Chemistry–A European Journal

Supporting Information

Frustrated Radical Pairs: From Fleeting Intermediates to Isolable Species

Lars J. C. van der Zee, Jelle Hofman, Simon Mathew, Anne de Visser, Ekkes Brück, Bas de Bruin, and J. Chris Slootweg*

Supporting Information

Frustrated Radical Pairs: From Fleeting Intermediates to Isolable Species

Lars J. C. van der Zee, Jelle Hofman, Simon Mathew, Anne de Visser, Ekkes Brück, Bas de Bruin and J. Chris Slootweg*

Abstract:

We present the design and comprehensive investigation of stable *para*-substituted triarylamine–2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) radical ion pairs (RIPs) generated via single-electron transfer (SET). We quantified the degree of SET in both solution and solid phases, utilising a suite of spectroscopic techniques including IR, EPR, NMR, and single-crystal X-ray diffraction (SC–XRD). Our findings reveal that the extent of SET is significantly influenced by the nature of the substituents (MeO > ^{t}Bu > Br) and the polarity of the solvent (MeCN > DCM > toluene). The radical ion pair $[(p\text{MeOPh})_3\text{N}]^{\bullet+}[\text{DDQ}]^{\bullet-}$ was unambiguously identified using EPR and UV–vis spectroscopy, and its structure was confirmed by SC–XRD. Detailed analysis indicates an open-shell singlet ground state with a thermally accessible triplet state, as corroborated by EPR, magnetic susceptibility measurements, and DFT calculations. This study offers crucial insights into the mechanistic pathways of RIP formation and tuning both in solution and solid states, laying the groundwork for future exploration of their reactivity and potential applications.

DOI: 10.1002/anie.2023XXXXX

SUPPORTING INFORMATION

Table of Contents

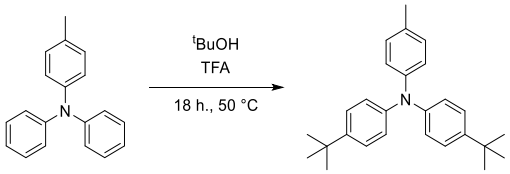
SUPPORTING INFORMATION

1. Experimental Section

1.1 General Procedures

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk and glovebox techniques. Toluene was distilled from potassium and stored over a sodium mirror. Dichloromethane (DCM) was distilled from CaH_2 and stored over activated molecular sieves. Acetonitrile was obtained from a MBraun Solvent Purification System, degassed and stored over molecular sieves (4 Å). Dichloromethane-*d*$_2$ (CD_2Cl_2), toluene-*d*$_8$ ($C_6D_5CD_3$), benzene-*d*$_6$ (C_6D_6) and acetonitrile-*d*$_3$ (CD_3CN) were distilled from P_2O_5, degassed and stored over activated molecular sieves (4 Å). DDQ, (*p*MePh)$_3$N and (*p*BrPh)$_3$N were obtained from commercial sources and used as received. NMR spectra (δ in ppm) were recorded using a Bruker Avance AMX 400 (^{1}H 400.1 MHz, ^{13}C 100.6 MHz) or a Bruker DRX 500 (^{1}H 500.1 MHz, ^{13}C 125.8 MHz spectrometer and were referenced to internal $CHCl_3$ (^{1}H δ = 7.26), $CDHCl_2$ (^{1}H δ = 5.32, ^{13}C δ = 53.84), CD_2HCN (^{1}H δ = 1.94), C_6D_5H (^{1}H δ = 7.16) or $C_6D_5CD_2H$ (^{1}H δ = 2.08). The EPR spectra were recorded on a Bruker EMXnano equipped with a variable temperature control and further analysed and simulated using EasySpin[1] and the application cwEPR.[2] UV–vis spectra were recorded on a Shimadzu UV2700 spectrophotometer in sealed cuvettes under nitrogen atmosphere. IR spectra were recorded on a Bruker Alpha-P spectrometer equipped with a single-reflection ATR sampling module. Mass spectra were measured on a AccuTOF GC v4g, JMS-T100GCV Mass spectrometer (JEOL, Japan). Melting points were measured in wax-sealed glass capillaries under nitrogen atmosphere using a Büchi M-565 melting point apparatus and are uncorrected.

1.2 Synthesis of (*p*^{t}BuPh)$_2$(*p*MePh)N



(*p*^{t}BuPh)$_2$(*p*MePh)N was prepared according to a modified literature procedure[3] as follows: 4-methyl-N,N-diphenylaniline (500 mg, 1.93 mmol, 1.0 eq) was dissolved in *tert*-butanol (1.9 mL, 20.0 mmol, 10.0 eq) and trifluoroacetic acid (5.8 mL, 76.0 mmol, 39.0 eq) and stirred for 18 hour at 50 °C, which resulted in a dark green solution. After cooling to room temperature, the mixture was slowly added to an ice-cold saturated $NaHCO_3$ solution. The aqueous layer was extracted trice with toluene, after which the organic layer was dried over $MgSO_4$, filtered and concentrated to afford a viscous green oil. The crude product was purified by column chromatography (eluent: 100% pentane to 5% DCM in pentane) to yield a yellow viscous oil. After storing overnight at 5 °C, a white precipitation (671 mg) was formed. Subsequent recrystallization from boiling ethanol (5 mL) and drying *in vacuo* obtained (*p*^{t}BuPh)$_2$(*p*MePh)N in 80% yield as a colourless solid (574 mg, 1.55 mmol).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.25–7.17 (m, 4H; C_6H_4–CH_3), 7.09–6.94 (m, 8H; C_6H_4–$C(CH_3)_3$), 2.30 (s, 3H; C_6H_4–CH_3), 1.30 (s, 18H; C_6H_4–$C(CH_3)_3$). [4]

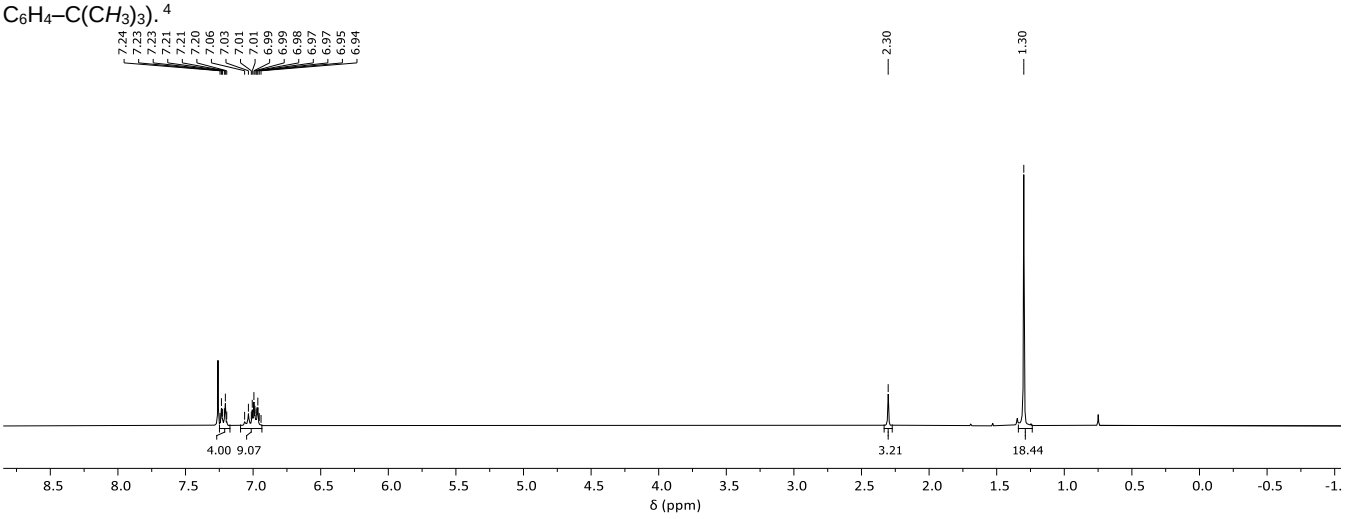
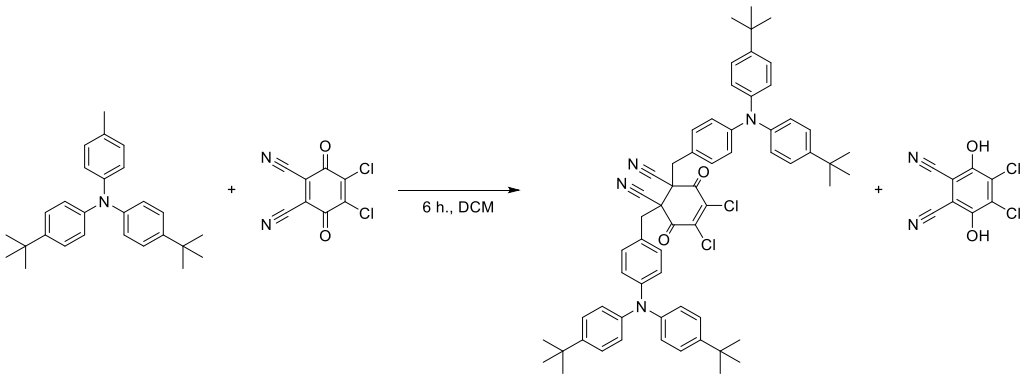


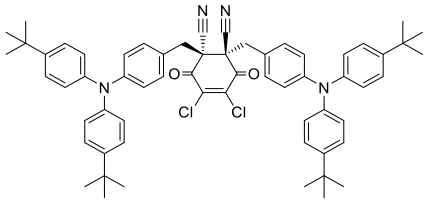
Figure S1. ^{1}H NMR spectrum (300.1 MHz, $CDCl_3$) of (*p*^{t}BuPh)$_2$(*p*MePh)N.

1.3 Reactivity of (p^tBuPh)$_2$(pMePh)N with DDQ: Synthesis of 5 and 6



4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ; 35.7 mg, 2.01 eq, 157 µmol) and 4-(*tert*-butyl)-N-(4-(*tert*-butyl)phenyl)-N-(*p*-tolyl)aniline ((p^tBuPh)$_2$(pMePh)N; 58.2 mg, 2.0 eq, 157 µmol) were dissolved in DCM (4.0 mL) and the solution turned directly green/blue. After stirring for 6 hours, the blue emulsion was concentrated to about a quarter of the original volume before pentane (10 mL) was added. Filtration and washing twice with pentane (4 mL) resulted in a blue solution and a grey residue.
The filtrate was concentrated *in vacuo* to yield 1,2-bis(4-(bis(4-(*tert*-butyl)phenyl)amino)benzyl)-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile **5** in 95% yield as a dark blue crystalline solid (76.8 mg, 74.5 µmol) that contained some residual pentane (0.87 eq). Single crystals suitable for XRD were obtained from a heptane solution at room temperature.
The grey residue was dried *in vacuo* to yield 2,3-dichloro-5,6-dicyanohydroquinone **6** in 38% yield as a grey powder (6.9 mg, 30 µmol).

Filtrate **5**



Melting point: 150-154 °C (decomposition).
^{1}H NMR (499.8 MHz, CD_2Cl_2, 300 K): δ 7.31 (d, $^3J_{HH}$ = 8.6 Hz, 8H; *m*-PhH_2–C$(CH_3)_3$), 7.00 (d, $^3J_{HH}$ = 8.6 Hz, 8H; *o*-PhH_2–C$(CH_3)_3$), 6.85 (d, $^3J_{HH}$ = 8.8 Hz, 4H; *o*-PhH_2–N), 6.78 (d, $^3J_{HH}$ = 8.8 Hz, 4H; *m*-PhH_2–N), 3.61 (ABq, 4H, $\Delta\delta_{AB}$ = 0.157, J_{AB} = 14.2 Hz, CH_2), 1.32 (s, 36H; C_6H_4–C(C$H_3)_3$).
^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 298 K): δ 179.3 (*C*=O), 149.7 (*ipso*-Ph*C*–CH_2), 147.4 (*ipso*-Ph*C*–C$(CH_3)_3$), 145.1 (*p*-Ph*C*–CH_2), 144.6 (*p*-Ph*C*–C$(CH_3)_3$), 131.4 (*o*-Ph*C*–CH_2), 126.7 (*m*-Ph*C*–C$(CH_3)_3$), 125.3 (o-Ph*C*–C$(CH_3)_3$), 122.0 (*C*–Cl), 121.5 (*m*-Ph*C*–CH_2), 114.9 (C–*C*N), 59.7 (*C*–CN), 45.3 (CH_2), 34.7 (*C*$(CH_3)_3$), 31.6 (C(*C*$H_3)_3$).
HR-MS (ESI): calcd for [$C_{62}H_{64}Cl_2N_4O_2$ – 3H]: 963.4172, found 963.4124 m/z.
IR (neat, cm^{-1}): v 3579, 3503, 2961, 1708 (C=O), 1601 (C=C), 1504, 1415, 1322, 1259, 1186, 1082, 1014, 791, 547, 481. C≡N stretch not visible.

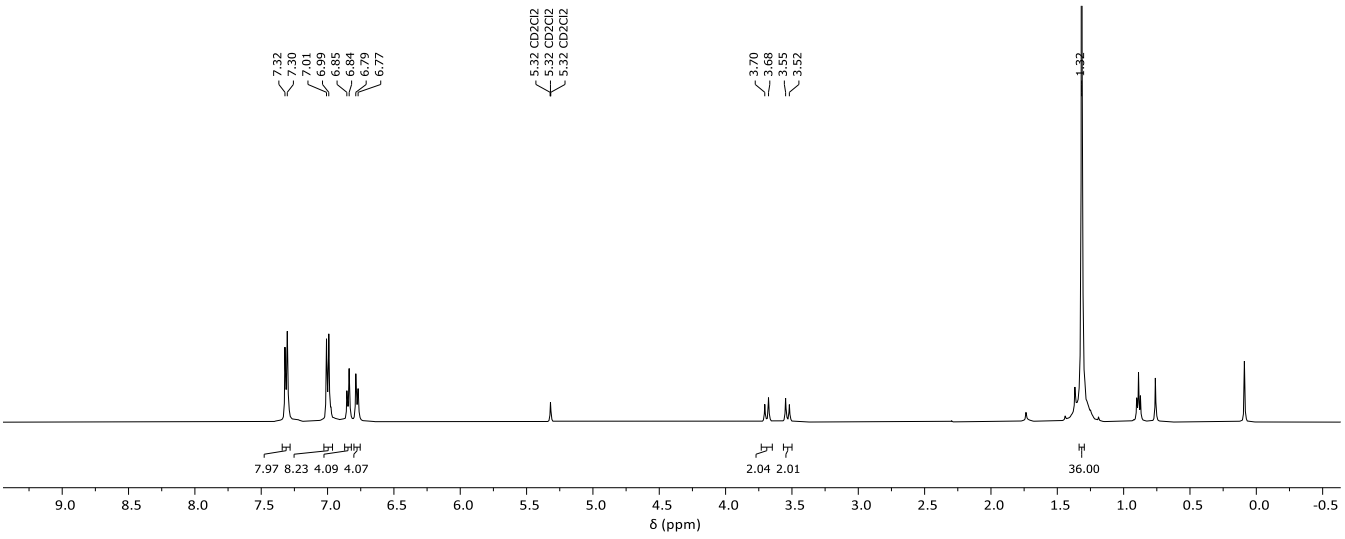


Figure S2. ^{1}H NMR spectrum (499.8 MHz, $CDCl_3$) of 1,2-bis(4-(bis(4-(*tert*-butyl)phenyl)amino)benzyl)-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile **5**.

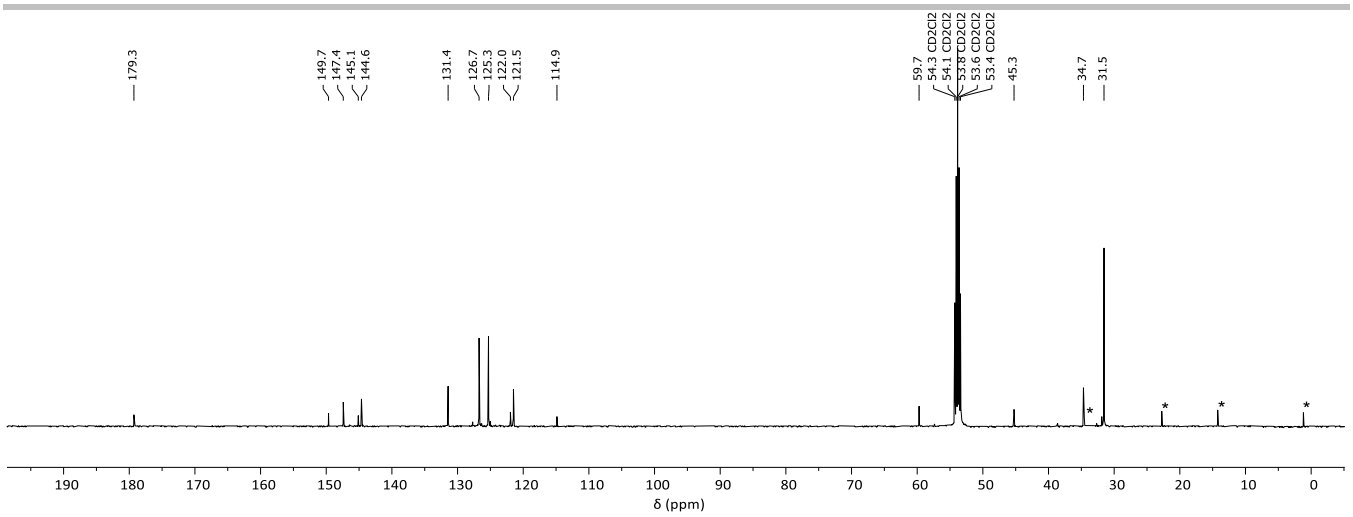


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (125.7 MHz, CD_2Cl2) of 1,2-bis(4-(bis(4-(*tert*-butyl)phenyl)amino)benzyl)-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile **5**. *residual pentane and silicon grease.

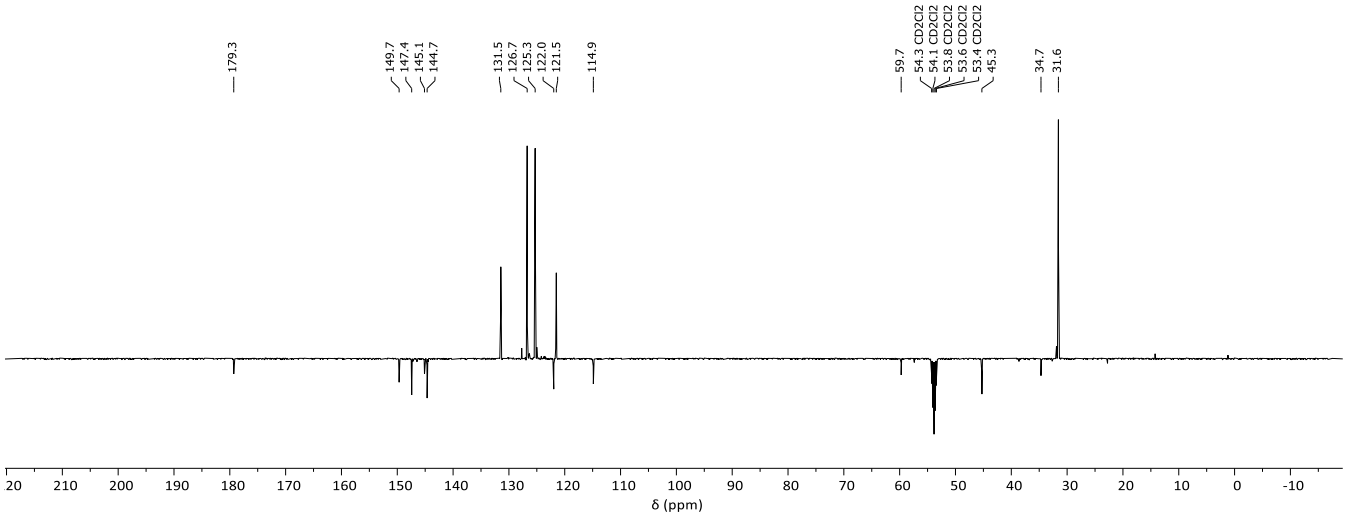


Figure S4. $^{13}C\{^{1}H\}$ APT NMR spectrum (125.7 MHz, CD_2Cl_2) of 1,2-bis(4-(bis(4-(*tert*-butyl)phenyl)amino)benzyl)-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile **5**.

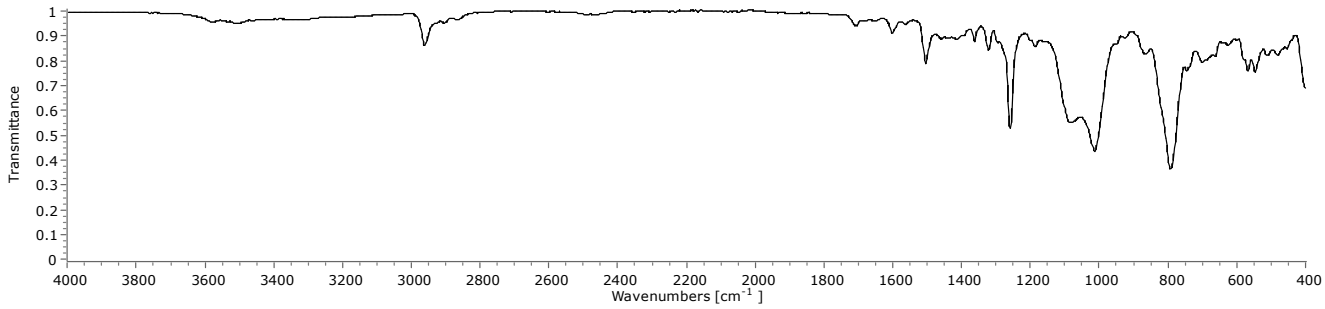
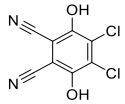


Figure S5. IR (neat) spectrum of 1,2-bis(4-(bis(4-(*tert*-butyl)phenyl)amino)benzyl)-4,5-dichloro-3,6-dioxocyclohex-4-ene-1,2-dicarbonitrile **5**.

SUPPORTING INFORMATION

Residue **6**



Melting point: 245-250 °C (decomposition).
^{1}H NMR (499.8 MHz, CD_3CN, 300 K): δ 8.2 (br s; O*H*).^{13}C{^{1}H} NMR (125.7 MHz, CD_3CN, 300 K): δ 151.3 (*C*–OH), 129.0 (*C*–Cl), 113.8 (C–*C*N), 102.5 (*C*–CN).
HR-MS (ESI): calcd. for $[C_8H_2Cl_2N_2O_2]$: 227.9493, found 227.9478.
IR (neat, cm^{-1}): v. 3225.5 (OH), 2254 (C≡N), 1573, 1510, 1451, 1359, 1268, 1189, 1075, 1000, 888, 826, 743, 688, 611, 430.

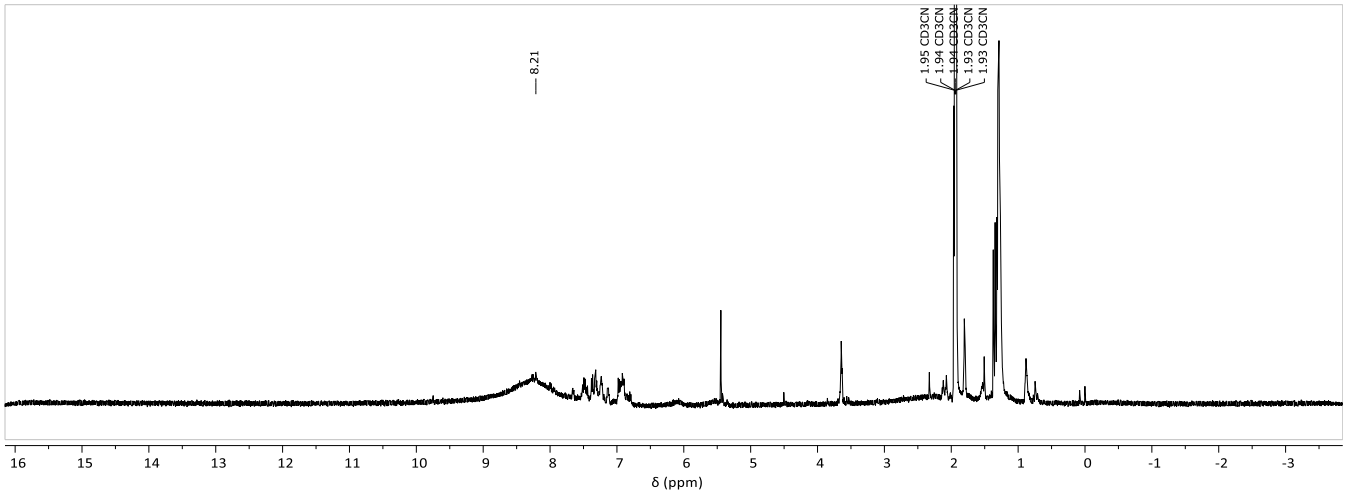


Figure S6. ^{1}H NMR spectrum (499.8 MHz, CD_3CN) of 2,3-dichloro-5,6-dicyanohydroquinone **6** including some residual filtrate.

