Supporting information for

Charge Transfer Through Cross-Hyperconjugated *versus* Cross-π-Conjugated Bridges: An Intervalence Charge Transfer Study

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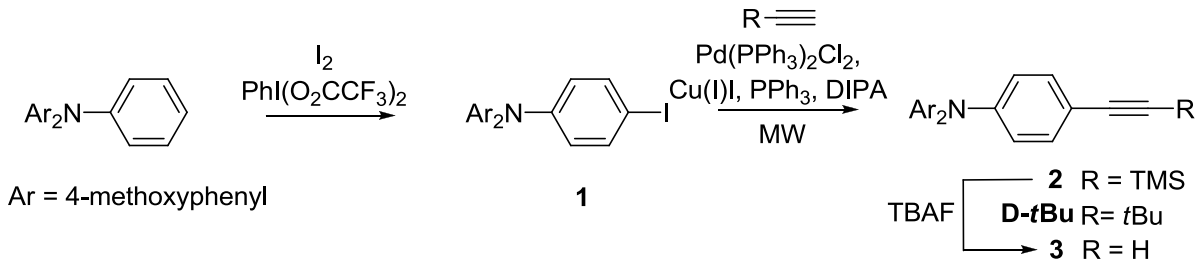
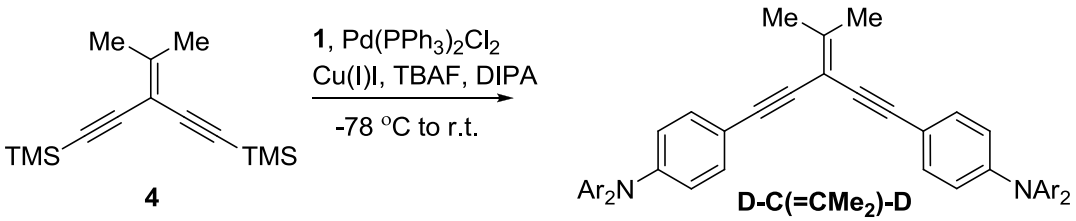
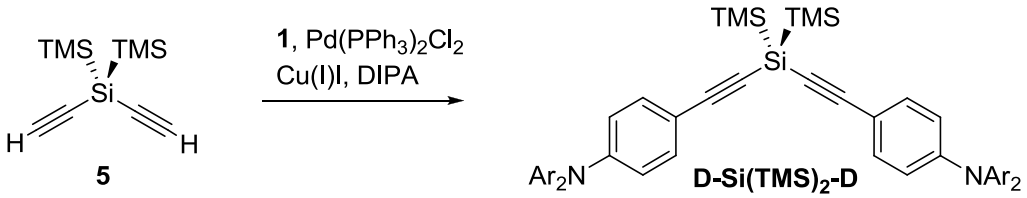
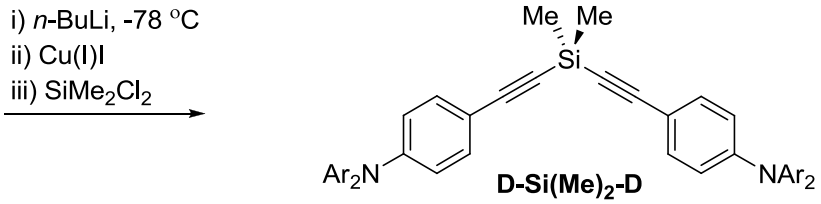
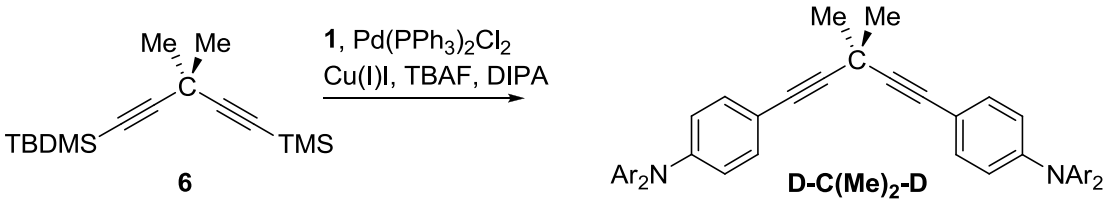










SI Scheme S1 Synthetic routes to reference compounds and dyads.

4-Iodo-*N*,*N*-bis(4-methoxyphenyl)aniline (1)

N,*N*-Bis(4-methoxyphenyl)aniline (4.23 g, 13.85 mmol) was dissolved in dry chloroform (100 mL). Separately, iodine (1.88 g, 7.41 mmol) and $PhI(O_2CCF_3)_2$ (3.19 g, 7.42 mmol) were dissolved in chloroform (70 mL) and after stirring for one hour, the iodine solution was added dropwise to the aniline solution. The solution was heated to 50 °C and stirred at this temperature for four hours and then left to cool to room temperature overnight. The reaction mixture was quenched with 10% Na_2SO_3 (aq), phases separated and the organic phases washed three times with 10% Na_2SO_3 (aq). The combined water phases were extracted with DCM and dried over $MgSO_4$. Following evaporation of the solvent, the residue was dissolved in DCM and put through a short silica column with DCM as eluent. Recrystallization from boiling ethanol yielded **1** (4.38 g, 73%) as pale yellow crystals.

^{1}H NMR (400 MHz, C_6D_6) δ 3.29 (s, 6H, O*Me*), 6.65-6.71 (m, 6H, ArH), 6.96 (m, 4H, ArH), 7.36 (m, 2H, ArH);

^{13}C NMR (100.6 MHz, C_6D_6) δ 55.0, 82.5, 115.2, 122.9, 127.0, 138.2, 140.9, 149.1, 156.7.

N,*N*-bis(4-methoxyphenyl)-4-[2-(trimethylsilyl)ethynyl]aniline (2)

Compound **1** (4.20 g, 10.93 mmol), ethynyltrimethylsilane (2.30 mL, 1.60 g, 16.27 mmol), Cu(I)I (208 mg, 1.09 mmol), $PdCl_2(PPh_3)_2$ (384 mg, 0.55 mmol), PPh_3 (430 mg, 1.64 mmol) and diisopropylamine (DIPA) (6.2 mL, 43.9 mmol) were dissolved in DMF and divided equally between two 20 mL microwave vials. The vials were heated to 130 °C in a microwave reactor and stirred at this temperature for 1 h. The reaction mixture was mixed with diethyl ether and filtered through a plug of celite before quenching with 1M HCl (40 mL). Phases were separated and the organic phase was washed twice with saturated NH_4Cl (aq) and twice with brine. The combined water phases were extracted once with DCM. The combined organic phases were dried over $MgSO_4$ and evaporated to remove most of the solvent. The remaining solution was purified by silica flash chromatography (pentane to pentane:DCM, 9:1 to 2:1) and **2** was obtained as solid material (3.07 g, 70%).

^{1}H NMR (400 MHz, C_6D_6) δ 0.26 (s, 9H, Si*Me*$_3$), 3.29 (s, 6H, O*Me*), 6.66 (m, 4H, ArH), 6.86 (m, 2H, ArH), 6.96 (m, 4H, ArH), 7.43 (m, 2H, ArH);

^{13}C NMR (100.6 MHz, C_6D_6) δ 0.2, 55.0, 92.6, 106.9, 114.8, 115.2, 119.5, 127.4, 133.3, 140.6, 149.5, 156.9.

4-*tert*-Butylethynyl-*N*,*N*-bis(4-methoxyphenyl)aniline (*t*Bu-D)

Compound **1** (0.22 g, 0.50 mmol), Cu(I)I (14 mg, 0.075 mmol), $PdCl_2(PPh_3)_2$ (18 mg, 0.025 mmol) and DIPA (7 mL, 49 mmol) were dissolved in THF (7 mL). 3,3-dimethyl-1-butyne (0.08 mL, 50 mg, 0.60 mmol) were added dropwise and the solution turned from clear orange to brown within a few minutes. The solution was left to stir in r.t. o.n. To the reaction mixture diethyl ether (20 mL) was added and thereafter the solution was filtered through a plug of celite. The clear red solution was quenched with saturated NH_4Cl (aq) and phases separated. The water layer extracted once with diethyl ether (50 mL). The combined organic phases were washed with Brine, dried over $MgSO_4$ and the solvent removed in vacou. The remaining solid was purified by silica flash chromatography (pentane:DCM, 4:1 to 2:1) and **D-*t*Bu** was obtained as a yellow solid (0.18 g, 94 %).

^{1}H NMR (400 MHz, C_6D_6) δ 1.28 (s, 9H, C*Me*$_3$), 3.31 (s, 6H, O*Me*), 6.66 (m, 4H, ArH), 6.92 (m, 2H, ArH), 7.00 (m, 4H, ArH), 7.39 (m, 2H, ArH);

^{13}C NMR (100.6 MHz, C_6D_6) δ 30.7, 31.0, 54.8, 92.5, 106.8, 114.7, 115.0, 119.4, 127.3, 133.2, 140.4, 149.4, 156.8;

MS: m/z = 386.2 ($M+H^+$);

Elemental analysis (%) calcd for $C_{26}H_{27}NO_2$: C, 81.01; H, 7.06; N, 3.63; O, 8.30. Found: C, 80.79 H, 6.98; N, 3.51; O, 7.99.

4-Ethynyl-*N*,*N*-bis(4-methoxyphenyl)aniline (3)

Compound **2** (2.99 g, 7.44 mmol) was dissolved in DCM (50 mL). TBAF (8.2 mL, 1M solution in THF, 8.2 mmol) was slowly added. The solution was stirred for 1 h when TLC analysis indicated complete reaction. The reaction mixture was quenched with saturated NH_4Cl (aq). Phases were separated and the organic phase was washed twice with saturated aqueous NH_4Cl and once with brine, dried and evaporated. The residue was purified by silica plug flash chromatography (pentane:DCM, 4:1 to 2:1 to 1:1) and **3** was obtained as an yellow oil (2.07 g, 85%).

^{1}H NMR (400 MHz, C_6D_6) δ 2.26 (s, 1H, CC*H*), 3.38 (s, 6H, O*Me*), 6.69 (m, 4H, ArH), 6.82 (m, 2H, ArH), 6.97 (m, 4H, ArH), 7.29 (m, 2H, ArH);

^{13}C NMR (100.6 MHz, C_6D_6) δ 55.1, 76.5, 84.6, 113.5, 115.2, 119.4, 127.4, 133.3, 140.4, 149.5, 156.8.

