Palladium-catalyzed annulative π-extension of *o*-halobiphenyls with *o*-chloropyridinecarboxylic acids to access azatriphenylenes

Shu-Lin, Cheng, Xin-Yue Fan, Ji-Fa Zhu, Bi-Qin Wang, Yingbo Shi,* Chun Feng,* and Shi-Kai Xiang*

College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610068, P. R. China
*E-mail: ybshi@sicnu.edu.cn (Y. S.); fengc@sicnu.edu.cn (C. F.); xiangsk@sicnu.edu.cn (S.-K. X.)

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General remarks

All of the manipulations were conducted with a Schlenk tube. ^{1}H NMR spectra were recorded on Bruker 600 MHz spectrometer. Chemical shifts (in parts per million (ppm)) were referenced to tetramethylsilane (δ = 0 ppm) as an internal standard in $CDCl_3$. $^{13}C\{^{1}H\}$ NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). High-resolution mass spectra (HRMS) were obtained using a quadrupole time-of-flight (Q-TOF) mass spectrometer with an electronspray ionization (ESI) resource, a quadrupole fourier-transform (Q-FT) mass spectrometer with an electronspray ionization (ESI) resource, or an orbitrap fourier-transform mass spectrometer with an electron ionization (EI) resource. Melting points were determined with a melting point apparatus. Unless otherwise noted, other materials obtained from commercial suppliers were used without further purification.

Synthesis of compounds 1

The compounds **1b-I**,[1] **1c-I**[2] and **1d-I**~**1o-I**[1] were synthesized according to the methods described in the literature. Compounds **1b-I**,[1] **1c-I**,[3] **1d-I**~**1e-I**,[1] **1f-I**,[4] **1g-I**,[1] **1h-I**,[5] **1i-I**,[1] **1j-I**,[6] **1k-I**,[7] **1l-I**,[1] **1m-I**,[4] **1n-I**,[6] and **1o-I**[1] are known, and the data are consistent with the literatures. The compounds **1b-Br**~**1c-Br**,[8] **1e-Br**~**1f-Br**,[8] **1h-Br**,[8] **1o-Br**[8] and **1p-Br**[9] were synthesized according to the methods described in the literature. Compounds **1b-Br**,[10] **1c-Br**,[11] **1e-Br**~**1f-Br,**[12] **1h-Br**,[13] **1o-Br**[14] and **1p-Br**[9] are known, and the data are consistent with the literatures.

The compound **1p-I** were synthesized from 1,2-bis(hexyloxy)-4,5-diiodobenzene (1.0604 g, 2.0 mmol) and 2-(3,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0110 g, 2.5 mmol) according to the methods described in the literature.[15] 490.1 mg (36% yield) of **1p-I** was afforded. White solid; mp 44.2−44.6 °C; IR (KBr, cm^{-1}) ν_{max} 2962, 2924, 2859, 1593, 1501, 1462, 1251, 1196; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.34 (s, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.84 (s, 1H), 6.82 (dd, J_1 = 8.4, J_2 = 2.4 Hz, 1H), 4.03 (t, J = 6.6 Hz, 4H), 3.99 (t, J = 6.6 Hz, 2H), 3.96 (t, J = 6.6 Hz, 2H), 1.87-1.78 (m, 8H), 1.52-1.42 (m, 8H), 1.38-1.31 (m, 16H), 0.93-0.86 (m, 12H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 149.1, 148.6, 148.5, 148.1, 139.1, 137.0, 123.9, 121.7, 115.5, 115.3, 112.8, 86.8, 69.5, 69.3, 69.1, 31.6, 31.5, 29.3, 29.2, 29.1, 29.1, 25.7, 25.7, 25.6, 25.6, 22.6, 22.6, 22.6, 14.0, 14.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{36}H_{58}IO_4$ 681.3380, Found 681.3378.

The compound **1d-Br** were synthesized from 4,4'-dimethoxy-biphenyl-2-amine (458.5 mg, 2.0 mmol) according to the methods described in the literature.[8] 457.3 mg (78% yield) of **1d-Br** was afforded. White solid; mp 69.9−70.3 °C; IR (KBr, cm^{-1}) ν_{max} 2945, 2899, 2830, 1602, 1484, 1458, 1285, 1248, 1215, 1178, 1029, 808, 544; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.31 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 6.89 (dd, J_1 = 8.4, J_2 = 3.0 Hz, 1H),

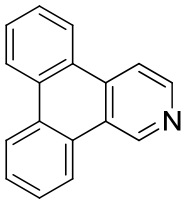
3.85 (s, 3H), 3.82 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 159.0, 158.8, 134.6, 133.2, 131.7, 130.7, 123.0, 118.1, 113.5, 113.3, 55.6, 55.2; HRMS (ESI) m/z: $[M]^+$ calcd for $C_{14}H_{13}BrO_2$ 292.0099, Found 292.0095.

The compound **1g-Br** were synthesized from 4,4'-bis(trifluoromethyl)-biphenyl-2-amine (610.4 mg, 2.0 mmol) according to the methods described in the literature.[8] 561.0 mg (76% yield) of **1g-Br** was afforded. Colourless liquid; IR (KBr, cm^{-1}) ν_{max} 3076, 1614, 1385, 1332, 1190, 1130, 828; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.97 (d, J = 1.8 Hz, 1H), 7.72 (d, J = 7.8 Hz, 2H), 7.65 (dd, J_1 = 7.8, J_2 = 1.8 Hz, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 7.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 144.8, 143.3, 131.7 (q, J = 33.15 Hz), 131.4, 130.5 (q, J = 32.4 Hz), 130.3 (q, J = 3.45 Hz), 129.6, 125.3 (q, J = 3.6 Hz), 124.4 (q, J = 3.45 Hz), 124.0 (q, J = 270.75 Hz), 123.1 (q, J = 270.9 Hz), 122.7; HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_7BrF_6$ 367.9635, Found 367.9623.

General procedure for synthesis of compounds 3

$Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol), K_2CO_3 (110.6 mg, 0.8 mmol), *o*-halobiphenyl derivatives **1** (0.2 mmol) and *o*-chloropyridinecarboxylic acids **2** (0.2 mmol) were placed into a 25 mL Schlenk tube equipped with a magnetic stir bar. To this mixture was added DMF (3.0 mL) with an injection syringe under nitrogen atmosphere. The reaction mixture was stirred for 12 h at the appointed temperature in an oil bath. Then the solution was cooled to room temperature, quenched by the addition of 30 mL water, and extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine (3 × 30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to afford the products **3**.

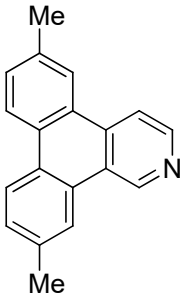
2-Azatriphenylene (3aa)



Method A: the reaction of 2-iodobiphenyl **1a-I** (56.0 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 41.7 mg (91% yield) of **3aa**. Method B: the reaction of 2-bromobiphenyl **1a-Br** (46.6, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 44.0 mg (96% yield) of **3aa**. Method C: the reaction of 2-iodobiphenyl **1a-I** (56.0 mg, 0.2 mmol) with 4-chloropyridine-3-carboxylic acid (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 35.8 mg (78% yield) of **3aa**. White solid; mp 171.2−172.0 °C; IR (KBr, cm^{-1}) ν_{max} 1595, 1408, 1274, 758; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.93 (s, 1H), 8.77 (d, J = 5.4 Hz, 1H), 8.73-8.69 (m, 1H), 8.64-8.58 (m,

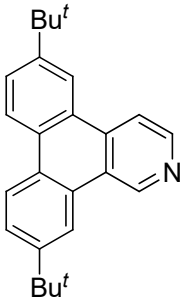
3H), 8.33 (d, J = 6.0 Hz, 1H), 7.77 -7.73 (m, 1H), 7.71-7.66 (m, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 146.8, 146.4, 135.1, 131.2, 129.9, 129.3, 128.0, 128.0, 127.8, 127.5, 127.4, 124.5, 123.7, 123.4, 122.6, 116.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{12}N$ 230.0970, Found 230.0973.

6,11-Dimethyl-2-azatriphenylene (3ba)



Method A: the reaction of 4,4'-dimethyl-2-iodobiphenyl **1b-I** (61.6 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 43.7 mg (85% yield) of **3ba**. Method B: the reaction of 4,4'-dimethyl-2-bromobiphenyl **1b-Br** (52.2, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 48.9 mg (95% yield) of **3ba**.Yellow solid; mp 163.4−163.7 °C; IR (KBr, cm^{-1}) ν_{max} 1595, 1412, 796; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.87 (s, 1H), 8.71 (d, J = 5.4 Hz, 1H), 8.42 (s, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.30 (s, 1H), 8.27 (d, J = 6.0 Hz, 1H), 7.50 (dd, J_1 = 8.4, J_1 = 1.2 Hz, 1H), 7.46 (dd, J_1 = 8.4, J_1 = 1.2 Hz, 1H), 2.59 (s, 3H), 2.57 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 146.7, 146.0, 137.1, 136.8, 135.1, 130.7, 129.4, 129.0, 127.7, 127.6, 127.0, 124.5, 123.6, 123.0, 122.4, 116.2, 21.8, 21.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}N$ 258.1283, Found 258.1287.

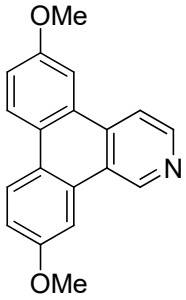
6,11-Di-tert-butyl-2-azatriphenylene (3ca)



Method A: the reaction of 4,4'-di-*tert*-butyl-2-iodobiphenyl **1c-I** (78.5 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 53.3 mg (78% yield) of **3ca**. Method B: the reaction of 4,4'-di-*tert*-butyl-2-bromobiphenyl **1c-Br** (69.1, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 50.5 mg (74% yield) of **3ca**. White solid; mp 151.5−152.2 °C; IR (KBr, cm^{-1}) ν_{max} 2961, 2901, 2865, 1616, 1266, 807,

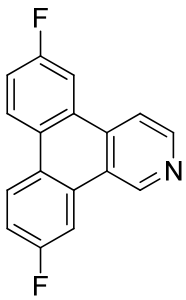
631; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 10.00 (s, 1H), 8.78 (d, J = 5.4 Hz, 1H), 8.73 (d, J = 1.8 Hz, 1H), 8.60 (d, J = 1.8 Hz, 1H), 8.55 (d, J = 9.0 Hz, 1H), 8.54 (d, J = 9.0 Hz, 1H), 8.41 (d, J = 6.0 Hz, 1H), 7.81 (dd, J_1 = 9.0, J_2 = 2.4 Hz, 1H), 7.76 (dd, J_1 = 8.4, J_2 = 2.4 Hz, 1H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, ppm) δ 150.3, 150.0, 146.8, 146.0, 135.6, 129.0, 127.6, 127.4, 127.4, 126.8, 126.0, 125.0, 123.1, 123.1, 119.6, 118.5, 116.3, 35.1, 35.0, 31.4, 31.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{28}N$ 342.2222, Found 342.2226.

6,11-Dimethoxy-2-azatriphenylene (3da)



Method A: the reaction of 4,4'-dimethoxy-2-iodobiphenyl **1d-I** (68.0 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 52.0 mg (90% yield) of **3da**. Method B: the reaction of 4,4'-dimethoxy-2-bromobiphenyl **1d-Br** (58.6, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 48.0 mg (83% yield) of **3da**. Yellow solid; mp 180.2−180.8 °C; IR (KBr, cm^{-1}) ν_{max} 1616, 1221, 814; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.74 (s, 1H), 8.69 (d, J = 5.4 Hz, 1H), 8.28 (d, J = 9.6 Hz, 1H), 8.27 (d, J = 9.0 Hz, 1H), 8.13 (d, J = 5.4 Hz, 1H), 7.93 (d, J = 2.4 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.24 (dd, J_1 = 9.0, J_2 = 3.0 Hz, 1H), 7.20 (dd, J_1 = 9.0, J_2 = 2.4 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, ppm) δ 158.4, 158.2, 146.7, 146.0, 135.0, 128.2, 127.6, 125.2, 124.4, 124.3, 124.3, 123.9, 118.0, 116.7, 116.2, 105.6, 104.6, 55.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}NO_2$ 290.1181, Found 290.1187.

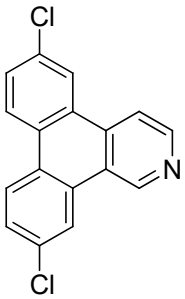
6,11-Difluoro-2-azatriphenylene (3ea)



Method A: the reaction of 4,4'-difluoro-2-iodobiphenyl **1e-I** (63.2 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 38.2 mg (72% yield) of **3ea**. Method B:

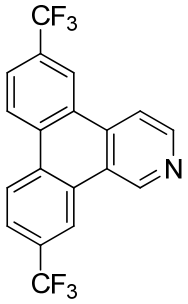
the reaction of 4,4'-difluoro-2-bromobiphenyl **1e-Br** (53.8, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 36.1 mg (68% yield) of **3ea**. White solid; mp 261.3−262.0 °C; IR (KBr, cm^{-1}) ν_{max} 1621, 1507, 1440, 1184, 793; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.84 (s, 1H), 8.83 (d, J = 5.4 Hz, 1H), 8.57-8.53 (m, 2H), 8.34 (dd, J_1 = 10.2, J_2 = 2.4 Hz, 1H), 8.24 (d, J = 6.0 Hz, 1H), 8.22 (dd, J_1 = 10.2, J_2 = 2.4 Hz, 1H), 7.53-7.48 (m, 1H), 7.47-7.43 (m, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 162.2 (d, J = 246.6 Hz), 162.0 (d, J = 246.0 Hz), 147.0 (d, J = 4.2 Hz), 134.9 (d, J = 3.45 Hz), 129.5 (d, J = 8.55 Hz), 128.9 (d, J = 7.65 Hz), 127.4 (d, J = 1.8 Hz), 126.1 (d, J = 1.65 Hz), 125.7, 125.6, 125.6, 124.2 (d, J = 3.6 Hz), 118.0 (d, J = 22.8 Hz), 116.7 (d, J = 22.8 Hz), 116.5, 109.4 (d, J = 22.65 Hz), 108.3 (d, J = 22.65 Hz); HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{10}F_2N$ 266.0781, Found 266.0785.

6,11-Dichloro-2-azatriphenylene (3fa)



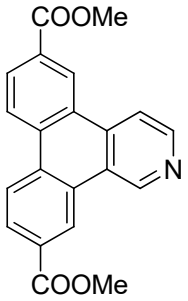
Method A: the reaction of 4,4'-dichloro-2-iodobiphenyl **1f-I** (69.8 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 35.8 mg (60% yield) of **3fa**. Method B: the reaction of 4,4'-dichloro-2-bromobiphenyl **1f-Br** (60.4, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 45.3 mg (76% yield) of **3fa**. Yellow solid; mp 277.4−277.8 °C; IR (KBr, cm^{-1}) ν_{max} 1600, 1417, 1099, 757; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.85 (s, 1H), 8.83 (d, J = 5.4 Hz, 1H), 8.64 (d, J = 1.8 Hz, 1H), 8.53 (d, J = 1.8 Hz, 1H), 8.47 (t, J = 8.4 Hz, 2H), 8.26 (d, J = 6.0 Hz, 1H), 7.71 (dd, J_1 = 8.4, J_2 = 1.8 Hz, 1H), 7.65 (dd, J_1 = 9.0, J_2 = 1.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 147.2, 146.9, 134.5, 134.4, 134.2, 129.9, 129.3, 129.0, 128.8, 128.6, 127.7, 125.0, 124.9, 123.7, 123.7, 122.5, 116.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{10}Cl_2N$ 298.0190, Found 298.0192.

6,11-Bis(trifluoromethyl)-2-azatriphenylene (3ga)



Method A: the reaction of 4,4'-bis(trifluoromethyl)-2-iodobiphenyl **1g-I** (83.2 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 56.3 mg (77% yield) of **3ga**. Method B: the reaction of 4,4'-bis(trifluoromethyl)-2-bromobiphenyl **1g-Br** (73.8, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 56.3 mg (77% yield) of **3ga**. White solid; mp 227.3−227.8 °C; IR (KBr, cm^{-1}) ν_{max} 1323, 1114, 823; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.97 (s, 1H), 8.96 (s, 1H), 8.91 (brs, 1H), 8.86 (s, 1H), 8.73 (t, J = 8.4 Hz, 2H), 8.37 (d, J = 5.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 147.6, 146.9, 134.7, 132.6, 131.2, 130.8 (q, J = 32.55 Hz), 130.5 (q, J = 32.55 Hz), 128.7, 128.2, 125.7 (q, J = 3.15 Hz), 124.8, 124.8, 124.5 (q, J = 3.3 Hz), 124.0 (q, J = 270.75 Hz), 123.9 (q, J = 270.75 Hz), 121.3 (q, J = 3.9 Hz), 120.1 (q, J = 4.2 Hz), 116.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{10}F_6N$ 366.0717, Found 366.0722.

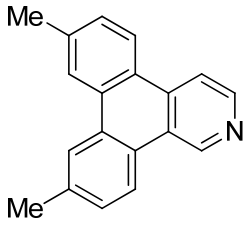
Dimethyl 2-azatriphenylene-6,11-dicarboxylate (3ha)



Method A: the reaction of dimethyl 2-iodobiphenyl-4,4'-dicarboxylate **1h-I** (79.2 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 46.3 mg (67% yield) of **3ha**. Method B: the reaction of dimethyl 2-bromobiphenyl-4,4'-dicarboxylate **1h-Br** (69.8, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 50.4 mg (73% yield) of **3ha**. White solid; mp 263.6−264.3 °C; IR (KBr, cm^{-1}) ν_{max} 1732, 1266, 1115, 751; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.93 (s, 1H), 9.29 (d, J = 1.8 Hz, 1H), 9.20 (d, J = 1.8 Hz, 1H), 8.82 (d, J = 6.0 Hz, 1H), 8.57 (t, J = 8.4 Hz, 2H), 8.38 (d, J = 5.4 Hz, 1H), 8.32 (dd, J_1 = 8.4, J_2 = 1.8 Hz, 1H), 8.27 (dd, J_1 = 8.4, J_2 = 1.8 Hz, 1H), 4.07 (s, 3H), 4.06 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 166.4, 166.3, 146.8, 146.6, 135.1, 133.6, 132.2, 130.0, 129.7, 129.6, 128.4, 128.3, 127.9, 125.8, 124.5,

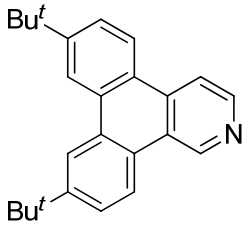
124.2, 124.2, 116.5, 52.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NO_4$ 346.1079, Found 346.1086.

7,10-Dimethyl-2-azatriphenylene (3ia)



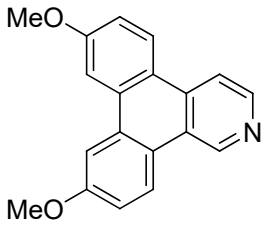
The reaction of 3',5-dimethyl-2-iodobiphenyl **1i-I** (61.6 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 44.3 mg (86% yield) of **3ia**. White solid; mp 143.8−144.5 °C; IR (KBr, cm^{-1}) ν_{max} 2918, 1617, 811; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.80 (s, 1H), 8.67 (d, J = 5.4 Hz, 1H), 8.49 (d, J = 7.8 Hz, 1H), 8.36 (d, J = 7.8 Hz, 1H), 8.29 (s, 1H), 8.28 (s, 1H), 8.19 (d, J = 5.4 Hz, 1H), 7.43 (d, J = 9.6 Hz, 1H), 7.41 (d, J = 9.0 Hz, 1H), 2.58 (s, 3H), 2.57 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 146.4, 145.7, 139.1, 137.6, 134.7, 131.0, 129.7, 129.0, 128.7, 125.7, 125.2, 124.2, 123.5, 123.2, 122.3, 116.0, 21.9, 21.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}N$ 258.1283, Found 258.1288.

7,10-Di-tert-butyl-2-azatriphenylene (3ja)



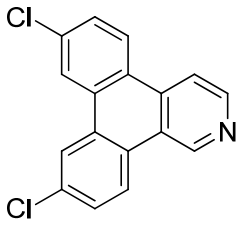
The reaction of 3',5-di-*tert*-butyl-2-iodobiphenyl **1j-I** (78.5 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 52.6 mg (77% yield) of **3ja**. Yellow solid; mp 209.8−210.6 °C; IR (KBr, cm^{-1}) ν_{max} 2964, 1615, 1266, 810; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.92 (s, 1H), 8.73 (d, J = 6.0 Hz, 1H), 8.68-8.65 (m, 3H), 8.55 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 5.4 Hz, 1H), 7.77 (td, J_1 = 8.4, J_2 = 1.8 Hz, 2H), 1.52 (s, 18H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 152.2, 150.8, 146.5, 145.8, 134.9, 131.2, 129.8, 125.8, 125.7, 125.4, 125.3, 124.4, 123.7, 122.5, 119.1, 119.1, 116.2, 35.3, 35.1, 31.4, 31.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{28}N$ 342.2222, Found 342.2230.

7,10-Dimethoxy-2-azatriphenylene (3ka)



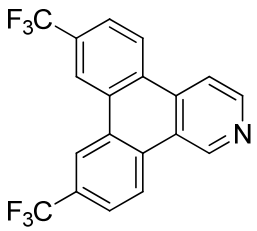
The reaction of 3',5-dimethoxy-2-iodobiphenyl **1k-I** (68.0 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 46.3 mg (80% yield) of **3ka**. White solid; mp 234.2−235.0 °C; IR (KBr, cm^{-1}) ν_{max} 1613, 1237, 1213, 1043, 814; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.77 (s, 1H), 8.66 (d, J = 5.4 Hz, 1H), 8.60 (d, J = 9.0 Hz, 1H), 8.48 (d, J = 9.0 Hz, 1H), 8.18 (d, J = 5.4 Hz, 1H), 7.88 (s, 2H), 7.29 (dd, J_1 = 8.4, J_1 = 2.4 Hz, 1H), 7.26 (dd, J_1 = 8.4, J_1 = 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 160.3, 159.2, 146.1, 145.4, 134.1, 132.6, 131.1, 125.6, 124.2, 123.7, 122.3, 121.7, 116.0, 115.8, 115.8, 106.4, 106.2, 55.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{16}NO_2$ 290.1181, Found 290.1189.

7,10-Dichloro-2-azatriphenylene (3la)



The reaction of 3',5-dichloro-2-iodobiphenyl **1l-I** (69.8 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 37.6 mg (63% yield) of **3la**. Yellow solid; mp 273.6−274.2 °C; IR (KBr, cm^{-1}) ν_{max} 1602, 797; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.89 (s, 1H), 8.81 (d, J = 6.0 Hz, 1H), 8.65 (d, J = 9.0 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 2.4 Hz, 1H), 8.49 (d, J = 2.4 Hz, 1H), 8.29 (d, J = 5.4 Hz, 1H), 7.69 (dd, J_1 = 9.0, J_1 = 2.4 Hz, 1H), 7.68 (dd, J_1 = 9.0, J_1 = 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 146.9, 146.8, 136.1, 134.6, 134.4, 131.6, 130.3, 128.9, 128.6, 126.9, 126.4, 125.5, 124.3, 123.8, 123.4, 123.4, 116.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{10}Cl_2N$ 298.0190, Found 298.0196.

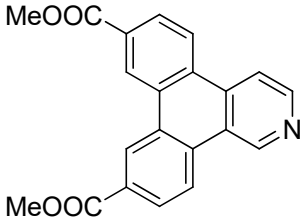
7,10-Bis(trifluoromethyl)-2-azatriphenylene (3ma)



The reaction of 3',5-bis(trifluoromethyl)-2-iodobiphenyl **1m-I** (83.2 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out

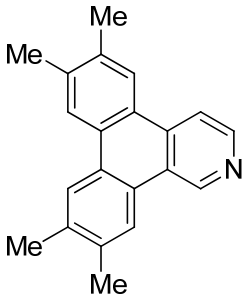
according to the general procedure to afforded 55.5 mg (76% yield) of **3ma**. White solid; mp 241.6−242.2 °C; IR (KBr, cm^{-1}) ν_{max} 1357, 1330, 1115, 819; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.90 (s, 1H), 8.88 (d, J = 5.4 Hz, 1H), 8.74 (d, J = 7.8 Hz, 3H), 8.65 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 6.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 147.8, 147.3, 134.5, 131.5 (q, J = 32.55 Hz), 130.7, 130.3, 130.27 (q, J = 32.55 Hz), 130.1, 128.9, 124.8, 124.8, 124.5 (q, J = 3.3 Hz), 124.0 (q, J = 270.75 Hz), 123.9 (q, J = 273.75 Hz), 123.8, 123.6, 120.6 (q, J = 3.45 Hz), 116.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{10}F_6N$ 366.0717, Found 366.0718.

