SUPPORTING INFORMATION

Multiple Adaptation of Constitutional Dynamic Networks and Information Storage in Constitutional Distributions of Acylhydrazones

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1. Instrumental methods

1.1. Heating setup. Sample solutions in sealed NMR tubes were immersed in an oil bath kept constantly at the indicated temperature. To interrupt the heating in order to measure an NMR spectra, the samples were taken out of the oil bath and immediately cooled down using a water-ice bath.

1.2. Mass measurements. Mass spectra were obtained on Bruker MicroTOF (HRMS on Bruker MicroTOF-Q), with electrospray ionization. Nominal precision of the HRMS analysis is 10 ppm.

1.3. NMR measurements. NMR spectra were recorded on Bruker Avance 400 (400.14 MHz for ^{1}H and 100.62 MHz for ^{13}C) and Bruker Avance III plus 400 (400.34 MHz for ^{1}H and 100.67 MHz for ^{13}C) NMR spectrometers at 25 ˚C, taking at least 15 min from injection sample into the magnet to finishing the acquisition. All the collected spectra were referenced on residual solvent signal according to Nudelman et al.[1] T1 relaxation times were determined, and the d1 delay parameter was adapted in order to have a total scan time of three times the longest T1 relaxation constant in the sample.

For the integration of overlapping peaks deconvolution was done by fitting experimental data with a combination of Lorentzian and Gaussian peak profiles as offered by the MestReNova v.10 software suite.

The experiment uncertainty of the measurement and integration was estimated by independently measuring 3.5 mM samples six times (including injection into the magnet, tuning and shimming) and determining the standard deviation of the absolute integral values after referencing to the internal standard (hexamethyldisiloxane, HMDSO). In all cases the obtained standard deviation was below 2% of the integral corresponding to one proton. Thus, for the ease of calculation, a maximum error of 2% of the absolute integral corresponding to one proton was assumed for all samples.[2]

In the ^{1}H NMR spectra shown in the figures below, the region between the domains of the aliphatic and aromatic proton signals has been deleted for clarity. In a few cases, other regions containing few signal(s) have also been deleted.

1.4. UV/Vis spectroscopy. UV/Vis spectra were recorded on a Jasco V670 UV/Vis spectrometer equipped with a peltier thermostated cell holder at 25 ˚C using HPLC grade solvents.

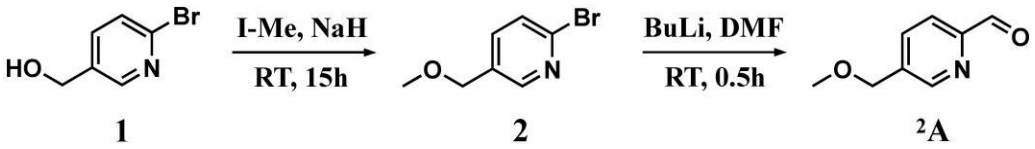
1.5. Irradiation setup. For irradiation experiments a 125 W high-pressure mercury lamp was used, whose light output was collimated using a quartz lens and filtered by passing

through a combination of a glass and a Schott UG11 bandpass filter allowing for a transmission centered at 360 nm (T = 27%) with a wavelength range of 310-400 nm. Samples were placed in front of the filtered light beam at a fixed distance of 10 cm using (sealed) NMR tubes (V = 0.5 mL). Thereby it was ensured that the full front of the solution was irradiated homogeneously. Mixing within NMR tubes was achieved by automatically turning them by 180° after every 5s-10s of irradiation using a small servomotor programmed with an Arduino microcontroller.[2]

1.6. Reagents and solvents. Reagents and solvents were purchased from Sigma-Aldrich, Alfa Aesar, and STREM and were used without further purification. Deuterated solvents were purchased from Euriso-TOP or Sigma-Aldrich and used without further purification.

2. Synthesis

2.1. Standard procedure for the preparation of relevant acylhydrazone constituents:



Scheme S1. Synthesis of pyridyl-aldehyde **2A**.

To a suspension of NaH (60% in paraffin oil, 0.1276 g, 3.19 mmol) in dry THF (20 mL), (6-bromopyridin-3-yl)methanol **1** (0.3 g, 1.6 mmol) in dry THF (80 mL) was added at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. MeI (0.2 mL, 3.19 mmol) was added to the reaction, and the resulting mixture was stirred at room temperature for 15 h. Upon completion of the reaction (as determined by TLC), the mixture was poured into ice water, and the resulting mixture was extracted with EtOAc (2 × 40 mL). The combined organic extracts were then washed with brine (25 mL), and dried ($MgSO_4$) before being concentrated in vacuo to yield 2-bromo-5-(methoxymethyl)pyridine oil **2**, yield 0.2345g.

To a solution of 2-bromo-5-(methoxymethyl)pyridine (0.13 g, 0.64 mmol) described in tetrahydrofuran (20 mL) was added n-butyl lithium (0.442 mL, 1.6 M hexane solution, 0.71 mmol) at -78 °C. This mixture was stirred for 55 minutes at -78 °C, and N,N-dimethylformamide (0.0598 mL, 0.772 mmol) was added at -78 °C. This mixture was warmed

to room temperature, and stirred for 20 minutes. The reaction solution was partitioned into water and ethyl acetate at 0 ˚C. The organic layer was washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate, and the solvent was evaporated under a reduced pressure. The residue was purified by silica gel column chromatography (DCM : ethyl acetate = 1 : 1) to obtain the title compound **^{2}A** (0.067g).

Aryl aldehydes **^{a}A** (1 equiv.) were added to ethanol solutions of hydrazides **^{b}B** (1 equiv.), respectively. After the mixtures were heated under reflux for 6 hours. The precipitates were collected on a Büchner funnel. The acylhydrazone products were obtained in a quantitative yield and were purified by recrystallization from certain proper solutions and washed with them. In all cases, the isomers obtained were E forms.

Nevertheless, several relevant components, constituents and complexes were reported before; the characterizations were consistent with the literature values.[3]-[10] The new compounds are described below:

^{2}A^{1}B: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.15 (s, 1H), 7.85 (s, 1H), 7.73 (dt, J = 9.1, 2.2 Hz, 2H), 7.68 (d, J = 1.3 Hz, 2H), 6.76 (dt, J = 9.1, Hz, 2H), 4.45 (s, 2H), 3.49 (s, 3H), 3.35 (s, 3H), 3..3 (s, 6H); ^{13}C NMR (100MHz, d_6-CD_3CN): δ 170.59, 154.46, 152.75, 149.24, 139.38, 136.52, 134.50, 132.81, 121.67, 119.71, 110.71, 71.91, 58.12, 39.89, 29.21; ESI-MS: calculated for $[C_{17}H_{20}N_4O_2+H]^+$ 312.16, found 312.17; Elemental analysis calculated (%) for $C_{17}H_{20}N_4O_2$: C 65.37, H 6.45, N 17.94 found C 64.98, H 6.46, N 17.90.

^{2}A^{8}B: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.59 (s, 1H), 8.35 (d, J = 7.2 Hz, 3H), 8.10 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 4.50 (s, 2H), 3.39 (s, 3H); ^{13}C NMR (100MHz, d_6-CD_3CN): δ 170.59, 154.46, 152.75, 149.24, 139.38, 136.52, 134.50, 132.81, 121.67, 119.71, 110.71, 71.91, 58.12, 39.89, 29.21; ESI-MS: calculated for $[C_{17}H_{20}N_4O_2+H]^+$ 312.16, found 312.20; Elemental analysis calculated (%) for $C_{17}H_{20}N_4O_2$: C 65.37, H 6.45, N 17.94 found C 64.98, H 6.46, N 17.90.

^{3}A^{1}B: ^{1}H NMR (400 MHz, CD_3CN): δ = 7.83 (s, 1H), 7.71 (dt, J = 9.0, 2.8 Hz, 2H), 7.53 (dt, J = 9.0, 2.8 Hz, 2H), 6.92 (dt, J = 9.0, 2.8 Hz, 2H), 6.74 (dt, J = 9.0, 2.8 Hz, 2H), 4.08 (q, J = 7.0 Hz, 2H), 3.46 (s, 3H), 3.02 (s, 6H), 1.36 (t, J = 7 Hz, 3H); ^{13}C NMR (100MHz, d_6-CD_3CN): δ 169.86, 159.96, 152.02, 138.63, 132.09, 128.36, 128.20, 121.93, 114.68, 110.13, 63.50, 39.36, 28.37, 14.04; ESI-MS: calculated for $[C_{19}H_{23}N_3O_2+H]^+$ 326.18, found 326.18; Elemental analysis calculated (%) for $C_{19}H_{23}N_3O_2$: C 70.13, H 7.12, N 12.91, found C 69.01, H 7.23, N 12.78.

^{3}A^{8}B: ^{1}H NMR (400 MHz, CD_3CN): δ = 10.24 (s, 1H, NH), 8.33 (d, J = 8.8 Hz, 2H), 8.27 (s, 1H), 8.07 (d, J = 12 Hz, 2H), 7.70 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.12 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100MHz, d_6-CD_3CN): δ 161.78, 161.07, 148.79, 129.06, 128.84, 126.55, 123.68, 114.81, 63.65, 14; ESI-MS: calculated for $[C_{16}H_{15}N_3O_4+H]^+$ 314.11, found 314.12; Elemental analysis calculated (%) for $C_{16}H_{15}N_3O_4$: C 61.34, H 4.83, N 13.41, found C 60.34, H 4.98, N 13.20.

^{4}A^{1}B: ^{1}H NMR (400 MHz, CD_3CN): δ = 7.83 (s, 1H), 7.71 (dt, J = 9.1, 2.8 Hz, 2H), 7.55 (dt, J = 9.1, 2.8 Hz, 2H), 6.95 (dt, J = 8.88, 2.8 Hz, 2H), 6.75 (dt, J = 9.1, 2.8 Hz, 2H), 3.80 (s, 3H), 3.46 (s, 3H), 3.02 (s, 6H); ^{13}C NMR (100MHz, d_6-CD_3CN): δ 170.40, 161.14, 152.54, 139.12, 132.65, 128.89, 128.87, 122.42, 117.90, 114.72, 110.64, 55.60, 55.57, 39.91, 28.91; ESI-MS: calculated for $[C_{18}H_{21}N_3O_2+H]^+$ 312.16, found 312.18; Elemental analysis calculated (%) for $C_{18}H_{21}N_3O_2$: C 69.43, H 6.80, N 13.49, found C 65.25, H 7.58, N 13.40.

^{4}A^{3}B: ^{1}H NMR (400 MHz, CD_3CN): δ = 9.85 (s, 1H, NH), 8.20 (s, J = 8.8 Hz, 1H), 7.67 (dt, J = 8.8, 1.9 Hz, 2H), 7.00 (dt, J = 8.8, 2.8 Hz, 2H), 6.78 (dt, J = 8.8, 2.8 Hz, 2H), 3.83 (s, 3H), 3.02 (s, 6H); ^{13}C NMR (100MHz, d_6-DMSO): δ 161.01, 152.85, 146.54, 129.46, 128.88, 127.73, 120.11, 114.77, 111.269, 55.75; ESI-MS: calculated for $[C_{17}H_{19}N_3O_2+H]^+$ 298.15, found 298.15; Elemental analysis calculated (%) for $C_{17}H_{19}N_3O_2$: C 68.67, H 6.44, N 14.13, found C 68.23, H 6.56, N 14.01.

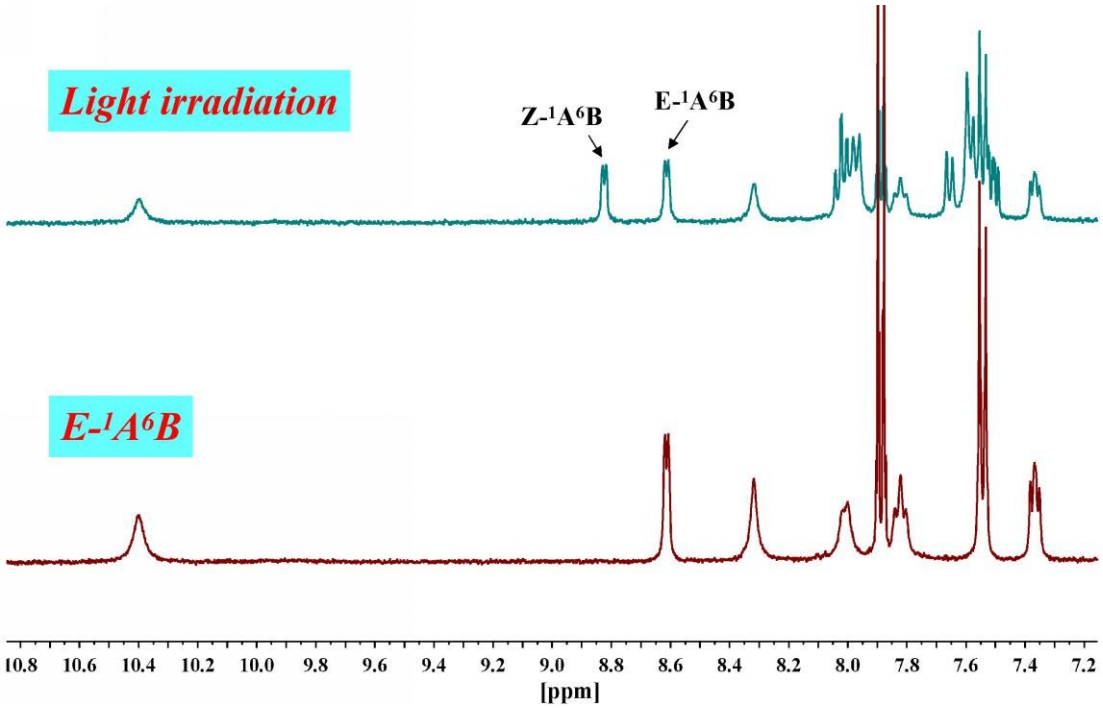


Figure S1a. A portion of the ^{1}H NMR spectra of E-**^{1}A^{6}B** and its transformation into Z-**^{1}A^{6}B** upon light irradiation (λ_{irr} = 310-400 nm) for 60 min in CD_3CN.

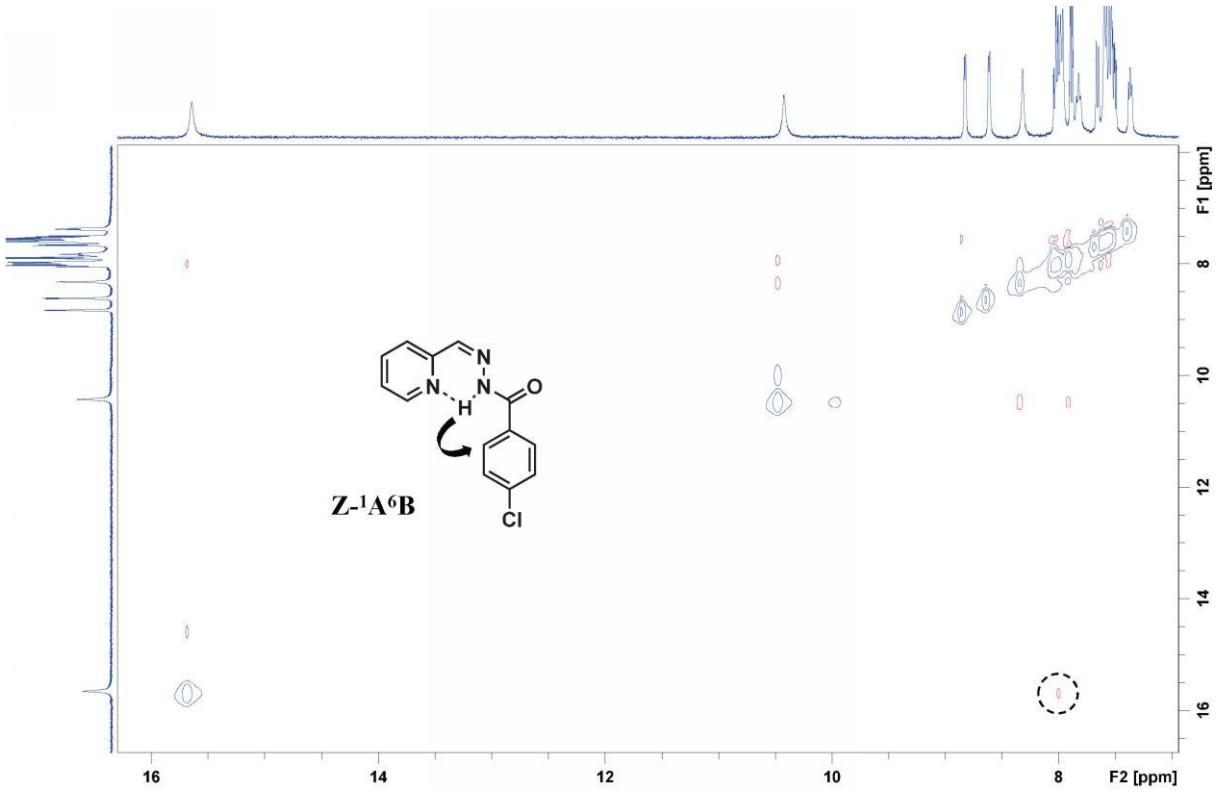


Figure S1b. 2D NOESY of a mixture of E and Z isomers of **^{1}A^{6}B**, which was obtained from pure E-**^{1}A^{6}B** upon light irradiation (λ_{irr} = 310-400 nm) for 60 min in CD_3CN. For the Z isomer, the N-H hydrogen is bound to N and have NOESY interaction with C-H of benzhydrazide (black circle) without the interaction with imine proton.

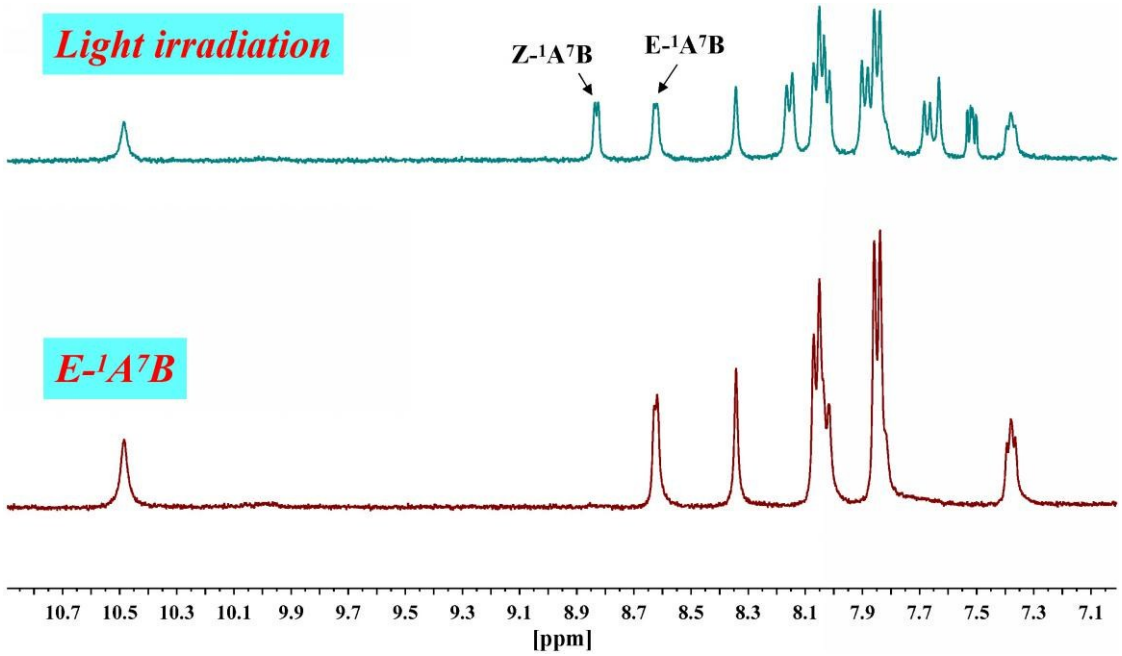


Figure S2a. A portion of the ^{1}H NMR spectra of E-**^{1}A^{7}B** and its transformation into Z-**^{1}A^{7}B** upon light irradiation (λ_{irr} = 310-400 nm) for 116 min in CD_3CN.

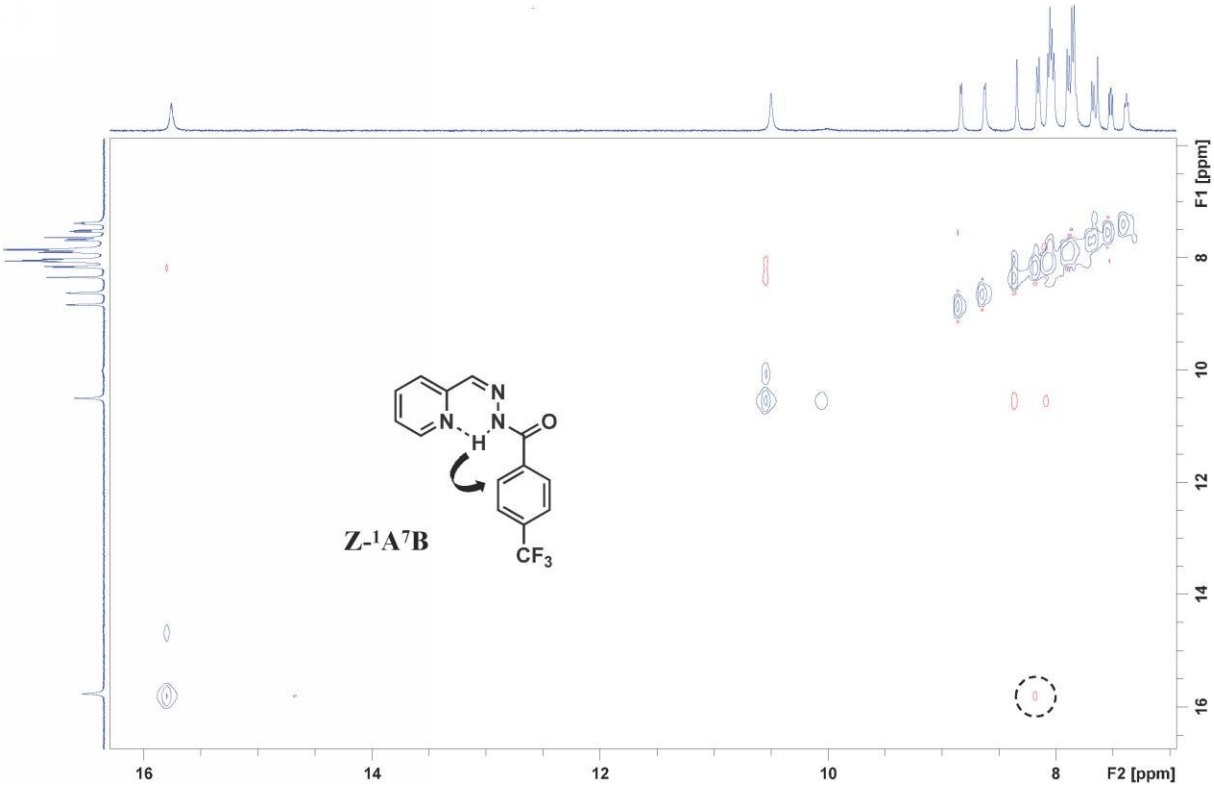


Figure S2b. 2D NOESY of a mixture of E and Z isomers of **^{1}A^{7}B**, which was obtained from pure E-**^{1}A^{7}B** upon light irradiation (λ_{irr} = 310-400 nm) for 116 min in CD_3CN. For the Z isomer, the N-H hydrogen is bound to N and have NOESY interaction with C-H of benzhydrazide (black circle) without the interaction with imine proton.

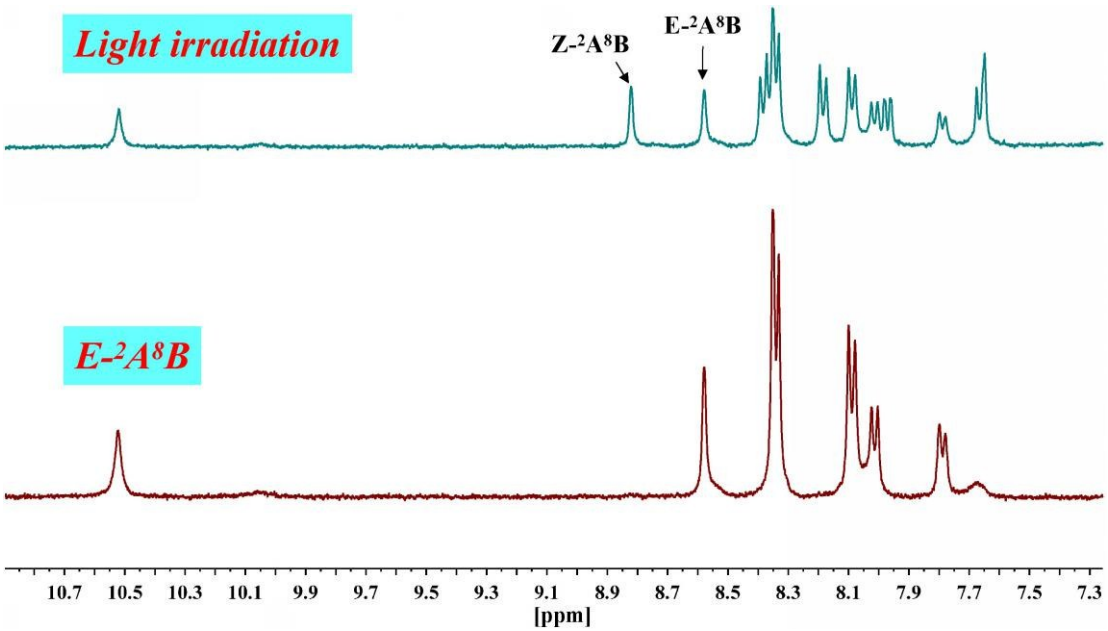


Figure S3a. A portion of the ^{1}H NMR spectra of E-^{2}**A**^{8}**B** and its transformation into Z-^{2}**A**^{8}**B** upon light irradiation (λ_{irr} = 310-400 nm) for 68 min in CD_3CN.

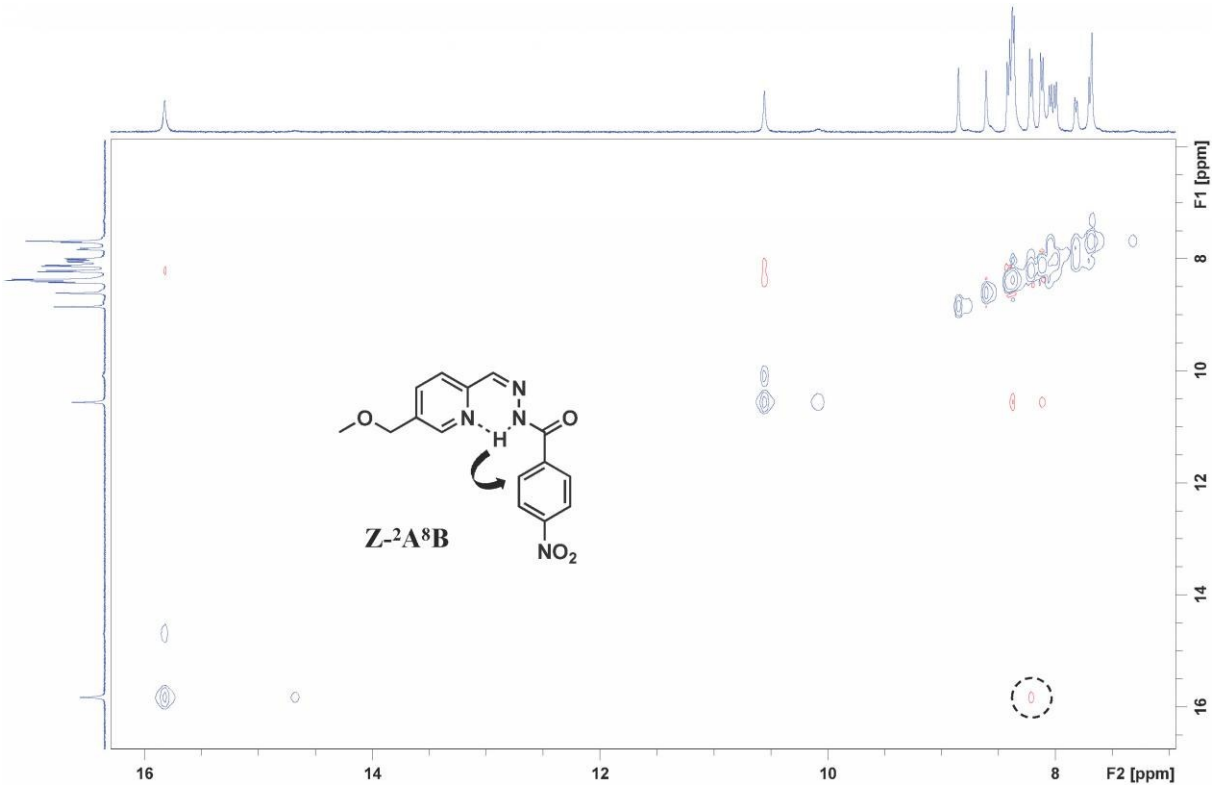


Figure S3b. 2D NOESY of a mixture of E and Z isomers of ^{2}**A**^{8}**B**, which was obtained from pure E-^{2}**A**^{8}**B** upon light irradiation (λ_{irr} = 310-400 nm) for 68 min in CD_3CN. For the Z isomer, the N-H hydrogen is bound to N and have NOESY interaction with C-H of benzhydrazide (black circle) without the interaction with imine proton.

