Supplementary information

Screening of the Carbazole-based Phosphonic Acids in Perovskite Solar Cells: Impact of the Substitution Pattern on Device Performance

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Contents:

KPFM measurements

General methods

All chemicals required for the synthesis were purchased from Merck (Sigma-Aldrich) or Tokyo Chemical Industry Co., Ltd., and used without additional purification.

[2-(3,6-Dimethoxy-9*H*-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz), [2-(3,6-Dimethyl-9*H*-carbazol-9-yl)ethyl]phosphonic acid (Me-2PACz) were purchased from Tokyo Chemical Industry Co., Ltd. [2-(2,7-Dimethoxy-9*H*-carbazol-9-yl) ethyl]phosphonic acid (DC-PA, 2,7-MeO-2PACz) was purchased from Luminescence Technology Corp. (Lumtec). All materials were used without additional purification.

Thin-layer chromatography (TLC) and Column chromatography: reactions were monitored on ALUGRAM SIL G/UV254 TLC plates and visualized under UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography.

Elemental Analysis: C, H, and N elemental composition were determined using an o.

UV/Vis Spectroscopy

UV/Vis spectra of sample solutions (10^{-4} M in THF) and thin films were recorded using a Shimadzu UV-2600 spectrophotometer. The diffraction grating crack width was set at 2 nm with a scan rate of 2 nm/s. Wavelengths (λ) are reported in nm.

Photoluminescence Spectroscopy

Edinburg instruments FLS920 Spectrometer, Xenon900. Sample solutions (10^{-5} M in THF)

Ionization potential measurements

Ip was determined using a low-energy photoelectron spectrometer (AC-2S, Riken-Keiki). The samples were prepared by a drop-casting solution (1 mg/ml, EtOH) of the investigated materials on pre-cleaned glass substrates.

Thermogravimetric Analysis (TGA)

Thermal stability was assessed using TA Instruments Q50 TGA under nitrogen. Decomposition temperatures are reported at 5% weight loss, with a heating rate of 20 °C/min.

Name	**3,6-Ph-2PACz**	**2,7-Ph-2PACz**	**4-Ph-2PACz**	**3,6-MeO-2PACz**	**2,7-MeO-2PACz**	**4-MeO-2PACz**	**3,6-Me-2PACz**	**2,7-Me-2PACz**	**2PACz**
TGA [°C]	338	234	255	289	297	301	331	299	347

Table S1 Thermogravimetric analysis (TGA) data (heating rate of 10°C min^{1}, N_2 atmosphere).

Contact angle measurements

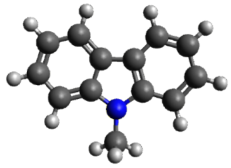
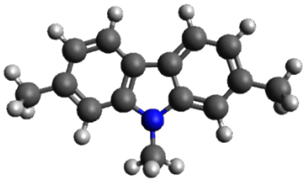
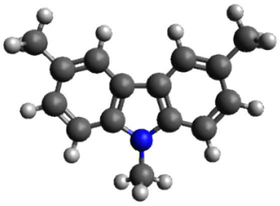
Contact angle (of water droplet) measurements were performed with optical goniometer (Ossila Contact Angle Goniometer). The values measured are given below:

Name	**3,6-Ph-2PACz**	**2,7-Ph-2PACz**	**4-Ph-2PACz**	**3,6-MeO-2PACz**	**2,7-MeO-2PACz**	**4-MeO-2PACz**	**3,6-Me-2PACz**	**2,7-Me-2PACz**	**2PACz**	**ITO**
Angle	72	74	80	70	69	76	72	74	72	54

Table S2. Contact angle values on ITO surface. Droplet volume 0.001 ml.

Theoretical DFT calculations

The DFT calculations for geometry optimization of compounds were performed using TURBOMOLE version 7.0 software,[1] with Becke's three parameter functional, B3LYP,[2], [3] and def2-SVP,[4], [5] basis set in vacuum.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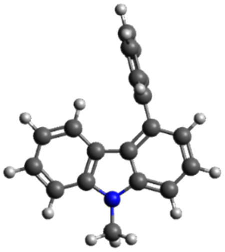	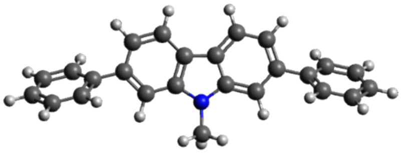	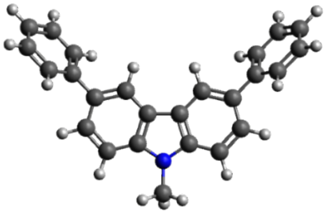
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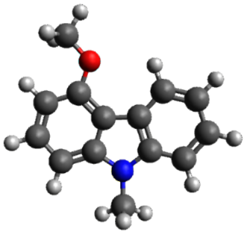	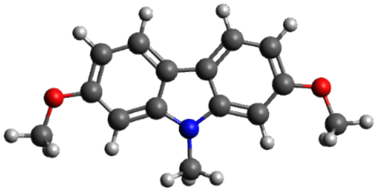	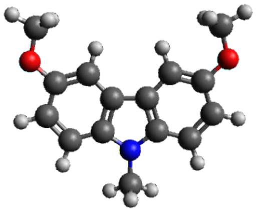
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	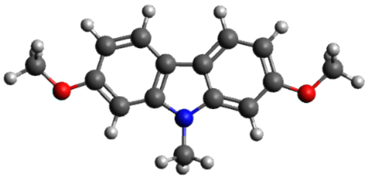	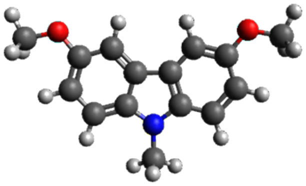
	0.25 D	0.19 D
	-784.788778	-784.785764

Table S3. Optimized molecular structures of chromophores (after ground state geometry optimization. Visualization by TMoleX). Dipoles, and energy values are given for each compound. For 2,7-MeO-2PACz and 3,6-MeO-2PACz the values of two rotamers with lowest energies are given, due to the rotation around C-O bond. Energy values reported in Hartrees.

Device fabrication

As substrates laser-patterned ITO on glass substrates were used with 6 independent ITO pixels confined by laser scribes (nominal ITO thickness of 150 nm, 15 Ω/sq sheet resistance, Automatic Research GmbH). The substrates were cleaned by ultra-sonication in H_2O with detergent (Hellmanex, 2%), H_2O, acetone, and IPA for 10 min each. For the hole transport layer (HTL), the PACz molecules described the text were dissolved in ethanol (1mmol/ml). The solution was then spin-coated in a nitrogen glovebox at 3000 rpm for 20 s and annealed at 100 °C for 10 min. All following spin-coating processes were also conducted in nitrogen gloveboxes. For the 1.4ᴍ triple-cation triple-halide (3Hal) perovskite ($Cs_{0.22}FA_{0.78}Pb(I_{0.85}Br_{0.15})_3$ + 5% $MAPbCl_3$) (1.68 eV) precursor, a $Cs_{0.22}FA_{0.78}Pb(Br_{0.15}\ I_{0.85})_3$ solution was prepared in a mixture of DMF and DMSO (volume ratio DMF:DMSO 3:1) and added to the $MAPbCl_3$ solids in a second step. The solution was spin-coated at 5000 rpm for 45 s, using 5 s acceleration and 250 µl anisole as antisolvent at 25 s from the beginning of the spin-coating process. The perovskite film was annealed at 100 °C for 20 min. Following the perovskite deposition 1 nm LiF and 16 nm C_{60} were deposited via thermal evaporation without breaking the vacuum. The SnO_x buffer layer was deposited by atomic layer deposition (ALD) in an Arradiance GEMStar reactor. Tetrakis(dimethylamino)tin(IV) (TDMASn) was used as the Sn precursor and was held at 60 °C in a stainless-steel container. Water was used as an oxidant, and was delivered from a stainless-steel container without active heating, whereas the precursor delivery manifold was heated to 115 °C. For the deposition at 80 °C, the TDMASn/purge/H_2O/purge times were 1 s/10 s/0.2 s/15 s with corresponding nitrogen flows of 30 sccm/90 sccm/90 sccm/90 sccm. With this 70, cycles lead 10 nm SnO_x, respectively. The 0.16 cm^2 active area was determined by the overlap between the area confined by the laser scribe and the 4 mm broad Ag stripes (100 nm thickness) that were thermally evaporated using shadow masks.

Current density-voltage measurement (J-V)

Current density-voltage (*J-V*) characteristics of perovskite single-junction solar cells were conducted in N_2 atmosphere and under 1-Sun AM1.5g equivalent illumination (1000 Wm^{-2}) from an Oriel LCS-100 class ABB sun simulator. The illumination intensity was calibrated to the J_{SC} of KG3 filtered silicon reference cell. For obtaining the *J-V* scans the voltage was swept in reverse (V_{OC} to J_{SC}) and forward direction (J_{SC} to V_{OC}) between 1.3 and -0.02 V in 0.02 V steps and with an integration time of 20 ms and settling time of 20 ms. The scans were recorded by a Keithley 2400 digital source measure unit, which was controlled by custom LabView software and using a two-wire arrangement. The devices were kept at a constant temperature of 25 °C.

trSPV measurements

Transient surface photovoltage (trSPV) measurements were carried out on an in-house-built setup. The samples were laser-excited with a tunable pumped pulse laser (Nd:YAG Laser, EKSPLA, NT230-50-SH/SF-SCU-2H). For the measurements in this work, an excitation energy of 1.7 eV and a pulse time of 3–6 ns at a frequency of 2 Hz were used. The laser fluence was controlled via neutral density filters and adjusted to yield charge carrier densities equivalent to 1 Sun. The transients were measured with an oscilloscope card (Gage, CSE 1622- 4GS, 200 MS s−1) using an in-house developed for logarithmic read-out.

KPFM measurements

For KPFM measurements glass/ITO/(SAM) samples were fabricated following the steps described above (device fabrication) The atomic force microscopy (AFM) measurements were conducted on a Park Systems NX12 AFM setup in air at room temperature. Contact potential difference (CPD) spatial maps were obtained using conductive cantilevers (PPP-EFM, Nanosensors)in a frequency modulated sideband KPFM mode.[6], [7] Work function (WF, ϕ) spatial maps were derived from CPD maps according to the formula $\phi = \phi_{\mathrm{tip}} - e{\cdot}\mathrm{CPD}$, where e is the elementary charge and ϕ_{tip} is the work function of the tip, measured using freshly cleaved highly oriented pyrolithic graphite (HOPG) as a reference sample. In these experiments, ϕ_{HOPG} was assumed to be 4.6 eV.[8] The work function values given in Table 1 are derived based on the median value from 3x3 μm CPD maps.

References:

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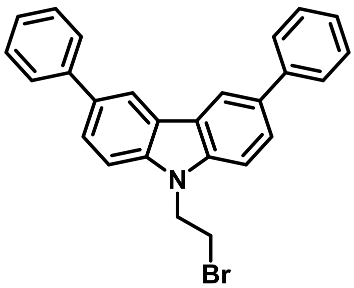
Synthesis of the compounds



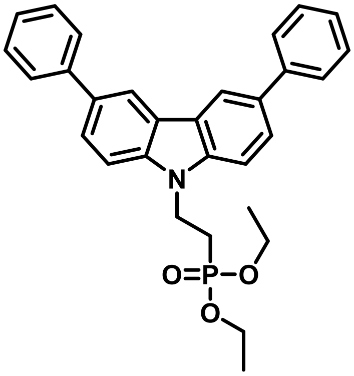
9-(2-bromoethyl)-3,6-diphenyl-9*H*-carbazole (1)

3,6-Diphenylcarbazole (1,24 g, 0.0039 mol) was dissolved in 1,2-Dibromoethane (10 ml, 0,1165 mol), and 50% KOH solution (10 ml) and Tetrabutylammonium bromide (0.037 g, 0.0001 mol) was added afterward. After 72 hours at 50 °C reaction was complete (TLC, acetone: n-hexane 1:4), the mixture was extracted with ethyl acetate, the organic layer was dried with anhydrous sodium sulfate, and the solvent was removed using a vacuum rotary evaporator. The product is purified by column chromatography (eluent, acetone: n-hexane 1:24) to yield 1.53 g (92% yield) of white powder.

Anal. Calcd. for $C_{26}H_{20}BrN$, %: C, 73.25; H, 4.73; N, 3.29, found, %: C, 73.36; H, 4.85; N, 3.38.

^{1}H NMR (400 MHz, DMSO) δ 8.64 (s, 2H), 7.91 – 7.66 (m, 8H), 7.49 (d, *J* = 7.5 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 2H), 4.91 (t, *J* = 6.2 Hz, 2H), 3.97 (t, *J* = 6.2 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 141.0, 140.0, 131.7, 128.9, 126.7, 126.6, 124.9, 123.2, 118.8, 110.2, 44.2, 31.5.



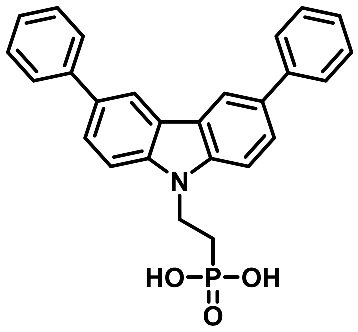
Diethyl (2-(3,6-diphenyl-9*H*-carbazol-9-yl)ethyl)phosphonate (2)

9-(2-bromoethyl)-3,6-diphenyl-9*H*-carbazole (1.5 g, 3.5 mmol, 1 eq) was dissolved in triethyl phosphite (5 ml, 8.24 eq) and refluxed for 20 h. After the reaction was finished (TLC acetone: n-hexane, 7:18) the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (eluent acetone: n-hexane, 1:4) to give 1.2 g (70%) of clear liquid.

Anal. Calcd. for $C_{30}H_{30}NO_3P$, %: C, 74.52; H, 6.25; N, 2.90, found, %: C, 74.04; H, 6.44; N, 2.95.

^{1}H NMR (400 MHz, DMSO) δ 8.64 (d, *J* = 1.8 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 6H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 4H), 7.34 (t, *J* = 7.3 Hz, 2H), 4.64 (dt, *J* = 14.0, 7.2 Hz, 2H), 3.93 (p, *J* = 7.3 Hz, 4H), 2.40 – 2.27 (m, 2H), 1.12 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, DMSO) δ 141.0, 139.6, 131.5, 128.9, 126.7, 126.5, 124.9, 123.2, 118.8, 109.9, 61.2 (d, *J* = 6.2 Hz), 36.9, 24.8 (d, *J* = 136.4 Hz), 16.1 (d, *J* = 6.2 Hz).



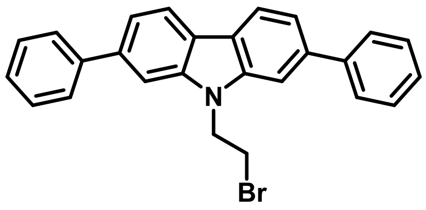
(2-(3,6-diphenyl-9*H*-carbazol-9-yl)ethyl)phosphonic acid (3; 3,6-Ph-2PACz)

Diethyl (2-(3,6-diphenyl-9*H*-carbazol-9-yl)ethyl)phosphonate (0.78 g, 1.61 mmol, 1 eq) was dissolved in anhydrous 1,4-dioxane (5.5 ml, 40 eq) and bromotrimethylsilane (2.34 ml, 17.74 mmol, 11 eq) was added dropwise. The reaction was stirred for 20 h at 25 °C under an argon atmosphere. Afterward, methanol (4 ml) was added, and stirring continued for 3h. Finally, distilled water was added dropwise (10 ml), until the solution became opaque, and it was left in a fridge overnight. The product was filtered off and washed with n-hexane, to yield 0.50 g (72 %) of white powder.

Anal. Calcd. for $C_{26}H_{22}NO_3P$, %:C, 73.06; H, 5.19; N, 3.28, found, %: C, 72.89; H, 5.47; N, 3.16.

^{1}H NMR (400 MHz, DMSO) δ 8.65 (d, *J* = 1.9 Hz, 2H), 7.86 – 7.78 (m, 6H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 2H), 4.62 (q, *J* = 7.9 Hz, 2H), 2.17 – 2.04 (m, 2H).

^{13}C NMR (101 MHz, DMSO) δ 141.0, 139.5, 131.5, 128.9, 126.7, 126.6, 125.0, 123.3, 118.9, 109.6, 37.7.



