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Supporting Information

Development of Emissive Aminopentaazaphenalene Derivatives Employing Design Strategy for Obtaining Luminescent Conjugated Molecules by Modulating Symmetry of Molecule Orbitals with the Substituent Effect

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Table of Contents

1. General

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on JEOL JNM-EX400 or JNM-AL400 spectrometers. ^{1}H and ^{13}C spectra were recorded by using tetramethylsilane (TMS) as an internal standard in $CDCl_3$. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher EXACTIVE for electron spray ionization (ESI). UV–vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4P spectrofluorometer. The absolute quantum yield was calculated by the integrating sphere method on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. The wavelength dependency of the detection sensitivity was corrected by the built-in program of Fluoromax-4. PL lifetime measurement was performed on a HORIBA FluoroCube spectrofluorometer system; excitation was carried out using a UV diode laser (NanoLED 375nm). The time resolution is ensured as 1.38×10^{-11} s. The lifetimes are described in 0.01 ns order. Cyclic voltammetry (CV) was carried out on a BAS ALS-Electrochemical-Analyzer Model 600D with a glassy carbon working electrode, a Pt counter electrode, an Ag/Ag^{+} reference electrode, and the ferrocene/ferrocenium external reference at a scan rate of 0.05 Vs^{-1}. All reactions were performed under argon atmosphere. X-ray crystallographic analysis was carried out by Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation diffractometer with an imaging plate. The analysis was carried out with direct methods (SHELXL-2014[1]) using Yadokari-XG[2]. Details of the structure refinement are described in the CIF file. The program ORTEP3[3] was used to generate the X-ray structural image.

2. Materials

Reagents (methyl *N*-cyanoacetimidate, 2,6-diaminopyridine, trichloroacetyl chloride, didodecylamine, *N*-bromosuccinimide, tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos), and cesium carbonate) and

solvents (dehydrated pyridine, chloroform, dichloromethane, and toluene) were purchased from commercial sources and used without further purification. Glyme (1,2-dimethoxyethane) was purchased from commercial source and degassed by Ar bubbling before use. Water for the Suzuki–Miyaura cross coupling reactions was degassed by Ar bubbling before use.

3. Synthetic Procedures

• *N*-Cyano-*N*′-(6-amino-2-pyridyl)acetamidine (**1**)

This compound was synthesized according to the literatures.[4,5] ^{1}H NMR (DMSO-d_6, ppm): 10.62 (s, 1H, NH), 7.45 (t, J = 8.0 Hz, 1H, Ar), 7.27 (d, J = 7.9 Hz, 1H, Ar), 6.33 (d, J = 7.9 Hz, 1H, Ar), 5.96 (s, 2H, NH_2), 2.47 (s, 3H, Me). ^{13}C NMR (DMSO-d_6, ppm): 170.7, 158.6, 148.8, 138.9, 116.5, 105.1, 103.0, 21.6. HRMS (p-ESI) calcd. for $C_8H_9N_5$+H $[M+H]^+$ 176.0932, found 176.0931.

• 2-Methyl-5-trichloromethyl-1,3,4,6,9b-pentaazaphenalene (**2**)

To a stirred cold slurry (0 °C) of **1** (10.0 g, 57 mmol) and dehydrated pyridine (5 mL, 57 mmol) in 100 mL of degassed glyme was slowly added trichloromethyl chloride (25 g, 140 mmol). Then the reaction mixture was refluxed for 4 h. (Gaseous HCl was evolved and trapped by saturated $NaHCO_3$ aq.) The reaction mixture was cooled to room temperature and quenched by the slow addition of MeOH (20 mL) and saturated $NaHCO_3$ aq. (ca. 100 mL, gaseous CO_2 was evolved). The mixture was extracted with 3 × 100 mL of $CHCl_3$ and the combined organic layers were washed with water (3 × 100 mL) and brine (1 × 100mL). Then the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed by a rotary evaporator. Recrystallization from $CHCl_3$ / MeOH (70 °C) gave **2** as a purple crystalline solid (9.62 g, 32 mmol, 56%). ^{1}H NMR ($CDCl_3$, ppm): 7.38 (t, J = 8.4 Hz, 1H, 5AP), 6.32 (dd, J = 8.4 Hz, 1.2 Hz, 1H, 5AP), 6.25 (dd, J = 8.4 Hz, 1.2 Hz, 1H, 5AP), 2.08 (s, 3H, Me) ^{13}C NMR (CD_2Cl_2): 179.1, 172.9, 162.5, 155.8, 154.7, 147.0, 114.4, 112.9, 95.0, 25.9. HRMS (p-ESI) calcd. for $C_{10}H_6Cl_3N_5$+H $[M+H]^+$ 301.9762, found 301.9759.

• 2-Didodecylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**3**)

The chloroform (50 mL) solution of **2** (2.67 g, 8.82 mmol) and didodecylamine (12.6 g, 35.6 mmol) was refluxed for 36 h. After cooling to room temperature, the solvent was removed by a rotary evaporator. The residual solid was purified by column chromatography on silica gel (eluent: $CHCl_3$ / EtOAc (v/v) = 8:1, then 20:1). After removal of the solvent, the product was obtained as a yellow solid (0.536 g, 1.0 mmol, 11%). ^{1}H NMR (CD_2Cl_2, ppm): 7.20 (t, *J* = 8.1 Hz, 1H, 5AP), 6.00 (d, *J* = 8.1 Hz, 1H, 5AP), 5.89 (d, *J* = 8.1 Hz, 1H, 5AP), 3.4–3.5 (m, *J* = 7.3 Hz, 4H, NC*H*$_2$), 2.04 (s, 3H, 5AP-C*H*$_3$), 1.0–1.4 (br, 40H, alkyl), 0.88 (br m, 6H, methyl in dodecyl groups). ^{13}C NMR (CD_2Cl_2, ppm): 174.5, 161.0, 157.7, 155.2, 153.0, 144.1, 109.7, 104.9, 47.7, 47.6, 32.3, 30.06, 30.04, 30.01, 29.95, 29.92, 29.75, 29.69, 28.7, 28.2, 27.3, 27.2, 26.0, 23.1, 14.3. Some peaks of two nonequivalent (due to the planarity around amino group) dodecyl groups were overlapped (in all A5AP derivatives). HRMS (p-ESI) calcd. for $C_{33}H_{56}N_6$+H $[M+H]^+$ 537.4639, found 537.4635.

• 7,9-Dibromo-2-dodecylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4**)

A dichloromethane (10 mL) solution of **3** (0.528 g, 0.984 mmol) and *N*-bromosuccinimide (0.357 g, 2.00 mmol) was stirred at room temperature for 46 h. Then the solvent was removed by a rotary evaporator. The crude material was dissolved in *n*-hexane, and the mixture was filtrated. After condensation, the residue was purified by column chromatography on silica gel (eluent: $CHCl_3$). The solvent was evaporated, and the *n*-hexane solution of the product was slowly evaporated to give the product as a red solid (0.617 g, 0.89 mmol, 91%). ^{1}H NMR (CD_2Cl_2, ppm): 7.83 (s, 1H, 5AP), 3.4–3.6 (m, 4H, NC*H*$_2$-), 2.16 (s, 3H, 5AP-C*H*$_3$), 1.5–1.7 (br m, 4H, NCH$_2$C*H*$_2$-), 1.1–1.4 (br, 36H, alkyl), 0.87 (br m, 6H, methyl groups of dodecyl groups). ^{13}C NMR (CD_2Cl_2): 175.8, 160.7, 157.4, 151.2, 149.3, 148.8, 101.0, 95.6, 48.5, 48.2, 32.4, 30.08, 30.02, 30.01, 29.88, 29.77, 29.72, 28.6, 28.3, 27.4, 27.3, 26.3, 23.1, 14.3. HRMS (p-ESI) calcd. for $C_{33}H_{54}Br_2N_6$+H $[M+H]^+$ 693.2849, found 693.2848.

•General procedure of the Suzuki−Miyaura cross coupling reaction (**5a**–**5f**)

To a toluene (1 mL) solution of **4** (0.10 mmol), arylboronic acid pinacol ester (0.21 mmol), Pd_2dba_3 (5 μmol), SPhos (20 μmol) and cesium carbonate (1.0 mmol) (an accurate amount of the reagents is described below) was added degassed water (1 mL). The mixture was stirred at 85 °C for 2 d. The reaction mixture was allowed to cool to room temperature and diluted by $CHCl_3$ (50 mL). The organic phase was washed by H_2O (3 × 30 mL) and brine (1 × 30 mL). The organic phase was dried over $MgSO_4$. After filtration, the solvent was removed by a rotary evaporator. The crude material (**5a**, **5b**, **5d**) was purified by column chromatography on silica gel (eluent: $CHCl_3$) and then the solvent was evaporated to give the products. The crude material (**5c**, **5e**, **5f**) was purified by reprecipitation into 50 mL of methanol. An accurate amount of the reagents and the reaction time is described below for each compound.

•7,9-Bis((4-trifluotromethyl)phenyl)-2-dodecylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**5a**)

From **4** (69.52 mg, 0.10 mmol), (4-trifluoromethyl)phenylboronic acid pinacol ester (55.00 mg, 0.20 mmol), Pd_2dba_3 (5.27 mg, 0.0058 mmol), SPhos (8.20 mg, 0.020 mmol) and Cs_2CO_3 (394 mg, 1.2 mmol), the product was obtained as a red oil (0.051 g, 0.062 mmol, 62% yield). ^{1}H NMR (CD_2Cl_2, ppm): 7.66–7.73 (m, 4H, Ar), 7.60–7.65 (m, 4H, Ar), 7.55 (s, 1H, 5AP), 3.2–3.6 (m, 4H, NC*H*$_2$-), 2.10 (s, 3H, 5AP-C*H*$_3$), 1.4–1.7 (br m, 4H, NCH$_2$C*H*$_2$-), 1.0–1.4 (br, 36H, alkyl), 0.87 (br m, 6H, methyl groups of dodecyl groups). ^{13}C NMR (CD_2Cl_2, ppm): 175.0, 160.5, 158.2, 152.6, 150.6, 144.9, 140.6, 140.5, 129.7, 129.0–130.0 (q, $J_{C\text{-}F}$ = 32.1 Hz), 129.5, 128.8–129.8 (q, $J_{C\text{-}F}$ = 32 Hz), 120.5–129.0 (two q peaks, $J_{C\text{-}F}$ = 272.1 Hz), 126.0, 125.3 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.4, 120.7, 119.3, 115.3, 48.4, 48.0, 32.3, 30.1, 30.04, 30.01, 29.99, 29.96, 29.93, 29.90, 29.83, 29.75, 28.68, 28.5, 27.4, 27.3, 26.1, 23.1, 14.3. HRMS (p-ESI) calcd. for $C_{47}H_{62}F_6N_6$+H $[M+H]^+$ 825.5013, found 825.5001.

•7,9-Diphenyl-2-dodecylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**5b**)

From **4** (69.06 mg, 0.10 mmol), phenylboronic acid pinacol ester (42.16 mg, 0.21 mmol), Pd_2dba_3 (4.67 mg, 0.0051 mmol), SPhos (8.69 mg, 0.021 mmol) and Cs_2CO_3 (338 mg, 1.0 mmol), the product was obtained as a red oil after reaction for 34 h (0.033 g, 0.047 mmol, 47% yield). ^{1}H NMR (CD_2Cl_2, ppm): 7.46–7.60 (m, 5H, Ar and 5AP), 7.32–7.40 (m, 4H, Ar), 7.24–7.32 (m, 2H, Ar), 3.2–3.6 (m, 4H, NCH_2-), 2.07 (s, 3H, 5AP-CH_3), 1.4–1.7 (br m, 4H, NCH_2CH_2-), 1.0–1.4 (br, 36H, alkyl), 0.87 (br m, 6H, methyl groups of dodecyl groups). ^{13}C NMR (CD_2Cl_2, ppm): 174.1, 160.6, 158.6, 152.3, 149.8, 145.2, 137.0, 136.9, 129.4, 129.,1, 128.4, 128.2, 127.7, 127.5, 121.0, 117.0, 48.2, 47.8, 32.4, 32.3, 30.1, 30.04, 30.03, 29.99, 29.92, 29.84, 29.76, 28.74, 28.60, 27.38, 27.33, 26.03, 23.10, 14.27. HRMS (p-ESI) calcd. for $C_{45}H_{64}N_6$+H $[M+H]^+$ 689.5265, found 689.5258.

•7,9-Bis(9,9-dimethylfluoren-2-yl)-2-dodecylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**5c**)

From **4** (69.59 mg, 0.10 mmol), 9,9-dimethylfluorene-2-boronic acid pinacol ester (67.67 mg, 0.21 mmol), Pd_2dba_3 (4.85 mg, 0.0053 mmol), SPhos (9.61 mg, 0.023 mmol) and Cs_2CO_3 (388 mg, 1.2 mmol), the product was obtained as a red powder after reaction for 24 h in 40% yield. ^{1}H NMR (CD_2Cl_2, ppm): 7.2–7.8 (m, 15H, Ar and 5AP), 3.3–3.6 (m, 4H, NCH_2-), 2.10 (s, 3H, 5AP-CH_3), 1.4–1.7 (br m, 4H, NCH_2CH_2-), 1.51 (two singlet peaks, 12H, methyl groups of fluorene), 1.0–1.4 (br, 36H, alkyl), 0.89 (br m, 6H, methyl groups of dodecyl groups). ^{13}C NMR (CD_2Cl_2, ppm): 174.1, 171.7, 160.8, 158.7, 154.46, 154.39, 153.81, 153.77, 152.4, 149.7, 145.2, 145.1, 139.30, 139.28, 138.85, 138.64, 136.14, 135.9, 128.3, 127.7, 127.4, 124.0, 123.9, 123.4, 123.3, 123.04, 123.02, 121.7, 120.4, 119.8, 119.6, 117.4, 47.7, 47.6, 47.34, 43.26, 32.35, 30.08, 30.06, 30.02, 29.94, 29.85, 29.77, 28.69, 28.55, 27.48, 27.37, 27.32, 26.1, 23.1, 14.3. HRMS (p-ESI) calcd. for $C_{63}H_{80}N_6$+H $[M+H]^+$ 921.6517, found 921.6503.

•7,9-Di(4-methoxyphenyl)-2-dodecylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**5d**)

From **4** (69.33 mg, 0.10 mmol), 4-methoxyphenylboronic acid pinacol ester (47.90 mg, 0.20 mmol), Pd_2dba_3 (4.53 mg, 0.0049 mmol), SPhos (8.31 mg, 0.020 mmol) and Cs_2CO_3 (400 mg, 1.2 mmol), the product was obtained as a red oil after reaction for 34 h (0.035 g, 0.046 mmol, 46% yield). ^{1}H NMR (CD_2Cl_2, ppm): 7.43–7.51 (m, 5H, Ar and 5AP), 6.87–6.91 (m, 4H, Ar), 3.81 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.2–3.6 (m, 4H, NCH_2-), 2.05 (s, 3H, 5AP-CH_3), 1.4–1.7 (br m, 4H, NCH_2CH_2-), 1.0–1.4 (br, 36H, alkyl), 0.87 (br m, 6H, methyl groups of dodecyl groups). ^{13}C NMR (CD_2Cl_2, ppm): 173.7, 160.7, 159.4, 159.3, 158.7, 152.1, 149.3, 144.6, 130.6, 130.3, 129.3, 120.8, 116.8, 113.8, 113.6, 55.7, 55.6, 48.1, 47.8, 32.4, 30.14, 30.11, 30.08, 30.06, 30.04, 29.94, 29.91, 29.79, 29.77, 28.8, 28.6, 27.5, 27.3, 26.0, 23.1, 14.3. HRMS (p-ESI) calcd. for $C_{47}H_{68}N_6O_2$+H $[M+H]^+$ 749.5477, found 749.5468.

