Supporting Information

N-monoarylated dihydrophenazines reduced and oxidized states as efficient organo-photocatalysts

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Summary

1.0 General Remarks

1.1 Instrumentation

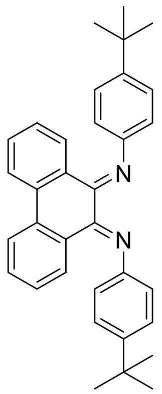
Thin layer chromatography (TLC) was performed on Sigma Aldrich pre-coated aluminium sheets (0.25 mm layer thickness, 60 Å porosity and fluorescent indicator GF254) and were visualized using 254 or 365 nm light. Flash column chromatography was carried out using Merck Gerduran silica gel 60 (particle size 40 63 μm). ***Nuclear magnetic resonance*** (NMR) ^{1}H, and ^{13}C spectra were obtained on Varian Inova spectrometer (500 MHz ^{1}H and 126 MHz ^{13}C) or Varian 400 MHz NMR spectrometer (400 MHz ^{1}H and 101 MHz ^{13}C). Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm, CD_3CN: δ_H = 1.94 ppm, δ_C = 1.32, 118.26 ppm, DMSO-*d6*: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Coupling constants (*J*) were given in Hz and were averaged. Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), m (multiplet), br (broad signal), dd (doublet of doublets), dt (doublet of triplets). Carbon spectra were acquired with a complete decoupling for the proton, unless specified. All spectra were recorded at 25°C unless specified. ***Infrared spectra*** (IR) were recorded on a Shimadzu IR Affinity 1S FTIR spectrometer in ATR mode with a diamond mono-crystal. Selected absorption bands are reported in wavenumber (cm^{-1}). ***ESI-High resolution mass spectrometry*** (ESI-HRMS). ESI-HRMS was performed at University of Trieste Chemistry department, High resolution mass spectra (HRMS) were obtained on Bruker micrOTOF-Q (ESI-TOF). ***Photophysical analysis*** Absorption spectra of compounds were recorded on air equilibrated solutions at room temperature with an Agilent Cary 5000 UV-Vis spectrophotometer, using quartz cells with path length of 1.0 cm. Emission measurements were performed on an Edinburgh instruments FS5 spectrofluorometer using a 150 W CW Ozone-free xenon arc lamp as source and a Photomultiplier R928P (spectral coverage 200 nm – 900 nm, cooled and stabilised) as detector. Quantum yields were performed using the integrating sphere setup SC-30 on a sample solution in a quartz cuvette and using the same solvent in another cuvette as reference. Luminescence lifetimes were measured with an Edinburgh Instruments FS5 time-correlated single-photon counting spectrofluorimeter, exciting the sample at 280 nm with a picosecond pulsed diode laser (EPLED - 280 Edimburgh Instruments). ***Cyclic voltammetry*** The electrochemical characterizations were carried out at room temperature, on an Autolab 302 N electrochemical workstation (Metrohm, The Netherlands) in a glass cell from CH Instruments (10 mL, CHI220). A typical three-electrode cell was employed, which was composed of glassy carbon (GC) working electrode (3 mm diameter), a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode (RE). RE was connected to the glass cell through a salt bridge. Oxygen was removed by purging the solution with Argon. The GC electrode was polished twice before use with 0.05 and 0.1 colloidal silica polishing suspension and ultrasonically rinsed with deionized water for 15 minutes. ***Photochemical reaction set up*** The light-driven reactions were set up under an argon atmosphere in Schlenk tubes or glass vials unless otherwise stated. The light sources used in this work were purchased from Kessil. Detail Kessil lamp 427 nm PR160L-427 (50W). https://www.kessil.com/science/PR160L.php

1.2 Materials and methods

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

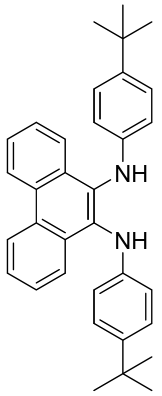
2.0 Synthetic procedures and spectral data

2.1 Synthesis of 2



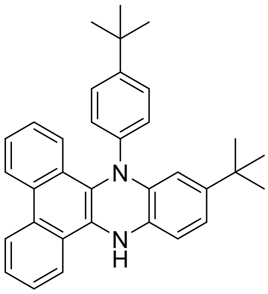
9,10-Phenanthroquinone (500 mg, 2.4 mmol) was added in a single necked flask and dissolved in CH_2Cl_2 (50 mL). The reaction was then cooled to 0°C and 4-*t*BuAniline (1.64 mL, 10.3 mmol) slowly added, followed by dry pyridine (1.95 mL, 24 mmol). $TiCl_4$ (0.87 mL, 7.92 mmol) was then added under Ar and the resulting dark mixture stirred at r.t. for 18 h. The solution was then diluted with diethyl ether (100 mL), stirred for 10 min, and filtered on celite to remove the solid. The solvent was evaporated to give a dark red viscous product, which was precipitated by addition of MeOH (20 mL), the final purification was performed on silica gel plug (PE/CH_2Cl_2 8/2) affording **2** as an orange powder (450 mg, 40%) along with diamine **3** (100 mg, 9%) as major byproduct.

2: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.59 (td, *J* = 7.6, 1.4 Hz, 2H), 7.47 (td, *J* = 7.5, 1.1 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 4H), 6.21 (d, *J* = 8.6 Hz, 4H), 1.32 (s, 18H).^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.55, 147.40, 146.91, 135.78, 134.73, 131.55, 128.92, 126.67, 125.65, 123.70, 119.39, 34.42, 31.57. IR (ATR) ν (cm^{-1}): 3063, 2957, 2866, 1593, 1504, 1449, 1362, 1267, 1180, 1119, 1022, 957, 829, 756, 725, 617, 563, 534, 476, 440, 419. ESI-HRMS: $[M-H]^+$ calc. for $[C_{34}H_{33}N_2]^+$: 469.2638; found 469.2649 (cyclization and oxidation occurs during analysis).



3: ^{1}H-NMR (400 MHz, ACN-*d3*) δ 8.80 (d, *J* = 8.2 Hz, 2H), 7.93 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.63 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 2H), 7.51 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 4H), 6.53 (d, *J* = 8.7 Hz, 4H), 6.48 (s, 2H), 1.21 (s, 18H).^{13}C-NMR (101 MHz, ACN-*d3*) δ 145.75, 142.58, 132.09, 131.00, 130.71, 127.61, 127.06, 126.72, 125.84, 124.06, 115.98, 34.46, 31.68. IR (ATR) ν (cm^{-1}): 3397, 3375, 2957, 2864, 1612, 1514, 1360, 1333, 1292, 1254, 1190, 1028, 818, 762, 725, 546, 419. ESI-HRMS: [M+H]$^+$ calc. for [$C_{34}H_{37}N_2$]$^+$: 473.2951; found 473.2963.

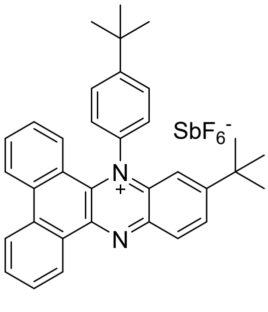
2.2 Synthesis of 1



In a round bottom flask equipped with a condenser **2** (300 mg, 0.64 mmol) was dissolved in a mixture of THF/EtOH (1/1, 15 mL). $NaBH_4$ (24 mg, 0.64 mmol) added, and the reaction heated at 80°C for 3h. The reaction was then evaporated and purified by filtration on a TEA neutralized silica plug using 8/2/0.5 PE/CH_2Cl_2/TEA as eluent to remove the main impurity, followed by 9.5/0.5 CH_2Cl_2/TEA to recover **1**. During the purification procedure **1** undergoes oxidation and thus after evaporation the residue, is suspended in MeOH (10 mL) and $NaBH_4$ added (24 mg, 0.64 mmol) until the colour of the solution becomes clear yellow, and precipitation occurs. Centrifugation of the suspension from MeOH affords clean **1** (189 mg, 63%). Alternatively, after heating at 80°C, the reaction can be evaporated and directly reprecipitated from MeOH followed by centrifugation and filtration on celite (CH_2Cl_2 100%).

^{1}H-NMR (400 MHz, DMSO-*d6*) δ 9.10 (s, 1H, N*H*), 8.91-8.88 (m, 1H), 8.77 (d, *J* = 8.1 Hz, 1H), 8.50-8.48 (m, 1H), 8.00 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.57 – 7.52 (m, 2H), 7.51 – 7.47 (m, 1H), 7.23 – 7.18 (m, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.69 (d, *J* = 8.9 Hz, 2H), 1.35 (s, 9H), 1.13 (s, 9H). ^{13}C-NMR (126 MHz, DMSO-*d6*) δ 148.00, 143.83, 143.08, 139.69, 135.64, 131.09, 129.64, 128.81, 127.30, 126.69, 126.60, 126.43, 125.37, 123.95, 123.85, 123.81, 123.57, 123.11, 122.47, 122.03, 121.36, 118.85, 116.48, 114.76, 33.99, 33.60, 31.37, 31.15. IR (ATR) ν (cm^{-1}): 3412, 2959, 2901, 2866, 1651, 1607, 1499, 1418, 1339, 1283, 1175, 1032, 937, 816, 754, 721, 615, 544, 438. ESI-HRMS: [M-H]$^+$ calc. for [$C_{48}H_{33}N_2$]$^+$: 469.2638; found 469.2637. Product gets oxidized to the monocation.

2.3 Synthesis of 1^{ox}



In a round bottom flask, **1** (35 mg, 0.07 mmol) was dissolved in CH_2Cl_2 (10 mL) and $AgSbF_6$ (72 mg, 0.21 mmol) added in a single portion. After 15 min. the reaction was filtered on a 0.1 μM PTFE filter to remove Ag^0, followed by washing with CH_2Cl_2. The resulting organic layers were then evaporated, and the residue precipitated and centrifuged 3× from Et_2O (46.5 mg, 94%) samples for catalysis were further purified by 2 × filtration on celite (CH_2Cl_2 100%).

^{1}H-NMR (400 MHz, ACN-*d3*) δ 9.42 – 9.38 (m, 1H), 8.84 – 8.80 (m, 1H), 8.75 – 8.71 (m, 1H), 8.66 (dd, *J* = 9.0, 0.4 Hz, 1H), 8.43 (dd, *J* = 9.0, 1.9 Hz, 1H), 8.06 – 7.88 (m, 5H), 7.64 – 7.59 (m, 2H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.30 (ddd, *J* = 8.6, 7.1, 1.3 Hz, 1H), 1.50 (s, 9H), 1.35 (s, 9H). ^{13}C-NMR (101 MHz, ACN-*d3*) δ 162.61, 157.76, 146.89, 143.21, 138.04, 138.00, 137.72, 135.46, 133.70, 133.40, 133.28, 132.39, 132.12, 131.31, 131.06, 129.75, 129.14, 128.46, 127.71, 127.14, 126.29, 124.68, 122.67, 116.01, 37.45, 36.08, 31.36, 30.45. IR (ATR) ν (cm^{-1}): 3067, 2963, 2878, 1601, 1504, 1450, 1360, 1177, 1107, 839, 758, 718, 652, 633, 581, 532. ESI-HRMS: $[M]^+$ calc. for $[C_{48}H_{33}N_2]^+$: 469.2638; found 469.2650.

3.0 Photophysical and electrochemical characterization

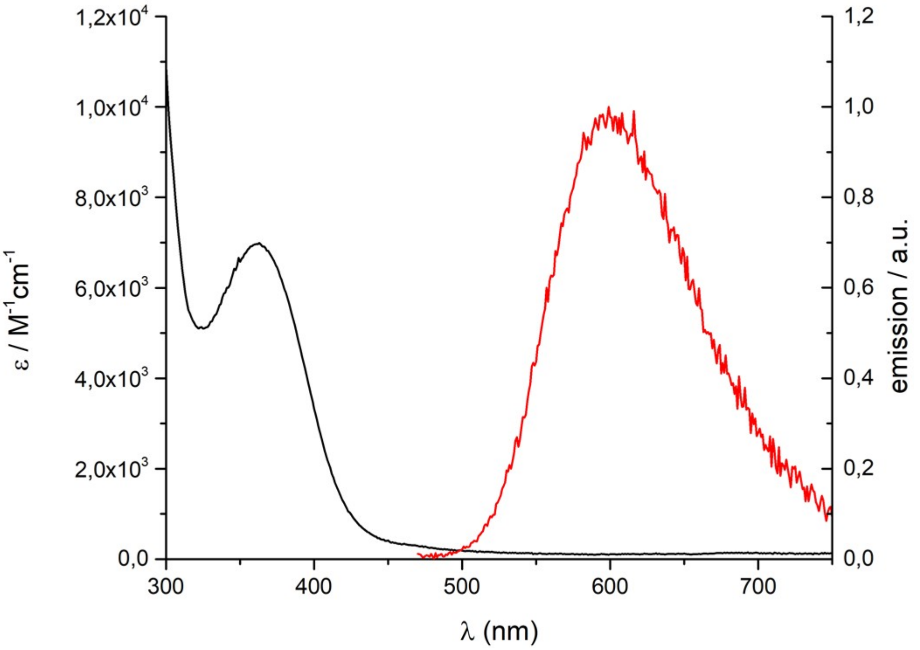


Figure S1. Normalized absorption and emission spectra of **1** in DMF.

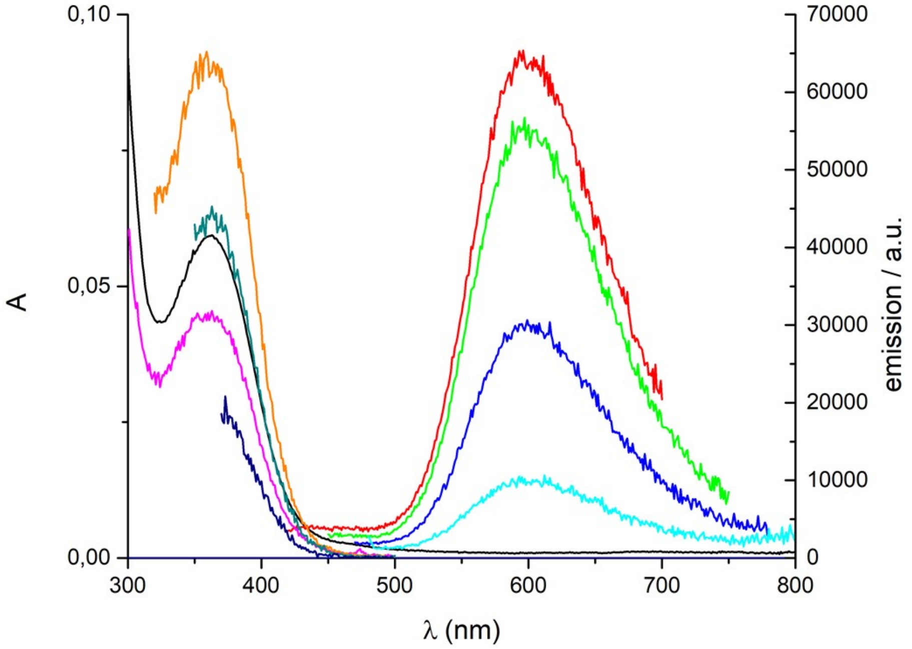


Figure S2. Absorption (black), emission (red, green, blue and cyan λ_{exc}= 360, 380, 400, 420 nm) and excitation (magenta, orange, dark green and navy blue λ_{em}= 550, 600, 650, 700 nm) spectra of **1** (8×10^{-6} M) in DMF.

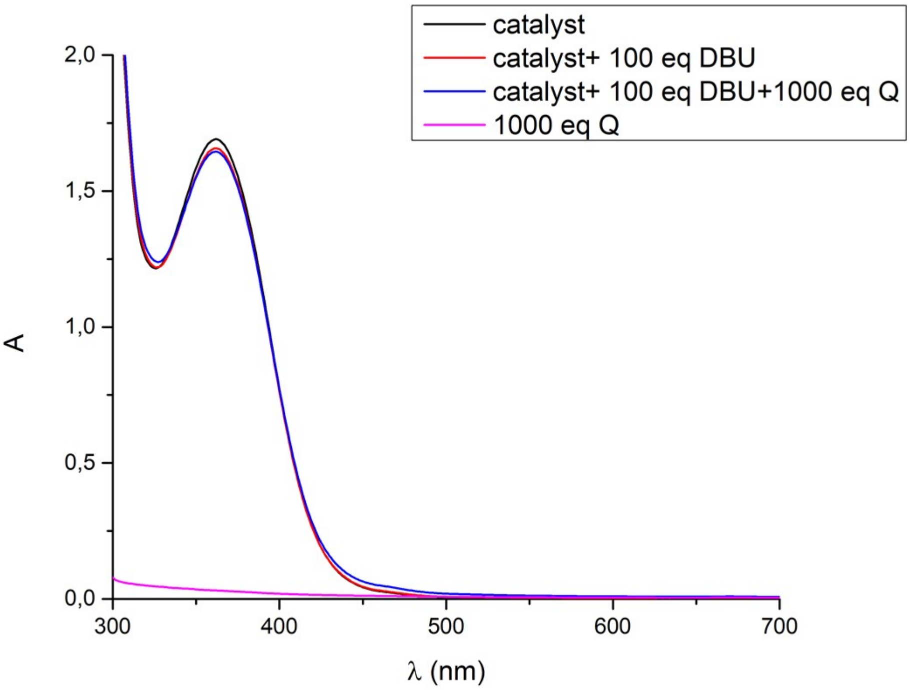


Figure S3. Absorption of **1** (2.5×10^{-4} M), **DBU** (0.025 M), **4a** (0.25 M) and relative mixtures in DMF.

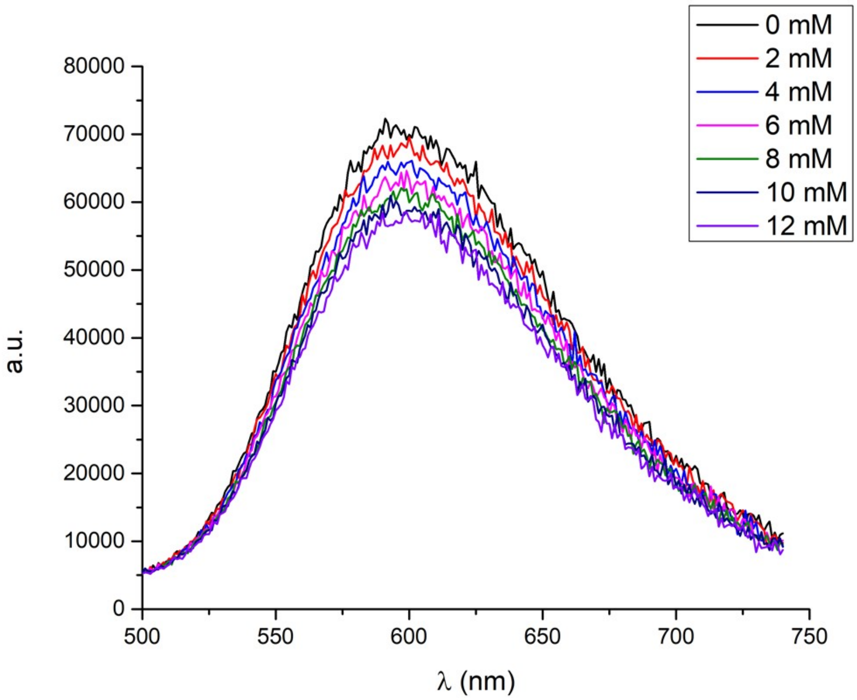


Figure S4. Stern-Volmer quenching study of **1** (1.0×10^{-5} M) in DMF upon the addition of **4a** ($2\text{-}12 \times 10^{-3}$ M) in presence of DBU (1.0×10^{-3} M).

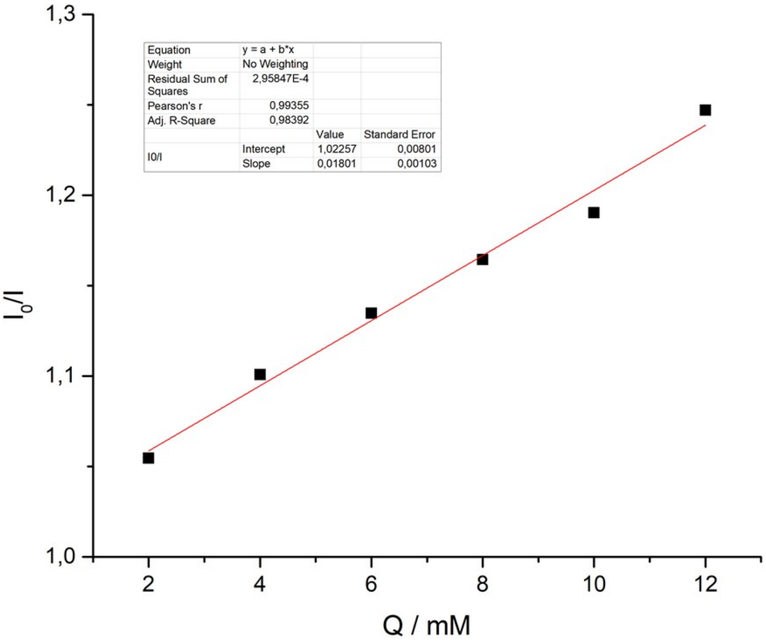


Figure S5. Stern-Volmer quenching study of **1** (1.0×10^{-5} M) in DMF upon the addition of **4a** ($2\text{-}12 \times 10^{-3}$ M) in presence of DBU (1.0×10^{-3} M). Kq= 5.1×10^{9} $M^{-1} \times s^{-1}$.

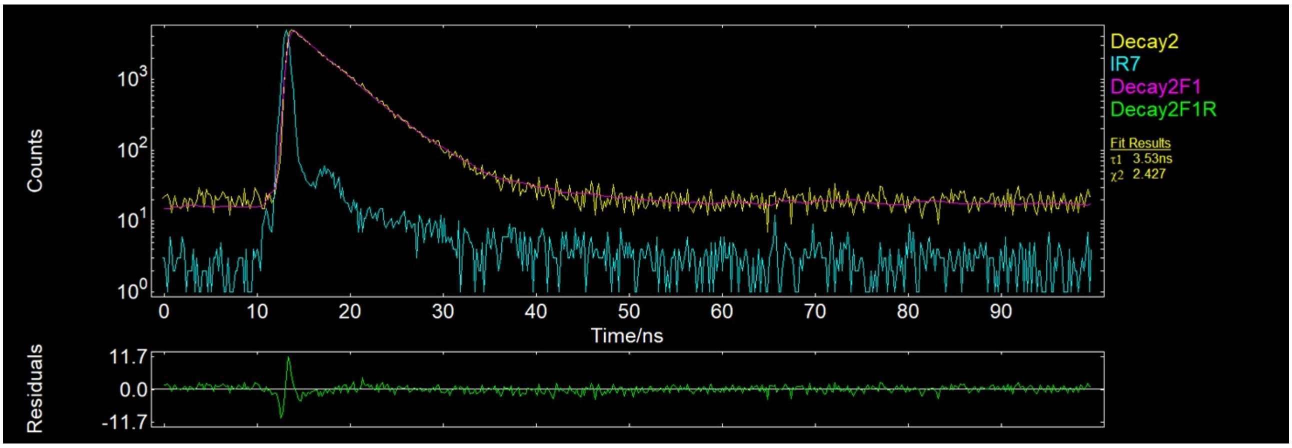


Figure S6. Emission lifetime of **1** (8×10^{-6} M) in DMF. The yellow curve corresponds to the sample fluorescence decay, the blue curve corresponds to the instrument response function and the magenta curve corresponds to the best fit, with their respective residuals (green line).

