

Synthesis of Indole-Fused Benzodiazepine Derivatives by Photocatalyzed Cascade Reaction

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1. General Methods

All operations were performed under nitrogen unless otherwise noted. NMR spectra for products data (^1H , ^{13}C and ^{19}F) were recorded on a Bruker AVANCE-III (400 MHz for ^1H , 100 MHz for ^{13}C , 376 MHz for ^{19}F) and JEOL ECZ400 (400 MHz for ^1H , 100 MHz for ^{13}C , 376 MHz for ^{19}F) spectrometer using CDCl_3 [tetramethylsilane (0 ppm) served as an internal standard in ^1H NMR and CDCl_3 (77.0 ppm) in ^{13}C NMR, hexafluorobenzene (-163.9 ppm) served as an internal or external standard in ^{19}F NMR]. Chemical shifts are expressed in parts per million (ppm). ESI mass analyses were performed on Bruker micrOTOF mass spectrometer. IR spectra were recorded on a FT/IR-4200 (JASCO Co., Ltd.). UV-Vis spectra were recorded on a V-670 UV-VIS-NIR spectrometer (JASCO Co., Ltd.). Emission spectra were recorded on a FP-6500 (JASCO Co., Ltd.). Cyclic Voltammetry was performed on ALS612E (BAS Co., Ltd.). UV light irradiation was performed with PR160L-370 nm (Kessil Co., Ltd.) for 370 nm LED. Visible light irradiation was performed with PR160L-427 nm (Kessil Co., Ltd.) for 427 nm blue LED.

Solvents were distilled according to the usual procedures and stored over molecular sieves unless otherwise noted. All of the substrates were purified by distillation (for liquid) or recrystallization (for solid). 10-Phenylphenothiazine (PTH) were synthesized according to the literature procedures.^{S1} Other chemicals were purchased and used as received.

2. Screening of conditions

Table S1. Optimization of reaction conditions

$\text{1a (x equiv)} + \text{2a (y equiv)} \xrightarrow[\text{solvent (0.1 M), rt, 20 h, 370 nm LED}]{\text{photocatalyst (10 mol\%), base (2 equiv)}} \text{3aa} + \text{1a'}$

Entry	x	y	photocatalyst	base	solvent	yield of 3aa / % ^{a)}	yield of 1a' / % ^{a)}
1	1.0	1.5	PTH	Na₂CO₃	CH₃CN	80^{b)}	3
2	1.0	1.0	PTH	Na ₂ CO ₃	CH ₃ CN	67	3
3	2.0	1.0	PTH	Na ₂ CO ₃	CH ₃ CN	62	2
4 ^{c)}	1.0	1.5	PTH	Na ₂ CO ₃	CH ₃ CN	51	4
5 ^{d)}	1.0	1.5	PTH	Na ₂ CO ₃	CH ₃ CN	43	3
6 ^{e)}	1.0	1.5	Ir(ppy) ₃	Na ₂ CO ₃	CH ₃ CN	67 ^{b)}	3
7 ^{e)}	1.0	1.0	Ir(ppy) ₃	Na ₂ CO ₃	CH ₃ CN	60	10
8 ^{e)}	2.0	1.0	Ir(ppy) ₃	Na ₂ CO ₃	CH ₃ CN	58	9
9	1.0	1.5	PTH	K ₂ CO ₃	CH ₃ CN	56	7
10	1.0	1.5	PTH	Cs ₂ CO ₃	CH ₃ CN	0	0
11	1.0	1.5	PTH	Et ₃ N	CH ₃ CN	18	24
12	1.0	1.5	PTH	2,6-lutidine	CH ₃ CN	51	4
13	1.0	1.5	PTH	DBU	CH ₃ CN	trace	33
14	1.0	1.5	PTH	<i>t</i> -BuOK	CH ₃ CN	0	0
15	1.0	1.5	PTH	Na ₂ CO ₃	toluene	20	6
16	1.0	1.5	PTH	Na ₂ CO ₃	CH ₂ Cl ₂	30	0
17	1.0	1.5	PTH	Na ₂ CO ₃	PhCN	69	0
18	1.0	1.5	PTH	Na ₂ CO ₃	DMF	52	11

a) Determined by ¹H NMR.

b) Isolated yield.

c) 5 mol% of PTH was used.

d) 2 mol% of PTH was used

e) 2 mol% of Ir(ppy)₃ was used. 427 nm LED.

