

Supporting Information

Controlling Structural and Photophysical Properties in Sequentially Methylated Phenoxazines

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1 GENERAL INFORMATION AND CONCEPT

Chemicals and synthesis

Commercially available chemicals were purchased from distributors *Deutero*, *TCI*, *Sigma Aldrich*, *abcr*, *Acros Organics*, *BLD Pharm*, or *Fisher Scientific* and used without further purification. Potassium carbonate and potassium phosphate were dried at 90 °C. *n*-Pentane used for chromatography was of technical grade and distilled before use. MilliQ water was obtained through purification by *MicroPure ultrapure*-System from TKA. Sensitive reactions were performed under an argon atmosphere using dried solvents and flame-dried glassware. Sonications were conducted using *Sonorex SUPER RK 514 BH* from Bandelin Electronics. The final compounds were freeze-dried using the *ALPHA 1-2* from Christ. For this, dispersions of the compounds in distilled water were frozen in liquid nitrogen under rotation.

Chromatography

Reaction monitoring was performed using thin-layer chromatography (TLC) using *POLYGRAM® SIL G/UV254* plates (0.2 mm) from *Macherey-Nagel*. Spots were visualized using a UV-hand lamp (254 nm, 365 nm, and 395 nm) from *Herolab* or *AHOME*. Flash-column chromatographic separations were carried out under argon on silica gel *MN 60 M* (40–63 µm) from *Macherey-Nagel*. For this, the crude materials were dry-mounted on *Celite® 545* from *Sigma Aldrich*. The purity of the target compounds was determined using analytical high-performance liquid chromatography (HPLC) using a *NUCLEODUR 100-5* normal-phase column (inner diameter 4.6 mm, length 250 mm, silica gel, particle size 5 µm) from *Macherey Nagel*. Two different setups were used: setup 1 was used as mentioned before¹ and consists of a *Gastorr AG-32* degasser, binary *Waters 1525 pump* with a flow of 1 mL/min, a *Waters 717plus autosampler* and a *Waters 2487 UV/Vis detector* (270 nm). Setup 2 consists of a *Hitachi Chromaster* HPLC system, including an organizer, a *5160 pump* with a flow rate of 1.3 mL/min, a *5280 autosampler*, a *5310 column oven* (set to 25 °C), and a *5420 UV/Vis detector* (monitored at 270 nm). All chromatograms were analyzed using the software *OriginPro* (2023) by *OriginLab Corporation*. HPLC-grade *n*-hexane and ethyl acetate were used with the gradient run *n*-hexane/ethyl acetate 90/10 → 0/100 over 35 min or *n*-hexane/ethyl acetate 98/2 → 0/100 over 35 min. The samples were dissolved in DCM (approximately 1 mM) and filtered using a syringe filter (0.22 µm, PTFE).

General analytical methods

NMR spectra were recorded at room temperature using the *AVNEO400* or *AVANCE III* (¹H: 400 MHz or 600 MHz, ¹³C: 101 MHz or 151 MHz, ¹⁹F: 376 MHz or 565 MHz) spectrometer from *Bruker* and analyzed with *MestReNova v15.01-35756* from *Mestrelab Research S.L.* Additionally, ¹H- and ¹⁹F-decoupled ¹³C-NMR spectra were obtained using the *JEOL400* spectrometer from *JEOL GmbH*. Analytical data are given with the respective frequency, solvent, temperature, chemical shift δ [ppm], multiplicity, integral, and assignment. The fine structure is abbreviated with s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = triplet of doublet, br = broad, ps = pseudo. Coupling constants $^nJ_{XY}$ are given in Hertz [Hz]. Here, *n* describes the number of bonds between coupling nuclei X and Y. For internal referencing, the residual proton signals of CDCl₃ (¹H: 7.26 ppm, ¹³C: 77.16 ppm), CD₂Cl₂ (¹H: 5.32 ppm, ¹³C: 53.84 ppm), acetone-*d*₆ (¹H: 2.05 ppm, ¹³C: 206.26 ppm, 29.84 ppm), or DMSO-*d*₆ (¹H: 2.50 ppm, ¹³C: 39.52 ppm) were used. Signals were assigned using conventional 2D-NMR methods (HSQC, HMBC, COSY). High-resolution mass spectra were recorded on a *Bruker maxis 4G (Q-TOF)* via electrospray-ionization. Samples were dissolved in acetone or dichloromethane and injected via flow-injection. FT-IR spectra were measured on a *FT/IR-4600* (*Jasco*). For this, concentrated DCM solutions of the compounds were drop-casted. Melting points were determined using a *BÜCHI B-540*.

Optical spectroscopy

UV-Vis spectra were measured on a *UV-2700 UV/Vis* double-beam, double-monochromator spectrophotometer from *Shimadzu Corporation* with baseline correction. Both monochromators use 1200 lines mm⁻¹ holographic gratings. A slit width of 2 nm with a data interval of 1 s/nm (high scan speed) was selected.

Excitation and emission spectra were recorded on an *RF-6000* spectrometer from *Shimadzu Corporation*. Diluted samples were prepared in the *Semi-Micro* quartz cuvettes (1.4 mL, 10x4 mm) from *Hellma Analytics*. Solid samples were placed between two quartz glass slides in 45° orientation to the excitation and emission slits. Appropriate long-pass filters (*Shimadzu Corporation*, *Edmund Optics GmbH*) were used to suppress the lamp signals. Measurements were conducted at room temperature. Slit widths of 5 nm with scan speeds of 2000 nm/min were used. The setup employed 600 lines mm⁻¹ blazed gratings at 500 nm.

Absolute photoluminescence (PL) quantum yields were measured with the *Quantaaurus-QY*® absolute PL quantum yield spectrometer C11347-11 by *Hamamatsu Photonics* equipped with a 3.3-inch Spectralon-coated integrating sphere, Czerny-Turner monochromator, continuous wave xenon light source (150 W), and a photonic multi-channel analyzer for simultaneous spectral acquisition. The data were acquired and analyzed using the U6039-05 software (*Hamamatsu Photonics*, Ltd., Shizuoka, Japan) with transmission and self-absorption corrections. Fluid samples were prepared in round quartz cuvettes, and solids were measured using quartz sample holders. The appropriate blank solvent or empty quartz sample holders were used for blank measurements. The instrument's internal spectral correction and RI calibration were applied according to the manufacturer's procedure. As excitation wavelengths, λ_{ex} = 400 nm (CH), 410 nm (DCM, MeOH, powders), or 420 nm (CCl₄, THF, aggregates, MeCN) were used. Each measurement was repeated five times, and the average value was reported with a relative deviation of 5%.

Time-resolved photoluminescence measurements were recorded on a *FluoTime 300* spectrometer from *PicoQuant* equipped with pulsed diode lasers (pulse widths <80 ps), operated by the computer-controlled laser driver PDL-820 "*Sepia II*", which allows repetition rates up to 80 MHz and burst mode operation for resolving slow and weak decay components. The system consists of a two double-grating emission monochromator (Bentham MSH300) with interchangeable gratings (blazed at 500 nm with 2.7 nm/mm dispersion and 1200 lines/mm, or blazed at 1200 nm with 5.4 nm/mm dispersion and 600 lines/mm) with adjustable slit widths between 25 μ m and 7 mm. The polarization of emission was controlled using Glan-Thompson polarizers placed after the sample. Depending on the experiment, appropriate sample holders were used, including a QNW TLC 50-cooled mounting unit with temperature control or a front-face adjustable sample holder for solid-state samples. Detection was performed using a PMA Hybrid-50 detector with transit time spread FWHM < 160 ps and a spectral range from 380–890 nm. Data acquisition was conducted in time-correlated single-photon counting (TCSPC) mode using a TH260 Pico module (base resolution down to 4 ps), and in multi-channel scaling (MCS) mode using a TimeHarp 260 (for long-lived species). The instrument response function (IRF) was determined using a diluted *Ludox*® dispersion. Data analysis was performed using the *EasyTau 2* software (*PicoQuant*). The quality of the fit was evaluated based on chi-squared (χ^2) values, reduced weighted residuals, and their respective autocorrelation plots. For data analysis and visualization, *OriginPro 2023* (*OriginLab*™) was used. CIE coordinates were constructed using an *OriginLab*™ Plugin (Chromaticity Diagram, File Version 1.20, License: Free). Radiative and non-radiative rate constants k_r and k_{nr} were reported using amplitude-weighted average lifetimes.

Photographs

Photographs of the samples were taken with a *Canon EOS R10* with a *Canon 18-150* lens.

2 SYNTHETIC PROCEDURES

GENERAL PROCEDURES

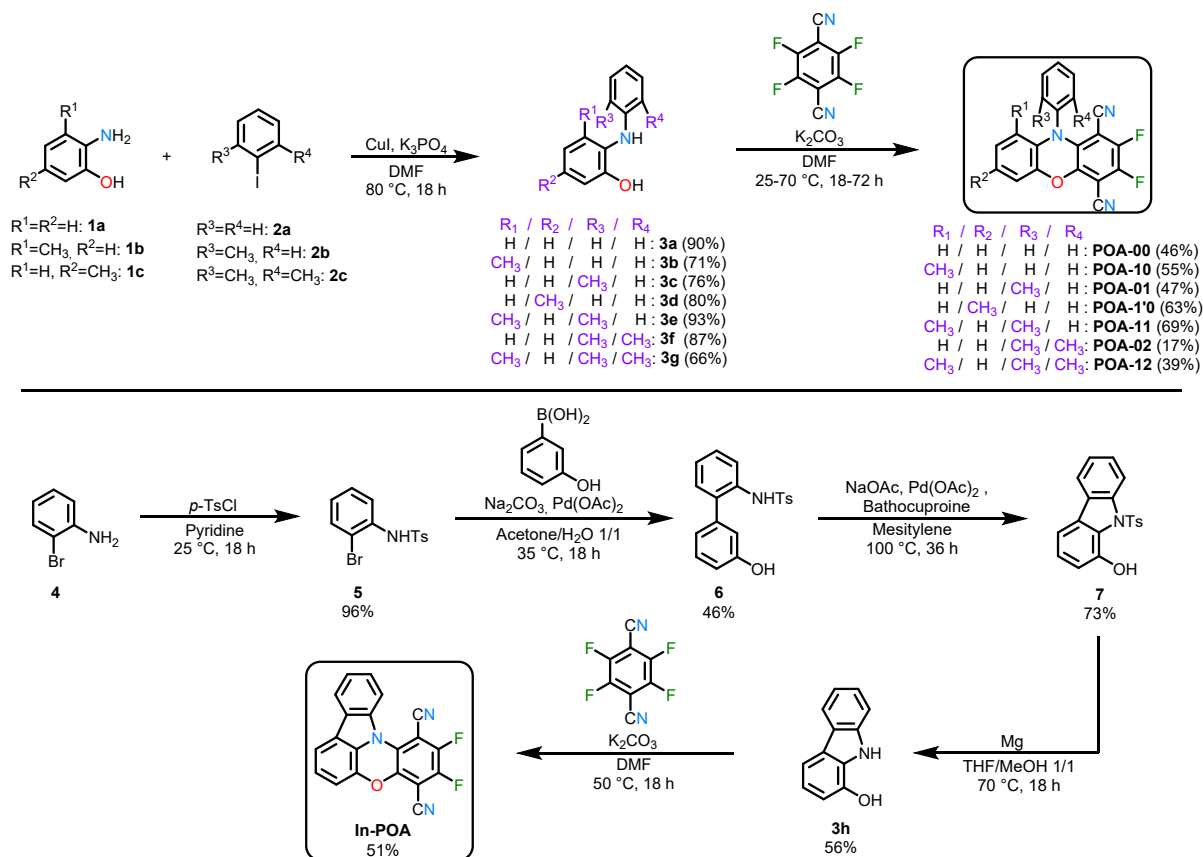
GENERAL PROCEDURE (GP1): COPPER-CATALYZED ULLMANN-GOLDBERG TYPE *N*-ARYLATION OF 2-AMINOPHENOLS

In a flame-dried pressure tube, corresponding 2-aminophenol (2 eq.), aryl iodide (1 eq.), copper(I)iodide (0.2 eq.), and dried potassium phosphate (2 eq.) were suspended in anhydrous *N,N*-dimethylformamide under argon atmosphere. The mixture was stirred at 80 °C until full consumption of the electrophile (TLC monitoring, FeCl₃-stain solution). Then, the reaction mixture was transferred into a round-bottom flask, concentrated, and dry-mounted over Celite® using ethyl acetate. The residue was purified by column chromatography and dried *in vacuo*.

GENERAL PROCEDURE (GP2): NUCLEOPHILIC AROMATIC SUBSTITUTIONS (S_NAr)

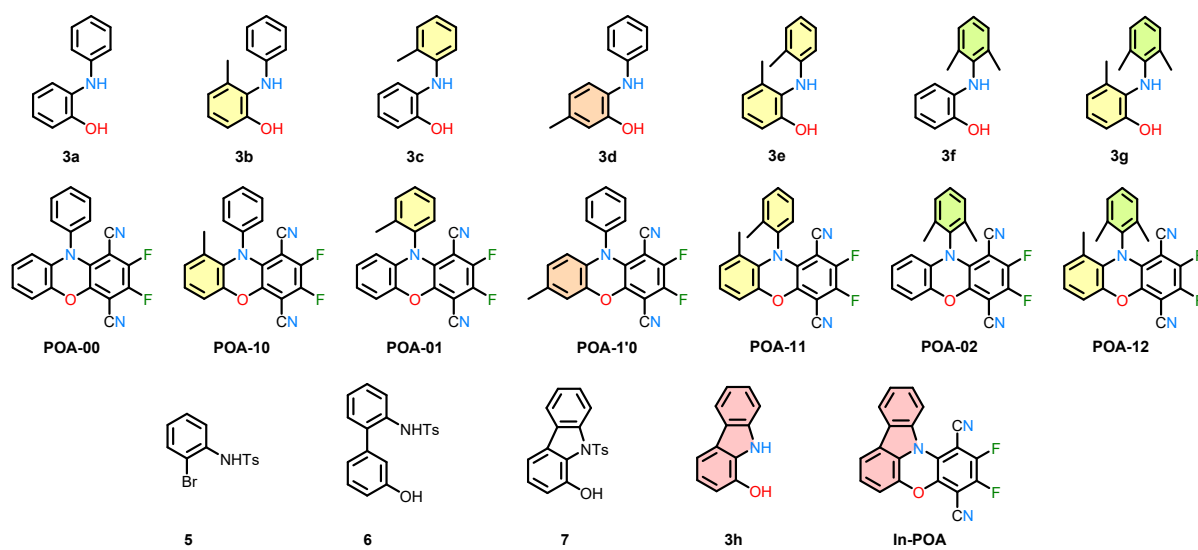
In an argon-flushed pressure tube, 2,3,5,6-tetrafluoroterephthalonitrile (1-2 eq.), 2-aminophenol-nucleophile (1 eq.), and dried potassium carbonate (3-10 eq.) were suspended in anhydrous *N,N*-dimethylformamide and stirred at 25–100 °C until full consumption of the electrophile (TLC monitoring). Then, the reaction mixture was transferred into a round-bottom flask, concentrated, and dry-mounted over Celite® using dichloromethane. The residue was purified by column chromatography and lyophilized.

OVERVIEW OF PERFORMED SYNTHESSES

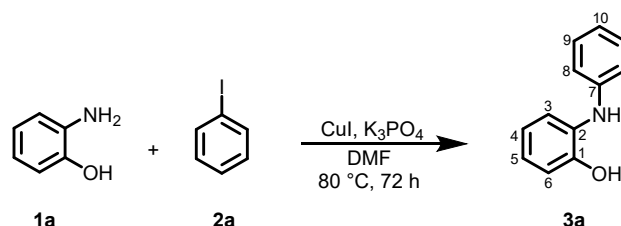


Scheme S1: Overview of performed syntheses.

OVERVIEW OF SYNTHESIZED COMPOUNDS

**Figure S1:** Overview of synthesized compounds.

SYNTHETIC PROCEDURES

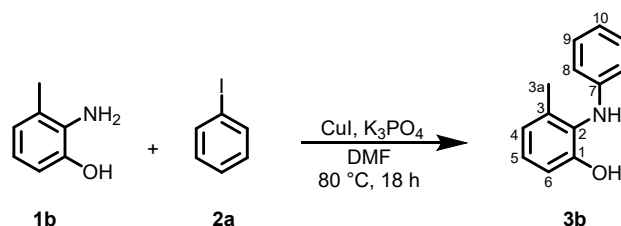
2-(Phenylamino)phenol (**3a**)²

3a was synthesized according to **GP1** using 2-aminophenol (**1a**, 0.218 g, 2.00 mmol, 2 eq.), iodobenzene (**2a**, 114 μ L, 0.208 g, 1.02 mmol, 1 eq.), copper(I)iodide (41.0 mg, 0.215 mmol, 0.2 eq.), and potassium phosphate (0.424 g, 2.00 mmol, 2 eq.) in anhydrous *N,N*-dimethylformamide (2 mL). Column chromatography (3x25 cm, cyclohexane/ethyl acetate 100/0 $\rightarrow$ 19/1 $\rightarrow$ 9/1 $\rightarrow$ 5/1) yielded the product **3a** as an off-white powder (0.170 g, 0.918 mmol, 90%).

M(C₁₂H₁₁NO): 199.25 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.22 (m, 3H), 7.11 (t, $^3J_{H-H}$ = 7.4 Hz, 1H), 7.00 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 6.89 (m, 2H), 6.79 (d, $^3J_{H-H}$ = 7.9 Hz, 1H), 5.76 (br s, 1H, OH), 5.27 (br s, 1H, NH).

Spectroscopic data match literature values.²

3-Methyl-2-(phenylamino)phenol (**3b**)³

3b was synthesized according to **GP1** using 2-amino-3-methylphenol (**1b**, 0.505 g, 4.10 mmol, 2 eq.), iodobenzene (**2a**, 227 μ L, 0.414 g, 2.03 mmol, 1 eq.), copper(I)iodide (77.8 mg, 0.409 mmol, 0.2 eq.), and potassium phosphate (0.901 g, 4.07 mmol, 2 eq.) in anhydrous *N,N*-dimethylformamide (5 mL). Column chromatography (5x33 cm, cyclohexane/ethyl acetate 5/1) yielded the product **3b** as an off-white powder (0.286 g, 1.43 mmol, 71%).

M(C₁₃H₁₃NO): 199.25 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.20 (m, 2H, H₉), 7.13 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, H₅), 6.90 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, H₆), 6.84 (tt, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.1 Hz, 1H, H₁₀), 6.79 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, H₄), 6.62 (m, 2H, H₈), 6.32 (br s, 1H, NH), 2.14 (s, 3H, H_{3a}). The OH signal is missing due to fast proton exchange processes.

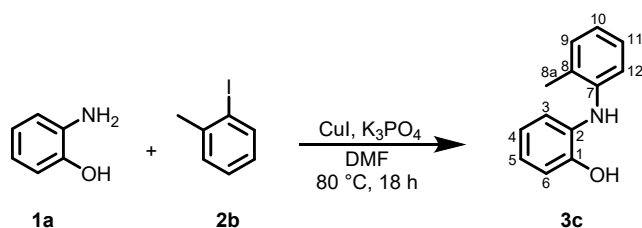
¹³C{¹H}-NMR (101 MHz, CDCl₃, 298 K): δ [ppm] = 154.3 (C₁), 146.2 (C₇), 137.3 (C₃), 129.7 (C₉), 128.2 (C₅), 126.2 (C₂), 122.3 (C₄), 120.0 (C₁₀), 114.4 (C₈), 112.6 (C₆), 17.9 (C₁₁).

HR-MS (ESI-pos, 70 eV): m/z = 200.1071 [M + H]⁺, calculated for [C₁₃H₁₃N₁O₁ + H]⁺ = 200.1070.

IR: $\tilde{\nu}$ [cm⁻¹] = 3380, 3080, 3047, 3013, 2941, 2917, 1933, 1597, 1495, 1471, 1441, 1410, 1350, 1284, 1256, 1231, 1176, 1076, 1025, 950, 874, 787, 747, 691, 615.

Melting point: 120 °C.

Spectroscopic data match literature values.³

2-(*o*-Tolylamino)phenol (3c)²

3c was synthesized according to **GP1** using 2-aminophenol (**1a**, 0.300 g, 2.75 mmol, 2 eq.), 1-iodo-2-methylbenzene (**2b**, 170 μL , 0.291 g, 1.34 mmol, 1 eq.), copper(I)iodide (52.0 mg, 0.275 mmol, 0.2 eq.), and potassium phosphate (0.584 g, 2.75 mmol, 2 eq.) in anhydrous *N,N*-dimethylformamide (3 mL). Column chromatography (4.5x40 cm, cyclohexane/ethyl acetate 6/1) yielded the product **3c** as an off-white powder (0.203 g, 1.02 mmol, 76%).

M(C₁₃H₁₃NO): 199.25 g/mol.

¹H-NMR (400 MHz, acetone-*d*₆, 298 K): δ [ppm] = 8.30 (s, 1H, OH), 7.17 (d, ³*J*_{H-H} = 7.4 Hz, 1H, H₉), 7.09 (t, ³*J*_{H-H} = 7.6 Hz, 1H, H₁₁), 7.03 (dd, ³*J*_{H-H} = 8.0 Hz, ⁴*J*_{H-H} = 1.3 Hz, 1, H₁₂), 7.01 – 6.97 (m, 1H, H₃), 6.92 – 6.88 (m, 1H, H₆), 6.86 – 6.80 (m, 1H, H₁₀), 6.79 – 6.73 (m, 2H, H₄, H₅), 6.05 (s, 1H, NH), 2.26 (s, 3H, H_{8a}).

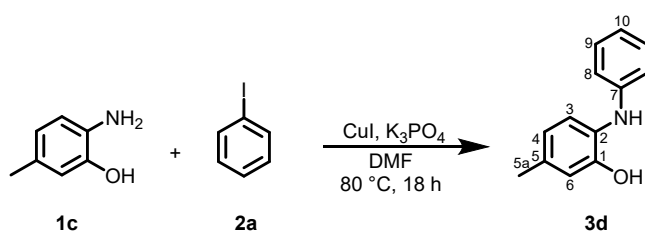
¹³C{¹H}-NMR (101 MHz, acetone-*d*₆, 298 K): δ [ppm] = 148.6 (C₁), 143.3 (C₇), 132.8 (C₂), 131.5 (C₉), 128.3 (C₈), 127.4 (C₁₁), 122.2 (C₅), 121.6 (C₁₀), 120.8 (C₄), 119.2 (C₃), 118.0 (C₁₂), 115.9 (C₆), 17.9 (C_{8a}).

HR-MS (ESI-pos, 70 eV): *m/z* = 200.1078 [M + H]⁺, calculated for [C₁₃H₁₃N₁O₁ + H]⁺ = 200.1070.

IR: $\tilde{\nu}$ [cm⁻¹] = 3388, 3047, 2970, 2922, 2855, 1581, 1491, 1461, 1382, 1354, 1293, 1262, 1237, 1179, 1130, 1113, 1067, 1044, 985, 928, 878, 844, 824, 738.

Melting point: 150 °C.

Spectroscopic data match literature values.²

5-Methyl-2-(phenylamino)phenol (3d)⁴

3d was synthesized according to **GP1** using 2-amino-5-methylphenol (**1c**, 0.753 g, 6.09 mmol, 2 eq.), iodobenzene (**2a**, 340 μL , 0.621 g, 3.04 mmol, 1 eq.), copper(I)iodide (118 mg, 0.610 mmol, 0.2 eq.), and potassium phosphate (1.30 g, 6.09 mmol, 2 eq.) in anhydrous *N,N*-dimethylformamide (10 mL). Column chromatography (6x28 cm, cyclohexane/ethyl acetate 5/1) yielded the product **3d** as an off-white powder (0.484 g, 2.43 mmol, 80%).

M(C₁₃H₁₃NO): 199.25 g/mol.

¹H-NMR (400 MHz, DMSO-*d*₆, 298 K): δ [ppm] = 9.26 (s, 1H, OH), 7.18 – 7.07 (m, 2H, H₉), 7.06 – 6.99 (m, 2H, H₃, NH), 6.93 – 6.84 (m, 2H, H₈), 6.74 – 6.64 (m, 2H, H₆, H₁₀), 6.54 (dd, ³*J*_{H-H} = 8.0 Hz, ⁴*J*_{H-H} = 1.4 Hz, 1H, H₄), 2.19 (s, 3H, H_{5a}).

¹³C{¹H}-NMR (101 MHz, DMSO-*d*₆, 298 K): δ [ppm] = 148.8 (C₁), 145.3 (C₇), 131.3 (C₅), 128.8 (C₂), 127.6 (C₂), 120.2 (C₃), 119.6 (C₄), 118.0 (CX), 116.3 (C₆), 115.1 (CX), 20.6 (C_{5a}).

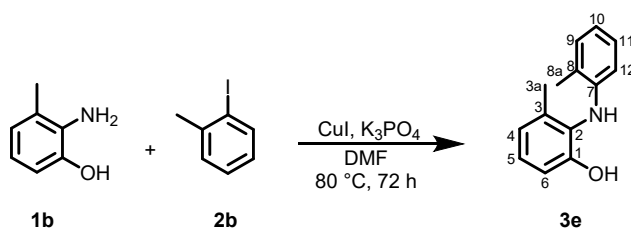
HR-MS (ESI-pos, 70 eV): $m/z = 200.1071$ $[M + H]^+$, calculated for $[C_{13}H_{13}N_1O_1 + H]^+ = 200.1070$.

IR: $\tilde{\nu}[\text{cm}^{-1}] = 3362, 3044, 2918, 2859, 1596, 1493, 1454, 1410, 1302, 1233, 1174, 1150, 1110, 1077, 1027, 998, 944, 795, 737, 689, 447$.

Melting point: 59 °C.

Spectroscopic data match literature values.⁴

3-Methyl-2-(*o*-tolylamino)phenol (**3e**)



3e was synthesized according to **GP1** using 2-amino-3-methylphenol (**1b**, 0.401 g, 3.26 mmol, 2 eq.), 1-iodo-2-methylbenzene (**2b**, 210 μL , 0.360 g, 1.65 mmol, 1 eq.), copper(I)iodide (62.1 mg, 0.326 mmol, 0.2 eq.), and potassium phosphate (0.691 g, 3.26 mmol, 2 eq.) in anhydrous *N,N*-dimethylformamide (6 mL). Column chromatography (6x24 cm, cyclohexane/ethyl acetate 5/1) yielded the product **3e** as a brownish powder (0.327 g, 1.53 mmol, 93%).

M($C_{14}H_{15}NO$): 213.28 g/mol.

$^1\text{H-NMR}$ (400 MHz, acetone- d_6 , 298 K): δ [ppm] = 7.80 (s, 1H, OH), 7.04 (d, $^3J_{H-H} = 7.4$ Hz, 1H, H9), 7.00 (t, $^3J_{H-H} = 7.8$ Hz, 1H, H5), 6.93 – 6.84 (t, $^3J_{H-H} = 7.8$ Hz, 1H, H11), 6.78 (d, $^3J_{H-H} = 8.1$ Hz, 1H, H6), 6.74 (d, $^3J_{H-H} = 7.6$ Hz, 1H, H4), 6.61 (td, $^3J_{H-H} = 7.4$, $^4J_{H-H} = 1.0$ Hz, 1H, H10), 6.08 (d, $^3J_{H-H} = 8.0$ Hz, 1H, H12), 5.70 (s, 1H, NH), 2.30 (s, 3H, H8a), 2.05 (s, 3H, H3a).

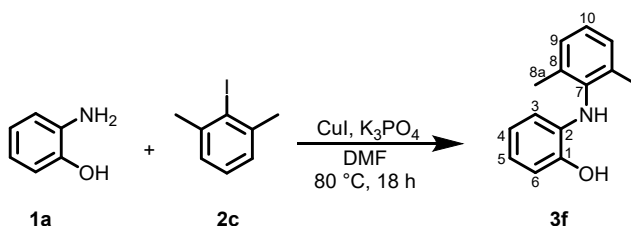
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, acetone- d_6 , 298 K): δ [ppm] = 155.0 (C1), 145.8 (C7), 137.9 (C3), 131.0 (C9), 128.2 (C2), 127.4 (2C, C5, C11), 124.0 (C8), 122.3 (C4), 118.9 (C10), 113.8 (C6), 112.4 (C12), 18.0 (C3a), 17.8 (C8a).

HR-MS (ESI-pos, 70 eV): $m/z = 214.1231$ $[M + H]^+$, calculated for $[C_{14}H_{15}N_1O_1 + H]^+ = 214.1226$.

IR: $\tilde{\nu}[\text{cm}^{-1}] = 3431, 3380, 3364, 3269, 3039, 3008, 2969, 2917, 2857, 1581, 1497, 1470, 1438, 1412, 1380, 1349, 1283, 1250, 1231, 1172, 1158, 1107, 1073, 1048, 1032, 984, 951, 874, 776, 746, 716, 702, 666$.

Melting point: 108 °C.

2-((2,6-dimethylphenyl)amino)phenol (**3f**)⁵



3f was synthesized according to **GP1** using 2-aminophenol (**1a**, 0.497 g, 4.55 mmol, 2 eq.), 2-iodo-1,3-dimethylbenzene (**2c**, 330 μL , 0.532 g, 2.29 mmol, 1 eq.), copper(I)iodide (78.6 mg, 0.413 mmol, 0.2 eq.), and potassium phosphate (0.986 g, 4.65 mmol, 2 eq.) in anhydrous *N,N*-dimethylformamide

(5 mL). Column chromatography (5x33 cm, cyclohexane/ethyl acetate 100/0 → 19/1 → 9/1 → 5/1) yielded the product **3f** as an orange-colored powder (0.424 g, 1.99 mmol, 87%).

M(C₁₄H₁₅NO): 213.28 g/mol.

¹H-NMR (400 MHz, acetone-*d*₆, 298 K): δ [ppm] = 8.39 (s, 1H, OH), 7.13 (d, ³*J*_{H-H} = 7.6 Hz, 2H, H₉), 7.05 (m, 1H, H₁₀), 6.83 (dd, ³*J*_{H-H} = 7.6 Hz, ⁴*J*_{H-H} = 1.5 Hz, 1H, H₆), 6.58 (td, ³*J*_{H-H} = 7.6 Hz, ⁴*J*_{H-H} = 1.4 Hz, 1H, H₄), 6.52 (td, *J* = 7.5 Hz, ⁴*J*_{H-H} = 1.6 Hz, 1H, H₅), 6.02 (dd, ³*J*_{H-H} = 7.7 Hz, ⁴*J*_{H-H} = 1.6 Hz, 1H, H₃), 5.91 (s, 1H, NH), 2.19 (s, 6H, H_{8a}).

¹³C{¹H}-NMR (101 MHz, acetone-*d*₆, 298 K): δ [ppm] = 145.2 (C₁), 140.1 (C₇), 136.7 (C₈), 136.2 (C₂), 129.2 (C₉), 126.3 (C₁₀), 120.9 (C₄), 118.2 (C₅), 115.0 (C₆), 112.1 (C₃), 18.3 (C_{8a}).

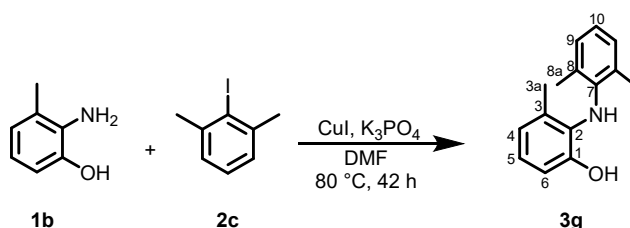
HR-MS (ESI-pos, 70 eV): *m/z* = 214.1228 [M + H]⁺, calculated for [C₁₄H₁₅N₁O₁ + H]⁺ = 214.1226.

IR: $\tilde{\nu}$ [cm⁻¹] = 3354, 3042, 2968, 2920, 2853, 1608, 1589, 1502, 1465, 1432, 1373, 1343, 1311, 1264, 1249, 1209, 1098, 1035, 880, 763, 737, 699.

Melting point: 120 °C.

Spectroscopic data match literature values.⁵

2-((2,6-dimethylphenyl)amino)-3-methylphenol (**3g**)



3g was synthesized according to **GP1** using 2-amino-3-methylphenol (**1b**, 0.401 g, 3.25 mmol, 1.9 eq.), 2-iodo-1,3-dimethylbenzene (**2c**, 252 μ L, 0.405 g, 1.74 mmol, 1 eq.), copper(I)iodide (63.2 mg, 0.332 mmol, 0.2 eq.), and potassium phosphate (0.691 g, 3.25 mmol, 1.9 eq.) in anhydrous *N,N*-dimethylformamide (6 mL). Column chromatography (6x26 cm, cyclohexane/ethyl acetate 9/1) yielded the product **3g** as an off-white powder (0.263 g, 1.16 mmol, 66%).

M(C₁₅H₁₇NO): 227.31 g/mol.

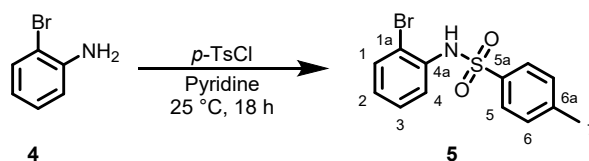
¹H-NMR (400 MHz, DMSO-*d*₆, 298 K): δ [ppm] = 8.96 (s, 1H, OH), 6.91 (d, ³*J*_{H-H} = 7.4 Hz, 2H, H₉), 6.76 (t, ³*J*_{H-H} = 7.4 Hz, 1H, H₁₀), 6.71 – 6.57 (m, 2H, H₆, H₅), 6.53 – 6.45 (m, 1H, H₄), 5.90 (s, 1H, NH), 1.97 (s, 6H, H_{8a}), 1.66 (s, 3H, H_{3a}).

¹³C{¹H}-NMR (101 MHz, DMSO-*d*₆, 298 K): δ [ppm] = 149.2 (C₁), 142.3 (C₇), 132.1 (C₂), 130.4 (C₈), 129.4 (C₃), 128.2 (C₉), 121.5 (C₁₀), 121.4 (C₄), 121.0 (C₅), 112.6 (C₆), 18.9 (C_{8a}), 18.4 (C_{3a}).

HR-MS (ESI-pos, 70 eV): *m/z* = 228.1389 [M + H]⁺, calculated for [C₁₅H₁₇N₁O₁ + H]⁺ = 228.1383.

IR: $\tilde{\nu}$ [cm⁻¹] = 3387, 3339, 3040, 2950, 2915, 2853, 1607, 1578, 1484, 1466, 1438, 1377, 1336, 1267, 1229, 1216, 1169, 1143, 1082, 1023, 989, 953, 922, 780, 761, 731, 688, 640.

Melting point: 120 °C.

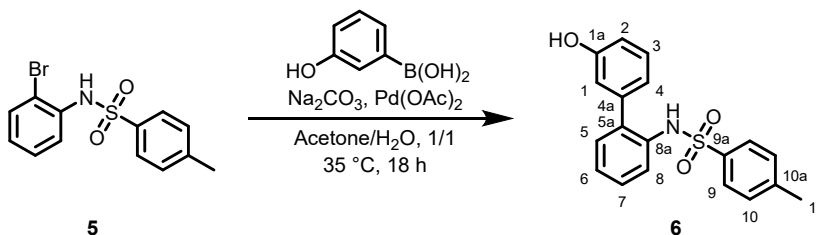
***N*-(2-Bromophenyl)-4-methylbenzenesulfonamide (5)⁶**

Compound **5** was synthesized according to a procedure by Youn *et al.*⁷ *p*-Toluenesulfonyl chloride (0.890 g, 4.67 mmol, 1.3 eq.) was added to a solution of 2-bromoaniline (0.617 g, 3.59 mmol, 1 eq.) in anhydrous pyridine (18 mL, 0.2 M) at 0 °C, and the mixture was stirred overnight at 25 °C. The solvent was removed *in vacuo*. Water (20 mL) and dichloromethane (20 mL) were added, the layers were separated, and the product was extracted three times using dichloromethane (20 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated. Column chromatography (4.5x30 cm, cyclohexane/ethyl acetate 100/1 → 100/2 → 100/5 → 10/1) yielded product **5** as an off-white powder (1.13 g, 3.46 mmol, 96%).

M(C₁₃H₁₂BrNO₂S): 326.21 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.66 (m, 3H), 7.41 (dd, ³*J*_{H-H} = 8.1 Hz, ⁴*J*_{H-H} = 1.5 Hz, 1H), 7.27 (td, ³*J*_{H-H} = 7.7 Hz, ⁴*J*_{H-H} = 1.5 Hz, 1H), 7.22 (d, ³*J*_{H-H} = 8.0 Hz, 2H), 6.97 (m, 2H), 2.38 (s, 3H).

Spectroscopic data match literature values.⁶

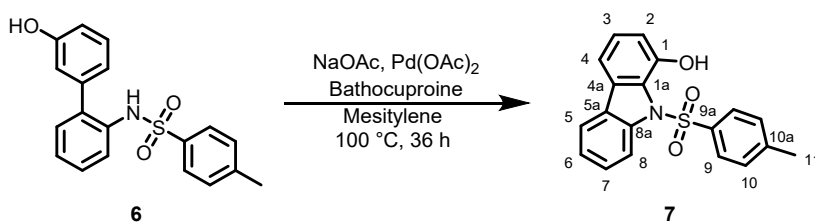
***N*-(3'-Hydroxy-[1,1'-biphenyl]-2-yl)-4-methylbenzenesulfonamide (6)⁷**

Compound **6** was synthesized according to a procedure by Youn *et al.*⁷ In a flame-dried round-bottom flask, *N*-Ts-2-bromoaniline (**5**, 1.01 g, 3.11 mmol, 1 eq.), 3-hydroxyphenylboronic acid (0.644 g, 4.67 mmol, 1.5 eq.), sodium carbonate (0.679 g, 6.40 mmol, 2.1 eq.), and palladium acetate (52.0 mg, 0.233 mmol, 0.05 eq.) were dissolved in a mixture of acetone (10 mL) and water (10 mL), and the mixture was stirred overnight at 35 °C. The mixture was filtered through a pad of Celite® and washed with ethyl acetate (50 mL). Brine (30 mL) was added, and the crude product was extracted three times using ethyl acetate (20 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated. Column chromatography (5.5x40 cm, cyclohexane/dichloromethane/ethyl acetate 10/20/1 → 10/20/1.5 → 10/20/2 → 10/20/3) yielded product **6** as a white powder (0.486 g, 1.43 mmol, 46%).

M(C₁₉H₁₇NO₃S): 339.41 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.66 (dd, ³*J*_{H-H} = 8.2 Hz, ⁴*J*_{H-H} = 1.1 Hz, 1H), 7.46 (dd, ³*J*_{H-H} = 8.3 Hz, ⁴*J*_{H-H} = 2.0 Hz, 2H), 7.31 (td, ³*J*_{H-H} = 7.6 Hz, ⁴*J*_{H-H} = 1.8 Hz, 1H), 7.19 (t, ³*J*_{H-H} = 8.4 Hz, 3H), 7.11 (m, 2H), 6.83 (ddd, ³*J*_{H-H} = 8.0 Hz, ⁴*J*_{H-H} = 1.8 Hz, 0.8 Hz, 1H), 6.71 (s, 1H), 6.44 (td, ³*J*_{H-H} = 7.5 Hz, ⁴*J*_{H-H} = 1.3 Hz, 1H), 6.31 (dd, ³*J*_{H-H} = 2.7 Hz, ⁴*J*_{H-H} = 1.5 Hz, 1H), 5.60 (br s, 1H), 2.39 (s, 3H).

Spectroscopic data match literature values.⁷

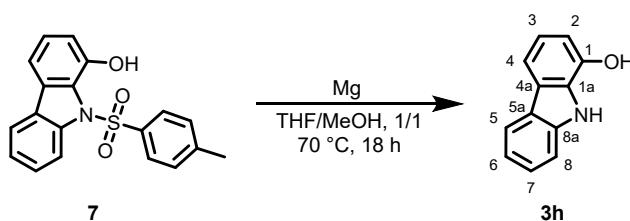
N-Ts-1-Hydroxycarbazole (7)⁷

Compound **7** was synthesized according to a modified procedure by Youn *et al.*⁷ In a flame-dried Schlenk flask, compound **6** (0.400 g, 1.18 mmol, 1 eq.), bathocuproine (0.042 g, 0.118 mmol, 0.1 eq.), sodium carbonate (0.096 g, 1.18 mmol, 1 eq.), and palladium acetate (28.0 mg, 0.123 mmol, 0.1 eq.) were dissolved in mesitylene (11 mL). The mixture was stirred at 100°C for 36 hours and flushed with oxygen twice, after 16 hours and 24 hours, respectively. After the reaction was completed (monitored by TLC), the mixture was concentrated *in vacuo*. Column chromatography (5.5x40 cm, cyclohexane/dichloromethane/ethyl acetate 10/1/1) yielded product **7** as a white powder (0.288 g, 0.854 mmol, 73%).

M(C₁₉H₁₅NO₃S): 337.39 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 9.26 (s, 1H), 8.29 (d, $^3J_{H-H}$ = 8.4 Hz, 1H), 7.73 (dd, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 0.8 Hz, 1H), 7.46 (m, 1H), 7.39 (d, $^3J_{H-H}$ = 8.5 Hz, 2H), 7.34 (td, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 0.8 Hz, 1H), 7.33 (dd, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.3 Hz, 1H), 7.25 (t, $^3J_{H-H}$ = 7.7 Hz, 1H), 7.08 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H), 6.98 (d, $^3J_{H-H}$ = 8.2 Hz, 2H), 2.20 (s, 3H).

Spectroscopic data match literature values.⁷

1-Hydroxycarbazole (3h)⁷

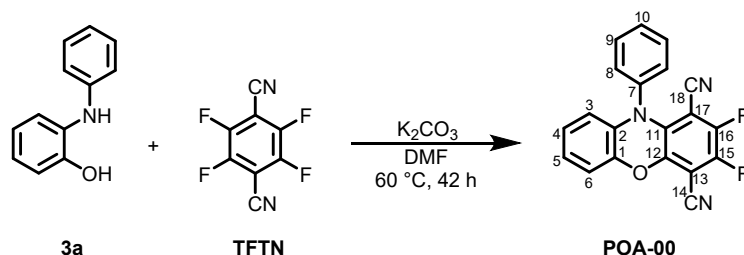
Compound **7** was synthesized according to a modified procedure by Youn *et al.*⁷ A Schlenk flask containing magnesium turnings (0.415 g, 17.1 mmol, 30 eq.) was flame-dried *in vacuo* under stirring. Then, a solution of compound **7** (0.190 g, 0.564 mmol, 1 eq.) in THF/MeOH 1/1 (each 13 mL) was added under argon atmosphere, and the mixture was stirred at 70 °C overnight. The mixture was filtered through a pad of Celite® and washed with dichloromethane (100 mL). Brine (200 mL), water (100 mL), and ethyl acetate (200 mL) were added, and the crude product was extracted three times using ethyl acetate (200 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. Product **3h** was obtained as a white powder (58.3 mg, 0.318 mmol, 56%).

M(C₁₂H₉NO): 183.21 g/mol.

¹H-NMR (400 MHz, acetone-*d*₆, 298 K): δ [ppm] = 10.19 (s, 1H), 8.72 (s, 1H), 8.06 (dd, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 0.6 Hz, 1H), 7.62 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 7.57 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 7.37 (ddd, $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H), 7.15 (ddd, $^3J_{H-H}$ = 7.9 Hz, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.0 Hz, 1H), 7.00 (t, $^3J_{H-H}$ = 7.5 Hz, 1H), 6.90 (dd, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 0.9 Hz, 1H).