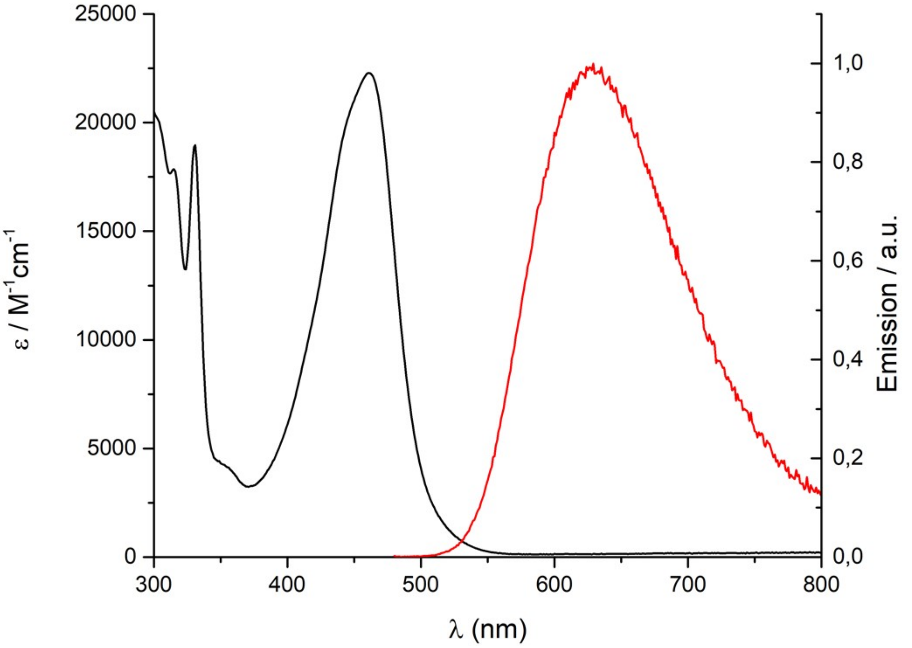


Figure S7. Normalized absorption and emission spectra of **1^{ox}** in CH_2Cl_2.

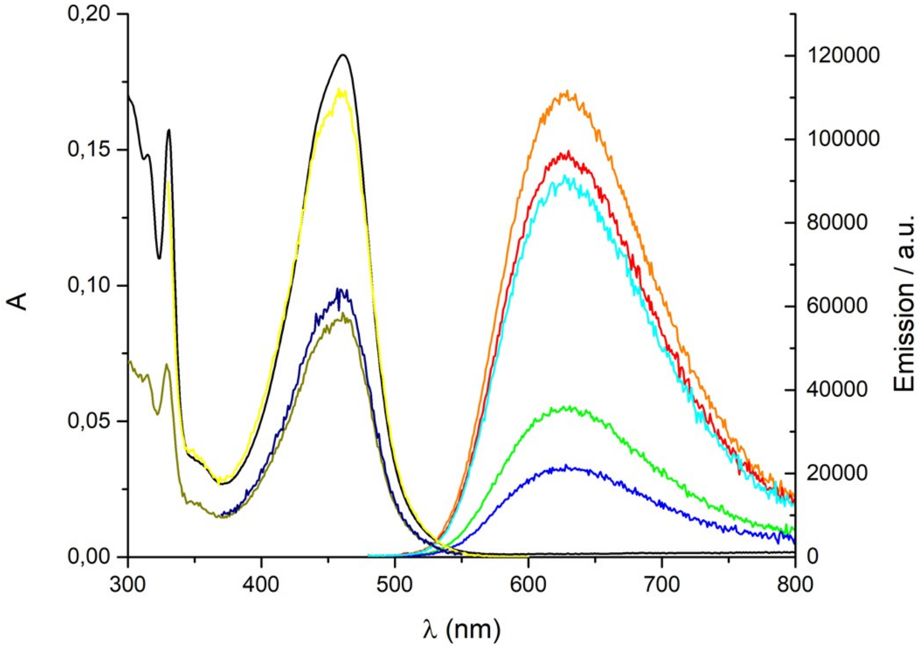


Figure S8. Absorption (black), emission (orange, red, cyan, green and blue λ_{exc}= 463, 330, 440, 400 and 360 nm) and excitation (yellow, navy blue and brown λ_{em}= 630, 575 and 700 nm) spectra of **1^{ox}** (8.3×10^{-6} M) in CH_2Cl_2.

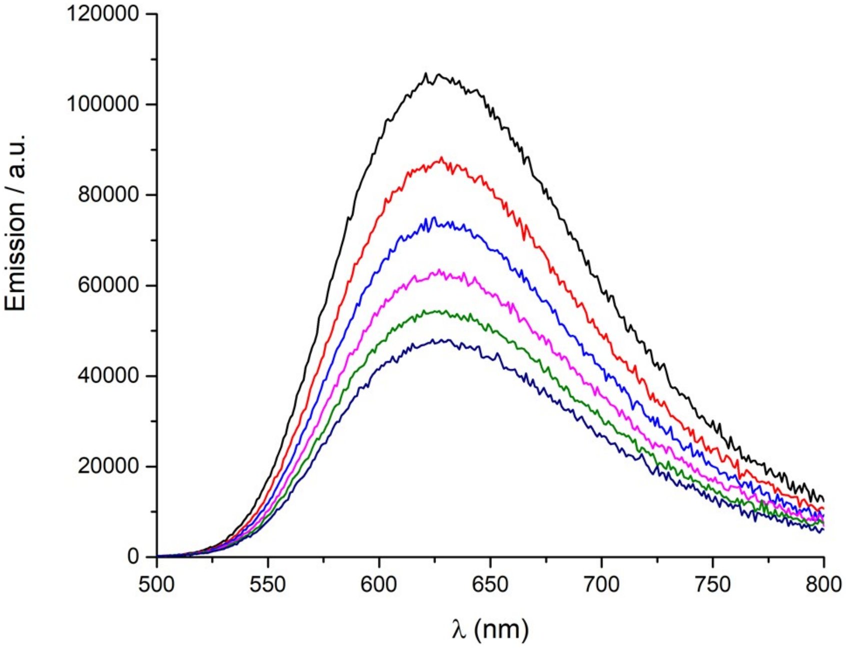


Figure S9. Stern-Volmer quenching study of **1**^{ox} (8.3×10^{-6} M) in CH_2Cl_2 upon the addition of **6a** ($8.3\text{-}40.0 \times 10^{-3}$ M).

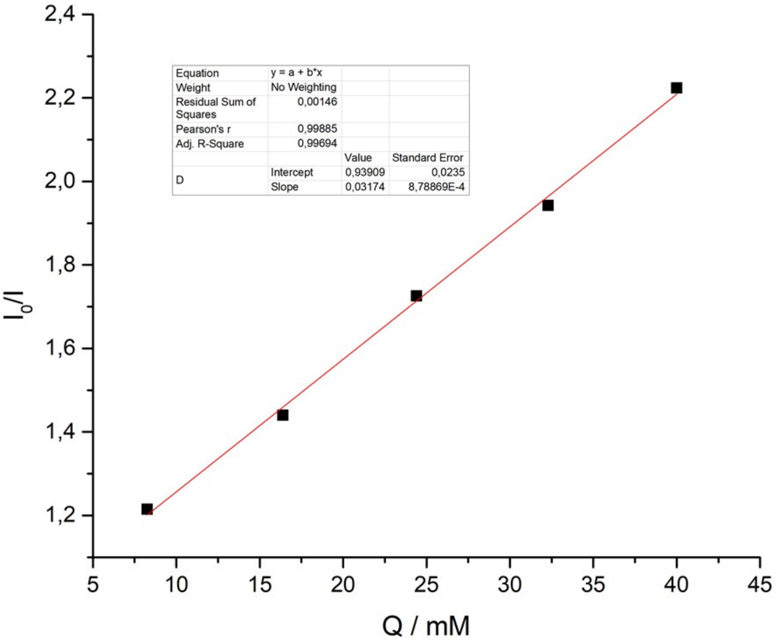


Figure S10. Stern-Volmer quenching study of **1**^{ox} (8.3×10^{-6} M) in CH_2Cl_2 upon the addition of **6a** ($8.3\text{-}40.0 \times 10^{-3}$ M). Kq= 8.5×10^{9} $M^{-1} \times s^{-1}$.

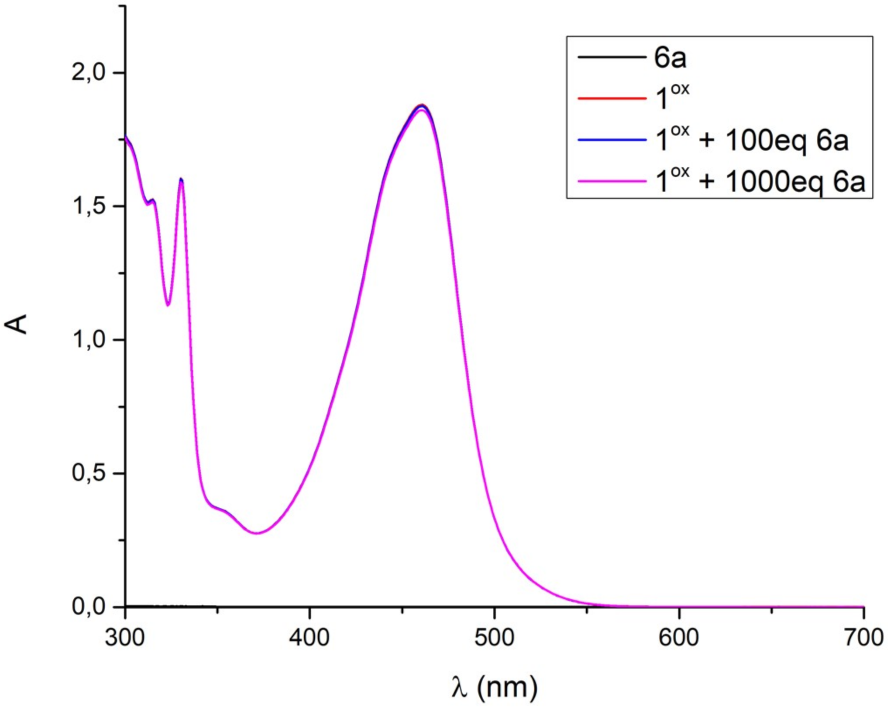


Figure S11. Absorption of **1**^{ox} (1.0 × 10^{-4} M), **6a** (0.01 M) and relative mixtures in CH_2Cl_2.

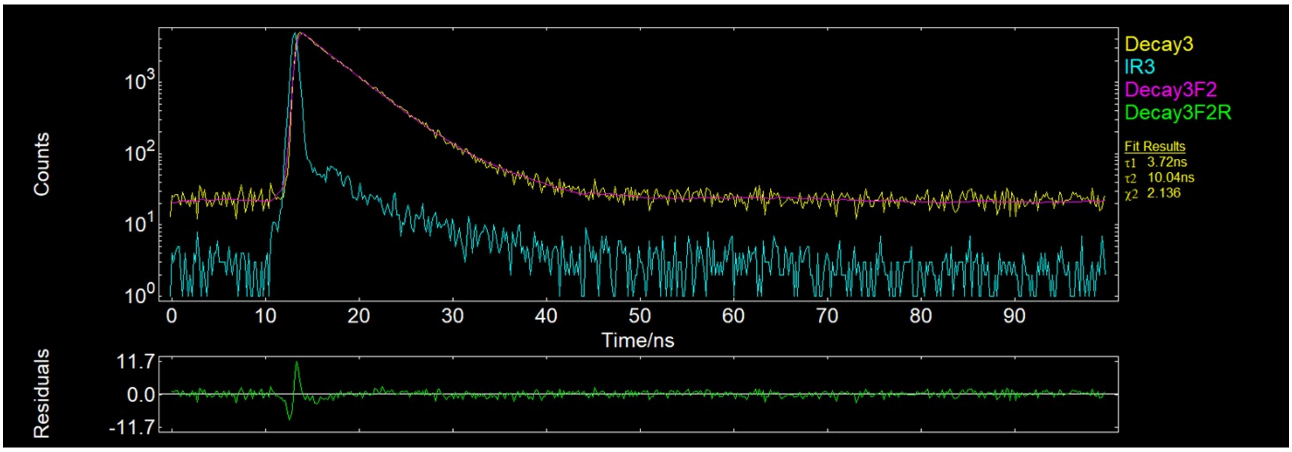


Figure S12. Emission lifetime of **1**^{ox} (8.3 × 10^{-6} M) in CH_2Cl_2. The yellow curve corresponds to the sample fluorescence decay, the blue curve corresponds to the instrument response function and the magenta curve corresponds to the best fit, with their respective residuals (green line).

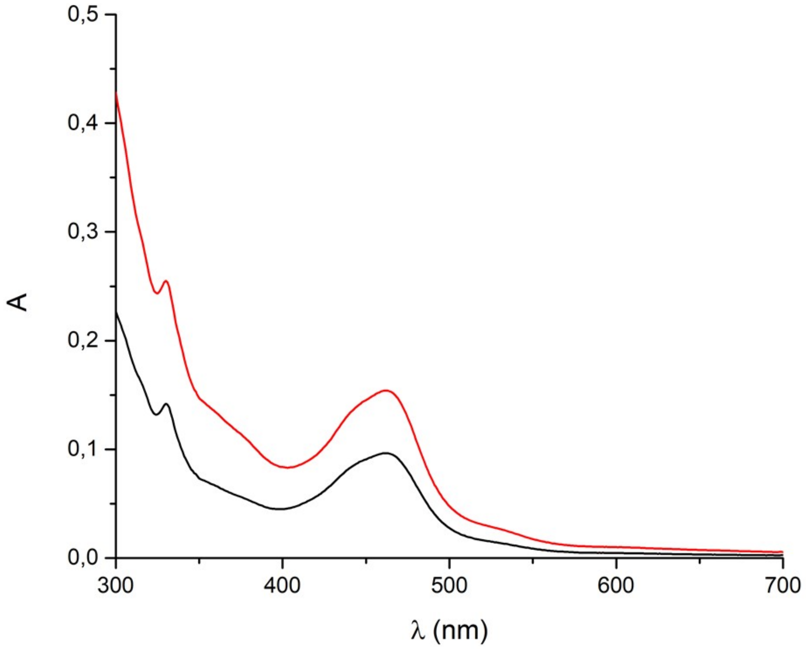


Figure S13. Absorption of **1** [1.67×10^{-5} M] (black), and [3.33×10^{-5} M] (red) after 2h irradiation under air in ODCB [0.01 M].

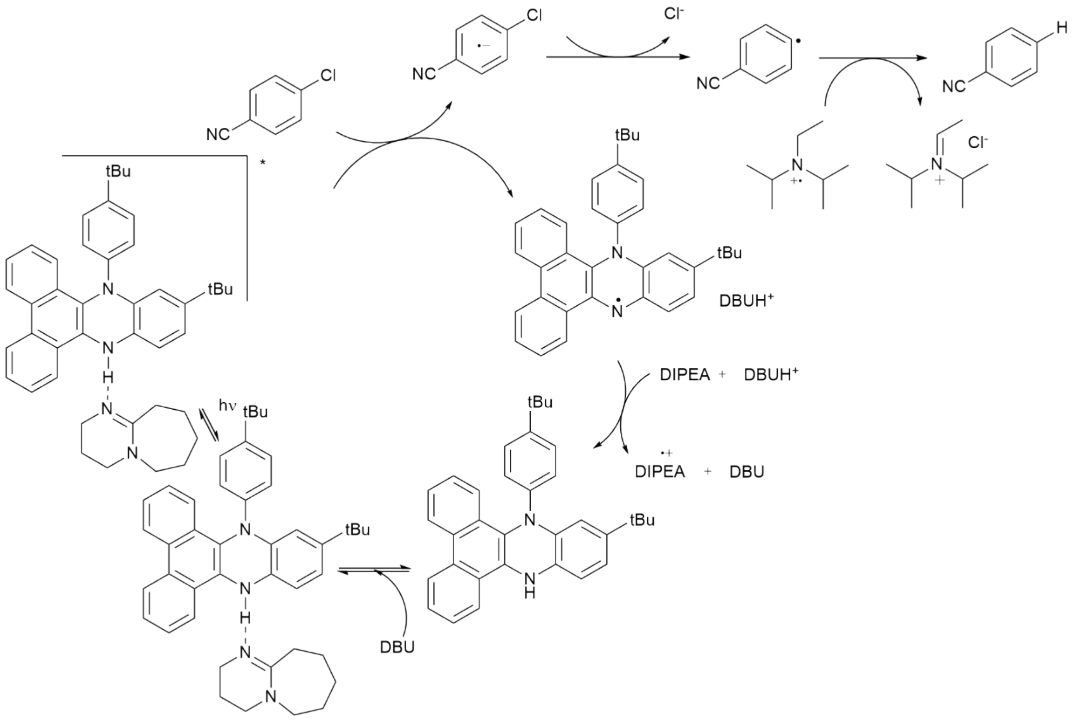


Figure S14. Proposed mechanism hypothesis for the catalytic activity of **1**.

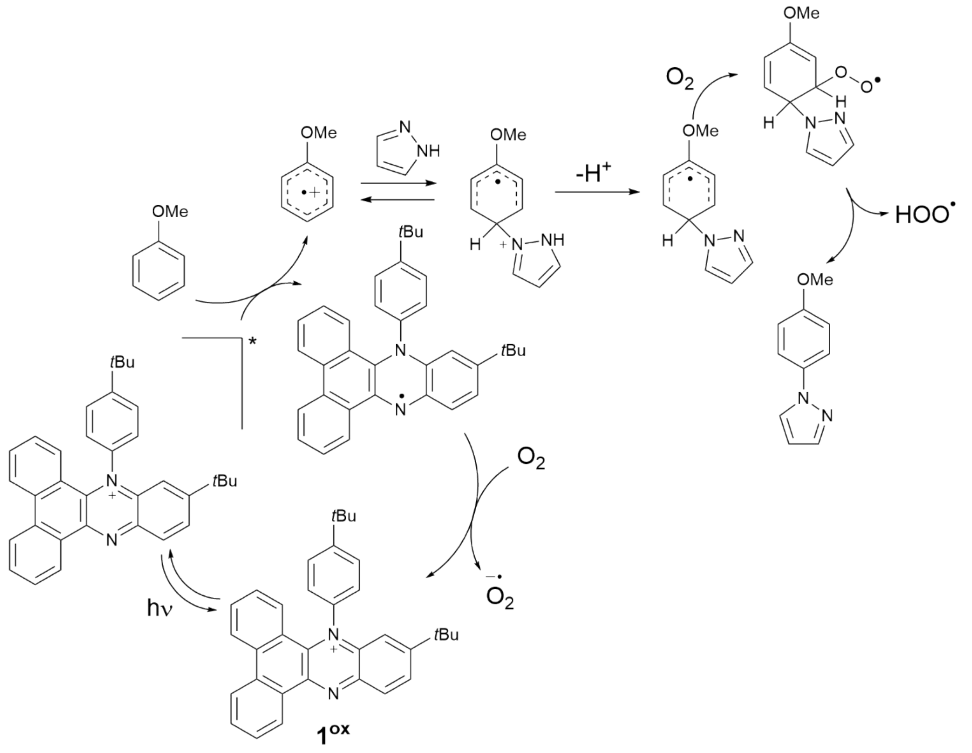


Figure S15. Proposed mechanism hypothesis for the catalytic activity of **1^{ox}**.

4.0 Electrochemical characterization

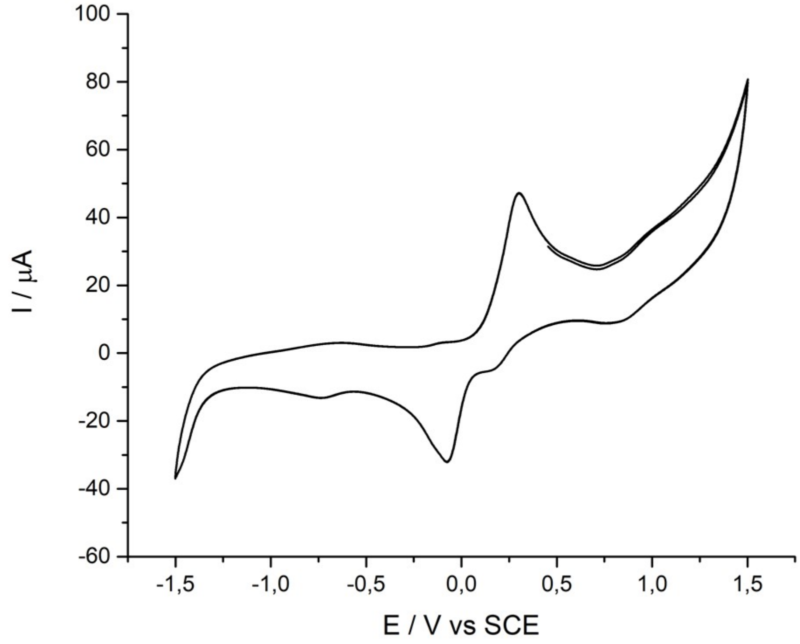


Figure S16. Cyclic voltammograms of **1** (1 mM), in DMF. Scan rates: 0.05 V s^{-1} (black line), TBAPF$_6$ (0.1 M) is used as a supporting electrolyte.

