Benz[*c*]indeno[2,1-*a*]fluorene: The First 2,3-Naphthoquinodimethane Isolated

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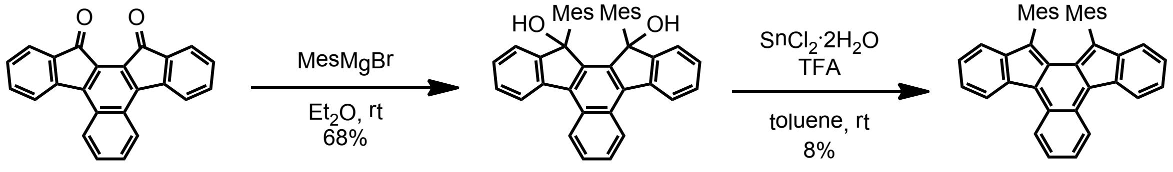
Supporting Information

Contents

1. General

Melting points were measured with a hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a Bruker AVANCEIII-400 spectrometer (400 MHz for ^{1}H, and 100 MHz for ^{13}C) in solvent at 30 °C. When chloroform-*d*, dichloromethane-d_2, acetone-d_6 and tolene-d_8 were used as solvent, the spectra were referenced to residual solvent proton signals in the ^{1}H NMR spectra (7.26 ppm for chloroform-*d*, 5.32 ppm for dichloromethane-d_2, 2.05 ppm for acetone-d_6 and 6.97 ppm for tolene-d_8) and to the solvent carbons in the ^{13}C NMR spectra (77.0 ppm for chloroform-*d*, 53.84 ppm for dichloromethane-d_2 and 29.48 ppm for acetone-d_6). IR spectra were recorded as KBr disks with a JASCO FT/IR-410 spectrometer. Mass spectral analyses were performed on a JEOL JMS-700 spectrometer for EI or FAB. Elemental analyses were carried out with a Perkin-Elmer 2400II analyzer. UV-vis-NIR and UV-vis spectra were recorded on a HITACHI U-3310 and a HITACHI U-3310 spectrophotometer, respectively. Cyclic voltammetric measurements were performed with an ALS-612DA electrochemical analyzer. Cyclic voltammograms were recorded with glassy carbon working electrode and Pt counter electrode in CH_2Cl_2 containing 0.1 M Bu_4NClO_4 as the supporting electrolyte. The experiments were done employing an Ag/$AgNO_3$ reference electrode at room temperature. Column chromatography and TLC were performed with Merck silica gel 60 (70–230 mesh ASTM) and Merck silica gel 60 F254, respectively. All reagents, except for benz[*c*]indeno[2,1-*a*]fluorene-13,14-dione (**10**),[1] were obtained from commercial suppliers and used as received. Toluene was dried over CaH_2 and distilled prior to use.

2. Synthesis of 9b, O_2 Adduct 12, DDQ Adduct 13, and Dimer 15



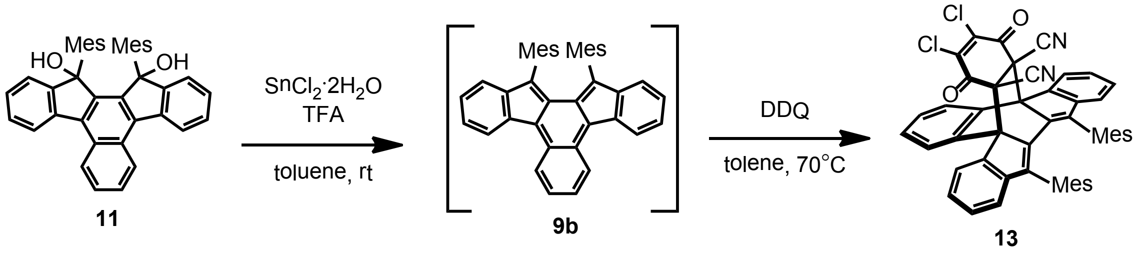
10 **11** **9b**

13,14-Dimesityl-13,14-dihydrobenz[*c*]indeno[2,1-*a*]fluorene-13,14-diol (11). To a solution of mesitylmagnesium bromide in ether freshly prepared from 2-bromomesitylene (1.80 g, 9.02 mmol), 1,2-dibromoethane (3.39 g, 18.1 mmol) and magnesium (659 mg, 27.1 mmol) in ether (20 mL), was added benz[*c*]indeno[2,1-*a*]fluorene-13,14-dione **10**[1] (500 mg, 1.50 mmol) at room temperature under an argon atmosphere, and the solution was stirred for 4.5 h. After addition of water and 1 M HCl, the organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. After column chromatography on silica gel (hexanes/$CHCl_3$ = 2/1) and recrystallization from a mixture of $CHCl_3$/CH_3OH, **11** (584 mg, 68%) was obtained as a colorless solid. mp 267.0–268.0 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 30 °C) δ 8.92–8.90 (m, 2H), 8.32 (d, J = 7.8 Hz, 2H), 7.75–7.73 (m, 2H), 7.45 (dd, J = 7.5, 7.5 Hz, 2H), 7.22 (dd, J = 7.3, 7.3 Hz, 2H), 7.13 (d, J = 7.3 Hz, 2H), 7.05 (s, 2H), 6.66 (s, 2H), 2.38 (s, 2H), 2.33 (s, 6H), 2.26 (s, 6H), 1.31 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2, 30 °C) δ 149.7, 146.0, 140.8, 140.3, 138.0, 136.8, 136.5, 136.3, 134.5, 132.2, 131.1, 129.5, 128.3, 127.3, 125.6, 124.6, 123.7, 86.8, 25.2, 21.4, 20.6; IR (KBr) 3506, 3033, 2965, 2920, 2857, 1608, 1474, 1461, 1385, 1041, 1014, 852, 826, 757, 678, 589 cm^{-1}; MS (EI) m/z 572.5 (M^+). Anal. Calcd for $C_{42}H_{36}O_2$: C, 88.08; H, 6.34. Found: C, 88.15; H, 6.43.

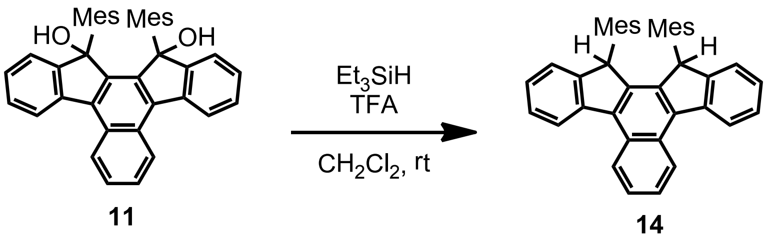
13,14-Dimesitylbenz[*c*]indeno[2,1-*a*]fluorene (9b). A mixture of **11** (200 mg, 0.349 mmol) and $SnCl_2 \cdot 2H_2O$ (316 mg, 1.40 mmol) in toluene (7.0 mL) placed in a Schlenk flask was degassed by freeze-pump-thaw cycles (7 times) and the flask was filled with argon. To the solution was added trifluoroacetic acid (0.50 mL) at room temperature, and the solution was stirred for 40 min. After removal of the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel (hexanes/CH_2Cl_2 = 9/1) to give a deep blue fraction. After removal of the solvents under reduced pressure, recrystallization from benzene/acetonitrile under an argon atmosphere gave **9b** (15.8 mg, 8%) as deep blue crystals. mp 200.0–201.0 °C (decomp.) ^{1}H NMR (400 MHz, CD_2Cl_2, 30 °C) δ 7.80–7.77 (m, 2H), 7.63 (d, J = 7.8 Hz, 2 H), 6.92 (dd, J = 7.3, 7.3 Hz, 2H), 6.85–6.82 (m, 2H), 6.79 (dd, J = 7.3, 7.3 Hz, 2H), 6.50 (s, 4H), 6.20 (d, J = 6.8 Hz, 2H), 2.22 (s, 6H), 1.89 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2, 30 °C) δ 146.1, 144.5, 140.9, 137.0, 136.6, 135.8, 133.9, 132.5, 131.6, 128.8, 128.3, 127.9, 127.1, 126.5, 124.5, 122.8, 21.2, 20.8; IR (KBr) 3060, 2914, 2852, 1611, 1464, 1438, 1375, 1348, 1130, 848, 759, 693 cm^{-1}; MS (EI) m/z 538.4 (M^+). Anal. Calcd for $C_{42}H_{34}$:

C, 93.64; H, 6.36. Found: C, 93.29; H, 6.00.

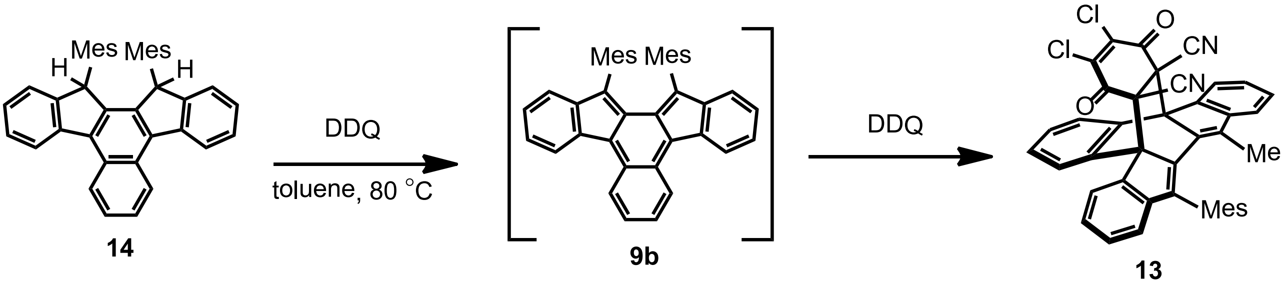
O_2 Adduct (12) Obtained from Crude Product of 9b Prepared from Diol 11 by Dehydroxylation. Dehydroxylation of **11** was carried out using **11** (50.1 mg, 87.4 μmol), $SnCl_2{\cdot}2H_2O$ (78.8 mg, 349 μmol), and TFA (0.2 mL) in toluene (3.0 mL) as described above. A blue fraction obtained by column chromatography was diluted with hexanes (approximately 800 mL) and the solution was left in a refrigerator while protecting from light with aluminum foils. After 3 days the blue color of the solution disappeared. The solvent was evaporated to give **12** (5.7 mg, 11% from **11**) as a pale yellow solid. An analytical sample of **12** was obtained by recrystallization from benzene/acetonitrile. mp 154.5–156.5 °C (decomp.), ^{1}H NMR (400 MHz, acetone-d_6, 30 °C) δ 7.87–7.84 (m, 2H), 7.50–7.47 (m, 6H), 7.37–7.35 (m, 2H), 6.83–6.81 (m, 2H), 6.59 (s, 2H), 6.50 (s, 2H), 2.24 (s, 6H), 1.96 (s, 6H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, acetone-d_6, 30 °C) δ 148.7, 139.6, 139.5, 138.5, 137.7, 136.5, 136.3, 136.2, 131.7, 130.2, 129.7, 128.6, 127.4, 123.0, 122.5, 89.6, 21.4, 20.6, 20.0; IR (KBr) 3059, 3003, 2948, 2917, 2855, 1720, 1613, 1576, 1494, 1475, 1460, 1377, 1348, 1300, 1287, 1267, 1119, 1030, 1015, 925, 846, 756, 732, 708, 696, 672, 656, 591. MS (EI) m/z 571.5 ([M+H]$^+$). HRMS (EI) *m/z* Calcd for $C_{42}H_{34}O_2$: 570.2560, Found:570.2564 (M$^+$).



DDQ Adduct (13) Obtained from Crude Product of 9b Prepared from Diol 11 by Dehydroxylation. Dehydroxylation of **11** was carried out using **11** (29.9 mg, 55.3 μmol), $SnCl_2{\cdot}2H_2O$ (47.0 mg, 208 μmol), and TFA (0.50 mL) in toluene (5.0 mL) as described above. The solvent of a blue fraction obtained by column chromatography was replaced by toluene (10 mL). After degassing the solution by bubbling Ar, DDQ (11.9 mg, 52.4 μmol) was added, and the mixture was heated at 70 °C for 30 min. The mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with brine and dried over anhydrous $MgSO_4$, After evaporation of the solvent, silica gel column chromatography ($CHCl_3$) followed by recrystallization from $CHCl_3$/hexane gave **13** (5.3 mg, 6.92 μmol, 13% from **11**) as a red solid. mp 224.0–225.0 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.49–7.35 (m, 10H), 6.82–6.80 (m, 2 H), 6.58 (s, 2H), 6.39 (s, 2H), 2.23 (s, 6H), 2.22 (s, 6H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 178.6, 148.1, 143.6, 143.0, 137.1, 136.7, 135.5, 135.3, 134.6, 130.5, 130.1, 129.2, 128.0, 127.4, 126.63, 126.57, 124.9, 123.3, 113.1, 64.6, 60.8, 21.4, 21.3, 20.0; IR (KBr) 3067, 2993, 2917, 2854, 2364, 2359, 1708, 1570, 1473, 1462, 1203, 1145, 778, 768, 744 cm^{-1}; MS (FAB) *m/z* 766.5 (M$^+$). Anal. Calcd for $C_{50}H_{34}Cl_2N_2O_2$: C, 78.43; H, 4.48; N, 3.66. Found: C, 78.58; H, 4.54; N, 3.49.



