MIT Open Access Articles

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

Synthesis, Reactivity and Electronic Properties of 6,6-Dicyanofulvenes
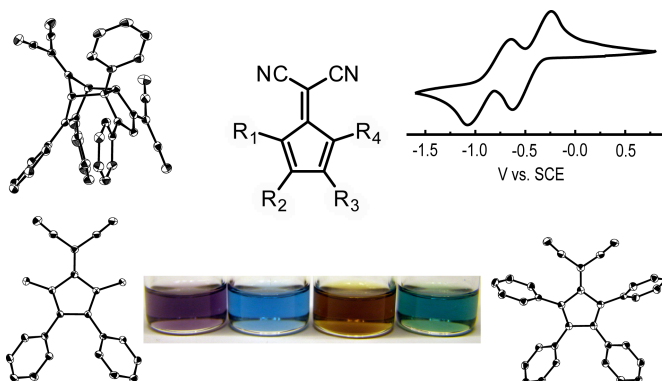
Trisha L. Andrew, Jason R. Cox, Timothy M. Swager*

Massachusetts Institute of Technology, Department of Chemistry, 77 Massachusetts Avenue, Cambridge, MA 02139

tswager@mit.edu

ABSTRACT

A series of 6,6-dicyanofulvene derivatives are synthesized starting from masked, dimeric or monomeric cyclopentadienones. The reactivities of 6,6-dicyanofulvenes relative to their parent cyclopentadienones are discussed. 6,6-Dicyanofulvenes are capable of undergoing two consecutive, reversible, one-electron reductions and are presented as potential n-type small molecules.

During the past decade, intense research efforts have yielded numerous optimized, air-stable, *p*-type (hole-transporting) organic semiconductors with conductivities and hole mobilities that are competitive with inorganic analogs.[1] Recently, several examples of *n*-type (electron-conducting) organic materials have been utilized in thin-film organic field-effect transistors (OFETs) and photovoltaic cells,[2] but the electronic and solid-state packing properties, air-stability, and processability of *n*-type semiconductors are far from being as optimized as their *p*-type counterparts.[3]

The discovery of new molecular building blocks for *n*-type materials remains germane, as the diversity in the chemical structures of proven electron-conductors does not match the large population of known organic hole-conductors. To date, polymeric / oligomeric / small molecule oxadiazoles,[4] benzothiadiazoles,[5] arylene imides,[6] perfluorinated[7] or perfluoroalkyl-containing

(1) (a) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986. (b) Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. *J. Am. Chem.Soc.* **2007**, *129*, 15732. (c) Subramanian, S.; Park, S. K.; Parkin, S. R.; Podzorov, V.; Jackson, T. N.; Anthony, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 2706. (d) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X.; Enkelmann, V.; Baumgarten, M.; Pisula, W.; Müllen, K. *Adv. Mater.* **2009**, *21*, 213. (e) Ortiz, R. P.; Facchetti, A.; Marks, T. J. *Chem Rev.* **2010**, *110*, 205.

(2) (a) Facchetti, A. *Mater. Today* **2007**, *10*, 28. (b) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194.

(3) (a) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953. (b) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Brédas, J.-L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436.

(4) (a) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969. (b) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem Mater.* **2004**, *16*, 4556.

(5) (a) Beaujuge, P. M.; Pisula, W.; Tsao Hoi, N.; Ellinger, S.; Müllen, K.; Reynolds, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 7514. (b) Linder, T.; Badiola, E.; Baumgartner, T.; Sutherland, T. C. *Org. Lett.* **2010**, *12*, 4520 and references therein.

(6) (a) Oriz, R. P.; Herrera, H.; Blanco, R.; Huang, H.; Facchetti, A.; Marks, T. J.; Zheng, Y.; Segura, J. L. *J. Am. Chem. Soc.* **2010**, *132*, 8440. (b) Letizia, J. A.; Salata, M. R.; Tribout, C. M.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 9679. (c) Gao,

arenes,[8] fullerenes,[9] pyridiniums,[10] and dicyanovinylene[11] or tricyanovinylene-substituted arenes[12] have been demonstrated as suitable *n*-type materials. Notably, nitrile incorporation is an interesting design strategy, as it both results in desirable electronic properties (low LUMO energies)[13] and is capable of transforming a *p*-type organic system into an electron-accepting material.[14]
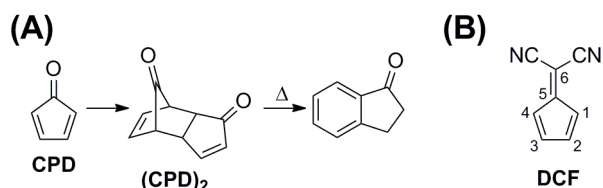

Figure 1. (A) Structures of the unisolable cyclopentadienone, **CPD**, and its isolable dimer, **(CPD)₂**. (B) Structure of 6,6-dicyanofulvene (DCF), depicting the numbering convention for a fulvene skeleton.

Cyclopentadienones (CPDs) and fulvenes have received little attention as *n*-type building blocks and have only been considered indirectly, as structural subunits in indenofluorenone and indenofluorene bis(dicyanovinylene) chromophores.[11a,b] Wudl et al. reported a donor-acceptor polymer containing a dithienylcyclopentadienone moiety in its repeat unit,

where the CPD served as the "acceptor" component;[15] however, this polymer displayed complex electrochemistry and did not demonstrate *n*-type behavior in an OFET. The paucity of CPD- or fulvene-based building blocks could also be attributed to the reactivity and instability of these classes of molecules: many CPDs are unisolable in their monomeric form[16] (see Figure 1A) and the electrochemical stability of fulvenes is suspect.[17]

We propose, instead, the use of 6,6-dicyanofulvenes (DCFs, Figure 1B) as building blocks for electron-transport materials. In this contribution, we explore the synthesis of DCFs, their chemical stabilities, and their optical and electrochemical properties.

Scheme 1. Synthesis of select 6,6-dicyanofulvene derivatives.
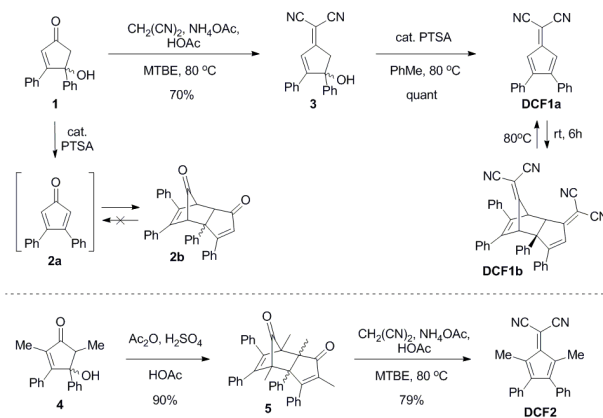
Informed by the instability of monomeric cyclopentadienone, we first synthesized a diphenyl derivative of 6,6-dicyanofulvene based on the hypothesis that two phenyl substituents would provide enough steric protection from dimerization. 2,3-Diphenyl-6,6-dicyanofulvene (**DCF1a**) was synthesized in two steps from the 4-hydroxy-2-cyclopenten-1-one derivative **1**, which was prepared by an aldol condensation between acetone and benzil.[18] Acid-catalyzed dehydration of **1** generates the corresponding cyclopentadienone **2a**, which either irreversibly undergoes a [4+2] homodimerization[16] or can be trapped by suitable dienophiles to generate 1,2-diphenylbenzene derivatives after decarbonylation.[18] To avoid such undesirable side reactions, only transformations of the masked cyclopentadienone **1** were pursued. The 1,2-addition of malononitrile to compound **1** proceeded smoothly to yield **3**. We initially anticipated

X.; Di, C.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *J. Am. Chem. Soc.* **2010**, *132*, 3697. (d) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Seigrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. *Nature,* **2000**, *404*, 478. (e) Schmidt, R.; Ling, M. M.; Oh, J. H.; Winkler, M.; Könemann, M.; Bao, Z.; Würthner, F. *Adv. Mater.* **2007**, *19*, 3692. (f) Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656.

(7) Bao, Z.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207.

(8) (a) Facchetti, A.; Letizia, J.; Yoon, M.-H.; Mushrush, M.; Katz, H.; Marks, T. J. *Chem. Mater.* **2004**, *16*, 4715. (b) Facchetti, A.; Mushrush, M.; Yoon, M.-H.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13859.

(9) (a) Haddon, R. C.; Perel, A. S.; Morris, R. C.; Palstra, T. T. M.; Hebard, A. F.; Fleming, R. M. *Appl. Phys. Lett.* **1995**, *67*, 121. (b) Kobayashi, S.; Takenobu, T.; Mori, S.; Fujiwara, A.; Iwasa, Y. *Appl. Phys. Lett.* **2003**, *82*, 4581. (c) Meijer, E. J.; De Leeuw, D. M.; Setayesh, S.; van Veenendaal, E.; Huisman, B. H.; Blom, P. W. M.; Hummelen, J. C.; Scherf, U.; Klapwijk, T. M. *Nat. Mater.* **2003**, *2*, 678.

(10) Izuhara, D.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 17724.

(11) (a) Usta, H.; Facchetti, A.; Marks, T. J. *Org. Lett.* **2008**, *10*, 1385. (b) Usta, H.; Fachetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 8580. (c) Handa, S.; Miyazaki, E.; Takiyama, K.; Kunugi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 11684. (d) Laquindanum, J. G.; Katz, H. E.; Dodabalapur, A.; Lovinger, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 11331. (e) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Raff, J. D.; Miller, L. L. *J. Am. Chem. Soc.* **2002**, *124*, 4184. (f) Moslin, R. M.; Andrew, T. L.; Kooi, S. E.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 20.

