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Electronic Supplementary Information

Carbazole-triazine based donor-acceptor porous organic frameworks for efficient visible-light photocatalytic aerobic oxidation reactions

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S-1. *Materials, reaction setup, redox potentials of photocatalysts, control experiments, reaction monitoring, synthesis of photocatalysts, and general procedures*

S1.1 Materials

All solvents and reagents were purchased from TCI Chemical or Sigma-Aldrich, unless otherwise noted, used without further purification. ^{1}H NMR were performed on a Bruker FT-NMR spectrometer (400 MHz or 300 MHz). Solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra were recorded on a Bruker Avance III three-channel spectrometer and acquired using CP-TOSS pulse sequences, which were cross-polarized and suppressed the spinning side bands. Mass spectra (MS) were tested on a Waters Q-TOF I mass spectrometer. Gas adsorption isotherms of the POFs were collected using the surface area analyzer, Micromeritics ASAP-2020. The solid-state and solution emission and excitation spectra were measured on a RF-5301PC spectrometer. The solid-state and solution UV-vis absorption spectra were measured on an Agilent Cary 300 UV-vis spectrometer. The FT-IR spectra were measured on a Nicolet Avatar 360 FT-IR. The EPR spectroscopy was collected on a Bruker EMX spectrometer. The CV curves were tested on an Epsilon RDE-2 electrochemical system.

S1.2 Redox potentials and spectral properties of the tBu-substituted monomers

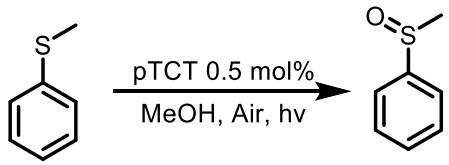
Table S1. Redox potentials and spectral properties of the tBu substituted monomers.

Compounds	$*E_{1/2}^{red}$	$*E_{1/2}^{ox}$	$E_{1/2}^{ox}$	$E_{1/2}^{red}$	$E_{0\text{-}0'}$	λ_{abs} (nm)	λ_{em} (nm)
tBuTCT	-1.69	+1.76	+1.52	-1.45	3.21	335	437/359
tBuTCT-P	-1.59	+1.29	+1.26	-1.56	2.85	352	518
tBuTCT-2P	-1.69	+1.18	+1.11	-1.62	2.80	382	504

*All potentials are given in volts versus the saturated calomel electrode (SCE). Measurements were performed in acetonitrile at room temperature.

S1.3 Control experiments and optimization studies

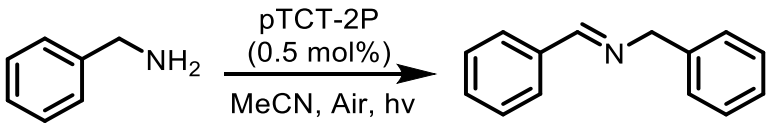
Table S2. Control experiments of photocatalytic aerobic oxidation of sulfides to sulfoxides.



Entry	Reaction Condition	Yield (%)[b]
1	Standard condition[a]	99
2	Without air	trace
3	Without light	NR.
4	Without pTCT	NR.
5	tBuTCT as photocat.	trace
6	tBuTCT-P as photocat.	trace (24 h)
7	tBuTCT-2P as photocat.	trace (32 h)
8	TCB as photocat.	trace (24 h)

[a]Standard condition: 0.5 mol% pTCT, 0.4 mmol thioanisole, 5 mL MeOH, 26 W white light at room temperature for 12 h. [b]Measured by ^{1}H-NMR.

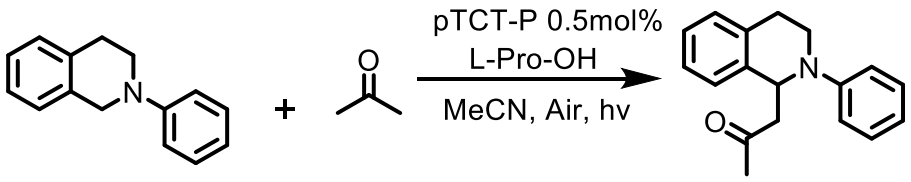
Table S3. Control experiments of photocatalytic aerobic oxidation of amine coupling.



Entry	Reaction Condition	Yield (%)[b]
1	Standard condition[a]	98
2	Without air	Trace
3	Without light	NR.
4	Without photocat.	NR.
5	tBuTCT as photocat.	14 (12 h)
6	tBuTCT-P as photocat.	32 (8 h)
7	tBuTCT-2P as photocat.	Trace (6 h)
8	TCB as photocat.	Trace (24 h)

[a]Standard condition: 0.5 mol% pTCT-2P, 0.4 mmol benzylamine, 5 mL MeCN, 26 W white CFL at room temperature for 6 h. [b]Measured by ^{1}H NMR.

Table S4. Control experiments of the direct Mannich reaction.



Entry	Reaction Condition	Yield (%)[b]
1	Standard condition[a]	98 (6 h)
2	Without air	Trace
3	Without light	NR.
4	Without photocat.	NR.
5	Without L-Pro-OH.	Trace

[a]Standard condition: 0.5 mol% pTCT-P, 0.25 mmol 2-phenyl-tetrahydroisoquinoline, 2.5 mmol acetone, 0.05 mmol L-Pro-OH, 5 mL MeCN, 26 W white CFL at room temperature for 6 h. [b]Isolated yield.

S1.4 Monitoring of the reactions

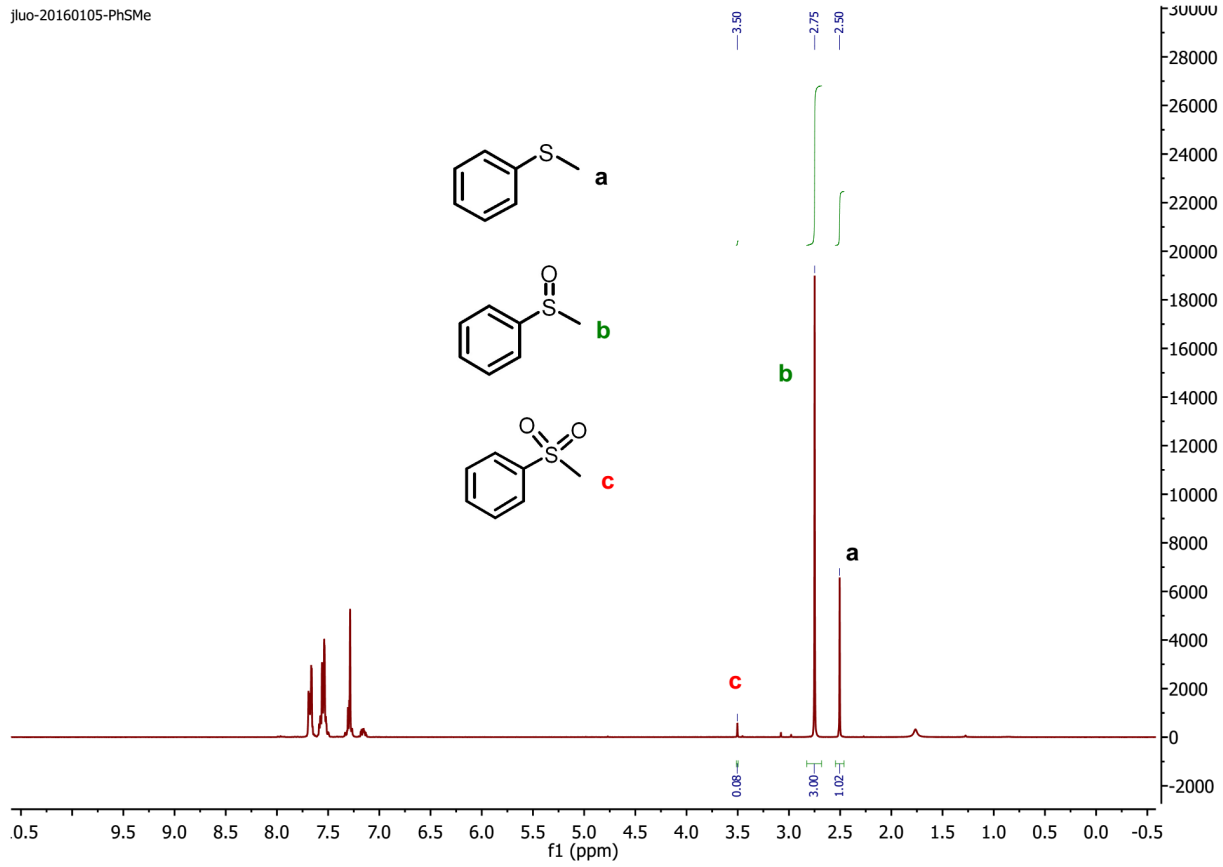


Fig. S1. ^{1}H NMR spectra of sulfide oxidation mixture.

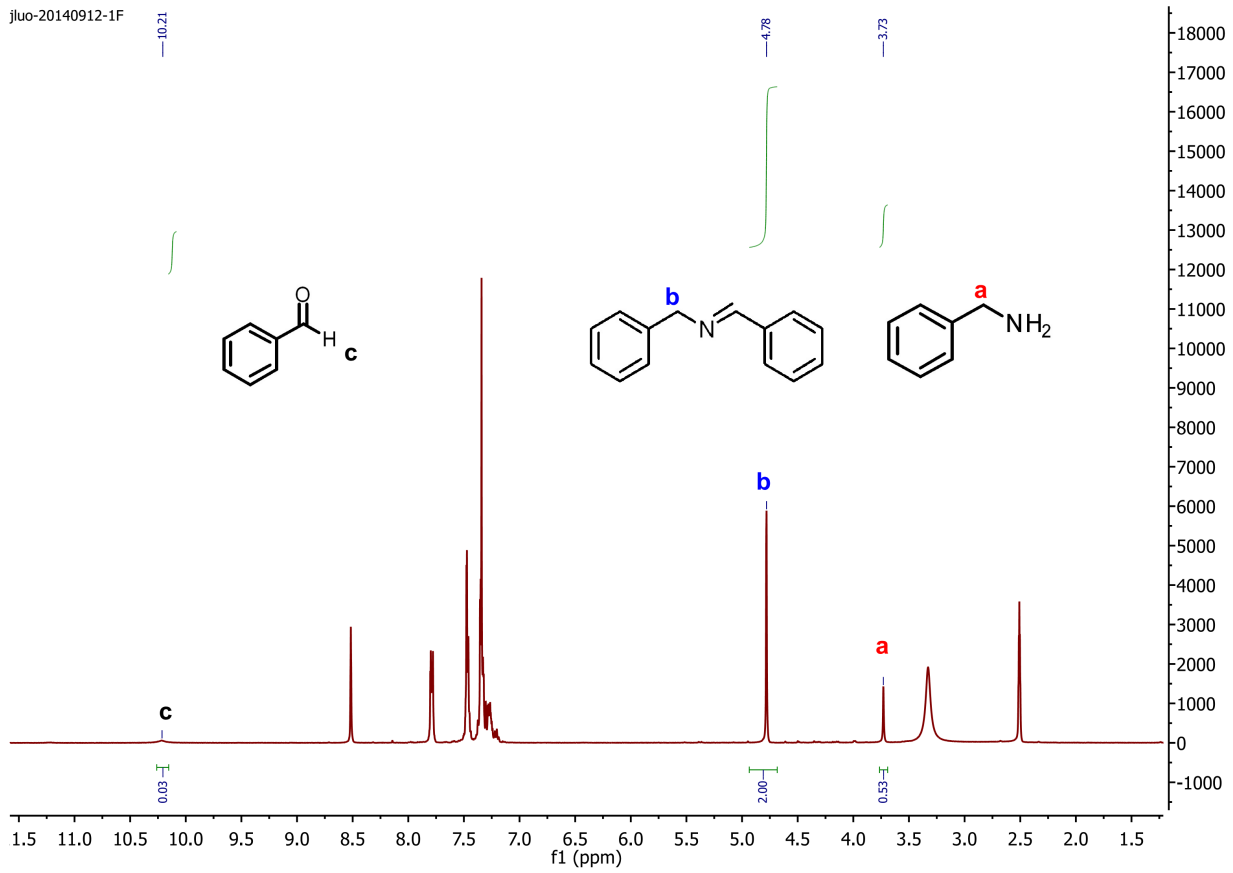


Fig. S2. ^{1}H NMR spectra of phenylmethanamine oxidation.

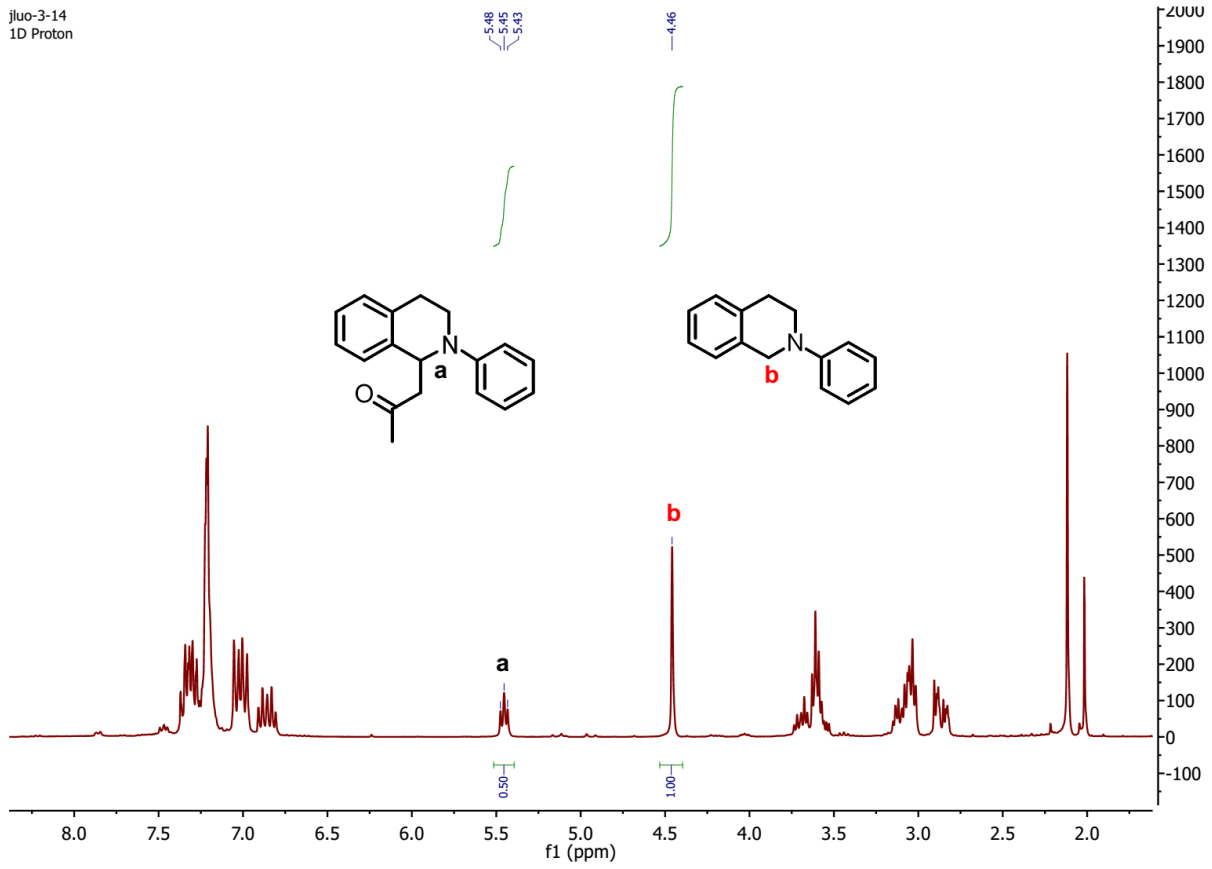
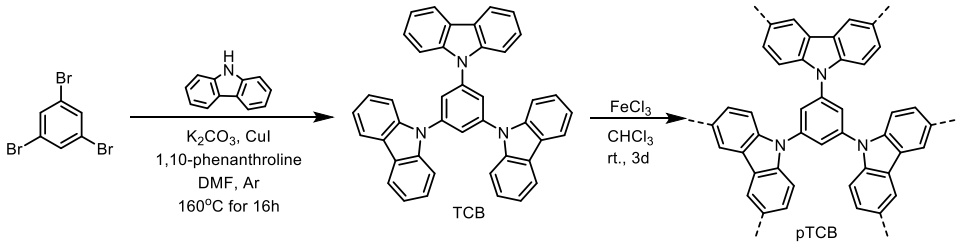


Fig. S3. ^{1}H NMR spectra of direct Mannich reaction.

S1.5 Synthesis of monomers and polymers



1,3,5-Tri(9*H*-carbazol-9-yl)benzene (TCB)

The TCB monomer was synthesized by the literature method.[1] The *N*-arylation reaction was proceeded with 1,3,5-tribromobenzene (0.32 g, 1.0 mmol), carbazole (0.67 g, 4.0 mmol), K_2CO_3 (0.69 g, 5.0 mmol), CuI (0.23 g, 1.2 mmol), and 1,10-phenanthroline (22 mg, 0.12 mmol) under argon. Anhydrous dimethylformamide (DMF) (20 mL) was injected into the reaction flask, and the resulting mixture was degassed for 15 min under stirring. The mixture was heated at 160 °C for 18 h. After cooling down to room temperature, the mixture was poured onto water. The precipitate was washed with ethanol (100 mL) and further purified by recrystallization in toluene to give a white powder as the product. Yield: 0.24 g (42% yield).

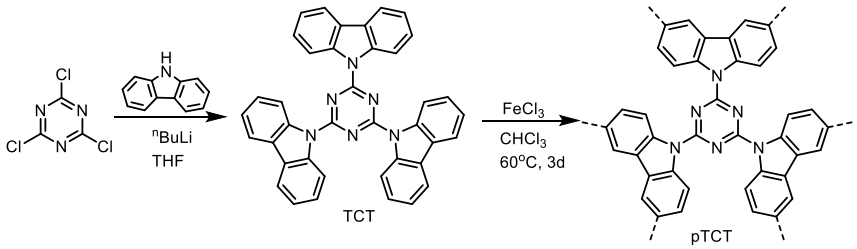
^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 7.36 (t, J = 7.5 Hz, 6H), 7.50 (t, J = 7.5 Hz, 6H), 7.70 (d, J = 7.5 Hz, 6H), 7.99 (s, 3H), 8.19 (d, J = 7.5 Hz, 6H).

ESI-MS [M^+]: 573.2216 (calc. 573.2205).

*p*TCB

The method of polymerization of carbazolic monomers was previously reported.[1-2] Under argon protection, TCB (172 mg, 0.3 mmol) was dissolved in anhydrous dichloromethane (20 mL). The monomer solution was added dropwise to a suspension of anhydrous $FeCl_3$ (322 mg, 2.0 mmol) in anhydrous dichloromethane (20 mL). The resulting reaction mixture was stirred for 3 days at room temperature. Methanol (50 mL) was added and stirred for 1 h to quench the reaction. The

obtained polymer was then washed with HCl (12 M) for 2 h, filtered and washed with water and THF. The polymer was further purified using Soxhelet extraction with THF for 24 h, and then dried at 120 °C under vacuum for 24 h to give a yellowish powder. Yield: 162 mg (94% yield). FT-IR (solid, ν, cm^{-1}): 1595, 1463, 1320, 1226, 1153, 1038, 878, 805, 743.



2,4,6-Tricarbazolo-1,3,5-triazine (TCT)

Monomer 2,4,6-tricarbazolo-1,3,5-triazine (TCT) was synthesized by the literature method.[3] ^{n}BuLi (6.59 mL, 1.6 M in hexane) was added dropwise to a solution of carbazole (1.6 g, 9.65 mmol) in dry THF (20 mL) under argon at –78 °C. The mixture was stirred for 1h and warmed to room temperature. Then cyanuric chloride (0.5 g, 2.73 mmol) was added into the carbazole–lithium mixture and refluxed for 12 h. After the solution was cooled to room temperature, 20 mL of water were added. The product was filtered, washed with water, hexane, and diethyl ether. The pure product was obtained by extractive filtering with hot chlorobenzene, recrystallizing repeatedly from the same solvent to afford 1.05 g (58% yield) of a white solid as the product.