Spectroscopic data match literature values.⁷

Compound POA-00



POA-00 was synthesized according to **GP2** using compound **3a** (84.0 mg, 0.453 mmol, 1 eq.), tetrafluoroterephthalonitrile (TFTN, 91.0 mg, 0.455 mmol, 1 eq.), and potassium carbonate (0.213 g, 1.54 mmol, 3.4 eq.) in anhydrous *N,N*-dimethylformamide (8 mL) at 60 °C for 42 hours. Column chromatography (4.7x35 cm, DCM) yielded product **POA-00** as a yellow powder (72.7 mg, 0.211 mmol, 46%).

M(C₂₀H₉F₂N₃O): 345.31 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.63 (m, 3H, *H*₁₀, *H*₉), 7.43 (m, 2H, *H*₈), 6.87 (m, 2H, *H*₅, *H*₆), 6.76 (1H, m, *H*₄), 6.14 (d, ³*J*_{H-H} = 8.0 Hz, 1H, *H*₃).

¹³C{¹H}-NMR (101 MHz, CDCl₃, 298 K): δ [ppm] = 146.5 (dd, ¹*J*_{C-F} = 254.0 Hz, ²*J*_{C-F} = 13.0 Hz, C15), 144.4 (t, ³*J*_{C-F} = 3.9 Hz, C12), 142.5 (dd, ¹*J*_{C-F} = 254.9 Hz, ²*J*_{C-F} = 15.2 Hz, C16), 141.8 (C1), 137.3 (C7), 134.6 (d, ³*J*_{C-F} = 2.6 Hz, C11), 131.3 (C10), 131.3 (C8), 131.3 (C9), 130.9 (C2), 125.6 (C4), 124.9 (C5), 116.3 (C6), 115.5 (C3), 108.8 (d, ³*J*_{C-F} = 3.8 Hz, C18), 108.1 (d, ³*J*_{C-F} = 3.8 Hz, C14), 95.6 (dd, ²*J*_{C-F} = 17.1 Hz, ³*J*_{C-F} = 2.6 Hz, C17), 91.8 (d, ²*J*_{C-F} = 18.5 Hz, C13).

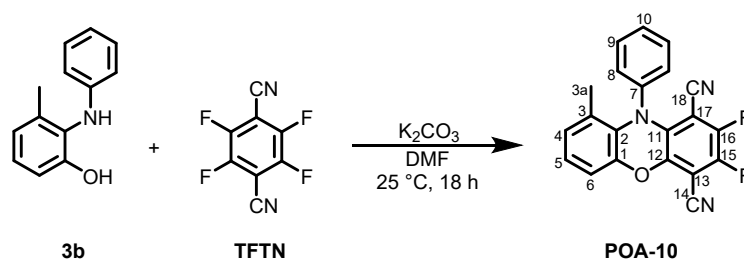
¹⁹F-NMR (376 MHz, CDCl₃, 298 K): δ [ppm] = -135.7 (d, ³*J*_{F-F}, 20.4 Hz, F15), -142.3 (d, ³*J*_{F-F}, 20.4 Hz, F16).

HR-MS (ESI-pos, 70 eV): *m/z* = 346.0780 [M + H]⁺, calculated for [C₂₀H₉F₂N₃O₁ + H]⁺ = 346.0786; 368.0604 [M + Na]⁺, calculated for [C₂₀H₉F₂N₃O₁ + Na]⁺ = 368.0606; 713.1317 [(M)₂ + Na]⁺, calculated for [(C₂₀H₉F₂N₃O₁)₂ + Na]⁺ = 713.1320.

IR: $\tilde{\nu}$ [cm⁻¹] = 2954, 2919, 2851, 2361, 2345, 1649, 1559, 1495, 1460, 1441, 1378, 1310, 1258, 1225, 1195, 1152, 1133, 1105, 1041, 1008, 967, 757, 733, 693, 674, 656.

Melting point: 310 °C.

Crystals suitable for X-ray diffractometry were grown using a concentrated solution of **POA-00** in dichloromethane overlaid with cyclohexane.

Compound POA-10³

POA-10 was synthesized according to **GP2** using compound **3b** (86.2 mg, 0.433 mmol, 1.1 eq.), tetrafluoroterephthalonitrile (TFTN, 83.6 mg, 0.418 mmol, 1 eq.), and potassium carbonate (0.156 g, 1.13 mmol, 2.7 eq.) in anhydrous *N,N*-dimethylformamide (8 mL) at 25 °C overnight. Column chromatography (5x33 cm, DCM) yielded an inseparable mixture of the phenoxazine product and the

corresponding heteropentacyclic congener. This mixture was recrystallized from diethyl ether, yielding product **POA-10** in the mother liquor, which was concentrated to obtain **POA-10** as a pale-yellow powder (82.2 mg, 0.229 mmol, 55%).

M(C₂₁H₁₁F₂N₃O): 359.34 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.49 (m, 2H, *H*8), 7.35 (m, 2H, *H*9), 7.25 (m, 1H, *H*10, overlapping with chloroform signal), 7.12 (m, 2H, *H*5, *H*6), 7.02 (m, 1H, *H*4), 2.25 (s, 3H, *H*19).

¹³C{¹H}-NMR (101 MHz, CDCl₃, 298 K): δ [ppm] = 151.4 (t, ³*J*_{C-F} = 2.7 Hz, C12), 150.2 (C1), 147.9 (C7), 147.9 (dd, ¹*J*_{C-F} = 260.0 Hz, ²*J*_{C-F} = 13.6 Hz, C16/C15), 147.4 (dd, ¹*J*_{C-F} = 260.0 Hz, ²*J*_{C-F} = 12.7 Hz, C15/C16), 137.0 (d, ³*J*_{C-F} = 4.3 Hz, C11), 135.2 (C3), 132.0 (C2), 130.0 (C9), 128.5 (C4), 127.4 (C10), 127.2 (C5), 127.1 (C8), 115.1 (C6), 110.3 (d, ³*J*_{C-F} = 3.9 Hz, C18/C14), 108.4 (d, ³*J*_{C-F} = 3.8 Hz, C14/C18), 103.8 (dd, ²*J*_{C-F} = 13.8 Hz, ³*J*_{C-F} = 2.5 Hz, C17/C13), 97.3 (dd, ²*J*_{C-F} = 15.6 Hz, ³*J*_{C-F} = 2.2 Hz, C13/C17), 18.1 (C19).

¹⁹F-NMR (376 MHz, CDCl₃, 298 K): δ [ppm] = -131.1 (d, ³*J*_{F-F}, 20.6 Hz), -133.5 (d, ³*J*_{F-F}, 20.6 Hz).

HR-MS (ESI-pos, 70 eV): *m/z* = 360.0948 [M + H]⁺, calculated for [C₂₁H₁₁F₂N₃O + H]⁺ = 360.0943; 382.0767 [M + Na]⁺, calculated for [C₂₁H₁₁F₂N₃O + Na]⁺ = 382.0762.

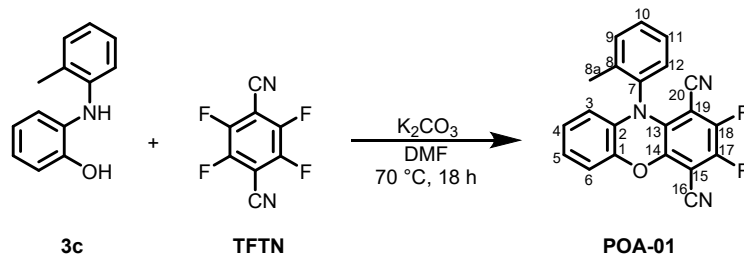
IR: $\tilde{\nu}$ [cm⁻¹] = 3069, 2956, 2921, 2853, 2320, 2240, 1636, 1590, 1469, 1447, 1382, 1310, 1257, 1214, 1190, 1137, 1092, 1076, 1037, 1000, 962, 932, 885, 783, 766, 752, 732, 700, 633, 611, 539, 479, 414.

Melting point: 192 °C.

Crystals suitable for X-ray diffractometry were grown using a concentrated solution of **POA-10** in chloroform overlaid with cyclohexane.

Spectroscopic data match literature values.³

Compound POA-01



POA-01 was synthesized according to **GP2** using compound **3c** (0.159 g, 0.798 mmol, 1 eq.), tetrafluoroterephthalonitrile (TFTN, 0.160 g, 0.800 mmol, 1 eq.), and potassium carbonate (1.15 g, 8.32 mmol, 10 eq.) in anhydrous *N,N*-dimethylformamide (9 mL) at 60 °C for 42 hours. Column chromatography (4.7x35 cm, DCM) yielded product **POA-01** as a yellow powder (0.134 g, 0.373 mmol, 47%).

M(C₂₁H₁₁F₂N₃O): 359.34 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.56 (td, ³*J*_{H-H} = 7.5 Hz, ⁴*J*_{H-H} = 1.2 Hz, 1H, *H*10), 7.47-7.41 (m, 2H, *H*9, *H*11), 7.31 (dd, ³*J*_{H-H} = 7.7 Hz, ⁴*J*_{H-H} = 1.2 Hz, 1H, *H*12), 6.86 (m, 2H, *H*5, *H*6), 6.75 (1H, m, *H*4), 5.94 (d, ³*J*_{H-H} = 8.0 Hz, 1H, *H*3), 2.31 (s, 3H, *H*8a).

¹³C{¹H}-NMR (101 MHz, CDCl₃, 298 K): δ [ppm] = 146.5 (dd, ¹*J*_{C-F} = 253.8 Hz, ²*J*_{C-F} = 13.1 Hz, C15), 144.2 (t, ³*J*_{C-F} = 3.7 Hz, C12), 142.2 (dd, ¹*J*_{C-F} = 254.1 Hz, ²*J*_{C-F} = 15.2 Hz, C16), 141.7 (C1), 139.8 (C8), 135.0 (C7), 134.0 (ps t, ³*J*_{C-F} = 2.9 Hz, C11), 132.4 (C9), 131.8 (C10), 131.2 (C12), 129.8 (C2), 128.8 (C11), 125.8 (C4), 124.8 (C5), 116.4 (C6), 114.8 (C3), 108.8 (d, ³*J*_{C-F} = 3.8 Hz, C18), 107.8 (d, ³*J*_{C-F} = 3.8 Hz, C14), 95.6 (dd, ²*J*_{C-F} = 17.4 Hz, ³*J*_{C-F} = 2.9 Hz, C17), 90.6 (d, ²*J*_{C-F} = 19.0 Hz, C13), 17.7 (C8a).

¹⁹F-NMR (376 MHz, CDCl₃, 298 K): δ [ppm] = -135.7 (d, $^3J_{F-F}$, 20.4 Hz, F17), -142.8 (d, $^3J_{F-F}$, 20.4 Hz, F18).

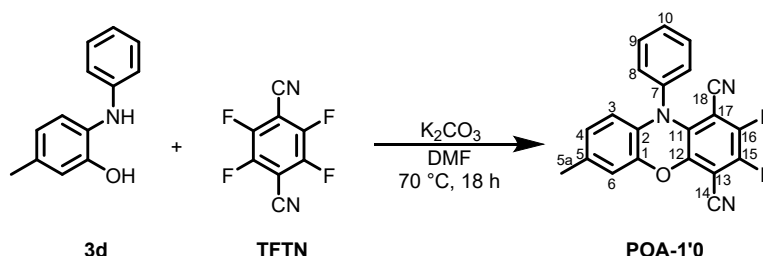
HR-MS (ESI-pos, 70 eV): m/z = 360.0937 [M + H]⁺, calculated for [C₂₁H₁₁F₂N₃O₁ + H]⁺ = 360.0943; 382.0761 [M + Na]⁺, calculated for [C₂₁H₁₁F₂N₃O₁ + Na]⁺ = 382.0762; 741.1621 [(M)₂ + Na]⁺, calculated for [(C₂₁H₁₁F₂N₃O₁)₂ + Na]⁺ = 741.1633.

IR: $\tilde{\nu}$ [cm⁻¹] = 3055, 2984, 2925, 2298, 2240, 2220, 1652, 1559, 1469, 1439, 1308, 1260, 1203, 1148, 1040, 1008, 896, 731, 701.

Melting point: 211 °C.

Crystals suitable for X-ray diffractometry were grown using a concentrated solution of **POA-01** in dichloromethane overlaid with butanone.

Compound POA-1'0



POA-1'0 was synthesized according to **GP2** using compound **3d** (0.400 g, 2.01 mmol, 1 eq.), tetrafluoroterephthalonitrile (TFTN, 0.400 g, 2.00 mmol, 1 eq.), and potassium carbonate (1.02 g, 7.40 mmol, 3.7 eq.) in anhydrous *N,N*-dimethylformamide (9 mL) at 60 °C for 42 hours. Column chromatography (6.5x35 cm, DCM) yielded product **POA-1'0** as an orange-colored powder (0.456 g, 1.27 mmol, 63%).

M(C₂₁H₁₁F₂N₃O): 359.34 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.62 (m, 3H, H10, H9), 7.41 (m, 2H, H8), 6.72 (d, $^4J_{H-H}$ = 1.7 Hz, 1H, H6), 6.76 (dd, $^3J_{H-H}$ = 8.2 Hz, $^4J_{H-H}$ = 1.7 Hz, 1H, H4), 6.03 (d, $^3J_{H-H}$ = 8.2 Hz, 1H, H3), 2.20 (s, 3H, H5a).

¹³C{¹H}-NMR (101 MHz, CDCl₃, 298 K): δ [ppm] = 146.5 (dd, $^1J_{C-F}$ = 253.6 Hz, $^2J_{C-F}$ = 13.2 Hz, C15), 144.5 (t, $^3J_{C-F}$ = 3.9 Hz, C12), 142.2 (dd, $^1J_{C-F}$ = 254.1 Hz, $^2J_{C-F}$ = 15.2 Hz, C16), 141.5 (C1), 137.5 (C7), 135.2 (C5), 134.7 (d, $^3J_{C-F}$ = 2.6 Hz, C11), 131.2 (C8), 131.2 (C9), 131.2 (C10), 128.4 (C2), 125.8 (C4), 116.9 (C6), 115.3 (C3), 108.9 (d, $^3J_{C-F}$ = 3.9 Hz, C18), 108.2 (d, $^3J_{C-F}$ = 3.7 Hz, C14), 95.5 (dd, $^2J_{C-F}$ = 17.0 Hz, $^3J_{C-F}$ = 2.0 Hz, C17), 91.5 (d, $^2J_{C-F}$ = 18.6 Hz, C13), 20.6 (C5a).

¹⁹F-NMR (376 MHz, CDCl₃, 298 K): δ [ppm] = -135.9 (d, $^3J_{F-F}$, 20.5 Hz, F15), -142.8 (d, $^3J_{F-F}$, 20.4 Hz, F16).

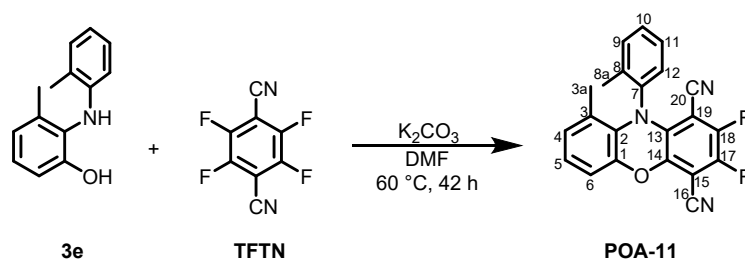
HR-MS (ESI-pos, 70 eV): m/z = 360.0938 [M + H]⁺, calculated for [C₂₁H₁₁F₂N₃O₁ + H]⁺ = 360.0943; 382.0763 [M + Na]⁺, calculated for [C₂₁H₁₁F₂N₃O₁ + Na]⁺ = 382.0762; 741.1630 [(M)₂ + Na]⁺, calculated for [(C₂₁H₁₁F₂N₃O₁)₂ + Na]⁺ = 741.1633.

IR: $\tilde{\nu}$ [cm⁻¹] = 2925, 2857, 2310, 2219, 1650, 1510, 1475, 1457, 1418, 1321, 1305, 1262, 1208, 1153, 1024, 817, 754, 697.

Melting point: 260 °C.

Crystals suitable for X-ray diffractometry were grown using a concentrated solution of **POA-1'0** in dichloromethane overlaid with methanol.

Compound POA-11



POA-11 was synthesized according to **GP2** using compound **3e** (0.252 g, 1.18 mmol, 1 eq.), tetrafluoroterephthalonitrile (TFTN, 0.236 g, 1.18 mmol, 1 eq.), and potassium carbonate (0.487 g, 3.52 mmol, 3 eq.) in anhydrous *N,N*-dimethylformamide (6 mL) at 60 °C for 42 hours. Column chromatography (6x28 cm, DCM/*n*-pentane 3/1) yielded product **POA-11** as a yellow powder (0.306 g, 0.819 mmol, 69%).

M(C₂₂H₁₃F₂N₃O): 373.36 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.98 (dd, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-H}$ = 2.2 Hz, 1H, *H*12), 7.35 (m, 2H, *H*10, *H*11), 7.24 (m, 1H, *H*9), 6.95 (t, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-H}$ = 7.5 Hz, 1H, *H*5), 6.90 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, *H*6), 6.79 (dd, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, *H*4), 2.29 (s, 3H, *H*8a), 1.91 (s, 3H, *H*3a).

¹³C{¹H}-NMR (101 MHz, CDCl₃, 298 K): δ [ppm] = 148.2 (t, $^3J_{C-F}$ = 3.0 Hz, *C*12), 147.2 (dd, $^1J_{C-F}$ = 256.1 Hz, $^2J_{C-F}$ = 13.3 Hz, *C*15), 147.1 (*C*1), 145.1 (dd, $^1J_{C-F}$ = 258.6 Hz, $^2J_{C-F}$ = 14.9 Hz, *C*16), 141.1 (*C*7), 138.8 (*C*8), 137.2 (*C*12), 135.7 (d, $^3J_{C-F}$ = 3.6 Hz, *C*11), 132.7 (*C*9), 131.0 (*C*3), 130.3 (*C*10), 130.0 (*C*4), 129.9 (*C*2), 126.4 (*C*11), 126.0 (*C*5), 114.8 (*C*6), 109.8 (d, $^3J_{C-F}$ = 3.7 Hz, *C*18), 108.7 (d, $^3J_{C-F}$ = 3.9 Hz, *C*14), 98.7 (dd, $^2J_{C-F}$ = 16.4 Hz, $^3J_{C-F}$ = 2.0 Hz, *C*17), 95.7 (dd, $^2J_{C-F}$ = 16.1 Hz, $^3J_{C-F}$ = 2.4 Hz, *C*13), 20.9 (*C*3a), 17.8 (*C*8a).

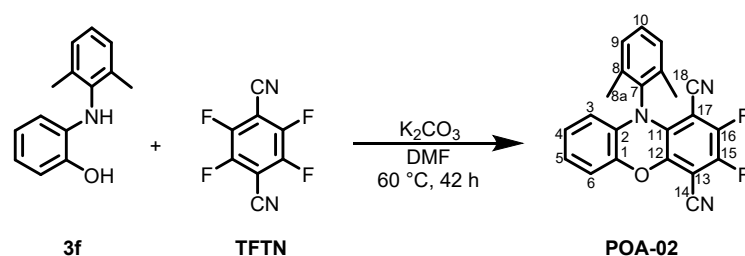
¹⁹F-NMR (376 MHz, CDCl₃, 298 K): δ [ppm] = -134.2 (d, $^3J_{F-F}$ = 20.6 Hz, *F*17), -136.6 (d, $^3J_{F-F}$ = 20.6 Hz, *F*18).

HR-MS (ESI-pos, 70 eV): *m/z* = 374.1096 [*M* + *H*]⁺, calculated for [C₂₂H₁₃F₂N₃O₁ + *H*]⁺ = 374.1099; 396.0919 [*M* + *Na*]⁺, calculated for [C₂₂H₁₃F₂N₃O₁ + *Na*]⁺ = 396.0919; 769.1944 [(*M*)₂ + *Na*]⁺, calculated for [(C₂₂H₁₃F₂N₃O₁)₂ + *Na*]⁺ = 769.1946.

IR: $\tilde{\nu}$ [cm⁻¹] = 2981, 2925, 2303, 2233, 2219, 1650, 1469, 1439, 1423, 1321, 1296, 1262, 1205, 1194, 1112, 1049, 1010, 978, 771, 731.

Melting point: 200 °C.

Compound POA-02



POA-02 was synthesized according to **GP2** using compound **3f** (0.227 g, 1.06 mmol, 1.2 eq.), tetrafluoroterephthalonitrile (TFTN, 0.173 g, 0.864 mmol, 1 eq.), and potassium carbonate (0.433 g, 3.13 mmol, 3.6 eq.) in anhydrous *N,N*-dimethylformamide (8 mL) at 60 °C for 42 hours. Column

chromatography (5x45 cm, DCM) yielded product **POA-02** as an orange-colored powder (55.6 mg, 0.149 mmol, 17%).

M(C₂₂H₁₃F₂N₃O): 373.36 g/mol.

¹H-NMR (600 MHz, CD₂Cl₂, 298 K): δ [ppm] = 7.43 (t, ³J_{H-H} = 7.6 Hz, 1H, H10), 7.26 (d, ³J_{H-H} = 7.6 Hz, 2H, H9), 6.87 (m, 2H, H5, H6), 6.76 (m, 1H, H4), 5.90 (dd, ³J_{H-H} = 8.1 Hz, ⁴J_{H-H} = 0.7 Hz, 1H, H3), 2.27 (s, 6H, H8a).

¹³C{¹H, ¹⁹F}-NMR (101 MHz, CD₂Cl₂, 298 K): δ [ppm] = 146.8 (C15), 144.6 (C12), 142.3 (C16), 142.1 (C1), 139.9 (C7), 133.6 (C11), 133.5 (C8), 131.7 (C10), 129.8 (C9), 129.0 (C2), 126.3 (C4), 125.1 (C5), 116.5 (C6), 114.3 (C3), 109.1 (C18), 107.9 (C14), 95.7 (C17), 90.0 (C13), 17.9 (C8a).

¹⁹F-NMR (564 MHz, CD₂Cl₂, 298 K): δ [ppm] = -137.3 (d, ³J_{F-F}, 20.6 Hz, F15), -144.5 (d, ³J_{F-F}, 20.6 Hz, F16).

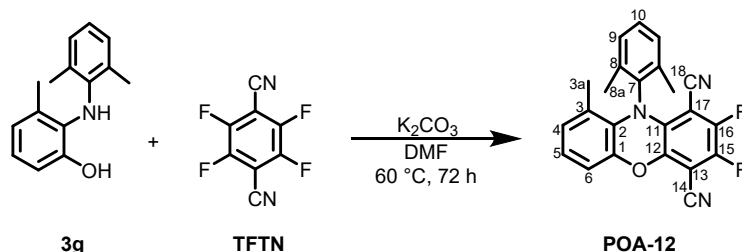
HR-MS (ESI-pos, 70 eV): m/z = 374.1097 [M + H]⁺, calculated for [C₂₂H₁₃F₂N₃O₁ + H]⁺ = 374.1099; 396.0915 [M + Na]⁺, calculated for [C₂₂H₁₃F₂N₃O₁ + Na]⁺ = 396.0919; 769.1949 [(M)₂ + Na]⁺, calculated for [(C₂₂H₁₃F₂N₃O₁)₂ + Na]⁺ = 769.1946.

IR: $\tilde{\nu}$ [cm⁻¹] = 2954, 2923, 2855, 2361, 2344, 2297, 2221, 1649, 1558, 1544, 1503, 1495, 1465, 1440, 1383, 1323, 1308, 1283, 1262, 1210, 1162, 1141, 1111, 1089, 1040, 1009, 967, 770, 750, 688, 674.

Melting point: 230 °C.

Crystals suitable for X-ray diffractometry were grown using a concentrated solution of **POA-02** in acetone.

Compound POA-12



POA-12 was synthesized according to **GP2** using compound **3g** (0.201 g, 0.885 mmol, 1 eq.), tetrafluoroterephthalonitrile (TFTN, 0.215 g, 1.08 mmol, 1.2 eq.), and potassium carbonate (0.368 g, 2.66 mmol, 3 eq.) in anhydrous *N,N*-dimethylformamide (12 mL) at 60 °C for 72 hours. Column chromatography (4.5x40 cm, DCM/*n*-pentane 1/3) and washing with cold cyclohexane yielded product **POA-12** as an orange-colored powder (0.133 g, 0.342 mmol, 39%).

M(C₂₃H₁₅F₂N₃O): 387.39 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.44 (t, ³J_{H-H} = 7.6 Hz, 1H, H10), 7.17 (d, ³J_{H-H} = 7.6 Hz, 2H, H9), 6.75 (m, 2H, H5, H6), 6.58 (m, 1H, H4), 2.33 (s, 6H, H8a), 1.31 (s, 3H, H3a).

¹³C{¹H, ¹⁹F}-NMR (101 MHz, CDCl₃, 298 K): δ [ppm] = 146.5 (C15), 143.8 (C12), 142.5 (C1), 142.1 (C16), 141.3 (C7), 136.3 (C8), 133.7 (C11), 132.3 (C10), 131.9 (C4), 129.1 (C9), 126.6 (C2), 124.7 (C3), 124.6 (C5), 115.8 (C6), 108.9 (C18), 107.2 (C14), 94.8 (C17), 89.9 (C13), 20.5 (C3a), 18.2 (C8a).

¹⁹F-NMR (376 MHz, CDCl₃, 298 K): δ [ppm] = -135.1 (d, ³J_{F-F}, 20.6 Hz, F15), -143.1 (d, ³J_{F-F}, 20.6 Hz, F16).

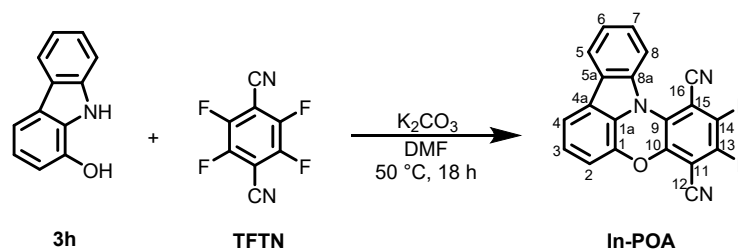
HR-MS (ESI-pos, 70 eV): m/z = 388.1256 [M + H]⁺, calculated for [C₂₃H₁₅F₂N₃O₁ + H]⁺ = 388.1256; 410.1079 [M + Na]⁺, calculated for [C₂₃H₁₅F₂N₃O₁ + Na]⁺ = 410.1075; 797.2257 [(M)₂ + Na]⁺, calculated for [(C₂₃H₁₅F₂N₃O₁)₂ + Na]⁺ = 797.2259.

IR: $\tilde{\nu}$ [cm⁻¹] = 2982, 2925, 2854, 2235, 2215, 1649, 1462, 1425, 1383, 1321, 1301, 1264, 1227, 1193, 1170, 1105, 1092, 1073, 1044, 1009, 978, 922, 888, 768, 754, 709, 673.

Melting point: 280 °C.

Crystals suitable for X-ray diffractometry were grown using a concentrated solution of **POA-12** in dichloromethane overlaid with ethyl acetate and chlorobenzene.

Compound In-POA



In-POA was synthesized according to **GP2** using compound **3h** (58.0 mg, 0.318 mmol, 1 eq.), tetrafluoroterephthalonitrile (TFTN, 0.131 g, 0.654 mmol, 2.1 eq.), and potassium carbonate (0.446 g, 3.22 mmol, 10 eq.) in anhydrous *N,N*-dimethylformamide (10 mL) at 50 °C overnight. Column chromatography (4.5x40 cm, cyclohexane/toluene 1/1) yielded product **In-POA** as an orange-colored powder (55.5 mg, 0.162 mmol, 51%).

M(C₂₀H₇F₂N₃O): 343.29 g/mol.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 8.01 (2 overlapping dd, 2H, *H*5, *H*8), 7.57 (overlapping td and dd, 2H, *H*4, *H*7), 7.45 (td, ³*J*_{H-H} = 7.4 Hz, ⁴*J*_{H-H} = 0.8 Hz, 1H, *H*6), 7.21 (t, ³*J*_{H-H} = 7.9 Hz, 1H, *H*3), 6.90 (dd, ³*J*_{H-H} = 7.9 Hz, ⁴*J*_{H-H} = 0.5 Hz, 1H, *H*2).

¹³C{¹H, ¹⁹F}-NMR (101 MHz, CDCl₃, 298 K): δ [ppm] = 147.5 (C10), 147.3 (C13), 144.8 (C14), 141.2 (C1), 136.3 (C8a), 129.6 (C9), 129.3 (C1a), 127.0 (C5a), 126.6 (C7), 126.1 (C3), 125.6 (C4a), 124.3 (C6), 121.8 (C5), 116.7 (C8), 116.6 (C4), 110.6 (C2), 110.5 (C16), 108.7 (C12), 98.0 (C15), 93.7 (C11).

¹⁹F-NMR (376 MHz, CDCl₃, 298 K): δ [ppm] = -134.8 (d, ³*J*_{F-F}, 20.6 Hz, *F*13), -137.9 (d, ³*J*_{F-F}, 20.6 Hz, *F*14).

HR-MS (ESI-pos, 70 eV): *m/z* = 344.0630 [M + H]⁺, calculated for [C₂₀H₇F₂N₃O₁ + H]⁺ = 344.0630; 366.0449 [M + Na]⁺, calculated for [C₂₀H₇F₂N₃O₁ + Na]⁺ = 366.0449; 709.1005 [(M)₂ + Na]⁺, calculated for [(C₂₀H₇F₂N₃O₁)₂ + Na]⁺ = 709.1007.

IR: $\tilde{\nu}$ [cm⁻¹] = 3068, 2919, 2850, 2559, 2461, 2425, 2361, 2225, 2189, 2108, 2087, 2040, 2016, 1968, 1946, 1913, 1870, 1833, 1745, 1715, 1701, 1653, 1627, 1593, 1564, 1475, 1451, 1431, 1315, 1278, 1238, 1162, 1143, 1068, 1040, 1004, 961, 873, 785, 742, 693, 637.

Melting point: 227 °C.

Crystals suitable for X-ray diffractometry were grown using a concentrated solution of **In-POA** in dichloromethane overlaid with methanol.

NMR SPECTRA

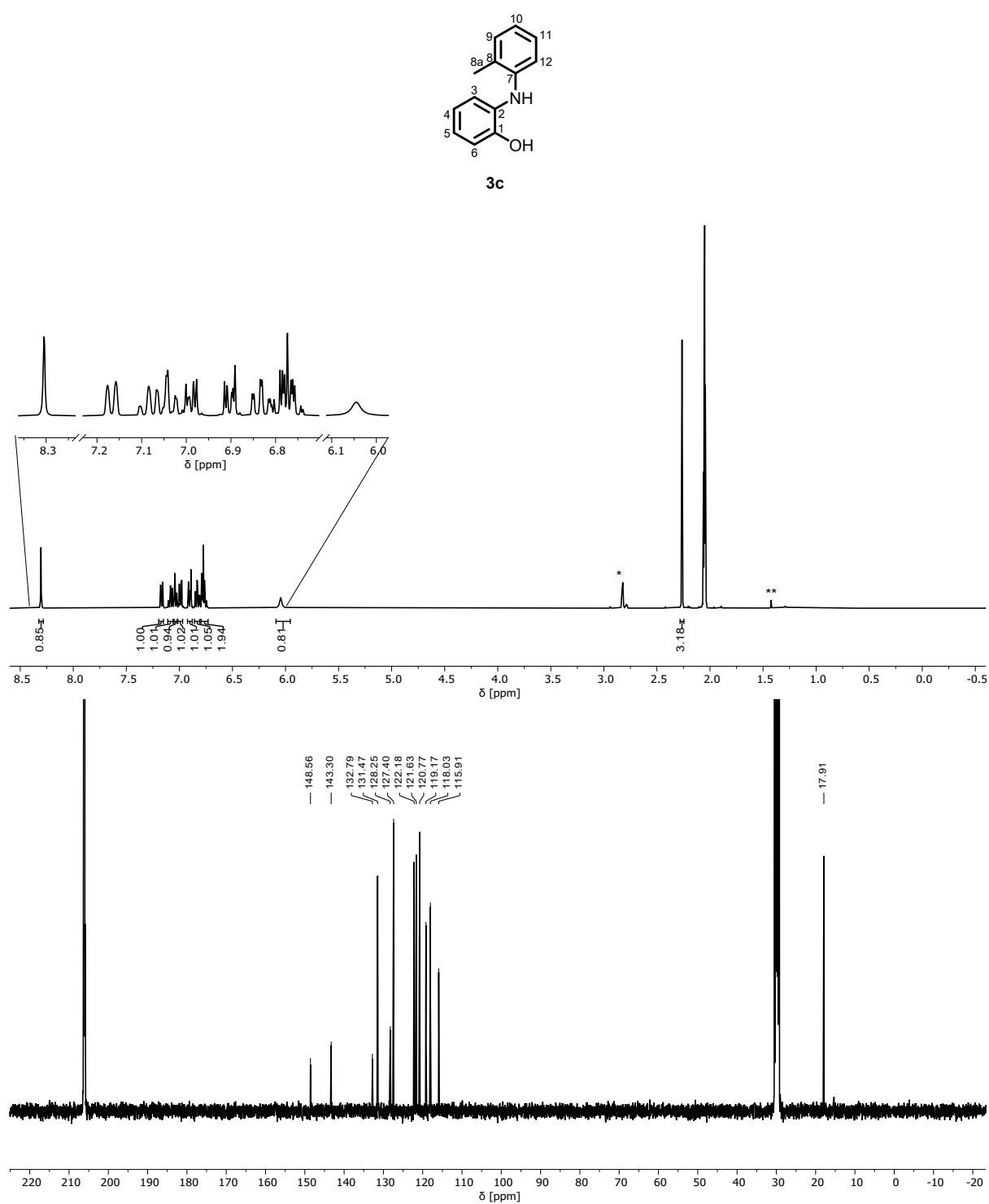


Figure S2: ¹H- (top, 400 MHz, acetone-*d*₆, 298 K) and ¹³C-NMR spectrum (bottom, 101 MHz, acetone-*d*₆, 298 K) of compound **3c** (* = water, ** = cyclohexane).

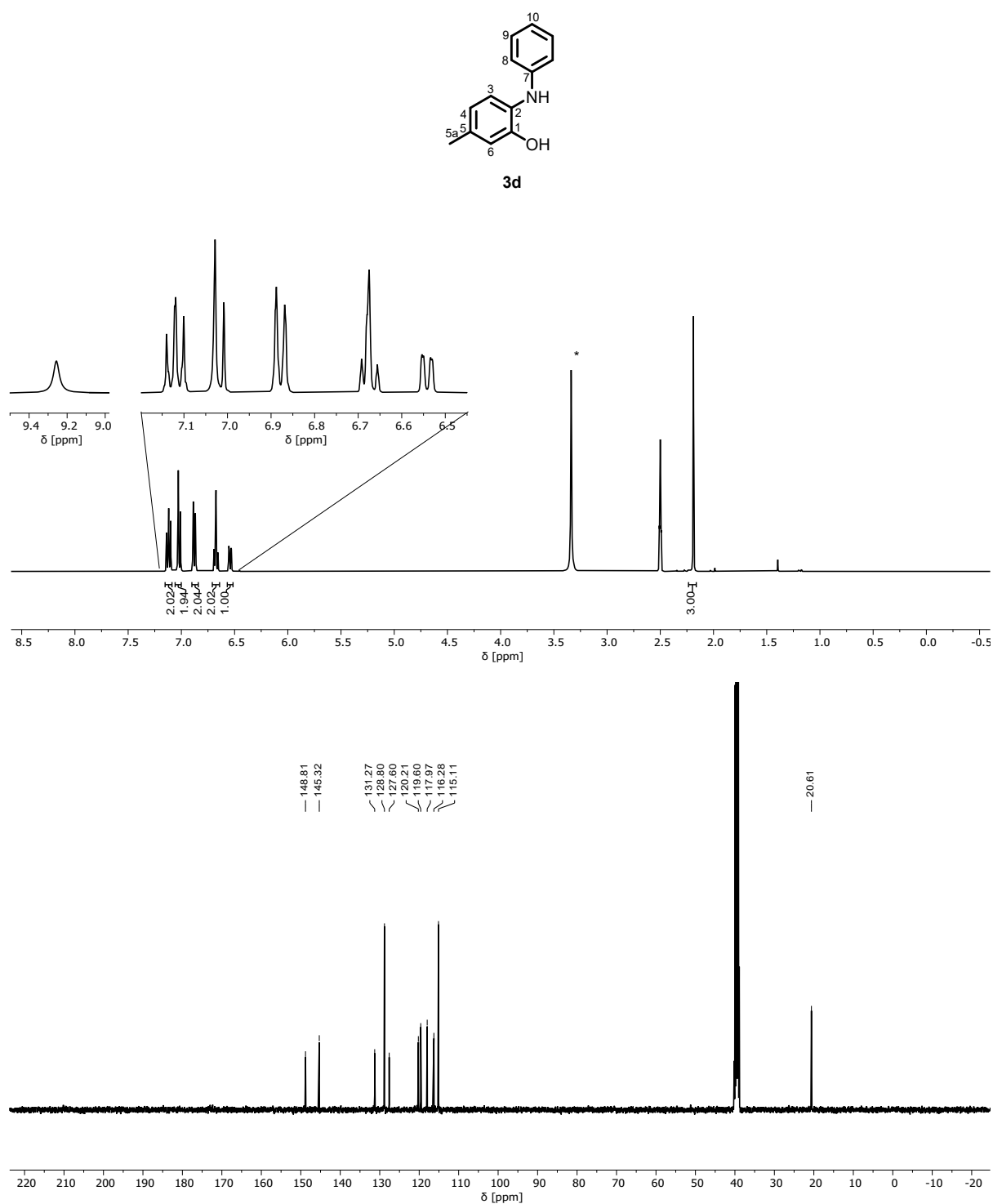


Figure S3: ^1H - (top, 400 MHz, $\text{DMSO}-d_6$, 298 K) and ^{13}C -NMR spectrum (bottom, 101 MHz, $\text{DMSO}-d_6$, 298 K) of compound **3d** (* = water).

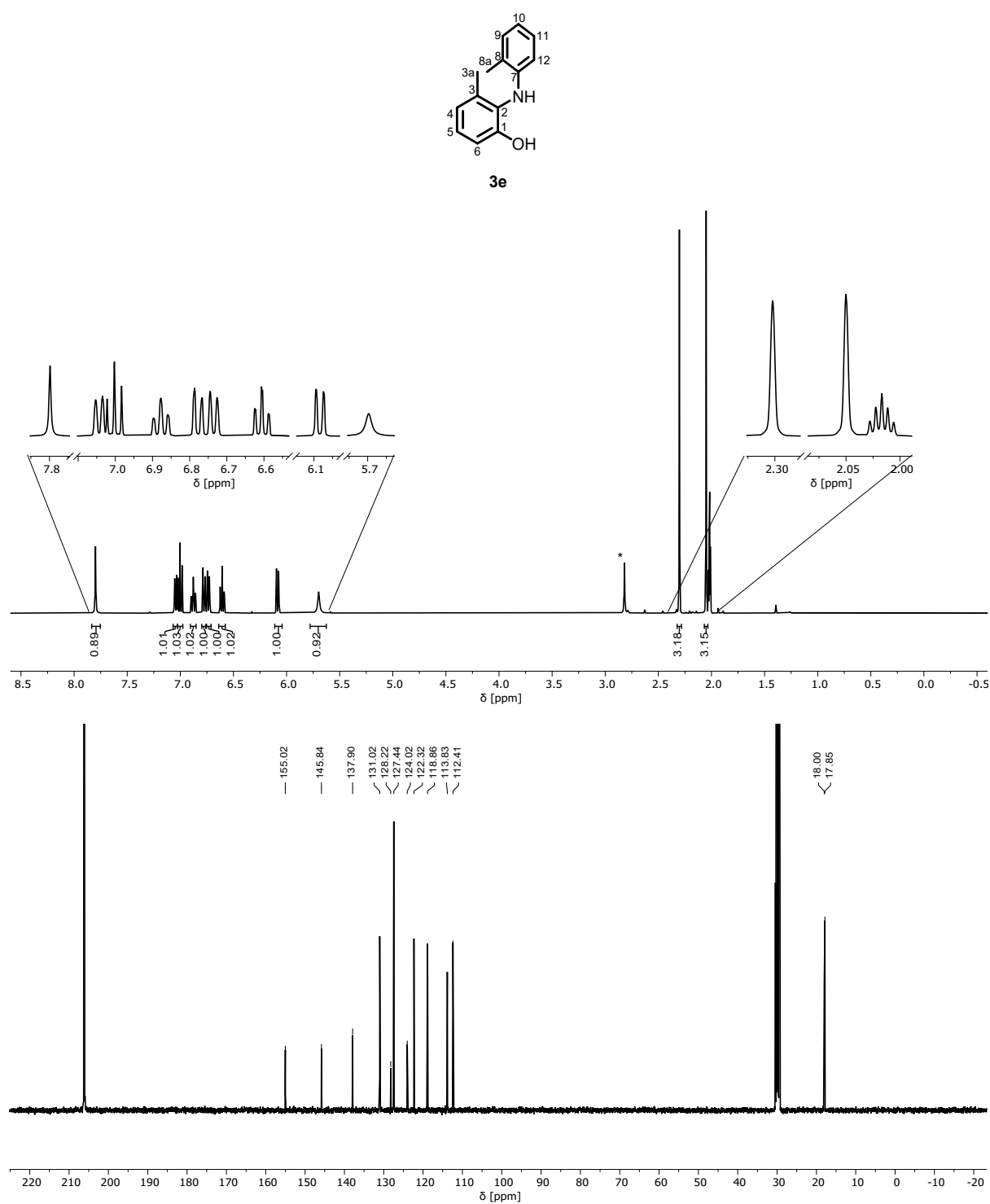


Figure S4: ^1H - (top, 400 MHz, $\text{DMSO}-d_6$, 298 K) and ^{13}C -NMR spectrum (bottom, 101 MHz, $\text{DMSO}-d_6$, 298 K) of compound **3e** (* = water).

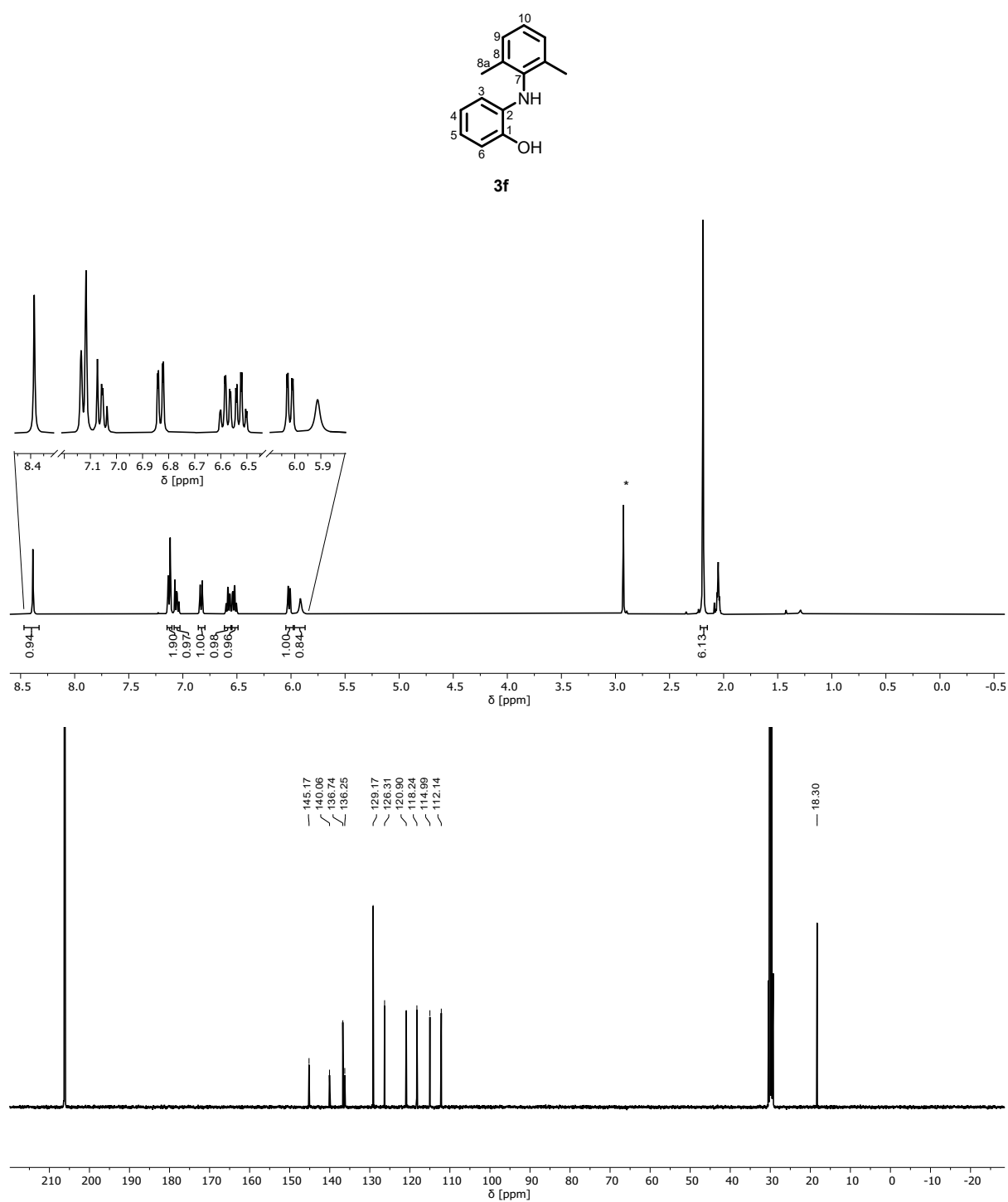


Figure S5: ^1H - (top, 400 MHz, acetone- d_6 , 298 K) and ^{13}C -NMR spectrum (bottom, 101 MHz, acetone- d_6 , 298 K) of compound **3f** (* = water).

