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# Evolution of pure hydrocarbon hosts: simpler structure, higher performance and universal application in RGB phosphorescent organic light-emitting diodes

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Keywords: universal host materials, RGB phosphorescent organic light-emitting diode, spirobifluorene, pure aromatic hydrocarbon, triplet energy

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# 1 General experimental methods

## 1.1 Synthesis

All manipulations of oxygen and moisture-sensitive materials were conducted with a standard Schlenk technique. Commercially available reagents and solvents were used without further purification other than those detailed below. THF was obtained through a PURE SOLV™ solvent purification system. Light petroleum refers to the fraction with bp 40-60°C. Analytical thin layer chromatography was carried out using aluminum backed plates coated with Merck Kieselgel 60 GF254 and visualized under UV light (at 254 and 360 nm). Flash chromatography was carried out using Teledyne Isco CombiFlash® Rf 400 (UV detection 200-360 nm), over standard silica cartridges (Redisep® Isco or Puriflash® columns Interchim). $^{1}H$ and $^{13}C$ NMR spectra were recorded using Bruker 300 MHz or 400 MHz instruments ($^{1}H$ frequency, corresponding $^{13}C$ frequency: 75 MHz or 101 MHz); chemical shifts were recorded in ppm and J values in Hz. The residual signals for the NMR solvents used are 5.32 or 7.26 ppm (proton); 53.84 or 77.09 ppm (carbon) for $CD_2Cl_2$ or $CDCl_3$, respectively.[1] Mass spectroscopy was performed using a Thermo Fisher ISQ Single Quadrupole GC-MS with direct probe system. High resolution mass spectra were recorded at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO-Rennes) on a Bruker MaXis 4G.

## 1.2 Spectroscopic studies

UV-visible spectra were recorded using an UV-vis spectrophotometer (Lambda 750) in toluene. Molar absorption coefficients ($\varepsilon$) were calculated from the gradients extracted from the plots of absorbance vs concentration with five solutions of different concentrations for each sample.

The fluorescent and phosphorescent (liquid nitrogen) spectra were tested by Hitachi F-4600 spectrophotometer, both in in toluene solution. The excitation wavelenght was 290 nm for both, modulated by a monochromator. Triplet energy levels were calculated from the maximum of the first phosphorescence emission peak, and conversion in electron-volt was obtained with the following formula: $E_T(eV) = \frac{hc}{\lambda}$ with $h = 6.62607 \times 10^{-34}$ J.s, $c = 2.99792 \times 10^{17}$ nm $s^{-1}$ and 1 J = $1.60218 \times 10^{-19}$ eV. This equation can be simplified as: $E_T(eV) = \frac{1239.84}{\lambda}$ with $\lambda$ formulated in nm.

The transient decay PL characteristics were evaluated using a HAMAMATSU (C11637) compact fluorescence lifetime spectrometer under a excitation light wavelenght of 373 nm.

## 1.3 Electrochemical studies

Electrochemical experiments were performed under argon atmosphere using a Pt disk electrode (diameter 1 mm). The counter electrode was a vitreous carbon rod. The reference electrode was either a silver wire in a 0.1 M $AgNO_3$ solution in $CH_3CN$ for the studies in oxidation or a Silver wire coated by a thin film of AgI (silver(I)iodide) in a 0.1 M $Bu_4NI$ solution in DMF for the studies in reduction. Ferrocene was added to the electrolyte solutions at the end of a series of experiments. The ferrocene/ferrocenium ($Fc/Fc^+$) couple served as internal standard. The three electrodes cell was connected to a PAR Model 273 potentiostat/galvanostat (PAR, EG&G, USA) monitored with the ECHEM Software. Activated $Al_2O_3$ was added in the electrolytic solution to remove excess moisture. All potentials are referred to the SCE electrode that was calibrated at –0.405 V *vs.* $Fc/Fc^+$ system. We estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionization potential (IP) or highest occupied molecular orbital (HOMO) from the redox data.[2-4] The LUMO level was calculated from: LUMO (eV) = − [$E_{onset}^{red}$ (*vs* SCE) + 4.4] and the HOMO level from: HOMO (eV) = − [$E_{onset}^{ox}$ (*vs* SCE) + 4.4], based on an SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from: $\Delta E^{el}$ =|HOMO − LUMO| (in eV).

## 1.4 Molecular modeling

Full geometry optimization of the ground state ($S_0$) and frequency calculation were performed with Density Functional Theory (DFT)[5, 6] using the hybrid Becke-3 0 parameter exchange functional[7, 8] and the Lee-Yang-Parr non-local correlation functional[9] (B3LYP) implemented in the Gaussian 16 (Revision B.01) program suite using the 6-31G(d) basis set and the default convergence criterion implemented in the program.

Geometry optimization of the first excited triplet state ($E_{T1}$) was performed using Time-Dependent Density Functional Theory (TD-DFT) calculations using the B3LYP functional and the 6-31+G(d) basis set.

Infrared spectra were calculated on the final geometry to verify that an energy minimum was reached (i.e. no negative frequency).

Transition diagrams were obtained through TD-DFT calculations performed using the B3LYP functional and the extended 6-311+G(d,p) basis set on the geometry of $S_0$.

$T_1$ to $S_0$ energy transition (ET) was calculated from the difference between the total energy of the molecule in its respective excited triplet state (found trough TD-DFT, B3LYP 6-

311+G(d,p)) and its ground singlet state (found through DFT, B3LYP 6-311+G(d,p)) in their optimized geometries.

Spin density (SD) representation was obtained through TD-DFT calculations performed using the extended 6-311+G(d,p) basis set and a triplet spin on the previously optimized geometry of $T_1$.

Calculations were carried out on the *OCCIGEN* calculator of the *Centre Informatique National de l'Enseignement Supérieur* (CINES (Montpellier) under project No. 2018-A0040805032). Figures were generated with GaussView 6.0 and GaussSum 3.0.

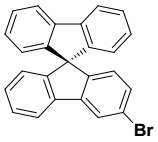
### 1.5 Thermal analysis

Thermal Gravimetric Analysis (TGA) was carried out by using a TA SDT 2960 instrument. TGA curved were measured at 10 °C $min^{-1}$ from 30 °C to 800 °C under a nitrogen flux. Differential Scanning Calorimetry (DSC) was carried out by using a TA DSC 2010 unit instrument equipped with an intracooler. DSC traces were measured at 10 °C $min^{-1}$, 2 heating/cooling cycles were successively carried out under a nitrogen flux.

### 1.6 Device fabrication and characterization

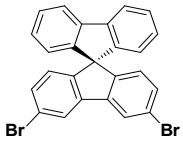
All organic compounds except the product of this paper were purchased from Lumtec Co., Ltd. ITO substrates (185 nm, R□ = 10 Ω $□^{-1}$ for blue PhOLEDs, 135 nm, R□ = 15 Ω $□^{-1}$ for green PhOLEDs, 110 nm, R□ = 18 Ω $□^{-1}$ for red PhOLEDs; activating area 0.1 $cm^2$; glass substrate, 32 mm × 32 mm × 0.7 mm) with patterned electrodes were ultrasonically cleaned in deionized water, acetone and ethanol for 15 min. Before loading to the vacuum chamber, the substrates were treated by UV ozone for 15 min at 40 °C. OLED devices were fabricated by depositing materials in a thermal evaporator chamber under a vacuum of $4.0 \times 10^{-6}$ Torr. The organic layers and cathode were defined by shallow masks placed under the substrates (0.15 $cm^2$), which define an active area of 0.1 $cm^2$. The evaporation rates and thicknesses of organic layers (2–4 Å $s^{-1}$) and aluminum cathode (4–8 Å $s^{-1}$) was monitored with oscillating quartz crystals. The devices were well encapsulated with glued glass lids before testing. A programmable spectra scan photometer (PHOTO RESEARCH, PR 655) connected to a KEITHLEY 2400 source meter was used to test the EL and luminescence characteristics, and the current–voltage characteristics.

## 2 Syntheses of materials



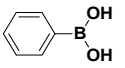

3-bromo-9,9'-spirobifluorene

Br-SBF



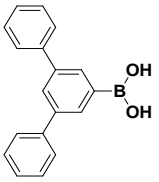

3,6-dibromo-9,9'-spirobifluorene

2Br-SBF




phenylboronic acid

Ph-B(OH)$_2$



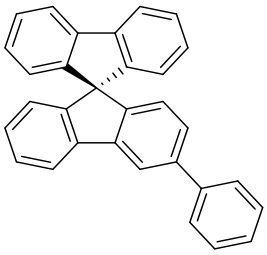

1,1':3',1''-terphenyl-5'-ylboronic acid

TPh-B(OH)$_2$

The above chemical intermediates were purchased from Suzhou Ge'Ao New Materials Co., Ltd and used without further purification. The four materials are synthesized in same condition by combining bromo spiro compound and boronic acid in a one-step typical method:

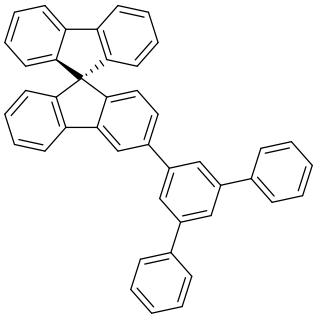
To a round bottom flask was charged Br-SBF (1 mmol, 1 eq), Ph-B(OH)$_2$ (1.1 mmol, 1.1 eq), $K_2CO_3$ (3 mmol, 3 eq), Pd($PPh_3$)$_4$ (0.04 mmol, 4% eq) and THF/$H_2O$ (4 ml/1.5 ml). The reaction mixture was refluxed under argon for 12 h. After cooling to r.t., it was diluted with brine (6 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL). The organic layer was then dried with $Na_2SO_4$ and the solvent was removed under reduced pressure. All the products were purified by silica gel column chromatography (20% $CH_2Cl_2$ in petroleum ether).

### 2.1 3-Phenyl-9,9'-spirobifluorene **[*m*SPh]**



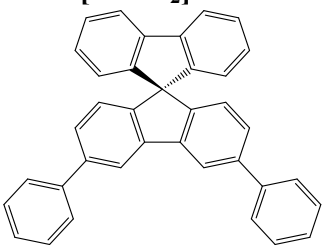
4.5 g of white solid was obtained, yield 92%; $^1$H NMR (300 MHz, $CD_2Cl_2$) δ = 8.11 (dd, *J* = 1.8, 0.6 Hz, 1H), 7.96 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.91 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.75–7.63 (m, 2H), 7.55–7.30 (m, 7H), 7.15 (tdd, *J* = 7.5, 2.5, 1.1 Hz, 3H), 6.80–6.69 (m, 4H); $^{13}$C NMR (75 MHz, CD2Cl2) δ = 149.73 (C), 149.28 (2C), 148.51 (C), 143.07 (C), 142.42 (2C), 142.24 (C), 141.79 (C), 141.69 (C), 129.39 (2CH) , 128.58 (CH), 128.44 (2CH), 128.42 (3CH), 127.95 (CH), 127.76 (2CH), 127.54 (CH), 124.58 (CH), 124.41 (CH), 124.40 (2CH), 120.79 (CH), 120.75 (2CH), 119.38 (CH), 66.35 (Cspiro); HRMS calculated for C31H21: 393.16433, found: 393.16378 $[M+H]^+$; elemental analysis calculated for C31H20: C, 94.86; H, 5.14; found: C, 94.39; H, 5.03.

2.2 3-Terphenyl-9,9'-spirobifluorene **[*m*STPh]**



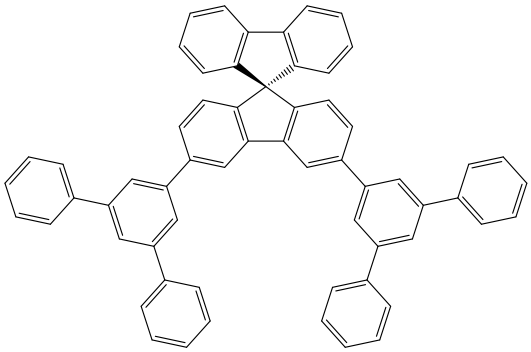
7.1 g of white solid was obtained, yield 96%; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.7 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.92–7.88 (m, 4H), 7.85 (t, *J* = 1.7 Hz, 1H), 7.79–7.74 (m, 4H), 7.53 (dd, *J* = 8.4, 6.8 Hz, 4H), 7.48–7.39 (m, 6H), 7.17 (td, *J* = 7.5, 1.1 Hz, 3H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.22 (Cqar), 148.73 (2Cqar), 148.28 (Cqar), 142.60 (Cqar), 142.42 (2Cqar), 141.85 (2Cqar), 141.59 (Cqar), 141.21 (2Cqar), 141.09 (Cqar), 128.94 (4CH), 128.14 (CH), 127.96 (2CH), 127.86 (2CH), 127.64 (2CH), 127.44 (4CH), 127.31 (CH), 125.39 (2CH), 125.26 (CH), 124.39 (CH), 124.16 (2CH), 120.11 (2CH), 119.02 (CH), 65.84 (Cspiro); MS (EI) calculated for $C_{34}H_{21}N_3O$: 544.70, found: 544.09 $[M]^+$; elemental analysis calculated for $C_{43}H_{28}$: C, 94.82; H, 5.18, found: C, 94.47; H, 5.03.

2.3 3,6-Diphenyl-9,9'-spirobifluorene **[*m*SPh$_2$]**



1.1 g of white solid was obtained, yield 90%; $^{1}$H NMR (300 MHz, $CD_2Cl_2$) δ = 8.18 (d, *J* = 1.6 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.74–7.69 (m, 4H), 7.54–7.35 (m, 10H), 7.16 (t, *J* = 7.5 Hz, 2H), 6.79 (dd, *J* = 7.8, 3.6 Hz, 4H); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) δ = 148.60 (2Cqar), 148.26 (2Cqar), 142.29 (2Cqar), 141.82 (2Cqar), 141.13 (4Cqar), 128.81 (4CH), 127.88 (2CH), 127.86 (2CH), 127.37 (2CH), 127.14 (4CH), 127.10 (2CH), 124.05 (2CH), 123.84 (2CH), 120.18 (2CH), 118.84 (2CH), 65.53 (Cspiro); IR (ATR, platinum): 3034, 3022, 1599, 1565, 1476, 1448, 1432, 1396, 1283, 1255, 1184, 1155, 1118, 1075, 1011, 953, 912, 884, 869, 827, 759, 745, 737, 721, 693, 681, 646, 619, 571, 517, 501, 474, 463, 423 $cm^{-1}$; HRMS (ASAP, 205 °C): Found $[M+H]^+$ 469.1950, $C_{37}H_{24}$ required 469.19508; elemental analysis calculated for $C_{37}H_{24}$: C, 94.84; H, 5.16, found: C, 94.58; H, 5.19.

2.4 3,6-diterphenyl-9,9'-spirobifluorene **[*m*STPh$_2$]**



1.8 g of white solid was obtained, yield 93%; $^1$H NMR (300 MHz, $CD_2Cl_2$) δ = 8.32 (d, *J* = 1.7 Hz, 2H), 7.97–7.91 (m, 6H), 7.85 (t, *J* = 1.7 Hz, 2H), 7.80–7.73 (m, 8H), 7.58–7.37 (m, 16H), 7.19 (td, *J* = 7.5, 1.2 Hz, 2H), 6.89–6.82 (m, 4H); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) δ = 149.07 (2Cqar), 148.98 (2Cqar), 142.83 (4Cqar), 142.80 (2Cqar), 142.72 (2Cqar), 142.31 (2Cqar), 141.53 (2Cqar), 141.47 (4Cqar), 129.29 (8CH), 128.40 (2CH), 128.36 (2CH), 128.04 (4CH), 127.81 (2CH), 127.73 (8CH), 125.59 (6CH), 124.63 (2CH), 124.31 (2CH), 120.68 (2CH), 119.61 (2CH), 66.06 (Cspiro); IR (ATR, platinum): 1596, 1575, 1496, 1474, 1447, 1409, 1389, 1076, 1031, 876, 832, 820, 761, 750, 729, 710, 698, 670, 650, 628, 614, 527, 501, 489, 420 cm$^{-1}$; HRMS (ASAP, 330 °C): Found $[M+H]^+$ 773.3203, $C_{61}H_{40}$ required 773.32028; elemental analysis calculated for $C_{61}H_{40}$: C, 94.78; H, 5.22, found: C, 94.75, H, 5.08.

## 3 Structural properties

The X-ray data were collected by a Bruker AXS Kappa CCD diffractometer with Mo-Kα source (λ = 0.71073 Å) at 296(2) K.