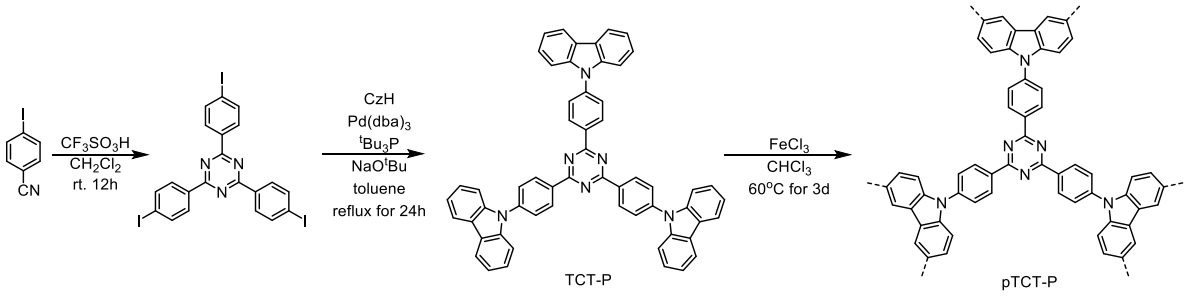
^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 7.43~7.54 (m, 12H), 8.13~8.20 (m, 6H), 9.01~9.10 (m, 6H).

ESI-MS [M^{+}]: 576.2048 (calc. 576.2062).

pTCT

A suspension of monomer TCT (288 mg, 0.5 mmol) in anhydrous chloroform (40 mL) was added dropwise into a suspension of $FeCl_3$ (1.3 g, 8.1 mmol) in anhydrous chloroform (50 mL) in 30 min. The mixture was stirred for 3 days under nitrogen at 60 °C. Methanol (50 mL) was added and stirred for 1 h to quench the reaction. The obtained polymer was then washed with HCl (12 M) for 2 h, filtered, and washed with water and THF. The polymer was further purified using Soxhelet extractor with methanol and THF for 24 h, and then dried at 120 °C under vacuum for 24 h to give a brown powder (265 mg, 93% yield).

FT-IR (solid, ν, cm^{-1}): 1545, 1383, 1310, 1220, 1062, 879, 817, 751.



2,4,6-Tris(4-iodophenyl)-1,3,5-triazine

4-Iodobenzonitrile (2.29 g. 10 mmol) was dissolved in dichloromethane (40 ml) and cooled to 0°C. Trifluoroacetic acid (4.42 mL, 50 mmol) was added dropwise under nitrogen atmosphere. After stirring 1h, the temperature was raised to room temperature and stirred for 12 h. Water was added after the reaction, and the mixture was stirred for 1 h. The resulting precipitate was filtered, washed with water and ethanol (1.65 g, 72 % yield).

^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 8.07 (d, J = 8.4 Hz, 6H), 8.50 (d, J = 8.4Hz, 6H).

ESI-MS [M^+]: 686.8172 (calc. 686.8165).

2,4,6-Tris(4-(9*H*-carbazol-9-yl)phenyl)-1,3,5-triazine (TCT-P)

The mixture of 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (0.90 g, 1.31mmol, 1.0 equiv), carbazole (0.766 g, 4.59 mmol, 3.5 equiv), $Pd_2(dba)_3$ (72 mg, 6 mol%), $^tBu_3P$ (40 mg, 5 mol%) was stirred in dry toluene (25 mL) under argon atmosphere at room temperature for 10 min. NaO^tBu (0.57 g, 5.9 mmol, 4.5 equiv) was added. And then the mixture was refluxed for 24 h. After the solution was cooled to room temperature, the solvent was removed under vacuum. The residue was purified by washing with 3 M HCl, MeOH, and diethyl ether to give the product as a gray solid (0.86 g, 82% yield).

^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 7.38 (t, J = 9.0 Hz, 6H), 7.50 (t, J = 9.0 Hz, 6H), 7.64 (d, J = 9.0 Hz, 6 H), 7.93 (d, J = 8.4 Hz, 6H), 8.23 (d, J = 8.4 Hz, 6H), 9.15 (d, J = 9.0 Hz, 6H).

ESI-MS [M^+]: 804.3007 (calc. 804.3001).

pTCT-P

The suspension of monomer TCT-P (402 mg, 0.5 mmol) in anhydrous chloroform (40 mL) was added dropwise to a suspension of $FeCl_3$ (1.3 g, 8.1 mmol) in anhydrous chloroform (50 mL) in 30 min. The mixture was stirred for 3 days under nitrogen at 60 °C. Methanol (50 mL) was added and stirred for 1 h to quench the reaction. The obtained polymer was then washed with HCl (12 M) for 2 h, filtered, and washed with water and THF. The polymer was further purified using Soxhelet extractor with methanol and THF for 24 h and then dried at 120 °C under vacuum for 24 h to give a yellow powder (380 mg, 95% yield).

FT-IR (solid, ν, cm^{-1}): 1606, 1505, 1452, 1414, 1365, 1265, 1226, 1174, 1018, 805, 732.

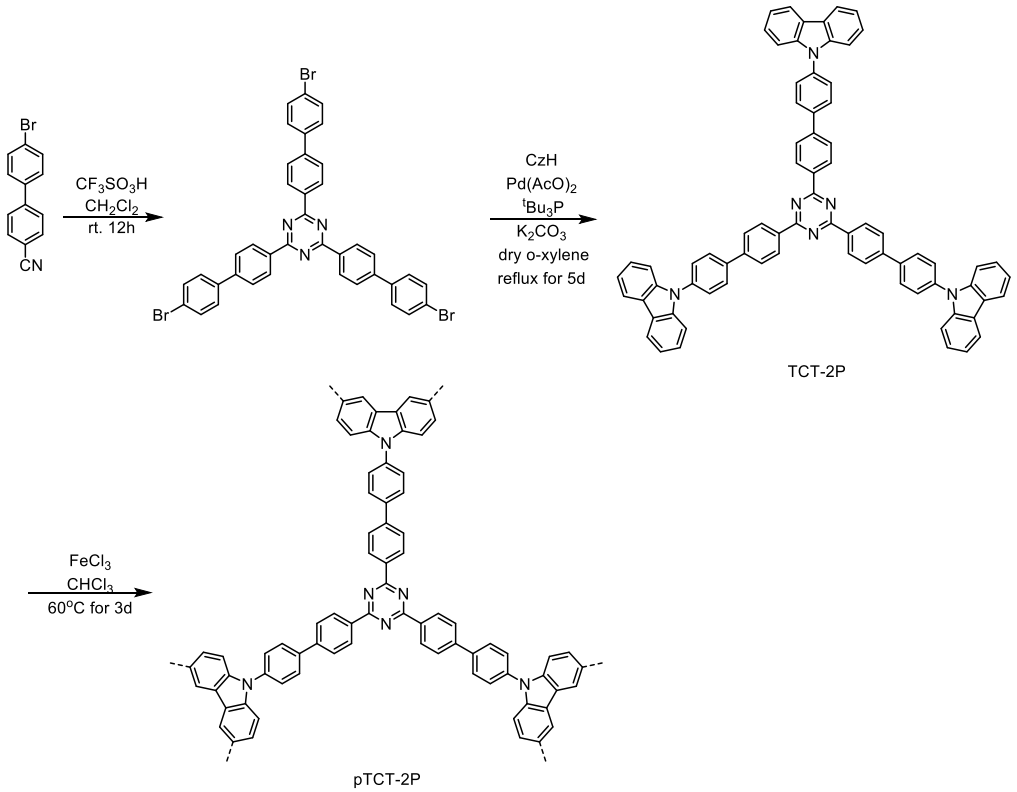


Fig. S4. Synthetic scheme of pTCT-2P.

2,4,6-Tris(4'-bromo-[1,1'-diphenyl]-4-yl)-1,3,5-triazine

2,4,6-Tris(4'-bromo-[1,1'-diphenyl]-4-yl)-1,3,5-triazine was synthesized by the same method as 2,4,6-tris(4-iodophenyl)-1,3,5-triazine using 4'-bromo-[1,1'-diphenyl]-4-carbonitrile (2.57 g. 10 mmol) as starting material. A white solid was obtained as the product (1.57 g, 61 % yield).

^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 7.58~7.67 (m, 12H), 7.81 (d, J = 8.1 Hz, 6H), 8.89 (d, J = 8.1 Hz, 6H).

ESI-MS [M^+]: 772.9506 (calc. 772.9500).

2,4,6-Tris(4'-(9H-carbazol-9-yl)-[1,1'-diphenyl]-4-yl)-1,3,5-triazine (TCT-2P)

A mixture of 2,4,6-Tris(4'-bromo-[1,1'-diphenyl]-4-yl)-1,3,5-triazine (0.5 g, 0.65 mmol, 1.0 equiv), carbazole (0.54 g, 3.2 mmol, 5.0 equiv), $Pd(AcO)_2$ (16 mg, 10 mol%), and ^{t}Bu$_3$P (52 mg,

40 mol%) was stirred in dry *o*-xylene (25 mL) under argon atmosphere at room temperature for 10 min. K_2CO_3 (0.50 g, 3.6 mmol, 5.5 equiv) was added. The mixture was then refluxed at 165 °C for 5 d. After the mixture was cooled to room temperature, the solvent was removed under vacuum. The residue was purified by washing with 3 M HCl, MeOH, and diethyl ether to give a grey solid as the product (0.59 g, 89% yield).

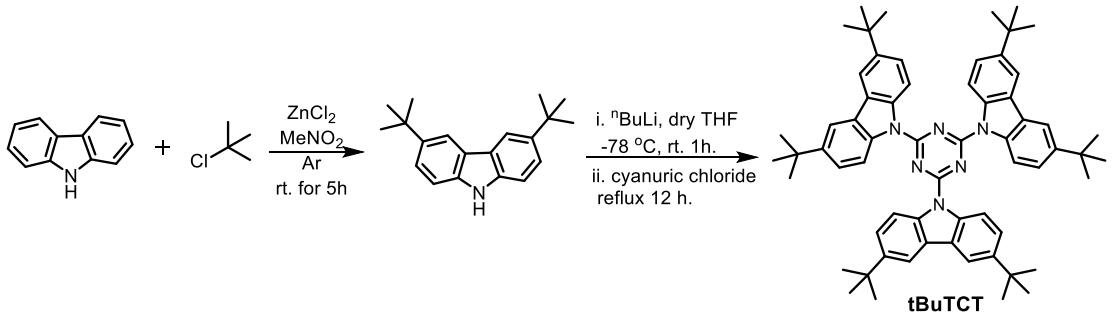
^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 7.38 (t, J = 7.5 Hz, 6H), 7.51 (t, J = 7.5 Hz, 6H), 7.57 (d, J = 8.1 Hz, 6H), 7.77 (t, J = 8.1Hz, 6H), 7.92~8.04 (m, 12H), 8.22 (d, J = 7.5 Hz, 6H), 9.02 (d, J = 8.1 Hz, 6H).

ESI-MS [M^+]: 1032.3948 (calc. 1032.3940).

pTCT-2P

The suspension of monomer TCT-2P (310 mg, 0.3 mmol) in anhydrous chloroform (40 mL) was added dropwise to a suspension of $FeCl_3$ (0.8 g, 5.0 mmol) in anhydrous chloroform (50 mL) in 30 min. The mixture was stirred for 3 days under nitrogen at 60 °C. Methanol (50 mL) was added and stirred for 1 h to quench the reaction. The obtained polymer was then washed with HCl (12 M) for 2 h, filtered, and washed with water and THF. The polymer was further purified using Soxhelet extractor with methanol and THF for 24 h and then dried at 120 °C under vacuum for 24 h to give an orange powder (275 mg, 89% yield).

FT-IR (solid, ν, cm^{-1}): 1608, 1573, 1493, 1445, 1421, 1362, 1231, 1179, 1003, 810, 744, 655.



3,6-Di-*tert*-butyl-9*H*-carbazole

2-Chloro-2-methylpropane (6.5 mL, 60 mmol) was added dropwise into the mixture of 9*H*-carbazole (3.3 g, 20 mmol) and $ZnCl_2$ (8.1 g, 60 mmol) in $MeNO_2$ (100 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 5 h. Water (100 mL) was added to quench the reaction, and the mixture was extracted using EtOAc (100 mL × 3) to the crude product. The crude mixture was then purified by column chromatography using hexane/ethyl acetate (10:1 – 5:1) as the eluent to yield the product as a white solid (4.07 g, 73% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 1.49 (s, 18H), 7.37 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 12.0 Hz, 2H), 7.85 (brs, 1H), 8.11 (s, 2H).

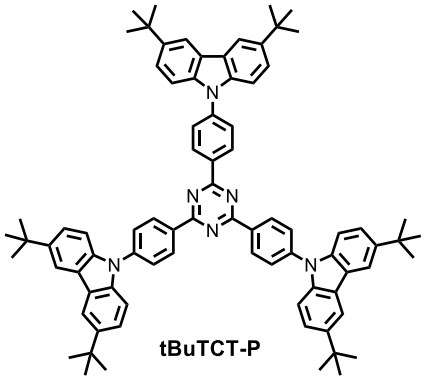
ESI-MS [M^+]: 279.1973 (calc. 279.1987).

2,4,6-Tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-1,3,5-triazine (tBuTCT)

The synthesis of tBuTCT is similar to that of TCT by using 3,6-di-*tert*-butyl-9*H*-carbazole (2.69 g, 9.65 mmol) and cyanuric chloride (0.5 g, 2.73 mmol) as the starting materials. The product was purified by column chromatography on a silica gel column using hexane/ethyl acetate (100:1) as eluent to yield the product as a white solid (1.56 g, 63% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 1.53 (s, 54H), 7.55 (d, *J* = 8.0 Hz, 6H), 8.14 (s, 6H), 8.94 (d, *J* = 8.0 Hz, 6H).

ESI-MS [M^+]: 912.5824 (calc. 912.5818).

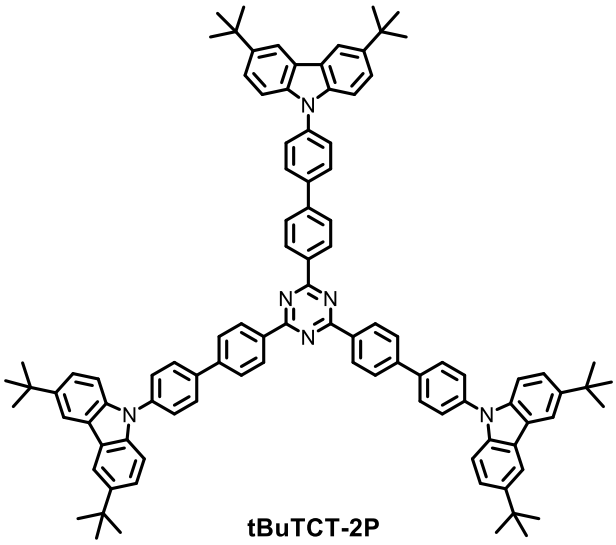


2,4,6-tris(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-1,3,5-triazine (tBuTCT-P)

The synthesis of tBuTCT-P is similar as that of TCT-P by using 3,6-di-*tert*-butyl-9*H*-carbazole (1.28 g, 4.59 mmol) and 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (0.90 g, 1.31mmol) as the starting materials. The product was purified by column chromatography on a silica gel column using hexane/ethyl acetate (100:1) as eluent to yield the product as a white solid (0.82 g, 55% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 1.52 (s, 54H), 7.48~7.59 (m, 12H), 7.90 (d, *J* = 8.4 Hz, 6H), 8.20 (s, 6H), 9.10 (d, *J* = 8.4Hz, 6H).

ESI-MS [M^+]: 1140.6748 (calc. 1140.6757).



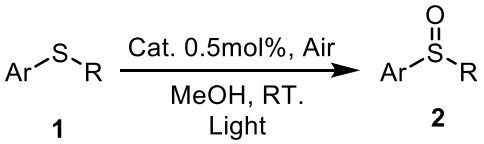
2,4,6-tris(4'-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-[1,1'-diphenyl]-4-yl)-1,3,5-triazine (tBuTPT-2P)

The synthesis of tBuTCT-2P is similar as that of TCT-2P by using 3,6-di-*tert*-butyl-9*H*-carbazole (0.63 g, 2.28 mmol) and 2,4,6-tris(4'-bromo-[1,1'-diphenyl]-4-yl)-1,3,5-triazine (0.5 g, 0.65 mmol) as the starting materials. The product was purified by column chromatography on a silica gel column using hexane/ethyl acetate (100:1) as eluent to yield the product as a white solid (0.51 g, 58% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 1.52 (s, 54H), 7.45~7.57 (m, 12H), 7.76 (d, J = 8.0 Hz, 6H), 7.99 (d, J = 8.0 Hz, 12H), 8.20 (s, 6H), 9.01 (d, J = 8.0 Hz, 6H).

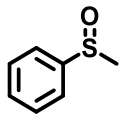
ESI-MS [M^+]: 1369.7741 (calc. 1369.7730).

S1.6 General procedure of aerobic oxidation of sulfide to sulfoxide:



1 2

A mixture of pTCT (1.4 mg, 2.5 μmol, 0.5 mol% based on the monomer TCT) and sulfide (0.5 mmol) in MeOH (5 mL) was stirred under air at room temperature over 26 W white compact fluorescent lamp (CFL) irradiation (distance app. 5 cm). Reaction progress was monitored by TLC (hexane : EtOAc v/v 5:1) and ^{1}H NMR. The reaction was stopped following disappearance of the starting material. The catalyst was then removed by filtration, and the filtrate was dried under vacuum. ^{1}H NMR was taken for the crude product, and the ratio between the integrated peaks of the starting material and product was used to calculate the conversions. The integrated peaks of the sulfoxide and sulfone were used to calculate selectivity. The product was purified by column chromatography on a silica gel column using hexane/ethyl acetate as eluent to yield the product. The ^{1}H NMR spectra of the sulfoxides are consistent with our previous report and the literature values.[4]

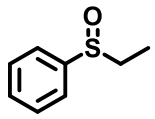


(Methylsulfinyl)benzene (2A)

The title compound was made following the general procedure using thioanisole (56 μL, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (95% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.75 (s, 3H), 7.55 (m, 3H), 7.67 (d, J = 8.0 Hz, 2H).

ESI-MS [M^+]: 140.0311 (calc. 140.0296).

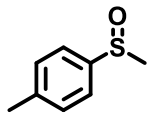


(Ethylsulfinyl)benzene (2B)

The title compound was made following the general procedure using ethyl(phenyl)sulfane (69 μL, 0.5 mmol) as the starting material. The product was obtained as a colorless liquid (94% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.75 (s, 3H), 2.92 (m, 1H), 2.80 (m, 1H), 7.54 (m, 3H), 7.65 (m, 2H).

ESI-MS $[M+H]^+$: 155.0533 (calc. 155.0525).

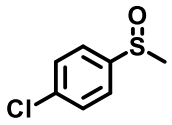


1-Methyl-4-(methylsulfinyl)benzene (2C)

The title compound was made following the general procedure using methyl(p-tolyl)sulfane (67 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (95% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.75 (s, 3H), 2.92 (m, 1H), 2.80 (m, 1H), 7.54 (m, 3H), 7.65 (m, 2H).

ESI-MS $[M+H]^+$: 155.0530 (calc. 155.0525).

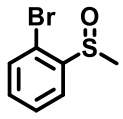


1-Chloro-4-(methylsulfinyl)benzene (2D)

The titled compound was made following the general procedure using (4-chlorophenyl)-(methyl)sulfane (95 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (97% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.75 (s, 3H), 7.54 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H).

ESI-MS [M^+]: 173.9906 (calc. 173.9906).

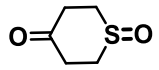


1-bromo-2-(methylsulfinyl)benzene (2E)

The titled compound was made following the general procedure using (2-bromophenyl)(methyl)sulfane (101 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (98% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.84 (s, 3H), 7.36~7.42 (m, 1H), 7.55~7.63 (m, 2H), 7.97 (dd, J_1=8.0 Hz, J_2= 4.0 Hz, 1H).

ESI-MS [M^+]: 217.9410 (calc. 217.9401).

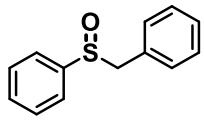


tetrahydro-4H-thiopyran-4-one 1-oxide (2F)

The titled compound was made following the general procedure using tetrahydro-4H-thiopyran-4-one (58 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (98% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 1.98 (d, *J* = 12.0Hz,1H), 2.37 (t, *J* = 12.0Hz, 1H), 2.70 (t, *J* = 12 Hz,1H), 2.95 (d, *J* =12.0 Hz, 1H), 3.19 (s, 2H), 3.25 (s, 2H).

ESI-MS $[M–O]^+$: 116.0291 (calc. 116.0296).

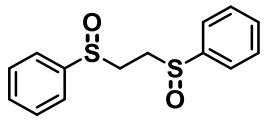


(benzylsulfinyl)benzene (2G)

The titled compound was made following the general procedure using benzyl(phenyl)sulfane (100 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (93% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 4.07 (m, 2H), 7.01 (d, *J* = 8.0Hz, 2H), 7.22~7.36 (m, 3H), 7.36~7.53 (m, 5H).

ESI-MS $[M^+]$: 216.0618 (calc. 216.0609).