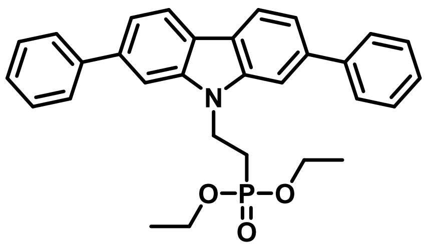
9-(2-bromoethyl)-2,7-diphenyl-9*H*-carbazole (4)

2,7-diphenyl-9*H*-carbazole (0.6 g, 1.9 mmol) was dissolved in 1,2-dibromoethane (4.8 ml, 56.4 mmol), and tetrabutylammonium bromide (0.012 g, 0.02 mmol) with 50% KOH aqueous solution (5 ml) were added subsequently. The reaction was stirred at 70°C for 6 h (TLC, acetone: n-hexane, 4:21, v:v). After completion of the reaction, extraction was done with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was distilled off under reduced pressure. The crude product was purified with column chromatography to yield 0.62 g (77 %) of white powder.

Anal. Calcd. for $C_{26}H_{20}BrN$, %: C, 73.25; H, 4.73; N, 3.29, found, %: C, 73.34; H, 4.81; N, 3.32

^{1}H NMR (400 MHz, DMSO) δ 8.23 (d, *J* = 8.1 Hz, 2H), 7.96 (s, 2H), 7.88 – 7.82 (m, 4H), 7.57 – 7.47 (m, 6H), 7.39 (t, *J* = 7.4 Hz, 2H), 5.02 (t, *J* = 6.3 Hz, 2H), 4.01 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 141.2, 141.1, 138.2, 128.9, 127.3, 127.2, 121.4, 120.7, 118.6, 107.9, 43.8, 31.7.



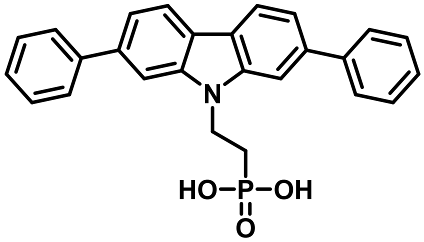
Diethyl (2-(2,7-diphenyl-9*H*-carbazol-9-yl)ethyl)phosphonate (5)

9-(2-bromoethyl)-2,7-diphenyl-9*H*-carbazole 2,7PhCz (0.42 g, 0.9 mmol, 1 eq) was dissolved in triethyl phosphite (6 ml, 80 eq) and heated at reflux for 20 h. When reaction was finished (TLC acetone: n-hexane 7:18 v:v) the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (acetone: n-hexane, 1:4, v:v) to yield 0.40 g (83%) of clear liquid.

Anal. Calcd. for $C_{30}H_{30}NO_3P$, %: C, 74.52; H, 6.25; N, 2.90, found C, 74.14; H, 6.45; N, 2.98

^{1}H NMR (400 MHz, DMSO) δ 8.22 (d, *J* = 1.7 Hz, 2H), 7.90 – 7.81 (m, 6H), 7.52 (t, 6H), 7.39 (t, *J* = 7.4 Hz, 2H), 4.75 (dt, *J* = 14.5, 7.0 Hz, 2H), 3.87 (p, *J* = 7.2 Hz, 4H), 2.39 (dt, *J* = 18.0, 6.9 Hz, 2H), 1.03 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, DMSO) δ 141.2, 140.8, 138.1, 128.9, 127.2, 121.4, 120.8, 118.4, 107.7, 61.1 (d, *J* = 6.2 Hz), 36.5, 24.3 (d, *J* = 136.4 Hz), 15.9 (d, *J* = 6.2 Hz).



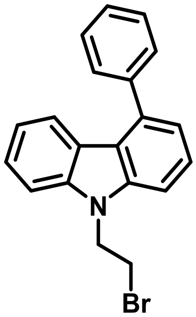
(2-(2,7-diphenyl-9*H*-carbazol-9-yl)ethyl)phosphonic acid (6; 2,7-Ph-2PACz)

diethyl (2-(2,7-diphenyl-9*H*-carbazol-9-yl)ethyl)phosphonate (0.31 g, 0.64 mmol, 1 eq) was dissolved in anhydrous 1,4-dioxane (2.7 ml, 50 eq) and bromotrimethylsilane (0.93 ml, 7.06 mmol, 11 eq) was added dropwise. The reaction was stirred for 20 h at 25 °C under an argon atmosphere. Afterward, methanol (1 ml) was added, and stirring continued for 3h. Finally, distilled water was added dropwise (10 ml), until the solution became opaque, and it was left in a fridge overnight. The product was filtered off and washed with n-hexane, to yield 0.23 g (83 %) of white powder.

Anal Calcd. for: $C_{26}H_{22}NO_3P$, %: C, 73.06; H, 5.19; N, 3.28, found, %: C, 72.82; H, 5.34; N, 3.15.

^{1}H NMR (400 MHz, DMSO) δ 8.23 (d, *J* = 8.6 Hz, 2H), 7.89 – 7.80 (m, 6H), 7.56 – 7.47 (m, 6H), 7.39 (t, *J* = 7.3 Hz, 2H), 4.70 (q, *J* = 8.1 Hz, 2H), 2.14 (dt, *J* = 17.1, 7.9 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 141.1, 140.7, 138.3, 128.9, 127.3, 127.2, 121.5, 120.9, 118.4, 107.3, 40.2, 37.3, 27.4 (d, *J* = 130.6 Hz).



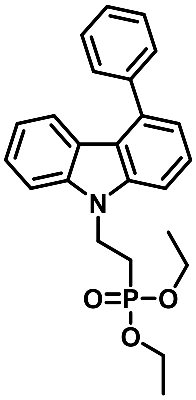
9-(2-bromoethyl)-4-phenyl-9*H*-carbazole (7)

4-Phenyl-9*H*-carbazole (0,6 g, 0.0025 mol, 1eq) was dissolved in 1,2-Dibromoethane (4.9 ml, 0.0567 mol 23 eq). After, 50% KOH solution (7 ml) and Tetrabutylammonium bromide (16 mg, 0.04 mmol, 0.02 eq) were added to the reaction mixture. After 72 hours at 50 °C reaction was complete (TLC in acetone: hexane v:v 1:4), the mixture was extracted with ethyl acetate, the organic layer was dried with anhydrous sodium sulfate, and the solvent was removed using a vacuum rotary evaporator. The product is purified by column chromatography (eluent, acetone: n-hexane 1:24) to yield 0.735 g, (85%) white powder.

Anal. Calcd. for $C_{20}H_{16}BrN$, %: C, 68.58; H, 4.60; N, 4.00, found, %: C, 68.68; H, 4.74; N, 4.12.

^{1}H NMR (400 MHz, DMSO) δ 7.69 (t, *J* = 9.0 Hz, 2H), 7.60 – 7.48 (m, 6H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 4.90 (t, *J* = 6.4 Hz, 2H), 3.94 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 140.7, 140.3, 140.2, 137.0, 128.9, 128.6, 127.7, 125.6, 121.7, 121.4, 120.6, 119.4, 118.8, 109.7, 108.8, 31.2, 25.1.



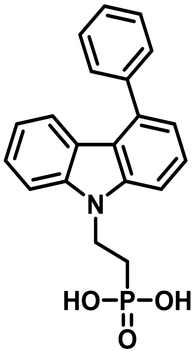
diethyl (2-(4-phenyl-9*H*-carbazol-9-yl)ethyl)phosphonate (8)

9-(2-bromoethyl)-4-phenyl-9*H*-carbazole (0.7 g, 1.9 mmol, 1 eq) was dissolved in triethyl phosphite (5.15 ml, 16 eq) and heated at reflux for 20 h. When the reaction was finished (TLC acetone: n-hexane 7:18 v:v) the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (acetone: n-hexane, 1:4, v:v) to give 0.8 g (98%) of clear liquid.

Anal. Calcd. for $C_{24}H_{26}NO_3P$, %: C, 70.75; H, 6.43; N, 3.44, found, %: C, 70.59; H, 6.61; N, 3.53.

^{1}H NMR (400 MHz, DMSO) δ 7.69 (t, *J* = 9.0 Hz, 2H), 7.60 – 7.48 (m, 6H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 4.90 (t, *J* = 6.4 Hz, 2H), 3.94 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 140.8, 139.8, 139.7, 137.2, 128.9, 128.7, 127.8, 125.8, 121.3, 121.2, 120.4, 119.4, 118.6, 109.1, 108.4, 61.0 (d, *J* = 6.2 Hz), 37.5, 25.8 (d, *J* = 134.6 Hz), 16.0 (d, *J* = 6.2 Hz).



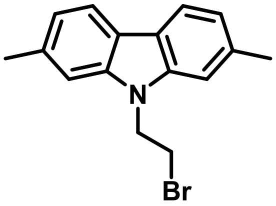
(2-(4-phenyl-9*H*-carbazol-9-yl)ethyl)phosphonic acid (9; 4-Ph-2PACz)

diethyl (2-(4-phenyl-9*H*-carbazol-9-yl)ethyl)phosphonate (0.78 g, 1.91 mmol) was dissolved in anhydrous 1,4-dioxane (6.5 ml, 76.5 mmol) and bromotrimethylsilane (2.78 ml, 21 mmol) was added dropwise. The reaction was stirred for 22 h at 25 °C under an argon atmosphere. Afterward, methanol (5 ml) was added, and stirring continued for 6h. Finally, distilled water was added dropwise (10 ml), until the solution became opaque, and it was stirred overnight. The product was filtered off, washed with water, dissolved in tetrahydrofuran (1 ml), and precipitated into n-hexane (12 ml). The product was filtered off and washed with n-hexane, to give 0.54 g (80 %) of white powder.

Anal. Calcd. for $C_{20}H_{18}NO_3P$, %: C, 68.37; H, 5.16; N, 3.99 found, %: C, 67.98; H, 5.38; N, 3.65.

^{1}H NMR (400 MHz, DMSO) δ 7.55 (h, *J* = 7.9 Hz, 8H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 4.60 (q, *J* = 7.3 Hz, 2H), 2.07 (dt, *J* = 17.2, 8.1 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 140.7, 139.8, 139.7, 137.1, 128.8, 128.6, 127.7, 125.8, 121.7, 121.5, 120.5, 119.4, 118.6, 109.0, 108.1, 37.5, 27.3 (d, *J* = 130.9 Hz)



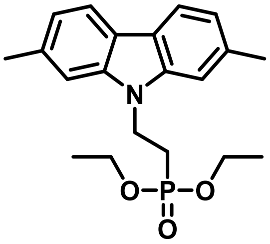
9-(2-bromoethyl)-2,7-dimethyl-9*H*-carbazole (10)

3-Bromo-9-(4-bromophenyl)-9*H*-carbazole (0.78 g, 0.0019 mol) was dissolved in 1,2-Dibromoethane (8 ml). After, 50% KOH solution (10 ml) and Tetrabutylammonium bromide (0.124 g, 0.0004 mol) were added to the reaction mixture. After 48 hours at 65 °C reaction was complete (TLC, acetone: n-hexane 1:4), the mixture was extracted with ethyl acetate, the organic layer was dried with anhydrous sodium sulfate, and the solvent was removed using a vacuum rotary evaporator. The product is purified by column chromatography (eluent, acetone: n-hexane 1:24) to yield 0.536 g (92%) white powder.

Anal. Calcd. for: $C_{16}H_{16}BrN$, %: C, 63.59; H, 5.34; N, 4.63, found % C, 63.68; H, 5.46; N, 4.78

^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.43 (s, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 4.75 (t, *J* = 6.5 Hz, 2H), 3.88 (t, *J* = 6.5 Hz, 2H), 2.50 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 140.3, 134.8, 120.5, 120.1, 119.6, 109.5, 43.8, 31.0, 21.8.



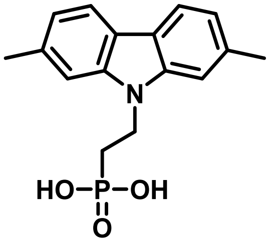
Diethyl (2-(2,7-dimethyl-9*H*-carbazol-9-yl)ethyl)phosphonate (11)

9-(2-bromoethyl)-2,7-dimethyl-9*H*-carbazole (0.5 g, 0.002 mol) was dissolved in triethyl phosphite (5.1 ml, 0.066 mol) and refluxed for 20 h. After the reaction was finished (TLC acetone: n-hexane, 7:18) the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (eluent acetone: n-hexane, 4:21) to give 0,58 g (98%) of clear liquid.

Anal.Calcd. for $C_{20}H_{26}NO_3P$, %: C, 66.84; H, 7.29; N, 3.90 found, %: C, 66.65; H, 7.36; N, 4.06.

^{1}H NMR (400 MHz, DMSO) δ 7.94 (d, J = 7.9 Hz, 2H), 7.32 (s, 2H), 7.00 (d, J = 7.9 Hz, 2H), 4.50 (dt, J = 12.3, 7.4 Hz, 2H), 3.94 (p, J = 7.2 Hz, 4H), 2.51 (s, 6H), 2.25 (dt, J = 18.0, 7.3 Hz, 2H), 1.14 (dd, J = 7.9, 6.4 Hz, 6H).

^{13}C NMR (101 MHz, DMSO) δ 139.9, 134.7, 120.3, 120.2, 119.7, 109.2, 61.2 (d, *J* = 6.2 Hz), 36.4 (d, *J* = 2.4 Hz), 24.3 (d, *J* = 135.7 Hz), 21.8, 16.1 (d, *J* = 6.1 Hz).



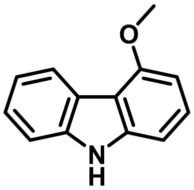
(2-(2,7-dimethyl-9*H*-carbazol-9-yl)ethyl)phosphonic acid (12; 2,7-Me-2PACz)

diethyl (2-(2,7-dimethyl-9*H*-carbazol-9-yl)ethyl)phosphonate (0.4 g, 0.001 mol) was dissolved in 1,4-Dioxane (3.8 ml, 0.445 mol) Then, C (1.6 ml, 0.0123 mol) was added dropwise, and stirring was continued at room temperature for 21 hours. After the reaction was completed (TLC analysis was performed using acetone: hexane v:v 20:5) methanol (2 ml, 0.049 mol) was added to the reaction mixture and left for another 3 hours. The resulting solution was then removed using a rotary evaporator, and the product was solidified by adding distilled water dropwise to the reaction mixture to give 0.28 g (83%) of white power.

Anal. Calcd. for $C_{16}H_{18}NO_3P$, %: C, 63.36; H, 5.98; N, 4.62, found, %: C, 63.04; H, 6.12; N, 4.46.

^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.30 (s, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 4.53 – 4.43 (m, 2H), 2.50 (s, 6H), 2.03 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 139.9, 134.9, 120.4, 120.2, 119.8, 108.9, 37.3, 27.3 (d, *J* = 130.2 Hz), 21.9.



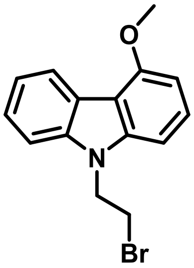
4-Methoxy-9*H*-carbazole (13)

4-hydroxycarbazole (1.5 g, 1 eq) was dissolved in ethyl acetate (6.5 ml, 10 eq). Afterward, Tetrabutylammonium hydrogen sulfate (0.027g, 0.08 mmol, 0.01 eq), methyl iodide (1.74 g., 12.3 mmol, 1.5 eq), and potassium carbonate (1.35g, 9.8 mmol, 1.2 eq) were added. The resulting suspension was refluxed for 16h.), the mixture was extracted with ethyl acetate, the organic layer was dried with anhydrous sodium sulfate, and the solvent was removed using a vacuum rotary evaporator. The product is purified by column chromatography (eluent acetone: n-hexane 3:22 v:v) to give 0.82 g (51%) white material.

Anal. Calcd. for: $C_{13}H_{11}NO$, %: C, 79.17; H, 5.62; N, 7.10, found C, 79.22; H, 5.74; N, 7.23

^1H NMR (400 MHz, DMSO) δ 11.27 (s, 1H), 8.16 (d, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 5.8 Hz, 1H), 7.33 (dt, *J* = 11.8, 7.6 Hz, 2H), 7.21 – 7.06 (m, 2H), 6.70 (t, *J* = 5.2 Hz, 1H), 4.06 – 3.98 (m, 3H).

