Supporting Information for:

Synthesis, Reactivity and Electronic Properties of 6,6-Dicyanofulvenes

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Experimental:

Materials: Synthetic manipulations that required an inert atmosphere (where noted) were carried out under argon using standard Schlenk techniques. All solvents were of ACS reagent grade or better unless otherwise noted. Anhydrous tetrahydrofuran, toluene and dichloromethane were obtained from J. T. Baker and dried on a solvent column purification system. Silica gel (40-63 μm) was obtained from SiliCycle Inc. Benzil, 3-pentanone, malononitrile, 1,3-diphenylacetone, acenaphthenequinone, tetracyclone, and $TiCl_4$ were purchased from Aldrich and used without further purification.

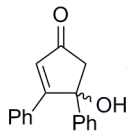
NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra for all compounds were acquired in $CHCl_3$ on a Bruker Avance Spectrometer operating at 400 and 100 MHz, respectively. The chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual $CHCl_3$.

Mass Spectrometry: High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion, employing either electron impact or electrospray as the ionization technique.

Infrared (IR) spectroscopy: IR spectra were recorded on a Perkin-Elmer Model 2000 FT-IR spectrophotometer at the MIT Department of Chemistry Instrumentation Facility and are reported as strong (s), medium (m) or weak (w).

X-Ray Diffraction: X-ray crystal structures were determined with a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), performing □- and ω-scans. All structures were solved by direct methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[2] All non-hydrogen atoms were refined anisotropically.

[1] Sheldrick, G. M. *Acta Cryst. A* **1990**, *46*, 467.
[2] Sheldrick, G. M. SHELXL 91, Universtität Göttingen, Göttingen, Germany, 1997



1

4-hydroxy-3,4-diphenylcyclopent-2-enone (1). 15 mL of 10% methanolic potassium hydroxide was added to a solution of benzil (30g, 143 mmol) and acetone (23 mL, 317 mmol) in 300 mL refluxing methanol. The mixture was heated at 90°C for 30 minutes, cooled to room temperature and poured into 500 mL ice/water. The resulting solids were filtered, washed with water and dried to yield 30 g of a faint-yellow powder (84%).

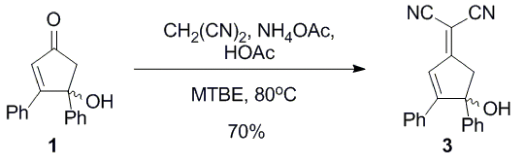
^{1}H NMR (400 MHz, $CHCl_3$) δ 2.85 (d, *J* = 18.4 Hz, 1H), 2.90 (broad singlet, 1H), 2.93 (d, *J* = 18.4 Hz, 1H), 6.65 (s, 1H), 7.30 (m, 6H), 7.41 (m, 2H), 7.49 (m, 2H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 56.7, 81.8, 124.3, 127.6, 128.9, 129.1, 129.2, 129.3, 131.1, 131.5, 144.2, 174.2, 205.1.

HRMS (ESI) calc for $C_{17}H_{14}O_2$ $[M-H]^-$ 249.0921, found 249.0915.

IR (KBr plate) 700 (s), 766 (m), 976 (m), 1049 (m), 1210 9s), 1249 (m), 1324 (w), 1447 (m), 1569 (s), 1685 (s), 3027 (m), 3061 (m), 3388 (s) cm-^{1}.

m.p. 146-148°C



2-(4-hydroxy-3,4-diphenylcyclopent-2-en-1-ylidene)malononitrile (3). Compound **1** (10g, 40 mmol) and malononitrile (13.1g, 198 mmol) were dissolved in 200 mL t-butyl methyl ether and to this solution was added 15 g ammonium acetate and 10 mL acetic acid. The resulting mixture was heated to 80°C for 30 h with a Dean-Stark trap to remove excess water. Upon cooling, diethyl ether (50 mL) was added to the reaction and a yellow solid started to precipitate. The solids were isolated by filtration, washed with cold diethyl ether and dried. Purification by flash column chromatography with 1% methanol in dichloromethane afforded 8.3 g of a bright yellow solid (70%).

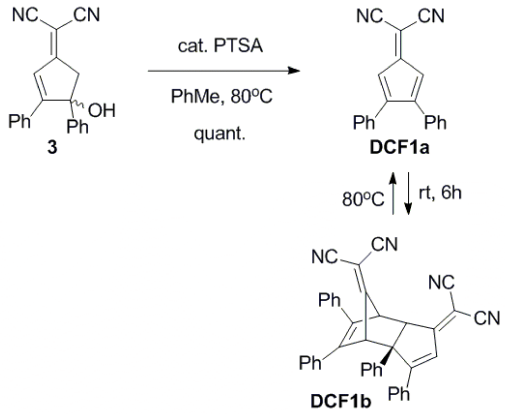
^{1}H NMR (400 MHz, $CHCl_3$) δ 2.83 (broad singlet, 1H), 3.43 (s, 2H), 7.25 (s, 1H), 7.35 (m, 8H), 7.62 (m, 2H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 27.1, 53.1, 75.2, 85.5, 112.6, 112.98, 124.13, 126.42, 128.3, 129.3, 129.3, 129.6, 130.8, 132.1, 143.2, 169.5, 177.4.

HRMS (ESI) calc for $C_{20}H_{14}N_2O$ $[M-H]^-$ 297.1033, found 297.1023.

IR (KBr plate) 1564 (m), 1586 (m), 2225 (m), 3426 (m) cm^{-1}.

m.p. 192-194°C



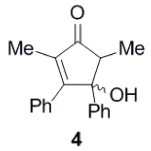
2,3-Diphenyl-6,6-dicyanofulvene dimer (DCF1b). A mixture of compound **3** (0.10g, 0.33 mmol) and PTSA (20 mg, 105 mmol) in toluene (20 mL) was heated to 80°C for 3 hours. The initially inhomogeneous reaction mixture was observed to turn homogenous after 5 minutes and the reaction mixture turned dark brown with heating. If, at this point, the reaction mixture was taken off the heat and cooled to room temperature, the dark brown solution was observed to turn bright yellow after approximately 6 hours. If, instead, the solvent from the reaction was evaporated under reduced pressure, the dark brown reaction mixture was observed to turn bright yellow almost immediately as the solvent evaporated. The monomeric **DCF1a** could therefore not be isolated as a solid directly from the reaction mixture. After complete solvent evaporation, the remaining yellow residue was purified by flash column chromatography with 70% dichloromethane in hexanes to afford approximately 0.09g of **DCF1b** as a bright yellow solid (97%). Heating a solution of **DCF1b** to approximately 80°C turned the initially yellow solution dark brown and subsequent cooling reverts the color back to bright yellow.

^{1}H NMR (400 MHz, $CHCl_3$) δ 3.95 (d, *J* = 4.4 Hz, 1H), 4.60 (dd, *J* = 2 Hz, 4.4 Hz, 1H), 4.92 (d, *J* = 2 Hz, 1H), 6.82 (m, 2H), 6.90 (m, 2H), 6.99 (m, 1H), 7.13 (m, 2H), 7.26 (m, 7H), 7.34 (m, 6H), 7.46 (m, 3H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 27.1, 53.5, 56.5, 60.2, 67.1, 72.3, 110.3, 111.6, 112.2, 113.1, 125.6, 128.2, 128.4, 128.5, 128.9, 129.0, 129.2, 129.3, 129.4, 129.7, 130.4, 130.7, 131.6, 132.2, 132.4, 132.8, 139.1, 139.9, 140.2, 168.6, 177.0, 184.6.

HRMS (ESI) calc for $C_{40}H_{24}N_4$ $[M-H]^-$ 559.1928, found 559.1930.

IR (KBr plate) 695 (s), 736 (m), 764 (m), 1345 (m), 1445 (s), 1546 (s), 1566 (s), 1648 (m), 2225 (s), 3028 (m), 3058 (m) cm^{-1}.



4

4-hydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-enone (4). 15 mL of 10% methanolic potassium hydroxide was added to a solution of benzil (30g, 143 mmol) and 3-pentanone (15 mL, 150 mmol) in 300 mL refluxing methanol. The mixture was heated at 90°C for 30 minutes, cooled to room temperature and poured into 500 mL ice/water. The resulting solids were filtered, washed with water and dried to yield 33 g of **4** as an approximately 3:1 mixture of diastereomers, by ^{1}H-NMR (85% total). The diastereomeric mixture was carried on to the next step without further purification.

