Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Substituted Benzophenone Imines for COF Synthesis via Transimination

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S1. Materials and Methods

Reactions were performed using reagent grade chemicals, purchased from various suppliers (ABCR, BLDpharm, fluorochem, Sigma-Aldrich, and TCI) and used without further purification, unless otherwise specified. Solvents utilized for synthesis were dried using a Pure Solv Micro Solvent Purification System (Innovative Technology) and stored over molecular sieves 3–4 Å. All non-aqueous reactions were performed in oven-dried glassware and under an Ar atmosphere. Automated Medium Pressure Column Chromatography (MPLC) was performed on a Teledyne ISCO CombiFlash Rf+ system, equipped with a 200–800 nm UV/Vis variable wavelength detector. Thin layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2-60 F254 (Merck); visualized with a UV lamp (254 or 366 nm). Evaporation in vacuo was performed at 40–60 °C and 700–10 mbar. All products were dried under vacuum (ca. 1 mbar) before analytical characterization. Reported yields refer to spectroscopically and chromatographically pure compounds, unless otherwise specified.

Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance II 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) and a Bruker Avance II 500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) at 298 K and are reported as follows: chemical shift (δ) in ppm (multiplicity, coupling constant *J* in Hz, number of protons; assignment). The residual deuterated solvent was used as the internal reference ($CDCl_3$: δ_H = 7.26 ppm, CD_2Cl_2: δ_H = 5.32 ppm, CD_3OD: δ_H = 3.31 ppm, $(CD_3)_2SO$: δ_H = 2.50 ppm; $CDCl_3$: δ_C = 77.16 ppm, CD_2Cl_2: δ_C = 54.00 ppm, CD_3OD: δ_C = 49.00 ppm, $(CD_3)_2SO$: δ_C = 39.52 ppm; The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept. (septet), m (multiplet), and br. (broad).

Infrared (IR) spectra were recorded on a Vertex 70v spectrometer by Bruker equipped with a diamond ATR attachment and are baseline-corrected. The spectra were measured between 4000 and 400 cm^{-1}. Absorption bands are reported in wavenumbers (cm^{-1}) and their relative intensities described as s (strong), m (medium), or w (weak).

Ultraviolet–visible (UV–vis) absorbance spectroscopy was performed on Agilent Cary 50 and Cary 60 instruments equipped with a temperature control sample chamber in 10 × 10 mm quartz cuvettes with 3 mL volume. Weighing of small quantities was performed on a Sartorius ME5 analytical microbalance.

High resolution mass spectra (HRMS) were recorded using a LTQ-FT-ICR-MS with a 7 T magnet and resolution of 100,000 from Thermo Fisher Scientific.

Supercritical CO_2 drying of COFs was performed using a samdri-PVT-3B supercritical point dryer. COFs were placed into teabags (drawstring teabag, Amazon) while wet, the teabags were sealed with a staple and stored in MeOH for at least 18 h before drying. The tea bags containing the material were placed in the drying chamber and the chamber was topped up with absolute EtOH. The apparatus was cooled by opening the “cool” valve and the chamber was filled with liquid CO_2 by opening the “fill” valve.

By opening the “purge” valve the chamber was flushed to replace the EtOH with CO_2. The “fill” valve was opened and closed at least five times consecutively. The “purge” valve was then closed and the pressure was allowed to rise to 58–62 bar. Next, the “fill” valve was closed and the heating was switched on. The temperature and pressure were allowed to rise above the critical point but also below 100 bar by venting using the “purge” valve. The chamber was held above the critical point of CO_2 (T_c = 31 °C, p_c = 73.8 bar) for 30 min. By opening the “purge” valve, the pressure was released as slowly as possible. The dried COF material was collected from the tea bags. 1–4 COF-containing teabags were dried in the chamber simultaneously.

Powder X-Ray Diffraction (PXRD) measurements were conducted using the MOUSE (Methodology Optimization for Ultrafine Structure Exploration) at the Bundesanstalt für Materialforschung und -prüfung (BAM).[1] X-rays were generated from a microfocus X-ray tube, followed by multilayer optics to parallelize and monochromatize the X-ray beams to wavelengths of Cu Kα (λ = 0.154 Å). Scattered radiation was detected on an *in-vacuum* Eiger 1M detector (Dectris, Switzerland), which was placed at multiple distances between 55–2307 mm from the sample. The resulting data has been processed using the DAWN software package in a standardized complete 2D correction pipeline with uncertainty propagation.[2,3] The experimental patterns were fitted using Pawley refinement to computational COF models constructed using Materials Studio program package.[4]

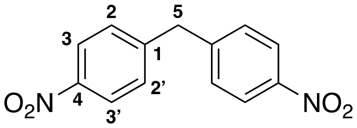
Nitrogen sorption isotherms were collected using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosity Analyzer and a Quantachrome Instruments Autosorb 1C surface area analyzer. 10–40 mg samples were transferred to dried and tared analysis tubes equipped with filler rods and capped with a seal frit. The samples were heated to 40 °C at a rate of 1 °C min^{-1} and evacuated at 40 °C for 60 min, then heated to 120 °C at a rate of 1 °C min^{-1} and evacuated at 100 °C for 10 h. The tube was weighed again to determine the mass of the activated sample and transferred to the analysis port of the instrument. N_2 gas (99.999% purity) was used for all adsorption measurements. N_2 isotherms were measured from a relative pressure p/p_0 of 0.01 to 1 in a liquid nitrogen (77 K) bath. Brunauer–Emmett–Teller (BET) surface areas were calculated from the N_2 isotherm at 77 K within the pressure range p/p_0 of 0.05–0.07.

Pore size distributions were evaluated using NL-DFT employing the SAIEUS program by Micromeritics. N_2-adsorption isotherms with data points down to 10^{-6} p/p_0 were used.

Structural Models of the COF were constructed using the Accelrys Materials Studio software package. *P*6/m symmetry was applied. The structure models were optimized using the Forcite module of Materials Studio performing an “ultra-fine” optimization using Universal force field and “Smart” algorithm including optimizing the cell. Structural refinements were carried out using the Reflex module with a Pawley-refinement.

S2. Experimental Procedures

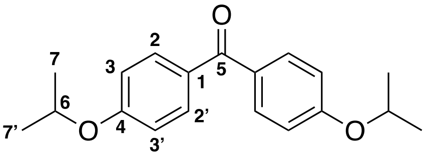
4,4'-Dinitrodiphenylmethane (S1)[5]



Adapted with changes from procedures reported in the literature[5] diphenylmethane (20.0 g, 119 mmol) was added to a mixture of concentrated sulfuric acid (68 mL) and concentrated nitric acid (76 mL) at -40 °C. The mixture was allowed to warm to room temperature and stirred for 6 h then poured into ice water (100 mL). The resulting solid was collected by filtration and washed with water. The crude solid was dissolved in CH_2Cl_2, filtered to remove insoluble impurities and recrystallized from toluene to yield **S1** (7.60 g, 29.4 mmol, 25%) as pale-yellow solid.

***R*f** = 0.70 (SiO_2; 100% CH_2Cl_2); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 8.18 (d, *J* = 8.8 Hz, 4H, 2x 2HC(3,3')), 7.34 (d, *J* = 8.9 Hz, 4H, 2x 2HC(2,2')), 4.19 (s, 2H, HC(5)); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 147.1, 146.8, 129.9, 124.2, 41.5; **IR (ATR)**: $\tilde{\nu}_{max}$ = 3111 (s), 3082 (s), 2943 (s), 2840 (s), 2450 (s), 2360 (m), 1736 (m), 1604 (m), 1505 (m), 1336 (m), 1108 (s), 884 (m), 818 (m), 742 (s), 706 (m), 509 (m).

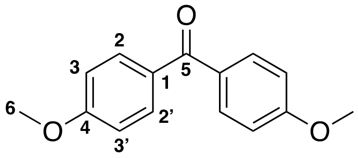
Bis(4-isopropoxyphenyl)methanone (1b)



Based on a procedure reported in the literature, a solution of bis(4-hydroxyphenyl)ketone (3.00 g, 14.0 mmol) in DMF (21 mL) was treated with potassium carbonate (7.73 g, 55.9 mmol) while stirring vigorously for 5 min. The mixture was treated with 2-iodopropane (4.2 mL, 42.0 mmol) and stirred for 64 h. The reaction mixture was diluted with water (10 mL) and the mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were concentrated under reduced pressure and washed with water (2 x 15 mL), dried over $MgSO_4$, and evaporated. The crude product (4.04 g) was loaded onto silica and purified by an automated MPLC (SiO_2; gradient hexane/EtOAc 1:0 → 3:2) to yield **1b** (3.69 g, 12.4 mmol, 88%) as a colorless solid.

***R*f** = 0.4 (SiO_2; hexane/EtOAC 9:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.82–7.73 (m, 4H, 2x 2H-C(2,2')), 6.98–6.89 (m, 4H, 2x 2HC(3,3')), 4.66 (quint. , *J* = 6.1 Hz, 2H, 2x HC(6)), 1.38 ppm (dd, *J* = 6.1, 0.7 Hz, 12H, 2x H_3C(7,7')); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 194.6, 161.4, 132.4, 115.0, 70.2, 22.1 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 1598 (s), 1242 (m), 1164 (m), 1152 (w), 1121 (m), 1108 (w), 928 (m), 846 (s), 770 (s), 617 cm^{-1} (m).

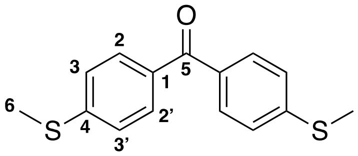
Bis(4-(hydroxymethyl)phenyl)methanone (1c)



A solution of bis(4-hydroxyphenyl)methanone (5.00 g, 23.2 mmol) in dry THF (150 mL) was treated with portions of NaH (60% w/v dispersion in mineral oil, 2.0 g, 49.0 mmol) at 0 °C. The reaction mixture was stirred at 0 °C until no gas formation was observed anymore. MeI (10.2 g, 72.0 mmol) was added, the reaction was allowed to warm up to room temperature, and it was stirred for 3 d in total. The reaction was diluted with aq. NaOH (1 M, 100 mL) and extracted with EtOAc (3 x 75 mL). The organic phase was dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by automated MPLC (SiO_2; gradient hexane/EtOAc 1:0 → 3:2) to yield **1c** (2.33 g, 9.62 mmol, 41%) as a colorless solid.

R_f = 0.3 (SiO_2; hexane/EtOAc 9:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.84–7.73 (m, 4H, 2x 2H-C(2,2')), 7.01–6.91 (m, 4H, 2x 2HC(3,3')), 3.89 ppm (s, 6H, 2x $H_3C(6)$). **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C): δ = 194.6, 1623.0, 132.4, 130.9, 113.6, 55.6 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 3672 (s), 3328 (w), 2951 (m), 2868 (s), 1706 (s), 1651 (s), 1257 (s), 1090 (s), 877 (s), 767 (s), 651 cm^{-1} (s).

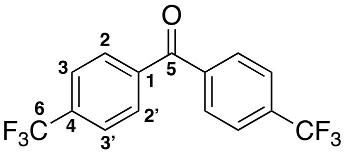
Bis(4-(thiomethyl)phenyl)methanone (1f)[6]



Based on a procedure reported in the literature,[6] a solution of 4-bromothioanisol (5.01 g, 24.7 mmol) in diethyl ether (50 mL) was treated dropwise with *n*-butyllithium (11.0 mL, 24.6 mmol, 2.2 M in hexane) at –30 °C over 5 min. More *n*-butyllithium (6.0 mL, 13.2 mmol) was added dropwise after 1.5 h. The reaction mixture was stirred for 1 h at –30 °C and treated dropwise with dimethyl carbamic chloride (1.1 mL, 12.3 mmol) over 5 min, the reaction mixture was allowed to warm to 25 °C, and diluted with sat. aq. NH_4Cl (30 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated. The crude product (4.11 g) was loaded onto silica and purified by automated MPLC (SiO_2; gradient hexane/EtOAc 1:0 → 3:2) to yield **1f** (1.10 g, 4.0 mmol, 16%) as a colorless solid.

R_f = 0.29 (SiO_2; hexane/EtOAc 9:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.73–7.70 (m, 4H, 2x 2H-C(2,2')), 7.26 ppm (m, 4H, 2x 2HC(3,3')), 2.54 ppm (s, 6H, 2x $H_3C(6)$); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 195.0, 145.1, 134.0, 130.6, 125.0, 15.0 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 2889 (m), 2361 (m), 1581 (m), 1520 (m), 1359 (m), 1186 (m), 1139 (m), 824 (m), 676 (m), 485 cm^{-1} (m); **ESI(+)-MS**: *m*/*z*: $[M + H]^+$ calcd. for $C_{15}H_{15}S_2O^+$, 275.0559; found, 274.9946.

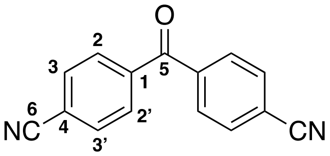
Bis(4-(trifluoromethyl)phenyl)methanone (1j)[7]



Based on a procedure reported in the literature,[7] a solution of oxalyl chloride (5.0 mL, 58.0 mmol) in CH_2Cl_2 (150 mL) was cooled to –78 °C and treated with a solution of DMSO (7.6 mL, 107 mmol) in CH_2Cl_2 (50 mL). After 15 min of stirring the reaction mixture was treated dropwise with a solution of bis(4-(trifluoromethyl)phenyl)methanol (11.46 g, 35.8 mmol) in CH_2Cl_2 (20 mL) over 5 min and subsequently triethylamine (46.6 mL, 322 mmol) over 20 min. After another 15 min of stirring the reaction mixture was allowed to warm up to room temperature and subsequently diluted with sat. aq. NH_4Cl (60 mL). The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography (SiO_2; hexane/EtOAc; gradient 1:0 → 3:2) to afford **1j** (9.97 g, 31.3 mmol, 88%) as a colorless solid.

$\boldsymbol{R_f}$ = 0.30 (SiO_2; hexane); **^{1}H NMR** (300 MHz, CD_2Cl_2, 25 °C): δ = 7.93–7.89 (m, 4H, 2x 2HC(3,3')), 7.80–7.77 ppm (m, 4H, 2x 2HC(2,2')); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 194.5, 139.9, 134.5 (q, J = 32.9 Hz), 130.4, 125.8 (q, J = 3.8 Hz), 123.7 ppm (q, J = 272 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$, 25 °C): δ = –63.1 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 1654 (m), 1323 (m), 1312 (w), 1129 (s), 1114 (s), 1107 (s), 1065 (s), 1016 (s), 931 (m), 865 (s), 694 (s), 665 cm^{-1} (m).

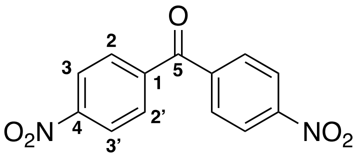
4,4'-Carbonyldibenzonitrile (1k)[6]



Based on a procedure reported in the literature,[6] a solution of 4-bromobenzonitrile (5.04 g, 27.7 mmol) in THF (165 mL) was treated dropwise with n-butyllithium (12.0 mL, 27.7 mmol, 2.3 m in hexane) at –85 °C (acetone/LN2 cooling bath) over 5 min. The mixture was stirred for 15 min and treated dropwise with dimethyl carbamic chloride (1.3 mL, 13.9 mmol) over 5 min. After 15 min of stirring the cooling bath was removed and the reaction mixture was allowed to warm up to 0 °C. The reaction mixture was diluted with sat. aq. NH_4Cl (30 mL), the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and evaporated. The crude product (4.12 g) was loaded onto silica and purified by an automated MPLC (SiO_2; gradient hexane/EtOAc 1:0 → 3:2) to yield **1k** (1.34 g, 5.8 mmol, 21%) as a yellow solid.

$\boldsymbol{R_f}$ = 0.76 (SiO_2; hexane/EtOAc 9:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.89–7.85 (m, 4H, 2x 2H-C(3,3')), 7.84–7.81 ppm (m, 4H, 2x 2HC(2,2')); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 193.6, 139. 9, 132.6, 130.4, 117.8, 116.7 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 2227 (m), 1665 (s), 1305 (m), 1274 (s), 928 (m), 869 (m), 849 (w), 762 (s), 728 (w), 674 (s), 556 cm^{-1} (m); **ESI(+)-HR-MS**: *m*/*z*: [*M* + H]$^+$ calcd. for $C_{15}H_9N_2O^+$, 233.0709; found, 233.2421.

Bis(4-(nitro)phenyl)methanone (1l)[5]



To a suspension of **S1** (5.70 g, 22.0 mmol) in acetic acid (85 mL) was added a solution of CrO_3 (9.24 g, 92.4 mmol) in water (56 mL). The solution was heated to reflux for 24 h and then poured into ice water. The resulting precipitate was filtered and washed subsequently with water, sat. $NaHCO_3$ and water. Drying under vacuum afforded **1l** (5.74 g, 21.1 mmol, 96%) as a pale-yellow solid.

***R*$_\mathbf{f}$** = 0.57 (SiO_2; 100% CH_2Cl_2); **^{1}H NMR** (300 MHz, CD_2Cl_2, 25 °C): δ = 8.37 (d, *J* = 8.8 Hz, 4H, 2x 2HC(3,3')), 7.96 (d, *J* = 8.8 Hz, 4H, 2x 2HC(2,2')); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 139.1, 150.5, 141.4, 131.0, 124.1; **IR (ATR)**: $\tilde{\nu}_{max}$ = 3111 (s), 2798 (s), 2360 (s), 1604 (m), 1578 (m), 1518 (m), 1324 (m), 1227 (s), 935 (s), 822 (m).

Synthesis of Benzophenone Imines

General Preparation Procedure

Based on a procedure reported in the literature,[8] benzidine (0.364 g, 1.98 mmol, 1.0 equiv.), 1,4-diazobicyclo[2.2.2]octane (DABCO) (1.33 g, 11.9 mmol, 6.0 equiv.) and benzophenone (4.15 mmol, 2.1 equiv.) were suspended in chlorobenzene (80 mL) in an oven-dried three-necked flask equipped with a dropping funnel and reflux condenser under a nitrogen atmosphere. The suspension was purged with nitrogen for 10 min and then treated dropwise with a solution of $TiCl_4$ (0.33 mL, 2.97 mmol, 1.5 equiv.) in chlorobenzene (20 mL) over 15–20 min. A wash bottle with NaOH was installed. The reaction mixture was heated to 120 °C and stirred until completion of the reaction. From here on three different procedures were used to purify the crude product.

Work up procedure 1 (WUP 1)

To the reaction mixture sat. aq. $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and filtered through a short silica plug. The crude product was then further purified by recrystallization (chlorobenzene, chloroform or chloroform/ethanol mixtures).

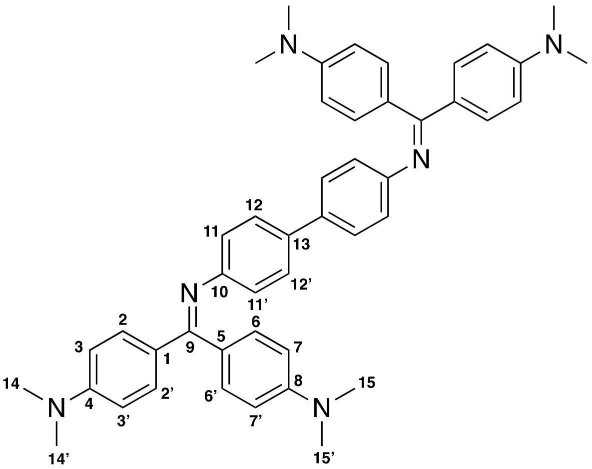
Work up procedure 2 (WUP2)

The reaction mixture was filtered through a short silica plug with CH_2Cl_2. The remaining solid and silica were suspended in CH_2Cl_2 with MeOH and filtered. The filtrates were combined, the solvents were removed under reduced pressure, and the crude product was purified by recrystallization (chlorobenzene, chloroform or chloroform/ethanol mixtures).

Work up procedure 3 (WUP3)

A hot filtration of the reaction mixture was performed to remove any TiO_2 and the solvent of the filtrate was removed under reduced pressure. The crude was dissolved in hot $CHCl_3$. If the solution remained cloudy, a hot filtration was performed. The filtrate was then slowly dripped into EtOH or EtOAc depending on the solubility of the respective starting material. The precipitate was filtered and washed with more EtOH or EtOAc. If the resulting product did not show the desired purity, a recrystallization from chlorobenzene was performed.

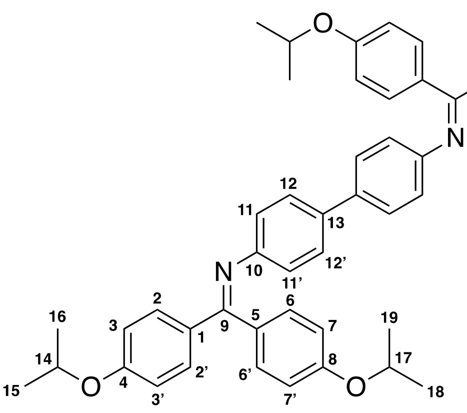
***N*,*N*‘-Bis(4,4‘-di(*N”,N’”*-dimethylamino-benzophenone)benzidine imine (2a)**



Following the general procedure, a solution of BND (0.36 g, 2.0 mmol) in chlorobenzene (77 mL) was treated with 4,4’dimethylamino-benzophenone (1.11 g, 4.2 mmol) and DABCO (1.33 g, 11.9 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (327 µL, 3.0 mmol) in chlorobenzene (20 mL) over 20 min. The reaction mixture was heated to 125 °C and stirred for 5 h. The reaction mixture was worked up according to WUP3 to yield **2a** (0.64 g, 0.9 mmol, 48%) as a yellow solid.

***R*f** = 0.1 (SiO_2; cHex/EtOAc 1:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.65 (d, *J* = 9.0 Hz, 4H), 7.40–7.34 (m, 4H), 7.06–7.01 (m, 4H), 6.78 (d, *J* = 8.5 Hz, 4H), 6.68 (d, *J* = 9.1 Hz, 4H), 6.53 (d, *J* = 8.9 Hz, 4H), 3.02 (s, 12H), 2.94 ppm (s, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$, 25 °C): δ = 168.2, 152.1, 151.5, 150.2, 134.7, 131.8, 131.3, 129.9, 128.8, 126.6, 122.2, 111.3, 111.0, 40.4, 40.3 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 1578 (m), 1523 (m), 1479 (m), 1355 (m), 1229 (s), 1137 (m), 942 (s), 821 (s) cm^{-1}; **ESI(+)-HR-MS**: *m*/*z*: [*M* + H]$^{+}$ calcd. for $C_{46}H_{49}N_6^{+}$, 685.4013; found, 685.4016.

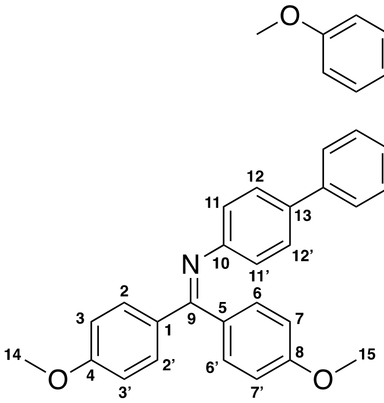
N,N‘-Bis(4,4‘-diisopropoxy-benzophenone)benzidine imine (2b)



Following the general procedure, a solution of BND (0.75 g, 4.1 mmol) in chlorobenzene (200 mL) was treated with **1b** (2.98 g, 10.0 mmol) and DABCO (2.74 g, 24.4 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (700 µL, 6.1 mmol) in chlorobenzene (15 mL). The reaction mixture was heated to 125 °C and stirred overnight. A hot filtration was performed, the solid was washed with CH_2CL_2 and the solvent of the filtrate was removed under reduced pressure. The solid was suspended in EtOH, filtrated, washed with EtOH and dried under reduced pressure to give **2b** (2.44 g, 3.3 mmol, 81%) as a yellow-brown solid.

R_f = 0.16 (SiO_2; hexane/EtOAC 9:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.68 (d, *J* = 8.8 Hz, 4H), 7.41–7.30 (m, 4H), 7.11–6.98 (m, 4H), 6.91–6.83 (m, 4H), 6.78–6.63 (m, 8H), 4.62 (p, *J* = 32.9, 6.0 Hz, 2H), 4.52 (p, *J* = 6.0 Hz, 2H), 1.36 (d, *J* = 6.0 Hz, 12H), 1.31 ppm (d, *J* = 6.0 Hz, 12H); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 167.5, 160.2, 158.1, 150.7, 135.2, 132.8, 131.6, 131.3, 128.4, 126.7, 121.9, 115.2, 115.0, 70.0, 69.9, 22.2, 22.1 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 1598 (m), 1242 (m), 1166 (w), 1137 (w), 1120 (s), 1106 (w), 951 (w), 928 (w), 844 (s), 771 cm^{-1} (m); **ESI(+)-HR-MS**: *m*/*z*: [M + H]$^+$ calcd. for $C_{50}H_{53}N_2O_4^+$, 745.4000; found, 745.4001.

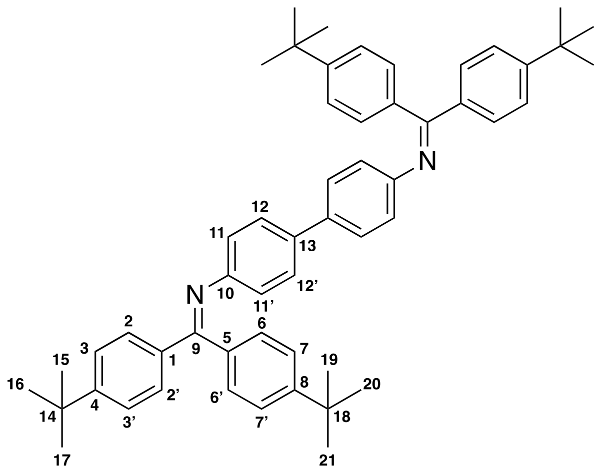
N,N‘-Bis(4,4‘-dihydroxymethyl-benzophenone)benzidine imine (2c)



Following the general procedure, a solution of BND (0.50 g, 2.7 mmol) in chlorobenzene (30 mL) was treated with bis(4-hydroxymethylbenzophenone) (1.45 g, 5.97 mmol) and DABCO (1.84 g, 16.4 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (450 µL, 4.1 mmol) in chlorobenzene (15 mL) over 15 min. The reaction mixture was heated to 125 °C and stirred for 16 h. The reaction mixture was worked up according to WUP1. The crude product was recrystallized from chloroform/EtOH 1:3 to yield **2c** (0.7 g, 1.1 mmol, 41%) as a yellow solid.

R_f = 0.2 (SiO_2; cHex/EtOAc 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.67 (d, J = 8.6 Hz, 4H), 7.30 (d, J = 8.5 Hz, 4H), 7.04 (d, J = 8.6 Hz, 4H), 6.86 (d, J = 8.8 Hz, 4H), 6.78 (s, 4H), 6.72 (d, J = 8.7 Hz, 4H), 3.80 (s, 6H), 3.72 (s, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$, 25 °C): δ = 132.0 (broad), 126.9, 122.5 (broad), 113.7, 113.6, 55.5, 55.3 ppm; **IR (ATR)**: $\tilde{\nu}_{\max}$ = 3672 (s), 3328 (w), 2951 (m), 2868 (s), 1706 (s), 1651 (s), 1257 (s), 1090 (s), 877 (s), 767 (s), 651 cm^{-1} (s); **ESI(+)-HR-MS**: m/z: $[M + H]^+$ calcd. for $C_{42}H_{37}N_2O_4^+$, 633.2748; found, 633.2737.

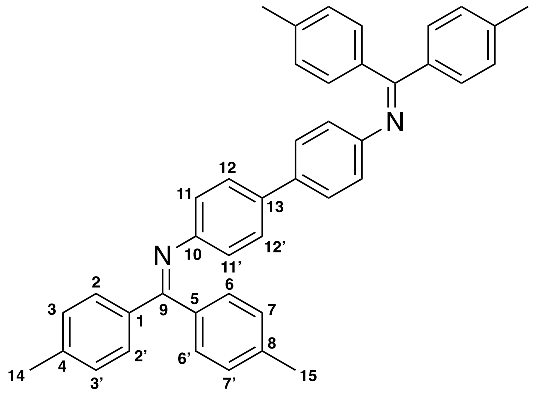
N,*N*‘-Bis(4,4‘-di-*tert*-butyl-benzophenone)benzidine imine (2d)



Following the general procedure, a solution of BND (0.36 g, 2.0 mmol) in chlorobenzene (80 mL) was treated with bis(4-(*t*-butyl)phenyl)methanone (1.22 g, 4.2 mmol) and DABCO (1.33 g, 11.9 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (330 µL, 3.0 mmol) in chlorobenzene (20 mL) over 20 min. The reaction mixture was heated to 120 °C and stirred for 8 h. The reaction mixture was worked up according to WUP3 and recrystallized from chlorobenzene to yield **2d** (1.24 g, 1.8 mmol, 85%) as a yellow solid.

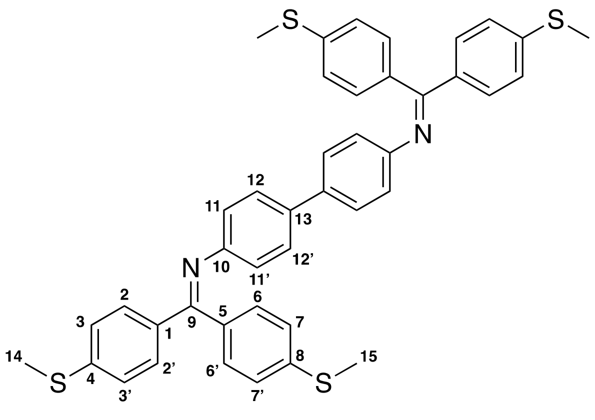
R_f = 0.53 (SiO_2; hexane/EtOAC 9:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.86–7.55 (m, 4H), 7.46–7.39 (m, 4H), 7.39–7.32 (m, 4H), 7.30–7.22 (m, 4H), 7.13–7.02 (m, 4H), 6.80–6.73 (m, 4H), 1.34 (s, 19H), 1.28 ppm (s, 19H); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 168.1, 154.1, 151.8, 150.4, 137.6, 135.4, 133.4, 129.6, 129.3, 126.7, 125.2, 124.9, 121.8, 35.0, 34.8, 31.4 (6C) ppm; **IR (ATR)**: $\tilde{\nu}_{\max}$ = 2963 (w), 1612 (w), 1597 (m), 1486 (w), 1109 (w), 963 (w), 860 (w), 831 (s), 818 (w), 686 cm^{-1} (m); **ESI(+)-HR-MS**: m/z: $[M + H]^+$ calcd. for $C_{54}H_{61}N_2^+$, 737.4829; found, 737.4819.

***N*,*N*‘-Bis(4,4‘-dimethyl-benzophenone)benzidine imine (2e)**



Following the general procedure, a solution of BND (0.50 g, 2.7 mmol) in chlorobenzene (30 mL) was treated with di-*p*-tolylmethanone (1.20 g, 5.7 mmol) and DABCO (1.84 g, 16.4 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (450 µL, 4.1 mmol) in chlorobenzene (15 mL) over 20 min. The reaction mixture was heated to 125 °C and stirred for 20 h, then treated dropwise with $TiCl_4$ (250 µL, 2.3 mmol) in chlorobenzene (15 mL) over 5 min and stirred for 2 h. The reaction mixture was worked up according to WUP1. The crude product (1.23 g) was recrystallized from chloroform/EtOH 1:2 to yield **2e** (0.35 g, 0.6 mmol, 22%) as a red solid. **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.72–7.63 (m, 4H), 7.43–7.33 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 4H), 7.15–7.02 (m, 8H), 6.84 (d, *J* = 8.1 Hz, 4H), 2.44 (s, 6H), 2.35 ppm (s, 6H); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 168.3, 150.5, 141.1, 138.6, 137.5, 135.3, 133.6, 129.7, 129.5, 129.0, 128.8, 126.7, 121.7, 21.6, 21.5 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 1621 (m), 1600 (m), 1484 (m), 1292 (m), 1180 (m), 1139 (m), 835 (w), 827 (s), 734 (m), 727 cm^{-1} (w); **ESI(+)-HR-MS**: (*m*/*z*): [*M* + H]$^+$ calcd. for $C_{42}H_{37}N_2^+$, 569.2951; found, 569.2935.

***N*,*N*‘-Bis(4,4‘-dithiomethyl-benzophenone)benzidine imine (2f)**

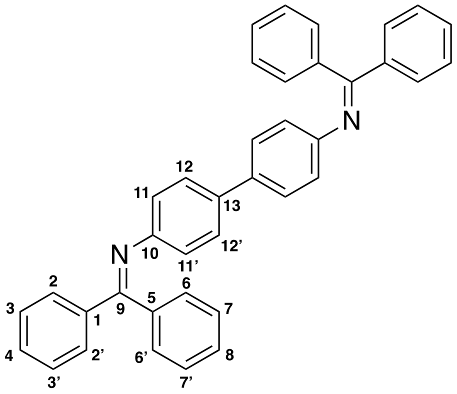


Following the general procedure, a solution of BND (0.31 g, 1.67 mmol) in chlorobenzene (20 mL) was treated with **1f** (0.96 g, 3.5 mmol) and DABCO (1.13 g, 10.1 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (280 µL, 2.5

mmol) in chlorobenzene (15 mL) over 20 min. The reaction mixture was heated to 125 °C and stirred for 18 h. The reaction mixture was treated dropwise with $TiCl_4$ (140 µL, 1.3 mmol) over 5 min and stirred for another hour. The reaction mixture was worked up according to WUP1 and the crude product was recrystallized from chloroform/EtOH 1:1 to yield **2f** as a yellow solid (0.33 g, 0.5 mmol, 19%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.69–7.61 (m, 4H), 7.42–7.34 (m, 4H), 7.26–7.21 (m, 4H), 7.13–7.01 (m, 8H), 6.78–6.71 (m, 4H), 2.52 (s, 6H), 2.46 ppm (s, 6H); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 167.1, 150.2, 142.5, 139.9, 136.5, 135.5, 132.5, 130.3, 129.9, 126.8, 125.4, 125.3, 121.7, 15.3, 15.2 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 1582 (s), 1547 (m), 1485 (m), 1291 (m), 1089 (m), 957 (m), 937 (w), 828 (s), 757 (m), 736 cm^{-1} (m); **ESI(+)-HR-MS**: *m/z*: [*M* + H]$^+$ calcd. for $C_{42}H_{37}N_2S_4$, 697.1834; found, 697.1837.

