Chemical Communications

Electronic Supplementary Information (ESI)

Expanding the chemical space for push-pull chromophores by non-concerted [2+2] and [4+2] cycloadditions: access to a highly functionalised 6,6-dicyanopentafulvene with an intense, low-energy charge-transfer band

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General experimental methods (ESI)

General: Chemicals were purchased from Acros, Aldrich, Fluka, and TCI and used as received. CH_2Cl_2 was freshly distilled from CaH_2 under nitrogen atmosphere. Column chromatography (CC) and plug filtrations were carried out with SiO_2 60 (particle size 0.040–0.063 mm, 230–400 mesh; Aldrich). Compound **1**,[1] was prepared according to literature procedure. Melting points (M.p.) were measured in open capillaries with a Büchi melting point B540 apparatus and are uncorrected. "Decomp" refers to decomposition. ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker DRX 400 MHz, Bruker AV 400 MHz or Bruker Avance II 600 MHz instruments at 25 °C. Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference. Chemical shifts (δ) are reported in ppm downfield from $SiMe_4$, with the residual solvent signal as an internal reference. Coupling constants (J) are given in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), dd (doublet of doublet) and m (multiplet). Infrared spectra (IR) were recorded on a Perkin-Elmer BX FT-IR spectrometer; signal designations: s (strong), m (medium) and w (weak). Selected absorption bands are reported in wavenumbers (cm^{-1}). UV/Vis spectra were recorded on a Varian CARY-500 spectrophotometer. The spectra were measured in a quartz cuvette of 1 cm at 298 K. The absorption maxima (λ_{max}) are reported in nm with the extinction coefficient (ε) in $dm^3\ mol^{-1}\ cm^{-1}$ in brackets. Shoulders are indicated as sh. High-resolution (HR) ESI-TOF spectra were measured on a Bruker maXis ESI-Q-TOF spectrometer. HR FT-ICR-MALDI spectra were measured on a IonSpec Ultima Fourier transform (FT) instrument with 3-hydroxypicolinic acid (3-HPA). The most important signals are reported in m/z units with M as the molecular ion. Liquid chromatography/mass spectrometry (LC/MS) was performed on an Ultimate 3000 series LC instrument combined with an

MSQ Plus mass spectrometer from Dionex, using a Zorbax Eclipse Plus *C18* column (30 × 3 mm; 3.5 μm pore size) from Agilent. The preparative HPLC separation was carried out using a Merck Hitachi L-7150 pump, equipped with a Merck Hitachi D-7000 interface and a Merck Hitachi L-7614 degasser. For detection, a Merck Hitachi L-7400 UV detector (254 nm) was used. The column used was Hibar, LiChrospher RP-18, 250x25mm with a flow rate of 12 mL/min.

Electrochemistry: The electrochemical experiments were carried out at 20 °C in CH_2Cl_2 (except for **5** in CH_3CN) containing 0.1 M *n*-Bu_4NPF_6 in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). CH_2Cl_2 was purchased in spectroscopic grade from Merck, dried over molecular sieves (4 Å), and stored under Ar prior to use. *n*-Bu_4NPF_6 was purchased in electrochemical grade from Fluka and used as received. The working electrode was a glassy carbon disk electrode (3 mm in a diameter), the auxiliary electrode a Pt wire, and the pseudo-reference electrode a Pt wire. All potentials are referenced to the ferricinium/ferrocene (Fc^+/Fc) couple, used as an internal standard, and uncorrected from ohmic drop. The cell was connected to an Autolab PGSTAT 30 potentiostat (Eco Chemie, The Netherlands) driven by a GPSE software running on a personal computer.

Solvent screening on selectivity between [2+2] and [4+2] cycloaddition reactions (ESI)

Table 1 (ESI). Solvent screening of the regioselective [2+2] and [4+2] cycloaddition reactions. The yields were determined by both LC-MS and ^{1}H NMR except for entry 3 (only LC-MS).

Entry	Conditions	Yield [%]			
		3	**4**	**5**	**6**
1	CH_2Cl_2, 25 ^oC, 15 h	69	29	0	0
2	THF, 25 ^oC, 24 h	62	32	4	0
3	1,4-Dioxane, 25 ^oC, 24 h	78	19	2	0
4	Toluene, 100 ^oC, 15 h	90	10	0	0
5	CH_3CN, 25 ^oC, 15 h	31	22	47	0
6	DMF, 25 ^oC, 15 h	16	25	46	0

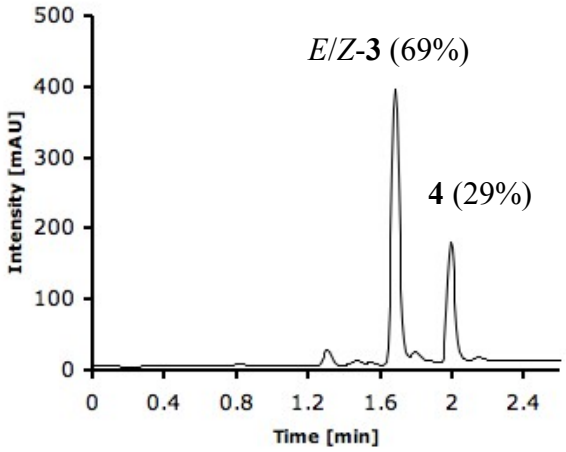


Fig. 1 (ESI). LC-MS profile for entry 1 in Table 1 (ESI).

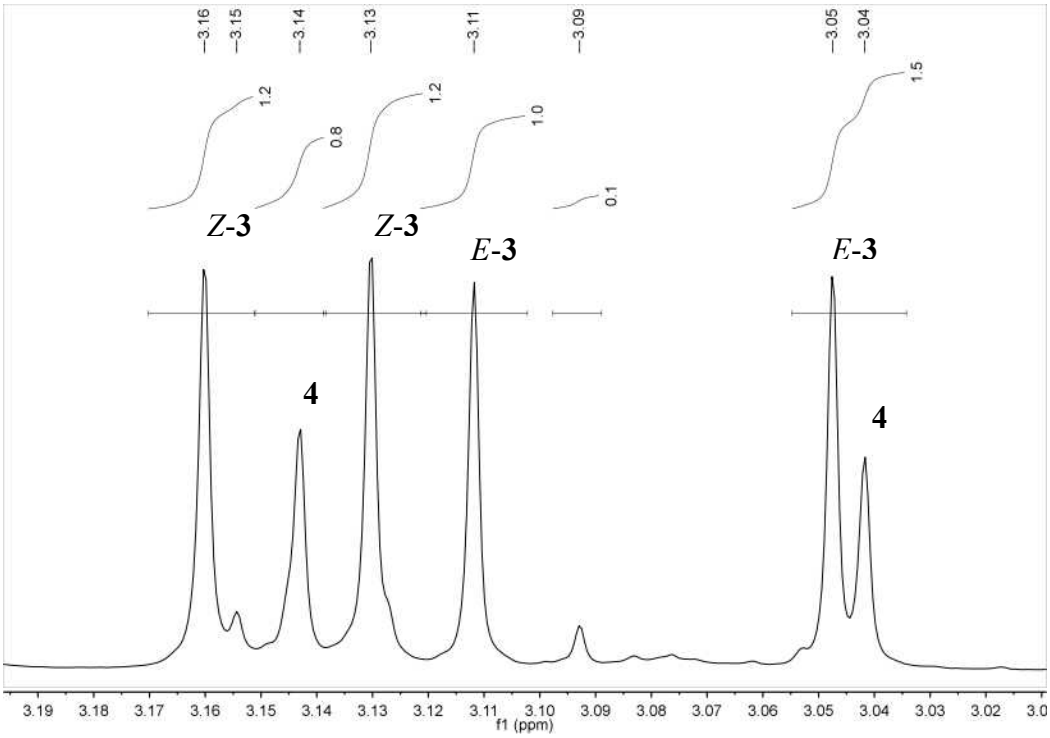


Fig. 2 (ESI). NMe_2 signals in the ^1H NMR spectrum (300 MHz, 298 K) in CD_2Cl_2 for entry 1 in Table 1 (ESI).

Synthetic procedures and characterisation of the products (ESI)

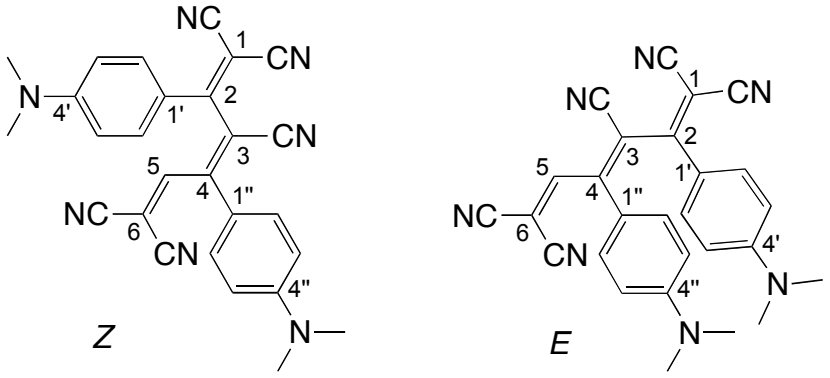
Cycloaddition of 2 to 1: a) A solution of **1** (88 mg, 0.3 mmol) in toluene (25 mL) was heated under nitrogen atmosphere to 100 °C, treated with **2** (38 mg, 0.27 mmol) and stirred for 15 h. After evaporation, reverse-phase HPLC (H_2O/CH_3CN 1:1) gave *E*/*Z*-**3** (101 mg, 86%) and **4** (13 mg, 11%).

b) A solution of **1** (125 mg, 0.42 mmol) in CH_2Cl_2 (25 mL) under nitrogen atmosphere was treated with **2** (55 mg, 0.38 mmol) and stirred at 25 °C for 15 h. After evaporation, reverse-phase HPLC (H_2O/CH_3CN 1:1) gave *E*/*Z*-**3** (100 mg, 60%) and **4** (40 mg, 24%).

c) A solution of **1** (74 mg, 0.25 mmol) in CH_3CN (20 mL) under nitrogen atmosphere was treated with **2** (32 mg, 0.22 mmol), stirred at 25 °C for 15 h when

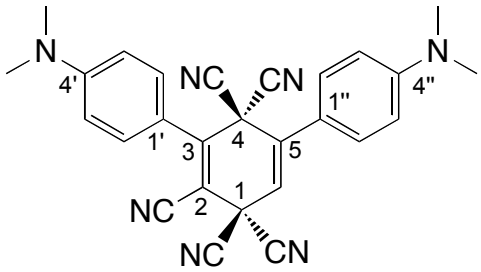
LC-MS revealed a mixture *E*/*Z*-**3**/**4**/**5** 31:22:47. After evaporation, a suspension of the residue in $CHCl_3$/hexane 1:1 was filtered through a sintered funnel. The solid was washed with $CHCl_3$ to afford analytically pure **5** (41.5 mg, 42%).

(*E*/*Z*)-2,4-Bis[4-(dimethylamino)phenyl]hexa-1,3,5-triene-1,1,3,6,6-pentacarbonitrile (*E*/*Z*-**3**):



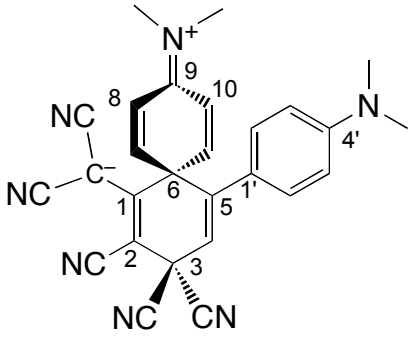
Deep-green solid. ν_{max}(neat)/cm^{-1} 2213 (w), 1602 (s), 1488 (m), 1437 (m), 1379 (m), 1344 (m), 1206 (m), 1167 (m), 943 (w), 821 (w); δ_H(400 MHz; $CDCl_3$; 298 K; *E*/*Z* ca. 1:1) 3.04 (s, 3 H; 0.5 NMe_2), 3.12 (s, 3 H; 0.5 NMe_2), 3.17 (s, 6 H; NMe_2), 6.60 (d, J = 9.0 Hz, 1 H), 6.76–6.73 (m, 3 H), 7.06 (d, J = 9.0 Hz, 1 H), 7.45 (d, J = 9.1 Hz, 1 H), 7.49 (s, 0.5 H; 0.5 H–C(5)), 7.67 (d, J = 9.2 Hz, 1 H), 7.82 (d, J = 9.2 Hz, 1 H), 8.22 ppm (s, 0.5 H; 0.5 H–C(5)); δ_C(100 MHz; $CDCl_3$; 298 K; *E*/*Z* ca. 1:1) 39.97/40.12/40.19/40.26 (2 NMe_2), 75.20/76.14 (C(1)), 93.54/95.56 (C(6)), 108.89/108.98/109.35/109.62/111.55/112.27/112.37/114.19/114.31/114.89/115.44/116.59 (C(3), 5 C≡N), 112.00/112.02/112.10/112.35 (C(3',5',3'',5'')), 118.45/118.57/119.60/120.55 (C(1',1'')), 131.15/132.28/132.70/133.18 (C(2',6',2'',6'')), 152.95/153.54/154.08/154.37/154.53/155.57 (C(2,4',4'')), 157.09/158.47 (C(5)), 161.39/161.57 ppm (C(4)); HR-MALDI-MS (negative mode): *m*/*z* (%): 445.1986 (13), 444.1925 (62), 443.1867 (100, $[M]^-$, calcd for $C_{27}H_{21}N_7^-$: 443.1858), 417.1829 (26), 416.1770 (26, $[M - HCN]^-$, calcd for $C_{26}H_{20}N_6^-$: 416.1749).

3,5-Bis[4-(dimethylamino)phenyl]cyclohexa-2,5-diene-1,1,2,4,4-pentacarbonitrile (**4**):



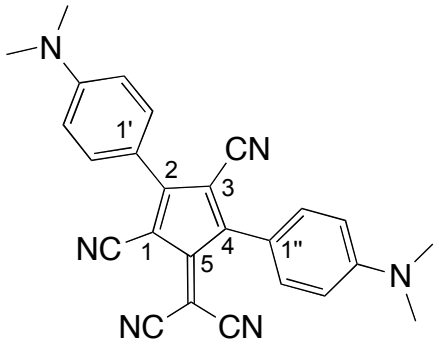
Light brown solid. M.p. > 259 °C (decomp); ν_{max}(neat)/cm^{-1} 2917 (w), 2860 (w), 2811 (w), 2218 (w), 2158 (w), 1605 (s), 1526 (s), 1484 (w), 1444 (w), 1372 (m), 1293 (w), 1271 (w), 1218 (w), 1198 (m), 1173 (m), 1124 (w), 1064 (w), 946 (w), 817 (m), 789 (w); δ_H(600 MHz; CD_2Cl_2; 298 K) 3.05 (s, 6 H; NMe_2), 3.11 (s, 6 H; NMe_2), 6.32 (s, 1 H; H–C(5)), 6.78 (d, J = 9.1 Hz, 2 H) and 6.83 (d, J = 9.2 Hz, 2 H) (H–C(2',6',2'',6'')), 7.54 (d, J = 9.2 Hz, 2 H) and 7.72 ppm (d, J = 9.2 Hz, 2 H) (H–C(3',5',3'',5'')); δ_C(150 MHz; CD_2Cl_2; 298 K) 35.93 (C(1)), 40.19 (2 NMe_2), 40.32 (C(4)), 100.55 (C(2)), 110.73 (C(C≡N)$_2$), 111.49 (C(C≡N)$_2$), 111.91/112.07 (C(3',5',3'',5'')), 113.41 (C(6)), 114.50 (C≡N), 117.85/119.66 (C(1',1'')), 129.11/130.82 (C(2',6',2'',6'')), 136.31 (C(5)), 149.04 (C(3)), 152.63/153.77 ppm (C(4',4'')); HR-MALDI-MS (negative mode): m/z (%): 444.1883 (19), 443.1842 (50, [M]$^-$, calcd for $C_{27}H_{21}N_7^-$: 443.1858), 417.1788 (33), 416.1733 (100, [M – HCN]$^-$, calcd for $C_{26}H_{20}N_6^-$: 416.1749).

Dicyano{2,3,3-tricyano-5-[4-(dimethylamino)phenyl]-9 (dimethyliminio)-spiro[5.5]undeca-1,4,7,10-tetraen-1-yl}methanide (**5**):



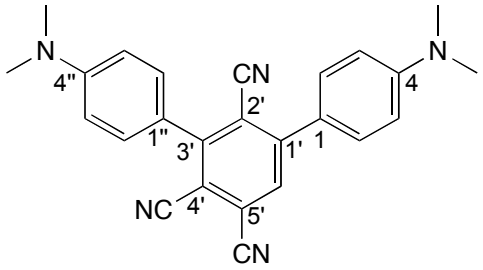
Maroon solid. M.p. > 213 °C (decomp); λ_{max}(CH_3CN)/nm 362 (ε/dm^3 mol^{-1} cm^{-1} 13 237), 461 (727); ν_{max}(neat)/cm^{-1} 3058 (w), 2923 (w), 2819 (w), 2197 (m), 2178 (s), 2161 (m), 1650 (s), 1606 (s), 1519 (s), 1445 (w), 1360 (m), 1226 (w), 1197 (m), 819 (m); δ_H(400 MHz; CD_3CN; 298 K; assignments based on NOE experiments) 2.90 (s, 6 H; Me_2N–C(4')), 3.37 (s, 6 H; Me_2N^+=C(9)), 6.20 (s, 1 H; irradiation at 6.85 ppm → NOE of 8 %; H–C(4)), 6.56 (d, J = 8.9 Hz, 2 H; irradiation at 2.90 ppm → NOE of 10 %; irradiation at 6.85 ppm → NOE of 4 %; H–C(3',5')), 6.85 (d, J = 8.9 Hz, 2 H; irradiation at 6.56 ppm → NOE of 5 %; irradiation at 7.14 ppm → NOE of 2 %; H–C(2',6')), 7.01 (d, J = 10.2 Hz, 2 H; irradiation at 3.37 ppm → NOE of 8 %; irradiation at 7.14 ppm → NOE of 3 %; H–C(8,10)), 7.14 ppm (d, J = 10.2 Hz, 2 H; irradiation at 6.85 ppm → NOE of 4 %; irradiation at 7.01 ppm → NOE of 9 %; H–C(7,11)); δ_C(150 MHz; CD_3CN; 298 K; assignments based on comparison with related structures in refs.[2]) 36.39 ($C^-(CN)_2$), 39.43 (NMe_2), 43.47 (N^+Me_2), 43.88 (C(6)), 51.45 (C(3)), 70.49 (C(2)), 110.48 (C(3',5')), 113.96 (C(1)), 117.66 (C(C≡N)$_2$), 119.58 (C≡N), 121.71 (C(8,10)), 122.57 (C(1')), 130.30 (C(2',6')), 140.43 (C(4)), 148.68 (C(5)), 150.75 (C(4')), 152.24 (C(7,11)), 162.57 ppm (C(9)), signal for (C^-(C≡N)$_2$) hidden by the CD_3CN signal; HR-MALDI-MS (negative mode): m/z (%): 444.1888 (41), 443.1845 (100, [M]$^-$, calcd for $C_{27}H_{21}N_7^-$: 443.1858), 417.1804 (27), 416.1740 (57, [M – HCN]$^-$, calcd for $C_{26}H_{20}N_6^-$: 416.1749).

5-(Dicyanomethylene)-2,4-bis[(4-dimethylamino)phenyl]cyclopenta-1,3-diene-1,3-dicarbonitrile (**6**).



A solution of *E*/*Z*-**3** 1:1 (104 mg, 0.23 mmol) in MeCN/H_2O 1:1 (20 mL) was treated with $(NH_4)_2Ce(NO_3)_6$ (CAN) (64 mg, 0.12 mmol) and stirred at room temperature for 12 h when LC-MS showed complete conversion. The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to afford **6** (88 mg, 90%) as a maroon metallic solid. An analytical sample was obtained by recrystallisation in CH_2Cl_2/hexane. M.p. > 400 °C; $\lambda_{max}(CH_2Cl_2)$/nm 782 (ε/dm^3 mol^{-1} cm^{-1} 27 522); ν_{max}(neat)/cm^{-1} 2924 (w), 2210 (w), 1596 (s), 1486 (m), 1427 (m), 1371 (s), 1356 (s), 1218 (m), 1197 (m), 1170 (m), 1091 (w), 944 (w), 823 (w); δ_H(600 MHz; CD_2Cl_2; 298 K): 3.14 (s, 6 H; NMe_2), 3.25 (s, 6 H; NMe_2), 6.84 (d, *J* = 9.0 Hz, 2 H; H–C(3'',5'')), 6.90 (d, *J* = 9.4 Hz, 2 H; H–C(3',5')), 7.45 (d, *J* = 9.1 Hz, 2 H; H–C(2'',6'')), 8.26 ppm (d, *J* = 9.4 Hz, 2 H; H–C(2',6')); δ_C(150 MHz; CD_2Cl_2; 298 K) 40.64 (br., NMe_2), 40.99 (NMe_2), 80.01 (*C*(C≡N)$_2$), 87.88 (C(1)), 108.48 (C(3)), 112.54 (br., C(3'',5'')), 113.32/114.05 (C(*C*≡N)$_2$), 113.61 (C(3',5')), 116.17 (C≡N), 116.72 (C≡N), 117.18 (br., C(1'')), 119.29 (br., C(1')), 132.97/134.18 (C(2',6',2'',6'')), 153.79 (br., C(4'')), 155.68 (C(4')), 157.48/159.13 (C(2,4)), 160.70 ppm (C(5)); HR-MALDI-MS (negative mode): *m*/*z* (%): 418.1857 (17), 417.1824 (79), 416.1754 (100, [*M*]$^-$, calcd for $C_{26}H_{20}N_6^-$: 416.1749).

4,4''-Bis(dimethylamino)-[1,1':3',1''-terphenyl]-2',4',5'-tricarbonitrile (**7**).



A solution of **4** (40 mg, 0.09 mmol) in CH_2Cl_2 (10 mL) was treated with SiO_2 (3 g), stirred at room temperature for 2 h and filtered through a pad of Celite. Evaporation gave sufficiently pure **7** (34 mg, 95%) as an orange solid. M.p. 211–213 °C; $\lambda_{max}(CH_2Cl_2)$/nm 384 (ε/dm^3 mol^{-1} cm^{-1} 12 041), 435 (9511, sh); ν_{max}(neat)/cm^{-1} 2912 (w), 2823 (w), 2222 (w), 2162 (very w), 1607 (s), 1567 (m), 1530 (m), 1515 (s), 1435 (w), 1420 (w), 1370 (s), 1344 (m), 1235 (w), 1199 (s), 1176 (m), 1156 (w), 1065 (w), 946 (w), 813 (m); δ_H(400 MHz; CD_2Cl_2; 298 K) 3.06 (s, 6 H; NMe_2), 3.07 (s, 6 H; NMe_2), 6.84 (d, J = 8.9 Hz, 2 H; H–C(3,5)), 6.87 (d, J = 9.0 Hz, 2 H; H–C(3'',5'')), 7.45 (d, J = 9.0 Hz, 2 H; H–C(2,6)), 7.55 (d, J = 9.0 Hz, 2 H; H–C(2'',6'')), 7.79 ppm (s, 1 H; H–C(6')); δ_C(100 MHz; $CDCl_3$; 298 K) 40.50 (2 NMe_2), 100.57 (C(4')), 112.12/112.49 (C(3,5,3'',5'')), 113.18 (C≡N), 115.60 (C≡N), 115.86 (C≡N), 117.26 (C(2')), 119.83 (C(5')), 121.29/122.71 (C(1,1'')), 130.67/131.05 (C(2,6,2'',6'')), 132.33 (C(6')), 151.53/152.25/152.38/152.85 ppm (C(4,1',3',4'')); HR-MALDI-MS: m/z (%): 393.1906 (20), 392.1872 (75), 391.1798 (100, $[M]^+$, calcd for $C_{25}H_{21}N_5^+$: 391.1797), 390.1720 (42), 377.1639 (25, $[M - CH_2]^+$, calcd for $C_{24}H_{19}N_5^+$: 377.1640), 376.1566 (11), 374.1404 (20, $[M - CH_4 - H]^+$, calcd for $C_{24}H_{16}N_5^+$: 374.1406).