Table S1. Crystal data and structure refinement for ***m*SPh.**

| | |
|---|---|
| Identification code | shelx |
| Empirical formula | C31 H20 |
| Formula weight | 392.47 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | $P2_1/a$ |
| Unit cell dimensions | a = 13.3029(16) Å α= 90°. |
| | b = 9.8247(10) Å, β= 107.451(3)°. |
| | c = 16.8935(19) Å, γ = 90°. |
| Volume | 2074.7(4) Å$^3$ |
| Z | 4 |

| | |
|---|---|
| Density (calculated) | 1.256 Mg $m^{-3}$ |
| Absorption coefficient | 0.071 $mm^{-1}$ |
| F(000) | 824 |
| Crystal size | 0.13 x 0.09 x 0.03 $mm^3$ |
| Theta range for data collection | 3.167 to 27.530°. |
| Index ranges | −17<=h<=17, −12<=k<=11, −21<=l<=21 |
| Reflections collected | 20027 |
| Independent reflections | 4750 [R(int) = 0.0710] |
| Completeness to theta = 25.242° | 99.2 % |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4750/0/280 |
| Goodness-of-fit on $F^2$ | 1.029 |
| Final R indices [I>2sigma(I)] | R1 = 0.0479, wR2 = 0.1021 |
| R indices (all data) | R1 = 0.0811, wR2 = 0.1149 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.259 and -0.233 e $Å^{-3}$ |

Table S2. Crystal data and structure refinement for ***m*SPh$_2$.**

| | |
|---|---|
| Identification code | shelx |
| Empirical formula | C37 H24 |
| Formula weight | 468.56 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | $P2_1/a$ |
| Unit cell dimensions | a = 16.6398(11) Å α= 90°. |
| | b = 9.5620(6) Å, β= 106.273(4)°. |
| | c = 16.8786(11) Å, γ = 90°. |
| Volume | 2578.0(3) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.207 Mg $m^{-3}$ |
| Absorption coefficient | 0.068 $mm^{-1}$ |
| F(000) | 984 |
| Crystal size | 0.24 x 0.23 x 0.02 $mm^3$ |
| Theta range for data collection | 2.473 to 27.480°. |
| Index ranges | −16<=h<=21, −12<=k<=12, −21<=l<=21 |
| Reflections collected | 17443 |

| | |
|---|---|
| Independent reflections | 5857 [R(int) = 0.0856] |
| Completeness to theta = 25.242° | 99.6 % |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5857/0/334 |
| Goodness-of-fit on $F^2$ | 0.967 |
| Final R indices [I>2sigma(I)] | R1 = 0.0612, wR2 = 0.1113 |
| R indices (all data) | R1 = 0.1906, wR2 = 0.1533 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.168 and -0.204 e.$Å^{-3}$ |

Table S3. Crystal data and structure refinement for mSTPh.

| | |
|---|---|
| Identification code | shelx |
| Empirical formula | C43 H28 |
| Formula weight | 468.56 |
| Temperature | 299(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | $P2_1/a$ |
| Unit cell dimensions | a = 11.2023(16) Å α= 90°. |
| | b = 18.855(2) Å, β= 108.220(5)°. |
| | c = 14.855(2) Å, γ = 90°. |
| Volume | 2951.3(7) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.226 Mg $m^{-3}$ |
| Absorption coefficient | 0.069 $mm^{-1}$ |
| F(000) | 1144 |
| Crystal size | 0.19 x 0.15 x 0.12 $mm^3$ |
| Theta range for data collection | 2.282 to 30.056°. |
| Index ranges | −15<=h<=15, −26<=k<=20, −20<=l<=20 |
| Reflections collected | 38725 |
| Independent reflections | 83725 [R(int) = 0.0856] |
| Completeness to theta = 25.242° | 99.4% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 8304/0/388 |
| Goodness-of-fit on $F^2$ | 1.015 |
| Final R indices [I>2sigma(I)] | R1 = 0.0504, wR2 = 0.1195 |
| R indices (all data) | R1 = 0.0794, wR2 = 0.1352 |

| | |
|---|---|
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.166 and −0.140 e Å$^{-3}$ |

## 4 Thermal properties

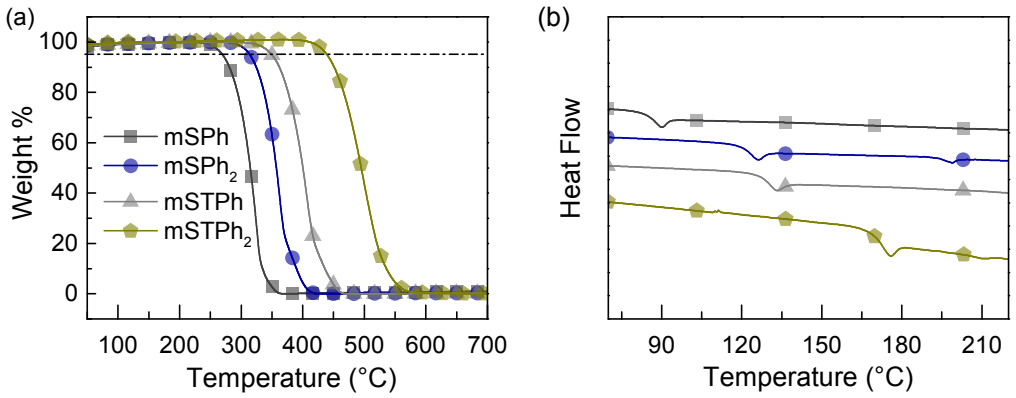



Figure S1. (a) The TGA and (b) DSC curves of **mSPh**, **mSPh$_2$**, **mSTPh** and **mSTPh$_2$**, which turns out the $T_d$ were 262, 287, 318 and 407 °C, and the $T_g$ were 90, 126, 133 and 175 °C for **mSPh**, **mSPh$_2$**, **mSTPh** and **mSTPh$_2$**, respectively.

## 5 Photophysical properties

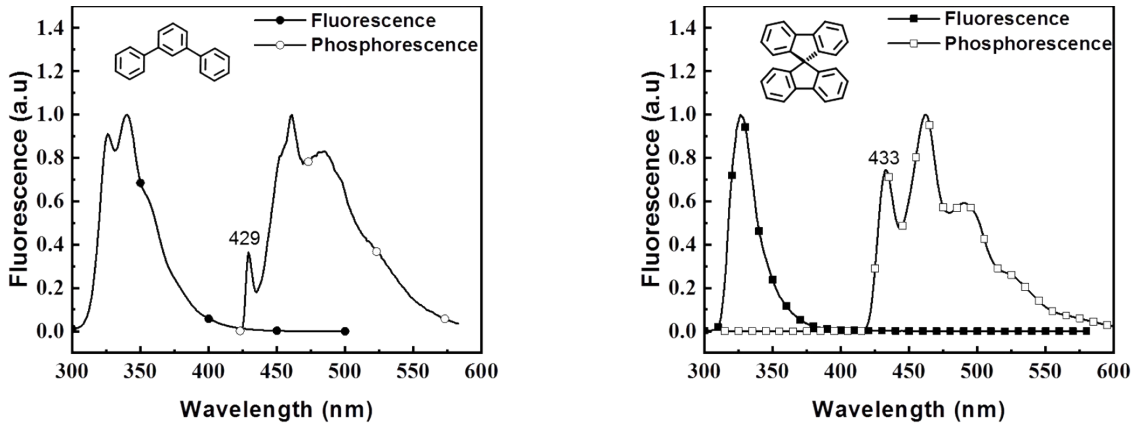



Figure S2. The PL and low temperature (77 k) phosphorescence spectra of *m*-terphenyl (left) and SBF (right) in toluene solution.

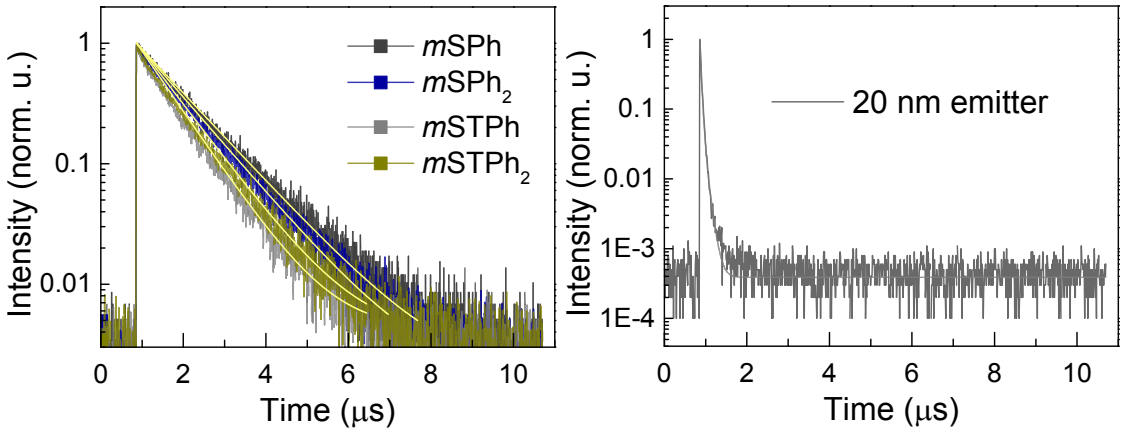



Figure S3. The transient PL curves of thin films of (left): 20 wt% of fac-Ir(iprpmi)$_3$ doped into *m*SPh, *m*SPh$_2$, *m*STPh and *m*STPh$_2$, respectively, on quartz and (right): 20 nm pure emitter thin film deposited on quartz (excitation peak 373 nm).

## 6 Electrochemical studies

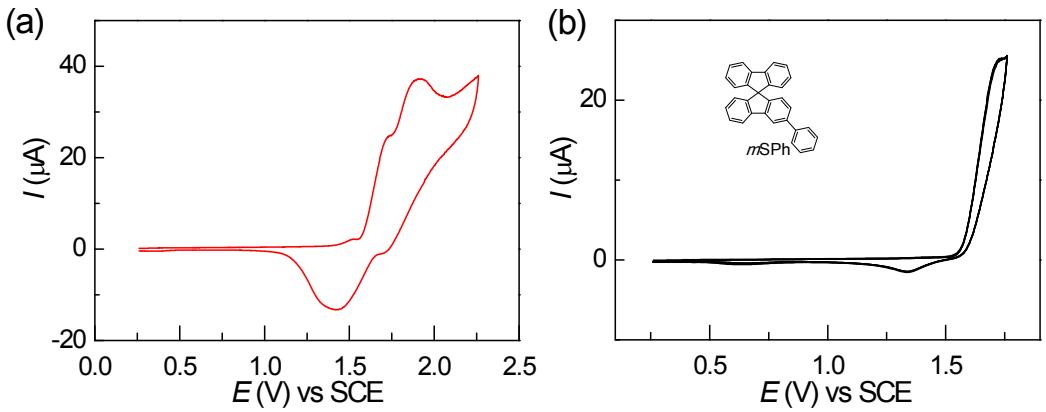



Figure S4. Cyclic voltammetry (CV) in oxidation recorded in $CH_2Cl_2$/[$Bu_4NPF_6$] 0.2 M of **mSPh** [5 × $10^{-3}$ M], platinum disk working electrode; sweep-rate: 100 $mV^{-1}$. (a) One cycle between 0.26 and 2.26V. (b) One cycle between 0.22 and 1.76V.

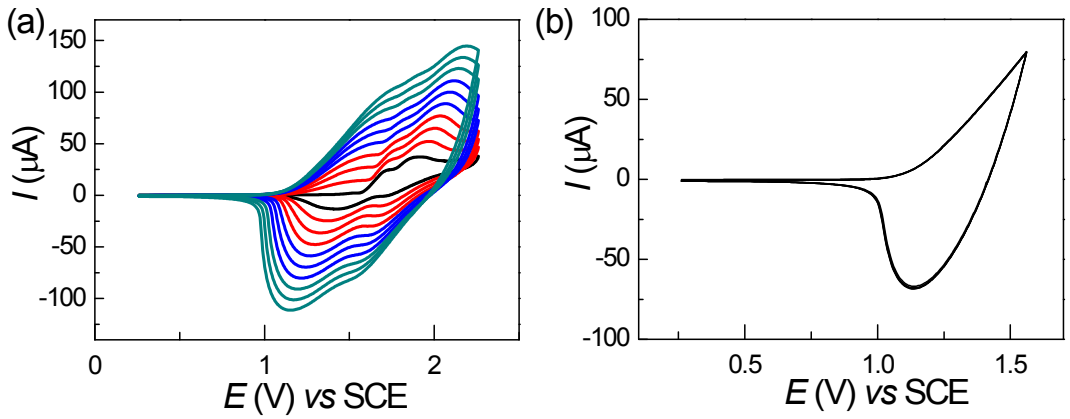



Figure S5. Cyclic voltammetry (CV) in oxidation recorded in $CH_2Cl_2$/[$Bu_4NPF_6$] 0.2 M of ***m*SPh** [5 × $10^{-3}$ M]. (a) Ten cycles between 0.27 and 2.27 V, platinum disk working electrode. (b) Three cycles between 0.29 and 2.1 V, platinum electrode modified in left. Sweep-rate: 100 $mV^{-1}$

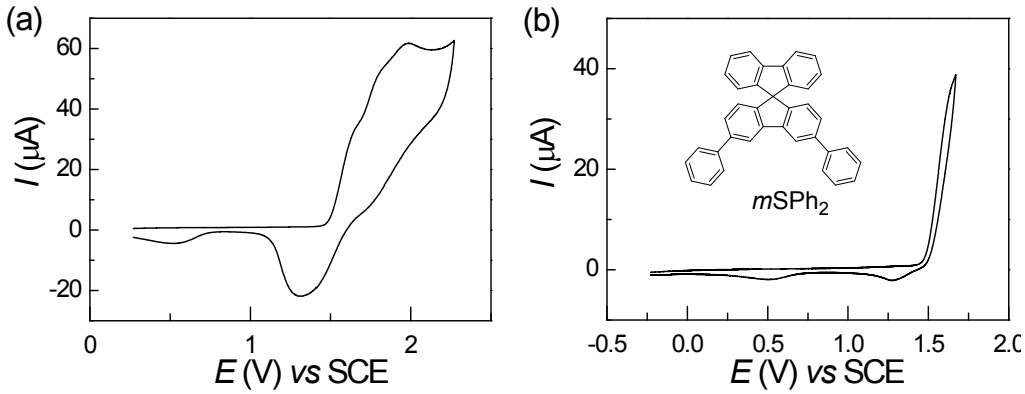



Figure S6. Cyclic voltammetry (CV) in oxidation recorded in $CH_2Cl_2/[Bu_4NPF_6]$ 0.2 M of **mSPh₂** [$5 \times 10^{-3}$ M], platinum disk working electrode; sweep-rate: 100 $mV^{-1}$. (a) One cycle between 0.3 and 2.3 V. (b) One cycle between 0.22 and 1.67 V.

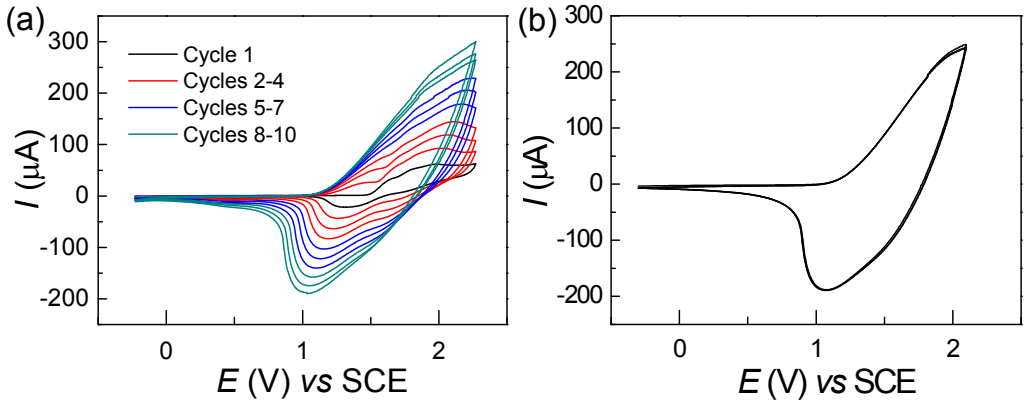



Figure S7. Cyclic voltammetry (CV) in oxidation recorded in $CH_2Cl_2/[Bu_4NPF_6]$ 0.2 M of ***m*SPh₂** [$5 \times 10^{-3}$ M]. (a) Ten cycles between 0.23 and 2.3 V, platinum disk working electrode. (b) Three cycles between −0.29 and 2.1 V, platinum electrode modified in left. Sweep-rate: 100 $mV^{-1}$

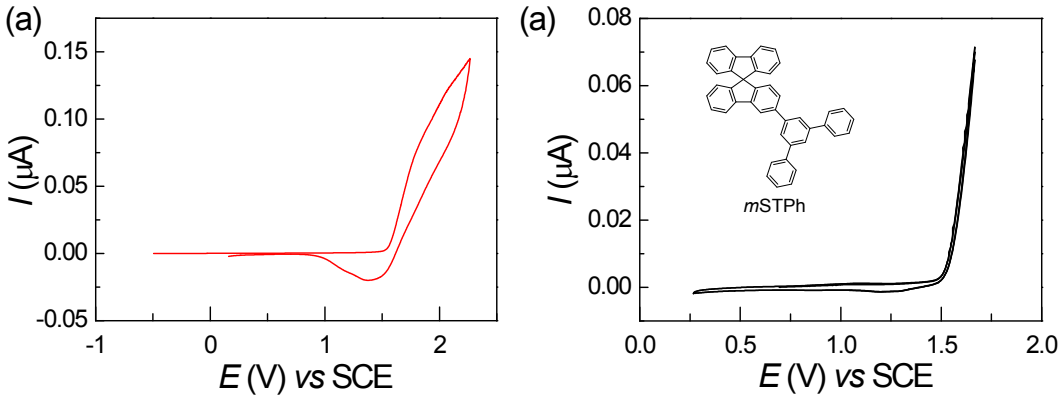



Figure S8. Cyclic voltammetry (CV) in oxidation recorded in $CH_2Cl_2/[Bu_4NPF_6]$ 0.2 M of ***m*STPh** [$5 \times 10^{-3}$ M], platinum disk working electrode; sweep-rate: 100 $mV^{-1}$. (a) Three cycles between0.26 and 1.66 V. (b) One cycle between 0.22 and 1.67 V.

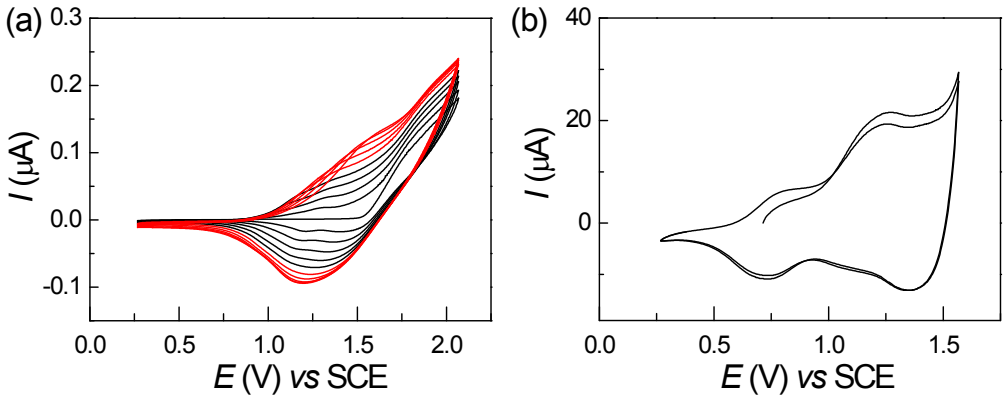



Figure S9. Cyclic voltammetry (CV) in oxidation recorded in $CH_2Cl_2/[Bu_4NPF_6]$ 0.2 M of ***m*STPh** [$5 \times 10^{-3}$ M]. (a) Ten cycles between 0.27 and 2.07V, platinum disk working electrode. (b) Three cycle between 0.26 and 1.56 V, platinum electrode modified in left. Sweep-rate: 100 $mV^{-1}$

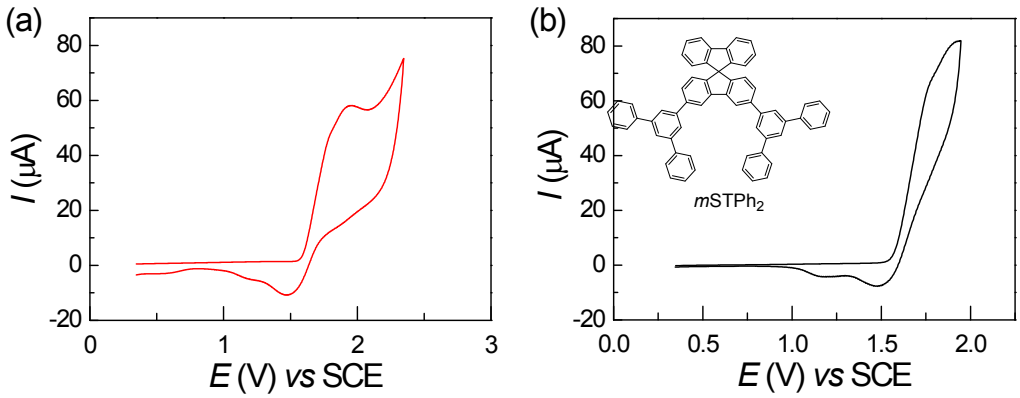



Figure S10. Cyclic voltammetry (CV) in oxidation recorded in $CH_2Cl_2/[Bu_4NPF_6]$ 0.2 M of ***m*STPh$_2$** [$5 \times 10^{-3}$ M], platinum disk working electrode; sweep-rate: 100 $mV^{-1}$. (a) One cycle between 0.3 and 2.3 V. (b) One cycle between 0.22 and 1.67 V.

