SUPPORTING INFORMATION

[2+2] Light-driven Cycloaddition Synthesis of an Organic Polymer and Photocatalytic Activity Enhancement via Monomer Truncation

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Summary

S1. SYNTHESIS AND CHARACTERIZATION

Characterization techniques

Nuclear Magnetic Resonance (NMR) spectra were acquired on a BRUKER AVANCE spectrometer running at 300 MHz for ^{1}H or at 75 MHz for ^{13}C, and are internally referenced to the residual $CDCl_3$ signal: δ 7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant *J* (Hz) and integration. Data for ^{13}C NMR are reported as chemical shift (δ ppm). ^{13}C and ^{19}F Solid State Nuclear Magnetic Resonance (SSNMR) were recorded at a frequency of 100.61 MHz (9.4 T) and 376.49 MHz (9.4 T), respectively, with a Bruker AV400 SSNMR spectrometer using a 2.5 mm double-resonance magic angle spinning (MAS) probe at a spinning speed of 10 kHz. To avoid baseline distortions, a rotor-synchronous echo sequence (τ_R-π-τ_R) was applied prior to signal acquisition, where τ_R denotes one rotor cycle. The π- and π/2-pulse widths for ^{13}C were 6.0 μs and 3 μs, respectively. Recycle delays of 20 s were used. Resonance positions were referenced with respect to tetramethylsilane (TMS) using the CH_2 resonance of adamantane at 38.56 ppm as a secondary reference.

Electrospray Ionization Mass Spectra (ESI-MS) were obtained on an Agilent Technologies 6120 Quadrupole LC/MS coupled with a Supercritical Fluid Chromatograph (SFC) Agilent Technologies 1260 Infinity Series instrument. High-Resolution Mass Spectra (HRMS) were obtained on the same equipment and using MassWorks software version 4.0.0.0 (Cerno Bioscience) for the formula identification. MassWorks is an MS calibration software which calibrates isotope profiles to achieve high mass accuracy and enables elemental composition determination on conventional mass spectrometers of unit mass resolution allowing highly accurate comparisons between calibrated and theoretical spectra. [1]

Fourier Transformed IR (FTIR) were recorded on a Thermo Nicolet Avatar 380 FT-IR equipped with a Michelson filter interferometer in transmission mode. For the preparation of the samples, 200 mg of dry KBr were mixed with 2 mg of the sample in a mortar. Pressure was then applied with a hydraulic press until a fine pellet was generated.

Scanning Electron Microscopy (SEM) images were acquired on a Hitachi S-3000 N electron microscope with a coupled ESED detector and an analyser from energy dispersive X-ray from Oxford Instruments, INCAx-sight model.

For the elemental analysis measurements, a LECO CHNS-932 Analyser (Model NO: 601-800-500) was used.

Powder X-ray difraction was performed in a X'Pert PRO difractometer θ/2θ geometry from Panalytical equipped with a Johansson Ge monochromator for λ Kα, a X'Celerator fast detector in an alumina holder. The θ/2θ swept was performed from 2 to 60º with an angular increase of 0.01º for 1s each step.

Textural analysis was done using N_2 adsorption at 77 K on a Micromeritics 3Flex instrument. Before the experiments, the samples were outgassed at 150 °C for 24 h under vacuum (pressure below 10^{-3} Pa). The apparent surface area (S_{BET}) was determined from the N_2-adsorption isotherm using the BET equation in the range of P/P° between 0.05 and 0.2.[2]

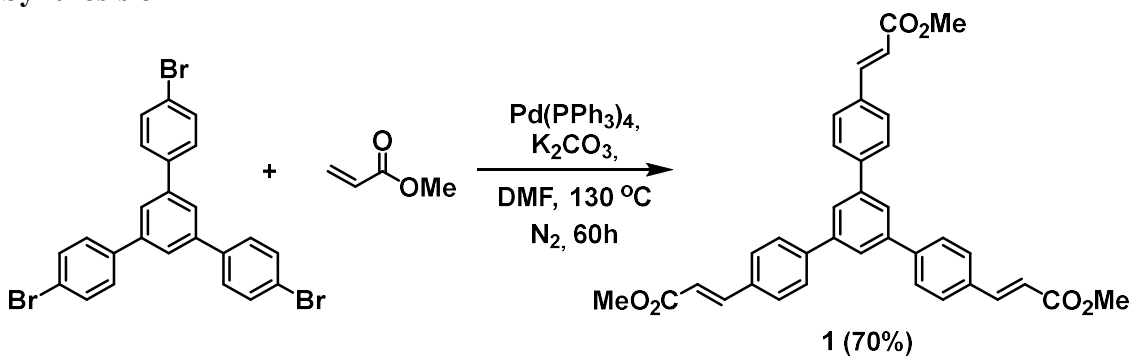
The photoelectron spectroscopies have all been carried out under ultra-high vacuum (UHV) conditions. The experimental chamber has a base pressure of 2×10^{-10} mbar and is equipped with an X-ray source with a Mg anode whose K_α emission line produces photons of energy $h\nu$ = 1253.6 eV which are used for X-ray photoemission spectroscopy (XPS) measurements. A He discharge lamp provides He-I ($h\nu$ = 21.2 eV) and He-II ($h\nu$ = 40.8 eV) photons for ultraviolet photoemission spectroscopy (UPS). For both techniques a hemispherical energy analyzer (LEYBOLD LHS10) has been used. The pass energy of the analyzer was set to 50 eV for the XPS measurements to reach a resolution of 0.7 eV and 5 eV for the UPS measurements reaching a final resolution of 0.1 eV. Sample preparation consisted on glueing the powders using a Ag liquid colloid to avoid samples falling in the UHV chamber and sample charging. All the core levels are referred to the Ag $3d_{5/2}$ XPS core level (BE = 367.4 eV). The energies of the UPS spectra are referred also to the Fermi edge of the Ar^+-ion sputtered Au(111) crystal. The measured spectra have been deconvoluted using a Richardson–Lucy algorithm in order to eliminate the Mg K_α intrinsic line width and satellites.[3],[4] An iterative Richardson–Lucy procedure was applied until convergence, using as stopping criteria the appearance of a maximum in the Shannon entropy. The core level peaks, have been fitted, after subtraction of a Tougaard background with a Doniach-Sunjic combination of Lorentzian and Gaussian lineshapes.[5] The measured XPS intensity were corrected by the corresponding atomic sensitive factor of each edge. Thus, the corrected intensity is proportional to the average

atomic composition of the films following standard procedures and using the atomic sensitivities determined previously for this spectrometer type.[6],[7] Assuming that the films are strictly homogeneous within the escape depth of the electrons, the ratio of the intensities of two atoms core level peaks is related to the atomic density ratio (X_A/X_B) by $X_A/X_B = A\ I_A\ /I_B$ where $A = 1/S_A\ /\ 1/S_B$ and S_A and S_B are the atomic sensitive factor determined for the pure chemical elements for the specific electron analyzer used.[8]

UV-Vis Diffuse Reflectance Spectroscopy was performed on a PerkinElmer Lambda850+ equipped with a spherical detector of 110 mm in the 250-800 nm range. The reflectance spectra were plotted as the Tauc plot and the Kubelka-Munk function.[9] UV-Vis absorption spectra were collected at a Cary 50 spectrometer (Varian), in the 200–800 nm range by natural solution of the molecules in dichloromethane. Photoluminiscence measurements were carried out in a freshly prepared suspension of 1 mg of the material in 5 mL of DMF, using a JASCO Spectrofluorometer FP-8600 controlled by Spectra Manager Version 2.10.01. A 10x10 mm precision cell made of quartz was used for all emission measurements. Emission spectra of the light sources used for the photochemical reactions were recorded on an optical spectrometer StellarNet model Blue-Wave UV-NB50 (see Figure S1).

Synthesis

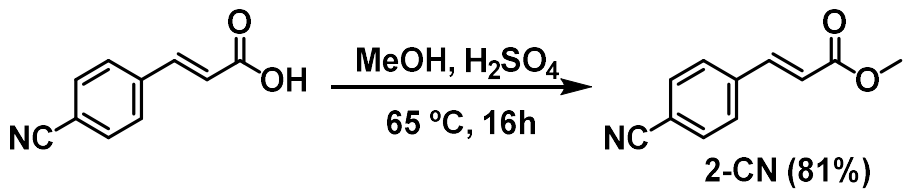
Synthesis of 1



Scheme S1. Synthesis of compound **1**.[10]

4,4''-dibromo-5'-(4-bromophenyl)-1,1':3',1''-terphenyl (0.51 g, 1 mmol), methyl acrylate (0.55 mL, 6 mmol) and tetrakis(triphenylphosphine)palladium (23 mg, 0.01 mmol) were dissolved under inert atmosphere in 5 mL of anhydrous *N,N*-dimethylformamide and stirred for 10 min. Then, potassium carbonate (0.552 g, 4 mmol) was added, and the mixture was stirred at 130 ºC for 60 h. After cooling to room temperature, the mixture was diluted in 15 mL of dichloromethane (DCM) and extracted 4 times with 15 mL of a 10%wt. LiCl aqueous solution, and 2 times with brine. After that, the organic phase was filtered through a pad of Celite® and profusely washed with DCM (4x10mL). Finally, the organic solution was dried over Mg_2SO_4, the solvent was evaporated under reduced pressure and the crude was purified by two successive flash chromatographies (Silica gel, Cyclohexane (CyH): Ethyl acetate (EtOAc) (80:20), and then DCM:EtOAc (95:5)). Monomer **1** was obtained as a white solid (0.38 g, 0.70 mmol, 70% yield). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.73 (s, 3H), 7.72 (d, J = 16.1 Hz, 3 H), 7.65 and 7.59 (AA'BB' system, 12H), 6.47 (d, J = 16.1 Hz, 3H), 3.81 (s, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)):** δ 167.3, 144.1, 142.4, 141.5, 133.9, 128.7, 127.7, 125.2, 118.1, 51.78. **MS (ESI)** [$M+H^+$] calculated for $C_{36}H_{31}O_6$: 559.21, found 559.21.

