

From phosphorescence to delayed fluorescence in one step: tuning photophysical properties by quaternisation of an sp^2 -hybridised nitrogen atom

Anastasia Klimash¹, Antonio Prlj², Dmitry S. Yufit², Abhijit Mallick², Basile F. E. Curchod², Paul R. McGonigal², Peter J. Skabara^{1*} and Marc K. Etherington^{3,4*}

¹WestCHEM, School of Chemistry, University of Glasgow, University Ave, Glasgow G12 8QQ

²Department of Chemistry and ³Department of Physics, Durham University, South Road, DH1 3LE, UK

⁴Department of Mathematics, Physics and Electrical Engineering, Northumbria University, Ellison Place, NE1 8ST, UK.

Table of Contents

1. General Methods	S1
2. Synthetic Procedures	S4
3. ¹ H and ¹³ C NMR Spectroscopic Characterisation of Synthesised Compounds	S11
4. Cyclic Voltammetry	S27
5. Thermal Analysis	S31
6. Photophysical Studies	S32
7. Calculations and Crystallography	S46
8. References	S52

Supporting Information

1. General Methods

Materials: Unless stated otherwise, all reagents were purchased from Sigma Aldrich, TCI, Alfa Aesar or Fluorochem and used without further purification.

Instrumentation and Analytical Techniques: Microwave syntheses were performed using Biotage Initiator Classic microwave heating apparatus in 10-20 mL vials. Melting points were determined using a Stuart Scientific SMP1 Melting Point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVIII 400 apparatus at 400 MHz and 100 MHz, respectively, or a Bruker AV500 at 500MHz and 125MHz, respectively, at room temperature. NMR data are presented in the following order: chemical shifts (δ) in ppm; multiplicity as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m); coupling constants (J) in Hz. Multiplets are reported over the range they appeared (in ppm). Signals were sharp unless stated as broad (br). Samples were referenced to residual solvent peaks. The high-resolution mass measurements were performed on a Waters Xevo G2S instrument (ASAP-TOF-MS) or on a Finnigan MAT 95XP (EI). Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Thermogravimetric Analyser TGA7 or on a NETZSCH TG 209 F3 - Tarsus thermogravimeter under a constant flow of Argon or Nitrogen (20 mL/min). The temperature was increased at a rate of 10 °C/min from 40 °C to 500 °C. Differential scanning calorimetry (DSC) was carried out on a TA Instruments Q1000 with a RC-90 refrigerated cooling unit attached or on a NETZSCH DSC 214 – Polyma differential scanning calorimeter. The test procedure was a standard Heat-Cool-Reheat, and the temperature range was from 20 °C to 300 °C at 10 °C min⁻¹. The absorption measurements were performed on a Shimadzu UV-3600 double beam spectrophotometer, with slit width 1 nm, at a medium scan rate and 0.2 nm step size. A clean quartz substrate was used as the blank. The steady-state photoluminescence measurements were

performed on a Jobin-Yvon Horiba Fluorolog system. The aggregation-induced emission measurements were performed on a Shimadzu RF-5301PC Spectrofluorophotometer. Phosphorescence (PH), prompt fluorescence (PF), and delayed fluorescence (DF) spectra, fluorescence decay curves and fluence measurements were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using either third harmonics of a high energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA) or a N₂ laser ((LTBMNL 100, Lasertechnik Berlin) emitting at 337 nm. Emission was focused onto a spectrograph and detected on a sensitive gated ICCD camera (Stanford Computer Optics) having sub-nanosecond resolution. PF/DF time resolved measurements were performed by exponentially increasing gate and integration times. Temperature-dependent experiments were conducted using a continuous flow liquid nitrogen cryostat (Janis Research) under nitrogen atmosphere, while measurements at room temperature were recorded in vacuum in the same cryostat. The absolute PLQY measurements were performed using 365 nm excitation from an Ocean Optics LLS-LED and an integrating sphere connected to an Ocean Optics HR2000 Spectrometer. The mechanochromic emission measurements were performed by exciting the samples with a UV torch of emission peak 410 nm and collecting the emission into an optical fibre attached to an Ocean Optics USB 4000 spectrometer with a 500 ms integration time. LabView software was used to interface with the spectrometer and collect the data. The measurements were performed before and after the sample was ground in a pestle and mortar. Due to the nature of the measurement emission intensities cannot be directly compared.

The X-ray single crystal data have been collected using λ MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker D8Venture (Photon III MM C14 CPAD detector, I μ S-III-microsource, focusing mirrors; for compound

MeQ1·OTf λ CuK α radiation, $\lambda = 1.54178\text{\AA}$, Photon III MM C7 CPAD detector, μ S-microsource, focusing mirrors) 3-circle diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat at the temperature 120.0(2)K. All structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2¹ and SHELXTL² software. All non-disordered non-hydrogen atoms were refined in anisotropic approximation, hydrogen atoms in structure **Q2** were found in the Fourier map and refined isotropically. The hydrogen atoms in other structures were placed in the calculated positions and refined in riding mode. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2149620-2149624.

Computational details

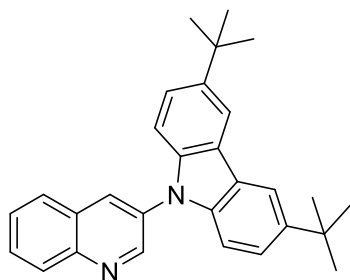
Ground state geometries of **Q1**, **Q2**, **MeQ1**⁺ and **MeQ2**⁺ were optimized with SCS-MP2 method (spin-component-scaled Møller-Plesset perturbation theory of second order)³ along with def2-SVP basis set.⁴ Excited states and excited state optimizations were performed with SCS-ADC(2) method (spin-component-scaled adiabatic diagrammatic construction up to second order)⁵ along with def2-SVP basis set. However, triplet lifetimes for **Q1** and **Q2** were estimated using related CC2 method (approximate coupled cluster singles and doubles),⁶ because spin-orbit coupling calculations are currently not supported for ADC(2).

All calculations were performed *in vacuo*, using Turbomole 7.4.0 program package.⁷ Default parameters for SCS treatment were employed (cos=1.2, css=0.33333). Excited state analysis was performed with Theodore 1.5.1 package.⁸] Charge Transfer (CT) numbers were computed following

Plasser.⁸ Note that CT numbers close to 0 indicate pure locally excited state, while CT numbers close to 1 indicate pure charge transfer excited state.

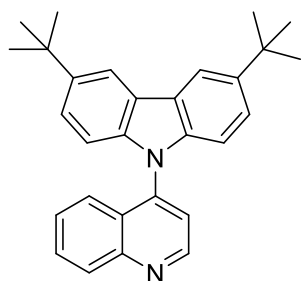
Sample Preparation: To prepare the polymer films. Firstly, PMMA molecular weight 15,000 was dissolved in chlorobenzene at 100 mg/ml. The compounds apart from **MeQ1**·OTf were dissolved in chlorobenzene at 0.5 mg/ml. **MeQ1**·OTf due to solubility issues in chlorobenzene was dissolved in chloroform at 0.5 mg/ml. The compound and polymer solutions were then mixed to give overall 1 wt% of compound to polymer. These mixed solutions were then drop cast onto a quartz substrate in air and at room temperature. After half an hour the substrates were then transferred to a vacuum oven at room temperature for a further 2 hours to remove any trace solvent. Neat films were dropcast directly from the compound solution onto a quartz substrate in air and at room temperature. After half an hour the substrates were then transferred to a vacuum oven at room temperature for a further 2 hours to remove any trace solvent.

2. Synthetic Procedures



3,6-Di-tert-butyl-9-(quinolin-3-yl)-9H-carbazole (Q1): 3,6-Di-tert-butyl-9H-carbazole (485 mg, 1.73 mmol, 1.2 eq.) was added in a dried 3-neck flask and dissolved in 120 mL of anhydrous toluene. 3-Bromoquinoline **1** (300 mg, 1.44 mmol, 1 eq.) was added and the mixture was bubbled with N₂ for 15 minutes while stirring. Tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (66 mg, 0.075 mmol, 0.05 eq.) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (137 mg, 0.29 mmol, 0.2 eq.) were

added and the mixture was degassed for another 15 minutes. Sodium *tert*-butoxide was added (167 mg, 1.73 mmol, 1.2 eq.) followed by *tert*-butanol (4 mL) and the mixture was degassed for 15 more minutes. It was next stirred at 110 °C for 18 hours. The mixture was then cooled to room temperature, washed with water (2×100 mL), dried over MgSO₄ and concentrated under reduced pressure. The crude product was then purified by column chromatography with dichloromethane followed by recrystallisation from ethyl acetate giving the material **Q1** as colourless crystals (350 mg, 60%). **M.P.** 248 – 250 °C; **HRMS** (LMMS) calculated for C₂₉H₃₀N₂ 406.2408, found 406.2468 [M+H⁺]; **¹H NMR** (400 MHz, CDCl₃) δ 9.17 (d, *J* = 2.5 Hz, 1H), 8.33 (d, *J* = 2.3 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 1.6 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.50 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 1.48 (s, 18H). **¹³C NMR** (100 MHz, CDCl₃) δ 149.6, 146.8, 143.7, 139.2, 132.1, 132.0, 129.7, 129.6, 128.4, 127.7, 127.6, 124.0, 123.8, 116.6, 108.8, 34.8, 32.0.

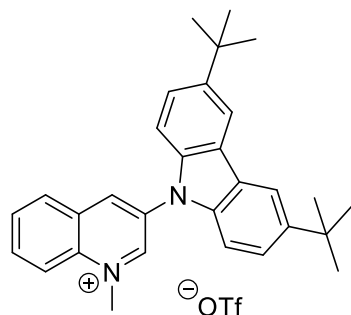


3,6-Di-*tert*-butyl-9-(quinolin-4-yl)-9H-carbazole (Q2): This was synthesised according to the general procedure leading to **Q1**. 3,6-Di-*tert*-butyl-9H-carbazole **3** (2.41 g, 8.6 mmol, 1 eq.), 4-bromoquinoline **2** (1.5 g, 7.2 mmol, 1.2 eq.), Pd₂(dba)₃ (0.33 g, 0.36 mmol, 0.05 eq.), XPhos (0.69

mg, 1.44 mmol, 0.2 eq.), sodium *tert*-butoxide (0.83 mg, 8.6 mmol, 1.2 eq.) and *tert*-butanol (16.5 mL) were used. The crude product was purified by column chromatography with a hexane: ethyl acetate (10 : 1) mixture followed by recrystallisation from methanol giving the material **Q2** as a yellow powder (360 mg, 12%). **M.P.** 168 – 170 °C; **HRMS** (EI) calculated for C₂₉H₃₀N₂ 406.2408, found 406.2419 [M⁺]; **¹H NMR** (400 MHz, CDCl₃) δ 9.10 (d, *J* = 4.6 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 1.7 Hz, 2H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.62 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.54 (d, *J* = 4.6 Hz, 1H), 7.45 (t,

$J = 7.6$ Hz, 1H), 7.41 (dd, $J = 8.6, 1.9$ Hz, 2H), 7.01 (d, $J = 8.6$ Hz, 2H), 1.48 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 150.3, 143.6, 143.6, 139.7, 130.3, 130.1, 127.1, 125.6, 124.2, 123.9, 123.9, 119.9, 116.4, 109.8, 34.8, 32.0.

Crystal data for Q2: $\text{C}_{29}\text{H}_{30}\text{N}_2$, $M = 406.55$, triclinic, space group P -1, $a = 5.6945(2)$, $b = 10.5970(4)$, $c = 18.3344(7)$ Å, $\alpha = 88.680(2)$, $\beta = 86.036(2)$, $\gamma = 89.722(2)^\circ$; $U = 1103.44(7)$ Å³, $F(000) = 436.0$, $Z = 2$, $D_c = 1.224$ mg m⁻³, $\mu = 0.071$ mm⁻¹ (Mo-K α , $\lambda = 0.71073$ Å), $T = 120(1)$ K. 23352 reflections were collected yielding 6384 unique data ($R_{\text{int}} = 0.0387$). Final $wR_2(F^2) = 0.1344$ for all data (400 refined parameters), conventional $R_1(F) = 0.0578$ for 5246 reflections with $I \geq 2\sigma$, GOF = 1.125.

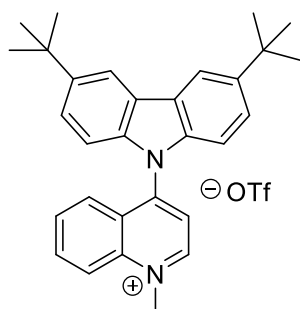


3-(3,6-Di-tert-butyl-9H-carbazol-9-yl)-1-methylquinolin-1-ium

trifluoromethanesulfonate (MeQ1-OTf): Compound **Q1** (50 mg, 0.123 mmol, 1 eq.) was dissolved in dry dichloromethane (2 mL) and cooled down to 0 °C under N_2 atmosphere. Methyl trifluoromethanesulfonate (14 μL , 0.123 mmol, 1 eq.) was added and

the mixture was stirred for 20 h at room temperature. The formed precipitate was filtered off and washed with cool methanol (100 mL) to give the product **MeQ1-OTf** as a bright yellow solid (58 mg, 82%). **M.P.** 356 – 358 °C; **HRMS** (LMMS) calculated for $\text{C}_{20}\text{H}_{33}\text{N}_2^+$ 421.2643, found 421.2625 [M^+]; ^1H NMR (400 MHz, DMSO-d_6) δ 10.15 (s, 1H), 9.73 (s, 1H), 8.67 (d, $J = 8.9$ Hz, 1H), 8.59 (d, $J = 7.8$ Hz, 1H), 8.44 (d, $J = 1.5$ Hz, 2H), 8.40 (t, $J = 8.0$ Hz, 1H), 8.19 (t, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 8.7$ Hz, 2H), 7.61 (dd, $J = 8.7, 1.8$ Hz, 2H), 4.78 (s, 3H), 1.49 (s, 18H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.0, 144.7, 142.9, 138.6, 137.6, 135.8, 132.1, 131.0, 130.9, 130.3, 124.7, 124.0, 119.7, 117.5, 109.7, 46.0, 35.1, 32.2.

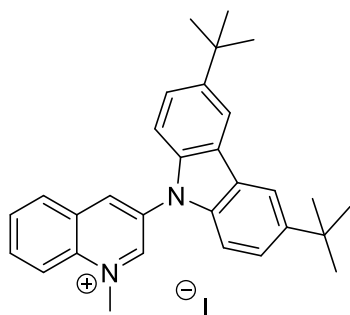
Crystal data for MeQ1·OTf C₃₁H₃₃F₃N₂O₃S, M = 570.65, monoclinic, space group P 2₁/c, a = 11.3872(4), b = 11.2494(4), c = 44.8900(16) Å, β = 93.284(2)°; U = 5740.9(4) Å³, F(000) = 2400.0, Z = 8, D_c = 1.320 mg m⁻³, μ = 1.467 mm⁻¹ (Cu-Kα, λ = 1.54178 Å), T = 120(1)K. 78024 reflections were collected yielding 11394 unique data (R_{int} = 0.1419). Final wR₂(F²) = 0.2852 for all data (736 refined parameters), conventional R₁ (F) = 0.0935 for 8764 reflections with I ≥ 2σ, GOF = 1.051.



4-(3,6-Di-tert-butyl-9H-carbazol-9-yl)-1-methylquinolin-1-ium trifluoromethanesulfonate (MeQ2·OTf): This was synthesized according to the general procedure leading to **MeQ1·OTf**. **Q2** (50 mg, 0.123 mmol, 1 eq.), dichloromethane (2 mL) and methyl trifluoromethanesulfonate (14 μL, 0.123 mmol, 1 eq.) were used. Hexane was added to the solution of

the product, then the formed precipitate was filtered off and washed with cold hexane (100 mL) giving the product **MeQ2·OTf** as a bright yellow solid (51 mg, 72%). **M.P.** 302 – 304 °C; **HRMS** (LMMS) calculated for C₂₀H₃₃N₂⁺ 421.2643, found 421.618 [M⁺]; **¹H NMR** (400 MHz, CDCl₃) δ 9.66 (d, J = 6.5 Hz, 1H), 8.45 (d, J = 9.1 Hz, 1H), 8.30 – 8.19 (m, 2H), 8.14 (d, J = 1.6 Hz, 2H), 8.10 (d, J = 6.5 Hz, 1H), 7.84 (t, J = 7.7 Hz, 1H), 7.45 (dd, J = 8.7, 1.8 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 4.83 (s, 3H), 1.46 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 153.16, 150.83, 146.76, 138.52, 136.43, 129.49, 127.73, 125.87, 125.32, 124.86, 119.30, 118.87, 116.96, 110.59, 45.61, 34.99, 31.80.

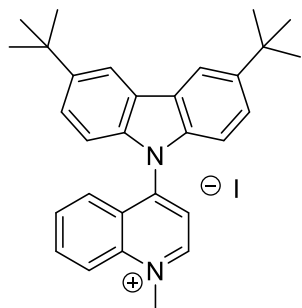
Crystal data for MeQ2·OTf: C₃₁H₃₃F₃N₂O₃S, M = 570.65, monoclinic, space group P 2₁/c, a = 11.1903(8), b = 11.7941(8), c = 44.243(3) Å, β = 93.521(2)°; U = 5828.1(7) Å³, F(000) = 2400.0, Z = 8, D_c = 1.301 mg m⁻³, μ = 0.165 mm⁻¹ (Mo-Kα, λ = 0.71073 Å), T = 120(1)K. 74784 reflections were collected yielding 11579 unique data (R_{int} = 0.1034). Final wR₂(F²) = 0.2120 for all data (736 refined parameters), conventional R₁ (F) = 0.0930 for 7820 reflections with I ≥ 2σ, GOF = 1.116.



3-(3,6-Di-tert-butyl-9H-carbazol-9-yl)-1-methylquinolin-1-ium

iodide (MeQ1·I): Compound **Q1** (50 mg, 0.123 mmol, 1 eq.) was dissolved in toluene (10 mL) and methyl iodide (0.38 mL, 6.15 mmol, 50 eq.) was then added. The mixture was heated to 100 °C for 2 hours in a microwave. The formed yellow precipitate was filtered off and

washed with diethyl ether (100 mL) to afford the material **MeQ1·I** as a bright yellow solid (40 mg, 60%). **M.P.** 242–244 °C; **HRMS** (LMMS) calculated for $C_{20}H_{33}N_2^+$ 421.2643, found 421.2620 [M^+]; **1H NMR** (400 MHz, $CDCl_3$) δ 9.57 (d, J = 2.0 Hz, 1H), 9.00 (d, J = 1.8 Hz, 1H), 8.50 (d, J = 9.0 Hz, 1H), 8.26 – 8.17 (m, 2H), 8.15 (d, J = 1.6 Hz, 2H), 7.98 (t, J = 7.6 Hz, 1H), 7.74 (d, J = 8.7 Hz, 2H), 7.56 (dd, J = 8.7, 1.9 Hz, 2H), 4.99 (s, 3H), 1.47 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 145.6, 141.6, 138.2, 137.5, 136.1, 133.5, 131.3, 130.4, 130.0, 124.9, 124.6, 119.4, 116.8, 109.2, 49.0, 34.9, 31.9.

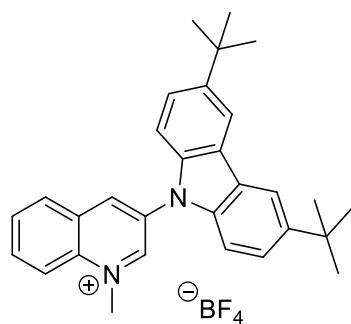


4-(3,6-Di-tert-butyl-9H-carbazol-9-yl)-1-methylquinolin-1-ium iodide

(MeQ2·I): This was synthesized and purified according to the general procedure leading to **MeQ1·I**. **Q2** (50 mg, 0.123 mmol, 1 eq.), toluene (10 mL) and methyl iodide (0.38 mL, 6.15 mmol, 50 eq.) were used. The material **MeQ2·I** was isolated as a bright yellow solid (35 mg, 52%). **M.P.**

240–242 °C; **HRMS** (LMMS) calculated for $C_{20}H_{33}N_2^+$ 421.2643, found 421.2622 [M^+]; **1H NMR** (400 MHz, $CDCl_3$) δ 10.45 (d, J = 6.7 Hz, 1H), 8.50 (d, J = 8.6 Hz, 1H), 8.30 – 8.26 (m, 2H), 8.19 – 8.16 (m,

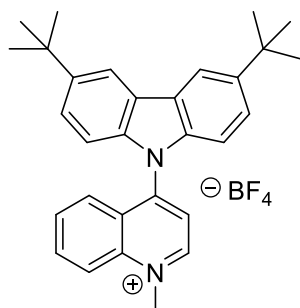
3H), 7.93 – 7.82 (m, 1H), 7.48 (dd, $J = 8.7, 1.9$ Hz, 2H), 7.26 (d, $J = 8.7$ Hz, 2H), 4.99 (s, 3H), 1.49 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.0, 150.8, 146.8, 140.7, 138.5, 136.4, 129.5, 127.8, 125.9, 125.3, 124.9, 119.3, 119.0, 117.0, 110.7, 46.1, 35.0, 31.8



3-(3,6-Di-tert-butyl-9H-carbazol-9-yl)-1-methylquinolin-1-ium tetrafluoroborate (MeQ1·BF₄): A mixture of **Q1** (250 mg, 0.6 mmol, 1 eq.) and NH_4BF_4 (80 mg, 0.77 mmol, 1.25 eq.) was dissolved in trimethyl orthoformate (10 mL). The solution was heated at 100 °C for 2 h in a microwave. The solvent was evaporated, the crude product

was diluted with methanol (100 mL) and filtered through a basic aluminium oxide plug. The solution was concentrated under reduced pressure. The material was then dissolved in chloroform and reprecipitated with hexane affording the product **MeQ1·BF₄** as a bright yellow powder (170 mg, 54%). **M.P.** 296–298 °C; HRMS (LMMS) calculated for $\text{C}_{20}\text{H}_{33}\text{N}_2^+$ 421.2643, found 421.2642 [M^+]; ^1H NMR (400 MHz, CDCl_3) δ 9.20 (s, 1H), 8.89 (s, 1H), 8.37 (d, $J = 8.9$ Hz, 1H), 8.27 – 7.94 (m, 4H), 7.88 (t, $J = 7.6$ Hz, 1H), 7.53 (s, 4H), 4.76 (s, 3H), 1.46 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 145.5, 141.6, 138.3, 137.4, 136.0, 133.2, 131.2, 130.1, 129.8, 125.0, 124.5, 119.0, 116.7, 108.6, 47.0, 35.0, 31.9.