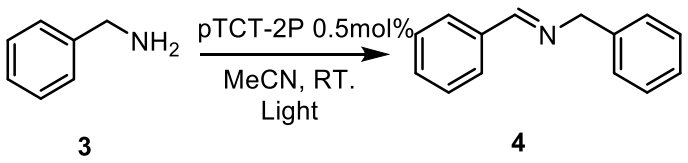
((2-(benzylsulfinyl)ethyl)sulfinyl)benzene (2H)

The titled compound was made following the general procedure using benzyl(2-(phenylthio)ethyl)sulfane (123 mg, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (94% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.69~2.85 (m, 1H), 3.08 (s, 2H), 3.33~3.52 (m, 1H), 7.46~7.64 (m, 10H).

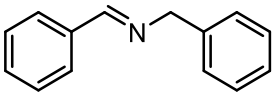
ESI-MS [M^+]: 292.0543 (calc.292.0592).

S1.8 General procedure for aerobic oxidation coupling of amine:



3 **4**

The mixture of pTCT-2P (2.6 mg, 2.5 μmol, 0.5 mol% based on the monomer TCT-2P) and respective amine (0.5 mmol) in MeCN (5 mL) was stirred under air at room temperature over 26W household white bulb irradiation (distance app. 5 cm). Reaction progress was monitored by TLC (Hexane : EtOAc v/v 4:1) and ^{1}H NMR, the reaction was stopped following disappearance of the starting material. The catalyst was then removed by filtration, and the filtrate was dried under vacuum. ^{1}H NMR was taken for the crude product, and ratio between the integrated peak of the starting material and product was used to calculate the conversion, integrated peak of the product and byproduct was used to calculate selectivity. The ^{1}H NMR spectra of the products are consistent with our previous report and the literature values.[5]

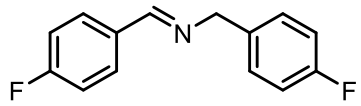


(E)-N-benzyl-1-phenylmethanimine (4A)

The titled compound was made following the general procedure using phenylmethanamine (55 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% conversion).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 4.86 (s, 2H), 7.26~7.33 (m, 1H), 7.33~7.41 (m, 4H), 7.42~7.47 (m, 3H), 7.77~7.85 (m, 2H), 8.43 (s, 1H).

ESI-MS [M^+]: 195.1047 (calc. 195.1048).

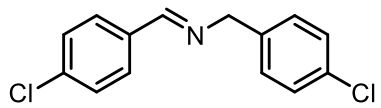


(E)-N-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (4B)

The titled compound was made following the general procedure using (4-fluorophenyl)methanamine (57 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% conversion).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 4.79 (s, 2H), 7.05 (t, J =8.0 Hz, 2H), 7.13 (t, J = 8.0 Hz, 2H), 7.31 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.80 (dd, J_1 = 8.0 Hz, J_2 = 4.1 Hz, 2H), 8.37 (s, 1H).

ESI-MS [M^+]: 231.0867 (calc. 231.0860).

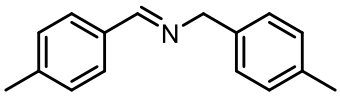


(E)-N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (4C)

The titled compound was made following the general procedure using (4-chlorophenyl)-methanamine(61 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% conversion).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 4.80 (s, 2H), 7.25~7.32 (m, 2H), 7.32~7.38 (m, 2H), 7.42 (d, J = 12.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 8.37 (s, 1H).

ESI-MS [M^+]: 263.0270 (calc. 263.0269).

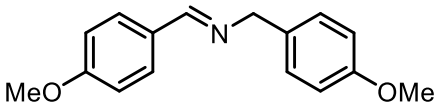


(E)-N-(4-methylbenzyl)-1-(p-tolyl)methanimine (4D)

The titled compound was made following the general procedure using *p*-tolylmethanamine (64 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% conversion).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.36 (s, 3H), 2.41 (s, 3H), 4.79 (s, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 4.0 Hz, 4H), 7.69 (d, J = 8.0 Hz, 2H), 8.37 (s, 1H).

ESI-MS [M^+]: 223.1362 (calc. 223.1361).

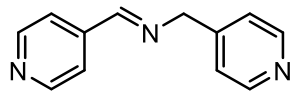


(E)-N-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (4E)

The titled compound was made following the general procedure using (4-methoxyphenyl)methanamine (65 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% conversion).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 3.82 (s, 3H), 3.86 (s, 3H), 4.75 (s, 2H), 6.93 (m, 4H), 7.27 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 8.32 (s, 1H).

ESI-MS [M^+]: 255.1257 (calc. 255.1259).

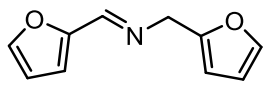


(E)-1-(pyridin-4-yl)-N-(pyridin-4-ylmethyl)methanimine (4F)

The titled compound was made following the general procedure using pyridin-4-ylmethanamine (51 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% conversion).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 4.88 (s, 2H), 7.33 (d, *J* = 12.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 8.44 (s, 1H), 8.60 (d, *J* = 8.0 Hz, 2H), 8.75 (d, *J* = 4.0 Hz, 2H).

ESI-MS [$M^{+\cdot}$]: 197.0953 (calc. 197.0953).

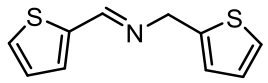


(E)-1-(furan-2-yl)-N-(furan-2-ylmethyl)methanimine (4G)

The titled compound was made following the general procedure using furan-2-ylmethanamine (44 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% conversion).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 4.98 (s, 2H), 6.87~7.05 (m, 2H), 7.10 (t, *J* = 4.0 Hz, 1H), 7.26 (d, *J* = 4.0 Hz, 1H), 7.35 (d, *J* = 4.0 Hz, 1H), 7.44 (d, *J* = 4.0 Hz, 1H), 8.45 (s, 1H).

ESI-MS [M+·]: 175.1090 (calc. 175.0633).



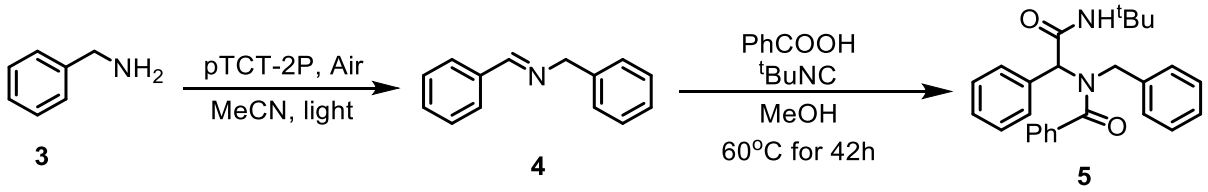
(E)-1-(thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine (4G)

The titled compound was made following the general procedure using thiophen-2-ylmethanamine (51 μL, 0.5 mmol) as starting material. The product was obtained as a colorless liquid (> 99% conversion).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 4.98 (s, 2H), 6.90~7.05 (m, 2H), 7.10 (dd, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 1H), 7.26 (dd, J_1 = 4.0 Hz, J_2 = 2.0Hz, 1H), 7.35 (d, J = 4.0 Hz, 1H), 7.44 (d, J = 4.0 Hz, 1H), 8.45 (s, 1H).

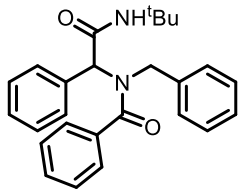
ESI-MS [M^+]: 207.0179 (calc. 207.0176).

S1.8 General procedure for the Ugi-type reaction:



The mixture of pTCT-2P (2.6 mg, 2.5 μmol, 0.5 mol% based on the monomer TCT-2P) and respective amine (0.5 mmol) in MeCN (5 mL) was stirred under air at room temperature over 26W household white bulb irradiation (distance app. 5 cm). Reaction progress was monitored by TLC (Hex : EtOAc v/v 4 :1) and the reaction was stopped following disappearance of the starting material. The solvent was removed under vacuum. And then benzoic acid (25 μL, 0.25 mmol), *tert*-butyl isocyanide (34 μL, 0.3 mmol) and MeOH (3 mL) was added to the residue. After stirred at 60 °C for 42 h, the mixture was filtrated to remove the polymer, and the filtrate was dried under vacuum. The crude mixture was purified by column chromatography on a silica gel column using hexane/ethyl acetate (10:1 ~ 2:1) as eluent to yield the corresponding products.

Fig. S4. Photocatalytic oxidative amine coupling reaction followed by the Ugi-type reaction.

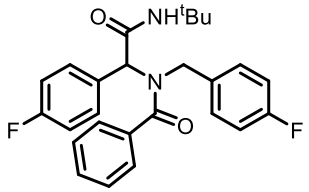


N-benzyl-N-(2-(tert-butylamino)-2-oxo-1-phenylethyl)benzamide (5A)

The titled compound was made following the general procedure using phenylmethanamine (55 μL, 0.5 mmol) as starting material. The product was obtained as a white solid (65 mg, 97% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ1.34 (s, 9H), 4.38~4.62 (m, 1H), 4.79 (d, *J* = 18.0 Hz, 1H), 5.49 (s, 1H), 5.59 (brs, 1H), 6.92 ~7.10 (m, 2H), 7.10~7.25 (m, 3H), 7.25~7.44 (m, 8H), 7.44~7.56 (m, 2H).

ESI-MS [$M^{+\cdot}$]: 400.2159 (calc. 400.2151).



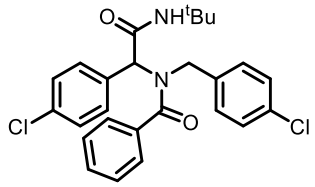
N-(2-(tert-butylamino)-1-(4-fluorophenyl)-2-oxoethyl)-N-(4-fluorobenzyl)benzamide (5B)

The titled compound was made following the general procedure using phenylmethanamine (57 μL, 0.5 mmol) as starting material. The product was obtained as a white solid (94 mg, 86% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ1.33 (s, 9H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.66~4.86 (m, 1H), 5.46 (s, 1H), 5.56 (brs, 1H), 6.75~6.87 (m, 2H), 6.88~7.06 (m, 4H), 7.21~7.57 (m, 7H).

^{19}F NMR ($CDCl_3$, 25 °C): δ -115.51 (s, 1F), -112.64 (s,1F).

ESI-MS [$M^{+\cdot}$]: 436.1954 (calc. 436.1962).

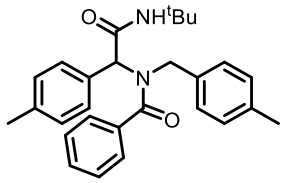


N-(2-(tert-butylamino)-1-(4-chlorophenyl)-2-oxoethyl)-N-(4-chlorobenzyl)benzamide (5C)

The titled compound was made following the general procedure using phenylmethanamine (61 μL, 0.5 mmol) as starting material. The product was obtained as a white solid (94 mg, 80% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ1.33 (s, 9H), 4.40 (d, *J* = 9.0 Hz, 1H), 4.66~4.84 (m, 1H), 5.46 (s, 1H), 5.64 (brs, 1H), 6.77~7.01 (m, 2H), 7.13 (d, *J* = 6.0Hz, 2H), 7.26~7.54 (m,9H).

ESI-MS [$M^{+\cdot}$]: 468.1392 (calc. 468.1371).

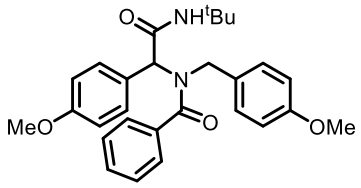


N-(2-(tert-butylamino)-2-oxo-1-(p-tolyl)ethyl)-N-(4-methylbenzyl)benzamide (5D)

The titled compound was made following the general procedure using phenylmethanamine (64 μL, 0.5 mmol) as starting material. The product was obtained as a white solid (88 mg, 88% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ1.29 (s, 9H), 2.27 (s, 3H), 2.32 (s, 3H), 4.19~4.49 (m, 1H), 4.49~4.77 (m, 1H), 5.35 (s, 1H), 5.64 (brs, 1H), 6.82~7.03 (m, 4H), 7.03~7.16 (m, 2H), 7.16~7.41 (m, 5H), 7.41~7.55 (m, 2H).

ESI-MS [$M^{+\cdot}$]: 428.2451 (calc. 428.2464).



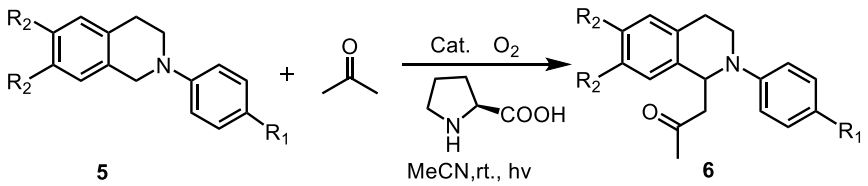
N-(2-(tert-butylamino)-1-(4-methoxyphenyl)-2-oxoethyl)-N-(4-methoxybenzyl)benzamide (5E)

The titled compound was made following the general procedure using phenylmethanamine (65 μL, 0.5 mmol) as starting material. The product was obtained as a white solid (87 mg, 76% yield).

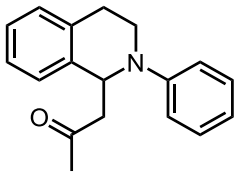
^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ1.30 (s, 9H), 3.75 (s, 3H), 3.79 (s,3H), 4.23~ 4.46 (m, 1H), 4.64 (d, *J* = 12 Hz, 1H), 5.37 (s, 1H), 5.60 (brs, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 6.0 Hz, 2H), 6.86~7.02 (m, 2H), 7.19~7.41 (m, 5H), 7.41~7.49 (m, 2H).

ESI-MS [$M^{+\cdot}$]: 460.2367 (calc. 460.2362).

S1.10 General procedure for photocatalytic direct Mannich reaction



In a 10 mL vial the polymer pTCT-P (1.0 mg, 1.25 μmol, 0.5 mol% based on the monomer TCT-P), L-proline (2.9 mg, 0.025 mmol) and substrate (0.25 mmol) were dissolved in 6 mL MeCN. Then acetone (183 μL, 2.5 mmol) were added via syringe and the reaction mixture was stirred at room temperature over 26W household white bulb irradiation (distance app. 5 cm). The reaction was monitored via TLC (hexanes : ethylacetate). Upon consumption of starting material, the crude mixture was purified by column chromatography on a silica gel column using hexane/ethyl acetate (10:1 ~ 5:1) as eluent to yield the corresponding products. The ^{1}H NMR spectra of the products are identical with our previous report and the literature values.[5b,6]

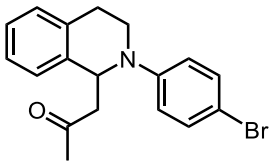


1-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6A)

The titled compound was made following the general procedure using 1,2,3,4-tetrahydro-2-phenylisoquinoline (52 mg, 0.25 mmol) as starting material. The product was obtained as a white solid (65 mg, 97% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.00 (s, 3H), 2.70~2.80 (m, 2H), 2.92~ 3.04 (m, 2H), 3.42~3.50 (m, 1H), 3.53~3.63 (m, 1H), 5.33 (t, J = 6.4 Hz, 1H), 6.70 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 8.0 Hz, 2H), 7.03~7.12 (m, 4H), 7.15~7.21 (m, 2H).

ESI-MS [$M^{+\cdot}$]: 265.1941 (calc. 265.1467).

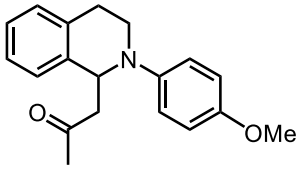


1-(2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6B)

The titled compound was made following the general procedure using 1,2,3,4-tetrahydro-2-(4-bromophenyl)isoquinoline (72 mg, 0.25 mmol) as starting material. The product was obtained as a white solid (82 mg, 96% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.11 (s, 3H), 2.80~2.90 (m, 2H), 3.01~3.11 (m, 2H), 3.50~3.58 (m, 1H), 3.58~3.66 (m, 1H), 5.36 (t, J = 6.0 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.14~7.21 (m, 4H), 7.31~7.35 (m, 2H).

ESI-MS [$M^{+\cdot}$]: 343.0588 (calc. 343.0572).

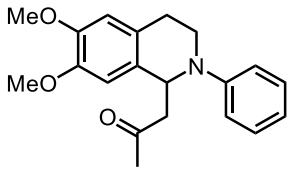


1-(2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6C)

The titled compound was made following the general procedure using 1,2,3,4-tetrahydro-2-(4-methoxyphenyl)isoquinoline (60 mg, 0.25 mmol) as starting material. The product was obtained as a white solid (68 mg, 91% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.08 (s, 3H), 2.72~2.82 (m, 2H), 2.97~3.08 (m, 2H), 3.44~3.53 (m, 1H), 3.55~3.62 (m, 1H), 3.78 (m, 3H), 5.27 (t, J = 6.4 Hz, 1H), 6.84 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 9.2 Hz, 2H), 7.21~ 7.11 (m, 4H).

ESI-MS [$M^{+\cdot}$]:296.2001 (calc. 296.1651).

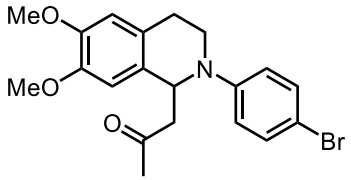


1-(6,7-Dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6D)

The titled compound was made following the general procedure using 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (67 mg, 0.25 mmol) as starting material. The product was obtained as a white solid (77 mg, 96% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.12 (s, 3H), 2.69~2.78 (m, 1H), 2.79~2.89 (m, 1H), 2.95~3.11 (m, 2H), 3.48~3.56 (m, 1H), 3.65~3.74 (m, 1H), 3.78 (d, *J* = 4.0 Hz, 6H), 5.33 (t, *J* = 6.4 Hz, 1H), 6.63 (s, 1H), 6.79 (s, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 1.6 Hz, 2H).

LCQ ESI-MS $[M+H]^+$:326.3 (calc. 326.2).

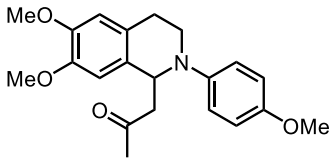


1-(2-(4-Bromophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6E)

The titled compound was made following the general procedure using 6,7-dimethoxy-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (87 mg, 0.25 mmol) as starting material. The product was obtained as a white solid (95 mg, 90% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.13 (s, 3H), 2.69~2.77 (m, 1H), 2.80~2.89 (m, 1H), 2.93~3.08 (m, 2H), 3.48~ 3.54 (m, 1H), 3.59~3.67 (m, 1H), 3.87 (d, *J* = 5.6 Hz, 6H), 5.27 (t, *J* = 6.0 Hz, 1H), 6.63 (s, 1H), 6.69 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 2H),7.33 (d, *J* = 8.8 Hz, 2H).

ESI-MS $[M+Na]^+$: 426.0688 (calc. 426.0681).

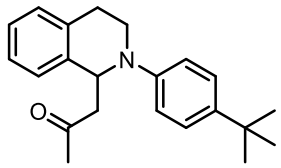


1-(6,7-Dimethoxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6F)

The titled compound was made following the general procedure using 6,7-dimethoxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (75 mg, 0.25 mmol) as starting material. The product was obtained as a white solid (79 mg, 86% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 2.09 (s, 3H), 2.59~2.69 (m, 1H), 2.74~2.82 (m, 1H), 2.90~3.06 (m, 2H), 3.41~ 3.50 (m, 1H), 3.54~3.63 (m, 1H), 3.77 (s, 3H), 3.86 (d, *J* = 1.6 Hz, 6H), 5.16 (t, *J* = 6.0 Hz, 1H), 6.61 (s, 1H), 6.69 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 9.2 Hz, 2H).

ESI-MS $[M+Na]^+$:378.1696 (calc. 378.1681).



1-(2-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6G)

The titled compound was made following the general procedure using 2-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (66 mg, 0.25 mmol) as starting material. The product was obtained as a white solid (68 mg, 93% yield).

^{1}H NMR ($CDCl_3$, 300 MHz, TMS, ppm): δ 1.30 (s, 9H), 2.09 (s, 3H), 2.75~2.89 (m, 2H), 3.00~3.16 (m, 2H), 3.47~3.61 (m, 1H), 3.61~3.73 (m, 1H), 5.39 (t, *J* = 6.3 Hz, 1H), 6.92 (d, *J* = 9.2 Hz, 2H), 7.10~7.21 (m, 3H), 7.25~ 7.34 (m, 3H).

ESI-MS $[M^{+\cdot}]$:321.2087 (calc. 321.2093).

S-2. ***Physical Measurements***

Scanning electron microscopy (SEM) images were taken on Hitachi S4700 field-emission scanning electron microscope (FE-SEM). Thermogravimetric Analysis (TGA) was performed on a Perkin Elmer STA 6000 Thermogravimetric Analyzer, heated from 30 °C to 800 °C at a rate of 10 °C/minute under N_2 atmosphere. X-ray diffraction patterns were acquired from 5° to 80° by a PANalytical Empyrean diffractometer with a PIXcel 3D detector. The copper target X-ray tube was set to 45 kV and 40 mA.