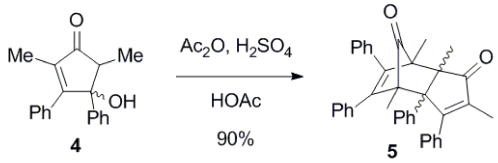
^{1}H NMR (Major diastereomer) (400 MHz, $CHCl_3$) δ 1.19 (d, *J* = 7.2 Hz, 3H), 1.94 (s, 3H), 2.42 (broad singlet, 1H), 2.68 (quartet, *J* = 7.2 Hz, 1H), 7.23 (m, 10H).

^{13}C NMR (mixture of diastereomers) (100 MHz, $CHCl_3$) δ 10.0, 10.1, 10.3, 10.4, 56.1, 55.9, 82.7, 85.1, 125.1, 125.8, 127.2, 127.8, 128.4, 128.6, 128.8, 129.1, 129.2, 129.2, 129.5, 130.1, 132.9, 133.6, 135.1, 137.6, 137.9, 141.6, 144.3, 166.4, 167.7, 207.1, 209.8.

HRMS (ESI) calc for $C_{19}H_{18}O_2$ $[M+H]^+$ 279.1380, found 279.1374.

IR (KBr plate) 699 (s), 1341 (m), 1448 (m), 1622 (m), 1693 (s), 2934 (m), 2977 (m), 3060 (m), 3437 (s) cm^{-1}.

m.p. 172-174°C



4 5

Compound 5. Compound **4** (20 g, 71.9 mmol) was dissolved in 50 mL acetic acid and to this solution was added 20 ml acetic anhydride and 1 mL concentrated sulfuric acid. The reaction was stirred at room temperature for 3 hours and then poured over ice (200 g). The solids were filtered, washed with saturated sodium bicarbonate and water, and dried to yield 33.5 g of a yellow powder (90%)

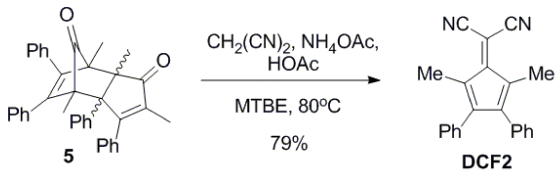
^{1}H NMR (400 MHz, $CHCl_3$) δ 0.57 (s, 3H), 1.25 (s, 3H), 1.63 (s, 3H), 2.24 (s, 3H), 6.66 (d, *J* = 2 Hz, 2H), 7.3 (m, 18H), 7.52 (m, 2H), 7.65 (m, 1H), 7.98 (m, 1H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 10.0, 12.5, 12.6, 18.2, 58.6, 59.9, 61.2, 66.9, 127.0, 127.1, 127.2, 127.4, 127.5, 128.1, 129.2, 129.5, 130.1, 130.3, 1301.0, 132.0, 133.5, 134.1, 135.1, 140.3, 143.4, 203.3

HRMS (ESI) calc for $C_{38}H_{32}O_2$ $[M+H]^+$ 521.2475, found 521.2472.

IR (KBr plate) 700 (m), 732 (m), 911 9w), 1211 (m), 1335 (m), 1447 (m), 1494 (m), 1598 (m), 1685 (s), 1768 (s), 2938 (m), 2980 (m), 3058 (m) cm^{-1}.

m.p. (decomp) 190°C



1,4-Dimethyl-2,3-diphenyl-6,6-dicyanofulvene (DCF2). Compound **5** (10g, 19.2 mmol) and malononitrile (8g , 121 mmol) were dissolved in 200 mL t-butyl methyl ether and to this solution was added 15 g ammonium acetate and 10 mL acetic acid. The resulting mixture was heated to 80°C for 20 h with a Dean-Stark trap to remove excess water. Water (100 mL) was added to the cooled reaction, the layers separated and the aqueous phase extract with ether (3x 30 mL). The organic layers were combined and dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue thus obtained was purified by flash column chromatography with 40% dichloromethane in hexanes as eluent to yield 4.6 g of a dark purple powder (79%).

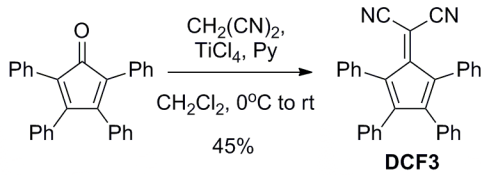
^{1}H NMR (400 MHz, $CHCl_3$) δ 2.21 (s, 3H), 6.85 (m, 2H), 7.22 (m, 3H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 12.9, 82.7, 113.3, 125.8, 128.1, 128.8, 129.6, 133.0, 151.8, 171.2.

HRMS (ESI) calc for $C_{22}H_{16}N_2$ $[M+H]^+$ 309.1386, found 309.1371.

IR (KBr plate) 700 (s), 764 (s), 1343 (m), 1444 (m), 1560 (m), 2222 (s), 2919 (m), 2951 (m), 3080 (w) cm^{-1}.

m.p. 148-150°C



DCF3

1,2,3,4-Tetraphenyl-6,6-dicyanofulvene (DCF3). To an ice-cooled solution of tetracyclone (3g , 7.8 mmol) and malononitrile (1g, 15 mmol) in 100 mL dry dichloromethane was added dropwise $TiCl_4$ (4.4 mL) over 5 minutes under argon. After the addition was complete, 15 mL pyridine was added to the reaction dropwise over 10 minutes. The reaction mixture was allowed to warm to room temperature and stir under argon for an additional 2 hours. The solvents were evaporated under reduced pressure, and the remaining solids were taken up in 50 mL dichloromethane and washed with 0.1M HCl. The organic layer was dried over magnesium sulfate, solvents evaporated under reduced pressure and the residue purified by flash column chromatography with 40% dichloromethane in hexanes as eluent. 1.5 g of a yellow-green powder was thus obtained (45%).

^{1}H NMR (400 MHz, $CHCl_3$) δ 6.83 (m, 2H), 7.02 (t, *J* = 8 Hz, 2H), 7.13 (m, 1H), 7.29 (m, 2H), 7.37 (m, 2H).

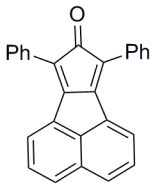
^{13}C NMR (100 MHz, $CHCl_3$) δ 86.7, 111.5, 1127.7, 128.8, 128.9, 129.3, 130.0, 131.3, 131.9, 131.9, 132.6, 151.3, 168.7

HRMS (DART) calc for $C_{32}H_{20}N_2$ [M-] 432.1632, found 432.1618.

IR (KBr plate) 697 (m), 1027 (m), 1246 (m), 1376 (m), 1457 (m), 2221 (m), 2868 (m), 2923 (s), 2954 (s) cm^{-1}.

Tetracyclone: IR (KBr plate) 1712 cm^{-1}.

m.p. 220-222°C



6

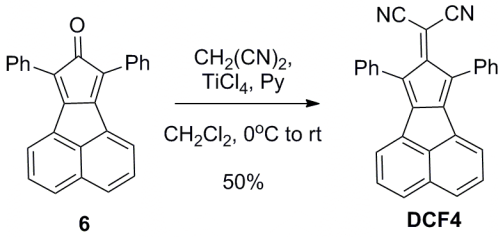
7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one (6). 5 mL of 10% methanolic potassium hydroxide was added to a solution of acenaphthenequinone (5g, 27 mmol) and 1,3-diphenylacetone (6 g, 28.5 mmol) in 200 mL refluxing methanol. The mixture was heated at 90^{o}C for 30 minutes and then placed in a -4^{o}C refrigerator. After 3 hours, the resulting black crystals were filtered, washed with methanol and dried to yield 7.8g of **6** (80%).

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.38 (m, 1H), 7.47 (m, 2H), 7.55 (m, 1H), 7.82 (m, 3H), 8.03 (m, 1H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 121.1, 121.8, 127.9, 128.5, 128.6, 128.8, 129.2, 131.6, 131.7, 154.4, 202.1

HRMS (ESI) calc for $C_{27}H_{15}O$ $[M-H]^-$ 355.1128, found 355.1134.

IR (KBr plate) 697 (m), 799 (m), 1121 (m), 1297 (m), 1696 (m), 2923 (m) cm^{-1}.



6 **DCF4**

2-(7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-ylidene)malononitrile (DCF4). To an ice-cooled solution of **6** (3g , 16.8 mmol) and malononitrile (1.5g, 22.7 mmol) in 100 mL dry dichloromethane was added dropwise $TiCl_4$ (5.5 mL) over 5 minutes under argon. After the addition was complete, 18 mL pyridine was added to the reaction dropwise over 10 minutes. The reaction mixture was allowed to warm to room temperature and stir under argon for an additional 2 hours. The solvents were evaporated under reduced pressure, and the remaining solids were taken up in 50 mL dichloromethane and washed with 0.1M HCl. The organic layer was dried over magnesium sulfate, solvents evaporated under reduced pressure and the residue purified by flash column chromatography with 40% dichloromethane in hexanes as eluent. 1.7 g of a forest green powder was thus obtained (50%).