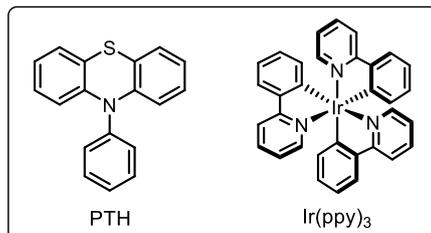
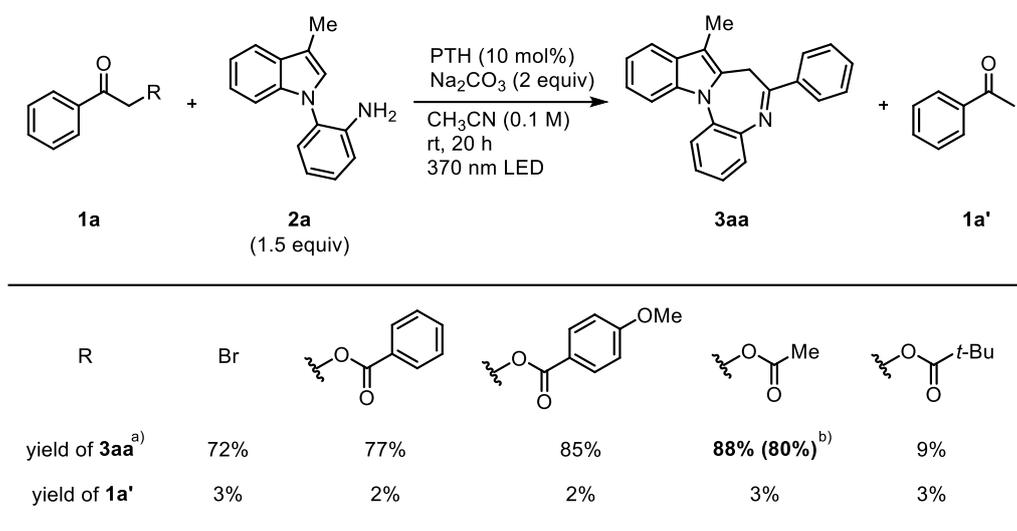
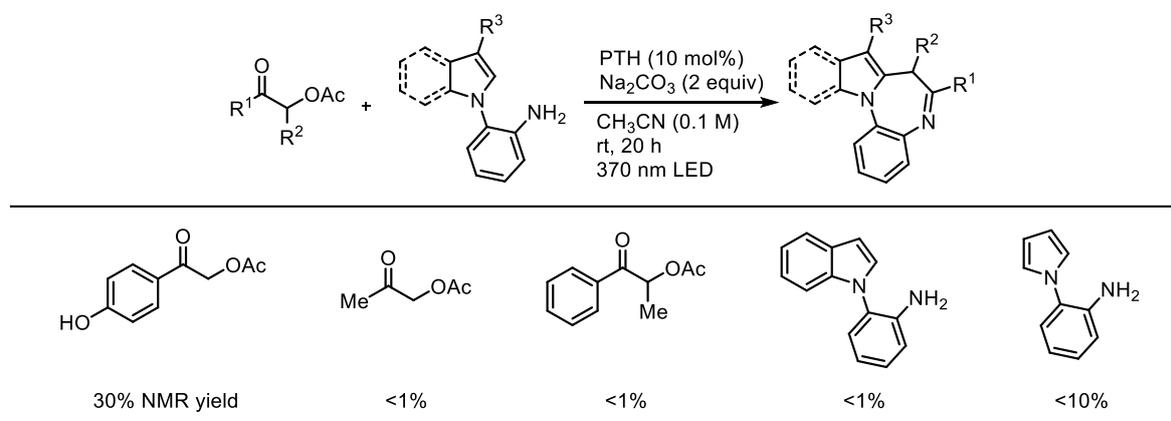
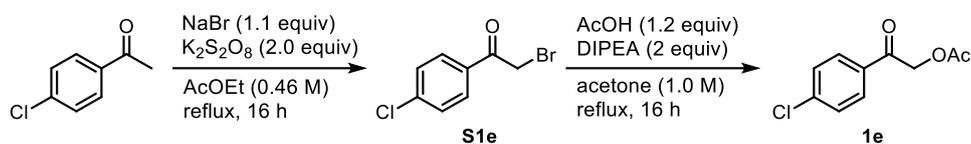


Table S2. Effect of leaving groupa) Determined by ¹H NMR.

b) Isolated yield.

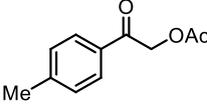
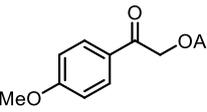
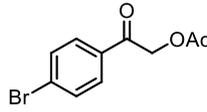
Table S3. Other tested substrates

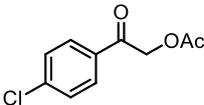
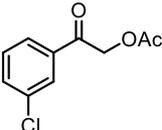
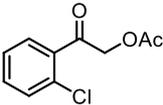
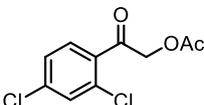
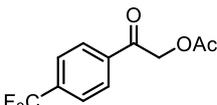
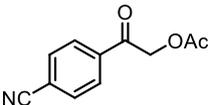
Method B.^{S4}