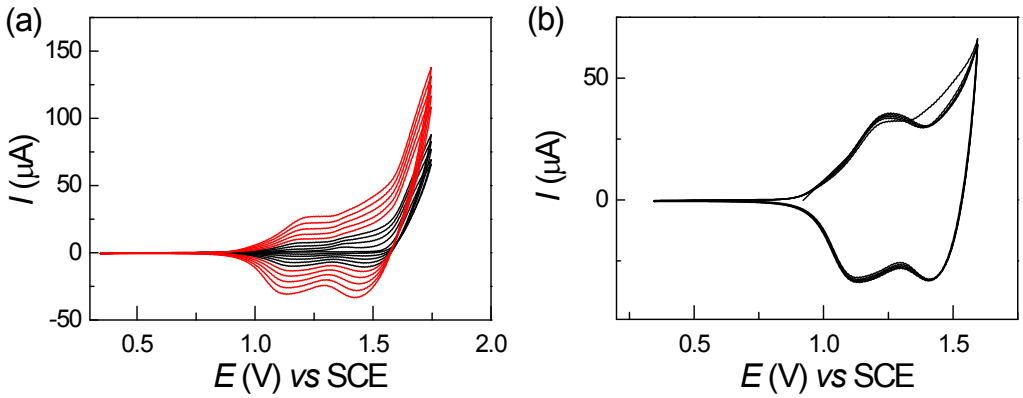



Figure S11. Cyclic voltammetry (CV) in oxidation recorded in $CH_2Cl_2/[Bu_4NPF_6]$ 0.2 M of ***m*STPh$_2$** [$5 \times 10^{-3}$ M]. (a) Ten cycles between 0.23 and 2.3 V, platinum disk working electrode. (b) Three cycle between 0.35 and 1.6 V, platinum electrode modified in left. Sweep-rate: 100 $mV^{-1}$

## 7 Molecular modelling

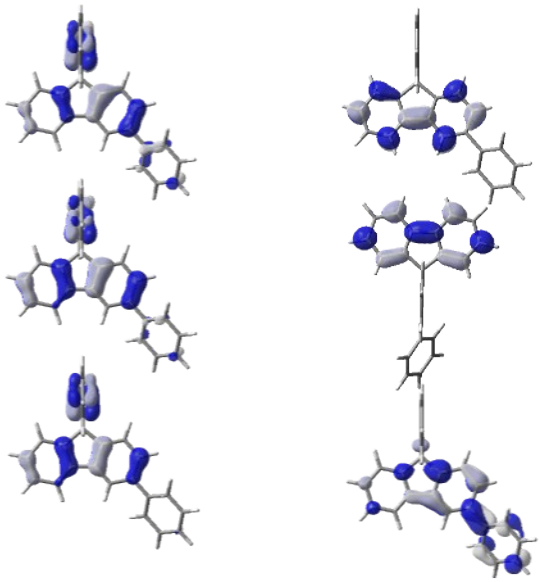


Figure S 12. The dominant natural transition orbital pairs for the first three excited singlet states of **mSPh**. The first excited state is at the top of the figure, the second at the middle and the third at the bottom; for each state, the ‘‘hole’’ is on the left, the “electron’’ on the right (td-dft, b3lyp, 6-311+g(d,p), shown with an isovalue of 0.04 [ebohr$^{-3}$]$^{1/2}$).

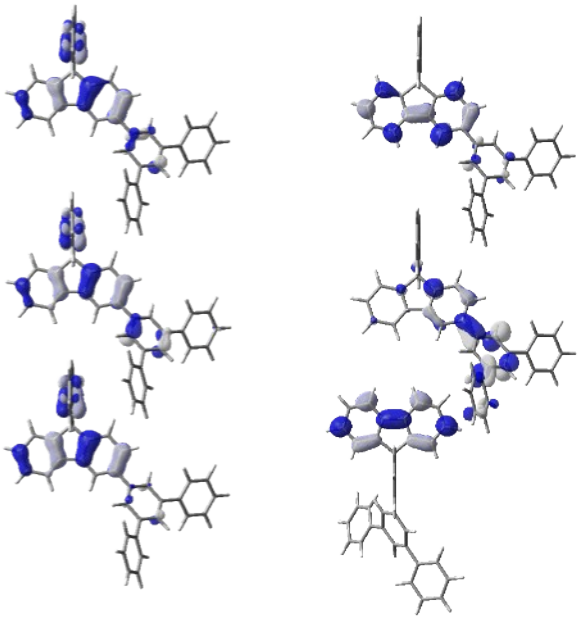


Figure S 13. The dominant natural transition orbital pairs for the first three excited singlet states of **mSTPh**. The first excited state is at the top of the figure, the second at the middle and the third at the bottom; for each state, the ‘‘hole’’ is on the left, the “electron’’ on the right (td-dft, b3lyp, 6-311+g(d,p), shown with an isovalue of 0.04 [ebohr$^{-3}$]$^{1/2}$).

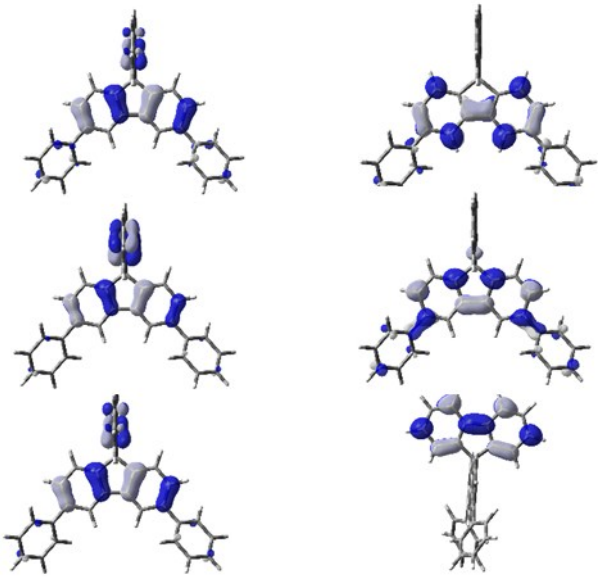


Figure S 14. The dominant natural transition orbital pairs for the first three excited singlet states of **mSPh$_2$**. The first excited state is at the top of the figure, the second at the middle and the third at the bottom; for each state, the ‘‘hole’’ is on the left, the “electron’’ on the right (td-dft, b3lyp, 6-311+g(d,p), shown with an isovalue of 0.04 [ebohr$^{-3}$]$^{1/2}$).

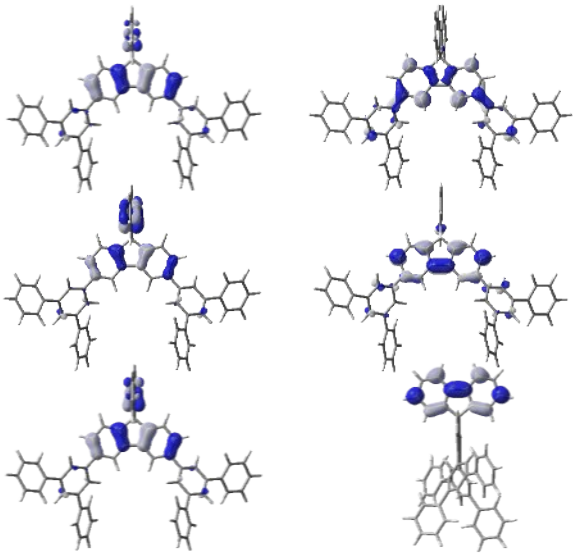


Figure S 15. The dominant natural transition orbital pairs for the first three excited singlet states of **mSTPh$_2$**. The first excited state is at the top of the figure, the second at the middle and the third at the bottom; for each state, the ‘‘hole’’ is on the left, the “electron’’ on the right (td-dft, b3lyp, 6-311+g(d,p), shown with an isovalue of 0.04 [ebohr$^{-3}$]$^{1/2}$).

Table S4. Results of TD-DFT calculations for ***m*SPh** (b3lyp/6-311+g(d,p))

| $\lambda$ (nm) | Oscillator Strength | Major contributions | Minor contributions |
|---|---|---|---|
| 306 | 0.089 | HOMO→LUMO (42%), HOMO→L+2 (42%) | H-2→LUMO (5%), H-1→LUMO (4%), H-1→L+2 (3%) |
| 303 | 0.048 | HOMO→L+1 (93%) | H-1→L+3 (3%) |
| 299 | 0.058 | HOMO→LUMO (49%), HOMO→L+2 (42%) | H-2→LUMO (4%) |
| 283 | 0.0004 | HOMO→L+3 (86%) | H-3→L+1 (4%), H-1→L+3 (4%) |
| 279 | 0.015 | H-2→LUMO (13%), H-1→LUMO (36%), H-1→L+2 (42%) | HOMO→L+2 (4%), HOMO→L+4 (2%) |
| 276 | 0.059 | H-1→LUMO (51%), H-1→L+2 (36%) | HOMO→LUMO (5%), HOMO→L+2 (3%) |
| 273 | 0.142 | H-1→L+1 (77%) | H-3→L+1 (5%), H-3→L+3 (2%), H-2→L+1 (4%), H-1→L+3 (8%) |
| 268 | 0.060 | H-3→LUMO (20%), H-2→LUMO (19%), HOMO→L+4 (35%) | H-6→LUMO (3%), H-1→LUMO (4%), H-1→L+2 (5%), H-1→L+4 (4%) |
| 264 | 0.101 | H-1→L+1 (11%), H-1→L+3 (69%) | H-3→L+1 (3%), HOMO→L+1 (4%), HOMO→L+3 (8%) |
| 262 | 0.820 | H-2→LUMO (41%), HOMO→L+4 (29%) | H-2→L+2 (8%), H-1→L+2 (8%), HOMO→L+2 (6%) |
| 260 | 0.019 | H-2→L+1 (91%) | H-3→L+1 (2%), H-1→L+1 (3%) |
| 259 | 0.049 | H-2→L+2 (10%), HOMO→L+5 (41%) | H-5→LUMO (4%), H-5→L+2 (9%), H-4→L+1 (9%), H-2→L+5 (5%), H-1→L+4 (3%), H-1→L+5 (4%), HOMO→L+6 (2%) |
| 258 | 0.093 | H-4→L+1 (29%), H-1→L+4 (12%), HOMO→L+5 (18%) | H-5→L+2 (4%), H-3→LUMO (2%), H-2→L+2 (8%), H-2→L+5 (2%), H-1→L+6 (4%), HOMO→L+6 (8%) |
| 254 | 0.005 | H-2→L+2 (62%) | H-4→L+1 (9%), H-2→LUMO (4%), HOMO→L+4 (9%), HOMO→L+6 (5%) |
| 247 | 0.116 | H-3→LUMO (39%), HOMO→L+4 (15%) | H-4→LUMO (6%), H-4→L+1 (6%), H-2→LUMO (6%), H-2→L+2 (4%), H-2→L+4 (3%), H-1→L+2 (3%), H-1→L+4 (6%), H-1→L+6 (3%) |
| 246 | 0.007 | H-4→LUMO (91%) | H-3→LUMO (2%) |
| 244 | 0.059 | H-3→L+1 (75%) | H-6→L+1 (6%), H-3→L+2 (2%), H-1→L+1 (2%), H-1→L+3 (7%) |
| 244 | 0.018 | H-3→LUMO (13%), H-3→L+2 (63%), H-1→L+4 (11%) | H-3→L+1 (3%), HOMO→L+6 (2%) |
| 243 | 0.013 | H-2→L+3 (83%) | HOMO→L+5 (5%) |
| 241 | 0.010 | H-5→LUMO (12%), H-5→L+2 (17%), H-2→L+3 (10%), H-2→L+5 (25%), HOMO→L+5 (27%) | |

Table S5. Results of TD-DFT calculations for **mSPh$_2$** (b3lyp/6-311+g(d,p))

| $\lambda$ (nm) | Oscillator Strength | Major contributions | Minor contributions |
|---|---|---|---|
| 312 | 0.146 | HOMO→L+1 (42%), HOMO→L+2 (44%) | H-3→LUMO (7%), H-1→LUMO (4%) |
| 308 | 0.002 | HOMO→LUMO (95%) | H-1→LUMO (3%) |
| 306 | 0.041 | HOMO→L+1 (49%), HOMO→L+2 (46%) | H-1→L+4 (2%) |
| 290 | 0.032 | H-2→LUMO (23%), | H-3→L+3 (3%), H-2→L+1 (5%), H- |

| | | | |
|---|---|---|---|
| | | HOMO→L+3 (57%) | 2→L+2 (7%), H-1→L+3 (3%) |
| 285 | 0.0001 | HOMO→L+4 (88%) | H-1→L+4 (4%) |
| 281 | 0.022 | H-1→LUMO (61%), H-1→L+1 (12%), H-1→L+2 (16%) | HOMO→L+1 (3%), HOMO→L+2 (4%) |
| 280 | 0.019 | H-1→LUMO (30%), H-1→L+1 (26%), H-1→L+2 (32%) | H-3→LUMO (9%) |
| 274 | 0.278 | H-2→LUMO (22%), H-1→L+3 (13%), HOMO→L+3 (39%) | H-3→L+3 (3%), H-2→L+1 (9%), H-2→L+2 (9%) |
| 273 | 0.134 | H-1→L+1 (39%), H-1→L+2 (32%), H-1→L+4 (12%) | H-5→L+1 (2%), H-3→L+1 (5%), H-3→L+2 (3%) |
| 268 | 0.058 | H-2→L+1 (74%), H-2→L+2 (15%) | H-2→LUMO (8%) |
| 267 | 0.271 | H-2→LUMO (37%), H-2→L+2 (56%) | |
| 265 | 0.123 | H-1→L+1 (10%), H-1→L+4 (64%) | H-5→L+1 (2%), H-1→L+2 (6%), HOMO→L+4 (7%) |
| 262 | 0.883 | H-3→LUMO (71%) | H-2→L+3 (2%), H-1→L+1 (3%), H-1→L+2 (7%), HOMO→L+1 (3%), HOMO→L+2 (3%), HOMO→L+6 (2%) |
| 262 | 0.070 | H-4→L+1 (10%), H-1→L+3 (50%) | H-4→L+2 (8%), H-2→L+1 (3%), H-2→L+2 (6%), H-1→L+7 (4%), HOMO→L+5 (5%), HOMO→L+7 (4%) |
| 260 | 0.021 | HOMO→L+5 (58%) | H-7→LUMO (7%), H-6→L+3 (7%), H-4→L+1 (2%), H-2→L+6 (9%), H-1→L+3 (2%), H-1→L+5 (3%) |
| 259 | 0.074 | H-2→L+5 (11%), HOMO→L+6 (56%) | H-7→L+3 (8%), H-6→LUMO (9%), H-3→LUMO (3%), H-1→L+6 (3%) |
| 254 | 0.220 | H-2→L+3 (94%) | H-3→LUMO (2%) |
| 254 | 0.0006 | H-4→L+1 (20%), H-4→L+2 (14%), H-1→L+3 (28%), HOMO→L+7 (19%) | H-1→L+7 (9%) |
| 253 | 0.060 | H-3→L+1 (70%), H-3→L+2 (19%) | H-1→L+1 (2%), H-1→L+2 (2%), H-1→L+4 (2%) |
| 252 | 0.043 | H-3→L+1 (19%), H-3→L+2 (72%) | |