X-ray data for compounds 1, 4, 5, 6 and 7 (ESI)

Crystals of compounds **5**, **6** and **7** were measured on a Bruker Nonius Kappa-CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å), compounds **1** and **4** on a Bruker Kappa Apex II Duo equipped with a Cu microfocus tube (λ =1.54178 Å) at 100 K. The structures were solved by direct methods with SHELXS-97[3] and refined by full-matrix least-squares analysis (SHELXL-97),[4] using an isotropic extinction correction. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically for compounds **1** and **5**. Hydrogen positions for compounds **4**, **6** and **7** are based on stereochemical considerations and included in the final structure factor calculation. CCDC 802217 (**1**), CCDC 801746 (**4**), CCDC 801743 (**5**), CCDC 801744 (**6**) and CCDC 801745 (**7**) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac. uk/data _request/cif

X-ray crystal structure of 1: Crystal data for $C_{17}H_{10}N_6$, M_r = 298.3, tetragonal space group $P4_3$, D_{calcd} = 1.310 Mg m^{-3}, Z = 4, a = 11.5737 (3) Å, b = 11.5737 (3) Å, c = 11.5001(5) Å, V = 1540.43 (10) Å^3; μ = 0.084 mm^{-1}. A dark green crystal (cubic dimensions ca. 0.15 × 0.16 × 0.16 mm) was obtained from CH_2Cl_2/hexane solution at 25 °C. Numbers of measured and unique reflections were 10808 and 8470, respectively (R_{int} = 0.0153). The tricyanovinyl moiety is disordered and refined over two positions. Final $R(F)$ = 0.057, $wR(F2)$ = 0.153 for 828 parameters and 8470 reflections with $I > 2\sigma(I)$ and $1.76 < \theta < 26.46°$ (corresponding R values based on all 8470 reflections are 0.056 and 0.154, respectively).

X-ray crystal structure of 4: Crystal data for $C_{27}H_{21}N_7$, M_r = 443.514, monoclinic space group $P2_1/c$, D_{calcd} = 1.337 Mg m^{-3}, Z = 4, a = 23.1039(7) Å, b = 6.0941(2) Å, c = 15.7821(5) Å, β = 92.218(2)°, V = 2204.0(1) Å^3; μ = 0.663 mm^{-1}. A brownish red crystal (linear dimensions ca. 0.12 × 0.04 × 0.01 mm) was obtained from CH_2Cl_2/hexane solution at 25 °C. Numbers of measured and unique reflections were 8349 and 2263, respectively (R_{int} = 0.036). Final $R(F)$ = 0.034, $wR(F2)$ = 0.106 for 391 parameters and 1873 reflections with $I > 2\sigma(I)$ and $1.91 < \theta < 50.31°$ (corresponding R values based on all 2263 reflections are 0.096 and 0.101, respectively).

X-ray crystal structure of 5: Crystal data for $C_{27}H_{21}N_7$, M_r = 443.514, orthorhombic space group $Pbca$, D_{calcd} = 1.336 Mg m^{-3}, Z = 8, a = 11.2924(4) Å, b = 15.4265(7) Å, c = 25.3239(11) Å, V = 4411.5(3) Å^3; μ = 0.084 mm^{-1}. A brownish red crystal (linear dimensions ca. 0.33 × 0.18 × 0.03 mm) was obtained from CH_3CN/THF solution at 25 °C. Numbers of measured and unique reflections were 7442 and 3818, respectively (R_{int} = 0.093). Final $R(F)$ = 0.069, $wR(F2)$ = 0.177 for 391 parameters and 3026 reflections with $I > 2\sigma(I)$ and $2.75 < \theta < 24.71°$ (corresponding R values based on all 3818 reflections are 0.092 and 0.188, respectively).

X-ray crystal structure of 6. 0.5 $CHCl_3$: Crystal data for 2 $(C_{26}H_{20}N_6)\cdot CHCl_3$, M_r = 868.312, Triclinic, space group $P\bar{1}$, D_{calcd} = 1.201 g cm^{-3}, Z = 1, a = 9.1282(3) Å, b = 11.1896(3) Å, c = 12.4251(4) Å, α = 102.417(1)°, β = 90.498(1)°, γ = 103.968 (1)°, V = 1200.32(6) Å^3; μ = 0.242 mm^{-1}. A metallic maroon crystal (linear dimensions ca. 0.27 × 0.24 × 0.21 mm) was obtained from $CHCl_3$/hexane solution at 25 °C. Numbers of measured and unique reflections were 9624 and 5472, respectively (R_{int} = 0.045). Structure contains one disordered $CHCl_3$ molecule close

to an inversion centre in the unit cell. Final $R(F) = 0.071$, $wR(F2) = 0.221$ for 328 parameters and 4453 reflections with $I > 2\sigma(I)$ and $2.91 < \theta < 27.48°$ (corresponding R values based on all 5472 reflections are 0.087 and 0.232, respectively).

X-ray crystal structure of 7. 0.25 $C_2H_4Cl_2$: Crystal data for 2 $(C_{25}H_{21}N_5)\cdot 0.5\ C_2H_4Cl_2$, $M_r = 832.436$, Triclinic, space group $P\bar{1}$, $D_{calcd} = 1.292$ Mg m^{-3}, $Z = 2$, $a = 9.8044(6)$ Å, $b = 12.8651(10)$ Å, $c = 18.011(2)$ Å, $\alpha = 93.245(5)°$, $\beta = 91.748(5)°$, $\gamma = 109.113(3)°$, $V = 2140.3(3)$ Å^3; $\mu = 0.139$ mm^{-1}. A dark red crystal (linear dimensions ca. 0.24 × 0.075 × 0.009 mm) was obtained from CH_2ClCH_2Cl/THF solution at 25 °C. Numbers of measured and unique reflections were 11481 and 7214, respectively ($R_{int} = 0.037$). Final $R(F) = 0.074$, $wR(F2) = 0.21$ for 570 parameters and 5920 reflections with $I > 2\sigma(I)$ and $2.75 < \theta < 24.71°$ (corresponding R values based on all 7214 reflections are 0.092 and 0.220, respectively).

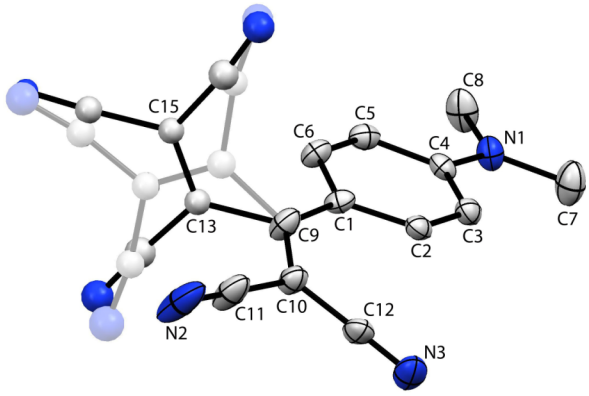


Fig. 3 (ESI). ORTEP plot of **1**, arbitrary numbering, H-atoms are omitted for enhanced clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths (Å), and torsional angle [°]: C1–C2: 1.416(3), C2–C3: 1.359(3), C3–C4: 1.421(3), C4–C5: 1.425(3), C5–C6: 1.355(4), C6–C1: 1.417(3), C1–C9: 1.424(3), C10–C9–C13–C15: 107.8(4), C2–C1–C9–C10: –9.3(5).

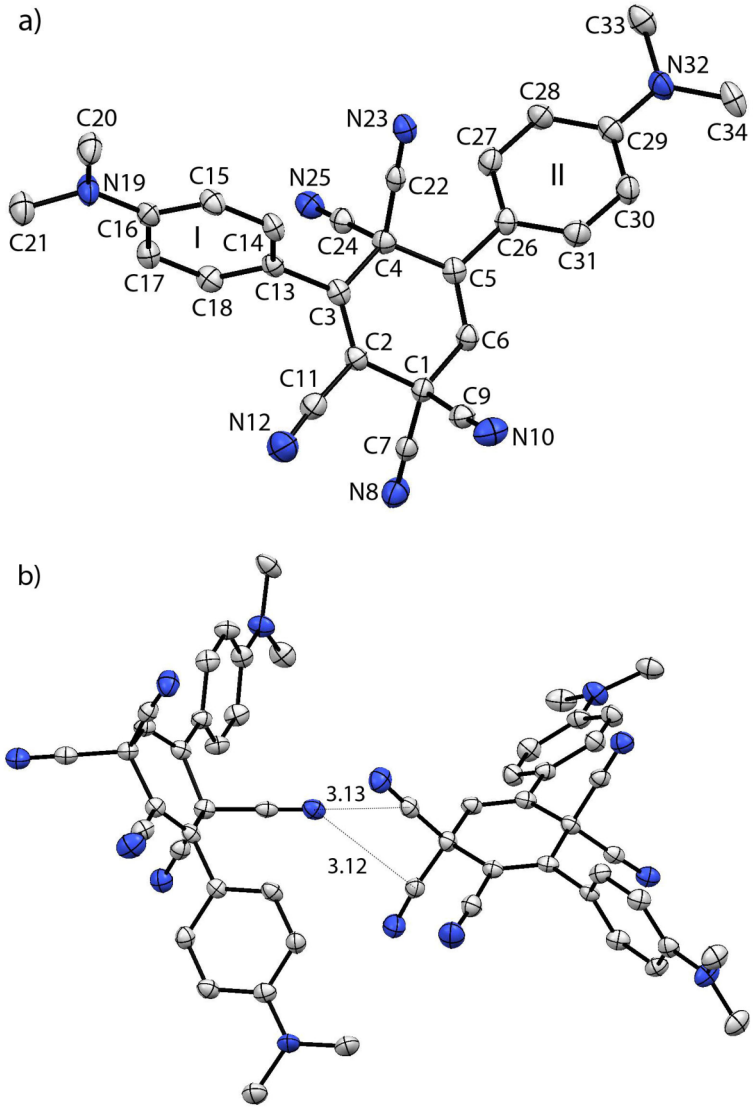


Fig. 4 (ESI). a) ORTEP plot of **4**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths (Å), angles (°), and torsional angles (°): C3–C13: 1.487(3), C13–C18: 1.395(3), C18–C17: 1.378(3), C17–C16: 1.407(3), C16–C15: 1.407(3), C15–C14: 1.375(3), C14–C13: 1.383(3), C5–C26: 1.482(3), C26–C27: 1.390(3), C27–C28: 1.380(3), C28–C29: 1.403(3), C29–C30: 1.398(3), C30–C31: 1.377(3), C31–C26: 1.401(3), C3–C2–C1: 124.98(19), C3–C4–C5: 115.19(18), C2–C1–C6: 112.56(18), C2–C3–C13–C18 (θ_I): –74.87(18), C6–C5–C26–C31(θ_{II}): –32.45(18). b) Arrangement of neighbouring molecules in the crystal packing of **4** (distances given in Å).

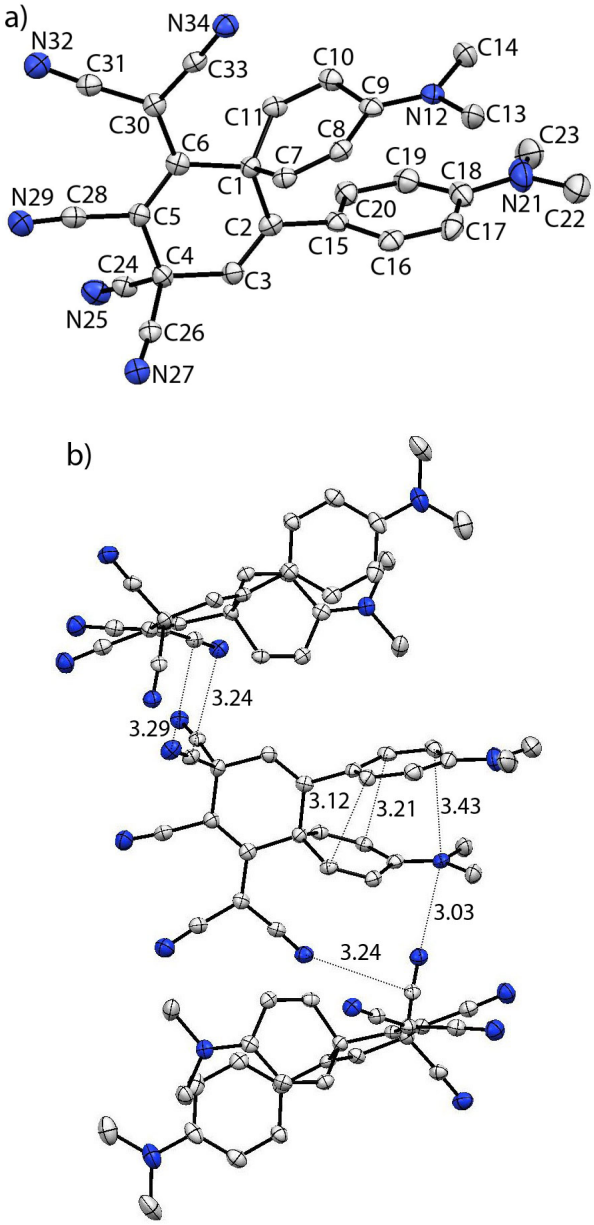
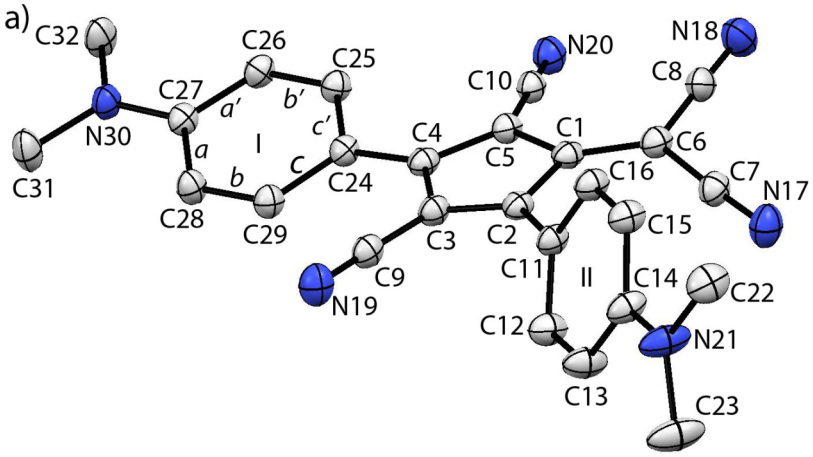


Fig 5 (ESI). a) ORTEP plot of **5**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths (Å), angles (°), and torsional angles (°): C1–C2: 1.570(4), C2–C3: 1.313(4), C3–C4: 1.519(4), C4–C5: 1.532(4), C5–C6: 1.368(4), C6–C1: 1.536(4), C2–C15: 1.491(4), C15–C16: 1.388(4), C16–C17: 1.392(5), C17–C18: 1.404(5), C18–C19: 1.403(5), C19–C20: 1.382(4), C20–C15: 1.399(4), C3–C4–C5: 113.2(2), C5–C6–C1: 120.8(3), C6–C1–C2: 112.4(2), C11–C1–C7: 110.6(2), C10–C9–C8: 117.1(3), C11–C1–C2: 107.1(2), C30–C6–C1–C11: –46.4(3), C3–

C2–C15–C16 (θ): –98.3(4). b) Arrangement of neighbouring molecules in the crystal packing of **5**. The crystal packing of **5** show that adjacent molecules of each of these species interact *via* various orthogonal dipolar interactions, such as CN···CN, CN···N^+ and π···π interactions (distances given in Å). The electron-rich DMA ring and the electron-deficient cyclohexa-2,5-diene-1-dimethylimminium ring are aligned in a parallel-displaced π -π stacking mode with short intramolecular C···C contacts of 3.12 (C_{11}···C_{20}) and 3.21 Å (C_8···C_{16}). The cyclohexadiene ring adopts a flat boat conformation, and the *C*=N^+ moiety deviates 16° out of the plane to point towards the DMA ring and most probably engage in stabilising cation-π interactions.



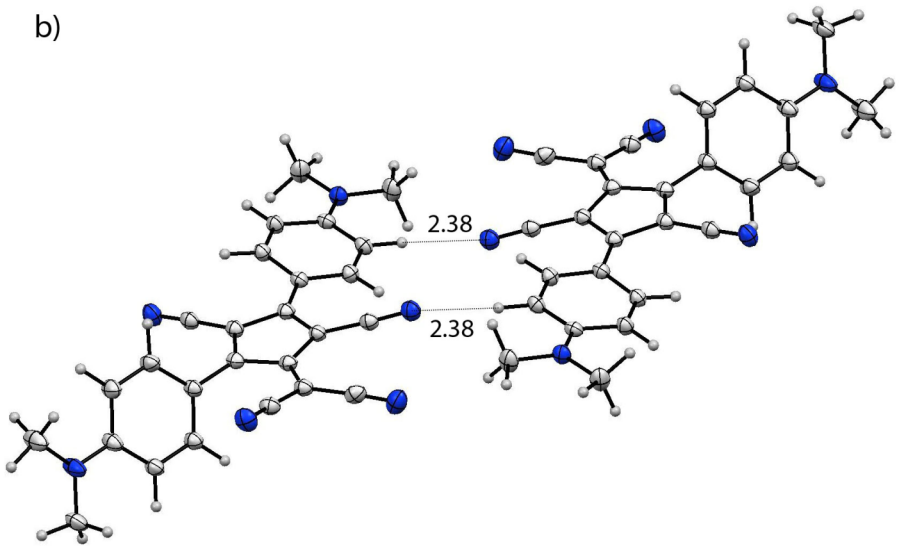


Fig. 6 (ESI). a) ORTEP plot of **6**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths (Å), angles (°), and torsional angles (°): C1–C6: 1.378(6), C6–C8: 1.435(6), C6–C7: 1.435(6), C1–C5: 1.434(5), C5–C4: 1.408(6), C4–C24: 1.423(6), C24–C25: 1.431(5), C25–C26: 1.362(6), C26–C27: 1.424(6), C27–C28: 1.436(6), C28–C29: 1.365(6), C29–C24: 1.425(6), C27–N30: 1.339(5), C2–C11: 1.463(6), C11–C12: 1.405(6), C12–C13: 1.378(6), C13–C14: 1.418(6), C14–C15: 1.409(6), C15–C16: 1.376(6), C16–C11: 1.398(6), C8–C6–C7: 112.9(4), C2–C1–C5: 106.6(4), C5–C4–C3: 105.3(3), C3–C4–C24–C29 (θ_{I}): –13.6(4), C3–C2–C11–C12 (θ_{II}): 59.3(5). b) Arrangement of neighbouring molecules in the crystal packing of **6** show that adjacent molecules interact *via* week CN···HC_{arom} interactions.

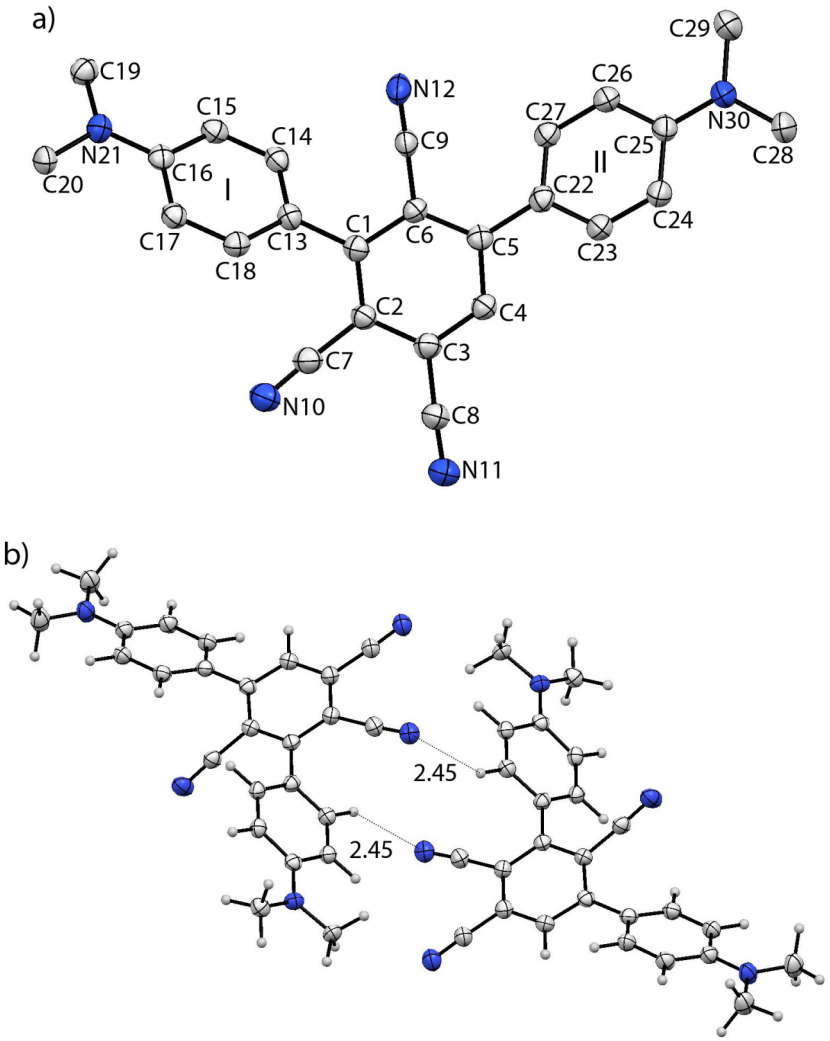


Fig. 7 (ESI). a) ORTEP plot of **7**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths (Å), angles (°), and torsional angles (°): C1–C13: 1.481(4), C13–C14: 1.402(4), C14–C15: 1.379(4), C15–C16: 1.415(4), C16–C17: 1.414(4), C17–C18: 1.382(4), C18–C13: 1.398(4), C16–N21: 1.371(4), C5–C22: 1.472(4), C22–C23: 1.402(4), C23–C24: 1.377(4), C24–C25: 1.404(4), C25–C26: 1.412(4), C26–C27: 1.387(4), C27–C22: 1.387(4), C7–N10: 1.155(4), C8–N11: 1.149(4), C2–C1–C6: 117.3(2), C4–C5–C6: 116.6(2), C3–C4–C5: 121.7(3), C2–C1–C13–C18 (θ_{I}): 46.4(4), C6–C5–C22–C27 (θ_{II}): –33.6(4). b) Arrangement of neighbouring molecules in the crystal packing of **7** show that adjacent molecules interact *via* week CN···HC_{arom} interactions.

Quinoid character of compounds 1, 4, 5, 6 and 7 (ESI)

1: δr = 0.063 Å, θ = –9.3°.

4: δr_{I} = 0.022 Å, θ = –74.9°; δr_{II} = 0.02 Å, θ = –32.5°.

5: δr = 0.012 Å, θ = –98.3°.

6: δr_{I} = 0.065 Å, θ = –13.6°; δr_{II} = 0.031 Å, θ = 59.3°.

7: δr_{I} = 0.027 Å, θ = 46.4°; δr_{II} = 0.019 Å, θ = –33.6°.

UV/Vis spectroscopic data (ESI)

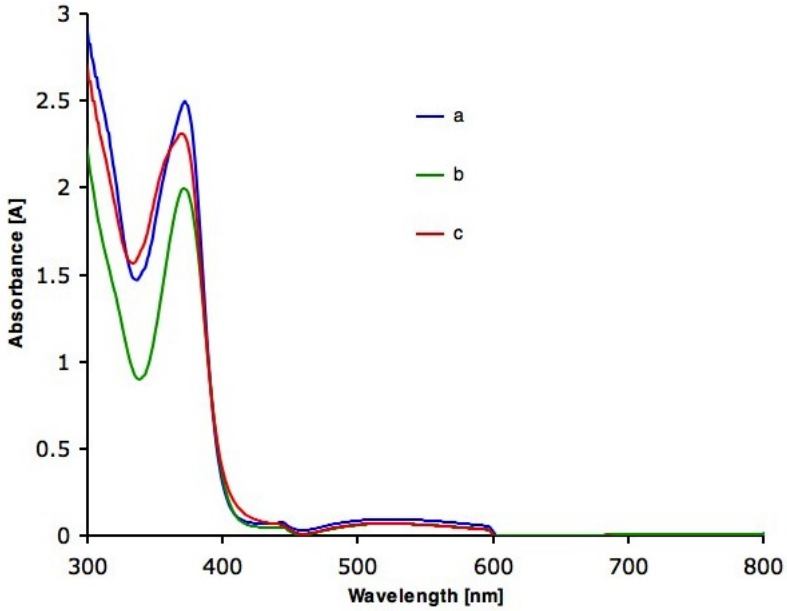


Fig. 8 (ESI). UV/Vis absorption spectra of **5** in CH_3CN at 298 K recorded a) neat, b) after acidification with trifluoroacetic acid (TFA) and c) after neutralisation with Et_3N. Four equivalents of TFA in CH_3CN were required due to the low acidity of TFA in this solvent (pK_a = 12.7).[5] The protonation occurring at the DMA group was evidenced by strong downfield shifts for the NMe_2 and the H–C(3′,5′) signals. The NMR pattern of **5** was completely restored upon addition of Et_3N evidencing a reversible protonation.

