Electronic Supplementary Information

1. General Information.

The NMR spectra (400 MHz for ^{1}H; 100.6 MHz for ^{13}C) were recorded using a JEOL NMR spectrometer (JNM-AL400). Chemical shift δ and coupling constant J values are expressed in ppm and Hz, respectively. The IR spectra were obtained using a JASCO FT/IR-470 spectrometer, and wavenumber ν is expressed in cm^{-1}. High resolution mass spectroscopic analyses were performed using a JEOL mass spectrometer (JMS-T100LP AccuTOF LC-plus) in a direct analysis in real time (DART) mode and detected by the time-of-flight (TOF) method.

The experimental setup for the reductive coupling reactions under visible-light irradiation is shown in Figure S1. For the irradiation, a HOZAN LED (model L – 711) was used. Its emission spectrum is shown in Figure S2.

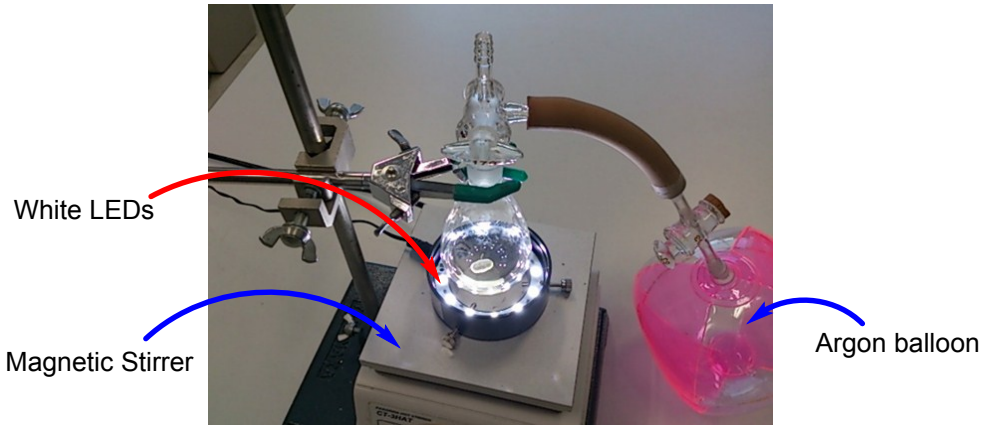


Figure S1. Experimental setup

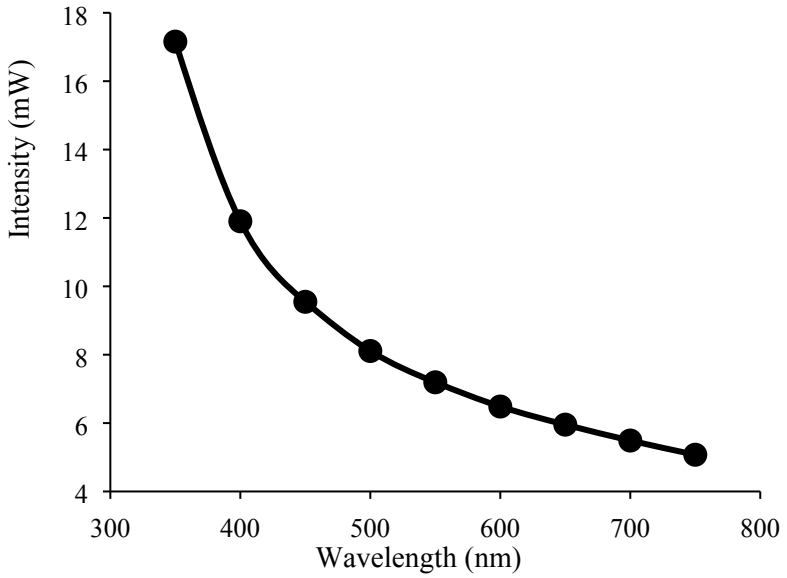


Figure S2. Emission spectrum of the LED used for irradiating visible light.

2. Procedures for reductive coupling reactions

Reductive coupling reaction of benzaldehyde. Benzaldehyde (53.0 mg, 0.500 mmol), perylene (15.1 mg, 60.0 μmol), *i*-Pr_2EtN (0.70 mL, 4.0 mmol), and acetonitrile (25 mL) were added to a 100 mL flask under argon. The resulting solution was irradiated using a LED light under stirring at room temperature. After 16 h, the solution was concentrated under reduced pressure to obtain a mixture containing diol **1a**.

To the mixture, acetic anhydride (5 mL), pyridine (10 mL), and DMAP (5 mg) were added, and the solution was left at room temperature for 24 h. Then, it was concentrated under reduced pressure. The residue was passed through a short silica gel column (eluent: hexane/ethyl acetate = 3:1). The fractions were combined and concentrated under reduced pressure. The residue was purified by preparative TLC (eluent: hexane/ethyl acetate = 5:1 twice), affording diacetate **2a** (mixture of *dl*- and *meso*-diastereomers; 49.2 mg, 0.165 mmol, 66% yield) as a pale yellow solid: ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.28 (t, J = 3.4 Hz, 6H), 7.21–7.18 (m, 10H), 7.15–7.13 (m, 4H), 6.09 (s, 2H, *meso*), 6.05 (s, 2H, *dl*), 2.08 (s, 6H, *dl*), 2.01 (s, 6H, *meso*); ^{13}C-NMR ($CDCl_3$, r.t.) δ 169.88, 169.69, 136.25, 136.11, 128.48, 128.29, 128.15, 127.67, 127.60, 77.25, 76.51, 21.13, 21.04; IR (KBr) v 3034, 2949, 1737, 1496, 1241 cm^{-1}

Reductive coupling reaction of 4-methylbenzaldehyde. The reductive coupling reaction of 4-methylbenzaldehyde (53.2 mg, 0.501 mmol) was performed under the same conditions as those for benzaldehyde. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 3:1), furnishing diol **1b** (mixture of *dl*- and *meso*-diastereomers; 33.9 mg, 0.140 mmol, 56% yield) as a yellow solid: ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.13 (dd, J = 8.3, 13.7 Hz, 8H), 7.01 (dd, J = 8.3, 14.2 Hz, 8H), 4.70 (s, 2H, *meso*), 4.61 (s, 2H, *dl*), 2.95 (br s, 4H), 2.33 (s, 6H, *meso*), 2.28 (s, 6H, *dl*); ^{13}C-NMR ($CDCl_3$, r.t.) δ 137.9, 137.5, 137.1 (2C), 129.06, 128.90, 127.15, 126.97, 78.87, 78.11, 21.29, 21.26; IR (KBr) v 3346, 3028, 2914, 2857, 1516 cm^{-1}.

Reductive coupling reaction of 4-methoxybenzaldehyde. The reductive coupling reaction of 4-methoxybenzaldehyde (68.0 mg, 0.500 mmol) was performed under the same conditions as those for benzaldehyde. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate =3/1), producing diol **1c** (mixture of *dl*- and *meso*-diastereomers; 38.2 mg, 0.139 mmol, 56% yield): ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.18 (d, J = 8.8 Hz, 4H, *meso*), 7.02 (d, J = 8.8 Hz, 4H, *dl*), 6.85 (d, J = 8.8 Hz, 4H, *meso*), 6.75 (d, J = 8.8 Hz, 4H, *dl*), 4.72 (s, 2H, *meso*), 4.60 (s, 2H, *dl*), 3.79 (s, 6H, *meso*), 3.75 (s, 6H, *dl*), 2.90 (br s, 4H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 159.5, 159.3, 132.2 (2C), 128.5, 128.3, 113.8, 113.6, 78.9, 77.9, 55.4, 55.3; IR (KBr) v 3345, 2916, 2360, 1516, 1491 cm^{-1}.

Reductive coupling reaction of 4-fluorobenzaldehyde. The reductive coupling reaction of 4-fluorobenzaldehyde (62.1 mg, 0.500 mmol) was performed under the same conditions as those for benzaldehyde. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 3:1), affording diol **1d** (mixture of *dl*- and *meso*-diastereomers; 39.9 mg, 0.159 mmol, 64% yield): ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.15–7.11 (m, 4H), 7.05–6.88 (m, 12H), 4.81 (s, 2H, *meso*), 4.60 (s, 2H, *dl*), 2.71 (br s, 4H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 163.8, 161.3, 135.5, 135.3, 128.9, 128.8, 128.7, 115.3, 115.1, 78.8, 77.4; IR (KBr) v 3322, 2898, 1900, 1608, 1513 cm^{-1}.