4-[3-(2-{4-[Bis(4-methoxyphenyl)amino]phenyl}ethynyl)-4-methylpent-3-en-1-yn-1-yl]-*N,N* bis(4-methoxyphenyl)aniline (D-C(=CMe$_2$) -D)

To THF (30 mL), **4** (187 mg, 0.75 mmol), **1** (0.680 g, 1.58 mmol), CuI (48 mg, 0.25 mmol), $PdCl_2(PPh_3)_2$ (55 mg, 0.08 mmol) and DIPA (1 mL, 7.08 mmol) were added. The solution was cooled to -78 °C and TBAF (1.6 mL, 1 M solution in THF, 1.60 mmol) was added dropwise. The cooling bath was removed and the solution was allowed to warm to room temperature overnight while stirring. The mixture was quenched with saturated NH_4Cl (aq). The phases were separated and the organic phase was washed twice with NH_4Cl (aq) and twice with brine. Combined water phases were extracted with DCM and the combined organic phases were dried over $MgSO_4$. After evaporation of most of the solvent purification by silica flash chromatography (ethyl acetate: pentane, 1:9 to 1:2) yielded **D-C(=CMe$_2$)-D** (163 mg, 31%) as a pale solid.

^{1}H NMR (400 MHz, C_6D_6) δ 2.01 (s, 6H, C(*CH$_3$*)$_2$), 3.31 (s, 12H, O*Me*), 6.69 (m, 4H, ArH), 6.91 (m, 2H, ArH), 6.99 (m, 4H, ArH), 7.36 (m, 2H, ArH);

^{13}C NMR (100.6 MHz, C_6D_6) δ 22.6, 55.0, 86.4, 92.5, 103.1, 115.2, 115.3, 120.0, 127.3, 132.8, 140.8, 149.0, 151.7, 156.8;

MS: m/z = 710.6 ($M+H^+$);

Elemental analysis (%) calcd for $C_{48}H_{42}N_2O_4$: C, 81.10; H, 5.96; N, 3.94; O, 9.00. Found: C, 80.90; H, 6.17; N, 3.89; O, 9.45.

4-{2-[(2-{4-[bis(4-methoxyphenyl)amino]phenyl}ethynyl)-dimethylsilyl] ethynyl}-*N,N*-bis(4-methoxyphenyl)aniline (D-Si(Me)$_2$-D)

Compound **3** (0.363 g, 1.1 mmol) was added to dry THF (10 mL) and the solution was cooled to -78 °C with an acetone/dry ice bath. *n*-BuLi (0.7 mL, 1.6 M in hexanes, 1.12 mmol) was added dropwise under stirring. A clear red color developed over several minutes. After stirring for 1 h, Cu(I)I (216 mg, 1.13 mmol) was added and a change of colour to purple was observed. After further stirring for 1 h, dichlorodimethylsilane (0.06 mL, 0.50 mmol) was added dropwise. The solution was then allowed to reach room temperature overnight. The reaction mixture was quenched with NH_4Cl (sat) and washed three times with NH_4Cl (sat). The water phases were extracted with diethyl ether and the combined organic phases were washed with brine and dried over $MgSO_4$. Solvent was evaporated and silica flash chromatography (pentane:DCM, 2:1 to 1:1 to 1:2) yielded **D-Si(Me)$_2$-D** (97 mg, 27%) as a pale yellow solid.

^{1}H NMR (400 MHz, C_6D_6) δ 0.53 (s, 6H, Si(*Me*)$_2$), 3.32 (s, 12H, O*Me*), 6.67 (m, 8H, ArH), 6.82 (m, 4H, ArH), 6.95 (m, 8H, ArH), 7.38 (m, 4H, ArH);

^{13}C NMR (100.6 MHz, C_6D_6) δ 1.1, 55.0, 90.0, 107.5, 114.2, 115.2, 119.3, 127.5, 133.5, 140.4, 149.6, 156.9;

MS: m/z = 714.6 ($M+H^+$);

Elemental analysis (%) calcd for $C_{46}H_{42}N_2O_4Si$: C, 77.28; H, 5.92; N, 3.92; O, 8.95; Si, 3.93. Found: C, 76.97; H, 5.97; N, 3.84 O, 8.56.

N-(4-{2-[2-(2-{4-[bis(4-methoxyphenyl)amino]phenyl}ethynyl)-1,1,1,3,3,3-hexamethyl-trisilan-2-yl]ethynyl}phenyl)-4-methoxy-*N*-(4-methylphenyl)aniline (D-Si(TMS)$_2$-D)

To THF (10 mL), **5** (56 mg g, 0.25 mmol), **1** (216 mg, 0.50 mmol), CuI (7 mg, 0.015 mmol), $PdCl_2(PPh_3)_2$ (9 mg, 0.0125 mmol) and DIPA (5 mL) were added. The solution was stirred at room temperature overnight. The mixture was quenched with 1M HCl and diluted with diethyl ether. The phases were separated and the organic phase was washed twice with NH_4Cl (aq) and twice with brine. The combined organic phases were dried over $MgSO_4$ and the solvent evaporated. The residue was purified by silica flash chromatography (pentane: DCM 3:1, 1:1 to 1:3) yielding **D-Si(TMS)$_2$-D** (31 mg, 14%) as a yellow solid.

^{1}H NMR (400 MHz, C_6D_6) δ 0.46 (s, 18H, Si(Si*Me*$_3$)$_2$), 3.28 (s, 12H, O*Me*), 6.68 (m, 8H, ArH), 6.84 (m, 4H, ArH), 6.96 (m, 8H, ArH), 7.37 (m, 4H, ArH);

^{13}C NMR (100.6 MHz, C_6D_6) δ -1.2, 55.0, 85.4, 111.0, 115.2, 115.4, 119.9, 127.2, 133.3, 140.7, 149.3, 156.9;

MS: m/z = 830.6 ($M+H^+$);

Elemental analysis (%) calcd for $C_{50}H_{54}N_2O_4Si_3$: C, 72.25; H, 6.55; N, 3.37; O, 7.70; Si, 10.14. Found: C, 71.89; H, 6.82; N, 3.43; O, 7.41.

N-[4-(5-{4-[bis(4-methoxyphenyl)amino]phenyl}-3,3-dimethylpenta-1,4-diyn-1-yl)phenyl]-4-methoxy-*N*-(4-methylphenyl)aniline (D-C(Me)$_2$-D)

To a solution of **1** (0.593 g, 1.375 mmol), CuI (20 mg, 0.10 mmol), $PdCl_2(PPh_3)_2$ (48 mg, 0.069 mmol) and DIPA (5 mL) in THF (15 mL), TBAF (1M in THF, 1.03 mL) was added. The solution was stirred for 5 min before **6** (0.170 mg, 0.69 mmol) were added dropwise and stirred at room temperature over night. The mixture was quenched with 1M HCl and diluted with diethyl ether. The phases were separated and the organic phase was washed twice with NH_4Cl (aq) and twice with brine. The combined organic phases were dried over $MgSO_4$ and the solvent evaporated. The residue was purified by silica flash chromatography (pentane to pentane:DCM 3:1) yielding **D-C(Me)$_2$-D** (55 mg, 11%) as a pale solid.

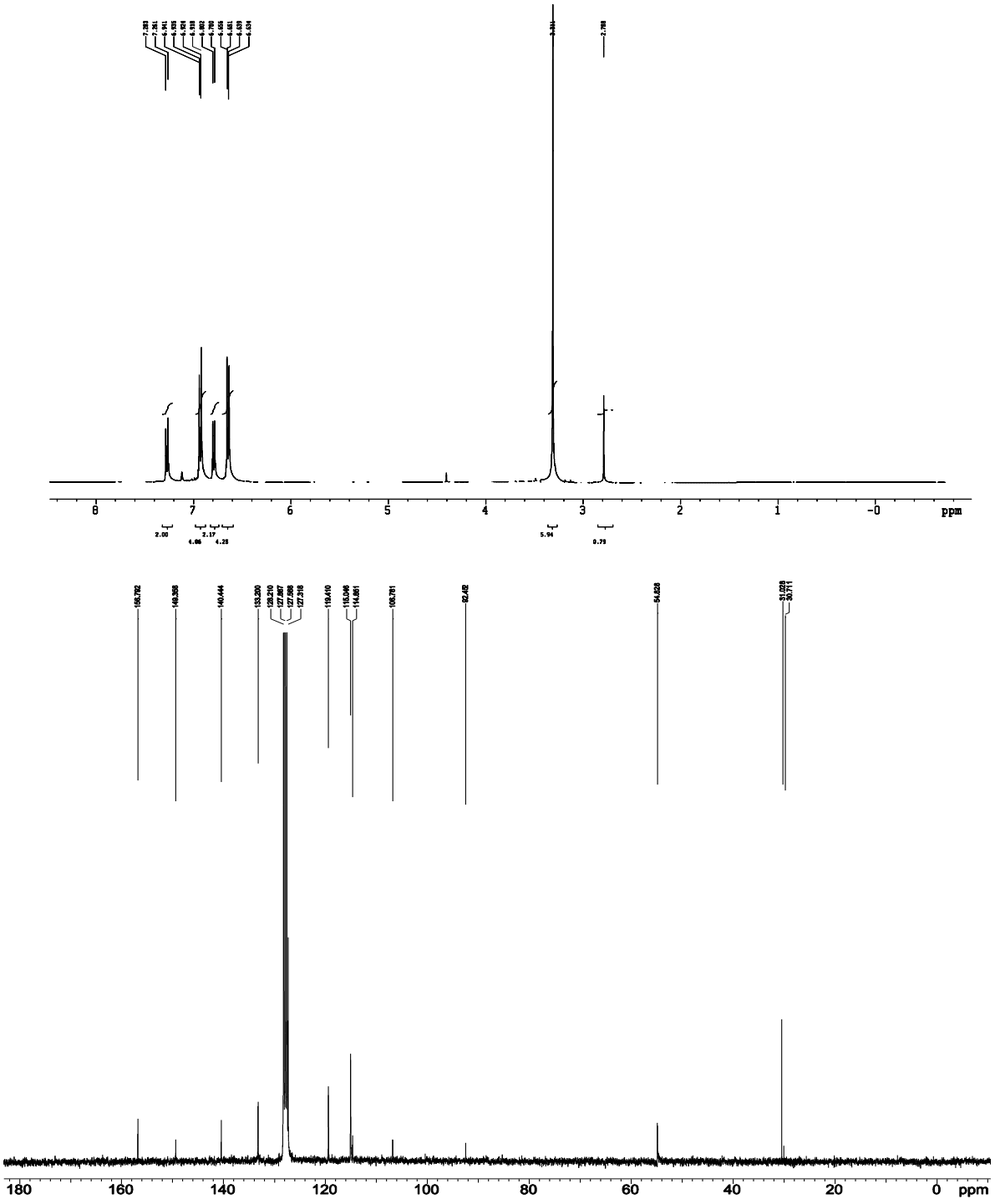
^{1}H NMR (400 MHz, C_6D_6) δ 1.74 (s, 6H, C*Me*$_2$), 3.28 (s, 12H, O*Me*), 6.67 (m, 8H, ArH), 6.90 (m, 4H, ArH), 6.98 (m, 8H, ArH), 7.38 (m, 4H, ArH);