Dimethyl 2-azatriphenylene-7,10-dicarboxylate (3na)



The reaction of dimethyl 6-iodobiphenyl-3,3'-dicarboxylate **1n-I** (79.2 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 43.5 mg (63% yield) of **3aa**. White solid; mp 282.6−283.0 °C; IR (KBr, cm^{-1}) ν_{max} 1727, 1251, 761; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.88 (s, 1H), 9.23 (s, 2H), 8.82 (d, J = 6.0 Hz, 1H), 8.66 (d, J = 9.0 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 8.29-8.24 (m, 3H), 4.078 (s, 3H), 4.076 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 166.6, 166.5, 147.5, 147.4, 134.9, 131.4, 130.7, 130.7, 130.6, 129.5, 129.3, 128.4, 128.0, 125.4, 125.4, 124.2, 123.9, 122.7, 116.7, 52.6, 52.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NO_4$ 346.1079, Found 346.1087.

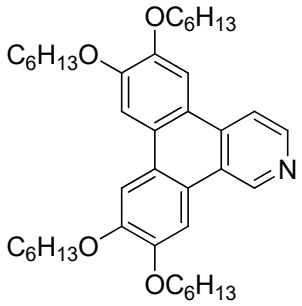
6,7,10,11-tetramethyl-2-azatriphenylene (3oa)



Method A: the reaction of 3',4,4',5-tetramethyl-2-iodobiphenyl **1o-I** (67.2 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 52.5 mg (92% yield) of **3oa**. Method B: the reaction of 3',4,4',5-tetramethyl-2-bromobiphenyl **1o-Br** (57.8, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 33.1 mg (58% yield) of **3oa**. White solid; mp 227.6−228.3 °C; IR (KBr, cm^{-1}) ν_{max} 2963, 1596, 1446, 1414, 863, 816; ^1H

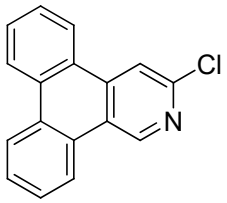
NMR (600 MHz, $CDCl_3$, ppm) δ 9.81 (s, 1H), 8.67 (d, J = 6.0 Hz, 1H), 8.34 (s, 1H), 8.22-8.19 (m, 4H), 2.47 (s, 9H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 146.4, 145.5, 138.3, 136.8, 136.2, 135.9, 134.6, 129.2, 127.9, 125.8, 125.2, 124.2, 124.0, 123.6, 123.6, 122.9, 116.0, 20.4, 20.3, 20.2, 20.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}N$ 286.1596, Found 286.1603.

6,7,10,11-Tetrakis(hexyloxy)-2-azatriphenylene (3pa)



Method A: the reaction of 3',4,4',5-tetrakis(hexyloxy)-2-iodobiphenyl **1p-I** (136.1 mg, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 104.6 mg (83% yield) of **3pa**. Method B: the reaction of 3',4,4',5-tetrakis(hexyloxy)-2-bromobiphenyl **1p-Br** (126.7, 0.2 mmol) with 3-chloropyridine-4-carboxylic acid **2a** (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 60.5 mg (48% yield) of **3pa**. Yellow solid; mp 170.8−171.5 °C; IR (KBr, cm^{-1}) ν_{max} 2954, 2927, 2853, 1615, 1514, 1435, 1266, 1179; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.78 (s, 1H), 8.67 (d, J = 5.4 Hz, 1H), 8.20 (d, J = 6.0 Hz, 1H), 8.07 (s, 1H), 7.94 (s, 1H), 7.81 (s, 1H), 7.80 (s, 1H), 4.28-4.21 (m, 8H), 1.99-193 (m, 8H), 1.62-1.5 (m, 8H), 1.45-1.36 (m, 16H), 0.94 (t, J = 7.2 Hz, 12H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 151.1, 149.9, 149.5, 149.1, 146.2, 144.6, 134.0, 126.0, 124.2, 123.7, 121.9, 121.0, 115.9, 106.8, 106.7, 106.2, 105.5, 69.6, 69.4, 69.3, 69.2, 31.6, 31.6, 29.3, 29.2, 25.8, 25.8, 22.6, 14.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{41}H_{60}NO_4$ 630.4522, Found 630.4518.

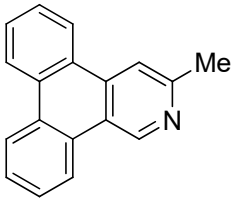
3-Chloro-2-azatriphenylene (3ab)



Method A: the reaction of 2-iodobiphenyl **1a-I** (56.0 mg, 0.2 mmol) with 2,5-dichloropyridine-4-carboxylic acid (38.4 mg, 0.2 mmol) was carried out according to the general procedure to afforded 31.1 mg (59% yield) of **3ab**. Method B: the reaction of 2-iodobiphenyl **1a-I** (56.0 mg, 0.2 mmol) with 2,4-dichloropyridine-5-carboxylic acid (38.4 mg, 0.2 mmol) was carried out according to the general procedure to afforded 29.0 mg (55% yield) of **3ab**. White solid; mp 160.6−161.2 °C; IR (KBr, cm^{-1}) ν_{max} 1611, 1107, 747; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.64 (s, 1H), 8.62-8.58 (m, 3H), 8.49 (d, J = 7.8 Hz, 1H), 8.33 (s, 1H), 7.78 (t,

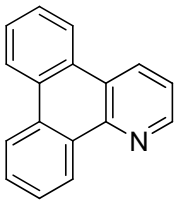
J = 7.2 Hz, 1H), 7.73-7.67 (m, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 149.1, 146.9, 137.9, 131.6, 130.0, 129.7, 128.4, 128.1, 127.7, 127.4, 126.6, 123.9, 123.6, 123.5, 122.5, 116.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{11}ClN$ 264.0580, Found 264.0582.

3-Methyl-2-azatriphenylene (3ac)



The reaction of 2-iodobiphenyl **1a-I** (56.0 mg, 0.2 mmol) with 5-chloro-2-methylpyridine-4-carboxylic acid **2a** (34.3 mg, 0.2 mmol) was carried out according to the general procedure to afforded 35.5 mg (73% yield) of **3ac**. Yellow solid; mp 122.5−123.3 °C; IR (KBr, cm^{-1}) ν_{max} 1602, 1435, 755, 717; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.85 (s, 1H), 8.72-8.70 (m, 1H), 8.67-8.61 (m, 3H), 8.23 (s, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.71-7.68 (m, 3H), 2.81 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 155.1, 146.2, 135.7, 131.4, 129.5, 129.2, 128.3, 127.8, 127.6, 127.5, 127.4, 123.7, 123.4, 123.4, 122.4, 122.3, 115.2, 24.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{14}N$ 244.1126, Found 244.1131.

1-Azatriphenylene (3ad)



Method A: the reaction of 2-iodobiphenyl **1a-I** (56.0 mg, 0.2 mmol) with 2-chloropyridine-3-carboxylic acid (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 13.8 mg (30% yield) of **3ad**. Method B: the reaction of 2-iodobiphenyl **1a-I** (56.0 mg, 0.2 mmol) with 3-chloropyridine-2-carboxylic acid (31.5 mg, 0.2 mmol) was carried out according to the general procedure to afforded 10.5 mg (23% yield) of **3ad**. White solid; mp 171.5−172.0 °C; IR (KBr, cm^{-1}) ν_{max} 1406, 754; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.33-9.31 (m, 1H), 8.96 (dd, J_1 = 4.2, J_2 = 1.2 Hz, 1H), 8.83 (dd, J_1 = 8.4, J_2 = 1.8 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.60 (dd, J_1 = 7.2, J_1 = 2.4 Hz, 1H), 8.53 (dd, J_1 = 7.8, J_1 = 0.6 Hz, 1H), 7.76-7.71 (m, 2H), 7.70-7.63 (m, 2H), 7.55 (dd, J_1 = 7.8, J_1 = 4.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 148.8, 146.4, 131.3, 130.8, 130.8, 129.7, 128.8, 128.7, 127.8, 127.5, 127.3, 125.3, 124.4, 123.4, 123.2, 122.5, 122.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{12}N$ 230.0970, Found 230.0970.

Synthesis of compounds 5

The compound **5** was synthesized according to the methods described in the literature.[16] Compound **5** is known, and the data are consistent with the literature.[16]

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Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 1p-I