Synthesis of 2-CN

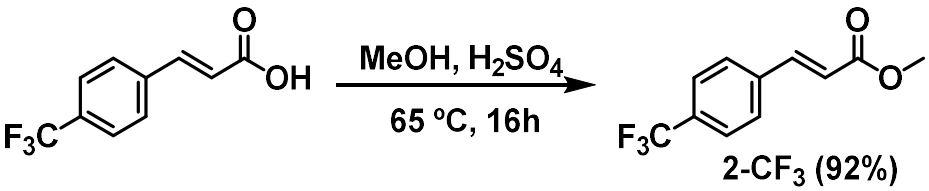


Scheme S2. Synthesis of compound **2-CN**. [11]

p-cyano-*trans*-cinnamic acid (0.38 g, 2.2 mmol) was dissolved in 5 mL of methanol with the help of magnetic stirring. To this solution, 0.2 mL of concentrated sulfuric acid were added, and the reaction was mantained at 65 ºC for 16 h. After that time, solvent was

removed under reduced pressure and the crude was dissolved in 20 mL of diethyl ether. After transferring to a separatory funnel, it was extracted with a saturated $NaHCO_3$ solution (3x10 mL), water (2x10 mL) and brine (2x10mL). The organic layer was dried over $MgSO_4$ and the crude was purified by flash chromatography (Silica gel, CyH: EtOAc (90:10)) to obtain **2-CN** as a white solid (0.33 g, 1.8 mmol, 81% yield). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.64 (m, 5H), 6.52 (d, J = 16.1 Hz, 1H), 3.83 (s, 3H).[11]

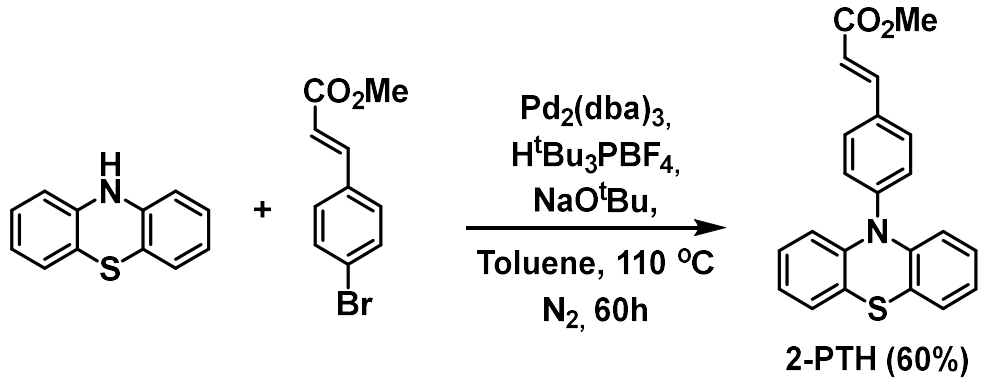
Synthesis of 2-CF_3



Scheme S3. Synthesis of compound **2-CF_3**. [11]

p-trifluoromethyl-*trans*-cinnamic acid (0.50 g, 2.2 mmol) was dissolved in 5 mL of methanol with the help of magnetic stirring. To this solution, 0.2 mL of concentrated sulfuric acid were added, and the reaction was mantained at 65 ºC for 16 h. After that time, solvent was removed under reduced pressure and the crude was dissolved in 20 mL of diethyl ether. After transferring to a separatory funnel, it was extracted with a saturated $NaHCO_3$ solution (3x10 mL), water (2x10 mL) and brine (2x10 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under reduce pressure to obtain pure **2-CF_3** as a white powder (0.46 g, 2.0 mmol 92% yield). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.66 (d, J = 16.0 Hz, 1H), 7.58 (m, 4H), 6.47 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H).[11]

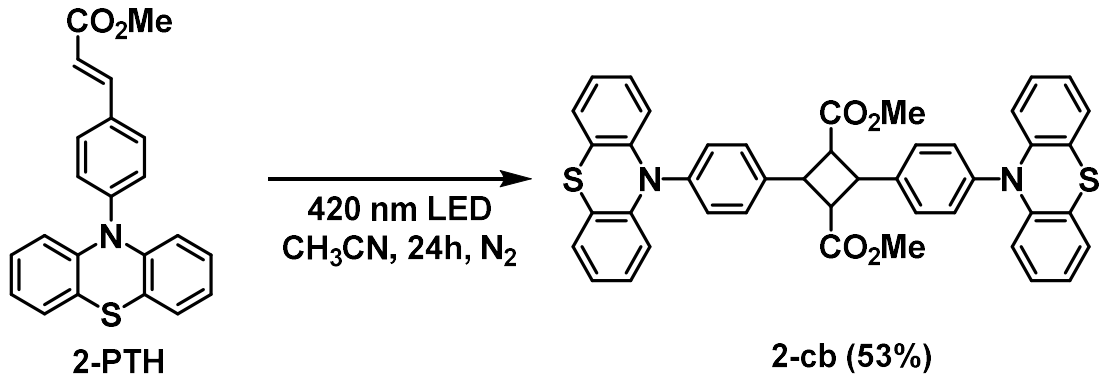
Synthesis of 2-PTH



Scheme S4. Synthesis of compound **2**.[12]

Phenothiazine (0.4 g, 2 mmol), methyl (*E*)-3-(4-bromophenyl)acrylate (0.53 g, 2.2 mmol), $Pd_2(dba)_3$ (3.5 mg, 0.04 mmol) and $HP^tBu_3BF_4$ (29 mg, 0.1 mmol) were added to a sealed tube under inert atmosphere. Then, 10 mL of toluene was added, and the mixture was stirred for 15 min at room temperature. Finally, NaO^tBu (0.22 g, 2.3 mmol) was added, and the mixture was heated at 110 °C for 60 h. After cooling to room temperature, the resulting mixture was diluted with DCM (20 mL), filtered through a pad of Celite® and washed with DCM (4 x 10 mL). The solvent was evaporated under reduced pressure and the crude was purified by flash chromatography (Silica gel, CyH:DCM (80:20)). Compound **2** was obtained as a yellow solid (0.43 g, 1.2 mmol, 60% yield). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.73 (d, J = 16.0 Hz, 1H), 7.64 and 7.31 (AA'BB' system, 4H), 7.15 (d, J = 7.6 Hz, 2H), 7.04 – 6.89 (m, 4H), 6.56 (d, J = 8.1 Hz, 2H), 6.45 (d, J = 16.0 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)):** δ 167.4, 144.2, 143.8, 143.2, 132.3, 130.1, 127.4, 127.0, 126.9, 124.3, 123.7, 119.1, 117.8, 51.8 **MS (HR-MS)** [$M+H^+$]: calculated for $C_{22}H_{18}NO_2S$: 360.1053, found 360.0927.

Synthesis of 2-cb



Scheme S5. Synthesis of compound **2-cb**.

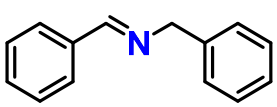
In a vial charged with a magnetic stirring bar, a solution of **2** (0.036 g, 0.1 mmol) in 1 mL of acetonitrile was prepared. The vial was sealed and degassed by 3 N_2-freeze-pump-thaw cycles. Then, the reaction was irradiated by 420 nm LED for 24 h at room temperature. After that time, the vial was opened, the solvent eliminated by reduced pressure and the residue purified by flash chromatography (Silica, CyH:EtOAc (95:5)). Compound **2-cb** was obtained as a light green solid (0.019 g, 0.026 mmol, 53% yield). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.56 and 7.39 (AA'BB' system, 8H), 7.07 – 6.99 (m, 4H), 6.89 - 6.75 (m, 8H), 6.26 - 6.05 (m, 4H), 4.63 (dd, J = 10.5, 7.2 Hz, 2H), 4.13 (dd, J = 10.5, 7.2 Hz, 2H), 3.43 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 172.0, 144.1, 140.1, 138.5, 130.7, 129.8, 126.8, 126.7, 122.5, 120.4, 116.0, 51.6, 47.7, 41.1. **MS (ESI)** [M+H^+] calculated for $C_{44}H_{35}N_2O_4S_2$: 719.20, found 719.20.

<u>Photocatalytic oxidative benzylamine homocoupling</u>

A vial was charged with a magnetic stirring bar, the amine **4a-k** (0.2 mmol), the catalyst (2 mg of the [2+2] photocycloaddition polymers or 5 mol% of the homogeneous catalysts) and the solvent (MeCN, 2 mL). The vial was sealed and irradiated with a 410 nm LED

while stirring at room temperature for the desired time, typically 24 h. Yield was determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

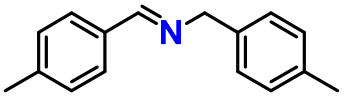
***N*-Benzylidene benzylamine (5a).**



It was prepared according to general photooxidation procedure from benzylamine. ^{1}H-NMR yield = 75%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.79-7.77 (m, 2H), 7.41-7.24 (m, 8H), 4.81 (s, 2H). [12]

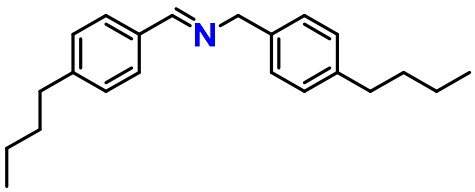
***N*-(4-methylbenzylidene)-4-methylbenzylamine (5b).**



It was prepared according to general photooxidation procedure from 4-methylbenzylamine. ^{1}H-NMR yield = 69%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 6.3 Hz, 4H), 7.12 (d, J = 8.2 Hz, 2H), 4.75 (s, 2H), 2.35 (s, 3H), 2.31 (s, 3H). [13]

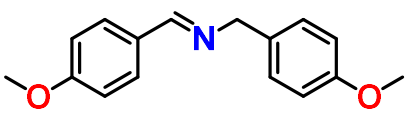
***N*-(4-butylbenzylidene)-4-butylbenzylamine (5c).**



It was prepared according to general photooxidation procedure from 4-butylbenzylamine. ^{1}H-NMR yield = 45%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.36-7.28 (m, 4H), 7.23 (d, J = 8.1 Hz, 2H), 4.87 (s, 2H), 2.81-2.67 (m, 4H), 1.78-1.74 (m, 4H), 1.53-1.49 (m, 4H), 1.07-1.0 (m, 6H). [14]

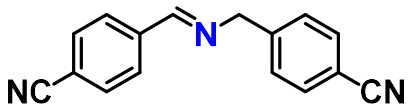
***N*-(4-methoxybenzylidene)-4-methoxybenzylamine (5d).**



It was prepared according to general photooxidation procedure from 4-methoxybenzylamine. ^{1}H-NMR yield = 69%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.71 (d, J = 9.0 Hz, 2H), 7.25 (d, J = 9.0 Hz, 2H), 6.94-6.86 (m, 4H), 4.72 (s, 2H), 3.83 (s, 3H), 3.79 (s, 3H). [13]

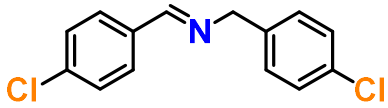
***N*-(4-cyanobenzylidene)-4-cyanobenzylamine (5e).**



It was prepared according to general photooxidation procedure from 4-(aminomethyl)benzonitrile. ^{1}H-NMR yield = 59%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 1H), (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 4.90 (s, 2H). [13]

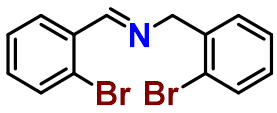
***N*-(4-chlorobenzylidene)-4-chlorobenzylamine (5f).**



It was prepared according to general photooxidation procedure from 4-chlorobenzylamine. ^{1}H-NMR yield = 48%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.31 (m, 4H), 4.77 (2H). [13]

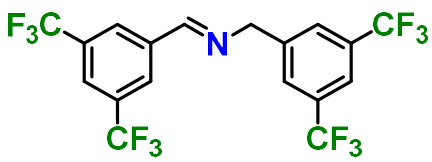
***N*-(2-bromobenzylidene)-2-bromobenzylamine (5g).**



It was prepared according to general photooxidation procedure from 2-bromobenzylamine. ^{1}H-NMR yield = 51%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.11 (dd, J = 7.6, 2.0 Hz, 1H), 7.59 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.38 – 7.27 (m, 3H), 7.18-7.08 (m,, 1H), 4.93 (s, 2H). [15]

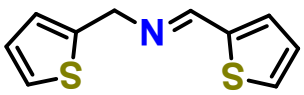
***N*-(3,5-bis(trifluoromethyl)benzylidene)-3,5-bis(trifluoromethyl)benzylamine (5h).**



It was prepared according to general photooxidation procedure from 3,5-bis(trifluoromethyl)benzylamine. ^{1}H-NMR yield = 69%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.25 (s, 2H), 7.97 (s, 1H), 7.83 (s, 3H), 4.95 (s, 2H). [13]

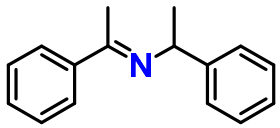
1-(thiophen-2-yl)-*N*-(thiophen-2-ylmethyl)methanimine (5i).