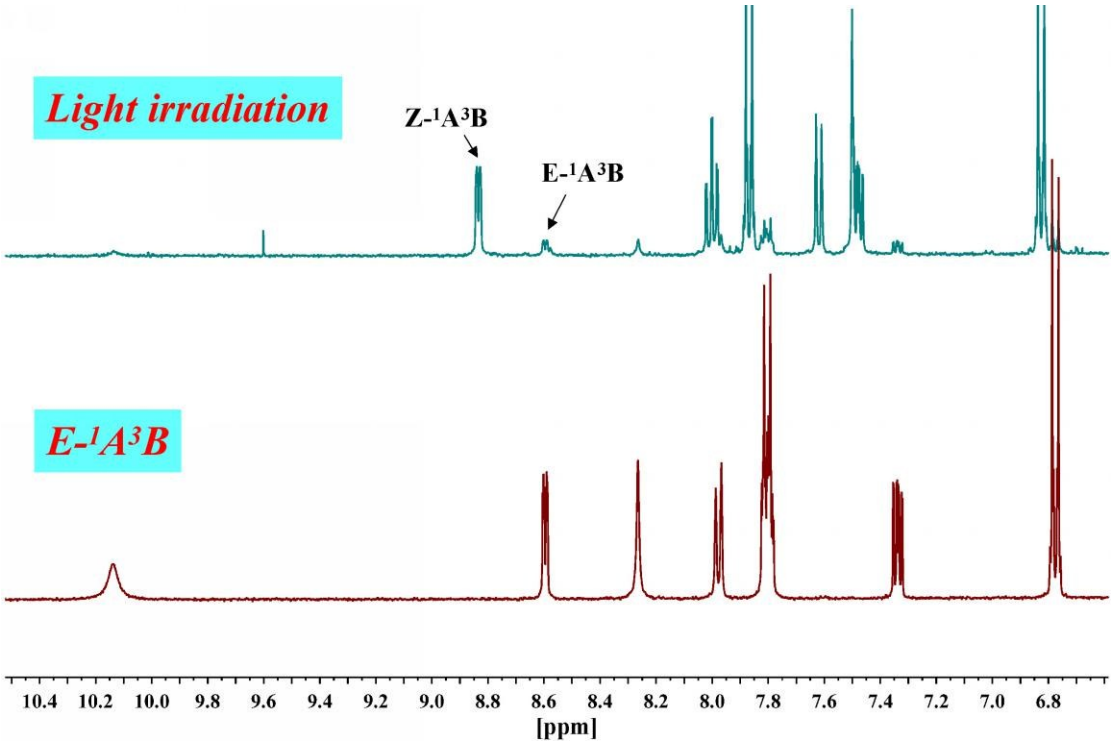


Figure S4a. A portion of the ^{1}H NMR spectra of E-^{1}**A**^{3}**B** and its transformation into Z-^{1}**A**^{3}**B** upon light irradiation (λ_{irr} = 310-400 nm) for 148 min in CD_3CN.

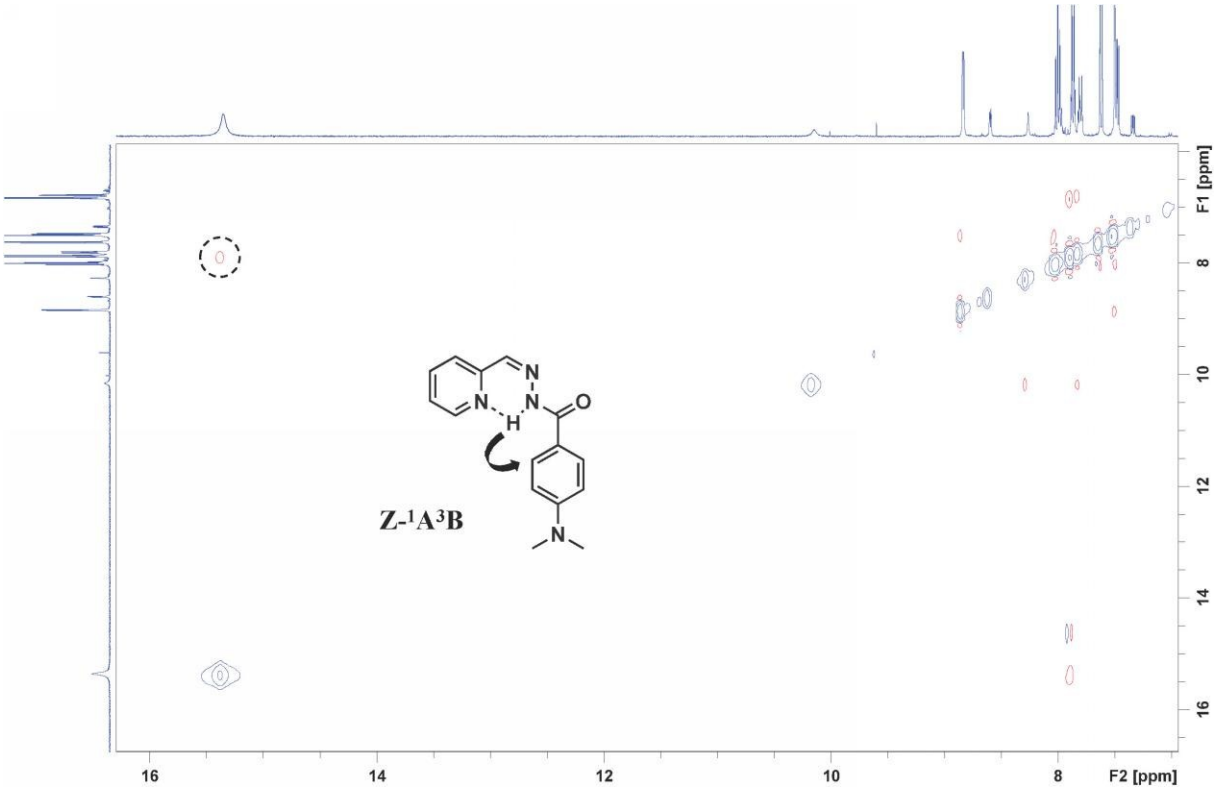


Figure S4b. 2D NOESY of a mixture of E and Z isomers of ^{1}**A**^{3}**B**, which was obtained from pure E-^{1}**A**^{3}**B** upon light irradiation (λ_{irr} = 310-400 nm) for 148 min in CD_3CN. For the Z isomer, the N-H hydrogen is bound to N and have NOESY interaction with C-H of benzhydrazide (black circle) without the interaction with imine proton.

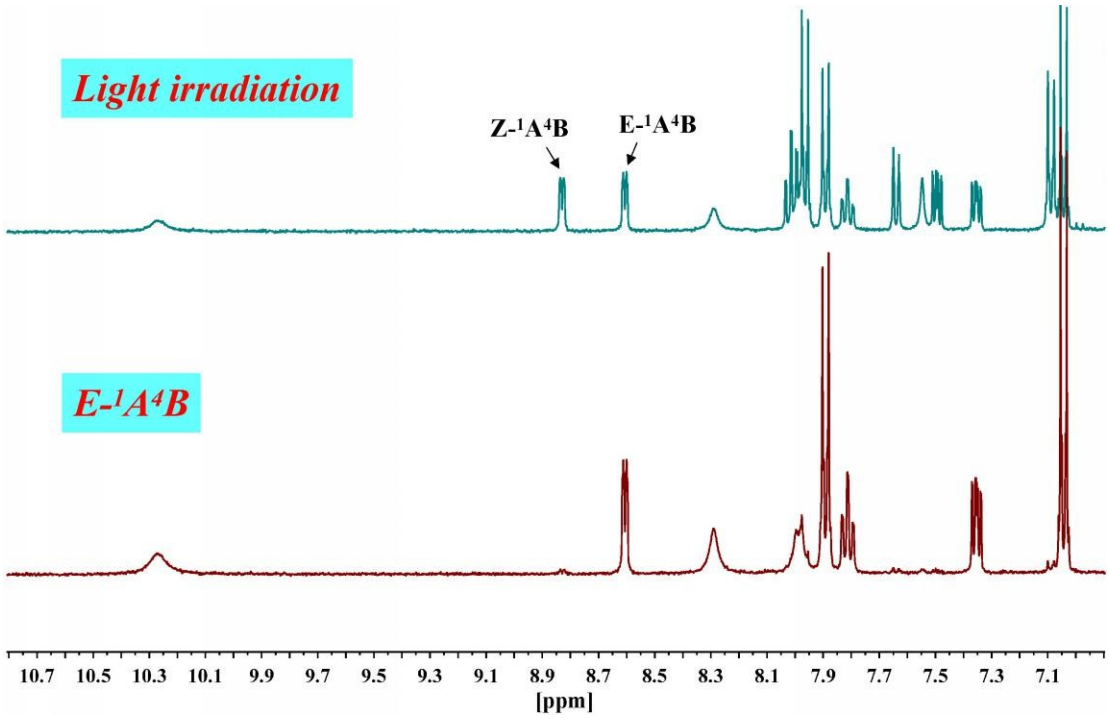


Figure S5a. A portion of the ^{1}H NMR spectra of E-**^{1}A^{4}B** and its transformation into Z-**^{1}A^{4}B** upon light irradiation (λ_{irr} = 310-400 nm) for 116 min in CD_3CN.

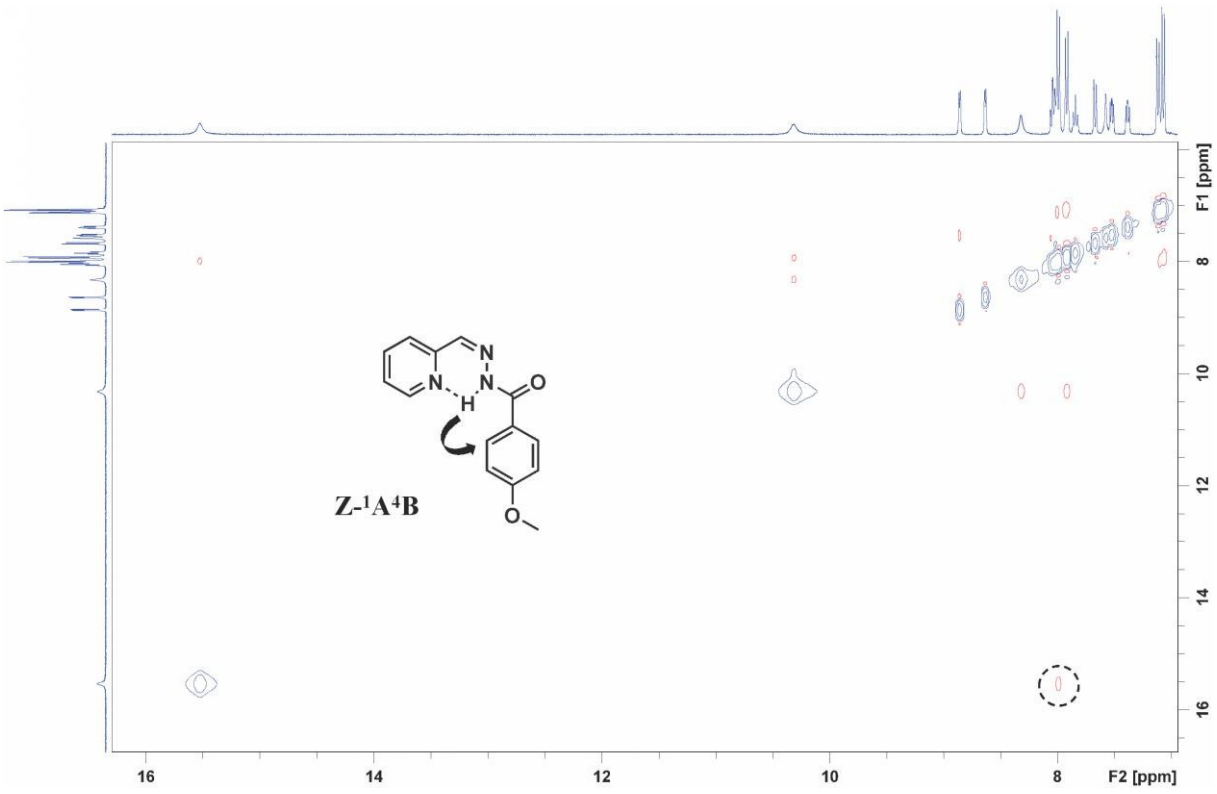


Figure S5b. 2D NOESY of a mixture of E and Z isomers of **^{1}A^{4}B**, which was obtained from pure E-**^{1}A^{4}B** upon light irradiation (λ_{irr} = 310-400 nm) for 116 min in CD_3CN. For the Z isomer, the N-H hydrogen is bound to N and have NOESY interaction with C-H of benzhydrazide (black circle) without the interaction with imine proton.

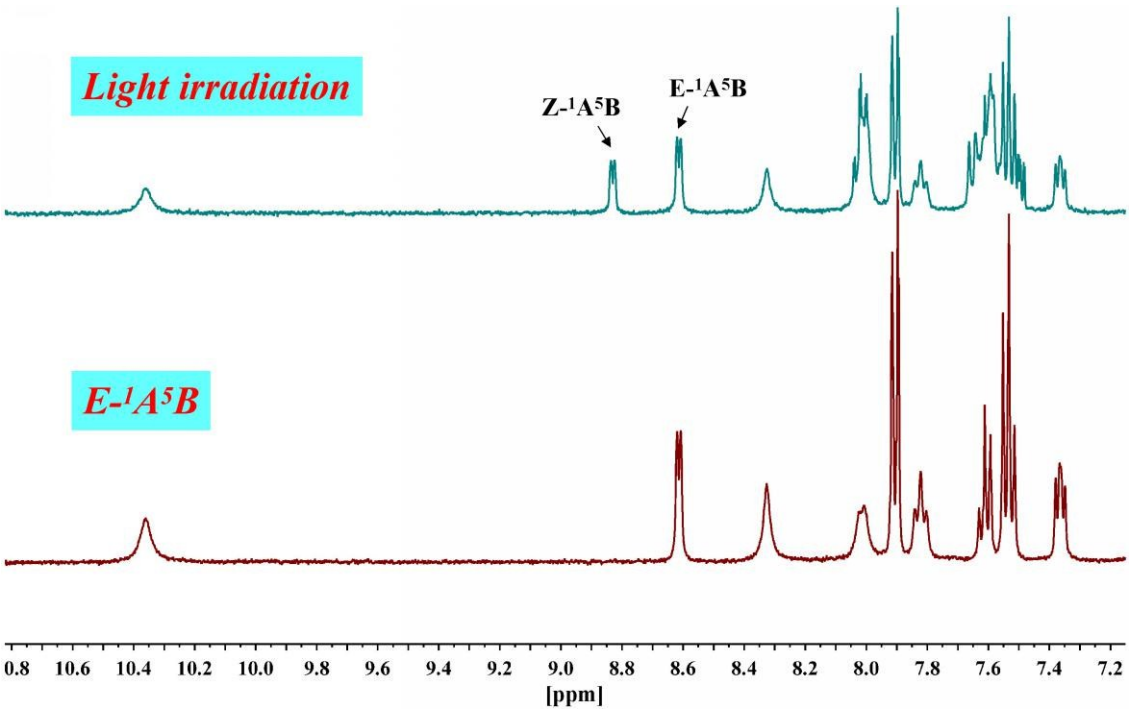


Figure S6a. A portion of the ^{1}H NMR spectra of E-**^{1}A^{5}B** and its transformation into Z-**^{1}A^{5}B** upon light irradiation (λ_{irr} = 310-400 nm) for 148 min in CD_3CN.

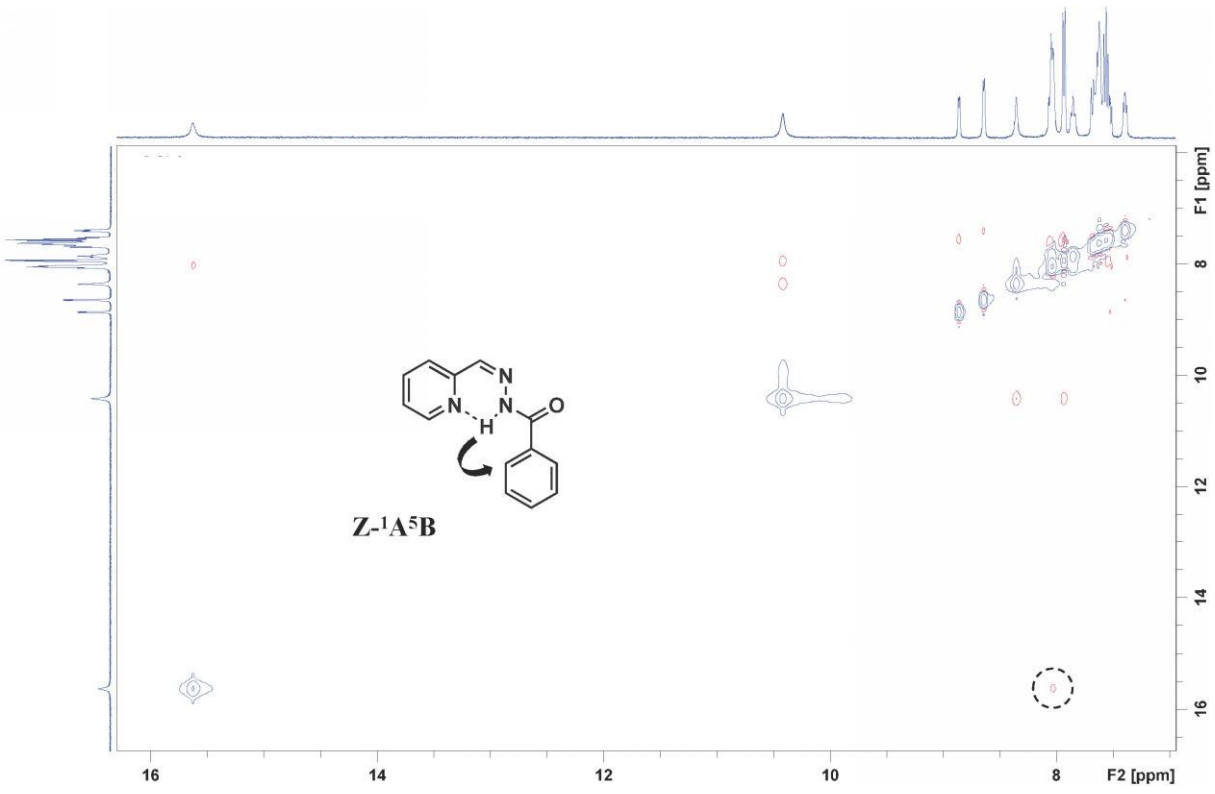


Figure S6b. 2D NOESY of a mixture of E and Z isomers of **^{1}A^{5}B**, which was obtained from pure E-**^{1}A^{5}B** upon light irradiation (λ_{irr} = 310-400 nm) for 148 min in CD_3CN. For the Z isomer, the N-H hydrogen is bound to N and have NOESY interaction with C-H of benzhydrazide (black circle) without the interaction with imine proton.

2.2. Standard procedure for the preparation of the relevant complexes: 0.5 equiv. of metal ions were added to the CD_3CN solutions of 1 equiv. of the ligand constitients (regardless the isomer) with or without 1.1 equiv. of Et_3N. The mixtures were heated overnight at 70 °C. The complexes were always freshly prepared prior to every new experiments. The complexes were never isolated, all the present experiments and analysis were done in CD_3CN solution.

$Zn^{II}(\mathbf{^2A^1B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.62 (s, 1H), 8.20 (s, 1H), 8.15 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 7.8 Hz, 2H), 6.76 (dt, J = 9.1, 3.0 Hz, 2H), 4.44 (s, 2H), 3.87 (s, 3H), 3.32 (s, 3H), 3.04 (s, 6H); ^{13}C NMR (100MHz, d_6-DMSO): δ 172.79, 154.51, 148.95, 146.02, 141.41, 140.99, 140.65, 132.54, 128.03, 114.41, 111.28, 70.85, 58.63, 39.80, 38.50. ESI-MS: calculated for $[C_{36}H_{44}N_8O_4Zn]^{2-}$ 358.14, found 358.15.

$Zn^{II}(\mathbf{^2A^8B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.94 (s, 1H), 8.38 (dt, J = 9.0, 2.3 Hz, 2H), 8.31 (s, 1H), 8.20 (m, 3H), 8.09 (d, J = 8.0 Hz, 1H), 4.45 (s, 2H), 3.32 (s, 3H); ^{13}C NMR (100MHz, d_6-DMSO): δ 151.18, 148.76, 145.12, 140.66, 129.77, 127.83, 124.17, 119.46, 70.27, 58.14. ESI-MS: calculated for $[C_{30}H_{27}N_8O_8Zn]^-$ 691.12, found 691.12.

$Zn^{II}(\mathbf{^1A^2B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.76 (s, 1H), 8.42 (d, J = 4.8 Hz, 1H), 8.26 (t, J = 6.8 Hz, 1H), 8.10 (d, J = 7 Hz, 1H), 7.71 (m, 4H), 7.58 (m, 2H), 3.77 (s, 3H); ^{13}C NMR (100MHz, d_6-DMSO): δ 173.53, 150.42, 146.48, 143.97, 143.00, 133.62, 130.46, 129.43, 129.08, 37.34. ESI-MS: calculated for $[C_{28}H_{26}N_6O_2Zn]^{2-}$ 271.07, found 271.07.

$Zn^{II}(\mathbf{^1A^3B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.81 (s, 1H), 8.25 (d, J = 4.8 Hz, 1H), 8.17 (td, J = 7.8, 3.9 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.86 (dt, J = 9.2, 3.0 Hz, 2H), 7.57 (ddd, J = 6.0, 5.1, 1.1 Hz, 1H), 6.78 (dt, J = 9.2, 3.0 Hz, 2H), 3.05 (s, 6H); ^{13}C NMR (100MHz, d_6-DMSO): δ 167.69, 155.43, 149.83, 147.01, 142.41, 142.20, 130.99, 128.75, 127.97, 111.77, 39.84. ESI-MS: calculated for $[C_{30}H_{31}N_8O_2Zn]^-$ 559.18, found 559.25.

$Zn^{II}(\mathbf{^1A^4B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.85 (s, 1H), 8.31 (d, J = 4.7 Hz, 1H), 8.21 (td, J = 7.8, 1.2 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.98 (dt, J = 9.0, 3.0 Hz, 2H), 7.62 (ddd, J = 6.2, 5.0, 1.1 Hz, 1H), 7.10 (dt, J = 9.0, 3.0 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100MHz, d_6-DMSO): δ 165.60, 150.05, 143.95, 142.60, 131.29, 129.02, 128.27, 115.21, 56.20. ESI-MS: calculated for $[C_{28}H_{25}N_6O_4Zn]^-$ 573.12, found 573.12.

$Zn^{II}(\mathbf{^1A^5B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.97 (s, 1H), 8.35 (s, 1H), 8.25 (td, J = 7.8, 1.5 Hz, 1H), 8.10 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 7.6 Hz, 2H), 7.77 (t, J = 7.4 Hz, 1H), 7.67 (t, J = 5.6 Hz, 1H), 7.62 (t, J = 7.9 Hz, 2H); ^{13}C NMR (100MHz, d_6-DMSO): δ 169.00,

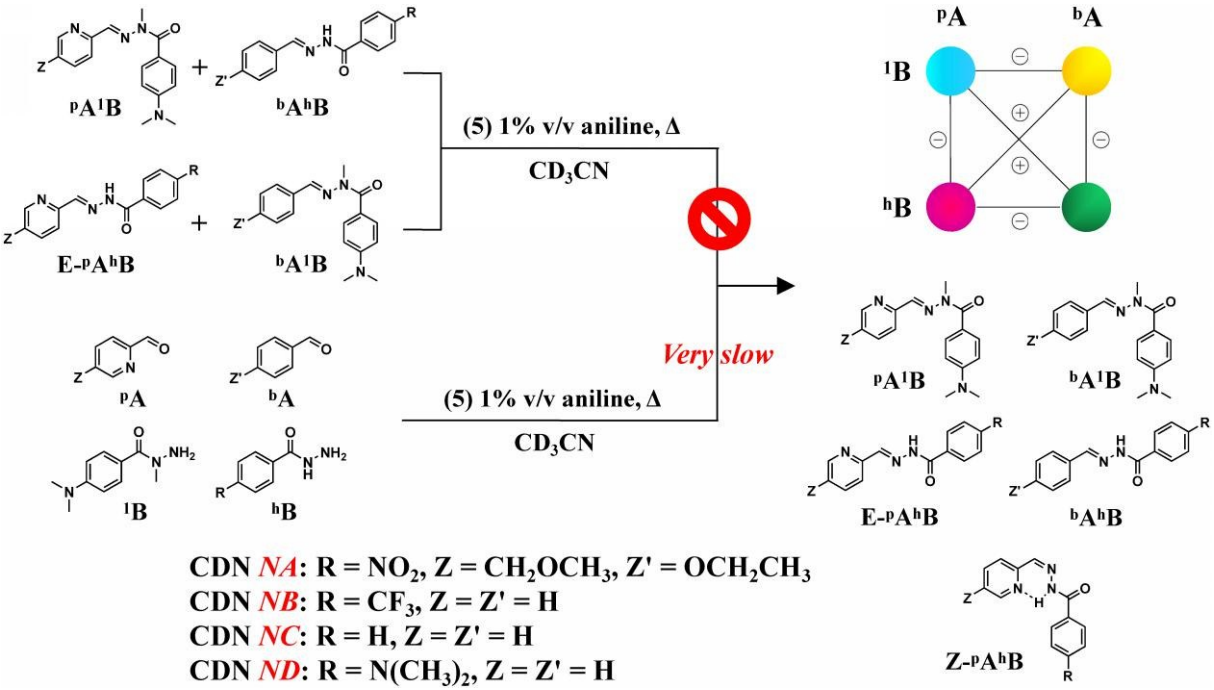
150.36, 146.55, 142.82, 135.61, 129.89, 129.42, 128.99, 128.78, 128.54. ESI-MS: calculated for $[C_{26}H_{21}N_6O_2Zn]^-$ 513.10, found 513.10.

$Zn^{II}(\mathbf{^1A^6B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.95 (s, 1H), 8.34 (d, J = 4.7 Hz, 1H), 8.26 (td, J = 7.8, 1.6 Hz, 1H), 8.11 (dt, J = 7.8, 0.8 Hz, 1H), 7.97 (dt, J = 8.8, 2.5 Hz, 2H), 7.67 (ddd, J = 6.2, 5.1, 1.2 Hz, 1H), 7.62 (dt, J = 8.8, 2.5 Hz, 2H); ^{13}C NMR (100MHz, d_6-DMSO): δ 168.14, 150.39, 146.49, 145.36, 142.90, 141.34, 130.64, 130.11, 129.46, 128.83, 127.36. ESI-MS: calculated for $[C_{28}H_{19}Cl_2N_6O_2Zn]^-$ 581.02, found 581.02.

$Zn^{II}(\mathbf{^1A^7B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.95 (s, 1H), 8.37 (d, J = 4.7 Hz, 1H), 8.27 (td, J = 7.8, 1.4 Hz, 1H), 8.14 (d, J = 8.2 Hz, 2H), 8.11 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.62 (ddd, J = 6.0, 5.1, 0.8 Hz, 1H); ^{13}C NMR (100MHz, d_6-DMSO): δ 168.33, 150.18, 146.70, 145.51, 143.14, 133.18, 129.83, 129.32, 128.72, 126.69. ESI-MS: calculated for $[C_{28}H_{19}F_6N_6O_2Zn]^-$ 649.08, found 649.08.

$Zn^{II}(\mathbf{^1A^1B})_2$: ^{1}H NMR (400 MHz, CD_3CN): δ = 8.57 (s, 1H), 7.85 (s, 1H), 7.75 (m, 4H), 7.29 (ddd, J = 6.5, 4.9, 1.5 Hz, 1H), 6.77 (dt, J = 9.1, 2.8 Hz, 2H), 3.50 (s, 3H), 3.02 (s, 6H); ^{13}C NMR (100MHz, d_6-DMSO): δ 154.56, 149.89, 146.94, 142.75, 141.47, 132.56, 128.95, 128.41, 111.30, 39.81, 38.53. ESI-MS: calculated for $[C_{32}H_{36}N_8O_2Zn]^{2-}$ 314.12, found 314.11.

3. Design and construction of the acylhydrazone-based DCLs from suitably selected components and catalysts.



Scheme S2. Generation of four [2×2] CDNs with four constituents $^{p}\mathbf{A}^{1}\mathbf{B}$, $^{b}\mathbf{A}^{1}\mathbf{B}$, $^{p}\mathbf{A}^{h}\mathbf{B}$ and $^{b}\mathbf{A}^{h}\mathbf{B}$ (3.5 mM each) by component exchange between either $^{p}\mathbf{A}^{1}\mathbf{B}$ and $^{b}\mathbf{A}^{h}\mathbf{B}$ (left top) or $^{p}\mathbf{A}^{h}\mathbf{B}$ and $^{b}\mathbf{A}^{1}\mathbf{B}$ (left middle), or by component condensation of $^{p}\mathbf{A}$, $^{b}\mathbf{A}$, $^{1}\mathbf{B}$ and $^{h}\mathbf{B}$ with 1% v/v aniline as the catalyst, giving the same statistical distribution. $^{p}\mathbf{A}^{h}\mathbf{B}$ exist in both E and Z isomers.

