

Electronic Supplementary Information

Light Swing CO₂ Capture: Photoirradiation-Type Chemical CO₂ Release Based on Photoisomerization of Azobenzene-Amine/Guanidine Derivatives

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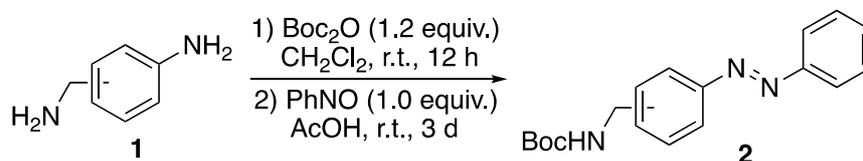
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1. Instrumentation and Chemicals

^1H (400 MHz), ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Bio Spin Inc., Ascend 400 spectrometer. Chemical shifts values for ^1H , ^{13}C NMR spectra are referenced to Me_4Si . Chemical shifts are reported in δ ppm. High-resolution mass spectra were recorded on a Bruker micrOTOF-Q mass spectrometer. IR spectra were measured with a Thermo ScientificTM NicoletTM iSTTM 5 FT-IR. UV spectra were measured with a JASCO V-750 spectrophotometer. Elemental analysis was measured J-Science Lab Micro Corder JM-10 at the Research Institute for Instrumental Analysis, Advanced Science Research Center, Kanazawa University. Single-crystal X-ray data were collected on a Dual Thickness MicroLoops (MiTeGen, 50 mm in diameter) with a XtaLAB mini II (Rigaku), Dualflex, HyPix diffractometer. □ Concentration of CO_2 was measured with Good ability GC-02 (sealed space). Oil-free air compressor (SILENTAIR, SA2000S) and mass flow controller (Fujikin, FCS-T1000L) were used. CO_2 concentration was monitored by using nondispersive infrared CO_2 meters (VAISALA, GMP252). 3 UV Multi-Wavelength Lamp (analytik Jena) was used as the light source. Biotage Selekt was used for Silica-gel column chromatography. Flash cartridge (Sfär Silica HC D High Capacity Duo 20 μm) was used for column chromatography. TLC analysis were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Commercially available 2-Aminobenzylamine (Tokyo Chemical Industry), 3-Aminobenzylamine (FUJIFILM Wako Pure Chemical Industry), Di-*t*-butyl Dicarboxylate (Boc_2O , WATANABE Chemical Industry), Nitrosobenzene (Aldrich), Acetic Acid (Tokyo Chemical Industry), Trifluoroacetic Acid (Tokyo Chemical Industry), 4-Nitroaniline (Aldrich), Hydrochloric Acid (FUJIFILM Wako Pure Chemical Industry), Sodium Nitrite (Tokyo Chemical Industry), N,N-Dimethylaniline (Tokyo Chemical Industry), Sodium hydroxide (Kishida Chemical), Sodium Sulfide (Na_2S , FUJIFILM Wako Pure Chemical Industry), Hydrogen Chloride in 1,4-Dioxane Solution (FUJIFILM Wako Pure Chemical Industry), Cyanamide (FUJIFILM Wako Pure Chemical Industry) were employed for reactions. All other chemicals and solvents were purchased from commercial sources and used without further purification.

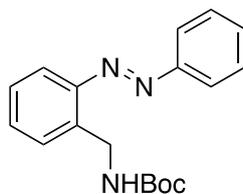
2. Preparation of Azobenzene Derivatives

2.1. General Procedure for Azobenzene-Amines (**o-3a** and **m-3b**)¹



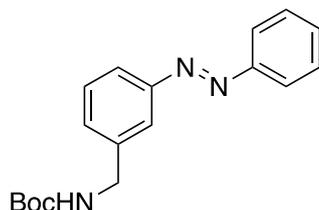
In a nitrogen gas atmosphere, Aminobenzylamine **1** (7.32 g, 60 mmol), CH_2Cl_2 (70 mL) were placed in 200 mL flask containing a magnetic stirring bar. The flask was sealed with a Precision Seal Septa. Boc_2O (15.7 g, 72 mmol) in CH_2Cl_2 (72 mL) solution was slowly added to the mixture using a syringe at 0 °C. The mixture was stirred at room temperature until the starting material had been consumed (TLC monitoring). The solvent was concentrated to dryness under reduced pressure. The resulting product was used to the next reaction without further purification. Then, in a nitrogen gas atmosphere, Boc-protected product (2.23 g, 10 mmol), nitroso benzene (1.07 g, 10 mmol) and acetic acid (5 mL) were placed in 100 mL flask containing a magnetic stirring bar. The flask was sealed with a Precision Seal Septa. After stirring for 3 days at room temperature, the reaction mixture was neutralized with 1M NaOH aq and the mixture was extracted with AcOEt. The combined organic layers were washed twice with 1M NaOH aq, water, brine, and concentrated to dryness. The residue was purified by Silica-gel column chromatography to afford **2**.

Tert-butyl (*E*)-[2-(phenyldiazenyl)benzyl]carbamate (**2a**)

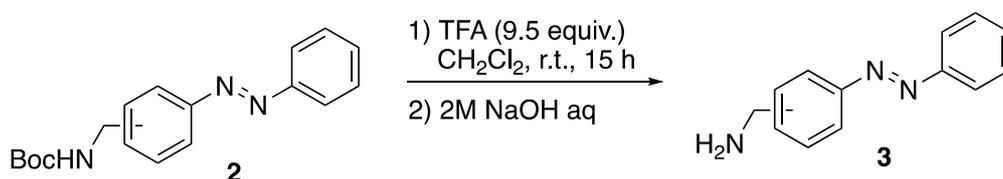


Compound **2a** was an orange solid (60% yield). ¹H NMR (CDCl_3) δ 1.36 (s, 9H), 4.74 (s, 2H), 5.00 (br, 1H), 7.29 (td, $J = 7.8, 1.2$ Hz, 1H), 7.34 (td, $J = 7.8, 1.2$ Hz, 1H), 7.41-7.47 (m, 4H), 7.63 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.83 (dd, $J = 8.4, 1.6$ Hz, 2H). ¹³C NMR (CDCl_3) δ 28.4, 41.0, 79.4, 115.8, 123.0, 128.2, 129.1, 129.6, 131.2, 131.4, 137.9, 149.9, 152.7, 155.8. IR (ATR): 2359, 2341, 1686, 1653, 1526, 1506, 1388, 1363, 1166, 776 cm^{-1} .

Tert-butyl (*E*)-[3-(phenyldiazenyl)benzyl]carbamate (**2b**)

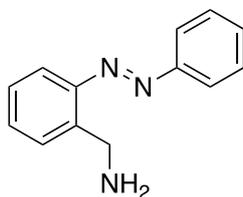


Compound **2b** was an orange solid (60% yield). $^1\text{H NMR}$ (CDCl_3): δ 1.49 (s, 9H), 4.43 (s, 2H), 5.02 (br, 1H), 7.41–7.42 (m, 1H), 7.47–7.56 (m, 4H), 7.83–7.85 (m, 2H), 7.92–7.94 (m, 2H). $^{13}\text{C NMR}$ (CDCl_3): δ 28.4, 44.4, 79.6, 121.2, 122.2, 122.8, 129.1, 129.3, 129.9, 131.1, 140.1, 152.5, 152.8, 155.9. IR (ATR): 2360, 2341, 1700, 1675, 1558, 1540, 1533, 1456, 1168, 766 cm^{-1} .



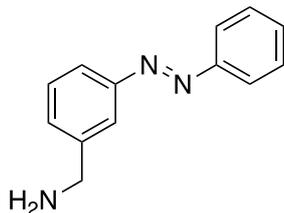
In a nitrogen gas atmosphere, **2** (1.8 g, 5.8 mmol), CH_2Cl_2 (15 mL) were placed in 100 mL flask containing a magnetic stirring bar. TFA (4.2 mL, 9.5 equiv.) was added to the flask was sealed with a Precision Seal Septa using a syringe. After stirring at room temperature for 1 day, solvent was concentrated to dryness under reduced pressure. The residue was dissolved in AcOEt and the solution was neutralized with 2M NaOH aq. The mixture was extracted with AcOEt and the combined organic layers were washed with 1M NaOH and brine. The organic phase was dried by Na_2SO_4 and concentrated to dryness under reduced pressure to afford **3**.

(E)-[2-(phenyldiazenyl)phenyl]methanamine (o-3a).



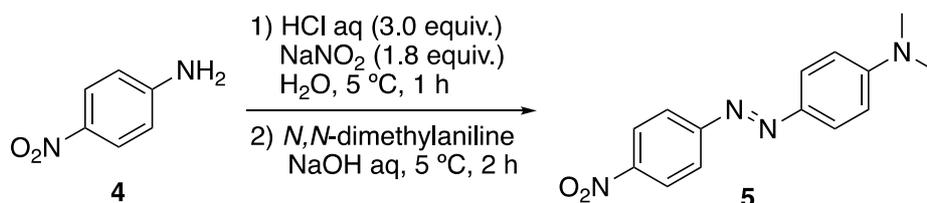
Compound **o-3a** was an orange liquid (97% yield). UV-vis (CH_2Cl_2): $\lambda_{\text{max}} = 326 \text{ nm}$. $^1\text{H NMR}$ (CDCl_3): δ 1.66 (br, 2H), 4.31 (s, 2H), 7.34–7.38 (m, 1H), 7.43–7.55 (m, 5H), 7.72 (d, $J = 8.4 \text{ Hz}$, 1H), 7.92 (d, $J = 8.4 \text{ Hz}$, 2H). $^{13}\text{C NMR}$ (CDCl_3): δ 43.7, 115.9, 123.2, 127.9, 129.26, 129.30, 131.3, 131.6, 142.8, 150.1, 152.9. IR (ATR): 3365, 2933, 1960, 1597, 1451, 1297, 1150, 1070 cm^{-1} .

(E)-[3-(phenyldiazenyl)phenyl]methanamine (m-3b).