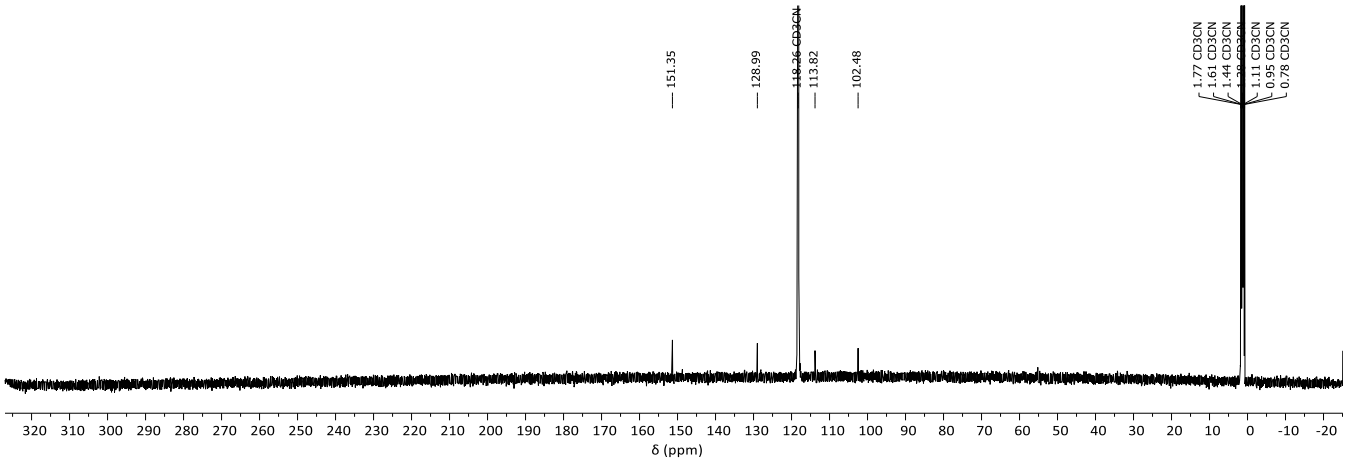


Figure S7. ^{13}C{^{1}H} NMR spectrum (125.7 MHz, CD_3N) of 2,3-dichloro-5,6-dicyanohydroquinone **6**.

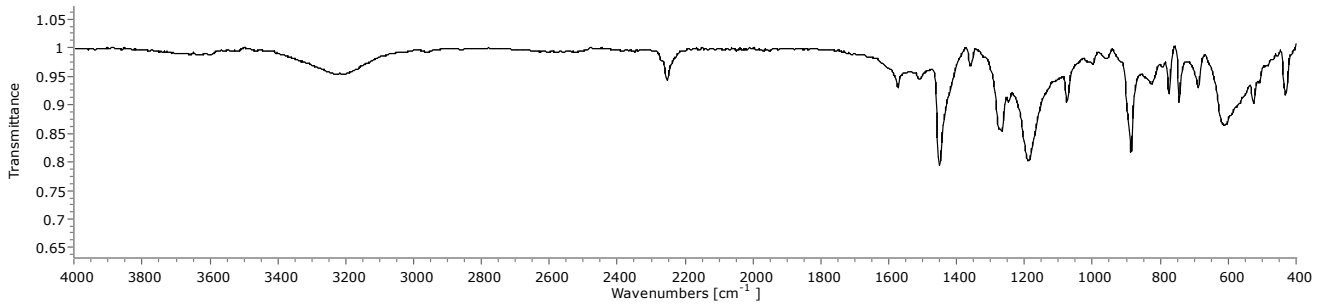
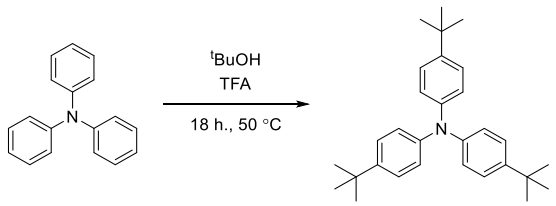


Figure S8. IR (neat) spectrum of 2,3-dichloro-5,6-dicyanohydroquinone **6**.

1.4 Synthesis of (p^tBuPh)$_3$N



(p^tBuPh)$_3$N was prepared according to a literature procedure.[3]

^{1}H NMR (300.1 MHz, $CDCl_3$) δ 7.23 (d, $^3J_{HH}$ = 7.9 Hz, 6H; Ph*H*), 7.00 (d, $^3J_{HH}$ = 7.9 Hz, 6H; Ph*H*), 1.30 (s, 27H; C(C*H*$_3$)$_3$).

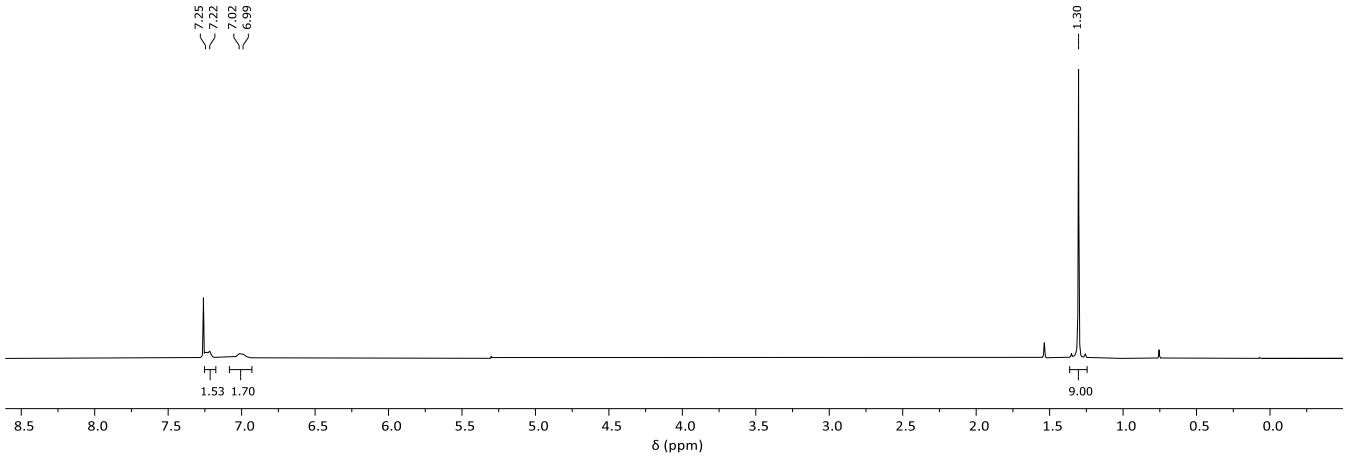
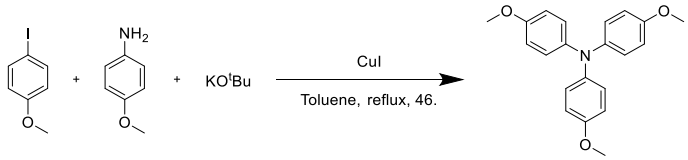


Figure S9. ^{1}H NMR spectrum (300.1 MHz, $CDCl_3$, 298 K) of (p^tBuPh)$_3$N.

1.5 Synthesis of (*p*MeOPh)$_3$N



(*p*MeOPh)$_3$N was prepared according to a literature procedure[4] and recrystallized twice from ethanol before use.

^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 7.14–7.05 (m, 6H; *o*-Ph*H*–OMe), 6.81–6.66 (m, 6H; *m*-Ph*H*–OMe), 3.31 (s, 9H; OC*H*$_3$).

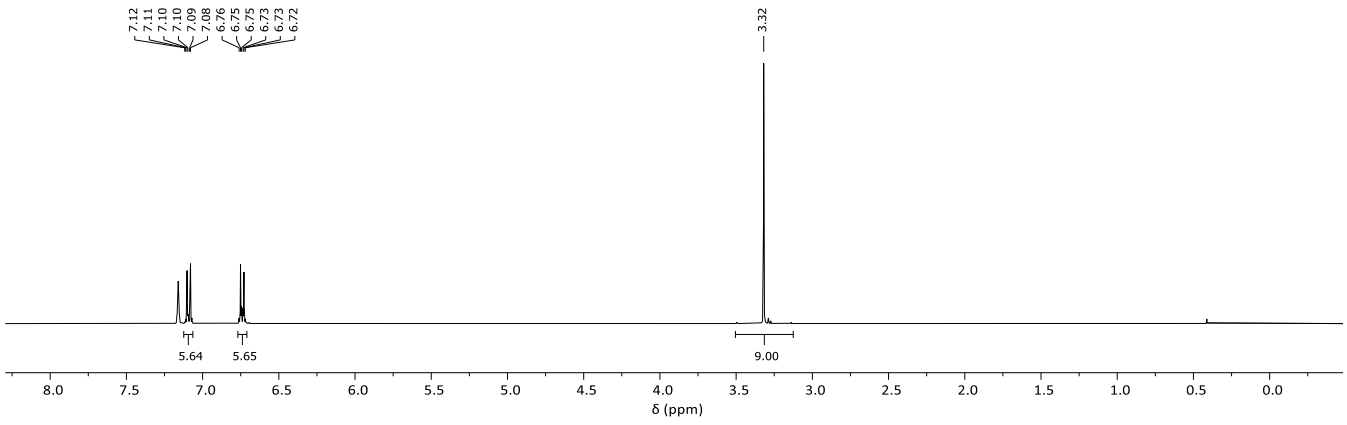


Figure S10. ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 300 K) of (*p*MeOPh)$_3$N.

2. NMR Spectroscopy

2.1 Reactivity of (*p*MePh)(*p*^{t}BuPh)$_3$N with DDQ

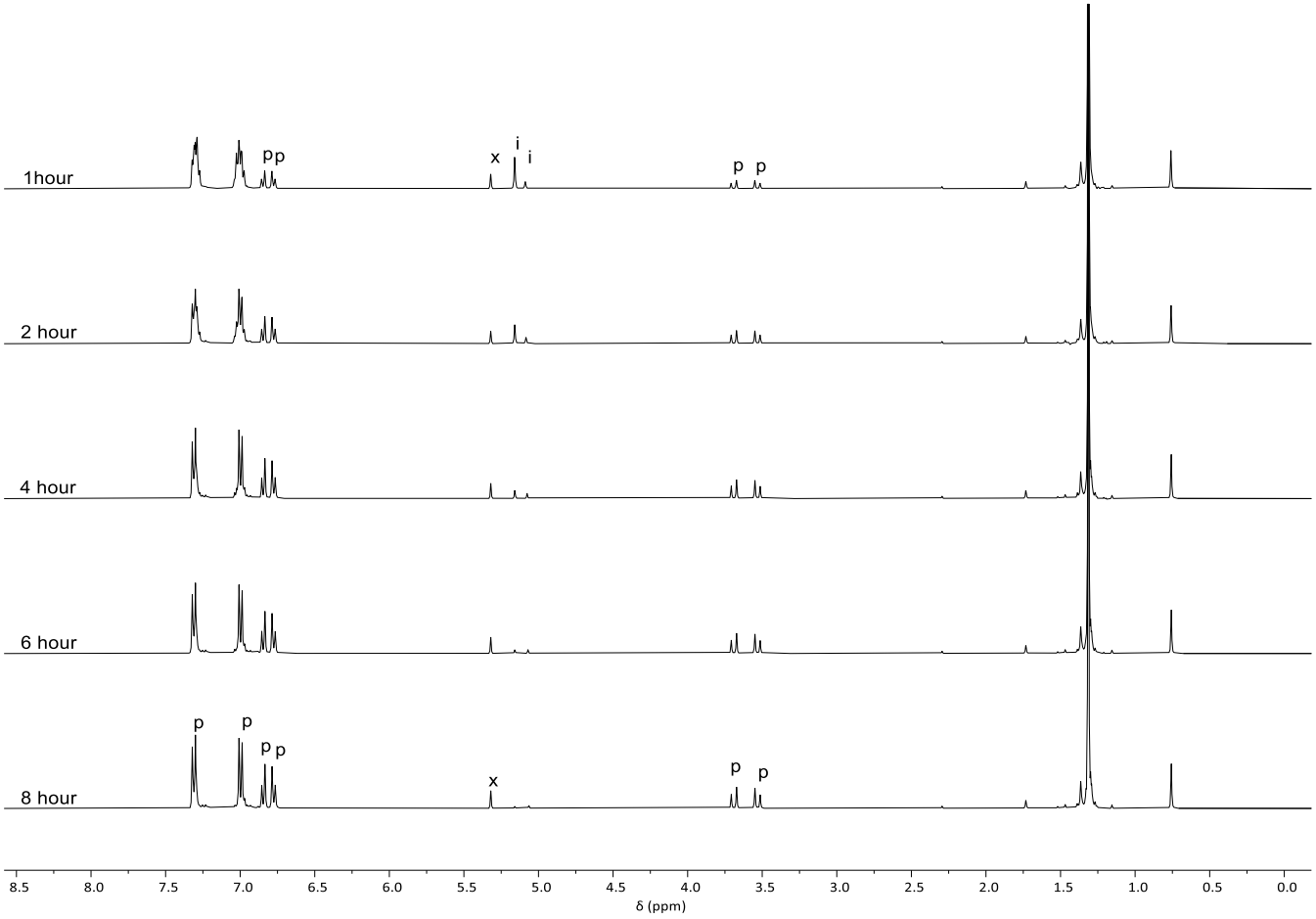


Figure S11. Time resolved 400.1 MHz *in situ* NMR spectra of a solution of (*p*MePh)(*p*^{t}BuPh)$_2$N (40 mM) and DDQ (40 mM) in CD_2Cl_2. x = solvent residue, i = unidentified intermediate, p = product.

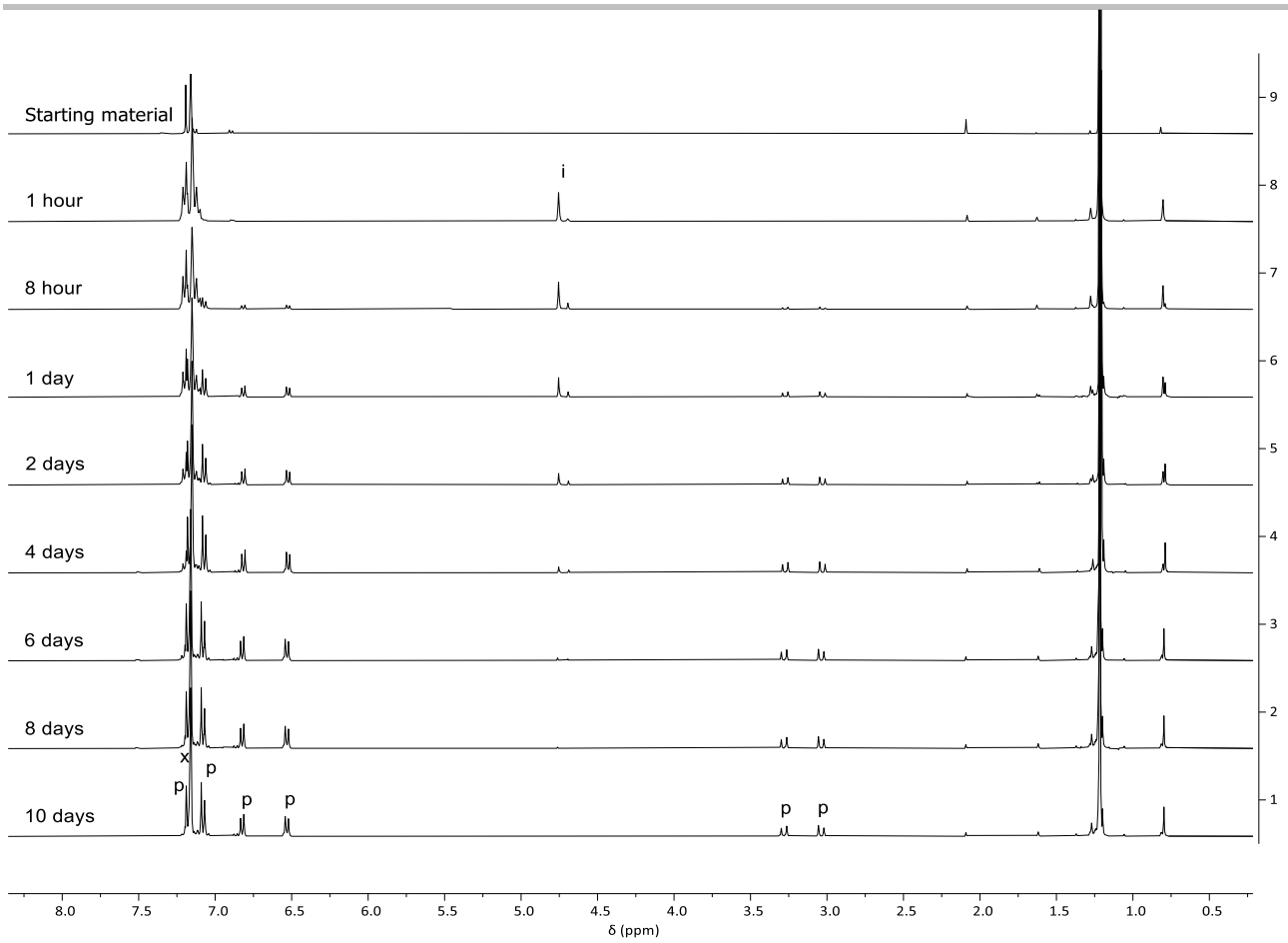


Figure S12. Time resolved 400.1 MHz *in situ* NMR spectra of a solution of (*p*MePh)(*p*^{t}BuPh)$_2$N (40 mM) and DDQ (40 mM) in C_6D_6. x = solvent residue, i = unidentified intermediate, p = product.

2.2 Reactivity of (*p*MePh)$_3$N with DDQ

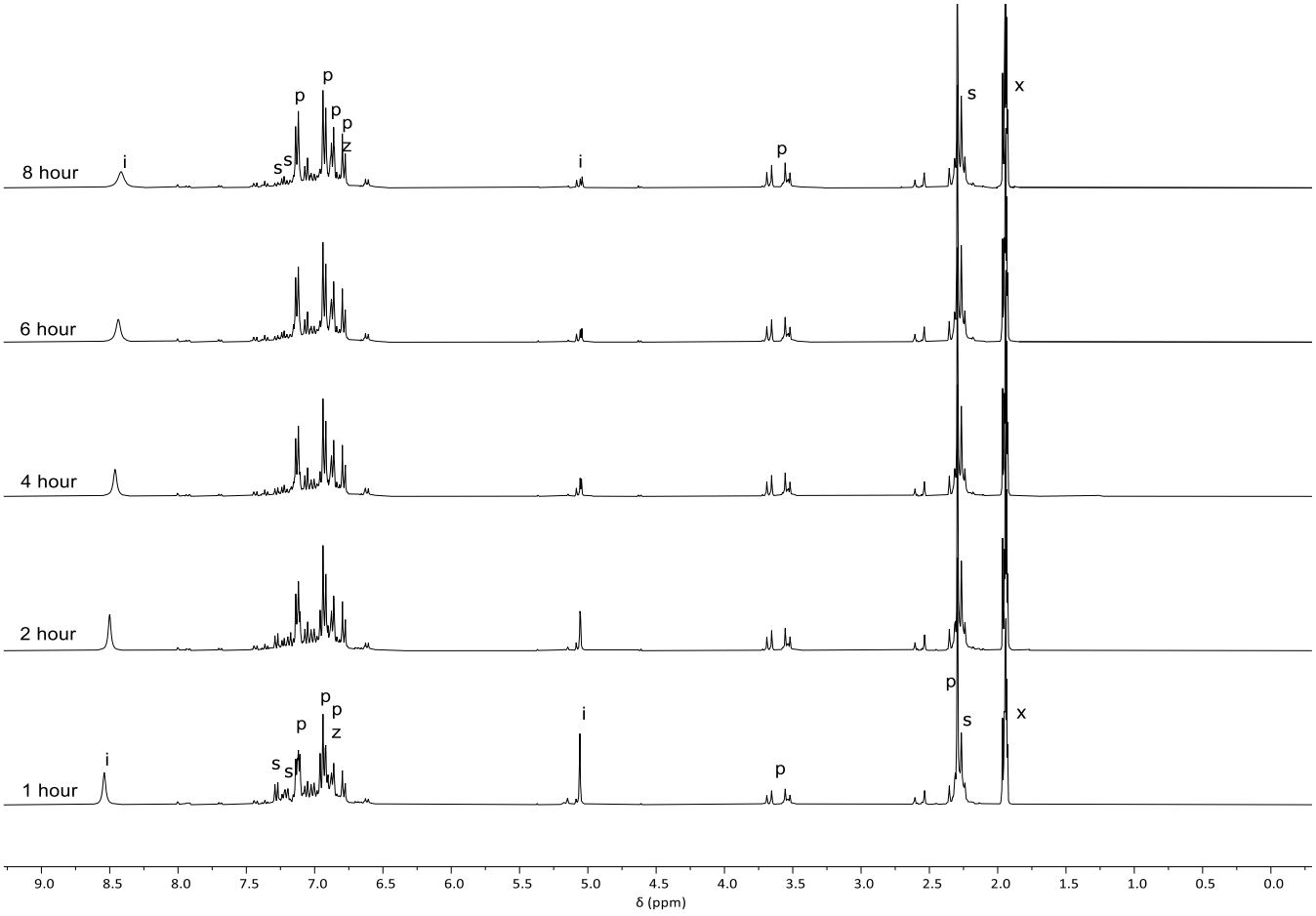


Figure S13. Time resolved 400.1 MHz *in situ* NMR spectra of a solution of (*p*MePh)$_3$N (40 mM) and DDQ (40 mM) in CD_3CN. x = solvent residue, s = starting material, i = unidentified intermediate, p = product.

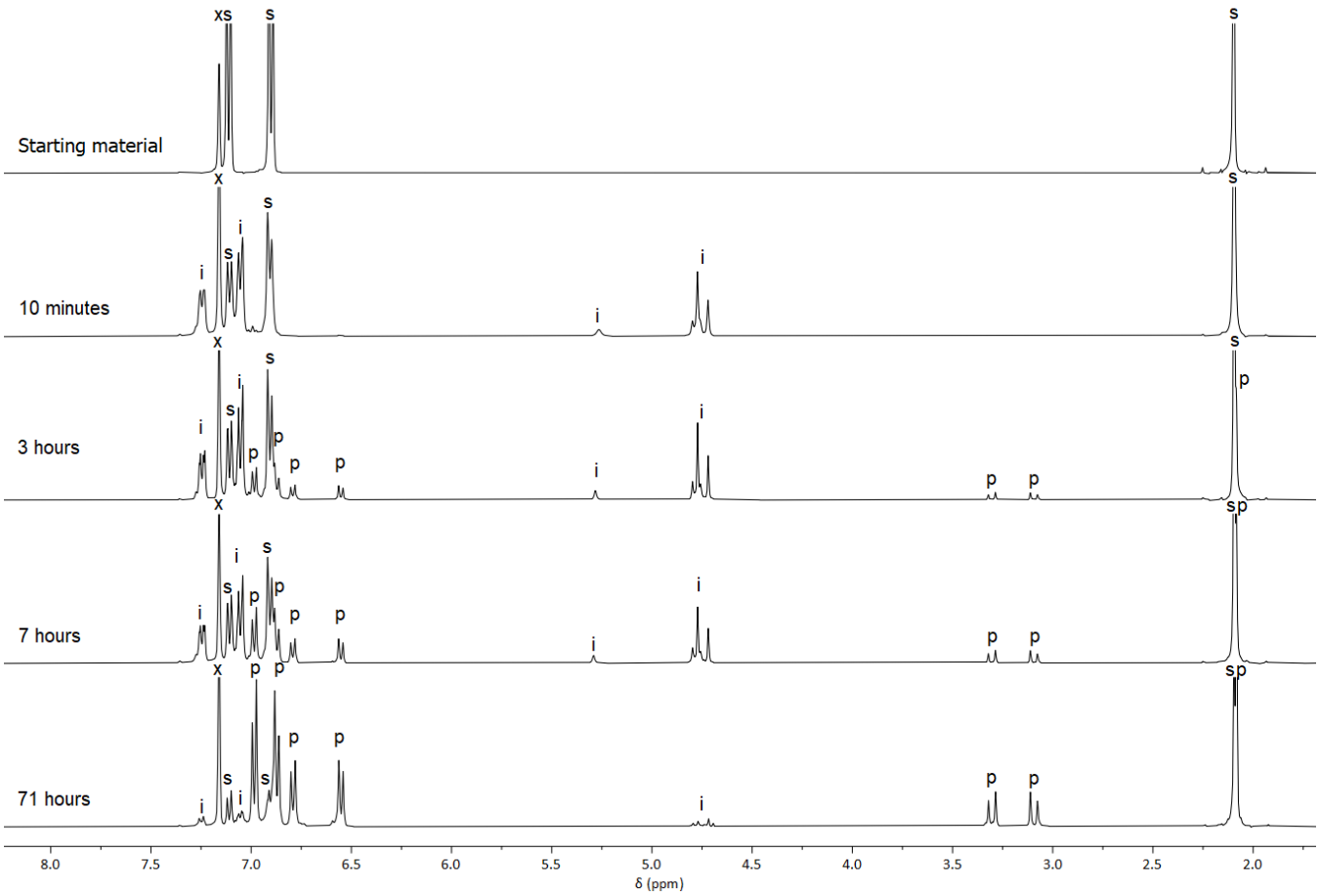


Figure S14. Time resolved 400.1 MHz *in situ* NMR spectra of a solution of (*p*MePh)$_3$N (40 mM) and DDQ (40 mM) in C_6D_6. x = solvent residue, s = starting material, i = unidentified intermediate, p = product.

