Supporting Information

Synthesis of a Novel Tetra-Phenol π-Extended Phenazine and its Application as Organo-Photocatalyst

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1. General Remarks

1.1 Instrumentation

Thin layer chromatography (TLC) was performed on Sigma Aldrich pre-coated aluminium sheets (0.25 mm layer thickness, 60 Å porosity and fluorescent indicator GF254) and were visualized using 254 or 365 nm light. Flash column chromatography was carried out using Merck Gerduran silica gel 60 (particle size 40 63 μm). ***Melting points*** (M.P.) were measured on a Gallenkamp apparatus. All of melting points have been measured in open capillary tubes and have not been corrected. ***Nuclear magnetic resonance*** (NMR) ^{1}H, and ^{13}C spectra were obtained on Varian Inova spectrometer (500 MHz ^{1}H and 126 MHz ^{13}C) or Varian 400 MHz NMR spectrometer (400 MHz ^{1}H and 101 MHz ^{13}C). Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm, CD_3CN: δ_H = 1.94 ppm, δ_C = 1.32, 118.26 ppm, DMSO-*d6*: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Coupling constants (*J*) were given in Hz. Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), m (multiplet), br (broad signal), dd (doublet of doublets), dt (doublet of triplets). Carbon spectra were acquired with a complete decoupling for the proton, unless specified. All spectra were recorded at 25°C unless specified. ***Infrared spectra*** (IR) were recorded on a Shimadzu IR Affinity 1S FTIR spectrometer in ATR mode with a diamond mono-crystal. Selected absorption bands are reported in wavenumber (cm^{-1}). ***ESI-High resolution mass spectrometry*** (ESI-HRMS). ESI-HRMS was performed at University of Trieste Chemistry department, High resolution mass spectra (HRMS) were obtained on Bruker micrOTOF-Q (ESI-TOF). ***High Performance Liquid Chromatography*** *(HPLC)*: HPLC-UV Agilent 1260 Infinity II was used to perform samples analysis. Infinity Lab PoroShell 120 EC-C18 4 μm column (4.6 × 100 mm) was used for HPLC analysis under the following conditions: Flow rate (0.750 mL/min); Injection volume 5 mL; Temperature 44°C. Solvent A: H_2O + H_2CO_2 (0.1 %); solvent B: acetonitrile; gradient: 0 min (30% B), 2.5 min (30% B), 15 min (100 % B), 18 min (100 % B). ***Photophysical analysis:*** Absorption spectra of compounds were recorded on air equilibrated solutions at room temperature with an Agilent Cary 5000 UV-Vis spectrophotometer, using quartz cells with path length of 1.0 cm. Emission spectra were recorded on an Agilent Cary Eclipse fluorescence spectrofluorometer. Luminescence lifetimes were measured with an Edinburgh Instruments FS5 time-correlated single-photon counting spectrofluorimeter, exciting the sample at 375 nm with a picosecond pulsed diode laser (EPL-375 Edimburgh Instruments). ***Cyclic voltammetry.*** The electrochemical characterizations were carried out in DMF/0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$), at room temperature, on an Autolab 302 N electrochemical workstation (Metrohm, The Netherlands) in a glass cell from CH Instruments (10 mL, CHI220). A typical three-electrode cell was employed, which was composed of glassy carbon (GC) working electrode (3 mm diameter), a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode (RE). RE was connected to the glass cell through a salt bridge in 0.1 M $TBAPF_6$ DMF solution. Oxygen was removed by purging the DMF solution with Argon. The GC electrode was polished twice before use with 0.05 and 0.1 colloidal silica polishing suspension and ultrasonically rinsed with deionized water for 15 minutes. ***Photochemical reaction set up.*** The light-driven reactions were set up under

an argon atmosphere in Schlenk tubes or glass vials unless otherwise stated. The light sources used in this work were purchased from Kessil. Detail Kessil lamp 427 nm PR160L-427 (50W). https://www.kessil.com/science/PR160L.php

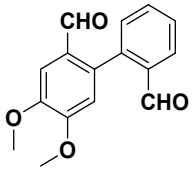
X-Ray Data: CCDC **2299130**, contains the supplementary crystallographic data for **7**. Related files can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

1.2 Materials and methods

Chemicals were purchased from Sigma Aldrich, TCI, Alfa Aesar and Fluorochem and were used as received unless otherwise stated. Solvents were purchased from Sigma Aldrich and Alfa Aesar, while deuterated solvents from Eurisotop and Sigma Aldrich. Anhydrous conditions were achieved by repeated cycles of flaming with a heat gun under vacuum and purging with Argon (Ar). The inert atmosphere was maintained using Argon-filled balloons equipped with a syringe and needle that was used to penetrate the silicon stoppers used to close the flask's necks. Additions of liquid reagents were performed using plastic syringes. Degassing of solutions was performed by bubbling argon in the reaction under sonication for at least 10 minutes or alternatively by 3 freeze pump thaw cycles. The latter was performed by freezing the solution with liquid N_2 and keeping the frozen solvent under vacuum for 5 to 10 min., followed by thawing. Dry solvents were obtained commercially. MilliQ water was obtained from a Millipore Milli-Q Plus 185 apparatus and presented a resistivity of 18.2 MΩcm. MilliQ water was always used unless otherwise specified.

2. Synthetic procedures and spectral data

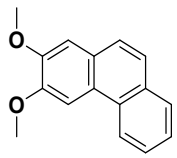
2.1 Synthesis of 4



In a 250 mL round bottom flask, 4-bromoveratraldehyde (4.0 g, 16.3 mmol) was added together with (2-formylphenyl)boronic acid (2.5 g, 16.6 mmol), PPh_3 (321 mg, 1.2 mmol) and K_2CO_3 (4.5 g, 32.6 mmol). The solids were suspended in a mixture of toluene/EtOH/H_2O (40/20/10 mL) and the suspension was degassed by argon bubbling and sonication. After 5 min. $Pd(OAc)_2$ (65 mg, 0.3 mmol) was added and the mixture degassed for further 5 min. before being heated under argon at 90°C for 2 h. The reaction was the cooled to r.t., diluted with EtOAc (100 mL) and washed with H_2O (100 mL × 2) and brine (50 mL). The organic layers were then dried over Na_2SO_4 and filtered over silica washing with plenty of solvent. The filtered solution was evaporated under reduced pressure and the residue reprecipitated from PE and filtered to give **4** as a grey solid (4.3 g, 98%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.86 (s, 1 H), 9.63 (s, 1 H), 8.06 (d, *J* = 7.6 Hz, 1 H), 7.67 (t, *J* = 7.5 Hz, 1 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.56 (s, 1 H), 7.39 (d, *J* = 7.6 Hz, 1 H), 6.77 (s, 1 H), 4.01 (s, 3 H), 3.94 (s, 3 H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 191.23, 189.81, 153.41, 149.57, 141.01, 136.59, 135.13, 133.51, 132.14, 129.00, 128.32, 113.59, 109.01, 56.52, 56.34. ESI-HRMS: $[M+Na]^+$ calc. for $[C_{16}H_{14}O_4Na]^+$: 293.0784; found 293.0787.

2.2 Synthesis of 5

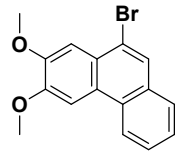


In a 50 mL microwave vial **4** (1.0 g, 3.7 mmol) was added together with tosylhydrazide (1.45 g, 7.7 mmol) and suspended in *n*BuOH (7.0 mL). The mixture was then degassed 10 min. with argon bubbling and sonication. The resulting suspension was then heated under MW irradiation at 120°C for 30 min. during which time a pressure build up occurs. After cooling to r.t. the solvent was evaporated under reduced pressure and the residue purified using SCC (CH_2Cl_2/PE 1/1), followed by reprecipitation from cold MeOH and filtration, resulting in the isolation of **5** as an off-white solid (466 mg, 53%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 8.3 Hz, 1 H), 8.02 (s, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.66 (s, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.54 (t, *J* = 7.54 Hz, 1 H), 7.25 (s, 1 H), 4.13 (s, 3 H), 4.05 (s, 3 H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.44, 149.42, 131.46, 129.85, 128.80, 127.27, 126.30, 126.07, 125.66, 125.34,

124.96, 122.25, 108.42, 103.37, 56.12, 56.04. ESI-HRMS: $[M+Na]^+$ calc. for $[C_{16}H_{14}O_2Na]^+$: 261.0886; found 261.0889.

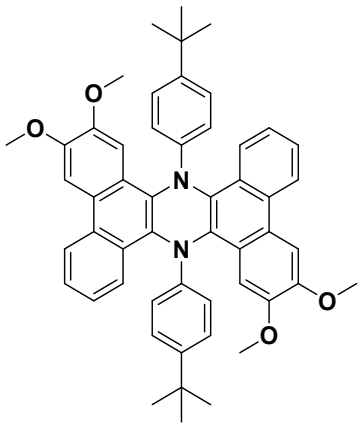
2.3 Synthesis of 6



In a 100 mL round bottom flask **5** (1.4 g, 5.9 mmol) was added and dissolved in $CHCl_3$ (EtOH 0.6% stabilized) (50 mL). NBS (1.05 g, 5.9 mmol) was then added at r.t. and the reaction stirred under argon for 18 h. The resulting solution was then filtered on a silica plug (CH_2Cl_2 100%) and the solvent evaporated. Reprecipitation from cold MeOH and filtration, afforded **6** as an off-white solid (1.42 g, 76%).

M.P.: 129-131°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.52 (d, J = 8.0 Hz, 1 H), 8.34 (d, J = 7.8 Hz, 1 H), 8.00 (s, 1 H), 7.96 (s, 1 H), 7.69-7.62 (m, 2 H), 7.14 (s, 1 H), 4.12 (s, 3 H), 4.04 (s, 3 H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 149.87, 149.79, 130.86, 129.70, 129.64, 128.24, 127.56, 127.12, 126.63, 124.57, 122.49, 119.68, 107.59, 103.38, 56.17, 56.12. IR (ATR) ν (cm^{-1}): 3055, 2997, 2961, 2936, 2853, 2826, 2349, 1614, 1597, 1572, 1526, 1501, 1443, 1433, 1408, 1387, 1364, 1327, 1294, 1250, 1231, 1209, 1198, 1153, 1117, 1043, 1024, 970, 945, 918, 899, 887, 845, 820, 770, 754, 733, 719, 685, 665. ESI-HRMS: $[M+Na]^+$ calc. for $[C_{16}H_{13}BrO_2]^+$: 338.9991; found 338.9992.

2.4 Synthesis of 7



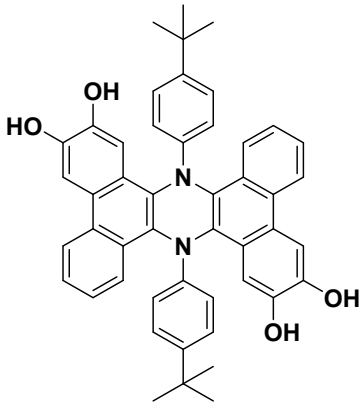
In a double necked flask, **6** (668 mg, 2.1 mmol), 4-*t*Bu aniline (350 µL, 2.2 mmol), $Pd(OAc)_2$ (24 mg, 0.11 mmol) and dppf (116 mg, 0.21 mmol) were added and purged with Ar (3 × vacuum/Ar cycles). Anhydrous toluene (10 ml) was then added, and the resulting suspension degassed for 10 min. with Ar bubbling and sonication. NaOtBu (444 mg, 4.6 mmol) was then added in one portion under Ar and the reaction degassed for further 10 min. The resulting dark suspension was then placed in a preheated silicon oil bath at 100°C and stirred for 2 h at the same temperature. At this point, a compressed air inlet equipped with a 12 cm needle was used to bubble air (passed on a column filled with drierite™) in the reaction solution at 100°C for 2 h. After complete conversion of the intermediate from the previous step, the reaction was diluted with PE

(100 mL) and filtered on a silica plug (PE 100% to CH_2Cl_2 100%). The obtained material (776 mg)* was transferred in a 100 mL single necked round bottom flask and dissolved in CH_2Cl_2 (20 mL) under Ar. The solution was cooled to 0°C, DDQ (275 mg, 1.21 mmol) added in one portion and the black reaction stirred at r.t. for 2 h. The resulting suspension was diluted with CH_2Cl_2 (50 mL) and filtered on a silica plug using CH_2Cl_2 as eluent. The organic phase was evaporated and the resulting solid purified by reprecipitation from MeOH (3 ×, 6000 rpm, 2 min.) to afford **7** as a white powder (284 mg, 35%, respectively to the phenanthrene).

* for subsequent step all material was considered as product.

