Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

for

Visible light photoredox by a ($^{ph, Ar}$NacNac)$_2$Zn photocatalyst: Photophysical properties and mechanistic understanding

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Contents

1. General Considerations

1.1 Materials:

All reactions were carried out in flame-dried glassware using standard Schlenk techniques unless otherwise mentioned. Styrene, TEA, DIPEA and $CDCl_3$ were obtained from Sigma Aldrich. Substituted styrenes, dibenzoylmethane and DMSO were obtained from TCI-chemicals. Substituted anilines, Titanium trichloride (98%), diethyl Zinc (1 M in hexane) and CBr_4 were supplied by AVRA chemicals. All chemicals were used as obtained except specifically mentioned.

1.2 Drying and purification methods:

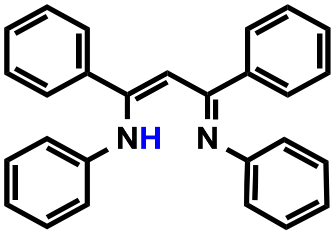
Toluene was refluxed and freshly distilled over sodium/benzophenone. Chloroform, dichloromethane (DCM) and DMSO were refluxed over calcium hydride and collected via distillation. DCM and DMSO were degassed using three freeze-pump-thaw cycles for reactions and spectroscopic measurements. Styrenes were stored overnight over 4 Å molecular sieves. Triethylamine (TEA) and diisopropylethylamine (DIPEA) were distilled under high vacuum and stored over KOH. The *p*-Nitrophenyl diazonium salt was freshly synthesized using procedure reported in literature [S1] and stored at -20 ^{o}C. The substrate CBr_4 and the catalysts **2a** and **2b** were dried under high vacuum for half- an-hour before catalysis experiments.

1.3 Physical Measurements.

Absorption spectra were recorded using LAB-INDIAUV/VIS Spectrophotometer UV 3000 in an air sensitive cuvette of path length 10 mm fitted with screw cap. Emission spectra were obtained in 10 mm path length quartz cuvettes equipped with screw cap using Fluoromax-4 (Horiba Jobin Yvon, NJ) spectrofluorophotometer and the graphs are plotted using Originpro8. Photo-luminescent lifetime data were collected using a Fluorolog-3 spectrofluorophotometer (Horiba Jobin Yvon, NJ) equipped with a single photon counting module in multi-channel scaler mode. The excitation laser source excited the molecule at 374 nm. The lifetime was determined using the decay analysis software package, DAS v6.1. ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on a Bruker 400 MHz spectrometer. All chemical shifts are reported with respect to the ^{1}H (residual) chemical shifts of the d-solvent. High resolution mass spectra were obtained on Waters Synapt-G2S, analyser configuration Q-ToF with ion mobility analysed using Masslynx41. Crystals suitable for X-ray diffraction were mounted on a nylon loop in paratone oil. Diffraction data were collected using a Rigaku XtaLABmini Xray diffractometer equipped with a Mercury charge-coupled device detector and graphite monochromatic Mo Kα (λ = 0.71 Å) radiation source. For high quality data, the crystals were cooled to 100 K with an Oxford Cryostream 700 system. The software SHELXT was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. Data reduction and refinement was further processed using olex2. Cyclic Voltammetry experiments were performed on Keithley 2450 potentiostat. For the measurement, the electrode setup consisted of a glassy carbon working electrode, a Pt-wire as counter electrode, and an Ag/Ag$^+$ (3 M KCl) as the reference electrode.

2. Experimental procedures with spectroscopic data.

2.1 Synthesis of Ligand.

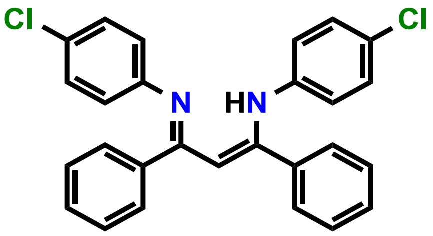


Synthesis of 1a: In an oven-dried Schlenk flask, dibenzoylmethane (1 g, 4.5mmol, 1 equiv), aniline (0.82 mL, 9.0 mmol, 2 equiv), TEA (3.74 mL, 26.8 mmol, 6 equiv) and toluene (50 mL) were stirred under nitrogen to give a clear solution. The mixture was cooled down to 0 ^{o}C and $TiCl_4$ (98% solution, 1.0 ml, 9.0 mmol, 2 equiv) was added dropwise during which colour of the solution turned from colourless to deep brown with heavy precipitation. The reaction mixture was stirred at 0 ^{o}C until fume subsides and then gradually brought to room temperature. The reaction mixture was refluxed at 120 ^{o}C under nitrogen flow for 2 hrs.

Workup procedure A: After completion of the reaction, all the volatiles were evaporated under vacuum and acetone (100 mL) was added to the dried mixture. The resulting solution was warmed to facilitate product dissolution and was filtered. The residue was again boiled in acetone (25 mL) and filtered. The same process was repeated three times until washed acetone solution became colourless. The acetone solution was fully dried to get a brown solid, which was further dissolved in DCM and methanol mixture (3:1) and left at room temperature to give yellow crystalline precipitate. The precipitate was filtered to obtain pure product (1.5 g, 85%).

Workup procedure B: After completion of the reaction, all the volatiles were evaporated and water (100mL) was added. The aqueous layer was washed with 30 × 3 mL DCM. The organic layer was collected and dried over $MgSO_4$. The ligand was purified by flash chromatography using ethyl acetate: hexane (1:1) to obtain bright yellow solid (1.4 g, 83%). Recrystallization of the ligand was done in chloroform and methanol mixture (3:1) at 4 ^{o}C to result bright yellow crystals of **1a**.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 13.00 (s, 1H), 7.35 – 7.28 (m, 10H), 7.11 (t, *J* = 7.8 Hz, 4H), 6.91 (t, *J* = 7.3 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 4H), 5.38 (s, 1H, C*H*). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.55, 150.57, 141.84, 129.53, 128.93, 128.84, 128.39, 127.99, 125.44, 122.82, 106.77.

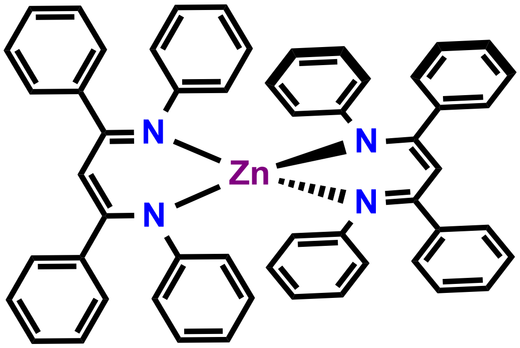
HRMS (ESI+, m/z) calcd for $C_{27}H_{23}N_2$, $[M+H]^+$ m/z = 375.1861, found 375.1874



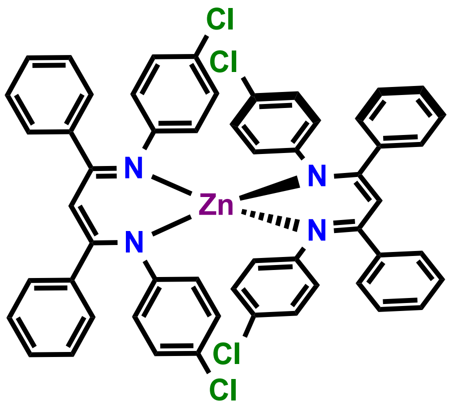
Synthesis of 1b: Ligand **1b** was synthesized according to the procedure used for **1a** using following reagents: dibenzoylmethane (1 g, 4.5 mmol, 1 equiv), 4-chloroaniline (1.14 g, 9.0 mmol, 2 equiv), TEA (3.74 mL, 26.8 mmol, 6 equiv), $TiCl_4$ (1.0 mL, 9.0 mmol, 2 equiv, 98% solution) and toluene (50mL). Using workup procedure, A, bright yellow solid in high yields (1.3 g, 70%) was obtained. The recrystallization of the ligand was done in DCM and methanol mixture (3:1) at 4 ^{o}C to result yellow crystals of **1b**. ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 12.94 (s, 1H, NH), 7.30 (s, 10H, aromatic), 7.07 (d, *J* = 8.0 Hz, 4H, aromatic), 6.66 (d, *J* = 8.0 Hz, 4H, aromatic), 5.39 (s, 1H, C*H*). ^{13}**C NMR** (101 MHz, $CDCl_3$): δ 161.53, 144.10, 137.73, 128.92, 128.72, 128.50, 128.41, 128.06, 123.63, 102.63.

HRMS (ESI+, m/z) calcd for $C_{27}H_{20}Cl_2N_2$, $[M+H]^+$ m/z = 443.1037, found 443.1063

2.2 The synthesis of Zinc complexes



Synthesis of the complex 2a: In an oven dried Schlenk flask, ligand **1a** (500 mg, 1.34 mmol) was taken with a stir-bar added to it. Freshly distilled toluene (5 mL) was added and stirred to get a bright yellow clear solution. $ZnEt_2$ (0.67 ml, 1.0 M in hexane, 0.67 mmol) was added in a dropwise manner and stirred at room temperature for 3 hours. The yellow precipitate was filtered and washed with toluene (10 ml) to give pure zinc complex, **2a** in high yields (456 mg, 84%). The saturated solution of **2a** in DCM was layered with DMSO to obtain yellow rhombus shaped crystals.^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.17 (dt, *J* = 13.1, 3.9 Hz, 20H), 6.93 (t, *J* = 7.7 Hz, 8H), 6.78 (t, *J* = 7.3 Hz, 4H), 6.55 (d, *J* = 7.6 Hz, 8H), 5.05 (s, 2H,-C*H).* ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 168.11, 150.12, 141.39, 129.07, 127.93, 127.53, 124.99, 122.25, 100.92. **HRMS (ESI+, m/z)** calcd for $C_{54}H_{43}N_4Zn$, $[M+H]^+$ m/z = 811.2779, found 811.2782. Anal. calcd for $C_{54}H_{46}N_4O_2Zn$: C, 76.45; H, 5.46; N, 6.60. Found: C, 75.86; H, 4.93; N, 6.53.



Synthesis of 2b: Zinc-complex **2b** was synthesized according to the procedure used for **2a** using following reagents: ligand **1b** (500 mg, 1.13 mmol), $ZnEt_2$ (0.56 ml, 1.0 M in hexane, 0.56 mmol) and freshly distilled toluene (5 mL). **2b** was obtained as yellow precipitate in moderate yield (374 mg, 73%). The saturated solution of **2b** in DCM was layered with DMSO to obtain yellow block of crystals.**^{1}H NMR** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.12 (m, 14H), 6.88 (d, *J* = 8.7 Hz, 3H), 6.42 (d, *J* = 8.7 Hz, 3H), 5.11 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.78, 148.56, 140.64, 129.14, 128.35, 128.09, 127.95, 125.94. **HRMS (ESI+, m/z)** calcd for $C_{54}H_{43}N_4Zn$, $[M+H]^+$ m/z = 947.1220, found 947.1159. Anal. calcd for $C_{54}H_{40}Cl_4N_4OZn$: C, 66.99; H, 4.16; N, 5.79. Found: C, 66.27; H, 4.32; N, 5.36.

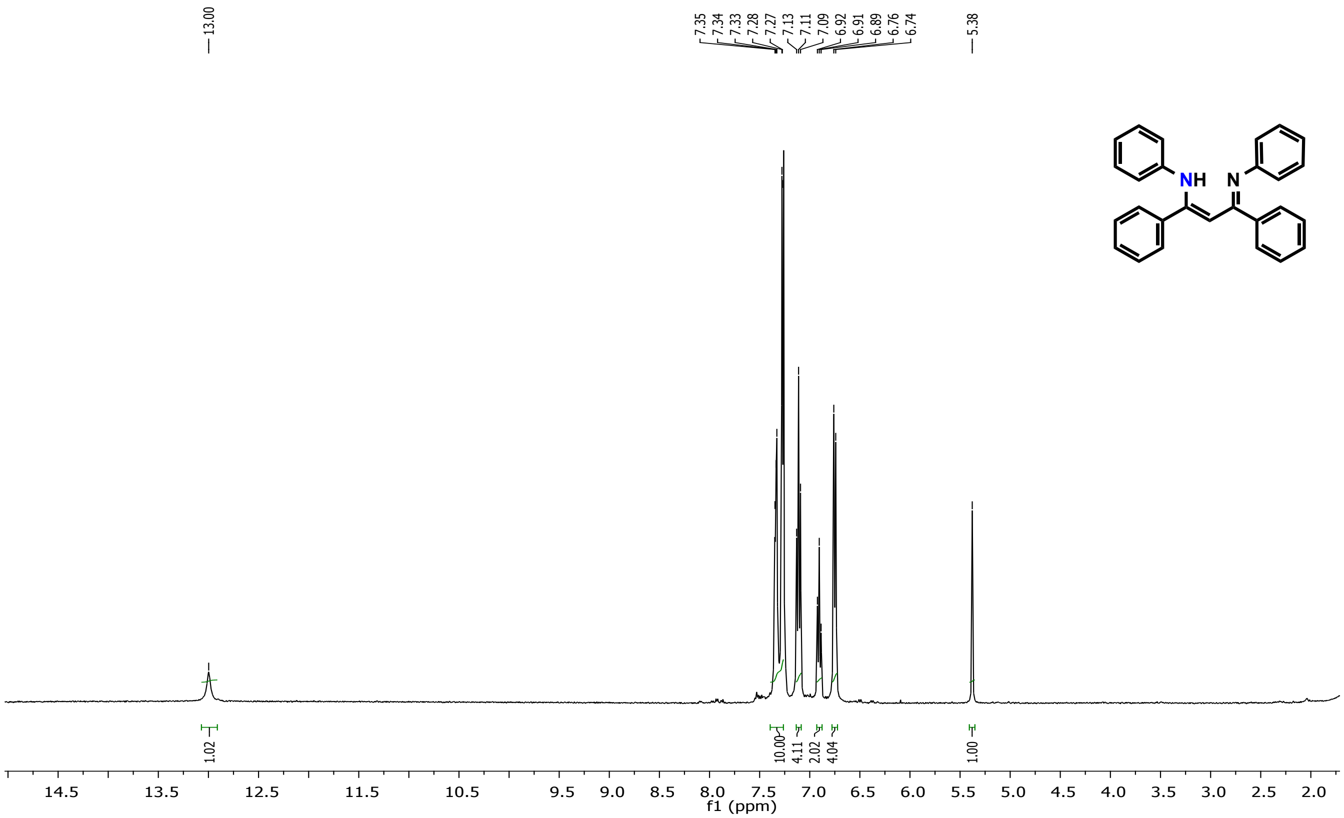
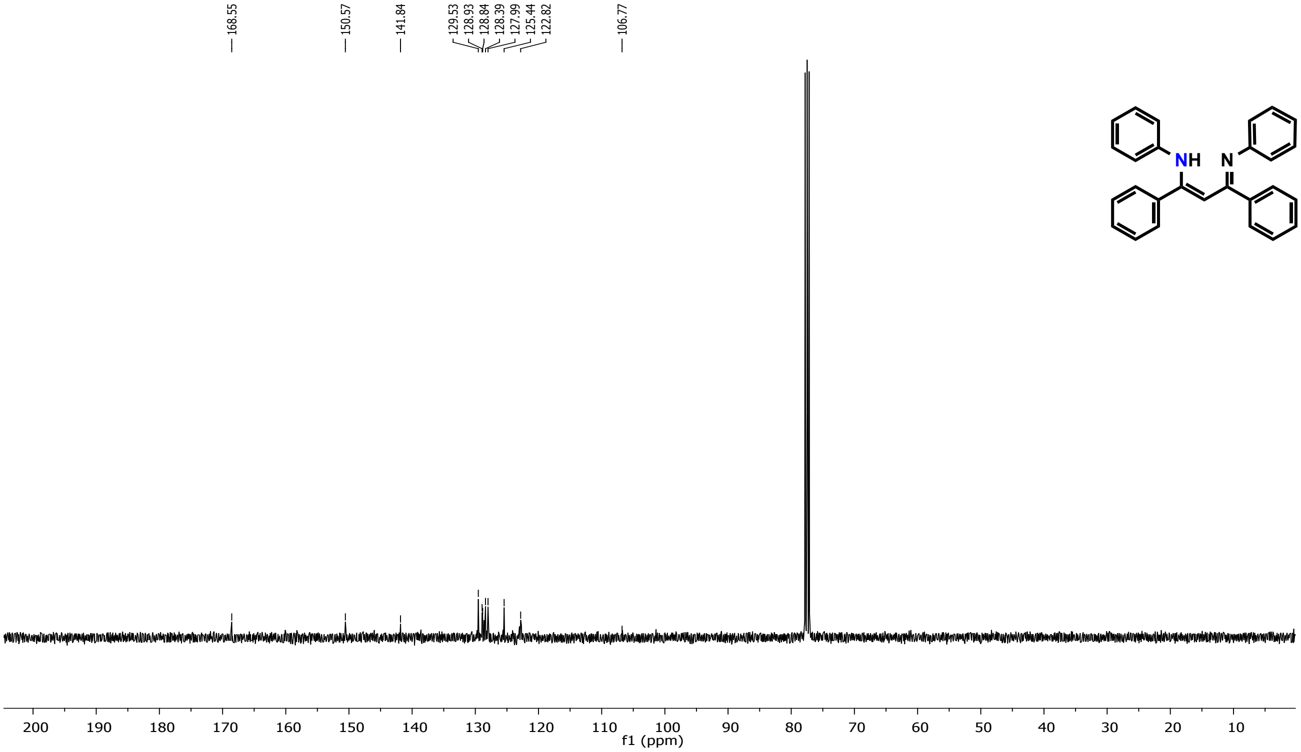


Fig S1: ^{1}H NMR spectrum of **1a** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.



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g S2:^{13}C NMR spectrum of **1a** recorded in $CDCl_3$, solvent residual peak is at 77.36 ppm.