2.3 Evans NMR Spectroscopy

To determine the concentration of radicals using the Evans method for NMR spectroscopy,[5] the use of an internal capillary with the same deuterated solvent as the analyte was used during the measurements. Using the solvent residue signals of the analyte and the capillary, the presence of radicals results in a change in magnetic susceptibility of the sample and therewith changes frequency of the solvent residue. The paramagnetic susceptibility (χ_M) is related to both the effective magnetic moment (μ_{eff}) and the concentration (c) of the radicals in solution via the following relation for an high-field NMR spectrometer: $\mu_{eff}{}^2 = \frac{3*k*T}{N_A*\mu_B{}^2} * \chi_M \approx 8.00 * T * \chi_M$.[6] Here is k is the Boltzmann constant, T the temperature, N_A the constant of Avegadro and μ_B the Bohr magneton. For radicals with S = 1/2 and g = 2 (as observed in this manuscript, see chapter S3), the effective moment is 1.73. The concentration of radicals is related to the paramagnetic susceptibility χ_M via the following equation: $\chi_M = \frac{-3*\Delta f}{4\pi*f*c}$ where Δf is the change in frequency in Hz upon addition of the radicals and f the frequency of the spectrometer in MHz. Together with the equation for the effecitive moment, this yields the following equation: $c \approx \frac{6*T}{\pi*f*\mu_{eff}{}^2} * \Delta f$.

To correct Δf for the diamagnetic contribution, the shift in frequency of both (*p*MeOPh)$_3$N and DDQ separately was measured in CD_3CN with ^{t}BuOH as internal standard. For a 191 mM solution of DDQ a shift of –1.23 Hz was observed and a 103 mM solution of (*p*MeOPh)$_3$N resulted in a shift of ^{t}BuOH of –5.08 Hz, both at 400.13 MHz and 300.0 K. As the shift in Hz linearly relates to both the frequency of the spectrometer and the concentration of the substrate, is the applied diamagnetic correction to the change in frequency is –0.0064 Hz/mM and –0.049 Hz/mM at a 400.13 mHz spectrometer and –0.0080 Hz/mM and –0.062 Hz/mM at a 499.84 mHz spectrometer for DDQ and (*p*MeOPh)$_3$N, respectively.

2.3.1 (pMeOPh)$_3$N–DDQ in MeCN

Table S1. Evans NMR spectroscopy results of (*p*MeOPh)$_3$N–DDQ in CD_3CN using internal capillary with CD_3CN. Measured at a 400.13 MHz spectrometer.

Concentration DDQ (mM)	Concentration (*p*MeOPh)$_3$N (mM)	Temperature (K)	Solvent residue shift (Hz)	Diamagnetic contribution to solvent residual shift (Hz)	Calculated concentration radicals (mM)
9.99	9.88	298.1	9.88	–0.55	4.96
15.0	15.21	298.2	15.95	–0.85	7.99
21.1	20.9	298.1	20.86	–1.17	10.5
26.4	25.6	298.1	29.27	–1.43	14.6

2.3.2 (pMeOPh)$_3$N–DDQ in DCM

Table S2. Evans NMR spectroscopy results of (*p*MeOPh)$_3$N–DDQ in CD_2Cl_2 using internal capillary with CD_2Cl_2. Measured at a 499.84 MHz spectrometer at 298.0 K.

Concentration DDQ (mM)	Concentration (*p*MeOPh)$_3$N (mM)	Solvent residue shift (Hz)	Diamagnetic contribution to solvent residual shift (Hz)	Calculated concentration radicals (mM)
10.1	10.1	9.34	–0.70	3.82
15.4	14.9	18.31	–1.04	7.36
20.3	20.9	29.45	–1.45	11.8
25.6	25.6	40.61	–1.78	16.1

3. EPR Spectrometry

3.1 (*p*BrPh$_3$)N–DDQ in MeCN

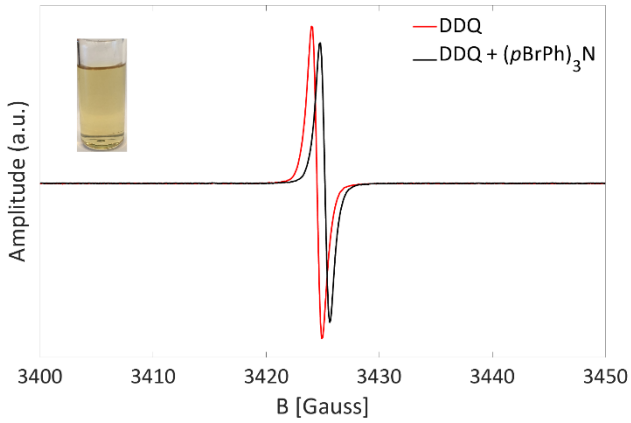


Figure S15. EPR spectra of (*p*BrPh)$_3$N and DDQ (both 5.0 mM) in MeCN and control EPR spectrum of DDQ (5.0 mM) in MeCN and photo of the DDQ + (*p*BrPh)$_3$N solution. Experimental details: (*p*BrPh)$_3$N + DDQ: microwave frequency = 9.611961 GHz, power = 0.3162 mW, modulation amplitude = 1.000 G; DDQ: microwave frequency = 9.611334 GHz, power = 0.3162 mW, modulation amplitude = 1.000 G.

3.2 (*p*^{t}BuPh)$_2$(*p*MePh)N–DDQ in DCM *in situ*

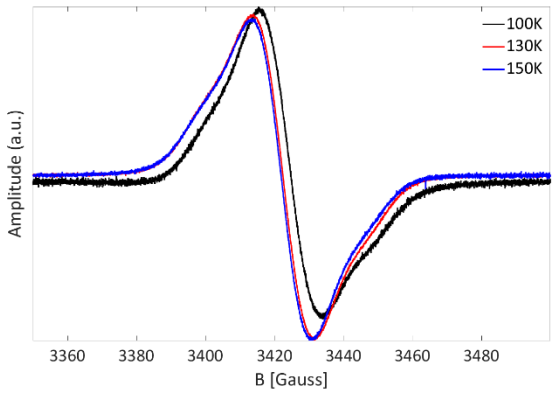


Figure S16. EPR spectrum of a flash frozen solution of (*p*MePh)$_3$N and DDQ (both 20 mM) in DCM at various temperatures. Experimental details: 100K: Microwave frequency = 9.598377 GHz, power = 0.01000 mW, modulation amplitude = 0.200 G; 130K: Microwave frequency = 9.597067 GHz, power = 0.3162 mW, modulation amplitude = 0.200 G; 150K: Microwave frequency = 9.595733 GHz, power = 0.3162 mW, modulation amplitude = 0.200 G.

3.3 (*p*MePh)$_3$N–DDQ in MeCN *in situ*

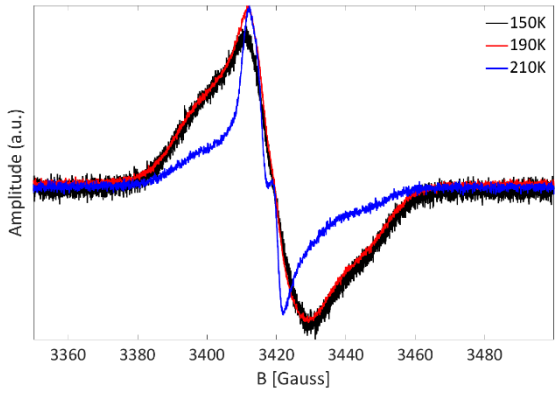


Figure S17. EPR spectrum of a flash frozen solution of (*p*MePh)$_3$N and DDQ (both 20 mM) in MeCN at various temperatures. Experimental details: 150K: Microwave frequency = 9.591875 GHz, power = 0.3162 mW, modulation amplitude = 0.200 G; 190K: Microwave frequency = 9.591443 GHz, power = 0.3162 mW, modulation amplitude = 0.500 G; 210K: Microwave frequency = 9.590550 GHz, power = 0.3162 mW, modulation amplitude = 0.500 G.

3.4 (*p*^{t}BuPh)$_3$N–DDQ in DCM

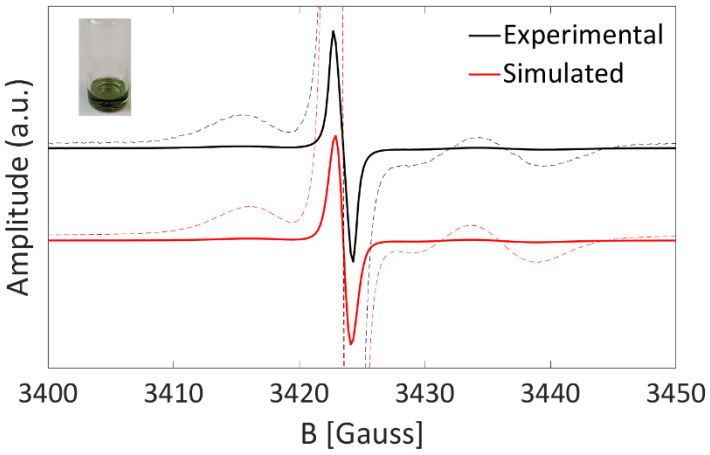


Figure S18. EPR spectrum of (*p*^{t}BuPh)$_3$N and DDQ (both 20 mM) in DCM and photo of the solution. Experimental details: Microwave frequency = 9.608842 GHz, power = 1.000 mW, modulation amplitude = 2.000 G. Simulation details: DDQ$^{\bullet-}$: S = ½, g_{iso} = 2.0054, lwpp = 0.106 & 0.038 (Gaussian & Lorentzian), weight = 1.00; (*p*^{t}BuPh)$_3$N$^{\bullet+}$: S = ½, g_{iso} = 2.0031, $^{14N}a_{iso}$ = 23.76 MHz, lwpp = 0.511 & 0.195 (Gaussian & Lorentzian), weight = 1.15.

3.5 (*p*MeOPh)$_3$N–DDQ

3.5.1 (pMeOPh)$_3$N–DDQ in MeCN

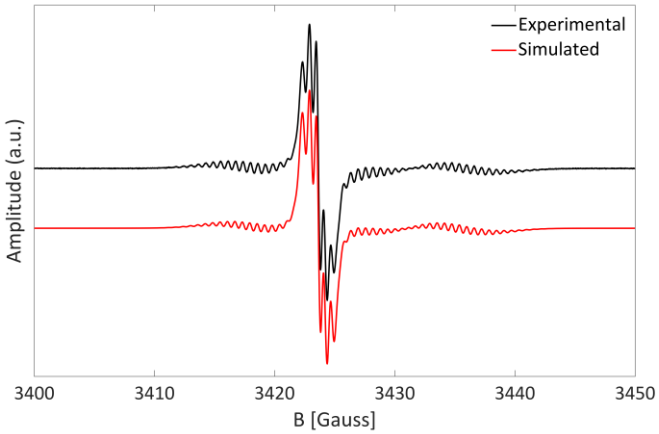


Figure S19. EPR spectrum of (*p*MeOPh)$_3$N and DDQ (both 1.0 mM) in MeCN. Experimental details: Microwave frequency = 9.608854 GHz, power = 3.162 mW, modulation amplitude = 0.250 G. Simulation details: DDQ$^{\bullet-}$: S = ½, g_{iso} = 2.0053, lwpp = 0.0232 & 0.0386 (Gaussian & Lorentzian), $^{14N}a_{iso}$ = 1.60 MHz (2x), weight = 1.00; (*p*MeOPh)$_3$N$^{\bullet+}$: S = ½, g_{iso} = 2.0034, $^{14N}a_{iso}$ = 23.59 MHz, $^{1H}a_{iso}$ = 5.18 MHz (6x, *o*-Ph*H*), $^{1H}a_{iso}$ = 1.71 MHz (6x, *m*-Ph*H*), $^{1H}a_{iso}$ = 1.71 MHz (9x, C*H*$_3$O), lwpp = 0.0282 & 0.0418 (Gaussian & Lorentzian), weight = 0.96.

3.5.2 (pMeOPh)$_3$N–DDQ in DCM

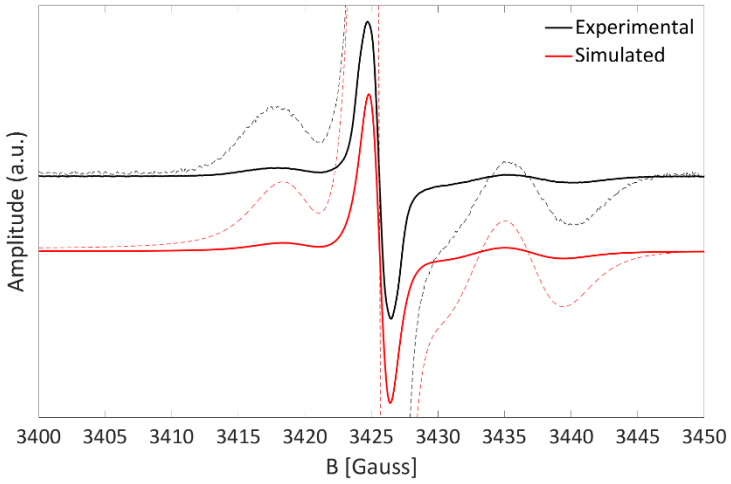


Figure S20. EPR spectrum of (*p*MeOPh)$_3$N and DDQ (both 1.0 mM) in DCM and zoomed in (dashed lines). Experimental details: Microwave frequency = 9.613624 GHz, power = 1.000 mW, modulation amplitude = 1.000 G. Simulation details: DDQ$^{\bullet-}$: S = ½, g_{iso} = 2.0051, lwpp = 0.0963 & 0.1033 (Gaussian & Lorentzian), weight = 1.00; (*p*MeOPh)$_3$N$^{\bullet+}$: S = ½, g_{iso} = 2.0033, $^{14N}a_{iso}$ = 23.23 MHz, lwpp = 0.3553 & 0.2435 (Gaussian & Lorentzian), weight = 1.00.

3.5.3 *(pMeOPh)$_3$N–DDQ in toluene*

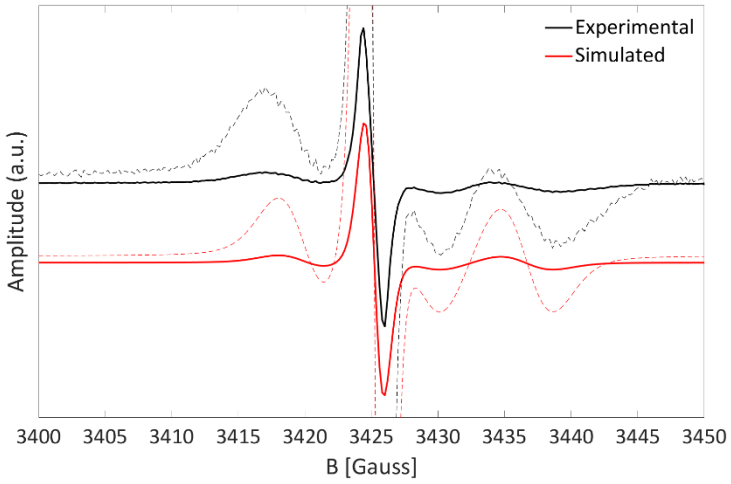


Figure S21. EPR spectrum of (*p*MeOPh)$_3$N and DDQ (both 40 mM) in toluene. Experimental details: Microwave frequency = 9.611441 GHz, power = 1.000 mW, modulation amplitude = 2.000 G. Simulation details: DDQ$^{\bullet-}$: S = ½, g_{iso} = 2.0049, lwpp = 0.1219 & 0.0431 (Gaussian & Lorentzian), weight = 1.00; (*p*MeOPh)$_3$N$^{\bullet+}$: S = ½, g_{iso} = 2.0031, $^{14N}a_{iso}$ = 23.52 MHz, lwpp = 0.3458 & 0.1145 (Gaussian & Lorentzian), weight = 1.13.

3.5.4 *Single crystal of {(pMeOPh)$_3$N}$_2${DDQ}$_3${CD$_3$CN}$_4$*

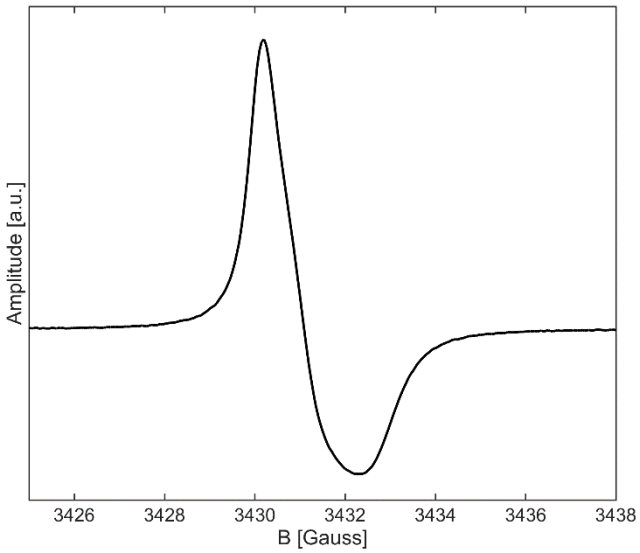


Figure S22. Room temperature EPR spectrum of a single crystal of {(*p*MeOPh)$_3$N}$_2${DDQ}$_3${CD$_3$CN}$_4$. Experimental details: Microwave frequency = 9.627267 GHz, power = 0.001000 mW, modulation amplitude = 0.500 G.

Table S3. Temperature dependence of signal intensity of a single crystal of {(*p*MeOPh)$_3$N}$_2${DDQ}$_3${CD$_3$CN}$_4$ of Figure S22.

Temperature (K)	Double integral	Q-value
295	126.0636	5506
290	124.1140	5509
280	123.2162	5536
270	121.2217	5553
260	118.1270	5487
250	113.9956	5444
240	111.6551	5443
230	108.3941	5492
210	97.5893	5457
200	94.1834	5402
190	87.9837	5347
180	85.4173	5456
220	101.4600	5505

Settings used: frequency ~9.61 GHz, power 0.0001 mW with a modulation of 0.050 G, 150 G wide, centre of spectrum 3425 G, 45 seconds per scan. Integration of the spectra was performed using the easyspin[1] via the GUI cwEPR (version 3.3).[7] Settings used for integration: first order baseline correction of the original spectrum over the whole spectrum and first order integral over 40% of the spectrum.

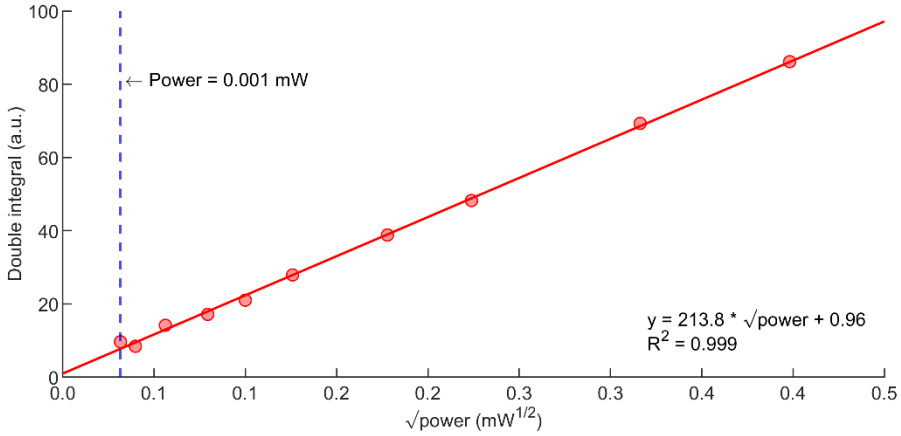


Figure S23. Power saturation of the single crystal at 180 K. Modulation used: 0.050 G

3.1.1. Quantitative EPR (qEPR)

For the calibration, TEMPO was used as the standard analyte. To obtain samples used for qEPR experiments, stock solutions of the required concentration were prepared. In case of MeCN or DCM as solvent were three capillaries filled (10 mm) with the solution and loaded in an EPR tube, while for toluene as solvent the solution (0.10 mL) was directly loaded in one specific EPR tube which was used for all measurements. All samples were measured in triplo using the same settings: frequency ~9.61 GHz, power 0.1000 mW with a modulation of 1.000 G, 150 G wide, centre of spectrum 3425 G, 45 seconds per scan and in total 4 scans. Integration of the spectra was performed using the easyspin[1] via the GUI cwEPR (version 3.3).[7] Settings used for integration: first order baseline correction of both spectrum and first order integral over 30% (toluene), 25% (MeCN) or 10% (DCM) of the spectrum. For the linear regression, the LINEST function in Excell was used.

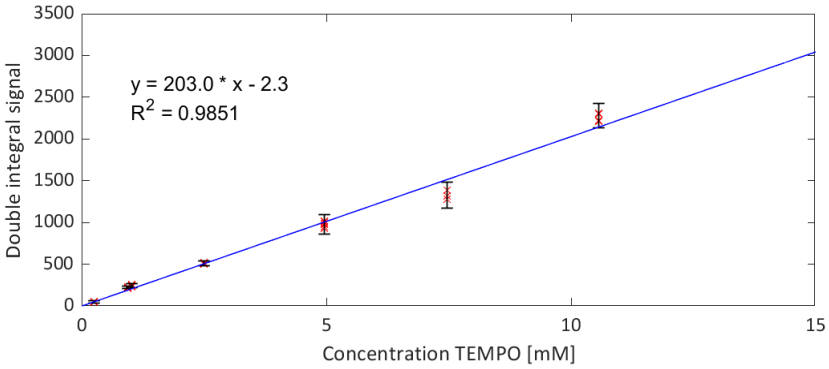


Figure S24. Calibration curve of qEPR measurements using TEMPO (0.26–10.6 mM) in MeCN. Error bars drawn at 90% for confidence intervals.

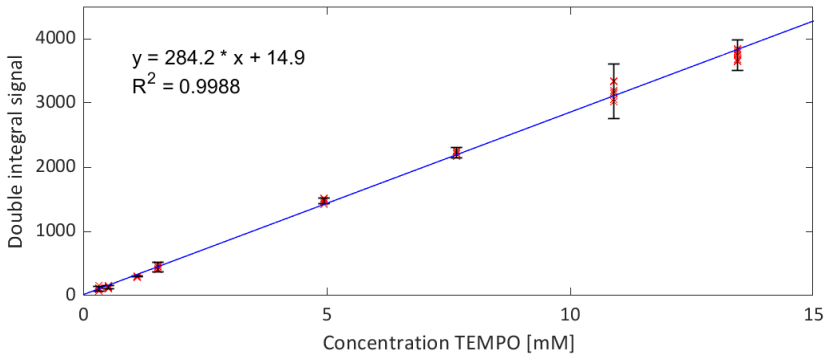


Figure S25. Calibration curve for qEPR measurements using TEMPO (0.32–13.4 mM) in DCM. Error bars drawn at 90% for confidence intervals.

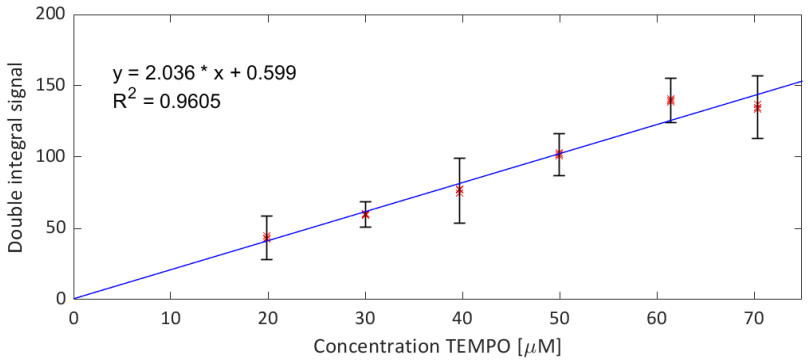


Figure S26. Calibration curve for qEPR measurements using TEMPO (20–70 µM) in toluene. Error bars drawn at 90% for confidence intervals.

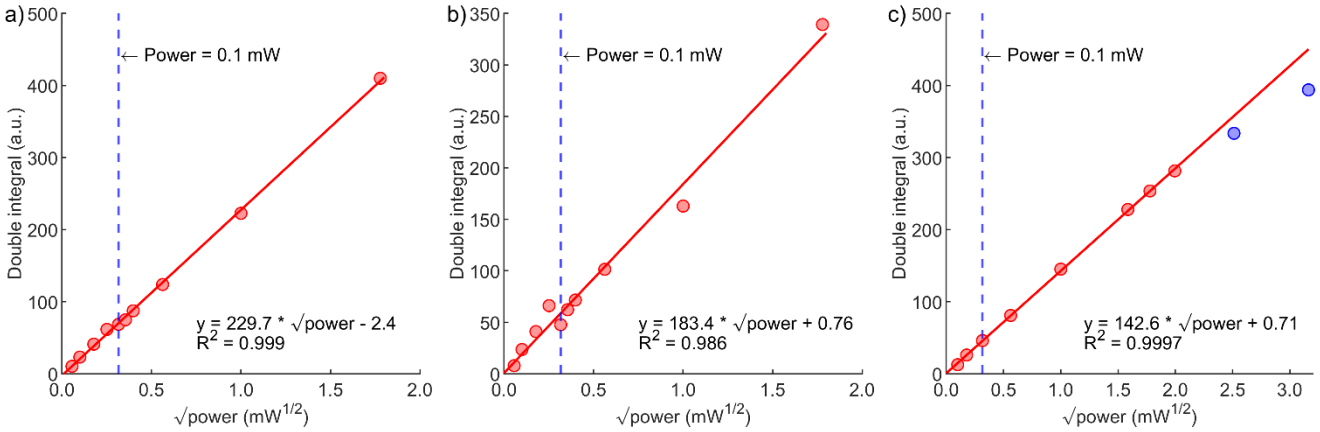


Figure S27. Power saturation of the TEMPO qEPR signal in different solvents. a) 0.256 mM in acetonitrile, b) 0.249 mM in DCM, c) 0.019 mM in toluene (measurements at 6.310 and 10.00 mW not used for fitting).