^{13}C NMR (100.6 MHz, C_6D_6) δ 27.7, 32.0, 55.0, 80.9, 92.6, 115.2, 115.3, 120.1, 127.2, 133.0, 140.9, 149.0, 156.7;

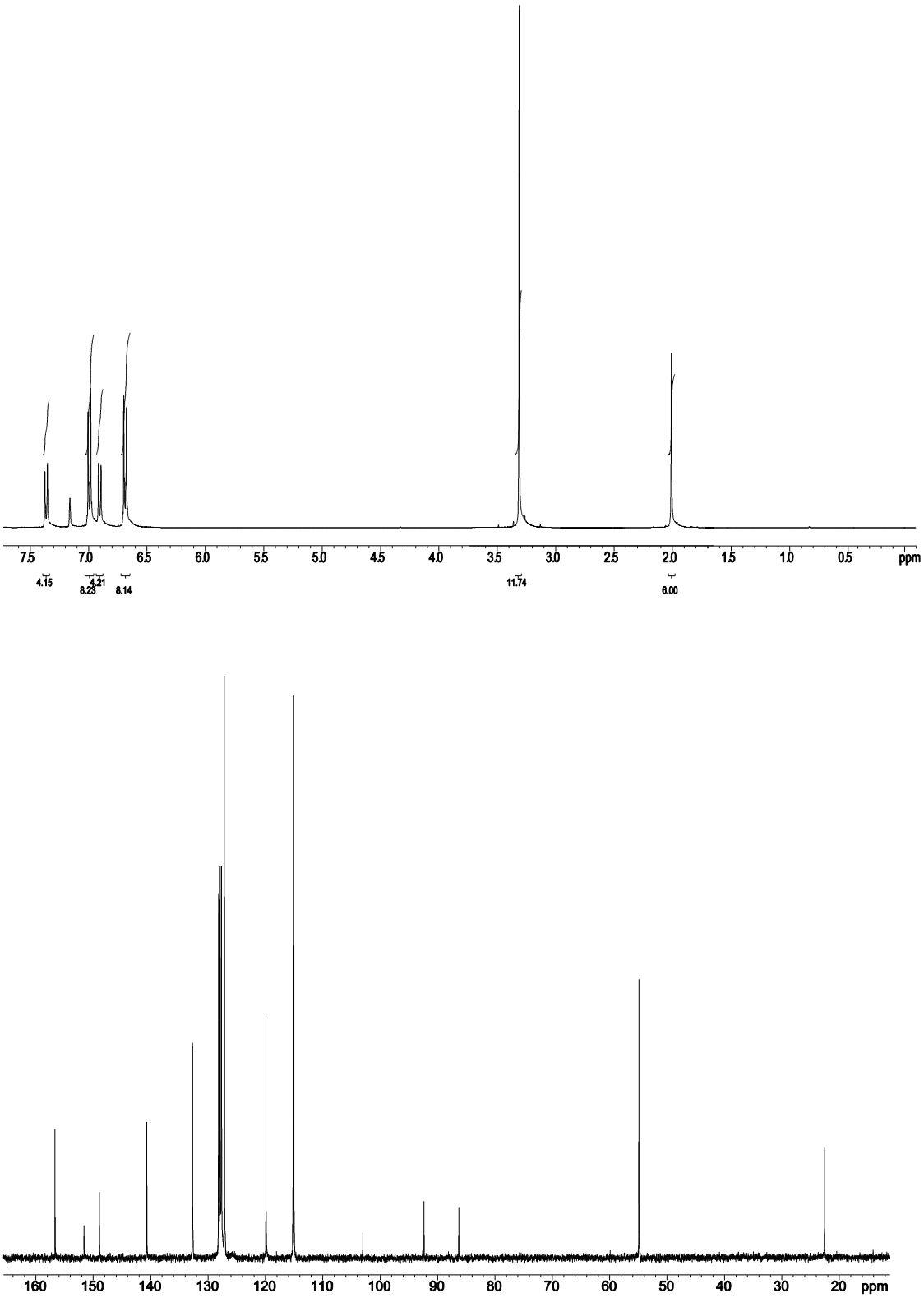
MS: m/z = 698.6 ($M+H^+$)

Elemental analysis (%) calcd for $C_{47}H_{42}N_2O_4$: C, 80.78; H, 6.06; N, 4.01; O, 9.16. Found: C, 80.40; H, 6.15; N, 4.01; O, 8.80.