Reductive coupling reaction of 4-chlorobenzaldehyde. The reductive coupling reaction of 4-chlorobenzaldehyde (70.3 mg, 0.500 mmol) was performed under the same conditions as those for benzaldehyde. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 3:1), furnishing diol **1e** (mixture of *dl*- and *meso*-diastereomers; 47 mg, 0.17 mmol, 67% yield): ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.27 (d, J = 8.8 Hz, 4H, *meso*), 7.21 (d, J = 8.3 Hz, 4H, *dl*), 7.11 (d, J = 8.8 Hz, 4H, *meso*), 7.03 (d, J = 8.3 Hz, 4H, *dl*), 4.84 (s, 2H, *meso*), 4.63 (s, 2H, *dl*), 2.89 (s, 2H, *dl*), 2.33 (s, 2H, *meso*); ^{13}C-NMR ($CDCl_3$, r.t.) δ 138.1, 137.9, 134.0,

128.5 (3C), 78.7, 77.3; IR (KBr) *v* 3329, 2918, 2355, 1598, 1491 cm^{-1}.

Reductive coupling reaction of benzophenone. Benzophenone (91.1 mg, 0.500 mmol), perylene (15.1 mg, 60.0 μmol), *i*-Pr_2NEt (0.7 mL, 4.0 mmol), and acetonitrile (25 mL) were added to a 100 mL flask under argon. The resulting solution was irradiated using a LED light under stirring at room temperature. After 16 h, the solution was concentrated under reduced pressure. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 8:1), producing diol **1f** (35.2 mg, 0.0955 mmol, 38% yield): ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.31–7.28 (m, 8H), 7.18–7.16 (m, 12H), 3.03 (s, 2H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 144.3, 128.76, 127.4, 127.1, 83.1; IR (KBr) *v* 3558, 3054, 2965, 2360, 1493 cm^{-1}.

Reductive coupling reaction of acetophenone. The reductive coupling reaction of acetophenone (60.2 mg, 0.501 mmol) was performed under the same conditions as those for benzophenone. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 3:1), affording a mixture containing diol **1g**. Further purification by preparative TLC (eluent: hexane/ethyl acetate = 10:1) furnishing **1g** (mixture of *dl*- and *meso*-diastereomers; 14.0 mg, 0.0575 mmol, 23%): ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.26–7.19 (m, 20H), 2.55 (s, 2H, *dl*), 2.25 (s, 2H, *meso*), 1.59 (s, 6H, *meso*), 1.51 (s, 6H, *dl*); ^{13}C-NMR ($CDCl_3$, r.t.) δ 143.9, 143.6, 127.5, 127.4, 127.3, 127.2, 127.0 (2C), 79.0, 78.7, 25.3, 25.1; IR (KBr) *v* 3491, 3056, 2983, 2361, 1446 cm^{-1}.

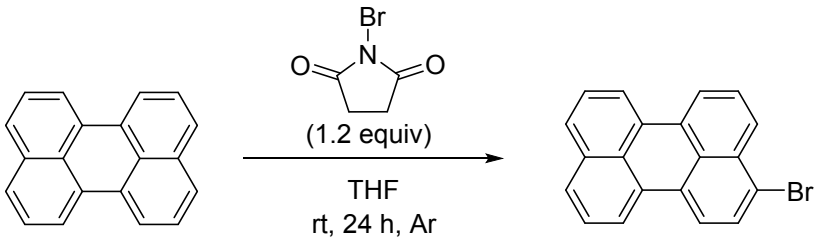
Synthesis of imine 3 and its reductive coupling reaction. To a solution of benzaldehyde (1.06 g; 10.0 mmol) in dichloromethane (20 mL), 4 Å molecular sieves (2.0 g) and benzylamine (1.07 g, 10.0 mmol) were added, and the reaction mixture was stirred at room temperature under argon. After 16 h, the mixture was filtered through a Celite pad, and the filtrate was concentrated under reduced pressure. The resulting residue was distilled using a Kugelrohr (230 °C, 20 mbar), furnishing imine **3** (1.65 g, 8.46 mmol, 85% yield) as a colourless oil: ^{1}H-NMR

($CDCl_3$, r.t.) δ 8.39 (s, 1H), 7.78 (dd, J = 2.0, 3.9 Hz, 2H), 7.40–7.42 (m, 3H), 7.34 (d, J = 4.4 Hz, 4H), 7.23–7.28 (m, 1H), 4.82 (s, 2H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 162.13, 139.40, 136.26, 130.89, 128.72, 128.62, 128.40, 128.10, 127.10, 65.17; IR (KBr) ν 3026, 2837, 1644, 1452, 752, 694 cm^{-1}.

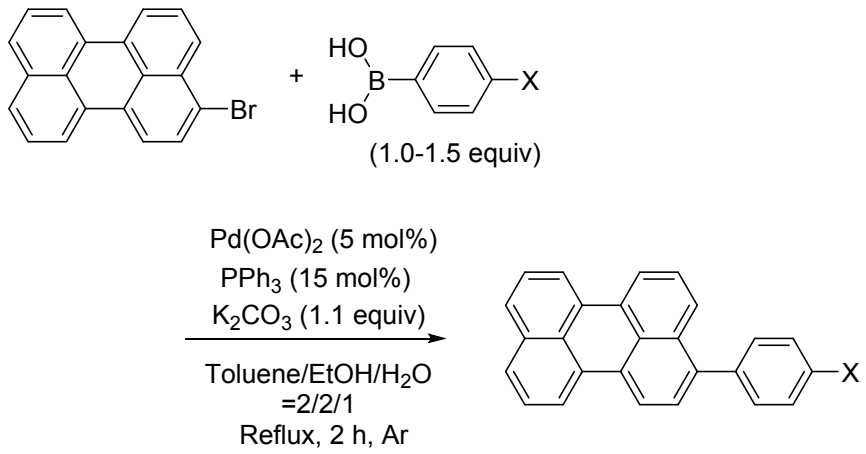
The reductive coupling reaction of imine **3** (97.6 mg, 0.500 mmol) was performed under the same conditions as those for benzaldehyde. The mixture was purified by silica gel column chromatography (eluent: hexane/ethyl acetate/triethylamine = 400:50:9), producing diamine **4** (mixture of *dl*- and *meso*-diastereomers; 64.7 mg, 0.165 mmol, 66% yield) as a yellow solid: ^{1}H-NMR ($CDCl_3$, r.t.) δ 7.13–7.35 (m, 32H), 7.04 (d, J = 7.8 Hz, 4H, *meso*), 6.97 (d, J = 6.3 Hz, 4H, *dl*), 3.75 (s, 2H, *dl*), 3.71 (s, 2H, *meso*), 3.68 (s, 2H, *meso*), 3.64 (s, 2H, *dl*), 3.51 (d, J = 13.7 Hz, 2H, *dl*), 3.48 (d, J = 6.3 Hz, 2H, *meso*), 3.30 (d, J = 13.7 Hz, 2H, *dl*), 1.70 (br s, 2H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 141.32, 140.95, 140.75, 140.46, 128.74, 128.50, 128.44, 128.33, 128.23, 128.12, 128.10, 128.02, 127.78, 127.05, 126.91, 126.80, 68.51, 67.33, 51.51, 50.88; IR (KBr) ν 3275, 3060, 3021, 1491, 1463, 754, 695 cm^{-1}.

3. Synthesis of perylene derivatives

3-Arylperylenes were synthesized from perylene via 1) the 3-bromination of perylene (Scheme S1) and 2) Suzuki–Miyaura coupling reaction of 3-bromoperylene with an arylboronic acid (Scheme S2).



Scheme S1. Synthesis of 3-bromoperylene



Scheme S2. Synthesis of 3-arylperylenes from 3-bromoperylene by Suzuki–Miyaura coupling reaction.

3-Bromoperylene. To a mixture of perylene (200 mg, 0.792 mmol) and *N*-bromo succinimide (169 mg, 0.948 mmol) under argon, tetrahydrofuran (20 mL) was added. The resulting solution was stirred at room temperature. After 24 h, the solution was diluted with dichloromethane (150 mL) and washed with water (150 mL × 2). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure; the crude solid was recrystallized from acetone, affording 3-bromoperylene (188 mg, 0.568 mmol, 72% yield) as a yellow solid: mp = 240–242 °C; ^{1}H-NMR ($CDCl_3$, r.t.) δ 8.22–8.12 (m, 3H), 8.07 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.75–7.66 (m, 3H), 7.56 (t, J = 7.3 Hz, 1H), 7.50–7.45 (m, 2H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 134.4, 132.9, 131.4, 131.0, 130.5 (2C), 130.4, 130.3, 129.7, 128.0 (2C), 127.4, 126.7, 126.4 (2C), 121.3, 120.7, 120.5, 120.3, 120.2; IR (KBr) ν 1492, 1379, 816, 804, 764 cm^{-1}.