4. UV–vis spectroscopy

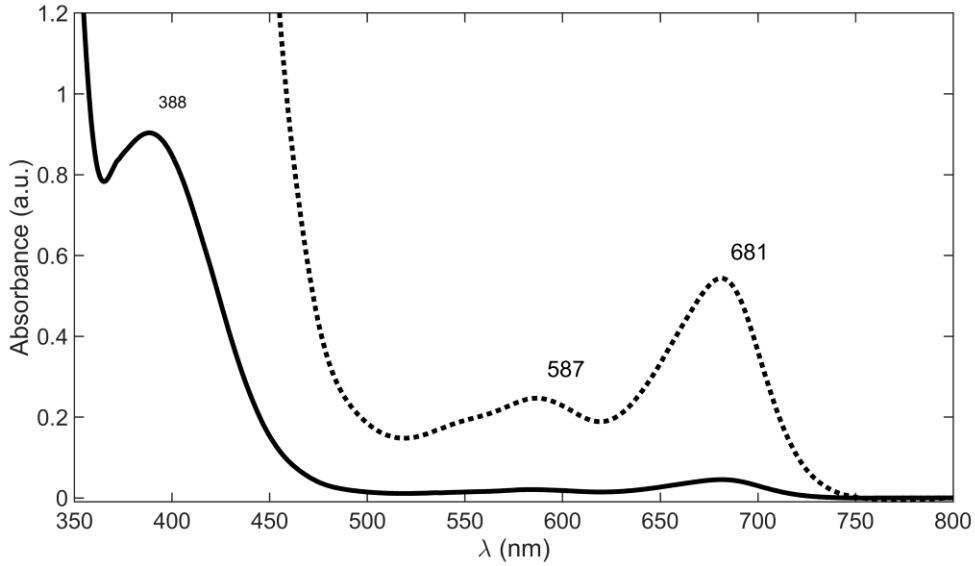


Figure S28. UV–vis spectra of (*pt*BuPh)$_3$N (continues: 1.0 mM, dotted: 10 mM) and DDQ (continues: 1.0 mM, dotted: 10 mM) in DCM.

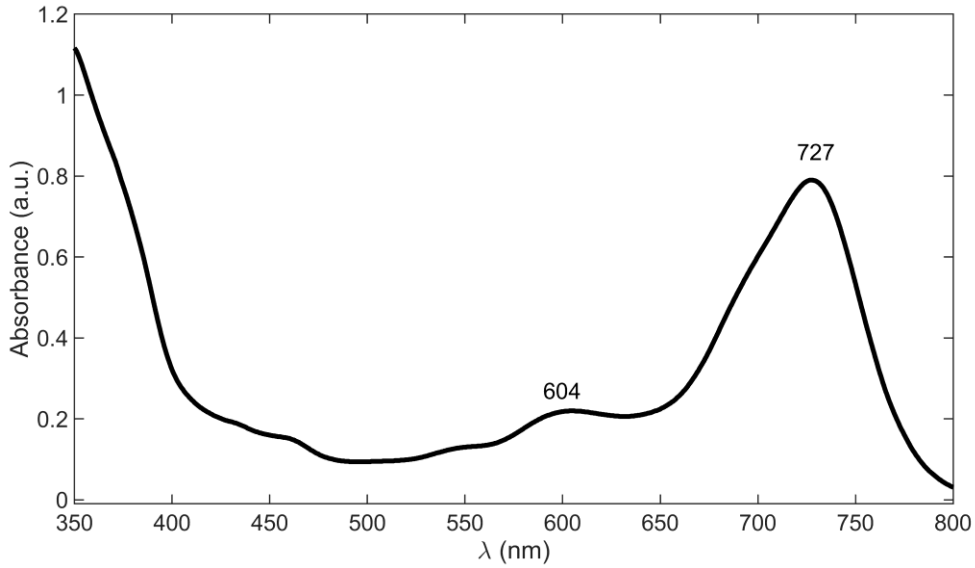


Figure S29. UV–vis spectrum of (*p*MeOPh)$_3$N (0.27 mM) and DDQ (0.27 mM) in DCM.

5. IR spectroscopy

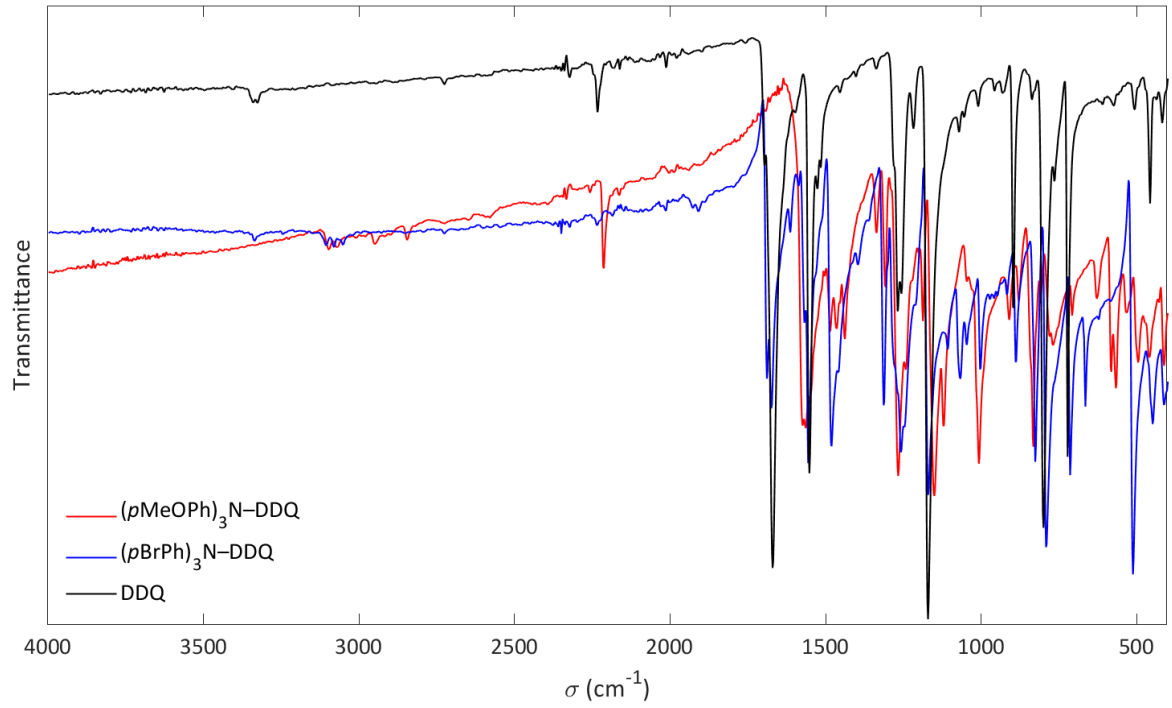


Figure S30. Powder IR spectra of the (pMeOPh)$_3$N–DDQ crystal, the (pBrOPh)$_3$N–DDQ crystal, and DDQ.

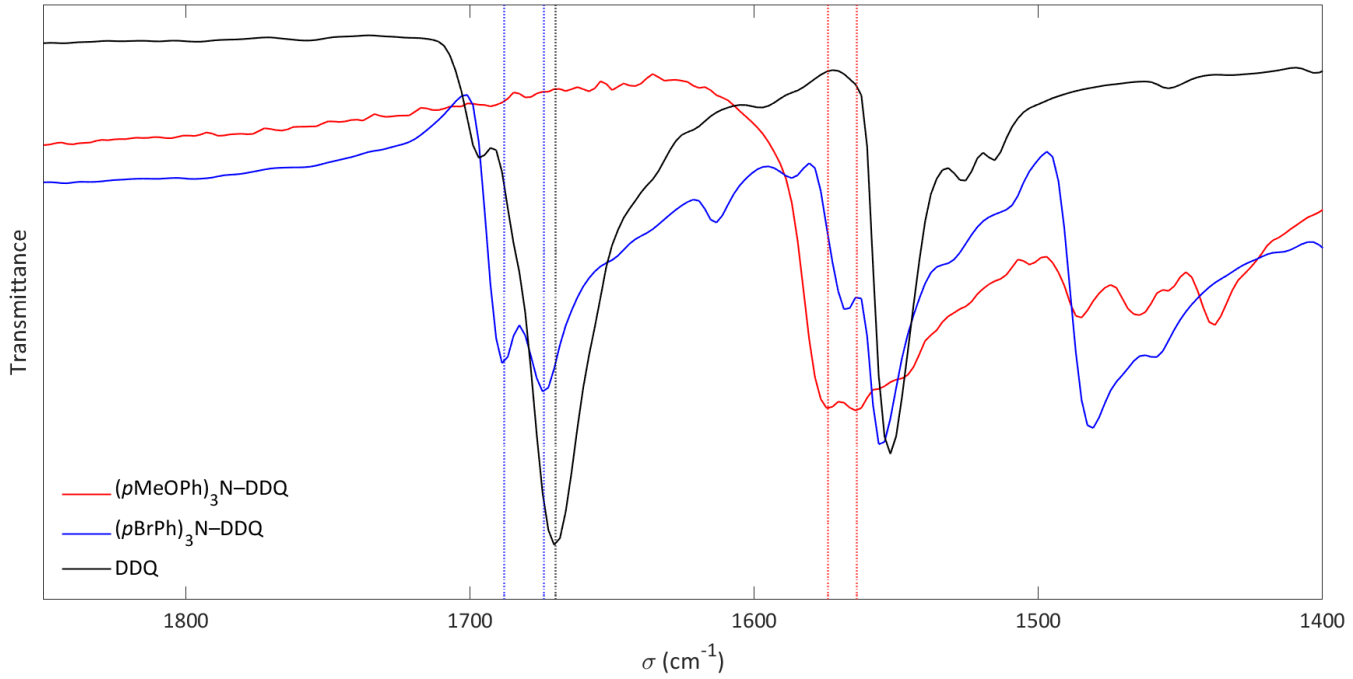


Figure S31. Zoom-in of the powder IR spectra of the (pMeOPh)$_3$N–DDQ crystal, the (pBrPh)$_3$N–DDQ crystal, and DDQ (full spectra shown in Figure S30) and marks of the C–O bond stretches (1574 and 1564 cm^{-1} for (pMeOPh)$_3$N–DDQ, 1688 amd 1674 cm^{-1} for (pBrPh)$_3$N–DDQ and 1670 cm^{-1} for DDQ).

6. Single Crystal X-Ray Crystallography (SC–XRD)

6.1 General procedures

Single crystals suitable for SC–XRD of (*p*BrPh)$_3$N–DDQ were obtained by layering an equimolar solution of (*p*BrPh)$_3$N (35 mM) and DDQ (35 mM) in *ortho*-difluorobenzene with cyclohexane at room temperature as green needles. Single crystals suitable for XRD of (*p*MeOPh)$_3$N–DDQ were obtained by cooling a equimolar solution of (*p*BrPh)$_3$N (15 mM) and DDQ (15 mM) in CD_3CN to -30 °C.

Single crystal X-ray diffraction data of [*p*BrPh)$_3$N][DDQ], [(*p*MeOPh)$_3$N][DDQ] and (*p*^{t}BuPh)$_2$(*p*MePh)N–DDQ product **5** were measured on a Bruker D8 Quest Eco diffractometer using graphite-monochromated (Triumph) Mo Kα radiation (λ = 0.71073 Å) and a CPAD Photon III C14 detector. The sample was cooled with N_2 to 100 K with a Cryostream 700 (Oxford Cryosystems). Intensity data were integrated using the SAINT software.[8] Absorption correction and scaling was executed with SADABS 2016/2.[9] The structures were solved using intrinsic phasing with the program SHELXT 2018/2[10] against F^2 of all reflections.

The initial structure solution for [*p*BrPh)$_3$N][DDQ] was initially $P\bar{1}$, but ADDSYM (PLATON[11] version 250424) revealed higher $P2_1/n$ symmetry. In a similar manner, the initial solution for [(*p*MeOPh)$_3$N][DDQ] was $P1$, but the use of ADDSYM during refinement found $P\bar{1}$, symmetry. The structure solution of (*p*^{t}BuPh)$_2$(*p*MePh)N–DDQ product **5** revealed the presence of a heptane solvent residue that could not be reliably refined. Thus, the SQUEEZE[12] procedure in PLATON (version 250424) was applied, showing the presence of two large (~408 Å^3) and two small (~20 Å^3) voids (total solvent accessible volume = 857 Å^3) accounting for 226 electrons per unit cell, congruent with the presence of 4 heptane molecules (58 e^-/molecule, 232 e^- total) in the unit cell (Z=4).

Least-squares refinement was performed with SHELXL-2019/3.[13] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions with a riding model. CheckCIF revealed no A-level alerts. The X-ray crystallographic data for [*p*BrPh)$_3$N][DDQ], [(*p*MeOPh)$_3$N][DDQ] and (*p*^{t}BuPh)$_2$(*p*MePh)N–DDQ product **5** was deposited at the Cambridge Crystallographic Data Centre (CCDC) under the deposition numbers CCDC 2375239–2375241.

6.2 Single-Crystal data

Table S4. Single-Crystal X-Ray Crystallographic data

Compound	[*p*BrPh)$_3$N][DDQ] Complex	(*p*^{t}BuPh)$_2$(*p*MePh)N–DDQ product **5**	[(*p*MeOPh)$_3$N][DDQ] Complex
CCDC number	2375239	2375241	2375240
Empirical formula	$C_{34}H_{12}Br_3Cl_4N_5O_4$	$C_{69}H_{80}Cl_2N_4O_2$	$C_{37}H_{27}Cl_3N_6O_6$
Formula weight	936.02	1068.27	757.99
Temperature [K]	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	triclinic
Space group (number)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a [Å]	14.2083(9)	12.6542(5)	10.1342(7)
b [Å]	8.5922(6)	15.0794(6)	13.1376(9)
c [Å]	27.8045(16)	32.6986(12)	14.5218(10)
α [°]	90	90.332(2)	100.041(3)
β [°]	93.411(3)	99.968(2)	97.703(3)
γ [°]	90	104.023(2)	110.105(3)
Volume [Å^3]	3388.4(4)	5954.7(4)	1748.0(2)
Z	4	4	2
ρ_{calc} [g cm^{-3}]	1.835	1.192	1.440
μ [mm^{-1}]	3.936	0.157	0.319
F(000)	1824	2288	780
Crystal size [mm^3]	0.412×0.203×0.160	0.606×0.123×0.092	0.643×0.362×0.038
Crystal colour	green	blue	violet
Crystal shape	block	block	block
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	4.96 to 55.08 (0.77 Å)	4.83 to 55.05 (0.77 Å)	4.38 to 55.14 (0.77 Å)
Index ranges	−18 ≤ h ≤ 18 −11 ≤ k ≤ 11 −36 ≤ l ≤ 36	−16 ≤ h ≤ 16 −19 ≤ k ≤ 19 −42 ≤ l ≤ 42	−13 ≤ h ≤ 13 −17 ≤ k ≤ 17 −18 ≤ l ≤ 18
Reflections collected	201766	405690	92003
Independent reflections	7785 R_{int} = 0.0560 R_{sigma} = 0.0176	27299 R_{int} = 0.1069 R_{sigma} = 0.0412	8044 R_{int} = 0.0681 R_{sigma} = 0.0312
Completeness to θ = 25.242°	99.9 %	99.8 %	99.8 %
Data / Restraints / Parameters	7785/0/451	27299/1200/1325	8044/439/554
Goodness-of-fit on F^2	1.265	1.021	1.229
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0379 wR_2 = 0.0850	R_1 = 0.0752 wR_2 = 0.1854	R_1 = 0.0931 wR_2 = 0.2074
Final *R* indexes [all data]	R_1 = 0.0426 wR_2 = 0.0872	R_1 = 0.1146 wR_2 = 0.2149	R_1 = 0.1140 wR_2 = 0.2195
Largest peak/hole [e Å^{-3}]	0.94/-0.55	1.22/-1.11	0.72/-0.76

6.3 Crystal bond length analysis

Table S5. C–C and C–O of DDQ bond lengths in Å in the crystal structure (and computations). Changes in bond length compared to the crystal structure of DDQ are shown in curly brackets {}.

Bond	DDQ[a]	$[Et_4N][DDQ]$ [a]	DDQ[b]	$DDQ^{\bullet-}$[b]	DDQ^{2-}[b]	$(p\text{BrPh})_3N$ –DDQ: B	$(p\text{BrPh})_3N$ –DDQ: C	$(p\text{MeOPh})_3N$ –DDQ: B	$(p\text{MeOPh})_3N$ –DDQ: C
C–O	1.214	1.237 {+0.023}	1.206 {-0.008}	1.236 {+0.022}	1.257 {+0.043}	1.212(4) {-0.002}	1.209(4) {-0.005}	1.217(6) {+0.003}	1.231(10) {+0.017}
	1.219	1.240 {+0.021}	1.206 {-0.013}	1.236 {+0.017}	1.257 {+0.038}	1.213(4) {-0.006}	1.213(4) {-0.006}	1.230(6) {+0.011}	1.235(12) {+0.016}
OC–CCl	1.481	1.468 {-0.013}	1.497 {+0.017}	1.478 {-0.003}	1.764 {+0.283}	1.476(5) {-0.005}	1.476(5) {-0.005}	1.481(6) {0}	1.45(3) {-0.03}
	1.487	1.472 {-0.015}	1.497 {+0.010}	1.478 {-0.009}	1.764 {+0.277}	1.486(5) {-0.001}	1.492(5) {+0.005}	1.484(7) {-0.003}	1.476(12) {-0.011}
ClC–CCl	1.354	1.359 {+0.005}	1.348 {-0.006}	1.358 {+0.004}	1.372 {+0.018}	1.351(5) {-0.003}	1.345(5) {-0.009}	1.346(7) {-0.008}	1.365(12) {+0.011}
OC–CCN	1.497	1.447 {-0.050}	1.502 {+0.005}	1.455 {-0.042}	1.428 {-0.069}	1.485(5) {-0.008}	1.485(5) {-0.012}	1.473(7) {-0.024}	1.463(12) {-0.034}
	1.499	1.454 {-0.055}	1.502 {+0.003]	1.455 {-0.044}	1.428 {-0.071}	1.498(5) {-0.001}	1.492(5) {-0.007}	1.475(6) {-0.024}	1.53(2) {+0.03}
NCC–CCN	1.354	1.384 {+0.030}	1.349 {-0.005}	1.395 {+0.041}	1.448 {+0.094}	1.344(5) {-0.010}	1.344(5) {-0.010}	1.366(6) {+0.012}	1.375(13) {+0.021}

[a] Bond lengths reported in reference 14 and corresponding crystal data in the CCDC database under numbers 1127101 and 1108285. [c] Computed at the UωB97X-D/6-31G(d) level of theory.

7. Magnetic Susceptibility Measurements

Temperature dependence of the magnetic susceptibility was determined using a Quantum Design MPMS Squid magnetometer equipped with the reciprocating sample option (RSO). Samples were prepared by charging a capsule with crystaline material (1.58 mg of (pBrPh)$_3$N–DDQ or 0.234 mg of (pBrPh)$_3$N–DDQ) and subsequently the temperature dependence of the magnetic susceptibility was determined both in zero field cooled (ZFC) and field cooling (FC) mode in applied magnetic fields of 25 and 100 mT. The results for both (pBrPh)$_3$N–DDQ and (pBrPh)$_3$N–DDQ using 25 mT are shown in figure S32. The 100 mT data of (pBrPh)$_3$N–DDQ is displayed in figure S33, which shows a lower response compared to the 25 mT data, demonstrating the rather strong diamagnetic background. Above 50 K we observe an almost temperature independent susceptibility of Van Vleck type for both (pMeOPh)$_3$N–DDQ and (pBrPh)$_3$N–DDQ, where the latter has a significant lower response indicating a much lower concentration of radicals. The most striking feature is a sharp maximum in the susceptibility observed in the FC curve at 45 and 48 K for (pMeOPh)3N-DDQ and (pBrPh)3N-DDQ, respectively, followed by a Curie type tail. The Curie type tail is reproduced also in the ZFC susceptibility but the sharp maximum is absent. Such peculiar magnetic response may indicate a charge ordering transition at the respective temperatures.

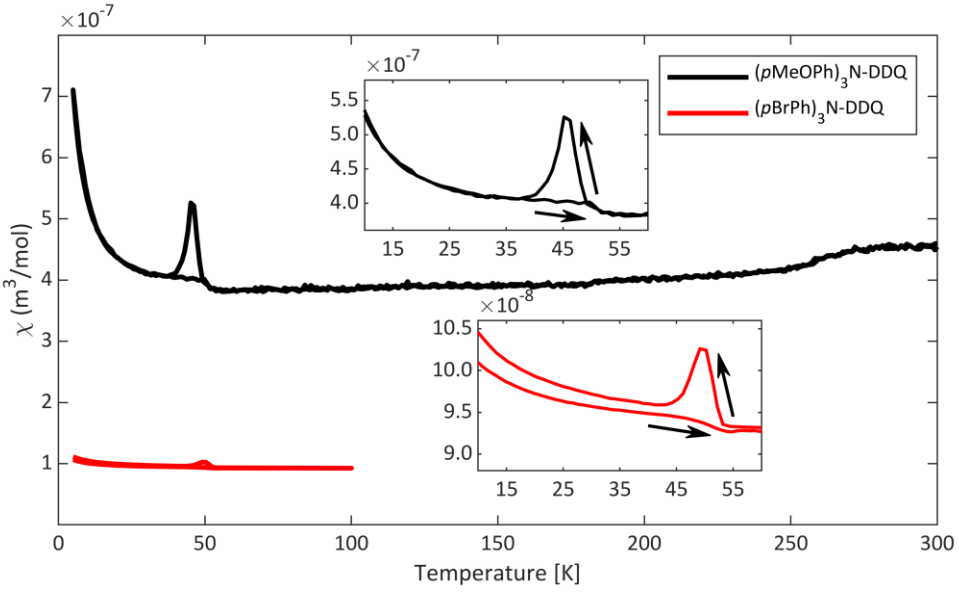


Figure S32. Magnetic susceptibility measurements using a field of 25 mT, including indication of scan direction in the zoom in.

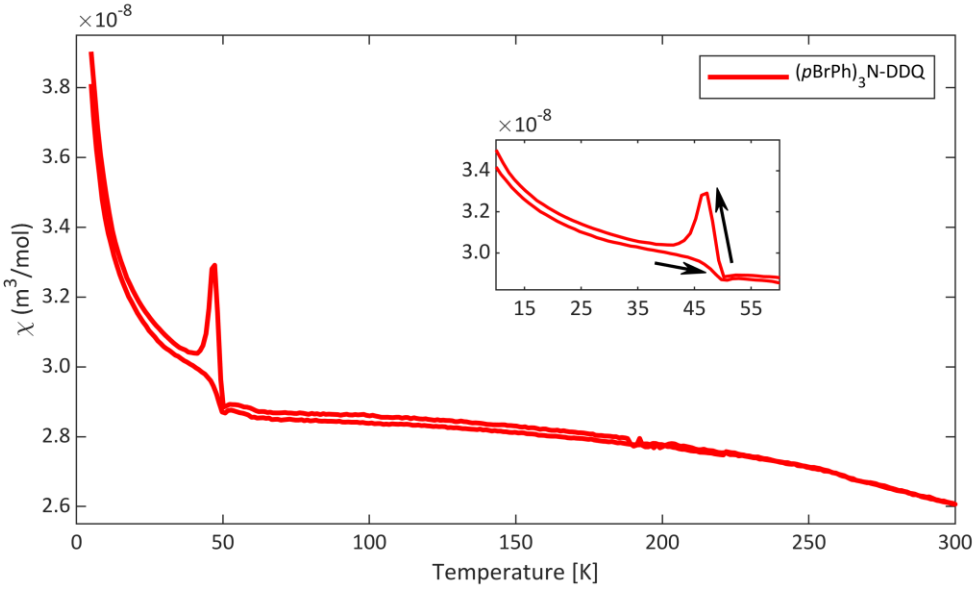


Figure S33. Magnetic susceptibility measurements using a field of 100 mT, including indication of scan direction in the zoom in.

8. Electrical Resistance Measurements

Electrical resistance measurements were carried out in a Quantum Design Dynacool Physical Properties Measurement System (PPMS). Single crystals of both (*p*MeOPh)$_3$N–DDQ and (*p*BrPh)$_3$N–DDQ were mounted on a sample puck with double sided sticky tape. Two current and voltage contacts were attached to the crystals by silver paint in a four point configuration as shown in Figure S34. Currents between 1 nA and 1 mA were applied. The resistance was measured using the Resistivity Option in the four point geometry and the Electro Transport Option in a two-point geometry. In both cases the resistance exceeded the measurement range of 40 MΩ and 5 GΩ, respectively. We conclude the crystals are insulating at room temperature. Upon cooling down to 10 K the crystals remained insulating.