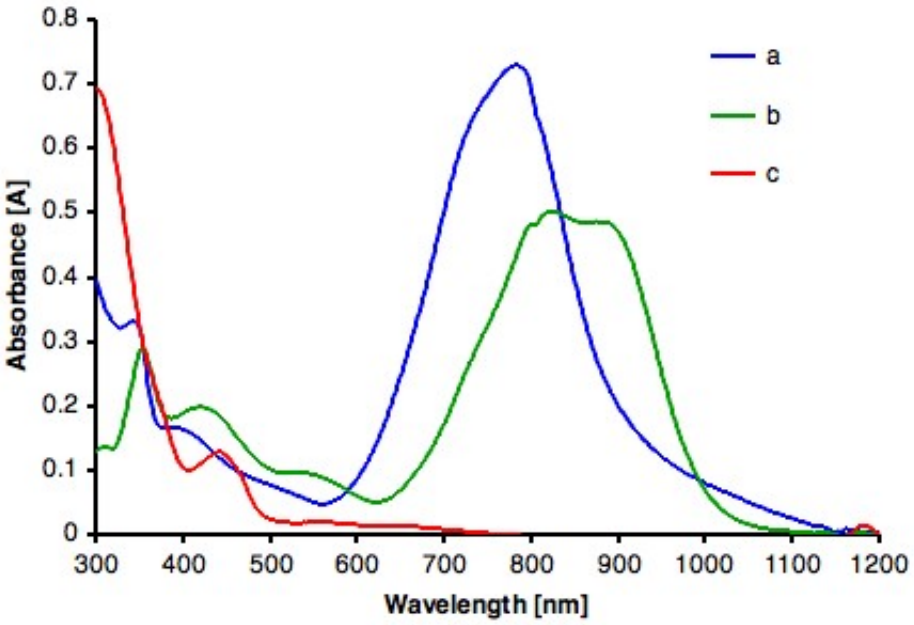


Fig. 9 (ESI). UV/Vis absorption spectra of **6** in CH_2Cl_2 at 298 K recorded a) neat, b) after acidification with TFA and c) after neutralisation with Et_3N.

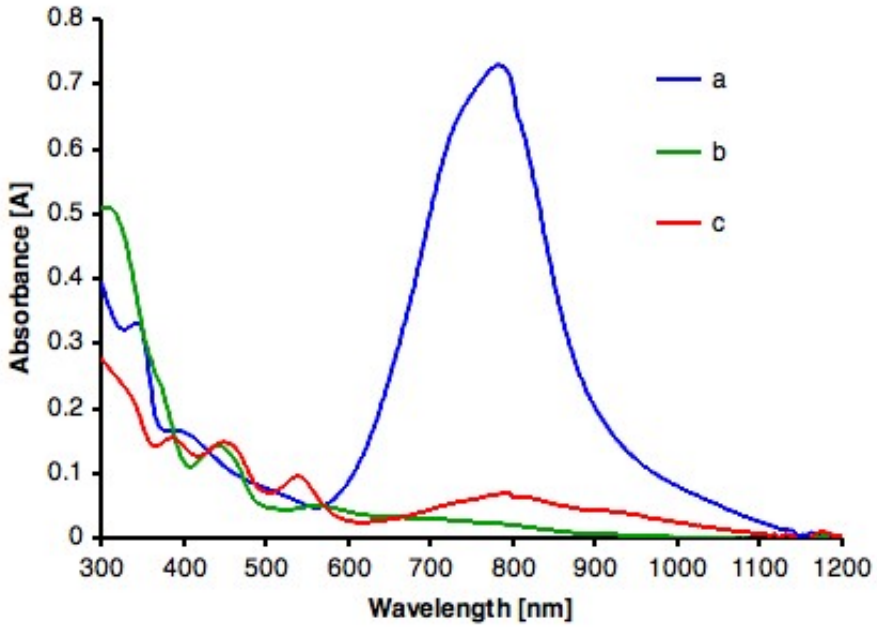


Fig. 10 (ESI). UV/Vis absorption spectra of **6** in CH_2Cl_2 at 298 K recorded a) neat, b) after basification with Et_3N and c) after neutralisation with TFA.

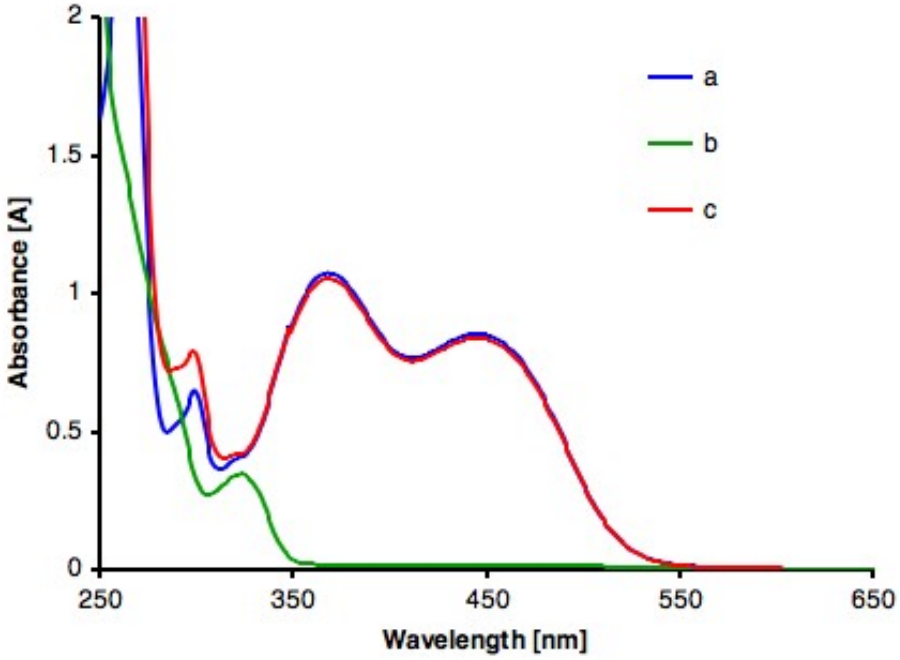


Fig. 11 (ESI). UV/Vis absorption spectra of **7** in CH_2Cl_2 at 298 K recorded a) neat, b) after acidification with TFA and c) after neutralisation with Et_3N.

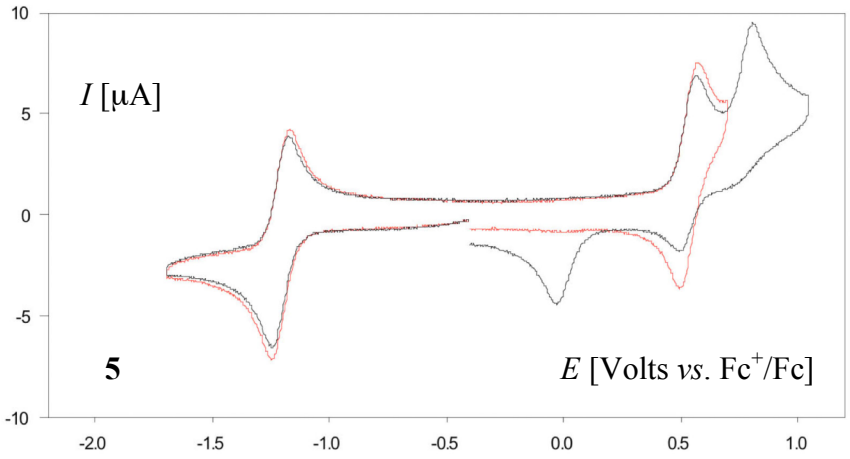
Electrochemistry (ESI)

Table 2 (ESI). Electrochemical data of chromophores **5**, **6** and **7** observed by cyclic voltammetry (CV) (scan rate v = 0.1 V s^{-1}) and rotating disk voltammetry (RDV) in CH_2Cl_2 (in the presence of 0.1 M nBu$_4$NPF$_6$). All potentials are given *vs.* ferricinium/ferrocene (Fc^+/Fc) couple used as internal standard.

	Cyclic Voltammetry			Rotating-Disk Voltammetry	
	$E°$ [V][a]	ΔE_p [mV][b]	E_p V[c]	$E_{1/2}$ [V][d]	Slope [mV][e]
5			+0.81	+0.78 (1e$^-$)	60
	+0.53	70		+0.53 (1e$^-$)	60
	–1.21	60		–1.23 (1e$^-$)	60
5[f]			+0.78	+0.79 (1e$^-$)	75
	+0.53	70		+0.54 (1e$^-$)	60
	–1.22	70		–1.23 (1e$^-$)	60

6			+0.90	*g*	
	+0.67	60		+0.67 (1e$^-$)	60
	–0.45	60		–0.47 (1e$^-$)	60
			–0.96	–0.97 (1e$^-$)	80
7				*g*	
			+0.67	+0.67 (1e$^-$)	
	–1.71	75		–1.72 (1e$^-$)	60
			–2.43	–2.50 (1e$^-$)	40

[a] $E^o = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = E_{pa} - E_{pc}$. [c] E_p = Irreversible peak potential. [d] $E_{1/2}$ = Half-wave potential. [e] Slope = Slope of the linearised plot of E versus log $[I/(I_{lim} - I)]$, where I_{lim} is the limiting current and I the current. [f] in CH_3CN. [g] Poorly resolved second oxidation due to strong electrode inhibition.



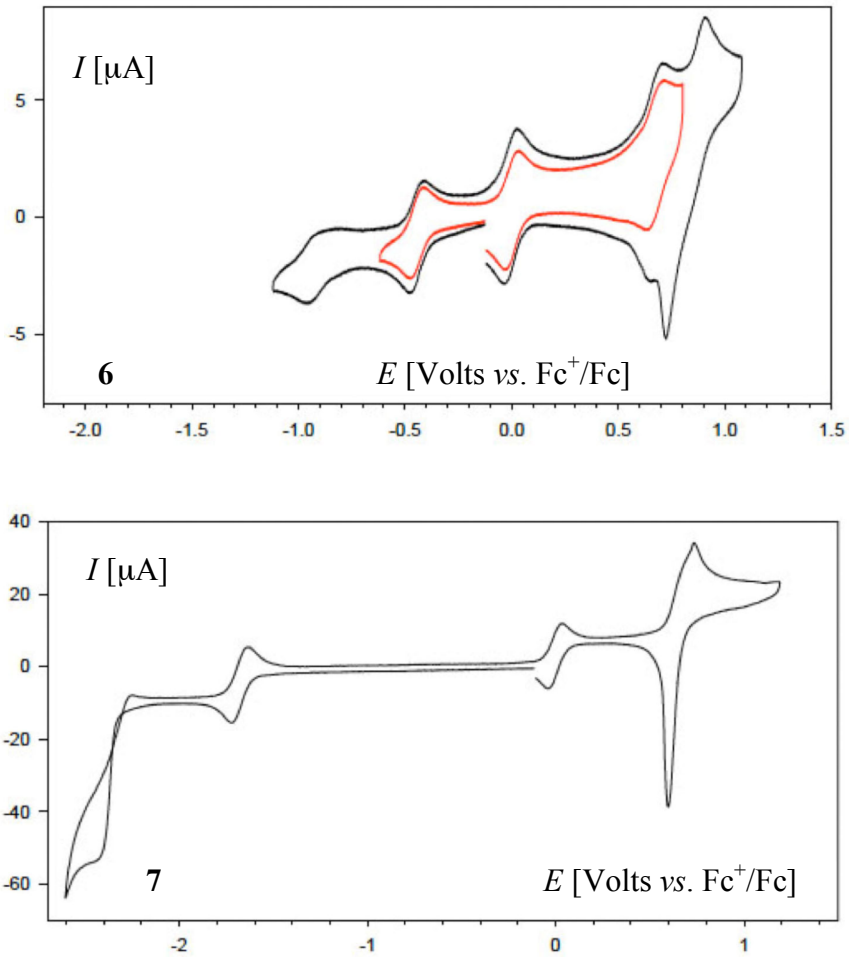


Fig. 14 (ESI). Cyclic voltammetry of **5** (top), **6** (middle) and **7** (bottom) in the presence of ferrocene (for **6** and **7**) in CH_2Cl_2 and in the presence of 0.1 M nBu$_4$NPF$_6$ and at a scan rate of 0.1 V/s.

Discussion of the electrochemical data for chromophores 5 and 7

Similar cyclic voltammograms were observed for zwitterion **5** in both CH_3CN and CH_2Cl_2, with only one reversible one-electron ($1e^-$) reduction and two $1e^-$ oxidations. The first oxidation at +0.53 V is reversible whereas the second oxidation (E_p = +0.78 V) is irreversible at any scan rate. It is noteworthy that the optical band gap (1.71 eV) from the end absorption at ca. 725 nm and the electrochemical gap (1.74 eV) are well correlated.

Tricyanobenzene **7** shows a single reversible 1e$^-$ reduction at –1.71 V as well as an irreversible reduction close to the electrolyte discharge at E_p = –2.43 V and a first unresolved irreversible oxidation at 0.67 V. However, RDV shows two well-resolved 1e$^-$ reductions and one oxidation as well as an unresolved second oxidation peak due to strong electrode inhibition.

Summary table of the optical and electrochemical data (ESI)

Table 3 (ESI). Optical and electrochemical (CV) data of **5** in CH_3CN and of **6** and **7** in CH_2Cl_2 at 298 K.

	λ_{max}, nm ($\log \varepsilon$]	λ_{end} [nm (eV)][a]	$\Delta(E_{ox,1}–E_{red,1})$ [V]	E^o [V][b]	EA[c] [eV]
5	461 (2.69), 365 (4.1)	725 (1.71)	1.74	+0.78,[d] +0.53, –1.22	3.58
6	782 (4.4)	1100 (1.13)	1.12	+0.90,[d] +0.67, –0.45, –0.96[d]	4.35
7	435 (3.98), 386 (4.1)	520 (2.38)	2.38	[e], +0.67, [d] –1.71, –2.43	3.09

[a]Optical gap; [b]$E^o = (E_{pc} + E_{pa})/2$; [c]$EA = E_{red}$ (V *vs* Fc^+/Fc) + 4.8 eV;[6] [d]Irreversible peak potential; [e]Due to electrode inhibition, the second oxidation could not be determined.

Theoretical calculations for 5 (ESI)

Calculations were performed using the Gaussian 09 program package.[7] Molecular properties in the electronic ground state were computed at the B3LYP/6-31G* level of theory. TD calculations for **5** were performed at the CAM-B3LYP/6-31G* level of theory.

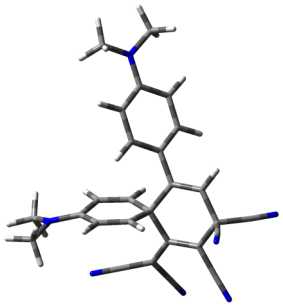
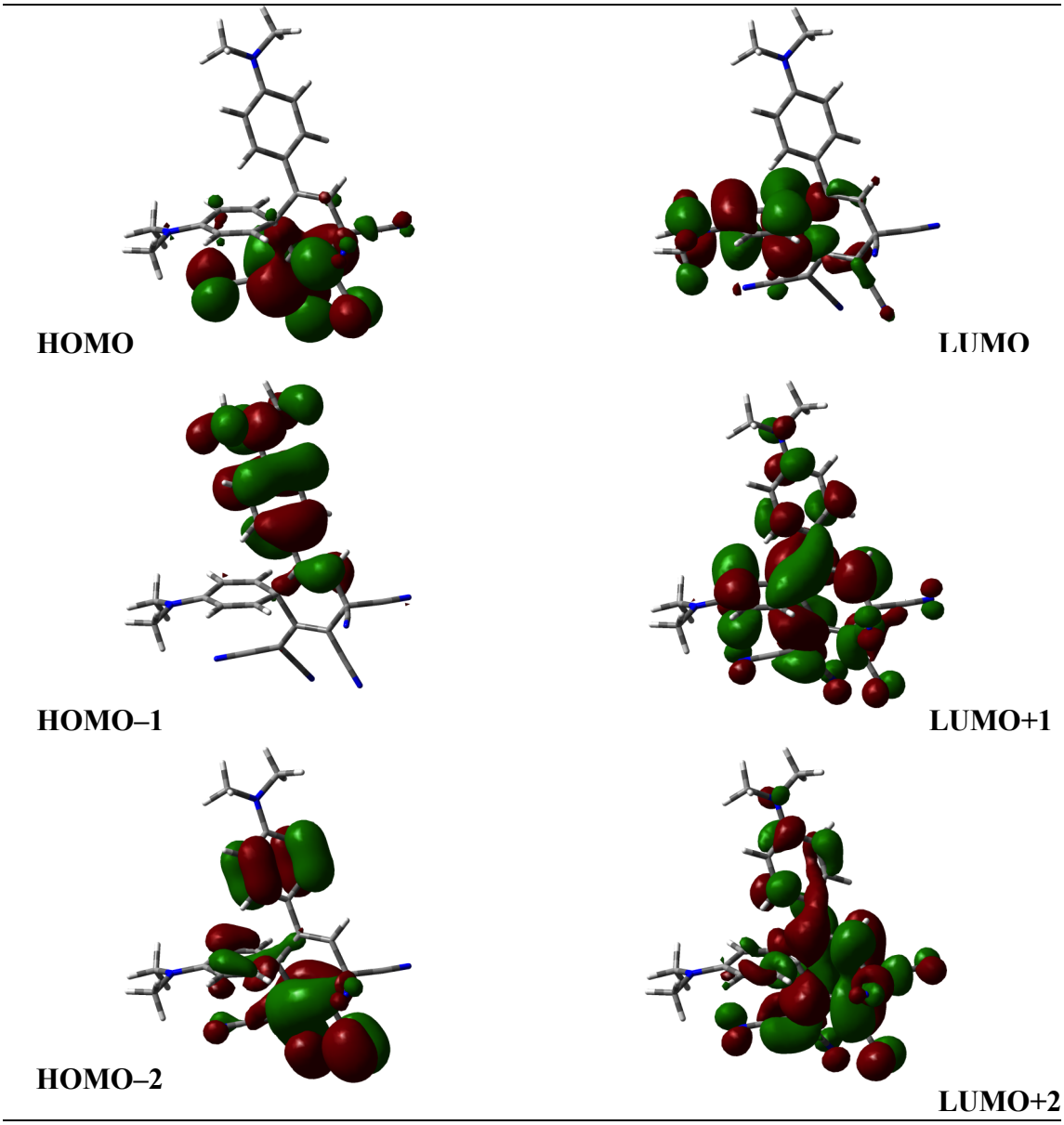
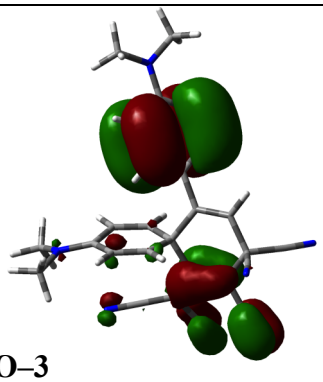


Fig. 15 (ESI). Optimised structure of **5**, calculated at the B3LYP/6-31G*(d) level of theory.





HOMO–3

Fig. 16 (ESI). Selected molecular orbital plots of **5**, calculated at the B3LYP/6-31G* level.

Table 4 (ESI). Selected data of vertical electronic transitions of **5**, calculated at the CAM-B3LYP/6-31G* level.[a][b][c]

State	λ [nm] (eV)	f	Composition of band and CI coefficiencies
1	881 (1.41)	0.0094	H→L, 0.70
2	439 (2.82)	0.0043	H–1→L, 0.70
3	358 (3.46)	0.0823	H→L+1, 0.69
4	320 (3.87)	0.0727	H–3→L, 0.14; H→L+2, 0.53; H→L+3, 0.16; H→L+4, 0.16
5	308 (4.03)	0.0540	H–8→L, 0.11; H–3→L, –0.16; H–2→L, 0.53; H→L+2, 0.34

[a] Calculations were carried out for the lowest 20 excited states, and only energies above 300 nm are shown. [b] f = oscillator strength; CI = configuration interaction; H = HOMO; L = LUMO. [c] Based on the calculated oscillation strengths (f), we assign state 3 (358 nm, 3.46 eV) to be associated with the absorption experimentally observed at 461 nm (2.69 eV). A shift of 0.77 eV is large, but not uncommon for TD-

DFT calculations, especially when charge-transfer states are involved, and when calculations were performed in the gas-phase and compared to experimental values measured in polar solvents.

Table 5 (ESI). Cartesian coordinates from the optimised structure of **5**.

Atomic Type	Coordinates [Å]		
	x	y	z
N	-0.043064	4.274476	0.472748
N	5.880931	-0.717681	-0.449952
N	-2.19531	-4.940205	-0.593579
N	-2.254415	-2.814255	3.227213
N	-5.16263	-2.172362	-0.042591
N	-4.756592	0.089067	-2.740845
N	-2.769951	3.257411	-0.539622
C	-0.712335	0.107391	0.092683
C	0.205711	-1.13173	0.243347
C	-0.304591	-2.340569	0.495034
C	-1.789053	-2.630019	0.625688
C	-2.663231	-1.517406	0.037113
C	-2.179219	-0.26861	-0.282741
C	-0.760374	0.839302	1.407593
C	-0.47424	2.148427	1.545977
C	-0.103647	2.950335	0.389547
C	0.167741	2.269961	-0.856474
C	-0.150813	0.967511	-1.006333
C	-0.479154	4.985272	1.686059
C	0.085825	5.090612	-0.747113
C	1.674485	-0.975658	0.064848
C	2.443284	-0.032507	0.766816
C	3.82049	0.050832	0.612095
C	4.513353	-0.808669	-0.274978
C	3.739791	-1.761479	-0.979042
C	2.364084	-1.835126	-0.807798
C	6.574174	-1.724496	-1.238802
C	-2.051795	-3.925878	-0.049507
C	-2.077751	-2.773046	2.080318
C	-4.042913	-1.847346	-0.05332
C	-2.959024	0.721543	-0.990075
C	-3.969189	0.348852	-1.918823
C	-2.858593	2.10648	-0.748604
H	0.35309	-3.19023	0.64646
H	-1.092333	0.259936	2.265164
H	-0.59637	2.618626	2.51242

H	0.538336	2.828092	-1.705169
H	-0.009933	0.481928	-1.966501
H	0.011654	4.581023	2.572604
H	-1.566647	4.90698	1.787736
H	-0.199238	6.03387	1.594756
H	1.005663	4.846917	-1.283256
H	0.124161	6.141012	-0.463067
H	-0.787719	4.914764	-1.383688
H	1.965161	0.632232	1.479316
H	4.36274	0.780905	1.200989
H	4.211644	-2.45005	-1.669183
H	1.804133	-2.572103	-1.377131
H	6.208734	-1.73853	-2.273006
H	6.460767	-2.737016	-0.822899
H	7.638272	-1.484782	-1.267989
C	6.660218	0.167064	0.399999
H	6.326547	1.207315	0.299028
H	6.602229	-0.108367	1.464417
H	7.706935	0.126074	0.094345

^{1}H and ^{13}C NMR spectra of the products (ESI)

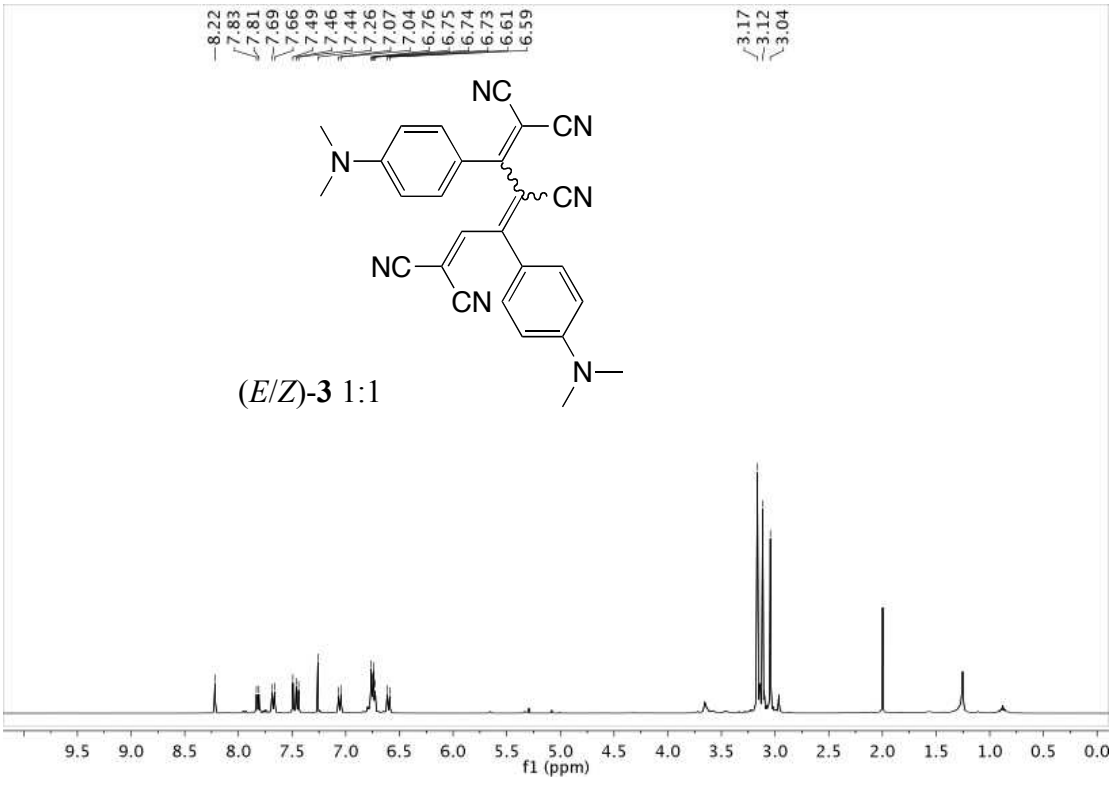


Fig. 17 (ESI). 400 MHz ^{1}H NMR spectrum of **3** recorded at 298 K in $CDCl_3$.