It was prepared according to general photooxidation procedure from thiophen-2-ylmethanamine. ^{1}H-NMR yield = 76%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.42 (d, J = 5.0 Hz, 1H), 7.33 (d, J = 3.7 Hz, 1H), 7.24 (dd, J = 4.7, 1.6 Hz, 1H), 7.07 (dd, J = 5.1, 3.6 Hz, 1H), 7.01-6.96 (m, 2H), 4.95 (s, 2H). [13]

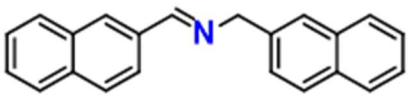
1-Phenyl-*N*-(1-phenylethyl)ethan-1-imine (5j).



It was prepared according to general photooxidation procedure from 1-phenylethan-1-amine. ^{1}H-NMR yield = 30%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88-7.82 (m, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.41-7.38 (m, 6H), 4.89 (q, J = 6.5 Hz, 1H), 2,31 (s, 3H), 1.60 (d, J = 6.5 Hz, 3H). [15]

1-(naphthalen-2-yl)-N-(naphthalen-2-ylmethyl)methanimine (5l).



It was prepared according to general photooxidation procedure from 2-naphtylmethylamine. ^{1}H-NMR yield = 42%.

^{1}H NMR (300 MHz, DMSO): δ 8.73 (s, 1H), 8.14-8.12 (m, 2H), 7.98-7.96 (m, 7H), 7.58-7.49 (m, 5H), 5.01 (s, 2H). [16]

S.2 EXTENDED CHARACTERIZATION DATA

The reactor used for the [2+2] photocycloaddition consisted of a custom-made temperature-controlled system, where the reaction mixture was kept at room temperature by passing coolant through the metallic system employing a recirculating chiller, and the irradiation was achieved with a single LED (21 mW purple LED (385 nm), 18 mW purple LED (410 nm), 22 mW blue LED (465 nm), 22 mW green LED (520 nm) and 40 mW white LED) located 1 cm beneath the base of the vial.

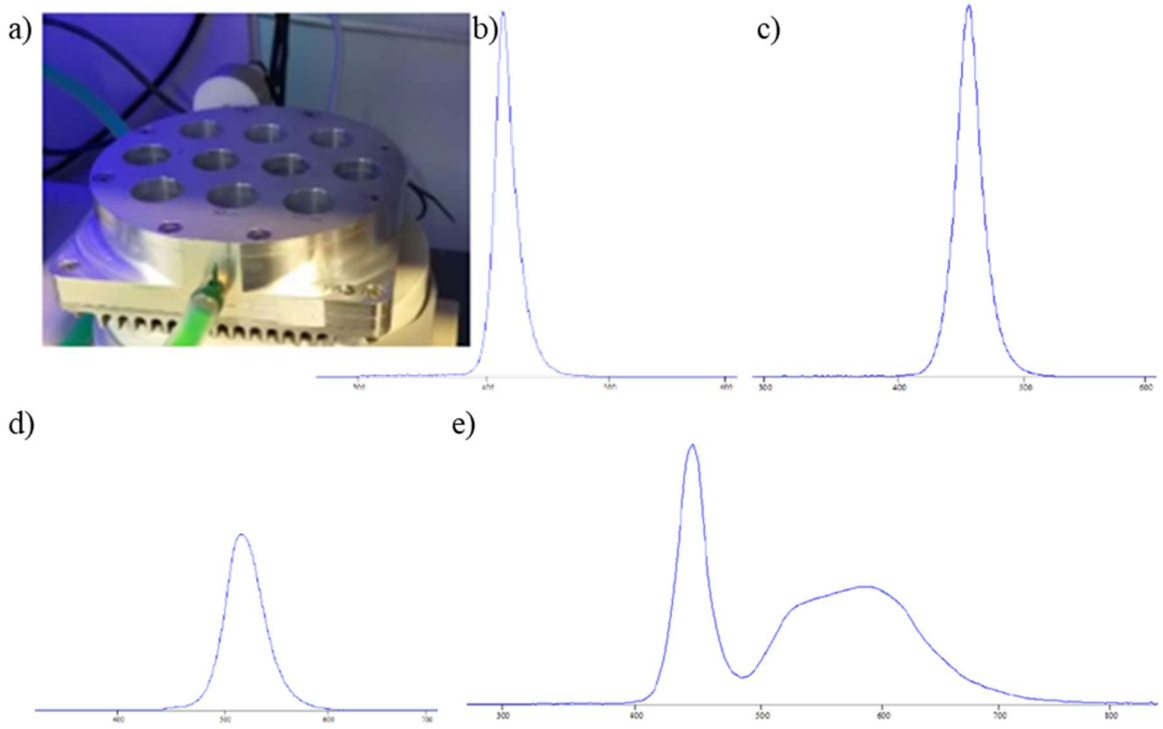


Figure S1: a) Digital photograph of the custom-made temperature-controlled system photoreactor. Emission spectrum of b) 18 mW purple LED (420 nm), c) 22 mW blue LED (450 nm), d) 22 mW green LED (520 nm) and e) 40 mW white LED.

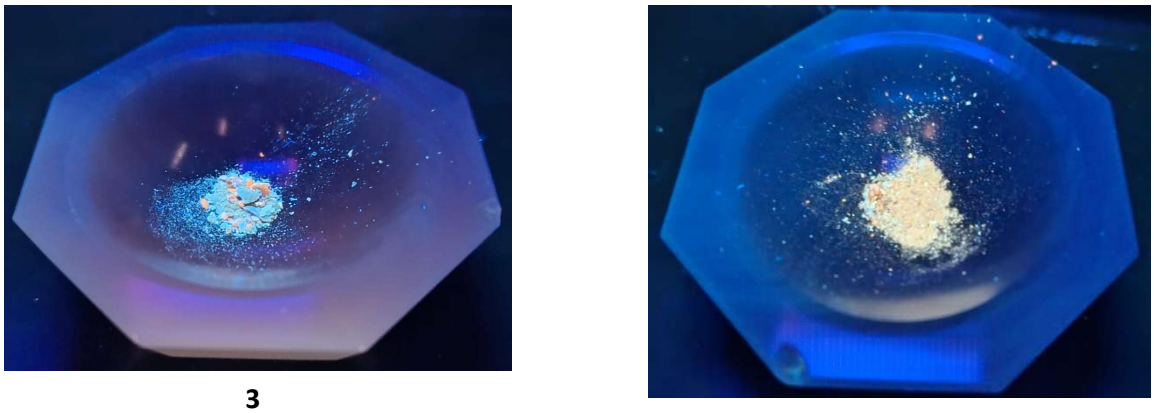


Figure S2. Pictures of **3** (on the left side) and **3-PTH** (on the right side) under a 365 nm lamp.

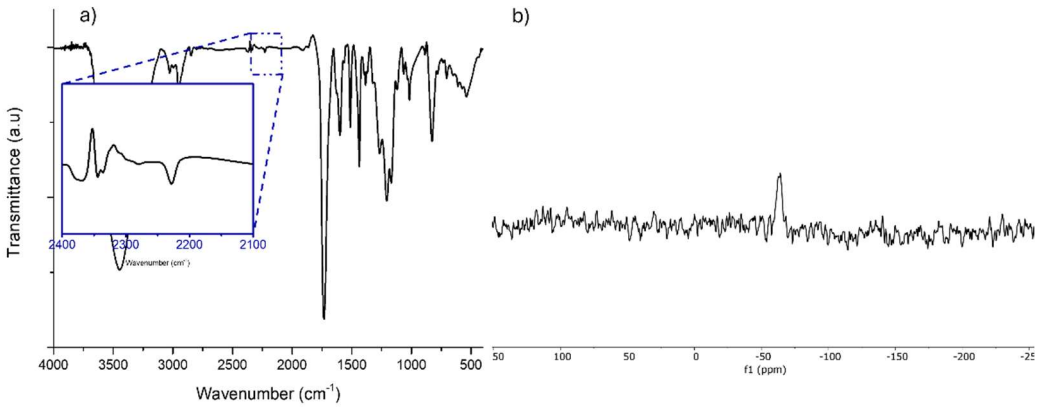


Figure S3. a) FTIR spectrum of **3-CN**. b) ^{19}F SS-NMR of **3-CF$_3$**.