M.P.:>300°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 8.0 Hz, 2 H), 8.49 (d, *J* = 8.2 Hz, 2 H), 8.10 (s, 2 H), 7.95 (s, 2 H), 7.69-7.61 (m, 4 H), 6.76 (d, *J* = 8.8 Hz, 4 H), 6.47 (d, *J* = 8.8 Hz, 4 H), 4.17 (s, 6 H), 4.06 (s, 6 H), 1.03 (s, 18 H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.12, 149.68, 146.20, 142.25, 141.99, 140.39, 130.09, 129.09, 126.34, 126.30, 124.84, 124.62, 124.50, 122.76, 115.34, 105.09, 103.82, 56.39, 56.27, 33.77, 31.41. IR (ATR) ν (cm^{-1}): 2951, 2901, 2868, 2826, 1614, 1591, 1504, 1472, 1454, 1433, 1416, 1396, 1368, 1341, 1319, 1310, 1271, 1256, 1207, 1198, 1173, 1043, 1024, 991, 947, 932, 853, 835, 818, 791, 775, 762, 733, 691, 633, 611, 584, 556, 540, 517. ESI-HRMS: $[M+Na]^+$ calc. for $[C_{52}H_{50}N_2O_4Na]^+$: 789.3663; found 789.3660.

2.5 Synthesis of 1



Molecule **7** (283 mg, 0.37 mmol) was added in a single necked flask and dissolved in CH_2Cl_2 (20 mL). The reaction was then cooled to 0°C and BBr_3 (2.22 mL, 1.0 M in CH_2Cl_2) slowly added. The reaction was then allowed to react r.t. and stirred for 18 h. The reaction was then slowly quenched by slow addition of H_2O and diluted with EtOAc (50 mL). The resulting mixture was then washed with H_2O (50 mL × 2), an aq. Solution of $Na_2S_2O_4$ (1g × 100 mL) and brine (50 mL × 1). The organic solution was then dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was finally purified by reprecipitation from CH_2Cl_2 (3 ×, 6000 rpm, 2 min.) to afford **1** as a grey powder (131 mg, 50%).

M.P.:>300°C. ^{1}H-NMR (400 MHz, CD_3CN) δ: 8.65-8.63 (m, 2 H), 8.34-8.31 (m, 2 H), 8.21 (s, 2 H), 7.81 (s, 2 H), 7.70-7.63 (m, 4 H), 7.38 (s, 2 H), 7.31 (s, 2 H), 6.90 (d, *J* = 9.1 Hz, 4 H), 6.51 (d, *J* = 9.1 Hz, 4 H), 1.07

(s, 18 H). ^{13}C-NMR (126 MHz, CD_3CN) δ 147.05, 146.96, 146.49, 143.12, 141.59, 139.69, 130.28, 130.07, 127.44, 127.09, 126.29, 126.02, 125.68, 125.18, 124.09, 115.92, 109.33, 108.96, 34.35, 31.55. IR (ATR) ν (cm^{-1}): 3491, 2959, 2903, 2866, 1609, 1595, 1504, 1443, 1393, 1364, 1337, 1300, 1265, 1248, 1221, 1196, 1159, 1144, 1038, 1016, 995, 947, 897, 866, 847, 820, 793, 781, 760, 733, 723, 708, 689, 656, 637, 619, 586, 567, 548, 538, 515. ESI-HRMS: $[M+Na]^+$ calc. for $[C_{48}H_{42}N_2O_4Na]^+$: 733.3037; found 733.3034.

3. Photophysical and electrochemical characterization

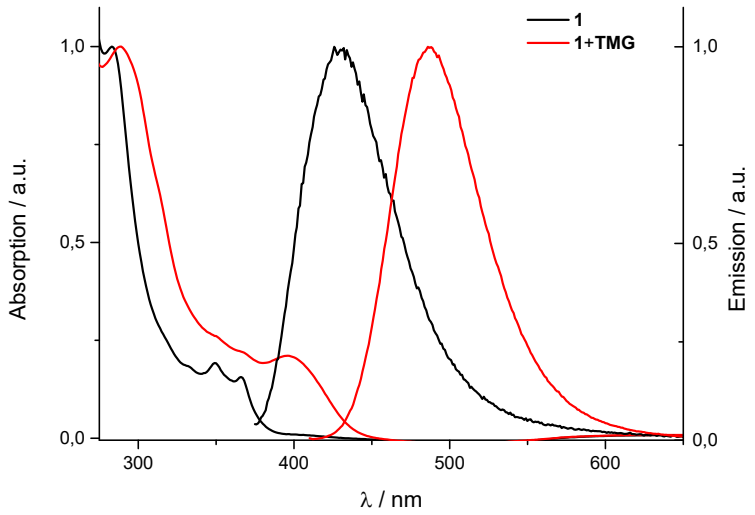


Figure S1. Normalized absorption and emission spectra of **1** (1.25×10^{-5} M) in DMF and upon the addition of **TMG** (1.25×10^{-3} M).

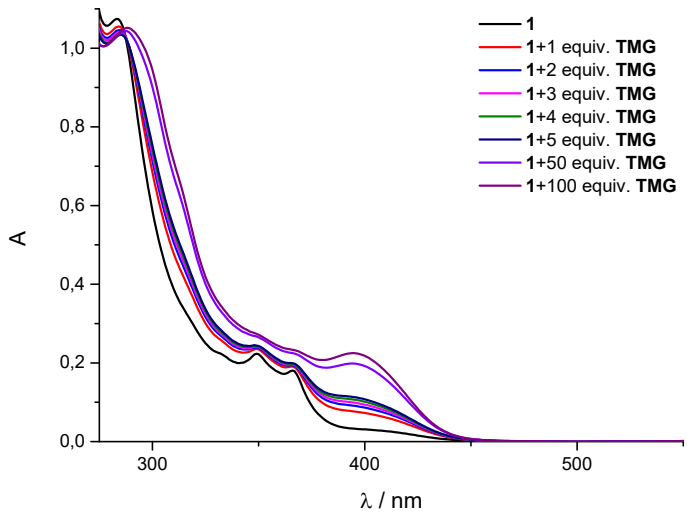


Figure S2. Absorption spectra of **1** (2×10^{-5} M) in DMF upon the addition of an increasing amount of **TMG**.

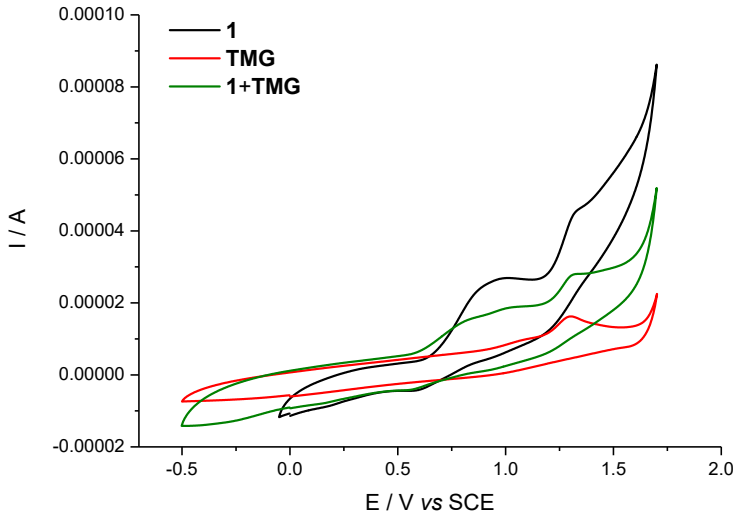


Figure S3. Cyclic voltammograms of **1** (1 mM), **TMG** (1 mM) and their mixture in DMF. Scan rates: 0.1 V s^{-1} (black line), $TBAPF_6$ (0.1 M) is used as a supporting electrolyte.

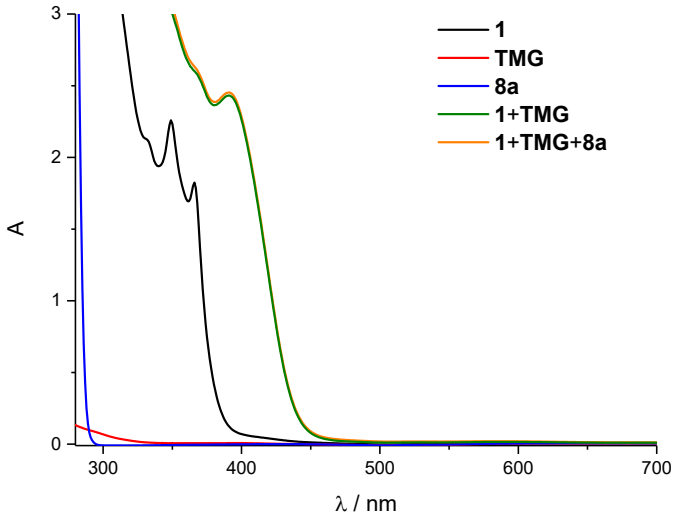


Figure S4. Absorption of **1** (2.5×10^{-4} M), **TMG** (0.025 M), **8a** (0.01 M) and relative mixtures in DMF.

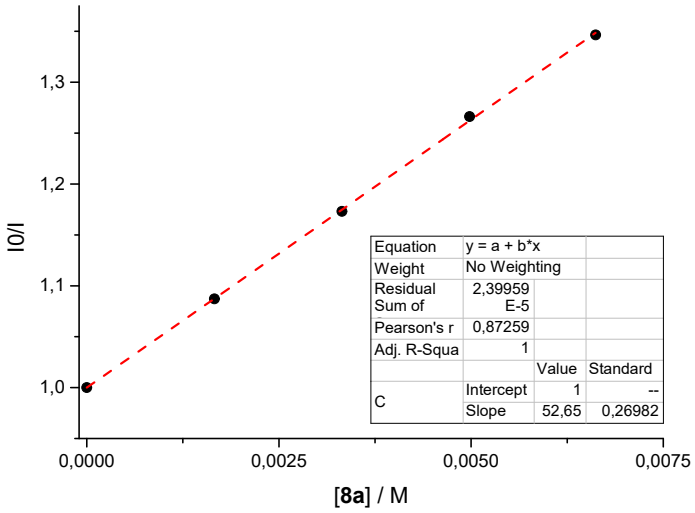


Figure S5. Stern-Volmer quenching study of **1** (3.6×10^{-5} M) and **TMG** (3.6×10^{-3} M) in DMF upon the addition of **8a** ($1.66\text{-}6.62 \times 10^{-3}$ M).

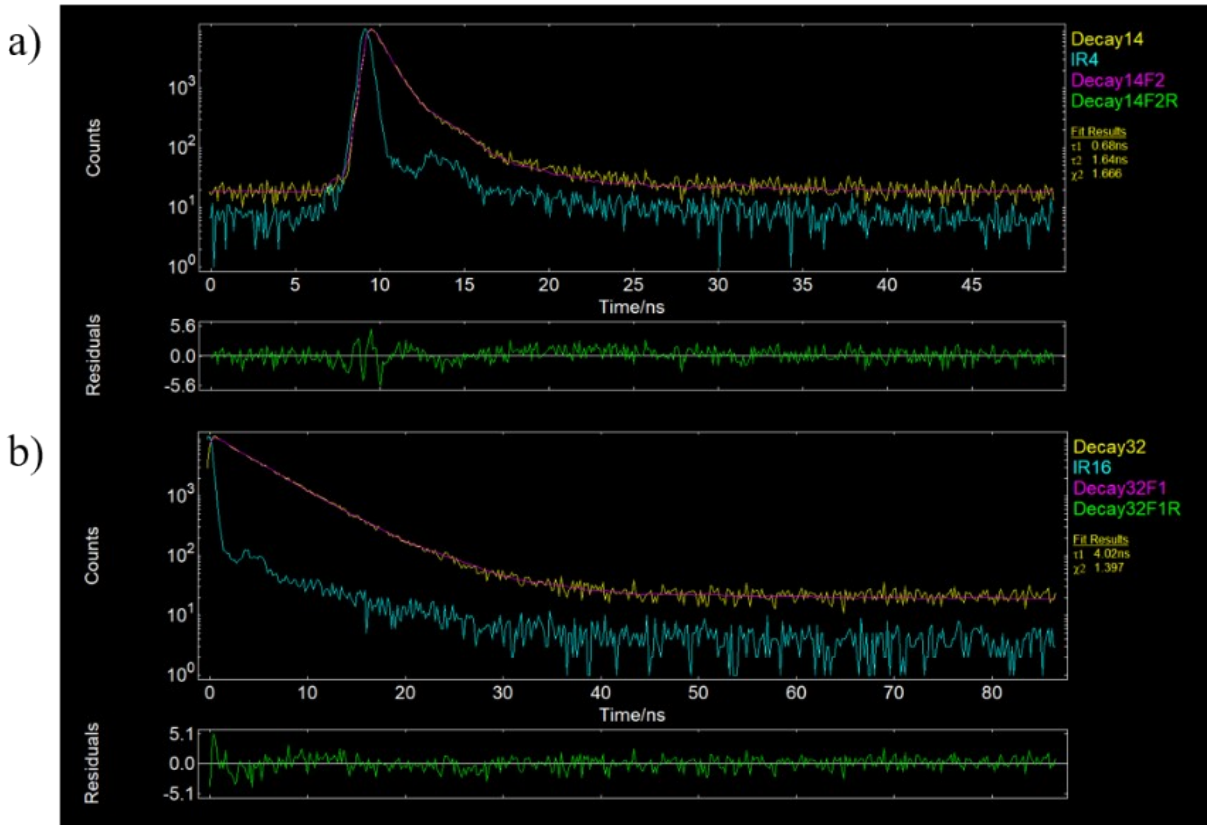


Figure S6. Emission lifetimes of a) **1** (1.25×10^{-5} M) in DMF and b) **1** upon the addition of **TMG** (1.25×10^{-3} M). The yellow curve corresponds to the sample fluorescence decay, the blue curve corresponds to the instrument response function and the magenta curve corresponds to the best fit, with their respective residuals (green line).