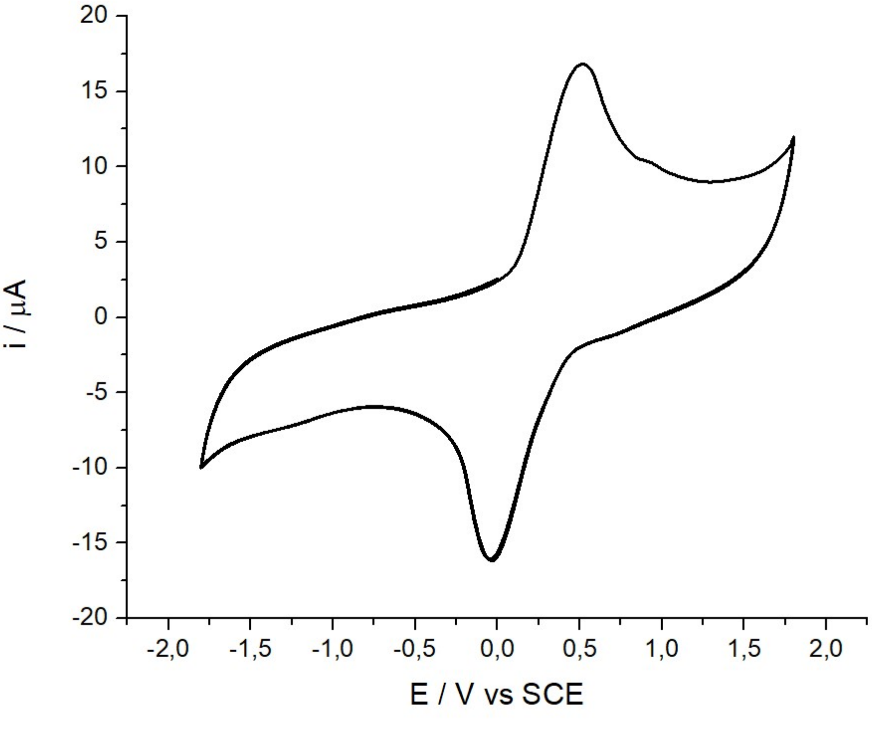


Figure S17. Cyclic voltammograms of **1** (1 mM), in CH$_2$Cl$_2$. Scan rates: 0.1 V s^{-1} (black line), TBAPF$_6$ (0.1 M) is used as a supporting electrolyte.

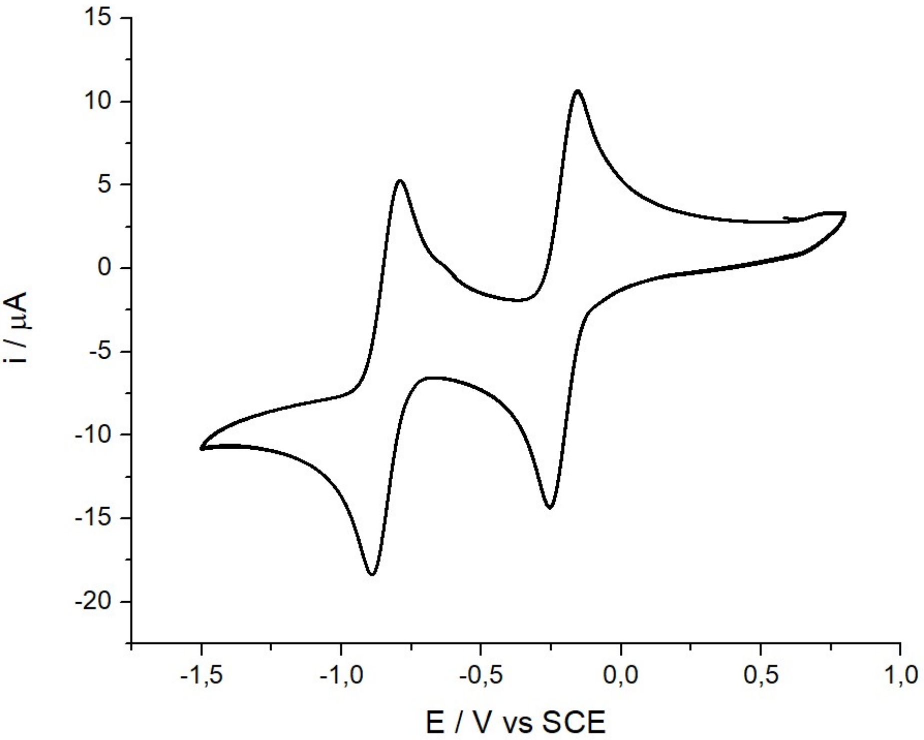
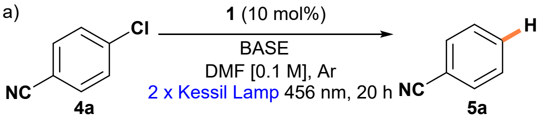


Figure S18. Cyclic voltammograms of **1^{ox}** (1 mM), in CH_2Cl_2. Scan rates: 0.05 V s^{-1} (black line), $TBAPF_6$ (0.1 M) is used as a supporting electrolyte.

5.0 Photocatalytic Reaction optimization and entries

5.1 Reduction reaction optimization and dehalogenation reactions

Reactions performed on 4-chlorobenzonitrile (0.05 mmol) as substrate [0.1 M]. Yields determined by NMR using 0.05 mmol of trichloroethylene as internal standard.



entry	conditions	solvent	T (h)	Base (vs 4a)	yield
1	/	DMF	20	Dipea 1 eq.	39%
2	/	DMF	20	Dipea 10 eq	46%
3	/	DMF	20	DBU 10 eq	84%
4	/	DMF	20	DBU 15 eq	70%
5	/	DMF	20	DBU 5 eq	26%
6	/	**DMF**	**20**	**DBU 10 eq-Dipea 1 eq**	**>95%**
7	no catalyst	DMF	20	DBU 10 eq- Dipea 1 eq	0%[a]
8	dark	DMF	20	DBU 10 eq-Dipea 1 eq	0%[a]
9	In air	DMF	20	DBU 10 eq-Dipea 1 eq	15%

Table S1. Optimization of reaction conditions with catalyst **1**.

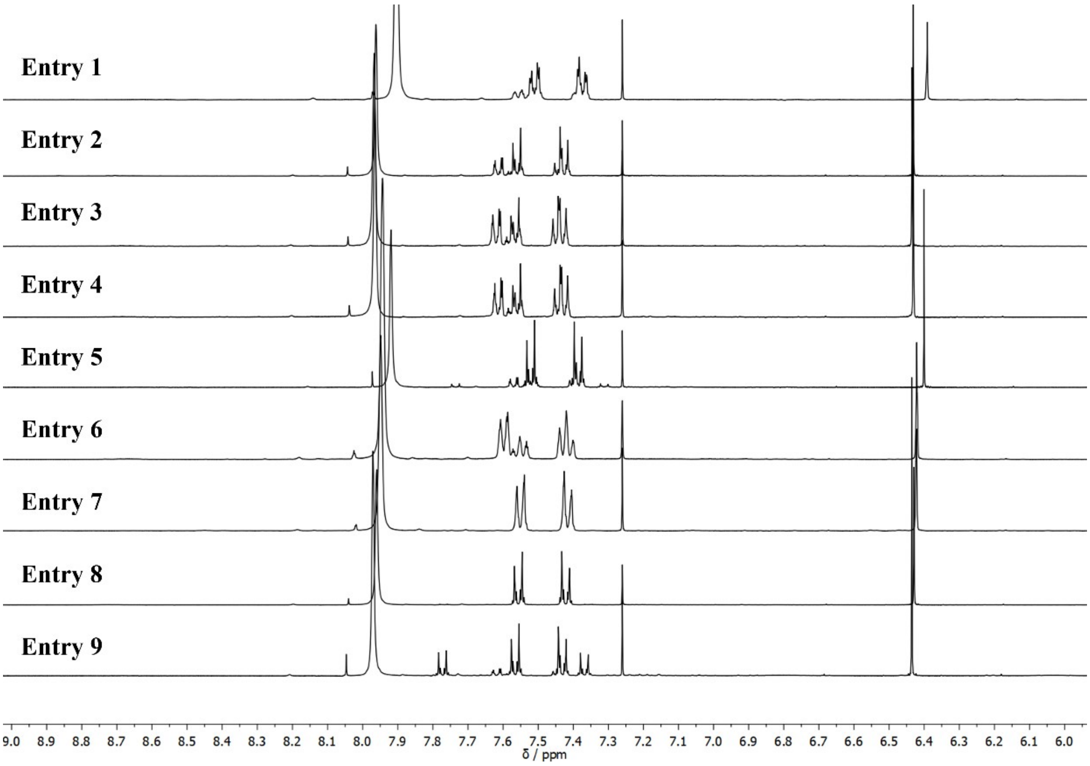


Figure S19. 400 MHz ^{1}H-NMR of entries 1-9 with **1**. Zoom on the aromatic region.

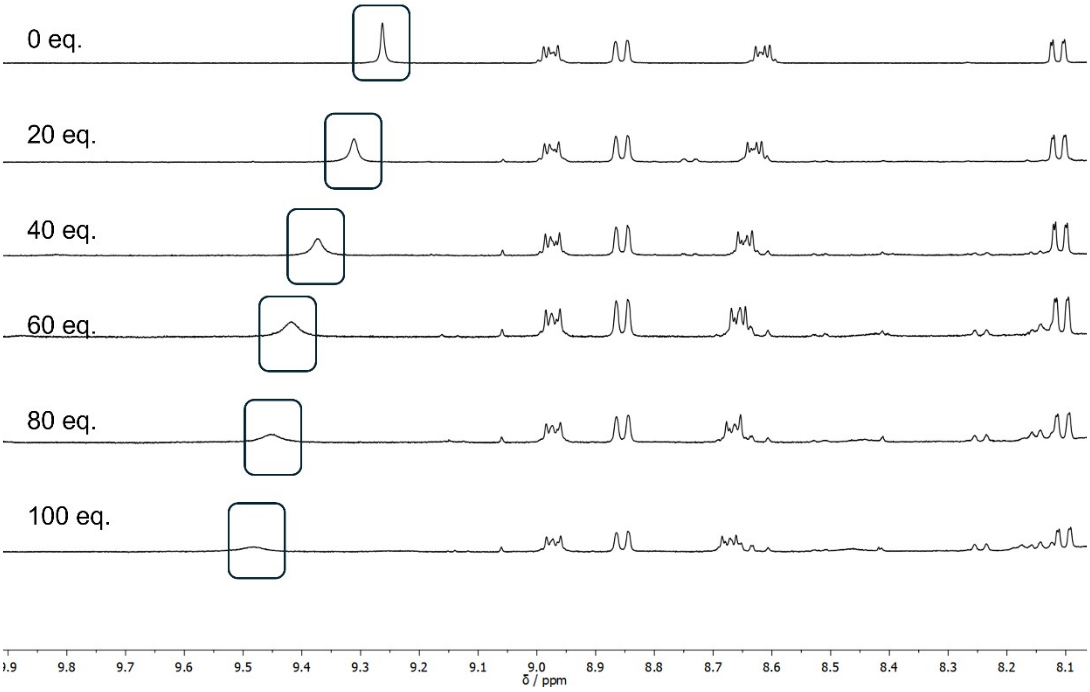


Figure S20. 400 MHz ^{1}H-NMR titration of **1** [0.01 M] in DMF-*d*7 with increasing amounts of DBU. Zoom on the aromatic region.

5.2 General procedure for photocatalytic reduction experiments

A 10 mL Schlenk tube equipped with magnetic stirring bar was charged the photocatalyst **1** (10 mol%, 0.005 mmol, 2.4 mg), DBU (75 μL, 0.5 mmol), DIPEA (8.7 μL, 0.05 mmol) and aryl halide (1 equiv., 0.05 mmol). Subsequently, DMF (0.5 mL) was introduced, the reaction mixture was thoroughly degassed via 3 cycles of freeze-pump-thaw, and the vessel refilled with argon. The Schlenk was irradiated for 20 hours through two 456 nm Kessil Lamp (each on opposite sides, ca. 4 cm distance from the flask). The temperature was kept at around 35°C by using a fan. After 20 h the reactions were quenched with 2M HCl (2 mL) and the reaction extracted 3 × with Et_2O (2 mL) and the organic layers evaporated. NMR yield was obtained adding 0.05 mmol of trichloroethylene to the reaction crude in $CDCl_3$.

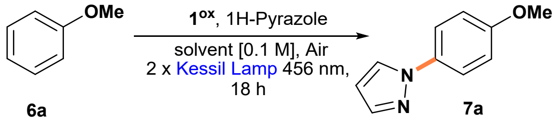
Dehalogenation Scope

entry	**Substrate**	**solv**	**T (h)**	**yield**
1	4-Br-Biphenyl (**4c**)	DMF	20	47%
2	4-Cl-Acetophenone (**4b**)	DMF	20	86%
3	1-Cl-Naphthalene (**4e**)	DMF	20	84%
4	4-Cl-Methylbenzoate (**4d**)	DMF	20	>95%

Table S2. Dehalogenation Scope using **1** as catalyst with conditions from paragraph **5.2**. NMR yields obtained with trichloroethylene (TCE) as internal standard.

5.3 Oxidation reaction optimization

Reactions performed on anisole (0.05 mmol) as substrate [0.1 M]. Yields determined by NMR using 0.05 mmol of trichloroethylene as internal standard.



Entry	Catalyst	Solvent	T (h)	Conditions	p yield	o yield	Total yield
1	10% cat	DCE	18h	/	60%	13%	73%
2	10% cat	DCE	18h	TEMPO 10%	56%	13%	69%
3	10% cat	DCE	18h	TEMPO 20%	48%	11%	59%
4	10% cat	odcb	18h	/	75%	17%	92%
5	0% cat	odcb	18h	/	0%	0%	0%
6	10% cat	odcb	18h	dark	0%	0%	0%
7	5% cat	odcb	18h	/	73%	15%	88%
8	5% cat	odcb	18h	525nm 1x	54%	9%	63%
9	**2.5% cat**	**odcb**	**18h**	**/**	**72%**	**16%**	**87% (80%) o:p 1:4.5**
10	1.0% cat	odcb	18h	/	60%	13%	73% o:p 1:4.6
11	0.5% cat	odcb	18h	/	55%	13%	68% o:p 1:4.2
12	2.5% cat	odcb	18h	Under Argon	10%	5%	15% o:p 1:2.0
13	2.5% **1**	odcb	18h	/	19%	4%	24% o:p 1:4.8
14	10% **1**	odcb	18h	/	32%	8%	40% o:p 1:4.75

Table S3. Optimization of reaction conditions using $\mathbf{1}^{ox}$ as catalyst.

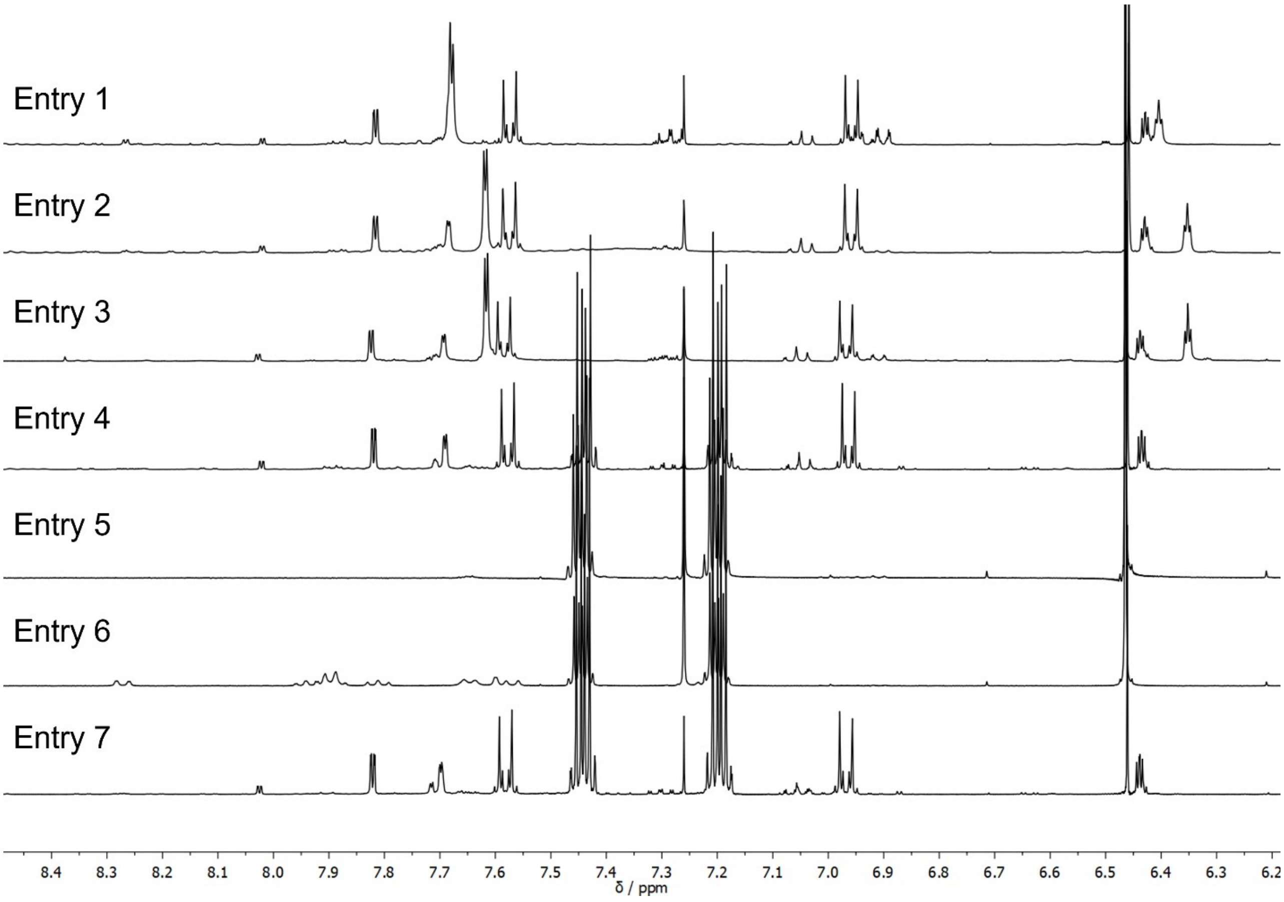


Figure S21. 400 MHz ^{1}H-NMR of entries 1-7 with $\mathbf{1}^{ox}$. Zoom on the aromatic region.

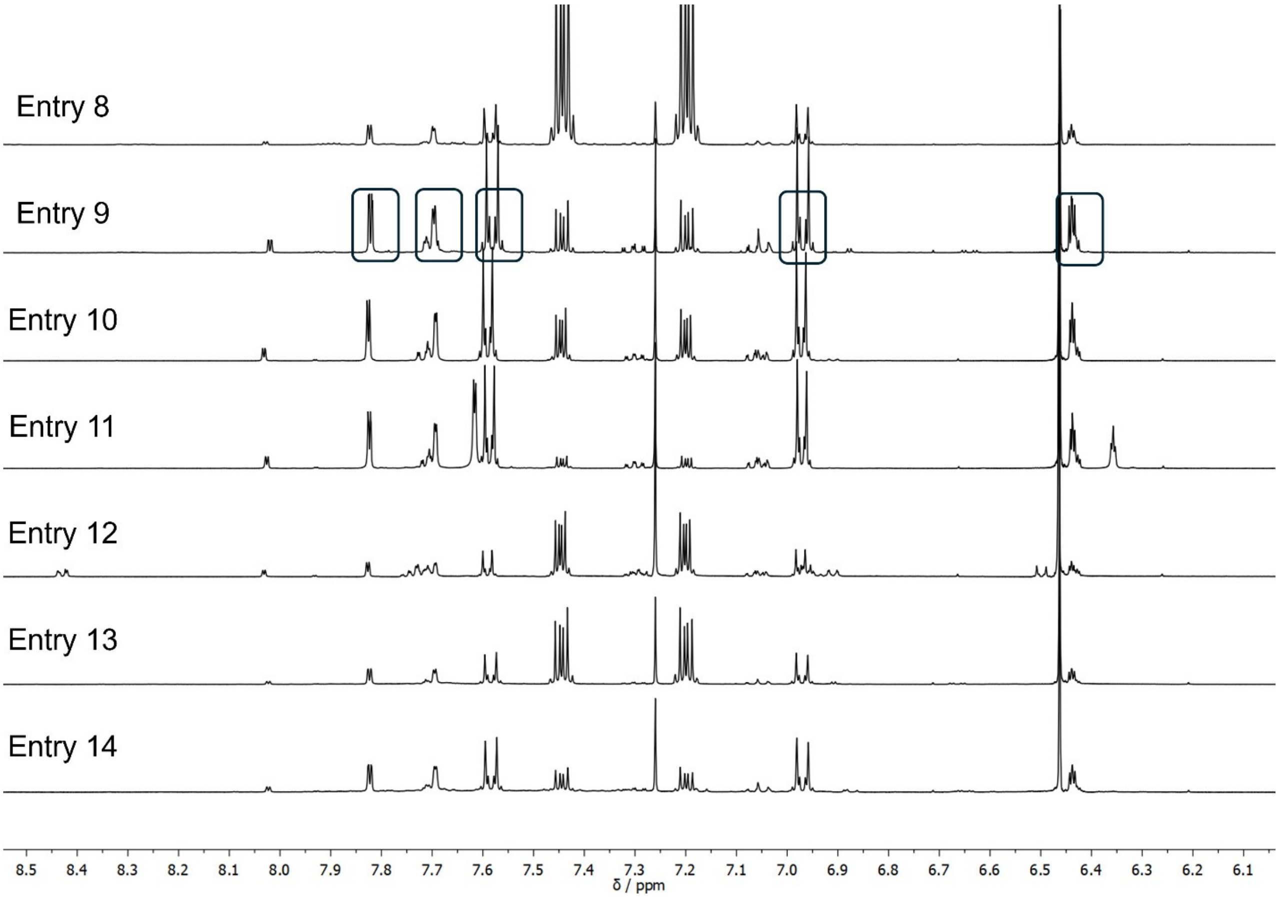


Figure S22. 400 MHz ^{1}H-NMR of entries 8-14 with **1^{ox}**. Zoom on the aromatic region. Blue boxes highlight the *para* product signals.

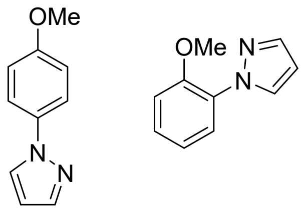
5.4 General procedure for photocatalytic oxidation experiments

A 10 mL Schlenk tube equipped with magnetic stirring bar was charged the photocatalyst **1^{ox}** (2.5 mol%, 0.00125 mmol, 0.9 mg), anisole (5,4 µL, 0.05 mmol) and pyrazole (0.1 mmol, 2 eq.). Subsequently, ODCB (0.5 mL) was introduced. The Schlenk was irradiated for 18 hours under air through two 456 nm Kessil Lamp (each on opposite sides, ca. 4 cm distance from the flask). The temperature was kept at around 35°C by using a fan. After 18 h the reactions were evaporated under reduced pressure. NMR yield was obtained adding 0.05 mmol of trichloroethylene to the reaction crude in $CDCl_3$.

5.5 Oxidation reaction scope

All reactions were carried out according with the general procedure **5.4**.