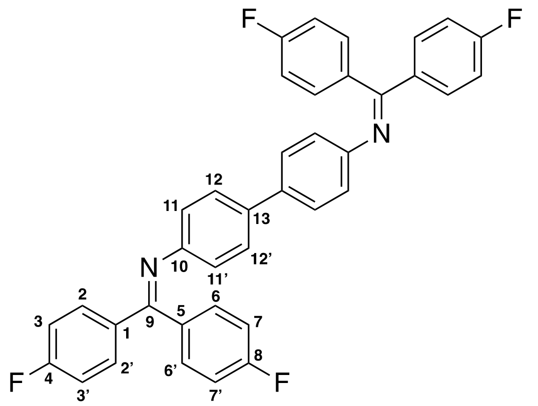
***N*,*N*'-Bis-benzophenone-benzidine imine (2g)**



Following the general procedure, a solution of BND (0.24 g, 1.3 mmol) in chlorobenzene (30 mL) was treated with benzophenone (0.72 g, 3.97 mmol) and DABCO (0.89 g, 7.95 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (450 µL, 4.1 mmol) in chlorobenzene (15 mL) over 15 min. The reaction mixture was heated to 125 °C and stirred for 20 h. The reaction mixture was treated dropwise with $TiCl_4$ (250 µL, 2.3 mmol) in chlorobenzene (15 mL) over 10 min and stirred for another 5 h. The reaction mixture was cooled down to 40°C and filtered through filter paper. The solvent was evaporated. A solution of chloroform and ethanol (1:3, 80 ml) was added to the residue. The mixture was slowly heated until all the product was dissolved. The solution was filtered hot through a cotton-plugged funnel and slowly cooled down until the crystallization started. The crude product (1.23 g) was recrystallized from $CHCl_3$/EtOH 1:3 to yield **2g** (0.18 g, 0.36 mmol, 27%) as a golden solid.

***R*$_f$** = 0.6 (SiO_2; cHex/EtOAc 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.67 (m, 4H), 7.41–7.36 (m, 2H), 7.35–7.30 (m, 4H), 7.27–7.23 (m, 4H), 7.21–7.16 (m, 6H), 7.08–7.04 (m, 4H), 6.69–6.65 ppm (m, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$, 25 °C): δ = 168.33, 150.16, 139.86, 136.40, 135.57, 130.85, 129.67, 129.48, 128.76, 128.33, 128.14, 126.72, 121.63, 77.16 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 3672 (s), 3328 (w), 2951 (m), 2868 (s), 1706 (s), 1651 (s), 1257 (s), 1090 (s), 877 (s), 767 (s), 651 cm^{-1} (s); **ESI(+)-MS**: *m/z*: [*M* + H]$^+$ calcd. for $C_{38}H_{29}N_2^+$, 513.2325; found, 513.2337.

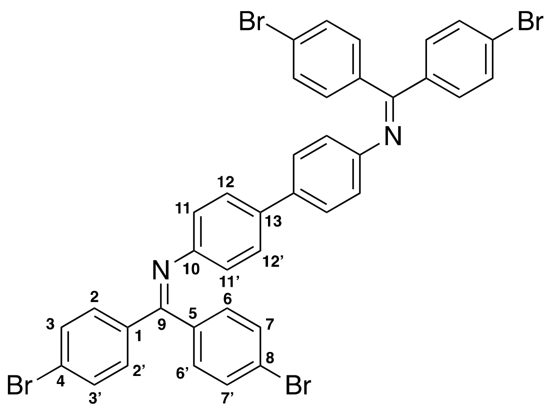
N,*N*‘-Bis(4,4‘-difluoro-benzophenone)benzidine imine (2h)



Following the general procedure, a solution of BND (0.50 g, 2.7 mmol) in chlorobenzene (30 mL) was treated with 4,4’difluoro-benzophenone (1.3 g, 5.97 mmol) and DABCO (1.84 g, 16.4 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (450 µL, 4.1 mmol) in chlorobenzene (15 mL) over 20 min. The reaction mixture was heated to 125 °C and stirred for 5 h. The reaction mixture was worked up according to procedure 1, but instead of recrystallization the organic phase was dried with $MgSO_4$ filtered and the solvent evaporated. The crude product was purified by an automated MPLC (SiO_2; gradient hexane/EtOAc 1:0 → 0:1) to yield **2h** (0.61 g, 1.1 mmol, 76%) as a yellow solid.

***R*$_f$** = 0.6 (SiO_2; cHex/EtOAc 9:1); **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.77–7.72 (m, 4H), 7.39–7.34 (m, 4H), 7.16–7.06 (m, 8H), 7.01–6.94 (m, 4H), 6.74 ppm (d, *J* = 8.4 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$, 25 °C): δ = 166.3, 165.7, 163.8, 163.7, 161.8, 149.7, 135.8, 132.0, 131.7, 131.6, 129.9, 128.7, 127.0, 126.6, 121.6, 115.6, 115.4 ppm; **^{19}F NMR** (282 MHz, $CDCl_3$, 25 °C): δ = –109.35, –111.08 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 3672 (s), 3328 (w), 2951 (m), 2868 (s), 1706 (s), 1651 (s), 1257 (s), 1090 (s), 877 (s), 767 cm^{-1} (s); **ESI(+)-HR-MS**: *m*/*z*: [*M* + H]$^+$ calcd. for $C_{38}H_{25}N_2O_4^+$, 585.1948; found, 585.1947.

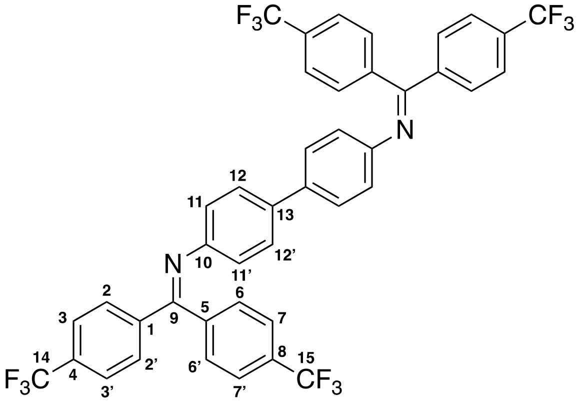
N,*N*‘-Bis(4,4‘-dibromo-benzophenone)benzidine imine (2i)



Following the general procedure, a solution of BND (0.51 g, 2.8 mmol) in chlorobenzene (30 mL) was treated with dibromo-benzophenone (1.97 g, 5.9 mmol) and DABCO (1.87 g, 16.7 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (450 µL, 4.1 mmol) in chlorobenzene (20 mL) over 20 min. The reaction mixture was heated to 125 °C and stirred for 18 h. The reaction mixture was worked up according to WUP1 and the crude product was recrystallized from chloroform to yield **2i** (0.56 g, 0.67 mmol, 24%) as a yellow solid.

***R*$_f$** = 0.6 (SiO_2; hexane/EtOAc 1:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.62–7.53 (m, 8H), 7.45–7.36 (m, 8H), 7.03–6.99 (d, *J* = 8.4 Hz, 4H), 6.76–6.73 ppm (d, *J* = 8.3 Hz, 4H); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 131.9, 131.7, 131.2, 130.9, 127.0, 121.5 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 1612 (m), 1583 (s), 1560 (m), 1485 (s), 1392 (m), 1070 (m), 1008 (m), 958 (m), 935 (m), 827 (s), 732 cm^{-1} (m); **ESI(+)-HR-MS**: *m*/*z* (%): [*M* + H]$^+$ calcd. for $C_{38}H_{26}{}^{79}Br_4N_2^+$, 824.8746; found, 824.8746 (20), 826.8725 (70), 828.8705 (100), 830.8684 (66), 831.8718 (28).

N,*N*‘-Bis(4,4‘-bis(trifluoromethyl)benzophenone)benzidine imine (2j)



Procedure 1

Following the general procedure, a solution of BND (0.58 g, 3.1 mmol) in chlorobenzene (30 mL) was treated with **1j** (2.11 g, 6.6 mmol) and DABCO (2.14 g, 19.0 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (520 µL, 4.7 mmol) in chlorobenzene (20 mL) over 20 min. The reaction mixture was heated to 125 °C and stirred for 18 h. The reaction mixture was worked up according to WUP2 and the crude product (2.25 g) was recrystallized from chloroform to yield **2j** (0.65 g, 0.82 mmol, 26%) as a gold-yellow solid.

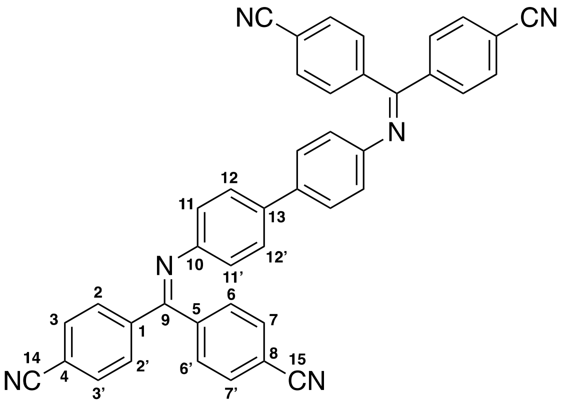
Procedure 2

Following the general procedure, a solution of BND (0.36 g, 2.0 mmol) in chlorobenzene (80 mL) was treated with **1j** (1.32 g, 4.2 mmol) and DABCO (1.33 g, 11.9 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (330 µL, 3.0 mmol) in chlorobenzene (20 mL) over 20 min. The reaction mixture was heated to 120 °C and stirred for 5 h. The reaction mixture was worked up according to yield **2j** (0.60 g, 0.76 mmol, 39%) as a gold-yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.65–7.59 (m, 4H), 7.59–7.53 (m, 4H), 7.47–7.42 (m, 4H), 7.42–7.36 (m, 4H), 7.06–6.99 (m, 4H), 6.75–6.68 ppm (m, 4H); **^{13}C NMR** (76 MHz, $CDCl_3$, 25 °C): δ = 165.4, 149.3, 142.3, 136.2, 129.9, 129.6, 128.8, 127.2, 125.6–125.5 (m, 4C, –CF_3), 125.4, 121.4 ppm, due to

^{13}C–^{19}F coupling the ^{13}C signals of the CF$_3$ group and the aromatic carbons *meta* to the CF$_3$ group are not observable; **^{19}F NMR** (282 MHz, CDCl$_3$, 25 °C): δ = –63.42, –63.44 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 1322 (m), 1160 (m), 1122 (w), 1108 (s), 1066 (s), 1017 (m), 858 (w), 846 (m), 835 (m), 673 cm^{-1} (m); **ESI(+)-HR-MS**: *m*/*z*: [*M* + H]$^+$ calcd. for $C_{42}H_{25}N_2F_{12}^+$, 785.1821; found, 785.1817.

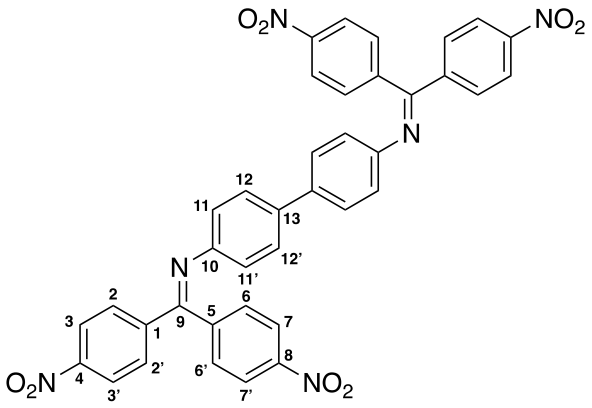
***N*,*N*‘-Bis(4,4‘-dicyano-benzophenone)benzidine imine (2k)**



Following the general procedure, a solution of BND (0.51 g, 2.7 mmol) in chlorobenzene (30 mL) was treated with **1k** (1.34 g, 5.8 mmol) and DABCO (1.86 g, 16.6 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of TiCl$_4$ (460 µL, 4.1 mmol) in chlorobenzene (15 mL) over 15 min. The reaction mixture was heated to 125 °C and stirred for 16 h. The reaction mixture was allowed to cool down to room temperature. Within two days, the product crystallized. The product was filtered of and washed with EtOH to yield **2k** (0.65 g, 1.1 mmol, 39%) as a golden solid.

^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.87–7.78 (m, 4H), 7.78–7.68 (m, 4H), 7.67–7.58 (m, 4H), 7.42–7.31 (m, 4H), 7.31–7.17 (m, 4H), 6.81–6.65 ppm (m, 4H); **^{13}C NMR** (76 MHz, CDCl$_3$, 25 °C): δ = 164.5, 148.9, 142.3, 139.9, 136.5, 132.6, 132.4, 132.4, 130.4, 130.1, 129.7, 127.2, 121.3, 114.8, 113.4 ppm; **IR (ATR)**: $\tilde{\nu}_{max}$ = 2230 (w), 1614 (w), 1598 (m), 1484 (w), 947 (w), 851 (w), 834 (m), 750 (w), 673 cm^{-1} (m); **ESI(+)-HR-MS**: *m*/*z*: [*M* + H]$^+$ calcd. for $C_{42}H_{25}N_6^+$, 635.1955; found, 635.1959.

***N*,*N*‘-Bis(4,4‘-di(*N’’,N’’’*-dinitro-benzophenone)benzidine imine (2l)**



Procedure 1

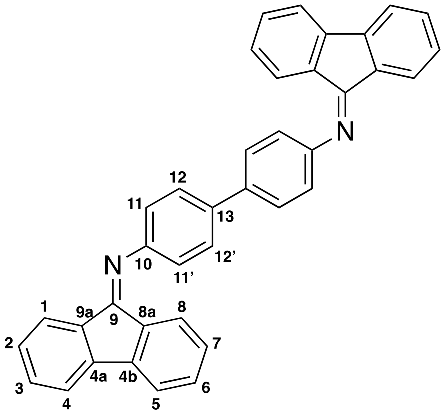
Following the general procedure, a solution of BND (0.36 g, 2.0 mmol) in chlorobenzene (80 mL) was treated with **1l** (1.13 g, 4.2 mmol) and DABCO (1.33 g, 11.9 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (330 µL, 3.0 mmol) in chlorobenzene (20 mL) over 20 min. The reaction mixture was heated to 120 °C and stirred for 8 h. The reaction mixture was worked up according to WUP3. Recrystallization from chlorobenzene afforded **2l** (0.27 g, 0.4 mmol, 20%) as a red solid.

Procedure 2

According to a procedure reported in the literature a suspension of BND (0.40 g, 2.2 mmol) and **1l** (0.65 g. 2.4 mmol) in $Si(OEt)_4$ (2 mL, 9 mmol) was treated with one drop of sulfuric acid and heated to 160 °C in a miniature distillation apparatus. The suspension was stirred overnight and allowed to cool to room temperature. The residue was suspended in CH_2Cl_2 and washed with $NaHCO_3$ (2x) and water. The organic phase was dried with $MgSO_4$ and the solvent removed under reduced pressure. The crude was washed with EtOAc and recrystallized from chlorobenzene to afford **2l** (0.43 g, 0.6 mmol, 28%) as a red solid.

***R*$_f$** = 0.36 (SiO_2; CH_2Cl_2/MeOH 99:1); **^{1}H NMR** (300 MHz, CD_2Cl_2, 25 °C): δ = 8.27 (d, *J* = 9.0 Hz, 4H), 8.18 (d, *J* = 8.8 Hz, 4H), 7.91 (d, *J* = 9.0 Hz, 4H), 7.38 (d, *J* = 8.4 Hz, 4H), 7.34 (d, *J* = 8.8 Hz, 4H), 6.74 (d, *J* = 8.4 Hz, 4H). **^{13}C NMR** (76 MHz, CD_2Cl_2, 25 °C): δ = 164.7, 150.0, 149.6, 148.6, 144.3, 142.3, 136.8, 130.9, 130.5, 127.6, 124.2, 124.1, 121.6; **IR (ATR)**: $\tilde{\nu}_{max}$ = 3110 (s), 3079 (s), 3032 (s), 2852 (s), 2362 (s), 2341 (s), 1636 (s), 1541 (s), 1513 (s), 1343 (m), 850 (s), 830 (s), 740 (s), 706 (m). **ESI(+)-HR-MS:** *m*/*z* (%): [*M* + H]$^+$ calcd. for $C_{38}H_{25}N_6O_8^+$, 683.1728; found, 693.1729

***N*,*N*'-([1,1'-biphenyl]-4,4'-diyl)bis(9*H*-fluoren-9-imine) (S2)**



Following the general procedure, a solution of BND (0.40 g, 2.2 mmol) in chlorobenzene (80 mL) was treated with fluorenone (0.82 g, 4.6 mmol) and DABCO (1.56 g, 13.0 mmol). After the addition, nitrogen was bubbled through the mixture for 10 min and it was treated dropwise with a solution of $TiCl_4$ (360 µL, 3.3 mmol) in chlorobenzene (20 mL) over 20 min. The reaction mixture was heated to 120 °C and stirred for 19 h. The reaction mixture was worked up according to WUP3 to afford **S2** (1.03 g, 2.0 mmol, 93%) as a bright orange solid.

***R*f** = 0.27 (SiO_2; CH2CL2/MeOH 99:1); **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ = 7.95 (d, J = 7.4 Hz, 2H), 7.77 (d, J = 8.3 Hz, 4H). 7.63 (d, J = 7.4 Hz, 4H), 7.49 (td, J = 7.5, 1.2Hz, 2H), 7.37 (m, 4H), 7.12 (d, J = 8.3 Hz, 4H), 6.99 (td, J = 7.6, 1.0 Hz, 2H), 6.83 (d, J = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, CD_2Cl_2, 25 °C): δ = 163.4, 151.5, 144.4, 142.5, 138.2, 136.9, 132.49, 132.47, 131.8, 129.0, 128.3, 128.1, 127.6, 123.7, 120.9, 120.3, 119.4; **IR (ATR)**: $\tilde{\nu}_{max}$ = 3046 (m), 3023 (m), 1307 (s), 1110 (s), 937 (m), 837 (m), 739 (m).

The compound was synthesized and its hydrolysis kinetics studied spectroscopically but ultimately not utilized in COF formation experiments.

Synthesis of BND-TFB COF

Synthesis and vacuum activation

To an oven-dried 25 mL high-pressure flask with vacuum valve, 1,3,5-triformylbenzene (61 mg, 0.667 equiv., 0.389 mmol) and the respective benzophenone imine **2a-l** (1.00 equiv. 0.581 mmol) were added, followed by the addition of mesitylene/1,4-dioxane (1:1, 3.6 mL). The flask was sonicated for 10 min and AcOH (6 M, 6 equiv. 581 µL) was added. After degassing by three freeze-pump-thaw cycles the flask was sealed under nitrogen and covered with aluminum foil and then placed in a pre-heated 120 °C oil bath. After three days the flask was removed from the oil bath, allowed to cool down and then transferred to a PTFE-filter using acetone. The solid was washed in succession with DMF (100 mL, 90 °C, twice), acetone (100 mL, 60 °C) and EtOH (100 mL, 80 °C) for 30 min each. The solid was then filtered, collected, placed in a small vial within a flask and then dried for at least one day in an oil bath at 120 °C under dynamic vacuum.

Synthesis and scCO₂ activation

To an oven-dried 10 mL high-pressure flask with vacuum valve, 1,3,5-triformylbenzene (30 mg, 0.667 equiv., 0.185 mmol) and the respective benzophenone imine **2a–l** (1.00 equiv. 0.276 mmol) were added, followed by the addition of mesitylene/dioxane (1:1, 1.8 mL). The flask was sonicated for 10 min, then pre-heated to 70°C. After cooling to room temperature, AcOH (6 M, 6 eqiv. 276 µL) was added. After degassing by three freeze-pump-thaw cycles the flask was sealed under nitrogen and covered with aluminum foil and then placed in a pre-heated 120 °C oil bath. After three days the flask was removed from the oil bath, allowed to cool down and then transferred to a PTFE-filter, using acetone. while using acetone to ensure all material was filtered. The solid was rinsed with acetone (100 mL) and MeOH (100 mL), placed into a teabag, secured with a staple and submerged in MeOH for 24 h. The material in the teabag was dried using *sc*CO_2.

Table S1 Crystallinity and porosity of BND-TFB COF synthesized from substituted benzophenone imines using vacuum activation.

Linear Linker	SA_{BET} [m^2g^{-1}]	Crystallinity
2a (–NMe_2)	971	Yes
2b (–O*i*Pr)	1884	Yes
2c (–OMe)	2322	Yes
2d (–*t*Bu)	1823	Yes
2e (–Me)	2147	Yes
2f (–SMe)	2388	Yes
2g (–H)	2119	Yes
2h (–F)	1986	Not determined
2i (–Br)	1847	Yes
2j (–CF_3)	1881	Yes
2k (–CN)	1295	Yes
2l (–NO_2)	348	Yes

Table S2 Crystallinity and porosity of BND-TFB COF synthesized from substituted benzophenone imines using supercritical CO_2 activation.

Linear Linker	SA_{BET} [m^2g^{-1}]	Crystallinity
2a (–NMe_2)	1926	Yes
2a (–NMe_2)	2382	Yes
2b (–O*i*Pr)	2320	Yes
2b (–O*i*Pr)	1664	Yes
2g (–H)	2332	Yes
2g (–H)	2376	Yes
2k (–CN)	1964	Yes
2k (–CN)	2783	Yes
2l (–NO_2)	542	Yes
2l (–NO_2)	1335	Yes

S3. Crystallographic Data

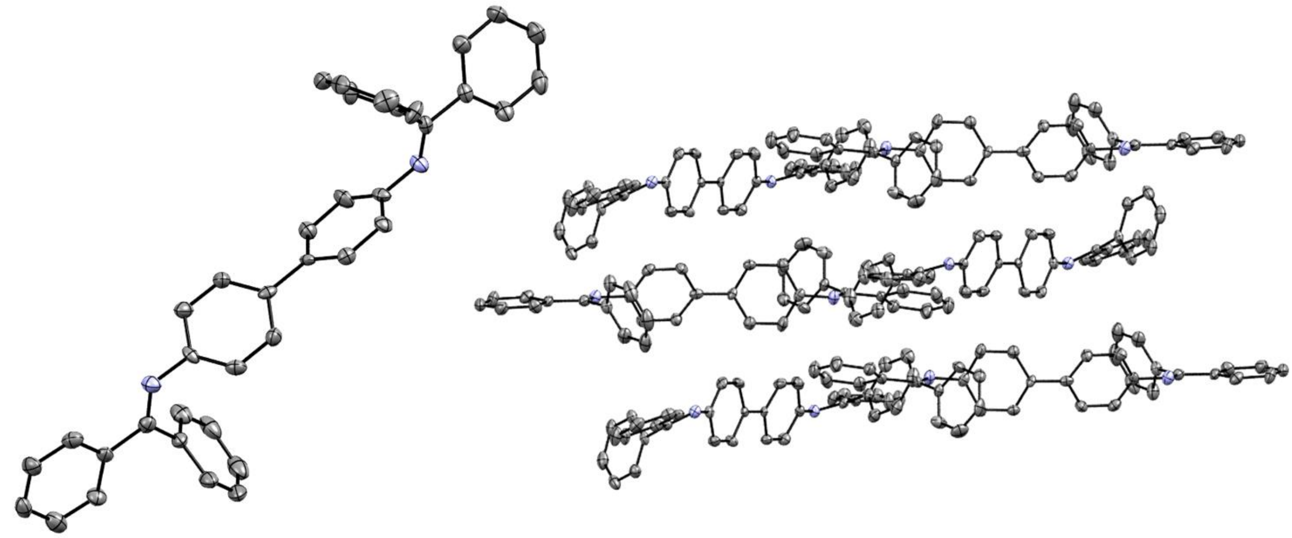


Figure S1 Single-crystal X-ray structure for imine **2g** at 100 K. Hydrogen atoms are omitted for clarity. The ellipsoids are displayed at 50% probability level. Color code: C: gray, N: blue.

Table S3 X-ray single crystal data and structure refinement for imine **2g**.

Identification code	2240743
Empirical formula	$C_{38}H_{28}N_2$
Formula weight	512.62
Temperature/K	100.01
Crystal system	triclinic
Space group	*P–1*
a/Å	9.5460(18)
b/Å	15.907(3)
c/Å	18.545(4)
α/°	88.246(4)
β/°	81.362(4)
γ/°	89.566(4)
Volume/Å^3	2782.8(9)
Z	4
ρ_{calc}/ g cm^{-3}	1.224
μ/mm^{-1}	0.071
F(000)	1080.0
Crystal size/mm^3	0.28 × 0.22 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.316 to 53.104
Index ranges	$-11 \leq h \leq 11$, $-19 \leq k \leq 20$, $-23 \leq l \leq 23$
Reflections collected	86855
Independent reflections	11521 [R_{int} = 0.4000, R_{sigma} = 0.3408]
Data/restraints/parameters	11521/0/721
Goodness-of-fit on F^2	0.977
Final R indexes [I>=2σ (I)]	R_1 = 0.0955, wR_2 = 0.1513
Final R indexes [all data]	R_1 = 0.3014, wR_2 = 0.2133
Largest diff. peak/hole / e Å^{-3}	0.27/–0.31

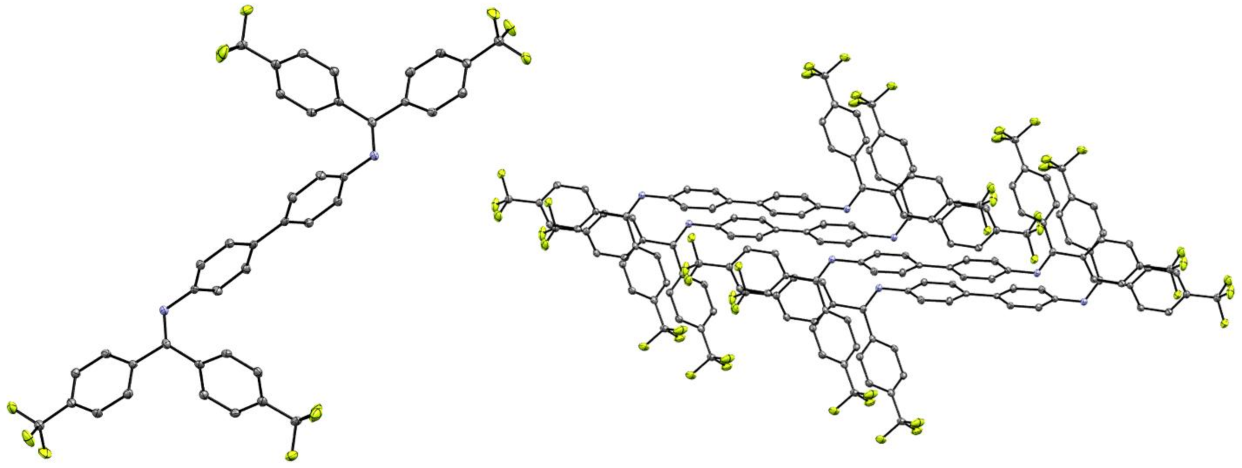


Figure S2 Single-crystal X-ray structure for imine **2j** at 100 K. Hydrogen atoms are omitted for clarity. The ellipsoids are displayed at 50% probability level. Color code: C: gray, N: blue, F: yellow.

Table S4 X-ray single crystal data and structure refinement for imine **2j**.

CCDC No.	1942397
Empirical formula	$C_{42}H_{24}F_{12}N_2$
Formula weight	784.63
Temperature/K	100.0
Crystal system	triclinic
Space group	*P–1*
a/Å	5.592(4)
b/Å	10.4164(7)
c/Å	14.6091(11)
α/°	80.515(4)
β/°	85.368(4)
γ/°	83.032(4)
Volume/Å^3	831.56(10)
Z	1
ρ_{calc}/ g cm^{-3}	1.567
μ/mm^{-1}	0.139
F(000)	398.0
Crystal size/mm^3	0.388 × 0.19 × 0.114
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.516 to 50.744
Index ranges	$-6 \leq h \leq 6, -12 \leq k \leq 12, -17 \leq l \leq 17$
Reflections collected	13993
Independent reflections	3048 [R_{int} = 0.0781, R_{sigma} = 0.0584]
Data/restraints/parameters	3048/0/253
Goodness-of-fit on F^2	1.030
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0547, wR_2 = 0.1151
Final R indexes [all data]	R_1 = 0.0875, wR_2 = 0.1280
Largest diff. peak/hole / e Å^{-3}	0.33/–0.28

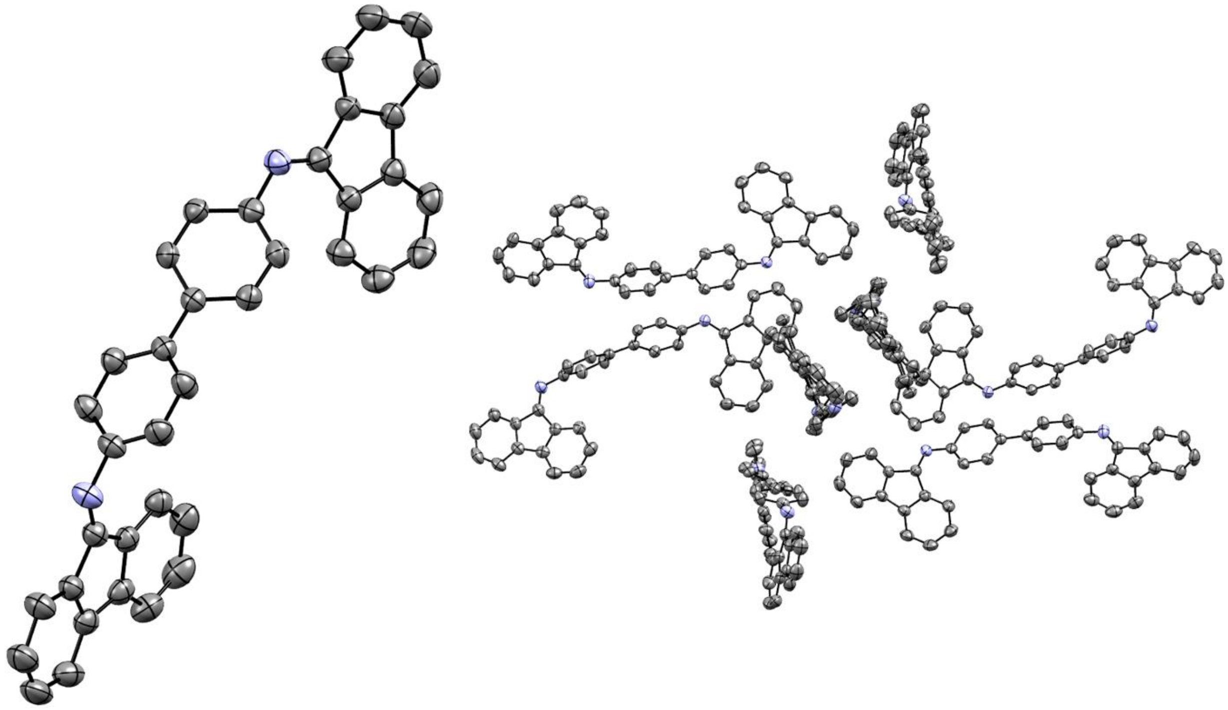


Figure 3 Single-crystal X-ray structure for imine **S2** at 100 K. Hydrogen atoms are omitted for clarity. The ellipsoids are displayed at 50% probability level. Color code: C: gray, N: blue.

Table 5 X-ray single crystal data and structure refinement for imine **S2**.

Identification code	2240744
Empirical formula	$C_{38}H_{24}N_2$
Formula weight	508.59
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbca
a/Å	17.0198(7)
b/Å	10.7650(5)
c/Å	29.1185(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5335.0(4)
Z	8
ρ_{calc}/ g cm^{-3}	1.266
μ/mm^{-1}	0.074
F(000)	2128.0
Crystal size/mm^3	0.409 × 0.173 × 0.058
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.682 to 46.5
Index ranges	$-18 \le h \le 18$, $-11 \le k \le 11$, $-32 \le l \le 32$
Reflections collected	111228
Independent reflections	3824 [R_{int} = 0.1406, R_{sigma} = 0.0312]
Data/restraints/parameters	3824/0/361
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.0723, wR_2 = 0.1331
Largest diff. peak/hole / e Å^{-3}	0.13/–0.21

S4. UV-vis Spectroscopy

Imine hydrolysis follows second-order kinetics.[9,10] Therefore, if $[I]$ is the concentration of imine, the rate law can be defined as follows

$$\frac{-\mathrm{d}[I]}{\mathrm{d}t} = k[I][\mathrm{H_2O}] \tag{1}$$

Due to the excess of acetic acid and water it can be assumed that $[\mathrm{H_2O}] = [\mathrm{H_2O}]_0$ and the observed reaction rate $k_{\mathrm{obs}} = k[\mathrm{H_2O}]_0$ can be introduced to distinguish it from the fundamental reaction rate constant. The rate law then becomes

$$\frac{-\mathrm{d}[I]}{\mathrm{d}t} = k_{\mathrm{obs}}[I] \tag{2}$$

$$\int_{[I]_0}^{[I]} \frac{1}{[I]}\mathrm{d}[I] = -k_{\mathrm{obs}} \int_0^t \mathrm{d}t \tag{3}$$

$$\ln\frac{[I]}{[I]_0} = -k_{\mathrm{obs}}t \tag{4}$$

$$\ln\frac{[I]}{[I]_0} = -k_{\mathrm{obs}}t \tag{5}$$

The observed reaction rate now only depends on the concentration of the imine. The hydrolysis reactions of the BP-imines with an excess of acetic acid are therefore pseudo first-order.

Plotting the logarithm of the relative absorption (A/A_0) against the time allows the determination of the observed kinetic constant k_{obs} as the slope of the linear fit.

If rate constants for the same reaction are measured at different temperatures the activation energy of a reaction, which is temperature-independent can be calculated with the Arrhenius equation (6) by plotting ln(k) versus T^{-1}. The slope of the linear fit will be $-E_{\mathrm{a}}\ \mathrm{R}^{-1}$.

$$\ln(k) = -\frac{E_{\mathrm{a}}}{\mathrm{R}}\cdot\frac{1}{T} + \ln(A) \tag{7}$$

For spectroscopic measurements, 1 mg of BP-imine was dissolved in 10 mL 1,4-dioxane. Depending on the absorption of the BP-imine between 0.5 and 2 mL of imine-solution were mixed with 1,4-dioxane and the solution added to a cuvette with a stir bar. The reaction mixture was heated in the spectroscopic chamber for 1 min. Afterwards, AcOH (1 mL, 6 M) was added to result in a total volume of 3 mL in the cuvette and the spectroscopic measurement was started. Full spectra were recorded every 0.25 min, 0.5 min, 1 min or 2 min depending on the speed of the imine hydrolysis.