4. Procedures for photocatalytic experiments

4.1 General procedure for dehalogenation reaction

Non volatile substrates (4-halobenzonitrile, halogen= fluoro, chloro, bromo, iodo)

In a 5 mL glass screw cap vial equipped with a magnetic stirring bar the photocatalyst (**1**) (2.5 mol%, 2.50 μmol, 1.77 mg), aryl halide (1 equiv., 0.1 mmol) were added. Subsequently, degassed MeCN (1 mL) was introduced followed by tributylamine (5.0 equiv., 0.5 mmol, 92.65 mg, 120 μL) and 1,1,3,3-tetramethylguanidine (2.5 equiv., 0.25 mmol, 28.75 mg, 32 μL). The vial was sealed, and the resulting mixture was degassed by bubbling dry Ar through a syringe needle for 5 minutes. The vial was irradiated for 24 hours through a 427 nm Kessil Lamp. The temperature was kept at around 30°C by using a fan. To analyse the sample, an aliquot was taken, diluted and analysed by HPLC-UV as described in the paragraph 4.3.

Volatile substrates

A 10 mL Schlenk tube equipped with magnetic stirring bar was charged the photocatalyst (**1**) (2.5 mol%, 2.50 μmol, 1.77 mg), aryl halide (1 equiv., 0.1 mmol) were added. Subsequently, degassed MeCN (1 mL) was introduced followed by tributylamine (5.0 equiv., 0.5 mmol, 92.65 mg, 120 μL) and 1,1,3,3-tetramethylguanidine (2.5 equiv., 0.25 mmol, 28.75 mg, 32 μL) vial was sealed. The reaction mixture was thoroughly degassed via 3 cycles of freeze-pump-thaw, and the vessel was refilled with argon. The vial was irradiated for 24 hours through a 427 nm Kessil Lamp. The temperature was kept at around 30°C by using a fan. To analyse the sample, an aliquot was taken, diluted and analysed by HPLC-UV as described in the paragraph 4.3.

4.2 General procedure for the reaction of aryl halides with *N*-alkylpyrroles

A 10 mL Schlenk tube equipped with magnetic stirring bar was charged the photocatalyst (**1**) (20 mol%, 0.02 mmol, 14.2 mg), aryl halide (1 equiv., 0.1 mmol) and *N*-alkylpyrroles (20 equiv., 2.0 mmol) were added. Subsequently, degassed DMF (1 mL) was introduced followed by 1,1,3,3-Tetramethylguanidine (2.5 equiv., 0.25 mmol, 28.75 mg, 32 mL) and *N*,*N*-diisopropiletilamine (2.5 equiv., 0.25 mmol, 32.3 mg, 44 μL). The reaction mixture was thoroughly degassed via 3 cycles of freeze-pump-thaw, and the vessel was refilled with argon. The reaction vessel was irradiated for 24 h through a 427 nm Kessil Lamp. After the irradiation time, the reaction mixture was transferred to a separating funnel containing 15 mL of 0.1 M HCl brine solution and extracted 3 times with ethyl acetate (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product was achieved by flash column chromatography using Cyclohexane/Ethyl acetate as eluent.

4.3 HPLC Analysis of the reaction crude

The chemical yield for the dehalogenation reaction was quantified via HPLC analysis. Biphenyl was used as internal standard and spiked into the reaction crude from a DMSO stock solution. An aliquot of the resulting

solution (10 or 100 µL) was collected and diluted to 1 mL of acetonitrile. Before the injection, the sample was filtered through a 0.2 µm PTFE membrane. The samples were then analyzed as described in the methods section. Figures S6 shows sample chromatograms for the analyzed mixtures; while Figure S7 reports the calibration curves.

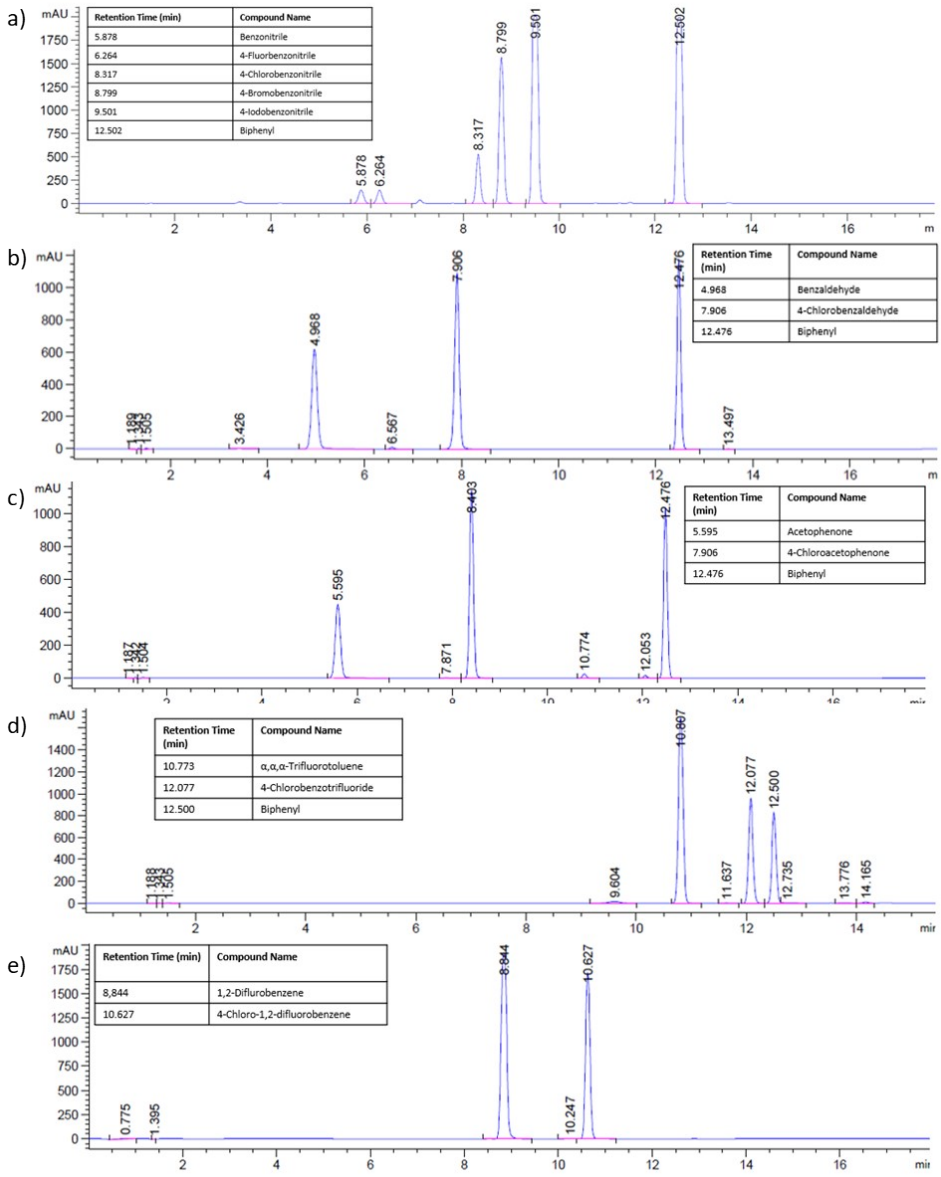


Figure S7. HPLC-UV chromatogram registered at 254 nm with a PoroShell 120 EC-C18 (4µm, 4.6 x 100 mm). a) mixture of Benzonitrile **9a**, 4-Fluorobenzonitrile **8b**, 4-Chlorobenzonitrile **8a**, 4-Bromobenzonitrile **8c** and internal standard; b) mixture of Benzaldehyde **9d** and 4-Chlorobenzaldehyde **8g**; c) mixture of acetophenone **9c** and 4-Chloroacetophenone **8f**; d) mixture of α,α,α-Trifluorotoluene **9b** and 4-Chlorobenzotrifluoride **8e**; e) mixture of 1,2-difluorobenzene **9e** and 4-chloro-1,2-difluorobenzene **8h**.

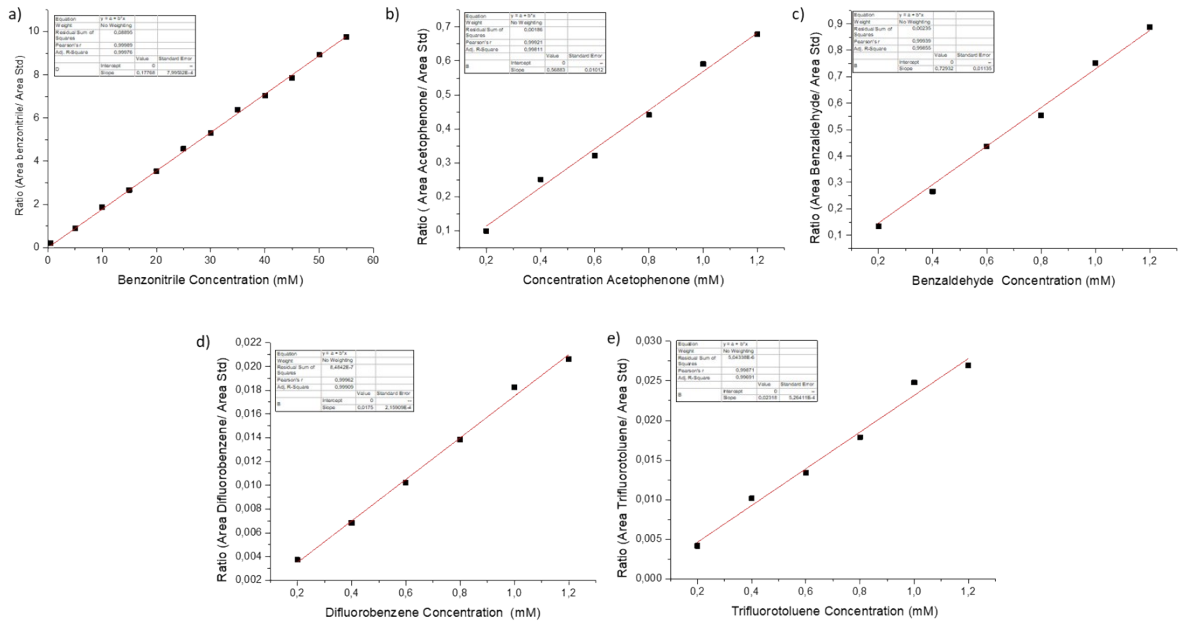
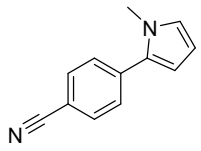


Figure S8. Internal standard calibration curve for: a) benzonitrile **9a**; b) acetophenone **9c**; c) benzaldehyde **9d**; d) difluorobenzene **9e**; e) Trifluorotoluene **9b**.

4.4 Spectral data for photocatalysis products

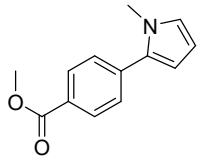


4-(1-methyl-1H-pyrrol-2-yl)benzonitrile (11a)

Prepared according to the general procedure using 4-Chlorobenzonitrile **8a** (0.1 mmol, 13.75 mg), and *N*-Methylpyrrole **10a** (20 mmol, 162 mg, 177 mL). The product **11a** was purified by flash chromatography (Hex/EtOAc) to afford a white solid. NMR Yield: 80%, Isolated yield: 76%, 13.8 mg. The characterization data matched with the reported one.[1]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.7 Hz, 2H), 7.57 – 7.45 (m, 2H), 6.78 (dd, *J* = 2.7, 1.8 Hz, 1H), 6.35 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.23 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.71 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 137.70, 132.62, 132.25, 128.28, 125.83, 119.03, 110.74, 109.69, 108.58, 35.45.

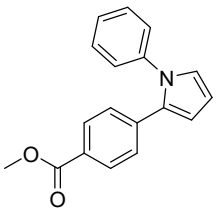


methyl 4-(1-methyl-1H-pyrrol-2-yl)benzoate (11b)

Prepared according to the general procedure using Methyl 4-bromobenzoate **8i** (0.1 mmol, 21.5 mg) and *N*-Methylpyrrole **10a** (20 mmol, 162 mg, 177 mL). The product **11b** was purified by flash chromatography (Hex/EtOAc) to afford the product as a white solid. NMR Yield: 45%, Isolated yield: 38%, 8.2 mg. The characterization data matched with the reported one.[1]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 6.76 (dd, *J* = 2.7, 1.8 Hz, 1H), 6.34 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.22 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.93 (s, 3H), 3.71 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.97, 137.74, 133.50, 129.74, 127.92, 127.86, 125.11, 110.03, 108.27, 52.09, 35.39.