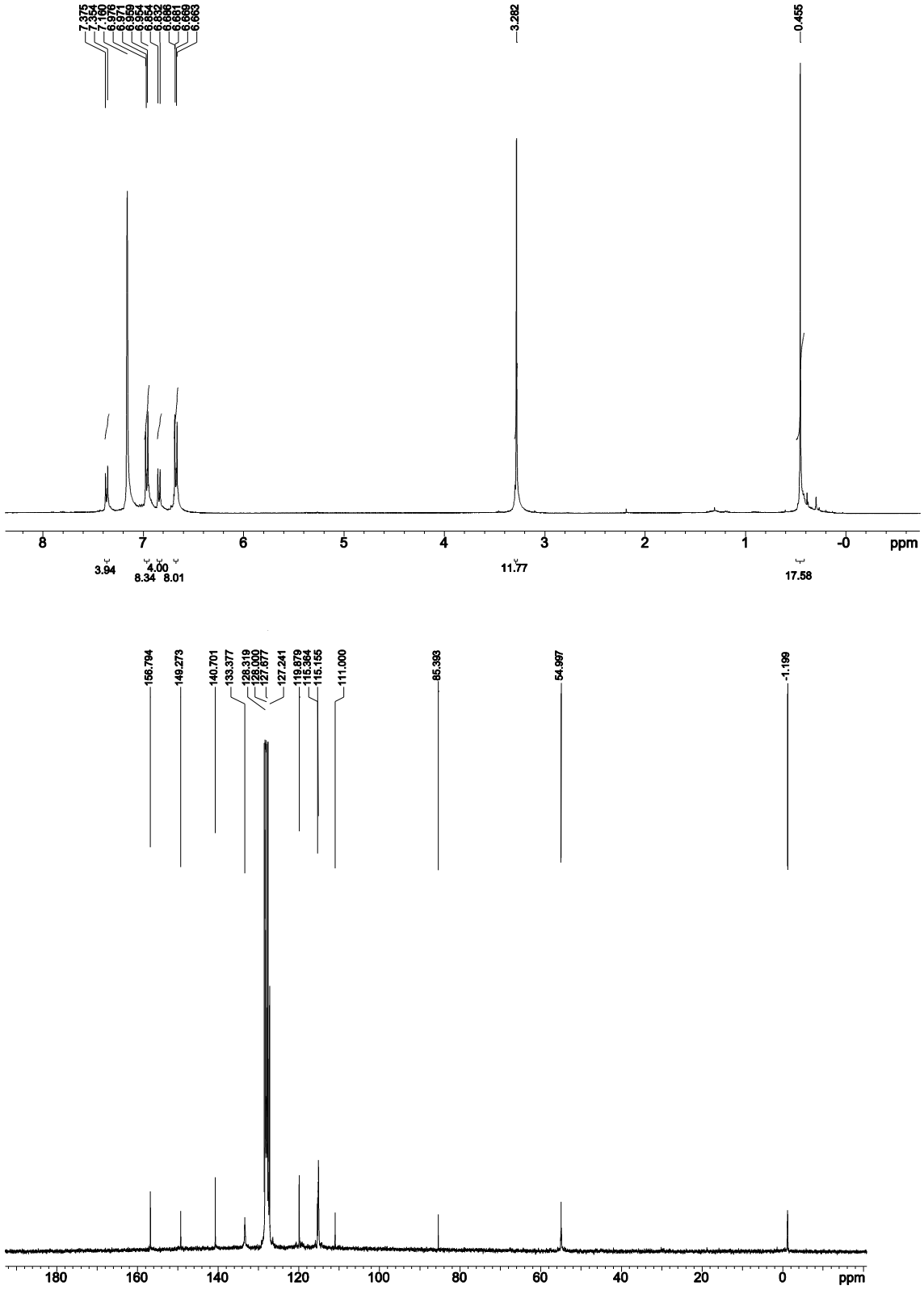
NMR spectra



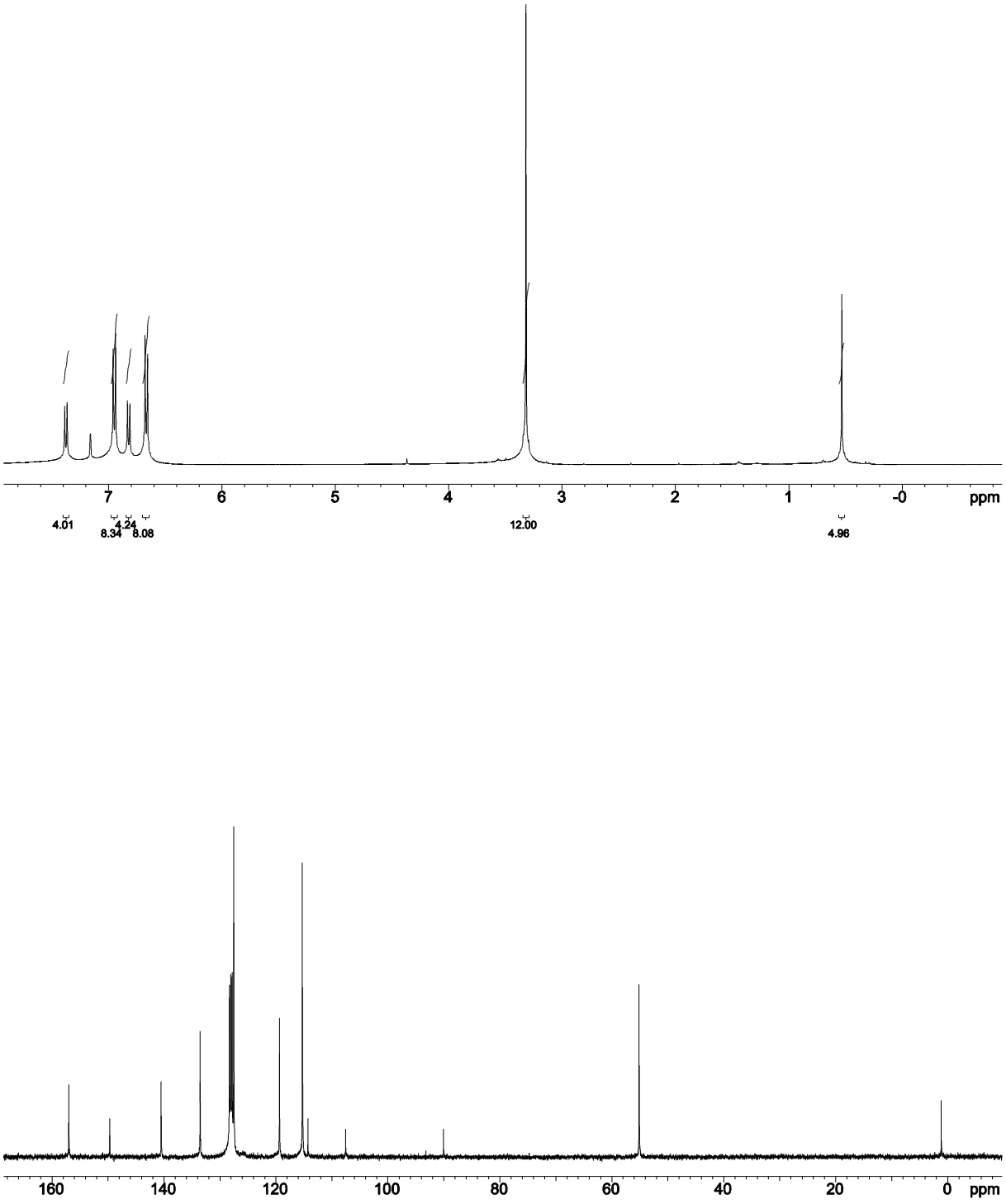
SI Figure S1 1H NMR (top) and 13C NMR spectra (bottom) of **D-tBu** in C6D6 recorded at 399.97 MHz (1H) and 100.57 MHz (13C).



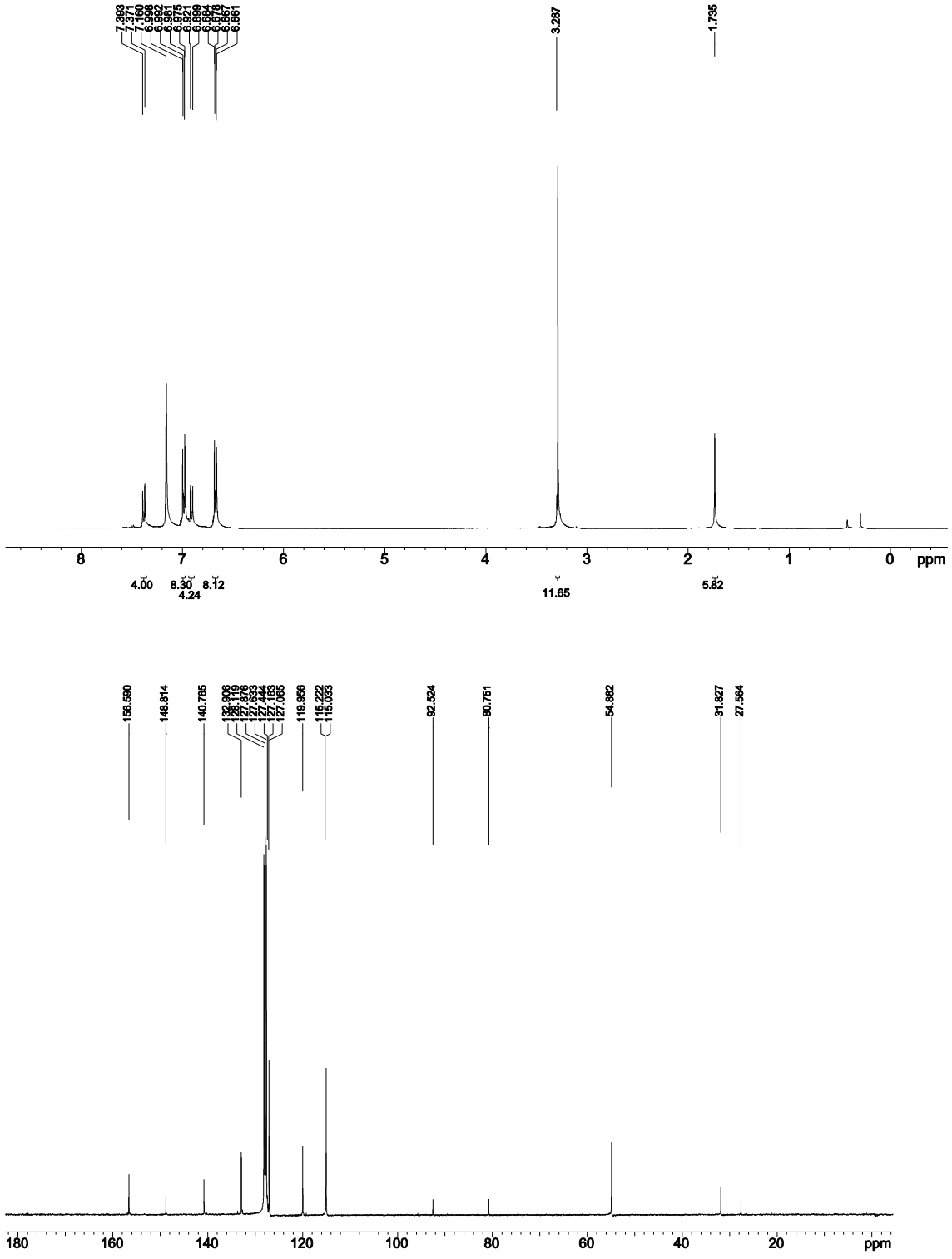
SI Figure S2 ^{1}H NMR (top) and ^{13}C NMR spectra (bottom) of **D-C(=CMe$_2$) -D** in C_6D_6 recorded at 399.97 MHz (^{1}H) and 100.57 MHz (^{13}C).



SI Figure S3 ^{1}H NMR (top) and ^{13}C NMR spectra (bottom) of D-Si(TMS)$_2$-D in C_6D_6 recorded at 399.97 MHz (^{1}H) and 100.57 MHz (^{13}C).

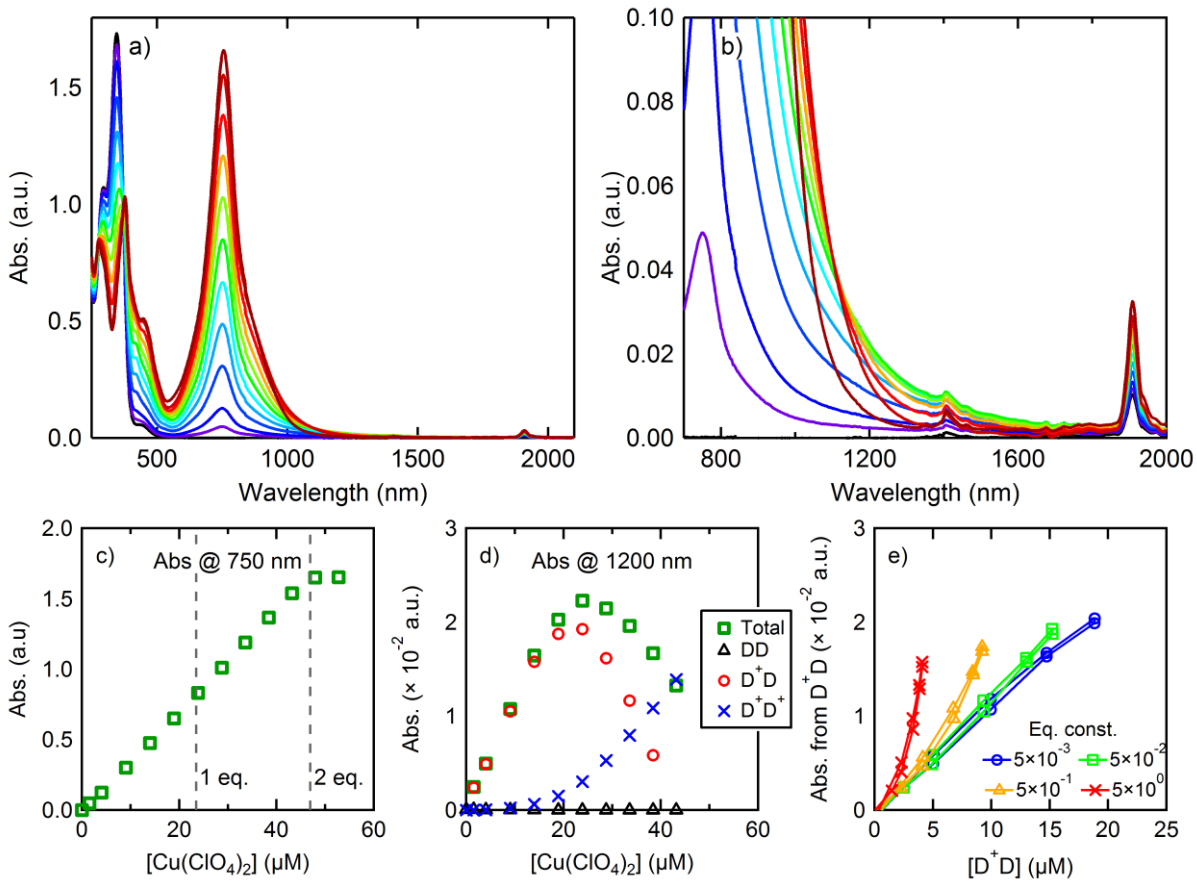


SI Figure S4 ^{1}H NMR (top) and ^{13}C NMR spectra (bottom) of **D-Si(Me)$_2$-D** in C_6D_6 recorded at 399.97 MHz (^{1}H) and 100.57 MHz (^{13}C).



SI Figure S5 ^{1}H NMR (top) and ^{13}C NMR spectra (bottom) **of D-C(Me)$_2$-D** in C_6D_6 recorded at 399.97 MHz (^{1}H) and 100.57 MHz (^{13}C).