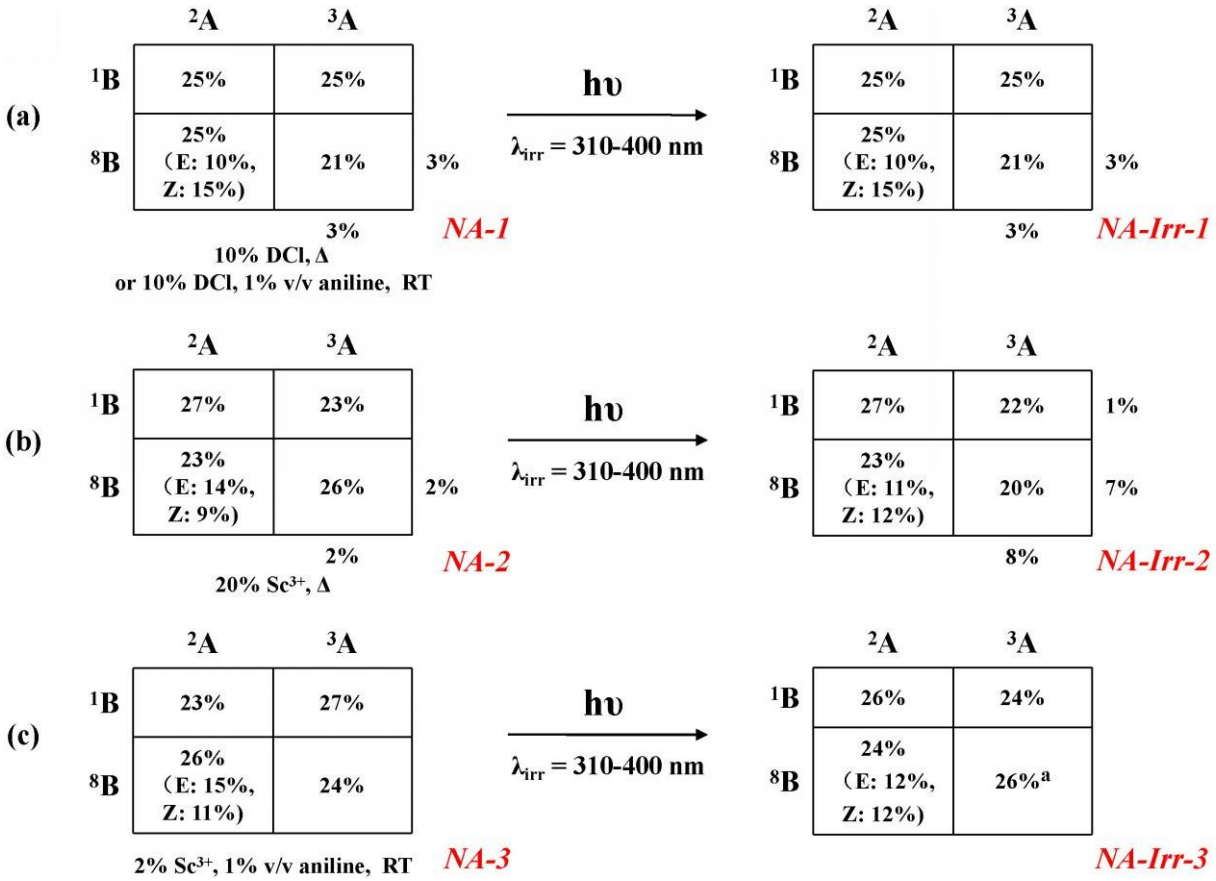


Table S1. Distribution of the four-membered [2×2] CDNs ***NA*** with four constituents ^{2}**A**^{1}**B**, ^{3}**A**^{1}**B**, ^{2}**A**^{8}**B** and ^{3}**A**^{8}**B** (3.5 mM each) generated from two constituents ^{2}**A**^{1}**B** and ^{3}**A**^{8}**B** or ^{2}**A**^{8}**B** and ^{3}**A**^{1}**B**, or from four components ^{2}**A**, ^{3}**A**, ^{1}**B** and ^{8}**B**, and distribution of CDNs ***NA-Irr*** stemmed from ***NA*** under light irradiation (λ_{irr} = 310-400 nm) with different catalysts and temperature conditions. Error on % determination: ±2%. See Figure S7a-S7c for ^{1}H NMR spectra.

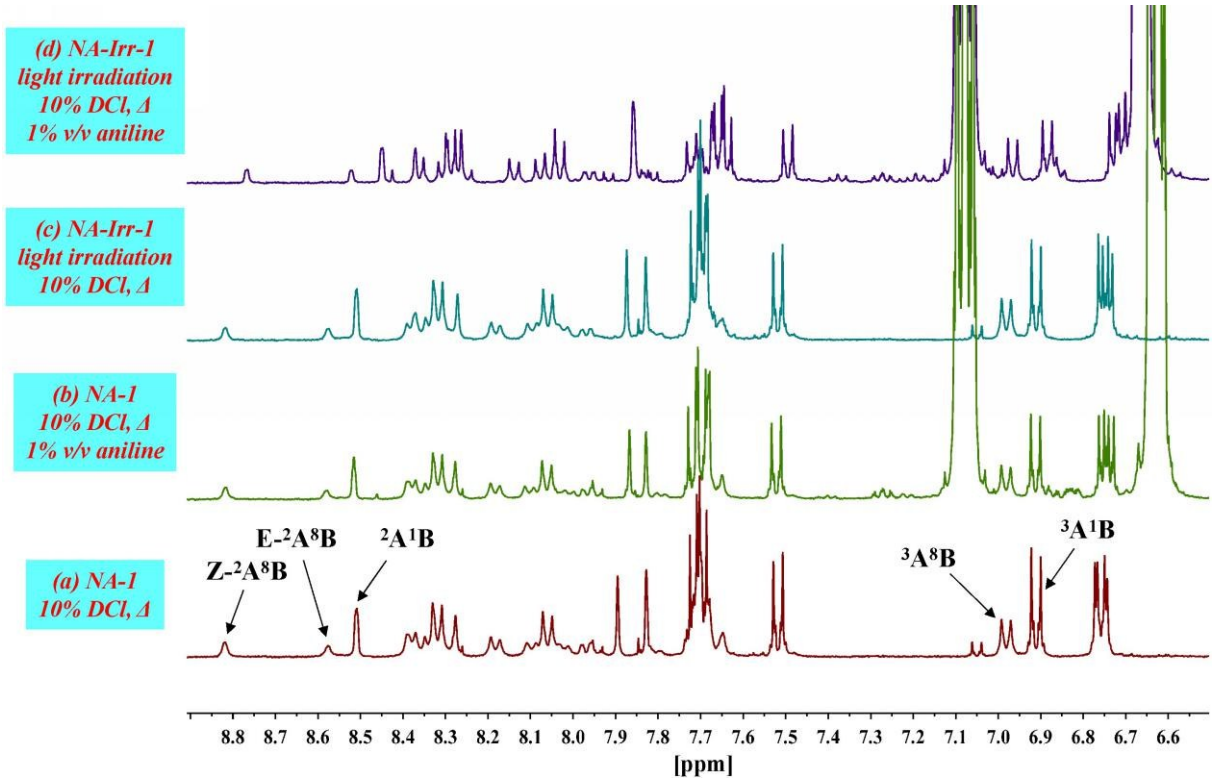


Figure S7a. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NA-1*** with 10% DCl after heating 60 °C for 54 h (a) or with 10% DCl and 1% v/v aniline at room temperature for 14 h (b), and ^{1}H NMR spectrum of library ***NA-Irr-1*** stemmed from ***NA-1*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (c) (d), generated from either the mixture of four components **^{2}A**, **^{3}A**, **^{1}B** and **^{8}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{2}A^{1}B** and **^{3}A^{8}B** or **^{3}A^{1}B** and **^{2}A^{8}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline in the case of (d), 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

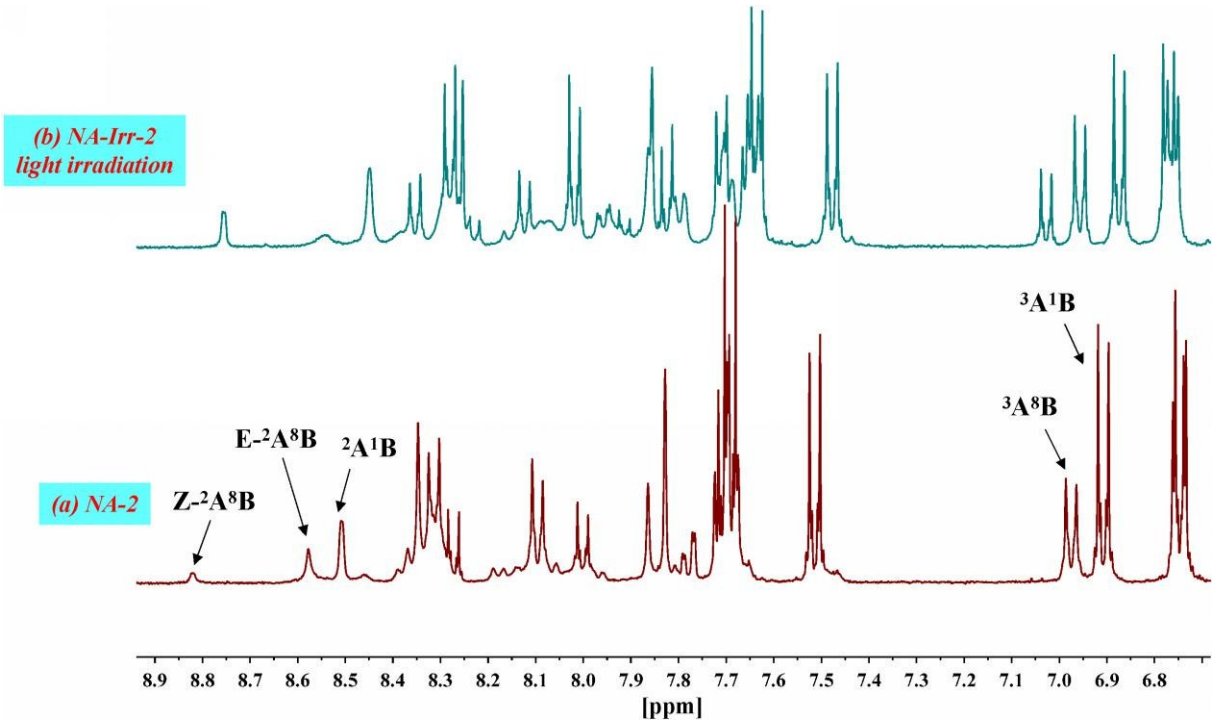


Figure S7b. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NA-2*** with 20% Sc^{3+} after heating 60 °C for 7 h, and ^{1}H NMR spectrum of library ***NA-Irr-2*** stemmed from ***NA-2*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (b), from either the mixture of four components **^{2}A**, **^{3}A**, **^{1}B** and **^{8}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{2}A^{1}B** and **^{3}A^{8}B** or **^{3}A^{1}B** and **^{2}A^{8}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline in the case of (b), 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

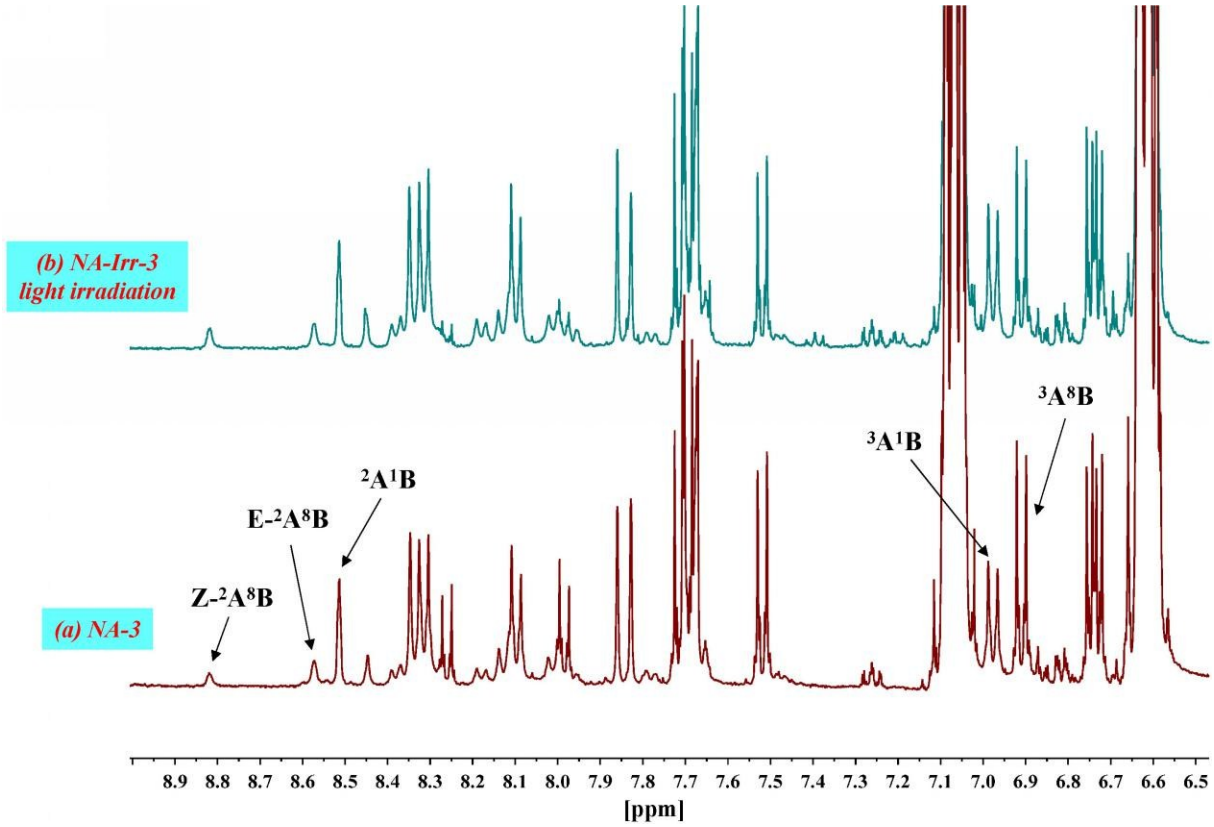


Figure S7c. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NA-3*** with 2% Sc^{3+} and 1% v/v aniline at room temperature for 30 h, and ^{1}H NMR spectrum of library ***NA-Irr-3*** stemmed from ***NA-3*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (b), from either the mixture of four components **^{2}A**, **^{3}A**, **^{1}B** and **^{8}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{2}A^{1}B** and **^{3}A^{8}B** or **^{3}A^{1}B** and **^{2}A^{8}B** (7 mM in CD_3CN).

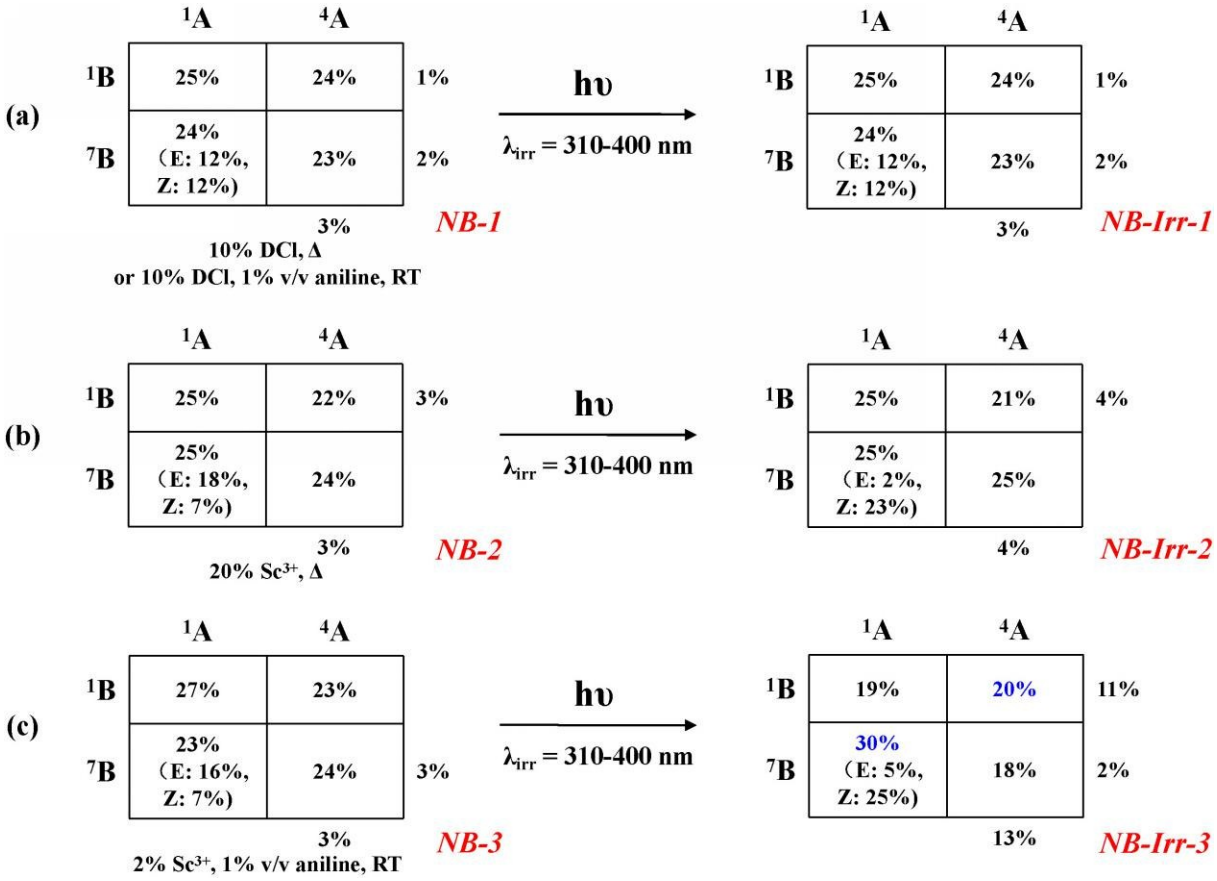


Table S2. Distribution of the four-membered [2×2] CDNs ***NB*** with four constituents ^{1}**A**^{1}**B**, ^{4}**A**^{1}**B**, ^{1}**A**^{7}**B** and ^{4}**A**^{7}**B** (3.5 mM each) generated from two constituents ^{1}**A**^{1}**B** and ^{4}**A**^{7}**B** or ^{4}**A**^{1}**B** and ^{1}**A**^{7}**B**, or from four components ^{1}**A**, ^{4}**A**, ^{1}**B** and ^{7}**B**, and distribution of CDNs ***NB-Irr*** stemmed from ***NB*** under light irradiation (λ_{irr} = 310-400 nm) with different catalysts and temperature conditions. Error on % determination: ±2%. See Figure S8a-S8c for ^{1}H NMR spectra.

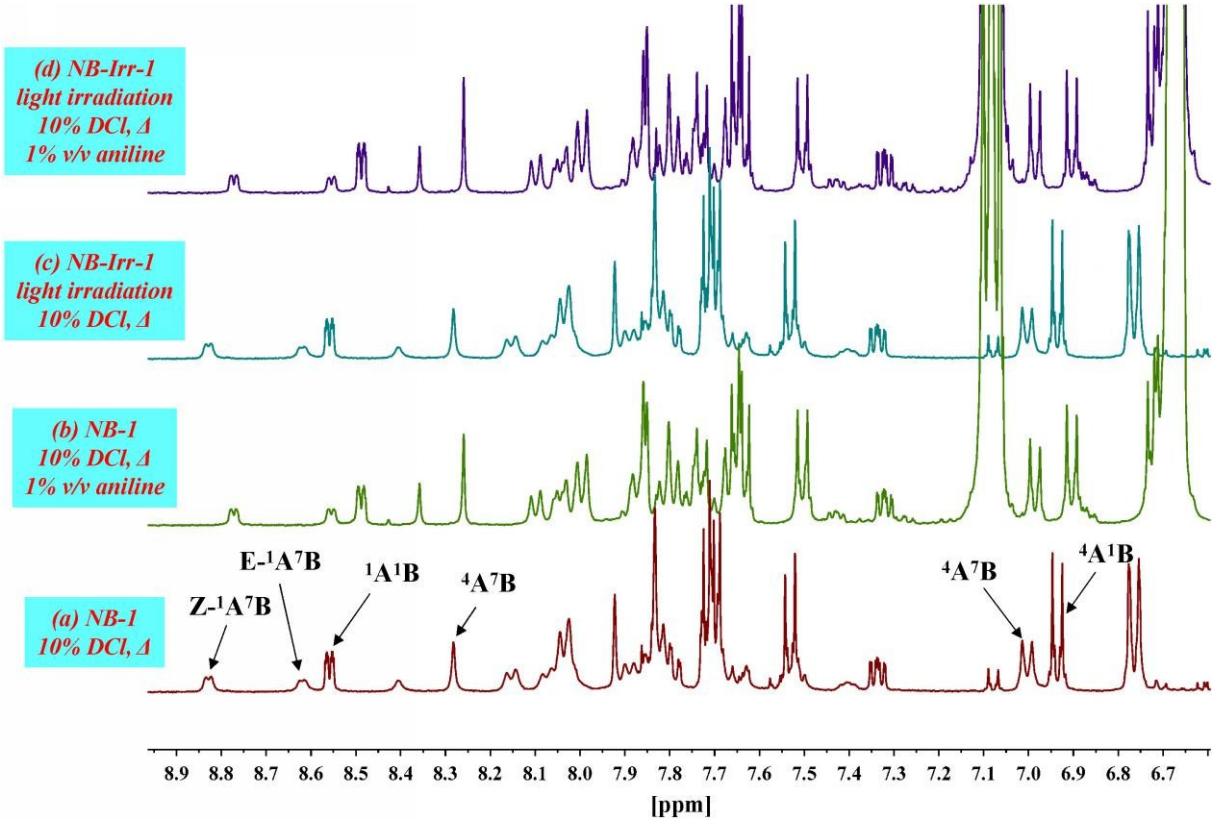


Figure S8a. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NB-1*** with 10% DCl after heating 60 °C for 35 h (a) or with 10% DCl and 1% v/v aniline at room temperature for 12 h (b), and ^{1}H NMR spectrum of library ***NB-Irr-1*** stemmed from ***NB-1*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (c) (d), generated from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{7}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{7}B** or **^{4}A^{1}B** and **^{1}A^{7}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline in the case of (b) (d), 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

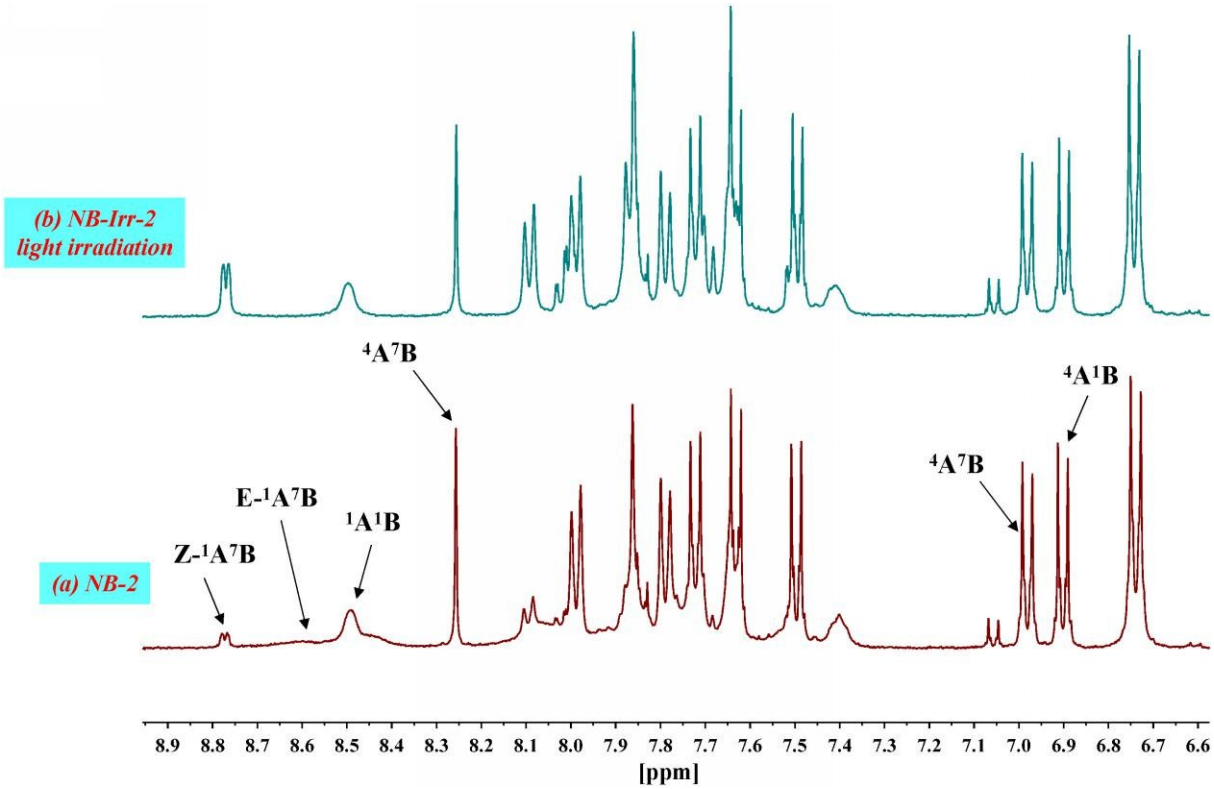


Figure S8b. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NB-2*** with 20% Sc^{3+} after heating 60 °C for 6.5 h, and ^{1}H NMR spectrum of library ***NB-Irr-2*** stemmed from ***NB-2*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (b), from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{7}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{7}B** or **^{4}A^{1}B** and **^{1}A^{7}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline, 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

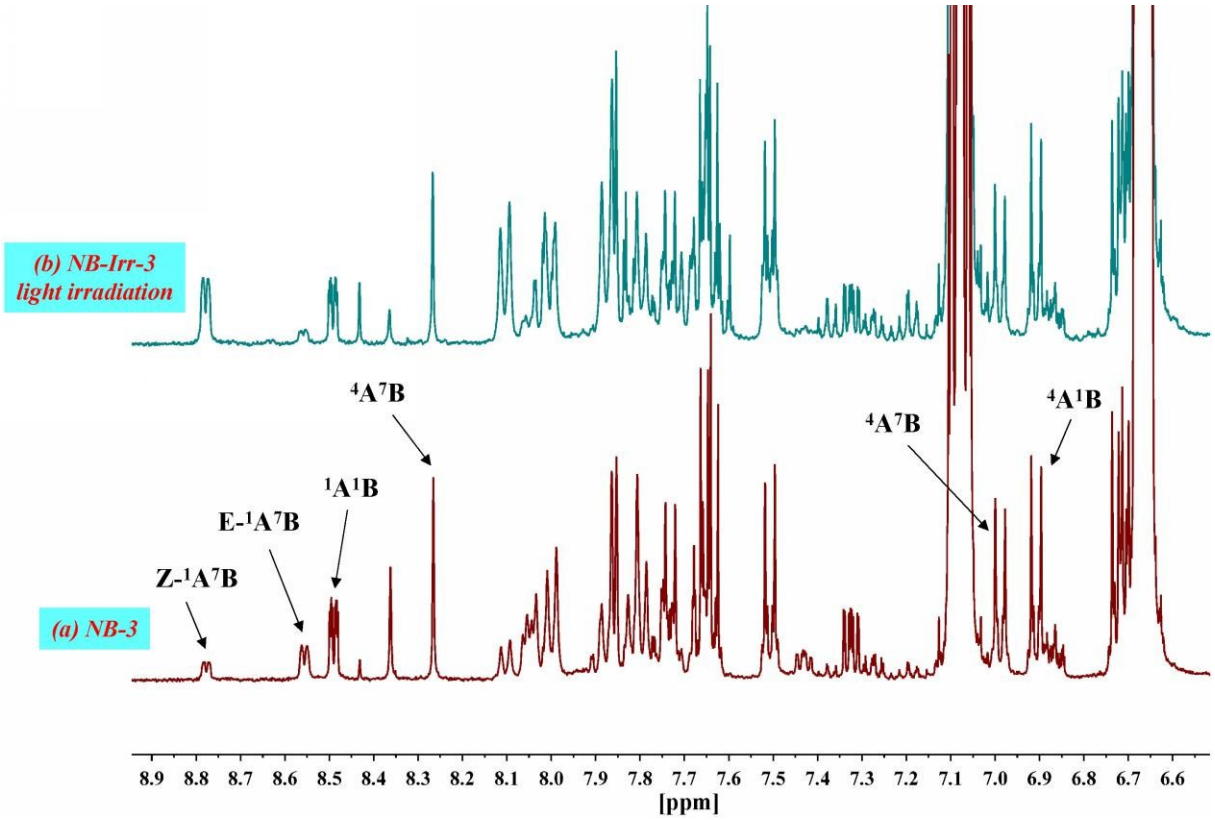


Figure S8c. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NB-3*** with 2% Sc^{3+} and 1% v/v aniline at room temperature for 20 h, and ^{1}H NMR spectrum of library ***NB-Irr-3*** stemmed from ***NB-3*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (b), from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{7}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{7}B** or **^{4}A^{1}B** and **^{1}A^{7}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline, 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

Table S3. Distribution of the four-membered [2×2] CDNs ***NC*** with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{5}B** and **^{4}A^{5}B** (3.5 mM each) generated from two constituents **^{1}A^{1}B** and **^{4}A^{5}B** or **^{4}A^{1}B** and **^{1}A^{5}B**, or from four components **^{1}A**, **^{4}A**, **^{1}B** and **^{5}B**, and distribution of CDNs ***NC-Irr*** stemmed from ***NC*** under light irradiation (λ_{irr} = 310-400 nm) with different catalysts and temperature conditions. Error on % determination: ±2%. See Figure S9a-S9c for ^{1}H NMR spectra.