^{13}C NMR (101 MHz, DMSO) δ 155.4, 140.8, 138.7, 126.3, 124.3, 122.0, 121.5, 118.4, 111.2, 110.2, 103.7, 99.5, 55.1.



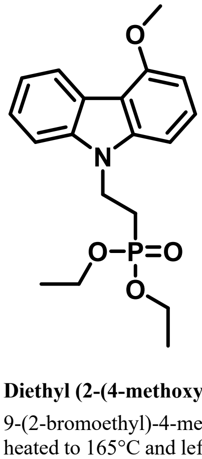
9-(2-bromoethyl)-4-methoxy-9*H*-carbazole (14)

4-methoxy-9*H*-carbazole (0.77 g, 0.0039 mol) was dissolved in 1,2-Dibromoethane (8 ml). After, 50% KOH solution (8 ml) and Tetrabutylammonium bromide (16,9 ml, 0,1954 mol) were added to the reaction mixture. After 24 hours at 60 °C reaction was complete (TLC, acetone: *n*-hexane 1:3), the mixture was extracted with ethyl acetate, the organic layer was dried with anhydrous sodium sulfate, and the solvent was removed using a vacuum rotary evaporator. The product is purified by column chromatography (eluent, acetone: n-hexane 1:12) to yield 0.6 g (50%) white powder.

Anal. Calcd. for $C_{15}H_{14}BrNO$, %: C, 59.23; H, 4.64; N, 4.60, found C, 53.78; H, 4.75; N, 4.70

^1H NMR (400 MHz, DMSO) δ 8.18 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.28 – 7.16 (m, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 4.82 (t, *J* = 6.3 Hz, 2H), 4.03 (s, 3H), 3.89 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 155.7, 141.3, 139.1, 126.8, 124.8, 122.4, 121.5, 119.3, 111.0, 109.2, 102.5, 100.6, 55.5, 44.1, 31.2.



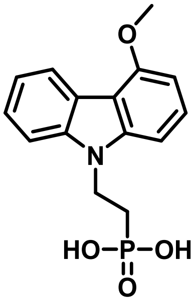
Diethyl (2-(4-methoxy-9*H*-carbazol-9-yl)ethyl)phosphonate (15)

9-(2-bromoethyl)-4-methoxy-9*H*-carbazole (0.58 g, 0.002 mol) was dissolved in triethyl phosphite (5.2 ml, 0.030 mol). The reaction mixture was heated to 165°C and left overnight. After 20 hours when the reaction was completed (TLC acetone: *n*-hexane v:v 7:18), the solvent was evaporated. The crude solution was purified using column chromatography (eluent: acetone: *n*-hexane v:v 4:21) to yield 0.68 g (98 %) of clear liquid.

Anal. Calcd. for $C_{19}H_{24}NO_4P$, %: C, 63.15; H, 6.69; N, 3.88, found, %: C, 62.89; H, 6.74; N, 3.99

^{1}H NMR (400 MHz, DMSO) δ 8.17 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.13 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.55 (dt, *J* = 12.6, 7.3 Hz, 2H), 4.02 (s, 3H), 3.91 (dq, *J* = 14.6, 7.1 Hz, 4H), 2.26 (dt, *J* = 18.0, 7.3 Hz, 2H), 1.11 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, DMSO) δ 155.7, 140.9, 138.7, 126.8, 124.8, 122.4, 121.6, 119.2, 111.1, 108.8, 102.1, 100.6, 61.2 (d, *J* = 6,2 Hz) , 55.5, 36.8 (d, *J* = 2,6 Hz), 24.3 (d, *J* = 136.1 Hz), 16.1 (d, *J* = 6,2 Hz).



(2-(4-methoxy-9*H*-carbazol-9-yl)ethyl)phosphonic acid (16; 4-MeO-2PACz)

Diethyl (2-(4-methoxy-9*H*-carbazol-9-yl)ethyl)phosphonate (0.58 g, 1,6 mmol) was dissolved in anhydrous 1,4-dioxane (5,5 ml, 0.064 mol) and bromotrimethylsilane (3,13 ml, 0.023 mol) was added dropwise. The reaction was stirred for 20 h at 25 °C under an argon atmosphere. Afterward, methanol (4 ml) was added, and stirring continued for 3h. Finally, distilled water was added dropwise (10 ml), until the solution became opaque, and it was left in a fridge overnight. The product was filtered off and washed with n-hexane, to yield 0.37 g (75%) of white power.

Anal. Calcd. for $C_{15}H_{16}NO_4P$, %: C, 59.02; H, 5.28; N, 4.59, found, %: C, 58.82; H, 5.59; N, 4.48

^{1}H NMR (400 MHz, DMSO) δ 8.18 (s, 1H), 7.54 – 7.48 (m, 1H), 7.40 (q, *J* = 7.9 Hz, 2H), 7.23 – 7.10 (m, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.58 – 4.47 (m, 2H), 4.02 (s, 3H), 2.07 – 1.94 (m, 2H).

^{13}C NMR (101 MHz, DMSO) δ 155.8, 140.8, 138.6, 126.9, 124.9, 122.5, 121.6, 119.1, 111.1, 108.5, 101.8, 100.5, 55.5, 37.7, 27.5 (d, *J* = 130.2 Hz).

NMR Spectroscopy:

^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 101 MHz using a Bruker Avance III spectrometer at 25 °C. Chemical shifts (δ) are calibrated and are reported relative to the residual solvent peak (2.50 for DMSO-d6) Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. 13C NMR spectra were measured with a Bruker 400 (at 101 MHz), and are reported relative to the residual solvent peak (39.5 for DMSO-d6). Data for ^{13}C NMR spectra is reported in terms of chemical shift (δ ppm) and expressed in ppm relative to tetramethylsilane (TMS).

