Supporting information

Macroscopic Heat Release in a Molecular Solar Thermal Energy Storage System

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S1. Materials and instruments

Cyclopentadiene was distilled by cracking dicyclopentadiene over iron filings prior to use in the Diels-Alder reaction. Tetrahydrofuran used for the Suzuki coupling reaction was distilled over a sodium/benzophenone couple. Precursor compounds **1**[1] and **3**[2] were made by their respective literature procedures. All other commercial chemicals were used as received. Activated carbon for catalyst adsorption was a 100 mesh particle size, powder. Thin-layer chromatography (TLC) was carried out using aluminium sheets precoated with silica gel. Purification of products were either carried out by flash chromatography on silica gel (40−63 μm, 60 Å) or using a Biotage Isolera. One instrument using pre-packed silica Biotage® SNAP Cartridges. Infrared (IR) spectra recorded on a Perkin-Elmer Frontier FT-IR instrument as films evaporated from $CDCl_3$ onto an ATR attachment. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian 400 MHz instrument using the residual solvent as the internal standard ($CDCl_3$, ^{1}H 7.26 ppm and ^{13}C 77.16 ppm or d_8-toluene, ^{1}H 2.09 ppm, ^{13}C 20.40 ppm). All chemical shifts are quoted on the δ scale (ppm), and all coupling constants (*J*) are expressed in Hz. The high resolution mass spectrum (HRMS) of **NBD1** was acquired using an Agilent 1260 Infinity fitted with an Agilent 6120 quadrupole using APCI mode for ionisation. Elemental analyses were performed at Mikrolab Kolbe AG, Germany. Melting point of **NBD1** and heat release of neat **QC1** were recorded on a Mettler Toledo DSC 2 apparatus, the sample was sealed in a 40 μL aluminium pan. TGA analysis of **NBD1** was measured by Mettler Toledo TGA/DSC 3+ with a 70 μL alumina crucible. All solution based spectroscopic measurements were performed in a 1-cm path length cuvette on either a Cary 100 UV-vis, Cary 50 UV-vis or a PerkinElmer UV-Vis-NIR Lambda 950 spectrophotometer, scanning the wavelength from 750 to 290 nm. Necessary temperature control during UV-vis experiments was achieved with Peltier temperature control. Photoswitching experiments for the kinetic study of NBD1 were performed at 365 nm, using a UVGL-58 Handheld

Lamp, otherwise photoconversions were achieved using a LED light source for photo conversion was from Thorlabs with a wavelength at either 340nm or 310nm. The thermal back reaction was performed by heating the sample (cuvette) by a Peltier unit in the UV-Vis spectrophotometer.

Luma 40^{TM}/Univ-Short sample holder from Quantum Northwest was used for temperature control during thermal cycling testing.

Absorption spectra for outdoor test were recorded by two micro flow cells and portable spectrometer which was purchased from Avantes.

Teflon plastic tubing used in outdoor testing and in the vacuum chamber heat release experiments were purchased from the Cole-Parmer Instrument Company.

XPS was carried out by a Quantum 2000 scanning ESCA microprobe from Physical Electronics, with an X-ray source of monochromatic Al Kα (1486.6 eV), and a beam size of 100 μm. The analysed area was approximately 400 x 600 μm. Take-off angle was 45^{o} with respect to the sample surface. The information depth was approximately 4-5 nm. Scanning electron microscopy (SEM) was performed on a LEO Ultra 55 SEM operating at 5.0 kV. Calculations for the catalytic mechanism of CoPc were performed using resources at Beronia Cluster, provided by Universidad de La Rioja (UR) and at Chalmers Centre for Computational Science and Engineering (C3SE) provided by the Swedish National Infrastructure for Computing (SNIC).

S2. Synthesis

Two synthetic strategies were successfully employed in the synthesis of **NBD1** (See Fig. S1), one following an established coupling procedure of **1** with boronic acid **2** under Suzuki conditions. Formation of **NBD1** was also made possible by an standard Diels-Alder [4+2π] approach, reacting 4-(methoxyphenyl)propiolonitrile **3** with freshly cracked cyclopentadiene. The synthesis of **3** was accomplished using a literature procedure.[1]

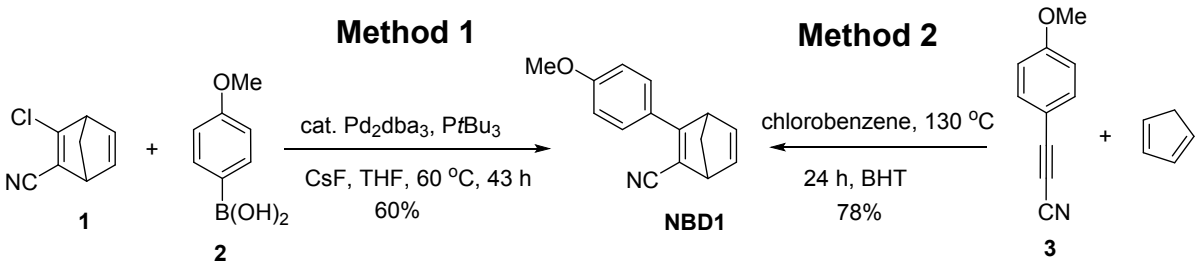


Figure S1. *Two synthetic routes for* ***NBD1****.*

2-Cyano-3-((4-methoxyphenyl)-norbornadiene (NBD1)

Method 1: To a dry degassed solution of 2-cyano-3-chloronorbornadiene (1.51 g, 9.96 mmol) in THF (20 mL) was added 4-methoxyphenylboronic acid (1.66 g, 10.9 mmol), cesium fluoride (4.99 g, 32.9 mol), *tris*(dibenzylideneacetone)dipalladium(0) (0.46 g, 0.50 mmol) and a solution of tri-*tert*-butylphosphine (1.5 mL, 1M in toluene, 1.5 mmol). The mixture was stirred under a nitrogen atmosphere for 2.5 h at ambient temperature and then heated to 60 °C for 43 h. The reaction mixture was allowed to cool to room temperature and was filtered through a pad of Celite®, washing with dichloromethane (50 mL). The solvent of the filtrate was removed under reduced pressure and purified on a Biotage Isolera One system using a Biotage KP-sil 100 g column (dichloromethane/hexane 1:1). The fractions containing **NBD1** were dried over sodium sulphate,

filtered, and the solvent removed under reduced pressure affording **NBD1** (1.34 g, 60%) as a white crystalline solid.

Method 2: A vial suitable for microwave reactions was charged with cyclopentadiene (7 mL, 8.3 mmol), 3-(4-methoxyphenyl)propiolontirile **3** (6.02 g, 38.3 mmol), BHT (5 mg) and chlorobenzene (7 mL). The vial was sealed and heated to 130 °C for 24 h. The resulting reaction mixture was subjected to flash column chromatography (gradient elution of CH_2Cl_2/petroleum spirit 1:1 to 3:1) to afford **NBD1** (6.68 g, 78%) as a white solid in addition to recovered **3** (1.27 g).

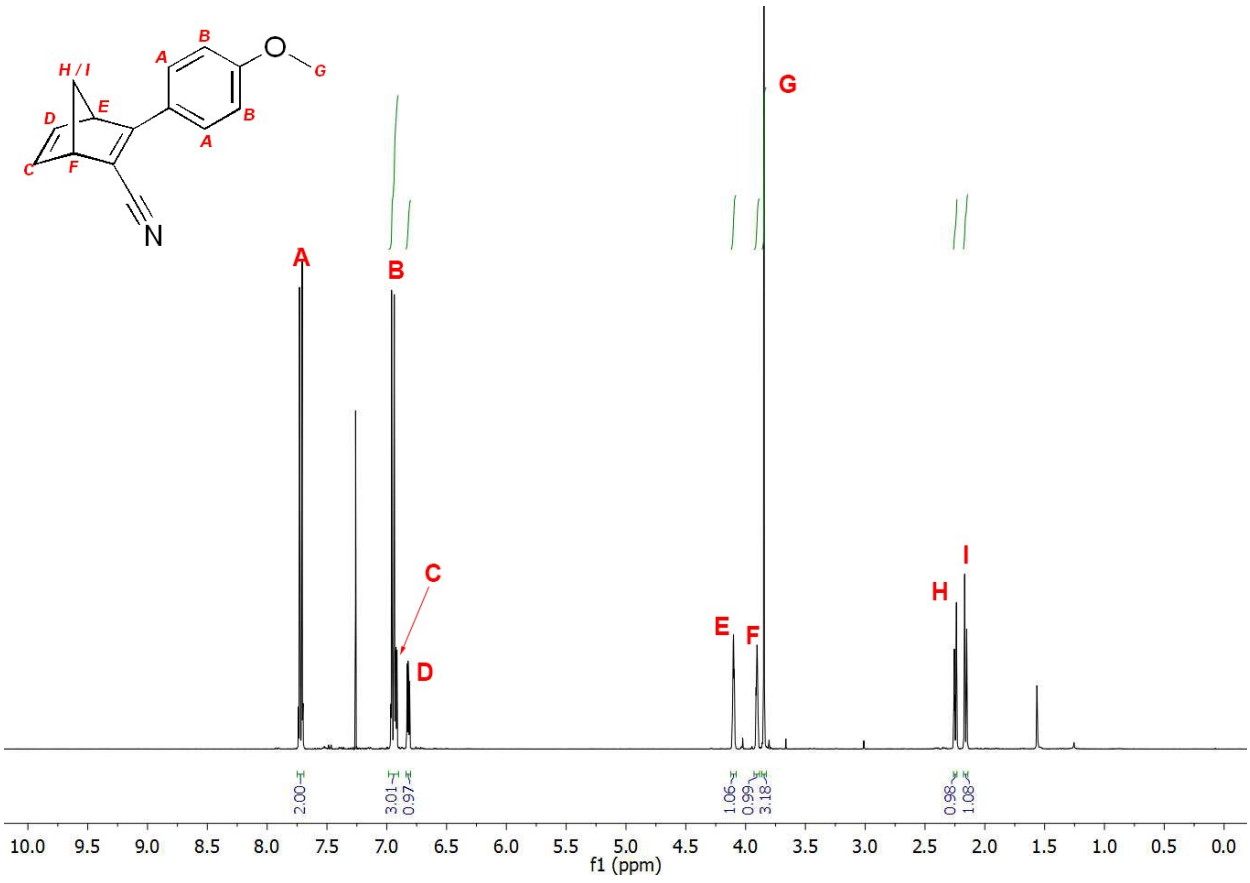
M.p. = 49.2–51.8 °C. R_f = 0.43 (CH_2Cl_2/n-hexane 7:3). IR: ν = 3071, 2997, 2976, 2945, 2913, 2872, 2839, 2192, 1604, 1587, 1565, 1508 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 6.92 (ddd, J = 5.1, 3.0, 0.7 Hz, 1H), 6.82 (ddd, J = 5.1, 3.2, 0.8 Hz, 1H), 4.10 (ddtd, J = 3.2, 2.5, 1.6, 0.7 Hz, 1H), 3.90 (ddtd, J = 3.0, 2.5, 1.6, 0.8 Hz, 1H), 3.84 (s, 3H), 2.24 (dt, J = 6.8, 1.6 Hz, 1H), 2.16 (dt, J = 6.8, 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.38, 161.21, 143.40, 140.08, 128.34, 126.11, 119.16, 114.40, 113.82, 70.85, 55.56, 54.84, 54.13 ppm. HRMS (ACPI, +ve) calcd. for $C_{15}H_{14}NO$ [$(M+H)^+$]: m/z = 224.1070; exp = 224.1073. Elemental analysis: Calculated for $C_{15}H_{13}NO$, C: 80.69, H: 5.87, N: 6.27. Found; C: 80.84, H: 5.99, N: 6.19.

2-Cyano-3-((4-methoxyphenyl)-quadricyclane (QC1) (preparative formation)

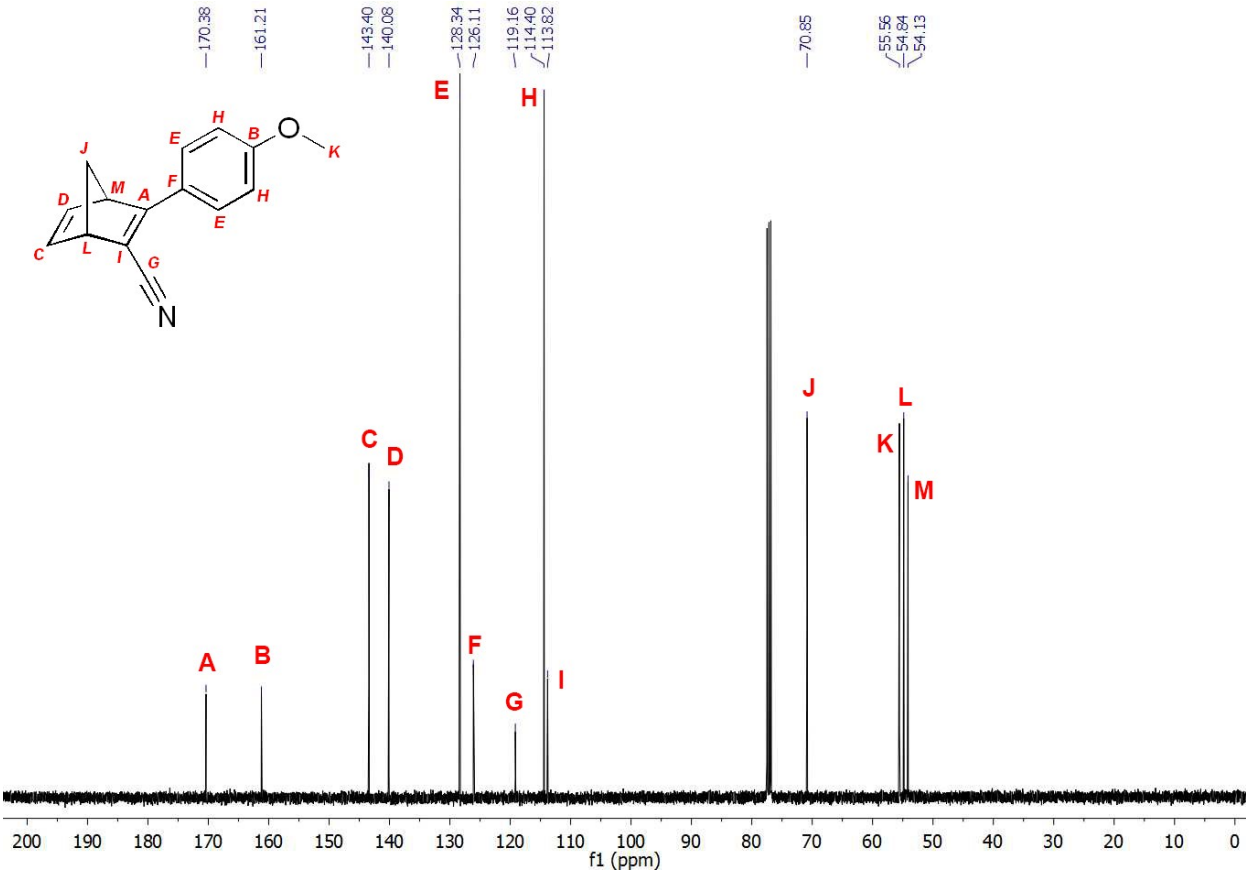
A solution of **NBD1** in $CDCl_3$ was irradiated using a 6W handheld UV lamp until complete conversion occurred. R_f = 0.35 (CH_2Cl_2/*n*-hexane 7:3). IR: ν = 3068, 3040, 3002, 2954, 2935, 2909, 2861, 2837, 2218, 1610, 1578, 1518 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, J = 8.9 Hz,

2H), 6.86 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 2.62 (dd, J = 4.9, 2.6 Hz, 1H), 2.43 (dt, J = 11.8, 1.4 Hz, 1H), 2.36 (dq, J = 4.9, 1.4 Hz, 1H), 2.20 (dt, J = 11.8, 1.4 Hz, 1H), 2.18 (dd, J = 5.0, 2.6 Hz, 1H), 1.84 (dq, J = 5.0, 1.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.64, 128.01, 127.56, 119.64, 114.19, 55.47, 35.36, 32.36, 30.95, 30.62, 26.70, 21.47, 14.68 ppm.

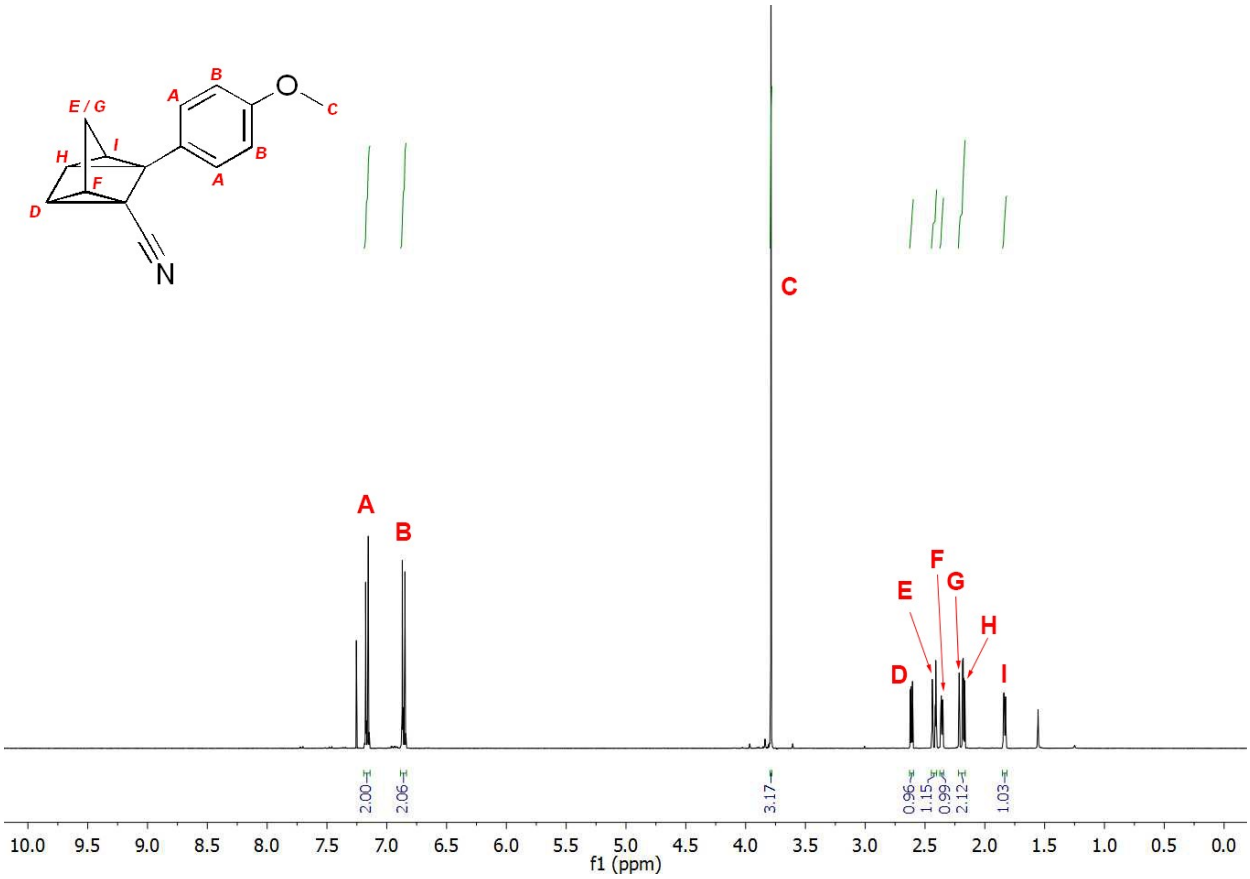
NMR Spectra of NBD1 and QC1



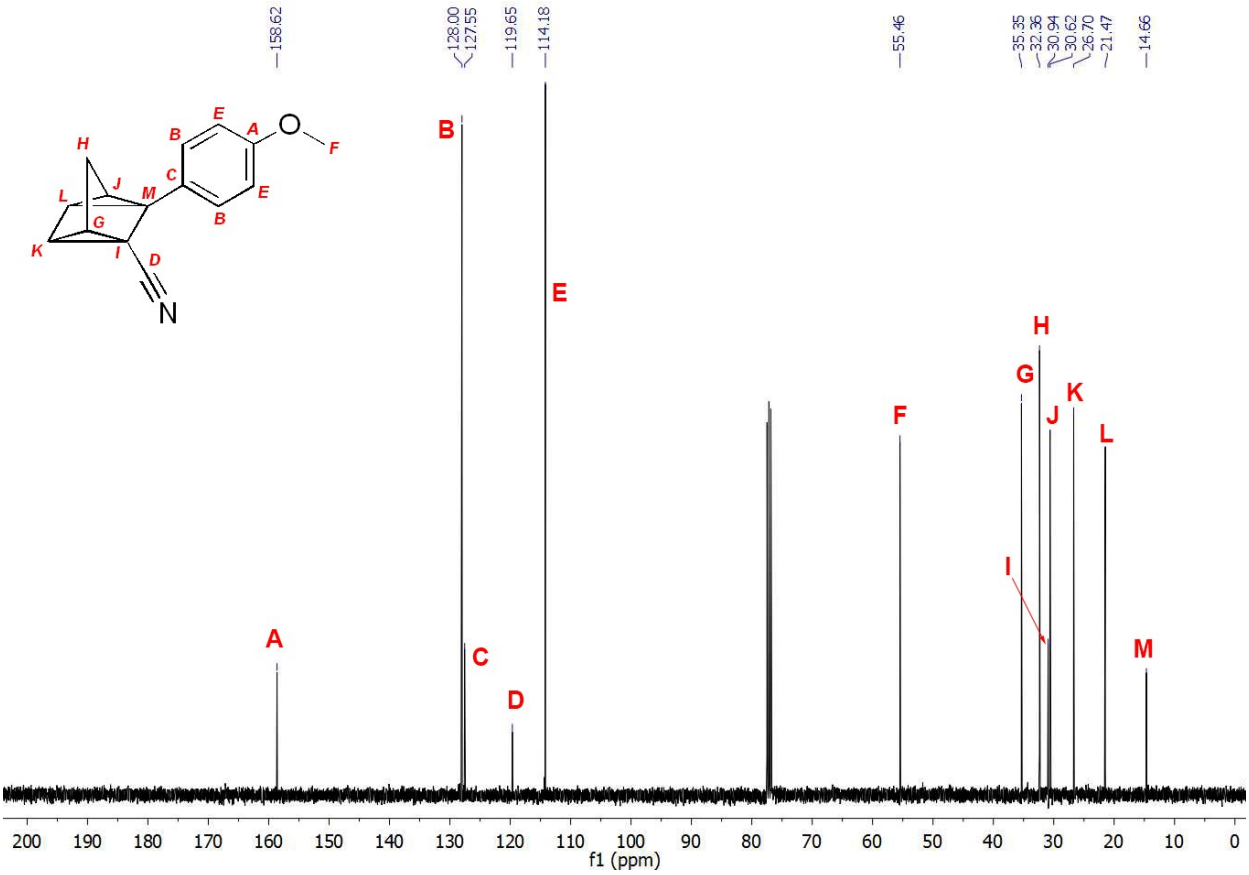
^{1}H NMR 400 MHz spectrum of **NBD1** in $CDCl_3$.



^{13}C NMR 100 MHz spectrum of **NBD1** in $CDCl_3$.



^{1}H NMR 400 MHz spectrum of **QC1** in $CDCl_3$.



^{13}C NMR 100 MHz spectrum of **QC1** in $CDCl_3$.

S3. Absorptivity determination of **NBD1**/**QC1**

To measure the absorption coefficient, three stock solutions were prepared, by dissolving **NBD1** (2.47 mg, 1.80 mg, 3.23 mg) in toluene (10.05 mL). The solutions were then diluted to bring the absorption below 1. The absorption spectra were measured on a Cary 4000 spectrophotometer, and the absorption coefficient calculated using the Beer-Lambert law. The reported absorption coefficient is the average of the three measurements.

Table S1. *Experimental details form the measurements of the absorption coefficient of* ***NBD1****.*

Concentration (M)	**Measured ε_{326} (M^{-1} cm^{-1})**	**Average ε_{326} (M^{-1} cm^{-1})**	**St. dev.**
8.467×10^{-5}	13130		
6.170×10^{-5}	13227	13292	203
4.429×10^{-5}	13521		

To calculate the absorption coefficient of the quadricyclane, a solution with a known concentration of norbornadiene was irradiated to achieve complete photoisomerization, the absorption spectrum recorded, and the absorption coefficient calculated using Beer-Lambert law. Onset of absorption was measured at 346 nm ($\log \varepsilon \approx 2$).

S4. Maximum solar absorption efficiency and energy storage efficiency of **NBD1**

The spectra of the suns spectral irradiation are shown in Figure S2, the yellow part shows the photos absorbed by a saturated solution of **NBD1**, blue line shows the absorption cut-off of the solution, black curve represent the solar spectrum AM 1.5. A maximum absorption of 4.0% of the solar spectrum was calculated by using the integration of the yellow part divided by the integration from the entire solar spectrum (Fig. S2). The maximum energy storage efficiency can be calculated from equation (1)[3]:

$$\eta_{MOST} = \frac{\int_0^{\lambda_{onset}} \frac{E_{AM\ 1.5}(\lambda) \cdot \phi_{iso} \cdot \Delta H_{stor}}{h\nu \cdot N_A} \cdot d\lambda}{\int E_{AM\ 1.5}(\lambda) \cdot d\lambda} \cdot 100\ \% \qquad (1)$$

Where $E_{\mathrm{AM\ 1.5}}(\lambda)$ represent the spectral irradiance (energy current density) in J s^{-1} m^{-2} nm^{-1}; h corresponds to the Plank constant in J s; ν is the frequency of incoming light in s^{-1}; and N_A represents Avogadro's constant. A maximum energy storage efficiency of 0.51% was finally obtained for an optically saturated solution of **NBD1**.

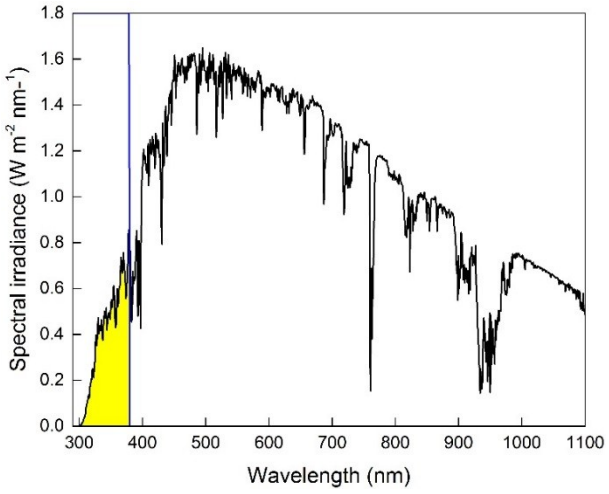


Figure S2. *Maximum solar absorption efficiency by* ***NBD1****. Blue line shows the transmittance of* ***NBD1*** *in a maximum concentration of 1.5 M. Yellow part shows the photons absorbed theoretically by* ***NBD1*** *in a toluene solution.*

S5. Quantum yield

The photoisomerization quantum yield measurement is based on the reported method using a high concentration regime[4]. By definition, the optical quantum yield for a photoisomerization determines the efficiency of a photoreaction:

$$\phi_{iso} = \frac{number\ of\ isomerization\ events}{number\ of\ photos\ absorbed}$$

Ideally, this factor should be unity for an ideal MOST candidate.