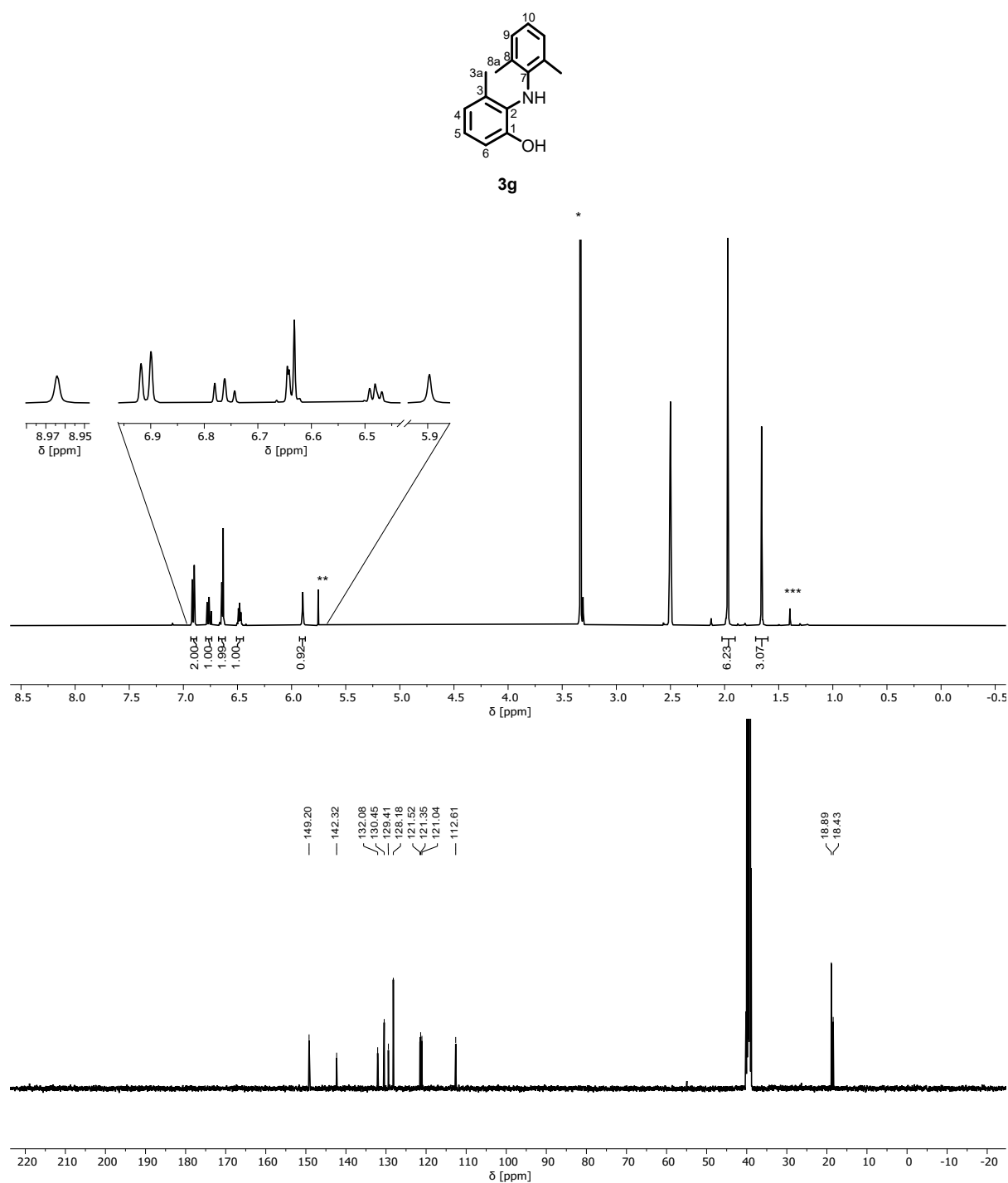


Figure S6: ¹H- (top, 400 MHz, DMSO-*d*₆, 298 K) and ¹³C-NMR spectrum (bottom, 101 MHz, DMSO-*d*₆, 298 K) of compound **3g** (* = water, ** = dichloromethane, *** = cyclohexane).

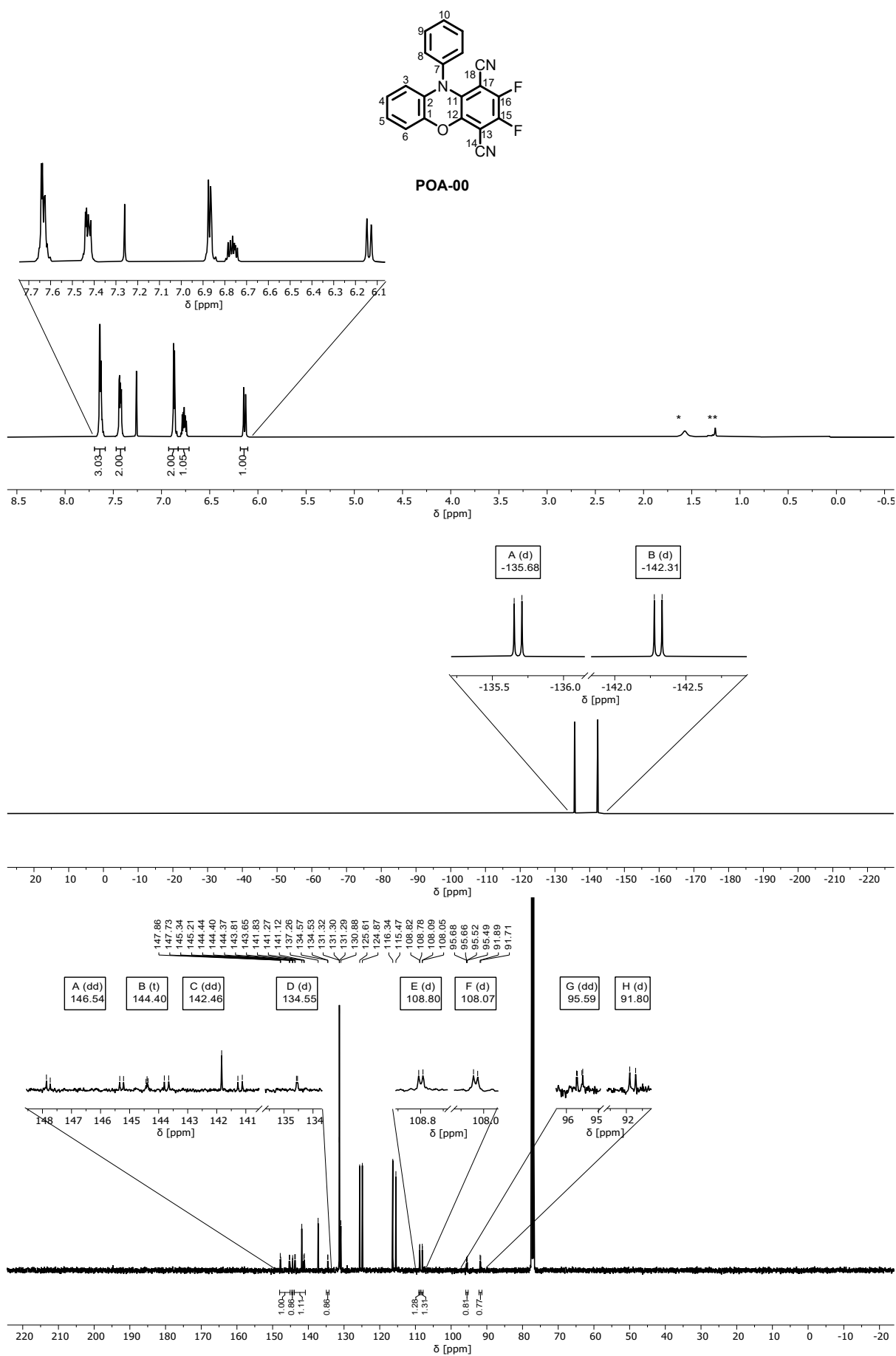


Figure S7: ¹H- (top, 400 MHz), ¹⁹F (center, 376 MHz) and ¹³C-NMR spectrum (bottom, 101 MHz) of compound **POA-00** (all spectra in CDCl₃ at 298 K; * = water, ** = H-grease).

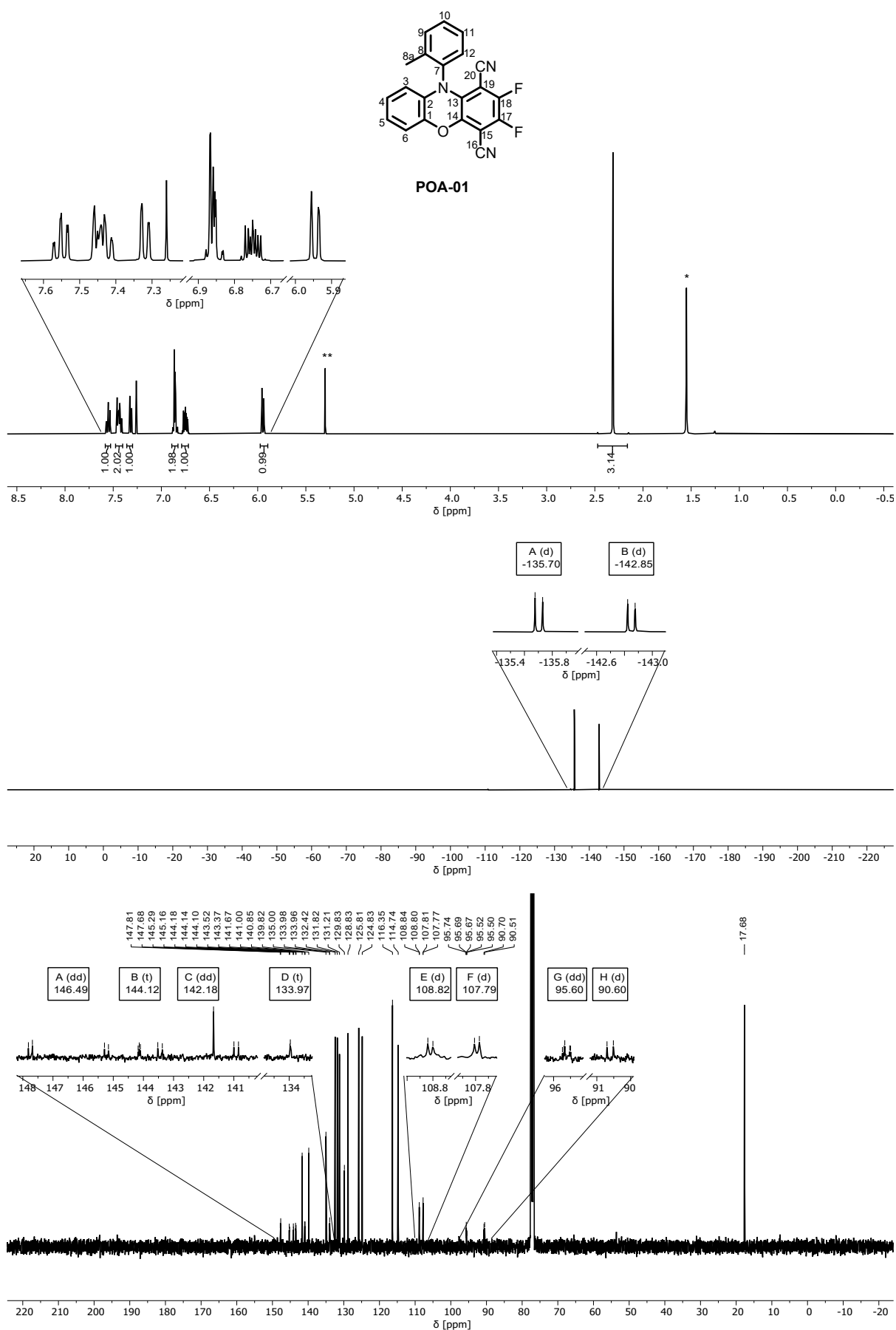


Figure S8: ¹H- (top, 400 MHz), ¹⁹F (center, 376 MHz) and ¹³C-NMR spectrum (bottom, 101 MHz) of compound **POA-01** (all spectra in CDCl₃ at 298 K; * = water, ** = dichloromethane).

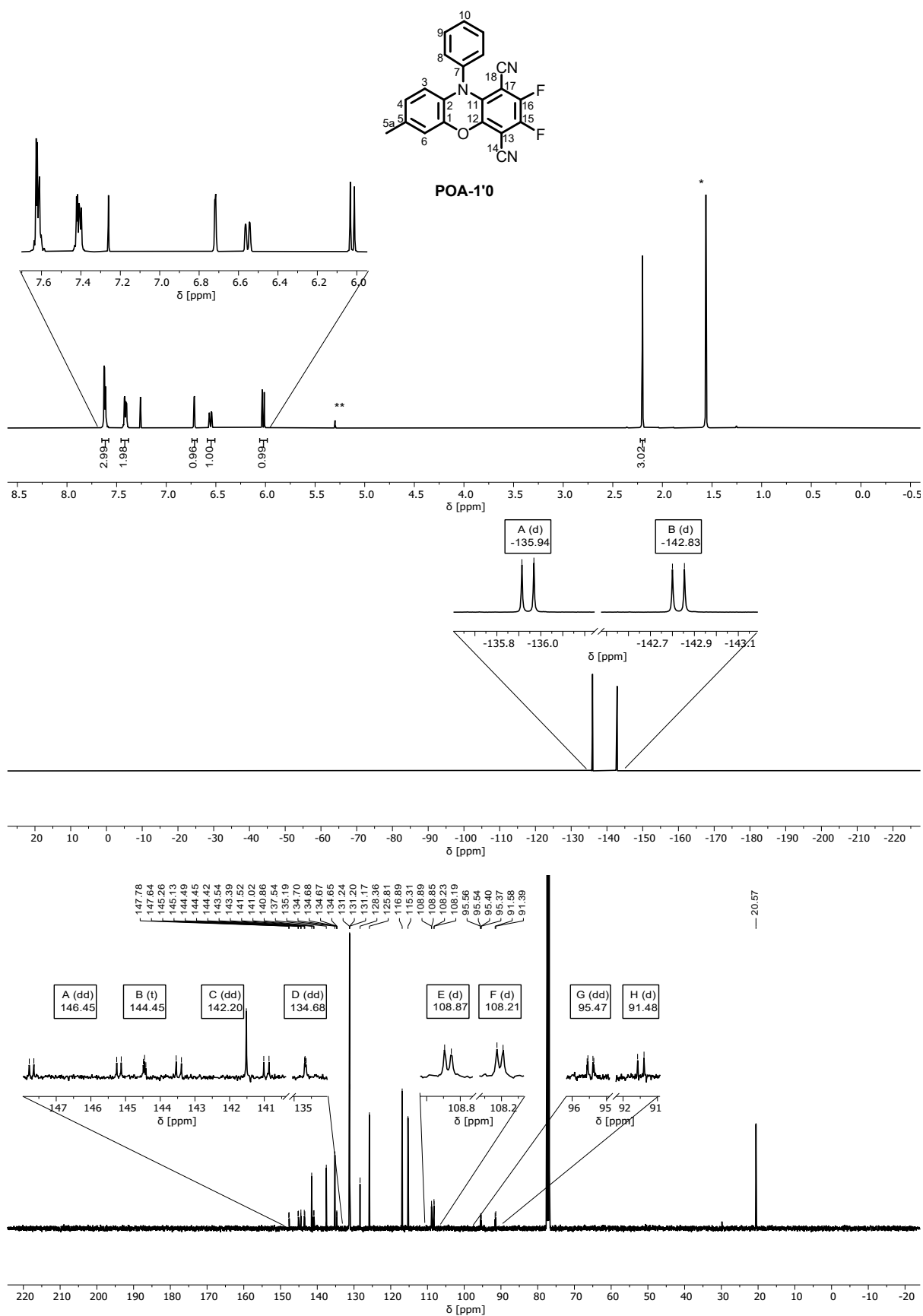


Figure S9: ¹H- (top, 400 MHz), ¹⁹F (center, 376 MHz) and ¹³C-NMR spectrum (bottom, 101 MHz) of compound POA-1'0 (all spectra in CDCl₃ at 298 K; * = water, ** = dichloromethane).

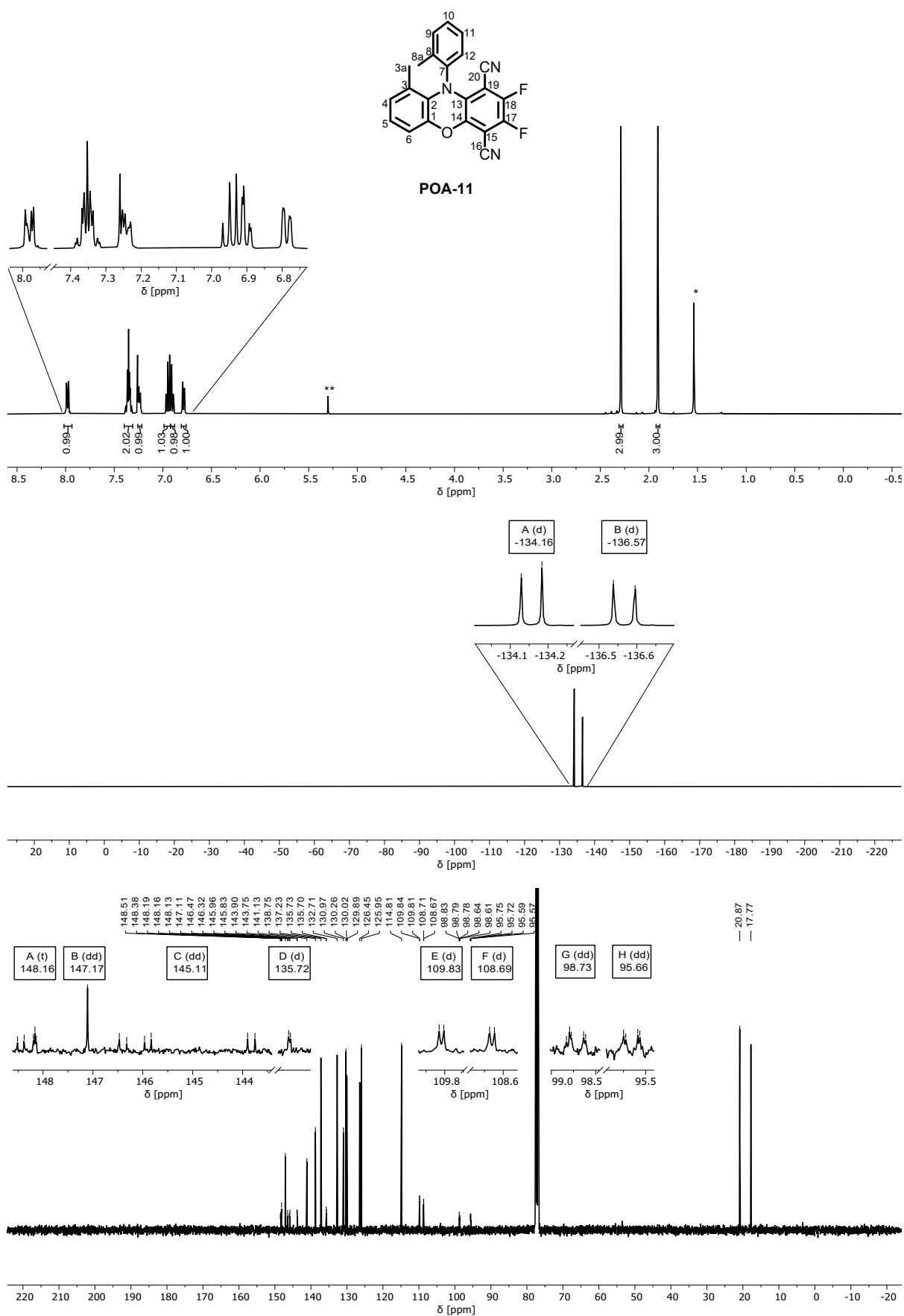


Figure S10: ¹H- (top, 400 MHz), ¹⁹F (center, 376 MHz) and ¹³C-NMR spectrum (bottom, 101 MHz) of compound POA-11 (all spectra in CDCl₃ at 298 K; * = water, ** = dichloromethane).

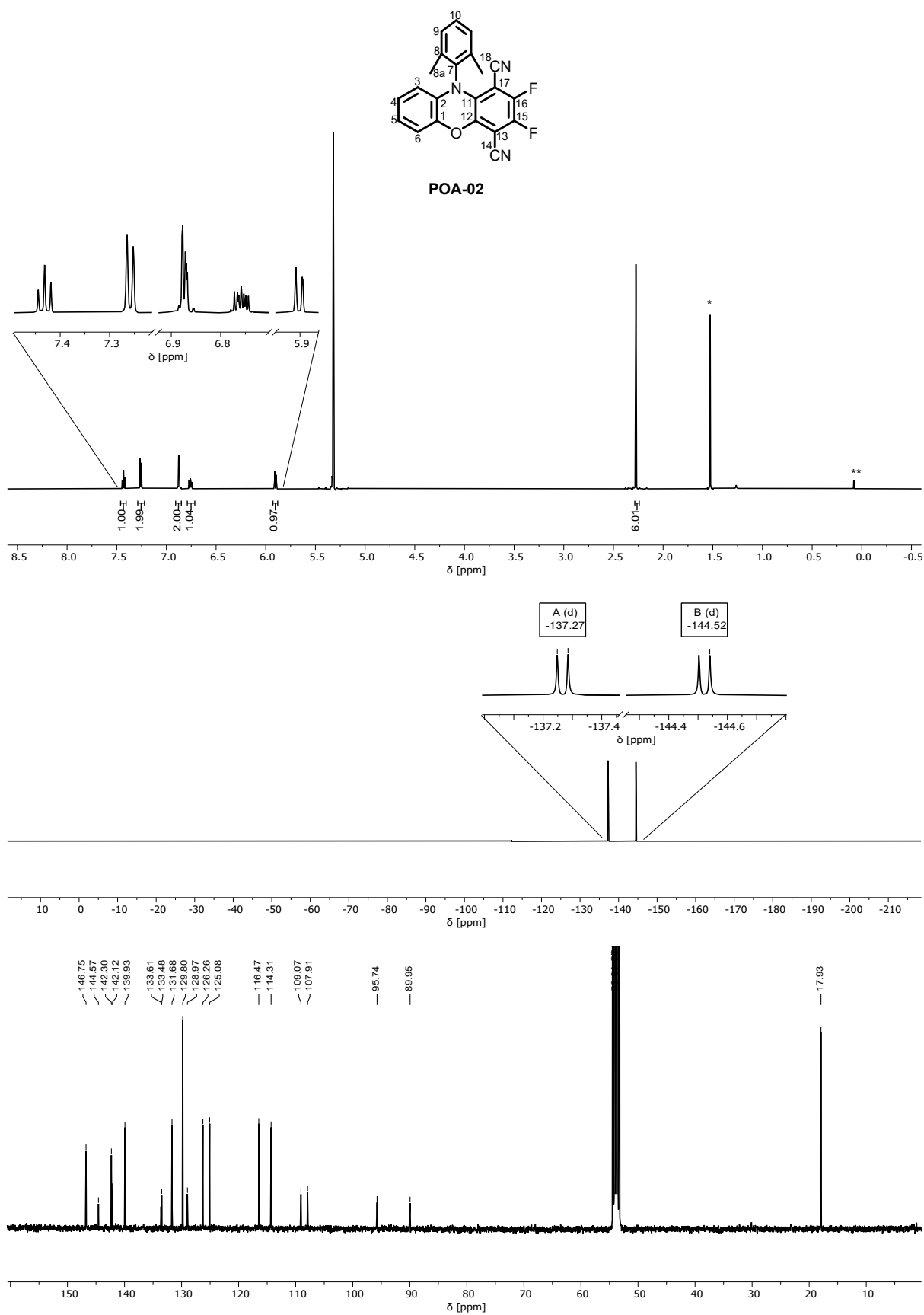


Figure S11: ¹H- (top, 600 MHz), ¹⁹F (center, 564 MHz) and ¹³C-NMR spectrum (bottom, 101 MHz, ¹H-&¹⁹F-decoupled) of compound **POA-02** (all spectra in CD₂Cl₂ at 298 K; * = water, ** = silicon grease).

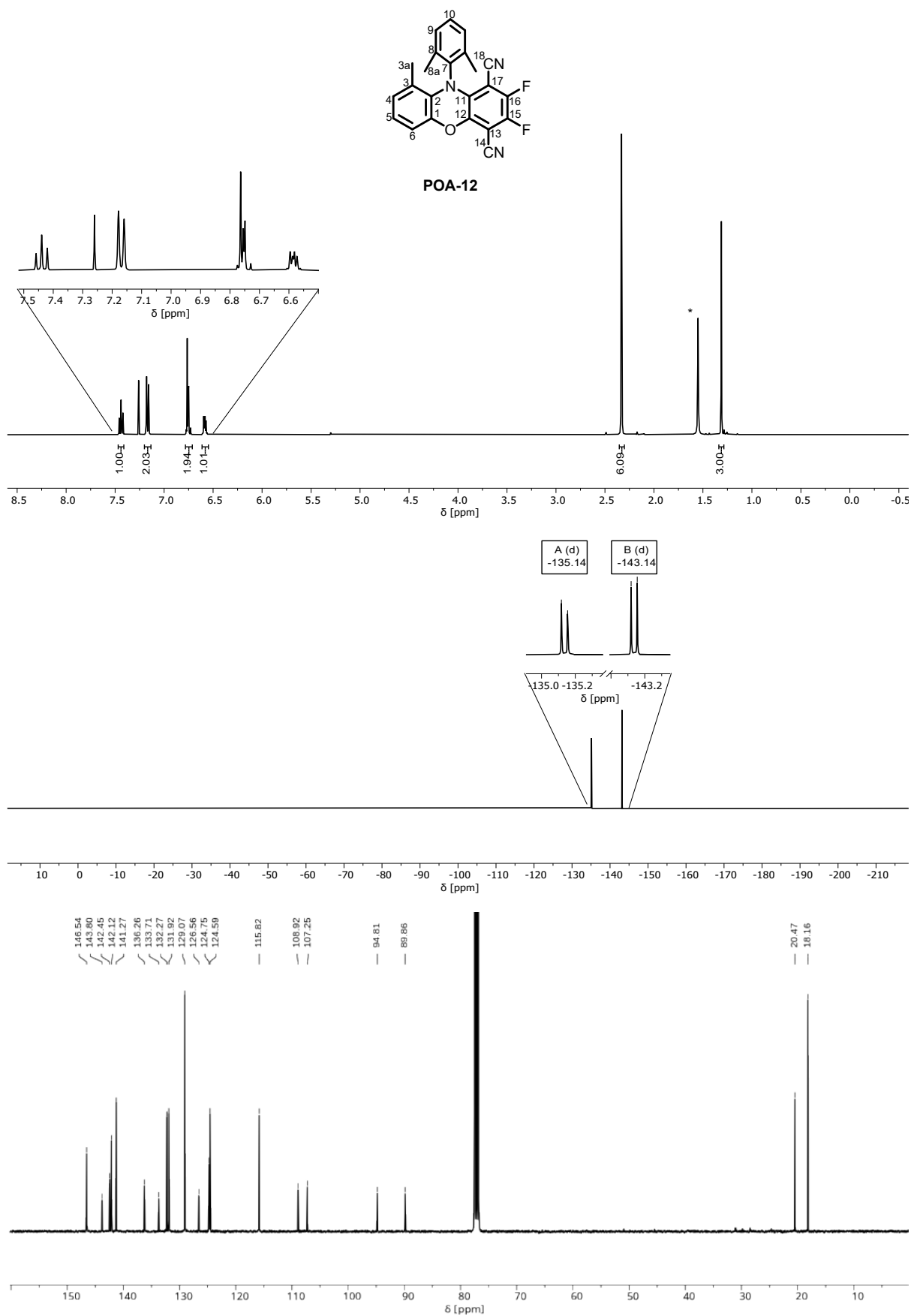


Figure S12: ¹H- (top, 400 MHz), ¹⁹F (center, 376 MHz) and ¹³C-NMR spectrum (bottom, 101 MHz, ¹H- & ¹⁹F-decoupled) of compound **POA-12** (all spectra in CDCl₃ at 298 K; * = water).

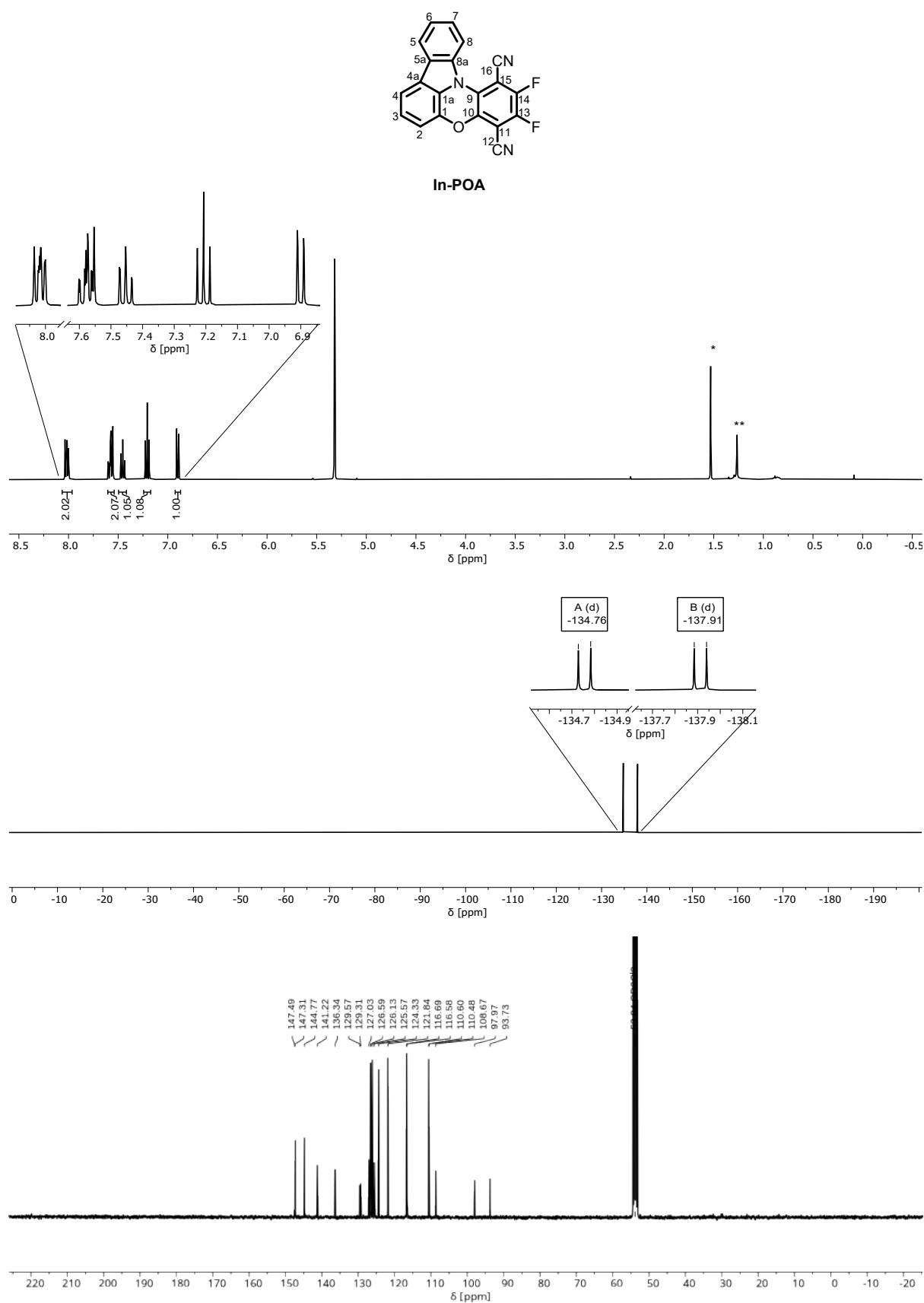


Figure S13: ¹H- (top, 400 MHz), ¹⁹F (center, 376 MHz) and ¹³C-NMR spectrum (bottom, 101 MHz, ¹H-&¹⁹F-decoupled) of compound **In-POA** (all spectra in CDCl₃ at 298 K; * = water, ** = H grease).

HPLC CHROMATOGRAMS

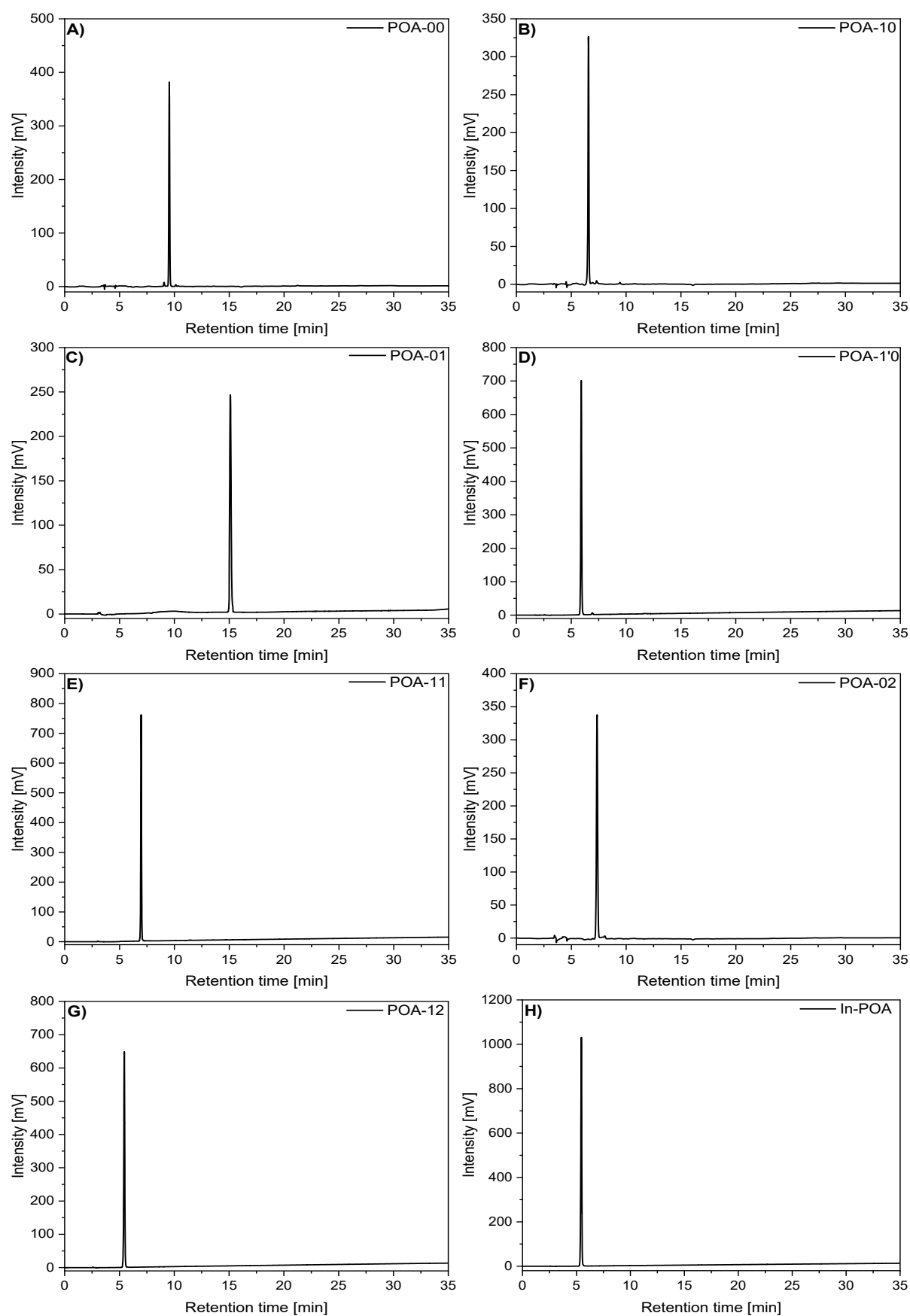
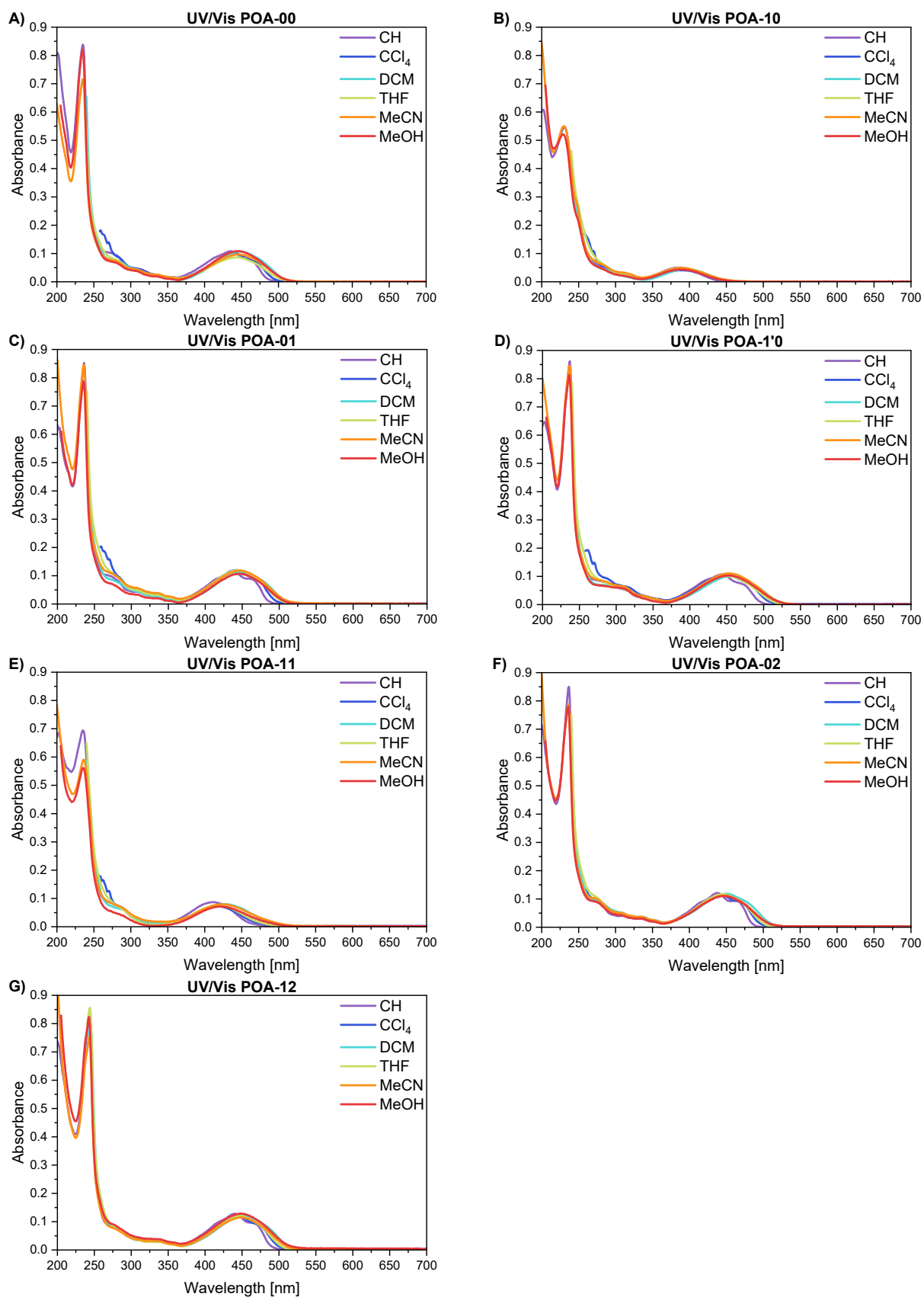
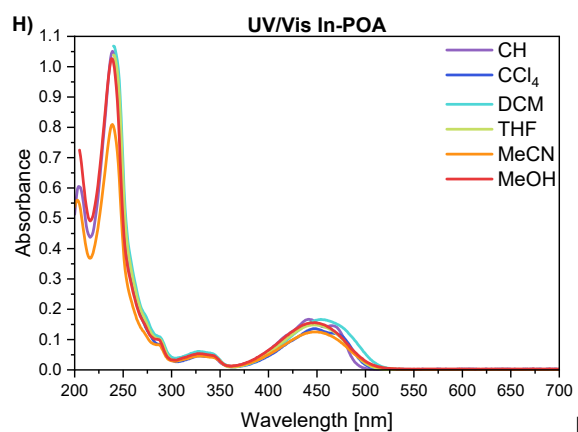


Figure S14: HPLC chromatograms of all compounds with HPLC setup 1 (A, B, F) or setup 2 (C, D, E, G, H). Run condition: *n*-hexane/ethyl acetate 90/10 → 0/100 over 35 min for A, B, C, D, F, G, H or 98/2 → 0/100 over 35 min for E.

3 PHOTOPHYSICAL PROPERTIES

UV/Vis ABSORPTION SPECTRA





compounds in all solvents (each 15 μ M).