•7,9-Bis((4-*N*,*N*-diphenylamino)phenyl)-2-dodecylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**5e**)

From **4** (64.66 mg, 93 μmol), 4-(*N*, *N*-diphenylamino)phenylboronic acid pinacol ester (79.51 mg, 0.21 mmol), Pd_2dba_3 (5.18 mg, 5.7 μmol), SPhos (8.53 mg, 21 μmol) and Cs_2CO_3 (349 mg, 1.1 mmol), the product was obtained as a red powder after reaction for 22 h in 91% yield. ^{1}H NMR (CD_2Cl_2, ppm): 7.56 (s, 1H, 5AP), 7.4–7.5 (dd, J = 15 Hz, 8.8 Hz, 4H, Ar), 7.2–7.4 (m, 9H, Ar), 7.0–7.2 (m, 14H, Ar), 3.3–3.5 (m, 4H, NCH_2-), 2.09 (s, 3H, 5AP-CH_3), 1.4–1.7 (br m, 4H, NCH_2CH_2-), 1.0–1.4 (br, 36H, alkyl), 0.87 (br m, 6H, methyl groups of dodecyl groups). ^{13}C NMR (CD_2Cl_2, ppm): 173.8, 160.6, 158.7, 152.0, 149.2, 148.1, 147.4, 147.3, 144.4, 130.8, 130.1, 19.8, 129.7, 125.0, 124.8, 123.4, 123.2, 123.1, 120.7, 116.6, 111.9, 111.5, 103.3, 102.8, 48.2, 47.8, 32.4, 30.08, 30.06, 30.04, 29.95, 29.78, 29.77, 28.8, 28.7, 27.40, 27.35, 26.0, 23.1, 14.3. HRMS (p-ESI) calcd. for $C_{69}H_{82}N_8$+H $[M+H]^+$ 1023.6735, found 1023.6717.

•7,9-Bis(2,2'-bithiophen-5-yl)-2-dodecylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**5f**)

From **4** (69.93 mg, 0.10 mmol), 2,2'-bithiophene-5-boronic acid pinacol ester (65 mg, 0.22 mmol), Pd_2dba_3 (4.87 mg, 5.3 μmol), SPhos (8.68 mg, 21 μmol) and Cs_2CO_3 (332 mg, 1.0 mmol), the product was obtained as a dark red powder after reaction for 18 h in 71% yield. ^{1}H NMR (CD_2Cl_2, ppm): 8.13 (s, 1H, 5AP), 7.32 (d, J = 4.0 Hz, 1H, Ar), 7.31 (d, J = 4.0 Hz, 1H, Ar), 7.23 (dd, J = 3.2 Hz, 1.2 Hz, 1H, Ar), 7.22 (dd, J = 3.2 Hz, 1.2 Hz, 1H, Ar), 7.18 (dd, J = 3.5 Hz, 1.2 Hz, 1H, Ar), 7.15 (dd, J = 3.5 Hz, 1.2 Hz, 1H, Ar), 7.12 (d, 4.0 Hz, 1H, Ar), 7.08 (d, 4.0 Hz, 1H, Ar), 7.03 (dd, 3.5 Hz, 2.0 Hz, 1H, Ar), 7.01 (dd, 3.5 Hz, 2.0 Hz, 1H, Ar). Two bithiophenes may be inequivalent because of the didodecylamino group. Therefore, ^{1}H NMR spectrum of bithiophene rings was complicated. 3.45–3.55 (m, 4H, NCH_2-), 2.17 (s, 3H, 5AP-CH_3), 1.5–1.7 (br m, 4H, NCH_2CH_2-), 1.0–1.4 (br, 36H, alkyl), 0.87 (br m, 6H, methyl groups of dodecyl groups). ^{13}C NMR (CD_2Cl_2, ppm): 173.7, 160.2, 157.4, 138.3, 138.12, 138.09, 138.04, 135.98, 135.92, 135.55, 128.2, 124.60, 124.43, 124.16, 124.06, 123.7, 123.6, 123.3, 123.1, 113.6, 110.6, 48.8, 48.4, 32.4, 30.13, 30.07, 30.05, 30.04, 29.96, 29.8, 28.7, 28.6, 27.7, 27.5, 25.8, 23.1, 14.3. HRMS (p-ESI) calcd. for $C_{49}H_{64}N_6S_4$+H $[M+H]^+$ 845.4148, found 865.4135.

4. ^{1}H and ^{13}C NMR spectra of the compounds

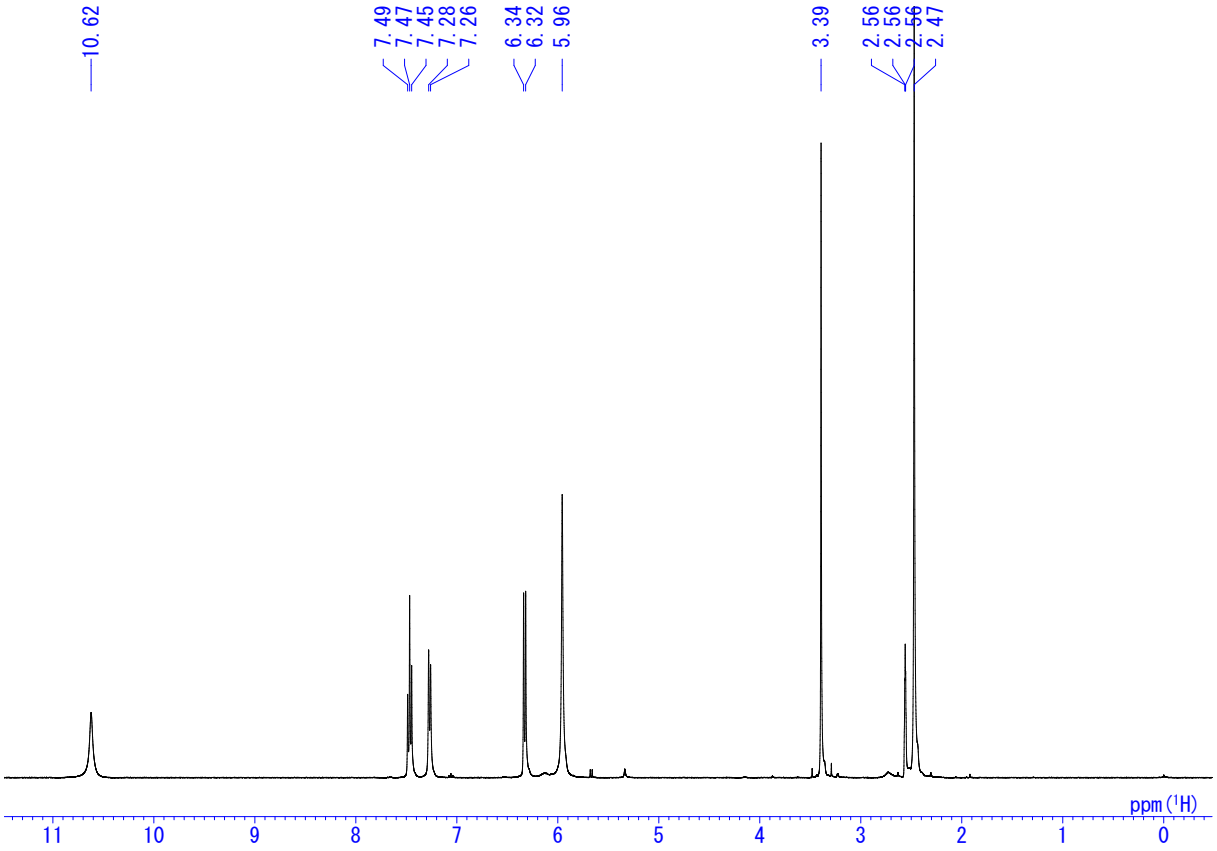


Figure S1. ^{1}H NMR spectrum of compound **1**.

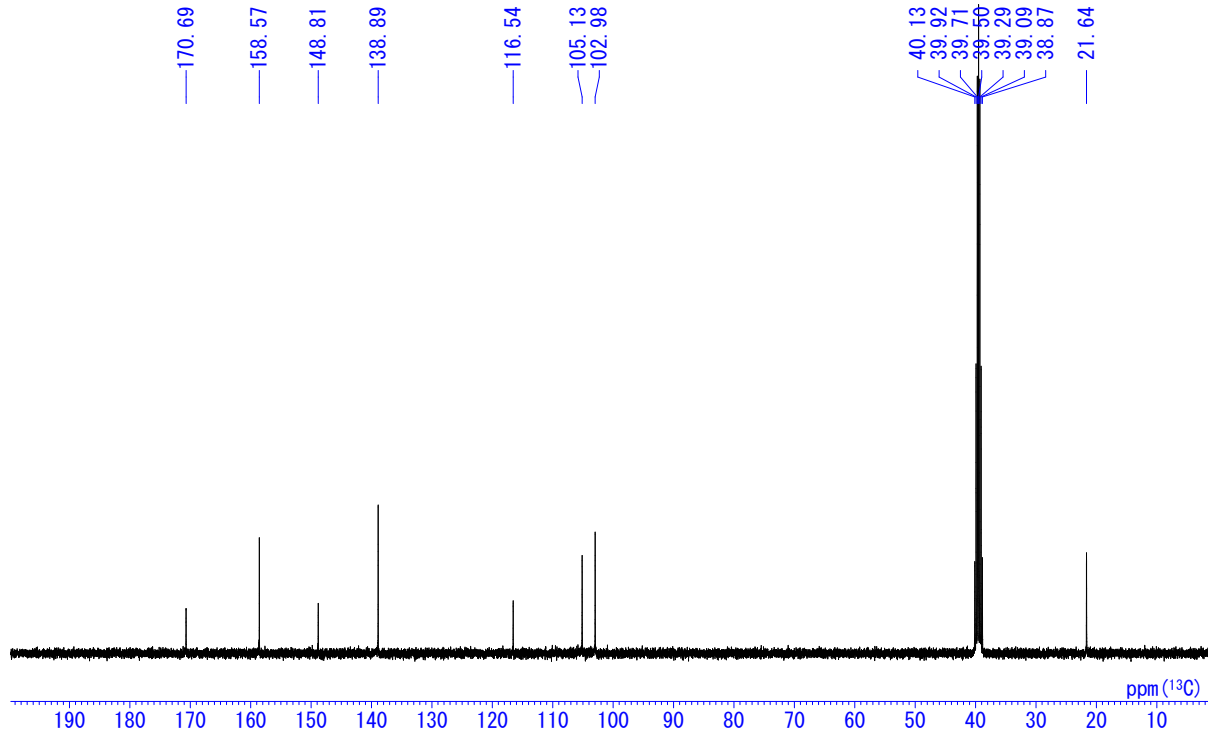


Figure S2. ^{13}C NMR spectrum of compound **1**.

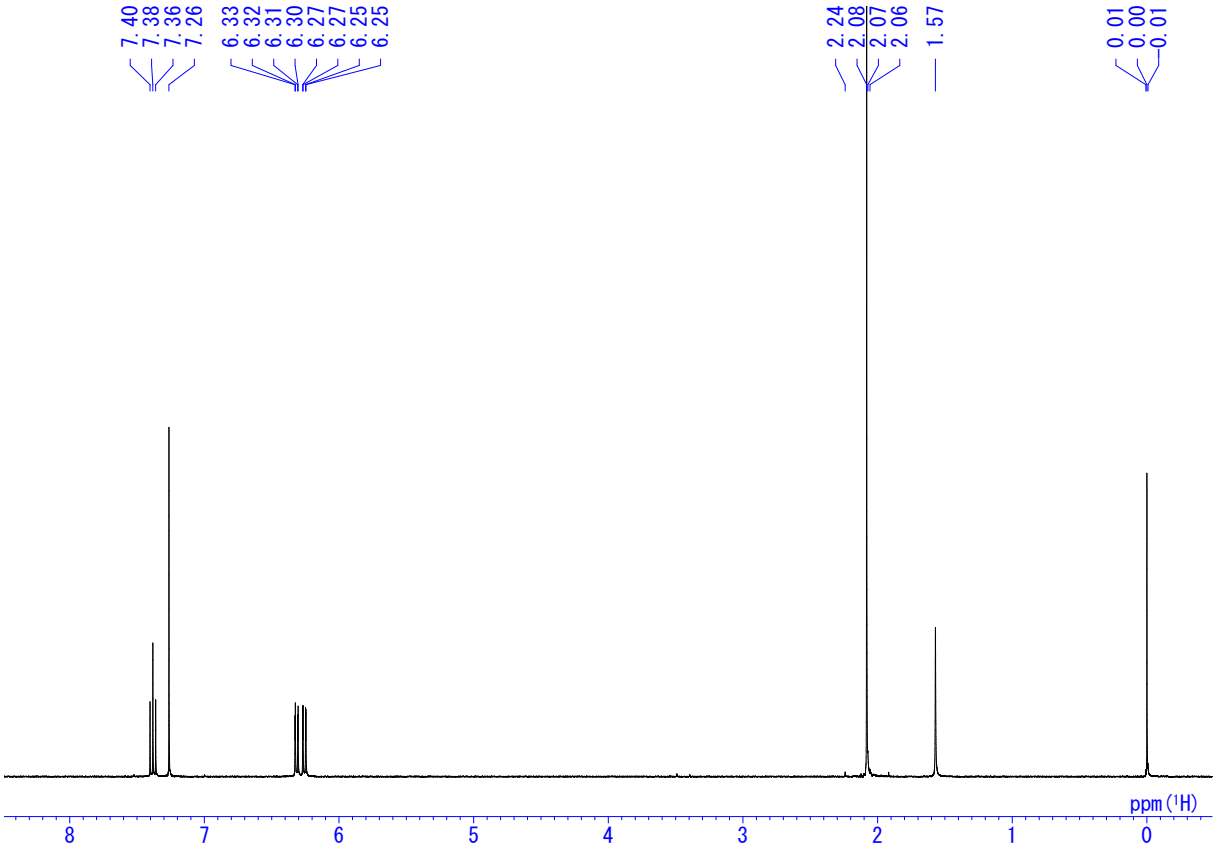


Figure S3. ^{1}H NMR spectrum of compound **2**.

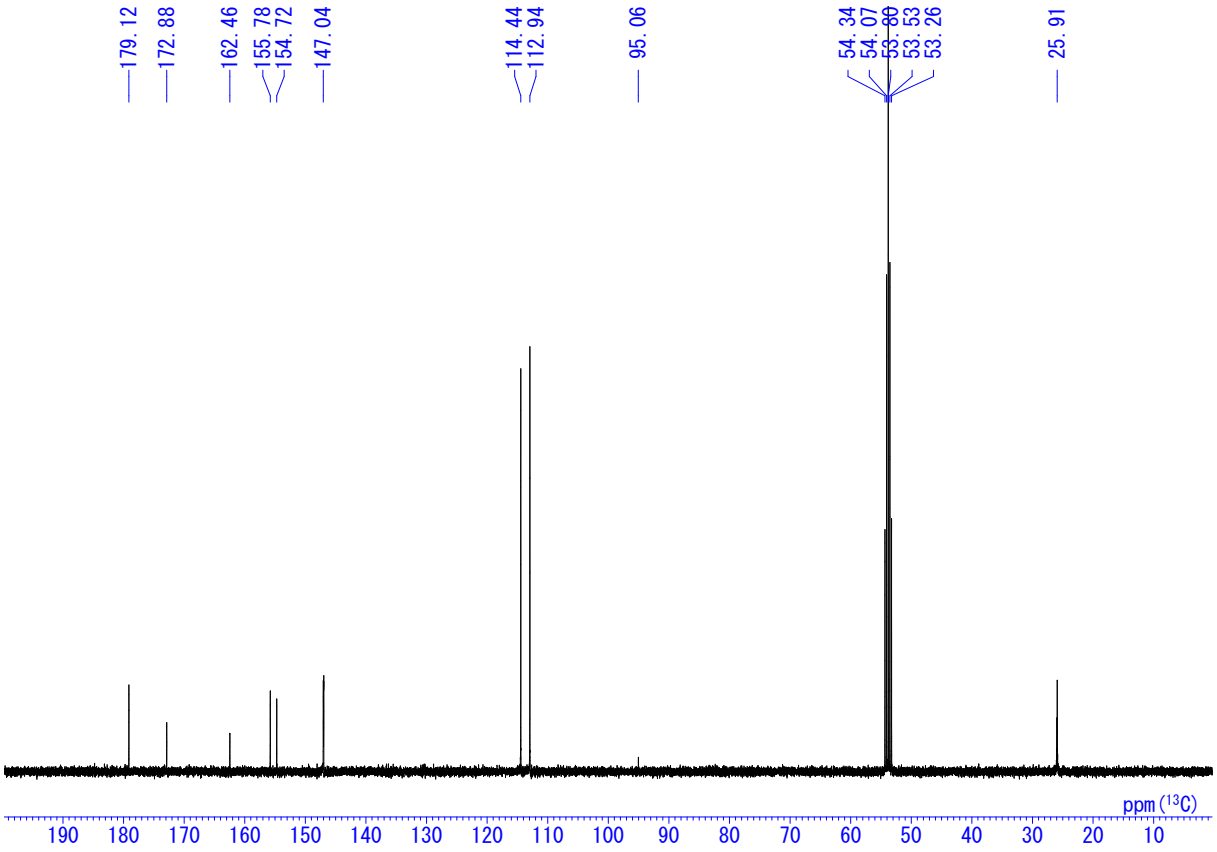


Figure S4. ^{13}C NMR spectrum of compound **2**.