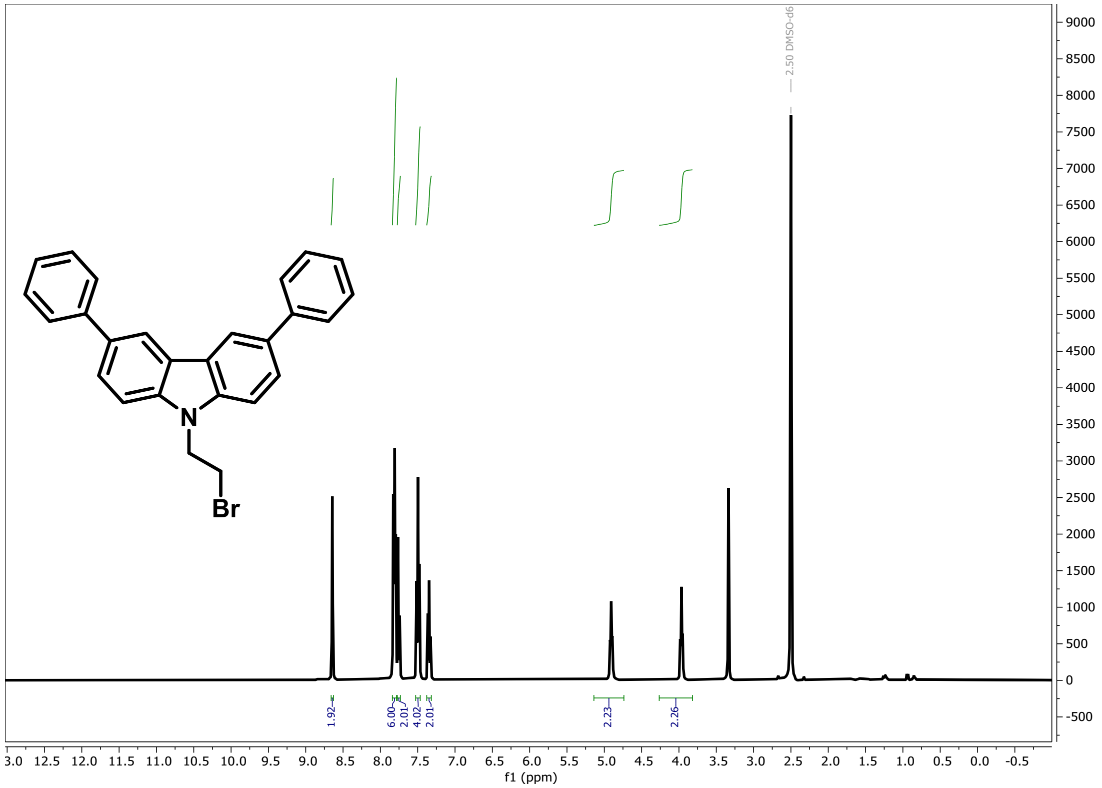


Fig. S1. ^{1}H NMR (400 MHz, DMSO-d6) of compound 1

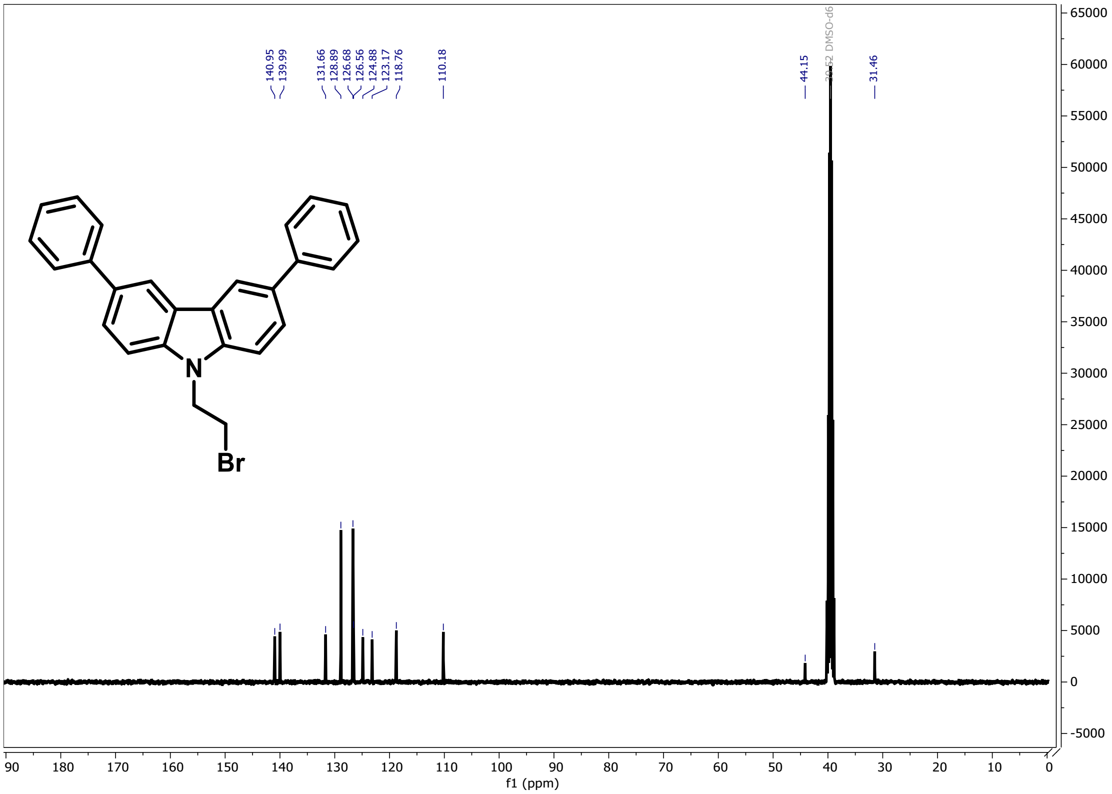


Fig. S2. ^{13}C NMR (101 MHz, DMSO-d6) of compound 1

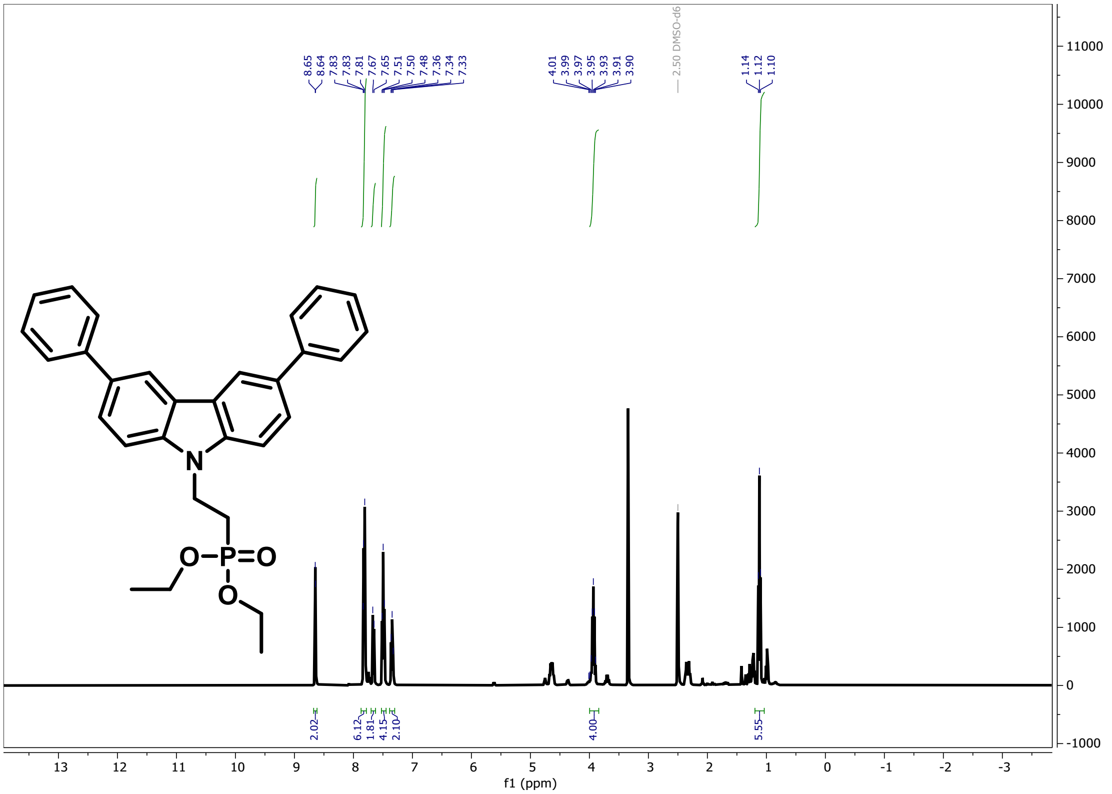


Fig. S3. ^{1}H NMR (400 MHz, DMSO-d6) of compound 2

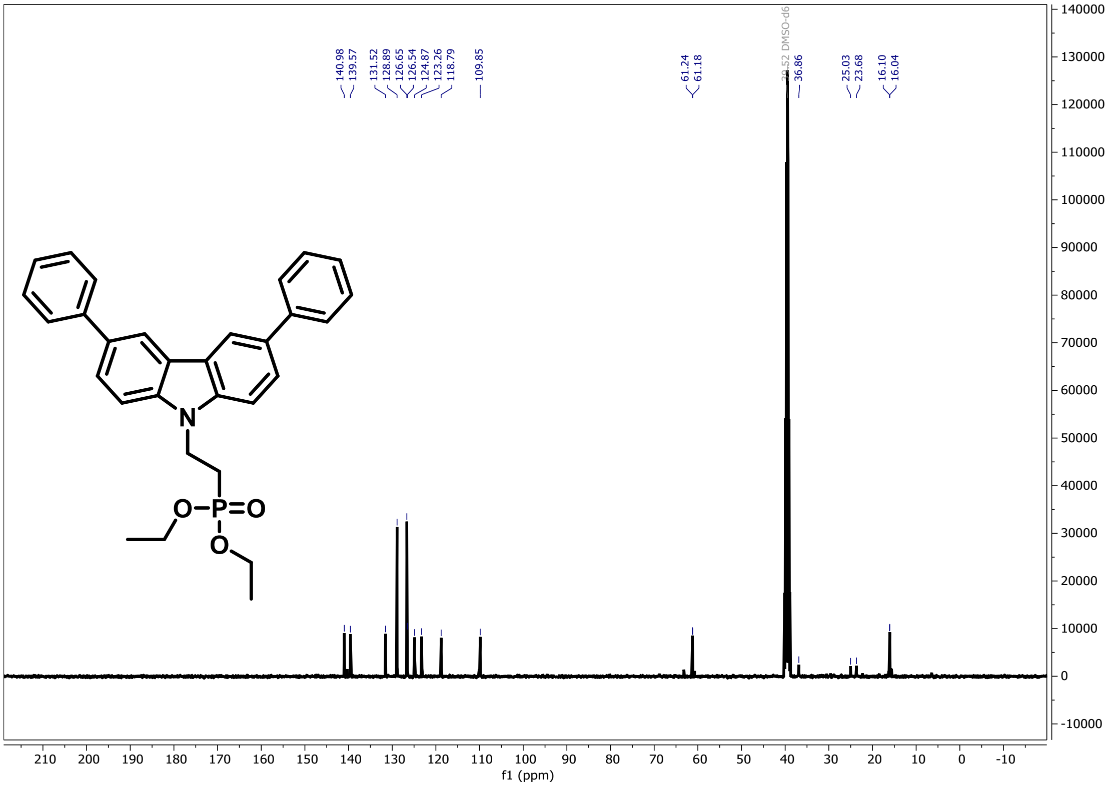


Fig. S4. ^{13}C NMR (101 MHz, DMSO-d6) of compound 2

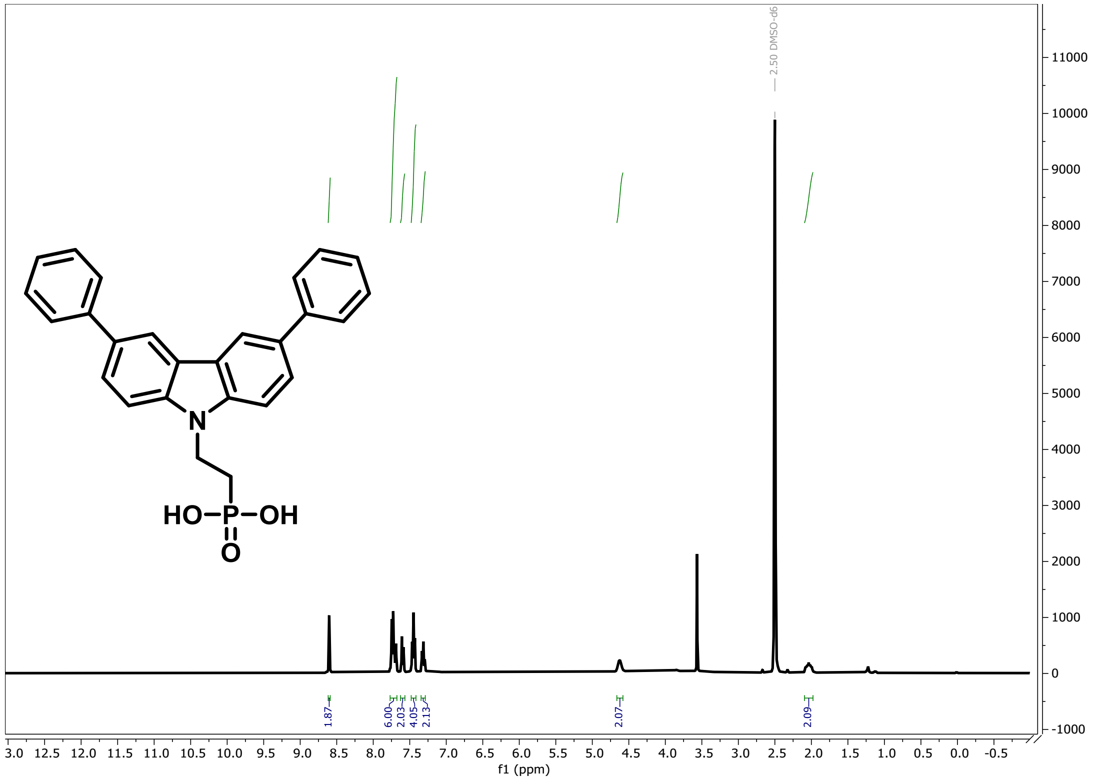


Fig. S5. ^{1}H NMR (400 MHz, DMSO-d6) of compound 3

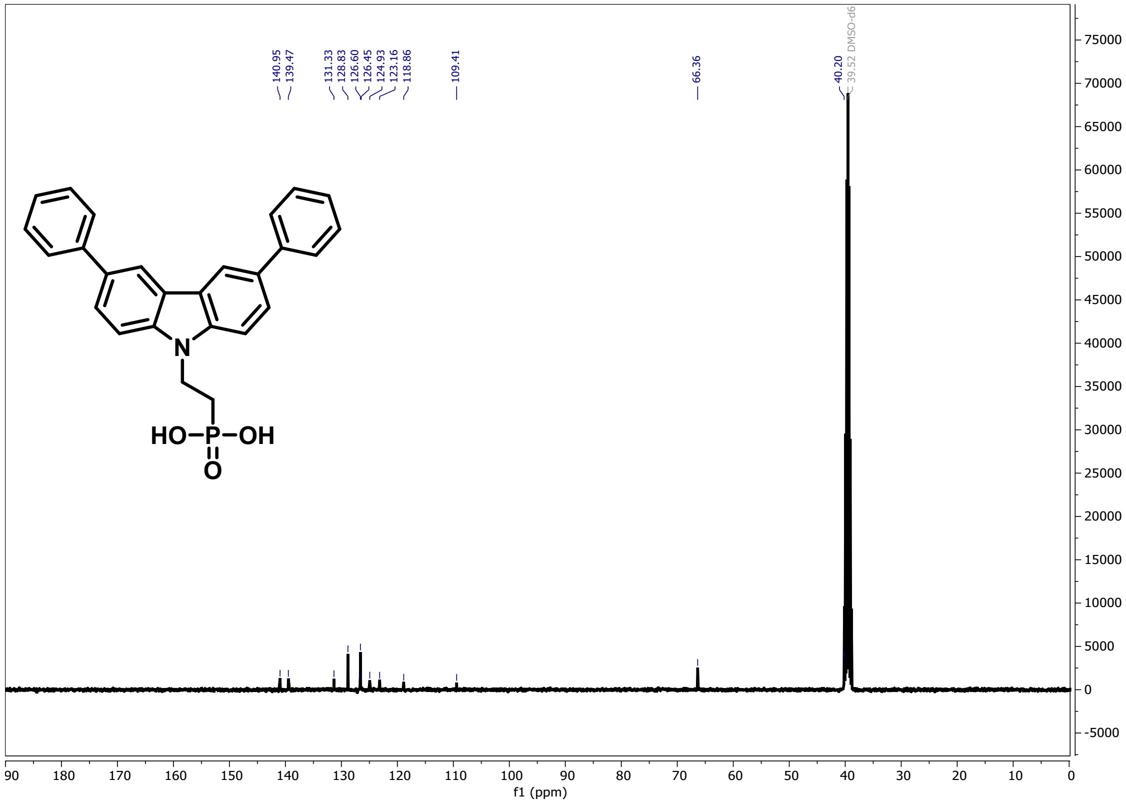


Fig. S6. ^{13}C NMR (101 MHz, DMSO-d6) of compound 3

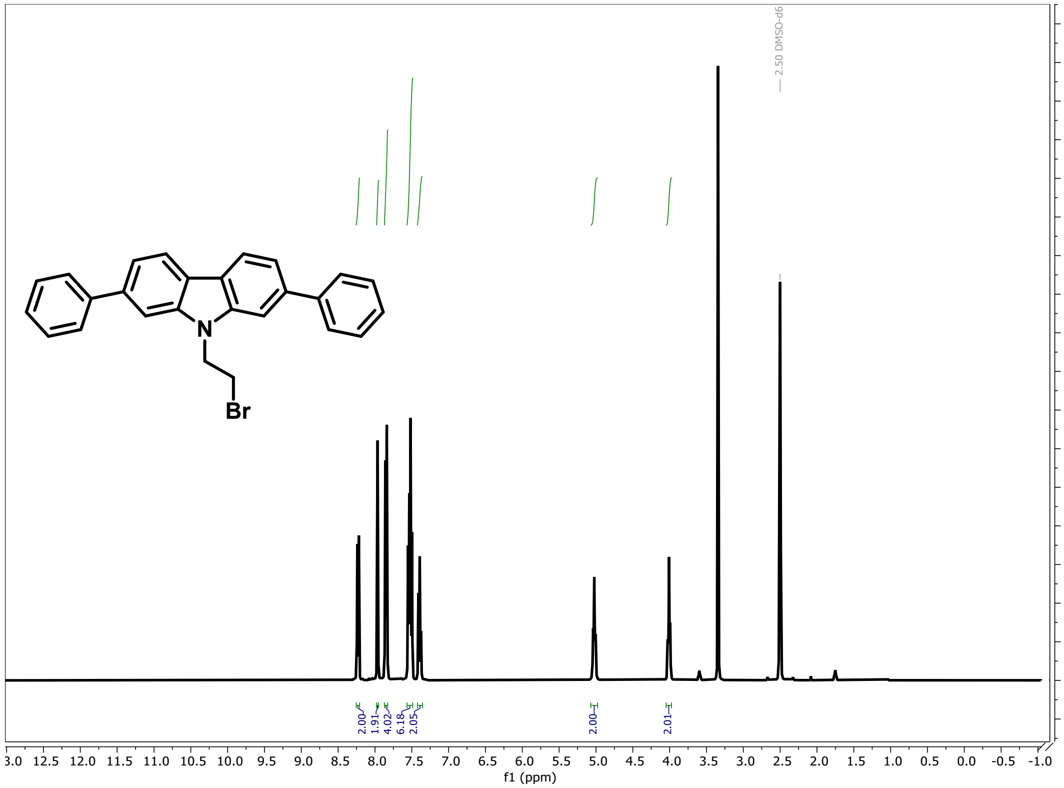


Fig. S7. ^{1}H NMR (400 MHz, DMSO-d6) of compound 4

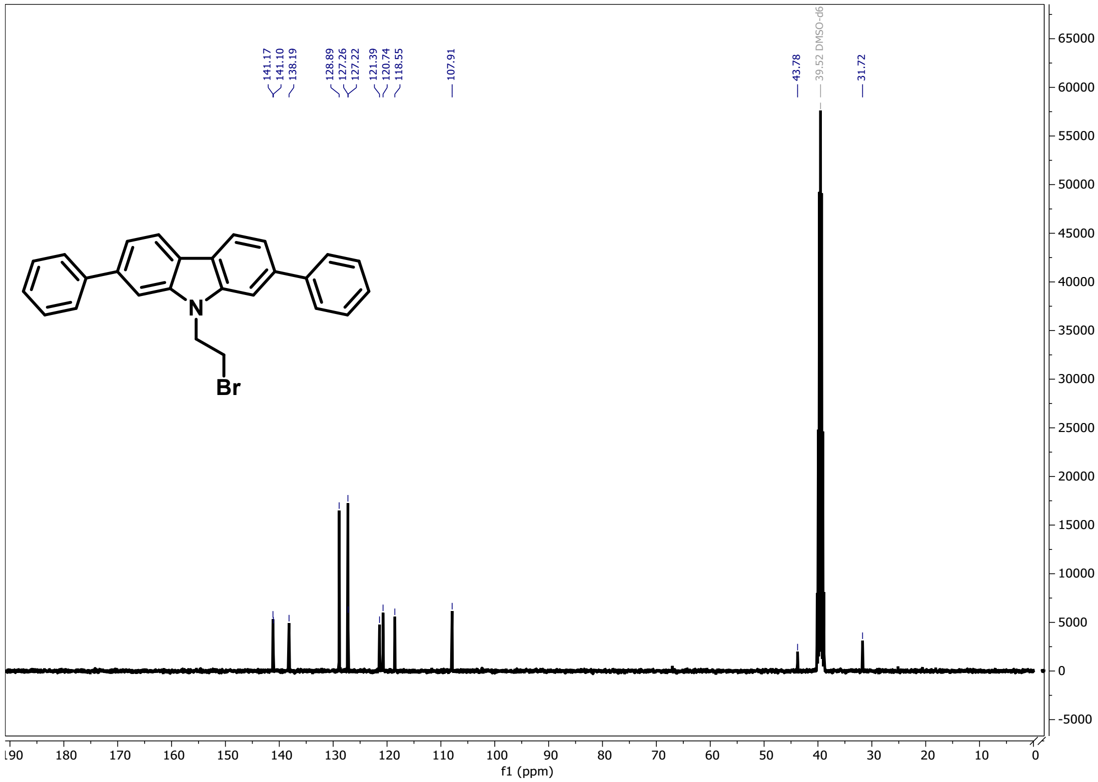


Fig. S8. ^{13}C NMR (101 MHz, DMSO-d6) of compound 4

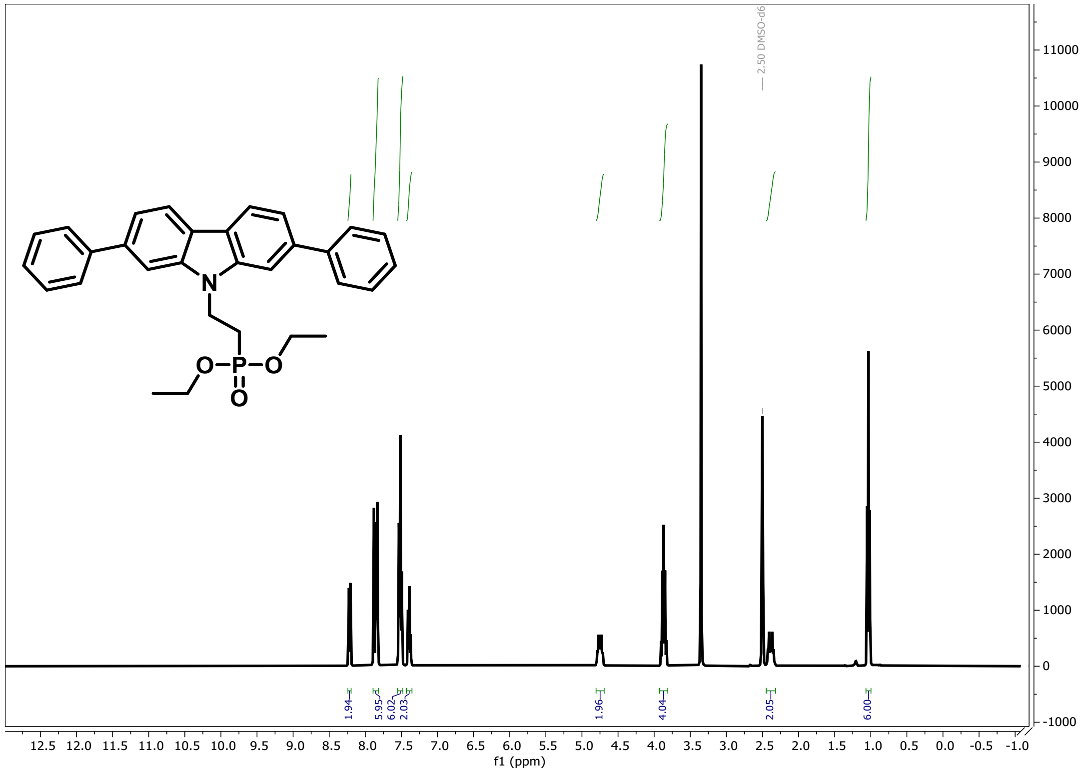


Fig. S9. ^{1}H NMR (400 MHz, DMSO-d6) of compound 5

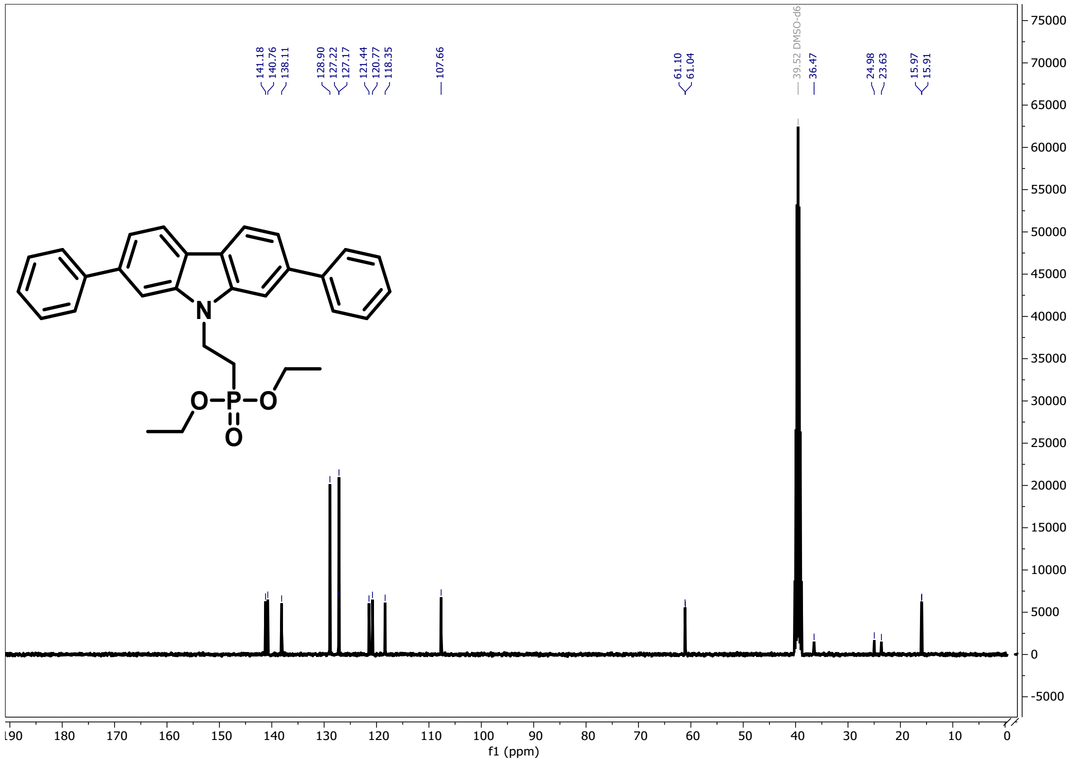