(12) Pappenfus, T. M.; Hermanson, B. J.; Helland, T. J.; Lee, G. G. W.; Drew, S. M.; Mann, K. R.; McGee, K. A.; Rasmussen, S. C. *Org. Lett.* **2008**, *10*, 1553 and references therein.

(13) Yamashita, Y.; Suzuki, T.; Saito, G.; Mukai, T. *Chem. Commun.* **1986**, 1489.

(14) Lim, Y.-F.; Shu, Y.; Parkin, S. R.; Anthony, J. E.; Malliaras, G. G. *J. Mater. Chem.* **2009**, *19*, 3049.

(15) (a) Yang, C.; Cho, S.; Chiechi, R. C.; Walker, W.; Coates, N. E.; Moses, D.; Heeger, A. J.; Wudl, F. *J. Am. Chem. Soc.* **2008**, *130*, 16524. (b) Walker, W.; Veldman, B.; Chiechi, R.; Partil, S.; Bendikov, M.; Wudl, F. *Macromolecules,* **2008**, *41*, 7278.

(16) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261.

(17) Day, J. H. *Chem. Rev.* **1953**, *53*, 167.

(18) Becker, H.; King, S. B.; Taniguchi, M.; Vanhessche, K. P. M.; Sharpless, K. B. *J. Org. Chem.* **1995**, *60*, 3940.

the occurance of a number of detrimental rearrangement reactions competing with the 1,2-addition of malononitrile; however, as supported by the crystal structure of **3** (Figure 2A), the desired product was the sole isolated compound. Dehydration of **3** by a catalytic amount of PTSA at elevated temperatures quantitatively generated a dark brown solution of **DCF1a**; however this dicyanofulvene was found to dimerize at room temperature to **DCF1b**. As seen in the crystal structure of dimer **DCF1b** (Figure 2B), the endo adduct was the major isolated product.
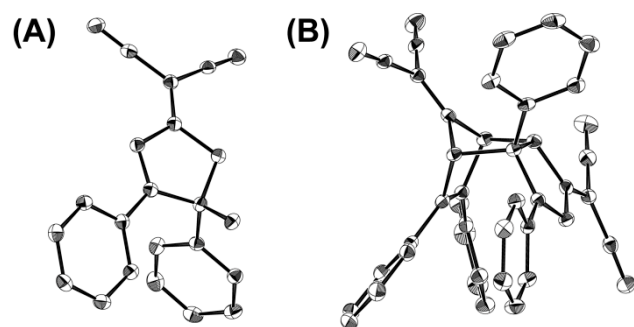

Figure 2. Crystal structures of (A) **3** and (B) **DCF1b**.

Dimerization was reversible and was accompanied by disappearance of the dark brown color of the starting **DCF1a** solution. The monomeric fulvene could be recovered by heating **DCF1b** to 80°C and we were able to cycle between monomeric and dimeric forms multiple times with little to no decomposition noticeable by ^{1}H-NMR spectroscopy. This observation is in contrast to the behavior of **2a**, for which dimerization is an irreversible phenomenon (heating results in decarbonylation).[16] Moreover, the tendency of **DCF1a** to undergo [4+2] dimerization is not shared by other 6,6-disubstituted fulvenes, such as a 6,6-dimethylfulvene.[17]

In an attempt to isolate a monomeric 6,6-dicyanofulvene, two methyl substituents were introduced at the 2- and 5-positions of the starting hydroxy-2-cyclopenten-1-one. Compound **4** was obtained from the aldol condensation of 3-pentanone with benzil and was subsequently dehydrated to yield the cyclopentadienone dimer **5**. Compound **5** is a member of a subclass of cyclopentadienones that can be reversibly cracked to their monomeric forms at elevated temperatures, unlike the parent CPD.[16] Therefore, **DCF2** was directly accessed from **5** by conducting the 1,2-addition of malononitrile at 80°C. Notably, dark purple, crystalline **DCF2** was isolated in its monomeric form (see Figure 3A) while the corresponding cyclopentadienone dimerizes at room temperature.

It was found that introduction of phenyl substituents at the 1,4-positions of the fulvene skeleton hindered the 1,2-addition of malononitrile and therefore, the reaction conditions used in the synthesis of **DCF1**-**2** failed to generate the dicyanofulvene analogs of tetracyclone and **6**. Nevertheless, the use of a strong lewis acid, such as BF$_3$·OEt$_2$ or TiCl$_4$, in combination with pyridine afforded the desired cyanofulvenes **DCF3** and **DCF4** (Scheme 2). In these instances, the progress of the reaction can be witnessed optically: deep purple tetracyclone forms pea green **DCF3** while navy blue **6** forms emerald green **DCF4**.

The crystal structure of **DCF3** is shown in Figure 3B. Both **DCF2** and **DCF3** do not display edge-to-face packing in the solid state, preferring instead to maximize the π-π interaction between fulvene cores (see Supporting Information, Figures S1 and S2).

Scheme 2. Synthesis of 1,4-diphenyl-6,6-dicyanofulvenes
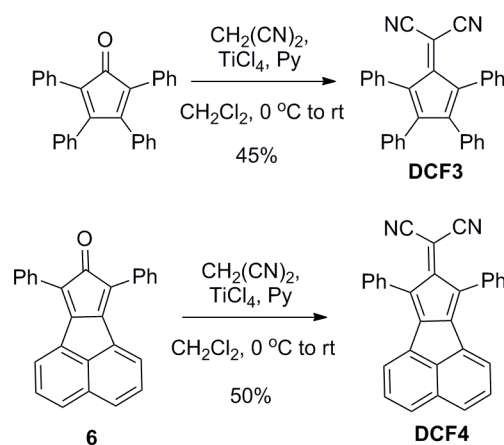
Cyclic voltammograms of all monomeric dicyanofulvenes were recorded in order to judge their suitability as electron-transport materials in electronic devices. The electrochemical properties of **DCF2**-**4** are summarized in Table 1. In general, the dicyanofulvenes displayed two distinct, reversible one-electron reduction peaks. The first one-electron reduction for **DCF3** and **DCF4**, which contain two phenyl substituents in the 1,4-positions, occurred at slightly less negative potentials than in DCFs with alkyl substituents in the 1,4-positions.

For cases where the parent CPDs are monomeric, such as with **DCF3**-**4**, it was possible to evaluate the effects of the dicyanovinylene moiety on the electronic properties of select cyclopentadiene systems. As previously reported, cyclic voltammograms of CPDs generally display a single two-electron reduction peak[19] (see Supporting Information, Figure S3) and the intermediate radical anion product of one-electron reduction is observed only in select cases.[15] In contrast, the intermediate radical anions of DCFs are stable and therefore, cyclic voltammograms of DCFs display two distinct, one-electron reduction peaks. Additionally, the

(19) Fox, M. A.; Campbell, K.; Maier, G.; Franz, L. H. *J. Org. Chem.* **1983**, *48*, 1762.

formal reduction potentials of DCFs are globally lower than those of the corresponding CPDs.
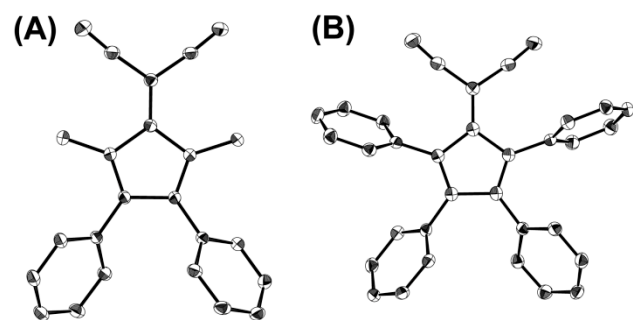

Figure 3. Crystal structures of (A) **DCF2** and (B) **DCF3**.

The electron affinities (EA) of **DCF2**-**4** were calculated from their formal reduction potentials using the formula $EA = E_{red} + 4.4$ eV[10] and are listed in Table 1. With average electron affinities of 3.9 eV, DCFs are comparable to PCBM (EA 4.0 eV) as electron acceptors.

In conclusion, a series of substituted 6,6-dicyanofulvenes were synthesized starting from masked, dimeric or monomeric cyclopentadienones. DCFs lacking sufficient steric bulk around the fulvene core tend to reversibly undergo a [4+2] dimerization. In addition to being highly crystalline, DCFs are darkly-colored compounds due to the presence of electronic transitions in the visible region of the electromagnetic spectrum. DCFs display two distinct, reversible one-electron reductions by cyclic voltammetry. Based on their high crystallinity and suitable electron affinities, and buoyed by their relatively cheap and straight-forward synthesis, DCFs are interesting candidates for organic electron-transport materials.
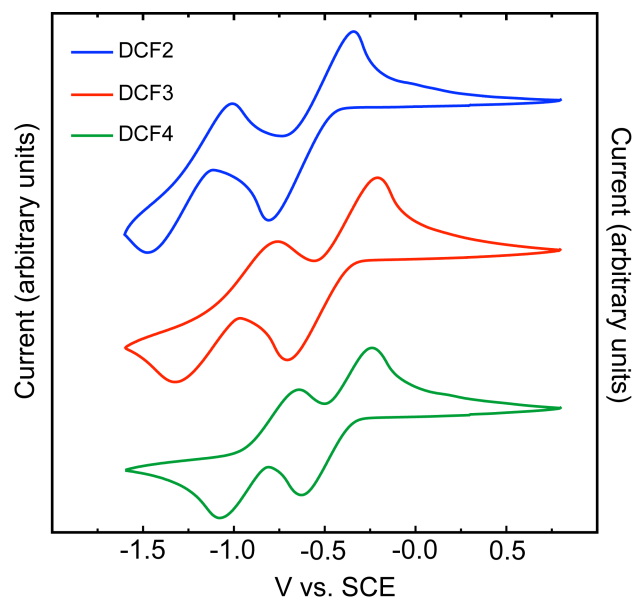

Figure 4. Cyclic voltammograms of **DCF2**-**4** recorded in 0.1M TBAPF$_6$ in CH$_2$Cl$_2$ using a Pt button electrode at a scan rate of 100 mV/s. Voltage values are reported vs. standard calomel electrode (SCE).