Table S6 Wavelengths used for obtaining k_{obs}.

Compound	Wavelength [nm]
2a	472
2b	363
2c	363
2d	366
2e	366
2f	374
2g	364
2h	366
2i	377
2j	379
2k	391
2l	405

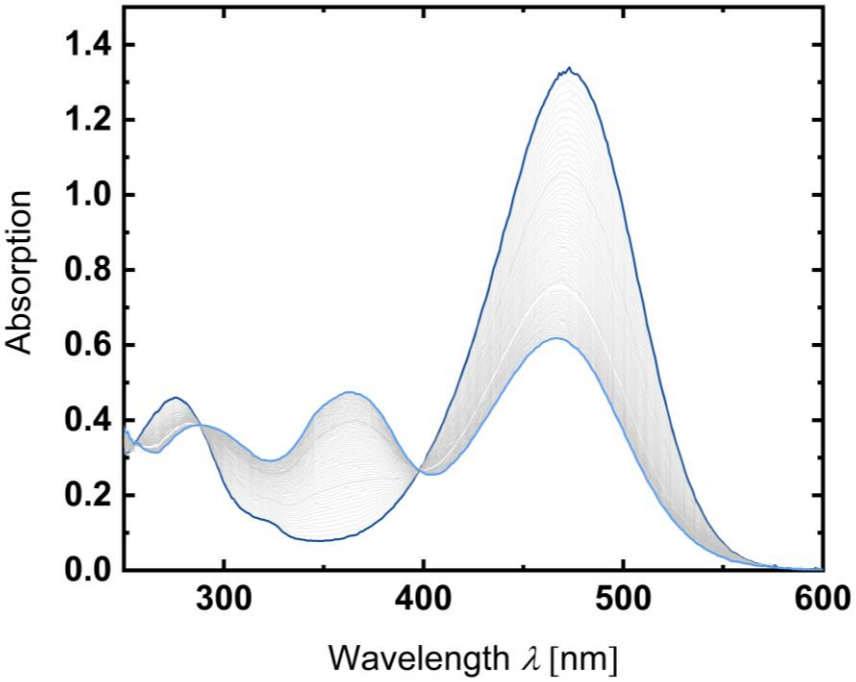


Figure S4 Absorption vs wavelength during hydrolysis of **2a** (–NMe$_2$). Spectra were recorded every 2 min. The spectrum at *t* = 0 is indicated with a dark blue line.

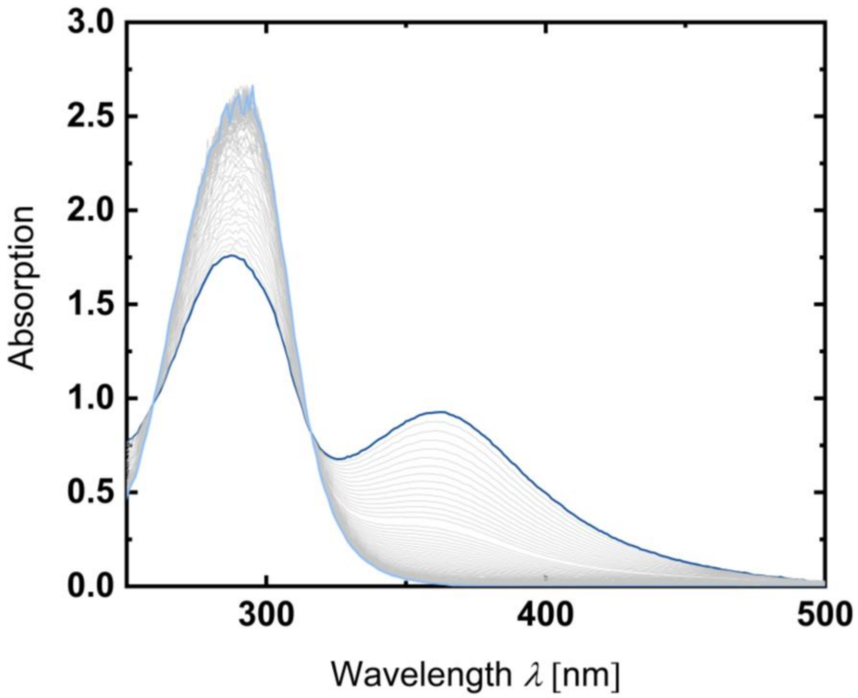


Figure S5 Absorption vs wavelength during hydrolysis of **2b** (–O$_i$Pr). Spectra were recorded every 0.5 min. The spectrum at *t* = 0 is indicated with a dark blue line.

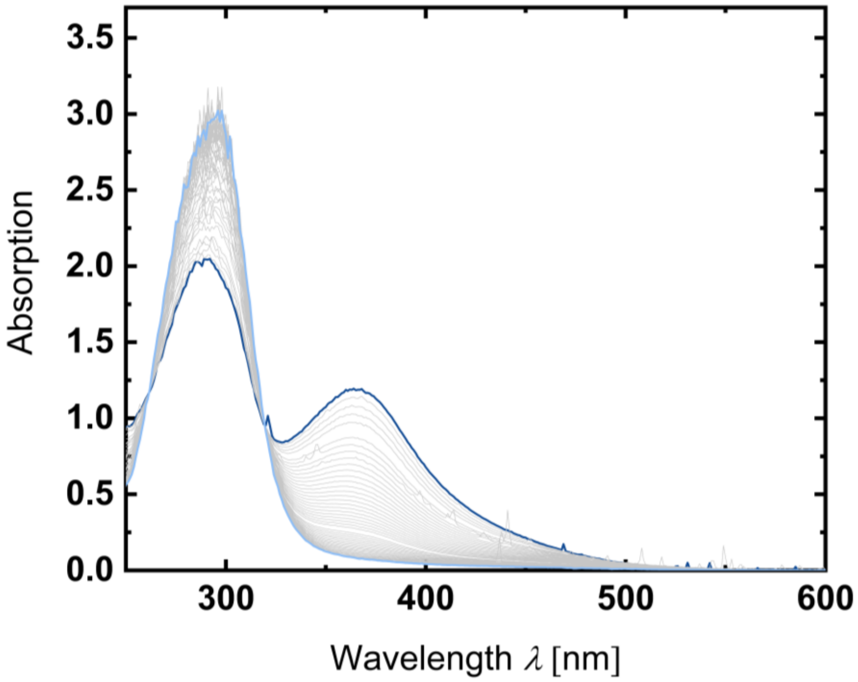


Figure S6 Absorption vs wavelength during hydrolysis of **2c** (–OMe). Spectra were recorded every 0.5 min. The spectrum at *t* = 0 is indicated with a dark blue line.

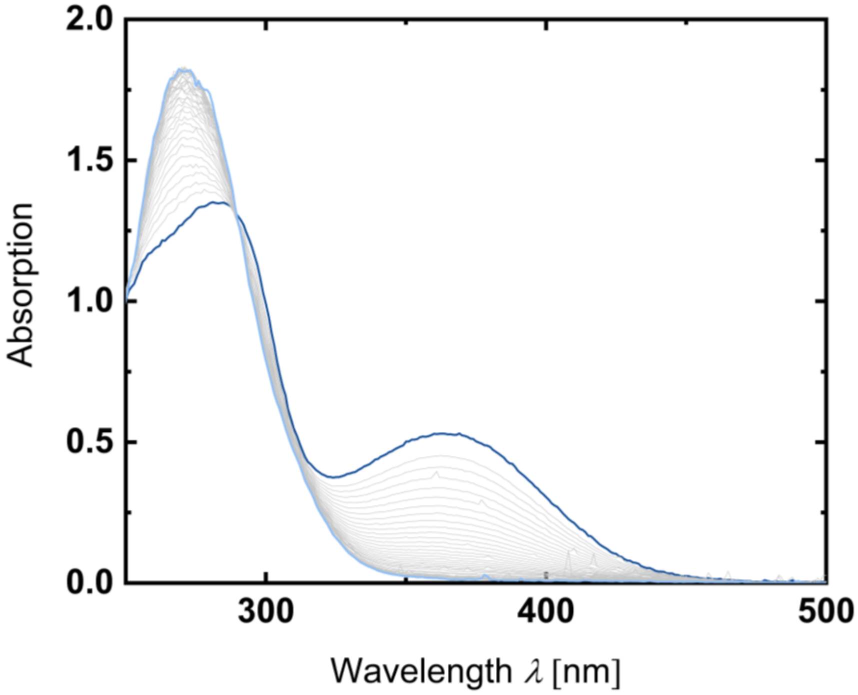


Figure S7 Absorption vs wavelength during hydrolysis of **2d** (–*t*Bu). Spectra were recorded every 0.5 min. The spectrum at *t* = 0 is indicated with a dark blue line.

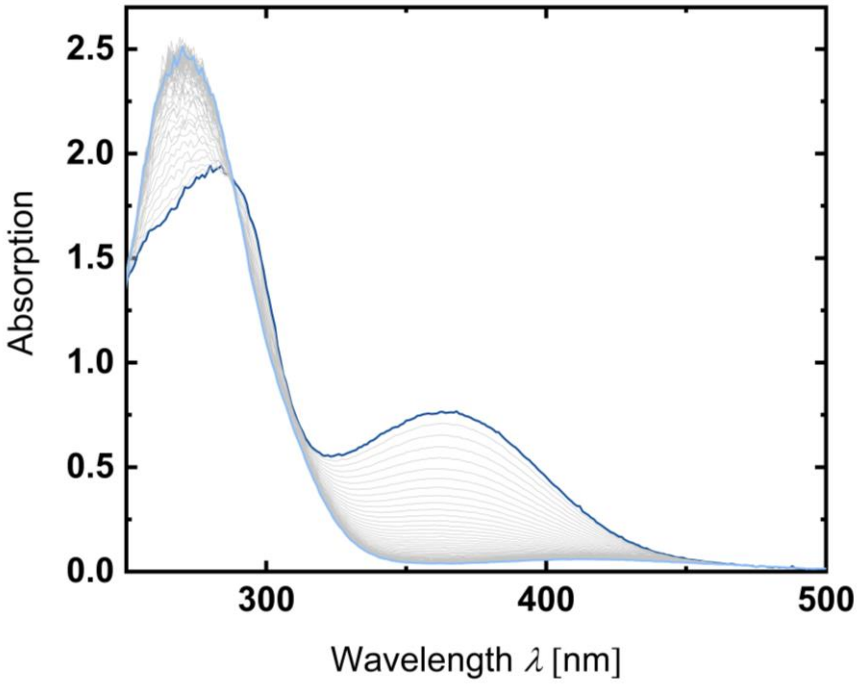


Figure S8 Absorption vs wavelength during hydrolysis of **2e** (–Me). Spectra were recorded every 0.5 min. The spectrum at *t* = 0 is indicated with a dark blue line.

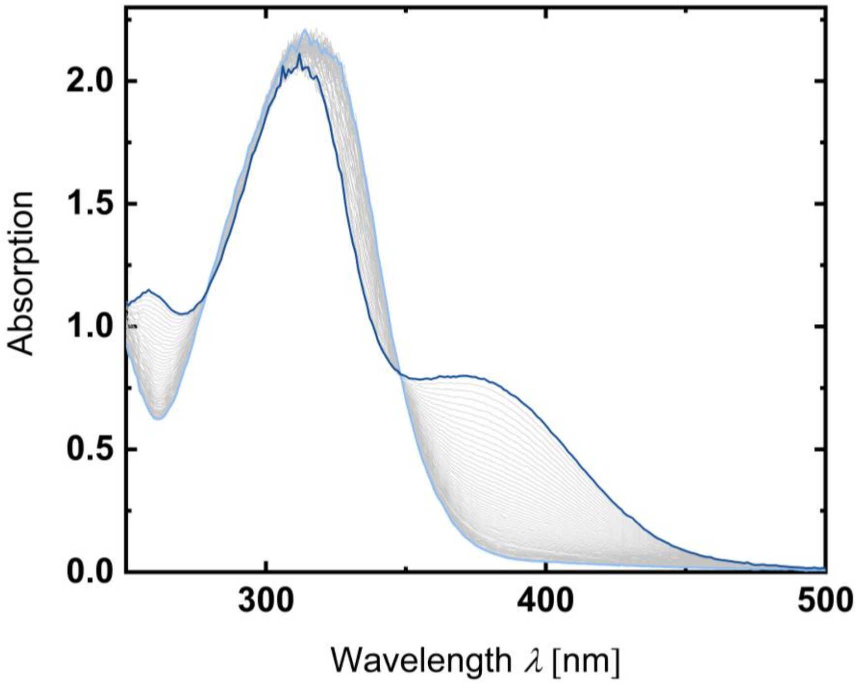


Figure S9 Absorption vs wavelength during hydrolysis of **2f** (–SMe). Spectra were recorded every 0.5 min. The spectrum at *t* = 0 is indicated with a dark blue line.

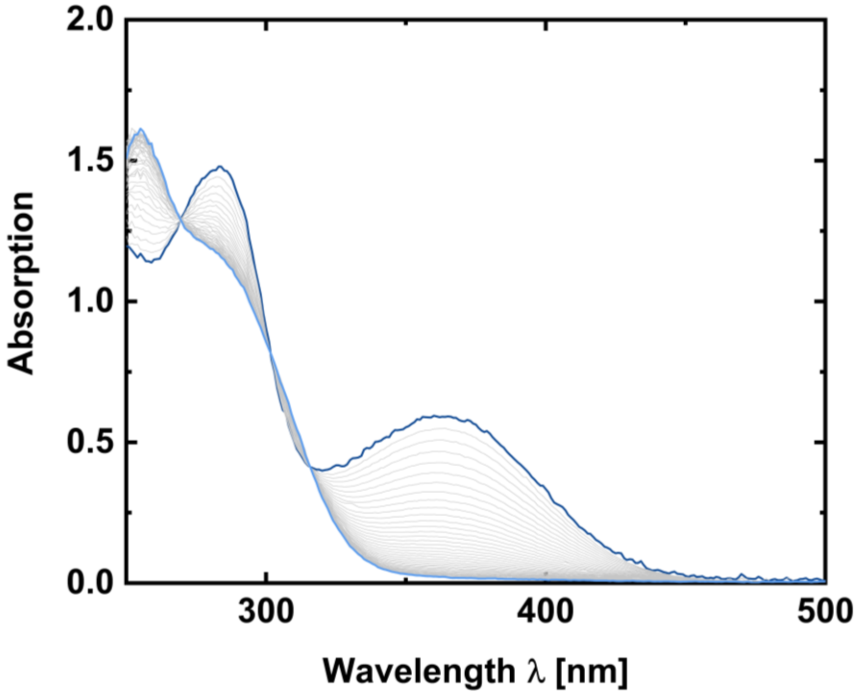


Figure S10 Absorption vs wavelength during hydrolysis of **2g** (–H). Spectra were recorded every 0.5 min. The spectrum at *t* = 0 is indicated with a dark blue line.

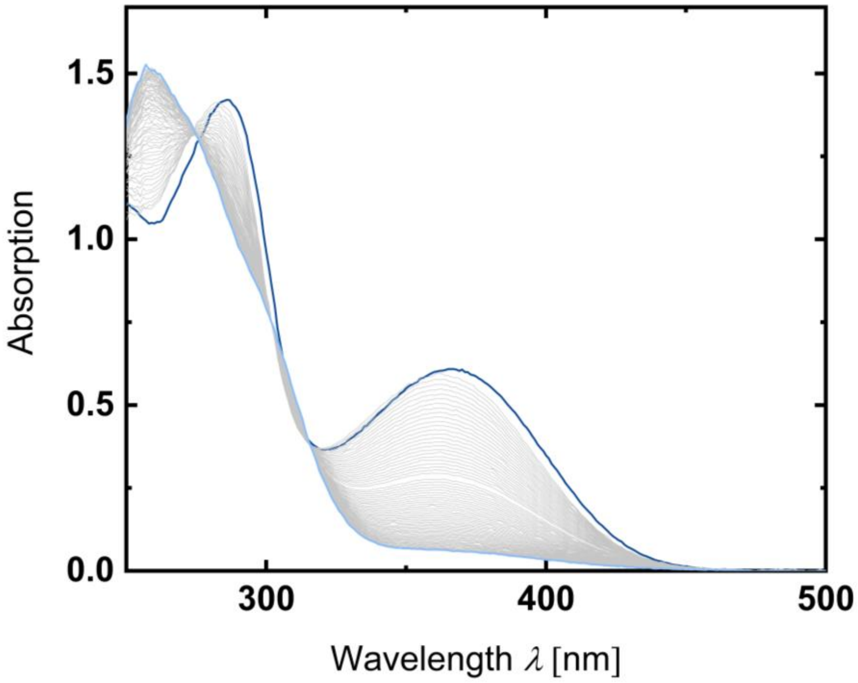


Figure S11 Absorption vs wavelength during hydrolysis of **2h** (–F). Spectra were recorded every 0.5 min. The spectrum at *t* = 0 is indicated with a dark blue line.

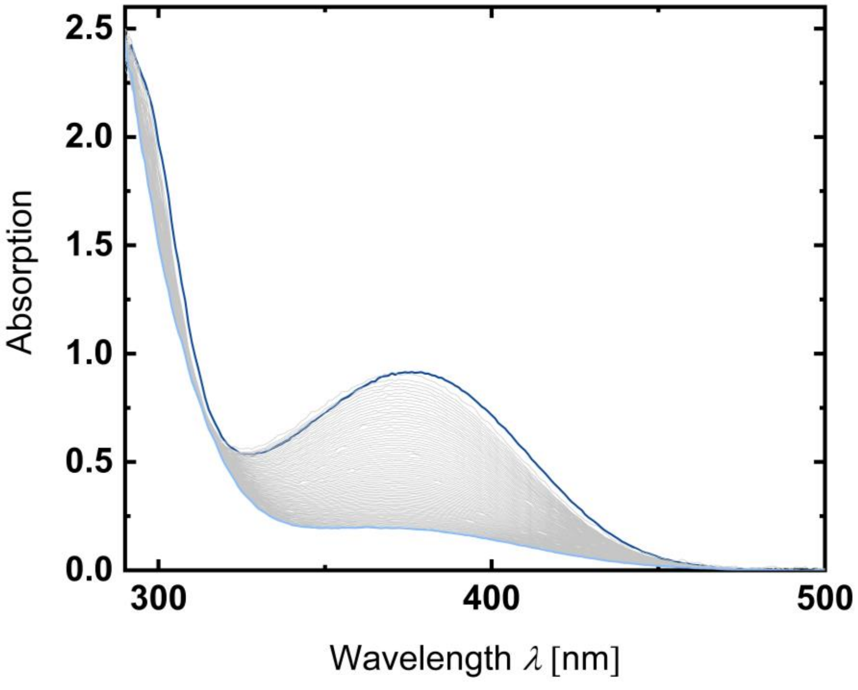


Figure S12 Absorption vs wavelength during hydrolysis of **2i** (–Br). Spectra were recorded every 0.5 min. The spectrum at *t* = 0 is indicated with a dark blue line.

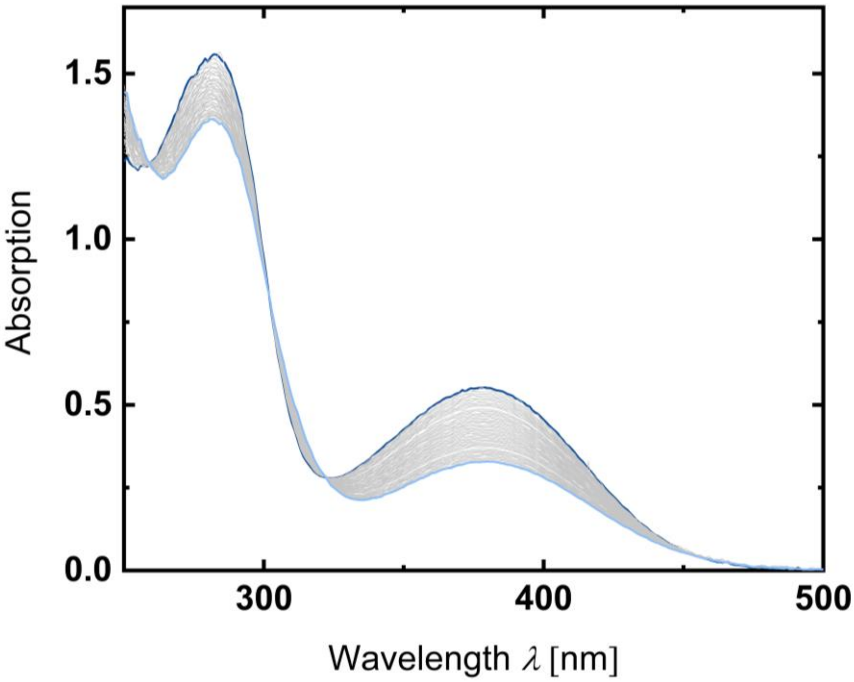


Figure S13 Absorption vs wavelength during hydrolysis of **2j** (–CF_3). Spectra were recorded every 1 min. The spectrum at *t* = 0 is indicated with a dark blue line.

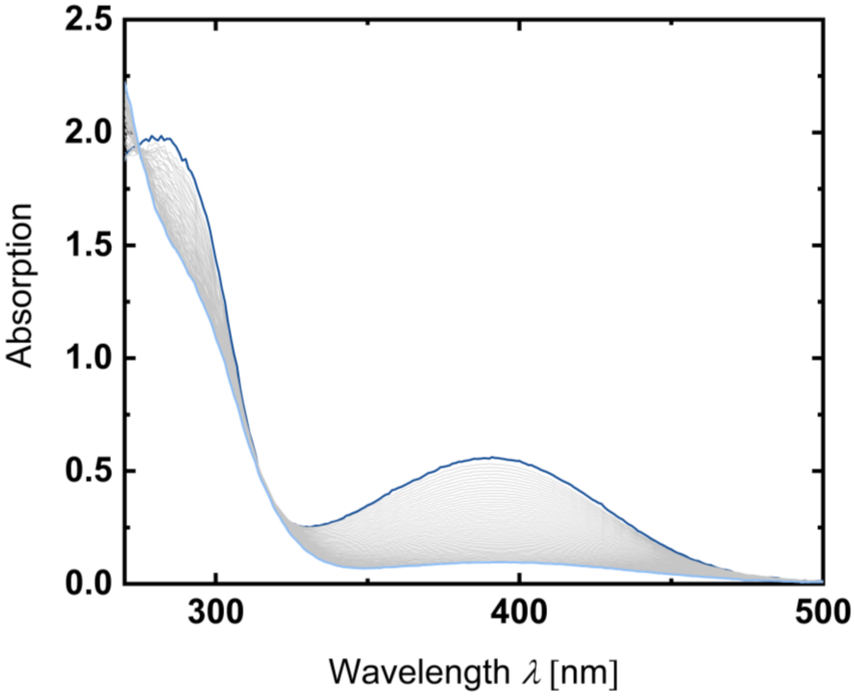


Figure S14 Absorption vs wavelength during hydrolysis of **2k** (–CN). Spectra were recorded every 1 min. The spectrum at *t* = 0 is indicated with a dark blue line.

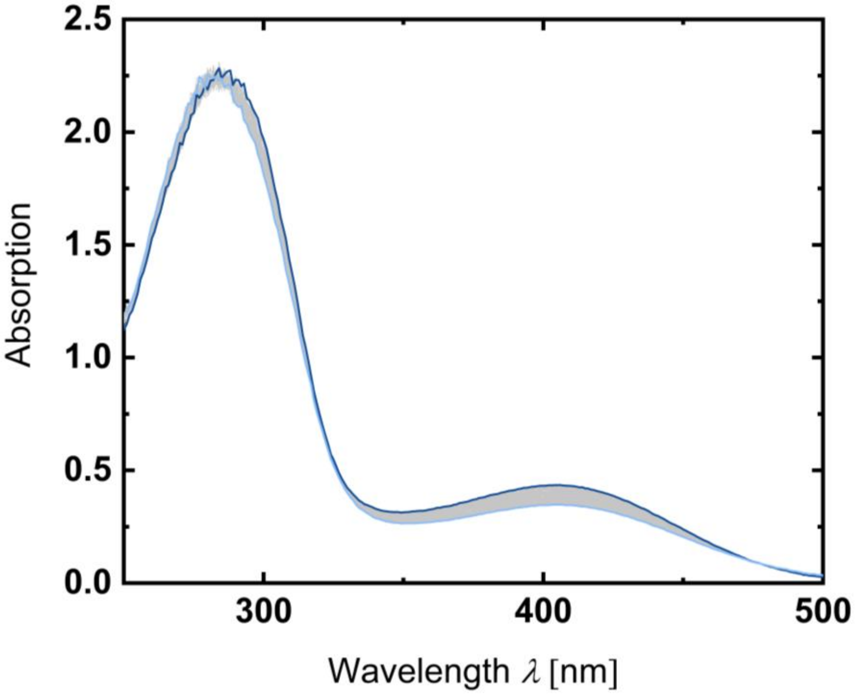


Figure S15 Absorption vs wavelength during hydrolysis of **2l** (–NO_2). Spectra were recorded every 2 min. The spectrum at *t* = 0 is indicated with a dark blue line.

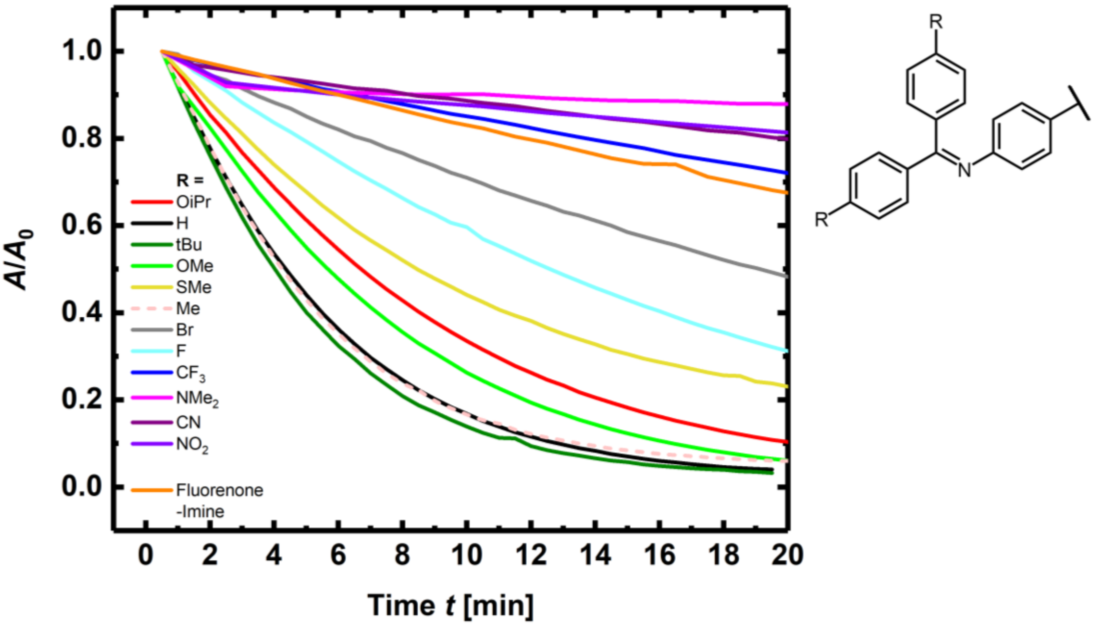


Figure S16. Absorption vs time during BP-imine hydrolysis in 50 °C 1,4-dioxane and 6 M AcOH, absorption was measured at the absorption maximum of the imine.

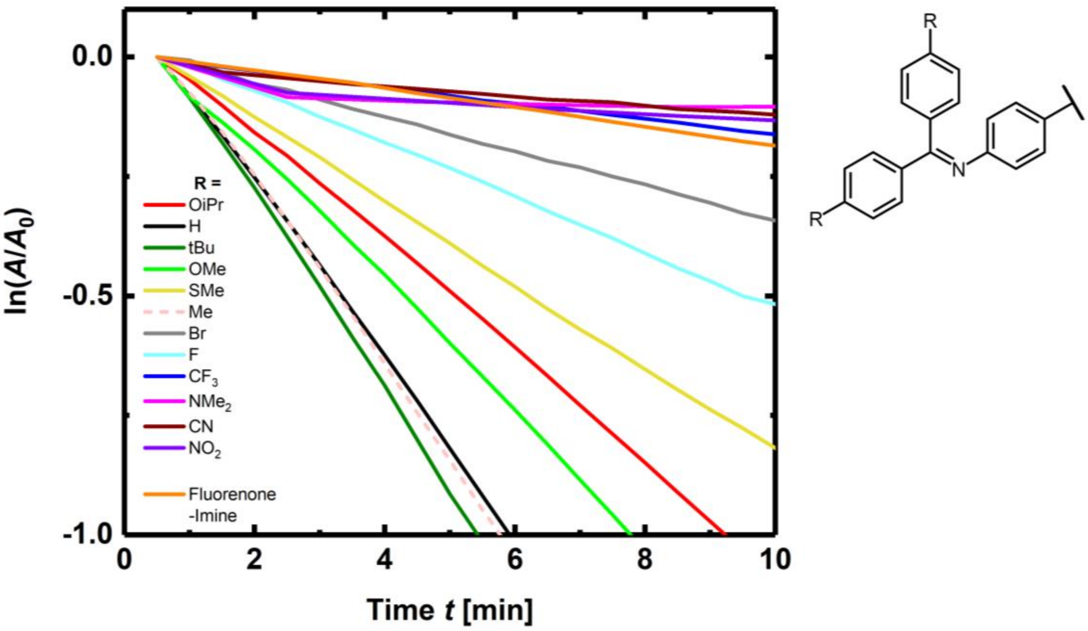


Figure S17. Logarithmic plot of absorption vs time during BP-imine hydrolysis in 50 °C 1,4-dioxane and 6 M AcOH, absorption was measured at the absorption maximum of the imine. The corresponding linear regressions are shown in the main text.

S5. Powder X-Ray Diffraction

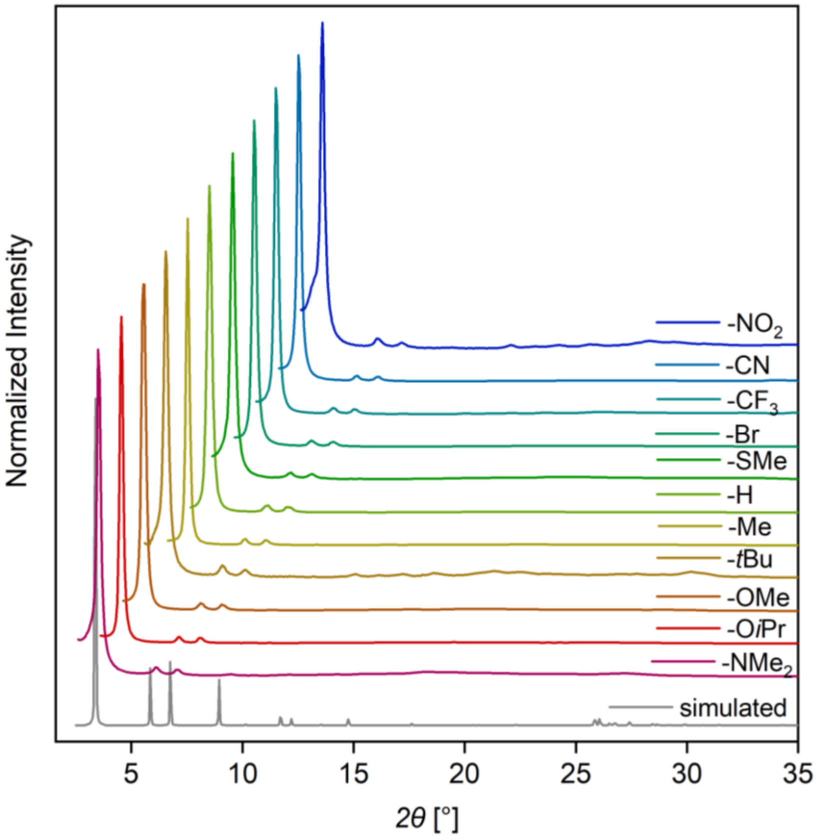


Figure S18 Staggered and stacked PXRD of BND-TFB COFs synthesized from various benzophenone imines, including simulated diffraction pattern (grey).

Domain sizes were estimated from the broadening of the <100> reflection by applying the Scherrer equation

$$\tau = \frac{\kappa\lambda}{\beta\cos\theta}$$

with

τ	domain size [nm]
κ	shape factor κ = 0.9 where it is assumed that the particles are spherical
λ	wavelength of the X-ray source, $\mathrm{CuK}_{\alpha 1} = 0.154056$
β	is the line broadening at half maximum intensity (FWHM) of the <100> peak in radians. This value is *uncorrected* for peak asymmetry and instrument line broadening.
θ	location of the <100> peak in degrees

Table 7 Line broadening and estimated domain size of BND-TFB COF synthesized from substituted benzophenone imines using vacuum activation.

Linear Linker	<100> 2θ [degrees]	β [radians]	τ [nm]
2a (–NMe$_2$)	3.55	0.00429	32.2
2b (–O*i*Pr)	3.55	0.00349	39.8
2c (–OMe)	3.55	0.00429	32.4
2d (–*t*Bu)	3.55	0.00472	29.4
2e (–Me)	3.54	0.00342	40.5
2f (–SMe)	3.56	0.00465	29.8
2g (–H)	3.52	0.00488	28.4
2i (–Br)	3.54	0.00431	32.2
2j (–CF$_3$)	3.54	0.00348	39.8
2k (–CN)	3.55	0.00398	34.9
2l (–NO$_2$)	3.59	0.00481	33.2

S6. Adsorption Desorption Isotherms and BET Plots

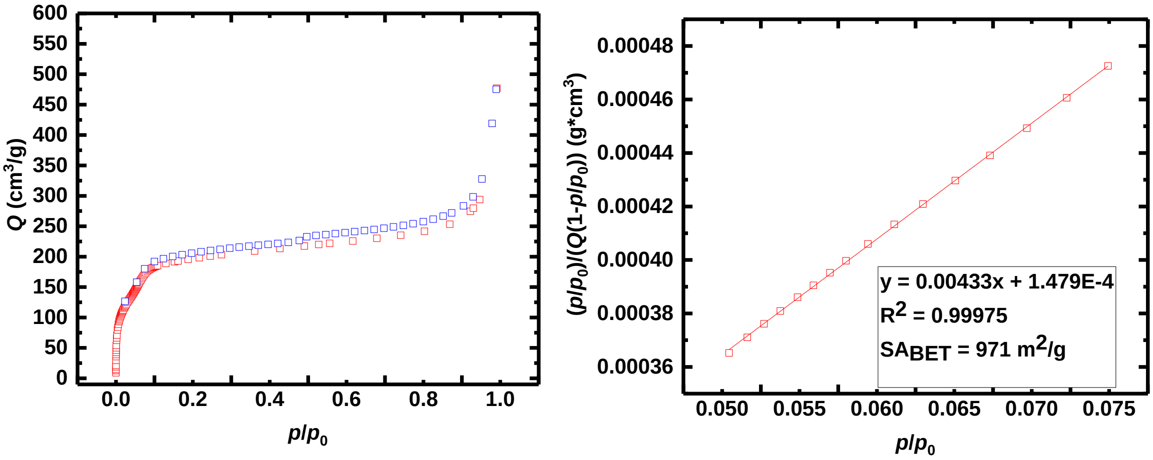


Figure S19 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2a** and vacuum activation.