13,14-Dimesityl-13,14-dihydrobenz[*c*]indeno[2,1-*a*]fluorene (14). To a mixture of **11** (100 mg, 175 µmol) and Et_3SiH (0.20 mL,1.25 mmol) in CH_2Cl_2 (10 mL) was added trifluoroacetic acid (0.40 mL) at room temperature under an argon atmosphere and the mixture was stirred for 20 h. After dilution with water, the organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed brine, dried over $MgSO_4$, and concentrated under reduced pressure. After column chromatography on silica gel (hexanes/$CHCl_3$=10/1), **14** (54.3 mg, 58%) was obtained as a colorless solid. mp 205.0–206.0 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2, 30 °C) δ 7.88 (d, *J* = 7.3 Hz, 2H), 7.61–7.59 (m, 2H), 7.35 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 2H), 7.27–7.25 (m, 2H), 7.23 (ddd, *J* = 7.5, 7.5, 0.8 Hz, 2H), 6.64 (d, *J* = 7.6 Hz, 2H), 6.53 (s, 2H), 6.44 (s, 2H), 5.09 (s, 2H), 2.22 (s, 6H), 1.95 (s, 6H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 147.9, 141.8, 139.7, 138.3, 138.1, 136.3, 136.1, 136.0, 131.9, 128.1, 128.0, 127.7, 126.9, 125.7, 125.5, 124.0, 121.8, 55.4, 21.3, 20.7, 20.2; IR (KBr) 3063, 3001, 2969, 2916, 1612, 1473, 1459, 1374, 1036, 1018, 851, 774, 753, 729, 686, 588 cm^{-1}; MS (EI) m/z 540.5 (M^+). HRMS (EI) *m/z* Calcd for $C_{42}H_{36}$: 540.2817, Found: 540.2828 (M^+).



DDQ Adduct (13) Obtained from Dihydro Derivative 14. Dihydro derivative **14** (29.9 mg, 55.3 µmol) was place in a Schlenk flask and the flask was filled with argon. After addition of toluene (5.0 mL) the solution was degassed by bubbling with argon. To this solution was added DDQ (28.1 mg, 0.124 mmol) and the mixture was heated at 50 °C for 30 min and then 80 °C for another 30 min. The mixture was passes through a short silica gel column chromatograph ($CHCl_3$) to give 35.9 mg of a yellow solid. Precipitation of this material from $CHCl_3$/hexane gave **13** (24.5 mg, 58%) as a red solid which was identical with the sample obtained by the above method.

Dimer (15). Degassed toluene-*d*$_8$ (degassed by freeze-pump-thaw cycles) was added by vacuum transfer to **9b** (3.80 mg, 7.05 μmol) placed in an NMR tube, and the tube was sealed. The solution was heated at 80 °C for 48 h (monitored by NMR). The product was isolated by silica gel column chromatography (hexanes/CH_2Cl_2 = 7/1) to give **15** (3.73 mg, 98%) as a purple solid. mp 208.0–209.0 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2, 30 °C) δ 8.14 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.48–7.44 (m, 3H), 7.38 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 7.29 (ddd, *J* = 6.9, 6.9, 2.0 Hz, 1H), 7.18 (dd, 10.4, 1.0 Hz, 1H), 7.12–7.05 (m, 2H), 7.00–6.85 (m, 6H), 6.81 (s, 1H), 6.69–6.51 (m, 7H), 6.44 (s, 3H), 6.40–6.37 (m, 2H), 6.12 (d, *J* = 7.2 Hz, 1H), 4.62 (d, *J* = 9.0 Hz, 1H), 3.41 (m, 1H), 2.29–2.17 (m, 21H), 1.91 (s, 3H), 1.84 (s, 3H), 1.83 (s, 3H), 1.69 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 30 °C) δ 148.0, 147.5, 145.0, 143.8, 142.3, 142.1, 141.4, 140.8, 138.8, 137.5, 137.0, 136.7, 136.6, 136.5, 136.17, 136.15, 136.0, 135.6, 135.3, 134.52, 134.46, 131.4, 131.3, 131.0, 128.6, 128.5, 128.42, 128.35, 128.24, 128.15, 128.1, 128.0, 127.8, 127.5, 127.2, 127.0, 126.8, 126.2, 125.9, 125.83, 125.78, 125.7, 124.49, 124.46, 123.9, 123.7, 122.5, 122.4, 122.1, 122.0, 121.3, 65.0, 63.9, 47.6, 41.3, 21.3, 21.2, 21.1, 20.91, 20.87, 20.8, 20.7, 20.4, 19.4; IR (KBr) 3062, 2922, 2852, 1732, 1612, 1460, 1442, 1375, 1261, 1095, 1024, 847, 804, 759, 743, 697 cm^{-1}; MS (FAB) *m/z* 1076.5 (M^+), HRMS (FAB) *m/z* Calcd for $C_{84}H_{67}$: 1075.5246, Found: 1075.5234 ($[M-H]^+$).

3. Decay of UV-vis Spectra of 9b at Room Temperature

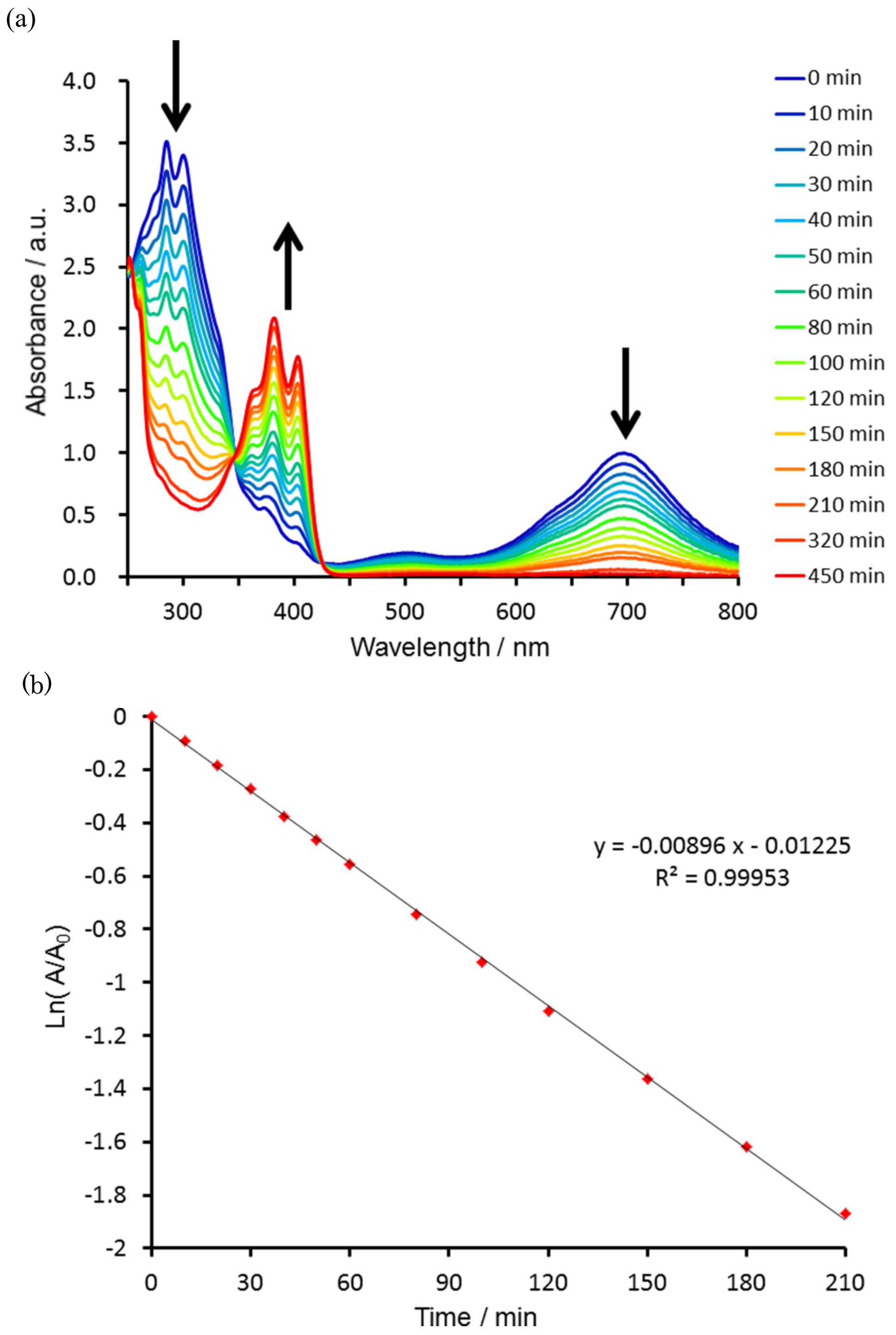


Figure S1. (a) Normalized absorbance-time profiles of **9b** under protection from light in CH_2Cl_2 at room temperature. (b) Time dependence of the electronic absorption of **9b** at 697 nm.

The half-life of **9b** was determined according to the following equation.

$$\tau_{1/2} = \frac{ln2}{k} = \frac{ln2}{0.00896} = 77 \text{ min}$$

4. Correlation NMR Spectra of 12

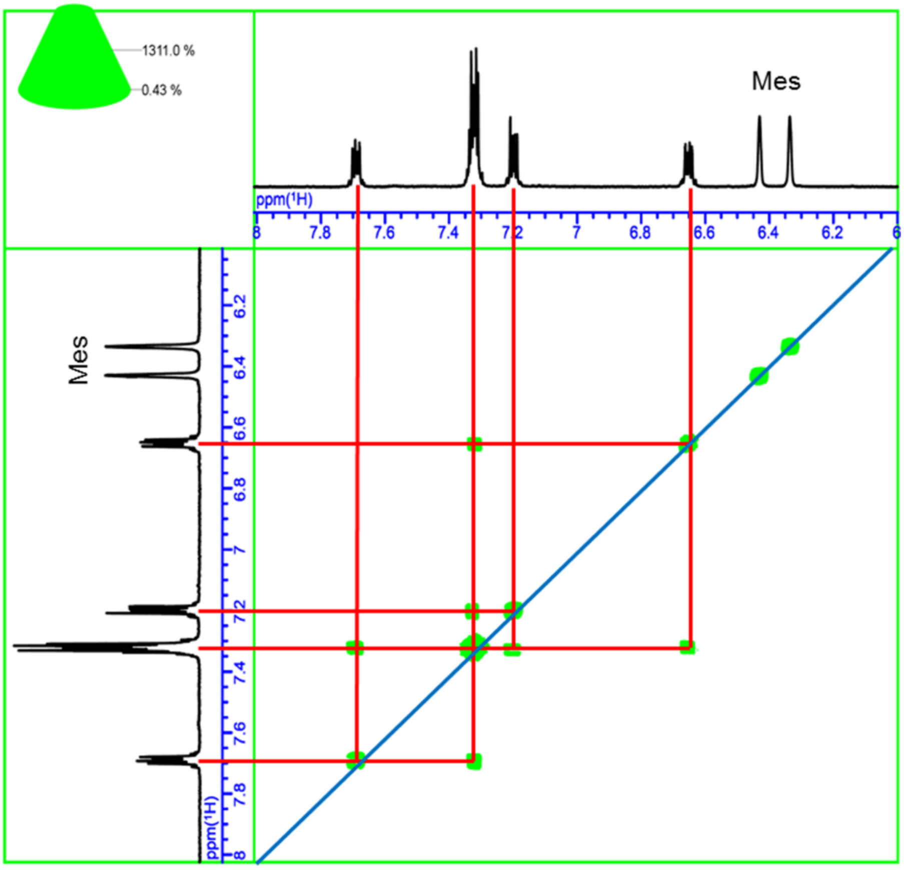


Figure S2. Partial H-H COSY (correlation spectroscopy) spectrum.

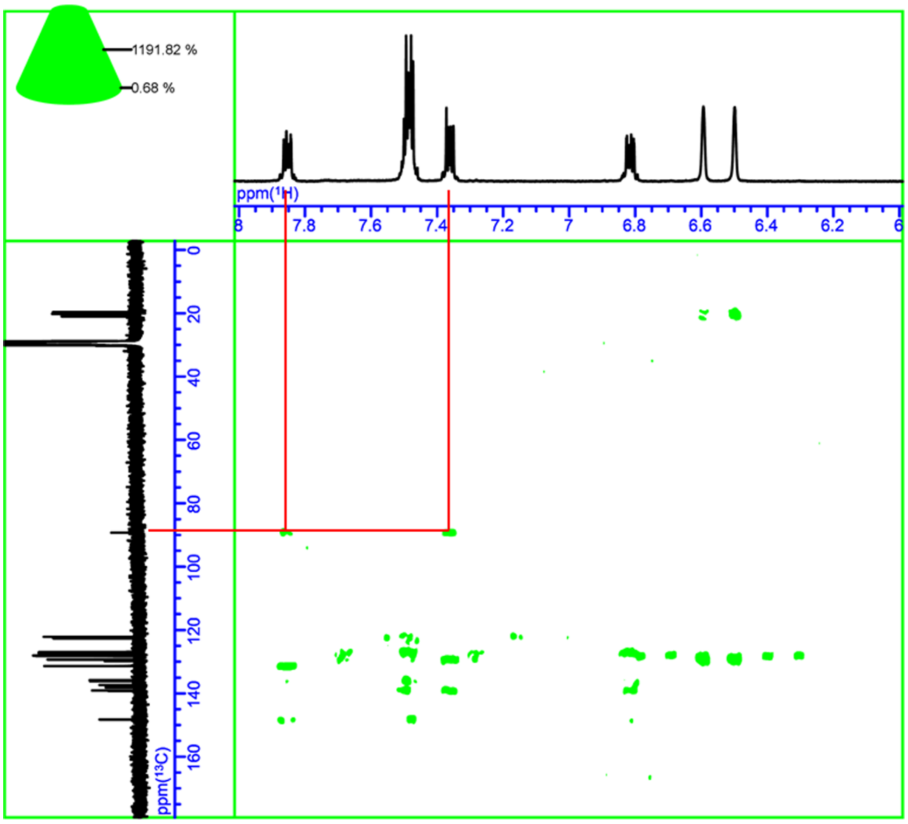
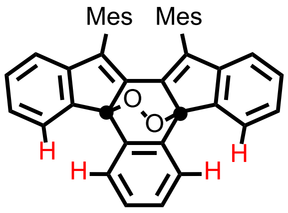
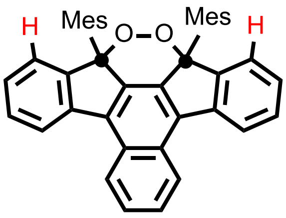


Figure S3. Partial HMBC (Heteronuclear Multiple Bond Coherence) spectrum.