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 8 Hz, 2H), 7.54 (m, 10H), 7.75 (d, *J* = 8 Hz, 2H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 85.3, 111.8, 121.2, 126.5, 127.9, 128.7, 129.2, 129.7, 129.9, 130.4, 131.8, 132.1, 148.1, 152.5, 174.0.

HRMS (DART) calc for $C_{30}H_{16}N_2$ [M-] 404.1319, found 404.1303.

IR (KBr plate) 701 (m), 761 (m), 1244 (m), 1551 (m), 2221 (s), 2927 (m) cm^{-1}.

m.p. 275^{o}C

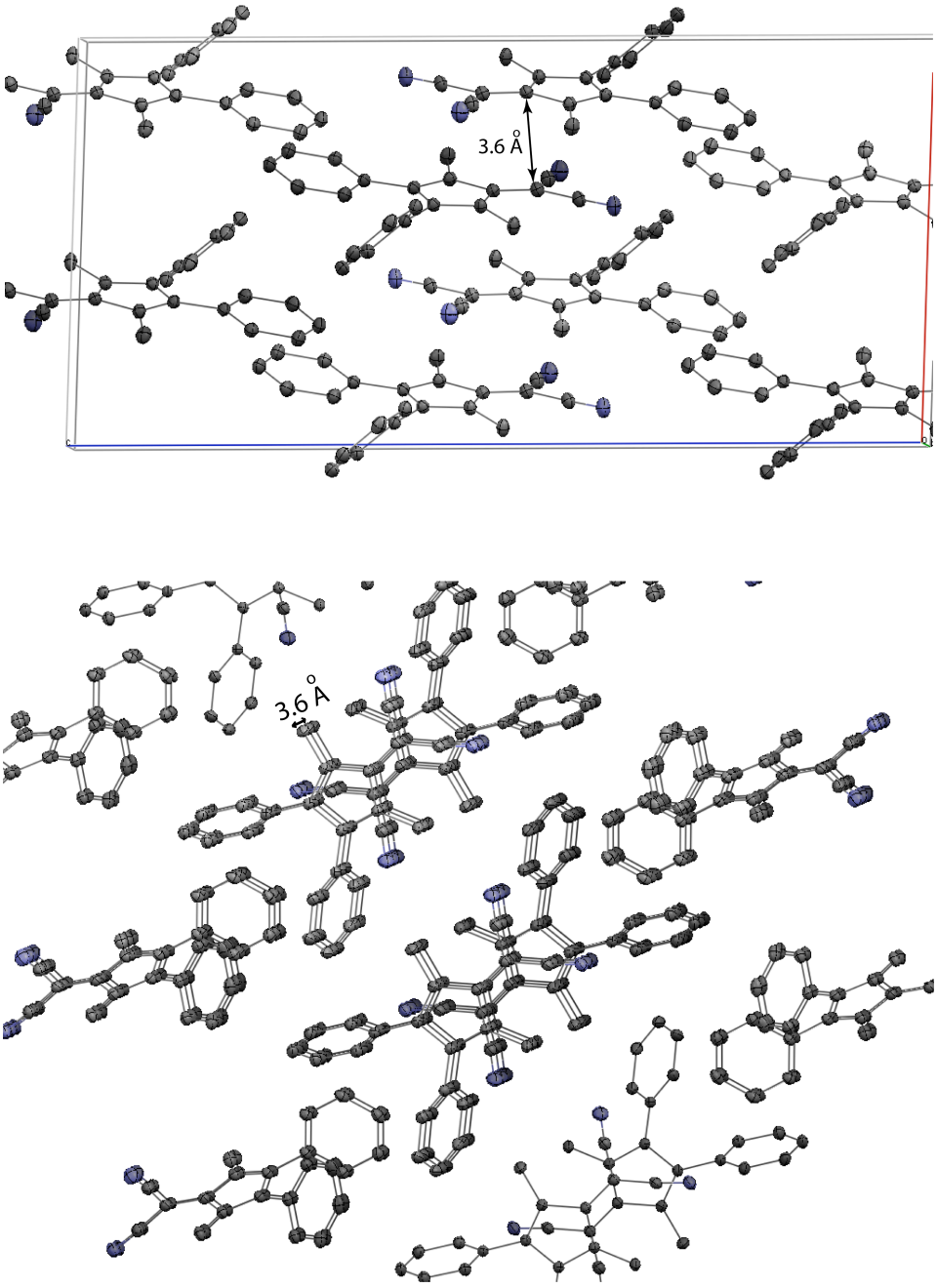


Figure S1. Select views of the packing structure of **DCF2**, showing the absence of herringbone packing between fulvene cores. The intermolecular separation between fulvene cores is ca. 3.6 Å, which is slightly higher than the characteristic π-π stacking distance (3.45 Å). The increased separation between fulvene cores is most likely due to steric crowding arising from the methyl substituents in the 1- and 4-positions.

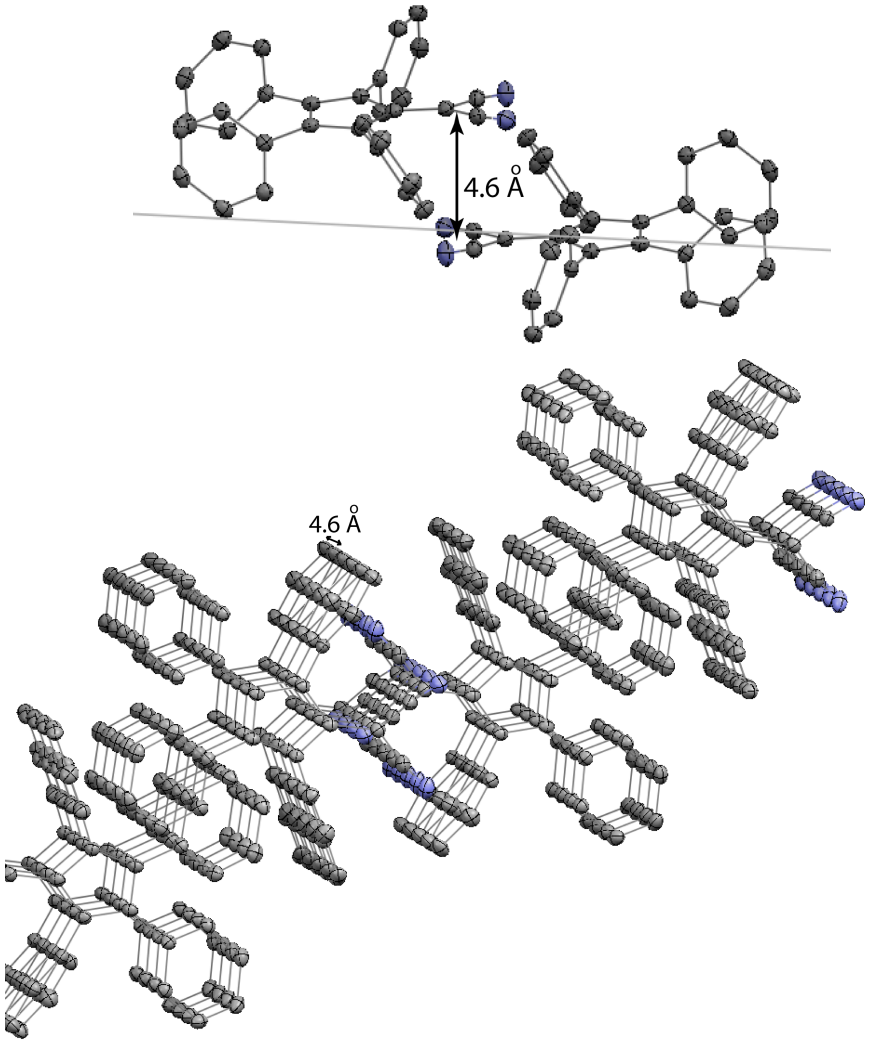


Figure S2. Select views of the packing structure of **DCF3**, showing the absence of herringbone packing between fulvene cores. The intermolecular separation between fulvene cores is ca. 4.6 Å, which is higher than that observed in **DCF2**. The increased separation between fulvene cores is most likely due to relatively greater steric crowding arising from the phenyl substituents in the 1- and 4-positions.

