Supporting Information

For

Synthesis of Substituted Picenes through Pd-Catalyzed Cross-Coupling Reaction/Annulation Sequences and Their Physicochemical Properties

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1. General

2. Experimental Procedures and Spectroscopic Data for New Compounds

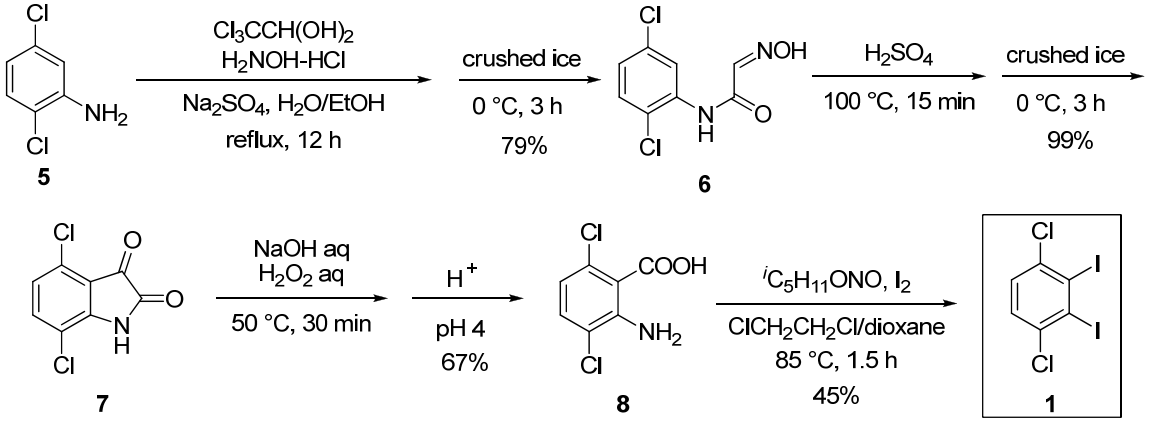
3. Structural Determination of Compounds by X-ray Analysis

4. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Charts for the New Compounds

1. General. All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. Dehydrated toluene, dichloromethane, hexane, and diethyl ether were purchased from Kanto Chemicals Co., Ltd. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 N (spherical, neutral, 40-100 μm) from Kanto Chemicals Co., Ltd. NMR spectra (^{1}H, ^{13}C{^{1}H}) were recorded on Varian INOVA-600 (600 MHz) or Mercury-300 (300 MHz) spectrometers. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. Melting Points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. The GC yields were determined using suitable hydrocarbon internal standards. GC/MS analyses were carried out on a SHIMADZU GC-17A equipped with a SHIMADZU QP-5050 GC-MS system. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer.

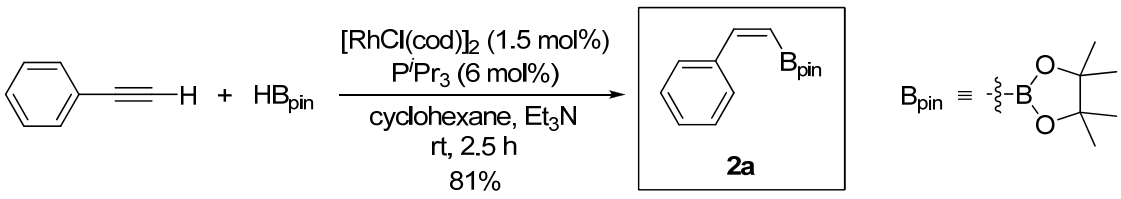
2. Experimental Procedures and Spectroscopic Data for New Compounds

2.1. Synthesis of 1,4-Dichloro-2,3-diiodobenzene (1). [1]



The first two steps followed the general procedure.[2] A commercially available 2,5-dichloroaniline (**5**) (4.86 g, 30 mmol), chloral hydrate (5.95 g, 36 mmol), hydroxylamine hydrochloride (3.13 g, 45 mmol), and Na_2SO_4 (30.0 g) were suspended in a mixture of H_2O (100 mL) and EtOH (100 mL). The mixture was stirred and kept at reflux temperature (80 °C) for 12 h and then concentrated by evaporation and poured into crushed ice, which caused precipitation of white solid. After being kept at 0 °C for 3 h, the suspension was filtered, and the white solid was dried in air to yield a crude 2,5-dichloroisonitroso-acetanilide (**6**) in 79% yield (5.52 g). Compound **6** was then heated in 86% H_2SO_4 (80 mL) at 100 °C for 15 min. The resulting dark red suspension was poured into crushed ice to yield 3,6-dichloroisatine (**7**) (5.07 g, 99%) as bright orange crystals, which were subsequently subjected to basic hydrolysis in aq H_2O_2 to yield off-white crystals of 3,6-dichloroanthranilic acid (**8**) (3.24 g, 67%).[3] Finally, compound **8** was converted into 1,4-dichloro-2,3-diiodobenzene (**1**) by employing the aprotic diazotization procedure.[4] After column chromatography on silica gel (hexanes as eluent) and bulb to bulb distillation (160 ºC/1.4 Torr), the desired product **1** was obtained as white crystals (2.83 g, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 7.41 (s, 2 H).

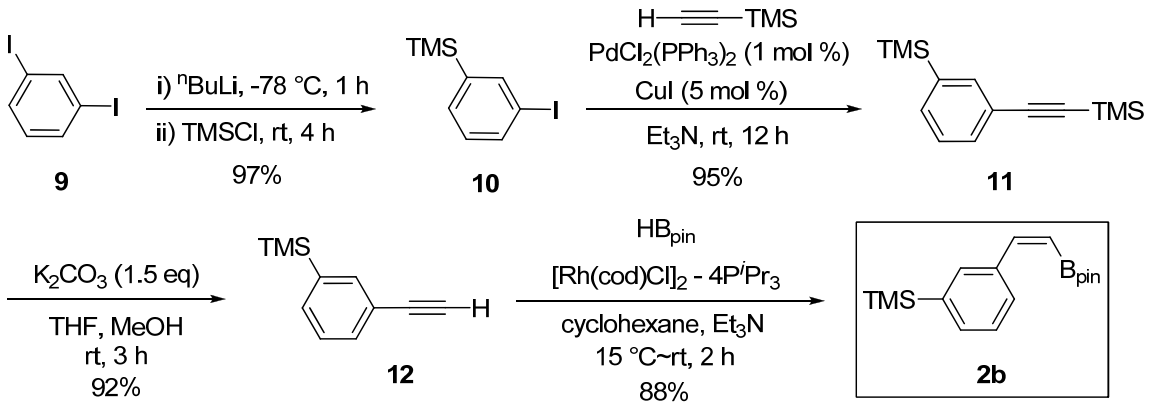
2.2. A General Procedure for (*Z*)-Alkenylboronates 2 by Hydroboration: Synthesis of 4,4,5,5-Tetramethyl-2-[(1*Z*)-2-phenylethenyl]-1,3,2-dioxaborolane (2a).[5]



A 50 mL Schlenk tube, equipped with a magnetic stir bar, was charged with $[RhCl(cod)]_2$ (37 mg, 0.075 mmol, 1.5 mol%) and then flushed with argon. Cyclohexane (15 mL), P^iPr_3 (0.057 mL, 0.3 mmol, 6 mol%), Et_3N (5 mL), and HB_{pin} (0.725 mL, 5 mmol) were successively added. After being stirred at room temperature for 30 min, phenylacetylene (1.1 mL, 10 mmol) was added in one-portion and the

mixture was stirred at room temperature for 2 h before quenching by MeOH. Filtration and evaporation afforded brown oil, which was purified by bulb to bulb distillation (130 °C/1.3 Torr) to obtain product **2a** as colorless liquid (0.93 g, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.30 (s, 12H), 5.60 (d, J = 14.7 Hz, 1H), 7.23 (d, J = 14.7 Hz, 1H), 7.26-7.31 (m, 3H), 7.54 (d, J = 7.9 Hz, 2H).

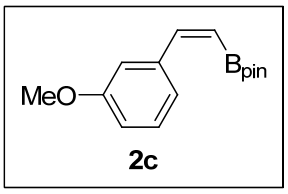
Synthesis of 4,4,5,5-Tetramethyl-2-[(1*Z*)-2-(3-trimethylsilane-phenylethenyl]-1,3,2-dioxaborolane (2b).



To a stirring solution of 1,3-diiodobenzene (**9**, 6.6 g, 20 mmol) in diethyl ether (50 mL) was cooled to -78 °C. Addition of n-BuLi (12.3 mL, 20 mmol, 1.63 M in hexane) over 10 min resulted in an off-white solution. After the mixture was stirred for 1 h at this temperature, chlorotrimtheylsilane (2.39 g, 22 mmol) was added. The solution was allowed to warm to room temperature for 4 h. Water (10 mL) was added to the above solution. The organic layer was extracted with diethyl ether and washed with brine, dried ($MgSO_4$), and concentrated under vacuum. The crude material (**10**, 5.38 g, 97%) was obtained as brown oil directly for next step. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 0.28 (s, 9H), 7.11 (t, J = 7.7 Hz, 1H), 7.47 (dt, J = 7.2 Hz, 1H), 7.70 (dt, J = 7.8 Hz, 1H), 7.83 (s, 1H). A 200 mL two necks round bottom flask equipped with a magnetic stir bar was charged with **10** (5.25 g, 19 mmol), $PdCl_2(PPh_3)_2$ (133 mg, 0.19 mmol, 1 mol%), CuI (181 mg, 0.95 mmol, 5 mol%), triethylamine (75 mL) and trimethylsilylacetylene (3.22 mL, 22.8 mmol) under argon atmosphere. The reaction mixture was stirred

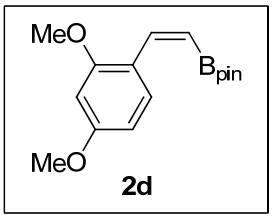
overnight at room temperature. After evaporation to remove Et_3N, the residue was filtrated with diethyl ether. The solvent was removed under reduced pressure and the desired compound **11** (4.45 g, 95% yield) was afford as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 0.28 (s, 18H), 7.30 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 6.0 Hz, 2H), 7.63 (s, 1H). To a solution of **11** (4.27 g, 17.3 mmol) in THF (50 mL) and MeOH (30 mL) was added K_2CO_3 (3.58 g, 26 mmol) and H_2O (1.2 mL). The solution was stirred at rt for 3 h before pouring the solution into saturated aq. NH_4Cl (50 mL). The mixture was extracted with diethyl ether. The organic layer was washed with 5% aq. NH_4Cl and brine, dried ($MgSO_4$) and the solvent was removed in vacuum. This crude product was purified via Florisil and afforded **12** (2.77 g, 92%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 0.28 (s, 9H), 3.09 (s, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.35-7.52 (m, 2H), 7.66 (s, 1H).

4,4,5,5-Tetramethyl-2-[(1*Z*)-2-(3-trimethylsilane-phenylethenyl]-1,3,2-dioxaborolane (2b) was obtained as a yellow liquid (2.11 g, 88% yield) via stereoselective hydroboration of **12**[6] with similar experimental procedure of **2a**. FT-IR (neat, cm^{-1}): 2978 (m), 2359 (m), 1620 (m), 1337 (m), 1250 (s), 1144 (s), 870 (m), 837 (s), 752 (m); ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 0.31 (s, 9H), 1.31 (s, 12H), 5.61 (d, J = 14.7 Hz, 1H), 7.23 (d, J = 14.7 Hz, 1H), 7.26-7.35 (m, 1H), 7.45 (d, J = 9.6 Hz, 1H), 7.56 (d, J = 10.5 Hz, 1H), 7.82 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt) δ -1.1, 24.8, 83.4, 127.3, 129.3, 133.1, 133.8, 137.5, 140.0, 149.0. The carbon signal adjacent to B was not observed due to low intensity. MS (EI, m/z (relative intensity)): 302 (M+, 41), 287 (100), 286 (25), 187 (35), 146 (15), 145 (98), 143 (16), 73 (39). Anal. Calcd for $C_{17}H_{27}BO_2Si$: C, 67.54; H, 9.00%. Found: C, 67.15; H, 8.83%.