1-(4-methoxyphenyl)-1H-pyrazole, 1-(2-methoxyphenyl)-1H-pyrazole (7a)



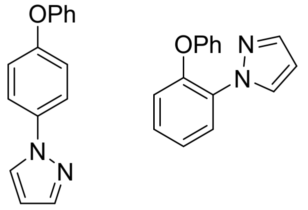
Prepared according to the general procedure using anisole **6a** (0.05 mmol, 5.4 μL), and pyrazole (0.1 mmol, 6.8 mg). The product **7a** was purified by flash chromatography (PE 100% to CH_2Cl_2 100%) to afford a pale-yellow oil composed by an inseparable mixture of *para* and *ortho* isomers in a ratio of 4.5:1. NMR Yield: 87%, Isolated yield: 80%, 7.0 mg. The characterization data matched with the reported one.[1]

para: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.59 (d, *J* = 9.2 Hz, 2H), 6.97 (d, *J* = 9.1 Hz, 2H), 6.44 (dd, *J* = 2.4, 1.9 Hz, 1H), 3.84 (s, 3H).

ortho: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.72 – 7.70 (m, 3H), 7.32 – 7.28 (m, 1H), 7.09 – 7.02 (m, 1H), 6.43 – 6.42 (m, 1H), 3.88 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 158.38, 140.74, 140.18, 134.14, 131.71, 128.20, 127.00, 125.46, 121.29, 121.08, 114.65, 112.40, 107.29, 106.28, 56.07, 55.70. Some *ortho* signals not visible due to low concentration.

1-(4-phenoxyphenyl)-1H-pyrazole and 1-(2-phenoxyphenyl)-1H-pyrazole (7b)



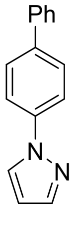
Prepared according to the general procedure using diphenylether **6b** (0.05 mmol, 7.9 μL), and pyrazole (0.1 mmol, 6.8 mg). The product **7b** was purified by flash chromatography (PE 100% to CH_2Cl_2 100%) to afford a yellowish solid composed by an inseparable mixture of *para* and *ortho* isomers in a ratio of 6.5:1. NMR Yield: >95%, Isolated yield: 89%, 10.8 mg. The characterization data matched with the reported one.[1]

para: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 2.5, 0.6 Hz, 1H), 7.72 (d, *J* = 1.3 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 2H), 7.36 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.16 – 7.07 (m, 3H), 7.06 – 7.02 (m, 2H), 6.46 (dd, *J* = 2.4, 1.8 Hz, 1H).

ortho: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 2.5, 0.6 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.27 (d, *J* = 2.3 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.01 – 6.94 (m, 2H), 6.37 (dd, *J* = 2.5, 1.8 Hz, 1H). One signal overlapped with *para* derivative.

^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.23, 155.89, 141.08, 140.60, 136.05, 131.33, 130.00, 129.87, 127.98, 126.99, 125.46, 124.65, 123.66, 123.35, 121.07, 120.72, 119.79, 118.99, 118.29, 107.63, 106.95. Some *ortho* signals not visible due to low concentration.

1-([1,1'-biphenyl]-4-yl)-1H-pyrazole (7c)

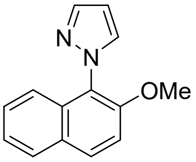


Prepared according to the general procedure using biphenyl **6c** (0.05 mmol, 7.7 mg), and pyrazole (0.1 mmol, 6.8 mg). The product **7c** was purified by flash chromatography (PE 100% to CH_2Cl_2 100%) to afford a beige solid. NMR Yield: 64%, Isolated yield: 64%, 7.0 mg. The characterization data matched with the reported one.[1]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.5 Hz, 1H), 7.79 – 7.75 (m, 3H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.62 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.50 – 6.49 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 141.32, 140.26, 139.53, 139.50, 129.02, 128.21, 127.64, 127.11, 126.85, 119.61, 107.85.

1-(2-methoxynaphthalen)-1H-Pyrazole (7d)

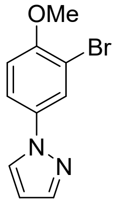


Prepared according to the general procedure using 2-methoxynaphthalene **6d** (0.05 mmol, 7.9 mg), and pyrazole (0.1 mmol, 6.8 mg). The product **7d** was purified by flash chromatography (PE 100% to CH_2Cl_2 100%) to afford a faint yellow oil. NMR Yield: 52%, Isolated yield: 40%, 4.5 mg. The characterization data matched with the reported one.[2]

^{1}H-NMR (499 MHz, $CDCl_3$-d) δ 7.96 (d, *J* = 9.1 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 2.3, 0.6 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 1H), 6.55 (t, *J* = 2.1 Hz, 1H), 3.89 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 152.75, 140.68, 133.10, 132.37, 130.83, 128.96, 127.96, 127.81, 124.49, 122.23, 113.69, 106.55, 106.08, 57.01.

1-(4-methoxy-2-bromophenyl)-1H-Pyrazole (7e)

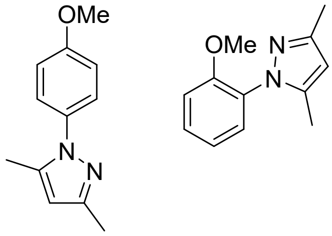


Prepared according to the general procedure using 2-bromoanisole **6e** (0.05 mmol, 6.2 μL), and pyrazole (0.1 mmol, 6.8 mg). The product **7e** was purified by flash chromatography (PE 100% to CH_2Cl_2 100%) to afford a faint yellow oil. NMR Yield: 38%, Isolated yield: 38%, 4.8 mg. The characterization data matched with the reported one.[3]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.7 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.70 (d, *J* = 1.4 Hz, 1H), 7.60 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 6.47 – 6.43 (m, 1H), 3.93 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 154.72, 141.18, 134.60, 126.94, 124.85, 119.55, 112.27, 112.25, 107.77, 56.72.

1-(4-methoxyphenyl)-3,5-dimethyl-1H-pyrazole, 1-(2-methoxyphenyl)-3,5 dimethyl-1H-pyrazole (7f)



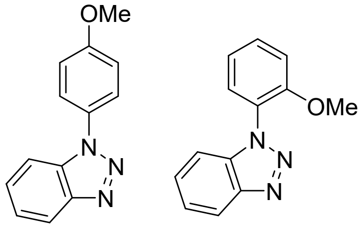
Prepared according to the general procedure using anisole **6a** (0.05 mmol, 5.4 µL), and 2,5-dimethylpyrazole (0.1 mmol, 9.6 mg). The product **7f** was purified by flash chromatography (PE 100% to CH_2Cl_2 100%) to afford a faint yellow solid composed by an inseparable mixture of *para* and *ortho* isomers in a ratio of 4:1. NMR Yield: 89%, Isolated yield: 52%, 5.3 mg. The characterization data matched with the reported one.[1]

Para: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 5.96 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H).

Ortho: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 1H), 7.04-7.00 (m, 2H), 5.96 (s, 1H), 3.79 (s, 3H), 2.30 (s, 3H), 2.09 (s, 3H). (one signal overlapped with *para* derivative).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 158.92, 154.82, 149.07, 148.67, 139.61, 133.26, 130.03, 129.41, 126.53, 120.94, 114.25, 112.02, 106.38, 105.30, 55.92, 55.67, 13.81, 13.65, 12.29, 11.40.

1-(4-methoxyphenyl)-1H-benzo[d][1,2,3]triazole, 1-(2-methoxyphenyl)-1H benzo[d][1,2,3]triazole (7g)



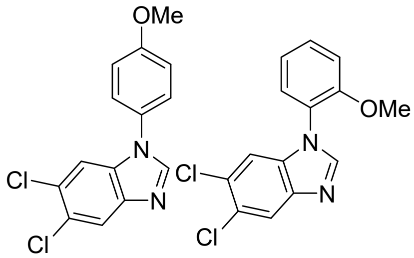
Prepared according to the general procedure using anisole **6a** (0.05 mmol, 5.4 µL), and benzotriazole (0.1 mmol, 11.9 mg). The product **7g** was purified by flash chromatography (PE 100% to CH_2Cl_2 100%) to afford a faint yellow solid composed by an inseparable mixture of *para* and *ortho* isomers in a ratio of 3:1. NMR Yield: >95%, Isolated yield: >95%, 11.0 mg. The characterization data matched with the reported one.[1]

para: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.68-7.66 (m, 3H), 7.55 – 7.51 (m, 1H), 7.49 – 7.35 (m, 1H), 7.12 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H).

ortho: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (dt, *J* = 1.0 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.46-7.44 (m, 1H), 7.38 (dt, *J* = 8.1, 1.0 Hz, 2H), 7.22 – 7.14 (m, 2H), 3.80 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.97, 146.44, 132.79, 131.16, 130.67, 130.13, 128.28, 128.15, 127.85, 127.66, 124.76, 124.37, 123.97, 121.24, 120.35, 120.00, 115.11, 112.51, 111.31, 110.38, 55.95, 55.81. (some *ortho* signals not visible due to low concentration).

1-(4-methoxyphenyl)-1H-5,6-dichlorobenzo[d]imidazole, 1-(2-methoxyphenyl)-1H 5,6-dichlorobenzo[d]imidazole (7h)



Prepared according to the general procedure using anisole **6a** (0.05 mmol, 5.4 μL), and 5,6-dichlorobenzimidazole (0.1 mmol, 18.6 mg). The product **7h** was purified by flash chromatography (PE 100% to CH_2Cl_2 100%) to afford a faint yellow solid composed by an inseparable mixture of *para* and *ortho* isomers in a ratio of 2.5:1. Isolated yield: 60%, 8.8 mg.

Para: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.67 (s, 1H), 7.11-7.10 (m, 3H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.63 (s, 3H).

Ortho: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.67 (s, 1H), 7.22 (td, J = 7.8, 1.6 Hz, 1H), 6.99 (s, 1H), 6.89 – 6.84 (m, 3H), 3.54 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.95, 154.03, 146.29, 145.66, 144.44, 143.20, 142.77, 133.68, 130.56, 128.32, 127.91, 127.58, 127.31, 126.96, 125.91, 121.80, 121.54, 121.34, 115.49, 112.67, 112.40, 111.96, 55.94, 55.84.

ESI-HRMS: $[M+H]^+$ calc. for $[C_{14}H_{11}{}^{35}Cl_2N_2O]^+$: 293.0243; found 293.0242.

6.0 NMR Reversibility studies

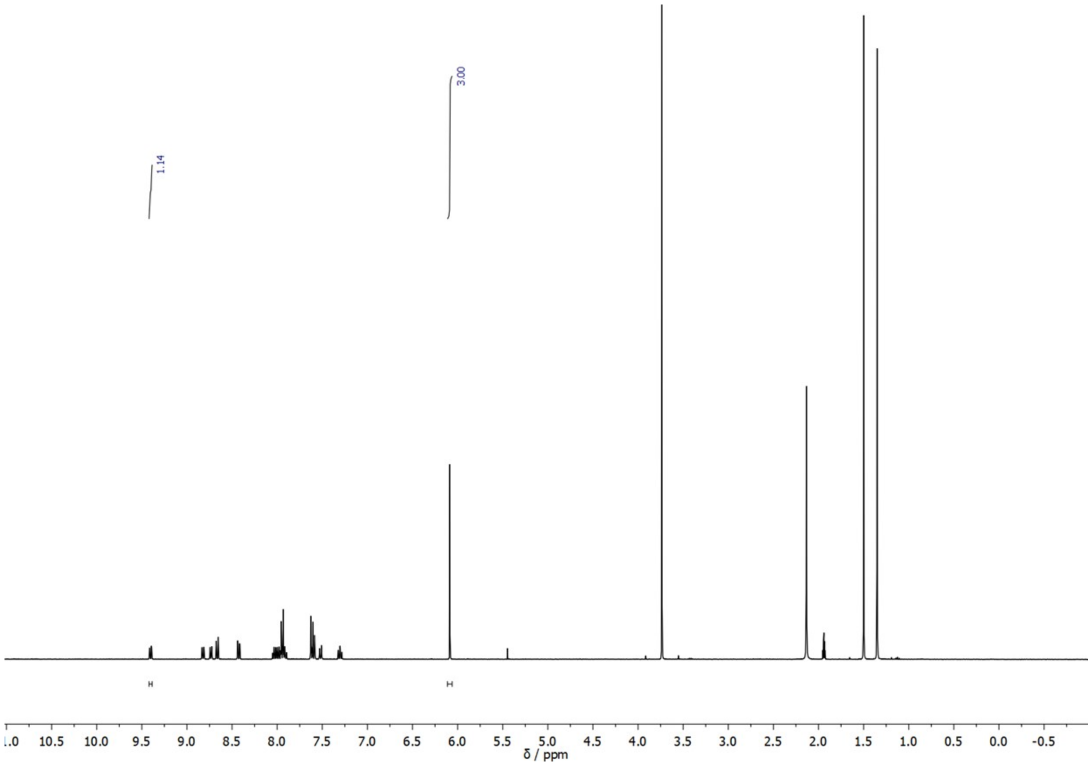


Figure S23. 400 MHz ^{1}H-NMR of **1^{ox}** in ACN-*d3* (0.9 eq. of 1,3,5-trimethoxy benzene as internal standard).

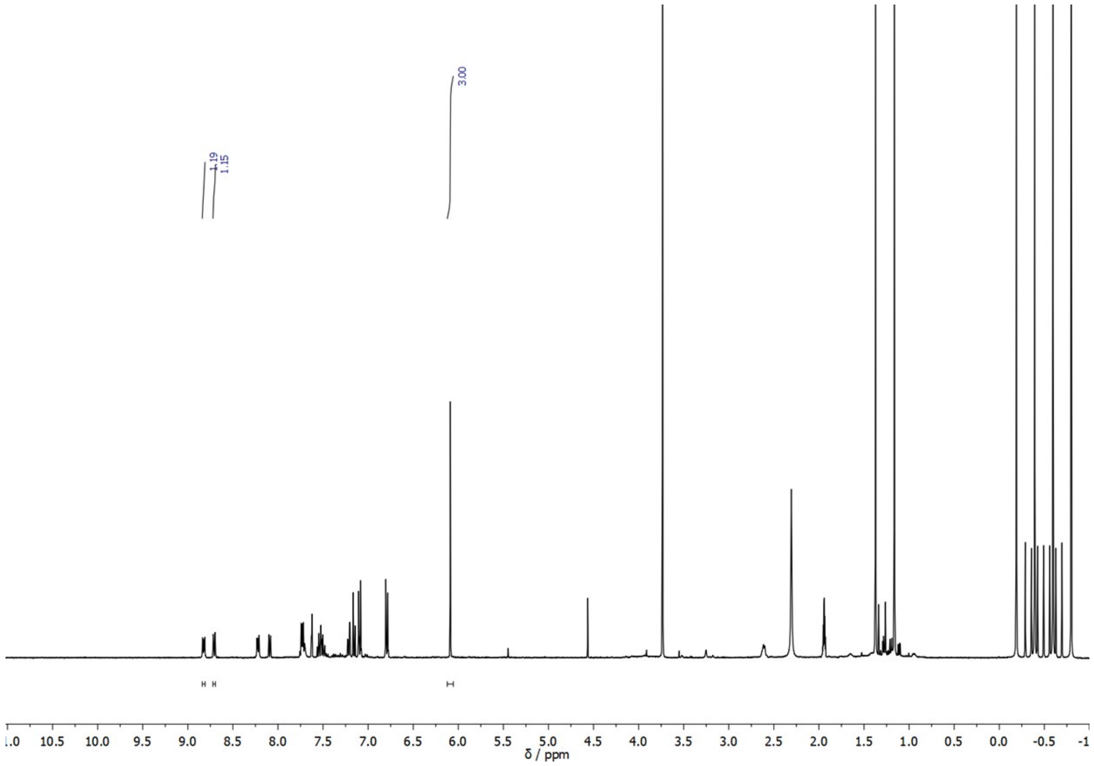


Figure S24. 400 MHz ^{1}H-NMR of **1** in ACN-*d3* (0.9 eq. of 1,3,5-trimethoxy benzene as internal standard) after addition of an excess of NaBH$_4$.

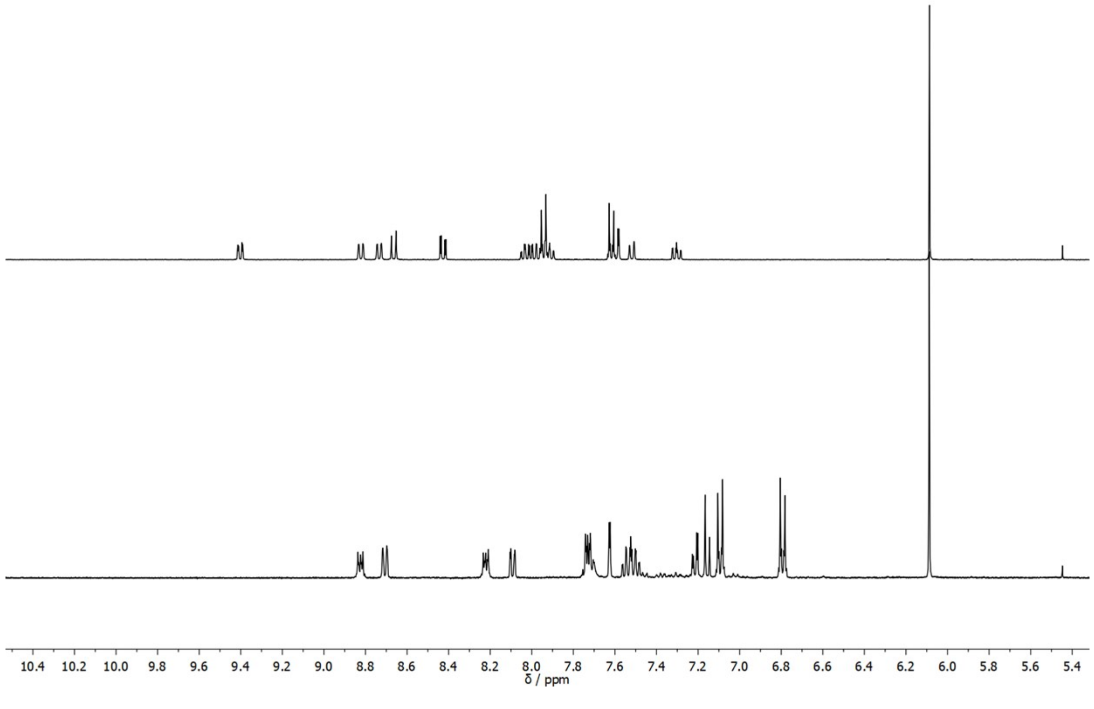


Figure S25. Detail of the aromatic region of the spectra a) before and b) after addition of NaBH$_4$.

7.0 NMR and HRMS spectroscopic characterization

Catalysts

7.1 Derivative 2

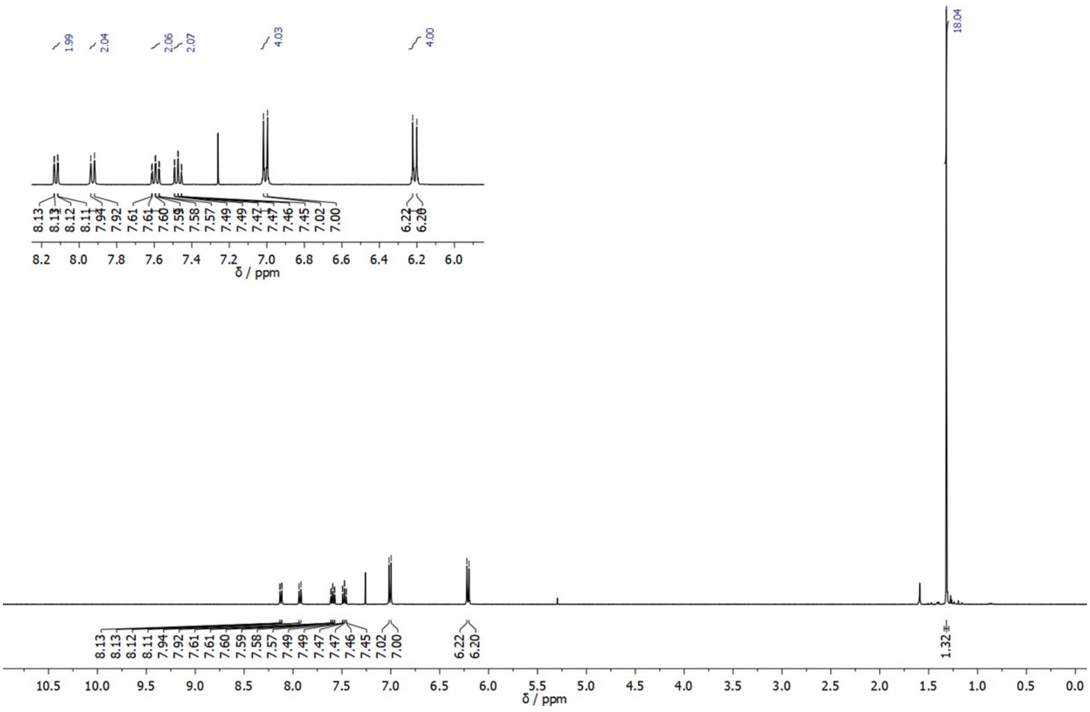


Figure S26. 400 MHz ^{1}H-NMR of **2** in CDCl$_3$.

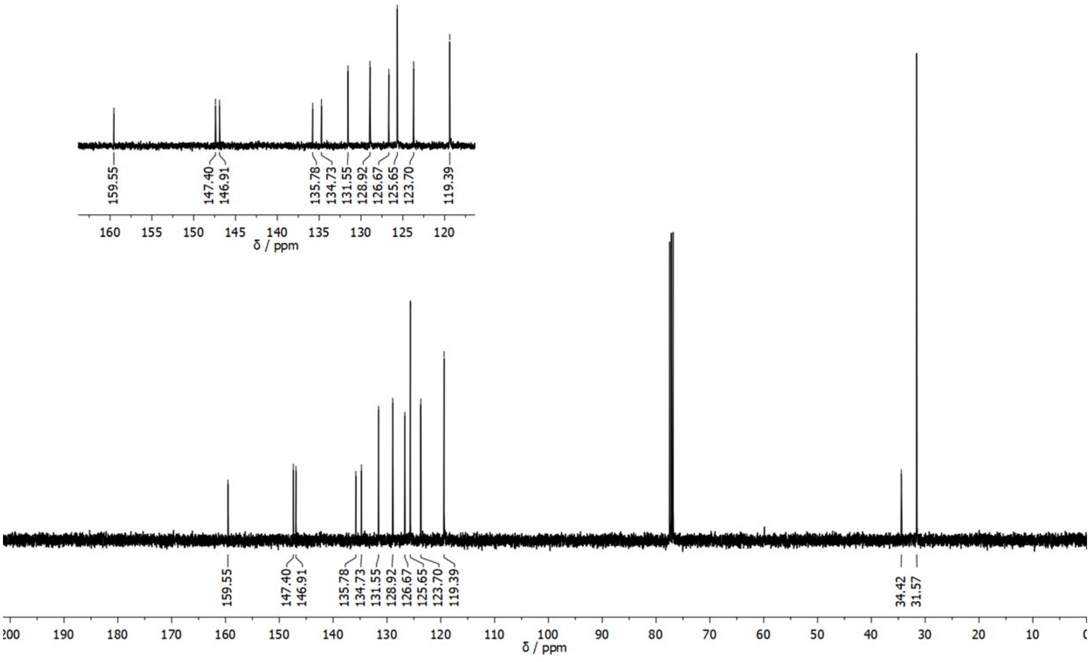


Figure S27. 101 MHz ^{13}C-NMR of **2** in CDCl$_3$.