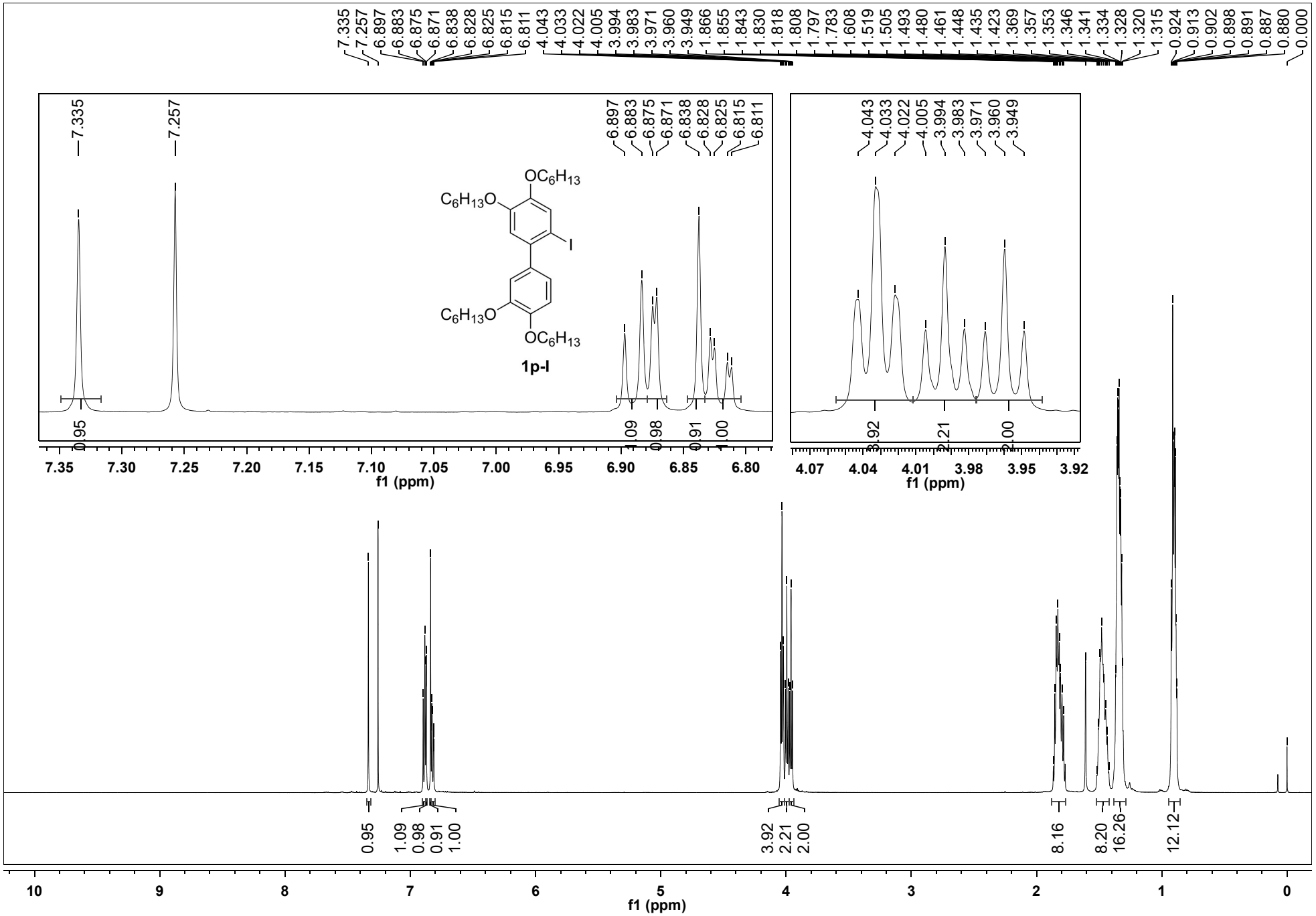

Figure S2. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 1p-I

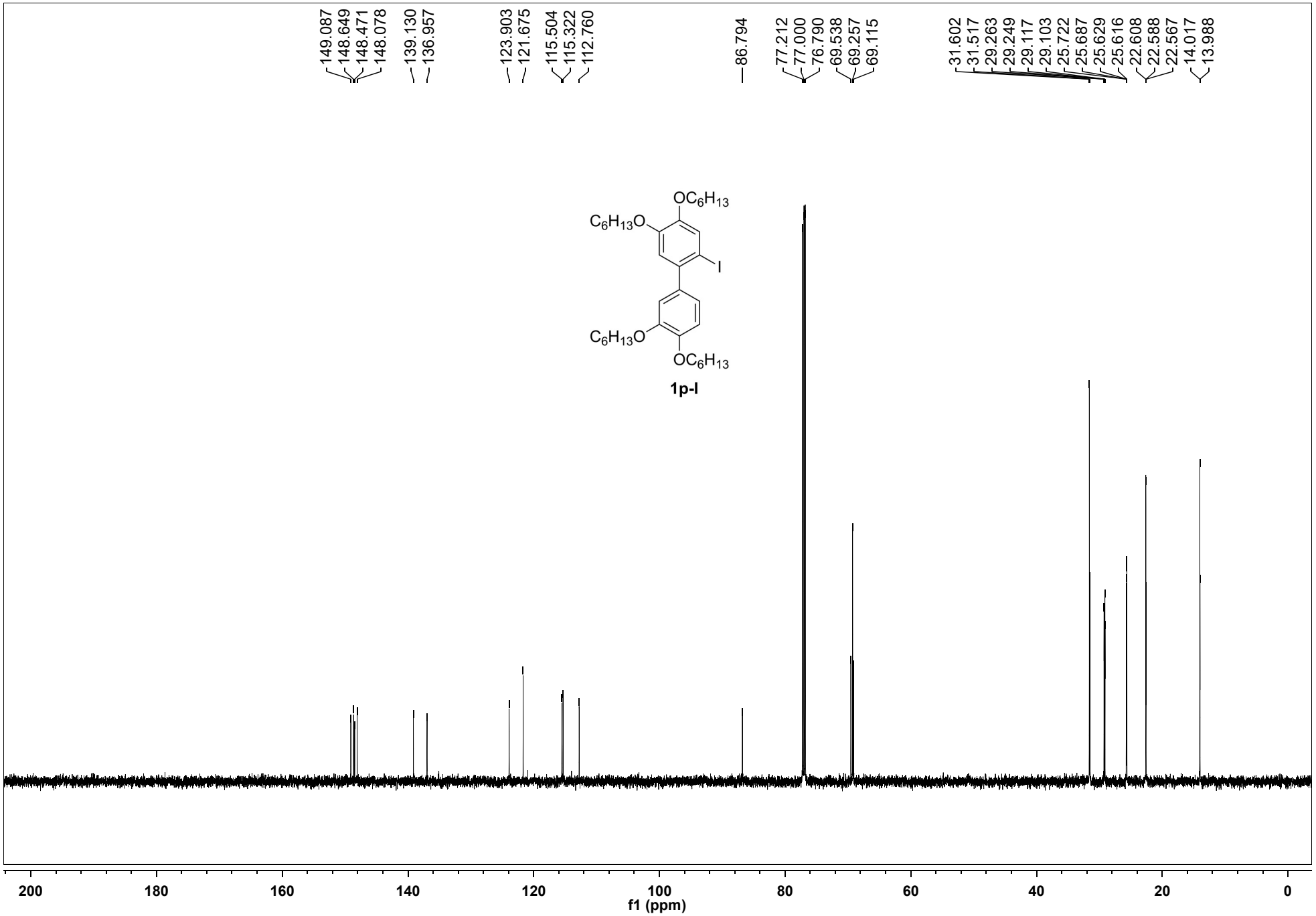

Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 1d-Br

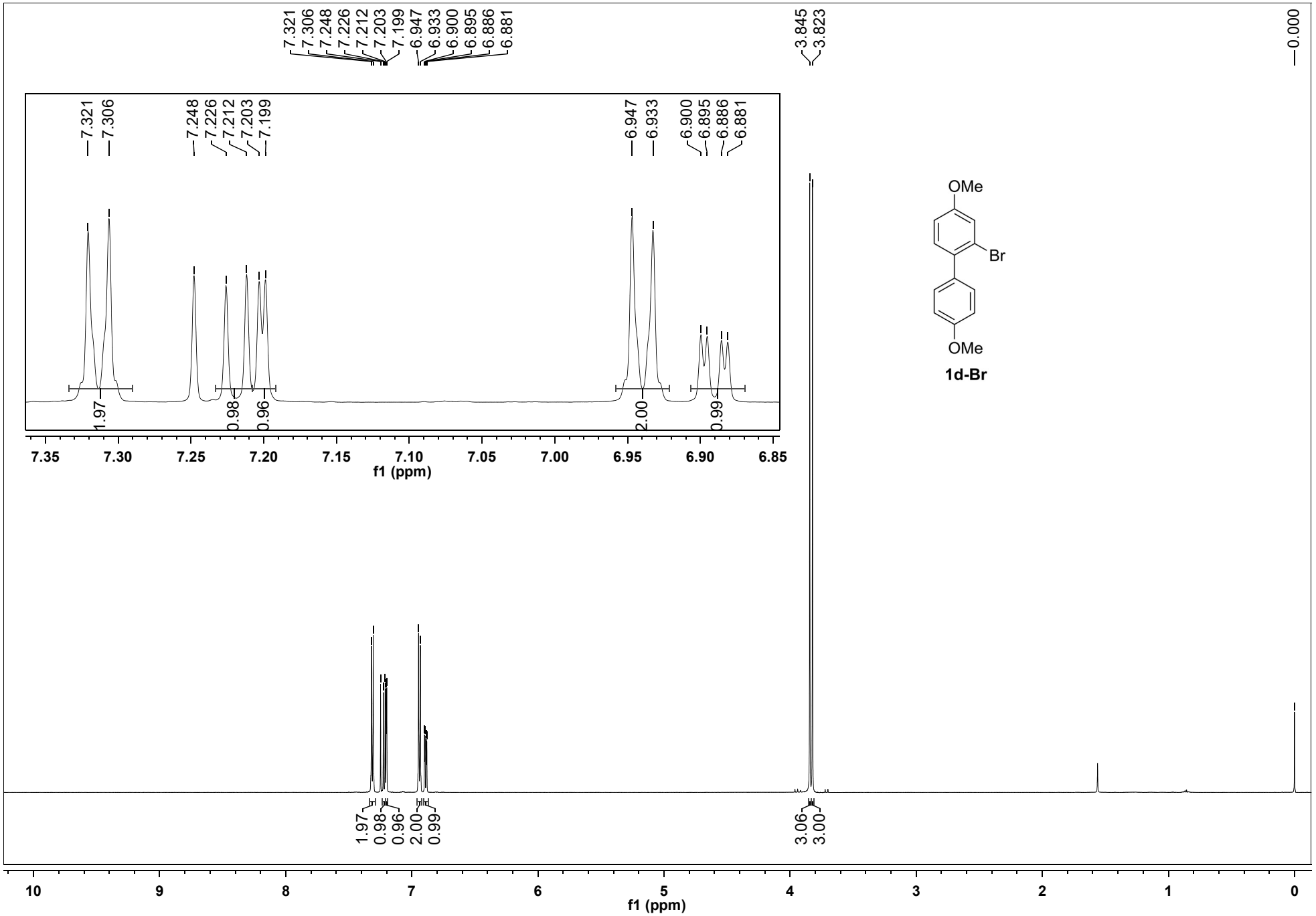

Figure S4. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 1d-Br

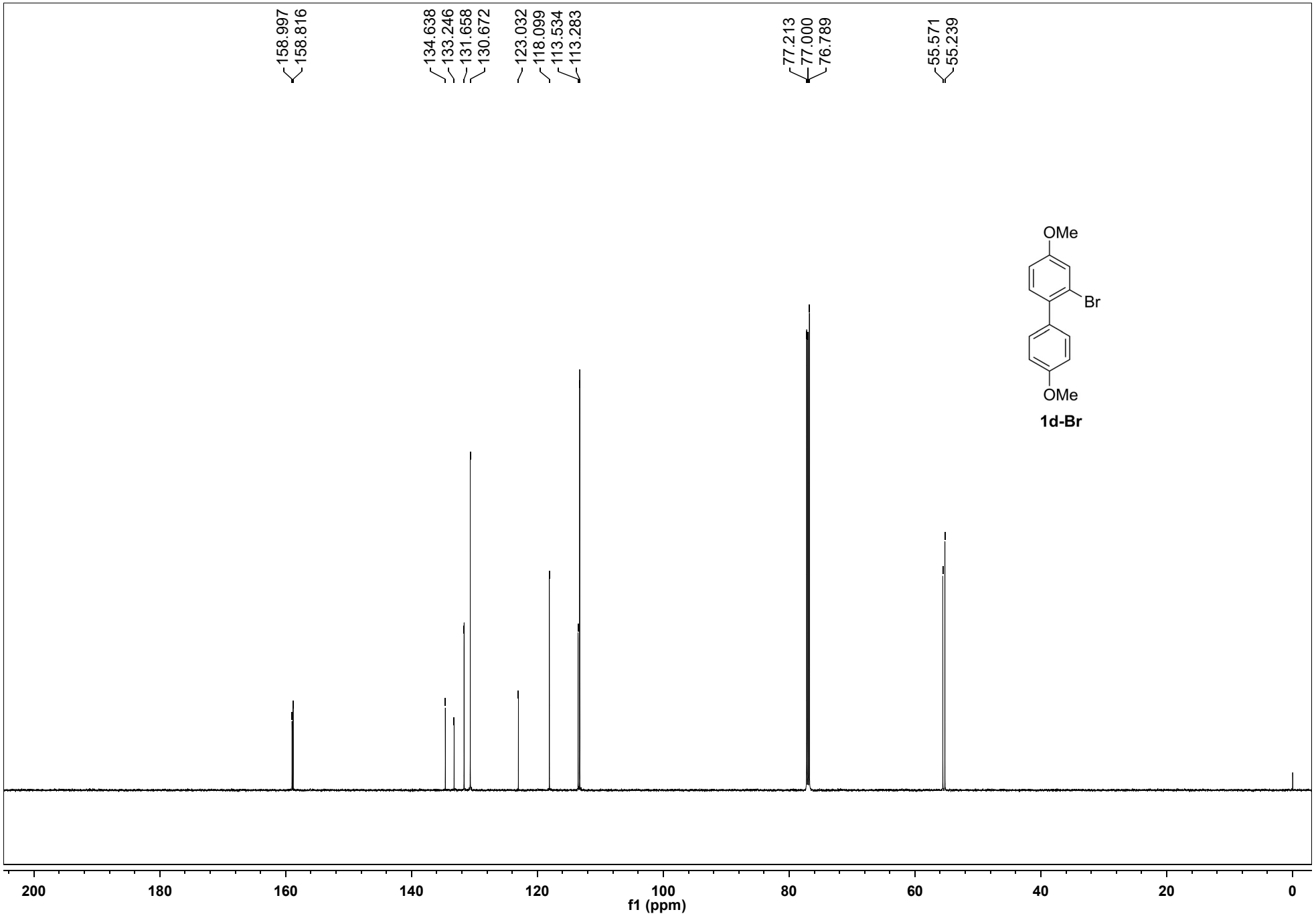

Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 1g-Br

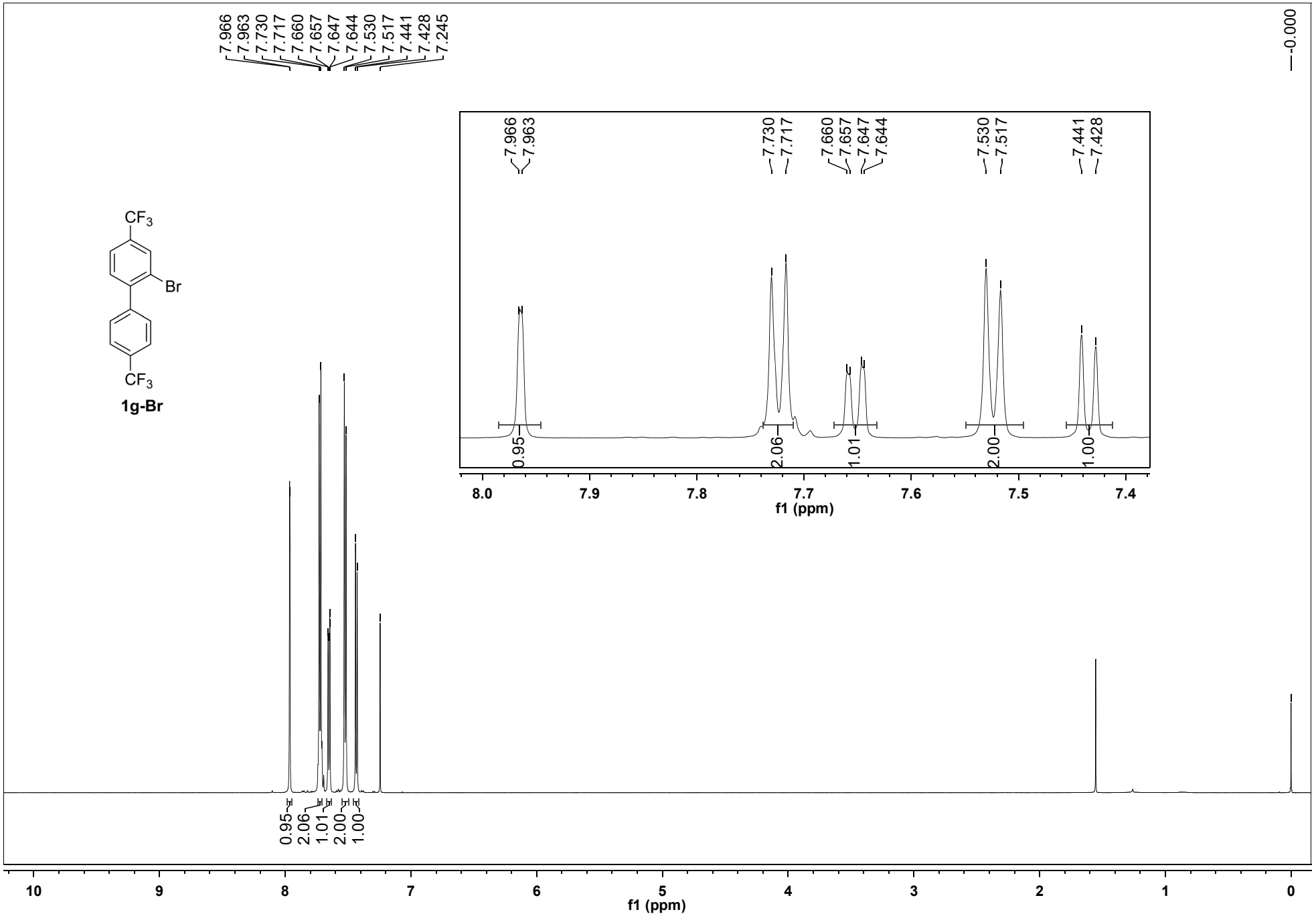

Figure S6. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 1g-Br

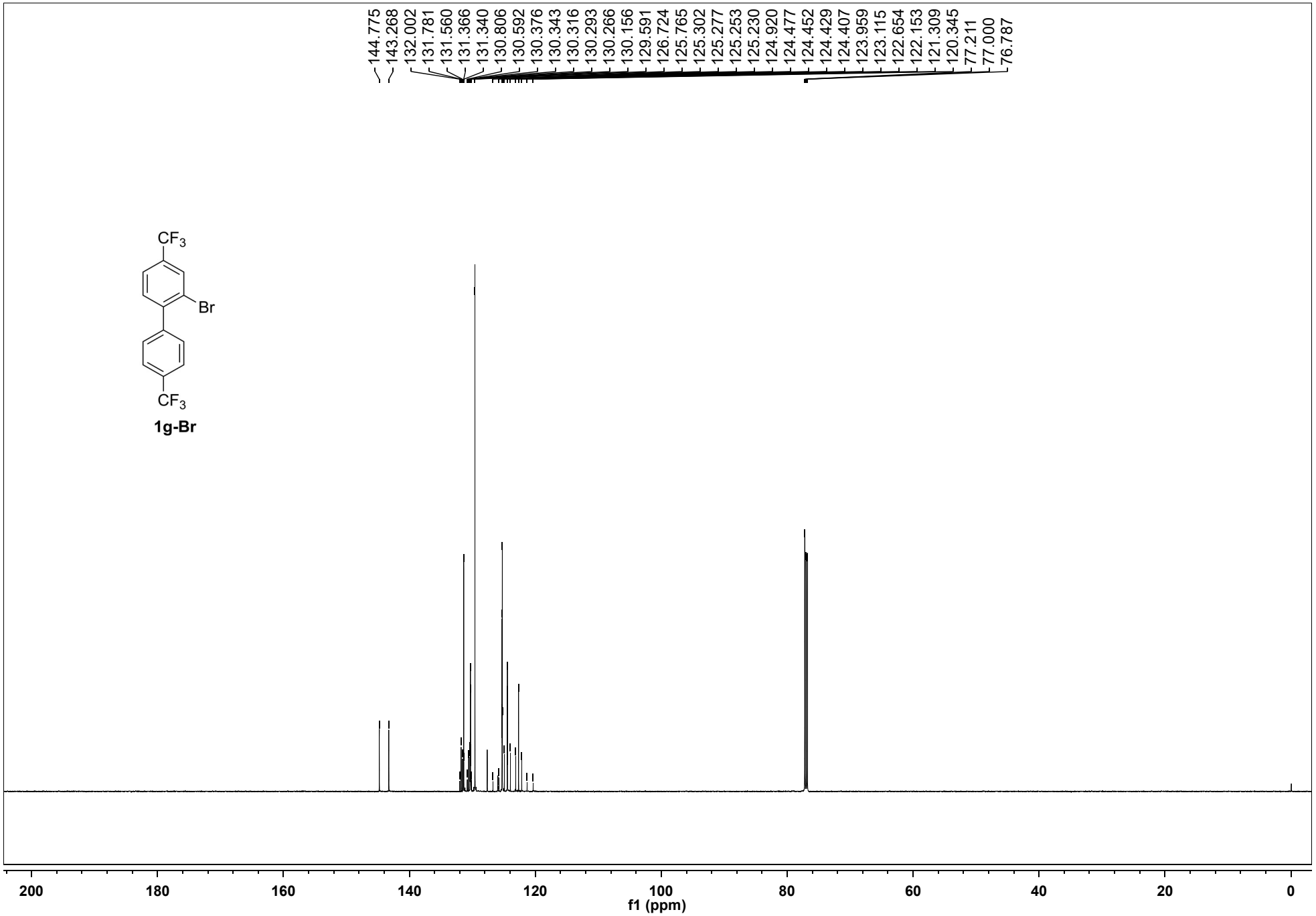

Figure S7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3aa

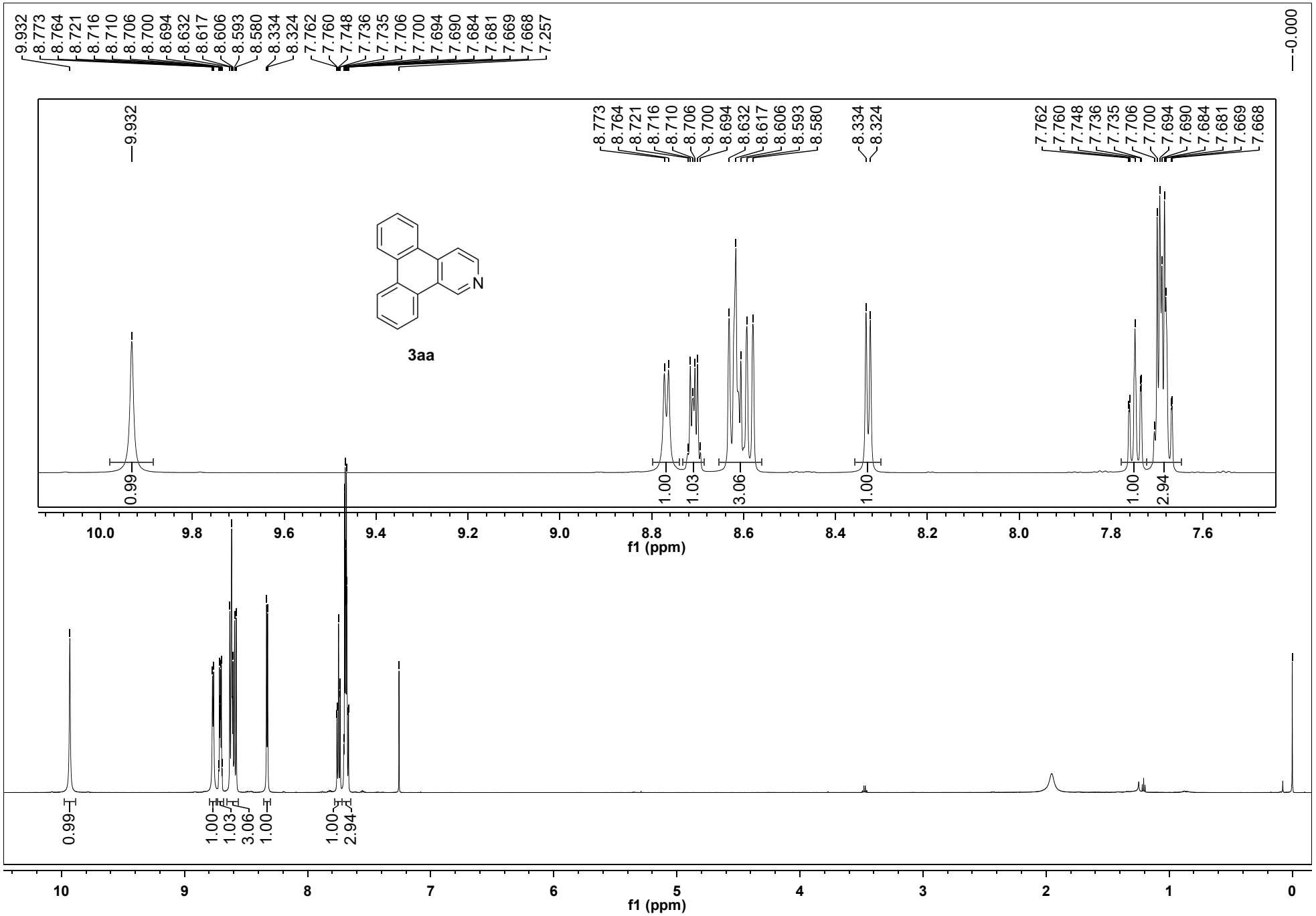

Figure S8. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3aa

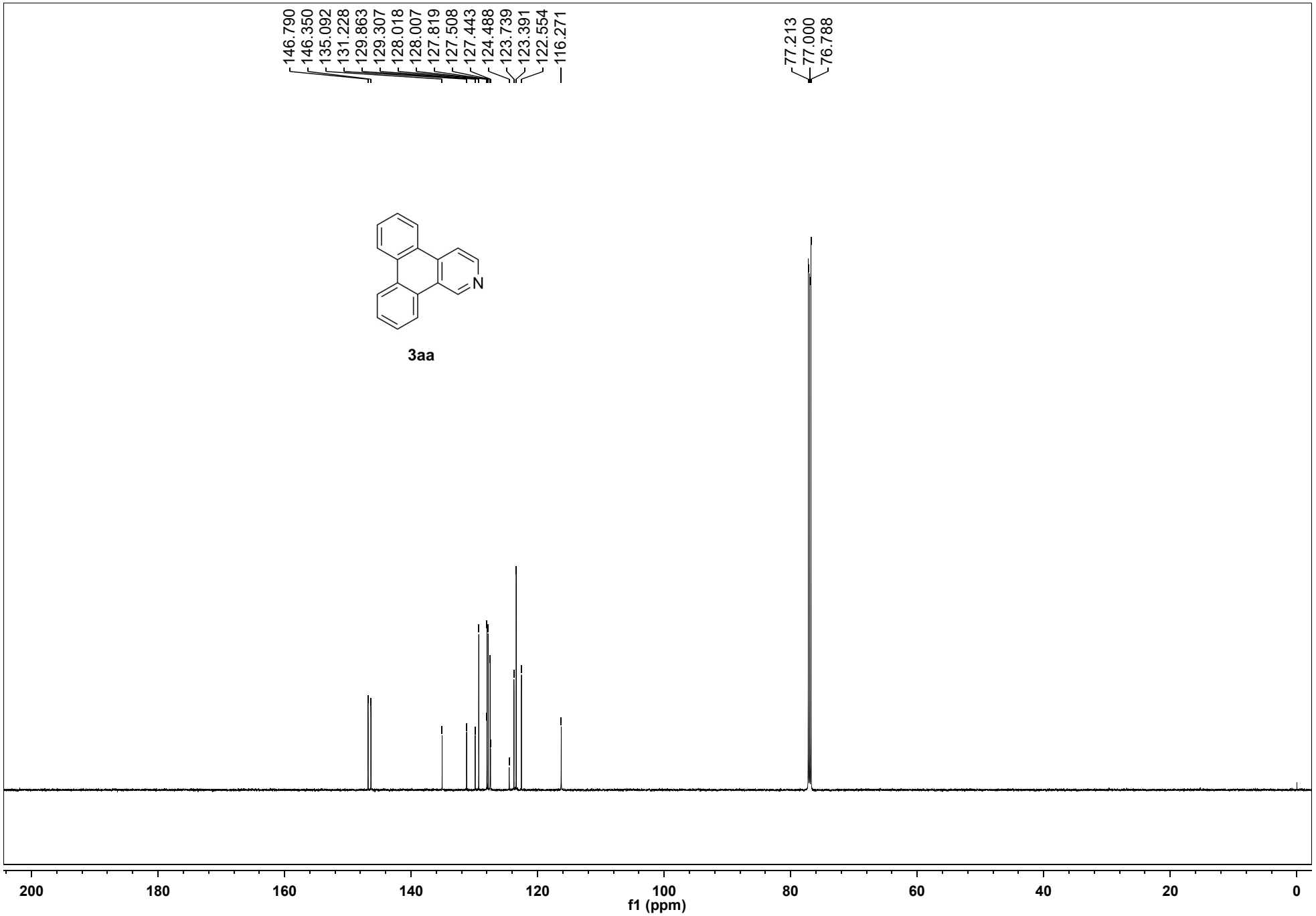