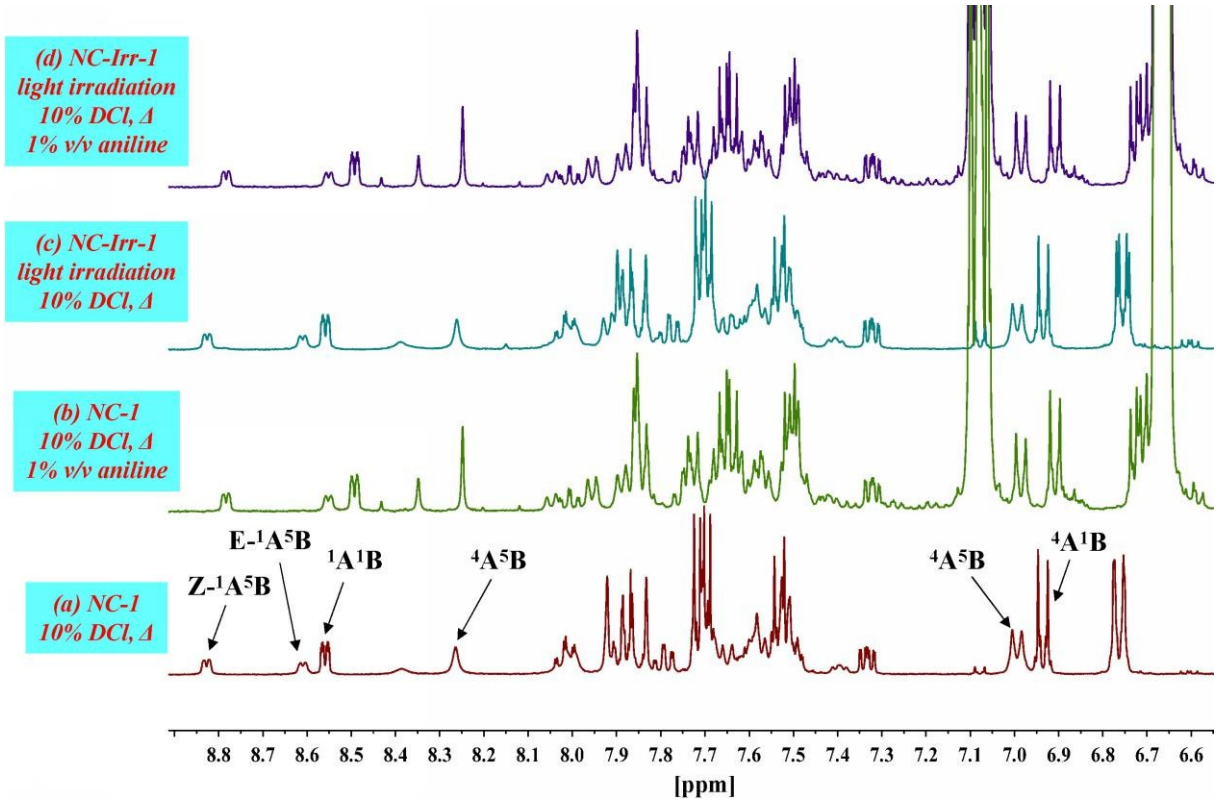


Figure S9a. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NC-1*** with 10% DCl after heating 60 °C for 18 h (a) or with 10% DCl and 1% v/v aniline at room temperature for 10 h (b), and ^{1}H NMR spectrum of library ***NC-Irr-1*** stemmed from ***NC-1*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (c) (d), generated from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{5}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{5}B** or **^{4}A^{1}B** and **^{1}A^{5}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline in the case of (b) (d), 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

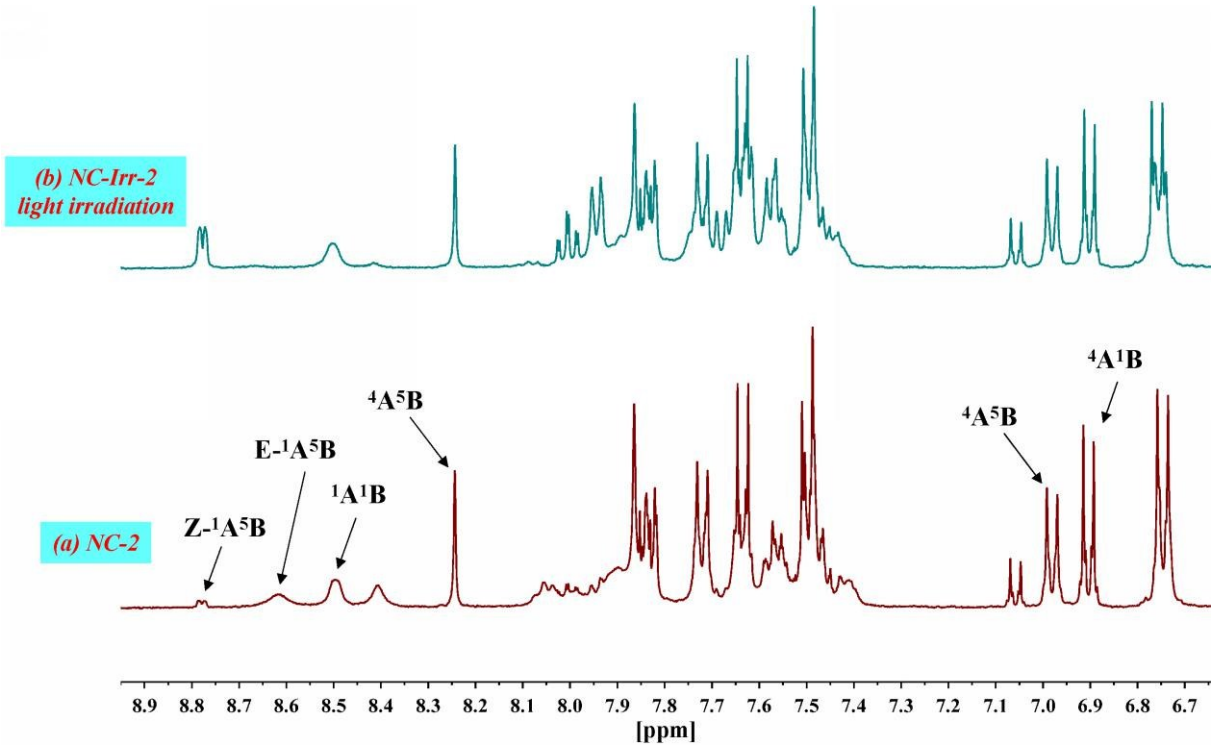


Figure S9b. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NC-2*** with 20% Sc^{3+} after heating 60 °C for 6 h, and ^{1}H NMR spectrum of library ***NC-Irr-2*** stemmed from ***NC-2*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (b), from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{5}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{5}B** or **^{4}A^{1}B** and **^{1}A^{5}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline, 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

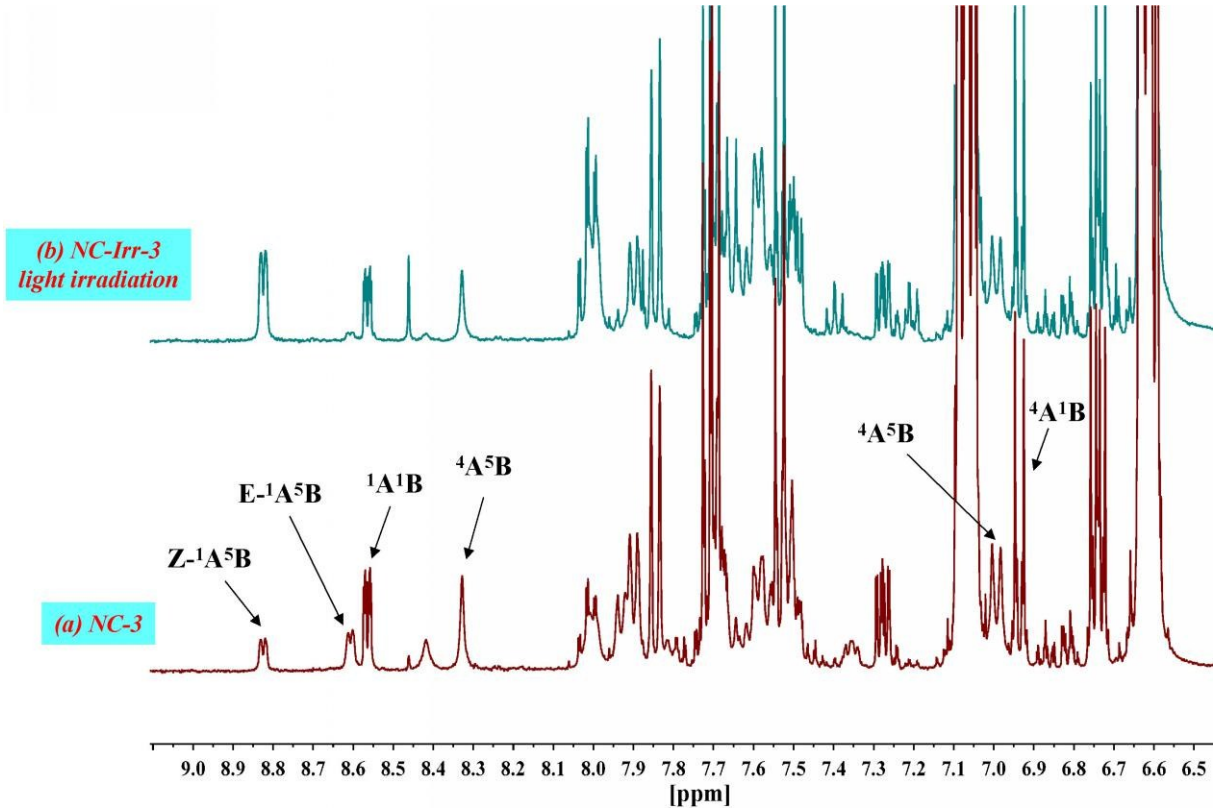


Figure S9c. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NC-3*** with 2% Sc^{3+} and 1% v/v aniline at room temperature for 20 h, and ^{1}H NMR spectrum of library ***NC-Irr-3*** stemmed from ***NC-3*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (b), from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{5}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{5}B** or **^{4}A^{1}B** and **^{1}A^{5}B** (7 mM in CD_3CN).

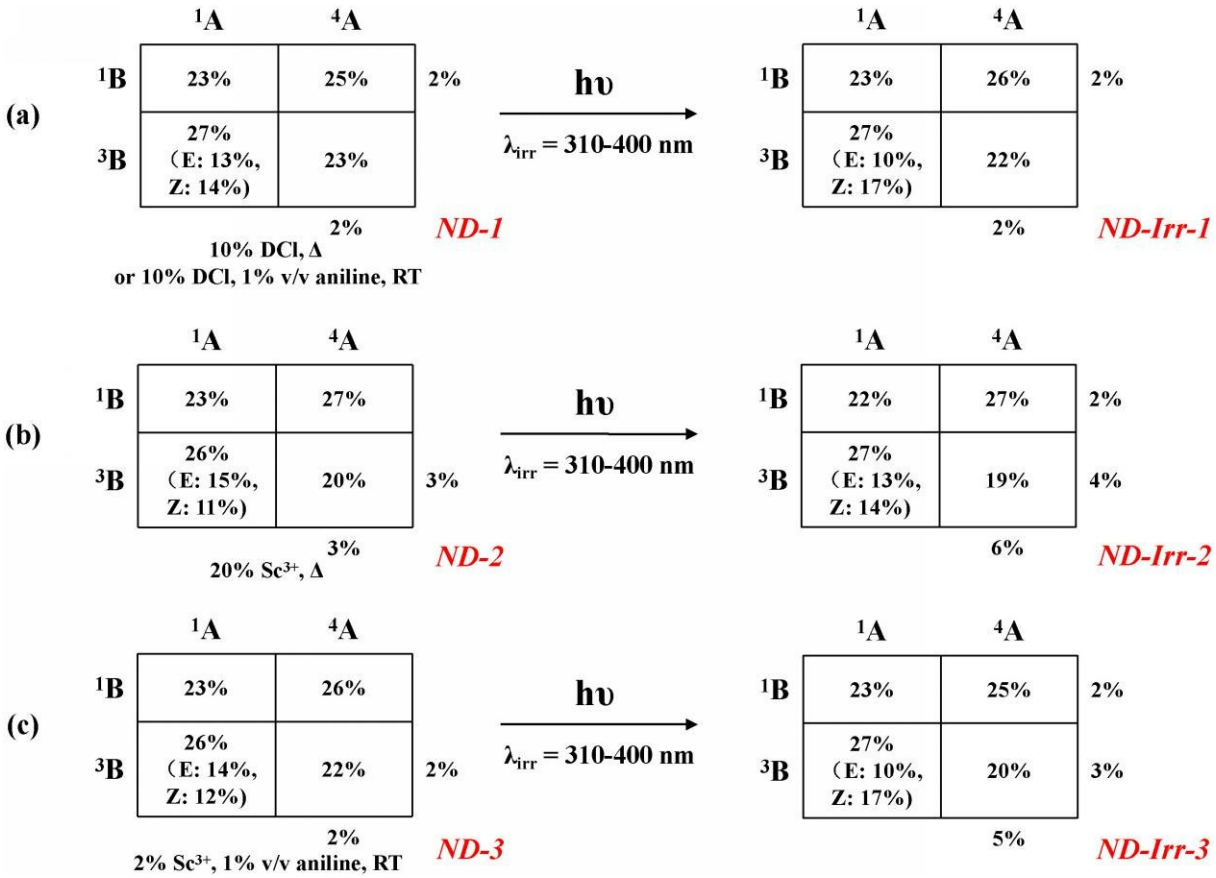


Table S4. Distribution of the four-membered [2×2] CDNs ***ND*** with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{3}B** and **^{4}A^{3}B** (3.5 mM each) generated from two constituents **^{1}A^{1}B** and **^{4}A^{3}B** or **^{4}A^{1}B** and **^{1}A^{3}B**, or from four components **^{1}A**, **^{4}A**, **^{1}B** and **^{3}B**, and distribution of CDNs ***ND-Irr*** stemmed from ***ND*** under light irradiation (λ_{irr} = 310-400 nm) with different catalysts and temperature conditions. Error on % determination: ±2%. See Figure S10a-S10c for ^{1}H NMR spectra.

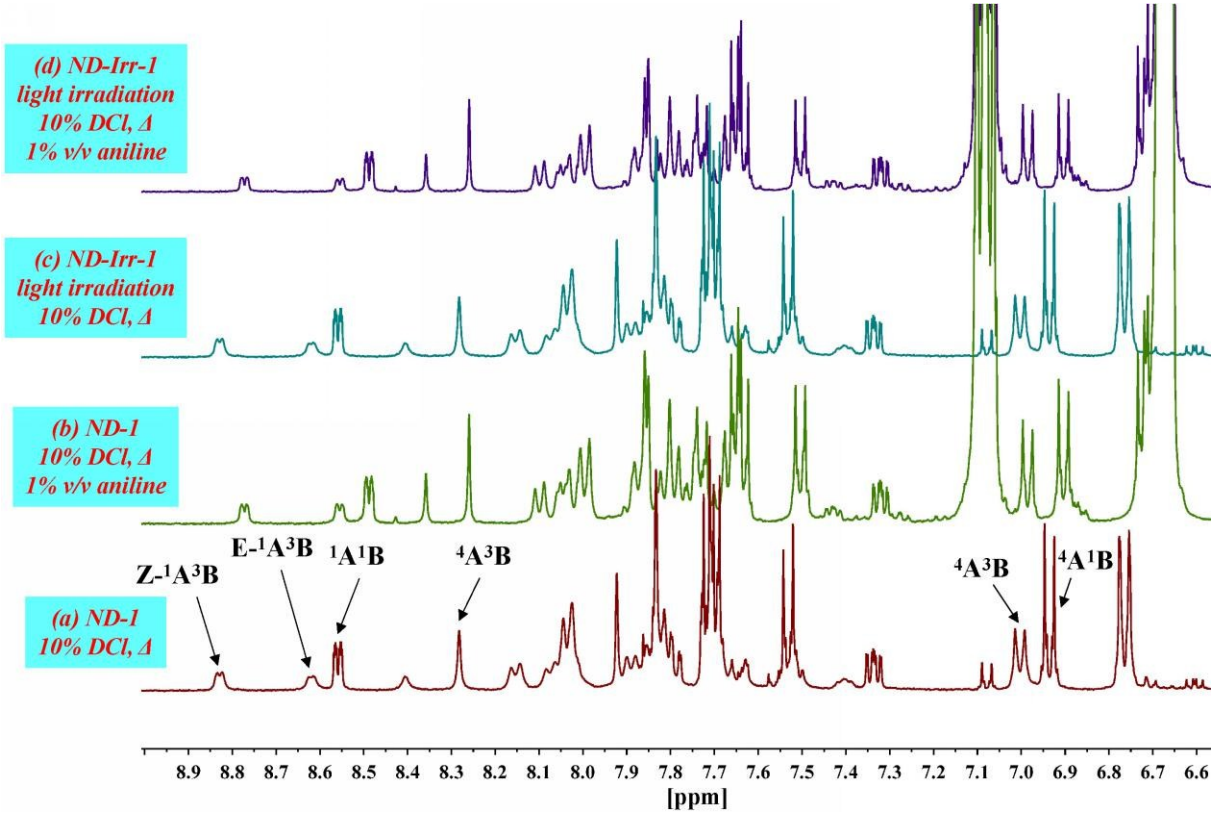


Figure S10a. A portion of the 400 MHz ^{1}H NMR spectrum of library ***ND-1*** with 10% DCl after heating 60 °C for 13 h (a) or with 10% DCl and 1% v/v aniline at room temperature for 9 h (b), and ^{1}H NMR spectrum of library ***ND-Irr-1*** stemmed from ***ND-1*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (c) (d), generated from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{3}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{3}B** or **^{4}A^{1}B** and **^{1}A^{3}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline in the case of (b) (d), 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

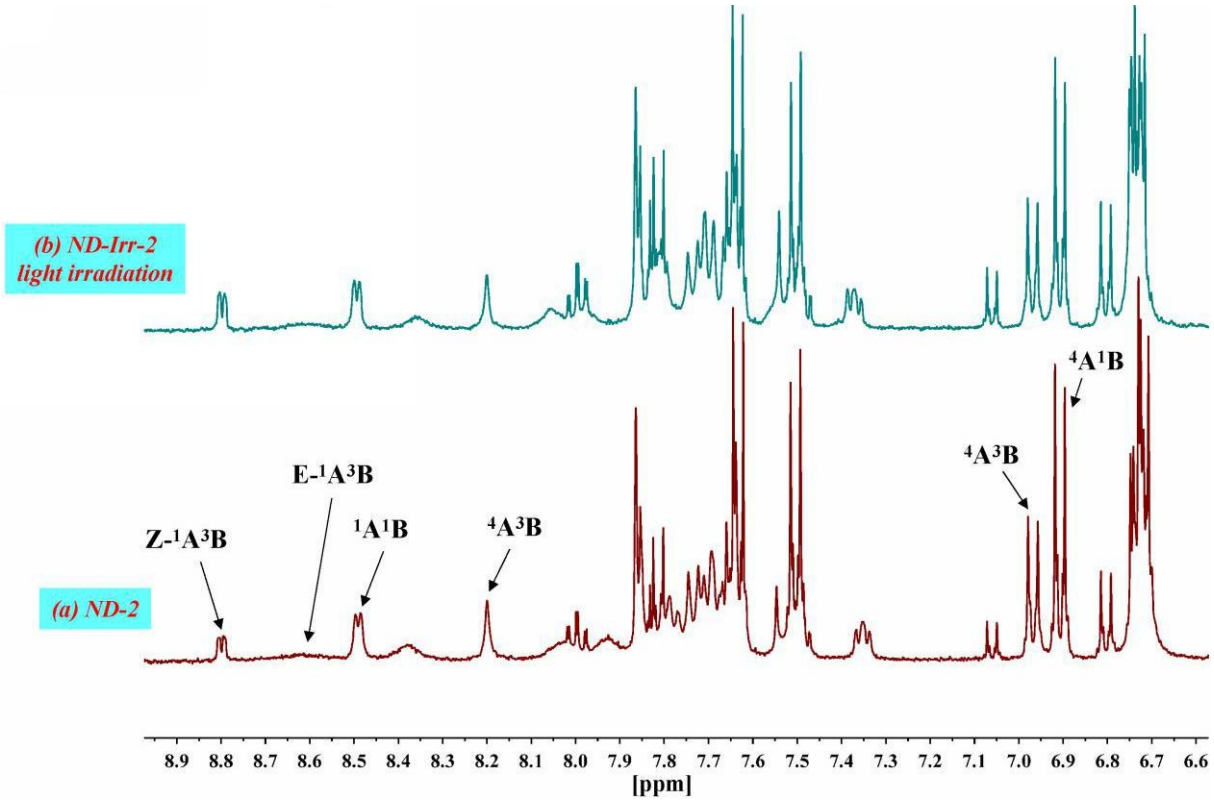


Figure S10b. A portion of the 400 MHz ^{1}H NMR spectrum of library ***ND-2*** with 20% Sc^{3+} after heating 60 °C for 6 h, and ^{1}H NMR spectrum of library ***ND-Irr-2*** stemmed from ***ND-2*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (b), from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{3}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{3}B** or **^{4}A^{1}B** and **^{1}A^{3}B** (7 mM in CD_3CN). For clarity of the spectrum and eliminating the interference of aniline, 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

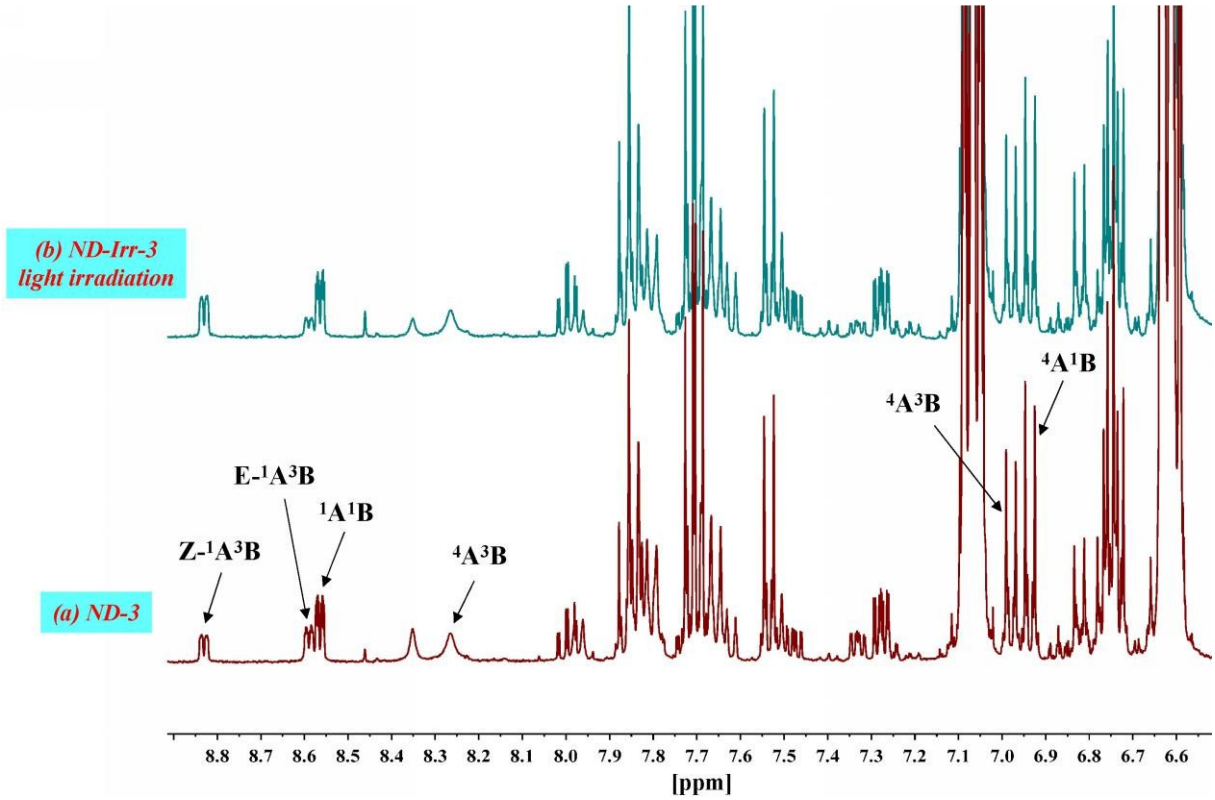
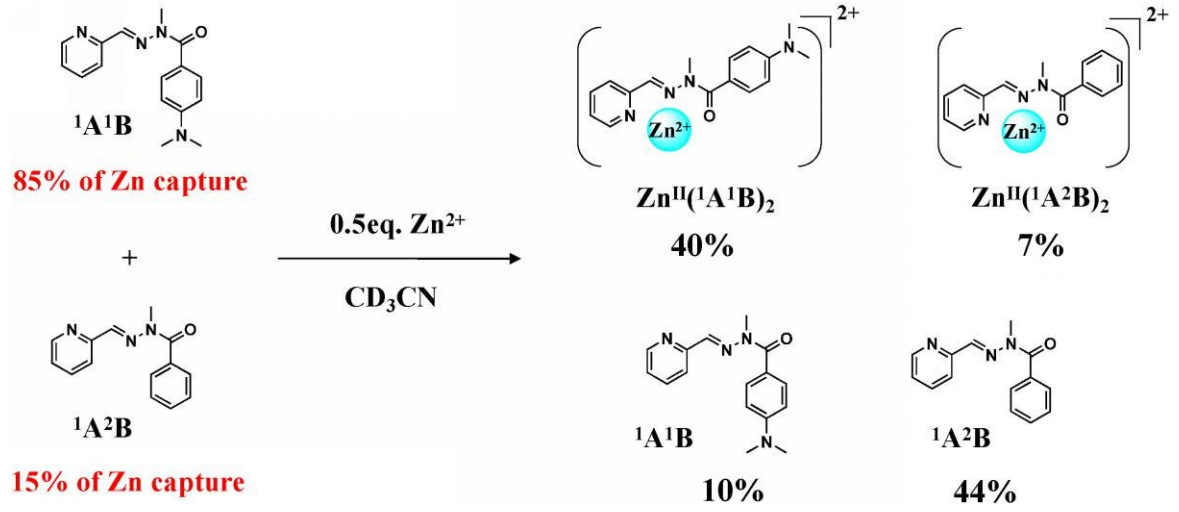


Figure S10c. A portion of the 400 MHz ^{1}H NMR spectrum of library ***ND-3*** with 2% Sc^{3+} and 1% v/v aniline at room temperature for 17 h, and ^{1}H NMR spectrum of library ***ND-Irr-3*** stemmed from ***ND-3*** under light irradiation (λ_{irr} = 310-400 nm) for 1 h (b), from either the mixture of four components **^{1}A**, **^{4}A**, **^{1}B** and **^{3}B** (7 mM in CD_3CN) or the mixtures of two constituents **^{1}A^{1}B** and **^{4}A^{3}B** or **^{4}A^{1}B** and **^{1}A^{3}B** (7 mM in CD_3CN).

4. Zn^{2+} binding competition and transfer among pyridyl-acylhydrazones.



Scheme S3. Distribution of products generated from a mixture of **$^1A^1B$** and **$^1A^2B$** (1 eq., 3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 °C for 6 h. The percentages for the Zn^{2+} ion capture between **$^1A^1B$** and **$^1A^2B$** are shown in red. Error on % determination: ±2%. See Figure S11 for ^1H NMR spectra.

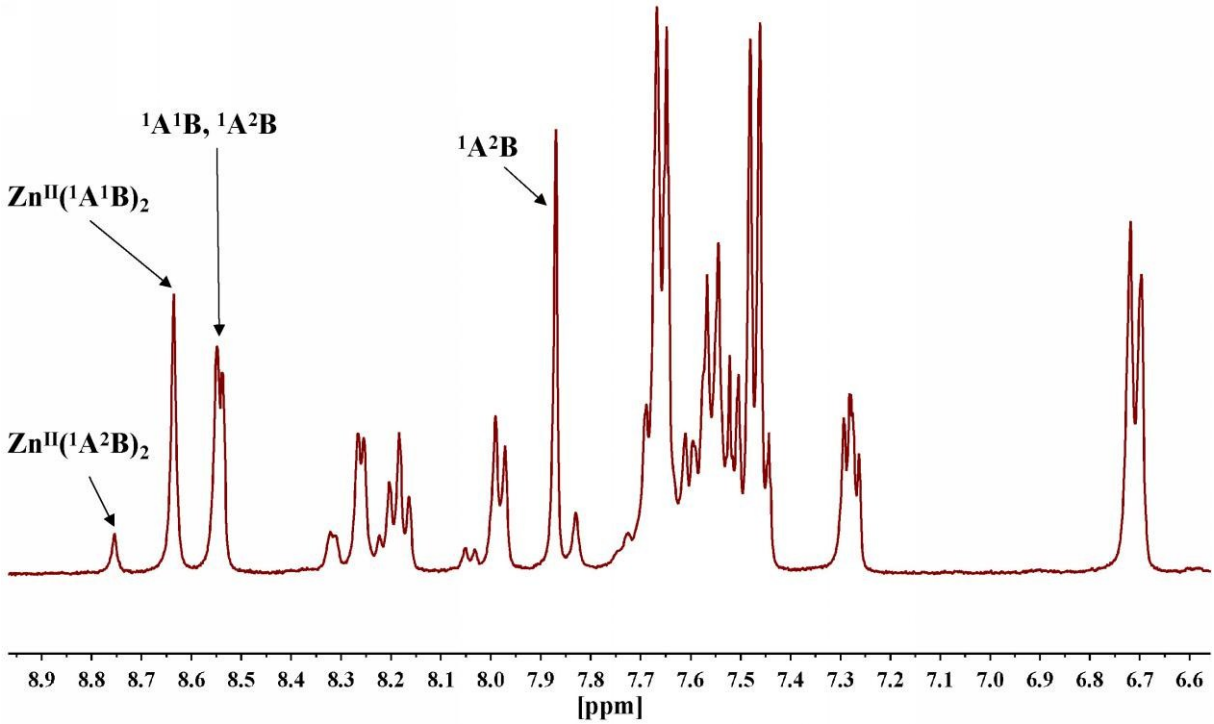
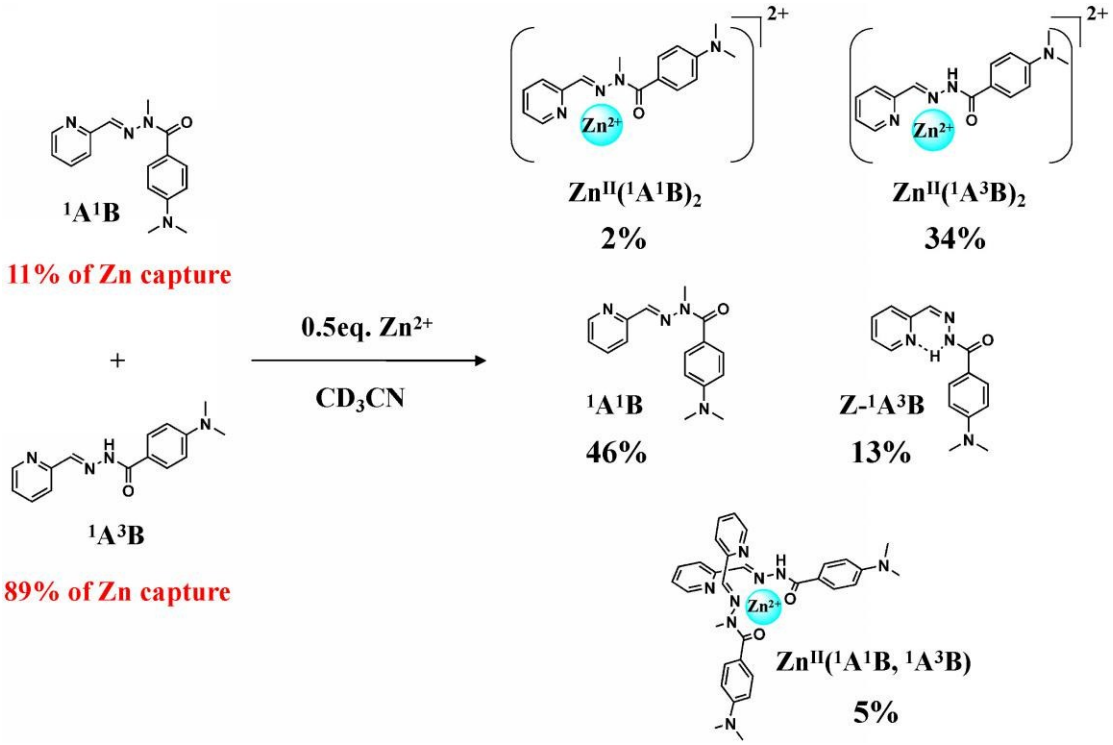


Figure S11. A portion of the 400 MHz ^1H NMR spectrum of the mixture of **$^1A^1B$** and **$^1A^2B$** (3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 °C for 6 h.