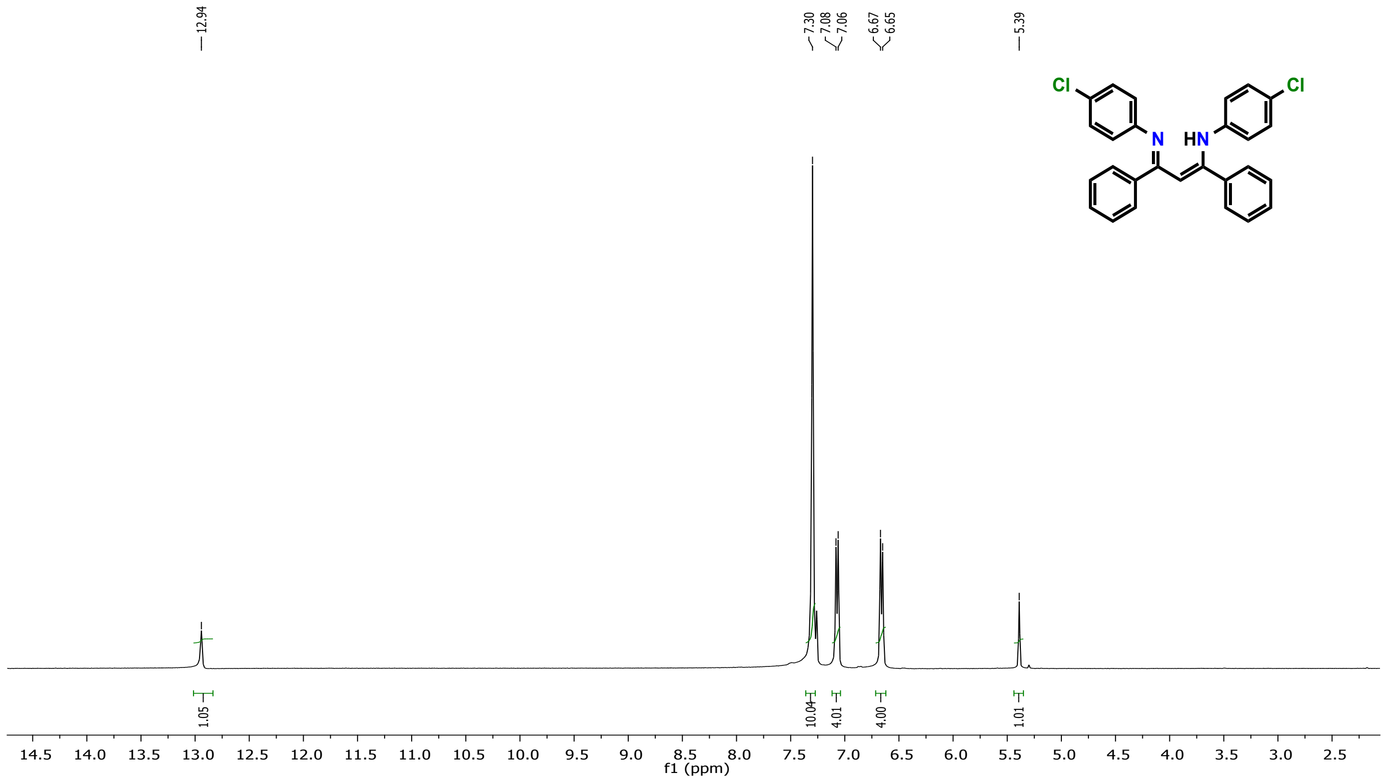


Fig S3: ^{1}H NMR spectrum of **1b** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.

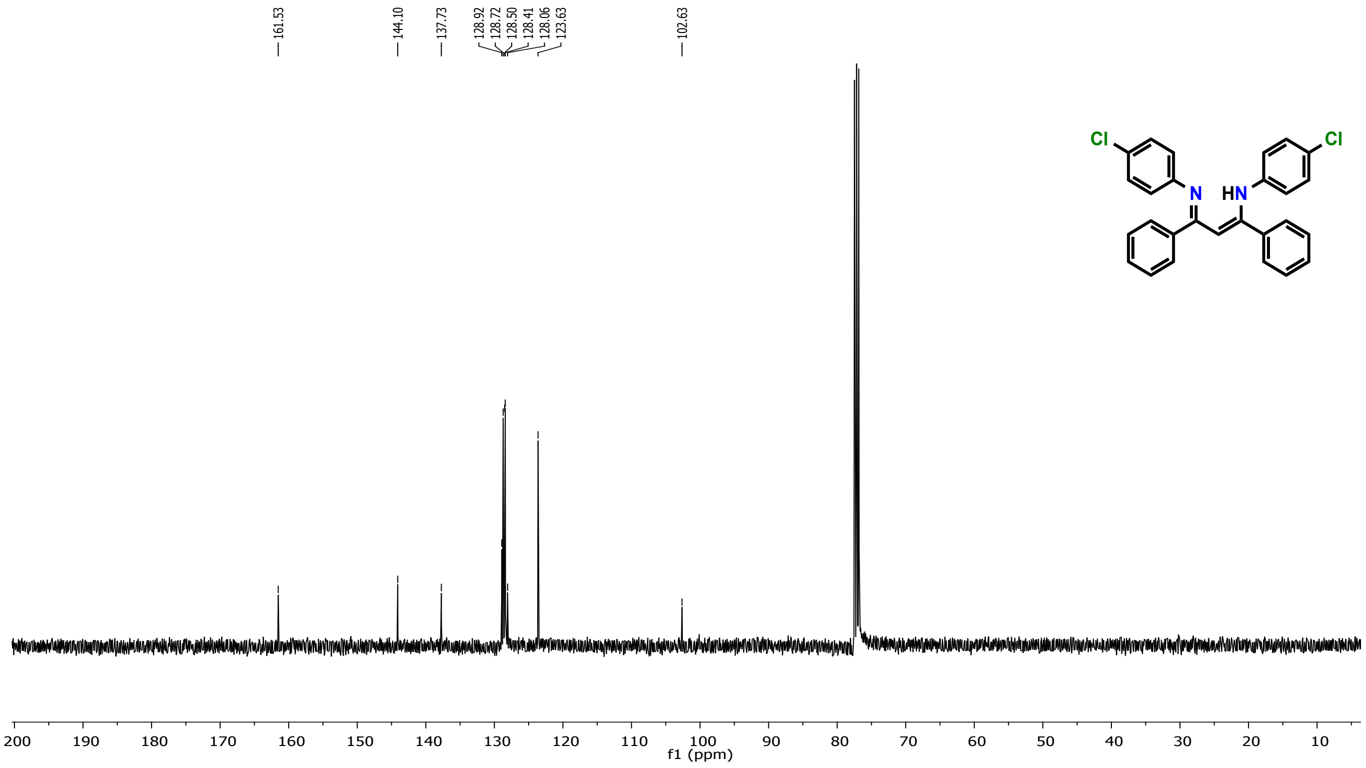


Fig S4:^{13}C NMR spectrum of **1b** recorded in $CDCl_3$, solvent residual peak is at 77.4 ppm.

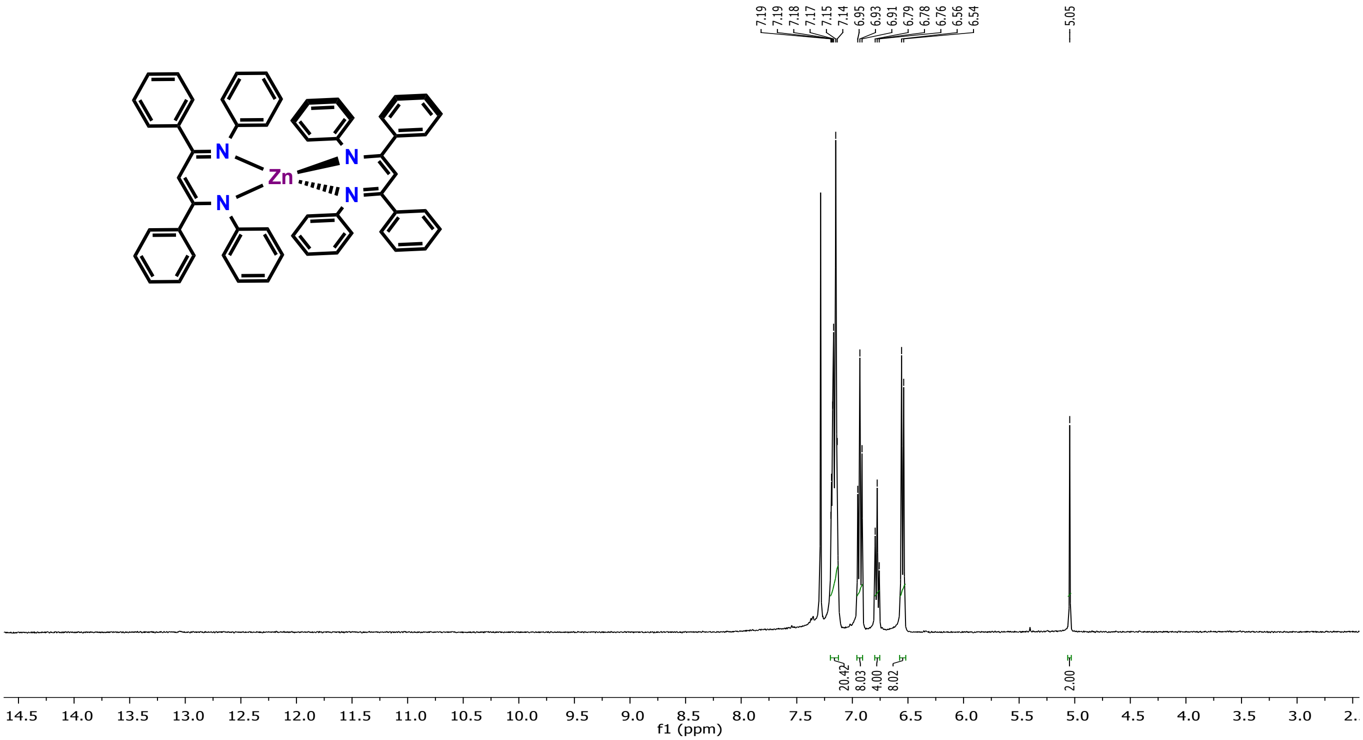


Fig S5: ^{1}H NMR spectrum of **2a** recorded in CDCl$_3$, residual proton peak of the solvent is at 7.26 ppm.

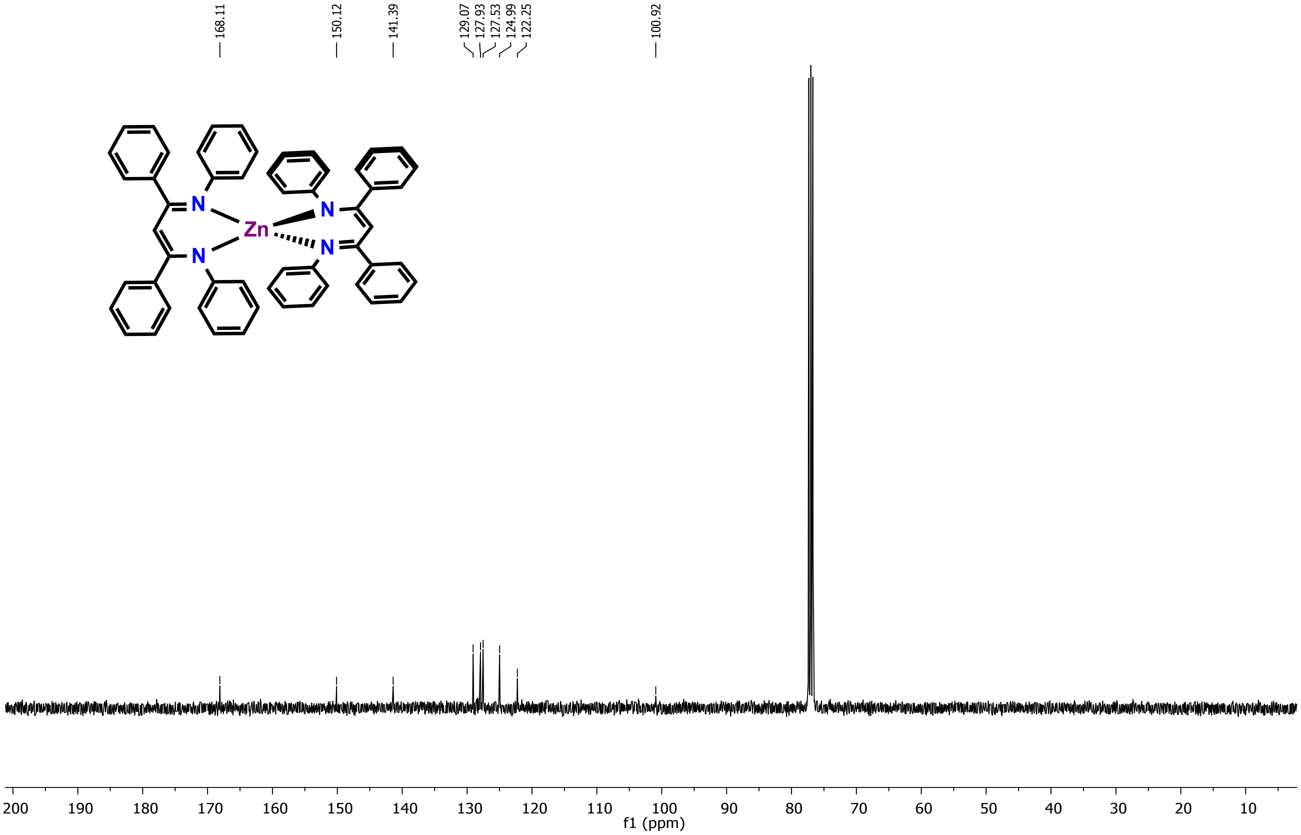
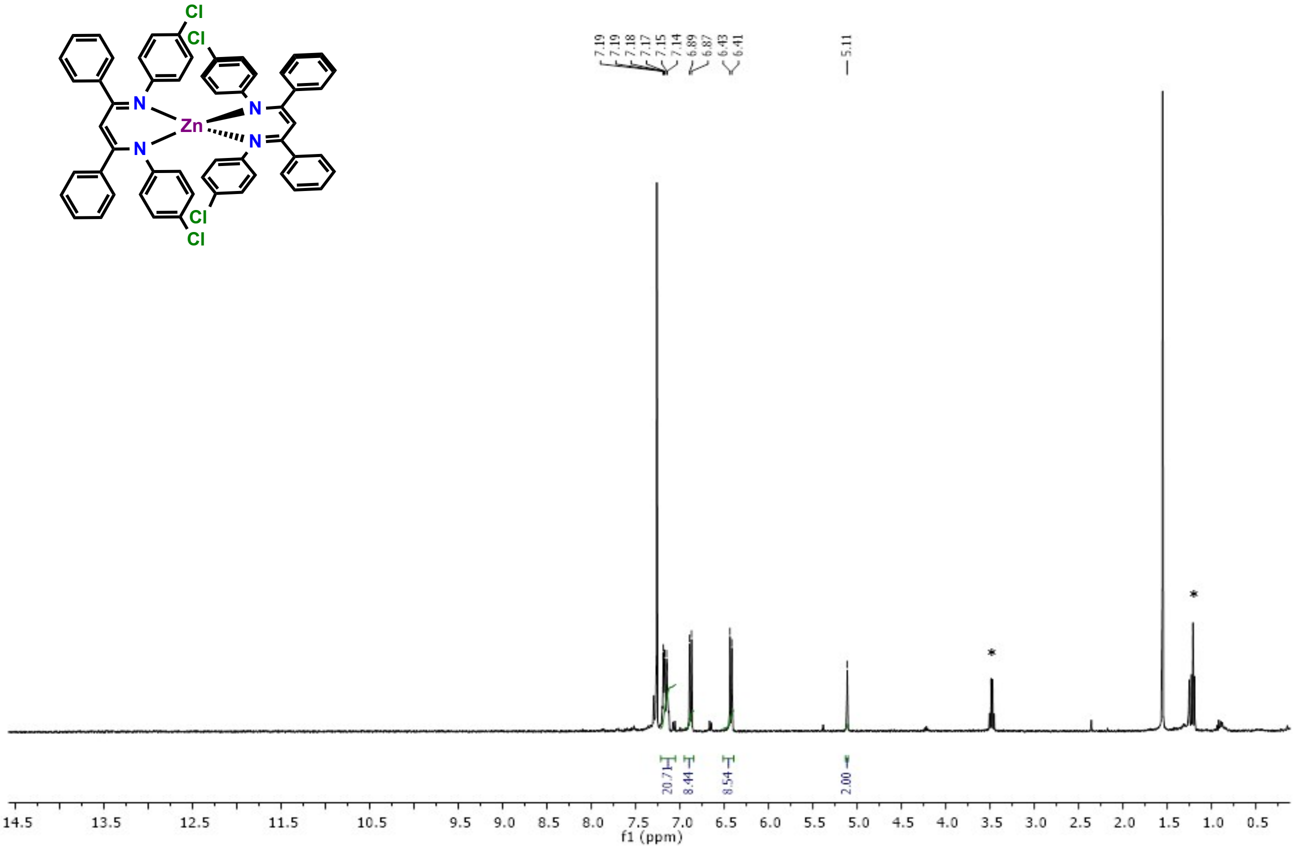


Fig S6: ^{13}C NMR spectrum of **2a** recorded in CDCl$_3$, solvent residual peak is at 77.4 ppm.



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ig S7: ^{1}H NMR spectrum of **2b** recorded in $CDCl_3$.(* denotes diethyl ether resonances)

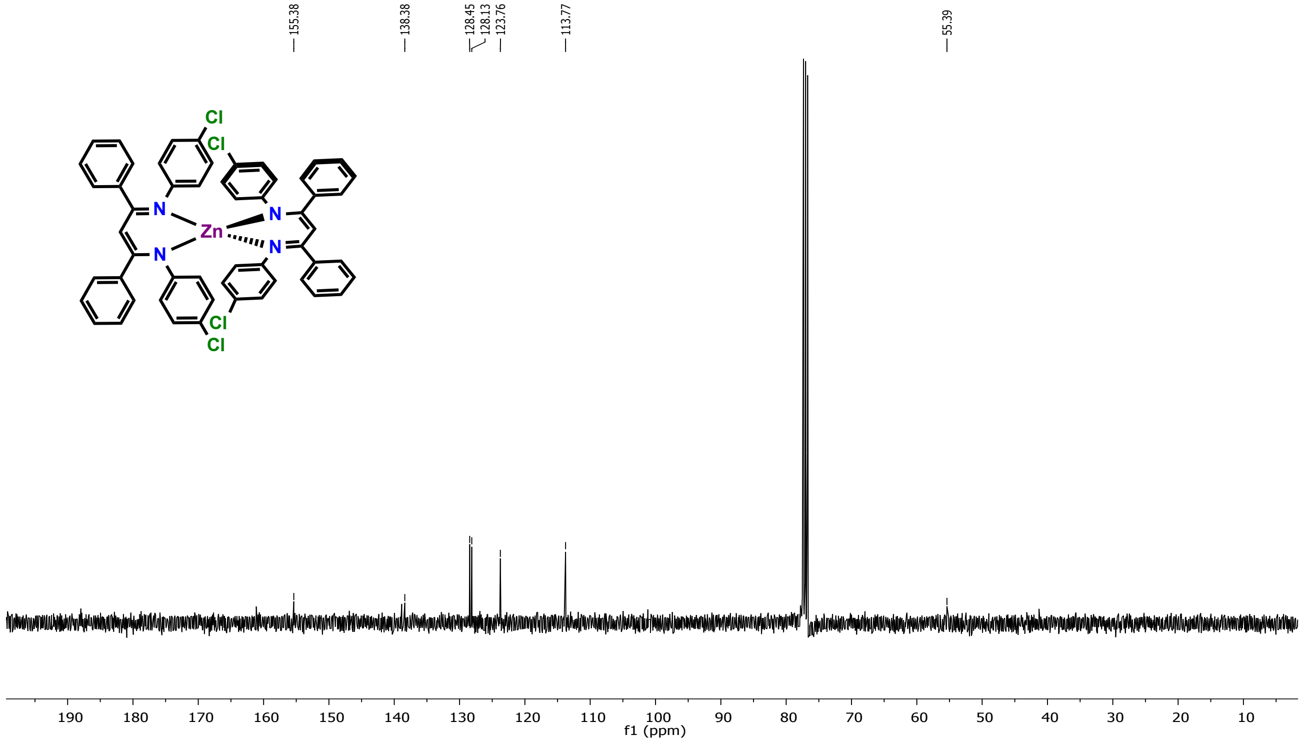


Fig S8:^{13}C NMR spectrum of **2b** recorded in $CDCl_3$, solvent residual peak is at 77.4 ppm