Before the measurements were performed, the photon flux of the irradiation source (LED lamp 340 nm) was firstly determined by potassium ferrioxalate actinometry.[5,6] 5 samples of 3 mL ferrioxalate solution (30 mM in 0.2 N H_2SO_4) was put into a 1 cm pathlength (l) quartz cuvette, then irradiated over 0 min, 2 mins, 4 mins, 6 mins and 8 mins respectively. Approximately 0.6 mL of each irradiated sample (V_1) was mixed with 1 mL buffer (V_2, 1.2 M NaAc + 0.72 N H_2SO_4) and 2 mL of phenanthroline solution (V_3, 6 mM), diluted into 25 mL volumetric flask with demineralized water under dark to react over 1 hour.

The photon flux I (E s^{-1}) can be then calculated from equation (2)[4]:

$$I = slope * \frac{V_1 \cdot V_3}{V_2 \cdot \varepsilon_{510nm} \cdot l \cdot \phi} \quad (2)$$

Where ε_{510nm} corresponds to the absorbance of tri-phenanthroline complex, which equals to 11100 M^{-1} cm^{-1}. And ϕ is the photonchemical quantum yields (1.23) of ferrioxalate

decomposition formed from 334 nm irradiation. Here the formation quantum yield of ferrioxalate decomposition at 340 nm was considered the same as 334 nm light source.

To ensure that all photons were absorbed, the concentration of the solutions were prepared to be optically thick at the irradiation wavelength, two solutions (one for measurements of sample 1, 2 and one for measurements of sample 3, 4) of **NBD1** where absorbance at 340 nm is over 2 were prepared ($A_{340\ nm} > 2$). By irradiating the sample with different time scale continuously, the absorbance changes have been recorded. When all photons were absorbed, a linear dependence between the decrease in absorption and the irradiation time can be obtained as in equation (3)[4]:

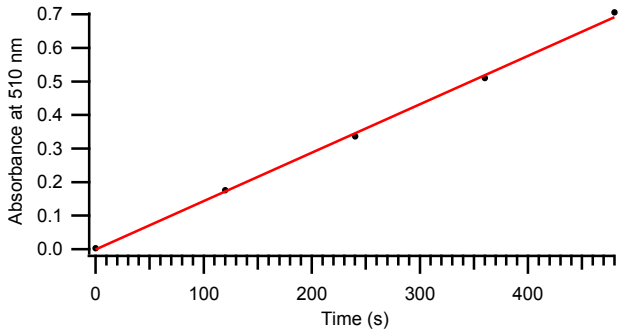
$$[NBD1] = [NBD1_{initial}] - \frac{\phi_{iso} \cdot I}{N_A \cdot V} \cdot t_{irr} \quad (3)$$

Where [***NBD1***] and [$\boldsymbol{NBD1}_{initial}$] correspond to the actual and initial concentration of the **NBD1** solution, respectivly. N_A is the Avogadro constant, V is the volume of the irradiated sample and t_{irr} is irradiation time.

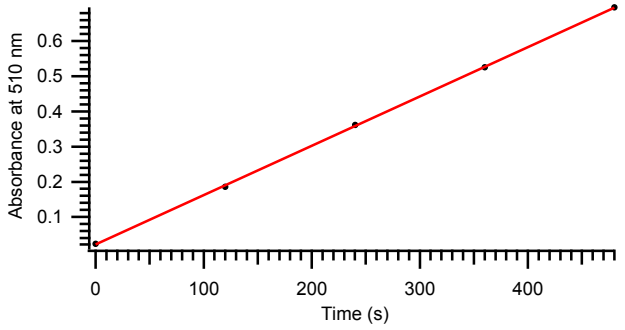
Two more comparaitive measurements were proformed with individual prepared reactant solutions. The reported quantum yield is an average of six measurements.

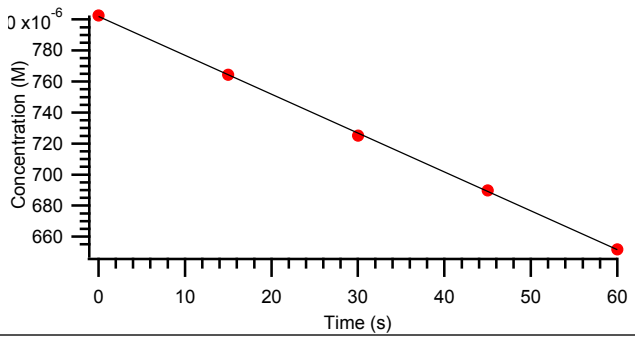
Table S2. *Experimental details form the measurements of the quantum yield of* ***NBD1****.*

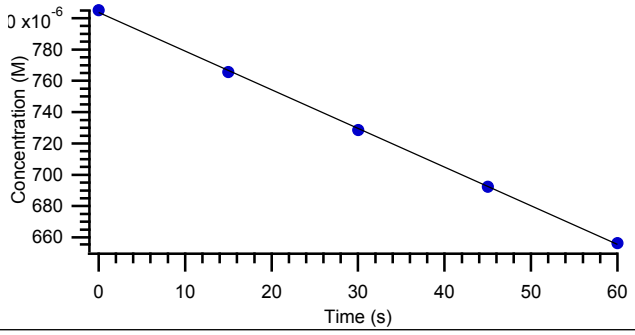
Photon flux before experiment*: *: **Value used for all quantum yield calculations**	
Irradiation time (s)	**Tri-phenanthroline complex absorbance at 510 nm (ε = 11100 M^{-1} cm^{-1})**
0	0.003
120	0.176
240	0.336
260	0.510
480	0.706
Photon flux before experiment* (E s^{-1}):	1.33 10^{-8}

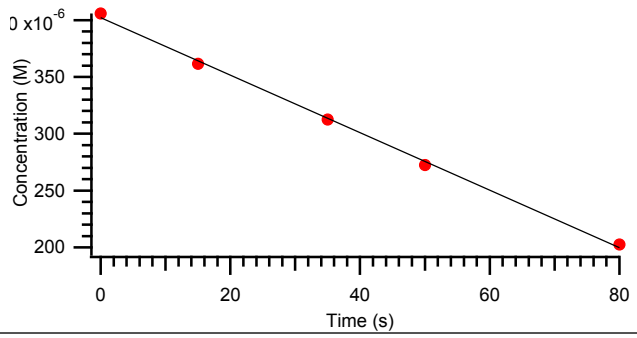


Photon flux after experiment:	
Irradiation time (s)	**Tri-phenanthroline complex absorbance at 510 nm (ε = 11100 M^{-1} cm^{-1})**
0	0.024
120	0.186
240	0.362
260	0.525
480	0.696
Photon flux before experiment* (E s^{-1}):	1.28 10^{-8}



Sample 1	
Sample weight (g): 2.79	
Irradiation time (s)	**NBD1 absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 30 45 60	1.03 0.98 0.93 0.89 0.84
Quantum yield: 60.7%	

Sample 2	
Sample weight (g): 2.85	
Irradiation time (s)	**Absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 30 45 60	1.03 0.98 0.94 0.89 0.84
Quantum yield: 61.2%	

Sample 3	
Sample weight (g): 2.81	
Irradiation time (s)	**NBD1 absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 35 50 80	0.52 0.46 0.40 0.35 0.26
Quantum yield: 61.8%	

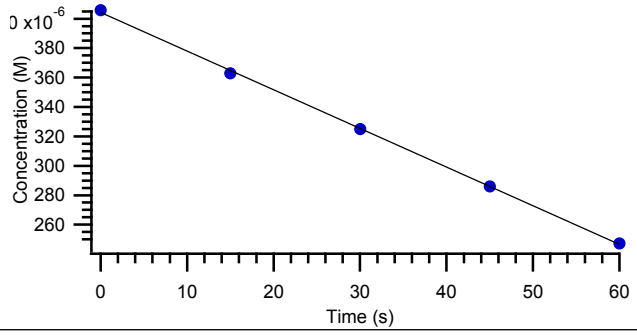
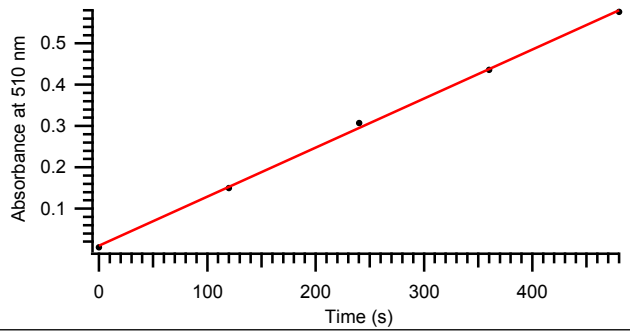
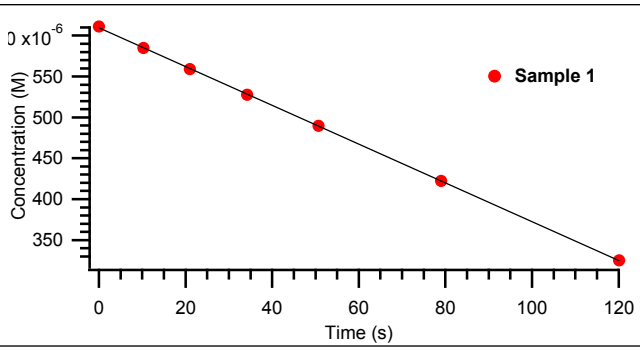
Sample 4	
Sample weight (g): 2.70	
Irradiation time (s)	**NBD1 absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 30 45 60	0.52 0.47 0.42 0.37 0.32
Quantum yield: 61.7%	

Table S3. *Repeating experimental details form the measurements of the quantum yield of* ***NBD1****.*

The measurement was performed with individual prepared reactant solutions.

Irradiation time (s)	**Tri-phenanthroline complex absorbance at 510 nm (ε = 11100 M^{-1} cm^{-1})**	
0	0.006	
120	0.150	
240	0.307	
260	0.436	
480	0.576	
Irradiated volume 3 mL, from here 0.5 mL was taking and diluted into 25 mL demineralized water, with the buffer in demineralized water (1.2 M NaAc + 0.72 N H_2SO_4, 1 mL) and phenanthroline in demineralized water (6 mM, 2 mL).		
Photon flux before experiment* (E s^{-1}):	1.31 10^{-8}	

Sample 1'	
Sample weight (g): 2.85	
Irradiation time (s)	**NBD1 absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0	0.79
10	0.75
21	0.72
34	0.68
51	0.63
79	0.54
120	0.42
Quantum yield: 59.7%	

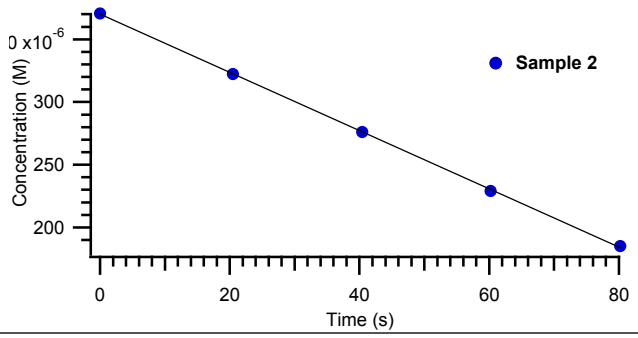
Sample 2’	
Sample weight (g): 2.90	
Irradiation time (s)	**NBD1 absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 21 40 60 80	0.48 0.41 0.36 0.30 0.24
Quantum yield: 59.4%	

Table S4. *Summary of measured quantum yield of* ***NBD1****.*

Measured quantum yield (%)		**Average quantum yield (%)**
Sample 1	60.7	61
Sample 2	61.2	
Sample 3	62.1	
Sample 4	62.0	
Sample 1’	59.7	
Sample 2’	59.4	

S6. Outdoor testing of NBD1

The experimental setup for outdoor tests is previously described in literature[3], the test was carried out in the morning on the 4th of May, 2016 in Gothenburg, Sweden. The weather was sunny all day without clouds. A solution of **NBD1** (Ca 30 mL, 4 x 10^{-3} M) was pumped thought the system with different flow speeds varies from 120 mL h^{-1} to 300 mL h^{-1}. Absorption spectra before and after the photo concentrator were recorded to calculate the conversion percentage and energy conversion efficiency. The highest energy storage efficiency was measured as 0.03% with a conversion percentage of 64%.

Table S5. *Flow speed with corresponding residence time, conversion percentage and energy storage efficiency for outdoor test.*

Flow speed (mL h^{-1})	**Residence time (s)**	**Conversion (%)**	**Energy storage efficiency (%)**
50	210	98.9	0.0108
150	180	99.3	0.0127
250	140	99.4	0.0164
360	114	99.4	0.0201
450	91	99.2	0.0250
500	68	91.2	0.0307
550	55	76.5	0.0322
600	46	64.0	0.0323

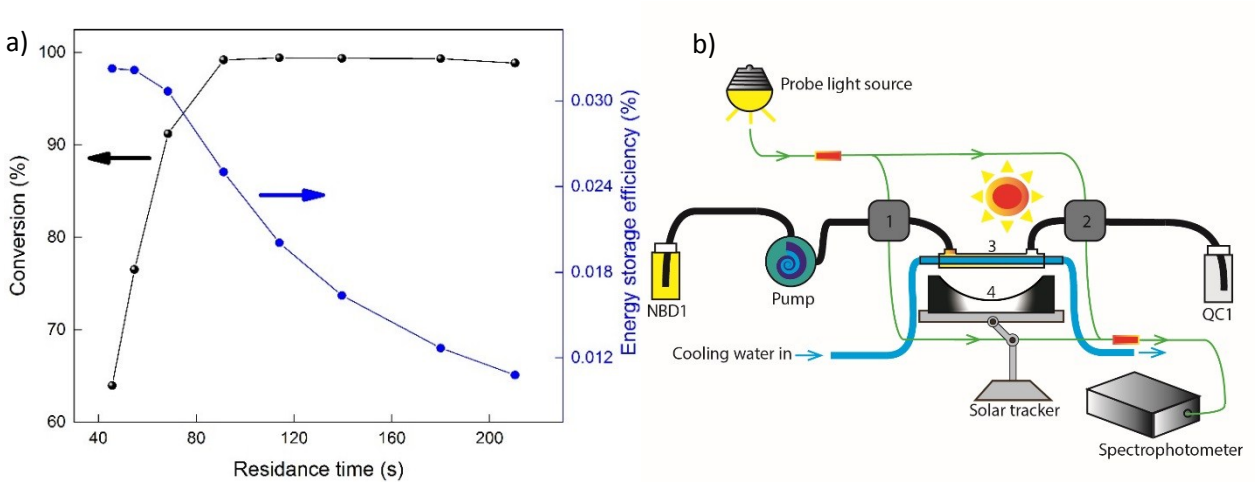


Figure S3. *a) Conversion percentage (black) and energy storage efficiency (blue) varies with residence time for outdoor test; b) Outdoor solar tracker setup. Box 1 and 2 shows the flow spectrometer, 3 represent a two layered glass flow cell. The inner layer serve to pass through cooling water and the outer layer serve to flow* ***NBD1*** *solution. 4 shows a custom made solar tracker.*

S7. DSC analysis

NBD1, (about 20 mg) was dissolved in deuterated chloroform (about 3 mL). After irradiation for about 30 minutes using a fiber-coupled LED (emitting at 310 nm), full conversion to **QC1** was confirmed by ^{1}H NMR spectroscopy. Complete photoconversion to **QC1** was possible by the irradiation of a solution of **NBD1** (ca. 20 mg) in $CDCl_3$ (ca. 3 mL) using using a LED (emitting at 310 nm), where the progress was monitored by ^{1}H NMR spectroscopy. After evaporation of the solvent, it was measured with ^{1}H NMR spectroscopy revealing that about 12% of **QC1** had backconverted to **NBD1**. About 1 mg of the obtained quadricyclane was sealed and inserted in the DSC at 0 °C. The DSC method involved running to consecutive cycles, each consisting of heating at 10 °C min^{-1} from 0 °C to 180 °C and in between cooling (at 40 °C min^{-1} from 180 °C to 0 °C). The first heating cycle showed the characteristic exothermic feature associated with back-isomerization to **NBD1**, and the second heating cycle did not show any evidence of any thermal transitions, confirming that the full back isomerization occurred in the first cycle. Integration of the exothermic peak and normalization respect to the amount of **QC1** present in the neat material gave an enthalpy difference ($\Delta H_{storage}$) between **NBD1** and **QC1**. This protocol was performed twice with good agreement, and the average $\Delta H_{storage}$ was calculated.

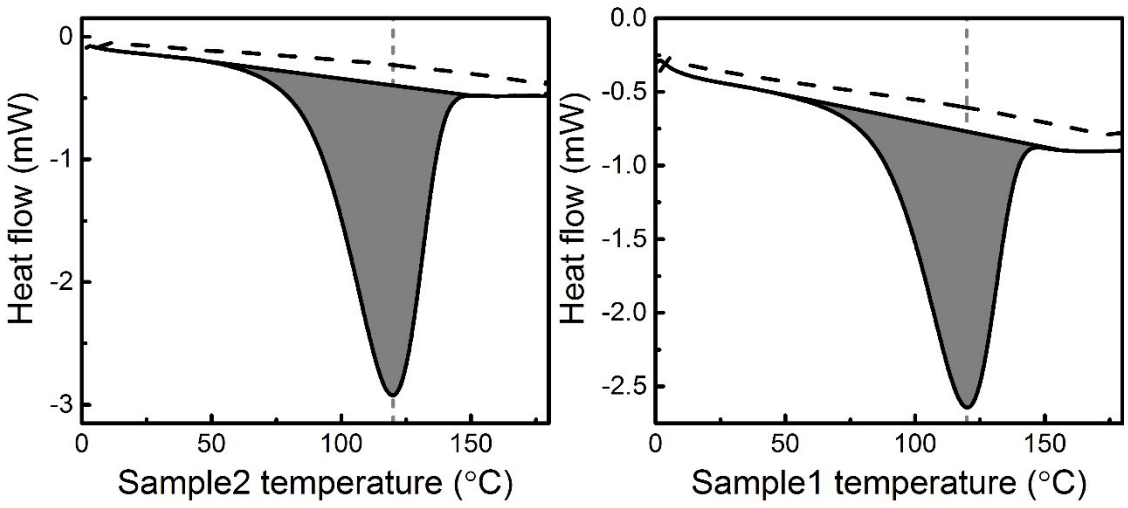


Figure S4. *DSC thermograms of* ***QC1****. The first heating cycle (full line) is accompanied by the typical exothermic peak associated to the back isomerization of QC to NBD. The second heating cycle (dashed line) does not present any exothermic peak showing full conversion during the first cycle.*

Table S6. *Measured and average values of released energy and* $\Delta H_{storage}$.

	Mass (mg)	**Energy released (mJ)**	$\Delta H_{storage}$ **(J g^{-1})**	$\Delta H_{storage}$ **(kJ mol^{-1})**	$\Delta H_{storage}$ **(kcal mol^{-1})**
1	1.20	490	398	89.0	21
2	0.89	350	394	88.1	21
Average	-	-	396	88.5	21

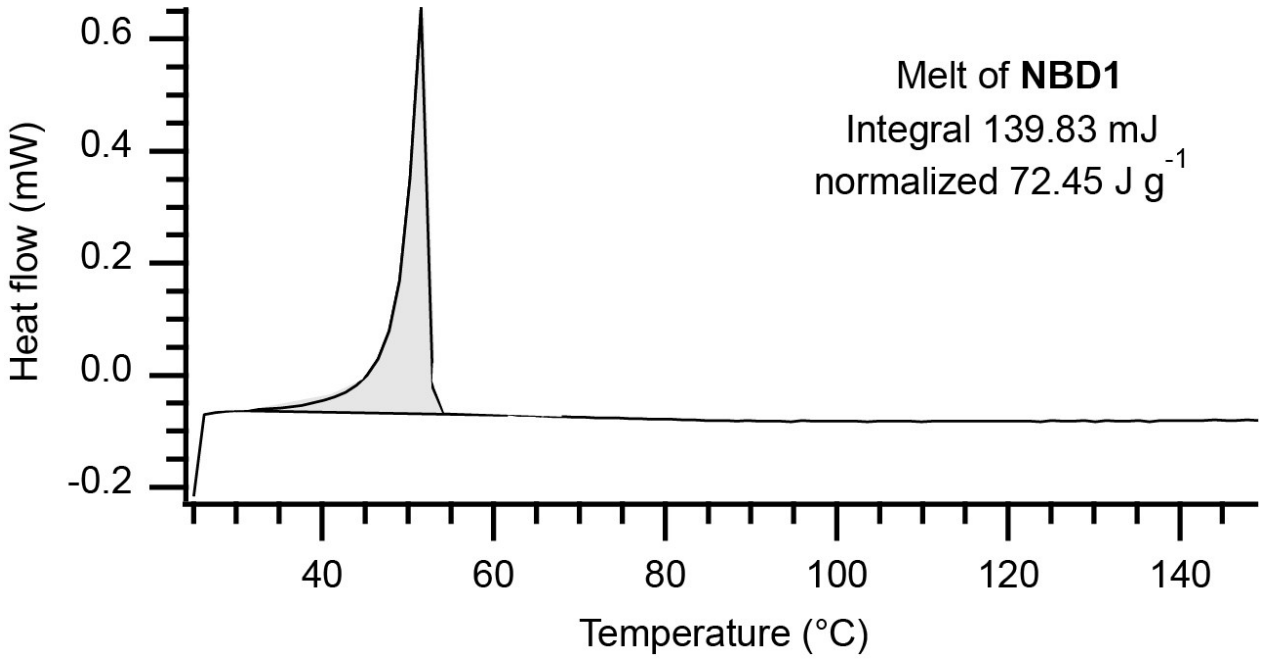


Figure S5. *Melting point of measurement of* ***NBD1*** *by DSC. The melting point site between 49.2 – 51.8 °C.* ΔH_{melt} *was normalized equals to 72.45 J* g^{-1}.

S8. MP2 coordinates for **NBD1**, **QC1**

Calculations were carried out using the MP2 method included in the Gaussian16[7] program package together with the standard basis set 6-31+G*[8]. **NBD1** and **QC1** structures were relaxed to the ground energy minima and characterized with frequency calculations to include ZPE and free energy corrections and verify the stationary points as minima (zero imaginary frequencies). The $\Delta H_{storage}$ energy shown in main text was calculated from the difference between both isomers free energy in frequency calculations.

Cartesian Coordinates (MP2/6-31G*)

NBD1

C	-8.624854	0.925243	1.182902
C	-9.629806	0.975958	0.259656
C	-9.373655	-0.208286	-0.687207
C	-8.852939	-1.235073	0.353055
C	-7.733131	-0.279632	0.838014
C	-7.074163	0.031395	-0.507950
C	-8.062451	0.072212	-1.425640
H	-10.227856	-0.503854	-1.301796
H	-8.464701	-2.149314	-0.109653

H	-9.586114	-1.471938	1.132296
H	-7.075739	-0.614458	1.644395
H	-7.983752	0.323131	-2.479380
H	-6.019031	0.245175	-0.648154
C	-8.322928	1.856783	2.205081
N	-8.044255	2.613112	3.078746
C	-10.690325	1.956795	0.084737
C	-11.220732	2.207591	-1.198968
C	-11.213555	2.678047	1.171965
C	-12.211872	3.163921	-1.388100
H	-10.834309	1.668718	-2.062284
C	-12.212739	3.637932	0.991780
H	-10.845926	2.487176	2.177745
C	-12.716239	3.883066	-0.293779
H	-12.615234	3.370120	-2.376997
H	-12.591179	4.168227	1.860161
O	-13.694530	4.796341	-0.589550
C	-14.223965	5.560665	0.497254

H	-14.966623	6.219046	0.048054
H	-14.704293	4.910955	1.236878
H	-13.439660	6.157361	0.975298

QC1

C	1.047530	0.770251	0.499762
C	0.254622	1.056848	-0.775922
C	0.413337	-0.430673	-1.198864
C	1.189461	-0.701983	0.078369
C	-0.440424	1.013137	0.581246
C	-0.242359	-1.186819	-0.050579
C	-1.188512	-0.293810	0.721032
H	1.803426	1.404381	0.952417
H	2.049503	-1.344349	0.242093
H	-0.801669	1.950771	0.998001
H	-0.424243	-2.249505	-0.196154
H	-1.286431	-0.596448	1.771435
H	-2.183995	-0.250117	0.262605
C	0.306399	2.188982	-1.634879

N	0.351769	3.136091	-2.349186
C	0.586847	-0.913847	-2.577897
C	1.603446	-1.823532	-2.915968
C	-0.288136	-0.482129	-3.584507
C	1.729385	-2.300126	-4.218487
H	2.309460	-2.152990	-2.155045
C	-0.162562	-0.940978	-4.900488
H	-1.083405	0.223203	-3.345822
C	0.849396	-1.858055	-5.217347
H	2.514508	-3.002539	-4.489418
H	-0.852779	-0.573704	-5.653574
O	1.066897	-2.381088	-6.468121
C	0.211354	-1.929309	-7.519577
H	0.557802	-2.447505	-8.413187
H	-0.832635	-2.195164	-7.319634
H	0.300634	-0.846570	-7.660873

S9. Kinetic Study of the back conversion of **QC1** to **NBD1**

A toluene solution of **NBD1** was irradiated to obtain **QC1** (until no further change was observed in the absorbance profile, ≈ 100% conversion percentage). Thereafter, the increase of the norbornadiene concentration over time were measured by monitoring the increase in absorption at 365 nm. The measurements were performed at five different temperatures (see Figure S6) (40 °C, 50 °C, 60 °C, 70 °C and 80 °C) and an exponential fit of the Eyring equation was applied to the data to determine the rate constants at the different temperatures. The enthalpy ($\Delta H^{\ddagger}_{therm}$) and entropy ($\Delta S^{\ddagger}_{therm}$) of activation was derived from the linear form of the Eyring equation presented in an Eyring plot (See Figure S6.) and the half-life at 25 °C was calculated to be 30 days in toluene.