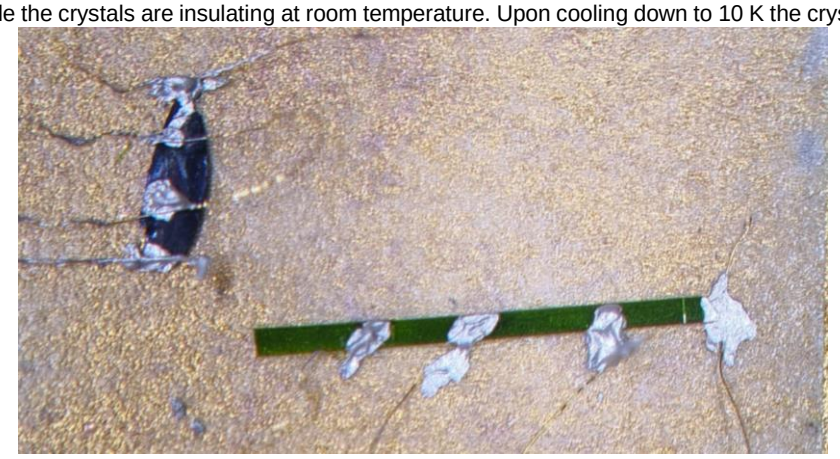


Figure S34. Photo of the crystals mounted on a PPMS resistance puck in a four-point geometry seen through a microscope. Top left: {(*p*MeOPh)$_3$N}$_2${DDQ}$_3${CD$_3$CN}$_4$. Bottom right: {(*p*BrPh)$_3$N}{DDQ}$_2$. For scale: the green crystal is 6 mm long.

9. Computational Section

9.1. General Computational Details

All geometry optimizations were calculated using the (U)ωB97X-D density functional[15] and the 6-31G(d)[16] basis set as implemented in Gaussian 16 (Revision C.01)[17] without symmetry constraints. The obtained geometries were characterized as true minima having no imaginary frequency via harmonic frequency calculation. Single-point calculations on the optimized structures were performed using (U)ωB97X-D and the 6-311+G(d,p)[16] basis set taking solvents effects (toluene, dichloromethane or acetonitrile where applicable) into account by means of the self-consistent reaction field (SCRF) method using the polarizable continuum model (PCM).[18]

9.2 Ionization Energies and Electron Affinities

Table S6. Calculated ionization energies (IEs) and electron affinities (EAs) (in Ev) (U)*ω*B97X-D/6-311+G(d,p)//(U)*ω*B97X-D/6-31G(d) with SCRF treatment of solvent were applicable and Hammett σ^+ values for the para-substituents of the arylamines.[a]

Compound	Gasphase	Toluene	Benzene	Dichloromethane	Acetonitrile	σ^+ [a]
DDQ	-3.84	-4.74	-4.71	-5.18	-5.28	
$DDQ^{\bullet-}$	1.02	-1.99	-1.89	-3.57	-4.01	
(*p*Me_2NPh)$_3$N	5.37	4.72	4.74	4.44	4.38	-1.70
(*p*MeOPh)$_3$N	6.12	5.36	5.39	5.01	4.91	-0.78
(*p*PhONPh)$_3$N	6.19	5.50	5.53	5.17	5.07	-0.50
(*p*MePh)$_3$N	6.45	5.64	5.66	5.25	5.15	-0.31
(*p*MePh)$_1$(*p*^{t}BuNPh)$_2$N	6.39	5.62	5.64	5.25	5.15	
(*p*^{t}BuNPh)$_3$N	6.36	5.61	5.64	5.26	5.16	-0.26
(*p*PhPh)$_3$N	6.50	5.77	5.80	5.41	5.31	-0.18
(*p*FPh)$_3$N	7.01	6.06	6.09	5.56	5.42	-0.07
(*p*ClPh)$_3$N	7.11	6.18	6.21	5.70	5.56	0.11
(*p*BrNPh)$_3$N	7.10	6.19	6.22	5.72	5.58	0.15
(*p*NO_2Ph)$_3$N	8.20	7.09	7.12	6.45	6.25	0.79

[a] Hammett σ^+ values taken from refence [19].

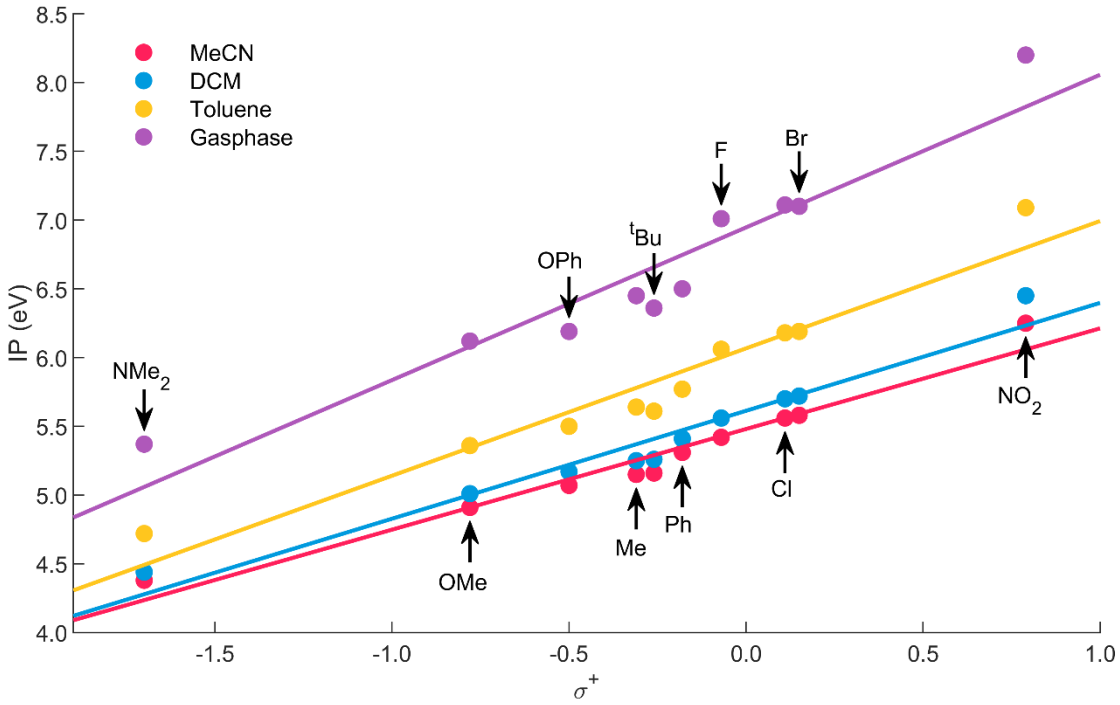


Figure S35. Hammett plot of the calculated IEs for different para-substituted triaryl amines in the gas phase, toluene, dichloromethane or acetonitrile. Trendlines: IP_{MeCN} = 0.73 eV * σ^+ + 5.48 eV, R^2 = 0.959; IP_{DCM} = 0.78 eV * σ^+ + 5.61 eV, R^2 = 0.953; $IP_{toluene}$ = 0.93 eV * σ^+ + 6.07 eV, R^2 = 0.934; $IP_{gasphase}$ = 1.11 eV * σ^+ + 6.95 eV, R^2 = 0.909.

9.3 Energies of Calculated Monomeric Structures

Table S7. Calculated energies and Gibbs free energy corrections (in Hartree) at the (U)ωB97X-D/6-311+G(d,p) level of theory with SCRF treatment of solvent were applicable for the different structures optimized at the (U)ωB97X-D/6-31G(d) level of theory.

Compound	Gas phase[a]	Gibbs free energy correction[a]	Gas phase	Toluene	Benzene	Dichloromethane	Acetonitrile
DDQ	-1484.84745756	0.023846	-1485.05915513	-1485.06573537	-1485.06543291	-1485.07217765	-1485.07472416
$DDQ^{\bullet-}$	-1484.97709284	0.023010	-1485.20016183	-1485.23999051	-1485.23864441	-1485.26243826	-1485.26894378
DDQ^{2-}	-1484.91800329	0.023048	-1485.16261997	-1485.31320605	-1485.30825190	-1485.39378009	-1485.41624399
$(p\mathrm{Me_2NPh})_3\mathrm{N}$	-1151.21312038	0.444091	-1151.50253264	-1151.50789785	-1151.50765806	-1151.51283208	-1151.51467982
$(p\mathrm{Me_2NPh})_3\mathrm{N}^{\bullet+}$	-1151.02455398	0.445801	-1151.30530129	-1151.33448525	-1151.33355763	-1151.34953475	-1151.35377383
$(p\mathrm{MeOPh})_3\mathrm{N}$	-1092.89490623	0.327935	-1093.17674881	-1093.18226118	-1093.18202354	-1093.18696793	-1093.18864040
$(p\mathrm{MeOPh})_3\mathrm{N}^{\bullet+}$	-1092.67936647	0.330418	-1092.95202386	-1092.98515458	-1092.98407864	-1093.00294920	-1093.00811870
$(p\mathrm{PhONPh})_3\mathrm{N}$	-1667.91516259	0.466482	-1668.32655363	-1668.33273004	-1668.33246124	-1668.33809720	-1668.34002438
$(p\mathrm{PhONPh})_3\mathrm{N}^{\bullet+}$	-1667.69656968	0.469306	-1668.09905528	-1668.13043582	-1668.12939427	-1668.14816604	-1668.15357017
$(p\mathrm{MePh})_3\mathrm{N}$	-867.354765041	0.313046	-867.565799851	-867.568622584	-867.568497383	-867.571172415	-867.572112680
$(p\mathrm{MePh})_3\mathrm{N}^{\bullet+}$	-867.126007743	0.313459	-867.328929710	-867.361502969	-867.360466888	-867.378287029	-867.383008792
$(p^t\mathrm{BuNPh})_2(p\mathrm{MePh})\mathrm{N}$	-1103.17178481	0.478031	-1103.44386282	-1103.44675409	-1103.44662428	-1103.44945072	-1103.45047911
$(p^t\mathrm{BuNPh})_2(p\mathrm{MePh})\mathrm{N}^{\bullet+}$	-1102.94486557	0.478745	-1103.20904703	-1103.24022171	-1103.23923439	-1103.25639460	-1103.26105433
$(p^t\mathrm{BuNPh})_3\mathrm{N}$	-1221.08030609	0.561802	-1221.38286491	-1221.38580662	-1221.38567358	-1221.38858850	-1221.38965738
$(p^t\mathrm{BuNPh})_3\mathrm{N}^{\bullet+}$	-1220.85425574	0.562411	-1221.14900824	-1221.17955615	-1221.17858988	-1221.19545287	-1221.20007427
$(p\mathrm{PhPh})_3\mathrm{N}$	-1442.36781099	0.464950	-1442.71033253	-1442.71574844	-1442.71550549	-1442.72074066	-1442.72259815
$(p\mathrm{PhPh})_3\mathrm{N}^{\bullet+}$	-1442.13826073	0.466103	-1442.47159539	-1442.50359099	-1442.50251816	-1442.52190100	-1442.52747607
$(p\mathrm{FNPh})_3\mathrm{N}$	-1047.05841515	0.209984	-1047.34220498	-1047.34598570	-1047.34583152	-1047.34887864	-1047.34983337
$(p\mathrm{FNPh})_3\mathrm{N}^{\bullet+}$	-1046.81252849	0.211739	-1047.08442279	-1047.12339878	-1047.12212008	-1047.14455917	-1047.15069150
$(p\mathrm{ClPh})_3\mathrm{N}$	-2128.17111392	0.203357	-2128.44133966	-2128.44486959	-2128.44472344	-2128.44765134	-2128.44858709
$(p\mathrm{ClPh})_3\mathrm{N}^{\bullet+}$	-2127.91673045	0.204137	-2128.18013540	-2128.21764890	-2128.21641183	-2128.23822120	-2128.24422914
$(p\mathrm{BrNPh})_3\mathrm{N}$	-8461.92742858	0.199184	-8470.33668509	-8470.34024879	-8470.34010060	-8470.34308027	-8470.34403760
$(p\mathrm{BrNPh})_3\mathrm{N}^{\bullet+}$	-8461.67357894	0.200084	-8470.07571416	-8470.11261451	-8470.11139588	-8470.13295134	-8470.13893399
$(p\mathrm{NO_2Ph})_3\mathrm{N}$	-1362.74161778	0.235954	-1363.10828909	-1363.11919446	-1363.11873798	-1363.12800471	-1363.13103304
$(p\mathrm{NO_2Ph})_3\mathrm{N}^{\bullet+}$	-1362.44956942	0.234573	-1362.80684413	-1362.85881349	-1362.85698311	-1362.89104193	-1362.90122651

[a] at the (U)ωB97X-D/6-31G(d) level of theory.

9.4 Analysis of Complexes

The crystal structures of both [*p*BrPh$_3$N][DDQ] and [*p*MeOPh$_3$N][DDQ] were optimized with a closed shell singlet state and triplet state. The triplet state geometry was used as a starting point for the open shell singlet state optimization, but yielded for [*p*MeOPh$_3$N][DDQ] a open shell state, while for [*p*BrPh$_3$N][DDQ] a closed shell singlet state was obtained. All wavefunctions were checked on their stability.

Table S8. Calculated energies at the (U)ωB97X-D/6-311+G(d,p) level of theory and Gibbs free energy corrections for the amine–DDQ crystal structures optimized at the (U)ωB97X-D/6-31G(d) level of theory. CS: closed shell singlet, OS: Open shell singlet, T: triplet state.

Compound	[*p*BrPh$_3$N][DDQ]	[*p*MeOPh$_3$N][DDQ]
E_{CS} (hartree)	-11440.4982905	-4063.35122671
Gibbs free energy correction CS (Hartree)[a]	0.290563	0.425043
E_{OS} (hartree)	–	-4063.35977924
Gibbs free energy correction OS (Hartree)[a]	–	0.424703
E_T (hartree)	-11440.4774104	-4063.35910342
Gibbs free energy correction T (Hartree)[a]	0.290919	0.423127
ΔE_{CS-T} (kcal/mol)	+13.1	–
ΔE_{OS-T} (kcal/mol)	–	+0.42

[a] at the (U)ωB97X-D/6-31G(d) level of theory.

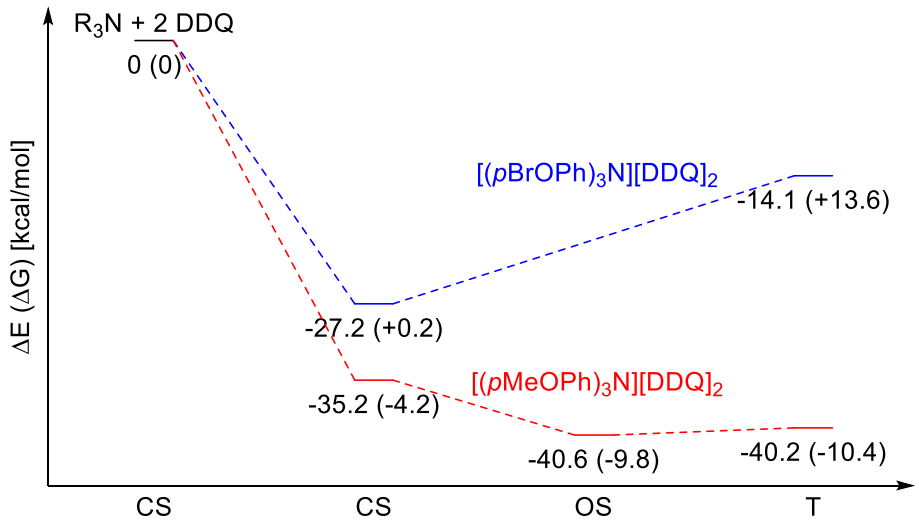


Figure S36. Energy diagram for the formation of [(*p*BrPh)$_3$N][DDQ]$_2$ (blue) and [(*p*MeOPh)$_3$N][DDQ]$_2$ (red) from separate starting materials with the Gibbs free energies in brackets.

Table S9. Total calculated Mulliken charges and spin densities for the different fragments at the (U)ωB97X-D/6-311+G(d,p)//(U)ωB97X-D/6-31G(d) level of theory. CS: closed shell singlet, OS: Open shell singlet, T: triplet state.

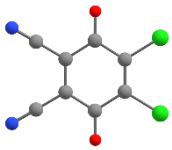
Compound	[*p*BrPh$_3$N][DDQ] (CS)	[*p*BrPh$_3$N][DDQ] (T)	[*p*MeOPh$_3$N][DDQ] (CS)	[*p*MeOPh$_3$N][DDQ] (OS)	[*p*MeOPh$_3$N][DDQ] (T)
Charge Amine	+0.12	+0.76	+0.19	+0.70	+0.72
Charge DDQ–B	–0.07	–0.69	–0.20	–0.62	–0.62
Charge DDQ–C	–0.05	–0.08	+0.01	–0.08	–0.10
Spin density Amine	–	+1.00	–	–0.95	+1.01
Spin density DDQ–B	–	+0.99	–	+0.90	+0.92
Spin density DDQ–C	–	+0.01	–	+0.05	+0.08

9.5 Coordinates of All Calculated Structures

DDQ

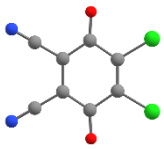
Cl	2.588616	1.609616	-0.000149
Cl	2.588617	-1.609616	-0.000038
O	-0.136448	2.662091	0.000057
O	-0.136447	-2.662091	-0.000035
N	-3.589748	2.052575	-0.000053
N	-3.589746	-2.052576	-0.000133
C	-1.399835	0.674580	0.000070
C	-1.399833	-0.674582	0.000118
C	-0.116963	1.456200	0.000129
C	-0.116963	-1.456197	0.000264
C	1.159125	0.674112	0.000024
C	1.159123	-0.674112	0.000079
C	-2.606773	1.440425	-0.000037
C	-2.606772	-1.440426	0.000070

DDQ$^{\bullet-}$



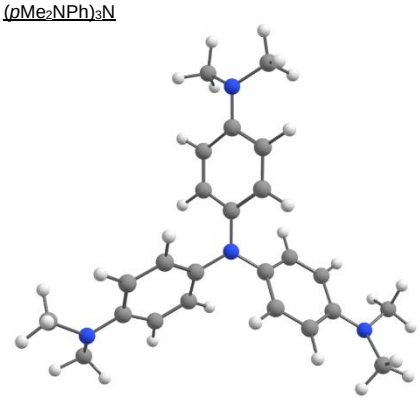
Cl	2.578928	1.597748	-0.000027
Cl	2.578933	-1.597744	0.000033
O	-0.121050	2.715152	-0.000337
O	-0.121045	-2.715152	0.000390
N	-3.583859	2.017926	0.000283
N	-3.583855	-2.017932	-0.000459
C	-1.356685	0.697420	0.000018
C	-1.356683	-0.697423	0.000028
C	-0.134649	1.479207	0.000153
C	-0.134646	-1.479208	-0.000225
C	1.108437	0.679058	-0.000010
C	1.108438	-0.679057	-0.000024
C	-2.581513	1.431783	0.000001
C	-2.581511	-1.431787	0.000177

DDQ^{2-}



Cl	2.577002	1.589283	0.000043
Cl	2.576645	-1.589707	0.000225
O	-0.100715	2.774678	-0.000136
O	-0.101341	-2.774505	-0.000039
N	-3.580399	2.013799	0.000661
N	-3.580191	-2.014042	0.000100
C	-1.336000	0.724272	-0.000290
C	-1.336160	-0.723824	-0.000176
C	-0.149498	1.518117	-0.000247
C	-0.149838	-1.517931	0.000018
C	1.062056	0.685969	-0.000053
C	1.061902	-0.686055	0.000027
C	-2.565352	1.435759	-0.000464
C	-2.565680	-1.435052	-0.000230

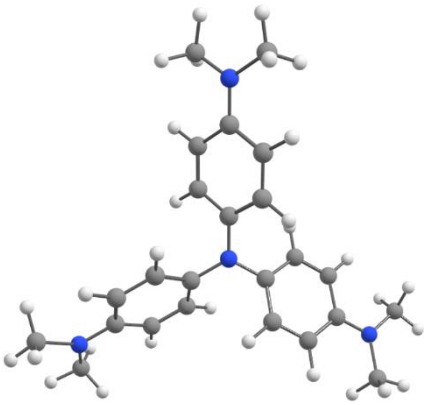
(*p*Me$_2$NPh)$_3$N



C	6.430636	-0.630784	-0.710790
N	5.475653	-1.533831	-0.105529
C	5.961033	-2.396466	0.950323
C	4.134605	-1.147122	-0.073824
C	3.657386	-0.080531	-0.856872
C	2.314509	0.270817	-0.858363
C	1.389344	-0.397134	-0.053436
N	0.024365	-0.024656	-0.044571
C	-0.335790	1.343740	-0.055124
C	-1.400276	1.803776	-0.832818
C	-1.768109	3.142257	-0.832038
C	-1.060728	4.095632	-0.077456
N	-1.398120	5.449765	-0.109707
C	-0.865367	6.309408	0.925605
C	-2.673209	5.820922	-0.684337
C	0.010611	3.623273	0.702388
C	0.355526	2.279075	0.717904
C	-0.980229	-1.020107	0.001170
C	-0.880324	-2.181545	-0.768111
C	-1.857627	-3.165490	-0.718064
C	-2.997544	-3.025509	0.094529
N	-3.972167	-4.022625	0.161632
C	-3.977009	-5.040894	-0.866887
C	-5.242833	-3.693962	0.770789
C	-3.102932	-1.840384	0.844684
C	-2.108205	-0.872640	0.810661
C	1.859195	-1.439898	0.748029
C	3.195573	-1.814153	0.733693
H	6.216481	-0.494971	-1.776665
H	6.446200	0.363899	-0.235107
H	7.430445	-1.063622	-0.635338
H	7.026966	-2.580805	0.800585
H	5.820700	-1.968125	1.956488
H	5.457466	-3.369171	0.921281
H	4.331818	0.483235	-1.490528
H	1.979234	1.091271	-1.485657
H	-1.960956	1.097258	-1.437452
H	-2.612139	3.438348	-1.443671
H	-1.135156	5.978599	1.942082
H	0.227299	6.363289	0.864003
H	-1.246568	7.322533	0.781191
H	-2.796096	6.903794	-0.614266
H	-3.529543	5.341095	-0.181987
H	-2.711889	5.558991	-1.747500
H	0.583242	4.302786	1.322562
H	1.182259	1.947937	1.339144
H	-0.018041	-2.318768	-1.413654
H	-1.726143	-4.045276	-1.336881

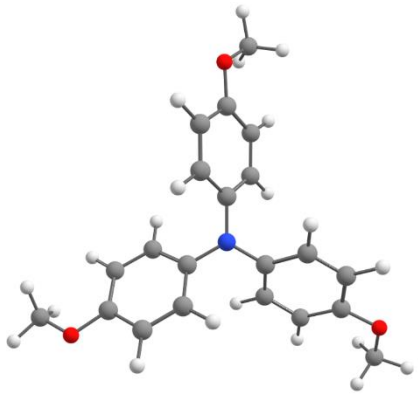
H	-4.813015	-5.721653	-0.692938
H	-4.072704	-4.626341	-1.883949
H	-3.059707	-5.638921	-0.828046
H	-5.753593	-2.850794	0.276722
H	-5.113098	-3.440478	1.828781
H	-5.897872	-4.566629	0.726147
H	-3.962375	-1.663726	1.480465
H	-2.216651	0.023943	1.413523
H	1.164079	-1.971171	1.391147
H	3.501813	-2.630776	1.376791

(pMe$_2$NPh)$_3$N$^{\bullet+}$



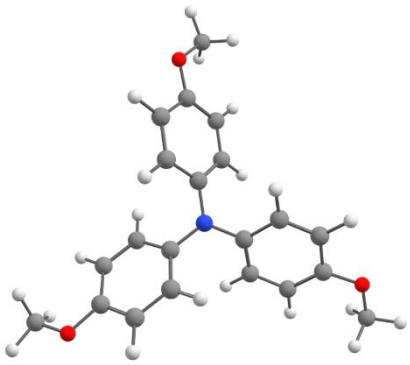
C	-6.353205	-0.840549	0.753561
N	-5.366282	-1.594150	-0.001068
C	-5.781292	-2.763242	-0.757636
C	-4.061497	-1.207170	0.000325
C	-3.624372	-0.086326	0.753718
C	-2.303871	0.303945	0.750788
C	-1.346067	-0.400920	0.002106
N	-0.000958	-0.000848	0.002256
C	0.325135	1.364154	0.002139
C	1.414179	1.841195	0.751178
C	1.736613	3.179864	0.754172
C	0.984915	4.118866	0.000384
N	1.302201	5.442346	-0.000886
C	0.497986	6.386329	-0.758201
C	2.447502	5.920318	0.754940
C	-0.111202	3.621417	-0.752015
C	-0.430177	2.281922	-0.747472
C	1.018462	-0.965486	0.001290
C	0.889022	-2.146934	0.751003
C	1.888386	-3.094248	0.753643
C	3.076788	-2.911684	-0.000891
N	4.065702	-3.846729	-0.001727
C	3.909516	-5.076760	0.755923
C	5.284486	-3.621213	-0.760085
C	3.191717	-1.714262	-0.754496
C	2.189947	-0.769542	-0.749603
C	-1.763052	-1.514239	-0.747134
C	-3.082520	-1.907934	-0.751689
H	-6.139478	-0.861289	1.829398
H	-6.395871	0.204174	0.422952
H	-7.337287	-1.281525	0.597639
H	-6.847367	-2.929102	-0.605475
H	-5.609506	-2.628921	-1.832799
H	-5.249473	-3.662989	-0.425678
H	-4.324739	0.471611	1.362149
H	-1.994467	1.151206	1.354134
H	1.992917	1.149624	1.354817
H	2.569826	3.507072	1.362979
H	0.528700	6.169892	-1.833251
H	-0.547251	6.376543	-0.426581
H	0.887956	7.392364	-0.606510
H	2.556993	6.993275	0.600160
H	3.374155	5.435858	0.424505
H	2.322073	5.744377	1.830507
H	-0.706047	4.290176	-1.361016
H	-1.259654	1.926921	-1.350399
H	0.001590	-2.303313	1.355645
H	1.756804	-3.979474	1.362755
H	4.785252	-5.706527	0.602014
H	3.819676	-4.878726	1.831209
H	3.027737	-5.639384	0.426506
H	5.797044	-2.709575	-0.430243
H	5.080892	-3.541641	-1.835140
H	5.962431	-4.460421	-0.607410
H	4.067293	-1.532556	-1.364658
H	2.295598	0.125856	-1.353487
H	-1.040802	-2.055157	-1.349901
H	-3.364036	-2.757690	-1.360516