3. Absorption and emission spectra

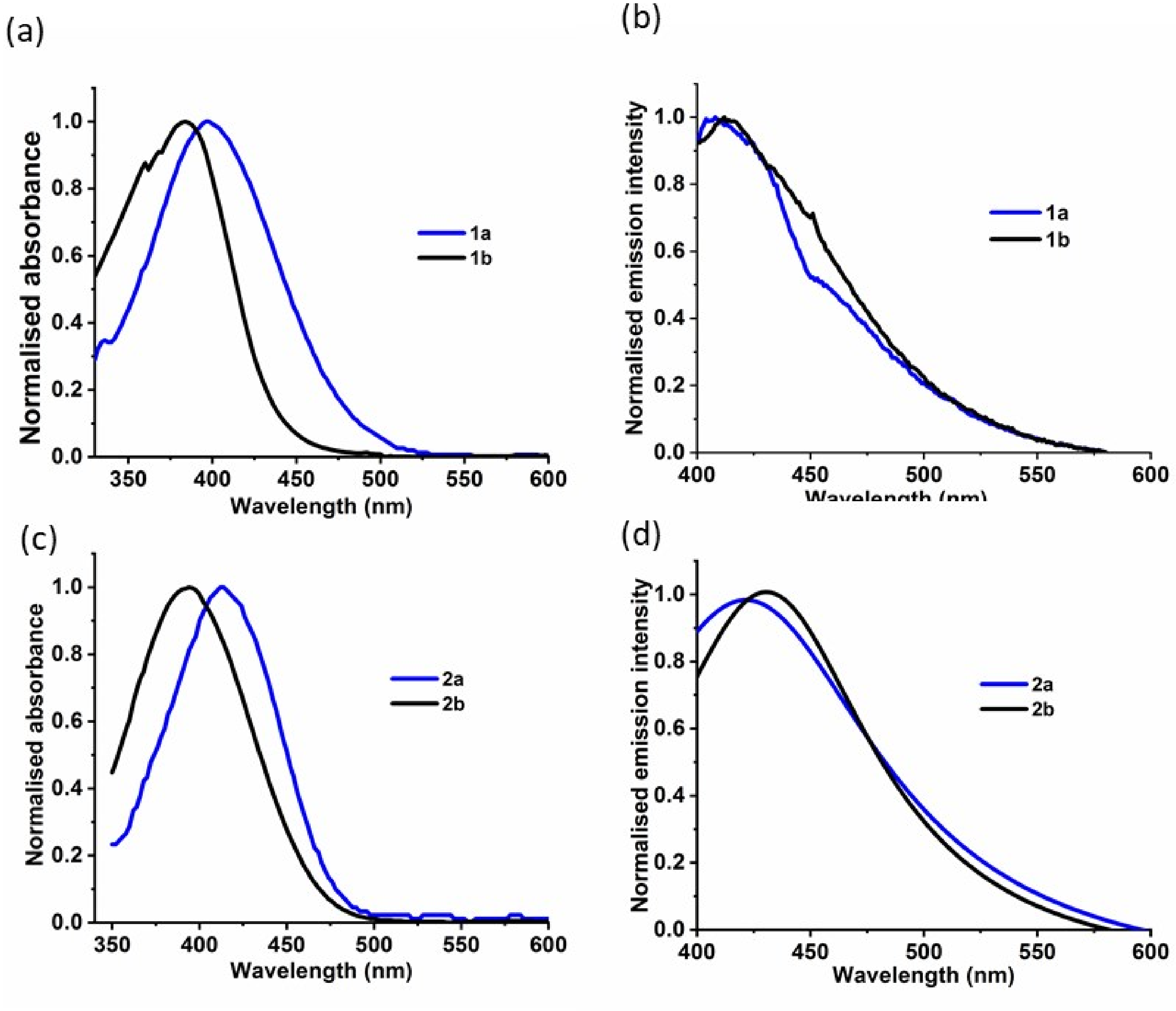


Fig S9: (a) Comparison of normalised absorption intensities of ligand **1a** and **1b,** (b) normalised emission intensities of ligands **1a** and **1b, (c**) normalised absorption intensities of zinc complexes **2a** and **2b**, (d) normalised emission intensity of zinc complexes **2a** and **2b**.

4. Measurement of emission quantum yield for ligand 1a and the photocatalyst 2a.

For the measurement of quantum yield, samples of reference compound, ligand and catalyst were prepared in dichloromethane, freshly distilled over calcium hydride and degassed using two freeze-pump-thaw cycles. The absorbance of each sample was measured in a 10 mm air sensitive cuvette fitted with screw cap. The absorption maxima was kept <0.1 for each case to prevent self-absorption. Immediate fluorescence measurement of same sample was followed to avoid chances of photo-bleach.

The ϕ_s values were obtained by comparing the photoluminescence intensities to $[Ru(bpy)_3](PF_6)_2$ and calculated using the following expression:

$$\boxed{\emptyset_s = \emptyset_{ref}\frac{Grad(s)}{Grad\ (ref)}}$$

Where, ϕ_{ref} is the known quantum yield of the reference compound. Here, $[Ru(bpy)_3](PF_6)_2$ dissolved in DCM (ϕ_{ref} = 0.029)[S2] was used as the reference, Grad(s) is slope of integrated emission intensity at absorbance maxima for sample and Grad (ref) is that for reference compound.

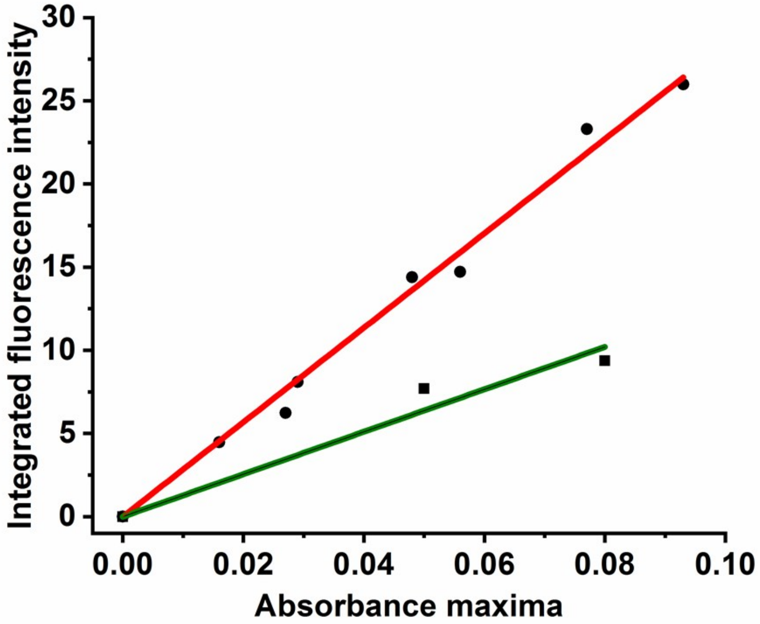


Fig S10: Linear fitted plots of integrated fluorescence intensity at absorbance maxima vs corresponding absorbance maxima, for emission quantum yield measurements of **1a** (sample) with **2a** (reference).

***absorbance of ligand below 0.05 was not considered due to high noise vs signal ratio.*

Quantum yield of **2a** and **1a** in DCM at room temperature was found to be **0.086** and **0.013**, respectively.

5. Time-correlated single photon counting (TCSPC) experiment details.

Excited state dynamics using triplet quenchers.

To assess the excited state dynamics, four triplet quenchers with different quenching mechanism and chemical property were employed. Two photophysical quenchers- cyclohexadiene (Q1), Cu(acac)$_2$ (Q2) and two photochemical quenchers- 4-nitrobiphenyl (Q3) and benzophenone (Q4) were used in this study. For measurement in TCSPC, each sample was prepared in freshly dried and degassed DCM. The quencher for this study was maintained with a concentration of 0.01 M. For lifetime measurement, a 374 nm laser was used for the excitation and 1% ludox was used as prompt. The slit width was maintained at 8 nm to keep α value close to 2%. Best fit of the decay traces were done using DAS6 software.

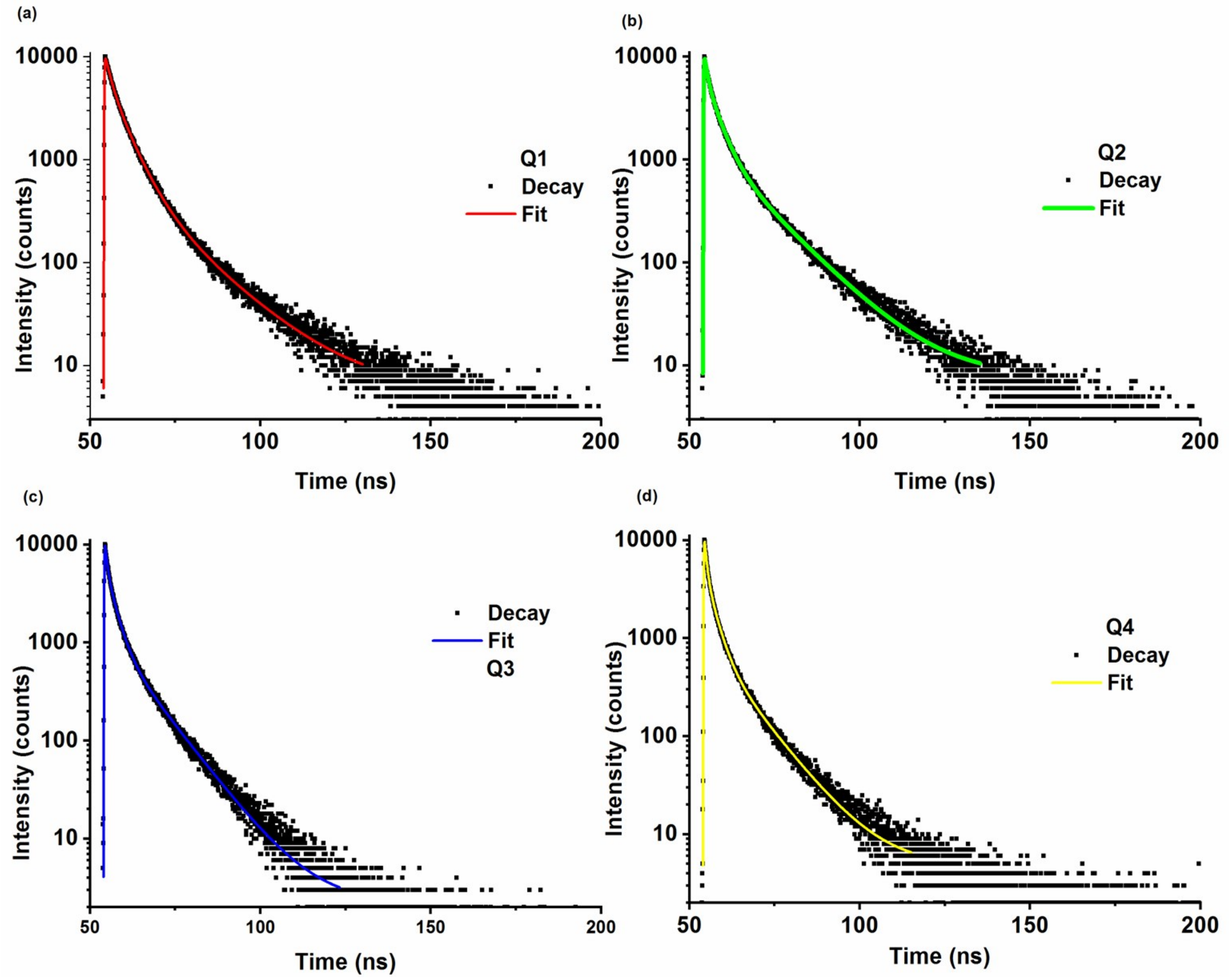


Fig S11: Tri-exponential fit of TCSPC data for **2a** when excitation was done with 374 nm laser and emitted photon was collected at 415 nm.

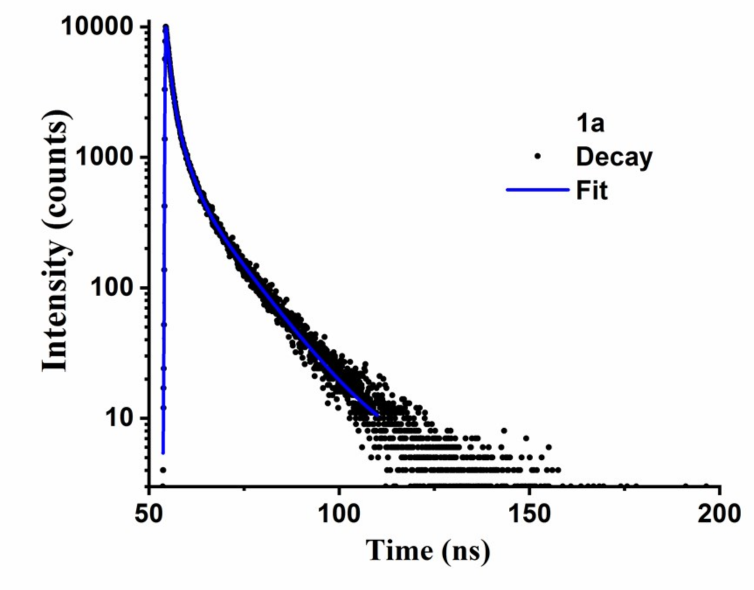


Fig S12: Bi-exponential fit for ligand **1a**, at 410 nm and 374 nm excitation laser.

Table 1 : Lifetimes of Zinc-complexes **2a** and **2b** under various conditions, including quenchers Q1-Q4.

Entry	Sample	τ_1	τ_2	τ_3	x^2	Condition
1[a]	**2a**	1.2±0.4	3.8±0.9	12.2±1.0	1.07	DCM/degassed
2	**2b**	1.9	4.7	10.4	1.01	DCM/degassed
4	**2a**	1.6	4.8	14.5	1.35	Q1
5	**2a**	0.8	3.5	12.9	1.30	Q2
6	**2a**	0.5	2.4	9.6	1.39	Q3
7	**2a**	0.6	2.6	9.7	1.29	Q4

[a] *Lifetime reported for catalyst **2a** is the mean lifetime calculated from 3 sets of experiments.*

5. Cyclic voltammetry and excited state calculation

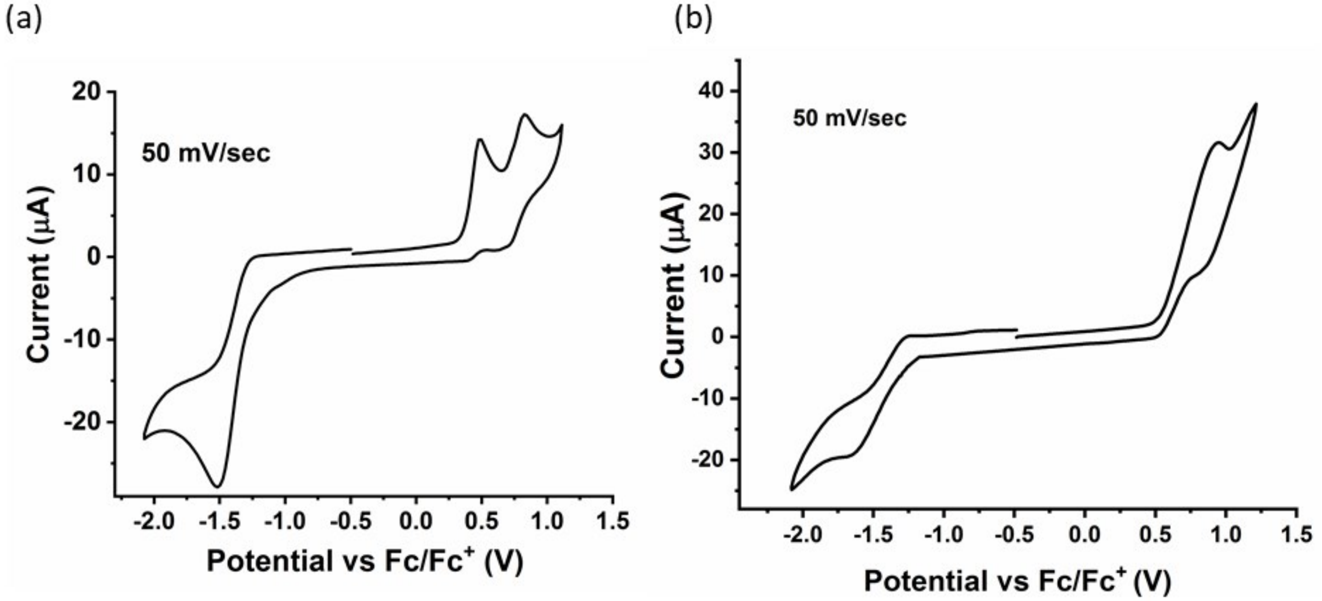


Fig S13: a) CV of 1 mM of **2a** in DCM where 0.1 M solution of tetrabutyl-ammonium hexafluorophosphate salt was used as an electrolyte, b) CV of **2b** in DCM under the same conditions.

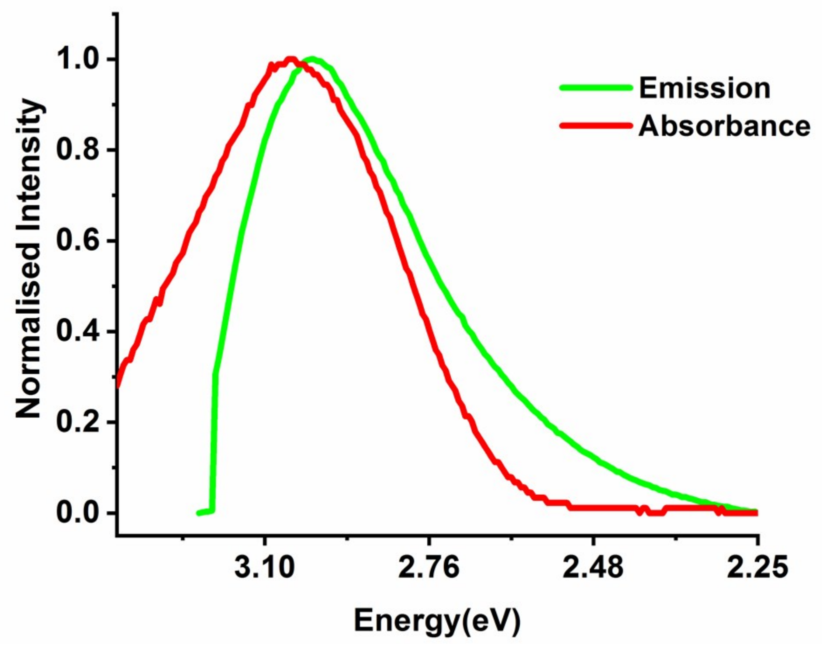


Fig S14: Normalized absorption and emission spectra of **2a** in DCM. The value of E_{00} has been considered as the energy at their point of intersection.

7. Optimisation of the procedure for ATRA reaction

Photochemical reaction setup: For all the photochemical reactions, the reaction tubes were packed with styrene, CBr_4, DCM, **2a** and DIPEA in an anaerobic environment. Experiments were performed using commercially available LED strips of 14 W power with emission maximum at 465 nm.