The structure of endoperoxide **12** was elucidated on the basis of the HMBC spectrum (*Figure S3*) using the correlation between the signals due to the sp^3 carbon atom attached to the oxygen atom (marked by dots in the following illustration) with the aromatic protons of the benzindenofluorene backbone (drawn in red). Namely, for **12** there are two aromatic protons (one in the external naphthalene ring and the other in the peripheral fused benzene ring) located within a three-bond range, whereas in alternative endoperoxide **12'** there is only one proton in the peripheral ring. In the HMBC spectrum, the signal for the sp^3 carbon (89.6 ppm) exhibits correlation peaks with two proton signals at 7.87–7.84 (m, 2H) and 7.37–7.35 (m, 2H) ppm, excluding the possibility of candidate **12'**.



12



12'

5. S-T Gaps, HOMO-LUMO Gaps, and Biradical Characters

Table S1. S-T Gaps, HOMO-LUMO Gaps, and Biradical Characters of NQD **6a**, **6b**, BIF **9a** and **9b**.

	S-T gap[a] (kJ/mol)	HOMO[b] (eV)	LUMO[b] (eV)	HOMO-LUMO[b] gap (eV)	Biradical Character[c] (%)
6a	47.8	−4.79	−2.20	2.59	55.7
6b	7.0	−4.07	−2.47	1.60	87.3
9a	31.2	−4.87	−3.21	1.66	62.8
9b	33.7	−4.75	−3.06	1.69	55.6

[a] Calculated at the UB3LYP/6-31G(d) level. [b] Calculated at the RB3LYP/6-31G(d) level.
[c] Calculated at the UHF/6-31G(d)//UB3LYP/6-31G(d) and Yamaguchi scheme.

6. Temperature Dependent ^{1}H NMR Spectra of 9b

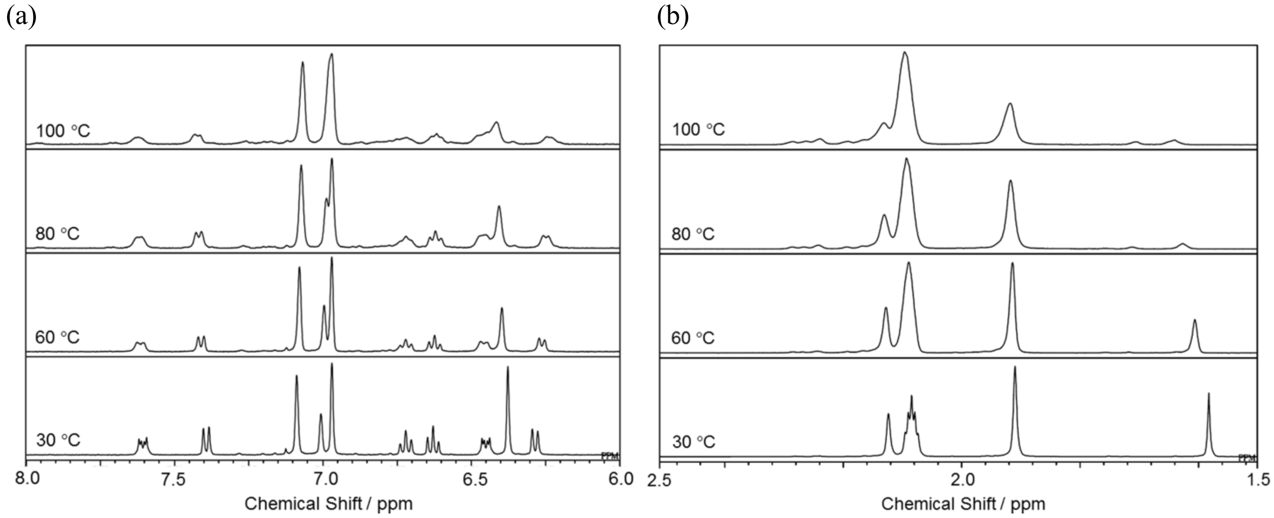
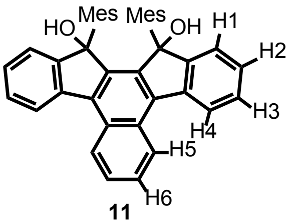


Figure S4. Partial variable temperature ^{1}H NMR spectra of **9b** in tolene-d_8. (a) 6.0−8.0 ppm, (b) 1.5−2.5 ppm.

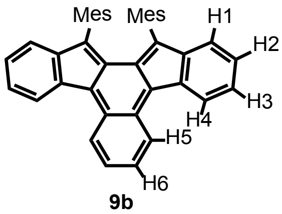
Table S2. Chemical Shifts (ppm) of Protons of **11** and **9b** in CD_2Cl_2.

Proton [a,b]	**11**	**9b**	Shift ($\delta_{9b}-\delta_{11}$)
H1	7.13 [c]	6.20 [c]	−0.93
H2	7.22	6.79	−0.43
H3	7.45	6.92	−0.53
H4	8.32	7.63	−0.69
H5	8.91	7.79	−1.12
H6	7.74	6.84	−0.90

[a] Proton positions are shown in the following drawings. [b] Identification of the signals was achieved by H-H COSY (correlation spectroscopy) and HMBC (Heteronuclear Multiple Bond Coherence) measurements. [c] The chemical shift is strongly affected by the ring current of mesityl groups.



11



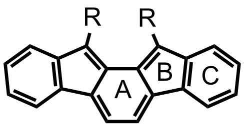
9b

7. NICS Calculations for 8 and 9

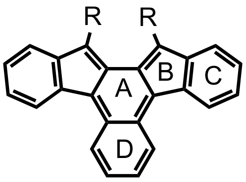
Table S3. NICS(0), NICS(1), and NICS(1)$_{zz}$ Values of Indeno[2,1-*a*]fluorenes **8a** and **8b** and Benz[c]indeno[2,1-*a*]fluorenes **9a** and **9b** Calculated at the RB3LYP/6-31G(d) and UB3LYP/6-31G(d) Levels, Respectively.

	8a			**8b**	**9a**			**9b**
Ring[a]	NICS(0)	NICS(1)	NICS(1)$_{zz}$	NICS(0)	NICS(0)	NICS(1)	NICS(1)$_{zz}$	NICS(0)
A	+5.42	+2.12	+13.81	+4.52	+1.96	−0.77	+5.98	+1.80
B	+9.20	+4.28	+22.02	+8.12	+10.05	+5.27	+25.14	+9.11
C	−3.94	−6.17	−12.62	−4.66	−2.96	−5.16	−9.41	−3.89
D	–[b]	–[b]	–[b]	–[b]	−1.37	−4.28	−6.47	−1.23

[a] Ring positions are shown in the following drawings. [b] Not applicable.



8a : R = H
8b : R = Mes



9a : R = H
9b : R = Mes

8. Molecular Orbitals for 9a

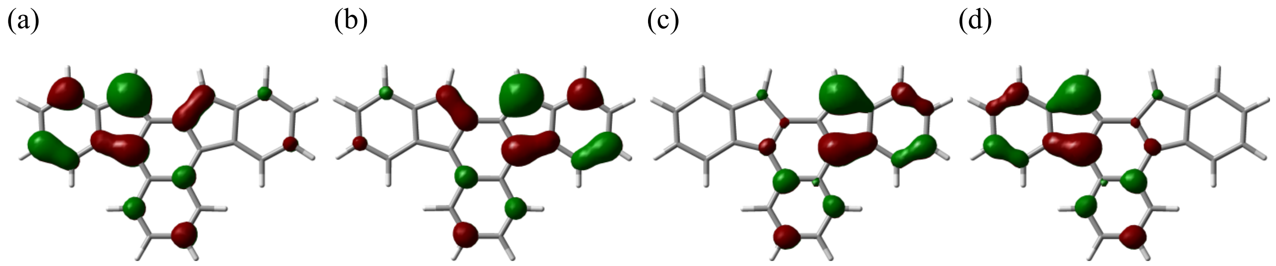


Figure S5. (a) α-HOMO, (b) β-HOMO, (c) α-LUMO, and (d) β-LUMO of 9a calculated at the UB3LYP/6-31G(d) level

9. TD-DFT Calculations for 9a

Table S4. Excitation Energies of **9a** Calculated at the TD-UB3LYP/6-31G(d) Level.[a]

Exited State	Excitation Energy / eV (Wavelength / nm)	Excitation Amplitudes		Oscillator Strength f	S^2
1	1.044 (1187)	−0.176	(α, HOMO−1 − LUMO)	0.0008	0.671
		0.682	(α, HOMO − LUMO)		
		−0.176	(β, HOMO−1 − LUMO)		
		0.682	(β, HOMO − LUMO)		
2	1.078 (1150)	0.674	(α, HOMO−1 − LUMO)	0.0024	1.606
		0.169	(α, HOMO − LUMO)		
		0.674	(β, HOMO−1 − LUMO)		
		0.169	(β, HOMO − LUMO)		
3	1.338 (927)	0.107	(α, HOMO−2 − LUMO)	0.0074	0.416
		0.605	(α, HOMO−1 − LUMO)		
		0.343	(α, HOMO − LUMO)		
		−0.107	(β, HOMO−2 − LUMO)		
		−0.605	(β, HOMO−1 − LUMO)		
		−0.343	(β, HOMO − LUMO)		
4	1.631 (760)	−0.342	(α, HOMO−1 − LUMO)	0.1148	0.033
		0.615	(α, HOMO − LUMO)		
		0.342	(β, HOMO−1 − LUMO)		
		−0.615	(β, HOMO − LUMO)		

[a] The excited state 3 is assigned to S1 state from the relative signs of excitation amplitudes, large oscillator strength and small $<S^2>$ value.

10. Electrochemical Properties of 9b

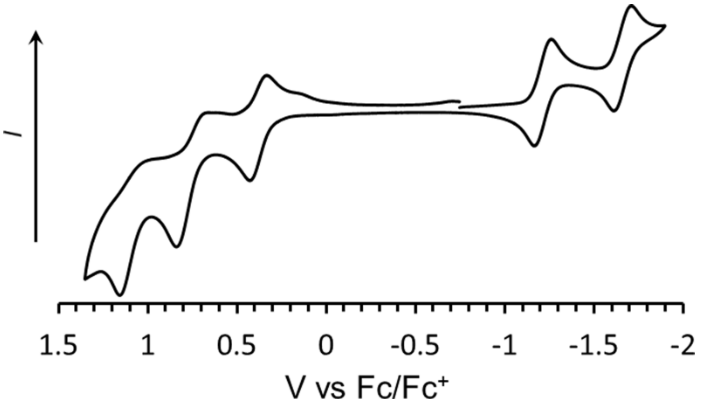


Figure S6. Cyclic voltammogram of **9b**. Conditions; in CH_2Cl_2 at rt, 0.1 M Bu_4NClO_4, working electrode: glassy carbon, counter electrode: Pt, reference electrode: $Ag/AgNO_3$, scan rate = 0.1 V/s.

11. X-ray Crystallographic Analyses of 9b, 13, and 15

Single crystals of **9b**, **13**, and **15** used for X-ray crystallographic analyses were obtained by recrystallization from a mixture of benzene/CH_3CN, AcOEt/hexane, and chlorobenzene/CH_3CN, respectively.

The X-ray diffraction data for **9b** and **13** were collected with a Rigaku R-AXIS-RAPID imaging plate diffractometer with graphite monochromated MoK_α radiation, respectively. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F_2 by the full-matrix least-squares method using SHELXL-97.[2] Hydrogen atoms were placed at calculated positions and refined "riding" on their corresponding carbon atoms.

For **15**, X-ray diffraction data were collected by using the synchrotron radiation (λ = 0.8000 Å). The cell refinements were performed by HKL2000 software.[3] Direct methods (Sir 2008) were used for the structure solution.[4] All calculations were performed with the observed reflections [$I>2\sigma(I)$] by the program CrystalStructure crystallographic software packages[5] except for refinement, which was performed using SHELXL-97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters.