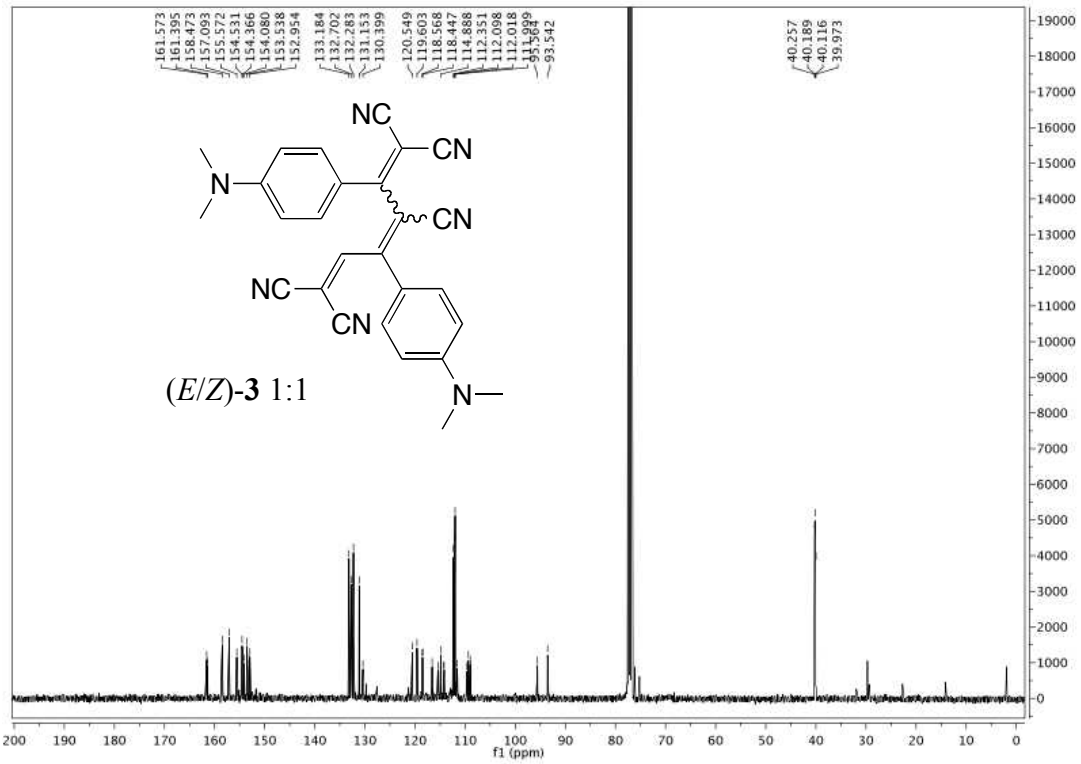


Fig. 18 (ESI). 100 MHz ^{13}C NMR spectrum of **3** recorded at 298 K in $CDCl_3$.

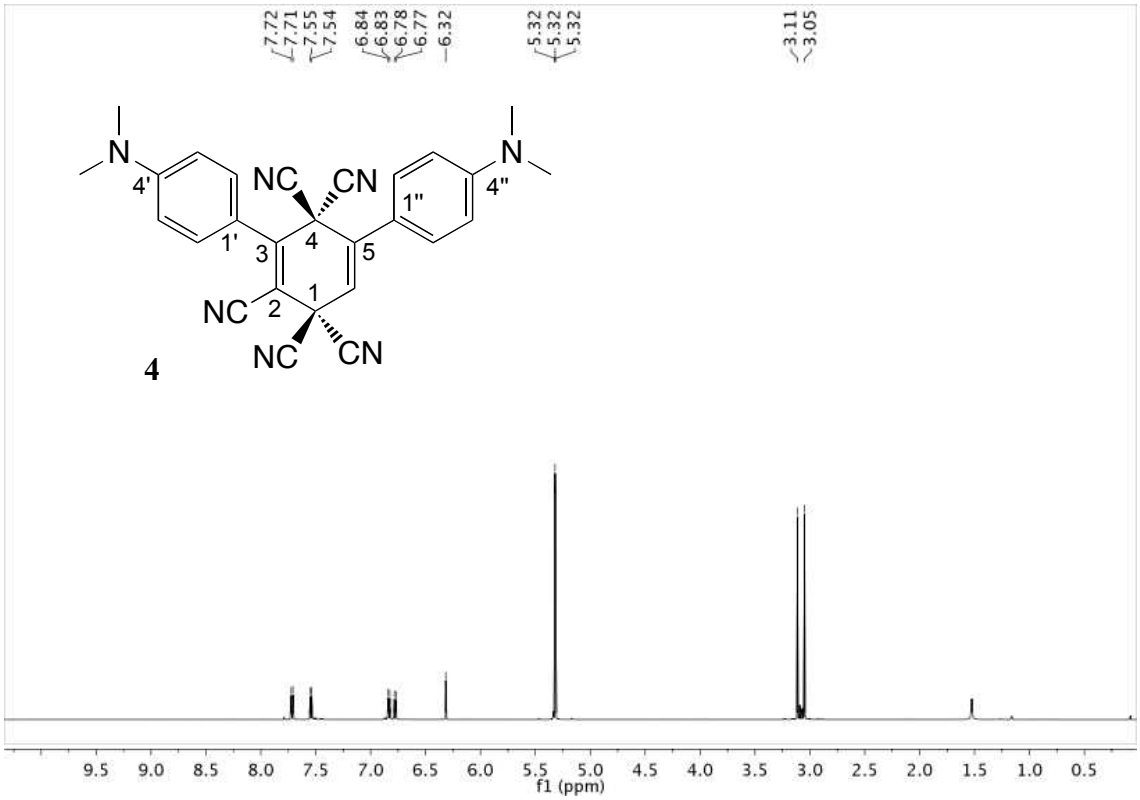


Fig. 19 (ESI). 600 MHz ^{1}H NMR spectrum of **4** recorded at 298 K in CD_2Cl_2.

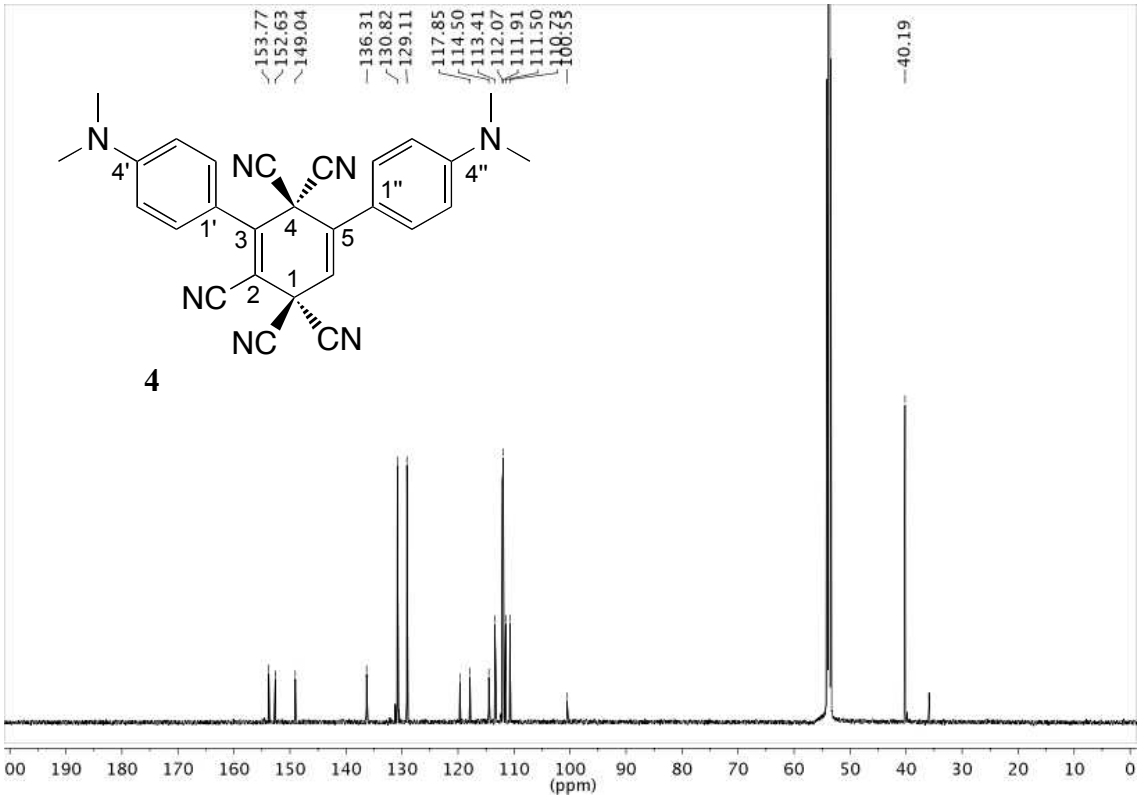


Fig. 20 (ESI). 150 MHz ^{13}C NMR spectrum of **4** recorded at 298 K in CD_2Cl_2.

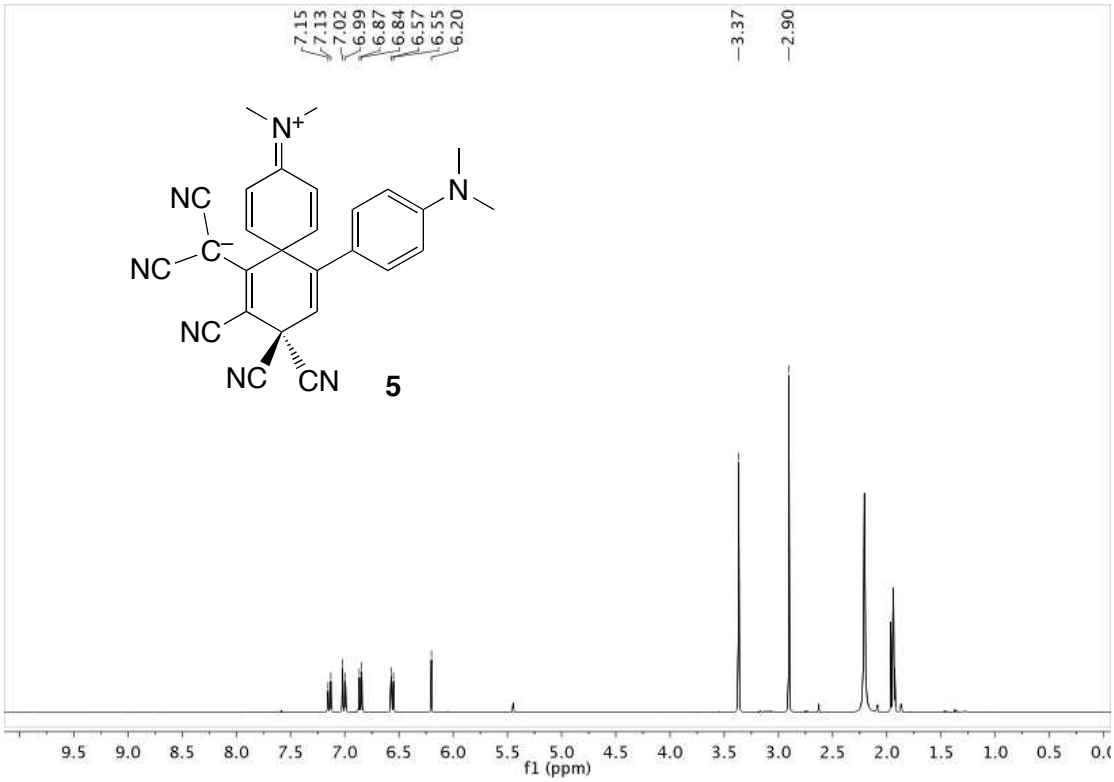


Fig. 21 (ESI). 400 MHz ^{1}H NMR spectrum of **5** recorded at 298 K in CD_3CN.

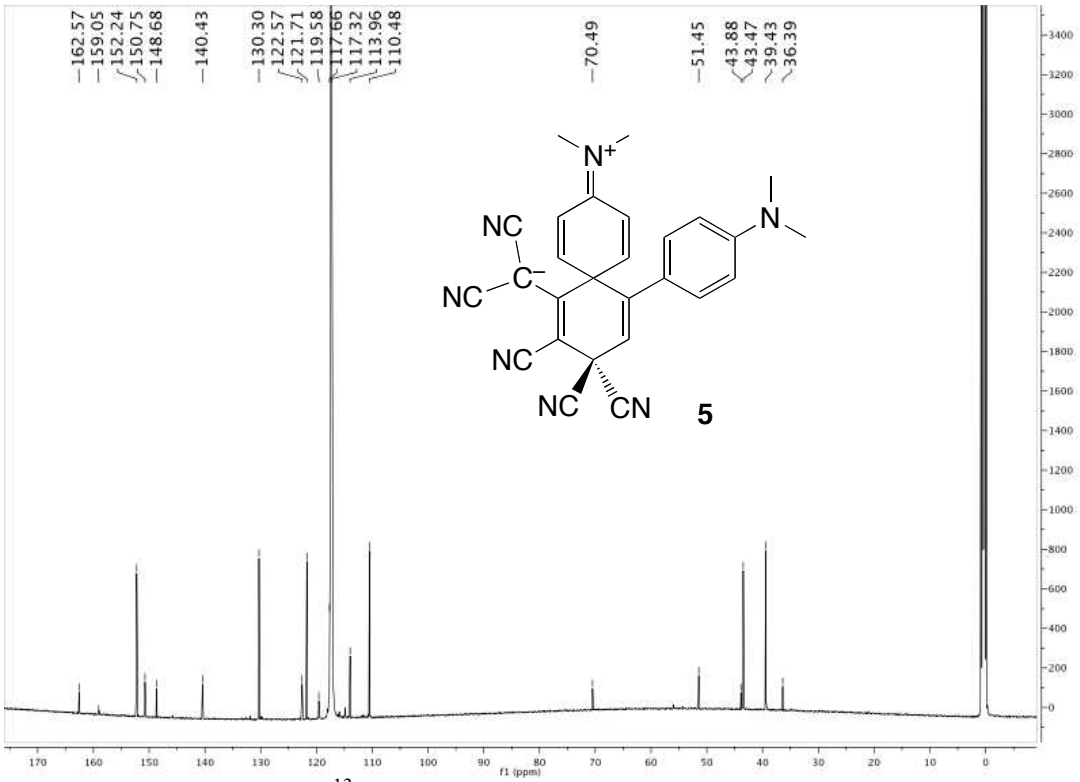


Fig. 22 (ESI). 100 MHz ^{13}C NMR spectrum of **5** recorded at 298 K in CD_3CN.

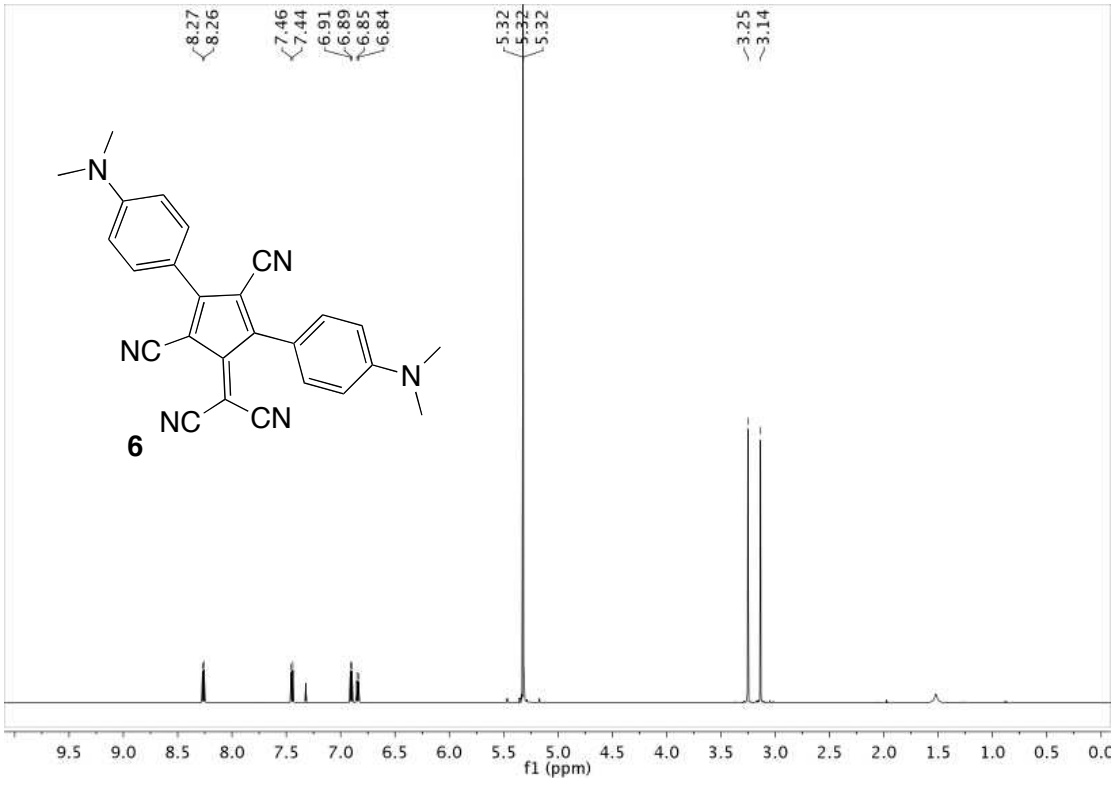


Fig. 23 (ESI). 400 MHz ^{1}H NMR spectrum of **6** recorded at 298 K in CD_2Cl_2.

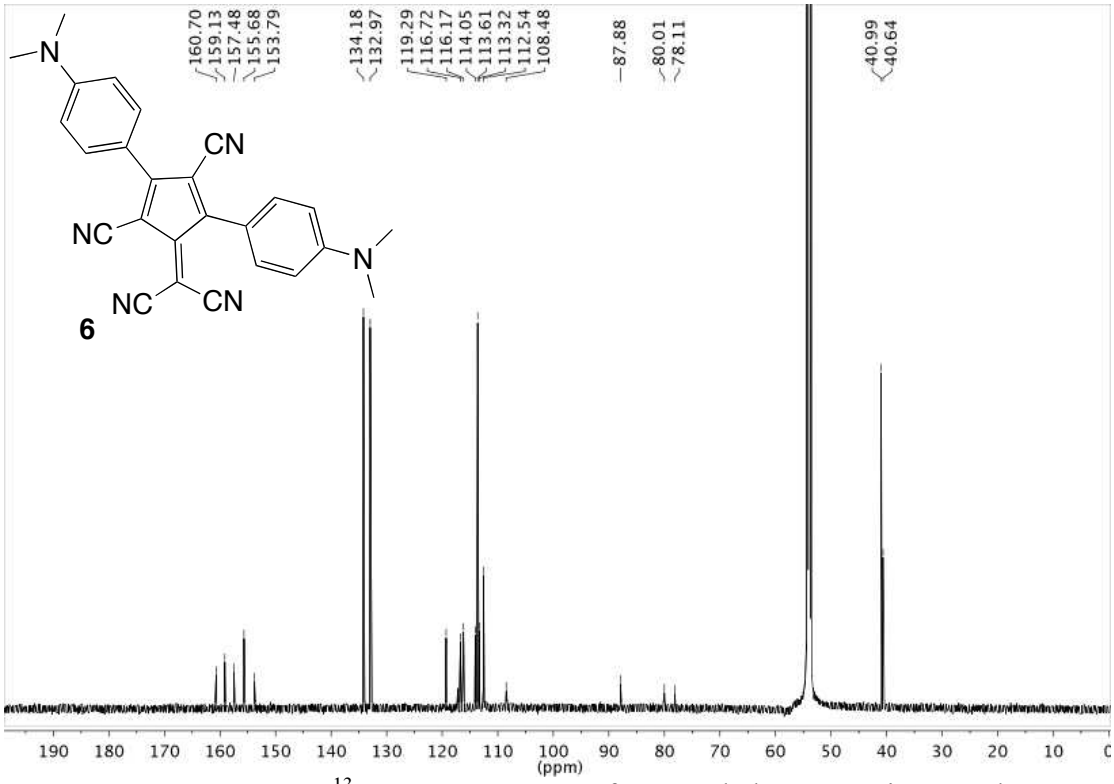


Fig. 24 (ESI). 100 MHz ^{13}C NMR spectrum of **6** recorded at 298 K in CD_2Cl_2.

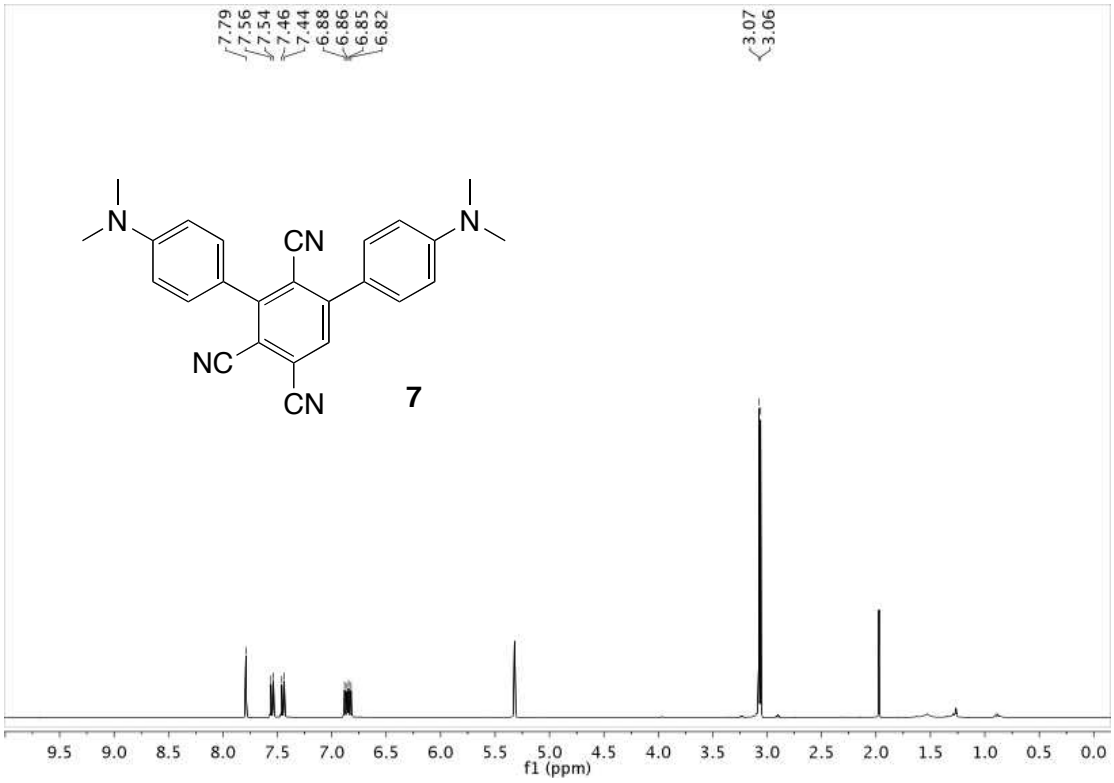


Fig 25 (ESI). 400 MHz ^{1}H NMR spectrum of **7** recorded at 298 K in CD_2Cl_2.