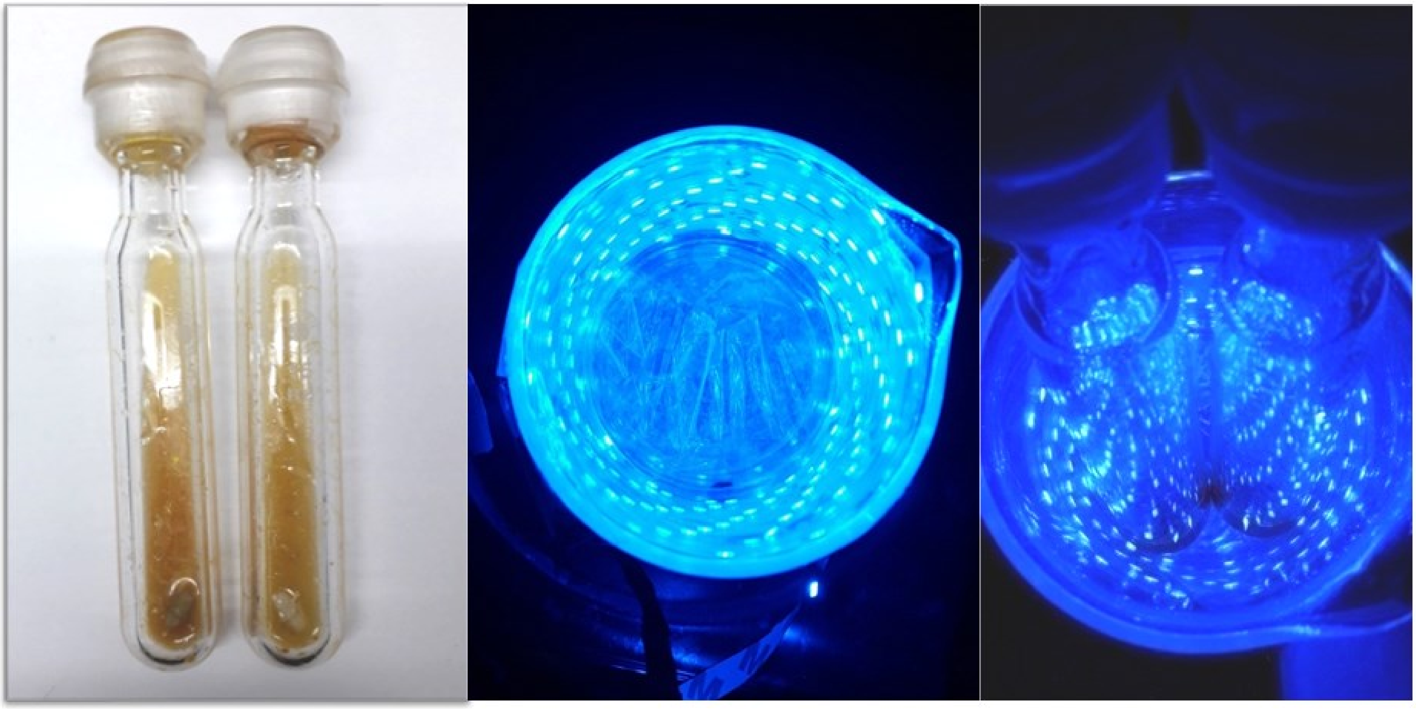


Fig S15: Sealed tubes packed under anaerobic atmosphere and kept for stirring in blue light setup.

A flame dried seal tube equipped with magnetic bead was packed with a solution of styrene (2 equiv), CBr_4 (1 equiv), DIPEA (1 equiv) and **2a** in DCM (2 mL) in glove box and irradiated with blue light. After 24 hours of reaction time, the reaction mixture was concentrated in vacuum and pure product was isolated by column chromatography using silica gel (100-200 mesh) and hexane as eluent.

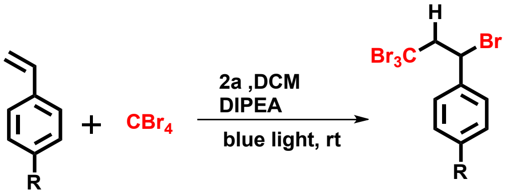


Table2: Optimisation condition for ATRA reaction with CBr_4 and styrene.

S.No.	Catalyst	mol%	Time	Yield ^{a}
1.	-	-	24	0
2.	2a	2%	24	70
3.	2b	2%	24	68
5.	2a	1%	24	74
6.	2a	0.5%	24	71
7.	2a	0.3%	24	45
8.	**2a**	**0.5%**	**18**	**71**
9.	2a	0.5%	12	59
10.	2a	0.5%	18^b	2
11.	2a	0.5%	18^c	No product
13.	2a	0.5%	18^d	38^e

NOTE: The reaction was conducted at room temperature. [a]The ^1H NMR yields in $CDCl_3$ using 4-chlorobenzaldehyde as the internal standard. [b]Dark reaction, where seal tubes were wrapped in aluminium foils and kept for stirring in dark. [c]Irradiation with white light LED strips. [d]TEA was used as photoreductant. [e]Isolated yield.

8. Mechanistic studies for the photo redox catalysis

8.1 Stern-Volmer kinetics in TEA and DIPEA.

Preparation of sample: In a Schlenk flask, 10^{-3} M solution of catalyst **2a** was prepared in 10 mL of dry and degassed DCM. Double dilution of the above solution was done to prepare a 10^{-9} M stock solution of **2a** in 10 mL DCM. Lifetime quenching experiments were done in 10^{-6} M **2b** concentration. For each quencher concentration, samples were prepared from the above stock solutions in 10 mm, 4 mL screw cap quartz cuvette. Integrated fluorescence intensities were plotted against absolute quencher concentration using Stern-Volmer equation given as;

$$\frac{I_o}{I} = 1 + K[Q] = 1 + k_q.\tau.[Q]$$

where, K = Stern-volmer constant which is product of radiative lifetime(τ) and quenching rate constant (k_q). I_o = fluorescence intensity of in absence of quencher, I = fluorescence intensity in the presence of quencher and [Q] is the concentration of quencher.

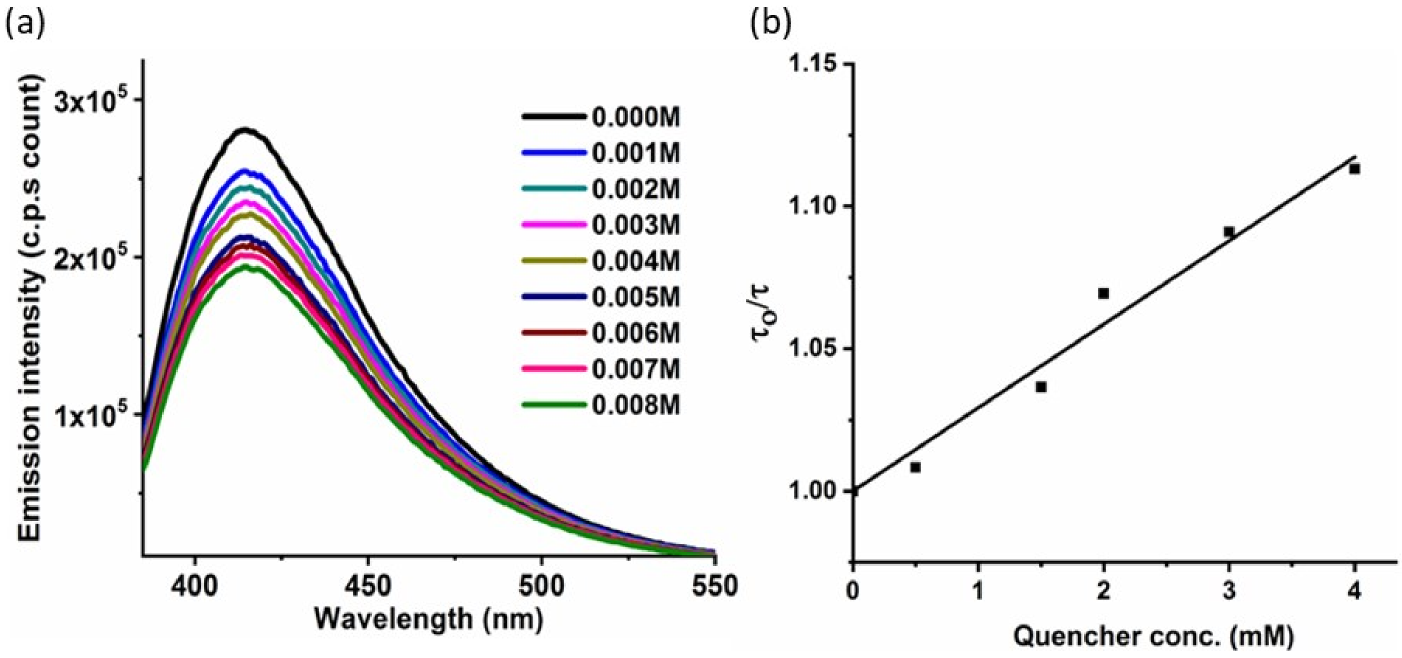


Fig S16: (a) Fluorescence-quenching of **2a** upon excitation at 370 nm in DCM (b) Lifetime-quenching of **2a** upon excitation at 374 nm laser in DCM in the presence of DIPEA

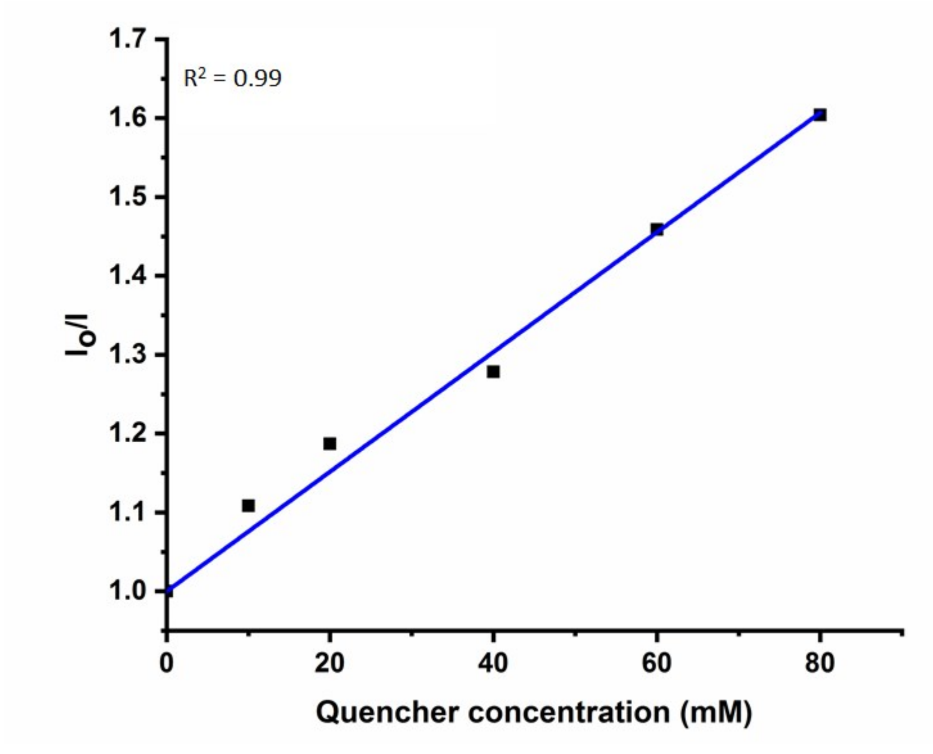


Fig S17: Stern-Volmer quenching of **2a** in anhydrous DCM under inert atmosphere when TEA is used as a sacrificial photoreductant.

8.2 Determination of the light intensity at 436 nm. [S3]

The photon flux of the spectrophotometer was determined by chemical actinometry experiment using standard ferrioxalate (0.15 M). Potassium ferrioxalate hydrate (0.73 g) was dissolved in 10 mL, 0.05 M H_2SO_4. Phenanthroline (10 mg) and sodium acetate (2.25 g) were dissolved in 10 ml, 0.5 M H_2SO_4. Both solutions were stored in the dark. The ferrioxalate solution (2.0 mL) was placed in a cuvette (10 mm) and irradiated for 90.0 seconds at λ = 436 nm with an emission slit width of 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm, using an UV-Visible spectrophotometer (7600 Photolab). A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using given equation.

$$Fe^{2+} = \frac{V \,.\, \Delta A}{l.\ \varepsilon}$$

$$Fe^{2+} = \frac{0.00235\ * 2.2}{1\ * 11{,}100} = 4.657 * 10^{-7}$$

Where, V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA (=2.2) is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux was calculated using given equation,

$$Photon\ flux = \frac{mol\ Fe^{2+}}{\emptyset\,.t\,.f}$$

$$Photon\ flux = \frac{4.65 \times 10^{-7}}{1.01 \times\ 90 \times 0.99} = \ = \ 5.17\ \times\ 10^{-9} sec^{-1}$$

Where, ϕ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 436 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ = 436 nm. Here f = 1- $10^{-2.2}$ = 0.99

8.3 Determination of reaction quantum yield.

In a 4 ml quartz cuvette, equipped with magnetic bead and fitted with screw cap, added styrene (114 µl, 1 mmol), DIPEA (174 µl, 1 mmol), CBr_4 (189 mg, 1 mmol), **2a** (5 mg, 0.005 mmol) and dry DCM (2ml) inside glove box. The reaction mixture was irradiated (λ = 436 nm, slit width= 10.0 nm) for 3600 sec at RT. Reaction quantum yield is calculated using the photon flux, determined above and moles of product formed using given equation:

$$\emptyset = \frac{mol\, product}{flux\, .t\, .f}$$

$$\emptyset = \frac{4.0 * 10^{-5}}{5.17 * 10^{-9} * 3600 * 0.99} = 2.1$$

8.4 Kinetics of reaction

In a flame dried seal tube equipped with septum and bead, ATRA reaction was set using general procedure as described in section 7. At a regular interval of 2 hrs, aliquot was syringed out and dried under high vacuum. Internal standard (IS), 4-chlorobenzaldehyde was added in a ratio, styrene: I.S. = 1:2 and recorded ^{1}H NMR in $CDCl_3$. The yield calculated from NMR spectroscopy, was plotted for product growth and rate vs. time.

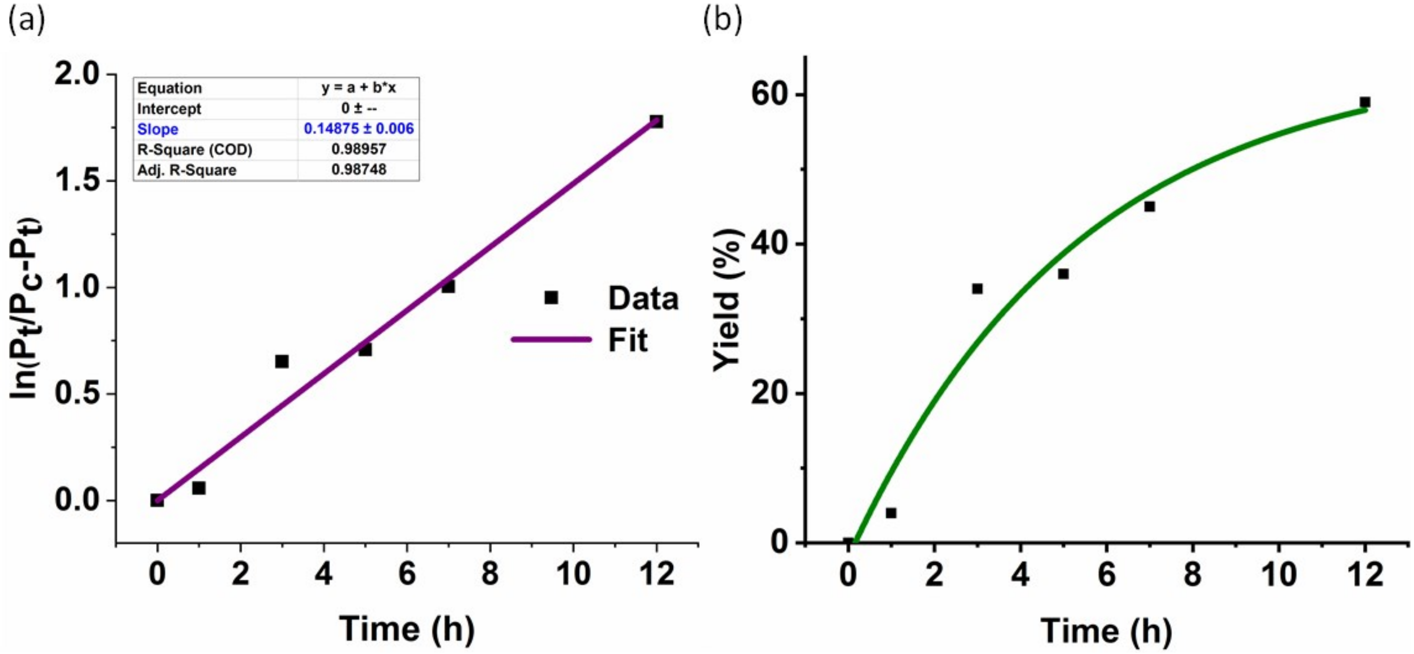
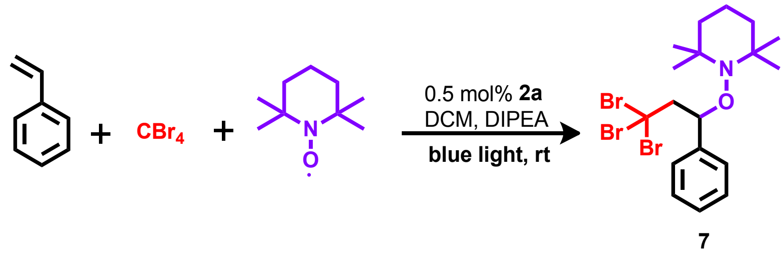


Fig S18: (a) Plot of $\ln P_t/P_c$-$P_t$vs. time for rate constant calculation (b) Product growth plot with time.

8.5 Radical-trapping experiment using TEMPO

In a flame dried Schlenk flask equipped with magnetic bead, styrene (0.10 mmol), CBr_4 (0.10 mmol), DIPEA (0.10 mmol), TEMPO (2 equiv) and catalyst **2a** (0.50 mol %) were added. To this was added freshly distilled and degassed DCM (2.0 mL) and irradiated with blue LED for 16 h. TEMPO adduct of the trapped intermediate radical was analysed by ESI high-resolution mass spectrometric method. $[M]^+$calcd. = 508.9564, found = 508.9487.