2c

4,4,5,5-Tetramethyl-2-[(1*Z*)-2-(3-methoxylphenylethenyl]-1,3,2-dioxaborolane (2c) was obtained in 68% yield as a yellow liquid via stereoselective hydroboration of the corresponding alkyne[7]. FT-IR (neat, cm^{-1}): 2978 (m), 2359 (m), 1618 (m), 1582 (m), 1371 (m), 1258 (s), 1144 (s), 872 (m), 799 (m); ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 1.30 (s, 12H), 3.83 (s, 3H), 5.60 (d, J = 15.3 Hz, 1H), 6.84 (d, J = 9.0 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 7.16-7.25 (m, 2H), 7.34 (t, J = 3.9 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt) δ 24.7, 55.1, 83.4, 113.1, 114.4, 121.7, 128.8, 139.7, 148.2, 159.3. The carbon signal adjacent to B was not observed due to low intensity. MS (EI, m/z (relative intensity)): 260 (M+, 60), 161 (24), 160 (38), 159 (65), 144 (100), 130 (20), 129 (26), 117 (22), 77(22). Anal. Calcd for $C_{15}H_{21}BO_3$: C, 69.26; H, 8.14%. Found: C, 69.29; H, 8.27%.

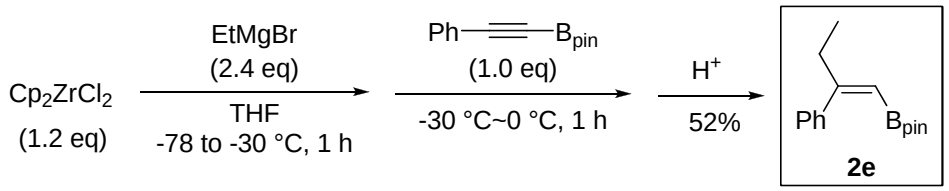


2d

4,4,5,5-Tetramethyl-2-[(1*Z*)-2-(2,4-dimethoxyl-phenylethenyl]-1,3,2-dioxaborolane (2d) was obtained in 74% yield as a yellow liquid via stereoselective hydroboration of the corresponding alkyne.[8] FT-IR (neat, cm^{-1}): 2974 (m), 1607 (s), 1429 (s), 1333 (m), 1283 (s), 1248 (s), 1161 (m), 1105 (w), 831 (m). ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 1.27 (s, 12H), 3.80 (s, 3H), 3.82 (s, 3H), 5.48 (d, J = 14.7 Hz, 1H), 6.40-6.44 (m, 2H), 7.43 (d, J = 12.0 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt) δ 24.7, 55.2, 55.3, 83.0, 97.7, 103.8, 120.6, 130.4, 143.4, 158.2, 161.0. The carbon signal adjacent to B was not observed due to low intensity. MS (EI, m/z (relative intensity)): 290 (M+, 59), 289 (15), 217 (100), 216 (27), 189 (10), 176 (15), 149 (37), 121 (11). Anal. Calcd for $C_{16}H_{23}BO_4$: C, 66.23; H, 7.99%. Found: C, 66.31; H, 8.08%.

Synthesis of (*Z*)-4,4,5,5-Tetramethyl-2-(2-phenyl-1-buten-1-yl)-1,3,2-dioxaborolane (2e).

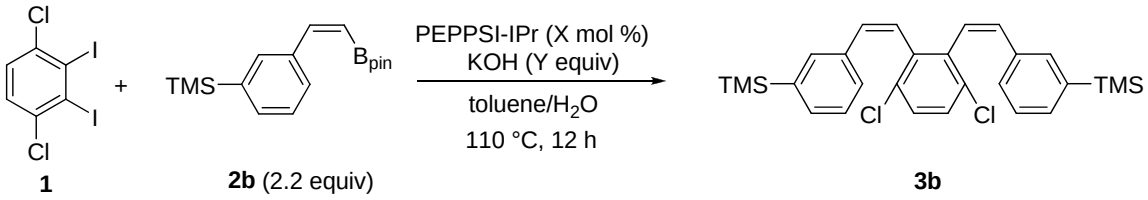
9



To a solution of zirconocene dichloride (1.75 g, 6 mmol) in THF (25 mL) was added dropwise EtMgBr (12.2 mL, 12 mmol, 0.98 M THF solution) at -78 °C. The reaction mixture was stirred for 1 h at -30 °C and then 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane was added. The reaction mixture was stirred for 1 h at 0 °C, quenched with 1 M HCl, and extracted with ethyl acetate. The combined organic layers were washed with brine, and dried over $MgSO_4$. Filtration and concentration under vacuum, followed by purification with bulb to bulb distillation (140 ºC/1.4 Torr) gave product **2f** as colorless liquid. (0.68 g, 52% yield). ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 1.05 (t, J = 7.5 Hz, 3H), 1.13 (s, 12H), 2.49 (q, J = 7.4 Hz, 2H), 5.46 (s, 1H), 7.24-7.28 (m, 5H).

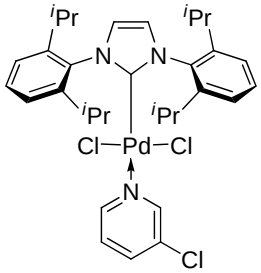
2.3. A General Procedure for Suzuki-Miyaura Coupling of 1,4-Dichloro-2,3-diiodobenzene with (*Z*)-Alkenylboronates: Formation of 3.

Table S1. Optimization of Suzuki-Miyaura Coupling of **1** with **2b**.



1 **2b** (2.2 equiv) **3b**

entry	PEPPSI-IPr (X mol %)	KOH (Y equiv)	toluene/H_2O (mL/mL)	yield[a] (%)
1	10	6	10/1	63
2	10	3	10/1	44
3	5	6	10/1	43
4	10	6	without water	ND
5	**10**	**6**	**5/1**	**68**
6[b]	10	6	5/1	51

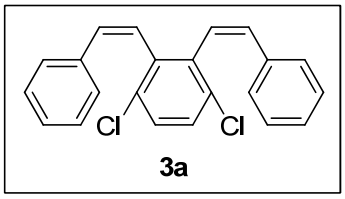


PEPPSI-IPr

[a] Isolated yields.
[b] 2.0 eq of **2b** was used.

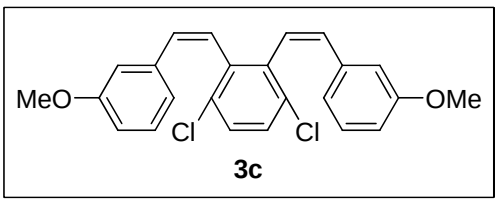
A 20 mL Schlenk tube, equipped with a magnetic stirrer bar, 1,4-dichloro-2,3-diiodobenzene (**1**, 199 mg, 0.5 mmol), (*Z*)-alkenylboranate **2b** (332 mg, 1.1 mmol), PEPPSI-IPr (34 mg, 0.05 mmol, 10 mol%), and KOH solid (168 mg, 3 mmol) were successively added. Then, 1 mL of toluene and 0.2 mL of H_2O were added in one-portion and the reaction mixture was stirred at 110 °C. After react for 12 h, the reaction mixture was quenched with 1 M HCl, and extracted with diethyl ether (3 × 10 mL). The combined ethereal layer was washed with brine and dried over anhydrous magnesium sulfate. Filtration and evaporation afforded brown oil, which was purified by chromatography (hexane as the eluent) to obtain product **3b** as pale yellow oil (169 mg, 68% yield). FT-IR (neat, cm^{-1}): 2953 (s), 1435 (m), 1248 (s), 1132 (w), 1113 (m), 837 (s), 800 (m), 754 (m), 691 (w). ^1H NMR ($CDCl_3$, 300 MHz, rt) δ 0.14 (s, 18H), 6.03 (d, J = 12.0 Hz, 2H), 6.53 (d, J = 12.3 Hz, 2H), 7.02 (s, 2H), 7.11 (s, 2H), 7.21-7.25 (m, 2H),

7.32-7.35 (m, 4H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, rt) δ -1.4, 125.5, 127.7, 128.9, 129.1, 132.3, 132.3, 132.8, 135.9, 137.5, 140.2; MS (EI, m/z (relative intensity)): 495 (M+, 1.18), 311 (22), 278 (10), 163 (34), 93 (20), 73 (100). Anal. Calcd for $C_{28}H_{32}Cl_2Si_2$: C, 67.85; H, 6.51%. Found: C, 68.15; H, 6.48%.



3a

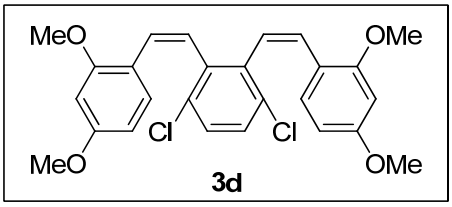
A yellow solid. 57% yield. FT-IR (neat, cm^{-1}): 3049 (w), 1493 (m), 1435 (s), 1121 (s), 870 (m), 810 (s), 773 (s), 745 (m), 691 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 6.06 (d, J = 12 Hz, 2H), 6.54 (d, J = 12 Hz, 2H), 6.93-7.01(m, 2H), 7.14-7.18 (m, 6H), 7.27-7.33 (m, 4H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, rt) δ 126.5, 128.6, 129.1, 129.2, 129.3, 129.6, 130.2, 133.2, 133.5, 137.9, 138.3. MS (EI, m/z (relative intensity)): 351 (M+, 5), 350 (17), 272 (15), 261 (32), 259 (49), 202 (28), 167 (56), 91 (100). Anal. Calcd for $C_{22}H_{16}Cl_2$: C, 75.22; H, 4.59%. Found: C, 74.93; H, 4.56%.



3c

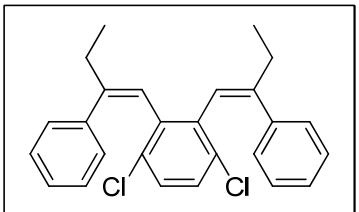
Yellow oil. 67% yield. FT-IR (neat, cm^{-1}): 2938 (w), 1597 (s), 1578 (s), 1489 (s), 1435 (s), 1260 (s), 1153 (m), 1042 (s), 860 (w), 795 (s), 689 (m). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 3.60 (s, 6H), 6.10 (d, J = 12 Hz, 2H), 6.49 (d, J = 3.9 Hz, 3H), 6.55 (t, J = 6.6 Hz, 3H), 6.68-6.75 (m, 2H), 7.05-7.10 (m, 2H), 7.31 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, rt) δ 54.9, 112.9, 113.6, 119.3, 124.0, 125.6, 128.7, 129.1, 129.2, 132.2, 133.2, 136.0, 137.4, 138.0. MS (EI, m/z (relative intensity)): 411 (M+, 5), 410 (19), 302

(16), 289 (27), 227 (79), 121 (100), 91 (14). Anal. Calcd for $C_{24}H_{20}Cl_2O_2$: C, 70.08; H, 4.90%. Found: C, 69.93; H, 4.78%.



3d

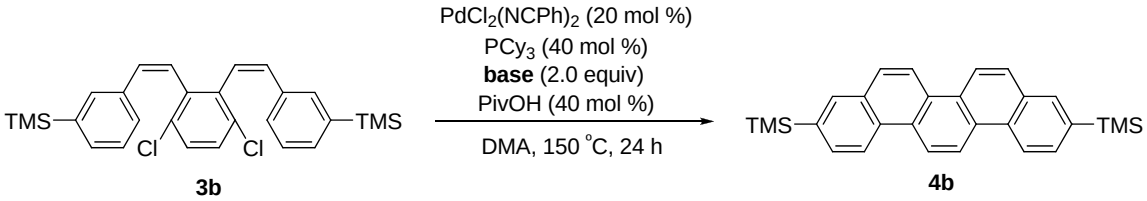
Yellow oil. 38% yield. FT-IR (neat, cm^{-1}): 2938 (w), 1608 (s), 1503 (s), 1464 (w), 1292 (s), 1290 (s), 1159, (s), 823 (w). ^1H NMR ($CDCl_3$, 300 MHz, rt) δ 3.76 (s, 6H), 3.80 (s, 6H), 6.17 (q, J = 8.7 Hz, 2H), 6.36 (s, 2H), 6.57 (q, J = 7.5 Hz, 2H), 6.78 (d, J = 12 Hz, 2H), 7.23 (s, 2H), 7.29 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt) δ 55.0, 55.4, 98.1, 104.1, 119.0, 123.5, 128.5, 128.9, 131.9, 137.9, 157.9, 160.3. MS (EI, m/z (relative intensity)): 471 (M+, 7), 470 (26), 332 (12), 151 (100), 121 (16). HRMS (EI) Calcd for $C_{26}H_{24}Cl_2O_4$: 470.1052. Found: 470.1043.