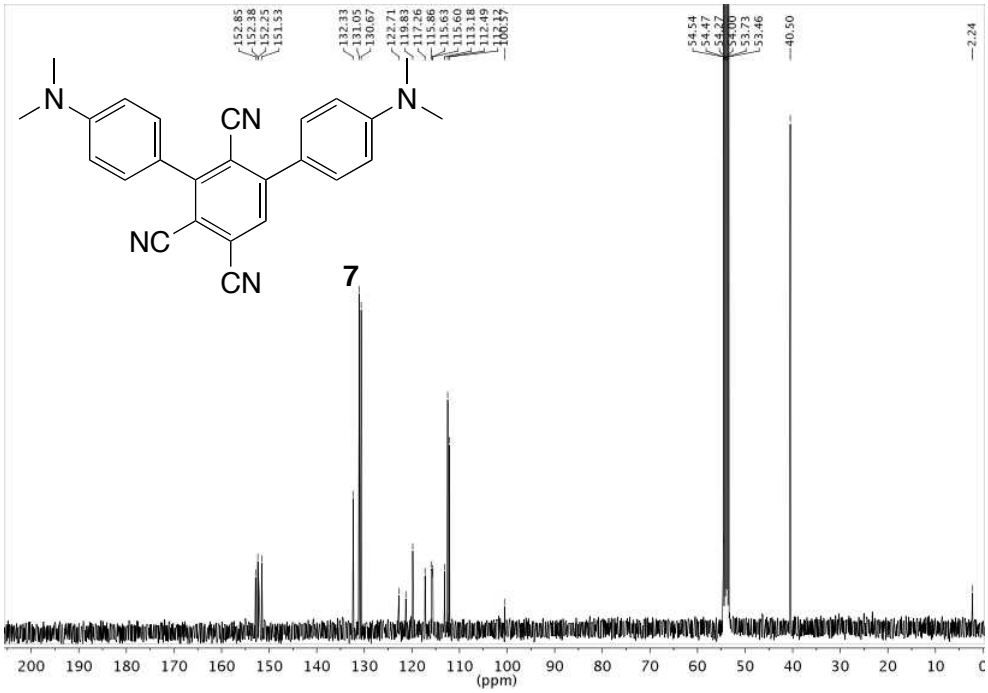


Fig. 26 (ESI). 100 MHz ^{13}C NMR spectrum of **7** recorded at 298 K in CD_2Cl_2.

Acid-base titration of 5 followed by ^1H NMR spectroscopy (ESI)

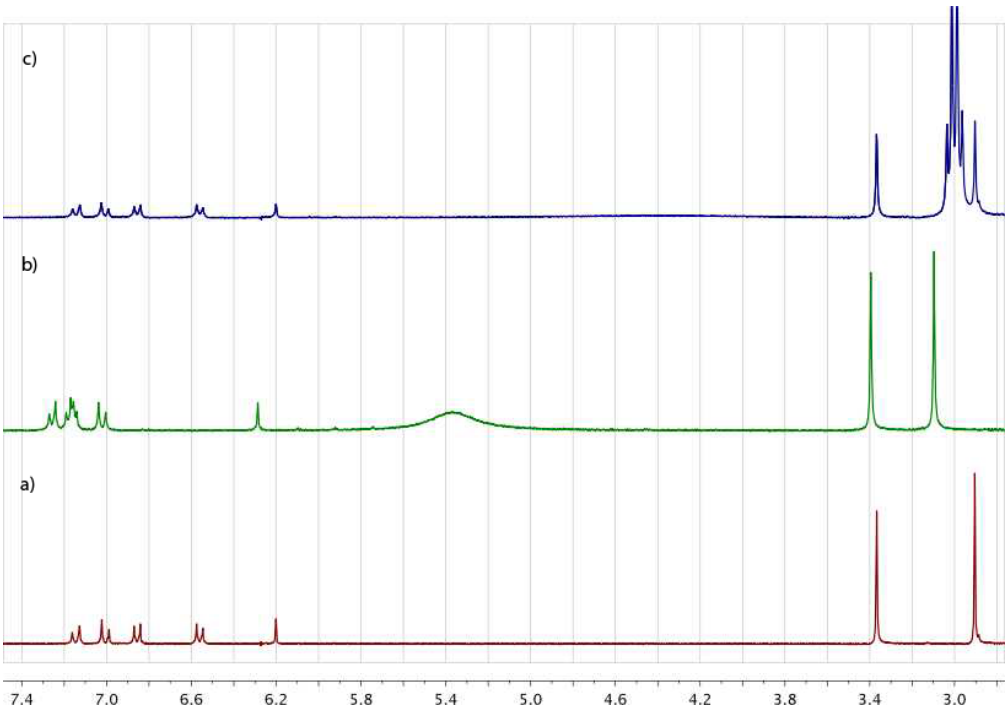


Fig. 27 (ESI). ^1H NMR spectra of **5** in CD_3CN at 298 K recorded (a) neat, (b) after acidification with TFA and (c) after neutralisation with Et_3N.

Thermal gravimetric analysis (ESI)

Table 6 (ESI). Thermal gravimetric analysis of chromophores **5** to **7**.

Compound	M.p. [°C][a]	T_d [°C][b]	$T_{95\%}$ [°C][c]
5	> 213 (decomp)	530	230
6	> 400	495	201
7	211–213	360	200

[a] Temperature at which melting or appearance change occurred (as observed by naked eye on a Büchi B-540 melting point apparatus). [b] Decomposition temperature determined by derivative thermogravimetry. [c] Temperature at which 5% weight loss occurred upon heating.

Computational details for mechanistic studies (ESI)

All calculations were performed with the Gaussian09 suite of programs.[7] Geometry optimisations in the gas-phase were performed at B3LYP/6-31G(d).[8] Optimisations in solvent were done with: CPCM (toluene or MeCN), B3LYP/6-31G(d). Frequency calculations were performed on all gas-phase and solution-phase optimised geometries to verify the nature of all the stationary points as either minima or transition states.

Summary

Path leading to 3 (pathway a, $\Delta G^{\ddagger}$ are with respect to the preceding intermediate

	gas-phase	toluene	MeCN
$\Delta G^{\ddagger}$ (in kJ/mol)	59.4	44.4	49.0

E-Z isomerisation

	gas-phase	toluene	MeCN
ΔG (in kJ/mol)	-10.9	-7.1	-2.5
$\Delta G^{\ddagger}$ (in kJ/mol)	33.9	46.9	69.0

Path leading to 4 ([4+2] cycloaddition after *E*/*Z* isomerisation)

	gas-phase	toluene	MeCN
$\Delta G^{\ddagger}$ (in kJ/mol)	16.7	31.8	20.5

Path leading to 5 ([4+2] cycloaddition from *E*, pathway c)

	gas-phase	toluene	MeCN
$\Delta G^{\neq}$ (in kJ/mol)	84.1	64.4	49.4

Toluene

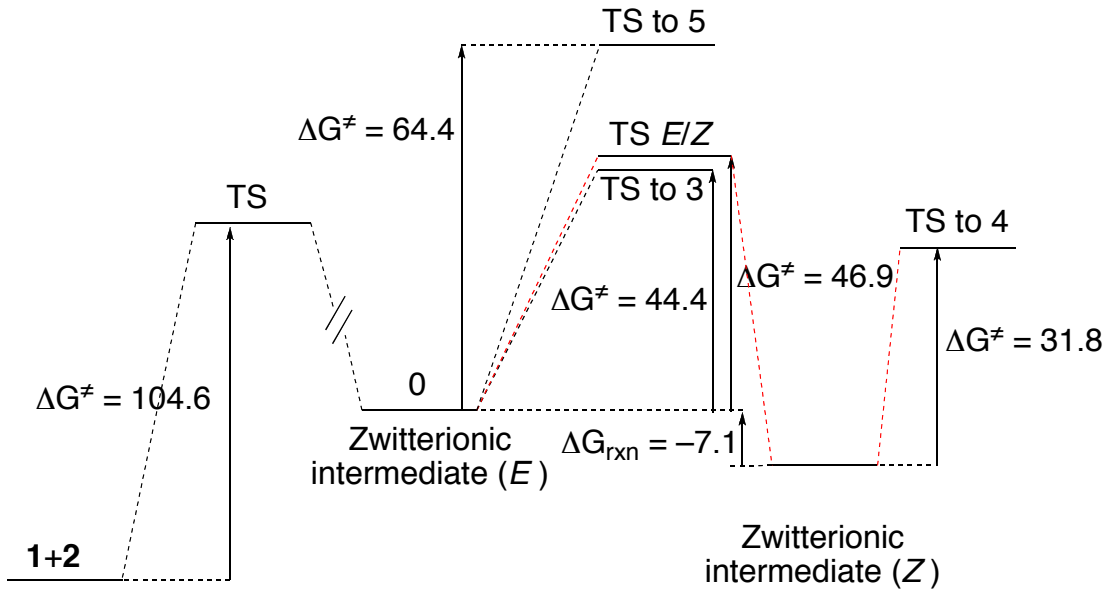


Fig. 28 (ESI). Reaction energy profile for the pathways leading to **3**, **4**, **5** in toluene (Energies in kJ/mol).

MeCN

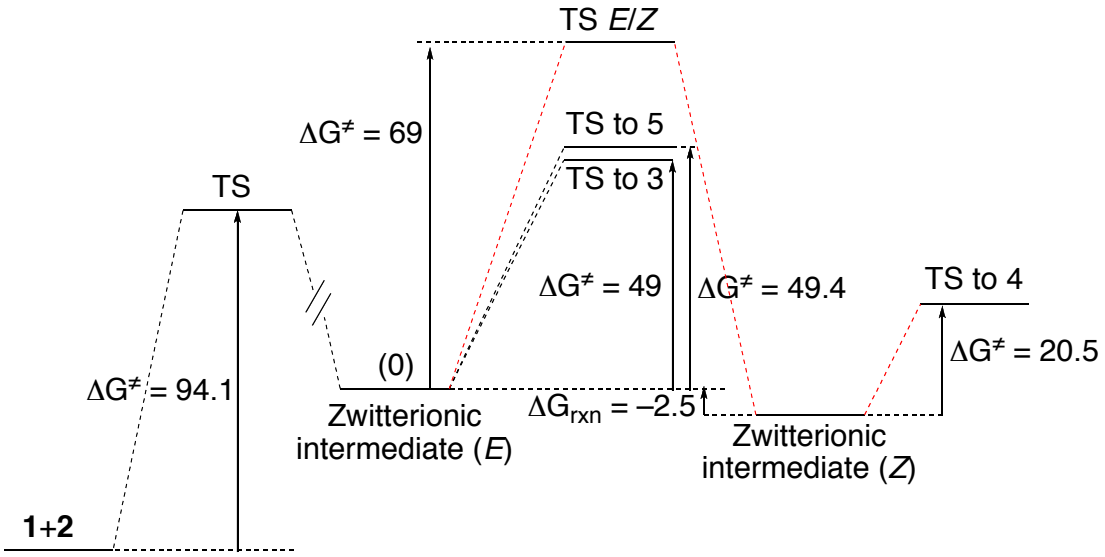


Fig. 29 (ESI). Reaction energy profile for the pathways leading to **3**, **4**, **5** in MeCN (Energies in kJ/mol).

XYZ coordinates and energies (ESI)

Initial bimolecular reaction of 1 and 2 to form the zwitterionic intermediate, optimised in gas-phase [at B3LYP/6-31G(d)] or solvent [at CPCM B3LYP/6-31G(d)]

1 optimised in gas-phase

C	-2.175800	-1.461517	0.632068
C	-1.972658	-0.538533	-0.353487
C	-1.551601	-1.334484	1.916465
C	-3.022481	-2.603053	0.448501
N	-3.694781	-3.542302	0.317222
N	-1.060409	-1.259440	2.967445
C	-1.063600	0.647690	-0.169512
C	-1.696526	1.871215	-0.055710
C	-1.017780	3.128064	-0.007611
N	-0.501552	4.171239	0.024279
C	-3.124193	1.952977	0.006168
N	-4.285428	2.018495	0.064260
C	0.363017	0.385247	-0.143902

C	0.888009	-0.780738	-0.754179
C	1.294210	1.251232	0.479801
C	2.239800	-1.053908	-0.772373
H	0.221936	-1.478171	-1.252845
C	2.646172	0.980988	0.483368
H	0.950545	2.135258	1.001581
C	3.171285	-0.177551	-0.152375
H	2.580699	-1.952350	-1.271087
H	3.305922	1.668087	0.997910
N	4.511755	-0.441508	-0.158151
C	5.020295	-1.651494	-0.793454
H	4.784684	-1.673007	-1.865194
H	6.104601	-1.682629	-0.685214
H	4.605361	-2.555166	-0.328865
C	5.445452	0.475412	0.486316
H	6.460925	0.101565	0.353845
H	5.391385	1.478134	0.044505
H	5.250781	0.559865	1.563286
C	-2.604871	-0.693143	-1.625305
N	-3.068046	-0.802487	-2.687425

Zero-point correction= 0.233360
Thermal correction to Energy= 0.255745
Thermal correction to Enthalpy= 0.256689
Thermal correction to Gibbs Free Energy= 0.179141
Sum of electronic and thermal Energies= -981.934344
Sum of electronic and thermal Enthalpies= -981.933400
Sum of electronic and thermal Free Energies= -982.010948

1 optimised in toluene

C	-2.106624	-1.533109	0.580852
C	-1.991666	-0.524502	-0.333334
C	-1.380446	-1.523164	1.816969
C	-2.974570	-2.654280	0.371090
N	-3.667858	-3.574188	0.216555
N	-0.817999	-1.552219	2.833669
C	-1.074560	0.649570	-0.133558
C	-1.698619	1.880415	0.008966
C	-1.011491	3.131638	0.036343
N	-0.496612	4.176376	0.045844
C	-3.120303	1.978615	0.122207
N	-4.277699	2.065401	0.222401
C	0.346282	0.385892	-0.121913
C	0.874414	-0.758749	-0.775296
C	1.279000	1.238312	0.523645
C	2.226037	-1.020176	-0.814974
H	0.209008	-1.443116	-1.291882
C	2.630820	0.977983	0.508558
H	0.932631	2.097610	1.083900
C	3.159254	-0.155975	-0.174233

H	2.569108	-1.898423	-1.346547
H	3.290625	1.647745	1.045029
N	4.496110	-0.407636	-0.202000
C	5.010980	-1.590895	-0.886815
H	4.763685	-1.573502	-1.955204
H	6.095829	-1.614241	-0.788945
H	4.607401	-2.512448	-0.450163
C	5.433086	0.496536	0.461179
H	6.448244	0.133062	0.304864
H	5.365145	1.510893	0.050726
H	5.248271	0.543765	1.541352
C	-2.750406	-0.577490	-1.544316
N	-3.326954	-0.607029	-2.554375

Zero-point correction= 0.233372
Thermal correction to Energy= 0.255723
Thermal correction to Enthalpy= 0.256667
Thermal correction to Gibbs Free Energy= 0.178981
Sum of electronic and thermal Energies= -981.946599
Sum of electronic and thermal Enthalpies= -981.945655
Sum of electronic and thermal Free Energies= -982.023341

1 optimised in MeCN

C	-2.035053	-1.600065	0.527856
C	-2.007731	-0.520966	-0.311299
C	-1.217214	-1.683185	1.702159
C	-2.915299	-2.709012	0.303201
N	-3.623395	-3.615040	0.135222
N	-0.593774	-1.799299	2.676098
C	-1.087953	0.645161	-0.108238
C	-1.704612	1.884674	0.054194
C	-1.012387	3.131271	0.039995
N	-0.501840	4.178583	0.011729
C	-3.116520	1.999397	0.228795
N	-4.267457	2.109880	0.377545
C	0.327734	0.385932	-0.108785
C	0.864786	-0.738415	-0.796953
C	1.257818	1.231789	0.555415
C	2.216269	-0.984340	-0.849984
H	0.204166	-1.412400	-1.332154
C	2.609494	0.984126	0.530795
H	0.903934	2.068388	1.145046
C	3.146346	-0.127801	-0.188065
H	2.565783	-1.843338	-1.407635
H	3.265872	1.640696	1.087065
N	4.479508	-0.365553	-0.227342
C	5.006165	-1.519891	-0.956787
H	4.743882	-1.469108	-2.019575
H	6.091735	-1.527197	-0.871909

H	4.620962	-2.459223	-0.543957
C	5.414422	0.523777	0.463551
H	6.429347	0.163441	0.303130
H	5.346018	1.546776	0.077063
H	5.221681	0.541060	1.542345
C	-2.886476	-0.496189	-1.441042
N	-3.571916	-0.463808	-2.380147

Zero-point correction= 0.233500
Thermal correction to Energy= 0.255743
Thermal correction to Enthalpy= 0.256687
Thermal correction to Gibbs Free Energy= 0.180138
Sum of electronic and thermal Energies= -981.957220
Sum of electronic and thermal Enthalpies= -981.956276
Sum of electronic and thermal Free Energies= -982.032825

2 optimised in gas-phase

C	-0.206088	1.209025	-0.000090
C	1.181202	1.202832	-0.000028
C	1.911496	0.000016	-0.000045
C	1.181214	-1.202815	-0.000101
C	-0.206071	-1.209025	-0.000173
C	-0.942543	-0.000001	-0.000225
H	-0.720555	2.162579	0.000002
H	1.718131	2.146873	0.000068
H	1.718164	-2.146845	-0.000081
H	-0.720532	-2.162581	-0.000205
C	3.338443	0.000014	0.000006
C	4.549656	-0.000004	0.000074
H	5.615473	-0.000127	0.001252
N	-2.325167	-0.000007	-0.000432
C	-3.052488	-1.256078	0.000329
H	-4.124228	-1.050363	0.000266
H	-2.825082	-1.862764	-0.888121
H	-2.824971	-1.861866	0.889382
C	-3.052483	1.256066	0.000182
H	-2.825535	1.861687	0.889502
H	-2.824499	1.862916	-0.888000
H	-4.124224	1.050358	-0.000626

Zero-point correction= 0.182669
Thermal correction to Energy= 0.192844
Thermal correction to Enthalpy= 0.193788
Thermal correction to Gibbs Free Energy= 0.147155
Sum of electronic and thermal Energies= -442.169223
Sum of electronic and thermal Enthalpies= -442.168278
Sum of electronic and thermal Free Energies= -442.214911

2 optimised in toluene

C	-0.206334	1.210150	-0.000096
C	1.180832	1.203742	0.000003
C	1.911664	0.000000	-0.000001
C	1.180832	-1.203741	-0.000085
C	-0.206334	-1.210149	-0.000187
C	-0.944552	0.000001	-0.000253
H	-0.720428	2.163726	-0.000029
H	1.716207	2.148819	0.000114
H	1.716206	-2.148818	-0.000053
H	-0.720429	-2.163725	-0.000230
C	3.339034	0.000000	0.000107
C	4.551263	0.000000	0.000194
H	5.617919	-0.000002	0.000244
N	-2.323487	0.000000	-0.000496
C	-3.052967	-1.257473	0.000379
H	-4.123824	-1.050105	0.000142
H	-2.824993	-1.863227	-0.887881
H	-2.825114	-1.862060	0.889485
C	-3.052970	1.257471	0.000109
H	-2.825482	1.862075	0.889303
H	-2.824634	1.863210	-0.888063
H	-4.123826	1.050101	-0.000578

Zero-point correction= 0.182593
Thermal correction to Energy= 0.192779
Thermal correction to Enthalpy= 0.193723
Thermal correction to Gibbs Free Energy= 0.147031
Sum of electronic and thermal Energies= -442.173057
Sum of electronic and thermal Enthalpies= -442.172113
Sum of electronic and thermal Free Energies= -442.218805

2 optimised in MeCN

C	-0.206554	1.211148	0.000051
C	1.180361	1.204519	0.000127
C	1.911890	0.000005	-0.000009
C	1.180360	-1.204513	-0.000195
C	-0.206552	-1.211143	-0.000274
C	-0.946380	0.000004	-0.000213
H	-0.720507	2.164677	0.000239
H	1.714430	2.150528	0.000325
H	1.714434	-2.150519	-0.000266
H	-0.720510	-2.164669	-0.000411
C	3.339458	0.000000	0.000072
C	4.552558	-0.000006	0.000134
H	5.619890	-0.000007	0.000193
N	-2.321884	-0.000002	-0.000424
C	-3.053237	-1.258581	0.000506

H	-4.123343	-1.049825	0.000371
H	-2.824954	-1.863298	-0.887804
H	-2.824926	-1.862103	0.889637
C	-3.053248	1.258572	-0.000072
H	-2.825474	1.862242	0.889105
H	-2.824439	1.863146	-0.888336
H	-4.123352	1.049808	-0.000850

Zero-point correction= 0.182512
Thermal correction to Energy= 0.192716
Thermal correction to Enthalpy= 0.193661
Thermal correction to Gibbs Free Energy= 0.146891
Sum of electronic and thermal Energies= -442.176175
Sum of electronic and thermal Enthalpies= -442.175230
Sum of electronic and thermal Free Energies= -442.222000

TS optimised in gas-phase

C	2.215946	-0.264437	-1.354359
C	-0.171571	-0.720214	-0.121026
C	-0.572810	0.529295	0.499719
C	0.968057	-0.225719	-1.538250
H	0.323703	0.167335	-2.308941
C	3.523710	-0.333873	-0.930152
C	4.399100	-1.366460	-1.380900
C	4.050190	0.643985	-0.030136
C	5.706178	-1.421982	-0.966102
H	4.015327	-2.117671	-2.063707
C	5.359117	0.593626	0.378954
H	3.388251	1.413964	0.352851
C	6.234396	-0.440640	-0.071361
H	6.336087	-2.224562	-1.328061
H	5.712769	1.343813	1.074498
N	7.528788	-0.495485	0.344751
C	8.055872	0.513205	1.261995
H	7.533729	0.491062	2.226425
H	9.112443	0.314088	1.440234
H	7.964771	1.520120	0.838742
C	8.401299	-1.585029	-0.085518
H	8.528754	-1.588727	-1.174916
H	9.382789	-1.456657	0.370405
H	8.005182	-2.559967	0.223504
C	-1.149654	-1.504693	-0.871641
C	0.663027	-1.604243	0.689125
N	1.328721	-2.311663	1.324304
N	-1.827910	-2.179224	-1.530088
C	-1.790549	1.254451	0.168196
C	-1.738824	2.627601	-0.084706
C	-2.898462	3.462051	-0.097356
N	-3.816252	4.180625	-0.109368

C	-0.514638	3.296815	-0.391134
N	0.468843	3.845668	-0.692355
C	-3.064052	0.525021	0.164524
C	-3.324682	-0.460392	1.138951
C	-4.075648	0.775310	-0.783774
C	-4.522015	-1.151428	1.176301
H	-2.574388	-0.667104	1.896699
C	-5.270313	0.079226	-0.771752
H	-3.908008	1.507146	-1.566959
C	-5.535556	-0.904551	0.215726
H	-4.673238	-1.886479	1.957160
H	-6.000802	0.292284	-1.542321
N	-6.726245	-1.590955	0.239896
C	-7.732979	-1.345425	-0.781217
H	-8.612824	-1.954653	-0.569482
H	-8.045717	-0.293588	-0.789616
H	-7.372017	-1.603900	-1.786973
C	-6.936877	-2.652088	1.212375
H	-6.196534	-3.457384	1.107056
H	-6.884461	-2.271807	2.241137
H	-7.928764	-3.081380	1.064478
C	0.429969	1.143282	1.291773
N	1.278850	1.599305	1.952611