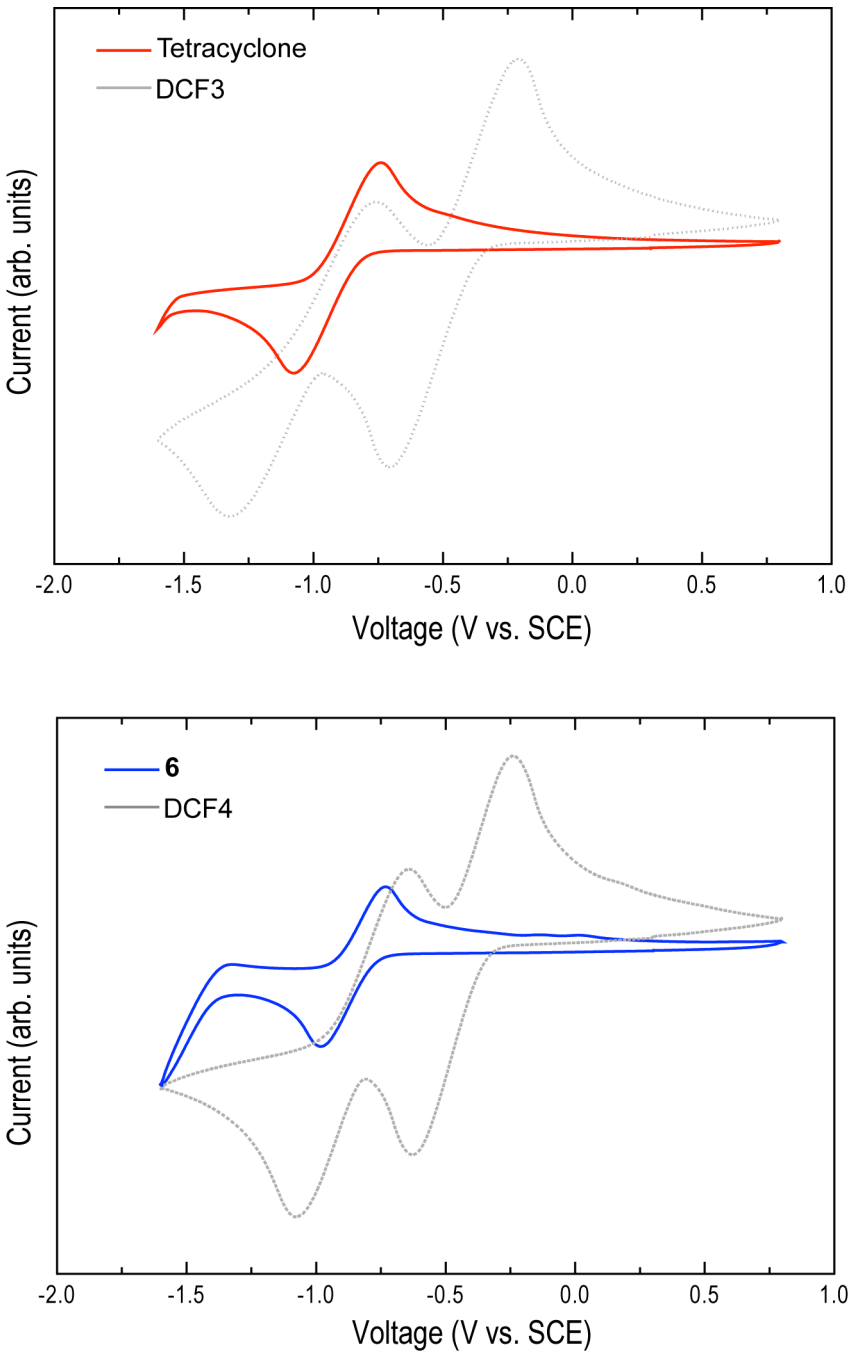


Figure S3. Cyclic voltammograms of monomeric CPDs (tetracyclone in red, **6** in blue) showing only a single reduction peak within the observation window of CH_2Cl_2. The cyclic voltammograms of the corresponding fulvenes are overlaid (dotted lines) for comparison. Pt button electrode, 0.1M $TBAPF_6$ in CH_2Cl_2, 100 mV/s.

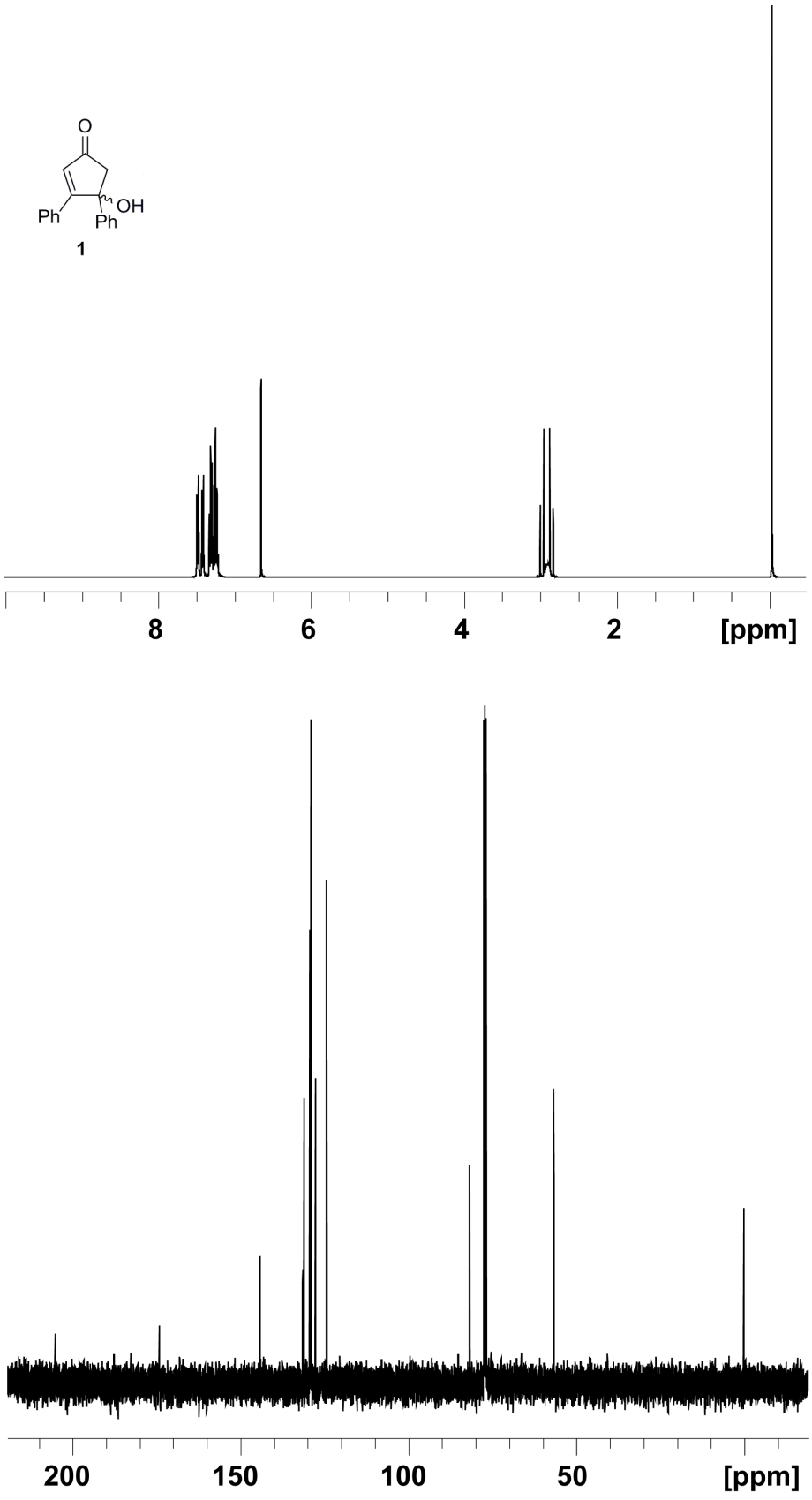


Figure S4. ^{1}H and ^{13}C NMR spectra of **1**.

