Supporting Information:

A tailored spirooxazine dimer as a photoswitchable binding tool

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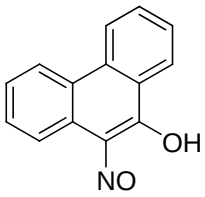
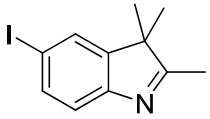
General information

Flash column chromatography was performed using Silica Gel 60 (230-400 mesh). ^{1}H NMR, ^{13}C NMR and 2D-NMR spectra were recorded on a 500 MHz Varian DirectDrive 500 MHz NMR spectrometer. IR spectra were recorded on a Nicolet 380 FT-IR spectrometer in KBr pellet. High resolution mass spectra were obtained at the University of California at Riverside Mass Spectroscopy Facility.

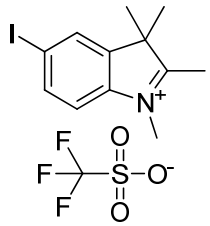
Synthetic procedures:



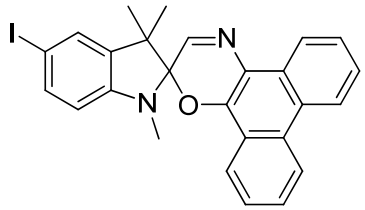
10-Nitroso-9-phenanthrol (2) 9-Phenanthrol (1.65g, 7.42 mmol) and ethanol (30 mL) were taken in a 150 ml flask. The mixture was cooled to 0 ^{o}C and H_2SO_4 (3 mL) was added slowly. This mixture was cooled to below 0 ^{o}C using ice-salt mixture. A solution of $NaNO_2$ (0.81 g, 12.89 mmol) in water was added cooled and added to reaction mixture dropwise keeping the solution around 0 ^{o}C. This reaction mixture was stirred at this temperature for 7 h. The precipitated product was filtered, washed with 50% aqueous ethanol and then with a little ethanol to give pure **2** (1.55 g, 81.7 %) as a greenish yellow solid. IR (KBr/ν cm^{-1}): 3445.0, 3058.0, 2925.1, 1600.0, 1525.7, 1143.6, 1107.5, 978.5. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.42 (dd, 1H, J= 8Hz), 8.37 (dd, 1H, J=8Hz), 8.20 (d, 1H, J=8Hz), 8.12 (d, 1H, J=8Hz), 7.80 (t, J=8Hz), 7.57-7.46 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 137.8, 136.5, 130.3, 129.6, 129.4, 129.3, 129.1, 128.9, 128.6, 128.5, 128.3, 124.2, 123.7, 123.6. HRMS (m/z): calcd. $[M+H]^+$ 224.0712; found 224.0710.



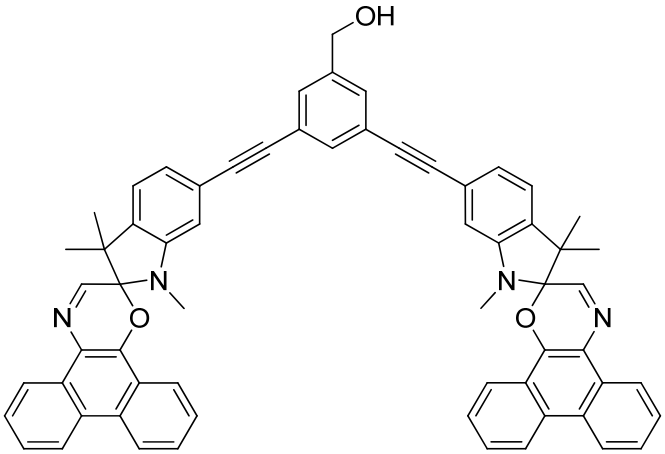
5-Iodo-2,3,3-trimethylindolenine (3) A solution of 4-Iodophenylhydrazine (1.37 g, 5.89 mmol), isopropylmethylketone (1.40 mL, 13.0 mmol), EtOH (20 mL) and concd H_2SO_4 (0.3 mL) in a 50 mL round bottom flask was heated under reflux for 12 h. After being cooled to ambient temperature, the mixture was filtered and filtrate was added to distilled water (50 mL). The product was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layer was washed 10 % $NaHCO_3$ (2 x 50 mL) and (3 x 20 mL) distilled water, dried over sodium sulfate, filtered, and evaporated under reduced pressure to yield **3** (1.63 g, 97.08%) as a brownish liquid. IR (KBr/ν cm^{-1}): 3041.7, 2960.2, 1656.6, 1574.7, 1448.2, 1122.2, 815.9. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.63-7.59 (m, 2H), 7.28 (d, 1H, J= 8 Hz), 2.26 (s, 3H), 1.29 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 153.4, 148.2, 136.7, 130.7, 121.8, 89.9, 54.0, 22.9, 15.4. HRMS (m/z): calcd. $[M+H]^+$ 286.0093; found 286.0094.



1,2,3,3-Tetramethyl-5-carboxy-3*H*-indolium triflate (4). A solution of **3** (2.69 g, 5.94 mmol) and Methyl triflate (0.85 mL, 7.07 mmol) in MeCN (20 mL) was refluxed under N_2 with stirring for 8 h. Solvent was evaporated under reduced pressure. The residue was washed with diethyl ether (100 mL) to afford **4** (3.87 g, 91.20 %) as an off white solid. IR (KBr/ν cm^{-1}): 2990.5, 1528.4, 1285.4, 15247.9, 1025.4. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.14 (d, 1H, J= 1.5 Hz), 8.01 (dd, 1H, J=8.5 Hz), 7.53 (d, 1H, J= 8.5 Hz), 3.91 (s, 3H), 2.69 (s, 3H), 1.56 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 202.0, 149.3, 147.6, 143.7, 138.2, 122.3, 100.5, 60.1, 40.3, 26.7, 19.4. HRMS (m/z): calcd. for $[M]^+$ 300.0244; found 300.0243.



5-iodo-1,3,3-trimethylspiro[indoline-2,2'-phenanthro[9,10-b][1,4]oxazine] (5):
A solution of **4** (5.61 g, 12.49 mmol) in aqueous NaOH (1 M, 100 mL) was stirred at ambient temperature for 2 h. The product was extracted into ethyl acetate. The organic layer was dried over sodium sulfate and evaporated under reduced pressure to give 3.39 g of dried reddish brown solid. The reddish brown solid (3.31 g), 10-nitroso-9-phenanthrol (2.50 g) and ethanol (50 mL) were taken in a 100 mL round bottom flask. The reaction mixture was refluxed for 12h, cooled, and ethanol was evaporated. The product was purified using column chromatography with 2% ether in hexane to give **5** (3.17 g, 51%) as light yellow solid. IR (KBr/ν cm^{-1}): 3072.6, 2957.4, 1588.8, 1479.2, 1321.8, 1170.0, 1102.6, 1026.7, 754.1, 720.4. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.67 (dd, 1H, J=8.5 Hz), 8.61 (d, 1H, J= 8 Hz), 8.58 (d, 1H, J=8.5 Hz), 8.08 (dd, 1H, J=8 Hz), 7.78 (s, 1H), 7.68 (t, 1H, J=8 Hz), 7.64 (t, 1H, J= 8 Hz), 7.58 (t, 1H, J=8 Hz), 7.52 (t, 1H, 8 Hz), 7.5 (dd, 1H, J=8 Hz),7.35 (d, 1H, J= 2 Hz), 6.36 (d, 1H, J=8 Hz), 2.73 (s, 3H), 1.36 (d, 6H, J=19 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 149.5, 147.3, 136.6, 130.4, 129.7, 127.3, 126.7, 126.4, 124.9, 124.0, 122.6, 122.5, 122.4, 122.1, 119.9, 109.4, 98.6, 80.8, 51.3, 29.5, 25.3, 20.6. HRMS (m/z): calcd. $[M+H]^+$ 505.0777; found 505.0772.



Synthesis of (3,5-bis((1,3,3-trimethylspiro[indoline-2,2'-phenanthro[9,10-b][1,4]oxazine]-6-yl)ethynyl)phenyl)methano (1) SPOD

DEBA (0.09 g, 0.56 mmol), **5** (0.50 g, 0.99 mmol), CuI (4.40 x 10^{-2} g, 2.31 x10^{-2}, mmol)dichlorobis(triphenylphosphine)palladium(II) (1.49 x 10^{-2} g, 2.12 x 10^{-2} mmol) were taken in a 50 mL 3-neck round bottom fitted with a condenser. The reaction flask was evacuated and N_2 was inserted. N-methylpyrrolidine (15 mL) was added to the reaction flask under N_2. The reaction flask was stirred at 70 ^oC for 48 h under N_2 atmosphere. The solid was dissolved in ethyl acetate and filtered. Ethyl acetate was evaporated and the residue was chromatographed on silica gel. The impurities were washed initially with 1:1 methylene chloride-hexane and then with methylene chloride. The product was eluted with 2% ethyl acetate in methylene chloride to give pure **1** (0.27 g, 59.9 %) as light blue product. IR (KBr/ν cm^{-1}): 3398.6, 3072.6, 2963.0, 2204.2, 1608.4, 1583.1, 1493.2, 1349.9, 1316.2, 1102.6, 754.1. ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 8.68 (dd, 2H, J=8.5 Hz), 8.62 (d, 2H, J= 8 Hz), 8.59 (d, 2H, J=8.5 Hz), 8.10 (dd, 2H, J=8 Hz), 7.81 (s, 2H), 7.69 (t, 2H, J= 7.75 Hz), 7.65-7.62 (m, 3H, J= 8 Hz), 7.58 (t, 1H, J=7.75 Hz), 7.52 (t, 1H, 7.75 Hz), 7.47 (brs, 2H), 7.45 (dd, 1H, J=8 Hz),7.29 (d, 2H, J= 1 Hz), 6.56 (d, 2H, J=8 Hz), 4.70 (d, 2H, J=5.5 Hz), 2.80 (s, 6H), 1.41 (d, 6H, J=10.5 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 149.6, 147.8, 141.3,138.1, 136.3, 133.1, 132.3, 131.3, 129.7, 128.9, 127.8 127.41, 126.7, 126.4, 125.1, 124.9, 124.3, 124.1, 122.7, 122.5, 122.4, 122.1, 119.9, 113.7, 107.06, 98.7, 91.0, 86.9, 64.6, 51.3, 29.5, 25.3, 20.7. HRMS (m/z): calcd. $[M+H]^+$ 909.3805; found 909.3787.