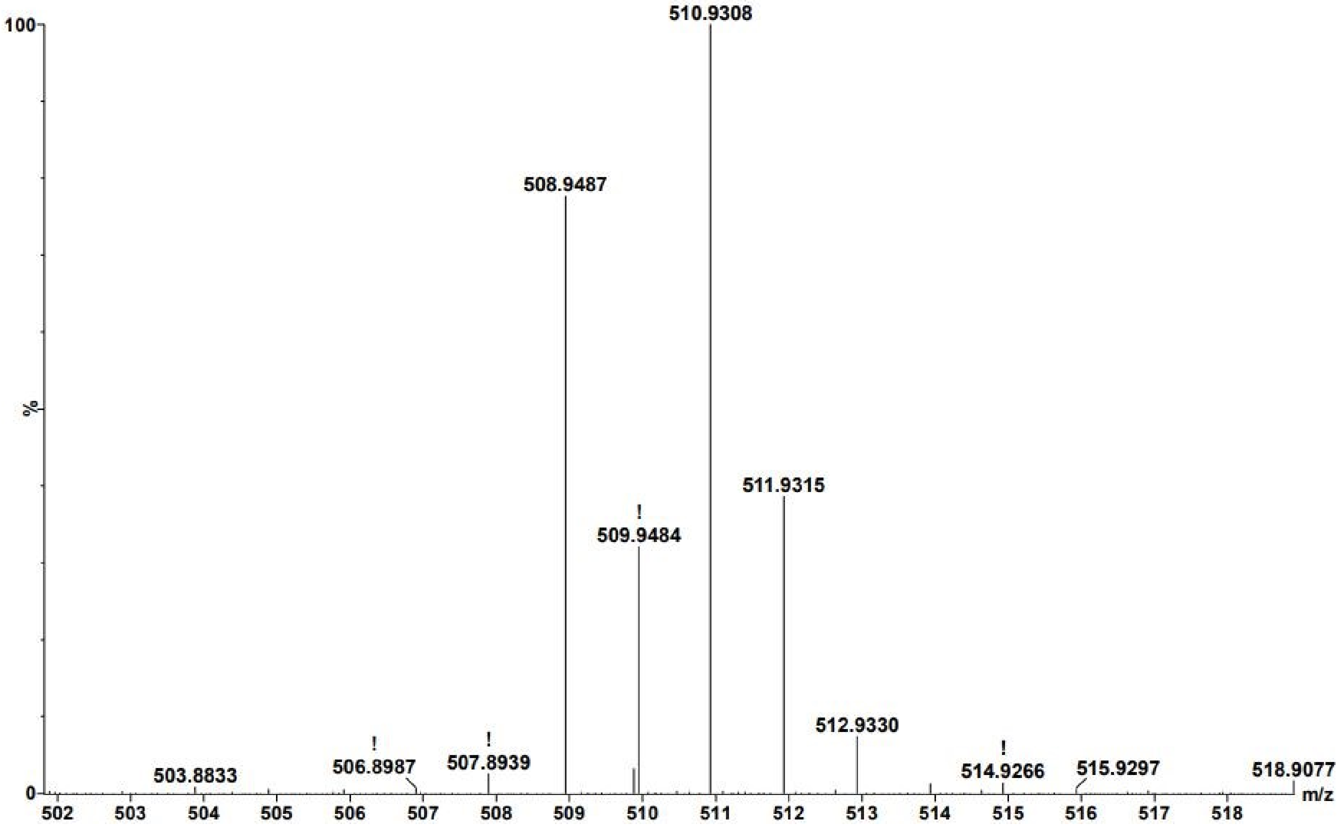
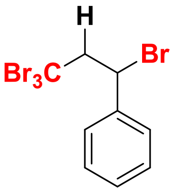
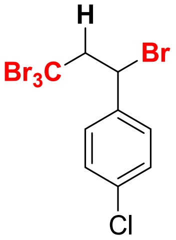


Fig S19. HRMS (ESI+, m/z), showing M+ peak and isotopic pattern for TEMPO-adduct, **7**.

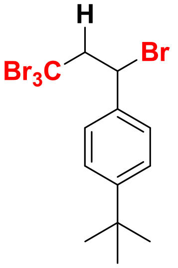
9. Spectroscopic characterization of products from ATRA reactions catalyzed by 2a



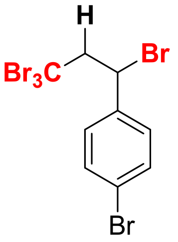
(1,3,3,3-tetrabromopropyl) benzene. Purified using column chromatography over silica (60-120 mesh) as colourless oil in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.31 (m, 3H), 5.38 – 5.27 (m, 1H), 4.16 – 4.02 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.78, 128.99, 128.91, 128.18, 66.44, 50.09, 35.04.



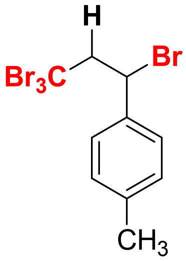
1-chloro-4-(1,3,3,3-tetrabromopropyl) benzene. Purified using column chromatography over silica (60-120 mesh) as white solid in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.29 (d, *J* = 4.8 Hz, 1H), 4.13 – 3.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.18, 134.78, 129.56, 129.10, 66.23, 48.92, 24.63



1-(tert-butyl)-4-(1,3,3,3-tetrabromopropyl) benzene. Purified using column chromatography over silica (60-120 mesh) as white solid in 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (q, *J* = 7.9 Hz, 4H), 5.40 – 5.30 (m, 1H), 4.12 (qd, *J* = 15.6, 5.0 Hz, 2H), 1.34 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.26, 137.94, 127.83, 125.94, 66.66, 50.35, 35.43, 34.83, 31.42.



1-(bromo)-4-(1,3,3,3-tetrabromopropyl)benzene. Purified using column chromatography over silica (60-120 mesh) as white solid in 68% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 36.8, 8.0 Hz, 4H), 5.44 – 5.25 (m, 1H), 4.16 – 3.92 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.29, 134.89, 129.69, 129.22, 66.34, 49.06, 34.78.



1-methyl-4-(1,3,3,3-tetrabromopropyl)benzene. Reaction mixture was dried under high vacuum and NMR yield was recorded with 2-chlorobenzaldehyde as internal standard revealing 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 5.40 – 5.16 (m, 1H), 4.12 – 3.92 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.84, 132.20, 131.72, 129.97, 66.32, 49.05, 34.75, 21.00.

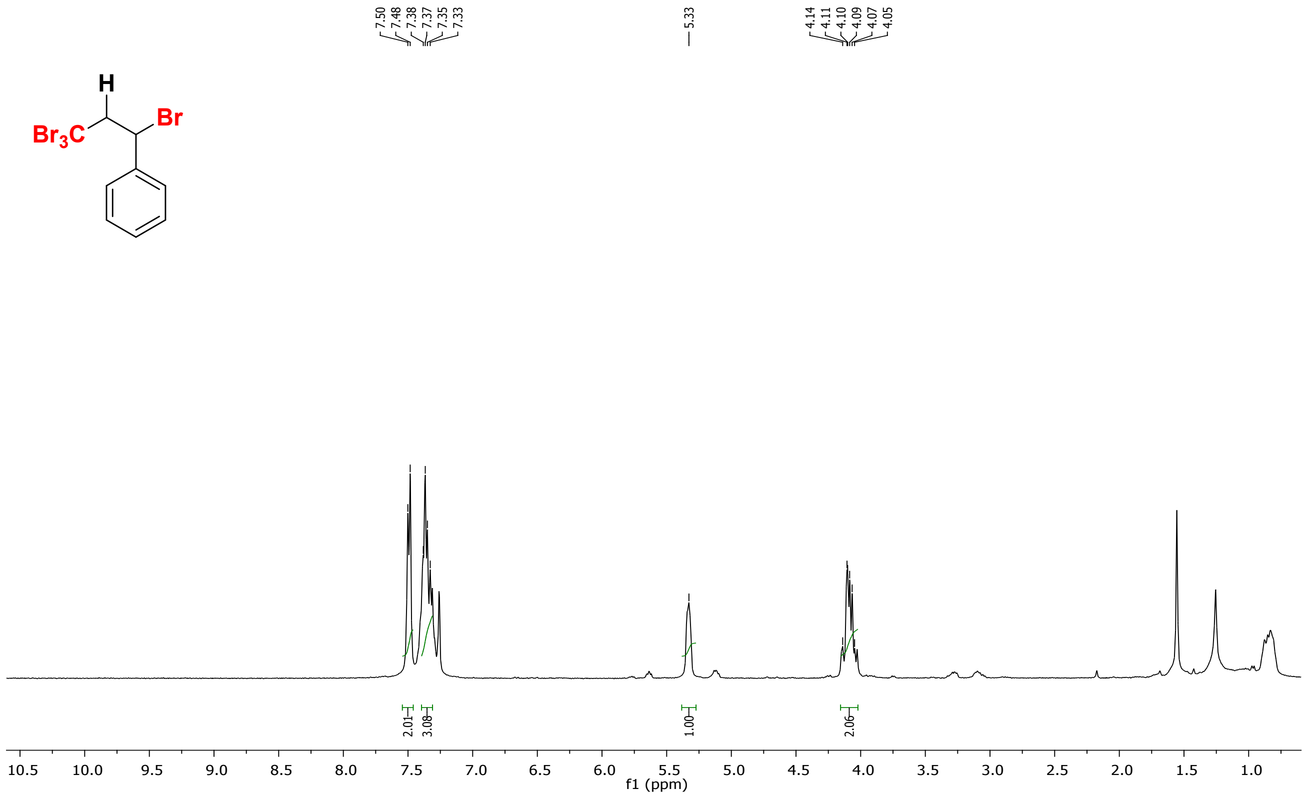


Fig S20: ^{1}H NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.

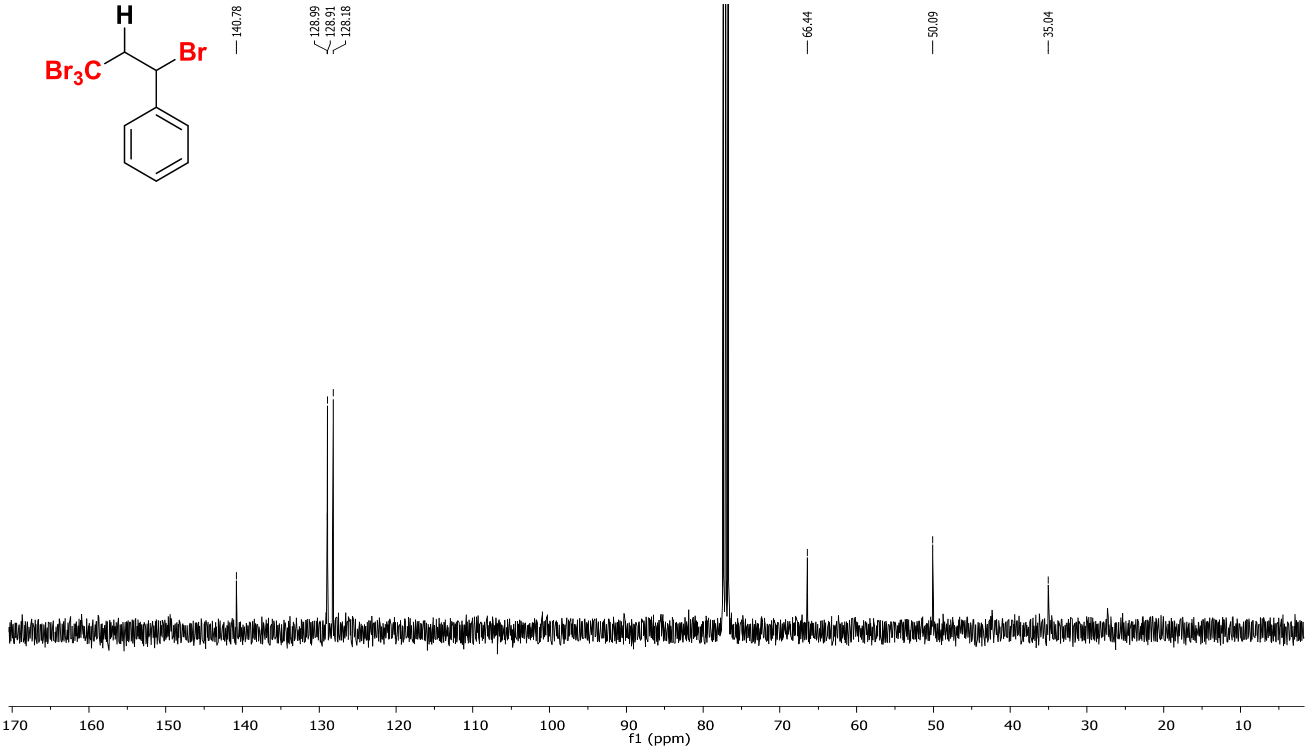


Fig S21: ^{13}C NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 77.4 ppm.

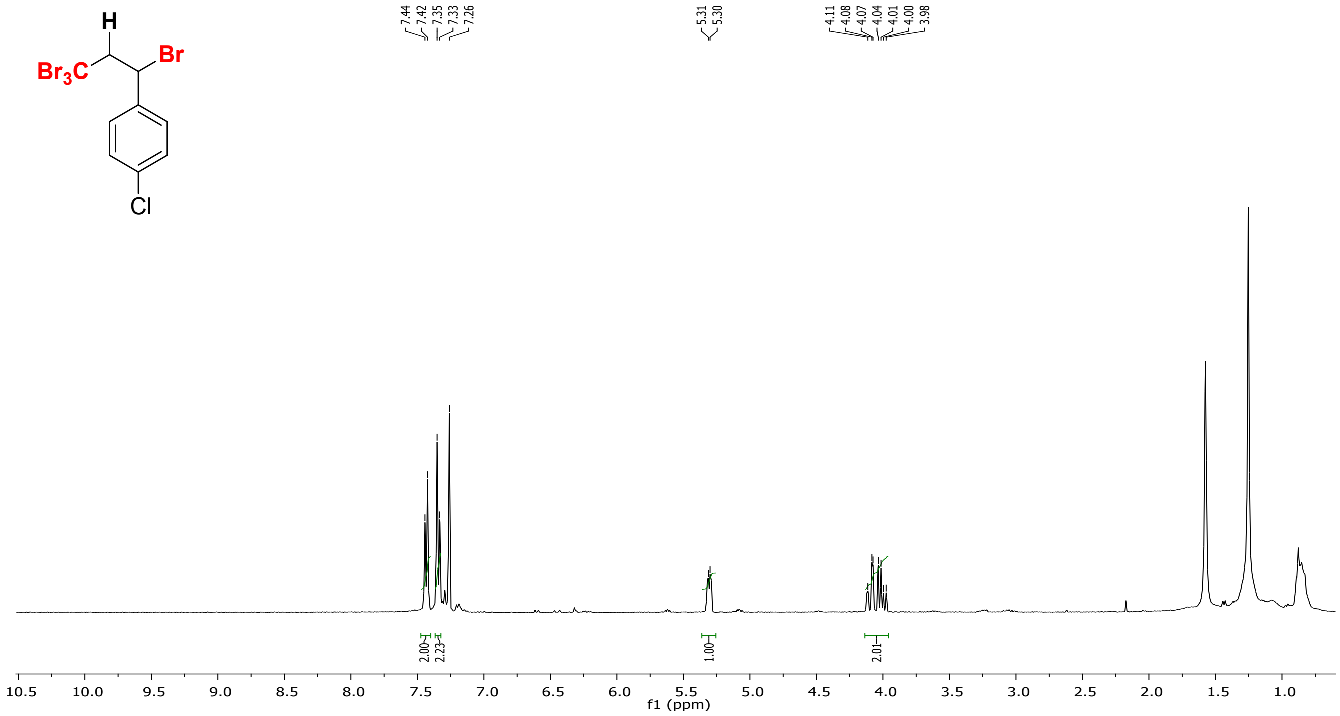


Fig S22: ^{1}H NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.

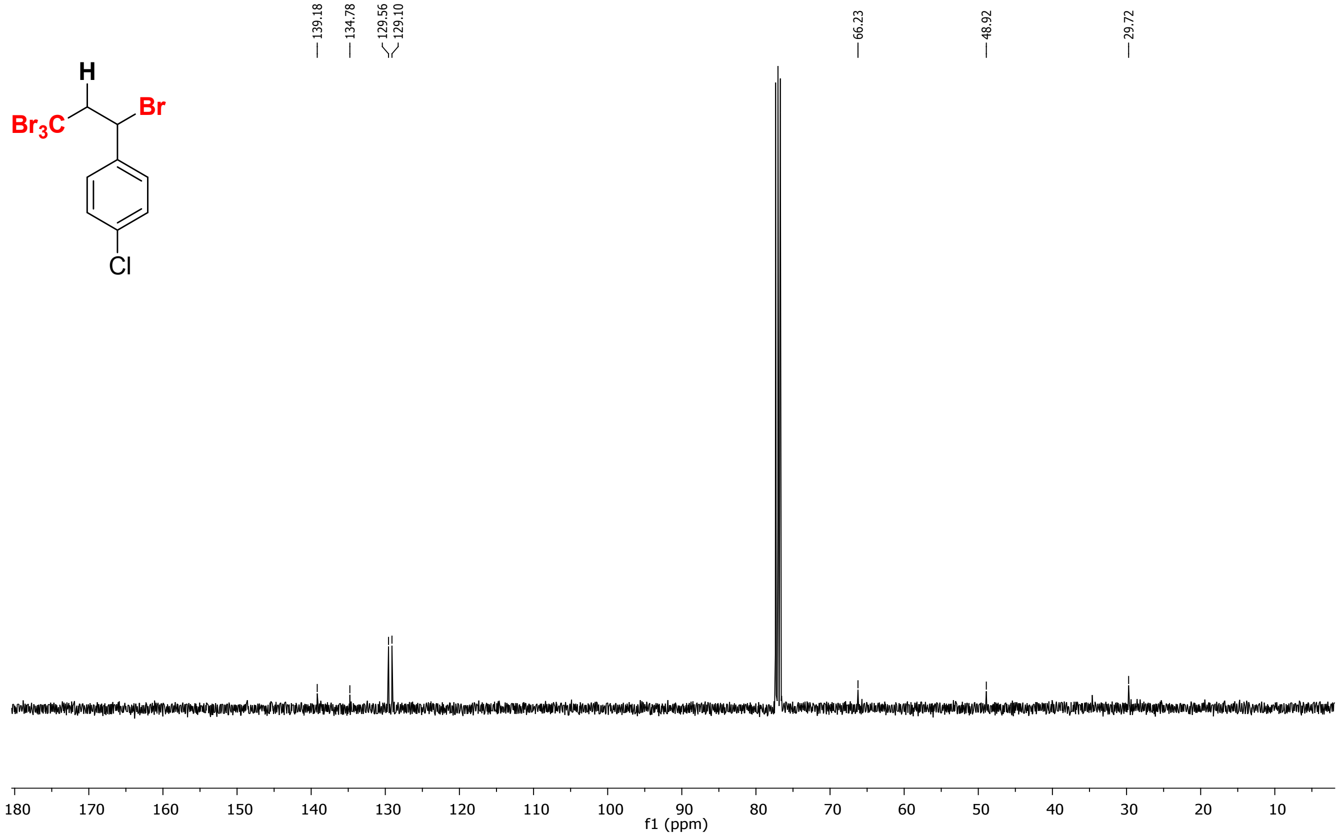


Fig S23: ^{13}C NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 77.4 ppm.