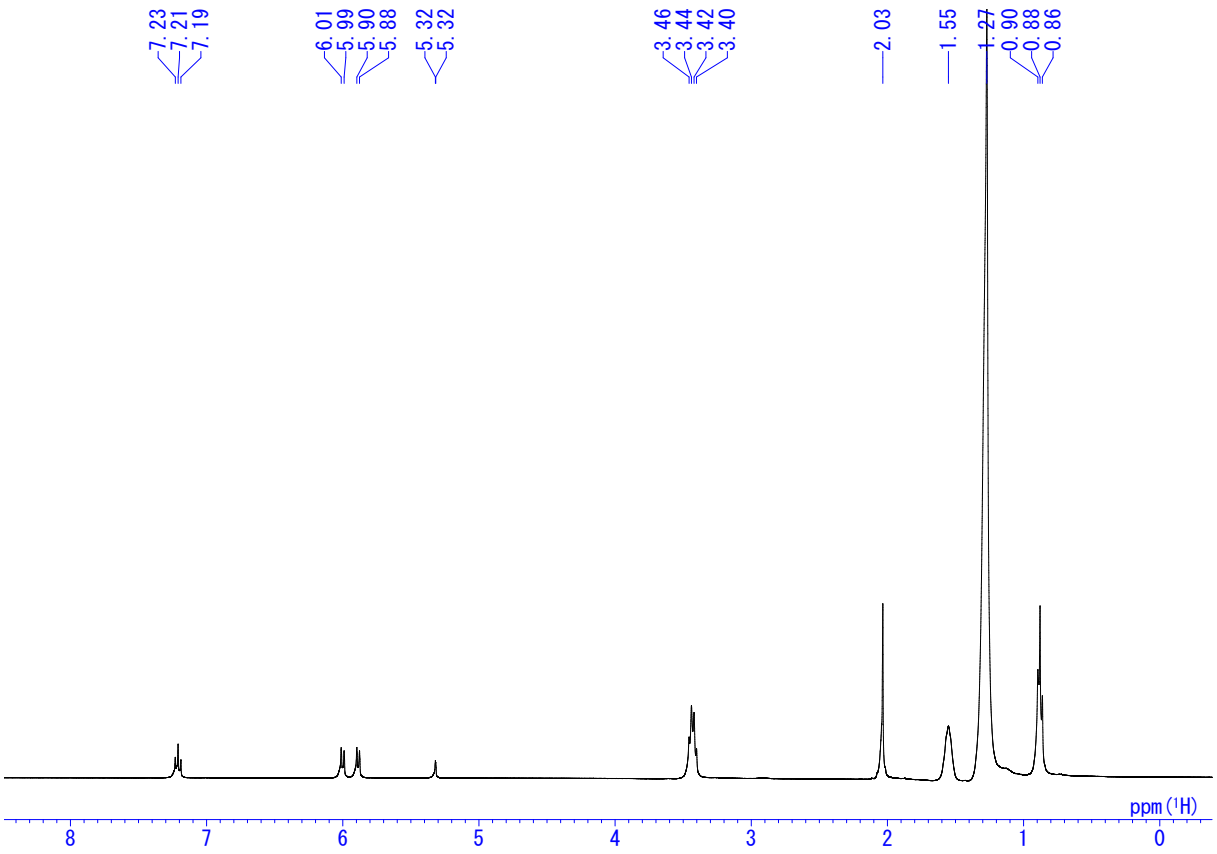


Figure S5. ^{1}H NMR spectrum of compound **3**.

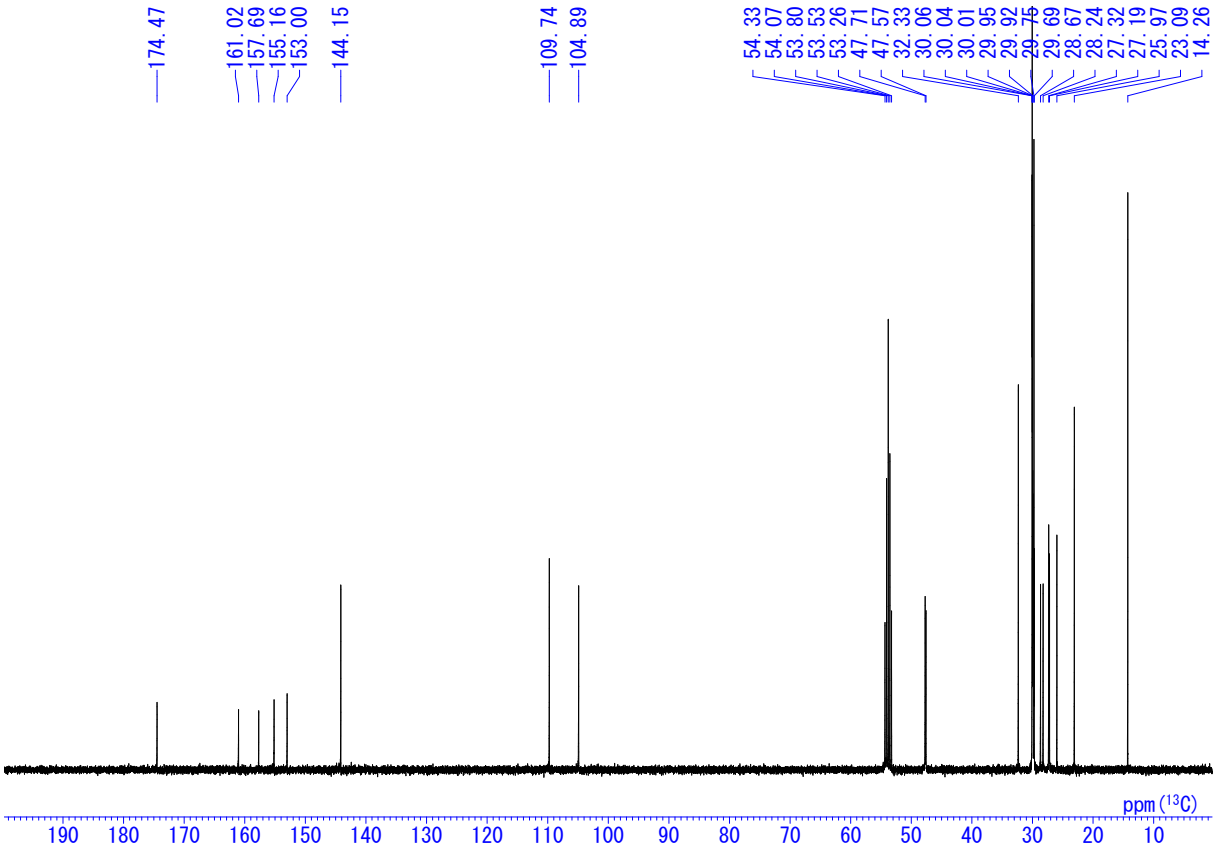


Figure S6. ^{13}C NMR spectrum of compound **3**.

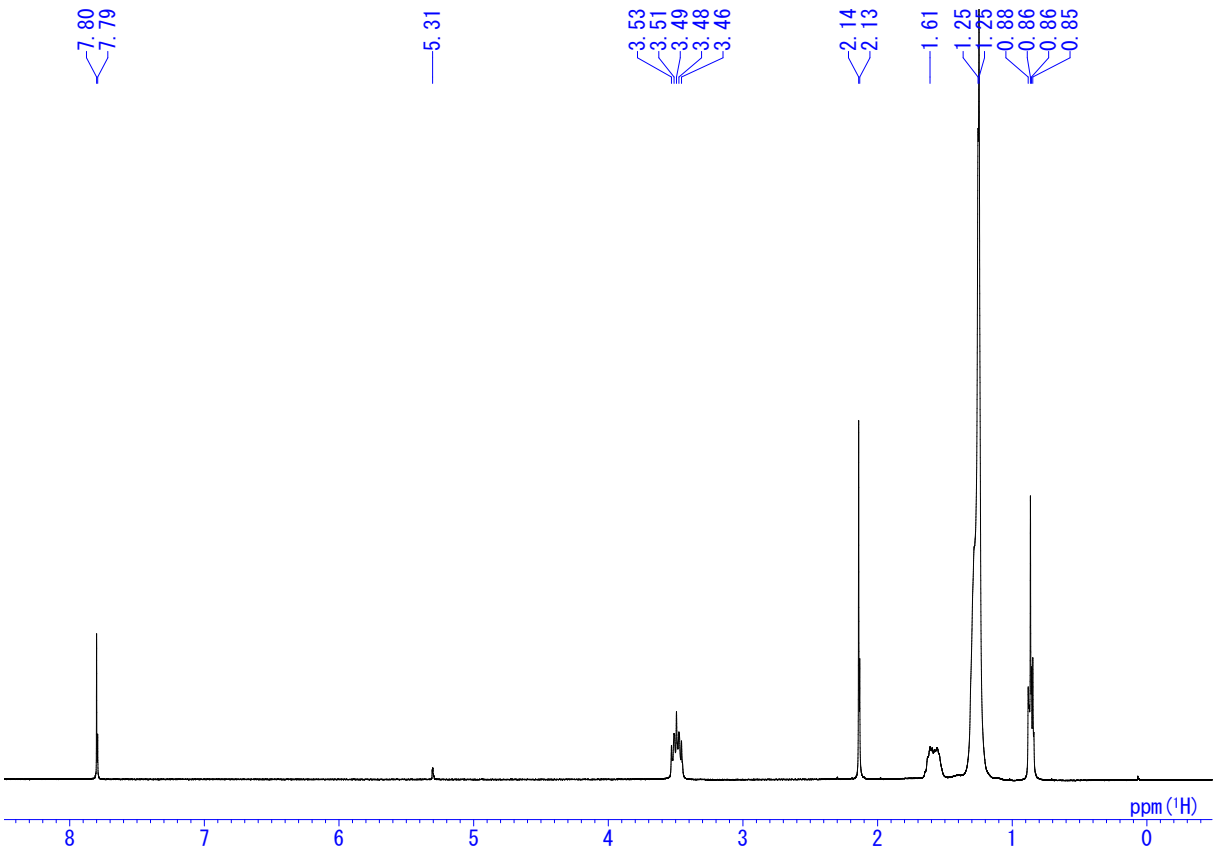


Figure S7. ^{1}H NMR spectrum of compound **4**.

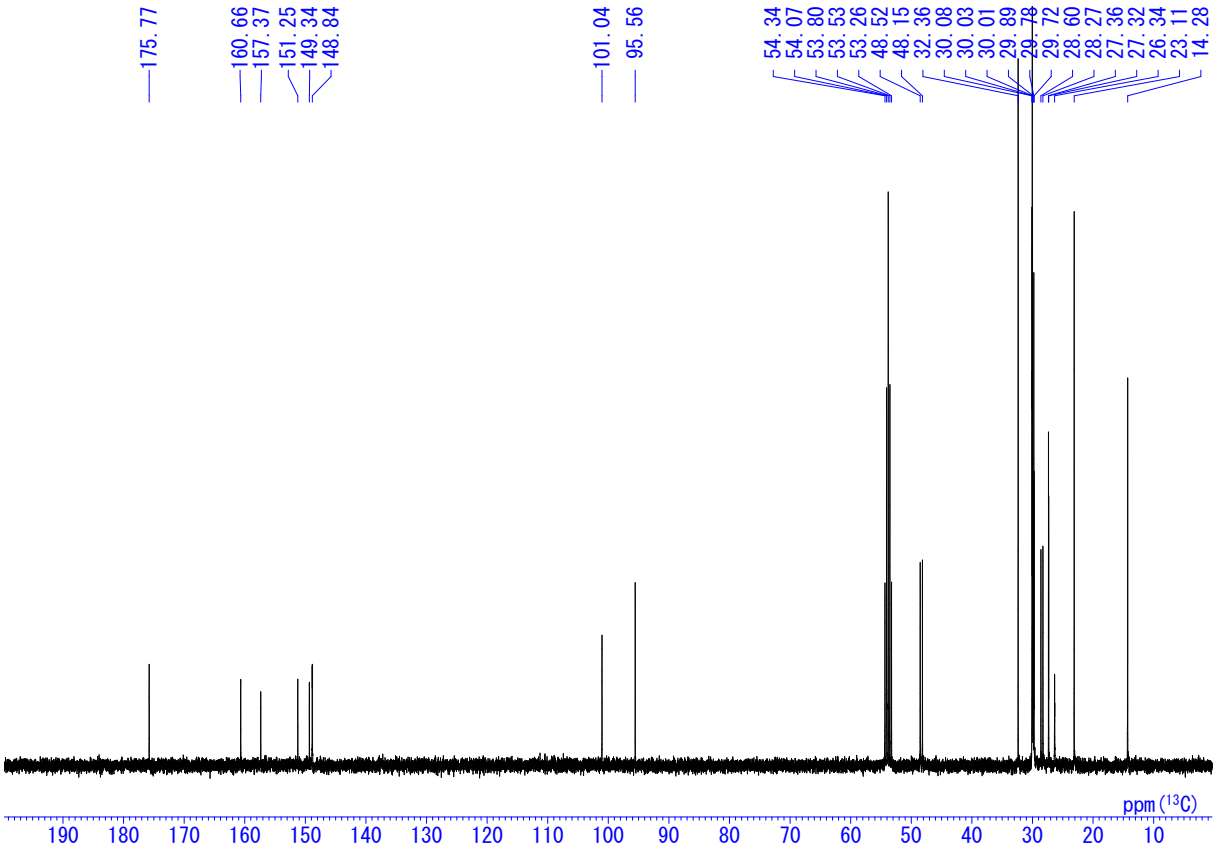


Figure S8. ^{13}C NMR spectrum of compound **4**.

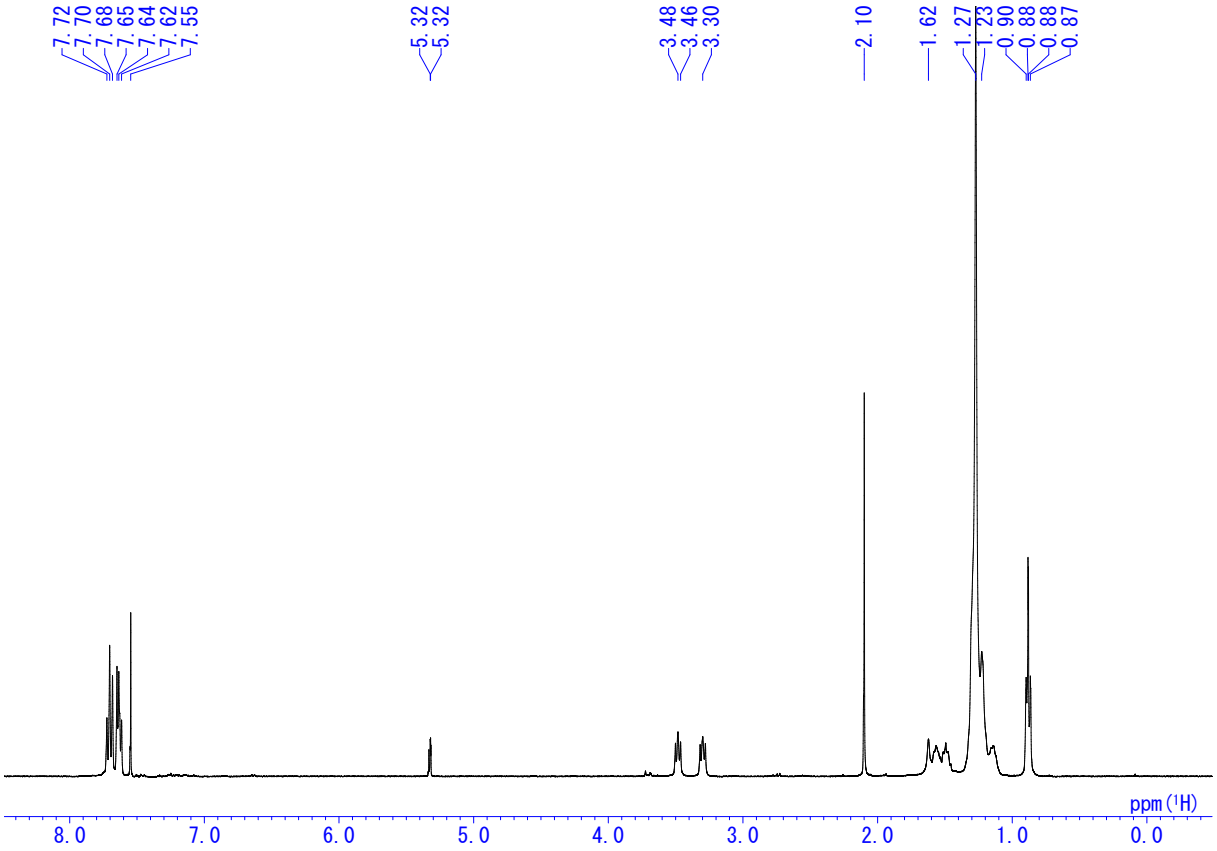


Figure S9. ^{1}H NMR spectrum of compound **5a**.