Zero-point correction= 0.417658
Thermal correction to Energy= 0.451548
Thermal correction to Enthalpy= 0.452492
Thermal correction to Gibbs Free Energy= 0.347402
Sum of electronic and thermal Energies= -1424.078394
Sum of electronic and thermal Enthalpies= -1424.077450
Sum of electronic and thermal Free Energies= -1424.182540

TS optimised in toluene

C	2.253890	-0.213613	-1.348805
C	-0.164424	-0.609255	-0.018697
C	-0.607795	0.655090	0.518152
C	1.013202	-0.151342	-1.541217
H	0.336299	0.217130	-2.293874
C	3.561640	-0.316779	-0.933004
C	4.391209	-1.404197	-1.345349
C	4.137555	0.679064	-0.083126
C	5.698612	-1.492178	-0.942776
H	3.971020	-2.169310	-1.989953
C	5.445356	0.595884	0.318685
H	3.513186	1.496648	0.262442
C	6.277055	-0.492575	-0.096116
H	6.292673	-2.333438	-1.275315
H	5.839038	1.363664	0.971931
N	7.568353	-0.577686	0.304139

C	8.149096	0.450060	1.170427
H	7.629629	0.496583	2.134336
H	9.194688	0.207810	1.355354
H	8.102823	1.437008	0.697120
C	8.402887	-1.708302	-0.105083
H	8.505117	-1.751079	-1.195406
H	9.395639	-1.590716	0.326981
H	7.984012	-2.657639	0.247470
C	-1.079225	-1.473442	-0.750815
C	0.732056	-1.396549	0.814666
N	1.450975	-2.025284	1.474706
N	-1.705870	-2.219126	-1.383884
C	-1.858361	1.305234	0.164666
C	-1.888943	2.679775	-0.100671
C	-3.097438	3.439362	-0.106849
N	-4.055464	4.104323	-0.106377
C	-0.715473	3.430187	-0.408606
N	0.221385	4.059267	-0.703048
C	-3.087969	0.509611	0.150205
C	-3.326310	-0.463664	1.144868
C	-4.087818	0.688874	-0.828780
C	-4.490721	-1.207727	1.172743
H	-2.588444	-0.614635	1.927466
C	-5.247078	-0.063400	-0.828865
H	-3.932149	1.405114	-1.629097
C	-5.491875	-1.035013	0.179587
H	-4.628882	-1.925997	1.971317
H	-5.965911	0.093335	-1.623415
N	-6.644093	-1.775347	0.191649
C	-7.648679	-1.589007	-0.847472
H	-8.498104	-2.241116	-0.642984
H	-8.012923	-0.554429	-0.871065
H	-7.257086	-1.838931	-1.842808
C	-6.842744	-2.805899	1.202500
H	-6.060418	-3.574900	1.156071
H	-6.847737	-2.381407	2.214717
H	-7.805257	-3.289513	1.034689
C	0.362441	1.347417	1.288896
N	1.177843	1.871013	1.941249

Zero-point correction= 0.417548
Thermal correction to Energy= 0.451504
Thermal correction to Enthalpy= 0.452448
Thermal correction to Gibbs Free Energy= 0.347233
Sum of electronic and thermal Energies= -1424.098030
Sum of electronic and thermal Enthalpies= -1424.097086
Sum of electronic and thermal Free Energies= -1424.202301

TS optimised in MeCN

C	2.316029	-0.043676	-1.213510
C	-0.133867	-0.331853	0.245250
C	-0.733639	0.913515	0.638287
C	1.080702	0.091631	-1.374708
H	0.368147	0.451343	-2.096355
C	3.632934	-0.234367	-0.864423
C	4.331714	-1.429088	-1.226832
C	4.357041	0.772501	-0.150157
C	5.649344	-1.606980	-0.900363
H	3.800060	-2.203324	-1.770067
C	5.675534	0.601549	0.176380
H	3.840881	1.682187	0.138457
C	6.376108	-0.596186	-0.187344
H	6.141350	-2.526048	-1.189881
H	6.186154	1.385487	0.719845
N	7.675745	-0.766991	0.131377
C	8.409975	0.270746	0.862023
H	7.956892	0.455680	1.841671
H	9.434730	-0.063250	1.013635
H	8.430941	1.208392	0.296627
C	8.382966	-1.995781	-0.242717
H	8.385310	-2.131465	-1.329251
H	9.414428	-1.926539	0.097820
H	7.921548	-2.872272	0.224500
C	-0.887501	-1.360531	-0.446881
C	0.846295	-0.906269	1.145441
N	1.638312	-1.365492	1.860044
N	-1.387144	-2.234817	-1.027087
C	-2.021643	1.392460	0.169355
C	-2.187838	2.742883	-0.180044
C	-3.468397	3.362068	-0.276000
N	-4.489559	3.922707	-0.343430
C	-1.095177	3.608848	-0.472014
N	-0.227474	4.338914	-0.747400
C	-3.151788	0.468981	0.122519
C	-3.362676	-0.472721	1.156174
C	-4.096168	0.495641	-0.928392
C	-4.447839	-1.326680	1.153136
H	-2.672775	-0.505760	1.994373
C	-5.171926	-0.369156	-0.960416
H	-3.952660	1.178834	-1.759494
C	-5.390746	-1.309278	0.086920
H	-4.574788	-2.009794	1.983546
H	-5.843708	-0.330765	-1.808605
N	-6.457331	-2.160085	0.065831
C	-7.420568	-2.108983	-1.029704
H	-8.206718	-2.840778	-0.846282
H	-7.886504	-1.119102	-1.106834
H	-6.949666	-2.345849	-1.992258

C	-6.640567	-3.139628	1.132498
H	-5.778216	-3.813165	1.209800
H	-6.787901	-2.653305	2.105076
H	-7.523133	-3.740594	0.915344
C	0.091676	1.766501	1.418431
N	0.769704	2.434793	2.095078

Zero-point correction= 0.417650
Thermal correction to Energy= 0.451518
Thermal correction to Enthalpy= 0.452462
Thermal correction to Gibbs Free Energy= 0.347723
Sum of electronic and thermal Energies= -1424.115239
Sum of electronic and thermal Enthalpies= -1424.114295
Sum of electronic and thermal Free Energies= -1424.219035

_E/Z_ isomerisation optimised in gas-phase [at B3LYP/6-31G(d)] or solvent [at CPCM B3LYP/6-31G(d)]

***E*-isomer optimised in gas-phase**

C	-2.24760500	-0.31258800	1.20125600
C	0.13283600	-0.58311000	0.30914300
C	0.55402500	0.73520500	-0.29807200
C	-0.98468700	-0.22577800	1.42958400
H	-0.54301800	0.18910400	2.33003500
C	-3.54510500	-0.38664200	0.80729500
C	-4.38892200	-1.47658400	1.21236200
C	-4.12387300	0.63906700	-0.02068100
C	-5.70036700	-1.53595200	0.83093000
H	-3.96631200	-2.25989400	1.83317000
C	-5.44130300	0.58376600	-0.38555600
H	-3.48222000	1.43805900	-0.38028000
C	-6.27942600	-0.50293400	0.02127500
H	-6.30305900	-2.37500500	1.15395400
H	-5.83539400	1.36630900	-1.02106000
N	-7.57918600	-0.56147800	-0.35568600
C	-8.16705700	0.50370800	-1.17112100
H	-7.69494600	0.55626600	-2.15923400
H	-9.22887700	0.30121000	-1.30712300
H	-8.06410500	1.47669000	-0.67914500
C	-8.41434500	-1.70550200	0.01303200
H	-8.52080900	-1.78617200	1.10112500
H	-9.40633700	-1.57426400	-0.41770400
H	-7.99492200	-2.64220000	-0.37125900
C	1.15967600	-1.33437900	1.06266700
C	-0.46679500	-1.50605700	-0.67772800
N	-0.94787800	-2.21796500	-1.45753200
N	1.82855200	-1.99069300	1.74722300
C	1.82631000	1.36397600	-0.10438600

C	1.92390800	2.75863100	0.04739400
C	3.14713300	3.46857100	-0.13760100
N	4.12546600	4.08649700	-0.28575000
C	0.80994600	3.55951500	0.43446800
N	-0.07991900	4.21848900	0.80224700
C	3.04781300	0.54006100	-0.13496400
C	3.20482400	-0.47034000	-1.10296300
C	4.10567500	0.73441300	0.77179800
C	4.34936100	-1.24756200	-1.16749500
H	2.41827400	-0.62906000	-1.83582700
C	5.24777900	-0.04598600	0.73270700
H	4.01668500	1.49374100	1.54222500
C	5.40829400	-1.06025400	-0.24508600
H	4.42241300	-2.00133600	-1.94195800
H	6.01970200	0.12963700	1.47182400
N	6.54979200	-1.82975000	-0.29795200
C	7.59201600	-1.65735000	0.70073400
H	8.41899200	-2.33241900	0.47498200
H	7.98456200	-0.63246000	0.69616100
H	7.23490400	-1.88177700	1.71653500
C	6.64461500	-2.92537000	-1.24834100
H	5.86015500	-3.67955900	-1.08970600
H	6.56776200	-2.56718300	-2.28347000
H	7.61361500	-3.41415800	-1.13584100
C	-0.51267200	1.39865400	-0.94303700
N	-1.44102500	1.86195700	-1.48441900

Zero-point correction= 0.419331
Thermal correction to Energy= 0.453229
Thermal correction to Enthalpy= 0.454174
Thermal correction to Gibbs Free Energy= 0.349556
Sum of electronic and thermal Energies= -1424.079366
Sum of electronic and thermal Enthalpies= -1424.078422
Sum of electronic and thermal Free Energies= -1424.183039

_E_-isomer optimised in toluene

C	-2.310800	-0.295298	1.174333
C	0.114751	-0.447726	0.468367
C	0.555190	0.904476	-0.103998
C	-1.061446	-0.168015	1.479968
H	-0.735914	0.241206	2.433141
C	-3.591829	-0.389858	0.774980
C	-4.392057	-1.554946	1.072940
C	-4.211246	0.687881	0.034367
C	-5.691793	-1.632766	0.677426
H	-3.937391	-2.371555	1.623504
C	-5.514820	0.609443	-0.351521
H	-3.601290	1.546011	-0.230721
C	-6.311095	-0.550280	-0.046976

H	-6.263637	-2.518723	0.919037
H	-5.943283	1.427134	-0.915434
N	-7.593286	-0.626875	-0.432786
C	-8.233439	0.487174	-1.147441
H	-7.766551	0.643435	-2.125339
H	-9.284985	0.250300	-1.297657
H	-8.166190	1.410307	-0.564698
C	-8.394190	-1.829698	-0.164521
H	-8.517095	-1.985429	0.912198
H	-9.378672	-1.703007	-0.610763
H	-7.926082	-2.714585	-0.605831
C	1.125926	-1.167789	1.277818
C	-0.354908	-1.371260	-0.593316
N	-0.732788	-2.062950	-1.445216
N	1.774643	-1.795438	2.006928
C	1.872346	1.429590	-0.052334
C	2.105327	2.824921	-0.009706
C	3.354915	3.398075	-0.377827
N	4.360113	3.909416	-0.681857
C	1.114404	3.753929	0.410212
N	0.329538	4.529456	0.793876
C	3.030457	0.516200	-0.103919
C	3.080096	-0.534078	-1.040516
C	4.139504	0.673947	0.747823
C	4.169643	-1.386727	-1.124882
H	2.258890	-0.661736	-1.740640
C	5.227338	-0.180173	0.690697
H	4.133384	1.467414	1.488849
C	5.277111	-1.241281	-0.251224
H	4.165307	-2.164340	-1.878791
H	6.045473	-0.025643	1.383304
N	6.356361	-2.090751	-0.314097
C	7.505848	-1.878488	0.553131
H	8.253149	-2.646246	0.349544
H	7.970328	-0.896894	0.385527
H	7.229753	-1.948227	1.613519
C	6.395778	-3.148540	-1.312475
H	5.549612	-3.839118	-1.200641
H	6.375943	-2.748829	-2.336256
H	7.315651	-3.721486	-1.190033
C	-0.518359	1.631829	-0.660792
N	-1.447772	2.153822	-1.146203

Zero-point correction= 0.419930
Thermal correction to Energy= 0.453727
Thermal correction to Enthalpy= 0.454671
Thermal correction to Gibbs Free Energy= 0.350361
Sum of electronic and thermal Energies= -1424.104921
Sum of electronic and thermal Enthalpies= -1424.103977
Sum of electronic and thermal Free Energies= -1424.208287

_E_-isomer optimised in MeCN

C	-2.379303	-0.076050	1.111518
C	0.077753	-0.161730	0.537330
C	0.641999	1.175907	0.005061
C	-1.146286	0.144337	1.445444
H	-0.898807	0.631940	2.386724
C	-3.647835	-0.259547	0.732432
C	-4.375566	-1.467286	1.072182
C	-4.340705	0.760860	-0.033826
C	-5.664886	-1.636197	0.686888
H	-3.869275	-2.234020	1.647982
C	-5.632012	0.591486	-0.412976
H	-3.794133	1.657182	-0.307907
C	-6.354699	-0.614281	-0.070906
H	-6.184439	-2.542560	0.965773
H	-6.116469	1.364143	-0.994232
N	-7.621380	-0.781235	-0.445251
C	-8.352056	0.279062	-1.161528
H	-7.951117	0.407069	-2.171533
H	-9.399360	-0.005965	-1.231629
H	-8.285421	1.223759	-0.617601
C	-8.343717	-2.033828	-0.161077
H	-8.529028	-2.136155	0.912446
H	-9.297730	-2.010980	-0.682727
H	-7.773583	-2.893923	-0.518623
C	1.007344	-0.917448	1.411169
C	-0.334112	-1.053292	-0.577548
N	-0.660822	-1.709815	-1.477029
N	1.606039	-1.547591	2.179713
C	2.006010	1.522568	-0.044770
C	2.433684	2.882219	-0.080432
C	3.717525	3.251014	-0.561068
N	4.757724	3.603505	-0.963547
C	1.626509	3.963777	0.354015
N	1.000529	4.873448	0.739924
C	3.046404	0.474314	-0.101586
C	2.963522	-0.582505	-1.028298
C	4.177480	0.508874	0.736091
C	3.942766	-1.560582	-1.112245
H	2.131223	-0.618339	-1.725233
C	5.155215	-0.470394	0.681099
H	4.273684	1.306643	1.466849
C	5.067486	-1.543950	-0.246358
H	3.838939	-2.336733	-1.860363
H	5.993152	-0.408003	1.364525
N	6.029704	-2.520150	-0.303364
C	7.210464	-2.438012	0.546854
H	7.853041	-3.295661	0.347155
H	7.789314	-1.524565	0.354358
H	6.943018	-2.454879	1.611309

C	5.922588	-3.596802	-1.278965
H	4.988308	-4.158327	-1.153400
H	5.960145	-3.221853	-2.311156
H	6.752786	-4.289154	-1.138523
C	-0.363764	2.047029	-0.469871
N	-1.225380	2.710857	-0.904157

Zero-point correction= 0.420365
Thermal correction to Energy= 0.454174
Thermal correction to Enthalpy= 0.455118
Thermal correction to Gibbs Free Energy= 0.350646
Sum of electronic and thermal Energies= -1424.131756
Sum of electronic and thermal Enthalpies= -1424.130812
Sum of electronic and thermal Free Energies= -1424.235285

_Z_-isomer optimised in gas-phase

C	-2.58973300	1.39058100	-0.30409300
C	-0.34403200	1.65443200	0.83245100
C	0.70353500	0.75897800	0.19626500
C	-1.48296400	2.03662300	-0.23978200
H	-1.15533400	2.81097100	-0.93647200
C	-3.69108700	0.59215100	-0.31143900
C	-4.93863200	1.03214800	0.24332400
C	-3.63403900	-0.73172500	-0.86755000
C	-6.04159400	0.22270400	0.23617100
H	-4.99613000	2.02772300	0.67107200
C	-4.74056200	-1.53682500	-0.88079400
H	-2.68072000	-1.09982900	-1.23373200
C	-5.98503200	-1.09279800	-0.32980400
H	-6.96491300	0.59010200	0.66505000
H	-4.65160400	-2.53605000	-1.28699700
N	-7.07544100	-1.89738500	-0.33101500
C	-7.01316200	-3.23496300	-0.92313400
H	-6.30496700	-3.87661300	-0.38575400
H	-8.00033000	-3.69289100	-0.86990600
H	-6.71514500	-3.18554100	-1.97604700
C	-8.32776500	-1.45889100	0.28662500
H	-8.73643200	-0.57839600	-0.22296300
H	-9.05900900	-2.26345200	0.21673400
H	-8.18312900	-1.21815100	1.34584900
C	0.18363800	2.90385500	1.41620500
C	-0.99888900	0.94034200	1.95435900
N	-1.52943000	0.38414400	2.82336900
N	0.53112000	3.87933300	1.93840200
C	2.02457900	1.12489400	-0.20781600
C	2.34983600	2.41402300	-0.68191900
C	3.67641300	2.93412700	-0.68816900
N	4.74762000	3.39562900	-0.70278000
C	1.35221700	3.23385400	-1.26825100
N	0.50194000	3.84012800	-1.79514800

C	3.06718300	0.08591900	-0.13158400
C	3.11257100	-0.82014900	0.94530800
C	4.05677300	-0.04606800	-1.12450100
C	4.08833400	-1.79812600	1.03686500
H	2.38029900	-0.73455600	1.74226500
C	5.03259000	-1.02548200	-1.05385600
H	4.04710800	0.62032700	-1.98072900
C	5.07902200	-1.93434400	0.03290100
H	4.08765900	-2.45222500	1.90012500
H	5.76205700	-1.08922000	-1.85192100
N	6.04711900	-2.91182600	0.10810300
C	7.10787100	-2.96517400	-0.88493200
H	7.78098800	-3.78985300	-0.64536100
H	6.70865300	-3.13873500	-1.89331700
H	7.69772500	-2.03786100	-0.90781000
C	6.09087500	-3.80662900	1.25242300
H	6.27499600	-3.26883800	2.19410200
H	5.15246200	-4.36621600	1.35872800
H	6.89635400	-4.52913800	1.11184300
C	0.22026700	-0.54734300	-0.05664500
N	-0.29290800	-1.56834200	-0.31043500

Zero-point correction= 0.419661
Thermal correction to Energy= 0.453330
Thermal correction to Enthalpy= 0.454274
Thermal correction to Gibbs Free Energy= 0.351224
Sum of electronic and thermal Energies= -1424.085113
Sum of electronic and thermal Enthalpies= -1424.084168
Sum of electronic and thermal Free Energies= -1424.187218

_Z_-isomer optimised in toluene

C	-2.589985	1.293550	-0.307383
C	-0.363708	1.647973	0.811791
C	0.722967	0.734739	0.235756
C	-1.476782	1.942649	-0.268478
H	-1.172967	2.665626	-1.026138
C	-3.704420	0.533191	-0.314889
C	-4.948660	1.012731	0.233037
C	-3.679455	-0.800681	-0.866345
C	-6.066986	0.234106	0.225966
H	-4.981264	2.012890	0.651732
C	-4.799913	-1.576223	-0.877950
H	-2.736640	-1.187795	-1.238735
C	-6.040478	-1.092687	-0.332667
H	-6.984431	0.626949	0.643481
H	-4.739343	-2.578459	-1.280628
N	-7.141787	-1.861555	-0.334949
C	-7.122089	-3.204072	-0.931321
H	-6.457178	-3.871729	-0.373065

H	-8.129473	-3.615542	-0.905188
H	-6.794531	-3.160198	-1.974012
C	-8.392249	-1.390053	0.274759
H	-8.783254	-0.516876	-0.257964
H	-9.131731	-2.187036	0.222680
H	-8.237812	-1.130241	1.326365
C	0.141381	2.931063	1.348365
C	-0.995720	0.973909	1.974623
N	-1.499459	0.447158	2.877014
N	0.467053	3.929991	1.838916
C	2.024025	1.108438	-0.189797
C	2.341552	2.398085	-0.690887
C	3.662652	2.925206	-0.679509
N	4.730489	3.397794	-0.673250
C	1.356610	3.206276	-1.308590
N	0.525562	3.822233	-1.856537
C	3.084500	0.086115	-0.120970
C	3.188396	-0.783474	0.982344
C	4.035671	-0.063666	-1.149083
C	4.182035	-1.744336	1.064859
H	2.488647	-0.680508	1.806177
C	5.027946	-1.027634	-1.089528
H	3.977897	0.573666	-2.025858
C	5.134122	-1.900552	0.024486
H	4.228010	-2.369729	1.947895
H	5.722346	-1.110451	-1.916550
N	6.117970	-2.857852	0.092186
C	7.117833	-2.956007	-0.961204
H	7.819312	-3.753733	-0.714361
H	6.662790	-3.192992	-1.932418
H	7.686870	-2.022882	-1.070536
C	6.200196	-3.741238	1.245718
H	6.391886	-3.186947	2.175152
H	5.275169	-4.317523	1.377788
H	7.018063	-4.447269	1.097694
C	0.274681	-0.598134	0.077856
N	-0.200840	-1.655608	-0.086130

Zero-point correction= 0.420001
Thermal correction to Energy= 0.453695
Thermal correction to Enthalpy= 0.454639
Thermal correction to Gibbs Free Energy= 0.351072
Sum of electronic and thermal Energies= -1424.108389
Sum of electronic and thermal Enthalpies= -1424.107445
Sum of electronic and thermal Free Energies= -1424.211012

_Z_-isomer optimised in MeCN

C	-2.628394	1.031888	-0.284579
C	-0.388661	1.433421	0.801086

C	0.787014	0.582114	0.276161
C	-1.487971	1.644596	-0.284051
H	-1.197579	2.311199	-1.094659
C	-3.796194	0.375112	-0.288195
C	-4.993824	0.967318	0.272665
C	-3.902525	-0.952063	-0.861626
C	-6.177343	0.302413	0.257178
H	-4.928685	1.960009	0.704165
C	-5.088161	-1.612838	-0.883607
H	-3.008072	-1.413919	-1.265196
C	-6.280988	-1.015717	-0.326996
H	-7.053843	0.776285	0.677556
H	-5.130636	-2.605394	-1.310798
N	-7.445360	-1.664410	-0.349705
C	-7.568767	-2.984467	-0.991209
H	-6.997818	-3.736985	-0.439009
H	-8.617399	-3.272856	-0.995726
H	-7.215345	-2.942562	-2.024153
C	-8.651913	-1.084689	0.264808
H	-8.965659	-0.186432	-0.275218
H	-9.453149	-1.818874	0.220001
H	-8.466615	-0.835664	1.312521
C	0.032467	2.753211	1.330128
C	-0.982323	0.740897	1.975036
N	-1.442161	0.202110	2.893279
N	0.296449	3.775557	1.809523
C	2.043782	1.040528	-0.166040
C	2.290556	2.353117	-0.671602
C	3.582200	2.941259	-0.639748
N	4.624010	3.471606	-0.611577
C	1.289063	3.128213	-1.300237
N	0.464321	3.744963	-1.858210
C	3.178251	0.095456	-0.120661
C	3.412794	-0.716612	1.006406
C	4.076960	-0.026821	-1.198654
C	4.480633	-1.597029	1.063934
H	2.757170	-0.630760	1.868046
C	5.140015	-0.914033	-1.166823
H	3.919019	0.568544	-2.093087
C	5.379943	-1.728987	-0.027858
H	4.627449	-2.178679	1.965673
H	5.785822	-0.983098	-2.033474
N	6.435039	-2.603750	0.015410
C	7.367692	-2.684003	-1.101392
H	8.142764	-3.413688	-0.866792
H	6.868070	-3.003670	-2.025416
H	7.854818	-1.718769	-1.292550
C	6.652281	-3.434281	1.192972
H	6.849192	-2.829556	2.088561
H	5.786012	-4.076323	1.398108

H	7.515797	-4.077062	1.021263
C	0.475524	-0.798066	0.220627
N	0.135706	-1.916272	0.154683

Zero-point correction= 0.420115
Thermal correction to Energy= 0.453946
Thermal correction to Enthalpy= 0.454890
Thermal correction to Gibbs Free Energy= 0.349819
Sum of electronic and thermal Energies= -1424.132129
Sum of electronic and thermal Enthalpies= -1424.131185
Sum of electronic and thermal Free Energies= -1424.236256