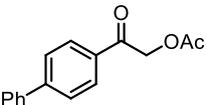
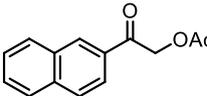
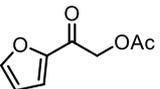
In a dried two-neck flask, 4'-chloroacetophenone (0.30 mL, 2.31 mmol), sodium bromide (0.26 g, 2.54 mmol), and potassium persulfate (1.25 g, 4.62 mmol) were mixed in ethyl acetate (5 mL). After being refluxed for 20 h, the mixture was cooled to room temperature, followed by filtration through Celite. Water was added to the mixture and the mixture was extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by column chromatography (SiO₂, hexane/ethyl acetate) to give **S1e**.

1e was synthesized according to synthetic procedure of **1a**.

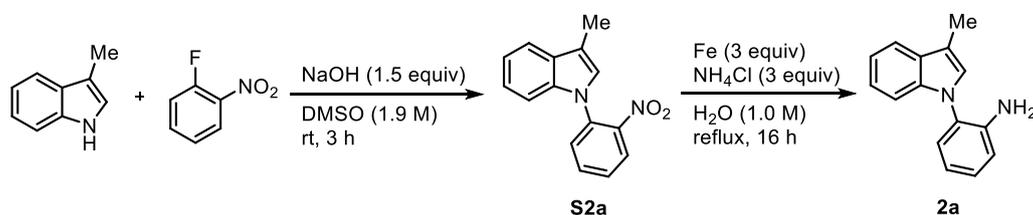
Data of 1

1b	70% (Method A.)	White powder.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.81 (d, <i>J</i> = 8.3 Hz, 2H), 7.28 (d, <i>J</i> = 8.3 Hz, 2H), 5.32 (s, 2H), 2.42 (s, 3H), 2.23 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	
1c	72% from S1c . (Method A. S1c was purified by column chromatography.)	
	White solid. ¹ H NMR (400 MHz, CDCl ₃) δ 7.93 – 7.86 (m, 2H), 6.99 – 6.92 (m, 2H), 5.30 (s, 2H), 3.88 (s, 3H), 2.23 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	
1d	48% (Method A.)	White powder.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.81 – 7.75 (m, 2H), 7.67 – 7.61 (m, 2H), 5.29 (s, 2H), 2.23(s, 3H). The NMR data was in accordance with literature data. ^{S2}	

1e	49% from S1e . (Method B.)	White powder.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.89 – 7.83 (m, 2H), 7.50 – 7.45 (m, 2H), 5.30 (s, 2H), 2.23 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	
1f	40% from S1f . (Method B.)	Pale yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.91 – 7.87 (m, 1H), 7.79 (m, 1H), 7.59 (m, 1H), 7.49 – 7.41 (m, 1H), 5.30 (s, 2H), 2.23 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	
1g	92% from S1g . (Method A. S1g was purified by column chromatography.)	Pale yellow liquid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.63 – 7.60 (m, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.33 (m, 1H), 5.20 (s, 2H), 2.18 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	
1h	52% (Method A.)	Yellow liquid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.61 (d, <i>J</i> = 8.5 Hz, 1H), 7.47 (d, <i>J</i> = 1.9 Hz, 1H), 7.35 (dd, <i>J</i> = 8.5, 1.9 Hz, 1H), 5.17 (s, 2H), 2.18 (s, 3H). The NMR data was in accordance with literature data. ^{S5}	
1i	47% (Method A.)	White powder.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.03 (d, <i>J</i> = 8.1 Hz, 2H), 7.77 (d, <i>J</i> = 8.1 Hz, 2H), 5.34 (s, 2H), 2.24 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	
1j	46% from S1j . (Method A. S1j was purified by column chromatography.)	White crystal.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.04 – 7.99 (m, 2H), 7.83 – 7.79 (m, 2H), 5.31 (s, 2H), 2.23 (s, 3H). The NMR data was in accordance with literature data. ^{S6}	

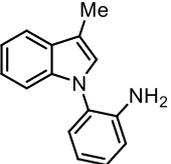
1k	60% (Method A.)	Pale yellow crystal.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.02 – 7.96 (m, 2H), 7.74 – 7.69 (m, 2H), 7.66 – 7.60 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 1H), 5.38 (s, 2H), 2.25 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	
1l	50% from S1l . (Method A. S1l was purified by column chromatography.)	
	Pale yellow crystal. ¹ H NMR (400 MHz, CDCl ₃) δ 8.43 (s, 1H), 8.01 – 7.86 (m, 4H), 7.67 – 7.54 (m, 2H), 5.49 (s, 2H), 2.26 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	
1m	38% from S1m . (Method A. S1m was purified by column chromatography.)	
	Pale yellow solid. ¹ H NMR (400 MHz, CDCl ₃) δ 7.61 (d, <i>J</i> = 1.8 Hz, 1H), 7.28 (d, <i>J</i> = 3.7 Hz, 1H), 6.58 (dd, <i>J</i> = 3.7, 1.8 Hz, 1H), 5.18 (s, 2H), 2.22 (s, 3H). The NMR data was in accordance with literature data. ^{S2}	