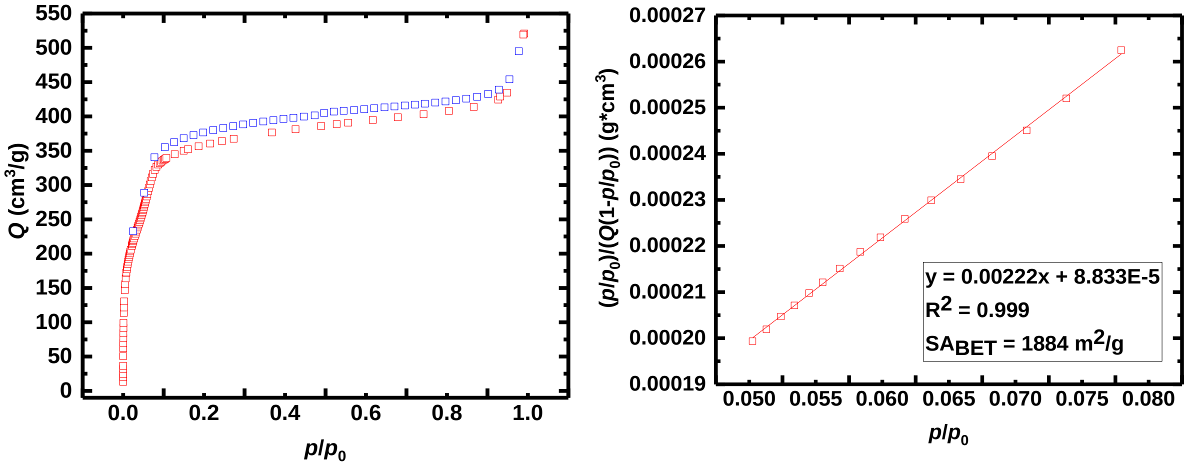


Figure S20 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2b** and vacuum activation.

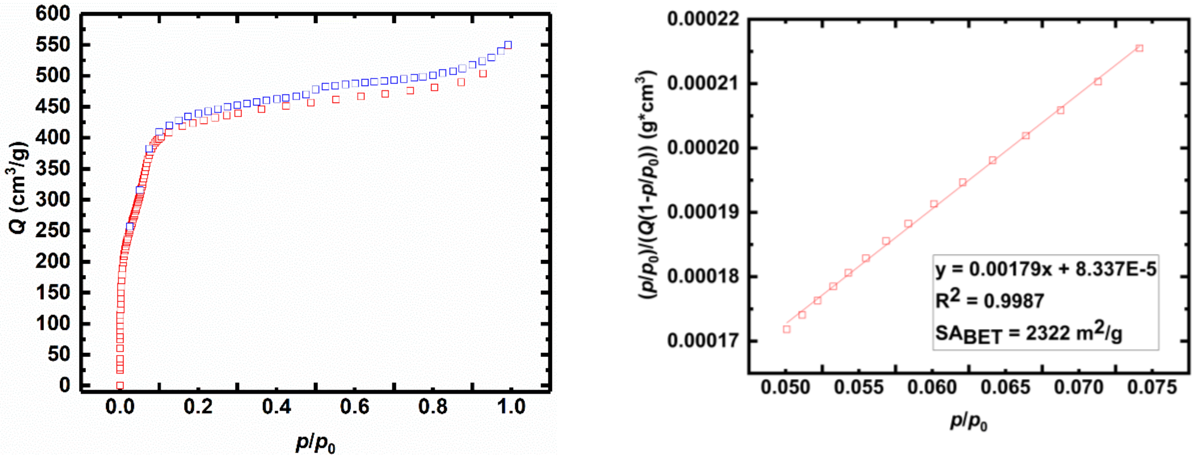


Figure S21 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2c** and vacuum activation.

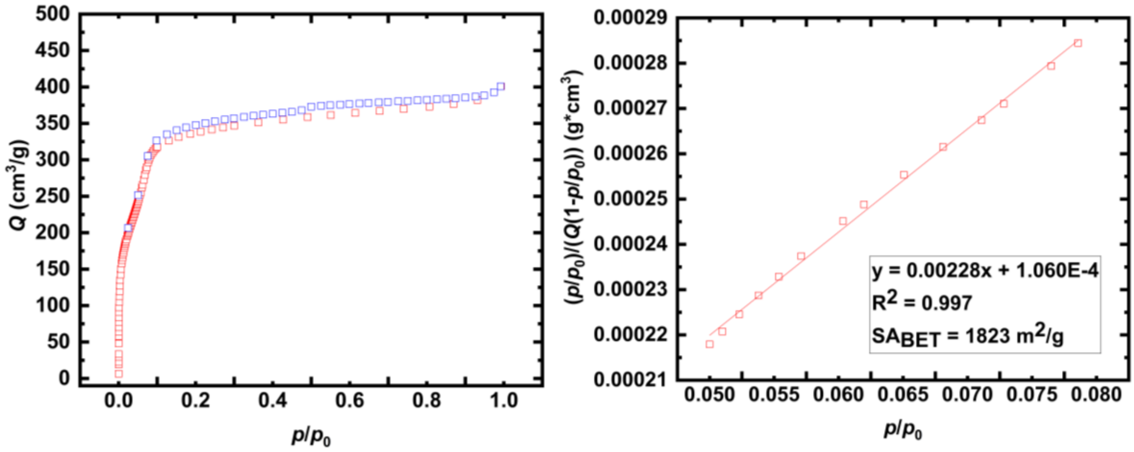


Figure S22 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2d** and vacuum activation.

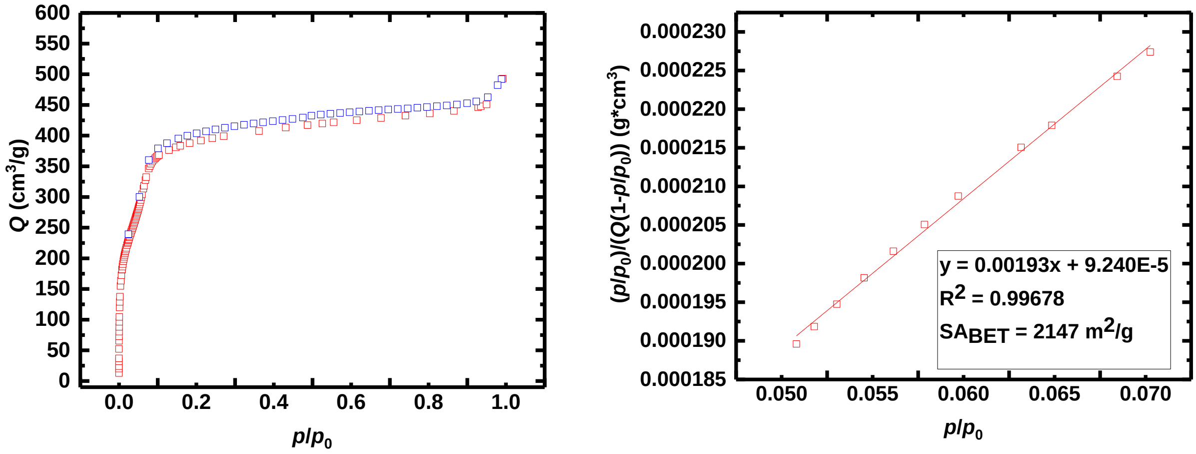


Figure S23 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2e** and vacuum activation.

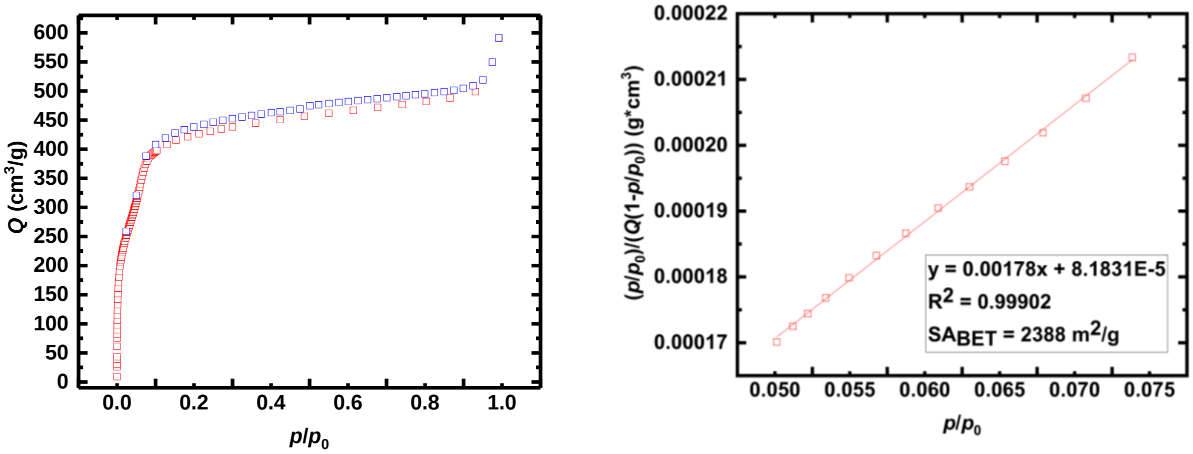


Figure S24 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2f** and vacuum activation.

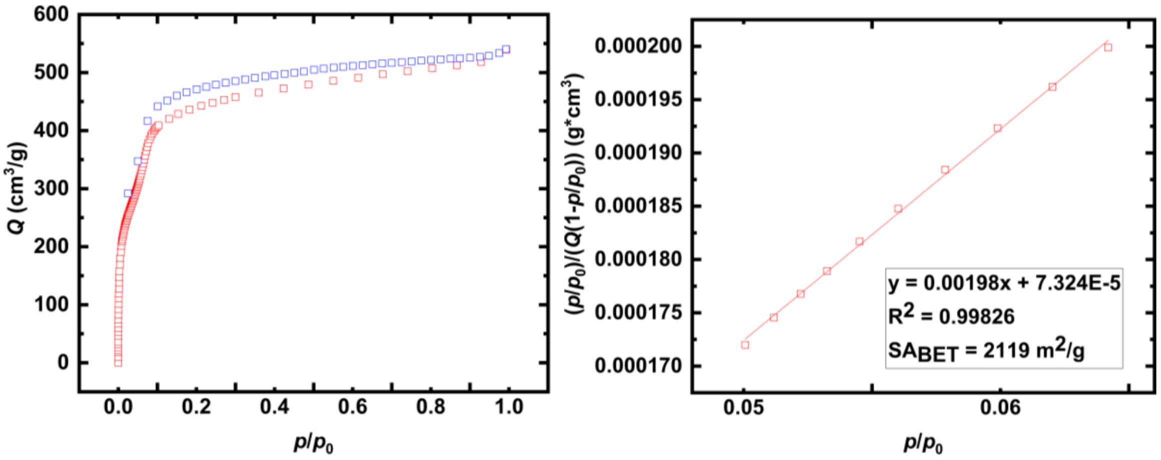


Figure S25 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2g** and vacuum activation.

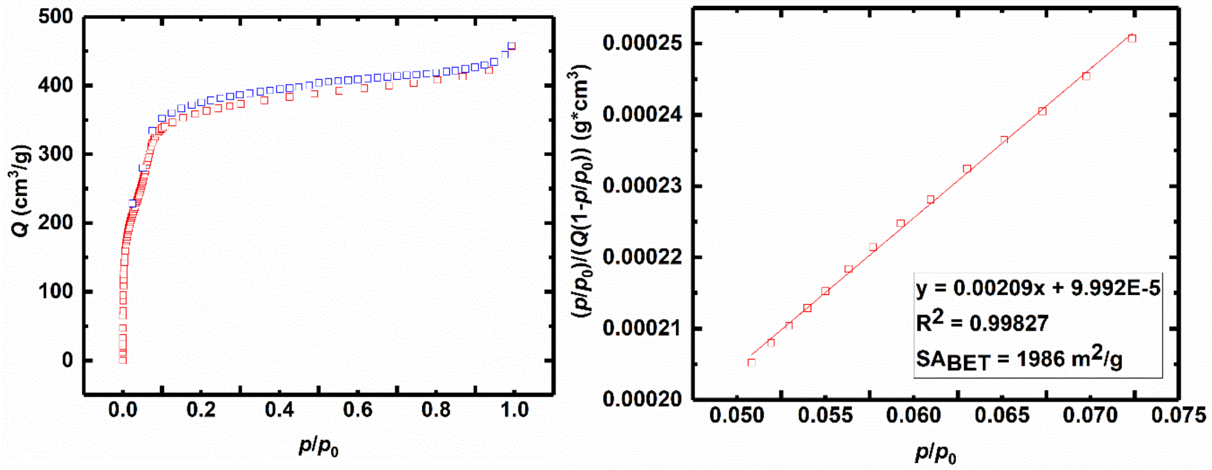


Figure S26 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2h** and vacuum activation.

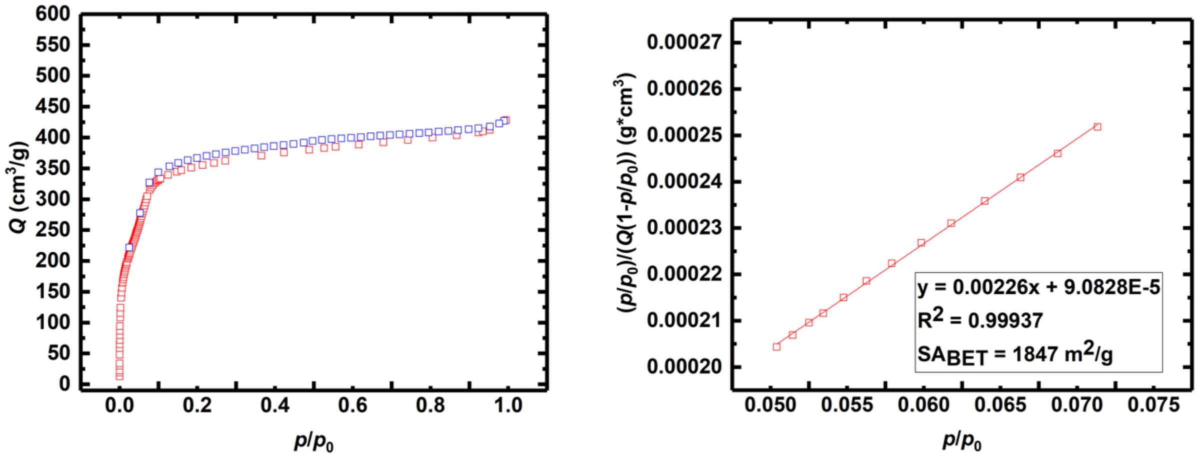


Figure S27 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2i** and vacuum activation.

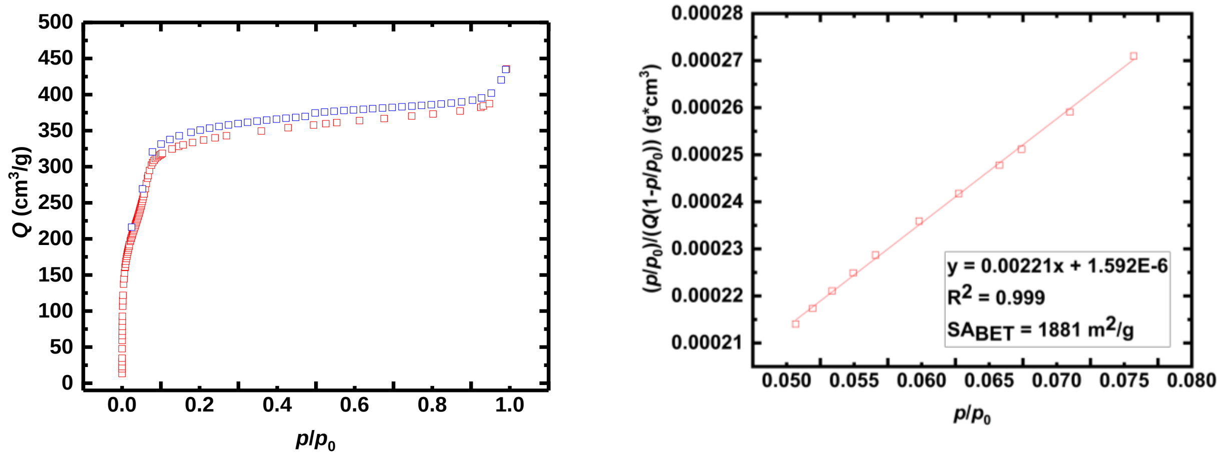


Figure S28 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2j** and vacuum activation.

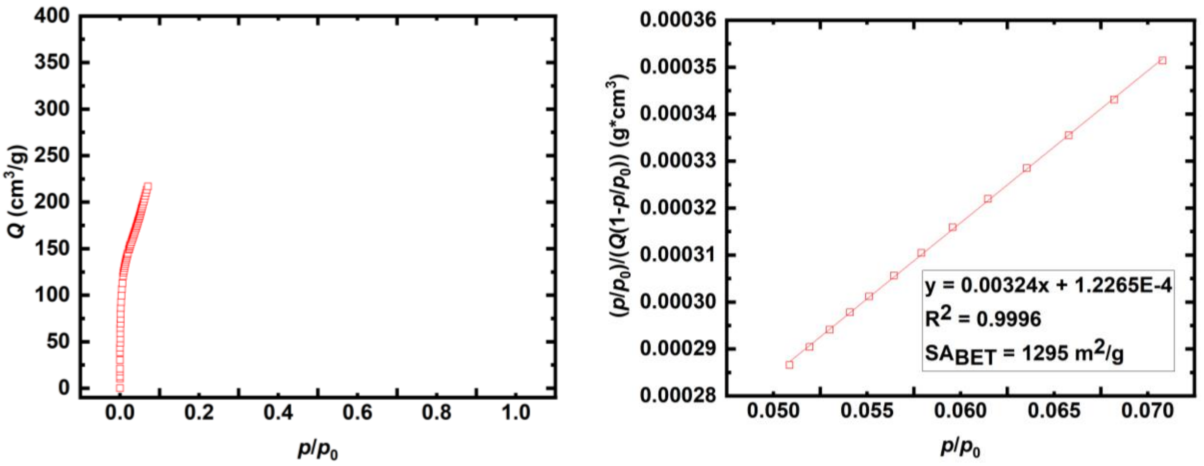


Figure S29 Nitrogen adsorption curve and BET surface analysis of BND-TFB COF synthesized from **2k** and vacuum activation.

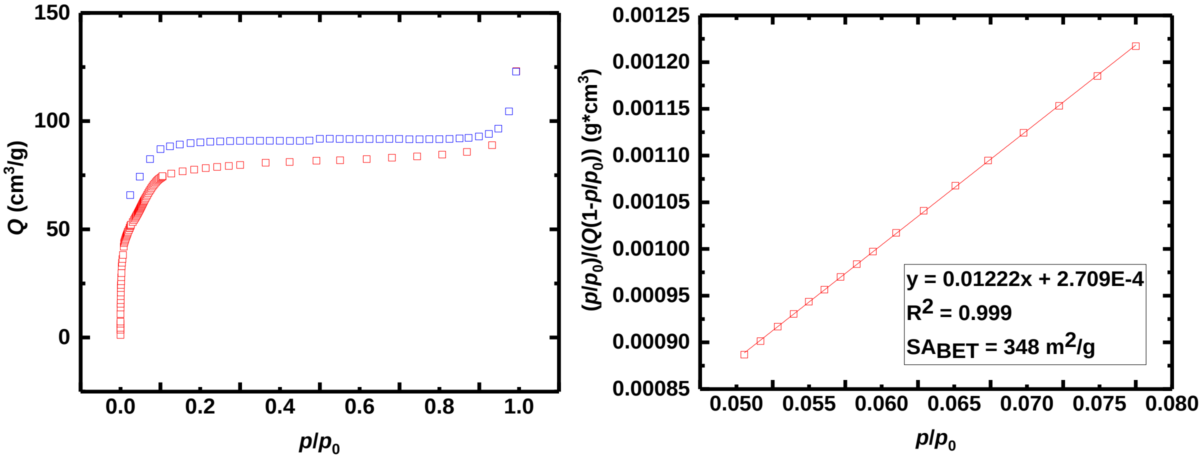


Figure S30 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2l** and vacuum activation.

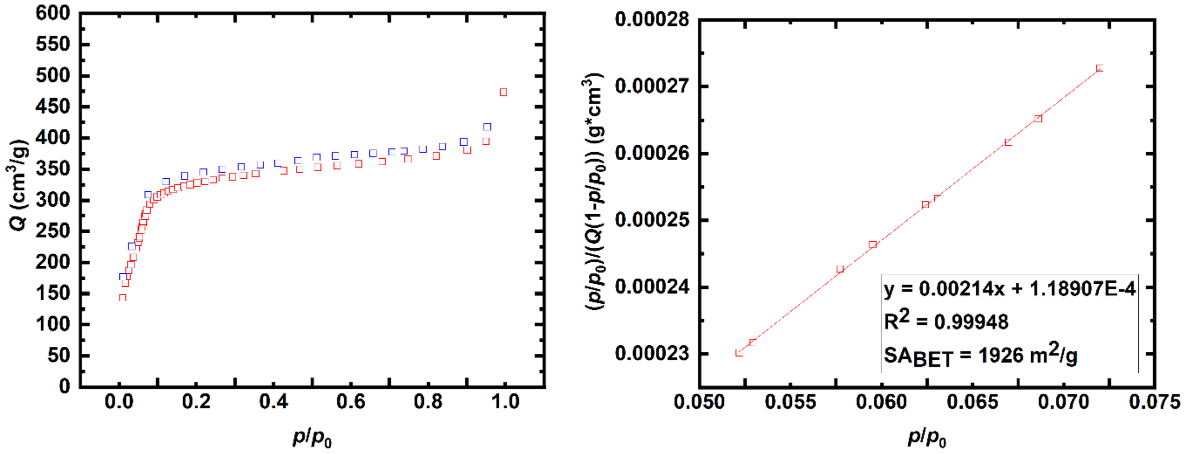


Figure S31 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2a** and *sc*CO_2 activation I.

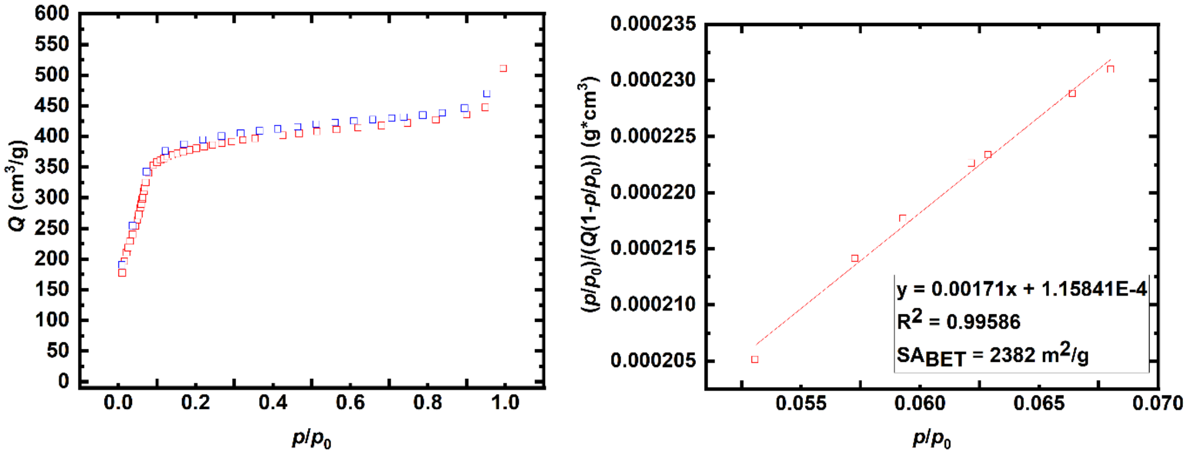


Figure S32 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2a** and *sc*CO_2 activation II.

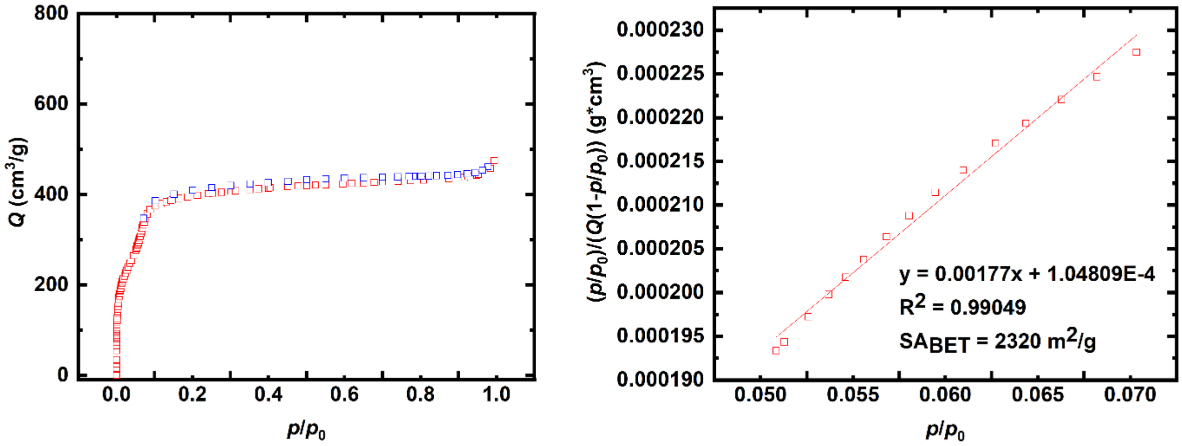


Figure S33 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2b** and *sc*CO_2 activation I.

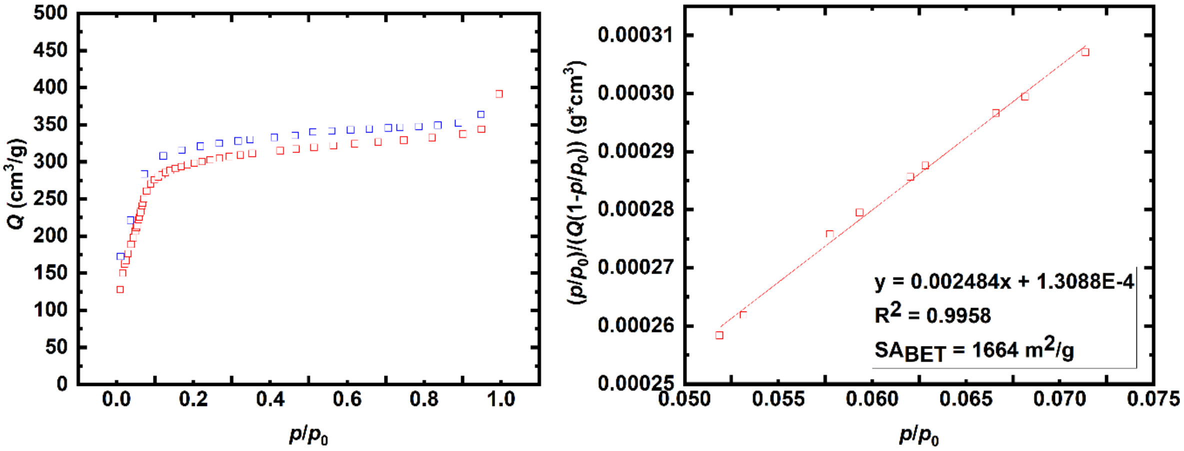


Figure S34 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2b** and *sc*CO_2 activation II.

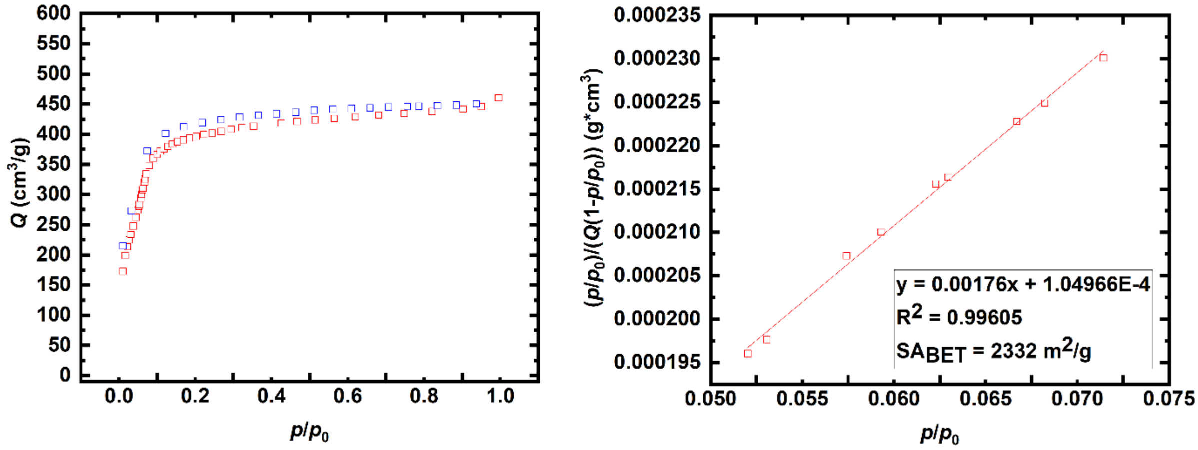


Figure S35 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2g** and *sc*CO_2 activation I.

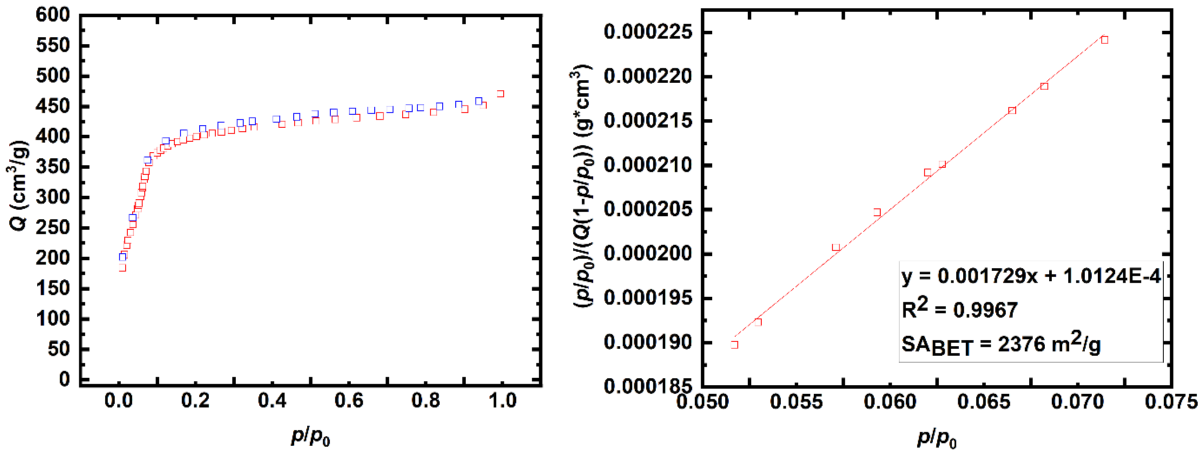


Figure S36 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2g** and *sc*CO_2 activation II.

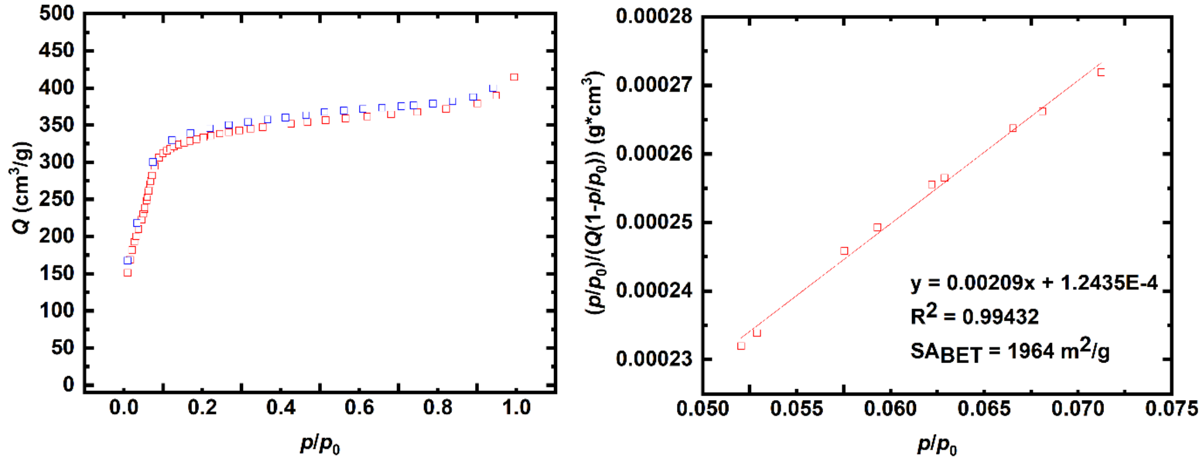


Figure S37 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2k** and *sc*CO_2 activation I.