Crystal data for MeQ1·BF₄: $\text{C}_{32}\text{H}_{36}\text{BF}_4\text{N}_3$, $M = 549.45$, monoclinic, space group $P 2_1/c$, $a = 22.3556(11)$, $b = 11.8909(6)$, $c = 10.7807(6)$ Å, $\beta = 100.600(2)^\circ$; $U = 2816.9(3)$ Å³, $F(000) = 1160.0$, $Z = 4$, $D_c = 1.296$ mg m⁻³, $\mu = 0.094$ mm⁻¹ (Mo-K α , $\lambda = 0.71073$ Å), $T = 120(1)$ K. 30314 reflections were collected yielding 5291 unique data ($R_{\text{int}} = 0.0905$). Final $wR_2(F^2) = 0.1630$ for all data (381 refined parameters), conventional $R_1(F) = 0.0770$ for 3797 reflections with $I \geq 2\sigma$, GOF = 1.054.



4-(3,6-Di-tert-butyl-9H-carbazol-9-yl)-1-methylquinolin-1-ium

tetrafluoroborate (MeQ2·BF₄): This was synthesised and purified according to the general procedure leading to **MeQ1·BF₄**. **Q2** (50 mg, 0.12 mmol, 1 eq.), NH₄BF₄ (16 mg, 0.15 mmol, 1.25 eq.) and trimethyl orthoformate (3 mL) were used. The trimethyl orthoformate was then

evaporated under reduced pressure, the product was diluted with methanol (100 mL) and filtered through a basic aluminium oxide plug. The solvent was evaporated under reduced pressure, and the material was recrystallised from isopropanol giving the product **MeQ2·BF₄** as a bright-yellow solid (30 mg, 48%). **M.P.** 322–324 °C; **HRMS** (LMMS) calculated for C₂₀H₃₃N₂⁺ 421.2643, found 421.2626 [M⁺]; **¹H NMR** (400 MHz, CDCl₃) δ 9.48 (d, *J* = 6.7 Hz, 1H), 8.49 (d, *J* = 8.9 Hz, 1H), 8.31 – 8.20 (m, 2H), 8.15 (d, *J* = 1.6 Hz, 2H), 8.11 (d, *J* = 6.5 Hz, 1H), 7.89 – 7.73 (m, 1H), 7.47 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 4.81 (s, 3H), 1.48 (s, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 153.0, 150.5, 146.6, 140.8, 138.6, 136.4, 129.4, 127.6, 125.8, 125.3, 124.9, 119.4, 119.0, 116.9, 110.6, 45.6, 35.0, 31.8.

Crystal data for MeQ2·BF₄: C₃₀H₃₄BF₄N₂O_{0.5}, *M* = 517.40, orthorhombic, space group P na₂₁, *a* = 11.4291(6), *b* = 42.045(2), *c* = 11.8480(6) Å; *U* = 5693.4(5) Å³, *F*(000) = 2184.0, *Z* = 8, *D_c* = 1.207 mg m⁻³, *μ* = 0.089 mm⁻¹ (Mo-Kα, λ = 0.71073 Å), *T* = 120(1)K. 56048 reflections were collected yielding 11014 unique data (*R*_{int} = 0.0665). Final *wR*₂(*F*²) = 0.2781 for all data (694 refined parameters), conventional *R*₁ (*F*) = 0.0918 for 6093 reflections with *I* ≥ 2σ, *GOF* = 1.043, *Flack x* = -0.1(4).

3. ^1H and ^{13}C NMR Spectroscopic Characterisation of Synthesised Compounds

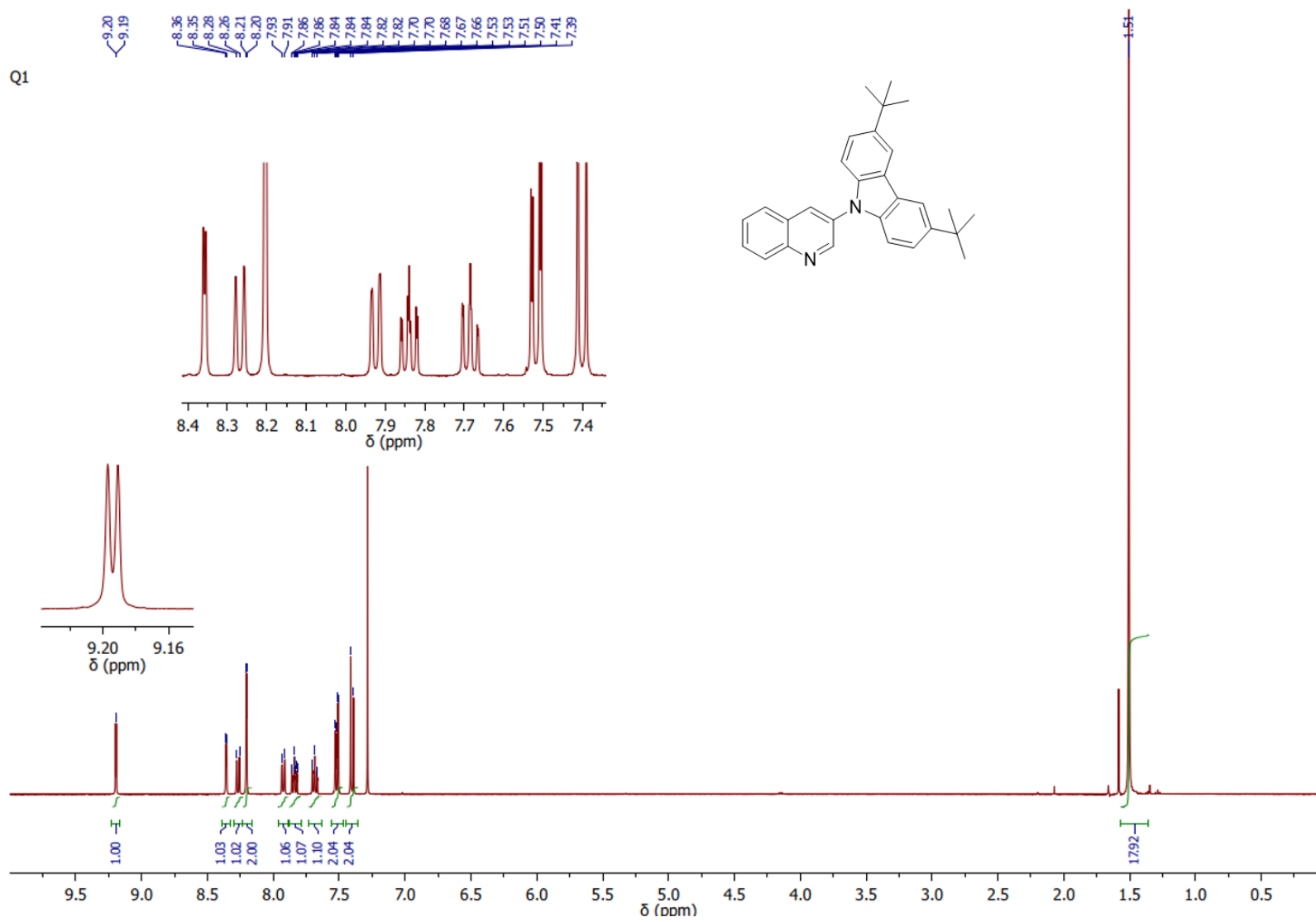


Figure S1. ^1H NMR spectrum of Q1 in CDCl_3 , 400MHz, 293 K.

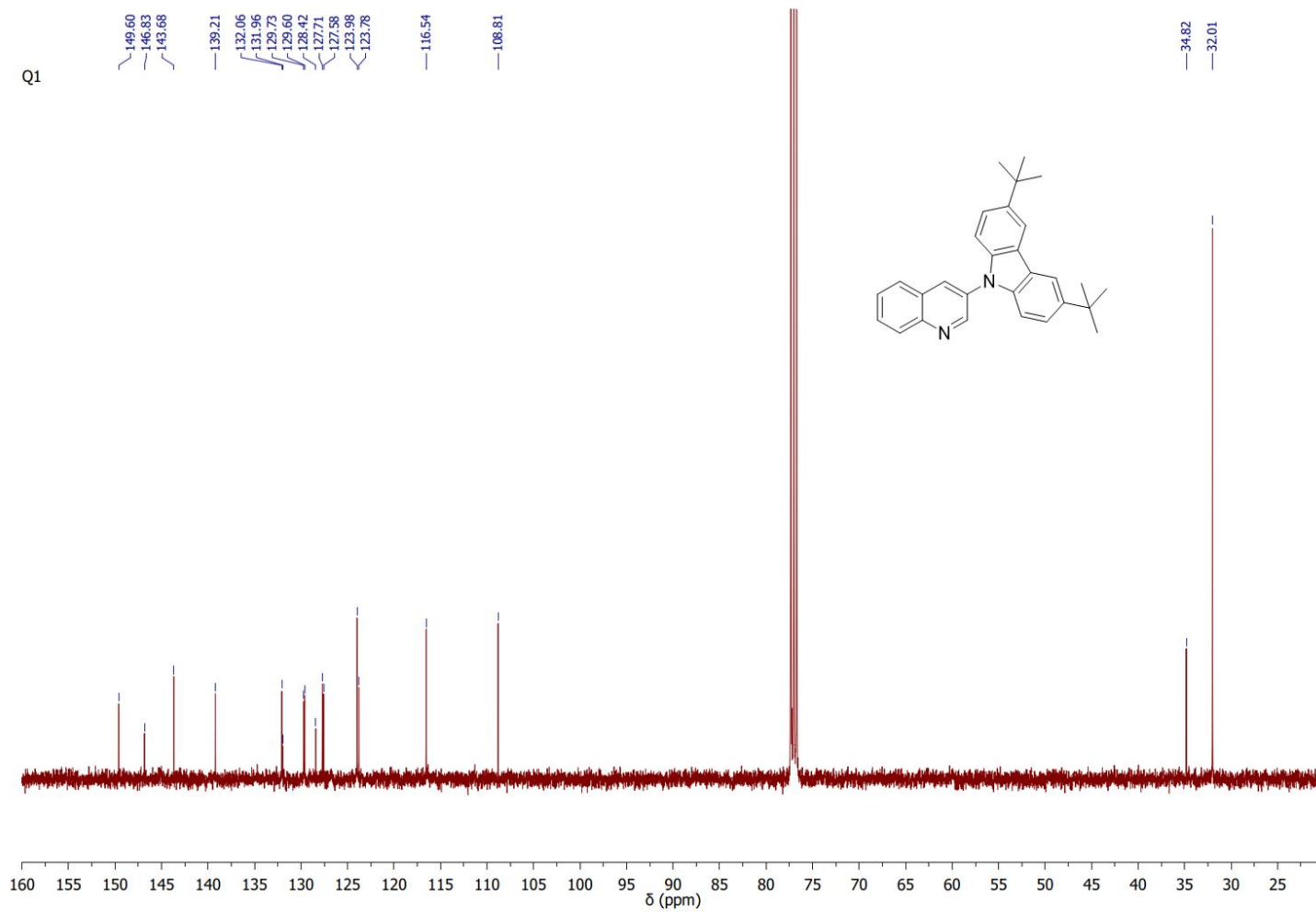


Figure S2. ^{13}C NMR spectrum of **Q1** in CDCl_3 , 400MHz, 293 K.

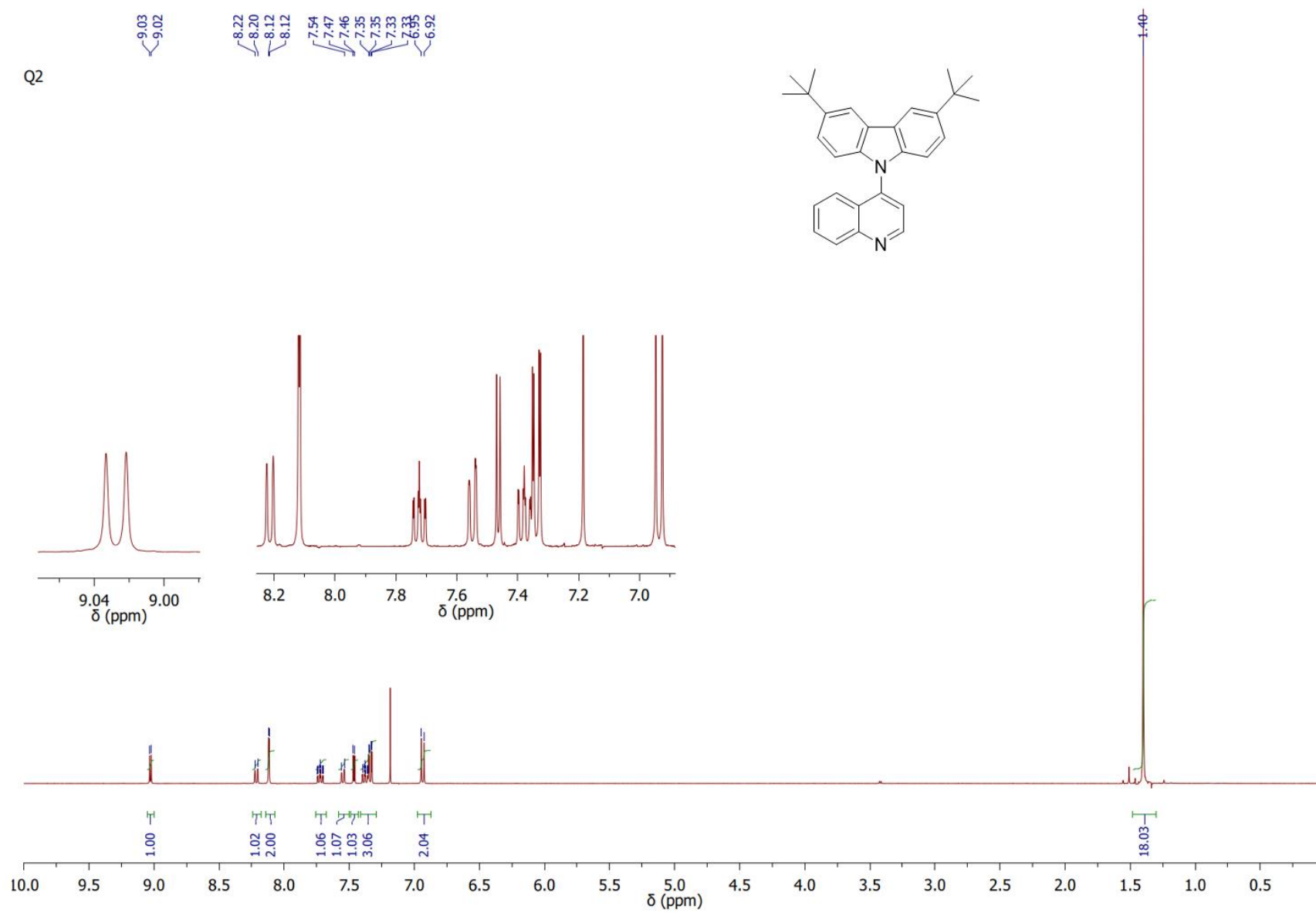


Figure S3. ¹H NMR spectrum of **Q2** in CDCl₃, 400MHz, 293 K.

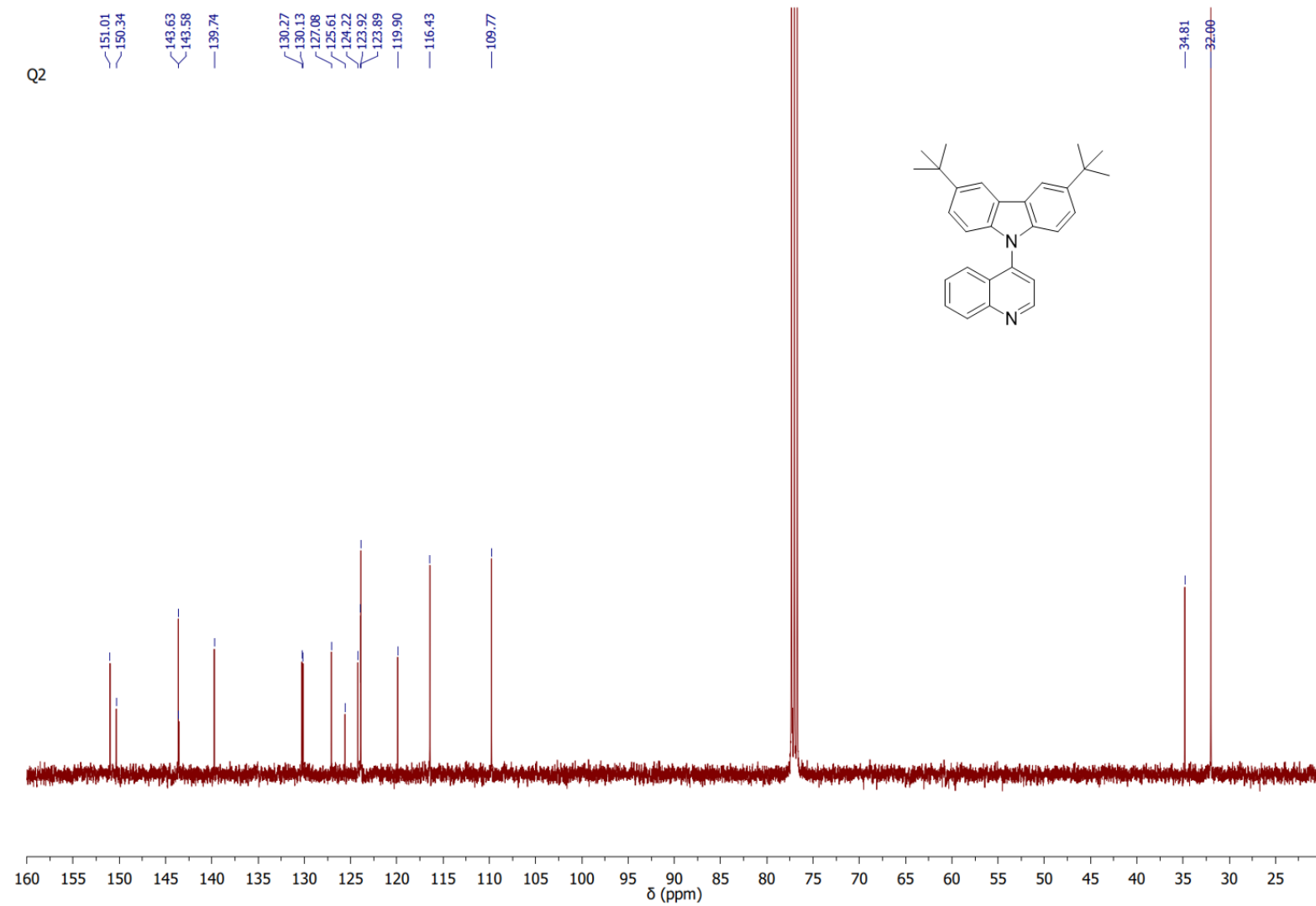


Figure S4. ^{13}C NMR spectrum of **Q2** in CDCl_3 , 400MHz, 293 K.