_E_/_Z_-isom TS in gas-phase

C	-2.55063100	1.25660000	0.77614400
C	-0.06532600	0.75990400	1.09576900
C	0.64530600	0.75431300	-0.23136000
C	-1.37472700	1.72445500	1.00436700
H	-1.10568300	2.77664000	1.03051500
C	-3.70484500	0.59186500	0.46476000
C	-4.71399200	0.33730400	1.44774100
C	-3.95598400	0.14200400	-0.87361600
C	-5.87814700	-0.31217500	1.12226300
H	-4.54467700	0.66699000	2.46772900
C	-5.12822400	-0.49473600	-1.19746400
H	-3.18823000	0.29045000	-1.62626100
C	-6.13127600	-0.74687900	-0.21461300
H	-6.61153100	-0.48812600	1.89917700
H	-5.27066500	-0.82755500	-2.21780900
N	-7.29127900	-1.38851400	-0.53862800
C	-7.53484000	-1.82733700	-1.90956700
H	-6.79424100	-2.56965700	-2.23303700
H	-8.52294900	-2.28401400	-1.96719100
H	-7.50850400	-0.98299200	-2.60879900
C	-8.28983100	-1.67564900	0.48607500
H	-8.67827200	-0.75420700	0.93772400
H	-9.12503500	-2.20790800	0.03077100
H	-7.87706200	-2.30637800	1.28326500
C	0.78899400	1.27746800	2.18228400
C	-0.51420100	-0.59609400	1.47607100
N	-0.86190500	-1.67211200	1.73846000
N	1.42502500	1.70648400	3.05220900
C	2.05473500	1.23981900	-0.40882200
C	2.19958300	2.59694200	-0.65034900
C	3.41925600	3.28985700	-0.92838700
N	4.38307100	3.89671500	-1.17380900
C	1.04965600	3.44942200	-0.64201700
N	0.13822000	4.17571000	-0.61263000
C	3.12074200	0.24983300	-0.31932600
C	2.79884900	-1.12978200	-0.28874700

C	4.49910600	0.56950300	-0.23143800
C	3.76306500	-2.11473100	-0.20666500
H	1.76104000	-1.43812900	-0.33907700
C	5.47241500	-0.40461500	-0.13832600
H	4.82418100	1.60054000	-0.21161800
C	5.14040600	-1.78525600	-0.13293200
H	3.44373100	-3.14950000	-0.19497000
H	6.50578700	-0.09016600	-0.05841100
N	6.10699400	-2.75363100	-0.05198800
C	7.51182500	-2.38264700	0.04750800
H	8.11933100	-3.28800600	0.07573300
H	7.83179200	-1.78665600	-0.81669900
H	7.71776000	-1.80447700	0.95850700
C	5.73189500	-4.15992100	-0.00732100
H	5.10915400	-4.38724400	0.86837400
H	5.17890800	-4.45746500	-0.90772900
H	6.63457000	-4.76926300	0.05083300
C	-0.06786500	0.27524500	-1.32949400
N	-0.70228000	-0.11481500	-2.23879300

Zero-point correction= 0.418905
Thermal correction to Energy= 0.452150
Thermal correction to Enthalpy= 0.453094
Thermal correction to Gibbs Free Energy= 0.350839
Sum of electronic and thermal Energies= -1424.068794
Sum of electronic and thermal Enthalpies= -1424.067850
Sum of electronic and thermal Free Energies= -1424.170104

_E_/_Z_-isom TS in toluene

C	-2.554515	1.189521	0.780305
C	-0.072220	0.720976	1.107450
C	0.639721	0.711256	-0.213949
C	-1.384780	1.669473	1.013831
H	-1.136525	2.726722	1.017803
C	-3.712877	0.554485	0.465635
C	-4.735143	0.321437	1.448754
C	-3.962117	0.103723	-0.878813
C	-5.905342	-0.302724	1.119090
H	-4.564257	0.653667	2.467367
C	-5.138237	-0.510628	-1.208582
H	-3.182914	0.237706	-1.622664
C	-6.156154	-0.739788	-0.225242
H	-6.649925	-0.460886	1.888280
H	-5.283428	-0.845669	-2.227178
N	-7.313132	-1.356386	-0.551012
C	-7.564307	-1.795595	-1.926789
H	-6.834783	-2.550694	-2.239906
H	-8.559228	-2.234624	-1.981496
H	-7.521330	-0.951247	-2.622787
C	-8.335445	-1.616819	0.466147

H	-8.708450	-0.682229	0.899334
H	-9.171596	-2.137402	0.001951
H	-7.939920	-2.247311	1.269811
C	0.775188	1.254178	2.193777
C	-0.511321	-0.635188	1.512474
N	-0.850292	-1.713268	1.779121
N	1.409275	1.689549	3.061692
C	2.042366	1.216109	-0.391811
C	2.166159	2.578360	-0.642582
C	3.367006	3.300645	-0.925100
N	4.309927	3.938306	-1.176434
C	1.002078	3.409579	-0.653124
N	0.091302	4.138508	-0.648813
C	3.130665	0.254610	-0.303623
C	2.839100	-1.133007	-0.256596
C	4.505850	0.601075	-0.239601
C	3.823097	-2.097778	-0.185144
H	1.805645	-1.457075	-0.287108
C	5.500313	-0.350841	-0.154545
H	4.811832	1.638119	-0.229838
C	5.196883	-1.740411	-0.136681
H	3.526088	-3.138930	-0.162305
H	6.528235	-0.015793	-0.091818
N	6.181710	-2.684959	-0.067389
C	7.583093	-2.285427	-0.004110
H	8.207378	-3.178603	0.022316
H	7.870881	-1.694139	-0.882211
H	7.794917	-1.692727	0.895218
C	5.838650	-4.101720	-0.023476
H	5.232324	-4.343118	0.859070
H	5.281486	-4.407111	-0.918072
H	6.755392	-4.689767	0.022167
C	-0.067469	0.214346	-1.304770
N	-0.703542	-0.192888	-2.207946

Zero-point correction= 0.418839
Thermal correction to Energy= 0.452119
Thermal correction to Enthalpy= 0.453064
Thermal correction to Gibbs Free Energy= 0.350502
Sum of electronic and thermal Energies= -1424.088855
Sum of electronic and thermal Enthalpies= -1424.087910
Sum of electronic and thermal Free Energies= -1424.190472

_E_/_Z_-isom TS in MeCN

C	-2.55658900	1.07399800	0.73776100
C	-0.07156300	0.72712000	1.06259900
C	0.66275300	0.76913200	-0.26004800
C	-1.39480300	1.58992200	0.96779200
H	-1.21731300	2.66233000	0.96979100
C	-3.72537800	0.47412300	0.44652300

C	-4.71440100	0.20814100	1.46644600
C	-4.03976600	0.09105000	-0.91311900
C	-5.90391000	-0.37507500	1.15778500
H	-4.49427500	0.49026600	2.49033600
C	-5.23475500	-0.48133100	-1.22242900
H	-3.28896100	0.25390300	-1.67978300
C	-6.22111900	-0.73813500	-0.20216700
H	-6.62387700	-0.55122000	1.94551500
H	-5.43261000	-0.76570200	-2.24714100
N	-7.39490700	-1.30268000	-0.50695200
C	-7.74464000	-1.61867700	-1.90040100
H	-7.10822700	-2.42019900	-2.28883700
H	-8.78138600	-1.94674700	-1.93494700
H	-7.64039300	-0.73381700	-2.53335700
C	-8.37606800	-1.62755300	0.53967300
H	-8.77873000	-0.71578600	0.99222700
H	-9.19450800	-2.18608600	0.09038300
H	-7.92018300	-2.24720200	1.31600100
C	0.74751500	1.29149300	2.15867100
C	-0.42084200	-0.66493800	1.45715700
N	-0.67354800	-1.77432200	1.69162600
N	1.36422400	1.74652800	3.02891700
C	2.08381600	1.23559100	-0.38190500
C	2.23697400	2.60896900	-0.58018900
C	3.44847400	3.33382400	-0.79684600
N	4.39902400	3.98071400	-0.99407100
C	1.08211000	3.45177700	-0.60166800
N	0.19334600	4.20876500	-0.61432000
C	3.15296700	0.25839400	-0.30027200
C	2.83600200	-1.12625700	-0.26859400
C	4.53770300	0.57524100	-0.23191200
C	3.79898000	-2.11050000	-0.20243300
H	1.79564000	-1.42616400	-0.30680800
C	5.51284200	-0.39495500	-0.15225400
H	4.86551400	1.60565000	-0.21651000
C	5.18210700	-1.78131500	-0.14516200
H	3.48264900	-3.14600400	-0.18990400
H	6.54748800	-0.08200000	-0.08773100
N	6.14403700	-2.74213500	-0.07907100
C	7.55566400	-2.37295700	-0.00399000
H	8.15841700	-3.27951900	0.03757000
H	7.86493300	-1.79560100	-0.88353200
H	7.76717900	-1.77904200	0.89352600
C	5.77448100	-4.15535000	-0.06525600
H	5.16155400	-4.40103400	0.81070500
H	5.21530200	-4.42948100	-0.96786100
H	6.68014700	-4.75978800	-0.02924200
C	-0.02176100	0.31104500	-1.37629200
N	-0.62919000	-0.06878700	-2.31430300

Zero-point correction= 0.419401

Thermal correction to Energy= 0.452631
Thermal correction to Enthalpy= 0.453575
Thermal correction to Gibbs Free Energy= 0.351131
Sum of electronic and thermal Energies= -1424.107542
Sum of electronic and thermal Enthalpies= -1424.106598
Sum of electronic and thermal Free Energies= -1424.209042

<u>Pathway leading to 3</u>, crucial points on the potential energy surface, optimised in gas-phase [at B3LYP/6-31G(d)] or solvent [at CPCM B3LYP/6-31G(d)]

Intermediate prior to TS (in gas-phase)

C	1.406792	-1.982744	1.770922
C	2.738083	-1.523126	1.192360
C	1.823527	-1.029688	-0.084925
C	0.637907	-1.593745	0.733836
C	3.385192	-0.430717	1.930043
C	3.689871	-2.608685	0.928104
N	4.402608	-3.510497	0.768935
N	3.838556	0.436464	2.554703
C	1.897099	0.471798	-0.428864
C	3.045967	0.951153	-1.010215
C	4.178173	0.128173	-1.319478
N	5.126844	-0.504577	-1.552232
C	3.250795	2.344223	-1.285854
N	3.470041	3.461040	-1.527370
C	0.756182	1.356052	-0.163024
C	0.277189	2.225462	-1.164129
C	0.128717	1.419736	1.097795
C	-0.769365	3.100115	-0.931506
H	0.719101	2.196901	-2.154973
C	-0.900585	2.309034	1.351498
H	0.484847	0.798058	1.911101
C	-1.388491	3.176727	0.341361
H	-1.104710	3.731707	-1.744608
H	-1.319965	2.340423	2.349411
N	-2.418303	4.053982	0.584610
C	-2.817512	5.009456	-0.438443
H	-3.181383	4.502075	-1.341360
H	-3.628935	5.628077	-0.052902
H	-1.989710	5.671704	-0.727468
C	-2.994464	4.152395	1.917264
H	-3.809139	4.877600	1.901653
H	-3.407665	3.190050	2.244889
H	-2.257897	4.481526	2.664231
H	1.230963	-2.510399	2.700315
C	-0.761331	-1.741679	0.387385
C	-1.262741	-1.399260	-0.881218
C	-1.670419	-2.284531	1.316648

C	-2.594464	-1.589821	-1.211379
H	-0.598816	-0.987355	-1.634014
C	-3.004082	-2.476321	1.004343
H	-1.322258	-2.565026	2.307481
C	-3.510683	-2.131339	-0.276039
H	-2.923370	-1.320781	-2.207313
H	-3.658303	-2.902600	1.754848
N	-4.837561	-2.313856	-0.593858
C	-5.305554	-2.040919	-1.944272
H	-4.805201	-2.672428	-2.692423
H	-6.377597	-2.235604	-1.997538
H	-5.140991	-0.991209	-2.219111
C	-5.732120	-2.962495	0.352348
H	-6.735913	-3.000237	-0.073091
H	-5.419278	-3.991387	0.582215
H	-5.789387	-2.404346	1.295653
C	2.033761	-1.830447	-1.297108
N	2.105094	-2.472495	-2.262174

Zero-point correction= 0.420959
Thermal correction to Energy= 0.454298
Thermal correction to Enthalpy= 0.455242
Thermal correction to Gibbs Free Energy= 0.353317
Sum of electronic and thermal Energies= -1424.128829
Sum of electronic and thermal Enthalpies= -1424.127885
Sum of electronic and thermal Free Energies= -1424.229809

Intermediate prior to TS (in toluene)

C	-0.428102	-1.719736	-2.040762
C	-1.791152	-2.038080	-1.451541
C	-1.086114	-1.612166	-0.011933
C	0.189645	-1.439187	-0.876522
C	-2.906951	-1.190118	-1.891010
C	-2.170770	-3.453243	-1.554489
N	-2.429942	-4.578199	-1.672829
N	-3.762631	-0.506043	-2.274390
C	-1.787865	-0.389667	0.614772
C	-2.956168	-0.600609	1.317165
C	-3.634133	-1.860573	1.385699
N	-4.229943	-2.859759	1.431286
C	-3.611575	0.446714	2.044559
N	-4.167095	1.245576	2.683297
C	-1.332978	0.974755	0.341941
C	-0.016471	1.424182	0.580628
C	-2.257556	1.930286	-0.142399
C	0.353145	2.738924	0.365419
H	0.721256	0.749975	0.994479
C	-1.893703	3.239286	-0.391429
H	-3.270751	1.621150	-0.376030
C	-0.571963	3.692990	-0.137428

H	1.368219	3.033194	0.601231
H	-2.638012	3.914366	-0.794477
N	-0.205640	4.990397	-0.369842
C	1.155871	5.430675	-0.092267
H	1.888434	4.856102	-0.672862
H	1.254365	6.480468	-0.368950
H	1.406792	5.332340	0.972414
C	-1.191095	5.959371	-0.835287
H	-0.708984	6.930156	-0.951011
H	-1.611040	5.670334	-1.807063
H	-2.017901	6.070202	-0.121866
H	-0.110437	-1.815865	-3.071162
C	1.575445	-1.216236	-0.508989
C	2.046640	-1.368207	0.809536
C	2.523908	-0.891516	-1.500170
C	3.385372	-1.203168	1.127073
H	1.361819	-1.642629	1.606032
C	3.862908	-0.719307	-1.198644
H	2.200420	-0.759384	-2.529211
C	4.339854	-0.868702	0.131678
H	3.693417	-1.344834	2.155409
H	4.547034	-0.465480	-1.998857
N	5.665692	-0.694962	0.439575
C	6.132604	-0.901342	1.803997
H	5.961166	-1.931723	2.144507
H	7.203656	-0.702321	1.848469
H	5.632959	-0.221276	2.505533
C	6.632346	-0.416407	-0.613948
H	7.622403	-0.308953	-0.170038
H	6.675637	-1.226485	-1.354831
H	6.395249	0.516869	-1.140800
C	-0.953810	-2.731687	0.926130
N	-0.758966	-3.605525	1.665532

Zero-point correction= 0.421180
Thermal correction to Energy= 0.454412
Thermal correction to Enthalpy= 0.455356
Thermal correction to Gibbs Free Energy= 0.353901
Sum of electronic and thermal Energies= -1424.142284
Sum of electronic and thermal Enthalpies= -1424.141339
Sum of electronic and thermal Free Energies= -1424.242795

Intermediate prior to TS (in MeCN)

C	-0.141403	-1.648448	-2.088158
C	-1.444889	-2.164764	-1.506966
C	-0.796882	-1.698055	-0.054481
C	0.443149	-1.333320	-0.913117
C	-2.675180	-1.472043	-1.914941
C	-1.634729	-3.615745	-1.645035

N	-1.749941	-4.762989	-1.777371
N	-3.629771	-0.918170	-2.273939
C	-1.673081	-0.621555	0.620006
C	-2.758417	-1.057070	1.369560
C	-3.233002	-2.405475	1.384390
N	-3.672557	-3.484709	1.388865
C	-3.519005	-0.179129	2.205142
N	-4.148719	0.471177	2.938372
C	-1.489450	0.794051	0.351791
C	-0.239063	1.458553	0.394468
C	-2.622432	1.596438	0.048671
C	-0.126067	2.815437	0.176320
H	0.655550	0.915178	0.662868
C	-2.520858	2.947100	-0.202528
H	-3.594274	1.126892	-0.056300
C	-1.263644	3.613586	-0.136269
H	0.852727	3.270269	0.259844
H	-3.415612	3.491946	-0.475333
N	-1.153485	4.949065	-0.368563
C	0.155379	5.598657	-0.344630
H	0.834108	5.154467	-1.082305
H	0.032175	6.653689	-0.586249
H	0.620731	5.525347	0.645851
C	-2.340079	5.748183	-0.666818
H	-2.047396	6.792222	-0.771535
H	-2.815036	5.428290	-1.602623
H	-3.078320	5.678859	0.140390
H	0.176121	-1.665556	-3.122533
C	1.790189	-0.970382	-0.525316
C	2.230933	-0.992694	0.813676
C	2.738376	-0.622261	-1.511582
C	3.537425	-0.686339	1.155633
H	1.545630	-1.263983	1.611201
C	4.044493	-0.309058	-1.186613
H	2.440280	-0.588247	-2.555908
C	4.491713	-0.332433	0.164297
H	3.821454	-0.724552	2.199675
H	4.727983	-0.042320	-1.982942
N	5.784232	-0.027583	0.492912
C	6.213066	-0.054375	1.886351
H	6.090078	-1.052148	2.326795
H	7.268680	0.211330	1.939330
H	5.649127	0.662879	2.496668
C	6.741728	0.335743	-0.545451
H	7.708817	0.533874	-0.083737
H	6.871946	-0.473478	-1.275375
H	6.429590	1.239014	-1.085503
C	-0.498624	-2.828254	0.832796
N	-0.177221	-3.708516	1.518372

Zero-point correction= 0.421213

Thermal correction to Energy= 0.454357
Thermal correction to Enthalpy= 0.455301
Thermal correction to Gibbs Free Energy= 0.354327
Sum of electronic and thermal Energies= -1424.156156
Sum of electronic and thermal Enthalpies= -1424.155212
Sum of electronic and thermal Free Energies= -1424.256186

TS $_{to\ 3}$ (in gas-phase)

C	-0.049324	-0.999306	2.000118
C	0.965387	-2.058612	1.895050
C	0.206099	-1.672365	-0.148356
C	-0.697848	-0.946565	0.805514
C	2.314259	-1.811431	2.306890
C	0.560627	-3.432413	1.957172
N	0.212538	-4.540495	2.049355
N	3.418752	-1.564099	2.584588
C	1.421672	-1.048842	-0.715082
C	2.310925	-1.791606	-1.483912
C	2.308937	-3.218061	-1.577683
N	2.389641	-4.377228	-1.658192
C	3.351982	-1.168892	-2.243544
N	4.193882	-0.713290	-2.907305
C	1.725973	0.365635	-0.429881
C	0.781328	1.396713	-0.603438
C	3.017343	0.745566	-0.008509
C	1.102043	2.725062	-0.385282
H	-0.219221	1.164716	-0.948902
C	3.345742	2.066566	0.237130
H	3.769520	-0.014879	0.168888
C	2.398848	3.104138	0.047728
H	0.340959	3.475603	-0.559945
H	4.346629	2.292127	0.582965
N	2.722016	4.418795	0.279922
C	1.737165	5.465526	0.055818
H	0.846605	5.320999	0.681645
H	2.175171	6.430405	0.314399
H	1.414368	5.508441	-0.993967
C	4.077451	4.779352	0.671143
H	4.137340	5.861108	0.797018
H	4.360031	4.311513	1.623321
H	4.813333	4.482239	-0.088142
H	-0.217150	-0.417393	2.901757
C	-2.007324	-0.409883	0.475281
C	-2.438149	-0.227615	-0.854289
C	-2.922651	-0.075297	1.495126
C	-3.695598	0.266963	-1.154426
H	-1.778336	-0.485143	-1.677942
C	-4.177716	0.431294	1.213988
H	-2.648910	-0.241820	2.533195

C	-4.606539	0.621350	-0.126474
H	-3.973390	0.378582	-2.195004
H	-4.842857	0.658054	2.038006
N	-5.852264	1.123198	-0.415179
C	-6.304662	1.203692	-1.796927
H	-6.324826	0.217144	-2.280207
H	-7.315057	1.613568	-1.818693
H	-5.660870	1.864015	-2.392174
C	-6.783342	1.433315	0.659714
H	-7.691260	1.861821	0.233506
H	-7.064110	0.539971	1.235757
H	-6.358840	2.169219	1.354140
C	-0.408731	-2.754873	-0.857536
N	-0.986353	-3.622130	-1.379136

Zero-point correction= 0.419608
Thermal correction to Energy= 0.452675
Thermal correction to Enthalpy= 0.453619
Thermal correction to Gibbs Free Energy= 0.352314
Sum of electronic and thermal Energies= -1424.106855
Sum of electronic and thermal Enthalpies= -1424.105910
Sum of electronic and thermal Free Energies= -1424.207216

TS $_{\text{to 3}}$ (in toluene)

C	-0.04932400	-0.99930600	2.00011800
C	0.96538700	-2.05861200	1.89505000
C	0.20609900	-1.67236500	-0.14835600
C	-0.69784800	-0.94656500	0.80551400
C	2.31425900	-1.81143100	2.30689000
C	0.56062700	-3.43241300	1.95717200
N	0.21253800	-4.54049500	2.04935500
N	3.41875200	-1.56409900	2.58458800
C	1.42167200	-1.04884200	-0.71508200
C	2.31092500	-1.79160600	-1.48391200
C	2.30893700	-3.21806100	-1.57768300
N	2.38964100	-4.37722800	-1.65819200
C	3.35198200	-1.16889200	-2.24354400
N	4.19388200	-0.71329000	-2.90730500
C	1.72597300	0.36563500	-0.42988100
C	0.78132800	1.39671300	-0.60343800
C	3.01734300	0.74556600	-0.00850900
C	1.10204300	2.72506200	-0.38528200
H	-0.21922100	1.16471600	-0.94890200
C	3.34574200	2.06656600	0.23713000
H	3.76952000	-0.01487900	0.16888800
C	2.39884800	3.10413800	0.04772800
H	0.34095900	3.47560300	-0.55994500
H	4.34662900	2.29212700	0.58296500
N	2.72201600	4.41879500	0.27992200
C	1.73716500	5.46552600	0.05581800

H	0.84660500	5.32099900	0.68164500
H	2.17517100	6.43040500	0.31439900
H	1.41436800	5.50844100	-0.99396700
C	4.07745100	4.77935200	0.67114300
H	4.13734000	5.86110800	0.79701800
H	4.36003100	4.31151300	1.62332100
H	4.81333300	4.48223900	-0.08814200
H	-0.21715000	-0.41739300	2.90175700
C	-2.00732400	-0.40988300	0.47528100
C	-2.43814900	-0.22761500	-0.85428900
C	-2.92265100	-0.07529700	1.49512600
C	-3.69559800	0.26696300	-1.15442600
H	-1.77833600	-0.48514300	-1.67794200
C	-4.17771600	0.43129400	1.21398800
H	-2.64891000	-0.24182000	2.53319500
C	-4.60653900	0.62135000	-0.12647400
H	-3.97339000	0.37858200	-2.19500400
H	-4.84285700	0.65805400	2.03800600
N	-5.85226400	1.12319800	-0.41517900
C	-6.30466200	1.20369200	-1.79692700
H	-6.32482600	0.21714400	-2.28020700
H	-7.31505700	1.61356800	-1.81869300
H	-5.66087000	1.86401500	-2.39217400
C	-6.78334200	1.43331500	0.65971400
H	-7.69126000	1.86182100	0.23350600
H	-7.06411000	0.53997100	1.23575700
H	-6.35884000	2.16921900	1.35414000
C	-0.40873100	-2.75487300	-0.85753600
N	-0.98635300	-3.62213000	-1.37913600

Zero-point correction= 0.419747
Thermal correction to Energy= 0.452690
Thermal correction to Enthalpy= 0.453634
Thermal correction to Gibbs Free Energy= 0.352677
Sum of electronic and thermal Energies= -1424.124152
Sum of electronic and thermal Enthalpies= -1424.123208
Sum of electronic and thermal Free Energies= -1424.224166