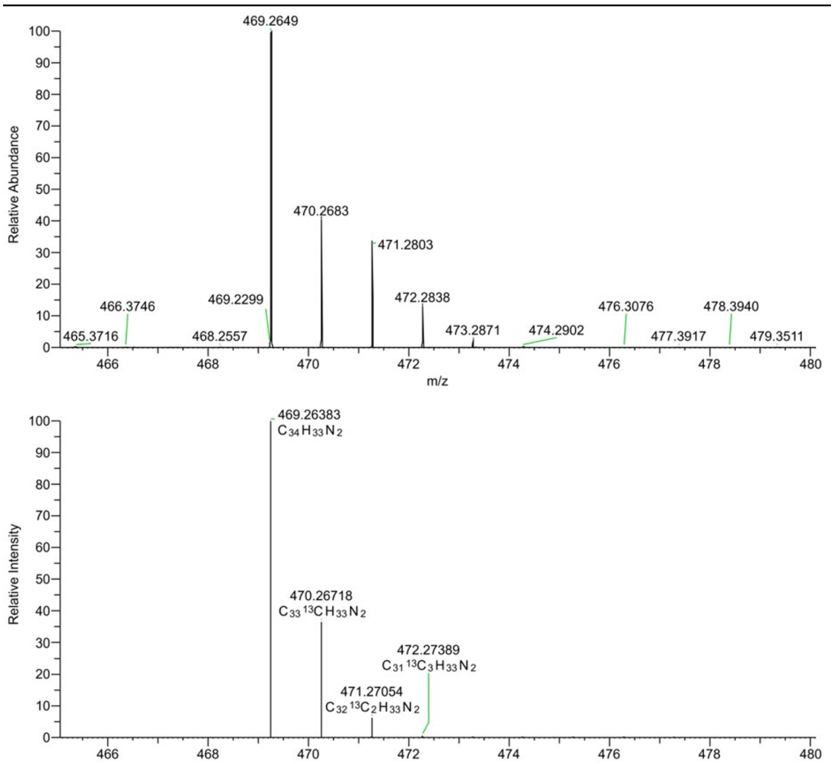


Figure S28. ESI-HRMS of **2**.

7.2 Derivative 3

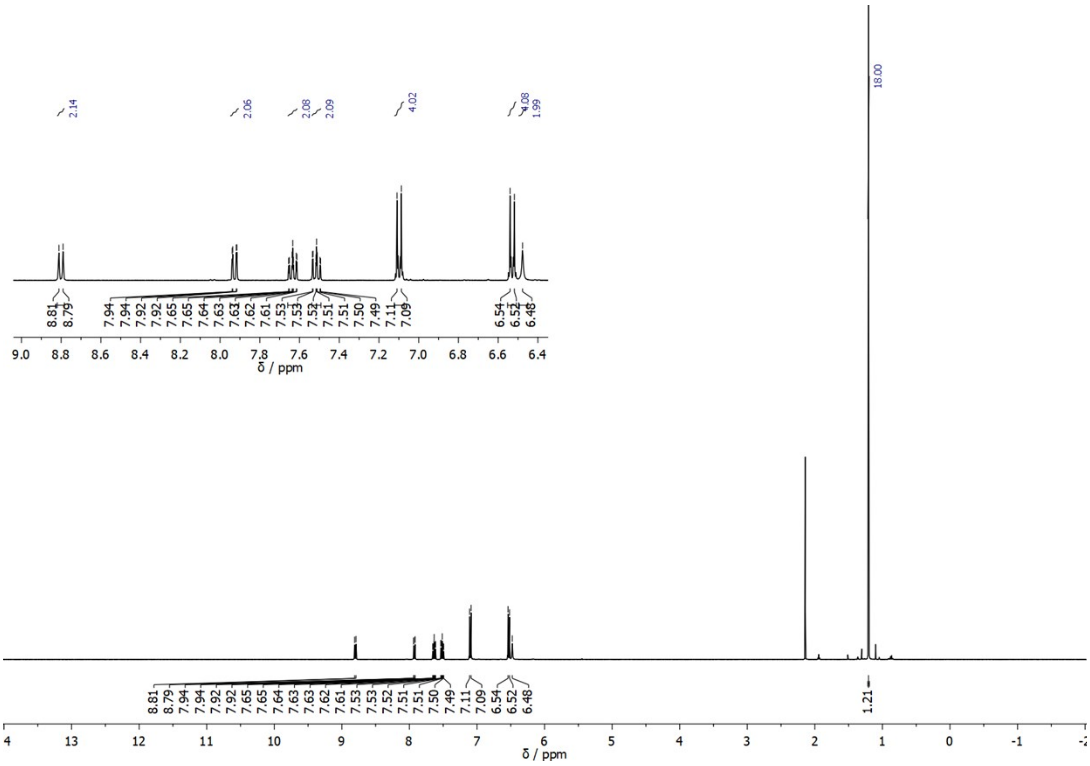


Figure S29. 400 MHz ^{1}H-NMR of **3** in $CDCl_3$.

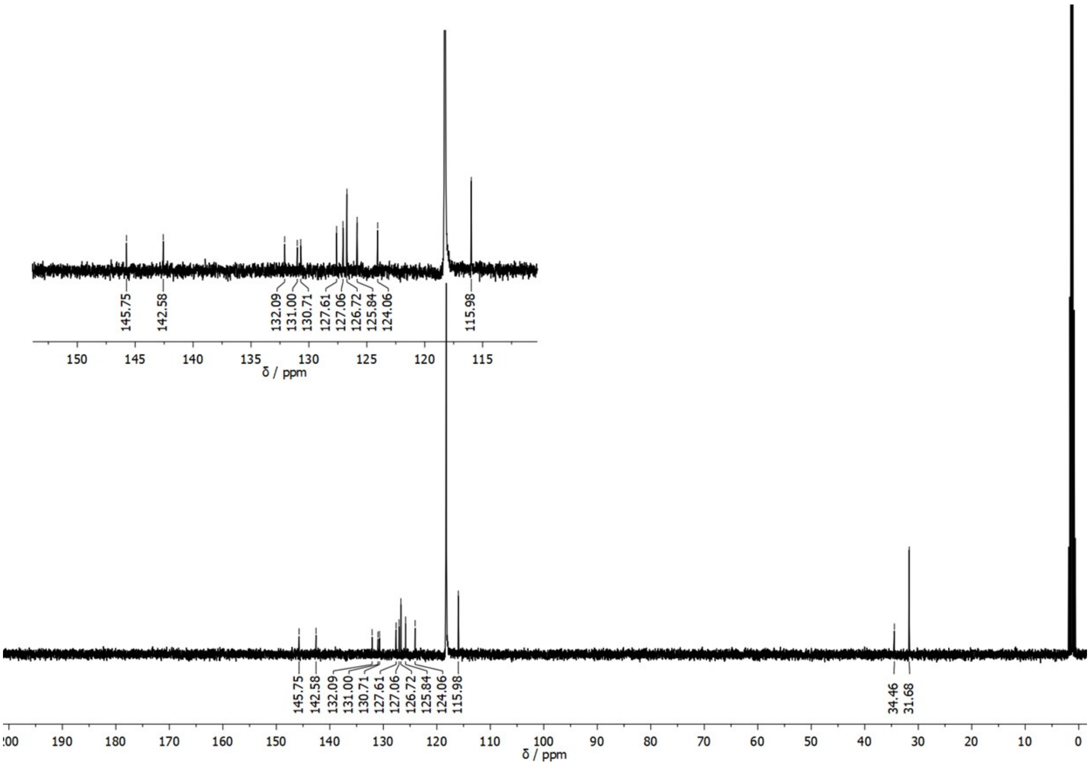


Figure S30. 101 MHz ^{13}C-NMR of **3** in $CDCl_3$.

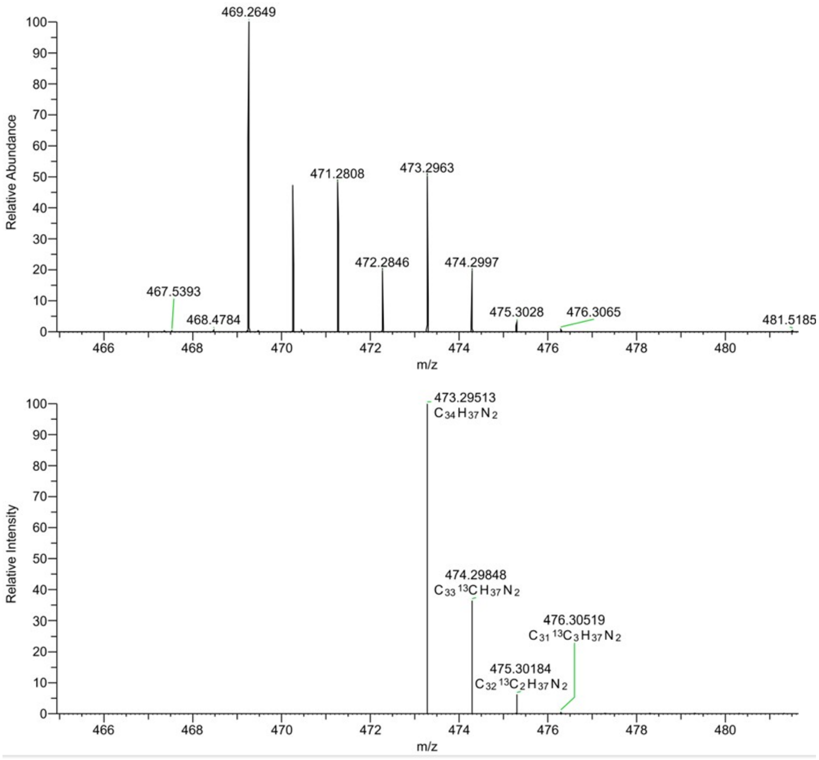


Figure S31. ESI-HRMS of **3**. Partial cyclization and oxidation of sample occurs during analysis.

7.3 Derivative 1

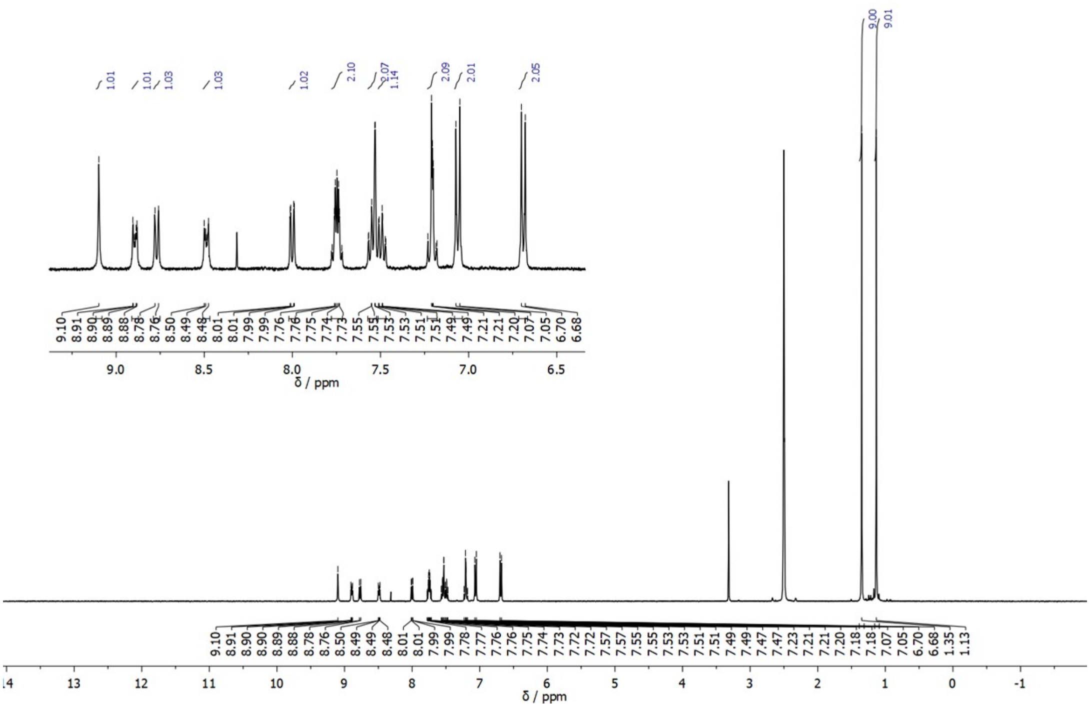


Figure S32. 400 MHz ^{1}H-NMR of **1** in DMSO-*d6*.

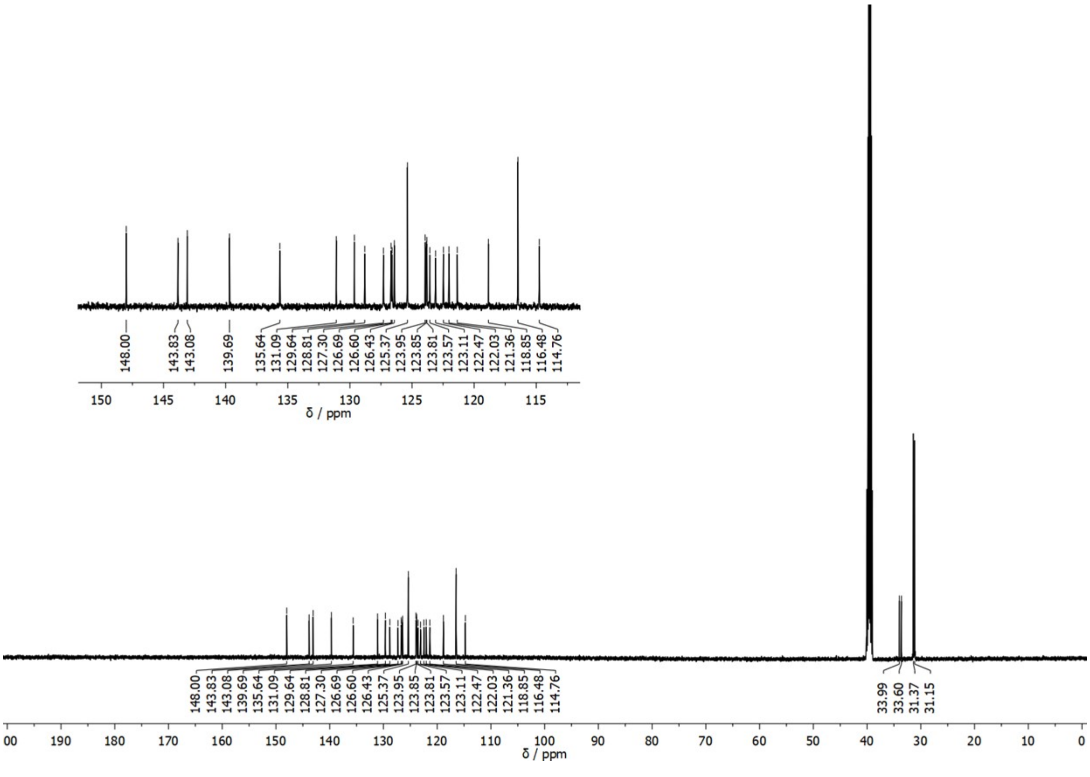


Figure S33. 126 MHz ^{13}C-NMR of **1** in in DMSO-*d6*.

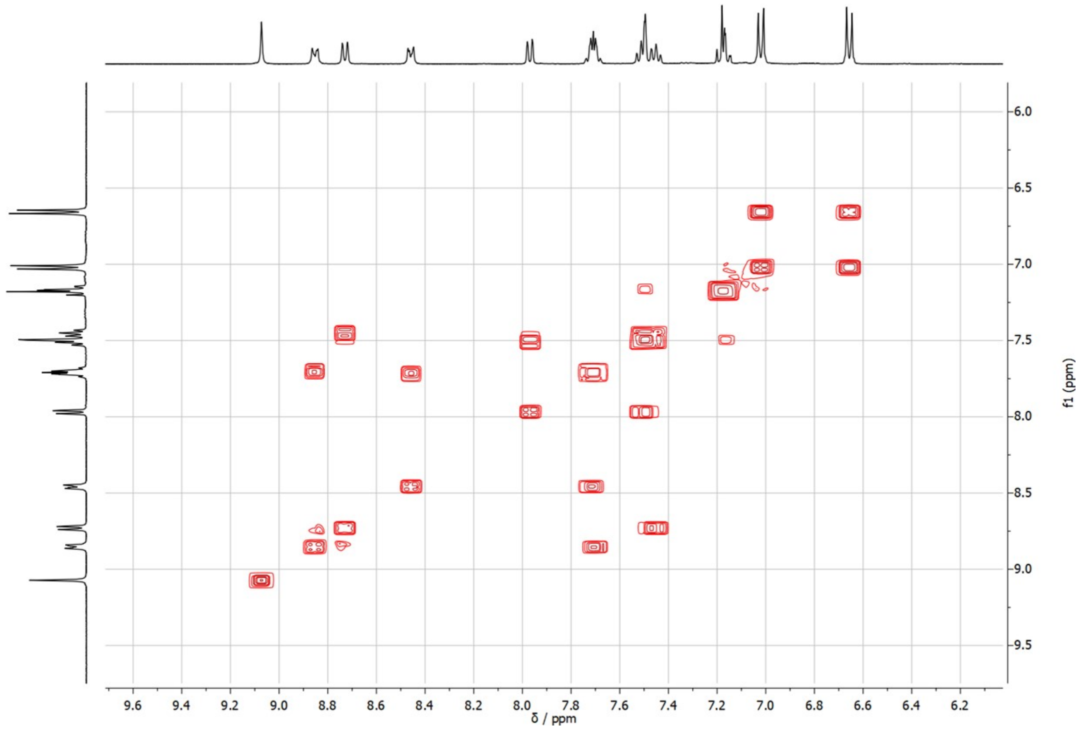


Figure S34. 400 MHz ^{1}H-^{1}H-NMR of **1** in DMSO-*d6* aromatic part detail

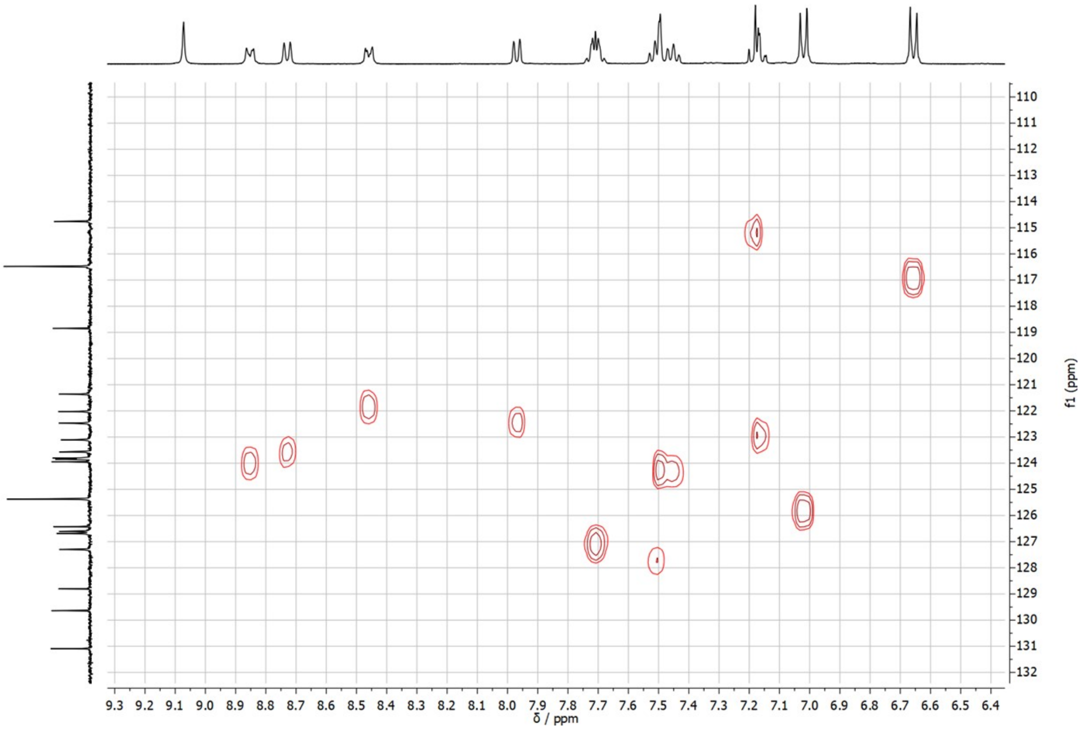


Figure S35. 400 MHz ^{1}H-^{13}C-NMR HSQC of **1** in DMSO-*d6* aromatic part detail

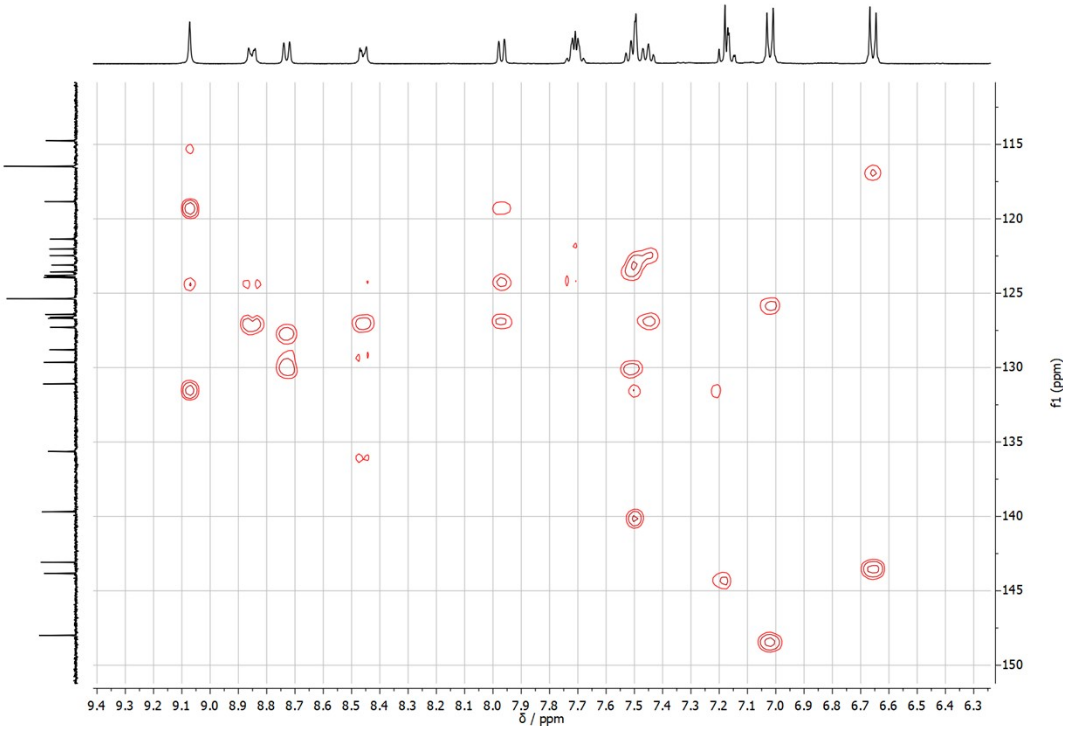


Figure S36. 400 MHz ^1H-^{13}C-NMR HMBC of **1** in DMSO-*d6* aromatic part detail

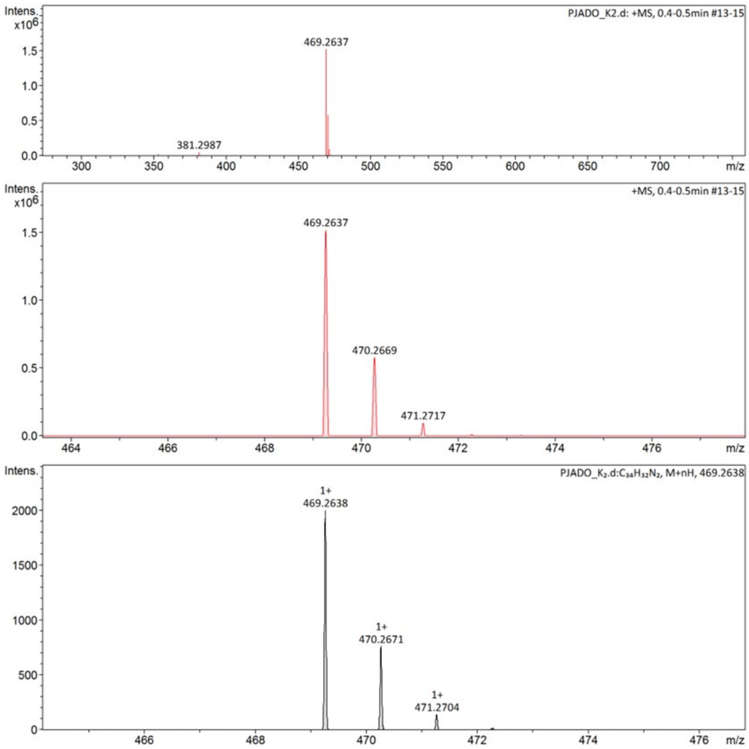


Figure S37. ESI-HRMS of **1**.