3.3. General procedure for the preparation of **2a**



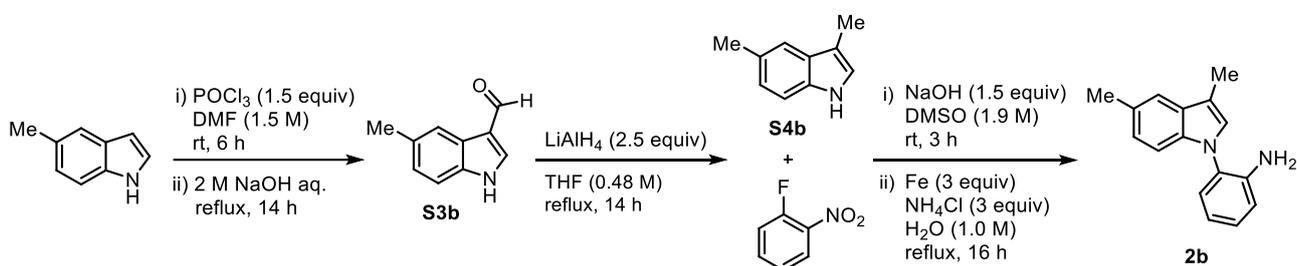
In a dried two-neck flask, 3-methylindole (1.26 g, 9.60 mmol), 2-fluoronitrobenzene (1 mL, 9.60 mmol), and NaOH (0.576 g, 14.4 mmol) were mixed in DMSO (5 mL). After stirred at room temperature for 3 h, the reaction mixture was quenched with 1N HCl aq. and extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator to afford crude **S2a**, which was directly used for the next reaction without further purification.

The above **S2a**, iron powder (1.61g, 28.8 mmol), and ammonium chloride (1.54 g, 28.8 mmol) were mixed in water (10 mL). After being reflux for 16 h, the mixture was cooled to room temperature, followed by filtration through Celite. The mixture was extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by column chromatography (SiO₂, hexane/ethyl acetate) to give **2a** in 71%.

2a	71%	Yellow oil.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 – 7.62 (m, 1H), 7.26 – 7.10 (m, 5H), 7.00 (s, 1H), 6.90 – 6.81 (m, 2H), 3.61 (s, 2H), 2.40 (s, 3H). The NMR data was in accordance with literature data. ^{S7}	

3.4. General procedure for the preparation of 2

3.4.1. General procedure for the preparation of 2b-2e

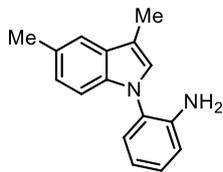
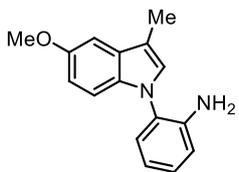
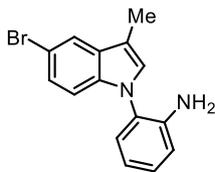
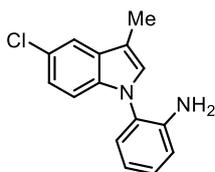


In a dried two-neck flask, phosphoryl chloride (0.3 mL, 3.32 mmol) was added by dropwise at 0 °C to anhydrous DMF (0.5 mL) and the mixture was stirred at 0 °C for 5 min. A solution of 5-methylindole (0.29 g, 2.22 mmol) in anhydrous DMF (1 mL) was added dropwise to the mixture at 0 °C and the solution was stirred for 6 h at rt. After cooling to 0 °C, 2 M NaOH aq. was added to adjust the pH value to 8~9. After being refluxed for 14 h, the precipitate was collected and dried *in vacuo* to give the desired product **S3b** in 65%, which was directly used for the next reaction without further purification.