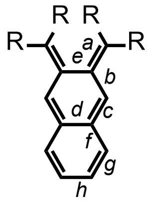
Table S5. Main Crystal Data for **9b**, **13**, and **15**

	9b	**13**	**15**
formula	$C_{42}H_{34}$	$C_{50}H_{34}Cl_2N_2O_2$	$C_{90}H_{73}Cl$
M	538.69	765.69	1190.02
T / K	113(2)	113(2)	123
color	deep blue	red	purple
crystal system	monoclinic	monoclinic	triclinic
space group	C 2/c	$P2_1/c$	P 1−
a / Å	14.515(2)	9.251(3)	8.5044(1)
b / Å	15.214(2)	18.592(6)	19.2480(2)
c / Å	13.311(2)	22.277(7)	20.4545(3)
α / deg.	90	90	82.0704(8)
β / deg.	99.134(3)	94.409(9)	78.1032(5)
γ / deg.	90	90	82.3308(7)
V / Å^3	2902.3(7)	3820(2)	3225.90(7)
Z value	4	4	2
GOF on F^2	1.145	1.062	1.044
R	0.0448	0.0959	0.0673
wR	0.1147	0.2259	0.1817

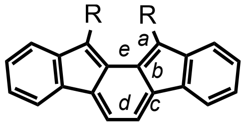
Table S6 Calculated and Experimental Bond Lengths (Å) of the Main Core Ring of NQD **6a**, **6b**, Indeno[2,1-*a*]fluorenes **8a**, **8b**, Benz[*c*]indeno[2,1-*a*]fluorenes **9a** and **9b**.

	Calculated data [b]						X-ray data	
Bond [a]	**6a**	**6b**	**8a**	**8b**	**9a**	**9b**	**8b**	**9b**
a	1.375	1.471	1.374	1.390	1.395	1.411	1.391(2)	1.403(2)
b	1.432	1.394	1.471	1.476	1.439	1.449	1.480(2)	1.468(2)
c	1.390	1.413	1.362	1.362	1.480	1.406	1.359(3)	1.398(2)
d	1.455	1.433	1.445	1.436	1.468	1.461	1.431(3)	1.465(3)
e	1.490	1.456	1.443	1.459	1.432	1.449	1.454(2)	1.453(3)
f	1.432	1.423	—[c]	—[c]	1.429	1.432	—[c]	1.441(2)
g	1.371	1.377	—[c]	—[c]	1.371	1.370	—[c]	1.363(3)
h	1.429	1.419	—[c]	—[c]	1.419	1.421	—[c]	1.419(4)

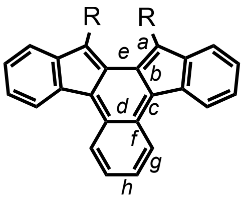
[a] Bond positions are shown in the following drawings. [b] Calculated at the RB3LYP/6-31G(d) or UB3LYP/6-31G(d) level for **8a**, **8b**, or **9a**, **9b**, respectively. [c] Not applicable.



6a: R = H
6b: R = Ph



8a: R = H
8b: R = Mes



9a: R = H
9b: R = Mes

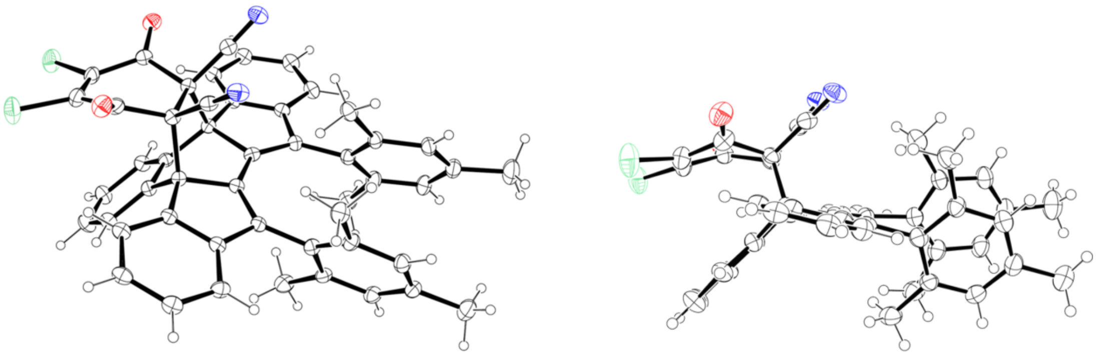


Figure S7. ORTEP drawings of DDQ adduct (**13**).

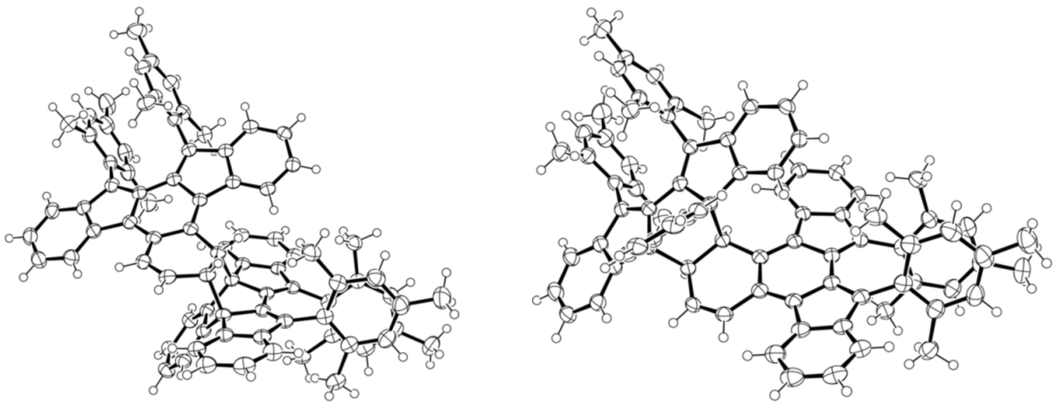


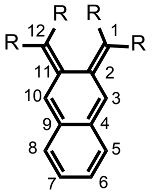
Figure S8. ORTEP drawings of dimer (**15**).

12. Spin Densities at NQD frameworks of 6a, 6b, 9a, and 9b

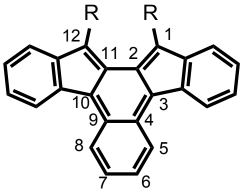
Table S7. Spin Densities (ρ) on Carbon Atoms of NQD frameworks of **6a, 6b, 9a** and **9b** Calculated at the Broken-Symmetry UBHandHLYP/6-31G(d)// UB3LYP/6-31G(d) Level.

	Spin Density (ρ)			
Position [a]	**6a**	**6b**	**9a**	**9b**
1	+0.711	+0.795	+0.646	+0.633
2	−0.422	−0.339	−0.397	−0.402
3	+0.581	+0.321	+0.485	+0.487
4	−0.404	−0.212	−0.345	−0.347
5	+0.353	+0.192	+0.304	+0.304
6	−0.352	−0.188	−0.301	−0.302
7	+0.352	+0.188	+0.301	+0.302
8	−0.353	−0.192	−0.304	−0.305
9	+0.404	+0.212	+0.345	+0.347
10	−0.581	−0.321	−0.485	−0.487
11	+0.422	+0.339	+0.397	+0.402
12	−0.711	−0.795	−0.646	−0.633

[a] Atom positions are shown in the following drawings.



6a R=H
6b R=Ph



9a: R = H
9b: R = Mes

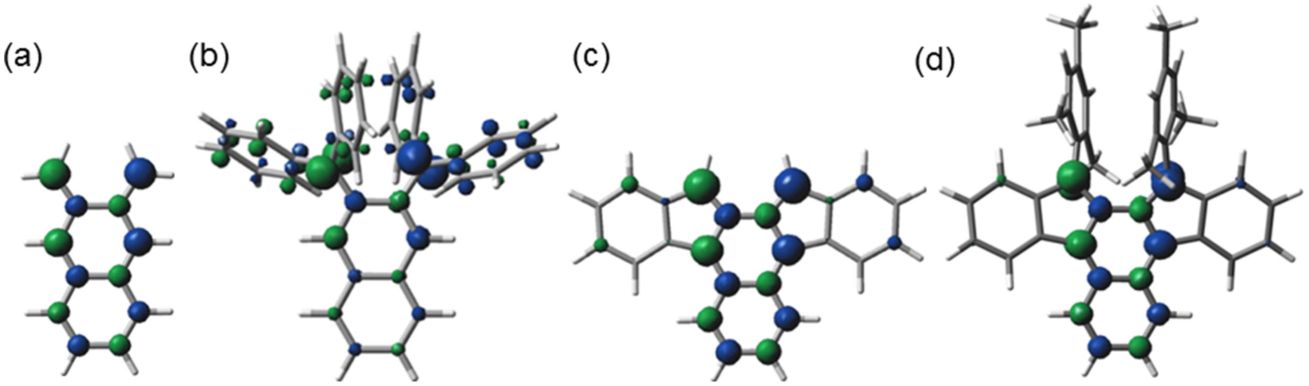


Figure S9. Spin densities of (a) NQD (**6a**), (b) tetraphenyl-NQD (**6b**), (c) BIF (**9a**), and (d) dimesityl-BIF (**9b**) calculated at the UB3LYP/6-31G(d) level.

13. NMR Spectra for 9b and 11–15

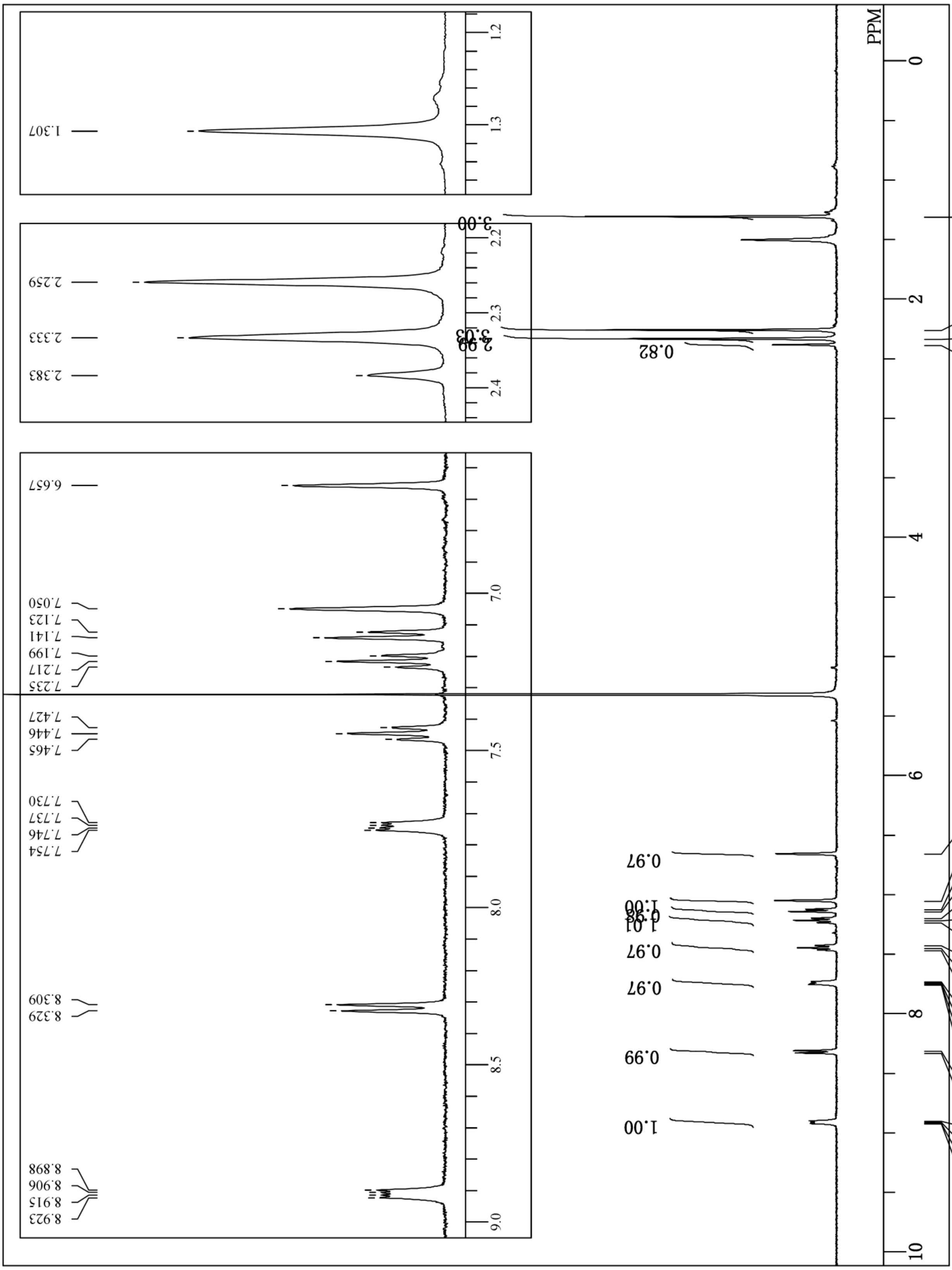


Figure S10. ^{1}H NMR spectrum of 13,14-dimesityl-13,14-dihydrobenz[*c*]indeno[2,1-*a*]fluorene-13,14-diol (**11**) (400 MHz, CD_2Cl_2).