7.4 Derivative 1^{ox}

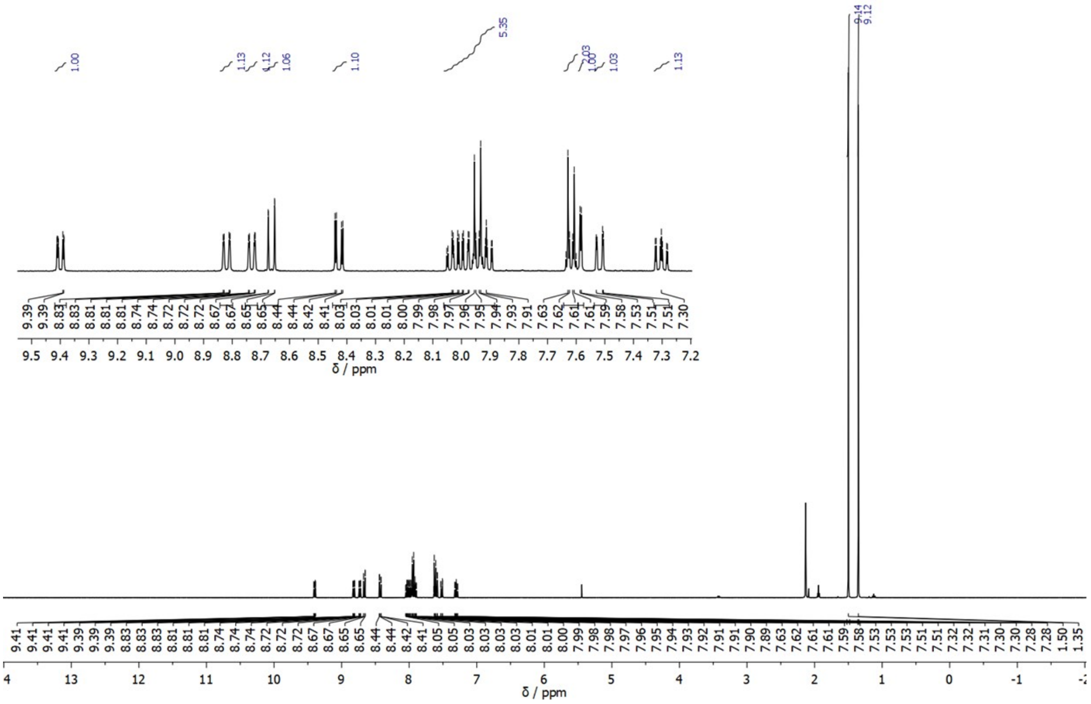


Figure S38. 400 MHz ^{1}H-NMR of $\mathbf{1^{ox}}$ in ACN-d3.

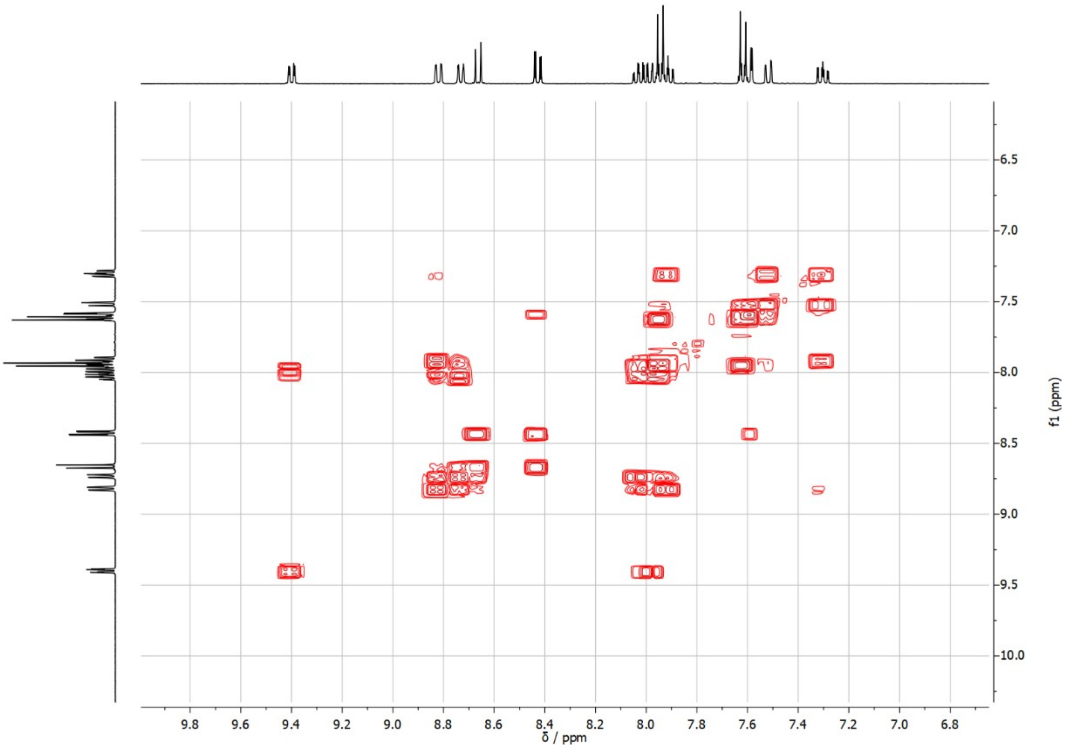


Figure S39. 400 MHz ^{1}H-^{1}H-NMR of $\mathbf{1^{ox}}$ in ACN-*d3* aromatic part detail

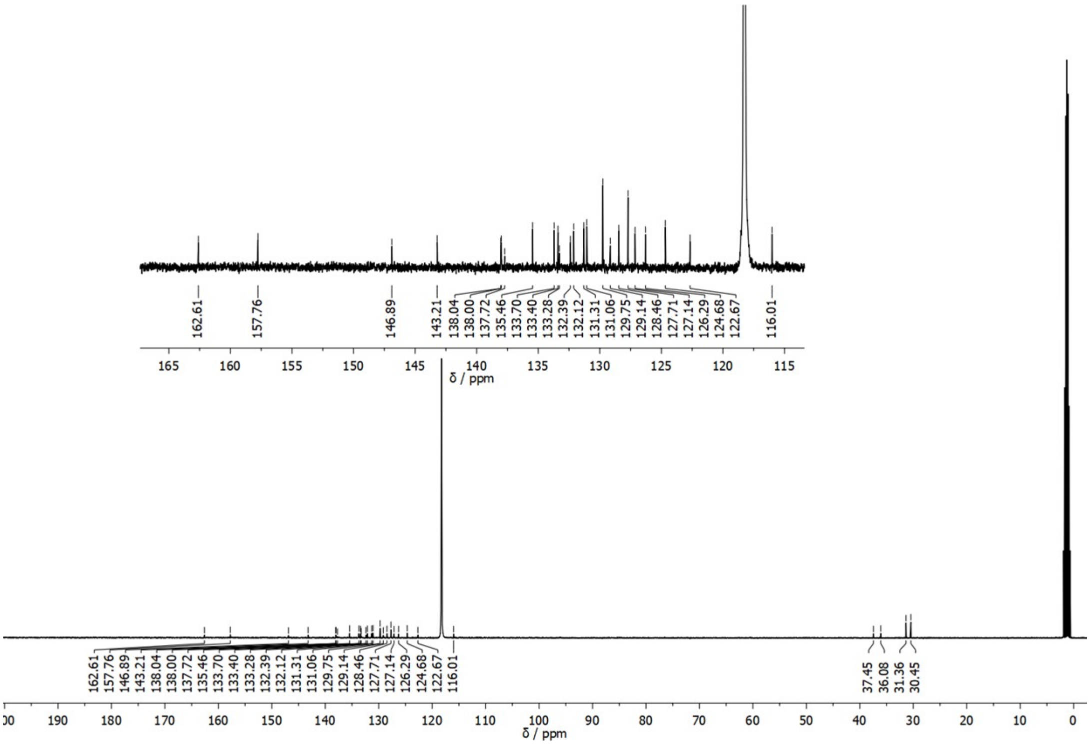


Figure S40. 101 MHz ^{13}C-NMR of **1^{ox}** in in ACN-*d3*.

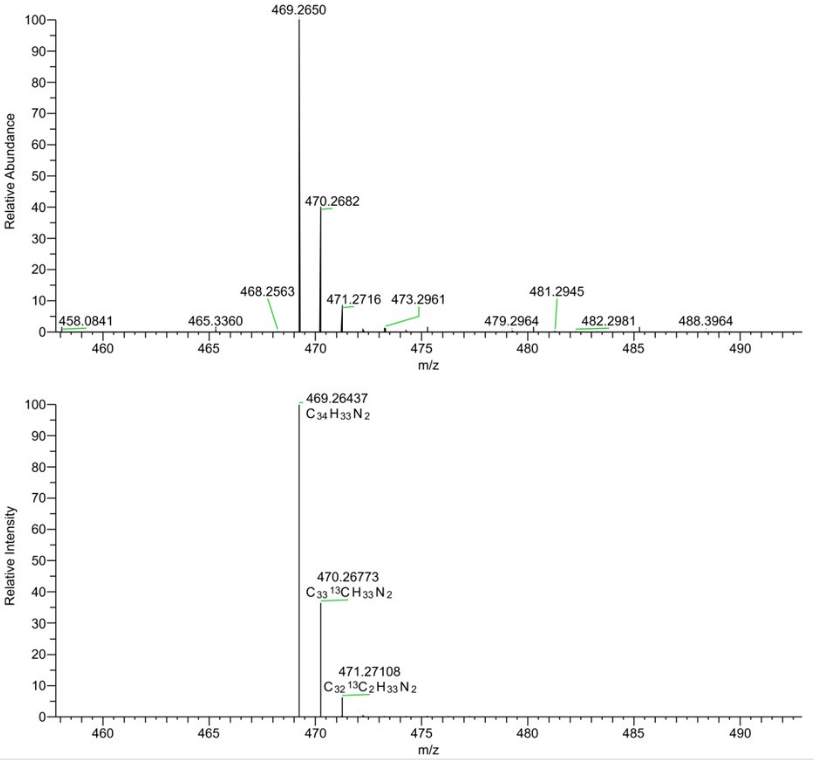


Figure S41. ESI-HRMS of **1^{ox}**.

8.0 Dehalogenation Reactions

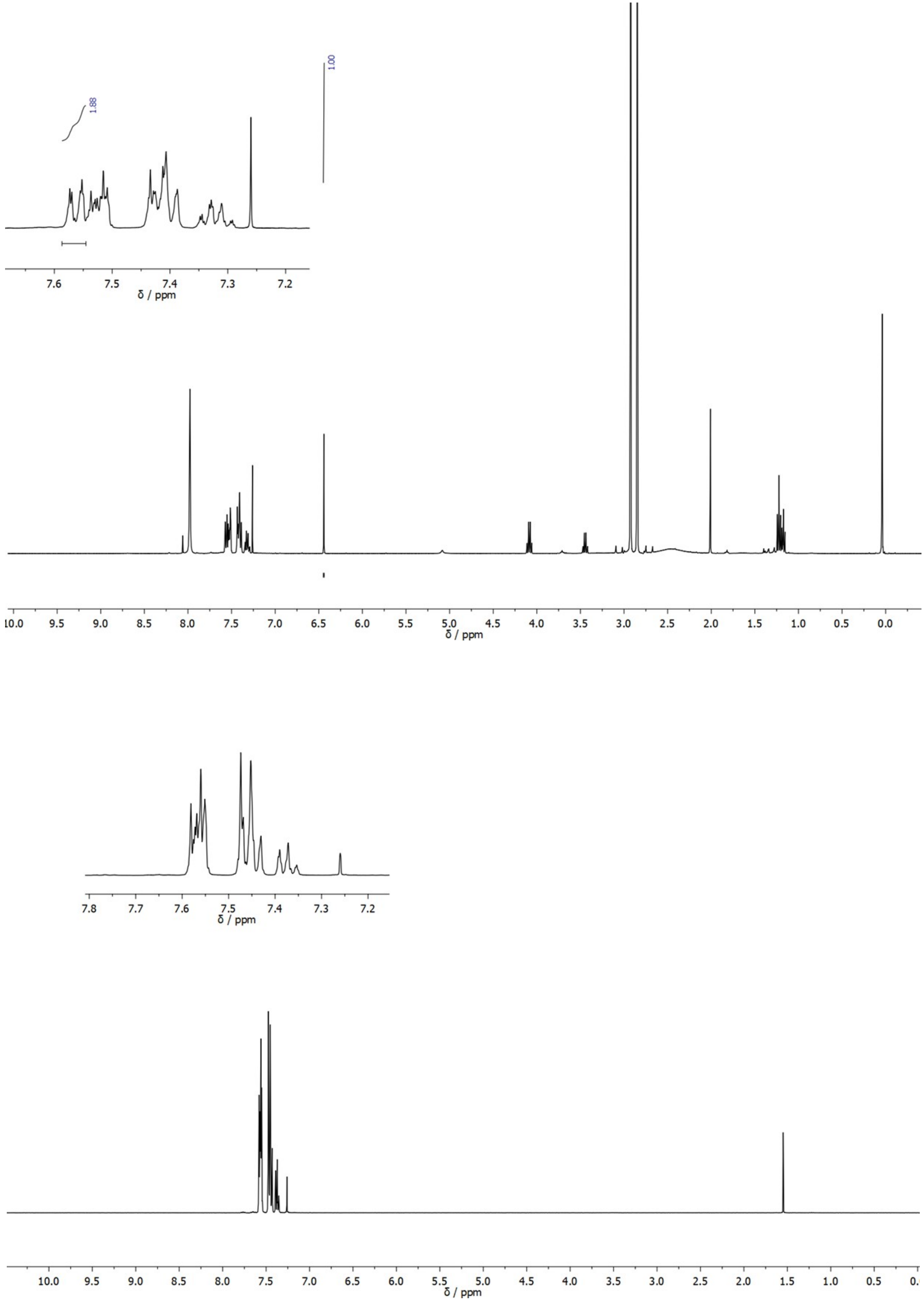


Figure S42. 400 MHz ^{1}H-NMR of top) **4c** dehalogenation in $CDCl_3$ bottom) starting material **4c**.

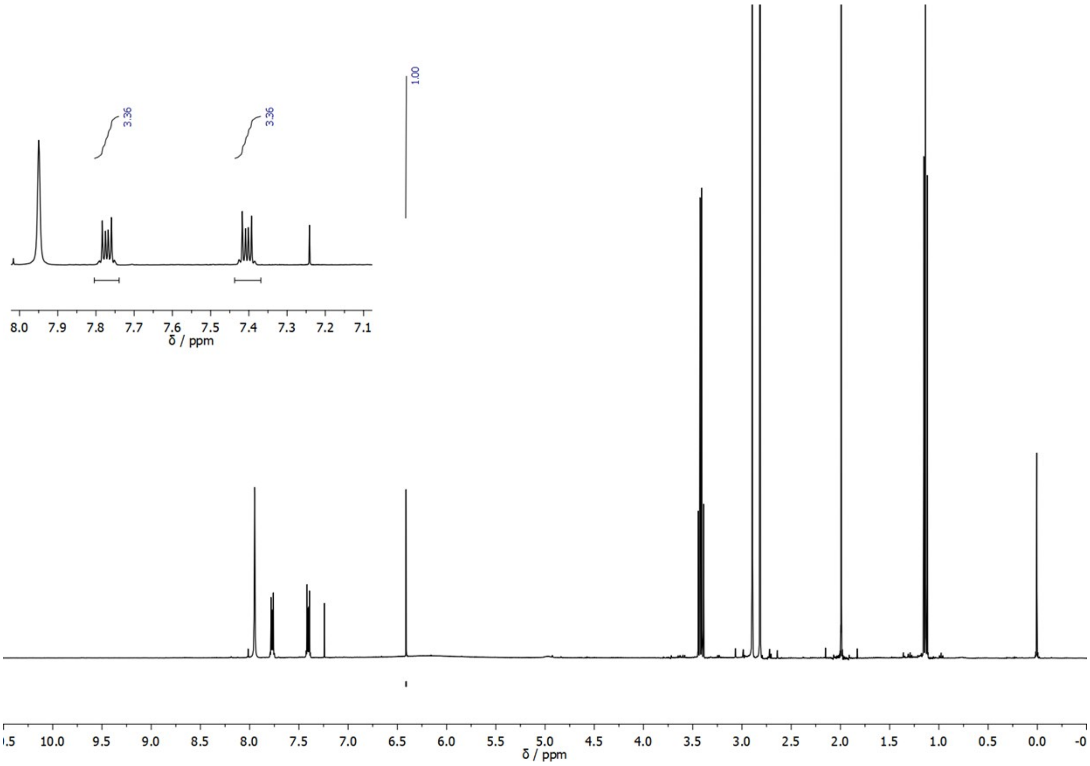


Figure S43. 400 MHz ^{1}H-NMR of **4e** reaction in CDCl$_3$.

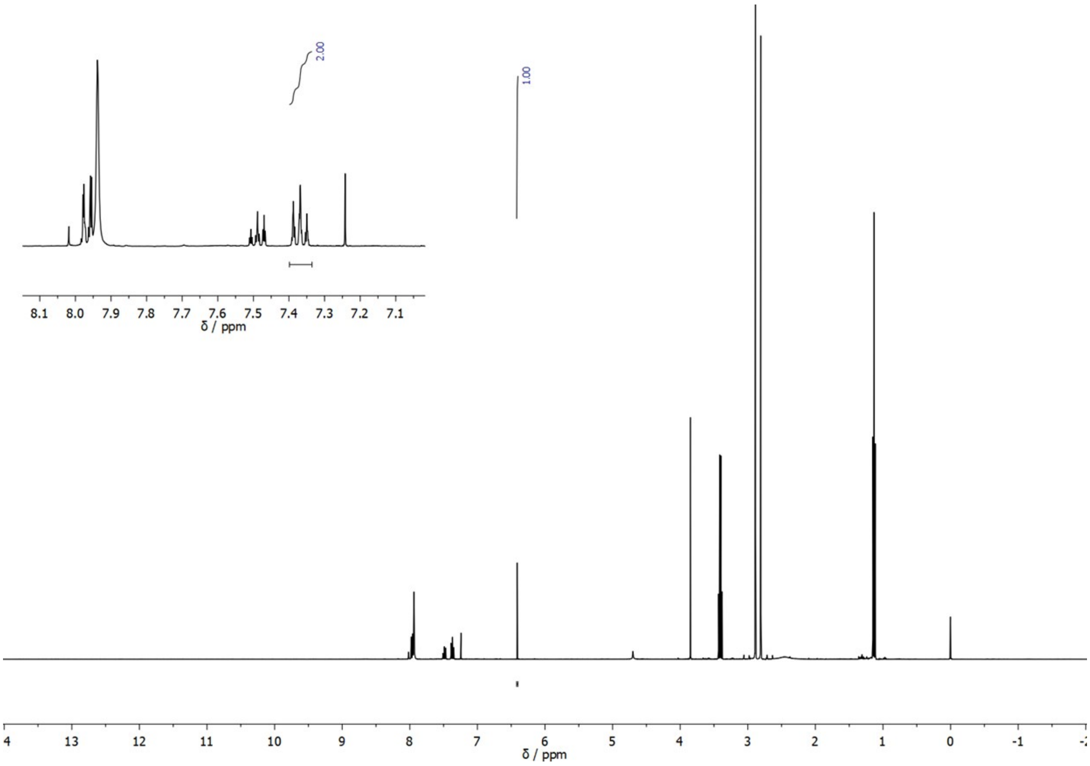


Figure S44. 400 MHz ^{1}H-NMR of **4d** reaction in CDCl$_3$.