3e

Yellow oil. 67% yield. FT-IR (neat, cm^{-1}): 2965 (s), 2929 (s), 2359 (s), 1427 (m), 1150 (m), 806 (w), 772 (m), 698 (s). ^1H NMR ($CDCl_3$, 600 MHz, rt) δ 1.04 (t, J = 7.2 Hz, 6H), 2.48-2.54 (m, 4H), 5.46 (s, 2H), 6.91-6.97 (m, 4H), 7.06 (s, 2H), 7.10-7.18 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz, rt) δ 13.1, 31.1, 122.0, 126.9, 127.6, 127.7, 127.7, 127.8, 127.8, 132.5, 137.9, 140.5. MS (EI, m/z (relative intensity)): 407 (M+, 7), 406 (24), 377 (26), 289 (24), 252 (23), 119 (43), 117 (40), 105 (39), 91(100). HRMS (EI) Calcd for $C_{26}H_{24}Cl_2$: 406.1255. Found: 406.1263.

Table S2. Optimization of the Bases in the Intramolecular Cyclization of **3b.**

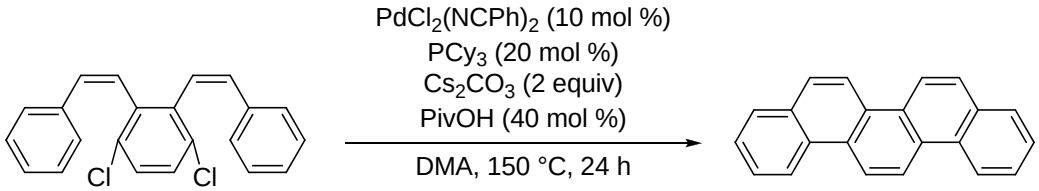


3b **4b**

entry	**base**	yield
1	Cs_2CO_3	47
2	K_2CO_3	57
3	**Na_2CO_3**	**60**
4	$CaCO_3$	0[a]
5	K_3PO_4	56
6	KOAc	18
7	^{t}BuOK	<1
8	DBU	<1[a,b]
9	NEt_3	0[a]

[a] The starting material was recovered.
[b] The ratio of the starting material and the product was 9:1.

2.4. General Procedure for Synthesis of Picene Derivatives via the Pd-Catalyzed Intramolecular Annulation. Synthesis of Picene (4a).[10]



3a **4a**

A 20 mL Schlenk tube equipped with a magnetic stirring bar was charged with PCy_3 (11.5 mg, 0.04 mmol, 20 mol%), $PdCl_2(NCPh)_2$ (7.6 mg, 0.02 mmol,10 mol%), and DMA (1 mL) under argon

atmosphere. After stirring for 10 min, Cs_2CO_3 (130 mg, 0.4 mmol, 2.0 equiv), PivOH (8.3 mg, 0.08 mmol, 40 mol%), and substrate (**3a**, 70.2 mg, 0.2 mmol, 1 equiv) were added into reaction mixture at room temperature. The tube was put into a preheated hot box at 150 °C for 24 h. The reaction mixture was cooled to room temperature, quenched with 1 M HCl (3 mL), and extracted with chloroform (3 × 10 mL). The combined organic extracts were washed adequately by water and dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude residue was then purified by chromatography and HPLC to afford the product (**4a**, 13 mg, 23% yield) as off-white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 7.68 (q, J = 9.0 Hz, 2H), 7.74 (q, J = 9.0 Hz, 2H), 8.00-8.06 (m, 4H), 8.80 (d, J = 9.3 Hz, 2H), 8.87 (d, J = 8.1 Hz, 2H), 8.97 (s, 2H).

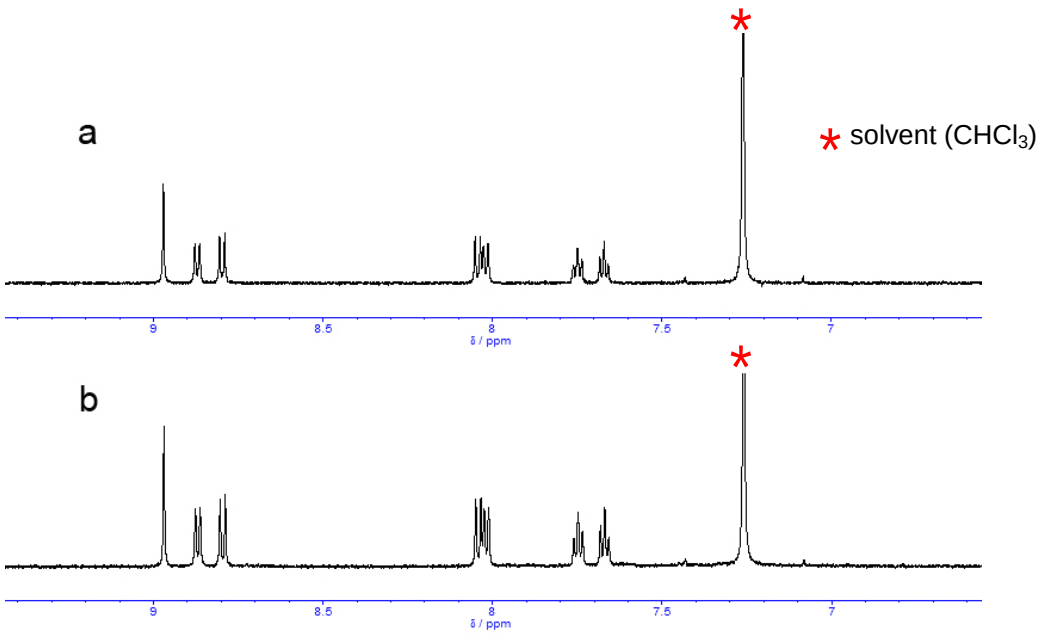
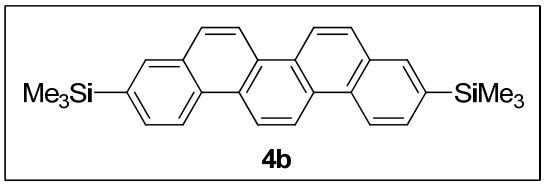
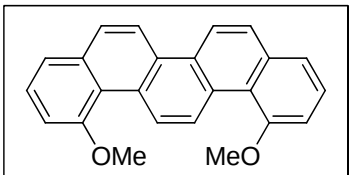


Figure S1. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of picene (**4a**): (a) purchased from TCI (Tokyo Chemical Industry Co., Ltd; (b) prepared by our synthetic method.



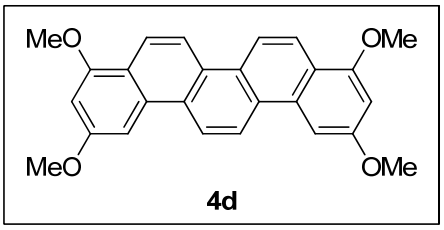
4b

White solid. Isolated yield was 47%. Mp. > 300 °C. FT-IR (KBr, cm^{-1}): 2953 (w), 1248 (m), 1109 (m), 910 (m), 845 (s), 808 (s), 759 (m), 689 (w), 637 (w). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 0.42 (s, 18H), 7.87 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 9.0 Hz, 2H), 8.16 (s, 2H), 8.81 (q, J = 9.0 Hz, 4H), 8.96 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, rt) δ 0.81, 121.82, 122.37, 127.81, 128.72, 128.89, 128.99, 130.95, 131.32, 131.44, 134.41, 138.96. MS (EI, m/z (relative intensity)): 422 (M+, 100), 409 (13), 408 (36), 407 (85), 196 (49), 73 (62). Anal. Calcd for $C_{28}H_{30}Si_2$: C, 79.56; H, 7.15%. Found: C, 79.66; H, 7.06%.



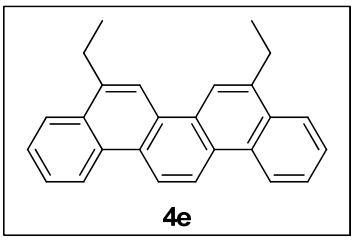
4c

White solid. Isolated yield was 24%. Mp. > 300 °C. FT-IR (KBr, cm^{-1}): 2930 (w), 1522 (m), 1450 (s), 1427 (s), 1269 (s), 1238 (s), 1140 (s), 1059 (s), 841 (s), 820 (s), 748 (s), 704 (w). ^{1}H NMR ($CDCl_3$, 600 MHz, rt) δ 4.21 (s, 6H), 7.21 (q, J = 12 Hz, 2H), 7.58-7.64 (m, 4H), 7.96 (d, J = 9.6 Hz, 2H), 8.83 (d, J = 9.0 Hz, 2H), 9.92 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz, rt) δ 55.9, 108.2, 121.1, 121.4, 122.5, 126.5, 126.6, 127.1, 128.5, 128.8, 134.3, 158.9. MS can not be detected because of high boiling point. Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%. Found: C, 85.52; H, 5.16%.



4d

White solid. Isolated yield was 31%. Mp. > 300 °C. FT-IR (KBr, cm^{-1}): 2999 (w), 1618 (s), 1454 (m), 1416 (m), 1383 (m), 1261 (s), 1148 (s), 1047 (s), 808 (m), 644 (w). ^{1}H NMR ($CDCl_3$, 600 MHz, rt) δ 4.06 (s, 6H), 4.08 (s, 6H), 6.70 (d, J = 2.4 Hz, 2H), 7.73 (d, J = 1.8 Hz, 2H), 8.37 (d, J = 9.6 Hz, 2H), 8.64 (d, J = 9.0 Hz, 2H), 8.74 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz, rt) δ 55.7, 56.0, 95.5, 97.9, 118.9, 119.2, 121.1, 121.6, 127.9, 129.8, 132.6, 157.3, 159.3. HRMS (EI) Calcd for $C_{26}H_{22}O_4$: 398.1518, Found: 398.1502.



4e

White solid. Isolated yield was 33%. Mp. > 300 °C. FT-IR (KBr, cm^{-1}): 2926 (m), 1452 (w), 1248 (w),1042 (w), 876 (m), 746 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 1.57 (t, J = 8.1 Hz, 6H), 3.35 (q, J = 18 Hz, 4H), 7.66-7.76 (m, 4H), 8.23 (q, J = 6.0 Hz, 2H), 8.65 (s, 2H), 8.87 (s, 2H), 8.91 (q, J = 9.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, rt) δ 15.2, 27.1, 120.2, 120.8, 123.7, 124.3, 126.2, 126.4, 127.9, 128.1, 130.9, 131.0, 138.9. MS can not be detected because of high boiling point. HRMS (EI) Calcd for $C_{26}H_{22}$: 334.1722, Found: 334.1700.