(pMeOPh)$_3$N



C	6.370808	0.143070	-0.659412
O	5.507424	0.919060	0.136175
C	4.177938	0.634132	0.092543
C	3.603792	-0.374027	-0.680294
C	2.223312	-0.568851	-0.655584
C	1.399771	0.211382	0.153931
N	0.000737	0.000135	0.195457
C	-0.516104	-1.317074	0.154281
C	0.054726	-2.328581	0.940102
C	-0.441390	-3.619456	0.900706
C	-1.540253	-3.933860	0.093673
O	-1.959110	-5.227361	0.137951
C	-3.061358	-5.587327	-0.659589
C	-2.123778	-2.933288	-0.682006
C	-1.601624	-1.640602	-0.657621
C	-0.881996	1.106013	0.154618
C	-0.620445	2.208194	-0.657187
C	-1.479844	3.305997	-0.681254
C	-2.638008	3.299843	0.094616
O	-3.549692	4.308517	0.139126
C	-3.311820	5.443148	-0.658754
C	-2.914068	2.190672	0.901592
C	-2.043271	1.116347	0.940658
C	1.989782	1.214012	0.937006

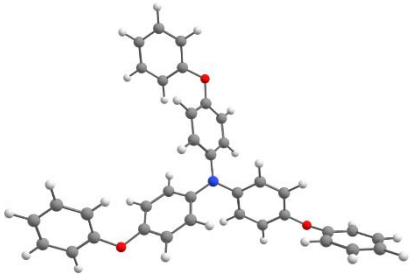
(pMeOPh)$_3$N$^{\bullet+}$



C	5.234406	-3.650197	-0.552465
O	4.952877	-2.457956	0.168376
C	3.732497	-1.925272	0.098757
C	2.672312	-2.448178	-0.659450
C	1.443841	-1.810685	-0.655443
C	1.249163	-0.643066	0.097418
N	-0.000104	-0.000832	0.096190
C	-1.181076	-0.761193	0.096853
C	-1.261766	-1.947189	0.854332
C	-2.421854	-2.685382	0.854961
C	-3.534650	-2.268379	0.097956
O	-4.606990	-3.057742	0.167713
C	-5.780877	-2.702853	-0.550878
C	-3.456575	-1.088246	-0.659376
C	-2.289536	-0.344322	-0.655253
C	-0.068321	1.402204	0.096713
C	0.846028	2.153865	-0.656265
C	0.784636	3.536492	-0.660744
C	-0.197983	4.193934	0.097249
O	-0.345847	5.517274	0.166750
C	0.547456	6.356408	-0.553102
C	-1.114589	3.438556	0.855182
C	-1.054758	2.064803	0.854806
C	2.315643	-0.119648	0.856011
C	3.535622	-0.754017	0.856797
C	3.355642	1.430401	0.897172
H	7.375892	0.527187	-0.479413
H	6.133500	0.239958	-1.727420
H	6.334670	-0.918289	-0.379129
H	4.209490	-1.008220	-1.317682
H	1.783394	-1.348299	-1.269833
H	0.899176	-2.092138	1.579955
H	-0.000184	-4.405025	1.505465
H	-2.856208	-5.432144	-1.727376
H	-3.232645	-6.649366	-0.478292
H	-3.962537	-5.024035	-0.382243
H	-2.974320	-3.141199	-1.321272
H	-2.054680	-0.870399	-1.273979
H	0.272997	2.216285	-1.273688
H	-1.235431	4.146811	-1.320486
H	-4.146631	6.121616	-0.477358
H	-2.373889	5.943082	-0.381827
H	-3.280062	5.187682	-1.726494
H	-3.814921	2.200502	1.506473
H	-2.259911	0.266502	1.580377
H	1.362476	1.828646	1.575063
H	3.814834	2.207282	1.499766

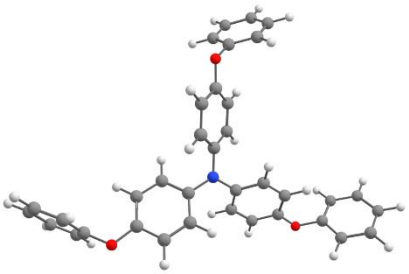
H	6.273008	-3.889002	-0.329542
H	5.117808	-3.493045	-1.630318
H	4.589637	-4.470788	-0.219467
H	2.802411	-3.337797	-1.263362
H	0.633471	-2.201634	-1.261712
H	-0.417673	-2.259429	1.459962
H	-2.511020	-3.589245	1.446948
H	-5.588246	-2.679653	-1.629019
H	-6.507834	-3.482009	-0.327558
H	-6.167034	-1.733916	-0.216183
H	-4.292024	-0.754771	-1.262599
H	-2.222270	0.553527	-1.260613
H	1.589698	1.646836	-1.262065
H	1.490369	4.093444	-1.264736
H	0.236435	7.375575	-0.329540
H	1.580111	6.206423	-0.219760
H	0.469835	6.177799	-1.631119
H	-1.852554	3.967571	1.447572
H	-1.746616	1.489675	1.460903
H	2.162877	0.766833	1.462304
H	4.362315	-0.378996	1.449512

(*p*PhONPh)$_3$N



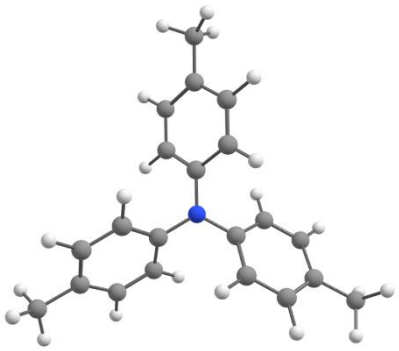
C	8.888249	0.082977	-1.828475
C	9.146355	-0.555698	-0.617273
C	8.175272	-0.601426	0.376668
C	6.939311	0.003382	0.158438
O	6.049638	-0.031324	1.203161
C	4.699101	-0.018293	0.944567
C	3.907565	0.860495	1.675583
C	2.527761	0.850295	1.512826
C	1.927258	-0.013650	0.591899
N	0.523815	-0.010376	0.409926
C	-0.174023	-1.233045	0.266461
C	-1.199691	-1.357651	-0.677908
C	-1.895055	-2.550815	-0.815845
C	-1.561116	-3.641814	-0.015483
O	-2.171703	-4.865226	-0.165854
C	-3.542148	-4.940601	-0.163098
C	-4.349464	-4.057385	0.552727
C	-5.729948	-4.236885	0.540149
C	-6.304982	-5.287679	-0.169227
C	-5.485270	-6.167869	-0.872804
C	-4.105583	-5.996907	-0.875895
C	-0.536312	-3.536261	0.917764
C	0.149239	-2.336082	1.062382
C	-0.183968	1.214046	0.377243
C	0.335125	2.319553	-0.303488
C	-0.361482	3.521759	-0.333579
C	-1.590916	3.626922	0.306221
O	-2.219679	4.850762	0.301923
C	-3.531783	4.932269	-0.092030
C	-4.267940	5.995751	0.426516
C	-5.589067	6.172498	0.031815
C	-6.181224	5.291429	-0.870991
C	-5.435012	4.233763	-1.382937
C	-4.108587	4.047972	-1.002758
C	-2.121594	2.533808	0.988495
C	-1.417420	1.338506	1.027638
C	2.737452	-0.883470	-0.147291
C	4.112801	-0.900648	0.038761
C	6.670270	0.653621	-1.045236
C	7.649628	0.684398	-2.034136
H	9.646549	0.112792	-2.604446
H	10.108878	-1.027920	-0.444255
H	8.355533	-1.096956	1.324858
H	4.381064	1.533009	2.382951
H	1.908945	1.525612	2.094930
H	-1.449682	-0.510461	-1.308571
H	-2.688404	-2.643191	-1.550663
H	-3.902660	-3.242694	1.112638
H	-6.358261	-3.548679	1.098018
H	-7.382127	-5.420956	-0.172623
H	-5.921445	-6.992216	-1.429230
H	-3.450885	-6.669203	-1.420418
H	-0.291904	-4.395968	1.532631
H	0.941602	-2.250065	1.798987
H	1.289593	2.233742	-0.812757
H	0.034467	4.383175	-0.860961
H	-3.790448	6.668698	1.130960
H	-6.160024	7.002262	0.437908
H	-7.214409	5.429371	-1.173509
H	-5.883515	3.544475	-2.092394
H	-3.526860	3.227469	-1.409071
H	-3.076707	2.626564	1.495535
H	-1.822878	0.489720	1.568975
H	2.280952	-1.559727	-0.862982
H	4.735285	-1.583539	-0.530480
H	5.708206	1.129205	-1.203894
H	7.439563	1.190844	-2.971677

(*p*PhONPh)$_3$N$^{\bullet+}$



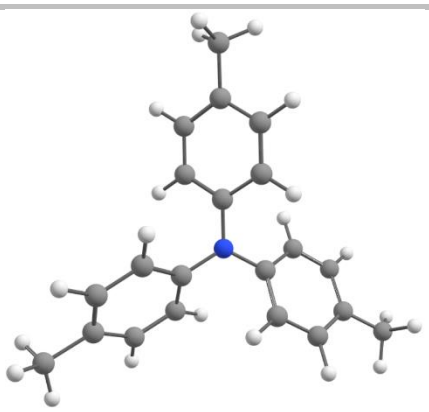
C	8.848240	-0.163711	0.724940
C	8.232990	-1.065661	1.590170
C	7.105649	-1.773381	1.180620
C	6.615049	-1.561061	-0.100330
O	5.515509	-2.303560	-0.531540
C	4.283359	-1.785440	-0.408820
C	4.008040	-0.541780	0.179470
C	2.701180	-0.098860	0.258710
C	1.650340	-0.885300	-0.241510
N	0.324590	-0.429050	-0.157830
C	-0.712021	-1.332949	0.128280
C	-1.955070	-1.209059	-0.513680
C	-2.977691	-2.097859	-0.239750
C	-2.769541	-3.127989	0.689610
O	-3.696471	-4.040259	1.022500
C	-4.963891	-3.969099	0.444240
C	-5.948591	-3.217508	1.071240
C	-7.224651	-3.190568	0.514660
C	-7.498121	-3.906338	-0.648950
C	-6.495511	-4.656448	-1.259700
C	-5.214931	-4.692329	-0.713810
C	-1.528151	-3.254689	1.336330
C	-0.509721	-2.370569	1.058540
C	0.035600	0.930441	-0.361370
C	0.725360	1.660870	-1.348210
C	0.438340	2.993070	-1.545800
C	-0.539140	3.628821	-0.761330
O	-0.743649	4.929391	-1.024570
C	-1.720669	5.624921	-0.312190
C	-1.352969	6.309591	0.838050
C	-2.322449	7.041761	1.518700
C	-3.632829	7.079871	1.047260
C	-3.978979	6.387691	-0.111260
C	-3.019659	5.651611	-0.801710
C	-1.229290	2.907911	0.224680
C	-0.942180	1.569681	0.418340
C	1.933929	-2.134070	-0.827570
C	3.235369	-2.575850	-0.911250
C	7.214430	-0.669981	-0.980540
C	8.340310	0.031609	-0.557710
H	9.728700	0.382109	1.047750
H	8.632680	-1.224841	2.586450
H	6.615849	-2.488191	1.833640
H	4.812720	0.060780	0.583470
H	2.482720	0.850160	0.736950
H	-2.104130	-0.428609	-1.252350
H	-3.928151	-2.008939	-0.752120
H	-5.715811	-2.677389	1.983170
H	-8.007341	-2.613568	0.996560
H	-8.495381	-3.885568	-1.076000
H	-6.709511	-5.221228	-2.161310
H	-4.421391	-5.277979	-1.166250
H	-1.399381	-4.049209	2.062600
H	0.440019	-2.454570	1.575950
H	1.461700	1.164780	-1.971430
H	0.944040	3.568560	-2.312860
H	-0.324069	6.273921	1.180800
H	-2.049729	7.587421	2.416220
H	-4.383289	7.655521	1.579020
H	-4.997309	6.424361	-0.484640
H	-3.263819	5.114281	-1.712310
H	-1.971250	3.400341	0.841810
H	-1.454870	1.016581	1.198230
H	1.128719	-2.733250	-1.239070
H	3.477229	-3.525110	-1.375730
H	6.808790	-0.542721	-1.978980
H	8.824250	0.727029	-1.235860

(*p*MePh)$_3$N



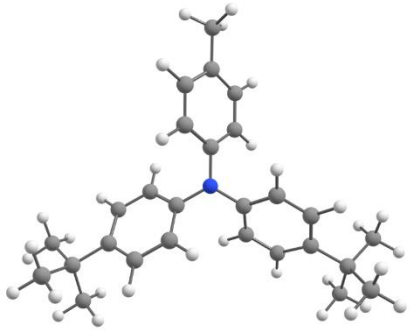
C	1.364462	-5.581901	0.014738
H	0.498185	-6.212505	0.238767
H	1.775292	-5.902710	-0.948132
H	2.124814	-5.784810	0.779169
H	1.812536	3.979756	-1.376630
N	-0.001818	0.002132	-0.002401
C	-0.391549	-2.281633	0.778341
H	-1.212750	-1.924197	1.391693
C	0.329786	-1.373452	-0.002432
C	-0.068294	-3.632969	0.761939
H	-0.647526	-4.321325	1.372995
C	1.024452	0.976438	0.000066
C	-2.299693	-0.265487	-0.792574
H	-1.980056	-1.095590	-1.414804
C	-1.359048	0.402784	-0.001639
C	1.708986	-3.203010	-0.776411
H	2.532304	-3.552560	-1.395146
C	1.383485	-1.852693	-0.787383
H	1.946520	-1.160150	-1.405232
C	0.915895	2.129541	-0.782753
H	0.034516	2.275359	-1.399428
C	0.990728	-4.120830	-0.006375
C	-4.068703	1.203862	-0.004993
C	-3.631546	0.127518	-0.781397
H	-4.345024	-0.406726	-1.404713
C	-5.521312	1.609406	0.013103
H	-5.641099	2.651228	0.326423
H	-5.978476	1.499950	-0.975974
H	-6.097193	0.987707	0.709835
C	3.073002	2.922665	0.009029
C	1.922034	3.087983	-0.763891
C	3.173762	1.762854	0.781277
H	4.052414	1.609539	1.403682
C	4.181783	3.944990	-0.008421
H	4.673043	4.017636	0.967482
H	4.952102	3.680812	-0.743607
H	3.804780	4.938495	-0.270999
C	2.166391	0.806727	0.789705
H	2.259768	-0.079787	1.409180
C	-3.118357	1.872007	0.769055
H	-3.425865	2.713830	1.385019
C	-1.786038	1.476223	0.785078
H	-1.066917	2.004987	1.402857

$(p\text{MePh})_3N^+$



C	-2.730831	-5.018494	-0.010491
H	-3.466039	-5.030411	-0.824277
H	-2.046053	-5.855114	-0.173106
H	-3.271763	-5.189293	0.924175
H	3.983632	1.785670	-1.342081
N	0.000618	-0.000560	-0.001406
C	-1.844308	-1.398518	0.752655
H	-2.218476	-0.577960	1.355625
C	-0.668596	-1.236887	0.000299
C	-2.490214	-2.621579	0.753036
H	-3.386170	-2.747198	1.353385
C	1.406097	0.038580	0.000194
C	-1.915309	1.296903	-0.759590
H	-2.241884	0.459586	-1.367106
C	-0.735562	1.197357	-0.002923
C	-0.827220	-3.524301	-0.737811
H	-0.438590	-4.347532	-1.329625
C	-0.160278	-2.312608	-0.747223
H	0.732016	-2.179989	-1.349753
C	2.082797	1.011900	-0.754401
H	1.521150	1.713664	-1.361813
C	-2.000978	-3.705022	0.008522
C	-2.200673	3.588920	-0.008660
C	-2.627003	2.482936	-0.758747
H	-3.526042	2.561569	-1.362487
C	-3.001438	4.860411	0.011166
H	-2.365034	5.732196	0.185026
H	-3.542335	5.007197	-0.927615
H	-3.743701	4.826950	0.817904
C	4.209592	0.121447	0.008674
C	3.465444	1.041415	-0.744922
C	3.516760	-0.838903	0.760033
H	4.073828	-1.546968	1.365977
C	5.711963	0.149087	-0.011024
H	6.091585	1.166592	-0.138207
H	6.132733	-0.265984	0.908610
H	6.089918	-0.450583	-0.847965
C	2.134416	-0.892399	0.759588
H	1.611680	-1.622596	1.368197
C	-1.021776	3.470128	0.741926
H	-0.680952	4.311317	1.337928
C	-0.289630	2.296642	0.750013
H	0.606668	2.210714	1.355147

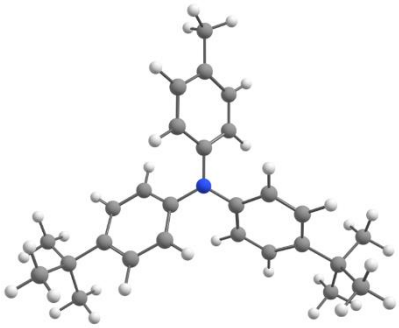
$(p^t\text{BuNPh})_3N$



C	-5.028630	-2.103372	-0.005518
C	-3.709245	-1.322684	-0.020749
C	-3.513916	-0.165469	-0.777107
C	-2.299431	0.514492	-0.778194
C	-1.234314	0.066545	0.003394
N	-0.000791	0.758782	0.018699
C	0.015550	2.174145	0.008304
C	-0.881266	2.901716	0.796734
C	-0.869494	4.290558	0.772635
C	0.043803	4.999026	-0.011757
C	0.079056	6.506811	0.001762
C	0.939442	4.261627	-0.788987
C	0.924674	2.872188	-0.792121
C	1.216156	0.038587	0.004173
C	2.306852	0.464731	0.770383
C	3.500060	-0.240842	0.744930
C	3.660344	-1.405033	-0.018586
C	4.997605	-2.154642	-0.002207
C	2.558825	-1.821790	-0.768467
C	1.361239	-1.112627	-0.770562
C	-1.416456	-1.085134	0.777046
C	-2.625497	-1.763213	0.750950
H	-4.312428	0.224065	-1.399204
H	-2.178133	1.404695	-1.387560
H	-1.593697	2.371831	1.421319
H	-1.580388	4.835331	1.389593
H	1.655576	4.783340	-1.419679
H	1.620663	2.319821	-1.415739
H	2.213944	1.356019	1.383107
H	4.323341	0.125023	1.352883
H	2.620400	-2.712131	-1.384779
H	0.528875	-1.458594	-1.375458
H	-0.601291	-1.447790	1.395441
H	-2.725106	-2.654688	1.364658
C	-6.090043	-1.468220	-0.914525
H	-6.335155	-0.447454	-0.600295
H	-5.763659	-1.439201	-1.960199
H	-7.012129	-2.058353	-0.871651
C	-5.585719	-2.139763	1.430616
H	-4.891581	-2.627305	2.122991
H	-5.771874	-1.125536	1.800589
H	-6.531115	-2.694796	1.459344
C	-4.777487	-3.542888	-0.494202
H	-4.378684	-3.542455	-1.514577
H	-4.061764	-4.069528	0.145565
H	-5.712699	-4.115621	-0.491194
C	5.314958	-2.605125	1.436720
H	6.269158	-3.144875	1.465945
H	5.392394	-1.753846	2.120994
H	4.532345	-3.271028	1.816562

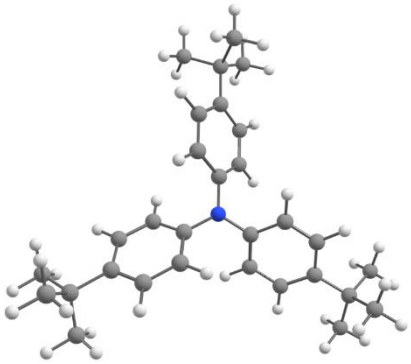
C	6.114793	-1.219905	-0.504452
H	6.213784	-0.330524	0.126504
H	7.079460	-1.741521	-0.500481
H	5.910070	-0.884852	-1.527219
C	4.976628	-3.399911	-0.899548
H	4.784009	-3.141913	-1.946989
H	5.949615	-3.901635	-0.855607
H	4.217357	-4.120589	-0.575616
H	0.735422	6.880062	0.797704
H	-0.916575	6.928094	0.174310
H	0.454469	6.905615	-0.946142

(p^tBuNPh)$_3$N$^{\bullet+}$



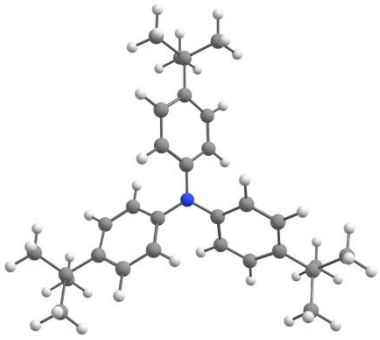
C	-4.994890	-2.100077	-0.000680
C	-3.679966	-1.319846	-0.021552
C	-2.578390	-1.787143	0.719658
C	-1.369239	-1.121269	0.730005
C	-1.224584	0.064636	-0.011249
N	-0.001232	0.755107	-0.007659
C	1.209446	0.042363	-0.010601
C	1.332174	-1.136473	-0.760268
C	2.531595	-1.829887	-0.760207
C	3.637619	-1.389173	-0.019743
C	4.971411	-2.136674	0.002584
C	3.487443	-0.205503	0.727122
C	2.305549	0.507562	0.736771
C	0.011480	2.162390	-0.002299
C	0.967485	2.858893	-0.759436
C	0.970332	4.242294	-0.746936
C	0.039763	4.966565	0.012112
C	0.036613	6.469532	-0.003863
C	-0.903135	4.253611	0.766361
C	-0.929452	2.870260	0.763064
C	-2.308982	0.554200	-0.753787
C	-3.509663	-0.136844	-0.754779
H	-2.672950	-2.689304	1.314853
H	-0.544440	-1.488163	1.331621
H	0.500367	-1.483124	-1.364396
H	2.602703	-2.726460	-1.363828
H	4.313435	0.161517	1.327184
H	2.208490	1.402507	1.342226
H	1.677742	2.312073	-1.370511
H	1.701974	4.775987	-1.346058
H	-1.619540	4.795508	1.376370
H	-1.647028	2.331531	1.372759
H	-2.194918	1.451914	-1.352176
H	-4.323157	0.254540	-1.353335
C	-5.512519	-2.168383	1.450833
H	-4.810539	-2.681287	2.116074
H	-5.692341	-1.165525	1.852603
H	-6.457735	-2.720316	1.479658
C	-6.075244	-1.444584	-0.871835
H	-6.323861	-0.434950	-0.526254
H	-5.777104	-1.392733	-1.924937
H	-6.991360	-2.040692	-0.821673
C	-4.739759	-3.526470	-0.528807
H	-4.362519	-3.504183	-1.556781
H	-4.018273	-4.072269	0.087693
H	-5.675424	-4.095141	-0.522756
C	5.284069	-2.557913	1.453209
H	4.504459	-3.217757	1.848580
H	6.234962	-3.099974	1.482920
H	5.374094	-1.696973	2.123317
C	4.948561	-3.395709	-0.874951
H	4.759340	-3.158381	-1.927793
H	5.922891	-3.890791	-0.822732
H	4.197285	-4.117870	-0.536320
C	6.080443	-1.198984	-0.516446
H	6.188927	-0.304151	0.104846
H	7.041209	-1.724129	-0.508975
H	5.876456	-0.878630	-1.543726
H	-0.351940	6.878959	0.932500
H	1.040620	6.870388	-0.167317
H	-0.602169	6.837887	-0.815705