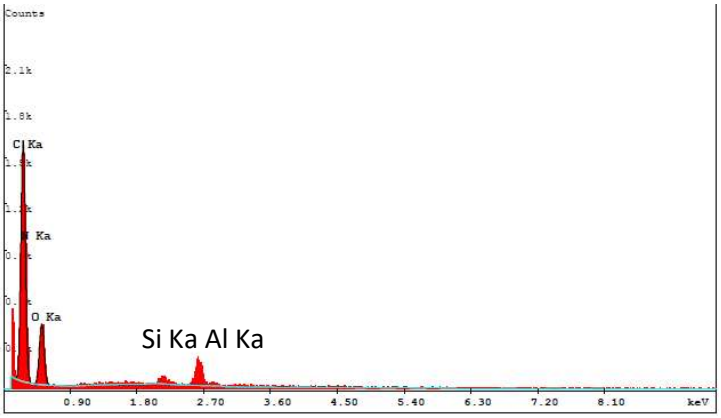


Figure S4. a) *in situ* Multielemental EDX spectrum of sample **3.**

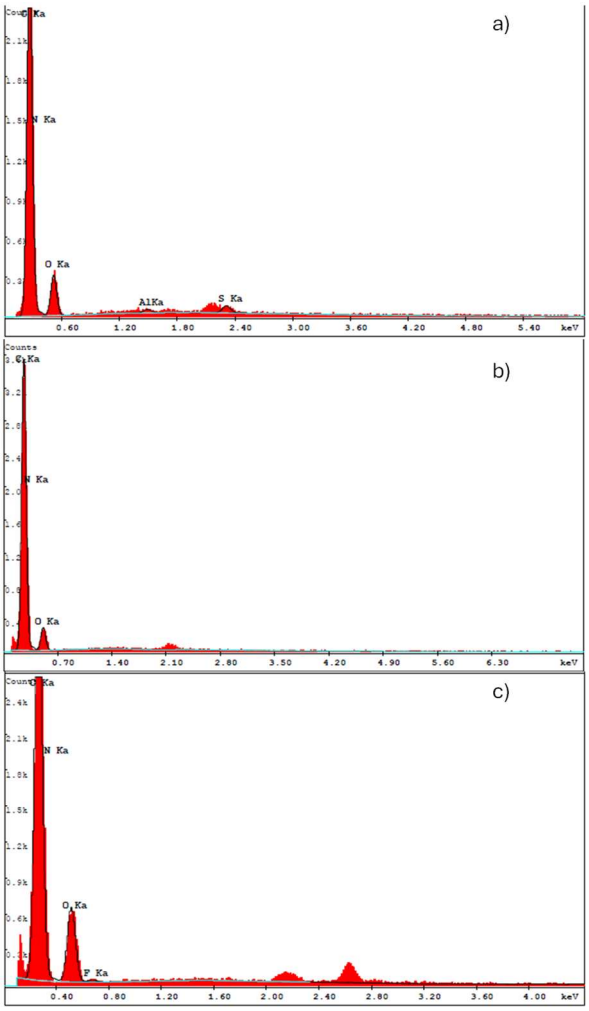


Figure S5. Multielemental EDX spectra of samples a) **3-CN**, b) **3-CF$_3$** and c) **3-PTH**

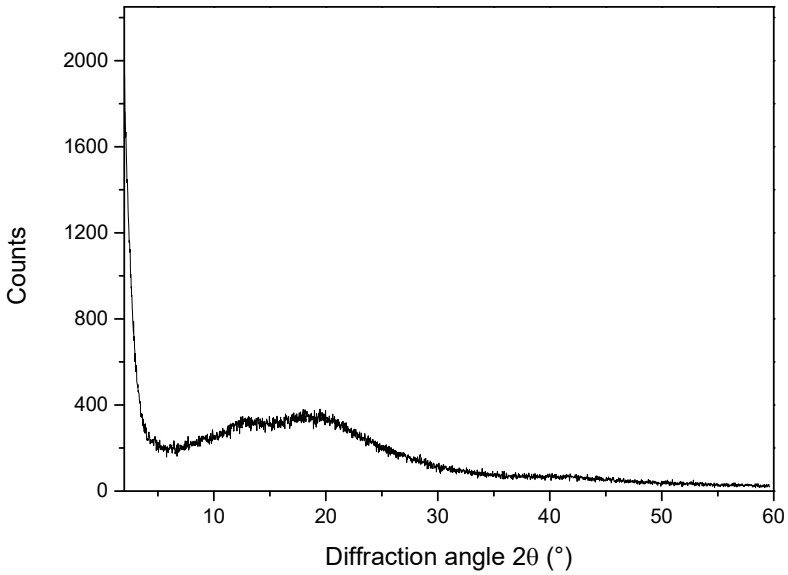


Figure S6. XRD pattern of **3.**

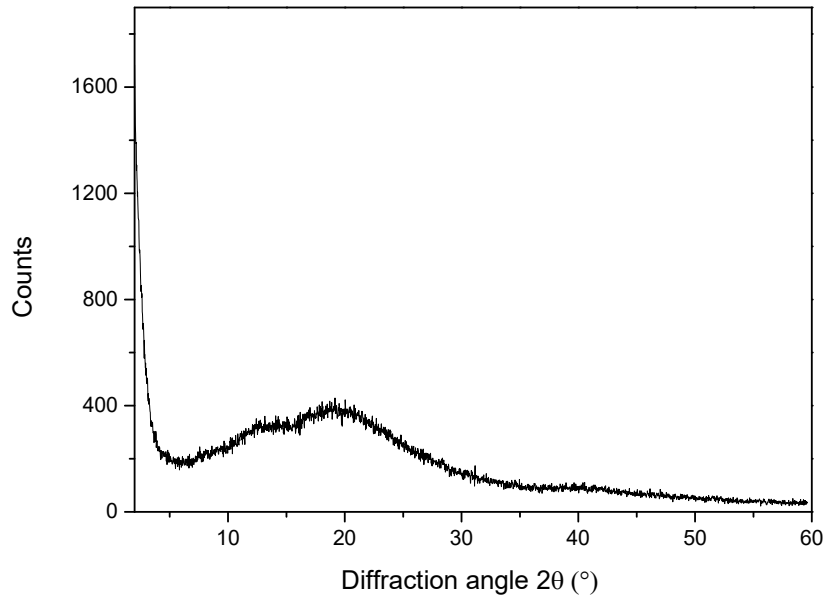


Figure S7. XRD pattern of **3-PTH.**

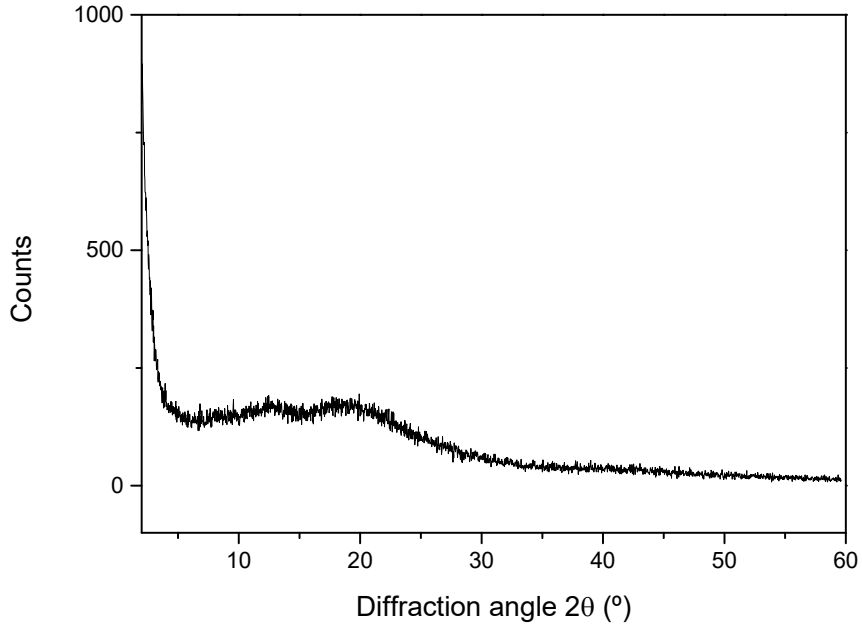


Figure S8. XRD pattern of **3-CN**.

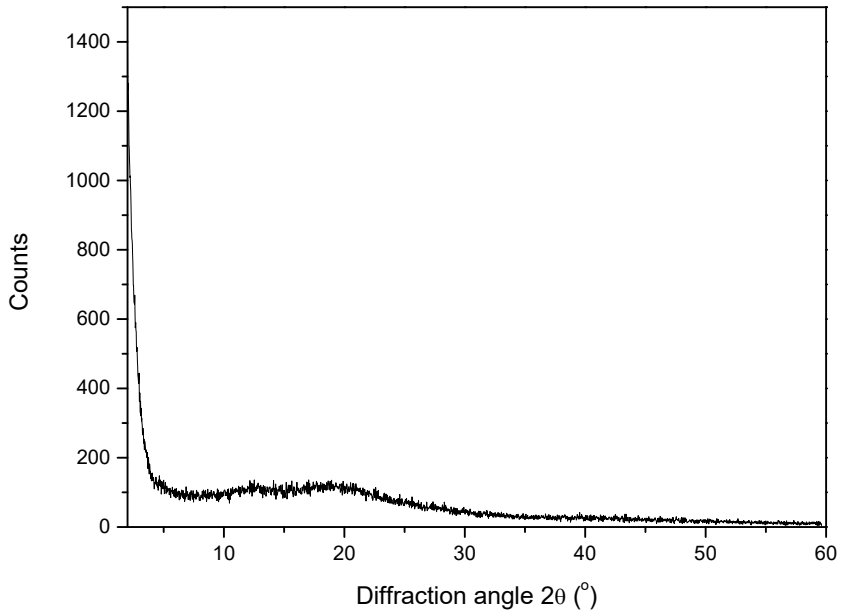
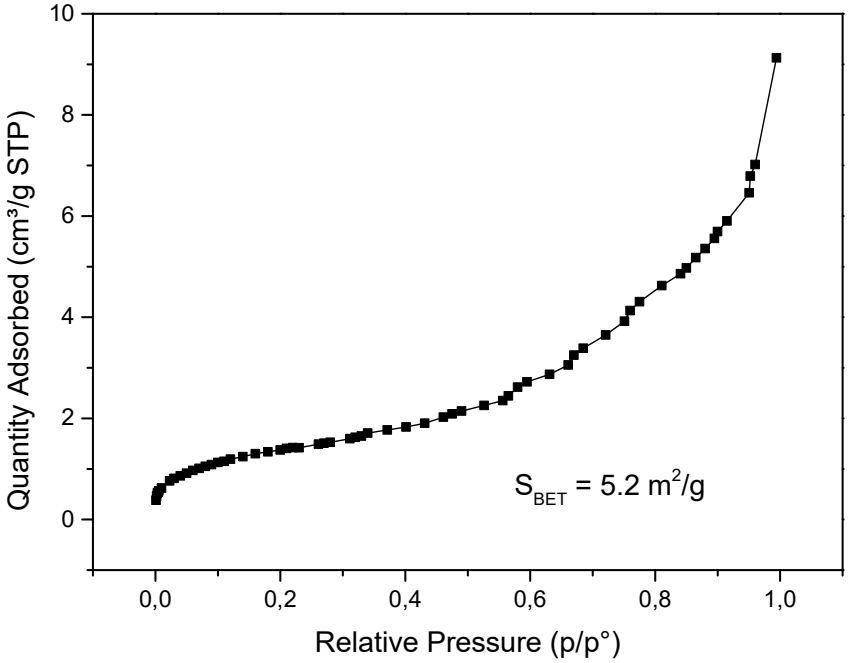


Figure S9. XRD pattern of **3-CF_3**.