Analysis of titration data



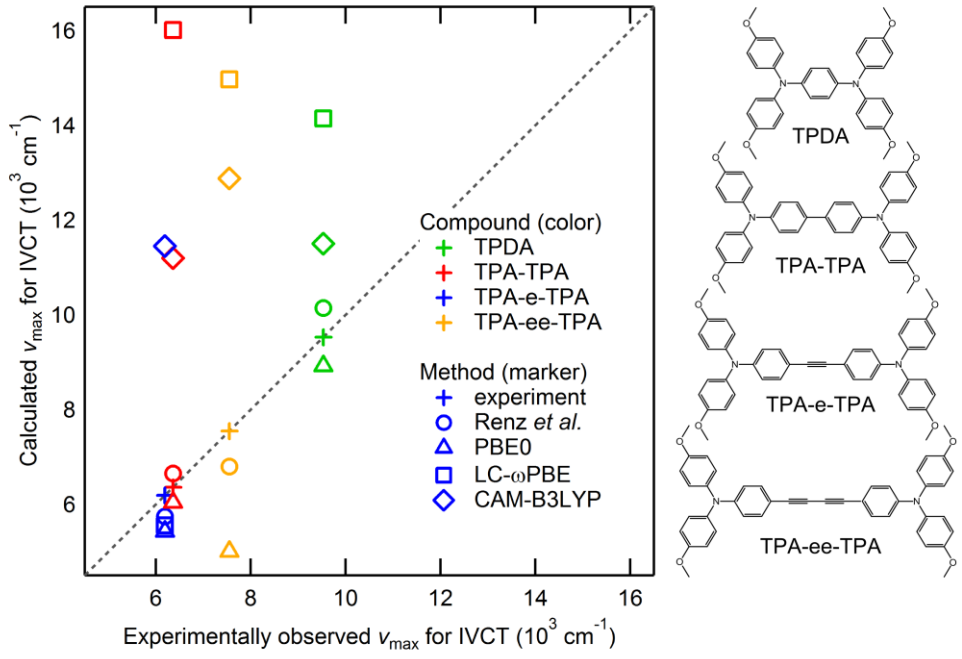
SI Figure S6. This figure illustrates the analytical procedure to extract the spectra of the neutral (DD), singly oxidized (D^+D) and doubly oxidized (D^+D^+) form of the dyads. As an example we show the data for **D-C(=CMe$_2$) -D**. Panel a) show absorption spectra of **D-C(=CMe$_2$) -D** in MeCN, with increasing amount of $Cu(ClO_4)_2$ added. Cu concentration increasing from blue → green → red. Absorption bands belonging to the aminium radical are growing in at 400 nm and 750 nm and the absorption band of the neutral species is disappearing at 320 nm. Panel b) displays the same data as a), zoomed in on the region where the IVCT band is expected. Notice the initial rise and then disappearance of absorption at wavelengths longer than 1200 nm. The narrow peaks at 1400 nm and 1900 nm are vibrational overtones, which occur due to imperfect background correction. Panel c) show the absorption at 750 nm plotted versus the added concentration of Cu^{2+}. The rise in absorption follows Beer-Lambert's law until two equivalents of Cu^{2+} has been added. The spectra taken at zero and two equivalents of Cu was used to calculate the extinction coefficients of DD and D^+D^+ respectively. Panel d) show the absorption at 1200 nm. To explain the observed absorption one need to account for the presence of all three form of the dyad (DD, D^+D and D^+D^+). The concentration of each species can be calculated the disproportionation equilibrium. To find the equilibrium constant (K_{disp}) we plotted the estimated absorption contribution of D^+D *vs.* the estimated concentration D^+D (see panel e). We then varied the equilibrium constant so that the absorption followed Beer-Lambert's law. Panel e) shows how an under or over estimation of K_{disp} will result in a deviation from a linear trend. The relative error of K_{disp} is ~30%. Finally, when K_{disp} has been determined one can use the slope to calculate the extinction coefficients for D^+D.

Benchmarking of the computational method.

The computational protocol used in this work is an adaptation on the work by Renz *et al.*.[1] In their work they systematically varied that amount of exact exchange (HF) that is included in the hybrid functional and found that custom hybrid functional with 35% HF exchange could account for the IVCT character (Robin Day classification and IVCT band energy) of a series of bis-triarylamine dyads. They used a double zeta basis set (SVP) and a dielectric model for the solvent COSMO. Wishing to use more established functional we decided to benchmark three functionals, PBE0, LC-ωPBE and CAM-B3LYP, which are already included in the Gaussian 09 computational package.[2] PBE0 is a hybrid functional that has been shown to work well for both ground state optimization and for TD-DFT. LC-ωPBE and CAM-B3LYP are two fairly new hybrid functionals, which have been designed to compensate for the problem DFT has with charge transfer transitions.[3] These three functional were benchmarked against the four bis-triarylamin dyads studied in Renz *et al.* (SI Figure S2). The cation radical (+1) of the four dyads was geometry optimized starting from a C1-symmetry. 6-31G(d) was used as basis set, this is a smaller basis set than SVP but it includes silicon, which is important for this study. In gas phase all three functionals indicated that the four dyads had the electron hole delocalized over the whole molecule. Introducing a solvent model (IEFPCM, acetonitrile) changed the behaviour results for the three larger dyads, which now has the electron hole mainly localized on one of the triarylamines. This follows the trend from Renz *et al.* and also matched the Robin-Day classification expected from experiments.

The optical IVCT band was modelled by TD-DFT, using 6-31G(d,p) as basis set. For PBE0 all dyads have a lowest transition dominated by a β-HOMO → β-LUMO orbital transition. This is what one would expect for IVCT and for the larger dyads one can clearly see that β-HOMO and the β-LUMO is located on different triarylamines (β-LUMO corresponding to the electron hole). The PBE0 transition energies for the dyad series follow the same trend as the experiment, but with slightly lower energies (SI Figure S2). Employing the other two functionals, LC-ωPBE and CAM-B3LYP, for TD-DFT resulted in transitions that had large contributions from other orbital transitions than β-HOMO → β-LUMO. They also reported too high transition energies and the trend within the benchmark series is not the same as in the experiments. Because of these results we decided to use PBE0 as our functional, knowing that the reported transition energies might be too low, but hoping that it still would represent the charge transfer transitions correctly.

We also tested expanding the basis-set to include diffuse functions (6-31+G(d,p)), but it did not change the results significantly (SI Table S1). Consequently we decided against including diffuse function since they caused convergence problems and higher computational cost.

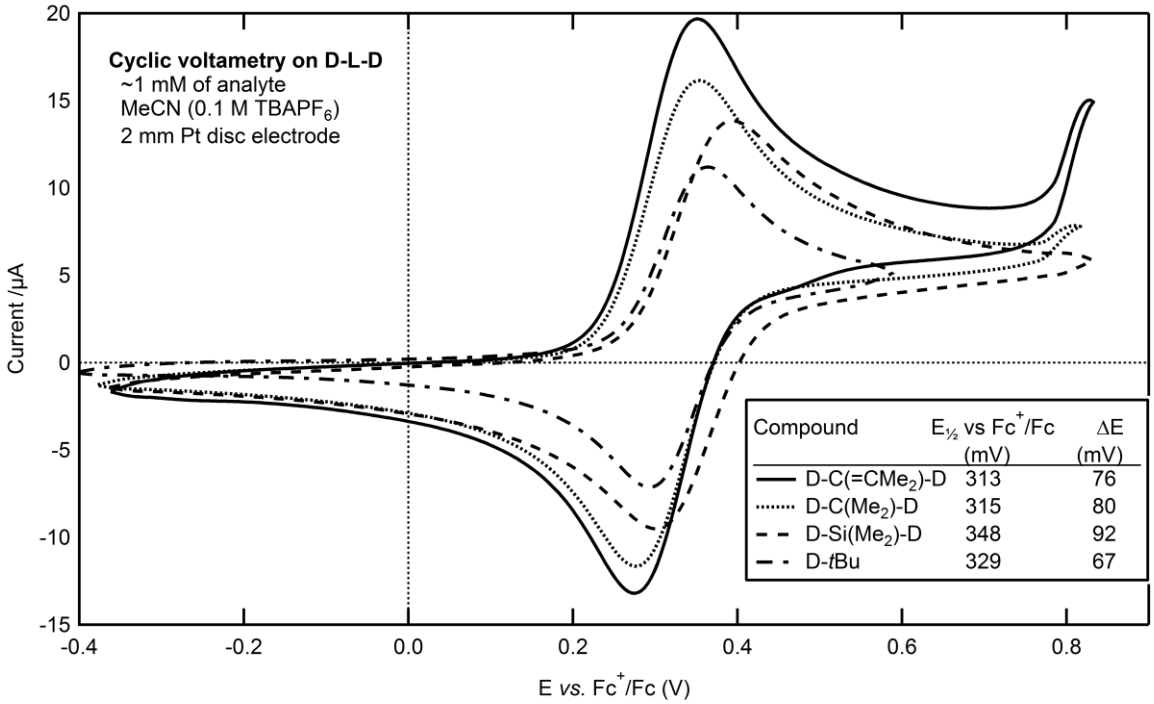


SI Figure S7. To the left is a summary of the calculated IVCT energies and how those compare to Renz *et al.* and to experiments. To the right is the structure of the four dyads used to benchmark the computational protocol.

SI Table S1. Comparison between TD-DFT results using PBE0/6-31G(d,p) and PBE0/6-31+G(d,p).