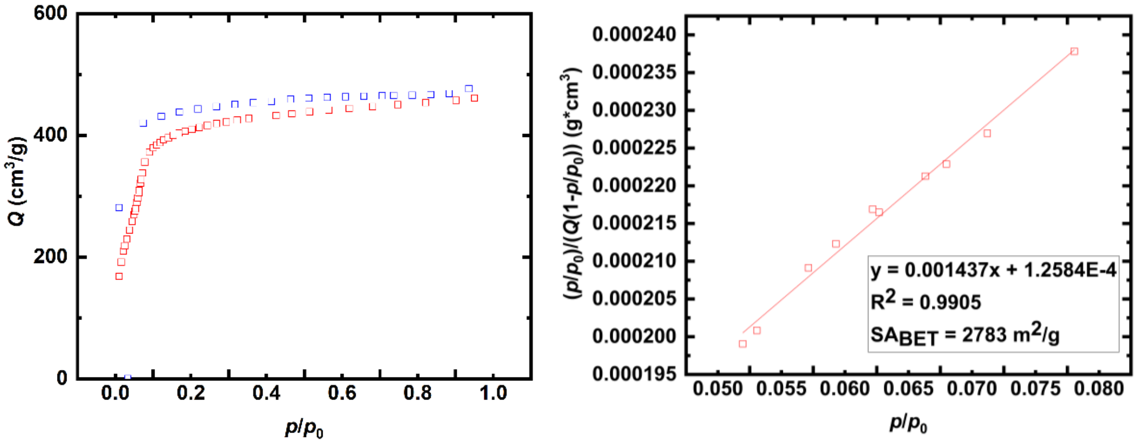


Figure S38 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2k** and *sc*CO_2 activation II.

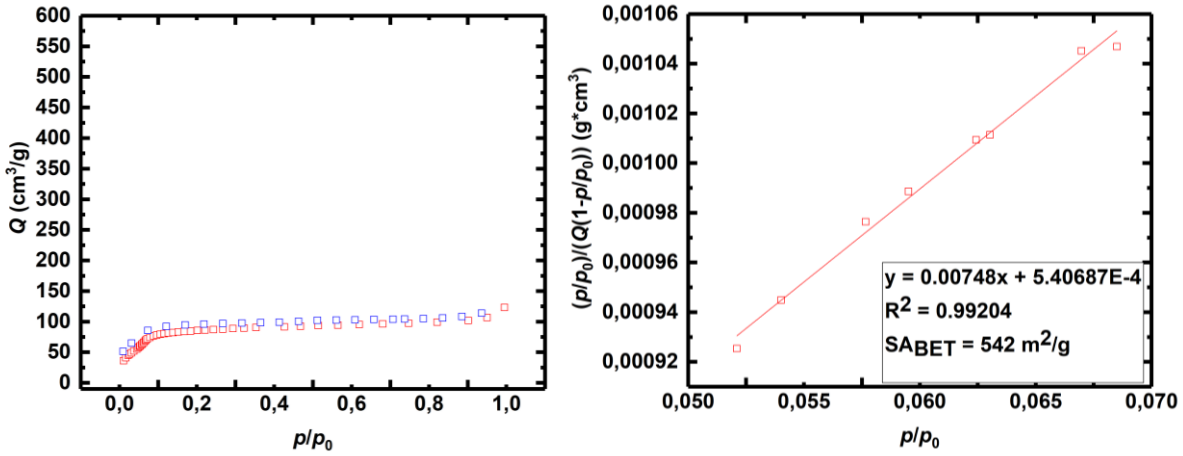


Figure S39 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2l** and *sc*CO_2 activation I.

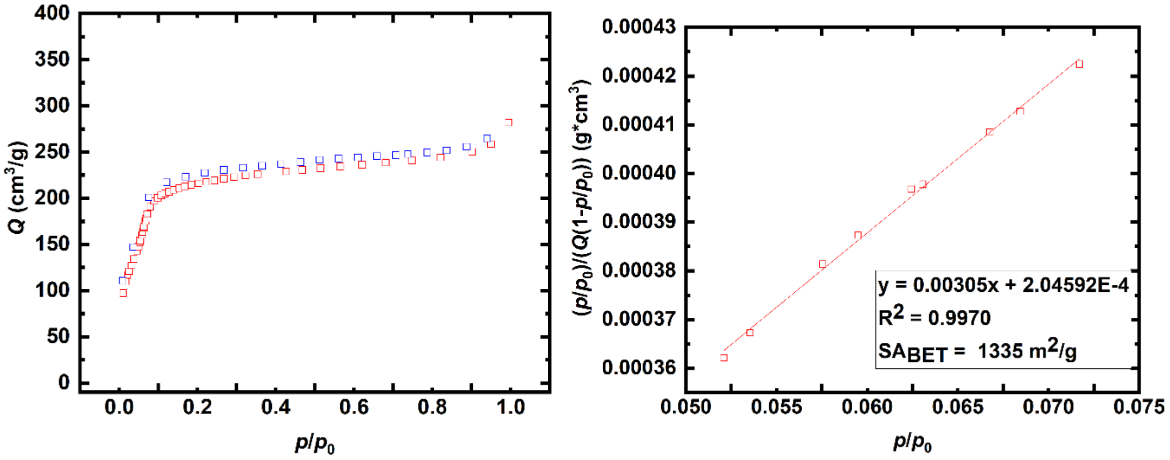


Figure S40 Nitrogen adsorption/desorption curves and BET surface analysis of BND-TFB COF synthesized from **2l** and *sc*CO_2 activation II.

S7. NMR Spectra

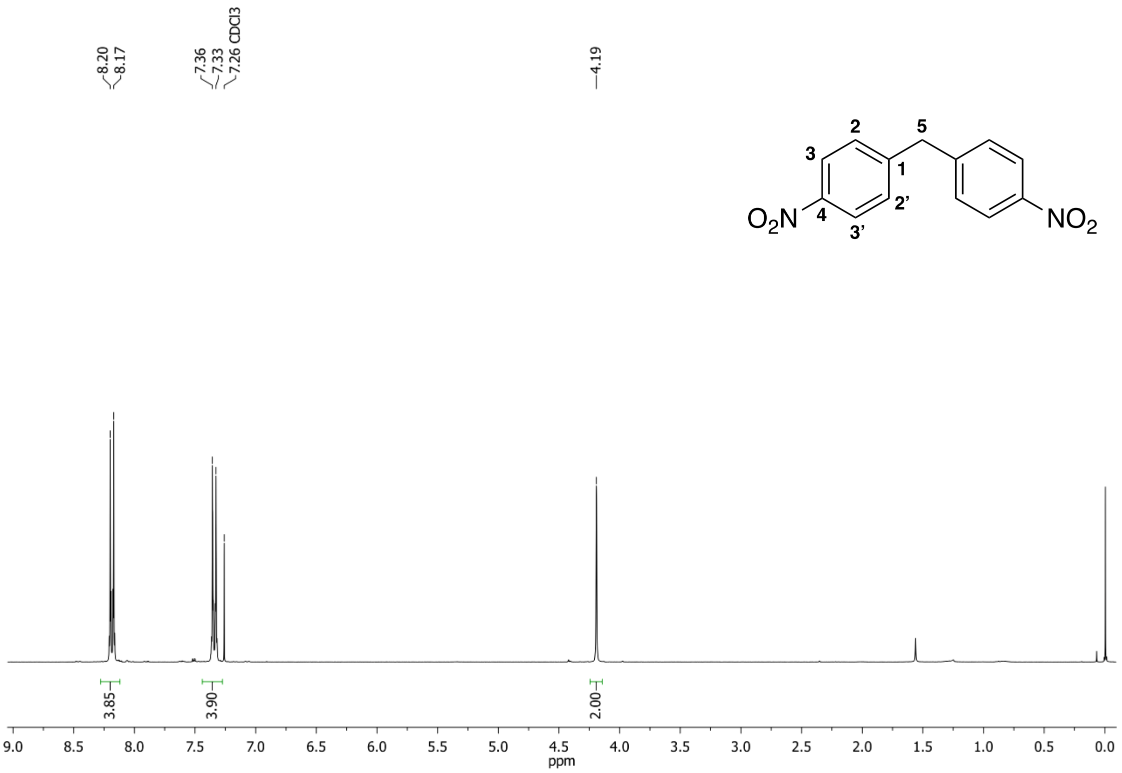


Figure S41 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of 4,4’-dinitrodiphenylmethane (**S1**).

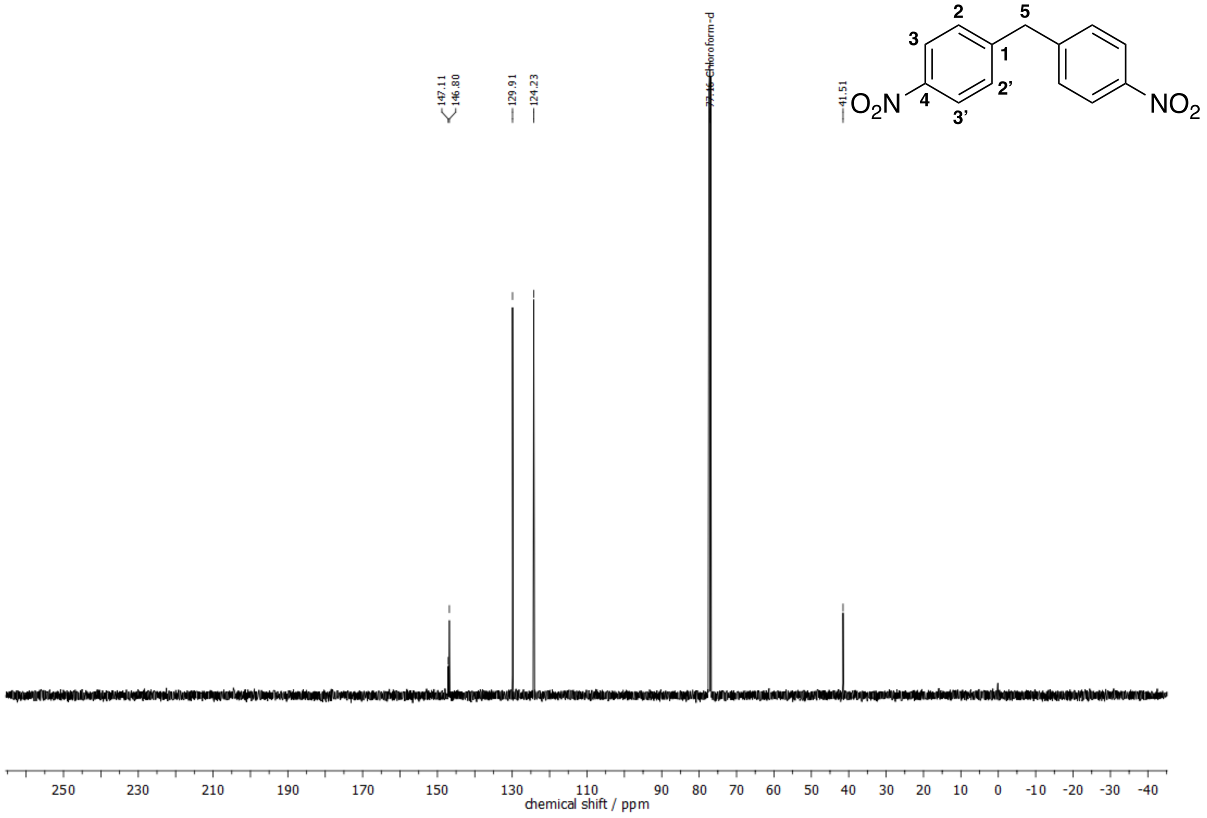


Figure S42 ^{13}C NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of 4,4’-dinitrodiphenylmethane (**S1**).

Figure S43 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of Bis(4-isopropoxyphenyl)-methanone (**1b**).

Figure S44 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of Bis(4-isopropoxyphenyl)-methanone (**1b**).

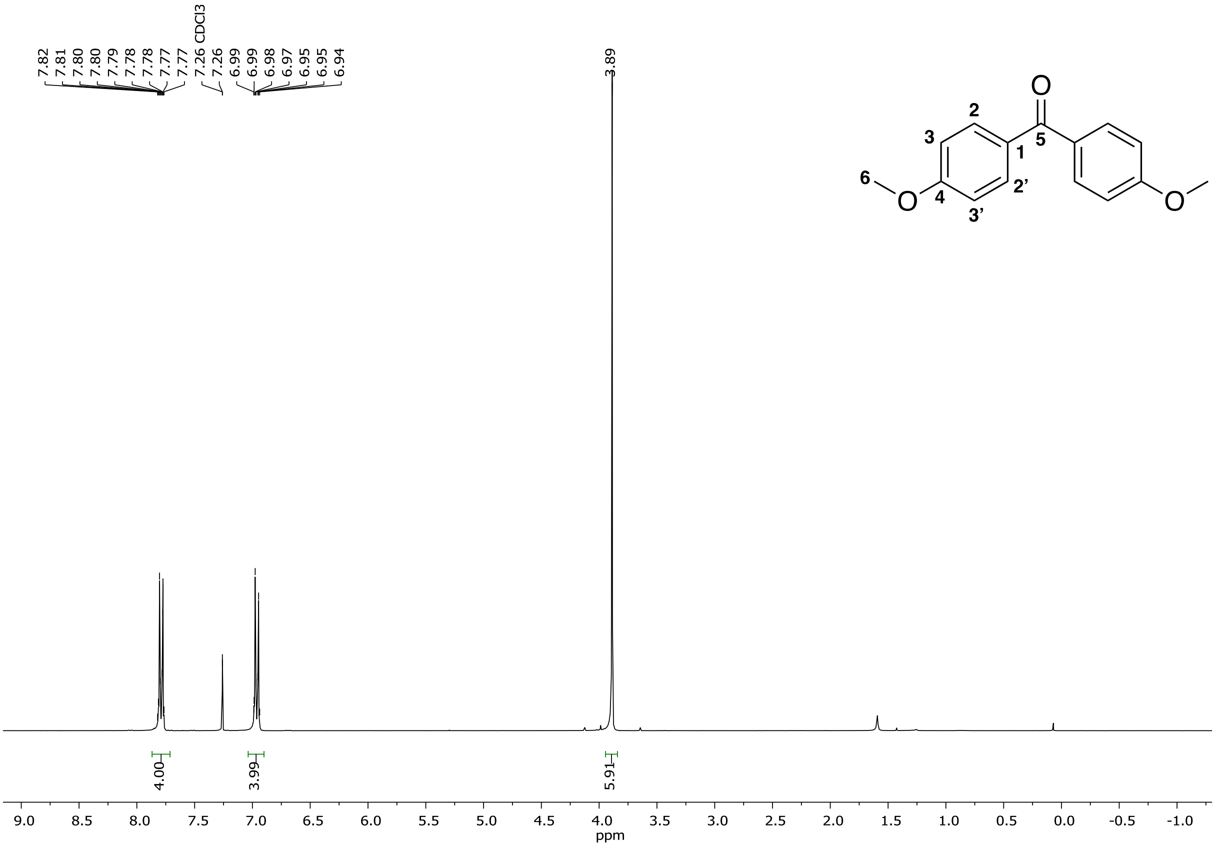


Figure S45 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of Bis(4-(hydroxymethyl)phenyl)-methanone (**1c**).

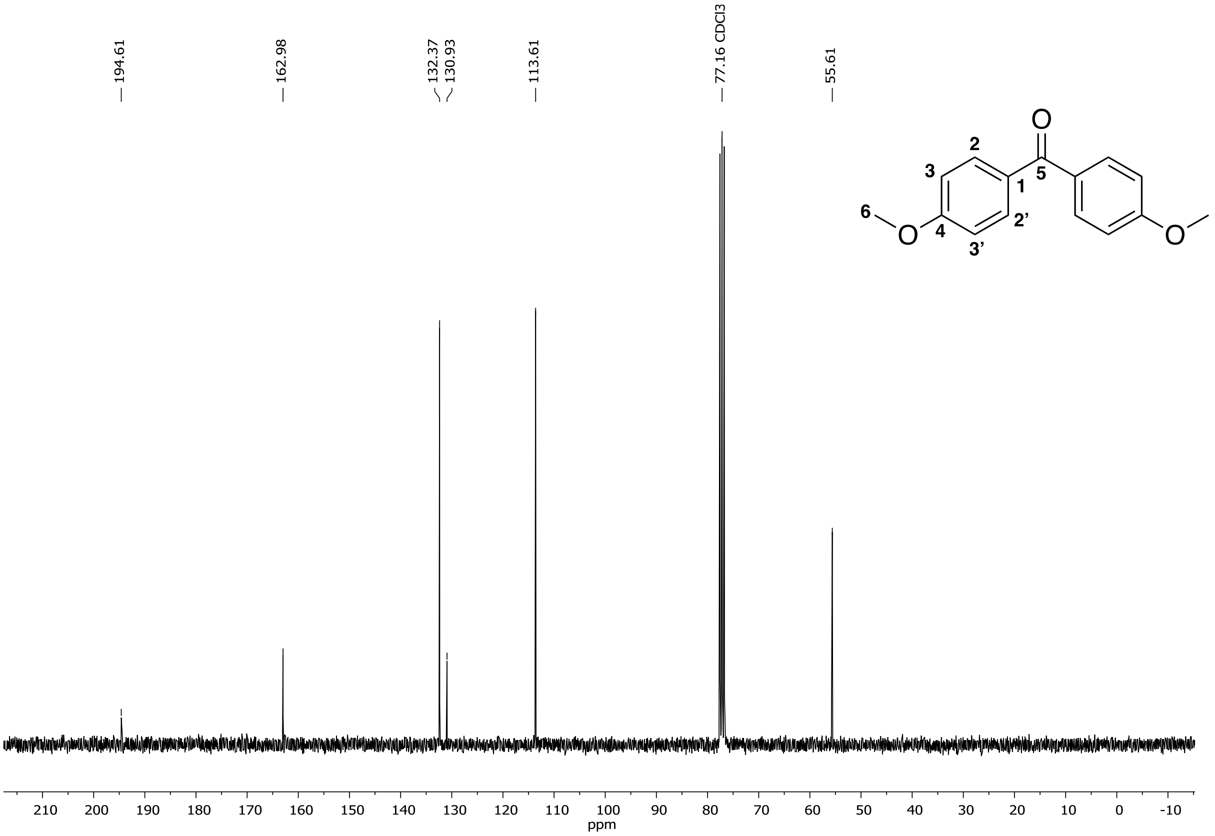


Figure S46 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of Bis(4-(hydroxymethyl)phenyl)-methanone (**1c**).

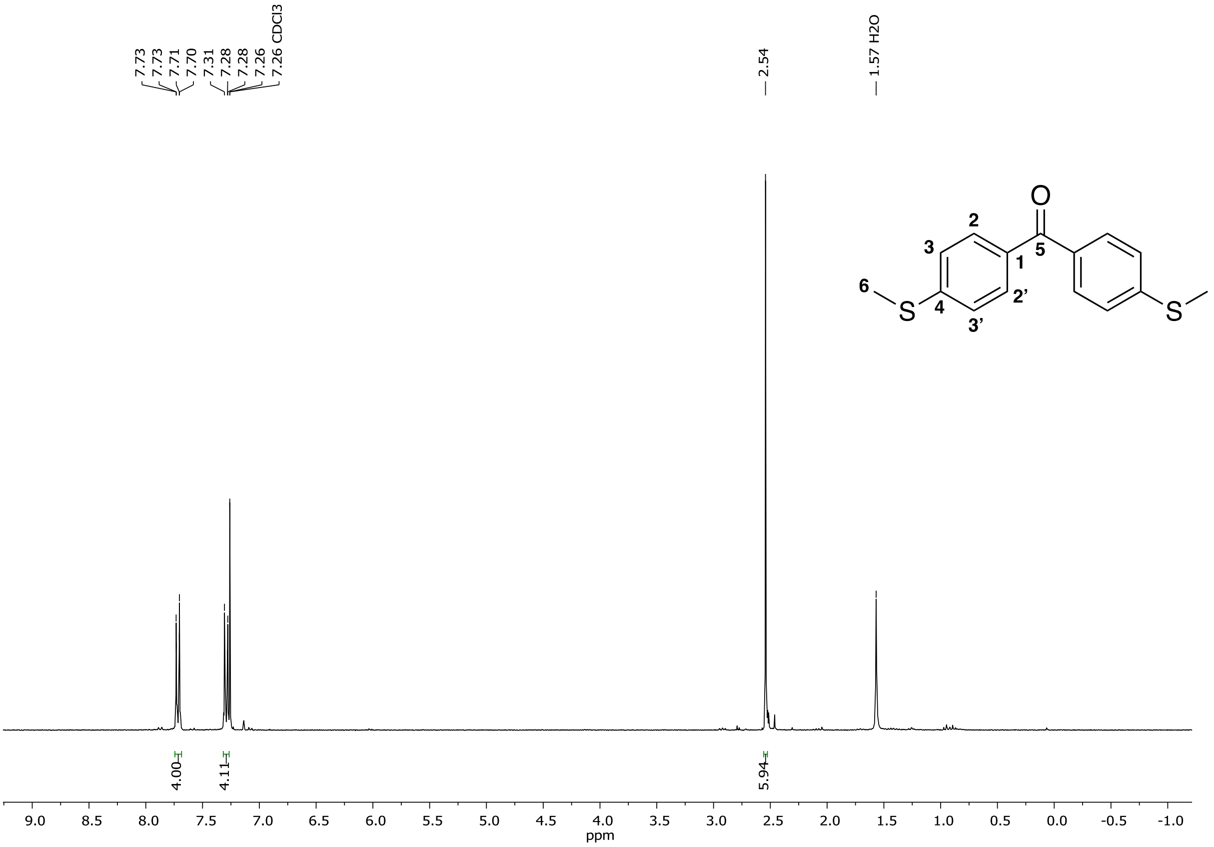


Figure S47 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of Bis(4-(methylthio)phenyl)-methanone (**1f**).

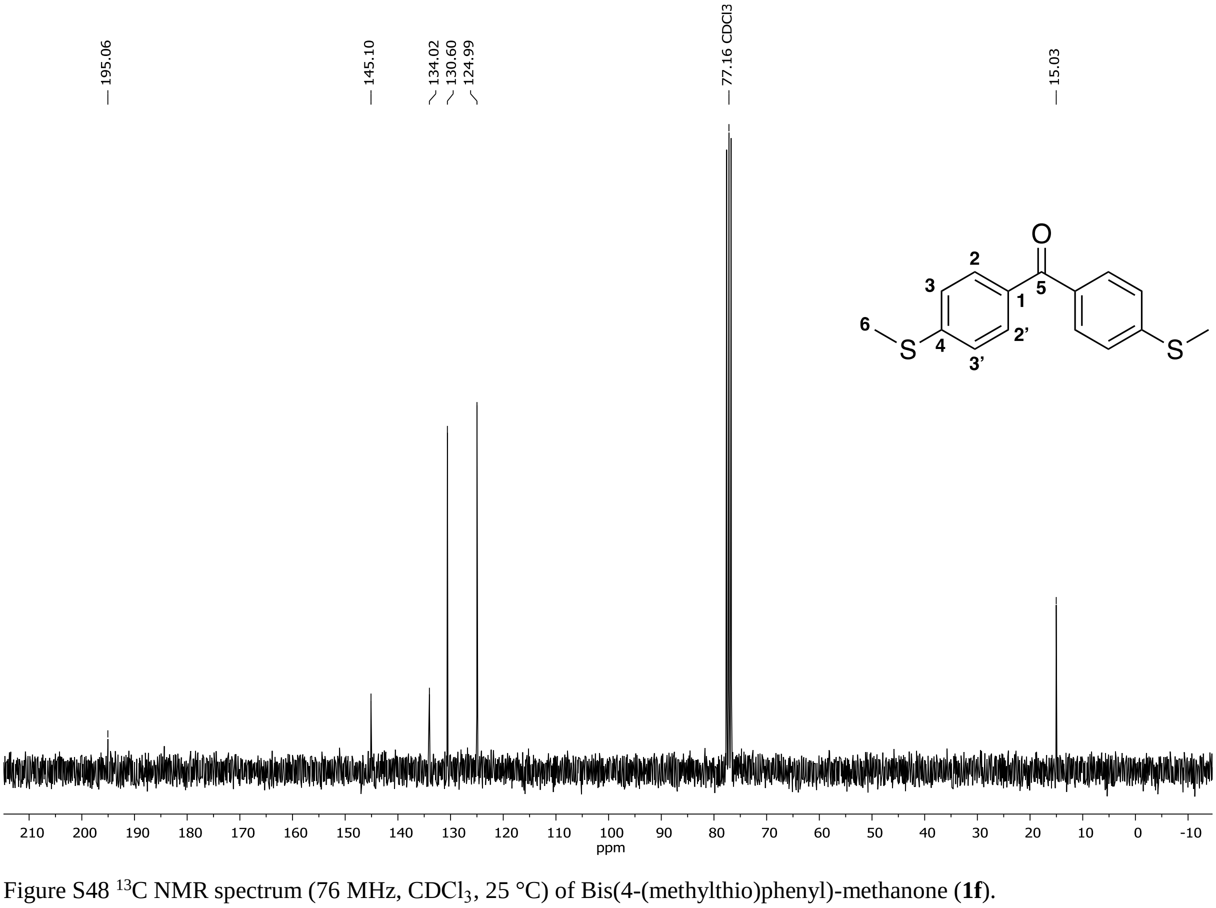


Figure S48 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of Bis(4-(methylthio)phenyl)-methanone (**1f**).

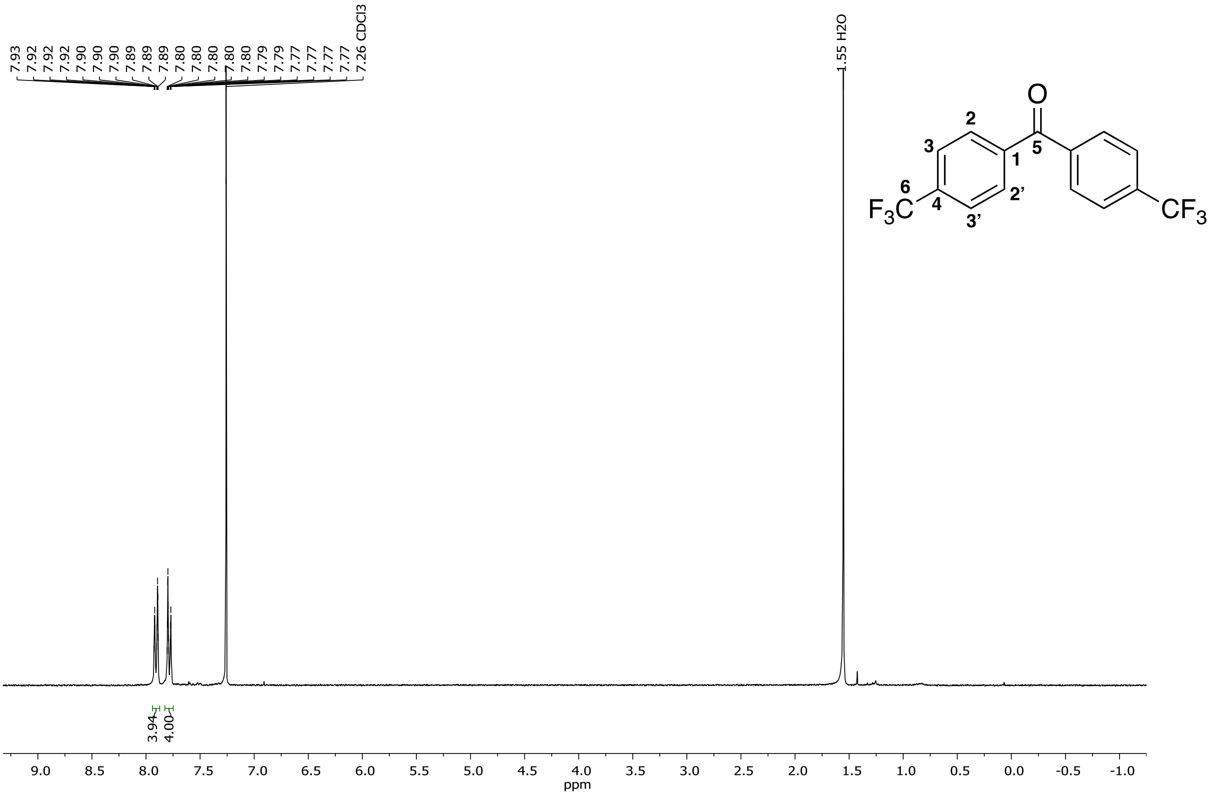


Figure S49 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of Bis(4(trifluoromethyl)phenyl)-methanone (**1j**).

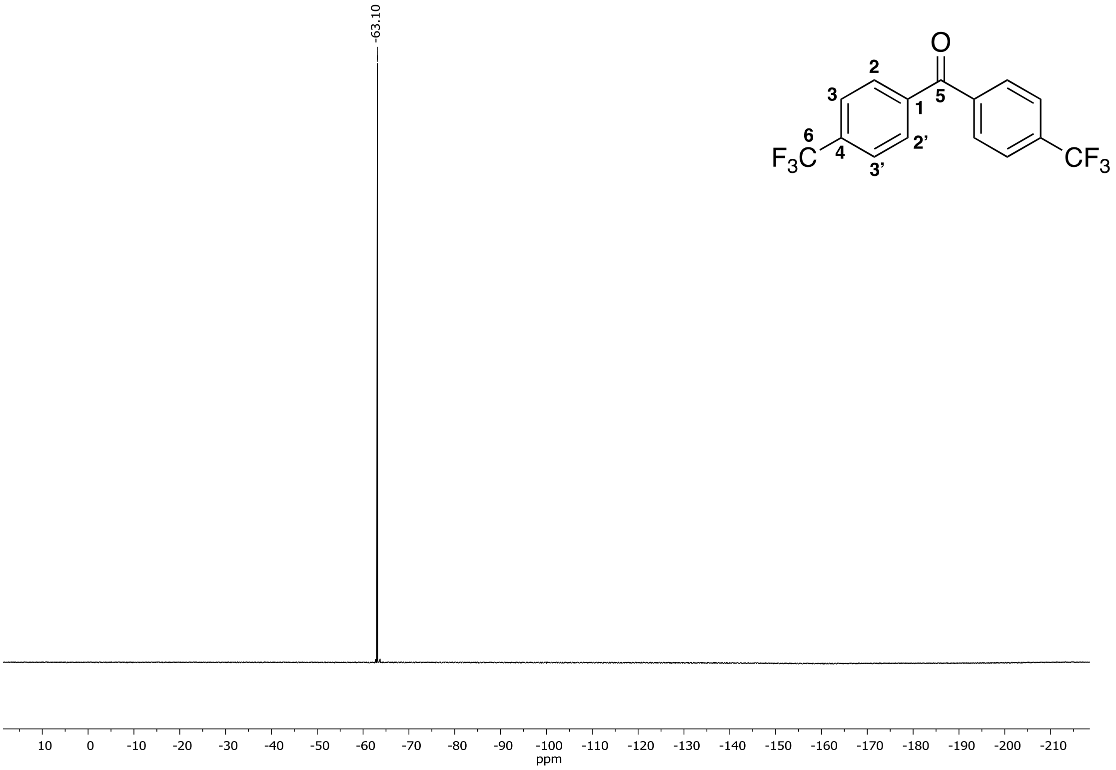


Figure S50 ^{19}F NMR spectrum (282 MHz, $CDCl_3$, 25 °C) of Bis(4-(trifluoromethyl)phenyl)-methanone (**1j**).

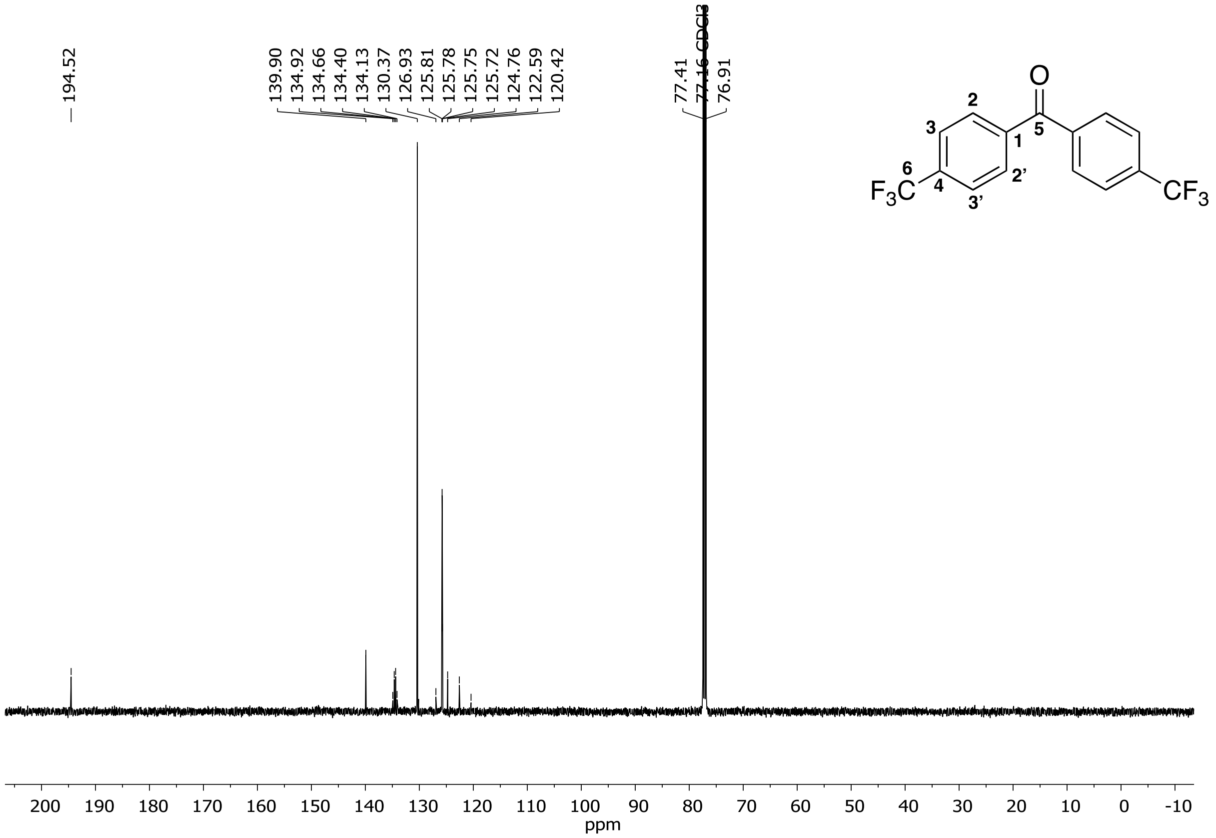


Figure S51 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of Bis(4-(trifluoromethyl)phenyl)-methanone (**1j**)

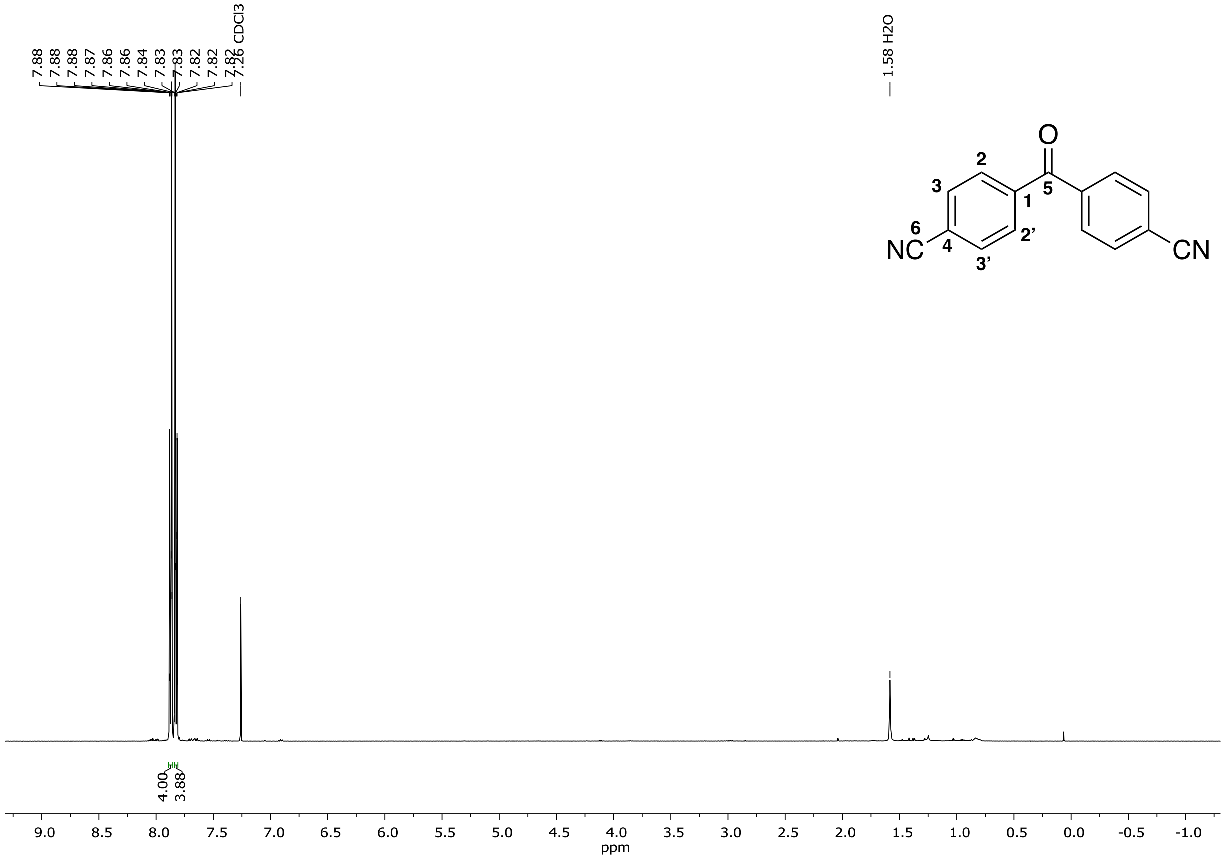


Figure S52 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of 4,4'-carbonyldibenzonitrile (**1k**).