3-Phenylperylene. To a suspension of 3-bromoperylene (115 mg, 0.350 mmol), phenylboronic acid (42.6 mg, 0.350 mmol), and K_2CO_3 (140 mg, 1.10 mmol) in a mixture of ethanol/toluene/water (v/v/v = 2:2:1, 25 mL), a solution of Pd(II) diacetate (3.9 mg, 0.018

mmol) and triphenylphosphine (18.4 mg, 0.0700 mmol) was added. The reaction mixture was refluxed and stirred under argon for 8 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (150 mL) and washed with water (150 mL) twice. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC (eluent: hexane/toluene = 5:1), furnishing 3-phenylperylene (54.3 mg, 0.165 mmol, 47% yield) as a yellow solid: mp = 171–174 °C; ^{1}H-NMR ($CDCl_3$, r.t.) δ 8.20–8.11 (m, 4H), 7.74 (t, J= 8.3 Hz, 1H), 7.69–7.62 (m, 3H), 7.55–7.36 (m, 8H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 143.1, 142.3, 137.0, 135.3, 133.7, 133.6, 133.0, 132.3, 131.3, 130.7, 130.1 (2C), 130.0 (2C), 129.6, 128.9, 128.8, 122.8, 122.6 (2C), 122.4, 122.2, 122.1; IR (KBr) ν 1600, 1492, 1388, 810, 763 cm^{-1}.

3-(4-Methoxyphenyl)perylene. The title compound was synthesized from 3-bromoperylene (230 mg, 0.700 mmol) and *p*-methoxyphenylboronic acid (155 mg, 1.05 mmol) and purified following the purification procedure for 3-phenylperylene. 3-(4-Methoxylphenyl)perylene was obtained as a yellow solid (157 mg, 0.434 mmol, 62% yield). It was further purified by recrystallization from acetone: mp = 168–170 °C; ^{1}H-NMR ($CDCl_3$, r.t.) δ 8.20–8.17 (m, 4H), 7.77 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.48–7.38 (m, 6H), 7.04 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 157.8, 138.4, 133.4, 131.9, 130.2, 130.1 (2C), 129.8, 129.0, 127.8, 127.4, 126.6, 126.5, 126.4 (2C), 125.3 (2C), 125.1, 124.9, 119.0 (2C), 118.7 (2C), 112.6; IR (KBr) ν 2953, 1609, 1510, 811, 768 cm^{-1}. HRMS Calcd for $C_{27}H_{19}O$: $[M+H]^+$, 359.1436; Found: 359.1420.

3-[4-(Trifluoromethyl)phenyl]perylene. The title compound was synthesized from 3-bromoperylene (230 mg, 0.700 mmol) and 4-(trifluoromethyl)phenylboronic acid (159 mg, 1.05 mmol) and purified following the procedure for 3-phenylperylene. 3-[4-Trifluoromethyl]phenyl]perylene was obtained as a yellow solid (178 mg, 0.449 mmol, 64%

yield). It was further purified by recrystallization from acetone: mp = 248–251 °C; ^{1}H-NMR ($CDCl_3$, r.t.) δ 8.26–8.16 (m, 4H), 7.78–7.62 (m, 7H), 7.51–7.38 (m, 4H); ^{13}C-NMR ($CDCl_3$, r.t.) δ 144.6, 138.3, 134.7, 132.7, 132.6, 131.7, 131.5, 131.3, 131.0, 130.4, 128.7, 128.2, 128.1, 128.0, 127.9, 127.1, 127.0, 126.8, 126.7, 125.5 (2C), 125.4, 120.6 (2C), 120.5, 119.9; IR (KBr) ν 1614, 1499, 1389, 811, 768 cm^{-1}. HRMS Calcd for $C_{27}H_{16}F_3$: $[M+H]^+$, 397.1204; Found: 397.1188.

4. NMR spectra

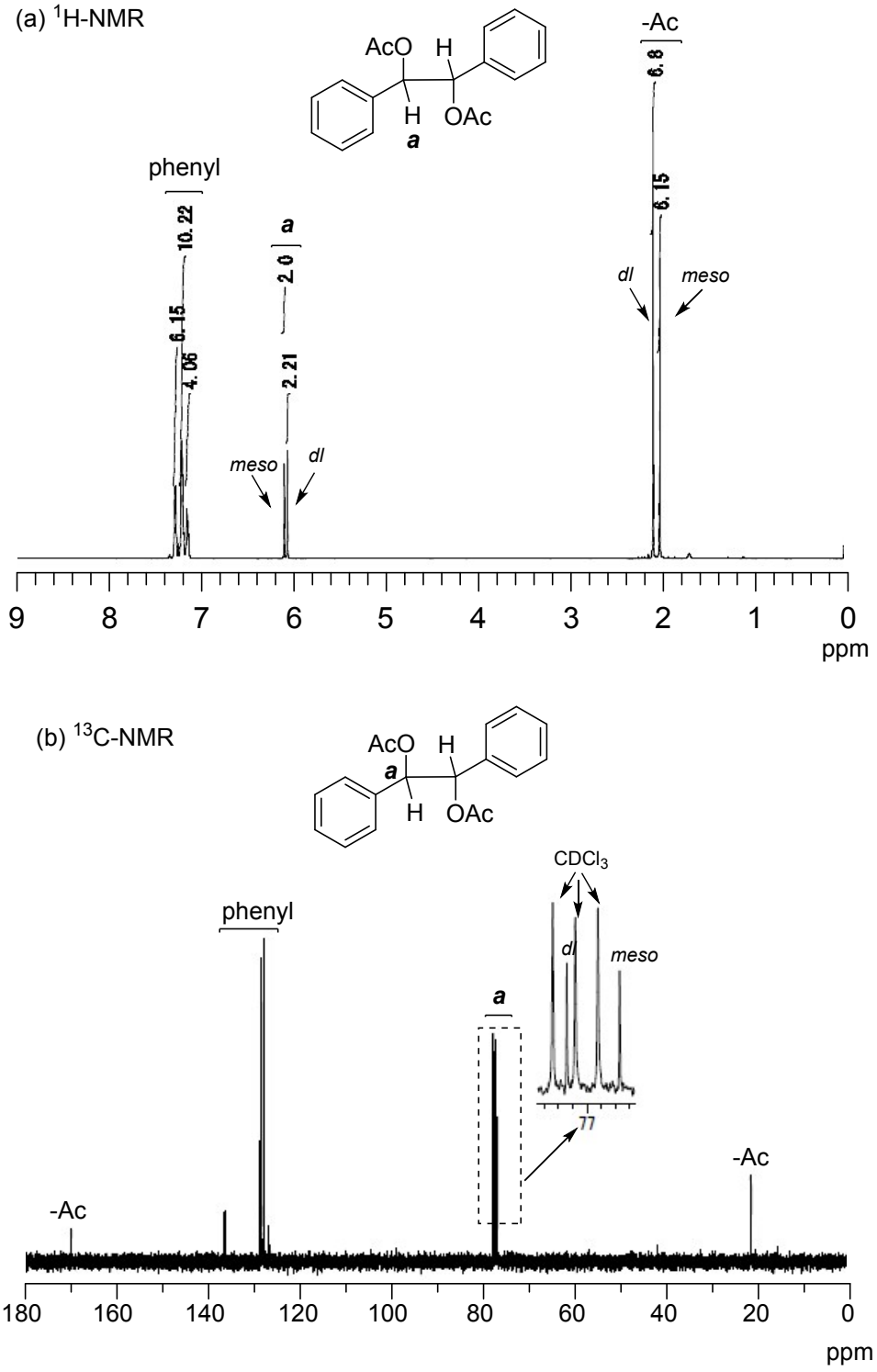
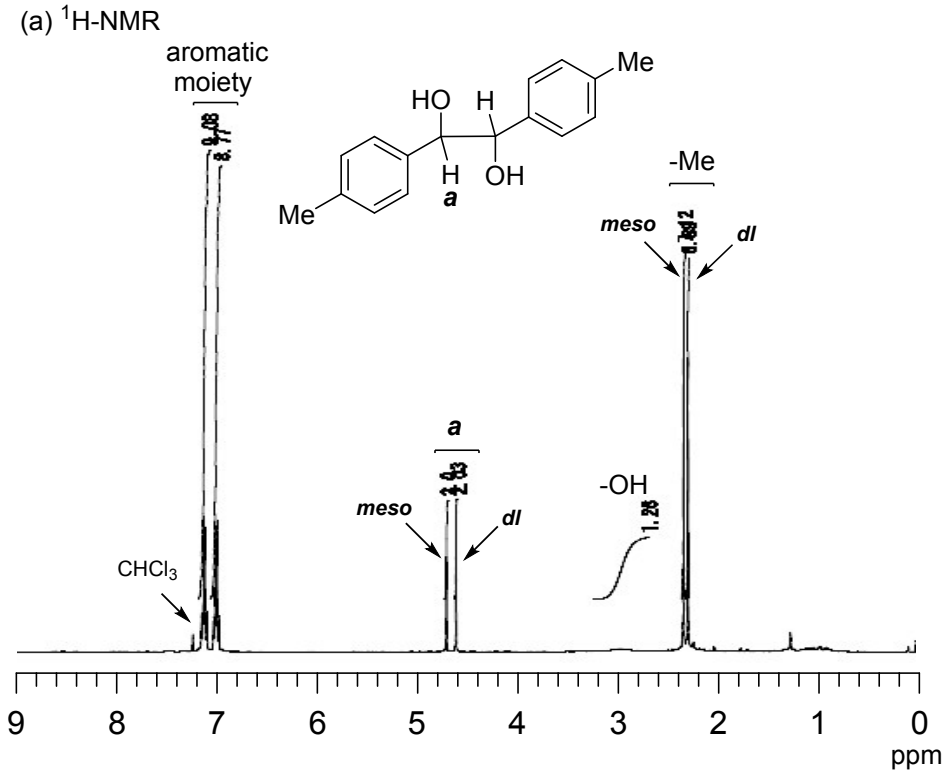