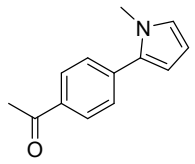


methyl 4-(1-phenyl-1H-pyrrol-2-yl)benzoate (11c)

Prepared according to the general procedure using Methyl 4-bromobenzoate **8i** (0.1 mmol, 21.5 mg) and *N*-phenylpyrrole **10b** (20 mmol, 286.3 mg). The product **11c** was purified by flash chromatography (Hex/EtOAc) to afford the product **11c** as a white solid. NMR Yield: 61%, Isolated yield: 58%, 16.1 mg. The characterization data matched with the reported one.[2]

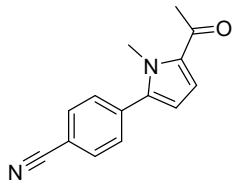
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.37 – 7.29 (m, 3H), 7.21 – 7.14 (m, 4H), 6.98 (dd, *J* = 2.8, 1.7 Hz, 1H), 6.55 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.39 (dd, *J* = 3.6, 2.8 Hz, 1H), 3.88 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.97, 140.28, 137.36, 132.69, 129.41, 129.20, 127.62, 127.48, 126.99, 125.74, 125.72, 112.05, 109.65, 51.99.



1-(4-(1-methyl-1H-pyrrol-2-yl)phenyl)ethan-1-one (11d)
Prepared according to the general procedure using 4'-Chloroacetophenone **8f** (0.1 mmol, 15.4 mg, 13 mL) and *N*-Methylpyrrole **10a** (20 mmol, 162 mg, 177 mL). The product **11d** was purified by flash chromatography (Hex/EtOAc) to afford the product as a white solid. NMR Yield: 26%, Isolated yield: 22%, 4.4 mg. The characterization data matched with the reported one.[3]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.56 – 7.36 (m, 2H), 6.77 (dd, *J* = 2.7, 1.8 Hz, 1H), 6.35 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.23 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.72 (s, 3H), 2.62 (s, 3H).
^{13}C-NMR (101 MHz, $CDCl_3$) δ 197.59, 137.92, 134.92, 133.40, 128.59, 127.95, 125.32, 110.22, 108.36, 35.44, 26.57.



4-(5-acetyl-1-methyl-1H-pyrrol-2-yl)benzonitrile (11e)
Prepared according to the general procedure using 4-Chlorobenzonitrile **8a** (0.1 mmol, 13.75 mg) and 2-Acetyl-1-methylpyrrole **10c** (20 mmol, 246.3 mg, 237 mL). The product **11e** was purified by flash chromatography (Hex/EtOAc) to afford the product a white solid.
NMR Yield: 41%, Isolated yield: 37%, 8.3 mg. The characterization data matched with the reported one.[4]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.53 – 7.51 (m, 2H), 7.04 (dd, *J* = 4.1, 1.1 Hz, 1H), 6.29 (dd, *J* = 4.1, 1.1 Hz, 1H), 3.89 (s, 3H), 2.49 (s, 3H).
^{13}C-NMR (101 MHz, $CDCl_3$) δ 189.08, 140.58, 136.43, 132.51, 132.17, 129.86, 119.79, 118.65, 111.96, 110.53, 35.52, 27.68.

5. NMR and HRMS spectroscopic characterization

5.1 Derivative 4

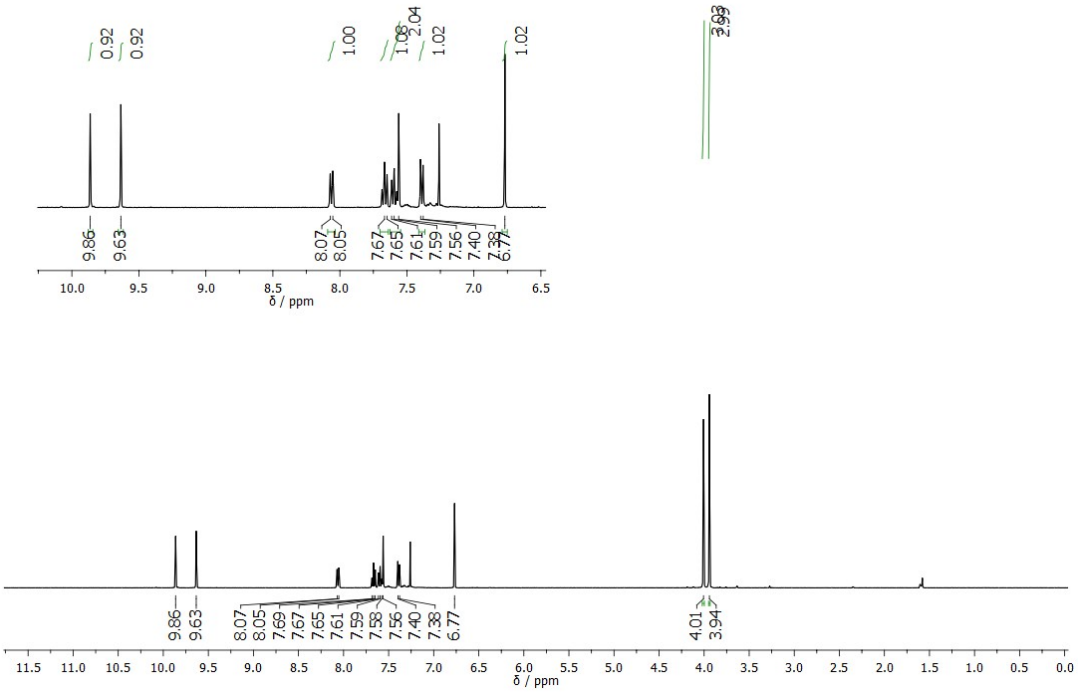


Figure S9. 400 MHz ^{1}H-NMR of **4** in $CDCl_3$.

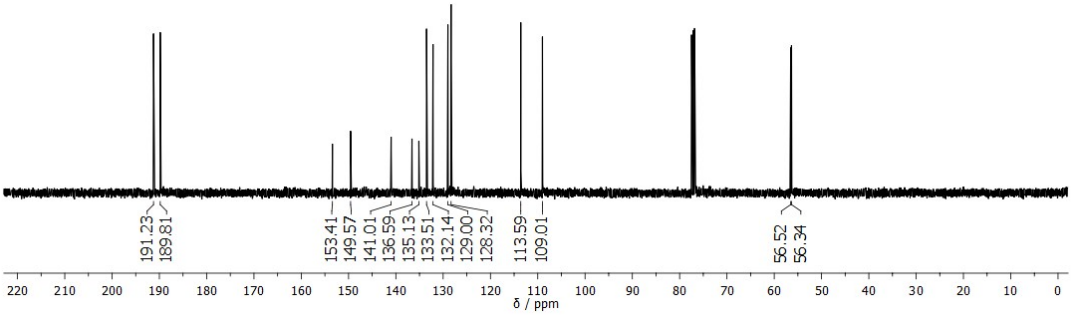


Figure S10. 101 MHz ^{13}C-NMR of **4** in $CDCl_3$.

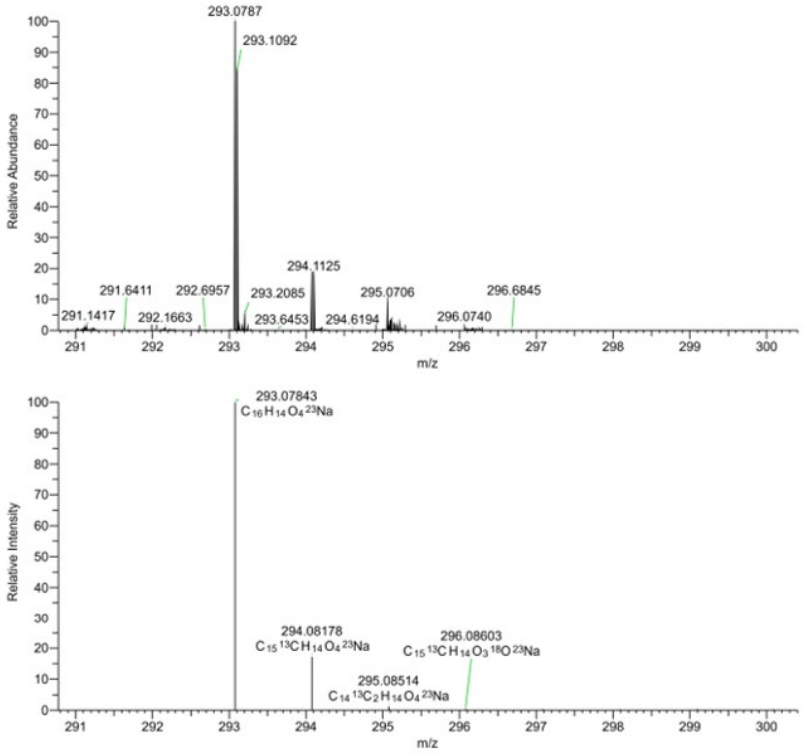


Figure S11. ESI-HRMS of **4**.

5.2 Derivative 5

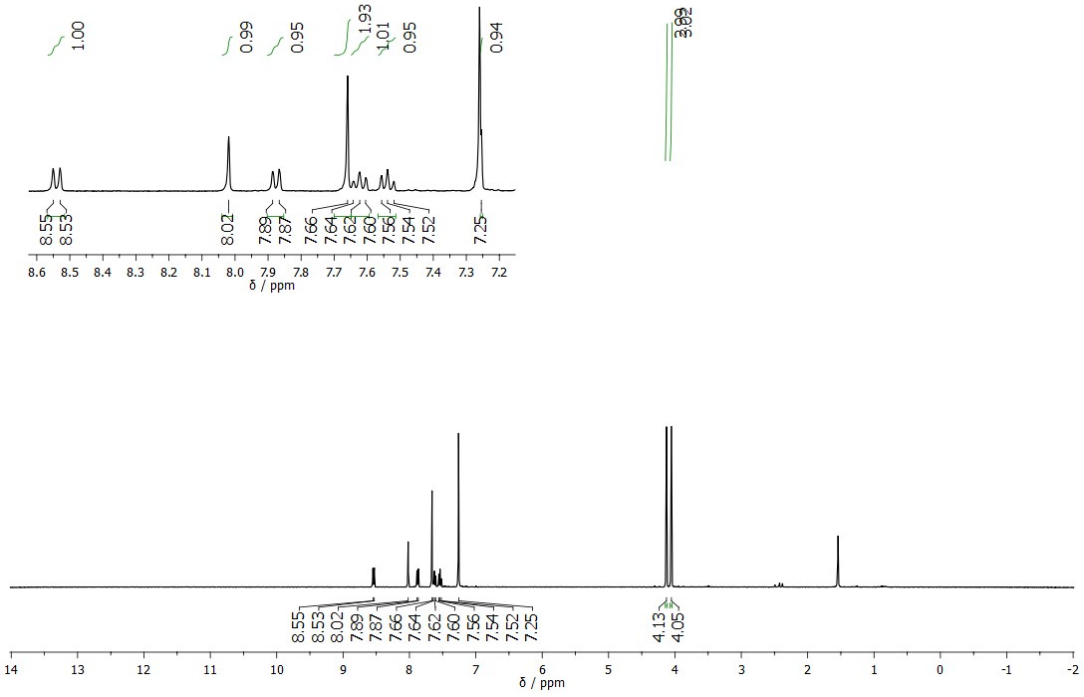


Figure S12. 400 MHz ^{1}H-NMR of **5** in $CDCl_3$.

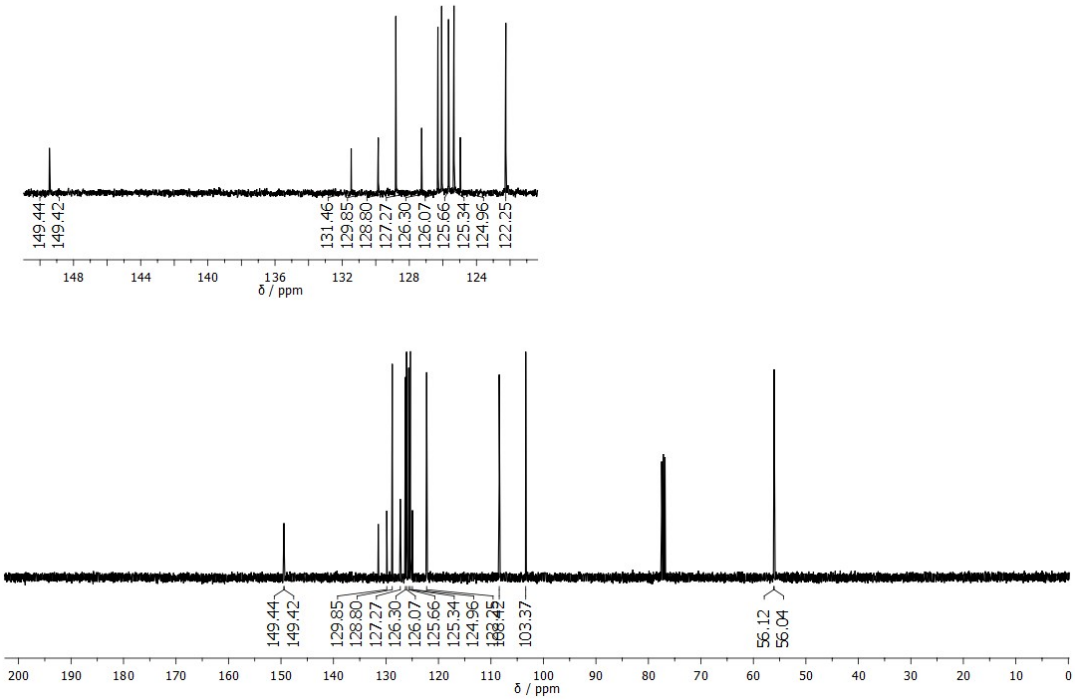


Figure S13. 101 MHz ^{13}C-NMR of **5** in $CDCl_3$.