Figure S9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ba

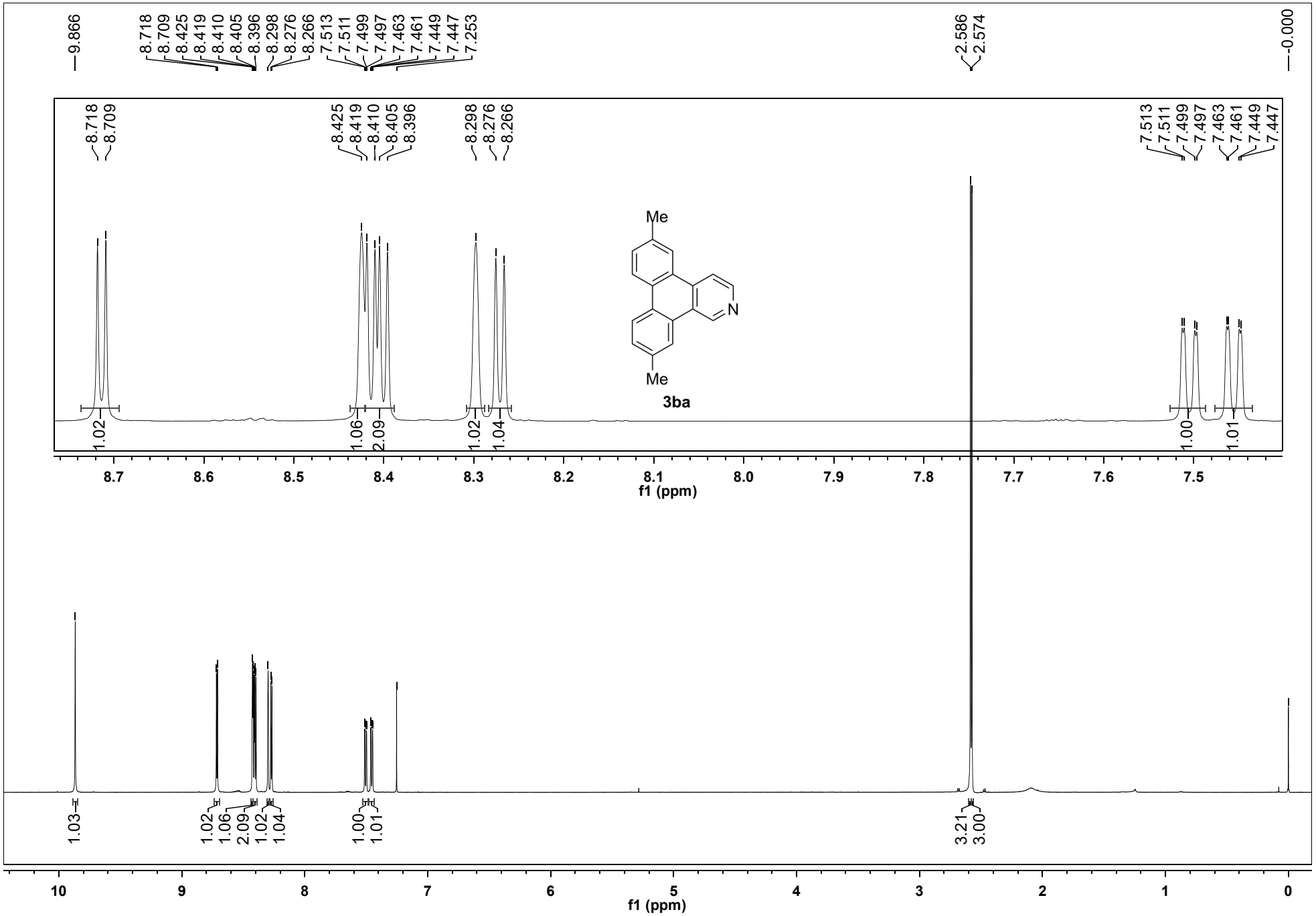

Figure S10. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ba

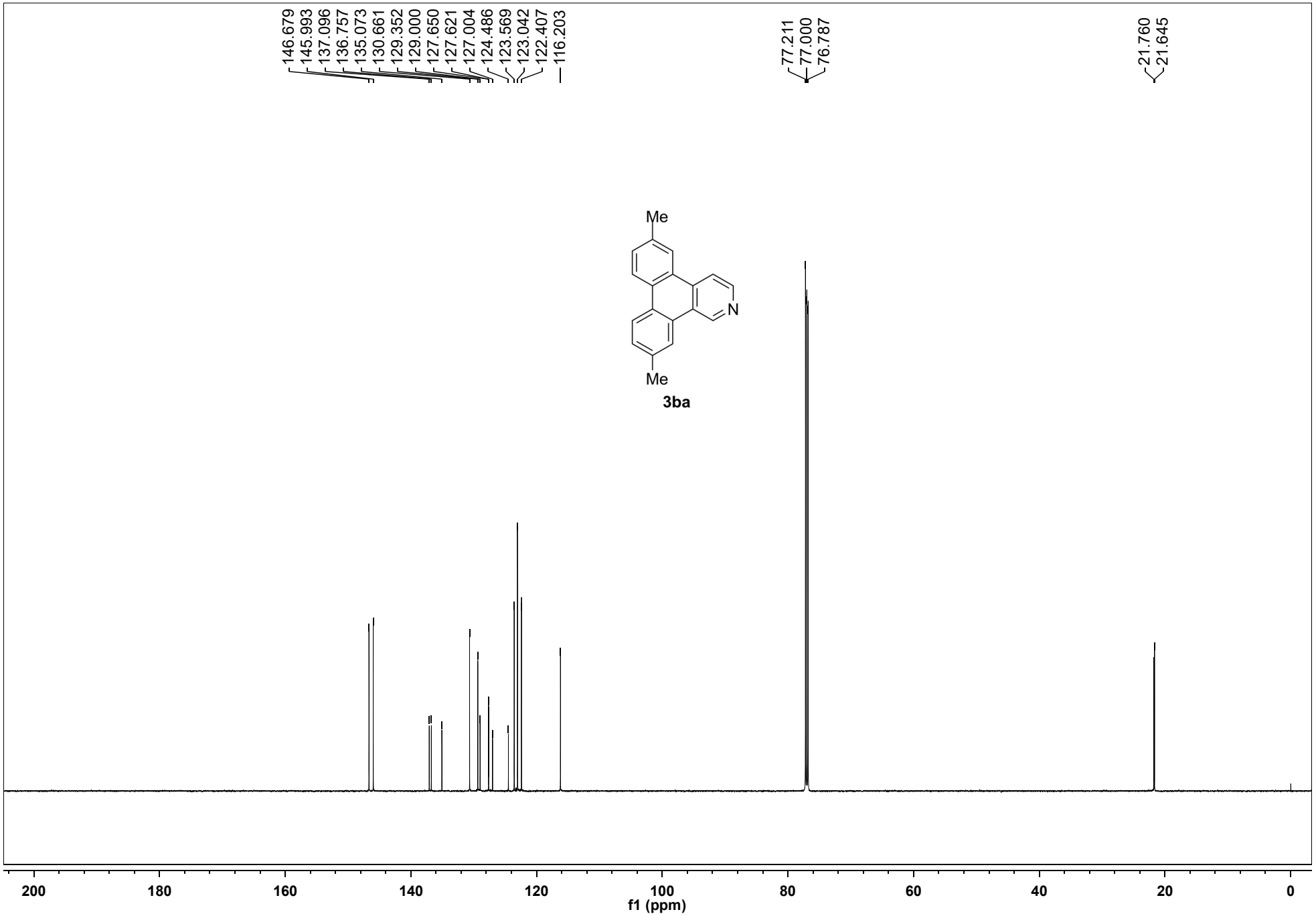

Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ca

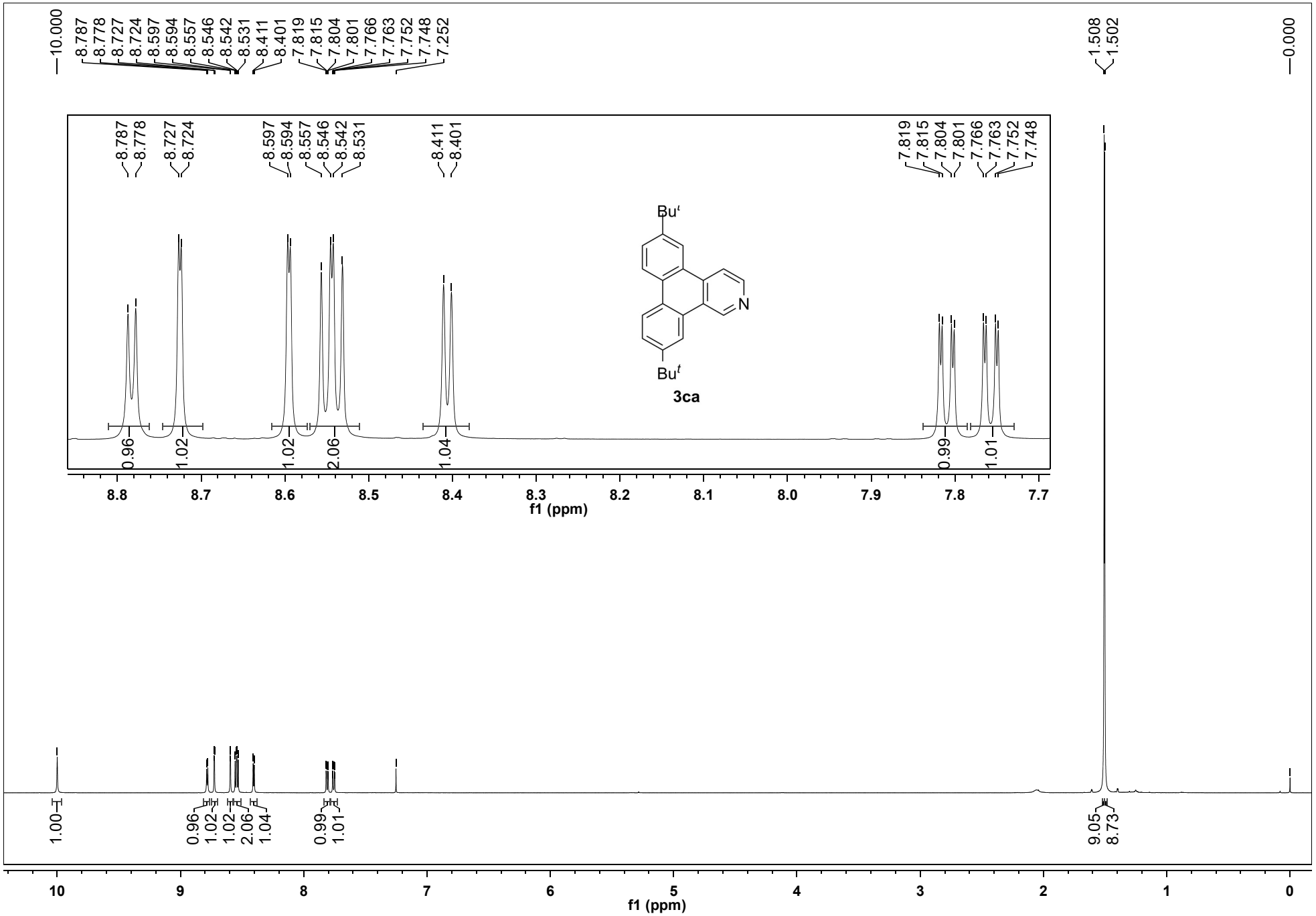

Figure S12. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ca

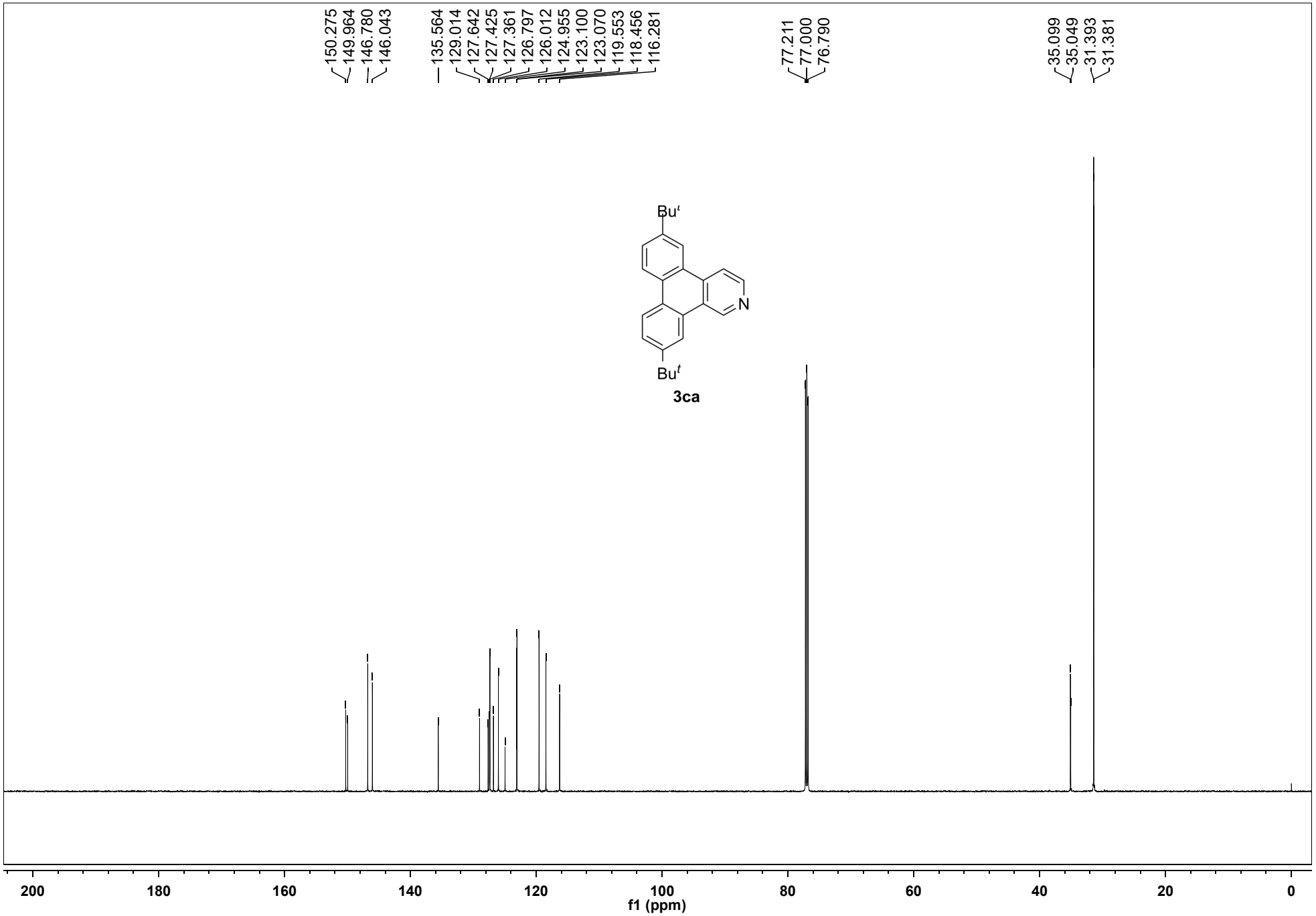

Figure S13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3da

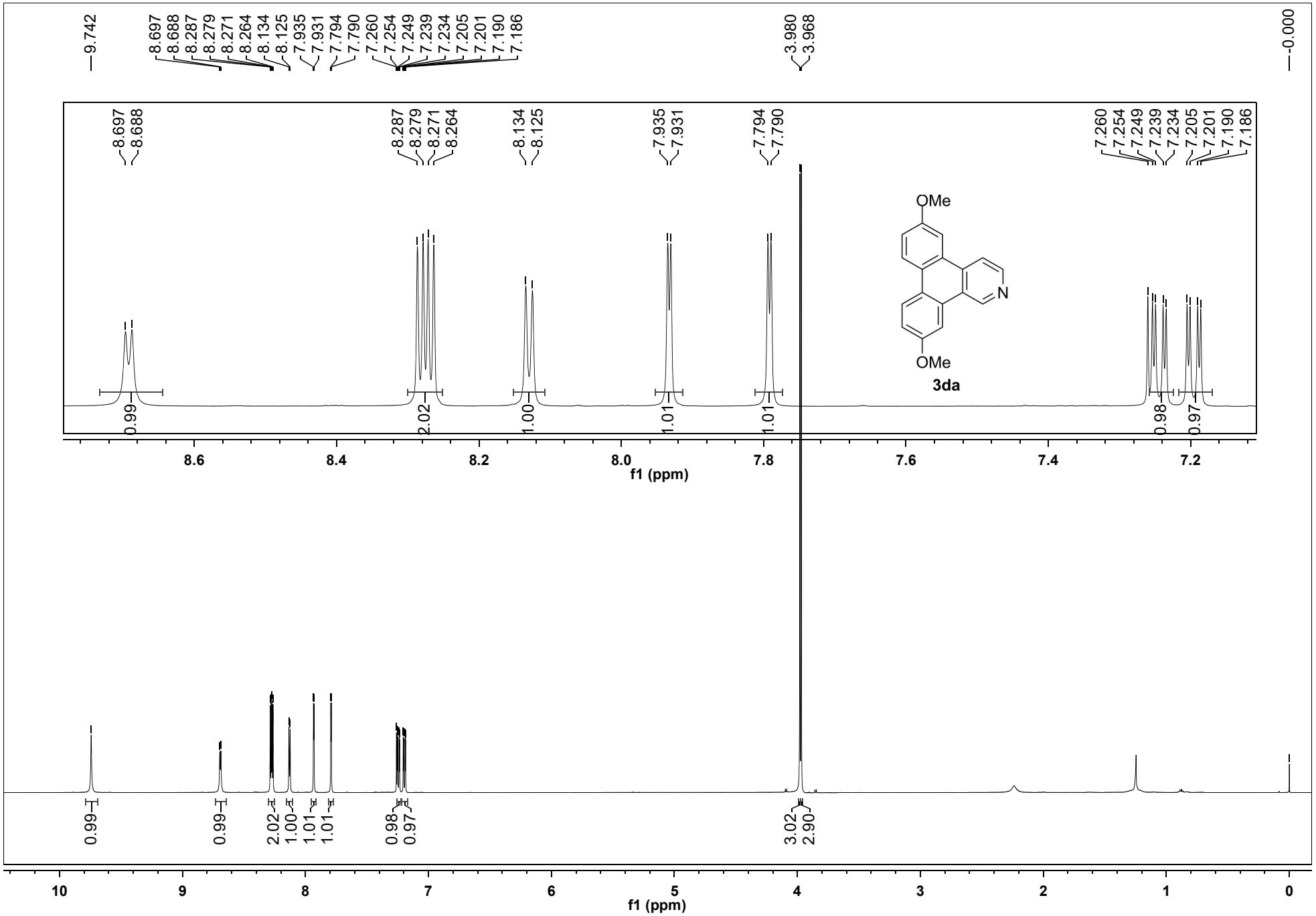

Figure S14. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3da

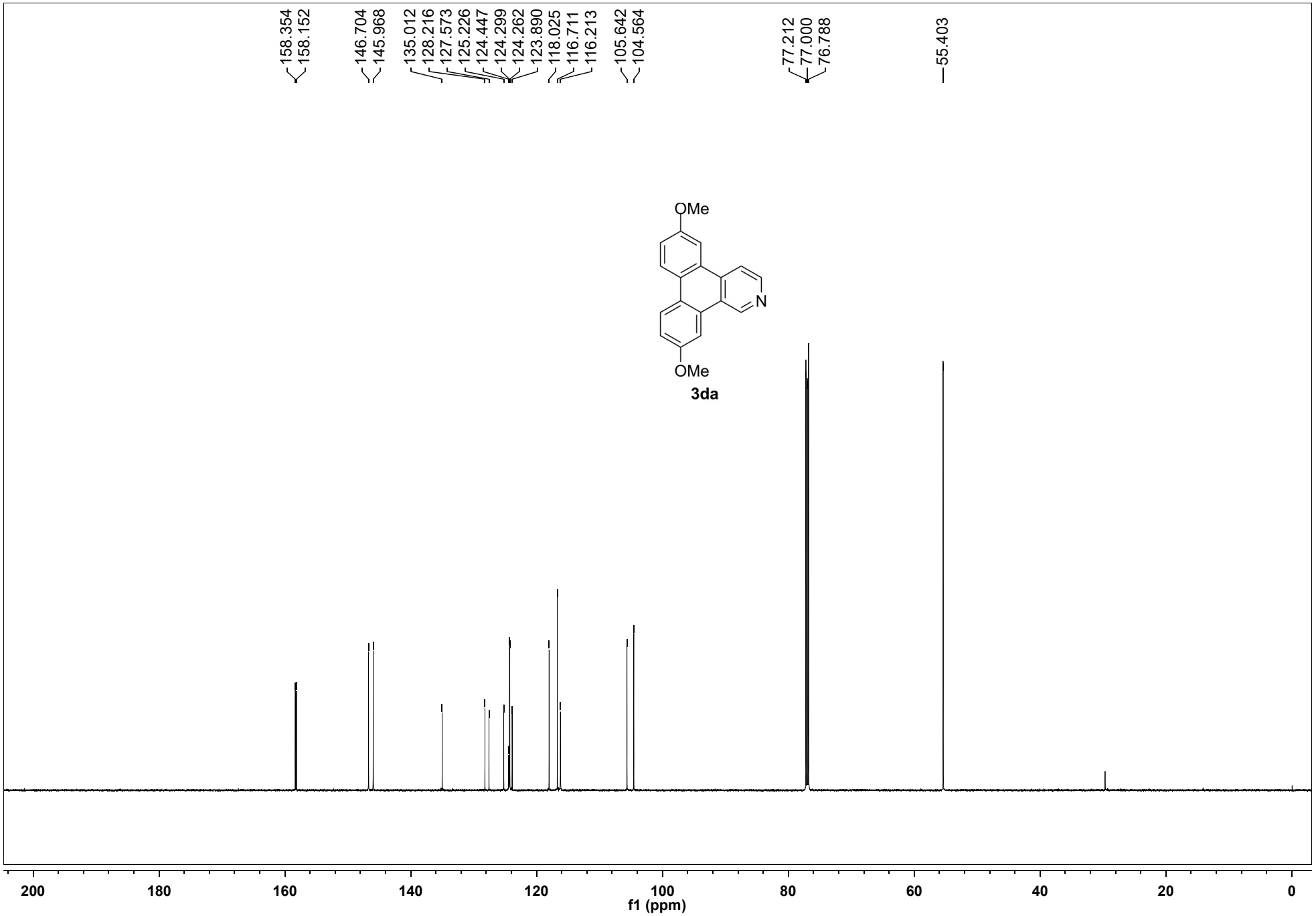

Figure S15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ea

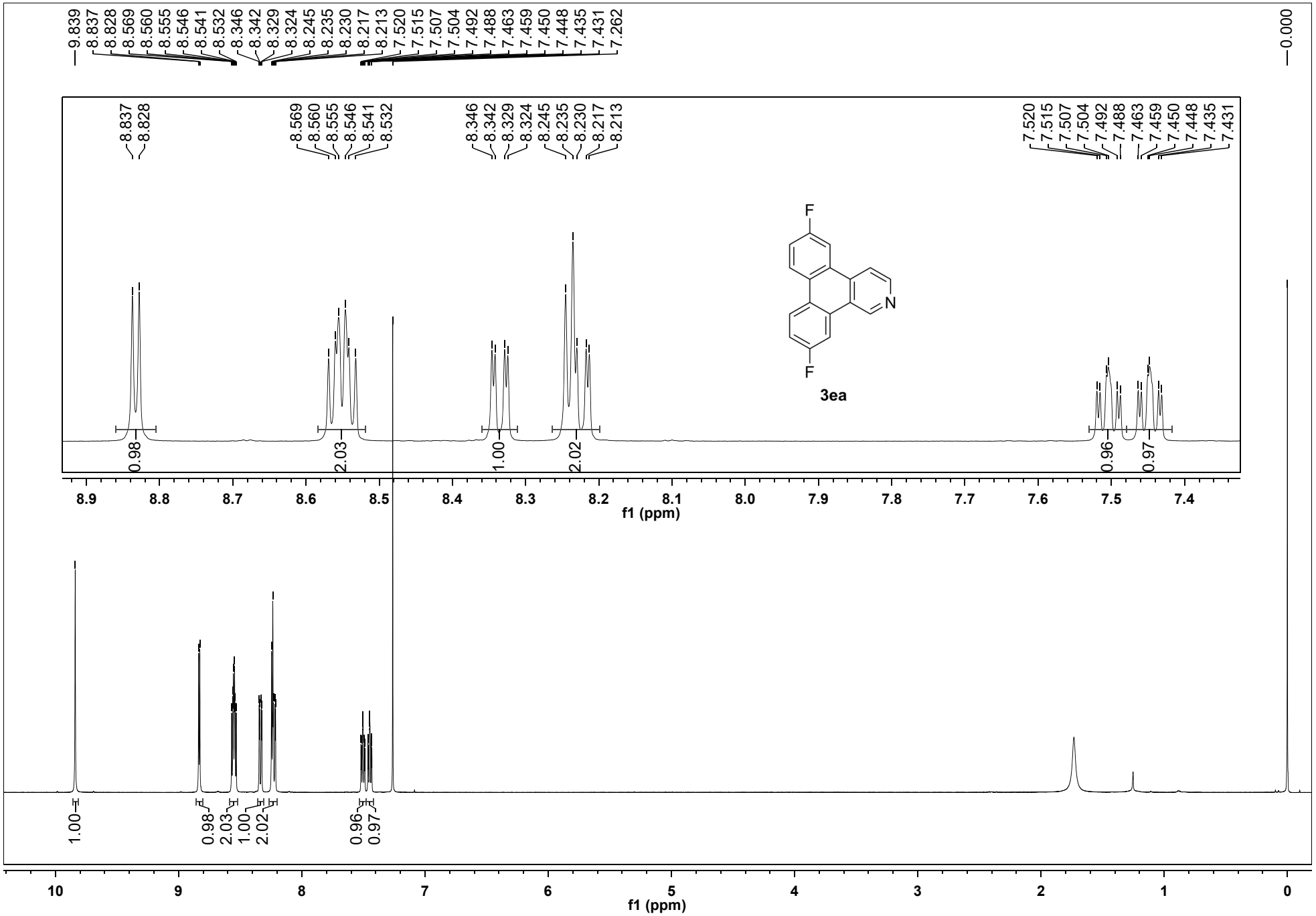

