---
Largest diff. peak and hole (e.Å^{-3})		0.197, −0.232	0.244, −0.233	0.226, −0.268