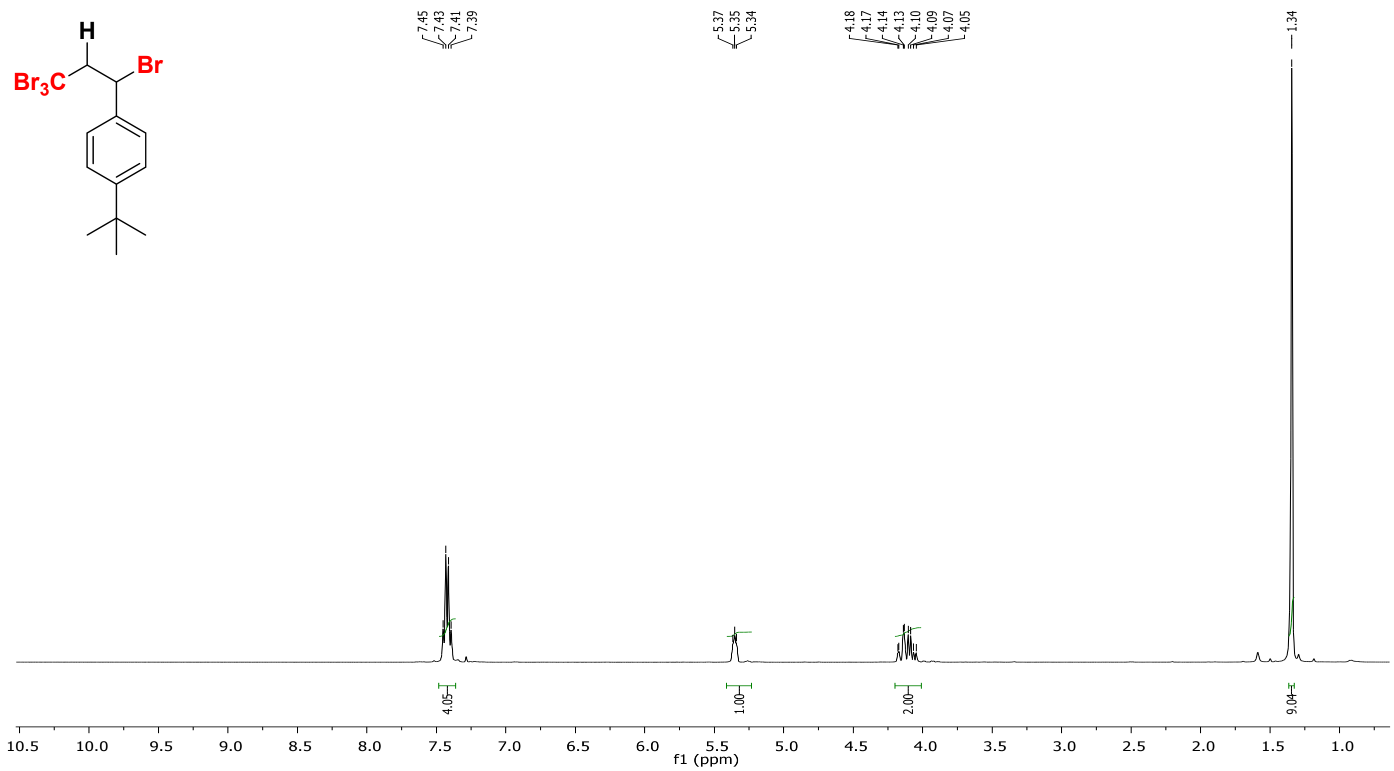


Fig S24: ^{1}H NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.

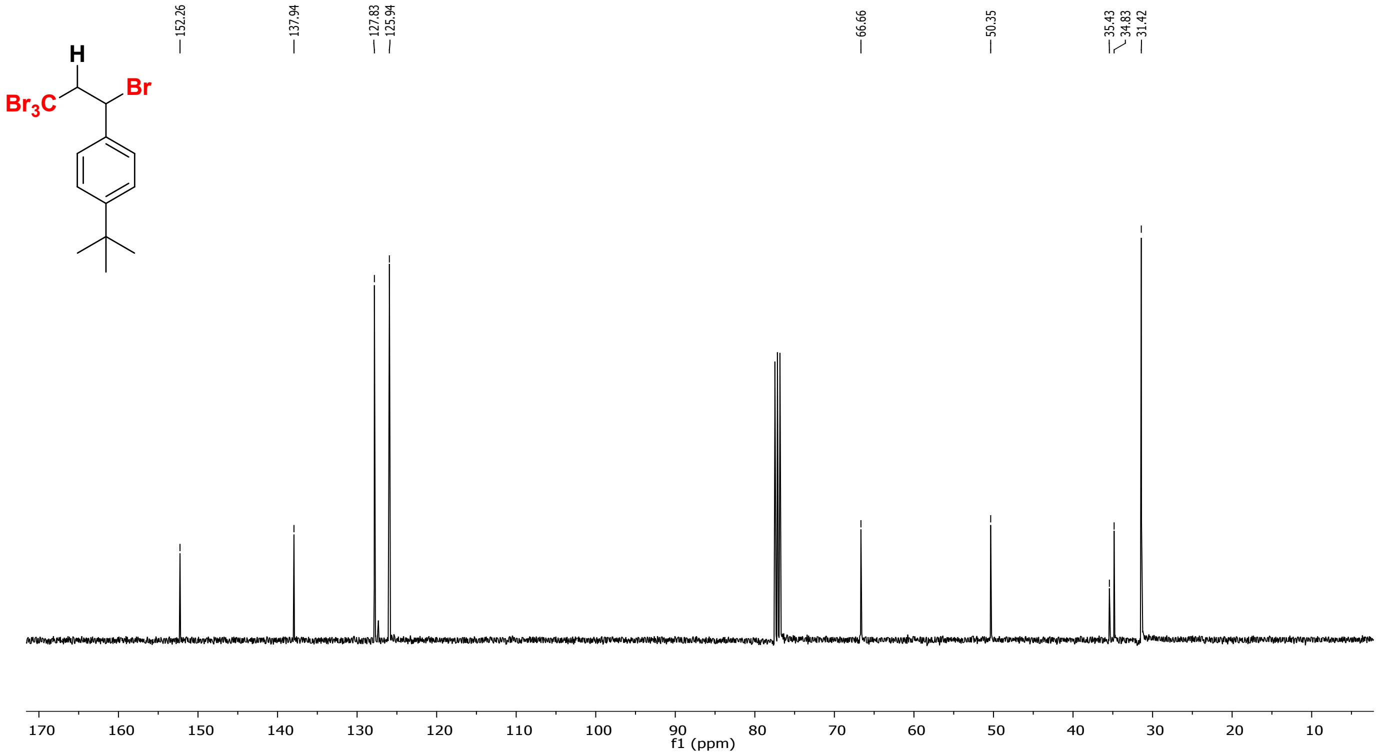
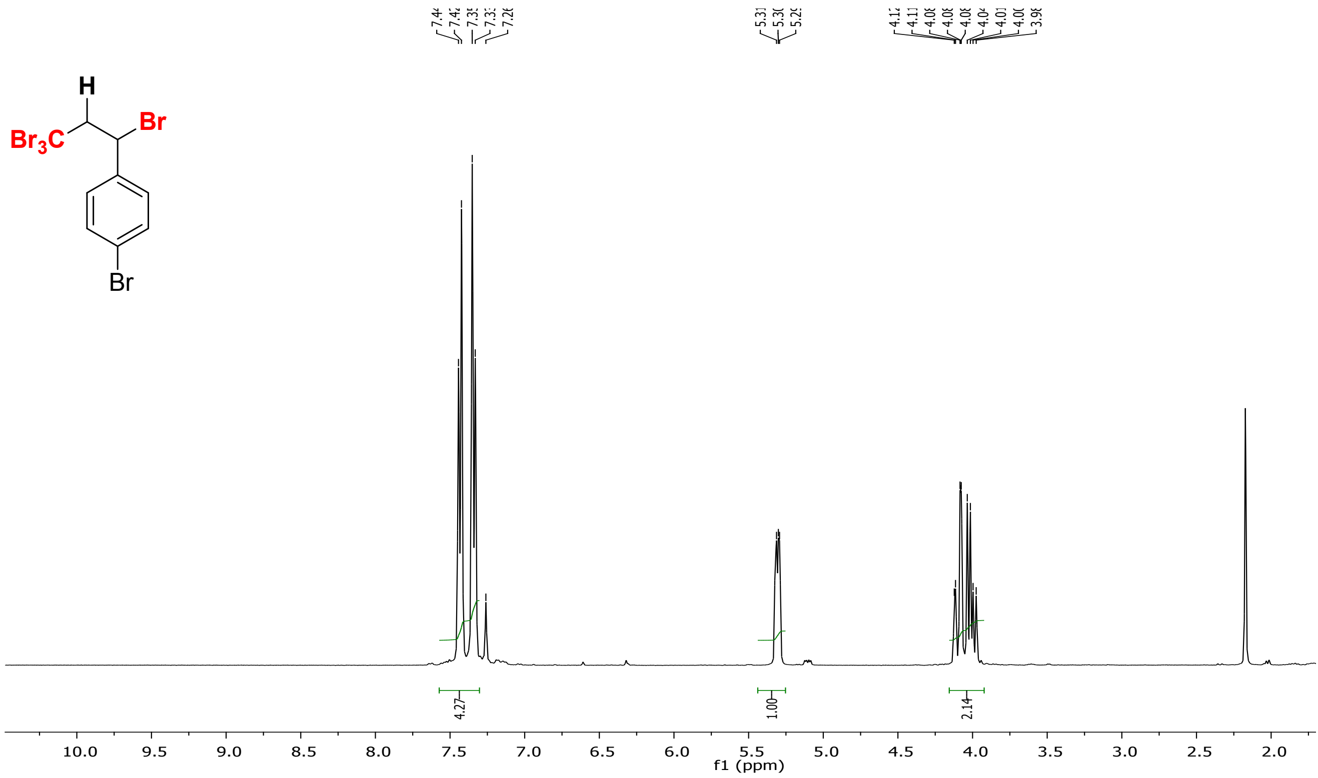
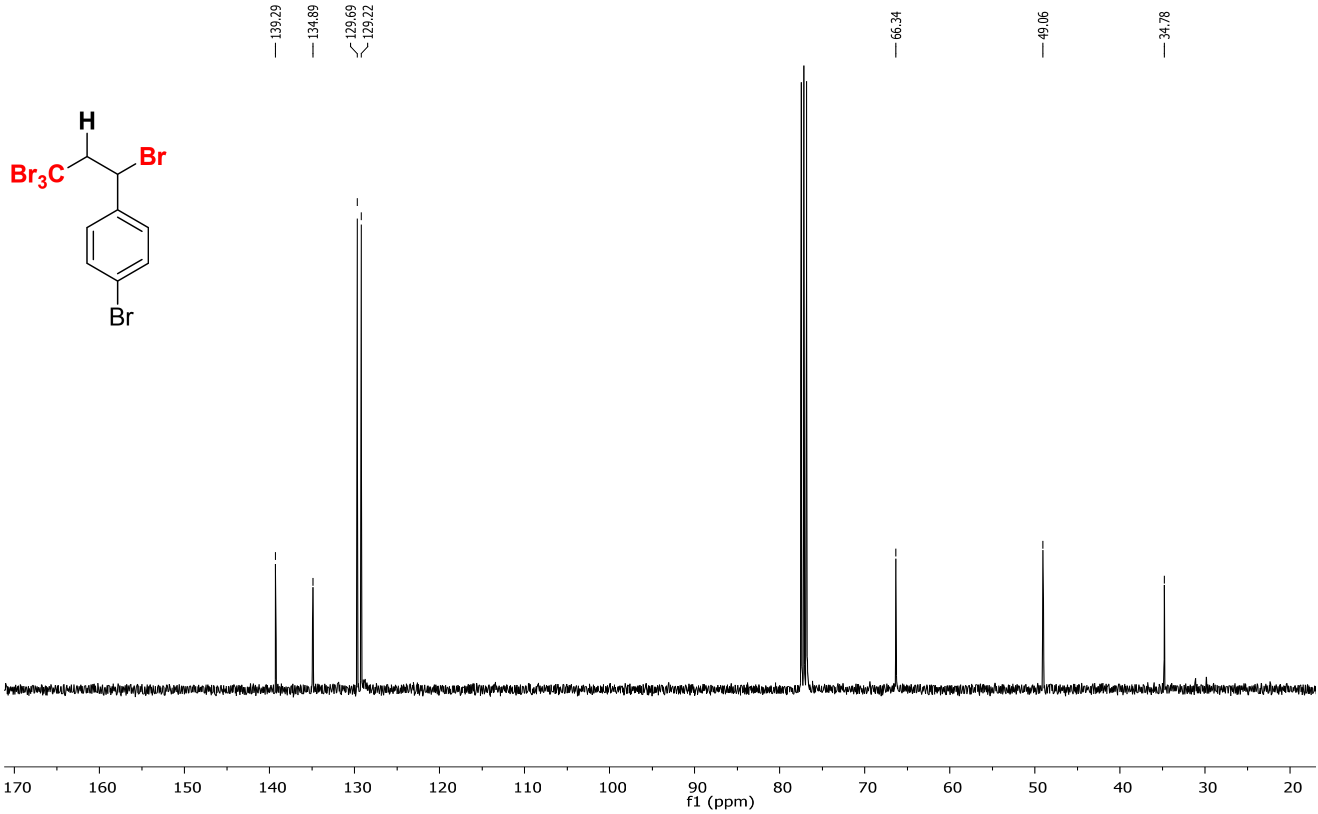


Fig S25: ^{13}C NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 77.4 ppm.



F

ig S26: ^{1}H NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.



F

ig S27: The ^{13}C NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 77.4 ppm.

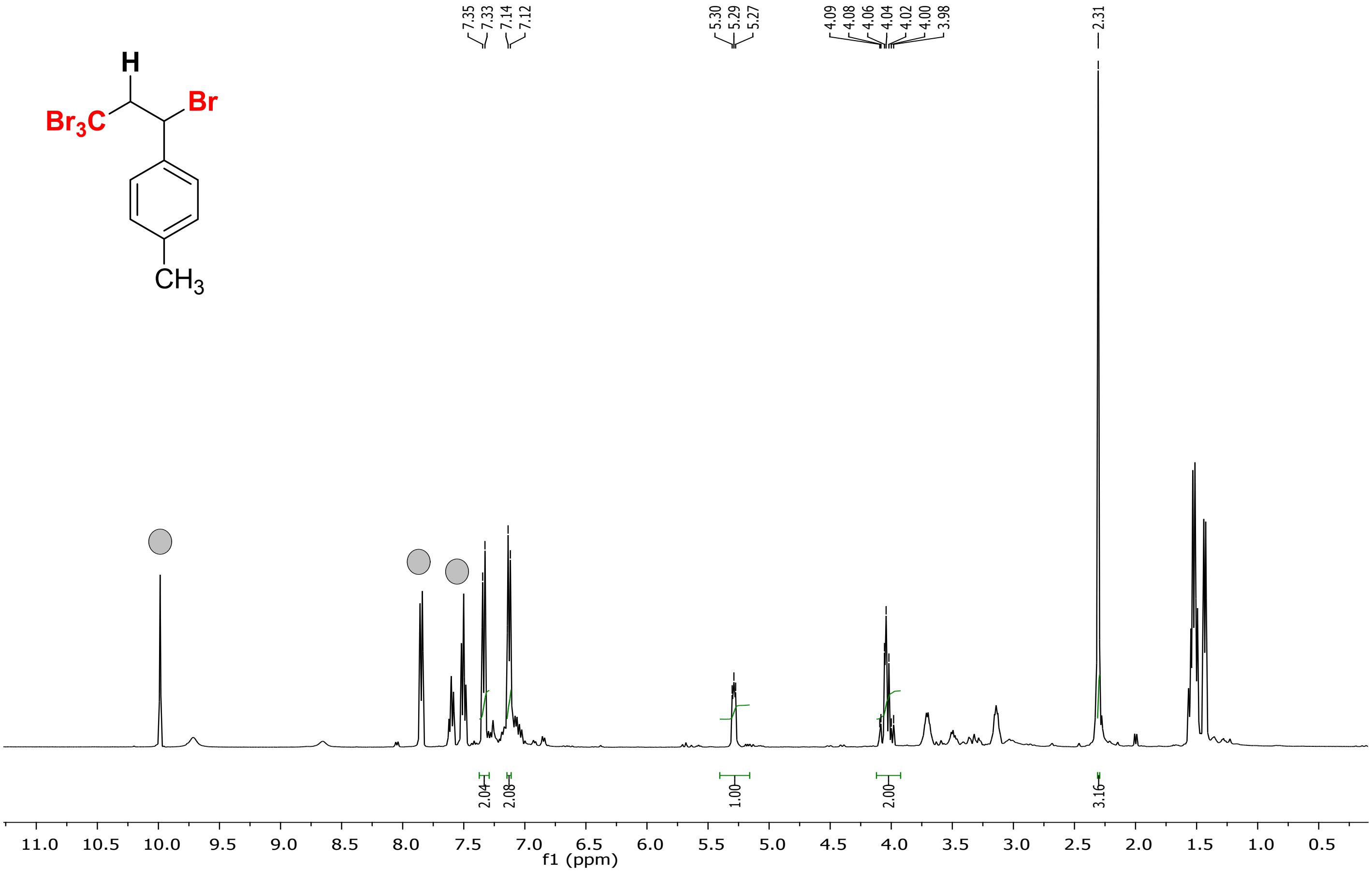


Fig S28: ^{1}H NMR spectrum recorded in $CDCl_3$, the symbol (●) designates the resonances for internal standard 4-chlorobenzaldehyde.

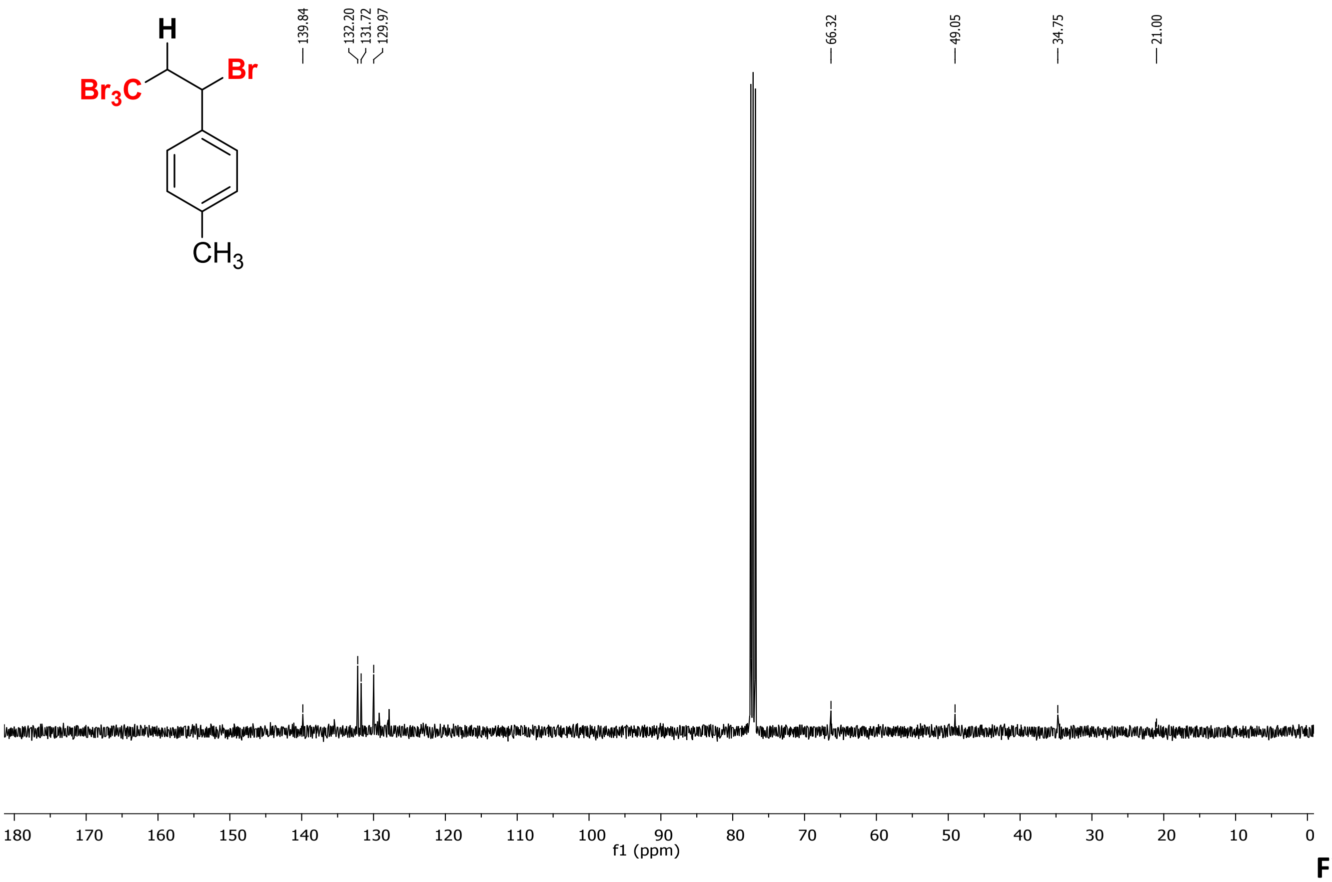


Fig S29: The ^{13}C NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 77.4 ppm.