Table S6. Results of TD-DFT calculations for ***m*STPh** (b3lyp/6-311+g(d,p))

| **$\lambda$ (nm)** | **Oscillator Strength** | **Major contributions** | **Minor contributions** |
|---|---|---|---|
| 307 | 0.115 | HOMO→L+1 (39%), HOMO→L+3 (41%) | H-3→LUMO (6%), H-1→LUMO (3%) |
| 304 | 0.067 | HOMO→LUMO (71%) | H-2→LUMO (6%), HOMO→L+3 (9%), HOMO→L+5 (2%) |
| 303 | 0.047 | HOMO→L+2 (90%) | H-1→L+4 (3%) |
| 301 | 0.016 | H-2→LUMO (13%), HOMO→LUMO (19%), HOMO→L+1 (24%), HOMO→L+3 (23%) | H-3→L+1 (4%), H-2→L+1 (3%), H-1→LUMO (5%), H-1→L+1 (2%), HOMO→L+2 (2%) |
| 284 | 0.043 | H-2→LUMO (30%), HOMO→L+1 (23%), HOMO→L+4 (15%) | H-3→LUMO (2%), H-3→L+1 (8%), H-3→L+3 (2%), H-2→L+1 (4%), HOMO→L+3 (8%) |
| 282 | 0.010 | HOMO→L+4 (69%) | H-4→L+2 (3%), H-2→LUMO (7%), H-1→L+4 (5%), HOMO→L+1 (5%) |
| 281 | 0.007 | H-3→LUMO (12%), H-1→L+1 (25%), H-1→L+3 (49%) | HOMO→L+3 (2%) |
| 279 | 0.042 | H-1→LUMO (83%) | H-1→L+5 (2%), HOMO→L+3 (7%) |
| 273 | 0.135 | H-1→L+2 (75%) | H-4→L+2 (6%), H-4→L+4 (2%), H-3→L+2 (5%), H-1→L+4 (8%) |

| | | | |
|---|---|---|---|
| 273 | 0.151 | H-2→LUMO (20%), H-2→L+1 (44%), H-2→L+3 (26%) | H-3→L+3 (2%) |
| 271 | 0.221 | H-3→LUMO (10%), HOMO→L+5 (59%) | H-4→L+3 (2%), H-3→L+1 (2%), HOMO→LUMO (2%), HOMO→L+3 (3%), HOMO→L+8 (6%) |
| 271 | 0.528 | H-3→LUMO (32%), H-2→L+3 (25%) | H-5→LUMO (2%), H-3→L+3 (7%), H-2→L+1 (3%), H-1→L+1 (9%), H-1→L+3 (4%), HOMO→L+5 (2%), HOMO→L+8 (3%) |
| 268 | 0.067 | H-1→L+1 (51%), H-1→L+3 (28%) | H-3→L+3 (2%), H-2→L+1 (6%), H-2→L+3 (2%), H-1→LUMO (3%) |
| 267 | 0.019 | H-3→LUMO (13%), H-2→L+1 (25%), H-2→L+3 (32%) | H-4→LUMO (3%), H-3→L+1 (6%), H-1→L+3 (9%), HOMO→L+8 (3%) |
| 264 | 0.260 | H-3→L+1 (66%), H-2→LUMO (12%) | H-2→L+3 (8%), HOMO→L+5 (5%) |
| 263 | 0.077 | H-3→L+2 (10%), H-1→L+4 (59%) | H-4→L+2 (2%), H-3→L+4 (2%), H-2→L+2 (2%), H-1→L+2 (6%), HOMO→L+2 (4%), HOMO→L+4 (7%) |
| 263 | 0.039 | H-3→L+2 (51%), H-2→L+2 (25%) | H-5→L+2 (3%), H-1→L+2 (9%), H-1→L+4 (5%) |
| 262 | 0.224 | H-3→LUMO (14%), H-3→L+3 (51%) | H-2→LUMO (3%), H-2→L+1 (4%), HOMO→L+5 (9%), HOMO→L+8 (2%) |
| 261 | 0.004 | H-3→L+2 (25%), H-2→L+2 (70%) | |
| 259 | 0.002 | H-6→L+2 (41%), H-1→L+8 (10%), HOMO→L+8 (19%) | H-1→L+5 (6%), H-1→L+9 (5%), HOMO→L+9 (9%) |

Table S7. Results of TD-DFT calculations for ***m*STPh$_2$** (b3lyp/6-311+g(d,p))

| **$\lambda$ (nm)** | **Oscillator Strength** | **Major contributions** | **Minor contributions** |
|---|---|---|---|
| 314 | 0.210 | HOMO→LUMO (25%), HOMO→L+1 (49%), HOMO→L+4 (12%) | H-5→LUMO (5%) |
| 311 | 0.001 | HOMO→LUMO (69%), HOMO→L+1 (19%) | H-1→LUMO (4%), HOMO→L+4 (3%) |
| 306 | 0.038 | HOMO→L+3 (93%) | H-1→L+6 (2%) |
| 303 | 0.0005 | H-3→L+5 (10%), H-2→LUMO (16%), HOMO→L+2 (55%) | H-4→L+1 (6%), H-4→L+4 (5%), H-1→L+2 (3%) |
| 302 | 0.006 | H-3→LUMO (15%), HOMO→L+4 (45%) | H-4→L+2 (9%), H-2→L+2 (2%), H-2→L+5 (8%), HOMO→L+1 (8%) |
| 295 | 0.063 | HOMO→L+5 (71%) | H-4→LUMO (6%), H-4→L+1 (6%), H-4→L+4 (3%), HOMO→L+8 (2%) |
| 287 | 0.024 | H-3→LUMO (24%), HOMO→L+1 (12%), HOMO→L+4 (19%), HOMO→L+6 (15%) | H-5→L+4 (2%), H-4→L+2 (6%), H-2→L+5 (8%), H-1→LUMO (4%) |
| 286 | 0.041 | H-3→L+5 (10%), H-2→LUMO (29%), HOMO→L+2 (40%) | H-5→L+2 (5%), H-4→L+1 (4%), H-4→L+4 (5%), HOMO→L+5 (2%) |
| 284 | 0.025 | H-1→LUMO (61%), HOMO→L+6 (25%) | HOMO→L+1 (2%) |
| 283 | 0.021 | H-1→LUMO (20%), HOMO→L+4 (13%), HOMO→L+6 (45%) | H-3→LUMO (6%), H-1→L+1 (3%), H-1→L+6 (3%) |
| 281 | 0.015 | H-1→L+1 (60%), H-1→L+4 (21%) | H-5→LUMO (7%), H-1→LUMO (3%) |
| 281 | 0.198 | H-4→LUMO (33%), H-4→L+1 (14%), HOMO→L+5 (23%) | H-5→L+5 (3%), H-4→L+4 (9%), H-2→L+1 (3%), H-1→L+5 (5%) |
| 275 | 0.074 | H-3→LUMO (11%), H-3→L+1 | H-4→LUMO (7%), H-4→L+2 (2%), H- |

| | | | |
|---|---|---|---|
| | | (38%), H-2→L+1 (20%) | 3→L+4 (4%), H-2→LUMO (3%), H-2→L+4 (5%) |
| 275 | 0.045 | H-4→LUMO (12%), H-3→L+1 (24%), H-2→L+1 (33%) | H-3→LUMO (7%), H-3→L+4 (3%), H-2→LUMO (4%), H-2→L+4 (8%) |
| 274 | 0.156 | H-4→LUMO (27%), H-4→L+1 (39%), H-2→LUMO (18%) | H-4→L+4 (3%), H-2→L+4 (2%), H-1→L+5 (3%) |
| 273 | 0.118 | H-1→L+3 (69%), H-1→L+6 (12%) | H-6→L+3 (5%), H-5→L+3 (6%) |
| 272 | 0.962 | H-5→LUMO (31%), H-3→L+4 (24%), H-2→L+2 (19%) | H-4→L+5 (5%), H-1→L+1 (4%) |
| 270 | 0.0001 | H-4→L+3 (76%), H-2→L+3 (15%) | H-7→L+3 (4%) |
| 269 | 0.155 | H-4→L+2 (14%), H-3→LUMO (21%), H-3→L+1 (16%), H-2→L+2 (19%) | H-5→LUMO (3%), H-5→L+1 (3%), H-4→L+5 (6%), H-1→L+1 (5%), H-1→L+4 (4%), HOMO→L+7 (3%) |
| 269 | 0.016 | H-2→LUMO (13%), H-2→L+1 (17%), H-1→L+2 (15%), H-1→L+5 (25%) | H-4→LUMO (4%), H-4→L+1 (4%), H-4→L+3 (2%), H-4→L+4 (9%), H-3→L+5 (2%) |

Table S8. Atomic coordinates of ***m*SPh** at the fundamental state after geometry optimization (DFT b3lyp/6-31g(d))

| Atom | X (Å) | Y (Å) | Z (Å) |
|---|---|---|---|
| C | −2.10102 | 3.92523 | −0.57806 |
| C | −0.77307 | 4.3623 | −0.64014 |
| C | 0.28115 | 3.45645 | −0.50423 |
| C | −0.01182 | 2.10565 | −0.30543 |
| C | −1.34904 | 1.66941 | −0.24378 |
| C | −2.39665 | 2.57227 | −0.379 |
| C | 0.8696 | 0.9424 | −0.12955 |
| C | 0.07117 | −0.20455 | 0.03564 |
| C | −1.41611 | 0.15461 | −0.02002 |
| C | 2.25997 | 0.84648 | −0.11722 |
| C | 2.87361 | −0.40512 | 0.06271 |
| C | 2.05738 | −1.54077 | 0.22779 |
| C | 0.66388 | −1.44805 | 0.21426 |
| C | −2.19181 | −0.59445 | −1.10891 |
| C | −3.26303 | −1.31667 | −0.5493 |
| C | −3.26592 | −1.10205 | 0.90454 |
| C | −2.19663 | −0.24807 | 1.23571 |
| C | −4.11215 | −1.59199 | 1.90155 |
| C | −3.87815 | −1.22081 | 3.22743 |
| C | −2.81409 | −0.37228 | 3.55299 |
| C | −1.96521 | 0.1199 | 2.55559 |
| C | −1.95518 | −0.62275 | −2.47797 |
| C | −2.80102 | −1.3815 | −3.29432 |
| C | −3.86712 | −2.10002 | −2.7417 |
| C | −4.10602 | −2.07336 | −1.36592 |
| C | 4.35436 | −0.52813 | 0.0771 |
| C | 4.99464 | −1.62424 | −0.52582 |
| C | 6.38395 | −1.73906 | −0.51409 |
| C | 7.16583 | −0.75893 | 0.09985 |
| C | 6.54452 | 0.3362 | 0.70286 |
| C | 5.15506 | 0.44942 | 0.69205 |
| H | −2.91025 | 4.64247 | −0.68565 |
| H | −0.55994 | 5.41656 | −0.79568 |
| H | 1.31095 | 3.80128 | −0.55312 |
| H | −3.42861 | 2.2347 | −0.33179 |
| H | 2.87422 | 1.72923 | −0.27318 |
| H | 2.52424 | −2.50713 | 0.39499 |

| | | | |
|---|---|---|---|
| H | 0.05635 | −2.33875 | 0.35073 |
| H | −4.93987 | −2.25176 | 1.65394 |
| H | −4.52854 | −1.59471 | 4.01376 |
| H | −2.64486 | −0.093 | 4.58944 |
| H | −1.13941 | 0.77873 | 2.81074 |
| H | −1.12784 | −0.0652 | −2.90901 |
| H | −2.62816 | −1.41253 | −4.36671 |
| H | −4.51535 | −2.68465 | −3.38912 |
| H | −4.93525 | −2.63413 | −0.942 |
| H | 4.39729 | −2.37914 | −1.02968 |
| H | 6.85668 | −2.59208 | −0.99408 |
| H | 8.24881 | −0.84783 | 0.10858 |
| H | 7.1423 | 1.10101 | 1.19199 |
| H | 4.6808 | 1.29175 | 1.18816 |

Table S9. Atomic coordinates of ***m*SPh$_2$** at the fundamental state after geometry optimization (DFT b3lyp/6-31g(d))

| Atom | X (Å) | Y (Å) | Z (Å) |
|---|---|---|---|
| C | 9.9649 | 1.8168 | 12.3665 |
| C | 9.2161 | 0.7353 | 11.5768 |
| C | 9.4935 | 0.2257 | 10.3266 |
| H | 10.2532 | 0.4964 | 9.8635 |
| C | 8.6222 | −0.6971 | 9.7715 |
| H | 8.8012 | −1.0321 | 8.9227 |
| C | 7.4829 | −1.1388 | 10.4483 |
| C | 7.2317 | −0.6254 | 11.7228 |
| H | 6.4838 | −0.9091 | 12.1972 |
| C | 8.0919 | 0.3041 | 12.2821 |
| C | 8.0076 | 1.0604 | 13.54 |
| C | 7.0677 | 1.0107 | 14.5553 |
| H | 6.3656 | 0.4025 | 14.5092 |
| C | 7.1732 | 1.8694 | 15.6436 |
| C | 8.238 | 2.7768 | 15.6765 |
| H | 8.3157 | 3.3573 | 16.399 |
| C | 9.1836 | 2.8342 | 14.6577 |
| H | 9.8835 | 3.4454 | 14.6977 |
| C | 9.0677 | 1.9707 | 13.5846 |
| C | 6.5139 | −2.0616 | 9.8128 |
| C | 6.1794 | −1.9373 | 8.4745 |
| H | 6.6108 | −1.2989 | 7.9541 |
| C | 5.2158 | −2.7453 | 7.8966 |
| H | 5.0014 | −2.6435 | 6.9974 |
| C | 4.5789 | −3.6957 | 8.6488 |
| H | 3.93 | −4.2401 | 8.2649 |
| C | 4.9002 | −3.8363 | 9.9637 |
| H | 4.4713 | −4.4845 | 10.4739 |
| C | 5.85 | −3.0331 | 10.5479 |
| H | 6.0511 | −3.1432 | 11.4494 |
| C | 6.162 | 1.8273 | 16.7325 |
| C | 4.8222 | 1.6322 | 16.4545 |
| H | 4.5439 | 1.5581 | 15.5702 |
| C | 3.8884 | 1.5462 | 17.4727 |
| H | 2.9923 | 1.403 | 17.2703 |
| C | 4.2852 | 1.6724 | 18.7867 |
| H | 3.6607 | 1.604 | 19.4713 |
| C | 5.6015 | 1.899 | 19.077 |
| H | 5.8679 | 2.0101 | 19.9611 |
| C | 6.5353 | 1.964 | 18.0671 |
| H | 7.4296 | 2.1012 | 18.2798 |

| | | | |
|---|---|---|---|
| C | 11.3902 | 1.3951 | 12.7297 |
| C | 11.8006 | 0.3767 | 13.5522 |
| H | 11.1772 | −0.1642 | 13.9805 |
| C | 13.1658 | 0.1654 | 13.7364 |
| H | 13.4605 | −0.5195 | 14.2929 |
| C | 14.0852 | 0.9763 | 13.0899 |
| H | 14.9945 | 0.825 | 13.2122 |
| C | 13.6728 | 2.0013 | 12.2722 |
| H | 14.2989 | 2.5327 | 11.8363 |
| C | 12.3129 | 2.2366 | 12.1004 |
| C | 11.5944 | 3.2664 | 11.3605 |
| C | 12.0444 | 4.345 | 10.5952 |
| H | 12.9553 | 4.4881 | 10.473 |
| C | 11.1226 | 5.1912 | 10.0249 |
| H | 11.4161 | 5.9111 | 9.515 |
| C | 9.7692 | 4.9875 | 10.1981 |
| H | 9.1615 | 5.5711 | 9.8048 |
| C | 9.306 | 3.9185 | 10.9549 |
| H | 8.3938 | 3.7792 | 11.0713 |
| C | 10.2275 | 3.0675 | 11.5304 |

Table S10. Atomic coordinates of ***m*STPh** at the fundamental state after geometry optimization (DFT b3lyp/6−31g(d))

| Atom | X (Å) | Y (Å) | Z (Å) |
|---|---|---|---|
| C | −3.66185 | −0.1237 | −0.10685 |
| C | −2.1551 | 0.09131 | 0.06035 |
| C | −1.48709 | 1.08245 | 0.76826 |
| H | −2.0388 | 1.84328 | 1.31397 |
| C | −0.09048 | 1.08437 | 0.78047 |
| H | 0.43534 | 1.84162 | 1.3548 |
| C | 0.65378 | 0.10766 | 0.09143 |
| C | −0.03515 | −0.88823 | −0.6217 |
| H | 0.52351 | −1.6332 | −1.18175 |
| C | −1.42897 | −0.89373 | −0.63427 |
| C | −2.3804 | −1.79894 | −1.29467 |
| C | −2.17069 | −2.92192 | −2.09776 |
| H | −1.16399 | −3.25955 | −2.33072 |
| C | −3.2786 | −3.60795 | −2.59998 |
| C | −4.57727 | −3.17859 | −2.30411 |
| H | −5.42899 | −3.72325 | −2.70256 |
| C | −4.78938 | −2.05369 | −1.49968 |
| H | −5.79869 | −1.72174 | −1.27125 |
| C | −3.68825 | −1.36928 | −0.99939 |
| C | 2.14019 | 0.13043 | 0.12001 |
| C | 2.84048 | 1.34332 | 0.04847 |
| H | 2.28582 | 2.26953 | −0.06712 |
| C | 4.24226 | 1.38062 | 0.05687 |
| C | 4.94427 | 0.16937 | 0.13764 |
| H | 6.02821 | 0.18762 | 0.19815 |
| C | 4.27514 | −1.06089 | 0.20902 |
| C | 2.87316 | −1.06212 | 0.19975 |
| H | 2.3428 | −2.00794 | 0.25549 |
| C | −4.41038 | −0.29887 | 1.21889 |
| C | −4.1994 | −1.24446 | 2.21507 |
| H | −3.41784 | −1.99263 | 2.11229 |
| C | −5.01096 | −1.21809 | 3.35452 |
| H | −4.85737 | −1.95144 | 4.14156 |
| C | −6.01808 | −0.25586 | 3.4889 |
| H | −6.64017 | −0.24851 | 4.38 |

| | | | |
|---|---|---|---|
| C | −6.23157 | 0.69525 | 2.48875 |
| H | −7.01547 | 1.44042 | 2.59832 |
| C | −5.42267 | 0.67074 | 1.35064 |
| C | −5.41194 | 1.5267 | 0.15611 |
| C | −6.20735 | 2.61922 | −0.1959 |
| H | −6.99615 | 2.96919 | 0.46524 |
| C | −5.9738 | 3.25875 | −1.41529 |
| H | −6.58521 | 4.11026 | −1.70204 |
| C | −4.96018 | 2.81359 | −2.27126 |
| H | −4.7909 | 3.32184 | −3.2167 |
| C | −4.1621 | 1.71917 | −1.92057 |
| H | −3.37543 | 1.37478 | −2.58666 |
| C | −4.39314 | 1.08154 | −0.70767 |
| C | 5.03503 | −2.3345 | 0.31107 |
| C | 4.58713 | −3.38043 | 1.13552 |
| C | 6.22177 | −2.52601 | −0.41638 |
| C | 5.29957 | −4.57523 | 1.2284 |
| H | 3.68667 | −3.2444 | 1.72805 |
| C | 6.93535 | −3.72002 | −0.32329 |
| H | 6.57322 | −1.74002 | −1.07916 |
| C | 6.47721 | −4.75062 | 0.49948 |
| H | 4.93813 | −5.36726 | 1.87913 |
| H | 7.84673 | −3.84827 | −0.90154 |
| H | 7.03294 | −5.68159 | 0.57218 |
| C | 4.968 | 2.67564 | −0.0182 |
| C | 4.48956 | 3.81194 | 0.65572 |
| C | 6.1519 | 2.79825 | −0.76494 |
| C | 5.16944 | 5.02697 | 0.58524 |
| H | 3.59015 | 3.7338 | 1.26019 |
| C | 6.83337 | 4.01241 | −0.83491 |
| H | 6.52622 | 1.93953 | −1.31533 |
| C | 6.345 | 5.13279 | −0.16026 |
| H | 4.78435 | 5.89042 | 1.12149 |
| H | 7.74304 | 4.08518 | −1.42534 |
| H | 6.87556 | 6.07954 | −0.21496 |
| H | −3.1306 | −4.48343 | −3.22661 |