Scheme S4. Distribution of products generated from a mixture of **^{1}A^{1}B** and **^{1}A^{3}B** (1 eq., 3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 ˚C for 6 h. The percentages for the Zn^{2+} ion capture between **^{1}A^{1}B** and **^{1}A^{3}B** are shown in red. Error on % determination: ±2%. See Figure S12a and Figure S12b for ^{1}H NMR and ESI mass spectra, respectively.

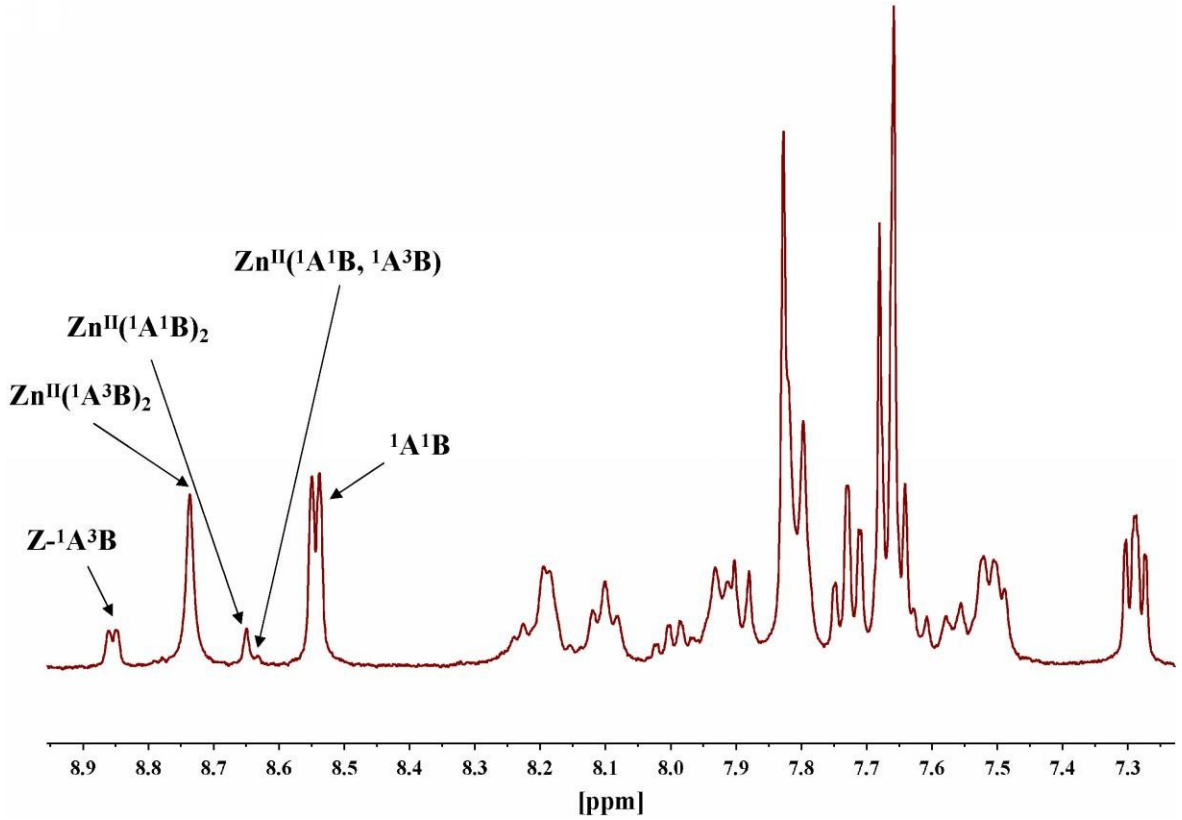


Figure S12a. A portion of the 400 MHz ^{1}H NMR spectrum of the mixture of **^{1}A^{1}B** and **^{1}A^{3}B** (3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 ˚C for 6 h. The NMR measurement was conducted at -30 ˚C.

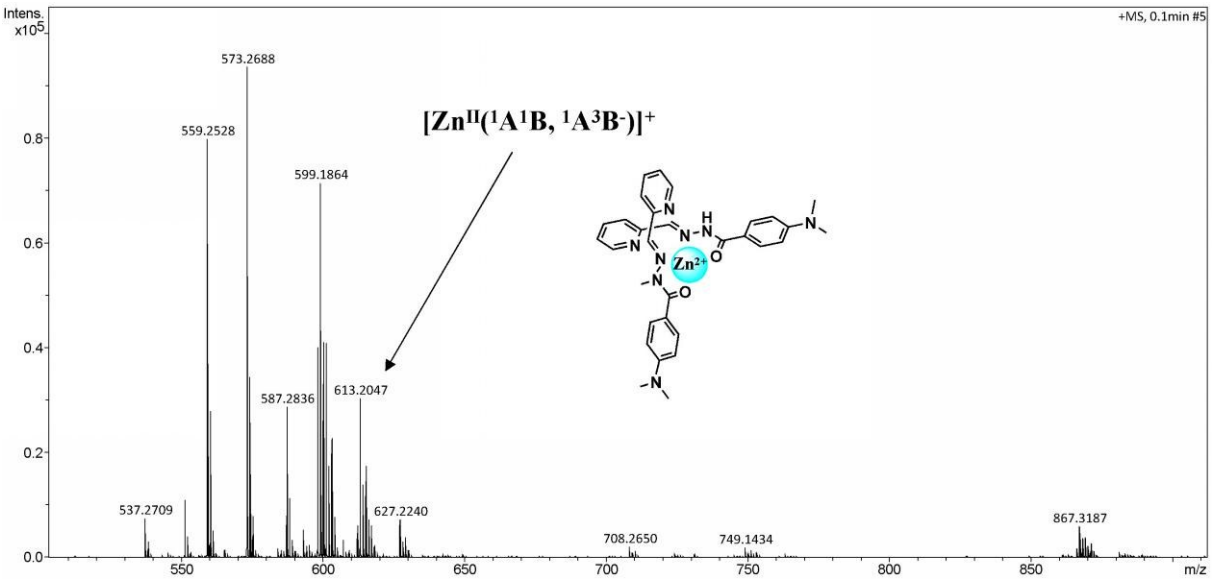
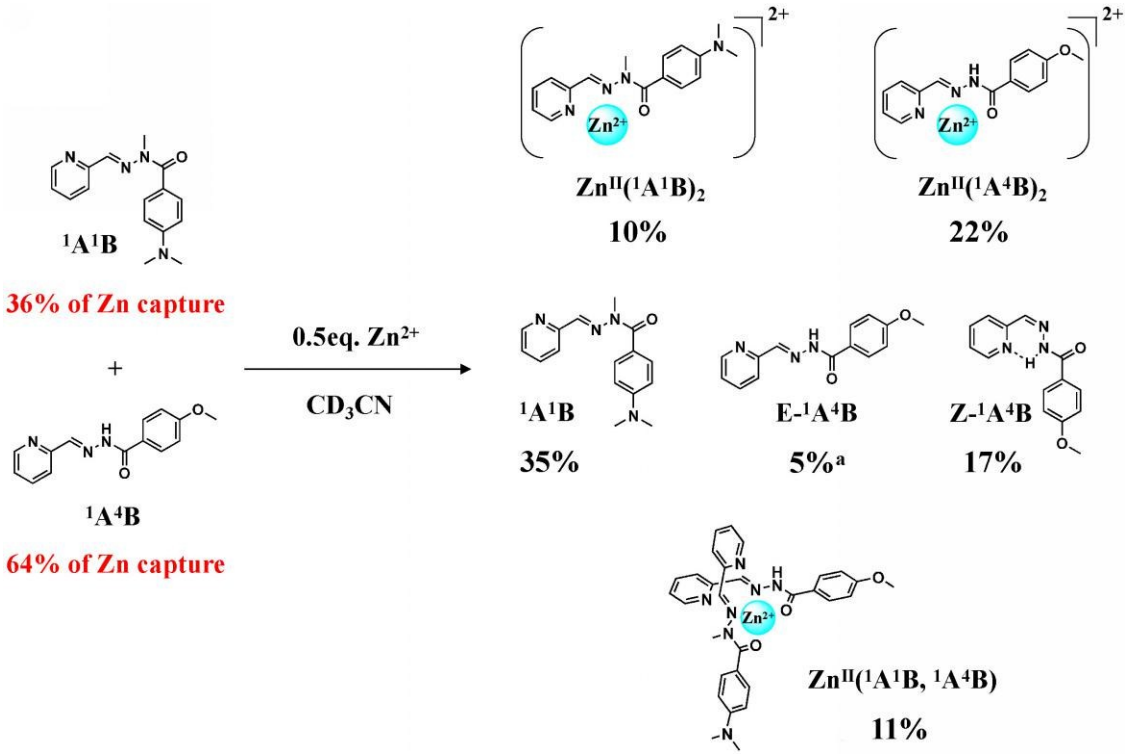


Figure S12b. ESI mass spectrum of the mixture of **^{1}A^{1}B** and **^{1}A^{3}B** (3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 ˚C for 6 h.



Scheme S5. Distribution of products generated from a mixture of **^{1}A^{1}B** and **^{1}A^{4}B** (1 eq., 3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 °C for 6 h. The percentages for the Zn^{2+} ion capture between **^{1}A^{1}B** and **^{1}A^{4}B** are shown in red. Error on % determination: ±2%. [a]The percentage was obtained by calculations. See Figure S13a and Figure S13b for ^{1}H NMR and ESI mass spectra, respectively.

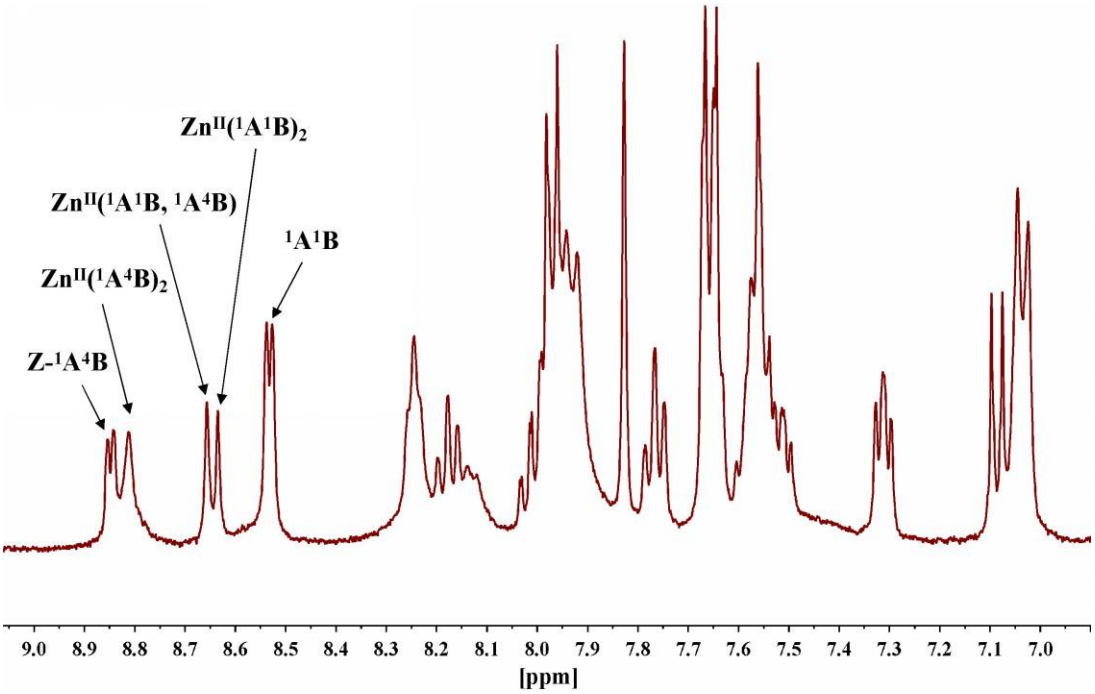


Figure S13a. A portion of the 400 MHz ^{1}H NMR spectrum of the mixture of **^{1}A^{1}B** and **^{1}A^{4}B** (3.5 mM each) in presence of 0.5 equiv. Zn^{II}(OTf)$_2$ in CD_3CN after heating at 60 ˚C for 6 h. The NMR measurement was conducted at -30 ˚C.

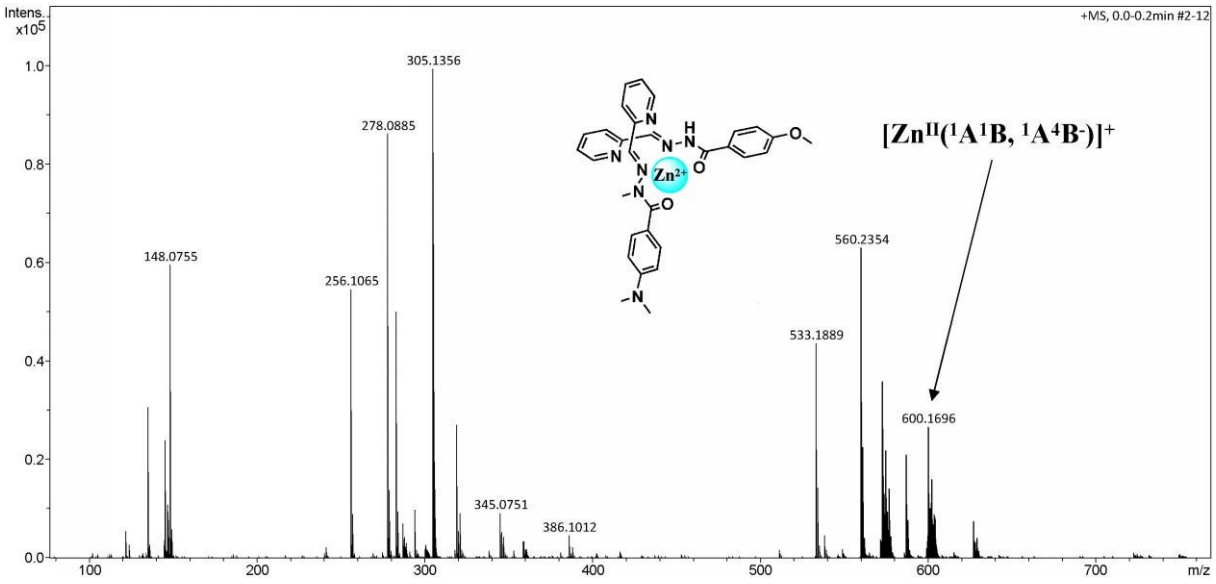
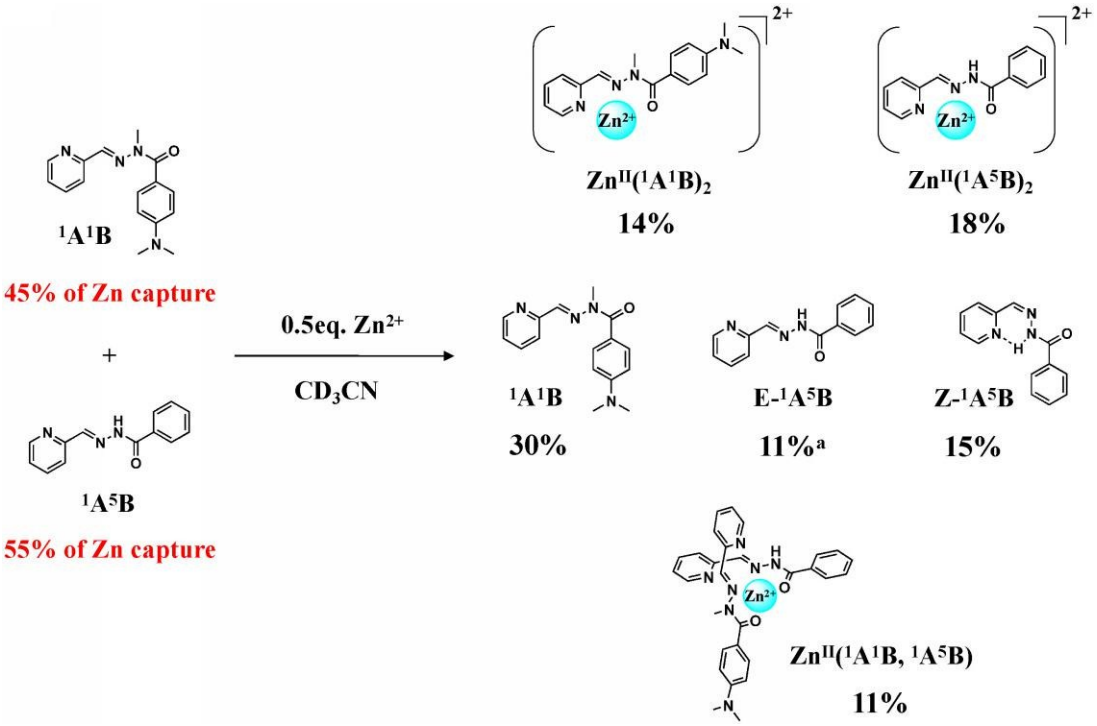


Figure S13b. ESI mass spectrum of the mixture of **^{1}A^{1}B** and **^{1}A^{4}B** (3.5 mM each) in presence of 0.5 equiv. Zn^{II}(OTf)$_2$ in CD_3CN after heating at 60 ˚C for 6 h.



Scheme S6. Distribution of products generated from a mixture of **^{1}A^{1}B** and **^{1}A^{5}B** (1 eq., 3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 °C for 6 h. The percentages for the Zn^{2+} ion capture between **^{1}A^{1}B** and **^{1}A^{5}B** are shown in red. Error on % determination: ±2%. [a]The percentage was obtained by calculations. See Figure S14a and Figure S14b for ^{1}H NMR and ESI mass spectra, respectively.

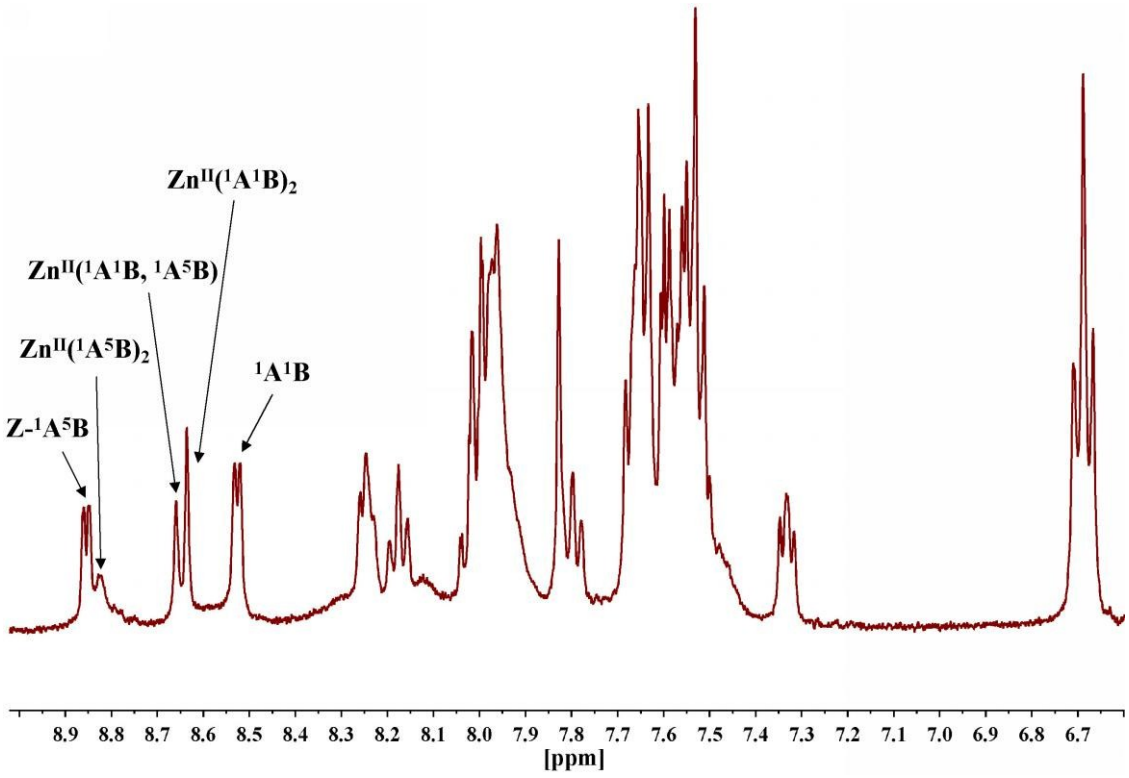


Figure S14a. A portion of the 400 MHz ^{1}H NMR spectrum of the mixture of **^{1}A^{1}B** and **^{1}A^{5}B** (3.5 mM each) in presence of 0.5 equiv. Zn^{II}(OTf)$_2$ in CD_3CN after heating at 60 ˚C for 6 h. The NMR measurement was conducted at -30 ˚C.

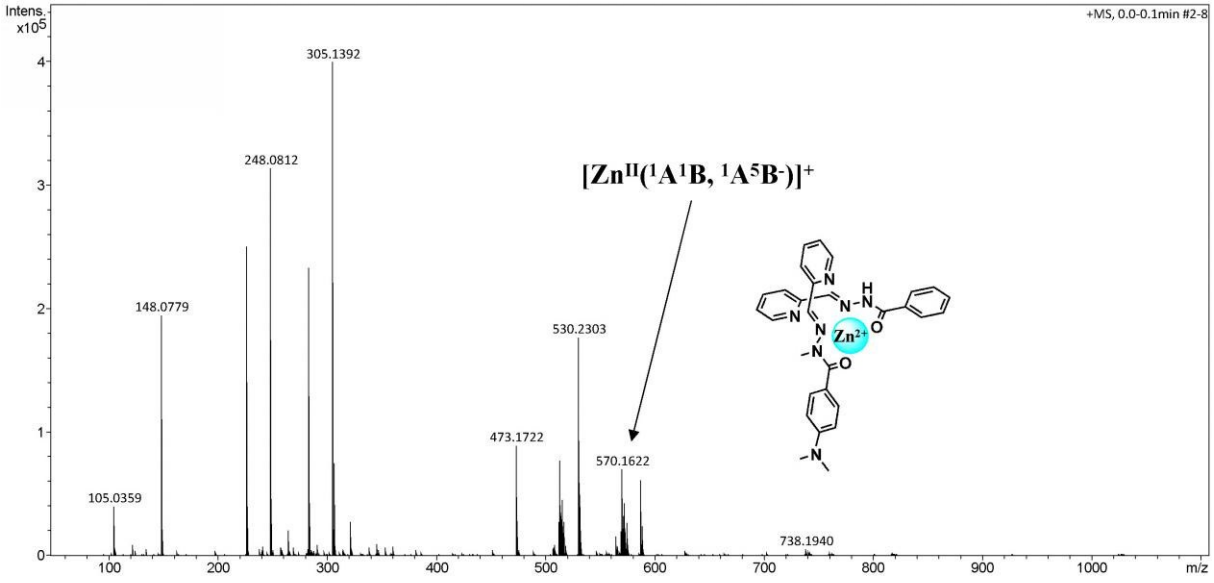
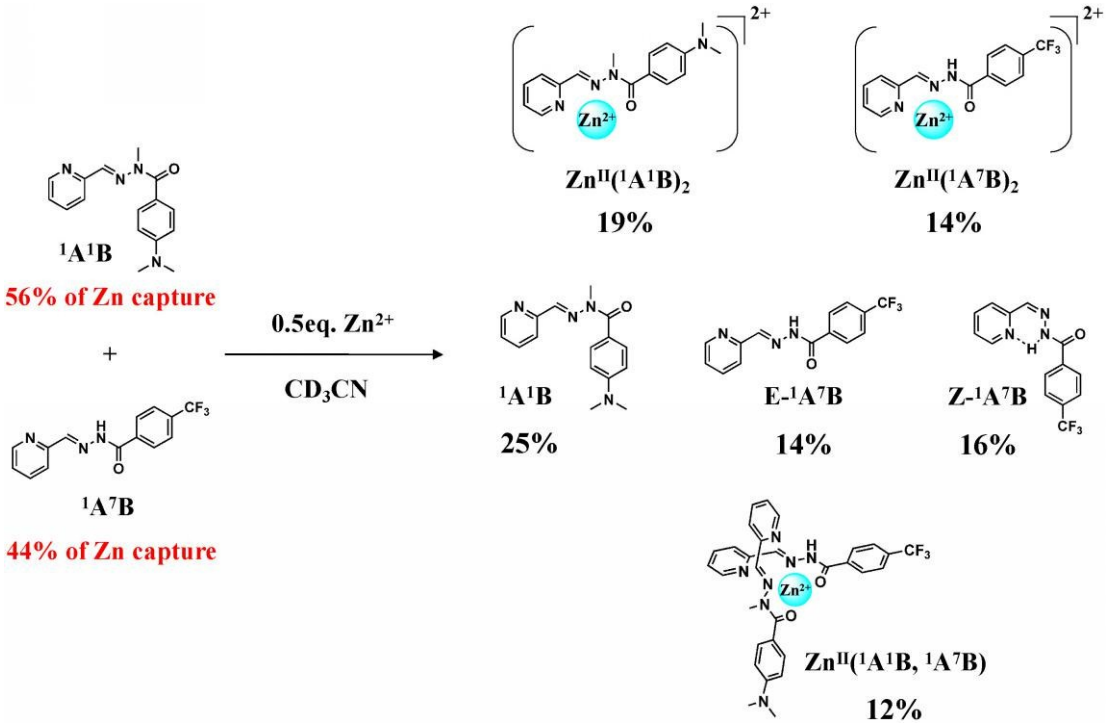


Figure S14b. ESI mass spectrum of the mixture of **^{1}A^{1}B** and **^{1}A^{5}B** (3.5 mM each) in presence of 0.5 equiv. Zn^{II}(OTf)$_2$ in CD_3CN after heating at 60 ˚C for 6 h.



Scheme S7. Distribution of products generated from a mixture of **^{1}A^{1}B** and **^{1}A^{7}B** (1 eq., 3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 °C for 6 h. The percentages for the Zn^{2+} ion capture between **^{1}A^{1}B** and **^{1}A^{7}B** are shown in red. Error on % determination: ±2%. See Figure S15a and Figure S15b for ^{1}H NMR and ESI mass spectra, respectively.

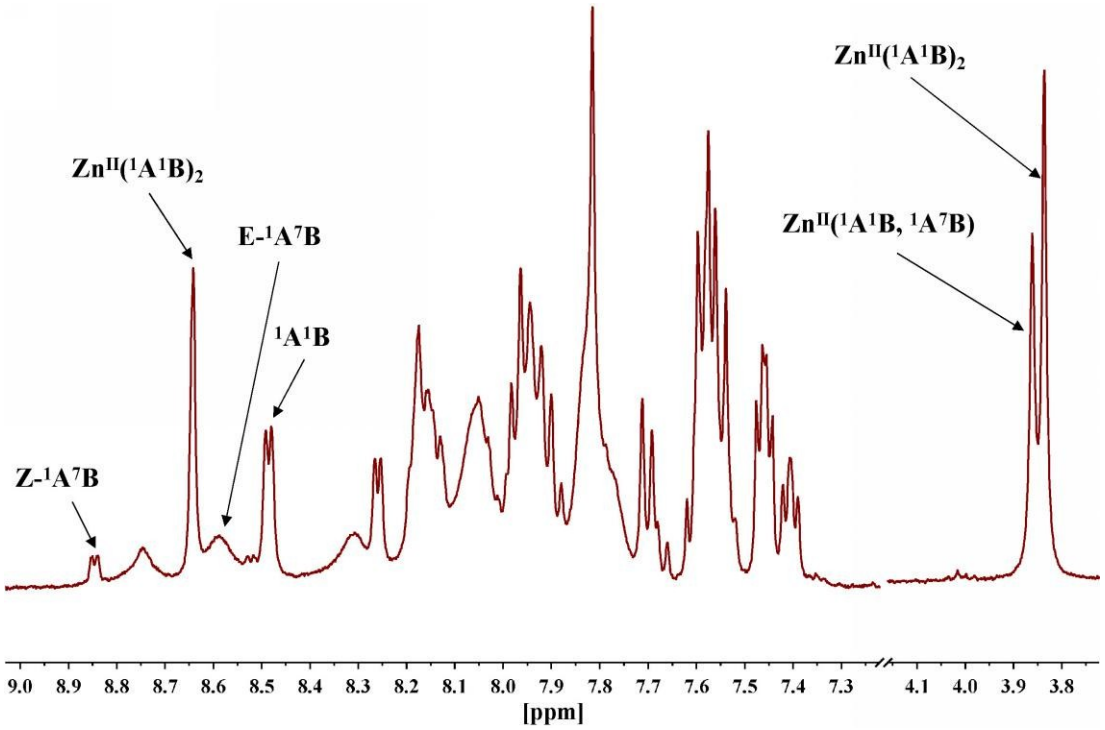


Figure S15a. A portion of the 400 MHz ^{1}H NMR spectrum of the mixture of **^{1}A^{1}B** and **^{1}A^{7}B** (3.5 mM each) in presence of 0.5 equiv. Zn^{II}(OTf)$_2$ in CD_3CN after heating at 60 ˚C for 6 h. The NMR measurement was conducted at -30 ˚C.