Supporting Information Available Experimental procedures, spectral characterization data and crystallographic information.

Table 1. Optical and electrochemical properties of **DCF2**-**5**

compound	λ_{max}/nm (log ε)	E_{red} / V vs. SCE	EA[a] / eV
DCF2	275 (4.2), 370 (4.1), 555 (2.5)	-0.57, -1.24	3.83
DCF3	270 (4.2), 387 (4.1), 543 (2.6)	-0.45, -1.04	3.95
Tetracyclone	265 (4.3), 338 (3.8), 509 (3.1)	-1.06	--
DCF4	333 (4.7), 638 (2.6)	-0.43, -0.85	3.97
6	334 (4.2), 381 (3.9), 580 (3.1)	-0.95	--

[a] EA = E_{red} (V vs. SCE) + 4.4 eV

Supporting Information for:

Synthesis, Reactivity and

Electronic Properties of 6,6-Dicyanofulvenes

Trisha L. Andrew, Jason R. Cox, Timothy M. Swager*

Department of Chemistry, Massachusetts Institute of Technology,

77 Massachusetts Avenue, Cambridge, Massachusetts 02139

tswager@mit.edu

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
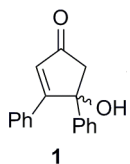
4-hydroxy-3,4-diphenylcyclopent-2-enone (1). 15 mL of 10% methanolic potassium hydroxide was added to a solution of benzil (30g, 143 mmol) and acetone (23 mL, 317 mmol) in 300 mL refluxing methanol. The mixture was heated at 90°C for 30 minutes, cooled to room temperature and poured into 500 mL ice/water. The resulting solids were filtered, washed with water and dried to yield 30 g of a faint-yellow powder (84%).
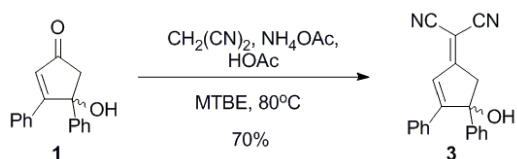
^{1}H NMR (400 MHz, CHCl$_3$) δ 2.85 (d, J = 18.4 Hz, 1H), 2.90 (broad singlet, 1H), 2.93 (d, J = 18.4 Hz, 1H), 6.65 (s, 1H), 7.30 (m, 6H), 7.41 (m, 2H), 7.49 (m, 2H).

^{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%).
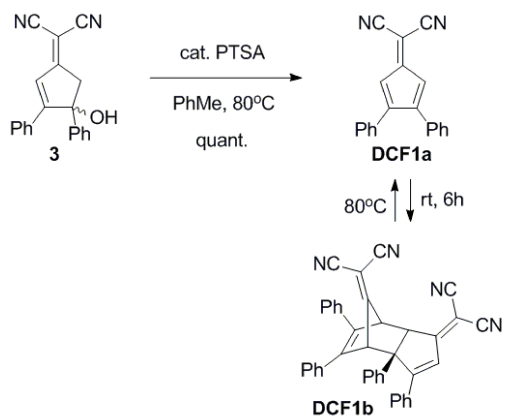
^{1}H NMR (400 MHz, CHCl$_3$) δ 2.83 (broad singlet, 1H), 3.43 (s, 2H), 7.25 (s, 1H), 7.35 (m, 8H), 7.62 (m, 2H).

^{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$_2$O [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}.
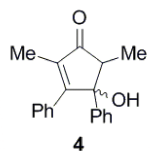
4-hydroxy-2,5-dimethyl-3,4-diphenylcyclopent-2-enone (4). 15 mL of 10% methanolic potassium hydroxide was added to a solution of benzil (30g, 143 mmol) and 3-pentanone (15 mL, 150 mmol) in 300 mL refluxing methanol. The mixture was heated at 90°C for 30 minutes, cooled to room temperature and poured 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
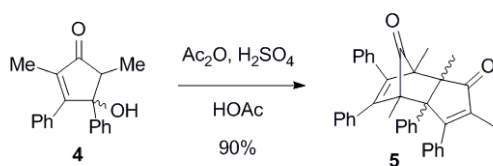
Compound 5. Compound **4** (20 g, 71.9 mmol) was dissolved in 50 mL acetic acid and to this solution was added 20 ml acetic anhydride and 1 mL concentrated sulfuric acid. The reaction was stirred at room temperature for 3 hours and then poured over ice (200 g). The solids were filtered, washed with saturated 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
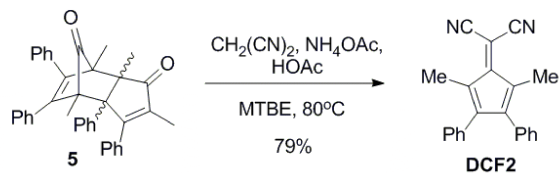
1,4-Dimethyl-2,3-diphenyl-6,6-dicyanofulvene (DCF2). Compound **5** (10g, 19.2 mmol) and malononitrile (8g , 121 mmol) were dissolved in 200 mL t-butyl methyl ether and to this solution was added 15 g ammonium acetate and 10 mL acetic acid. The resulting mixture was heated to 80°C for 20 h with a Dean-Stark 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
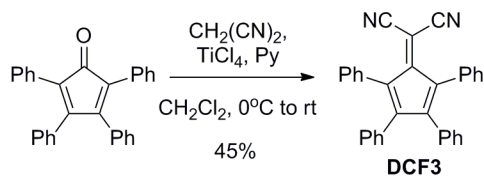
1,2,3,4-Tetraphenyl-6,6-dicyanofulvene (DCF3). To an ice-cooled solution of tetracyclone (3g , 7.8 mmol) and malononitrile (1g, 15 mmol) in 100 mL dry dichloromethane was added dropwise $TiCl_4$ (4.4 mL) over 5 minutes under argon. After the addition was complete, 15 mL pyridine was added to the reaction 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
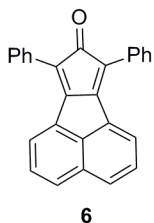
7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one (6). 5 mL of 10% methanolic potassium hydroxide was added to a solution of acenaphthenequinone (5g, 27 mmol) and 1,3-diphenylacetone (6 g, 28.5 mmol) in 200 mL refluxing methanol. The mixture was heated at 90°C for 30 minutes and then placed in a -4°C 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}.
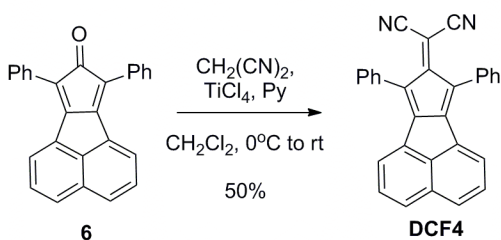
2-(7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-ylidene)malononitrile (DCF4). To an ice-cooled solution of **6** (3g , 16.8 mmol) and malononitrile (1.5g, 22.7 mmol) in 100 mL dry dichloromethane was added dropwise TiCl$_4$ (5.5 mL) over 5 minutes under argon. After the addition was complete, 18 mL pyridine 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}.
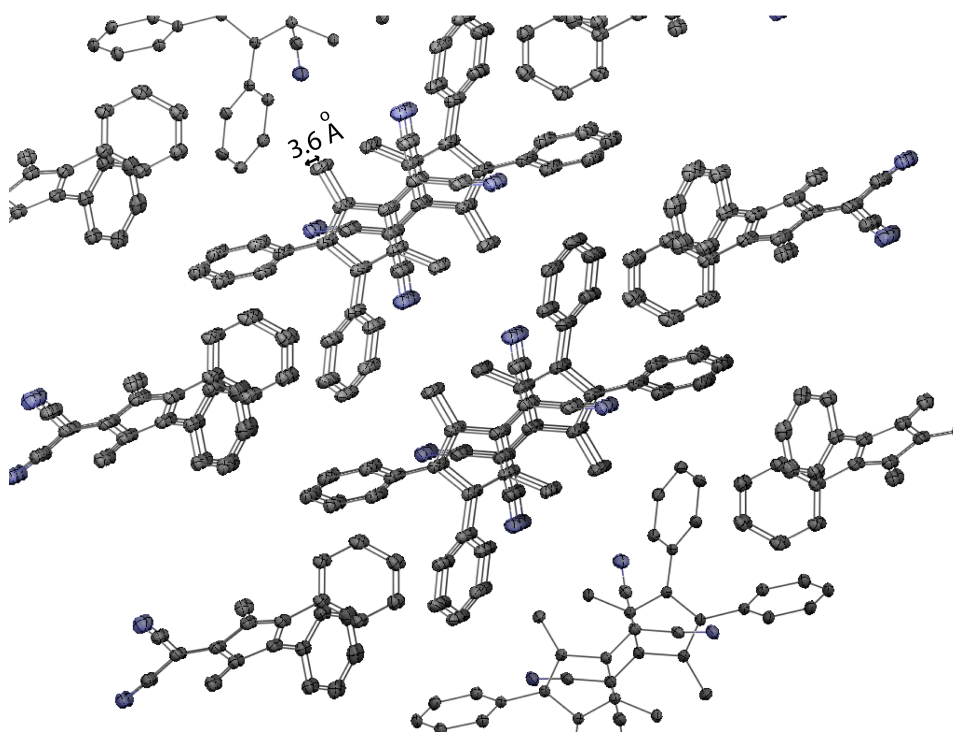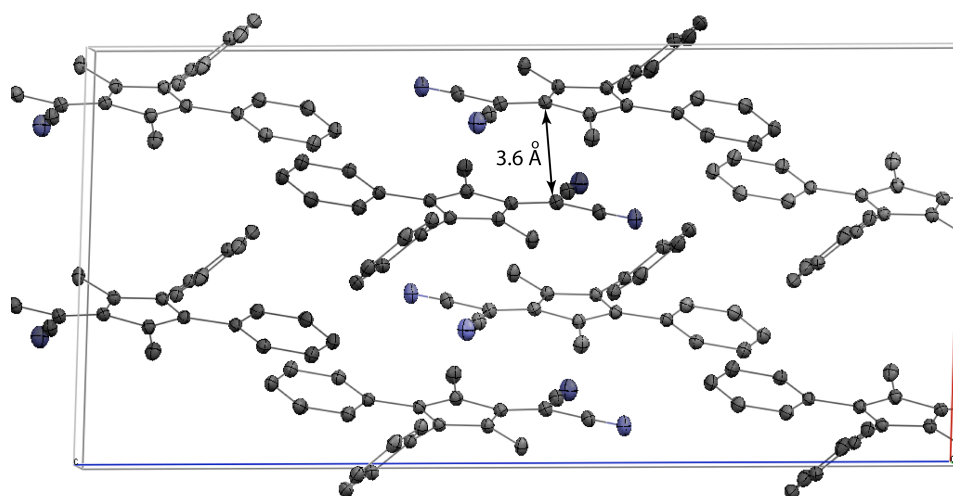
m.p. 275°C