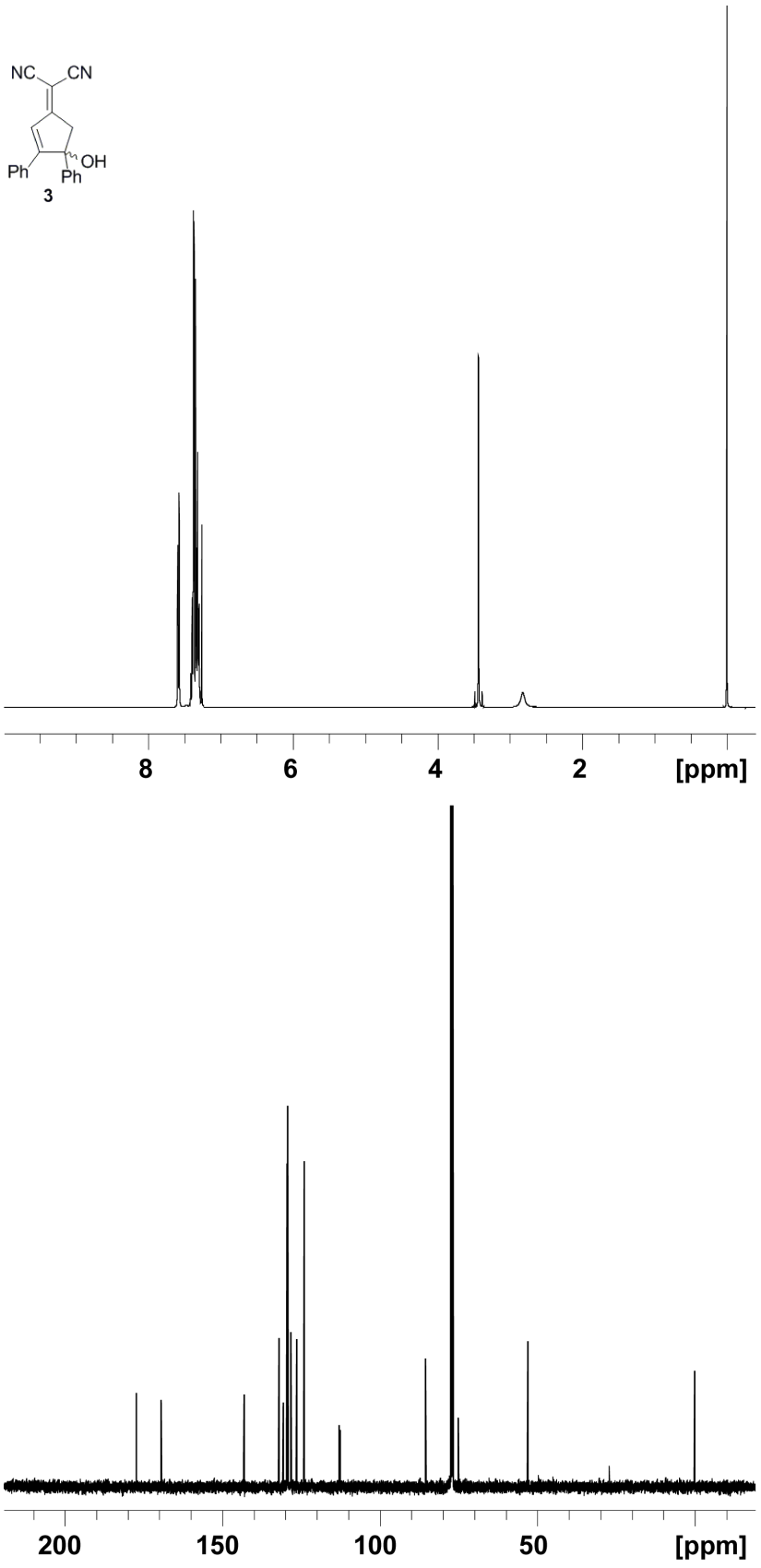


Figure S5. ^{1}H and ^{13}C NMR spectra of **3**.

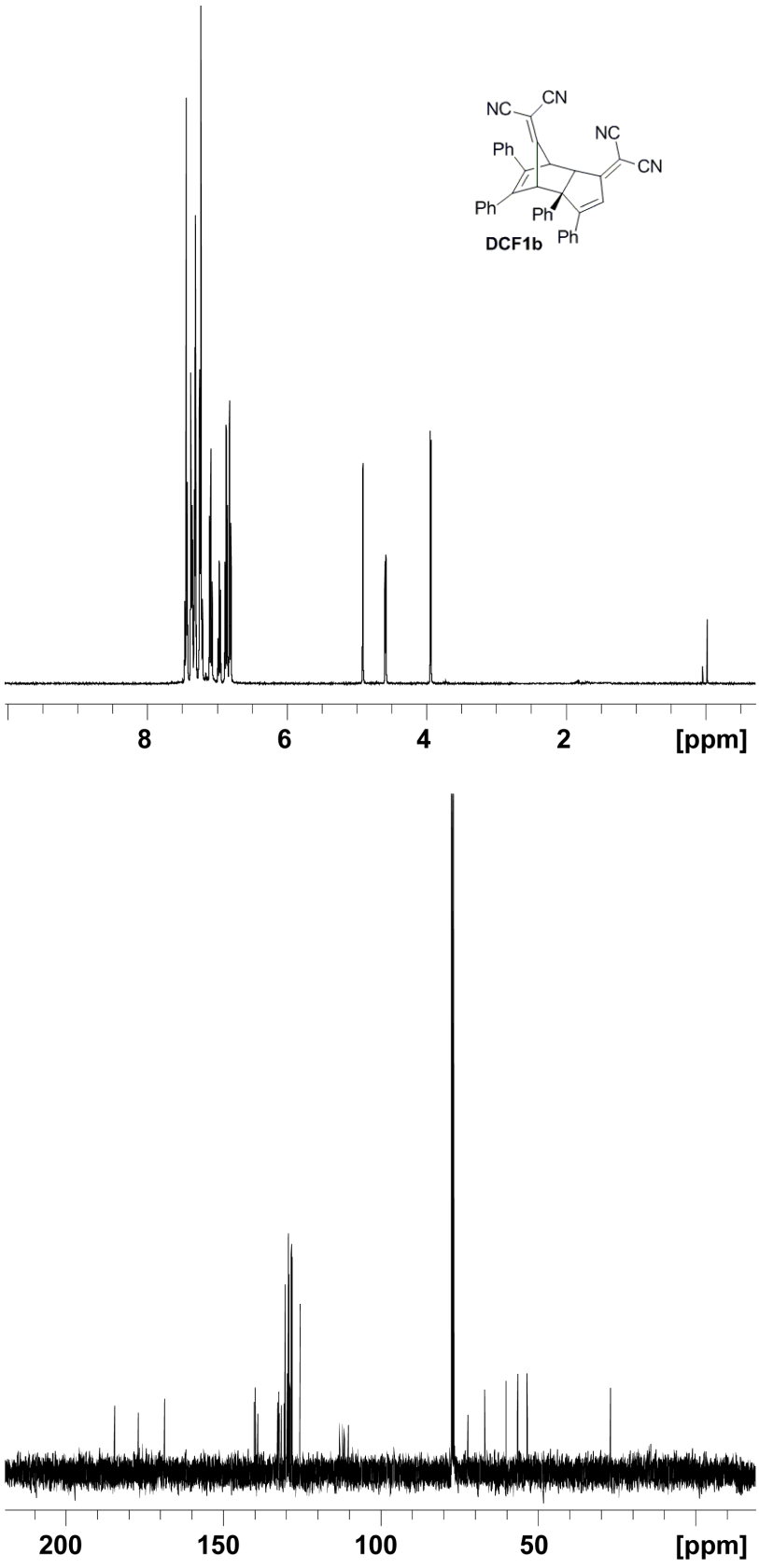


Figure S6(a). ^{1}H and ^{13}C NMR spectra of **DCF1b** in $CHCl_3$.