Figure S15: UV/Vis absorption spectra of the target

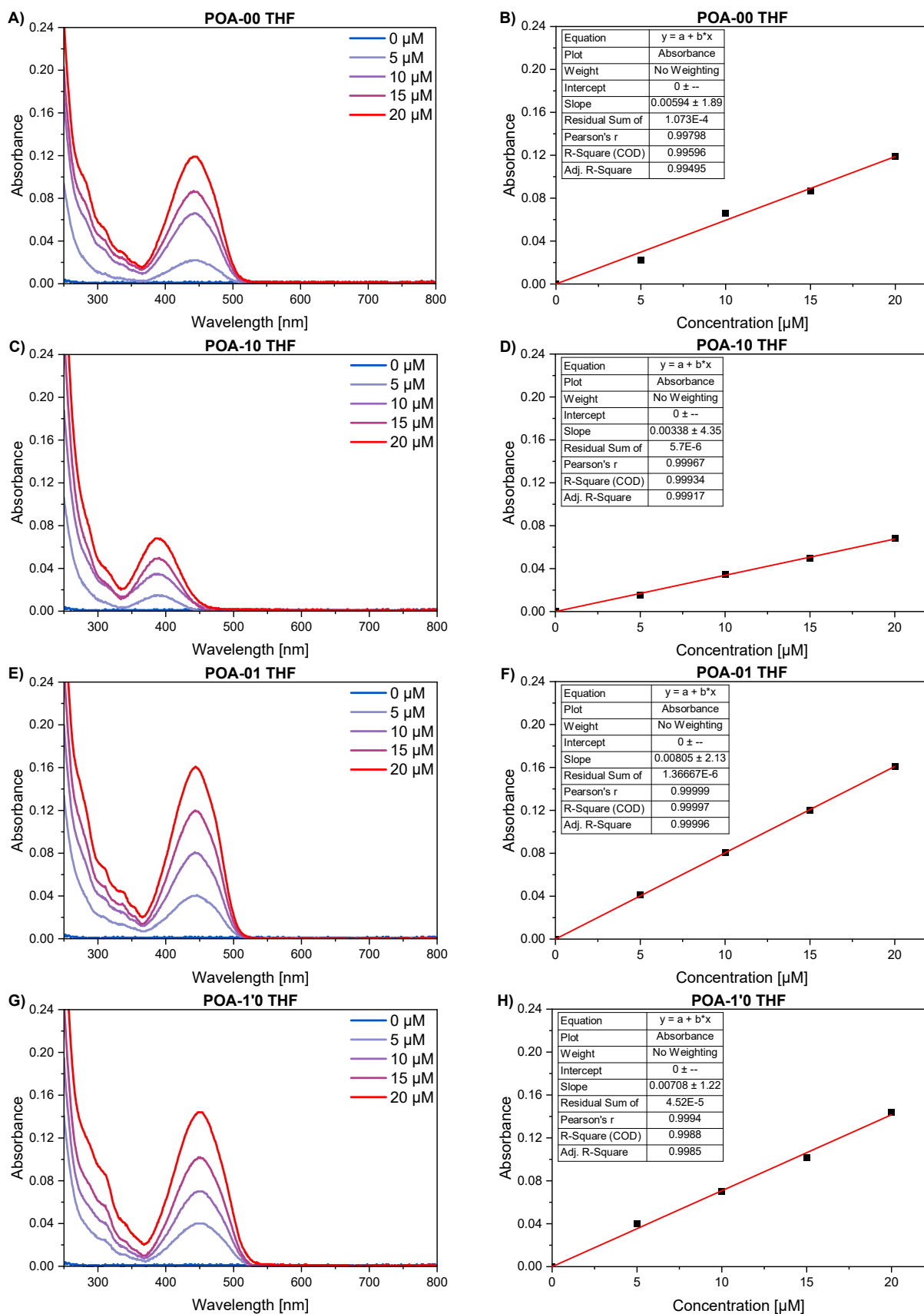
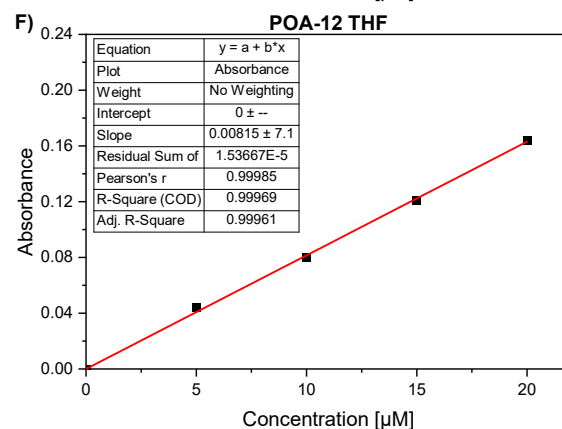
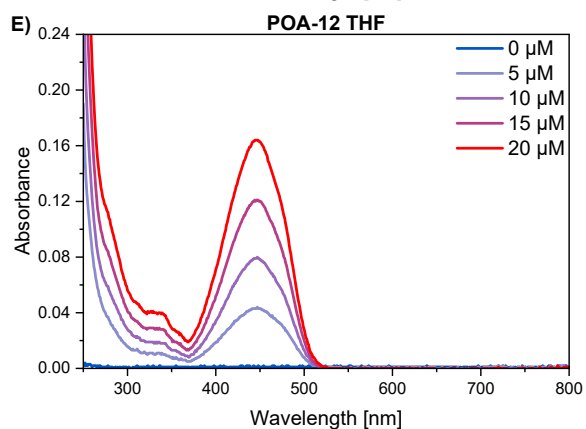
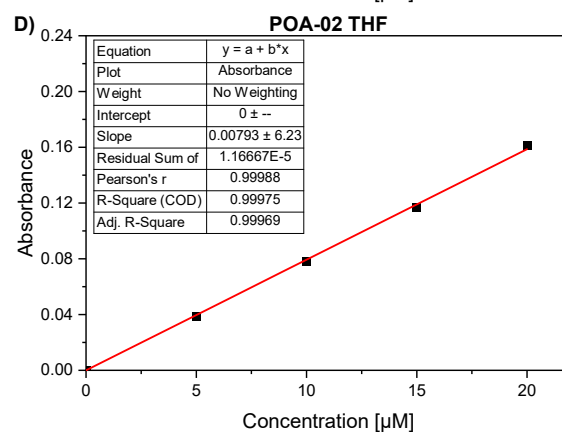
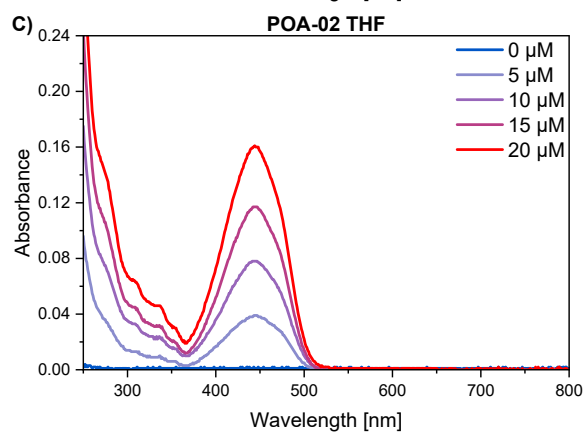
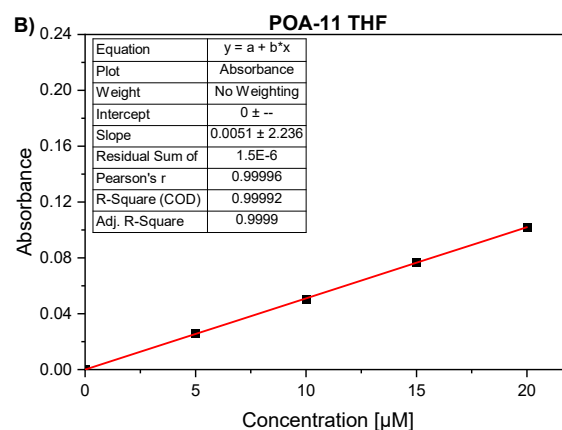
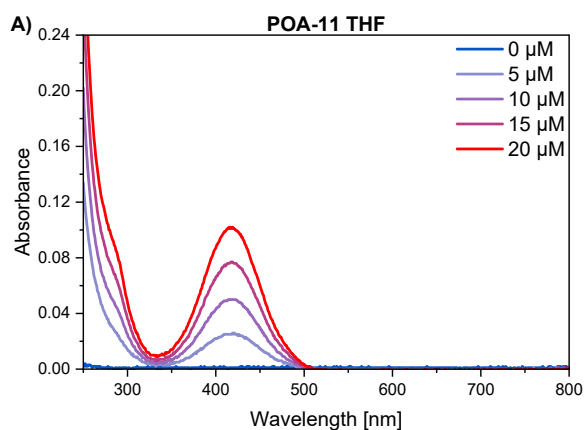


Figure S16: Left: UV/Vis absorption spectra of **POA-00 (A)**, **POA-10 (C)**, **POA-01 (E)**, and **POA-1'0 (G)** in THF; right: linear plot of the respective absorption maxima for determination of molar extinction coefficient ϵ .



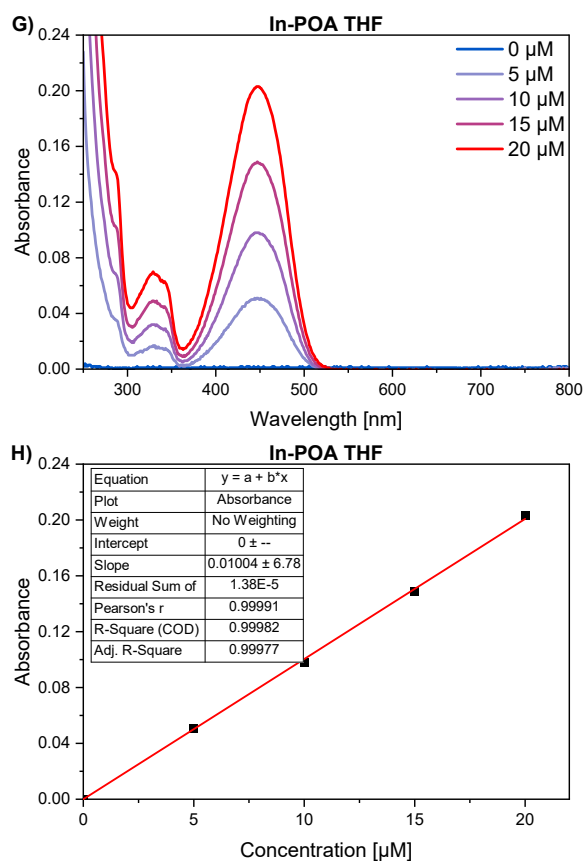


Figure S17: Left: UV/Vis absorption spectra of **POA-11** (A), **POA-02** (C), **POA-12** (E), and **In-POA** (G) in THF; right: linear plot of the respective absorption maxima for determination of molar extinction coefficient ϵ .

Table S1: Summary of UV/Vis absorption maxima and overview of all molar absorption coefficients in THF.

Solvent	POA-00	POA-10	POA-01	POA-1'0	POA-11	POA-02	POA-12	In-POA
CH	235, 436	231, 388	236, 436, 460	237, 442	235, 412	237, 438, 462	243, 441, 462	204, 239, 441, 465
CCl ₄	441	389	442	451	416	442	446	447
DCM	449	396	451	457	427	450	245, 454	454
THF	445	389	444	450	417	444	244, 446	448
MeCN	235, 446	230, 389	236, 446	236, 454	236, 424	236, 446	243, 449	203, 239, 449
MeOH	235, 446	229, 389	235, 446	236, 453	235, 422	236, 447	243, 449	239, 447
ϵ (THF) [L·mol ⁻¹ ·cm ⁻¹]	5940	3380	8050	7080	5100	7930	8150	10040

PHOTOLUMINESCENCE IN SOLUTION

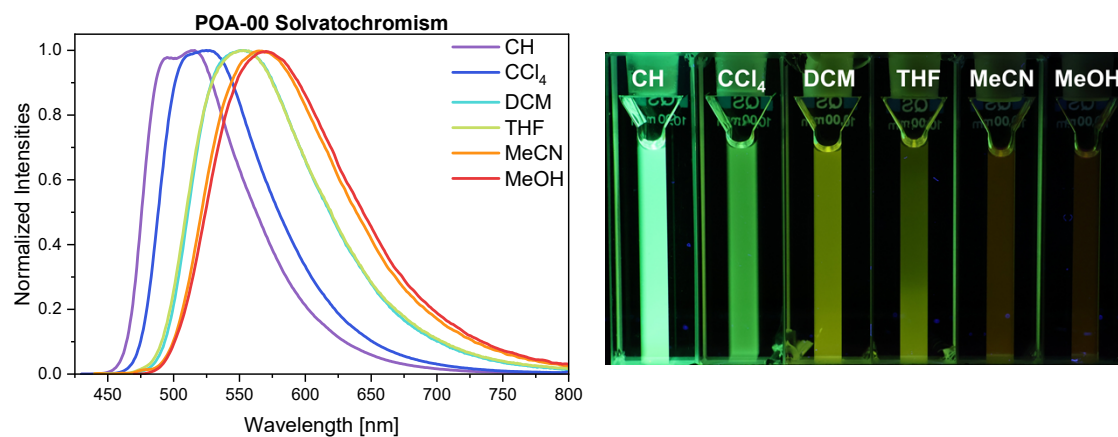


Figure S18: Normalized emission spectra (left, each 15 μM , emission at $\lambda_{\text{ex}} = 410 \text{ nm}$) of **POA-00** in cyclohexane (CH), CCl₄, DCM, THF, MeCN, MeOH (f.l.t.r.) and corresponding pictures taken under UV-light (365 nm, right).

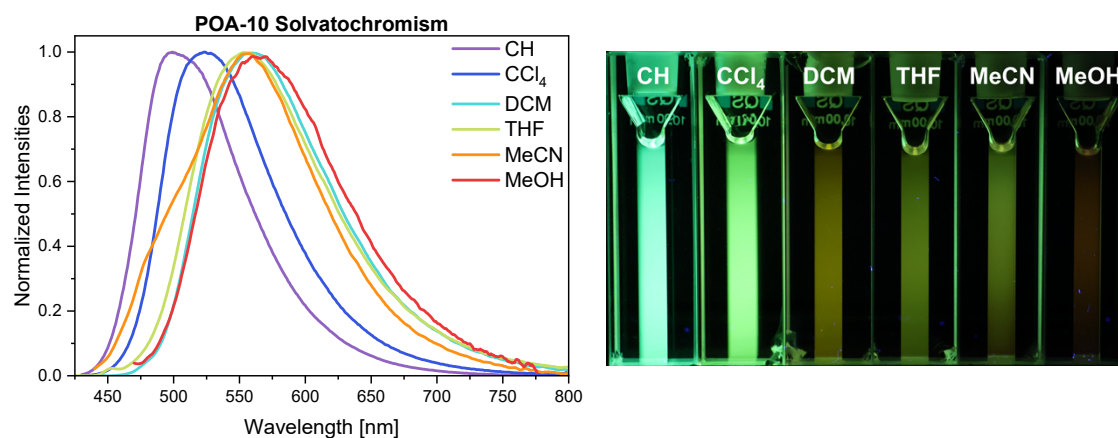


Figure S19: Normalized emission spectra (left, each 15 μM , emission at $\lambda_{\text{ex}} = 410 \text{ nm}$) of **POA-10** in cyclohexane (CH), CCl₄, DCM, THF, MeCN, MeOH (f.l.t.r.) and corresponding pictures taken under UV-light (365 nm, right).

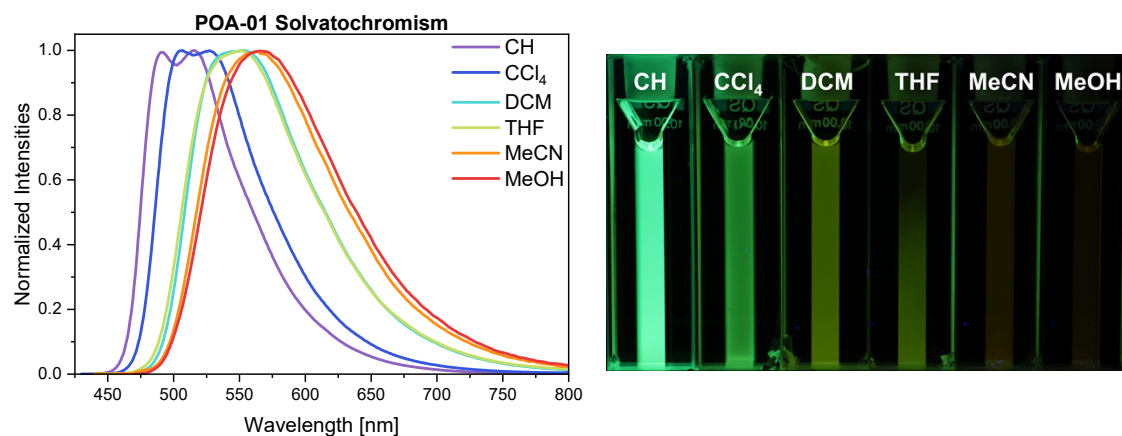


Figure S20: Normalized emission spectra (left, each 15 μM , emission at $\lambda_{\text{ex}} = 410 \text{ nm}$) of **POA-01** in cyclohexane (CH), CCl₄, DCM, THF, MeCN, MeOH (f.l.t.r.) and corresponding pictures taken under UV-light (365 nm, right).

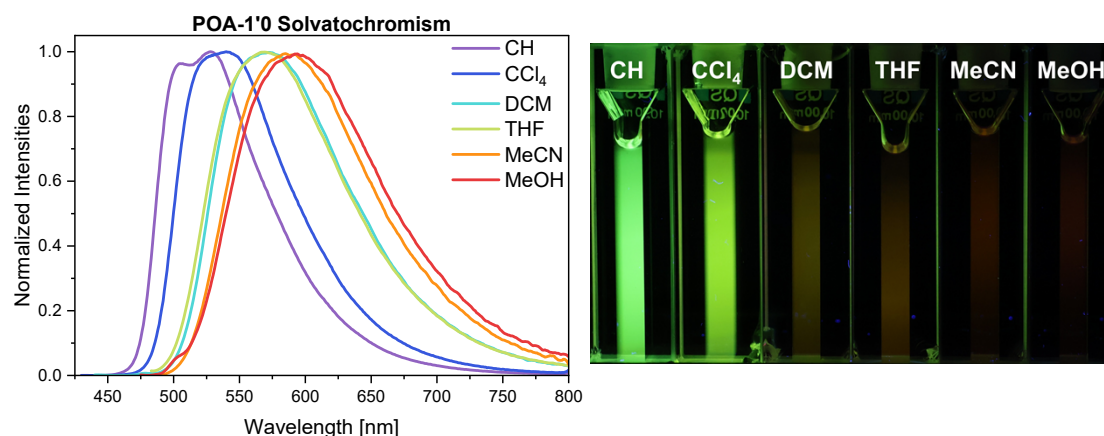


Figure S21: Normalized emission spectra (left, each 15 μ M, emission at $\lambda_{\text{ex}} = 410$ nm) of **POA-1'0** in cyclohexane (CH), CCl₄, DCM, THF, MeCN, MeOH (f.l.t.r.) and corresponding pictures taken under UV-light (365 nm, right).

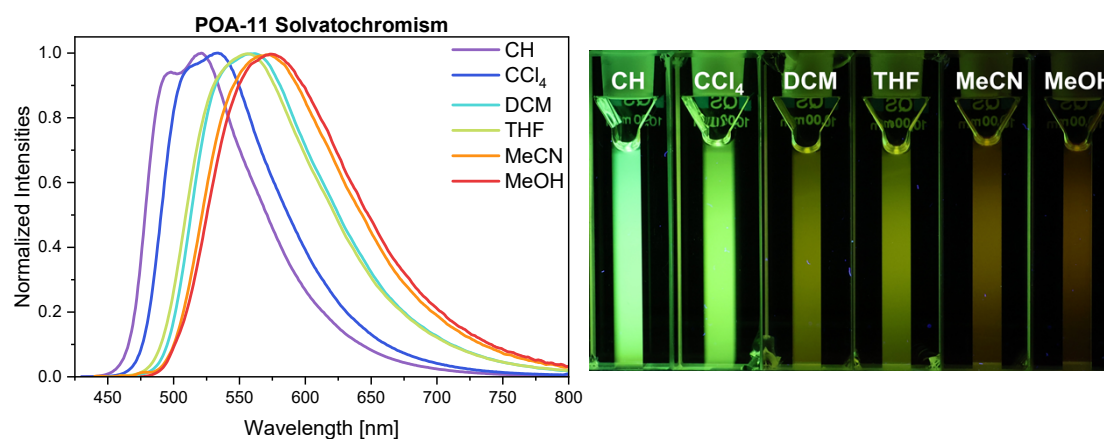


Figure S22: Normalized emission spectra (left, each 15 μ M, emission at $\lambda_{\text{ex}} = 410$ nm) of **POA-11** in cyclohexane (CH), CCl₄, DCM, THF, MeCN, MeOH (f.l.t.r.) and corresponding pictures taken under UV-light (365 nm, right).

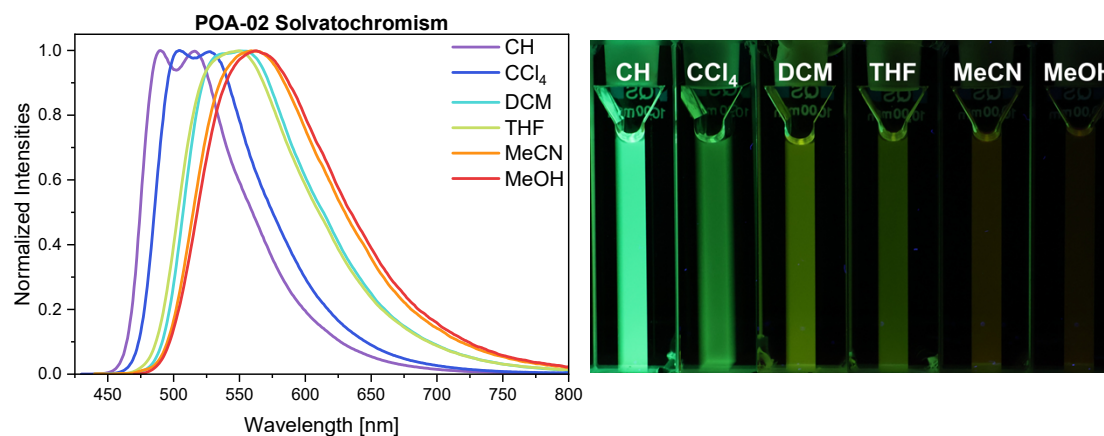


Figure S23: Normalized emission spectra (left, each 15 μ M, emission at $\lambda_{\text{ex}} = 410$ nm) of **POA-02** in cyclohexane (CH), CCl₄, DCM, THF, MeCN, MeOH (f.l.t.r.) and corresponding pictures taken under UV-light (365 nm, right).

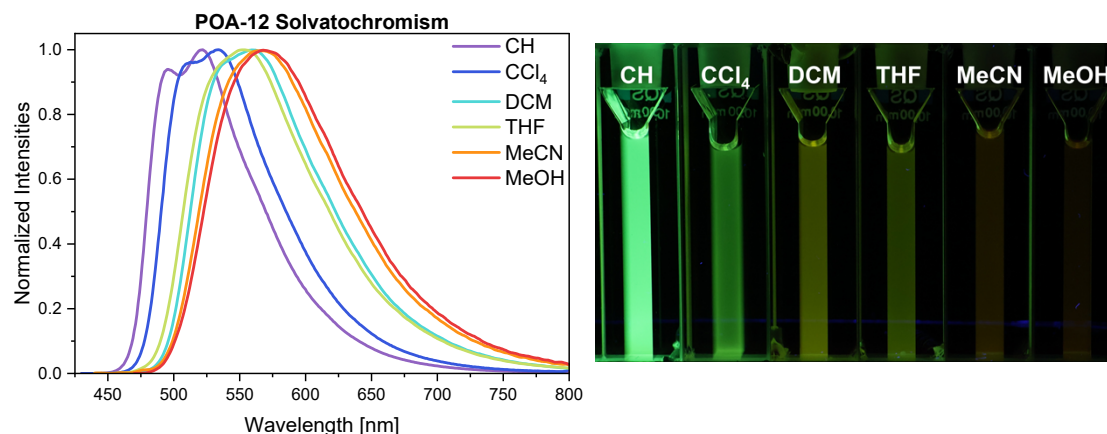


Figure S24: Normalized emission spectra (left, each 15 μ M, emission at $\lambda_{\text{ex}} = 410$ nm) of **POA-12** in cyclohexane (CH), CCl_4 , DCM, THF, MeCN, MeOH (f.l.t.r.) and corresponding pictures taken under UV-light (365 nm, right).

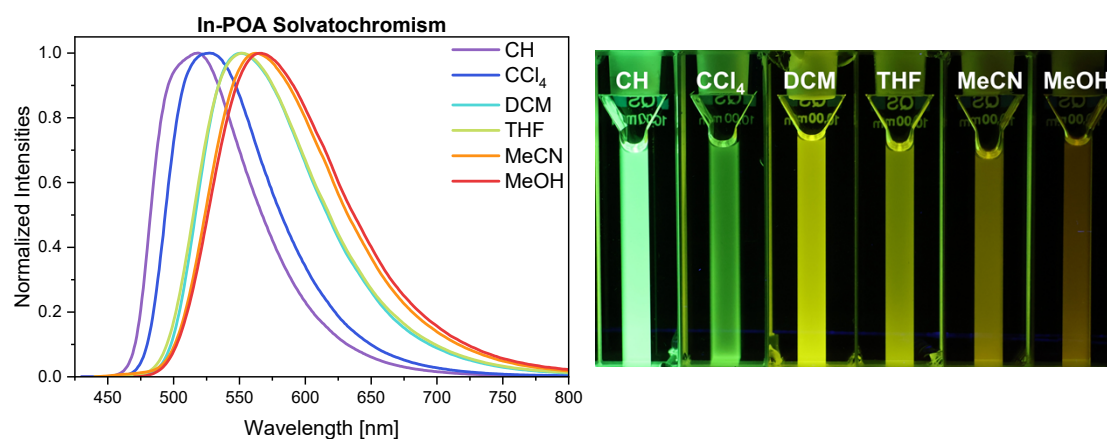


Figure S25: Normalized emission spectra (left, each 15 μ M, emission at $\lambda_{\text{ex}} = 410$ nm) of **In-POA** in cyclohexane (CH), CCl_4 , DCM, THF, MeCN, MeOH (f.l.t.r.) and corresponding pictures taken under UV-light (365 nm, right).

Table S2: Overview of emission maxima in solution.

Solvent	POA-00	POA-10	POA-01	POA-1'0	POA-11	POA-02	POA-12	In-POA
CH	495, 516	499	492, 516	507, 528	498, 521	490, 516	495, 522	518
CCl_4	525	524	507, 526	540	533	504, 528	512, 534	527
DCM	553	559	554	569	561	552	560	551
THF	553	553	550	572	556	549	554	552
MeCN	566	556	563	585	572	559	565	562
MeOH	570	564	566	594	574	562	568	568

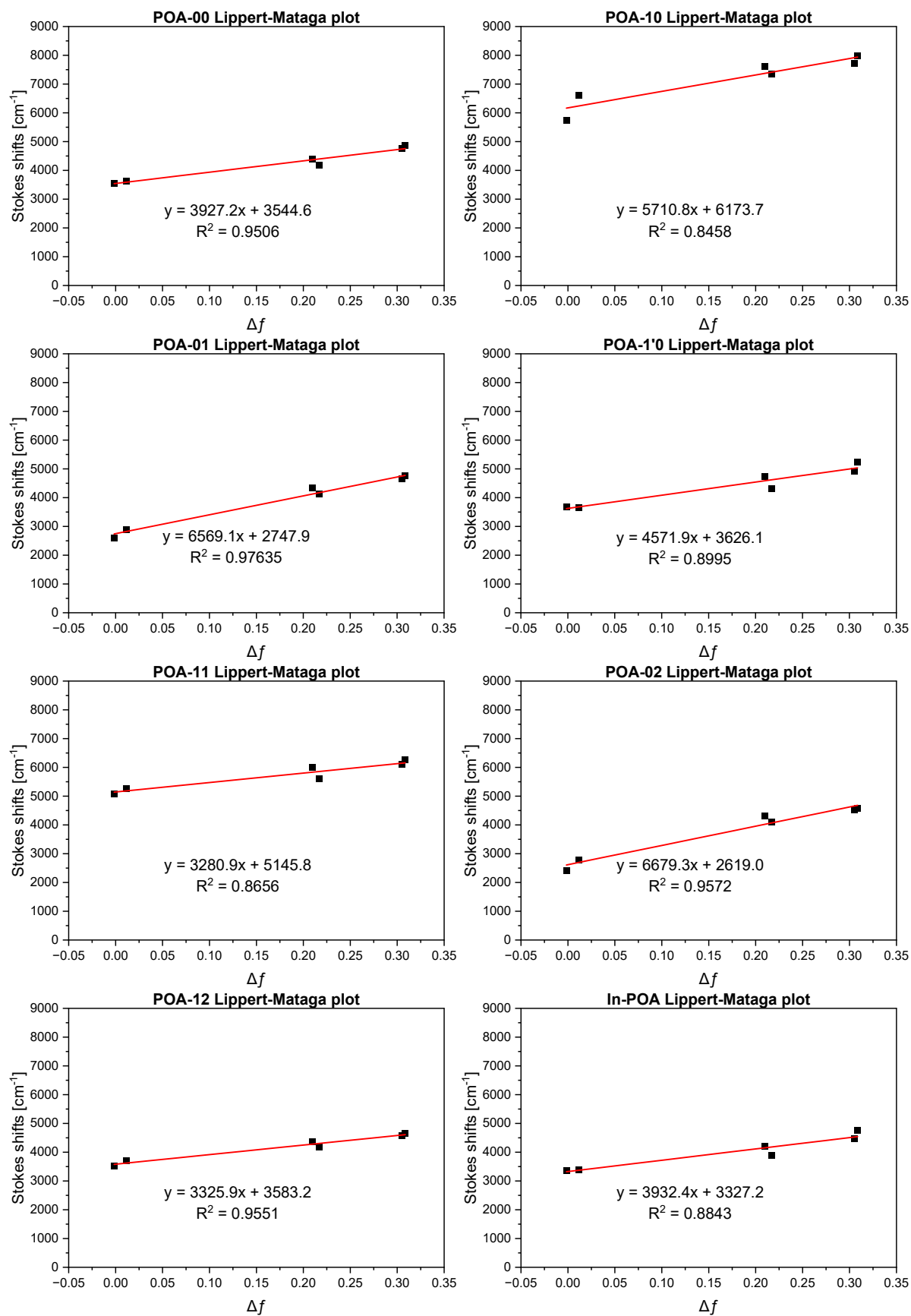


Figure S26: Lippert-Mataga plots for all compounds with fitted linear regression.

Comment: Specific solvent-solute interactions can lead to deviations from linearity, especially for compounds with hydrogen-bond accepting groups.

Table S3: Summary of the photophysical properties of **POA-00** in solution (orientation polarization factor Δf , measured wavelengths λ [nm] for absorption λ_{ab} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes τ_{av_amp} [ns] and non-radiative deactivation rate constants (k_r and k_{nr}); n.d. = not determined).

Solvent	Δf	λ_{ab} [nm]	λ_{em} [nm]	$\Delta\lambda_{em-ab}$ [nm]	$\Delta\nu_{ab-em}$ [cm^{-1}]	Φ_{PL}	τ_{av_amp} [ns]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
CH	-0.0016	436	516	80	3556	0.52 ± 0.03	8.88 ± 0.01	0.59 ± 0.03	0.54 ± 0.03
CCl_4	0.0113	441	525	84	3628	0.41 ± 0.02	8.70 ± 0.01	0.47 ± 0.04	0.68 ± 0.03
DCM	0.2172	449	553	104	4189	0.10 ± 0.02	2.50 ± 0.01	0.4 ± 0.1	3.6 ± 0.1
THF	0.2099	445	553	108	4389	0.08 ± 0.02	2.07 ± 0.01	0.4 ± 0.1	4.4 ± 0.2
MeCN	0.3050	446	566	120	4754	0.03 ± 0.02	n.d.	-	-
MeOH	0.3086	446	570	124	4878	$\leq 0.02 \pm 0.02$	n.d.	-	-

Table S4: Summary of the photophysical properties of **POA-10** in solution (orientation polarization factor Δf , measured wavelengths λ [nm] for absorption λ_{ab} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes τ_{av_amp} [ns] and non-radiative deactivation rate constants (k_r and k_{nr}); n.d. = not determined).

Solvent	Δf	λ_{ab} [nm]	λ_{em} [nm]	$\Delta\lambda_{em-ab}$ [nm]	$\Delta\nu_{ab-em}$ [cm^{-1}]	Φ_{PL}	τ_{av_amp} [ns]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
CH	-0.0016	388	499	111	5733	0.31 ± 0.02	8.88 ± 0.01	0.35 ± 0.03	0.78 ± 0.03
CCl_4	0.0113	389	524	135	6623	0.27 ± 0.02	8.34 ± 0.02	0.32 ± 0.04	0.88 ± 0.03
DCM	0.2172	396	559	163	7363	0.05 ± 0.02	2.22 ± 0.02	0.2 ± 0.1	4.3 ± 0.1
THF	0.2099	389	553	164	7624	0.04 ± 0.02	2.08 ± 0.10	0.2 ± 0.1	4.6 ± 0.2
MeCN	0.3050	389	556	167	7721	0.04 ± 0.02	n.d.	-	-
MeOH	0.3086	389	564	175	7976	$\leq 0.02 \pm 0.02$	n.d.	-	-

Table S5: Summary of the photophysical properties of **POA-01** in solution (orientation polarization factor Δf , measured wavelengths λ [nm] for absorption λ_{ab} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes τ_{av_amp} [ns] and non-radiative deactivation rate constants (k_r and k_{nr}); n.d. = not determined).

Solvent	Δf	λ_{ab} [nm]	λ_{em} [nm]	$\Delta\lambda_{em-ab}$ [nm]	$\Delta\nu_{ab-em}$ [cm^{-1}]	Φ_{PL}	τ_{av_amp} [ns]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
CH	-0.0016	436	492	56	2611	0.55 ± 0.03	9.36 ± 0.01	0.59 ± 0.03	0.48 ± 0.03
CCl_4	0.0113	442	507	65	2901	0.45 ± 0.02	8.75 ± 0.01	0.51 ± 0.04	0.68 ± 0.03
DCM	0.2172	451	554	103	4122	0.11 ± 0.02	2.63 ± 0.01	0.4 ± 0.1	3.4 ± 0.1
THF	0.2099	444	550	106	4341	0.09 ± 0.02	2.21 ± 0.01	0.4 ± 0.2	4.1 ± 0.2
MeCN	0.3050	446	563	117	4660	0.04 ± 0.02	n.d.	-	-
MeOH	0.3086	446	566	120	4754	$\leq 0.02 \pm 0.02$	n.d.	-	-

Table S6: Summary of the photophysical properties of **POA-1'0** in solution (orientation polarization factor Δf , measured wavelengths λ [nm] for absorption λ_{ab} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes τ_{av_amp} [ns] and non-radiative deactivation rate constants (k_r and k_{nr}); n.d. = not determined).

Solvent	Δf	λ_{ab} [nm]	λ_{em} [nm]	$\Delta\lambda_{em-ab}$ [nm]	$\Delta\nu_{ab-em}$ [cm^{-1}]	Φ_{PL}	τ_{av_amp} [ns]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
CH	-0.0016	442	528	86	3685	0.40 ± 0.02	6.01 ± 0.01	0.67 ± 0.05	1.00 ± 0.05
CCl_4	0.0113	451	540	89	3654	0.24 ± 0.02	5.22 ± 0.01	0.46 ± 0.06	1.46 ± 0.06
DCM	0.2172	457	569	112	4307	0.04 ± 0.02	1.10 ± 0.01	0.4 ± 0.3	8.7 ± 0.3
THF	0.2099	450	572	122	4740	0.04 ± 0.02	1.00 ± 0.01	0.4 ± 0.3	9.6 ± 0.3
MeCN	0.3050	454	585	131	4932	$\leq 0.02 \pm 0.02$	n.d.	-	-
MeOH	0.3086	453	594	141	5240	$\leq 0.02 \pm 0.02$	n.d.	-	-

Table S7: Summary of the photophysical properties of **POA-11** in solution (orientation polarization factor Δf , measured wavelengths λ [nm] for absorption λ_{ab} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes τ_{av_amp} [ns] and non-radiative deactivation rate constants (k_r and k_{nr}); n.d. = not determined).

Solvent	Δf	λ_{ab} [nm]	λ_{em} [nm]	$\Delta\lambda_{em-ab}$ [nm]	$\Delta\nu_{ab-em}$ [cm^{-1}]	Φ_{PL}	τ_{av_amp} [ns]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
CH	-0.0016	412	521	109	5078	0.46 ± 0.02	7.07 ± 0.01	0.65 ± 0.04	0.76 ± 0.04
CCl_4	0.0113	416	533	117	5277	0.34 ± 0.02	6.64 ± 0.01	0.51 ± 0.05	0.99 ± 0.05
DCM	0.2172	427	561	134	5594	0.08 ± 0.02	1.84 ± 0.01	0.4 ± 0.2	5.0 ± 0.2
THF	0.2099	417	556	139	5995	0.07 ± 0.02	1.90 ± 0.01	0.4 ± 0.2	4.9 ± 0.2
MeCN	0.3050	424	572	148	6102	0.03 ± 0.02	n.d.	-	-
MeOH	0.3086	422	574	152	6275	$\leq 0.02 \pm 0.02$	n.d.	-	-

Table S8: Summary of the photophysical properties of **POA-02** in solution (orientation polarization factor Δf , measured wavelengths λ [nm] for absorption λ_{ab} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes τ_{av_amp} [ns] and non-radiative deactivation rate constants (k_r and k_{nr}); n.d. = not determined).

Solvent	Δf	λ_{ab} [nm]	λ_{em} [nm]	$\Delta\lambda_{em-ab}$ [nm]	$\Delta\nu_{ab-em}$ [cm^{-1}]	Φ_{PL}	τ_{av_amp} [ns]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
CH	-0.0016	438	490	52	2423	0.55 ± 0.03	8.73 ± 0.02	0.63 ± 0.04	0.52 ± 0.03
CCl_4	0.0113	442	504	62	2783	0.45 ± 0.02	8.84 ± 0.02	0.51 ± 0.03	0.62 ± 0.03
DCM	0.2172	450	552	102	4106	0.12 ± 0.02	2.82 ± 0.01	0.4 ± 0.1	3.1 ± 0.1
THF	0.2099	444	549	105	4308	0.10 ± 0.02	2.53 ± 0.01	0.4 ± 0.1	3.6 ± 0.1
MeCN	0.3050	446	559	113	4532	0.04 ± 0.02	n.d.	-	-
MeOH	0.3086	447	562	115	4578	$\leq 0.02 \pm 0.02$	n.d.	-	-

Table S9: Summary of the photophysical properties of **POA-12** in solution (orientation polarization factor Δf , measured wavelengths λ [nm] for absorption λ_{ab} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes τ_{av_amp} [ns] and non-radiative deactivation rate constants (k_r and k_{nr}); n.d. = not determined).

Solvent	Δf	λ_{ab} [nm]	λ_{em} [nm]	$\Delta\lambda_{em-ab}$ [nm]	$\Delta\nu_{ab-em}$ [cm^{-1}]	Φ_{PL}	τ_{av_amp} [ns]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
CH	-0.0016	441	522	81	3519	0.49 ± 0.02	7.69 ± 0.01	0.64 ± 0.04	0.66 ± 0.04
CCl_4	0.0113	446	534	88	3695	0.37 ± 0.02	7.16 ± 0.01	0.52 ± 0.04	0.88 ± 0.04
DCM	0.2172	454	560	106	4169	0.09 ± 0.02	2.17 ± 0.01	0.4 ± 0.1	4.2 ± 0.1
THF	0.2099	446	554	108	4371	0.08 ± 0.02	2.08 ± 0.01	0.4 ± 0.1	4.4 ± 0.1
MeCN	0.3050	449	565	116	4573	0.04 ± 0.02	n.d.	-	-
MeOH	0.3086	449	568	119	4666	$\leq 0.02 \pm 0.02$	n.d.	-	-

Table S10: Summary of the photophysical properties of **In-POA** in solution (orientation polarization factor Δf , measured wavelengths λ [nm] for absorption λ_{ab} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes τ_{av_amp} [ns] and non-radiative deactivation rate constants (k_r and k_{nr}); n.d. = not determined).

Solvent	Δf	λ_{ab} [nm]	λ_{em} [nm]	$\Delta\lambda_{em-ab}$ [nm]	$\Delta\nu_{ab-em}$ [cm^{-1}]	Φ_{PL}	τ_{av_amp} [ns]	k_r [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
CH	-0.0016	441	518	77	3371	0.65 ± 0.03	9.40 ± 0.01	0.69 ± 0.03	0.37 ± 0.03
CCl_4	0.0113	447	527	80	3396	0.61 ± 0.03	9.28 ± 0.02	0.66 ± 0.03	0.42 ± 0.03
DCM	0.2172	454	551	97	3878	0.30 ± 0.02	5.64 ± 0.01	0.53 ± 0.05	1.24 ± 0.05
THF	0.2099	448	552	104	4205	0.22 ± 0.02	4.51 ± 0.01	0.49 ± 0.07	1.73 ± 0.07
MeCN	0.3050	449	562	113	4478	0.12 ± 0.02	n.d.	-	-
MeOH	0.3086	447	568	121	4766	0.07 ± 0.02	n.d.	-	-

Table S11: Summary of dipole moment differences $\Delta\mu$ in Debye calculated using the Lippert-Mataga equation and applying either lower-bound a_1 or upper-bound a_2 cavity radius in Å, which were obtained from DFT calculations (PBE0-D3BJ/TZVP, *vide infra*) using the volume keyword.

Compound	a_1 [Å]	a_2 [Å]	$\Delta\mu$ [D] for a_1	$\Delta\mu$ [D] for a_2
POA-00	4.47	5.42	5.9	7.9
POA-10	4.6	5.57	6.2	8.2
POA-01	4.55	5.5	6.1	8.1
POA-1'0	4.53	5.48	6.0	8.0
POA-11	4.45	5.39	5.9	7.8
POA-02	4.53	5.49	6.0	8.0
POA-12	4.8	5.79	6.6	8.7
In-POA	4.42	5.36	5.8	7.8

PHOTOLUMINESCENCE IN POWDERS

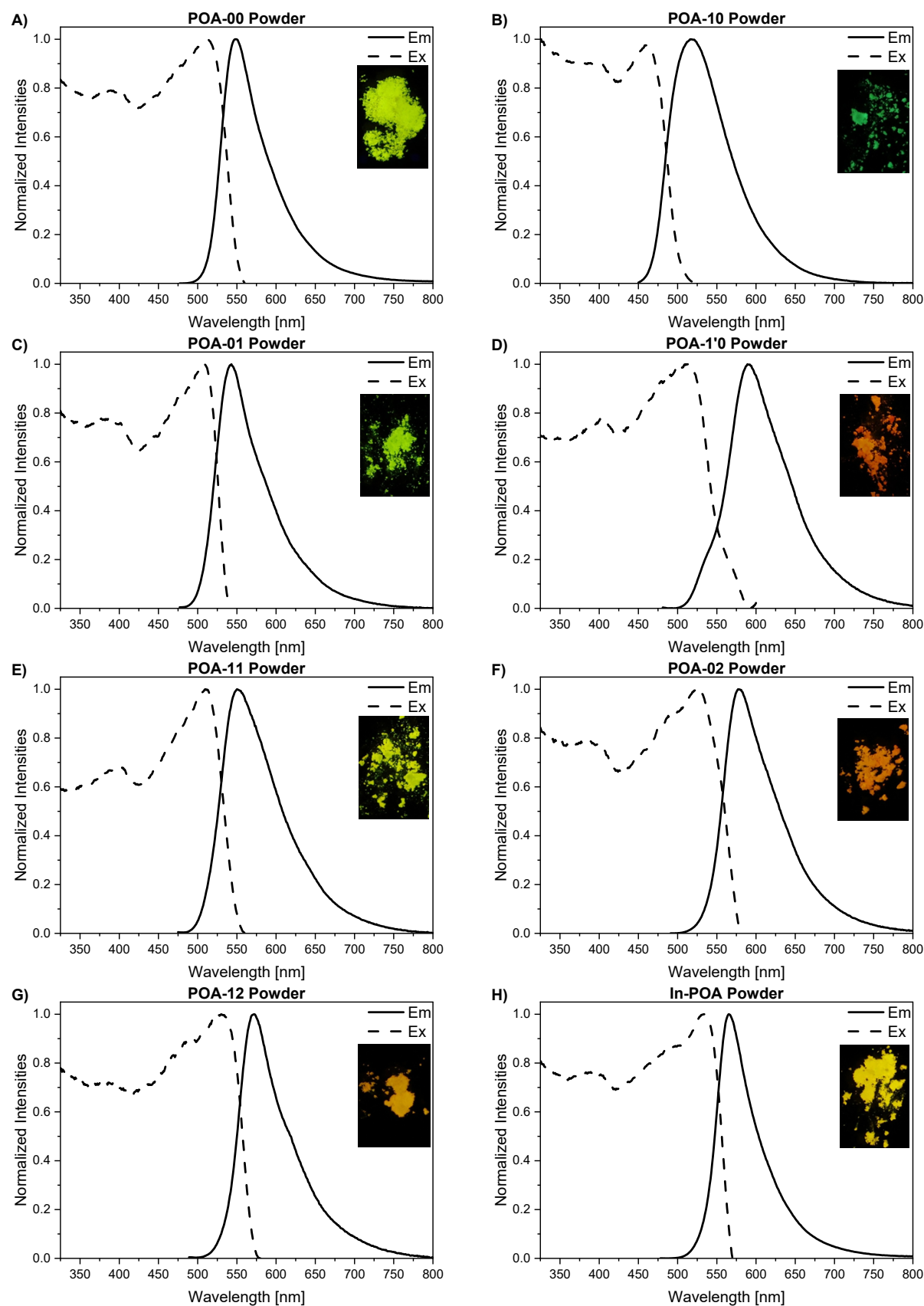


Figure S27: Normalized excitation (dotted line) and emission (solid line) spectra of the powders with corresponding pictures taken under UV-light (395 nm); all emission spectra measured at $\lambda_{\text{ex}} = 430$ nm, excitation measured at $\lambda_{\text{ex}} = 580$ nm (A, E, H), $\lambda_{\text{ex}} = 550$ nm (B, C), $\lambda_{\text{ex}} = 600$ nm (F, G), or $\lambda_{\text{ex}} = 620$ nm (D).