Figure S3. ^{1}H and ^{13}C-NMR spectra of diacetate **2a**



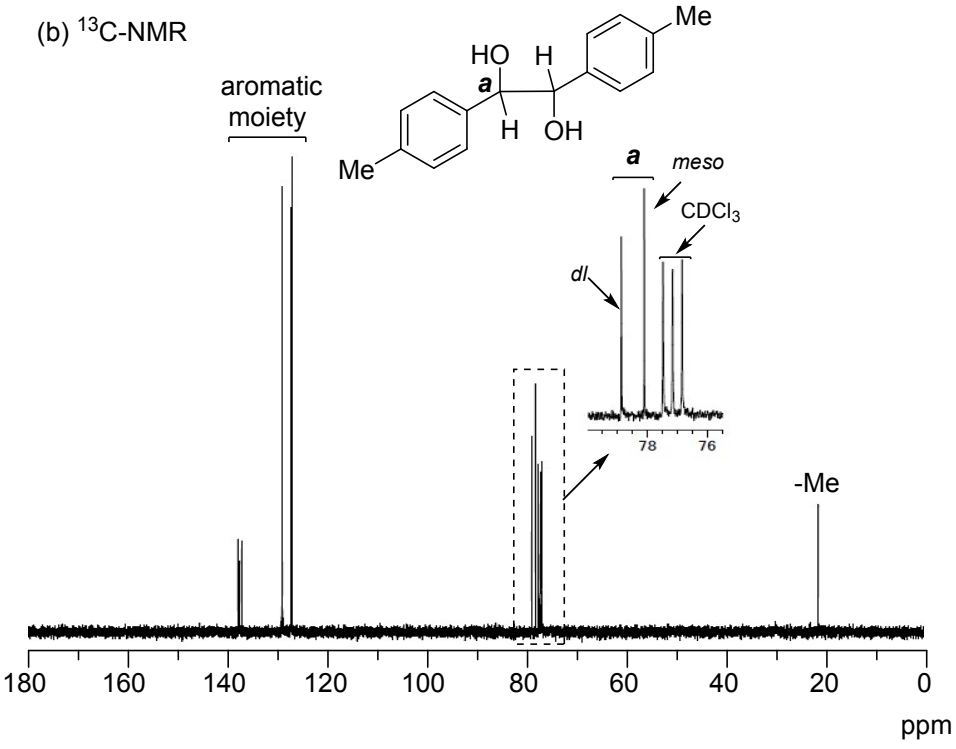
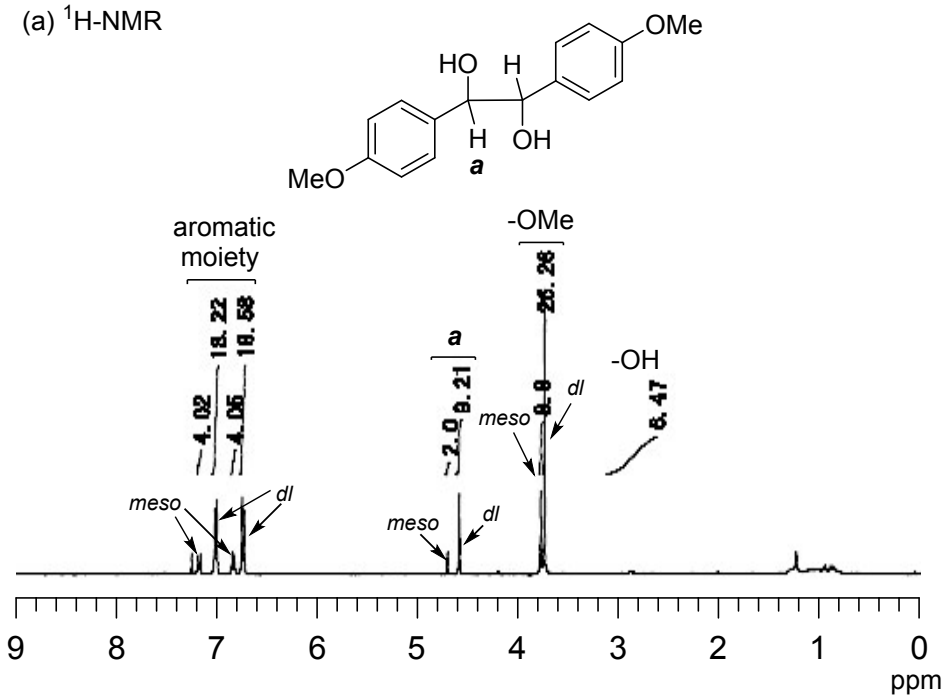