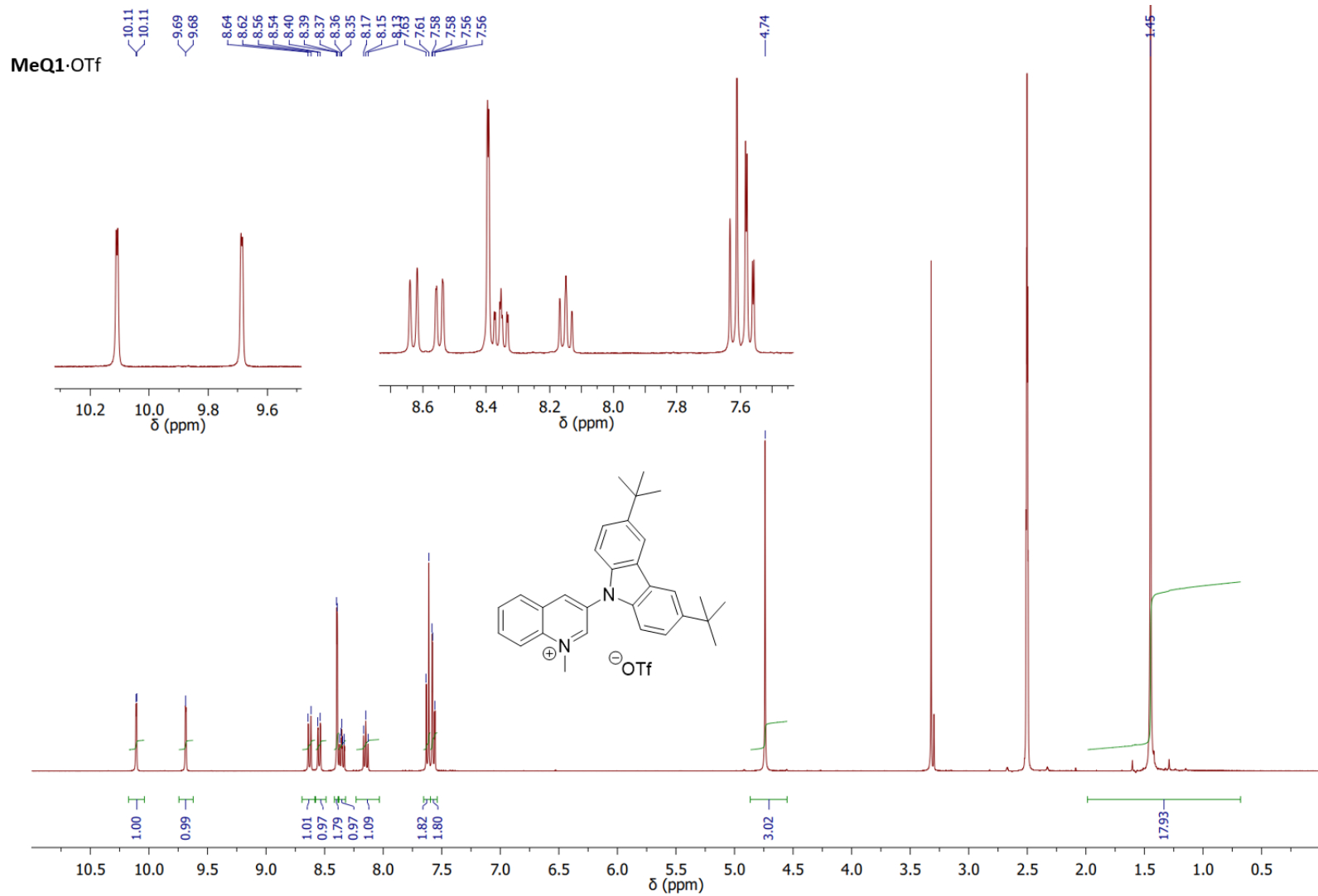
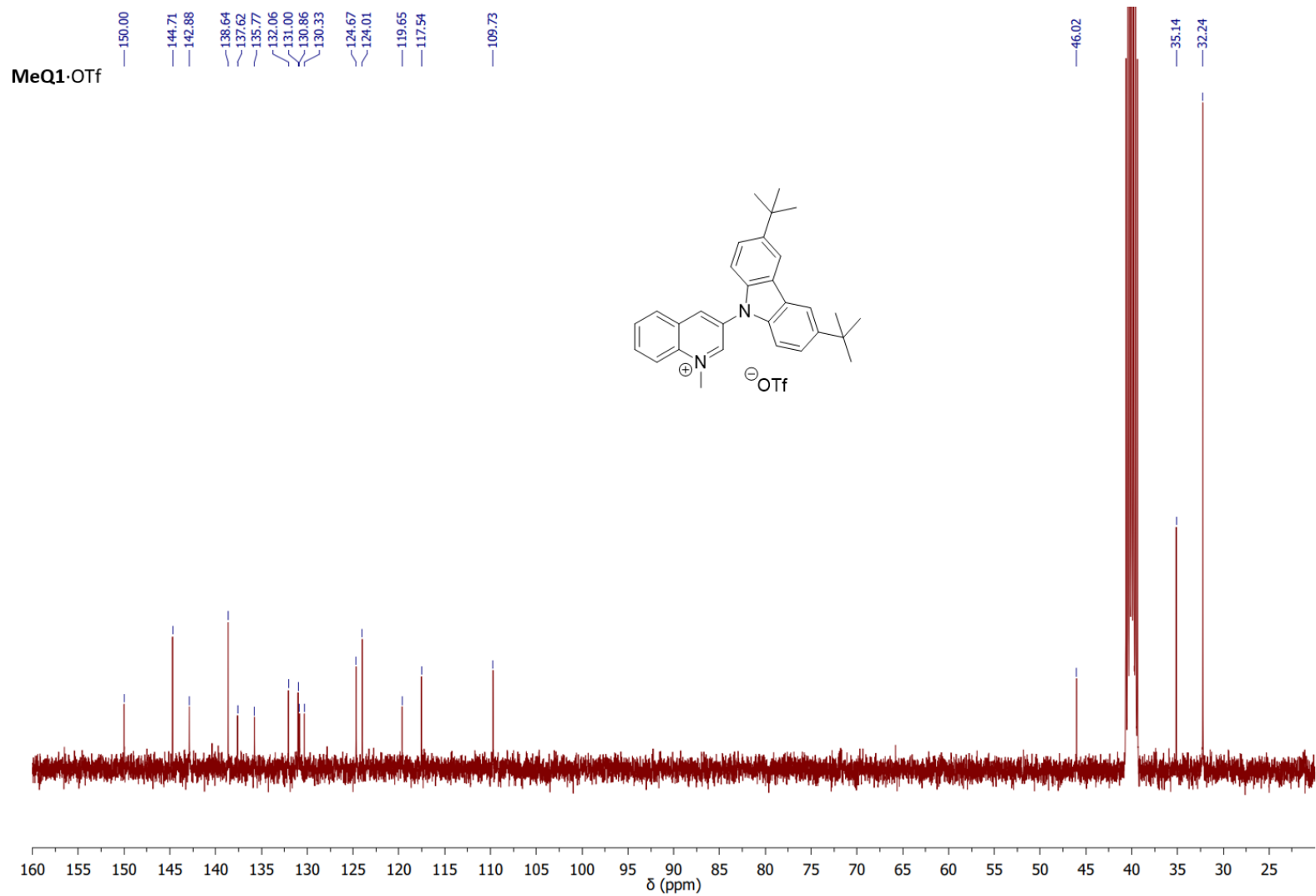


Figure S5. ¹H NMR spectrum of **MeQ1·OTf** in DMSO-d₆, 400MHz, 293 K.



MeQ2-OTf

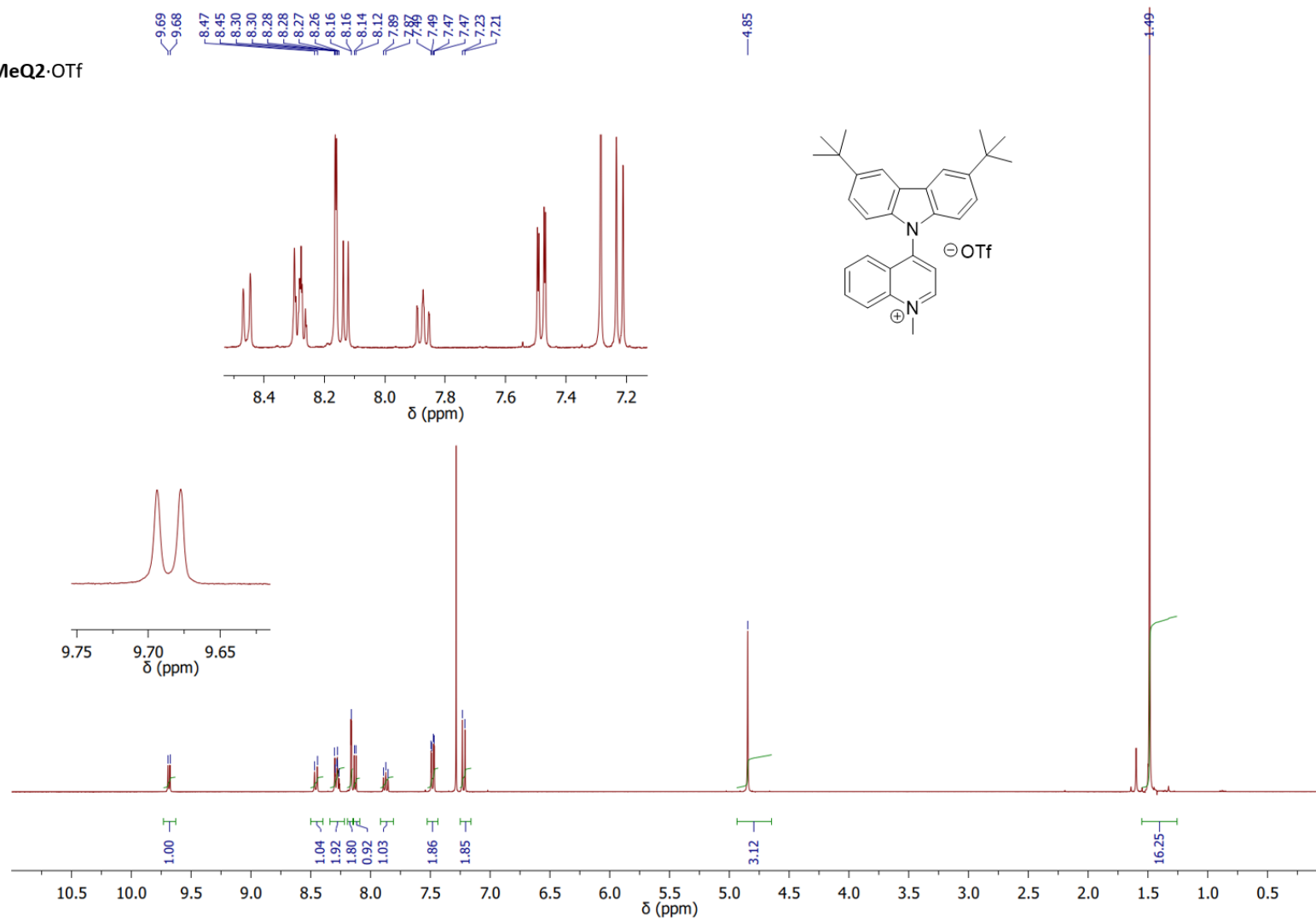


Figure S7. ¹H NMR spectrum of MeQ2-OTf in CDCl₃, 400MHz, 293 K.

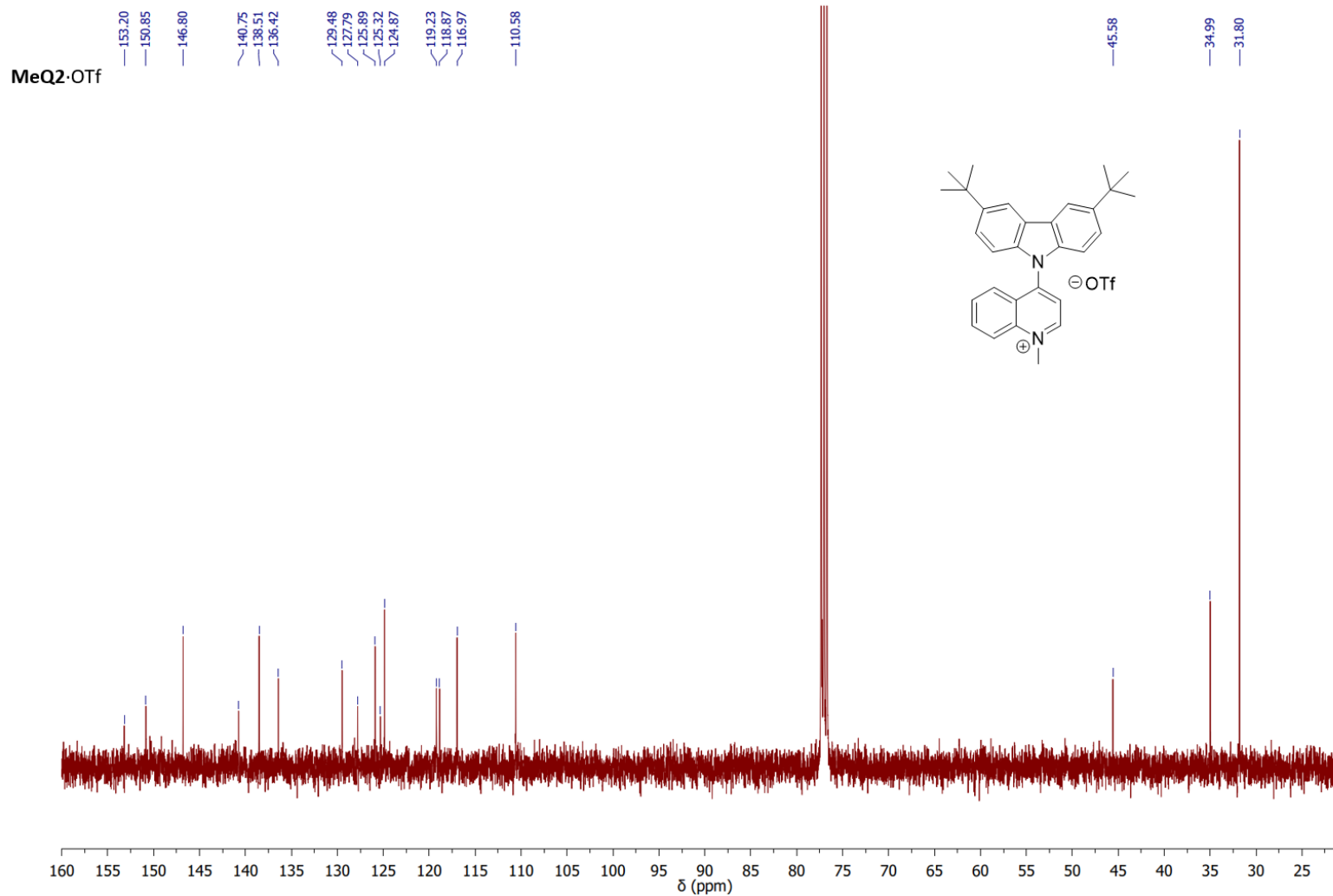


Figure S8. ^{13}C NMR spectrum of **MeQ2·OTf** in CDCl_3 , 400MHz, 293 K.

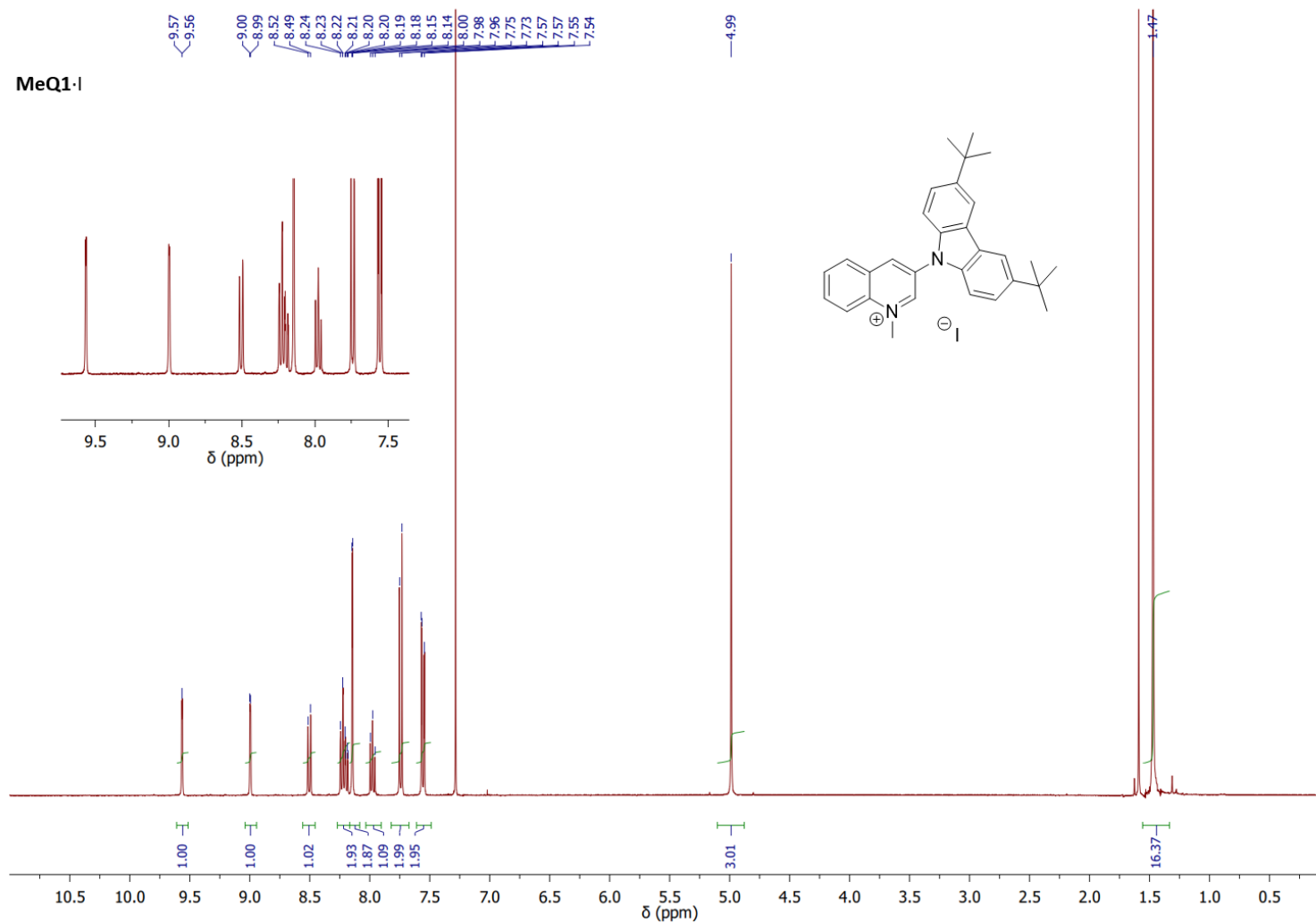


Figure S9. ^1H NMR spectrum of **MeQ1-I** in CDCl_3 , 400MHz, 293 K.

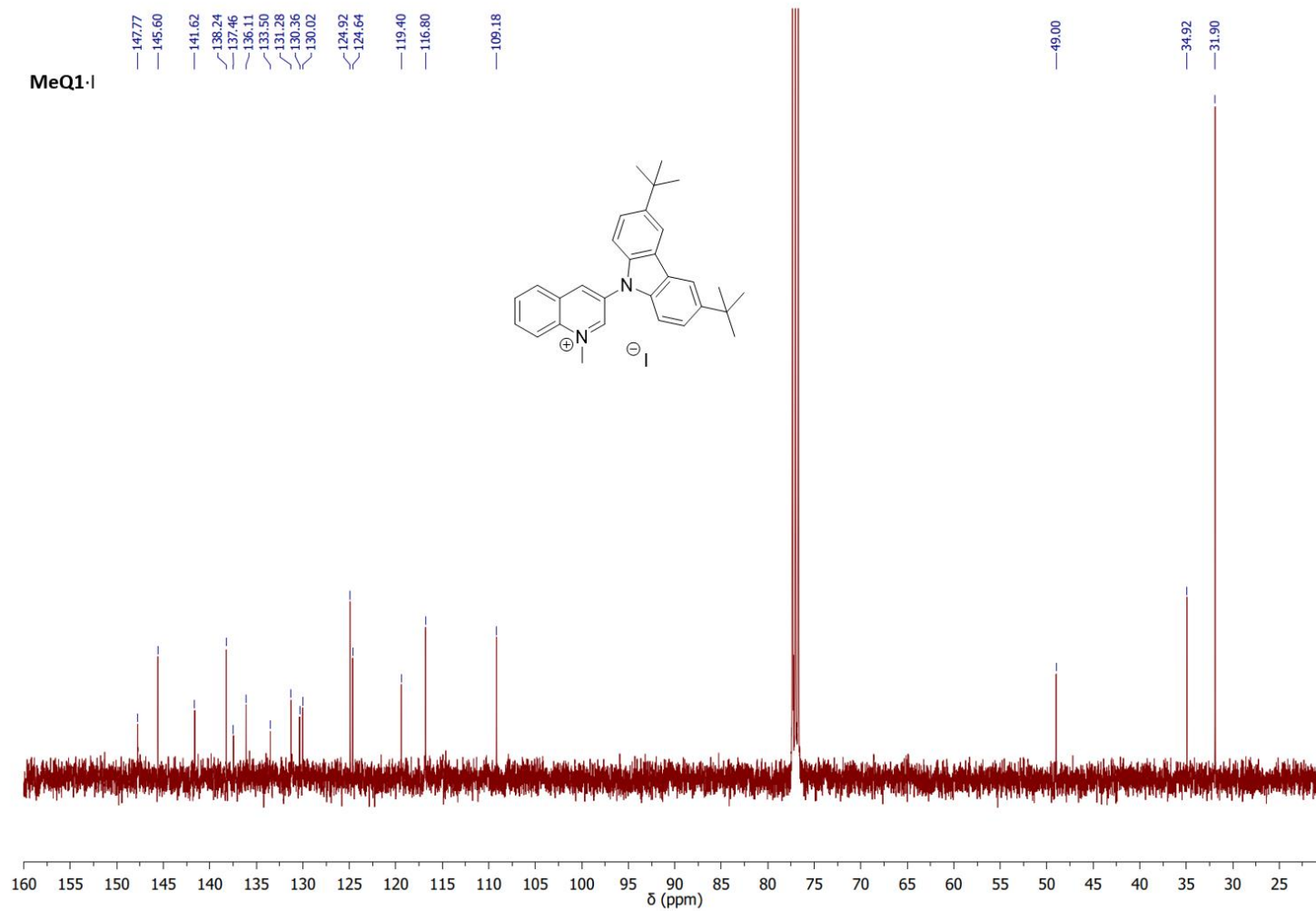


Figure S10. ^{13}C NMR spectrum of **MeQ1·I** in CDCl_3 , 400MHz, 293 K.

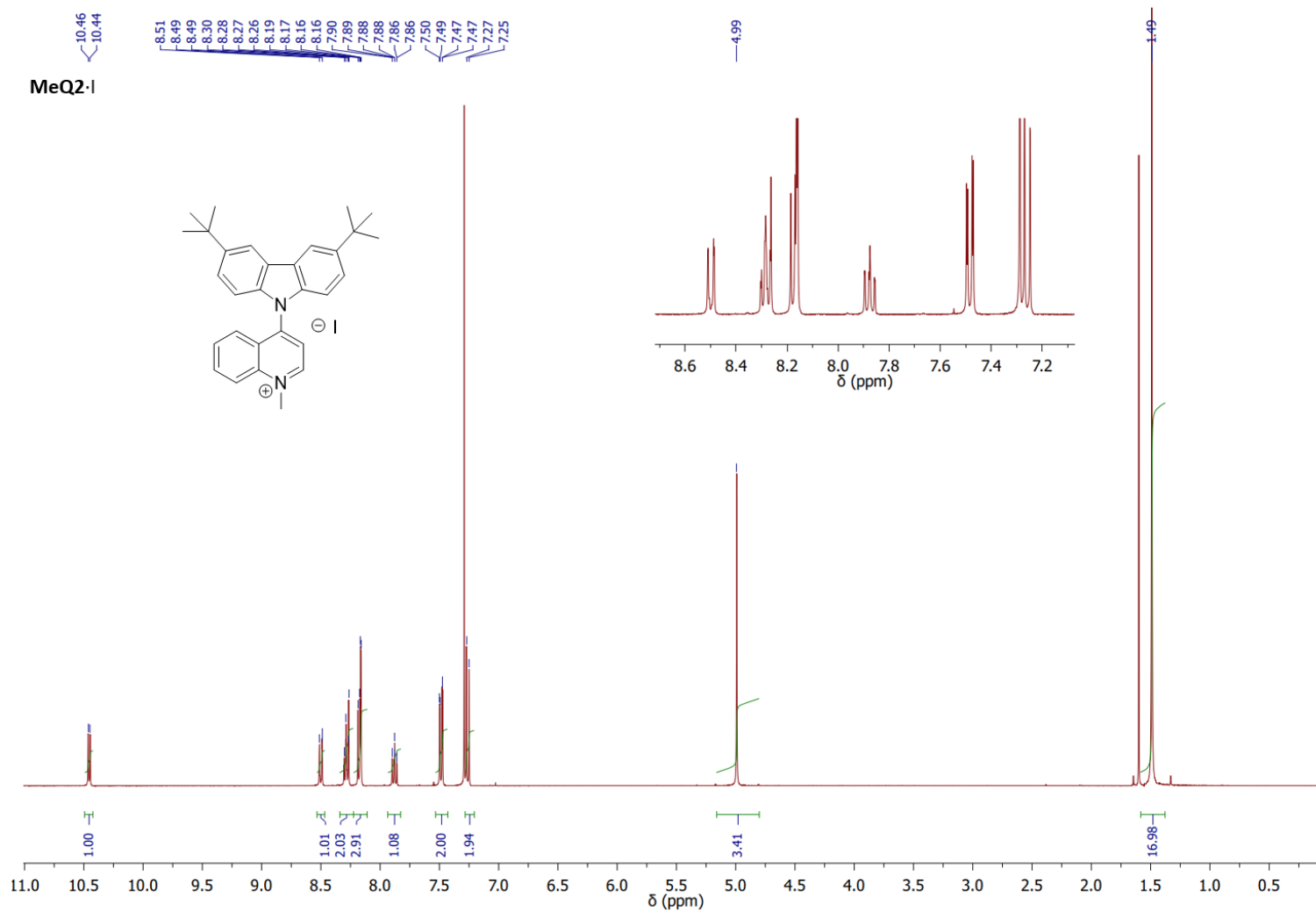


Figure S11. ¹H NMR spectrum of **MeQ2-I** in CDCl₃, 400MHz, 293 K.