Fig. S10. ^{13}C NMR (101 MHz, DMSO-d6) of compound 5

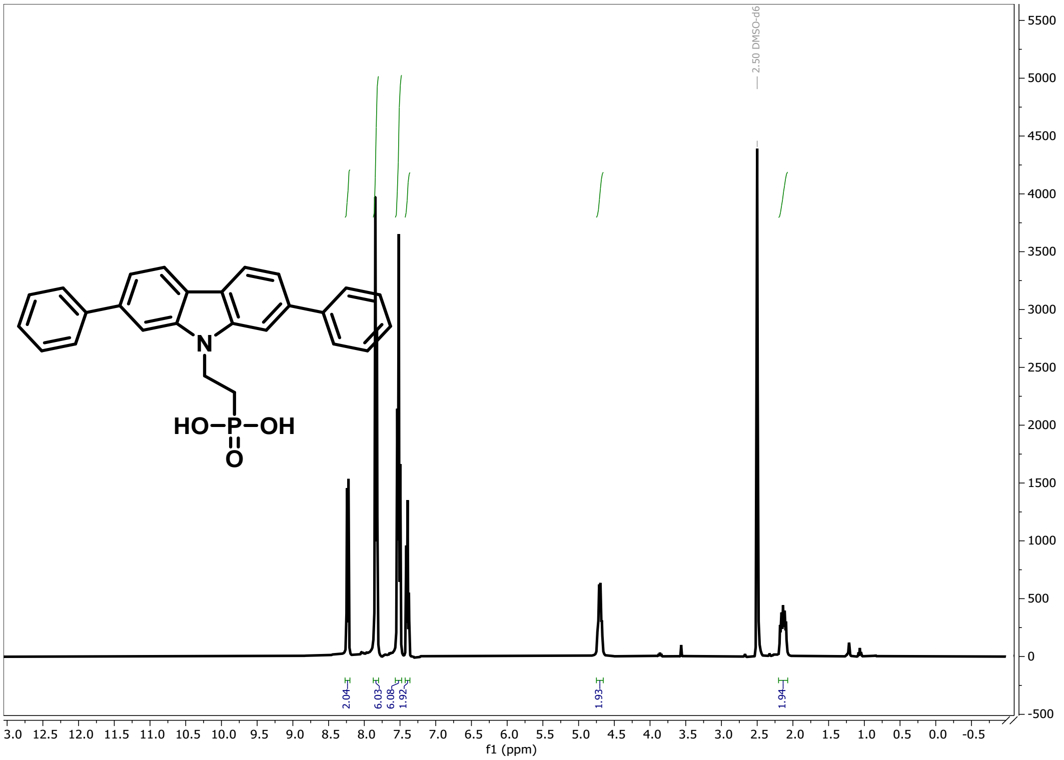


Fig. S11. ^{1}H NMR (400 MHz, DMSO-d6) of compound 6

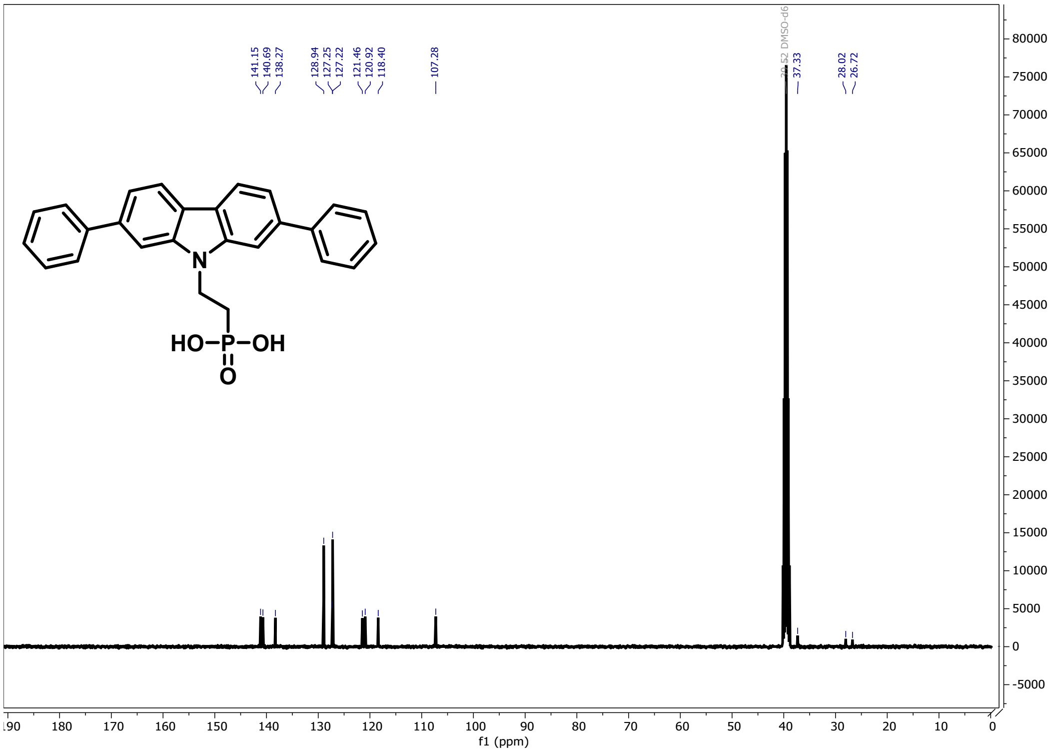


Fig. S12. ^{13}C NMR (101 MHz, DMSO-d6) of compound 6

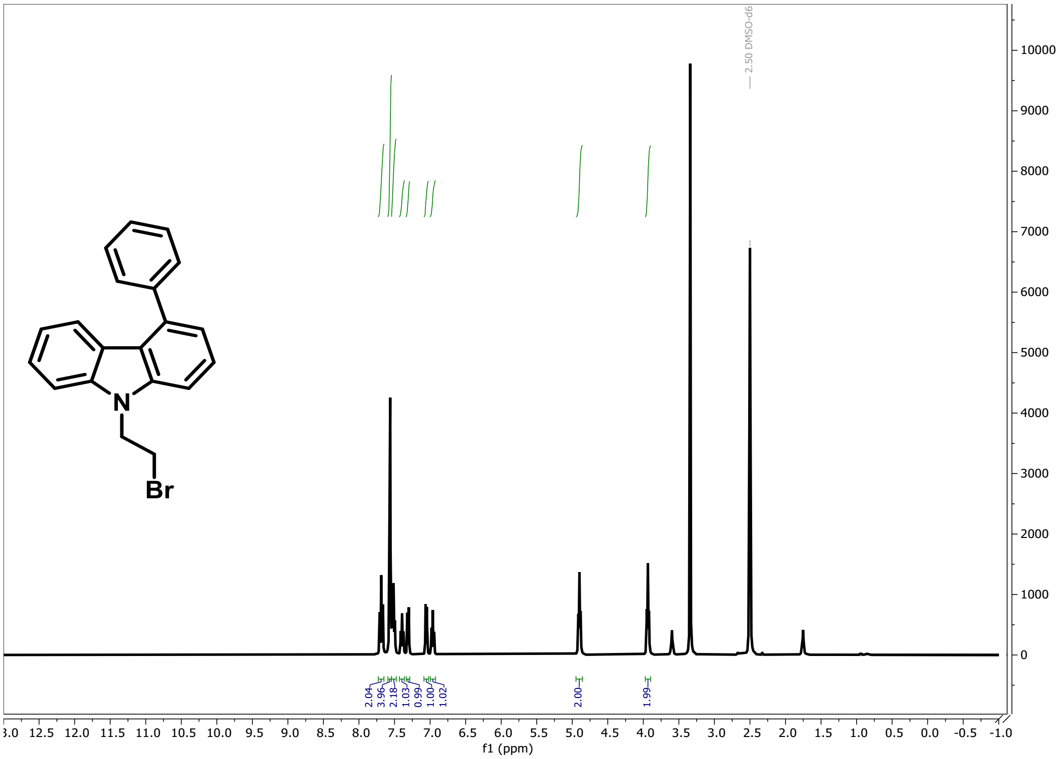


Fig. S13. ^{1}H NMR (400 MHz, DMSO-d6) of compound 7

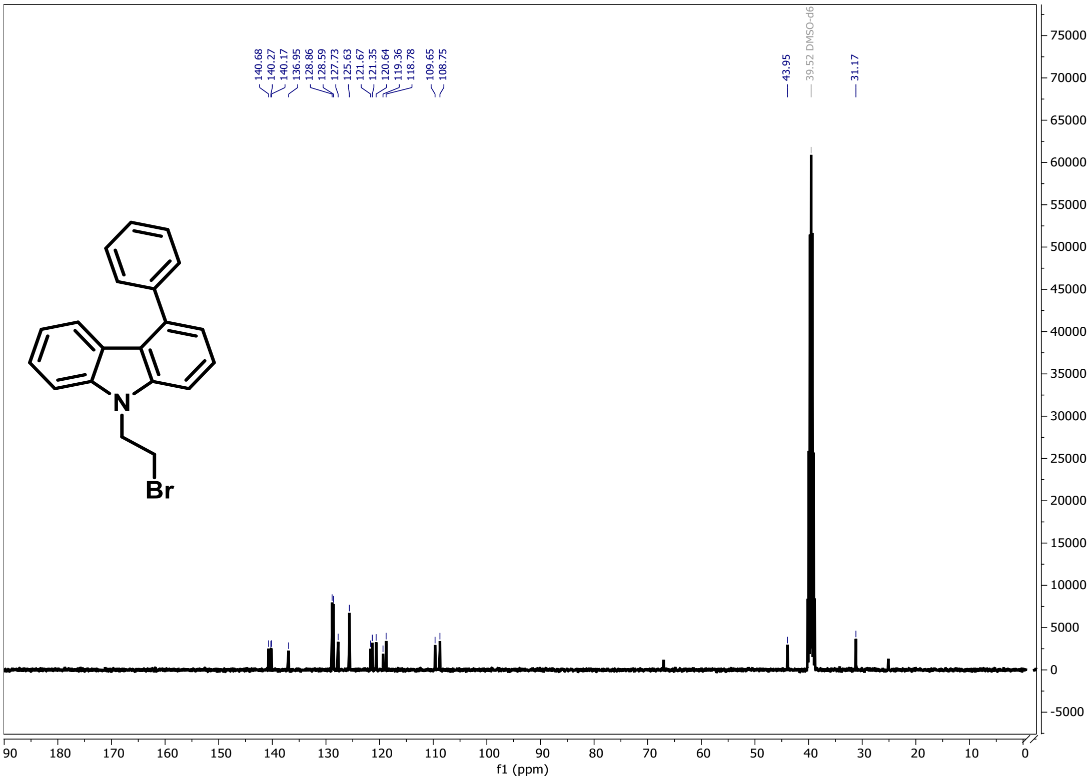


Fig. S14. ^{13}C NMR (101 MHz, DMSO-d6) of compound 7

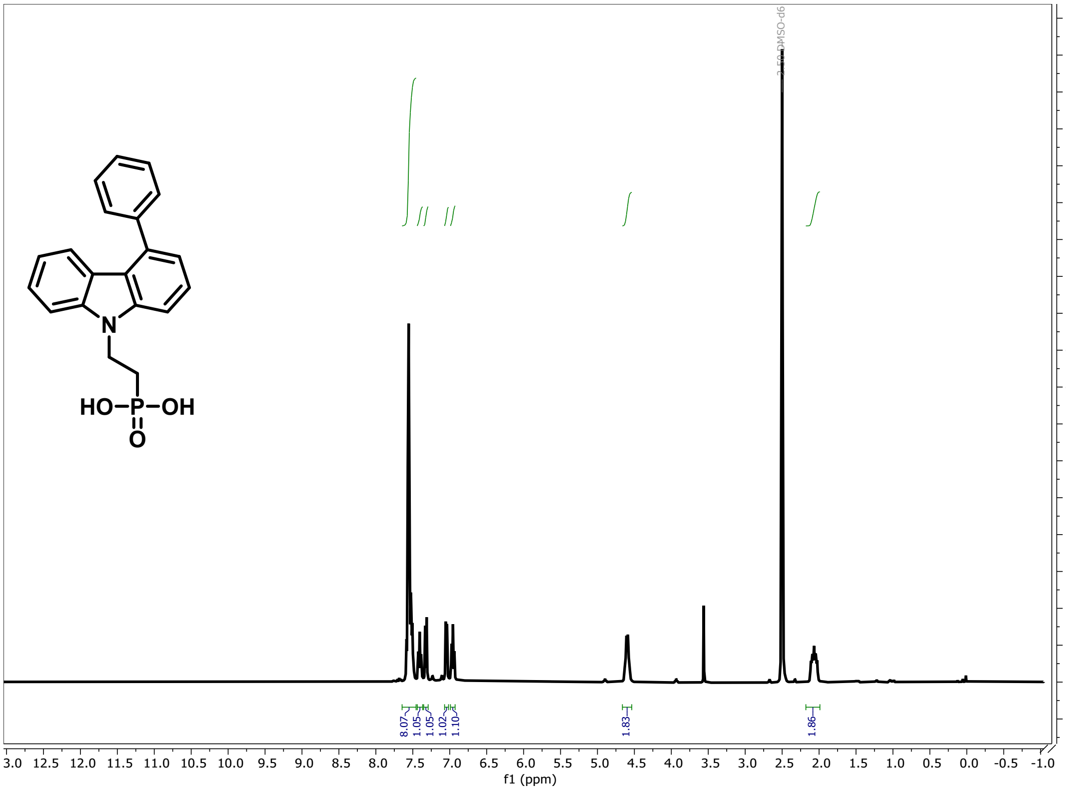


Fig. S15. ^{1}H NMR (400 MHz, DMSO-d6) of compound 9

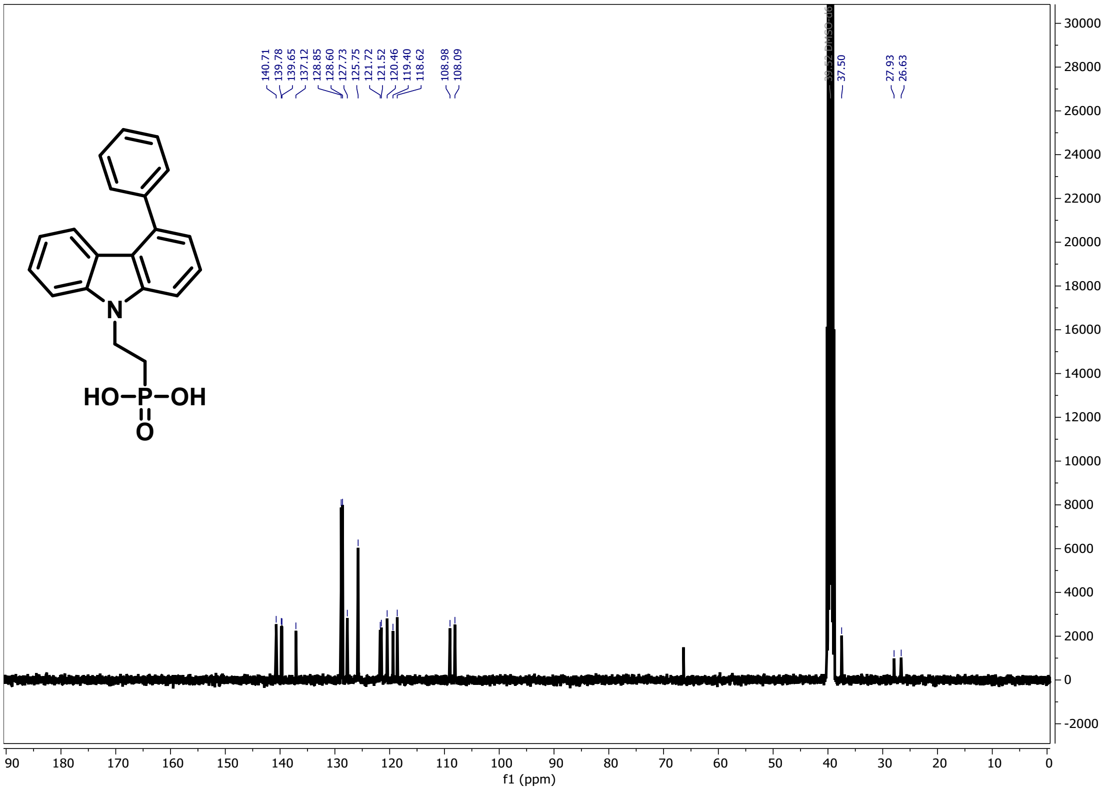


Fig. S16. ^{13}C NMR (101 MHz, DMSO-d6) of compound 9

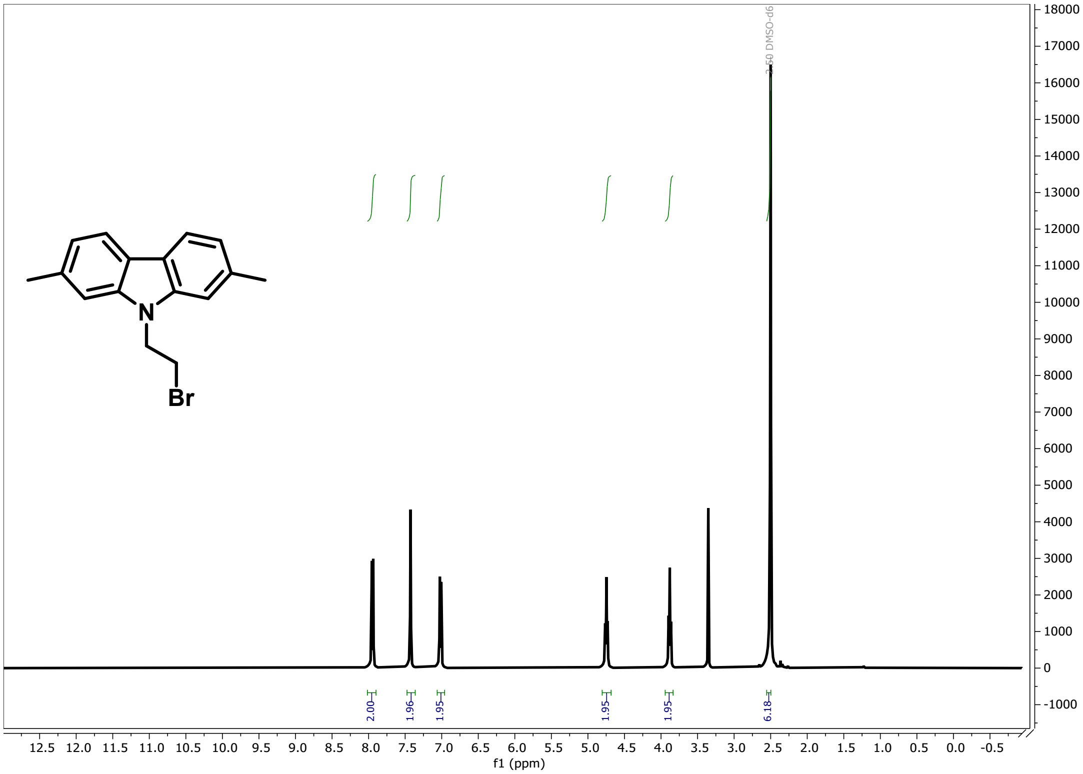


Fig. S17. ^{1}H NMR (400 MHz, DMSO-d6) of compound 10

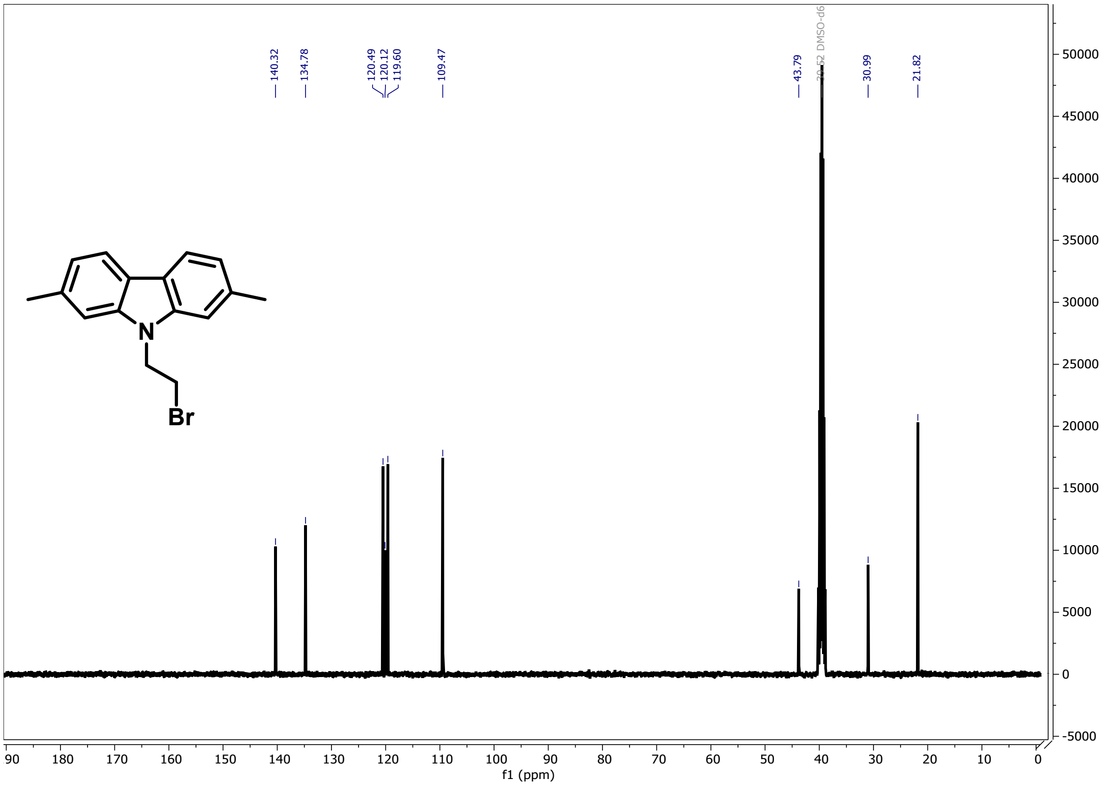


Fig. S18. ^{13}C NMR (101 MHz, DMSO-d6) of compound 10

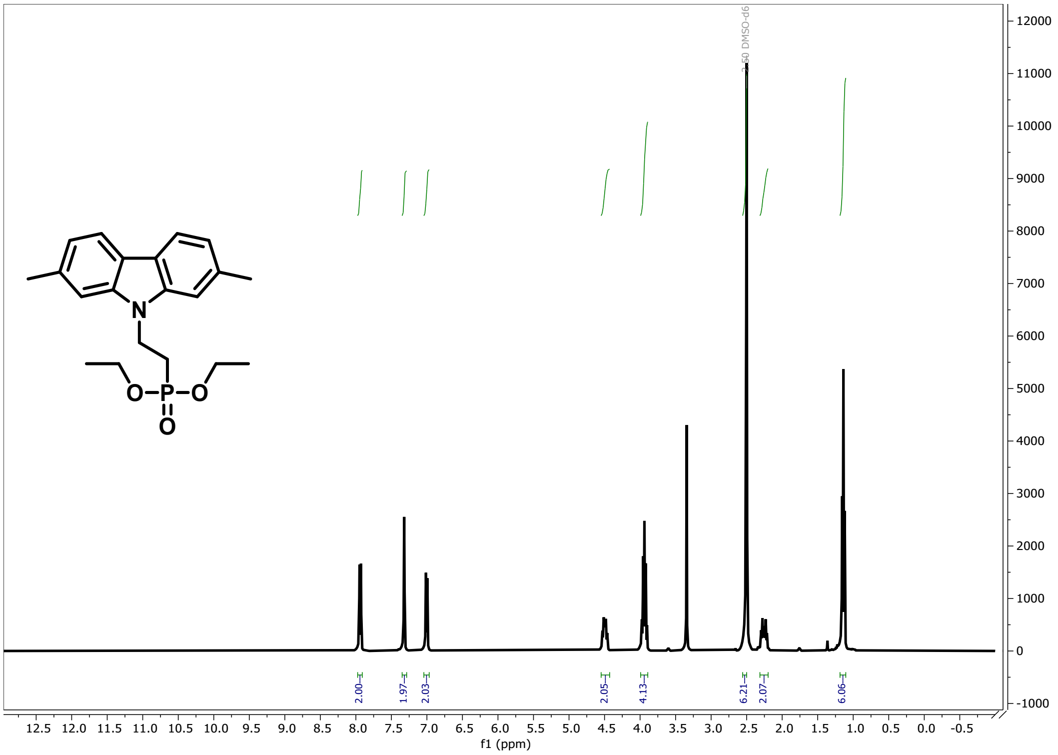


Fig. S19. ^{1}H NMR (400 MHz, DMSO-d6) of compound 11