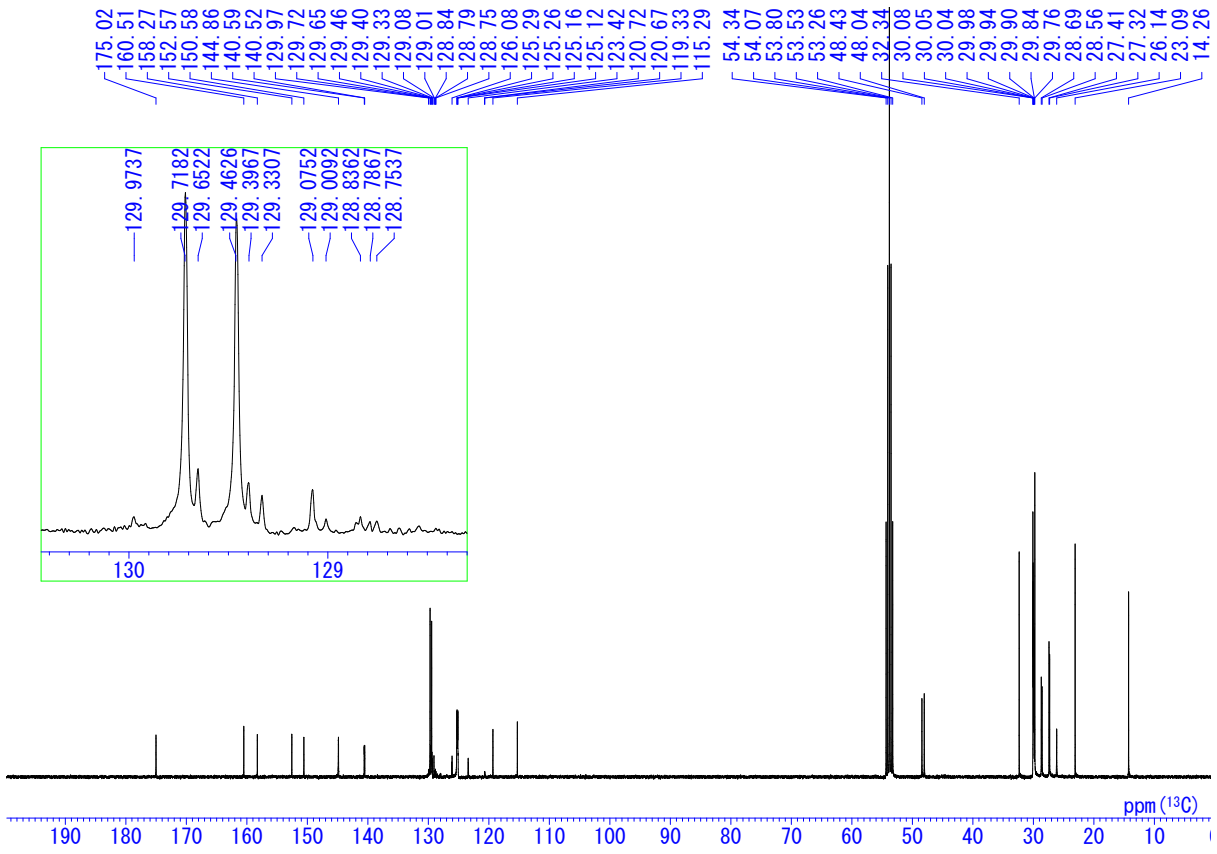


Figure S10. ^{13}C NMR spectrum of compound **5a**.

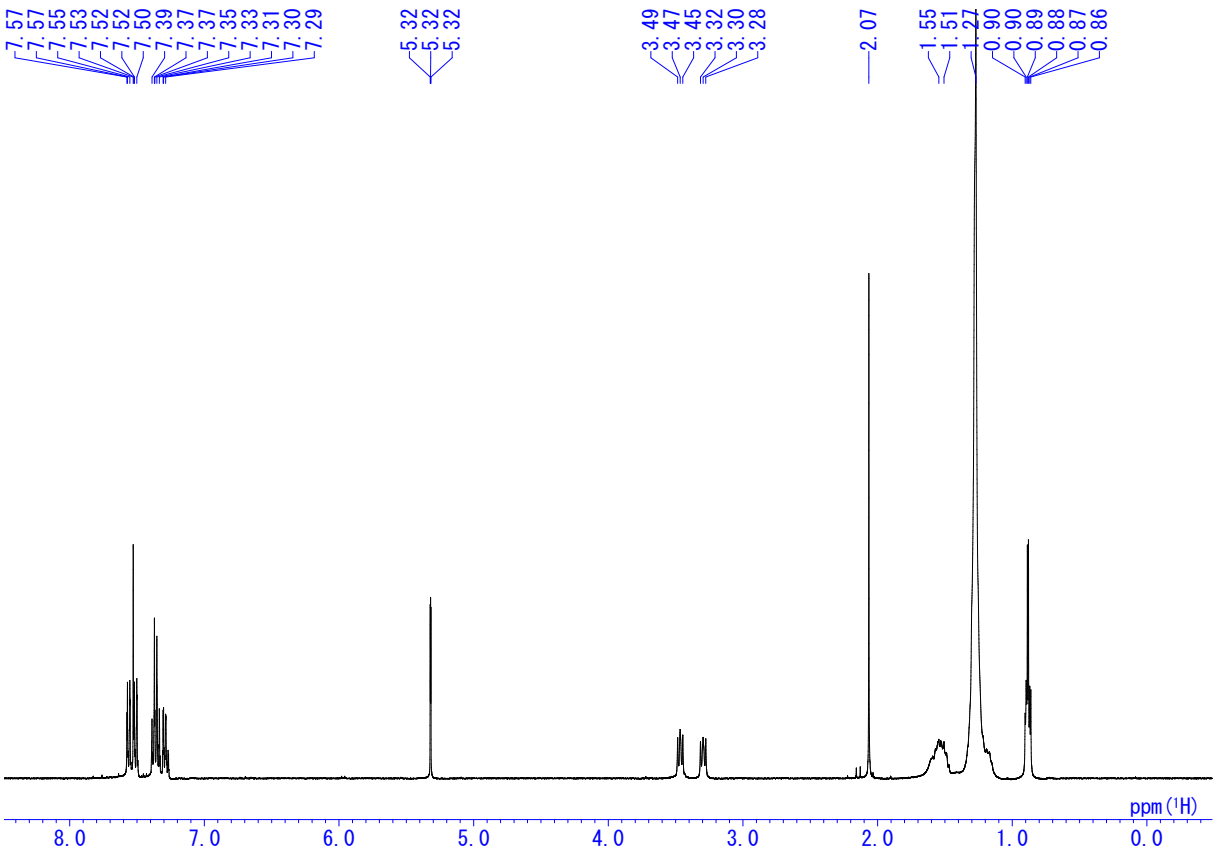


Figure S11. ^{1}H NMR spectrum of compound **5b**.

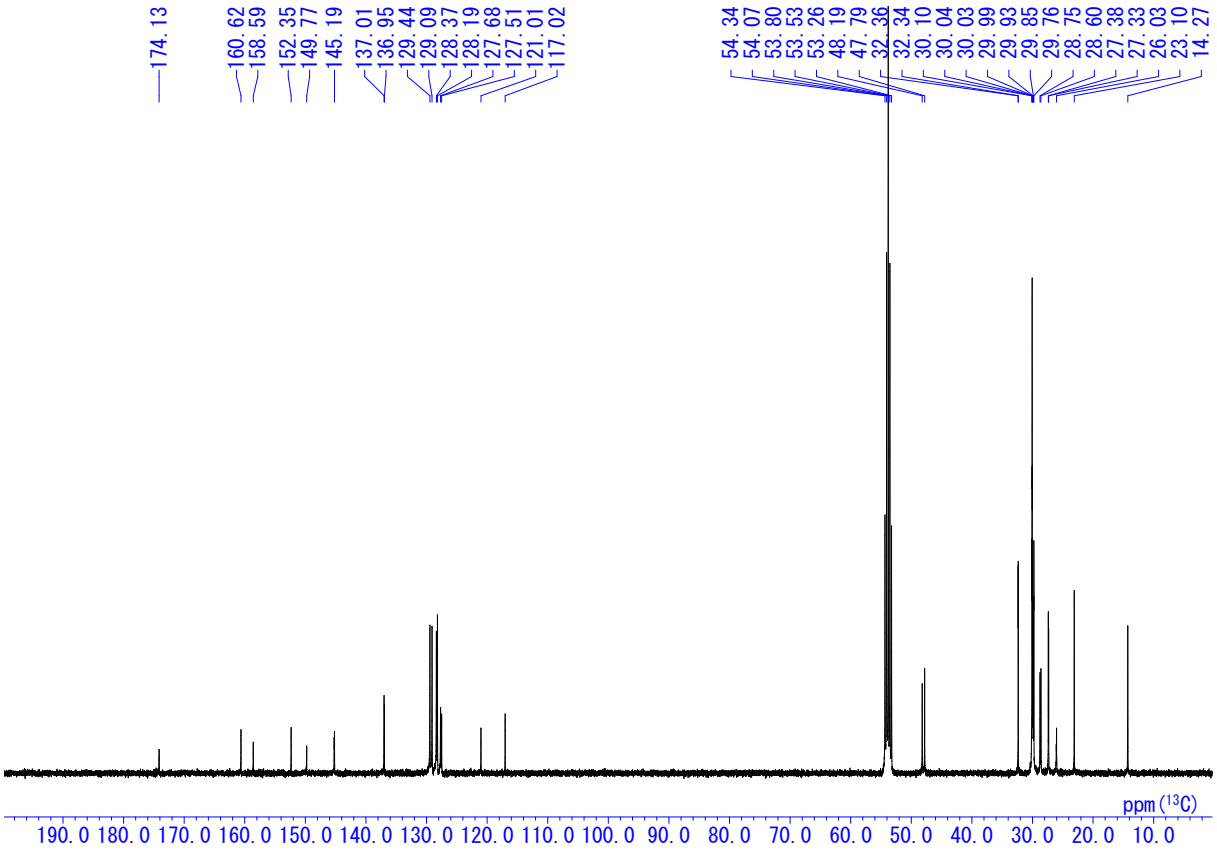


Figure S12. ^{13}C NMR spectrum of compound **5b**.

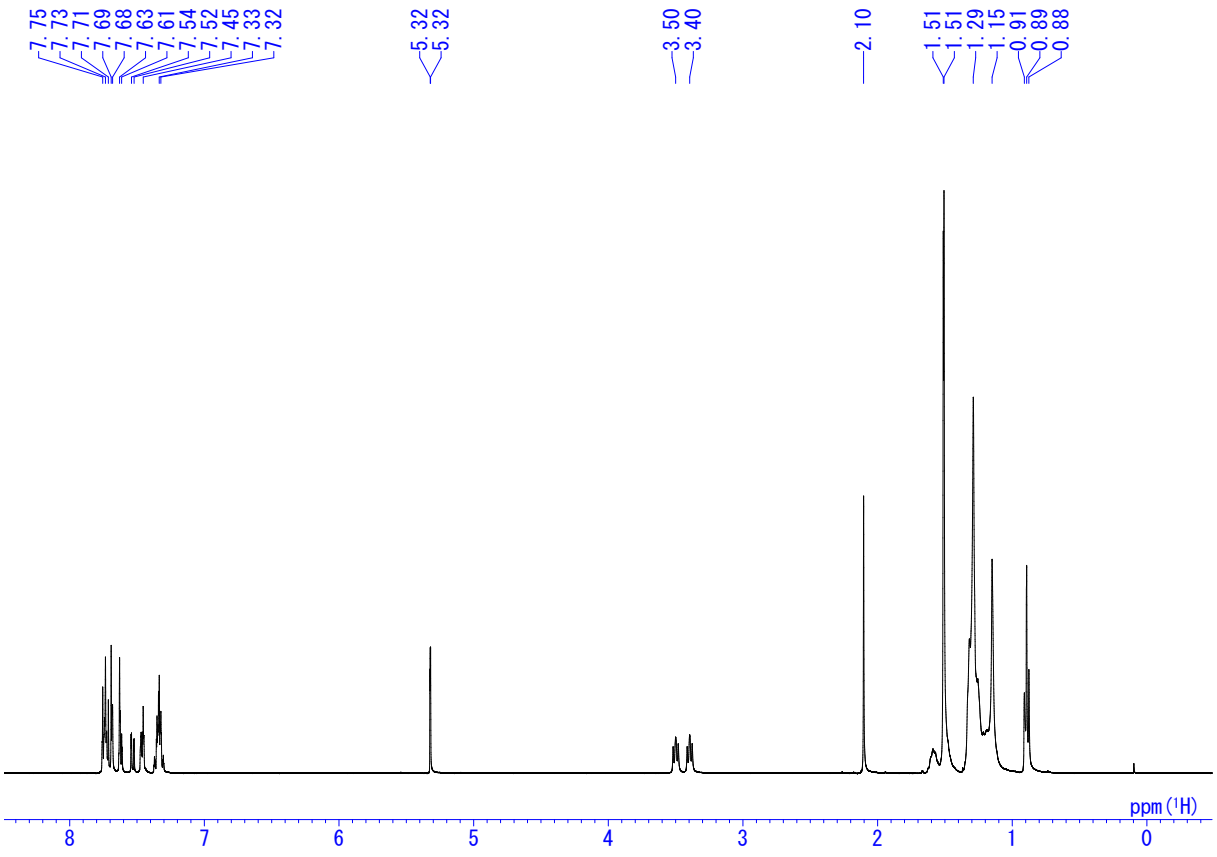


Figure S13. ^{1}H NMR spectrum of compound **5c**.