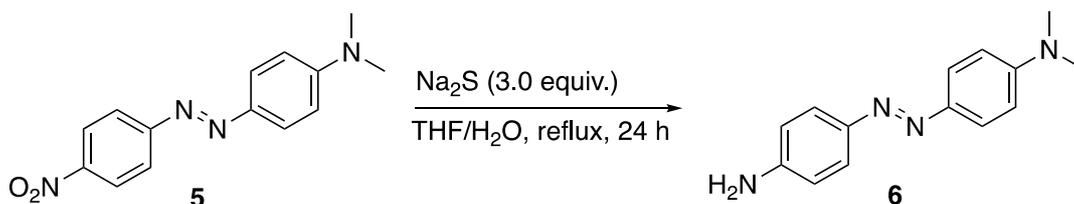


Compound **m-3b** was an orange liquid (94% yield). **UV-vis** (CH_2Cl_2): $\lambda_{\text{max}} = 321 \text{ nm}$. **^1H NMR** (CDCl_3): δ 1.52 (br, 2H), 3.99 (s, 2H), 7.44 (d, $J = 7.2 \text{ Hz}$, 1H), 7.49 (t, $J = 7.2 \text{ Hz}$, 2H), 7.48–7.54 (m, 2H), 7.81 (d, $J = 7.6 \text{ Hz}$, 1H), 7.87 (s, 1H), 7.92 (d, $J = 7.6 \text{ Hz}$, 2H). **^{13}C NMR** (CDCl_3): δ 46.4, 120.9, 122.1, 123.0, 129.2, 129.4, 129.9, 131.2, 144.7, 152.8, 153.1. **IR** (ATR): 3365, 2856, 1585, 1446, 1304, 1150, 1070, 1019 cm^{-1} .

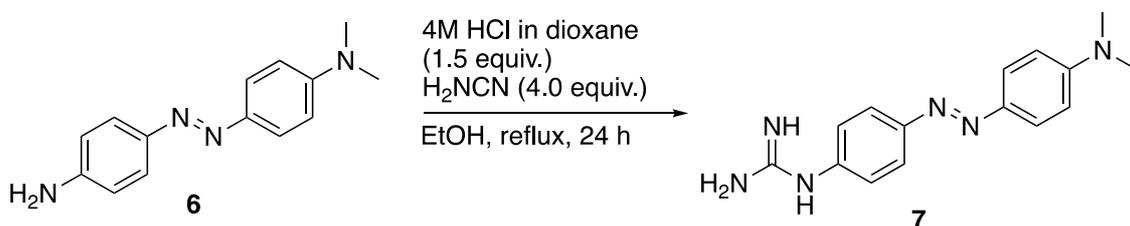
2.2 General Procedure for Azobenzene-Guanidine 7



4-nitroaniline **4** (6.9 g, 50 mmol), water (90 mL) and 36 wt% HCl aq (13 mL, 150 mmol) were placed in 500 mL flask containing a magnetic stirring bar. The mixture was stirred at room temperature for 30 minutes. After stirred mixture cooled at 5 °C and was dropwise added Sodium Nitrite (6.2 g, 90 mmol) as an aqueous solution. The mixture was further stirred at 5 °C for 1 hour. Then, *N,N*-dimethylaniline (6.4 mL, 50.5 mmol) and 10 wt% NaOH aq (36 mL, 90 mmol) slow added to the mixture. After stirring at 5 °C for 1.5 hours, allowed to stand for 2 hours at 5 °C. The residue was filtered on a Büchner funnel and sucked as dry as possible. Dried reddish brown solid washed with AcOH (100mL) on a Büchner funnel and dried under reduced pressure to afford **5** as a reddish brown solid in 78% yield². **^1H NMR** (400 MHz, d-DMSO): δ 3.11 (s, 6H), 6.88 (d, $J = 9.2 \text{ Hz}$, 2H), 7.86 (d, $J = 9.2 \text{ Hz}$, 2H), 7.93 (d, $J = 9.2 \text{ Hz}$, 2H), 8.35 (d, $J = 9.2 \text{ Hz}$, 2H). **^{13}C NMR** (100 MHz, d-DMSO): δ 39.5, 111.5, 122.2, 124.6, 125.5, 142.8, 146.8, 153.4, 156.1.



5 (5.4 g, 20 mmol), solvent (160 mL, THF 75%, H₂O 25%) and Na₂S (4.7 g, 60 mmol) were placed in 300 mL flask containing a magnetic stirring bar. The mixture was refluxed at 95 °C for 24 hours. The residue was concentrated to dryness under reduced pressure, filtered on a Büchner funnel. The product was dried in vacuo to afford **6** as a reddish brown solid in 78% yield². **¹H NMR** (400 MHz, DMSO-d₆): δ 3.00 (s, 6H), 5.70 (s, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 9.2 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H). **¹³C NMR** (100 MHz, d-DMSO): δ 39.5, 111.5, 122.2, 124.6, 125.5, 142.8, 146.8, 153.4, 156.1.



6 (4.7 g, 19.6 mmol), ethanol (20 mL), Cyanamide (1.65 g, 39.2 mmol) and 4 M HCl in dioxane (4.9 mL 19.6 mmol) were placed in 100 mL flask containing a magnetic stirring bar. The mixture was refluxed at 95 °C for 24 hours. Then Cyanamide (1.65 g, 39.2 mmol) and 4 M HCl in dioxane (4.9 mL 19.6 mmol) added to the mixture. After refluxing for 3 hours, the mixture was added CH₂Cl₂ (100 mL) and 1M NaOH aq (250 mL) just then precipitate solid. The solid was collected to afford 4-Guanidino-4'-dimethylaminoazobenzene **7** as an orange solid in 53% yield. **UV-vis** (DMSO): λ_{max} = 457 nm. **¹H NMR** (400 MHz, DMSO-d₆): δ 3.02 (s, 6H), 5.38 (br, 4H), 6.81 (dd, *J* = 2.0, 9.2 Hz, 2H), 6.90 (dd, *J* = 2.0, 8.8 Hz, 2H), 7.65 (dd, *J* = 2.0, 8.8 Hz, 2H), 7.71 (dd, *J* = 2.0, 9.2 Hz, 2H). **¹³C NMR** (125 MHz, d-DMSO): δ 39.8, 111.6, 122.9, 123.0, 123.7, 142.9, 146.0, 151.6, 152.8, 153.4. **IR** (ATR): 1661, 1600, 1549, 1362, 1303, 1152, 865, 826. **HRMS-ESI** (*m/z*): [M+H]⁺ Calcd for C₁₅H₁₈N₆, 283.1665; found 283.1668.

3. Experimental Procedures

3.1. General Procedure for CO₂ Absorption Experiment on Scale

Aminomethylated azobenzene derivatives **3** (2.11 g, 10 mmol) was set on the petri dish. The increment was measured with scale. The results are summarized in Figure 2b, Table S1.

Table S1. Increment of *o*-**3a** and *m*-**3b** in air.

time (h)	increment (g)	
	<i>o</i> - 3a	<i>m</i> - 3b
0	0	0
2	0.08	0.07
4	0.14	0.12
6	0.14	0.16
8	0.15	0.17
10	0.15	0.17
12	0.16	0.18
14	0.16	0.18
16	0.16	0.17
18	0.16	0.18

3.2. General Procedure for CO₂ Absorption Experiment in Elemental Analysis

Amine **3** (2.11 g, 10 mmol) was set on the petri dish. The sample was allowed to set overnight in a desiccator (35.7 L) under 1 vol% CO₂ and 99 vol% N₂ gas atmospheres. CO₂-absorbed amino methyl azobenzene **3** was measured for elemental analysis. The results are summarized in Figure 2c and Table S2.

Table S2. CO₂ absorption under 1 vol% CO₂ and 99 vol% N₂ gas atmospheres

Amine		Elemental analysis (%)		
		C	H	N
<i>o</i> - 3	calcd.	69.51	5.62	18.01
	found	69.51	5.55	18.05
<i>m</i> - 3	calcd.	69.51	5.62	18.01
	found	69.66	5.57	18.02

Amine **3** (2.11 g, 10 mmol) was set on the petri dish. The sample was allowed to set overnight in air. CO₂-absorbed amino methyl azobenzene **3** was measured for elemental analysis three times. The results are summarized in Figure 2d and Table S3.

Table S3. CO₂ absorption in air

Amine		Elemental analysis (%)		
		C	H	N
<i>o</i> - 3	calcd.	70.32	5.73	18.36
	found	70.72	5.73	18.32
<i>m</i> - 3	calcd.	70.32	5.73	18.36
	found	70.35	5.77	18.2

3.3. General Procedure for Measurement of UV-vis Absorption Spectra

UV-vis spectra of CO₂-absorbed aminomethylazobenzene **3** (1.0×10⁻⁵ M) were recorded using CH₂Cl₂ as a solvent (Figure 3a). UV-vis spectra of CO₂-absorbed azobenzene-guanidine **7** (1.0×10⁻⁵ M) were recorded using DMSO as a solvent (Figure 5a). The corresponding absorption spectra were measured on a JASCO V-750 spectrophotometer using a screw-top quartz cuvette (10 × 10 mm, 3.5 mL).

3.4. General Procedure for CO₂ Desorption of CO₂-Absorbed Azobenzene-Amines under UV Irradiation

Test tube in CO₂-absorbed aminomethylazobenzene (*o*-**3a** and *m*-**3b**; amine : CO₂ = 5 : 2; derived from **3** in 10 mmol) put on the UV lamp (λ = 302 nm). The flow rate of nitrogen gas was set to 200 ml/min using a mass flow controller (MFC), and the CO₂ concentration at the outlet side was measured over time for 12 h while nitrogen gas flowed through the test tube. The CO₂ concentration was measured by CO₂ monitor for 15 h. The results are summarized in Figure 3c and Table S4.