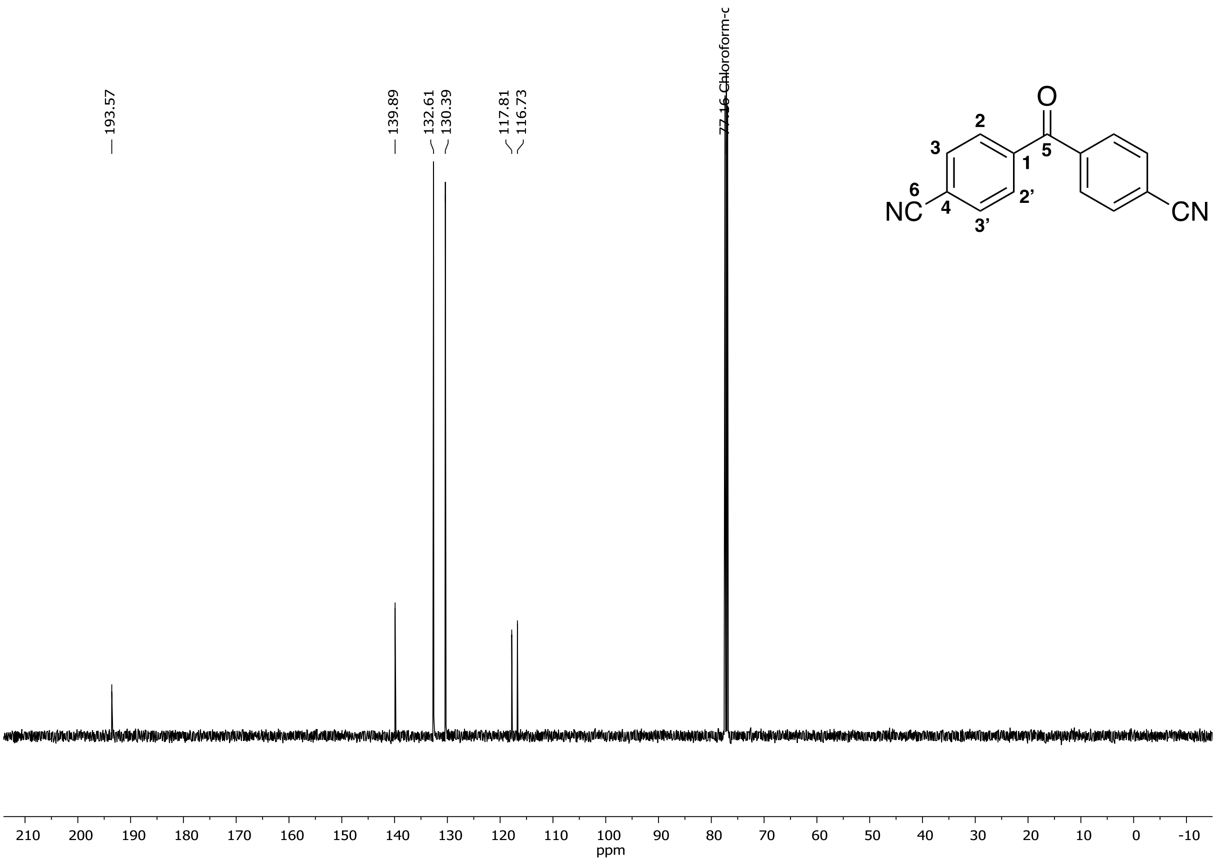


Figure S53 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of 4,4'-carbonyldibenzonitrile (**1k**).

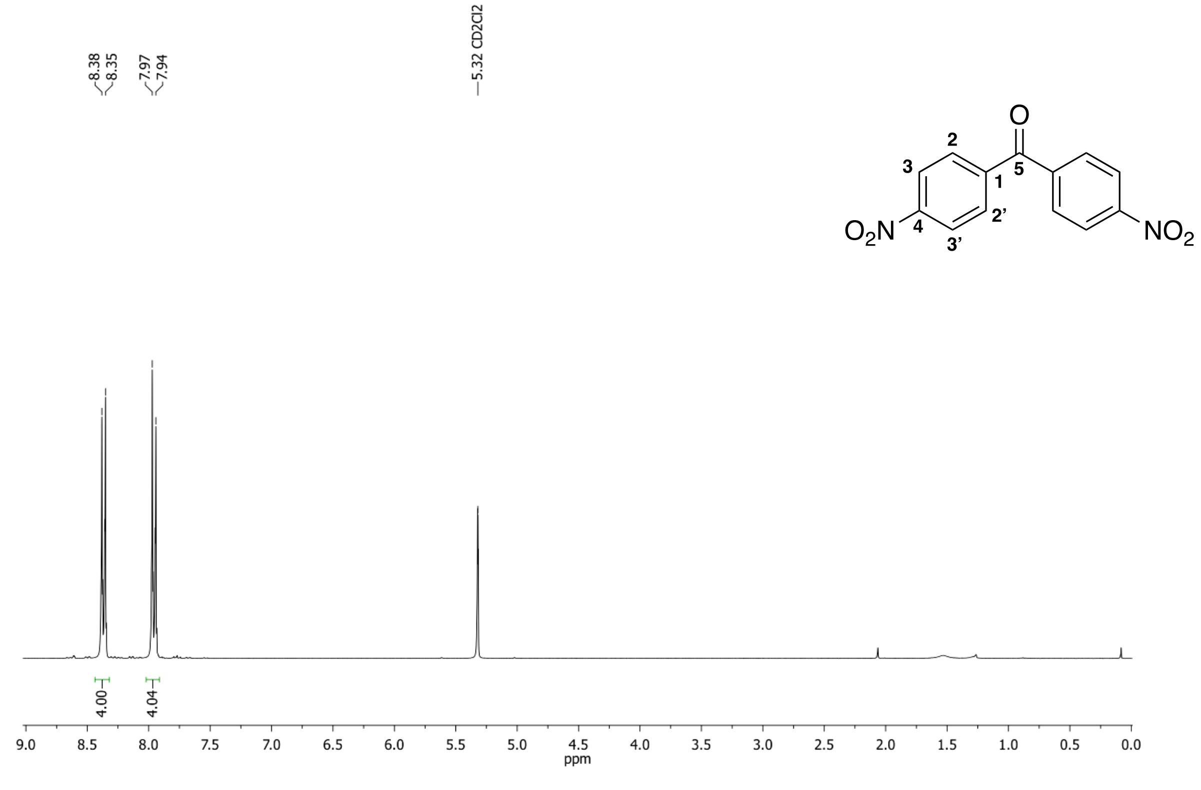


Figure S54 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of Bis(4-(nitro)phenyl)methanone (**1l**).

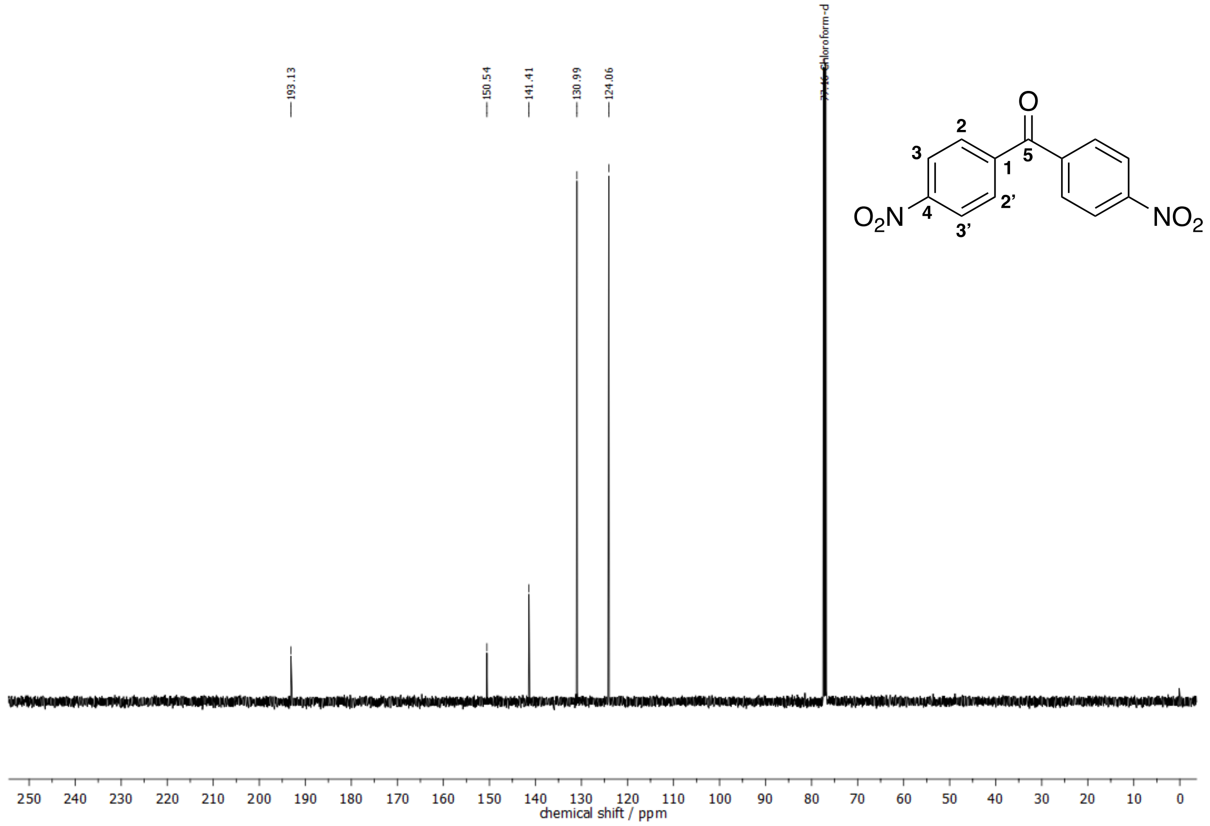


Figure S55 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of Bis(4-(nitro)phenyl)methanone (**1l**).

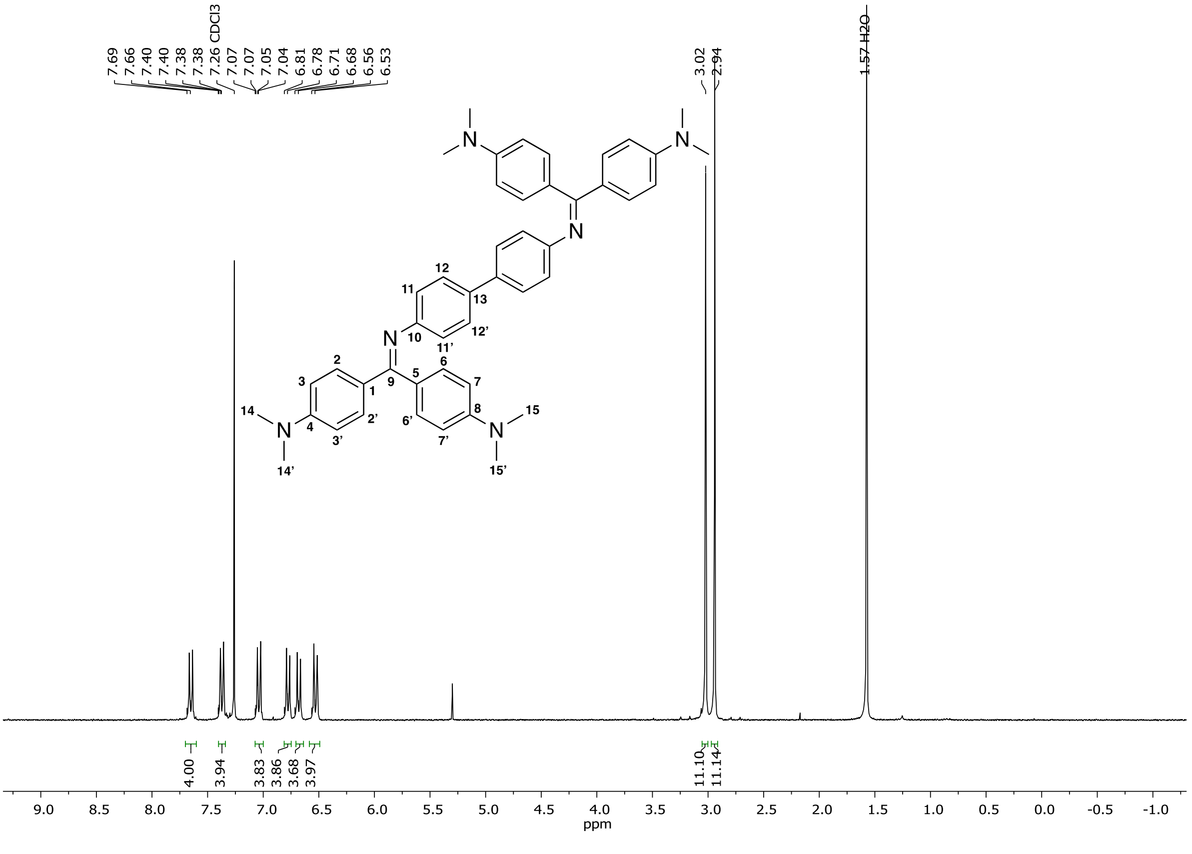


Figure S56 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-di(*N'',N'''*-dimethylamino-benzophenone)benzidine imine (**2a**).

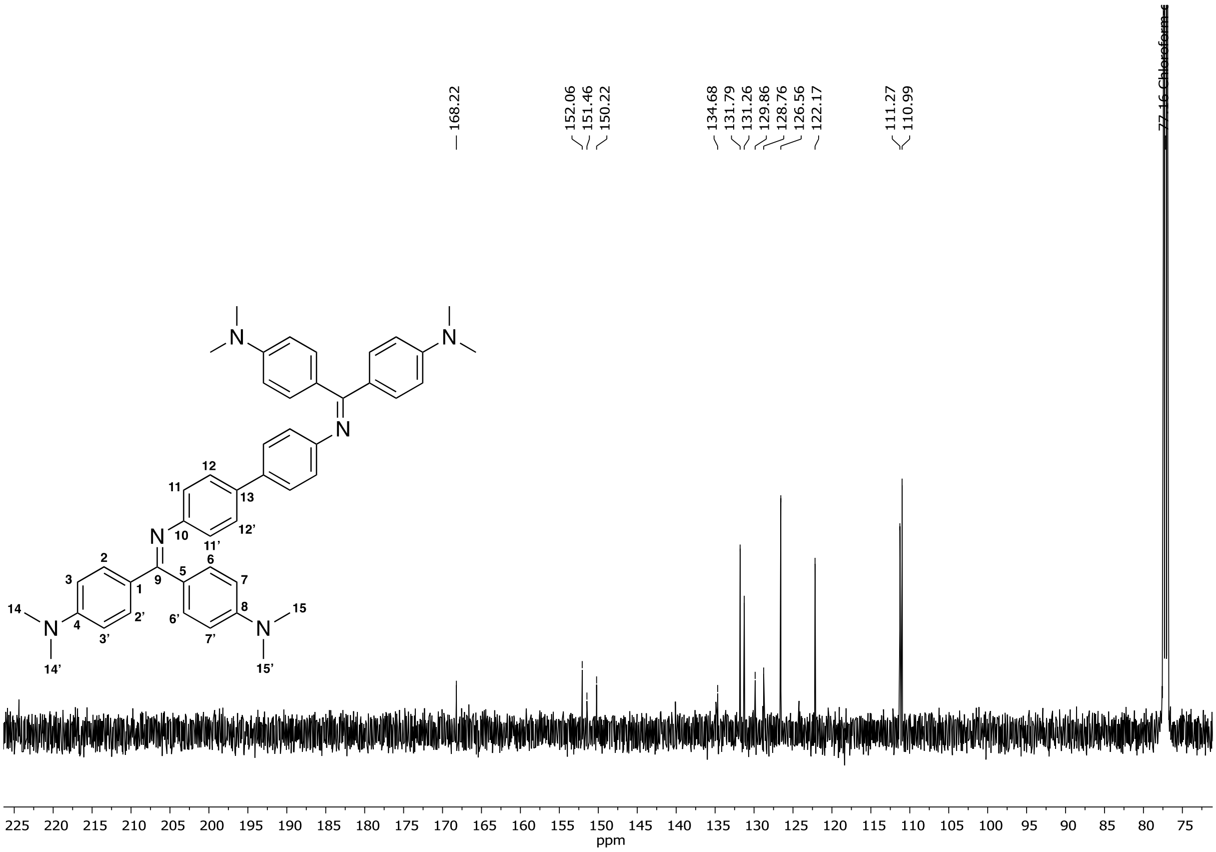


Figure S57 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-di(*N'',N'''*-dimethylamino-benzophenone)benzidine imine (**2a**).

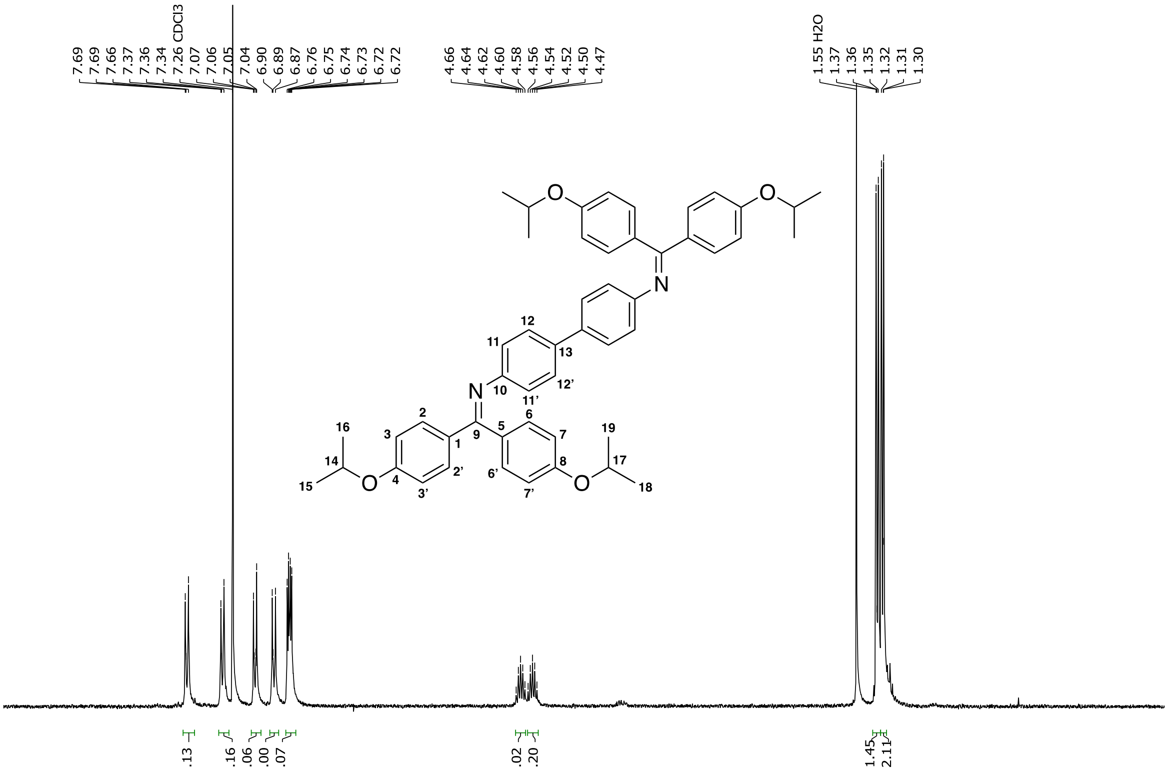


Figure S58 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-diisopropoxy-benzophenone)benzidine imine (**2b**).

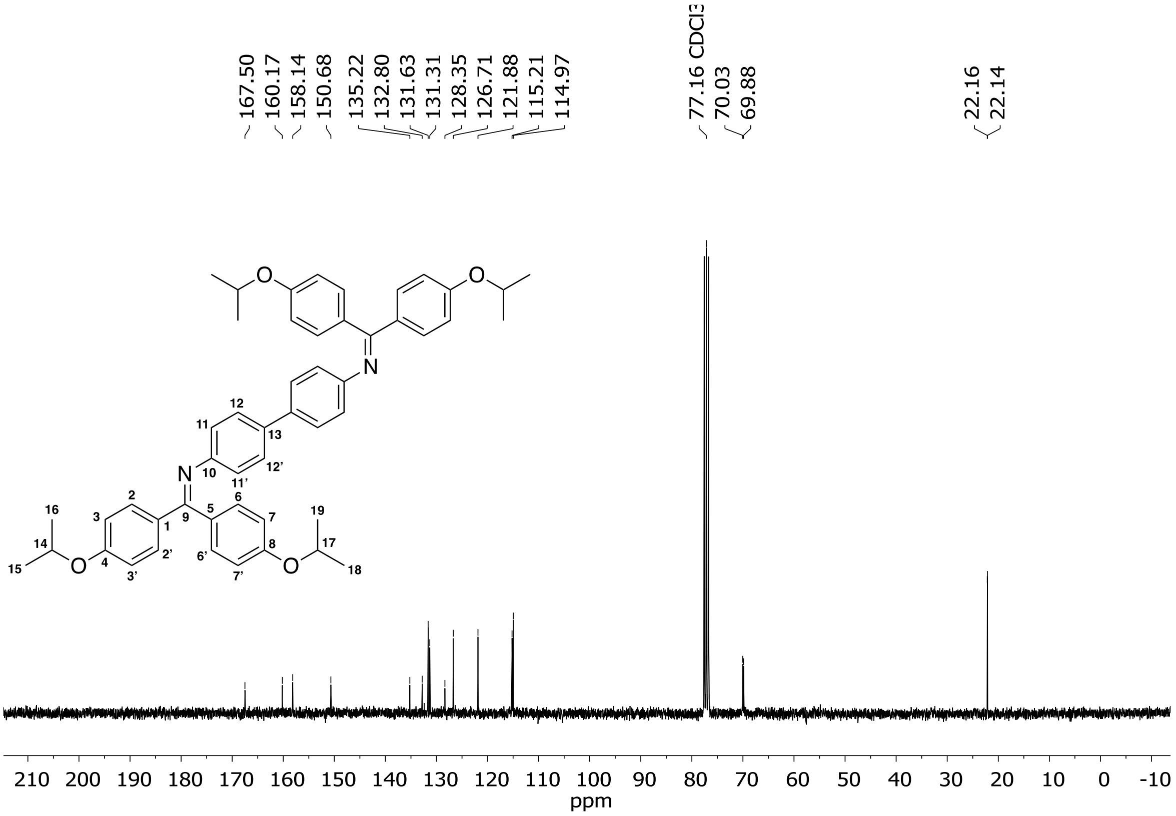


Figure S59 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-diisopropoxy-benzophenone)benzidine imine (**2b**).

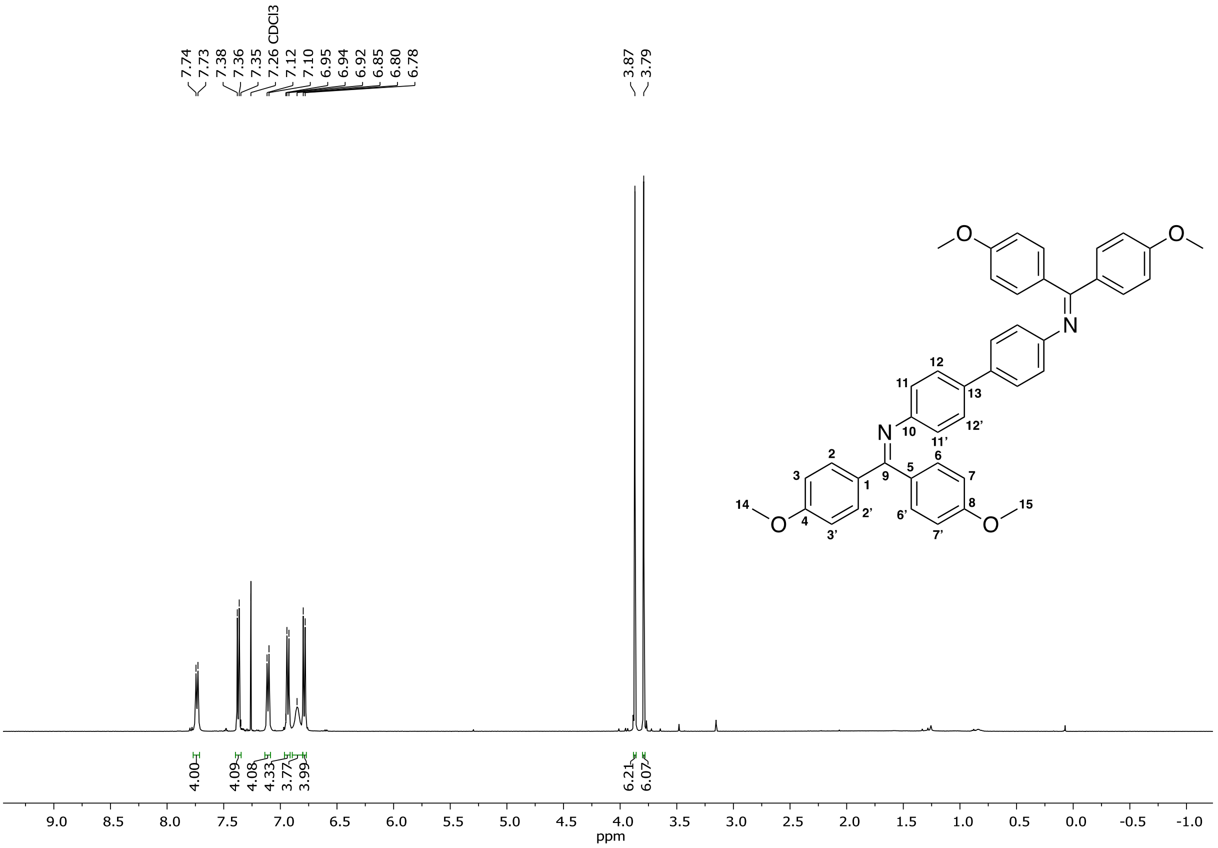


Figure S60 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-dihydroxymethyl-benzophenone)benzidine imine (**2c**).

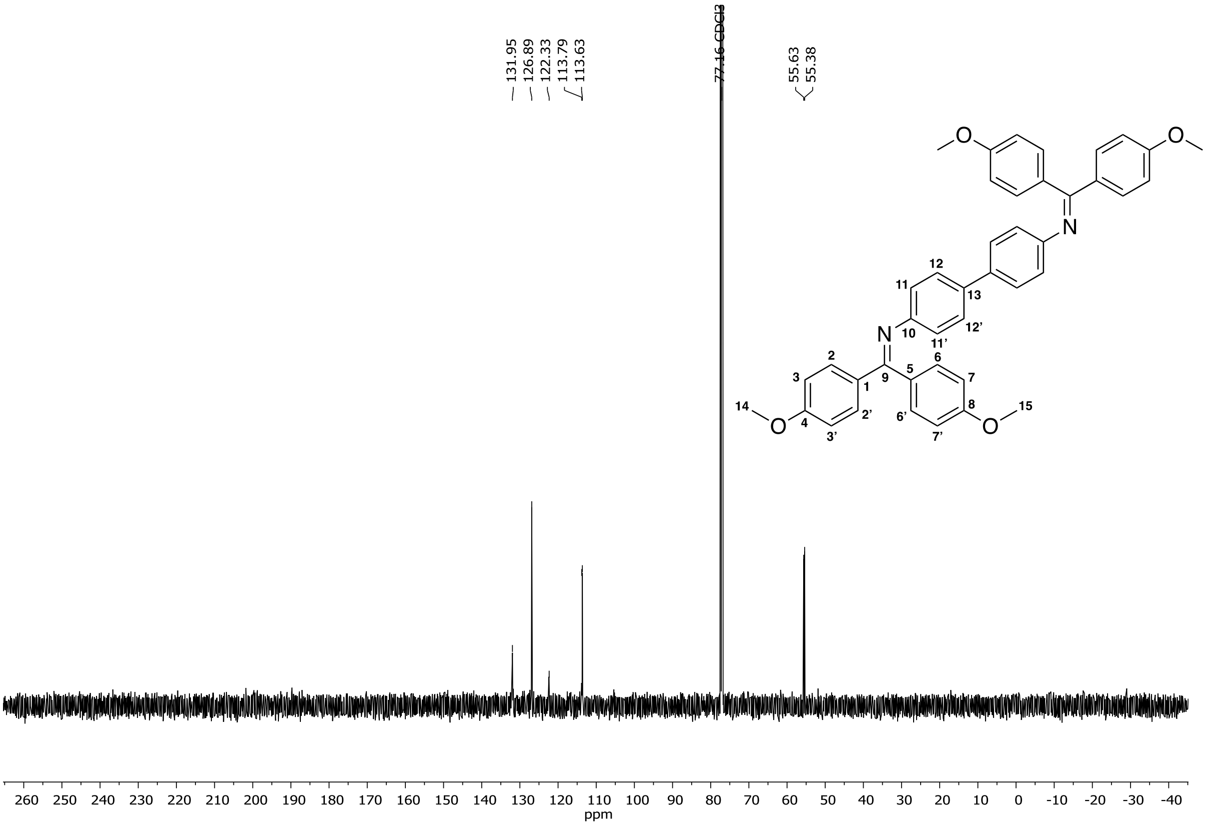


Figure S61 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-dihydroxymethyl-benzophenone)benzidine imine (**2c**).

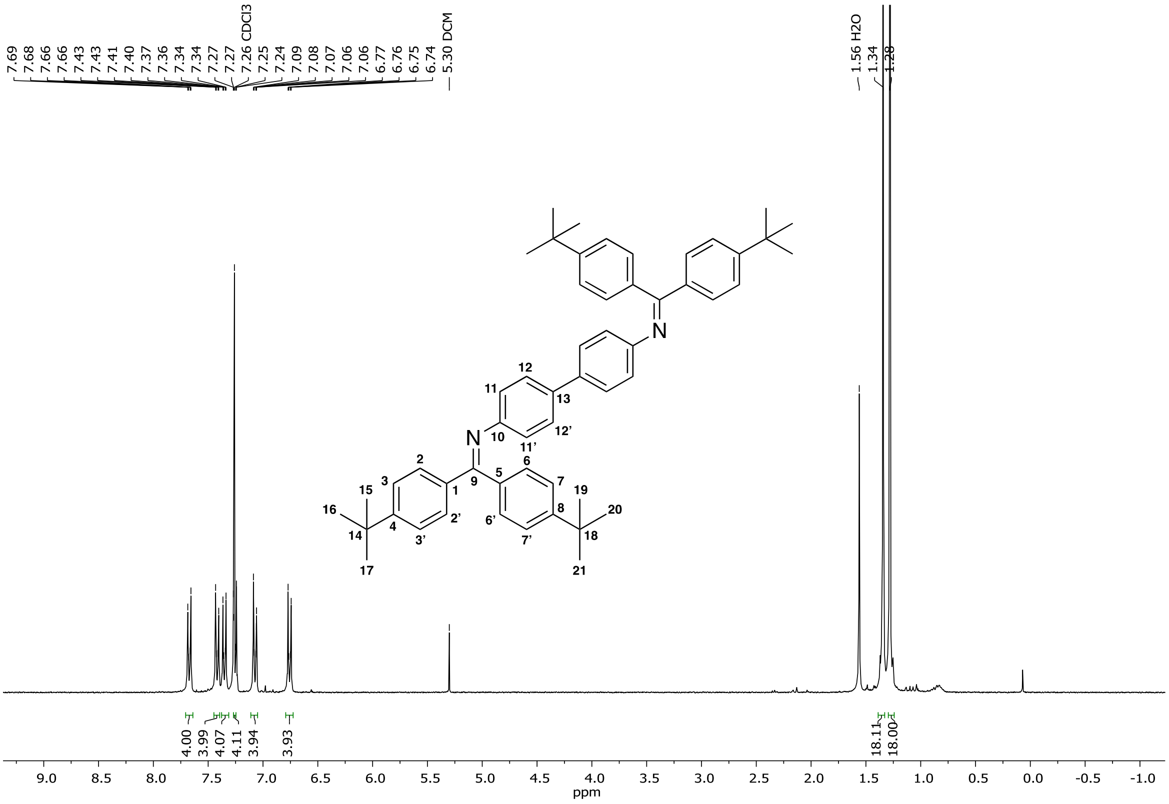


Figure S62 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-ditert-butyl-benzophenone)benzidine imine (**2d**).