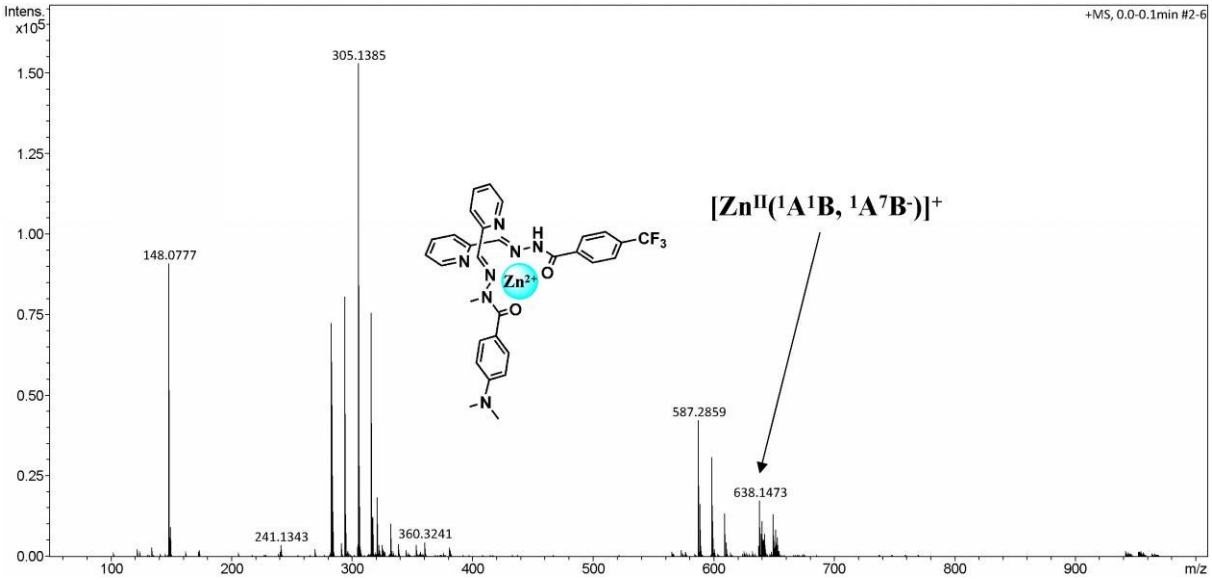
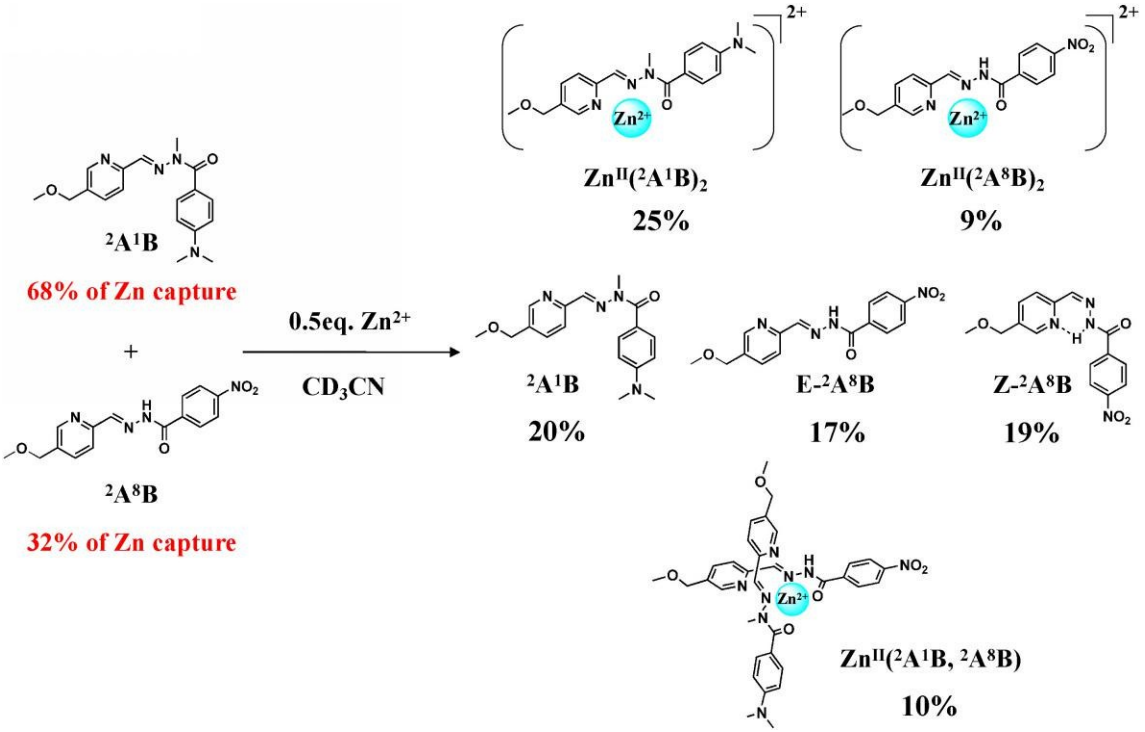


Figure S15b. ESI mass spectrum of the mixture of **^{1}A^{1}B** and **^{1}A^{7}B** (3.5 mM each) in presence of 0.5 equiv. Zn^{II}(OTf)$_2$ in CD_3CN after heating at 60 ˚C for 6 h.



Scheme S8. Distribution of products generated from a mixture of **^{2}A^{1}B** and **^{2}A^{8}B** (1 eq., 3.5 mM each) in presence of 0.5 equiv. $Zn^{II}(OTf)_2$ in CD_3CN after heating at 60 ºC for 6 h. The percentages for the Zn^{2+} ion capture between **^{2}A^{1}B** and **^{2}A^{8}B** are shown in red. Error on % determination: ±2%. See Figure S16a and Figure S16b for ^{1}H NMR and ESI mass spectra, respectively.

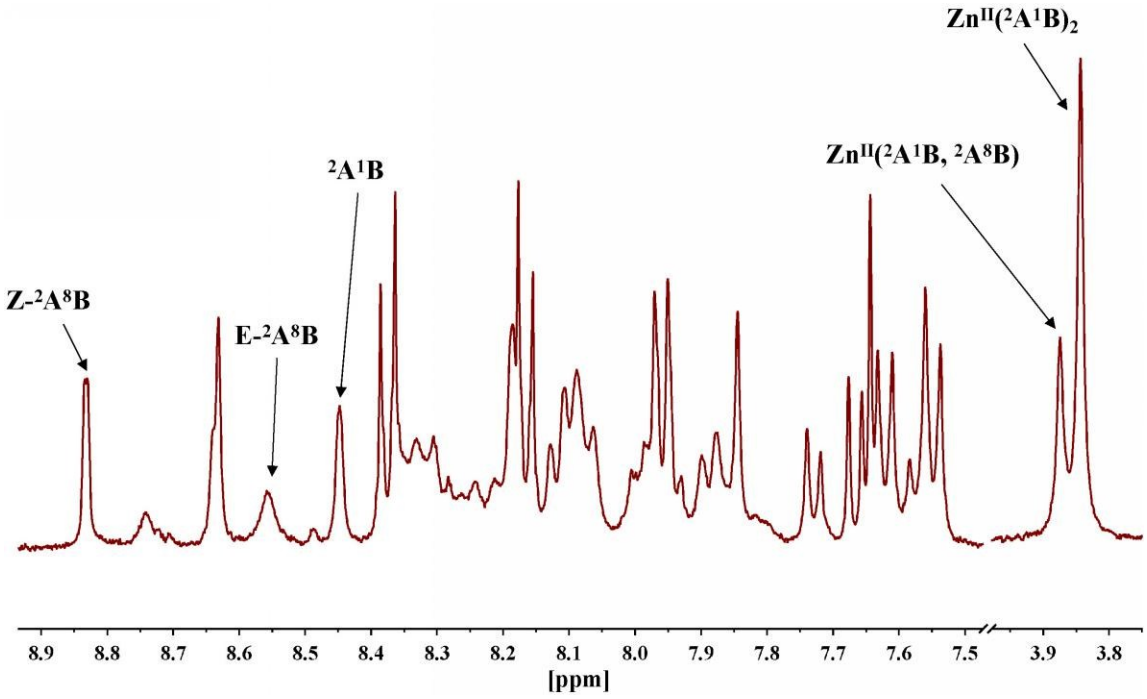


Figure S16a. A portion of the 400 MHz ^{1}H NMR spectrum of the mixture of **^{2}A^{1}B** and **^{2}A^{8}B** (3.5 mM each) in presence of 0.5 equiv. Zn^{II}(OTf)$_2$ in CD_3CN after heating at 60 ˚C for 6 h. The NMR measurement was conducted at -30 ˚C.

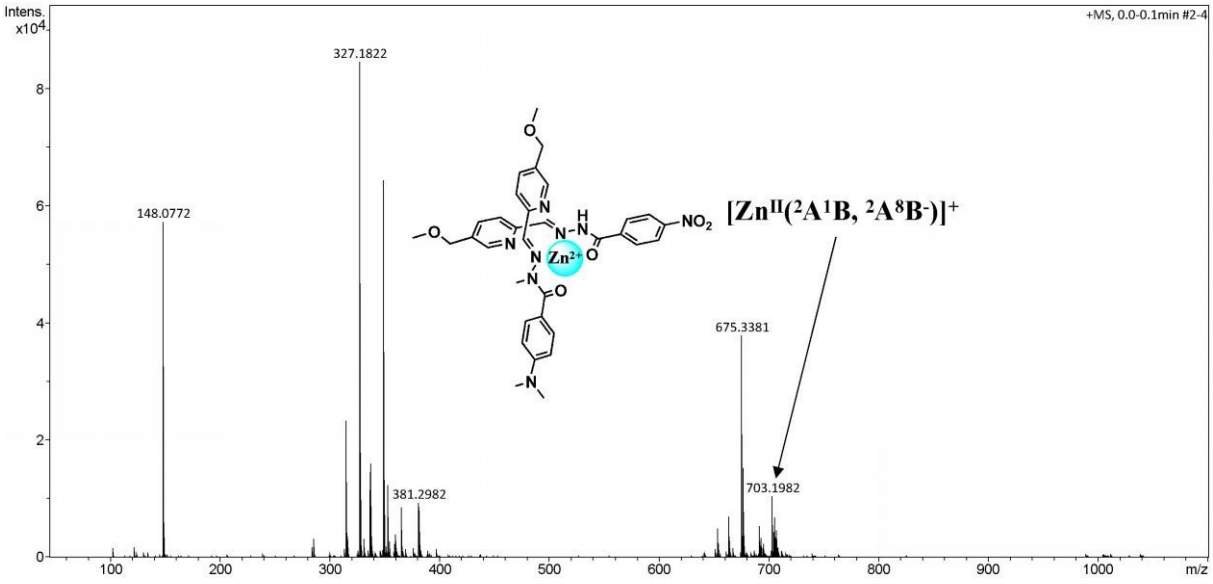


Figure S16b. ESI mass spectrum of the mixture of **^{2}A^{1}B** and **^{2}A^{8}B** (3.5 mM each) in presence of 0.5 equiv. Zn^{II}(OTf)$_2$ in CD_3CN after heating at 60 ˚C for 6 h.

5. Photoselection in CDLs of acylhydrazones.

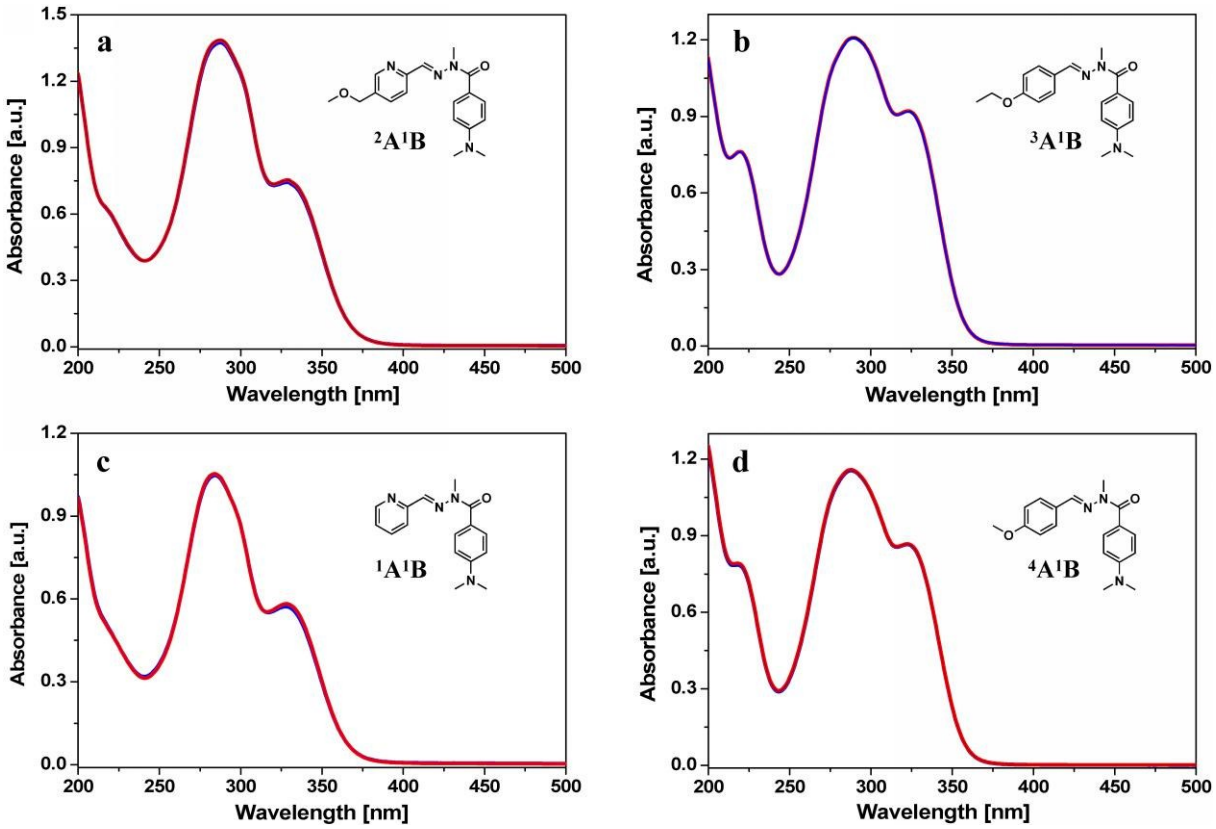


Figure S17. Photoisomerization of ^{1}**B** involved acylhydrazones (a) ^{2}**A**^{1}**B**, (b) ^{3}**A**^{1}**B**, (c) ^{1}**A**^{1}**B** and (d) ^{4}**A**^{1}**B** (^{p}**A**^{1}**B** and ^{b}**A**^{1}**B** in the CDNs) from its E-isomer (red line) in CH_3CN (30 μM) to Z-isomer (blue line) in function of time from 0 to 1380 sec under constant irradiation (λ_{irr} = 310-400 nm).

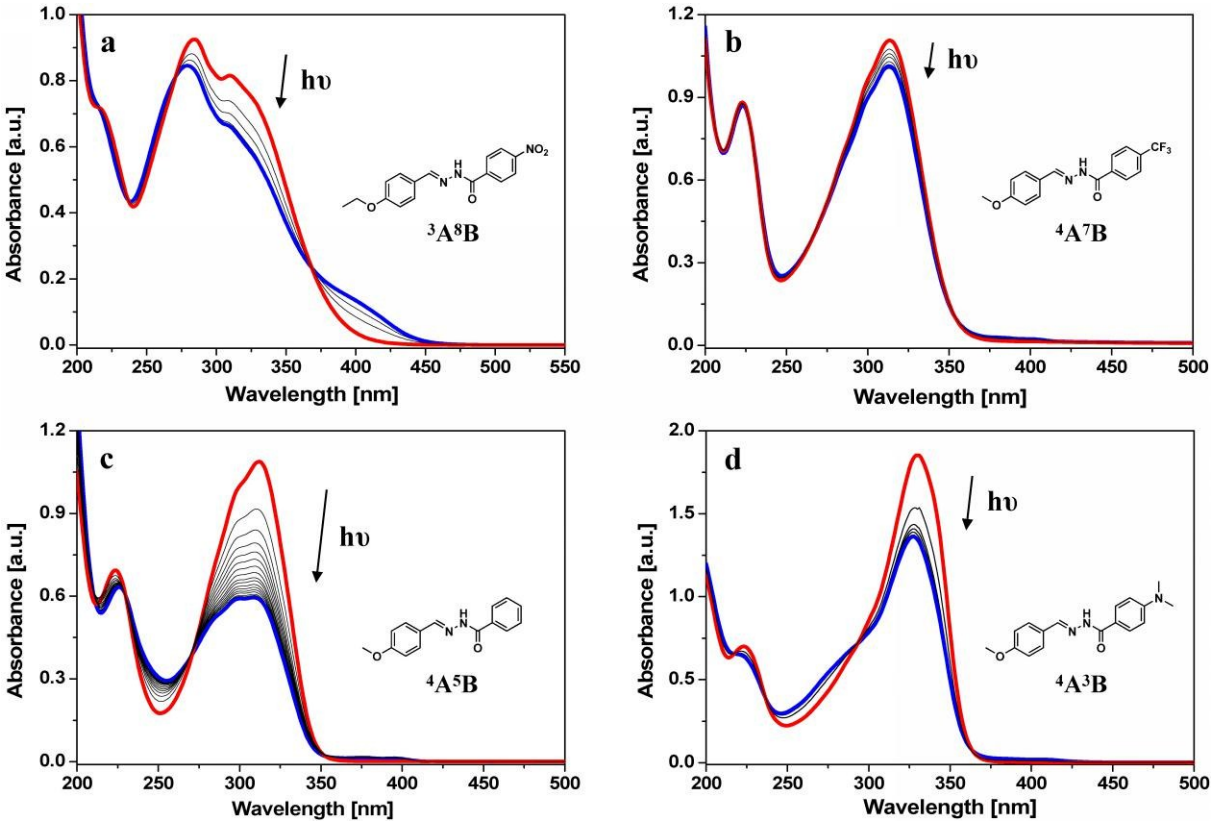


Figure S18. Photoisomerization of N-H phenyl-acylhydrazones (a) **^{3}A^{8}B**, (b) **^{4}A^{7}B**, (c) **^{4}A^{5}B** and (d) **^{4}A^{3}B** (**^{b}A^{h}B** in the CDNs) from its E-isomer (red line) in CH_3CN (30 μM) to Z-isomer (blue line) in function of time from 0 to 1080 sec under constant irradiation (λ_{irr} = 310-400 nm).

Thermal half-life for Z to E isomerization:[11]

Time evolution absorption spectra of all acylhydrazones were recorded in CH_3CN at 25 °C using the instruments described in this section to estimate thermal half-lives $t_{1/2}$. After full conversion of the respective photoswitch until a photostationary state was reached, the solution was monitored for 30 min in the dark. For each spectrum, the corresponding amount of Z-isomer was derived from the value of the absorbance at λ_{max} using the following equations:

$$x(t) = \frac{A(t) - A_Z}{A_E - A_Z} \text{ and } y(t) = \frac{A_E - A(t)}{A_E - A_Z}$$

where at time t, x(t) is the amount of E-isomer, y(t) is the amount of Z-isomer, and A(t) is the total absorbance of the mixture, and A_Z and A_E are the absorbances of the pure E- and Z-isomers, respectively.

Plotting the percentage of Z-isomer against the time gives the rate constant k from the first order kinetic equation:

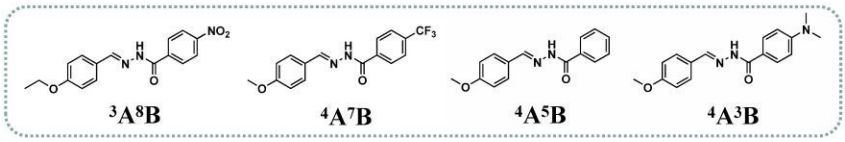
$$[Z] = [Z]_0 \times e^{-k \cdot t}$$

The corresponding thermal half-life then follows from:

$$t_{1/2} = \frac{\ln(2)}{k}$$

Table S5. Photochromic properties of N-H phenyl-acylhydrazones $^{b}\mathbf{A}^{h}\mathbf{B}$ derived from benzaldehyde and N-H hydrazide.

Compd	λ_{max}[a] [nm]	$t_{1/2}$[b] [min]	$t_{1/2}$(20%Sc^{3+})[c] [sec]	$t_{1/2}$(10%HCl)[d] [sec]
$^{3}\mathbf{A}^{8}\mathbf{B}$	284	26.64	18.35	1.86
$^{4}\mathbf{A}^{7}\mathbf{B}$	313	28.92	7.08[e]	1.81
$^{4}\mathbf{A}^{5}\mathbf{B}$	312	40.11	2.25	2.55
$^{4}\mathbf{A}^{3}\mathbf{B}$	330	330.05	8.04[e]	4.88



[a]For the E-isomer. [b]Thermal half life of the back reaction (from Z to E isomer) at 25 ºC. [c]Thermal half life of the back reaction for acylhydrazones with 0.2 eq. Sc^{3+} at 25 ºC. [d]Thermal half life of the back reaction for acylhydrazones with 0.1 eq. HCl at 25 ºC. [e]Thermal half life of the back reaction monitoring from 0 to 35 sec.

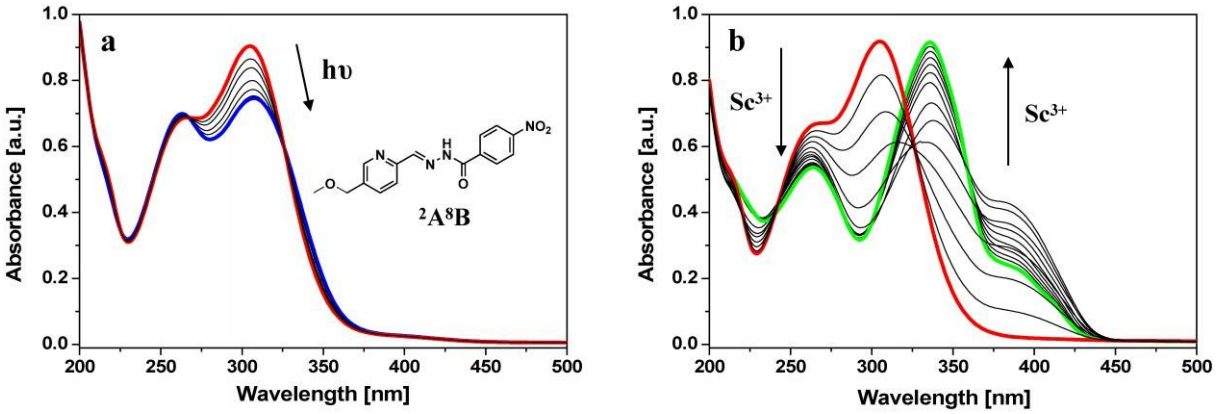


Figure S19. (a) Photoisomerization of **^{2}A^{8}B** from its E-isomer (red line) in CH_3CN (30 μM) to Z-isomer (blue line) in function of time from 0-240 sec under constant irradiation (λ_{irr} = 310-400 nm). (b) Absorption spectra of **^{2}A^{8}B** (red line) in CH_3CN (30 μM) solution upon addition of increasing concentrations of Sc^{3+} from 0 to 1eq. (green line).

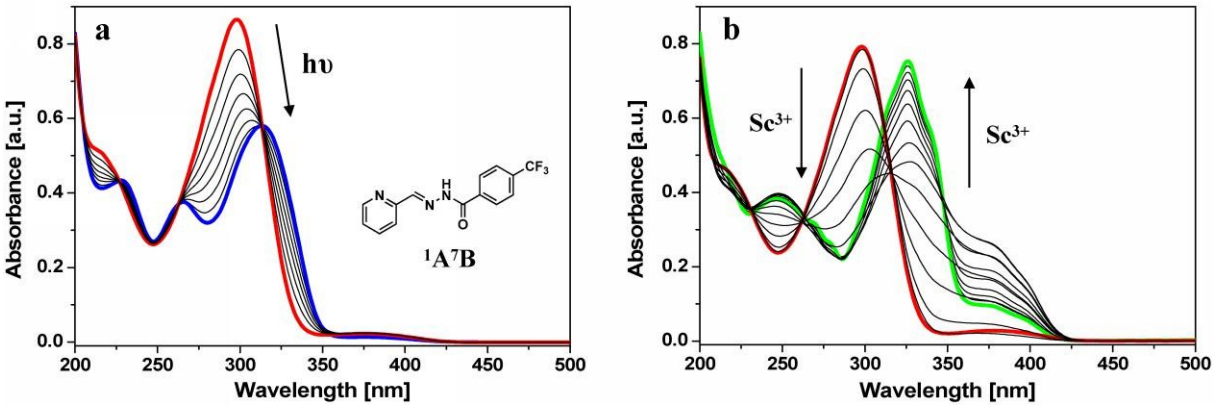


Figure S20. (a) Photoisomerization of **^{1}A^{7}B** from its E-isomer (red line) in CH_3CN (30 μM) to Z-isomer (blue line) in function of time from 0-240 sec under constant irradiation (λ_{irr} = 310-400 nm). (b) Absorption spectra of **^{1}A^{7}B** (red line) in CH_3CN (30 μM) solution upon addition of increasing concentrations of Sc^{3+} from 0 to 1eq. (green line).

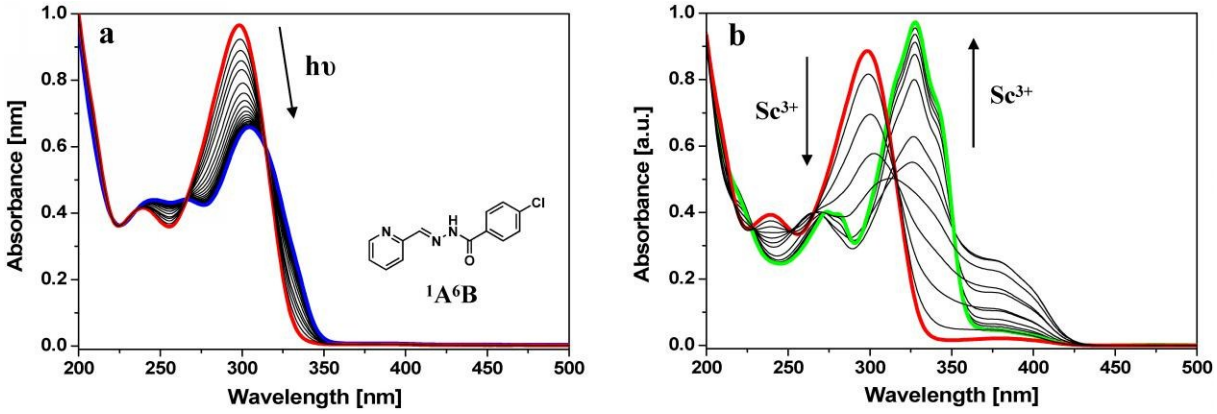


Figure S21. (a) Photoisomerization of **^{1}A^{6}B** from its E-isomer (red line) in CH_3CN (30 μM) to Z-isomer (blue line) in function of time from 0-960 sec under constant irradiation (λ_{irr} = 310-400 nm). (b) Absorption spectra of **^{1}A^{6}B** (red line) in CH_3CN (30 μM) solution upon addition of increasing concentrations of Sc^{3+} from 0 to 1eq. (green line).

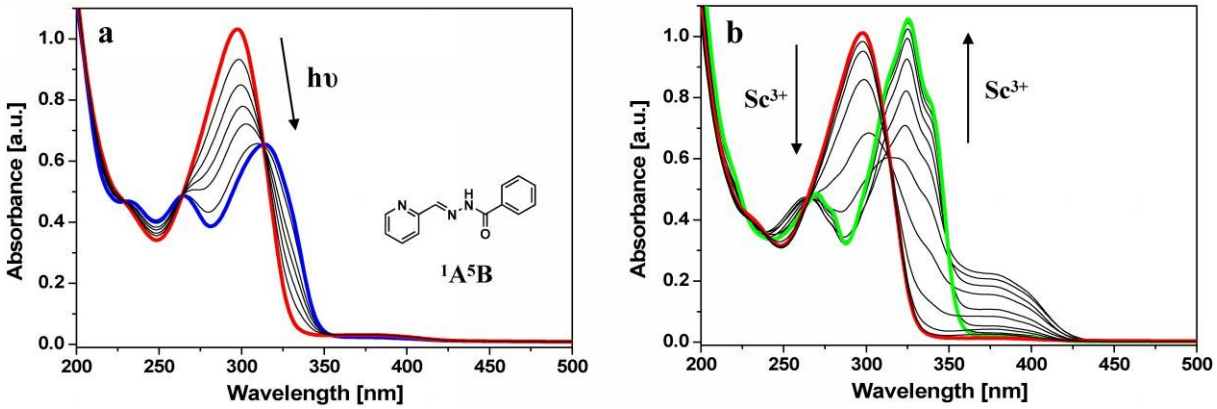


Figure S22. (a) Photoisomerization of **^{1}A^{5}B** from its E-isomer (red line) in CH_3CN (30 μM) to Z-isomer (blue line) in function of time from 0-300 sec under constant irradiation (λ_{irr} = 310-400 nm). (b) Absorption spectra of **^{1}A^{5}B** (red line) in CH_3CN (30 μM) solution upon addition of increasing concentrations of Sc^{3+} from 0 to 1eq. (green line).