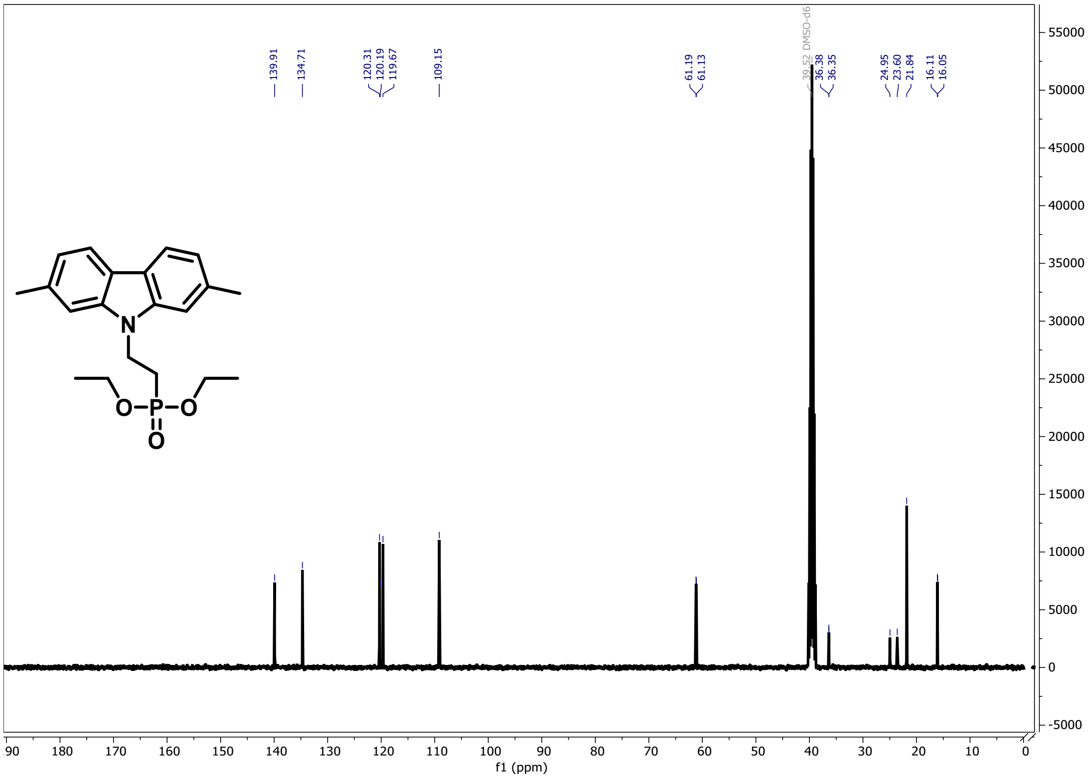


Fig. S20.^{13}C NMR (101 MHz, DMSO-d6) of compound 11

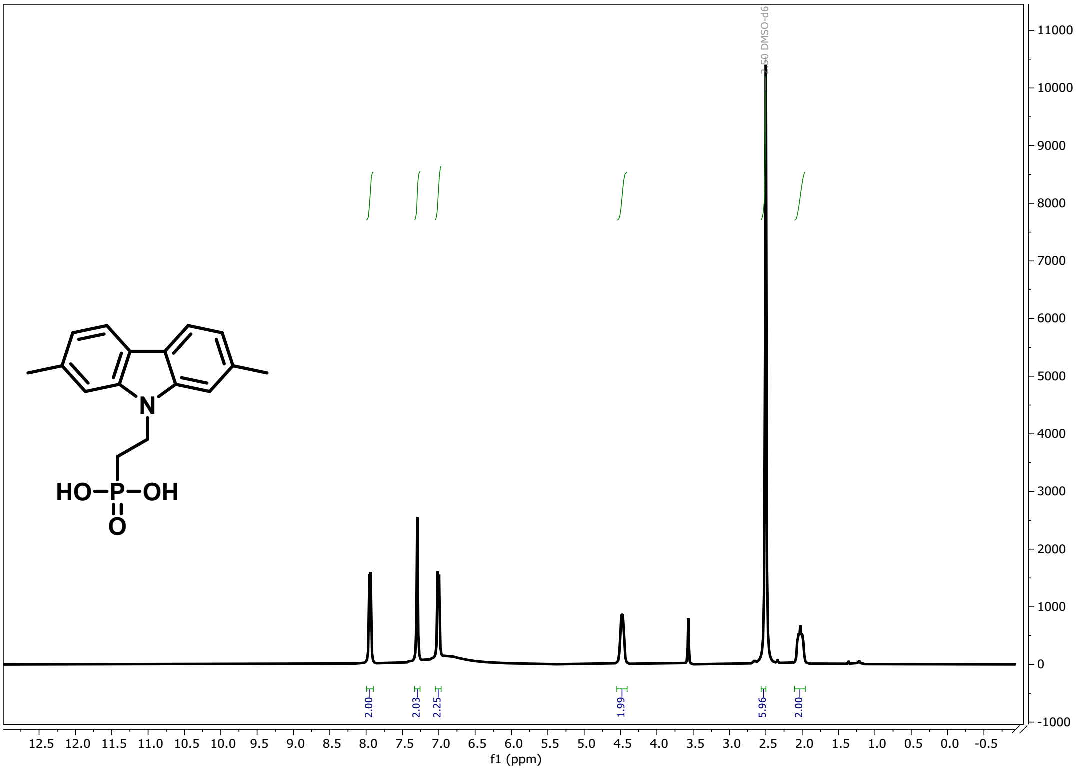


Fig. S21. ^{1}H NMR (400 MHz, DMSO-d6) of compound 12

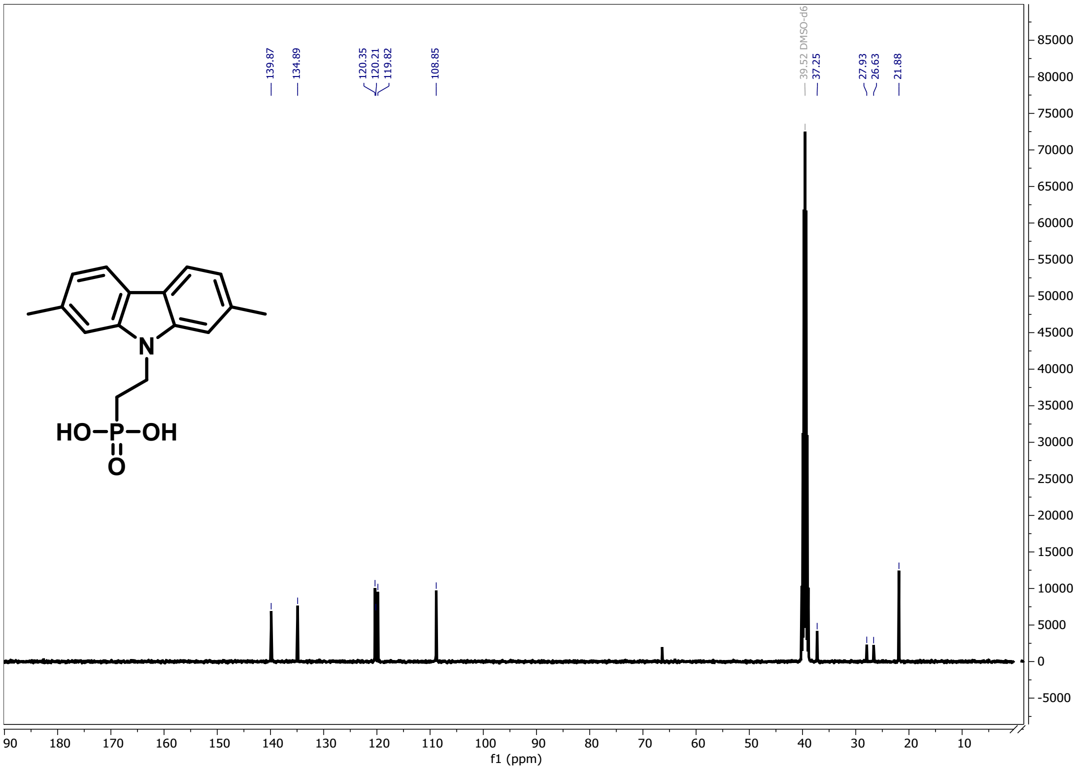


Fig. S22. ^{13}C NMR (101 MHz, DMSO-d6) of compound 12

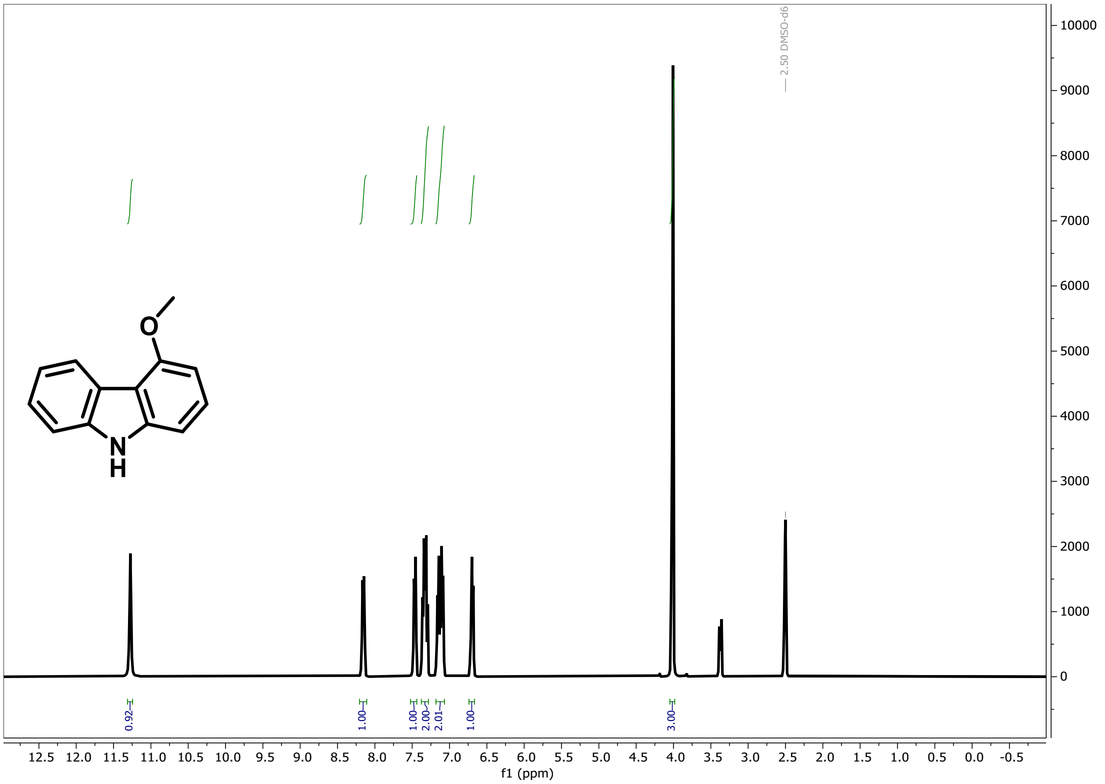


Fig. S23. ^{1}H NMR (400 MHz, DMSO-d6) of compound 13

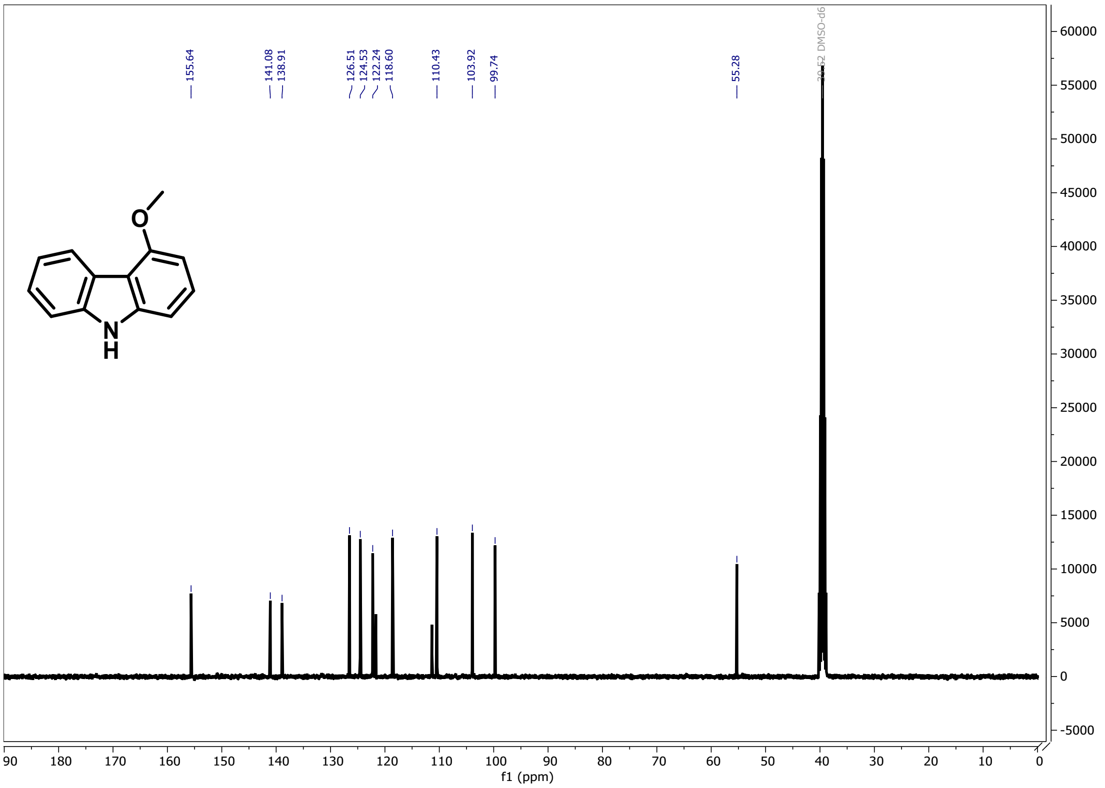


Fig. S24. ^{13}C NMR (101 MHz, DMSO-d6) of compound 13

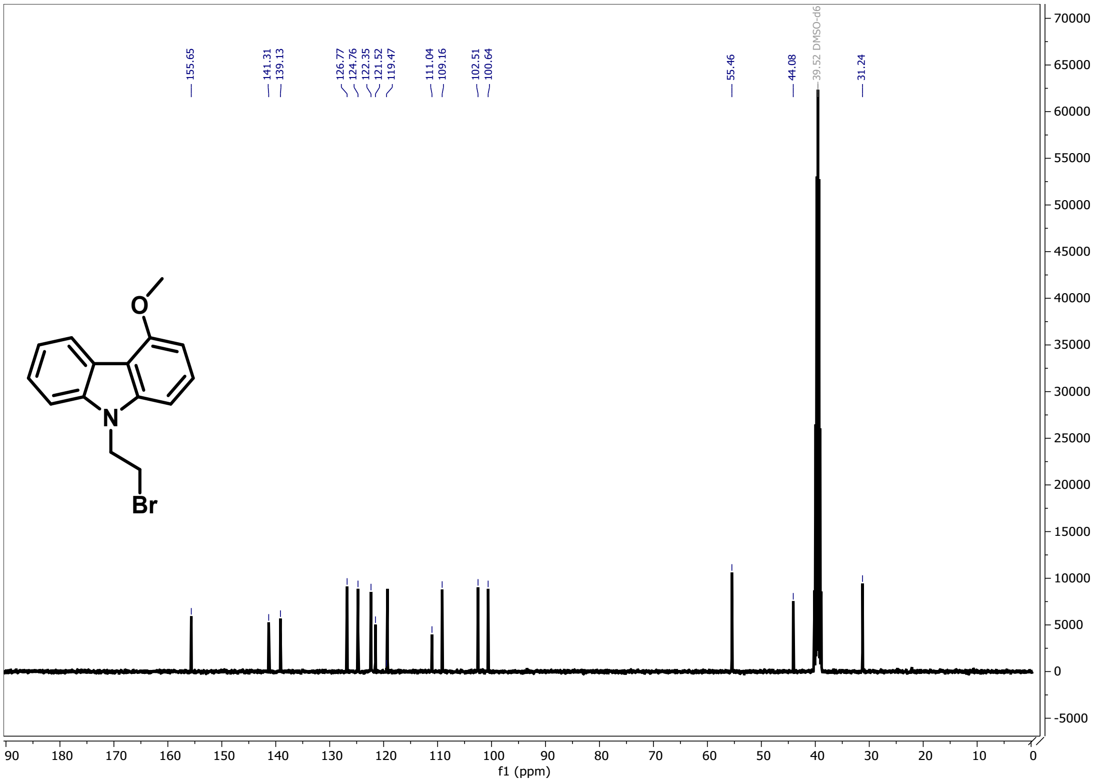


Fig. S25. ^{1}H NMR (400 MHz, DMSO-d6) of compound 14

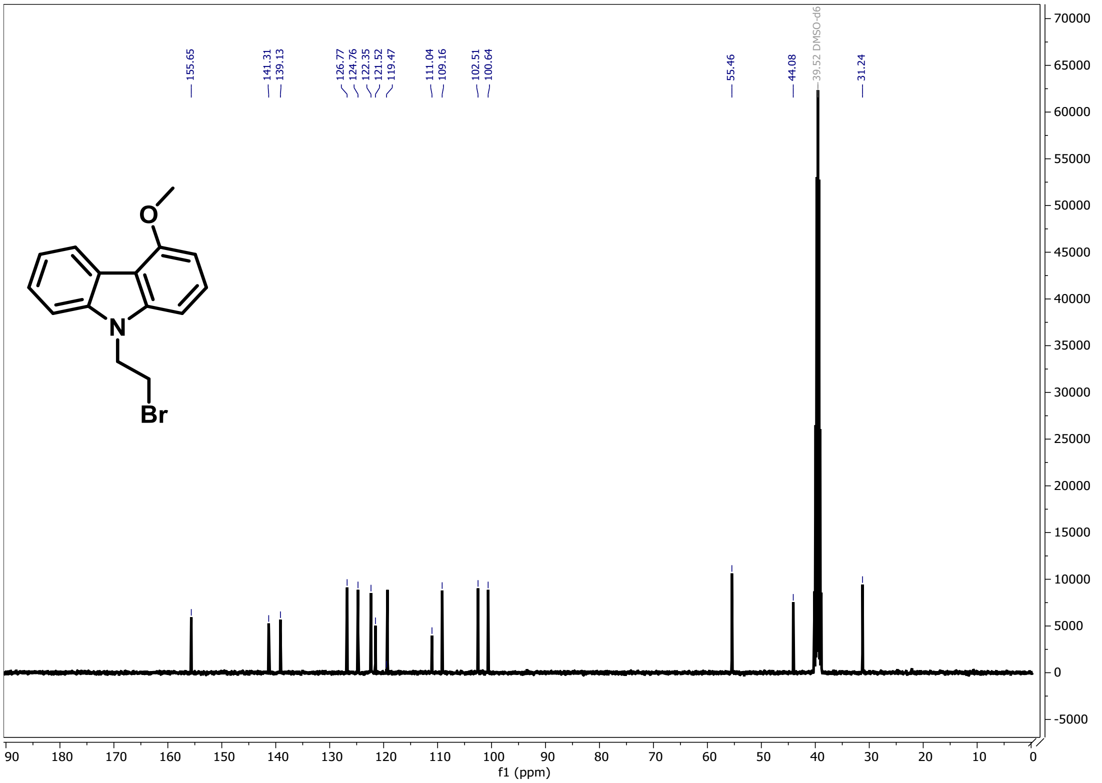


Fig. S26. ^{13}C NMR (101 MHz, DMSO-d6) of compound 14

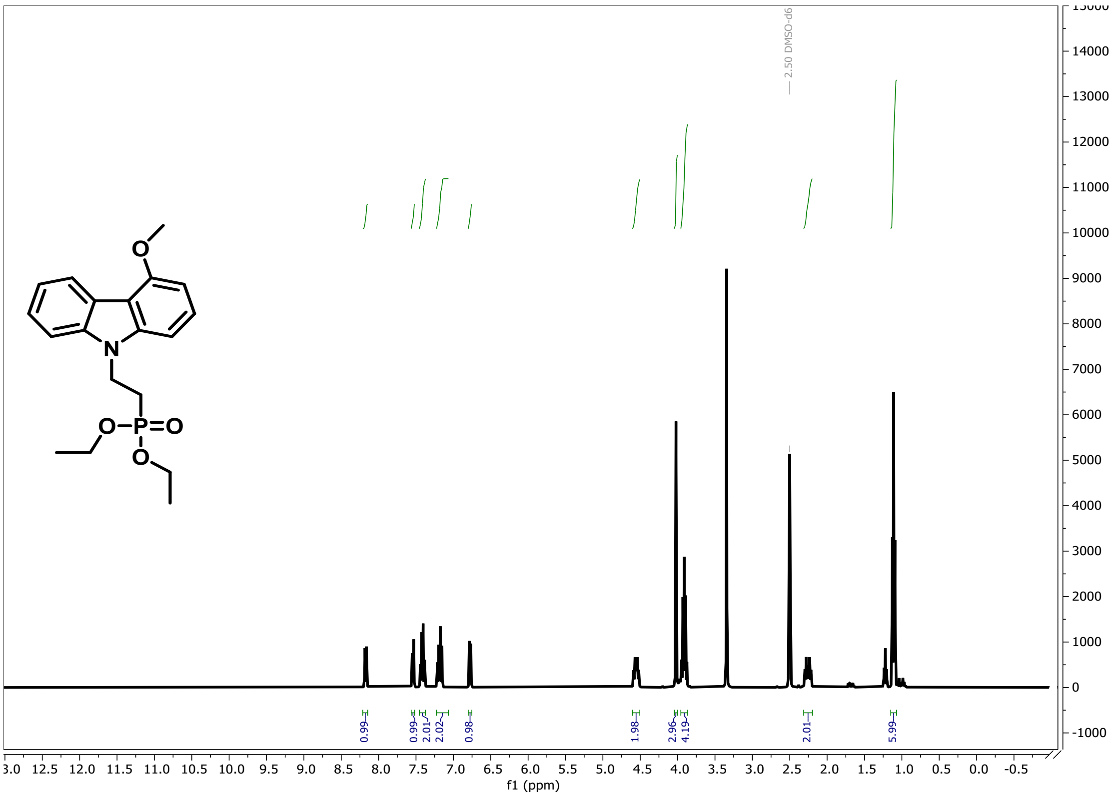


Fig. S27. ^{1}H NMR (400 MHz, DMSO-d6) of compound 15

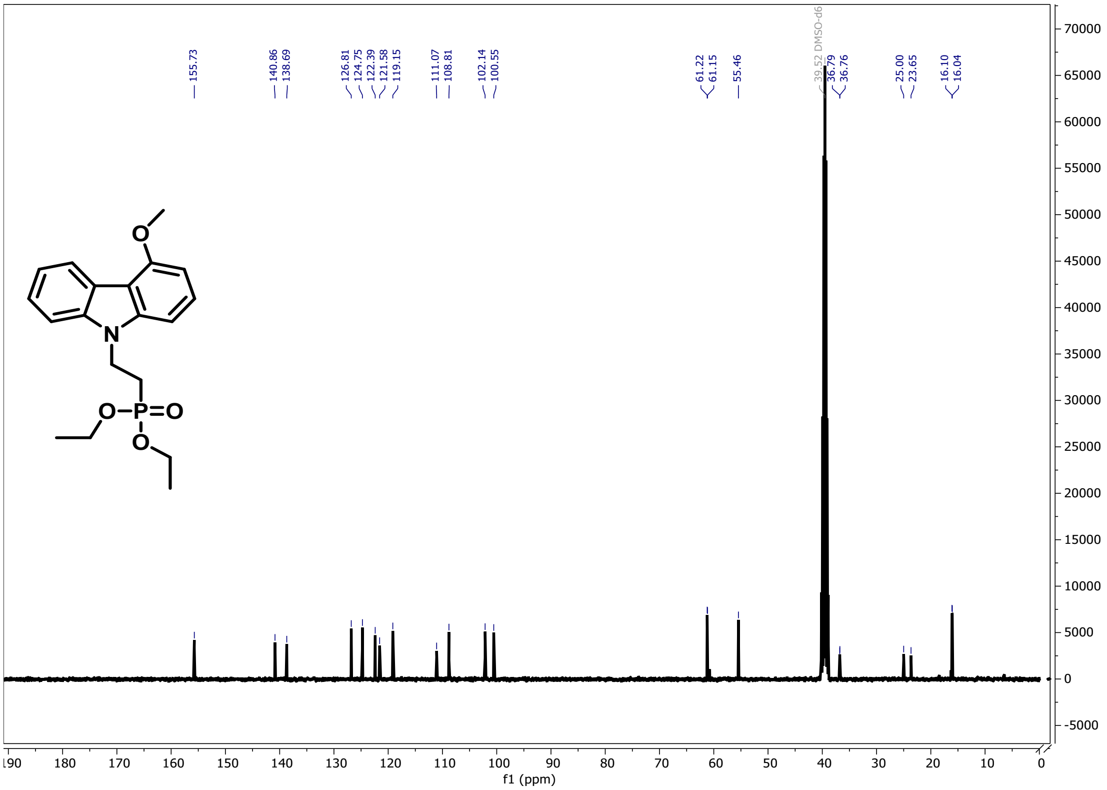


Fig. S28. ^{13}C NMR (101 MHz, DMSO-d6) of compound 15

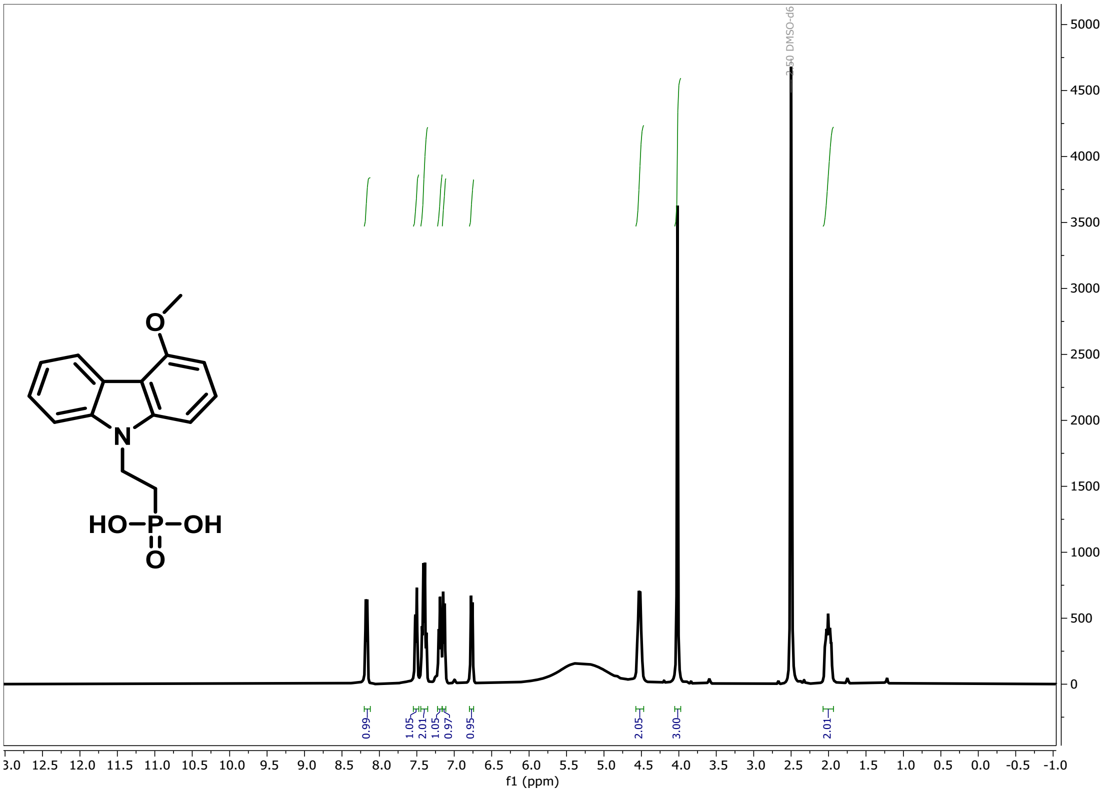