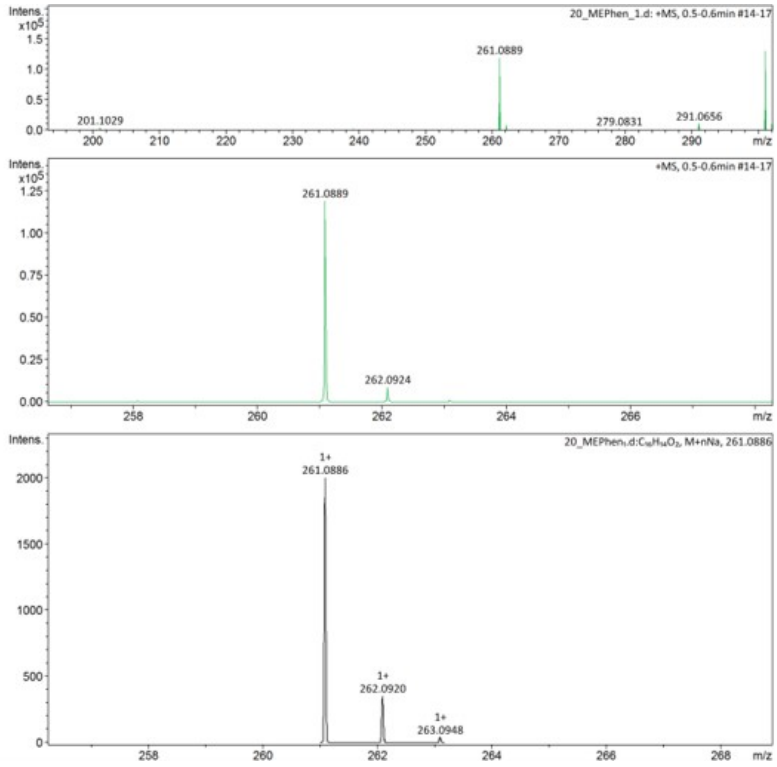


Figure S14. ESI-HRMS of **5**.

5.3 Derivative 6

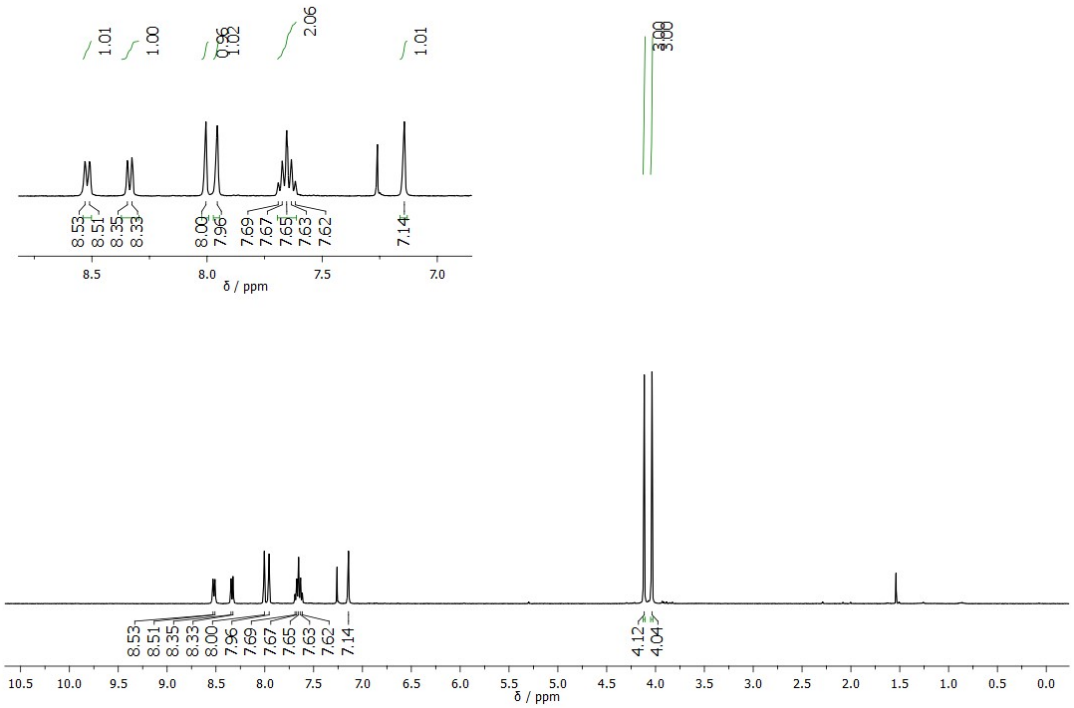


Figure S15. 400 MHz ^{1}H-NMR of **6** in $CDCl_3$.

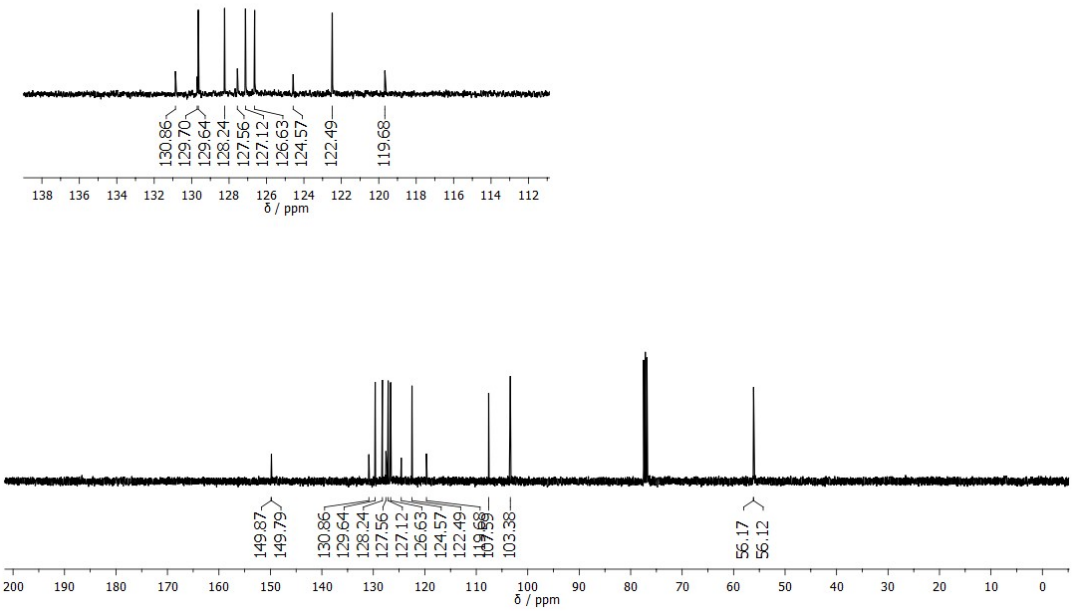


Figure S16. 101 MHz ^{13}C-NMR of **6** in $CDCl_3$.

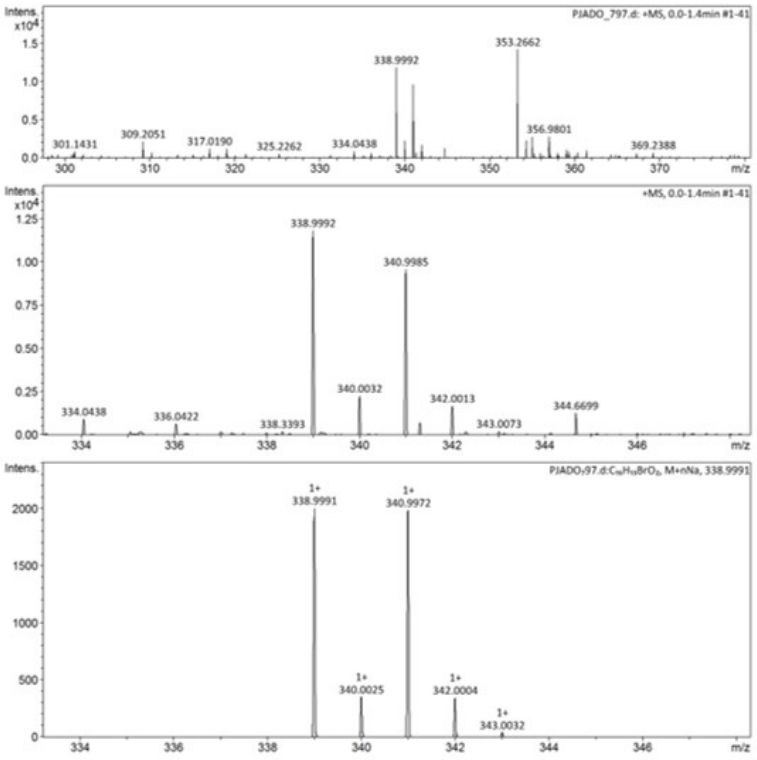


Figure S17. ESI-HRMS of **6**.

5.4 Derivative 7

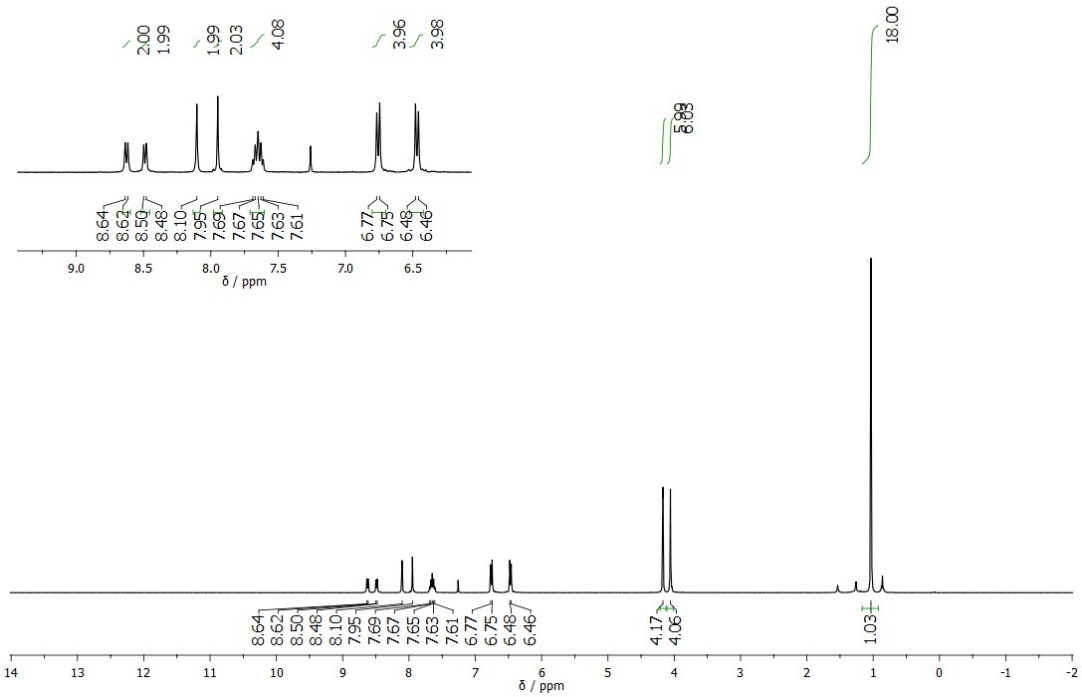


Figure S18. 400 MHz ^{1}H-NMR of **7** in $CDCl_3$.

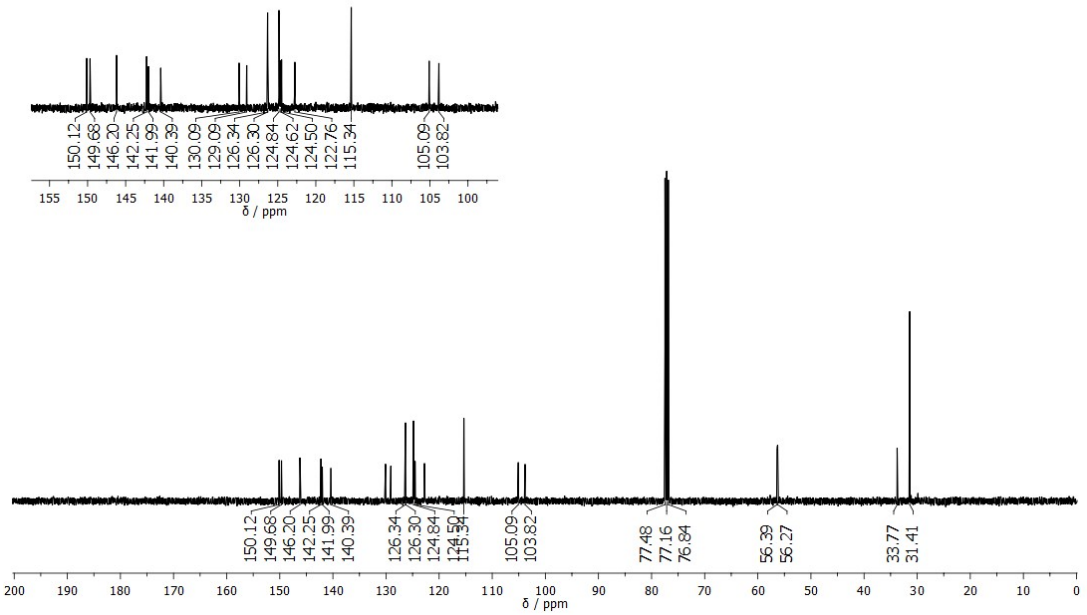


Figure S19. 101 MHz ^{13}C-NMR of **7** in $CDCl_3$.