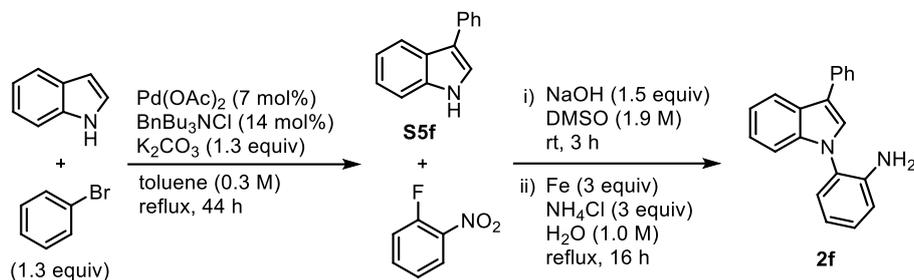
In a dried two-neck flask, a solution of **S3b** (0.23 g, 1.44 mmol) in anhydrous THF (1.4 mL) was added by dropwise to a suspension of LiAlH₄ (0.14 g, 3.69 mmol) in anhydrous THF (1.5 mL) at 0 °C, and the mixture was stirred at 70 °C for 14 h. The reaction mixture was cooled to 0 °C, ethyl acetate (10 mL) and a saturated aqueous potassium sodium tartrate tetrahydrate solution (20 mL) was added dropwise and the mixture was stirred at room temperature for 2 h. Then, the mixture was extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by column chromatography (SiO₂, hexane/ethyl acetate) to give **S4b** in 82%.

2b was synthesized according to synthetic procedure of **2a**.

Data of 2b-2e

2b	65% from S4b .	Yellow oil.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 (s, 1H), 7.26 – 7.12 (m, 2H), 7.02 (d, J = 1.2 Hz, 2H), 6.94 (d, J = 1.2 Hz, 1H), 6.87 – 6.79 (m, 2H), 3.55 (s, 2H), 2.50 (s, 3H), 2.38 (d, J = 1.2 Hz, 3H).	
	$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.0, 135.0, 129.1, 128.7, 128.6, 128.4, 126.1, 125.2, 123.7, 118.7, 118.4, 116.1, 111.8, 110.3, 21.4, 9.6.	
	LRMS (ESI): m/z = 237 [M+H].	
	HRMS (ESI): Calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2$: 237.1392. Found 237.1393.	
	IR (neat, cm^{-1}): 3467, 3375, 1617, 1508, 1455, 1230, 750.	
2c	81% from S4c .	Orange oil.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.25 – 7.15 (m, 2H), 7.06 (d, J = 2.5 Hz, 1H), 7.02 (d, J = 8.8 Hz, 1H), 6.98 (d, J = 1.3 Hz, 1H), 6.90 – 6.80 (m, 3H), 3.89 (s, 3H), 3.61 (s, 2H), 2.36 (d, J = 1.3 Hz, 3H). The NMR data was in accordance with literature data. ^{S8}	
2d	57% from S4d .	Pale yellow solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, J = 1.6 Hz, 1H), 7.29 – 7.20 (m, 2H), 7.15 (dd, J = 7.8, 1.6 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.91 – 6.80 (m, 2H), 3.57 (s, 2H), 2.34 (d, J = 1.1 Hz, 3H).	
	$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.9, 135.2, 130.6, 129.1, 128.4, 127.2, 124.9, 124.4, 121.6, 118.5, 116.2, 112.8, 112.1, 111.9, 9.5.	
	LRMS (ESI): m/z = 299 [M-H].	
	HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{12}\text{BrN}_2$: 299.0178. Found 299.0180.	
	IR (neat, cm^{-1}): 3381, 1618, 1506, 1447, 790, 750.	
2e	67% from S4e .	Pale yellow solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 (d, J = 1.9 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.18 – 7.10 (m, 2H), 7.02 (m, 2H), 6.91 – 6.80 (m, 2H), 3.58 (s, 2H), 2.35 (d, J = 1.3 Hz, 3H). The NMR data was in accordance with literature data. ^{S8}	

3.4.2. General procedure for the preparation of 2f-2h^{S9}

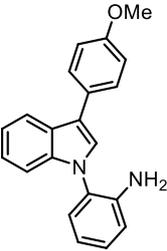


In a dried two-neck flask, indole (0.28 g, 2.44 mmol), bromobenzene (0.33 mL, 3.15 mmol), palladium(II) acetate (0.039 g, 0.17 mmol), benzyltributylammonium chloride (0.09 g, 0.34 mmol), and potassium carbonate (0.45 g, 3.27 mmol) were mixed in toluene (8 mL). After being refluxed for 44 h, the mixture was cooled to room temperature, followed by filtration through Celite. Water was added to the mixture and the mixture was extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by column chromatography (SiO₂, hexane/ethyl acetate) to give **S5f**.

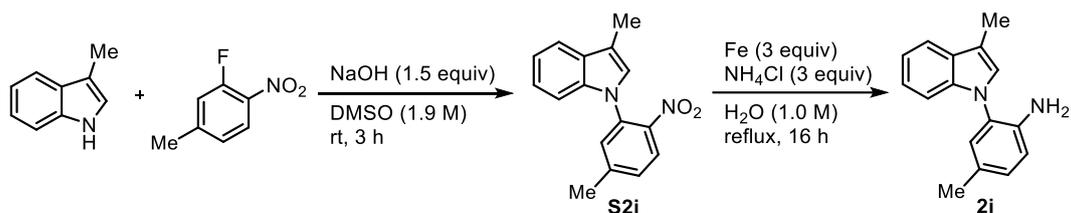
2f was synthesized according to synthetic procedure of **2a**.