Table S4. CO₂ concentration using CO₂ releasing measurement device.

time (h)	CO ₂ conc. (ppm)	
	<i>o</i> - 3a	<i>m</i> - 3b
0	2	2
1	58	52
2	72	82
3	62	76
4	52	82
5	48	68
6	46	52
7	36	48
8	32	32
9	28	12
10	12	6
11	4	8
12	2	8

3.5. General Procedure for 1 vol% CO₂ Absorption of Azobenzene-Guanidine **7**

A mixed gas containing 1 vol% CO₂ and 99 vol% N₂ was flowed into azobenzene-guanidine **7** (7.6 mmol) in MeOH at a speed of 20 mL per minute by mass flow controller (MFC), and the resulting CO₂ concentration on the outlet side was measured over time. The results are summarized in Figure 4c and Table S5.

Table S5. CO₂ concentration on the outlet side.

time (min)	CO ₂ conc. (ppm)
0	10000
0.5	2342
0.75	1756
1	2352
1.5	3070
2	3280
2.5	3386
3	3480
3.5	3598
4	3726
4.5	3884
5	4098
5.5	4418
6	4798
6.5	5252
7	5752
7.5	6294
8	6896
8.5	7448
9	7928
9.5	8350
10	8712
10.5	8972
11	9188
11.5	9364
12	9444
12.5	9534
13	9610
13.5	9640
14	9684
14.5	9690
15	9690
15.5	9714
16	9700
16.5	9620
17	9560

3.6. General procedure for CO₂ desorption of CO₂-absorbed azobenzene-guanidine **7** under blue light irradiation

Separable flask in CO₂-absorbed azobenzene-guanidine **7** (amine : CO₂ : MeOH = 1 : 1 : 1; derived from **7** (7.6 mmol)) put on the Blue LED (440 nm). The flow rate of nitrogen gas was set to 50 ml/min using a mass flow controller (MFC), and the CO₂ concentration at the outlet side was measured over time for 6 h while nitrogen gas flowed through the separable flask. The results are summarized in Figure 5c and Table S6.

Table S6. CO₂ concentration on the outlet side.

time (min)	CO ₂ conc. (ppm)
10	2568
20	3346
30	3644
40	3608
50	3482
60	3326
70	3124
80	2888
90	2640
100	2388
110	2156
120	1932
130	1726
140	1540
150	1384
160	2568
170	3346
180	3644
190	3608
200	3482
210	3326
220	3124
230	2888
240	2640
250	2388
260	2156
270	1932
280	1726
290	1540
300	1384

3.7. General Procedure for CO₂ Desorption of CO₂-Absorbed Azobenzene-Guanidine **7 under Thermal Condition without Photoirradiation**

Separable flask in CO₂-absorbed azobenzene-guanidine **7** (amine : CO₂ : MeOH = 1 : 1 : 1; derived from **7** (7.6 mmol)) put on oil bath. Nitrogen gas was flowed into the separable flask at a rate of 50 mL/min using a mass flow controller (MFC), gradually heated (10 °C/30 min), and the CO₂ concentration at the outlet side was measured over time. The results are summarized in Figure 5d and Table S7.

Table S7. CO₂ concentration on the outlet side.

time (min)	CO ₂ conc. (ppm)	temp (°C)
10	16	30
20	18	30
30	16	30
40	20	40
50	20	40
60	24	40
70	30	50
80	30	50
90	30	50
100	40	60
110	46	60
120	50	60
130	90	70
140	106	70
150	130	70
160	190	80
170	240	80
180	490	80
190	872	90
200	1234	90
210	2346	90
220	3240	100
230	3832	100
240	4092	100
250	4058	100
260	3842	100
270	3520	100
280	3114	100
290	2708	100
300	2332	100
310	1972	100
320	1644	100
330	1364	100
340	1124	100
350	912	100
360	732	100
370	586	100
380	476	100
390	380	100
400	306	100

time (min)	CO ₂ conc. (ppm)	temp (°C)
410	244	100
420	202	100
430	166	100
440	136	100
450	110	100
460	94	100
470	74	100
480	64	100
490	54	100
500	50	100
510	46	100
520	40	100
530	40	100
540	36	100
550	34	100
560	30	100
570	24	100
580	20	100
590	24	100
600	24	100

3.8. General Procedure for Recyclable Visible Light Swing CO₂ Capture using Azobenzene-Guanidine **7** in Air

Air was flowed into 0.2 M of Azobenzene-guanidine **7** (10 mmol) ethanol solution in separable flask at a speed of 100 mL per minute by mass flow controller (MFC), and the resulting CO₂ concentration at the outlet side was measured over time. After CO₂ absorption, the separable flask was placed under a nitrogen atmosphere. The CO₂-absorbed azobenzene-guanidine **7** in ethanol solution was irradiated with a blue light LED (Kessil PR 160L, 440 nm) by flowing N₂ gas at a speed of 50 mL per minute by MFC, and the resulting CO₂ concentration at the outlet side was measured over time. The results of investigating CO₂ absorption and release in three repeated cycles are summarized in Scheme 2, Table S8 and S9.

Table S8. CO₂ concentration on the outlet side during CO₂ absorption.

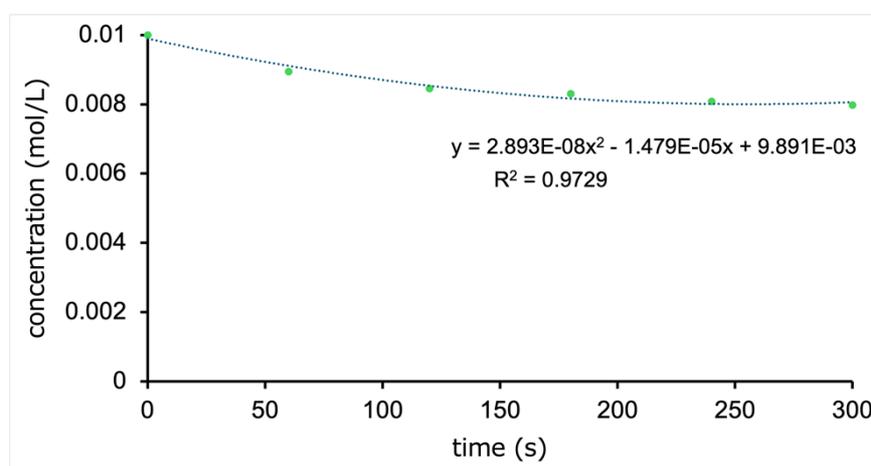
time (min)	<i>1st</i> _CO ₂ conc. (ppm)	<i>2nd</i> _CO ₂ conc. (ppm)	<i>3rd</i> _CO ₂ conc. (ppm)
0	492	428	456
5	442	376	282
10	392	296	226
15	358	258	248
20	326	248	266
25	316	256	268
30	310	266	266
35	302	282	272
40	302	288	278
45	306	282	272
50	302	282	262
55	308	282	262
60	308	288	266
65	308	288	276
70	302	292	276
75	300	292	282
80	308	296	292
85	302	298	298
90	302	302	302
95	306	302	302
100	302	306	302
105	308	306	302
110	308	308	308
115	308	304	308
120	306	302	302

Table S9. CO₂ concentration on the outlet side during CO₂ emission.

time (min)	<i>1st</i> _CO ₂ conc. (ppm)	<i>2nd</i> _CO ₂ conc. (ppm)	<i>3rd</i> _CO ₂ conc. (ppm)
0	30	52	62
5	70	52	62
10	176	90	310
15	358	398	844
20	598	742	1406
25	840	1024	1884
30	1030	1230	2172
35	1166	1366	2308
40	1244	1426	2314
45	1270	1426	2254
50	1260	1366	2112
55	1224	1282	1938
60	1176	1170	1754
65	1114	1074	1588
70	1050	970	1436
75	988	878	1306
80	918	798	1190
85	864	730	1080
90	804	658	980
95	754	602	878
100	698	552	796
105	660	498	724
110	616	448	650
115	578	408	592
120	544	366	538

3.10. Determination of light intensity

The photon flux of the LED lamp (Kessil PR 160L, 440 nm) was determined by chemical actinometry using 2,4-Dinitrobenzaldehyde.⁶ Separable flask vessel were added 50 mL of a solution of 2,4-Dinitrobenzaldehyde (10 mM) in EtOH and 1,3,5-Triisopropylbenzene (10mM). The aliquot of the mixture ($t = 0$ min) was analyzed by ¹H-NMR and calculated the integration ratio of 2,4-Dinitrobenzaldehyde to 1,3,5-Triisopropylbenzene. The solution was irradiated with a LED lamp. The reaction mixture was irradiated with an LED lamp, and aliquots taken out of the reaction mixture were analyzed every 1 min to determine the concentration of 2,4-Dinitrobenzaldehyde. The 2,4-Dinitrobenzaldehyde concentrations were plotted as a function of the irradiation time (Supplementary Figure 1).



Supplementary Figure 1. Concentration of 2,4-Dinitrobenzaldehyde as a function of irradiation time.

The given polynomial is

$$[Act] = 2.893 \times 10^{-8} \times t^2 - 1.479 \times 10^{-5} \times t + 9.891 \times 10^{-3}$$

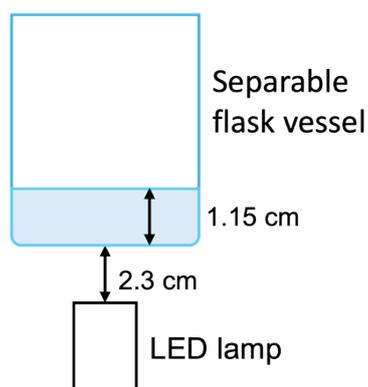
where [Act] represents the concentration of 2,4-Dinitrobenzaldehyde in mol L⁻¹ and t functions as the irradiation time in s. The calculation formula of light intensity from the light source is given in the following form:

$$I_0 = -\frac{Vd[Act]}{dt} \left(\frac{1}{\phi} \right) \left(\frac{1}{1 - 10^{\epsilon b [Act]}} \right)$$

where I_0 is the light intensity in einstein s⁻¹, V is the volume of reaction solution in L, ϕ is the quantum yield, ϵ is the molar absorption coefficient in L mol⁻¹ cm⁻¹, and b is the path length of light in cm. The path length of the light is b = 2.3 cm (Supplementary Figure 2). The molar absorption coefficient of 2,4-Dinitrobenzaldehyde at 440 nm (the average

wavelength range over which LED lamp emits light) was $\epsilon = 23.4 \text{ L mol}^{-1} \text{ cm}^{-1}$, the reaction volume was $V = 5.0 \times 10^{-2} \text{ L}$, the quantum yield of photochemical degradation of 2,4-Dinitrobenzaldehyde is known to be $\phi = 0.08$, and the concentration of 2,4-Dinitrobenzaldehyde was $[\text{Act}] = 1.0 \times 10^{-2} \text{ mol L}^{-1}$. Based on these, the rightmost term can be assumed to be almost unity. The light intensity of the LED lamp can be calculated as follows:

$$I_0 = -\frac{5.0 \times 10^{-2} \times (-1.479 \times 10^{-5})}{0.08} \times 1 = 9.244 \times 10^{-6} \text{ (einstein / s)}$$



Supplementary Figure 2. Illustration of the reaction set.