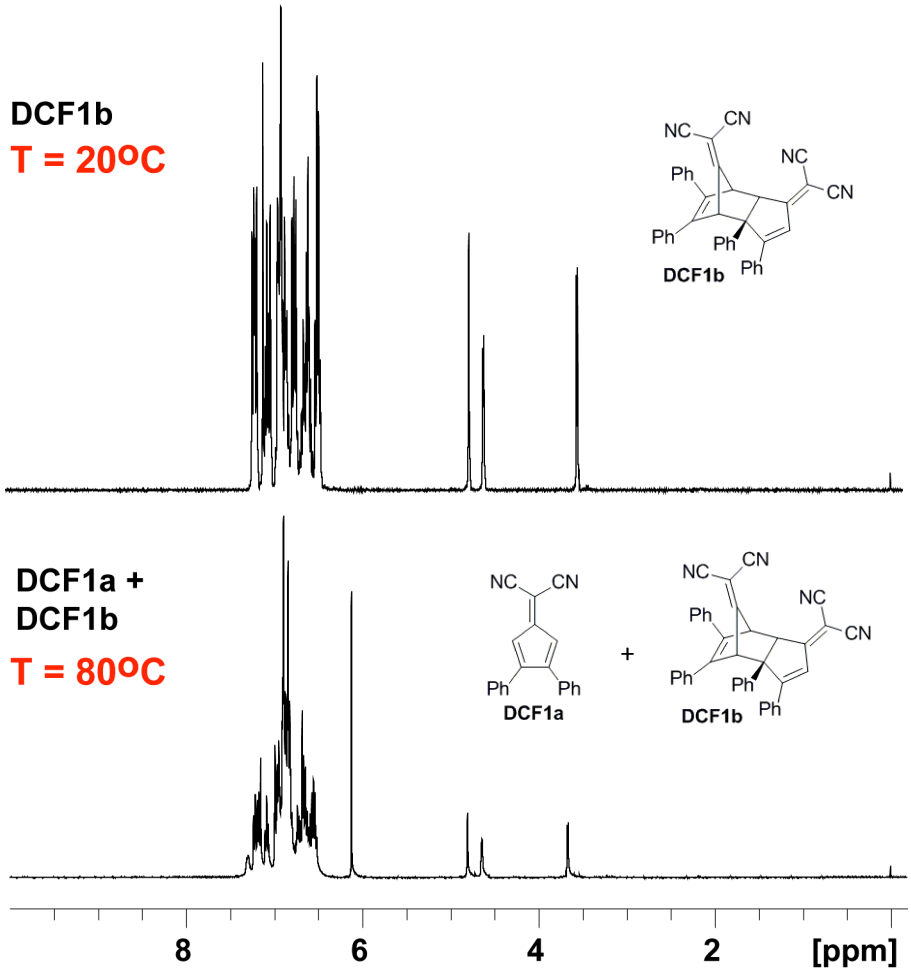


Figure S6(b). ^{1}H-NMR spectrum of **DCF1b** in toluene-d_8 at room temperature and at 80^{o}C, showing the evolution of **DCF1a** upon heating.

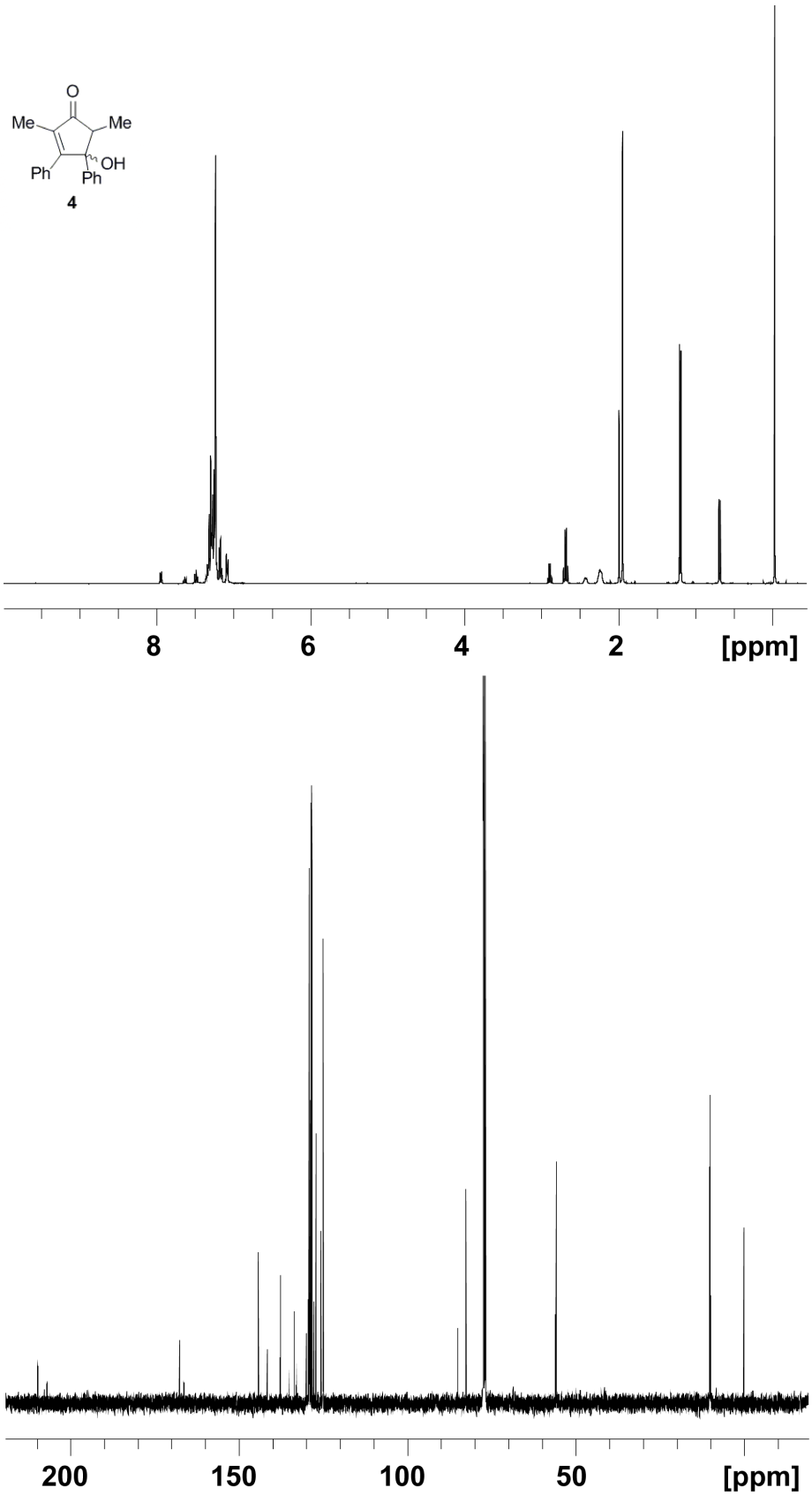


Figure S7. ^{1}H and ^{13}C NMR spectra of **4**.