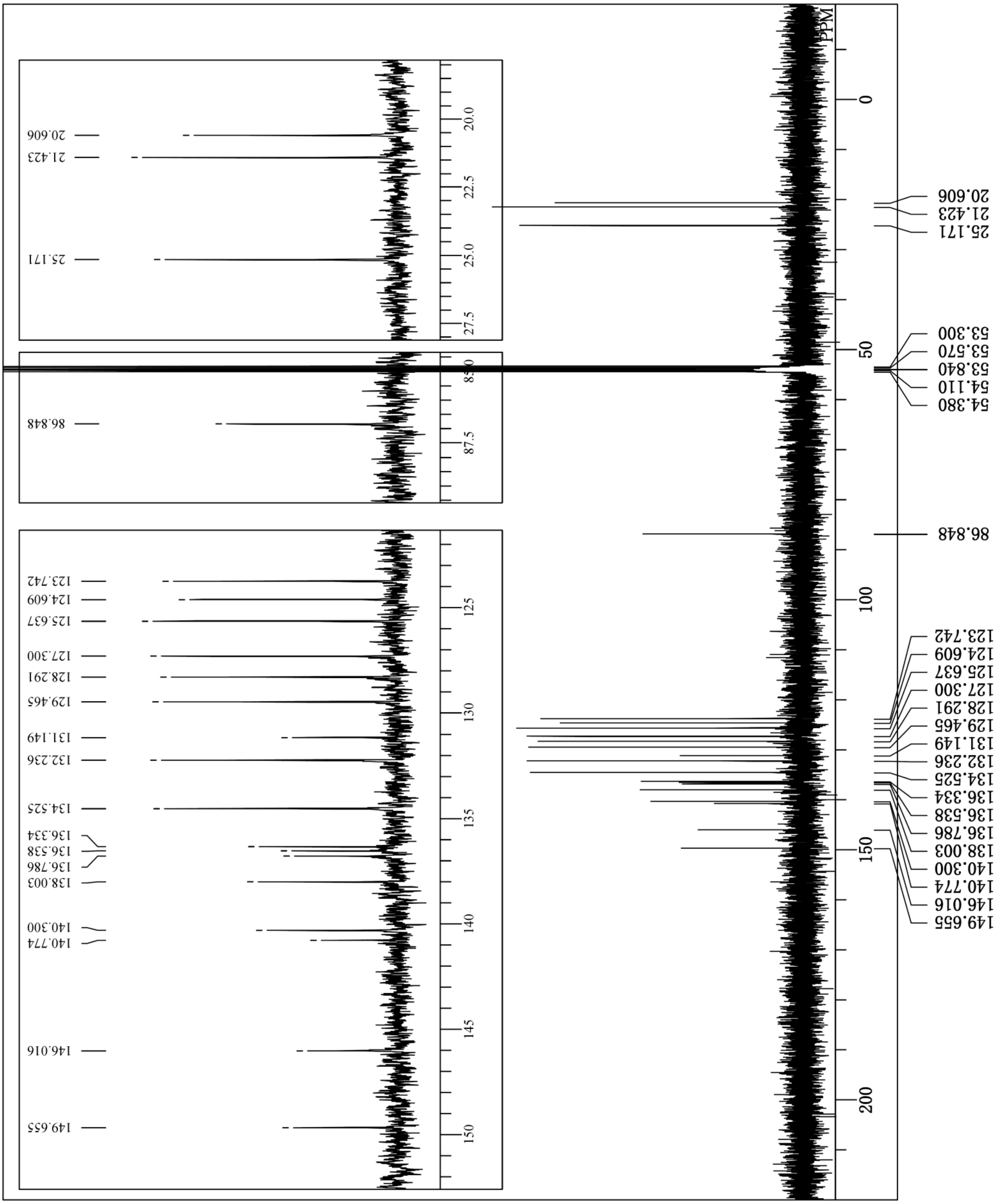


Figure S11. ^{13}C NMR spectrum of 13,14-dimesityl-13,14-dihydrobenz[*c*]indeno[2,1-*a*]fluorene-13,14-diol (**11**) (100 MHz, CD_2Cl_2).

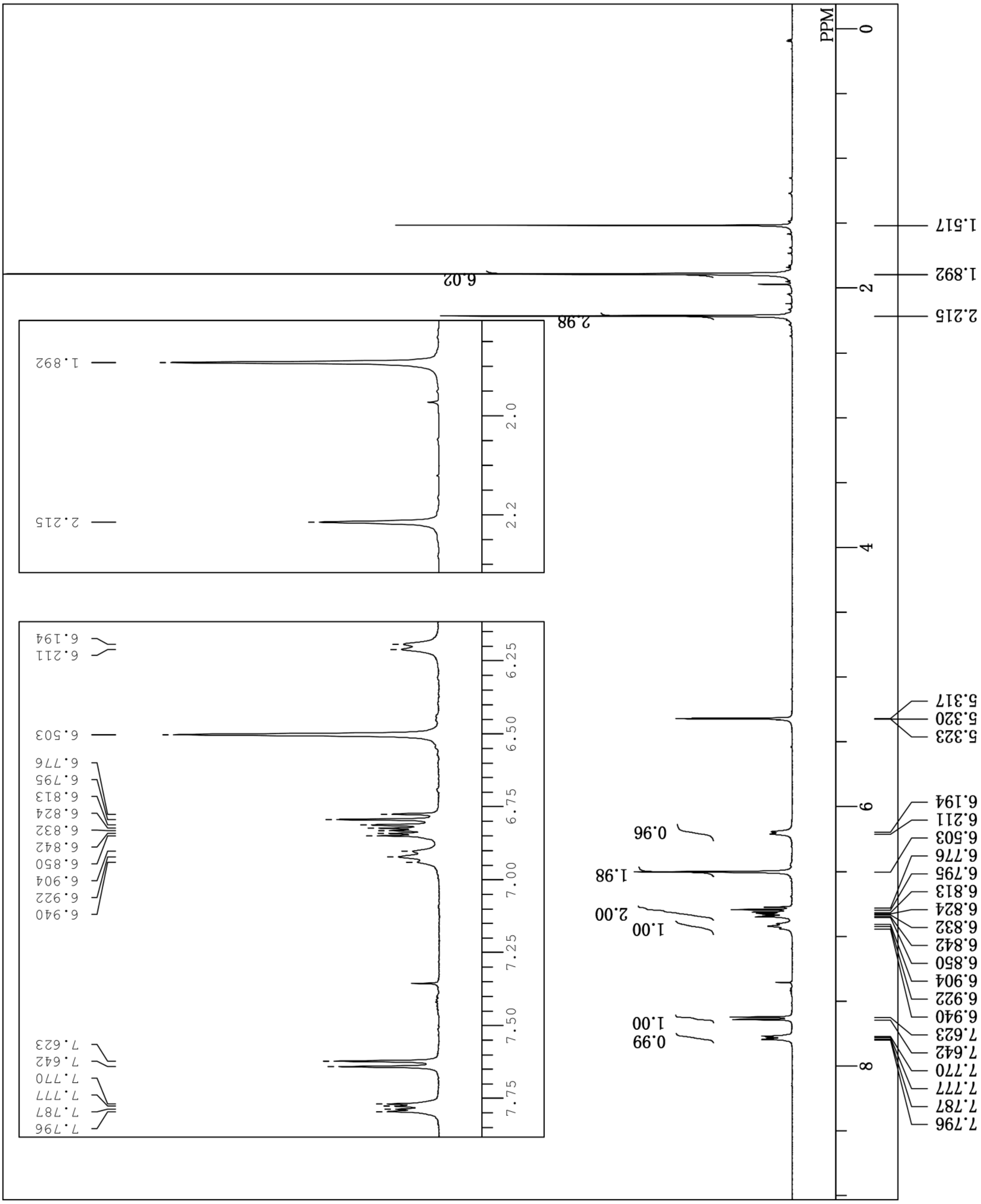


Figure S12. ^{1}H NMR spectrum of 13,14-dimesitylbenz[*c*]indeno[2,1-*a*]fluorene (**9b**) (400 MHz, CD_2Cl_2).

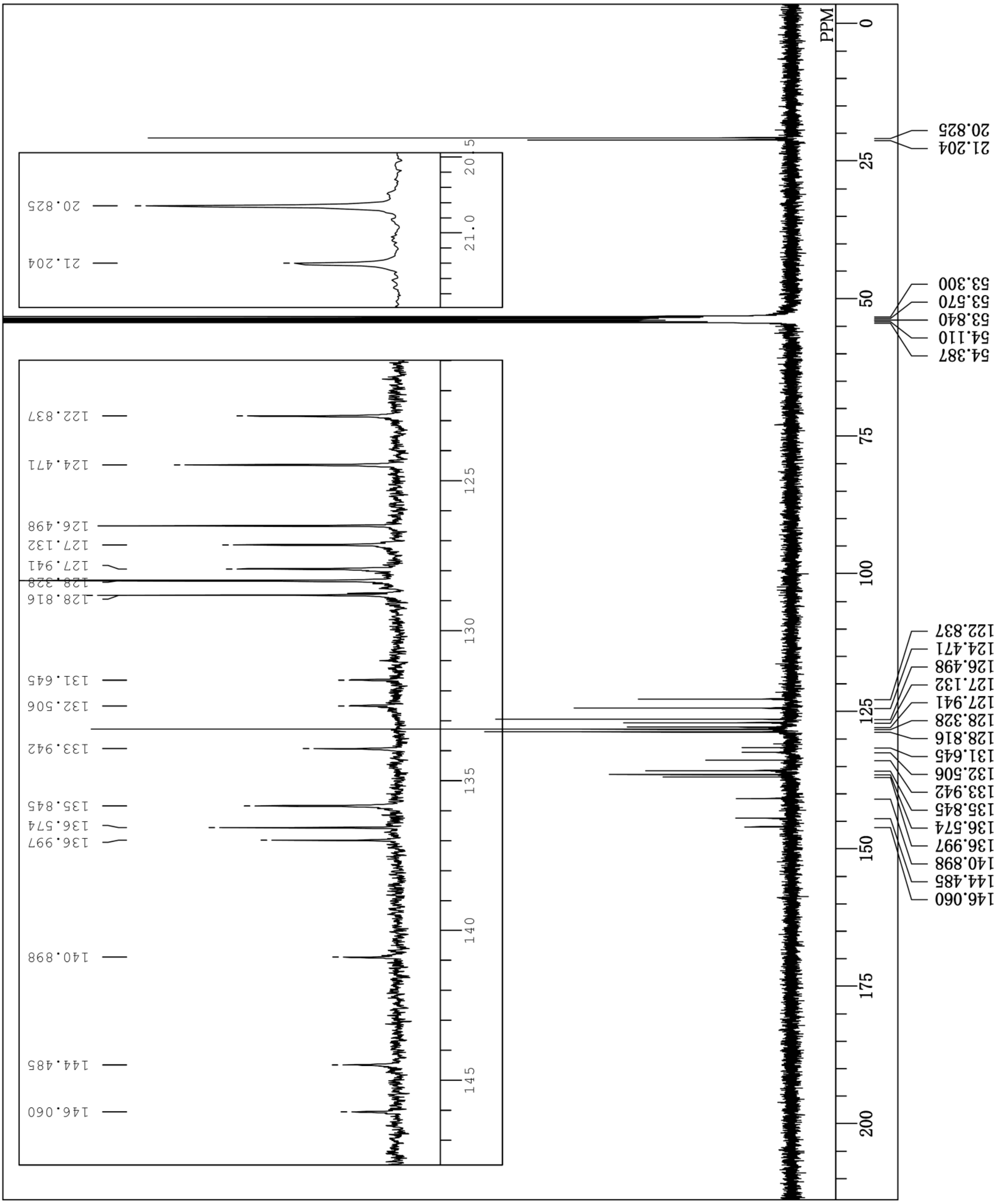


Figure S13. ^{13}C NMR spectrum of 13,14-dimesitylbenz[*c*]indeno[2,1-*a*]fluorene (**9b**) (100 MHz, CD_2Cl_2).