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.
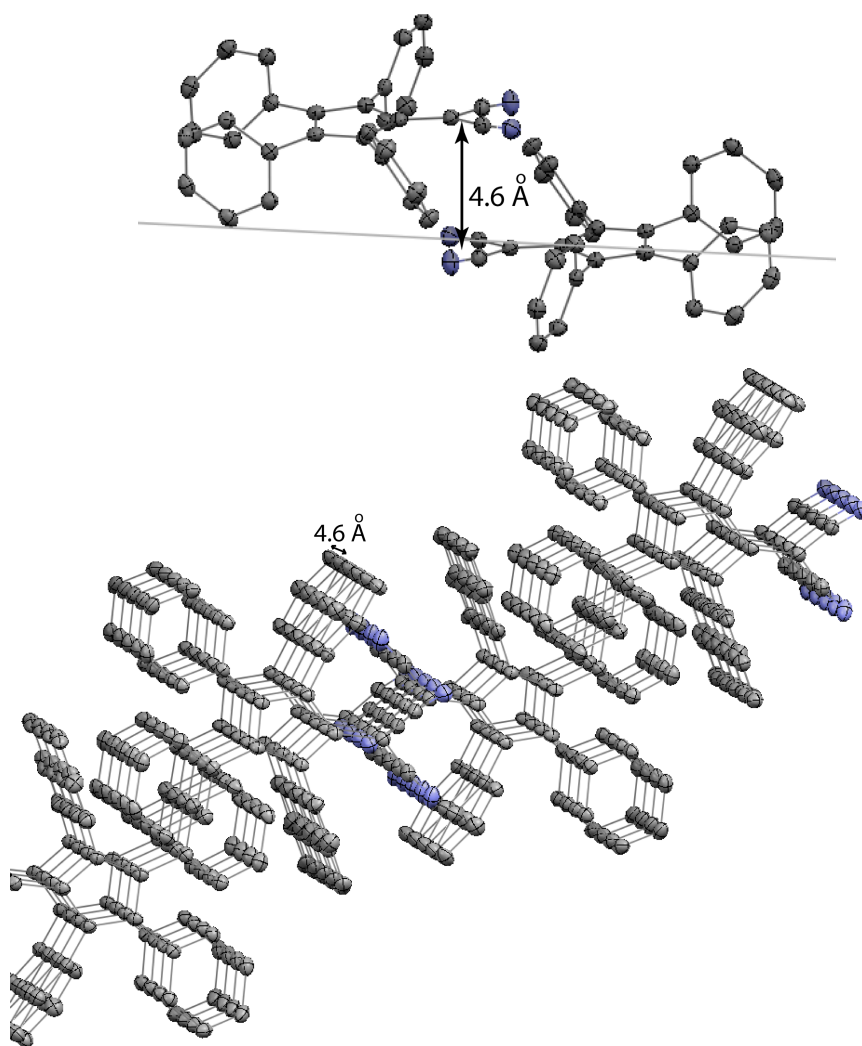
Figure S2. Select views of the packing structure of **DCF3**, showing the absence of herringbone packing between fulvene cores. The intermolecular separation between fulvene cores is ca. 4.6 Å, which is higher than that observed in **DCF2**. The increased separation between fulvene cores is most