Table S12: Summary of the photophysical properties of all powders (measured wavelengths λ [nm] for excitation λ_{ex} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$) (calculated for excitation wavelengths since no absorption wavelengths were determined), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes $\tau_{\text{av_amp}}$ [ns] and non-radiative deactivation rate constants (k_{r} and k_{nr} ; n.d. = not detectable).

Compound d	λ_{ex} [nm]	λ_{em} [nm]	$\Delta\lambda_{\text{em-ex}}$ [nm]	$\Delta\nu_{\text{ex-em}}$ [cm^{-1}]	$\Phi_{\text{PL}} \pm 0.02$	$\tau_{\text{av_amp}}$ [ns]	k_{r} [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
POA-00	512	548	36	1283	0.30	12.59 ± 0.05	0.24 ± 0.02	0.56 ± 0.02
POA-10	462	516	54	2265	0.38	9.21 ± 0.04	0.41 ± 0.03	0.67 ± 0.03
POA-01	509	543	34	1230	0.20	5.57 ± 0.05	0.36 ± 0.06	1.44 ± 0.06
POA-1'0	513	590	77	2544	0.19	9.56 ± 0.01	0.20 ± 0.03	0.85 ± 0.03
POA-11	510	550	40	1426	0.21	3.95 ± 0.07	0.53 ± 0.09	2.00 ± 0.09
POA-02	525	577	52	1717	0.15	4.24 ± 0.06	0.35 ± 0.08	2.00 ± 0.08
POA-12	530	572	42	1385	0.19	4.40 ± 0.04	0.43 ± 0.07	1.84 ± 0.07
In-POA	533	565	32	1063	0.44	6.89 ± 0.02	0.64 ± 0.05	0.81 ± 0.04

PHOTOLUMINESCENCE IN AGGREGATES

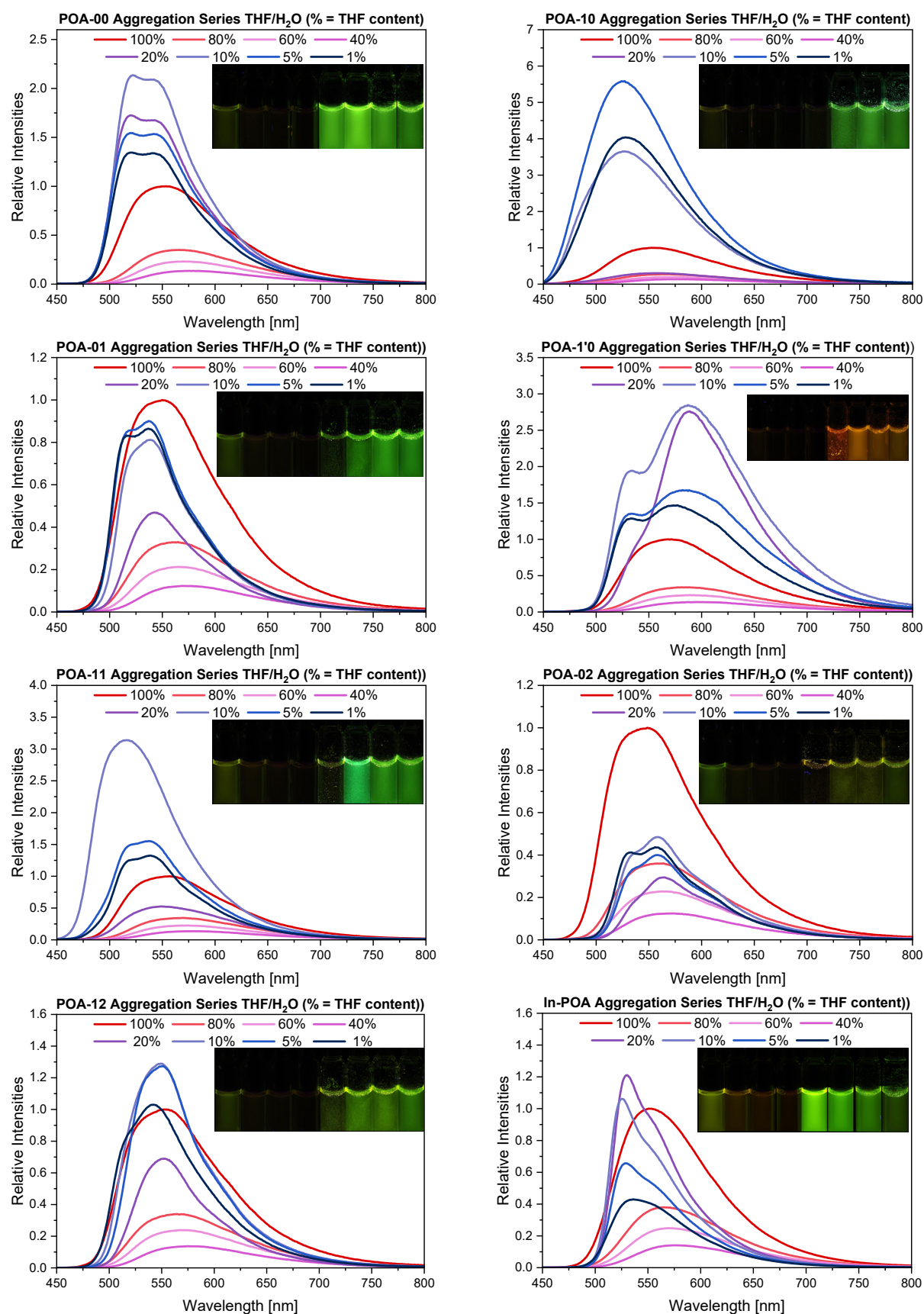


Figure S28: Relative intensities of the emission spectra (15 μ M, measured at $\lambda_{\text{ex}} = 420$ nm) for binary mixtures (THF/H₂O) of all compounds with corresponding pictures taken under UV-light (365 nm). The intensities were relativized to the measured maximum in 100% THF.

For the aggregation series in binary mixtures, stock solutions of the compounds in THF (1.5 mM) were first diluted with THF and subsequently with water to achieve final concentrations of 15 μM compound in the following THF/H₂O ratios: 100/0, 80/20, 60/40, 40/60, 20/80, 10/90, 5/95, 1/99. Measurements were conducted employing a 455 nm long-pass filter (*Edmund Optics GmbH*) to reduce scattering artefacts.

Table S13: Summary of the photophysical properties of all compounds in binary mixtures of THF/H₂O (100/0, 10/90): measured wavelengths λ [nm] for excitation λ_{ex} and emission λ_{em} , Stokes shifts in nm ($\Delta\lambda$) and cm^{-1} ($\Delta\nu$) (calculated for excitation wavelengths since no absorption wavelengths were determined), absolute photoluminescence quantum yields Φ_{PL} , amplitude-weighted average fluorescence lifetimes $\tau_{\text{av_amp}}$ [ns] and non-radiative deactivation rate constants (k_{r} and k_{nr}).

Compound	THF/H ₂ O ratio	λ_{ex} [nm]	λ_{em} [nm]	$\Phi_{\text{PL}} \pm 0.02$	$\tau_{\text{av_amp}}$ [ns]	k_{r} [10^8 s^{-1}]	k_{nr} [10^8 s^{-1}]
POA-00	THF/H ₂ O 100/0	445	553	0.08	2.07 ± 0.01	0.4 ± 0.1	4.4 ± 0.2
	THF/H ₂ O 10/90	482	522, 542	0.32	7.45 ± 0.08	0.43 ± 0.04	0.91 ± 0.04
POA-10	THF/H ₂ O 100/0	389	553	0.04	2.08 ± 0.10	0.2 ± 0.1	4.6 ± 0.2
	THF/H ₂ O 10/90	405	527	0.25	5.34 ± 0.15	0.47 ± 0.07	1.40 ± 0.07
POA-01	THF/H ₂ O 100/0	444	550	0.09	2.21 ± 0.01	0.4 ± 0.2	4.1 ± 0.2
	THF/H ₂ O 10/90	479	539	0.26	4.70 ± 0.08	0.55 ± 0.07	1.57 ± 0.07
POA-1'0	THF/H ₂ O 100/0	450	572	0.04	1.00 ± 0.01	0.4 ± 0.3	9.6 ± 0.3
	THF/H ₂ O 10/90	495	586	0.18	3.76 ± 0.07	0.48 ± 0.09	2.2 ± 0.1
POA-11	THF/H ₂ O 100/0	417	556	0.07	1.90 ± 0.01	0.4 ± 0.2	4.9 ± 0.2
	THF/H ₂ O 10/90	458	517	0.35	4.53 ± 0.05	0.77 ± 0.07	1.43 ± 0.07
POA-02	THF/H ₂ O 100/0	444	549	0.10	2.53 ± 0.01	0.4 ± 0.1	3.6 ± 0.1
	THF/H ₂ O 10/90	497	559	0.22	3.50 ± 0.07	0.6 ± 0.1	2.2 ± 0.1
POA-12	THF/H ₂ O 100/0	446	554	0.08	2.08 ± 0.01	0.4 ± 0.1	4.4 ± 0.1
	THF/H ₂ O 10/90	491	550	0.26	3.69 ± 0.07	0.70 ± 0.09	2.0 ± 0.1
In-POA	THF/H ₂ O 100/0	448	552	0.22	4.51 ± 0.01	0.49 ± 0.07	1.73 ± 0.07
	THF/H ₂ O 10/90	509	525	0.32	3.63 ± 0.06	0.9 ± 0.1	1.87 ± 0.09

DYNAMIC LIGHT SCATTERING (DLS) OF THE AGGREGATES

For the THF/H₂O 10/90 mixtures, dynamic light scattering measurements were performed using a *Zetasizer Nano-ZS* from *Malvern Panalytic* (Malvern, United Kingdom). The measurements were conducted at an angle of 173° with a HeNe-Laser (633 nm) in triplicate, and the mean values were calculated based on the number of particles.

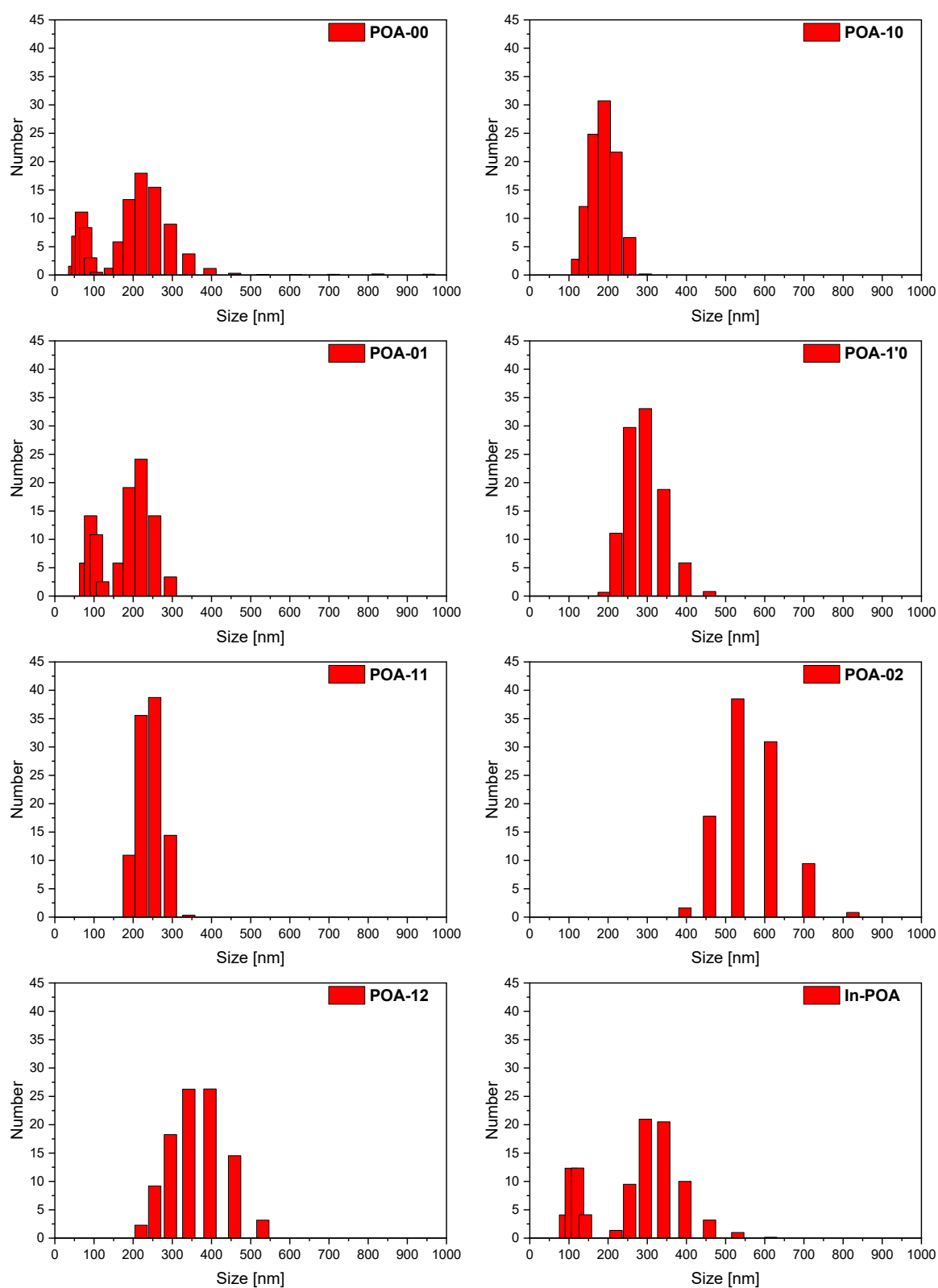


Figure S29: Average sizes [nm] for all target **POA**-compounds at a THF/H₂O ratio of 10/90.

LIFETIME REPORTS

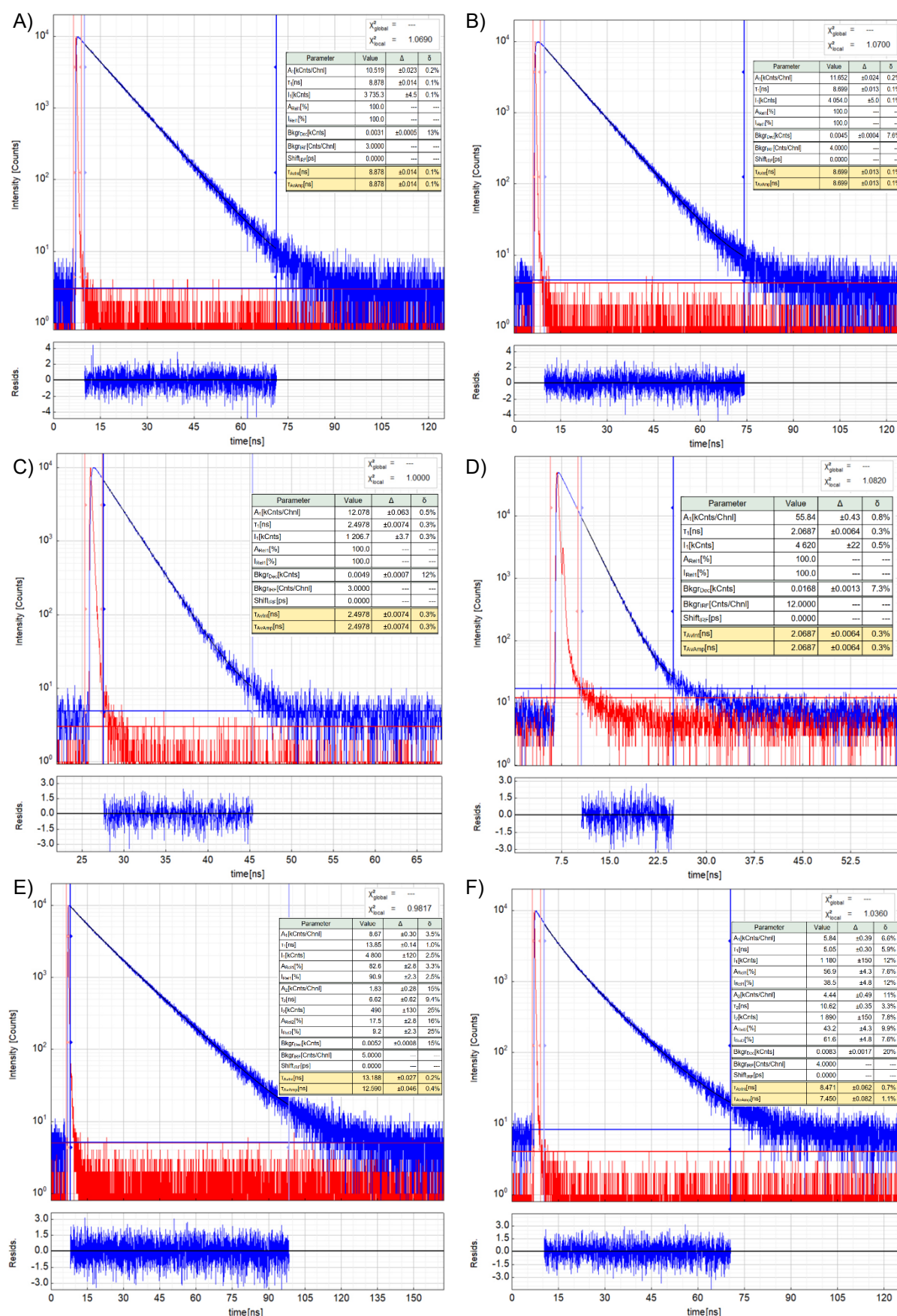


Figure S30: Raw time-resolved photoluminescence decay (blue) of **POA-00** (**A:** CH, **B:** CCl₄, **C:** DCM, **D:** THF, **E:** powder, **F:** aggregates in THF/H₂O 10/90) at r.t. with instrumental response functions (red), including the residuals ($\lambda_{\text{ex}} = 405.8$ nm) and fitting parameters with pre-exponential factors and confidence limits.

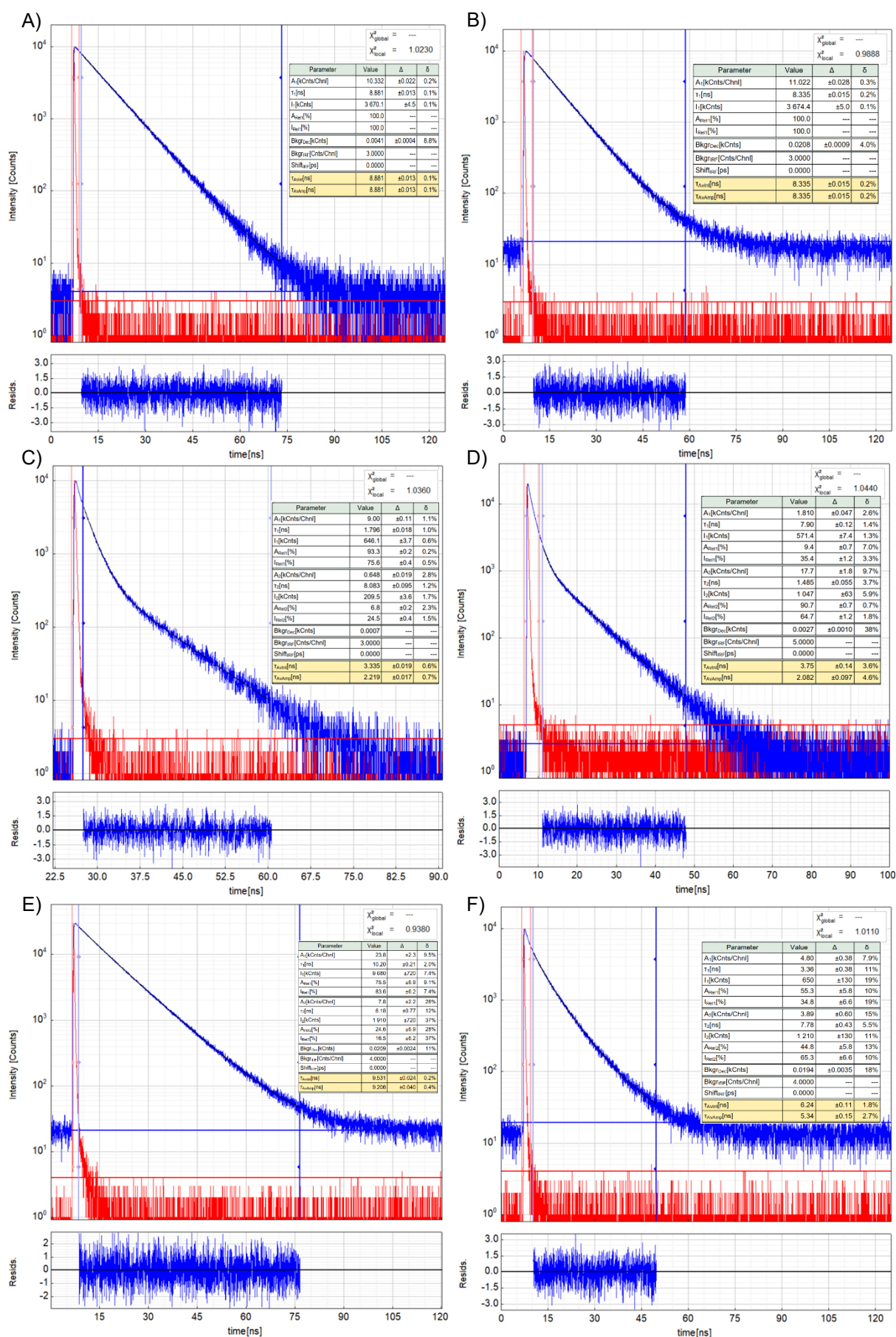


Figure S31: Raw time-resolved photoluminescence decay (blue) of **POA-10** (**A:** CH, **B:** CCl_4 , **C:** DCM, **D:** THF, **E:** powder, **F:** aggregates in THF/ H_2O 10/90) at r.t. with instrumental response functions (red), including the residuals ($\lambda_{\text{ex}} = 405.8 \text{ nm}$) and fitting parameters with pre-exponential factors and confidence limits.

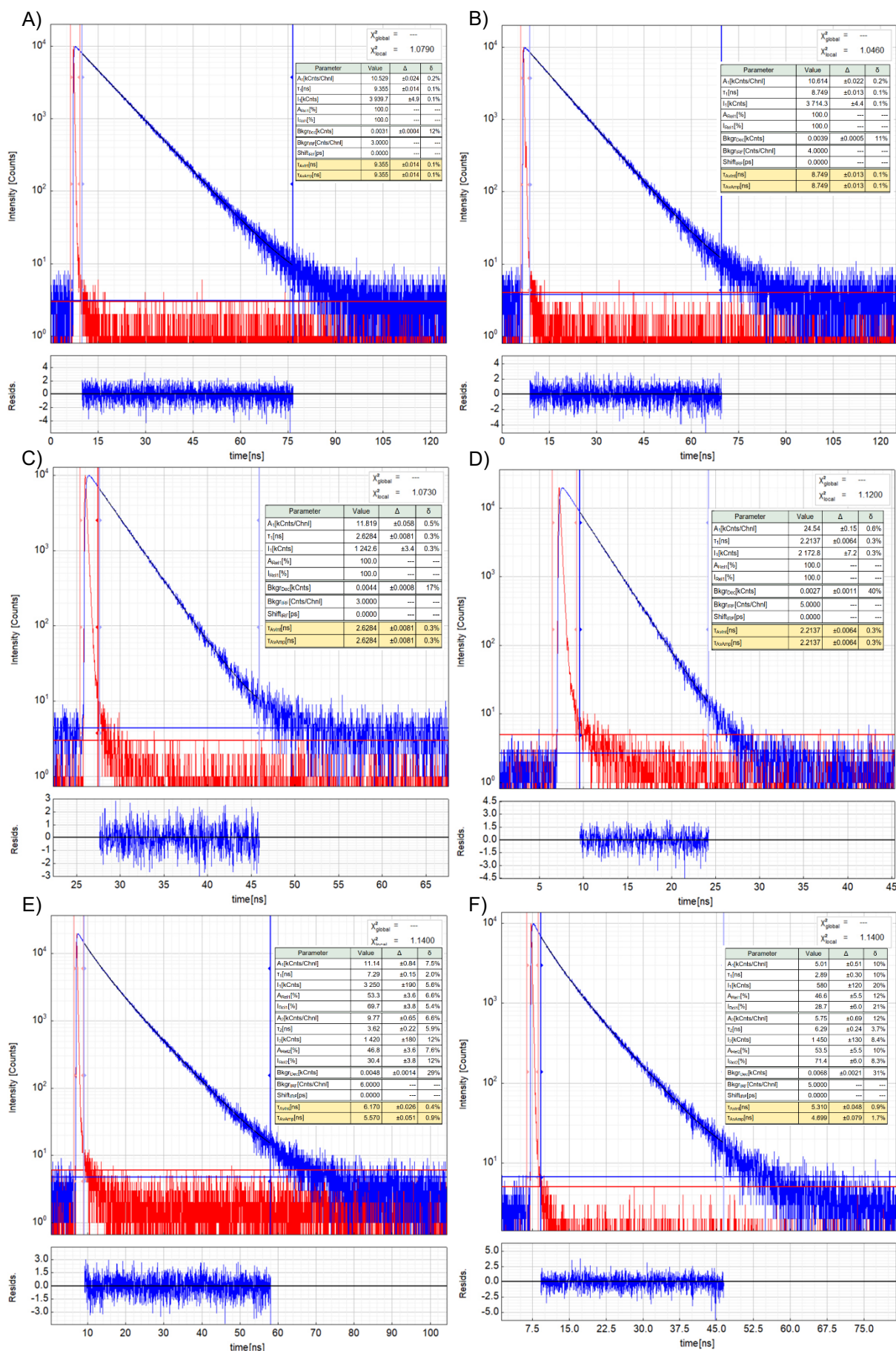


Figure S32: Raw time-resolved photoluminescence decay (blue) of **POA-01** (**A:** CH, **B:** CCl₄, **C:** DCM, **D:** THF, **E:** powder, **F:** aggregates in THF/H₂O 10/90) at r.t. with instrumental response functions (red), including the residuals ($\lambda_{\text{ex}} = 405.8$ nm) and fitting parameters with pre-exponential factors and confidence limits.

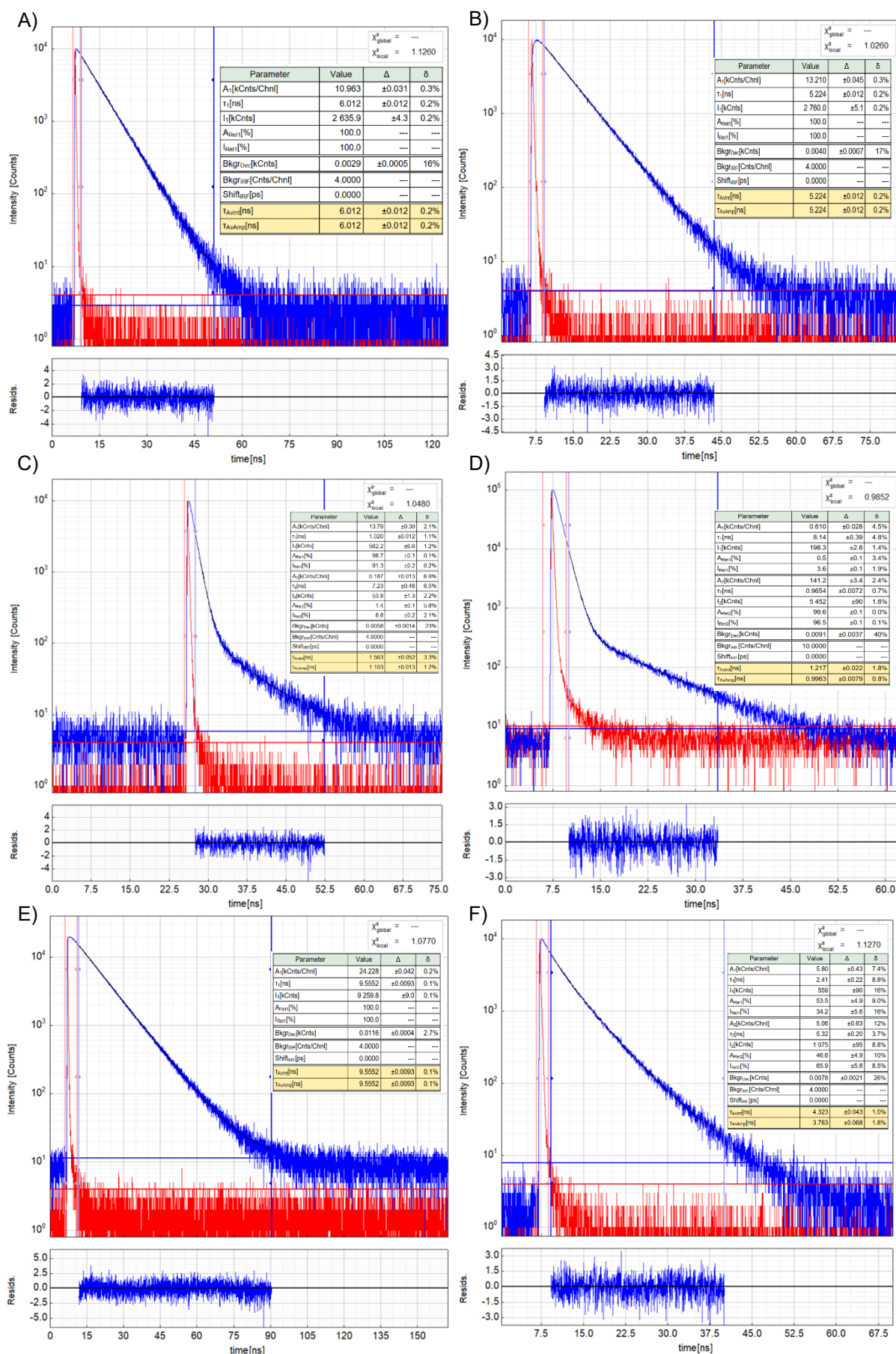


Figure S33: Raw time-resolved photoluminescence decay (blue) of **POA-1'0** (**A**: CH, **B**: CCl₄, **C**: DCM, **D**: THF, **E**: powder, **F**: aggregates in THF/H₂O 10/90) at r.t. with instrumental response functions (red), including the residuals ($\lambda_{\text{ex}} = 405.8$ nm) and fitting parameters with pre-exponential factors and confidence limits.

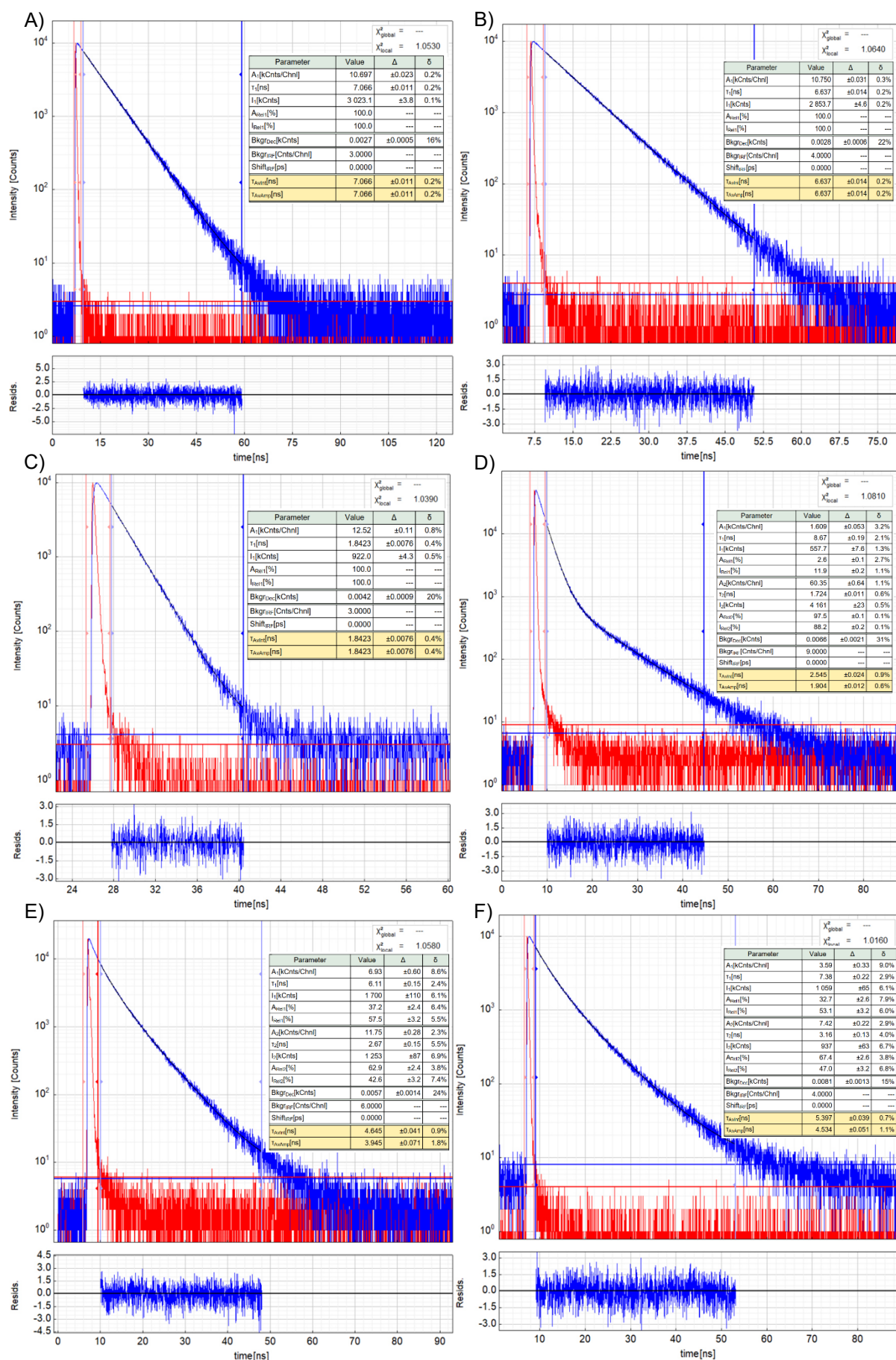


Figure S34: Raw time-resolved photoluminescence decay (blue) of **POA-11** (**A:** CH, **B:** CCl₄, **C:** DCM, **D:** THF, **E:** powder, **F:** aggregates in THF/H₂O 10/90) at r.t. with instrumental response functions (red), including the residuals ($\lambda_{\text{ex}} = 405.8$ nm) and fitting parameters with pre-exponential factors and confidence limits.

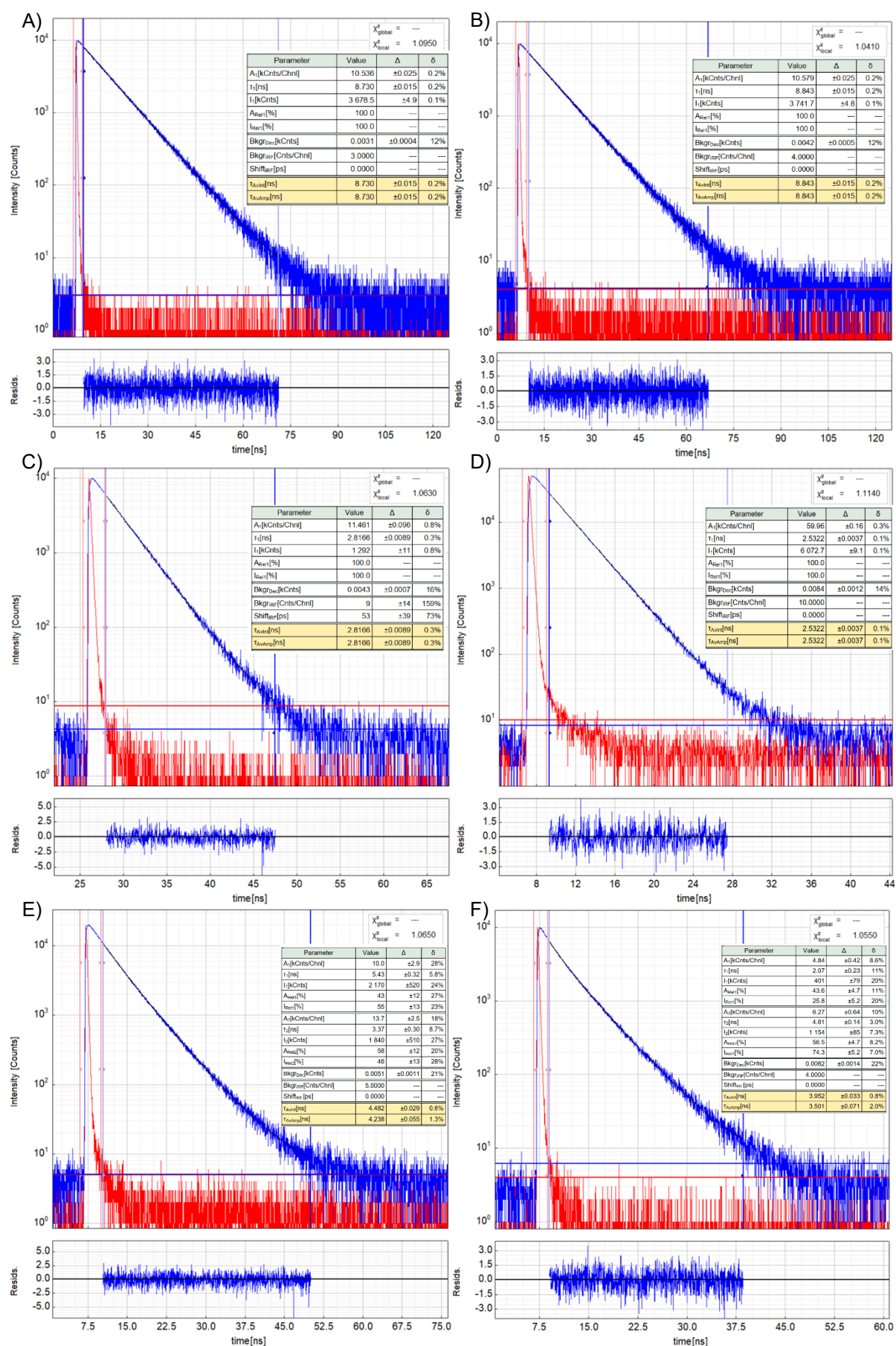


Figure S35: Raw time-resolved photoluminescence decay (blue) of **POA-02** (**A:** CH, **B:** CCl₄, **C:** DCM, **D:** THF, **E:** powder, **F:** aggregates in THF/H₂O 10/90) at r.t. with instrumental response functions (red), including the residuals ($\lambda_{\text{ex}} = 405.8$ nm) and fitting parameters with pre-exponential factors and confidence limits.

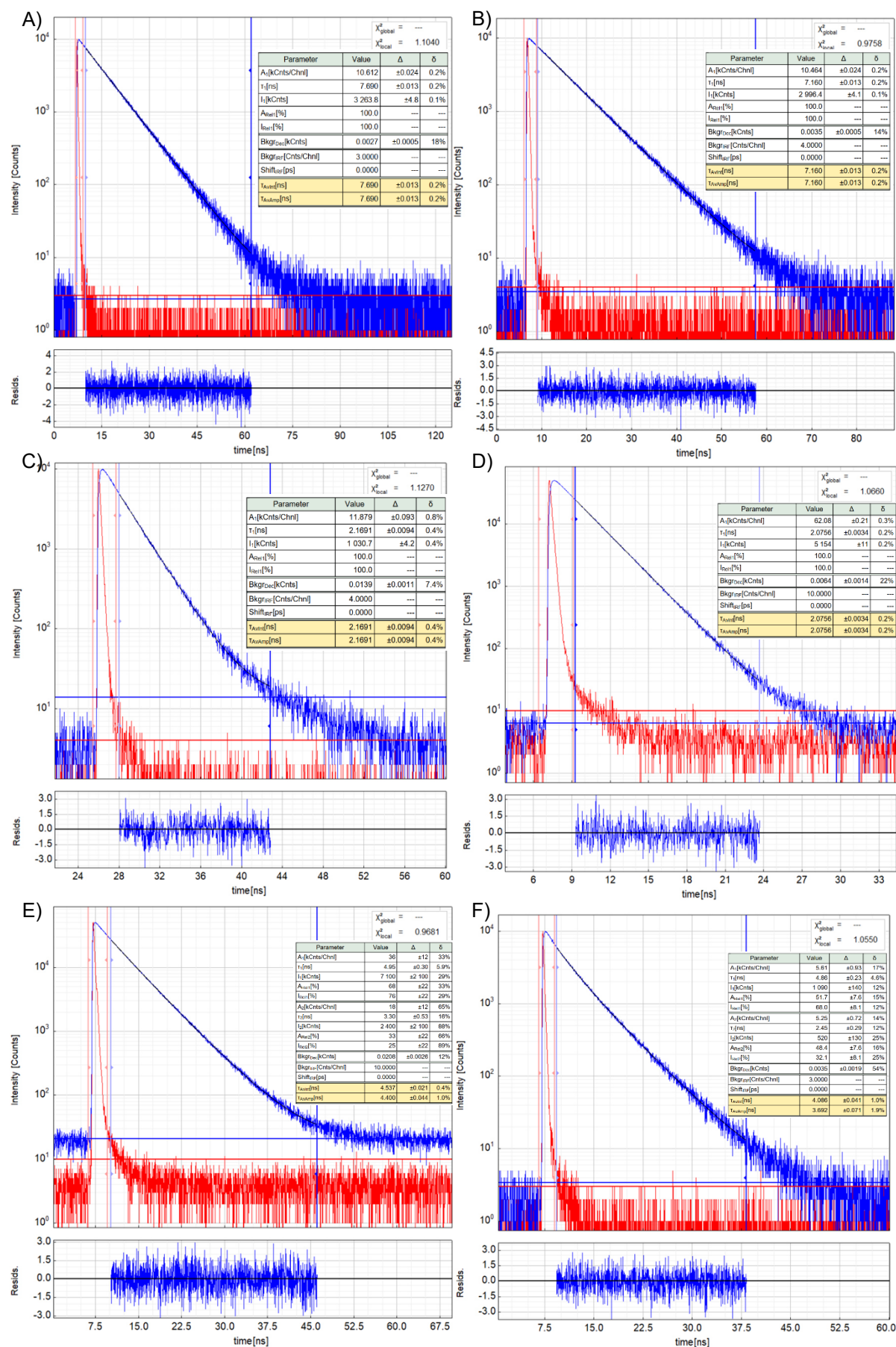


Figure S36: Raw time-resolved photoluminescence decay (blue) of **POA-12** (**A:** CH, **B:** CCl₄, **C:** DCM, **D:** THF, **E:** powder, **F:** aggregates in THF/H₂O 10/90) at r.t. with instrumental response functions (red), including the residuals ($\lambda_{\text{ex}} = 405.8$ nm) and fitting parameters with pre-exponential factors and confidence limits.