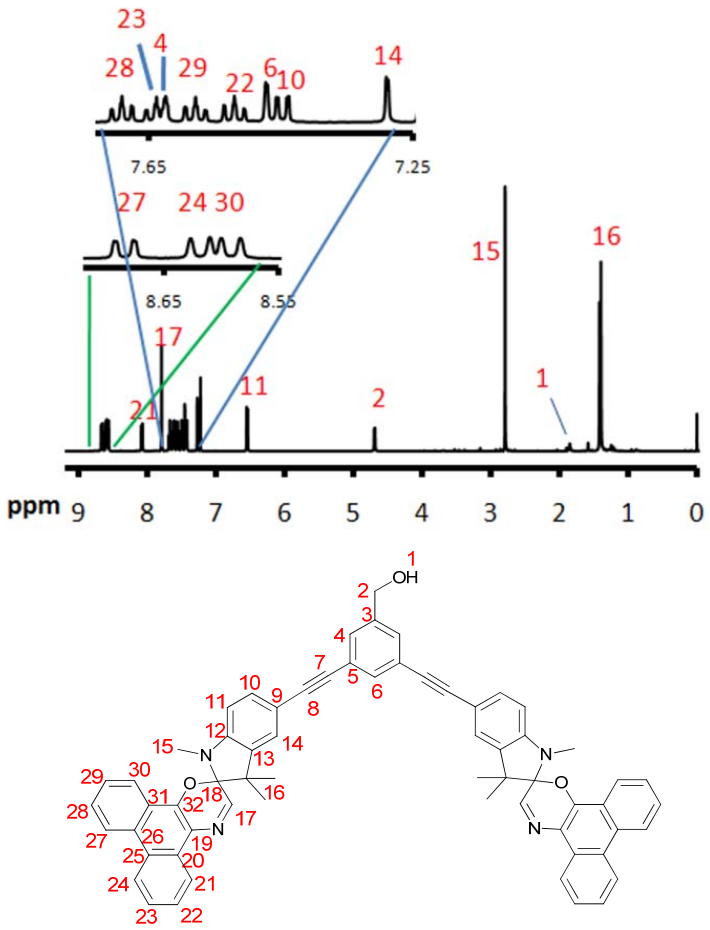


Figure S1. ^{1}H NMR (500 MHz) characterization of spirooxazine dimer **1**.

Procedure for determination of first order rate constant for thermal bleaching: A 5 mL solution of **1** (8.35 x 10^{-7} M) was prepared in a cuvette containing a micro stir bar, maintained at 25°C. Light from a 200W Mercury Xenon lamp, filtered by 340 nm colored glass filter (FSR-U340), was directed through the side of a cuvette. The absorbance was recorded every 0.1 or 1s using the Ocean Optics software. The solution was irradiated, stirred while monitoring the change in absorbance till no further change in absorbance was detected in visible region. The shutter was closed and the sample was left in the dark till the spectrums resemble that of original solution. The thermal closing data was fit to first order reaction kinetics to obtain first order rate constants.

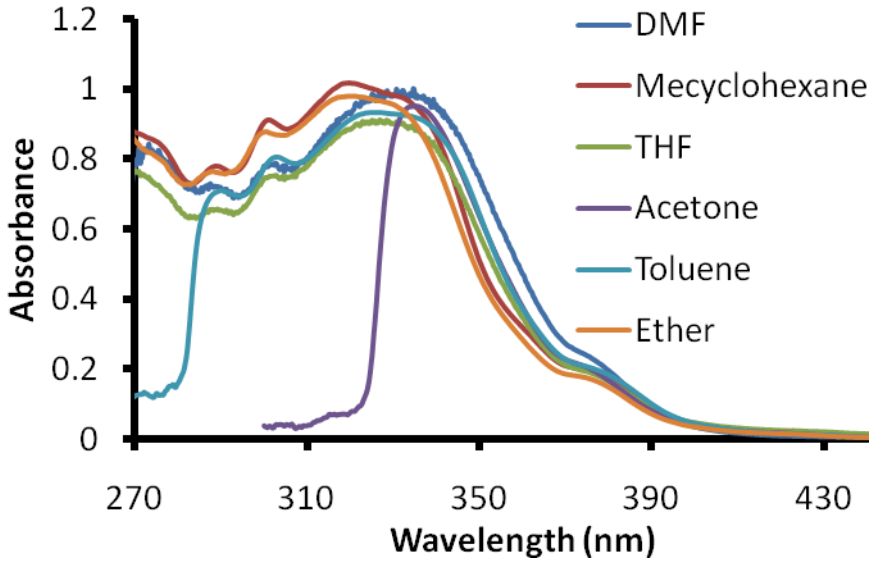


Figure S2. UV-Vis spectra of closed form of **1** ([**1**]=8.35 x 10^{-7} M) with different solvents. (Mecyclohexane= Methylcylcohexane)

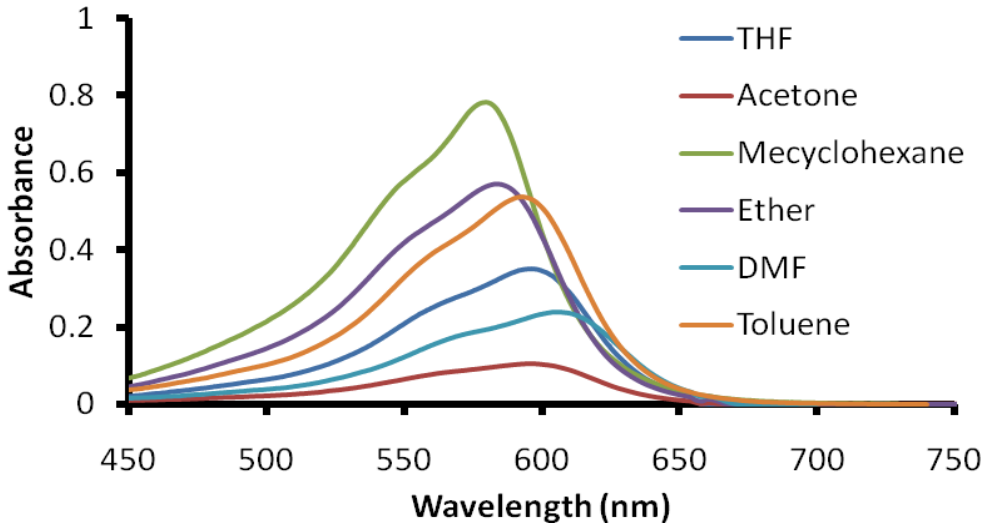


Figure S3. UV-Vis spectra of open form of **1** ([**1**]=8.35 x 10^{-7} M) with in different solvents (1 min UV 340 nm light irradiation). (Mecyclohexane = Methylcyclohexane)

Table S1. Brooker red parameter and wave numbers of the absorption maxima in different solvents.

Solvent	χ_R	Wavenumber cm^{-1}
methylcyclohexane	50.1	17265.27
ether	48.3	17020.11
toluene	47.2	16877.94
THF	46.6	16807.72
Acetone	45.7	16759.92
DMF	43.7	16542.51

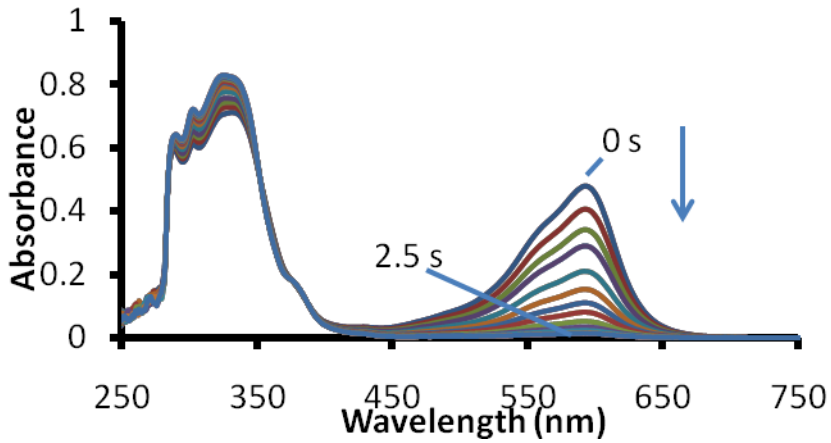


Figure S4. Thermal fading of a solution of **1** in methylcyclohexane in dark over time [**1**]=8.35 x 10^{-7} M