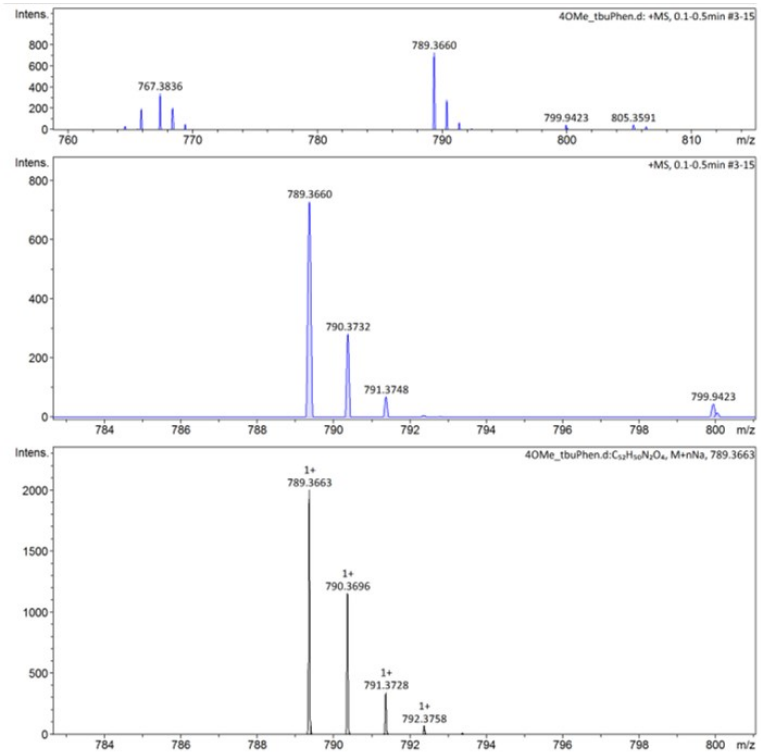


Figure S20. ESI-HRMS of **7**.

5.5 Derivative 1

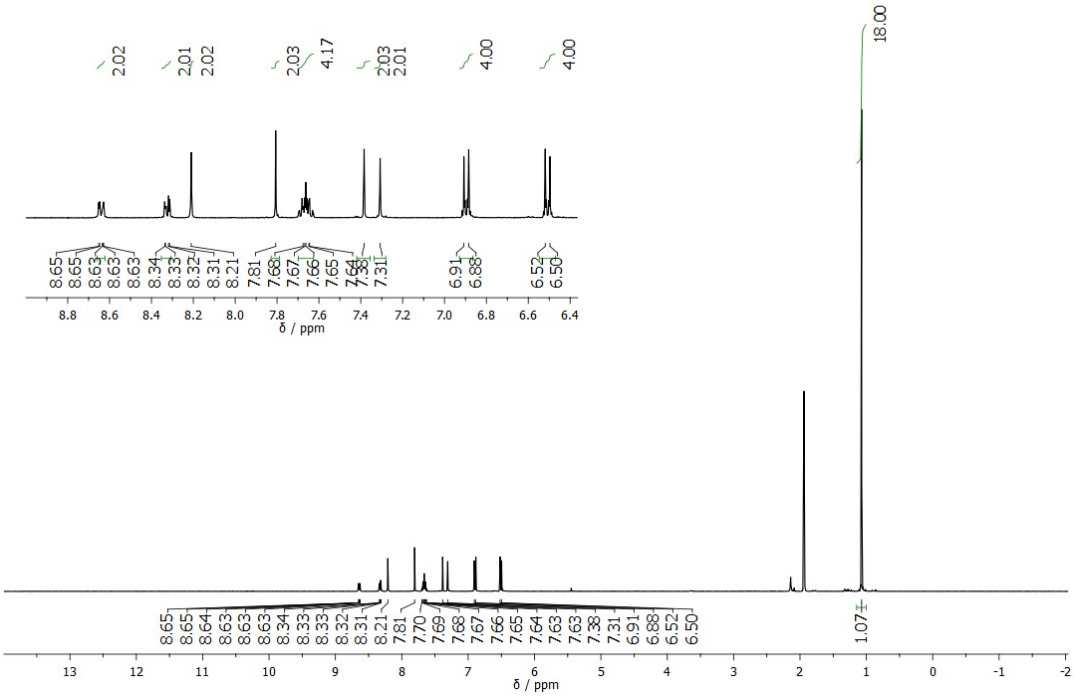


Figure S21. 400 MHz ^{1}H-NMR of **1** in CD_3CN.

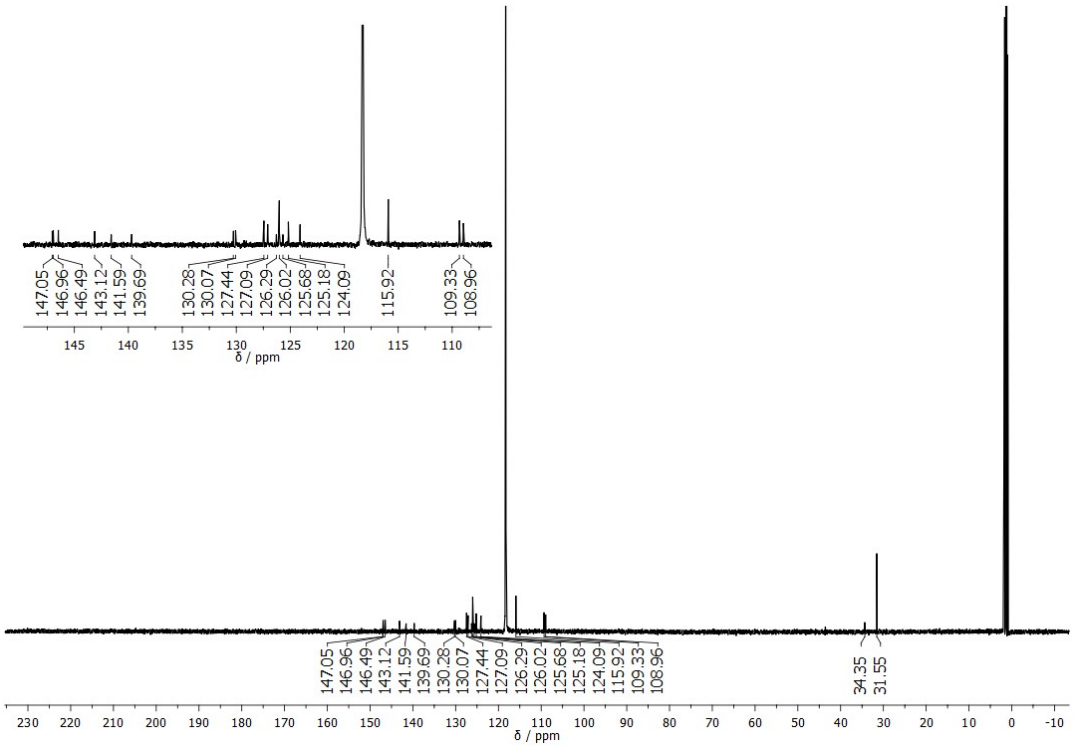


Figure S22. 126 MHz ^{13}C-NMR of **1** in CD_3CN.

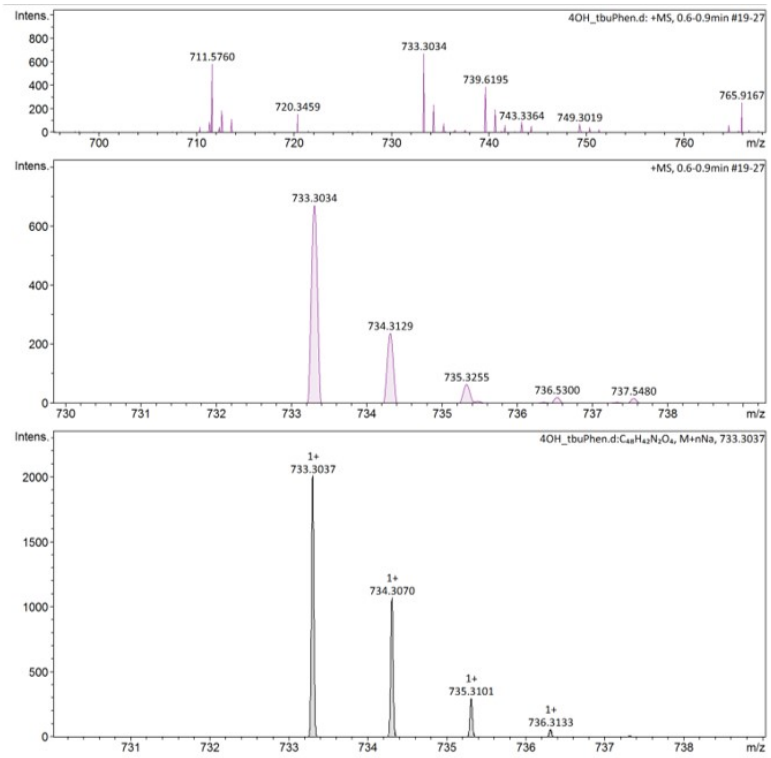


Figure S23. ESI-HRMS of **1**.

5.6 ^{1}H- and ^{13}C-NMR spectra of scope entries 11a-e

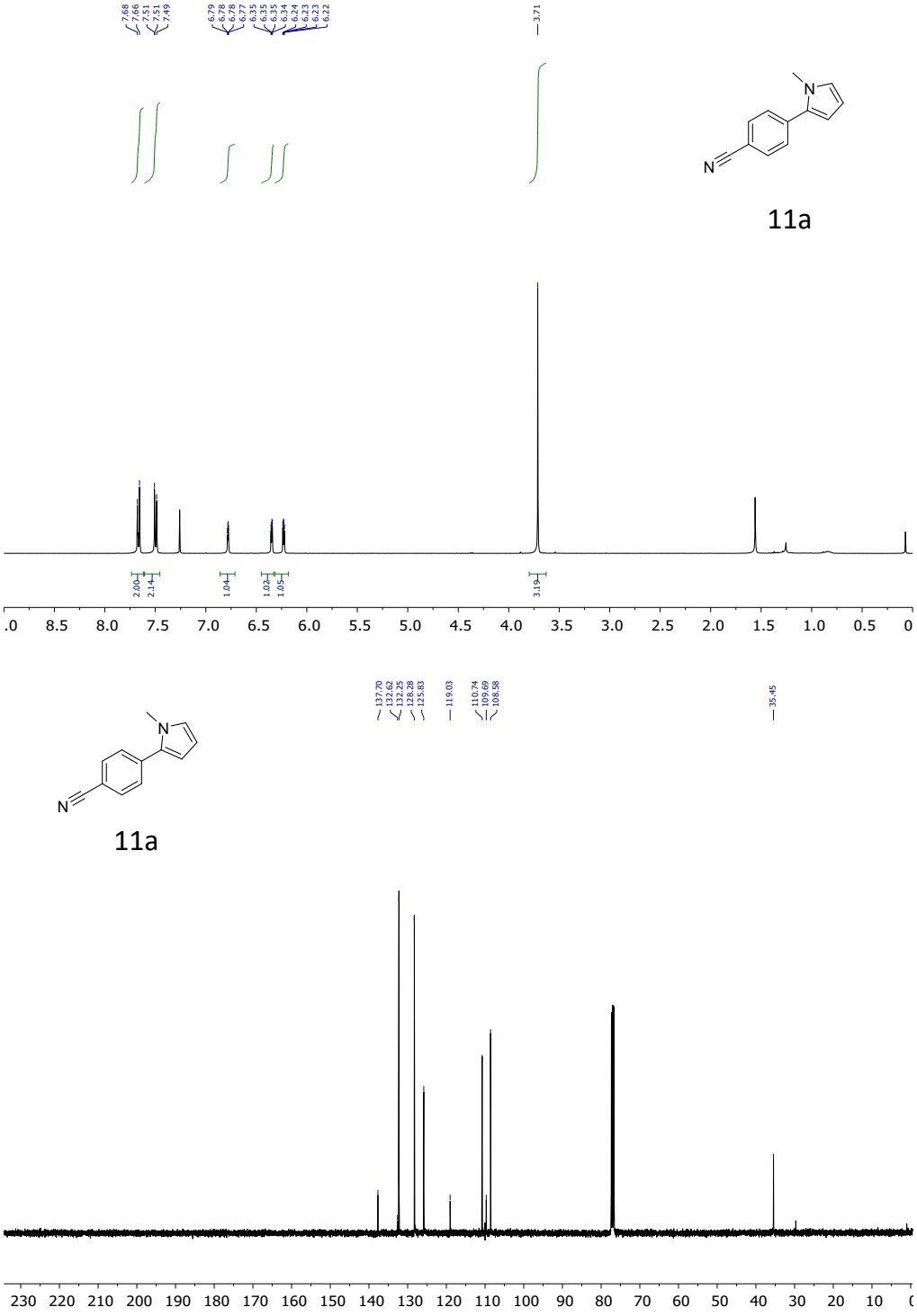


Figure S24. ^{1}H-NMR and ^{13}C-NMR of **11a** in $CDCl_3$.