Figure S16. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ea

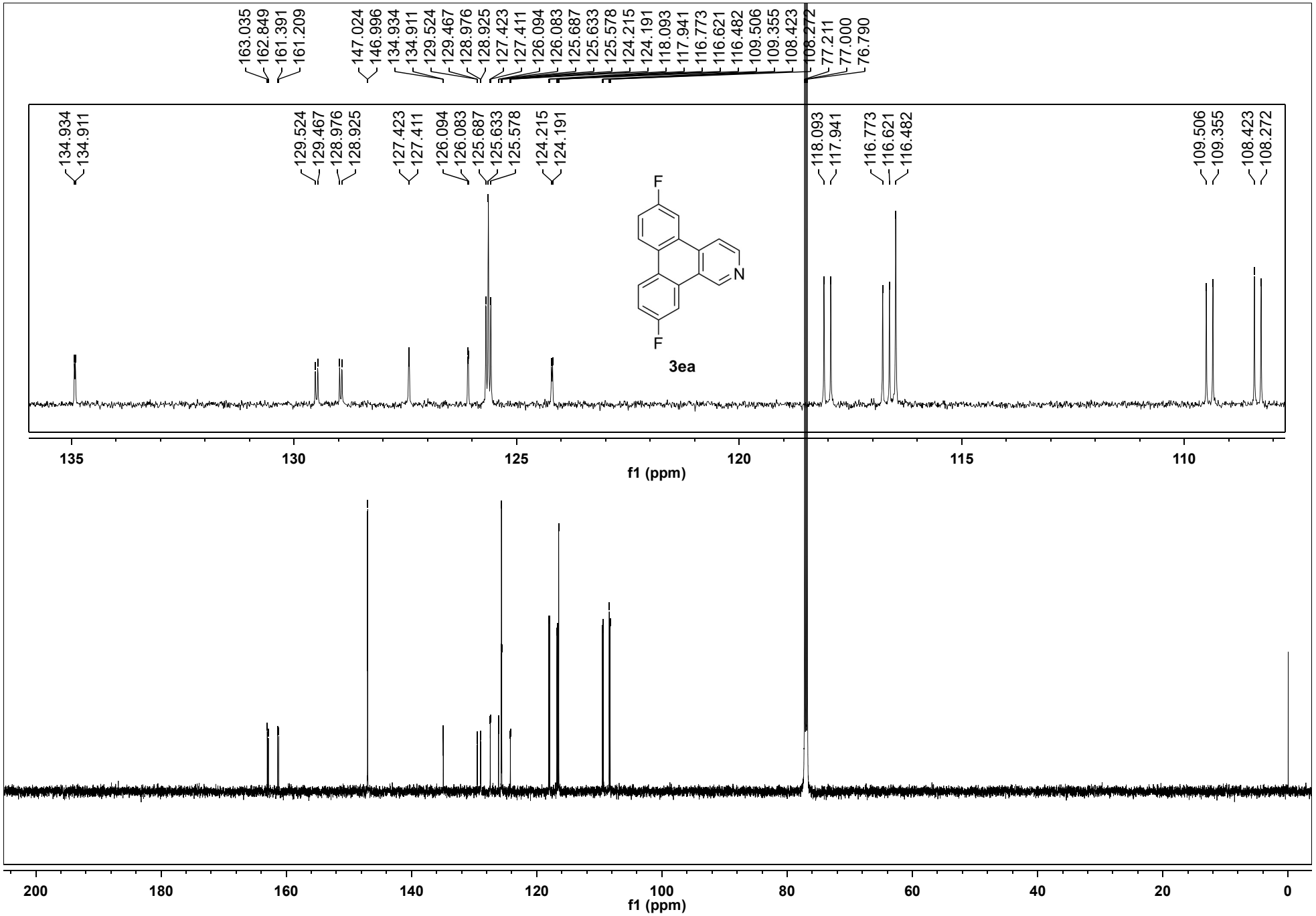

Figure S17. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3fa

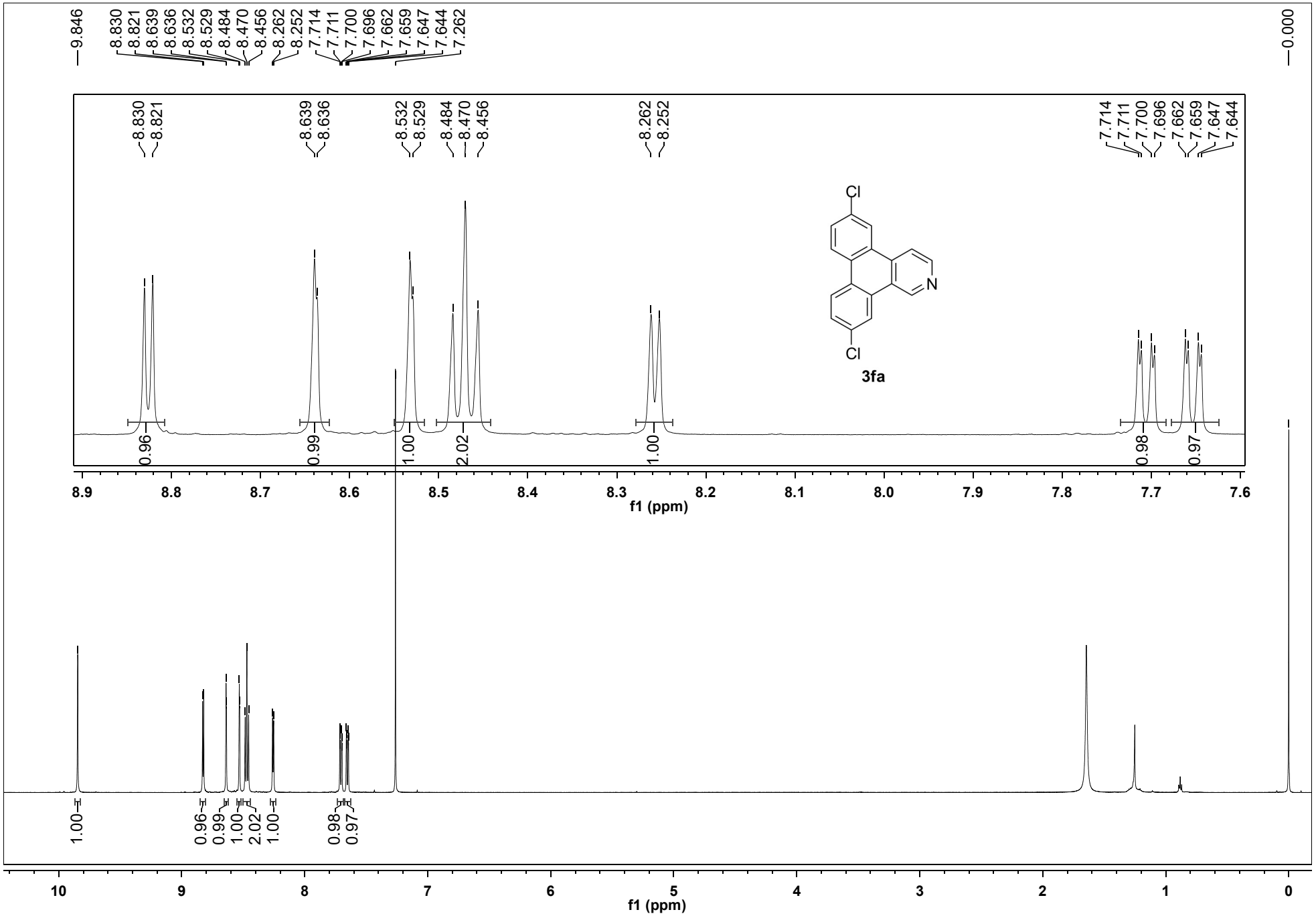

Figure S18. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3fa

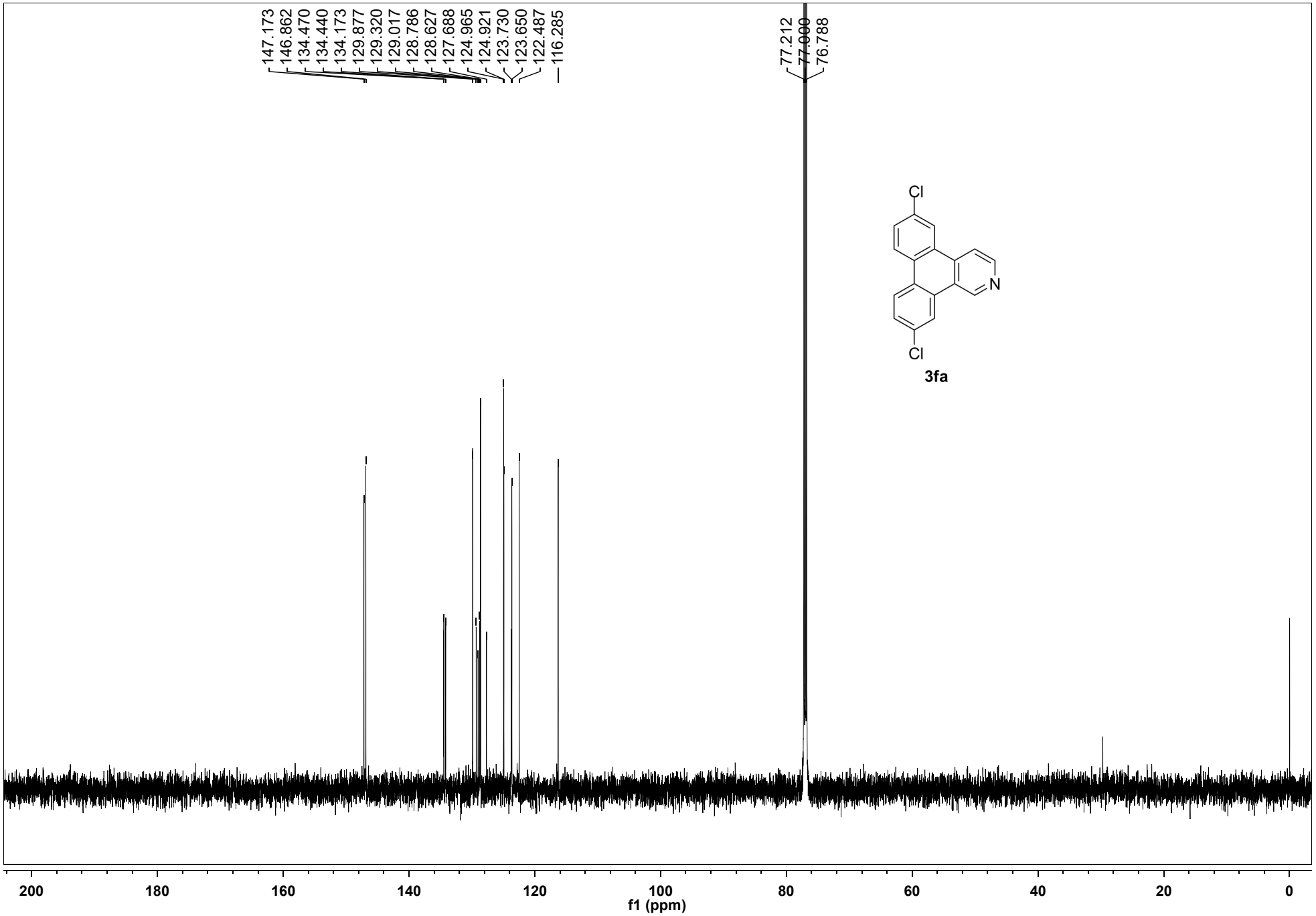

Figure S19. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ga

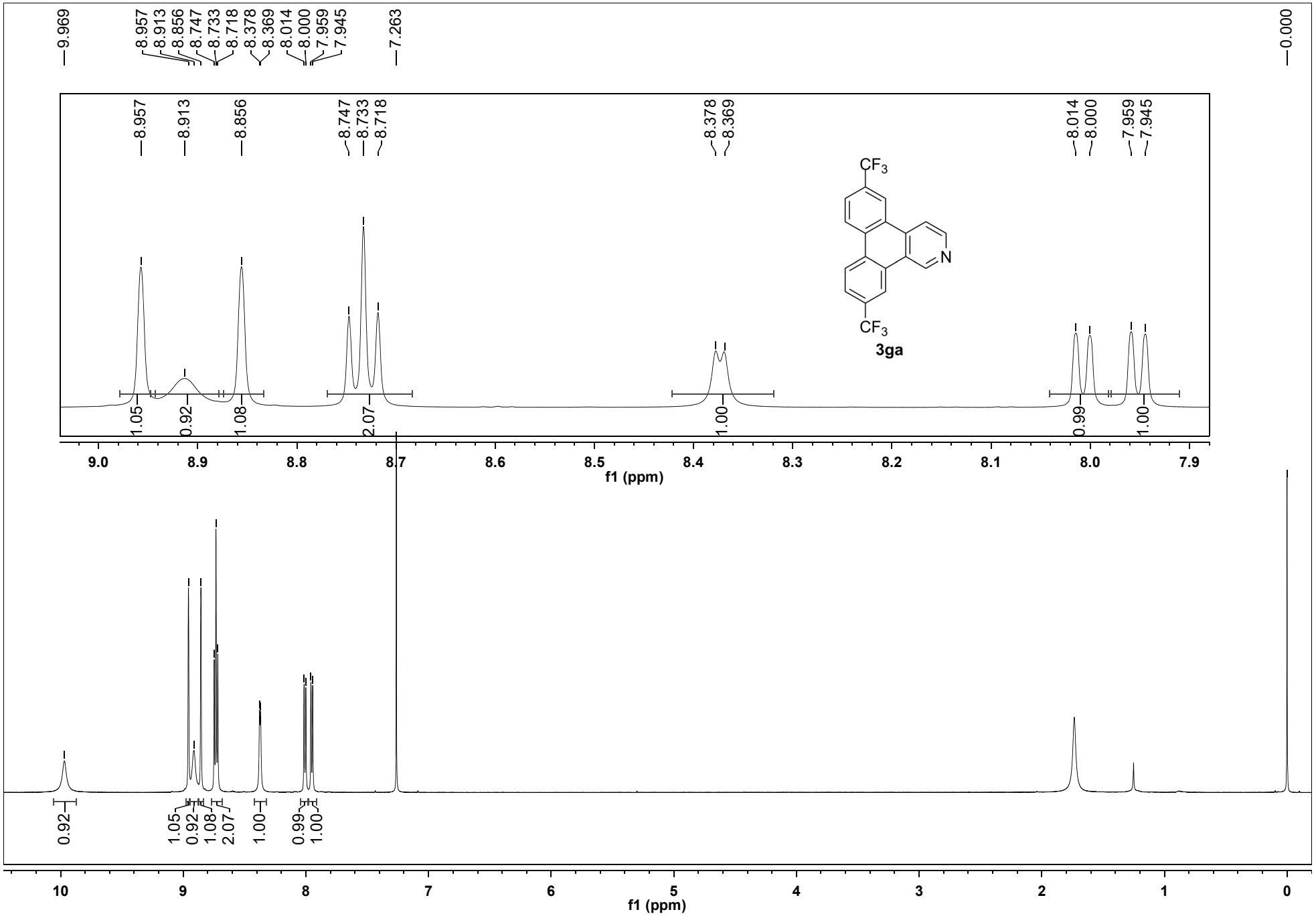

Figure S20. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ga

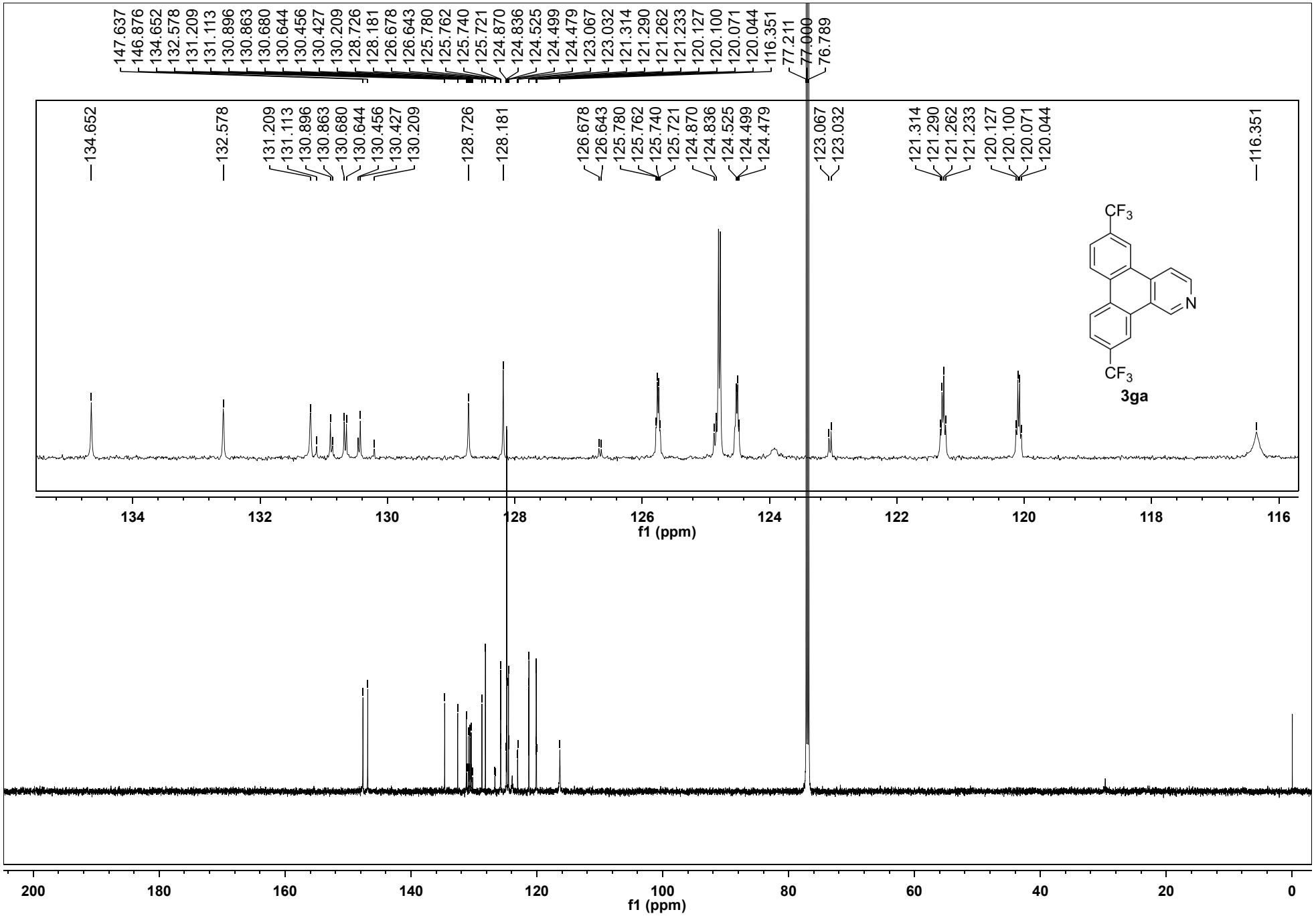

Figure S21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ha

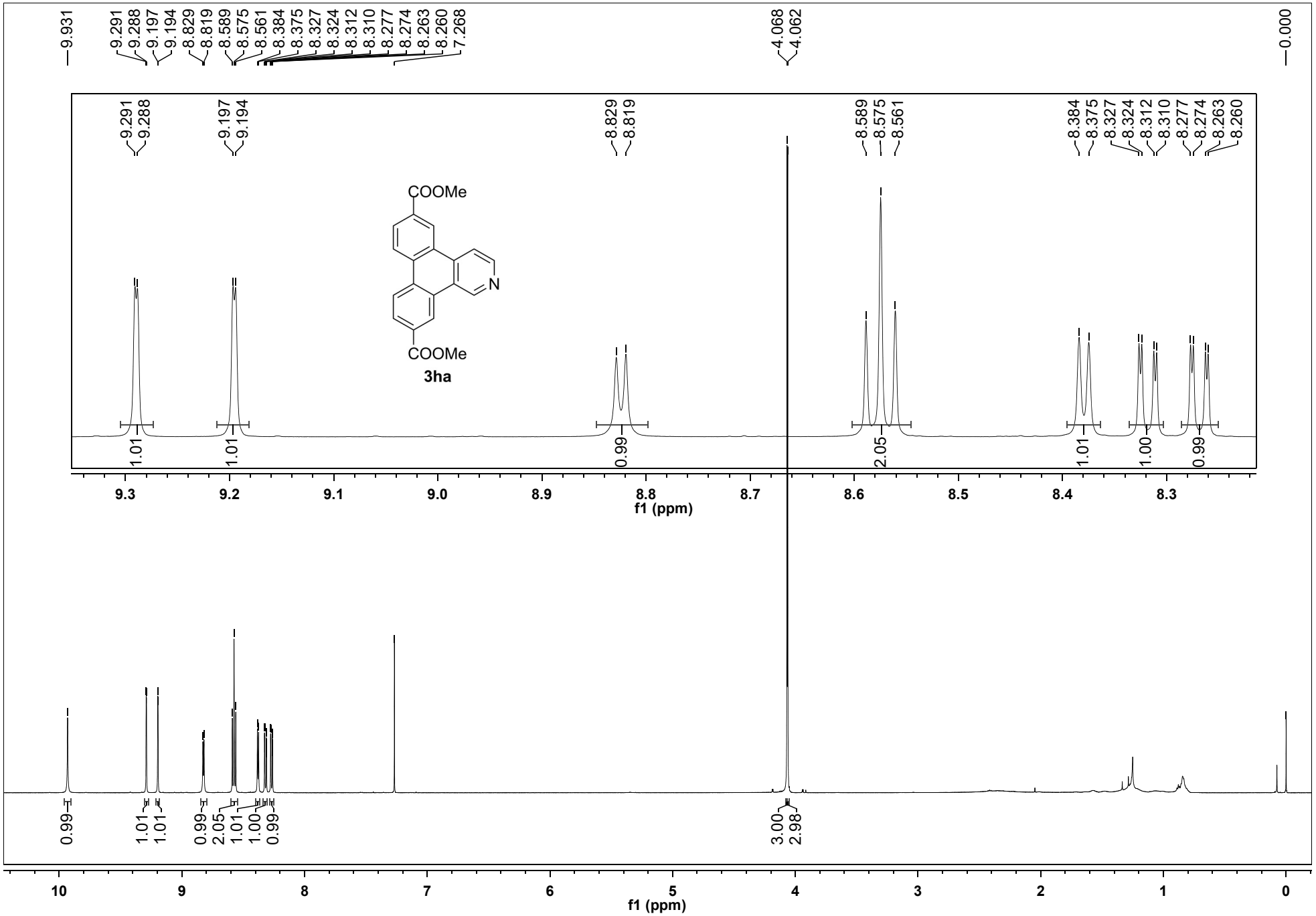

Figure S22. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ha

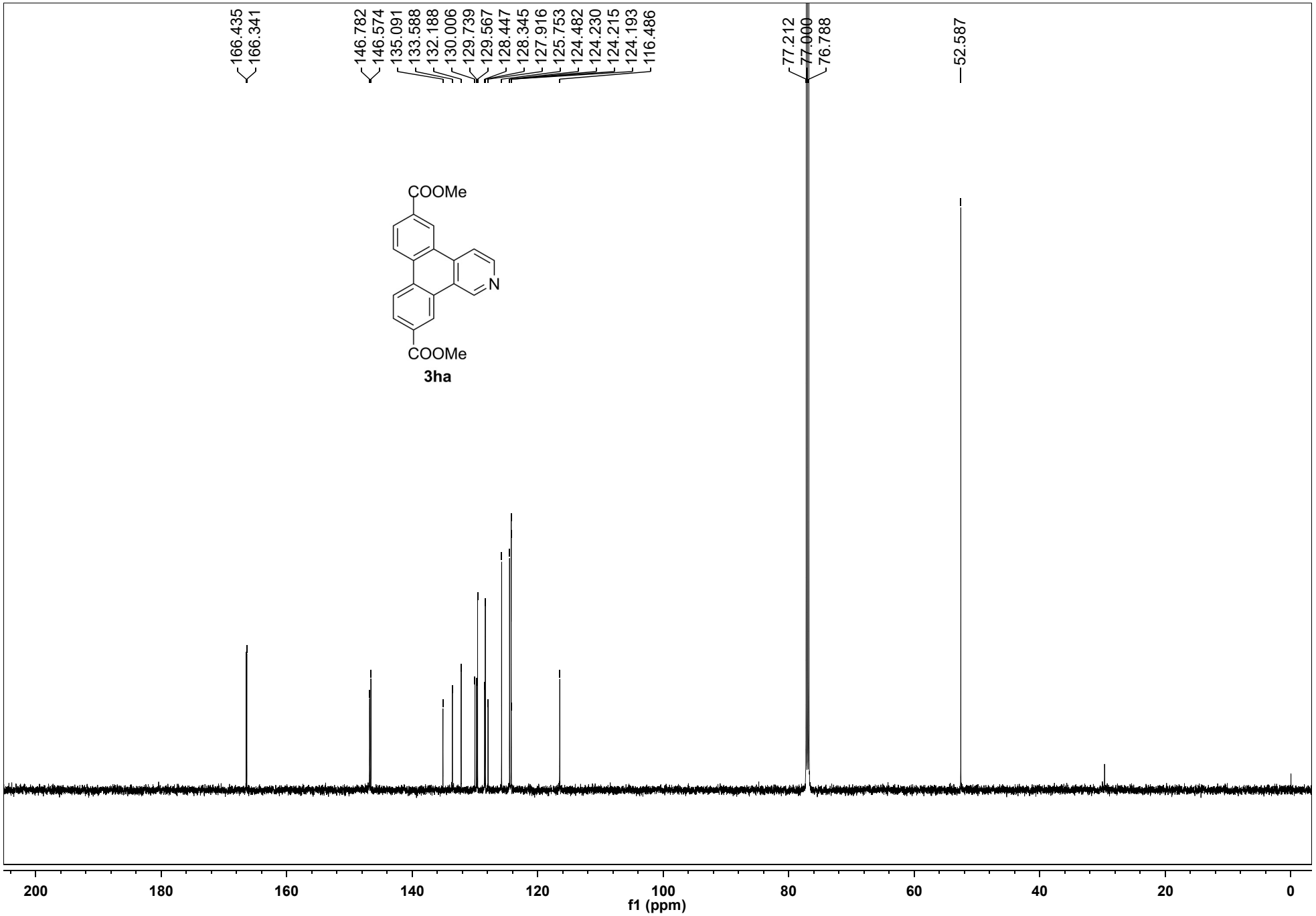