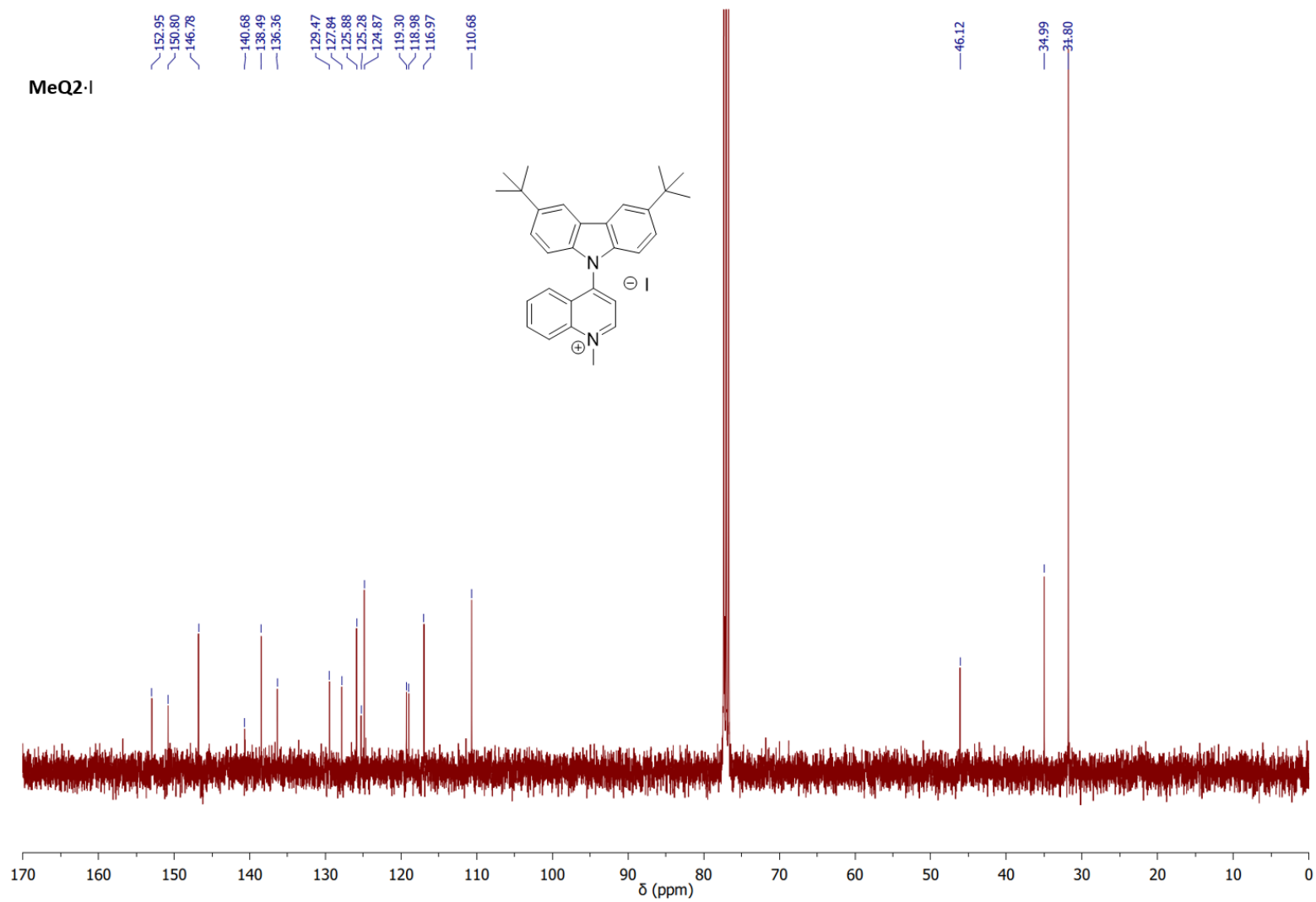


Figure S12. ^{13}C NMR spectrum of **MeQ2⁺I⁻** in CDCl_3 , 400MHz, 293 K.

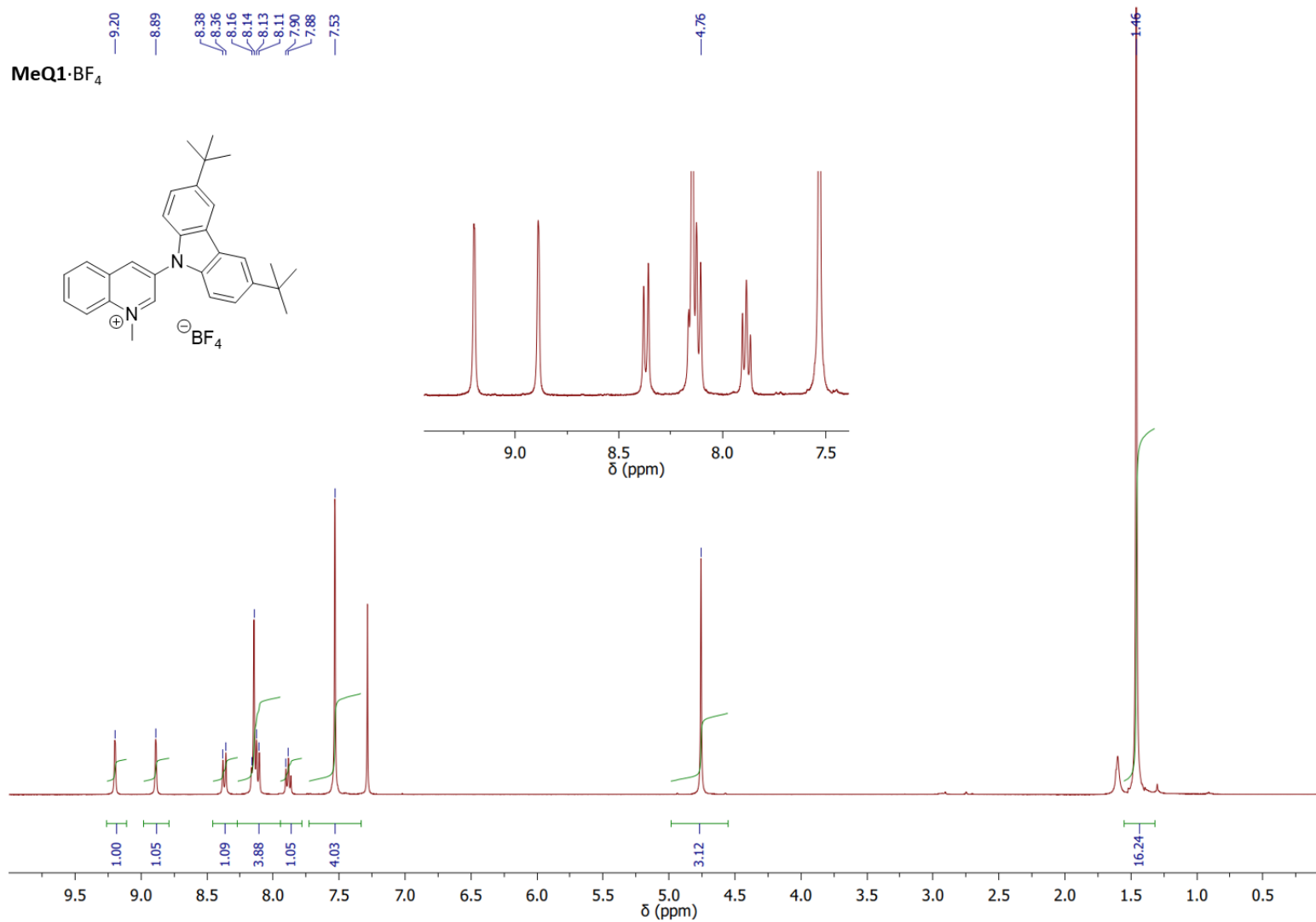
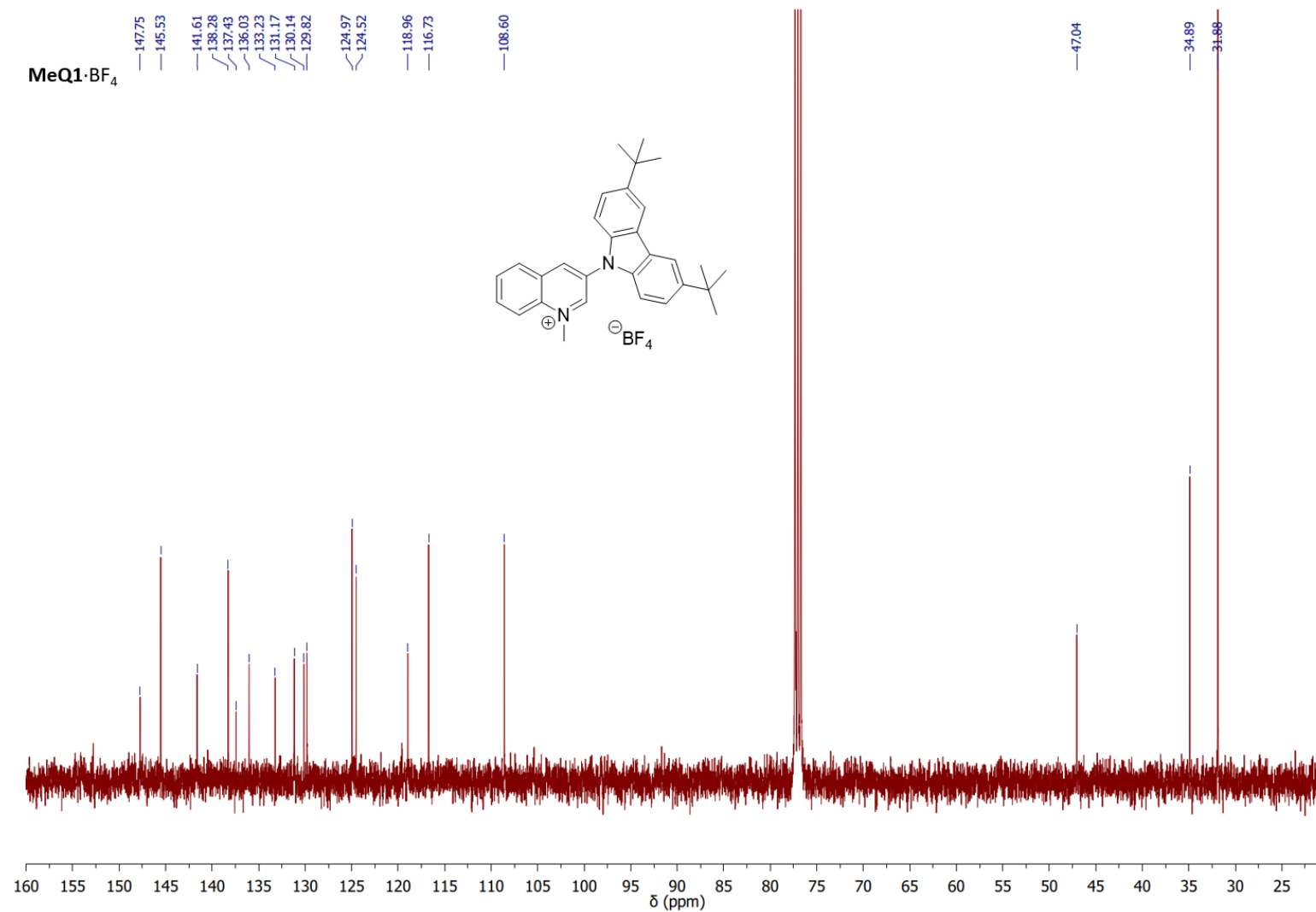


Figure S13. ¹H NMR spectrum of **MeQ1**·BF₄ in CDCl₃, 400MHz, 293 K.



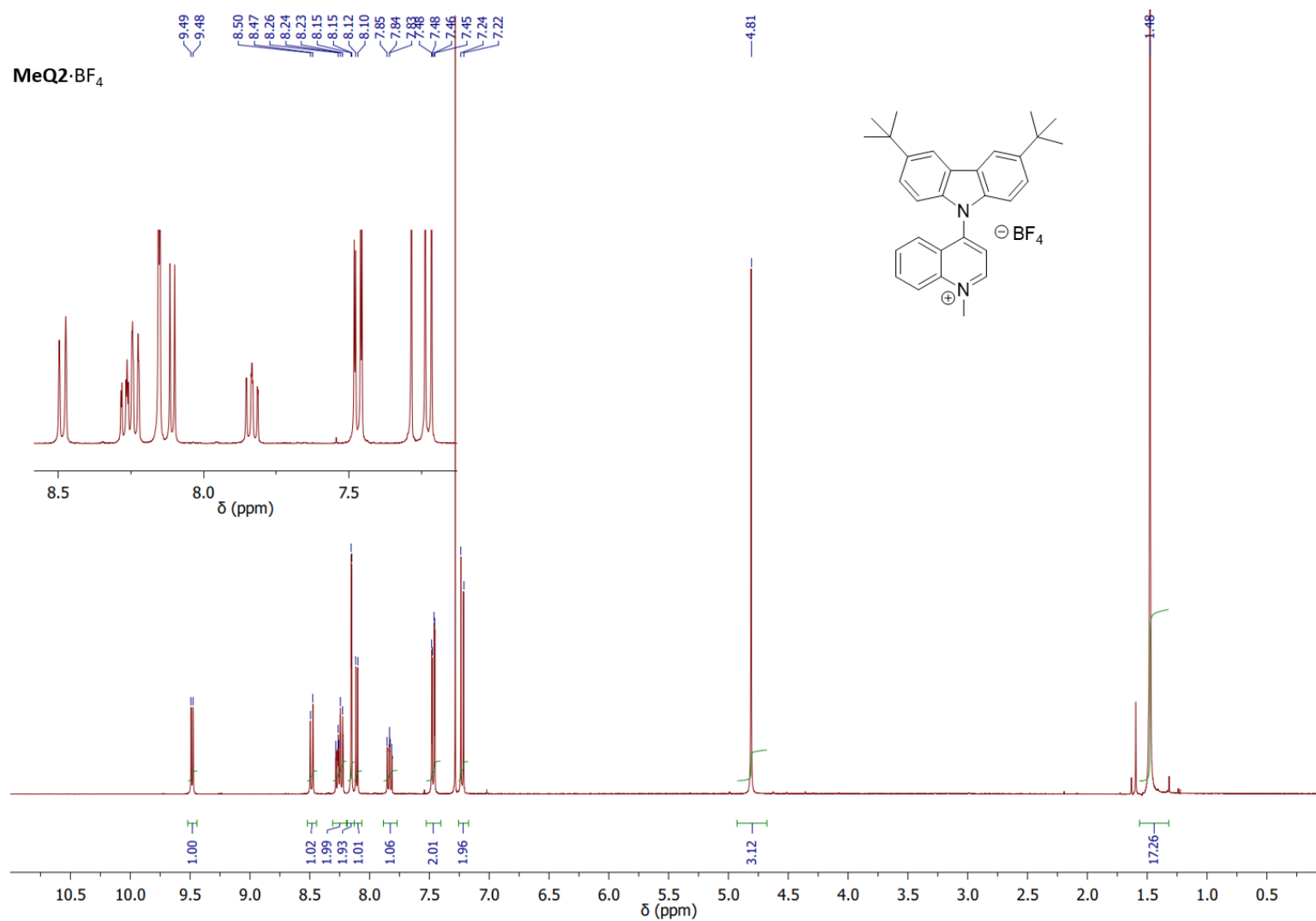


Figure S15. ¹H NMR spectrum of **MeQ2·BF₄** in CDCl₃, 400MHz, 293 K.

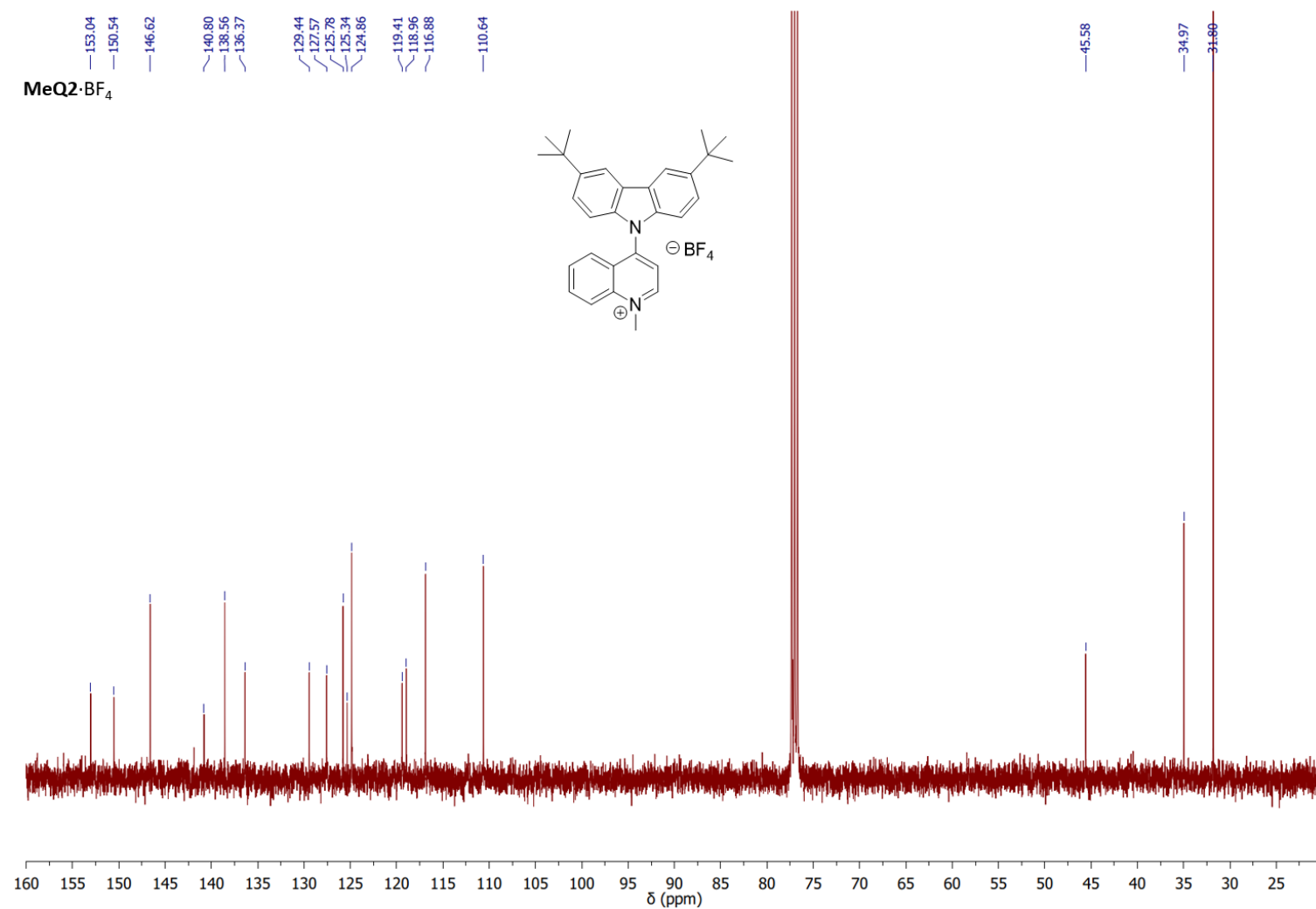


Figure S16. ¹³C NMR spectrum of **MeQ2·BF₄** in CDCl₃, 400MHz, 293 K.