likely due to relatively greater steric crowding arising from the phenyl substituents in the 1- and 4-positions.
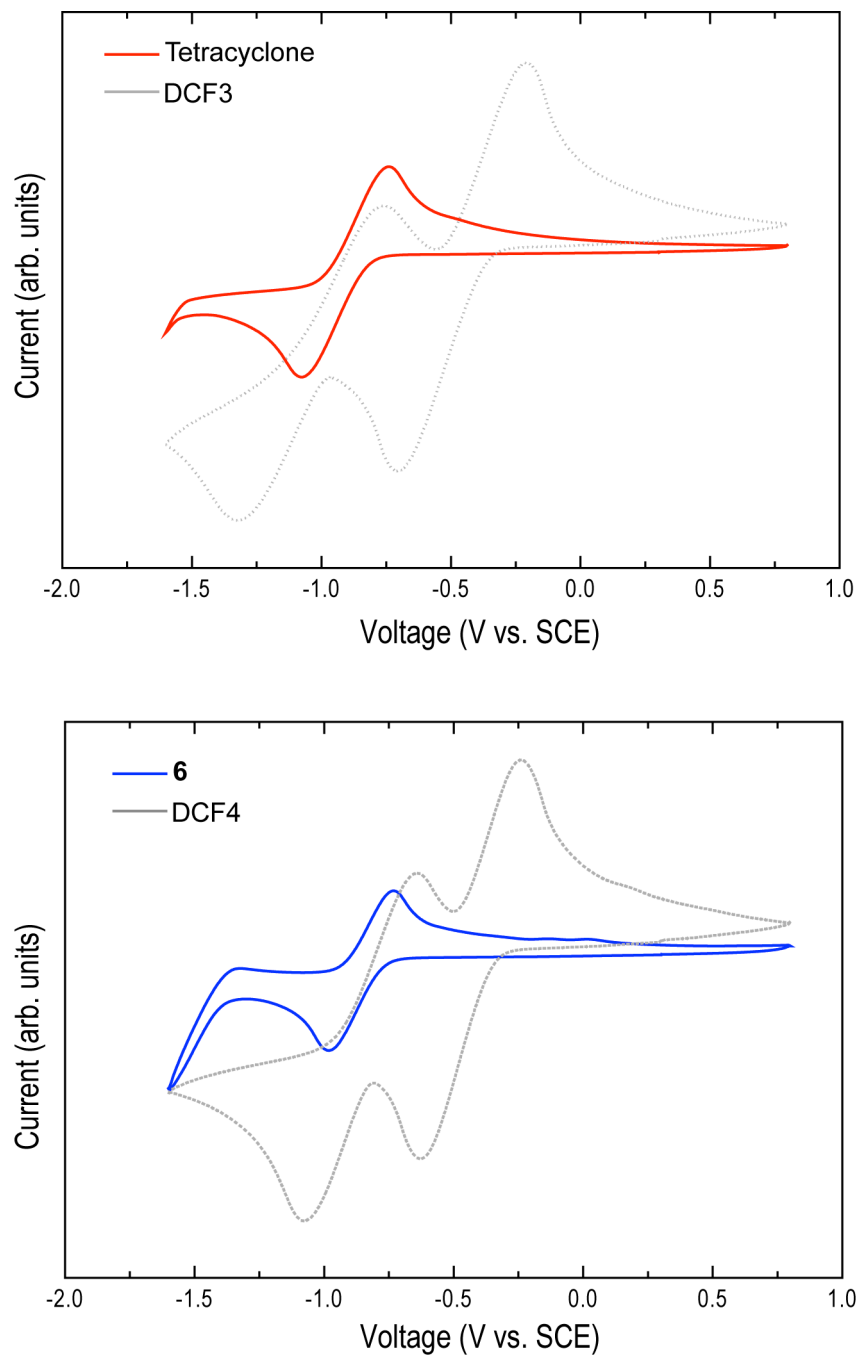
Figure S3. Cyclic voltammograms of monomeric CPDs (tetracyclone in red, **6** in blue) showing only a single reduction peak within the observation window of CH_2Cl_2. The cyclic voltammograms of the corresponding fulvenes are overlaid (dotted