4. X-ray Crystallographic Analysis

Data were collected on a Dual-thickness MicroLoops (MiTeGen, 50 μm in diameter) with a XtaLAB Synergy, Dualflex, HyPix Diffractometer. The crystal was kept at 100 K using $\text{CuK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by a ShelXT³ structure solution program with Olex2⁴ (Rigaku) and refined with the ShelXL⁵ refinement package using Least Squares minimisation.

Crystal data for **3** (recrystallization from EtOH). $\text{C}_{18}\text{H}_{24}\text{N}_6\text{O}_3$, $M = 372.43$, monoclinic, space group = $P2_1/n$ (#14), $a = 7.6781(4) \text{ \AA}$, $b = 27.9980(13) \text{ \AA}$, $c = 9.1512(3) \text{ \AA}$, $\beta = 93.736(4)^\circ$, $V = 1963.07(15) \text{ \AA}^3$, $Z = 4$, density (calc.) = 1.260, total reflections collected = 45123, unique reflections = 5917 ($R_{\text{int}} = 0.0386$), GOF = 1.034 The final R_1 factor was 0.0747 ($I > 2\sigma(I)$) ($wR_2 = 0.1742$, all data).

Table S8. Fractional Atom coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O001	12315(2)	8118.1(6)	6053.3(15)	68.8(5)
O002	9756(2)	7812.7(7)	5437.2(16)	77.0(5)
O003	10537(2)	7919.2(7)	7790.2(16)	83.1(6)
N3	5120(3)	6937.0(7)	7537.3(19)	65.6(5)
N5	6904(3)	7214.4(8)	5741.2(19)	70.9(6)
N4	7544(3)	7375.0(9)	8146(2)	90.5(8)
C007	10781(3)	7940.7(8)	6485(2)	59.5(6)
C008	3882(3)	6663.9(8)	6682(2)	60.7(6)
C009	6508(3)	7172.4(9)	7115(2)	60.8(6)
N00A	-4850(3)	4361.7(8)	969(3)	89.3(7)
C00B	-3716(3)	4664.3(8)	1720(3)	67.8(6)
N1	355(4)	5593.8(10)	3853(3)	103.6(9)
C00D	4345(4)	6360.7(9)	5579(3)	74.4(7)
N2	-366(4)	5788.1(12)	4662(3)	116.5(11)
C00F	-1330(4)	5282.5(10)	3215(3)	84.6(9)
C00G	13599(3)	8275.2(11)	7163(3)	77.1(7)
C00H	1347(5)	6096.1(12)	5285(4)	97.4(11)
C00I	-1984(4)	4697.6(10)	1378(3)	84.5(8)
C00J	2167(4)	6677.1(11)	7055(3)	82.2(8)
C00K	3054(5)	6080.2(10)	4870(3)	91.2(10)
C00L	-848(4)	4999.1(11)	2105(4)	90.4(9)
C00M	-4208(4)	4951.8(10)	2862(3)	88.3(8)
C00N	-3024(5)	5253.7(10)	3598(3)	94.9(9)
C00O	15125(4)	8458.8(12)	6393(3)	93.2(9)
C00P	923(4)	6398.1(12)	6380(4)	98.9(10)
C00Q	-4301(5)	4091.5(12)	-274(4)	116.4(12)
C00R	-6622(4)	4309.8(13)	1342(5)	121.6(13)

Table S9. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3**. The Anisotropic displacement factor exponent takes the form: $-2p^2 [h^2a^*2U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
O001	77.2(11)	84.1(12)	45.3(8)	-6.3(7)	6.0(7)	-15.0(9)
O002	88.8(12)	101.6(13)	39.7(8)	6.5(8)	-2.9(8)	-27.7(10)
O003	88.9(12)	122.5(16)	37.9(8)	-0.3(9)	4.3(8)	-21.6(11)
N3	75.6(13)	82.3(14)	39.1(9)	-4.9(9)	5.9(8)	-14.6(11)
N5	82.6(14)	90.1(15)	39.5(9)	1.6(9)	0.5(9)	-17.8(11)
N4	103.9(17)	129(2)	37.5(9)	-2.1(11)	0.2(10)	-48.4(15)
C007	75.1(15)	63.7(13)	39.9(10)	2.7(9)	4.9(10)	-4.7(11)
C008	72.2(15)	63.7(14)	45.0(11)	5.3(10)	-5.7(10)	-4.9(11)
C009	73.2(15)	69.1(14)	39.4(10)	-1.3(10)	-0.9(10)	-5.2(12)
N00A	86.2(17)	74.6(15)	104.0(18)	-7.8(13)	-16.2(14)	-8.2(13)
C00B	74.6(16)	52.4(13)	74.9(15)	3.4(11)	-7.7(13)	3.2(12)
N1	141(2)	88.9(18)	85.3(17)	28.7(14)	37.3(17)	49.4(17)
C00D	94.4(19)	71.7(16)	56.6(13)	-5.5(12)	1.5(13)	-5.9(14)
N2	122(2)	129(2)	103(2)	52.2(18)	42.7(18)	64(2)
C00F	98(2)	60.5(16)	90(2)	14.3(15)	-31.4(17)	-20.4(15)
C00G	74.8(16)	96.0(19)	60.3(14)	-16.3(13)	1.8(12)	-9.1(14)
C00H	102(2)	84(2)	99(2)	37.1(18)	-49(2)	-38.7(18)
C00I	95(2)	70.8(17)	88.3(19)	-12.5(14)	7.6(16)	-7.7(15)
C00J	78.8(18)	85.0(19)	82.2(18)	1.2(15)	1.4(15)	-2.8(15)
C00K	145(3)	67.4(17)	58.1(15)	-4.5(12)	-20.1(17)	-14.9(18)
C00L	81.4(19)	75.3(18)	113(2)	-5.0(18)	-4.4(17)	-8.2(15)
C00M	86(2)	74.3(18)	105(2)	-6.0(17)	14.1(17)	2.6(15)
C00N	139(3)	65.7(17)	79.8(19)	-13.6(14)	1.8(19)	-4.1(19)
C00O	79.4(19)	110(2)	91(2)	-16.2(17)	8.7(15)	-13.6(17)
C00P	84(2)	96(2)	113(3)	9(2)	-22.1(19)	-15.9(18)
C00Q	159(3)	86(2)	101(2)	-19.8(19)	-14(2)	-25(2)
C00R	84(2)	103(3)	173(4)	5(3)	-32(2)	-7.7(19)

Table S10. Bond Lengths for **3**.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
O001	C007	1.361(3)	C00B	C00M	1.391(4)
O001	C00G	1.438(3)	N1	N2	1.097(3)
O002	C007	1.253(3)	N1	C00F	1.636(4)
O003	C007	1.222(2)	C00D	C00K	1.392(4)
N3	C008	1.416(3)	N2	C00H	1.643(4)
N3	C009	1.332(3)	C00F	C00L	1.359(4)
N5	C009	1.317(3)	C00F	C00N	1.372(4)
N4	C009	1.322(3)	C00G	C00O	1.497(4)
C008	C00D	1.383(3)	C00H	C00K	1.389(5)
C008	C00J	1.382(4)	C00H	C00P	1.367(5)
N00A	C00B	1.368(3)	C00I	C00L	1.357(4)
N00A	C00Q	1.451(4)	C00J	C00P	1.352(4)
N00A	C00R	1.432(4)	C00M	C00N	1.384(4)
C00B	C00I	1.389(4)			

Table S11. Bond Angles for **3**.

Atom Atom Atom	Angle/°	Atom Atom Atom	Angle/°
C007 O001 C00G	118.25(17)	N2 N1 C00F	94.7(3)
C009 N3 C008	128.90(18)	C008 C00D C00K	118.5(3)
O002 C007 O001	113.23(18)	N1 N2 C00H	93.8(3)
O003 C007 O001	119.5(2)	C00L C00F N1	109.3(3)
O003 C007 O002	127.3(2)	C00L C00F C00N	117.7(3)
C00D C008 N3	122.7(2)	C00N C00F N1	133.0(3)
C00J C008 N3	117.7(2)	O001 C00G C00O	107.1(2)
C00J C008 C00D	119.4(2)	C00K C00H N2	129.5(4)
N5 C009 N3	124.1(2)	C00P C00H N2	110.8(3)
N5 C009 N4	118.5(2)	C00P C00H C00K	119.6(3)
N4 C009 N3	117.42(19)	C00L C00I C00B	121.7(3)
C00B N00A C00Q	120.6(3)	C00P C00J C008	121.9(3)
C00B N00A C00R	121.8(3)	C00H C00K C00D	120.7(3)
C00R N00A C00Q	117.6(3)	C00I C00L C00F	122.2(3)
N00A C00B C00I	121.0(3)	C00N C00M C00B	121.1(3)
N00A C00B C00M	122.8(3)	C00F C00N C00M	121.0(3)
C00I C00B C00M	116.2(3)	C00J C00P C00H	119.8(3)