4. Cyclic voltammetry

Cyclic voltammetry measurements were performed using a CH Instruments 660E electrochemical workstation with iR compensation at a scan rate of 0.1 Vs^{-1} . The electrochemical cell comprised of glassy carbon, platinum wire and silver wire as working, counter and reference electrodes respectively. The experiments were conducted at room temperature in degassed (Ar) 0.1 M solutions of tetrabutylammonium tetrafluoroborate in anhydrous solvent with *ca.* $5 \cdot 10^{-4} \text{ M}$ concentrations of the studied compounds. All measurements were referenced against the half-wave potential ($E_{1/2}$) of the Fc/Fc^+ redox couple. The cathodic and anodic peaks are shown for reversible and irreversible (irr) processes. The HOMO and LUMO levels were determined according to the following equations:

$$\text{LUMO} = -(E_{\text{ox}} + 4.8) \text{ (eV)}; \text{HOMO} = -(E_{\text{red}} + 4.8) \text{ (eV)}$$

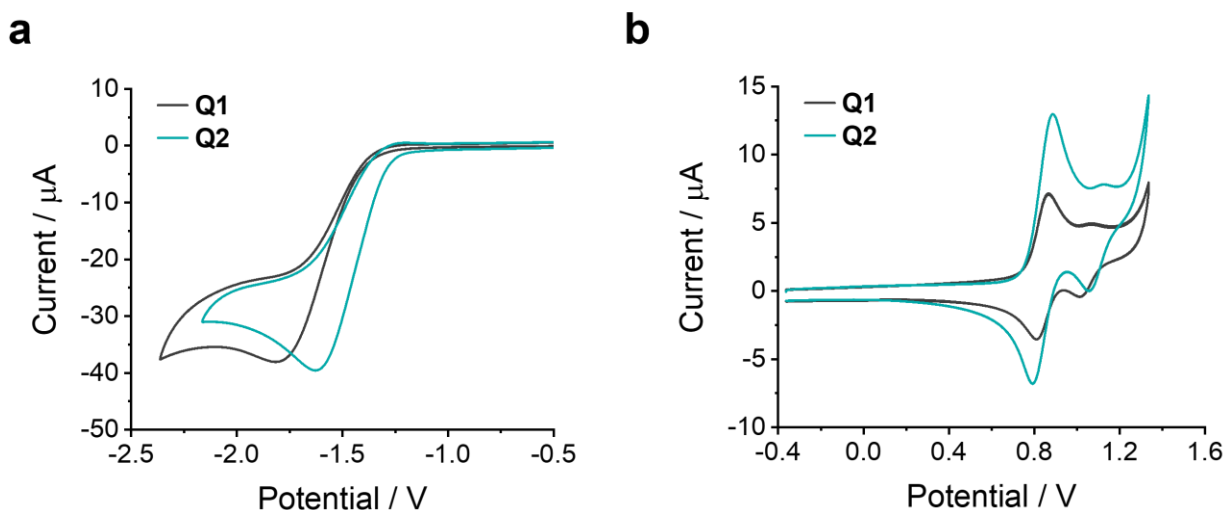


Figure S17. (a) Reduction and (b) oxidation curves from cyclic voltammetry of **Q1** and **Q2** referenced against the $E_{1/2}$ of the Fc/Fc^+ redox couple; $5 \cdot 10^{-4} \text{ M}$ solutions in $0.1 \text{ M } n\text{-Bu}_4\text{NPF}_6 (\text{CH}_2\text{Cl}_2)$.

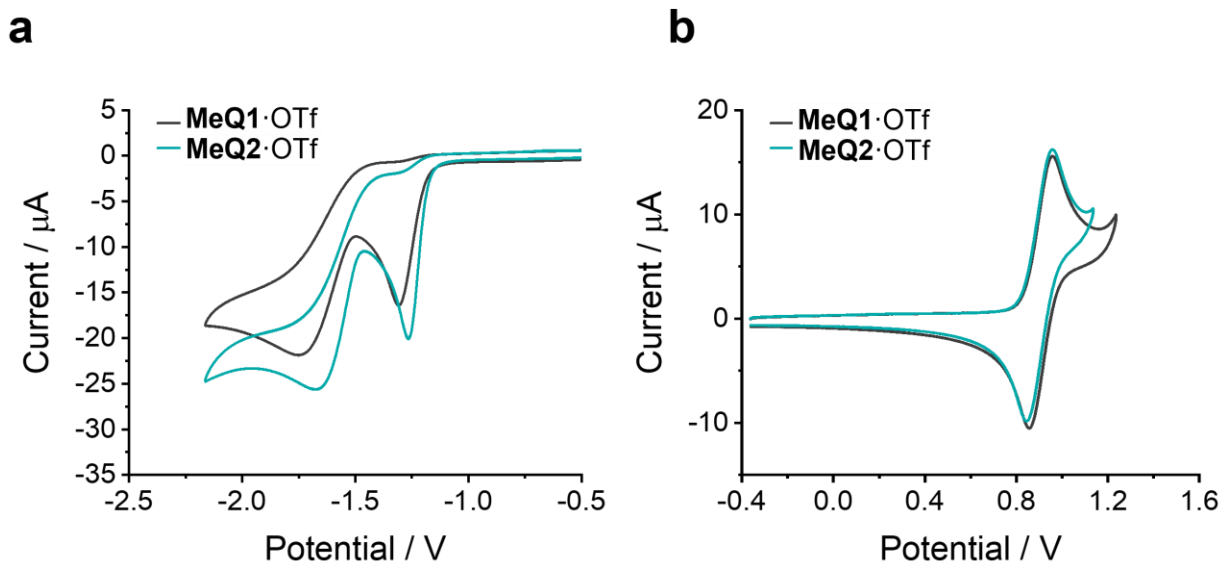


Figure S18. (a) Reduction and (b) oxidation curves from cyclic voltammetry of **MeQ1·OTf** and **MeQ2·OTf** referenced against the $E_{1/2}$ of the Fc/Fc⁺ redox couple; $5 \cdot 10^{-4}$ M solutions in 0.1 M *n*-Bu₄NPF₆ (CH₂Cl₂).

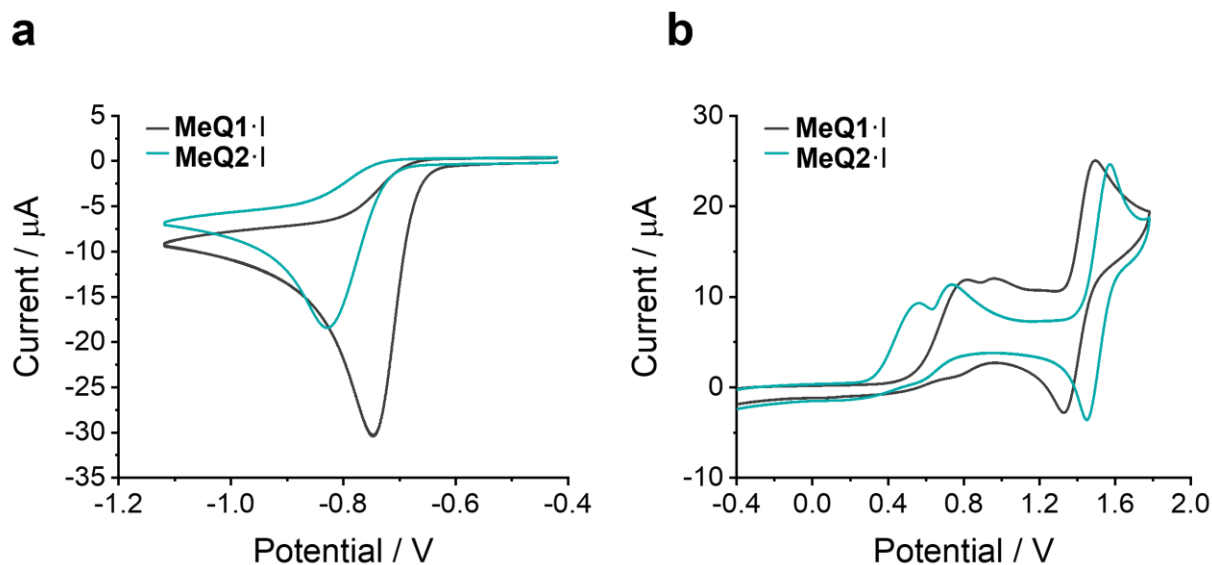


Figure S19. (a) Reduction and (b) oxidation curves from cyclic voltammetry of **MeQ1·I** and **MeQ2·I** referenced against the $E_{1/2}$ of the Fc/Fc⁺ redox couple; $5 \cdot 10^{-4}$ M solutions in 0.1 M *n*-Bu₄NPF₆ (CH₂Cl₂).

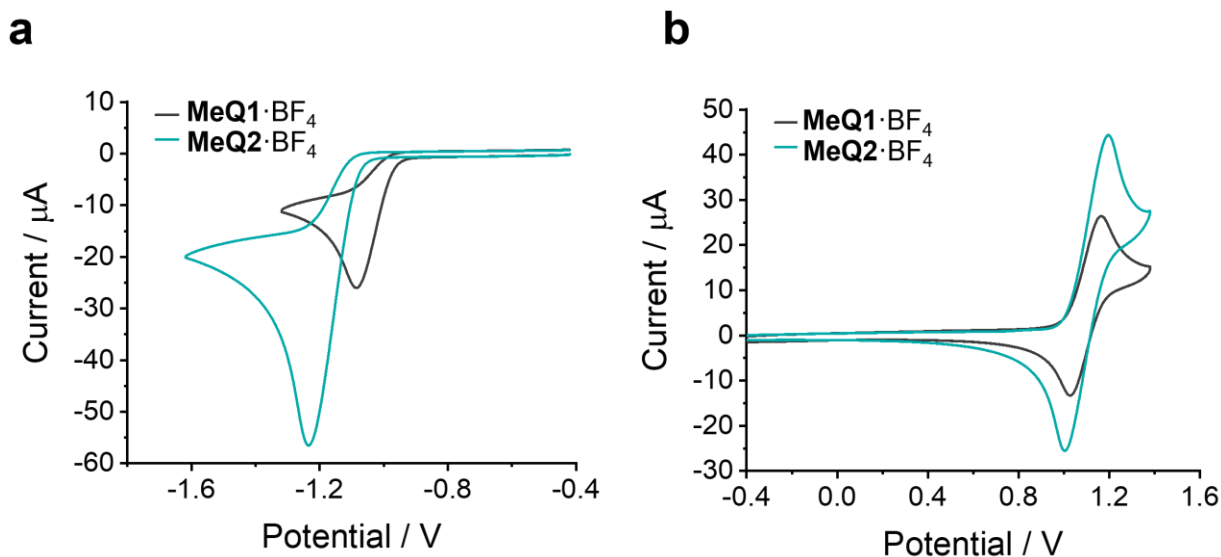


Figure S20. (a) Reduction and (b) oxidation curves from cyclic voltammetry of **MeQ1**·BF₄ and **MeQ2**·BF₄ referenced against the E_{1/2} of the Fc/Fc⁺ redox couple; 5·10⁻⁴ M solutions in 0.1 M *n*-Bu₄NPF₆ (CH₂Cl₂).

The electrochemistry data are presented in Table S1. The cathodic and anodic peaks are shown for reversible, quasi-reversible (q-r) and irreversible (irr) processes.

Table S1. HOMO-LUMO levels and electrochemical bandgap E_{g(CV)} for the **Q** series.

	E _{ox}	E _{red}	HOMO ^c (eV)	LUMO ^c (eV)	E _{g(CV)} (eV)
Q1	0.87 1.06 (q-r) ^a	-1.80 (irr) ^b	-5.67	-3.00	2.67
Q2	0.89 1.14 (q-r)	-1.63 (irr)	-5.69	-3.17	2.52
MeQ1 ·OTf	0.95	-1.31 (irr) -1.74 (irr)	-5.75	-3.49	2.26
MeQ2 ·OTf	0.95	-1.27 (irr) -1.67 (irr)	-5.75	-3.53	2.22
MeQ1 ·I	0.81 (irr) 0.96 (irr) 1.49	-0.75 (irr)	-5.61	-4.05	1.56

MeQ2 ·I	0.55 (irr) 0.73 (irr) 1.57	-0.83 (irr)	-5.35	-3.97	1.38
MeQ1 ·BF ₄	1.16	-1.09 (irr)	-5.96	-3.71	2.25
MeQ2 ·BF ₄	1.19	-1.23 (irr)	-5.99	-3.57	2.42

^a (q-r) denotes quasi-reversible; ^b (irr) denotes irreversible; ^c HOMO(LUMO) calculated from the peak of the corresponding redox wave and referenced to ferrocene.

The pairs of **Q1** and **Q2** derivatives demonstrate very similar electrochemical behaviour for all four sets of compounds. Materials **Q1** and **Q2** both show one reversible and one quasi-reversible oxidation peak (Figure S17, Table S1). The reduction demonstrates one irreversible peak. HOMO energies of materials are almost identical (-5.67 eV for **Q1** and -5.69 eV for **Q2**) while the LUMO energy is 0.17 eV higher for **Q1** material compared to **Q2** (-3.00 eV and -3.17 eV, respectively) which is probably due to a less efficient conjugation between carbazole and quinoline moiety for **Q1**.

The oxidation of materials **MeQ1**·OTf and **MeQ2**·OTf demonstrates one reversible wave and the reduction shows two irreversible waves (Figure S18, Table S1). The methylated materials have lower $E_{g(CV)}$ (2.26 eV for **MeQ1**·OTf and 2.22 eV for **MeQ2**·OTf) compared to **Q1** (2.67 eV) and **Q2** (2.52 eV).

The materials **MeQ1**·I and **MeQ2**·I show one reversible and two irreversible oxidation peaks, and one irreversible reduction peak (Figure S19, Table S1). These compounds demonstrate the smallest $E_{g(CV)}$ (1.56 eV for **MeQ1**·I and 1.38 eV for **MeQ2**·I) out of the whole series.

For the compounds **MeQ1**·BF₄ and **MeQ2**·BF₄ there is one reversible oxidation peak and one irreversible reduction peak (Figure S20, Table S1). These compounds demonstrate the lowest HOMO energy levels in the series ($\approx$ 6 eV).

5. Thermal Analysis

Thermal properties of the materials were investigated using TGA and DSC (Table S2). All compounds demonstrate high thermal stability with 5% weight loss above 290 °C for **Q1**, **Q2**, and **MeQ1**- and **MeQ2**- derivatives with triflate and tetrafluoroborate counter-ions. The materials with iodine counter ions exhibited a slightly lower thermal stability with 5% weight loss at 211 °C for **MeQ1**·I and 251 °C for **MeQ2**·I. Some of the materials demonstrate thermal transitions when measured by differential scanning calorimetry (Table S2). Lower temperature transitions are most likely glass transitions (T_g). All salts exhibit mechanochromic properties which suggests that the conformational changes can occur in the solid state for these compounds. Thus, some of the higher temperature transitions (T_{st}) can be attributed to the solid-solid phase transformations.

Table S2. Thermal properties of the quinoline-based materials.

	Q1	Q2	MeQ1 · OTf	MeQ2 · OTf	MeQ1 ·I	MeQ2 ·I	MeQ1 · BF ₄	MeQ2 · BF ₄
5% weight loss (°C)	290	310	330	315	211	251	328	319
DSC transitions (°C)	-	92 (T_g)	91 (T_g)	110 (T_g) 251 (T_{st})	-	95 (T_g)	129 (T_g) 222 (T_{st}) 273 (T_{st})	-

6. Photophysical Studies

Table S3. Absorption peaks in eV (nm) for **Q1**, **Q2**, **MeQ1·OTf** and **MeQ2·OTf** in MCH, 2-MeTHF, dichloromethane and chloroform.

	Q1	Q2	MeQ1·OTf ^a	MeQ2·OTf ^a
MCH	4.36 (284), <u>4.32</u> (<u>287</u>), 4.20 (295), 4.00 (310), 3.77 (329), 3.62 (343), 3.48 (356), <u>3.32</u> (<u>373</u>)	4.29 (289), 3.92 (316), 3.80 (326), 3.68 (337), 3.46 (358)	-	-
2-MeTHF	4.38 (283), 4.20 (295), 3.96 (313), 3.77 (329), 3.60 (344), 3.42 (363)	4.35 (285), 3.91 (317), 3.79 (327), 3.67 (338), 3.44 (360)	4.21 (294), 3.88 (<u>320</u>), 3.71 (334), 2.74 (452)	4.34 (286), 3.85 (322), 3.59 (345), 2.76 (450)
Dichloromethane	4.37 (284), 4.22 (294), 3.95 (314), 3.76 (330), 3.60 (344), 3.41 (364)	4.29 (289), 3.91 (317), 3.79 (327), 3.66 (339), 3.45 (359)	4.28 (290), <u>4.05</u> (<u>306</u>), 3.89 (319), 3.72 (333), 2.52 (493)	4.37 (284), 3.97 (312), 3.83 (324), 2.58 (480)
Chloroform	4.34 (286), 4.20 (295), 3.94 (315), 3.76 (330), 3.60 (344), 3.37 (368)	4.26 (291), 3.91 (317), 3.79 (327), 3.66 (339), 3.40 (365)	4.25 (292), 4.05 (306), 3.86 (321), 3.71 (334), 2.52 (493)	4.35 (285), 3.96 (313), 3.82 (325), 2.62 (473)
Acetonitrile	4.37 (284), 4.22 (294), 3.77 (329), 3.60 (344), 3.43 (361)	4.31 (288), 3.91 (317), 3.80 (326), 3.67 (338), 3.41 (364)	4.23 (293), 3.85 (322), 3.72 (333), 2.76 (450)	4.38 (283), 3.90 (318), 2.77 (448)

^a compound insoluble in MCH

Table S4 Emission peaks in eV(nm) for **Q1** and **Q2** in solutions of MCH, 2-MeTHF, dichloromethane and chloroform

	MCH	2-MeTHF	Dichloromethane	Chloroform	Acetonitrile
Q1	3.24 (383)	2.86 (434)	2.63 (471)	2.67 (465)	2.57 (482)
Q2	3.09 (401)	2.79 (444)	2.58 (479)	2.63 (472)	2.51 (494)

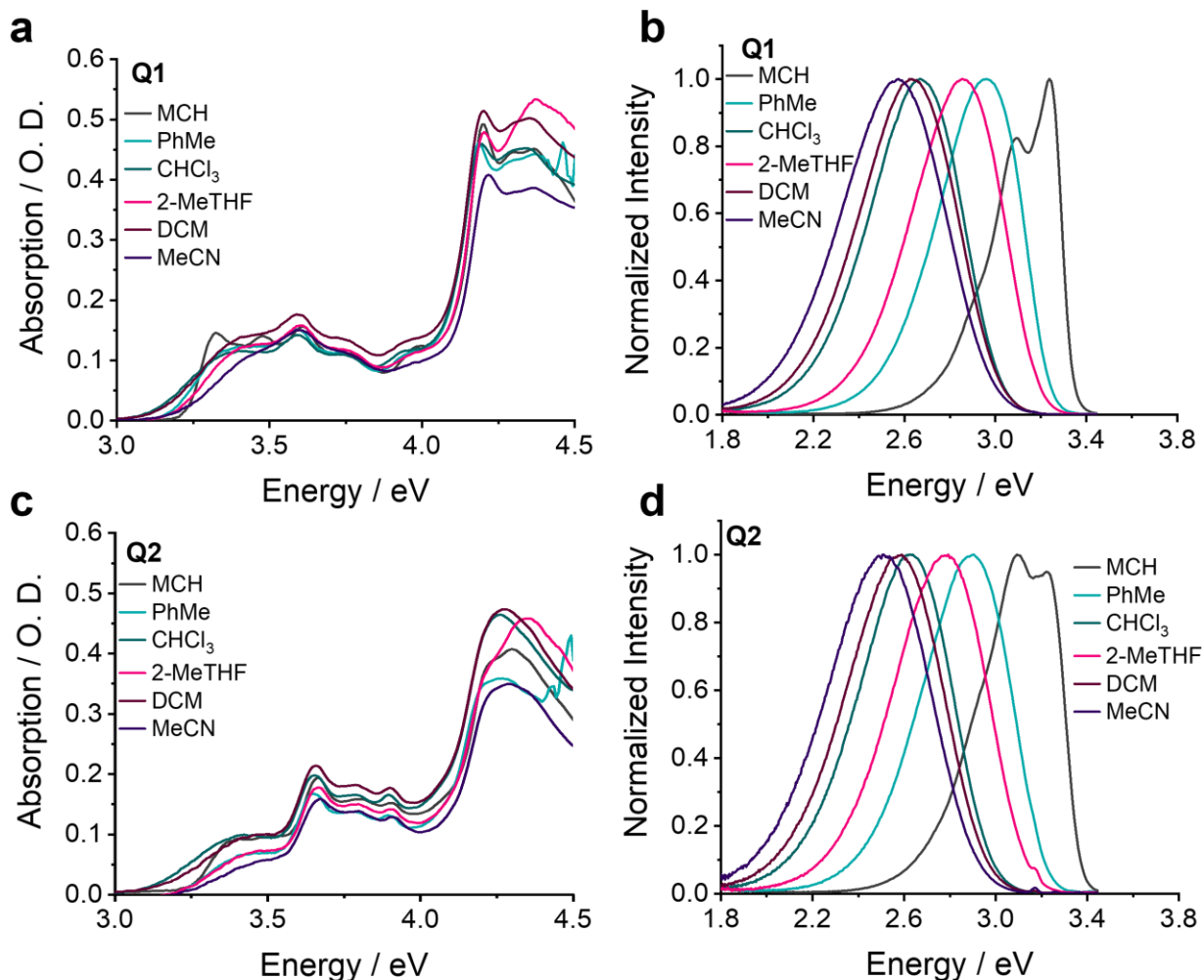


Figure S21. Solvatochromic a) UV-vis absorption and b) emission spectra for **Q1** at a concentration of 20 μ M. Solvatochromic c) UV-vis absorption and d) emission spectra for **Q2** at a concentration of 20 μ M.

Table S5 Absorption and emission maxima in eV (nm) for **Q**-series in PMMA matrix film.