(p^tBuNPh)$_3$N



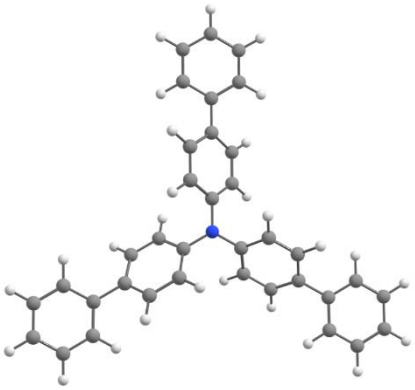
C	5.555825	-1.617340	-0.003237
C	4.076967	-1.213466	-0.020047
C	3.110878	-1.879483	-0.776537
C	1.777133	-1.481309	-0.778777
C	1.356445	-0.404683	0.002203
N	0.000829	-0.000967	0.017481
C	-1.027092	-0.972645	0.001956
C	-0.923352	-2.133821	0.775908
C	-1.931226	-3.085490	0.750632
C	-3.089987	-2.921972	-0.020520
C	-4.180456	-3.999464	-0.003420
C	-3.181844	-1.752755	-0.777945
C	-2.169008	-0.798004	-0.780040
C	-0.327254	1.375051	0.002365
C	-1.382693	1.865256	0.779326
C	-1.704410	3.213567	0.754152
C	-0.986833	4.135420	-0.020093
C	-1.376576	5.618073	-0.003377
C	0.069965	3.630945	-0.780278
C	0.391794	2.276749	-0.782370
C	2.309621	0.267498	0.775332
C	3.638169	-0.127970	0.750198
H	3.388034	-2.724235	-1.397826
H	1.054346	-2.014421	-1.388565
H	-0.044336	-2.287109	1.394202
H	-1.810931	-3.974160	1.364690
H	-4.051239	-1.569629	-1.400048
H	-2.267814	0.094159	-1.390563
H	-1.952330	1.180473	1.399836
H	-2.532593	3.553267	1.370556
H	0.660678	4.292486	-1.404610
H	1.212374	1.916502	-1.395008
H	2.002071	1.105638	1.392883
H	4.347072	0.422075	1.363532
C	5.839044	-2.823452	-0.909562
H	5.276016	-3.709089	-0.594226
H	5.592501	-2.611332	-1.955994
H	6.904412	-3.075145	-0.864904
C	5.968889	-1.989140	1.433871
H	5.835566	-1.150026	2.124531
H	5.369946	-2.827944	1.805176
H	7.025392	-2.281687	1.463717
C	6.414925	-0.436117	-0.493906
H	6.137409	-0.152009	-1.514919
H	6.294857	0.445587	0.144122
H	7.477055	-0.709128	-0.490016
C	-1.254815	6.163457	1.432551
H	-1.529564	7.224728	1.462313
H	-1.911829	5.629290	2.126747
H	-0.227315	6.064611	1.799516
C	-2.831305	5.770623	-0.487726
H	-3.531854	5.226186	0.153921
H	-3.126173	6.826885	-0.483519
H	-2.943029	5.387216	-1.507894
C	-0.477888	6.465455	-0.914773
H	-0.541848	6.143616	-1.960293
H	-0.793476	7.513708	-0.871066
H	0.571812	6.422405	-0.603231
C	-4.710522	-4.168957	1.433408
H	-5.136256	-3.229806	1.803446
H	-5.493419	-4.936317	1.463365
H	-3.918308	-4.473726	2.125090
C	-3.588143	-5.335374	-0.491876
H	-4.356485	-6.117865	-0.487507
H	-3.202451	-5.238872	-1.512728
H	-2.765353	-5.672244	0.147214
C	-5.365340	-3.641405	-0.911261
H	-6.116715	-4.437517	-0.866723
H	-5.850322	-2.710336	-0.597107
H	-5.057160	-3.534960	-1.957431

(p^tBuNPh)$_3$N$^{\bullet+}$



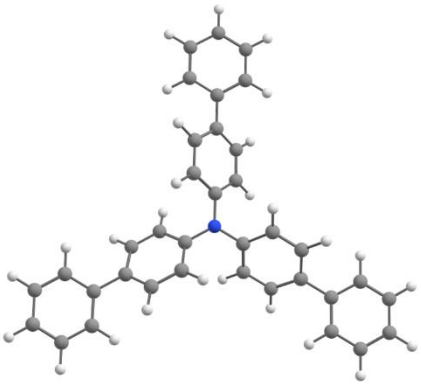
C	-4.677756	3.349021	-0.004992
C	-3.448630	2.439458	0.020206
C	-2.306859	2.787396	-0.725450
C	-1.171534	2.001923	-0.732987
C	-1.146888	0.812658	0.015770
N	0.000176	0.000488	0.015044
C	1.277171	0.587501	0.015741
C	1.519087	1.748733	0.763277
C	2.782605	2.317334	0.761044
C	3.837441	1.766193	0.020011
C	5.240019	2.375158	-0.005128
C	3.567467	0.603206	-0.725176
C	2.319270	0.013366	-0.732600
C	-0.129857	-1.399027	0.015716
C	0.754023	-2.188888	0.764439
C	0.614791	-3.567448	0.762303
C	-0.388909	-4.205589	0.020093
C	-0.562517	-5.724769	-0.005058
C	-1.260139	-3.390545	-0.726461
C	-1.147034	-2.014620	-0.733897
C	-2.273151	0.441226	0.763660
C	-3.397732	1.250604	0.761539
H	-2.310254	3.690731	-1.326357
H	-0.314658	2.279728	-1.337534
H	0.726997	2.179080	1.366972
H	2.944542	3.203063	1.363176
H	4.351365	0.153785	-1.325710
H	2.130994	-0.867890	-1.336621
H	1.522067	-1.717918	1.368890
H	1.300132	-4.150443	1.365392
H	-2.040366	-3.844963	-1.328026
H	-1.815332	-1.411061	-1.338872
H	-2.249234	-0.459819	1.367497
H	-4.245408	0.947655	1.363983
C	-5.188687	3.458636	-1.456302
H	-4.439463	3.892396	-2.126321
H	-5.470110	2.476148	-1.850038
H	-6.073047	4.103483	-1.488458
C	-5.817434	2.813042	0.872286
H	-6.167640	1.831211	0.534693
H	-5.524151	2.739067	1.925429
H	-6.668536	3.498541	0.818497
C	-4.278592	4.746125	0.511951
H	-3.903514	4.693358	1.539610
H	-3.506590	5.211280	-0.109461
H	-5.151780	5.406735	0.502635
C	5.591423	2.761119	-1.456640
H	4.881954	3.496136	-1.851497
H	6.592358	3.203901	-1.488705
H	5.592276	1.894722	-2.125782
C	5.345847	3.631019	0.870869
H	5.134967	3.415179	1.924221
H	6.365176	4.025008	0.816847
H	4.670947	4.425064	0.532335
C	6.249533	1.330943	0.513499
H	6.266359	0.429181	-0.107021
H	7.258438	1.756362	0.504429
H	6.015486	1.033626	1.541294
C	-0.400783	-6.222273	-1.456150
H	-1.150182	-5.789976	-2.126918
H	0.591287	-5.975234	-1.848936
H	-0.517534	-7.310521	-1.488337
C	0.470474	-6.443928	0.873291
H	0.302232	-7.523726	0.819357
H	1.496252	-6.256505	0.536760
H	0.386859	-6.152929	1.926347
C	-1.972596	-6.077150	0.510641
H	-2.760765	-5.641264	-0.111689
H	-2.108309	-7.163634	0.501605
H	-2.115359	-5.725529	1.538034

(pPhPh)$_3$N



C	-6.077123	-5.986239	-0.003710
C	-4.733198	-6.350783	-0.002170
C	-3.742988	-5.373991	-0.002820
C	-4.076096	-4.014212	-0.000950
C	-3.019364	-2.973222	0.000550
C	-3.146237	-1.812137	-0.770330
C	-2.156047	-0.839905	-0.780240
C	-1.007228	-0.992454	0.002890
N	0.000580	-0.000480	0.003920
C	1.363596	-0.377002	0.003180
C	1.806108	-1.449347	-0.778280
C	3.143364	-1.820043	-0.768130
C	4.085348	-1.127807	0.001240
C	5.515457	-1.521650	-0.000380
C	5.888013	-2.871155	0.001430
C	7.228959	-3.240699	-0.002300
C	8.224259	-2.266827	-0.003860
C	7.867203	-0.920901	-0.003670
C	6.525918	-0.552666	-0.003960
C	3.632486	-0.050972	0.771840
C	2.294331	0.316283	0.783920
C	-0.354949	1.368246	0.003120
C	-1.419326	1.827905	0.785510
C	-1.770441	3.170382	0.773360
C	-1.065806	4.100629	0.000920
C	-1.439762	5.536053	-0.000570
C	-0.457245	6.533364	-0.001150
C	-0.807481	7.879481	-0.004540
C	-2.148507	8.254606	-0.003380
C	-3.135686	7.272514	-0.000880
C	-2.784151	5.926747	-0.001510
C	0.003292	3.630661	-0.770190
C	0.350928	2.287233	-0.780200
C	-0.873726	-2.144358	0.785000
C	-1.861376	-3.119109	0.772760
C	-5.430859	-3.661279	-0.000540
C	-6.422029	-4.637141	-0.003910
H	-6.850569	-6.748474	-0.004760
H	-4.453549	-7.400319	-0.009960
H	-2.696982	-5.667142	-0.028650
H	-4.019093	-1.683715	-1.404490
H	-2.265396	0.042881	-1.402170
H	1.096334	-1.986895	-1.399030
H	3.468815	-2.641123	-1.400930
H	5.117988	-3.637319	0.029670
H	7.496908	-4.293276	0.005510
H	9.271264	-2.554928	-0.005220
H	8.635808	-0.153466	-0.012840
H	6.256008	0.499561	-0.030870
H	4.333820	0.486944	1.403770
H	1.961309	1.141462	1.405390
H	-1.966269	1.127178	1.408340
H	-2.585723	3.509042	1.406720
H	0.591300	6.249383	0.024890
H	-0.029795	8.637737	0.001420
H	-2.422447	9.305402	-0.004450
H	-4.184581	7.554575	-0.007940
H	-3.560607	5.167012	-0.026640
H	0.550417	4.322838	-1.404300
H	1.170210	1.940954	-1.402230
H	0.006539	-2.268259	1.407790
H	-1.747438	-3.994605	1.406040
H	-5.708749	-2.611133	0.026290
H	-7.467376	-4.342180	0.002820

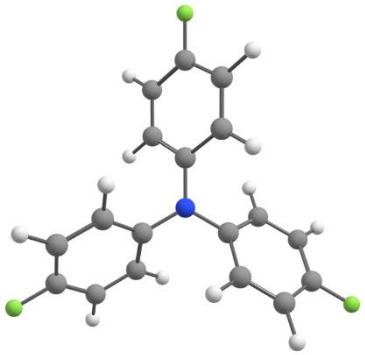
(pPhPh)$_3$N$^{\cdot+}$



C	-8.422858	-1.075639	-0.001626
C	-7.577625	-2.182584	0.019443
C	-6.199229	-2.007036	0.024306

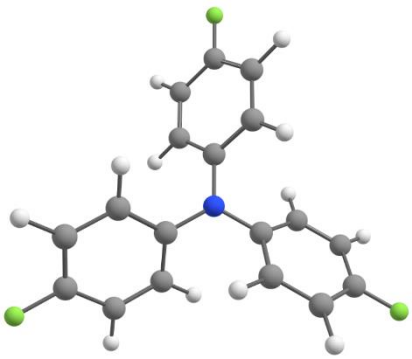
C	-5.645798	-0.720051	-0.000140
C	-4.180827	-0.532837	0.000533
C	-3.582966	0.497108	-0.747662
C	-2.214023	0.682413	-0.749459
C	-1.394175	-0.177692	0.001038
N	-0.000607	-0.000247	0.001114
C	0.849961	-1.118329	0.001266
C	0.515413	-2.258487	-0.749258
C	1.360759	-3.351079	-0.747482
C	2.551617	-3.353513	0.000756
C	3.446824	-4.528165	-0.000042
C	2.919585	-5.826076	-0.025697
C	3.762956	-6.930436	-0.022429
C	5.144553	-6.754481	-0.001779
C	5.679831	-5.468714	0.019726
C	4.838011	-4.363209	0.024713
C	2.866140	-2.205305	0.749599
C	2.037972	-1.099673	0.751861
C	0.542559	1.295351	0.000935
C	-0.067116	2.315149	0.751542
C	0.476903	3.584927	0.749256
C	1.628631	3.886141	0.000363
C	2.199252	5.248350	-0.000237
C	3.587048	5.439608	-0.025769
C	4.122728	6.721765	-0.022277
C	3.280429	7.830958	-0.001534
C	1.899143	7.652727	0.019830
C	1.361696	6.371341	0.024590
C	2.221320	2.853384	-0.748072
C	1.697191	1.575254	-0.749820
C	-1.972351	-1.215845	0.751445
C	-3.344003	-1.379773	0.749180
C	-6.505565	0.386019	-0.025386
C	-7.883743	0.208554	-0.021979
H	-9.499378	-1.213448	-0.002196
H	-7.992973	-3.185207	0.025874
H	-5.548858	-2.877199	0.014268
H	-4.203203	1.135555	-1.367988
H	-1.766317	1.458796	-1.360794
H	-0.380806	-2.259262	-1.360600
H	1.118239	-4.207388	-1.367980
H	1.843412	-5.974465	-0.015383
H	3.341063	-7.930318	-0.029785
H	5.802657	-7.617490	-0.002457
H	6.755720	-5.326478	0.026399
H	5.265876	-3.364659	0.015028
H	3.756222	-2.199702	1.369944
H	2.277322	-0.236243	1.363521
H	-0.934597	2.091149	1.363298
H	0.027437	4.353096	1.369732
H	4.252973	4.581290	-0.015540
H	5.199702	6.855528	-0.029535
H	3.699599	8.832046	-0.002031
H	1.238672	8.513856	0.026557
H	0.282889	6.243493	0.014754
H	3.084215	3.071169	-1.368639
H	2.145482	0.799217	-1.361178
H	-1.344440	-1.855164	1.362946
H	-3.784443	-2.153361	1.369414
H	-6.095386	1.391961	-0.014852
H	-8.538290	1.074197	-0.028993

(*p*FNPh)$_3$N



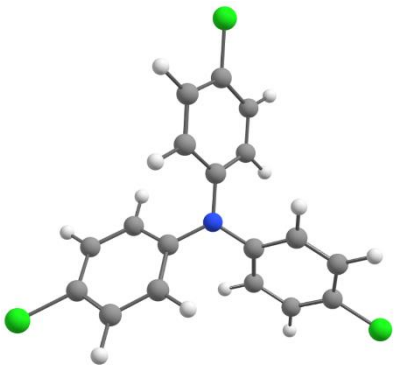
F	2.869124	-4.733118	-0.000825
C	2.172957	-3.584590	-0.000449
C	2.602205	-2.532332	-0.794932
C	1.871859	-1.350101	-0.801598
C	0.733627	-1.210342	0.000182
N	-0.000082	-0.000078	0.000336
C	-1.415063	-0.030112	0.000009
C	-2.105386	-0.945409	-0.802240
C	-3.494407	-0.986679	-0.795385
C	-4.190864	-0.089213	-0.000275
F	-5.533605	-0.117842	-0.000351
C	-3.533426	0.837141	0.794911
C	-2.143914	0.855062	0.802006
C	0.681334	1.240443	0.000329
C	0.235148	2.295213	-0.803561
C	0.893921	3.518777	-0.796547
C	2.017975	3.673797	0.000437
F	2.664548	4.850956	0.000461
C	2.490123	2.641954	0.797381
C	1.810863	1.429643	0.804239
C	0.331329	-2.284411	0.801722
C	1.041715	-3.478735	0.794411
H	3.487709	-2.649282	-1.409931
H	2.187924	-0.523240	-1.429349
H	-1.547530	-1.632315	-1.430421
H	-4.038597	-1.694693	-1.410700
H	-4.107355	1.521371	1.410103
H	-1.615883	1.565061	1.430284
H	-0.637526	2.154854	-1.433142
H	0.554018	4.343585	-1.413130
H	3.368527	2.797495	1.413997
H	2.160546	0.617743	1.433686
H	-0.547825	-2.182479	1.429695
H	0.735984	-4.318163	1.409168

(*p*FNPh)$_3$N$^{\bullet+}$



F	-5.484403	-0.012257	-0.000000
C	-4.162050	-0.009308	-0.000000
C	-3.486442	-0.958513	-0.765400
C	-2.104290	-0.957018	-0.763290
C	-1.406233	-0.003152	0.000010
N	-0.000160	-0.000009	0.000010
C	0.700148	1.219225	0.000130
C	0.222891	2.300929	-0.762720
C	0.912849	3.498533	-0.764880
C	2.073079	3.608628	-0.000020
F	2.731971	4.755170	-0.000160
C	2.562229	2.550954	0.765020
C	1.874989	1.351778	0.763010
C	0.705606	-1.216091	-0.000120
C	1.881050	-1.343349	-0.762960
C	2.573654	-2.539439	-0.764970
C	2.089221	-3.599319	0.000010
F	2.753232	-4.742893	0.000140
C	0.928476	-3.494435	0.764830
C	0.233161	-2.299932	0.762680
C	-2.108550	0.947586	0.763290
C	-3.490695	0.942902	0.765400
H	-4.050408	-1.668910	-1.358540
H	-1.558806	-1.668194	-1.374100
H	-0.665956	2.184536	-1.373310
H	0.579545	4.342316	-1.357730
H	3.459134	2.687939	1.357760
H	2.221828	0.525142	1.373560
H	2.224223	-0.515151	-1.373460
H	3.471184	-2.672374	-1.357680
H	0.598928	-4.339726	1.357640
H	-0.656218	-2.187544	1.373240
H	-1.566251	1.661204	1.374110
H	-4.057832	1.650778	1.358540

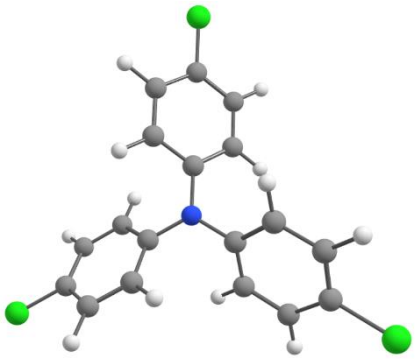
(*p*ClPh)$_3$N



Cl	-2.429858	5.428554	-0.002727
C	-1.715095	3.833966	-0.000510
C	-0.596930	3.579670	-0.787404
C	-0.037907	2.308119	-0.792561
C	-0.575968	1.290879	0.002399
N	0.001441	-0.000460	0.003618
C	1.408231	-0.146337	0.002129
C	2.208566	0.688700	0.788675
C	3.591106	0.555471	0.780586
C	4.180318	-0.432843	-0.000562
Cl	5.918465	-0.612655	-0.002191
C	3.399916	-1.279516	-0.780446
C	2.019313	-1.127183	-0.785879

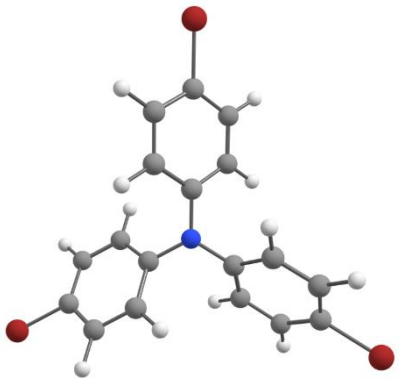
C	-0.829094	-1.145461	0.002320
C	-0.511178	-2.253704	0.794179
C	-1.319223	-3.383475	0.785981
C	-2.465968	-3.400779	-0.000670
Cl	-3.492167	-4.815161	-0.002679
C	-2.804066	-2.303771	-0.785772
C	-1.980395	-1.185366	-0.790893
C	-1.693744	1.568296	0.796047
C	-2.270372	2.831914	0.787976
H	-0.175179	4.365416	-1.404539
H	0.825828	2.101646	-1.416178
H	1.744265	1.449212	1.408040
H	4.207169	1.206554	1.391088
H	3.868603	-2.042699	-1.392052
H	1.408233	-1.776411	-1.404429
H	0.376690	-2.230809	1.417665
H	-1.067397	-4.240823	1.400560
H	-3.696495	-2.328982	-1.401480
H	-2.233088	-0.333062	-1.413210
H	-2.115235	0.787599	1.420871
H	-3.138027	3.041563	1.403907

(pClPh)$_3$N$^{\bullet+}$



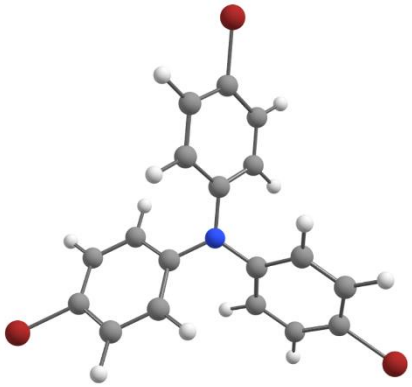
Cl	4.437815	-3.890114	0.001831
C	3.141681	-2.754716	0.000612
C	3.247916	-1.586244	0.761803
C	2.210332	-0.672513	0.759149
C	1.055838	-0.928372	-0.001119
N	-0.001208	-0.001493	-0.001554
C	0.274163	1.377235	-0.001002
C	1.345358	1.877521	-0.761604
C	1.612755	3.234033	-0.762850
C	0.818209	4.095746	0.000145
Cl	1.156048	5.785305	0.000827
C	-0.246783	3.605438	0.762647
C	-0.522083	2.250499	0.760329
C	-1.332510	-0.452355	-0.001409
C	-2.302706	0.228923	-0.757177
C	-3.611216	-0.217426	-0.758090
C	-3.959070	-1.340070	0.000060
Cl	-5.591506	-1.891480	0.001361
C	-3.000642	-2.021344	0.757290
C	-1.689605	-1.582408	0.754927
C	0.955333	-2.107027	-0.760755
C	1.998205	-3.014809	-0.761534
H	4.134179	-1.408085	1.359962
H	2.273153	0.222385	1.368886
H	1.939347	1.206328	-1.372554
H	2.423904	3.632603	-1.361314
H	-0.842068	4.284964	1.361724
H	-1.328517	1.859224	1.371151
H	-2.019429	1.081543	-1.364905
H	-4.363021	0.288855	-1.352623
H	-3.290549	-2.879611	1.352552
H	-0.946566	-2.088144	1.362112
H	0.077588	-2.288162	-1.371733
H	1.939331	-3.917197	-1.359233

(pBrNPh)$_3$N



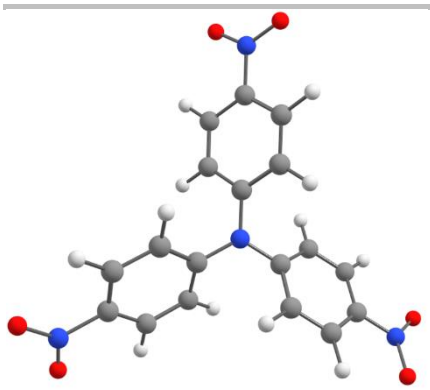
Br	-5.310619	-2.993915	-0.000360
C	-3.660398	-2.063353	0.000010
C	-2.608189	-2.527031	0.781860
C	-1.402427	-1.837464	0.788960
C	-1.232078	-0.694854	0.000440
N	0.000020	-0.000460	0.000380
C	0.014382	1.413832	0.000180
C	-0.888586	2.132361	0.790570
C	-0.883253	3.521371	0.783690
C	0.042636	4.201107	-0.000020
Br	0.061927	6.095475	-0.000130
C	0.954517	3.502599	-0.783680
C	0.931675	2.113774	-0.790380
C	1.217626	-0.719888	0.000240
C	1.364085	-1.866614	-0.787150
C	2.555568	-2.580530	-0.780350
C	3.617685	-2.137504	0.000090
Br	5.248807	-3.101132	-0.000140
C	3.493058	-0.993486	0.780610
C	2.292667	-0.294653	0.787530
C	-2.297611	-0.248575	-0.788130
C	-3.511975	-0.922884	-0.781550
H	-2.732523	-3.413044	1.394380
H	-0.584267	-2.188906	1.409180
H	-1.600654	1.599255	1.412160
H	-1.587188	4.071825	1.397780
H	1.669474	4.038576	-1.397860
H	1.632769	1.566269	-1.411930
H	0.538457	-2.202032	-1.406350
H	2.661287	-3.469536	-1.392040
H	4.322719	-0.657041	1.392270
H	2.187986	0.590370	1.406720
H	-2.174370	0.633522	-1.408080
H	-4.334122	-0.570300	-1.394260