Table S11. Atomic coordinates of ***m*STPh$_2$** at the fundamental state after geometry optimization (DFT b3lyp/6-31g(d))

| Atom | X (Å) | Y (Å) | Z (Å) |
|---|---|---|---|
| C | 0.000001 | 3.782188 | −0.000017 |
| C | −1.174764 | 2.80969 | −0.139058 |
| C | −2.526725 | 3.089428 | −0.293152 |
| H | −2.879866 | 4.116128 | −0.340005 |
| C | −3.431312 | 2.030705 | −0.399506 |
| H | −4.485809 | 2.245053 | −0.547308 |
| C | −3.005348 | 0.689369 | −0.351946 |
| C | −1.634979 | 0.420986 | −0.193951 |
| H | −1.292007 | −0.607964 | −0.127832 |
| C | −0.729753 | 1.475686 | −0.089301 |
| C | 0.729741 | 1.475679 | 0.089324 |
| C | 1.634956 | 0.420971 | 0.19399 |
| H | 1.291971 | −0.607977 | 0.127918 |
| C | 3.005333 | 0.689343 | 0.351943 |
| C | 3.431314 | 2.030674 | 0.39945 |
| H | 4.485817 | 2.245016 | 0.547218 |
| C | 2.526737 | 3.089406 | 0.293085 |
| H | 2.879893 | 4.116102 | 0.339896 |
| C | 1.174771 | 2.809679 | 0.139032 |

| | | | |
|---|---|---|---|
| C | −3.988262 | −0.420208 | −0.468236 |
| C | −5.239735 | −0.338123 | 0.159139 |
| H | −5.472358 | 0.531393 | 0.766365 |
| C | −6.171081 | −1.382945 | 0.073375 |
| C | −5.827327 | −2.528378 | −0.658957 |
| H | −6.559312 | −3.321549 | −0.777259 |
| C | −4.584054 | −2.643349 | −1.297274 |
| C | −3.676564 | −1.579811 | −1.192023 |
| H | −2.710559 | −1.655767 | −1.681979 |
| C | 3.988233 | −0.420246 | 0.468234 |
| C | 3.676543 | −1.579827 | 1.192062 |
| H | 2.710558 | −1.655765 | 1.682061 |
| C | 4.584027 | −2.643371 | 1.297302 |
| C | 5.827287 | −2.528433 | 0.65895 |
| H | 6.559258 | −3.321619 | 0.777238 |
| C | 6.171025 | −1.38302 | −0.073417 |
| C | 5.23969 | −0.338193 | −0.159183 |
| H | 5.472317 | 0.531314 | −0.766418 |
| C | 0.139715 | 4.753929 | −1.176934 |
| C | 0.300153 | 4.463539 | −2.526368 |
| H | 0.341036 | 3.433503 | −2.870617 |
| C | 0.408387 | 5.520624 | −3.436611 |
| H | 0.53413 | 5.308549 | −4.494913 |
| C | 0.356043 | 6.8477 | −2.995719 |
| H | 0.441547 | 7.657725 | −3.715188 |
| C | 0.19496 | 7.141364 | −1.639876 |
| H | 0.154993 | 8.174141 | −1.302948 |
| C | 0.086722 | 6.087841 | −0.729639 |
| C | −0.086515 | 6.087823 | 0.729693 |
| C | −0.194655 | 7.141325 | 1.639967 |
| H | −0.154568 | 8.17411 | 1.303077 |
| C | −0.355797 | 6.847628 | 2.995796 |
| H | −0.441229 | 7.657637 | 3.715293 |
| C | −0.408298 | 5.520542 | 3.436637 |
| H | −0.534095 | 5.308442 | 4.494928 |
| C | −0.300156 | 4.463478 | 2.526358 |
| H | −0.341164 | 3.433435 | 2.870568 |
| C | −0.139655 | 4.753902 | 1.17694 |
| C | 7.493346 | −1.278621 | −0.744213 |
| C | 8.194067 | −0.061101 | −0.774184 |
| C | 8.078014 | −2.39454 | −1.366436 |
| C | 9.433893 | 0.037674 | −1.403905 |
| H | 7.77313 | 0.808465 | −0.277079 |
| C | 9.318438 | −2.297243 | −1.995223 |
| H | 7.542319 | −3.339721 | −1.3781 |
| C | 10.00216 | −1.080295 | −2.017205 |
| H | 9.960925 | 0.988262 | −1.407385 |
| H | 9.747269 | −3.172263 | −2.476737 |
| H | 10.968809 | −1.003879 | −2.507671 |
| C | 4.243082 | −3.857751 | 2.08405 |
| C | 3.530427 | −3.761468 | 3.291139 |
| C | 4.624283 | −5.134998 | 1.639644 |
| C | 3.209431 | −4.901369 | 4.026853 |
| H | 3.248759 | −2.782078 | 3.667784 |
| C | 4.304661 | −6.275268 | 2.375259 |
| H | 5.153983 | −5.234949 | 0.696262 |
| C | 3.595232 | −6.16371 | 3.572413 |
| H | 2.664259 | −4.801647 | 4.961841 |
| H | 4.603048 | −7.253584 | 2.007456 |
| H | 3.345382 | −7.052265 | 4.14587 |
| C | −4.243098 | −3.85775 | −2.083981 |

| | | | |
|---|---|---|---|
| C | −3.530499 | −3.761503 | −3.291107 |
| C | −4.624251 | −5.134991 | −1.639515 |
| C | −3.209501 | −4.901427 | −4.026785 |
| H | −3.24888 | −2.782127 | −3.667819 |
| C | −4.304628 | −6.275284 | −2.375092 |
| H | −5.153912 | −5.234925 | −0.696109 |
| C | −3.595247 | −6.163761 | −3.572278 |
| H | −2.664369 | −4.801726 | −4.961798 |
| H | −4.602982 | −7.253591 | −2.007236 |
| H | −3.345397 | −7.052333 | −4.145708 |
| C | −7.493417 | −1.27852 | 0.744132 |
| C | −8.194065 | −0.060957 | 0.774184 |
| C | −8.078183 | −2.394457 | 1.366239 |
| C | −9.433903 | 0.037844 | 1.403871 |
| H | −7.773068 | 0.808619 | 0.277152 |
| C | −9.318623 | −2.297136 | 1.994983 |
| H | −7.542541 | −3.339667 | 1.377861 |
| C | −10.002265 | −1.080145 | 2.017049 |
| H | −9.960883 | 0.98846 | 1.407421 |
| H | −9.747538 | −3.172165 | 2.476408 |
| H | −10.968928 | −1.00371 | 2.507485 |

Table S12. Atomic coordinates of ***m*SPh** at the first triplet state after geometry optimization (TD-DFT b3lyp/6-31+g(d))

| Atom | X (Å) | Y (Å) | Z (Å) |
|---|---|---|---|
| C | −2.051804 | 3.951125 | −0.559706 |
| C | −0.691538 | 4.382134 | −0.605151 |
| C | 0.348079 | 3.488649 | −0.471223 |
| C | 0.048444 | 2.089588 | −0.280966 |
| C | −1.348653 | 1.665753 | −0.235535 |
| C | −2.366553 | 2.579437 | −0.373336 |
| C | 0.877811 | 0.980859 | −0.119315 |
| C | 0.047684 | −0.225907 | 0.034168 |
| C | −1.437831 | 0.147187 | −0.021738 |
| C | 2.309486 | 0.858051 | −0.099574 |
| C | 2.900371 | −0.380611 | 0.064893 |
| C | 2.052661 | −1.554593 | 0.215728 |
| C | 0.639523 | −1.454456 | 0.19561 |
| C | −2.2229 | −0.587322 | −1.113624 |
| C | −3.302236 | −1.302755 | −0.558413 |
| C | −3.302664 | −1.096075 | 0.89718 |
| C | −2.223608 | −0.254271 | 1.23176 |
| C | −4.15498 | −1.582535 | 1.892887 |
| C | −3.916271 | −1.219728 | 3.222031 |
| C | −2.841687 | −0.382633 | 3.551892 |
| C | −1.987727 | 0.105588 | 2.554811 |
| C | −1.986891 | −0.608984 | −2.484595 |
| C | −2.841133 | −1.354152 | −3.307204 |
| C | −3.915748 | −2.066659 | −2.757801 |
| C | −4.154392 | −2.046401 | −1.380159 |
| C | 4.372515 | −0.534026 | 0.080471 |
| C | 4.989711 | −1.682236 | −0.45581 |
| C | 6.378472 | −1.818201 | −0.45996 |
| C | 7.187912 | −0.815326 | 0.081679 |
| C | 6.591441 | 0.326332 | 0.628025 |
| C | 5.203985 | 0.463573 | 0.629248 |
| H | −2.850254 | 4.679064 | −0.668201 |
| H | −0.479056 | 5.438747 | −0.749143 |
| H | 1.380319 | 3.826378 | −0.508026 |

| | | | |
|---|---|---|---|
| H | −3.406434 | 2.262643 | −0.340364 |
| H | 2.923063 | 1.741088 | −0.254741 |
| H | 2.515168 | −2.519958 | 0.3913 |
| H | 0.037963 | −2.352544 | 0.316456 |
| H | −4.990454 | −2.232504 | 1.64373 |
| H | −4.570357 | −1.590623 | 4.007193 |
| H | −2.669617 | −0.109985 | 4.589997 |
| H | −1.155323 | 0.755394 | 2.81416 |
| H | −1.154274 | −0.0567 | −2.91374 |
| H | −2.66943 | −1.379881 | −4.380264 |
| H | −4.570183 | −2.640615 | −3.409092 |
| H | −4.989964 | −2.601894 | −0.960785 |
| H | 4.378169 | −2.46212 | −0.90108 |
| H | 6.829187 | −2.708509 | −0.891696 |
| H | 8.269355 | −0.924122 | 0.084089 |
| H | 7.208748 | 1.106699 | 1.066429 |
| H | 4.754513 | 1.341012 | 1.086134 |

Table S13 Atomic coordinates of ***m*SPh$_2$** at the first triplet state after geometry optimization (TD-DFT b3lyp/6-31+g(d))

| Atom | X (Å) | Y (Å) | Z (Å) |
|---|---|---|---|
| C | 0.00208 | 1.77379 | −0.00002 |
| C | 1.18206 | 0.79457 | 0.03102 |
| C | 2.5328 | 1.05356 | 0.06034 |
| H | 2.90422 | 2.07571 | 0.07447 |
| C | 3.45091 | −0.02149 | 0.08216 |
| H | 4.51361 | 0.18735 | 0.14752 |
| C | 3.00272 | −1.39943 | 0.07257 |
| C | 1.64484 | −1.66557 | 0.04199 |
| H | 1.29004 | −2.69143 | −0.00406 |
| C | 0.69734 | −0.58846 | 0.02199 |
| C | −0.69883 | −0.58679 | −0.02194 |
| C | −1.6489 | −1.66164 | −0.04191 |
| H | −1.29655 | −2.68833 | 0.00434 |
| C | −3.00614 | −1.39228 | −0.07268 |
| C | −3.45104 | −0.01322 | −0.08251 |
| H | −4.51322 | 0.19817 | −0.14805 |
| C | −2.53035 | 1.05964 | −0.06069 |
| H | −2.89934 | 2.08267 | −0.07501 |
| C | −1.18024 | 0.79743 | −0.03113 |
| C | 3.99919 | −2.49613 | 0.088 |
| C | 5.22813 | −2.37008 | −0.58934 |
| H | 5.44381 | −1.46136 | −1.1447 |
| C | 6.15959 | −3.40924 | −0.59014 |
| H | 7.09541 | −3.29101 | −1.13093 |
| C | 5.89089 | −4.59843 | 0.09391 |
| H | 6.61861 | −5.40579 | 0.09781 |
| C | 4.67931 | −4.73656 | 0.77924 |
| H | 4.46445 | −5.6507 | 1.32733 |
| C | 3.7475 | −3.69881 | 0.77764 |
| H | 2.82422 | −3.80823 | 1.34017 |
| C | −4.00522 | −2.48658 | −0.08807 |
| C | −3.75621 | −3.69007 | −0.77729 |
| H | −2.83303 | −3.80187 | −1.33952 |
| C | −4.69048 | −4.7256 | −0.77884 |
| H | −4.47764 | −5.6404 | −1.3266 |
| C | −5.90193 | −4.58439 | −0.09389 |
| H | −6.63157 | −5.39 | −0.09777 |
| C | −6.16798 | −3.39436 | 0.58975 |

| | | | |
|---|---|---|---|
| H | −7.10365 | −3.27375 | 1.13025 |
| C | −5.23405 | −2.35742 | 0.58889 |
| H | −5.44772 | −1.44803 | 1.14394 |
| C | −0.0274 | 2.74674 | 1.18408 |
| C | −0.0629 | 2.4553 | 2.54408 |
| H | −0.07278 | 1.42485 | 2.89129 |
| C | −0.0855 | 3.51232 | 3.46275 |
| H | −0.113 | 3.29998 | 4.52846 |
| C | −0.07265 | 4.84165 | 3.01891 |
| H | −0.09044 | 5.65136 | 3.74411 |
| C | −0.03697 | 5.13661 | 1.65251 |
| H | −0.02703 | 6.17042 | 1.31528 |
| C | −0.01422 | 4.08207 | 0.73494 |
| C | 0.02421 | 4.08209 | −0.73475 |
| C | 0.04962 | 5.13666 | −1.65221 |
| H | 0.04232 | 6.17046 | −1.31488 |
| C | 0.08451 | 4.84175 | −3.01864 |
| H | 0.10433 | 5.65148 | −3.74377 |
| C | 0.09397 | 3.51243 | −3.46262 |
| H | 0.12087 | 3.30013 | −4.52836 |
| C | 0.06871 | 2.45539 | −2.54406 |
| H | 0.07596 | 1.42495 | −2.89137 |
| C | 0.03399 | 2.74678 | −1.18402 |

Table S14 Atomic coordinates of ***m*STPh** at the first triplet state after geometry optimization (TD-DFT b3lyp/6-31+g(d))

| Atom | X (Å) | Y (Å) | Z (Å) |
|---|---|---|---|
| C | −3.690204 | −0.134402 | −0.095484 |
| C | −2.1841 | 0.098438 | 0.067142 |
| C | −1.51522 | 1.125855 | 0.686114 |
| H | −2.058363 | 1.935936 | 1.167586 |
| C | −0.098761 | 1.128424 | 0.706308 |
| H | 0.424019 | 1.918299 | 1.234837 |
| C | 0.672896 | 0.062988 | 0.082235 |
| C | 0.004188 | −0.972523 | −0.54337 |
| H | 0.55983 | −1.755728 | −1.051338 |
| C | −1.431945 | −0.993514 | −0.573627 |
| C | −2.330203 | −1.89573 | −1.142518 |
| C | −2.119374 | −3.11647 | −1.882245 |
| H | −1.110518 | −3.470011 | −2.077439 |
| C | −3.213465 | −3.820261 | −2.33509 |
| C | −4.543573 | −3.365651 | −2.086672 |
| H | −5.386386 | −3.942237 | −2.456015 |
| C | −4.771039 | −2.167191 | −1.361265 |
| H | −5.788735 | −1.830185 | −1.178327 |
| C | −3.697166 | −1.444757 | −0.896867 |
| C | 2.152249 | 0.112202 | 0.119907 |
| C | 2.834405 | 1.341153 | 0.061496 |
| H | 2.267082 | 2.261716 | −0.037589 |
| C | 4.235727 | 1.402119 | 0.05373 |
| C | 4.962631 | 0.203041 | 0.11957 |
| H | 6.0469 | 0.240924 | 0.173324 |
| C | 4.313666 | −1.041028 | 0.193212 |
| C | 2.912942 | −1.068789 | 0.193632 |
| H | 2.402826 | −2.025358 | 0.256059 |
| C | −4.44915 | −0.218026 | 1.233811 |
| C | −4.240754 | −1.090296 | 2.297462 |
| H | −3.455304 | −1.841086 | 2.254697 |
| C | −5.060962 | −0.987574 | 3.42819 |

| | | | |
|---|---|---|---|
| H | −4.909965 | −1.66243 | 4.266863 |
| C | −6.074921 | −0.021833 | 3.486892 |
| H | −6.703453 | 0.045579 | 4.371349 |
| C | −6.286048 | 0.85558 | 2.418793 |
| H | −7.074889 | 1.602305 | 2.47079 |
| C | −5.467712 | 0.7537 | 1.289894 |
| C | −5.452325 | 1.522088 | 0.036615 |
| C | −6.251106 | 2.583598 | −0.398867 |
| H | −7.046802 | 2.977598 | 0.22899 |
| C | −6.011178 | 3.135112 | −1.661202 |
| H | −6.624278 | 3.960968 | −2.013251 |
| C | −4.98805 | 2.633457 | −2.477201 |
| H | −4.814556 | 3.073163 | −3.456044 |
| C | −4.187368 | 1.570008 | −2.041589 |
| H | −3.394484 | 1.182797 | −2.677064 |
| C | −4.424521 | 1.019946 | −0.78582 |
| C | 4.938256 | 2.711717 | −0.017796 |
| C | 4.474318 | 3.822358 | 0.709229 |
| C | 6.085602 | 2.873405 | −0.81452 |
| C | 5.133532 | 5.051188 | 0.642324 |
| H | 3.604251 | 3.714974 | 1.351817 |
| C | 6.746043 | 4.101528 | −0.882478 |
| H | 6.448721 | 2.035945 | −1.404709 |
| C | 6.272889 | 5.196665 | −0.154166 |
| H | 4.761079 | 5.893373 | 1.220389 |
| H | 7.626345 | 4.204629 | −1.512255 |
| H | 6.786589 | 6.153152 | −0.20661 |
| C | 5.098159 | −2.301543 | 0.292076 |
| C | 4.697051 | −3.338418 | 1.153221 |
| C | 6.261839 | −2.489156 | −0.474748 |
| C | 5.432773 | −4.521511 | 1.243949 |
| H | 3.81561 | −3.206045 | 1.775324 |
| C | 6.99854 | −3.671681 | −0.384953 |
| H | 6.57855 | −1.711197 | −1.164712 |
| C | 6.587251 | −4.693909 | 0.475044 |
| H | 5.108117 | −5.30565 | 1.923576 |
| H | 7.890423 | −3.797215 | −0.994033 |
| H | 7.160622 | −5.61465 | 0.545772 |
| H | −3.068105 | −4.741418 | −2.894205 |