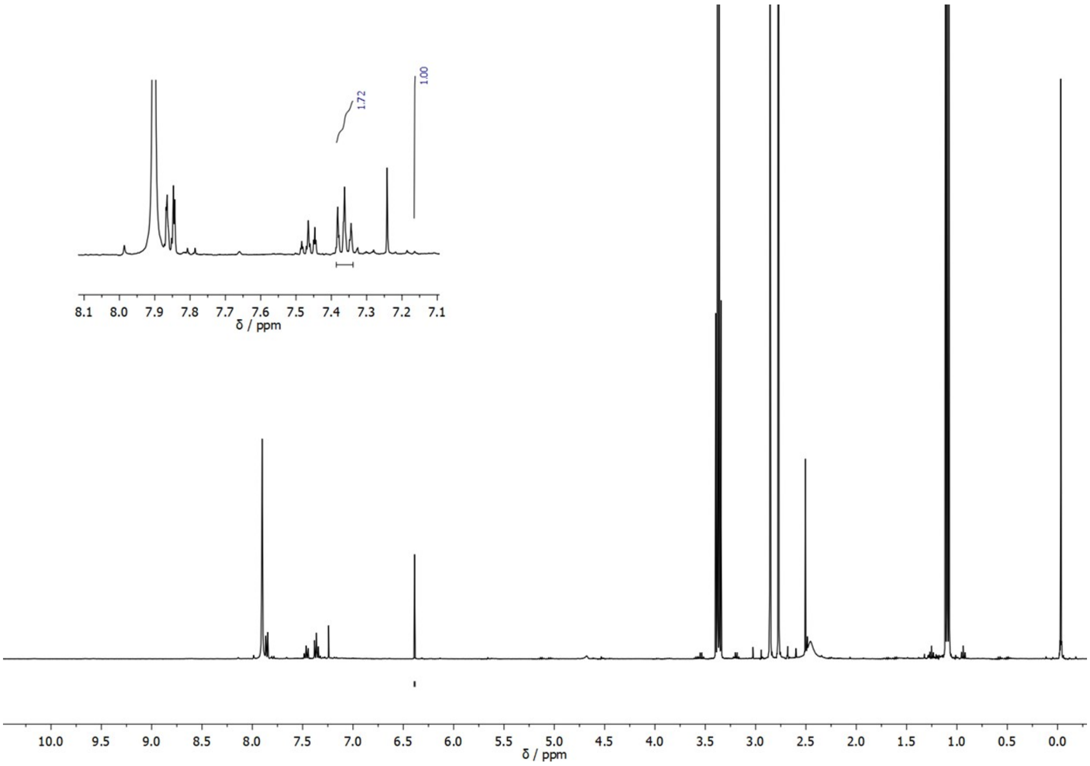


Figure S45. 400 MHz ^{1}H-NMR of **4b** reaction in $CDCl_3$.

9.0 Oxidation Reactions products

9.1 7a NMR Spectra

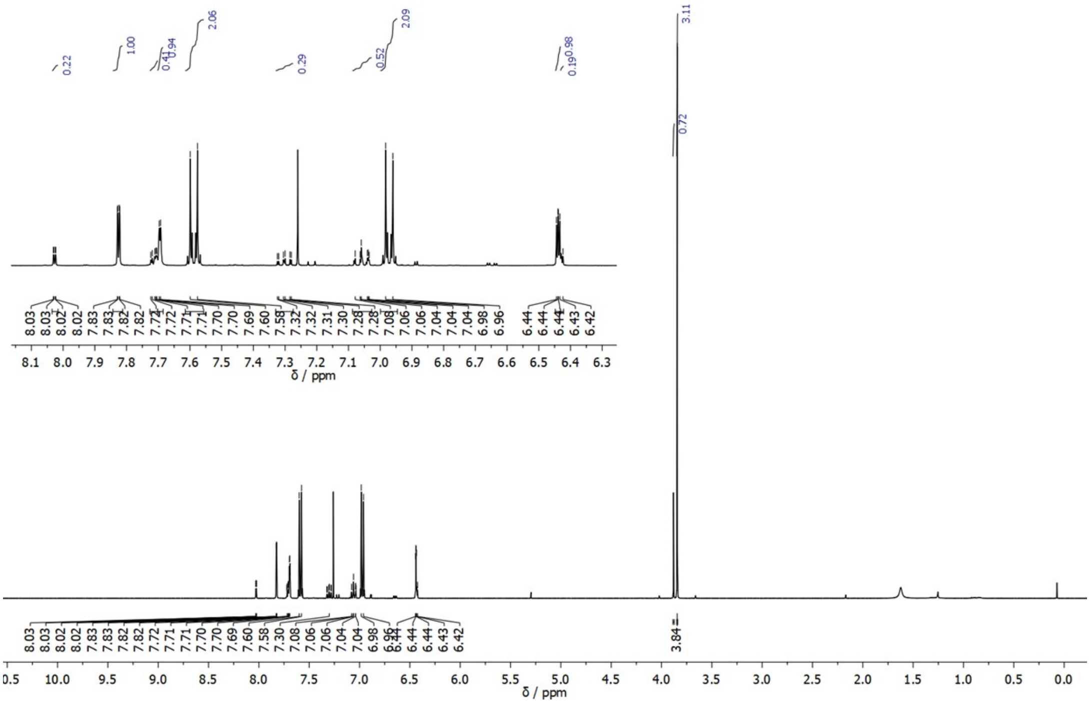


Figure S46. 400 MHz ^{1}H-NMR of **7a** in CDCl$_3$.

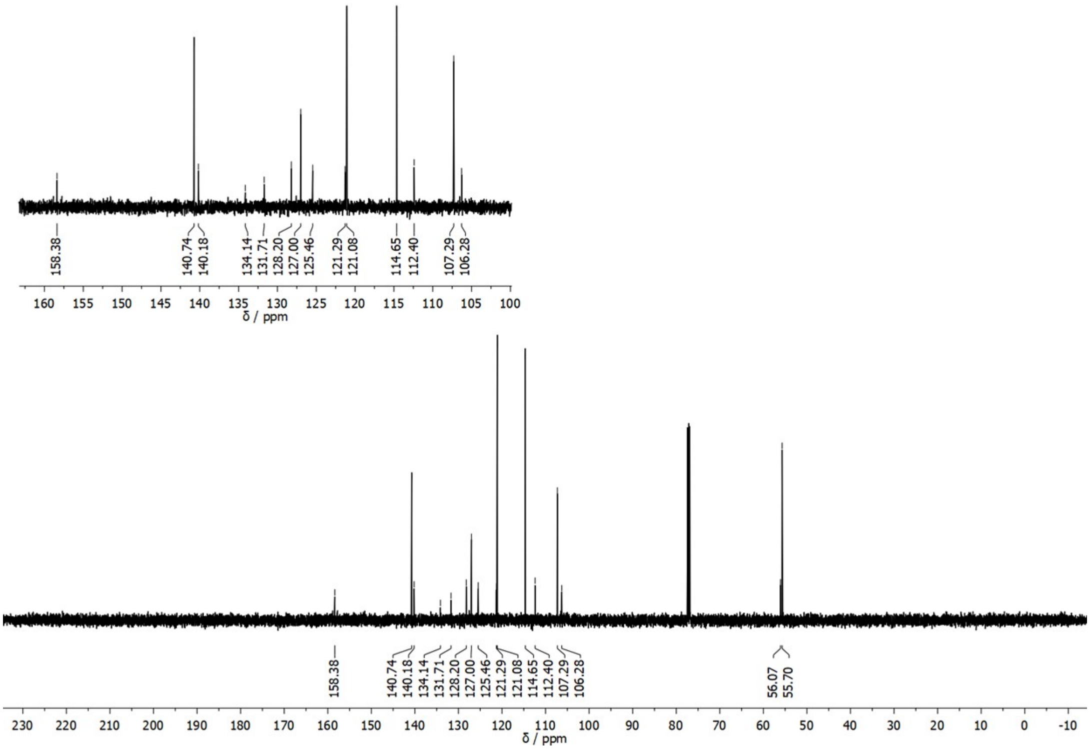


Figure S47. 126 MHz ^{13}C-NMR of **7a** in CDCl$_3$.

9.2 7b NMR Spectra

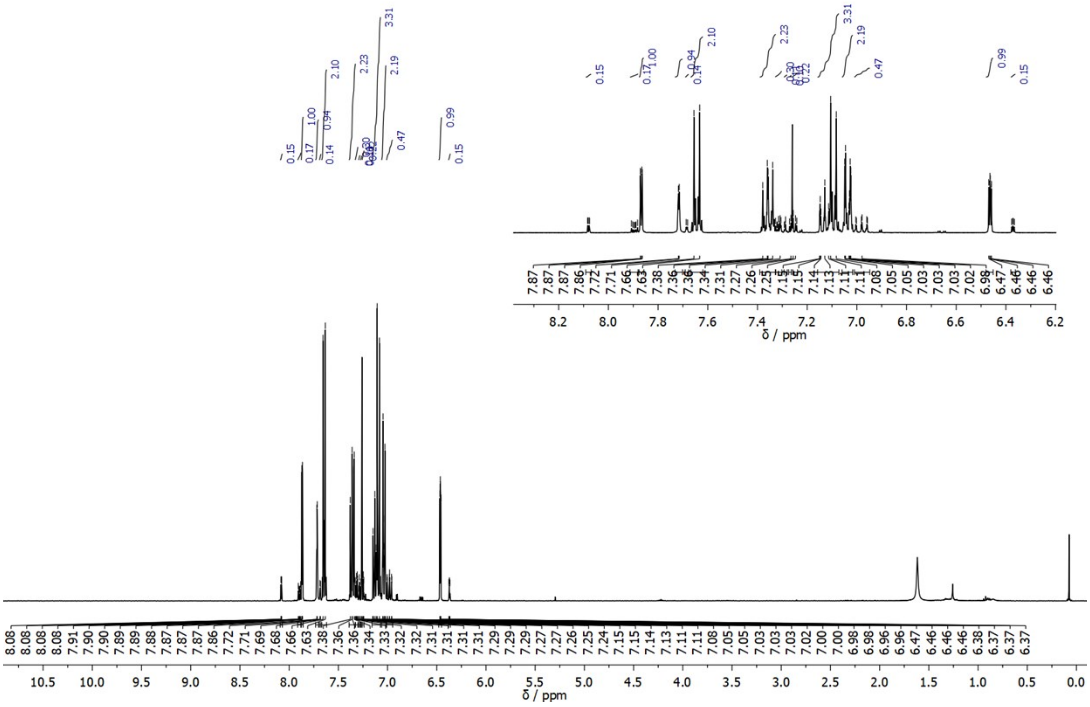


Figure S48. 400 MHz ^{1}H-NMR of **7b** in CDCl$_3$.

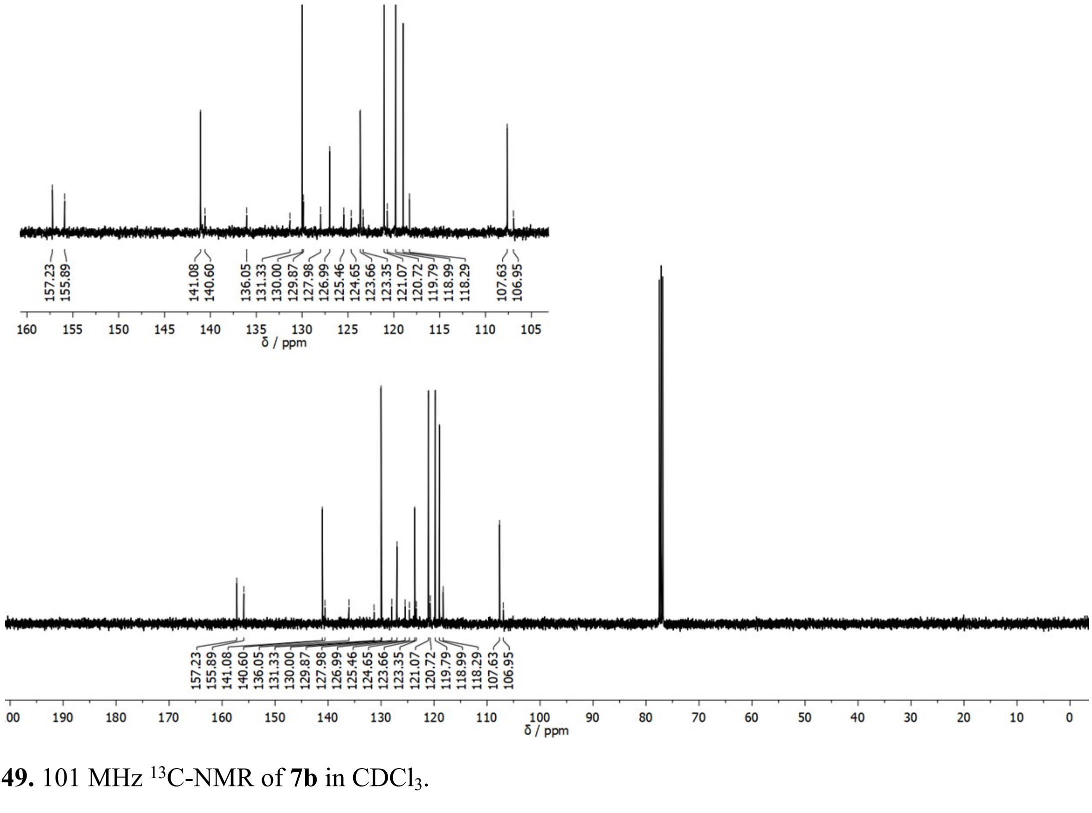


Figure S49. 101 MHz ^{13}C-NMR of **7b** in CDCl$_3$.

9.3 7c NMR Spectra

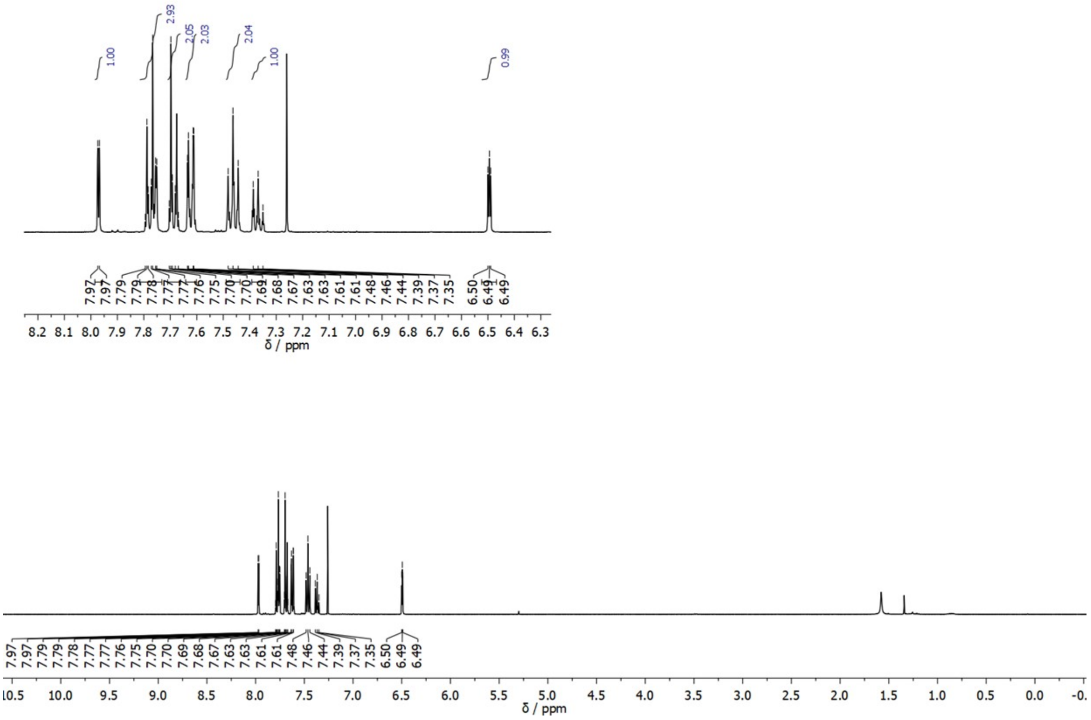


Figure S50. 400 MHz ^{1}H-NMR of **7c** in $CDCl_3$.

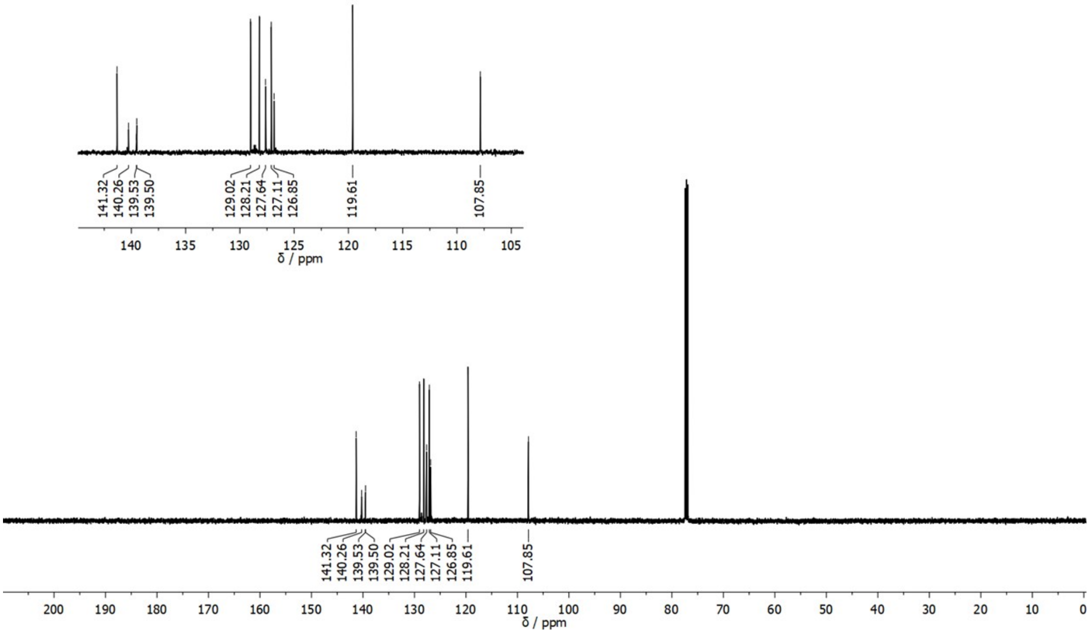


Figure S51. 101 MHz ^{13}C-NMR of **7c** in $CDCl_3$.

9.4 7d NMR Spectra

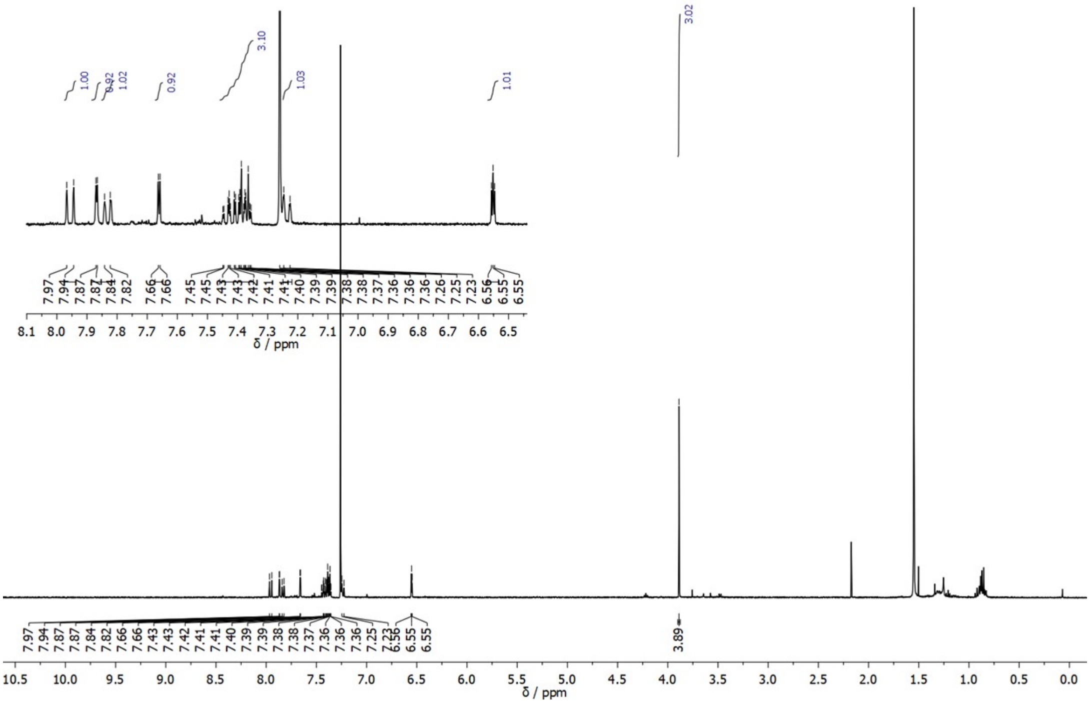


Figure S52. 500 MHz ^{1}H-NMR of **7d** in CDCl$_3$.

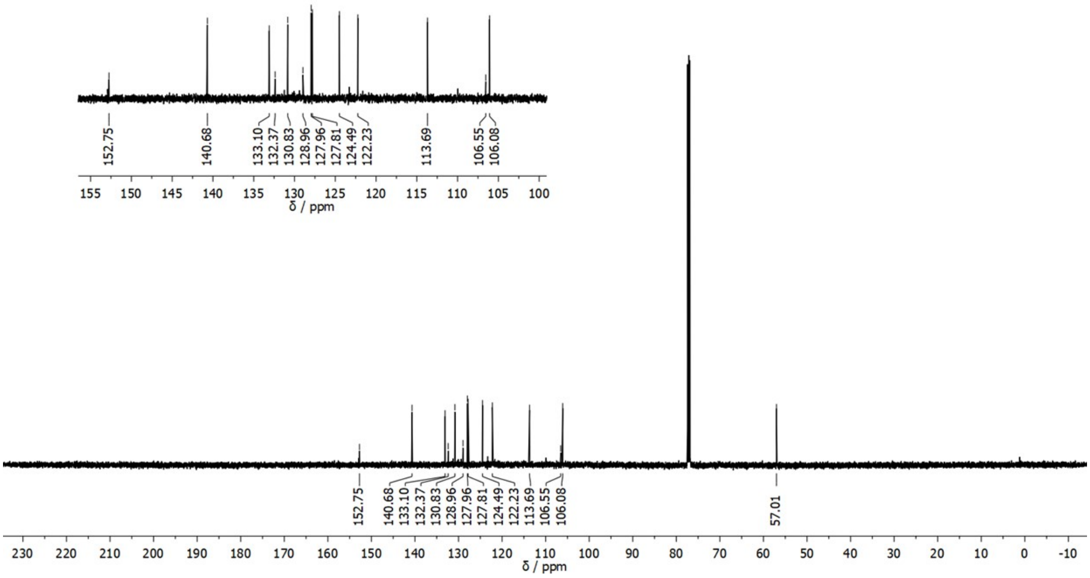


Figure S53. 126 MHz ^{13}C-NMR of **7d** in CDCl$_3$.