Figure S4. ^{1}H and ^{13}C-NMR spectra of diol **1b**



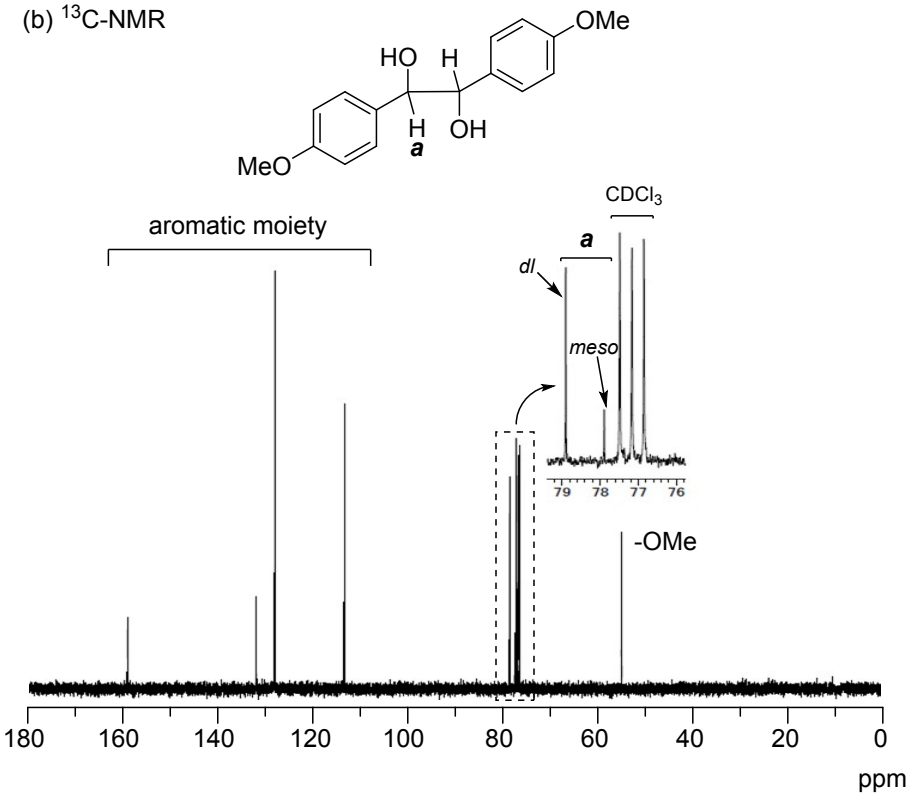


Figure S5. ^{1}H and ^{13}C-NMR spectra of diol **1c**

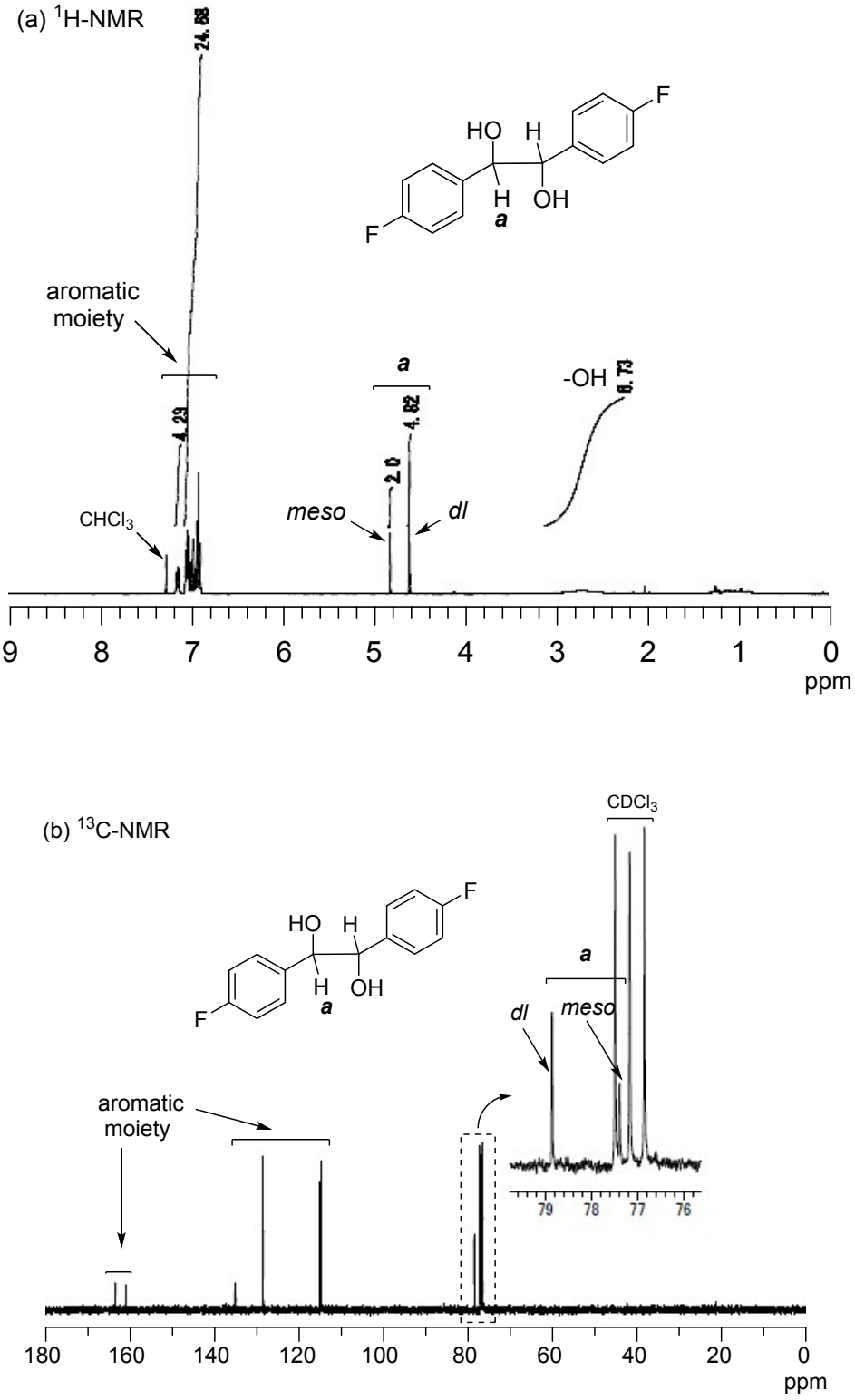