Figure S23. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ia

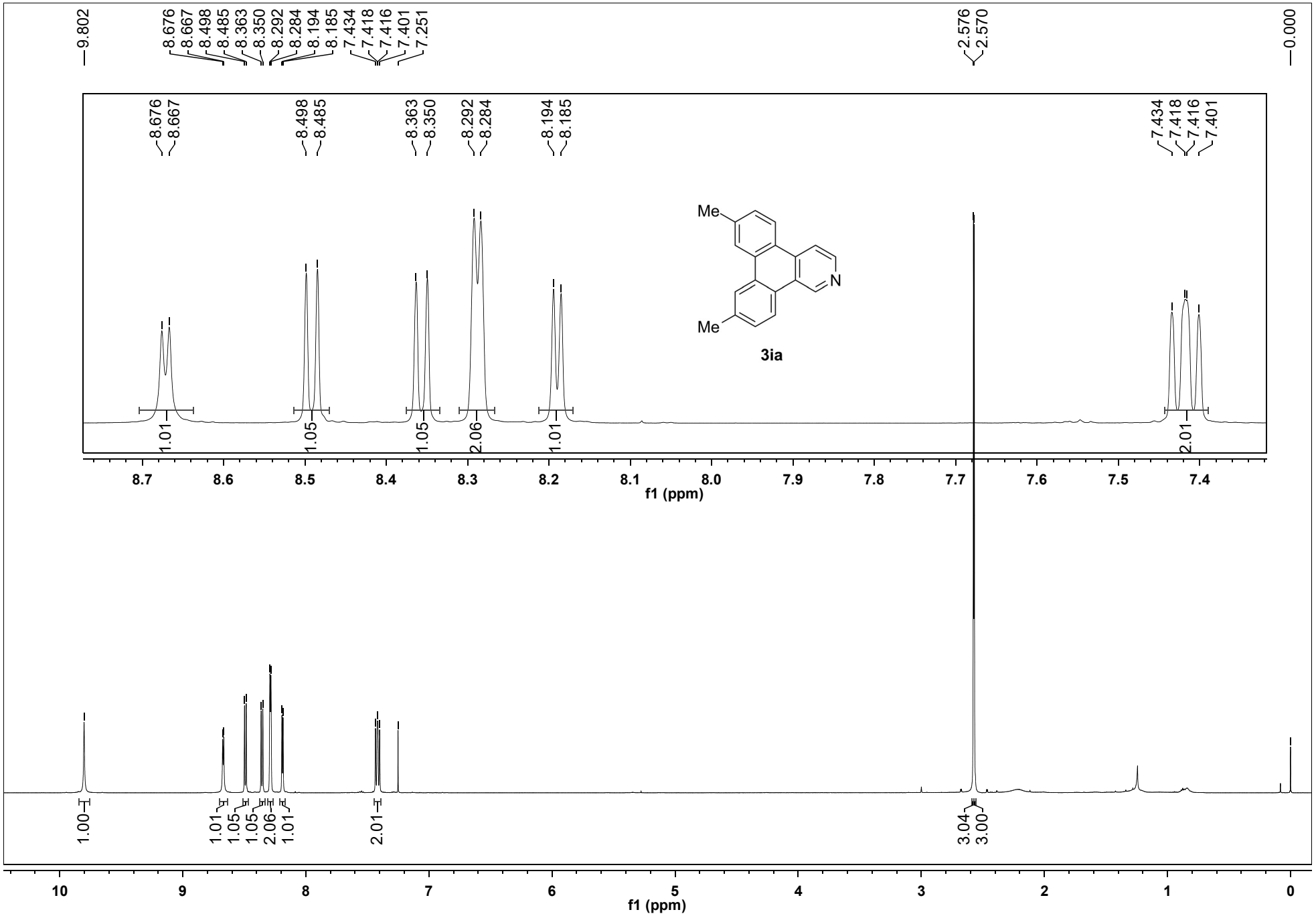

Figure S24. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ia

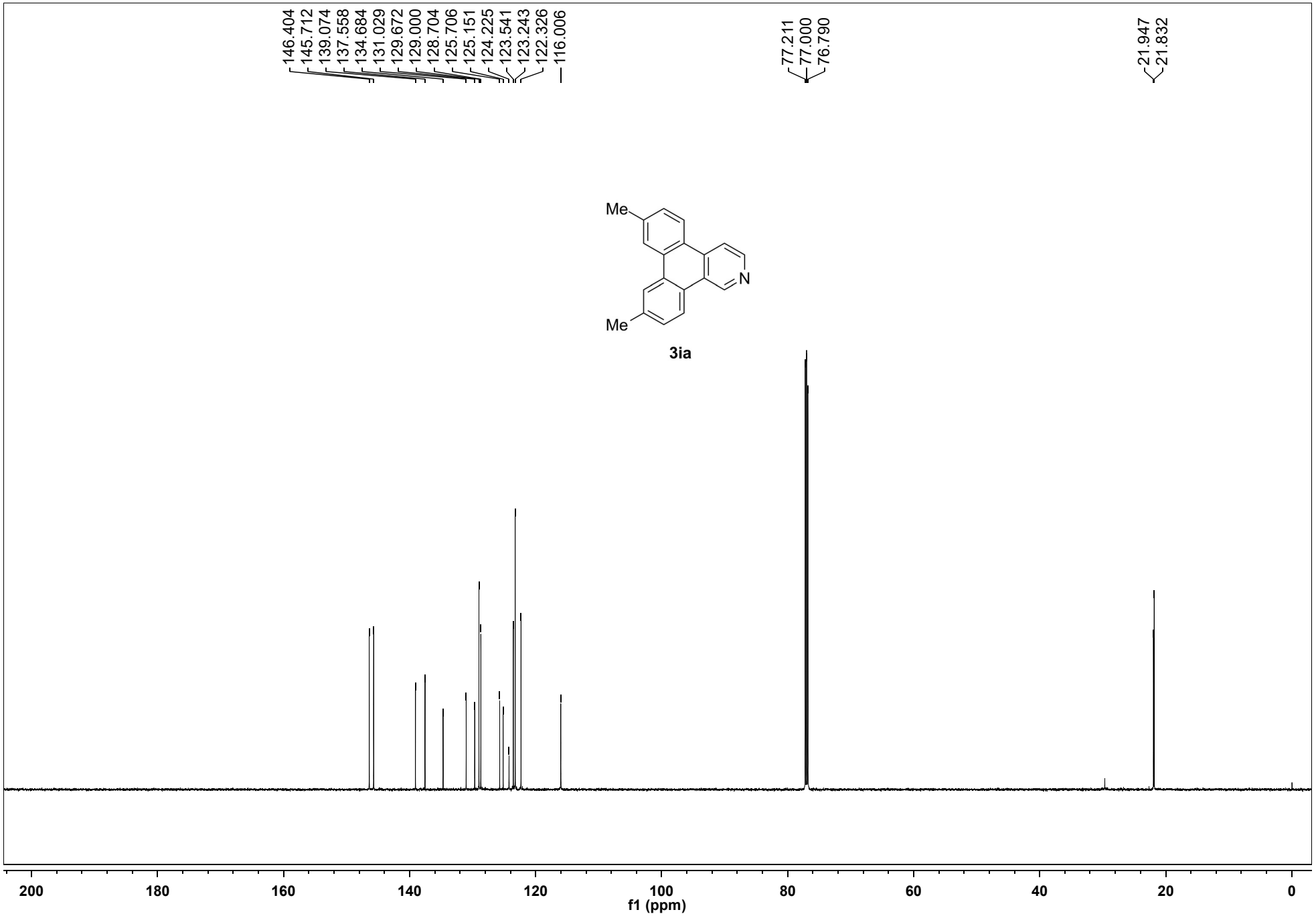

Figure S25. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ja

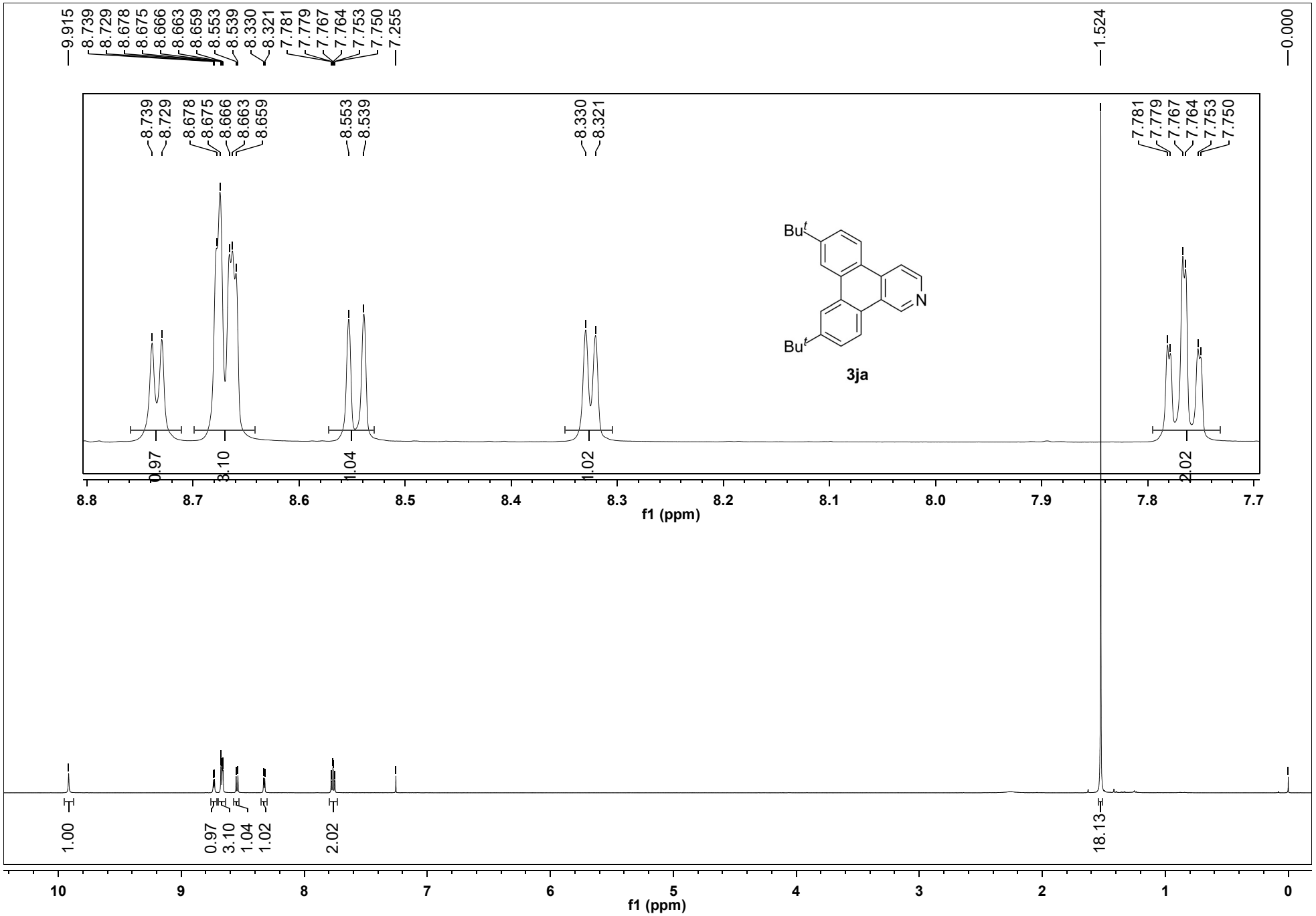

Figure S26. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ja

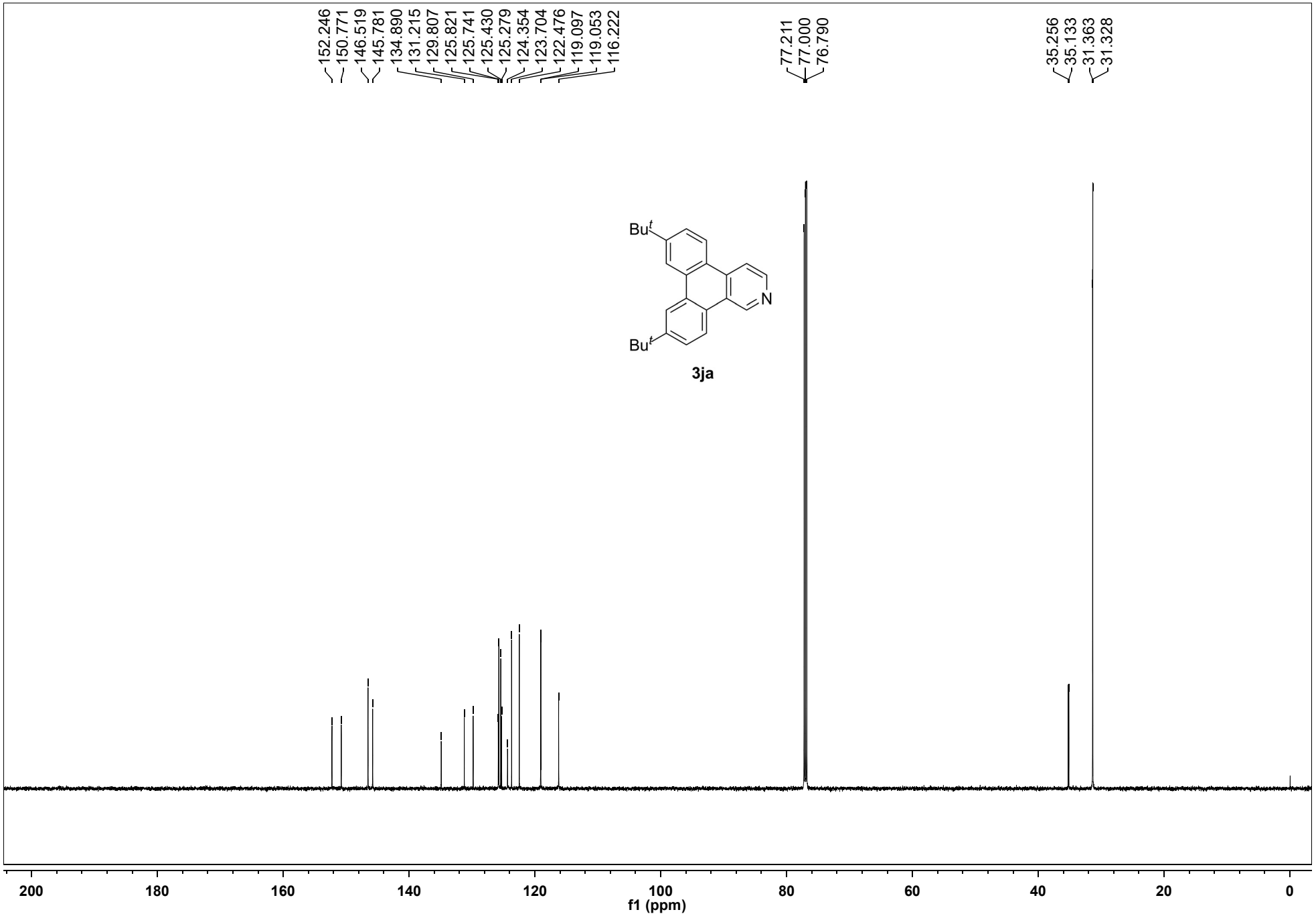

Figure S27. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ka

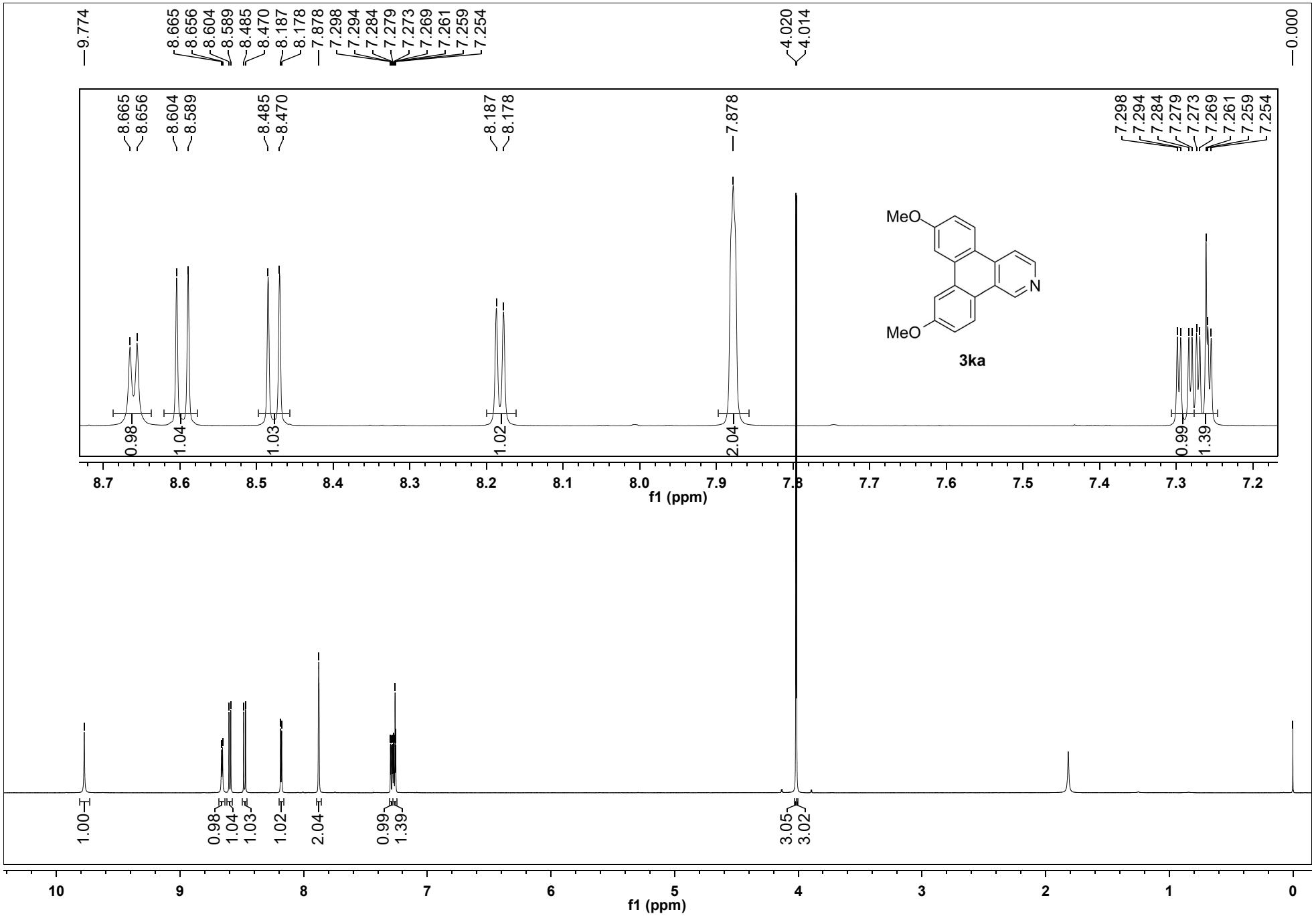

Figure S28. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ka

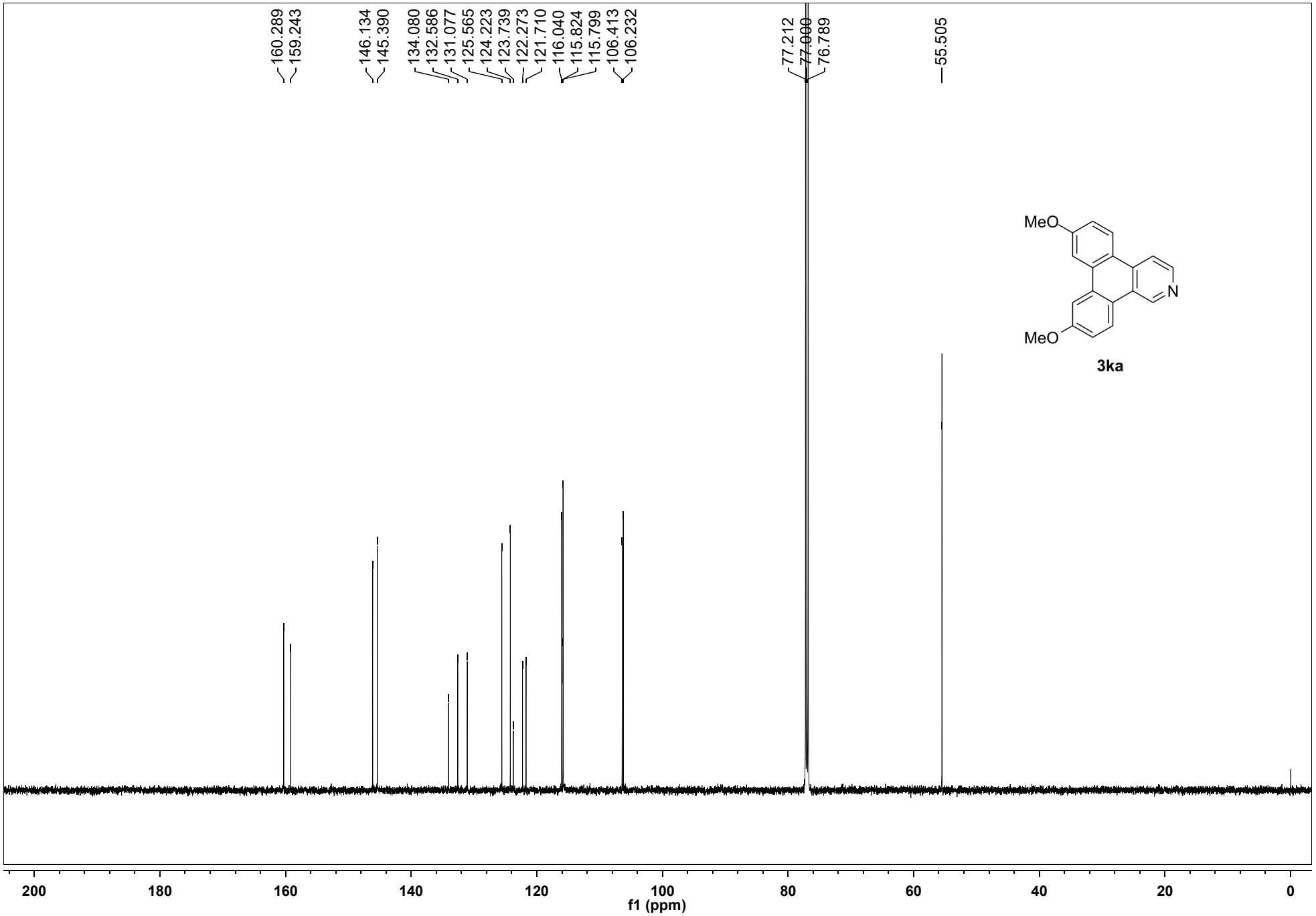

Figure S29. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3la

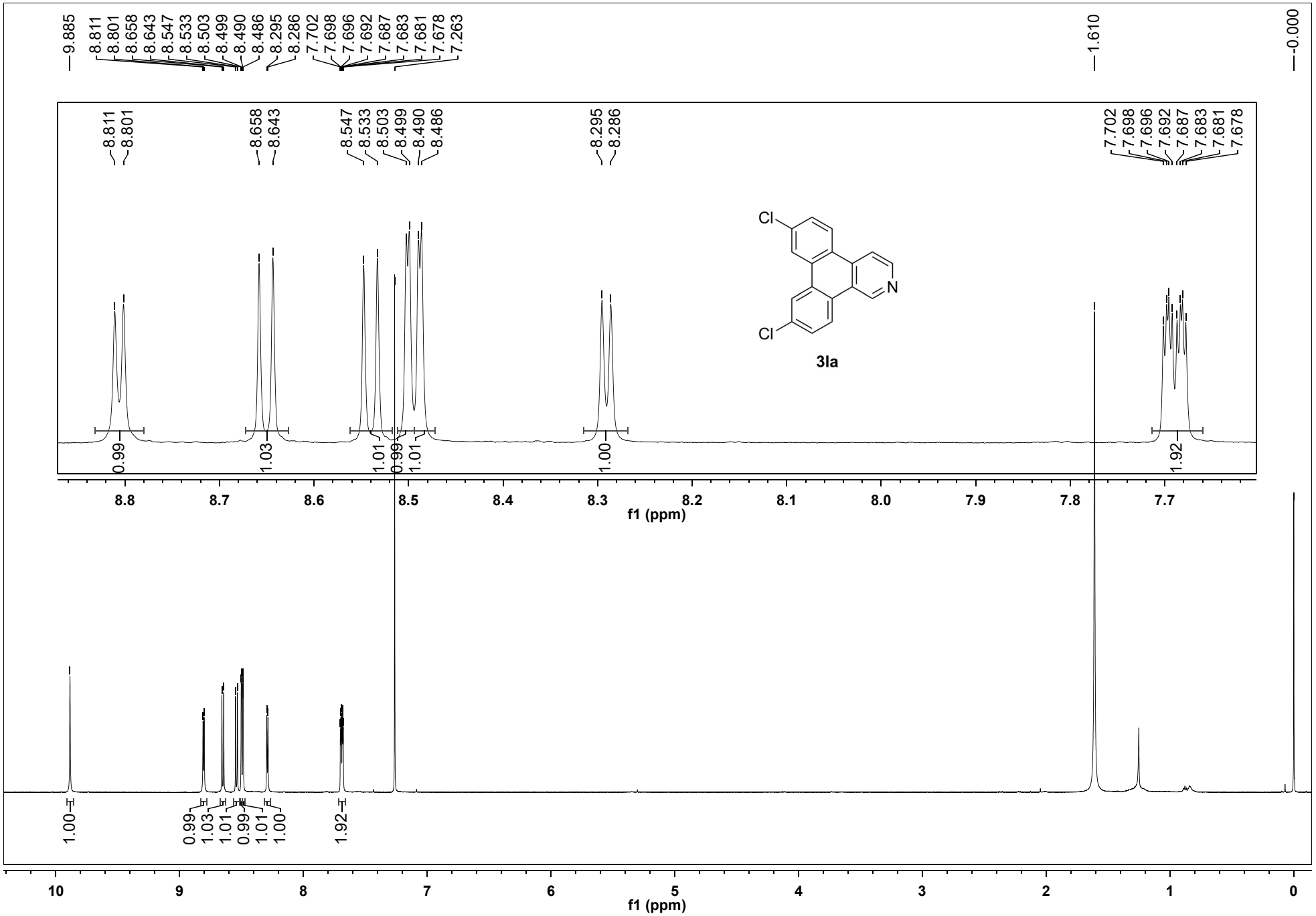

Figure S30. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3la