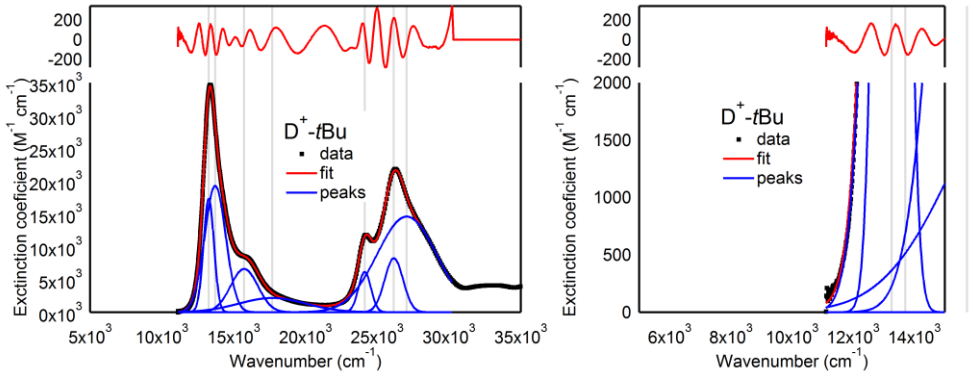
	Oscillation strength				Transition energy (eV)			
	6-31G(d,p)		6-31+G(d,p)		6-31G(d,p)		6-31+G(d,p)	
	0°,0°	90°,90°	0°,0°	90°,90°	0°,0°	90°,90°	0°,0°	90°,90°
D-Si(TMS)$_2$-D	0.0143	0.0246	0.0142	0.0237	0.5470	0.5156	0.5907	0.5567
D-Si(Me)$_2$-D	0.0301	0.0012	0.0291	0.0010	0.5628	0.5513	0.6062	0.5959
D-C(Me)$_2$-D	0.0596	0.0019	0.0547	0.0015	0.5175	0.5064	0.5609	0.5542
D-C(=CMe$_2$) -D	0.0532	0.1097	0.0499	0.1073	0.5300	0.4659	0.5728	0.4990

Electrochemsitry

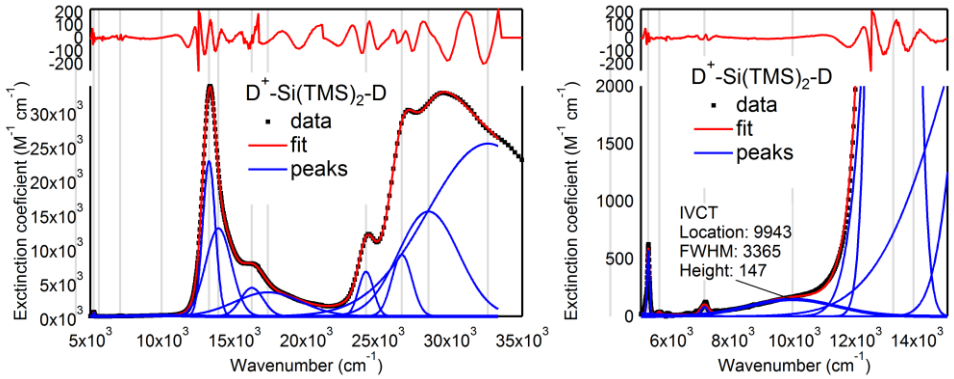


SI Figure S8. Cyclic voltammograms for the reference and dyads.

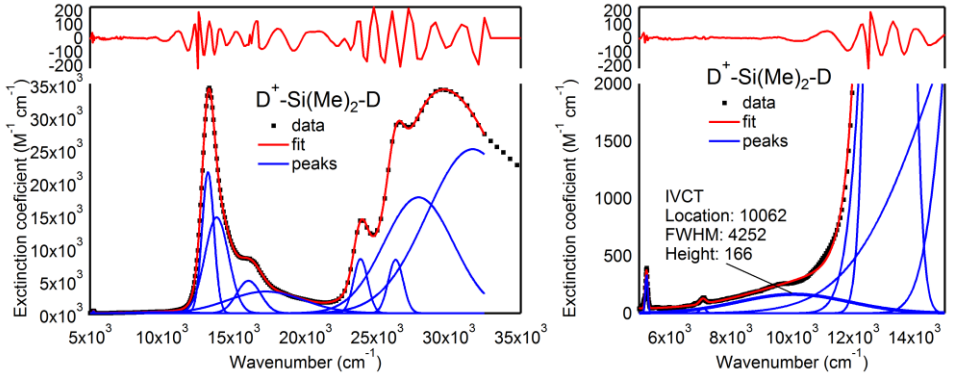
Spectral deconvolution



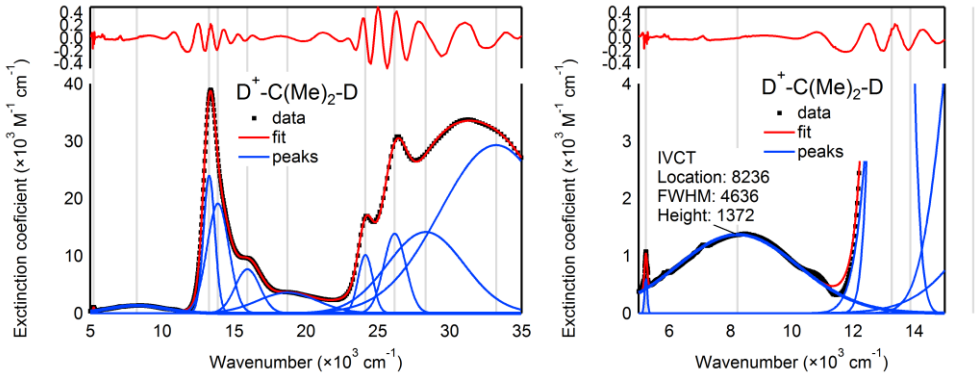
SI Figure S9. Spectal deconcoulution of the singly oxidized refrence. The result from this fit was used as starting point of the fit for the four dyads.



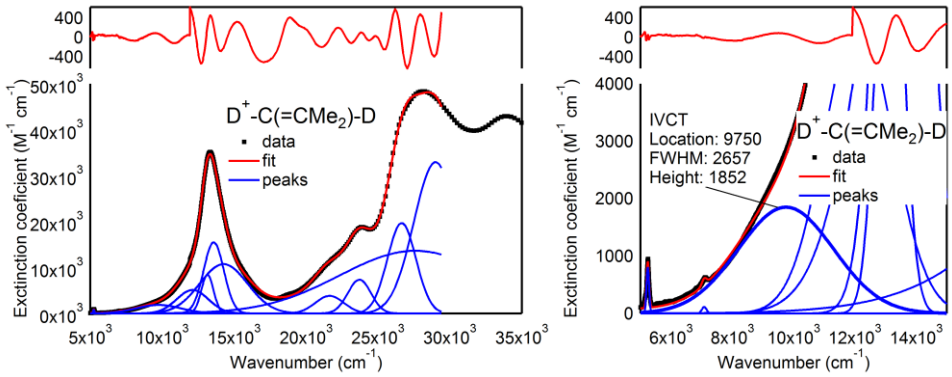
SI Figure S10. Results for the peak fit of **D-Si(TMS)$_2$-D**. Compared to the reference four more peaks have been added. The first is to account for the band from the neutral triarylamine around 34000 cm^{-1}. The second is for the IVCT band around 10000 cm^{-1}. The last two is to fit the bands from vibrational overtones found at ~5200 cm^{-1} and ~7500 cm^{-1}.



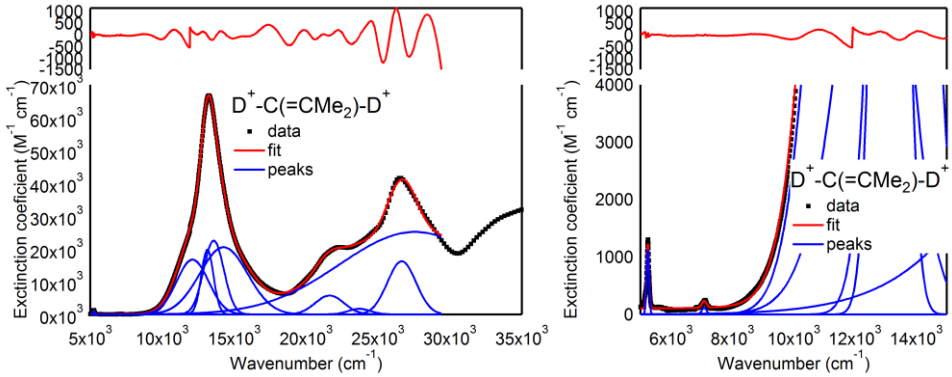
SI Figure S11. Results for the peak fit of **D-Si(Me)$_2$-D**. Just as in SI Figure S5 four more peaks have been added compared to the reference. The first is to account for the band from the neutral triarylamine around 34000 cm^{-1}. The second is for the IVCT band around 10000 cm^{-1}. The last two is to fit the bands from vibrational overtones found at ~5200 cm^{-1} and ~7500 cm^{-1}.



SI Figure S12. Results for the peak fit of **D-C(Me)$_2$-D**. Just as in the figures above four more peaks have been added compared to the reference. The first is to account for the band from the neutral triarylamine around 34000 cm^{-1}. The second is for the IVCT band around 8000 cm^{-1}. The last two is to fit the bands from vibrational overtones found at ~5200 cm^{-1} and ~7500 cm^{-1}.

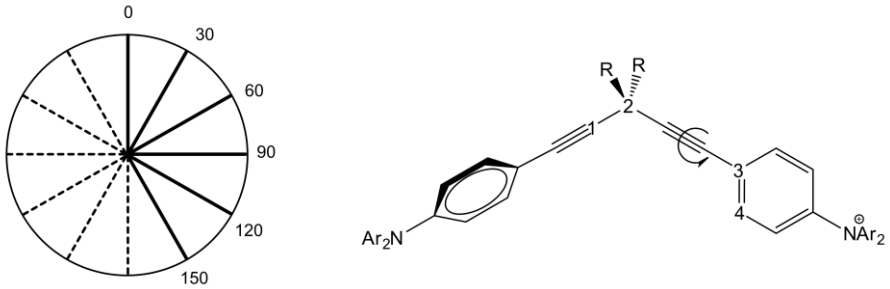


SI Figure S13 Multi-peak fit analysis of the singly oxidized form of **D-C(Me)$_2$-D**. The peaks in this analysis globally fitted together with hose of the doubly oxidized form (see below). Peak positions and peak widths were linked between the two spectra, while peak heights were allowed to vary. For the singly oxidized form two additional peaks were added; one for the IVCT band and the other one for the band of the neutral triarylamine.