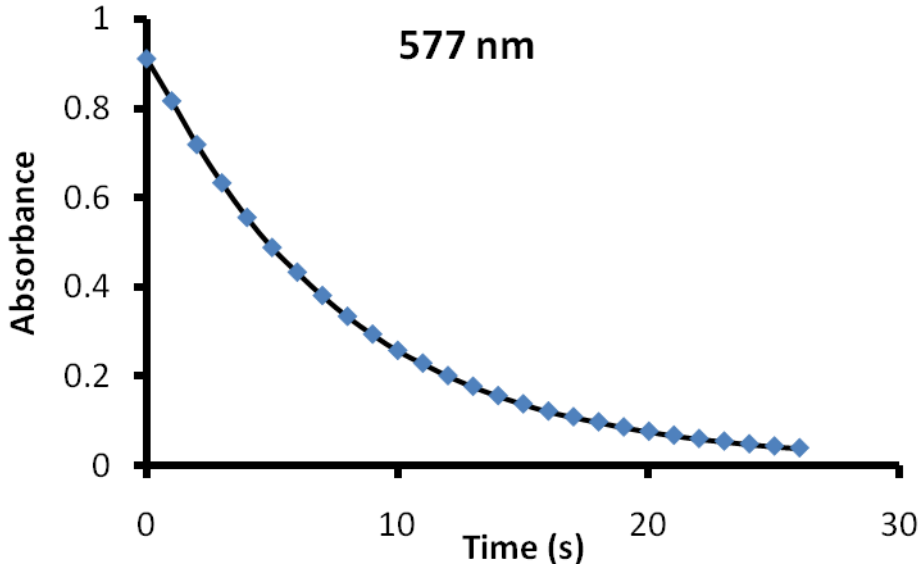


Figure S5a. The rate of thermal decay of a solution of **1** in methylcyclohexane over time at 577 nm [**1**]=1.67 x 10^{-6} M.

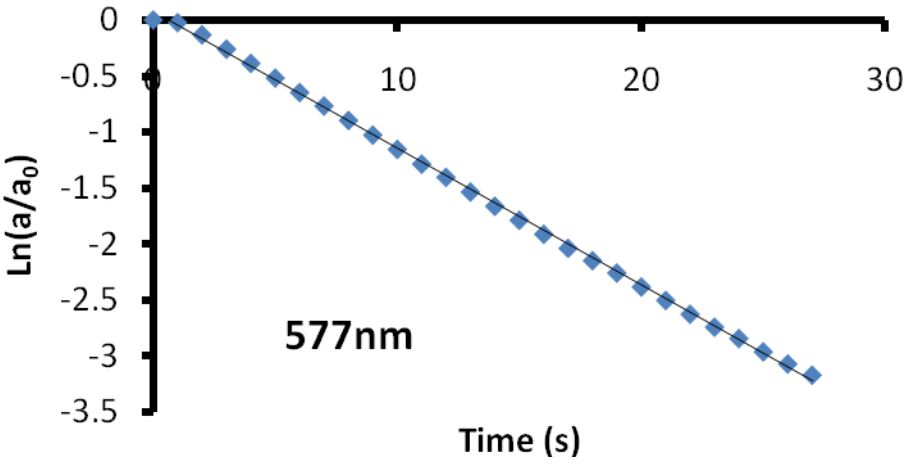


Figure S5b. The first-order kinetic plot for the thermal decay of the open form of **1** in methylcyclohexane at 25°C.

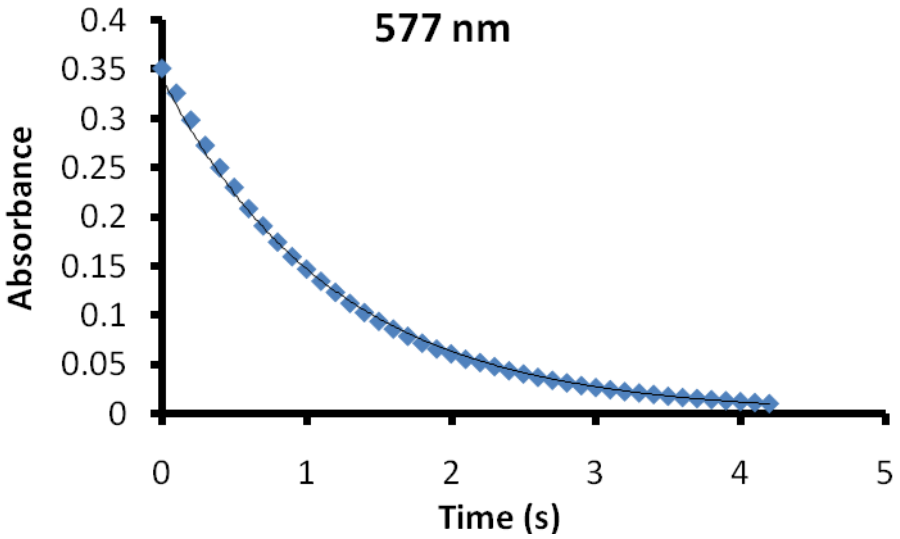


Figure S6a. The rate of thermal decay of a solution of **5** in methylcyclohexane over time at 577 nm [**1**]= 2.02 x 10^{-6} M.

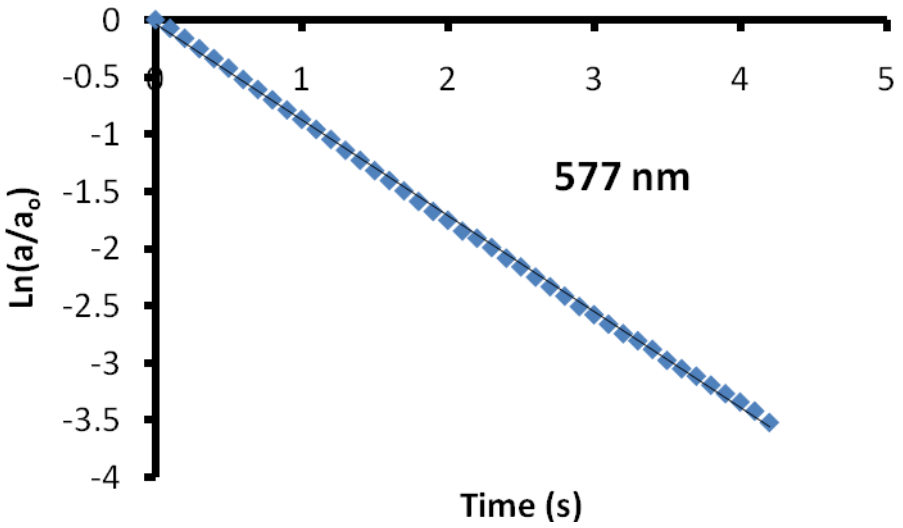


Figure S6b. The first-order kinetic plot for the thermal decay of the open form of **5** in methylcyclohexane at 25^{o}C.

Fatigue study procedures: A 5 mL solution of **1** (8.35 x 10^{-7} M) was prepared in a cuvette containing a micro stir bar, maintained at 25^{0}C. Light from a 200W Mercury Xenon lamp, filtered by 340 nm colored glass filter (FSR-U340), was directed through the side of a cuvette. The absorbance was recorded every 0.1 or 1s using the Ocean Optics software. The solution was irradiated, stirred while monitoring the change in absorbance until no further change in absorbance was detected in visible region. The shutter was closed and the sample was left in the dark until the spectrum resembles that of original solution. This process was repeated 4 additional times for each sample.

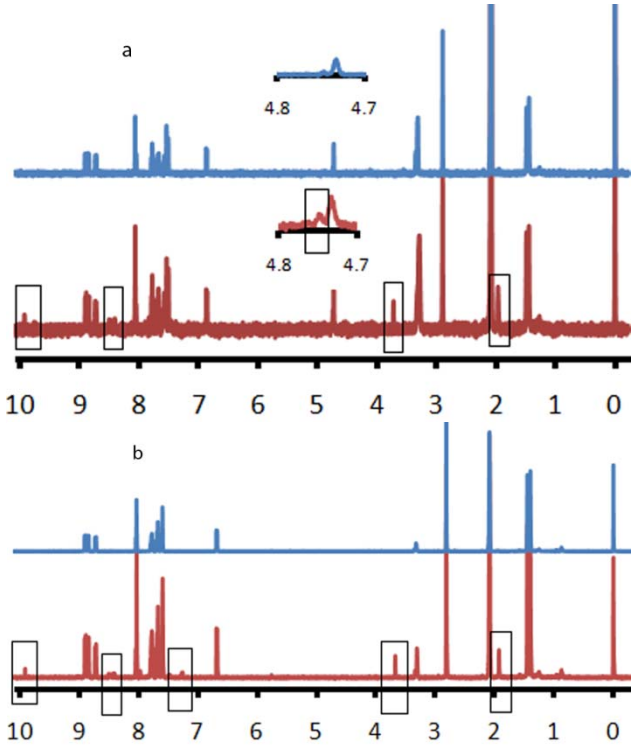


Figure S7. A comparison of ^{1}H-NMR spectra of SPOD **1** (a) and I-SPO **5** (b) in acetone-d_6 at -40^{o}C; Before (upper) and after (lower) UV irradiation of each compound.