Table S7. *Enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation derived from the Eyring equation and the calculated half-life at 25 °C.*

$\Delta H^{\ddagger}_{therm}$ (kJ mol^{-1})	$\Delta S^{\ddagger}_{therm}$ (J K^{-1} mol^{-1})	$t_{1/2}$ (days)
103.8	-22	30

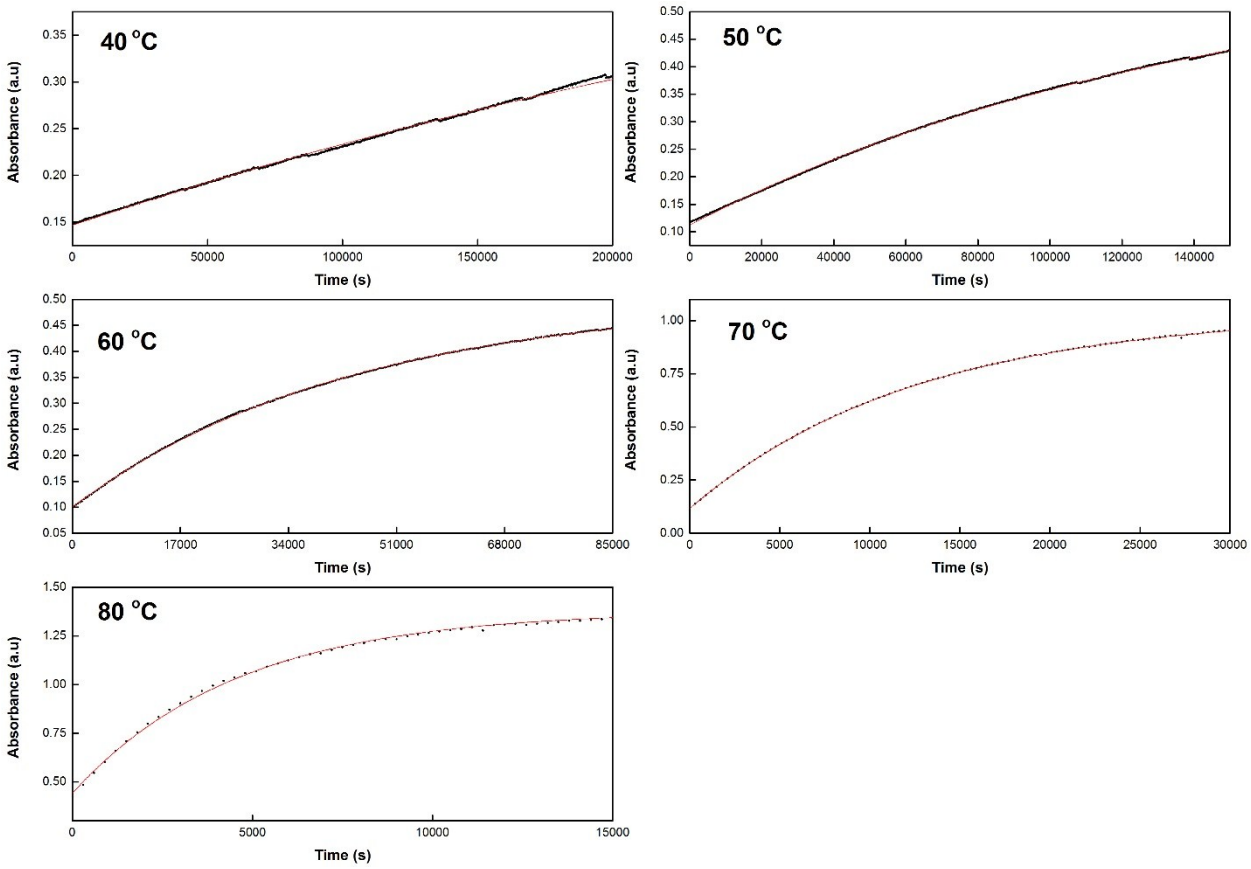


Figure S6. *Kinetic data for the back conversion of QC1 to NBD1 in toluene at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C.*

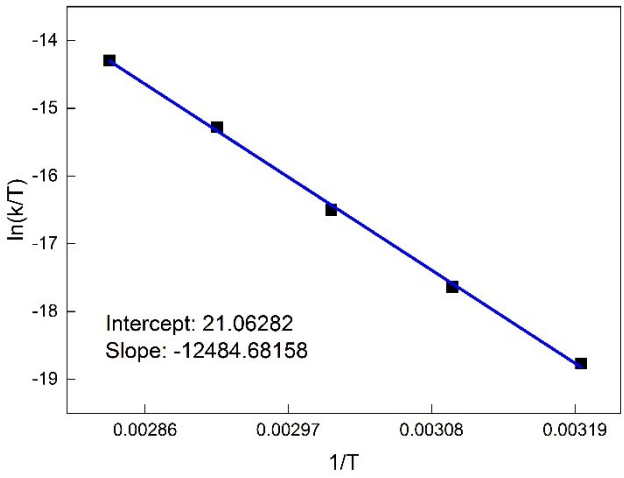


Figure S7. *Eyring plot from the kinetic study.*

S10. TGA analysis of **NBD1**

A crucible containing **NBD1** (9.6 mg) was heated from 20 °C to 600 °C, a TGA method of 10 °C min^{-1} heating flow was used under air condition (60 mL min^{-1}). Mass loss was estimated to have begun at around 150 °C, as indicated by weight loss.

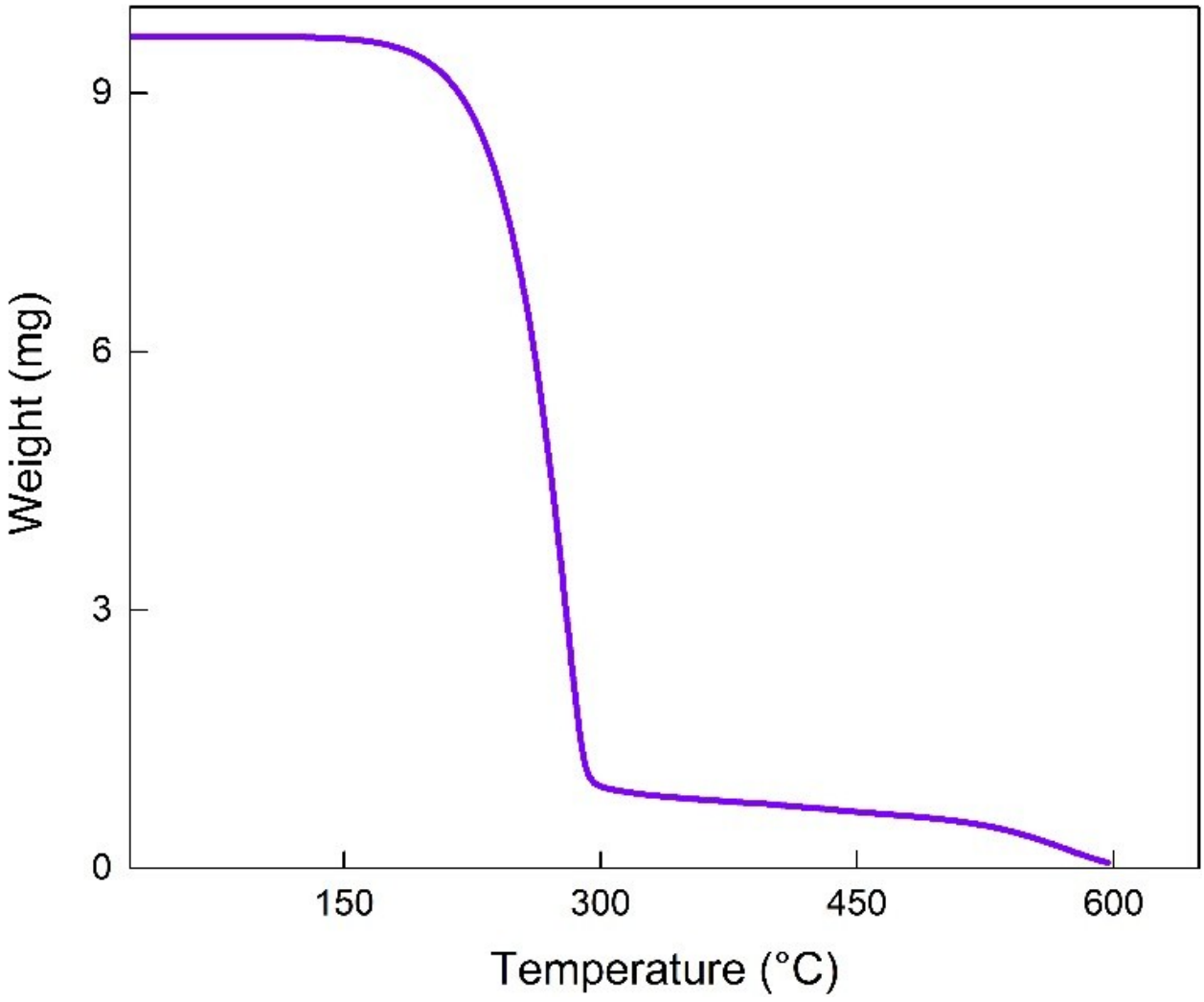


Figure S8. *TGA thermogram of* ***NBD1****.*

S11. Cycling test

A 0.7 x 10^{-4} M solution was prepared in toluene and pre-degassed under nitrogen over three hours. The cycling test was recorded on absorbance at λ = 325 nm. A LED light of 310 nm was switched on for ca. 800 s and off for 8000 s to preform conversion and thermally back conversion. The whole system was continually heat around 85 °C. A degradation of 0.14% per cycle over 43 cycles was finally observed. The UV-Vis spectrometer setup is shown below.

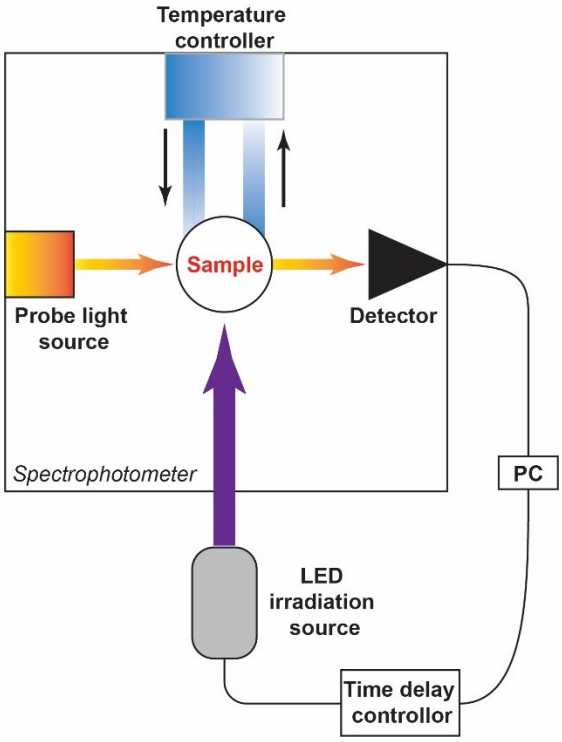


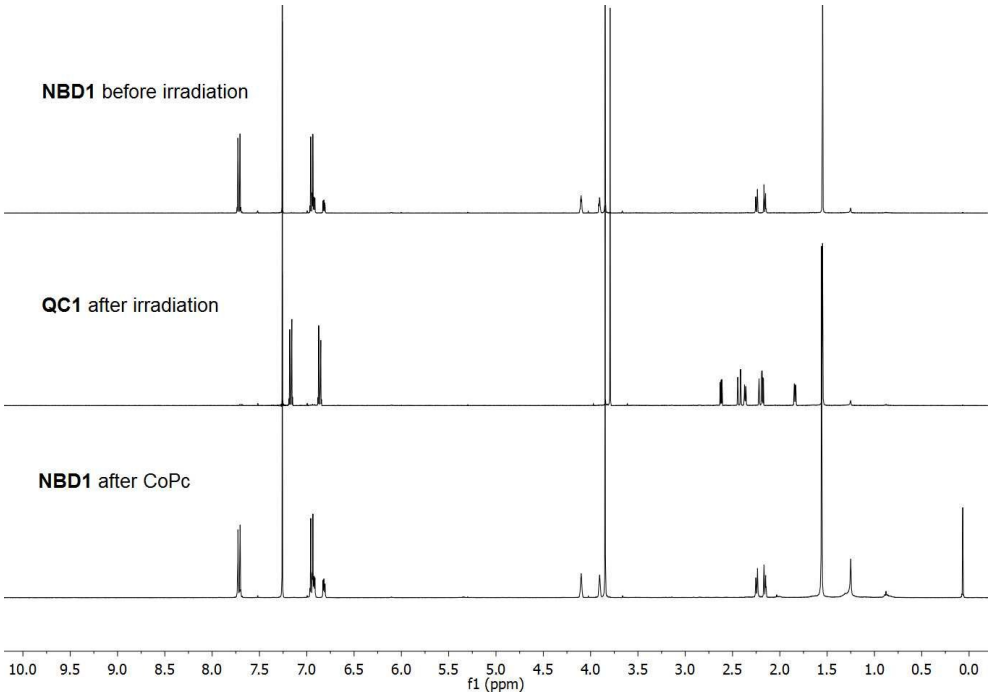
Figure S9. *Cycling test UV-Vis spectrometer setup for* ***NBD1****.*

S12. Catalyst screening

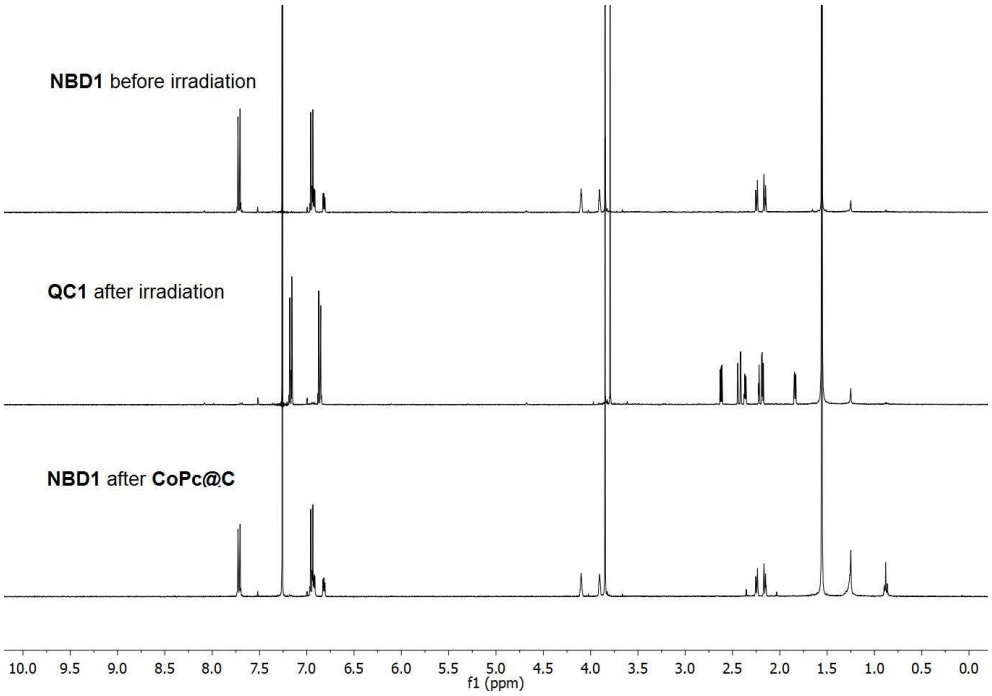
^{1}H NMR check

NBD1 (about 4 mg) was dissolved in $CDCl_3$ or Toluene-d_8 (1 mL) in a NMR-tube, ^{1}H NMR analysis was obtained to confirm starting point. Then the samples was irradiated overnight at 365 nm and full conversion to **QC1**was established by ^{1}H NMR analysis. The catalyst candidate was added to the NMR-tube, and left to react for at least 6 hours, after which the progress of the reaction back to **NBD1** was determined by ^{1}H NMR.

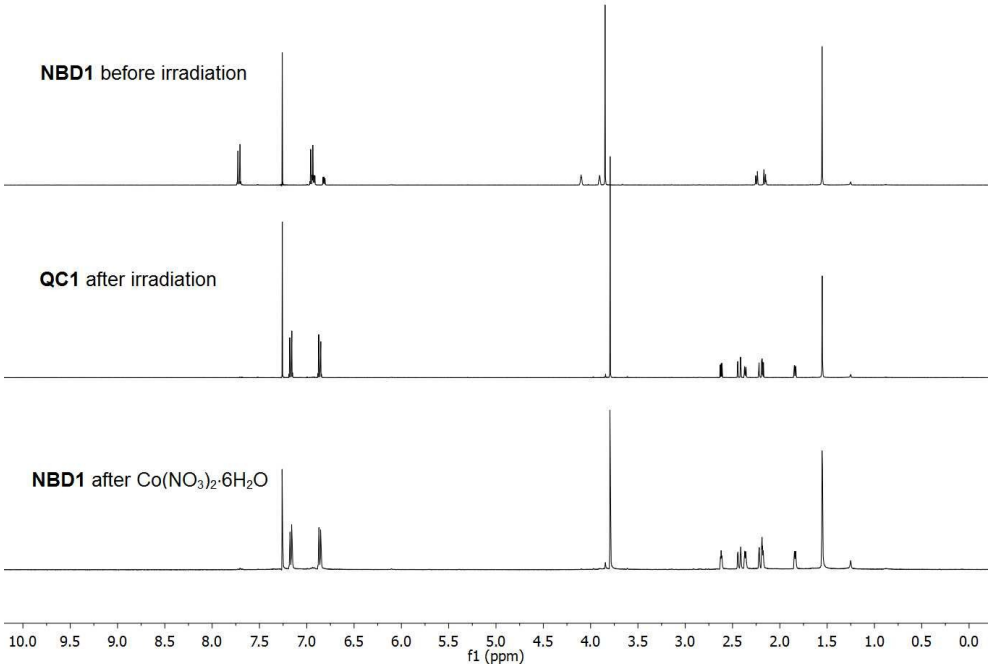
CoPc (in $CDCl_3$, ^1H NMR 400 MHz)



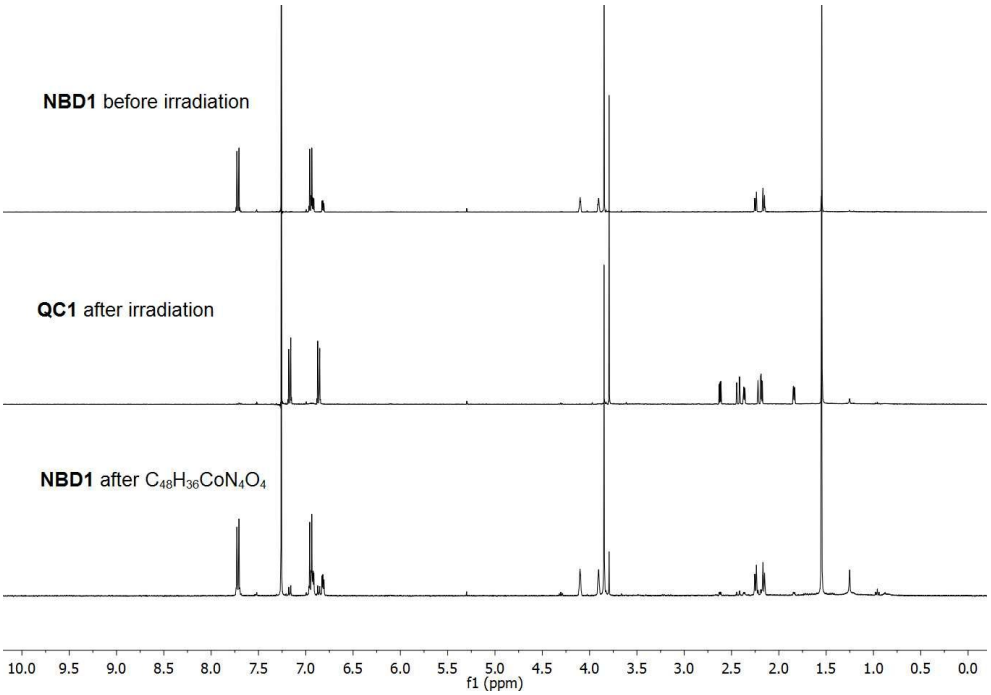
CoPc@C (in $CDCl_3$, ^1H NMR 400 MHz)



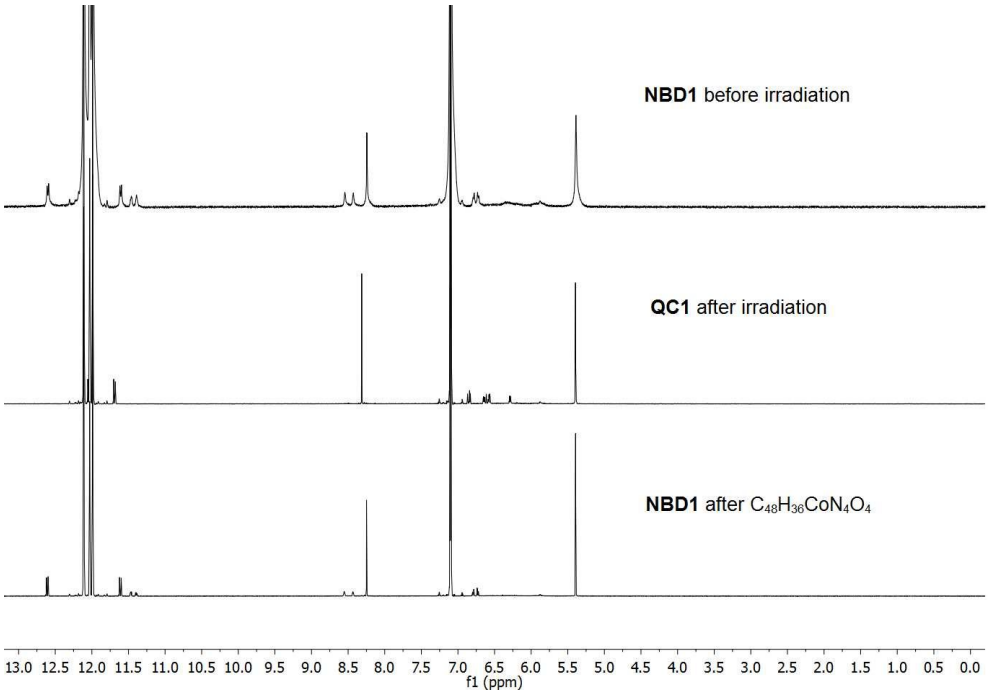
$Co(NO_3)_2 \cdot 6H_2O$ (in $CDCl_3$, ^1H NMR 400 MHz)



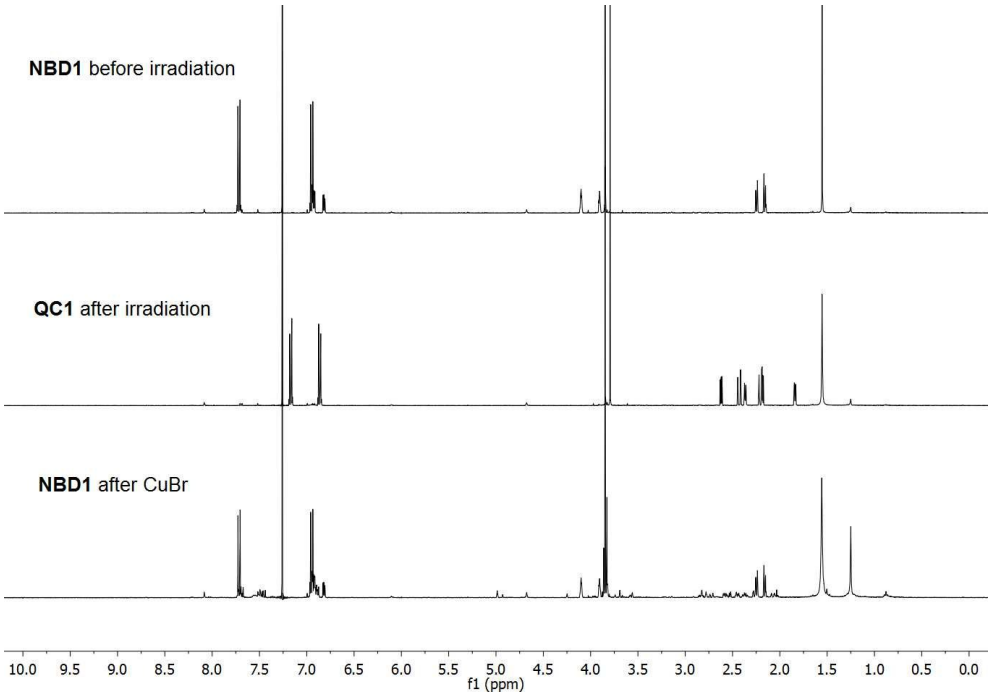
$C_{48}H_{36}CoN_4O_4$ (in $CDCl_3$, ^1H NMR 400 MHz)



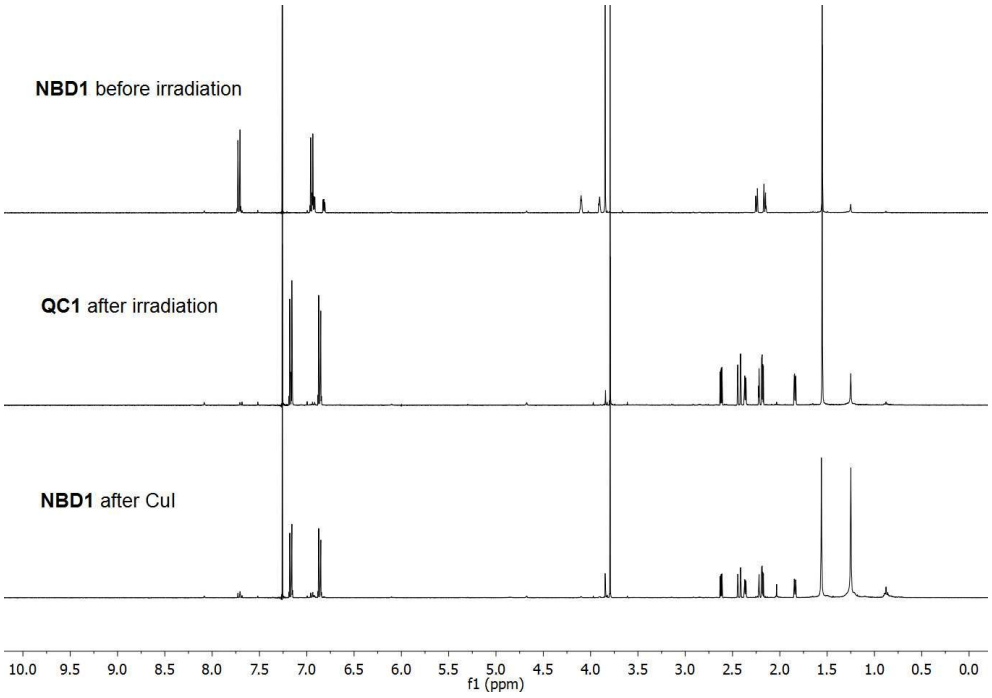
$C_{48}H_{36}CoN_4O_4$ (in toluene-d_8, ^{1}H NMR 400 MHz)