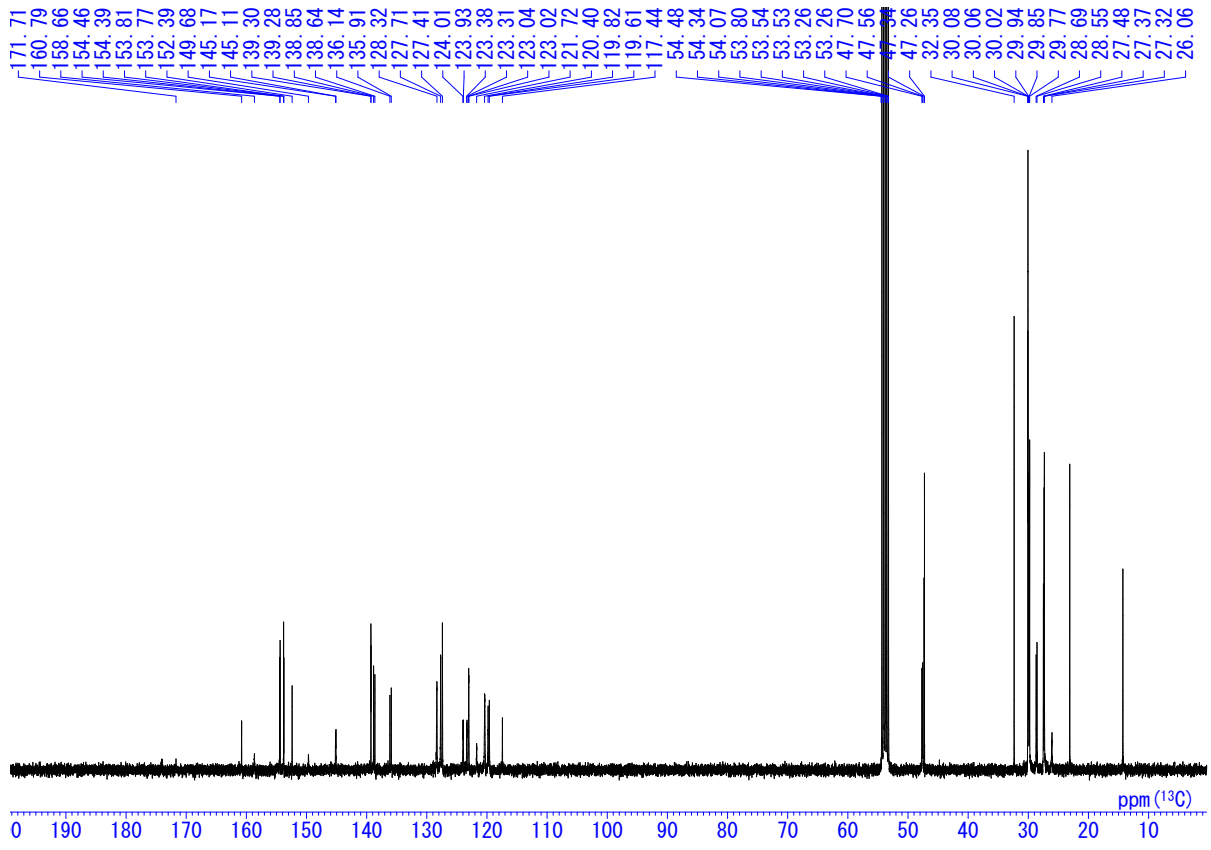


Figure S14. ^{13}C NMR spectrum of compound **5c**.

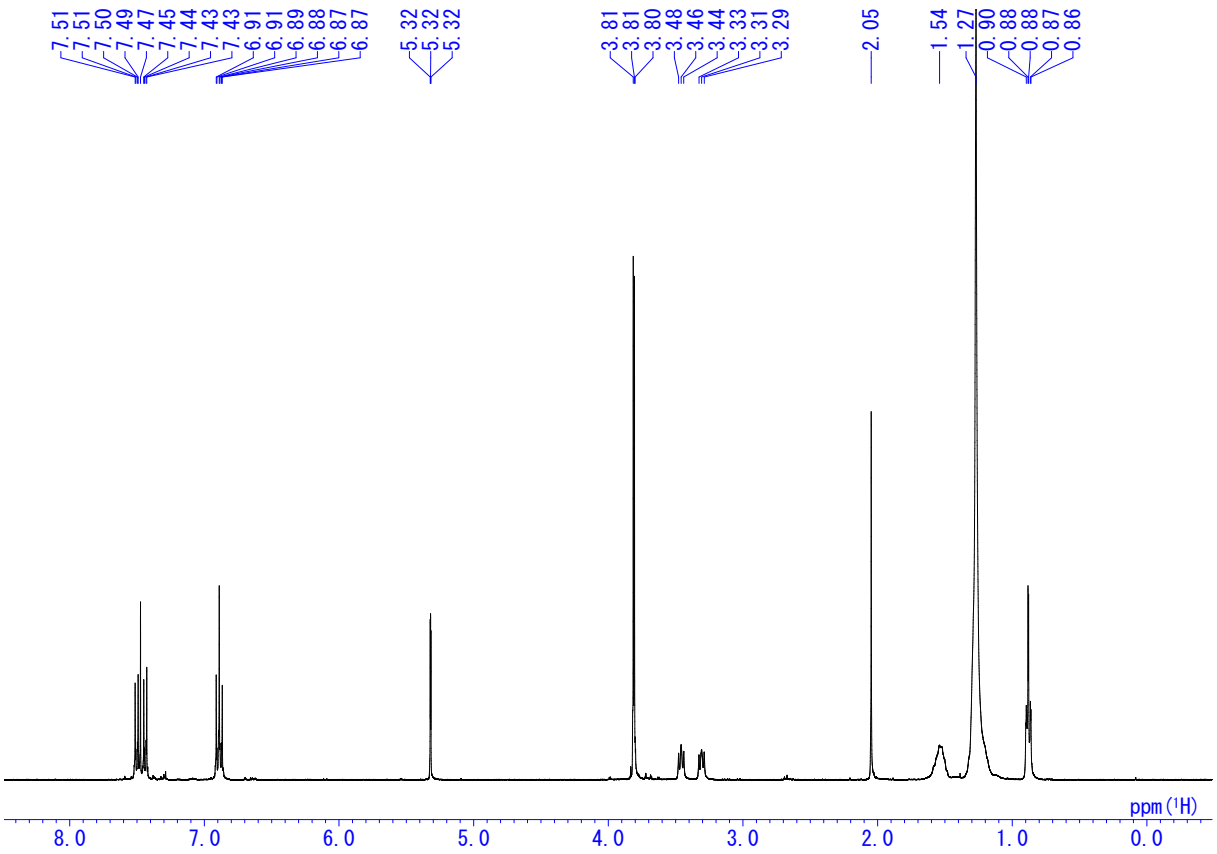


Figure S15. ^{1}H NMR spectrum of compound **5d**.

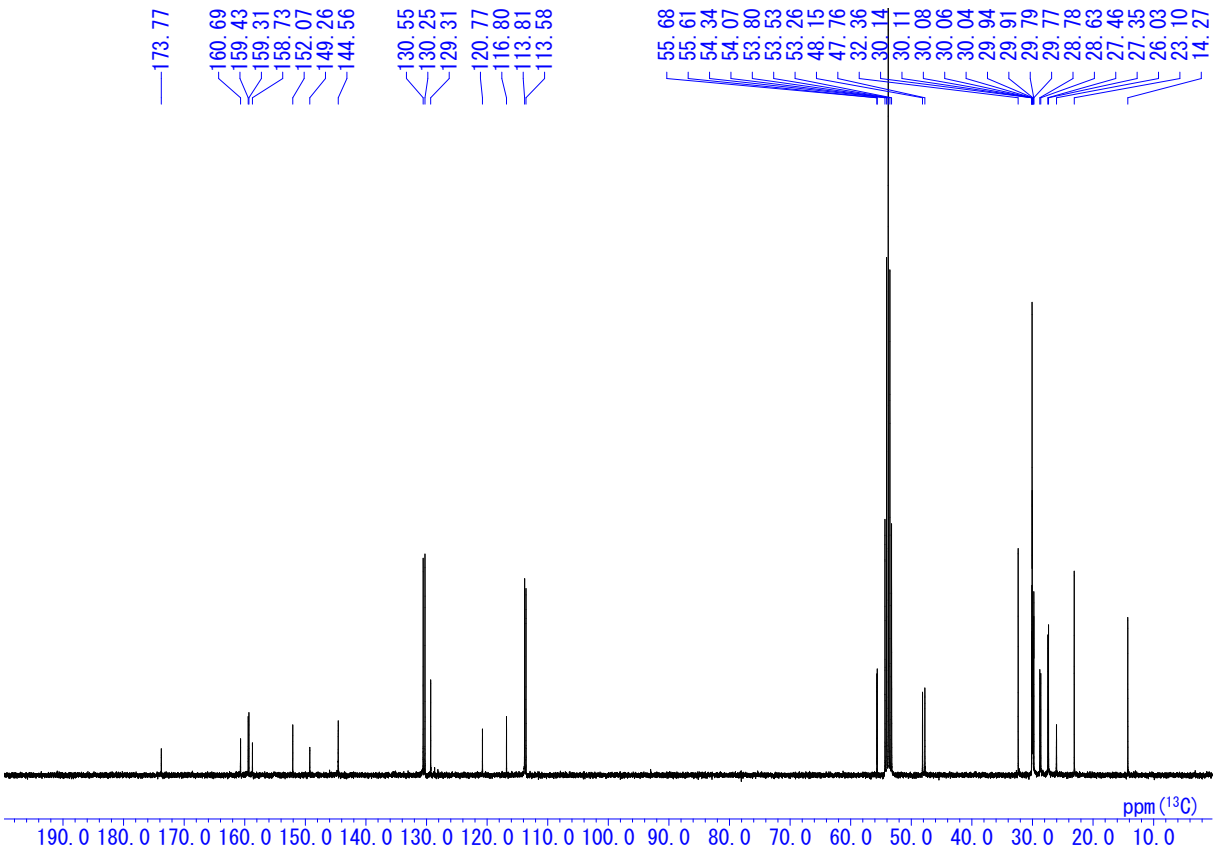


Figure S16. ^{13}C NMR spectrum of compound **5d**.

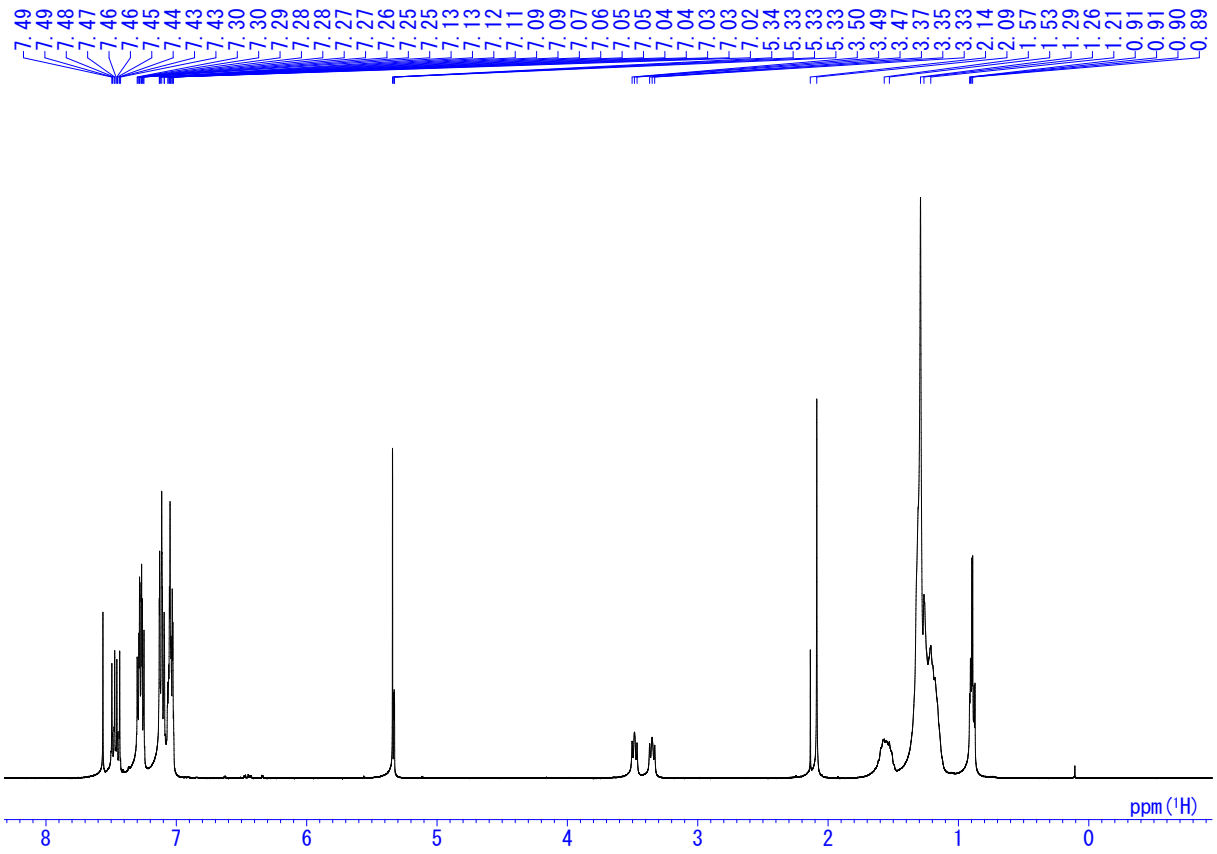


Figure S17. ^{1}H NMR spectrum of compound **5e**.

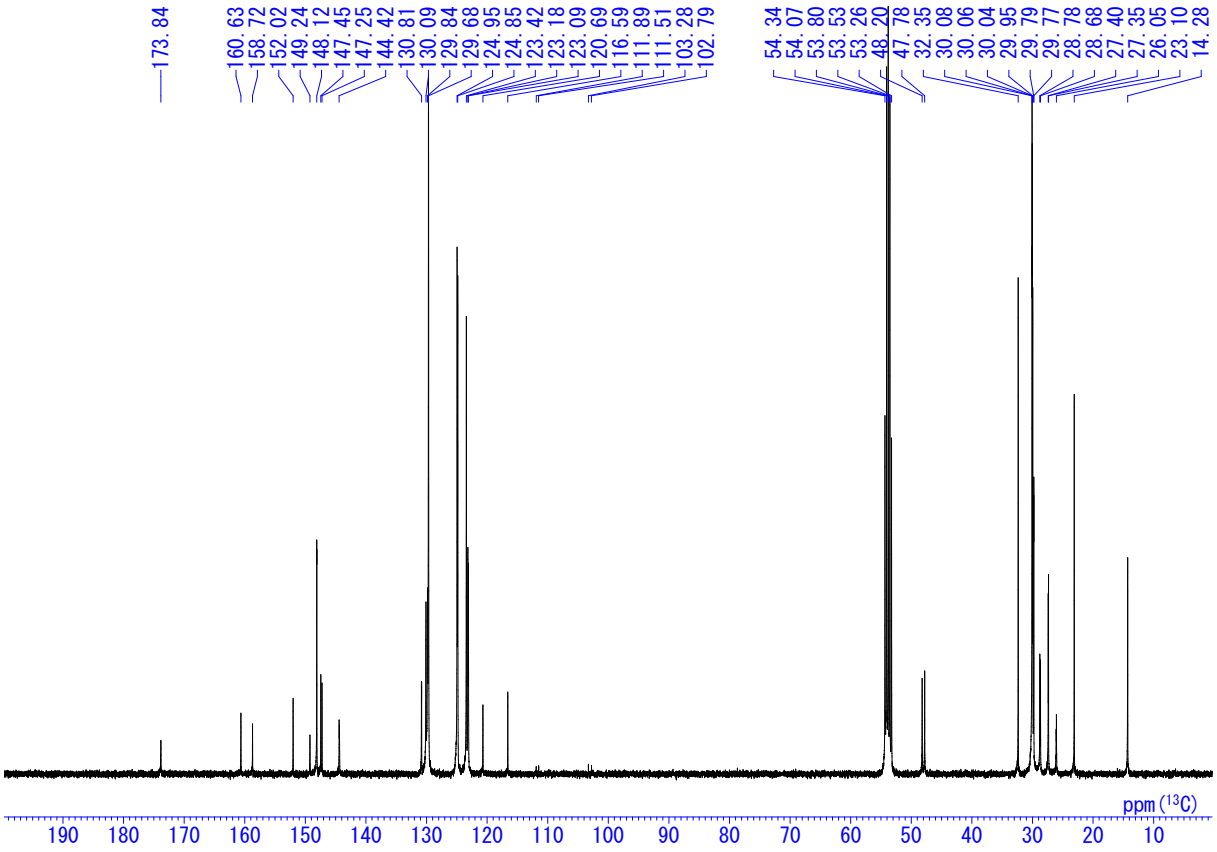


Figure S18. ^{13}C NMR spectrum of compound **5e**.