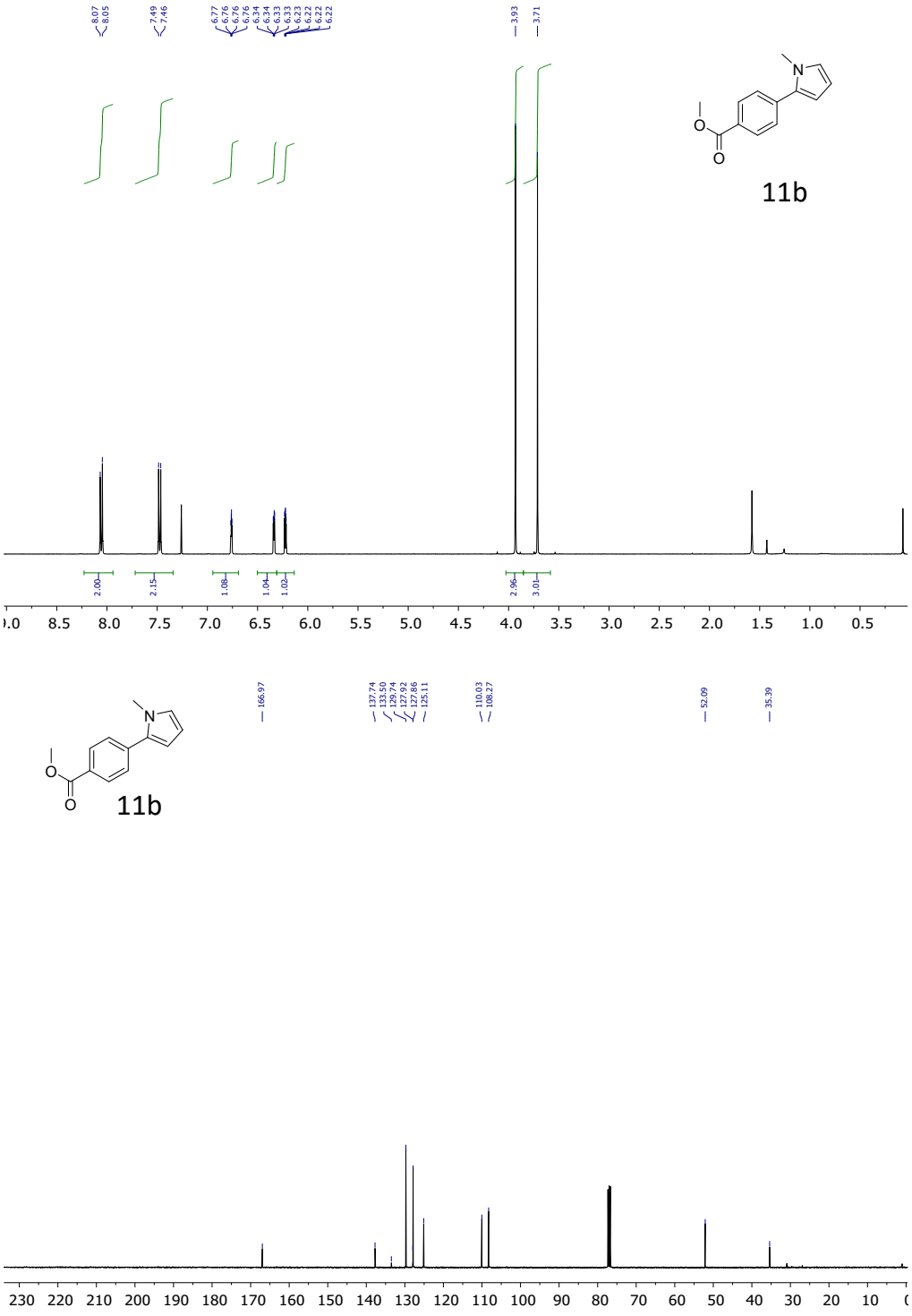


Figure S25. ^{1}H-NMR and ^{13}C-NMR of **11b** in $CDCl_3$.

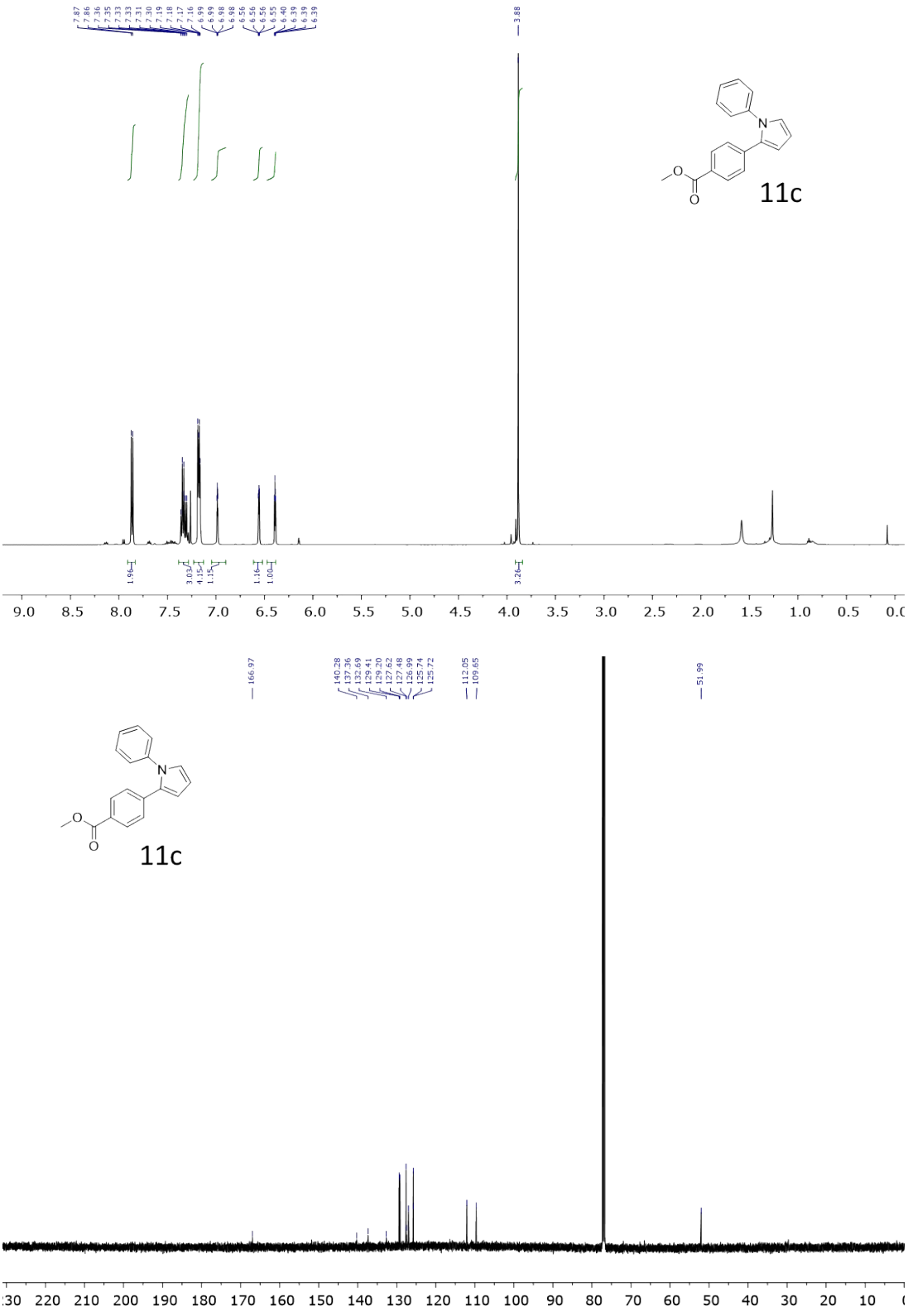


Figure S26. ^{1}H-NMR and ^{13}C-NMR of **11c** in $CDCl_3$.

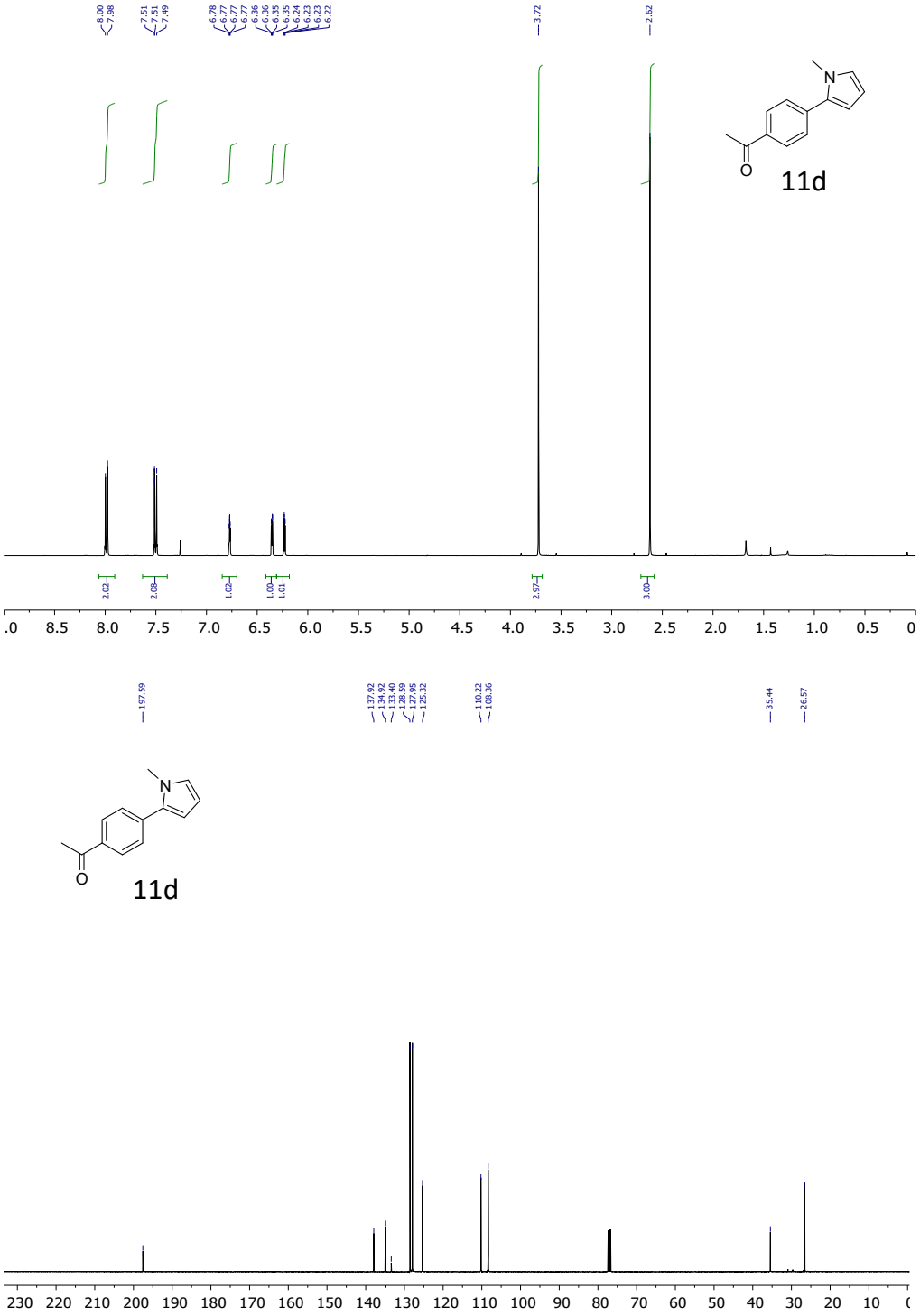


Figure S27. ^{1}H-NMR and ^{13}C-NMR of **11d** in $CDCl_3$.