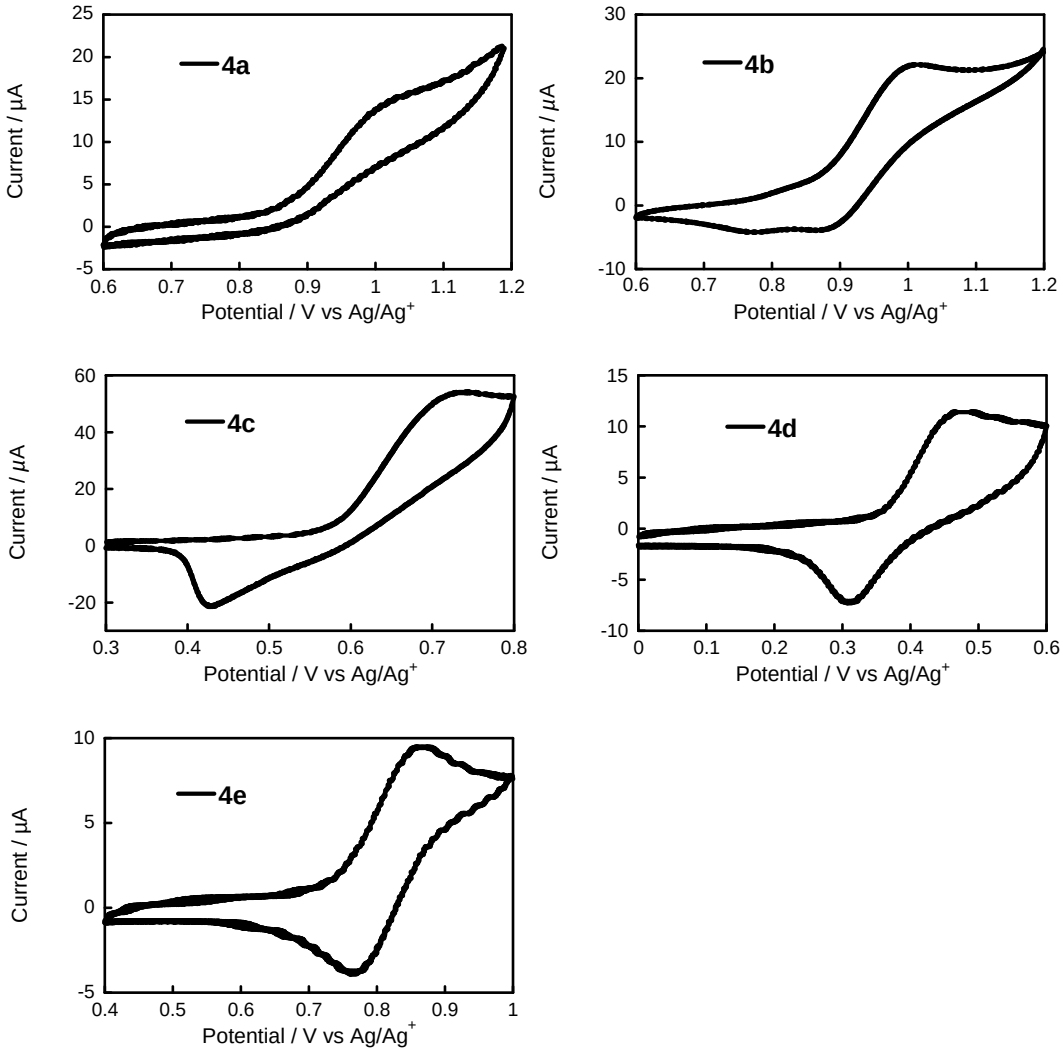


Figure 2S. Cyclic Voltammetry Diagrams of Compounds **4a-4e.**

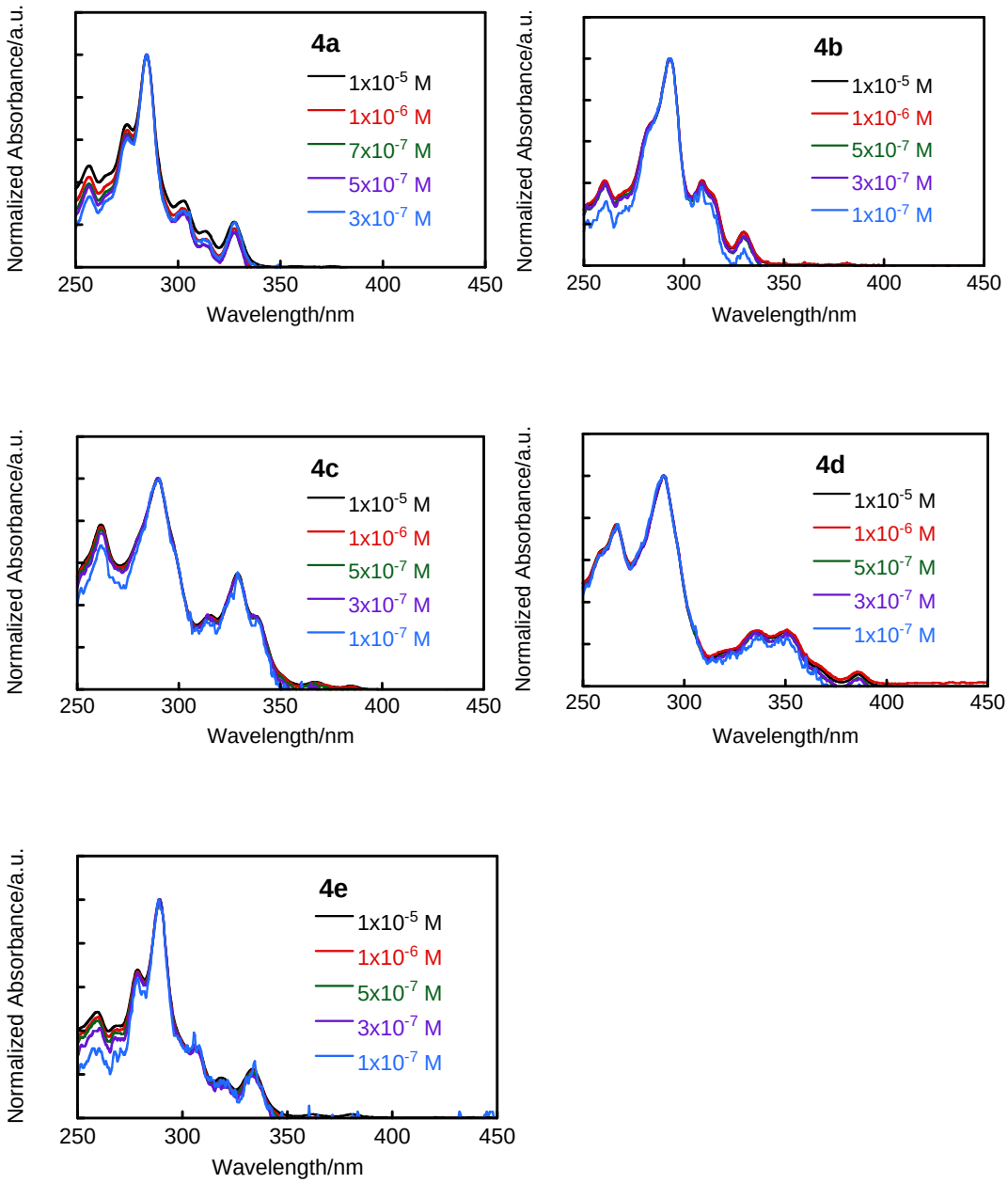


Figure 3S. UV-vis Absorption Spectra of **4a-4e** in Different Concentrations (CH_2Cl_2, 10^{-5}-10^{-7} M).

Reorganization Energy

Reorganization energies of hole were calculated using Gaussian 09, Revision A. 02 at the B3LYP/6-31G(d) level following the procedures described.[11]

Table S3. B3LYP/6-31G(d) Estimates of the Reorganization Energies of Hole λ^h in **4a**-**4e**.

Compound	λ^h/meV
4a	185
4b	240
4c	168
4d	277
4e	203

Calculation of Transfer Integrals of HOMO in 4c. The calculations of transfer integrals (*t*) between HOMOs in the semiconducting layer elucidated by the single crystal X-ray analysis. Calculations of *t*s were performed with PW91 functional and Slater-type triple-ξ plus polarization (TZP) basis sets using the Amsterdam Density Functional (ADF) program package.[12]

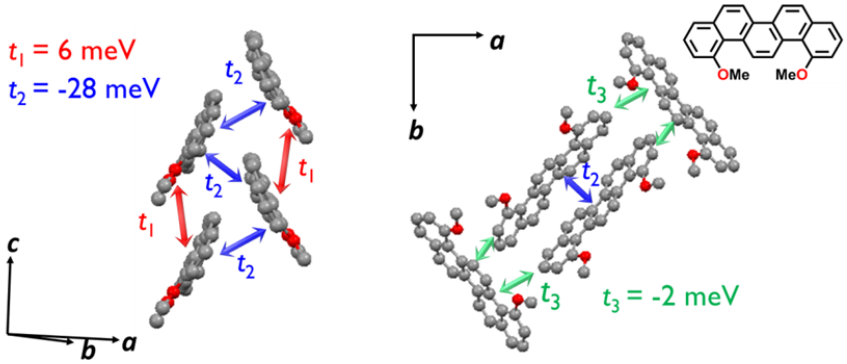


Figure S4. Transfer Integrals of HOMO in **4c**.

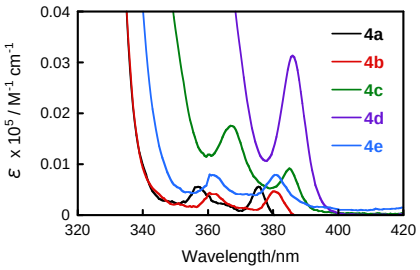
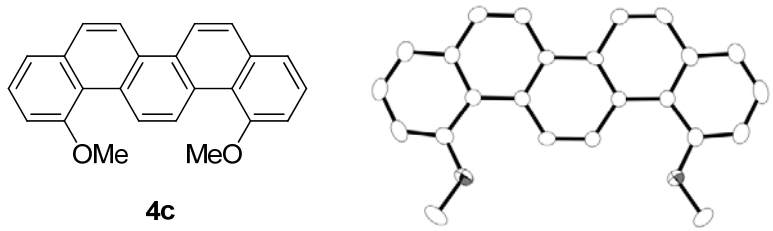


Figure S5. The Enlarged UV-vis Absorption Spectra of **4a**-**4e**.

3. Structural Determination of Compounds by X-ray Analysis



4c

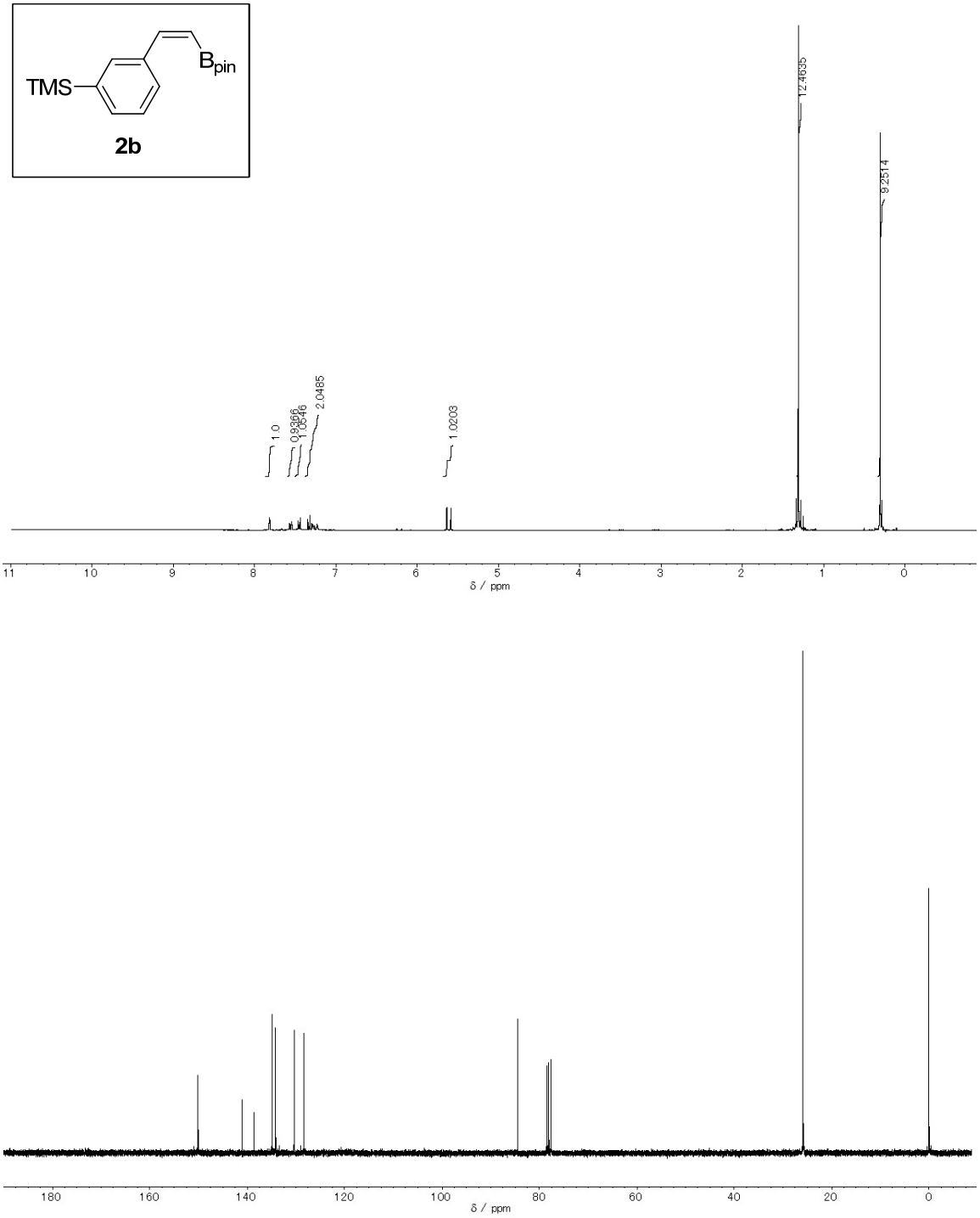
Figure S6. An ORTEP Drawing of **4c.**

Empirical Formula	$C_{24}H_{18}O_2$
Formula Weight	338.41
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.50 X 0.15 X 0.10 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2q range)	12327 (6.3 - 55.5^o)
Lattice Parameters	a = 17.528(2) Å
	b = 13.8570(16) Å
	c = 6.9178(8) Å
	V = 1680.2(3) Å^3
Space Group	$Pna2_1$ (#33)
Z value	4
D_{calc}	1.338 g/cm^3
F_{000}	712.00
m(MoKa)	0.837 cm^{-1}