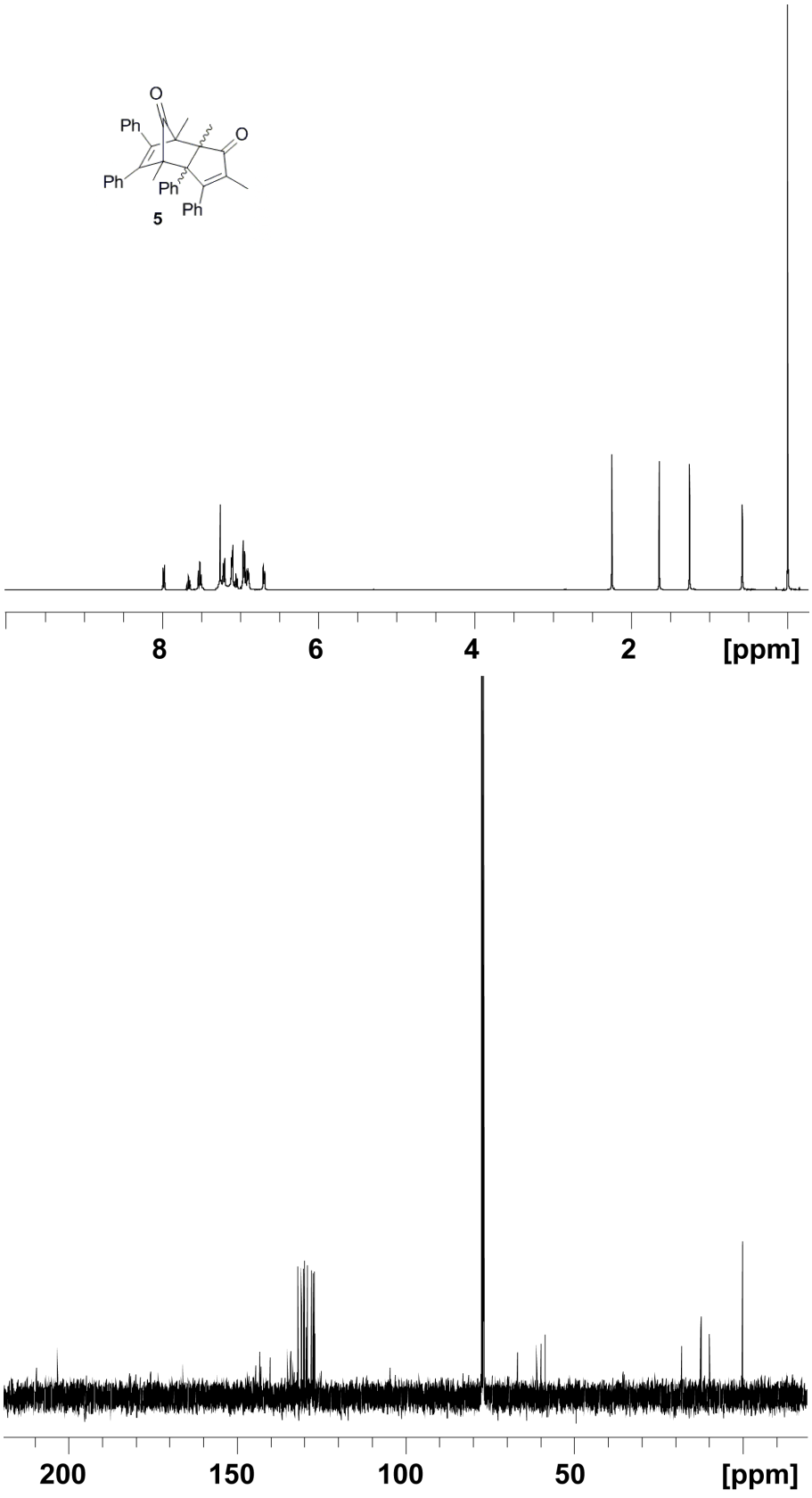


Figure S8. ^{1}H and ^{13}C NMR spectra of **5**.

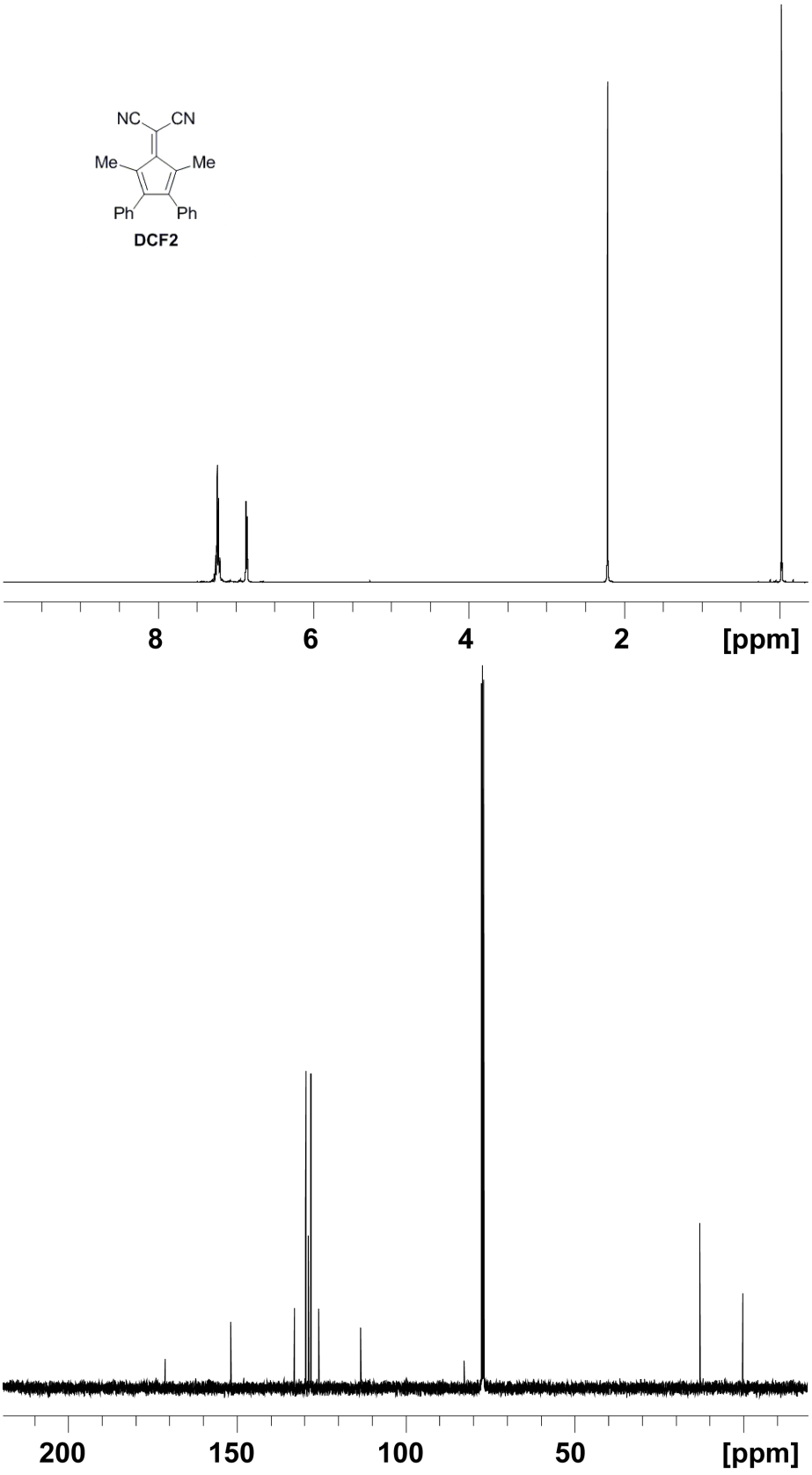


Figure S9. ^{1}H and ^{13}C NMR spectra of **DCF2**.

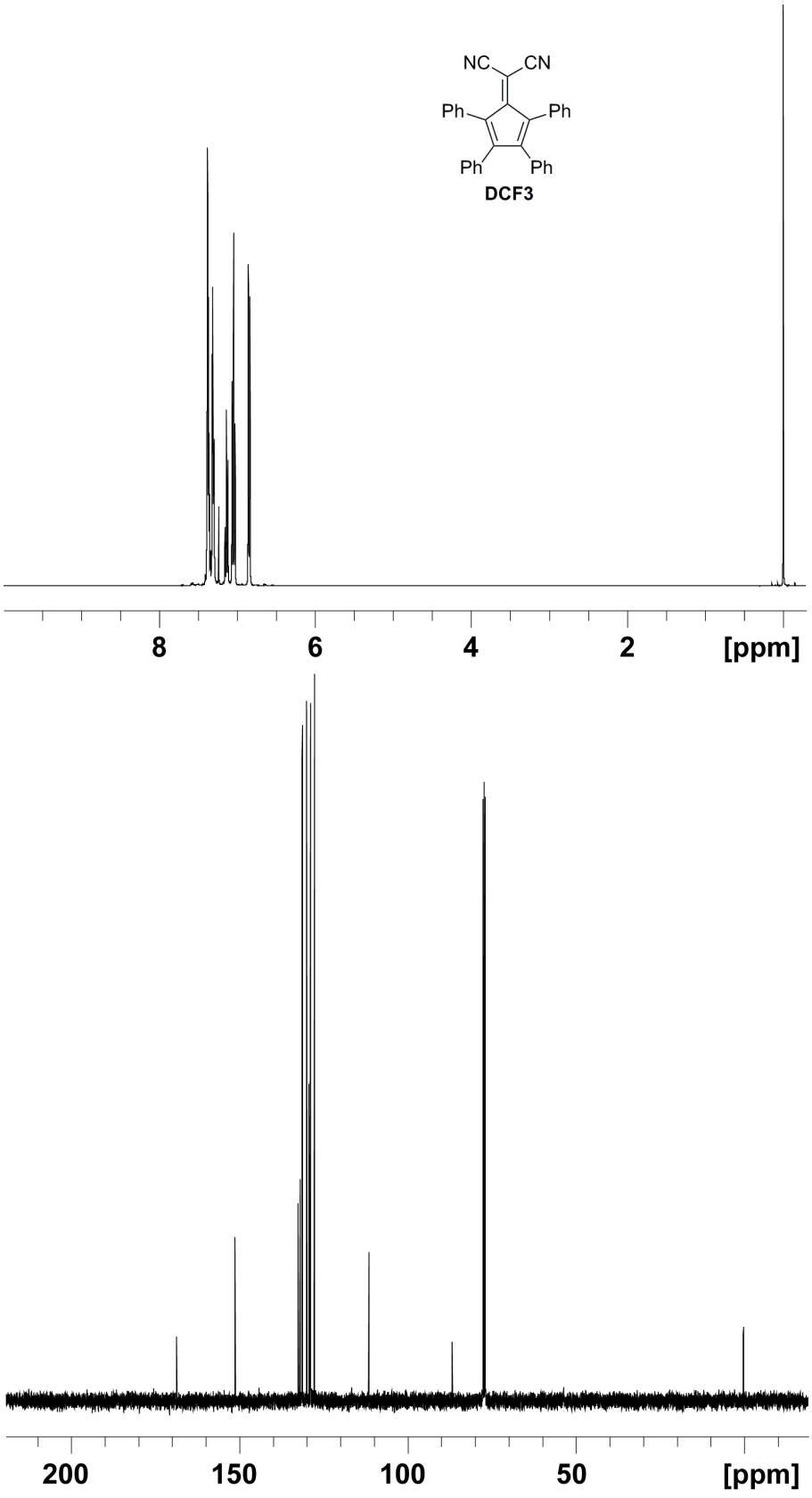


Figure S10. ^{1}H and ^{13}C NMR spectra of **DCF3**.