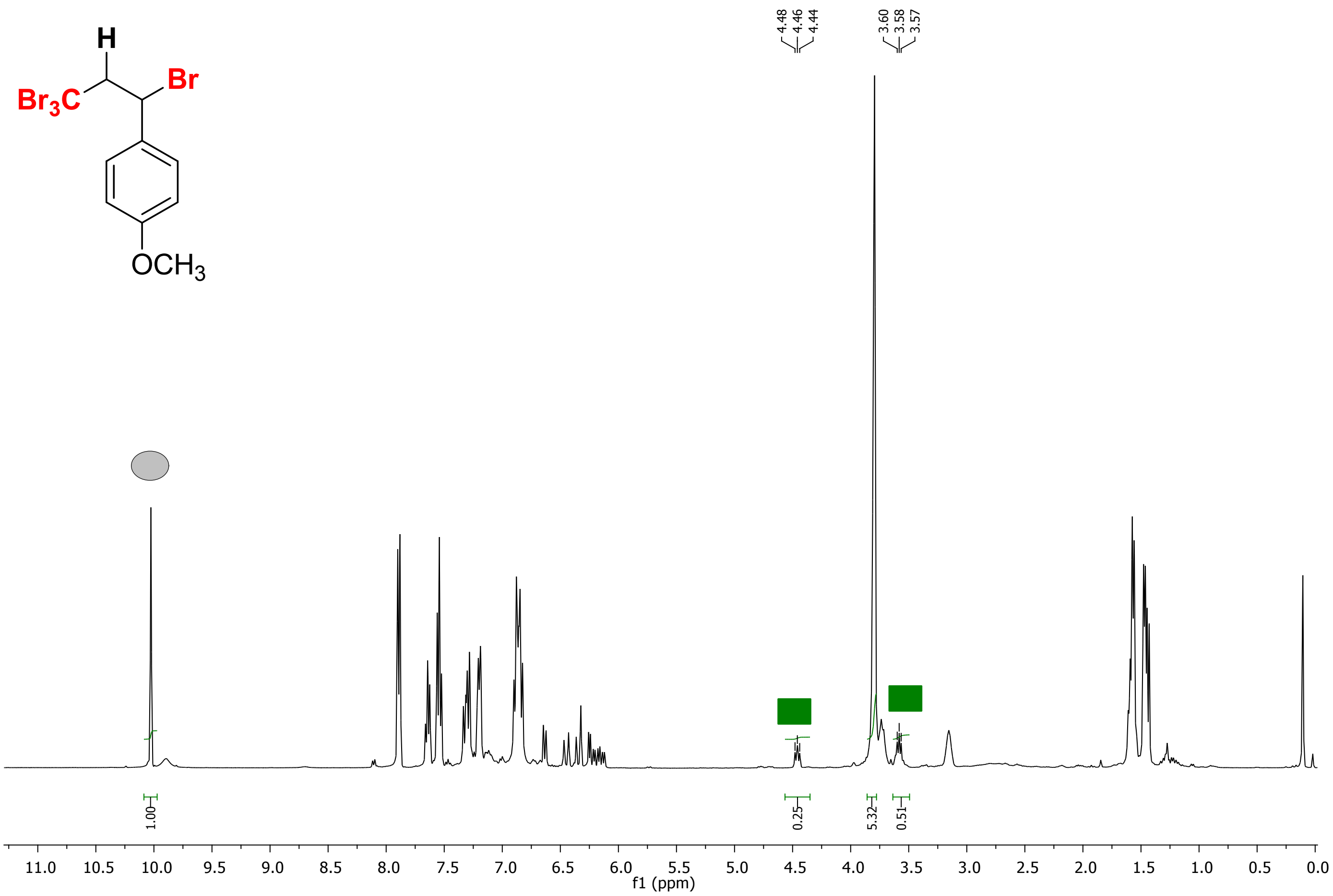
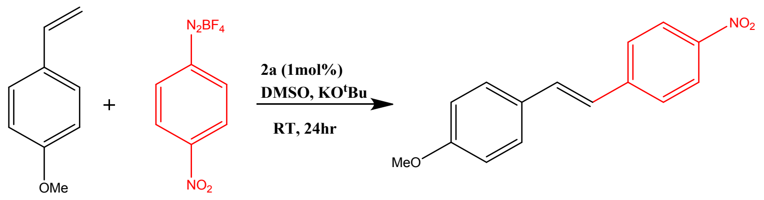


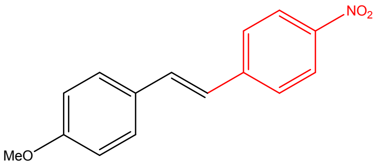
Fig. S30: ^{1}H NMR spectrum recorded in $CDCl_3$, the symbol (●) designates the resonances for internal standard 4-chlorobenzaldehyde.

NB: The final ATRA product from 4-methoxystyrene undergoes hydrolysis in silica gel quickly.

10. Photochemical Meerwein arylation reaction



Styrene (0.1 mmol, 1 equiv), 4-nitro-phenyldiazonium salt (0.2 mmol, 3 equiv), **2a** (1 mol %), and KO^{t}Bu (0.2 equiv) were taken in a 15 mL seal tube, and DMSO (2 mL) was added to it. The reaction mixture was stirred for 24 hrs, at room temperature. After completion of the reaction, product was extracted in ethyl-acetate and washed with ice-cold water. Organic layer was collected over $MgSO_4$. Product was purified by column chromatography on silica gel using hexane/EtOAc (9:1) in high yield (92%)



1-methoxy-4-(4-nitrostyryl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 16.4 Hz, 1H), 7.01 (d, *J* = 16.2 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 3.85 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.26, 144.31, 132.92, 128.96, 128.44, 126.52, 124.18, 124.10, 114.36, 55.40.1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 147.36, 134.26, 131.02, 129.22, 128.63, 117.46.

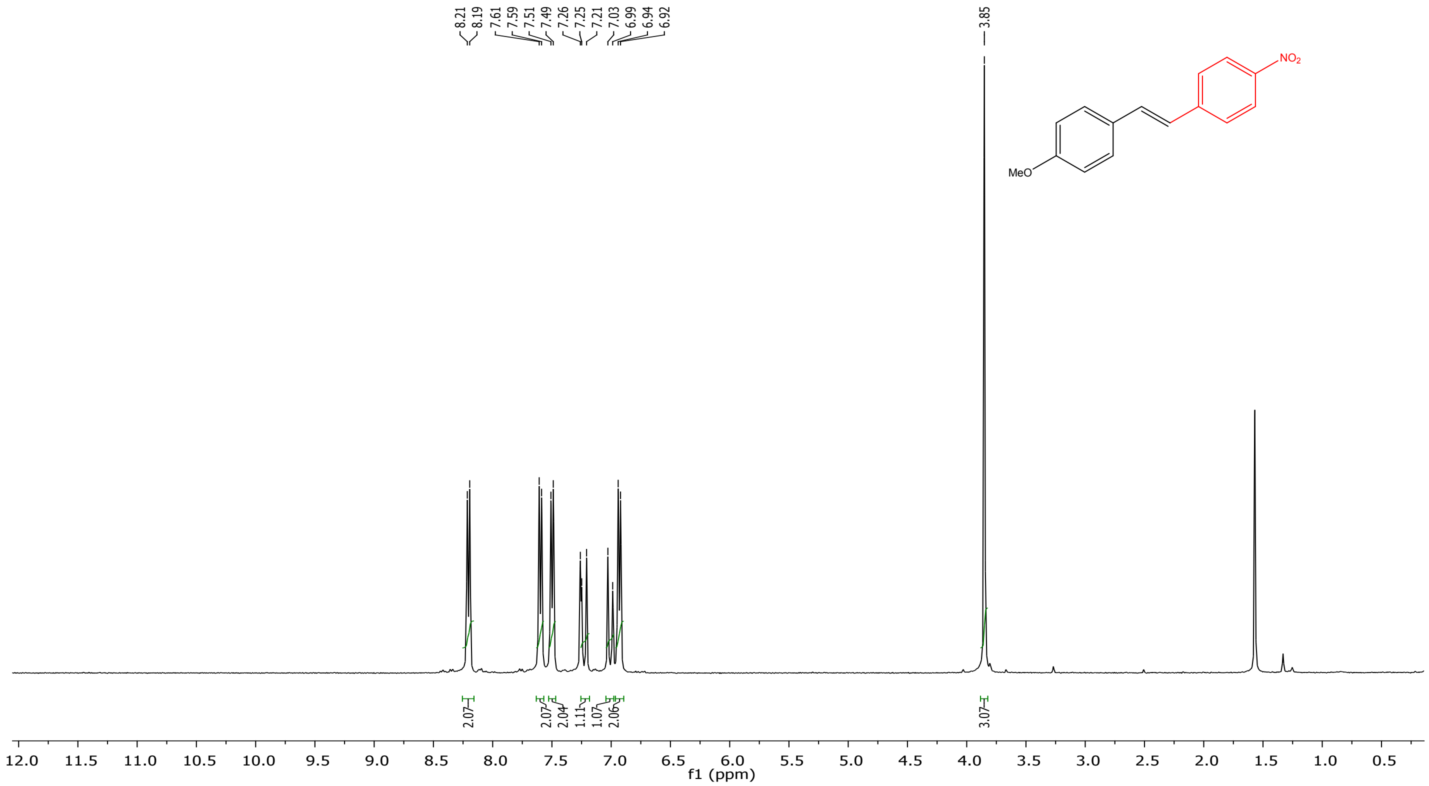


Fig S31: ^{1}H NMR spectrum recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.

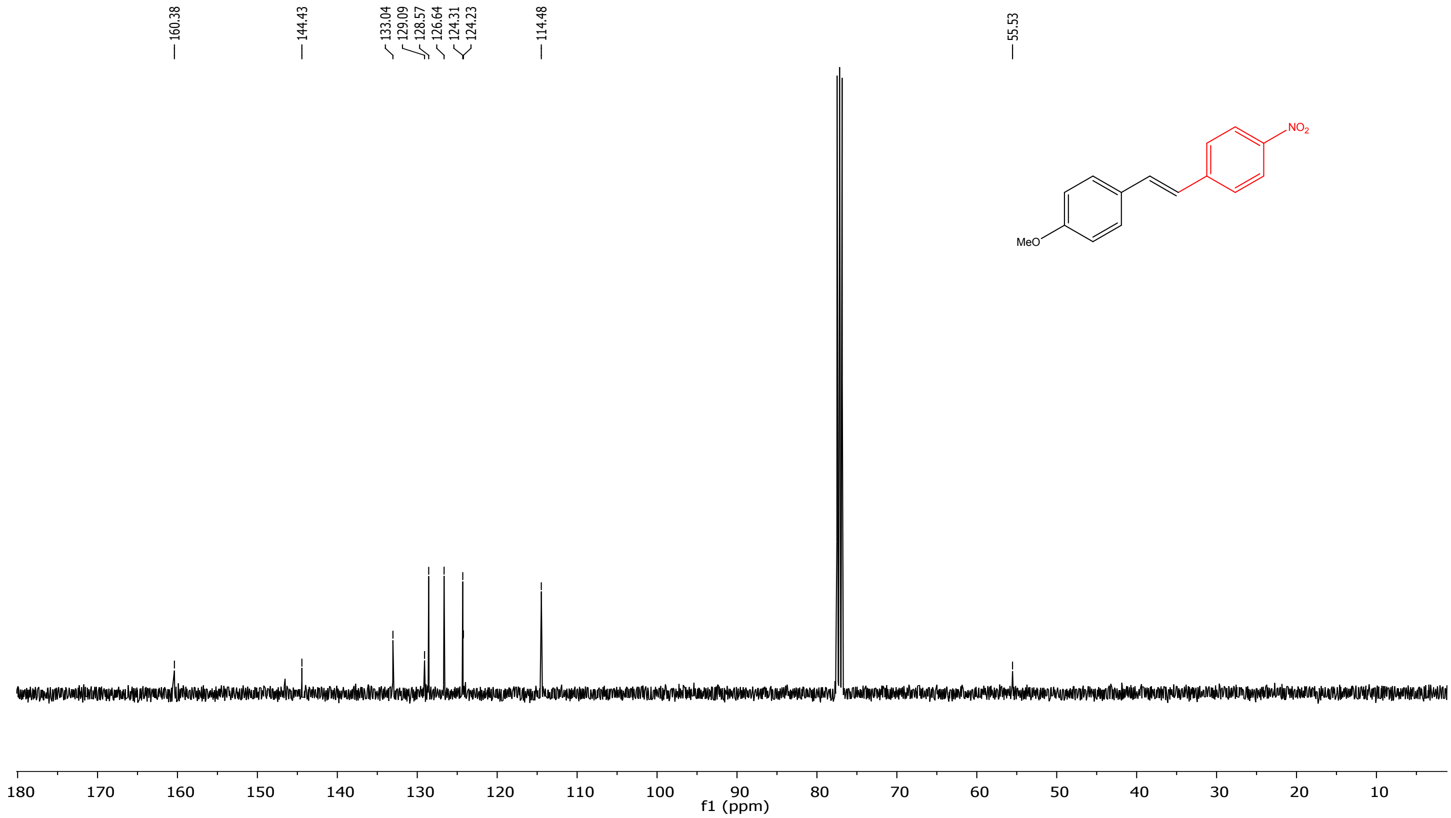


Fig S32: ^{13}CNMR spectrum recorded in $CDCl_3$, solvent residual peak is at 77.4 ppm.

11. Crystallographic data, bond length and bond angles of 2a and 2b

Crystallographic data for catalyst (2a)

Empirical formula	$C_{54}H_{42}N_4Zn$
Formula weight	812.28
Temperature/K	296(2)
Crystal system	Monoclinic
Space group	C2/c
a/Å	21.5494(6)
b/Å	10.5308(3)
c/Å	19.1721(5)
α/°	90
β/°	106.179(3)
γ/°	90
Volume/Å^3	4178.47(19)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.630
F(000)	1696.0
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/° 5.794 to 65.65	
Index ranges	-32 ≤ h ≤ 26, -15 ≤ k ≤ 8, -16 ≤ l ≤ 29
Reflections collected	16101
Independent reflections	7335[R_{int} = 0.0232, R_{sigma} = 0.0315]
Data/restraints/parameters	7335/0/267
Goodness-of-fit on F^2	1.03
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.1023
Final R indexes [all data]	R_1 = 0.00560, wR_2 = 0.1146
Largest diff. peak/hole / e Å^{-3} 0.37/-0.43	

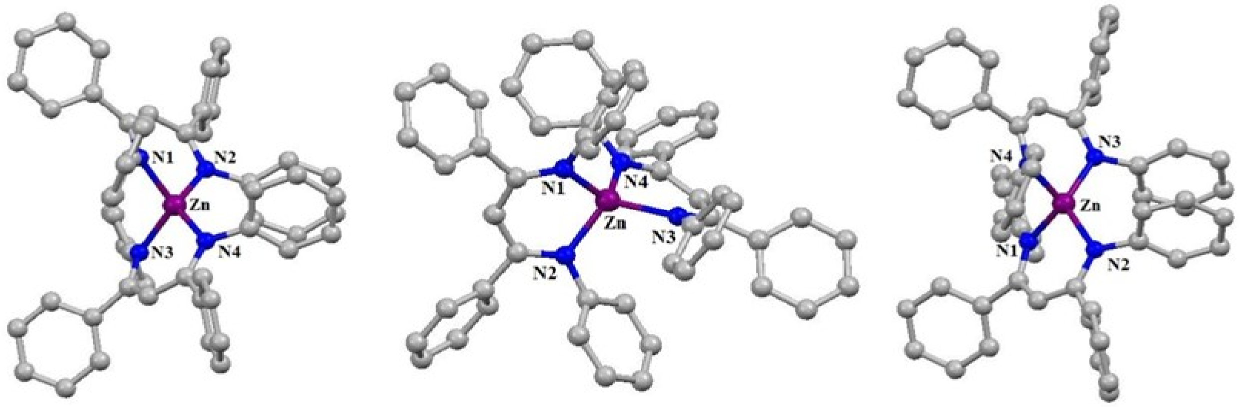


Fig S33: View of **2a** along different axes

Table 4: Bond Distances (Å) for 2a, R = 0.004

Zn1	-N1	1.9939(11)	C19	-C20	1.379(3)
Zn1	-N2	1.9885(12)	C20	-C21	1.387(2)
Zn1	-N1_a	1.9939(11)	C22	-C23	1.390(2)
Zn1	-N2_a	1.9885(12)	C22	-C27	1.384(2)
N1	-C1	1.4208(19)	C23	-C24	1.389(3)
N1	-C7	1.3356(17)	C24	-C25	1.371(3)
N2	-C15	1.3336(17)	C25	-C26	1.374(3)
N2	-C22	1.4271(18)	C26	-C27	1.391(3)

Table 5: Bond Angles (Degrees) for 2a, R = 0.04

N1	-Zn1	-N2	95.46(5)	C10	-C11	-C12	119.93(19)
N1	-Zn1	-N1_a	117.31(5)	C11	-C12	-C13	120.21(19)
N1	-Zn1	-N2_a	112.71(5)	C8	-C13	-C12	120.35(16)
N1_a	-Zn1	-N2	112.71(5)	C7	-C14	-C15	128.97(13)
N2	-Zn1	-N2_a	124.91(5)	N2	-C15	-C14	124.20(13)
N1_a	-Zn1	-N2_a	95.46(5)	N2	-C15	-C16	121.44(12)
Zn1	-N1	-C1	118.53(9)	C14	-C15	-C16	114.24(12)
Zn1	-N1	-C7	120.04(9)	C15	-C16	-C17	120.26(13)

C1	-N1	-C7	120.80(12)	C15	-C16	-C21	120.78(12)
Zn1	-N2	-C15	119.70(9)	C17	-C16	-C21	118.55(13)
Zn1	-N2	-C22	118.25(9)	C16	-C17	-C18	120.92(15)
C15	-N2	-C22	122.03(12)	C17	-C18	-C19	119.96(16)
N1	-C1	-C2	120.94(13)	C18	-C19	-C20	119.92(19)
N1	-C1	-C6	119.60(14)	C19	-C20	-C21	120.44(17)

Crystallographic information for 2b

For data collection, yellow block like crystals were mounted on nylon loop at 100 K. It was noted that the single crystal developed a crack due to temperature shock, thus affecting the data quality. We used solvent mask for DMSO, to correct the disorder.