The fluorescence quenching experiments were carried out on an RF-5301PC spectrometer. A suspension of polymer (0.05 mg/mL) with varying concentrations of NEt_3 was respectively prepared to test the emission spectra, and the emission intensity at the maximum emission wavelength were recorded. The O_2 emission quenching experiment was performed by testing the emission intensity of polymer suspension (0.05 mg/mL in MeCN) after bubbling of Ar or O_2 for 2 min.

The experiment of photo-bleaching of DPBF were carried out by irradiating the mixture of polymers (0.3 mM, based on monomer) and DPBF (10 mM) in MeCN. UV-vis absorption spectra of the mixture were tested every 2 or 5 min after dilution for 400 times.

Electrochemical measurements of cyclic voltammetry (CV) was performed by an Epsilon Electrochemical Workstation (a BASi C-3 cell stand) with a three-electrode cell system, in which a glassy carbon electrode after loading the polymers was used as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl (KCl, 3 M) electrode as the reference electrode with ferrocenium-ferrocene (Fc^+/Fc) as an internal standard. The CV scans were carried out at a rate of 100 mV/s in MeCN containing 0.1 M Bu_4NPF_6 as supporting electrolyte.

Electrode preparation. POFs (2 mg) were dispersed in the solvent mixture containing 10 μL of nafion (5 wt%) and 0.49 mL of ethanol by sonication for 2 h to obtain a stable suspension. The sample (15 μL) was slightly dropped on the disk surface of the pre-polished glassy carbon electrode. The electrode was then dried at 45 °C for 30 min for measurement.

Electron paramagnetic resonance (EPR) spectra were collected on a Bruker EMX spectrometer, equipped with a frequency counter and nitrogen flow temperature control (130–300 K). The mixtures of polymers and TEMP (2,2,6,6-tetramethylpiperidine) in air-saturated CH_3CN or MeOH were stirred under irradiation of 26 W white CFL at room temperature for 4 h, respectively. The mixture was then filtrated to get the clean solution for the measurements.

Gas adsorption isotherms were collected using a Micromeritics ASAP 2020-accelerated surface area and porosimetry analyzer after degassing at 110 °C for 10 h under vacuum. The obtained adsorption–desorption isotherms were evaluated to give the pore parameters, including Brunauer–Emmett–Teller (BET) (SA_{BET}) and pore volume. The SA_{BET} for POFs was calculated using the N_2 adsorption branch in the pressure range of $P/P_0 = 0.01–0.10$. The pore size distribution was calculated from the adsorption branch with the nonlocal density function theory (NLDFT) approach.

S-3. ***Physical, photophysical, and electrochemical characterizations***

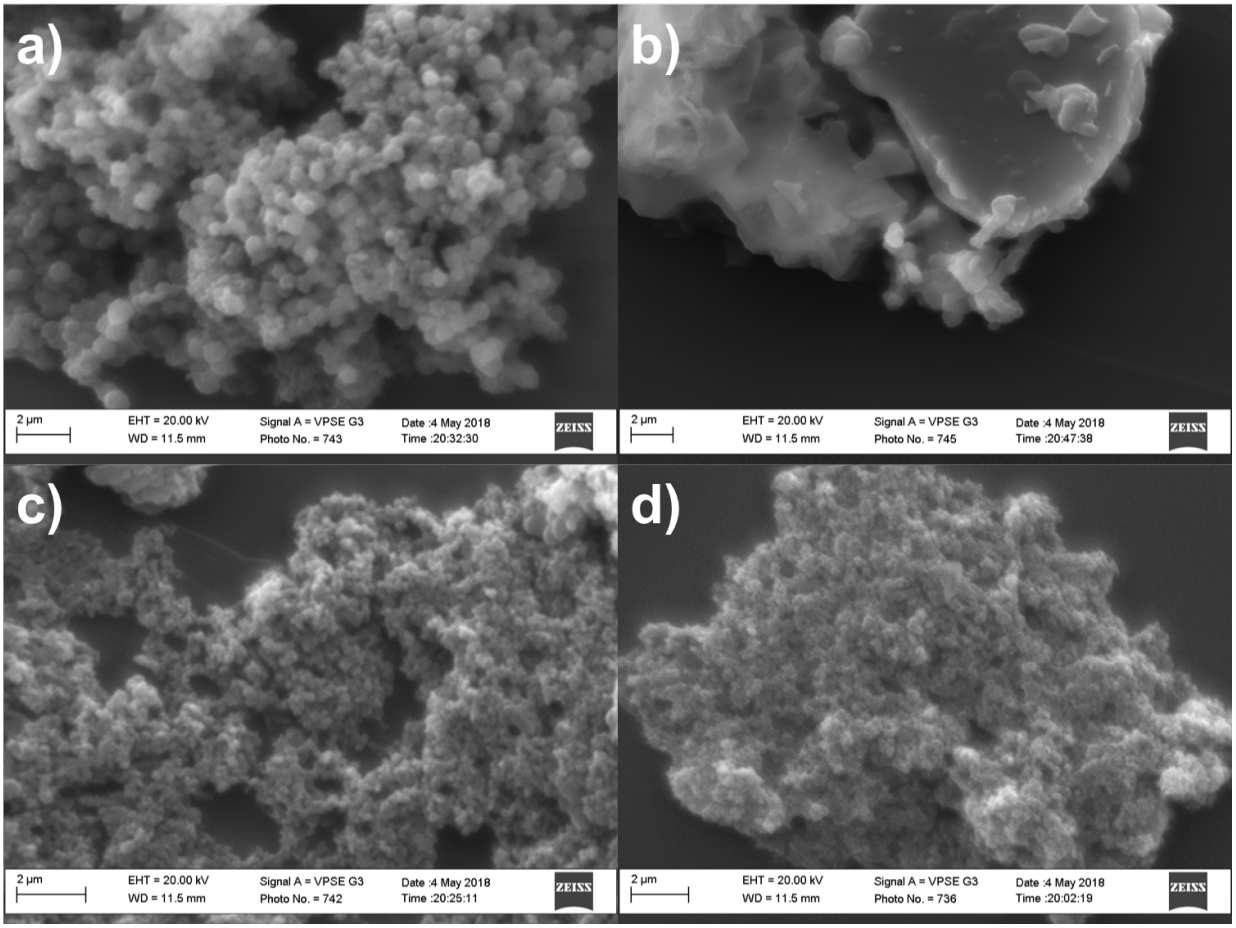


Fig. S5. SEM images of a) pTCB, b) pTCT, c) pTCT-P, and d) pTCT-2P.

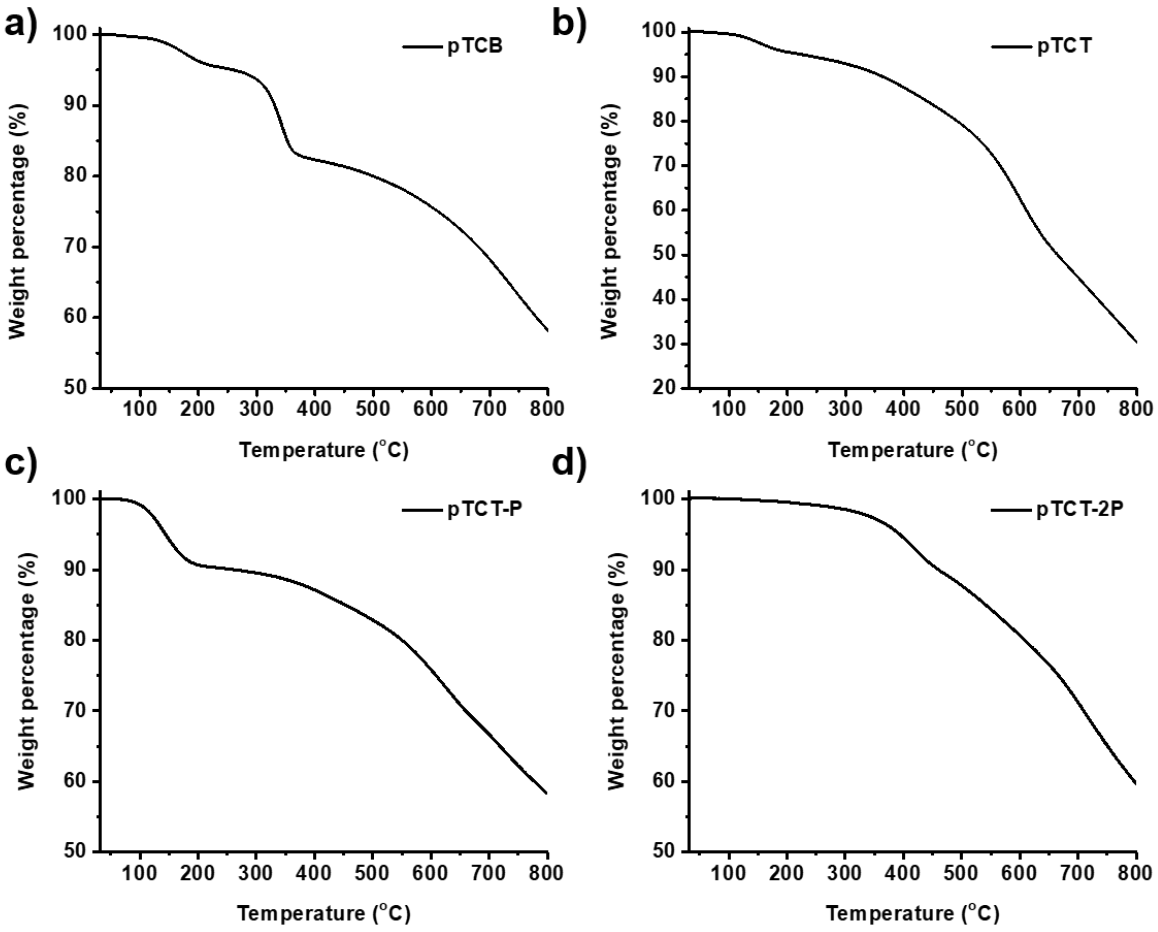


Fig. S6. Thermogravimetric analysis of a) pTCB, b) pTCT, c) pTCT-P, and d) pTCT-2P.

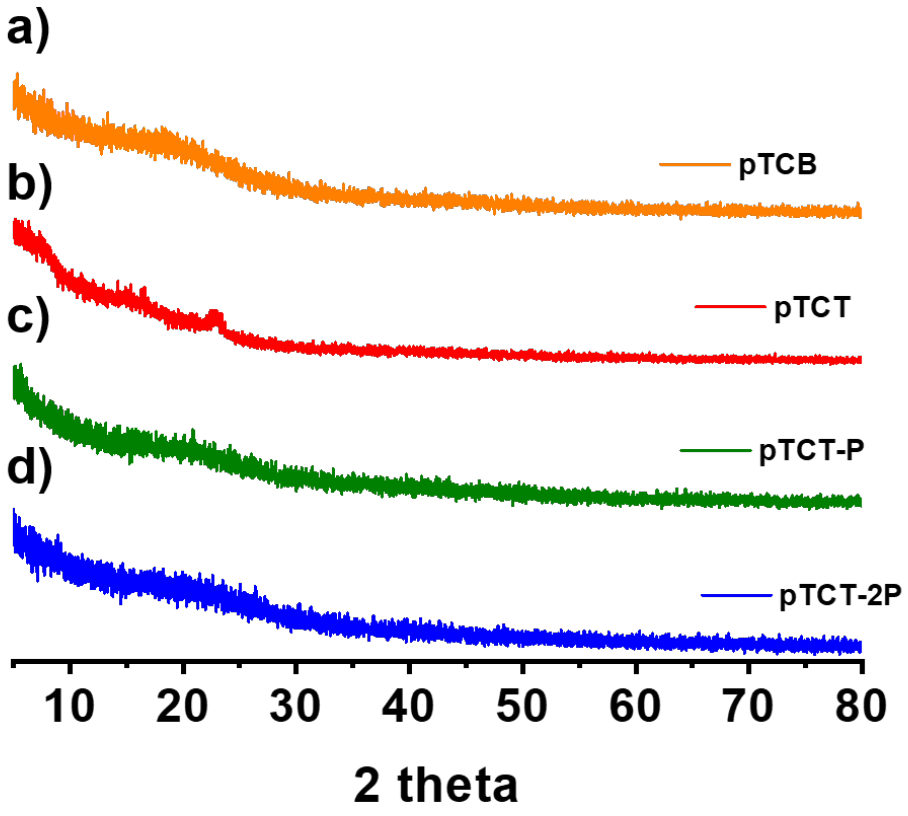


Fig. S7. Powder X-ray diffraction pattern of a) pTCB, b) pTCT, c) pTCT-P, and d) pTCT-2P.

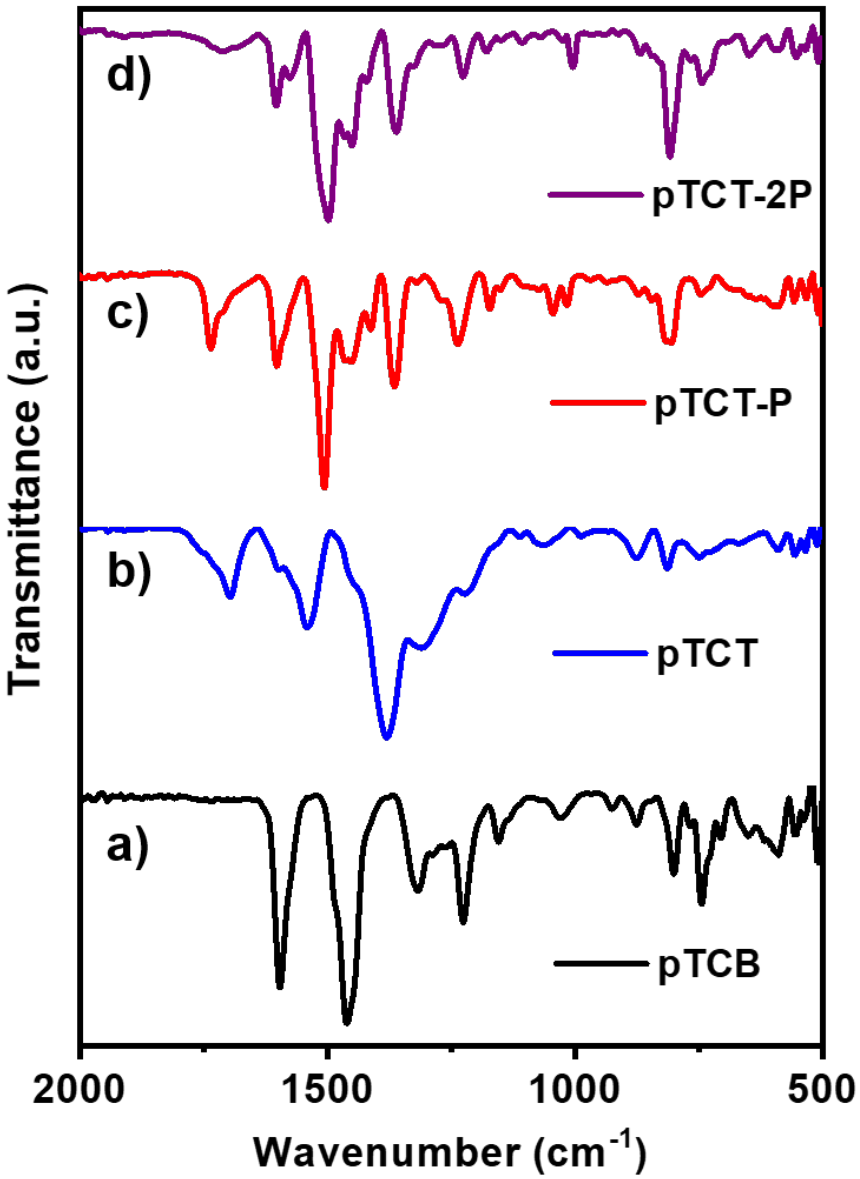


Fig. S8. FT-IR spectra of a) pTCB, b) pTCT, c) pTCT-P, and d) pTCT-2P.

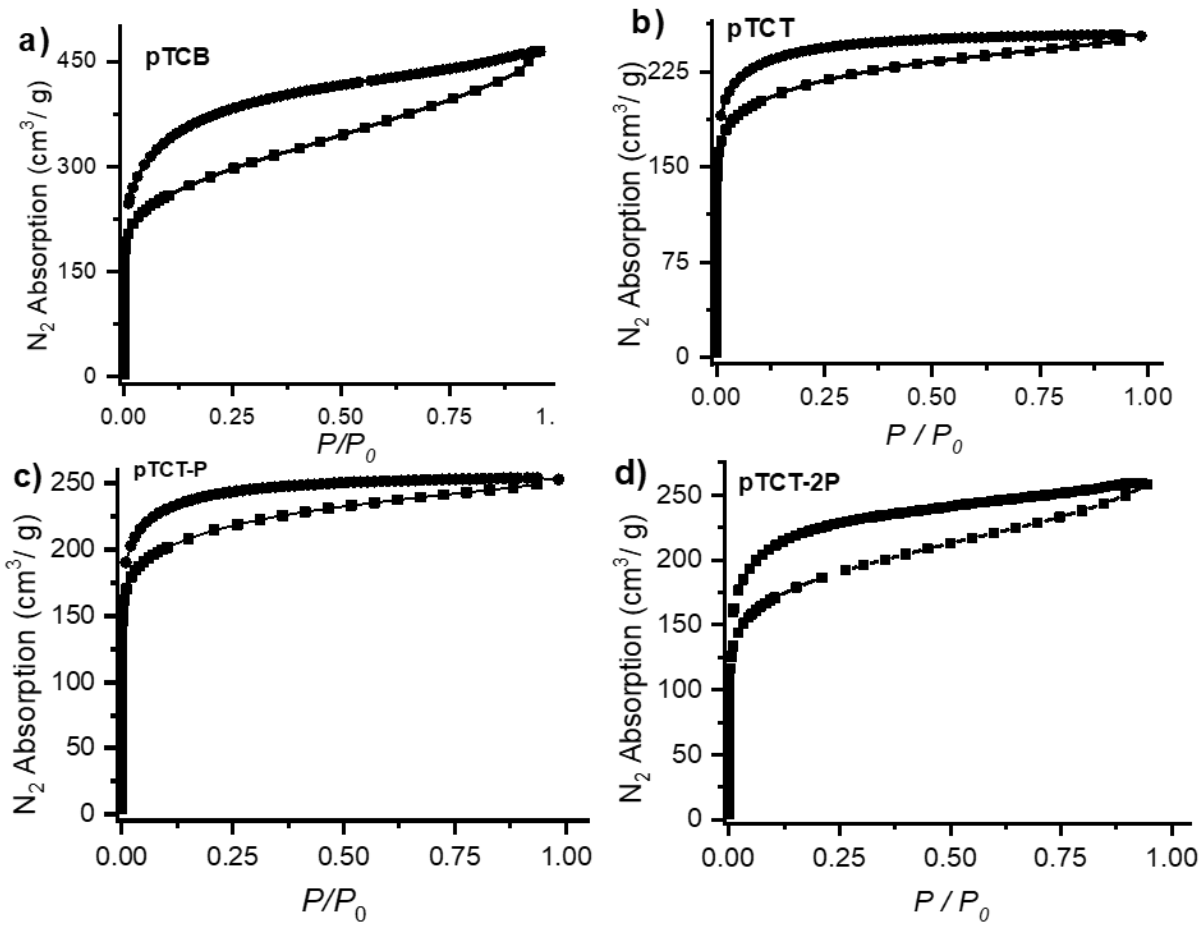


Fig. S9. Nitrogen adsorption and desorption isotherms of a) pTCB, b) pTCT, c) pTCT-P, and d) pTCT-2P.