TS $_{to\ 3}$ (in MeCN)

C	-0.081263	-1.082116	2.021200
C	0.964951	-2.103790	1.831266
C	0.240457	-1.647498	-0.137132
C	-0.710254	-0.969381	0.818344
C	2.313259	-1.847303	2.251631
C	0.604806	-3.494326	1.845741
N	0.295539	-4.617075	1.873600
N	3.416453	-1.595952	2.527875
C	1.447084	-0.987098	-0.693889
C	2.369037	-1.739724	-1.433820
C	2.422477	-3.164635	-1.436170

N	2.532031	-4.325668	-1.435215
C	3.365456	-1.131097	-2.254379
N	4.173494	-0.695441	-2.973508
C	1.719449	0.417261	-0.414794
C	0.728467	1.427089	-0.482982
C	3.034979	0.837895	-0.091707
C	1.024887	2.756391	-0.269471
H	-0.287870	1.173683	-0.754451
C	3.341798	2.158927	0.154428
H	3.818739	0.097607	0.024055
C	2.346437	3.173979	0.061354
H	0.229832	3.484835	-0.364689
H	4.355193	2.411349	0.439200
N	2.642978	4.482078	0.287589
C	1.597514	5.500681	0.217544
H	0.800765	5.305493	0.945212
H	2.033936	6.473090	0.442105
H	1.151627	5.547049	-0.783281
C	4.008978	4.884299	0.616427
H	4.042099	5.966923	0.732011
H	4.345837	4.427578	1.555099
H	4.708437	4.602122	-0.179080
H	-0.280572	-0.590381	2.967192
C	-2.015625	-0.448343	0.477518
C	-2.427986	-0.243016	-0.858183
C	-2.954991	-0.152643	1.493113
C	-3.688446	0.231579	-1.168388
H	-1.747020	-0.455525	-1.677739
C	-4.213232	0.332964	1.202341
H	-2.692260	-0.326498	2.532518
C	-4.626372	0.543865	-0.144889
H	-3.947846	0.373428	-2.209747
H	-4.893689	0.536324	2.019487
N	-5.868997	1.023987	-0.440116
C	-6.284621	1.188203	-1.829872
H	-6.244876	0.236873	-2.374487
H	-7.311758	1.550774	-1.852954
H	-5.652640	1.914845	-2.355790
C	-6.802431	1.364641	0.629328
H	-7.709902	1.778015	0.190263
H	-7.078282	0.483037	1.222105
H	-6.377080	2.116443	1.304943
C	-0.333430	-2.735889	-0.876906
N	-0.850211	-3.633723	-1.409924

Zero-point correction= 0.419864
Thermal correction to Energy= 0.452732
Thermal correction to Enthalpy= 0.453677
Thermal correction to Gibbs Free Energy= 0.353496
Sum of electronic and thermal Energies= -1424.140025
Sum of electronic and thermal Enthalpies= -1424.139080

Sum of electronic and thermal Free Energies= -1424.239261

<u>Pathway leading to 4</u>, crucial points on the potential energy surface, optimised in gas-phase [at B3LYP/6-31G(d)] or solvent [at CPCM B3LYP/6-31G(d)]

TS $_{to\ 4}$ optimised in gas-phase

C	-0.28793800	3.19201100	-0.49965000
C	1.18132900	2.71575000	-0.59502800
C	1.72458308	1.56126339	-0.33521761
C	-0.13047808	0.78771661	1.46766161
C	-1.20456000	0.96618400	0.52338000
C	-1.37434900	2.13763200	-0.21460400
H	1.84679900	3.48682900	-0.98812000
C	2.61751408	0.54444739	-0.32538161
C	3.44042308	0.25579739	0.82367739
C	2.79380308	-0.27462461	-1.49995361
C	4.38873208	-0.72098161	0.78170939
H	3.31256708	0.85161139	1.72076239
C	3.73527608	-1.25815361	-1.53843661
H	2.16743508	-0.08577361	-2.36494461
C	4.57984008	-1.52013161	-0.40129061
H	5.00435508	-0.89143861	1.65451839
H	3.84237608	-1.84664361	-2.43957861
C	-2.14936300	-0.15013500	0.33009700
C	-2.55028700	-0.56167600	-0.95646100
C	-2.68429500	-0.85498400	1.42704400
C	-3.43365700	-1.61110500	-1.14522700
H	-2.13260200	-0.06595600	-1.82778100
C	-3.58341400	-1.89430500	1.25861900
H	-2.41040600	-0.56036900	2.43590700
C	-3.99095200	-2.30731800	-0.03877400
H	-3.68547800	-1.90246000	-2.15743200
H	-3.97904400	-2.38671600	2.13828500
C	-0.35912900	4.33781300	0.45120400
N	-0.46287900	5.25323000	1.15664900
C	-0.54520200	3.76905900	-1.85074100
N	-0.70357000	4.21292600	-2.91038500
C	-2.64400200	2.44938800	-0.76662800
N	-3.68051300	2.77268300	-1.20043200
C	0.40889692	-0.50009576	1.71824481
N	0.92355322	-1.53011915	1.91982483
C	0.29194547	1.79181699	2.37513254
N	0.65441015	2.58655256	3.15252659
N	5.51408108	-2.47928761	-0.44285961
N	-4.88113500	-3.33424100	-0.21471700
C	-5.38705300	-4.07225400	0.93602200

H	-5.93482500	-3.41701200	1.62533000
H	-6.07253100	-4.84569100	0.58959400
H	-4.57726000	-4.55834300	1.49634000
C	-5.26750700	-3.74878000	-1.55755500
H	-5.71493600	-2.91903400	-2.11878800
H	-4.41131900	-4.12855400	-2.13173400
H	-6.00826000	-4.54520800	-1.48527500
C	5.76752086	-3.23338242	-1.67917748
H	6.02019952	-2.55586425	-2.49956296
H	6.60814831	-3.90404032	-1.51457544
H	4.89269855	-3.82913622	-1.95812089
C	6.30886073	-2.81225722	0.74842001
H	6.92034562	-1.95924877	1.05867799
H	5.65896017	-3.11144117	1.57571119
H	6.96774919	-3.64407564	0.50876886

Zero-point correction= 0.419209
Thermal correction to Energy= 0.452468
Thermal correction to Enthalpy= 0.453412
Thermal correction to Gibbs Free Energy= 0.350190
Sum of electronic and thermal Energies= -1424.078737
Sum of electronic and thermal Enthalpies= -1424.077793
Sum of electronic and thermal Free Energies= -1424.181014

TS $_{\text{to 4}}$ optimised in toluene

C	-0.28793800	3.19201100	-0.49965000
C	1.18132900	2.71575000	-0.59502800
C	1.73270700	1.56465100	-0.34311300
C	-0.13860200	0.78432900	1.47555700
C	-1.20456000	0.96618400	0.52338000
C	-1.37434900	2.13763200	-0.21460400
H	1.84679900	3.48682900	-0.98812000
C	2.62563800	0.54783500	-0.33327700
C	3.44854700	0.25918500	0.81578200
C	2.80192700	-0.27123700	-1.50784900
C	4.39685600	-0.71759400	0.77381400
H	3.32069100	0.85499900	1.71286700
C	3.74340000	-1.25476600	-1.54633200
H	2.17555900	-0.08238600	-2.37284000
C	4.58796400	-1.51674400	-0.40918600
H	5.01247900	-0.88805100	1.64662300
H	3.85050000	-1.84325600	-2.44747400
C	-2.14936300	-0.15013500	0.33009700
C	-2.55028700	-0.56167600	-0.95646100
C	-2.68429500	-0.85498400	1.42704400
C	-3.43365700	-1.61110500	-1.14522700
H	-2.13260200	-0.06595600	-1.82778100
C	-3.58341400	-1.89430500	1.25861900
H	-2.41040600	-0.56036900	2.43590700
C	-3.99095200	-2.30731800	-0.03877400

H	-3.68547800	-1.90246000	-2.15743200
H	-3.97904400	-2.38671600	2.13828500
C	-0.35912900	4.33781300	0.45120400
N	-0.46287900	5.25323000	1.15664900
C	-0.54520200	3.76905900	-1.85074100
N	-0.70357000	4.21292600	-2.91038500
C	-2.64400200	2.44938800	-0.76662800
N	-3.68051300	2.77268300	-1.20043200
C	0.35468164	-0.51100637	1.77714543
N	0.83242241	-1.55010393	2.01900036
C	0.32776747	1.80931566	2.33698871
N	0.72545659	2.62202532	3.07771345
N	5.52220500	-2.47590000	-0.45075500
N	-4.88113500	-3.33424100	-0.21471700
C	-5.38705300	-4.07225400	0.93602200
H	-5.93482500	-3.41701200	1.62533000
H	-6.07253100	-4.84569100	0.58959400
H	-4.57726000	-4.55834300	1.49634000
C	-5.26750700	-3.74878000	-1.55755500
H	-5.71493600	-2.91903400	-2.11878800
H	-4.41131900	-4.12855400	-2.13173400
H	-6.00826000	-4.54520800	-1.48527500
C	5.77564478	-3.22999481	-1.68707288
H	6.02832343	-2.55247663	-2.50745835
H	6.61627222	-3.90065270	-1.52247083
H	4.90082246	-3.82574861	-1.96601628
C	6.31698465	-2.80886960	0.74052462
H	6.92846953	-1.95586116	1.05078260
H	5.66708408	-3.10805356	1.56781580
H	6.97587311	-3.64068803	0.50087346

Zero-point correction= 0.419643
Thermal correction to Energy= 0.452670
Thermal correction to Enthalpy= 0.453614
Thermal correction to Gibbs Free Energy= 0.352587
Sum of electronic and thermal Energies= -1424.103108
Sum of electronic and thermal Enthalpies= -1424.102163
Sum of electronic and thermal Free Energies= -1424.203191

$TS_{to\ 4}$ optimised in MeCN

C	-0.287938	3.192011	-0.499650
C	1.181329	2.715750	-0.595028
C	1.732707	1.564651	-0.343113
C	-0.138602	0.784329	1.475557
C	-1.204560	0.966184	0.523380
C	-1.374349	2.137632	-0.214604
H	1.846799	3.486829	-0.988120
C	2.625638	0.547835	-0.333277
C	3.448547	0.259185	0.815782
C	2.801927	-0.271237	-1.507849

C	4.396856	-0.717594	0.773814
H	3.320691	0.854999	1.712867
C	3.743400	-1.254766	-1.546332
H	2.175559	-0.082386	-2.372840
C	4.587964	-1.516744	-0.409186
H	5.012479	-0.888051	1.646623
H	3.850500	-1.843256	-2.447474
C	-2.149363	-0.150135	0.330097
C	-2.550287	-0.561676	-0.956461
C	-2.684295	-0.854984	1.427044
C	-3.433657	-1.611105	-1.145227
H	-2.132602	-0.065956	-1.827781
C	-3.583414	-1.894305	1.258619
H	-2.410406	-0.560369	2.435907
C	-3.990952	-2.307318	-0.038774
H	-3.685478	-1.902460	-2.157432
H	-3.979044	-2.386716	2.138285
C	-0.359129	4.337813	0.451204
N	-0.462879	5.253230	1.156649
C	-0.545202	3.769059	-1.850741
N	-0.703570	4.212926	-2.910385
C	-2.644002	2.449388	-0.766628
N	-3.680513	2.772683	-1.200432
C	0.325009	-0.513948	1.809802
N	0.778922	-1.557381	2.077504
C	0.356388	1.820525	2.307089
N	0.777045	2.642998	3.023966
N	5.522205	-2.475900	-0.450755
N	-4.881135	-3.334241	-0.214717
C	-5.387053	-4.072254	0.936022
H	-5.934825	-3.417012	1.625330
H	-6.072531	-4.845691	0.589594
H	-4.577260	-4.558343	1.496340
C	-5.267507	-3.748780	-1.557555
H	-5.714936	-2.919034	-2.118788
H	-4.411319	-4.128554	-2.131734
H	-6.008260	-4.545208	-1.485275
C	5.733595	-3.271750	-1.668667
H	5.955809	-2.622556	-2.520182
H	6.580920	-3.935588	-1.510902
H	4.850771	-3.877533	-1.896032
C	6.359114	-2.767053	0.722490
H	6.979318	-1.903335	0.981595
H	5.739362	-3.038265	1.581934
H	7.010933	-3.605999	0.488417

Zero-point correction= 0.419949
Thermal correction to Energy= 0.452802
Thermal correction to Enthalpy= 0.453746
Thermal correction to Gibbs Free Energy= 0.353507
Sum of electronic and thermal Energies= -1424.124887

Sum of electronic and thermal Enthalpies= -1424.123943
Sum of electronic and thermal Free Energies= -1424.224182

Pathway leading to 5, crucial points on the potential energy surface, optimised in gas-phase [at B3LYP/6-31G(d)] or solvent [at CPCM B3LYP/6-31G(d)]

$TS_{to\ 5}$ optimised in gas-phase

C	0.800509	0.779214	1.556871
C	-0.452229	1.178603	1.990823
C	-1.377252	1.776952	1.097915
C	-0.967546	1.932904	-0.255560
C	0.282754	1.525289	-0.672309
H	1.501609	0.399945	2.289987
H	0.569058	1.675622	-1.707914
C	1.205292	0.916788	0.207680
C	0.217803	-1.629144	-0.266250
C	2.607162	0.689063	-0.235587
C	1.346090	-2.252083	-0.148133
C	3.314896	-0.491234	0.067712
C	2.699176	-1.818861	0.521813
H	1.373452	-3.289051	-0.488530
N	-2.615116	2.201362	1.518601
C	-2.968730	2.115513	2.929294
H	-2.339267	2.759432	3.560247
H	-4.008445	2.421347	3.056186
H	-2.874783	1.085143	3.290065
C	-3.431614	3.037287	0.645865
H	-2.911604	3.959477	0.352951
H	-3.716565	2.499366	-0.266242
H	-4.346984	3.312656	1.171705
C	2.456685	-1.884388	1.990435
N	2.267532	-1.935666	3.135221
C	3.634470	-2.940290	0.228010
N	4.271840	-3.878446	-0.011988
C	4.730814	-0.522779	-0.006728
N	5.897484	-0.573975	0.020538
C	3.197695	1.744844	-0.984752
C	4.288940	1.561336	-1.878117
N	5.134221	1.444690	-2.674506
C	2.707104	3.079401	-0.907108
N	2.324679	4.182053	-0.853720
H	-1.629526	2.396419	-0.976186
H	-0.689387	1.074776	3.042336
C	-1.123806	-1.439420	-0.463263
C	-2.057109	-1.741883	0.580259
C	-1.655846	-0.977507	-1.709308

C	-3.410680	-1.639495	0.378157
H	-1.673854	-2.076367	1.538473
C	-3.008944	-0.897786	-1.919601
H	-0.967917	-0.721885	-2.508022
C	-3.938024	-1.226279	-0.883937
H	-4.080023	-1.894681	1.189794
H	-3.367161	-0.573989	-2.888465
N	-5.279726	-1.149386	-1.095191
C	-6.219085	-1.492005	-0.029133
H	-6.114752	-2.540354	0.276358
H	-6.070614	-0.854835	0.850553
H	-7.236509	-1.341056	-0.388767
C	-5.805592	-0.769647	-2.405787
H	-5.470424	-1.462898	-3.186446
H	-6.894432	-0.794893	-2.373101
H	-5.495878	0.245051	-2.683232

Zero-point correction= 0.419139
Thermal correction to Energy= 0.452061
Thermal correction to Enthalpy= 0.453005
Thermal correction to Gibbs Free Energy= 0.352299
Sum of electronic and thermal Energies= -1424.055374
Sum of electronic and thermal Enthalpies= -1424.054430
Sum of electronic and thermal Free Energies= -1424.155137

$TS_{to\ 5}$ optimised in toluene

C	0.813236	0.753263	1.553189
C	-0.444799	1.147817	1.977336
C	-1.337899	1.808667	1.095497
C	-0.876451	2.056899	-0.228132
C	0.383003	1.656552	-0.633069
H	1.487699	0.316766	2.279618
H	0.700902	1.869303	-1.648612
C	1.261360	0.970306	0.230396
C	0.167534	-1.635319	-0.488599
C	2.656338	0.683820	-0.185280
C	1.332016	-2.204434	-0.457514
C	3.294918	-0.537014	0.110969
C	2.592377	-1.877689	0.403059
H	1.439749	-3.104302	-1.065428
N	-2.590156	2.203568	1.497979
C	-2.989036	2.036812	2.890834
H	-2.387345	2.652094	3.574932
H	-4.035408	2.325420	2.998038
H	-2.894944	0.989677	3.197703
C	-3.379915	3.094994	0.654174
H	-2.873001	4.053423	0.476447
H	-3.593319	2.633601	-0.316372
H	-4.332605	3.296110	1.145451
C	2.207844	-2.055774	1.833319

N	1.922282	-2.205376	2.948832
C	3.532820	-2.999167	0.126124
N	4.198756	-3.919853	-0.103151
C	4.707772	-0.606392	0.173025
N	5.867770	-0.682908	0.299468
C	3.338532	1.724442	-0.879921
C	4.451834	1.492076	-1.730752
N	5.330453	1.333259	-2.484277
C	2.942934	3.085970	-0.774838
N	2.648292	4.215020	-0.702341
H	-1.505328	2.583458	-0.934841
H	-0.716565	0.979086	3.011736
C	-1.163266	-1.407932	-0.598875
C	-2.066734	-2.012869	0.348364
C	-1.740145	-0.637983	-1.669765
C	-3.418977	-1.890538	0.215538
H	-1.648794	-2.580064	1.173191
C	-3.095074	-0.545189	-1.821609
H	-1.079840	-0.173067	-2.391788
C	-3.990306	-1.161982	-0.884537
H	-4.062243	-2.362618	0.946416
H	-3.489245	0.008362	-2.663650
N	-5.325278	-1.066725	-1.033120
C	-6.235442	-1.708386	-0.077091
H	-6.073538	-2.790767	-0.047715
H	-6.099094	-1.299053	0.929366
H	-7.261946	-1.522886	-0.388133
C	-5.903589	-0.329398	-2.162824
H	-5.600635	-0.773415	-3.116913
H	-6.989123	-0.370342	-2.092896
H	-5.595530	0.721002	-2.144382

Zero-point correction= 0.419807
Thermal correction to Energy= 0.452638
Thermal correction to Enthalpy= 0.453582
Thermal correction to Gibbs Free Energy= 0.353674
Sum of electronic and thermal Energies= -1424.087444
Sum of electronic and thermal Enthalpies= -1424.086500
Sum of electronic and thermal Free Energies= -1424.186408

$TS_{to\ 5}$ optimised in MeCN

C	0.762528	0.789248	1.478033
C	-0.451537	1.268934	1.909543
C	-1.368501	1.871163	0.993596
C	-0.953417	1.984641	-0.375118
C	0.267109	1.516885	-0.785040
H	1.453657	0.379292	2.207428
H	0.550785	1.621483	-1.826919
C	1.148864	0.834731	0.102197
C	0.209055	-1.349120	-0.137465

C	2.569602	0.622619	-0.283122
C	1.220029	-2.157032	0.059702
C	3.276910	-0.516205	0.112064
C	2.658237	-1.866916	0.513225
H	1.014359	-3.221201	-0.063965
N	-2.571915	2.333927	1.399232
C	-2.979614	2.209412	2.800007
H	-2.340245	2.810042	3.457705
H	-4.005925	2.558621	2.902402
H	-2.937849	1.164675	3.124504
C	-3.464186	3.024827	0.463658
H	-2.998062	3.935001	0.069925
H	-3.737116	2.375269	-0.374031
H	-4.375425	3.305450	0.989451
C	2.695254	-2.041385	1.995214
N	2.722377	-2.138253	3.151939
C	3.492328	-2.955107	-0.069797
N	4.122440	-3.806837	-0.541365
C	4.688105	-0.497569	0.215372
N	5.846887	-0.518059	0.374310
C	3.205397	1.671194	-1.020660
C	4.355008	1.460739	-1.822565
N	5.275137	1.317518	-2.530471
C	2.751238	3.014691	-0.982271
N	2.424093	4.137784	-0.964358
H	-1.603375	2.457323	-1.099695
H	-0.691875	1.208272	2.962831
C	-1.151075	-1.265596	-0.355364
C	-2.067079	-1.450186	0.730193
C	-1.703167	-1.025907	-1.654468
C	-3.422808	-1.449634	0.526788
H	-1.670985	-1.627054	1.724031
C	-3.055418	-1.033066	-1.864753
H	-1.030287	-0.864389	-2.489987
C	-3.971369	-1.244541	-0.780365
H	-4.078273	-1.618798	1.370848
H	-3.429612	-0.873707	-2.867381
N	-5.304555	-1.251319	-0.987426
C	-6.231825	-1.466369	0.127484
H	-6.062620	-2.441630	0.596314
H	-6.122531	-0.683987	0.886063
H	-7.251733	-1.438781	-0.251746
C	-5.856258	-1.047460	-2.330628
H	-5.509776	-1.824866	-3.019819
H	-6.942317	-1.095087	-2.275975
H	-5.572503	-0.067207	-2.727774

Zero-point correction= 0.420317
Thermal correction to Energy= 0.452980
Thermal correction to Enthalpy= 0.453924
Thermal correction to Gibbs Free Energy= 0.355046

Sum of electronic and thermal Energies= -1424.119399
Sum of electronic and thermal Enthalpies= -1424.118455
Sum of electronic and thermal Free Energies= -1424.217334

Attack at C4 in 1, optimised in gas-phase [at B3LYP/6-31G(d)]

C	1.921755	-0.987013	-0.743889
C	-1.984661	2.834815	0.277211
C	-1.021716	1.807745	0.315853
C	0.663635	-1.031748	-0.662882
H	-0.145349	-1.324563	-1.315447
C	3.290198	-0.850451	-0.635970
C	4.113355	-1.969384	-0.310963
C	3.931330	0.405865	-0.857114
C	5.477476	-1.844725	-0.209001
H	3.643970	-2.932615	-0.137926
C	5.296393	0.528865	-0.760546
H	3.319418	1.276066	-1.069363
C	6.118821	-0.588660	-0.430742
H	6.063624	-2.718398	0.046454
H	5.740198	1.503583	-0.918493
N	7.472328	-0.461259	-0.324482
C	8.112510	0.832490	-0.545841
H	7.777519	1.578283	0.185933
H	9.191856	0.717210	-0.446543
H	7.901500	1.213251	-1.552167
C	8.295972	-1.603952	0.058089
H	8.219733	-2.416826	-0.674823
H	9.338642	-1.290469	0.108914
H	8.008048	-1.994279	1.042102
C	-3.341878	2.671914	0.674950
C	-1.630681	4.157775	-0.113544
N	-1.368833	5.247253	-0.437097
N	-4.457097	2.626698	1.012731
C	-1.276183	0.426501	0.560762
C	-0.181923	-0.476689	0.911792
C	-0.552982	-1.804680	1.404446
N	-0.762334	-2.878546	1.794358
C	0.880351	0.045939	1.768435
N	1.730579	0.408690	2.470409
C	-2.595829	-0.145911	0.228283
C	-3.144071	0.045188	-1.057077
C	-3.360152	-0.895305	1.142600
C	-4.371085	-0.485777	-1.417227
H	-2.592257	0.628064	-1.790011
C	-4.595026	-1.420834	0.801975
H	-2.997936	-1.039125	2.155032
C	-5.138339	-1.238537	-0.493922
H	-4.740007	-0.305355	-2.419399

H	-5.150048	-1.962653	1.557550
N	-6.361905	-1.769051	-0.841323
C	-7.181780	-2.421237	0.168312
H	-8.096356	-2.790168	-0.298666
H	-6.660548	-3.281246	0.606289
H	-7.462728	-1.738621	0.983855
C	-6.958653	-1.432596	-2.124478
H	-7.136457	-0.352436	-2.231889
H	-6.321492	-1.758557	-2.956195
H	-7.915931	-1.947534	-2.219297
C	0.320967	2.231770	0.010496
N	1.388372	2.567384	-0.305450

Zero-point correction= 0.417439
Thermal correction to Energy= 0.451251
Thermal correction to Enthalpy= 0.452195
Thermal correction to Gibbs Free Energy= 0.348380
Sum of electronic and thermal Energies= -1424.073550
Sum of electronic and thermal Enthalpies= -1424.072606
Sum of electronic and thermal Free Energies= -1424.176421

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