	Q1	Q2	MeQ1 ·OTf	MeQ1 ·I	MeQ1 · BF ₄	MeQ2 · OTf	MeQ2 ·I	MeQ2 · BF ₄
Absorption	4.34 (286)	4.26 (291)	4.20 (295)	4.20 (295)	4.22 (294)	4.35 (285)	4.32 (287)	4.34 (286)
	4.19 (296)	3.90 (318)	3.84 (323)	3.84 (323)	3.82 (325)	3.86 (321)	3.91 (317)	3.90 (318)
	3.76 (330)	3.77 (329)	3.68 (337)	3.69 (336)	3.69 (336)	2.76 (449)	2.78 (446)	2.76 (449)
	3.60 (344)	3.66 (339)	2.75 (451)	2.74 (452)	2.73 (455)			
	3.39 (366)	3.43 (361)						
Emission	3.04 (407)	3.01 (412)	2.15 (578)	2.12 (586)	2.13 (581)	2.13 (581)	2.10 (590)	2.12 (585)

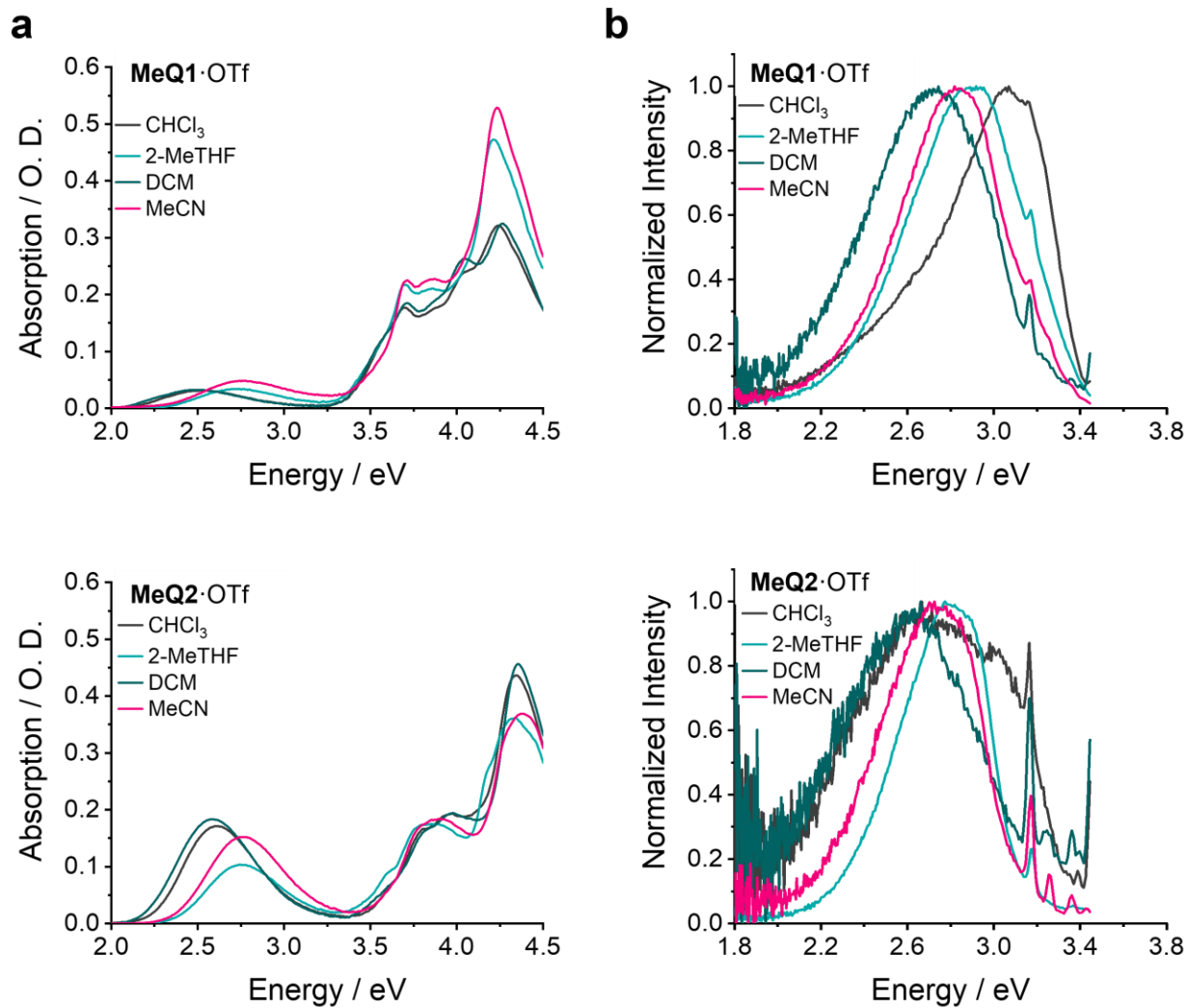


Figure S22. UV-vis absorption spectra and emission spectra for **MeQ1·OTf** (a,b) and **MeQ2·OTf** (c,d) in a series of solvents at 20 μM .

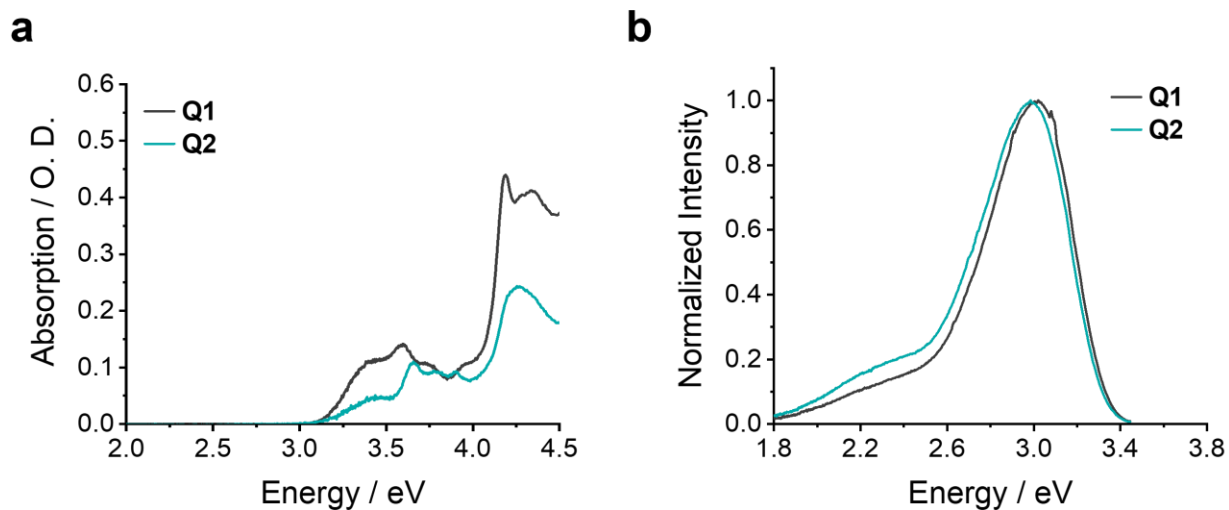


Figure S23. (a) UV-vis absorption and (b) emission spectra for **Q1** and **Q2** in 1 wt% PMMA film.

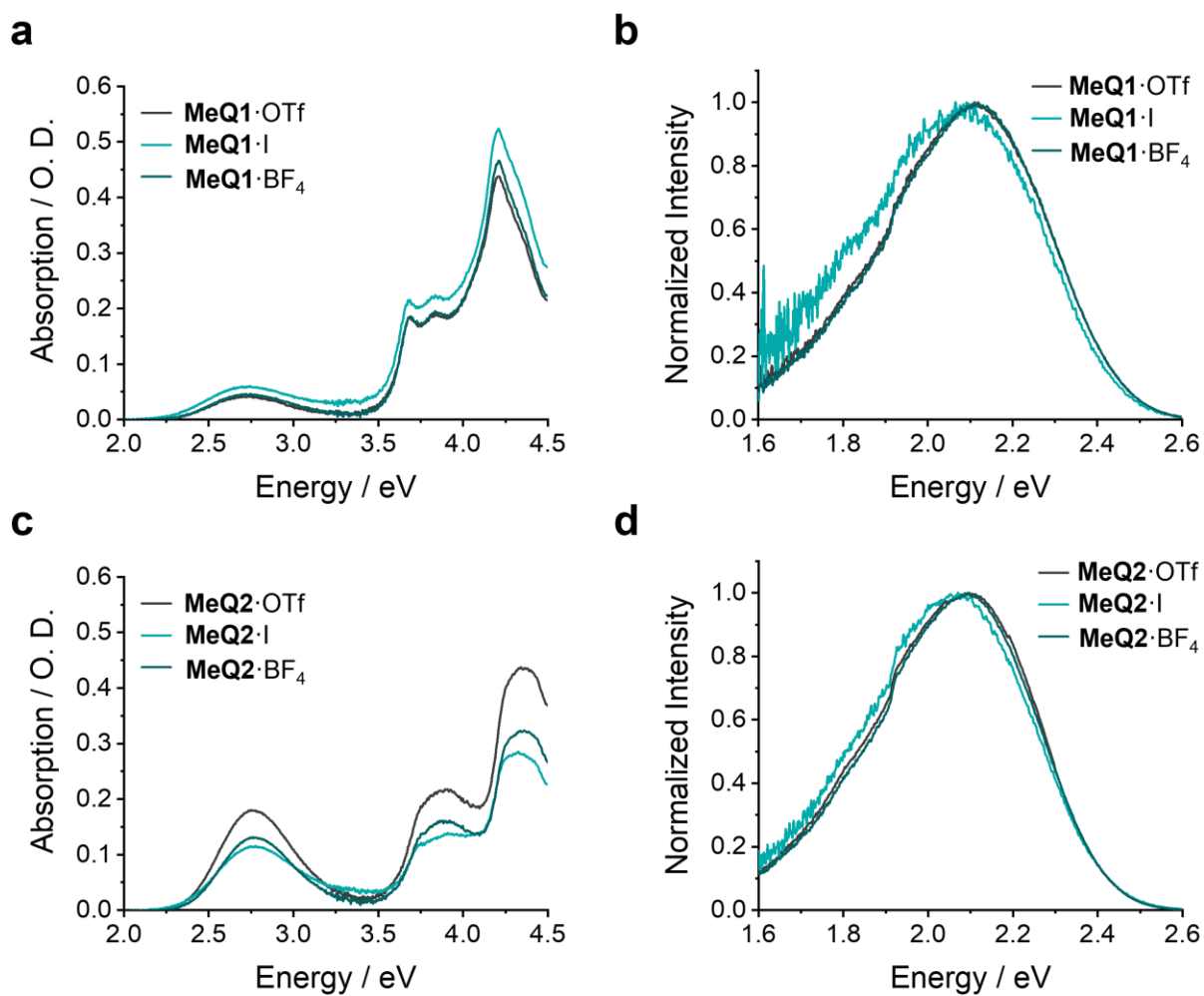


Figure S24. UV-vis absorption spectra and emission spectra for **MeQ1**-based (a,c) and **MeQ2**-based (b,d) salts in a 1 wt% PMMA film.

Table S6 Emission maxima in eV (nm) for powders of **MeQ1**·OTf, **MeQ2**·OTf, **MeQ1**·BF₄ and **MeQ2**·BF₄ before and after grinding.

	MeQ1 ·OTf	MeQ2 ·OTf	MeQ1 ·BF ₄	MeQ2 ·BF ₄
Before grinding	2.24 (554)	2.23 (557)	2.12 (585)	2.22 (559)
After grinding	2.13 (582)	2.07 (600)	2.07 (600)	2.02 (613)

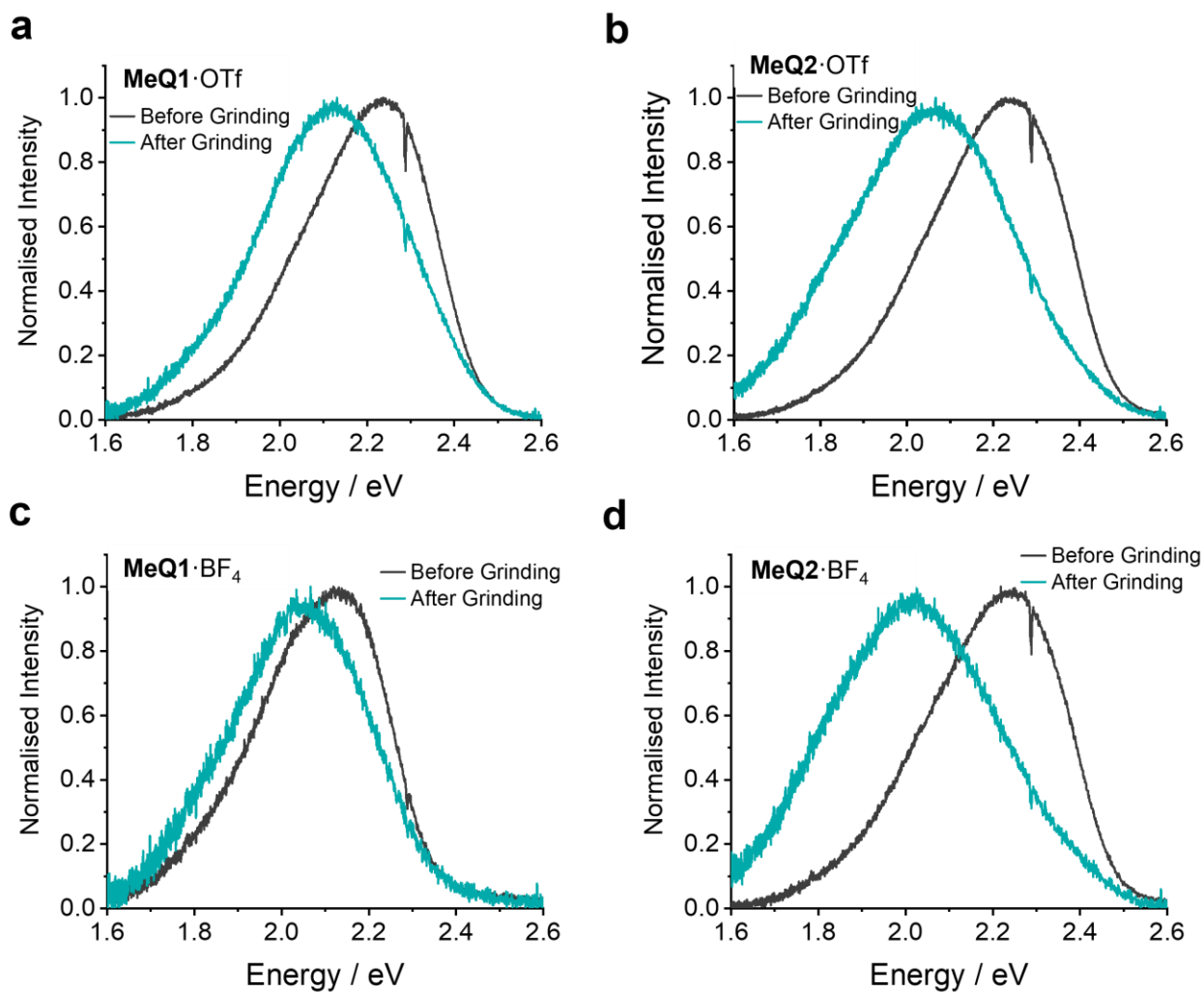


Figure S25 Mechanochromism of (a) **MeQ1**·OTf, (b) **MeQ2**·OTf, (c) **MeQ1**·BF₄ and (d) **MeQ2**·BF₄.

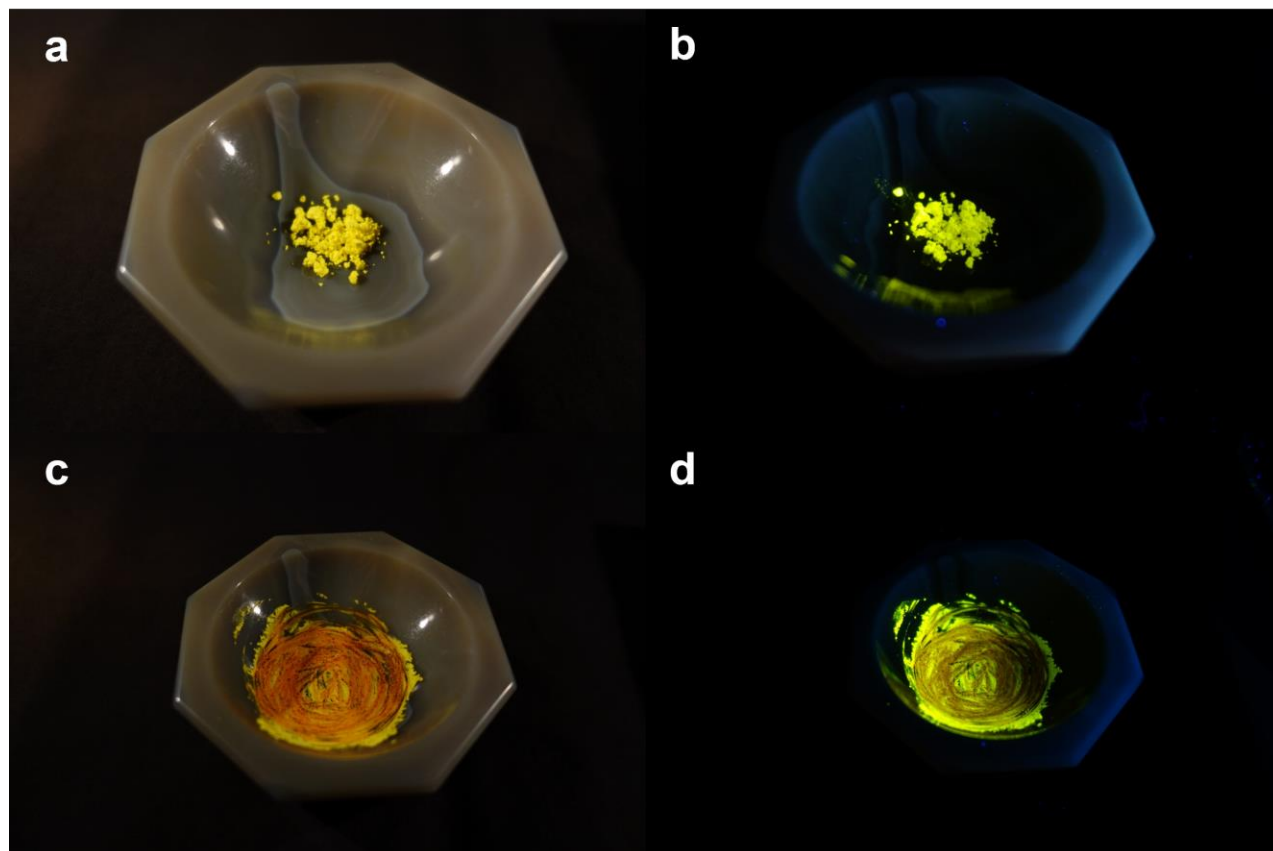


Figure S26 Mechanochromism of **MeQ1·OTf** (a) before grinding under normal light (b) before grinding under UV light (c) after grinding under normal light and (d) after grinding under UV light.

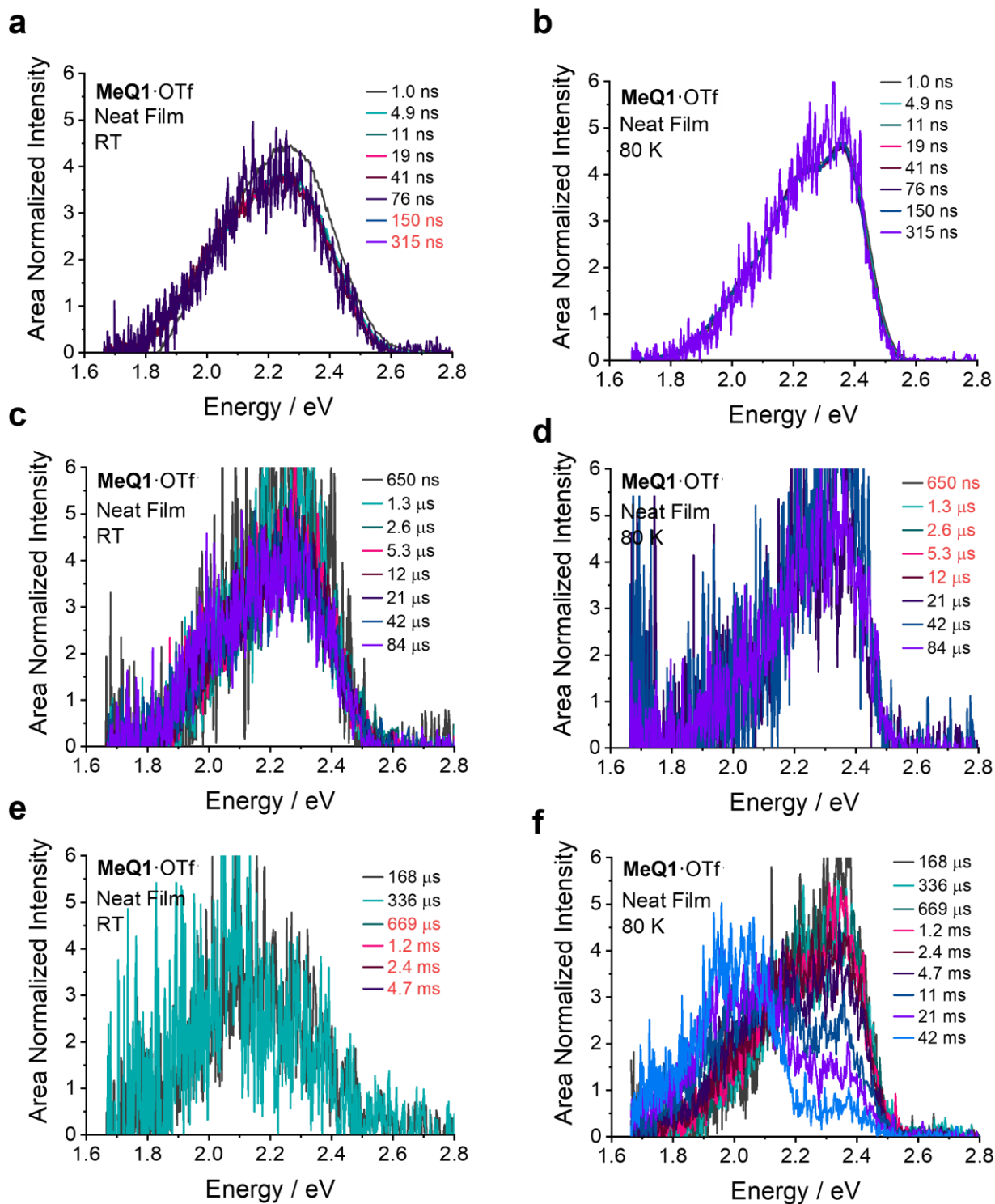


Figure S27. The time-resolved photoluminescence spectra of a neat film of **MeQ1·OTf**

measured at (a,c,e) room temperature (RT) and (b,d,f) 80 K. The times in red indicate times where no measurable signal was found.