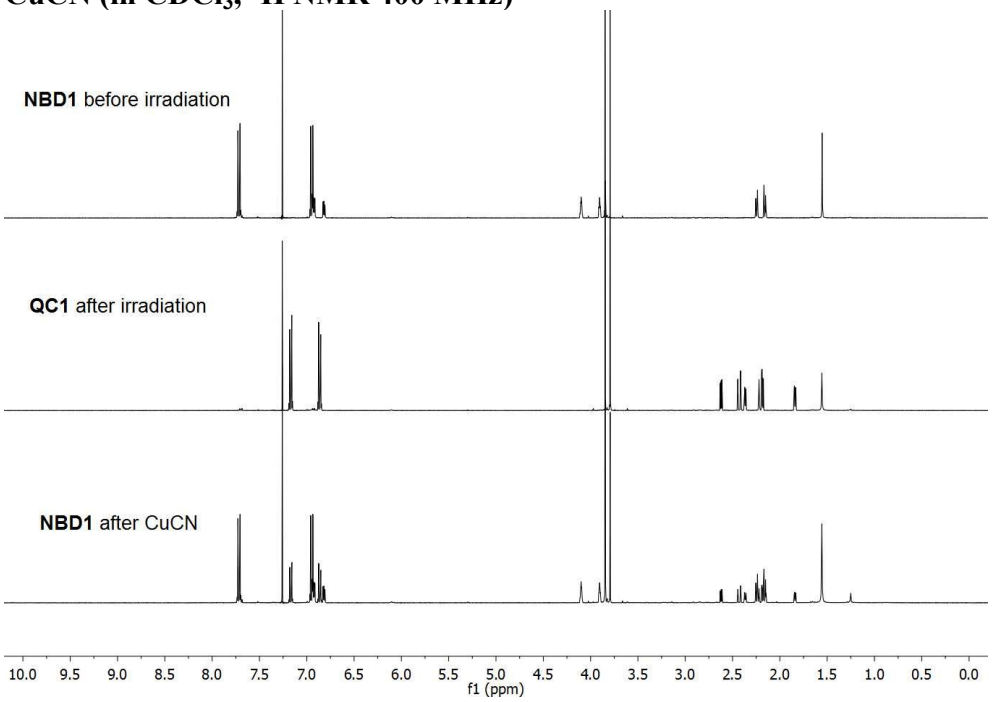
CuBr (in $CDCl_3$, ^{1}H NMR 400 MHz)



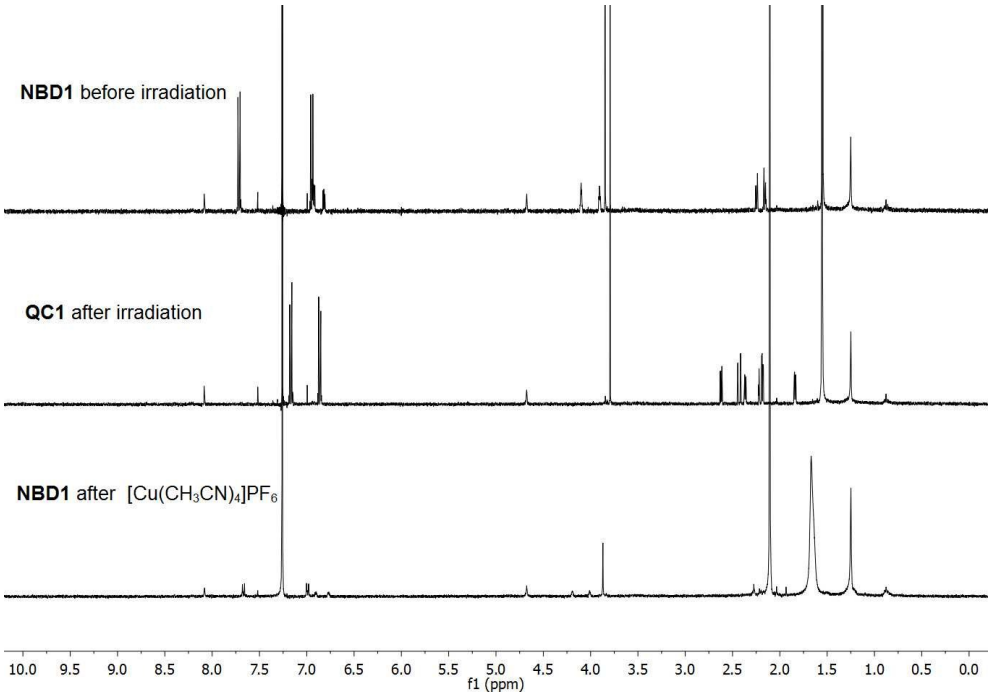
CuI (in $CDCl_3$, ^1H NMR 400 MHz)



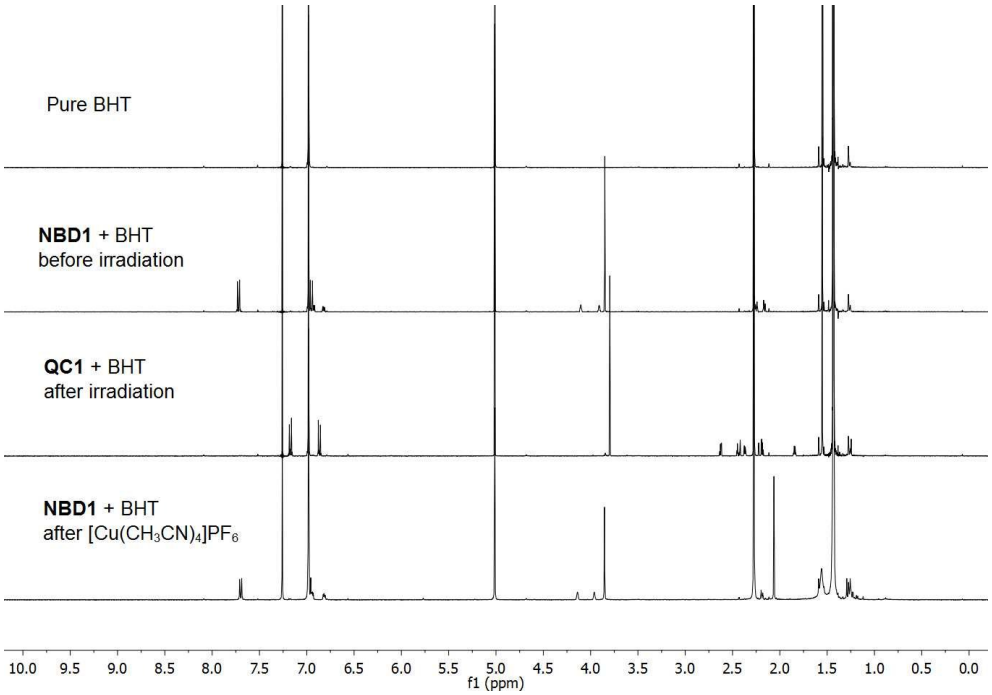
CuCN (in $CDCl_3$, ^1H NMR 400 MHz)



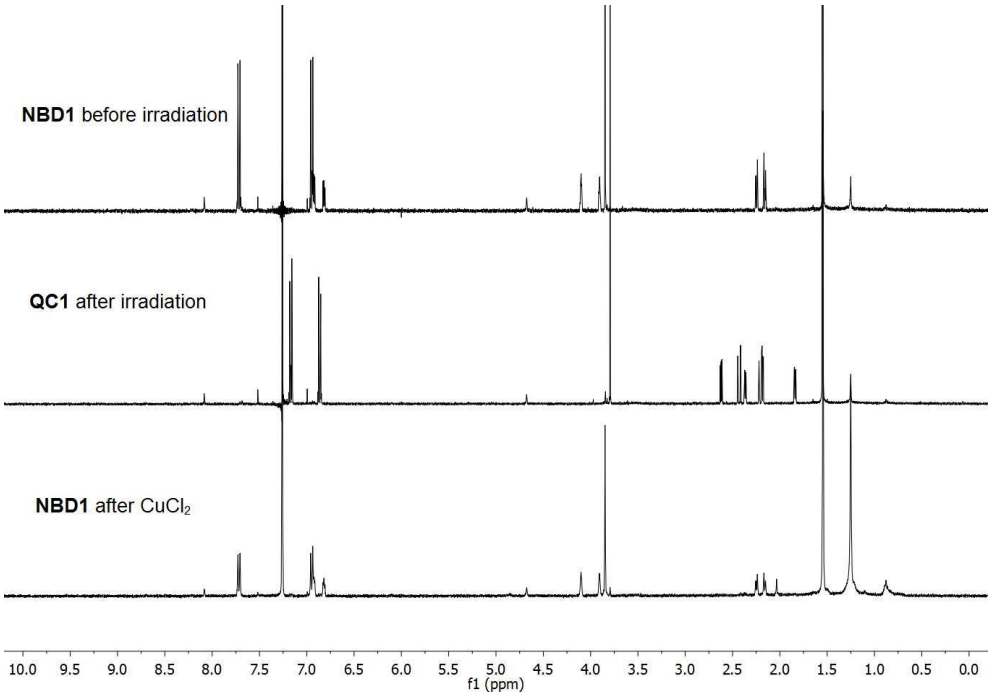
$[Cu(CH_3CN)_4]PF_4$ (in $CDCl_3$, ^1H NMR 400 MHz)



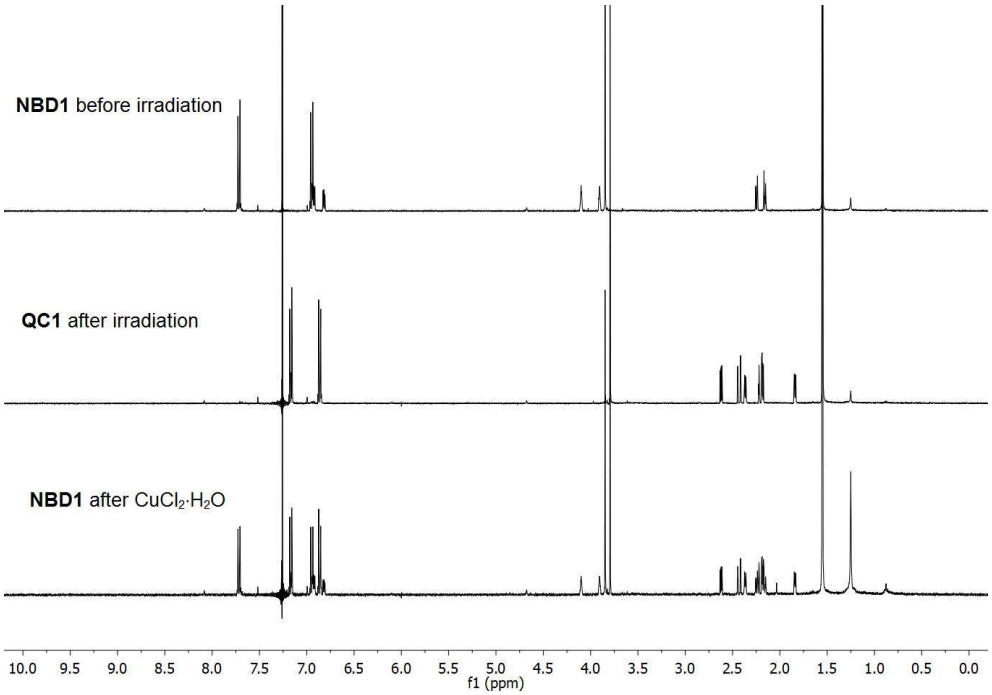
$[Cu(CH_3CN)_4]PF_4$+BHT (in $CDCl_3$, ^1H NMR 400 MHz)



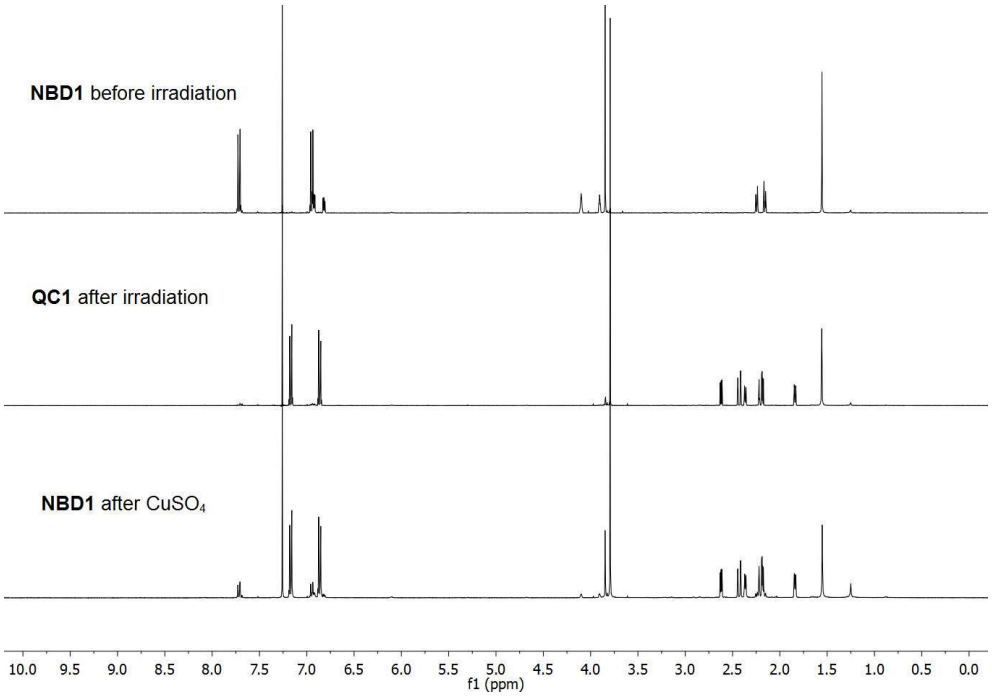
$CuCl_2$ (in $CDCl_3$, ^1H NMR 400 MHz)



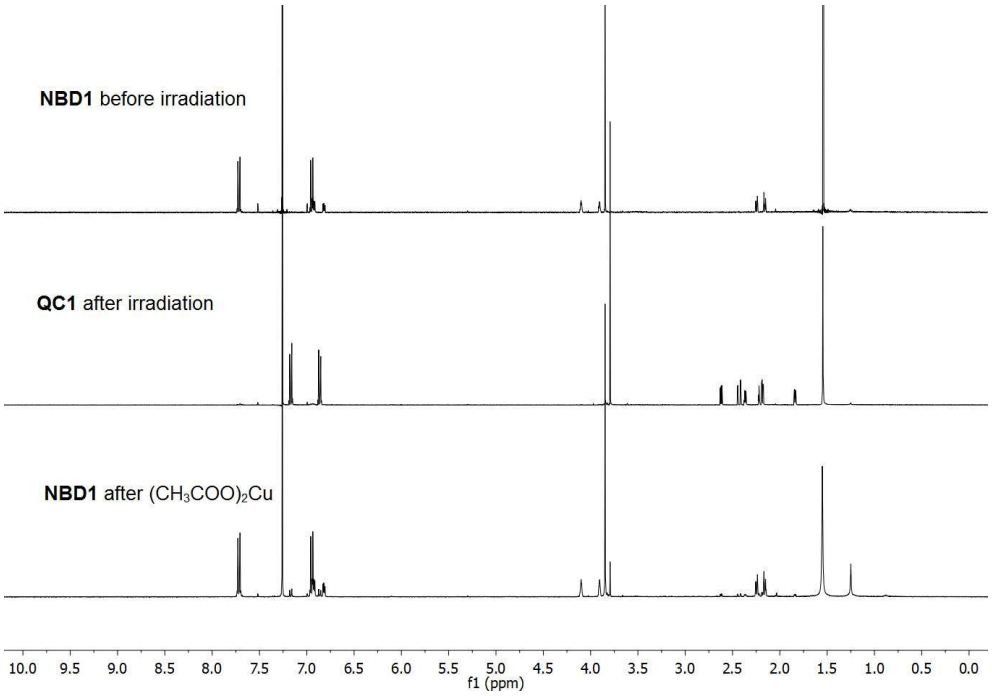
$CuCl_2 \cdot H_2O$ (in $CDCl_3$, ^1H NMR 400 MHz)



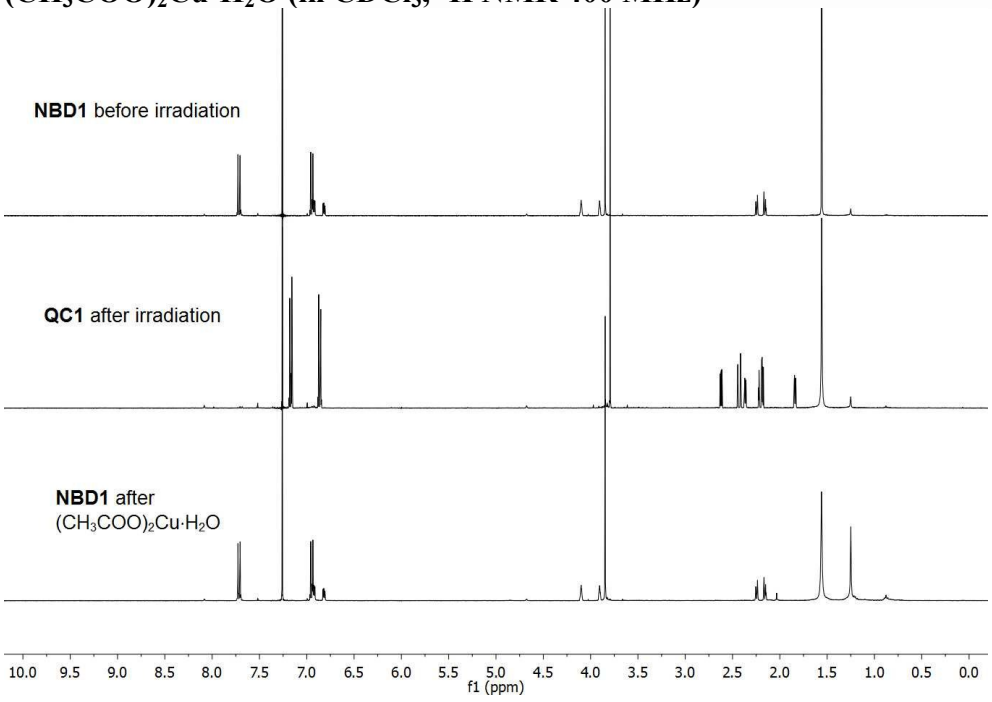
$CuSO_4$ (in $CDCl_3$, ^1H NMR 400 MHz)



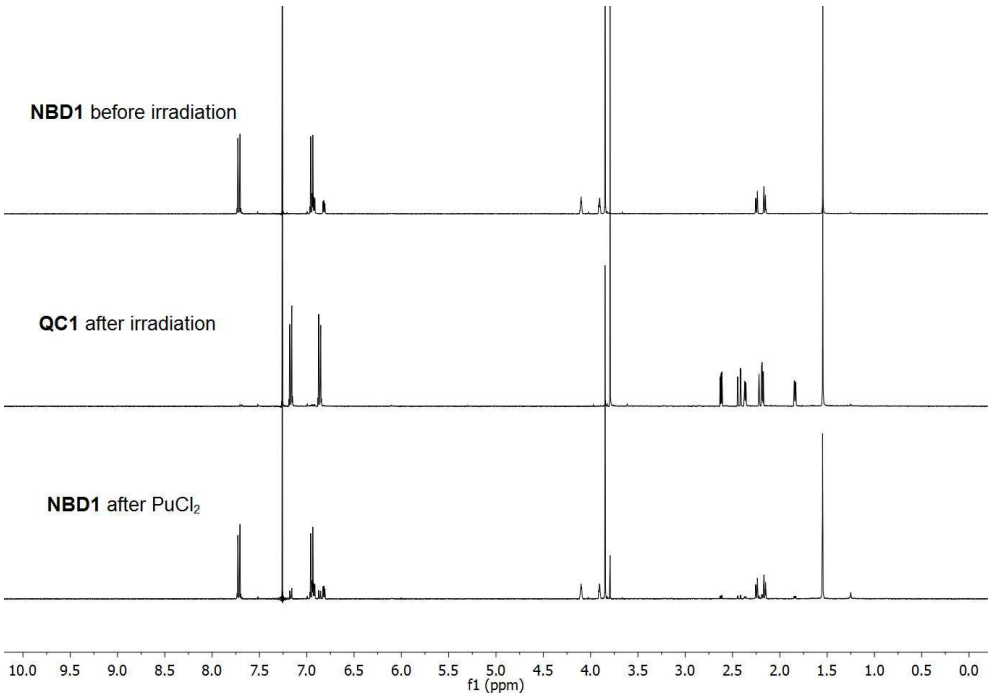
$(CH_3COO)_2Cu$ (in $CDCl_3$, ^1H NMR 400 MHz)



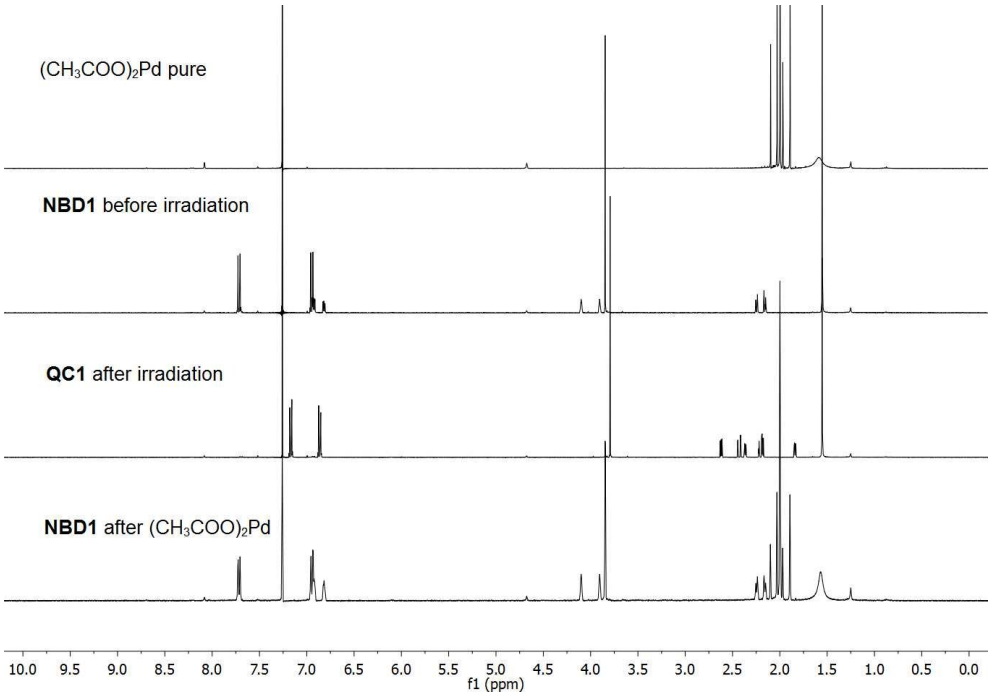
$(CH_3COO)_2Cu·H_2O$ (in $CDCl_3$, ^1H NMR 400 MHz)



$PdCl_2$ (in $CDCl_3$, ^1H NMR 400 MHz)



$(CH_3COO)_2Pd$ (in $CDCl_3$, ^1H NMR 400 MHz)



UV-Vis check

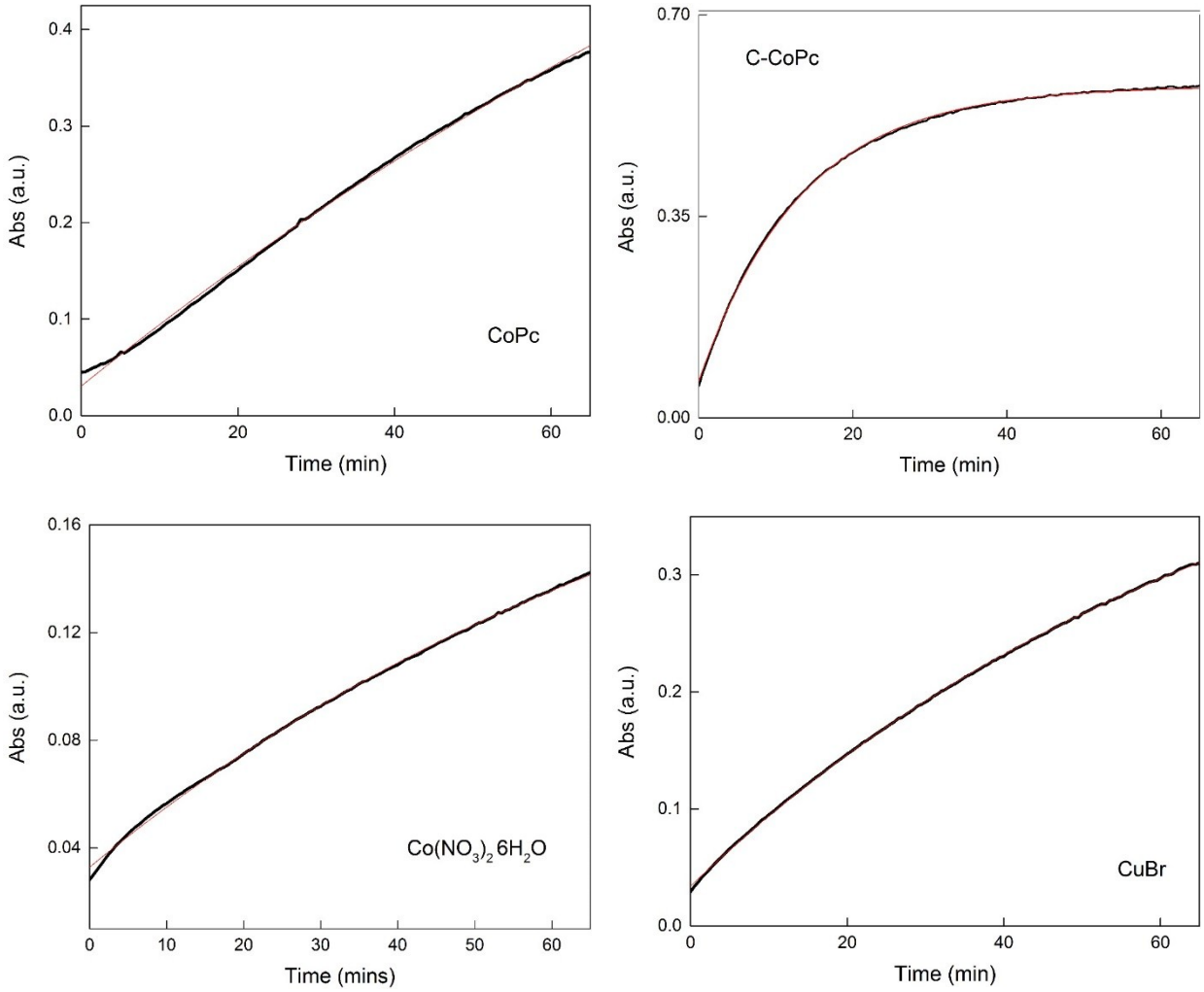
A 160mL **NBD1** solution of 7.52 x 10^{-5} M (Abs = 1) was prepared. For each catalyst candidate, 2.5 mL of the solution was transfered to a 1 cm pathlength cuvette, and irradiated until fully converted to **QC1**. A catalyst candidate was then added to the solution and the absorption change was recorded by a UV-Vis spectrometer at 347 nm over one hour.