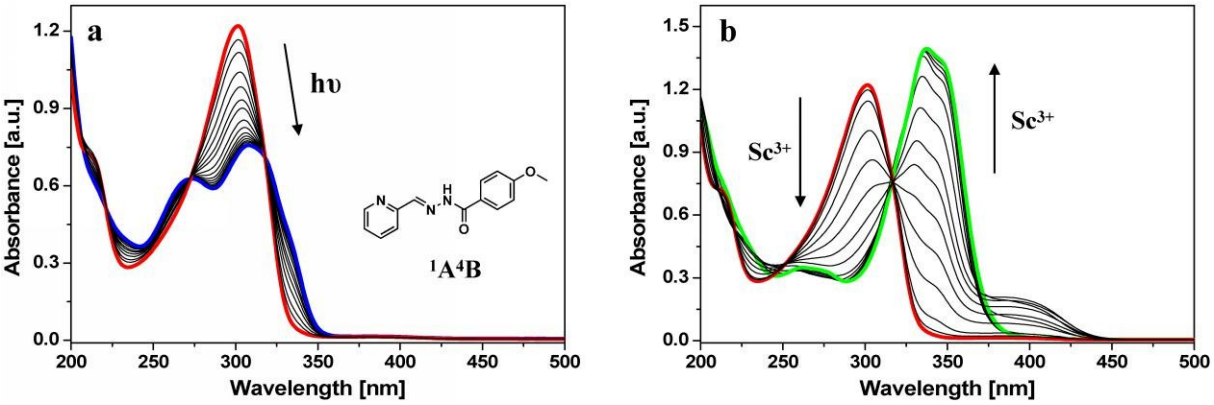


Figure S23. (a) Photoisomerization of **^{1}A^{4}B** from its E-isomer (red line) in CH_3CN (30 μM) to Z-isomer (blue line) in function of time from 0-1380 sec under constant irradiation (λ_{irr} = 310-400 nm). (b) Absorption spectra of **^{1}A^{4}B** (red line) in CH_3CN (30 μM) solution upon addition of increasing concentrations of Sc^{3+} from 0 to 1eq. (green line).

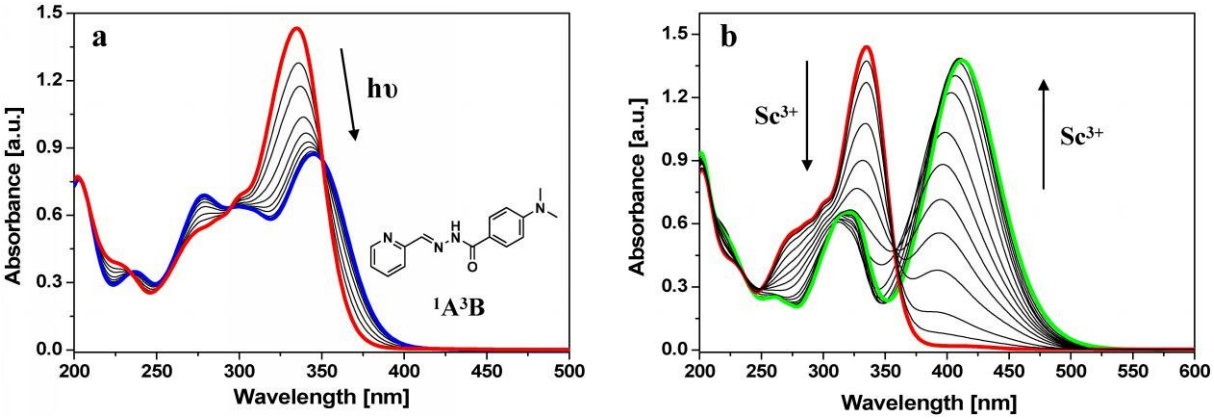
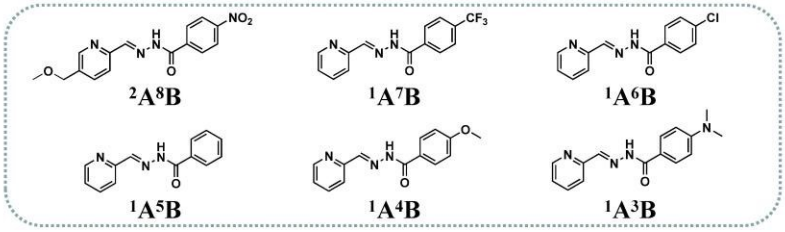


Figure S24. (a) Photoisomerization of **^{1}A^{3}B** from its E-isomer (red line) in CH_3CN (30 μM) to Z-isomer (blue line) in function of time from 0-780 sec under constant irradiation (λ_{irr} = 310-400 nm). (b) Absorption spectra of **^{1}A^{3}B** (red line) in CH_3CN (30 μM) solution upon addition of increasing concentrations of Sc^{3+} from 0 to 1eq. (green line).

Table S6. Photochromic properties of N-H pyridyl-acylhydrazones $^{p}\mathbf{A}^{h}\mathbf{B}$ derived from 2-pyridinecarboxaldehyde and N-H hydrazide.

Compd	R	λ_{max}[a] [nm]	λ_{max}(1eq. Sc^{3+})[b] [nm]	$t_{1/2}$[c] [min]	$t_{1/2}$(20%Sc^{3+})[d] [min]	$t_{1/2}$(10%HCl)[e] [min]
$^{2}\mathbf{A}^{8}\mathbf{B}$	NO_2	304	335	stable	stable	stable
$^{1}\mathbf{A}^{7}\mathbf{B}$	CF_3	298	326	stable	stable	stable
$^{1}\mathbf{A}^{6}\mathbf{B}$	Cl	298	328	stable	stable	stable
$^{1}\mathbf{A}^{5}\mathbf{B}$	H	297	325	stable	stable	stable
$^{1}\mathbf{A}^{4}\mathbf{B}$	OCH_3	301	337	stable	stable	stable
$^{1}\mathbf{A}^{3}\mathbf{B}$	$N(CH_3)_2$	335	411	stable	stable	stable



[a]For the E-isomer. [b]For the E-isomer with 1 eq. Sc^{3+}. [c]Thermal half life of the back reaction (from Z to E isomer) at 25 °C; stable photoswitches were defined as those where no thermal Z-E isomerization was observed for at least 30 min. [d]Thermal half life of the back reaction for acylhydrazones with 0.2 eq. Sc^{3+} at 25 °C. [e]Thermal half life of the back reaction for acylhydrazones with 0.1 eq. HCl at 25 °C.

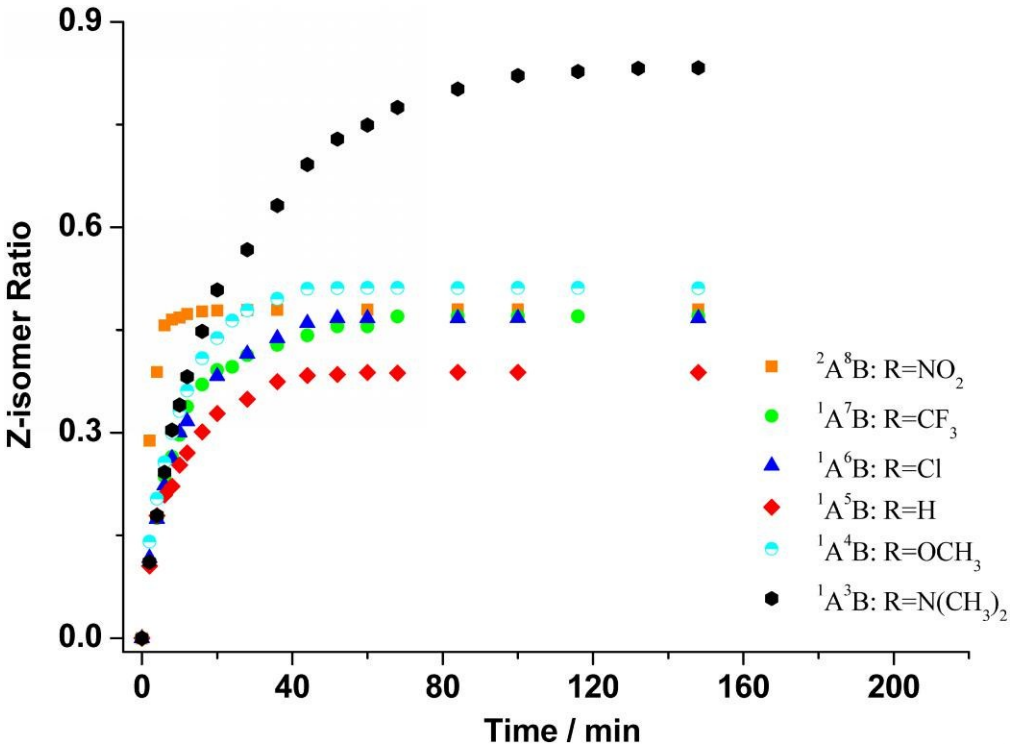


Figure S25. Time course of the Z-isomer ratio following the photo-isomerization from E to Z isomers of N-H pyridyl-acylhydrazones $^{p}\mathbf{A}^{h}\mathbf{B}$ (3.5 mM) under light irradiation (λ_{irr} = 310-400 nm).

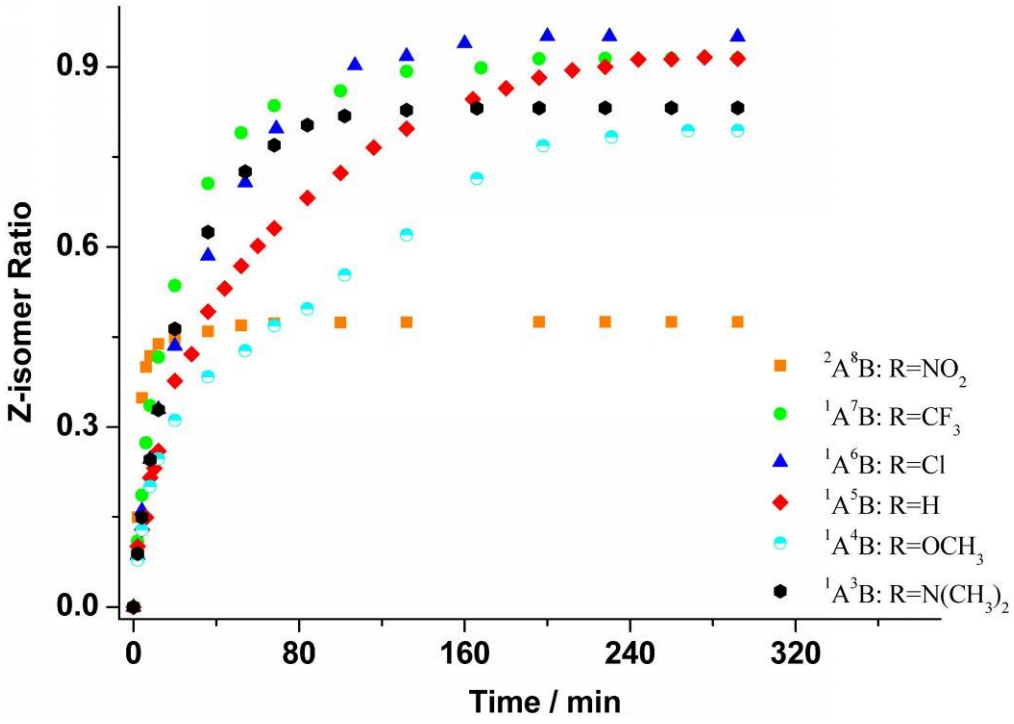


Figure S26. Time course of the Z-isomer ratio following the photo-isomerization from E to Z isomers of N-H pyridyl-acylhydrazones $^{p}\mathbf{A}^{h}\mathbf{B}$ (3.5 mM) under light irradiation (λ_{irr} = 310-400 nm) with catalytical amount of $Sc^{III}(OTf)_3$ (2%, 0.14 mM).

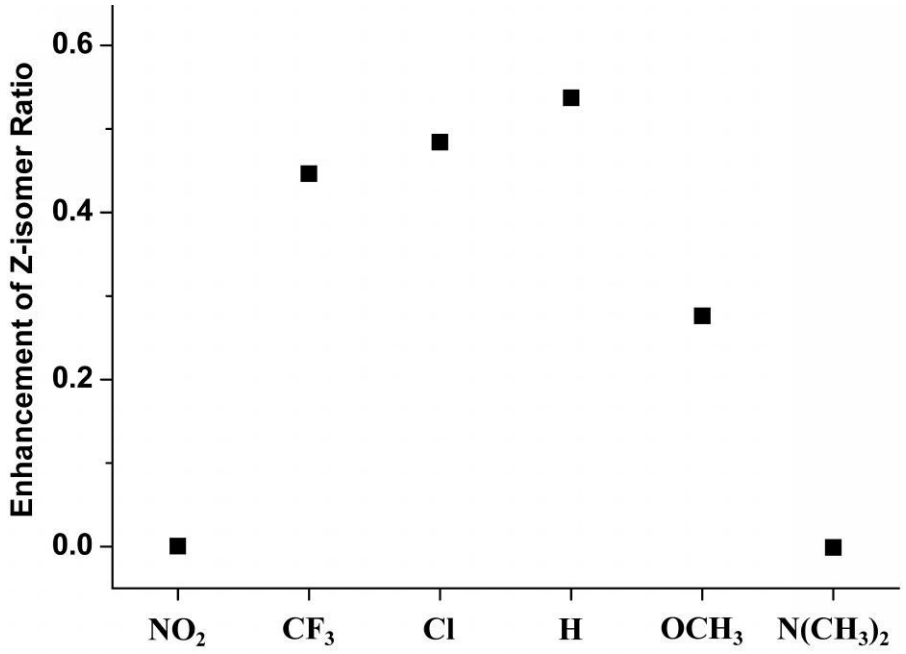
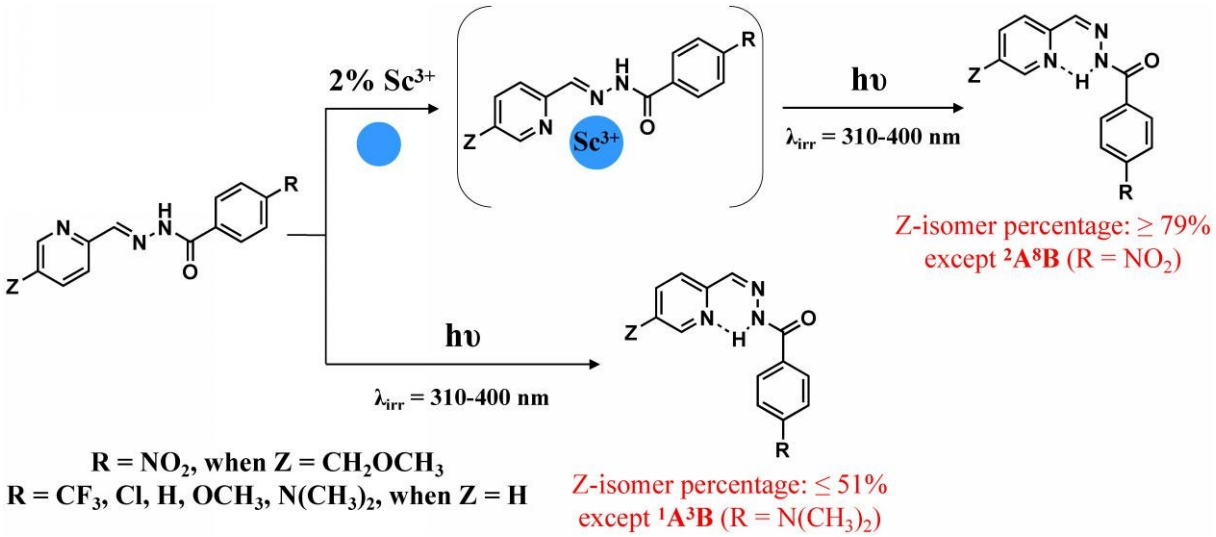


Figure S27. Enhancements of the Z-isomer ratio after the photo-isomerization from E to Z of 3.5 mM N-H pyridyl-acylhydrazones **^{p}A^{h}B** with different R groups under 300 min constant light irradiation (λ_{irr} = 310-400 nm) between presence and absence of $Sc^{III}(OTf)_3$ (2%, 0.07 mM).



Scheme S9. Photoisomerization of N-H pyridyl-acylhydrazones **^{p}A^{h}B** (3.5 mM) from E to Z under constant light irradiation (λ_{irr} = 310-400 nm) with or without catalytical amount of $Sc^{III}(OTf)_3$ (2%, 0.14 mM).

6. Triple adaptation in CDNs based on four acylhydrazone CDLs.

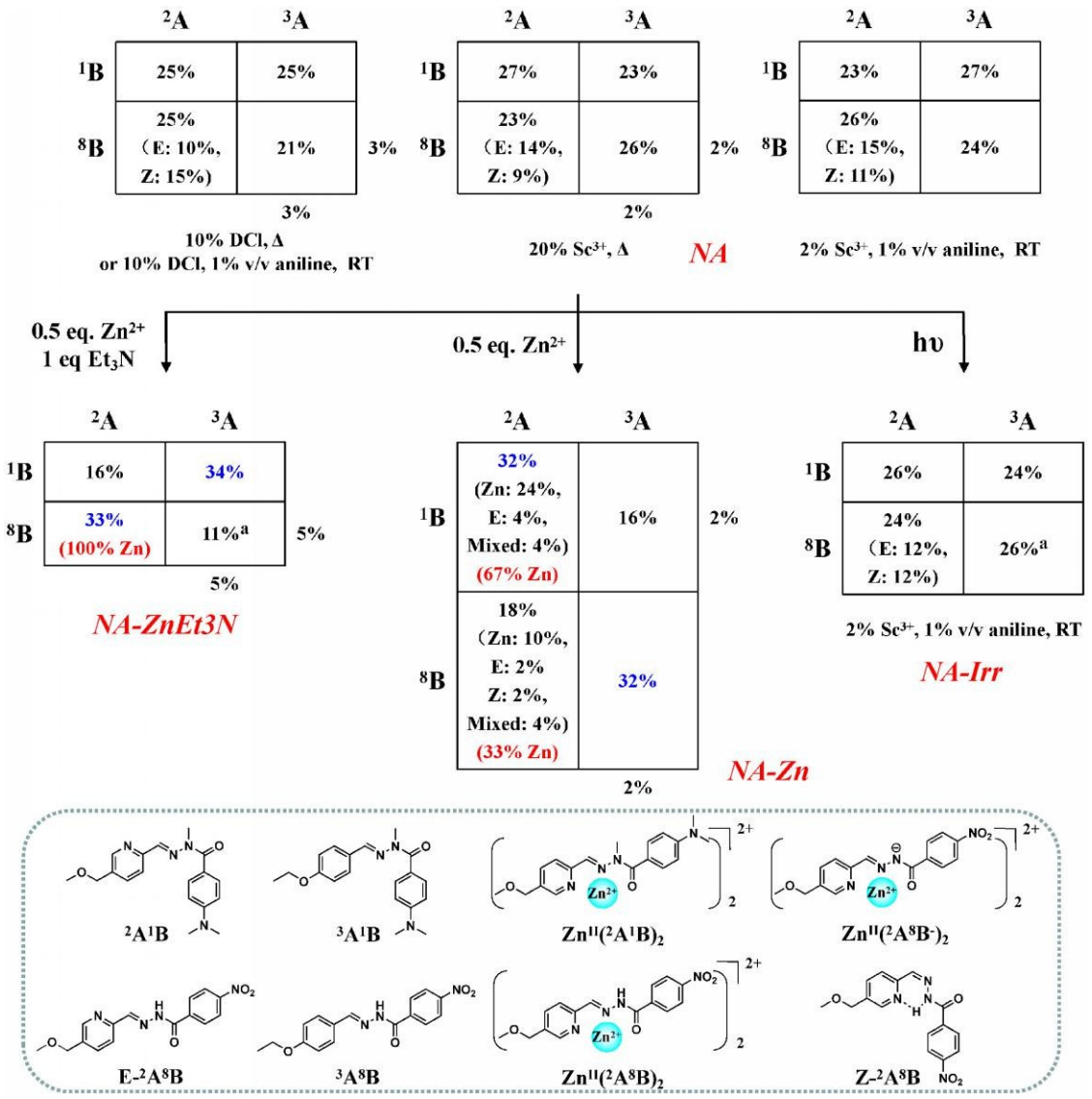


Table S7. Percentage distributions of the contituents forming the [2×2] CDN ***NA*** with four constituents **^{2}A^{1}B**, **^{3}A^{1}B**, **^{2}A^{8}B** and **^{3}A^{8}B** (3.5 mM each) in response to 0.5 eq. Zn^{2+} & 1 eq. Et_3N (middle left), 0.5 eq. Zn^{2+} (middle center) and light irradiation (λ_{irr} = 310-400 nm, middle right) from the statistical distribution (top) with corresponding catalyst and temperature conditions, undergoing the changes shown in Scheme 4 of the main text, listed in the [2×2] tables. The percentages of the unreacted free components are indicated out of the tables. Amplified or dominat constituents are marked by blue color. The percentage of the Zn^{2+} ion capture between constituents **^{2}A^{1}B** and **^{2}A^{8}B** are indicated by red color. [a]This percentage was obtained by calculation from the other corresponding constituents. Error on % determination: ±2%. See Figure S7a-S7c and Figure S28-S29 for ^{1}H NMR spectra.

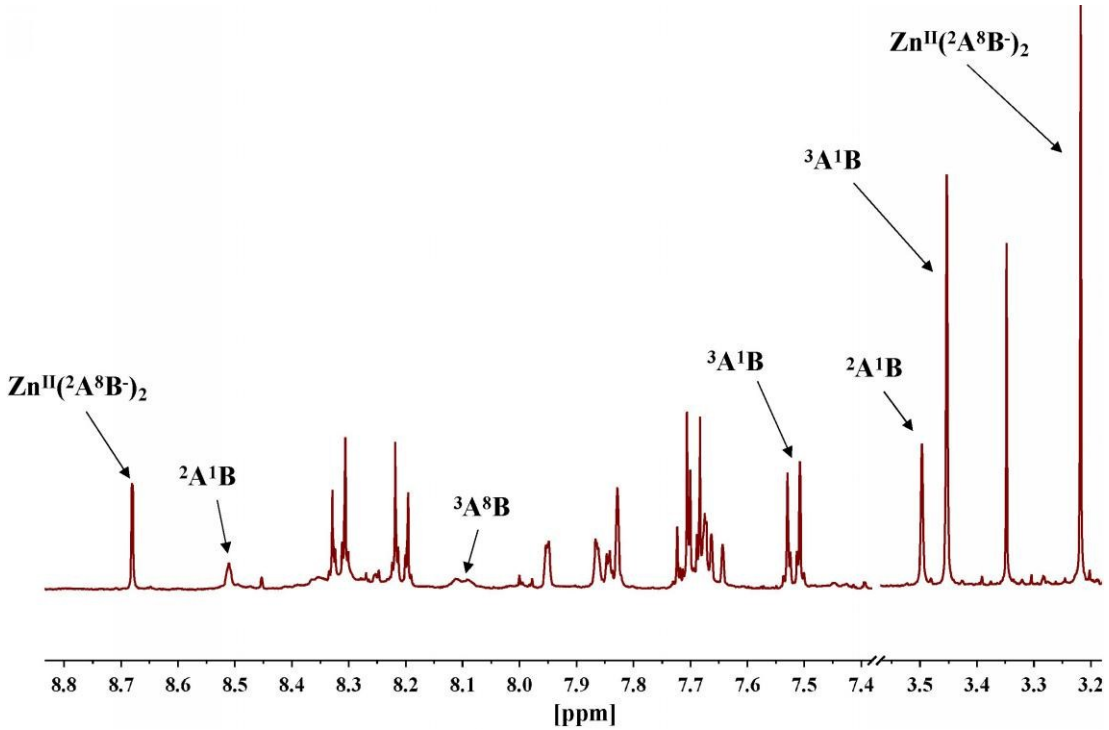


Figure S28. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NA-ZnEt3N*** generated from a statistically distributional library with four constituents **^{2}A^{1}B**, **^{3}A^{1}B**, **^{2}A^{8}B** and **^{3}A^{8}B** (3.5 mM each), treated with 0.5 equiv. of Zn^{2+} (3.5 mM) and 1 equiv. of Et_3N (7 mM) using 1% v/v aniline as a catalyst after heating at 78 ˚C for 40 h.

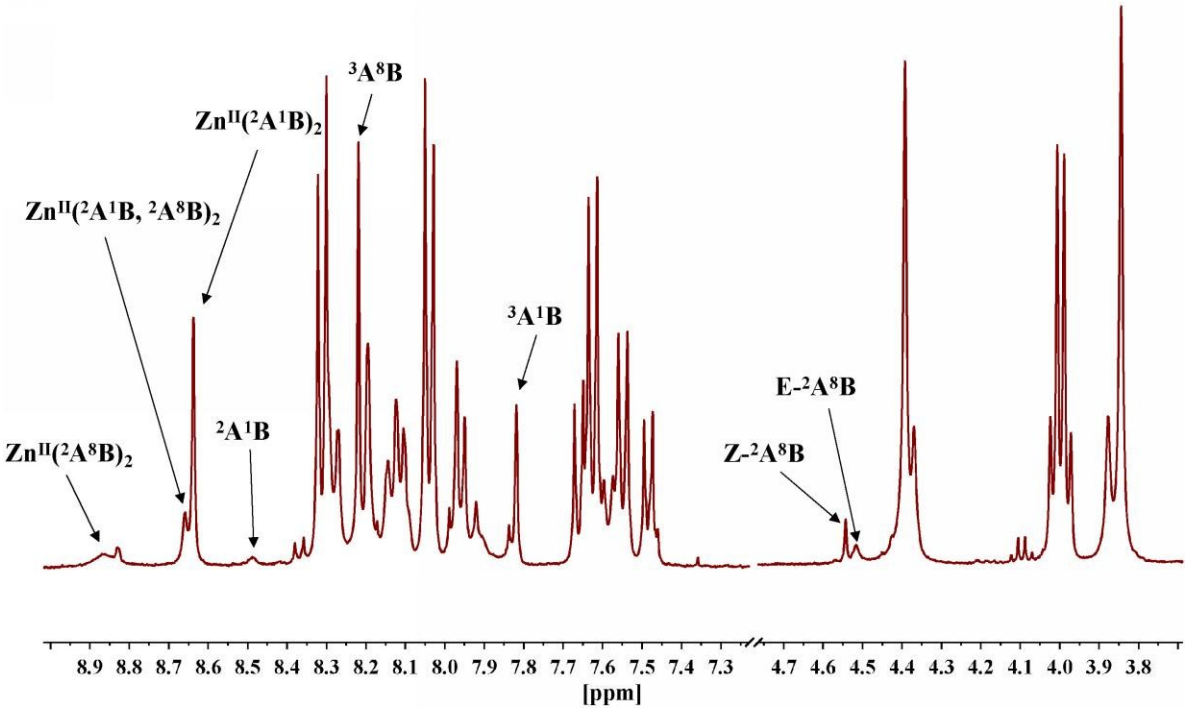


Figure S29. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NA-Zn*** generated from a statistically distributional library with four constituents **^{2}A^{1}B**, **^{3}A^{1}B**, **^{2}A^{8}B** and **^{3}A^{8}B** (3.5 mM each), treated with 0.5 equiv. of Zn^{2+} (3.5 mM) after heating at 60 ˚C for 10 h. The NMR measurement was conducted at -30 ˚C.

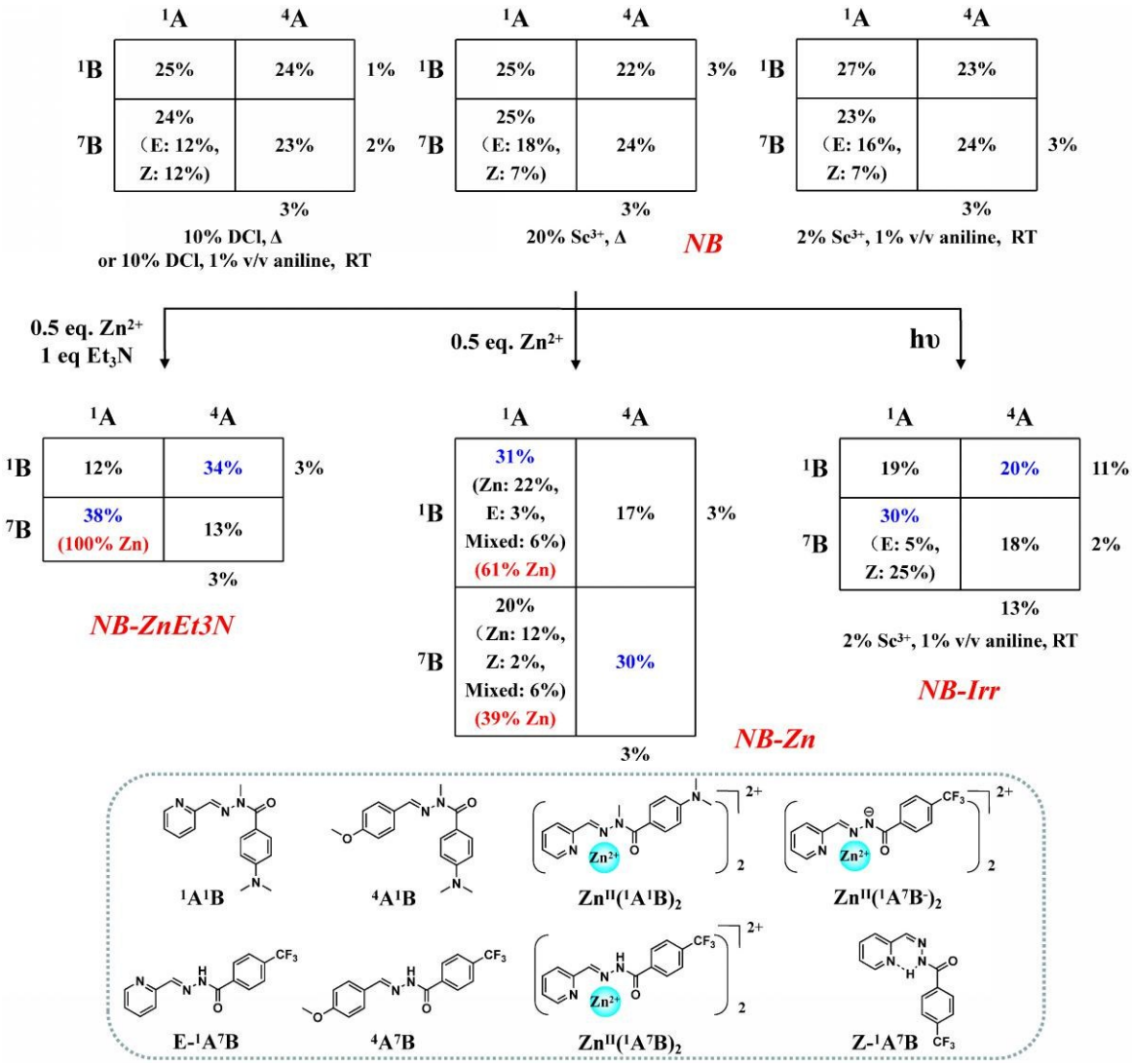


Table S8. Percentage distributions of the contituents forming the [2×2] CDN ***NB*** with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{7}B** and **^{4}A^{7}B** (3.5 mM each) in response to 0.5 eq. Zn^{2+} & 1 eq. Et_3N (middle left), 0.5 eq. Zn^{2+} (middle center) and light irradiation (λ_{irr} = 310-400 nm, middle right) from the statistical distribution (top) with corresponding catalyst and temperature conditions, undergoing the changes shown in Scheme 5 of the main text, listed in the [2×2] tables. The percentages of the unreacted free components are indicated out of the tables. Amplified or dominat constituents are marked by blue color. The percentage of the Zn^{2+} ion capture between constituents **^{1}A^{1}B** and **^{1}A^{7}B** are indicated by red color. Error on % determination: ±2%. See Figure S8a-S8c and Figure S30-S31 for ^{1}H NMR spectra.