Figure S6. ^{1}H and ^{13}C-NMR spectra of diol **1d**

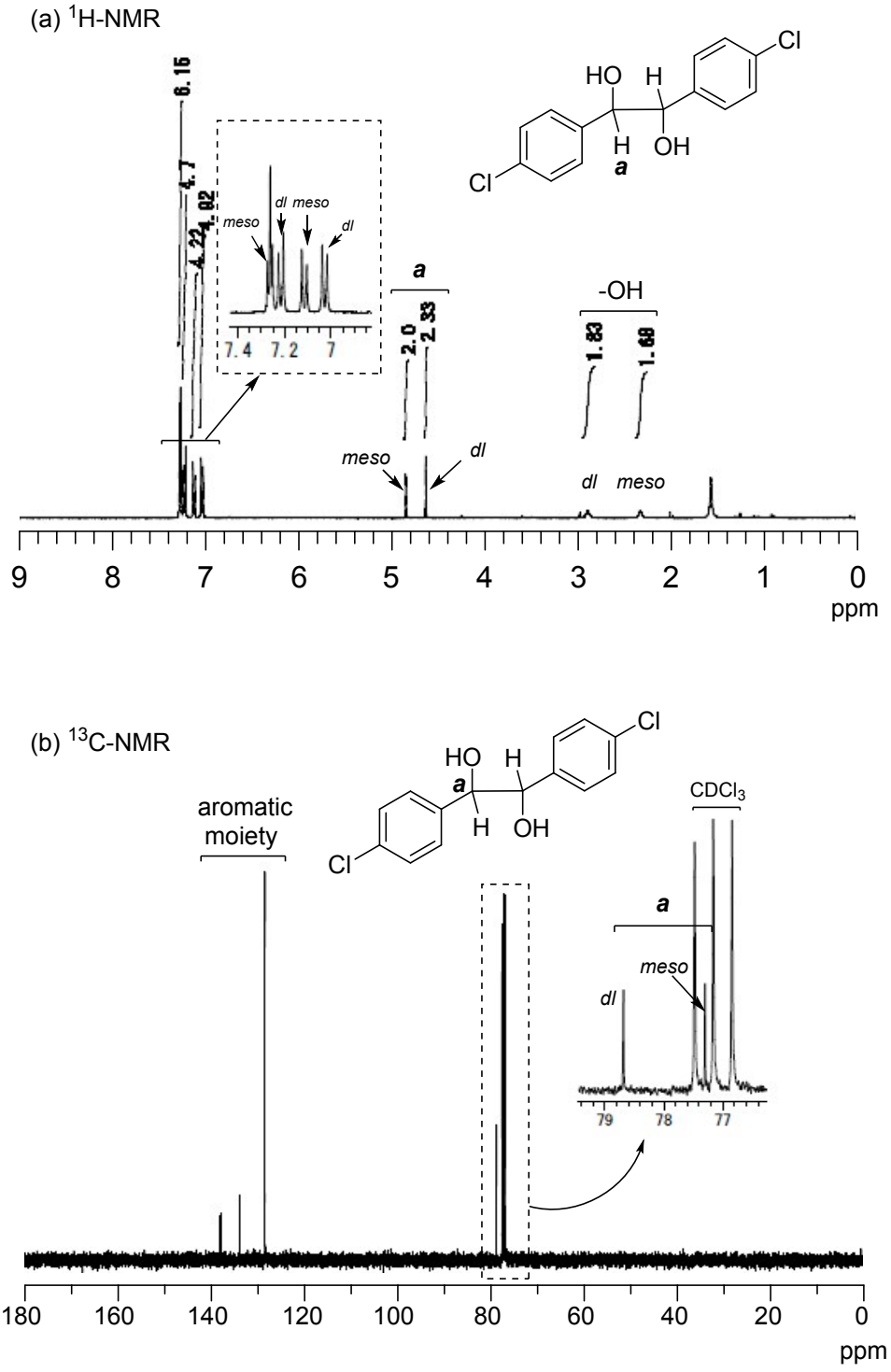


Figure S7. ^{1}H and ^{13}C-NMR spectra of diol **1e**

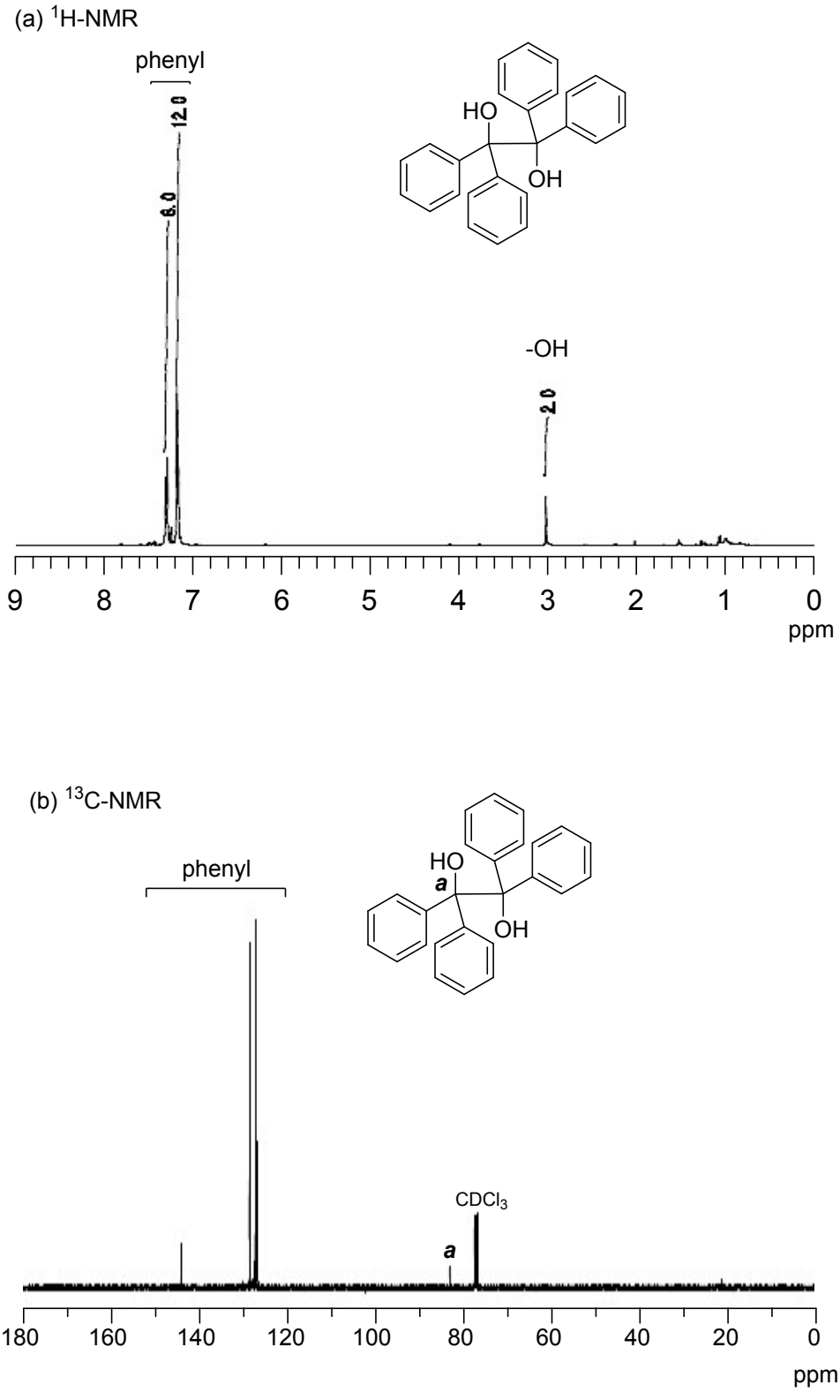
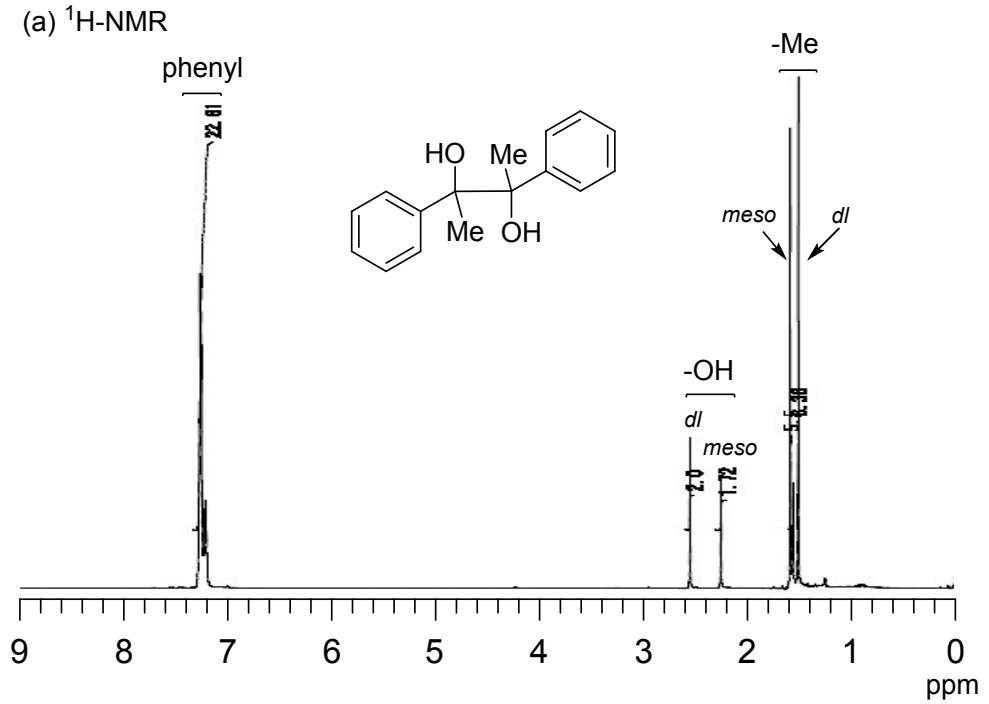