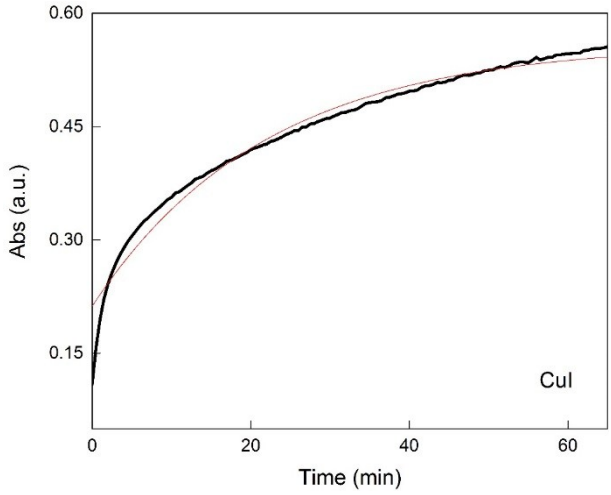
CoPc was chosen because of its high reaction rate in toluene. **CoPc@C** was then tested, given a clean fit to determine an even higher reaction rate. The fit curve can be explained by a pseudo-first order kinetic model. A function of $y(t) = y_0 + A_1 e^{-k\,c_{cata}\,(t_0 - t)}$ was used to fit all kinetic studies. k is the reaction constant, c_{cata} represent the concentration of the catalyst, supposing the suspension of insoluble catalyst was homogeneously distributed in solution. t represents the variable of time is s. y_0, A_1 are unitless parameter from the fit.

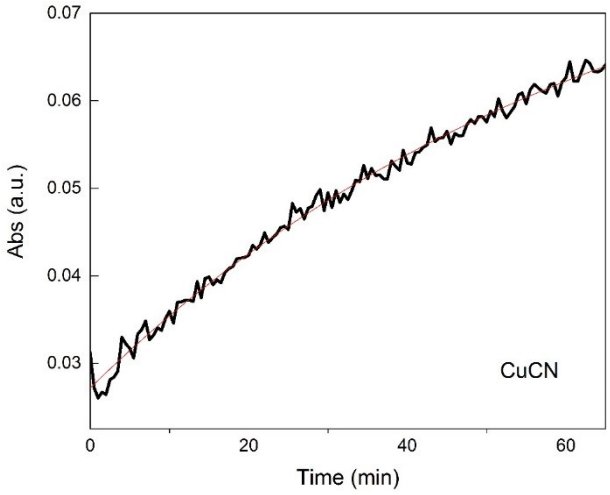
Table S8. *Screened metal salts and complexes as candidates for catalytically back-conversion of* ***QC1.*** ✓ *means an active catalytic behaviour by* ^{1}H *NMR,* ✕ *means no obvious behaviour of catalytic activation.*

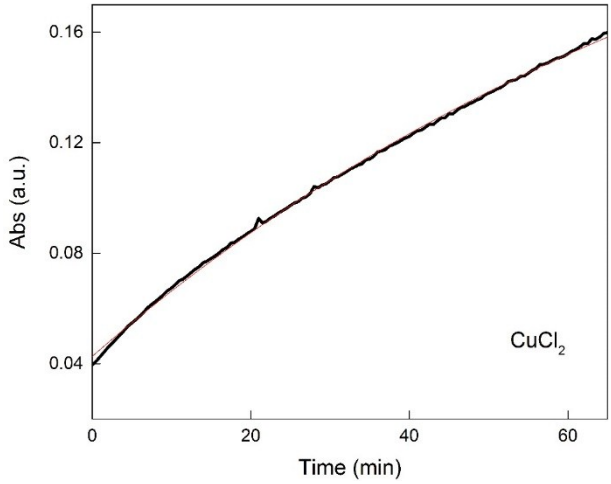
Number	Catalyst Name	Activity in $CDCl_3$	Activity in toluene	Reaction rate in toluene (s^{-1} M^{-1})
	Co(II)			
1	**CoPc**	✓	✓	172.05
2	**CoPc@C**	✓	✓	11788.22
3	**$Co(NO_3)_2.6H_2O$**	✕	✓	3.88
4	**5,10,15,20-Tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(II)**	✕	✓	Dissolve in toluene and spectral overlap with **NBD1**, hard to follow by UV-Vis.
	Cu(I)			
5	**CuBr**	**Degradation**	✓	2.41
6	**CuI**	✕	✓	8.73
7	**CuCN**	✓	✓	4.09
8	**$[Cu(CH_3CN)_4]PF_6$**	**Degradation**	/	/
8*	**$[Cu(CH_3CN)_4]PF_6$ + BHT**	**Low degradation**	/	/
	Cu(II)			
9	**$CuCl_2$**	**Degradation**	✓	2.52
10	**$CuCl_2$ $2H_2O$**	**Degradation**	✕	0.03
11	**$CuSO_4$**	✓	✓	6.07
12	**$(CH_3COO)_2Cu$**	✓	✓	0.02
13	**$(CH_3COO)_2Cu$ H_2O**	✓	✓	32.39
	Pd(II)			
14	**$PdCl_2$**	✓	✓	3.62
15	**$(CH_3COO)_2Pd$**	✓	✓	Slowly dissolve in toluene and spectral overlap with **NBD1**, hard to follow by UV-Vis.

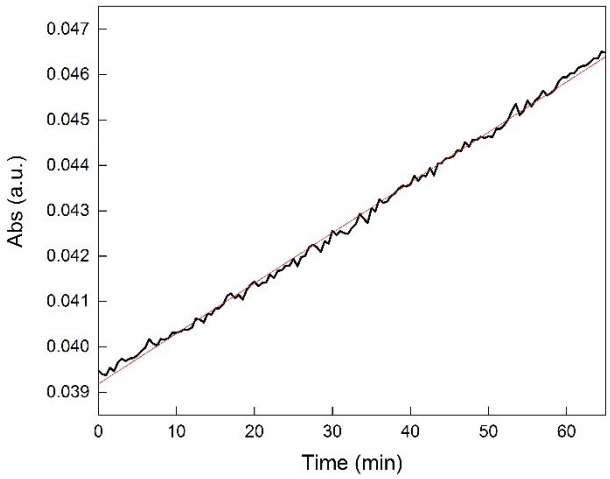
Figure S10. QC1 *Catalytic conversion of difference candidates in toluene during 65 min, red line corresponds to the pseudo first order kinetic fit.*

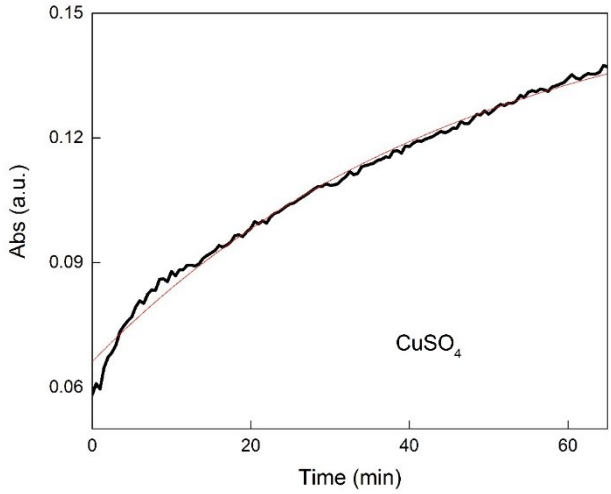


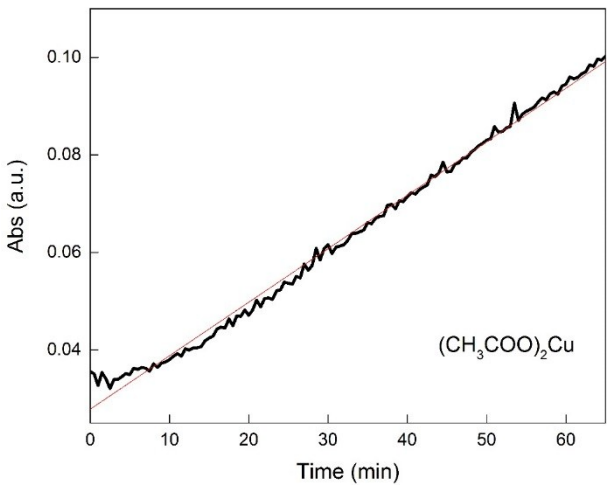

Abs (a.u.)
Time (min)
CuI

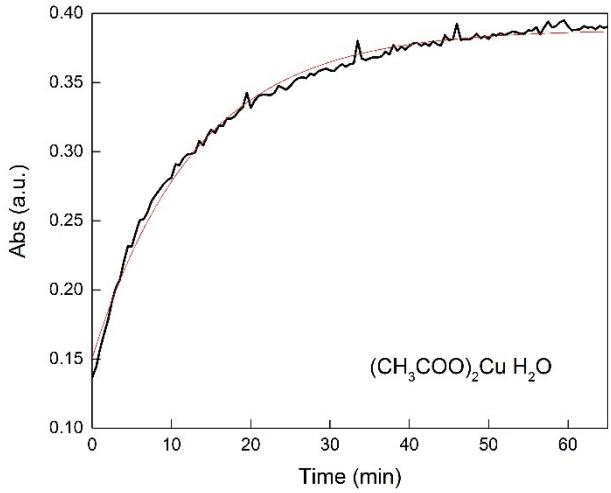

Abs (a.u.)
Time (min)
CuCN

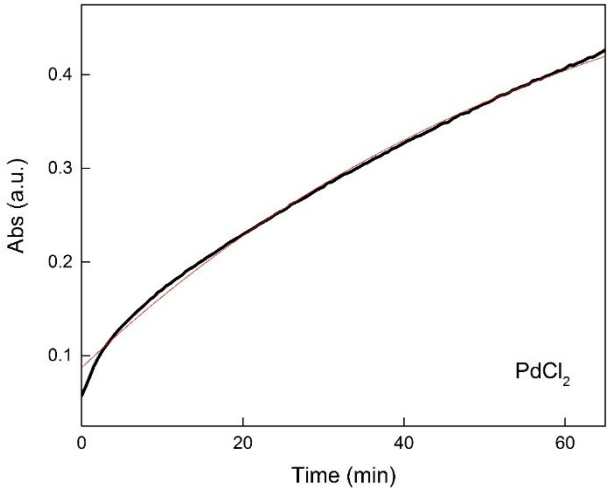

Abs (a.u.)
Time (min)
CuCl2


Abs (a.u.)
Time (min)


Abs (a.u.)
Time (min)
CuSO4


Abs (a.u.)
Time (min)
(CH3COO)2Cu


Abs (a.u.)
Time (min)
(CH3COO)2Cu H2O


Abs (a.u.)
Time (min)
PdCl2

S13. Preparation of **CoPc@C**

A suspension of CoPc (28.3 mg) in freshly distilled THF (1L), under a nitrogen atmosphere, was stirred overnight whereby complete dissolution occurred. Simultaneously, activated carbon (234.8 mg, Sigma-Aldrich 100 mesh particle size, powder) was dried at 150 °C overnight, and was added to the resulting CoPc solution and the contents of the vessel were allowed to stir for 3 days, after which time the blue colour had faded. The solvent was removed under reduced pressure and the remains were dried under high vacuum. The powder was washed with toluene (5 x 50 mL) by dispersing the material using sonication, followed by centrifugation and decantation to remove the toluene. In the last washing cycle, the discarded toluene was colourless. This sample of **CoPc@C** was then dried under high vacuum, the dry catalyst was the stored in a vial for several days prior to use.

X-ray photoelectron spectroscopy (XPS)

Atomic concentration Tables (%) of **CoPc@C** and activated carbon are shown below. Compared both tables, it is obvious that CoPc is absorbed on the surface of activated carbon. Si and part of O and C elements come from the conductive tape using as the substrate. Excluding the effect of the substrate, the loading percentage was then calculated as 13%, slightly higher than the theoretical value of 10%.

Table S9. *XPS atomic concentration table of* ***CoPc@C***

	C: 1s	**N: 1s**	**O: 1s**	**Na: 1s**	**Si: 2p**	**Co: 2p^3**
CoPc@C	91.75	2.01	5.14	0.10	0.74	0.27

Table S10. *XPS atomic concentration table of C*

	C: 1s	O: 1s	Si: 2p	Cl: 2p
Active carbon	89.99	9.66	0.27	0.08

Scanning electron microscope (SEM)

Figure S11 shows the SEM images of **CoPC@C** and activated carbon. It can be seen that the size of carbon particles is not uniform and big holes enlarge the surface area greatly. However, comparison of Figure S11(b) and (d) shows there is no obvious difference between the carbon with and without CoPc since the surface of activated carbon itself is not smooth and on which, small particles exist. There is no obvious clumping of CoPc, which would effectively lower the surface area of catalyst.

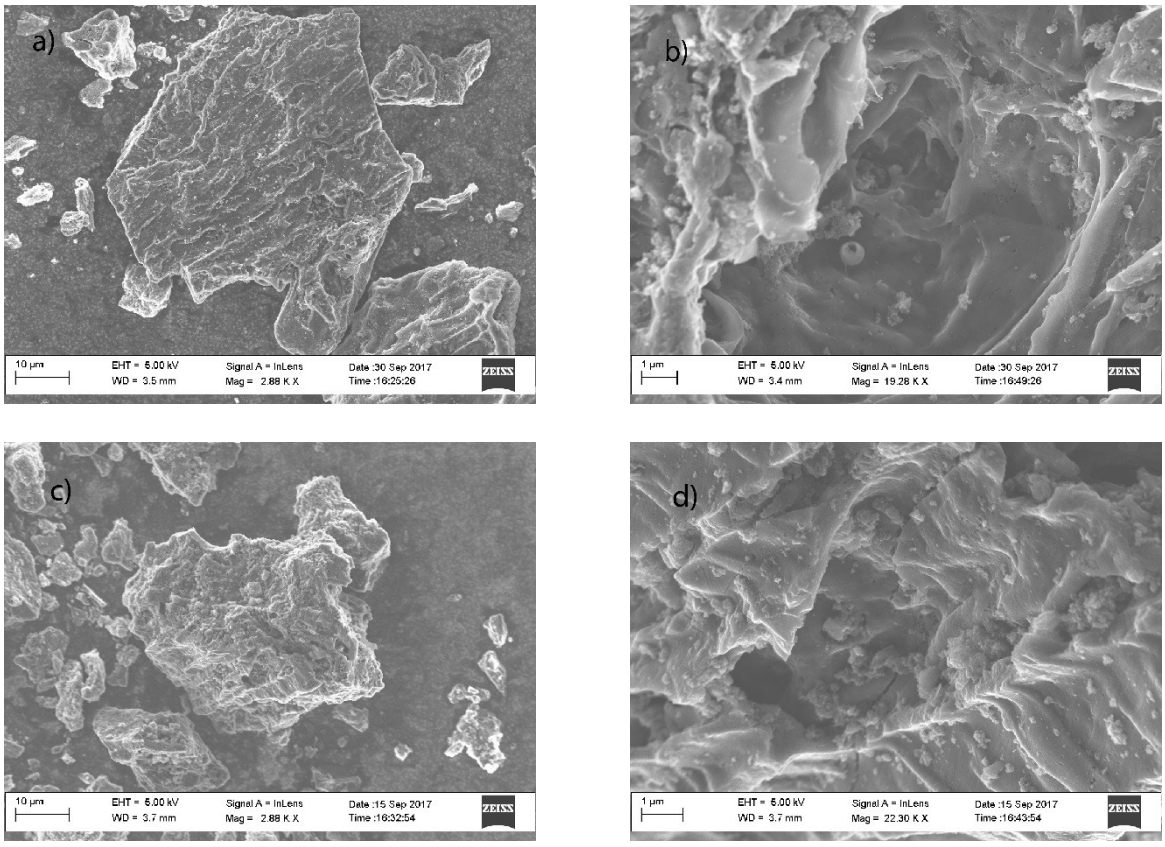


Figure S11. *SEM images a) low magnification image of activated carbon; b) higher magnification image of activated carbon; c) low magnification image of* ***CoPc@C****; d) higher low magnification image of* ***CoPc@C****.*

S14. Vacuum chamber setup

The schematic for the heat release set up shown in Figure 3 of main text, and for a picture of the actual see Figure S12. In the central part of the vacuum chamber, ca. 5 mg of the **CoPc@C** was loaded into a 2.5 cm Teflon tubing with cotton blocked each side (1.27 mm inner diameter, 1 cm loading length). A **QC1** solution was pumped through the catalytic center with a flow speed of 5 mL h^{-1}. During the heat release measurement, we observed that higher concentrations of **QC1** can result in a CoPc leaching from the activated carbon. (See Figure S13.)

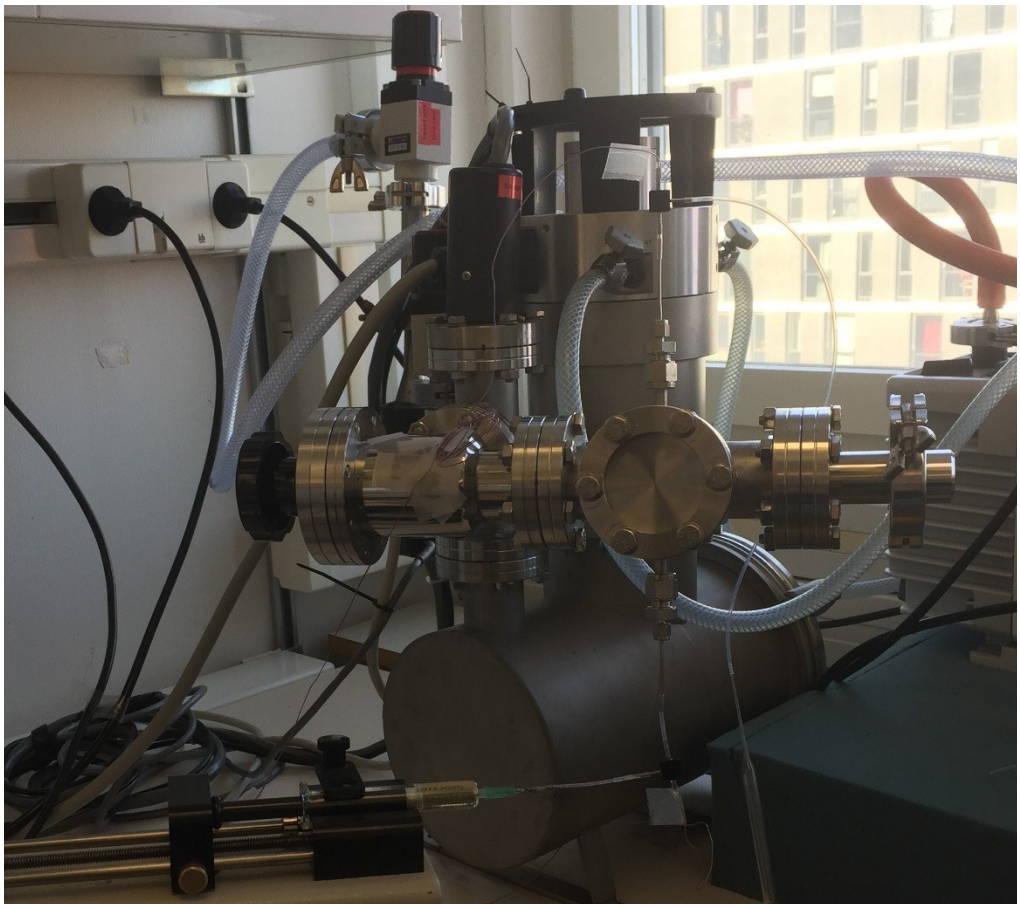


Figure S12. *Picture of vacuum chamber setup.*

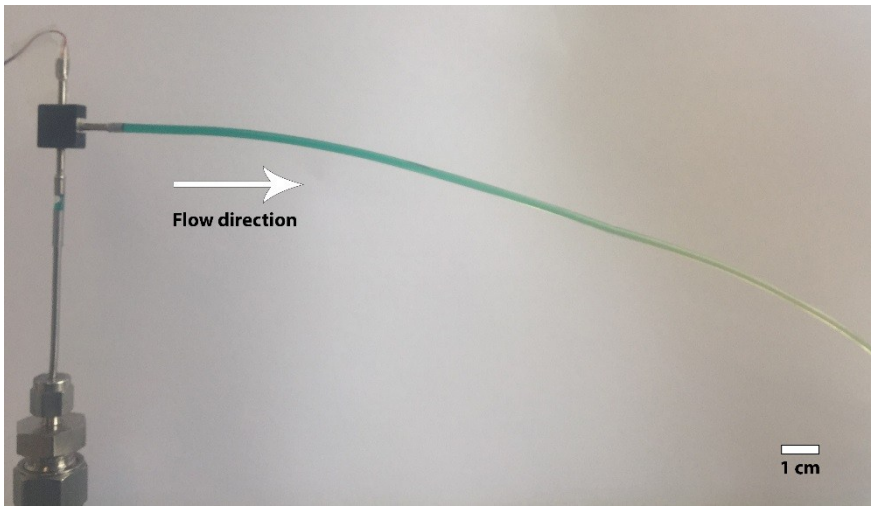


Figure S13. *A clear colour gradient shows a leaching problem of CoPc from the reaction centre when a high concentration (1.5M) of converted* ***NBD1*** *was used.*

To determine the effect of dissolved CoPc from CoPc@C for **NBD1** conversion, 1.97 mg of CoPc@C was loaded into a 4.5 cm Teflon tube with cotton blocked each side. The flow speed was selected at 5 mL h^{-1}. Catalytic back converted solution of **NBD1** with leached catalyst was collected by using a 1 M solution. Ca. 0.7 mL of the final blue solution was successfully collected. (See Figure S14)

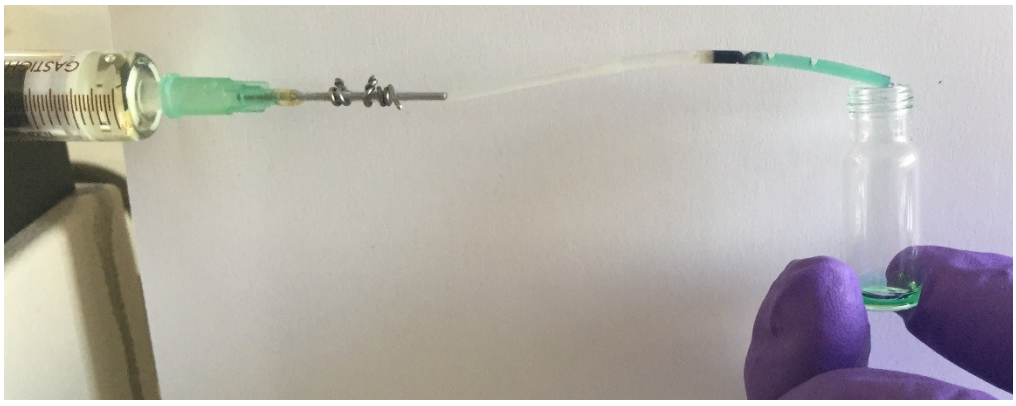


Figure S14. *With a flow speed of 5 mL h^{-1}, ca. 0.7 mL of the catalyst leached NBD1 solution was collected into a vial. Left syringe containing 1M* ***QC1*** *solution passing through catalytic centre.*

The collected solution was diluted immediately to fit in a high concentrated regime for quantum yield measurements ($A_{340\ nm} > 2$). In addition, the collected solution observed a colour change over time fading gradually to yellow under ambient conditions, likely the CoPc lost its catalytic activity. (See Figure S15) For this reason, the quantum yield was measured three times with a freshly collected solution, after 11 hours (11h) as well as after 3 days (3D).

For the freshly collected solution, around 4% decrease of the quantum yield was observed with the presence of catalytic depletion in **NBD1** solution. After 11 hours, the absorbance at 364 nm was increased over time, thus implying that CoPc had some effect on the photoconversion process. However, no significant change of quantum yield was observed.

After three days, two more diluted solutions from the collected sample were prepared ($A_{340\ nm} > 2$). The quantum yield went back to 61% as blue colour changed to yellow over time. ^{1}H NMR spectrum was checked after three days from the collected solution, no significant degradation was observed.