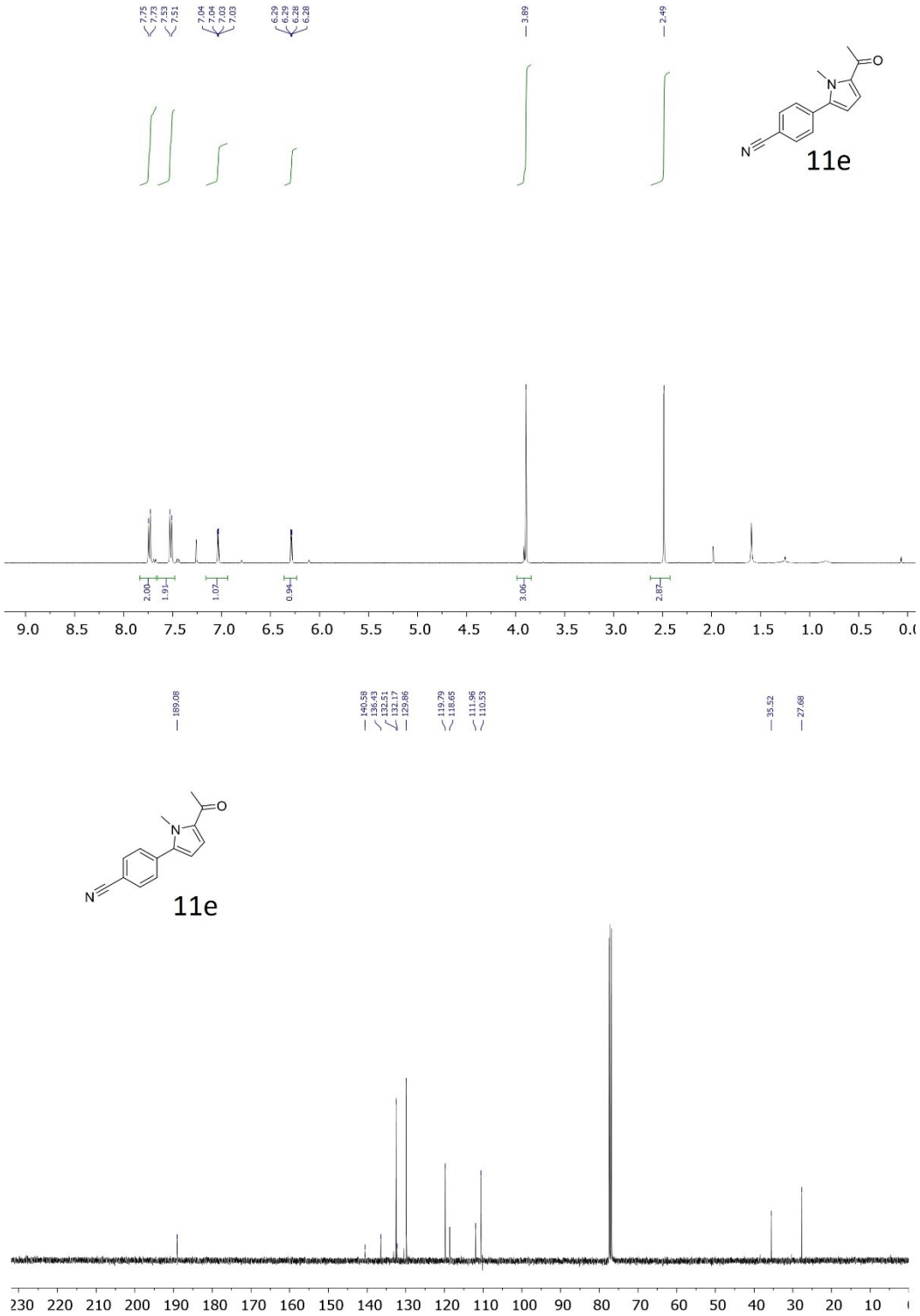


Figure S28. ^{1}H-NMR and ^{13}C-NMR of **11e** in $CDCl_3$.

6. XRD analysis of 7

Data collections were performed at the XRD2 beamline of the Elettra Synchrotron, Trieste (Italy).[5] The crystals were dipped in NHV oil (Jena Bioscience, Jena, Germany) and mounted on the goniometer head with kapton loops (MiTeGen, Ithaca, USA). Complete datasets were collected at 100 K (nitrogen stream supplied through an Oxford Cryostream 700) through the rotating crystal method. Data were acquired using monochromatic wavelength of 0.620 Å on Pilatus hybrid-pixel area detector (DECTRIS Ltd., Baden-Daettwil, Switzerland). The diffraction data were indexed, integrated and scaled using XDS.[6] The structures were solved by the dual space algorithm implemented in the SHELXT code.[7] Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F^2 implemented in SHELXL (Version 2018/3).[8] Coot program was used for modeling.[9] Anisotropic thermal motion refinement have been used for all atoms. Hydrogen atoms were included at calculated positions with isotropic $U_{factors} = 1.2 \bullet U_{eq}$ or $U_{factors} = 1.5 \bullet U_{eq}$ for methyl groups (U_{eq} being the equivalent isotropic thermal factor of the bonded non-hydrogen atom). Pictures were prepared using Ortep-3[10] and Pymol[11] software. Essential crystal and refinement data are reported below (Table S1).

Crystals of **7** show half crystallographic independent molecule in the asymmetric unit (ASU) and full molecular moieties are generated through crystallographic binary axis (Figure S28). **7** molecules are perfectly superimposable with related π-extended neutral phenazine compounds previously published[12] (Figure S29). Crystal packing for **7** show extensive hydrophobic interactions with π•••π stacking of phenanthrene moieties (e.g. $d_{\pi\cdots\pi}$ = 3.712(1) Å with 1.48 Å slippage between ring centroids) and CH•••π contacts (e.g. $d_{CH\cdots\pi}$ = 3.433(2) Å with 78° between CH and π-plane). No solvent molecules have been found in the crystal packing.

Table S1. Crystallographic data and refinement details for compound **7**.

	7
CCDC Number	**2299130**
Chemical Formula	$C_{52}H_{50}N_2O_4$
Formula weight	766.94 g/mol
Temperature	100(2) K
Wavelength	0.620 Å
Crystal system	Monoclinic
Space Group	*C* 2/*c*
Unit cell dimensions	*a* = 19.961(4) Å *b* = 14.527(3) Å *c* = 16.049(3) Å *α* = 90° *β* = 118.68(3)° *γ* = 90°
Volume	4082.7(17) Å^3
Z	4
Density (calculated)	1.248 g·cm^{-3}
Absorption coefficient	0.060 mm^{-1}
F(000)	1632
Theta range for data collection	1.6° to 31.1°
Index ranges	-30 ≤ h ≤ 29, -23 ≤ k ≤ 23, -26 ≤ l ≤ 26
Reflections collected	47689
Independent reflections (data with I>2σ(I))	8858 (5156)
Resolution	0.60 Å
Data multiplicity (max resltn)	4.75 (2.80)
I/σ(I) (max resltn)	9.49 (2.35)
R_{merge} (max resltn)	0.0711 (0.3557)
Data completeness (max resltn)	89.1% (73.3%)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8858 / 0 / 267
Goodness-of-fit on F^2	1.029
Δ/σ_{max}	0.000
Final R indices [I>2σ(I)]	R_1 = 0.0685, wR_2 = 0.1861
R indices (all data)	R_1 = 0.1200, wR_2 = 0.2201
Largest diff. peak and hole	0.477 and -0.299 eÅ^{-3}
R.M.S. deviation from mean	0.066 eÅ^{-3}

$R_1 = \Sigma \, ||Fo|-|Fc|| \, / \, \Sigma \, |Fo|$, $wR_2 = \{\Sigma \, [w(Fo^2 - F4)^2] \, / \, \Sigma \, [w(Fo^2)^2]\}^{½}$

Figure S29. Top) Ellipsoids representation of **7** molecule (50% probability); bottom) Hydrogens omitted for clarity.

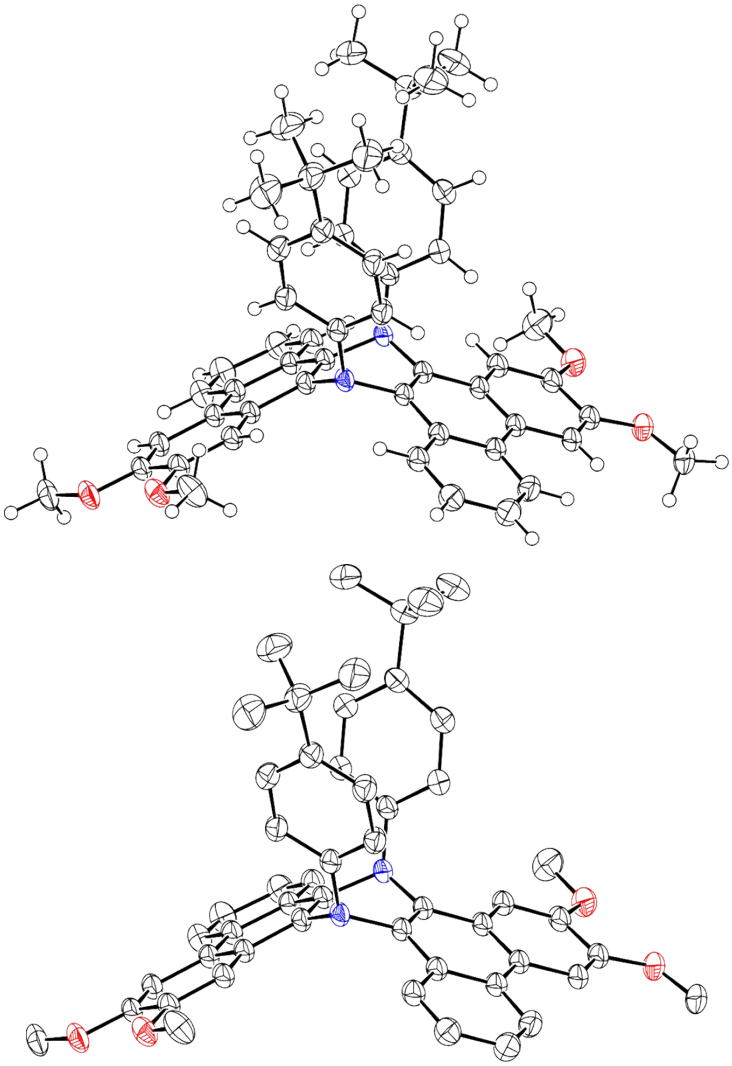
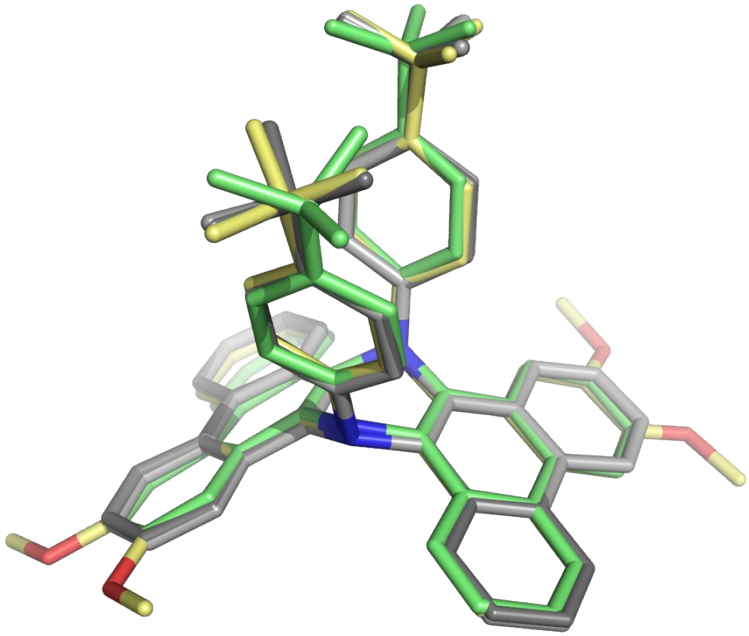


Figure S30. Stick representation for overlapped molecular models of **7** (yellow sticks), CCDC **2129306** and CCDC **2129307**[12] (green and grey sticks); R.M.S.D. ~0.5 Å.



7. References

1 N. G. W. Cowper, C. P. Chernowsky, O. P. Williams and Z. K. Wickens, *J. Am. Chem. Soc.*, 2020, **142**, 2093–2099.

2 Y. X. Liu, D. Xue, J. Di Wang, C. J. Zhao, Q. Z. Zou, C. Wang and J. Xiao, *Synlett*, 2013, **24**, 507–513.

3 G. Sun, S. Ren, X. Zhu, M. Huang and Y. Wan, *Org. Lett.*, 2016, **18**, 544–547.

4 B. Yiğit, N. Gürbüz, M. Yiğit, Z. Dağdeviren and İ. Özdemir, *Inorganica Chim. Acta*, 2017, **465**, 44–49.

5 A. Lausi, M. Polentarutti, S. Onesti, J. R. Plaisier, E. Busetto, G. Bais, L. Barba, A. Cassetta, G. Campi, D. Lamba, A. Pifferi, S. C. Mande, D. D. Sarma, S. M. Sharma and G. Paolucci, *Eur. Phys. J. Plus*, 2015, **130**, 2–8.

6 W. Kabsch, *Acta Crystallogr. Sect. D Biol. Crystallogr.*, 2010, **66**, 125–132.

7 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

8 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2015, **71**, 3–8.

9 P. Emsley, B. Lohkamp, W. G. Scott and K. Cowtan, *Acta Crystallogr. Sect. D Biol. Crystallogr.*, 2010, **66**, 486–501.

10 L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849–854.

11 L. L. C. Schröedinger, *PyMOL Mol. Graph. Syst. http//www.pymol.org*.

12 J. Dosso, B. Bartolomei, N. Demitri, F. P. Cossío and M. Prato, *J. Am. Chem. Soc.*, 2022, **144**, 7295–7301.