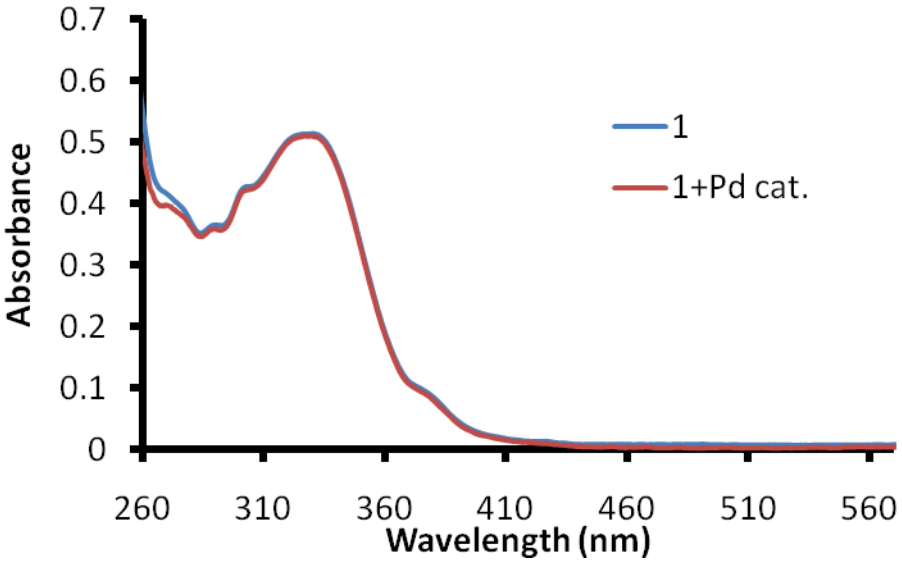


Figure S8. UV-Vis spectra of closed form of 1 (4.18 x 10^{-7} M) with $Pd(PPh_3)_2Cl_2$ (6.63 x 10^{-5} M) in THF.

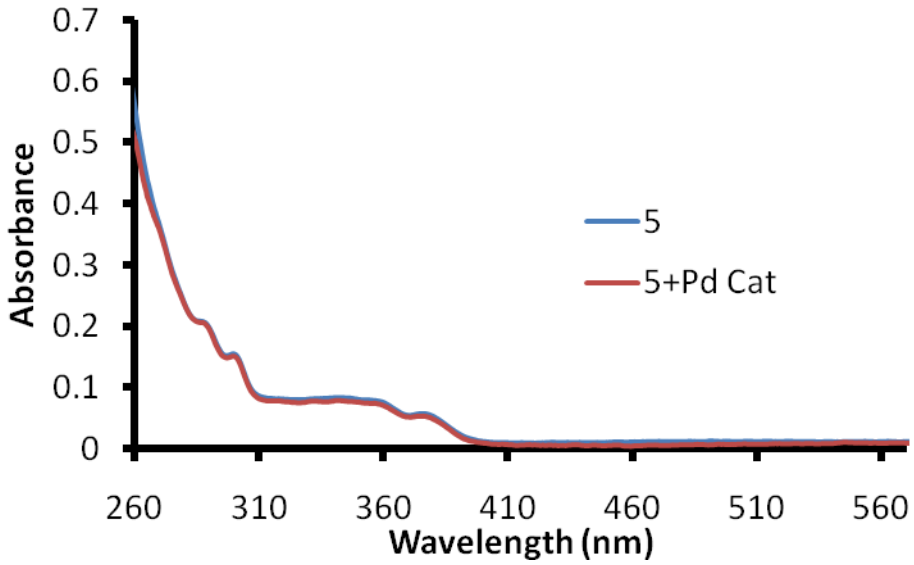


Figure S9. UV-Vis spectra of closed form of **5** (2.02 x 10^{-6} M) with $Pd(PPh_3)_2Cl_2$ (6.63 x 10^{-5} M) in THF.

Binding study of open form:

The binding constant of the open form of 1 and 5 with metal catalyst was determined indirectly using kinetics assuming the model equilibrium in Scheme S2 below. This model assumes that there is only 1:1 binding (Figure S7) in the open form and metal ion affinity of closed form of 1 or 5 has negligibly small (as evident from the UV visible spectrum of closed form of 1 and 5 in presence of large excess of metal catalyst, Figure S8 and S9) binding constant values, (Table S2 and S3). A series of experiments evaluating thermal closure rates of 1 and 5 at various metal catalyst concentrations were performed.

A 4 mL solution of chelator **1** or **5** in THF was prepared in a cuvette containing a micro stirrer bar. The cuvette was allowed to equilibrate to 25^{o}C for ~2 min. Light from a 200W Mercury Xenon lamp, filtered by 340 nm colored glass filter (FSR-U340), was directed through the side of a cuvette. The absorbance was recorded every 0.1 or 1s using the Ocean Optics software. Similarly, 4 mL solutions of **1** or **5** with different metal catalyst were prepared and their thermal fading rates determined after irradiation with 340 nm light.

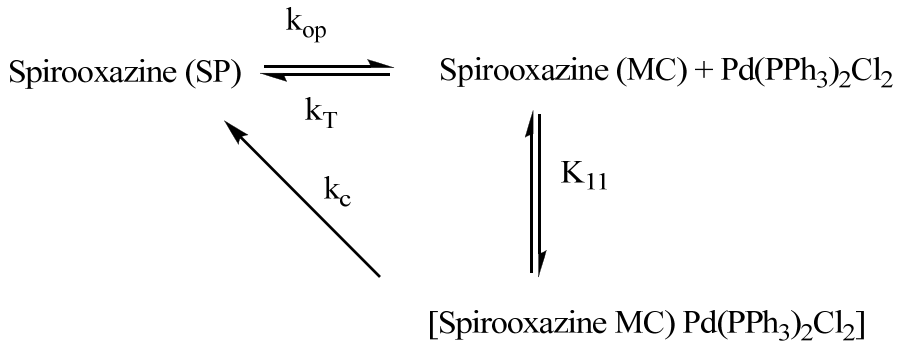


Figure S10. A graphical presentation of model used to determine the binding affinity of open form of **1** and **5**.

$$k_T^{ob} = \frac{k_T}{K_{11(eq)}[Pd(PPh_3)_2Cl_2]} + k_{op} + k_c \qquad \text{---------} \qquad \textbf{Equation S1}$$

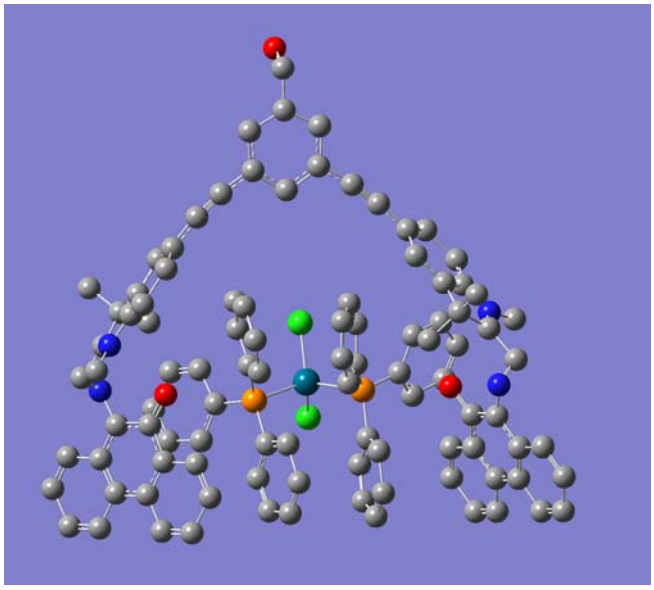


Figure S11. Optimized structure of SPOD (**1**) and $Pd(PPh_3)_2Cl_2$ using Ampac (PM6).

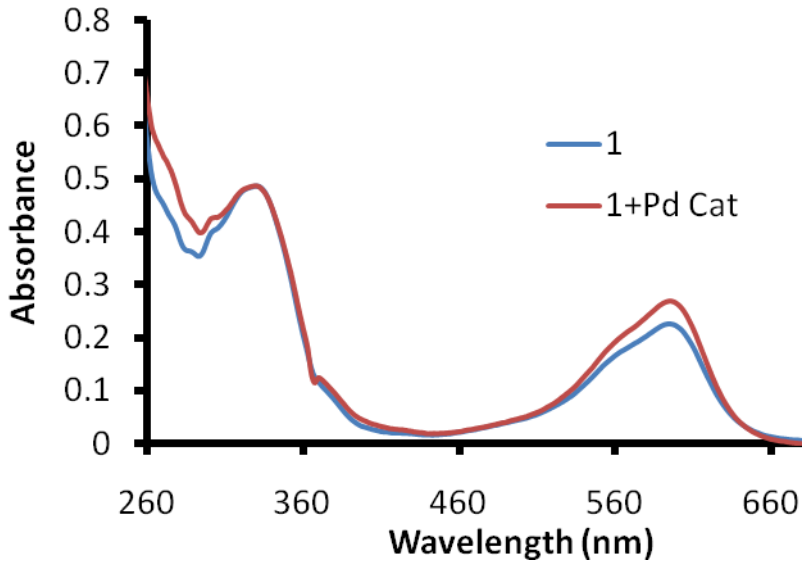


Figure S12. UV-Vis spectra of open form of **1** (4.18 x 10^{-7} M) with $Pd(PPh_3)_2Cl_2$ (6.63 x 10^{-5} M) in THF.

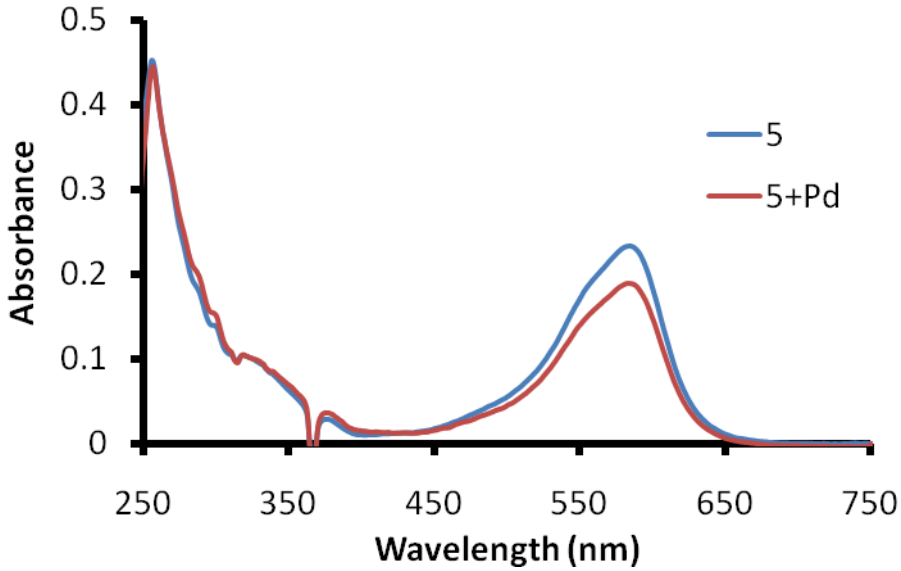


Figure S13. UV-Vis spectra of open form of **5** (2.02 x 10^{-6} M) with $Pd(PPh_3)_2Cl_2$ (6.63 x 10^{-5} M) in THF.