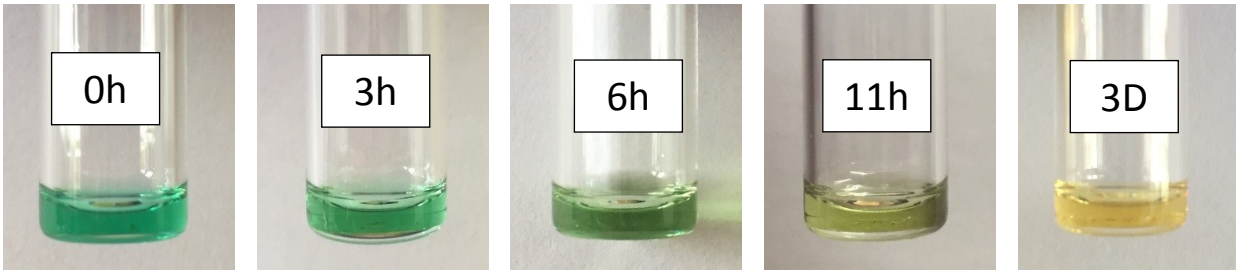


Figure S15. *Colour changes of* ***NBD1*** *solution with depleted catalyst over time.*

Collected catalyst depleted **NBD1** solution after 3 days
(in $CDCl_3$, ^1H NMR 400 MHz)

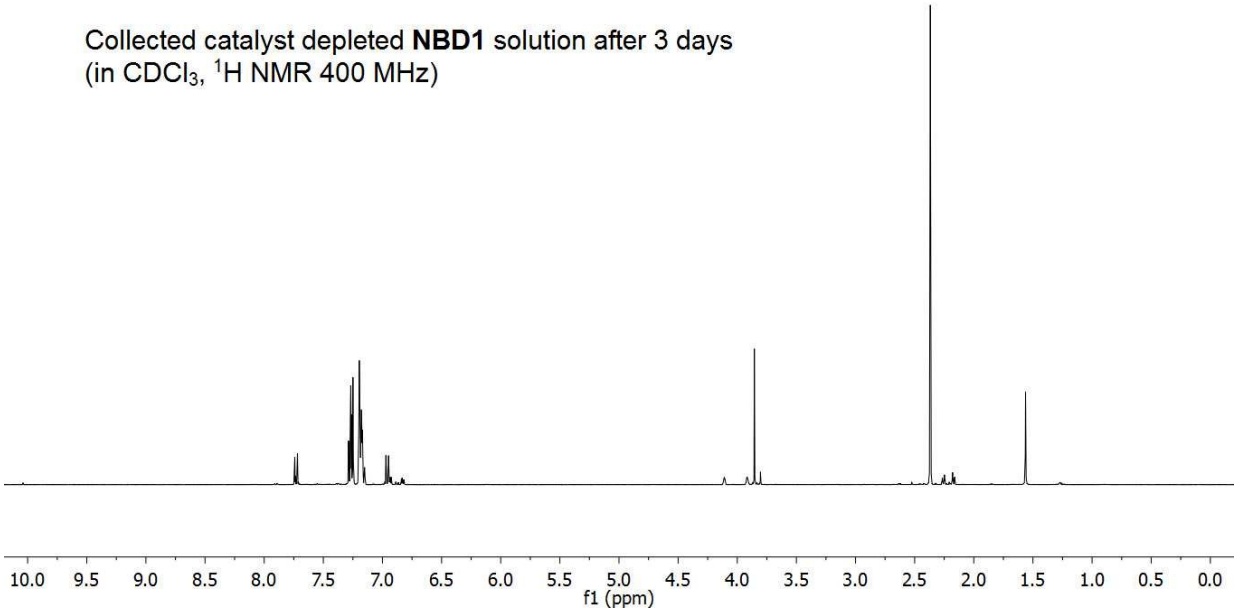
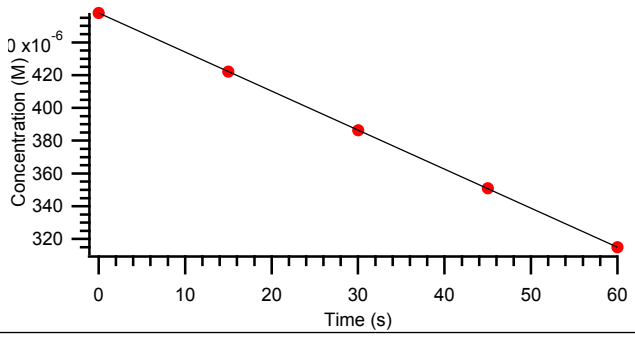
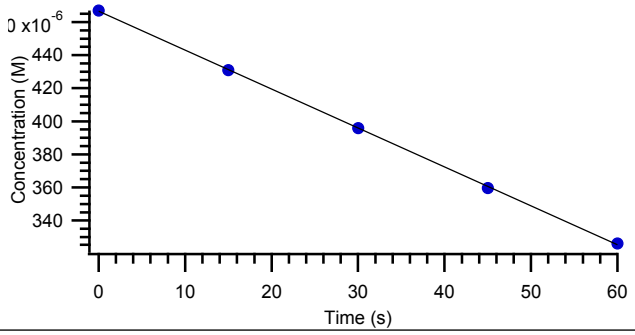
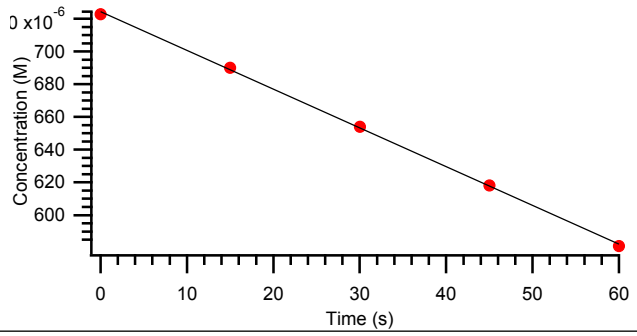


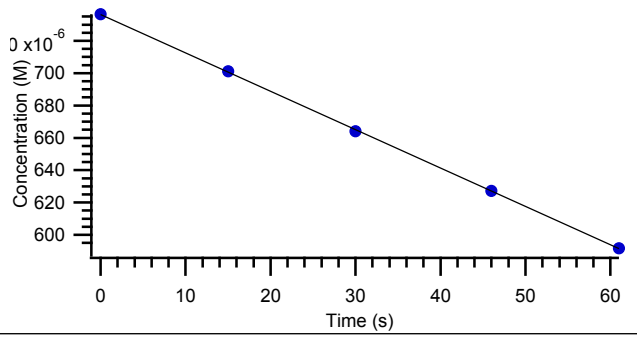
Table S11. *Determination of the quantum yield of NBD1 with depleted catalyst at 0 hours (sample 1, 2), 11 hours (sample 3, 4) and 3 days (sample 5, 6).*

Sample 1 (0h)	
Sample weight (g): 2.75 g	
Photon flux (E s^{-1}): 1.33 10^{-8}	
Irradiation time (s)	**Absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 30 45 60	0.59 0.54 0.50 0.45 0.40
Quantum yield: 56.8%	

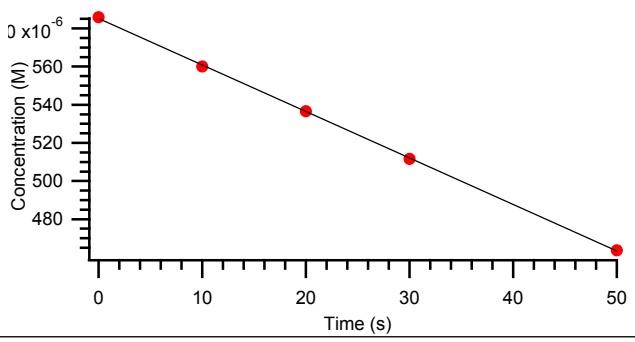
Sample 2 (0h)	
Sample weight (g): 2.79 g	
Photon flux (E s^{-1}): 1.33 10^{-8}	
Irradiation time (s)	**Absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 30 45 60	0.60 0.55 0.51 0.46 0.42
Quantum yield: 57.0%	

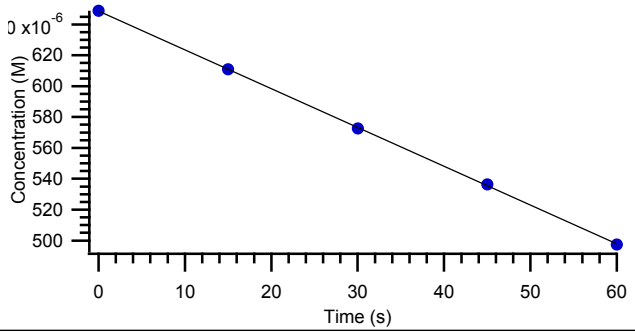
Measured quantum yield (%)		Average quantum yield (%)
Sample 1 (0h)	56.8	57
Sample 2 (0h)	57.0	

Sample 3 (11h)	
Sample weight (g): 2.74 g	
Photon flux (E s^{-1}): 1.33 10^{-8}	
Irradiation time (s)	**Absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 30 45 60	0.93 0.87 0.84 0.79 0.75
Quantum yield: 56.4%	

Sample 4 (11h)	
Sample weight (g): 2.78 g	
Photon flux (E s^{-1}): 1.33 10^{-8}	
Irradiation time (s)	**Absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 30 45 60	0.95 0.90 0.85 0.81 0.76
Quantum yield: 57.6%	

Measured quantum yield (%)		Average quantum yield (%)
Sample 3 (11h)	56.4	57
Sample 2 (11h)	57.6	

Sample 5 (3D)	
Sample weight (g): 2.81 g	
Photon flux (E s^{-1}): 1.31 10^{-8}	
Irradiation time (s)	**Absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 10 20 30 50	0.75 0.72 0.69 0.66 0.60
Quantum yield: 60.6%	

Sample 6 (3D)	
Sample weight (g): 2.72 g	
Photon flux (E s^{-1}): 1.31 10^{-8}	
Irradiation time (s)	**Absorbance at 364 nm (ε = 1284.5 M^{-1} cm^{-1})**
0 15 30 45 60	0.83 0.78 0.74 0.69 0.64
Quantum yield: 60.5%	

Measured quantum yield (%)		**Average quantum yield (%)**
Sample 5 (3D)	60.6	61
Sample 6 (3D)	60.5	

S15. Macroscopic heat release

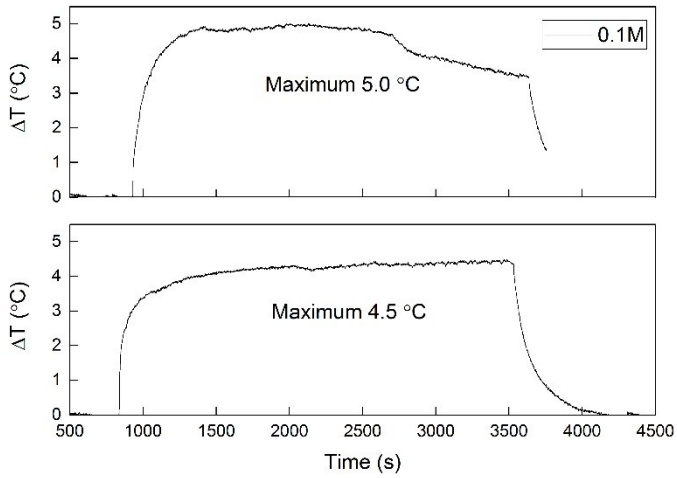


Figure S16. *0.1 M of* ***NBD1*** *heat release experiment. A maximum temperature of 5.0* °C *was observed for first attempt, vacuum pressure varied from 6.6* x *10^{-6} mbar to 4.5* x *10^{-4} mbar. A maximum temperature of 4.5* °C *was observed for second attempt, vacuum pressure varied from 8.7* x *10^{-6} mbar to 4.2* x *10^{-5} mbar.*

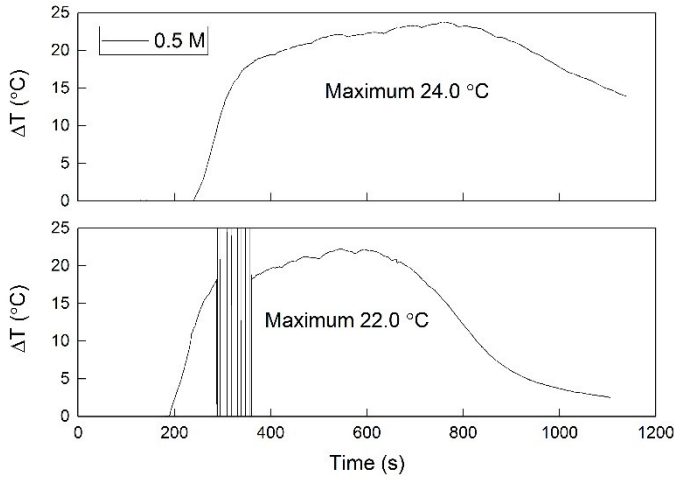


Figure S17. *0.5 M of* ***NBD1*** *heat release experiment. A maximum temperature of 24.0* °C *was observed for first attempt, vacuum pressure varied from 6.6* x *10^{-6} mbar to 8.5* x *10^{-6} mbar. A maximum temperature of 22.0* °C *was observed for second attempt, vacuum pressure varied from 1.6* x *10^{-4} mbar to 5.7* x *10^{-3} mbar.*

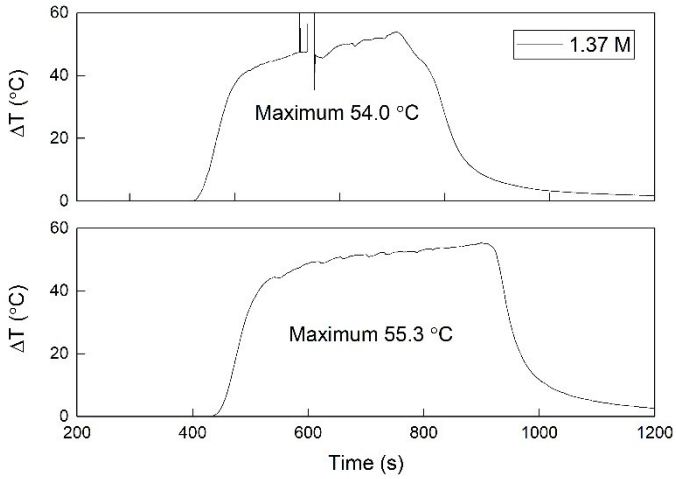


Figure S18. *1.37 M of* ***NBD1*** *heat release experiment. A maximum temperature of 54.0* °C *was observed for first attempt, vacuum pressure varied from 1.6* x 10^{-5} *mbar to 2.2* x 10^{-4} *mbar. A maximum temperature of 55.3* °C *was observed for second attempt, vacuum pressure varied from 6.2* x 10^{-5} *mbar to 9.0* x 10^{-4} *mbar.*

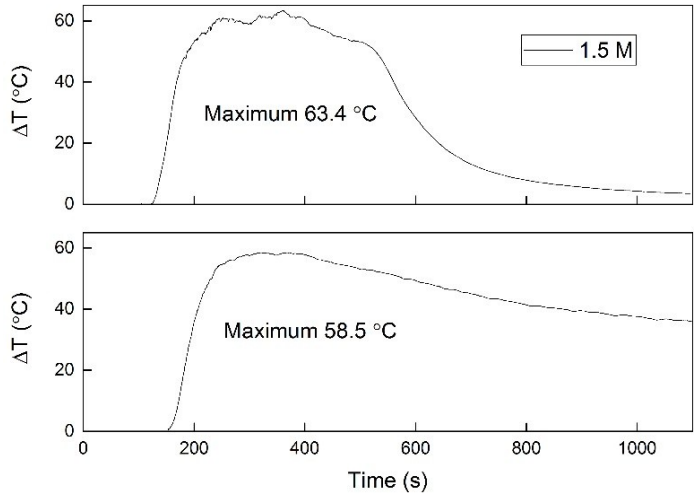
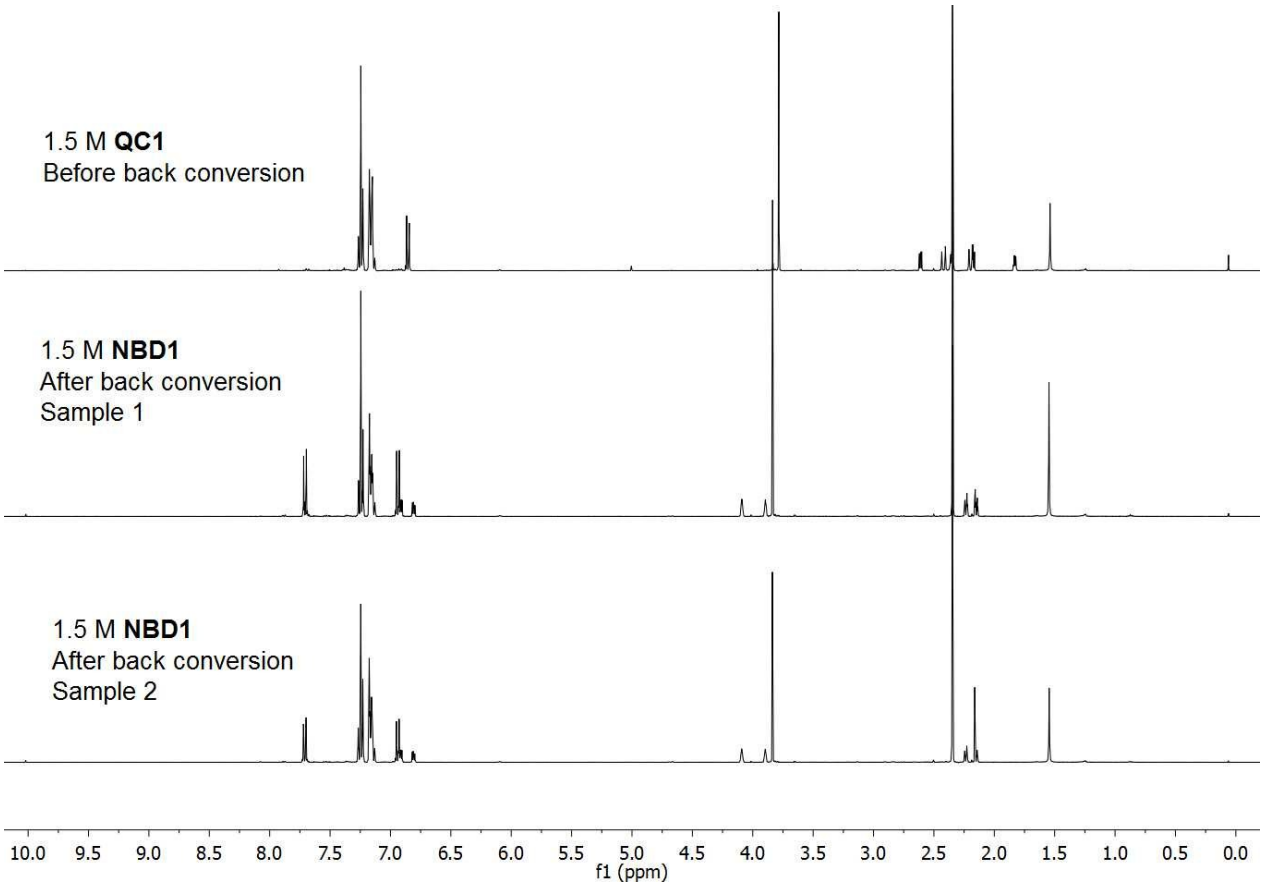


Figure S19. *1.5 M of* ***NBD1*** *heat release experiment. A maximum temperature of 63.4* °C *was observed for first attempt, vacuum pressure varied from 4.4* x 10^{-5} *mbar to 4.0* x 10^{-4} *mbar. A maximum temperature of 58.5* °C *was observed for sample second attempt, vacuum pressure varied from 5.5* x 10^{-5} *mbar to 6.6* x 10^{-5} *mbar.*



The back conversion was checked with NMR after both measurements for 1.5 M. A full back conversion can be confirmed for the highest concentration, which can implies all the lower concentration were fully back converted as well.

S16. Catalysis back conversion computational calculations

The reaction mechanism was studied by theoretical methods to understand the possible alternatives involved in the catalytical back reversion of **QC** to **NBD**.

An initial mechanistic proposal for the reaction with cobalt as catalyst has been previously reported [9]. The proposed mechanism involved an oxidative addition of **QC** to cobalt phtalocyanine followed by (a) a concerted step or (b) a multi-step pathway with cationic species. More recently[10], the catalytic activity of $CuSO_4$ and $SnCl_2$ was tested and two different mechanisms were proposed. In the case of the copper catalyst, a concerted rearrangement was observed due to the electronically available d orbitals in the metallic atom. In the tin species, as the d orbitals are not available the rearrangement is not possible.

Using these preliminary mechanistic proposals, we envisioned a multi-step pathway with participation of the d orbitals in cobalt phtalocyanine. In addition, an initial step involving an oxidative addition to C-C in **QC** bond was evaluated.

All calculations were carried out using the M06[11] or BP86[12] functionals included in the Gaussian09[13] and Gaussian16[7] program packages together with the standard basis set 6-31+G*[8]. All critical points in the PES were characterized with frequency calculations to include ZPE and free energy corrections and verify the stationary points as transition states (one imaginary frequency) or minima (zero imaginary frequencies). When stated, geometry optimizations were performed in solution with implicit solvent applying the PCM solvation model with toluene as solvent (ε=2.3741). In addition, stability of the wave function was checked for all critical points giving a stable wave function in all cases. The nature of the transition states was checked through IRC calculations.

A preliminary study on the parent **QC/NBD** system in gas phase was performed to find the key steps in the reaction pathway using BP86 as the functional and 6-31+G* as the basis set (see Figure S20).

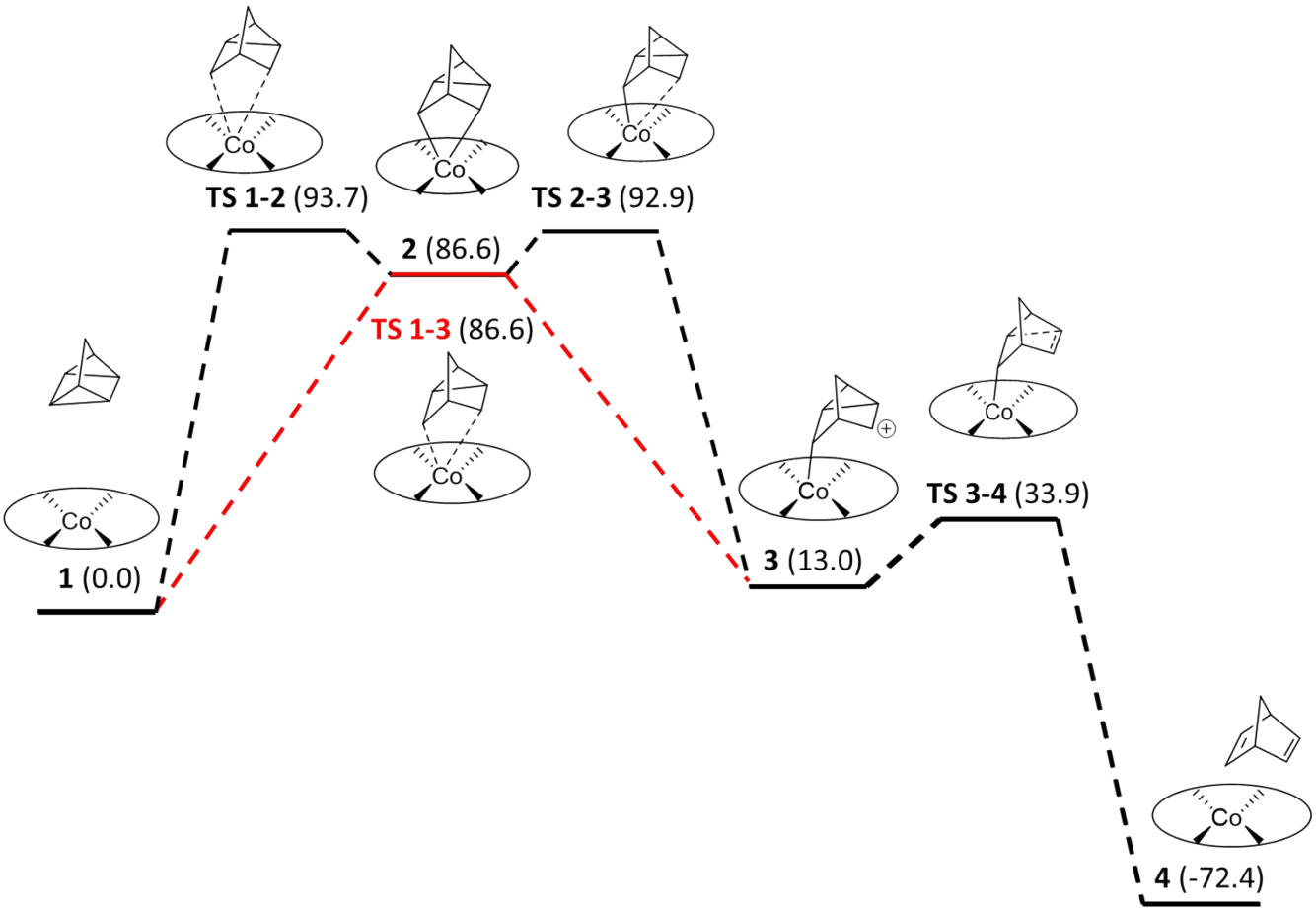


Figure S20. *QC to NBD conversion in gas phase. Energies in kJ mol^{-1} related to* ***1****. (BP86/6-31G*+)*

The first steps of the mechanism are clearly the rate limiting steps. The energy barriers are around 86 kJ mol^{-1} for the two possible alternatives and they differ in less than 8 kJ mol^{-1}. Path 1 (black

line, Figure S20) consists of an oxidative addition of the C-C QC bond to the cobalt atom to yield intermediate **2**. A small energy barrier then leads to the formation of the radical **3**.

Path 2 (red line, Figure S20) implies the direct formation of intermediate **3** through the transition state **TS1-3** combination of the two steps described in Path 1, oxidative addition and radical formation. A second mechanistic alternative[10] was also computed. The geometries of **TS 1-2** and **TS 1-3** were optimized as minima with quatriplet multiplicity. The high energy values obtained allowed us to discard this alternative as not competitive with the main path. The formation of NBD is completed through **TS3-4**. This step implies the elongation of the remaining C-C QC bond to yield the final NBD coordinated complex **4**.

The solvent effect was subsequently evaluated by using the PCM with toluene as solvent (Figure S21). In this case, only one reaction path could be found. The energy barrier of **TS1-3** is slightly higher than in gas phase, probably due to the higher dipolar moment of **TS1-3** in solvent.

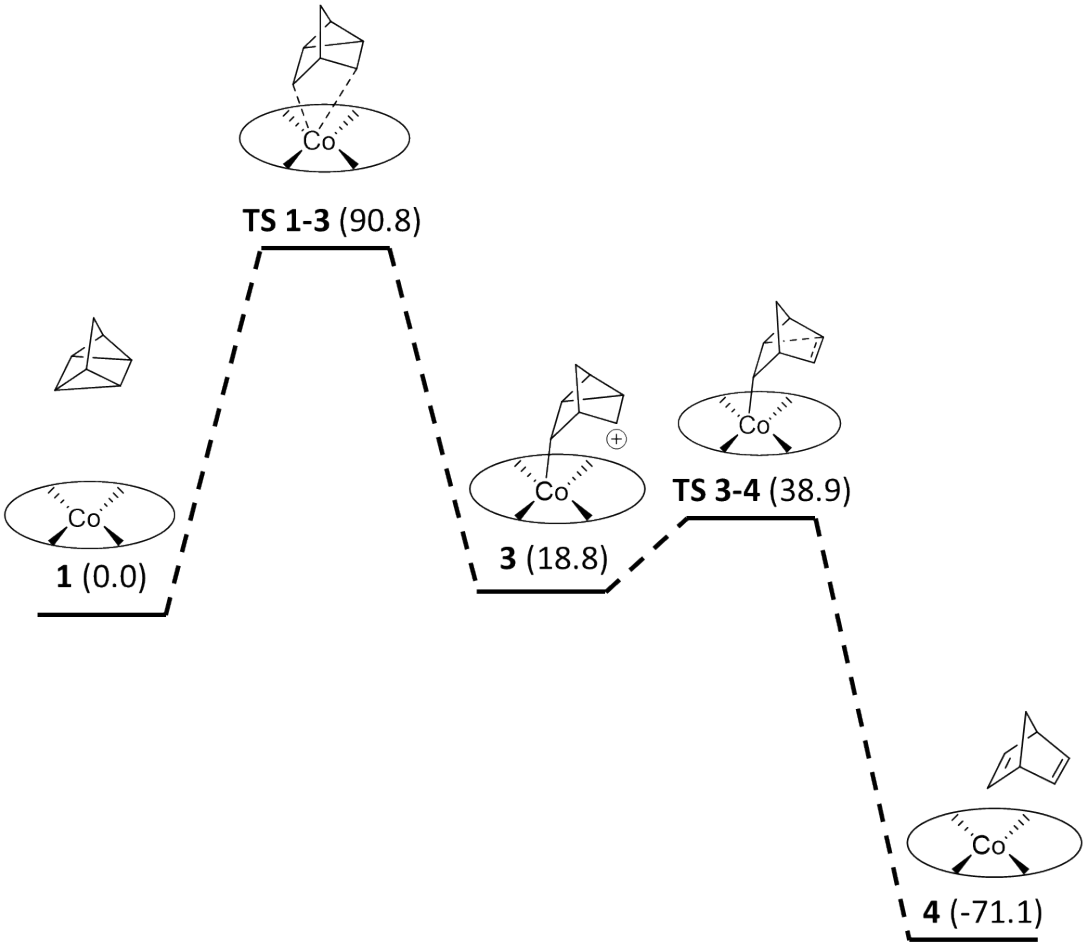


***Figure S21. QC** to **NBD** conversion in toluene reaction path. Energies in kJ mol^{-1} related to **1**. (BP86/6-31G*+; PCM Toluene)*

In order to check the effect of the functional used, we also re-evaluated the whole path at the M06/6-31G*+ level of theory (figure S22).