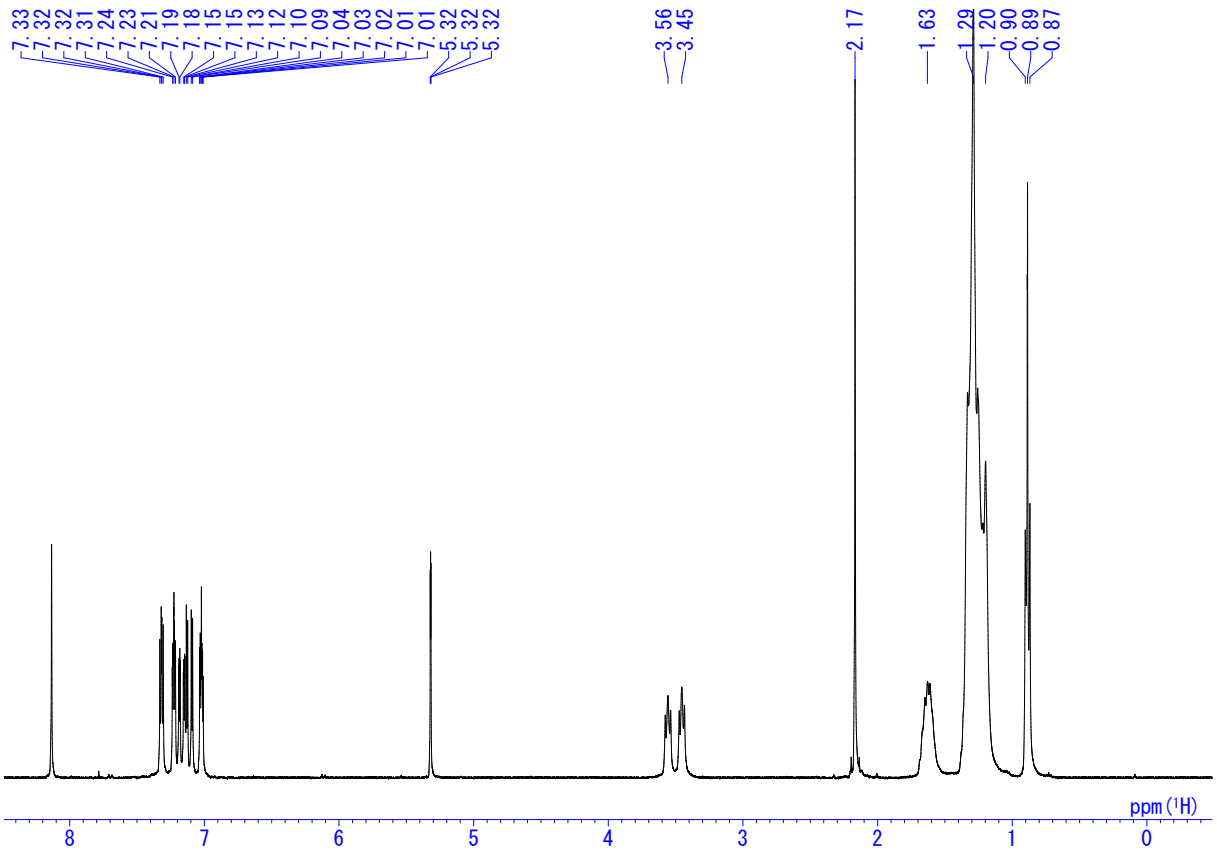


Figure S19. ^{1}H NMR spectrum of compound **5f**.

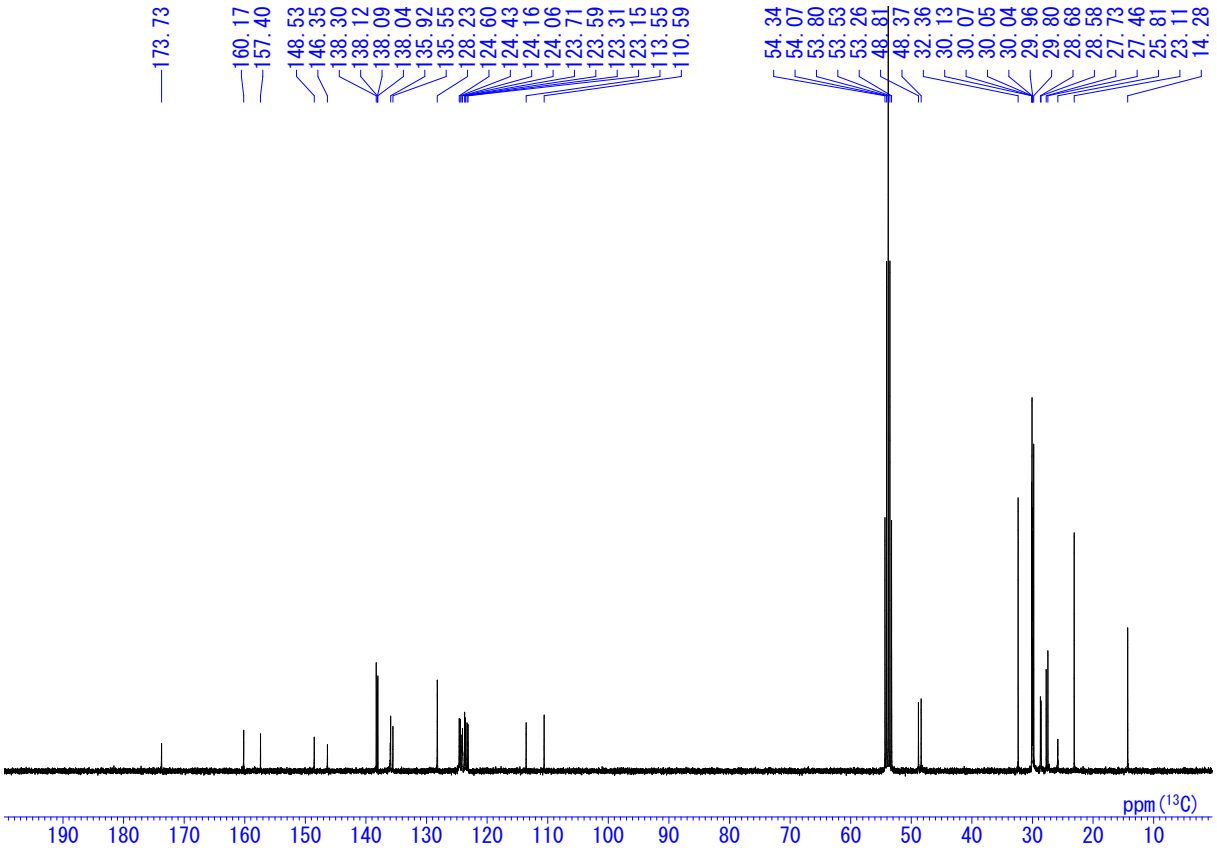


Figure S20. ^{13}C NMR spectrum of compound **5f**.

5. Supplementary Data

5-1. Theoretical consideration for optical properties of 5AP and A5AP based on the point group theory

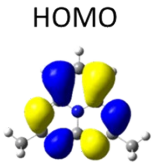
In this theoretical consideration, we only consider the electronic transition (vibronic coupling and other high-order perturbation terms were omitted).

π-Conjugated system of 5AP belongs to the D_{3h} symmetry. The character table of D_{3h} symmetry is shown in Table S1.[3] As shown in the following Figure S21, HOMO and LUMO are assigned to A_1'' and A_2'', respectively. The direct product $A_1'' \times A_2'' \; equals \; to \; A_2'$. x, y,or z first-order basis do not have A_2' symmetry. Therefore, all components in electronic transition dipole moment are zero because all components are odd functions and will be zero when they are integrated all over the space. As a result, HOMO–LUMO transition of 5AP is symmetry-forbidden.

Next, the same discussion is applied to A5AP. A5AP's π-conjugated system belongs to C_{2v} symmetry. The character table of C_{2v} symmetry is shown in Table S2.[6] As shown in the following Figure S22, HOMO and LUMO are assigned to A_2'' and B_1'', respectively. The direct product $A_2'' \times B_1'' \; equals \; to \; B_2''$. y basis have B_2''symmetry. Therefore, y component of electronic transition dipole moment is non-zero because the y component is an even function. As a result, HOMO–LUMO transition of A5AP is symmetry-allowed.

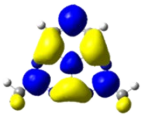
Table S1. Character table of D_{3h} point group

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2,z^2
A_1''	1	1	1	–1	–1	–1		
A_2'	1	1	–1	1	1	–1	R_z	
A_2''	1	1	–1	–1	–1	1	z	
E'	2	–1	0	2	–1	0	(x,y)	$(x^2–y^2,xy)$
E''	2	–1	0	–2	1	0	(R_x,R_y)	(xz,yz)



E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
1	1	1	–1	–1	–1

A_1''



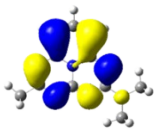
E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
1	1	–1	–1	–1	1

A_2''

Figure S21. Characters and irreducible representation for HOMO and LUMO of 5AP.

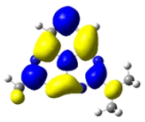
Table S2. Character table of C_{2v} point group

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	–1	–1	R_z	xy
B_1	1	–1	1	–1	x,R_y	xz
B_2	1	–1	–1	1	y,R_x	yz



E	C_2	σ_v	σ_v'
1	1	–1	–1

A_2



E	C_2	σ_v	σ_v'
1	–1	1	–1

B_1

Figure S22. Characters and irreducible representation for HOMO and LUMO of A5AP.

5-2. Results of DFT calculations

All DFT calculations were performed using Gaussian 09 package.[7] In DFT calculations, dodecyl groups were replaced by methyl groups for simplicity of calculation. Optimization was carried out at B3LYP/6–31G(d) level of theory. The absence of imaginary frequency was confirmed at the same level of calculation. Time-dependent (TD)-DFT calculations were performed at B3LYP/6–31+G(d) level of theory. We estimated the absorption spectra by TD-DFT single point calculations and the emission spectra by TD-DFT optimization calculations, respectively.

The following tables show the Cartesian coordinates (Table S3–10) of the optimized ground-state structure and the results of TD-DFT calculation in comparison with experimental values (Table S11) for 5AP, A5AP and arylated A5AP derivatives. MO patterns of HOMOs and LUMOs at optimized ground-state structure are shown in Figure S23–30.

Table S3. Cartesian coordinates of the optimized 5AP structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.210835	2.411899	-0.000132
2	6	0	-1.229504	1.012534	0.000066
3	7	0	0.000006	0.340257	0.000064
4	6	0	1.229500	1.012518	0.000167
5	6	0	1.210855	2.411895	0.000111
6	6	0	0.000018	3.094327	-0.000071
7	7	0	-2.386010	0.315207	0.000099
8	6	0	-2.292416	-1.010562	-0.000171
9	7	0	-1.158915	-1.734983	-0.000474
10	6	0	0.000000	-1.079263	-0.000097
11	7	0	1.158913	-1.734979	0.000076
12	6	0	2.292420	-1.010556	0.000001
13	7	0	2.386018	0.315209	-0.000039
14	6	0	-3.573001	-1.794426	0.000198
15	6	0	3.572959	-1.794469	0.000053
16	1	0	-2.168468	2.916472	-0.000310
17	1	0	2.168504	2.916438	0.000139
18	1	0	0.000015	4.180759	-0.000167
19	1	0	-3.606631	-2.448791	-0.878055
20	1	0	-3.607328	-2.446351	0.880306
21	1	0	-4.434889	-1.125808	-0.000819
22	1	0	3.606973	-2.447594	-0.879147
23	1	0	4.434904	-1.125910	-0.000016
24	1	0	3.606860	-2.447579	0.879250

Table S4. Cartesian coordinates of the optimized A5AP structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.563076	3.545418	0.000016
2	1	0	-1.879387	4.085018	0.000007
3	1	0	-3.307920	-3.323940	-0.879293
4	1	0	-3.308400	-3.323445	0.879781
5	1	0	-4.495862	-2.314396	-0.000336
6	1	0	4.876711	0.422216	0.889065
7	1	0	4.876620	0.422292	-0.889149
8	1	0	3.781514	1.517255	0.000060
9	1	0	4.286411	-2.053992	0.889164
10	1	0	2.814126	-2.537704	0.000032
11	1	0	4.286326	-2.054000	-0.889240
12	1	0	-3.566587	2.222753	-0.000012
13	6	0	3.670037	-1.866846	-0.000009
14	6	0	4.241793	0.532030	-0.000004
15	7	0	3.204779	-0.487694	0.000012
16	6	0	-3.471900	-2.690948	0.000017
17	7	0	1.560019	1.134595	0.000007
18	6	0	1.884791	-0.171079	0.000007
19	7	0	1.011049	-1.203683	0.000004
20	6	0	-0.282482	-0.925142	-0.000002
21	7	0	-1.190023	-1.902578	-0.000009
22	6	0	-2.488513	-1.554350	-0.000018
23	7	0	-2.982233	-0.320727	-0.000021
24	6	0	-1.549974	3.049430	0.000004
25	6	0	-0.192700	2.770302	0.000009
26	6	0	0.259778	1.438419	0.000005
27	7	0	-0.715310	0.427959	-0.000002
28	6	0	-2.093493	0.696641	-0.000009
29	6	0	-2.501437	2.031110	-0.000006

Table S5. Cartesian coordinates of the optimized BT structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.451804	-0.008168	-0.134327
2	6	0	1.376726	1.400709	-0.106631
3	7	0	0.112999	2.008587	-0.113710
4	6	0	-1.095766	1.302438	-0.159831
5	6	0	-1.022904	-0.118768	-0.190026
6	6	0	0.238606	-0.710409	-0.147767
7	7	0	2.484899	2.159218	-0.056061
8	6	0	2.342469	3.479792	-0.011497
9	7	0	1.178964	4.144355	-0.015511
10	6	0	0.051348	3.433136	-0.069330
11	7	0	-1.117700	4.047010	-0.084348
12	6	0	-2.236924	3.292315	-0.135037
13	7	0	-2.262465	1.945667	-0.159425
14	6	0	3.588464	4.315445	0.049513
15	6	0	2.727313	-0.726449	-0.127035
16	6	0	-2.217625	-0.961282	-0.260125
17	6	0	2.896265	-2.090446	-0.291045
18	6	0	4.235422	-2.529220	-0.188908
19	6	0	5.127362	-1.505260	0.051631
20	16	0	4.293850	0.036344	0.125629
21	6	0	-2.260500	-2.278325	-0.678860
22	6	0	-3.525429	-2.894373	-0.533801
23	6	0	-4.484201	-2.057086	-0.003297
24	16	0	-3.811826	-0.463563	0.285769
25	6	0	-5.879722	-2.331552	0.272958
26	6	0	6.565538	-1.574764	0.210367
27	16	0	7.473960	-2.960567	-0.377547
28	6	0	8.972093	-2.286802	0.182656
29	6	0	8.786113	-1.065959	0.770637
30	6	0	7.421354	-0.660740	0.788471
31	16	0	-6.715018	-3.657559	-0.522427
32	6	0	-8.190336	-3.307430	0.321492
33	6	0	-8.052694	-2.227905	1.150113
34	6	0	-6.741494	-1.673545	1.125036
35	7	0	-3.419067	3.950910	-0.167761

36	6	0	-3.494024	5.404025	-0.089526
37	6	0	-4.695421	3.253945	-0.231680
38	1	0	0.277105	-1.791161	-0.100114
39	1	0	3.606552	5.015707	-0.792898
40	1	0	3.584201	4.920118	0.963538
41	1	0	4.479350	3.686450	0.027176
42	1	0	2.077711	-2.774826	-0.482541
43	1	0	4.530784	-3.569775	-0.275543
44	1	0	-1.401210	-2.794615	-1.092191
45	1	0	-3.722494	-3.926434	-0.804415
46	1	0	9.895268	-2.832983	0.043311
47	1	0	9.594348	-0.475173	1.188197
48	1	0	7.074459	0.265705	1.233609
49	1	0	-9.066007	-3.920096	0.154578
50	1	0	-8.856407	-1.844459	1.769434
51	1	0	-6.432213	-0.831612	1.735285
52	1	0	-4.007693	5.797581	-0.975674
53	1	0	-4.065797	5.700494	0.799503
54	1	0	-2.489844	5.817380	-0.033709
55	1	0	-5.311590	3.702226	-1.020138
56	1	0	-4.534967	2.200890	-0.448447
57	1	0	-5.233449	3.349938	0.721088