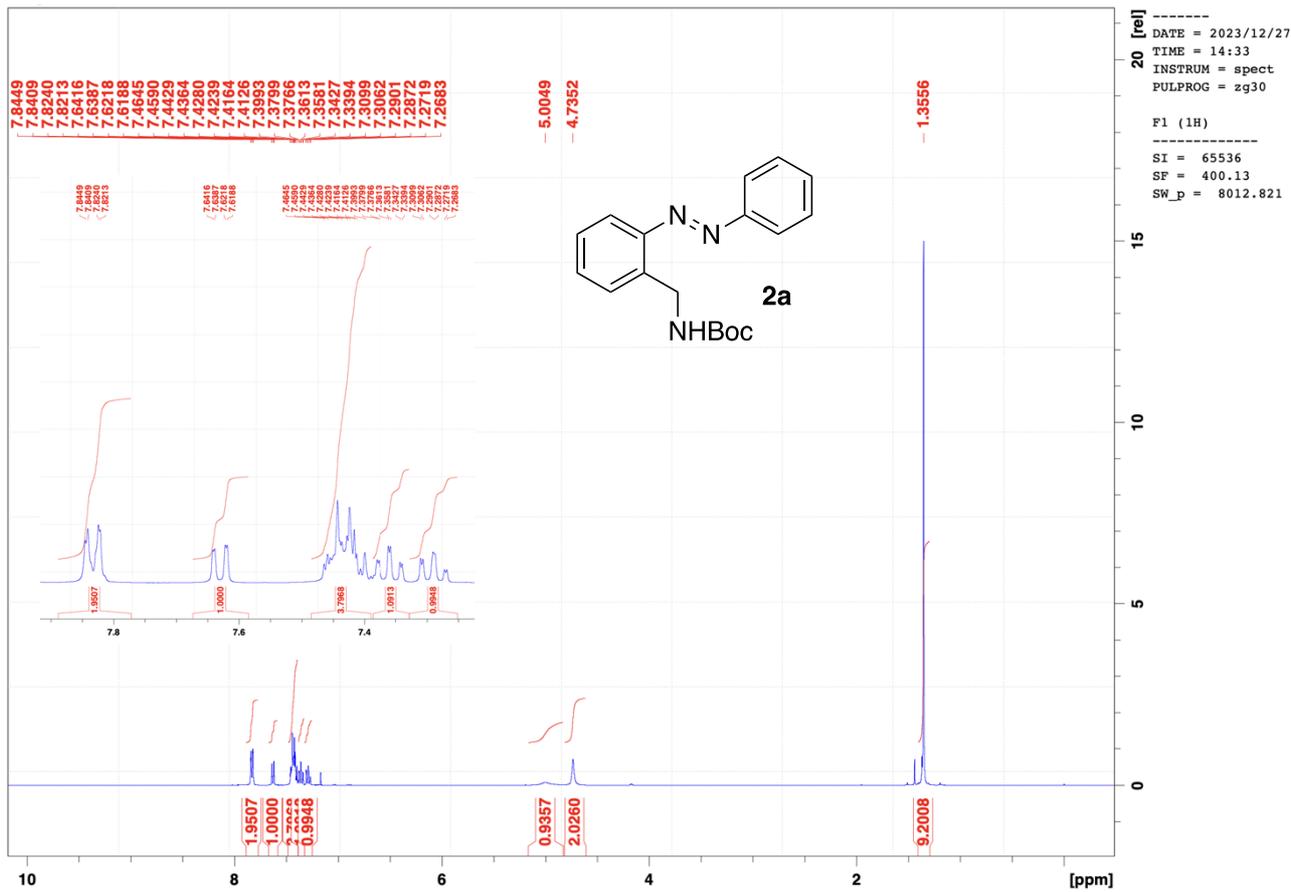
Table S12. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **3**.

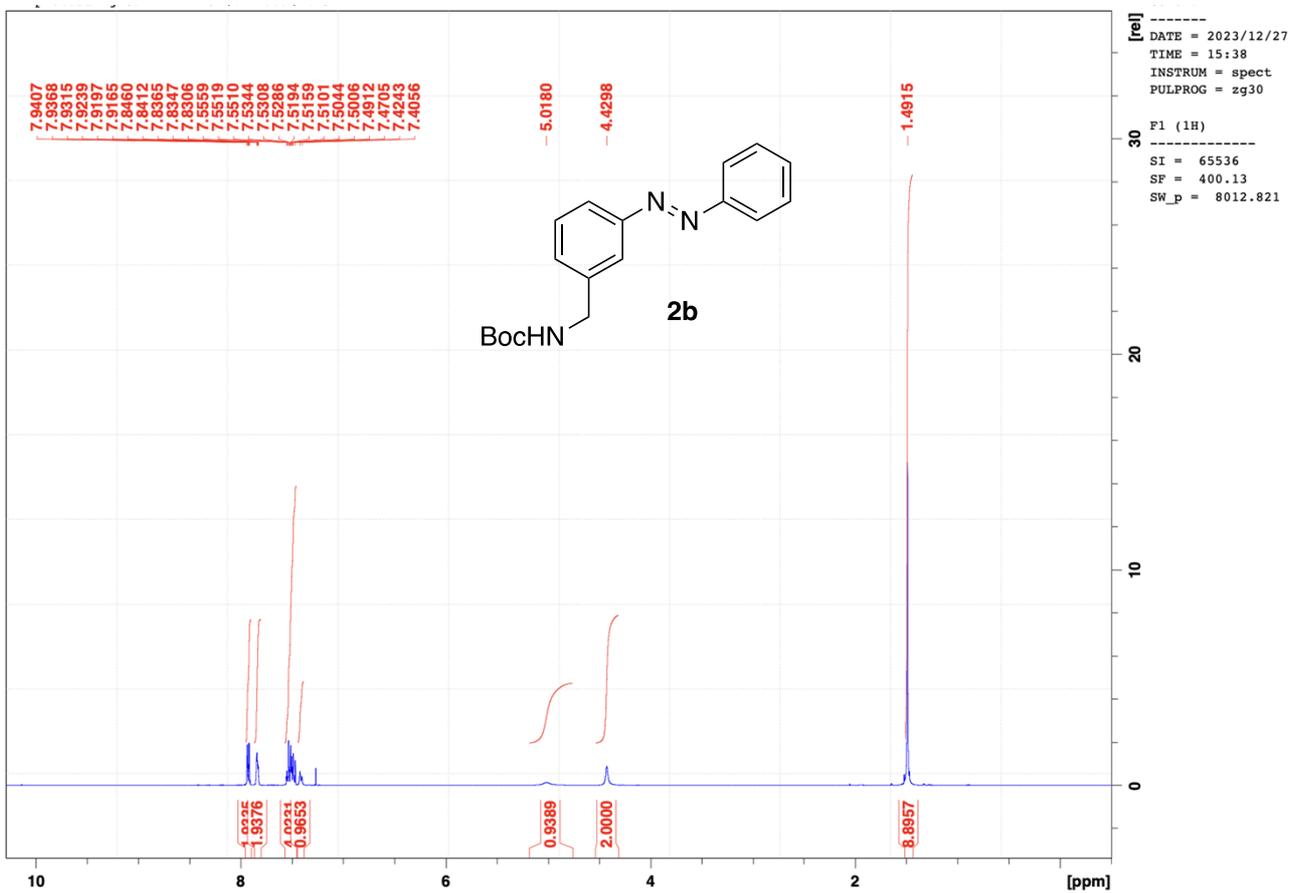
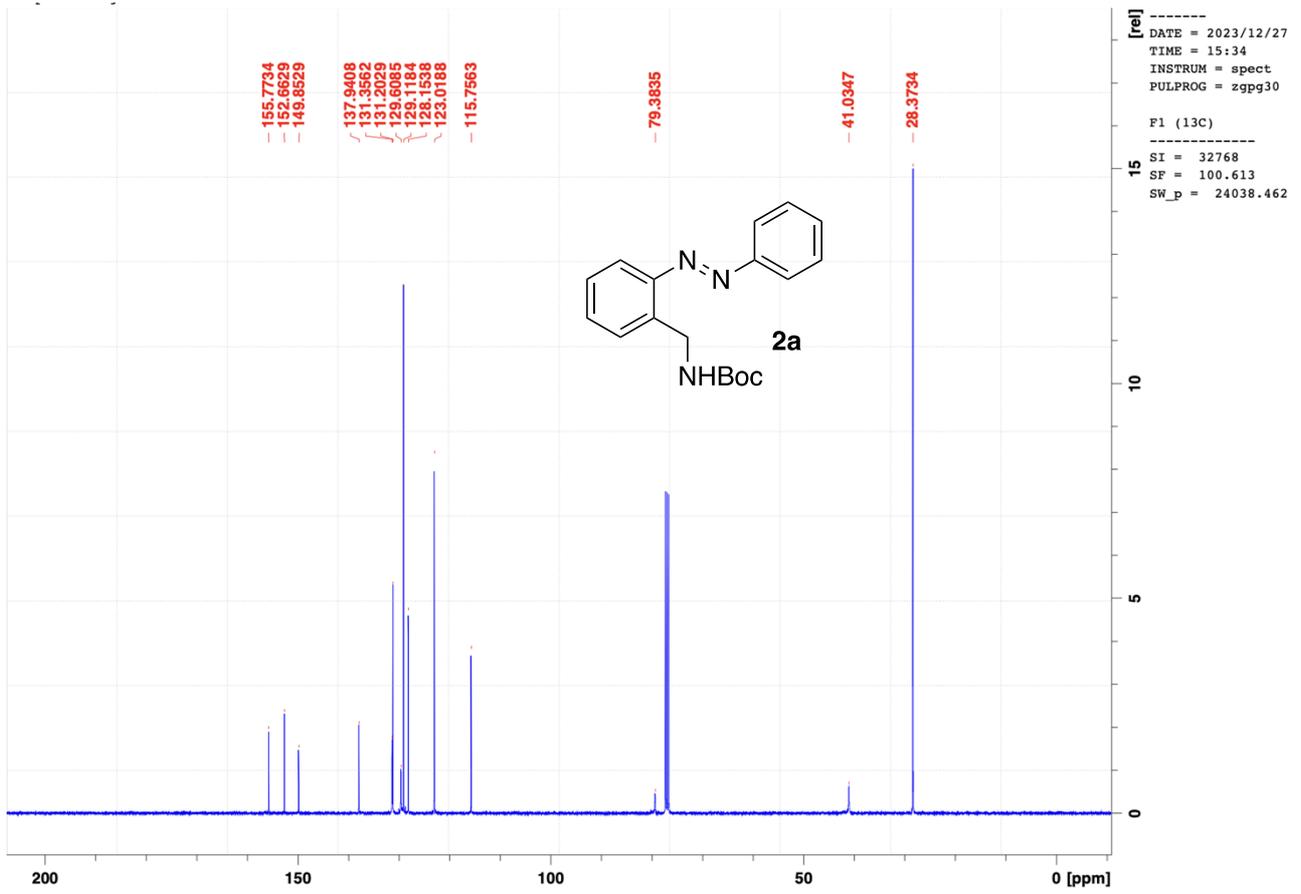
Atom	x	y	z	U(eq)
H3	4952.21	6953.17	8456.09	79
H5A	7819.32	7370.99	5532.56	85
H5B	6247.82	7085.35	5053.39	85
H4A	8452.9	7529.95	7914.08	109
H4B	7309.23	7351.79	9049.69	109
H00D	5493.48	6344.6	5317.22	89
H00H	13955.39	8011.63	7802.83	93
H00O	13123.27	8525.98	7750.42	93
H00I	-1593.38	4508.4	630.27	101
H00J	1860.78	6883.85	7790.57	99
H00K	3337.39	5879.92	4110.38	109
H00L	297.55	5012.26	1835.03	108
H00M	-5353.08	4940.96	3135.86	106
H00N	-3382.83	5439.91	4364.74	114
H00Q	14778.34	8735.27	5825.83	140
H00R	15526.67	8215.36	5757.46	140
H00S	16049.66	8543.68	7102.85	140
H00P	-218.28	6411.58	6660.42	119
H00A	-3737.26	4301.39	-925.26	175
H00B	-5301.68	3948.31	-782.41	175
H00C	-3499.61	3846.07	64.7	175
H00E	-6654.68	4276.28	2383.7	182
H00F	-7122.75	4031.36	868.29	182
H00G	-7277.83	4587.1	1023.68	182