Fig. S29. ^{1}H NMR (400 MHz, DMSO-d6) of compound 16

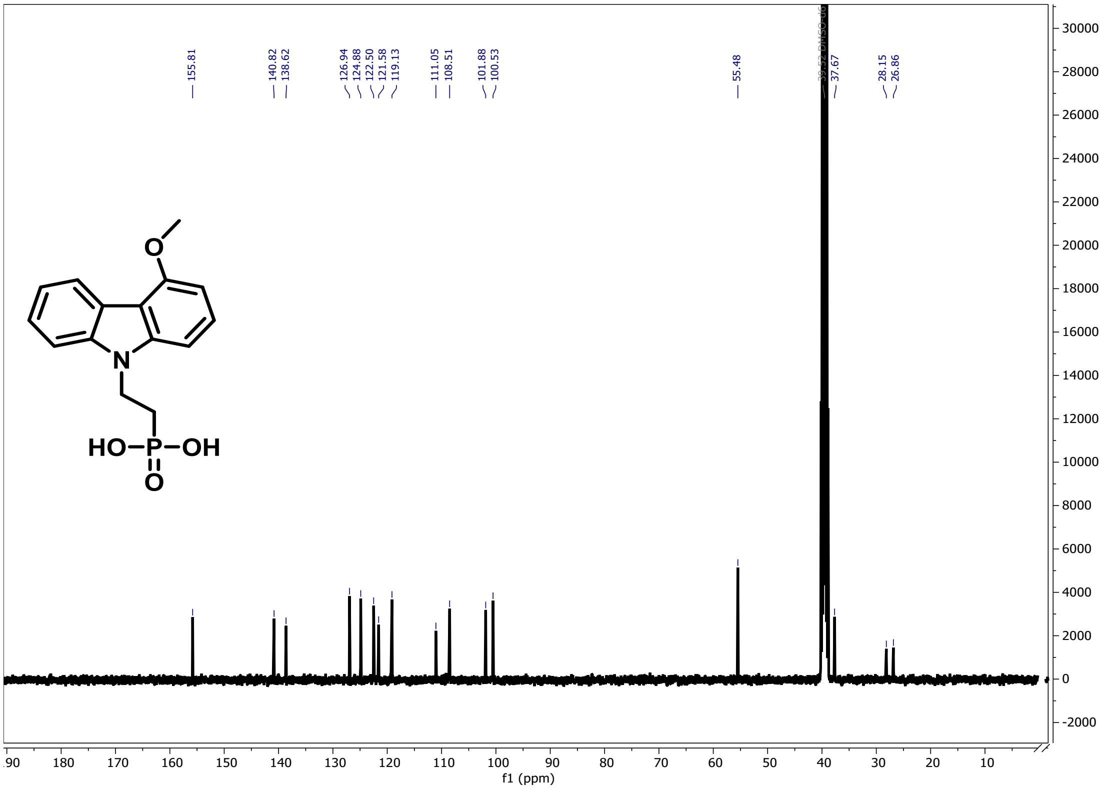


Fig. S30. ^{13}C NMR (101 MHz, DMSO-d6) of compound 16

Evaluation of the stability of the SAM materials

For the evaluation of the stability of the materials under heat and UV light, the samples of the materials were aged using 390 nm LED lamp, and their Ip measured using a low-energy photoelectron spectrometer (AC-2S, Riken-Keiki). The samples were prepared by a drop-casting solution (1 mg/ml, THF) of the investigated materials on pre-cleaned ITO substrates.

Lamp: 390 nm LED lamp (Kessil PR160L-390nm). Spectral range – 370 – 415 nm. Distance to samples 3cm. Intensity: ~250 mW/cm^2

Temperature: 85°C set on hotplate

Atmosphere: N_2 glovebox.

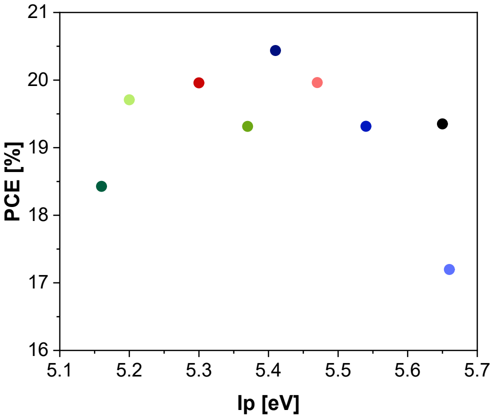
Time: up to 60 min.

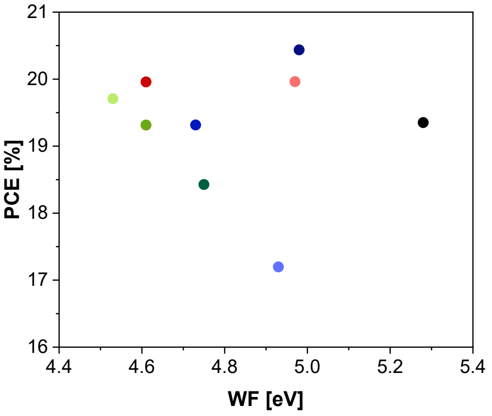