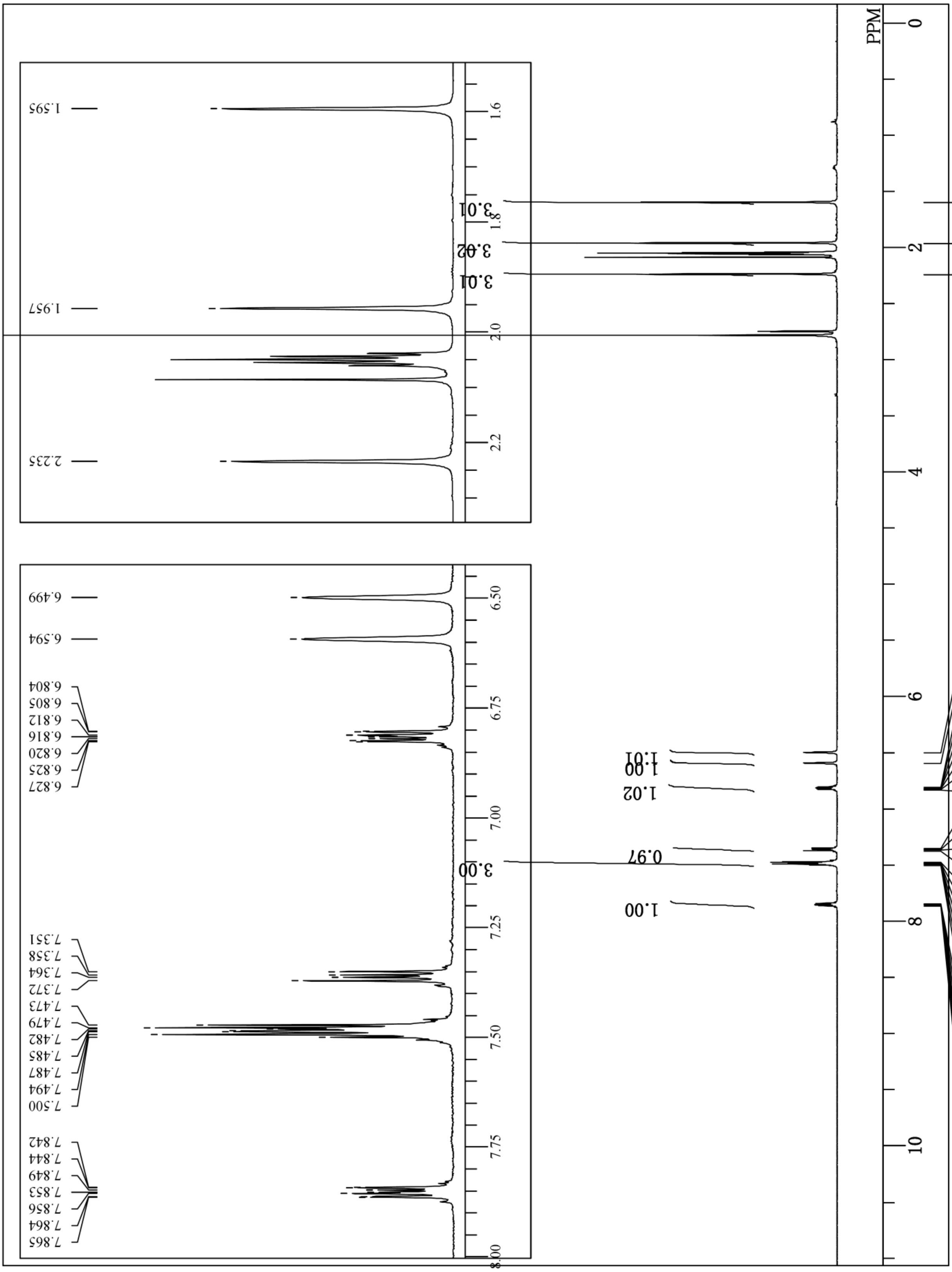


Figure S14. ^{1}H NMR spectrum of O_2 adduct **12** (400 MHz, acetone-d_6).

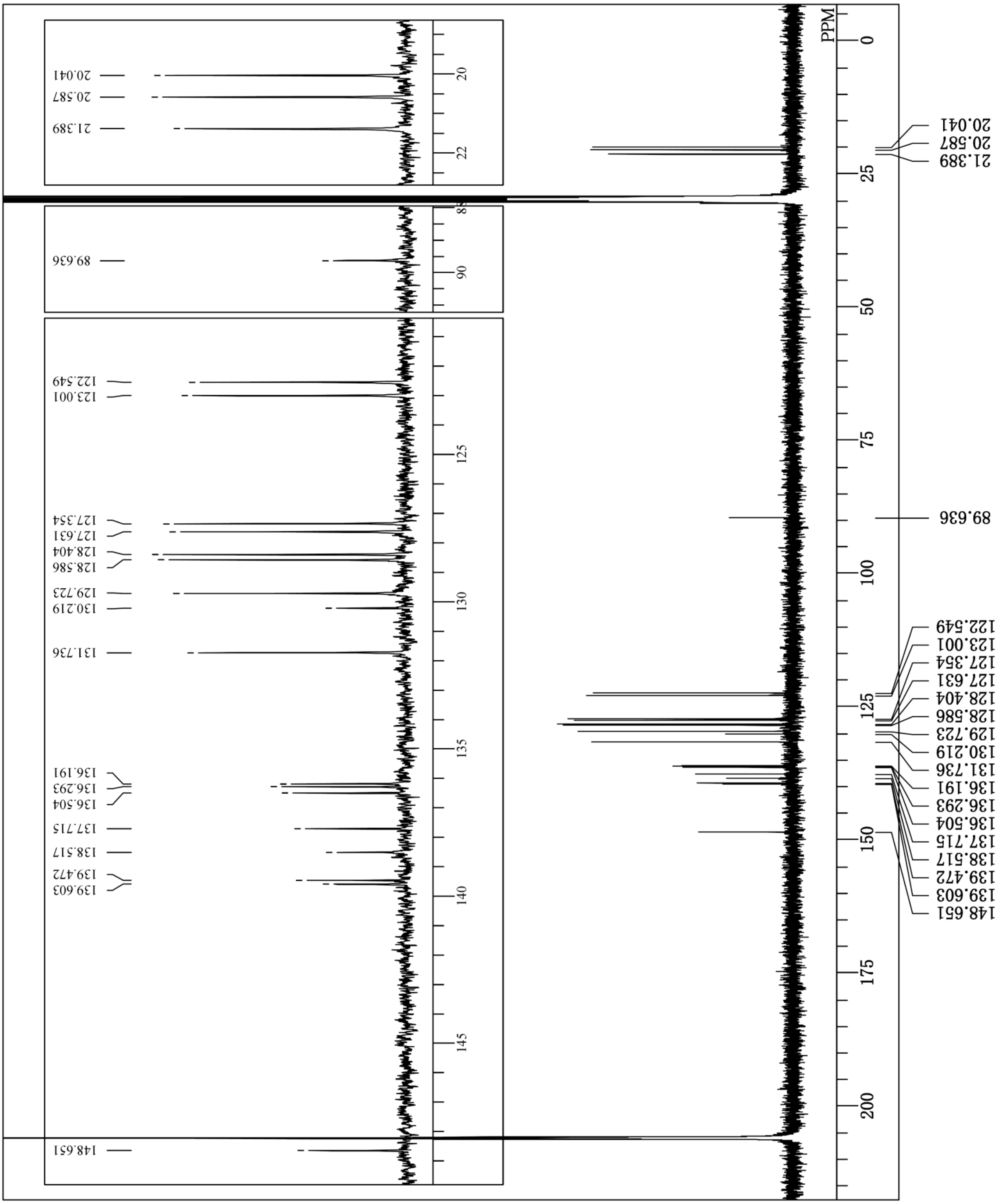


Figure S15. ^{13}C NMR spectrum of O_2 adduct **12** (100 MHz, acetone-d_6).

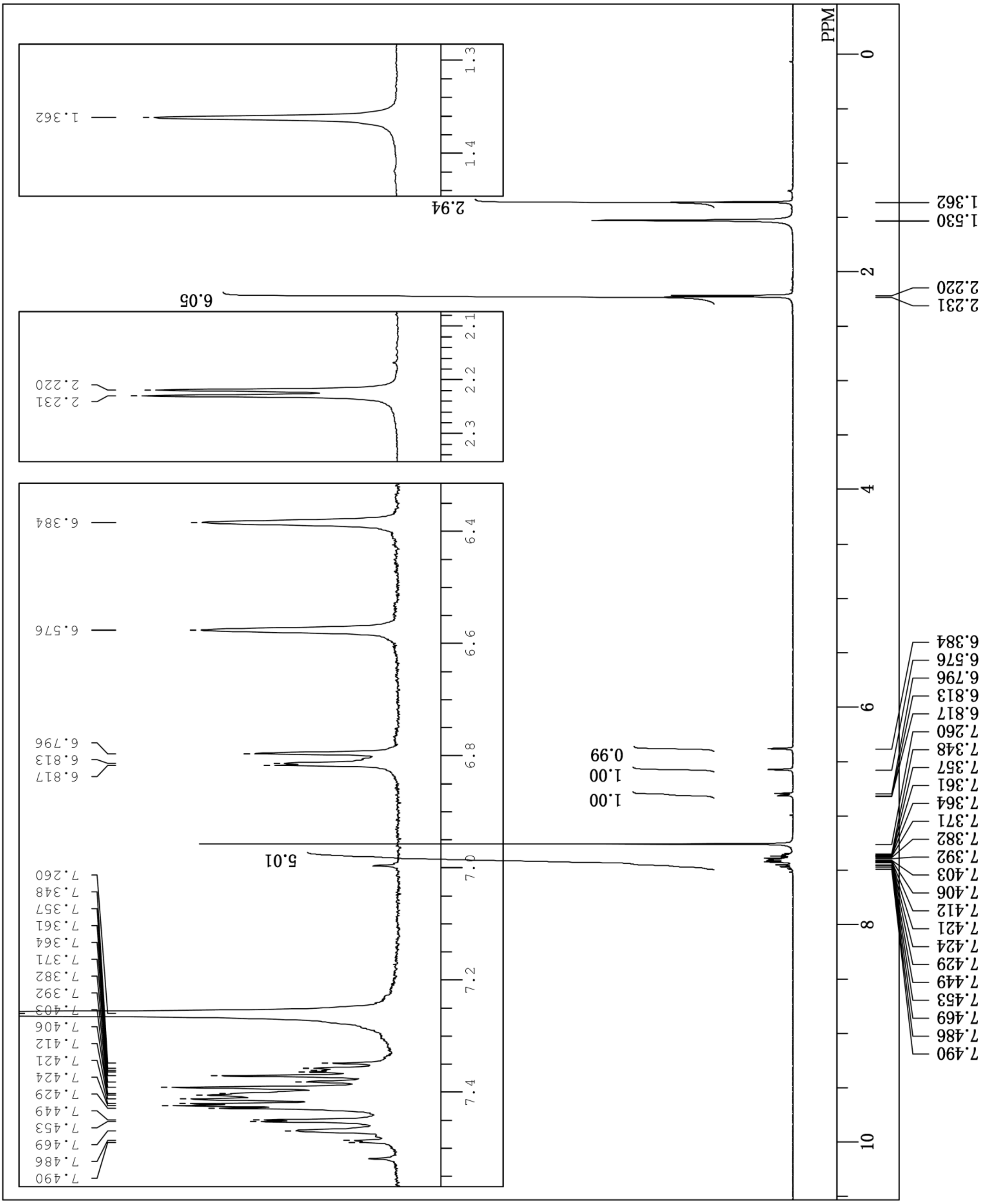


Figure S16. ^{1}H NMR spectrum of DDQ adduct **13** (400 MHz, $CDCl_3$).

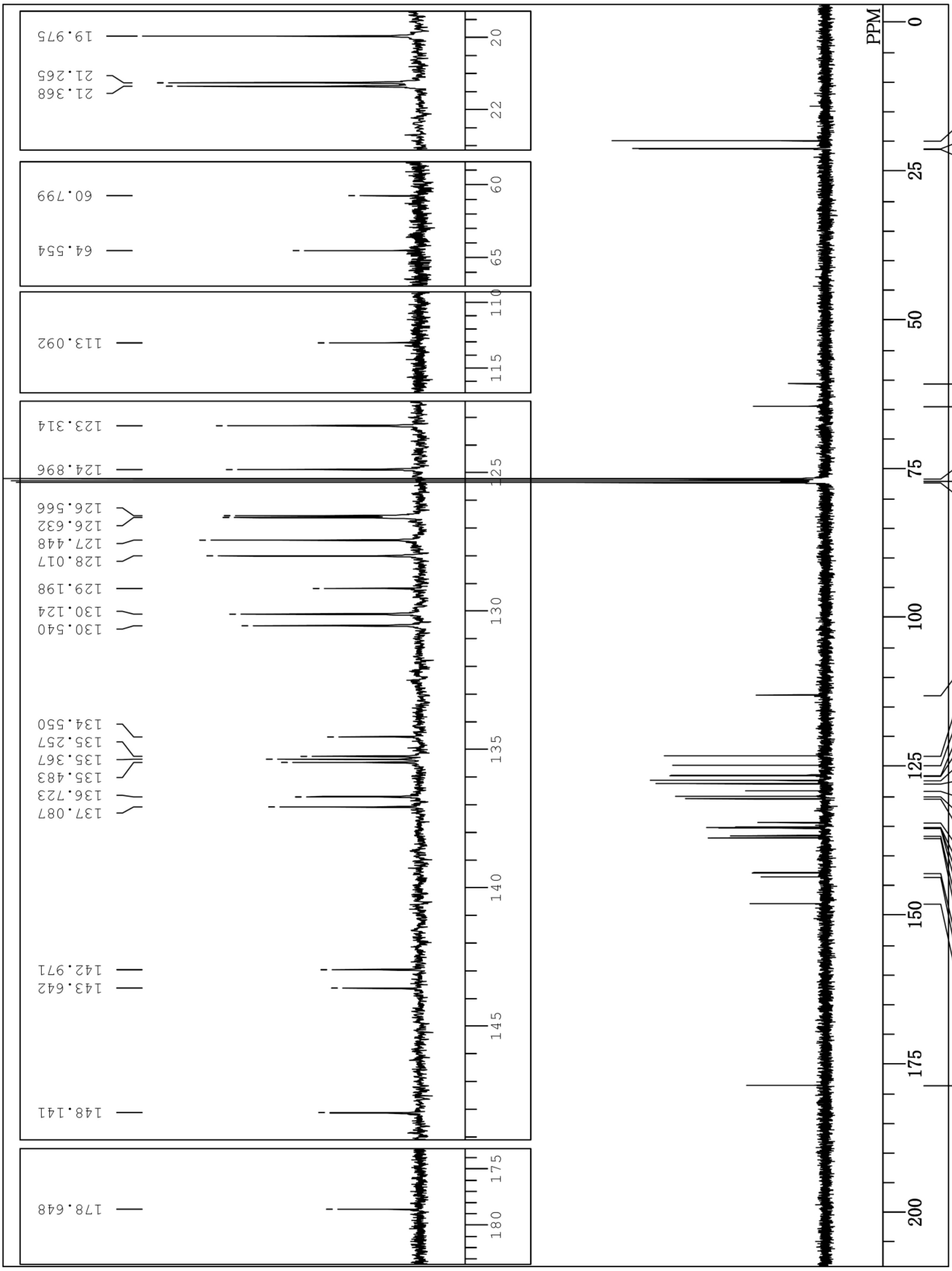


Figure S17. ^{13}C NMR spectrum of DDQ adduct **13** (100 MHz, $CDCl_3$).