Data of 2f-2h

2f	87% from S5f .	Pale yellow oil.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.05 – 7.97 (m, 1H), 7.72 (dd, <i>J</i> = 7.9, 2.4 Hz, 2H), 7.46 (td, <i>J</i> = 7.9, 2.4 Hz, 2H), 7.40 (s, 1H), 7.35 – 7.15 (m, 6H), 6.88 (m, 2H), 3.65 (s, 2H). The NMR data was in accordance with literature data. ^{S10}	
2g	83% from S5g .	Pale yellow oil.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.03 – 7.96 (m, 1H), 7.65 – 7.58 (m, 2H), 7.38 (s, 1H), 7.33 – 7.15 (m, 7H), 6.93 – 6.83 (m, 2H), 3.66 (s, 2H), 2.42 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 143.0, 137.1, 135.6, 132.1, 129.5, 129.1, 128.5, 127.3, 126.3, 125.8, 124.4, 122.5, 120.5, 120.0, 118.6, 118.4, 116.2, 111.0, 21.1.	
	LRMS (ESI): <i>m/z</i> = 321 [M+Na].	
	HRMS (ESI): Calcd for C ₂₁ H ₁₈ N ₂ Na: 321.1368. Found 321.1370.	
	IR (neat, cm ⁻¹): 3472, 3382, 1618, 1509, 1312, 1217, 746.	

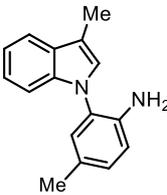
2h	46% from S5h .	Pale yellow oil.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.00 – 7.93 (m, 1H), 7.67 – 7.60 (m, 2H), 7.34 (s, 1H), 7.31 – 7.15 (m, 5H), 7.06 – 7.00 (m, 2H), 6.94 – 6.83 (m, 2H), 3.88 (s, 3H), 3.67 (s, 2H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 158.1, 143.0, 137.0, 129.1, 128.52, 128.47, 127.6, 126.4, 125.4, 124.5, 122.5, 120.5, 119.9, 118.4, 118.3, 116.2, 114.2, 111.0, 55.2.	
	LRMS (ESI): m/z = 315 [M+H].	
	HRMS (ESI): Calcd for C ₂₁ H ₁₉ N ₂ O: 315.1497. Found 315.1497.	
	IR (neat, cm ⁻¹): 3379, 1618, 1551, 1502, 1243, 747.	

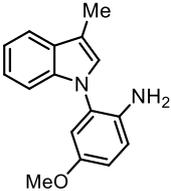
3.4.3. General procedure for the preparation of 2i-2k

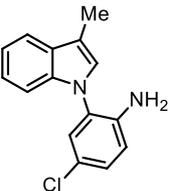


2i-2k were synthesized according to synthetic procedure of **2a**.

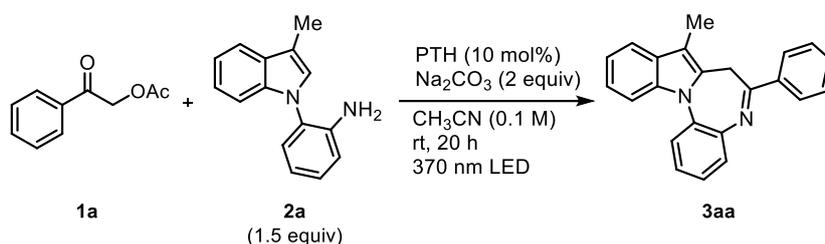
Data of 2i-2k

2i	24% from S2i .	Pale yellow oil.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.66 – 7.61 (m, 1H), 7.24 – 7.10 (m, 3H), 7.05 (dd, <i>J</i> = 8.2, 2.0 Hz, 1H), 7.00 (d, <i>J</i> = 3.0 Hz, 2H), 6.80 (d, <i>J</i> = 8.2 Hz, 1H), 3.48 (s, 2H), 2.40 (s, 3H), 2.29 (s, 3H).	
	The NMR data was in accordance with literature data. ^{S11}	

2j	73% from S2j .	Pale brown solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 – 7.62 (m, 1H), 7.24 – 7.13 (m, 3H), 7.01 (d, J = 1.3 Hz, 1H), 6.89 – 6.81 (m, 2H), 6.78 (d, J = 2.5 Hz, 1H), 3.75 (s, 3H), 3.35 (s, 2H), 2.40 (d, J = 1.2 Hz, 3H). The NMR data was in accordance with literature data. ^{S11}	