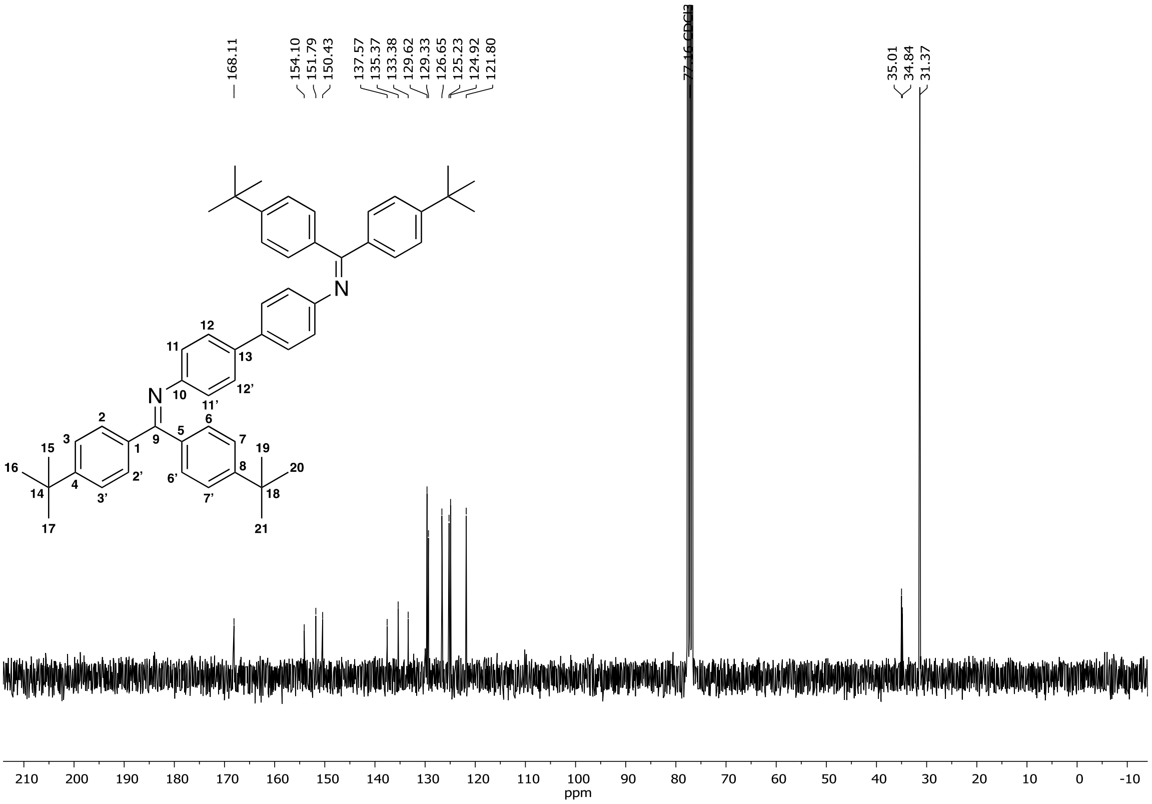


Figure S63 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of *N,N*‘-bis(4,4‘-ditert-butyl-benzophenone)benzidine imine (**2d**).

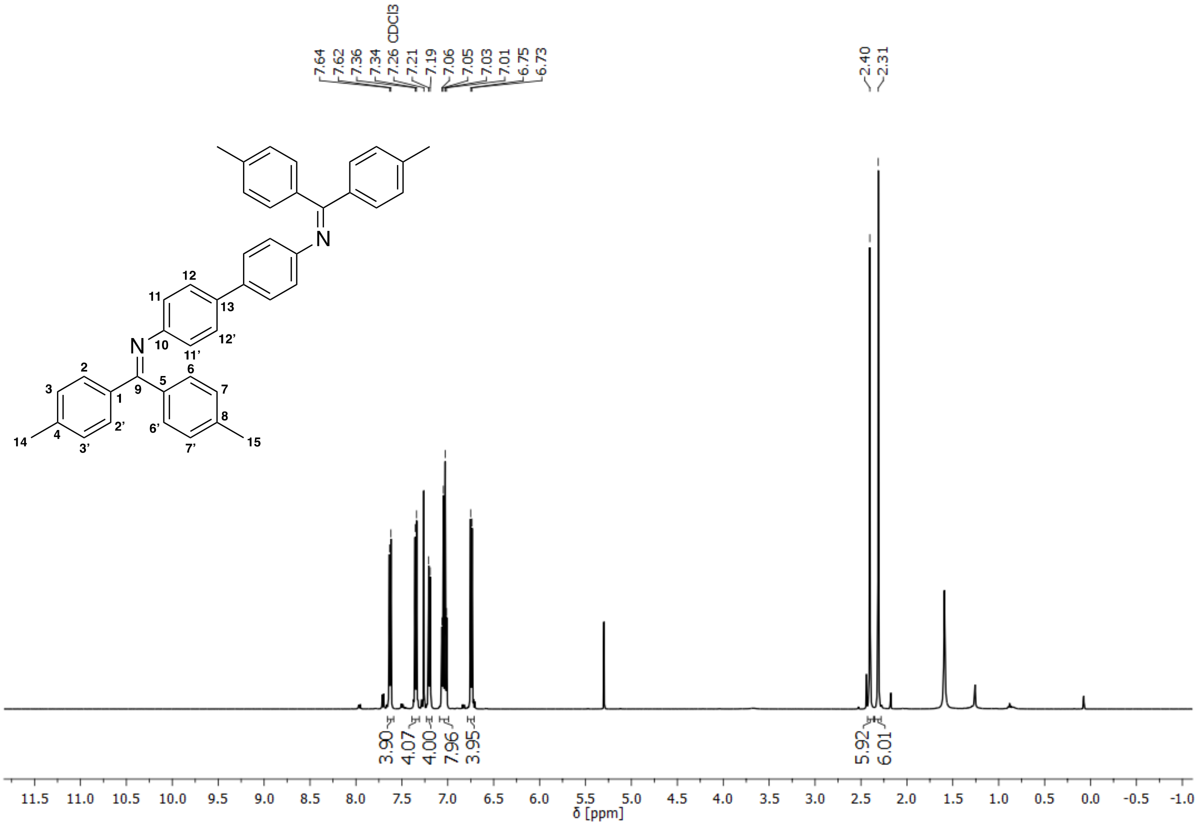


Figure S64 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of *N,N*‘-bis(4,4’-dimethyl-butyl-benzophenone)benzidine imine (**2e**)

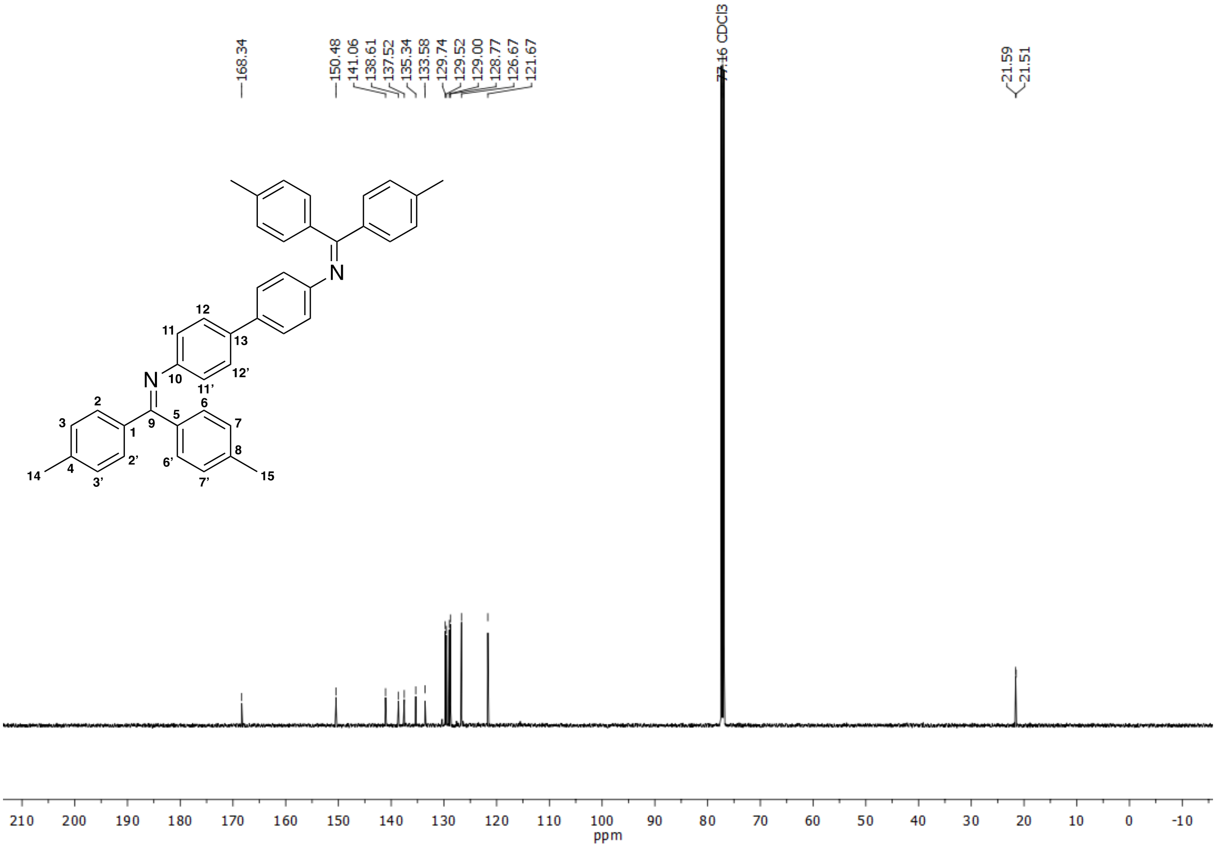


Figure S65 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-dimethyl-benzophenone)benzidine imine (**2e**).

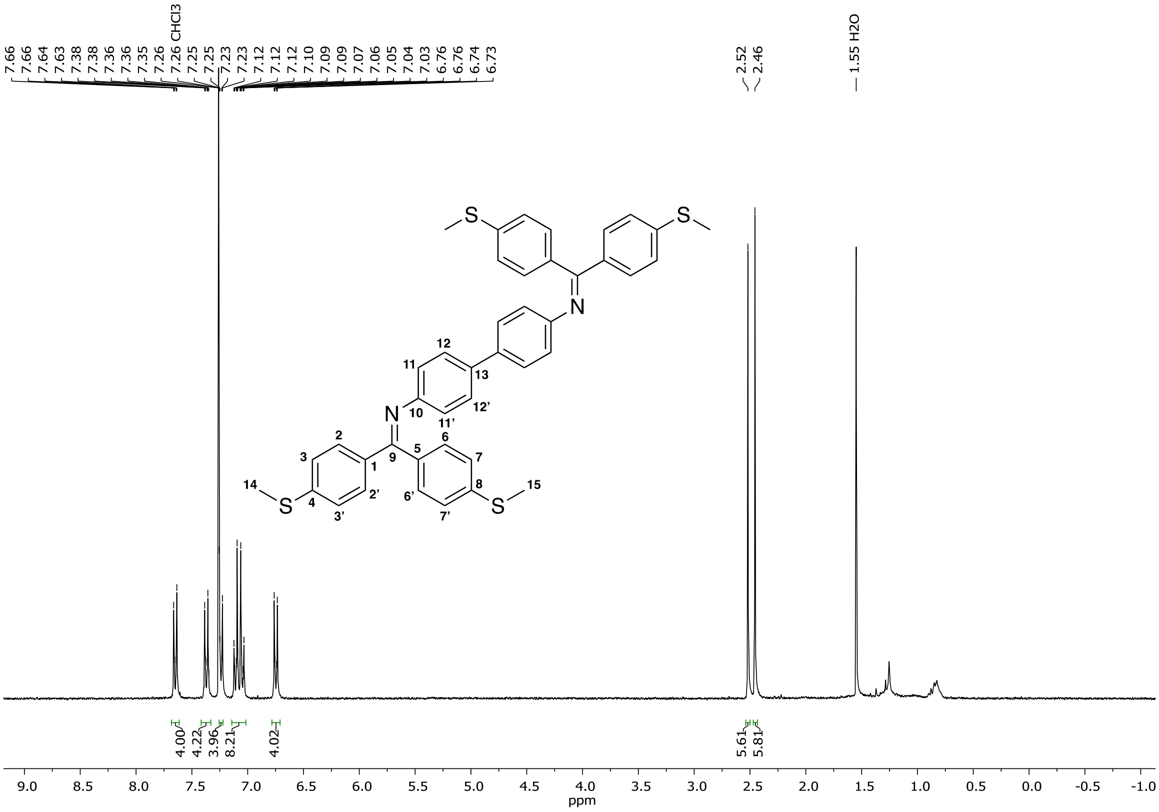


Figure S66 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-dithiomethyl-benzophenone)benzidine imine (**2f**).

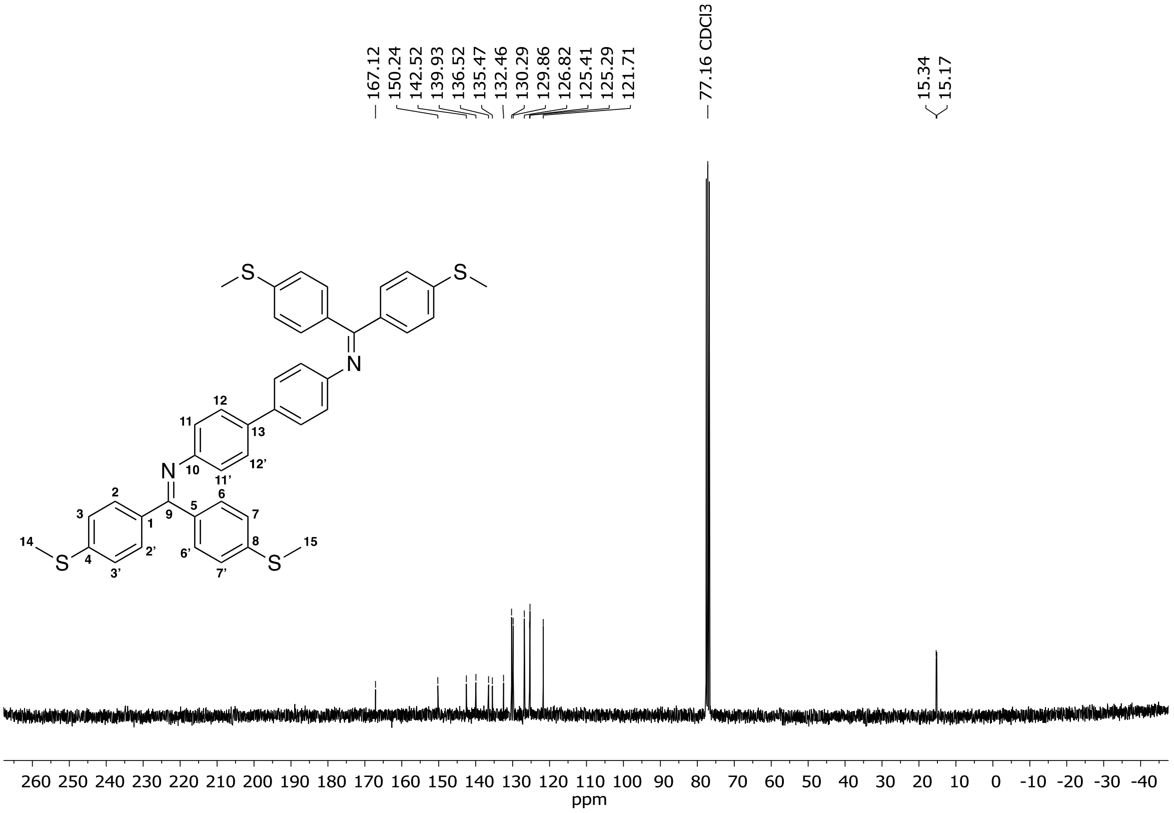


Figure S67 ^{13}C NMR spectrum (76 MHz, CDCl$_3$, 25 °C) of *N,N'*-bis(4,4'-dithiomethyl-benzophenone)benzidine imine (**2f**).

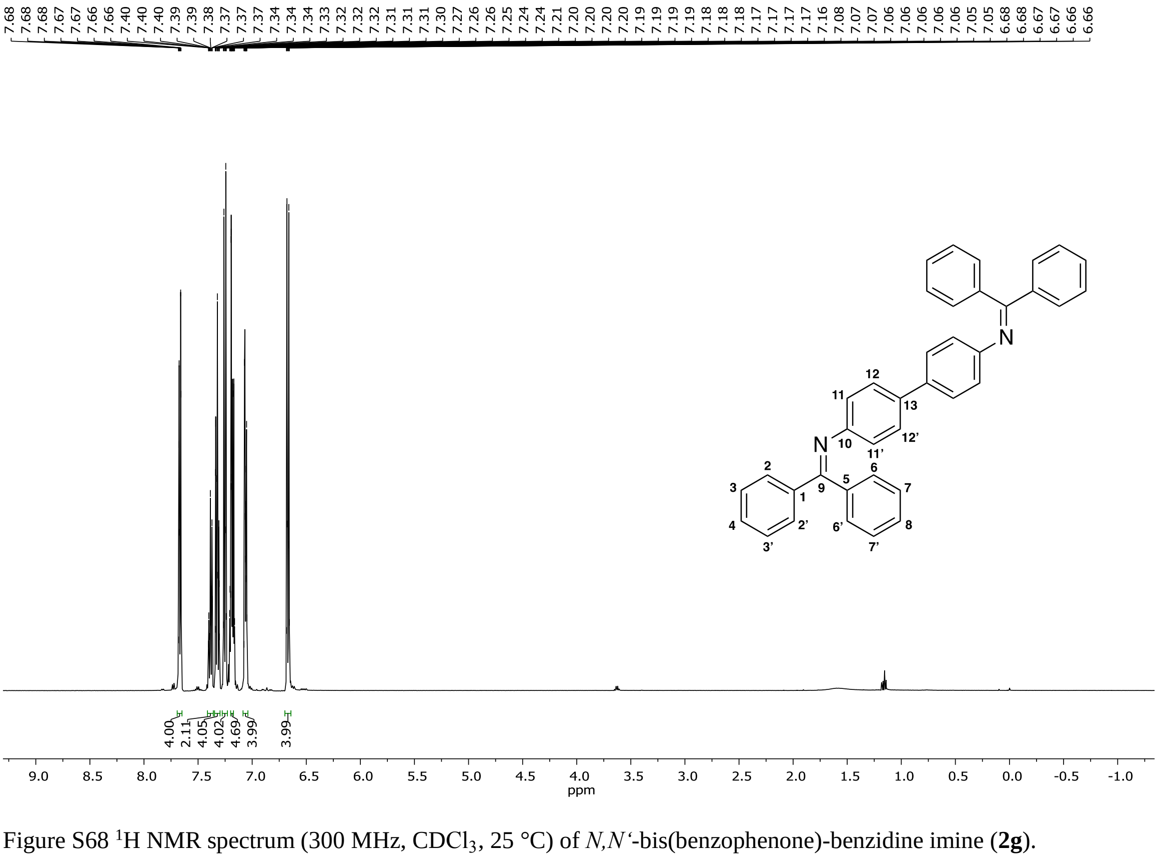


Figure S68 ^{1}H NMR spectrum (300 MHz, CDCl$_3$, 25 °C) of *N,N'*-bis(benzophenone)-benzidine imine (**2g**).

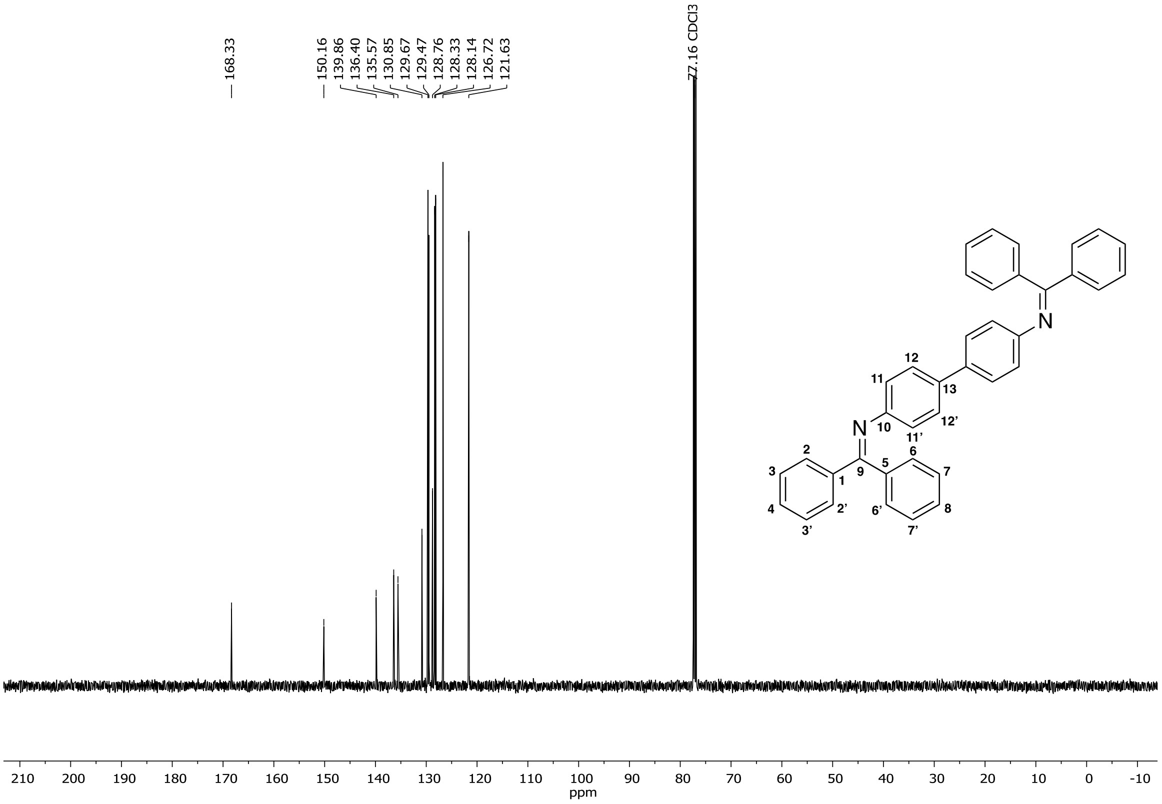


Figure S69 ^{13}C NMR spectrum (76 MHz, CDCl$_3$, 25 °C) of *N,N'*-bis(benzophenone)-benzidine imine (**2g**).

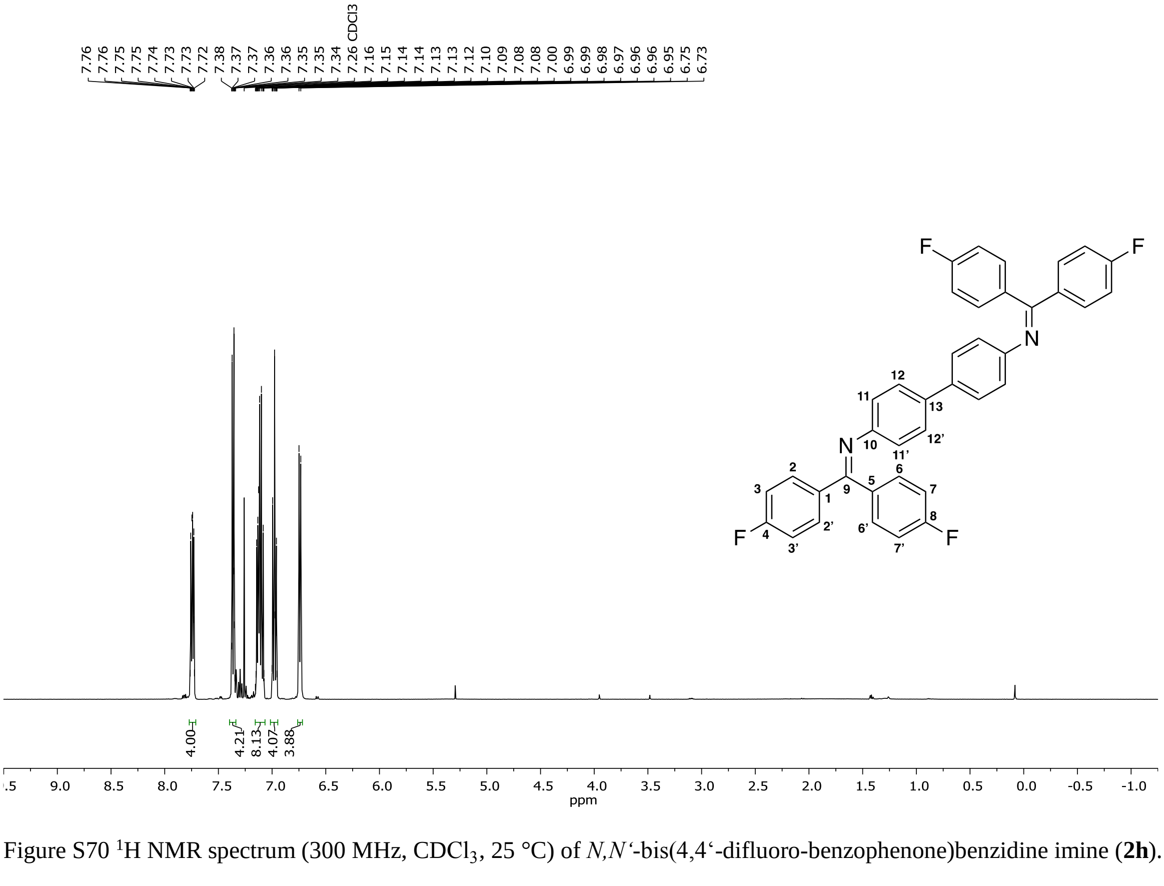


Figure S70 ^{1}H NMR spectrum (300 MHz, CDCl$_3$, 25 °C) of *N,N'*-bis(4,4'-difluoro-benzophenone)benzidine imine (**2h**).

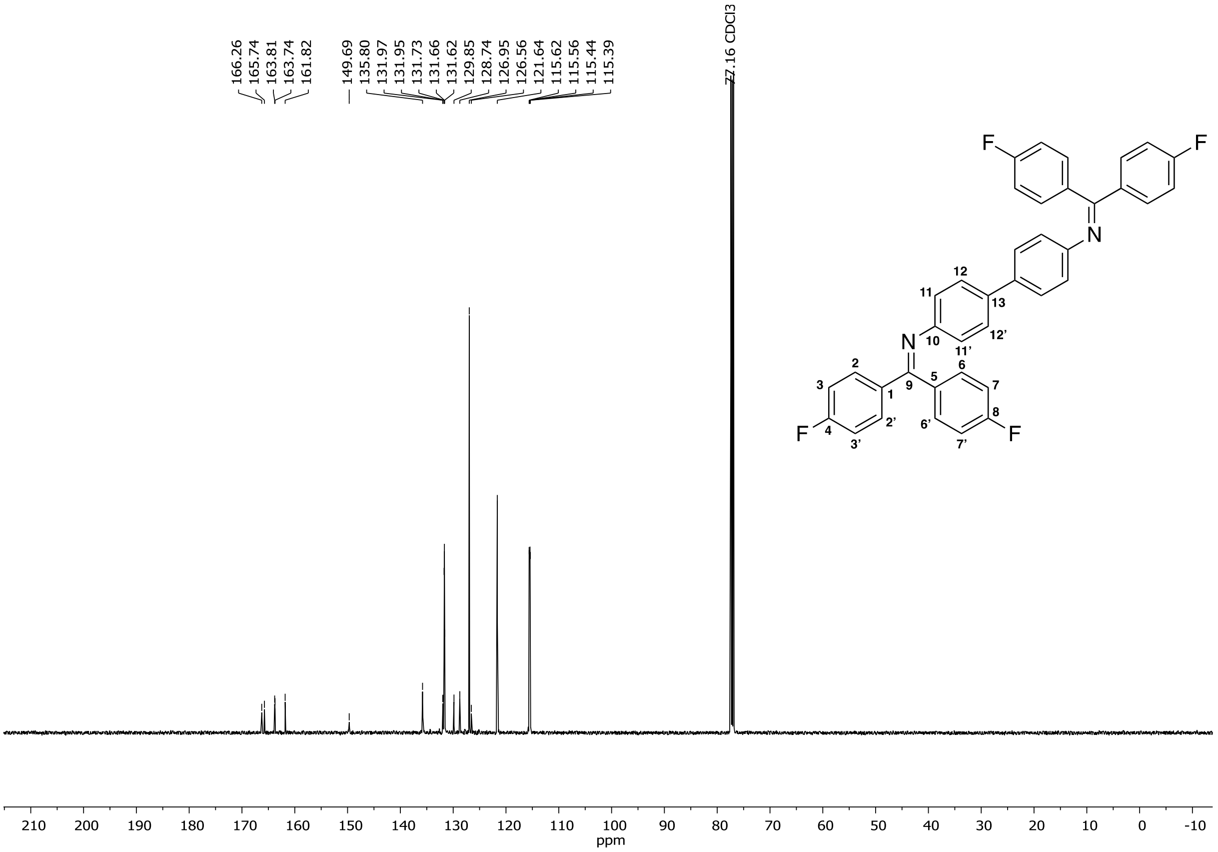


Figure S71 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-difluoro-benzophenone)benzidine imine (**2h**).

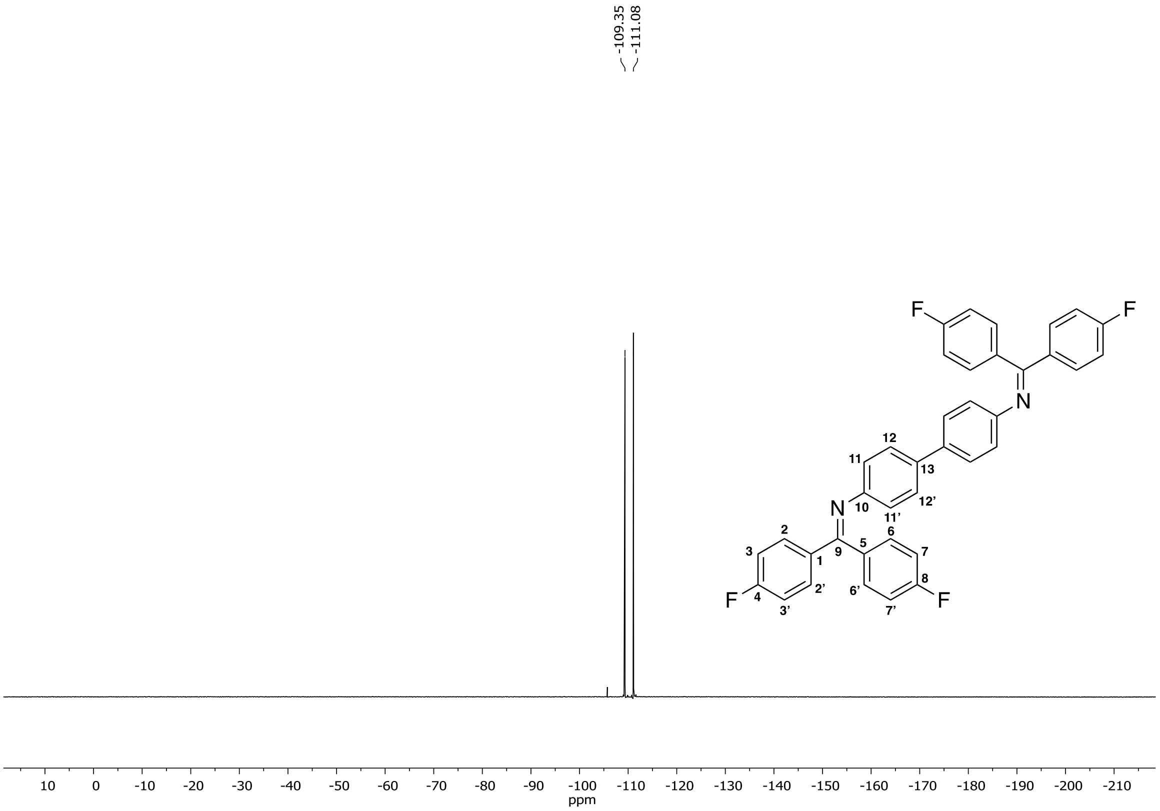


Figure S72 ^{19}F NMR spectrum (282 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-difluoro-benzophenone)benzidine imine (**2h**).