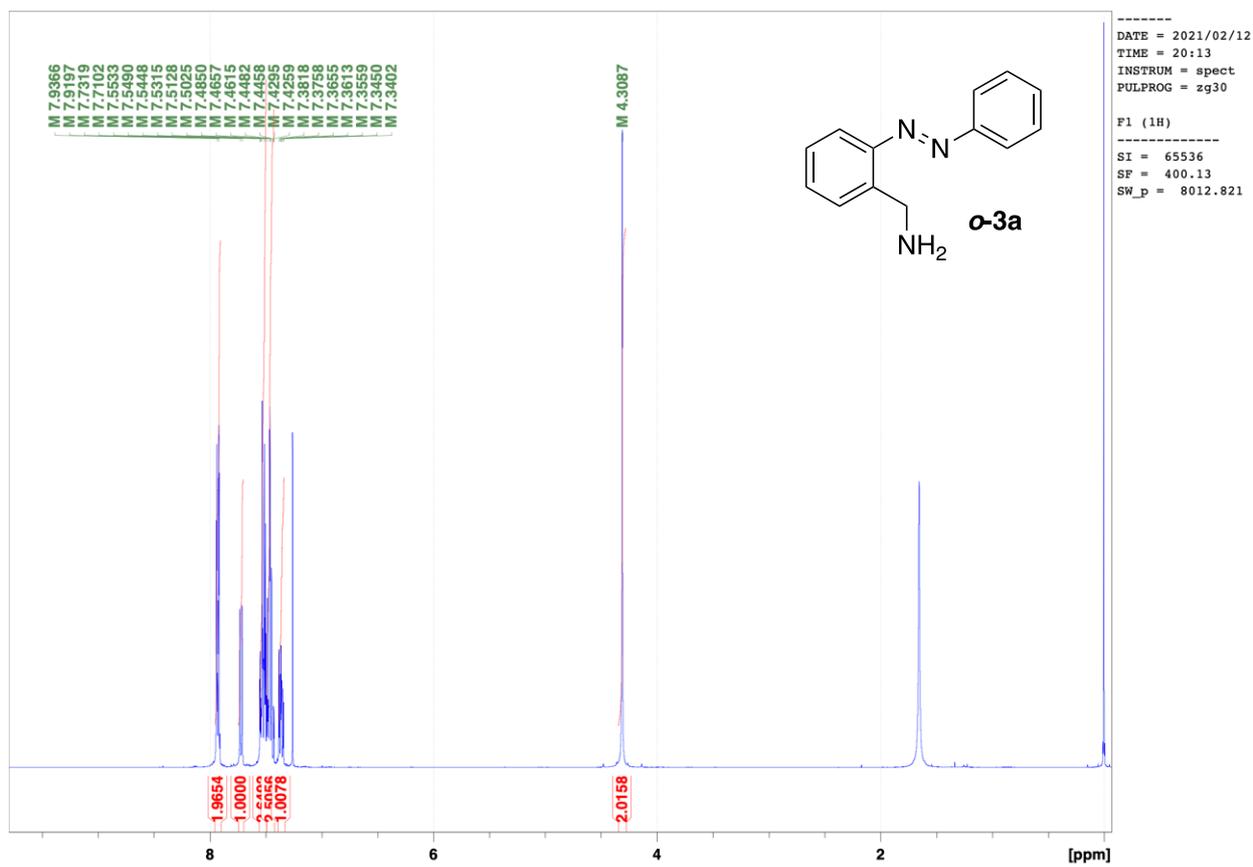
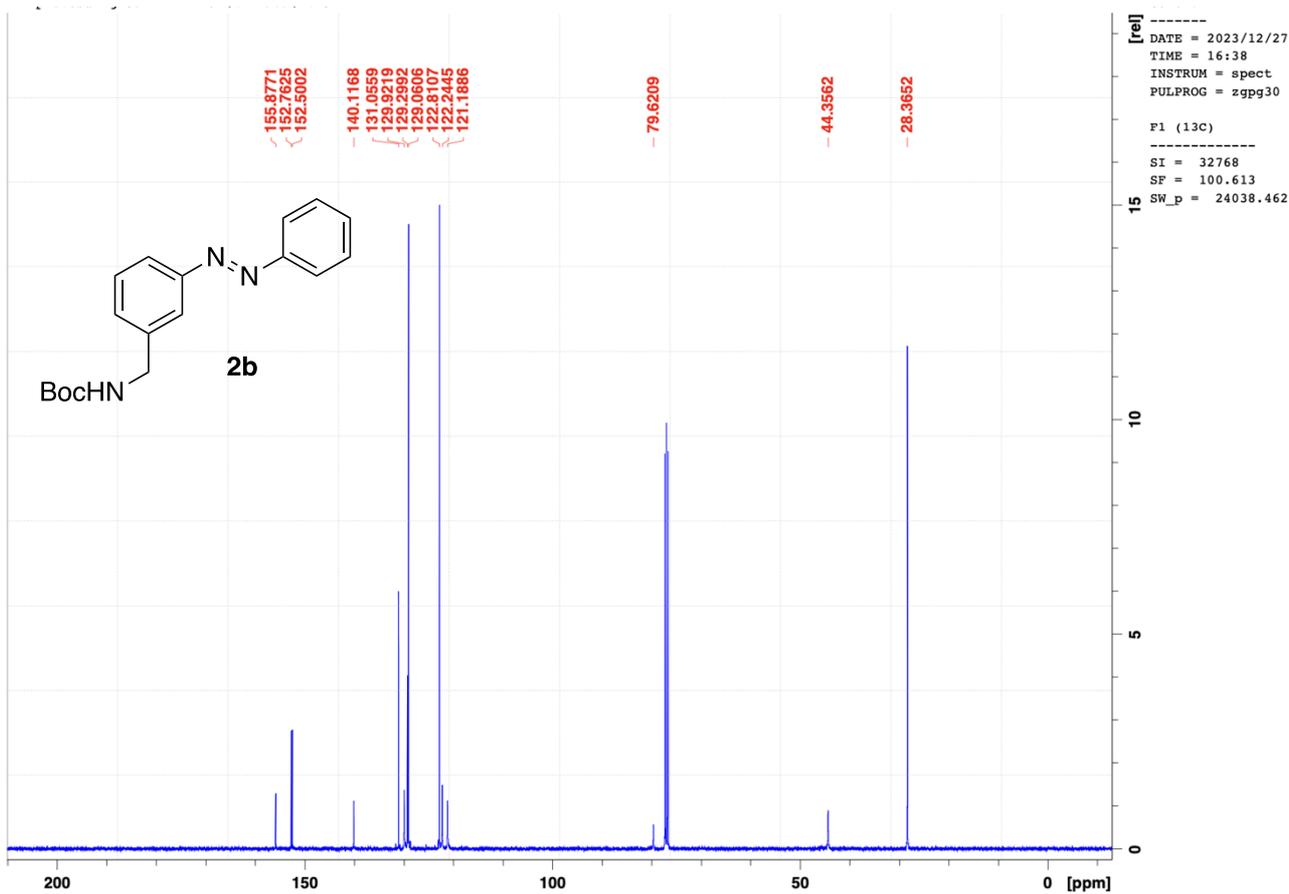
5. References