Figure S8. ^{1}H and ^{13}C-NMR spectra of diol **1f**



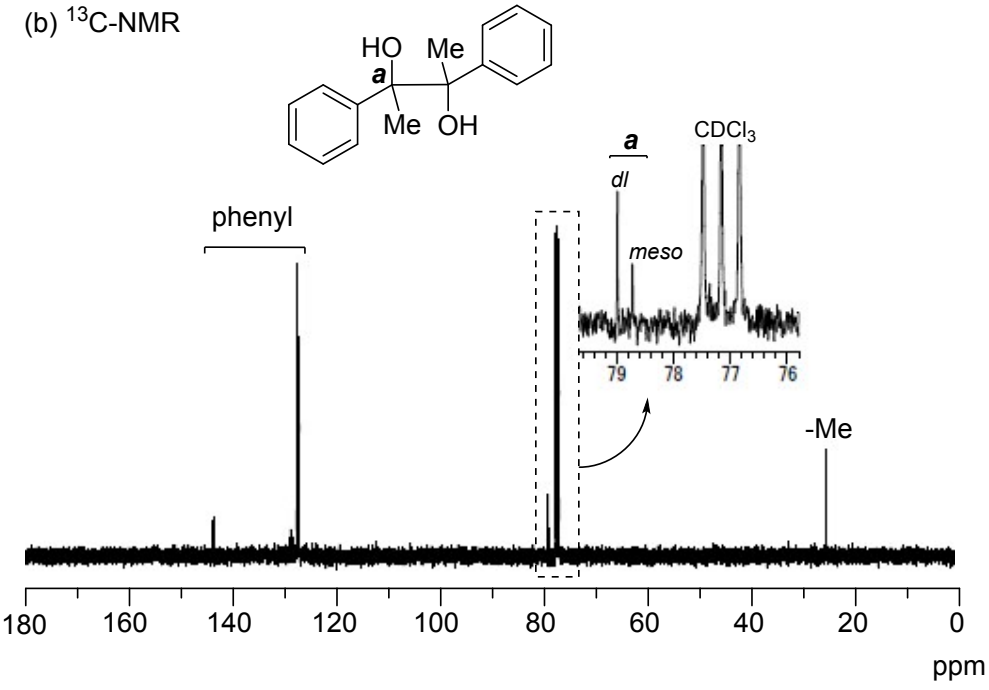


Figure S9. ^{1}H and ^{13}C-NMR spectra of diol **1g**

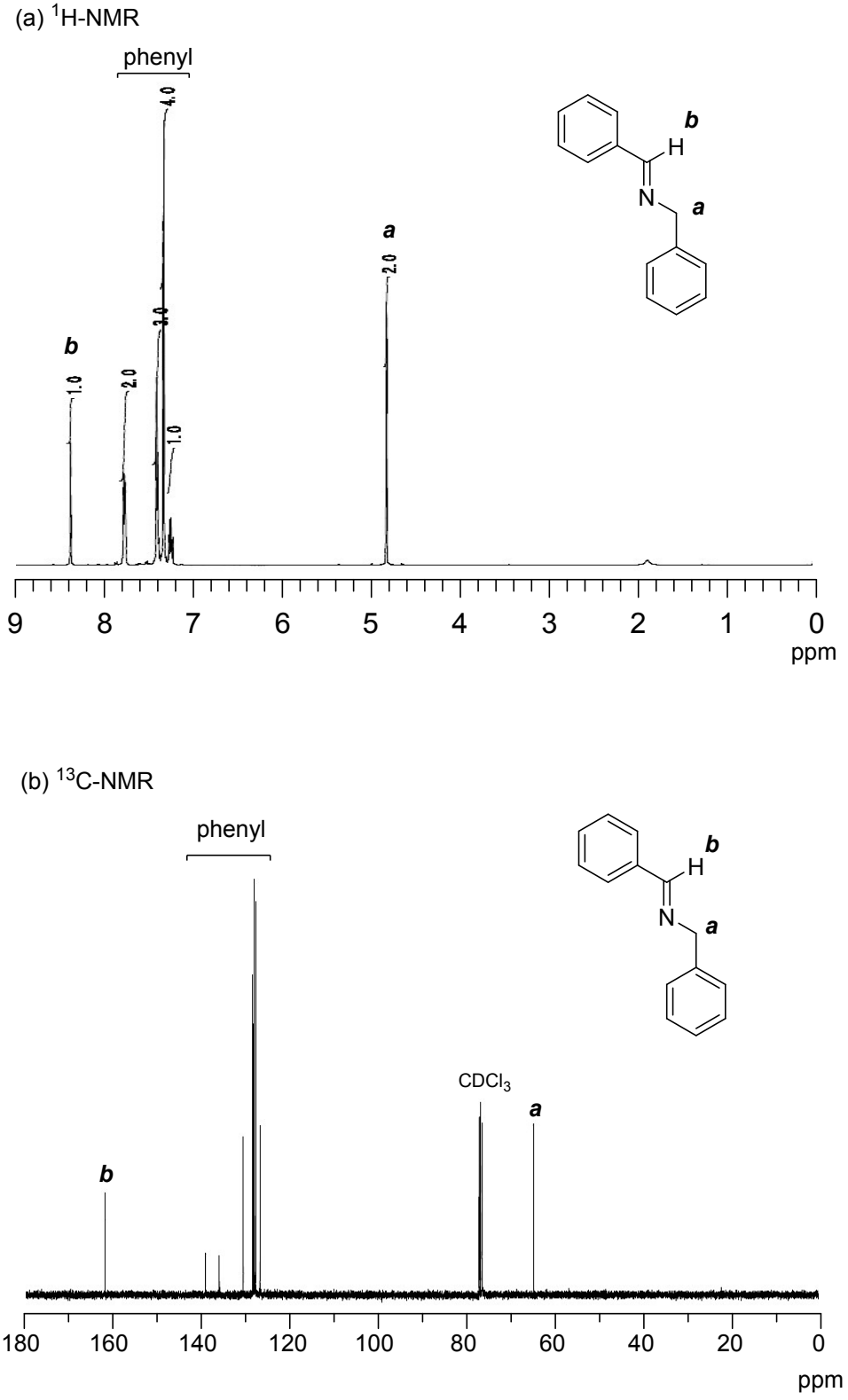


Figure S10. ^{1}H and ^{13}C-NMR spectra of imine **3**

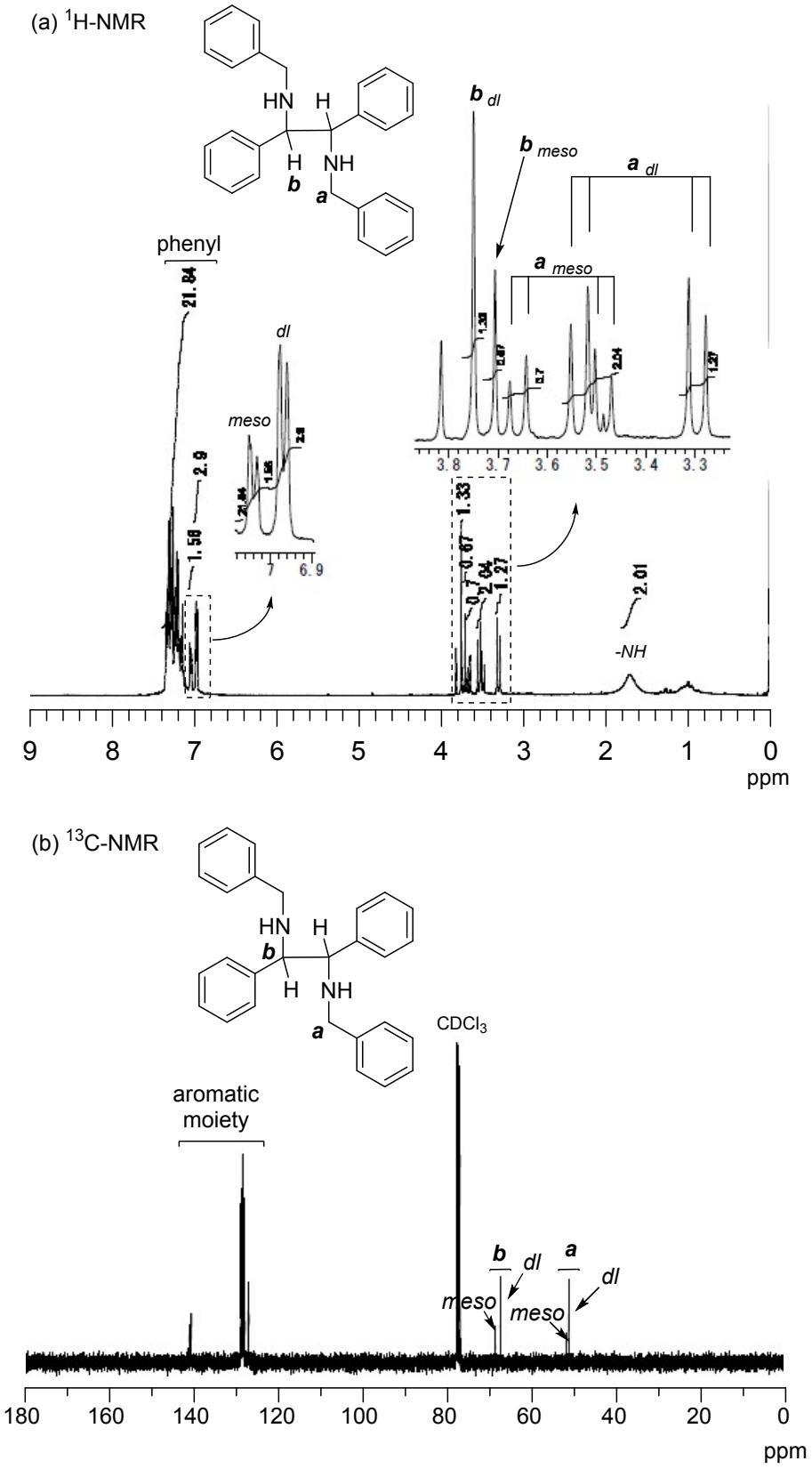


Figure S11. ^{1}H and ^{13}C-NMR spectra of diamine **4**

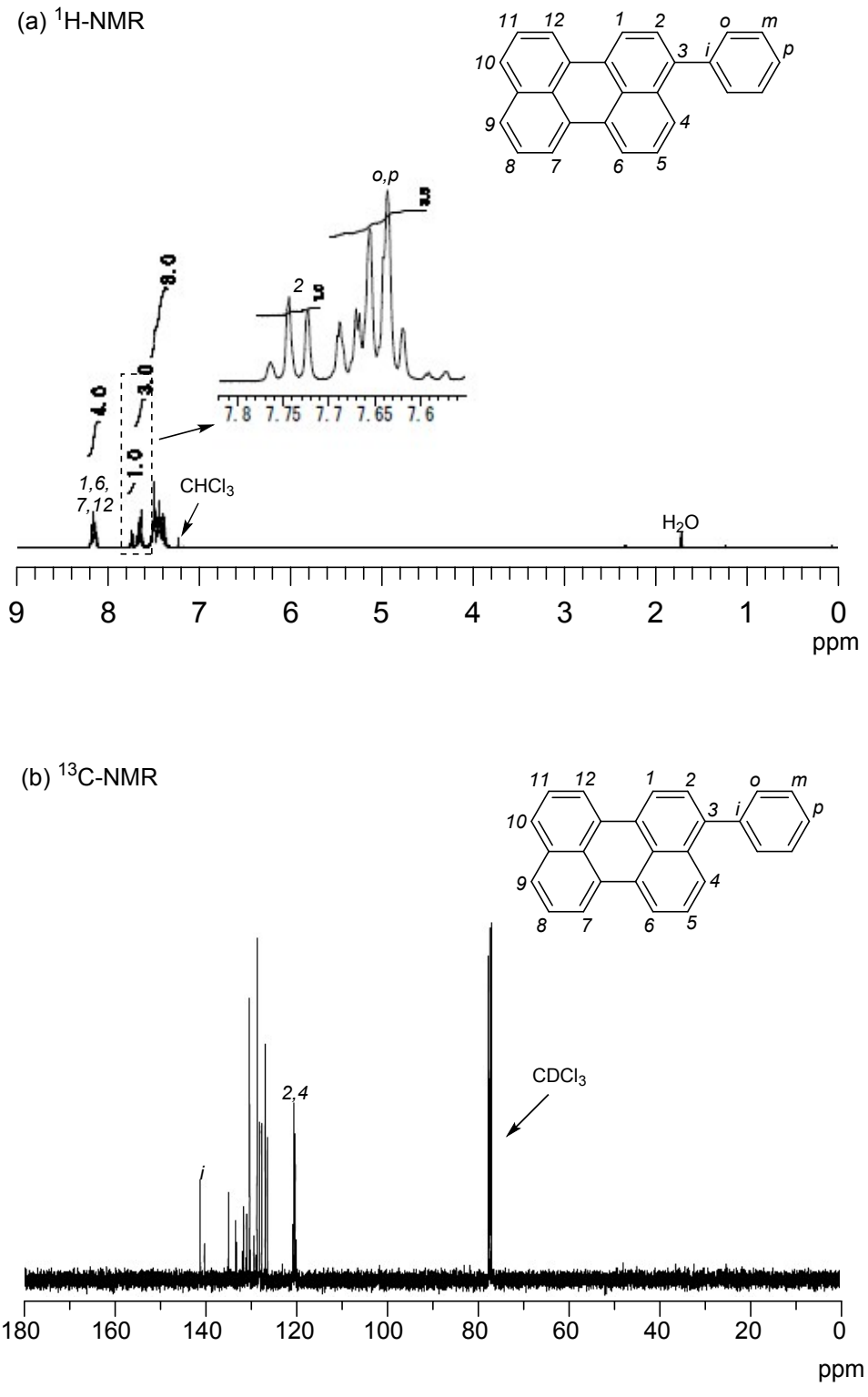
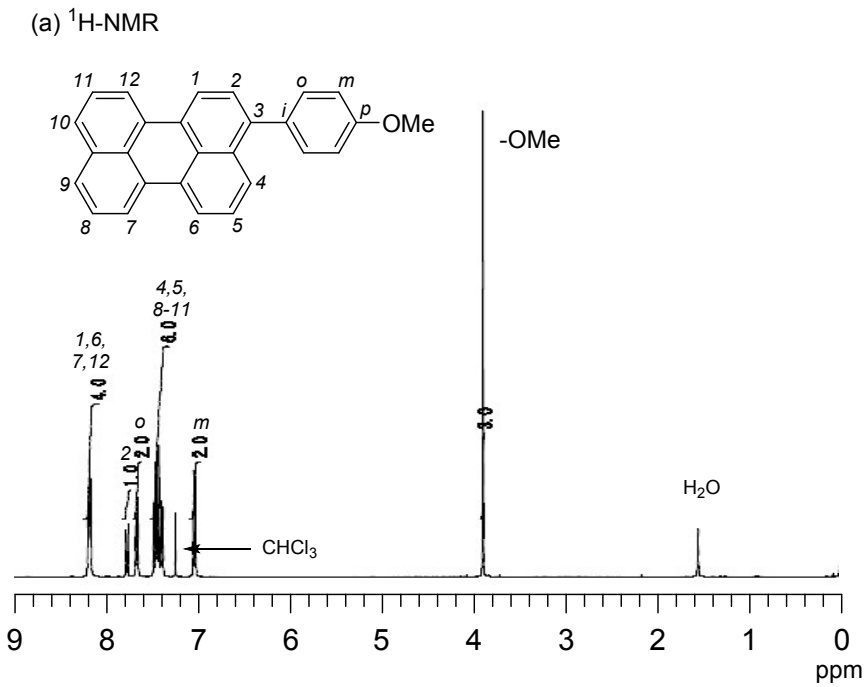