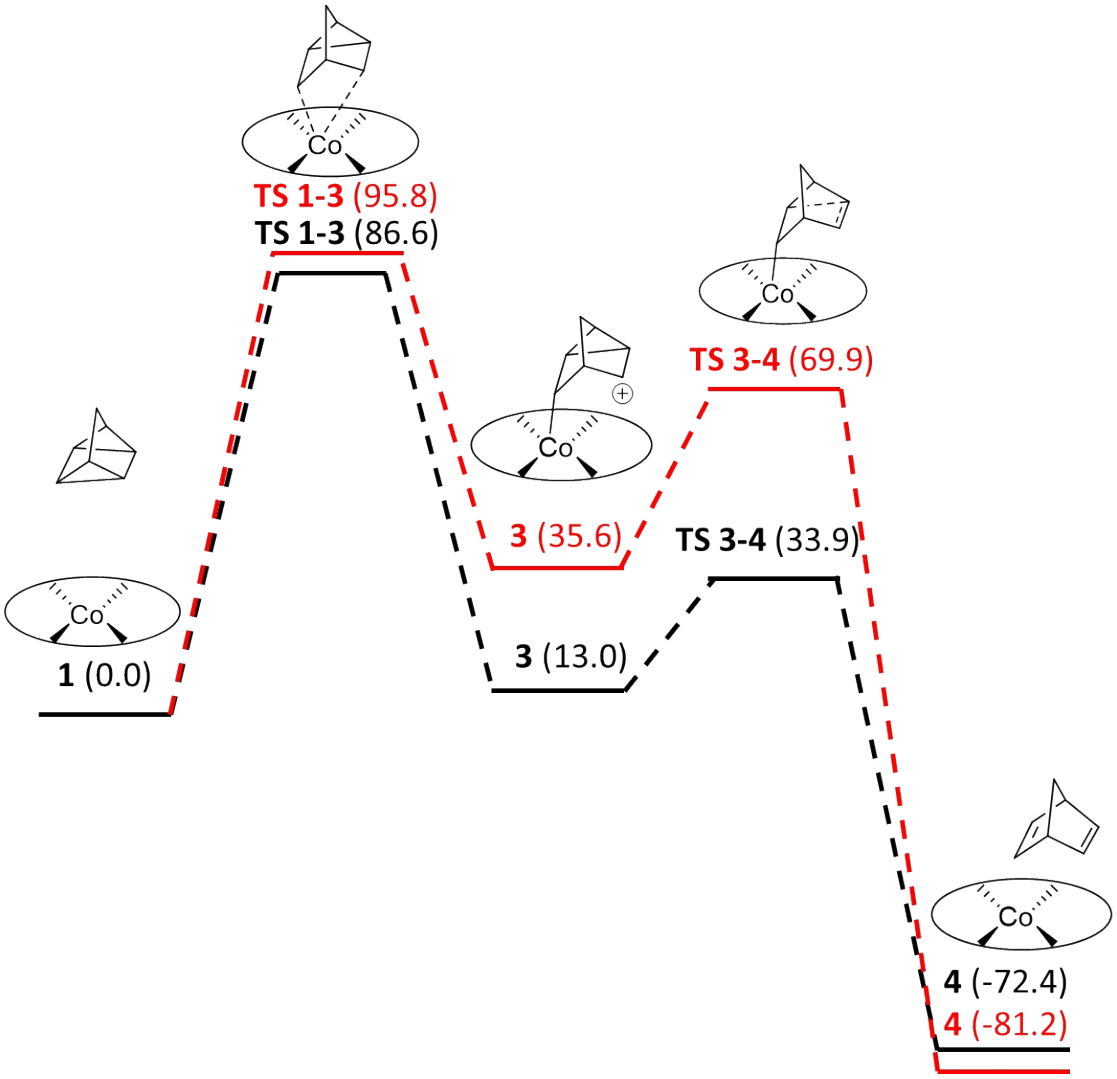
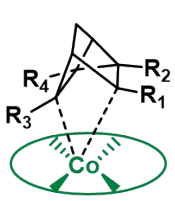


Figure S22. *QC to NBD conversion in gas phase for two different functionals (black line BP86/6-31G*+, red line, M06/6-31G*+). Energies in kJ mol^{-1} related to* ***1****.*

Both functionals shown a similar behavior in the form of the PES, being more energetic the intermediate **3** and **TS3-4** due to an over estimation of charge in the carbocation centre maybe due to the absence of the HF part in the BP86 functional, for that we choose the M06 functional instead. M06 gives reliable results in cobalt systems previously reported[14] and for non-covalent interactions, which are relevant to this system.

Once identified the main features of the mechanism, we performed a complete study of the reaction at our best level of theory: the full **NBD1/QC1** system, CoPc as catalyst in toluene and using M06 as functional. It should be noted that the parent NBD/QC system is highly symmetric, but up to four different orientations between the QC and the catalyst are possible for the **NBD1/QC1** system (Fig. S23).



QC) R_1, R_2, R_3, R_4 = H
i) R_1 = *p*-MeOPh, R_2 = CN, R_3,R_4 = H
ii) R_1 = CN, R_2 = *p*-MeOPh, R_3,R_4 = H
iii) R_1,R_2 = H, R_3 = CN, R_4 = *p*-MeOPh
iv) R_1,R_2 = H, R_3 = *p*-MeOPh, R_4 = CN

Figure S23. *Different orientations between QC and the catalyst. In all cases QC bonds the metal atom through the carbon substituted by* R_3.

Compared to the parent system, significantly lower energy barriers at the transition structures were found due to the stabilization of the charge centered in C_{R1} during the CC oxidative addition to the cobalt center (Fig.4a, main text). In the case of **TS1-2**, a strong stabilization was found for **QC1**, decreasing the energy of the TS from 95.8 to 58.6 or 50.8 kJ mol^{-1}. This energy difference is the key for an efficient heat release as measured experimentally and it is due to charge stabilization in the oxidative addition step. Thus, the relative energy of the four TSs coming from the different orientations are clearly different. Two of the possible intermediates (**2_iii** and **2_iv**) are too high in energy compared to the other two (**2_i** and **2_ii**). The combined effect of electronic stabilization and steric hindrance can explain the energy ordering of **2_i** to **2_iv** (Figure S24).

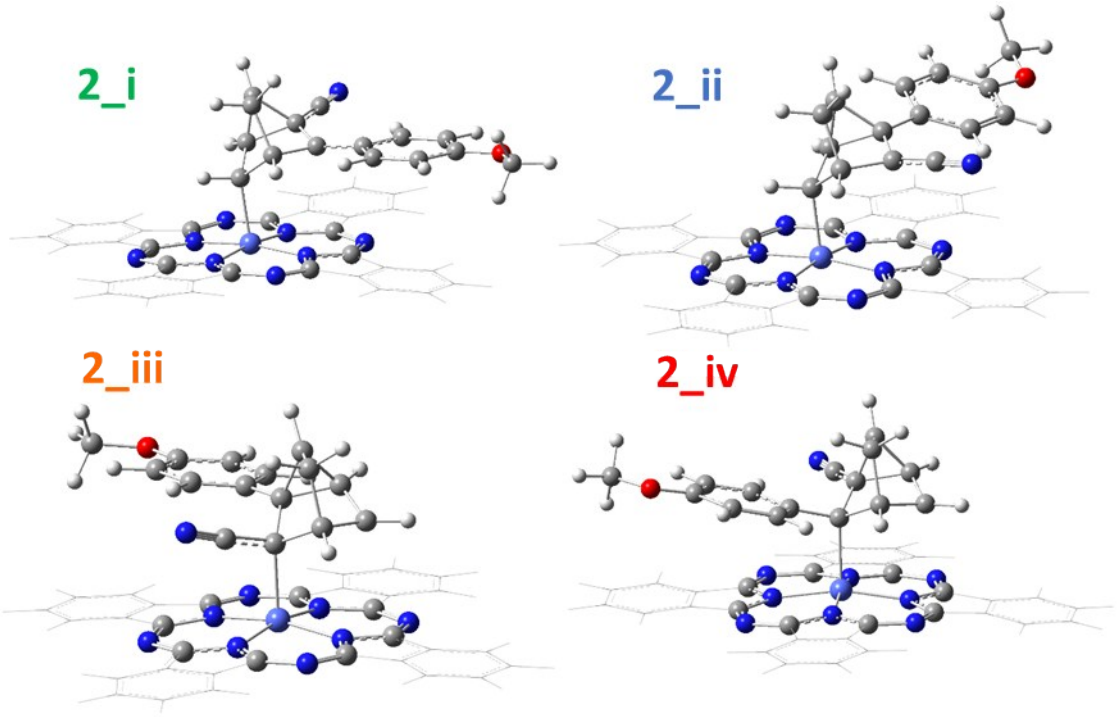


Figure S24. *Structures of the intermediates* ***2_i*** *–* ***2_iv****.*

Cartesian Coordinates (toluene, M06/6-31+G*).

1

Co	9.23050000	1.98849000	-5.93270200
N	9.21157900	3.16199400	-4.40793800
N	9.97366700	0.58645400	-4.84441300
N	8.48731800	3.39052300	-7.02098600
N	9.24938500	0.81497400	-7.45745700
C	8.77639600	4.46376400	-4.38916500
C	9.63074000	2.85197400	-3.13808000
C	10.27684800	0.66852900	-3.50812300
C	10.29858600	-0.68053200	-5.26099100
C	8.16243100	4.65751700	-6.60441600
C	8.18414900	3.30845100	-8.35728100
C	9.68452800	-0.48680800	-7.47622100
C	8.83016600	1.12497500	-8.72730100
C	8.91992600	5.01573000	-3.05643400
N	8.29076700	5.16442300	-5.39446900
C	9.45985800	3.99708500	-2.26577900
N	10.12358400	1.70667800	-2.71052500
C	10.81828800	-0.59347600	-3.04376500
C	10.83202100	-1.44604800	-4.15156900
N	10.17021500	-1.18744900	-6.47093000

C	7.62912300	5.42307700	-7.71387000
C	7.64283900	4.57049900	-8.82167100
N	8.33736500	2.27028700	-9.15486500
C	9.54098400	-1.03877900	-8.80894800
C	9.00103400	-0.02014000	-9.59959800
C	8.62827900	6.26899600	-2.52430500
C	9.72816900	4.19390900	-0.91369600
C	11.27040600	-1.01765800	-1.79694800
C	11.29837000	-2.75440200	-4.05365900
C	7.16289100	6.73147100	-7.81180800
C	7.19081800	4.99471700	-10.06851100
C	9.83263800	-2.29204300	-9.34107700
C	8.73271300	-0.21696800	-10.95167800
C	8.89508500	6.46855200	-1.17453100
H	8.20793400	7.05684000	-3.14690900
C	9.43801500	5.44424300	-0.37949700
H	10.14868400	3.39536800	-0.30499300
C	11.73665300	-2.32354100	-1.69604800
H	11.25632800	-0.34739900	-0.93928800
C	11.75045700	-3.18083900	-2.81000900
H	11.30567100	-3.41188100	-4.92123500
C	6.71088900	7.15793700	-9.05547800
H	7.15560000	7.38895200	-6.94423400
C	6.72467500	6.30063500	-10.16943600

H	7.20488000	4.32445300	-10.92616700
C	9.56580500	-2.49160800	-10.69084400
H	10.25299500	-3.07988400	-8.71847700
C	9.02285800	-1.46730600	-11.48587500
H	8.31218400	0.58156800	-11.56037900
H	8.68091200	7.43493500	-0.72091700
H	9.63350900	5.63774300	0.67400900
H	12.09876600	-2.69300600	-0.73797400
H	12.12298600	-4.19717500	-2.69246800
H	6.33844200	8.17430200	-9.17303900
H	6.36263100	6.67012400	-11.12752600
H	9.77997200	-3.45799500	-11.14445800
H	8.82734600	-1.66081200	-12.53937600
C	-0.34619900	-0.64530200	-1.37711100
C	-1.19703000	0.42375400	-2.05625600
C	-1.31028600	-0.48132500	-3.31044600
C	-0.47587700	-1.53580700	-2.61912000
C	-1.74664600	-0.41684700	-0.90959500
C	-1.95837800	-1.74224300	-2.76578900
C	-2.67271100	-1.46855100	-1.46609700
H	0.54424500	-0.46995800	-0.78232900
H	0.29371500	-2.17681300	-3.03963700
H	-1.91830900	0.07757200	0.04383200
H	-2.32339700	-2.46492100	-3.49345100

H	-2.71788400	-2.35371400	-0.81674200
H	-3.69156700	-1.08905300	-1.61867400
C	-1.02337500	1.82843600	-1.99893100
N	-0.87640200	2.98365500	-1.94752900
C	-1.33368500	-0.04899100	-4.71706800
C	-0.80471700	-0.86624000	-5.72634300
C	-1.90973700	1.16415600	-5.09157500
C	-0.86083200	-0.48837200	-7.05693300
H	-0.33547700	-1.81529300	-5.46283300
C	-1.96359500	1.56400100	-6.42700100
H	-2.32885300	1.82443900	-4.33215600
C	-1.43990100	0.73346800	-7.41700300
H	-0.44938800	-1.12115300	-7.84159400
H	-2.41416600	2.52208500	-6.67420400
O	-1.43912100	1.02239500	-8.74449800
C	-1.99987200	2.25087600	-9.15415200
H	-1.89489600	2.28773000	-10.24097900
H	-3.06592700	2.31135500	-8.89075100
H	-1.46500200	3.10233100	-8.70894700

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C	-1.52889171	-5.53046445	0.86785290
C	-0.75816980	-6.68324528	0.97221496
C	0.64604369	-6.62234534	0.98820194

C	1.31550130	-5.40692717	0.89998267
C	0.54126448	-4.25444801	0.79410761
C	-0.85618287	-4.31470349	0.77856460
C	0.88906386	-2.85020403	0.68751072
N	-0.24775991	-2.09022081	0.61185571
C	-1.31987559	-2.94533786	0.65925594
N	-2.60027425	-2.63606723	0.59052529
N	2.14214664	-2.43415807	0.65957531
C	-3.02134286	-1.38992562	0.47690656
C	2.45171445	-1.15394641	0.59454755
N	-2.25906853	-0.25115767	0.41681258
C	-3.11372807	0.81046903	0.27775268
C	-4.48573948	0.34162586	0.24369904
C	-4.42723303	-1.04996045	0.37680018
C	3.82450580	-0.68266868	0.61701108
C	3.75724350	0.71278858	0.59345059
C	2.34736810	1.05240528	0.56248600
N	1.58953538	-0.08956689	0.53113452
N	-2.80164301	2.09205917	0.21887534
N	1.92355868	2.29951954	0.58200016
C	-1.55512450	2.51176154	0.31467184
N	-0.41824023	1.74983166	0.39370025
C	0.64366524	2.60678545	0.50862865
C	0.17579563	3.97993042	0.52092704

C	-1.21401275	3.92050563	0.38403392
C	-5.70384027	1.00633504	0.12589497
C	-6.86004060	0.23422088	0.14101429
C	-6.80080312	-1.16405263	0.27407274
C	-5.58395766	-1.82518734	0.39514759
C	0.84327651	5.19629055	0.62639961
C	0.07263063	6.35380535	0.59679269
C	-1.32497222	6.29518400	0.45768921
C	-1.98806158	5.07681194	0.34881033
C	5.04558045	-1.34780360	0.64484715
C	6.19800091	-0.56904991	0.63291093
C	6.13020717	0.83342278	0.59545388
C	4.90705248	1.49563346	0.57888648
H	-2.61683696	-5.56988413	0.85608357
H	-1.24816955	-7.65300011	1.04391123
H	1.21655395	-7.54596777	1.07191231
H	2.40266149	-5.35115131	0.91316668
H	-5.74234887	2.08995681	0.02726536
H	-7.83133380	0.71802613	0.05040741
H	-7.72735327	-1.73589827	0.28404370
H	-5.53014583	-2.90721622	0.50239237
H	1.92763761	5.23411578	0.72282386
H	0.55919600	7.32513353	0.68020189
H	-1.89638708	7.22241742	0.44038228

H	-3.07059524	5.02323994	0.24514815
H	5.09180696	-2.43531601	0.66149000
H	7.17339476	-1.05271390	0.64325016
H	7.05429193	1.40901180	0.57833209
H	4.84355385	2.58270808	0.55071534
Co	-0.32900297	-0.17269639	0.39502231
C	0.63560934	0.71749810	-2.93072105
C	-0.50045826	-0.77582914	-2.18905031
C	0.71950177	-1.57761160	-2.55414772
C	1.58976411	-0.45695232	-3.07347032
C	-0.64073197	0.09675379	-3.39609965
C	0.90627629	-1.44935765	-4.04135210
C	-0.29871898	-0.75162618	-4.62414719
H	-1.37092238	-1.15971822	-1.66367747
H	1.13880084	-2.39280117	-1.97024774
H	-1.52478022	0.73507532	-3.43116138
H	1.52664696	-2.14969214	-4.59644435
H	-0.05547458	-0.14219185	-5.50451762
H	-1.09975902	-1.45847702	-4.87888075
C	0.93140036	2.10805584	-2.78531852
C	-0.07521123	3.08340183	-2.95165612
C	2.24329498	2.57545873	-2.52806009
C	0.19893443	4.43991388	-2.88750324
H	-1.10371352	2.77387565	-3.13281113

C	2.52771170	3.92361947	-2.47878826
H	3.05572570	1.86817669	-2.37033494
C	1.51022606	4.87078253	-2.65500416
H	-0.61408749	5.15131569	-3.01192073
H	3.54014674	4.27483623	-2.28536569
C	3.00057649	-0.47030326	-2.89605155
N	4.15632485	-0.52136350	-2.75821575
O	1.88677178	6.16620059	-2.57924534
C	0.91170795	7.16341130	-2.81376586
H	0.10819133	7.11660081	-2.06403561
H	1.43111926	8.12073512	-2.72942305
H	0.48410778	7.06837234	-3.82196988

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C	-1.82098700	-5.43112600	0.71328900
C	-1.18875700	-6.66463200	0.81293900
C	0.21193500	-6.76166300	0.89538900
C	1.01472900	-5.62746200	0.88008800
C	0.37933700	-4.39163900	0.77911700
C	-1.01449600	-4.29514700	0.69783800
C	0.88393200	-3.03467400	0.73977800
N	-0.15882600	-2.14935000	0.64185200
C	-1.31896200	-2.88233800	0.60582900

N	-2.55312900	-2.42884800	0.48102600
N	2.17395100	-2.75612900	0.79966600
C	-2.82623700	-1.14351800	0.38535300
C	2.62425500	-1.51825100	0.79596600
N	-1.93765400	-0.09451000	0.39894300
C	-2.66251900	1.06062600	0.27657300
C	-4.07505400	0.75048600	0.16703900
C	-4.17864500	-0.64240700	0.23954100
C	4.03319600	-1.20285300	0.93819100
C	4.12296400	0.19193000	0.93913800
C	2.77030000	0.68747500	0.77877700
N	1.89175200	-0.35980700	0.69583400
N	-2.21163300	2.30166300	0.28056100
N	2.49480300	1.97679100	0.74409000
C	-0.93065700	2.57790700	0.40757600
N	0.10979000	1.68958300	0.51377000
C	1.26367600	2.42402200	0.61520000
C	0.95870100	3.84069300	0.55909000
C	-0.42848100	3.93889600	0.43705000
C	-5.20289200	1.55453400	0.02519600
C	-6.43767300	0.91899500	-0.04382800
C	-6.54180700	-0.48093700	0.02957000
C	-5.41406600	-1.28129600	0.17312700
C	1.77076800	4.96915100	0.55994900

C	1.14325900	6.20561800	0.44295300
C	-0.25324600	6.30481600	0.33039700
C	-1.06028000	5.17170500	0.32550600
C	5.16520700	-2.00032000	1.08291000
C	6.38778900	-1.35404200	1.23657200
C	6.47480600	0.04875300	1.24684400
C	5.34347300	0.84204600	1.09170600
H	-2.90471200	-5.34813600	0.65104800
H	-1.78545600	-7.57527800	0.82917200
H	0.67182700	-7.74549100	0.97401200
H	2.09936700	-5.69443800	0.94619300
H	-5.11351800	2.63806100	-0.03006600
H	-7.34296100	1.51344800	-0.15605100
H	-7.52596100	-0.94343200	-0.02650500
H	-5.48691500	-2.36587800	0.23310900
H	2.85323400	4.87956300	0.64068400
H	1.74234300	7.11479700	0.43417000
H	-0.70868500	7.28936400	0.23666600
H	-2.14144500	5.24072000	0.22043400
H	5.08935400	-3.08648500	1.08524100
H	7.29524000	-1.94352100	1.36094700
H	7.44745400	0.52143400	1.38020300
H	5.40295700	1.92950500	1.08799700
Co	-0.02084400	-0.22915500	0.51238900

C	0.53460300	0.87995200	-2.97823800
C	-0.12509200	-0.97646400	-2.34878600
C	1.32248100	-1.26354100	-2.55947400
C	1.83329400	0.09535500	-2.99724300
C	-0.45631900	-0.11778000	-3.52237200
C	1.58549000	-1.00426300	-4.03188700
C	0.25999100	-0.75474200	-4.71652000
H	-0.83479200	-1.48452400	-1.70549900
H	1.91968700	-1.93088400	-1.94243100
H	-1.48670800	0.22329900	-3.63077900
H	2.43760100	-1.45451500	-4.53744600
H	0.34187800	-0.06457600	-5.56621200
H	-0.22815500	-1.68199700	-5.04522000
C	0.25434800	2.21555700	-2.73696400
N	-0.01721000	3.34619300	-2.56657600
C	3.18132400	0.60886700	-2.67358700
C	3.42709100	1.96524700	-2.42511200
C	4.27218000	-0.26491200	-2.63108200
C	4.70809800	2.42519700	-2.15797500
H	2.61137700	2.68707600	-2.43411100
C	5.56326100	0.18255900	-2.37165700
H	4.12451100	-1.33311900	-2.79854900
C	5.78602500	1.53939000	-2.13179800
H	4.88987400	3.47987900	-1.95598100

H	6.37667300	-0.53843800	-2.33956800
O	7.00260000	2.08010100	-1.85473000
C	8.12866800	1.23184100	-1.91447200
H	8.24362400	0.79397100	-2.91706500
H	8.99617900	1.85790800	-1.69195400
H	8.06361000	0.42327400	-1.17062600

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C	0.25713300	-5.52753500	0.62805000
C	1.30485800	-6.43752600	0.71727100
C	2.63440800	-6.00903600	0.86928900
C	2.95242200	-4.65739700	0.93804100
C	1.90223400	-3.75059700	0.83981000
C	0.58051300	-4.17519100	0.68465900
C	1.86702300	-2.30181700	0.84487300
N	0.58065900	-1.85864700	0.66739600
C	-0.22315900	-2.97093200	0.59988700
N	-1.53531800	-3.00465200	0.49261600
N	2.94928600	-1.57667500	1.03513700
C	-2.25795800	-1.90207200	0.42729600
C	2.91419400	-0.26142400	1.00581600
N	-1.80904100	-0.60671000	0.41281100
C	-2.91022100	0.20678000	0.29469900
C	-4.11705100	-0.59465000	0.26001500

C	-3.70397800	-1.92803700	0.34280800
C	4.09777100	0.54345400	1.23350100
C	3.70020600	1.87448400	1.08799100
C	2.28061700	1.84355000	0.79055100
N	1.83364200	0.54467500	0.74833000
N	-2.93173000	1.52139000	0.20924000
N	1.57749700	2.94191100	0.60824400
C	-1.83347200	2.24841000	0.26629400
N	-0.54281800	1.80497900	0.42223400
C	0.26881000	2.90937300	0.43829500
C	-0.52369100	4.11247700	0.28329500
C	-1.85403100	3.69392900	0.17763600
C	-5.46570200	-0.25948400	0.16718500
C	-6.38480600	-1.30234200	0.15722900
C	-5.96867800	-2.64289400	0.23955700
C	-4.62230600	-2.97475400	0.33429400
C	-0.18419000	5.46282600	0.24399600
C	-1.21845000	6.37859000	0.09021600
C	-2.55591200	5.95731300	-0.01609400
C	-2.89272500	4.60969900	0.02860900
C	5.41543200	0.20550500	1.52526600
C	6.32515400	1.24794400	1.66510600
C	5.92676500	2.58756200	1.51698100
C	4.60711800	2.92077300	1.22748400

H	-0.77398300	-5.85418300	0.50586100
H	1.09511800	-7.50448900	0.66368800
H	3.42741100	-6.75249000	0.92920200
H	3.97941100	-4.31319900	1.05080100
H	-5.78153900	0.78042300	0.10475800
H	-7.44836300	-1.08076900	0.08478000
H	-6.71809800	-3.43258700	0.22889000
H	-4.29125800	-4.00972100	0.39936000
H	0.85300000	5.78196300	0.33099100
H	-0.99312900	7.44316200	0.05267100
H	-3.33944600	6.70408800	-0.13390400
H	-3.92600100	4.27595400	-0.04903100
H	5.71750300	-0.83546100	1.62899800
H	7.36687000	1.02426100	1.89232700
H	6.66697400	3.37782700	1.63565800
H	4.29065900	3.95643200	1.11487100
Co	0.02431500	-0.03371400	0.42334600
C	0.00386600	-0.03938500	-1.54174700
C	-0.07411700	-1.38310600	-2.21850400
C	1.36458900	-1.76943400	-2.58271300
C	1.23789600	0.49037200	-2.29089200
C	0.38838500	-1.17243000	-3.62557800
C	0.77462100	0.28867100	-3.75973500
H	1.56746600	1.49869600	-2.02969300

H	0.03416500	-1.79211100	-4.44559400
H	1.58990900	0.45563300	-4.47667300
H	-0.08067600	0.92379700	-4.02768000
C	1.71841100	-3.14867400	-2.66475700
N	1.97459200	-4.28233600	-2.73582600
H	-0.79827900	-2.15807400	-1.97859900
C	2.23503800	-0.63514700	-2.16864700
C	3.64387500	-0.54627800	-2.09365500
C	4.29391300	0.71344800	-2.08787500
C	4.47947700	-1.69299200	-1.98153100
C	5.67096300	0.83376200	-1.97028700
H	3.70279200	1.62442000	-2.17984900
C	5.84583100	-1.57615200	-1.85368900
H	4.03683800	-2.68797100	-1.97135100
C	6.45813700	-0.31281700	-1.83851400
H	6.11535800	1.82661700	-1.96222600
H	6.47543600	-2.45905600	-1.75358200
O	7.80664300	-0.30819500	-1.68281200
C	8.47238000	0.93637600	-1.70824600
H	8.13282900	1.58921100	-0.89044900
H	9.53488700	0.71737000	-1.57852100
H	8.32177000	1.44847900	-2.66975100
H	-0.88696300	0.56474400	-1.76600700