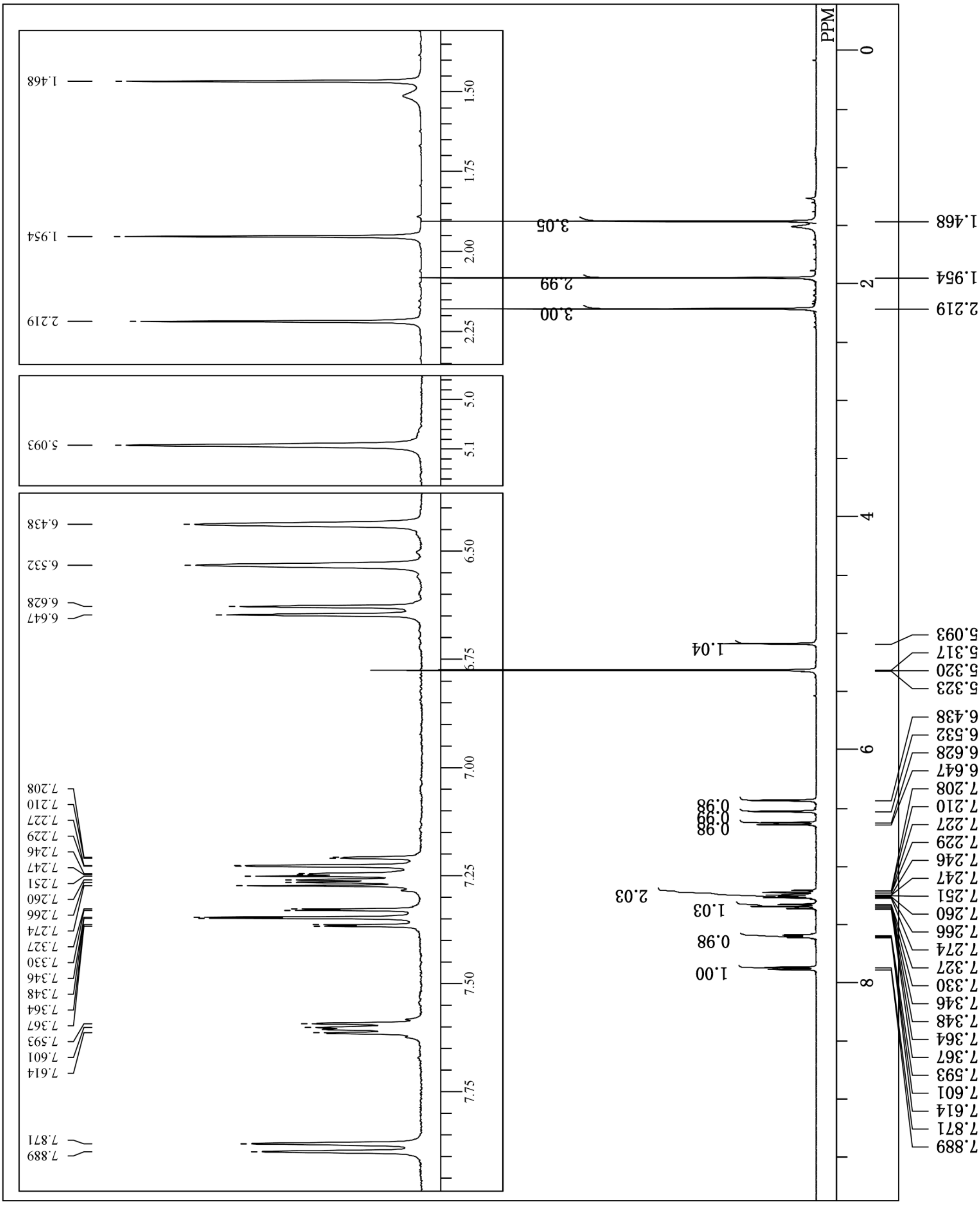


Figure S18. ^{1}H NMR spectrum of dihydro derivative **14** (400 MHz, CD_2Cl_2).

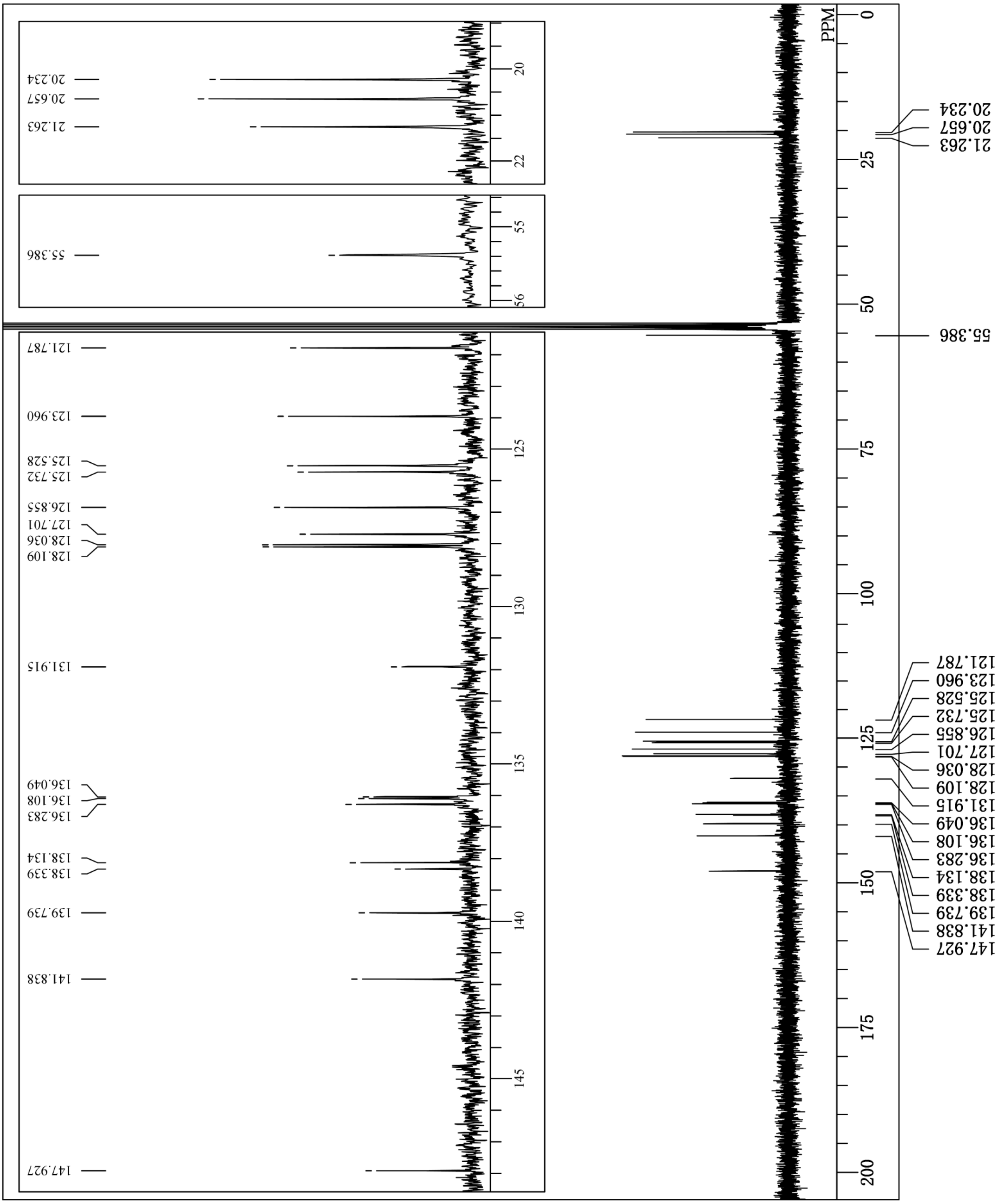


Figure S19. ^{13}C NMR spectrum of dihydro derivative **14** (100 MHz, CD_2Cl_2).

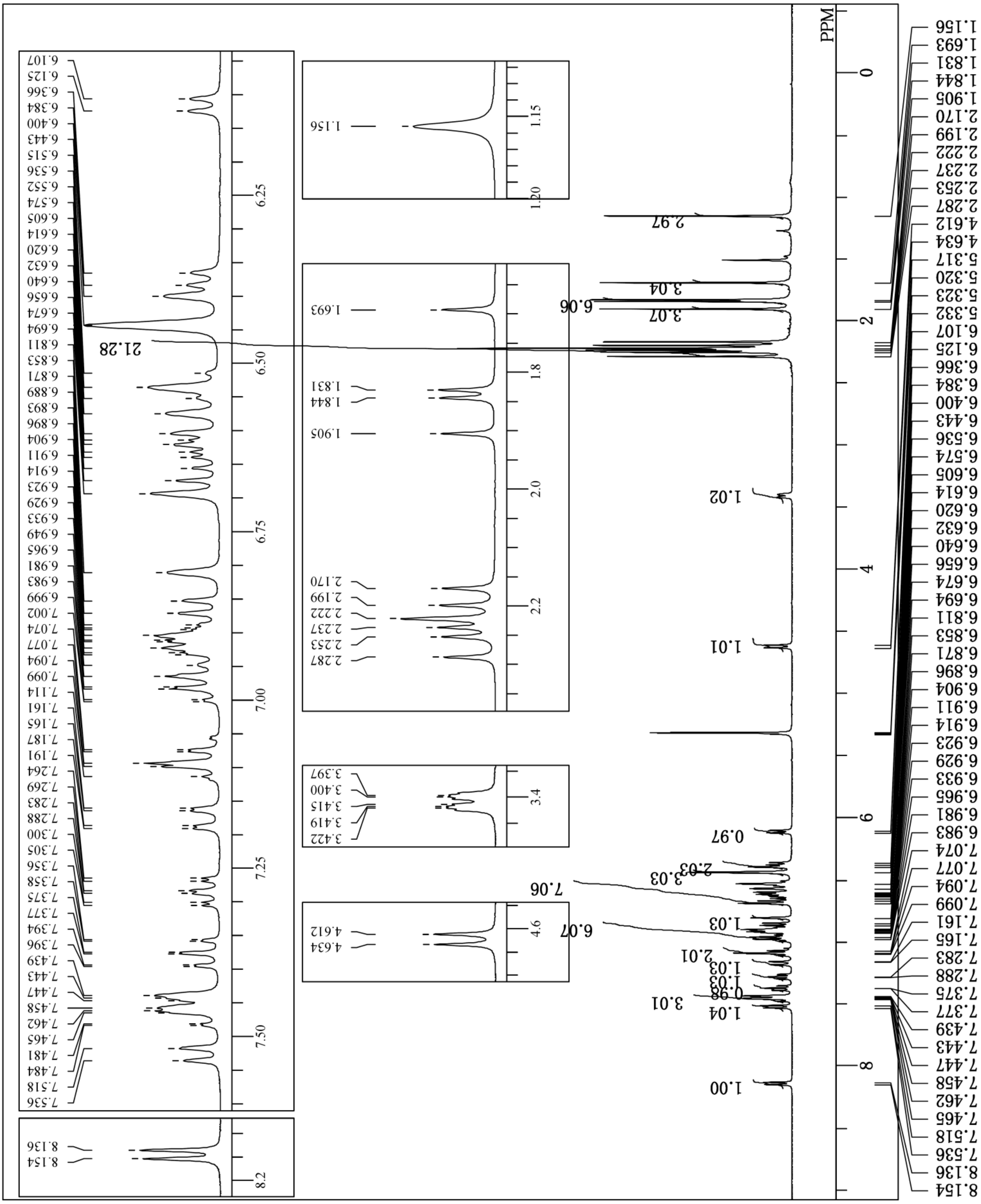


Figure S20. ^{1}H NMR spectrum of dimer **15** (400 MHz, CD_2Cl_2).