Table S6. Cartesian coordinates of the optimized NPh_2 structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.653977	7.215961	-0.033249
2	1	0	-4.167650	7.138721	0.912617
3	1	0	-4.232364	7.118217	-0.864589
4	1	0	-4.632613	3.548226	0.140376
5	1	0	-5.408192	4.822532	-0.840759
6	1	0	-5.407193	4.948548	0.932438
7	1	0	-5.999987	-0.799062	2.343747
8	1	0	-6.853639	-1.682332	4.489460
9	1	0	-7.583379	-4.057591	4.669027
10	1	0	-7.429092	-5.537235	2.670662
11	1	0	-6.545107	-4.659809	0.534834
12	1	0	-4.497892	-2.839823	-2.221702
13	1	0	-5.594880	-3.455393	-4.350972
14	1	0	-8.080152	-3.520566	-4.510178
15	1	0	-9.448365	-2.944546	-2.509569
16	1	0	-8.348268	-2.298496	-0.390774
17	1	0	5.205070	-2.174142	2.359124
18	1	0	6.440076	-2.520036	4.473536
19	1	0	8.923288	-2.325133	4.523840
20	1	0	10.147209	-1.763350	2.427833
21	1	0	8.906628	-1.387393	0.322202
22	1	0	6.313993	-0.305668	-2.384367
23	1	0	7.180210	-1.224755	-4.509558
24	1	0	8.156890	-3.515767	-4.582400
25	1	0	8.236753	-4.876285	-2.496837
26	1	0	7.338941	-3.966994	-0.379807
27	1	0	-1.575704	-0.858910	1.560335
28	1	0	-3.507683	-2.376743	1.567948
29	1	0	-5.384987	0.006997	-1.475948
30	1	0	-3.437695	1.507349	-1.503021
31	1	0	3.669773	1.981527	1.376984
32	1	0	5.756228	0.684424	1.377612
33	1	0	4.031279	-2.098694	-1.405587
34	1	0	1.956444	-0.787460	-1.426006
35	1	0	4.342185	5.147279	-0.207995

36	1	0	3.479204	6.445070	0.671513
37	1	0	3.416083	6.401926	-1.085722
38	1	0	0.191001	-0.372384	0.031967
39	6	0	-3.653226	6.788577	0.008153
40	6	0	-4.822161	4.616579	0.065164
41	7	0	-3.558542	5.336168	0.021610
42	6	0	-6.306710	-1.837393	2.420182
43	6	0	-6.788405	-2.340745	3.627055
44	6	0	-7.201740	-3.670800	3.728433
45	6	0	-7.118317	-4.497653	2.606196
46	6	0	-6.620533	-4.008694	1.399883
47	6	0	-5.581014	-2.856164	-2.290265
48	6	0	-6.204620	-3.202148	-3.487523
49	6	0	-7.597618	-3.243203	-3.577333
50	6	0	-8.363038	-2.923895	-2.453709
51	6	0	-7.748701	-2.558694	-1.257347
52	6	0	6.285972	-2.077982	2.379193
53	6	0	6.987179	-2.271529	3.567741
54	6	0	8.379441	-2.166691	3.596941
55	6	0	9.064187	-1.855716	2.420220
56	6	0	8.370362	-1.642426	1.230655
57	6	0	6.727901	-1.308564	-2.413669
58	6	0	7.217647	-1.831871	-3.608709
59	6	0	7.769409	-3.114087	-3.650441
60	6	0	7.817135	-3.873694	-2.479544
61	6	0	7.312498	-3.366620	-1.283613
62	6	0	-6.348074	-2.525261	-1.161498
63	6	0	-6.212927	-2.669090	1.292322
64	6	0	6.765437	-2.073959	-1.236594
65	6	0	6.970955	-1.755743	1.196212
66	7	0	6.258208	-1.548655	-0.016546
67	7	0	-5.715958	-2.162596	0.059905
68	6	0	-2.401001	-0.667530	0.879520
69	6	0	-3.495059	-1.527342	0.892588
70	6	0	-4.590555	-1.298114	0.046176
71	6	0	-4.547228	-0.187243	-0.813728
72	6	0	-3.444102	0.658192	-0.829583
73	6	0	3.736269	1.084583	0.773435

74	6	0	4.919459	0.355445	0.769723
75	6	0	5.048397	-0.805259	-0.011106
76	6	0	3.953700	-1.207534	-0.791032
77	6	0	2.777998	-0.463684	-0.792384
78	6	0	2.635161	0.695107	-0.009484
79	6	0	-2.342949	0.440389	0.017261
80	6	0	3.446400	5.769845	-0.191170
81	7	0	-2.382960	3.349109	-0.028502
82	6	0	-2.364749	4.691933	-0.021215
83	7	0	-1.255267	5.460764	-0.055154
84	6	0	-0.079761	4.854653	-0.075024
85	7	0	1.040049	5.576793	-0.119410
86	6	0	2.209482	4.918688	-0.126201
87	7	0	2.373656	3.603160	-0.077892
88	6	0	0.135890	0.711682	0.007760
89	6	0	-1.128486	1.292267	-0.017798
90	6	0	-1.211368	2.709972	-0.039329
91	7	0	-0.004514	3.429921	-0.049054
92	6	0	1.268625	2.829670	-0.034381
93	6	0	1.341981	1.423267	0.002582

Table S7. Cartesian coordinates of the optimized OMe structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.531180	-0.097891	0.067677
2	6	0	-1.295413	1.290416	0.045635
3	7	0	0.038635	1.739467	0.031439
4	6	0	1.153814	0.884819	0.047490
5	6	0	0.907882	-0.512837	0.088541
6	6	0	-0.414971	-0.943619	0.091223
7	6	0	2.529047	2.716026	-0.065756
8	7	0	2.391983	1.382552	0.002812
9	6	0	-3.115980	4.468089	0.094788
10	6	0	-2.899464	-0.672677	0.107682
11	6	0	-4.422235	-2.377477	0.965860
12	6	0	3.142293	-1.374516	0.922074
13	6	0	4.137865	-2.339642	0.938262
14	6	0	4.048084	-3.468137	0.108808
15	6	0	1.947122	-2.631282	-0.739109
16	6	0	4.959932	2.351798	-0.169719
17	7	0	-2.303541	2.188924	0.059232
18	6	0	-1.986930	3.476614	0.055331
19	7	0	-0.749057	3.994288	0.016286
20	1	0	4.998466	-2.246882	1.593752
21	6	0	0.278982	3.145838	-0.004722
22	7	0	1.516543	3.609633	-0.059026
23	1	0	-0.594069	-2.014266	0.113083
24	6	0	-5.207703	-0.791996	-0.680925
25	6	0	2.017879	-1.498489	0.082059
26	6	0	-3.171762	-1.775472	0.940390
27	6	0	-5.453415	-1.889963	0.151821
28	6	0	-3.945817	-0.196874	-0.694977
29	8	0	5.082553	-4.354778	0.198600
30	6	0	2.942542	-3.611798	-0.734943
31	7	0	3.789069	3.214892	-0.146732
32	6	0	4.050636	4.645560	-0.199572
33	6	0	5.038661	-5.519353	-0.609644
34	1	0	4.646665	1.310527	-0.197591
35	1	0	2.847943	-4.466248	-1.395368

36	1	0	-3.076210	5.114121	-0.789676
37	1	0	3.228143	-0.511648	1.572180
38	1	0	-3.775191	0.655946	-1.340758
39	1	0	-4.077885	3.954814	0.135996
40	1	0	5.567886	2.577087	-1.055300
41	1	0	-3.006391	5.121169	0.967855
42	1	0	-4.627503	-3.220597	1.618180
43	1	0	4.584954	4.895514	-1.125573
44	1	0	4.679886	4.943091	0.649711
45	1	0	1.105259	-2.747145	-1.416737
46	1	0	5.577751	2.525586	0.721745
47	1	0	3.107921	5.186753	-0.164156
48	1	0	5.944974	-6.081064	-0.375809
49	1	0	4.160062	-6.137166	-0.380759
50	1	0	-2.394222	-2.154682	1.598259
51	6	0	-7.731313	-2.080736	-0.541589
52	8	0	-6.648046	-2.545594	0.246556
53	1	0	-5.985183	-0.393598	-1.322950
54	1	0	5.033264	-5.269730	-1.679139
55	1	0	-8.574736	-2.732735	-0.306399
56	1	0	-7.994950	-1.043630	-0.294892
57	1	0	-7.509654	-2.148929	-1.615087

Table S8. Cartesian coordinates of the optimized FL structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-2.260231	6.789825	0.425826
2	1	0	-3.759271	6.715482	1.395027
3	1	0	-3.854430	6.942134	-0.366453
4	1	0	-4.555663	3.318157	0.140052
5	1	0	-5.236378	4.792176	-0.604002
6	1	0	-5.181344	4.638348	1.166105
7	1	0	-4.553997	-3.876198	3.042243
8	1	0	-4.900035	-2.148502	2.831078
9	1	0	-3.220517	-2.718411	2.895807
10	1	0	-2.249383	-4.084595	0.942243
11	1	0	-3.261354	-4.461472	-0.466477
12	1	0	-3.581540	-5.242463	1.094425
13	1	0	6.695504	-0.956345	3.012072
14	1	0	5.207468	-1.861384	2.670320
15	1	0	5.148165	-0.101170	2.890963
16	1	0	6.903370	0.768039	-0.348747
17	1	0	7.694872	0.599453	1.231405
18	1	0	6.146961	1.455159	1.101410
19	1	0	-6.222837	-5.235606	1.465601
20	1	0	-8.462348	-5.288642	0.396586
21	1	0	-9.144814	-3.505316	-1.180744
22	1	0	-7.596955	-1.638091	-1.715657
23	1	0	5.819148	-4.119521	-2.113053
24	1	0	8.086571	-4.979557	-1.575838
25	1	0	9.461905	-3.886613	0.170230
26	1	0	8.595446	-1.917313	1.407319
27	1	0	-1.880778	-1.441479	0.994533
28	1	0	-5.614674	0.082283	-1.933225
29	1	0	-3.524781	1.390487	-1.793780
30	1	0	1.587548	-1.317585	-2.093901
31	1	0	3.527215	-2.825020	-2.298529
32	1	0	3.562699	0.897875	1.019460
33	1	0	4.520522	4.164322	-0.195628
34	1	0	3.787580	5.417937	0.851213
35	1	0	3.698973	5.590222	-0.896969

36	1	0	-0.103372	-0.960483	-0.545293
37	6	0	-3.292818	6.448703	0.437658
38	6	0	-4.649824	4.397461	0.236442
39	7	0	-3.327822	5.005124	0.253453
40	6	0	-4.227457	-2.960231	2.536214
41	6	0	-3.272762	-4.305229	0.616965
42	6	0	5.740010	-0.924973	2.475464
43	6	0	6.725575	0.606324	0.719127
44	6	0	-6.512467	-4.447899	0.773850
45	6	0	-7.775808	-4.477029	0.170709
46	6	0	-8.161094	-3.469644	-0.720034
47	6	0	-7.292712	-2.418469	-1.022558
48	6	0	6.419308	-3.636309	-1.346016
49	6	0	7.694468	-4.117943	-1.041835
50	6	0	8.471341	-3.500732	-0.055781
51	6	0	7.983036	-2.389630	0.642455
52	6	0	5.932442	-2.528006	-0.649344
53	6	0	6.714358	-1.904910	0.344775
54	6	0	5.970718	-0.720169	0.961618
55	6	0	-4.229361	-3.154774	1.003193
56	6	0	-5.643066	-3.404466	0.476822
57	6	0	-6.032568	-2.389912	-0.421109
58	6	0	-2.693625	-1.122406	0.346079
59	6	0	-3.867865	-1.859627	0.275196
60	6	0	-4.929404	-1.430757	-0.543616
61	6	0	-4.805940	-0.256904	-1.290488
62	6	0	-3.626370	0.480669	-1.213729
63	6	0	2.443220	-1.174221	-1.439641
64	6	0	3.542226	-2.022957	-1.564853
65	6	0	4.653991	-1.815444	-0.747974
66	6	0	4.654713	-0.758440	0.183693
67	6	0	3.558809	0.082143	0.305844
68	6	0	-2.554035	0.064066	-0.401378
69	6	0	2.426158	-0.116590	-0.509056
70	6	0	3.683996	4.855808	-0.083883
71	7	0	-2.334033	2.947744	-0.079211
72	6	0	-2.196784	4.271771	0.099474
73	7	0	-1.023592	4.939366	0.136512

74	6	0	0.092558	4.241478	0.009562
75	7	0	1.271662	4.863963	0.028916
76	6	0	2.377145	4.113632	-0.091831
77	7	0	2.424487	2.793088	-0.213265
78	6	0	-0.061133	0.118707	-0.435044
79	6	0	-1.268270	0.806034	-0.360082
80	6	0	-1.225061	2.216702	-0.200783
81	7	0	0.041541	2.824245	-0.148451
82	6	0	1.256273	2.118415	-0.239387
83	6	0	1.203924	0.717288	-0.380267

Table S9. Cartesian coordinates of the optimized H structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.805756	0.358476	-0.001774
2	6	0	-1.318973	-0.963129	-0.023180
3	7	0	0.075089	-1.158665	-0.025082
4	6	0	1.014239	-0.112325	-0.016914
5	6	0	0.513249	1.215953	-0.011843
6	6	0	-0.866069	1.396081	0.001314
7	7	0	-2.143885	-2.029587	-0.063839
8	6	0	-1.595844	-3.237801	-0.097388
9	7	0	-0.284224	-3.519052	-0.077334
10	6	0	0.570558	-2.496672	-0.034165
11	7	0	1.872546	-2.726109	0.001071
12	6	0	2.703265	-1.662213	0.034199
13	7	0	2.321748	-0.374571	0.008964
14	6	0	-2.524162	-4.417945	-0.159962
15	6	0	1.419799	2.392849	0.020683
16	6	0	-3.258238	0.672372	-0.021167
17	6	0	-3.728112	1.722419	-0.829243
18	6	0	-5.075046	2.083447	-0.830481
19	6	0	-5.983912	1.399591	-0.022894
20	6	0	-5.531886	0.351409	0.781774
21	6	0	-4.186440	-0.010765	0.783383
22	6	0	2.528942	2.506297	-0.835384
23	6	0	3.324167	3.650635	-0.822594
24	6	0	3.034081	4.705483	0.045996
25	6	0	1.938361	4.605280	0.903422
26	6	0	1.141061	3.460833	0.890173
27	7	0	4.033715	-1.921343	0.095926
28	6	0	5.025069	-0.857726	0.147937
29	6	0	4.555848	-3.279964	0.107562
30	1	0	-1.240411	2.415115	0.014427
31	1	0	-2.359833	-5.066552	0.708031
32	1	0	-3.564097	-4.089136	-0.185226
33	1	0	-2.302358	-5.018256	-1.049365
34	1	0	-3.034315	2.247258	-1.480893
35	1	0	-5.413479	2.894159	-1.470497

36	1	0	-7.034697	1.676909	-0.023276
37	1	0	-6.230880	-0.187465	1.416285
38	1	0	-3.848262	-0.828589	1.408075
39	1	0	2.760759	1.694630	-1.515328
40	1	0	4.171823	3.721374	-1.499535
41	1	0	3.658009	5.595209	0.055264
42	1	0	1.705435	5.414583	1.590501
43	1	0	0.302195	3.383884	1.576981
44	1	0	5.660508	-0.986742	1.033523
45	1	0	5.667919	-0.894829	-0.741871
46	1	0	4.524908	0.106931	0.195882
47	1	0	5.228366	-3.429354	-0.747358
48	1	0	5.128264	-3.453948	1.028124
49	1	0	3.730015	-3.985398	0.051584