Table S15 Atomic coordinates of ***m*STPh$_2$** at the first triplet state after geometry optimization (TD-DFT b3lyp/6-31+g(d))

| Atom | X (Å) | Y (Å) | Z (Å) |
|---|---|---|---|
| C | −0.00008 | 3.81596 | −0.00044 |
| C | 1.17398 | 2.83827 | 0.13237 |
| C | 2.51681 | 3.09888 | 0.27872 |
| H | 2.8845 | 4.12143 | 0.32538 |
| C | 3.43105 | 2.02502 | 0.37897 |
| H | 4.48384 | 2.23547 | 0.53552 |
| C | 2.98682 | 0.64683 | 0.33005 |
| C | 1.63696 | 0.37872 | 0.18286 |
| H | 1.28829 | −0.64747 | 0.10677 |
| C | 0.69378 | 1.45485 | 0.08146 |
| C | −0.69383 | 1.4548 | −0.08181 |
| C | −1.63697 | 0.3786 | −0.18295 |
| H | −1.28827 | −0.64755 | −0.10651 |
| C | −2.98683 | 0.64662 | −0.33035 |
| C | −3.4311 | 2.02479 | −0.37978 |
| H | −4.48387 | 2.23515 | −0.53653 |

| | | | |
|---|---|---|---|
| C | −2.51691 | 3.09871 | −0.27976 |
| H | −2.88463 | 4.12123 | −0.3268 |
| C | −1.17408 | 2.8382 | −0.13316 |
| C | 3.9803 | −0.44952 | 0.42977 |
| C | 5.25755 | −0.31692 | −0.14214 |
| H | 5.52033 | 0.60421 | −0.65359 |
| C | 6.20225 | −1.35136 | −0.07355 |
| C | 5.8549 | −2.53626 | 0.59339 |
| H | 6.57993 | −3.34247 | 0.65832 |
| C | 4.59162 | −2.69847 | 1.18494 |
| C | 3.66829 | −1.64773 | 1.09546 |
| H | 2.69028 | −1.76135 | 1.55355 |
| C | −3.98025 | −0.44979 | −0.42981 |
| C | −3.66814 | −1.64822 | −1.09507 |
| H | −2.69008 | −1.76198 | −1.55303 |
| C | −4.59143 | −2.69901 | −1.18428 |
| C | −5.85478 | −2.53664 | −0.59291 |
| H | −6.57975 | −3.34292 | −0.65766 |
| C | −6.20223 | −1.35153 | 0.0736 |
| C | −5.25756 | −0.31705 | 0.14193 |
| H | −5.52041 | 0.60425 | 0.65303 |
| C | −0.13234 | 4.78892 | 1.17664 |
| C | −0.28373 | 4.49756 | 2.52864 |
| H | −0.32184 | 3.4671 | 2.87392 |
| C | −0.3863 | 5.55462 | 3.44181 |
| H | −0.50464 | 5.34239 | 4.50131 |
| C | −0.33713 | 6.88395 | 3.00043 |
| H | −0.41796 | 7.6937 | 3.72128 |
| C | −0.18483 | 7.17881 | 1.64208 |
| H | −0.14714 | 8.21259 | 1.30672 |
| C | −0.08231 | 6.12422 | 0.73006 |
| C | 0.082 | 6.12422 | −0.73093 |
| C | 0.18446 | 7.17882 | −1.64295 |
| H | 0.1467 | 8.21259 | −1.30759 |
| C | 0.33677 | 6.88397 | −3.0013 |
| H | 0.41756 | 7.69372 | −3.72215 |
| C | 0.38604 | 5.55465 | −3.44268 |
| H | 0.5044 | 5.34242 | −4.50218 |
| C | 0.28353 | 4.49758 | −2.52951 |
| H | 0.32171 | 3.46712 | −2.87479 |
| C | 0.13212 | 4.78893 | −1.1775 |
| C | −7.54715 | −1.19333 | 0.6908 |
| C | −8.70187 | −1.65707 | 0.03577 |
| C | −7.69845 | −0.57597 | 1.94517 |
| C | −9.96383 | −1.50911 | 0.61441 |
| H | −8.6125 | −2.11534 | −0.94582 |
| C | −8.95997 | −0.42725 | 2.52468 |
| H | −6.81801 | −0.2316 | 2.48163 |
| C | −10.09892 | −0.8933 | 1.86191 |
| H | −10.84327 | −1.86776 | 0.08514 |
| H | −9.05139 | 0.04582 | 3.49936 |
| H | −11.08125 | −0.77779 | 2.31272 |
| C | −4.24205 | −3.95972 | −1.89362 |
| C | −3.52525 | −3.93383 | −3.10313 |
| C | −4.61993 | −5.20994 | −1.37253 |
| C | −3.19708 | −5.11655 | −3.7685 |
| H | −3.24381 | −2.97814 | −3.53788 |
| C | −4.29247 | −6.39329 | −2.03717 |
| H | −5.15325 | −5.25616 | −0.42649 |
| C | −3.57929 | −6.35219 | −3.23857 |
| H | −2.6493 | −5.07137 | −4.70659 |

| | | | |
|---|---|---|---|
| H | −4.58751 | −7.34882 | −1.61048 |
| H | −3.32384 | −7.27324 | −3.75618 |
| C | 4.24233 | −3.95894 | 1.89473 |
| C | 3.52555 | −3.93268 | 3.10425 |
| C | 4.62029 | −5.20933 | 1.37409 |
| C | 3.19747 | −5.11519 | 3.77004 |
| H | 3.24405 | −2.97686 | 3.53867 |
| C | 4.29292 | −6.39246 | 2.03915 |
| H | 5.1536 | −5.25587 | 0.42805 |
| C | 3.57976 | −6.35099 | 3.24055 |
| H | 2.64969 | −5.06971 | 4.70812 |
| H | 4.58803 | −7.34813 | 1.6128 |
| H | 3.32437 | −7.27188 | 3.75849 |
| C | 7.5471 | −1.19333 | −0.69094 |
| C | 8.70191 | −1.65667 | −0.03577 |
| C | 7.69824 | −0.57655 | −1.94561 |
| C | 9.96381 | −1.50887 | −0.61458 |
| H | 8.61264 | −2.11448 | 0.94604 |
| C | 8.9597 | −0.42799 | −2.52528 |
| H | 6.81772 | −0.2325 | −2.48214 |
| C | 10.09874 | −0.89363 | −1.86239 |
| H | 10.84333 | −1.86719 | −0.08523 |
| H | 9.05102 | 0.04463 | −3.5002 |
| H | 11.08103 | −0.77825 | −2.31333 |

## 8 Charge Transport

Space-charged limited current (SCLC) diodes

The hole-only device (HOD) has a configuration of ITO/HAT-CN (10 nm)/Host (100 nm)/HATCN (10 nm)/ Al (120 nm), and electron-only device (EOD) is ITO/Liq (4 nm)/Host (100 nm)/Liq (4 nm)/Al (120 nm). After the fabrication, the devices were encapsulated before testing in dark.

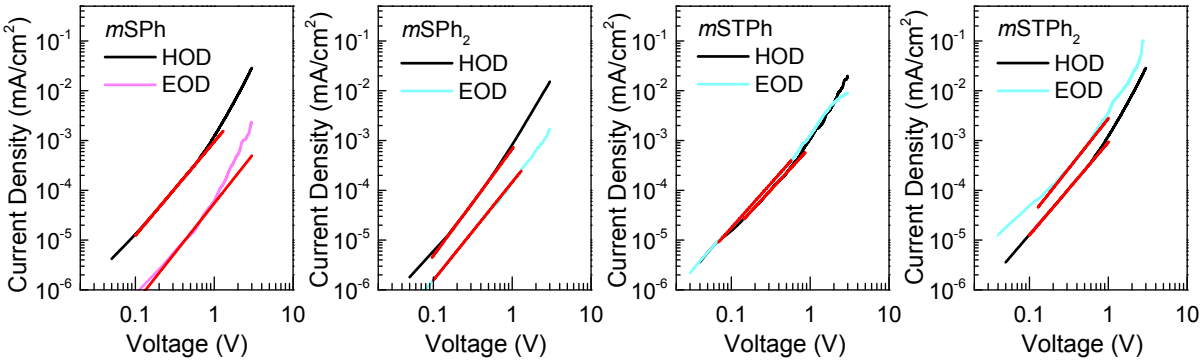



Figure S16. The *J*–*V* curves of hole-only (HOD) and electron-only devices using *m*SPh, *m*SPh$_2$, *m*STPh and *m*STPh$_2$, respectively.

The *J*–*V* curves of charge-only devices show the charge transport ability of the compounds. Based on the Schottky thermionic region and space-charge-limited current (SCLC) model, the curves can be divided into two parts under low bias. We assign the second region of the *J*–*V* curve as assigned as the SCLC region, which then can be described by an equation:

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu_0 exp(\beta\sqrt{\frac{V}{L}})\frac{V^2}{L^3}$$

in which $V$ is the driving voltage, $L$ is the thickness of the thin layer, $\varepsilon_0$ the permittivity of the free space, $\varepsilon$ is the relative dielectric constant (estimated to be 3.0 here), $\mu_0$ is the zero-field mobility and $\beta$ is Poole-Frenkel factor. The thickness $L$ equals to 100 nm, the zero-field mobility of the compounds was calculated and summarized Table 1.

## 9 Phosphorescent OLED characteristics

The architecture of the devices is the following: …

Blue PhOLEDs: ITO/HAT-CN (10 nm)/TAPC (35 nm)/TCTA (8 nm)/host: 15 wt% fac-Ir(iprpmi)$_3$, 20 nm)/TmPyPB (40 nm)/Liq (2nm)/Al (120 nm).

Green PhOLEDs: ITO/HAT-CN (10 nm)/TAPC (40 nm)/TCTA (8 nm)/host: 14 wt% $Ir(ppy)_2acac$, 20 nm)/TmPyPB (45 nm)/Liq (2nm)/Al (120 nm).

Red PhOLEDs: ITO/HAT-CN (10 nm)/TAPC (45 nm)/TCTA (8 nm)/host: 12 wt% $Ir(MDQ)_2acac$, 20 nm)/TmPyPB (55 nm)/Liq (2nm)/Al (120 nm).

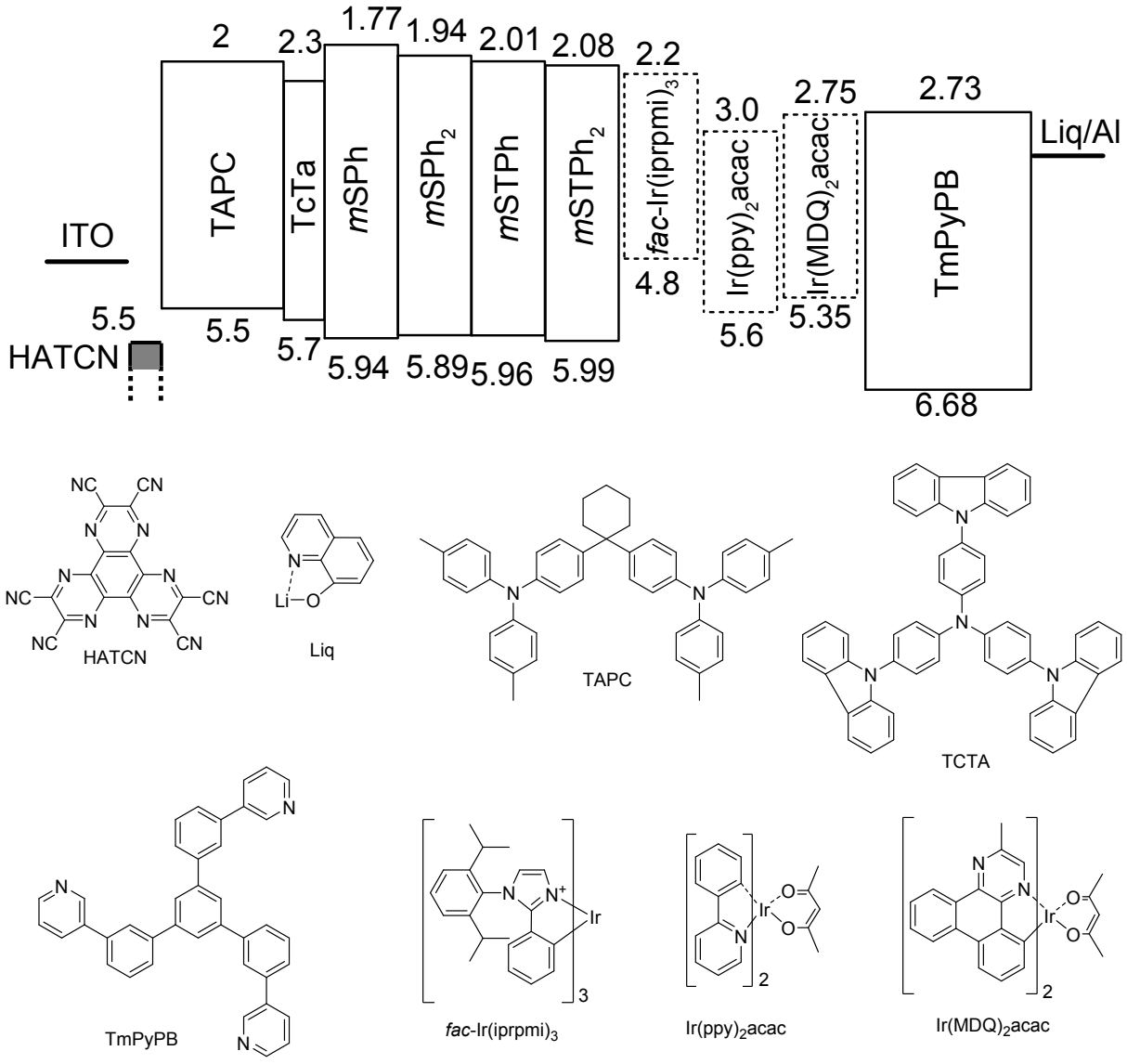



Figure S17. The energy level alignment of the deice and the molecular structures of materials in different layers. The LUMO/HOMO values of hosts were taken from the CV measurements and other material were taken from literature.

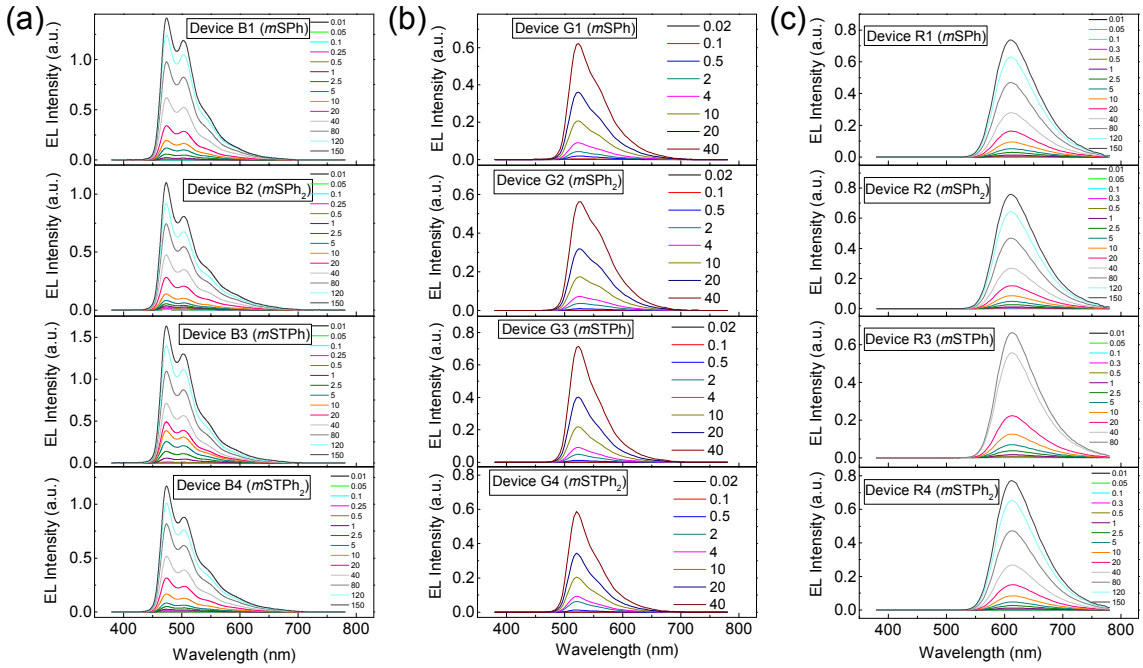



Figure S18. The EL spectrum of (a) blue (B1–4), (b) green (G1–4) and (c) red (R1–4) PhOLEDs using *m*SPh, *m*SPh$_2$, *m*STPh and *m*STPh$_2$, respectively. The legends show the driving current densities of each spectrum.

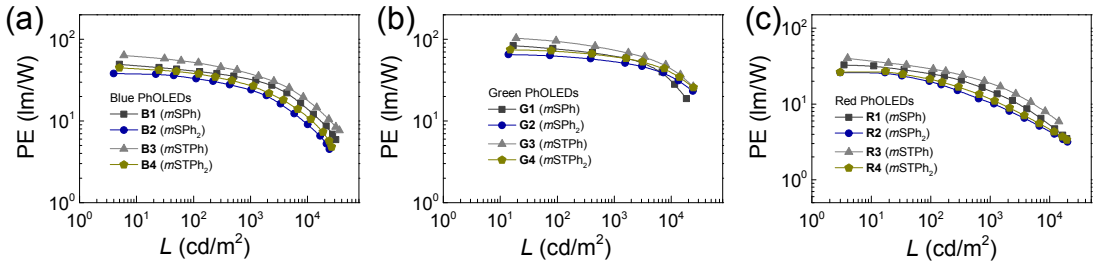



Figure S19 The PE–*L* curves of (a) blue (B1–4), (b) green (G1–4) and (c) red (R1–4) PhOLEDs using *m*SPh, *m*SPh$_2$, *m*STPh and *m*STPh$_2$, respectively.