Table S2. Thermal fading rates of **5** (2.02×10^{-6} M) in presence of different concentrations $Pd(PPh_3)_2Cl_2$ in THF at 25 °C.

$[Pd(PPh_3)_2Cl_2)]$	1/[Pd Cat]	k_T s^{-1}
0	0	2.216±0.0122
1.24E-06	8.04E+05	2.211±0.053
2.49E-06	4.02E+05	2.342±0.053
4.97E-06	2.01E+05	2.0941±0.019
9.94E-06	1.01E+05	2.365±0.065
1.99E-05	5.03E+04	2.3315±0.036

Table S3. Thermal fading rates of **1** (4.18×10^{-6} M) in presence of different concentrations $Pd(PPh_3)_2Cl_2$ in THF at 25 °C.

$[Pd(PPh_3)_2Cl_2)]$	1/[Pd Cat]	k_T s^{-1}
0	0	1.518±0.0204
1.24E-06	8.04E+05	1.278±0.053
2.49E-06	4.02E+05	1.123±0.047
3.48E-06	2.87E+05	1.115±0.05
4.97E-06	2.01E+05	1.072±0.05
9.94E-06	1.01E+05	1.050±0.056

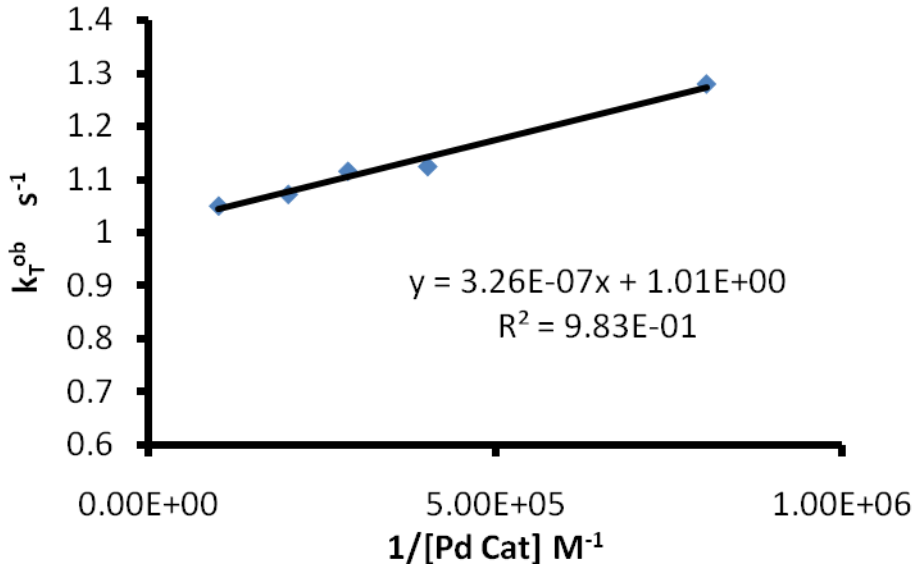


Figure S14. A plot of observed variation in the fading rate constant of **1** as a function of reciprocal of $Pd(PPh_3)_2Cl_2$ concentration in THF at 25°C. [**1**]=4.18×10^{-7} M;

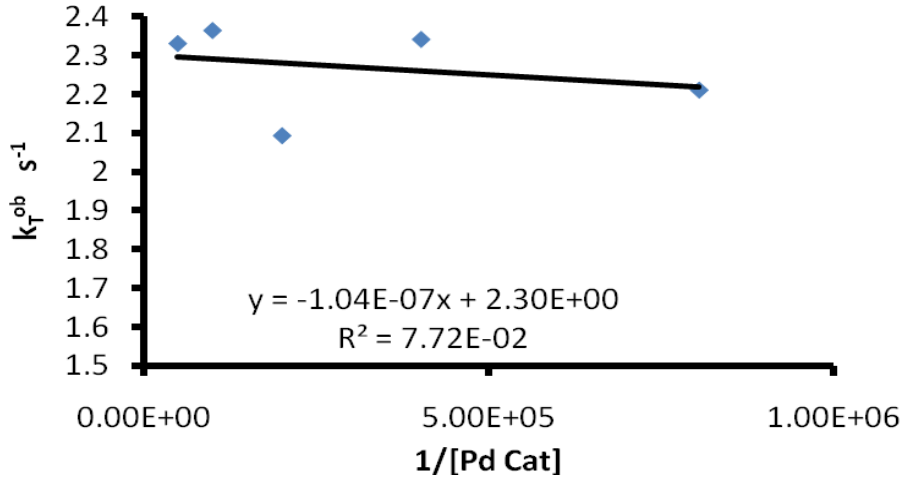


Figure S15. A plot of observed variation in the fading rate constant of **5** as a function of reciprocal of $Pd(PPh_3)_2Cl_2$ concentration in THF at 25°C. [**5**]=4.18×10^{-7} M;

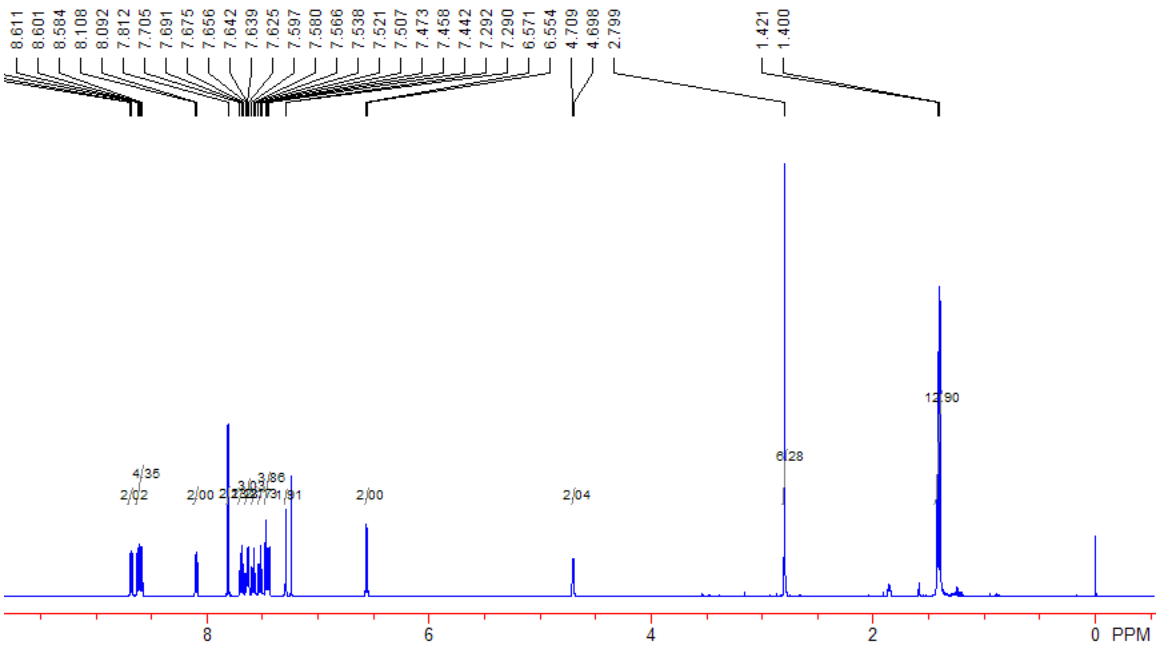


Figure S16. ^{1}H NMR of **1** in $CDCl_3$ recorded on 500 MHz NMR instrument.

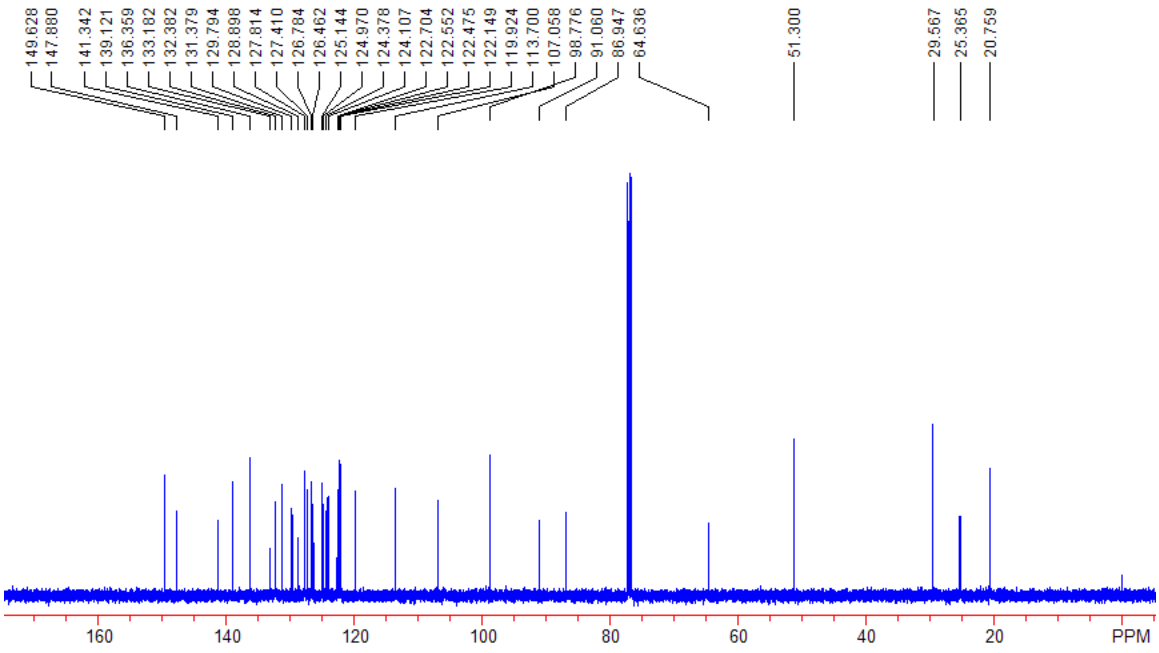


Figure S17. ^{13}C NMR of **1** in $CDCl_3$ recorded on 500 MHz NMR instrument.