Figure S12. ^{1}H and ^{13}C-NMR spectra of 3-phenylperylene



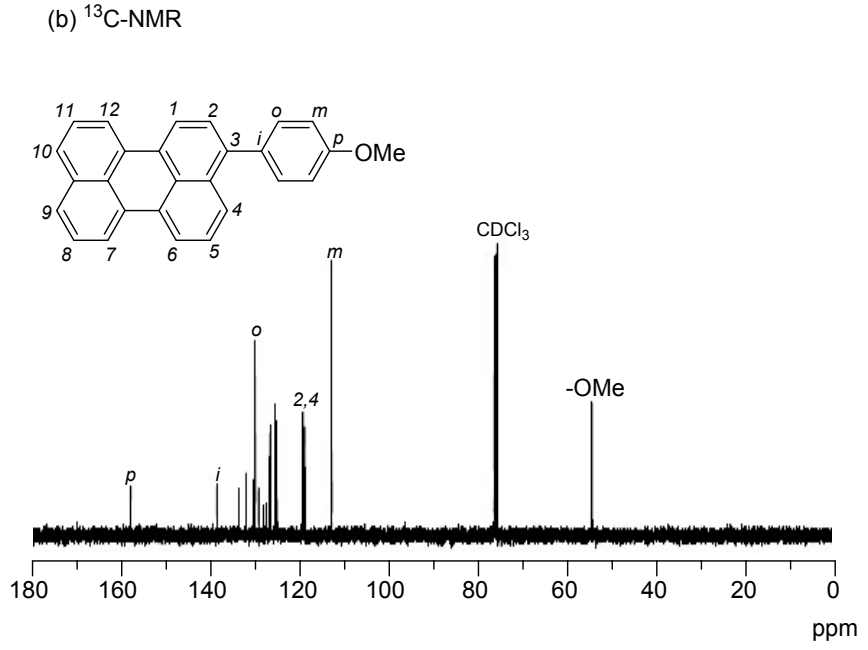


Figure S13. ^{1}H and ^{13}C-NMR spectra of 3-(4-methoxyphenyl)perylene

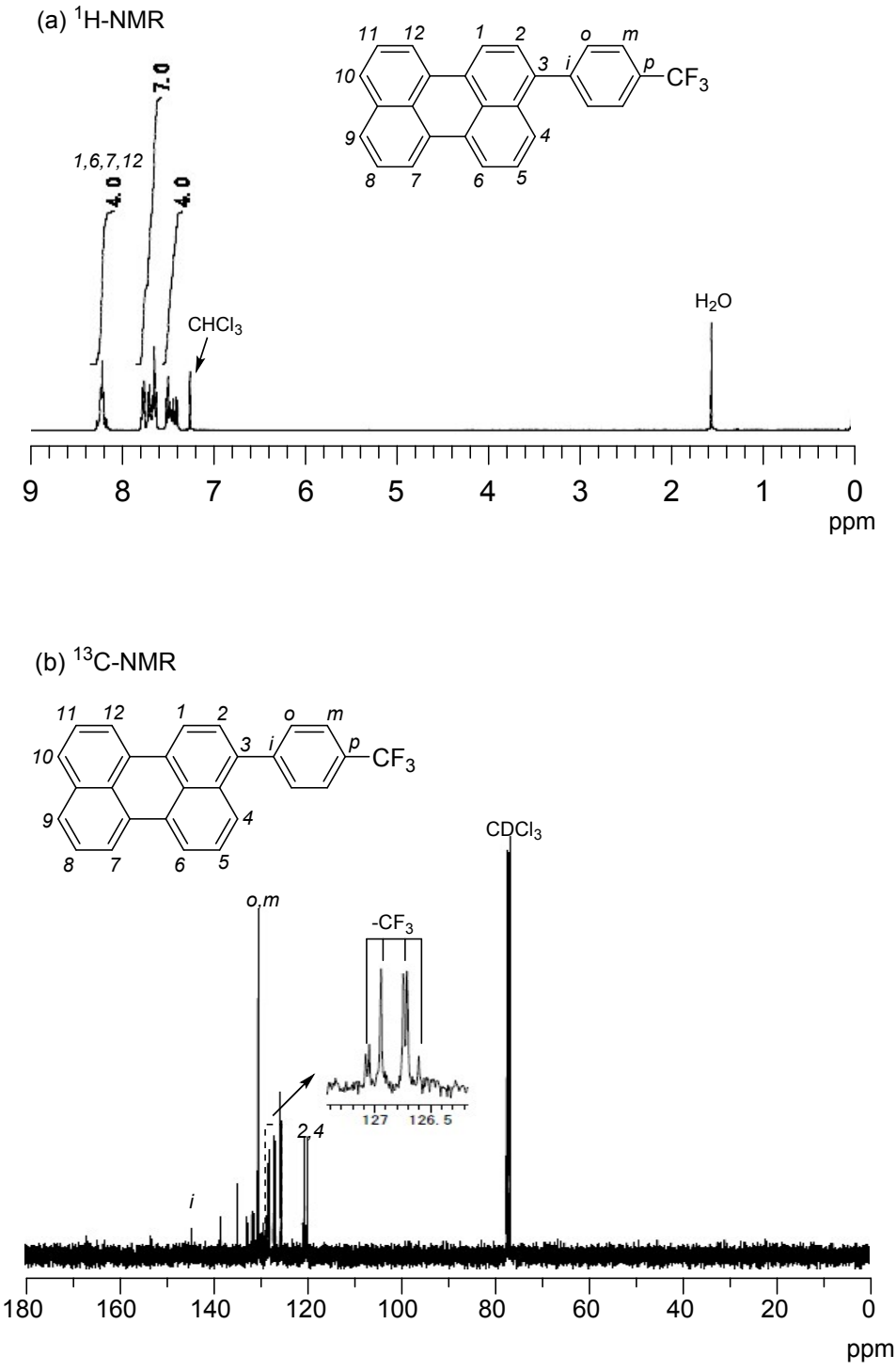


Figure S14. ^{1}H and ^{13}C-NMR spectra of 3-[4-(trifluoromethyl)phenyl]perylene