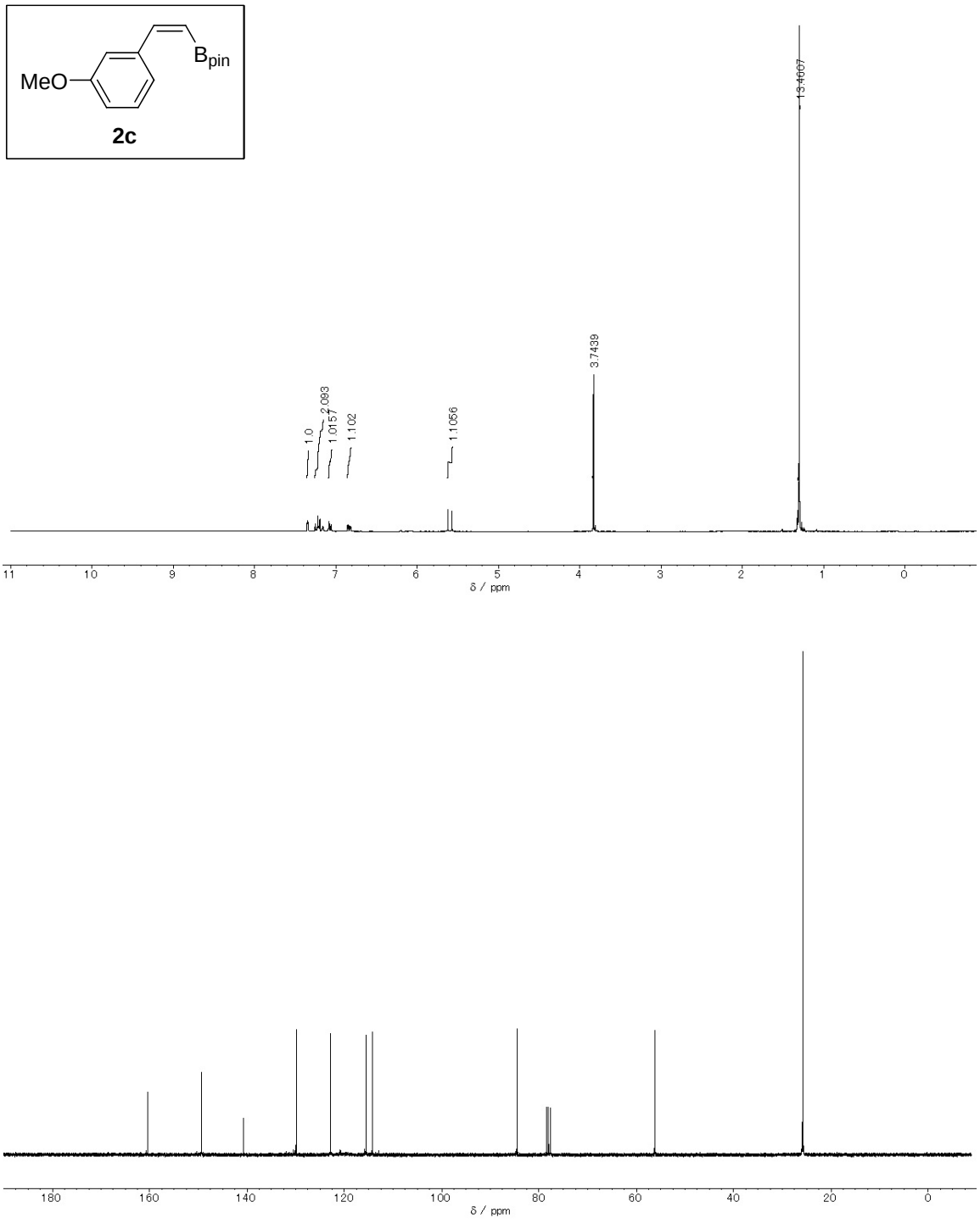
Diffractometer	AFC7
Radiation	MoKa (l = 0.71075 Å)
	graphite monochromated
Take-off Angle	2.8 ^{o}
Detector Aperture	2.0 - 2.5 mm horizontal
	2.0 mm vertical
Crystal to Detector Distance	21 mm
Temperature	24.9 ^{o}C
Scan Type	w-2q
$2q_{max}$	55.0 ^{o}
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.959 - 0.992)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	S w (|Fo| - |Fc|)^2
Least Squares Weights	1
$2q_{max}$ cutoff	55.0 ^{o}
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00s(I))	3849
No. Variables	307
Reflection/Parameter Ratio	12.54
Residuals: R (I>2.00s(I))	0.0705

Residuals: Rw (I>2.00s(I))	0.1170
Goodness of Fit Indicator	1.064
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.16 $e^-/Å^3$
Minimum peak in Final Diff. Map	0.00 $e^-/Å^3$

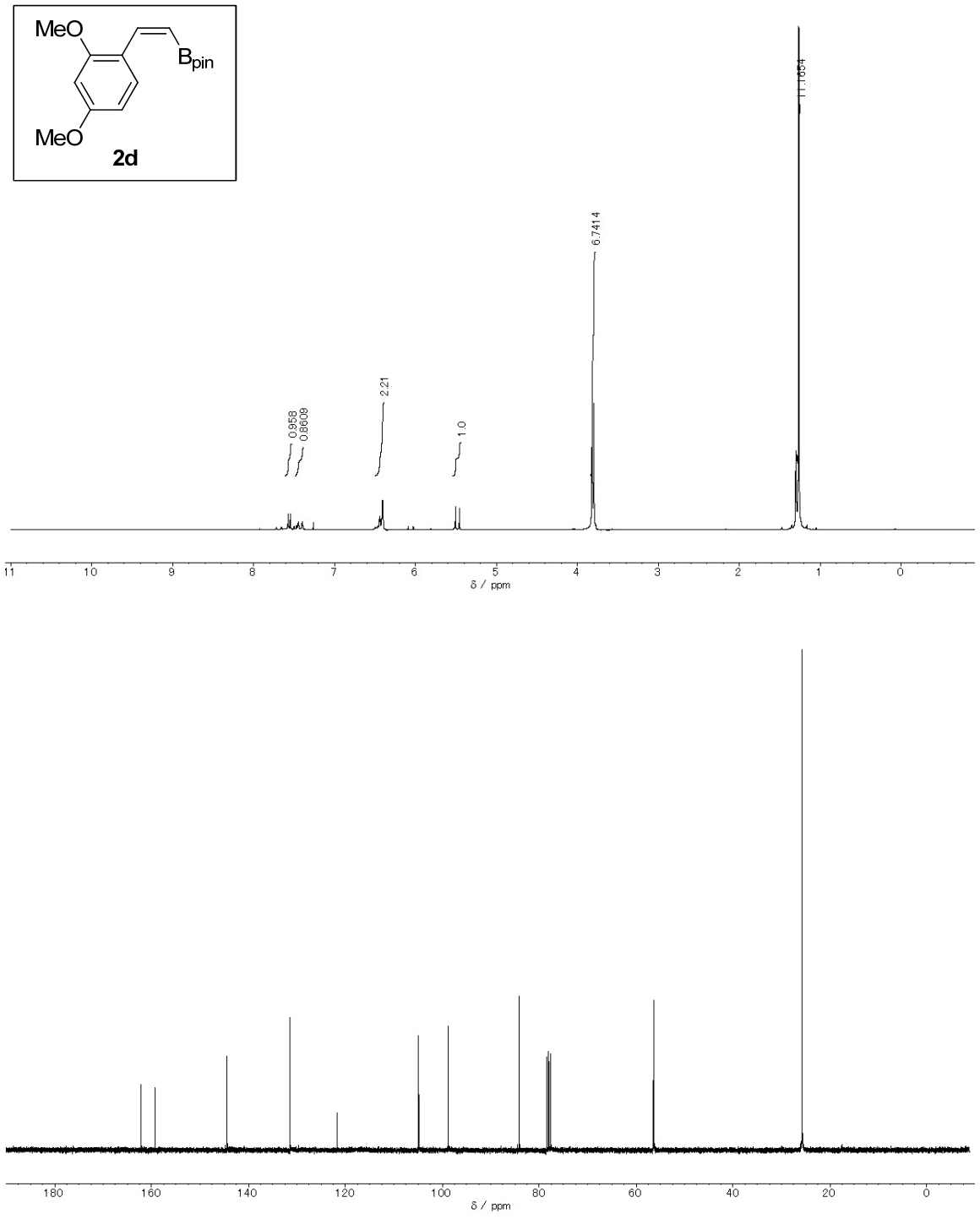
4. Copies of ^{1}H and ^{13}C NMR Charts for the New Compounds



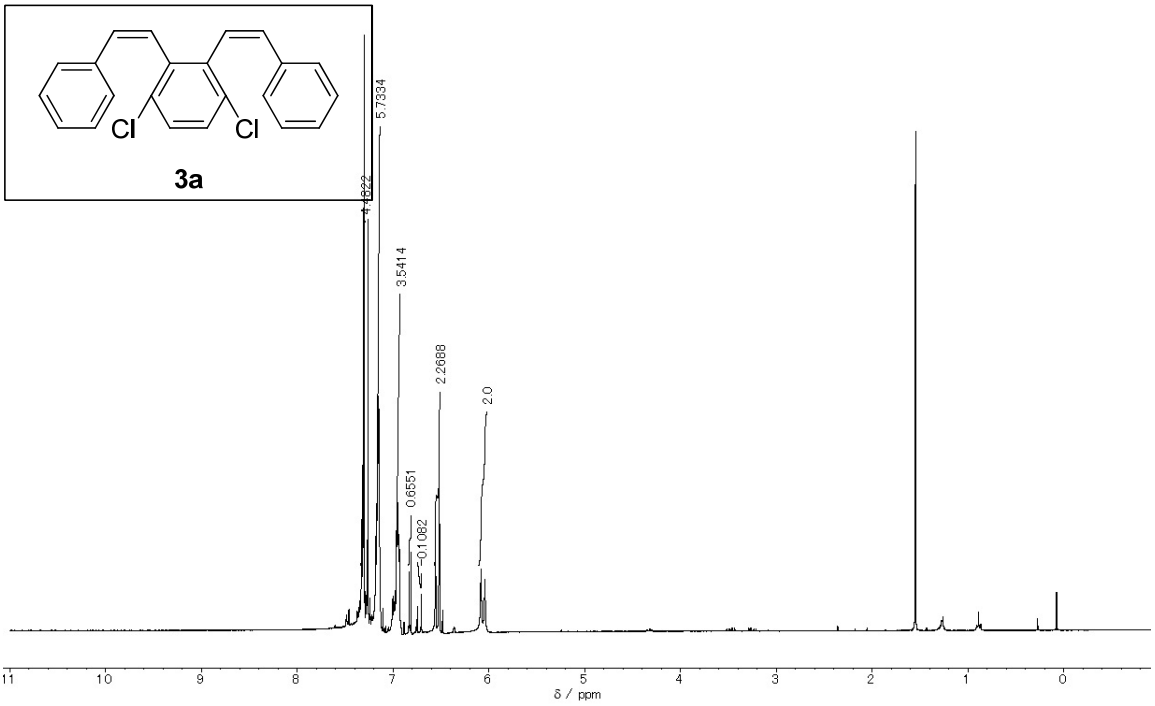
^{1}H (300 MHz) and $^{13}C\{^{1}H\}$ NMR (75 MHz) spectra of **2b** (rt, $CDCl_3$).