2k	77% from S2k .	Pale yellow solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 – 7.60 (m, 1H), 7.25 – 7.15 (m, 4H), 7.14 – 7.09(m, 1H), 6.96 (d, J = 1.2 Hz, 1H), 6.84 – 6.77 (m, 1H), 3.63 (s, 2H), 2.39 (d, J = 1.1 Hz, 3H). The NMR data was in accordance with literature data. ^{S11}	

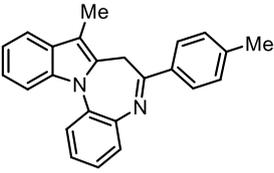
3.5. General procedure for the synthesis of indole-fused benzodiazepines

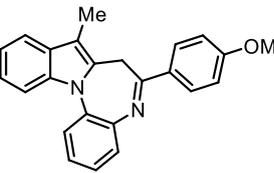


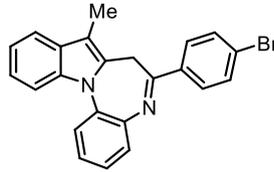
In a dried test tube, sodium carbonate (10.6 mg, 0.10 mmol) was dried up by heating gun under vacuum. **1a** (8.9 mg, 0.05 mmol), **2a** (16.7 mg, 0.075 mmol) and PTH (1.4 mg, 0.005 mmol) were mixed in CH₃CN (0.5 mL), and degassed 4 times by freeze-pump-thaw. The mixture was irradiated with 370 nm LED for 20 h. After irradiation, water was added to the mixture and extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator. The NMR yield was determined by ¹H NMR with 1,1,2-trichloroethane as an internal standard. The crude mixture was purified by flash column chromatography (SiO₂, hexane/ethyl acetate) to give **3aa** (12.9 mg, 0.040 mmol) in 80%.

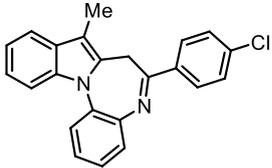
Data of products

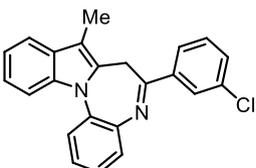
3aa	80%	Pale yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.09 – 8.00 (m, 2H), 7.82 (dd, <i>J</i> = 7.8, 1.6 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.59 – 7.50 (m, 2H), 7.46 (dd, <i>J</i> = 5.1, 1.8 Hz, 3H), 7.36 (td, <i>J</i> = 7.6, 1.6 Hz, 1H), 7.31 (td, <i>J</i> = 7.6, 1.8 Hz, 1H), 7.23 – 7.13 (m, 2H), 4.57 (d, <i>J</i> = 13.8 Hz, 1H), 3.44 (d, <i>J</i> = 13.8 Hz, 1H), 2.41 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 165.7, 141.5, 137.7, 136.6, 134.7, 130.8, 130.7, 130.5, 128.6, 127.8, 127.6, 125.663, 125.659, 123.7, 121.9, 120.2, 118.8, 110.8, 105.7, 28.1, 8.5.	
	LRMS (ESI): <i>m/z</i> = 345 [M+Na].	
	HRMS (ESI): Calcd for C ₂₃ H ₁₈ N ₂ Na: 345.1368. Found 345.1365.	
	IR (neat, cm ⁻¹): 1611, 1574, 1484, 1456, 1363, 1213, 754.	

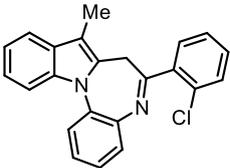
3ba	80%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.96 (d, <i>J</i> = 8.3 Hz, 2H), 7.82 (dd, <i>J</i> = 7.9, 1.6 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.59 – 7.50 (m, 2H), 7.36 (td, <i>J</i> = 7.6, 1.6 Hz, 1H), 7.33 – 7.24 (m, 3H), 7.24 – 7.14 (m, 2H), 4.56 (d, <i>J</i> = 13.7 Hz, 1H), 3.42 (d, <i>J</i> = 13.7 Hz, 1H), 2.40 (s, 6H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 165.5, 141.6, 141.3, 136.7, 134.9, 134.6, 130.6, 130.5, 129.3, 127.8, 127.6, 125.6, 125.5, 123.7, 121.8, 120.2, 118.7, 110.8, 105.6, 27.9, 21.4, 8.4.	
	LRMS (ESI): <i>m/z</i> = 337 [M+H].	
	HRMS (ESI): Calcd for C ₂₄ H ₂₁ N ₂ : 337.1705. Found 337.1707.	
	IR (neat, cm ⁻¹): 1605, 1566, 1484, 1456, 1363, 1212, 741.	