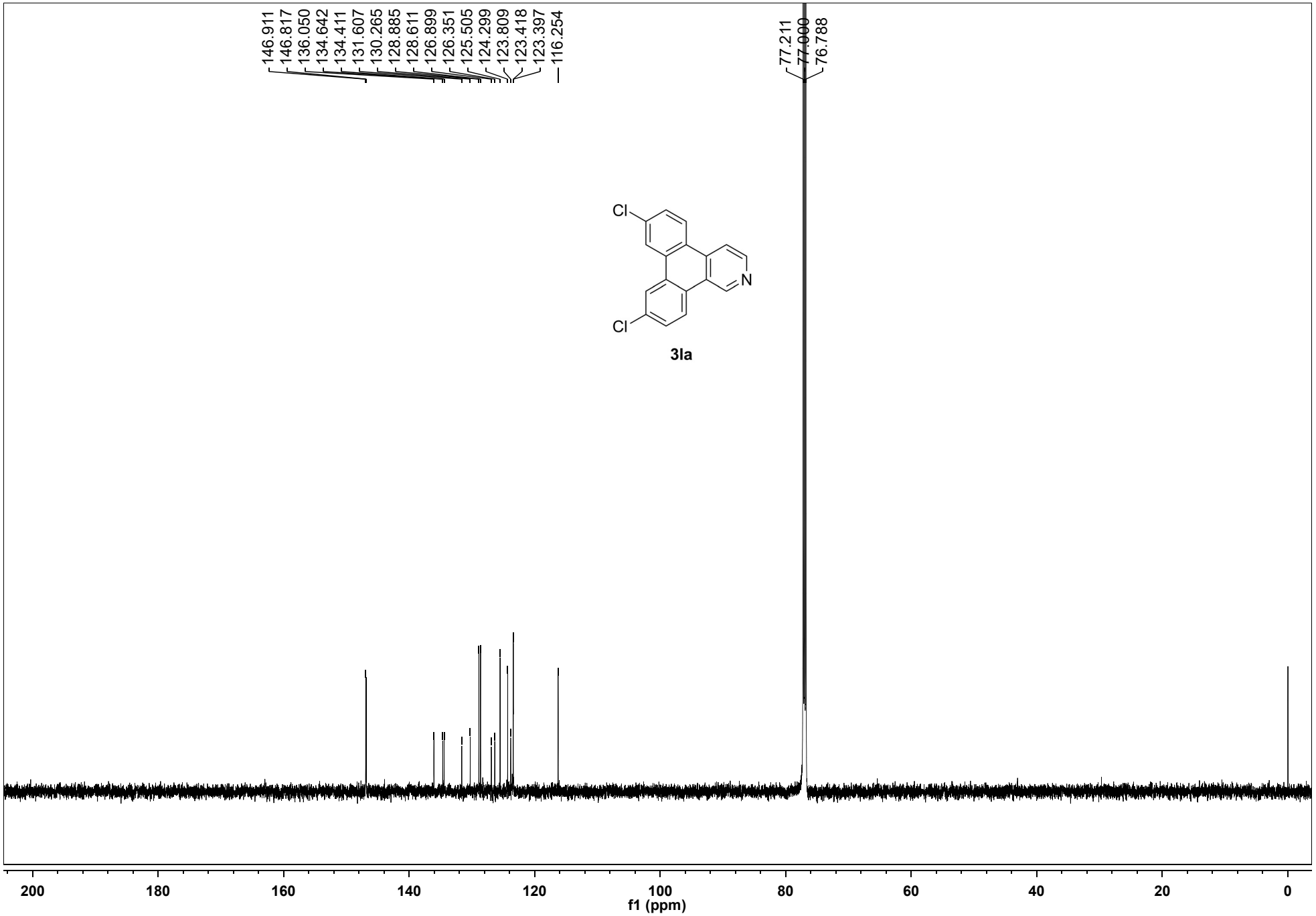

Figure S31. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ma

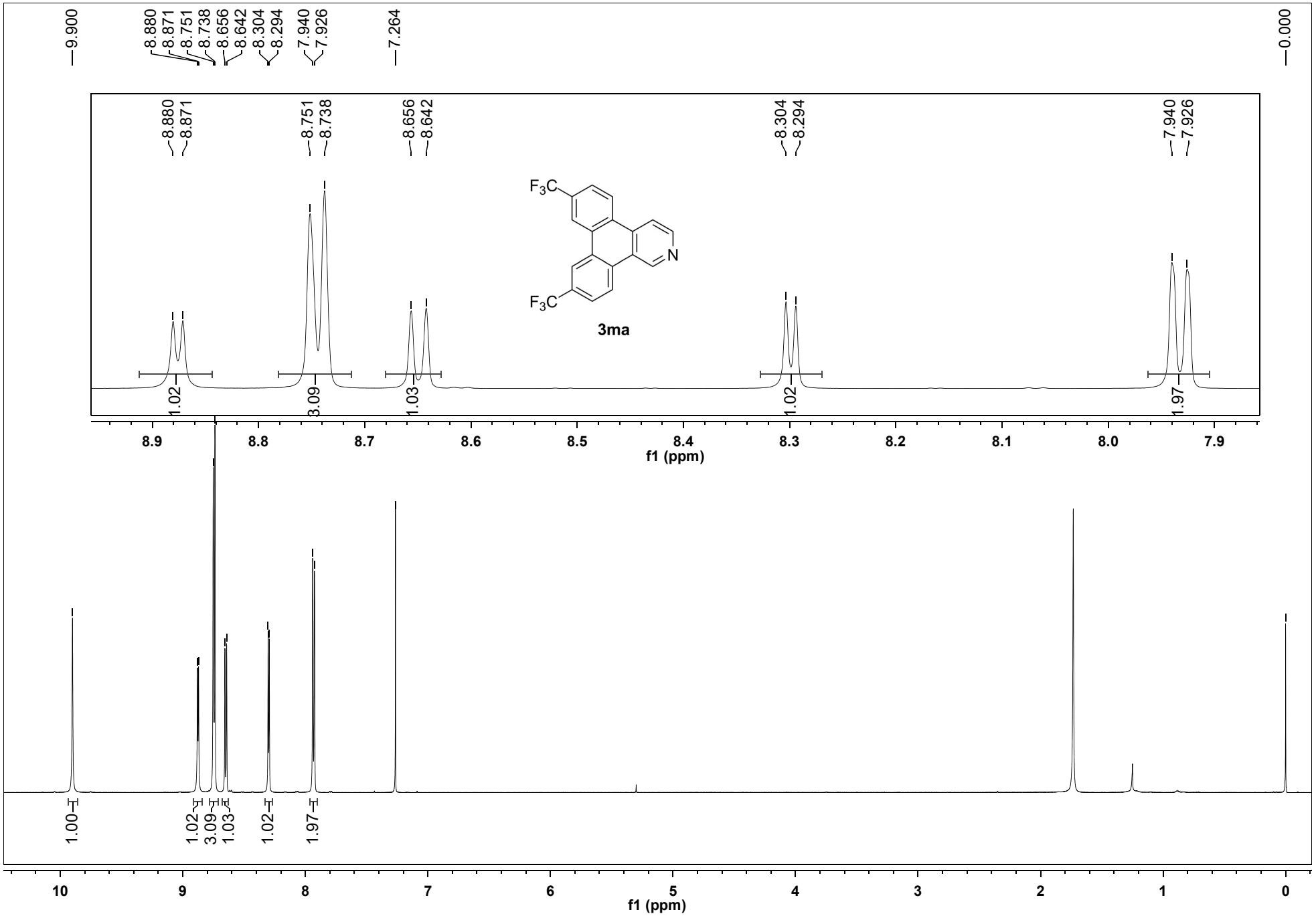

Figure S32. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ma

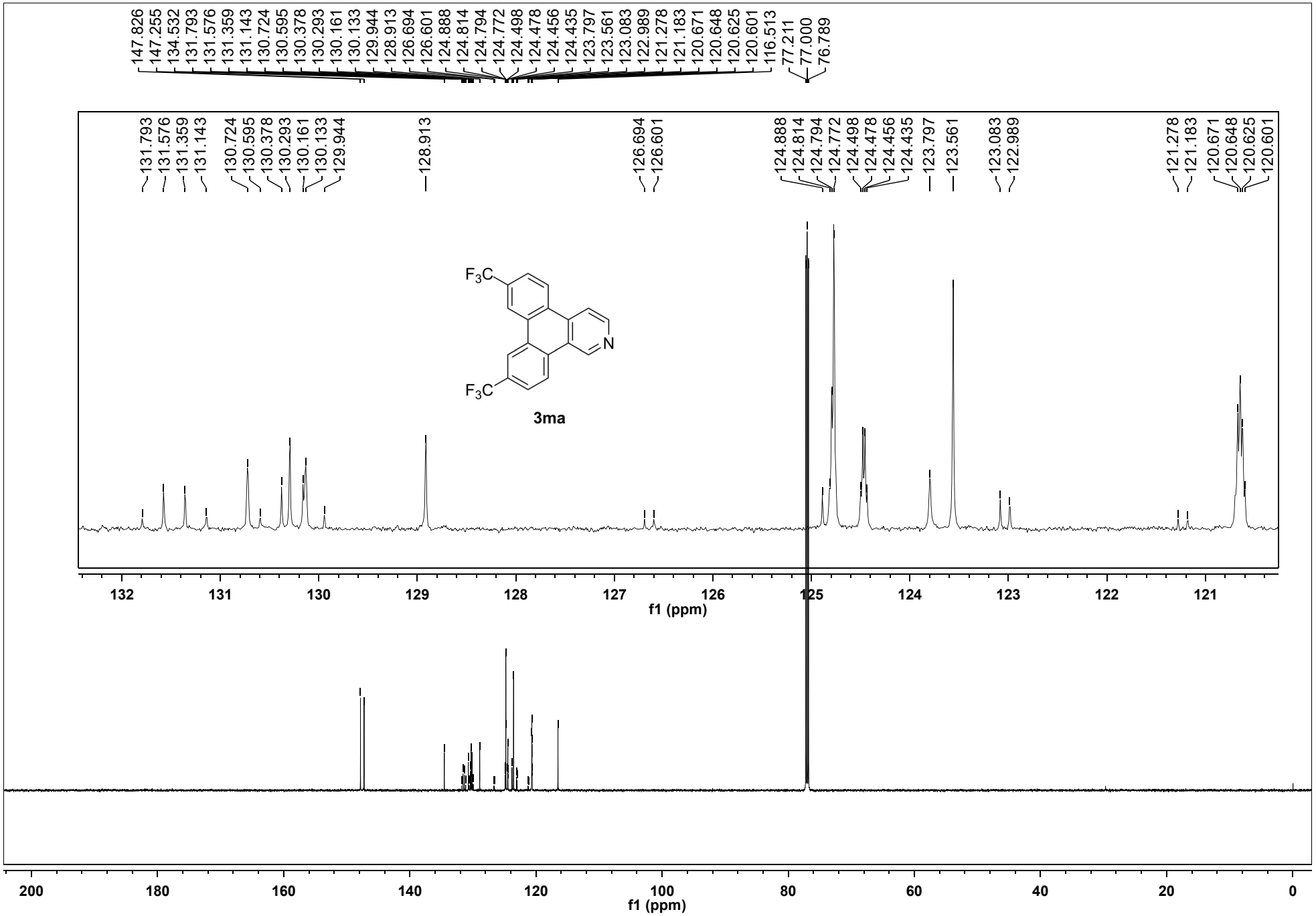

Figure S33. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3na

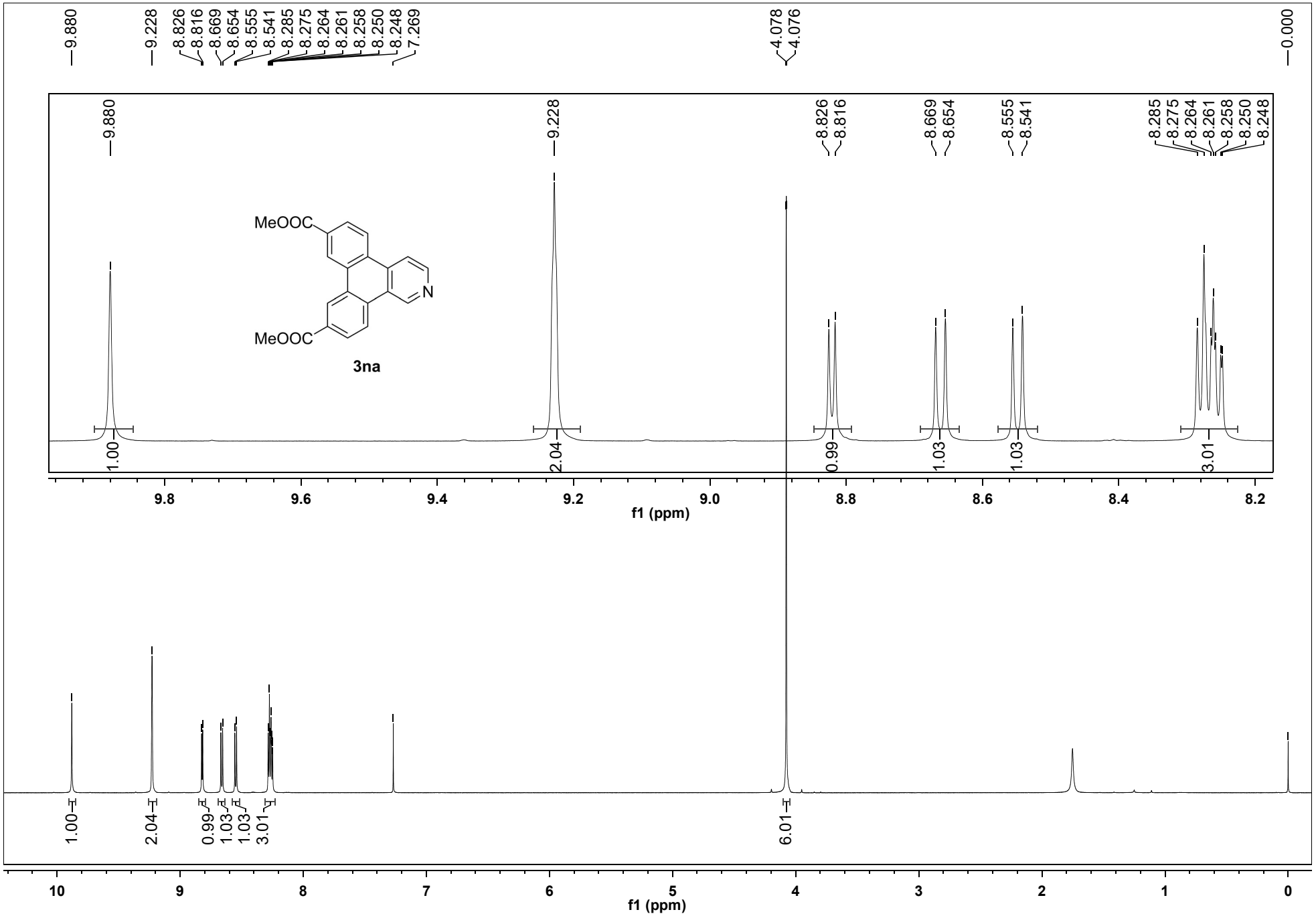

Figure S34. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3na

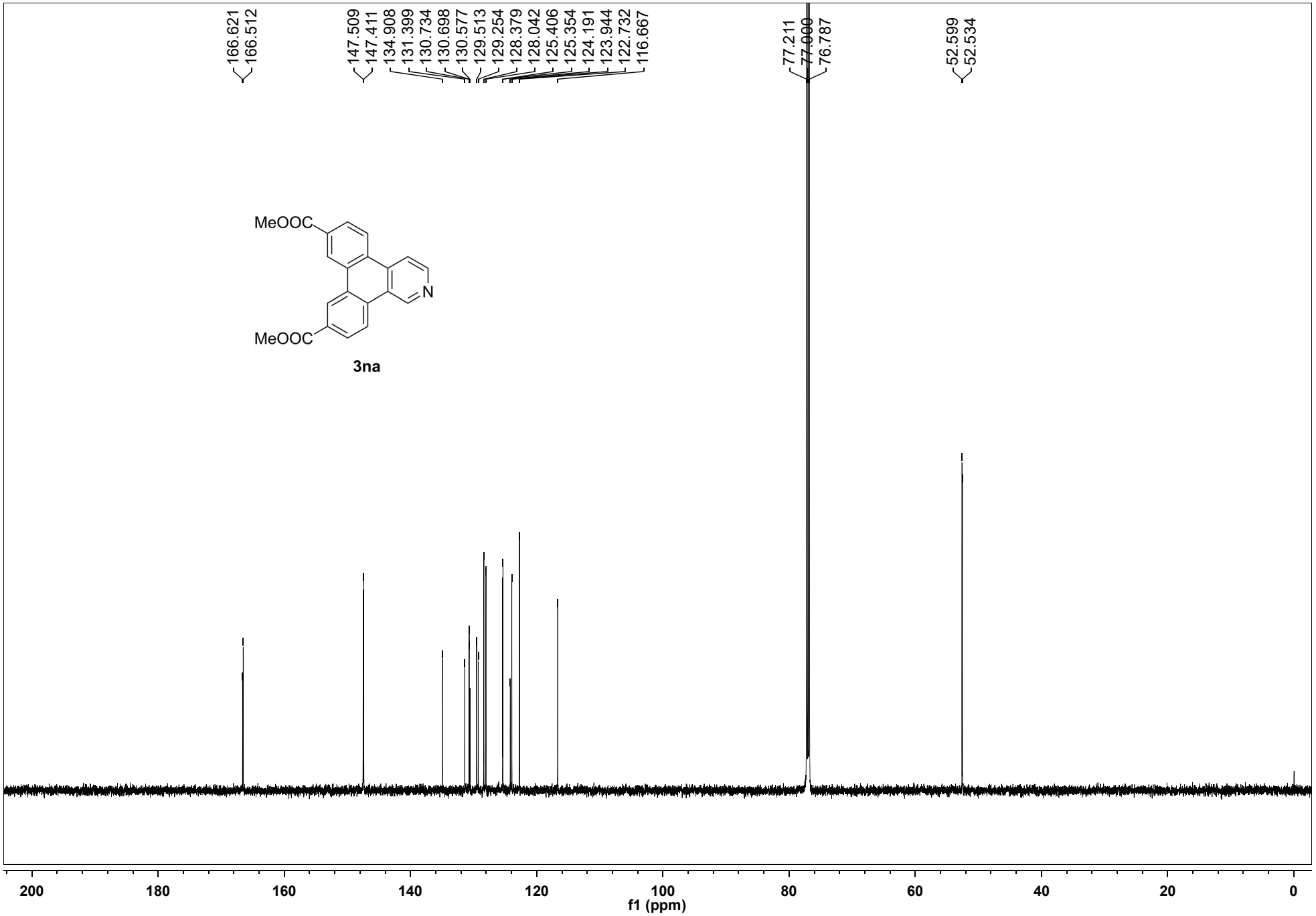

Figure S35. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3oa

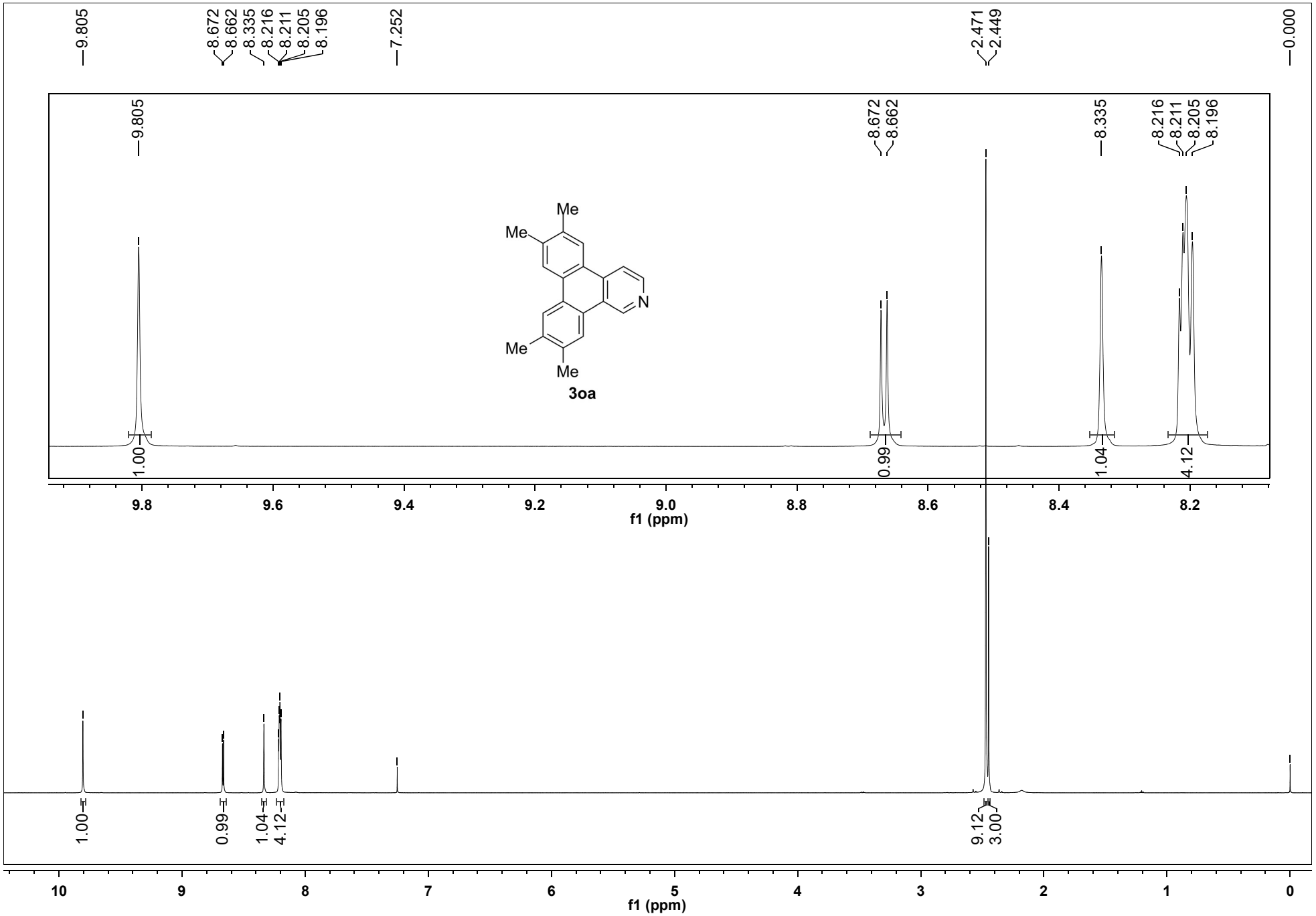

Figure S36. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3oa

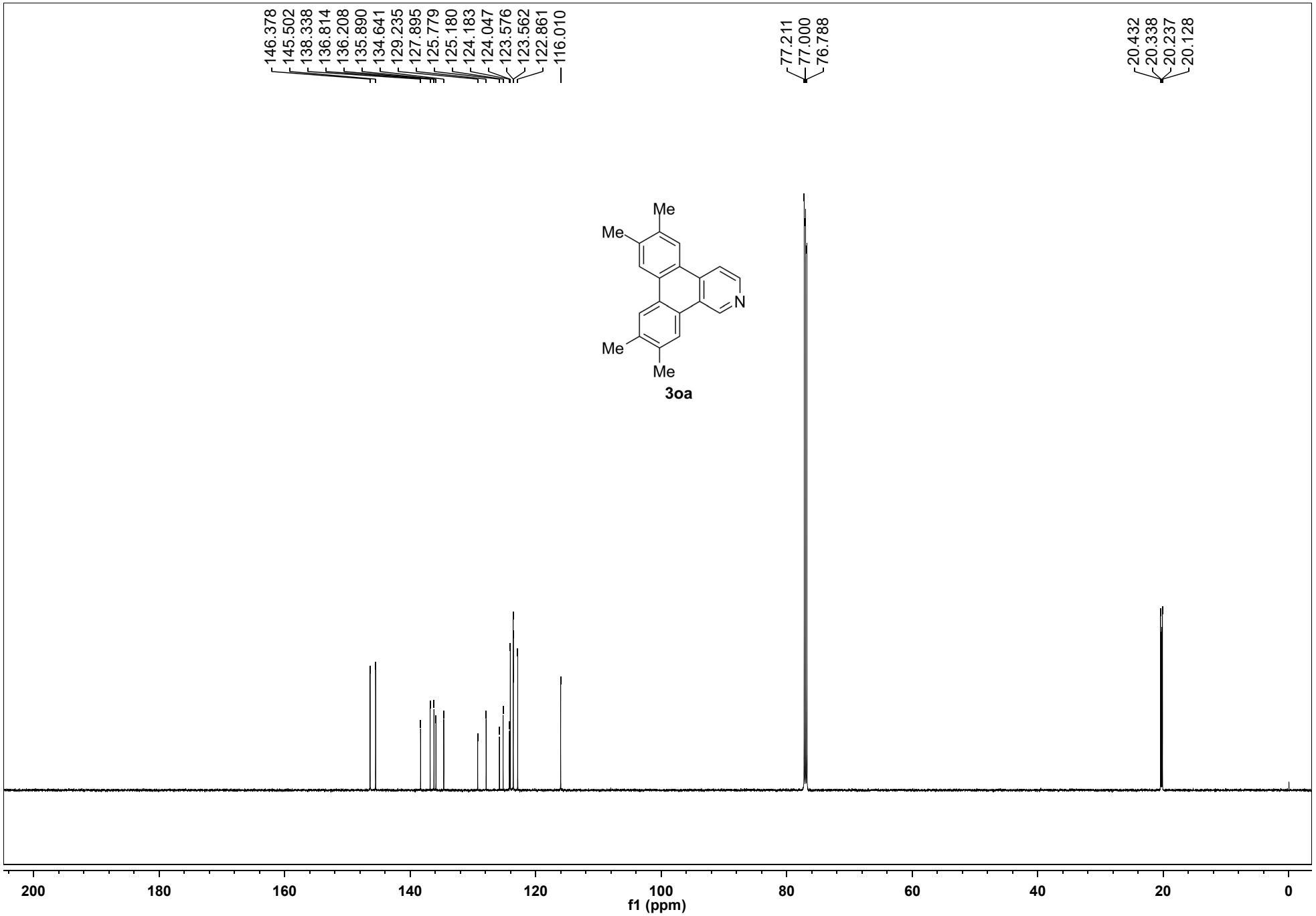

Figure S37. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3pa