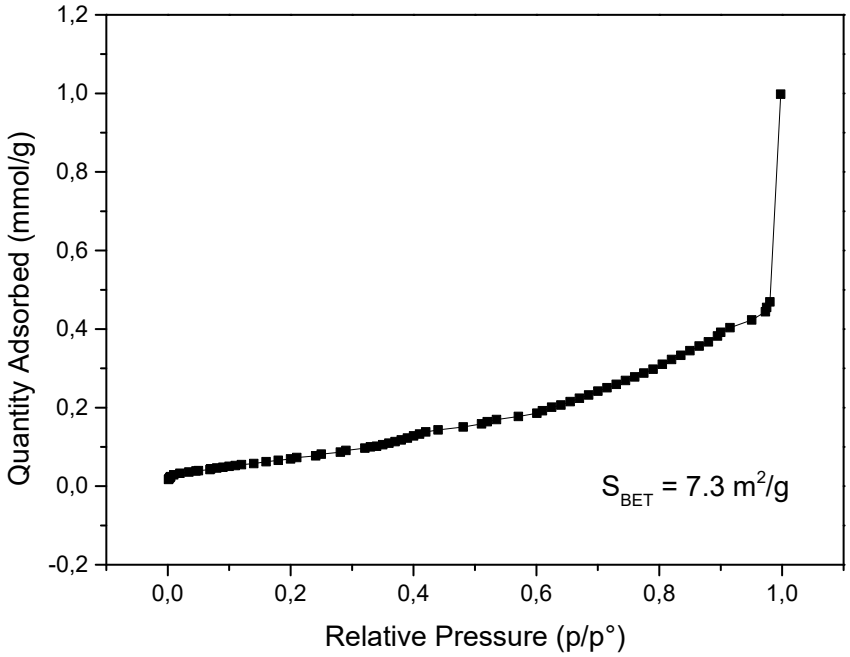


Figure S10. N_2 adsorption isotherm at 77K of **3** (upper) and **3-PTH** (lower)

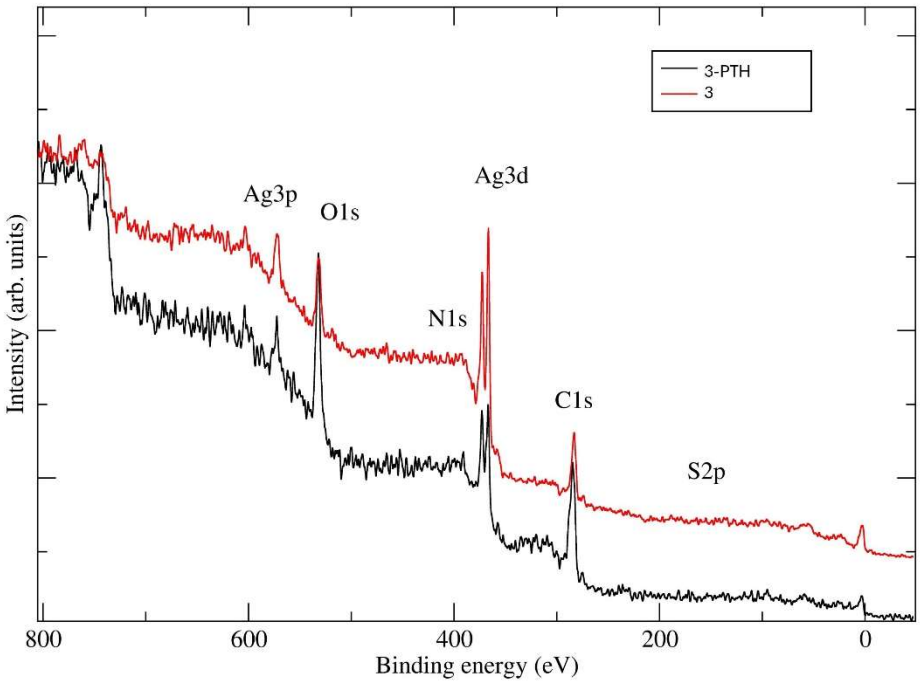


Figure S11. XPS Survey Spectrum of **3** (red) and **3-PTH** (black).

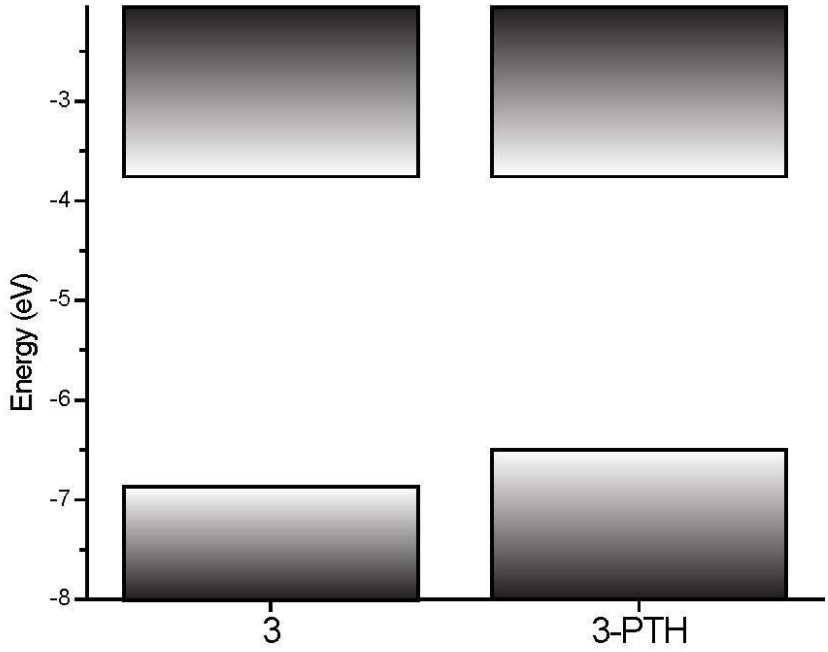
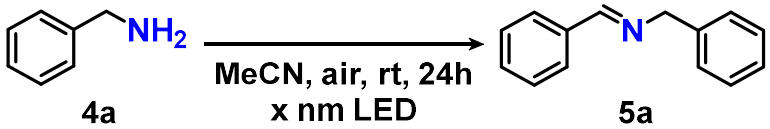


Figure S12. Band structure of **3** and **3-PTH.**

S3. EXTENDED CATALYTIC DATA

Table S1. Screening of reaction light in absence of catalyst.

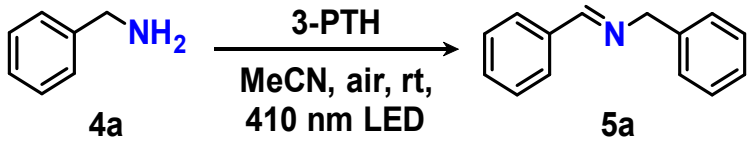


4a **5a**

Entry	*Light used*	*Yield (%)[a]*
1	385	11
2	410	9
3	455	3
4	520	3
5	White	4

Reaction conditions: substrate **4a** (0.2mmol) in acetonitrile (2 ml) under an air atmosphere was irradiated at x nm light for 24 h at rt. [a] Yield determined by ^{1}H-NMR using 1,3,5-trimetoxybenzene as internal standard.

Table S2. Mechanistic studies in the presence of ROS quenchers.



4a 5a

Entry	*Additive (equiv.)*	*Time (h)*	*Yield (%)[a]*
1	-	24	75
2	DABCO (0.5)	24	66
3	p-benzoquinone (0.5)	24	47
4	KI (0.5)	24	94
5	TBA (0.5)	24	16

Reaction conditions: substrate **4a** (0.2mmol), 2 mg of heterogeneous catalyst in acetonitrile (2 ml) under an air atmosphere with the quencher was irradiated at 410 nm light for 24 h at rt. [a] Yield determined by ^{1}H-NMR using 1,3,5-trimetoxybenzene as internal standard.

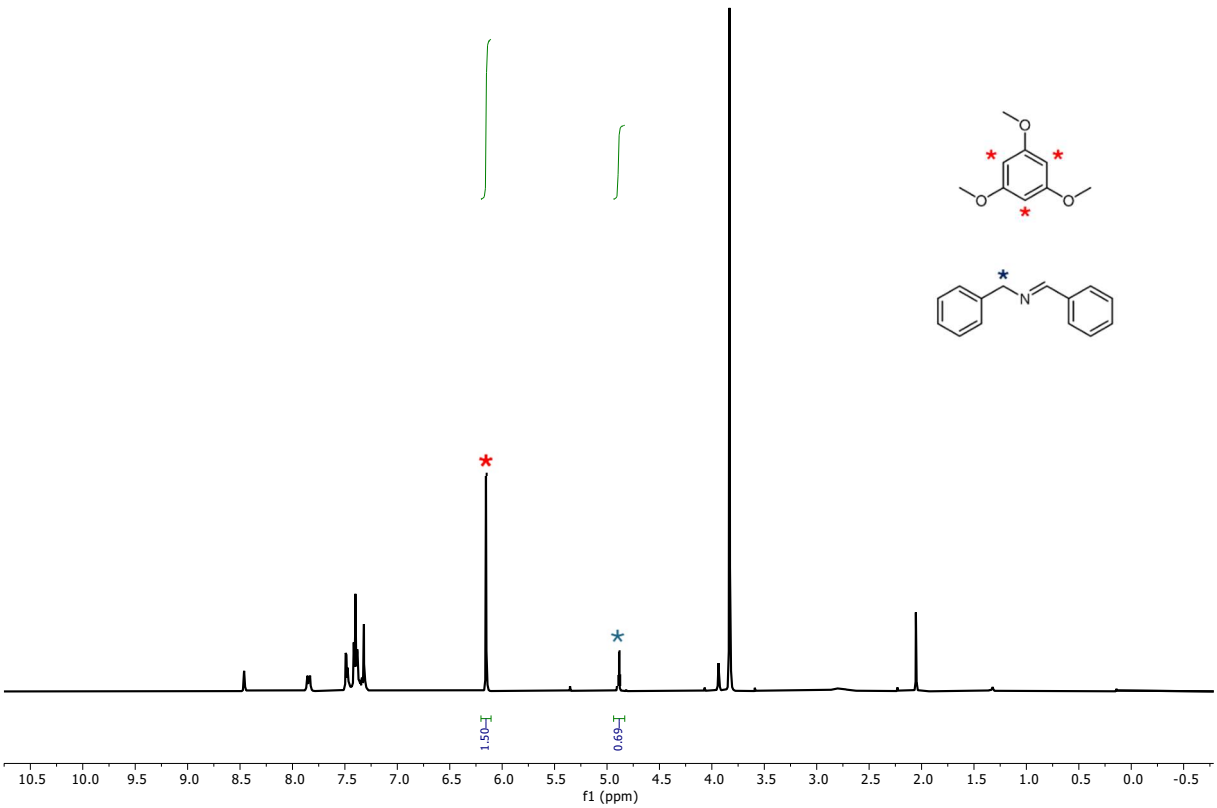


Figure S13. Example of crude of reaction and quantification of NMR yield via the use of 1,3,5-trimethoxybenzene as internal standard.

Table S3. State of the art for heterogenous catalysts for aryl amine homocoupling.