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C	-2.59603200	-5.58538400	1.14352800
C	-1.94375900	-6.79551300	1.34776800
C	-0.54858500	-6.85313400	1.51388100
C	0.22967900	-5.70196000	1.47987800
C	-0.42619400	-4.49077300	1.27272200
C	-1.81353000	-4.43374500	1.10735200
C	0.04944400	-3.12525200	1.18383300
N	-1.00455100	-2.27041100	0.98813800
C	-2.14320000	-3.03567000	0.92166200
N	-3.37877300	-2.62318400	0.71827300
N	1.32850700	-2.81602000	1.28313800
C	-3.68004000	-1.34847400	0.57853600
C	1.74861600	-1.56923500	1.23199000
N	-2.82017200	-0.27694200	0.60338100
C	-3.57486800	0.85545800	0.43965500
C	-4.97418400	0.50571400	0.30107900
C	-5.04087600	-0.88820200	0.38920400
C	3.15115200	-1.22033200	1.34996100
C	3.21499500	0.17321600	1.26901000
C	1.85055900	0.63184300	1.09780900
N	0.99009800	-0.43500000	1.06912300
N	-3.15520800	2.10620800	0.41900300
N	1.54680500	1.91049000	1.00762000

C	-1.88418500	2.41496800	0.56988300
N	-0.82590800	1.55116800	0.72392200
C	0.30569600	2.32039100	0.85027400
C	-0.03360300	3.72597100	0.77178100
C	-1.41715400	3.78744600	0.59217000
C	-6.11990500	1.27720800	0.12351600
C	-7.33426400	0.60680700	0.03421600
C	-7.40177300	-0.79471800	0.12424500
C	-6.25675200	-1.56194900	0.30521500
C	0.74750900	4.87631200	0.81697900
C	0.09430800	6.09487400	0.67274000
C	-1.29798700	6.15790500	0.49339100
C	-2.07518200	5.00551700	0.45296800
C	4.29942100	-1.99066700	1.51084300
C	5.51453600	-1.31763400	1.58531900
C	5.57803700	0.08403800	1.50640000
C	4.42823100	0.85019500	1.34887200
H	-3.67593000	-5.53260600	1.01669000
H	-2.52037500	-7.71844000	1.38182100
H	-0.07289100	-7.81948800	1.67312400
H	1.30990500	-5.73821900	1.61017900
H	-6.05968300	2.36210800	0.05780900
H	-8.25271900	1.17417800	-0.10689800
H	-8.37138000	-1.28469300	0.05167700

H	-6.30175600	-2.64712300	0.37914100
H	1.82658100	4.81562600	0.94944100
H	0.66871200	7.01943100	0.69242300
H	-1.77365300	7.13043000	0.37846800
H	-3.15306100	5.04812300	0.30721500
H	4.24228900	-3.07588500	1.57611300
H	6.43620600	-1.88461700	1.70959400
H	6.54725600	0.57786400	1.56465800
H	4.46941600	1.93604300	1.28273700
Co	-0.90431200	-0.36821700	0.70724000
C	0.04213500	1.35950400	-2.15676100
C	-0.81167100	-0.66462900	-1.23407200
C	0.56292700	-0.93765200	-1.78385400
C	1.13579300	0.37849600	-2.32159900
C	-1.18061000	0.47347300	-2.19702900
C	0.49953700	-0.67957900	-3.25665200
C	-0.91658100	-0.22058900	-3.56326200
H	-1.49028600	-1.51913700	-1.36775700
H	1.24471600	-1.67924500	-1.37330200
H	-2.15261800	0.95918600	-2.08046100
H	1.12955600	-1.20939400	-3.96830000
H	-0.97339500	0.48563700	-4.40206200
H	-1.60561700	-1.05585000	-3.74921100
C	0.02183600	2.71534100	-2.44737700

N	-0.03753000	3.86907100	-2.66677100
C	2.58709700	0.66937300	-2.26563700
C	3.06742700	1.94732000	-1.94929000
C	3.52775800	-0.34369500	-2.46396400
C	4.42547400	2.19483200	-1.83003900
H	2.37482200	2.76844200	-1.76890600
C	4.89583100	-0.11288100	-2.33886900
H	3.19983100	-1.35530200	-2.70751600
C	5.35006300	1.16437900	-2.01014900
H	4.79164300	3.18763900	-1.57251800
H	5.58738700	-0.93923200	-2.48508300
O	6.65653100	1.49495500	-1.83157900
C	7.62190100	0.47867700	-1.98929500
H	7.61037600	0.07031500	-3.01052100
H	8.59174300	0.94520900	-1.80022400
H	7.46517200	-0.33865100	-1.26891600

2_iii

C	-0.46811000	0.24953500	0.43340400
C	0.26858500	-0.87635300	0.78492500
C	1.64594400	-0.79167000	1.05679500
C	2.32433700	0.41902400	0.97508200
C	1.58437000	1.54065200	0.61293900
C	0.21512000	1.46003200	0.35182400

C	1.95569600	2.92652400	0.41653100
N	0.85756000	3.66174900	0.03715300
C	-0.21657300	2.80485400	0.02466300
N	-1.47958700	3.10209100	-0.19517600
N	3.17835900	3.35775200	0.62841400
C	-1.87068900	4.33635900	-0.43282400
C	3.50327600	4.62509200	0.48324900
N	-1.09444200	5.46780300	-0.48719100
C	-1.93013700	6.51794000	-0.78355300
C	-3.29181900	6.04547700	-0.92889700
C	-3.25455500	4.66830700	-0.69769900
C	4.84523300	5.10534300	0.73693300
C	4.80389800	6.49181700	0.56933100
C	3.43553800	6.81762000	0.22109100
N	2.68414100	5.66972100	0.13370800
N	-1.61174500	7.79074500	-0.88994800
N	3.02816100	8.06009100	0.07176300
C	-0.38377800	8.21985600	-0.67208500
N	0.72776100	7.46971000	-0.38232300
C	1.77444500	8.34464000	-0.21358200
C	1.32174700	9.70516100	-0.41196500
C	-0.04161700	9.62617800	-0.71125600
C	-4.48666100	6.70126100	-1.21345500
C	-5.64082200	5.92841600	-1.26806300

C	-5.60222000	4.54177400	-1.03936300
C	-4.40854300	3.89171100	-0.74883700
C	1.98209400	10.93059400	-0.35536100
C	1.23241800	12.07259100	-0.61039100
C	-0.13991200	11.99319100	-0.90898800
C	-0.79707500	10.76994700	-0.96070600
C	6.02369100	4.44851100	1.08244200
C	7.16172800	5.22838100	1.25331900
C	7.11948300	6.62490400	1.09154400
C	5.93993000	7.27704500	0.75125400
H	-1.53521600	0.19347700	0.22591200
H	-0.22794500	-1.84278500	0.85662600
H	2.18855900	-1.69449000	1.33465600
H	3.39284600	0.49286700	1.17325700
H	-4.50863000	7.77535400	-1.38894200
H	-6.59487800	6.40225300	-1.49333300
H	-6.52699800	3.96971800	-1.09318700
H	-4.36910100	2.81860200	-0.57157300
H	3.04363100	10.98366900	-0.11974700
H	1.71236900	13.04936800	-0.57816000
H	-0.69425700	12.91009700	-1.10232900
H	-1.85922400	10.70078000	-1.18881600
H	6.04370300	3.36689000	1.20841400
H	8.10489500	4.75365000	1.51902500

H	8.03071200	7.20294200	1.23657900
H	5.89954700	8.35782800	0.62730200
Co	0.82826500	5.54285900	-0.37438100
C	2.51451800	7.14118700	-2.84350400
C	1.07913300	5.31193600	-2.38469500
C	2.41759800	4.74478100	-2.89817600
C	3.30507100	5.94468700	-3.17499200
C	1.13339100	6.66053000	-3.17763100
C	2.54904500	5.28162900	-4.32331000
C	1.35592700	6.16223500	-4.62846800
H	0.28935400	7.33922200	-3.03292100
H	3.06113600	4.66876700	-5.06208900
H	1.60357500	6.99562400	-5.30032600
H	0.49818700	5.61740400	-5.04319500
C	-0.04084900	4.51728500	-2.84224500
N	-0.92974500	3.89970800	-3.27399300
H	4.38723300	5.89166200	-3.09278300
C	2.96753900	3.38755400	-2.62730300
C	4.30496000	3.19624000	-2.26017900
C	2.17939400	2.24662700	-2.80081700
C	4.82464400	1.92838200	-2.04803700
H	4.95664400	4.05711300	-2.10953000
C	2.67963300	0.96587100	-2.57949200
H	1.14068200	2.34572200	-3.11374500

C	4.01050800	0.80290900	-2.19348500
H	5.86248100	1.78973200	-1.74788000
H	2.01668100	0.11197900	-2.70373200
O	4.59445100	-0.39726400	-1.93674500
C	3.81566500	-1.56148000	-2.11431700
H	3.47366400	-1.65719700	-3.15519200
H	4.46638200	-2.40454900	-1.86956800
H	2.94380000	-1.56664600	-1.44235500
H	2.85589300	8.16679900	-2.96489000

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C	-0.44653400	-5.81271600	1.42704300
C	0.48852100	-6.80271200	1.70781400
C	1.86447900	-6.51850800	1.73664200
C	2.34188100	-5.23700200	1.48388000
C	1.40275600	-4.25125300	1.19496500
C	0.03605000	-4.53383200	1.17088600
C	1.52937300	-2.83871500	0.89436800
N	0.29220900	-2.28765900	0.66541800
C	-0.63142400	-3.28954900	0.84552400
N	-1.94175800	-3.20052900	0.76673000
N	2.69285300	-2.22175000	0.90906400
C	-2.54651500	-2.04495400	0.57077600
C	2.79088400	-0.91815200	0.74193500

N	-1.96697800	-0.81630600	0.41244000
C	-2.98554700	0.09956200	0.30391700
C	-4.26917000	-0.57142400	0.36084700
C	-3.99198000	-1.93066300	0.52239500
C	4.06151000	-0.22779400	0.82170600
C	3.78654400	1.12537000	0.60501200
C	2.35576800	1.22022000	0.40022900
N	1.78036300	-0.02348300	0.49174400
N	-2.88393000	1.40070300	0.15028200
N	1.75652000	2.36916600	0.16109800
C	-1.71519700	2.00436500	0.06482600
N	-0.46861200	1.43604800	0.12438900
C	0.44613300	2.45734600	0.04937800
C	-0.23394700	3.72459100	-0.12478600
C	-1.60255800	3.43745200	-0.10983000
C	-5.57438800	-0.10444200	0.24100300
C	-6.59596000	-1.04753600	0.28516100
C	-6.31800900	-2.41603800	0.44863600
C	-5.01128200	-2.87719500	0.57327400
C	0.23051400	5.03016000	-0.26840800
C	-0.71931600	6.03476600	-0.41152200
C	-2.09545800	5.74469300	-0.40413900
C	-2.55680800	4.44244200	-0.24950400
C	5.35845200	-0.67608200	1.05936800

C	6.37225500	0.27494800	1.06770900
C	6.09598100	1.63643400	0.84967300
C	4.79941700	2.08139600	0.61819700
H	-1.51379800	-6.02421200	1.39845100
H	0.15262200	-7.81900900	1.90723200
H	2.56710700	-7.31965000	1.96044900
H	3.40603800	-5.00865700	1.50635800
H	-5.77890400	0.95634900	0.10360400
H	-7.63158700	-0.72400600	0.18993200
H	-7.14359000	-3.12549900	0.47761200
H	-4.78777200	-3.93563500	0.69556600
H	1.29720300	5.24792400	-0.27021600
H	-0.39575500	7.06742200	-0.53185200
H	-2.80957100	6.55840500	-0.52023700
H	-3.62016500	4.20864000	-0.23777600
H	5.56247300	-1.73160900	1.23088000
H	7.40021100	-0.03567200	1.24745700
H	6.91576000	2.35290600	0.86481800
H	4.57778000	3.13434300	0.45267700
Co	-0.07270100	-0.44948900	0.20343500
C	2.41043700	-0.41456400	-2.17693900
C	0.01642700	-0.64860500	-1.88640800
C	0.62017200	-1.97677700	-2.36327500
C	2.13437000	-1.80570900	-2.55733800

C	1.11418600	0.24109100	-2.55243000
C	1.21195400	-1.71306500	-3.75224000
C	1.02062000	-0.23569800	-4.03315300
H	3.38654600	0.06049700	-2.23112100
H	2.80351300	-2.64806600	-2.40218000
H	1.04109200	1.31925600	-2.39373100
H	1.16750700	-2.49265900	-4.50868900
H	1.84209000	0.17358600	-4.63699300
H	0.06633800	-0.00224900	-4.51873000
C	-1.36158100	-0.38431400	-2.40512000
C	-2.30770700	-1.40399700	-2.56271500
C	-1.76686800	0.91154600	-2.77429300
C	-3.59991400	-1.15745900	-3.01401500
H	-2.06111600	-2.43015100	-2.29327400
C	-3.04202100	1.17621800	-3.24108400
H	-1.06929500	1.74499400	-2.69247800
C	-3.98056000	0.14496900	-3.34282800
H	-4.29944900	-1.98760500	-3.08367200
H	-3.34312800	2.18945900	-3.50396200
O	-5.22071900	0.49948400	-3.75781000
C	-6.21844800	-0.50113800	-3.79084300
H	-6.36978800	-0.94246200	-2.79366800
H	-7.13696000	-0.00455400	-4.11220300
H	-5.96527900	-1.29429900	-4.50875000

C	0.13062300	-3.29759700	-2.14187400
N	-0.22734000	-4.40016100	-2.02646600

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C	0.34196300	-5.50877700	0.57415400
C	1.38795200	-6.41845700	0.68951200
C	2.71573500	-5.98783200	0.84663200
C	3.03293800	-4.63441200	0.89420600
C	1.98429300	-3.72883600	0.77417200
C	0.66379000	-4.15603400	0.61383700
C	1.94493300	-2.27898700	0.77477500
N	0.66074100	-1.84007900	0.59287600
C	-0.14185300	-2.95133400	0.52796300
N	-1.45667900	-2.98570100	0.43886900
N	3.02358500	-1.54891400	0.97520500
C	-2.18569000	-1.88448200	0.40763300
C	2.98516400	-0.23268700	0.94572300
N	-1.74235400	-0.58831200	0.40272400
C	-2.84689000	0.22344200	0.32867000
C	-4.05339300	-0.58114800	0.30772700
C	-3.63438000	-1.91493800	0.35473900
C	4.15761000	0.57596000	1.21686900
C	3.75973900	1.90626500	1.06413700
C	2.34839700	1.87147500	0.72810900

N	1.91142200	0.57063900	0.65931500
N	-2.87285600	1.54058300	0.26562600
N	1.64116200	2.96980500	0.55788800
C	-1.77573500	2.27240900	0.30317700
N	-0.48012500	1.83314000	0.41279300
C	0.32825700	2.93690300	0.41253200
C	-0.47106200	4.14097100	0.28997500
C	-1.80375500	3.71984300	0.22660400
C	-5.40488100	-0.24963500	0.25473400
C	-6.32146400	-1.29521600	0.24716600
C	-5.89961400	-2.63536700	0.29322100
C	-4.54982400	-2.96388800	0.34844500
C	-0.13703400	5.49236300	0.24988700
C	-1.17802300	6.40728400	0.13823800
C	-2.51694600	5.98358100	0.07369700
C	-2.84840500	4.63422200	0.11933600
C	5.46288100	0.24260400	1.56468700
C	6.36048500	1.28773200	1.75328400
C	5.96278200	2.62702400	1.59573300
C	4.65552700	2.95553300	1.25067700
H	-0.68844400	-5.83744600	0.45042500
H	1.17760800	-7.48609400	0.65327800
H	3.50808200	-6.73000800	0.92894900
H	4.05878900	-4.28874400	1.01534300

H	-5.72549100	0.79022100	0.22102400
H	-7.38715100	-1.07556000	0.20595600
H	-6.64656000	-3.42753100	0.28624000
H	-4.21406600	-3.99877500	0.38637700
H	0.90169500	5.81391000	0.30499100
H	-0.95622700	7.47272200	0.10195900
H	-3.30606100	6.72904100	-0.01117800
H	-3.88304500	4.29836500	0.07488500
H	5.76451000	-0.79795300	1.67644800
H	7.39135000	1.06724300	2.02899200
H	6.69262300	3.41993600	1.75478100
H	4.33833100	3.99074600	1.13552400
Co	0.09625800	-0.01061100	0.36994100
C	-0.03057100	-0.00178800	-1.75489200
C	-0.35453800	-1.27576600	-2.35635300
C	1.41603000	-1.83107400	-2.88532700
C	1.17865400	0.42314900	-2.63250200
C	0.24075200	-1.34260300	-3.70762200
C	0.60752800	0.09806100	-4.03894900
H	1.53579800	1.44393700	-2.47924100
H	-0.17430300	-2.02644800	-4.44708700
H	1.36135500	0.18174400	-4.83271500
H	-0.27098700	0.70421500	-4.29473100
C	1.71381000	-3.21019500	-2.79610000

N	1.92518100	-4.35645400	-2.74608500
H	-1.04065300	-2.02925400	-1.97537900
C	2.18233800	-0.70227600	-2.49798500
C	3.56820300	-0.59401700	-2.16983400
C	4.19763200	0.66781400	-2.12256000
C	4.39084500	-1.72911900	-1.95306900
C	5.55901500	0.80492900	-1.89307500
H	3.61210900	1.57190200	-2.28387800
C	5.73840400	-1.59974200	-1.70021900
H	3.95632800	-2.72765300	-1.96393600
C	6.33903200	-0.33159500	-1.66888600
H	5.99256200	1.80180100	-1.86575000
H	6.36049600	-2.47443100	-1.51726200
O	7.66634500	-0.31193800	-1.40770700
C	8.32370100	0.93972800	-1.38957200
H	7.90944800	1.59460000	-0.60817200
H	9.37262700	0.72888900	-1.16913600
H	8.25040600	1.43941200	-2.36604100
H	-0.86201900	0.71125100	-1.74311500

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C	-2.58216000	-5.52729800	1.26586500
C	-1.93346800	-6.73526300	1.49301300
C	-0.53543300	-6.79723100	1.63170200

C	0.24866600	-5.65267700	1.54675500
C	-0.40334900	-4.44324300	1.31726400
C	-1.79421500	-4.38189000	1.17929600
C	0.07821500	-3.08396300	1.17654300
N	-0.97539100	-2.22945800	0.97905300
C	-2.11877100	-2.98783300	0.95652000
N	-3.35511100	-2.57419800	0.74761400
N	1.36196700	-2.77835800	1.23052900
C	-3.65466800	-1.30351000	0.57191300
C	1.78726100	-1.53449300	1.14430200
N	-2.79405300	-0.23231900	0.57434200
C	-3.54419900	0.89650200	0.38979700
C	-4.94389100	0.54663400	0.24330600
C	-5.01421300	-0.84528000	0.36091700
C	3.19303200	-1.18800200	1.23415300
C	3.25662600	0.20664400	1.15846400
C	1.88869100	0.66654100	1.01191800
N	1.03036000	-0.39911100	0.98463000
N	-3.12447700	2.14853900	0.38493300
N	1.57837800	1.94810700	0.96688400
C	-1.85507800	2.45494500	0.55412200
N	-0.79004400	1.59141400	0.64841400
C	0.33434700	2.35856500	0.83757800
C	-0.01797000	3.76397900	0.86509000

C	-1.40021000	3.82623000	0.68041500
C	-6.08660500	1.31622600	0.04218600
C	-7.30219800	0.64670700	-0.04264400
C	-7.37330600	-0.75216100	0.07619600
C	-6.23097200	-1.51760900	0.28256800
C	0.75082600	4.91472000	0.99904200
C	0.08666200	6.13501800	0.93790500
C	-1.30440000	6.19806600	0.75388700
C	-2.06945800	5.04350200	0.62524900
C	4.34271200	-1.95943500	1.38091300
C	5.55941900	-1.28822300	1.44750400
C	5.62290200	0.11383100	1.37747200
C	4.47197900	0.88102100	1.23383700
H	-3.66418600	-5.47113400	1.15967000
H	-2.51508700	-7.65277500	1.56705400
H	-0.06226800	-7.76149100	1.81042300
H	1.33119300	-5.69261300	1.65578400
H	-6.02344900	2.39950600	-0.04476100
H	-8.21827800	1.21305300	-0.20240300
H	-8.34334700	-1.24183800	0.00673100
H	-6.27923400	-2.60082400	0.38030300
H	1.82955300	4.85545600	1.13464800
H	0.65211100	7.06092400	1.02977400
H	-1.78928000	7.17180500	0.70685200

H	-3.14688300	5.08576400	0.47577400
H	4.28486500	-3.04479400	1.44401900
H	6.48164300	-1.85674000	1.56173700
H	6.59215400	0.60806000	1.43368900
H	4.51535300	1.96748000	1.17591000
Co	-0.87268600	-0.32966700	0.64707000
C	0.01081900	1.27710400	-2.42050900
C	-0.84077600	-0.74370900	-1.38745000
C	0.45662600	-1.17630700	-1.88322500
C	1.13435000	0.45019200	-2.65819000
C	-1.17789900	0.33566700	-2.44351700
C	0.58839400	-0.79822000	-3.30884700
C	-0.83219700	-0.44269200	-3.73717100
H	-1.58556400	-1.54597700	-1.32003500
H	1.17771400	-1.80768200	-1.36893100
H	-2.16857100	0.79450500	-2.38654100
H	1.25125400	-1.36871000	-3.95965700
H	-0.86657100	0.19119500	-4.63253900
H	-1.45922700	-1.33194300	-3.88551200
C	-0.07668600	2.66132400	-2.31172200
N	-0.19562500	3.82853900	-2.28840900
C	2.55653600	0.73424300	-2.46708200
C	3.00105200	1.99301800	-2.02349500
C	3.52430300	-0.25454100	-2.67892100

C	4.34241200	2.24130200	-1.80517500
H	2.28887900	2.79497600	-1.83546200
C	4.87586200	-0.02489600	-2.44040400
H	3.22696400	-1.24832800	-3.01395000
C	5.29012400	1.22959200	-1.99126300
H	4.68058400	3.21584600	-1.45599800
H	5.58598300	-0.83407600	-2.59252500
O	6.57208600	1.55584600	-1.69696600
C	7.56363000	0.56306200	-1.85626300
H	7.63013900	0.23004600	-2.90203100
H	8.50918500	1.02653000	-1.56519800
H	7.36732100	-0.30376200	-1.20736900

3

Co	9.23050000	1.98849000	-5.93270200
N	9.21157900	3.16199400	-4.40793800
N	9.97366700	0.58645400	-4.84441300
N	8.48731800	3.39052300	-7.02098600
N	9.24938500	0.81497400	-7.45745700
C	8.77639600	4.46376400	-4.38916500
C	9.63074000	2.85197400	-3.13808000
C	10.27684800	0.66852900	-3.50812300
C	10.29858600	-0.68053200	-5.26099100

C	8.16243100	4.65751700	-6.60441600
C	8.18414900	3.30845100	-8.35728100
C	9.68452800	-0.48680800	-7.47622100
C	8.83016600	1.12497500	-8.72730100
C	8.91992600	5.01573000	-3.05643400
N	8.29076700	5.16442300	-5.39446900
C	9.45985800	3.99708500	-2.26577900
N	10.12358400	1.70667800	-2.71052500
C	10.81828800	-0.59347600	-3.04376500
C	10.83202100	-1.44604800	-4.15156900
N	10.17021500	-1.18744900	-6.47093000
C	7.62912300	5.42307700	-7.71387000
C	7.64283900	4.57049900	-8.82167100
N	8.33736500	2.27028700	-9.15486500
C	9.54098400	-1.03877900	-8.80894800
C	9.00103400	-0.02014000	-9.59959800
C	8.62827900	6.26899600	-2.52430500
C	9.72816900	4.19390900	-0.91369600
C	11.27040600	-1.01765800	-1.79694800
C	11.29837000	-2.75440200	-4.05365900
C	7.16289100	6.73147100	-7.81180800
C	7.19081800	4.99471700	-10.06851100
C	9.83263800	-2.29204300	-9.34107700
C	8.73271300	-0.21696800	-10.95167800

C	8.89508500	6.46855200	-1.17453100
H	8.20793400	7.05684000	-3.14690900
C	9.43801500	5.44424300	-0.37949700
H	10.14868400	3.39536800	-0.30499300
C	11.73665300	-2.32354100	-1.69604800
H	11.25632800	-0.34739900	-0.93928800
C	11.75045700	-3.18083900	-2.81000900
H	11.30567100	-3.41188100	-4.92123500
C	6.71088900	7.15793700	-9.05547800
H	7.15560000	7.38895200	-6.94423400
C	6.72467500	6.30063500	-10.16943600
H	7.20488000	4.32445300	-10.92616700
C	9.56580500	-2.49160800	-10.69084400
H	10.25299500	-3.07988400	-8.71847700
C	9.02285800	-1.46730600	-11.48587500
H	8.31218400	0.58156800	-11.56037900
H	8.68091200	7.43493500	-0.72091700
H	9.63350900	5.63774300	0.67400900
H	12.09876600	-2.69300600	-0.73797400
H	12.12298600	-4.19717500	-2.69246800
H	6.33844200	8.17430200	-9.17303900
H	6.36263100	6.67012400	-11.12752600
H	9.77997200	-3.45799500	-11.14445800
H	8.82734600	-1.66081200	-12.53937600

C	-1.36958400	0.27237400	-2.21741500
C	-1.45885700	-0.50551700	-3.32931200
C	-1.46438200	-1.95189300	-2.81085000
C	-2.27462100	-1.74765400	-1.51252300
C	-1.30333100	-0.66690700	-0.99886300
C	0.01037400	-1.44406500	-1.11116300
C	-0.08604300	-2.21428100	-2.19857600
H	-1.83351700	-2.69880800	-3.51947200
H	-2.29807000	-2.64570900	-0.88329300
H	-3.29178400	-1.37265300	-1.68393700
H	-1.51480700	-0.19312000	-0.03650800
H	0.66887700	-2.86092100	-2.63763400
H	0.86298100	-1.31580300	-0.45044300
C	-1.22353500	1.66970200	-2.12249700
N	-1.10924100	2.82639900	-2.00656700
C	-1.47054200	-0.15377500	-4.73684900
C	-1.12015600	-1.10834400	-5.71066000
C	-1.81349500	1.13168400	-5.18086900
C	-1.09646700	-0.78881500	-7.05502200
H	-0.83883500	-2.11575600	-5.40643300
C	-1.80487600	1.46331400	-6.52920800
H	-2.10918100	1.89304600	-4.46088400
C	-1.44058800	0.50090000	-7.47642000
H	-0.81364800	-1.52388000	-7.80617500

H	-2.08579700	2.46982600	-6.82835800
O	-1.39527200	0.71906800	-8.80914400
C	-1.72275900	2.00808500	-9.29082900
H	-1.61235400	1.96278700	-10.37635100
H	-2.75962100	2.27360800	-9.04169600
H	-1.03970600	2.76815900	-8.88682900

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