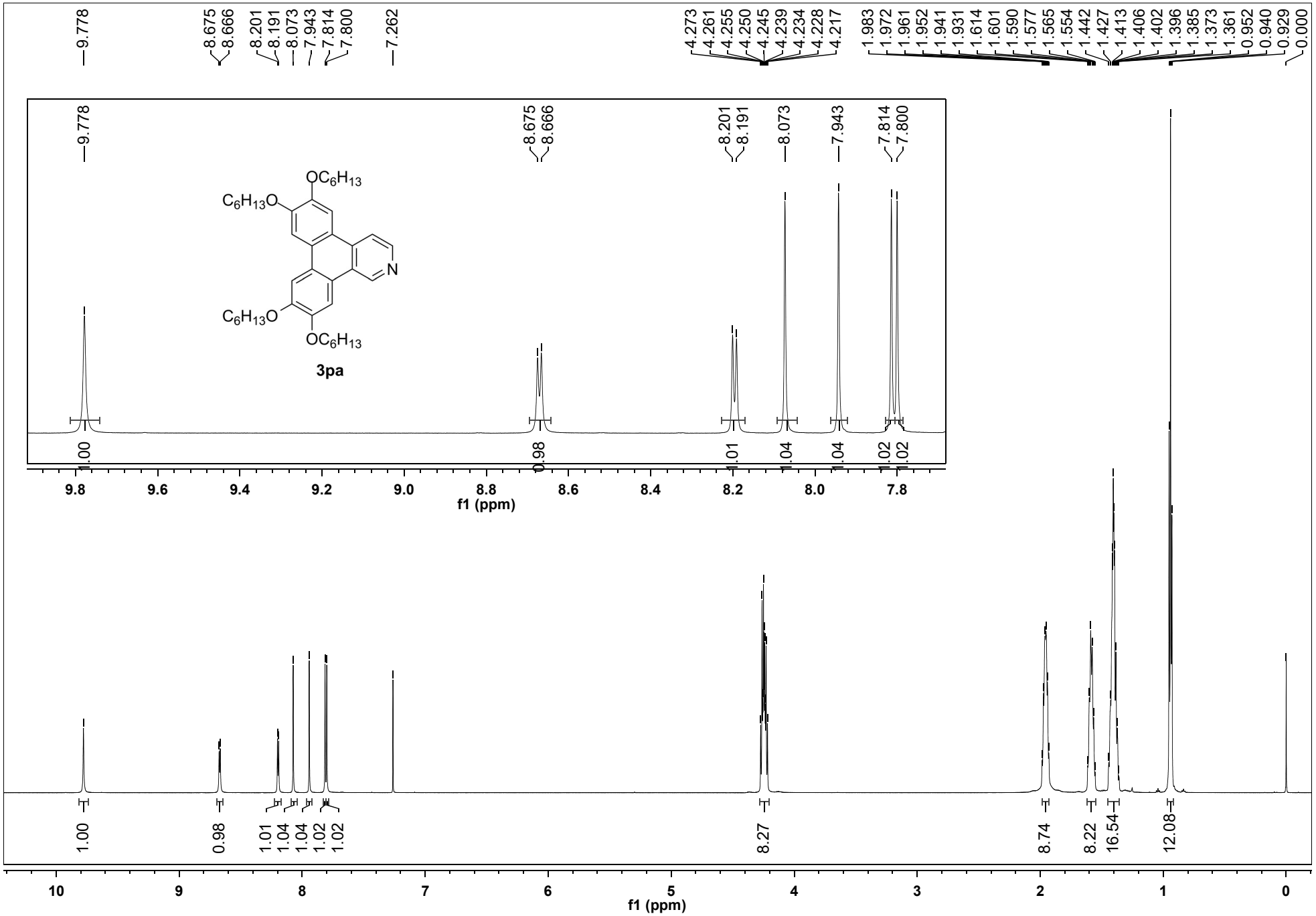

Figure S38. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3pa

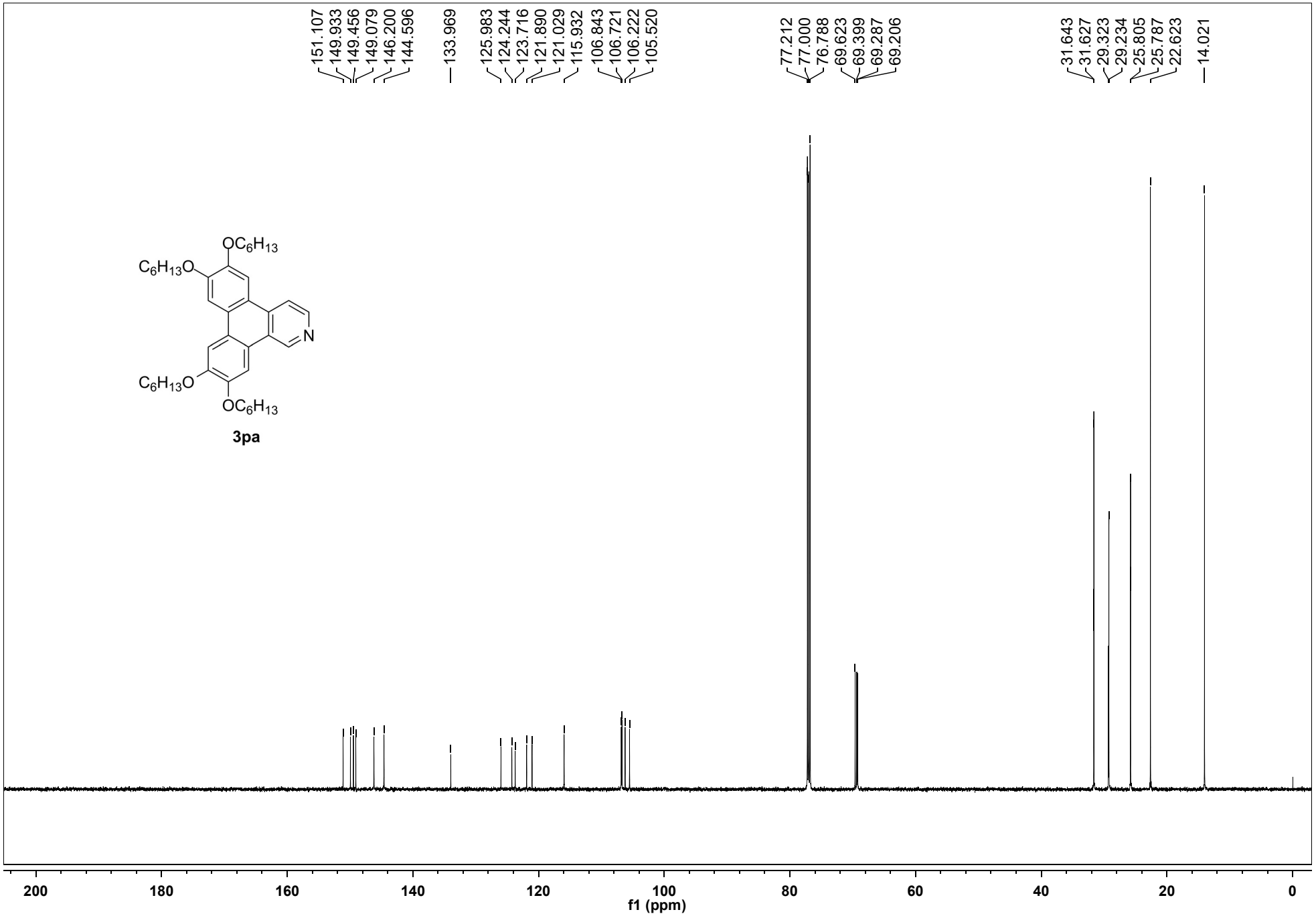

Figure S39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ab

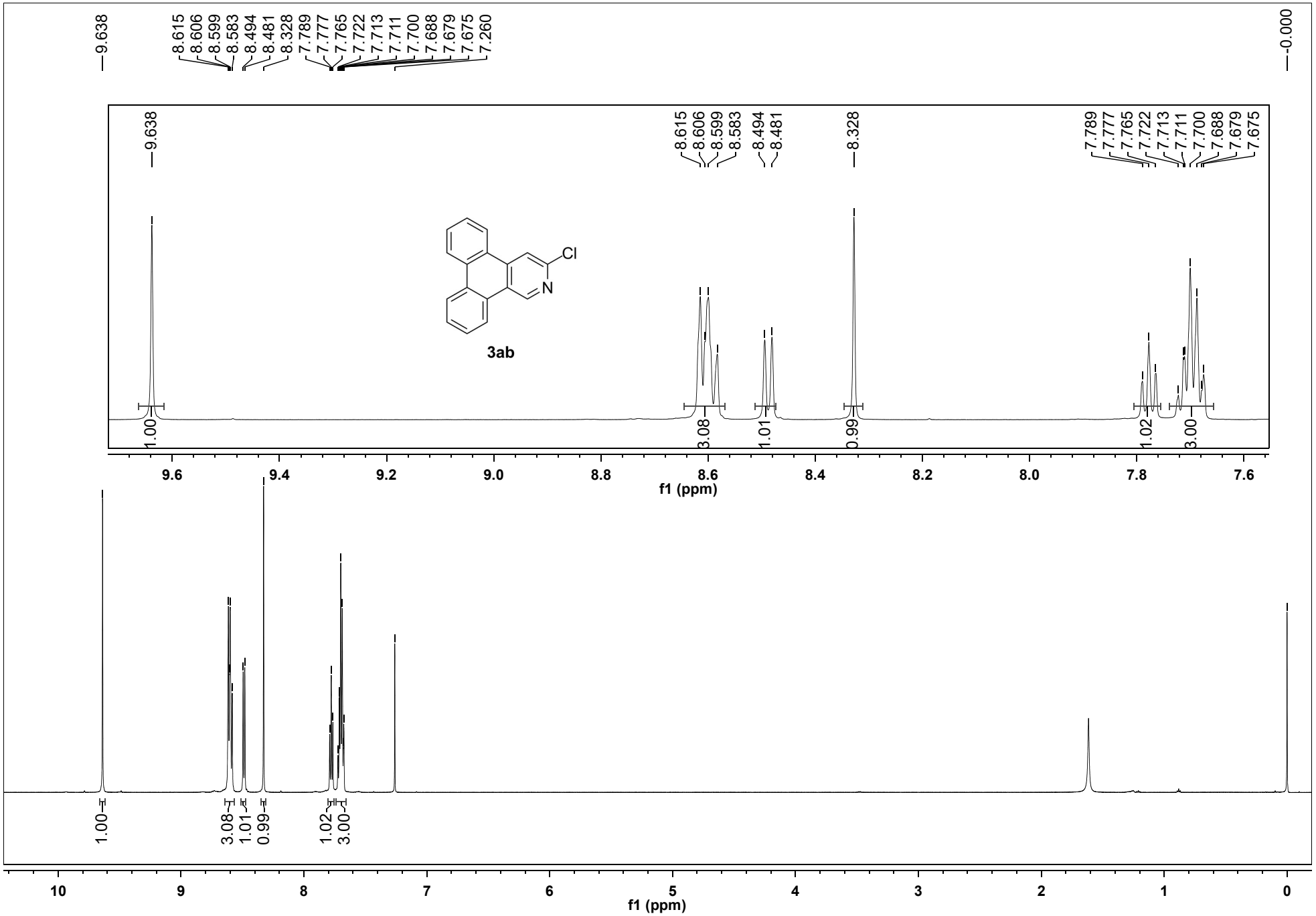

Figure S40. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ab

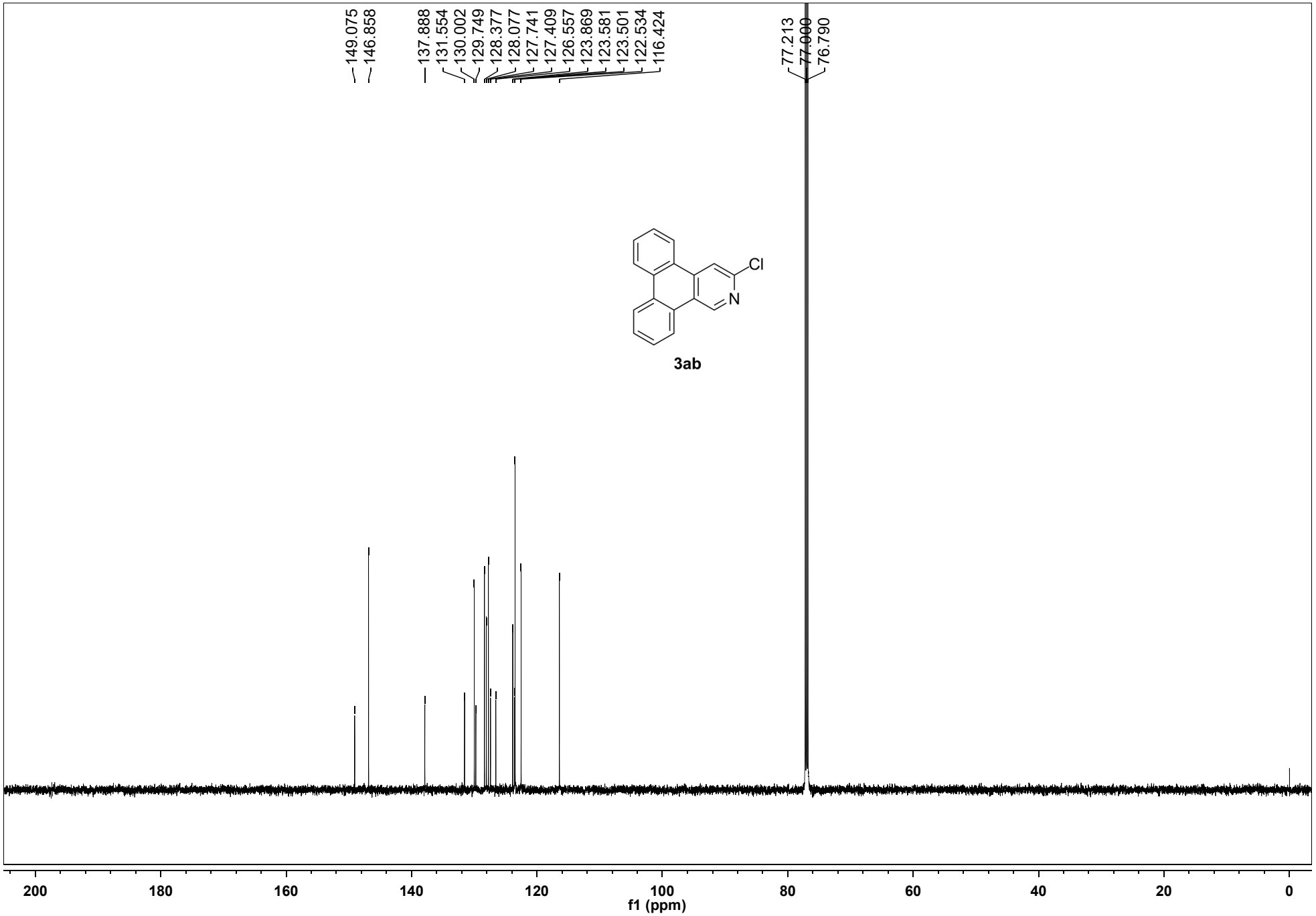

Figure S41. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ac

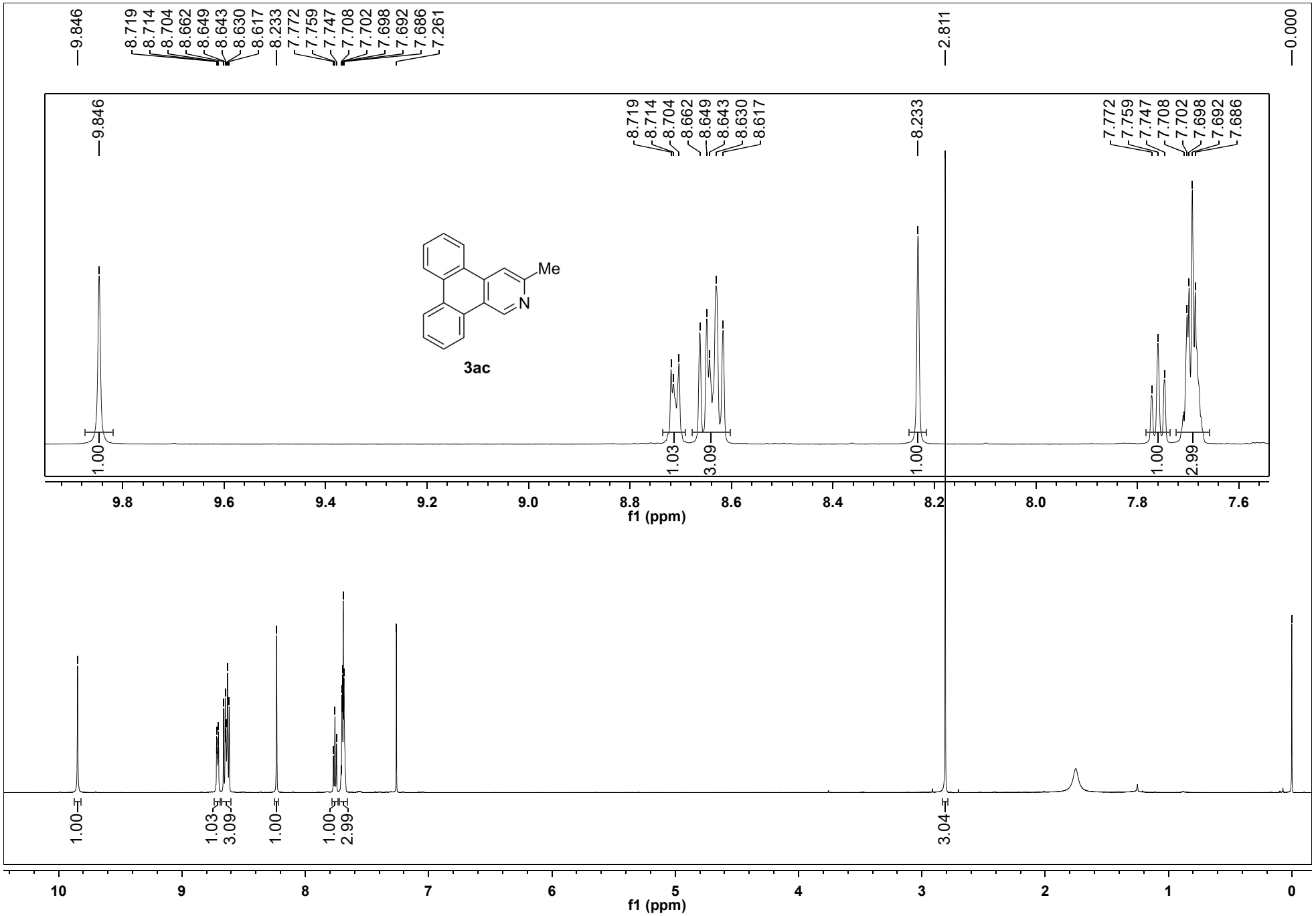

Figure S42. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ac

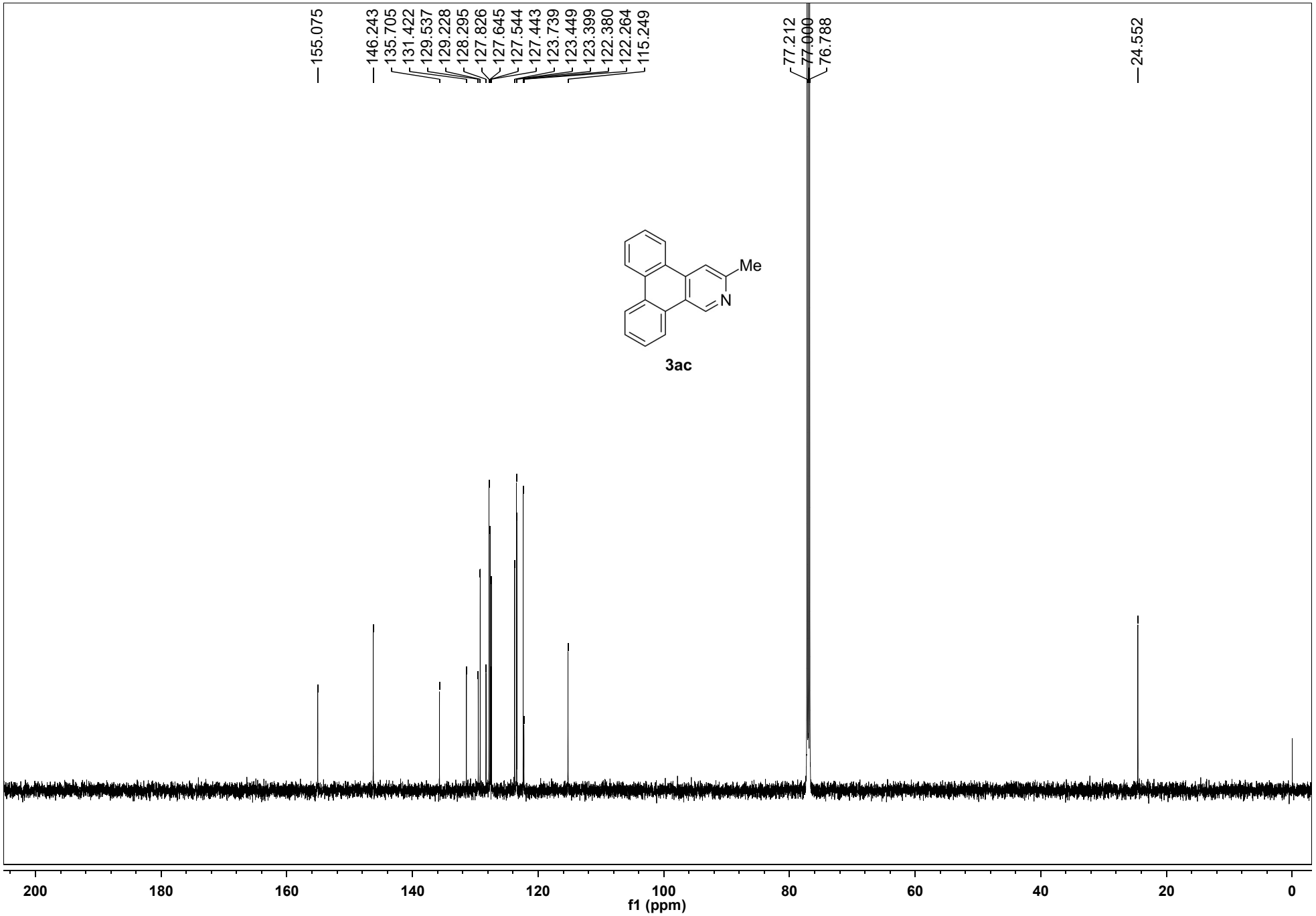

Figure S43. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ad

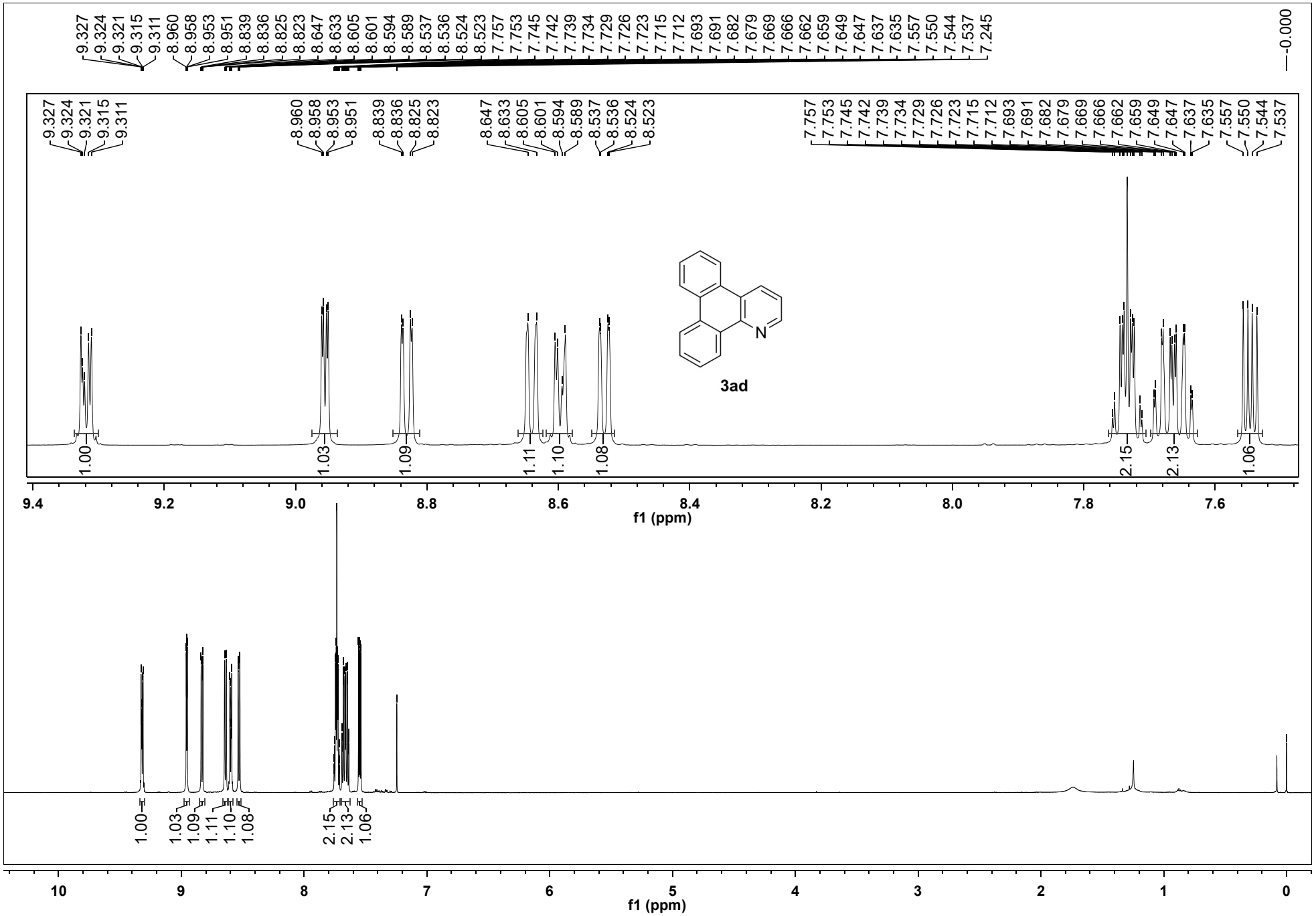

Figure S44. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ad