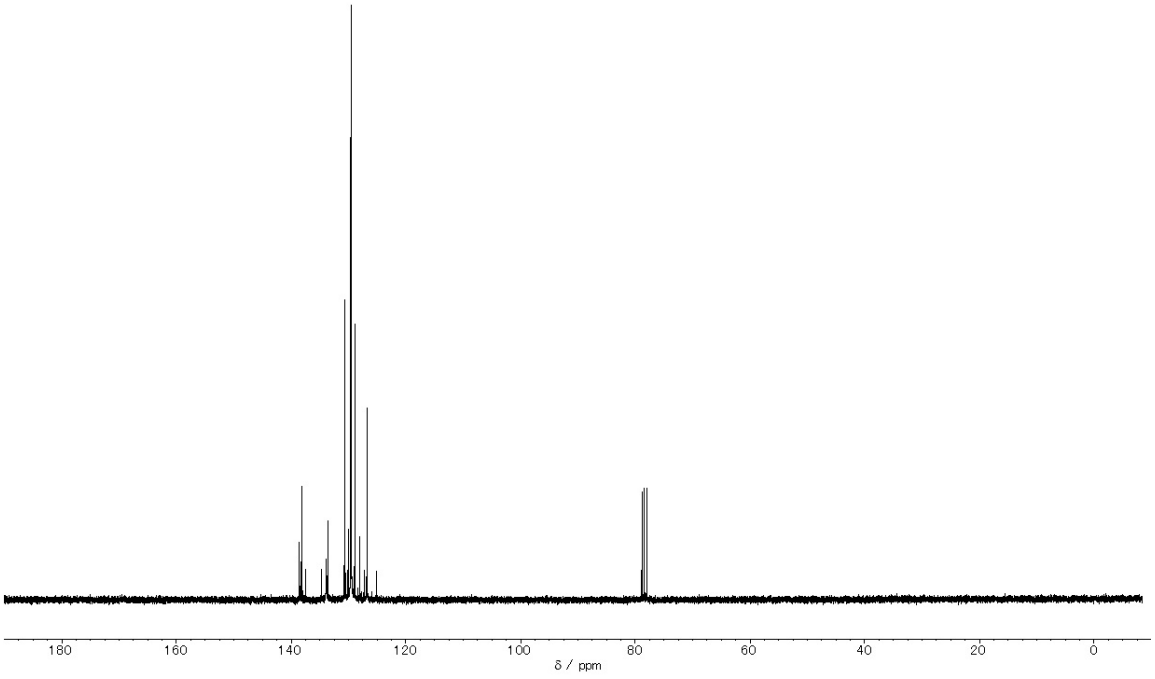


^{1}H (300 MHz) and $^{13}C\{^{1}H\}$ NMR (75 MHz) spectra of **2c** (rt, $CDCl_3$).

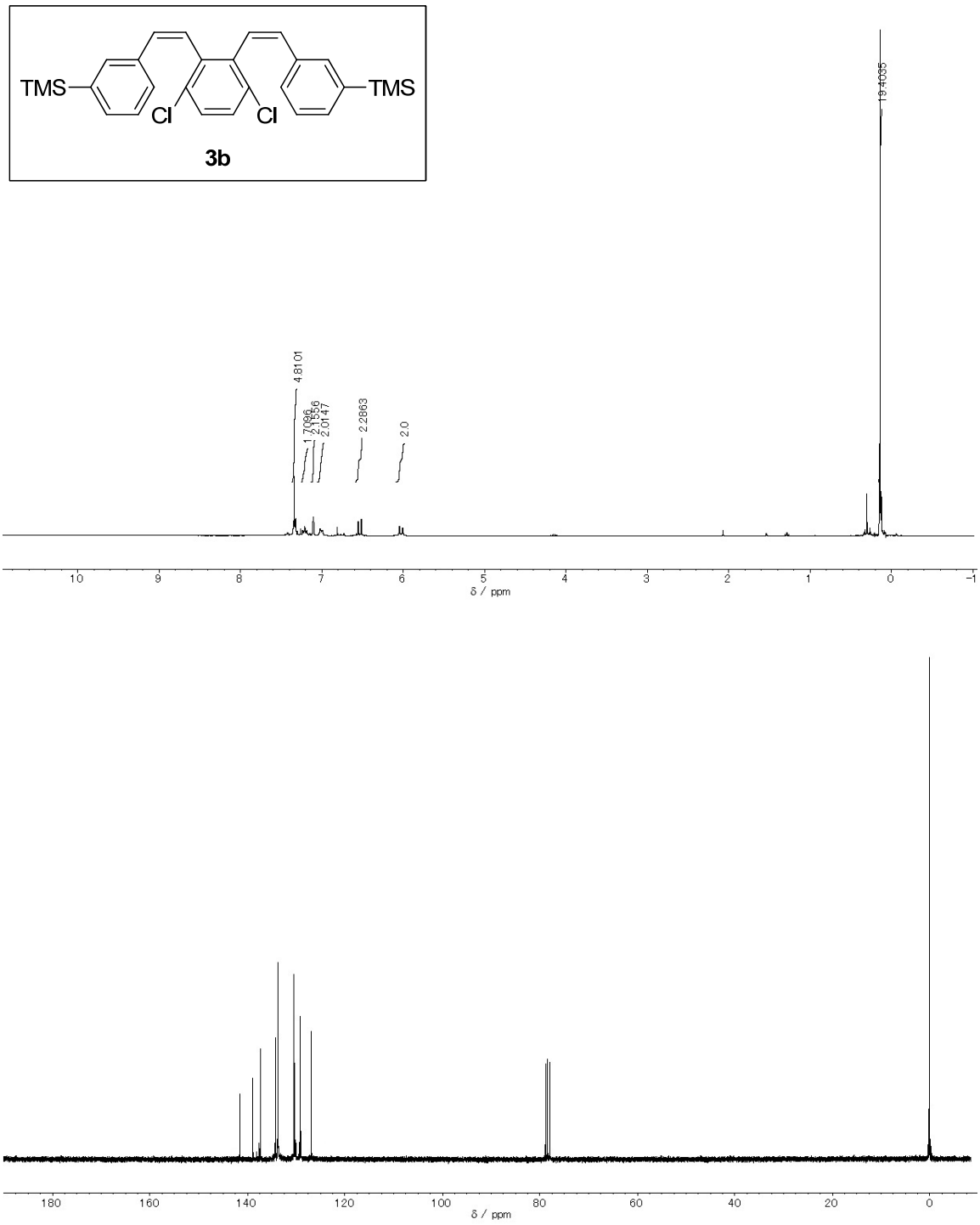


^{1}H (300 MHz) and $^{13}C\{^{1}H\}$ NMR (75 MHz) spectra of **2d** (rt, $CDCl_3$).