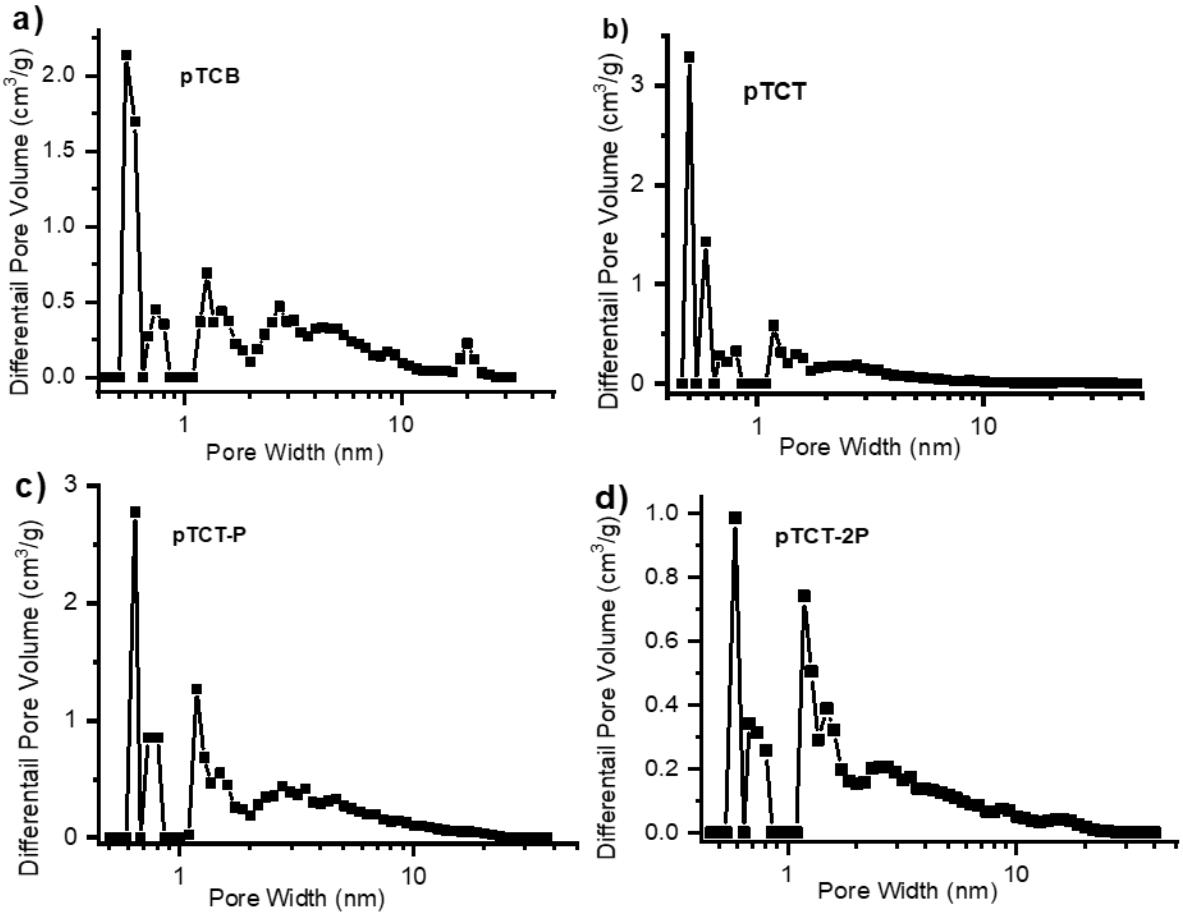


Fig. S10. Pore size distributions of a) pTCB, b) pTCT, c) pTCT-P, and d) pTCT-2P (calculated with NLDFT method).

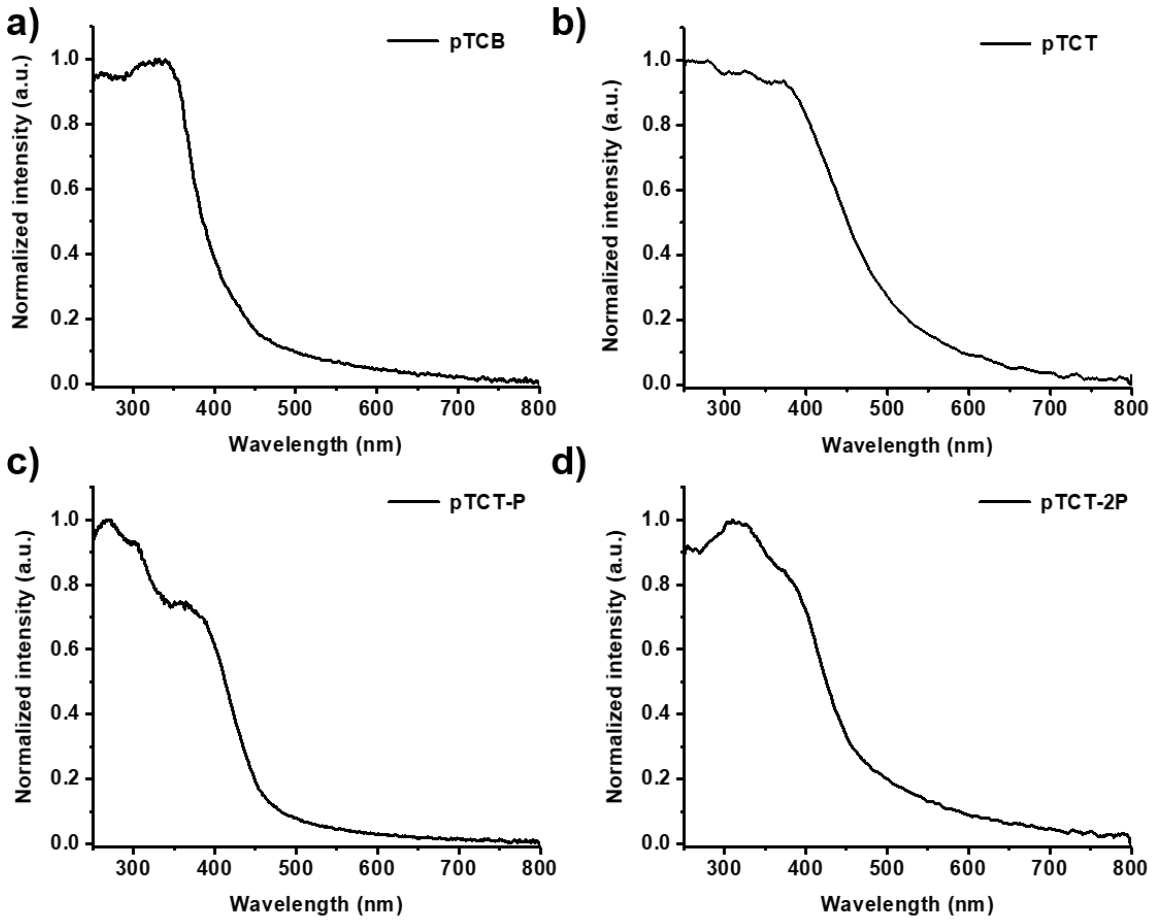


Fig. S11. Absorption spectra of a) pTCB, b) pTCT, c) pTCT-P, and d) pTCT-2P in polyethylene glycol 400 (0.05 mg/mL suspension).

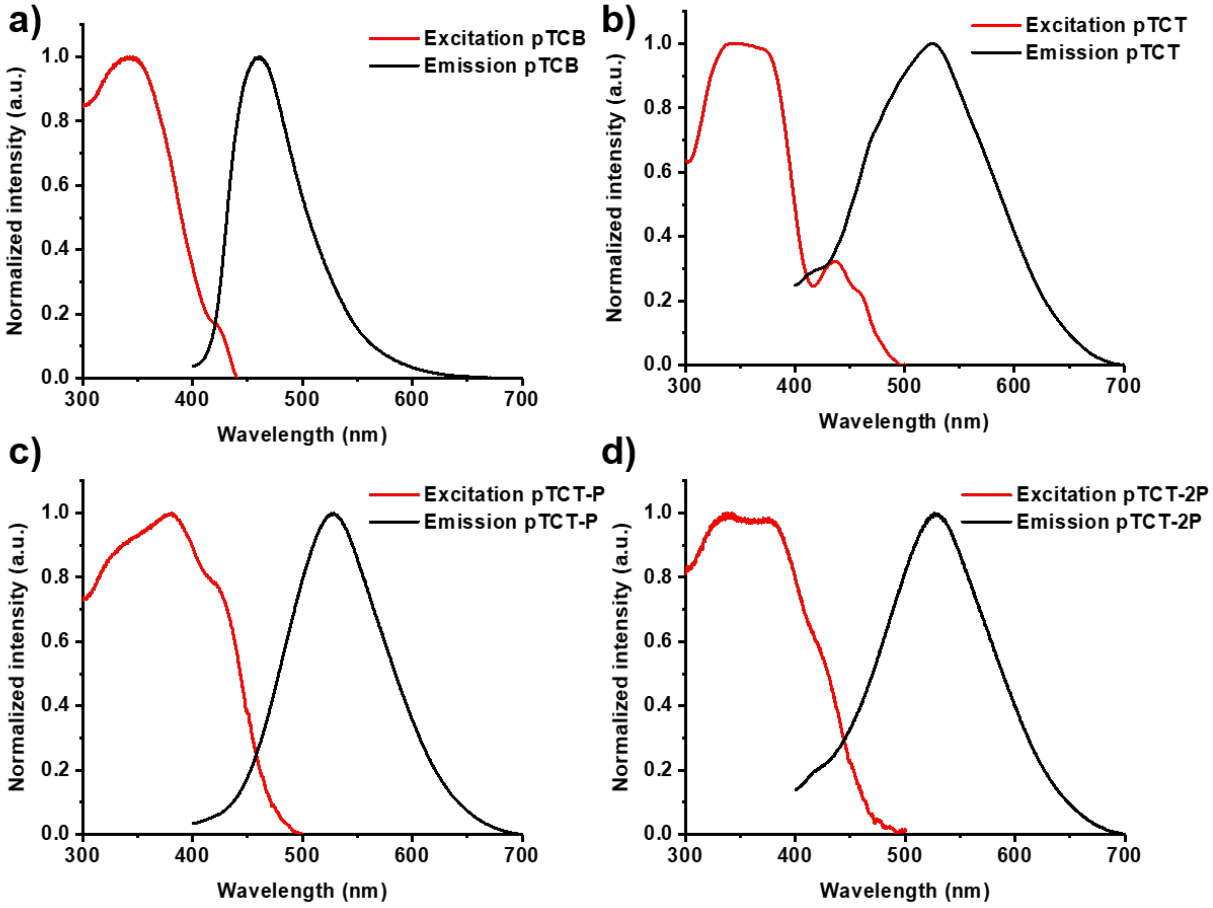


Fig. S12. Fluorescence emission and excitation spectra of a) pTCB, b) pTCT, c) pTCT-P, and d) pTCT-2P in polyethylene glycol 400 (0.05 mg/mL suspension).

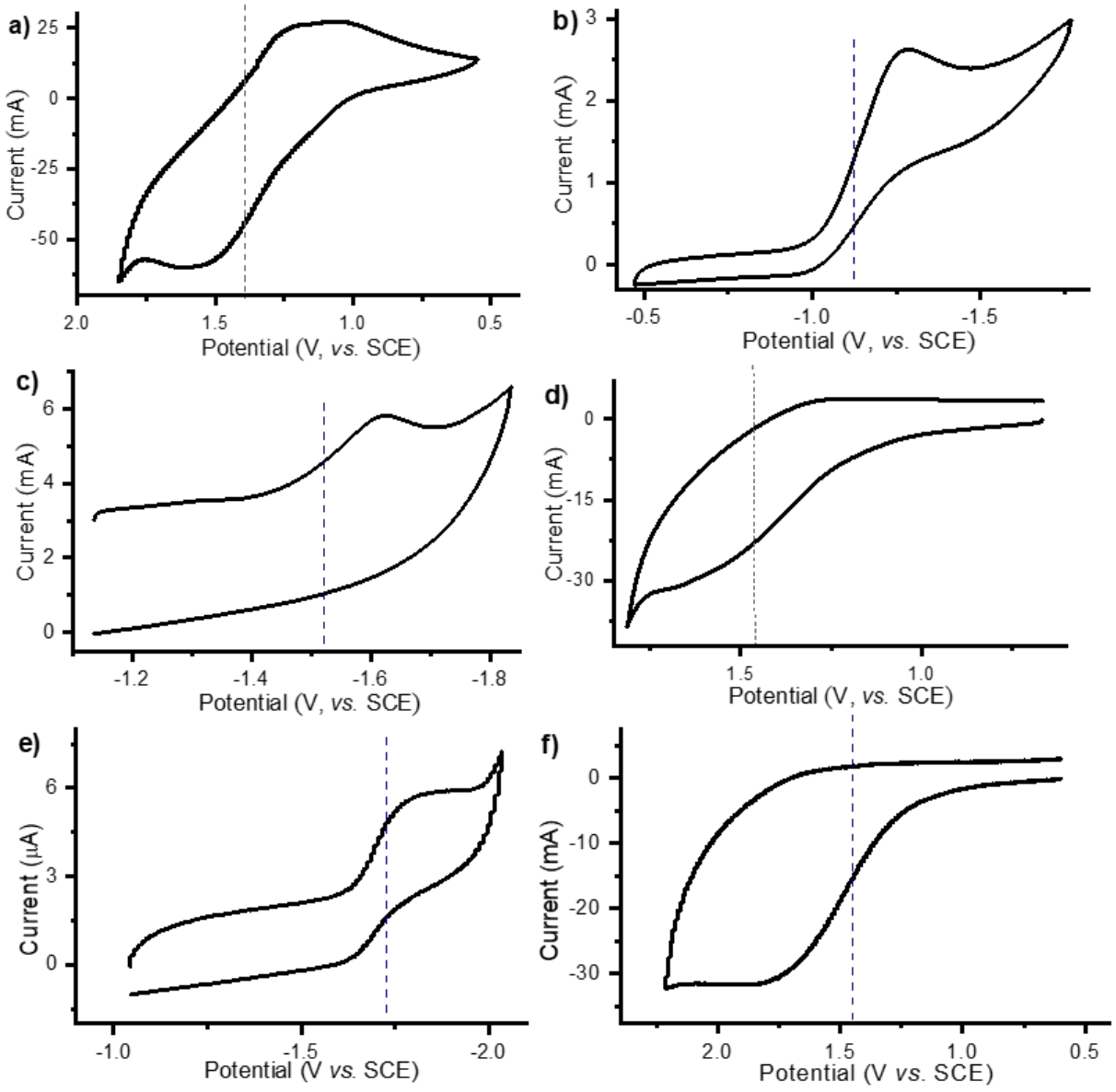


Fig. S13. Cyclic voltammetry of pTCB (a), pTCT (b), pTCT-P (c and d), pTCT-2P (e and f). (MeCN, scan rate: 100 mV s^{-1}).

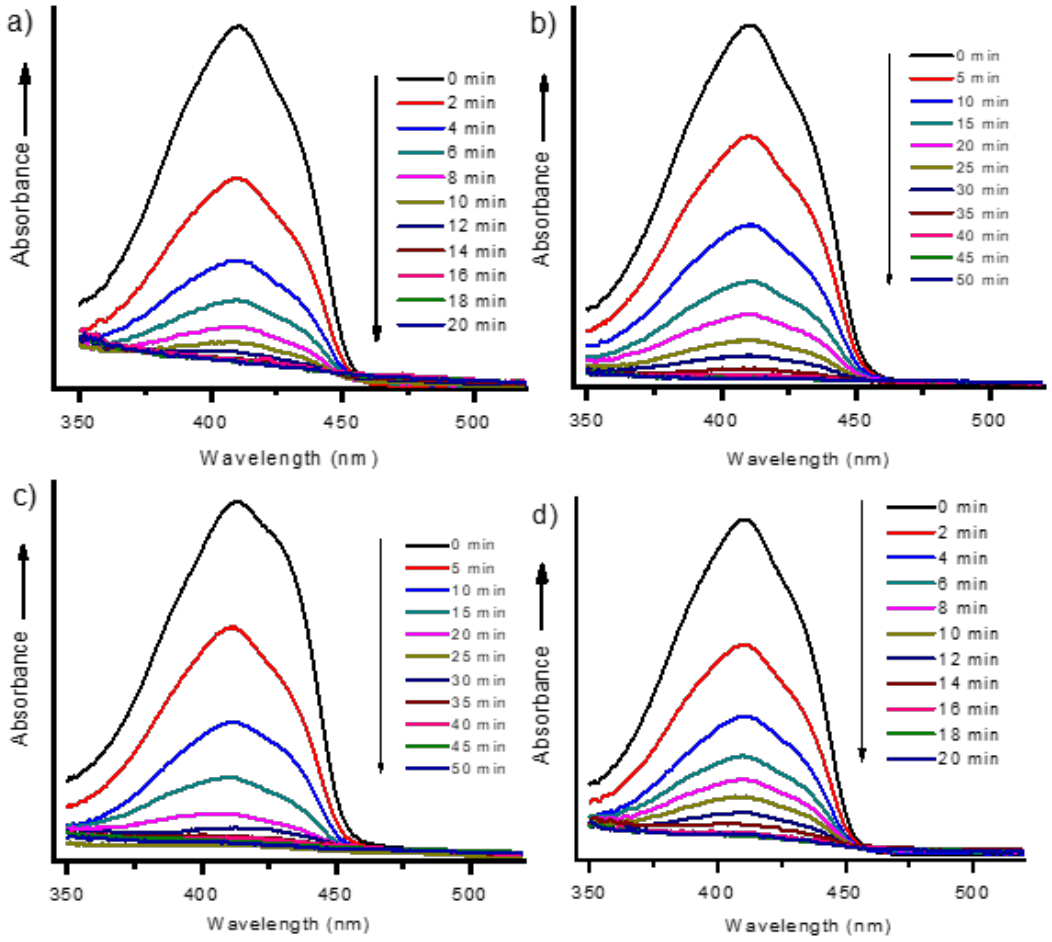


Fig. S14. Bleach of DPBF (10 mM) in MeCN in the presence of (a) pTCB, (b) pTCT, (c) pTCT-P, and (d) pTCT-2P (0.3 mM, diluted 400 times before UV-vis measurement).

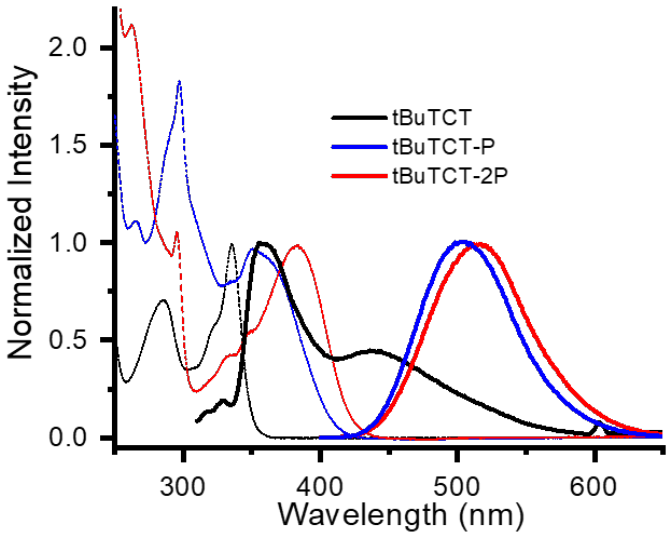


Fig. S15. Absorption (dash) and emission (solid) spectra of the tBu substituted monomers: tBuTCT, tBuTCT-P, and tBuTCT-2P (CH_2Cl_2, λ_{ex} = 280 nm, 380 nm, and 360 nm, respectively).

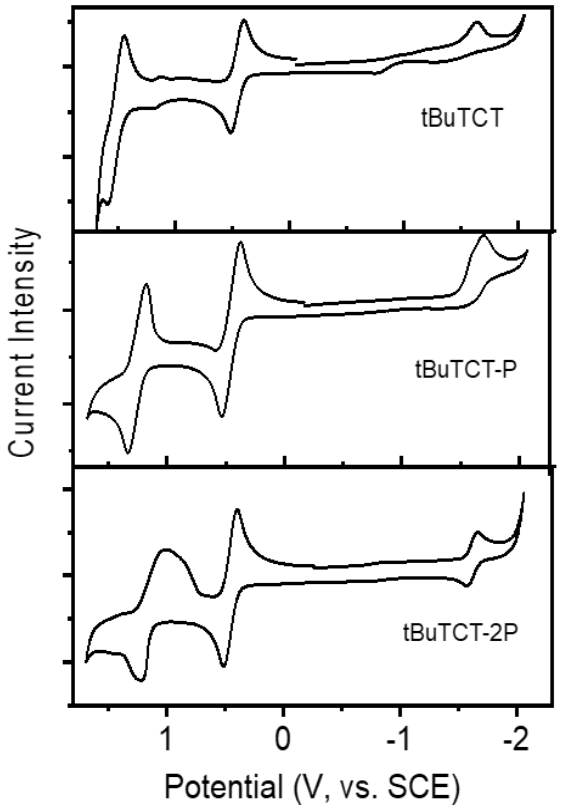


Fig. S16. Cyclic voltammetry of tBuTCT, tBuTCT-P, and tBuTCT-2P (CH_2Cl_2, Fc was used as internal standard, scan rate: 100 mV s^{-1}).