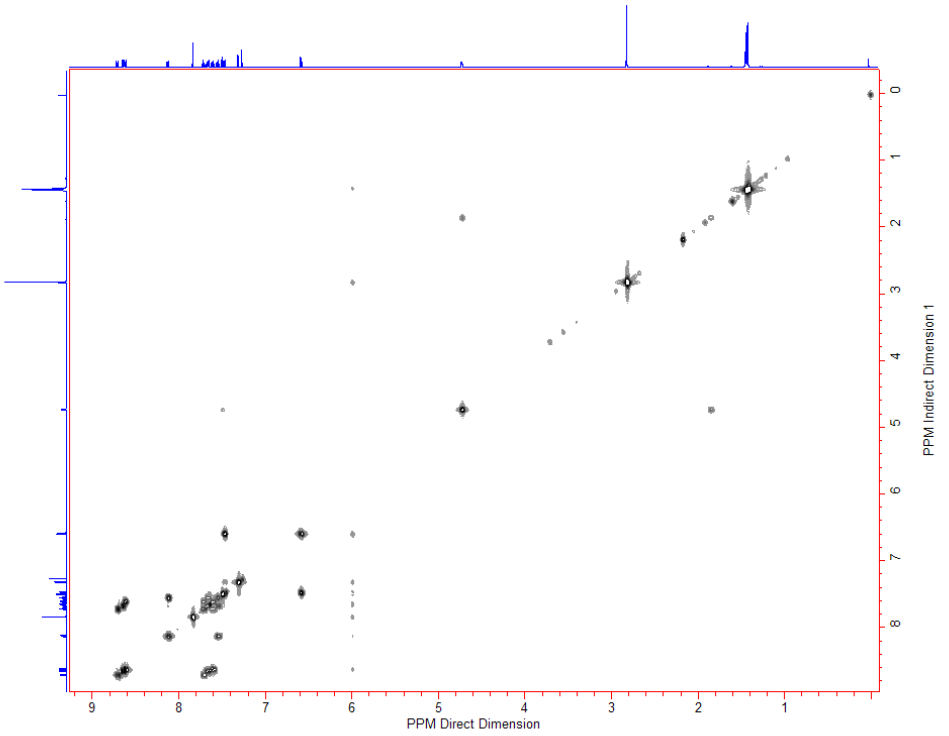


Figure S18. COSY NMR of **1** in $CDCl_3$ recorded on a 500 MHz instrument.

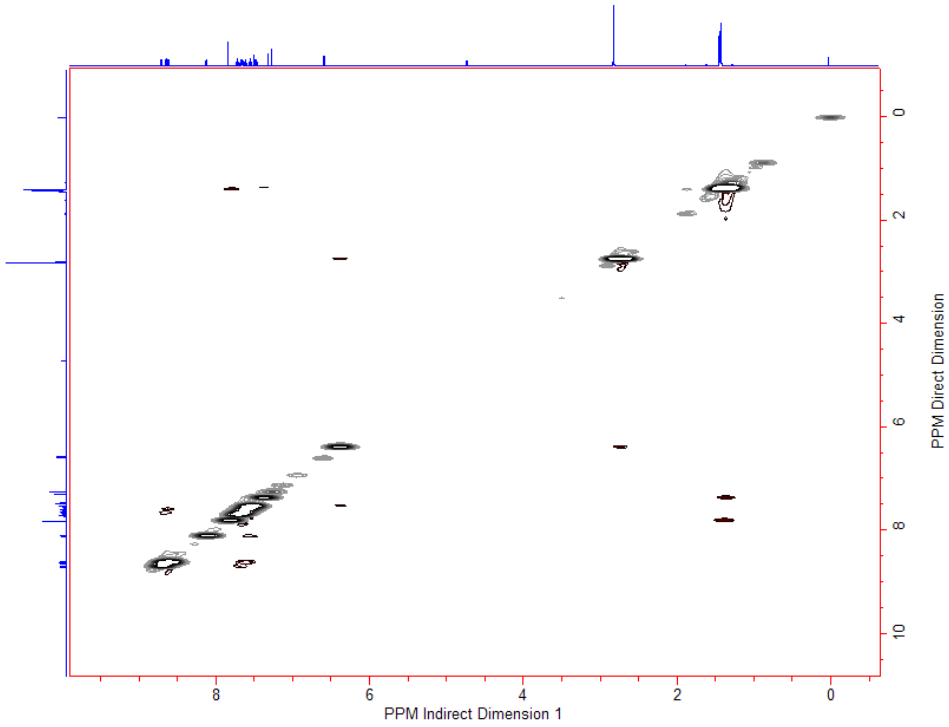


Figure S19. ROSEY NMR of **1** in $CDCl_3$ recorded on a 500 MHz instrument.

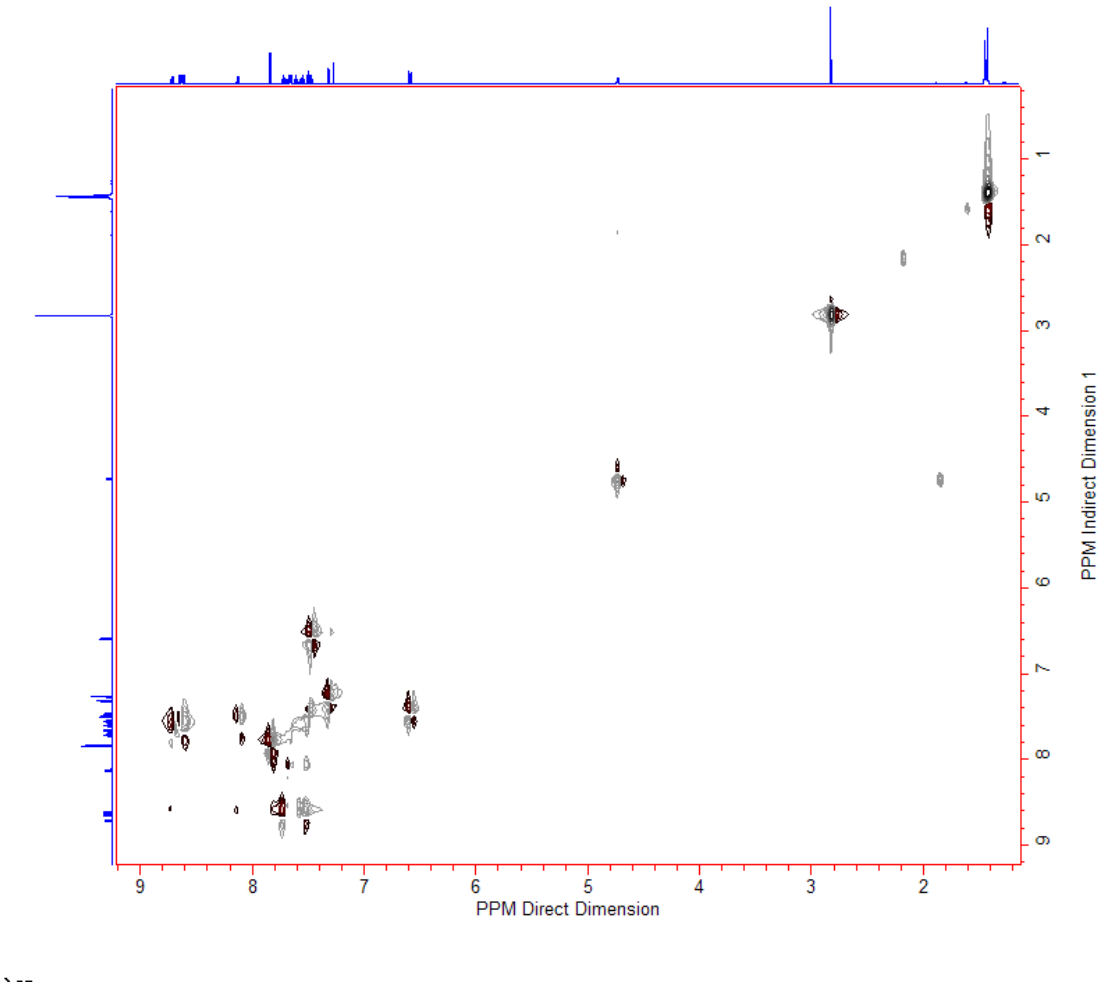


Figure S20. TOCSY NMR of **1** in $CDCl_3$ recorded on a 500 MHz instrument.