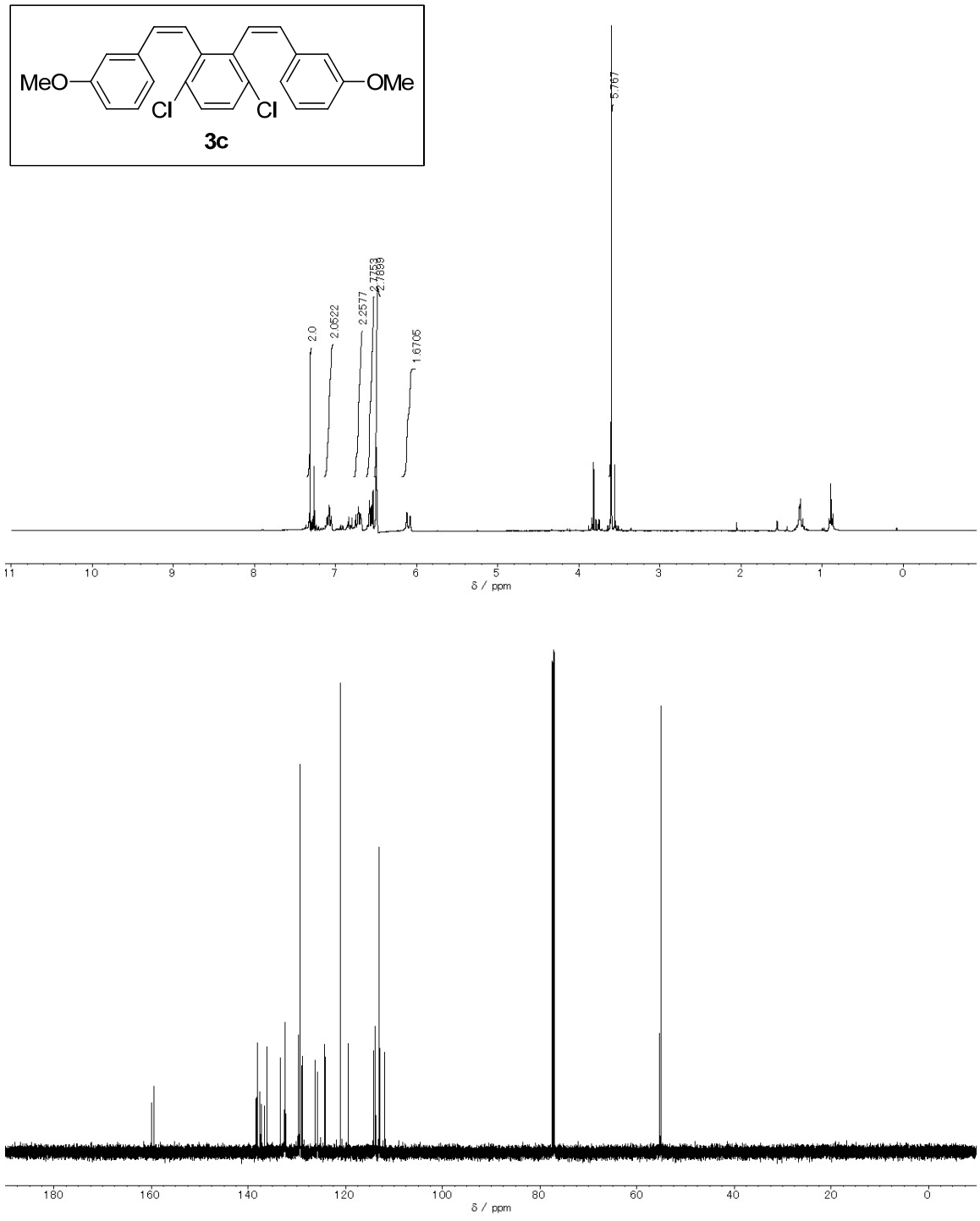




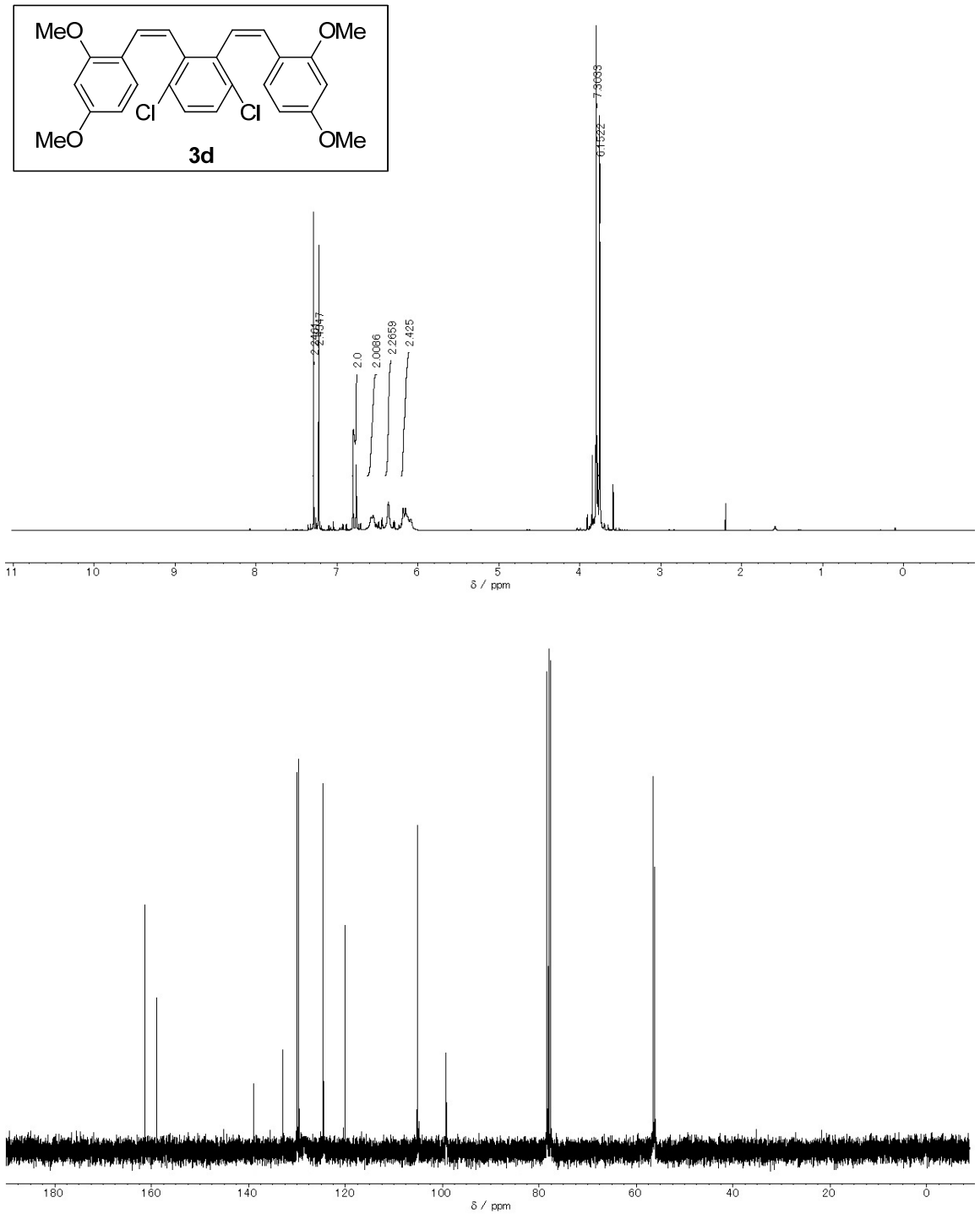
^{1}H (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3a** (rt, $CDCl_3$).



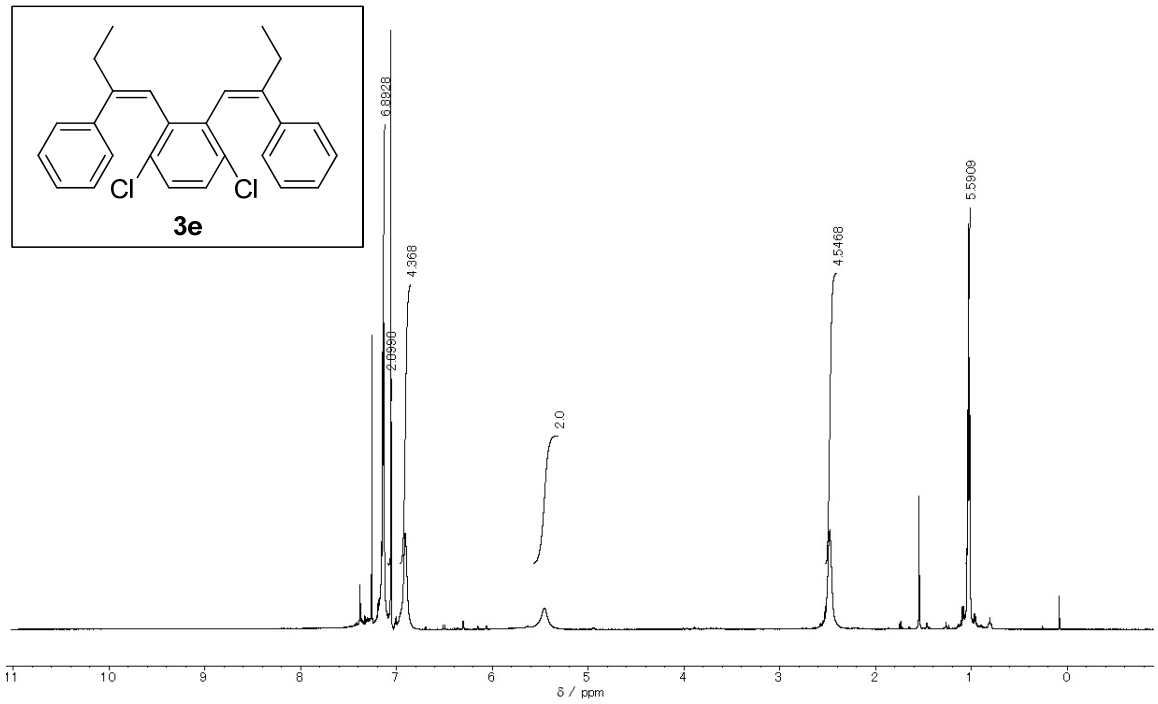
^{1}H (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3b** (rt, $CDCl_3$).

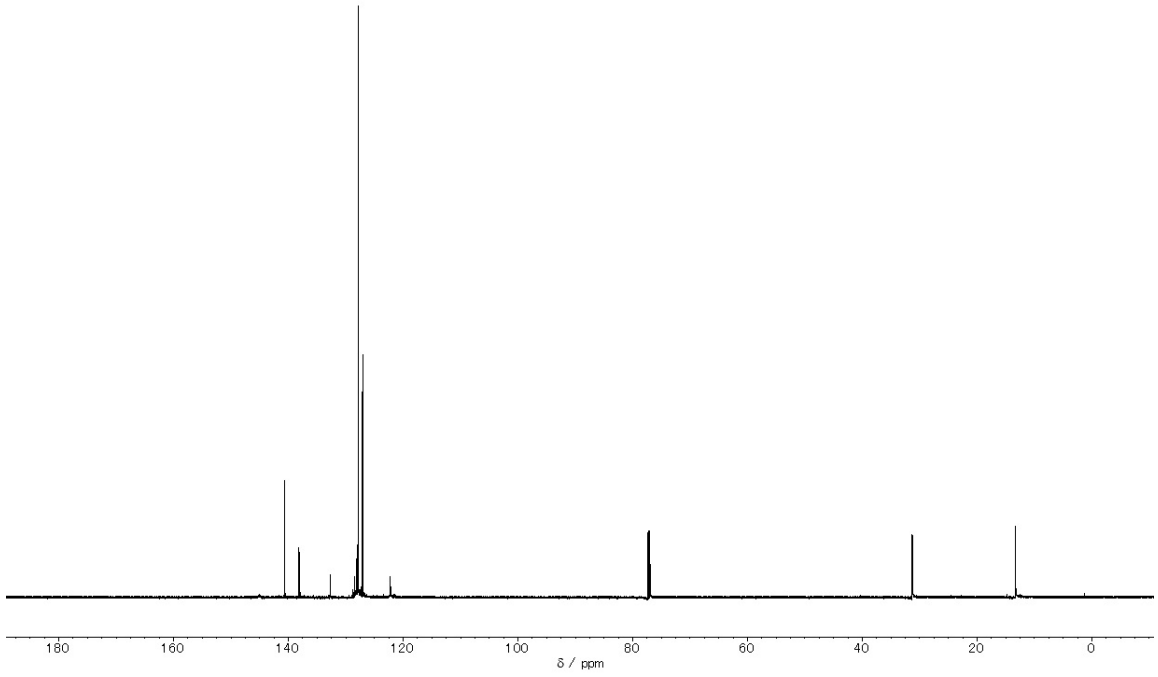


^{1}H (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3c** (rt, $CDCl_3$).

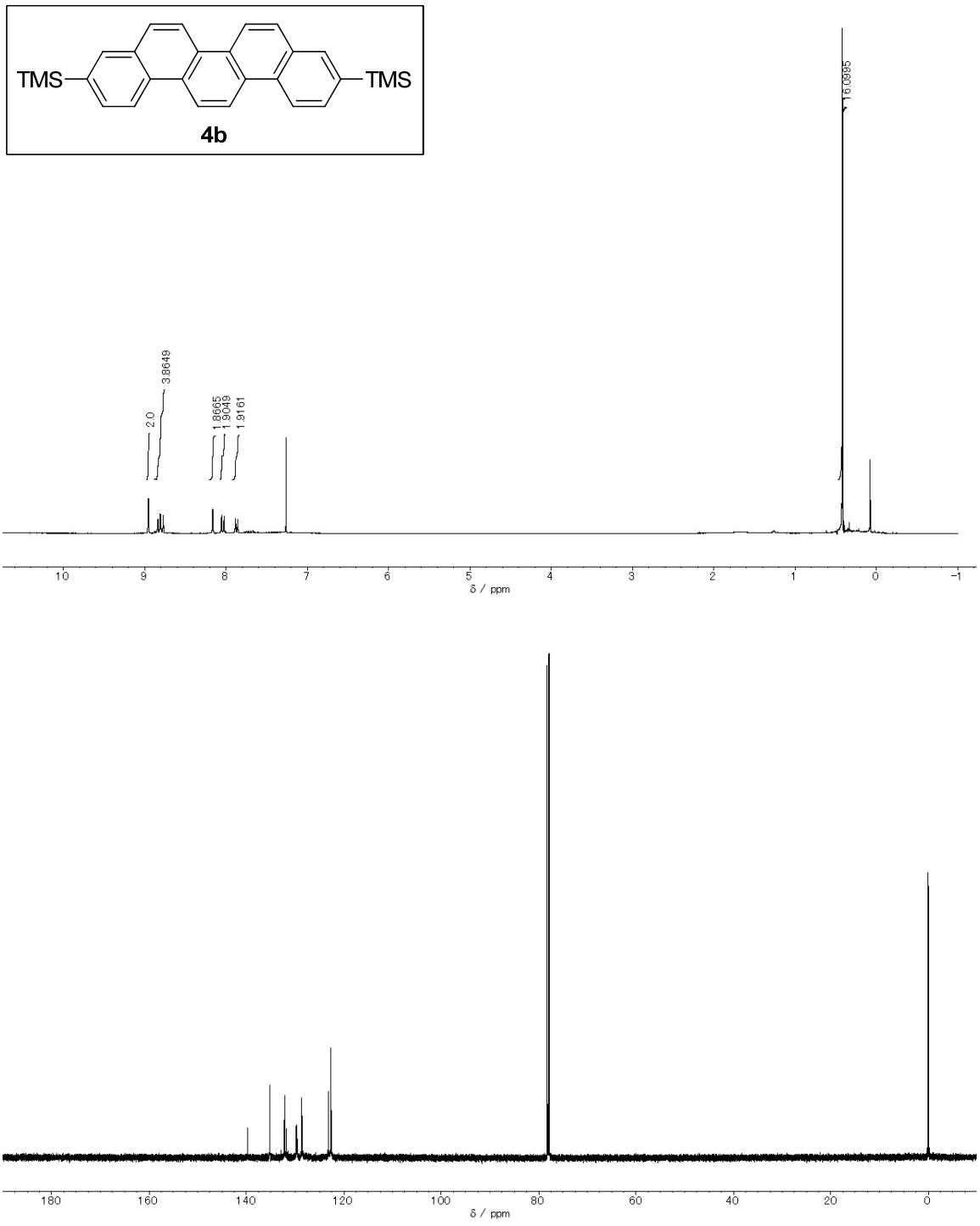


^{1}H (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **3d** (rt, $CDCl_3$).