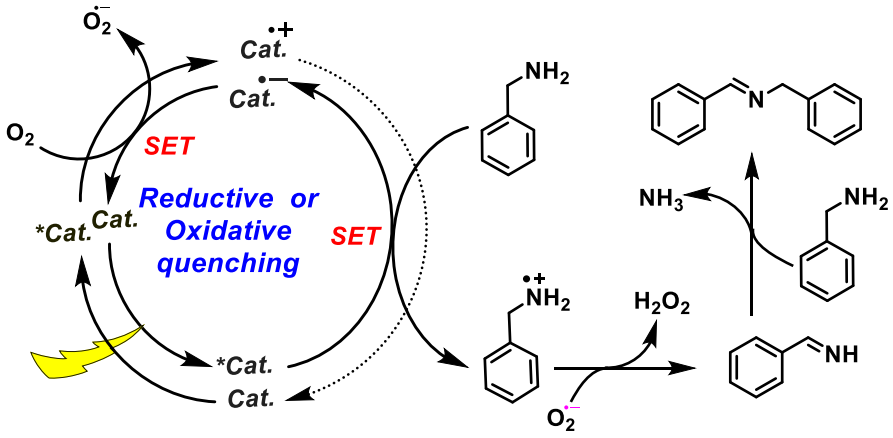


Fig. S17. Proposed mechanism for the photocatalytic oxidative amine coupling reaction.

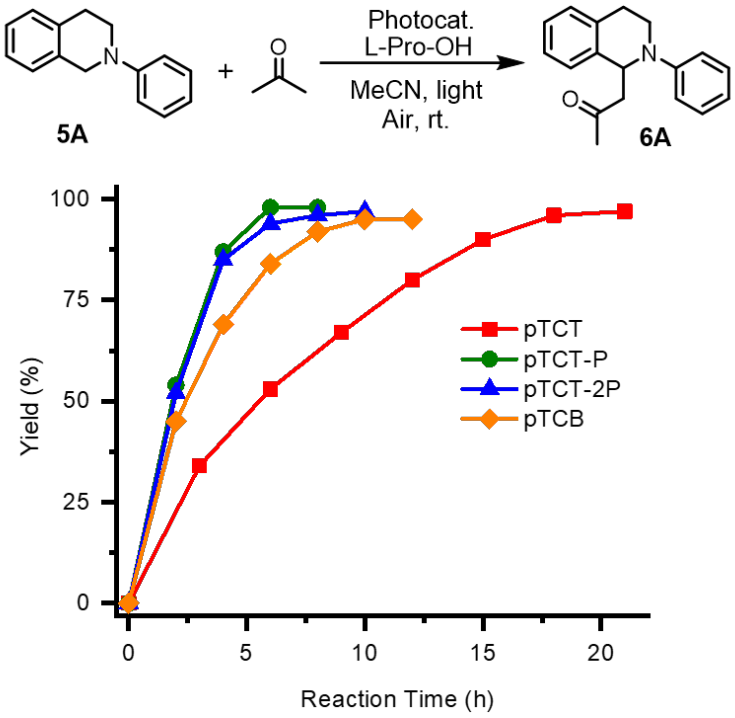


Fig. S18. Plots of yield of **6A** versus time in Mannich reaction using POFs as photocatalysts.

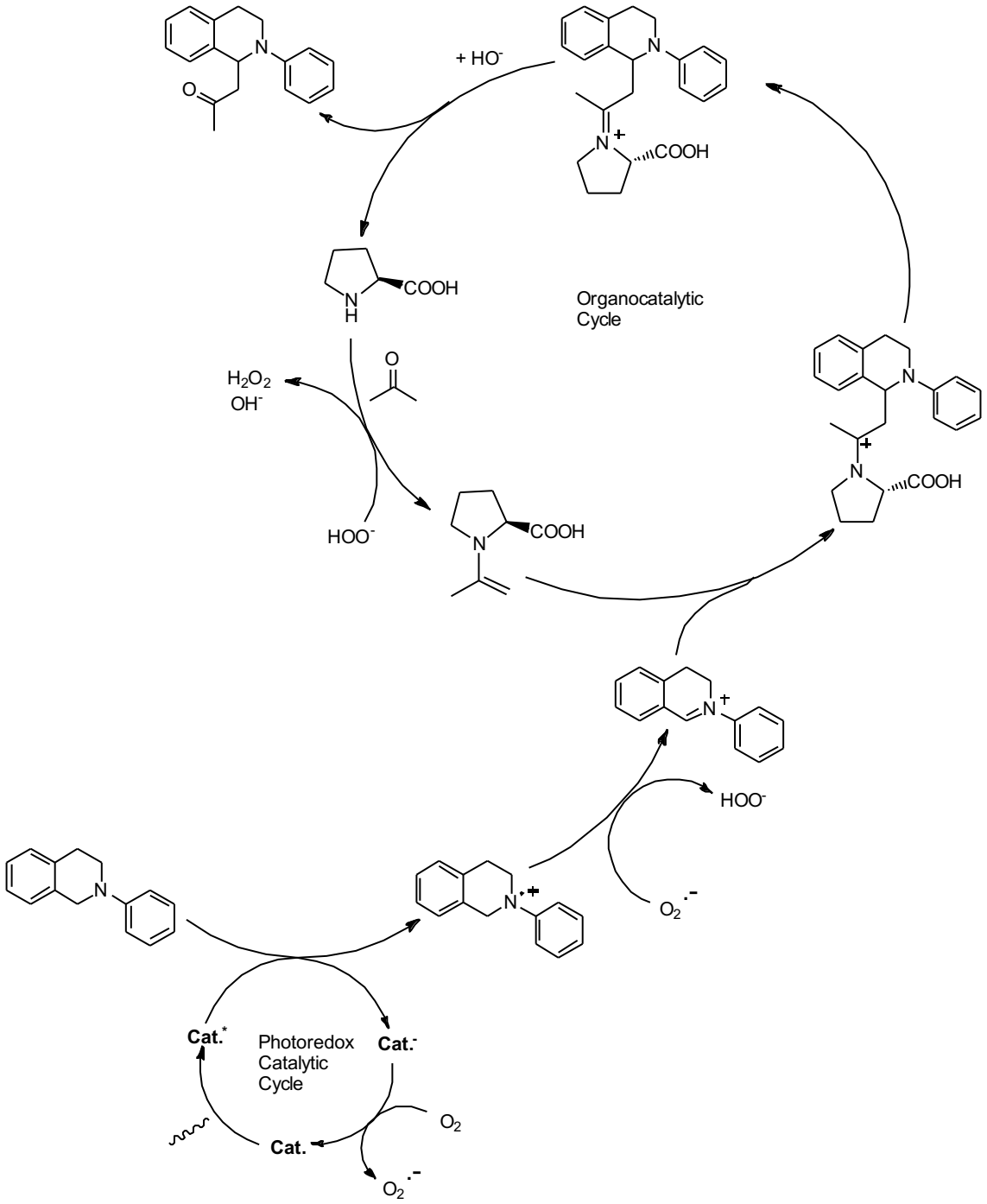


Fig. S19. Proposed mechanism for the aerobic photooxidative Mannich reaction.

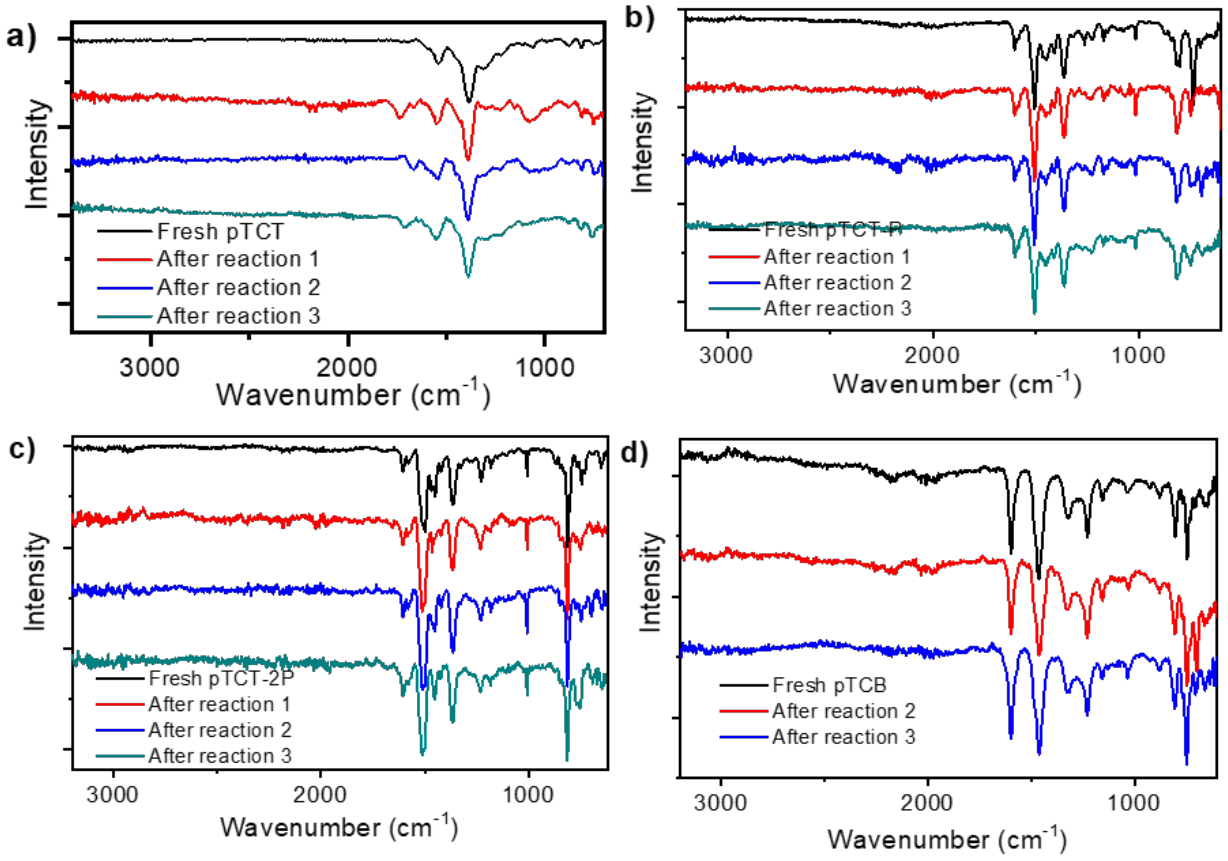


Fig. S20. The FT-IR spectra of the fresh and recovered POFs. (Reaction 1 is the sulfides oxidation, reaction 2 is the oxidative amine coupling, and reaction 3 is the Mannich reaction.)

S-4. ***References***

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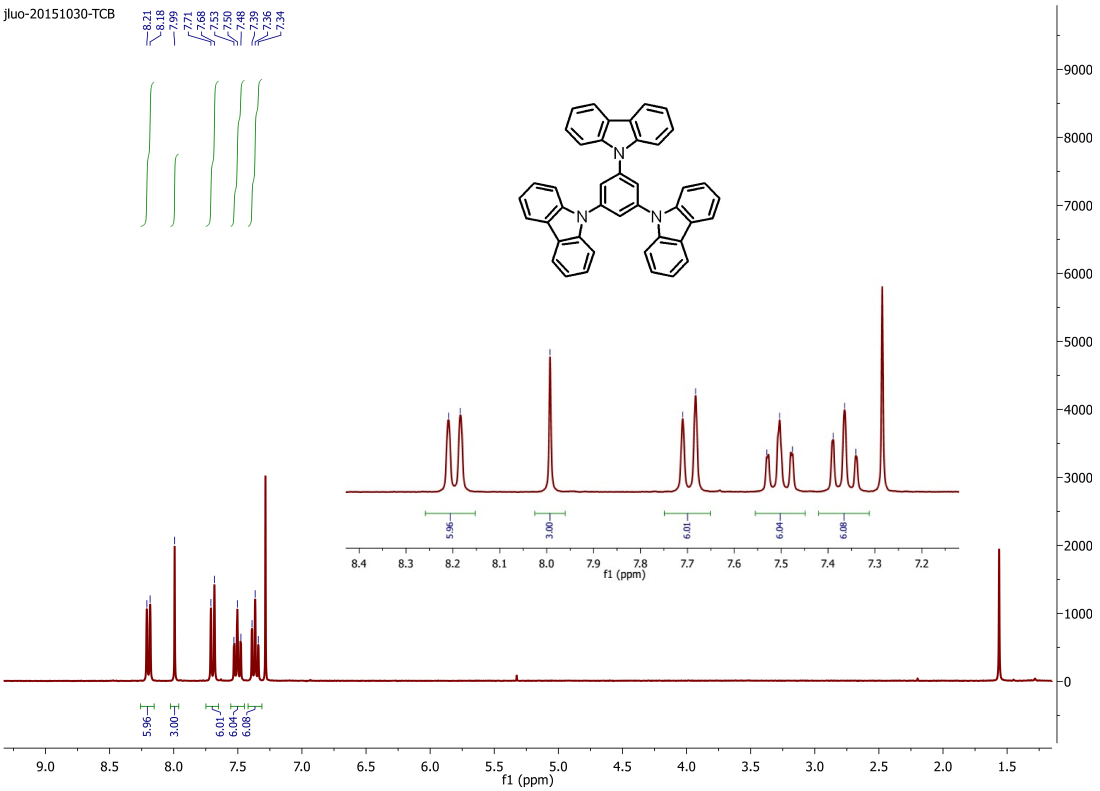
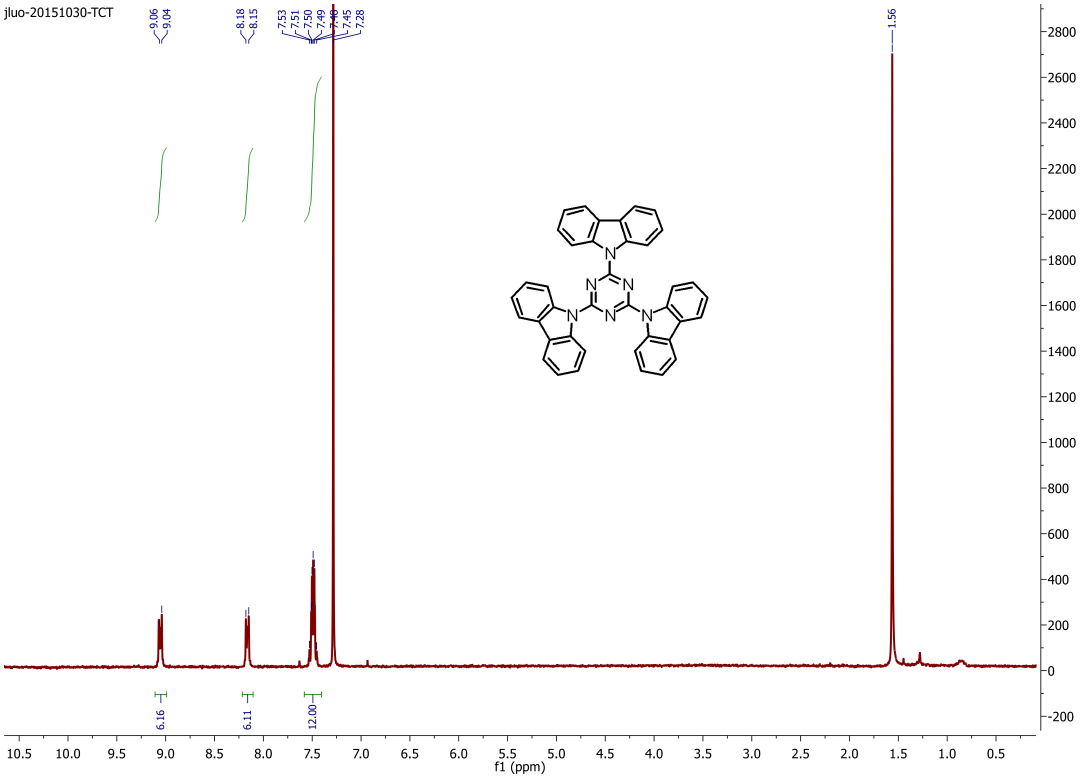
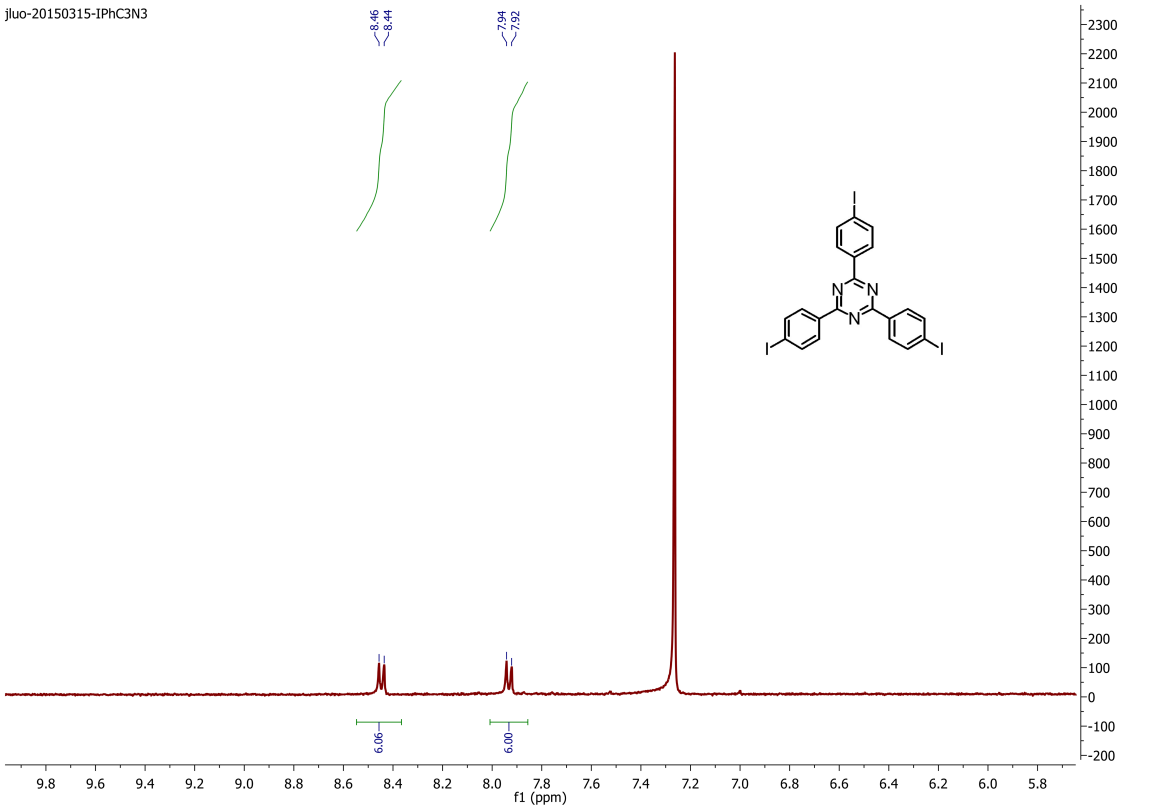
S-5. *NMR spectra*