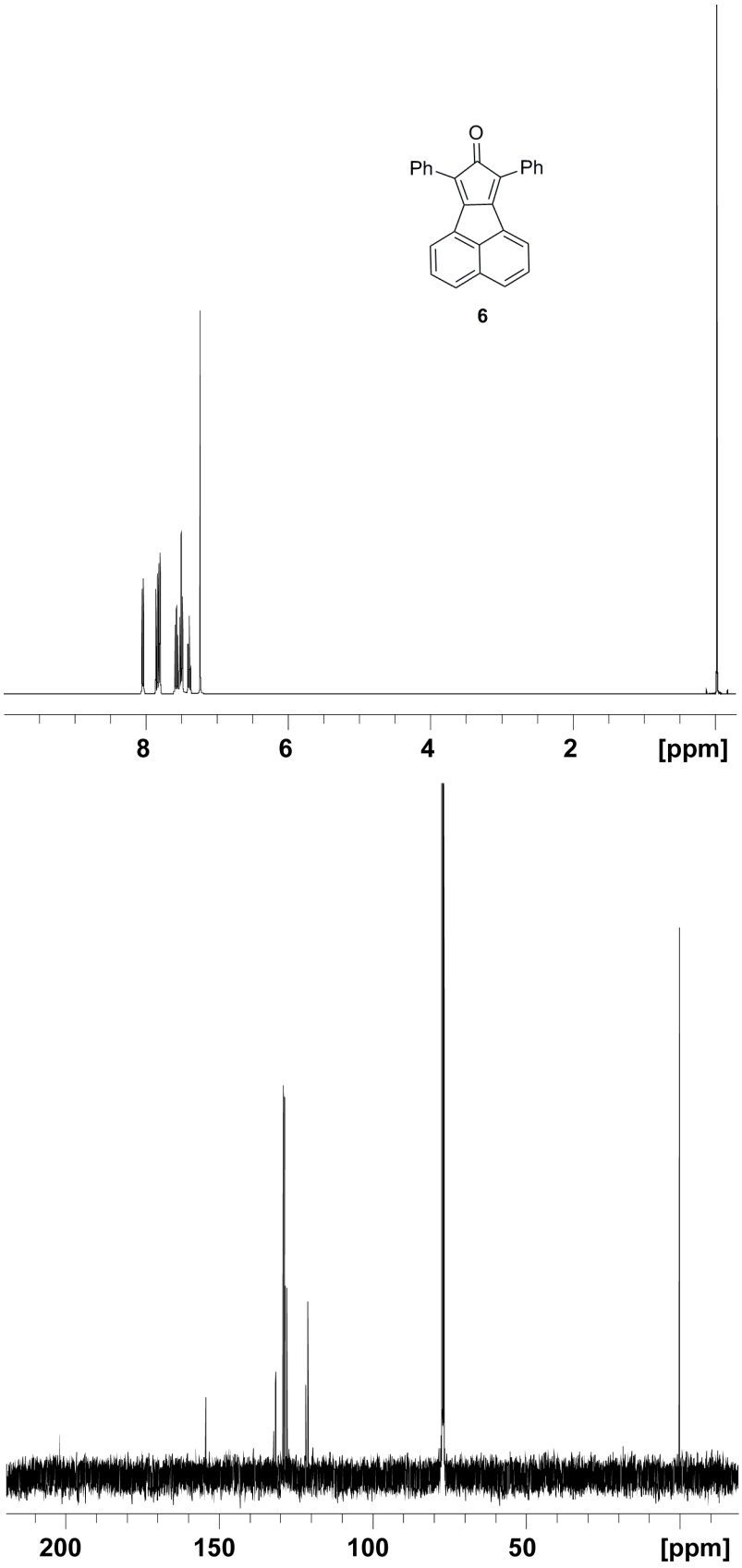


Figure S11. ^{1}H and ^{13}C NMR spectra of **6**.

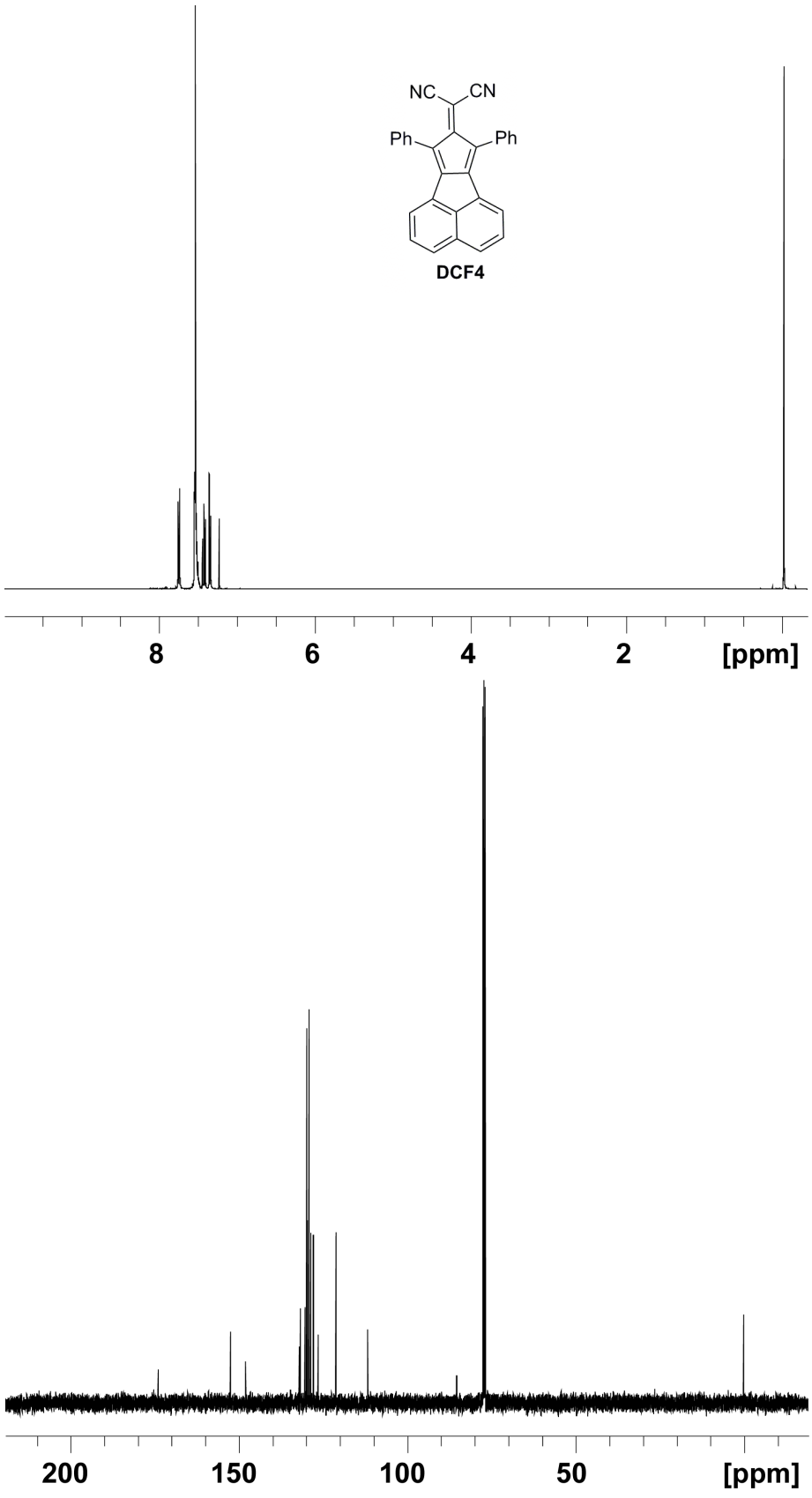


Figure S12. ^{1}H and ^{13}C NMR spectra of **DCF4**.