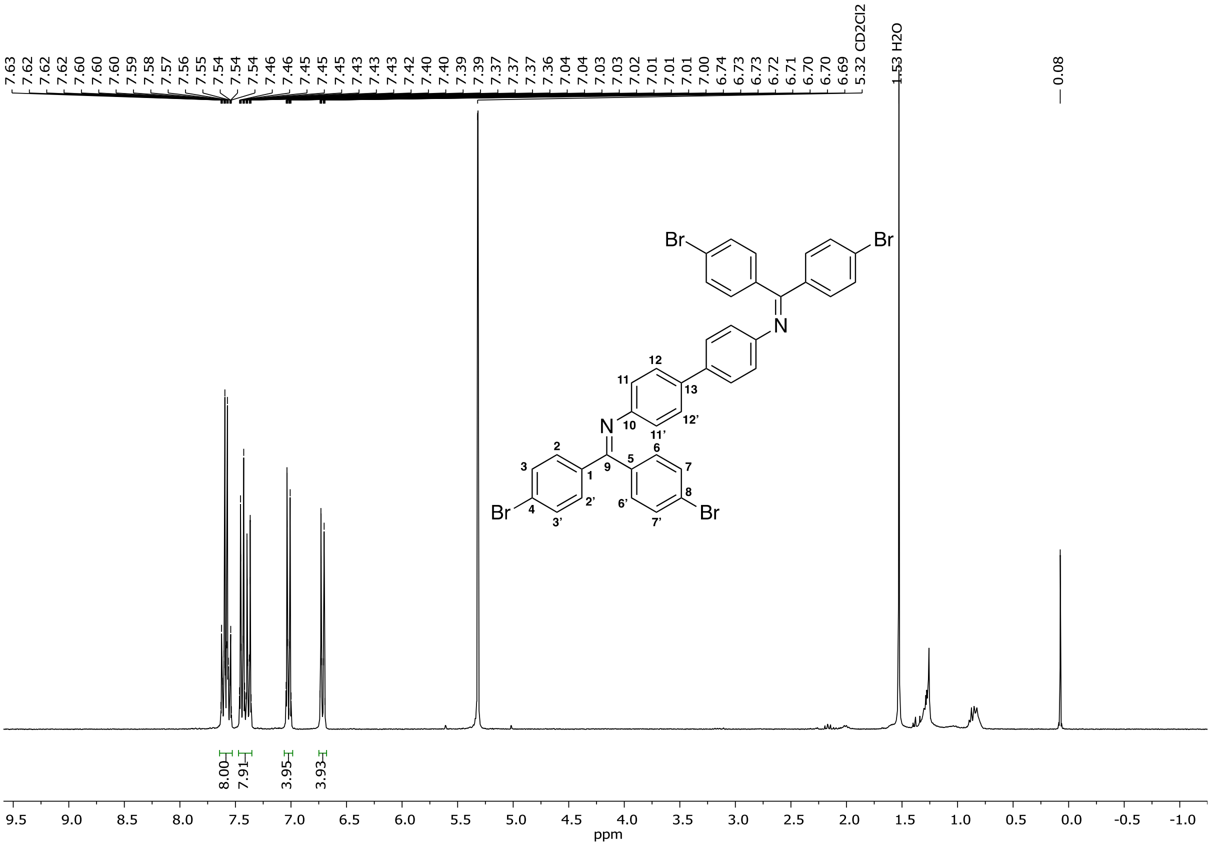


Figure S73 ^{1}H NMR spectrum (300 MHz, CD_2Cl_2, 25 °C) of *N,N*‘-bis(4,4‘-dibromobenzo-phenone)benzidine imine (**2i**).

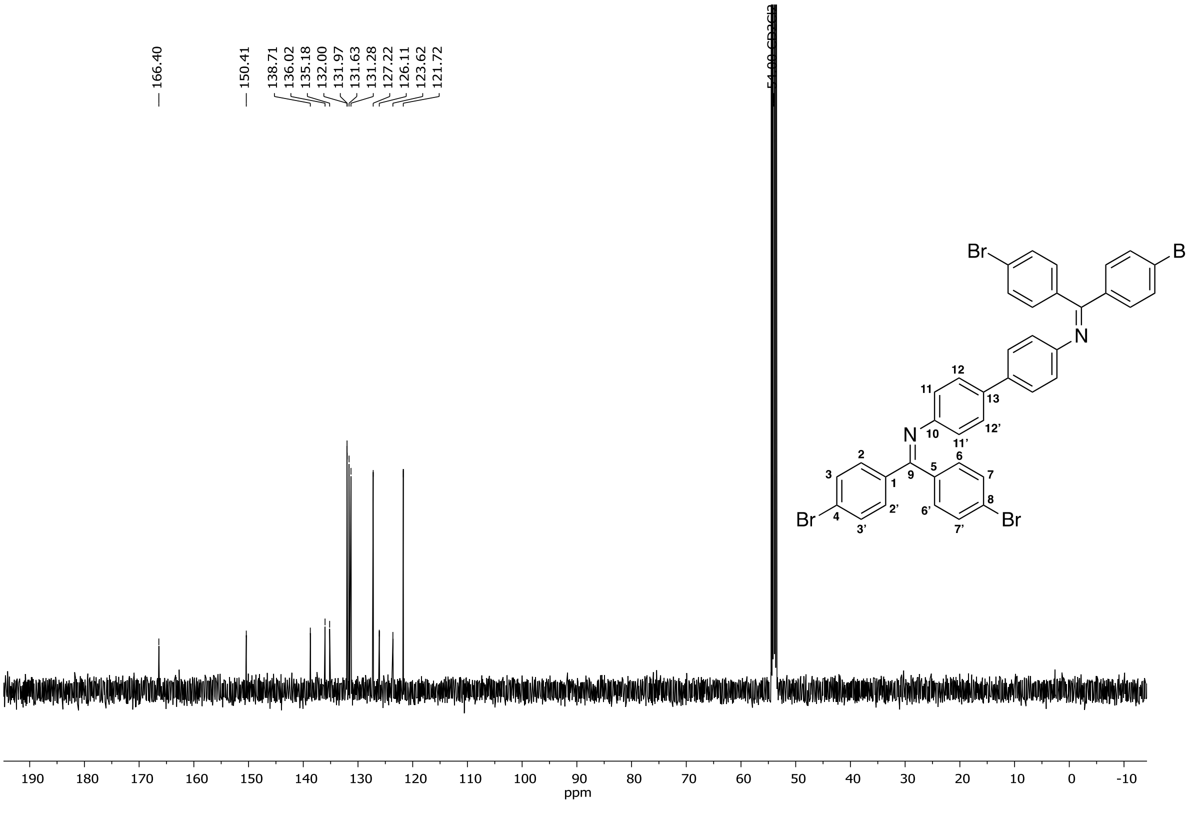


Figure S74 ^{13}C NMR spectrum (76 MHz, CD_2Cl_2, 25 °C) of *N,N*‘-bis(4,4‘-dibromobenzo-phenone)benzidine imine (**2i**).

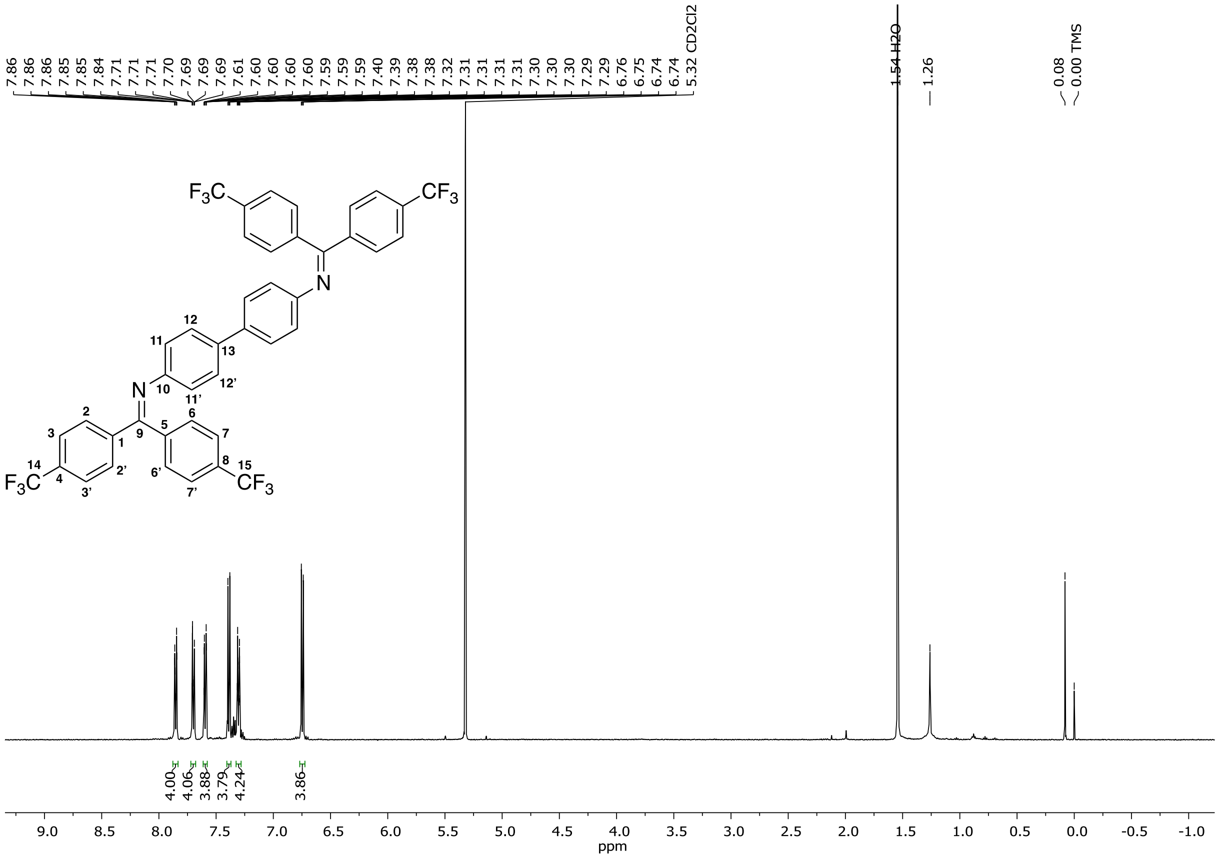


Figure S75 ^{1}H NMR spectrum (300 MHz, CD_2Cl_2, 25 °C) of *N,N'*-bis(4,4'-bis(trifluoro-methyl)benzophenone)benzidine imine (**2j**).

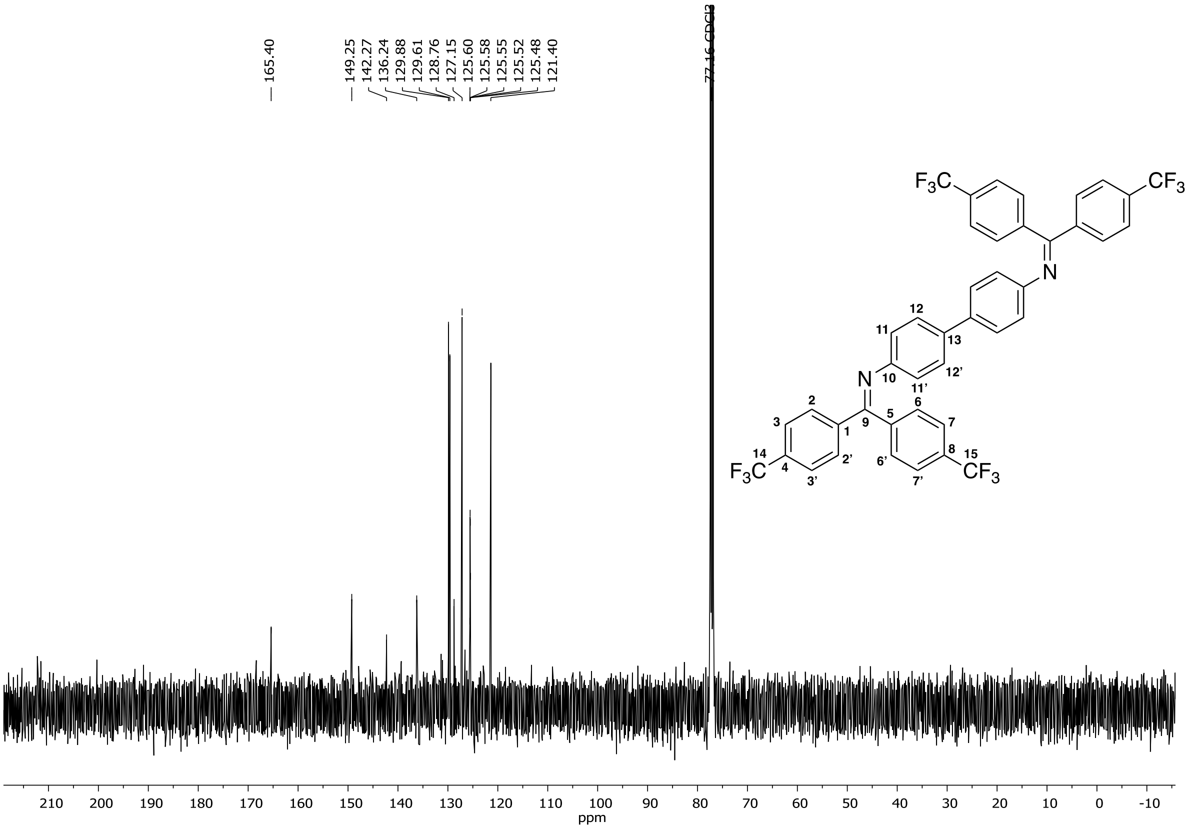


Figure S76 ^{13}C NMR spectrum (76 MHz, CD_2Cl_2, 25 °C) of *N,N‘*-bis(4,4‘-bis(trifluoro-methyl)benzophenone)benzidine imine (**2j**).

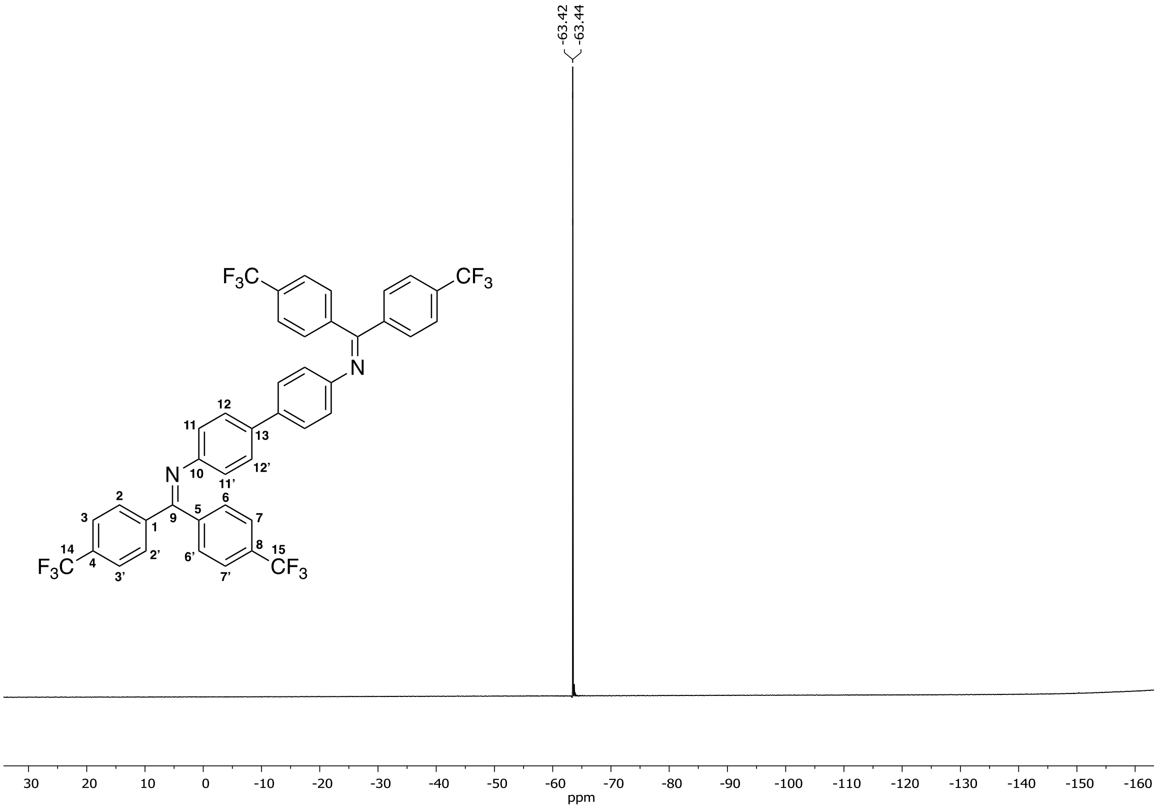


Figure S77 19F NMR spectrum (282 MHz, $CDCl_3$, 25 °C) of *N,N‘*-bis(4,4‘-bis(trifluoro-methyl)benzophenone)benzidine imine (**2j**).

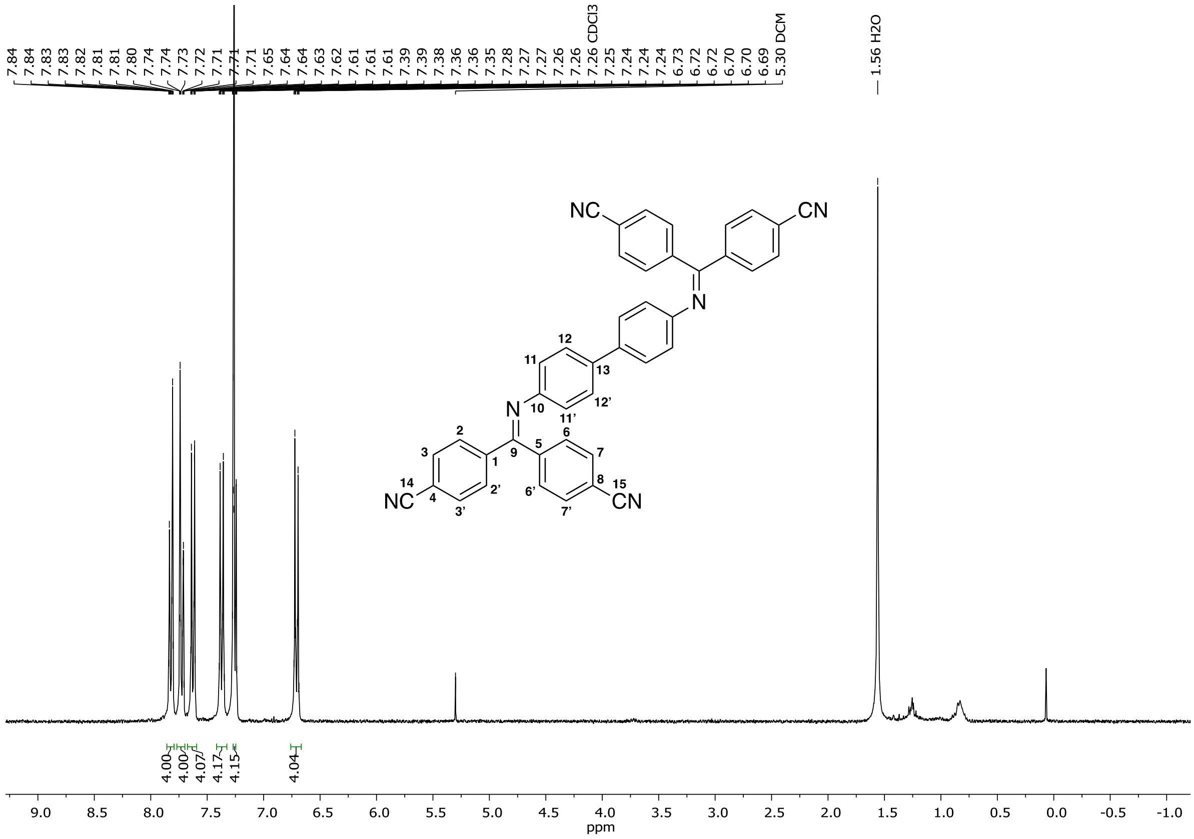


Figure S78 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-dicyano-benzophenone)benzidine imine (**2k**).

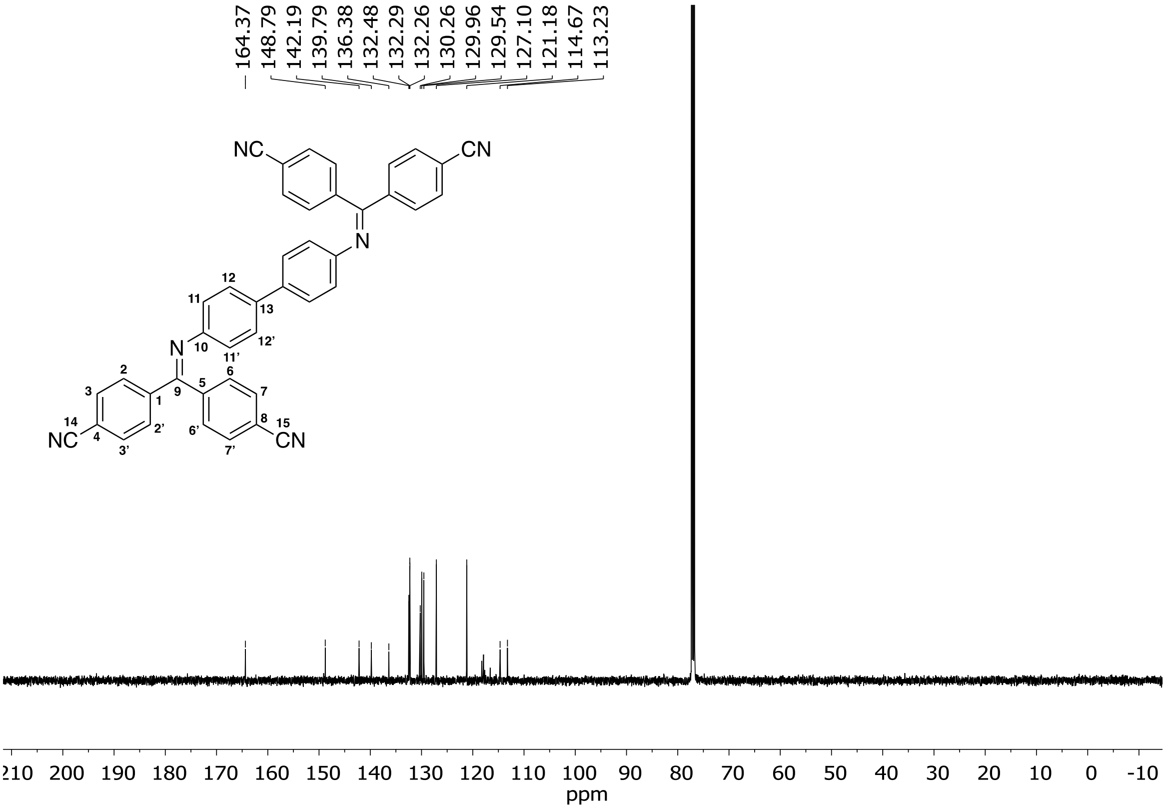


Figure S79 ^{13}C NMR spectrum (76 MHz, $CDCl_3$, 25 °C) of *N,N'*-bis(4,4'-dicyano-benzophenone)benzidine imine (**2k**).

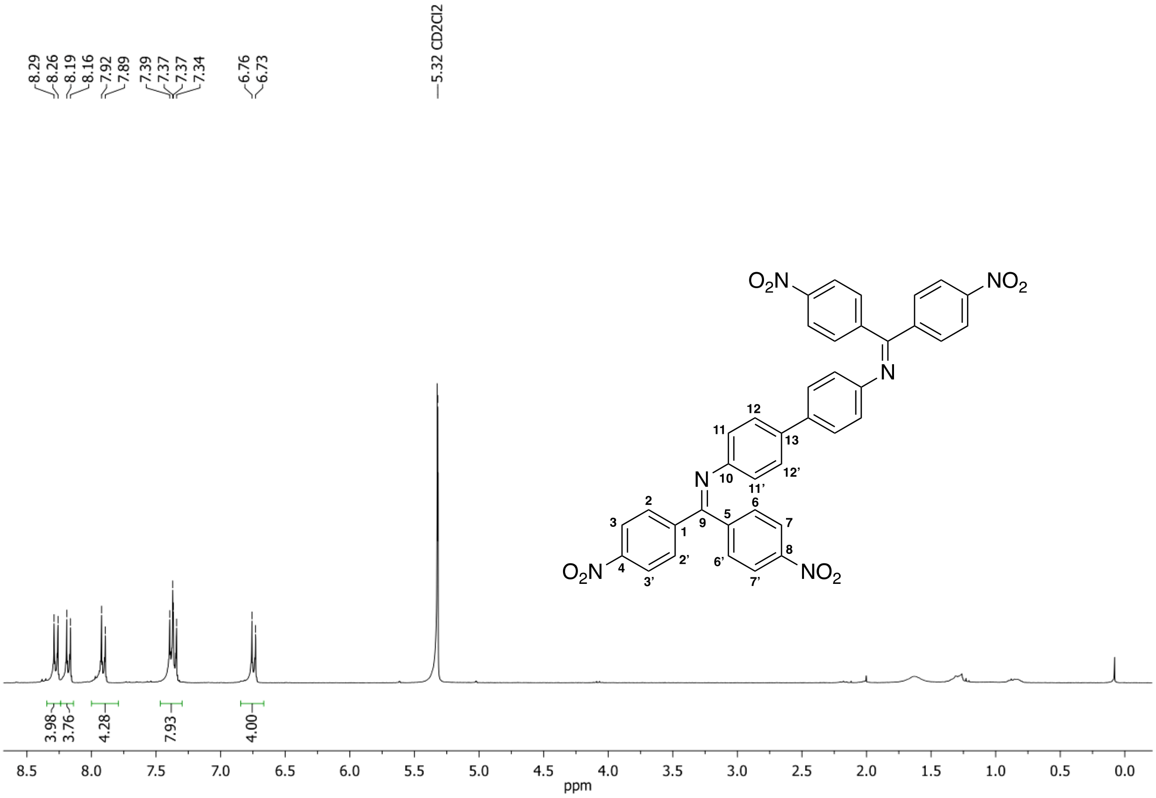


Figure S80 ^{1}H NMR spectrum (300 MHz, CD_2Cl_2, 25 °C) of *N*,*N*‘-bis(4,4‘-dinitrobenzo-phenone)benzidine imine (**2l**).

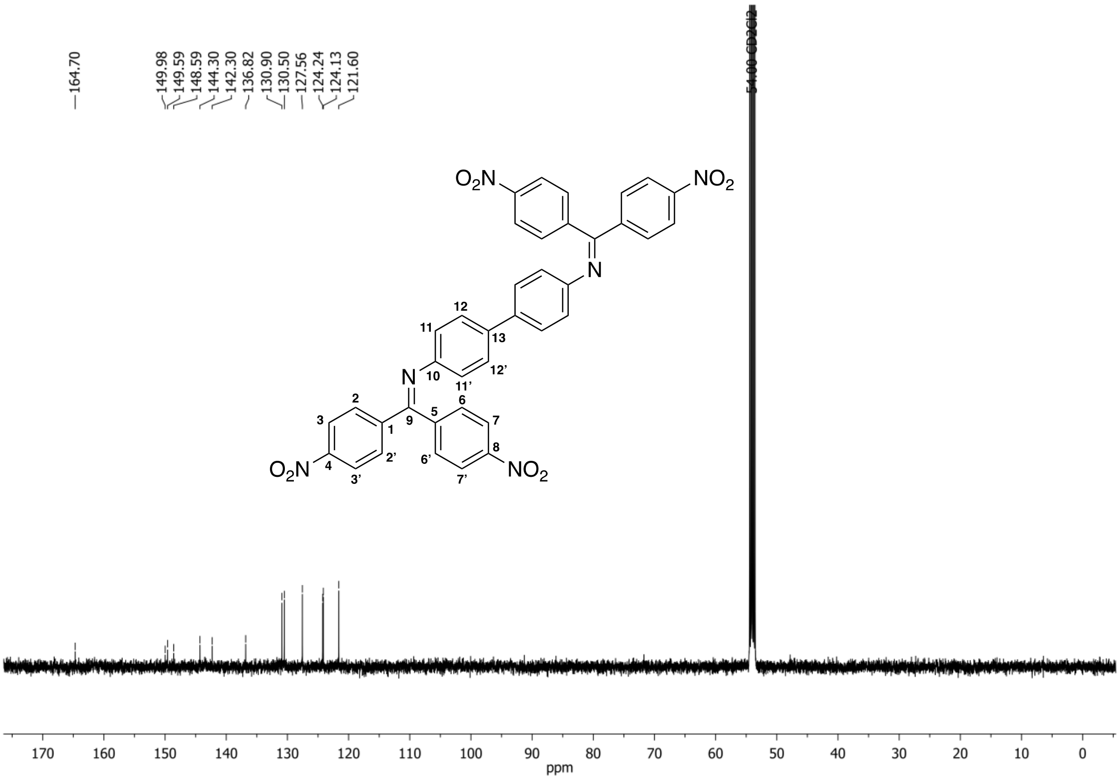


Figure S81 ^{13}C NMR spectrum (76 MHz, CD_2Cl_2, 25 °C) of *N*,*N*‘-bis(4,4‘-dinitrobenzo-phenone)benzidine imine (**2l**).

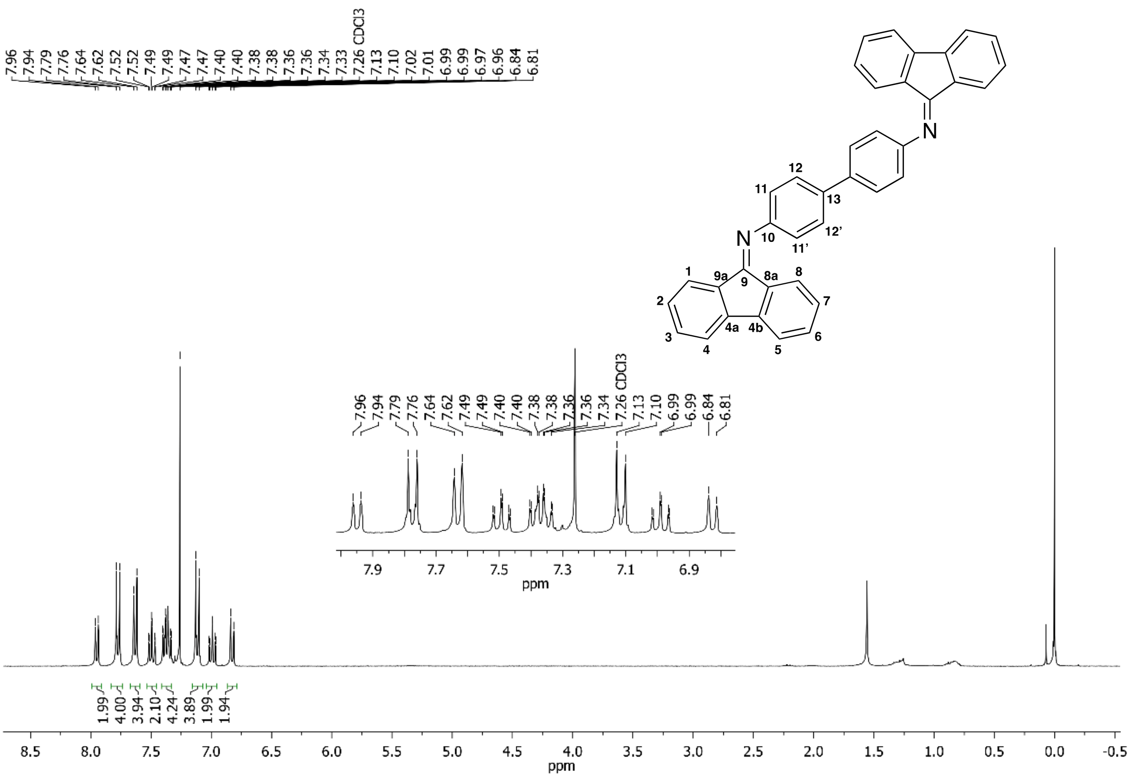


Figure S82 ^{1}H NMR spectrum (76 MHz, CDCl$_3$, 25 °C) *N*,*N*'-([1,1'-biphenyl]-4,4'-diyl)bis(9*H*-fluoren-9-imine) (**S2**).

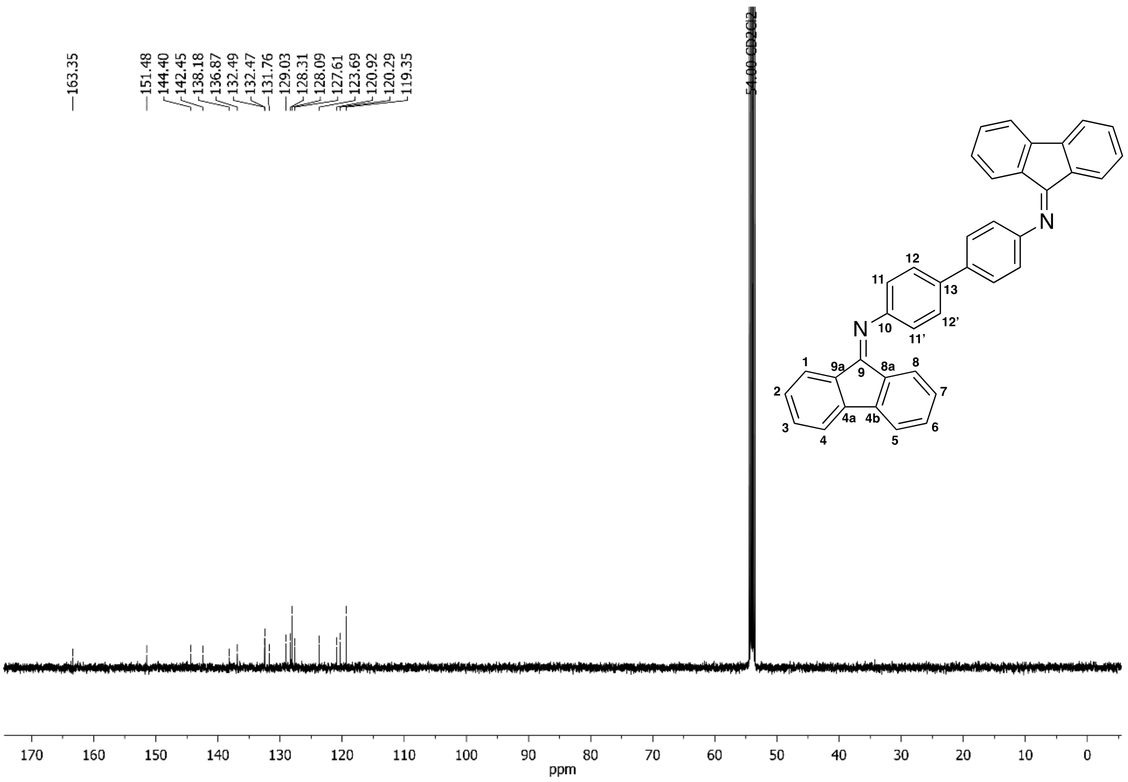


Figure S83 ^{13}C NMR spectrum (76 MHz, CDCl$_3$, 25 °C) *N*,*N*'-([1,1'-biphenyl]-4,4'-diyl)bis(9*H*-fluoren-9-imine) (**S2**).

S8. References

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