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6.00
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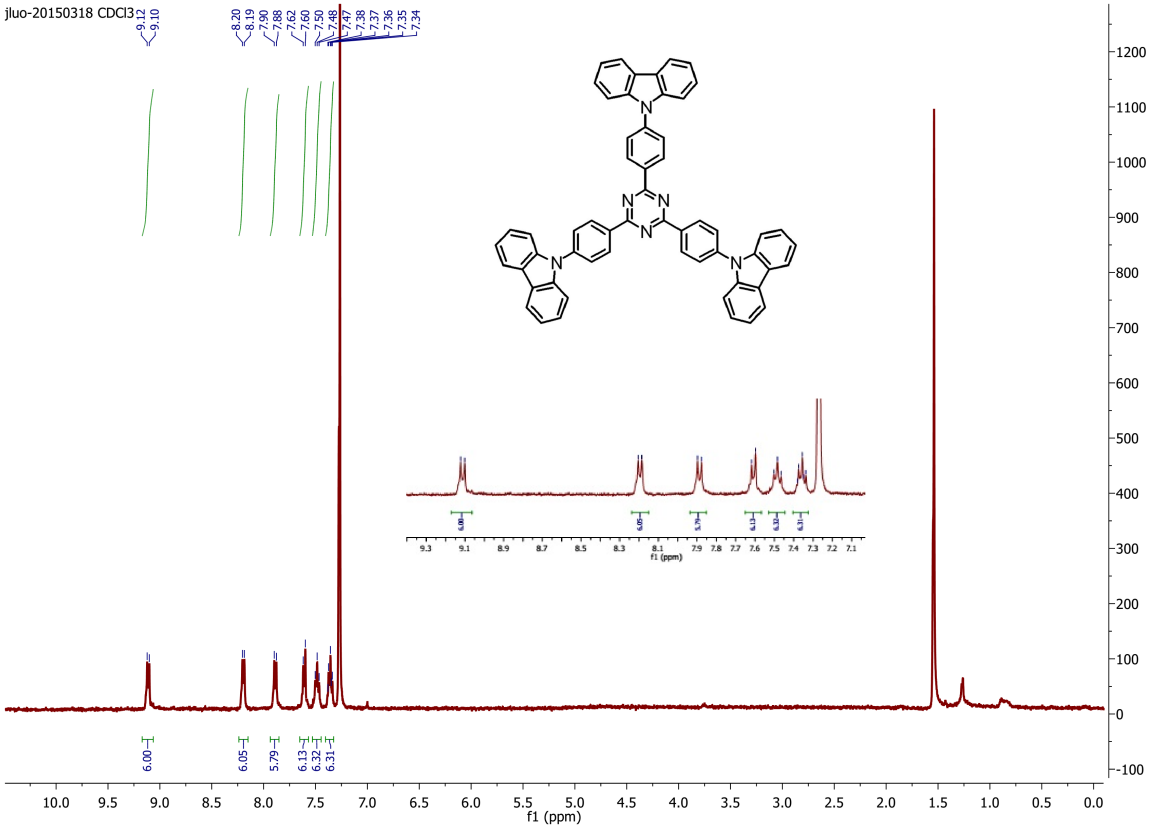
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6.13
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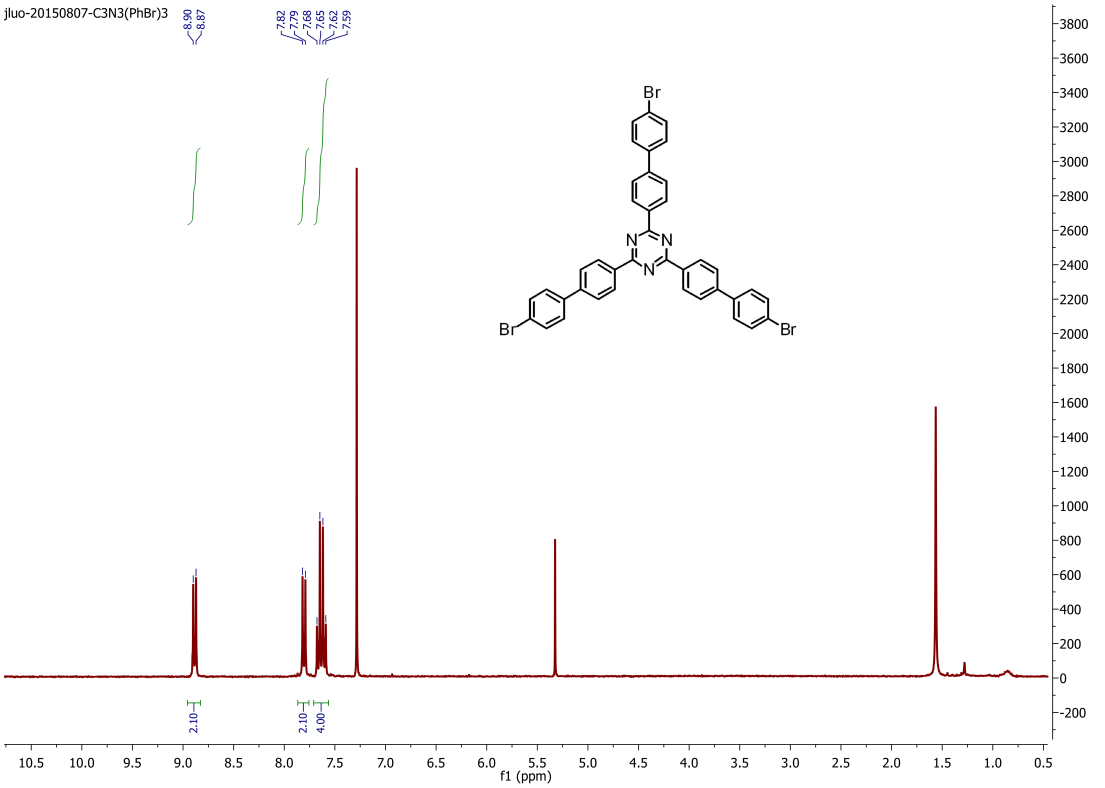
6.31
f1 (ppm)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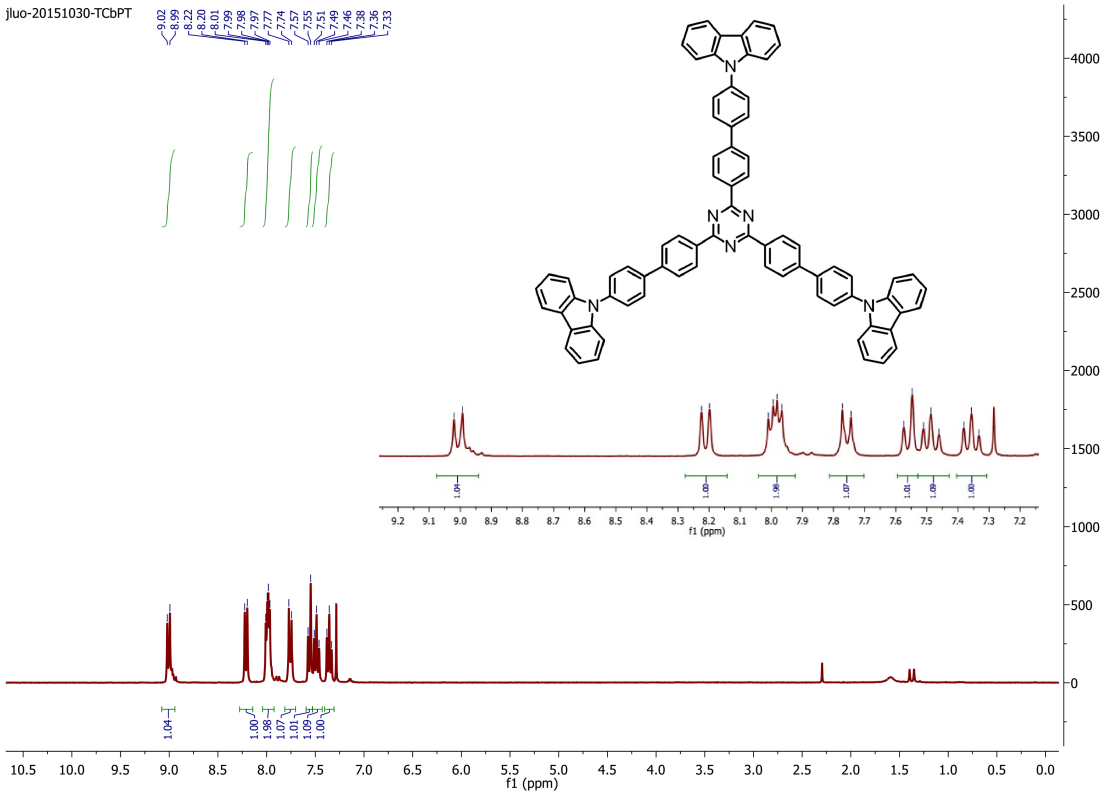
4.00
f1 (ppm)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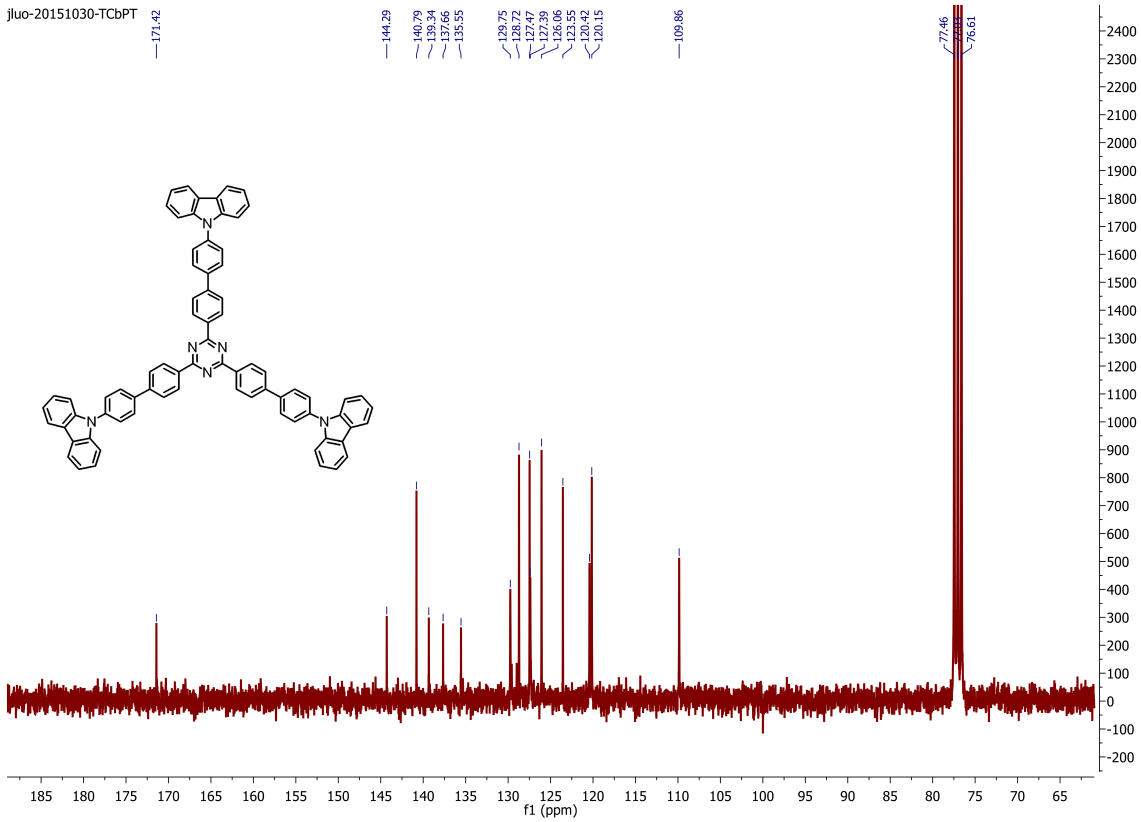
1.00
f1 (ppm)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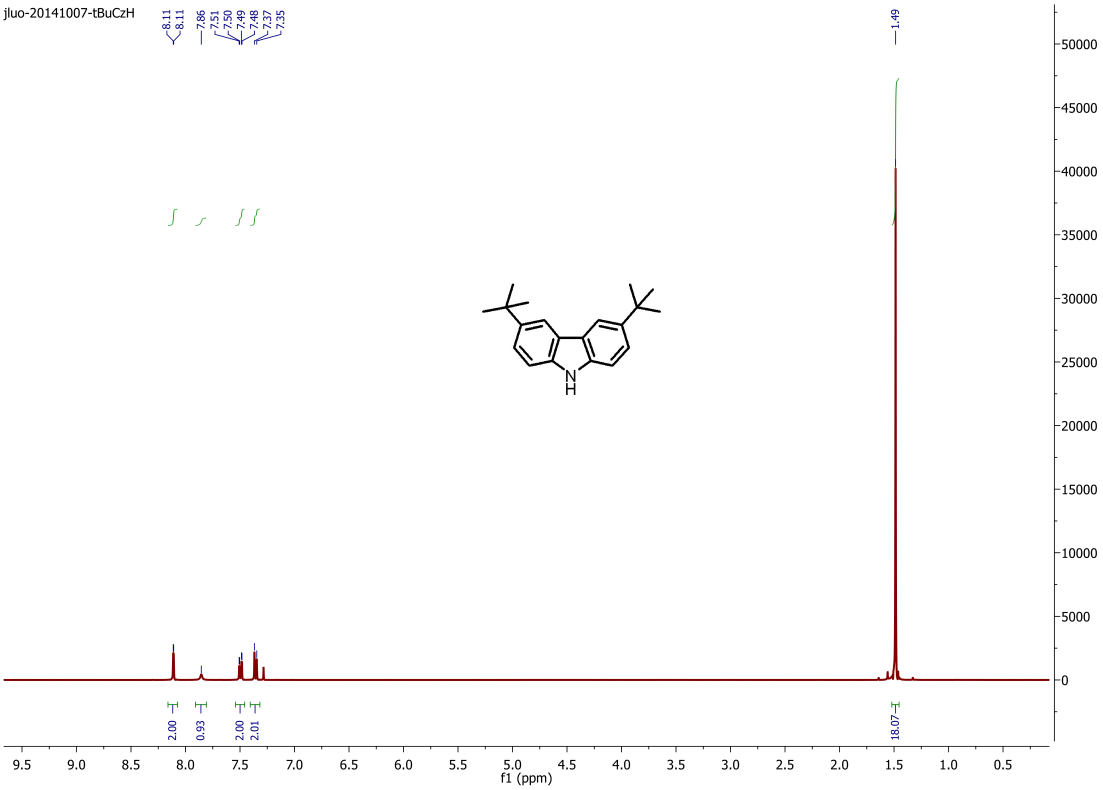
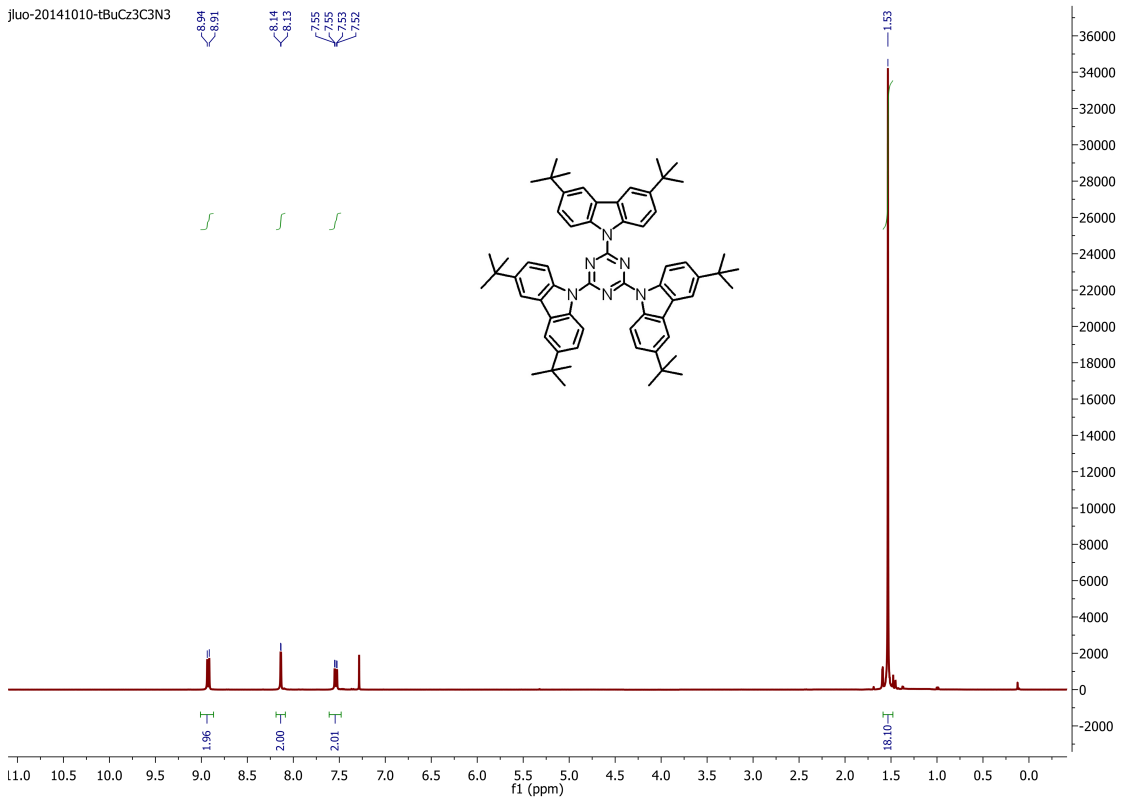
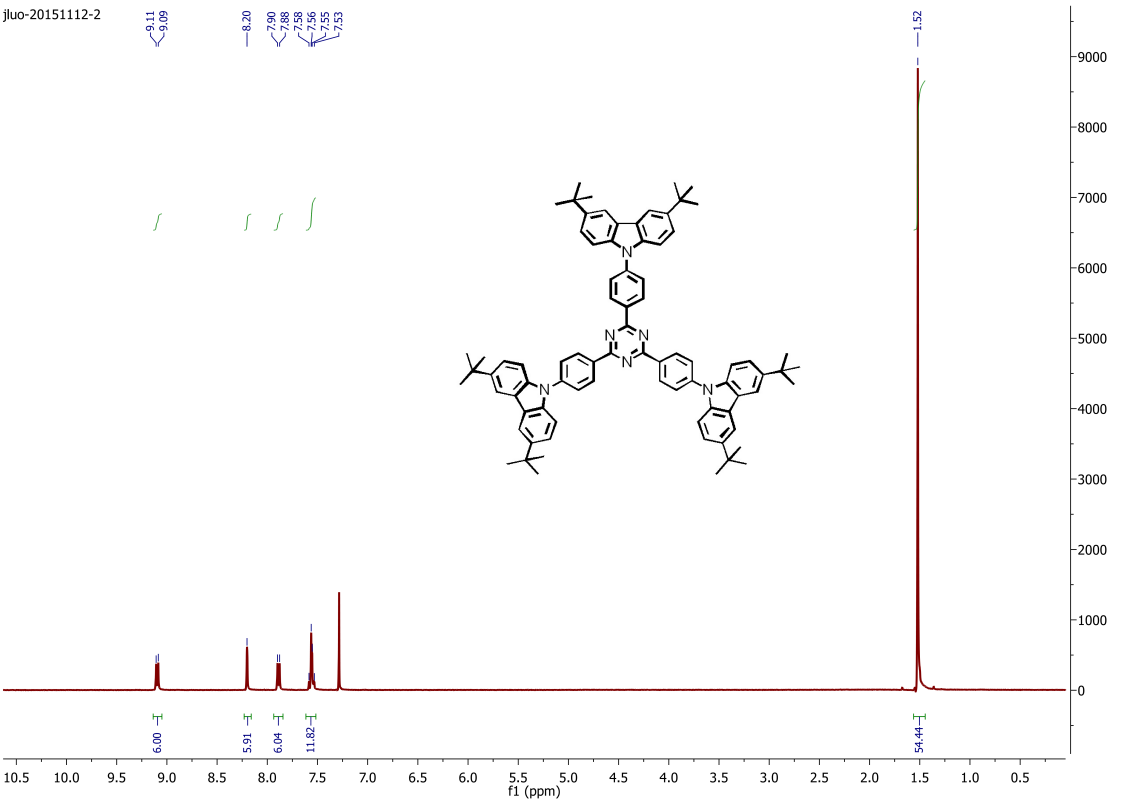
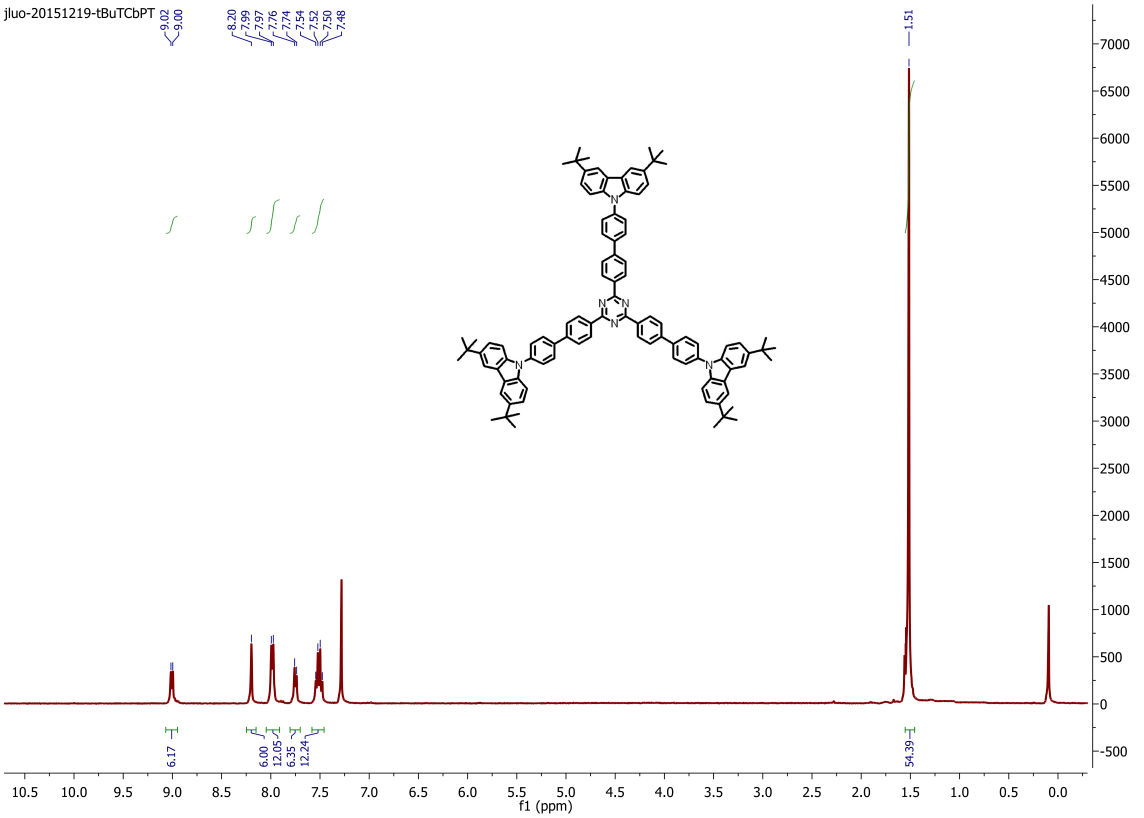
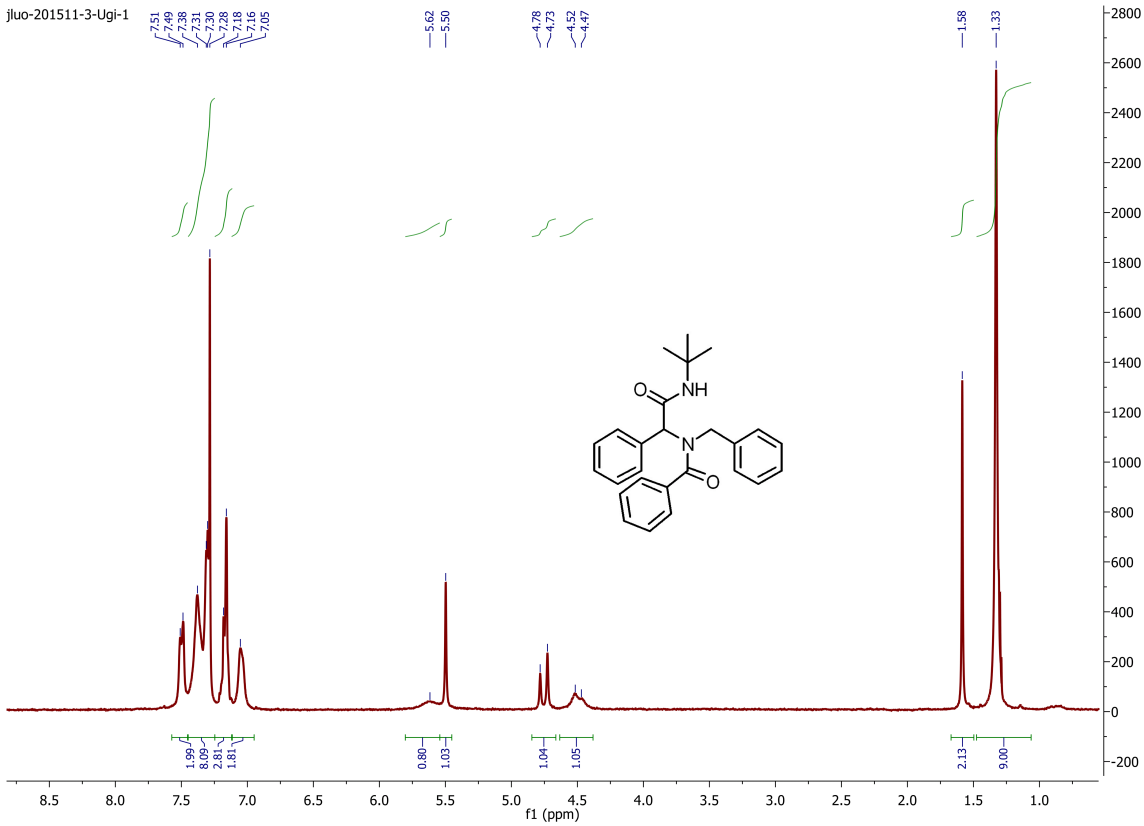
120.15
109.86
77.46
77.03
76.61
f1 (ppm)