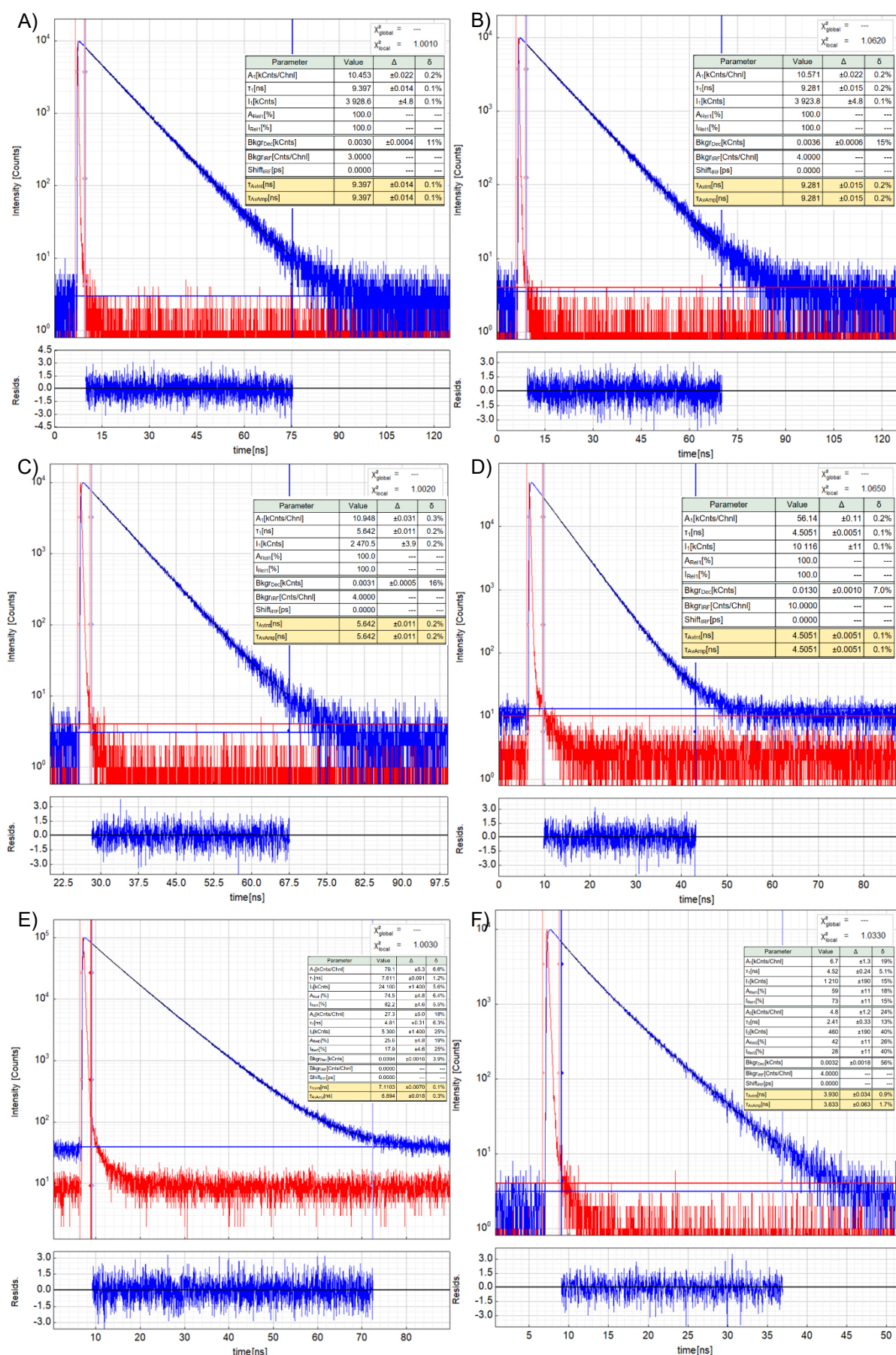


Figure S37: Raw time-resolved photoluminescence decay (blue) of In-POA (**A:** CH, **B:** CCl₄, **C:** DCM, **D:** THF, **E:** powder, **F:** aggregates in THF/H₂O 10/90) at r.t. with instrumental response functions (red), including the residuals ($\lambda_{\text{ex}} = 405.8$ nm) and fitting parameters with pre-exponential factors and confidence limits.

EXEMPLARY ABSOLUTE PHOTOLUMINESCENCE QUANTUM YIELD REPORT

	Quantum Yield	Internal Absorbance	Excitation Wavelength [nm]
DCM blank (black)	---	---	410.57
DCM blank sample 1 (green)	-0.261	0.001	410.57
DCM blank sample 2 (blue)	0.181	0.000	410.57
POA-00 (DCM)	0.100	0.221	410.57
POA-00 (DCM)	0.098	0.223	410.57
POA-00 (DCM)	0.100	0.222	410.57
POA-00 (DCM)	0.101	0.221	410.57
POA-00 (DCM)	0.099	0.221	410.57
POA-10 (DCM)	0.045	0.166	410.57
POA-10 (DCM)	0.044	0.166	410.57
POA-10 (DCM)	0.043	0.166	410.57
POA-10 (DCM)	0.045	0.164	410.57
POA-10 (DCM)	0.045	0.165	410.57
In-POA (DCM)	0.302	0.262	410.57
In-POA (DCM)	0.299	0.262	410.57
In-POA (DCM)	0.302	0.261	410.57
In-POA (DCM)	0.302	0.262	410.57
In-POA (DCM)	0.302	0.261	410.57

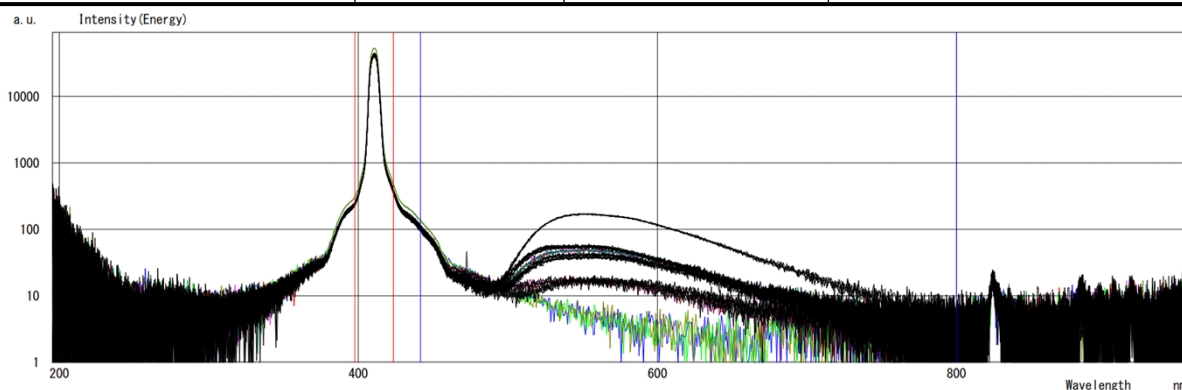


Figure S38: Exemplary absolute photoluminescence quantum yield report depicting the overview spectrum (top, logarithmic y axis, borders for excitation in red, for emission in blue) and the report file with the quantum yield, internal absorbance, and excitation wavelength [nm] for **POA-00**, **POA-10**, and **In-POA** in DCM.

4 X-RAY DIFFRACTOMETRIC ANALYSIS ON SINGLE CRYSTALS

The crystals were mounted on nylon loops in inert oil. Data of **POA-10** were collected on a *Bruker AXS D8 Kappa* diffractometer with *APEX2* detector (monochromated MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$) at 100(2) K. Data of all other compounds were collected on a *Bruker AXS D8 Venture* diffractometer with *Photon II* detector (monochromated CuK_α radiation, $\lambda = 1.54178 \text{ \AA}$, microfocus source) at 100(2) K. The structures were solved by *Direct Methods (SHELXS-2013)*⁸ and refined anisotropically by full-matrix least-squares on F^2 (*SHELXL-2017*).^{9–11} Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (*Bruker AXS APEX3*). Hydrogen atoms were refined using a riding model or rigid methyl groups.

CCDC 2490301-2490307 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

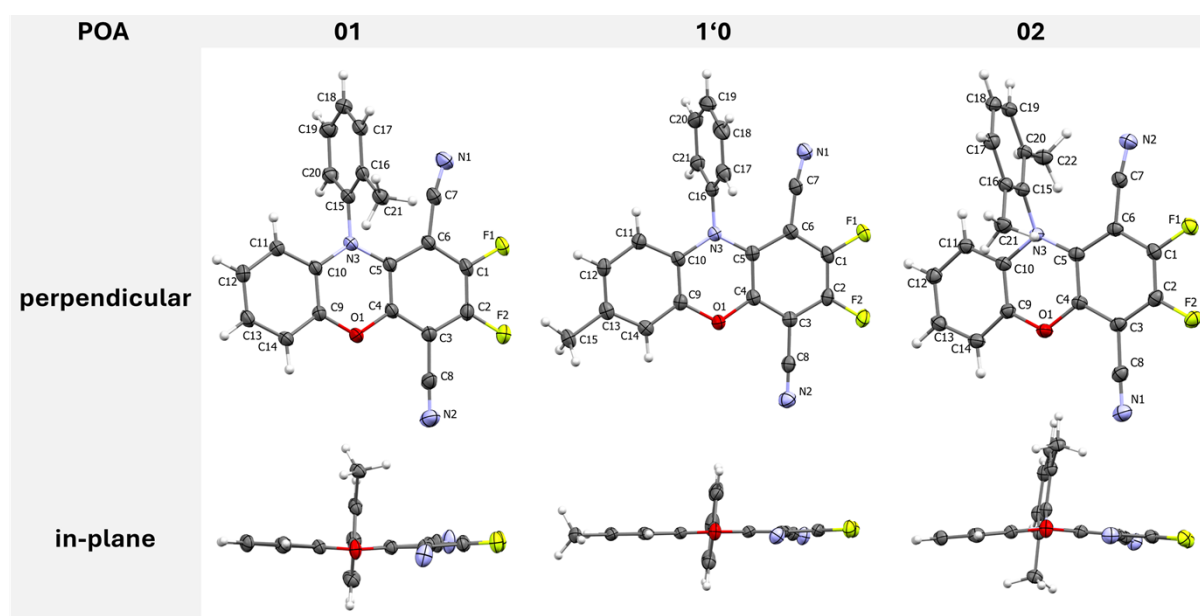


Figure S39: Molecular crystal structures of the compounds **POA-01**, **-1'0**, and **-02** (perpendicular and in-plane view). The displacement ellipsoids are displayed at 50% probability levels.

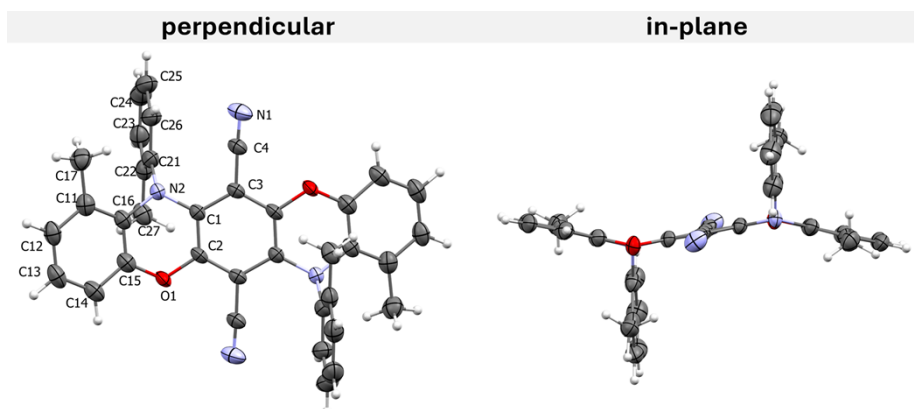


Figure S40: Molecular crystal structures of the heteropentacyclic side product of compounds **POA-11** (perpendicular and in-plane view, CCDC number 2490263). The displacement ellipsoids are displayed at 50% probability levels.¹²

Table S14: Crystallographic data for compounds **POA-00**, **POA-10**, **POA-01**, and **POA-1'0**.

Identification code	POA-00	POA-10	POA-01	POA-1'0
CCDC number	2490302	2490305	2490303	2490306
Name in cif	alh_141m	alh_fr18am	alh_171_1m	alh_169_2tm
Empirical formula	C ₂₀ H ₉ F ₂ N ₃ O	C ₂₁ H ₁₁ F ₂ N ₃ O	C ₂₁ H ₁₁ F ₂ N ₃ O	C ₂₁ H ₁₁ F ₂ N ₃ O
M [g/mol]	345.30	359.33	359.33	359.33
Crystal size [mm]	0.191 × 0.093 × 0.033	0.478 × 0.228 × 0.160	0.274 × 0.134 × 0.060	0.248 × 0.154 × 0.032
T [K]	101(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	10.7211(5)	14.2968(7)	7.3888(5)	6.8867(3)
<i>b</i> [Å]	7.0214(3)	7.0079(4)	10.9216(7)	10.6214(5)
<i>c</i> [Å]	20.9569(8)	33.5592(17)	11.4479(7)	12.6073(6)
α [°]	90	90	110.799(3)	66.398(2)
β [°]	103.1461(17)	98.488(3)	105.830(2)	81.051(2)
γ [°]	90	90	96.406(3)	75.150(2)
<i>V</i> [Å ³]	1536.23(11)	3325.5(3)	808.24(9)	815.35(7)
<i>Z</i>	4	8	2	2
<i>D</i> _{calc} [g·cm ⁻³]	1.493	1.435	1.476	1.464
$\mu(K_{\alpha})$ [mm ⁻¹]	0.943 (Cu)	0.106 (Mo)	0.919 (Cu)	0.911 (Cu)
Transmissions	0.75/0.57	0.75/0.69	0.75/0.61	0.75/0.59
<i>F</i> (000)	704	1472	368	368
Index ranges	-13 ≤ <i>h</i> ≤ 13	-22 ≤ <i>h</i> ≤ 22	-9 ≤ <i>h</i> ≤ 9	-8 ≤ <i>h</i> ≤ 8
	-8 ≤ <i>k</i> ≤ 8	-10 ≤ <i>k</i> ≤ 10	-13 ≤ <i>k</i> ≤ 13	-13 ≤ <i>k</i> ≤ 13
	-26 ≤ <i>l</i> ≤ 26	-51 ≤ <i>l</i> ≤ 51	-14 ≤ <i>l</i> ≤ 14	-16 ≤ <i>l</i> ≤ 16
$\theta_{\max}$ [°]	80.621	33.271	80.406	80.734
Reflections collected	49434	173742	37811	37230
Independent reflections	3355	12781	3493	3532
<i>R</i> _{int}	0.059	0.041	0.0579	0.0579
Refined parameters	236	489	245	246
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0359	0.0564	0.0409	0.04
<i>wR</i> ₂ [all data]	0.1027	0.1573	0.1196	0.1212
GooF	1.035	1.124	1.068	1.093
$\Delta\rho_{\text{final}}$ (max/min) [e·Å ⁻³]	0.250/-0.217	0.598/-0.282	0.259/-0.222	0.277/-0.239

Table S15: Crystallographic data for compounds **POA-02**, **POA-12**, and **In-POA**.

Identification code	POA-02	POA-12	In-POA
CCDC number	2490304	2490307	2490301
Name in cif	alh_fr10_2m	fv_004m	vh_poa_czm
Empirical formula	C ₂₂ H ₁₃ F ₂ N ₃ O	C ₃₁ H ₁₅ F ₂ N ₃ O	C ₂₀ H ₇ F ₂ N ₃ O
M [g/mol]	373.35	387.38	343.29
Crystal size [mm]	0.194 × 0.155 × 0.025	0.339 × 0.195 × 0.149	0.148 × 0.141 × 0.012
T [K]	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	<i>Pbca</i>
a [Å]	7.6351(4)	7.6214(3)	12.0178(9)
b [Å]	10.5974(6)	7.7485(3)	6.7446(5)
c [Å]	10.7660(6)	15.5892(6)	35.282(3)
α [°]	81.320(3)	77.1964(12)	90
β [°]	82.728(3)	80.0966(12)	90
γ [°]	78.023(3)	85.8218(12)	90
V [Å ³]	838.28(8)	883.77(6)	2859.8(4)
Z	2	2	8
D _{calc} [g·cm ⁻³]	1.479	1.456	1.595
μ(K _α [mm ⁻¹])	0.908 (Cu)	0.882 (Cu)	1.013 (Cu)
Transmissions	0.75/0.62	0.75/0.61	0.75/0.49
F(000)	384	400	1392
Index ranges	-9 ≤ h ≤ 9	-9 ≤ h ≤ 9	-15 ≤ h ≤ 15
	-13 ≤ k ≤ 13	-9 ≤ k ≤ 9	-8 ≤ k ≤ 7
	-13 ≤ l ≤ 13	-19 ≤ l ≤ 19	-44 ≤ l ≤ 45
θ _{max} [°]	80.343	80.683	80.395
Reflections collected	30396	42965	71344
Independent reflections	3640	3844	3132
R _{int}	0.0706	0.0301	0.183
Refined parameters	255	265	235
R ₁ [I > 2σ(I)]	0.0448	0.0354	0.0455
wR ₂ [all data]	0.1181	0.0933	0.1273
GooF	1.02	1.033	1.026
Δρ _{final} (max/min) [e·Å ⁻³]	0.267/-0.298	0.296/-0.339	0.274/-0.241

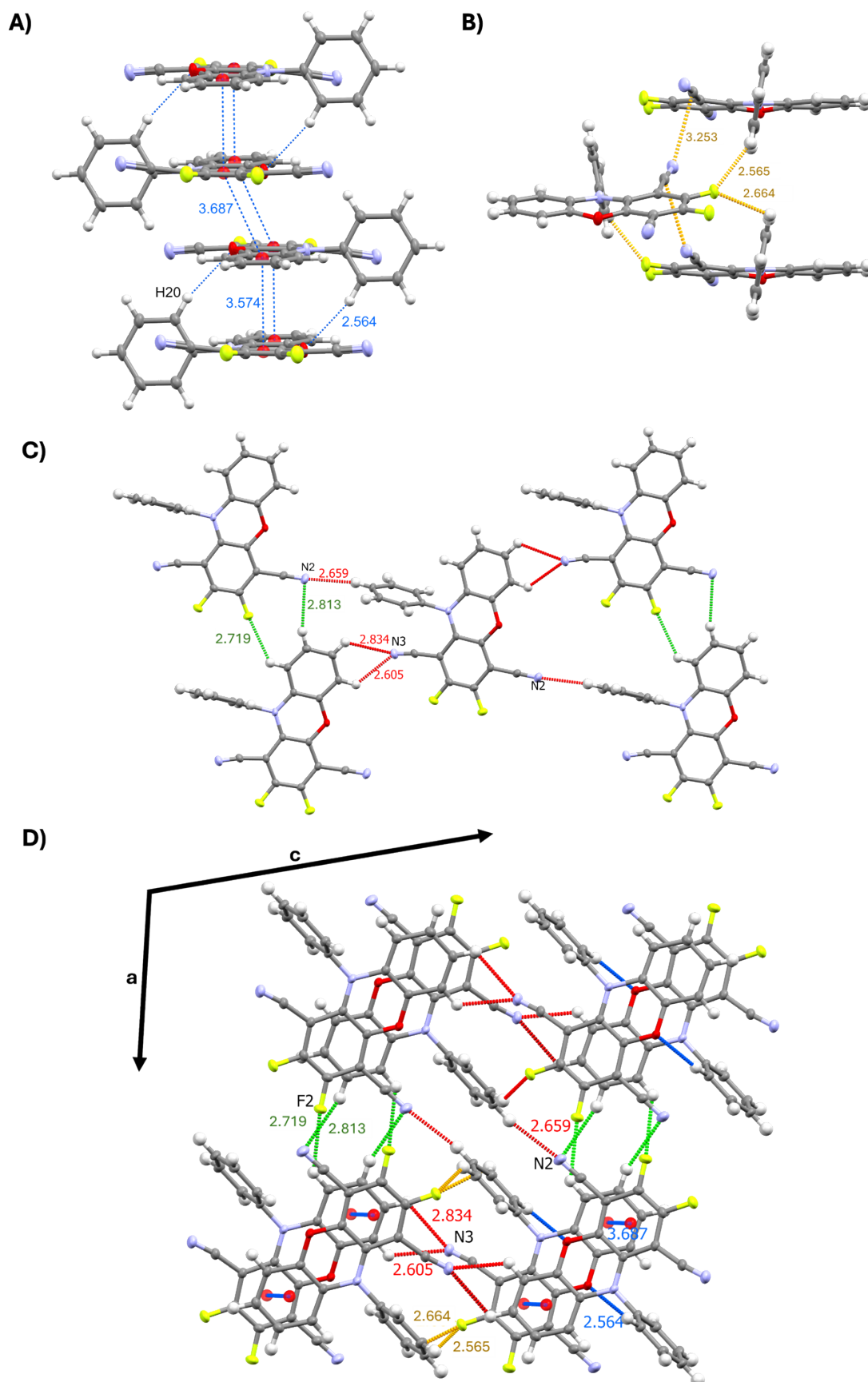


Figure S41: Excerpt of the packing of **POA-00** displaying all types of interactions: A) string formation through $\pi \cdots \pi$ stacking with additional hydrogen bonding (blue); B) hydrogen bonds and CN $\cdots\pi$ stacking interconnecting the strings (orange); C) layer formation through hydrogen bonding (green), forming a 3D-network (red); D) stacking of the layers. The displacement ellipsoids are displayed at 50% probability levels.

Comment: The C–H $\cdots$ N contacts in Figure S41C (2.813 Å) with H $\cdots$ N–C angles around 90° are shown for completeness but may not represent classic hydrogen bonds due to their near-orthogonal geometry.

In the following tables, the most relevant interactions ($\pi\cdots\pi$, CN $\cdots\pi$, X $\cdots\pi$, hydrogen bonds) are summarized quantitatively. For each contact, distances were measured for calculated planes and centroids (Cnt). Slippages, ring offsets and the atoms involved, including the symmetry operators for generated equivalent atoms, are reported.

Table S16: $\pi\cdots\pi$ and CN $\cdots\pi$ interactions in **POA-00** [Å]. Operators for generating equivalent atoms: \$1 -x, 2-y, -z; \$2 -x, 1-y, -z; \$3 -1+x, y, z; \$4 -1+x, 1.5-y, -1/2+z; \$5 x, 1.5-y, 1/2+z; \$6 -x, 1/2+y, -1/2-z. Cnt1 is the centroid involving atoms C10, C12, C14. Cnt2 is the centroid involving C10, O1, C5. Cnt3 is the centroid involving C1, C3, C5. Cnt4 is the centroid involving C15, C17, C19.

Plane $\cdots$ Cnt	<(Plane/Plane) [°]	Cnt $\cdots$ Cnt	Shift	
3.542	5.05	3.574	0.477	Cnt3...Cnt1_\$1 (blue)
3.386	5.05	3.687	1.459	Cnt3...Cnt1_\$2 (blue)
3.179	-	3.223	0.531	N3...Cnt4 (green)
3.217	-	3.253	0.483	N3...C8_\$6 (orange)

Table S17: Specified hydrogen bonds in **POA-00** (with esds except fixed and riding H) [Å]. Operators for generating equivalent atoms: \$1 -x, 2-y, -z; \$2 -x, 1-y, -z; \$3 -1+x, y, z; \$4 -1+x, 1.5-y, -1/2+z; \$5 x, 1.5-y, 1/2+z; \$6 -x, 1/2+y, -1/2-z.

D-H	H $\cdots$ A	D $\cdots$ A	<(DHA) [°]	
0.950	2.564	3.492	165.55	C20-H20...O1_\$1 (blue)
0.950	2.719	3.374	126.70	C11-H11...F2_\$3 (green)
0.950	2.813	3.658	148.71	C12-H12...N2_\$3 (green)
0.950	2.659	3.558	157.95	C18-H18...N2_\$4 (red)
0.950	2.605	3.274	127.76	C14-H14...N3_\$5 (red)
0.950	2.834	3.383	117.86	C13-H13...N3_\$5 (red)
0.950	2.565	3.281	132.26	C17H17...F1_\$6 (orange)
0.950	2.664	3.092	107.91	C19H19...F1_\$6 (orange)

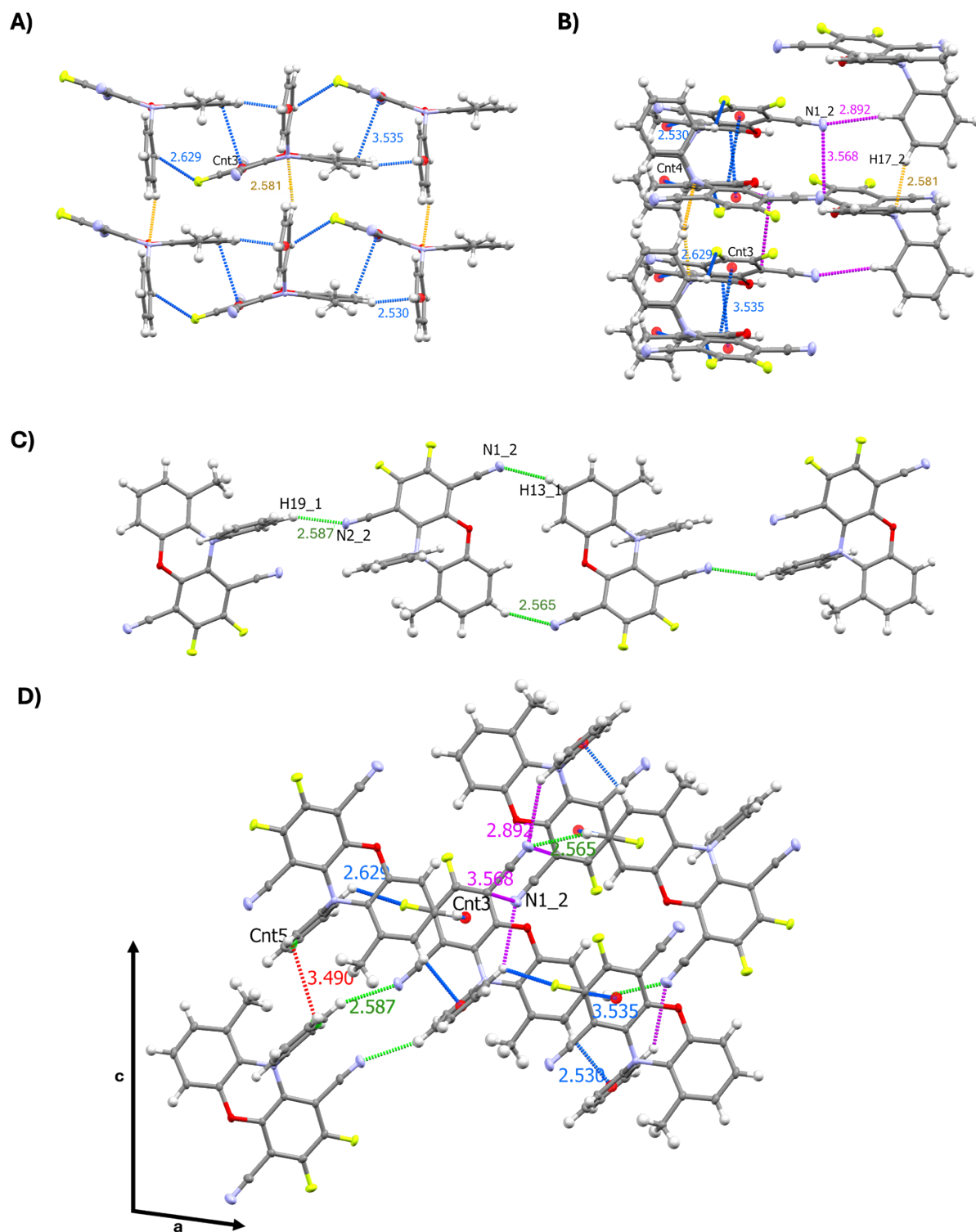


Figure S42: Excerpt of the packing of **POA-10** displaying all types of interactions: A) Dimer-like slipped stacking with additional C-H $\cdots$ π contacts (blue) and hydrogen bonds connecting the dimers (orange); B) hydrogen bonds and additional CN $\cdots$ π stacking interconnecting the strings (purple); C) layer formation through hydrogen bonding (green), D) stacking of the layers. The displacement ellipsoids are displayed at 50% probability levels.

Table S18: $\pi\cdots\pi$ and $CN\cdots\pi$ interactions in **POA-10** [Å]. Operators for generating equivalent atoms: \$1 1-x, -1/2+y, 1/2-z; \$2 x, 1+y, z; \$3 1-x, 1/2+y, 1/2-z; \$4 1+x, y, z; \$5 x, 1.5-y, -1/2+z; \$6 -x, -1/2+y, 1/2-z. Cnt1 is the centroid involving atoms C12 and C13. Cnt3 is the centroid involving C1, C3, C5. Cnt4 is the centroid involving C15, C17, C19. Cnt5 is the centroid involving C18_1 and C19_1.

Plane $\cdots$ X	$\angle(\text{Plane/Plane}) [^\circ]$	Cnt $\cdots$ X	Shift	
3.319	14.12	3.535	1.217	C13_2...Cnt3_1_\$1 (blue)
3.157	0	3.490	1.488	Cnt5_\$5...Cnt5_\$6 (red)
2.525	$\angle(DH\cdots\text{Cnt}) = 160.1$	2.530	0.159	C12_2-H12_2...Cnt4_1_\$1 (blue)
3.541	-	3.568	0.513	C3_2...N1_2_\$3 (purple)

Table S19: Specified hydrogen bonds in **POA-10** (with esds except fixed and riding H) [Å]. Operators for generating equivalent atoms: \$1 1-x, -1/2+y, 1/2-z; \$2 x, 1+y, z; \$3 1-x, 1/2+y, 1/2-z; \$4 1+x, y, z; \$5 x, 1.5-y, -1/2+z; \$6 -x, -1/2+y, 1/2-z.

D-H	H $\cdots$ A	D $\cdots$ A	$\angle(DHA) [^\circ]$	
0.950	2.631	3.167	116.18	C16_2-H16_2...F1_1_\$1 (blue)
0.950	2.581	3.453	152.83	N3_2-H17_2-C17_2_\$2 (orange)
0.950	2.892	3.682	141.28	N1_2...H16_2-C16_2_\$3 (purple)
0.950	2.565	3.464	158.02	C13_2-H13_2...N1_1_\$4 (green)
0.950	2.587	3.474	155.6	N2_2...H19_1-C19_1_\$5 (green)

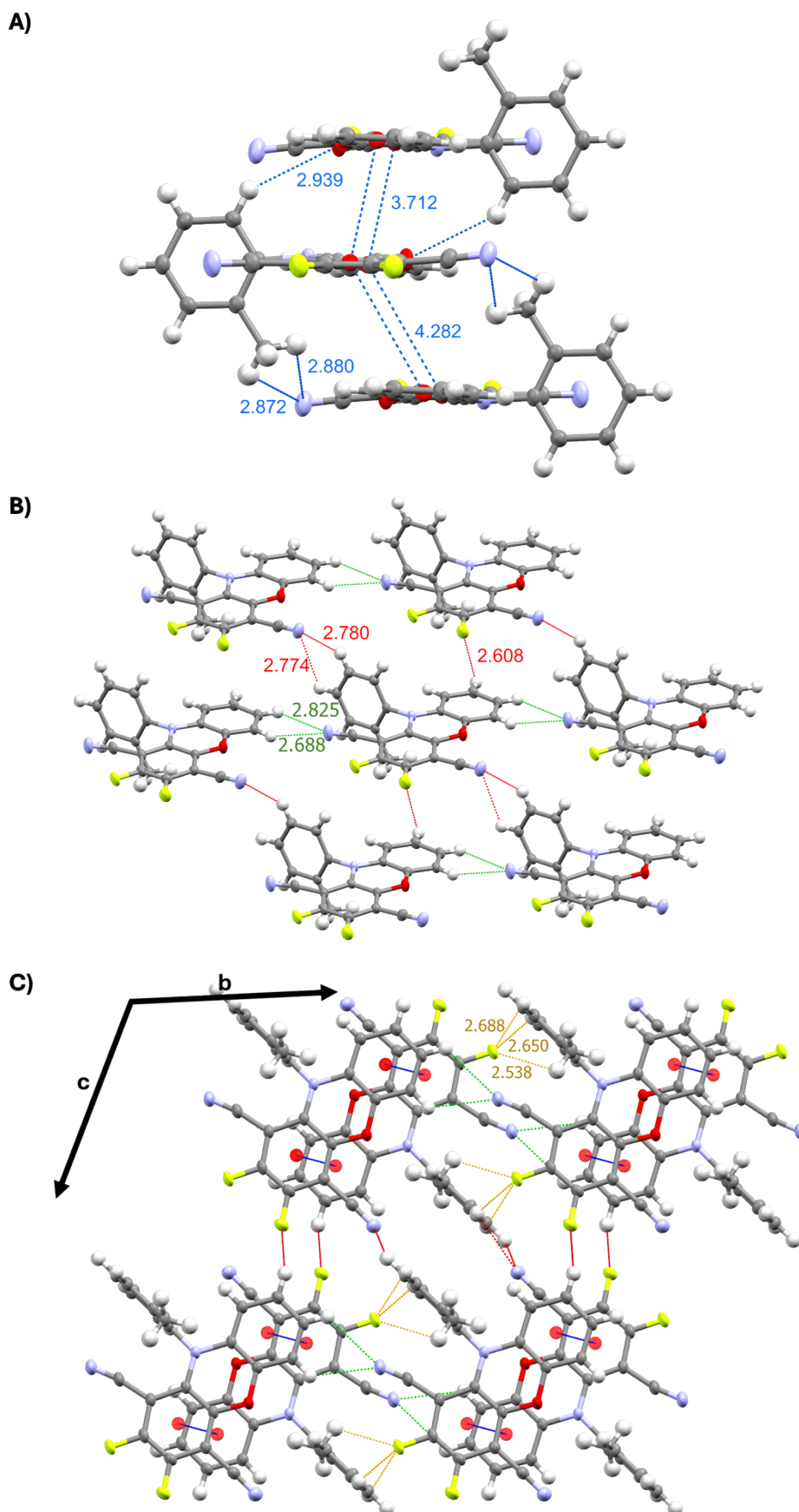


Figure S43: Excerpt of the packing of **POA-01** displaying all types of interactions: A) string formation through $\pi \cdots \pi$ stacking with additional hydrogen bonding (blue); B) layer formation through hydrogen bonding (green), forming a 3D-network (red); C) stacking of the layers, connecting the strings through hydrogen bonding (orange). The displacement ellipsoids are displayed at 50% probability levels.

Table S20: $\pi\cdots\pi$ and $CN\cdots\pi$ interactions in **POA-01** [Å]. Operators for generating equivalent atoms: \$1 -x, -y, 1-z; \$2 1-x, -y, 1-z; \$3 x, -1+y, z; \$4 x, 1+y, 1+z; \$5 x, y, 1+z; \$6 -x, 1-y, 1-z; \$7 1-x, 1-y, 1-z. Cnt1 is the centroid involving atoms C10, C12, C14. Cnt2 is the centroid involving C10, O1, C5. Cnt3 is the centroid involving C1, C3, C5. Cnt4 is the centroid involving C15, C17, C19.

Plane $\cdots$ Cnt	$\angle(\text{Plane/Plane}) [^\circ]$	Cnt $\cdots$ Cnt	Shift	
3.588	6.39	3.712	0.951	Cnt3...Cnt1_\$1 (blue)
3.166	-	3.201	0.472	N1...Cnt4 (green)

Table S21: Specified hydrogen bonds in **POA-01** (with esds except fixed and riding H) [Å]. Operators for generating equivalent atoms: \$1 -x, -y, 1-z; \$2 1-x, -y, 1-z; \$3 x, -1+y, z; \$4 x, 1+y, 1+z; \$5 x, y, 1+z; \$6 -x, 1-y, 1-z; \$7 1-x, 1-y, 1-z.

D-H	H $\cdots$ A	D $\cdots$ A	$\angle(\text{DHA}) [^\circ]$	
0.950	2.939	3.745	143.5	C20-H20...O1_\$1 (blue)
0.950	2.880	3.323	108.5	C21-H21A...N2_\$2 (blue)
0.950	2.872	3.323	109.1	C21-H21B...N2_\$2 (blue)
0.950	2.825	3.419	121.5	C13-H13...N1_\$3 (green)
0.950	2.688	3.353	127.6	C14-H14...N1_\$3 (green)
0.950	2.774	3.398	123.5	C18-H18...N2_\$4 (red)
0.950	2.780	3.394	123.7	C19-H19...N2_\$4 (red)
0.950	2.608	3.378	138.4	C12-H12...F2_\$5 (red)
0.950	2.688	3.395	131.6	C19H19...F1_\$6 (orange)
0.950	2.650	3.095	109.1	C17H17...F1_\$7 (orange)
0.950	2.538	3.030	111.0	C21H21C...F1_\$7 (orange)

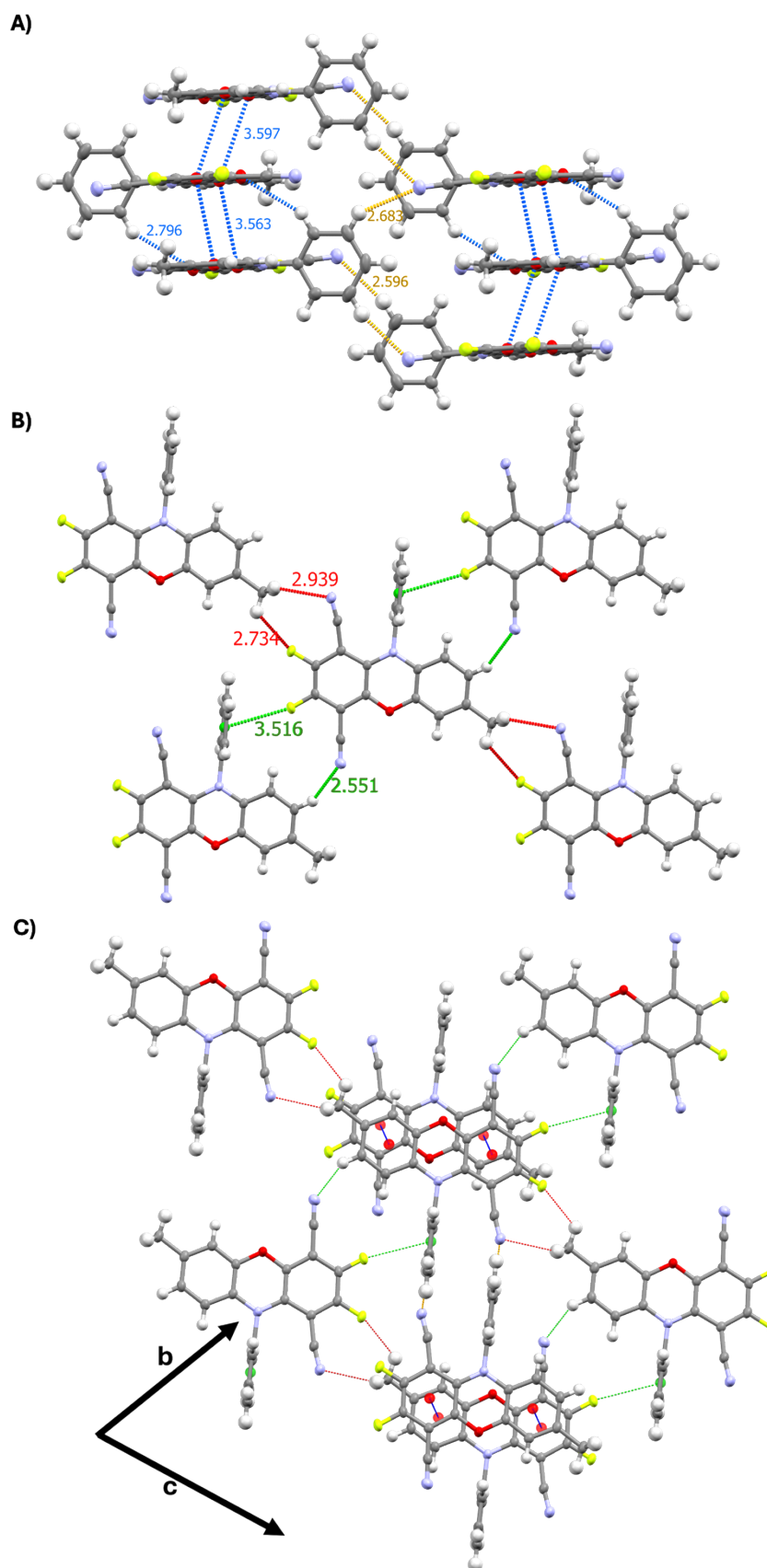


Figure S44: Excerpt of the packing of **POA-1'0** displaying all types of interactions: A) string formation through $\pi \cdots \pi$ stacking with additional hydrogen bonding (blue) and hydrogen bonding connecting the strings (orange); B) layer formation through hydrogen bonding and fluorine $\cdots\pi$ contacts (green), forming a 3D-network (red); C) stacking of the layers. The displacement ellipsoids are displayed at 50% probability levels.

Table S22: $\pi\cdots\pi$ and $X\cdots\pi$ interactions in **POA-1'0** [Å]. Operators for generating equivalent atoms: \$1 -x, -y, 1-z; \$2 1-x, -y, 1-z; \$3 x, -1+y, z; \$4 x, 1+y, z; \$5 x, y, -1+z; \$6 1-x, 1-y, 2-z; \$7 -x, 1-y, 2-z. Cnt1 is the centroid involving atoms C10, C12, C14. Cnt2 is the centroid involving C10, O1, C5. Cnt3 is the centroid involving C1, C3, C5. Cnt4 is the centroid involving C16, C18, C20.

Plane $\cdots$ Cnt	$\angle(\text{Plane/Plane}) [^\circ]$	Cnt $\cdots$ Cnt	Shift	
3.431	-0.38	3.563	0.961	Cnt3...Cnt1_\$1 (blue)
3.338	-0.38	3.597	1.340	Cnt3...Cnt1_\$2 (blue)
3.164	-	3.200	0.479	N1...Cnt4 (green)
2.983	-	3.516	1.861	F2...Cnt4_\$4 (green)

Table S23: Specified hydrogen bonds in **POA-1'0** (with esds except fixed and riding H) [Å]. Operators for generating equivalent atoms: \$1 -x, -y, 1-z; \$2 1-x, -y, 1-z; \$3 x, -1+y, z; \$4 x, 1+y, z; \$5 x, y, -1+z; \$6 1-x, 1-y, 2-z; \$7 -x, 1-y, 2-z.