Entry	Catalyst	Scale (mmol)	Catalyst loading	Time	Atmosphere	Light	Ref.	Yield (%)
1	BDF-MON	1.0	21 mg	20-40 h	Air	blue LED	[17]	62
2	CPP-PX-1	1.0	6 mg	3-5 h	O_2	20 W white LEF	[18]	68
3	MFC-CMP	0.5	5 mg	1 h	O_2	12 W 460 nm LED	[19]	64
4	CP-1/CP-2	-	1 mol%	1 h	Air (60 ºC)	450 W Xe Lamp	[20]	84
5	CTF-9	0.2	2 mg	14h	O_2	blue LED	[13]	98
6	Py-BSZ-COF	0.2	5 mg	12 h	Air	15 W 520 nm LED	[21]	99
7	POR-BC-COF	0.2	10 mg	70 min	Air	20 W White LED	[22]	97
8	COF-TpPa	0.9	10 mg	8 h	O_2	5 W 420 nm LED	[23]	99

S4. ORGANIC MOLECULES CHARACTERIZATION SPECTRA

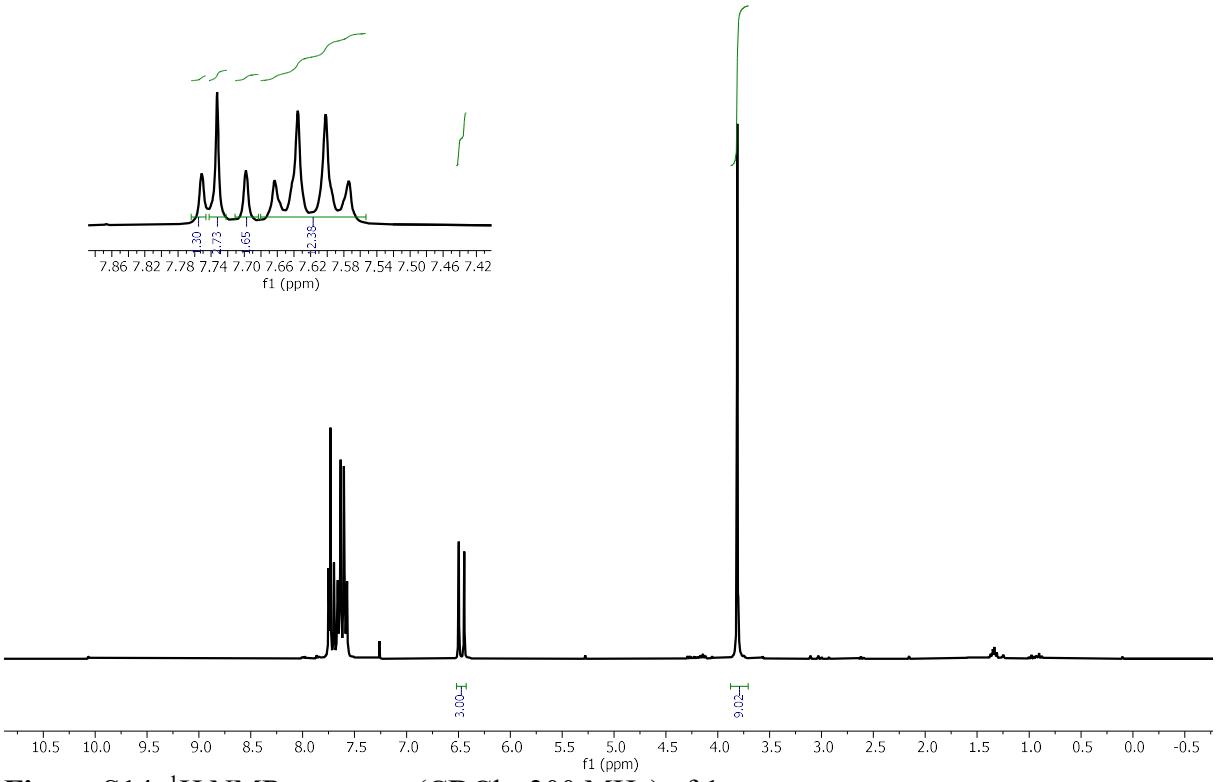


Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **1**.

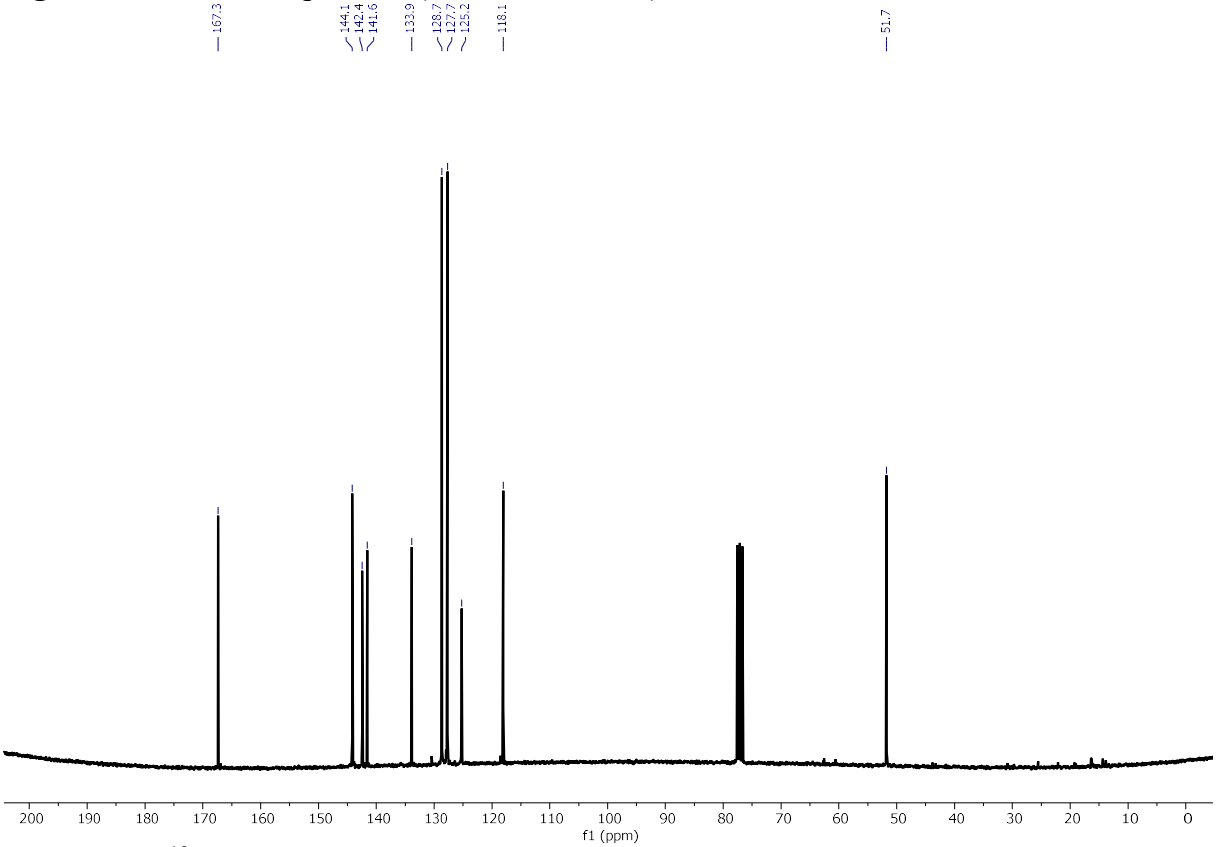


Figure S15. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **1**.

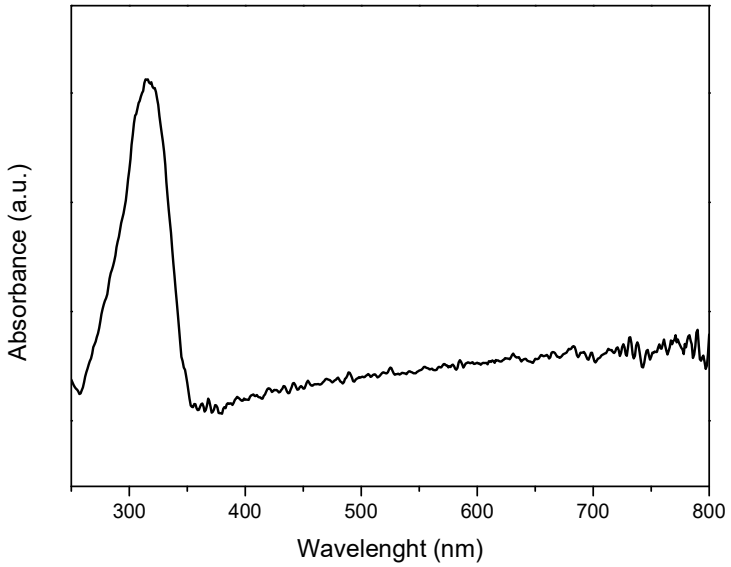


Figure S16. UV-Vis Absorption Spectrum of **1**.