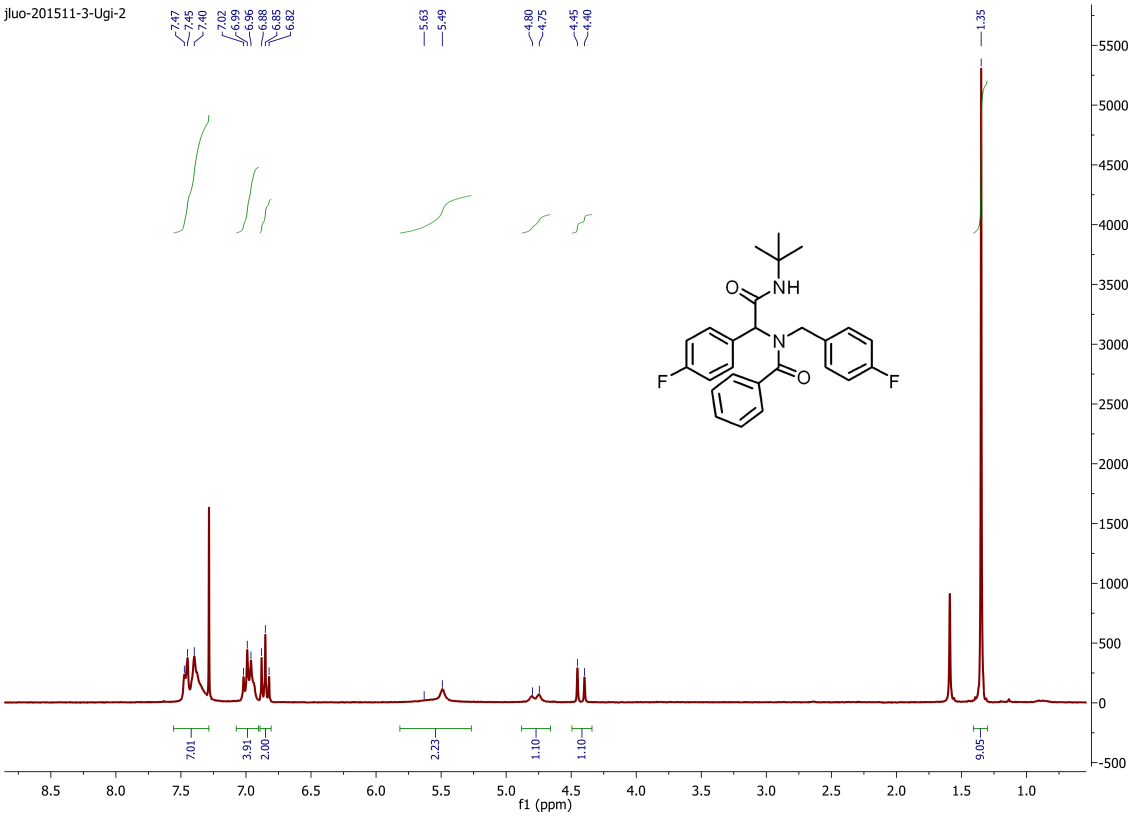

jluo-20141007-tBuCzH
8.11
8.11
7.86
7.51
7.50
7.49
7.48
7.37
7.35
1.49
2.00
0.93
2.00
2.01
18.07
f1 (ppm)

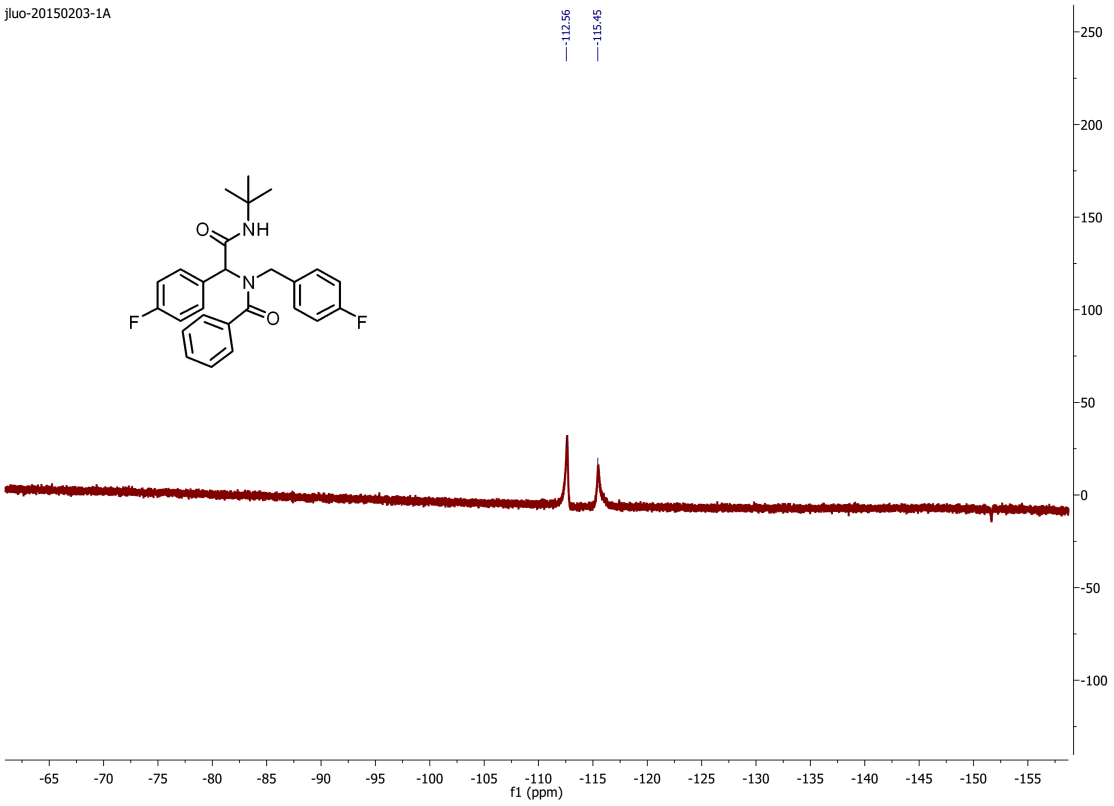

jluo-20141010-tBuCz3C3N3
8.94
8.91
8.14
8.13
7.55
7.55
7.53
7.52
1.53
1.96
2.00
2.01
18.10
f1 (ppm)

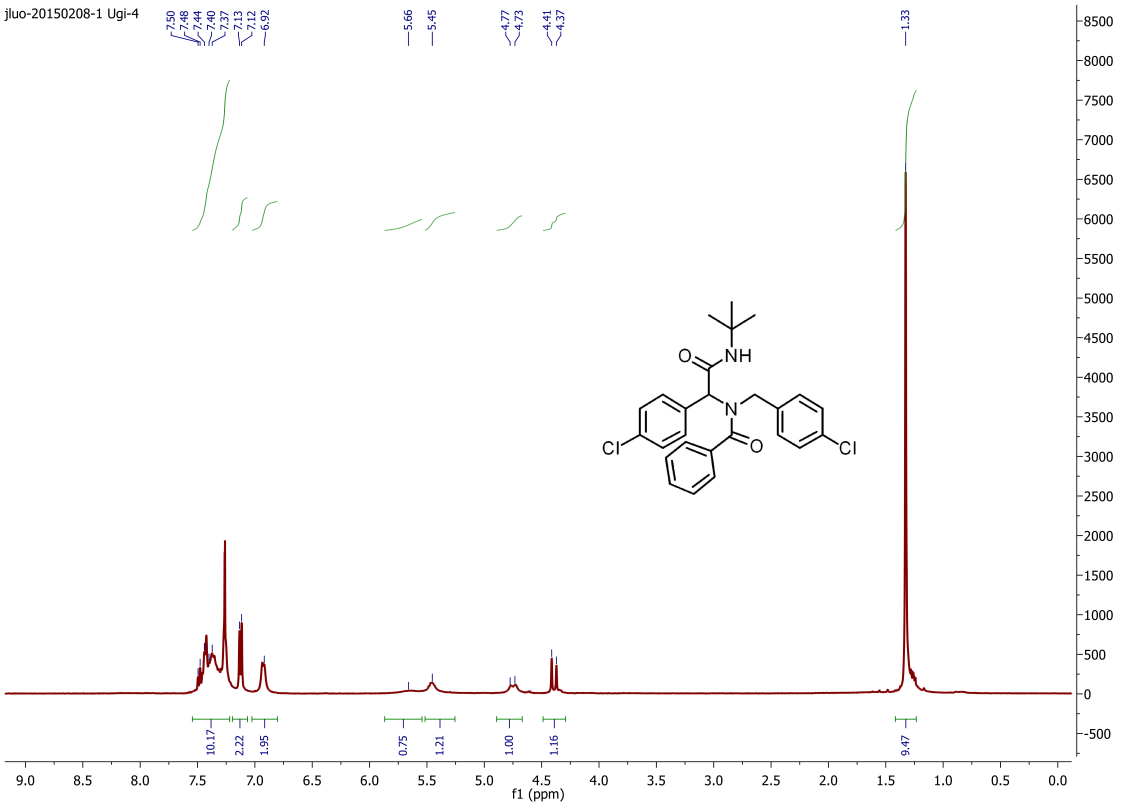

jluo-20151112-2
9.11
9.09
8.20
7.90
7.88
7.58
7.56
7.55
7.53
1.52
6.00
5.91
6.04
11.82
54.44
f1 (ppm)

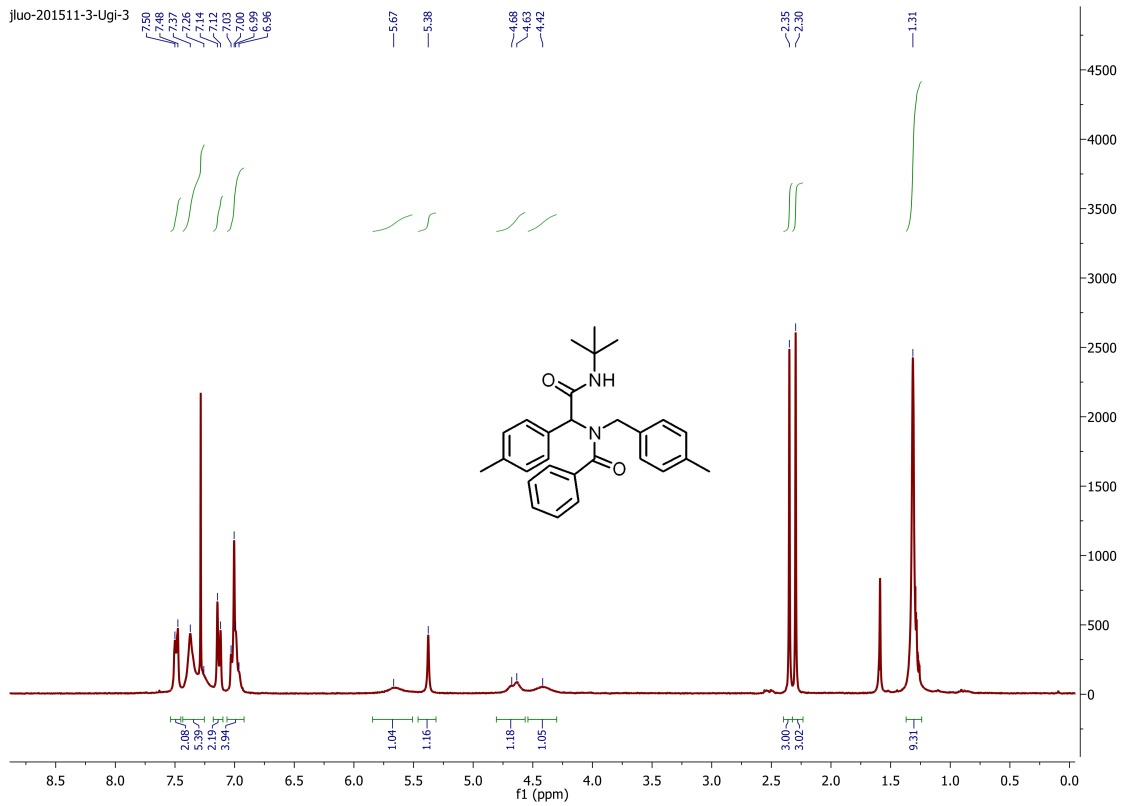

jluo-20151219-tBuTCbPT
9.02
9.00
8.20
7.99
7.97
7.76
7.74
7.54
7.52
7.50
7.48
1.51
6.17
6.00
12.05
6.35
12.24
54.39
f1 (ppm)

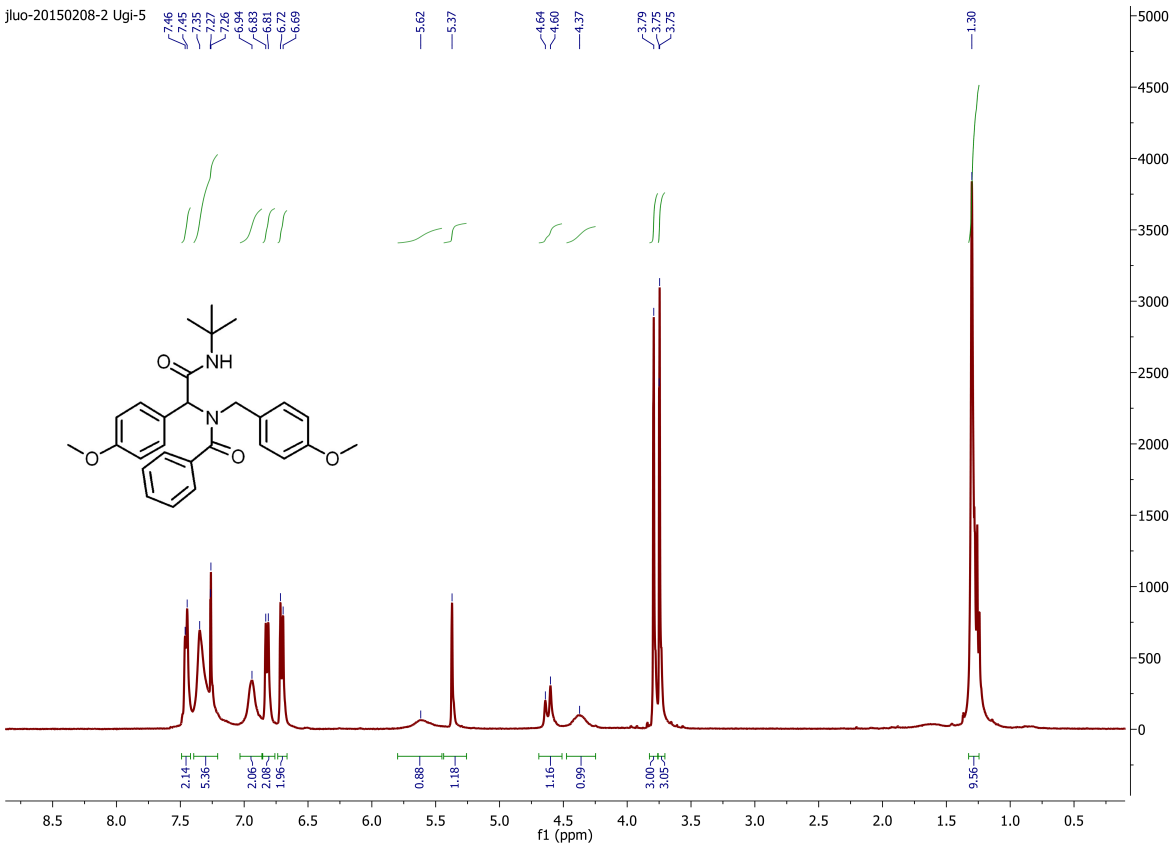

jluo-201511-3-Ugi-1
7.51
7.49
7.38
7.31
7.30
7.28
7.18
7.16
7.05
5.62
5.50
4.78
4.73
4.52
4.47
1.58
1.33
NH
O
O
N
1.99
8.09
2.81
1.81
0.80
1.03
1.04
1.05
2.13
9.00
f1 (ppm)


jluo-201511-3-Ugi-2
7.47
7.45
7.40
7.02
6.99
6.96
6.88
6.85
6.82
5.63
5.49
4.80
4.75
4.45
4.40
1.35
7.01
3.91
2.00
2.23
1.10
1.10
9.05
f1 (ppm)


jluo-20150203-1A
-112.56
-115.45
f1 (ppm)


jluo-20150208-1 Ugi-4
7.50
7.48
7.44
7.40
7.37
7.13
7.12
6.92
5.66
5.45
4.77
4.73
4.41
4.37
1.33
O
NH
N
O
Cl
Cl
10.17
2.22
1.95
0.75
1.21
1.00
1.16
9.47
f1 (ppm)


jluo-201511-3-Ugi-3
7.50
7.48
7.37
7.26
7.14
7.12
7.03
7.00
6.99
6.96
5.67
5.38
4.68
4.63
4.42
2.35
2.30
1.31
O
NH
N
O
2.08
5.39
2.19
3.94
1.04
1.16
1.18
1.05
3.00
3.02
9.31
f1 (ppm)


jluo-20150208-2 Ugi-5
7.46
7.45
7.35
7.27
7.26
6.94
6.83
6.81
6.72
6.69
5.62
5.37
4.64
4.60
4.37
3.79
3.75
3.75
1.30
NH
O
N
O
O
2.14
5.36
2.06
2.08
1.96
0.88
1.18
1.16
0.99
3.00
3.05
9.56
f1 (ppm)