lines) for comparison. Pt button electrode, 0.1M TBAPF$_6$ in CH_2Cl_2, 100 mV/s.
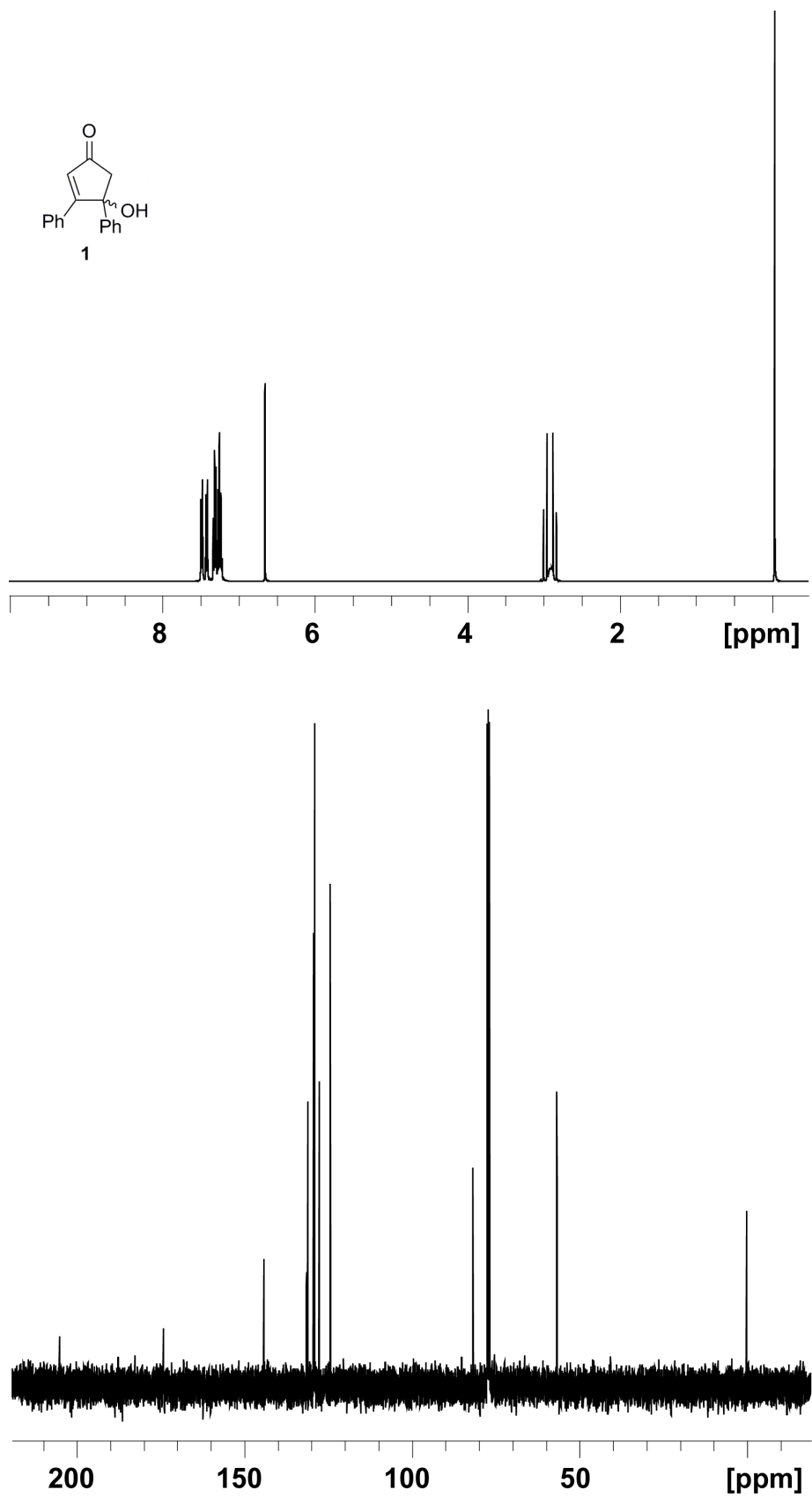
Figure S4. ^1H and ^{13}C NMR spectra of **1**.
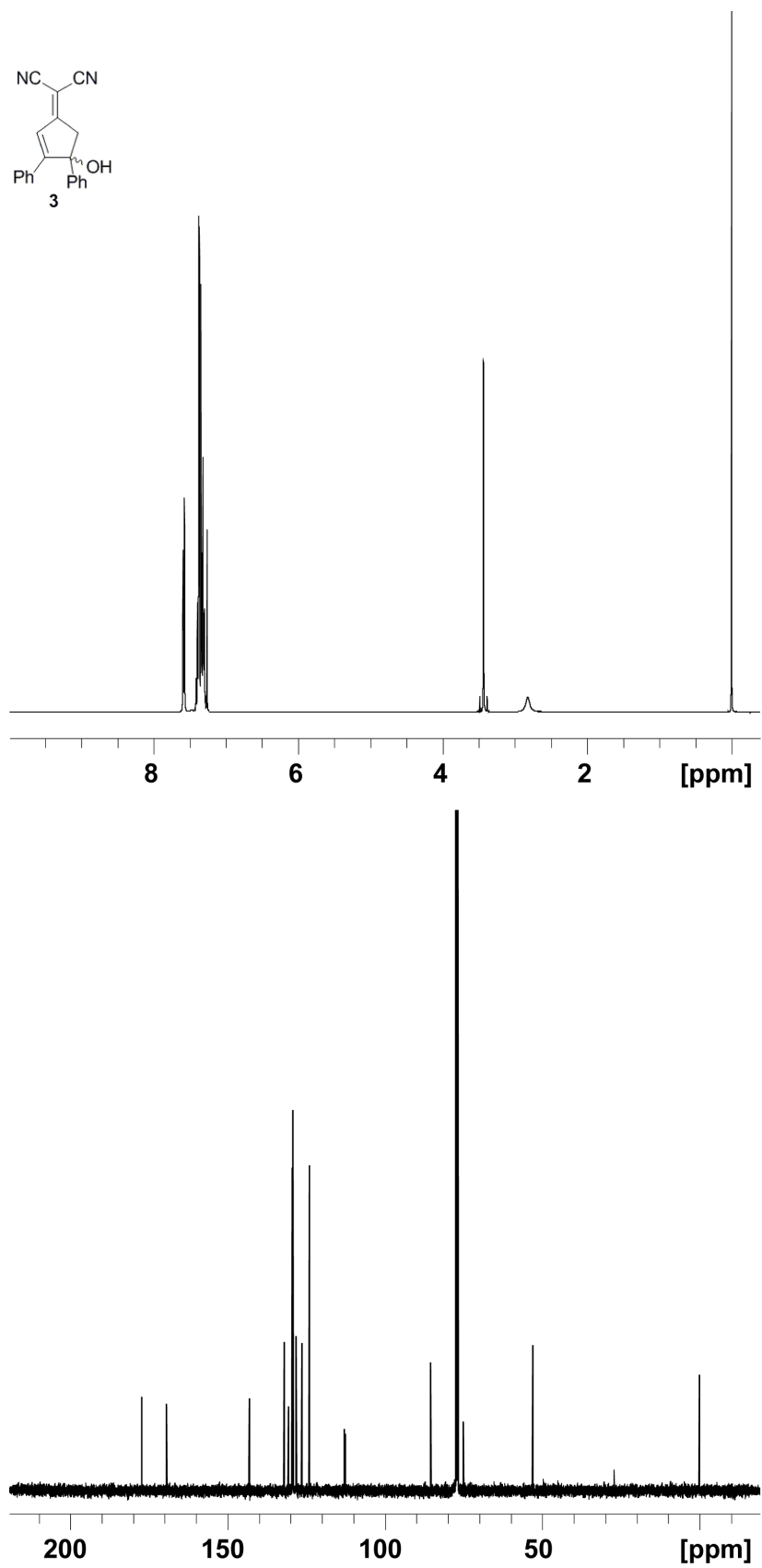
Figure S5. ^{1}H and ^{13}C NMR spectra of **3**.
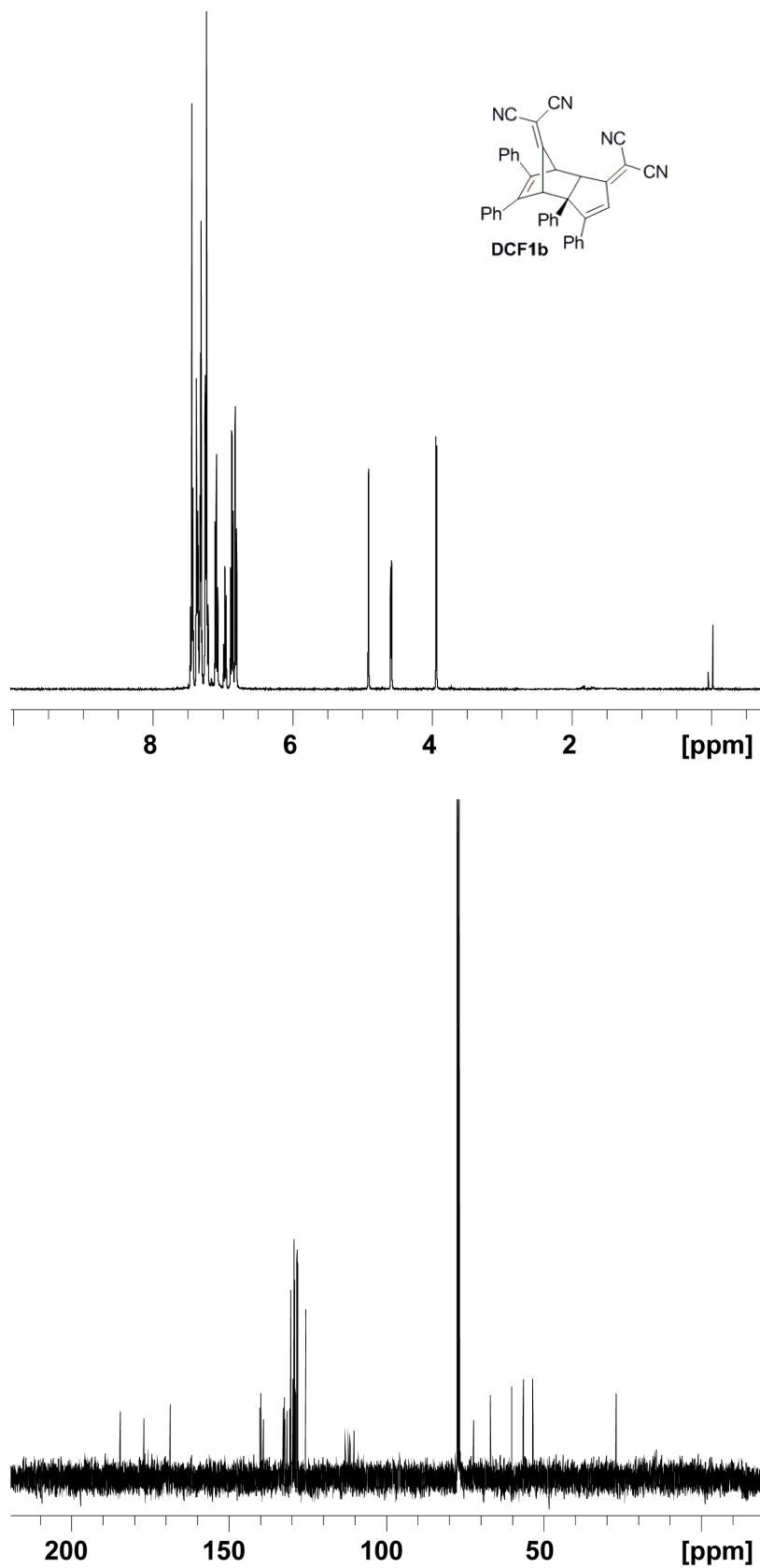
Figure S6(a). ^{1}H and ^{13}C NMR spectra of **DCF1b** in CHCl$_3$.