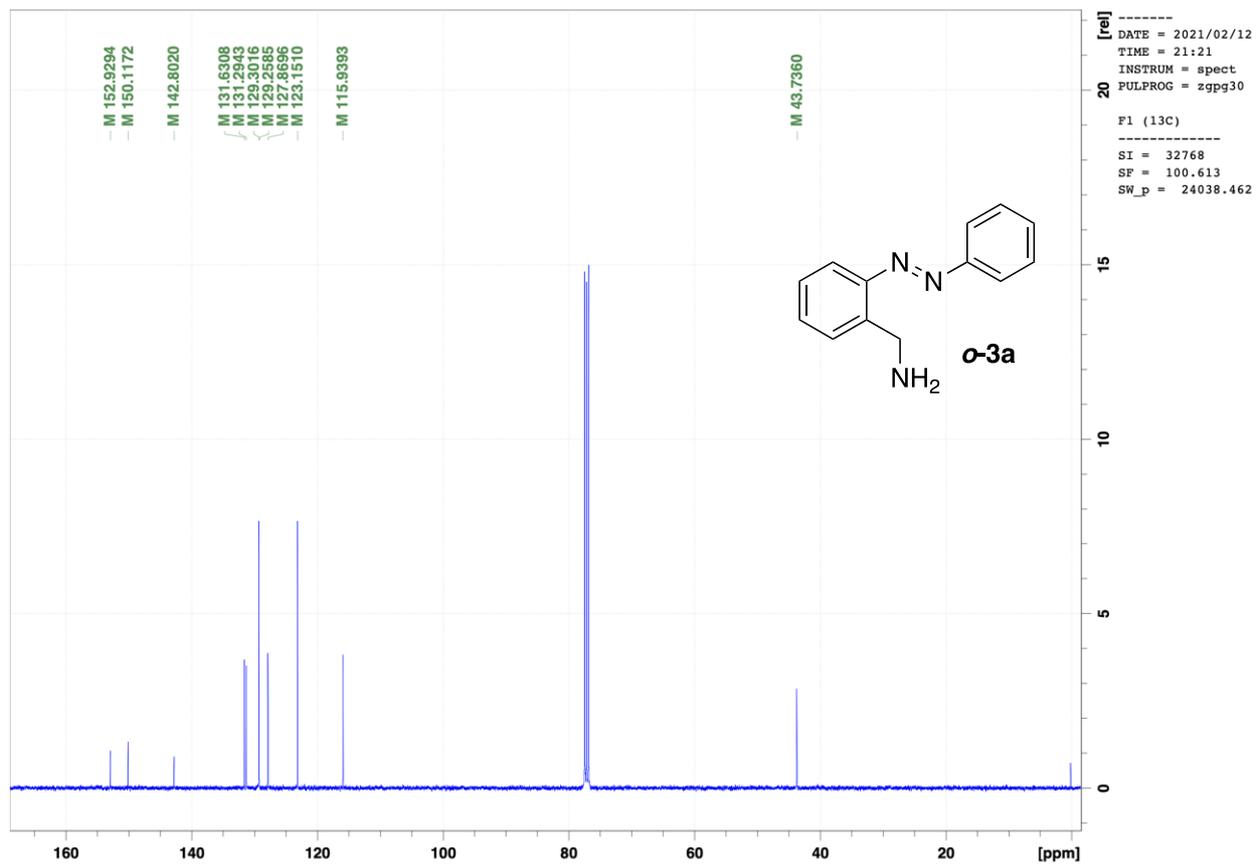
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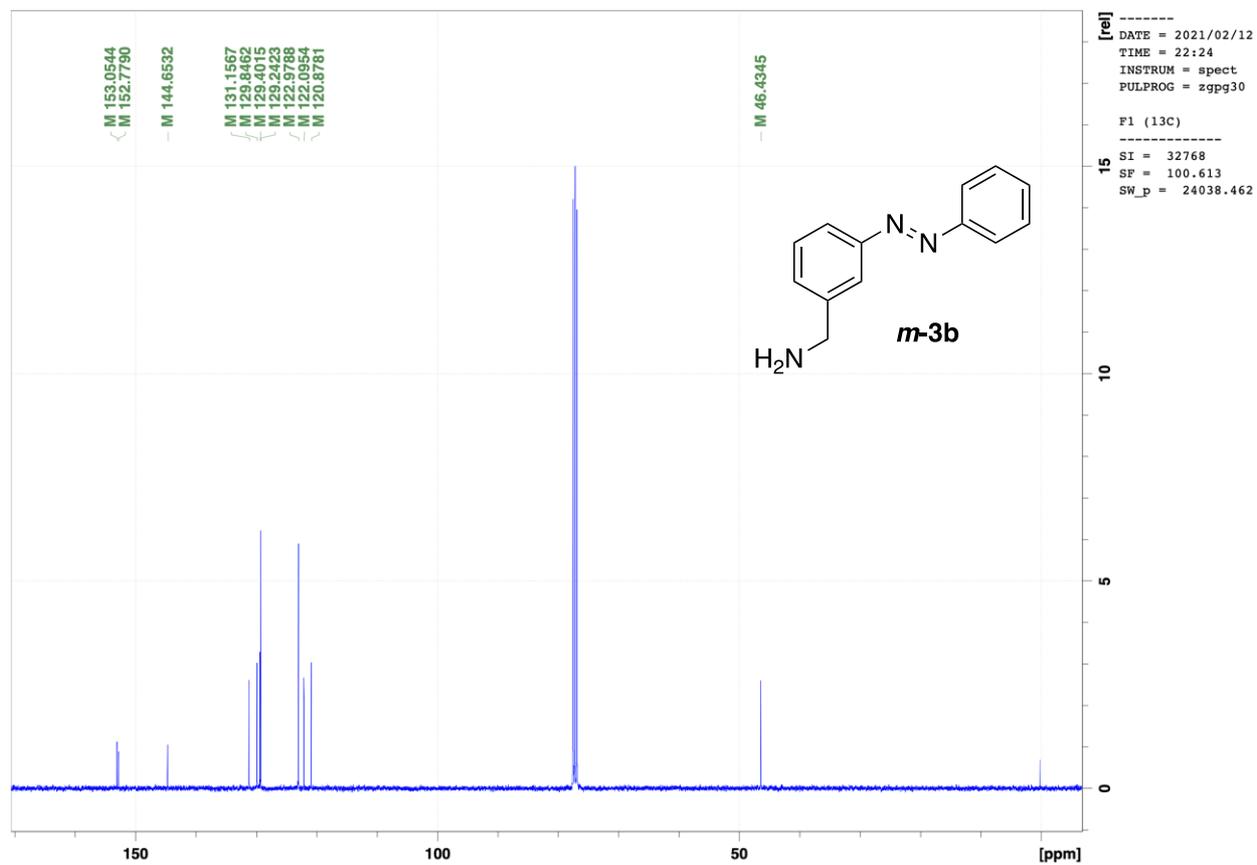
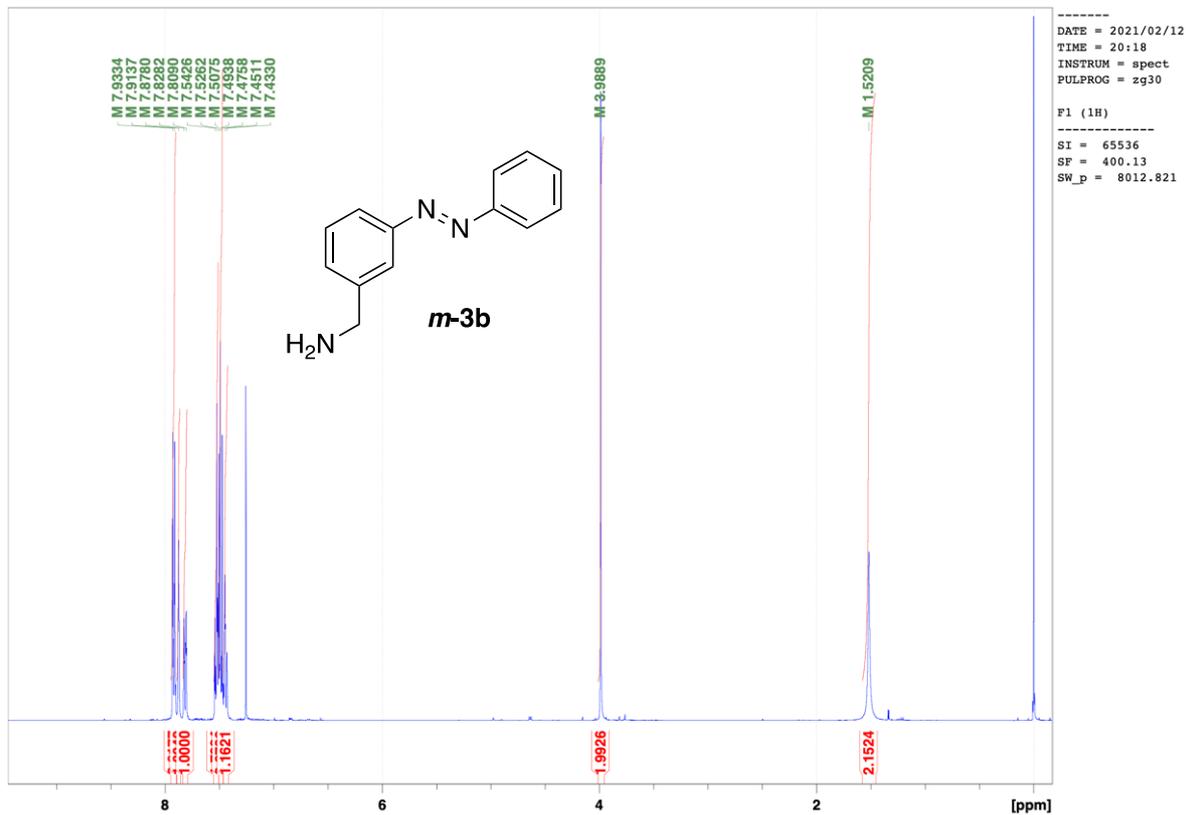
6. NMR Spectra