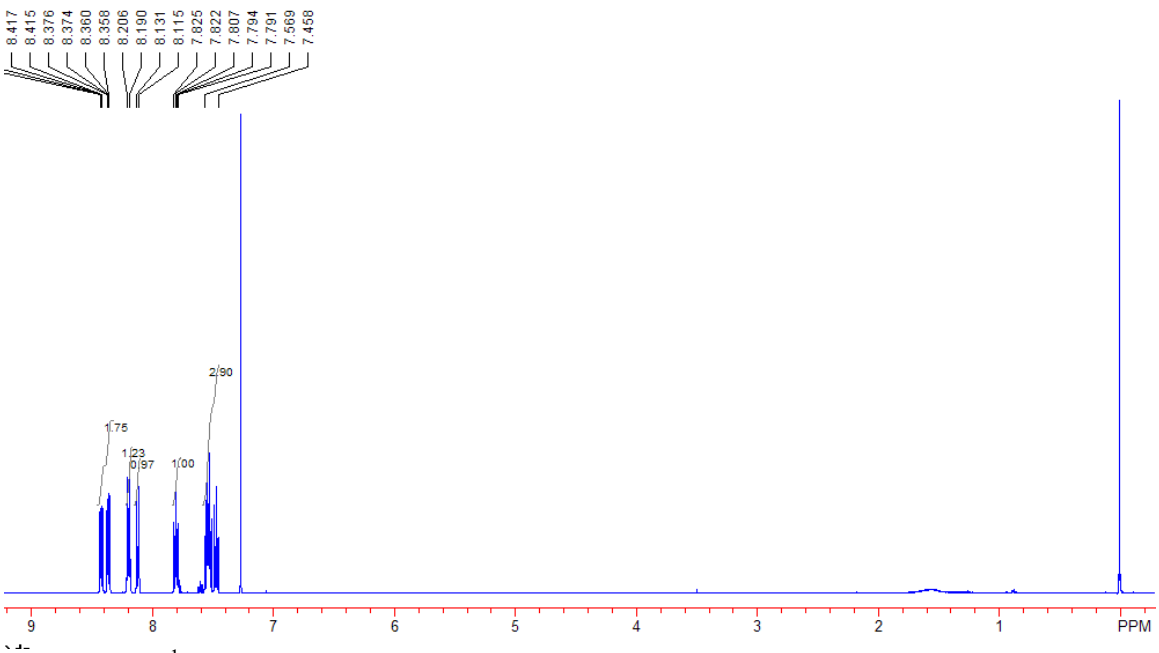


Figure S21. ^{1}H NMR of **2** in $CDCl_3$ recorded on 500 MHz NMR instrument.

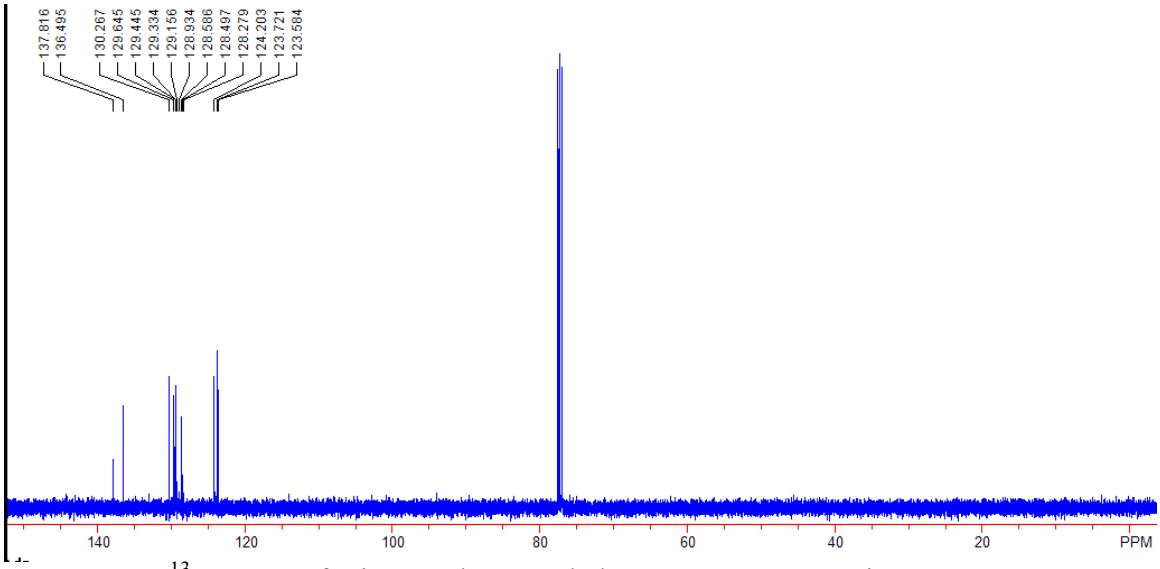


Figure S22. ^{13}C NMR of **2** in $CDCl_3$ recorded on 500 MHz NMR instrument.

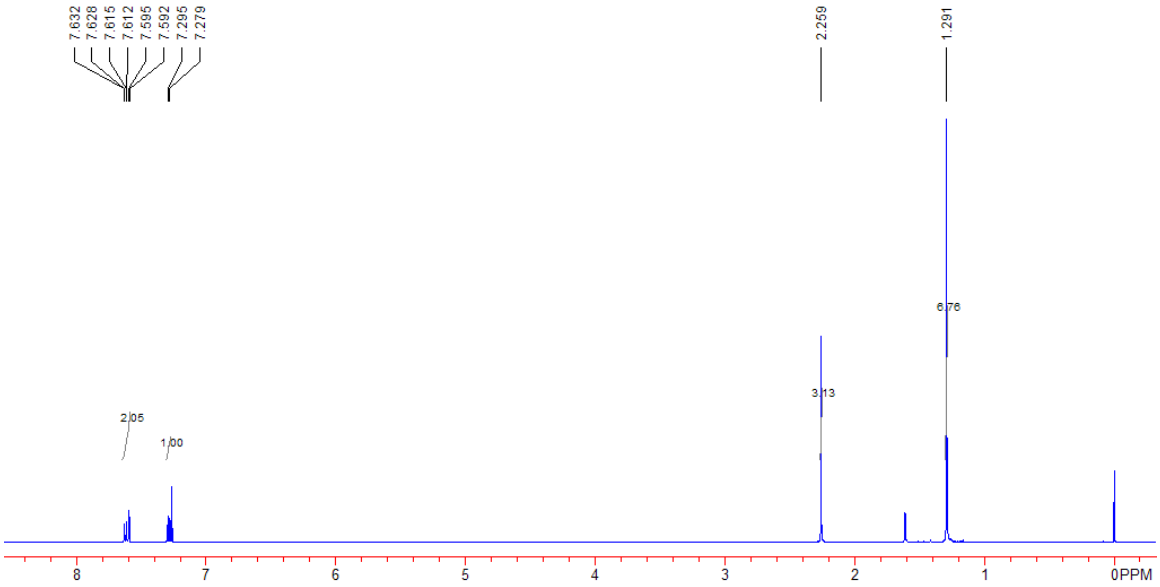


Figure S23. ^{1}H NMR of **3** in $CDCl_3$ recorded on 500 MHz NMR instrument.

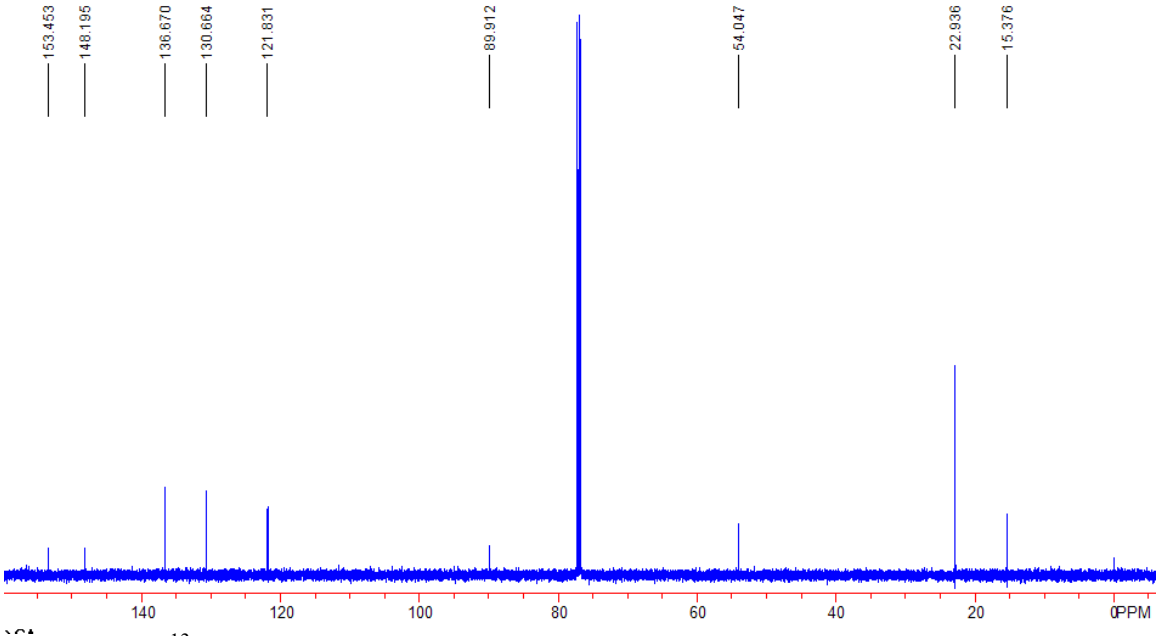


Figure S24. ^{13}C NMR of **3** in $CDCl_3$ recorded on 500 MHz NMR instrument.