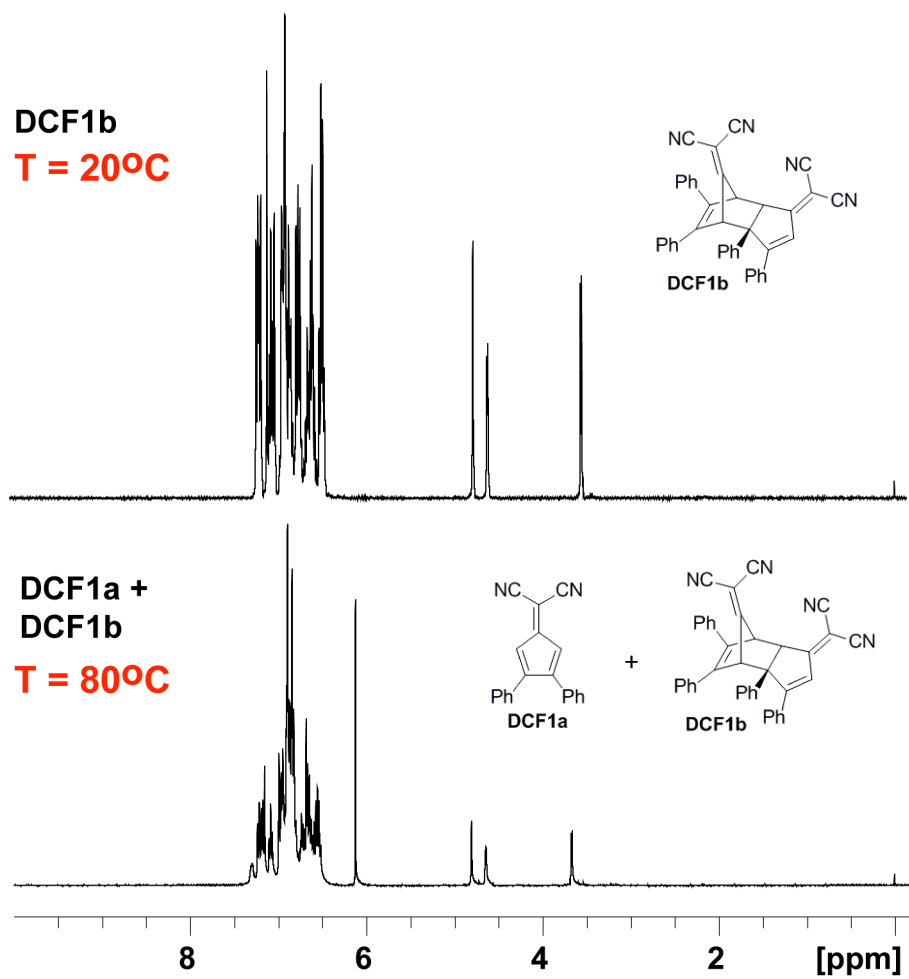
Figure S6(b). ^{1}H-NMR spectrum of **DCF1b** in toluene-d$_8$ at room temperature and at 80°C, showing the evolution of **DCF1a** upon heating.
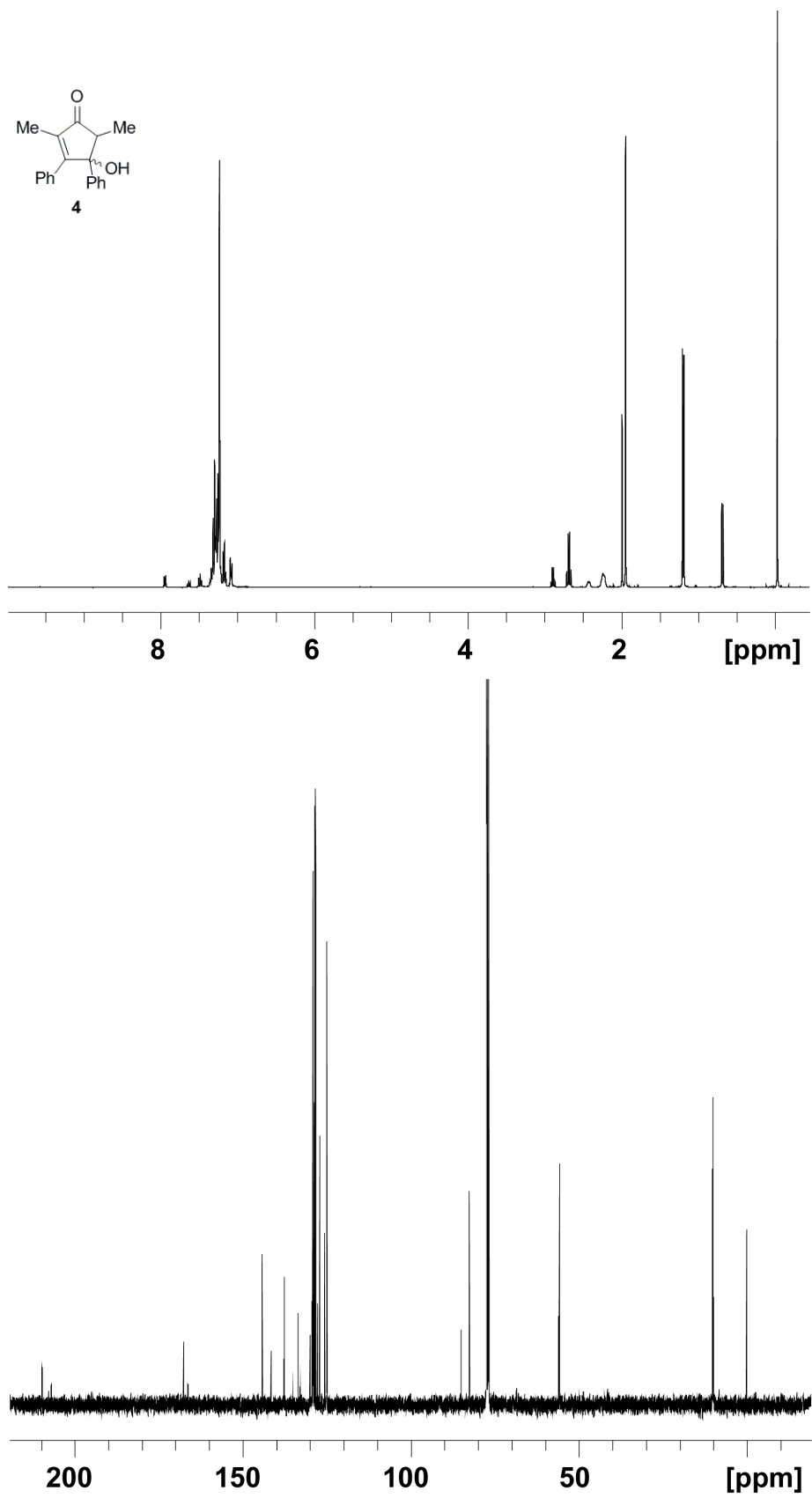
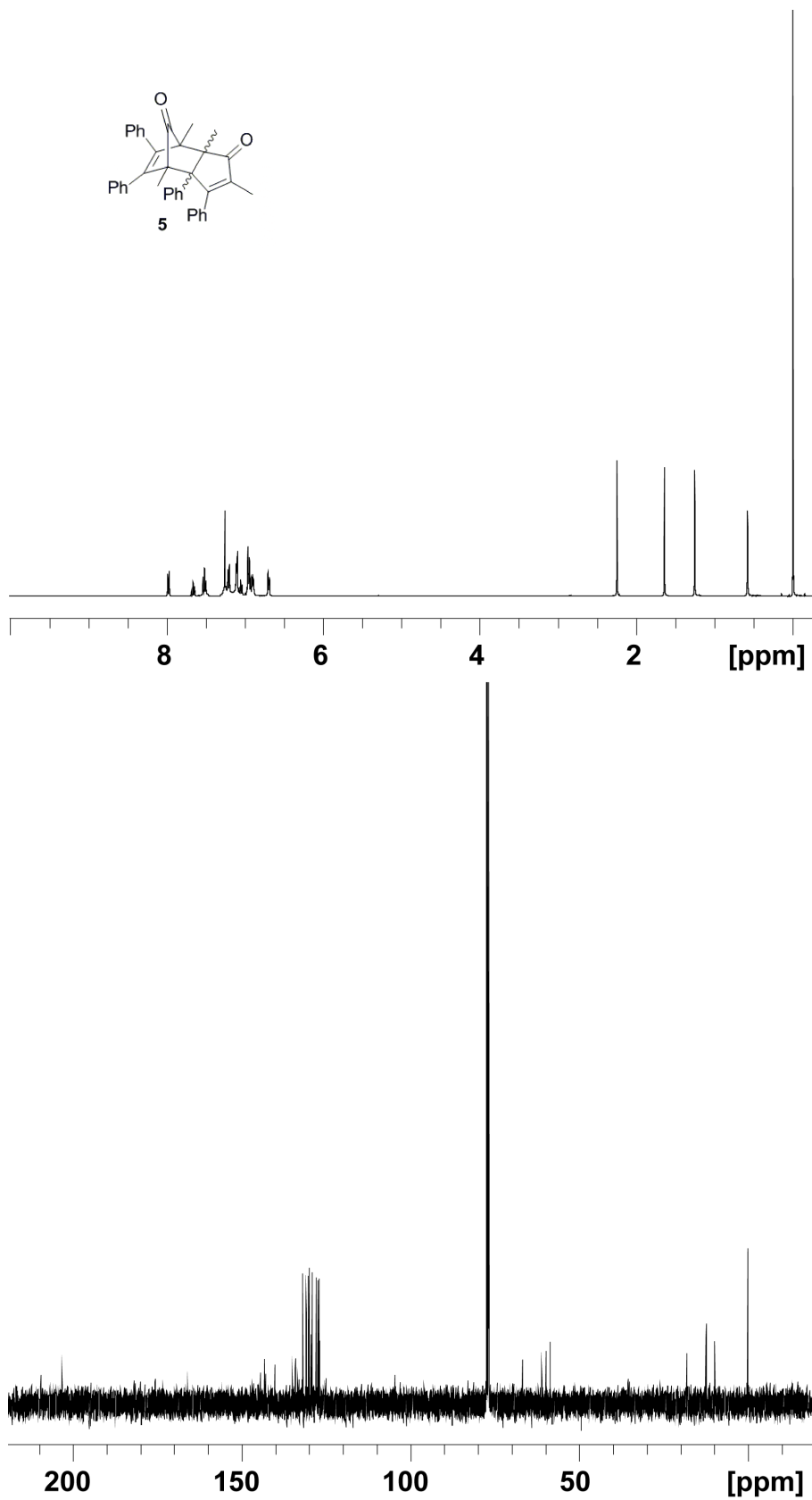**Figure S7**. ^{1}H and ^{13}C NMR spectra of **4**.
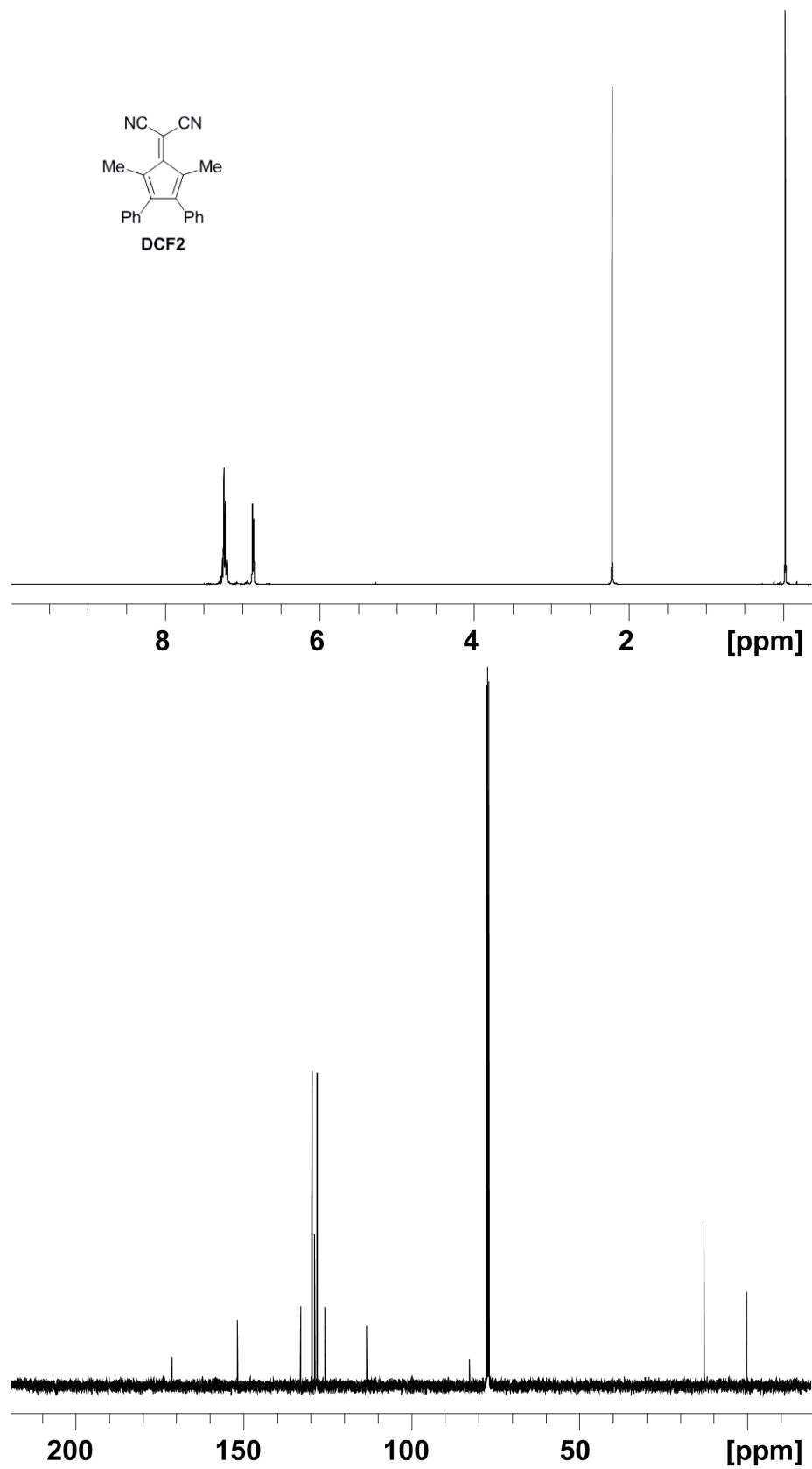
Figure S8. ^{1}H and ^{13}C NMR spectra of **5**.