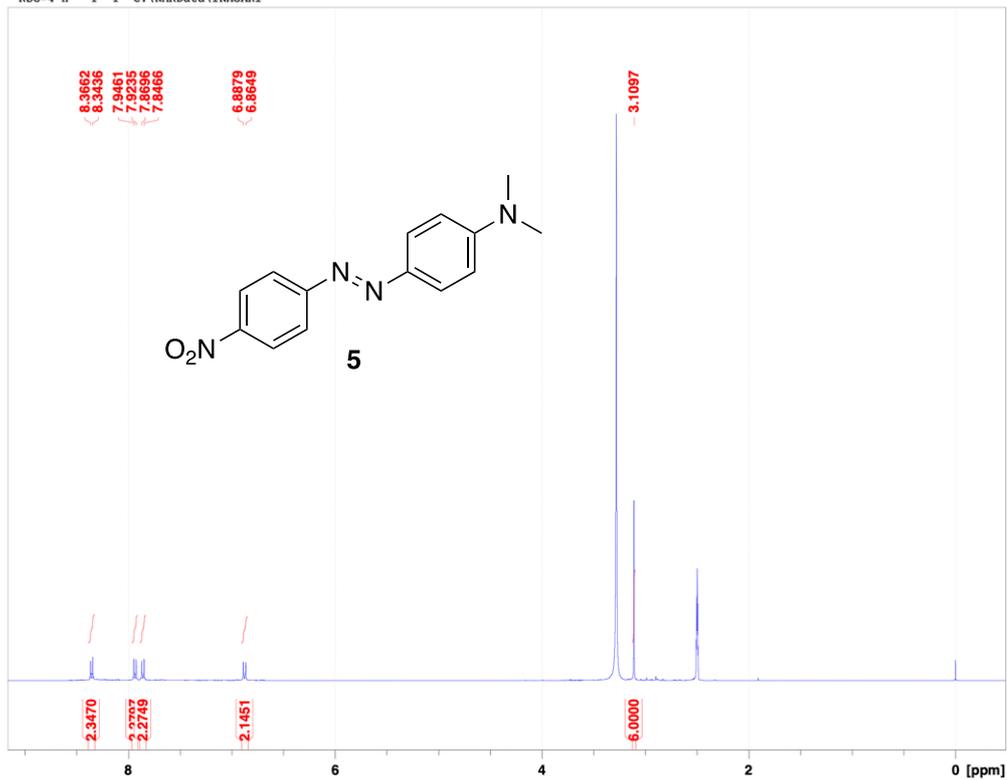








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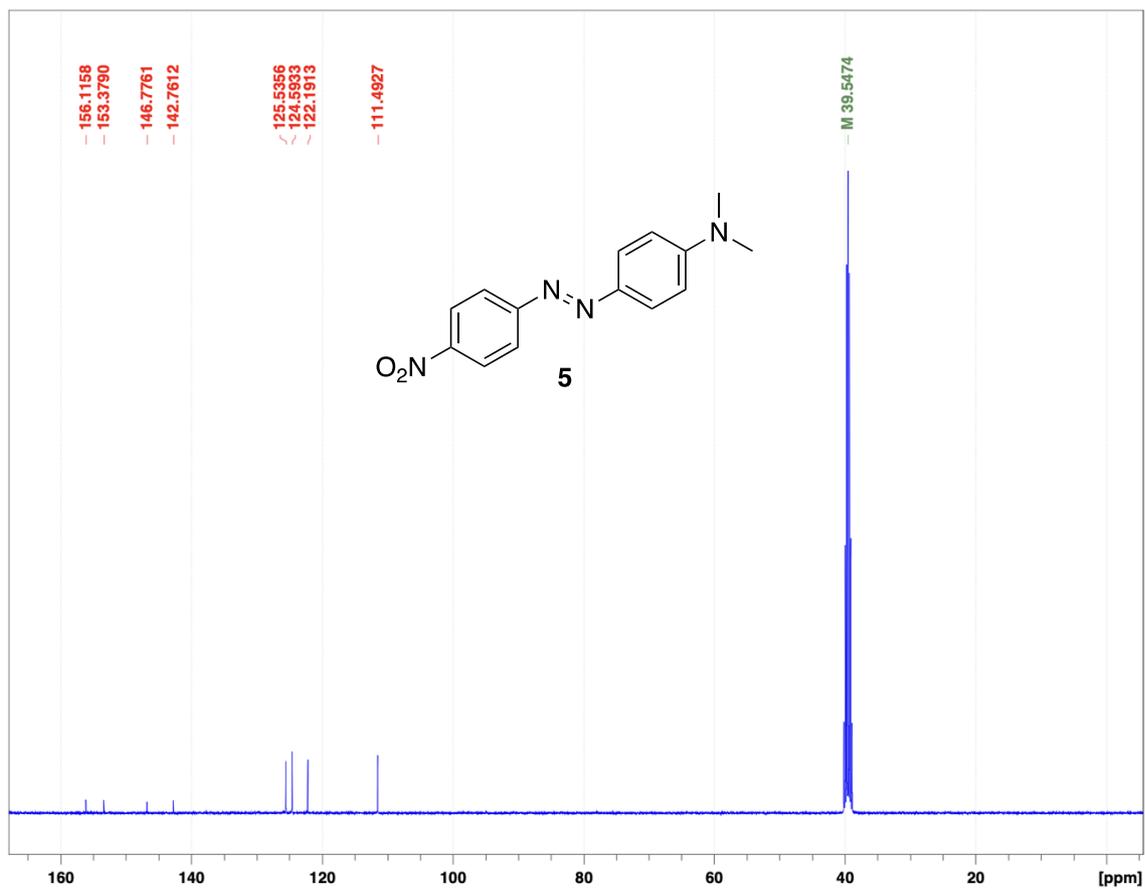


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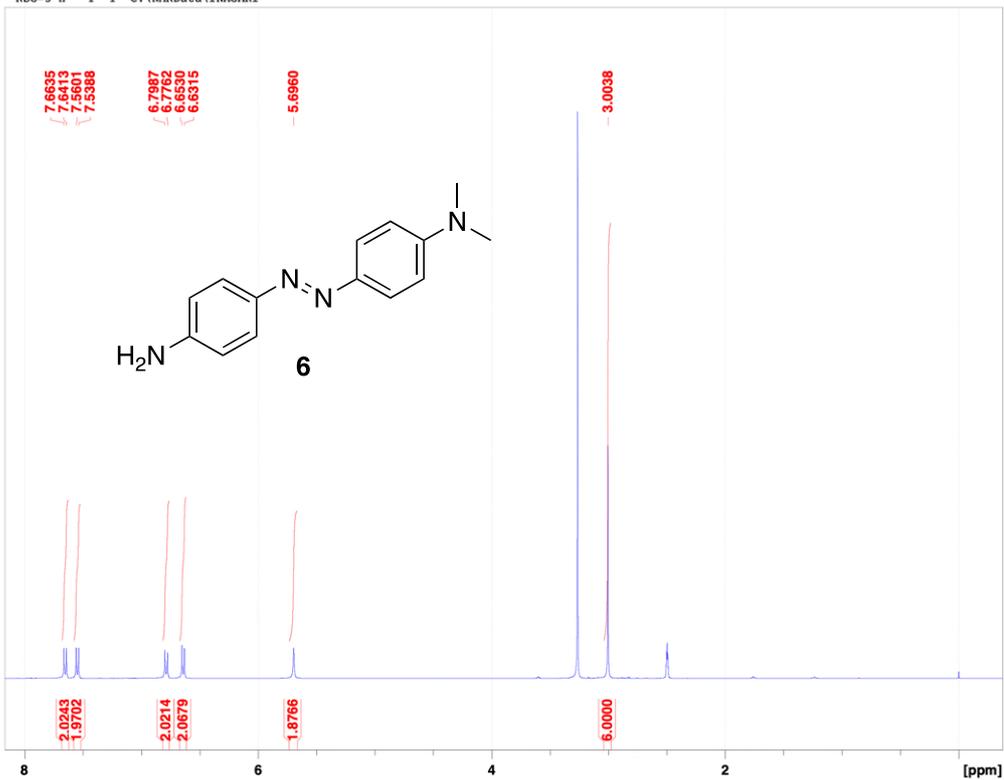


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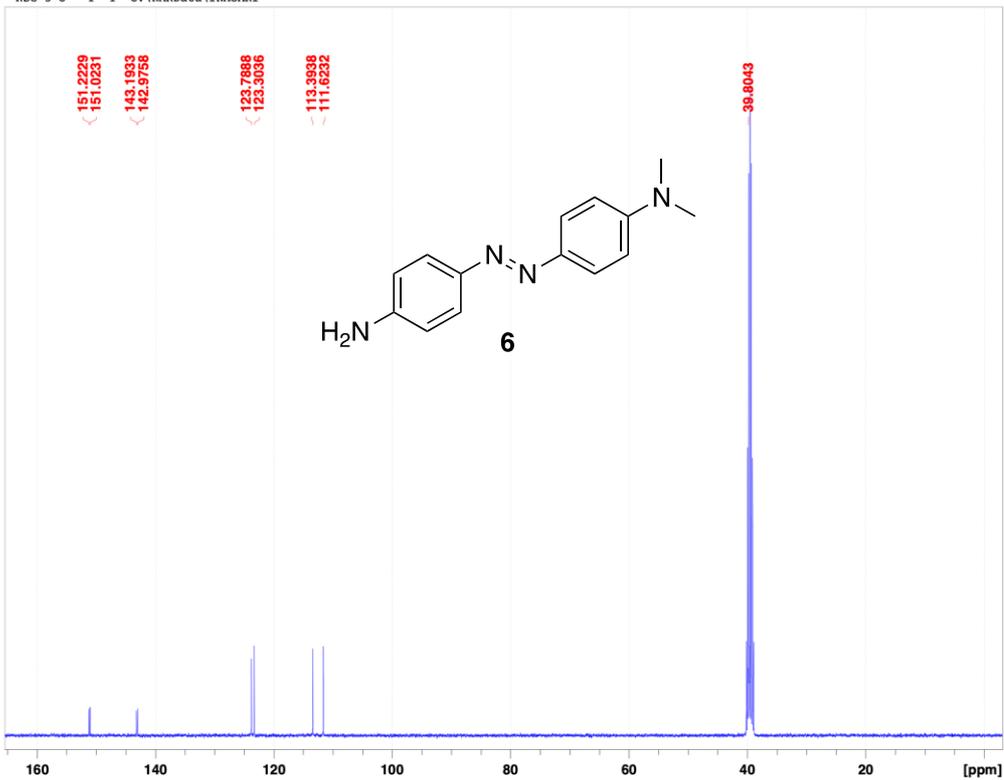
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