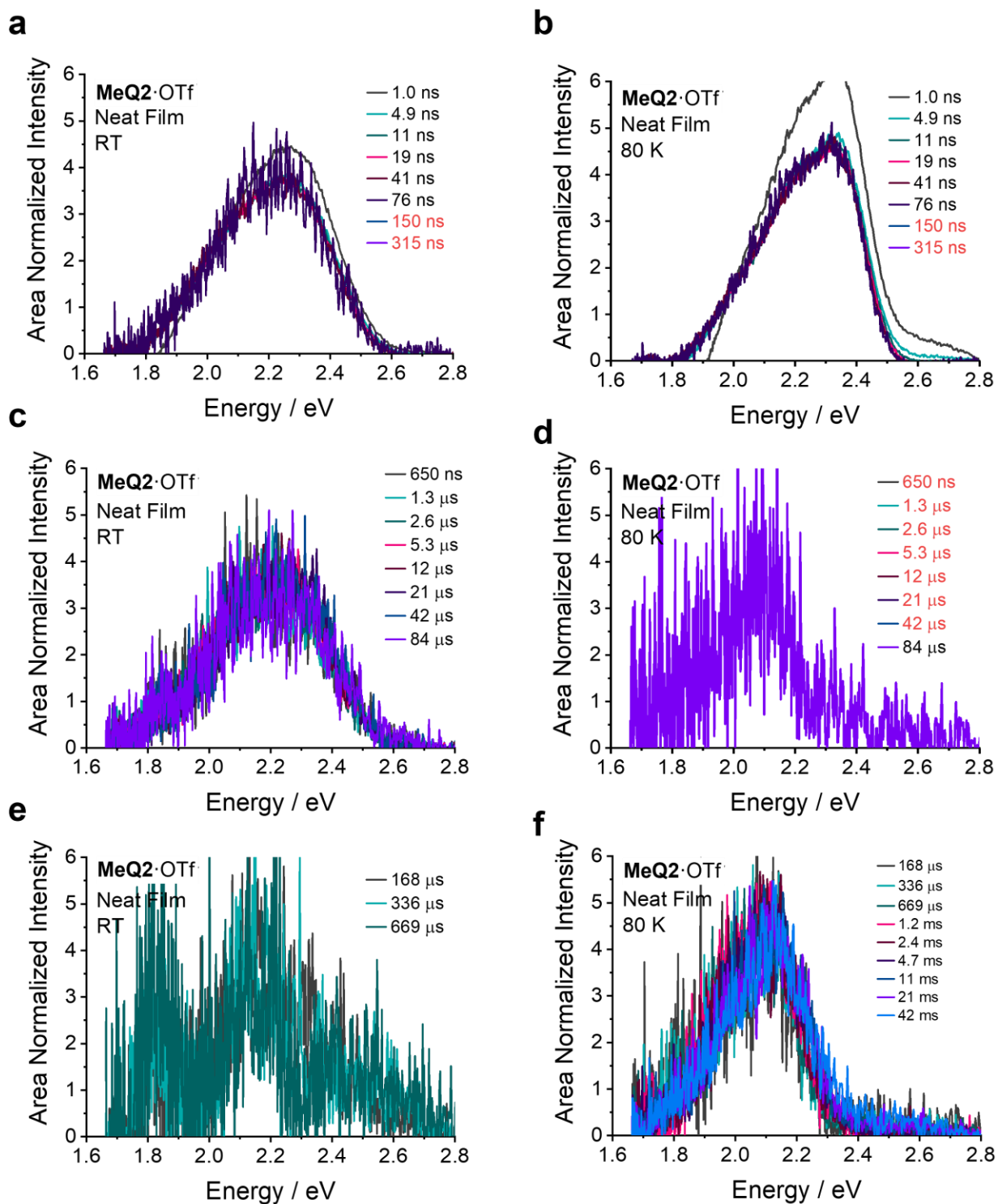


Figure S28. The time-resolved photoluminescence spectra of a neat film of **MeQ2·OTf**

measured at (a,c,e) room temperature (RT) and (b,d,f) 80 K. The times in red indicate times where no measurable signal was found.

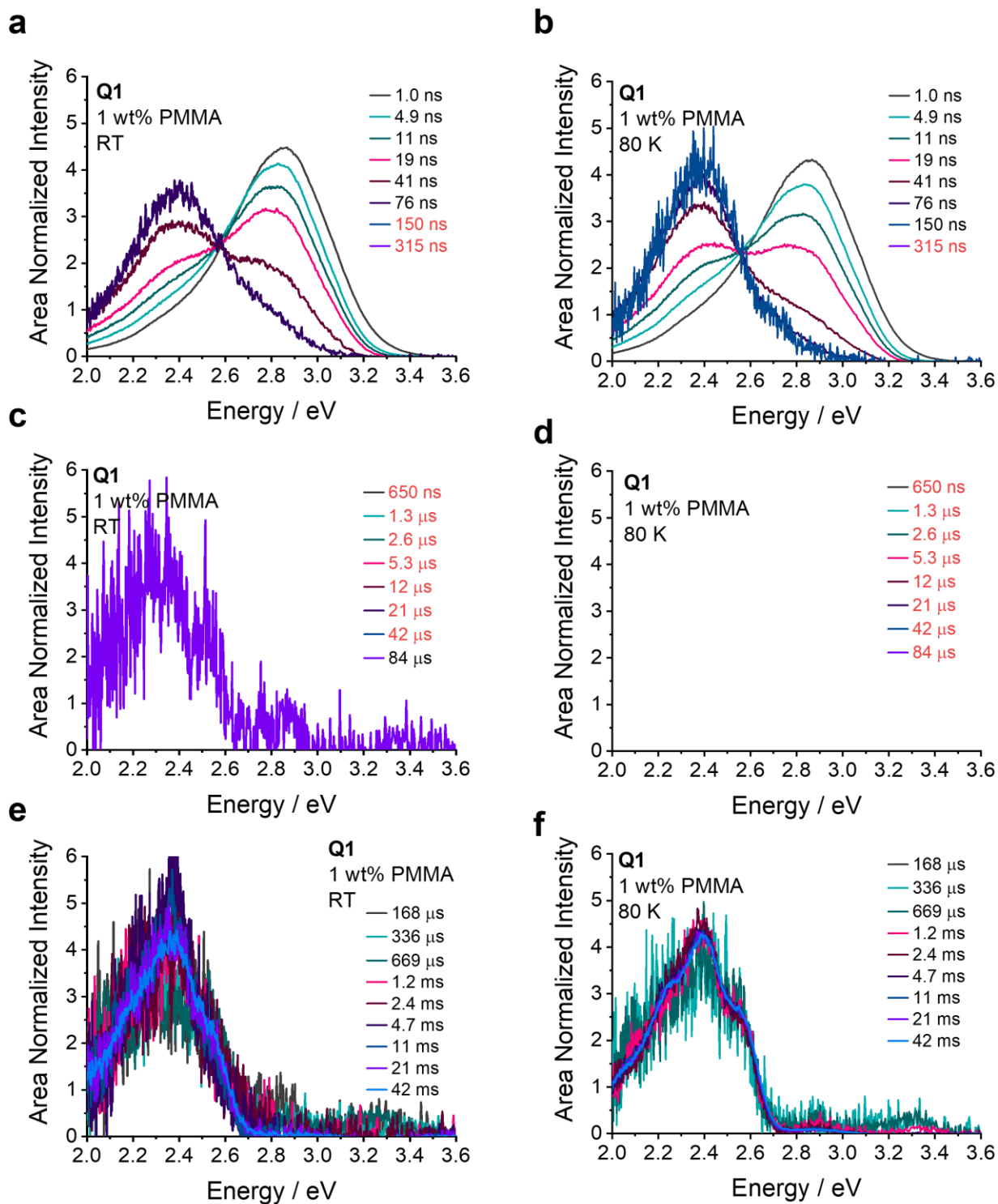


Figure S29. The time-resolved photoluminescence spectra of a 1 wt% PMMA film of **Q1**

measured at (a,c,e) room temperature (RT) and (b,d,f) 80 K. The times in red indicate times where no measurable signal was found.

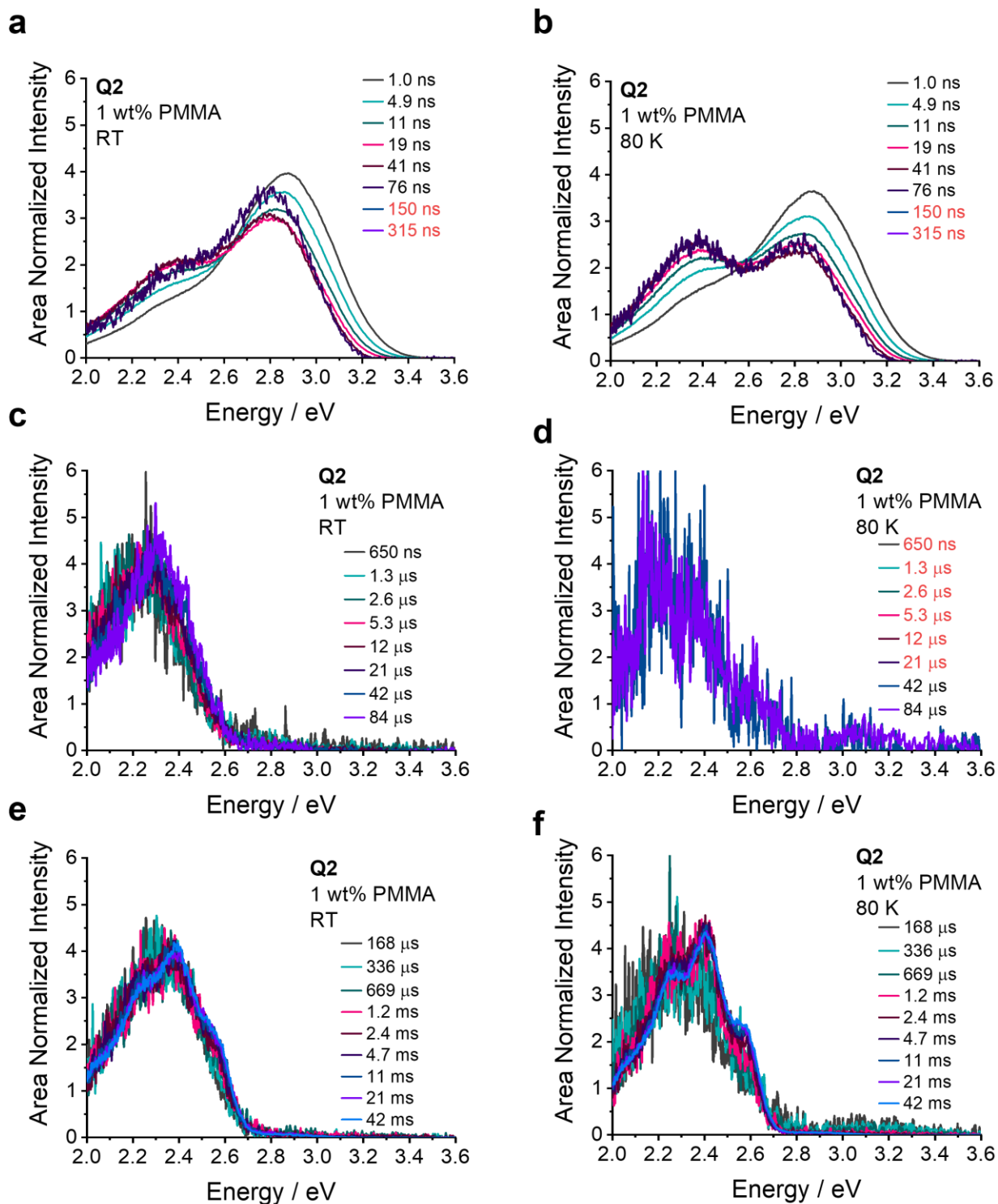


Figure S30. The time-resolved photoluminescence spectra of a 1 wt% PMMA film of **Q2** measured at (a,c,e) room temperature (RT) and (b,d,f) 80 K. The times in red indicate times where no measurable signal was found.

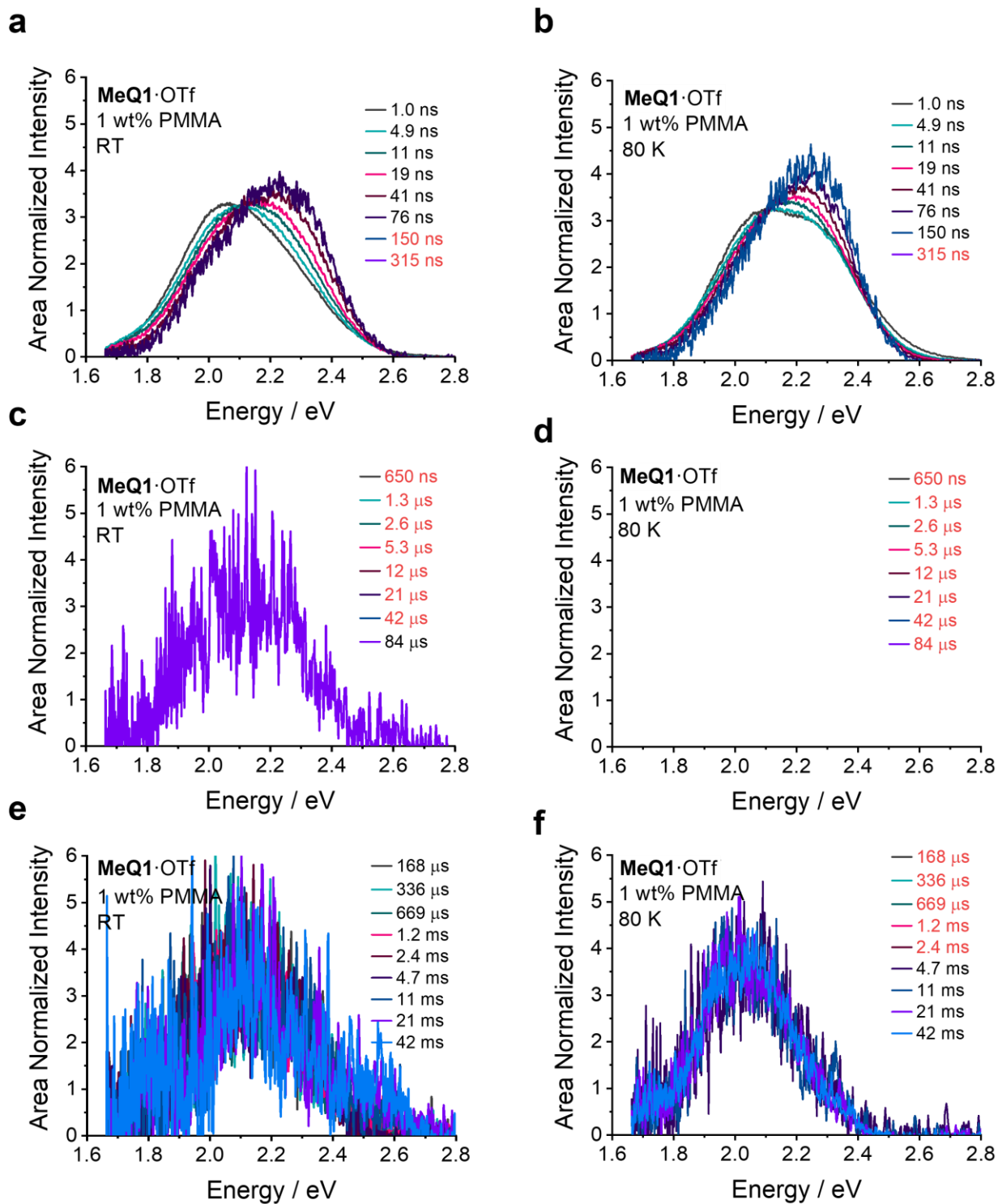


Figure S31. The time-resolved photoluminescence spectra of a 1 wt% PMMA film of **MeQ1·OTf** measured at (a,c,e) room temperature (RT) and (b,d,f) 80 K. The times in red indicate times where no measurable signal was found.

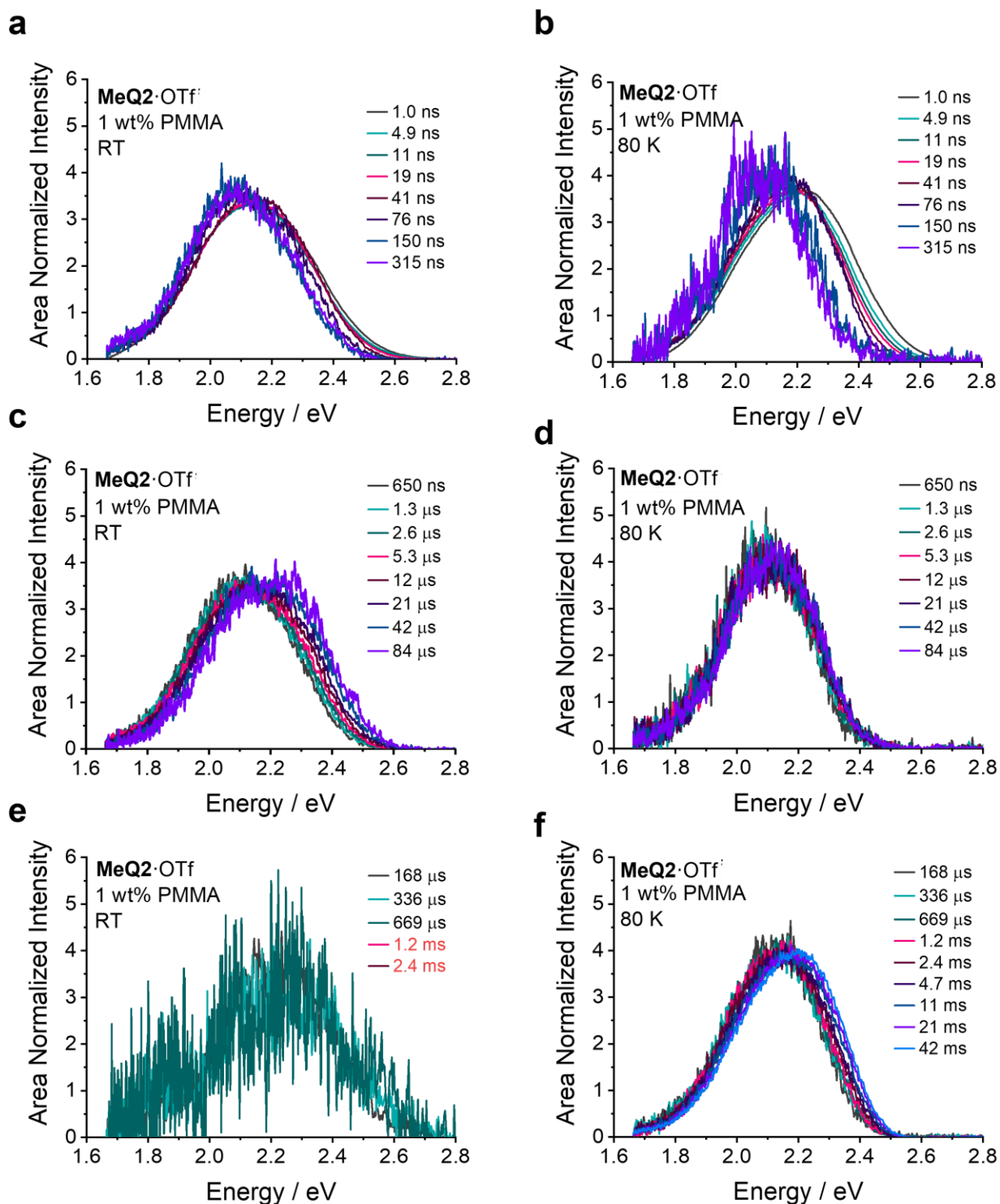


Figure S32. The time-resolved photoluminescence spectra of a 1 wt% PMMA film of **MeQ2·OTf** measured at (a,c,e) room temperature (RT) and (b,d,f) 80 K. The times in red indicate times where no measurable signal was found.

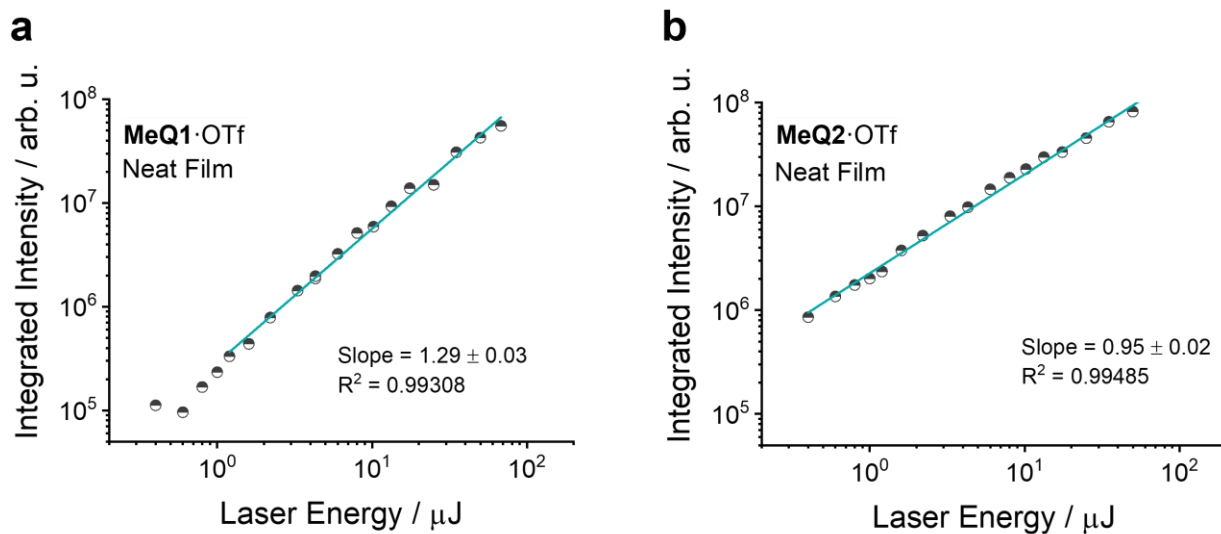


Figure S33. Power dependence of delayed fluorescence for neat films of (a) **MeQ1·OTf** and (b) **MeQ2·OTf** at 295 K.

Table S7 The measured energies of S_1 and T_1 , respective ΔE_{S-T} of **MeQ1·OTf** and **MeQ2·OTf** samples in neat film determined from the spectra recorded at 80 K. The reverse intersystem crossing rates have been estimated according to Approach B in previous work by dos Santos *et al.*⁹

Sample	S_1^a / eV	T_1^a / eV	ΔE_{S-T} / eV	$k_{\text{risc}} (\times 10^4 \text{ s}^{-1})$
MeQ1·OTf	2.51 (2.25)	2.23 (1.98)	0.28	0.3
MeQ2·OTf	2.51 (2.33)	2.40 (2.13)	0.11	6.6

^aPeak energies are in brackets.