9.5 7e NMR Spectra

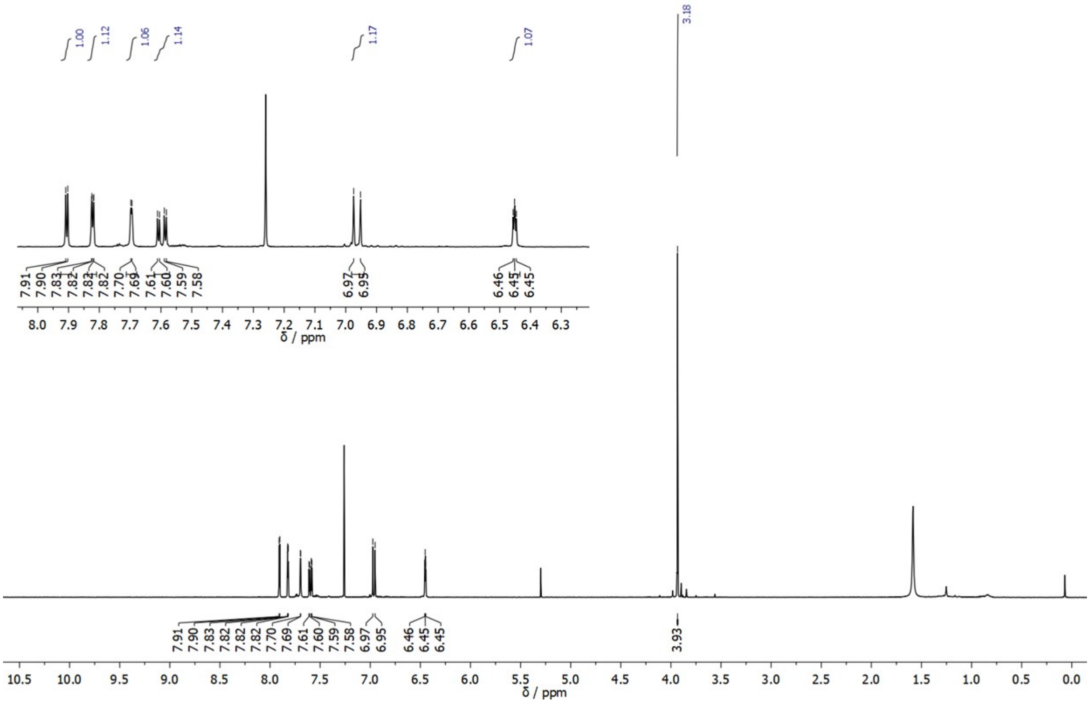


Figure S54. 400 MHz ^{1}H-NMR of **7e** in CDCl$_3$.

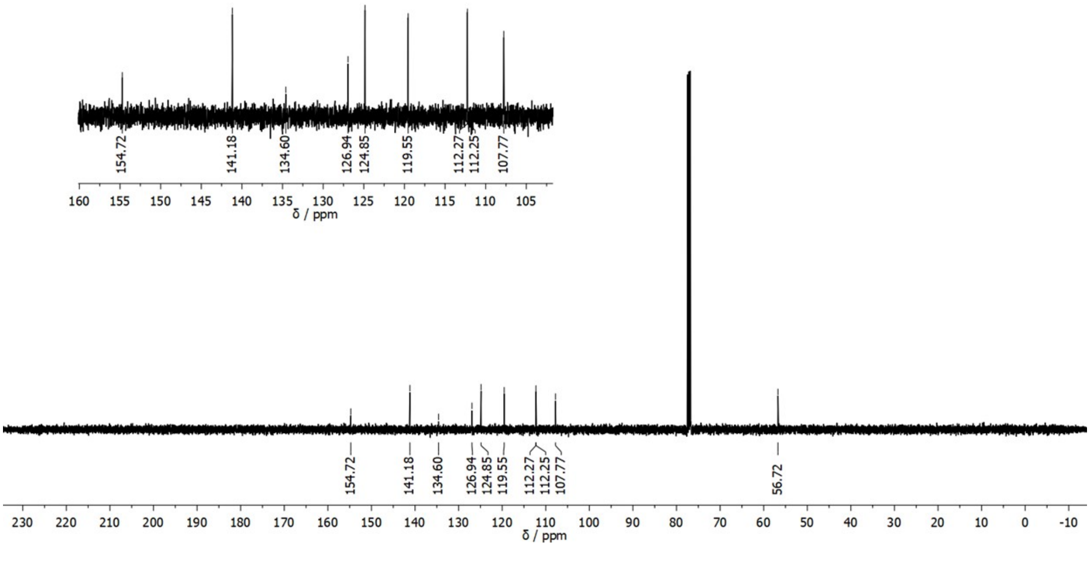


Figure S55. 101 MHz ^{13}C-NMR of **7e** in CDCl$_3$.

9.6 7f NMR Spectra

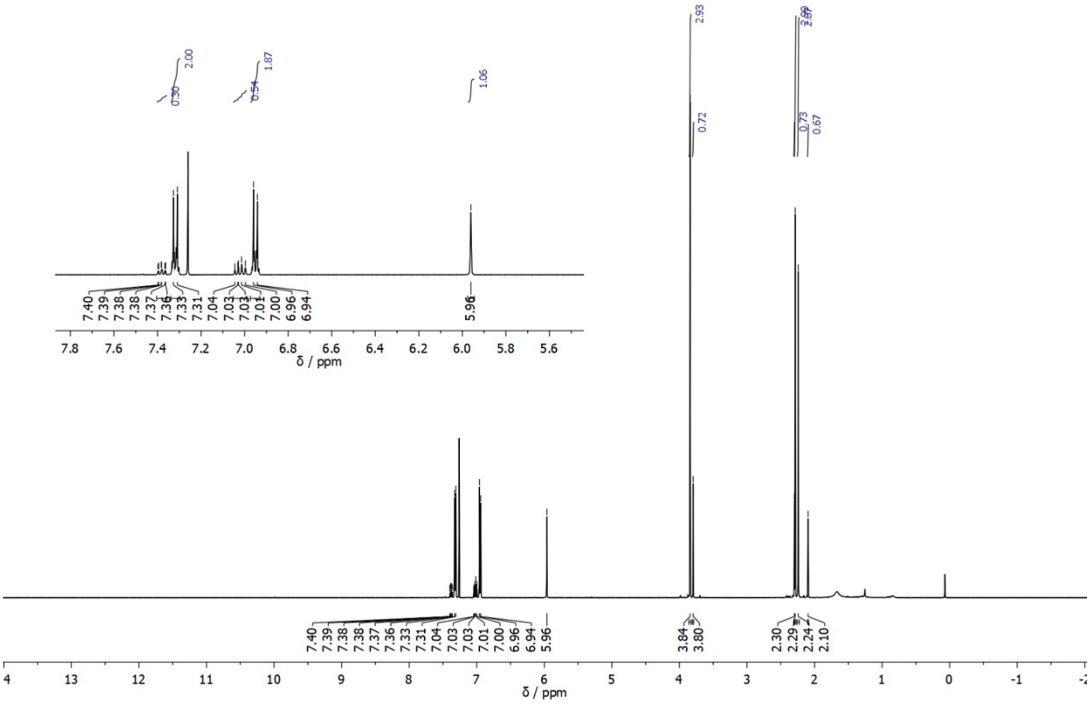


Figure S56. 500 MHz ^{1}H-NMR of **7f** in CDCl$_3$.

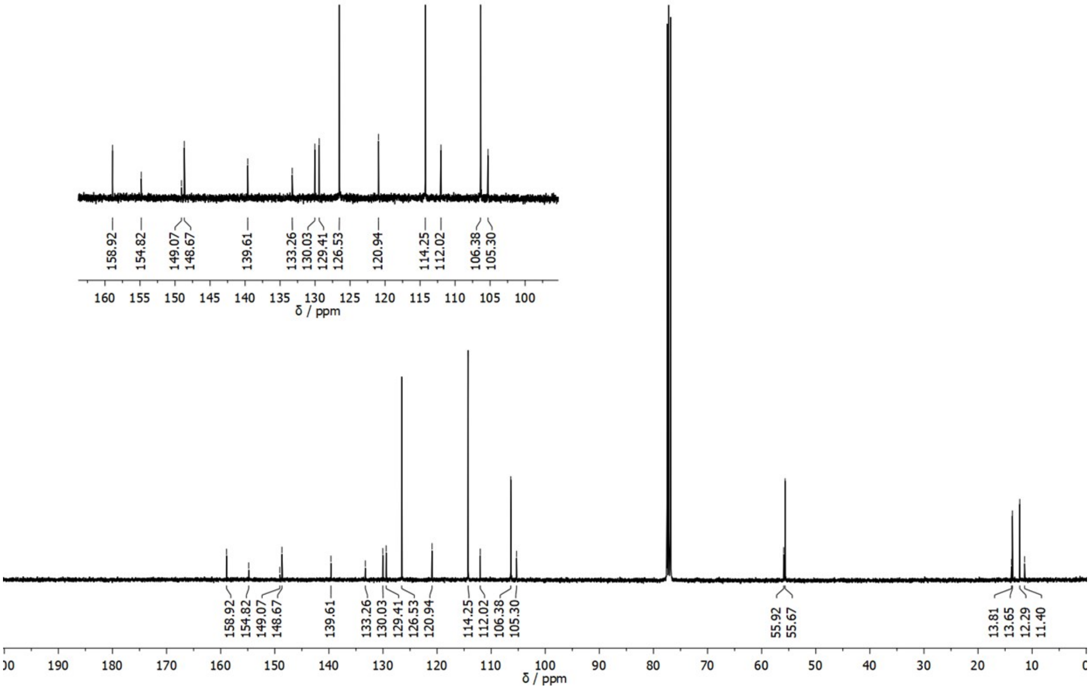


Figure S57. 126 MHz ^{13}C-NMR of **7f** in CDCl$_3$.

9.7 7g NMR Spectra

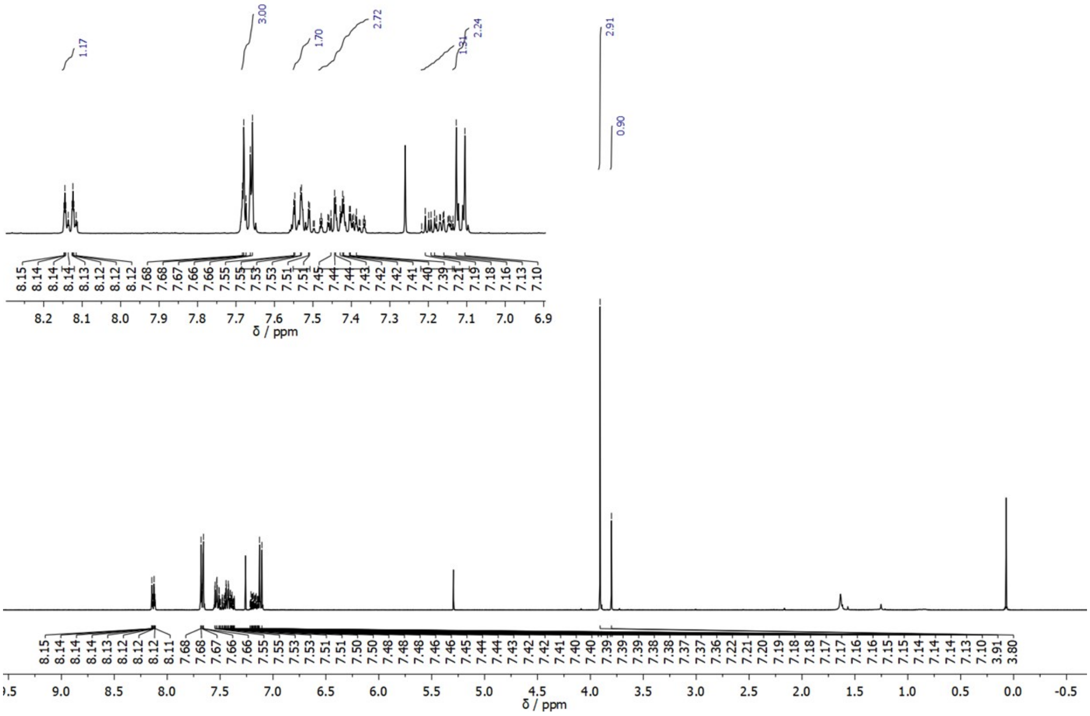


Figure S58. 400 MHz ^{1}H-NMR of **7g** in $CDCl_3$.

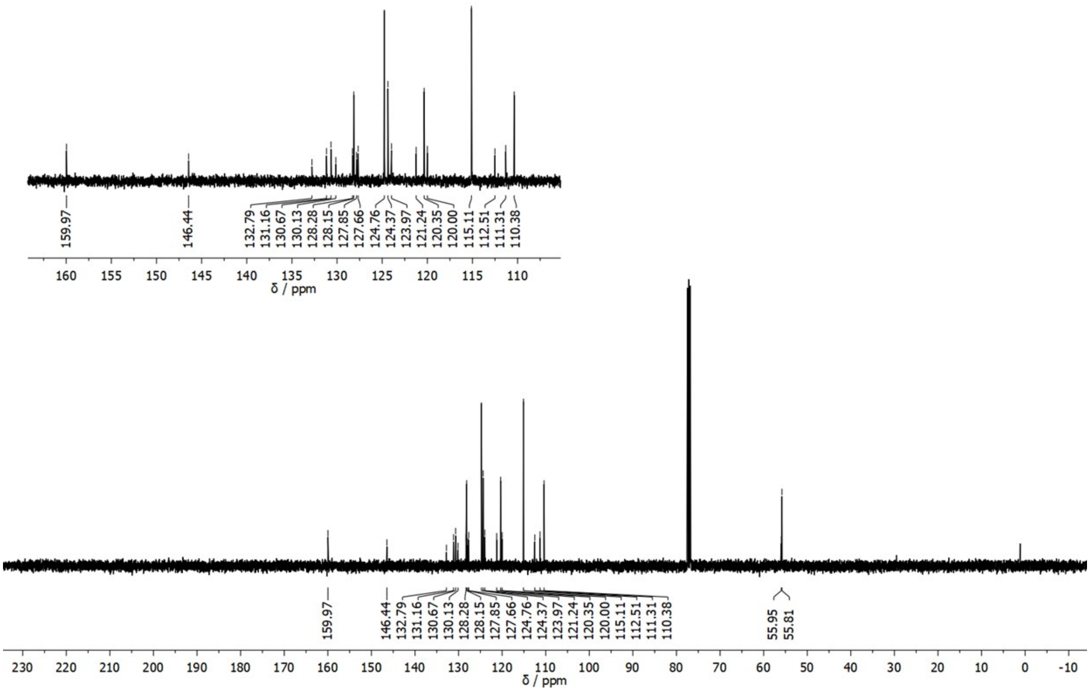


Figure S59. 101 MHz ^{13}C-NMR of **7g** in $CDCl_3$.

9.8 7h NMR Spectra

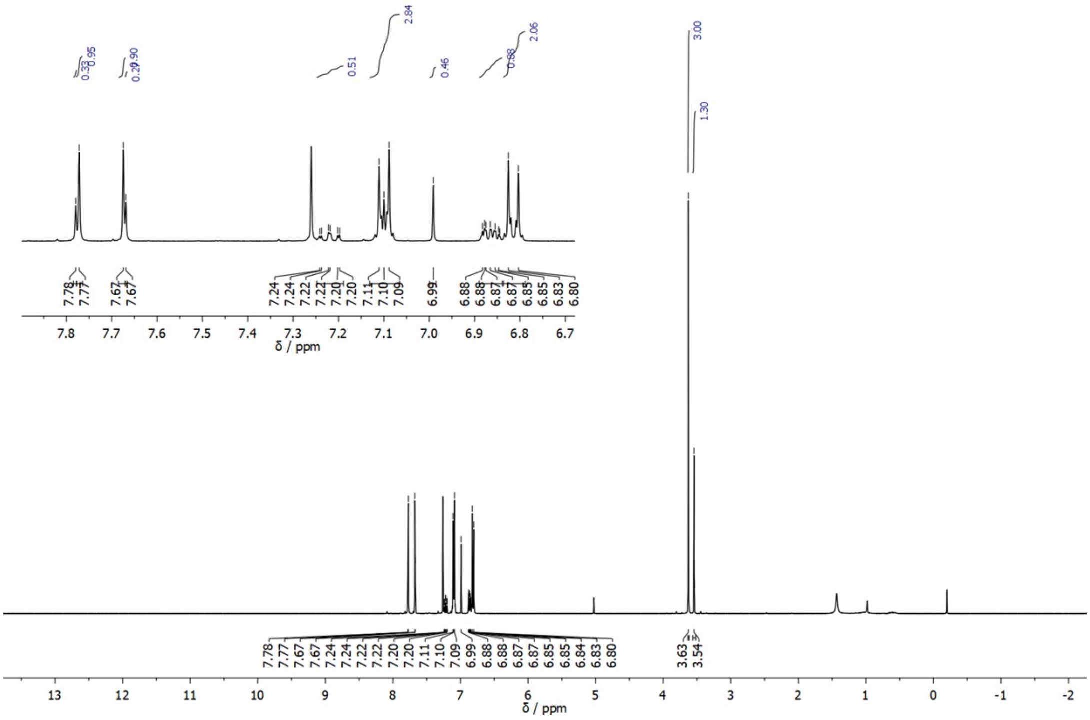


Figure S60. 400 MHz ^{1}H-NMR of **7h** in CDCl$_3$.

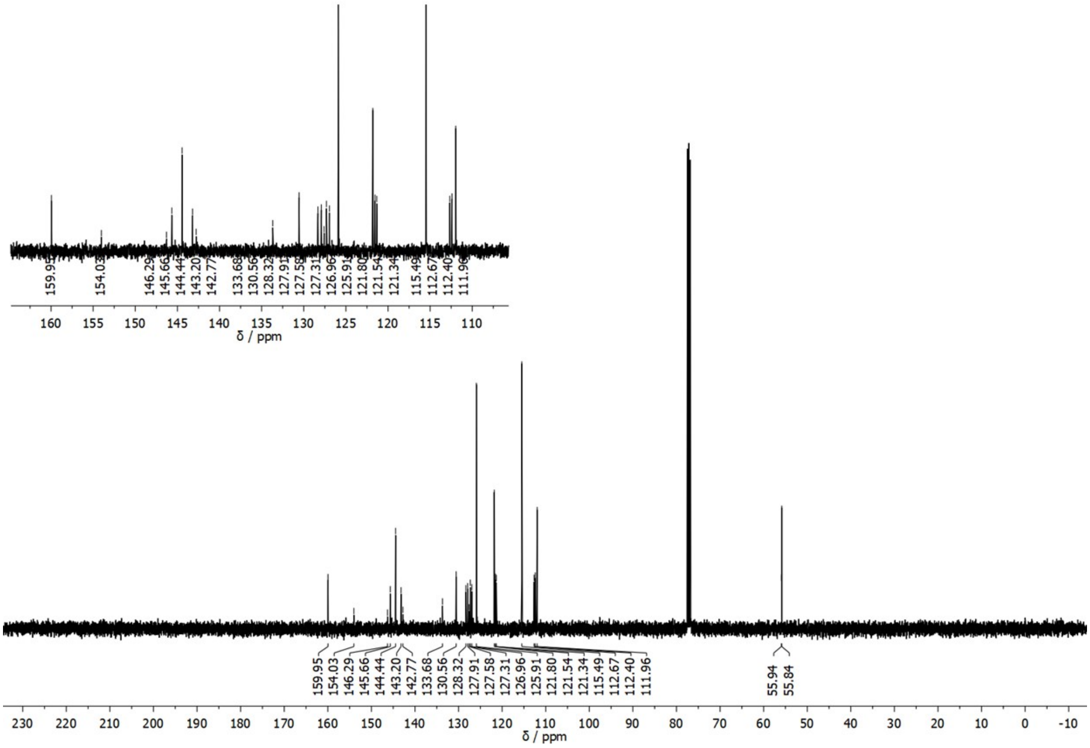


Figure S61. 101 MHz ^{13}C-NMR of **7h** in CDCl$_3$.

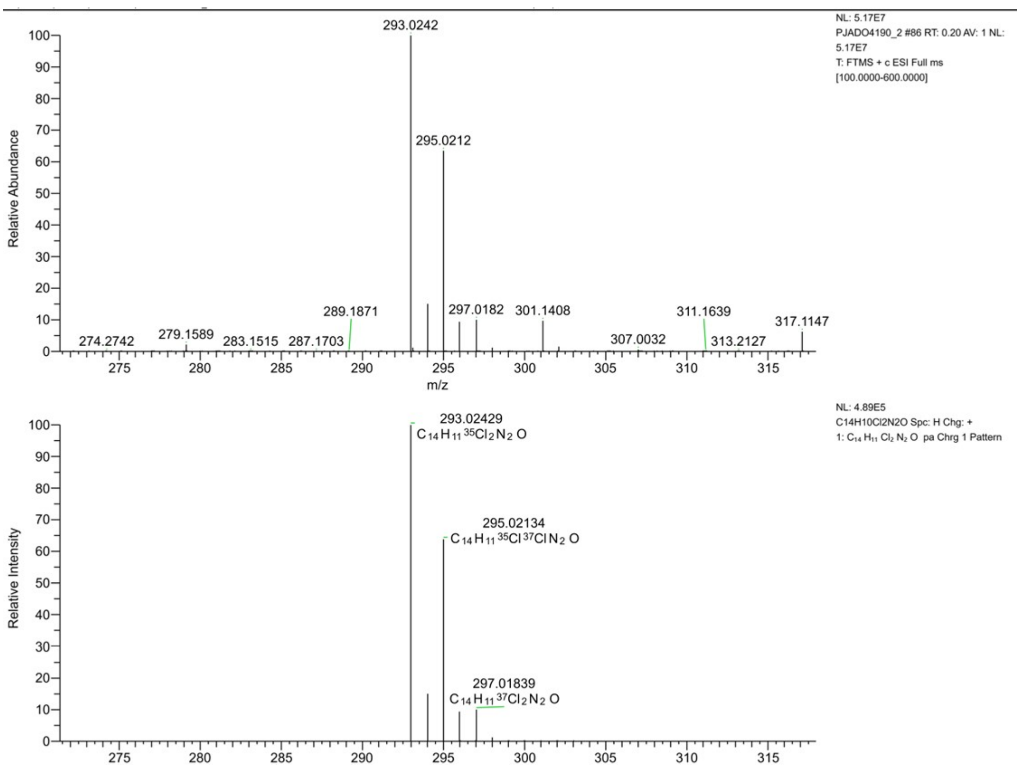


Figure S62. ESI-HRMS of **7h**.

10 References

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2 M. Zheng, I. Ghosh, B. König and X. Wang, *ChemCatChem*, 2019, **11**, 703–706.

3 Y. Wang, H. Simon, X. Chen, Z. Lin, S. Chen and L. Ackermann, *Angew. Chemie - Int. Ed.*, 2022, **61**, e202201595.