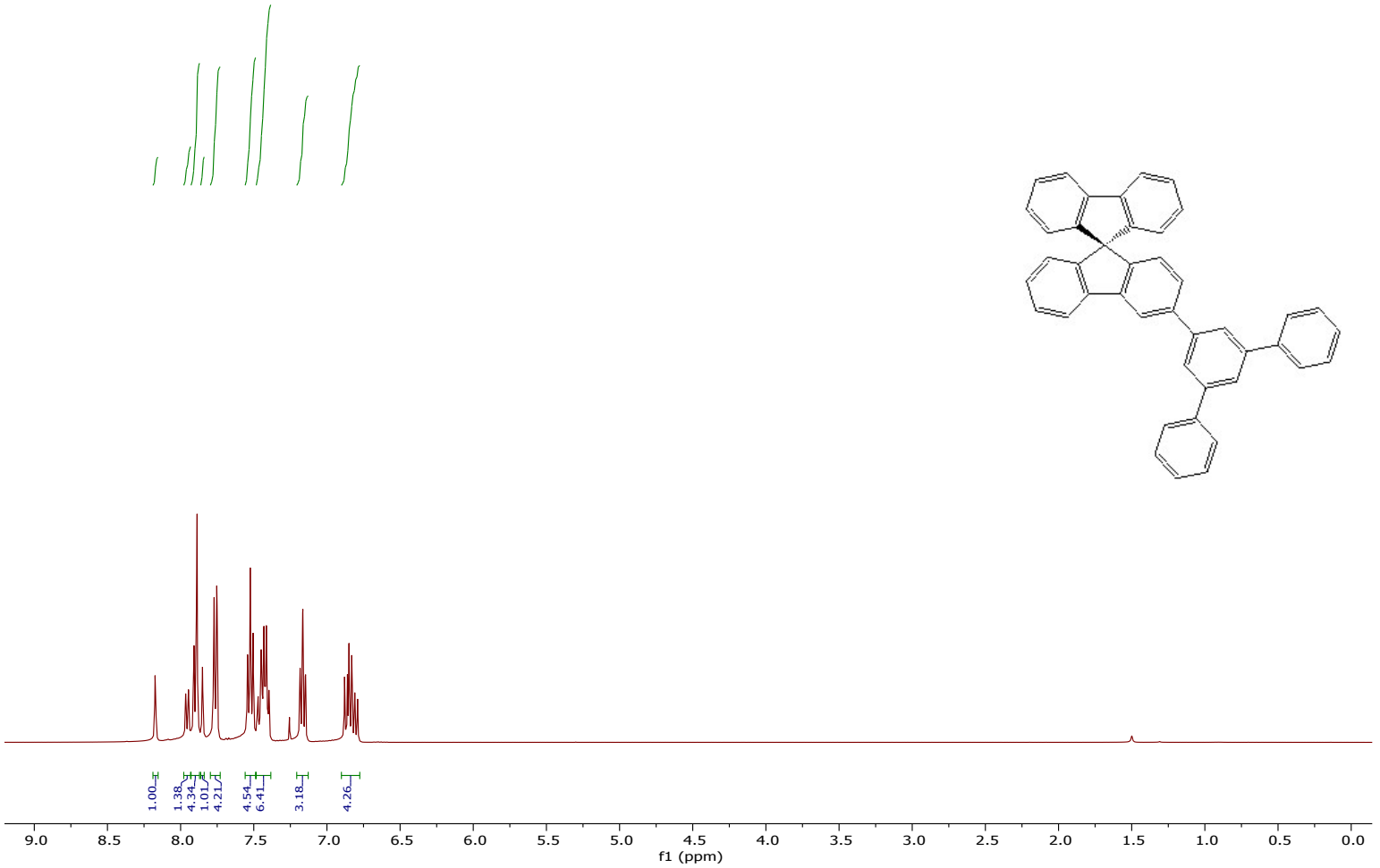
Table S16 The state-of-art device performance using universal hosts in red, green and blue PhOLEDs.

| Compound | Red PhOLED | | Green PhOLED | | Blue PhOLED | | $EQE_{AV.}$ | Reference |
|---|---|---|---|---|---|---|---|---|
| | $EQE_{max}$ [%] | CIE (x, y) | $EQE_{max}$ [%] | CIE (x, y) | $EQE_{max}$ [%] | CIE (x, y) | | |
| 4CzMC | 11.4 | (0.62, 0.38) | 16.6 | (0.32, 0.62) | 18.9 | (0.16, 0.31) | 15.6 | [10] |
| DPBP-DMAC | 14.8 | (0.68, 0.32) | 23.8 | (0.31, 0.63) | 22.9 | (0.19, 0.41) | 20.5 | [11] |
| DPMBP-DMAC | 15.6 | (0.67, 0.32) | 24.7 | (0.30, 0.64) | 22.6 | (0.19, 0.41) | 20.9 | [11] |
| *o*-CzTP | 15.8 | (0.60, 0.39) | 25 | (0.25, 0.64) | 27.1 | (0.15, 0.34) | 22.6 | [12] |
| BCPO | 17 | (0.67, 0.33) | 21.6 | (0.28, 0.65) | 23.5 | (0.13, 0.30) | 20.7 | [13] |
| 2 | 17 | (0.67, 0.33) | 26.9 | N/A | 24.3 | N/A | 22.7 | [14] |
| *m*-CzTP | 17.2 | (0.61, 0.38) | 22.3 | (0.26, 0.64) | 23.9 | (0.15, 0.33) | 21.1 | [12] |
| *o*-DiCbzBz | 20.1 | N/A | 20.4 | N/A | 27 | N/A | 22.5 | [15] |
| TPA-L-BN | 20.5 | (0.61, 0.39) | 20 | (0.31, 0.64) | 19.8 | (0.16, 0.32) | 20.1 | [16] |
| 1 | 20.5 | (0.52, 0.48) | 22.7 | (0.35, 0.62) | 16.1 | (0.18, 0.32) | 19.7 | [17] |
| $TCZSO_2$ | 21 | (0.63, 0.37) | 24 | (0.35, 0.61) | 22.8 | (0.15, 0.35) | 22.6 | [18] |
| BII–TPA | 22.1 | (0.68, 0.31) | 26.4 | (0.34, 0.62) | 21.2 | (0.17, 0.34) | 23.2 | [19] |
| m-DCz-S | 22.5 | (0.50, 0.50) | 22.6 | (0.29, 0.64) | 25.1 | (0.15, 0.29) | 23.4 | [20] |
| BII–BCz | 22.7 | (0.68, 0.31) | 27.8 | (0.35, 0.61) | 29.4 | (0.16, 0.33) | 26.6 | [19] |
| 4ICDPy | 25.3 | (0.67, 0.33) | 27 | (0.24, 0.64) | 22.1 | (0.14, 0.32) | 24.8 | [21] |
| ***m*-STPh** | 27.3 | (0.63, 0.37) | 26.0 | (0.32, 0.63) | 27.1 | (0.18, 0.38) | 26.8 | **This work** |

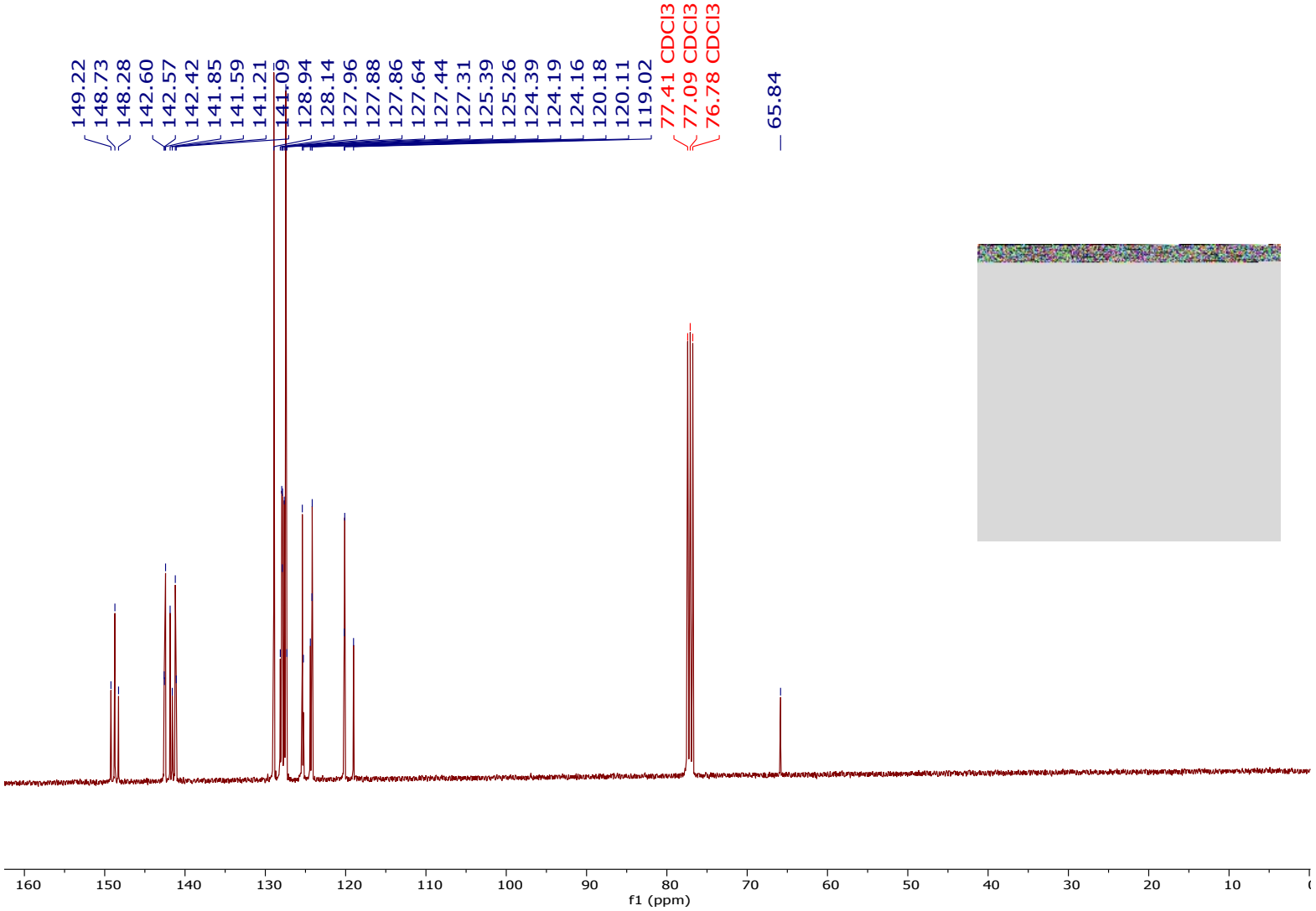
$EQE_{AV.}$: the average EQE value of each host in red, green and blue device performances.

## 10 Copy of NMR spectra

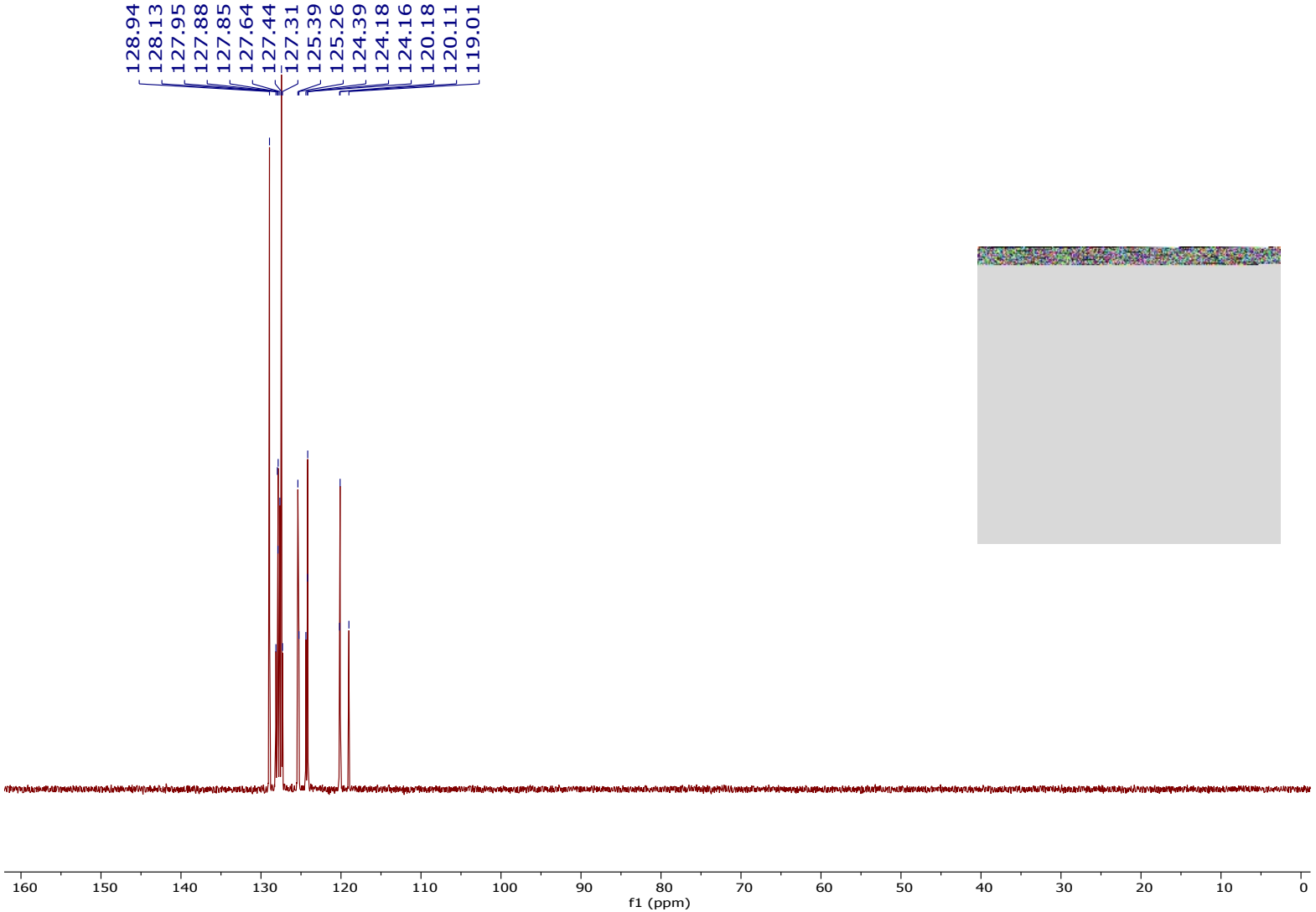
### 10.1 ***m*STPh — $^{1}$H— $CDCl_3$



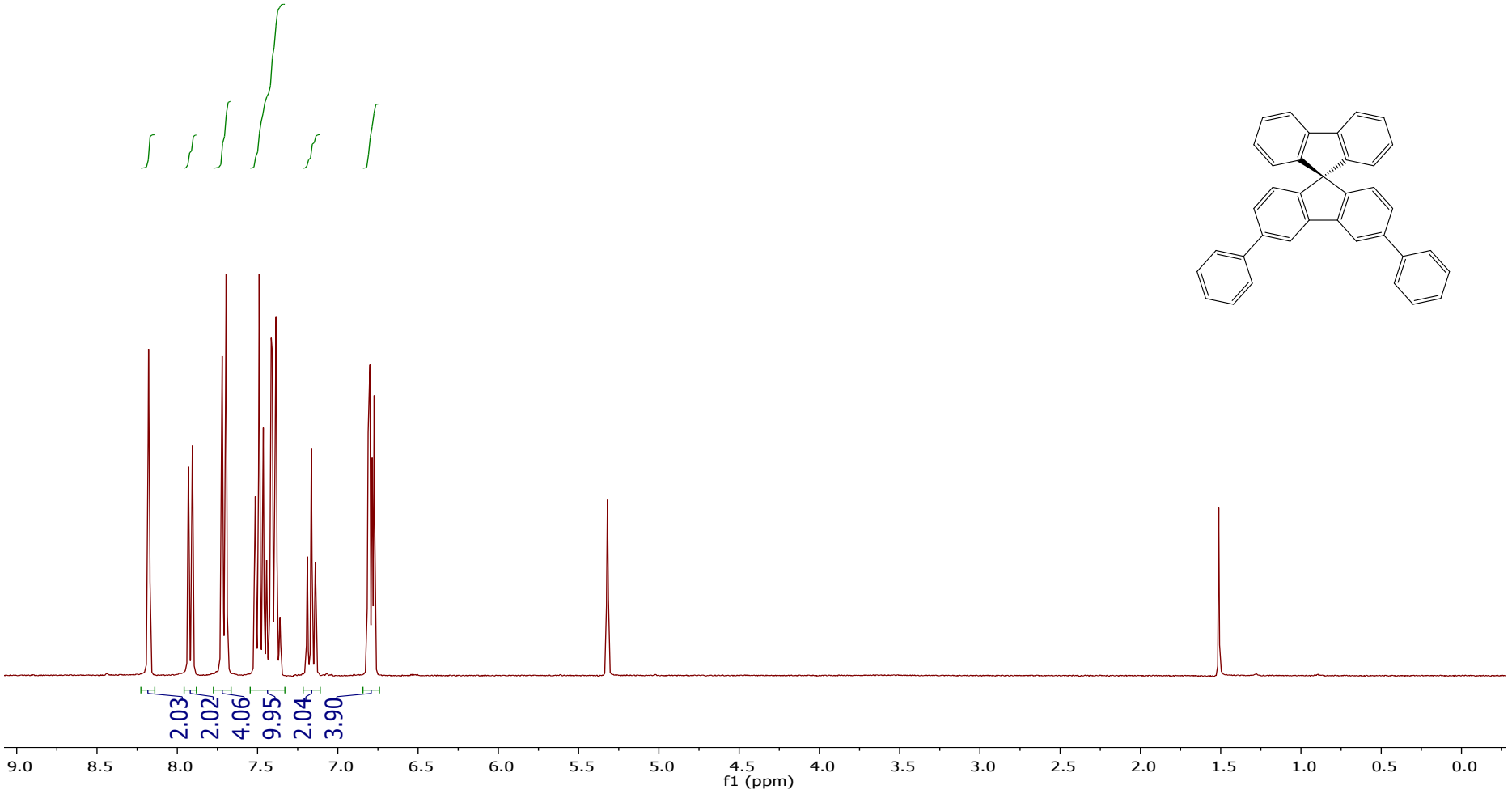
10.2 ***m*STPh — $^{13}C$ — $CDCl_3$**



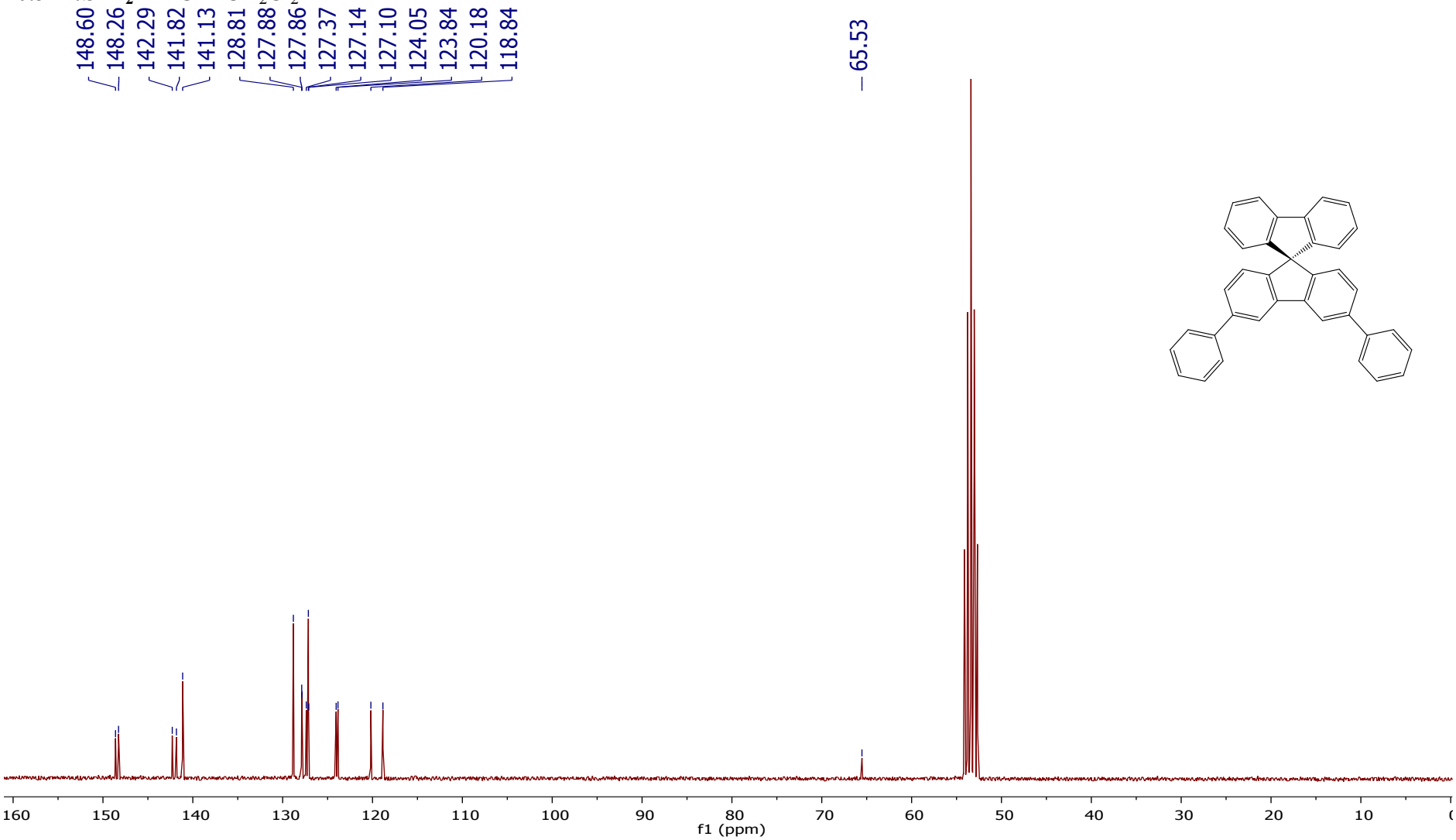
10.3 ***m*STPh — $^{13}C$ — DEPT135 — $CDCl_3$**