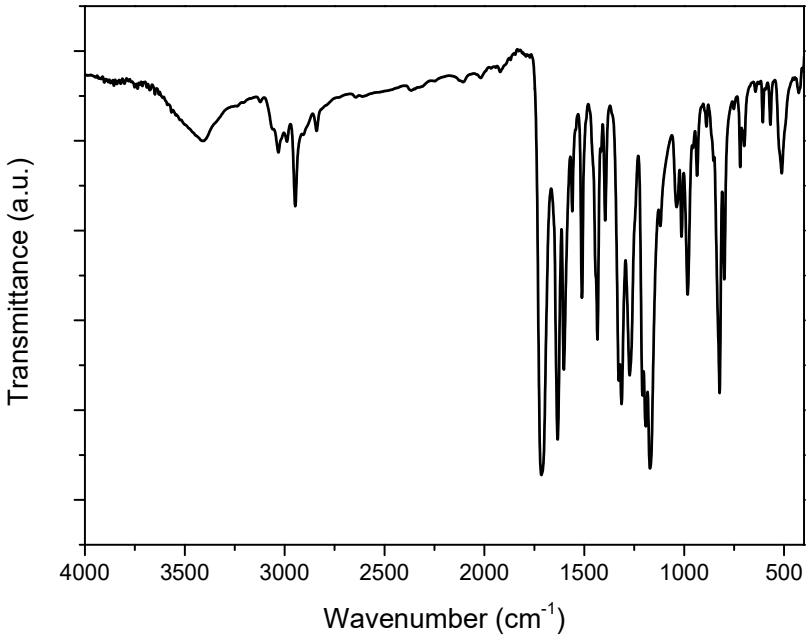


Figure S17. FT-IR Spectrum of **1.**

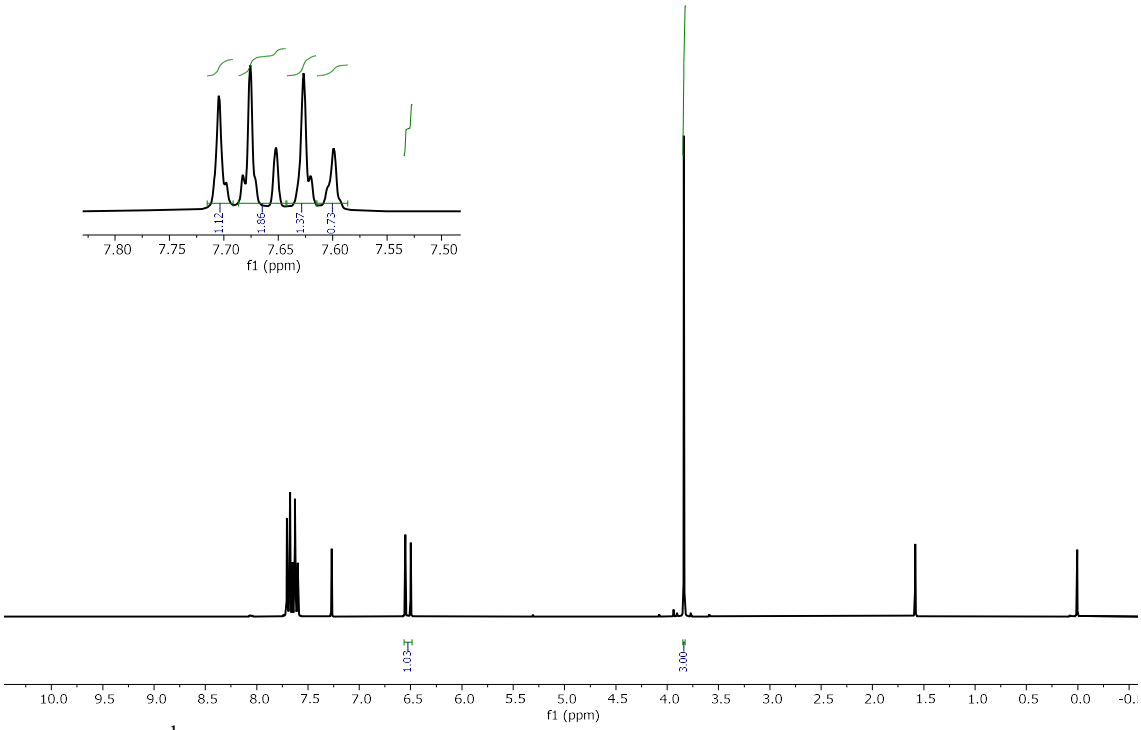


Figure S18. ^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of **2-CN**.

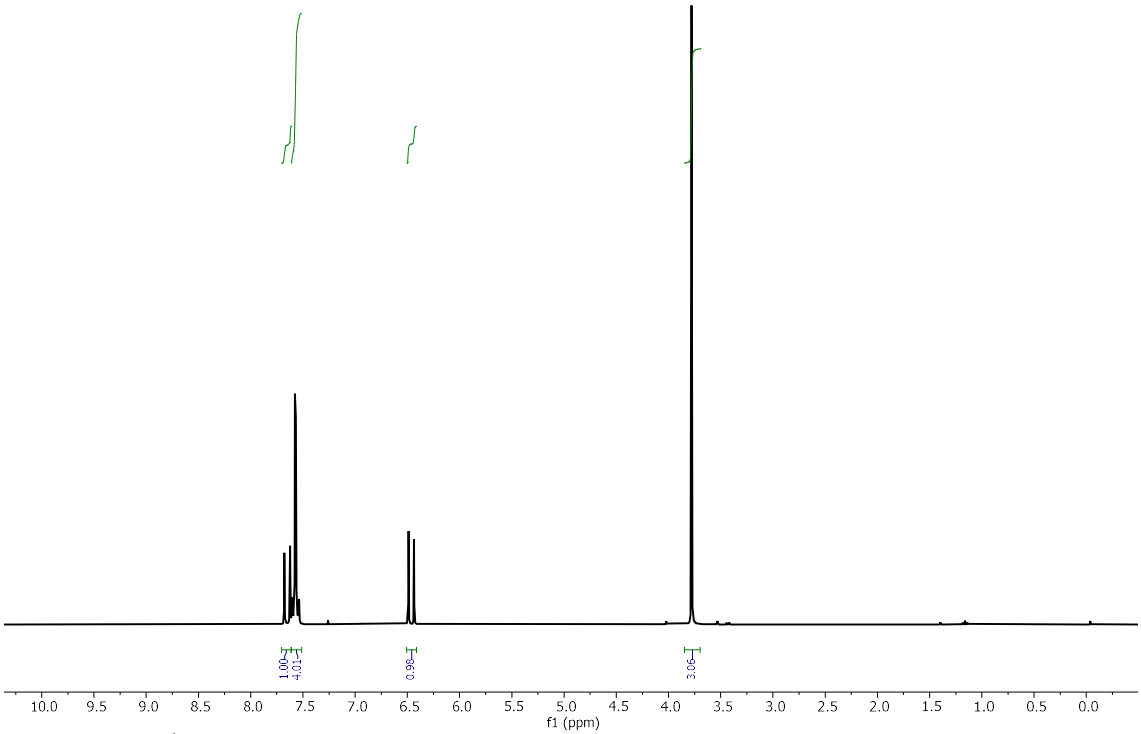


Figure S19. ^{1}H-NMR ($CDCl_3$, 300 MHz) spectrum of **2-CF$_3$**.

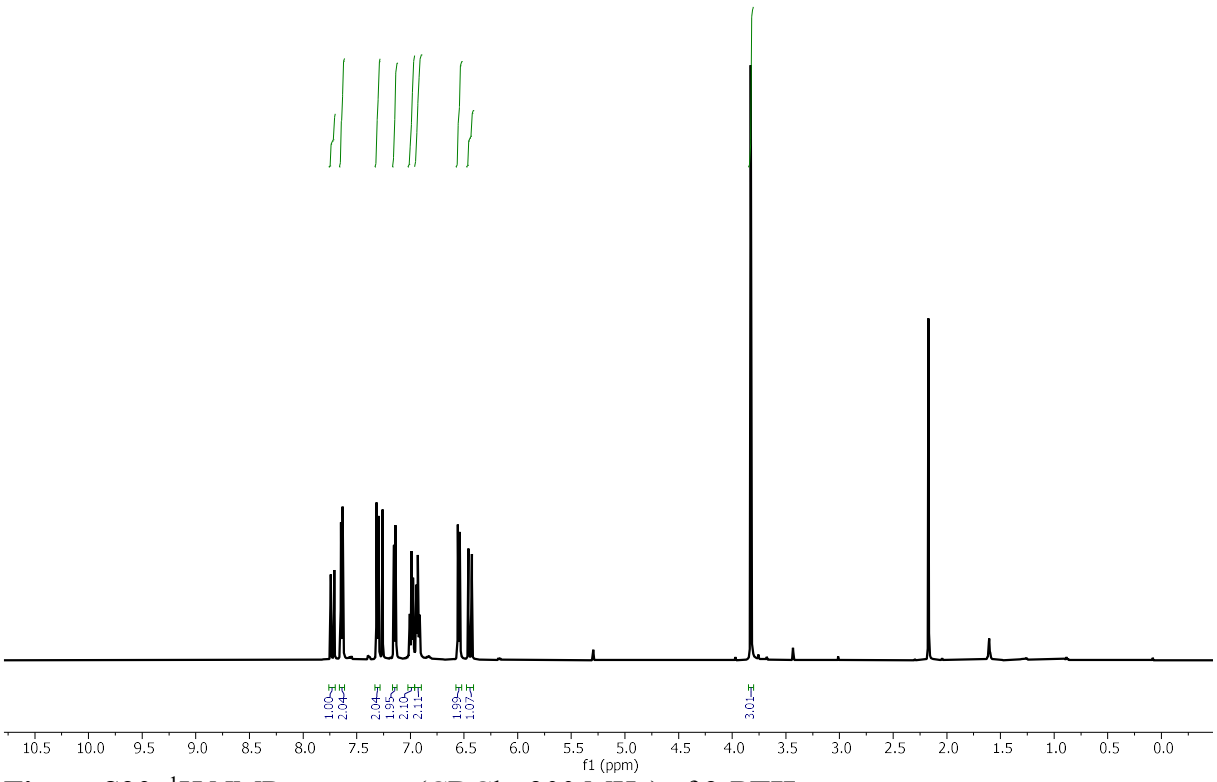


Figure S20. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **2-PTH**.

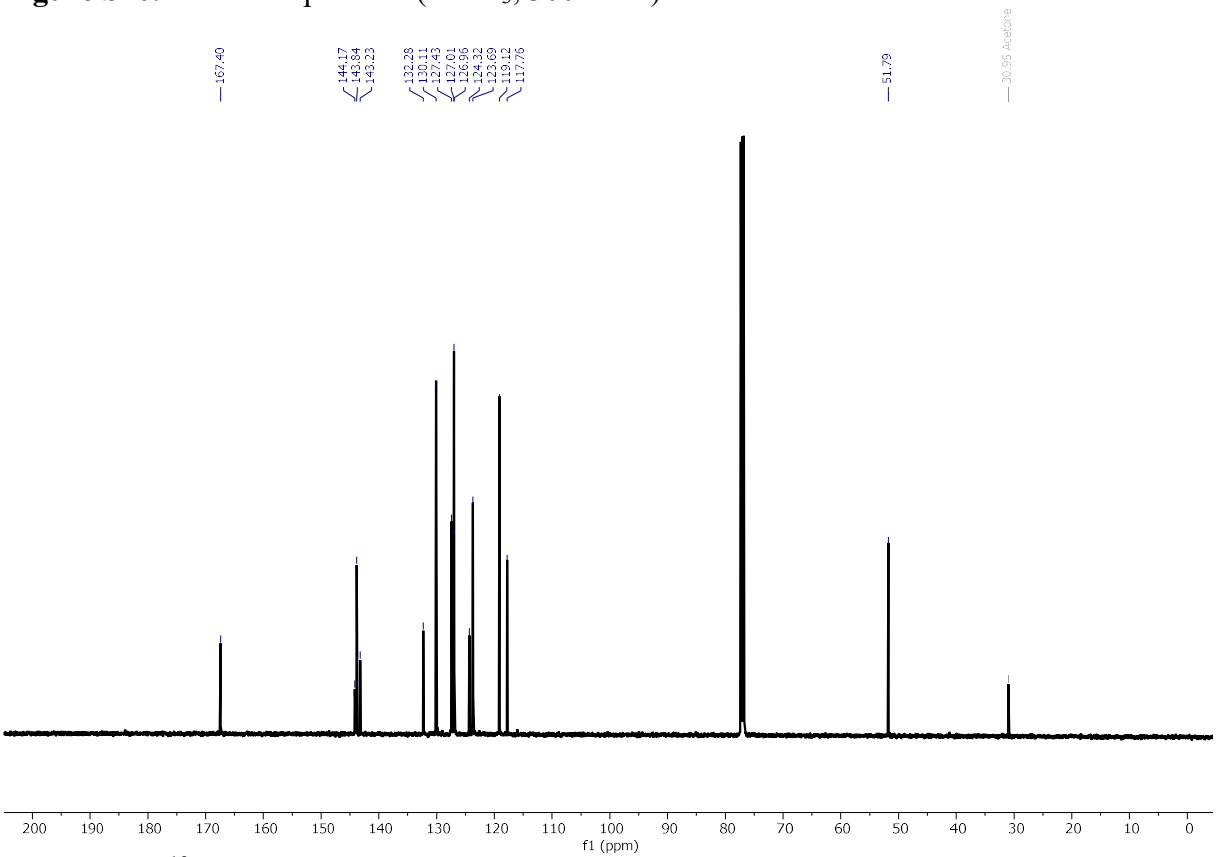


Figure S21. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **2-PTH**.