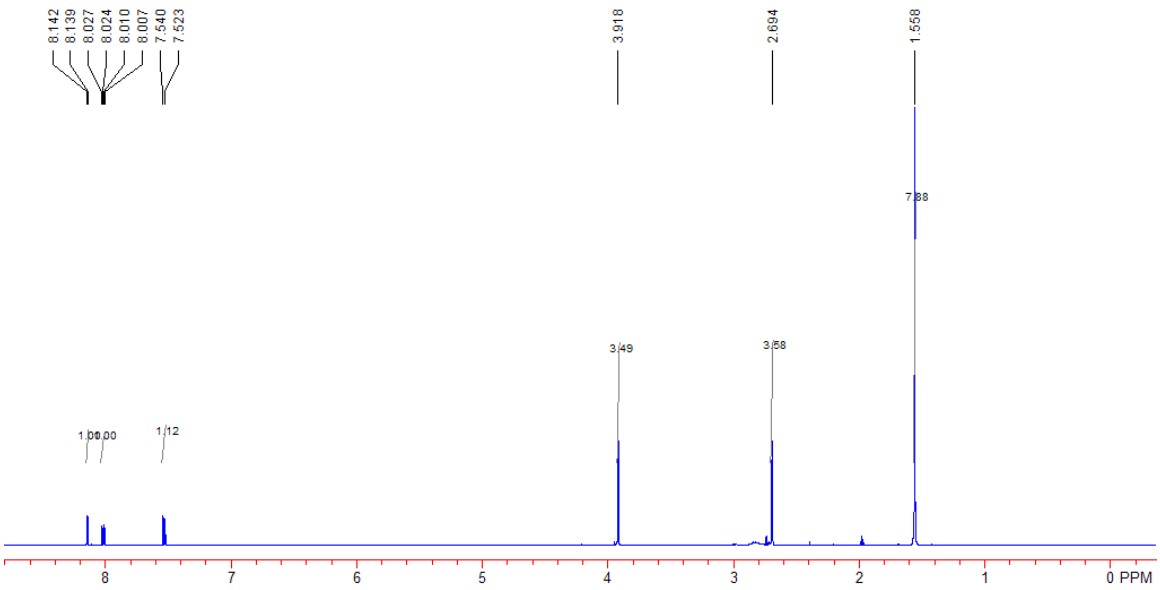


Figure S25. ^{1}H NMR of **4** in $CDCl_3$ recorded on 500 MHz NMR instrument.

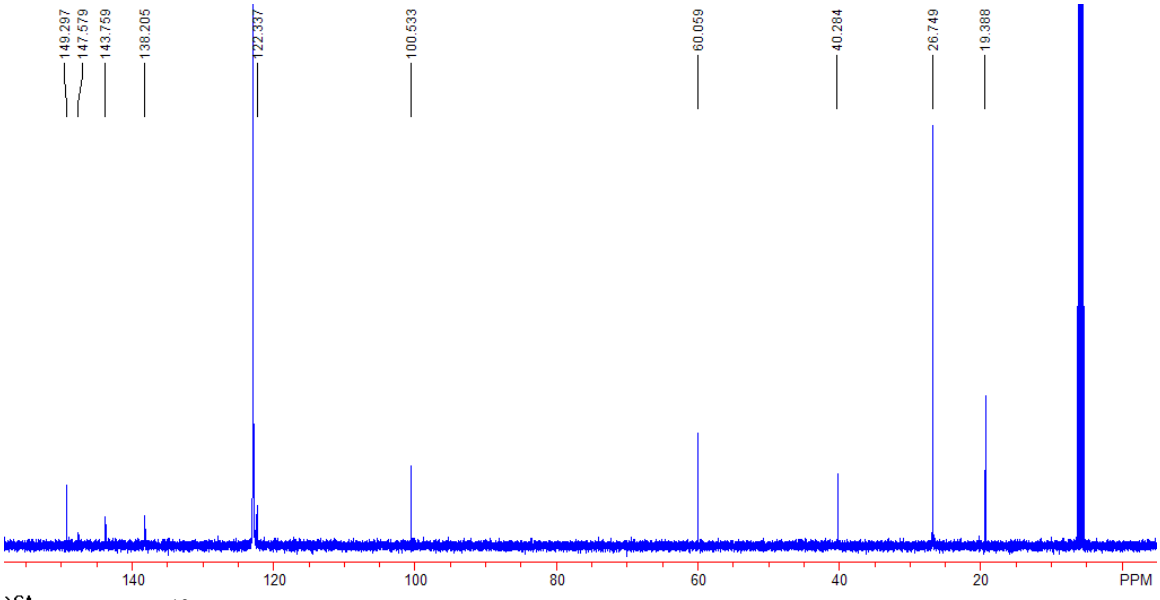


Figure S26. ^{13}C NMR of **4** in $CDCl_3$ recorded on 500 MHz NMR instrument.

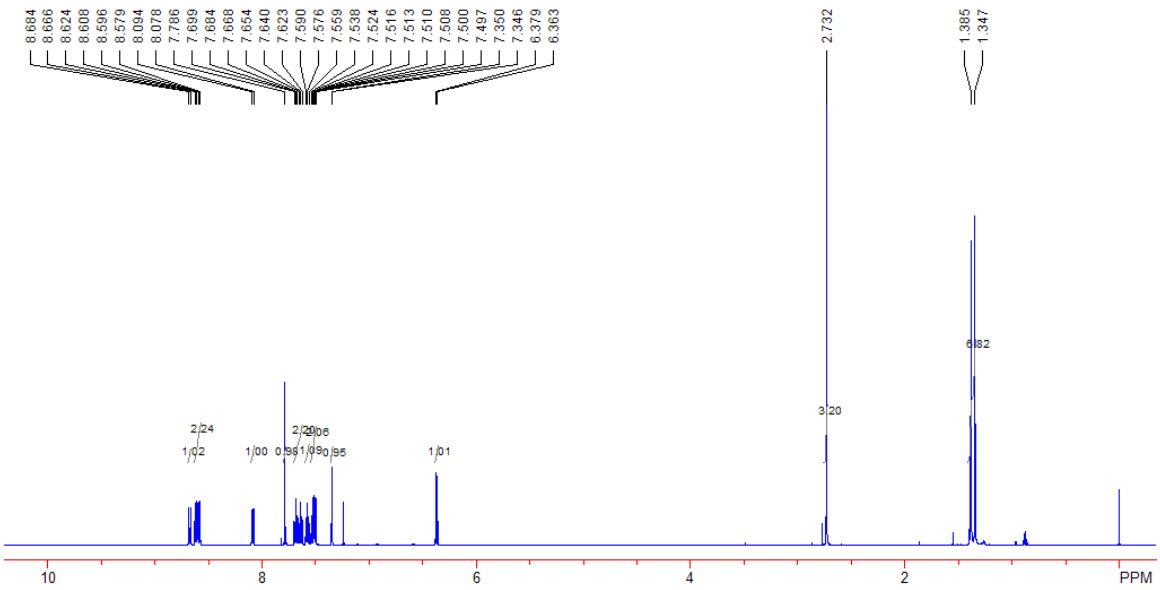


Figure S27. ^{1}H NMR of **5** in $CDCl_3$ recorded on 500 MHz NMR instrument.

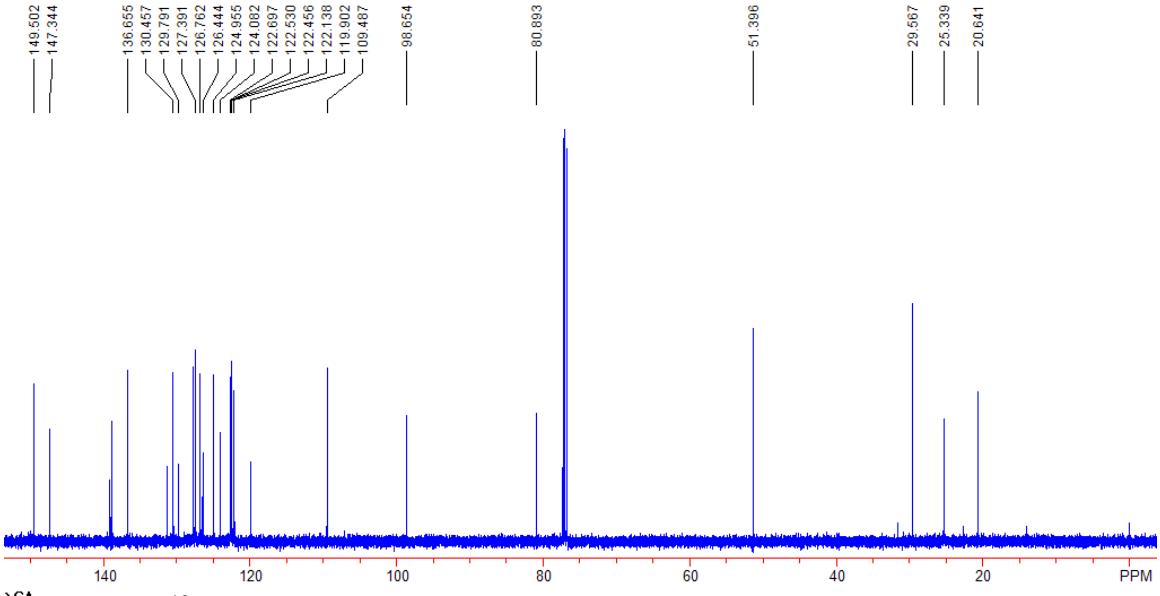


Figure S28. ^{13}C NMR of **5** in $CDCl_3$ recorded on 500 MHz NMR instrument.