(pBrNPh)$_3$N$^{\bullet+}$



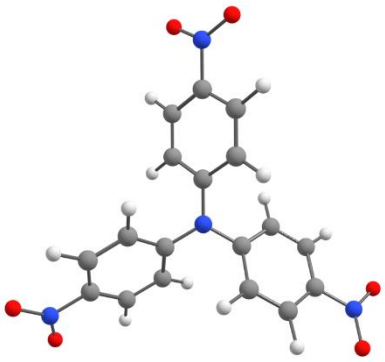
Br	-5.148993	3.180704	0.000508
C	-3.556329	2.197033	0.000060
C	-2.469935	2.641521	-0.759658
C	-1.290814	1.919103	-0.758951
C	-1.195818	0.739291	-0.000697
N	0.000118	0.000443	-0.000861
C	-0.042028	-1.404667	-0.000458
C	-1.017128	-2.076498	-0.757946
C	-1.053703	-3.458834	-0.758789
C	-0.125172	-4.177790	0.000103
Br	-0.180880	-6.048901	0.000288
C	0.844674	-3.515458	0.758832
C	0.890997	-2.133419	0.757444
C	1.237984	0.666509	-0.000812
C	1.402405	1.839440	0.756337
C	2.622464	2.490260	0.757781
C	3.681289	1.980828	-0.000087
Br	5.329955	2.867420	0.000526
C	3.523050	0.816844	-0.758426
C	2.307577	0.157490	-0.757730
C	-2.293026	0.295629	0.757802
C	-3.466999	1.026350	0.759333
H	-2.557498	3.541656	-1.356860
H	-0.454382	2.243823	-1.368496
H	-1.716940	-1.514191	-1.366781
H	-1.790148	-3.984418	-1.355441
H	1.548286	-4.083966	1.355735
H	1.623240	-1.613555	1.365888
H	0.585925	2.214139	1.364295
H	2.762867	3.384247	1.354133
H	4.346659	0.441454	-1.354519
H	2.170552	-0.729961	-1.366214
H	-2.208349	-0.598206	1.366528
H	-4.310843	0.701300	1.356694

(pNO$_2$Ph)$_3$N



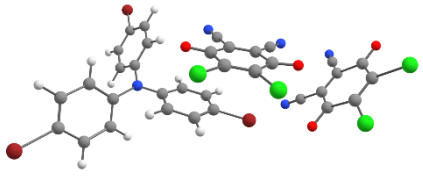
O	6.123410	-1.334666	-0.677307
N	5.303698	-1.933786	0.001271
O	5.545223	-2.919252	0.680874
C	3.927432	-1.432671	-0.000022
C	2.972037	-2.078125	0.775173
C	1.672567	-1.596629	0.778967
C	1.328217	-0.485631	-0.001823
N	0.000751	-0.001180	-0.002379
C	-0.243393	1.390848	-0.001612
C	0.543315	2.243677	0.783322
C	0.310903	3.609884	0.779614
C	-0.722180	4.115416	0.000185
N	-0.975908	5.558026	0.001231
O	-1.901307	5.969063	-0.681416
O	-0.246228	6.259292	0.684685
C	-1.521189	3.288976	-0.780174
C	-1.273871	1.925413	-0.785652
C	-1.083110	-0.907999	-0.001456
C	-2.215940	-0.650426	0.781351
C	-3.284013	-1.533396	0.777670
C	-3.205532	-2.682343	0.000406
N	-4.329040	-3.622101	0.001250
O	-5.302357	-3.338260	0.681988
O	-4.221932	-4.630686	-0.678913
C	-2.089466	-2.963808	-0.777754
C	-1.031092	-2.069208	-0.783372
C	2.307506	0.142862	-0.781928
C	3.612128	-0.324391	-0.776310
H	3.256667	-2.933461	1.375364
H	0.918866	-2.079013	1.391903
H	1.335182	1.831377	1.399270
H	0.906993	4.283164	1.383082
H	-2.311236	3.719631	-1.382803
H	-1.877986	1.268554	-1.402138
H	-2.254687	0.242552	1.395784
H	-4.165741	-1.351416	1.379521
H	-2.067894	-3.864475	-1.378731
H	-0.159659	-2.266128	-1.398427
H	2.041521	0.996775	-1.395541
H	4.381079	0.147105	-1.375695

(pNO$_2$Ph)$_3$N$^{\bullet+}$



O	5.870573	-2.105392	-0.663970
N	4.987075	-2.612861	0.000168
O	5.072499	-3.627837	0.664802
C	3.676493	-1.926472	-0.000321
C	2.645499	-2.460936	0.764547
C	1.417120	-1.823150	0.762977
C	1.246623	-0.653990	-0.000522
N	-0.000038	-0.000731	-0.000488
C	-0.057327	1.405640	-0.000452
C	0.869661	2.137379	0.763804
C	0.808363	3.520104	0.765633
C	-0.169095	4.146286	0.000036
N	-0.229490	5.624501	0.000358
O	-1.110235	6.136001	-0.664355
O	0.606580	6.205882	0.665313
C	-1.092273	3.442865	-0.765863
C	-1.040767	2.059735	-0.764558
C	-1.189277	-0.753348	-0.000129
C	-2.286985	-0.314972	0.762697
C	-3.454142	-1.058831	0.764513
C	-3.507350	-2.219452	0.000500
N	-4.757603	-3.010358	0.000241
O	-5.679967	-2.575698	0.663177
O	-4.759526	-4.029785	-0.663068
C	-2.436114	-2.668960	-0.763678
C	-1.263778	-1.933258	-0.762582
C	2.304854	-0.128323	-0.763898
C	3.528706	-0.774699	-0.765325
H	2.820316	-3.352693	1.354321
H	0.605897	-2.200001	1.376094
H	1.601130	1.622896	1.377236
H	1.493137	4.116700	1.356183
H	-1.823324	3.982040	-1.356171
H	-1.727869	1.487637	-1.378258
H	-2.207413	0.576444	1.375124
H	-4.313657	-0.762958	1.353806
H	-2.538043	-3.572672	-1.352397
H	-0.424415	-2.243329	-1.375236
H	2.152911	0.753156	-1.377025
H	4.361077	-0.410149	-1.355084

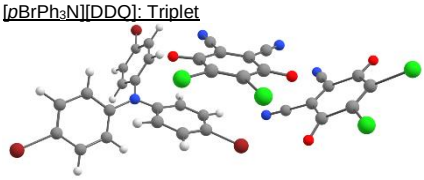
[pBrPh$_3$N][DDQ]: Closed shell singlet



Cl	0.140076	-2.490127	-2.545278
Cl	-3.012801	-2.779537	-1.980440
O	1.093185	0.190724	-1.878556
O	-4.159926	-0.238015	-1.100044
N	-3.685972	3.005486	0.015018
N	0.399707	3.396803	-0.684832
C	-0.087187	0.056094	-1.647081
C	-0.815197	-1.218231	-1.915565
C	-2.140846	-1.338520	-1.691477
C	-2.953270	-0.188752	-1.201579
C	-2.220417	1.075375	-0.887896
C	-0.891734	1.192663	-1.098875
C	-3.020415	2.147607	-0.387742
C	-0.181042	2.410611	-0.862401
Br	-1.909881	-1.134095	1.775826
Br	5.794435	5.705890	-0.677658
N	3.926470	0.032615	0.530581
C	2.592370	-0.243024	0.830020
C	2.045855	-1.516924	0.589271
H	2.660474	-2.293840	0.149790
C	0.720161	-1.788283	0.885087
H	0.312148	-2.774354	0.690737
C	-0.094489	-0.783661	1.404379
C	0.432764	0.482457	1.664934
H	-0.194171	1.254467	2.099598
C	1.763008	0.747263	1.385597
H	2.159798	1.734172	1.593125
C	4.893019	-1.005793	0.462962
C	5.743404	-1.093754	-0.640920
H	5.645692	-0.376609	-1.449537
C	4.354623	1.360379	0.245516
C	3.652548	2.152182	-0.664857
H	2.773548	1.753905	-1.160083
C	4.069758	3.450799	-0.928786
H	3.509835	4.070303	-1.619750
C	5.211728	3.943060	-0.306117
C	5.933108	3.156549	0.586117
H	6.820596	3.551137	1.067789
C	5.495712	1.868463	0.868851
H	6.043256	1.251564	1.574439
Cl	-8.702289	-0.852708	-1.651687
Cl	-6.671479	-2.895081	-0.213687
O	-8.340340	1.866691	-0.652235
O	-4.974760	-1.509884	1.710544
C	-7.592517	1.086093	-0.116731
C	-7.577634	-0.370292	-0.457750
C	-6.727149	-1.225016	0.141472
C	-5.746116	-0.756018	1.166066
C	-5.766302	0.700964	1.521778
C	-6.633414	1.553932	0.940233
N	-4.058869	1.454907	3.313994
N	-6.791898	4.049315	1.601675
C	-4.826406	1.119551	2.514258
C	-6.708605	2.936562	1.292636
Br	8.128206	-4.371703	0.244526
C	6.711887	-2.087784	-0.704634
H	7.372273	-2.153360	-1.561914
C	6.818448	-3.007459	0.333286
C	5.975804	-2.935303	1.437712
H	6.073715	-3.650386	2.246747
C	5.022411	-1.926873	1.505425

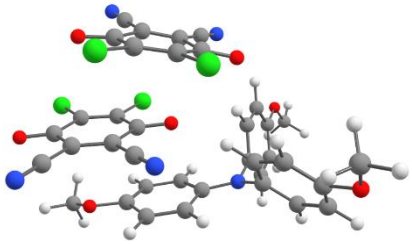
H	4.372080	-1.853009	2.371476

[*p*BrPh$_3$N][DDQ]: Triplet



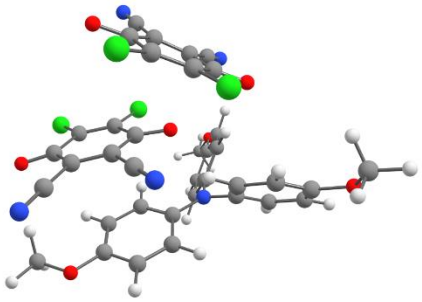
Cl	-0.241264	-2.541138	2.662734
Cl	2.862224	-2.897670	1.991178
O	-1.211813	0.136954	1.993989
O	4.090923	-0.417518	1.047158
N	3.701096	3.007453	0.538260
N	-0.314537	3.431482	1.159287
C	0.020207	0.035968	1.857380
C	0.727723	-1.235616	2.071306
C	2.053996	-1.389450	1.803343
C	2.889779	-0.275115	1.323981
C	2.217723	0.999374	1.211394
C	0.858309	1.145725	1.457436
C	3.028501	2.110545	0.835946
C	0.219008	2.409916	1.296665
Br	1.810436	-2.001014	-1.753887
Br	-4.992827	5.898778	0.365093
N	-3.706068	0.037239	-0.468313
C	-2.426576	-0.401073	-0.724867
C	-2.069664	-1.738633	-0.420176
H	-2.764826	-2.375881	0.111982
C	-0.815830	-2.205039	-0.732587
H	-0.529209	-3.217290	-0.473853
C	0.115387	-1.351191	-1.340042
C	-0.207365	-0.012042	-1.614281
H	0.532429	0.635971	-2.074100
C	-1.464772	0.461783	-1.309944
H	-1.725955	1.486405	-1.547274
C	-4.788237	-0.882895	-0.410359
C	-5.694168	-0.804370	0.650760
H	-5.546868	-0.067660	1.433215
C	-4.005065	1.409007	-0.264216
C	-3.203077	2.172512	0.587413
H	-2.381761	1.703085	1.125325
C	-3.495113	3.517691	0.768972
H	-2.857875	4.117845	1.407305
C	-4.591038	4.075465	0.117604
C	-5.406812	3.307930	-0.718664
H	-6.251813	3.762913	-1.222078
C	-5.116228	1.969109	-0.909836
H	-5.728000	1.365068	-1.571812
Cl	8.800762	-0.391014	1.194182
Cl	6.752264	-2.707066	0.285451
O	8.110801	2.160045	-0.054851
O	4.846631	-1.672460	-1.683936
C	7.310542	1.295759	-0.318211
C	7.461488	-0.110737	0.164414
C	6.605774	-1.079835	-0.208890
C	5.473792	-0.794226	-1.141750
C	5.209980	0.646293	-1.465199
C	6.100144	1.607500	-1.150558
N	2.997690	1.155736	-2.707528
N	5.887380	4.035652	-2.014128
C	3.999355	0.928284	-2.173151
C	5.965976	2.959438	-1.594558
Br	-8.370660	-3.839879	-0.218183
C	-6.759172	-1.690192	0.709699
H	-7.458196	-1.648713	1.536774
C	-6.919428	-2.641316	-0.297064
C	-6.024749	-2.716851	-1.362604
H	-6.168950	-3.452458	-2.145269
C	-4.955379	-1.834796	-1.420160
H	-4.261265	-1.870804	-2.253413

[*p*MeOPh$_3$N][DDQ]: Closed shell singlet



O	2.258920	-1.445532	-3.521441
O	-4.590046	4.897718	-0.897510
O	-5.182916	-3.999812	1.918476
N	-2.803792	-0.345435	-1.556654
C	-1.590235	-0.664883	-2.126608
C	-1.056373	-1.968549	-2.014507
H	-1.619861	-2.735210	-1.497792
C	0.199303	-2.275556	-2.503660
H	0.582993	-3.280180	-2.365688
C	0.976197	-1.285822	-3.122555
C	0.404110	-0.020778	-3.348422
H	0.981019	0.717590	-3.896065
C	-0.852678	0.282863	-2.873595
H	-1.256397	1.274290	-3.038038
C	-3.212127	1.018961	-1.394759
C	-2.405082	1.939190	-0.732577
H	-1.431765	1.632794	-0.364860
C	-2.826945	3.253203	-0.554674
H	-2.169169	3.945572	-0.044163
C	-4.081022	3.648088	-1.023291
C	-4.900503	2.719143	-1.675631
H	-5.871945	3.044169	-2.032517
C	-4.465162	1.418588	-1.863654
H	-5.097900	0.697816	-2.372415
C	-3.440329	-1.292842	-0.685859
C	-3.080464	-1.347396	0.665038
H	-2.323612	-0.667200	1.043009
C	-3.680543	-2.263211	1.509108
H	-3.405549	-2.320783	2.557109
C	-4.654646	-3.141422	1.013855
C	-5.015259	-3.091980	-0.333896
H	-5.764870	-3.760693	-0.740592
C	-4.401503	-2.164355	-1.176378
H	-4.668849	-2.123372	-2.228175
C	2.762152	-2.762996	-3.691270
H	2.165337	-3.307741	-4.431016
H	2.776723	-3.321862	-2.749550
H	3.784673	-2.644051	-4.048007
C	-3.803913	5.868018	-0.242388
H	-3.593264	5.580227	0.795749
H	-4.392337	6.786217	-0.249189
H	-2.856697	6.040659	-0.769484
C	-6.174229	-4.900845	1.480823
H	-7.055986	-4.372904	1.094969
H	-6.459069	-5.483540	2.357445
H	-5.790117	-5.577552	0.706268
Cl	3.980480	-3.425504	-0.044843
Cl	0.949195	-2.777530	0.786483
O	5.177977	-1.219823	-1.541216
O	0.200140	-0.060500	0.031823
N	1.068783	2.960392	-1.462344
N	4.882659	2.123156	-2.670473
C	4.058088	-0.956201	-1.162409
C	3.223400	-1.932382	-0.402660
C	1.944313	-1.663272	-0.060122
C	1.323865	-0.346967	-0.353458
C	2.163766	0.647711	-1.062192
C	3.440369	0.371091	-1.430178
C	1.562856	1.926676	-1.290014
C	4.247090	1.330296	-2.114220
C	0.020915	1.448061	2.542450
C	1.012122	2.470385	2.080990
C	2.325966	2.180833	1.984365
C	2.853228	0.833635	2.358826
C	1.890972	-0.127643	2.993608
C	0.569051	0.136781	3.029392
Cl	0.362577	3.997273	1.688992
Cl	3.494037	3.288253	1.412131
O	-1.166367	1.659516	2.558698
O	3.996461	0.504162	2.150564
N	2.907938	-2.329828	3.893117
N	-1.174361	-1.557957	3.912274
C	2.451368	-1.348346	3.481632
C	-0.391821	-0.798869	3.522128

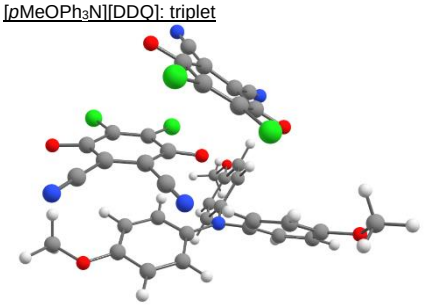
[*p*MeOPh$_3$N][DDQ]: Open shell singlet



O	-3.076846	1.441967	-4.285189
O	5.276308	-3.065875	-2.076528
O	3.428145	4.919795	2.117769
N	1.741010	1.179866	-1.609438
C	0.540601	1.288570	-2.280748
C	-0.472167	2.163815	-1.820731
H	-0.312543	2.741017	-0.918063
C	-1.684847	2.258258	-2.472719
H	-2.448716	2.915600	-2.074220
C	-1.938633	1.458186	-3.601245
C	-0.927667	0.593769	-4.076541
H	-1.138330	-0.006116	-4.954327
C	0.283913	0.513553	-3.441261
H	1.050869	-0.144297	-3.831232
C	2.604069	0.065324	-1.770684

C	2.113920	-1.240103	-1.727424
H	1.062682	-1.419812	-1.548220
C	2.980766	-2.315258	-1.839222
H	2.570508	-3.314421	-1.773275
C	4.353599	-2.093197	-1.984346
C	4.845762	-0.777843	-2.033104
H	5.912723	-0.626686	-2.152696
C	3.982634	0.290303	-1.918849
H	4.363599	1.305793	-1.949766
C	2.165392	2.171225	-0.685669
C	2.614865	1.768510	0.580615
H	2.588849	0.718455	0.849679
C	3.028488	2.714265	1.492837
H	3.340775	2.419760	2.488749
C	3.010035	4.077784	1.156475
C	2.576121	4.478661	-0.113366
H	2.569330	5.522704	-0.401870
C	2.157431	3.522325	-1.029757
H	1.835587	3.826642	-2.020957
C	-4.182264	2.221729	-3.832982
H	-3.937437	3.289391	-3.863568
H	-4.489811	1.927011	-2.825227
H	-4.988114	2.008059	-4.532898
C	4.848027	-4.409719	-1.947016
H	4.356671	-4.574912	-0.981042
H	5.751711	-5.015938	-2.006389
H	4.167239	-4.689730	-2.759687
C	3.392286	6.310127	1.865163
H	4.056342	6.582329	1.035499
H	3.743275	6.787534	2.779725
H	2.372164	6.648274	1.646384
Cl	-3.532673	2.983799	1.584434
Cl	-0.562349	1.952447	2.076305
O	-4.892938	1.470810	-0.509182
O	0.096459	-0.377987	0.427966
N	-1.038109	-2.660917	-1.988520
N	-4.756465	-1.268175	-2.711853
C	-3.798209	0.983092	-0.217699
C	-2.907765	1.595072	0.784932
C	-1.644072	1.138816	1.003858
C	-1.087840	-0.012687	0.282010
C	-1.992459	-0.673119	-0.633781
C	-3.269099	-0.197857	-0.885956
C	-1.474039	-1.780030	-1.371267
C	-4.098810	-0.798320	-1.879799
C	1.066726	-2.384892	1.845848
C	0.061056	-3.359209	1.326262
C	-1.227325	-3.323300	1.720245
C	-1.704027	-2.345543	2.748406
C	-0.677622	-1.435107	3.349113
C	0.590574	-1.417785	2.889301
Cl	0.666297	-4.525905	0.231220
Cl	-2.419313	-4.392765	1.122736
O	2.224480	-2.398439	1.501278
O	-2.858217	-2.289448	3.100317
N	-1.480016	0.131491	5.245159
N	2.384078	0.233189	3.757931
C	-1.129932	-0.563671	4.387537
C	1.576627	-0.504781	3.378098

[*p*MeOPh$_3$N][DDQ]: triplet



O	-2.427206	-2.046377	4.306019
O	4.007272	4.693981	1.559219
O	4.814755	-3.776489	-1.960751
N	2.174767	-0.526354	1.666366
C	1.059246	-0.971976	2.359370
C	0.335102	-2.096421	1.908064
H	0.653866	-2.615880	1.012169
C	-0.822373	-2.498600	2.543809
H	-1.378563	-3.338091	2.143316
C	-1.300912	-1.777277	3.651367
C	-0.558961	-0.678884	4.133282
H	-0.932098	-0.148498	5.001695
C	0.599256	-0.287503	3.509301
H	1.161976	0.552328	3.899470
C	2.600006	0.817088	1.708527
C	1.677852	1.868785	1.686785
H	0.618164	1.663446	1.629340
C	2.114903	3.180733	1.652060
H	1.373216	3.966830	1.598518
C	3.485677	3.460241	1.629091
C	4.414581	2.404577	1.672795
H	5.472077	2.643607	1.669433
C	3.979209	1.099299	1.702456
H	4.696139	0.285478	1.727414
C	2.863881	-1.384658	0.772597
C	3.114745	-0.943099	-0.535822
H	2.747460	0.025877	-0.854975
C	3.768350	-1.769370	-1.423291
H	3.933793	-1.455382	-2.448097
C	4.189237	-3.047543	-1.020768
C	3.945361	-3.485162	0.288011
H	4.271943	-4.461855	0.623703
C	3.282637	-2.651479	1.178904
H	3.100697	-2.979981	2.197523
C	-3.265727	-3.108217	3.859287
H	-2.740946	-4.068013	3.924033
H	-3.621200	-2.936882	2.838627
H	-4.116928	-3.106826	4.537823
C	3.121121	5.788219	1.392094
H	2.515313	5.665508	0.487020
H	3.754647	6.669406	1.294412
H	2.466334	5.904548	2.263580
C	5.223659	-5.091721	-1.641294
H	5.967208	-5.093410	-0.834837
H	5.674893	-5.491119	-2.549207
H	4.368151	-5.715362	-1.355212
Cl	-2.539504	-3.893988	-1.507025
Cl	0.091362	-2.141919	-1.891233
O	-4.360093	-2.731239	0.460130
O	0.010490	0.342999	-0.346320
N	-1.732421	2.249760	2.010403
N	-5.041726	-0.000369	2.574040
C	-3.415989	-1.982794	0.196157
C	-2.343051	-2.368948	-0.738372
C	-1.231456	-1.602701	-0.918749
C	-1.037381	-0.324937	-0.226295
C	-2.120706	0.090510	0.637615
C	-3.245490	-0.690990	0.845286
C	-1.921933	1.291274	1.384096
C	-4.247736	-0.306011	1.785621
C	0.218313	2.494518	-1.882590
C	-1.044220	3.107217	-1.374060
C	-2.254518	2.616003	-1.707861
C	-2.399490	1.470822	-2.661133
C	-1.141375	0.928074	-3.263497
C	0.070130	1.363880	-2.855916
Cl	-0.843813	4.478693	-0.368957
Cl	-3.722953	3.259909	-1.114828
O	1.312205	2.916143	-1.586965
O	-3.475865	1.005810	-2.953500
N	-1.415243	-0.913708	-5.059632
N	2.295501	0.353698	-3.707841
C	-1.298475	-0.098540	-4.245183
C	1.294638	0.803697	-3.337912

10. Author Contributions

Table S10. Author Contributions

Author	Contribution
L. J. C. van der Zee	Conceptualization, Data curation, DFT calculations, Formal Analysis, investigation, Writing – original draft
J. Hofman	Data curation, DFT calculations
S. Matthew	SC–XRD measurements
A de Visser	Electrical resistance measurements
E. H. Bruck	Magnetic susceptibiltiy measurements
B. de Bruin	Formal Analysis
J. C. Slootweg	Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing

11. References

1. S. Stoll, A. J. Schweiger *Magn. Reson*. **2006**, *178*, 42–55.
2. cwEPR, verstion 3.4.10, T. Casey, https://www.mathworks.com/matlabcentral/fileexchange/73292-cwepr), MATLAB Central File Exchange.
3. M. Stanoppi, A. Lorbach *Dalt. Trans.* **2018**, *47*(31), 10394-10398.
4. A. A. Kelkar, N. M. Patil, R. V. Chaudhari *Tetrahedron Lett.* **2002**, *43*(40), 7143-7146.
5. T. H. Crawford, J. Swanson *J. Chem. Educ.* **1971**, *48* (6), 382-386.
6. E. M. Schubert *J. Chem. Educ.* **1992**, *1992*, 69 (1), 62.
7. Thomas Casey (2021). cwEPR (https://www.mathworks.com/matlabcentral/fileexchange/73292-cwepr), MATLAB Central File Exchange.
8. Bruker, SAINT V8.40B, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
9. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke *J. Appl. Cryst.* **2015**, *48*(1), 3-10.
10. G. M. Sheldrick *Acta Crystallogr. Sect. A.* **2015**, *A71*(1), 3-8.
11. A. L. Spek (2001). PLATON. Utrecht University, The Netherlands. http://www.Cryst.Chem.uu.nl.
12. A. L. Spek *Acta Crystallogr.* **2015**, *C71*, 9-18.
13. G. M. Sheldrick *Acta Crystallogr.***2015**, *C71*(1), 3-8.
14. S. V. Rasokha, J. Lu, T. Y. Rosokha, J. K. Kochi *Phys. Chem. Chem. Phys.* **2009**, *11*, 324-332.
15. a) J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom, *J. Chem. Phys*. **1997**, *107*, 5016–5021; b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J.A. Pople, M. S. Gordon, *J. Chem. Phys*. **1982**, *77*, 3654–3665.
16. J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys*. **2008**, *10*, 6615–6620.
17. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji,X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B.Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson,D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M.Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M.J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R.Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J.Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT.
18. G. Scalmani, M. J. Frisch *J. Chem. Phys.* **2010**, *132*, 114110.
19. C. Hansch, A. Leo, R. W. Taft *Chem. Rev.* **1991**, *91*, 165-195.