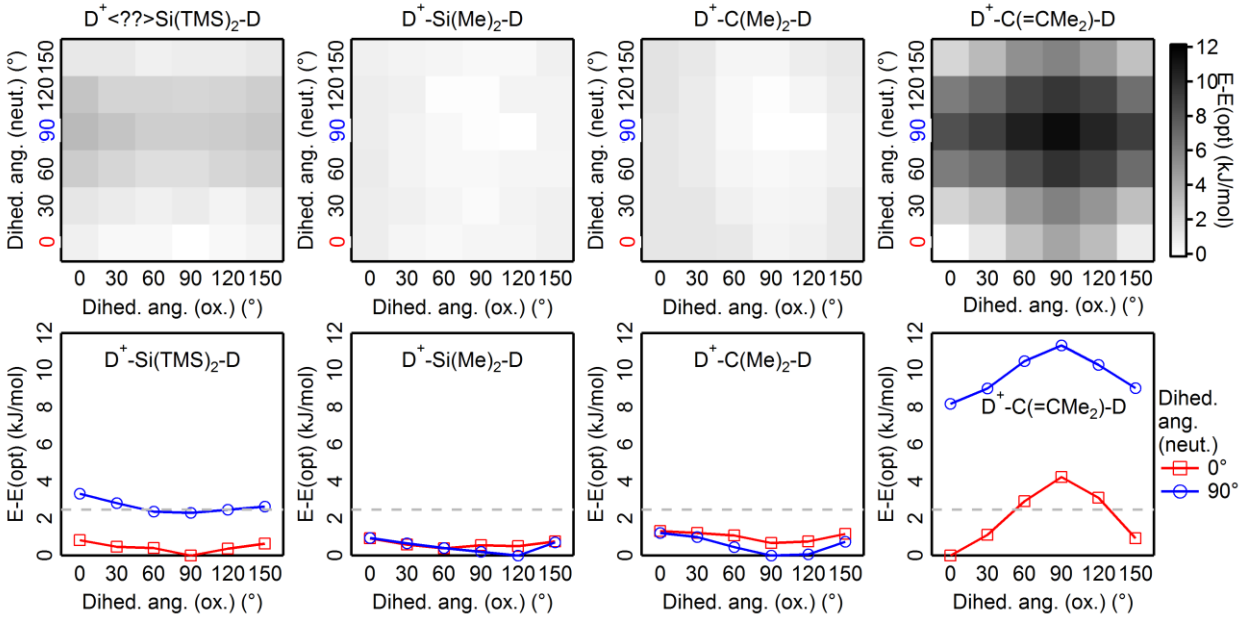


SI Figure S14. Multi-peak fit analysis of the doubly oxidized form of **D-C(Me)$_2$-D**. The peaks in this analysis globally fitted together with hose of the singly oxidized form (see above). Peak positions and peak widths were linked between the two spectra, while peak heights were allowed to vary.

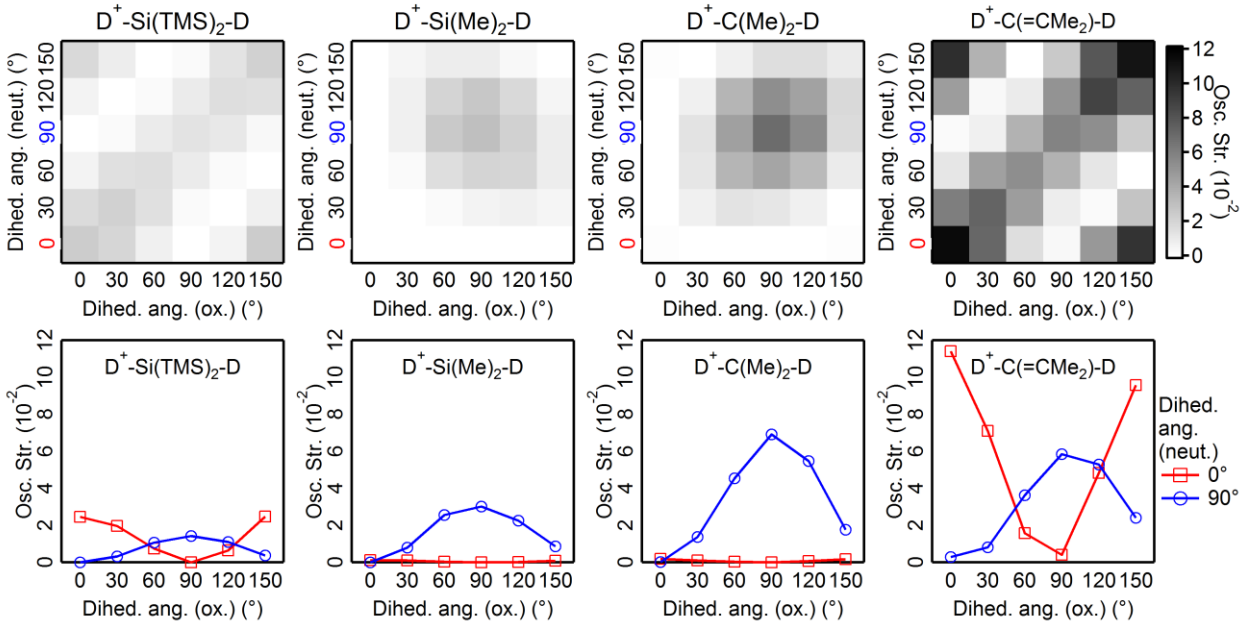
Results from the conformational scans



SI Figure S15. To the left illustration how a scan between 0° and 150° can represent the whole conformer space. Right: Illustration of which atoms (1-4) that were used to define the dihedral angle on the oxidized side. The neutral side was defined analogously.



SI Figure S16. Top row of panels show represent the 6×6 matrix of conformers that was calculated for each dyad. Gray scale to the right is applicable for all four panels. The bottom row shows the energy of conformers which have the dihedral angle on the neutral side at either 0° (red squares) or 90° (blue circles) and how the energy varies as a function of the dihedral angle on the oxidized side. The gray dashed line corresponds to the thermal energy at 298 K.



SI Figure S 17. Top row of panels show represent the oscillator strengths of the 6×6 matrix of conformers that was calculated for each dyad. Grey scale to the right is applicable for all four panels. The bottom row shows the oscillator strengths of conformers which have the dihedral angle on the neutral side at either 0° (red squares) or 90° (blue circles) and how the oscillator strengths changes as a function of the dihedral angle on the oxidized side. The red squares represent the contribution from the cross-conjugated mechanism to the electronic coupling. The blue circles represents the through space mechanism.

Evaluation of the static dipole moment

SI Table S2 contains the parameters for evaluating the change in static dipole moment between the two diabetic states, $\Delta\mu_{21}$. The data comes from the conformer which has the largest contribution to the overall electronic coupling. The static dipole moments of the ground state, μ_a, was evaluated from the SCF density, while the excited state dipole, μ_b, was evaluated from the CI density from the TD-DFT calculations at the same geometry. $\Delta\mu_{21}$ was estimated with Eq. 3 using the tabulated data combined with the experimentally determined transition dipole moment, μ_{ba}. The resulting $\Delta\mu_{21}$ are all somewhat shorter than what one would get from evaluating $\Delta\mu_{21}$ from the nitrogen-nitrogen distance, $|r_{N\text{-}N}|$, indicating that the values are reasonable. Note that the coordinate system is not the same between the four dyads. Furthermore, the dipoles expressed in [eÅ], rather than Debye, [D]. The conversion factor is 1 eÅ = 4.802 D

SI Table S2. Values for evaluating $\Delta\mu_{21}$.

	μ_a / eÅ			$\lvert\mu_a\rvert$ / eÅ	μ_b / eÅ			$\lvert\mu_b\rvert$ / eÅ	$\lvert\Delta\mu_{ba}\rvert$ / eÅ	$\lvert\Delta\mu_{21}\rvert$ / eÅ	$\lvert r_{N\text{-}N}\rvert$ / Å
	X	y	z		x	y	z				
D-Si(TMS)$_2$-D	6.556	1.152	-0.260	6.66	-6.541	0.619	0.259	6.58	13.1	13.1	14.4
D-Si(Me)$_2$-D	6.470	-0.919	-0.185	6.54	-6.784	-0.296	0.359	6.80	13.3	13.3	13.7
D-C(Me)$_2$-D	-6.269	0.478	-0.222	6.29	6.631	-0.133	0.292	6.64	12.9	13.0	13.6
D-C(=CMe$_2$)-D	5.769	-0.027	-0.252	5.77	-6.255	-0.712	0.230	6.30	12.1	12.1	13.7
D-C(TMS)$_2$-D	-5.855	0.409	0.209	5.87	7.378	0.001	-0.277	7.38	13.2	13.5	14.2
D-CH$_2$-D	-6.479	0.361	0.150	6.49	6.640	-0.352	-0.103	6.65	13.1	13.2	13.9

Cartesian coordinates and absolute electronic energies

Below we report the Cartesian coordinates and absolute energies for singly oxidized forms of the dyads at the same conformers that were used to evaluate the change in static dipole moment (SI Table S2). Geometries were optimized at the PBE0/6-31G(d) level, while the total energies comes from single point calculations at these geometries using PBE0/6-31G(d,p). Note that the coordinate system is not the same between the four dyads

D^{+}-$Si(TMS)_2$-D

Charge = +1 Multiplicity = 2
Dihedrals locked to [0,0]
Energy: -3213.44766003 Hartree

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D^{+}-Si(Me)$_2$-D

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Dihedrals locked to [90,90]
Energy: -2475.2061369 Hartree

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H,-5.689559286,0.5919349511,-2.077571589
H,-3.6012551027,-2.9698436099,0.6566196767
H,-3.6625042684,-0.5292233478,-2.882126729
H,-7.9265253327,1.1095367605,2.487134696
H,-8.0117282415,-2.3566746351,-0.0386742573
H,-9.5138177375,0.0031470552,4.0432946141
H,-9.5512293404,-3.4717170438,1.5118966316
H,-5.9560936116,4.5216005856,-0.4527389454
H,-9.9143935758,3.1904488239,-1.475338645
H,-8.0308011545,7.1757420631,-1.7393950266
H,-7.1754627628,6.4907635449,-0.3314020636
H,-6.6142288056,6.1202128589,-1.9892788662
H,-11.6414811887,-3.8467237443,4.4274409899
H,-11.5580318142,-3.6853200345,2.6526574266
C,0.2635795523,-5.6563111538,-1.9648980245
H,1.1761024401,-6.1637945455,-2.2968458644
H,0.2508641292,-5.6529887351,-0.8703645308
H,-0.5964760983,-6.2370360502,-2.3163299945
C,0.2363133157,-3.9015794476,-4.5283027224
H,-0.625038955,-4.4463068839,-4.9306173736
H,0.2095060823,-2.880034939,-4.9206337859
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D^{+}-C(Me)$_2$-D

Charge = +1 Multiplicity = 2
Dihedrals locked to [90,90]
Energy: -2223.85545394 Hartree