Table S10. Cartesian coordinates of the optimized CF_3 structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.455062	0.315885	0.003902
2	6	0	1.271120	1.714001	-0.016900
3	7	0	-0.045583	2.209645	-0.024089
4	6	0	-1.192624	1.395492	-0.019104
5	6	0	-0.993709	-0.011362	-0.012668
6	6	0	0.312019	-0.490866	0.003812
7	7	0	2.308875	2.570328	-0.053757
8	6	0	2.040825	3.872347	-0.092701
9	7	0	0.824160	4.432873	-0.078456
10	6	0	-0.235540	3.623623	-0.035627
11	7	0	-1.454239	4.133253	-0.003382
12	6	0	-2.499761	3.279618	0.029994
13	7	0	-2.408614	1.937111	0.004348
14	6	0	3.206831	4.817206	-0.155668
15	6	0	-2.135542	-0.959491	0.017460
16	6	0	2.803224	-0.305934	-0.009144
17	6	0	3.035460	-1.441588	-0.804648
18	6	0	4.267624	-2.089433	-0.797220
19	9	0	7.468085	-1.713731	-0.939710
20	1	0	0.453238	-1.567251	0.017585
21	1	0	3.127495	5.444554	-1.050491
22	1	0	4.148976	4.267580	-0.172222
23	6	0	-2.096211	-2.069951	0.877780
24	7	0	-3.738634	3.823403	0.091381
25	6	0	-4.941803	3.005057	0.140399
26	6	0	-5.310489	-3.888331	0.014263
27	1	0	-3.305393	0.033076	-1.497972
28	1	0	-5.542022	3.285112	1.015007
29	1	0	-4.669172	1.954425	0.207080
30	6	0	5.300266	-1.610717	0.010733
31	6	0	5.089116	-0.479191	0.803986
32	6	0	3.857062	0.165768	0.793390
33	6	0	-3.250248	-0.816114	-0.827691
34	6	0	-4.279370	-1.751680	-0.816641
35	9	0	6.562605	-3.587235	-0.315294

36	9	0	7.283129	-2.168455	1.175794
37	6	0	-4.222002	-2.851969	0.044159
38	6	0	-3.124754	-3.008522	0.892460
39	1	0	4.426123	-2.964537	-1.418827
40	1	0	3.184729	5.493141	0.706622
41	1	0	2.247560	-1.812379	-1.454051
42	1	0	5.886815	-0.111101	1.441081
43	9	0	-6.513655	-3.346541	-0.283453
44	6	0	-3.949851	5.264854	0.099303
45	9	0	-5.071458	-4.840968	-0.918761
46	9	0	-5.434242	-4.525976	1.199808
47	6	0	6.650118	-2.271413	-0.014975
48	1	0	-5.131489	-1.628239	-1.477408
49	1	0	3.706044	1.041634	1.411627
50	1	0	-3.082511	-3.851558	1.574151
51	1	0	-2.989614	5.772631	0.047843
52	1	0	-1.260873	-2.187121	1.562196
53	1	0	-5.549232	3.171087	-0.759103
54	1	0	-4.474989	5.559849	1.016684
55	1	0	-4.568561	5.555241	-0.759497

Table S11. Results of TD-DFT calculations in comparison with experimental values

Compound	Experimental		Calculated			
	λ_{abs}[a] / nm	λ_{em} / nm	λ_{abs} / nm	$f(S_0 \rightarrow S_1)$ (H–L CI coefficient)[b]	λ_{em} / nm	$f(S_1 \rightarrow S_0)$ (H–L CI coefficient)[b]
5AP	573	n.d.	505.77	0.0066 (0.69900)	570.21	0.0040 (0.70441)
A5AP	506	518	449.97	0.0241 (0.68685)	500.85	0.0184 (–0.69556)
BT	590	615	563.40	0.1562 (0.68282)	745.97	0.0477 (0.69242)
NPh_2	550	584	517.26	0.0995 (0.66237)	673.61	0.0386 (0.68472)
OMe	546	568	499.59	0.0628 (0.68375)	661.36	0.0237 (0.69804)
FL	544	566	499.05	0.0962 (0.67939)	644.70	0.0358 (–0.69437)
H	538	554	485.54	0.0555 (0.68463)	626.71	0.0218 (–0.69894)
CF_3	532	545	478.31	0.0667 (0.68267)	596.93	0.0279 (–0.69733)

[a]The peak maxima of the absorption band in the largest wavelength (i.e. not the absorption maxima). [b]The CI expansion coefficients of HOMO–LUMO transition in corresponding transitions. These values clearly indicate that S_0–S_1 transitions are largely composed of the HOMO–LUMO transition.

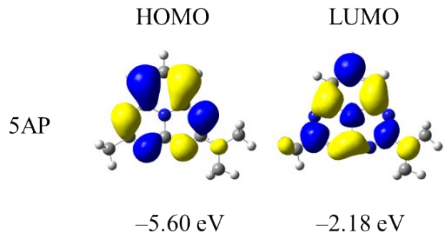


Figure S23. MO patterns of HOMO and LUMO of 5AP.

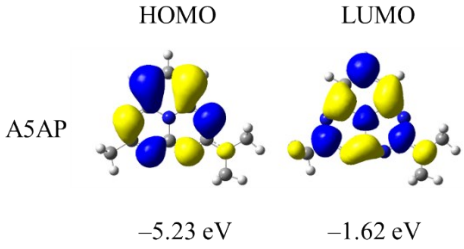


Figure S24. MO patterns of HOMO and LUMO of A5AP.

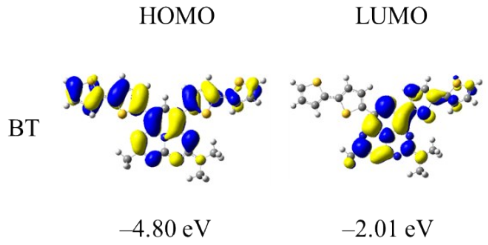


Figure S25. MO patterns of HOMO and LUMO of BT.

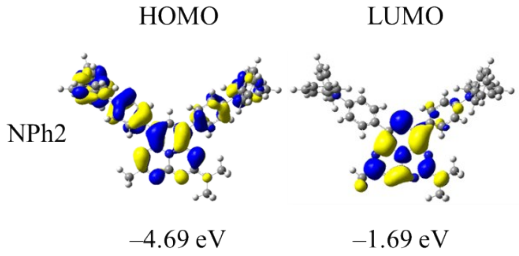


Figure S26. MO patterns of HOMO and LUMO of NPh2.

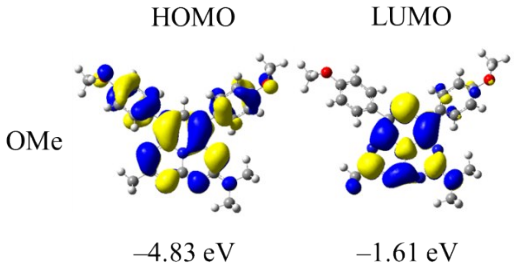


Figure S27. MO patterns of HOMO and LUMO of OMe.

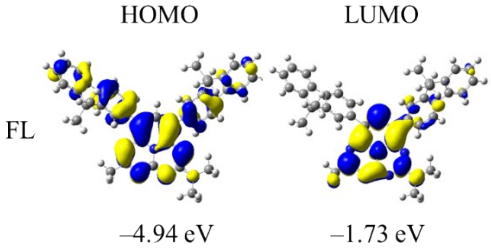


Figure S28. MO patterns of HOMO and LUMO of FL.

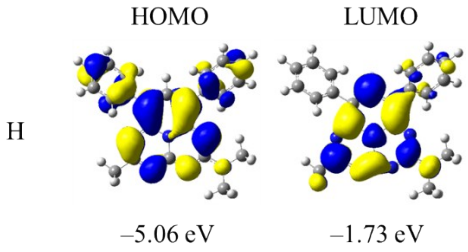


Figure S29. MO patterns of HOMO and LUMO of H.

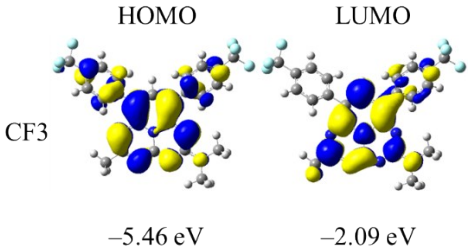


Figure S30. MO patterns of HOMO and LUMO of CF3.

5-4. Second emission peak of FL.

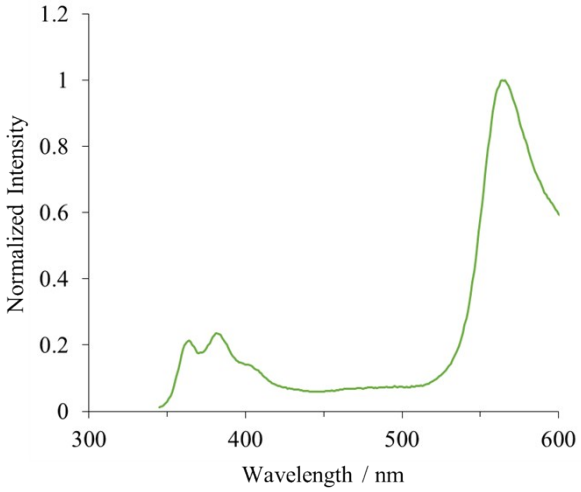


Figure S30. PL spectrum of FL including a second emission peak in shorter wavelength region. The spectrum was recorded with the excitation light at 325 nm.

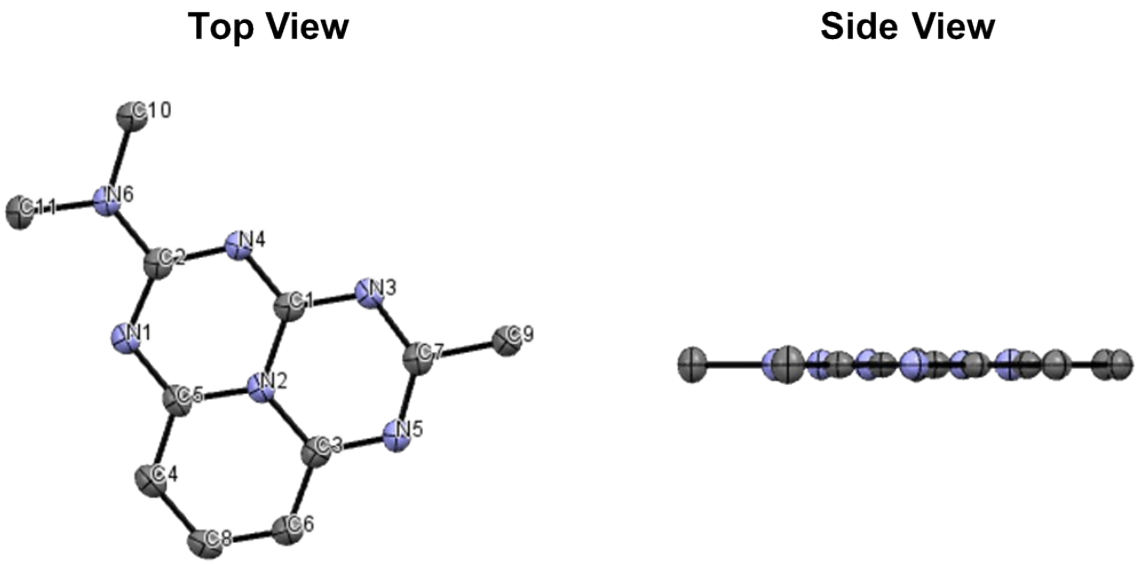


Figure S31. ORTEP drawings of A5AP-Me. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme S1. Synthetic scheme of A5AP derivatives

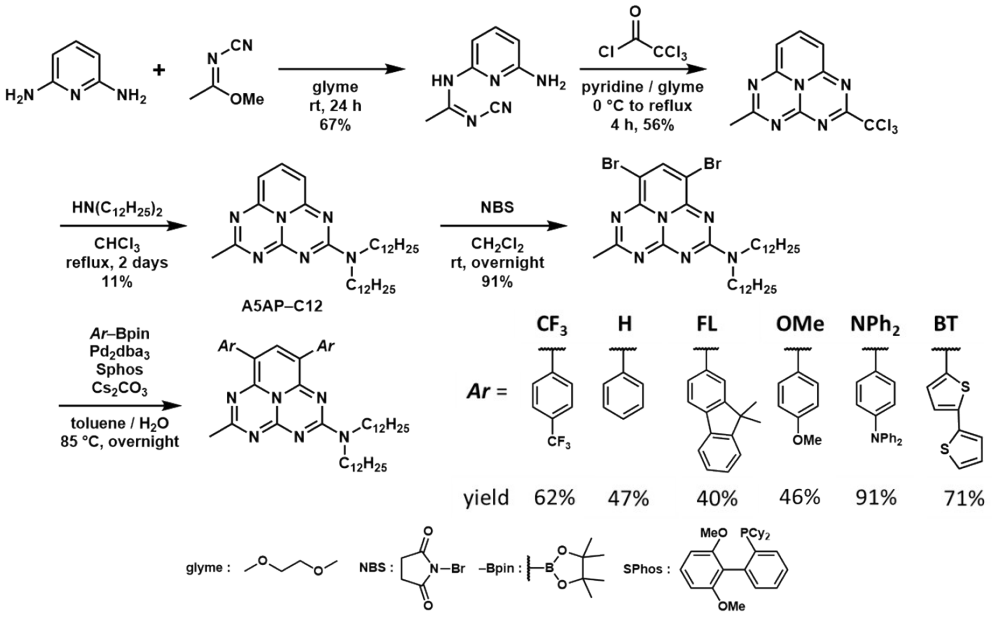


Table S12. Photophysical properties of A5AP derivatives

	Φ_{PL}	τ / ns	$\bar{\tau}$[a] / ns	k_r / 10^7 s^{-1}	k_{nr} / 10^9 s^{-1}	k_r^{th} [b] / 10^7 s^{-1}
A5AP –C12	0.03	1.77 (χ^2 = 1.19)	1.77	1.7	0.55	0.72
BT	0.01	0.27 (χ^2 = 1.12)	0.27	3.7	3.7	1.4
NPh2	0.02	0.27 (38%), 0.43 (62%) (χ^2 = 1.00)	0.37	5.4	2.6	1.3
OMe	0.01	0.42 (85%), 0.77 (15%) (χ^2 = 1.19)	0.47	2.1	2.1	0.79
FL	0.02	0.69 (χ^2 = 1.04)	0.69	2.9	1.4	1.2
H	0.02	0.83 (93%), 5.07 (7%) (χ^2 = 1.16)	1.12	1.8	0.88	0.75
CF3	0.08	1.97 (χ^2 = 1.09)	1.97	4.0	0.47	0.99

[a] Weighted average value of τ. [b] Calculated values determined from the absorption maxima of the S_0–S_1 band in the longer wavelength region (wavenumber / cm^{-1}: $\bar{\nu}_0^2$) and oscillator strength f ($S_1 \rightarrow S_0$)from DFT calculations (Table S11). These values and k_r^{th} are related with the following formula (N. J. Turro, V. Ramamurthy and J. C. Scaiano, *Principles of Molecular Photochemistry*, University Science Books, Sausalito, 2009. Japanese edition was published from Maruzen, 2013.):

$$k_r^{th} \cong \bar{\nu}_0^2 f$$

These k_r^{th} values qualitatively corresponded with the k_r values from PL litetime measurements.

Table S13. Electrochemical properties of A5AP derivatives[a]

Compound	E_{ox}^{onset} / V	E_{red}^{onset} / V	E_{HOMO}[b] / eV	E_{LUMO}[c] / eV	E_g[d] / eV	$E_{g,opt}$[e] / eV
A5AP–C12	0.40	–2.31	–5.20	–2.49	2.71	2.37
BT	0.19	–2.03	–4.99	–2.77	2.22	1.97
NPh2	0.19	–2.24	–4.99	–2.56	2.43	2.15
OMe	0.32	–2.27	–5.12	–2.53	2.59	2.16
FL	0.35	–2.25	–5.15	–2.55	2.60	2.19
H	0.43	–2.23	–5.23	–2.57	2.66	2.23
CF3	0.56	–2.13	–5.36	–2.67	2.66	2.26

[a]Measured in dichloromethane solution (1.0×10^{-3} M) containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as an electrolyte, using a glassy carbon working electrode, a Pt wire counter electrode, an Ag/AgCl reference electrode, and a ferrocene/ferrocenium external standard at room temperature with a scan rate of 0.05 Vs^{-1}. [b]$E_{HOMO} = -4.8 - E_{ox}^{onset}$. [c]$E_{LUMO} = -4.8 - E_{red}^{onset}$. [d]$E_g = E_{LUMO} - E_{HOMO}$. [e] Optical band gaps were estimated from onset wavelength of the absorption spectra.

6. References

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