7. Calculations and Crystallography

Table S8 Calculated excitation energies (eV), oscillator strengths (in parentheses) and CT numbers for singlet and triplet states of four compounds (ground state geometries). Singlet transitions with largest oscillator strength are indicated in grey.

	Q1	Q2	MeQ1 ⁺	MeQ2 ⁺
T ₁	3.29, CT=0.156	3.30, CT=0.103	1.96, CT=0.735	2.31, CT=0.733
T ₂	3.65, CT=0.032	3.66, CT=0.034	2.86, CT=0.979	2.87, CT=0.848
T ₃	3.80, CT=0.074	3.82, CT=0.088	3.32, CT=0.225	3.32, CT=0.173
T ₄	3.89, CT=0.309	4.08, CT=0.517	3.51, CT=0.580	3.67, CT=0.194
S ₁	3.98 (0.169), CT=0.463	4.09 (0.0004), CT=0.246	2.21 (0.051), CT=0.855	2.48 (0.263), CT=0.772
S ₂	4.07 (0.013), CT=0.105	4.13 (0.165), CT=0.630	2.86 (0.0003), CT=0.979	2.91 (0.0005), CT=0.910
S ₃	4.49 (0.057), CT=0.282	4.38 (0.010), CT=0.070	3.63 (0.242), CT=0.720	3.86 (0.051), CT=0.728
S ₄	4.68 (0.193), CT=0.064	4.66 (0.169), CT=0.148	3.91 (0.017), CT=0.972	4.09 (0.018), CT=0.572

Table S9 Calculated twist angles for ground state geometries of four compounds. Dihedrals were computed for 4 atoms around the chemical bond between carbazole and quinoline. Because different choices of atoms are possible, we report two angles which are usually very similar. Different values of two angles indicate slight bending from the twist axis (i.e. pyramidalisation on carbazole N-atom).

	Q1	Q2	MeQ1 ⁺	MeQ2 ⁺
φ ₁	-54.15°	-58.47°	-42.41°	-37.35°
φ ₂	-53.07°	-64.43°	-43.21°	-51.54°

Table S10 Calculated adiabatic excitation energies (i.e. energy difference between ground and excited state minimum) for S_1 and T_1 states of MeQ1^+ and MeQ2^+ . Energies are given in eV, along with corresponding excited state CT numbers, and two twist angles of excited state minimum geometries.

	T_1 (adiabatic)	S_1 (adiabatic)
MeQ1⁺	1.74 (CT=0.776, $\phi_1=-44.1^\circ$, $\phi_2=-43.3^\circ$)	1.88 (CT=0.949, $\phi_1=-61.8^\circ$, $\phi_2=-59.6^\circ$)
MeQ2⁺	1.92 (CT=0.939, $\phi_1=-78.4^\circ$, $\phi_2=-74.6^\circ$)	1.90 (CT=0.961, $\phi_1=-92.0^\circ$, $\phi_2=-88.4^\circ$)

Table S11 Dihedral angles (determined as the angles between mean planes of planar fragments) between carbazole and quinoline moieties in crystals of **Q2**, **MeQ1**·OTf, **MeQ2**·OTf, **MeQ1**·BF₄ and **MeQ2**·BF₄.

Q2	MeQ1 ·OTf	MeQ2 ·OTf	MeQ1 ·BF ₄	MeQ2 ·BF ₄
62.38(4)°	62.7(1)°	56.8(2)°	50.4(1)°	56.8(2)°

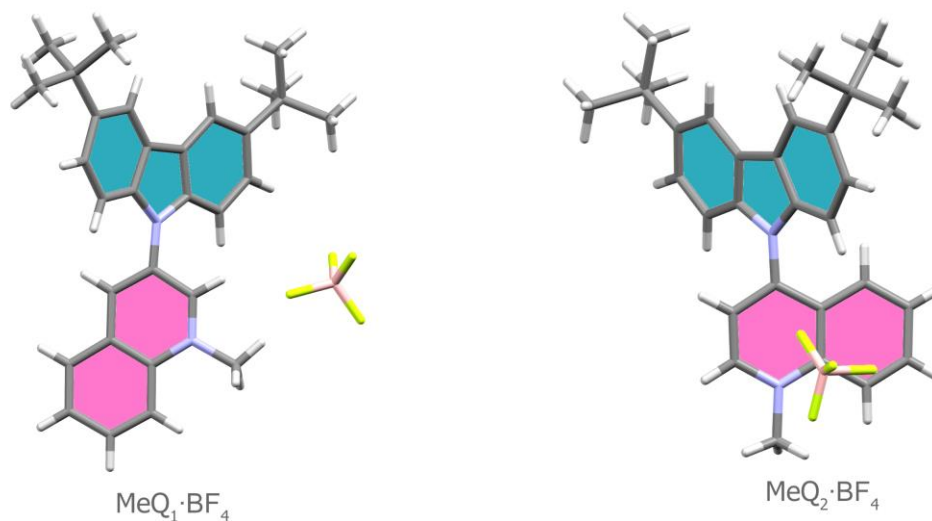


Figure S34. Molecular structures determined by X-ray crystallography for **MeQ1**·BF₄ and **MeQ2**·BF₄, the solvent molecules are omitted, only one out of two independent ionic pairs is shown in each case.

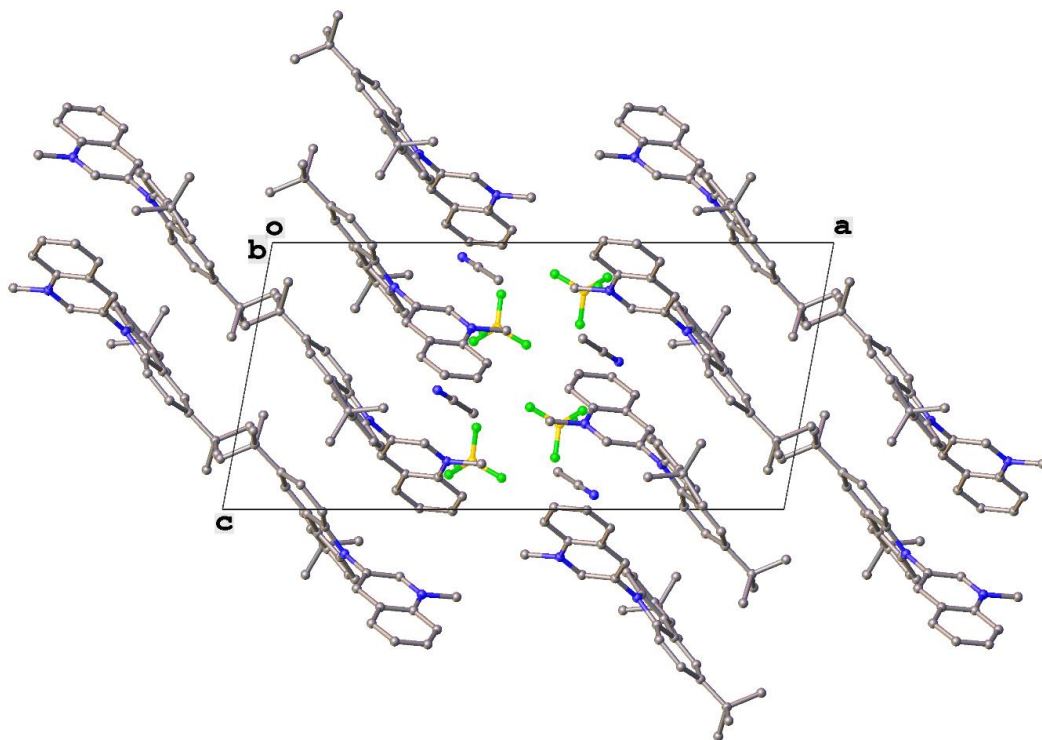


Figure S35. Crystal packing structure for **MeQ1**·BF₄. H-atoms omitted for clarity.

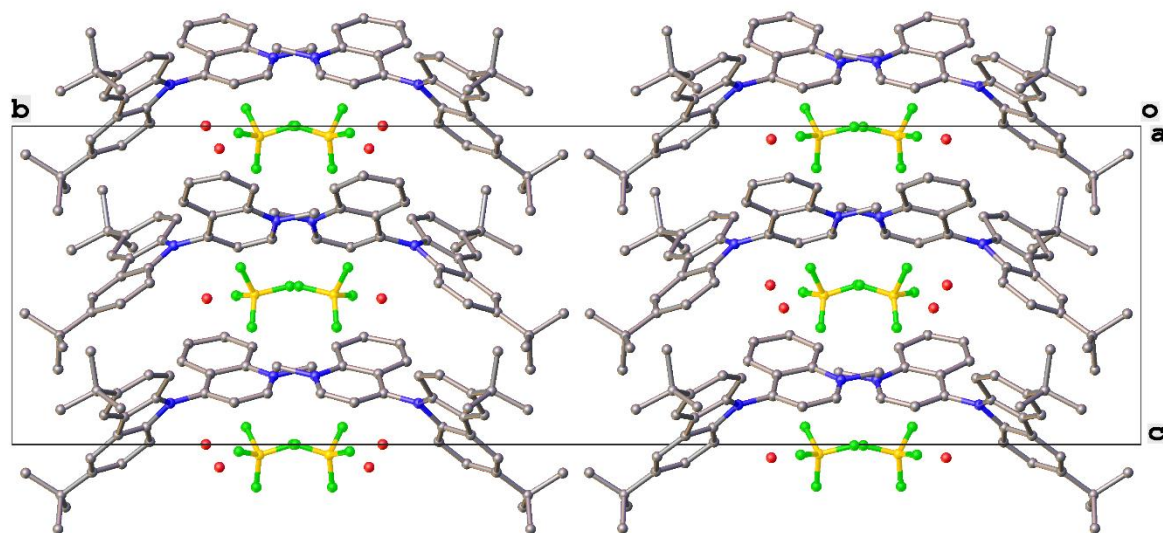


Figure S36. Crystal packing structure for **MeQ2**·BF₄. H-atoms omitted for clarity.

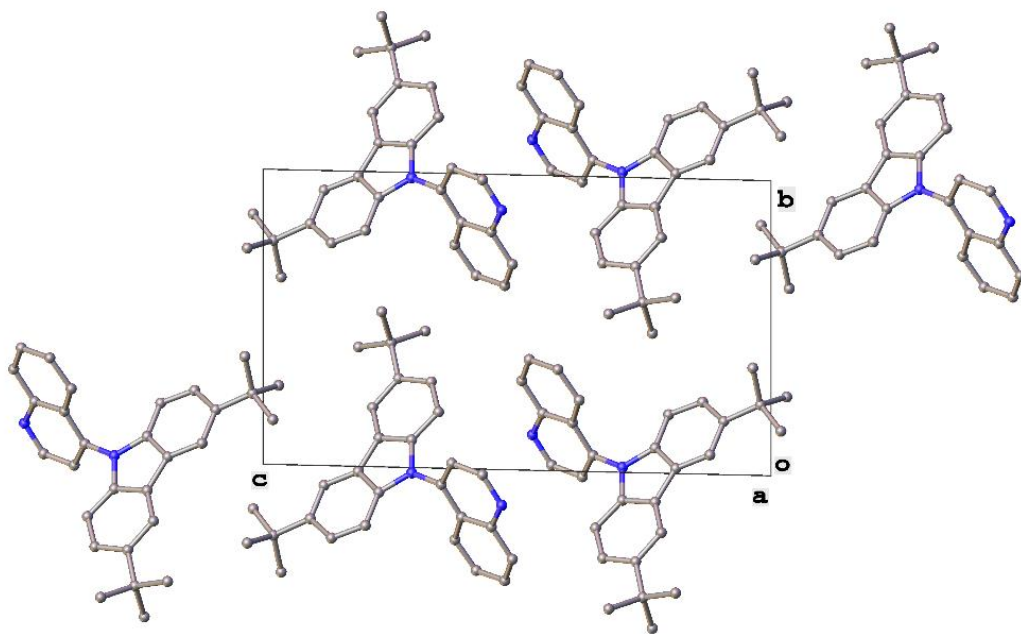


Figure S37. Crystal packing structure for **Q2**. H-atoms omitted for clarity.

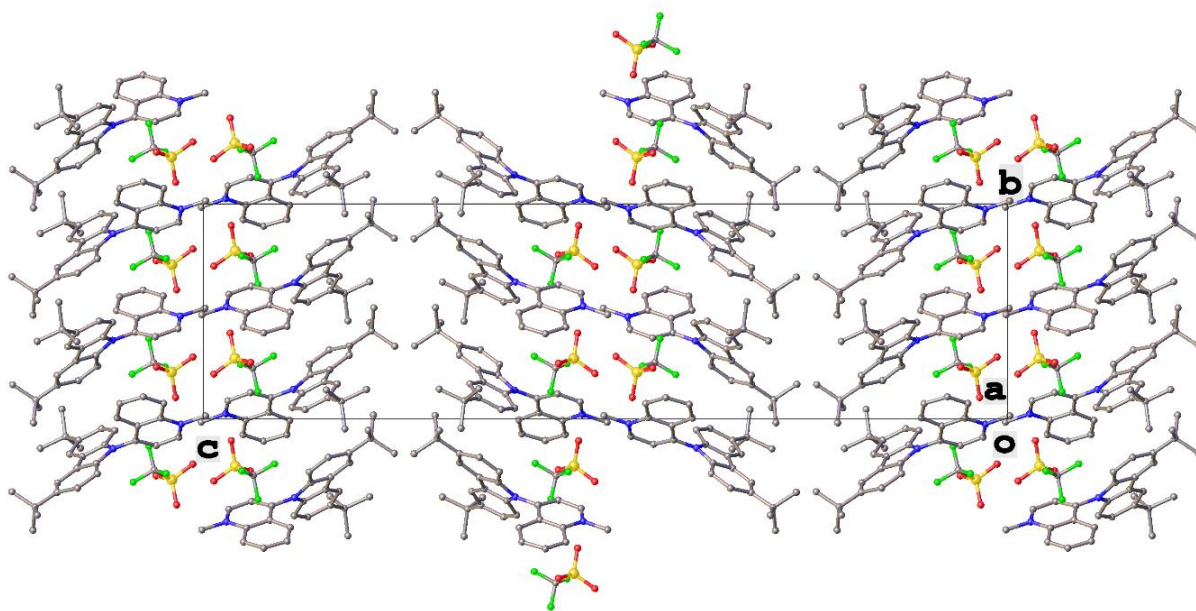


Figure S38. Crystal packing structure for **MeQ2·OTf**. H-atoms omitted for clarity

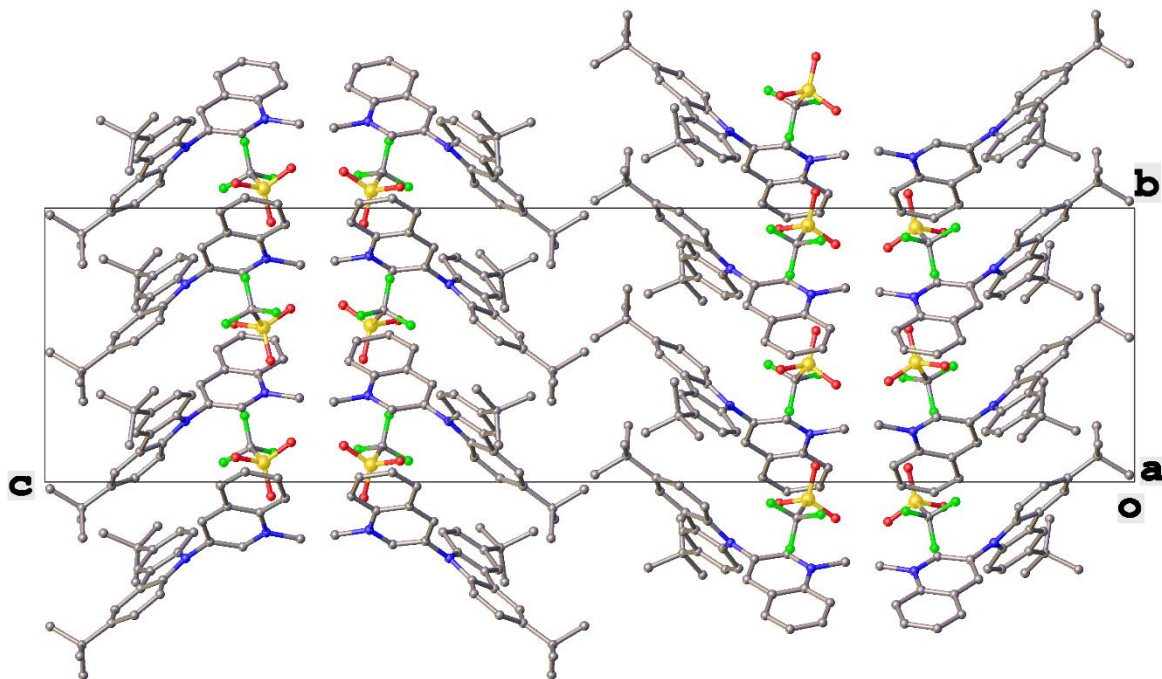


Figure S39. Crystal packing structure for **MeQ1·OTf**. H-atoms omitted for clarity

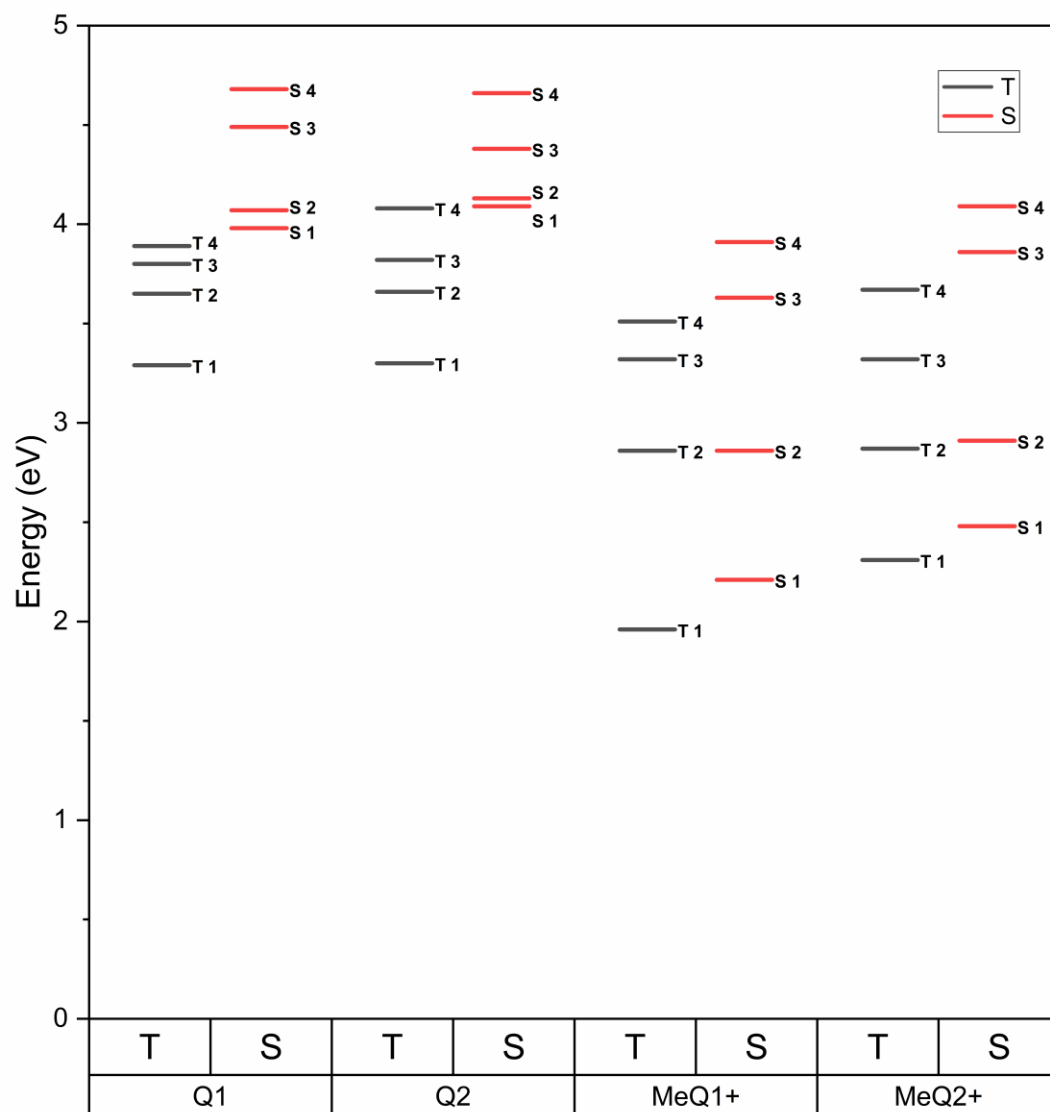


Figure S40. Energy diagram from calculated excitation energies (eV), for singlet and triplet states in **Q1**, **Q2**, **MeQ1⁺** and **MeQ2⁺**

8. References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, **42**, 339-341.
2. G. M. Sheldrick, *Acta Crystallogr A*, 2008, **64**, 112-122.
3. S. Grimme, L. Goerigk and R. F. Fink, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2012, **2**, 886-906.
4. F. Weigend and R. Ahlrichs, *Phys Chem Chem Phys*, 2005, **7**, 3297-3305.
5. A. Dreuw and M. Wormit, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2015, **5**, 82-95.
6. O. Christiansen, H. Koch and P. Jørgensen, *Chemical Physics Letters*, 1995, **243**, 409-418.
7. F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka and F. Weigend, *WIREs Computational Molecular Science*, 2013, **4**, 91-100.
8. F. Plasser, *J Chem Phys*, 2020, **152**, 084108.
9. P. L. Dos Santos, J. S. Ward, D. G. Congrave, A. S. Batsanov, J. Eng, J. E. Stacey, T. J. Penfold, A. P. Monkman and M. R. Bryce, *Adv Sci (Weinh)*, 2018, **5**, 1700989.