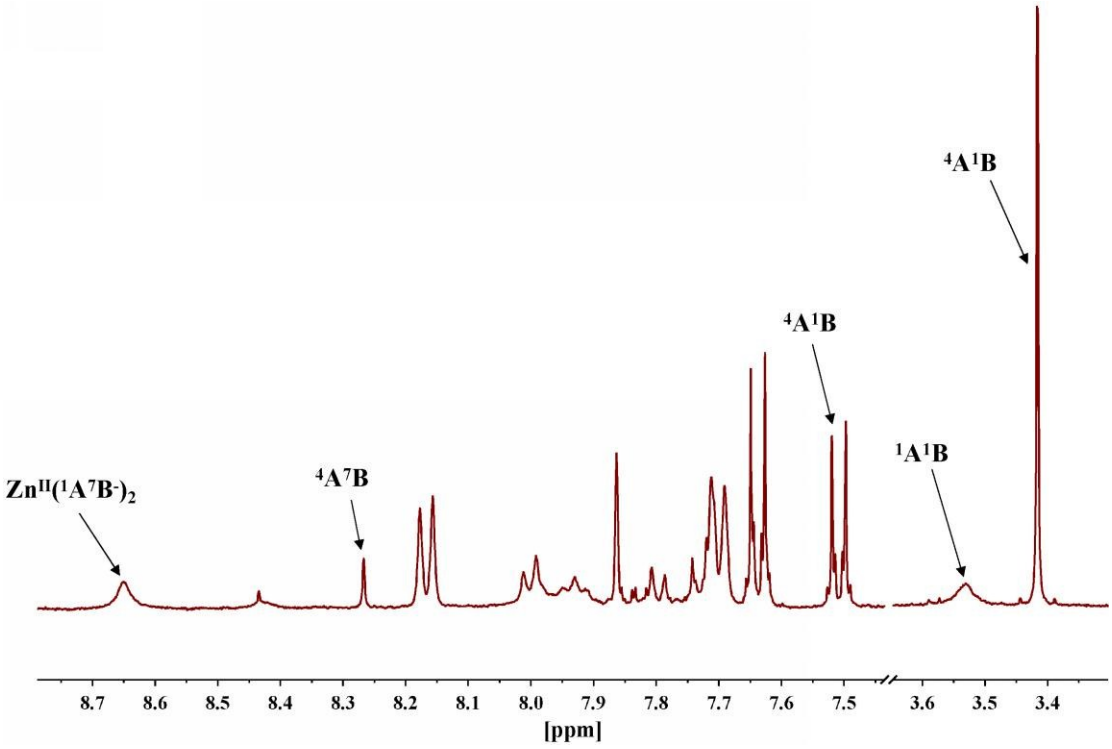


Figure S30. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NB-ZnEt3N*** generated from a statistically distributional library with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{7}B** and **^{4}A^{7}B** (3.5 mM each), treated with 0.5 equiv. of Zn^{2+} (3.5 mM) and 1 equiv. of Et_3N (7 mM) using 1% v/v aniline as a catalyst after heating at 78 °C for 18 h. For clarity of the spectrum and eliminating the interference of aniline, 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

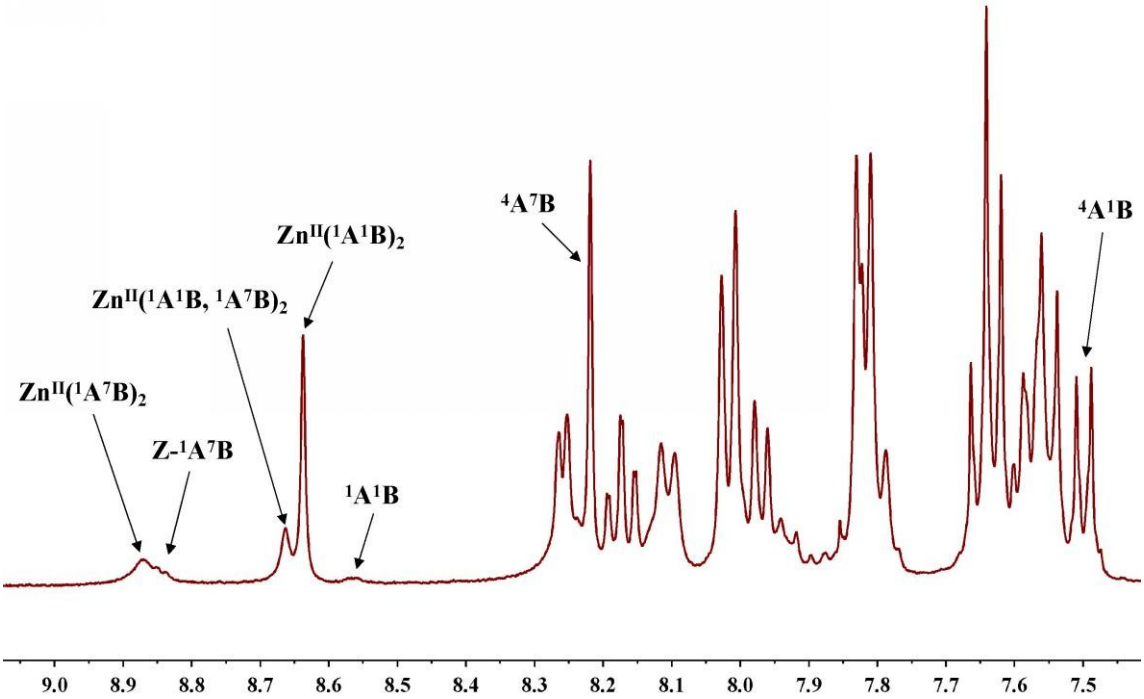


Figure S31. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NB-Zn*** generated from a statistically distributional library with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{7}B** and **^{4}A^{7}B** (3.5 mM each), treated with 0.5 equiv. of Zn^{2+} (3.5 mM) after heating at 60 °C for 10 h. The NMR measurement was conducted at -30 °C.

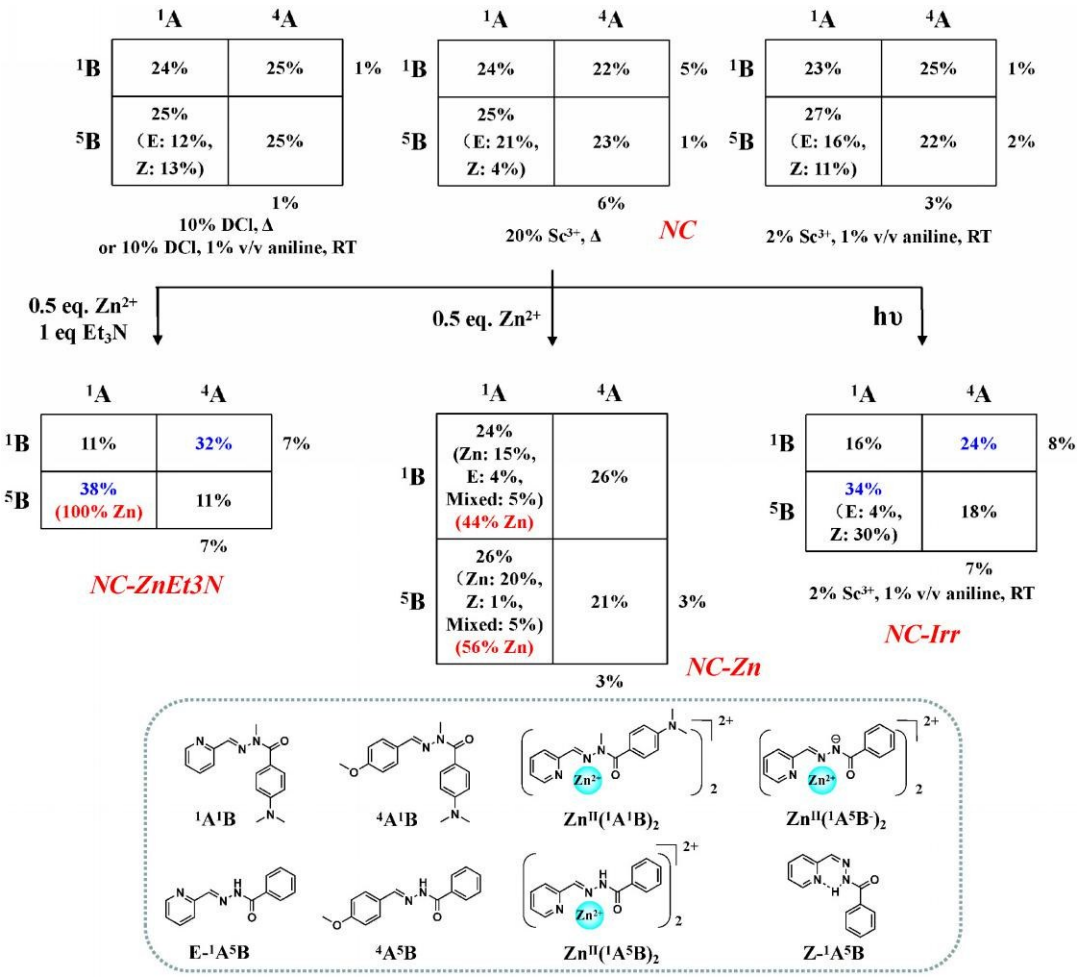


Table S9. Percentage distributions of the contituents forming the [2×2] CDN ***NC*** with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{5}B** and **^{4}A^{5}B** (3.5 mM each) in response to 0.5 eq. Zn^{2+} & 1 eq. Et_3N (middle left), 0.5 eq. Zn^{2+} (middle center) and light irradiation (λ_{irr} = 310-400 nm, middle right) from the statistical distribution (top) with corresponding catalyst and temperature conditions, undergoing the changes shown in Scheme 6 of the main text, listed in the [2×2] tables. The percentages of the unreacted free components are indicated out of the tables. Amplified or dominat constituents are marked by blue color. The percentage of the Zn^{2+} ion capture between constituents **^{1}A^{1}B** and **^{1}A^{5}B** are indicated by red color. Error on % determination: ±2%. See Figure S9a-S9c and Figure S32-S33 for ^{1}H NMR spectra.

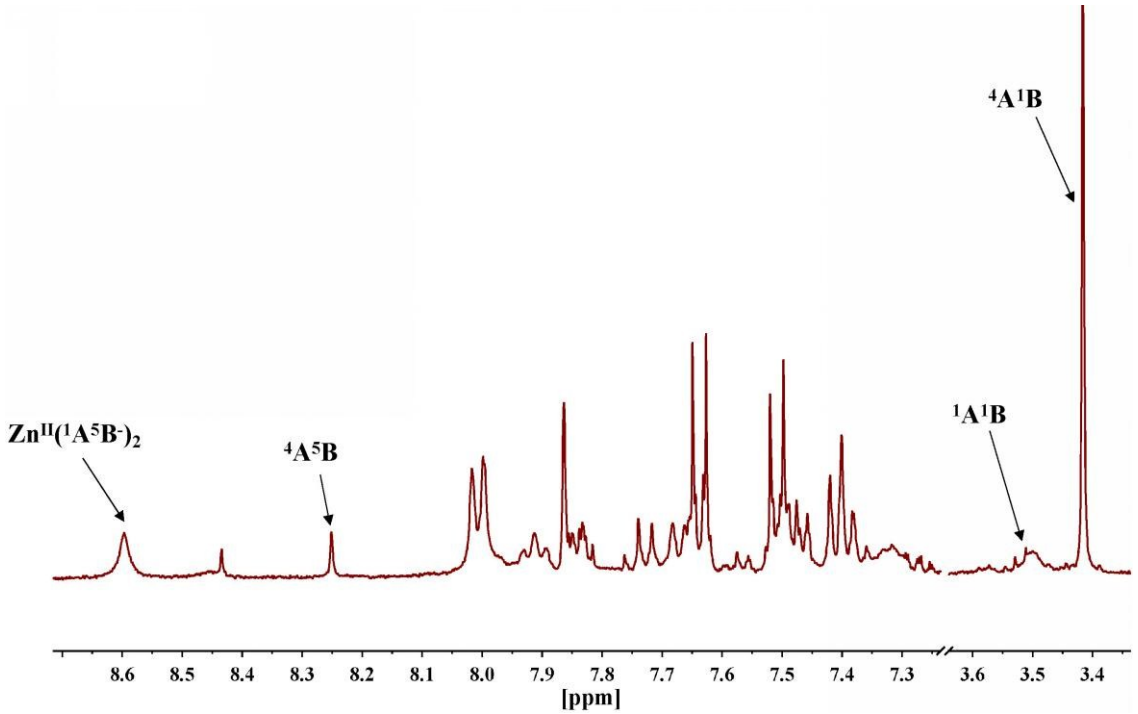


Figure S32. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NC-ZnEt3N*** generated from a statistically distributional library with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{5}B** and **^{4}A^{5}B** (3.5 mM each), treated with 0.5 equiv. of Zn^{2+} (3.5 mM) and 1 equiv. of Et_3N (7 mM) using 1% v/v aniline as a catalyst after heating at 78 ˚C for 17 h. For clarity of the spectrum and eliminating the interference of aniline, 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

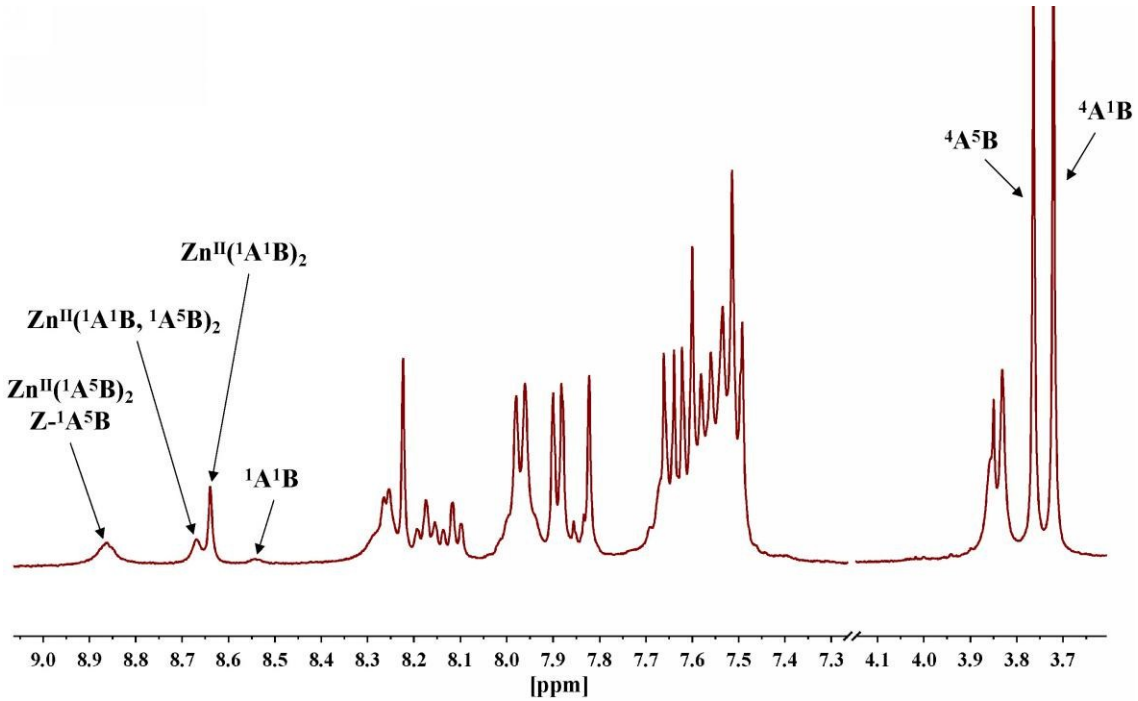


Figure S33. A portion of the 400 MHz ^{1}H NMR spectrum of library ***NC-Zn*** generated from a statistically distributional library with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{5}B** and **^{4}A^{5}B** (3.5 mM each), treated with 0.5 equiv. of Zn^{2+} (3.5 mM) after heating at 60 ˚C for 10 h. The NMR measurement was conducted at -30 ˚C.

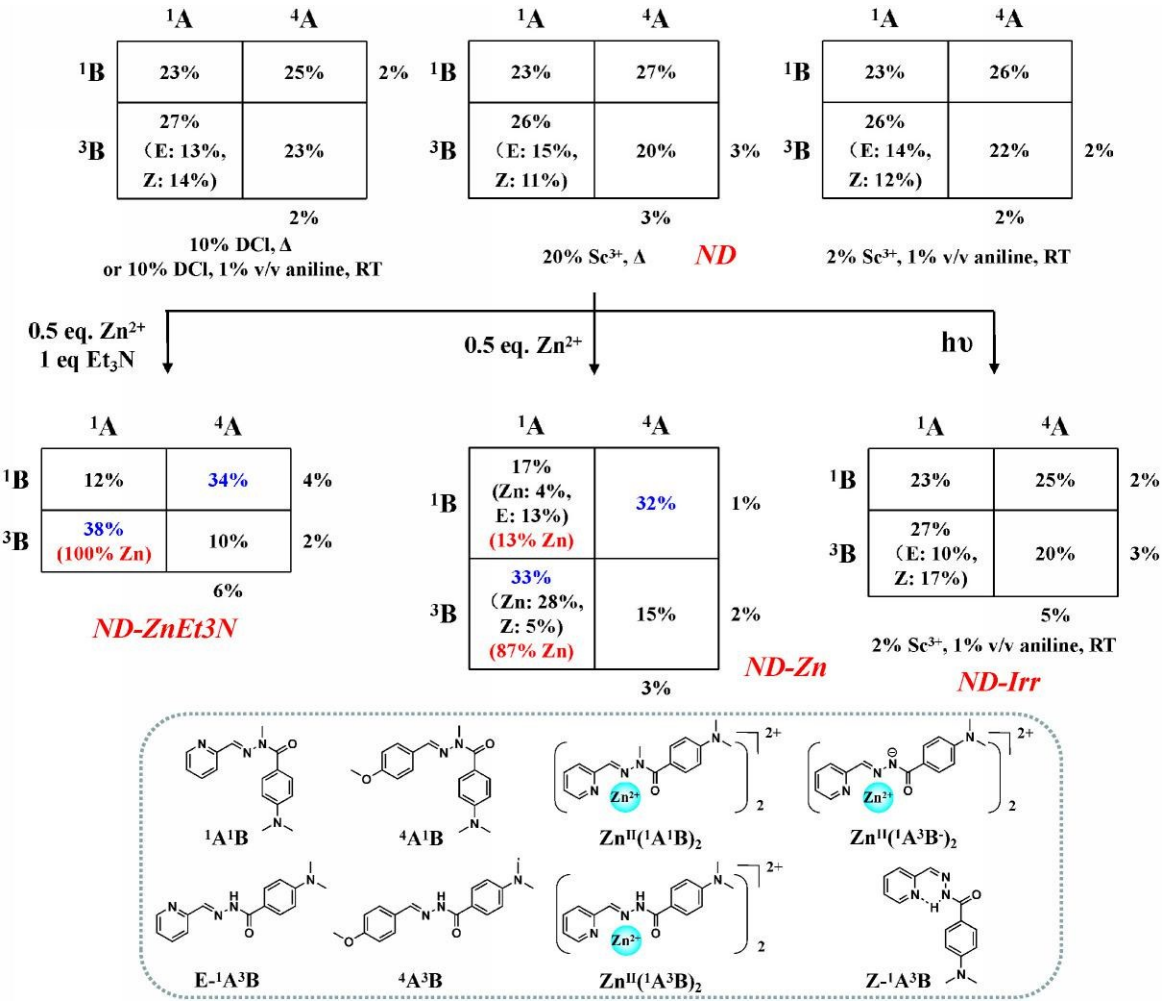


Table S10. Percentage distributions of the contituents forming the [2×2] CDN ***ND*** with four constituents ^{1}**A**^{1}**B**, ^{4}**A**^{1}**B**, ^{1}**A**^{3}**B** and ^{4}**A**^{3}**B** (3.5 mM each) in response to 0.5 eq. Zn^{2+} & 1 eq. Et_3N (middle left), 0.5 eq. Zn^{2+} (middle center) and light irradiation (λ_{irr} = 310-400 nm, middle right) from the statistical distribution (top) with corresponding catalyst and temperature conditions, undergoing the changes shown in Scheme 7 of the main text, listed in the [2×2] tables. The percentages of the unreacted free components are indicated out of the tables. Amplified or dominat constituents are marked by blue color. The percentage of the Zn^{2+} ion capture between constituents ^{1}**A**^{1}**B** and ^{1}**A**^{3}**B** are indicated by red color. Error on % determination: ±2%. See Figure S10a-S10c and Figure S34-S35 for ^{1}H NMR spectra.

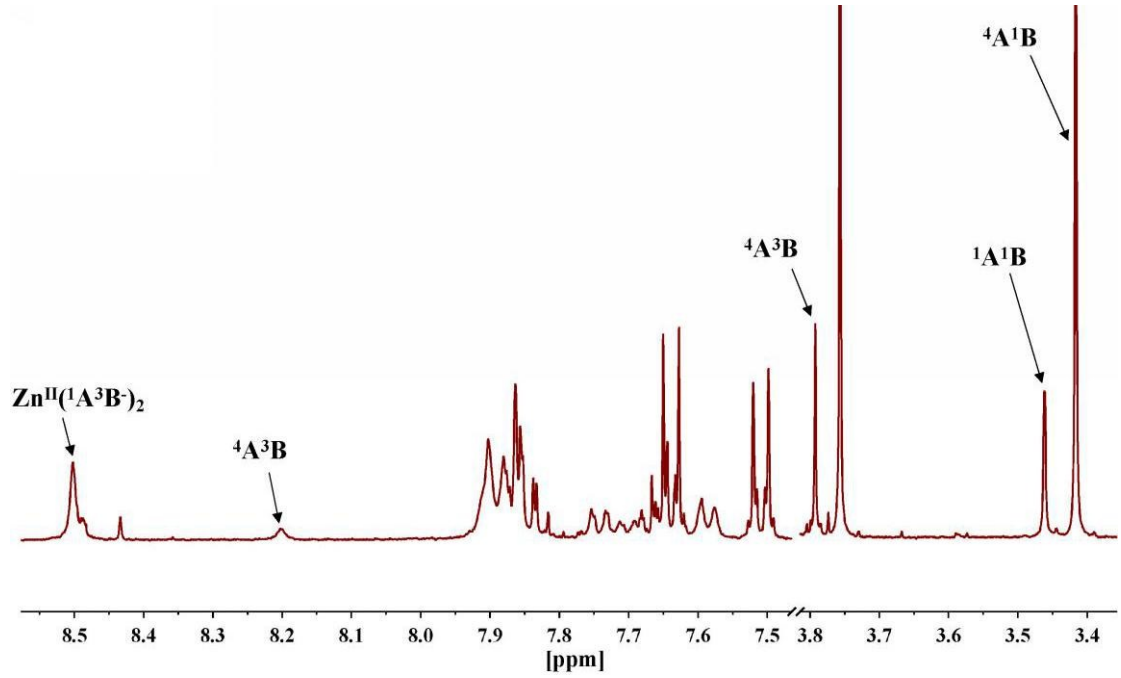


Figure S34. A portion of the 400 MHz ^{1}H NMR spectrum of library ***ND-ZnEt3N*** generated from a statistically distributional library with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{3}B** and **^{4}A^{3}B** (3.5 mM each), treated with 0.5 equiv. of Zn^{2+} (3.5 mM) and 1 equiv. of Et_3N (7 mM) using 1% v/v aniline as a catalyst after heating at 78 °C for 17 h. For clarity of the spectrum and eliminating the interference of aniline, 0.3 mL D_2O was added after the equilibrium of the library, before the NMR measurement.

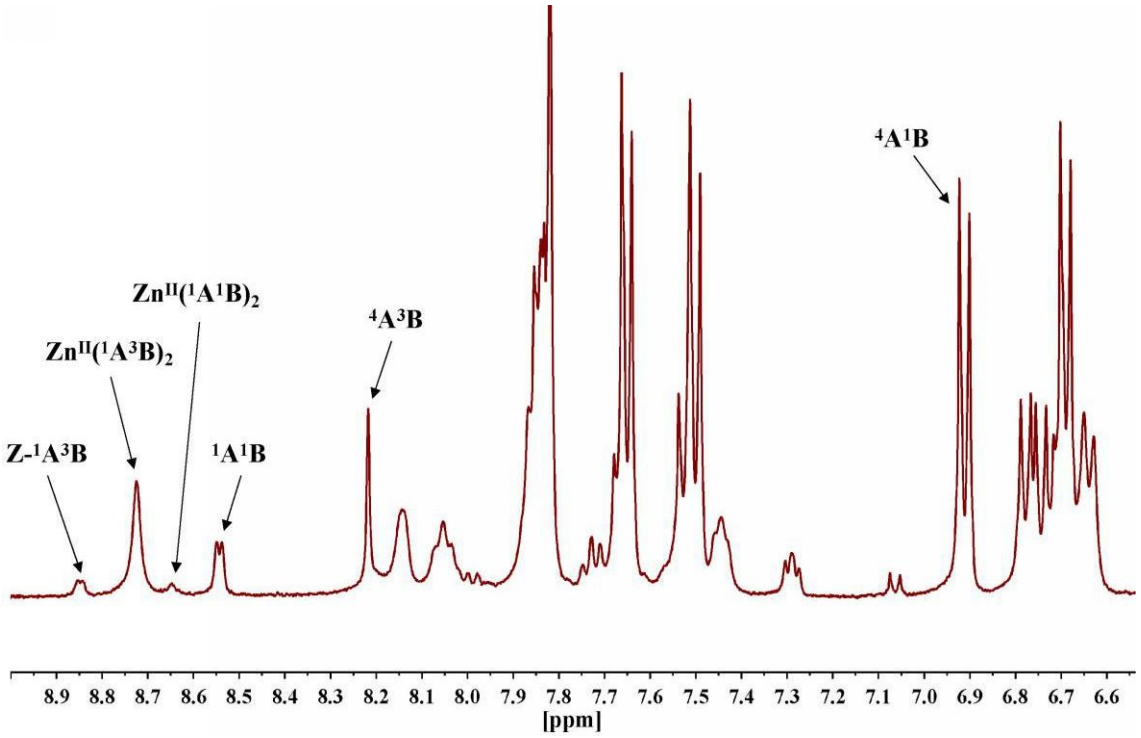


Figure S35. A portion of the 400 MHz ^{1}H NMR spectrum of library ***ND-Zn*** generated from a statistically distributional library with four constituents **^{1}A^{1}B**, **^{4}A^{1}B**, **^{1}A^{3}B** and **^{4}A^{3}B** (3.5 mM each), treated with 0.5 equiv. of Zn^{2+} (3.5 mM) after heating at 60 °C for 10 h. The NMR measurement was conducted at -30 °C.

7. Reference.

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(2) M. Herder, J.-M. Lehn, *J. Am. Chem. Soc.*, 2018, **140**, 7647-7657.

(3) For the compounds $^{1}\mathbf{A}^{1}\mathbf{B}$, $^{1}\mathbf{A}^{5}\mathbf{B}$, see for instance: G. Vantomme, S. M. Jiang, J.-M. Lehn, *J. Am. Chem. Soc.*, 2014, **136**, 9509-9518.

(4) For the compounds $^{1}\mathbf{A}^{2}\mathbf{B}$, see for instance: G. Vantomme, J.-M. Lehn, *Angew. Chem.*, *Int. Ed.*, 2013, **52**, 3940-3943.

(5) For the compounds $^{1}\mathbf{A}^{3}\mathbf{B}$, see for instance: R. Raveendran, S. Pal, *Polyhedron*, 2005, **24**, 57-63.

(6) For the compounds $^{1}\mathbf{A}^{4}\mathbf{B}$, see for instance: G. Majji, S. K. Rout, S. Guin, A. Gogoi, B. K. Patel, *RSC Adv.*, 2014, **4**, 5357-5362.

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(11) D. J. Dijken, P. Kova í ek, S. P. Ihrig, S. Hecht, *J. Am. Chem. Soc.*, 2015, **137**, 14982-14991.