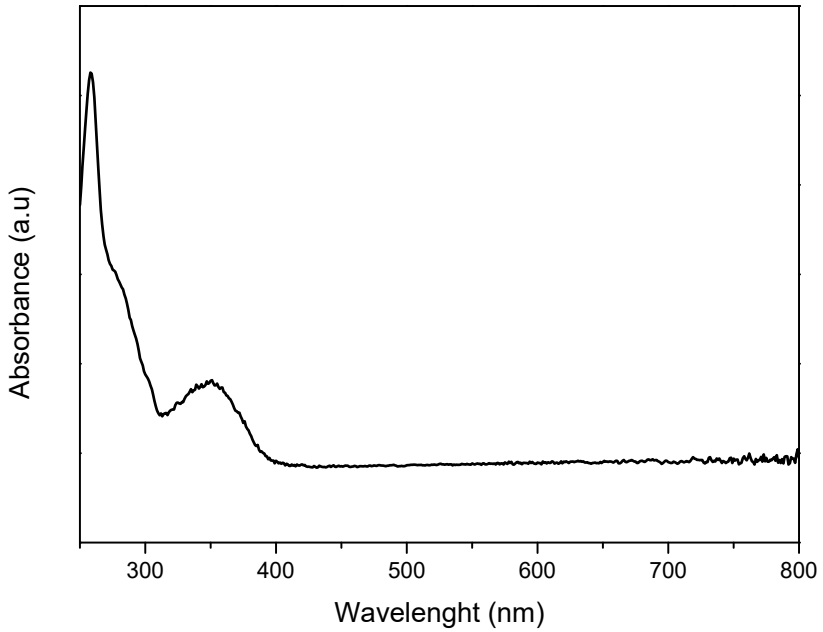


Figure S22. UV-Vis Absorption Spectrum of **2-PTH**.

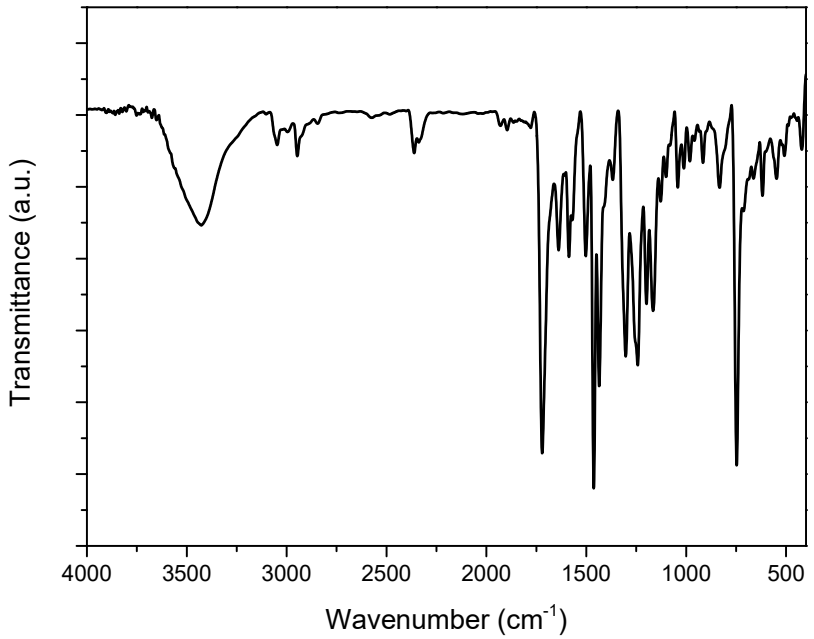


Figure S23. FT-IR Spectrum of **2-PTH.**

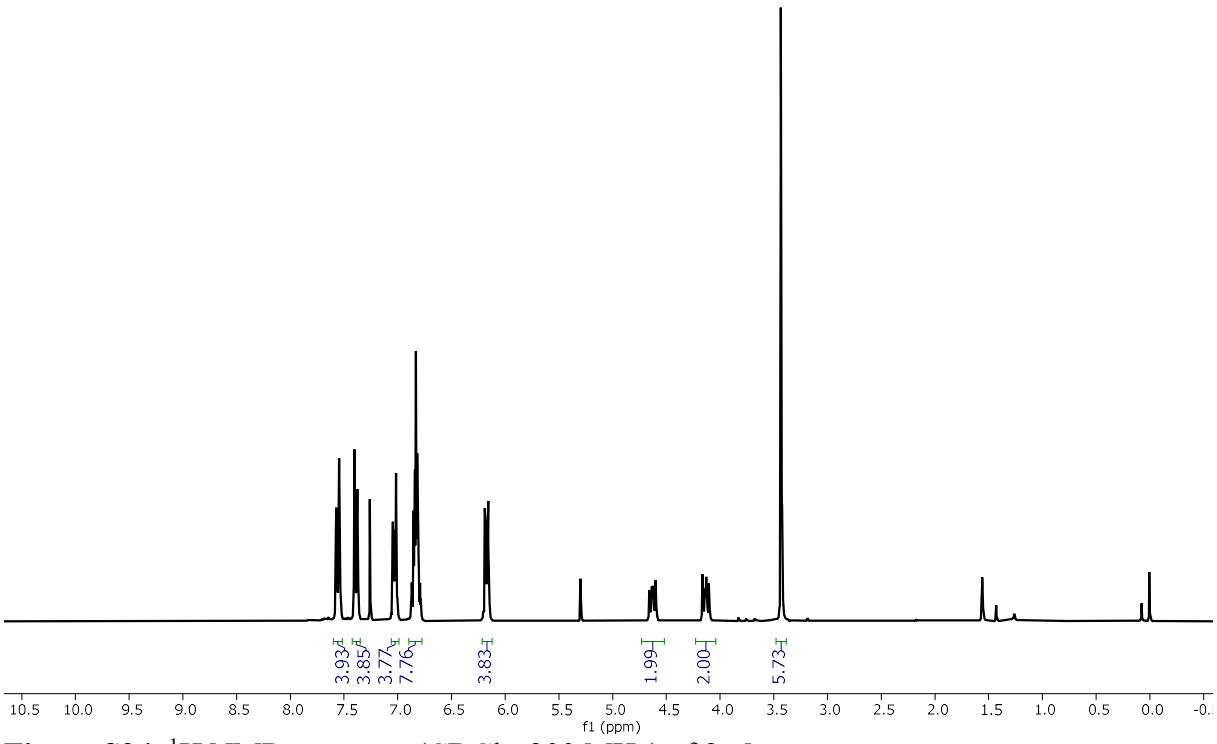


Figure S24. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **2-cb**.

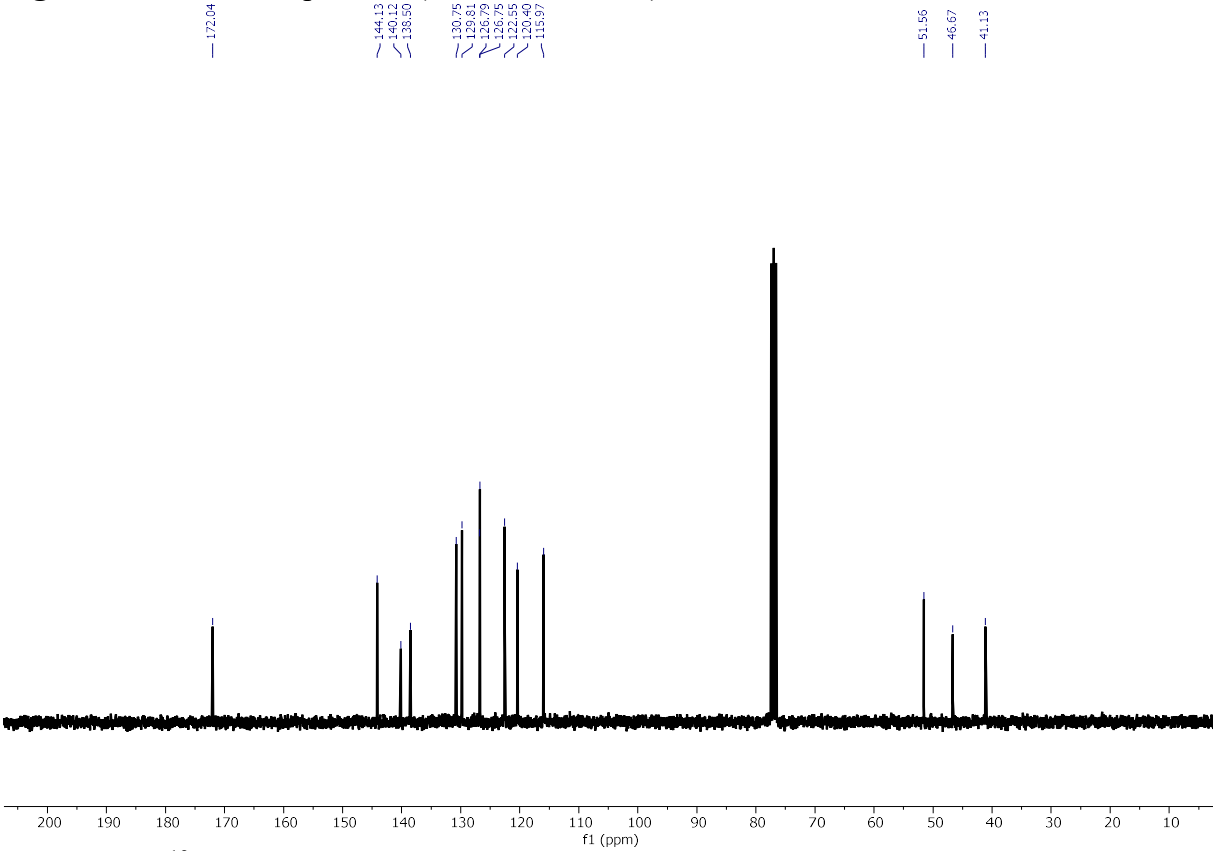


Figure S25. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **2-cb**.

S5. SUPPORTING REFERENCES

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