D-H	H $\cdots$ A	D $\cdots$ A	$\angle(\text{DHA}) [^\circ]$	
0.950	2.796	3.662	152.0	C21-H21...O1_\$1 (blue)
0.950	2.551	3.367	144.1	C12-H12...N2_\$3 (green)
0.950	2.939	3.750	140.8	C15-H15A...N2_\$5 (red)
0.950	2.734	3.331	119.8	C15-H15C...F1_\$5 (red)
0.950	2.596	3.519	164.2	C18H18...N1_\$6 (orange)
0.950	2.683	3.484	142.4	C18H18...N1_\$7 (orange)

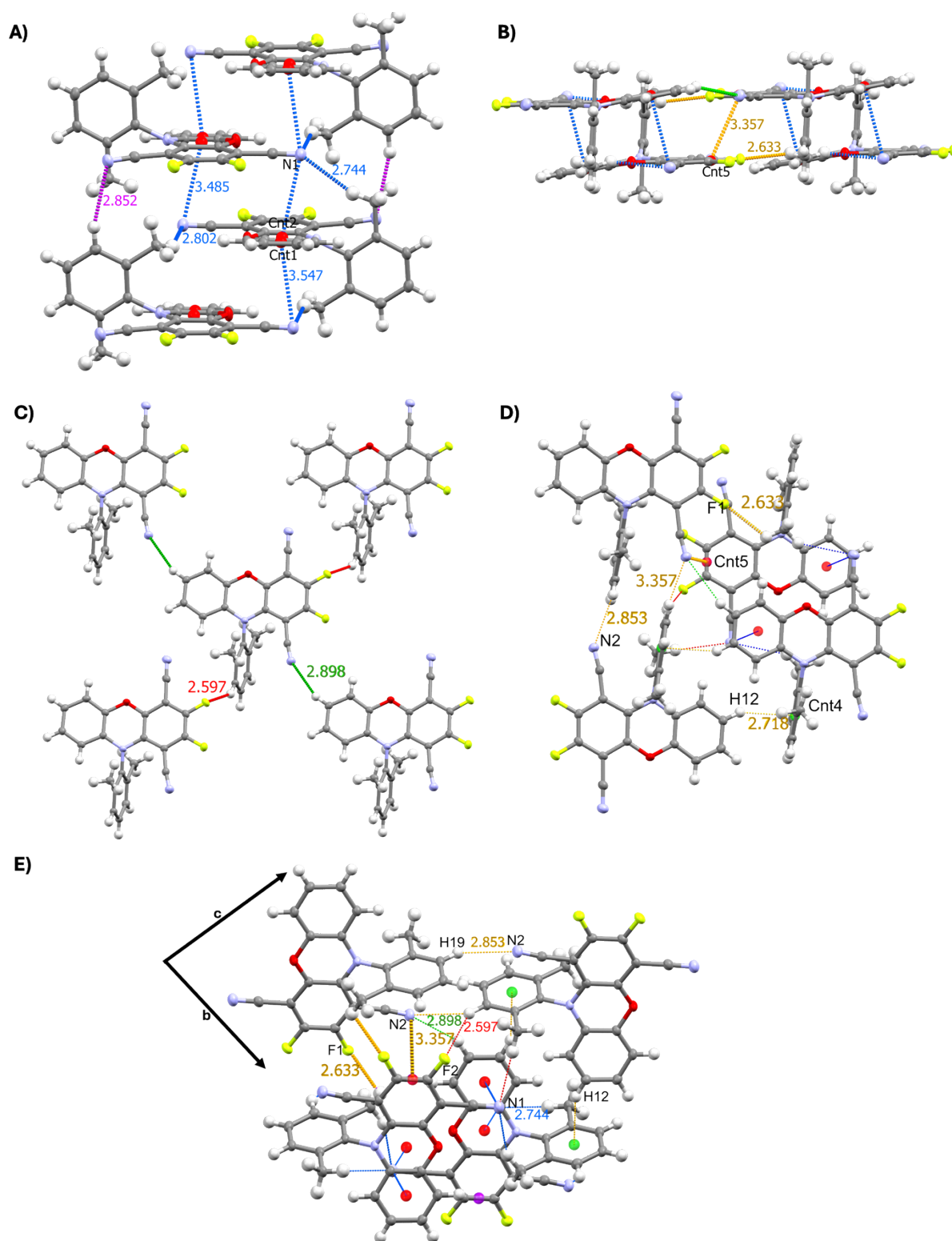


Figure S45: Excerpt of the packing of **POA-02** displaying all types of interactions: A) Slipped stacking with additional hydrogen bonds (blue, between dimers purple); B) hydrogen bonds and additional CN... π stacking interconnecting the strings (orange); C) layer formation through hydrogen bonding (green), forming a 3D-network (red); D) additional interactions between the layers and strings; E) stacking of the layers. The displacement ellipsoids are displayed at 50% probability levels.

Table S24: $\pi\cdots\pi$ and $\text{CH}\cdots\pi$ interactions in **POA-02** [Å]. Operators for generating equivalent atoms: \$1 1-x, 1-y, -z; \$2 -x, 1-y, -z; \$3 1+x, -1+y, z; \$4 x, y, 1+z; \$5 -x, 2-y, -z; \$6 1-x, 1-y, 1-z; \$7 -x, 2-y, 1-z; \$8: -1+x, y, z. Cnt1 is the centroid involving atoms C10, C12, C14. Cnt2 is the centroid involving C10, O1, C5. Cnt3 is the centroid involving C1, C3, C5. Cnt4 is the centroid involving C15, C17, C19. Cnt5 is the centroid involving C1 and C2.

Plane...X	<(Plane/Plane) [°]	Cnt...X	Shift	
3.371	8.87	3.547	1.103	Cnt1...N1_\$1 (blue)
3.295	4.23	3.485	1.135	Cnt2...N1_\$2 (blue)
3.056	3.41	3.357	1.389	Cnt5...N2_\$5 (orange)
2.706	<(DH...Cnt) = 148.3	2.718	0.255	C12-H12...Cnt4_\$6 (orange)

Table S25: Specified hydrogen bonds in **POA-02** (with esds except fixed and riding H) [Å]. Operators for generating equivalent atoms: \$1 1-x, 1-y, -z; \$2 -x, 1-y, -z; \$3 1+x, -1+y, z; \$4 x, y, 1+z; \$5 -x, 2-y, -z; \$6 1-x, 1-y, 1-z; \$7 -x, 2-y, 1-z; \$8: -1+x, y, z.

D-H	H...A	D...A	<(DHA) [°]	
0.950	2.802	3.634	143.2	C21-H21A...N1_\$1 (blue)
0.950	2.744	3.695	163.84	C22-H22A...N1_\$2 (blue)
0.950	2.852	3.678	146.02	N2...H17-C17_\$8 (purple)
0.950	2.633	3.213	118.1	C21-H21C...F1_\$5 (orange)
0.950	2.898	3.768	152.79	C13-H13...N2_\$3 (green)
0.950	2.597	3.441	148.2	C19-H19...F2_\$4 (red)
0.950	2.842	3.804	167.02	C22-H22C...N1_\$4 (red)
0.950	2.853	3.526	128.7	C19H19...N2_\$7 (orange)

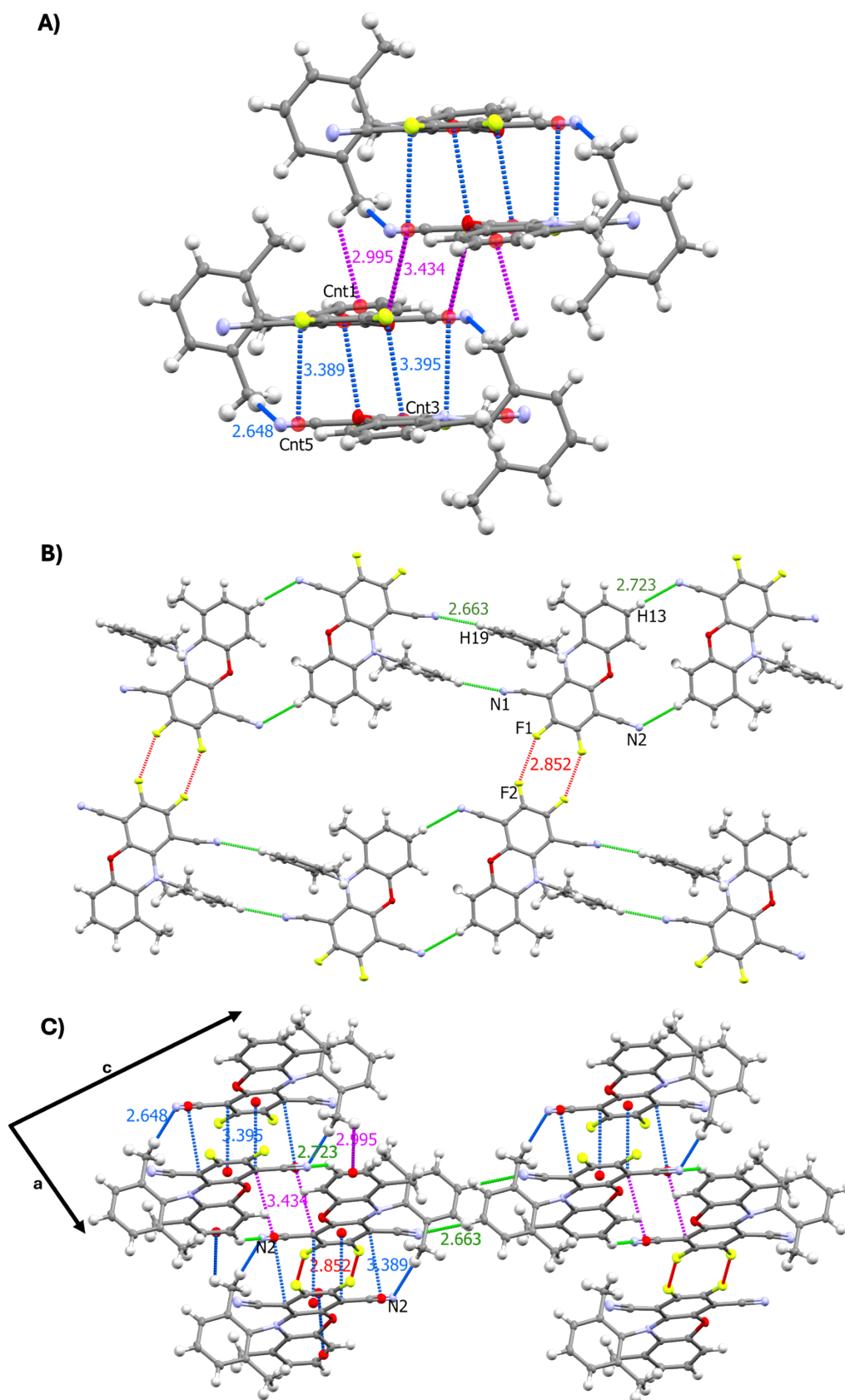


Figure S46: Excerpt of the packing of **POA-12** displaying all types of interactions: A) Dimer-like stacking with additional hydrogen bonds (blue, between dimers purple); B) layer formation through hydrogen bonding (green), forming a 3D-network (red); C) stacking of the layers. The displacement ellipsoids are displayed at 50% probability levels.

Table S26: $\pi\cdots\pi$ and $\text{CH}\cdots\pi$ interactions in **POA-12** [Å]. Operators for generating equivalent atoms: \$1 1-x, 1-y, 1-z; \$2 -x, 1-y, 1-z; \$3 -1+x, y, z; \$4 -x, -y, 1-z; \$5 1-x, 1-y, 2-z; \$6 1-x, 2-y, 1-z. Cnt1 is the centroid involving atoms C12 and C13. Cnt3 is the centroid involving C1, C3, C5. Cnt4 is the centroid involving C16, C18, C20. Cnt5 is the centroid involving C8 and C2.

Plane...X	<(Plane/Plane) [°]	Cnt...X	Shift	
3.328	0.51	3.389	0.640	C6..Cnt5_\$1 (blue)
3.32	0.51	3.395	0.710	C3..Cnt3_\$1 (blue)
2.952	0.15	3.434	1.754	C3..Cnt5_\$2 (purple)
2.958	-	2.995	0.469	Cnt1...H22B-C22_\$3 (purple)

Table S27: Specified hydrogen bonds in **POA-12** (with esds except fixed and riding H) [Å] and F...F contacts. Operators for generating equivalent atoms: \$1 1-x, 1-y, 1-z; \$2 -x, 1-y, 1-z; \$3 -1+x, y, z; \$4 -x, -y, 1-z; \$5 1-x, 1-y, 2-z; \$6 1-x, 2-y, 1-z.

D-H	H...A	D...A	<(DHA) [°]	
0.950	2.648	3.627	177.91	C22-H22C...N2_\$1 (blue)
0.950	2.723	3.575	149.58	C13-H13...N2_\$4 (green)
0.950	2.663	3.609	173.88	C19-H19...N1_\$5 (green)
-	2.852	-	-	F1...F2_\$6 (red)

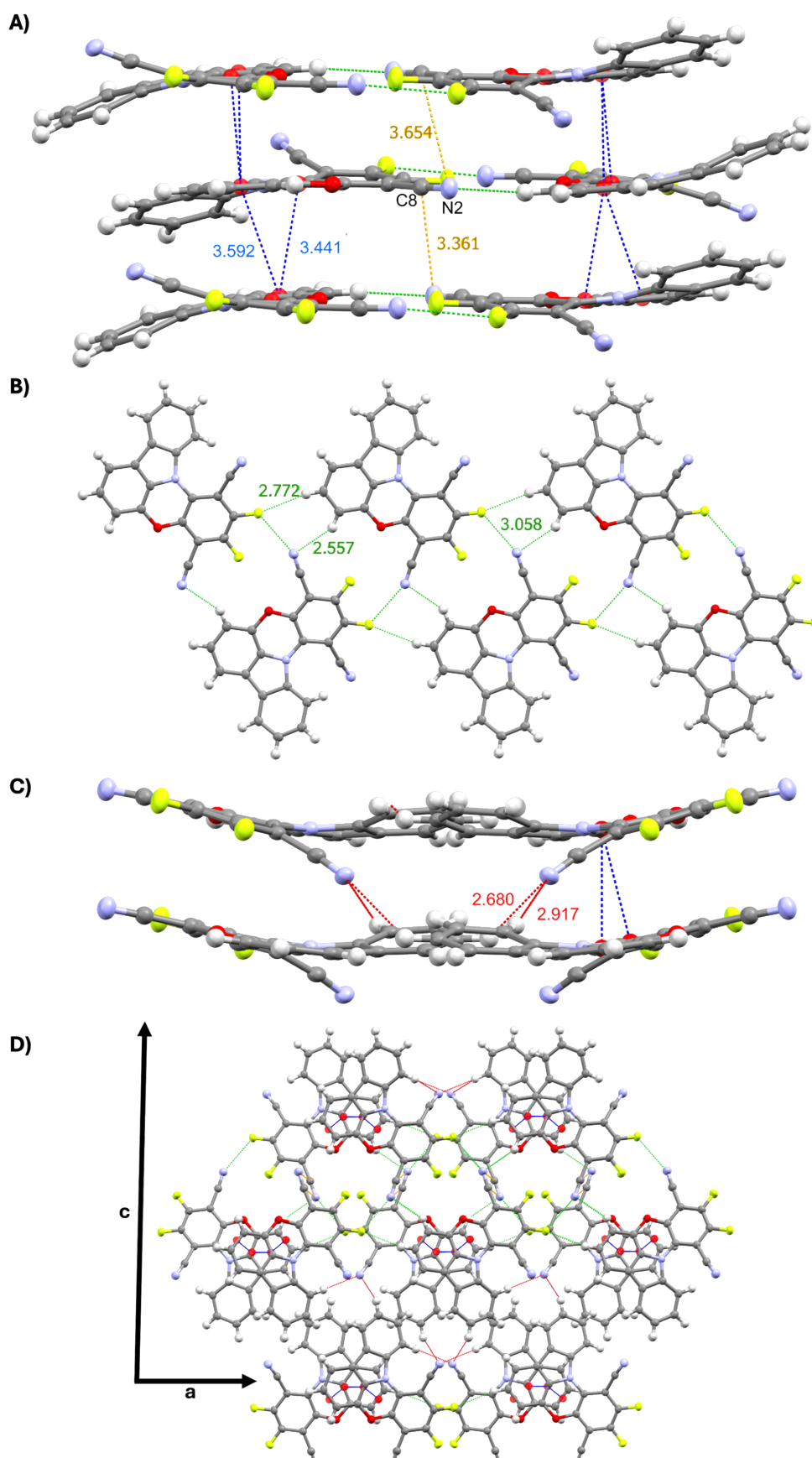


Figure S47: Excerpt of the packing of In-POA displaying all types of interactions: A) string formation through $\pi \cdots \pi$ stacking (blue) with additional $CN \cdots \pi$ stacking (orange) interconnecting the strings; B) layer formation through hydrogen bonding (green), C) formation of a 3D-network (red); D) stacking of the layers. The displacement ellipsoids are displayed at 50% probability levels.

Comment: The C–H···N contacts in Figure S47B (2.577 Å) with H···N–C angles around 90° are shown for completeness but may not represent classic hydrogen bonds due to their near-orthogonal geometry.

Table S28: $\pi\cdots\pi$ and CH $\cdots\pi$ interactions in **In-POA** [Å]. Operators for generating equivalent atoms: \$1 1.5-x, -1/2+y, z; \$2 1.5-x, 1/2+y, z; \$3 1+x, y, z; \$4 1/2+x, 1/2-y, 1-z; \$5 -1/2+x, 1/2-y, -1-z; \$6 1-x, 1/2+y, 1/2-z; \$7 1/2-x, -1/2+y, z; \$8 1-x, 1-y, 1-z; \$9 1-x, -y, 1-z. Cnt1 is the centroid involving atoms C9, C11, C13. Cnt2 is the centroid involving C9, N3, C5. Cnt3 is the centroid involving C1, C3, C5. Cnt4 is the centroid involving N3, C16, C11. Cnt5 is the centroid involving C16, C18, C20. Cnt6 is the centroid involving C8, N2.

Plane···X	<(Plane/Plane) [°]	Cnt···X	Shift	
3.318	3.04	3.441	0.912	Cnt1...Cnt2_\$1 (blue)
3.340	0.43	3.592	1.322	Cnt1...Cnt1_\$1 (blue)
3.308	-	3.361	0.595	C8...N2_\$8 (orange)
2.972	-	3.654	2.126	C8...N2_\$9 (orange)

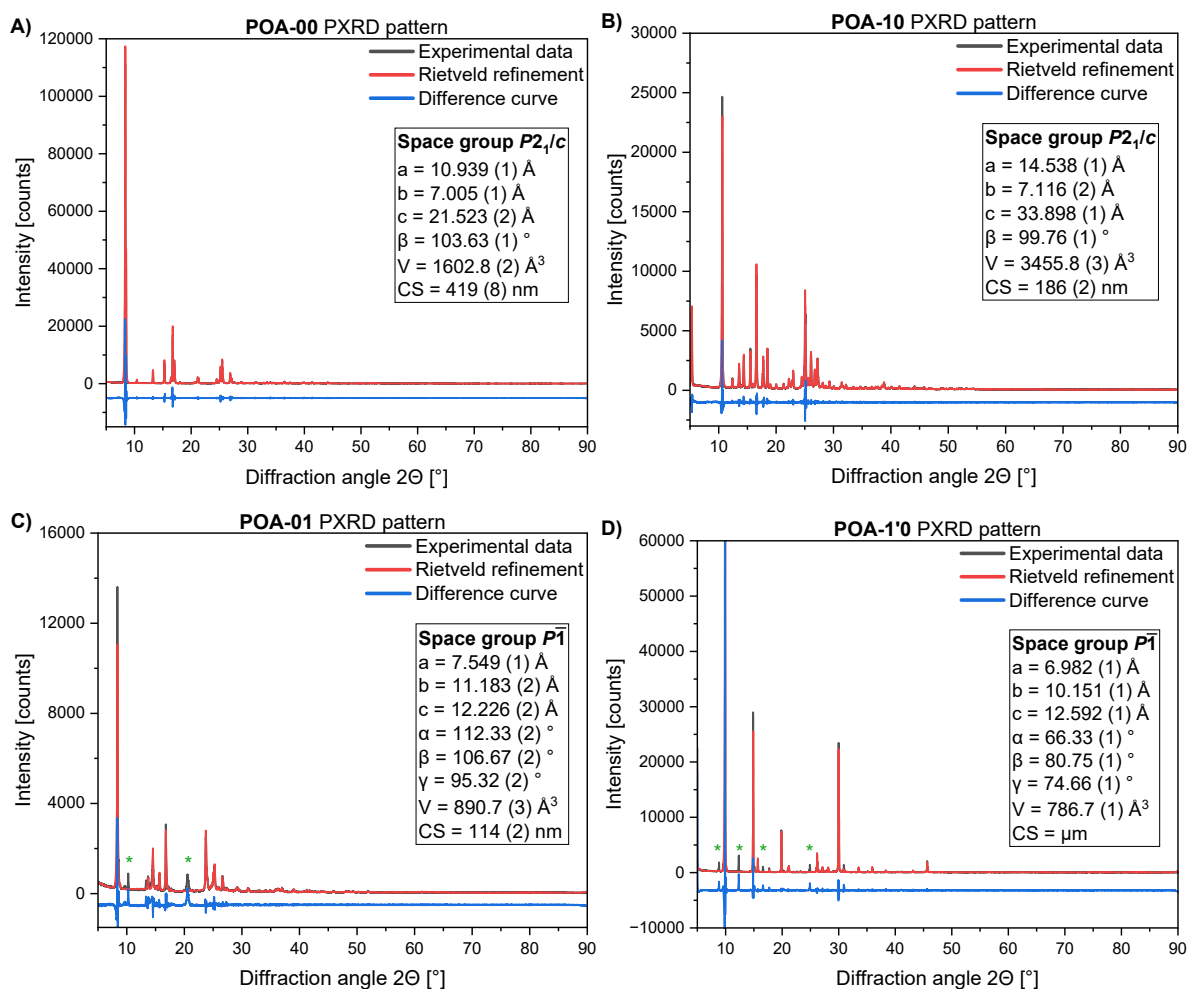
Table S29: Specified hydrogen bonds in **In-POA** (with esds except fixed and riding H) [Å]. Operators for generating equivalent atoms: \$1 1.5-x, -1/2+y, z; \$2 1.5-x, 1/2+y, z; \$3 1+x, y, z; \$4 1/2+x, 1/2-y, 1-z; \$5 -1/2+x, 1/2-y, -1-z; \$6 1-x, 1/2+y, 1/2-z; \$7 1/2-x, -1/2+y, z; \$8 1-x, 1-y, 1-z; \$9 1-x, -y, 1-z.

D-H	H···A	D···A	<(DHA) [°]	
0.950	2.772	3.703	166.83	C13-H13...F1_\$3 (green)
0.950	2.557	3.395	147.24	C14-H14...N2_\$4 (green)
0.950	2.68	3.419	135	N1...C18-H18_\$6 (red)
0.950	2.917	3.833	162.47	N1...C20-H20_\$7 (red)
D-X: 3.058			<DXC = 157.2	F1...N2_\$5 (green)

5 POWDER X-RAY DIFFRACTOMETRY

A *Bruker D8 Advance* powder diffractometer employing the Bragg-Brentano reflection mode with $\text{Cu}_{K\alpha}$ radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA) was used for collecting powder diffraction data. For this, the samples were prepared on a silicon single crystal sample holder for reduced scattering. Scanning was performed from $5\text{--}90^\circ 2\theta$ with a step size of 0.01° and a counting time of 0.85 s, with a total acquisition time of 2 h. The crystallite sizes (CS) were determined from diffraction peak broadening through Rietveld refinement using the software *TOPAS 7.0* from *Bruker*, after instrumental calibration with a standard reference material LaB_6 (SRM 660b of NIST).

For compounds **POA-01**, **-1'0**, **-12**, and **In POA**, additional minor phases were observed, and are marked with an asterisk.



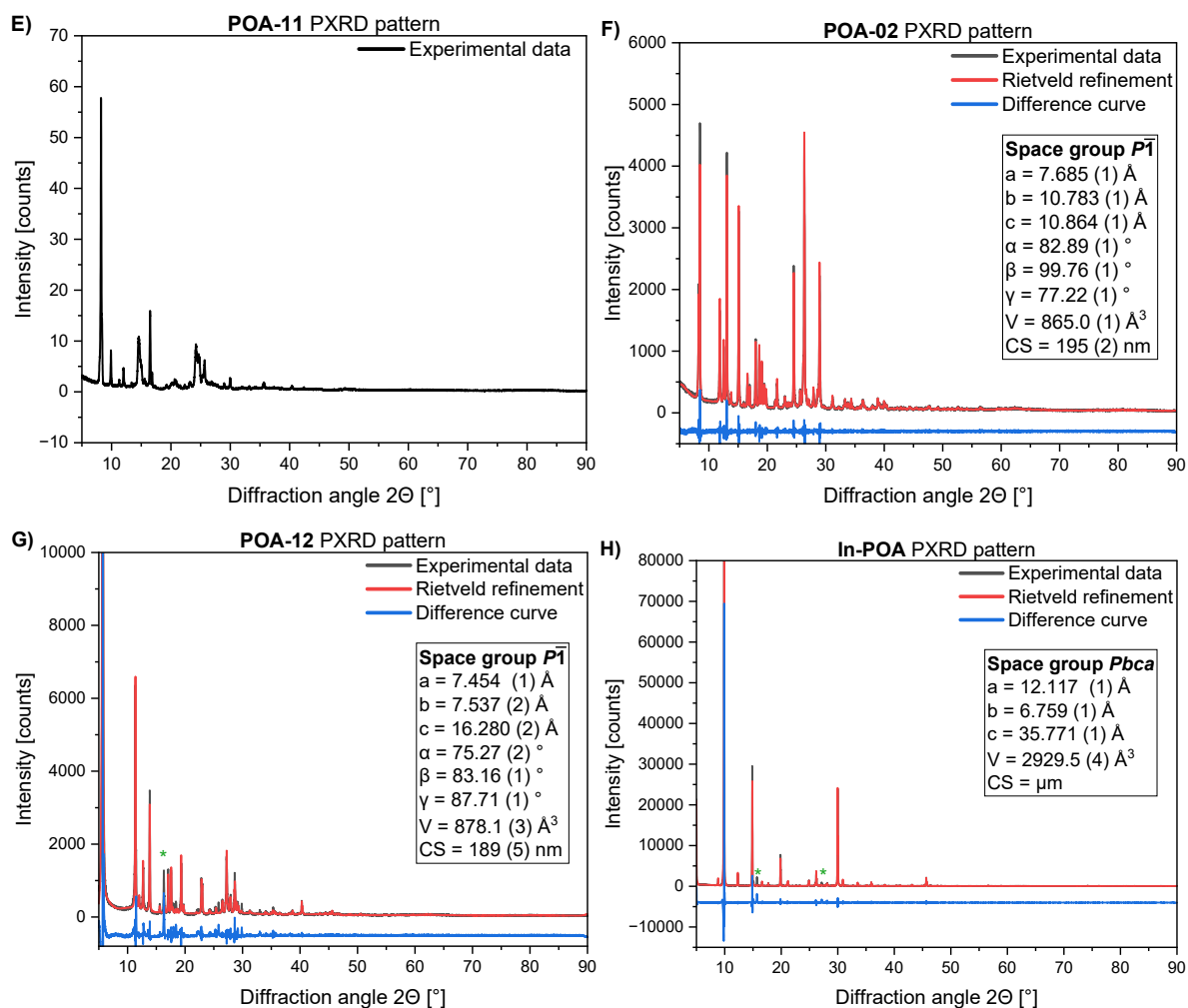


Figure S48: X-ray powder diffraction data (black), Rietveld refinement (red) and difference curves (blue) pattern of the target compounds

6 QUANTUM CHEMICAL CALCULATIONS

Gaussian 16 was used for the quantum chemical calculations.¹³ The compound geometries in the energetic ground states were calculated using PBE0/TZVP with the Grimme dispersion correction (D3BJ).^{14–16} For the initially guessed geometries, the structures obtained from X-ray diffractometry were used. In the case of **POA-11**, both out-of-plane (similar to **POA-10**) and in-plane (similar to **POA-00**) geometries were used. All four convergence criteria of *Gaussian* were fulfilled in every optimization. Frequency analysis revealed no imaginary frequencies, indicating that the obtained structures are energetic minima. To simulate UV/Vis-spectra, the first 40 transitions were calculated using the *TD* keyword.¹⁷ The optimized first excited state geometries and natural transition orbital (NTO) pairs were obtained using TD-PBE0/TZVP. For the scans, the keyword *opt=modredundant* was used in addition to the above-mentioned optimization parameters. The optimized structure of **POA-00** with an in-plane angle (α_{ONC}) of 178° was used as the initial geometry for the scans of all other compounds, and the respective methyl group was added at its corresponding position. 20 scan steps, each with a 5° increased bending angle, were calculated.

NICS(1) and NICS(1)_{zz} values were obtained using GIAO-PBE0/TZVP.^{18,19} The centroids of the oxazine rings were placed 1 Å above the ring planes in the z-direction. Using the same level of theory, the NICS(1) value of benzene was calculated to be -10.0 ppm, denoting aromaticity.²⁰ Bond length analysis was conducted using the harmonic oscillator model of aromaticity (HOMA).²¹ For this, equation S1 was applied with the parameters given in Table S29.²² The respective bond length R_i in Å was subtracted from the optimized value R_{opt} and the difference squared. For each bond, the respective normalization parameter α in Å⁻¹ was considered, with n as the number of bonds taken into summation. Table S31 provides an overview of NICS(1) and NICS(1)_{zz} values (GIAO-PBE0/TZVP) as well as HOMA indices (PBE0-D3BJ/TZVP) for **POA-00**, **POA-10**, and benzene.

The bond energy analysis (EDA)²³ calculations were performed using the density functional PBE0-D3BJ and the TZ2P²⁴ basis set within the Amsterdam Modeling Suite (AMS; Amsterdam Density Functional ADF).^{25,26} For treatment of relativistic effects, the zeroth-order regular approximation (ZORA)²⁷ to the Dirac equation was used for the bond energy analysis, which is shown in Table S35.

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_{\text{opt}} - R_i)^2 \quad \text{S1}$$

Table S30: Parameters used for HOMA calculations.²²

Bond type	R_{opt} [Å]	α [Å ⁻¹]
C–C	1.388	257.7
C–N	1.334	93.52
C–O	1.265	157.38

Table S31: an overview of NICS(1) and NICS(1)_{zz} values (GIAO-PBE0/TZVP) as well as HOMA indices (PBE0-D3BJ/TZVP) for **POA-00**, **POA-10**, and benzene.

Aromaticity Index	POA-00	POA-10	Benzene
NICS(1) [ppm]	6.2	-0.2	-10.0
NICS(1) _{zz} [ppm]	22.6	7.2	-29.7
HOMA	0.33	0.17	1.00

Table S32: Overview of the calculated energies [eV] of the respective HOMOs and LUMOs as well as the energy gap $\Delta E_{\text{H-L}}$, absorption wavelengths $\lambda_{\text{ab,calc}}$ with oscillator strengths f_{ab} for the absorption processes, and theoretical emission wavelengths $\lambda_{\text{em,calc}}$ [nm]; both stable conformations of **POA-11** were calculated with out-of-plane twisted ($\alpha_{\text{ONC}} = 129^\circ$) and in-plane conformer ($\alpha_{\text{ONC}} = 178^\circ$).

POA	E_{LUMO} [eV]	E_{HOMO} [eV]	$\Delta E_{\text{H-L}}$ [eV]	$\lambda_{\text{ab,calc}}$ [nm]	f_{ab}	$\lambda_{\text{em,calc}}$ [nm]
00	-2.518	-6.114	-3.596	421	0.158	565
10	-2.789	-6.713	-3.924	399	0.075	681
01	-2.525	-6.113	-3.588	420	0.153	543
1'0	-2.472	-6.008	-3.536	429	0.163	596
11 ($\alpha_{\text{ONC}}=129^\circ$)	-2.731	-6.525	-3.794	410	0.098	564
11 ($\alpha_{\text{ONC}}=178^\circ$)	-2.482	-6.097	-3.615	419	0.150	549
02	-2.52	-6.111	-3.591	421	0.154	536
12	-2.467	-6.042	-3.575	423	0.156	538
In	-2.901	-6.366	-3.465	438	0.196	543

Table S33: Comparison of the calculated absorption $\lambda_{\text{ab,calc}}$ and emission wavelengths $\lambda_{\text{em,calc}}$ with the experimentally determined ones in THF ($\lambda_{\text{ab,THF}}$, $\lambda_{\text{em,THF}}$) and energetical differences $\Delta\lambda_{\text{ab,THF-calc}}$ and $\Delta\lambda_{\text{em,THF-calc}}$ [eV]; both stable conformations of **POA-11** were calculated with out-of-plane twisted ($\alpha_{\text{ONC}} = 129^\circ$) and in-plane conformer ($\alpha_{\text{ONC}} = 178^\circ$).

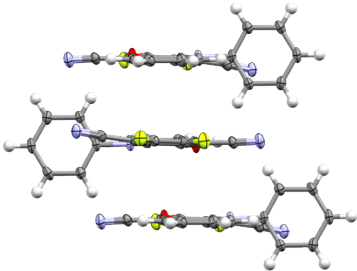
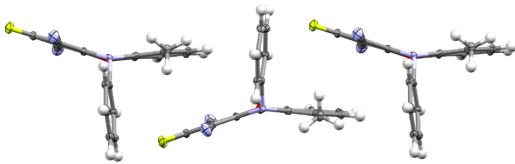
POA	$\lambda_{\text{ab,calc}}$ [eV]	$\lambda_{\text{ab,THF}}$ [eV]	$\Delta\lambda_{\text{ab,THF-calc}}$ [eV]	$\lambda_{\text{em,calc}}$ [eV]	$\lambda_{\text{em,THF}}$ [eV]	$\Delta\lambda_{\text{em,THF-calc}}$ [eV]
00	2.945	2.786	-0.159	2.194	2.242	0.048
10	3.107	3.187	0.080	1.821	2.242	0.421
01	2.952	2.792	-0.160	2.283	2.354	0.071
1'0	2.890	2.755	-0.135	2.080	2.168	0.087
11 ($\alpha_{\text{ONC}}=129^\circ$)	3.024	2.973	-0.051	2.198	2.230	0.032
11 ($\alpha_{\text{ONC}}=178^\circ$)	2.959		0.014	2.258		-0.028
02	2.945	2.792	-0.153	2.313	2.258	-0.055
12	2.931	2.780	-0.151	2.305	2.238	-0.067
In	2.831	2.768	-0.063	2.283	2.246	-0.037
average error			± 0.119			± 0.102

Table S34: Comparison of the different methods used for calculating the emission wavelengths λ_{em} in nm and eV for **POA-00** and **POA-10** with deviations from the experimental value in DCM.

$\lambda_{\text{em,METHOD}}$ nm (eV)	POA-00 nm (eV)	POA-00 deviation from DCM [eV]	POA-10 nm (eV)	POA-10 deviation from DCM [eV]
DCM (experimental)	553 (2.24)	-	559 (2.22)	-
TD-PBE0/TZVP	573 (2.16)	-0.08	680 (1.82)	-0.39
TD-cam-B3LYP-D3BJ/def2-TZVP	479 (2.59)	0.35	494 (2.51)	0.29
TD- ω B97X-D/def2-TZVP	467 (2.66)	0.41	472 (2.63)	0.41
CC2/def2-TZVP	542 (2.29)	0.05	535 (2.32)	0.10
CC2/cc-pVDZ	515 (2.41)	0.17	504 (2.46)	0.24
ADC(2)/cc-pVDZ	548 (2.26)	0.02	524 (2.36)	0.15

Table S35: Energy decomposition analysis (EDA) calculations of the extracted trimers of **POA-00** and **POA-10** from the crystal structure. Calculations were performed using PBE0-D3BJ/TZ2P. The total bonding energy ΔE_{total} in kcal/mol includes Pauli repulsion (ΔE_{pauli}), orbital (ΔE_{oi}) and electrostatic (ΔV_{elstat}) interactions, and dispersion energy (ΔE_{disp}).

	POA-00	POA-10
ΔE_{pauli}	27.7	11.7
ΔE_{oi}	-9.2	-4.9
ΔV_{elstat}	-21.3	-9.0
ΔE_{disp}	-35.7	-19.3
ΔE_{total}	-38.5	-21.5

Calculated for		
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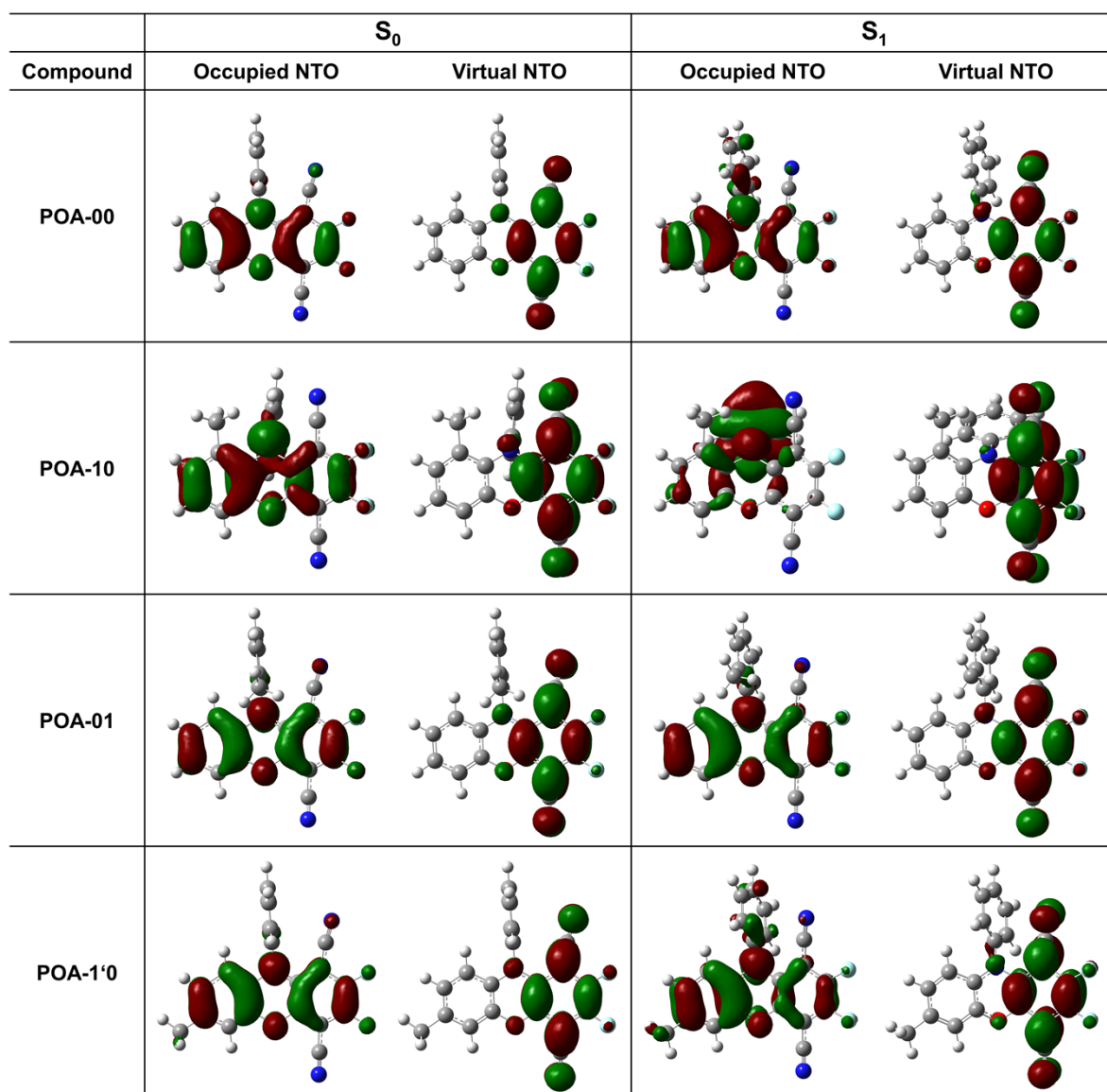


Figure S49: Occupied and virtual natural transition orbital pairs (isovalue 0.030 a.u.) for optimized S_0 (left) and S_1 (right) geometries for compounds **POA-00**, **-10**, **-01**, and **-1'0** using PBE0-D3BJ/TZVP (S_0) or TD-PBE0/TZVP (S_1).

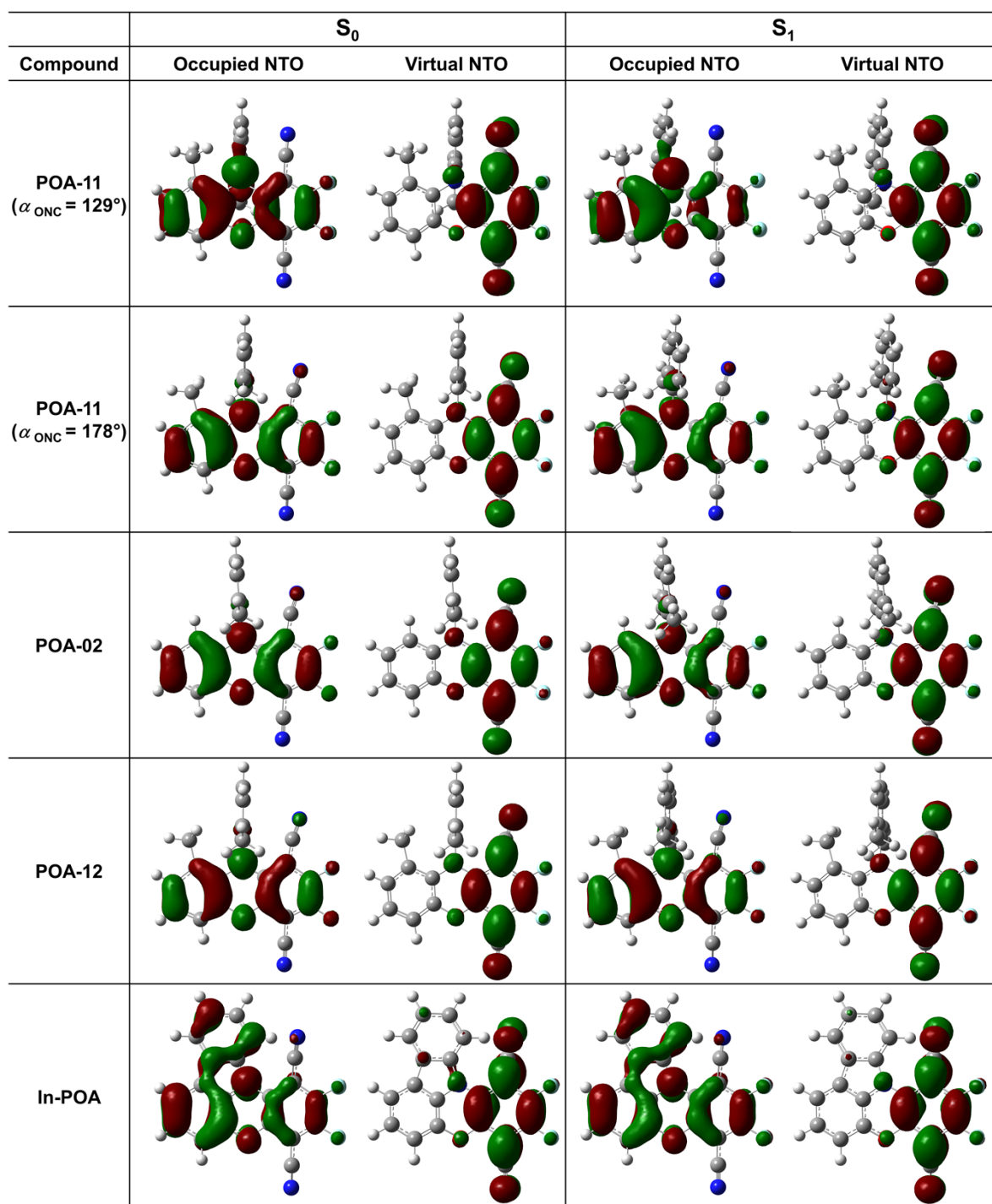


Figure S50: Occupied and virtual natural transition orbital pairs (isovalue 0.030 a.u.) for optimized S_0 (left) and S_1 (right) geometries for compounds **POA-11** (both conformers, $\alpha_{\text{ONC}} = 129^\circ$, $\alpha_{\text{ONC}} = 178^\circ$), **-02**, **-12**, and **In-POA** using PBE0-D3BJ/TZVP (S_0) or TD-PBE0/TZVP (S_1).