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C,-9.4554324232,0.743819417,2.8046011942
C,-8.1688864241,-1.2867808328,1.3899883354
C,-8.4769486627,1.0713989009,1.8951334216
C,-7.8165196735,0.0560921161,1.1734628544
N,-6.8171125752,0.3821204547,0.2491795807
C,-6.9366508834,1.5300747642,-0.5432816507
C,-5.685752873,-0.4429219628,0.1196070702
C,-5.0949274098,-1.0093203424,1.261020298
C,-5.1451614763,-0.6978169615,-1.1513677659
C,-4.0335706159,-1.5088914948,-1.2756175168
C,-3.9791677084,-1.8135732861,1.1303530522
C,-3.4293254577,-2.0794642037,-0.1386612898
C,-5.8027403092,2.3045179115,-0.8409887614
C,-8.1947075563,1.9203312334,-1.0457490053
C,-8.3047977908,3.0495993521,-1.8235110748
C,-5.912711764,3.4424223738,-1.6183790329
C,-7.1677264218,3.8260679931,-2.1193618038
C,-2.2827953139,-2.9067356197,-0.2688449413
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O,-7.3825958998,4.9021694786,-2.8811679112
O,-10.7724969389,-0.8121897628,3.9202322613
C,-11.1691527343,-2.1490208137,4.2012799525
C,-6.2757723138,5.7221267669,-3.2363660947
H,-5.5336304357,5.152841181,-3.8054746133
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H,-5.6198815042,-0.2819885536,-2.0339619046
H,-5.4965481667,-0.7874157564,2.2442503327
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H,-3.5107926232,-2.2349759504,2.013509199
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H,-9.2617080426,3.3505718552,-2.236828022
H,-5.0273048221,4.0346369749,-1.8165454257
H,-9.4225505359,-2.6584795561,2.4349084205
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H,-11.9424845283,-2.0715080916,4.9647291548
H,-11.5814238891,-2.6311548974,3.3088151097
H,-10.3282122969,-2.7341682285,4.5874840039
H,-6.6861067281,6.5153916875,-3.8602546104
H,-5.8101152728,6.1584778466,-2.3466204862
C,-0.1143776488,-4.4747588117,-0.5086030801
C,9.4134037452,0.531776388,-3.3816335403
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C,8.9797016615,1.6873943017,-2.7199947316
C,8.0722402102,-0.7964355488,-1.8761633072
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C,7.6233761303,0.3526804061,-1.2240537143
N,6.7332028923,0.2689849128,-0.1217007879
C,7.0532368312,1.0009479577,1.0521531318
C,5.5828416358,-0.5191940515,-0.1830404582
C,4.9505010688,-0.7828296958,-1.411931965
C,5.0222327728,-1.0724599551,0.9827147707
C,3.8809947385,-1.853324289,0.9195344795
C,3.8134555664,-1.5699491468,-1.4703051758
C,3.2510604183,-2.1238667538,-0.3073270669
C,6.1097648185,1.8279056101,1.6625747447
C,8.3371926784,0.9218765597,1.6068943825
C,8.6633010837,1.6526752864,2.7372239638
C,6.4223678624,2.5494770765,2.8123133828
C,7.7076219251,2.4693511603,3.3547395477
C,2.0810446777,-2.9329005437,-0.3714068652
C,1.0853783664,-3.6254447333,-0.4285852423
O,8.1208316662,3.135297736,4.4606593516
O,10.2744651072,0.7238865782,-4.4109524873
C,10.7404357376,-0.4192520649,-5.1011577885
C,7.1872461233,3.9758047396,5.1105536069
H,6.3185781597,3.4094224057,5.4680666946
H,7.7294313718,-1.7710266727,-1.540415271
H,7.751483537,2.5023563987,-1.1630450836
H,5.4943238979,-0.8912067497,1.9427268078
H,5.3557500754,-0.3592067221,-2.3250321062
H,3.4719614517,-2.2760794635,1.8326862828
H,3.3400308338,-1.7540444315,-2.4304307353
H,9.0823431151,0.2830100694,1.1415560605
H,5.1133142028,1.9074507604,1.2371942986
H,9.6581527436,1.5948363643,3.1689541507
H,5.6624518124,3.17903887,3.2617888451
H,9.2729743425,-1.6295254145,-3.440186062
H,9.344274976,2.6521003478,-3.0604617786
H,11.4078659793,-0.0492753237,-5.8805114912
H,11.2973518191,-1.0901886633,-4.4357500106
H,9.9142194338,-0.9725103214,-5.5641938108
H,7.7127877292,4.4061388979,5.9639872491
H,6.846681655,4.7828644684,4.4504641746
C,-0.1517213187,-5.2005019878,-1.8699593321
H,0.7324442518,-5.8375589744,-1.9675126033
H,-1.0479142948,-5.8254905978,-1.9317461119
H,-0.1627133723,-4.482699428,-2.6942034231
C,-0.1044674237,-5.5091361161,0.6363942792
H,-0.078620768,-5.0129131723,1.6099864219
H,-1.0024036678,-6.1320688363,0.5795725452
H,0.7778497971,-6.149296743,0.5421410576

D^{+}-C(=CMe_2)-D

Charge = +1 Multiplicity = 2
Dihedrals locked to [0,0]
Energy: -2261.91802955 Hartree

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C,6.1711090773,1.8954778255,-2.0909231602
C,7.557177422,2.7835886662,-0.3056727492
C,6.8670121052,1.7030861517,-0.8878718738
N,6.885356763,0.4409036995,-0.2720194435
C,8.0713026931,-0.0203685788,0.3218368496
C,5.732346149,-0.3479358441,-0.2488113167
C,4.4656990821,0.2546476684,-0.1217564657
C,5.8301062891,-1.7491183229,-0.3519543098
C,4.6899484519,-2.5240687155,-0.3319489251
C,3.3292491755,-0.5253295344,-0.0958066714
C,3.4156152225,-1.9304184602,-0.2024843436
C,8.0304823614,-0.7215706373,1.5366459943
C,9.313045686,0.2273401419,-0.2942701379
C,10.4744539322,-0.2238948089,0.2906546972
C,9.1972529687,-1.1731402498,2.1282322244
C,10.4327244309,-0.9286562652,1.5082551807
C,2.2500563831,-2.7242368787,-0.1769745373
C,1.2455082977,-3.4151536125,-0.1534004252
O,11.6163020503,-1.321087006,1.9927348019
O,6.8920488111,5.4473977877,-2.6287412207
C,6.2004050392,5.7138349663,-3.8418185952
C,11.6469774394,-2.0528134346,3.2111303291
H,11.0879363595,-2.9900875725,3.120540296
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H,6.801756448,-2.2139988851,-0.4813861972
H,4.3896103565,1.3310161928,-0.0097134528
H,4.7674750477,-3.6015323962,-0.4330716722
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H,6.5957370043,5.1039245831,-4.6609427476
H,5.1259625427,5.5348741546,-3.7288119307
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H,11.2446640923,-1.4573608231,4.0374972819
C,0.0445713081,-4.1747500105,-0.1197622707
C,0.0557393204,-5.5438051838,-0.213119238
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C,-10.4515738074,-0.4260457439,0.4300315639
C,-8.2005480625,-0.5929245195,-1.1862819486
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C,-8.0802635161,-0.0717358499,0.1022404918
N,-6.8321910308,0.4008956372,0.5882355018
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C,-5.6784392236,-0.373775255,0.4802442679
C,-5.7529048297,-1.7781873325,0.4154372036
C,-4.4050329669,0.2245437346,0.4313796407
C,-3.2619079774,-0.546849565,0.3228043093
C,-4.6078021332,-2.5453340989,0.3000864247
C,-3.3340184691,-1.94992983,0.2510921328
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C,-7.3774594161,2.7841055408,0.5093693021
C,-7.3704971046,4.0442877599,1.0833233955
C,-6.1730794758,3.1752457947,2.9920263381
C,-6.7629302167,4.2538710275,2.3277504734
C,-2.1604321917,-2.7378463977,0.1279044854
C,-1.1576252989,-3.4195016388,0.0156654503
O,-6.7987695722,5.5238411382,2.7993150514
O,-11.8036443362,-1.365904358,-1.2285164976
C,-11.9605797769,-1.9063712933,-2.5263289893
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H,-5.1273606751,5.5444692956,4.0417191304
H,-7.3240747614,-0.6475922829,-1.8257556378
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H,-4.318532658,1.3053392266,0.470510655
H,-6.7206823858,-2.2665151885,0.461814691
H,-2.2917403304,-0.0605514348,0.2777174681
H,-4.6918475012,-3.6274659925,0.2577176348
H,-7.8421029513,2.6336644511,-0.4609017939
H,-5.7584665692,1.0699895399,2.9476799291
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H,-9.4816378885,-1.4515825724,-2.6710485322
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H,-11.6977490284,-1.1743313798,-3.2996333074
H,-11.352583863,-2.8093116439,-2.6606355487
H,-6.3337458495,6.8436007674,4.242910314
H,-6.6844591484,5.2047313305,4.8544790209
C,1.3220671801,-6.3180950257,-0.357214161
H,2.2069982025,-5.6790574378,-0.3776313285
H,1.4226872968,-7.0337037146,0.4693339745
H,1.2964597926,-6.9144488688,-1.2787553295
C,-1.2048208953,-6.3392487046,-0.1765465315
H,-2.091563952,-5.7121571084,-0.0655863629
H,-1.3036392907,-6.9326689659,-1.0950518442
H,-1.1734106463,-7.0586086833,0.6523585867
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D^{+}-C(TMS)$_2$-D

Charge = +1 Multiplicity = 2
Dihedrals locked to [0,0]
Energy: -2962.12718955 Hartree

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H,2.4729347663,-4.647685115,1.5557188924
H,1.5516380382,-6.1225959894,1.1977682511
H,1.7422382923,-5.5822574107,2.871485293
C,-1.507341567,-5.2891226158,1.9269771347
H,-1.5917714153,-5.6271648134,2.9669005575
H,-1.4637517124,-6.1789131691,1.2915527439
H,-2.4190568069,-4.7340457636,1.6810800822
C,0.0381850612,-2.9070123024,3.1119688565
H,0.904323109,-2.2435300903,3.0161968137
H,0.0880373736,-3.3896535002,4.0951425042
H,-0.8676800874,-2.2917602288,3.0833183999
C,-1.6568208794,-5.2972763649,-1.6573976613
H,-1.606703296,-6.163874814,-0.9913414508
H,-1.7976614095,-5.6704278304,-2.6790583247
H,-2.5417745104,-4.7091453705,-1.3914581905
C,1.4468895909,-5.321197318,-1.743500091
H,2.3511191405,-4.7499861135,-1.5079614546
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C,-9.5411680342,0.6530811975,0.1428428903
C,-10.6477005937,0.1613493113,-0.5125714039
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C,-10.5150528817,-0.461836216,-1.76728002
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O,-11.6511404866,-0.9042911334,-2.319613977
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C,7.318185682,4.8918434766,-2.0317553961
C,2.2377032017,-1.8140345927,-0.0342984145
O,7.4459897627,6.152583359,-2.5131085942
O,11.8765551546,-1.0221005149,1.7418377277
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H,8.3974362854,5.469211,-0.2694493599
H,6.2162040742,4.0008194544,-3.6703701912
H,9.4917081142,-0.9863704406,3.081142082
H,11.5745957332,0.0316497687,-0.539197653
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D^+-CH_2-D

Charge = +1 Multiplicity = 2
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Energy: -2145.31824661 Hartee

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