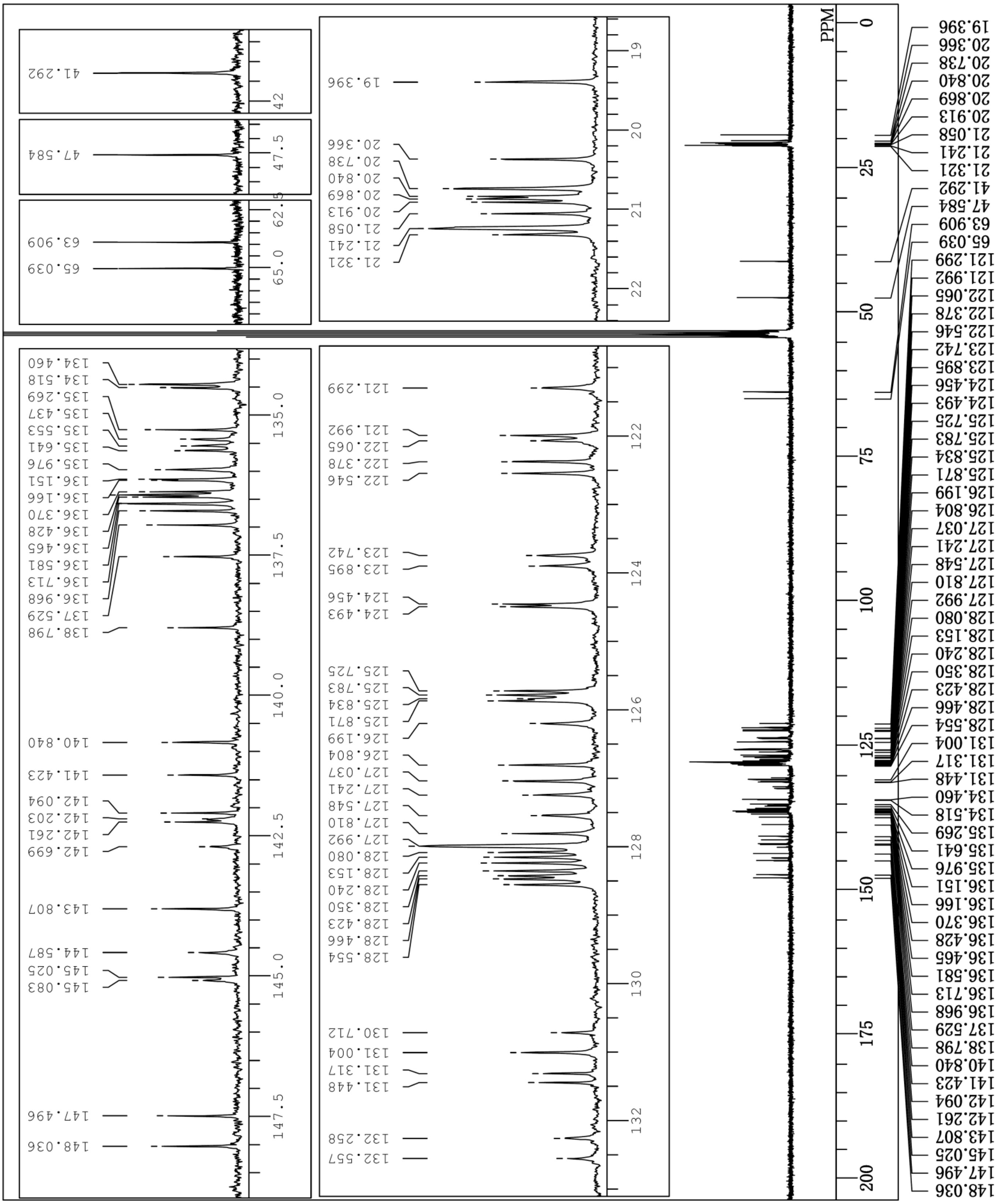


Figure S21. ^{13}C NMR spectrum of dimer **15** (100 MHz, CD_2Cl_2).

14. Cartesian Coordinates for Optimized Geometries

Table S8. Cartesian Coordinates (Å) of the Optimized Structure of 2,3-Naphthoquinodimetane (**6a**) (C_{2v} symmetry) Calculated at the UB3LYP/6-31G(d) Level.

Atom	X	Y	Z	Atom	X	Y	Z
C	0.000000	0.714647	3.088099	C	0.000000	1.500512	-2.985724
C	0.000000	1.409886	1.90704	H	0.000000	2.491926	-0.561262
C	0.000000	0.727391	0.648301	H	0.000000	1.247525	4.035022
C	0.000000	-0.727391	0.648301	H	0.000000	2.497396	1.905583
C	0.000000	-1.409886	1.90704	H	0.000000	-2.497396	1.905583
C	0.000000	-0.714647	3.088099	H	0.000000	-1.247525	4.035022
C	0.000000	1.404012	-0.566039	H	0.000000	-2.491926	-0.561262
C	0.000000	-1.404012	-0.566039	H	0.000000	-1.066992	-3.978968
C	0.000000	-0.74498	-1.836904	H	0.000000	-2.584566	-2.929011
C	0.000000	0.74498	-1.836904	H	0.000000	1.066992	-3.978968
C	0.000000	-1.500512	-2.985724	H	0.000000	2.584566	-2.929011

Table S9. Cartesian Coordinates (Å) of the Optimized Structure of Tetraphenyl-NQD (**6b**) (C_2 symmetry) Calculated at the UB3LYP/6-31G(d) Level.

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.368107	-0.606266	5.863104	C	1.635778	0.555607	-2.615459
C	-0.727868	-1.201616	4.674752	C	2.392742	-0.821626	-0.78095
C	-0.367746	-0.614742	3.430954	C	2.311542	-0.270342	-3.509636
C	0.367746	0.614742	3.430954	C	3.070148	-1.642897	-1.677048
C	0.727868	1.201616	4.674752	C	3.034162	-1.373714	-3.047873
C	0.368107	0.606266	5.863104	H	-1.345026	-2.079512	2.195482
C	-0.733234	-1.181791	2.18891	H	-0.646665	-1.064611	6.80817
C	0.733234	1.181791	2.18891	H	-1.292653	-2.130962	4.671166
C	0.406256	0.604097	0.962674	H	1.292653	2.130962	4.671166
C	-0.406256	-0.604097	0.962674	H	0.646665	1.064611	6.80817
C	0.977284	1.178919	-0.2652	H	1.345026	2.079512	2.195482
C	-0.977284	-1.178919	-0.2652	H	-0.812569	2.989508	0.68228
C	0.996407	2.626307	-0.446071	H	2.826541	2.683633	-1.601979
C	-0.007451	3.45135	0.121823	H	-0.785395	5.431723	0.393882
C	2.0217	3.275716	-1.179983	H	2.842627	5.122291	-1.898411
C	0.007451	4.83124	-0.045083	H	1.037503	6.525456	-0.90676
C	2.034127	4.65675	-1.34034	H	0.812569	-2.989508	0.68228
C	1.026701	5.446551	-0.778342	H	-2.826541	-2.683633	-1.601979
C	-0.996407	-2.626307	-0.446071	H	0.785395	-5.431723	0.393882
C	0.007451	-3.45135	0.121823	H	-2.842627	-5.122291	-1.898411
C	-2.0217	-3.275716	-1.179983	H	-1.037503	-6.525456	-0.90676
C	-0.007451	-4.83124	-0.045083	H	-2.449429	1.02469	0.284166
C	-2.034127	-4.65675	-1.34034	H	-1.058941	-1.395221	-2.989086
C	-1.026701	-5.446551	-0.778342	H	-3.636425	2.492353	-1.303839

C	-1.658192	-0.301094	-1.225112	H	-2.26712	0.055913	-4.574526

(*Continued*)

Atom	X	Y	Z	Atom	X	Y	Z
C	-2.392742	0.821626	-0.78095	H	-3.56277	2.015729	-3.747248
C	-1.635778	-0.555607	-2.615459	H	1.058941	1.395221	-2.989086
C	-3.070148	1.642897	-1.677048	H	2.449429	-1.02469	0.284166
C	-2.311542	0.270342	-3.509636	H	2.26712	-0.055913	-4.574526
C	-3.034162	1.373714	-3.047873	H	3.636425	-2.492353	-1.303839
C	1.658192	0.301094	-1.225112	H	3.56277	-2.015729	-3.747248

Table S10. Cartesian Coordinates (Å) of the Optimized Structure of Benz[*c*]indeno[2,1-*a*]fluorene (**9a**) (C_{2v} symmetry) Calculated at the UB3LYP/6-31G(d) Level.

Atom	X	Y	Z	Atom	X	Y	Z
C	0.000000	0.709639	3.841775	C	0.000000	4.196671	-2.248570
C	0.000000	1.398708	2.656188	C	0.000000	5.294464	-0.090955
C	0.000000	0.734138	1.390832	C	0.000000	5.369073	-1.483209
C	0.000000	-0.734138	1.390832	C	0.000000	2.963380	-1.599351
C	0.000000	-1.398708	2.656188	C	0.000000	4.053766	0.570931
C	0.000000	-0.709639	3.841775	H	0.000000	1.250523	4.784057
C	0.000000	-1.432957	0.166448	H	0.000000	2.479097	2.679864
C	0.000000	0.715803	-1.081495	H	0.000000	-2.479097	2.679864
C	0.000000	-0.715803	-1.081495	H	0.000000	-1.250523	4.784057
C	0.000000	-1.626196	-2.138633	H	0.000000	-1.381144	-3.194884
C	0.000000	-2.963380	-1.599351	H	0.000000	1.381144	-3.194884
C	0.000000	1.432957	0.166448	H	0.000000	-4.055499	1.654408
C	0.000000	1.626196	-2.138633	H	0.000000	-6.206903	0.499001
C	0.000000	-2.874713	-0.169381	H	0.000000	-4.246269	-3.334671
C	0.000000	-4.053766	0.570931	H	0.000000	-6.337762	-1.975241
C	0.000000	-5.294464	-0.090955	H	0.000000	4.055499	1.654408
C	0.000000	-4.196671	-2.248570	H	0.000000	4.246269	-3.334671
C	0.000000	-5.369073	-1.483209	H	0.000000	6.206903	0.499001
C	0.000000	2.874713	-0.169381	H	0.000000	6.337762	-1.975241

Table S11. Cartesian Coordinates (Å) of the Optimized Structure of the Triplet State of 13,14-Dimesitylbenz[*c*]indeno[2,1-*a*]fluorene (**9b**) (C_2 symmetry) Calculated at the UB3LYP/6-31G(d) Level.

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.714643	-0.045928	5.997284	C	1.095253	-2.899530	-0.494131
C	-1.398872	-0.126380	4.822841	C	-1.095253	2.899530	-0.494131
C	-0.728919	-0.106427	3.546374	C	1.662534	-2.028751	-5.428697
C	0.728919	0.106427	3.546374	C	-1.662534	2.028751	-5.428697
C	1.398872	0.126380	4.822841	H	-1.251265	-0.056832	6.941995
C	0.714643	0.045928	5.997284	H	-2.477847	-0.174945	4.842756
C	1.407379	0.227255	2.339725	H	2.477847	0.174945	4.842756
C	-0.725732	-0.044988	1.056341	H	1.251265	0.056832	6.941995
C	0.725732	0.044988	1.056341	H	3.893452	0.950440	3.871312
C	1.689076	-0.089020	0.058403	H	6.105199	0.949945	2.821817

C	3.004167	0.130171	0.666083	H	4.377296	-0.114320	-0.978257

(Continued)

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.407379	-0.227255	2.339725	H	6.377548	0.402418	0.418311
C	-1.689076	0.089020	0.058403	H	-3.893452	-0.950440	3.871312
C	2.845015	0.369488	2.058074	H	-4.377296	0.114320	-0.978257
C	3.968282	0.685715	2.823230	H	-6.105199	-0.949945	2.821817
C	5.235007	0.701734	2.220327	H	-6.377548	-0.402418	0.418311
C	4.267090	0.114344	0.077795	H	-1.162769	3.417991	-3.131270
C	5.387502	0.401815	0.866233	H	-2.084980	-0.518997	-4.546839
C	-2.845015	-0.369488	2.058074	H	1.162769	-3.417991	-3.131270
C	-3.004167	-0.130171	0.666083	H	2.084980	0.518997	-4.546839
C	-3.968282	-0.685715	2.823230	H	3.274472	1.937752	-1.995146
C	-4.267090	-0.114344	0.077795	H	1.943562	2.386863	-3.069637
C	-5.235007	-0.701734	2.220327	H	1.664915	2.197206	-1.331715
C	-5.387502	-0.401815	0.866233	H	-3.274472	-1.937752	-1.995146
C	-1.586086	0.544454	-1.350756	H	-1.943562	-2.386863	-3.069637
C	-1.335927	1.911594	-1.614404	H	-1.664915	-2.197206	-1.331715
C	-1.879989	-0.330364	-2.420361	H	0.959414	-3.909853	-0.892551
C	-1.355163	2.364385	-2.936661	H	1.940124	-2.923923	0.204655
C	-1.879989	0.167405	-3.727037	H	0.207001	-2.646810	0.094978
C	-1.622985	1.510443	-4.009698	H	-0.959414	3.909853	-0.892551
C	1.586086	-0.544454	-1.350756	H	-1.940124	2.923923	0.204655
C	1.335927	-1.911594	-1.614404	H	-0.207001	2.646810	0.094978
C	1.879989	0.330364	-2.420361	H	2.690744	-2.250044	-5.745664
C	1.355163	-2.364385	-2.936661	H	1.084281	-2.952792	-5.534166
C	1.879989	-0.167405	-3.727037	H	1.259157	-1.294510	-6.135096
C	1.622985	-1.510443	-4.009698	H	-2.690744	2.250044	-5.745664
C	2.204399	1.790084	-2.190214	H	-1.084281	2.952792	-5.534166
C	-2.204399	-1.790084	-2.190214	H	-1.259157	1.294510	-6.135096

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