Empirical formula	$C_{54}H_{38}Cl_4N_4Zn$
Formula weight	950.136
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	20.8033(4)
b/Å	21.5601(4)
c/Å	43.9515(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	19713.2(7)
Z	16
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	0.755
F(000)	7825.3
Crystal size/mm^3	0.25 × 0.25 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.08 to 65.62
Index ranges	$-22 \le h \le 31$, $-31 \le k \le 32$, $-66 \le l \le 64$
Reflections collected	166412
Independent reflections	35724 [R_{int} = 0.0769, R_{sigma} = 0.0927]
Data/restraints/parameters	35724/0/1135
Goodness-of-fit on F^2	1.065

Final R indexes [I>=2σ (I)]	R_1 = 0.0630, wR_2 = 0.1384
Final R indexes [all data]	R_1 = 0.1279, wR_2 = 0.1843

Largest diff. peak/hole / e Å^{-3} 1.63/-1.27

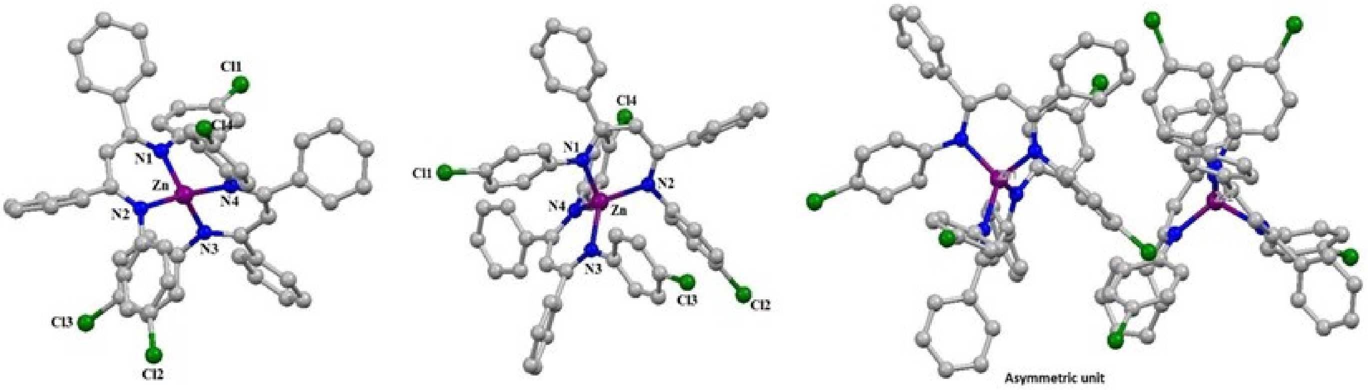


Fig S34: View of **2b** along different axes

Table 7: Bond distance (Å) for 2b, R = 0.06

Zn1	-N1	1.988(2)	N7	-C82	1.419(3)
Zn1	-N2	1.980(2)	N7	-C88	1.341(3)
Zn1	-N3	1.986(2)	N8	-C96	1.334(3)
Zn1	-N4	1.977(2)	N8	-C103	1.421(3)
Zn2	-N8	1.982(2)	C1	-C2	1.386(3)
Zn2	-N7	1.9994(19)	C1	-C6	1.403(4)
Zn2	-N5	1.983(2)	C2	-C3	1.383(4)
Zn2	-N6	1.992(2)	C3	-C4	1.387(4)
Cl1	-C4	1.738(3)	C4	-C5	1.387(4)
Cl2	-C25	1.740(3)	C5	-C6	1.383(4)
N1	-C7	1.341(3)	C11	-C12	1.382(5)
N1	-C1	1.425(3)	C12	-C13	1.390(4)
N2	-C22	1.439(3)	C14	-C15	1.410(4)
N2	-C15	1.323(3)	C15	-C16	1.507(3)

Table S6 - Bond Angles (Degrees) for 2b

N1	-Zn1	-N2	97.69(9)	Zn2	-N6	-C69	118.58(15)
N1	-Zn1	-N3	116.18(9)	Zn2	-N6	-C76	119.64(17)
N1	-Zn1	-N4	114.04(8)	Zn2	-N7	-C88	118.98(16)
N2	-Zn1	-N3	114.65(8)	C82	-N7	-C88	122.48(19)
N2	-Zn1	-N4	118.70(9)	Zn2	-N7	-C82	118.47(16)
N3	-Zn1	-N4	96.86(9)	C96	-N8	-C103	122.8(2)
N5	-Zn2	-N8	114.94(9)	Zn2	-N8	-C96	121.07(16)
N5	-Zn2	-N6	98.22(9)	Zn2	-N8	-C103	115.49(16)
N5	-Zn2	-N7	114.63(8)	N1	-C1	-C2	119.4(2)
N7	-Zn2	-N8	95.51(9)	N1	-C1	-C6	122.1(2)
N6	-Zn2	-N7	115.13(9)	C2	-C1	-C6	118.4(2)
N6	-Zn2	-N8	119.63(8)	C1	-C2	-C3	121.2(2)
Zn1	-N1	-C1	118.51(17)	C2	-C3	-C4	119.3(3)
C1	-N1	-C7	121.2(2)	C3	-C4	-C5	120.8(3)
Zn1	-N1	-C7	120.29(16)	Cl1	-C4	-C5	119.7(2)
Zn1	-N2	-C15	121.33(17)	Cl1	-C4	-C3	119.5(2)
C15	-N2	-C22	121.7(2)	C4	-C5	-C6	119.1(3)
Zn1	-N2	-C22	116.93(16)	C1	-C6	-C5	121.0(3)
C28	-N3	-C34	122.4(2)	N1	-C7	-C14	123.9(2)
Zn1	-N3	-C34	120.60(16)	N1	-C7	-C8	120.6(2)
Zn1	-N3	-C28	116.95(16)	C8	-C7	-C14	115.1(2)
C42	-N4	-C49	123.1(2)	C7	-C8	-C13	118.6(2)
Zn1	-N4	-C42	121.40(16)	C9	-C8	-C13	119.0(3)
Zn1	-N4	-C49	115.53(16)	C7	-C8	-C9	122.2(2)
Zn2	-N5	-C55	116.12(16)	C8	-C9	-C10	119.9(3)
Zn2	-N5	-C61	121.29(16)	C9	-C10	-C11	120.7(3)
C55	-N5	-C61	122.4(2)	C10	-C11	-C12	119.5(3)

C69	-N6	-C76	121.5(2)	C11	-C12	-C13	120.3(3)
C8	-C13	-C12	120.6(3)	Cl3	-C31	-C30	119.3(3)
C7	-C14	-C15	130.3(2)	Cl3	-C31	-C32	119.4(2)
C14	-C15	-C16	114.3(2)	C30	-C31	-C32	121.3(3)
N2	-C15	-C16	121.2(2)	C31	-C32	-C33	119.1(3)
N2	-C15	-C14	124.4(2)	C28	-C33	-C32	121.9(2)
C15	-C16	-C17	118.8(2)	N3	-C34	-C35	120.8(2)
C19	-C20	-C21	120.0(3)	C35	-C36	-C37	120.0(2)
C16	-C21	-C20	120.7(3)	C36	-C37	-C38	120.1(3)
N2	-C22	-C23	119.7(2)	C37	-C38	-C39	120.2(2)
N2	-C22	-C27	120.7(2)	C38	-C39	-C40	120.0(3)

Computational details:

All calculations were carried out using Density Functional Theory as implemented in the Gaussian 09[S4] quantum chemistry programs. The geometries of **2a-2b** were optimized with the B3PW91[S5,S6] density functional theory. We used double-ζ basis set with the relativistic effective core potential of Hay and Wadt (LANL2DZ) for the zinc atom and 6-31G(d) basis set for other elements (H, C, N, Cl, O). The geometries were optimized without any symmetry constraints. Vibration calculations were performed to check whether they are true minima. Time-dependent DFT calculations were performed on the molecule **2a** at the same level of theory. The PCM model[S7] was used to model the solvent effects in dichloromethane. The molecular orbitals, spin density plots were visualized using Gaussview.

Co-ordinates of optimized geometry

2a

0 1

Zn	0.00000200	-0.00003000	0.02144300
N	-1.63668400	0.68188400	1.05756000

N	-1.04920800	-1.41819400	-1.05836500
C	-0.30424500	-2.50451000	-1.56735800
C	-2.87264800	0.40675500	0.64743400
C	-4.05706400	1.09453600	1.25813900
C	-0.67326100	-3.84333100	-1.35139800
H	-1.59581700	-4.06286700	-0.82239400
C	-2.38243200	-1.35865300	-1.15174400
C	-3.19079300	-0.47221100	-0.41446000
H	-4.23279300	-0.45641500	-0.71090600
C	-1.38745200	1.37250200	2.26987900
C	-3.12460300	-2.19921800	-2.14800500
C	-4.10010100	2.49286900	1.34069900
H	-3.25168600	3.07497300	0.99375300
C	-0.51380200	2.46890100	2.26334200
H	-0.10698000	2.81532100	1.31658100
C	-4.28702500	-2.88936100	-1.78081700
H	-4.61856000	-2.85693900	-0.74615300
C	-5.16512800	0.35686800	1.69284800
H	-5.13738900	-0.72817300	1.63179900
C	0.91051500	-2.24468900	-2.22142300
H	1.21338600	-1.21283600	-2.38306800
C	-1.91591300	0.93556600	3.49322100
H	-2.56641400	0.06651800	3.51072900
C	-0.19808400	3.12702900	3.44976300
H	0.47138600	3.98360500	3.42339900
C	-2.70306100	-2.25463200	-3.48384700

H	-1.80560100	-1.72128000	-3.78334800
C	-6.28587600	0.99970500	2.21477800
H	-7.13314900	0.41239700	2.56013600
C	-6.32018600	2.39109100	2.29145200
H	-7.19583500	2.89460000	2.69340600
C	-5.22622200	3.13471700	1.84785000
H	-5.24945100	4.22044000	1.89636300
C	1.71622400	-3.28826600	-2.66870300
H	2.64992800	-3.06032000	-3.17690800
C	-0.73764400	2.69701600	4.66136300
H	-0.48802400	3.20960000	5.58672900
C	-5.00515100	-3.62530100	-2.72124700
H	-5.89892600	-4.16397100	-2.41626200
C	0.13635700	-4.88222500	-1.80207100
H	-0.16917600	-5.91058000	-1.62376300
C	-1.59483300	1.59668500	4.67484700
H	-2.01155700	1.24190400	5.61438400
C	-3.42804300	-2.97804100	-4.42599000
H	-3.09261600	-3.00208300	-5.45972600
C	-4.57930500	-3.66952100	-4.04769700
H	-5.14094300	-4.23934900	-4.78360400
C	1.33349500	-4.61403100	-2.46585700
H	1.96429200	-5.42805700	-2.81287800
N	1.63667300	-0.68268300	1.05710700
N	1.04923300	1.41888700	-1.05734500
C	0.30431100	2.50556200	-1.56562300

C	2.87265100	-0.40726800	0.64719100
C	4.05708000	-1.09549600	1.25737400
C	0.67342700	3.84421900	-1.34882900
H	1.59601200	4.06335400	-0.81970900
C	2.38245300	1.35942300	-1.15073300
C	3.19080700	0.47246000	-0.41407200
H	4.23281300	0.45688400	-0.71051100
C	1.38738800	-1.37413600	2.26894200
C	3.12460500	2.20077500	-2.14634000
C	4.10022400	-2.49389800	1.33872700
H	3.25187100	-3.07577000	0.99123900
C	0.51373900	-2.47053100	2.26160300
H	0.10697700	-2.81630600	1.31458000
C	4.28706900	2.89057900	-1.77865200
H	4.61867500	2.85728100	-0.74404000
C	5.16508300	-0.35812400	1.69274100
H	5.13727200	0.72696700	1.63261400
C	-0.91046000	2.24623300	-2.21986000
H	-1.21339300	1.21450200	-2.38216900
C	1.91575000	-0.93801900	3.49261900
H	2.56623200	-0.06897000	3.51076400
C	0.19795000	-3.12947100	3.44755400
H	-0.47151300	-3.98603400	3.42056200
C	2.70295200	2.25733900	-3.48209700
H	1.80543900	1.72428500	-3.78197100
C	6.28585500	-1.00132600	2.21416900

H	7.13307400	-0.41425200	2.56005900
C	6.32026100	-2.39277400	2.28966000
H	7.19593100	-2.89656300	2.69121800
C	5.22637000	-3.13609800	1.84537400
H	5.24967800	-4.22186000	1.89295300
C	-1.71610800	3.29014700	-2.66646400
H	-2.64982800	3.06258500	-3.17481100
C	0.73742600	-2.70027900	4.65948300
H	0.48774700	-3.21349400	5.58448200
C	5.00515400	3.62727800	-2.71852000
H	5.89897000	4.16566000	-2.41314900
C	-0.13612800	4.88345200	-1.79883300
H	0.16947800	5.91167400	-1.61988100
C	1.59459700	-1.59994400	4.67377300
H	2.01124800	-1.24579400	5.61358000
C	3.42789100	2.98151100	-4.42368700
H	3.09238300	3.00644000	-5.45737600
C	4.57921200	3.67262200	-4.04490100
H	5.14081700	4.24304700	-4.78037200
C	-1.33329300	4.61575800	-2.46277200
H	-1.96403900	5.43004500	-2.80926900

2b

0 1

Zn	0.00011800	-0.21092200	-0.00003000

N	0.29795900	-1.29258500	1.73698500
N	-1.63131700	0.81760900	0.70309400
N	-0.29805900	-1.29110700	-1.73794000
N	1.63169300	0.81783600	-0.70244400
C	-3.60804600	1.00894000	2.16320500
C	-2.28898500	0.40292100	1.78387400
C	3.60819500	1.01025400	-2.16274700
C	-0.66981900	-1.39046400	2.65428700
C	2.30739100	-1.59351000	3.14809100
H	1.83171700	-1.06219100	3.96698100
C	-1.59817600	-1.80068600	-1.95984600
C	-1.87272900	-0.65741400	2.62212300
H	-2.60498800	-0.95607900	3.36278800
C	2.28913600	0.40404700	-1.78370700
C	-0.57565500	-2.38314900	3.77588400
C	1.59795700	-1.80259200	1.95858700
C	-3.84289100	1.44816100	3.47183500
H	-3.03829600	1.39556200	4.20105200
C	0.66958400	-1.38833700	-2.65545300
C	-2.26268700	-2.45905800	-0.91024600
H	-1.74040100	-2.61982700	0.02984900
C	1.87261800	-0.65551200	-2.62280600
H	2.60473100	-0.95364400	-3.36383000
C	-4.65067300	1.07916300	1.22933300
H	-4.48346800	0.72816100	0.21551000
C	-0.87906900	-2.01143200	5.09180700

H	-1.12903300	-0.97532700	5.30532700
C	0.57512200	-2.38002800	-3.77790500
C	-0.24987600	-3.72130200	3.51383300
H	-0.01597100	-4.02436900	2.49744300
C	-1.96488600	2.03008500	0.04803000
C	-2.14091900	2.03387500	-1.34500500
H	-2.09163600	1.09314200	-1.88758300
C	3.61648300	-2.04921800	3.30481800
H	4.12676300	-1.86511700	4.24455000
C	2.26248500	-2.46011900	0.90846600
H	1.74028900	-2.61994100	-0.03184100
C	-3.56400100	-2.91448600	-1.05619900
H	-4.06990700	-3.42750200	-0.24360600
C	-6.11708500	2.02618000	2.90164600
H	-7.08936200	2.42078800	3.18619000
C	-5.08593900	1.96176600	3.83718100
H	-5.24859400	2.30934300	4.85452600
C	-0.23230600	-4.66061600	4.54036600
H	0.01192500	-5.69621000	4.31731500
C	-0.84803200	-2.94911600	6.12245200
H	-1.07674900	-2.64030700	7.13956200
C	3.56370000	-2.91590800	1.05416500
H	4.06961600	-3.42827000	0.24116600
C	0.24917200	-3.71836100	-3.51698400
H	0.01535700	-4.02228100	-2.50082700
C	-4.25357500	-2.71751800	-2.25934800

C	1.96545300	2.02971400	-0.04635300
C	-5.89629600	1.57822300	1.59873400
H	-6.69868500	1.61573900	0.86620600
C	3.84279400	1.45068600	-3.47101600
H	3.03801800	1.39889400	-4.20009000
C	-2.30772400	-1.59038700	-3.14906800
H	-1.83206000	-1.05839800	-3.96753000
C	4.25315900	-2.72016400	2.25758000
C	2.03932900	3.25155700	-0.72211200
H	1.87217900	3.27778700	-1.79452000
C	4.65106200	1.07943600	-1.22906400
H	4.48406300	0.72747800	-0.21553800
C	2.30774900	4.43947700	-0.04341000
H	2.35407000	5.36620500	-0.60570600
C	0.87841600	-2.00720600	-5.09354400
H	1.12850600	-0.97095100	-5.30619100
C	-2.03894500	3.25130800	0.72488900
H	-1.87208500	3.27655500	1.79736700
C	-0.52713600	-4.27759900	5.84939200
H	-0.50766500	-5.01162000	6.65106500
C	-3.61691500	-2.04572100	-3.30604800
H	-4.12728300	-1.86066400	-4.24554500
C	2.49825700	4.42436200	1.34067800
C	2.14183900	2.03222700	1.34664000
H	2.09267800	1.09100000	1.88837000
C	0.84709200	-2.94398000	-6.12500600

H	1.07571900	-2.63431400	-7.14187600
C	5.08582100	1.96447900	-3.83616800
H	5.24827800	2.31300800	-4.85321800
C	6.11719800	2.02786500	-2.90081700
H	7.08945900	2.42261800	-3.18521600
C	-2.30718200	4.43985000	0.04720700
H	-2.35365500	5.36606100	0.61034300
C	2.40953500	3.20917800	2.03025500
H	2.55900700	3.20948500	3.10614400
C	0.52602700	-4.27265200	-5.85306800
H	0.50633000	-5.00596600	-6.65538200
C	-2.49732100	4.42600700	-1.33694500
C	0.23131500	-4.65677100	-4.54433800
H	-0.01304800	-5.69252100	-4.32216300
C	-2.40842700	3.21145300	-2.02761200
H	-2.55762400	3.21274700	-3.10353900
C	5.89666300	1.57868300	-1.59828500
H	6.69923300	1.61538800	-0.86591300
O	2.76514200	5.52425500	2.10176800
O	5.52545000	-3.20622500	2.30289700
O	-5.52595800	-3.20331500	-2.30495200
O	-2.76399800	5.52659900	-2.09709600
C	2.87517800	6.76597600	1.44410300
H	1.93739100	7.04659400	0.94418900
H	3.10034300	7.50082000	2.22007400
H	3.68705800	6.76362000	0.70344800

C	-2.87426700	6.76770500	-1.43830800
H	-1.93662800	7.04790200	-0.93788000
H	-3.09925600	7.50325900	-2.21365600
H	-3.68634600	6.76462300	-0.69787400
C	-6.25533400	-3.02402100	-3.49812900
H	-7.23029100	-3.48587100	-3.32886000
H	-6.39725100	-1.95962800	-3.73220400
H	-5.76678800	-3.51553400	-4.35103700
C	6.25472700	-3.02811000	3.49631200
H	7.22963400	-3.48995200	3.32673100
H	6.39677500	-1.96394900	3.73135600
H	5.76601800	-3.52031800	4.34872600

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