Three representative materials: 2PACz (reference material), 3,6-MeO-2PACz (highest absorption in this range), and 3,6-Ph-2PACz (compound with highest efficiency).

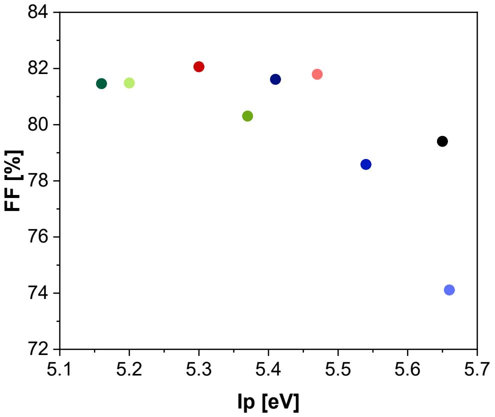
Time	2PACz	3,6-MeO-2PACz	3,6-Ph-2PACz
Ionization potential Ip, eV			
0 min	5.52	5.19	5.48
15 min	5.54	5.23	5.50
60 min	5.59	5.16	5.49
Gradient, Yield/eV			
0 min	18.1	19.0	14.8
15 min	17.2	24.2	18.5
60 min	18.0	23.5	23.2

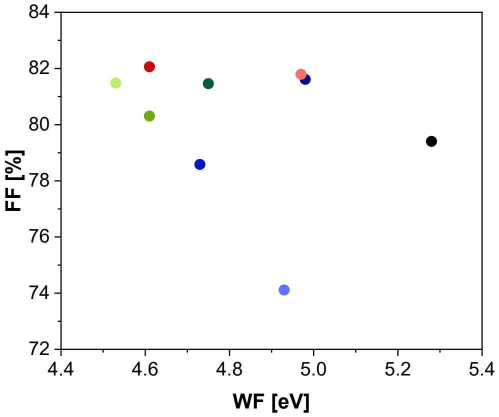
Table S4 Results of the aging of the SAM materials under UV light, at 85°C, N_2 atmosphere.

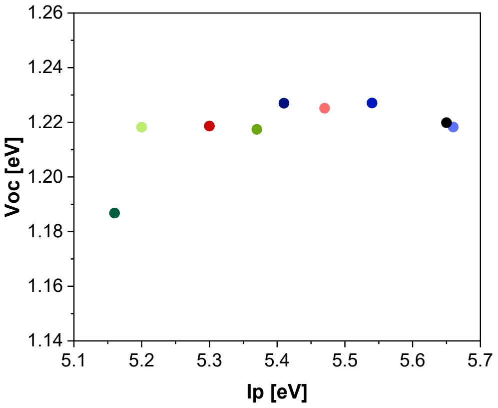
Investigation of the correlation between device parameters and materials/layers properties

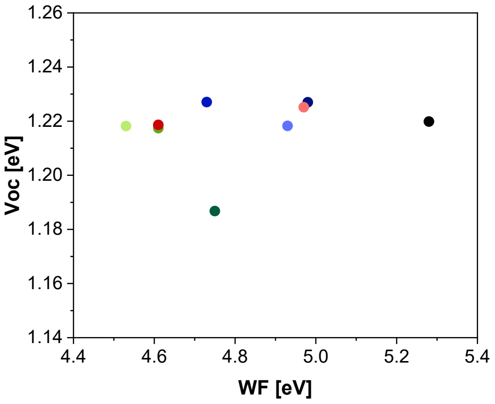












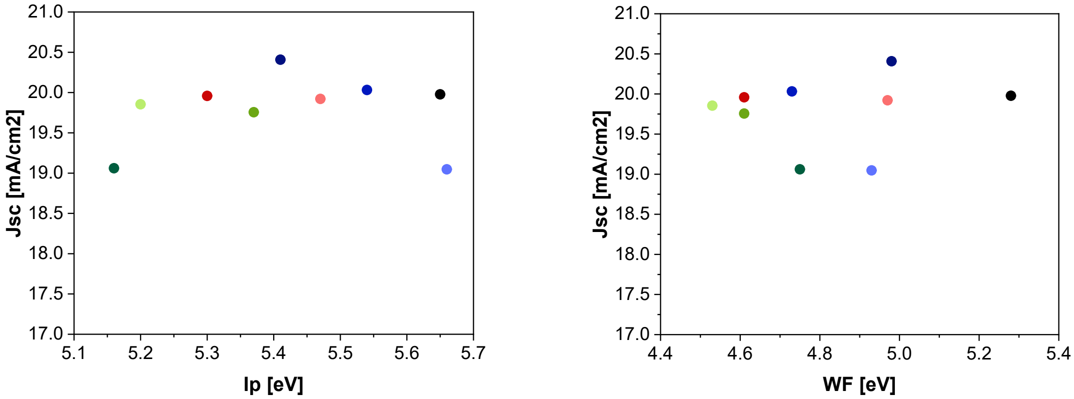


Fig. S31. Plots of the data from Table 1 and Fig. 5, showing the relationship between device parameters (y axis) and materials/layers properties (x axis). The color scheme follows the same pattern as in Fig. 5.