Figure S9. ^{1}H and ^{13}C NMR spectra of **DCF2**.
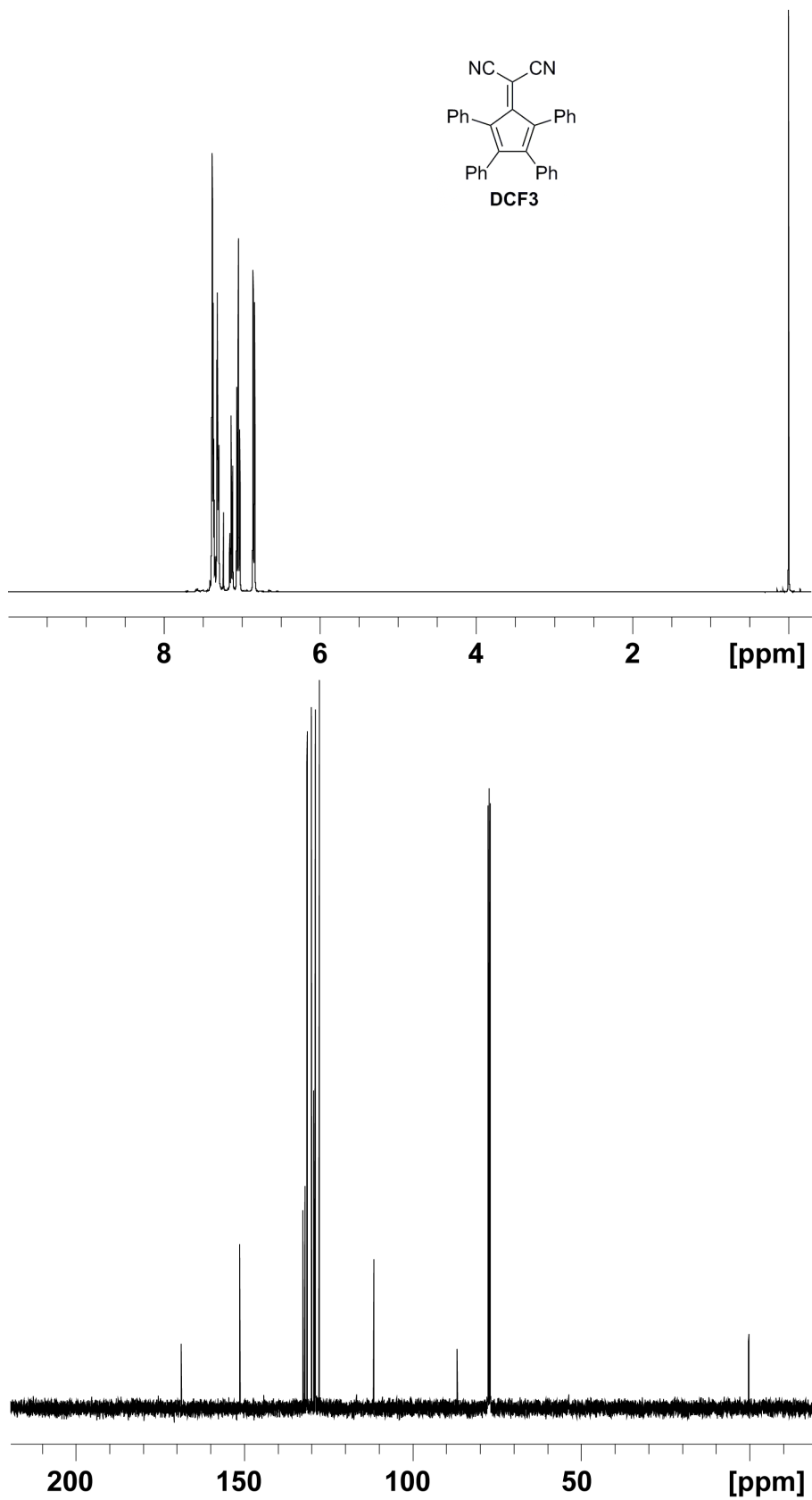
Figure S10. ^{1}H and ^{13}C NMR spectra of **DCF3**.
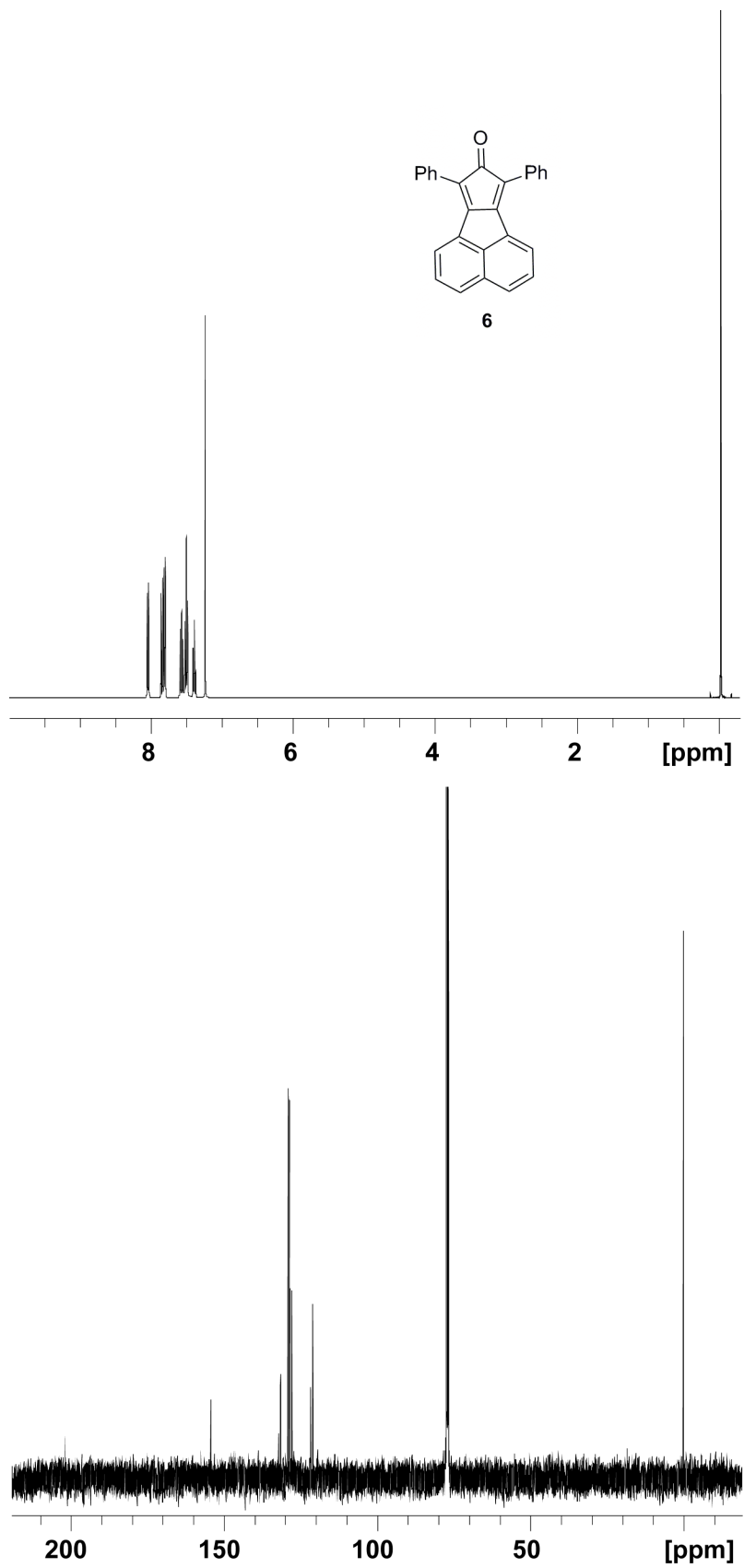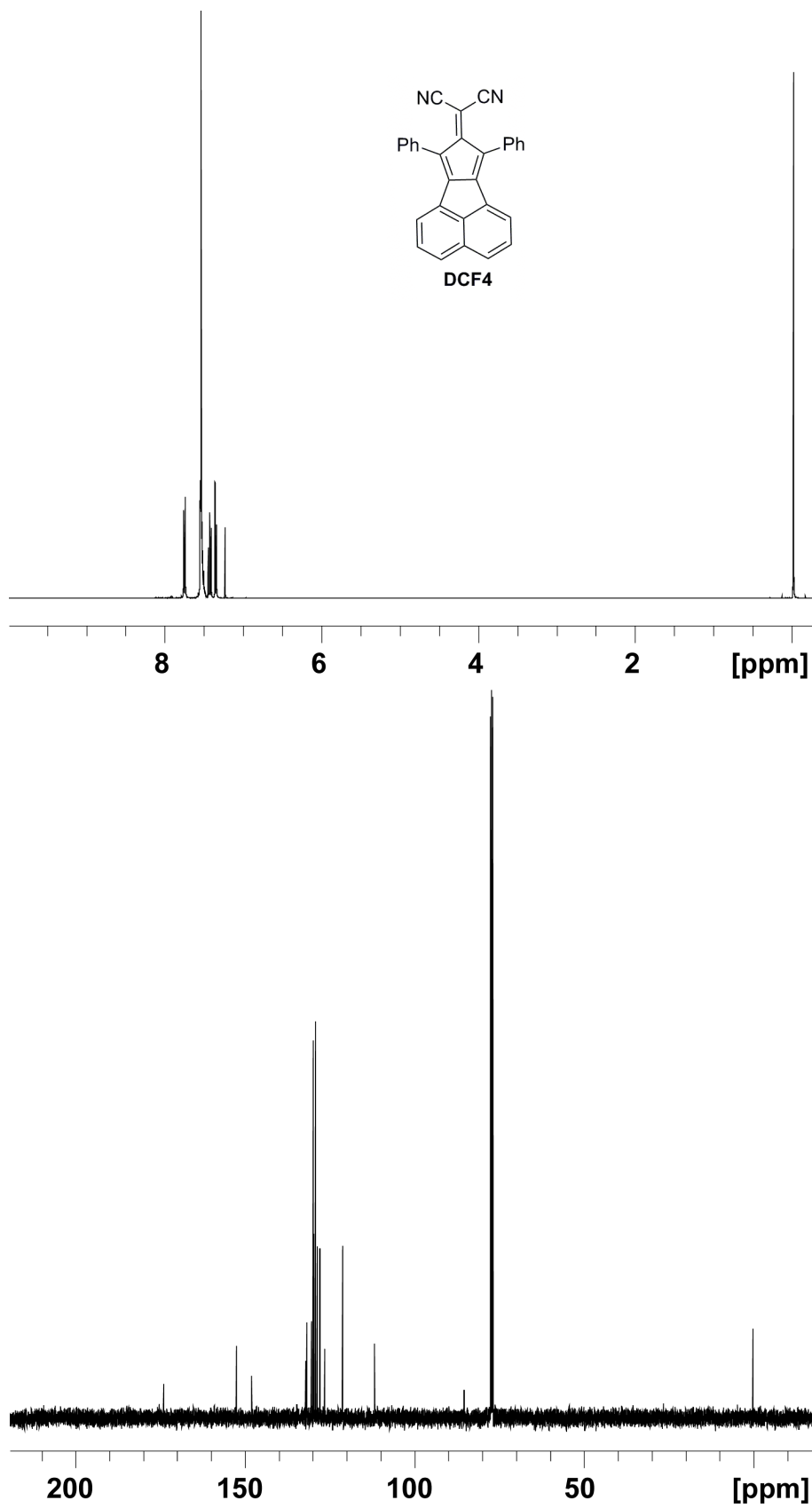
Figure S11. ^{1}H and ^{13}C NMR spectra of **6**.

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