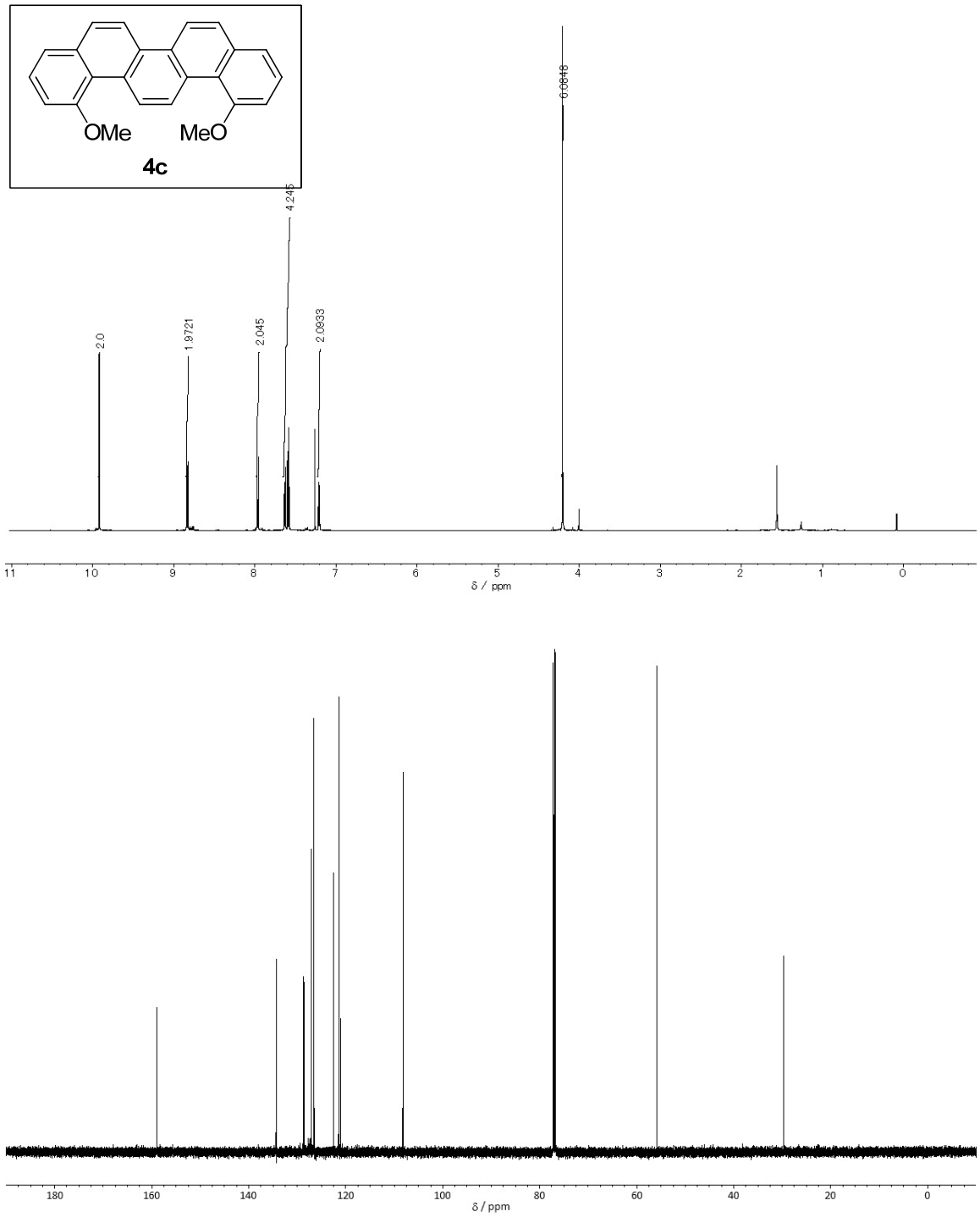




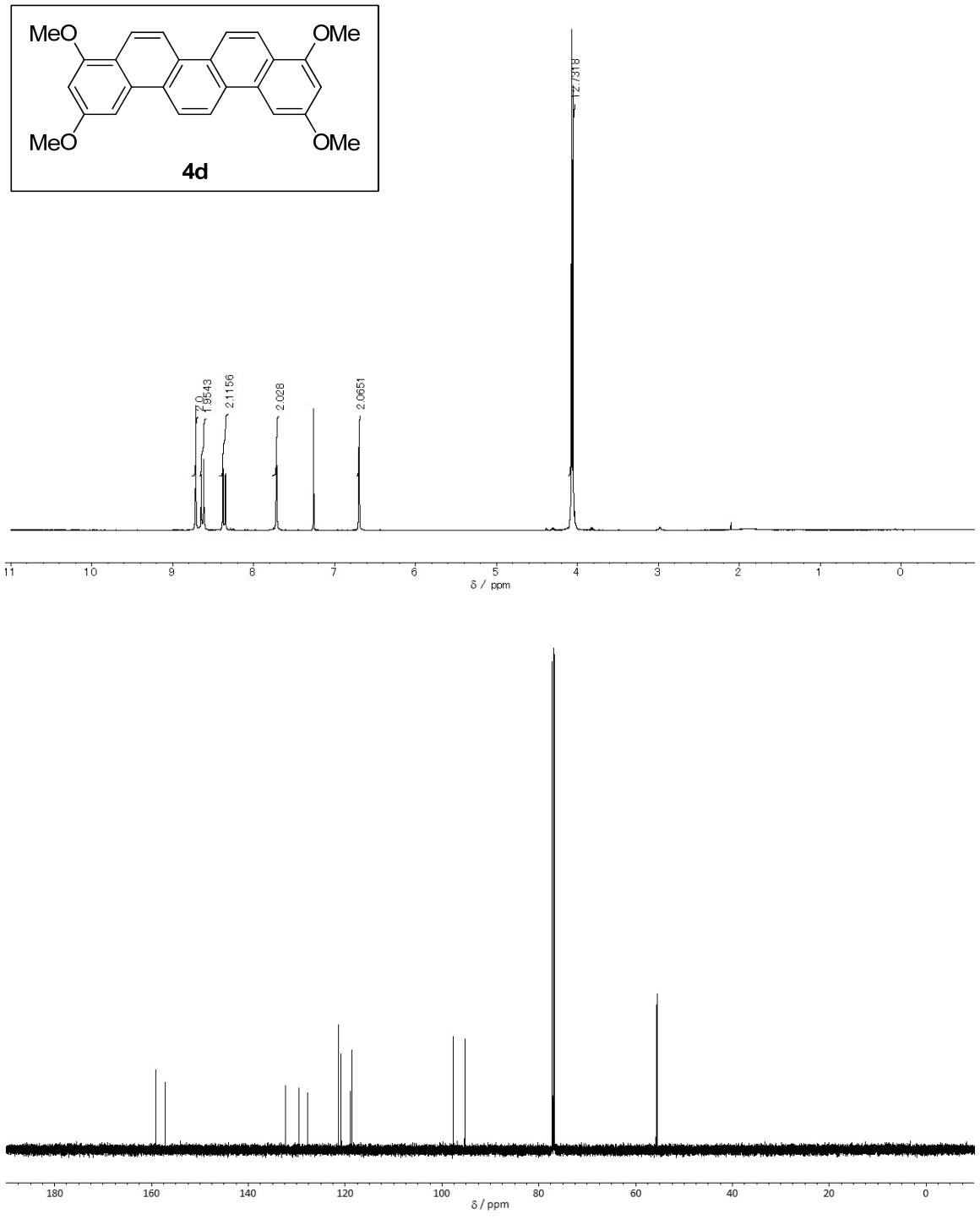
^{1}H (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **3e** (rt, $CDCl_3$).



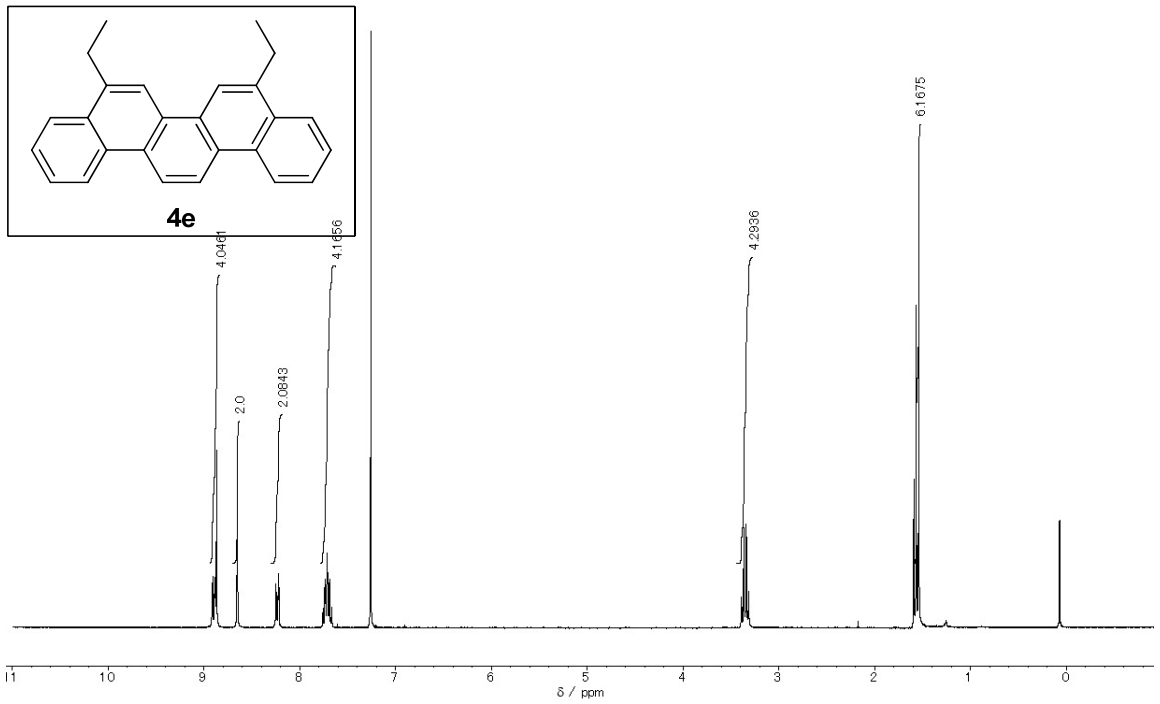
^{1}H (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **4b** (rt, $CDCl_3$).

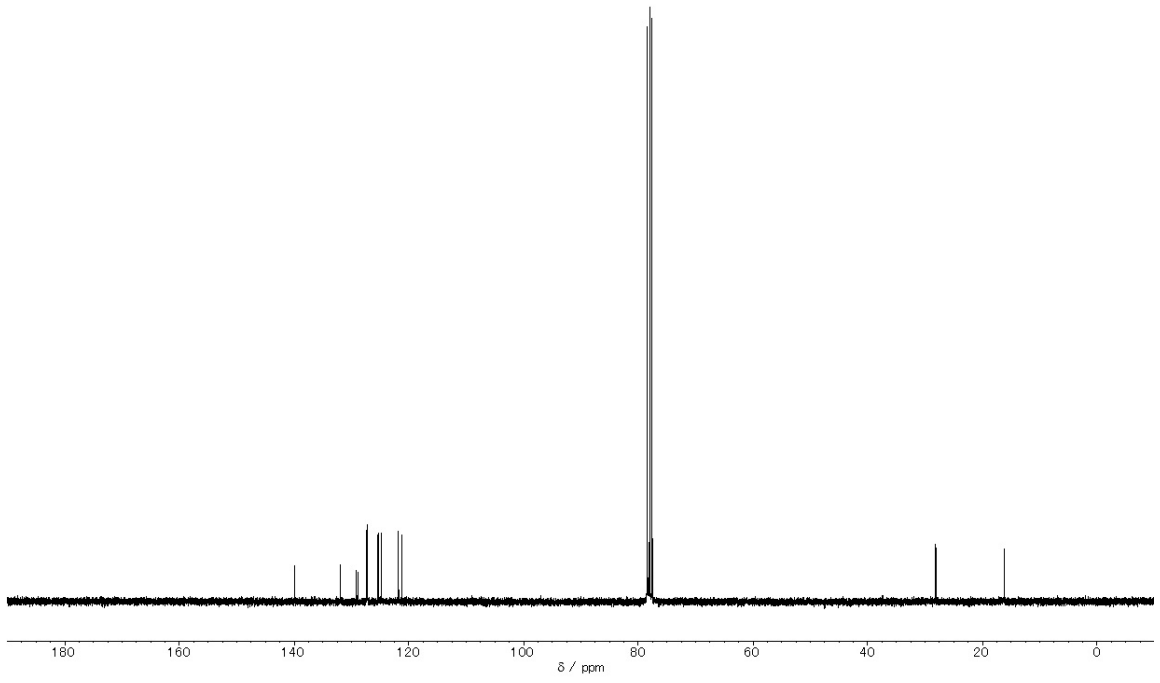


^{1}H (600 MHz) and $^{13}C\{^{1}H\}$ NMR (150 MHz) spectra of **4c** (rt, $CDCl_3$).



^{1}H (600 MHz) and ^{13}C{^{1}H} NMR (150 MHz) spectra of **4d** (rt, $CDCl_3$).





^{1}H (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra of **4e** (rt, $CDCl_3$).

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