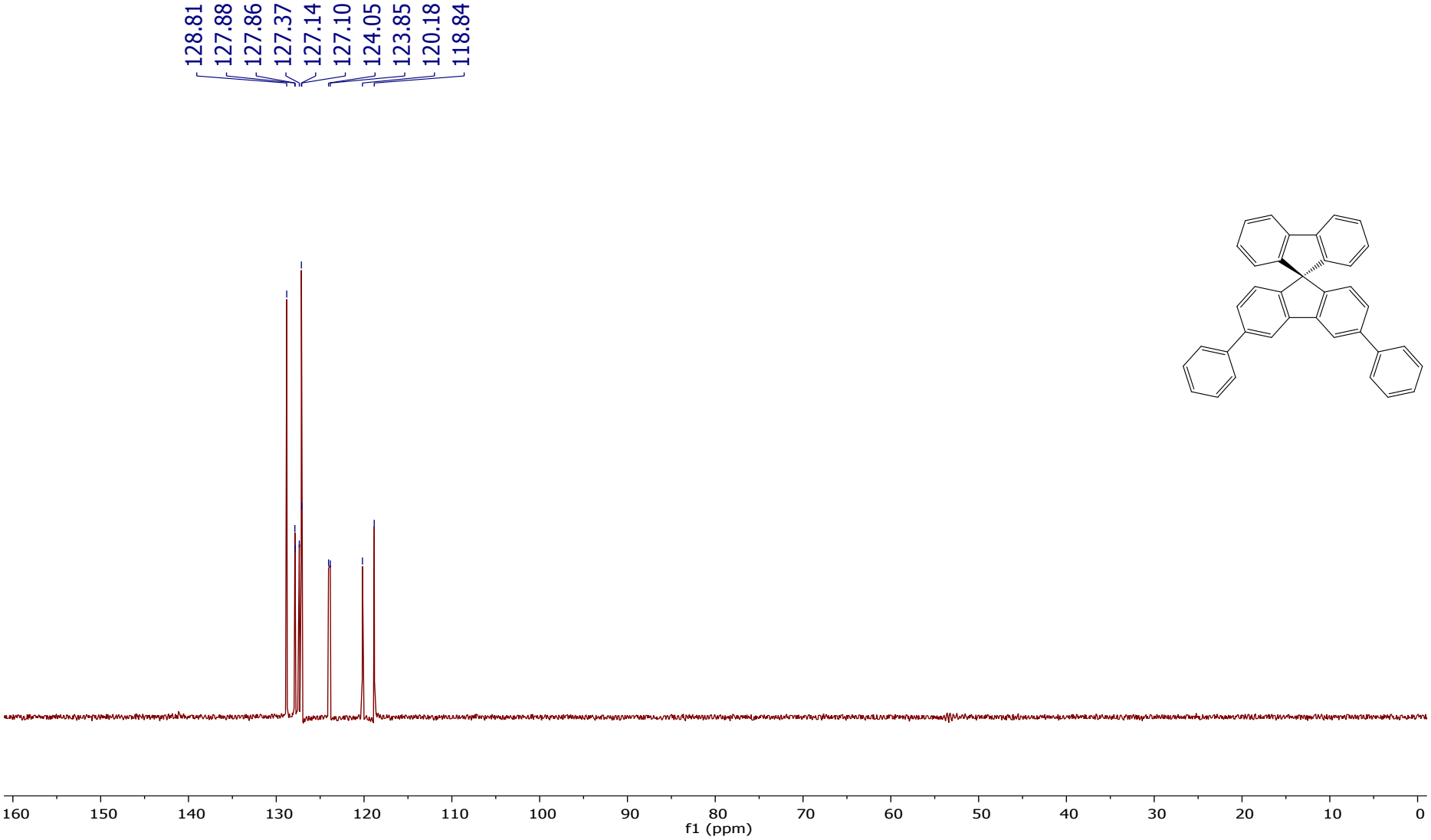
10.4 ***m*SPh$_2$ — $^1$H — $CD_2Cl_2$**



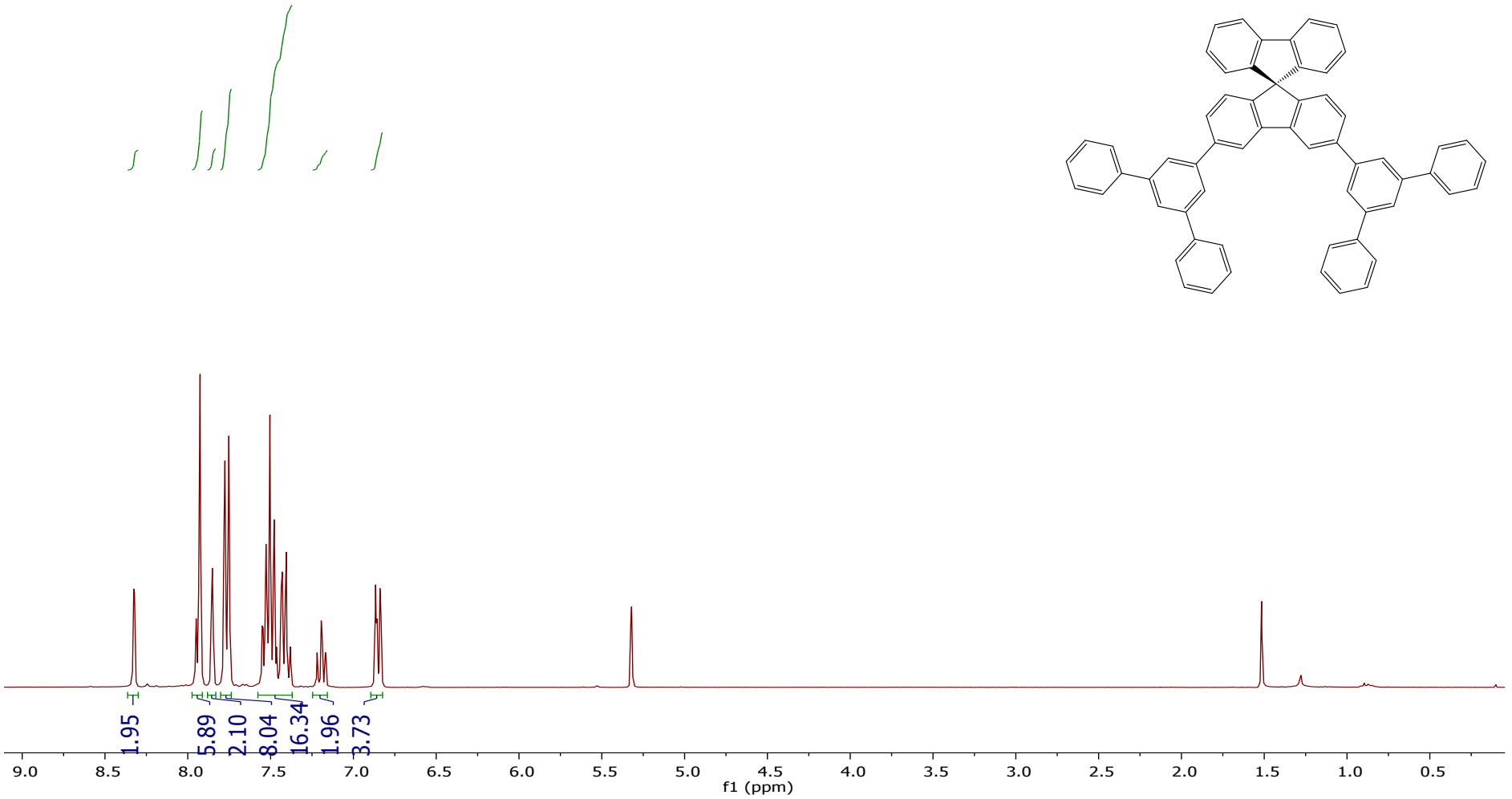
10.5 ***m*SPh$_2$ — $^{13}$C — $CD_2Cl_2$**



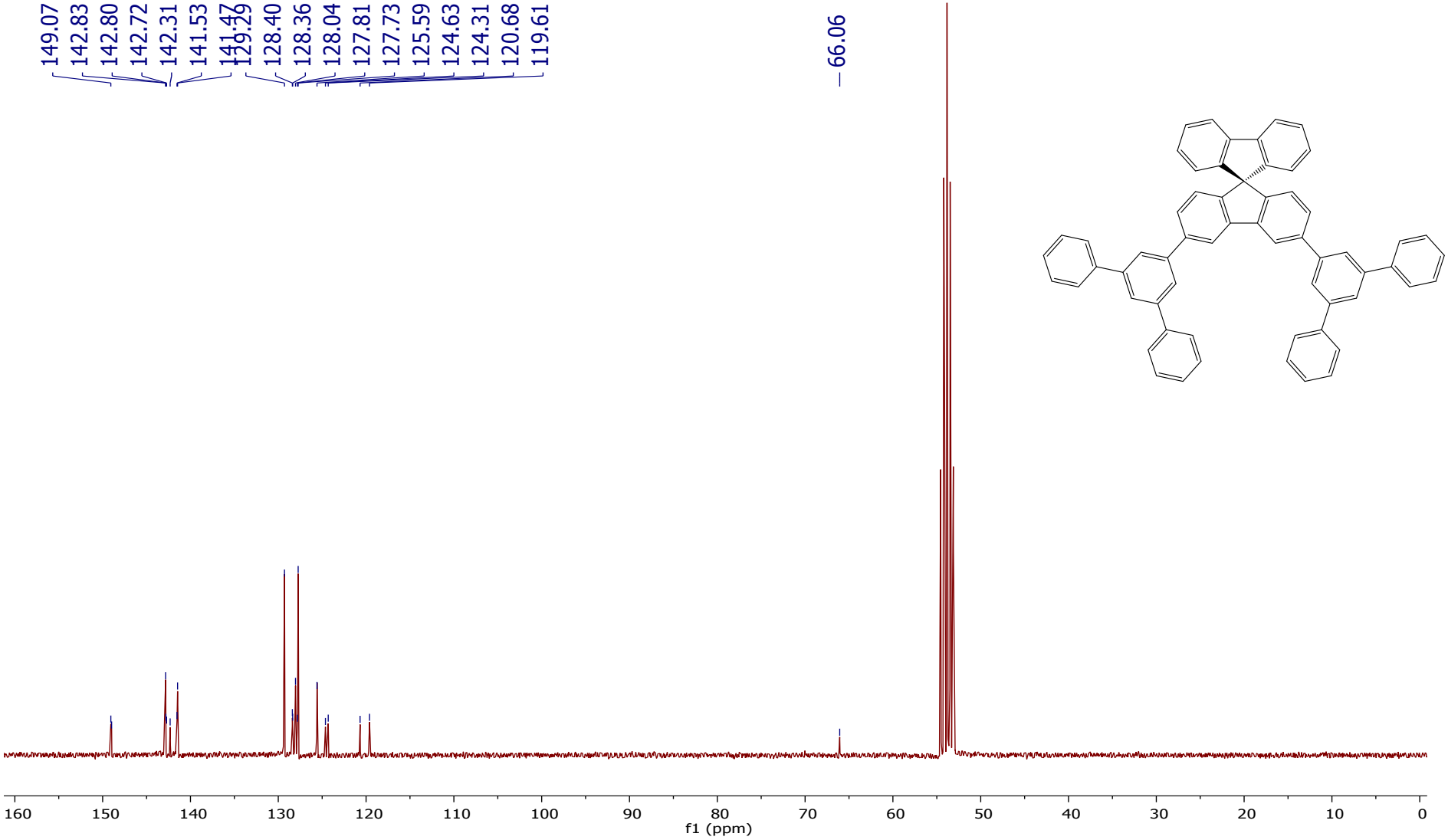
10.6 ***m*SPh$_2$ — $^{13}$C — DEPT135 — $CD_2Cl_2$**



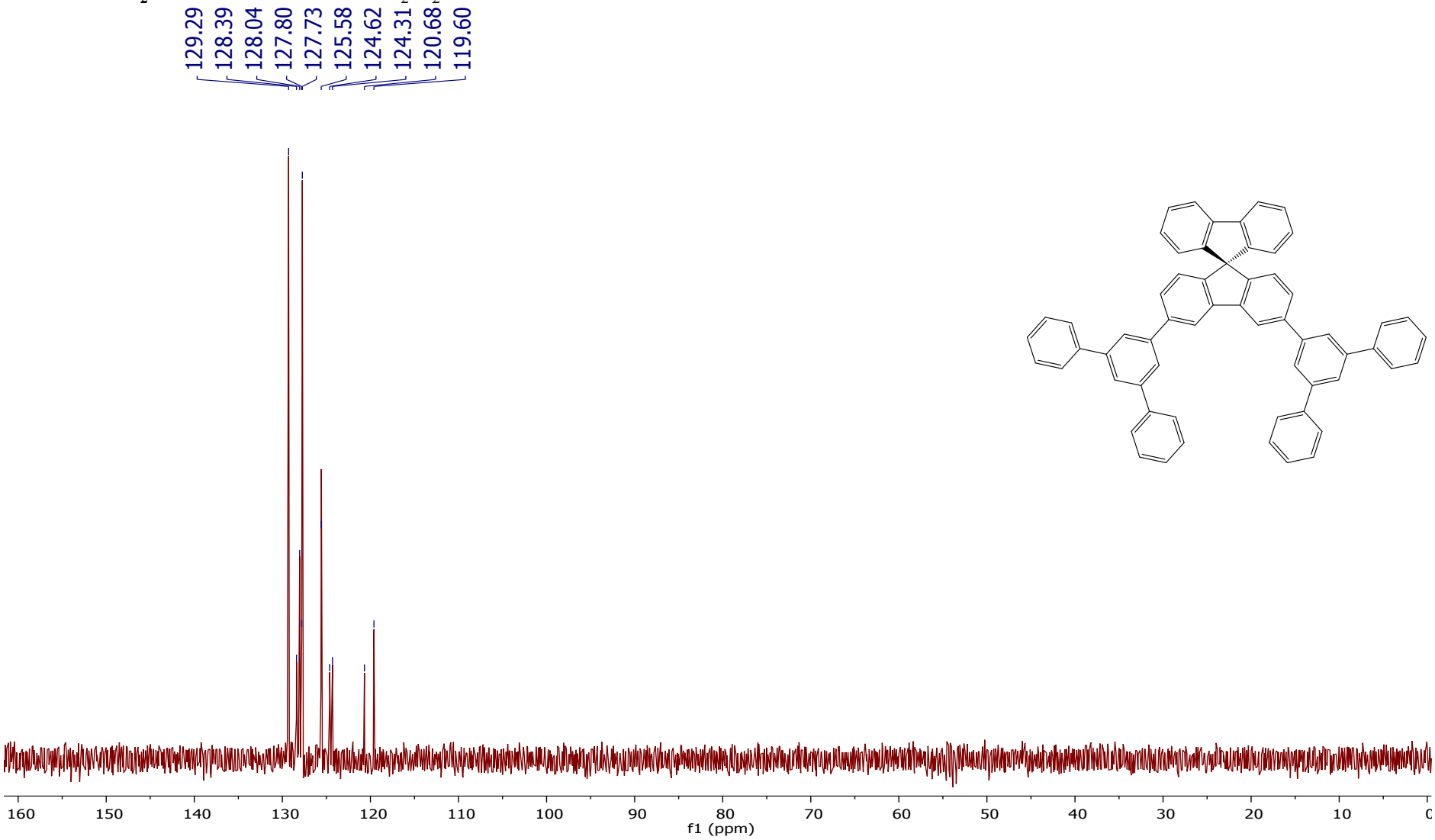
10.7 ***m*STPh$_2$ — $^1$H — $CD_2Cl_2$**



10.8 ***m*STPh$_2$ — $^{13}$C — $CD_2Cl_2$**



10.9 ***m*STPh$_2$ — $^{13}$C — DEPT135 — $CD_2Cl_2$**



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