Cartesian coordinates of the optimized S_0 geometry of **POA-00** using PBE0-D3BJ/TZVP.

```

F      2.24417800  -3.39611600  -0.01666400
F      4.32656600  -1.68745300  -0.01731100
O      1.41576100   1.97505800   0.03590700
N     -0.83038400   0.32015400   0.02057000
N      4.82547000   1.79241500   0.00273200
N     -0.98375600  -3.56721900   0.00418400

```

C	2.02351200	-2.09024500	-0.00802900
C	3.08446300	-1.22863100	-0.00783900
C	2.84685000	0.15047000	0.00227400
C	1.54356800	0.63002100	0.01520900
C	0.43351800	-0.23780800	0.01083700
C	0.69554500	-1.62101100	0.00152100
C	3.93723300	1.05937200	0.00296600
C	-0.29174100	-2.64482500	0.00274100
C	0.15523300	2.52447000	0.01153100
C	-0.97865200	1.71805200	0.00572700
C	-2.22365500	2.33454000	-0.01266300
H	-3.11737600	1.72490200	-0.01668800
C	-2.32076000	3.72045700	-0.02519600
H	-3.30170200	4.17979400	-0.03881700
C	-1.18120300	4.50586300	-0.02021800
H	-1.25437000	5.58618300	-0.03022000
C	0.06837900	3.89873300	-0.00233400
H	0.98592500	4.47441200	0.00273500
C	-2.01123200	-0.48097800	0.01066500
C	-2.59598900	-0.84924200	1.21343300
H	-2.13797400	-0.54002200	2.14590000
C	-3.74392400	-1.62476500	1.20105700
H	-4.19586000	-1.93413800	2.13594900
C	-4.30487000	-2.01424900	-0.00735200
H	-5.19599600	-2.63101700	-0.01437400
C	-3.72905300	-1.61884400	-1.20690100
H	-4.16939400	-1.92363600	-2.14880800
C	-2.58111500	-0.84347200	-1.20123800
H	-2.11198200	-0.52972700	-2.12670800

Cartesian coordinates of the optimized S_1 geometry of **POA-00** using TD-PBE0/TZVP.

F	2.16726800	-3.33577700	-0.72298800
F	4.20608700	-1.79178700	-0.07261400
O	1.35425100	1.90798900	0.41574600
N	-0.89338200	0.35032800	-0.12214100
N	4.78711900	1.63122700	0.82830500
N	-1.18784400	-3.23875900	-1.27954100
C	1.91842400	-2.07991800	-0.37321100
C	2.98919100	-1.27169500	-0.04292900
C	2.82845300	0.08243600	0.27040100
C	1.47767300	0.54664300	0.24148100
C	0.40788200	-0.23849100	-0.03979400
C	0.58708200	-1.62692700	-0.37750100
C	3.90093800	0.92683900	0.57312900
C	-0.41052800	-2.48254200	-0.86351400
C	0.21786600	2.47713000	-0.00563200
C	-0.96034700	1.71396900	-0.24905800
C	-2.14976300	2.41913500	-0.50534700
H	-3.07340100	1.87421900	-0.62888800
C	-2.14418000	3.79001300	-0.59588400
H	-3.07103900	4.31066200	-0.80374100
C	-0.96178500	4.51973900	-0.40702100
H	-0.97086200	5.59995000	-0.48443700
C	0.20992500	3.86211100	-0.10610100
H	1.13591500	4.38967200	0.08577300
C	-2.02390400	-0.43617800	0.22956400
C	-1.99448700	-1.13223200	1.43646000
H	-1.13217700	-1.04124900	2.08665500
C	-3.07106800	-1.92720500	1.79049600
H	-3.04940900	-2.46996800	2.72823900

C	-4.16568100	-2.03703200	0.94523300
H	-4.99924900	-2.67367300	1.21761200
C	-4.18400700	-1.34885400	-0.26214500
H	-5.02092300	-1.46381800	-0.94073900
C	-3.11557300	-0.55056500	-0.62703100
H	-3.09098900	-0.07946800	-1.60195100

Cartesian coordinates of the optimized S_0 geometry of **POA-10** using PBE0-D3BJ/TZVP.

F	3.43601400	-2.34190200	-1.01371800
C	2.72066400	-1.30234100	-0.61443400
O	0.55340300	1.97573400	0.61599500
N	3.80001100	2.89858400	1.45993900
F	4.66208200	-0.26431300	0.16366000
C	3.35319000	-0.23307500	-0.01635200
N	-0.82906700	-0.18878100	-0.45729700
C	1.23467100	0.88822900	0.20186800
C	0.57580500	-0.19989900	-0.36438000
C	1.33982300	-1.28369900	-0.81698900
C	3.27290000	1.99526400	0.97791500
C	0.74131600	-2.36664400	-1.51377300
C	-0.68342900	2.18619600	0.03245400
C	-1.38173000	1.12440000	-0.52767400
C	-2.61387100	1.35928600	-1.14216600
C	-3.11743600	2.65761600	-1.12458500
H	-4.07722700	2.84933400	-1.59126400
C	-2.41675000	3.70164500	-0.54038600
H	-2.82973700	4.70323900	-0.54677300
C	-1.17761700	3.47431000	0.03682300
H	-0.59224000	4.26701000	0.48574200
C	-1.49531500	-1.06576900	0.48770300
C	-1.55548700	-0.70653300	1.83020300
H	-1.11062400	0.22654300	2.15903300
C	-2.18898600	-1.53834300	2.73900100
H	-2.23423700	-1.25748700	3.78495400
C	-2.76209200	-2.72859200	2.30890700
H	-3.25570000	-3.38063900	3.02033100
C	-2.70245800	-3.08083500	0.96900800
H	-3.14855500	-4.00798400	0.62840200
C	-2.07329300	-2.24792900	0.05318900
H	-2.02240500	-2.51323600	-0.99403100
C	-3.37157600	0.24620700	-1.79049100
H	-3.86404100	-0.38657100	-1.04682400
H	-2.70082700	-0.39708800	-2.36382400
H	-4.13674500	0.64348900	-2.45781700
C	2.62053800	0.88470900	0.38178200
N	0.27892400	-3.23577100	-2.11137100

Cartesian coordinates of the optimized S_1 geometry of **POA-10** using TD-PBE0/TZVP.

F	3.14069600	-2.44162600	-1.47959500
C	2.53049600	-1.49217800	-0.77268400
O	0.69079600	1.66271600	1.15450400
N	4.13170900	2.22702600	1.87954900
F	4.60433900	-0.75706800	-0.03033500
C	3.28144800	-0.62675300	-0.02651400
N	-0.86487000	-0.08404300	-0.04821900

C	1.29943800	0.52915700	0.64964600
C	0.54692500	-0.38490700	-0.01532100
C	1.11438800	-1.40790500	-0.83901500
C	3.49399500	1.42127600	1.34093900
C	0.34160000	-2.24002900	-1.64544000
C	-0.28546400	2.15791200	0.34642600
C	-1.10130300	1.27316200	-0.37495200
C	-2.03717600	1.72720600	-1.30708900
C	-2.19543700	3.10572800	-1.40890900
H	-2.90228200	3.49939400	-2.13088300
C	-1.45156800	3.98283400	-0.62729100
H	-1.60365400	5.05074800	-0.73378700
C	-0.48317000	3.52163900	0.25119900
H	0.14180700	4.19129000	0.82837600
C	-1.76226500	-0.85523300	0.59668100
C	-3.08833200	-0.39571900	0.84020400
H	-3.35809200	0.61363100	0.56360100
C	-3.99250400	-1.21812900	1.45357600
H	-4.99777800	-0.86246500	1.64419600
C	-3.62144100	-2.50736100	1.86235800
H	-4.34652400	-3.14852200	2.34852400
C	-2.31279000	-2.95301200	1.66854000
H	-2.02230200	-3.94004200	2.00576600
C	-1.38463600	-2.14888500	1.06005500
H	-0.37031100	-2.48620600	0.91405300
C	-2.80594400	0.78710200	-2.18658600
H	-3.80551200	0.58451900	-1.79048900
H	-2.29526100	-0.16927900	-2.30797300
H	-2.93515100	1.22883600	-3.17560500
C	2.71441000	0.44761400	0.71102200
N	-0.34407500	-2.91676900	-2.29897300

Cartesian coordinates of the optimized S_0 geometry of **POA-01** using PBE0-D3BJ/TZVP.

F	-2.26249700	-3.41576300	0.00340700
F	-4.37102600	-1.74214900	0.08576800
O	-1.52917700	1.96482600	-0.21352800
N	0.96349000	-3.53368900	-0.17365700
N	-4.93032900	1.72944900	0.04401400
N	0.74091800	0.34864900	-0.24504200
C	-2.06472300	-2.10676900	-0.03446800
C	-3.13920500	-1.26264700	0.00625100
C	-2.92667900	0.12003700	-0.03522400
C	-1.63467300	0.61981100	-0.13109500
C	-0.51083900	-0.22894400	-0.15944500
C	-0.74724400	-1.61592300	-0.11752400
C	0.25811000	-2.62160300	-0.15324800
C	-4.03117500	1.01082800	0.00639000
C	-0.27941900	2.53419500	-0.13399000
C	0.86689600	1.74612300	-0.16031300
C	2.10231200	2.37936200	-0.10313500
H	3.00449200	1.78219200	-0.12722700
C	2.17750700	3.76434500	-0.02173300
H	3.15095300	4.23786900	0.01870500
C	1.02562600	4.53133100	0.00639700
H	1.08208200	5.61085000	0.06983500
C	-0.21454800	3.90699800	-0.04806300
H	-1.14071200	4.46849400	-0.03114500
C	1.93616800	-0.43316600	-0.22966500

C	2.50133400	-0.79536400	0.99441200
C	3.67279200	-1.54297500	0.95976700
H	4.12512700	-1.85451400	1.89500000
C	4.25871900	-1.90744400	-0.24326000
H	5.16522600	-2.50171300	-0.23934700
C	3.69152600	-1.51756000	-1.44750300
H	4.14838300	-1.80109300	-2.38789700
C	2.52700700	-0.76900300	-1.43786500
H	2.05601800	-0.45093500	-2.36092000
C	1.84804800	-0.41757600	2.28610500
H	1.66636800	0.65876800	2.34275300
H	2.47199700	-0.70488600	3.13221600
H	0.88140800	-0.91763200	2.39972500

Cartesian coordinates of the optimized S_1 geometry of **POA-01** using TD-PBE0/TZVP.

F	-2.28050700	-3.40998300	0.28953600
F	-4.35490800	-1.80918900	-0.00506400
O	-1.55382700	1.94784300	-0.19843800
N	1.04939600	-3.40472300	0.72857500
N	-4.99108400	1.70524600	-0.32774500
N	0.74238500	0.35072800	0.01993000
C	-2.05375400	-2.11172600	0.13841000
C	-3.14474600	-1.27474600	-0.00855000
C	-3.00170900	0.11003200	-0.11374500
C	-1.64827800	0.57246800	-0.13401100
C	-0.55978500	-0.23187400	0.00067600
C	-0.72489600	-1.65189400	0.14418000
C	0.28325800	-2.57486400	0.45838800
C	-4.08962100	0.98049100	-0.22971900
C	-0.34957600	2.50086000	-0.02378800
C	0.83543200	1.71377700	0.04834800
C	2.06805200	2.39043300	0.09216300
H	2.98131800	1.81147200	0.09216300
C	2.10967000	3.76348000	0.13177600
H	3.06935000	4.26414400	0.17378500
C	0.92895300	4.52003500	0.10558900
H	0.97537000	5.60158400	0.13742900
C	-0.29199300	3.88727000	0.01933200
H	-1.22394900	4.43585700	-0.03699300
C	1.90810300	-0.42391800	-0.29259400
C	2.85750700	-0.69390300	0.69630000
C	3.97677400	-1.42560700	0.31353800
H	4.72181200	-1.66750300	1.06379400
C	4.13774400	-1.88342700	-0.98569600
H	5.01435700	-2.46610500	-1.24471200
C	3.17555000	-1.61227300	-1.94658600
H	3.29172400	-1.97395200	-2.96135500
C	2.05868200	-0.87218800	-1.59885400
H	1.29304300	-0.64117900	-2.33117900
C	2.63885900	-0.31996400	2.12900800
H	2.30825500	0.71340400	2.25254900
H	3.55535700	-0.45493300	2.70409600
H	1.87249000	-0.96651400	2.56737100

Cartesian coordinates of the optimized S_0 geometry of **POA-1'0** using PBE0-D3BJ/TZVP.

F	4.20703400	1.02635400	-0.00572300
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F	4.50753700	-1.65092900	-0.00536600
O	-0.13315000	-2.24597800	0.01087600
N	2.01118800	3.40068400	0.00025300
N	2.43670600	-4.49207400	0.00149900
N	-0.58772500	0.50754500	0.00596500
C	3.13786800	0.24436800	-0.00284600
C	3.29719800	-1.11290200	-0.00251100
C	2.16468900	-1.93528900	0.00080400
C	0.89610400	-1.37033900	0.00462600
C	0.70566900	0.02650900	0.00307600
C	1.85907700	0.83465300	0.00003100
C	1.86532200	2.25675900	0.00009000
C	2.31194800	-3.34716100	0.00128000
C	-1.42028600	-1.76112700	0.00446800
C	-1.66934500	-0.39227600	0.00248000
C	-2.99195900	0.02433000	-0.00239700
H	-3.21650700	1.08277800	-0.00387800
C	-4.02378600	-0.90720000	-0.00516800
H	-5.04816400	-0.55198400	-0.00881300
C	-3.77074300	-2.27111900	-0.00341100
C	-2.43808700	-2.68562000	0.00132700
H	-2.17385700	-3.73727000	0.00301700
C	-4.87845100	-3.27934300	-0.00624700
H	-4.82943800	-3.92345300	0.87591200
H	-4.82165700	-3.92712700	-0.88522700
H	-5.85361700	-2.79077700	-0.01153800
C	-0.87804800	1.90432300	0.00309700
C	-1.03895400	2.57086700	1.20905500
H	-0.92310300	2.02612800	2.13897500
C	-1.32319400	3.92674900	1.20315300
H	-1.42997400	4.45953400	2.14057000
C	-1.45736700	4.60204500	-0.00208900
H	-1.66751500	5.66525500	-0.00411700
C	-1.32212800	3.92236700	-1.20476500
H	-1.42806600	4.45173900	-2.14421000
C	-1.03785900	2.56650900	-1.20547600
H	-0.92124400	2.01846900	-2.13337900

Cartesian coordinates of the optimized S₁ geometry of **POA-1'0** using TD-PBE0/TZVP.

F	4.16174800	0.52743500	0.89115700
F	4.26933000	-2.00702400	0.15546700
O	-0.37708600	-2.08057300	-0.55123200
N	1.95508300	3.08398500	1.36497000
N	2.01862500	-4.56058900	-0.97350400
N	-0.59774200	0.61974300	0.09302400
C	3.04722400	-0.05247400	0.46090800
C	3.10504200	-1.37945200	0.08503700
C	1.96748000	-2.08703000	-0.32130000
C	0.75648800	-1.32860300	-0.31452800
C	0.68459500	-0.01594400	0.01249800
C	1.85912400	0.70082100	0.43078800
C	1.87713900	2.00920200	0.93174100
C	1.99856200	-3.43907200	-0.67584300
C	-1.53432400	-1.58447600	-0.09332300
C	-1.68928800	-0.19932100	0.20212600
C	-2.99078200	0.25349800	0.48681300
H	-3.16217300	1.30649300	0.65197000
C	-4.03936400	-0.62721300	0.55177400
H	-5.02957400	-0.24954200	0.78173100
C	-3.86924100	-2.00829500	0.31479700

C	-2.60519100	-2.46083800	-0.01502600
H	-2.41910500	-3.50185200	-0.25120600
C	-5.02957200	-2.94059700	0.41856600
H	-5.36569800	-3.02068500	1.45739800
H	-4.77426100	-3.94072000	0.06914300
H	-5.87916400	-2.57528900	-0.16459300
C	-0.70333200	1.99403900	-0.25808300
C	-1.32304600	2.90934100	0.58777400
H	-1.68348900	2.59264300	1.55865400
C	-1.38460200	4.24139500	0.22008900
H	-1.84130800	4.95961000	0.89078300
C	-0.82345000	4.66545900	-0.97808600
H	-0.86058400	5.71318000	-1.25244800
C	-0.19402200	3.75132300	-1.81061700
H	0.25540300	4.07977000	-2.74049700
C	-0.12640500	2.41527400	-1.45408500
H	0.36697500	1.69308000	-2.09424900

Cartesian coordinates of the optimized S_0 geometry of **POA-11** ($\alpha_{\text{ONC}} = 129^\circ$) using PBE0-D3BJ/TZVP.

N	0.11586300	-3.35207900	-1.97192100
C	3.39805900	-0.50019900	-0.06266700
C	2.65201600	-1.54164500	-0.56375100
C	1.27295900	-1.40654400	-0.75512600
C	0.60308100	-2.47991100	-1.39861600
N	4.15828500	2.67284200	1.17753100
N	-0.77361600	-0.06622200	-0.45416000
O	0.84312400	2.00714200	0.45042200
C	0.61625000	-0.22515500	-0.37488300
C	1.39845200	0.83286800	0.09296300
C	2.77957800	0.70998300	0.25237300
C	3.54101100	1.79323000	0.76339100
C	-2.45151100	1.62523300	-1.12437800
C	-2.82861000	2.96742000	-1.12223600
H	-3.78689500	3.23291100	-1.55440200
C	-2.00852100	3.95961400	-0.61252500
H	-2.32657200	4.99492300	-0.63283900
C	-0.76594100	3.62864700	-0.09810100
H	-0.07953700	4.37106600	0.28946000
C	-0.39821500	2.29996800	-0.07785500
C	-1.22240000	1.28219100	-0.54928300
C	-3.34799300	0.60656000	-1.75209800
H	-4.10529300	1.10181000	-2.36025100
H	-2.77853200	-0.06975700	-2.39260700
H	-3.85743800	-0.00782600	-1.00642900
C	-1.58308200	-0.98771000	0.31928800
C	-1.68264500	-0.85170600	1.71084900
C	-2.48057900	-1.76517900	2.39554700
H	-2.56813500	-1.67200000	3.47290500
C	-3.15262100	-2.78330000	1.73795900
H	-3.76139700	-3.48063500	2.30219000
C	-3.03848900	-2.90814700	0.36298400
H	-3.54971700	-3.70358100	-0.16574700
C	-2.25726100	-2.00590300	-0.33964700
H	-2.15712000	-2.09113000	-1.41221400
C	-0.96682700	0.22176300	2.46878800
H	-1.17340500	0.13387700	3.53531400
H	0.11582800	0.15754900	2.33647400
H	-1.27580900	1.21873000	2.14721600

F	3.25359300	-2.67445200	-0.89217400
F	4.70141200	-0.64303000	0.10767800

Cartesian coordinates of the optimized S_0 geometry of **POA-11** ($\alpha_{\text{ONC}} = 178^\circ$) using PBE0-D3BJ/TZVP.

F	2.69345000	-3.21273400	0.09634800
F	4.63352600	-1.35088500	0.12830000
O	1.44546600	2.03973500	-0.34146100
N	-0.66140700	0.25282000	-0.27470400
N	4.85307900	2.16471900	-0.03090800
N	-0.43354400	-3.69648300	-0.07909400
C	2.37082300	-1.93020800	0.01767200
C	3.36301800	-0.99049900	0.03214900
C	3.02010700	0.36202300	-0.05546200
C	1.68584200	0.72619600	-0.17717400
C	0.64165000	-0.21305600	-0.16866000
C	1.01069500	-1.57206700	-0.08157900
C	4.03017800	1.35908000	-0.04537900
C	0.13031800	-2.69022100	-0.08670000
C	0.16432000	2.50798400	-0.15475300
C	-0.93431400	1.64243200	-0.15392000
C	-2.21651700	2.22197500	-0.05986500
C	-2.29768400	3.61245600	0.07713700
H	-3.28687100	4.04899600	0.15102300
C	-1.19338300	4.43804300	0.10782100
H	-1.30666800	5.50947700	0.21569000
C	0.06264900	3.87218200	-0.01140700
H	0.97244300	4.45927000	-0.01658300
C	-1.71891600	-0.70716900	-0.25854400
C	-2.23006000	-1.14564200	0.96346000
C	-3.25137500	-2.08724200	0.92750100
H	-3.66374300	-2.45215900	1.86187900
C	-3.73581200	-2.57709900	-0.27597100
H	-4.52416400	-3.32093700	-0.27309900
C	-3.21013000	-2.13010300	-1.47956400
H	-3.58216200	-2.51853300	-2.41984200
C	-2.19515600	-1.18946200	-1.46745500
H	-1.75913900	-0.82031000	-2.38882700
C	-3.53778100	1.50035800	-0.10249500
H	-3.64678800	0.86300800	-0.97842700
H	-3.70547800	0.87152000	0.77227000
H	-4.33524100	2.24305300	-0.13013900
C	-1.68570200	-0.62670900	2.25659900
H	-0.63665700	-0.90977500	2.38414800
H	-1.73093400	0.46493700	2.30375000
H	-2.24462800	-1.03074300	3.10047300

Cartesian coordinates of the optimized S_1 geometry of **POA-11** ($\alpha_{\text{ONC}} = 129^\circ$) using TD-PBE0/TZVP.

N	-0.00531500	-3.44513400	-1.85267100
C	3.41188700	-0.67773700	0.02367100
C	2.62158500	-1.68587500	-0.47894500
C	1.21944900	-1.58078500	-0.59971100
C	0.53017700	-2.58705500	-1.28087200
N	4.30706500	2.51316900	1.24346800
N	-0.74418800	-0.04262000	-0.35615800
O	0.96448200	1.93679800	0.50414200
C	0.65666900	-0.32340600	-0.18338800
C	1.46245900	0.66545500	0.27152700

C	2.87584000	0.55831300	0.42235100
C	3.66320300	1.62522500	0.86392900
C	-2.27406400	1.68022800	-1.22442700
C	-2.51429200	3.03325700	-1.32793600
H	-3.42168900	3.36053600	-1.82232800
C	-1.61554900	4.00133800	-0.84945500
H	-1.85555100	5.05220700	-0.95828300
C	-0.43033000	3.62579600	-0.26440000
H	0.28897000	4.33980500	0.11543900
C	-0.14333500	2.27292200	-0.15402300
C	-1.06107500	1.26717500	-0.60775900
C	-3.23941900	0.70734200	-1.82153800
H	-3.94208000	1.23620000	-2.46572900
H	-2.72080100	-0.04296100	-2.42077700
H	-3.80878000	0.17369100	-1.05824500
C	-1.71113700	-0.88303200	0.33033600
C	-2.01283200	-0.61144200	1.67307500
C	-2.94115600	-1.43924600	2.30020000
H	-3.18099500	-1.25144800	3.34158300
C	-3.54718800	-2.49338500	1.63525000
H	-4.26103700	-3.12106800	2.15662500
C	-3.23036000	-2.74615600	0.31046200
H	-3.68495700	-3.57338600	-0.22113100
C	-2.31214400	-1.93882600	-0.33981400
H	-2.05449600	-2.13338600	-1.37037300
C	-1.37152500	0.50257600	2.44373600
H	-1.66306900	0.44858100	3.49265700
H	-0.28152400	0.45339400	2.39974000
H	-1.67553400	1.48554300	2.07275500
F	3.21225800	-2.79720000	-0.90344400
F	4.72347400	-0.86236400	0.08220300

Cartesian coordinates of the optimized S_1 geometry of **POA-11** ($\alpha_{\text{ONC}} = 178^\circ$) using TD-PBE0/TZVP.

F	2.71881700	-3.21775500	-0.04522300
F	4.62906500	-1.40515500	-0.15311400
O	1.47562200	2.05100300	-0.02394800
N	-0.66478200	0.25731800	-0.08132100
N	4.91444100	2.17208700	-0.01849600
N	-0.47567500	-3.61876300	0.63671900
C	2.36685000	-1.93826600	-0.04407400
C	3.37404100	-0.99234500	-0.08811600
C	3.09472200	0.37247100	-0.02717700
C	1.70333100	0.69853300	-0.03308300
C	0.69123200	-0.20726000	-0.01595300
C	0.99960300	-1.61401300	0.03028100
C	4.08983500	1.35536300	-0.02011400
C	0.13143100	-2.66982300	0.35547000
C	0.21094900	2.49181300	0.01071100
C	-0.91319500	1.60866200	-0.10298000
C	-2.19799100	2.21685400	-0.26641100
C	-2.28238200	3.59373400	-0.13738400
H	-3.26122300	4.04807000	-0.23752100
C	-1.17911700	4.42036600	0.07380100
H	-1.31089400	5.49123600	0.16729900
C	0.07642700	3.86399500	0.12667000
H	0.97788200	4.45433900	0.23048600
C	-1.70877900	-0.71071800	-0.21154900
C	-2.50156100	-1.02526800	0.89411100
C	-3.48082300	-1.99488800	0.71419000
H	-4.09673500	-2.27922200	1.56057200

C	-3.65939500	-2.62856600	-0.50729200
H	-4.42183500	-3.39239400	-0.60824800
C	-2.85342500	-2.30599100	-1.58866200
H	-2.98018600	-2.80883200	-2.53996000
C	-1.87060800	-1.34368000	-1.43835900
H	-1.22196500	-1.07336200	-2.26400400
C	-3.48426900	1.50814900	-0.59256700
H	-3.37875500	0.80322800	-1.41552800
H	-3.89088700	0.95204900	0.25310100
H	-4.22260600	2.25587900	-0.88390300
C	-2.26521900	-0.40002400	2.23344200
H	-1.25645100	-0.62343000	2.59220600
H	-2.36685900	0.68886700	2.20787500
H	-2.97320000	-0.78734600	2.96619000

Cartesian coordinates of the optimized S_0 geometry of **POA-02** using PBE0-D3BJ/TZVP.

F	-2.32286000	-3.41795500	-0.00002300
F	-4.44291300	-1.75576500	-0.00032900
O	-1.61252700	1.97166200	0.00060700
N	-5.02002500	1.71228500	-0.00017200
N	0.90774500	-3.51638000	0.00064200
N	0.66696000	0.36078400	0.00010100
C	-2.13141100	-2.10744400	0.00000800
C	-3.21109500	-1.26939400	-0.00011800
C	-3.00495300	0.11529600	-0.00002900
C	-1.71287900	0.62382800	0.00024400
C	-0.58438200	-0.21954800	0.00018700
C	-0.81426700	-1.60807400	0.00020200
C	0.19923900	-2.60633100	0.00040200
C	-4.11577300	0.99906400	-0.00009300
C	-0.36247400	2.54514800	0.00023100
C	0.78613600	1.75968600	0.00009700
C	2.02045000	2.39782800	-0.00013500
H	2.92290400	1.80007200	-0.00022400
C	2.09305000	3.78540400	-0.00020700
H	3.06553200	4.26260800	-0.00036700
C	0.93924900	4.54994700	-0.00009800
H	0.99309500	5.63145700	-0.00016400
C	-0.29983900	3.92077800	0.00014100
H	-1.22715400	4.48065000	0.00025400
C	1.86566900	-0.41639200	-0.00004400
C	2.43959900	-0.75630200	1.22512500
C	3.61626100	-1.49423600	1.20325700
H	4.07504100	-1.78921200	2.14039000
C	4.19487600	-1.86414300	-0.00042200
H	5.10766200	-2.44900100	-0.00056900
C	3.61584900	-1.49428000	-1.20392500
H	4.07431100	-1.78929900	-2.14119800
C	2.43919300	-0.75634000	-1.22540800
C	1.78450900	-0.36060700	2.51109200
H	1.61681300	0.71847600	2.55923500
H	2.40075200	-0.64981400	3.36220100
H	0.81048100	-0.84608300	2.62325900
C	1.78374400	-0.36049700	-2.51114800
H	2.39895500	-0.65111400	-3.36252200
H	1.61762800	0.71881700	-2.55981100
H	0.80890100	-0.84454100	-2.62234000

Cartesian coordinates of the optimized S_1 geometry of **POA-02** using TD-PBE0/TZVP.

F	-2.30159000	-3.42869700	-0.25772200
F	-4.39334300	-1.84247800	-0.02834500
O	-1.63371600	1.94535400	0.10624200
N	-5.06492100	1.67187500	0.22341800
N	1.01112600	-3.45683800	-0.55293100
N	0.68080700	0.37378700	-0.08531200
C	-2.08845100	-2.12393400	-0.14991700
C	-3.18906100	-1.29511200	-0.03184600
C	-3.05977900	0.09238100	0.04286900
C	-1.71002100	0.56750400	0.05398000
C	-0.61131500	-0.22729800	-0.06944000
C	-0.76256500	-1.65273300	-0.15597300
C	0.25349500	-2.59579200	-0.37122000
C	-4.15577600	0.95430400	0.14180300
C	-0.43246900	2.51301300	-0.03808400
C	0.75905100	1.73628800	-0.11049700
C	1.98639200	2.42169300	-0.17200900
H	2.90227000	1.84688400	-0.19764000
C	2.01695000	3.79581400	-0.19782500
H	2.97195100	4.30433800	-0.25127200
C	0.83099900	4.54261200	-0.15243900
H	0.86875400	5.62477100	-0.17384400
C	-0.38546300	3.89955900	-0.06638000
H	-1.32164900	4.44081600	-0.00882200
C	1.88695100	-0.38356700	0.09603600
C	2.25005000	-0.74723900	1.39580400
C	3.43476200	-1.45673900	1.55649800
H	3.73380200	-1.76505100	2.55240500
C	4.22769900	-1.77017900	0.46528900
H	5.14513300	-2.32973500	0.60886300
C	3.85207700	-1.37934900	-0.80973200
H	4.46974300	-1.64087600	-1.66175700
C	2.67212100	-0.67767700	-1.02187800
C	1.39013300	-0.40117000	2.57280100
H	1.19434900	0.67316400	2.62977400
H	1.87520600	-0.70283400	3.50109400
H	0.42138600	-0.90589400	2.52200100
C	2.22625400	-0.32383600	-2.40684300
H	3.01894400	-0.52866800	-3.12659700
H	1.94783600	0.72878100	-2.49955800
H	1.35511800	-0.92097400	-2.69218900

Cartesian coordinates of the optimized S_0 geometry of **POA-12** using PBE0-D3BJ/TZVP.

F	2.73299800	-3.21887400	0.00070900
F	4.69321400	-1.37532900	0.00068600
O	1.52937400	2.06519800	-0.00166400
N	-0.39940500	-3.66773900	-0.00009200
N	4.94322900	2.13894100	-0.00015200
N	-0.59953700	0.28043400	-0.00123900
C	2.42181500	-1.93104000	0.00026500
C	3.42275900	-1.00164700	0.00024700
C	3.09024100	0.35683700	-0.00023800
C	1.75545100	0.73997500	-0.00080600
C	0.70324100	-0.19126400	-0.00071300
C	1.06217200	-1.55560700	-0.00015700
C	0.16906000	-2.66382700	-0.00012200

C	4.11127200	1.34244800	-0.00020500
C	0.23728100	2.53708400	-0.00054500
C	-0.86397000	1.67464500	-0.00060100
C	-2.14703900	2.26085400	-0.00025000
C	-2.23028800	3.65785500	0.00065200
H	-3.22027800	4.09863200	0.00097500
C	-1.12539700	4.48304800	0.00100600
H	-1.23894600	5.55985300	0.00170600
C	0.13221700	3.90897000	0.00037100
H	1.04355200	4.49373800	0.00042300
C	-3.46800800	1.53703900	-0.00094800
H	-3.60624300	0.90348300	-0.87651800
H	-4.26684200	2.27875700	-0.00101800
H	-3.60694600	0.90285800	0.87406900
C	-1.66252600	-0.67340000	-0.00024300
C	-2.15571800	-1.12309700	-1.22450400
C	-3.18463900	-2.05515800	-1.20268800
H	-3.58319200	-2.42903400	-2.13917800
C	-3.69128400	-2.51748900	0.00161000
H	-4.48679800	-3.25388200	0.00234200
C	-3.18366700	-2.05381600	1.20497800
H	-3.58147600	-2.42662300	2.14221300
C	-2.15474000	-1.12170500	1.22492600
C	-1.58384600	-0.61411100	-2.51013600
H	-1.64041700	0.47641400	-2.57058600
H	-2.11801000	-1.03328000	-3.36262900
H	-0.52884400	-0.88594600	-2.60867100
C	-1.58196800	-0.61116800	2.50954600
H	-0.52679400	-0.88253300	2.60752400
H	-2.11530000	-1.02960600	3.36291900
H	-1.63888600	0.47940200	2.56888400

Cartesian coordinates of the optimized S_1 geometry of **POA-12** using TD-PBE0/TZVP.

F	2.68606800	-3.25598400	-0.17313200
F	4.64148500	-1.50192100	-0.00687600
O	1.57632400	2.03140600	0.07899800
N	-0.52653000	-3.63980300	-0.44417800
N	5.01115800	2.06917100	0.14609900
N	-0.61280500	0.30314000	-0.03271300
C	2.36503900	-1.97072300	-0.10171900
C	3.39649300	-1.05499400	-0.01545700
C	3.15036800	0.31651300	0.02419800
C	1.76594800	0.67307900	0.04070000
C	0.72931000	-0.20103800	-0.05254100
C	1.00245000	-1.61467400	-0.10897500
C	0.09783100	-2.67264800	-0.29080800
C	4.16715300	1.27377700	0.09167300
C	0.33162400	2.51240500	-0.02955800
C	-0.82337300	1.66181700	-0.04058300
C	-2.10129600	2.30831700	-0.02891300
C	-2.12782500	3.69192300	-0.09553300
H	-3.09797000	4.17471500	-0.10037200
C	-0.98467300	4.49000900	-0.13887600
H	-1.07444700	5.56793700	-0.19229400
C	0.25112900	3.89269000	-0.09662600
H	1.17715500	4.45339000	-0.09540000
C	-3.44514700	1.63522500	0.04634900
H	-3.68317700	1.06884400	-0.85428600
H	-4.20818400	2.40512000	0.16440500
H	-3.53182700	0.94699300	0.88585900

C	-1.69571600	-0.63109600	0.07191000
C	-2.34550500	-1.03839800	-1.09459400
C	-3.38870200	-1.94532800	-0.96455200
H	-3.89952400	-2.29443900	-1.85510200
C	-3.75886200	-2.42722300	0.28048500
H	-4.56623600	-3.14623800	0.36114400
C	-3.09320300	-2.00980000	1.42150900
H	-3.38249600	-2.39819500	2.39193500
C	-2.04493000	-1.10121300	1.34063300
C	-1.90178000	-0.55972100	-2.44233300
H	-1.86423000	0.53136900	-2.50472700
H	-2.57778600	-0.92038700	-3.21775200
H	-0.89966500	-0.93197700	-2.67483000
C	-1.32262000	-0.63896600	2.56913300
H	-0.26329400	-0.90747600	2.53560600
H	-1.75486600	-1.09442000	3.46009500
H	-1.37705300	0.44751400	2.68623900

Cartesian coordinates of the optimized S_0 geometry of **In-POA** using PBE0-D3BJ/TZVP.

F	-3.16932500	-2.84541400	0.30366200
F	-4.71354800	-0.69162300	-0.18619600
O	-0.96732000	2.11140200	-0.19967800
N	-0.03826700	-3.60661700	1.17447900
N	-4.30578300	2.77648800	-0.48552700
N	0.77158800	-0.08170000	-0.10721200
C	-1.21413400	-1.53818900	0.20751600
C	-2.61066600	-1.65995200	0.12123600
C	-3.40047800	-0.56400400	-0.10441600
C	-2.81351500	0.70154900	-0.20482100
C	-1.42948600	0.83638600	-0.14940900
C	-0.59490700	-0.30264000	-0.04390400
C	-0.52676200	-2.67425900	0.70514500
C	-3.63364100	1.85007900	-0.35949000
C	0.36369500	2.31181700	0.09028400
C	1.19535900	1.22208400	0.11659200
C	2.57410900	1.30477200	0.23862700
C	3.13599100	2.56875200	0.43670100
H	4.20661800	2.69632800	0.53900900
C	2.29342800	3.66891000	0.46848700
H	2.71607200	4.65527300	0.61727200
C	0.90581600	3.56175900	0.28693100
H	0.27121100	4.43866500	0.26840600
C	1.92742600	-0.87037200	-0.24290000
C	3.05208100	-0.04376700	0.01084600
C	4.33293300	-0.57162800	-0.08608700
H	5.19622500	0.05358000	0.11058300
C	4.48838800	-1.89495400	-0.45997100
H	5.48145000	-2.32056700	-0.54050400
C	3.37649800	-2.67704800	-0.76884300
H	3.51598000	-3.70049000	-1.09598200
C	2.08673500	-2.17843400	-0.67606900
H	1.25089200	-2.80303800	-0.94946100

Cartesian coordinates of the optimized S_1 geometry of **In-POA** using TD-PBE0/TZVP.

F	-3.19518200	-2.84011600	0.22007600
F	-4.69772300	-0.70864600	-0.22238900

O	-0.95303900	2.10594100	-0.16738000
N	-0.04645700	-3.64285500	1.21932900
N	-4.28971800	2.82975700	-0.43744400
N	0.79836100	-0.08703500	-0.01958700
C	-1.19773500	-1.60041400	0.18889500
C	-2.59764100	-1.66689000	0.06723300
C	-3.38674900	-0.55342000	-0.13706400
C	-2.83967500	0.73296200	-0.20708800
C	-1.41725400	0.80091200	-0.13707200
C	-0.61296700	-0.30529100	-0.03771600
C	-0.53962500	-2.69883700	0.75640400
C	-3.63211900	1.88104600	-0.32689100
C	0.34111000	2.29403900	0.11501600
C	1.19655500	1.20070700	0.18141400
C	2.58757600	1.31321600	0.23808000
C	3.12844600	2.58040500	0.39396900
H	4.19890500	2.73375100	0.45815500
C	2.26178100	3.68768400	0.42178800
H	2.68504000	4.67779000	0.54137800
C	0.88867100	3.56703900	0.26715500
H	0.24113400	4.43367500	0.23140700
C	1.93603500	-0.85702100	-0.22142700
C	3.07421900	-0.02757300	-0.00163300
C	4.34843700	-0.55761900	-0.12087300
H	5.22123700	0.06095200	0.05403200
C	4.48856100	-1.88861000	-0.48687200
H	5.47867700	-2.31740700	-0.58594700
C	3.36697400	-2.67511900	-0.75956500
H	3.50024300	-3.70186200	-1.07860800
C	2.08292900	-2.17660500	-0.64553900
H	1.23473000	-2.79831000	-0.88592800

7 CYCLIC VOLTAMMETRY

To investigate the electrochemical response of representative compounds **POA-00**, **POA-10**, and **In-POA**, cyclic voltammetry (CV) measurements were carried out using an *Autolab PGSTAT204* potentiostat. A three-electrode arrangement with a glassy carbon (3 mm diameter) working electrode, a Pt sheet counter electrode, and an Ag/AgCl (3 M KCl) reference electrode was used. Before recording CVs, the GC was properly polished with alumina slurry and rinsed with acetone and Milli-Q water. The used electrolyte was 0.5 mM of the compound dissolved in 0.1 M *n*-Bu₄NPF₆ in acetonitrile. The solution was purged with Ar for at least 15 minutes before measurement. The CVs were recorded with 100 mV s⁻¹ in the proper potential window.

For the estimation of E_{HOMO} from CV, the measured oxidation potential was converted to the vacuum energy scale and Koopmans' approximation was applied as follows:

$$E_{\text{HOMO}}(\text{eV}) = E_f(\text{V vs ref.}) + E_{\text{ref}}^{\text{abs}}$$

Where, E_f is the formal potential of the redox couple and $E_{\text{ref}}^{\text{abs}}$ is the absolute potential of the reference electrode (here 4.44 eV for standard hydrogen electrode SHE was used and conversion from Ag/AgCl to SHE was considered).²⁸

The CVs of the three compounds (Figure S51) show a reversible redox peak between 0.8–1.1 V vs Fc/Fc⁺ as well as a second irreversible oxidation peak at 1.5–1.7 V. A shift in oxidation potentials can be observed. The formal redox potential of the reversible first peak was found to be 0.803, 0.934 and 0.999 V vs Fc/Fc⁺ for **POA-00**, **POA-10**, and **In-POA**, respectively. Using Koopmans' approximation, electrochemical E_{HOMO} values of –5.87, –6.01, and –6.07 eV are obtained for **POA-00**, **POA-10**, and **In-POA**, respectively. A deviation of 0.1–0.3 eV between computed and electrochemical values is common as Koopmans' approximation neglects solvation, entropy and structural relaxation effects. Nevertheless, both electrochemical E_{HOMO} and computed E_{HOMO} trends indicate that **POA-00** has the lowest energy for oxidation, while **POA-10** and **In-POA** differ only slightly ($\Delta = 0.06$ eV in electrochemical E_{HOMO}).

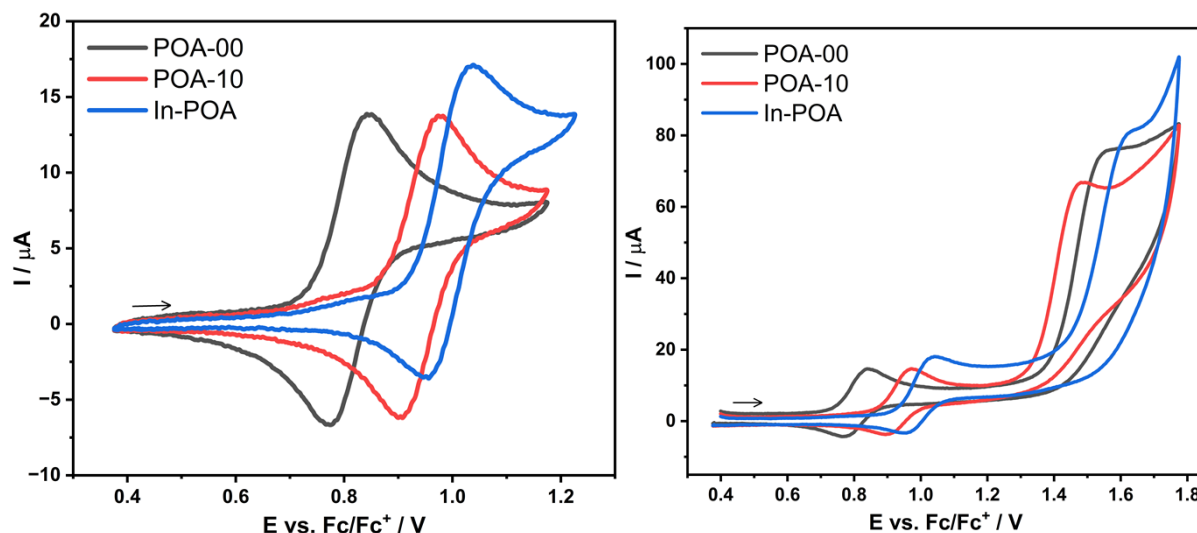


Figure S51: CVs of 0.5 mM compound in 0.1 M *n*-Bu₄NPF₆/MeCN recorded at GC electrode with 100 mV s⁻¹ in a narrow potential range (left panel) and larger potential window (right panel). The potential was normalized against the Fc/Fc⁺ redox couple.

8 LITERATURE

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