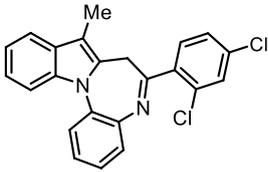
3ca	49%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.03 (d, <i>J</i> = 8.9 Hz, 2H), 7.81 (dd, <i>J</i> = 7.9, 1.5 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.59 – 7.53 (m, 1H), 7.51 (dd, <i>J</i> = 7.9, 1.7 Hz, 1H), 7.35 (td, <i>J</i> = 7.6, 1.5 Hz, 1H), 7.29 (td, <i>J</i> = 7.6, 1.7 Hz, 1H), 7.24 – 7.13 (m, 2H), 6.96 (d, <i>J</i> = 8.9 Hz, 2H), 4.55 (d, <i>J</i> = 13.8 Hz, 1H), 3.86 (s, 3H), 3.41 (d, <i>J</i> = 13.8 Hz, 1H), 2.40 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 164.8, 161.9, 141.7, 136.6, 134.6, 130.6, 130.5, 130.2, 129.4, 127.7, 125.6, 125.3, 123.7, 121.8, 120.2, 118.7, 113.9, 110.8, 105.5, 55.4, 27.7, 8.4.	
	LRMS (ESI): <i>m/z</i> = 353 [M+H].	
	HRMS (ESI): Calcd for C ₂₄ H ₂₁ N ₂ O: 353.1654. Found 353.1652.	
	IR (neat, cm ⁻¹): 1604, 1570, 1484, 1456, 1249, 1173, 742.	

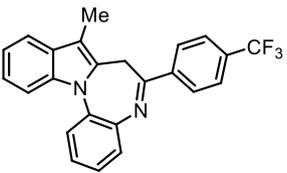
3da	61%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.92 (d, <i>J</i> = 8.6 Hz, 2H), 7.82 (dd, <i>J</i> = 7.8, 1.7 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.62 – 7.55 (m, 3H), 7.52 (dd, <i>J</i> = 7.7, 1.8 Hz, 1H), 7.41 – 7.29 (m, 2H), 7.25 – 7.15 (m, 2H), 4.50 (d, <i>J</i> = 13.9 Hz, 1H), 3.44 (d, <i>J</i> = 13.9 Hz, 1H), 2.40 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 164.5, 141.3, 136.6, 136.3, 134.7, 131.8, 130.6, 130.4, 129.2, 127.8, 125.9, 125.7, 125.6, 123.8, 122.0, 120.3, 118.8, 110.8, 105.8, 27.9, 8.5.	
	LRMS (ESI): <i>m/z</i> = 401 [M+H].	
	HRMS (ESI): Calcd for C ₂₃ H ₁₈ BrN ₂ : 401.0653. Found 401.0655.	
	IR (neat, cm ⁻¹): 1613, 1583, 1484, 1455, 1363, 1007, 754.	

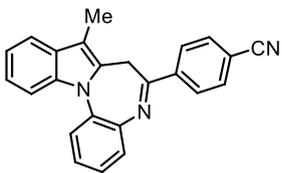
3ea	81%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.99 (d, <i>J</i> = 8.7 Hz, 2H), 7.82 (dd, <i>J</i> = 7.9, 1.6 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.60 – 7.55 (m, 1H), 7.51 (dd, <i>J</i> = 7.8, 1.7 Hz, 1H), 7.43 (d, <i>J</i> = 8.7 Hz, 2H), 7.37 (td, <i>J</i> = 7.6, 1.7 Hz, 1H), 7.32 (td, <i>J</i> = 7.6, 1.8 Hz, 1H), 7.25 – 7.15 (m, 2H), 4.51 (d, <i>J</i> = 13.9 Hz, 1H), 3.44 (d, <i>J</i> = 13.9 Hz, 1H), 2.40 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 164.4, 141.3, 137.1, 136.3, 136.1, 134.7, 130.6, 130.5, 129.0, 128.9, 127.8, 125.9, 125.7, 123.8, 122.0, 120.3, 118.8, 110.8, 105.8, 27.9, 8.5.	
	LRMS (ESI): <i>m/z</i> = 357 [M+H].	
	HRMS (ESI): Calcd for C ₂₃ H ₁₈ ClN ₂ : 357.1159. Found 357.1159.	
	IR (neat, cm ⁻¹): 1613, 1588, 1484, 1456, 1363, 840, 754.	

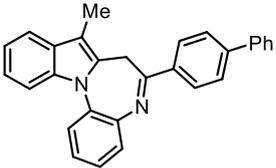
3fa	90%	Pale yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.05 (t, <i>J</i> = 1.9 Hz, 1H), 7.90 (dt, <i>J</i> = 7.5, 1.6 Hz, 1H), 7.82 (dd, <i>J</i> = 7.8, 1.7 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.60 – 7.55 (m, 1H), 7.53 (dd, <i>J</i> = 7.8, 1.8 Hz, 1H), 7.47 – 7.30 (m, 4H), 7.25 – 7.15 (m, 2H), 4.50 (d, <i>J</i> = 13.9 Hz, 1H), 3.46 (d, <i>J</i> = 13.9 Hz, 1H), 2.42 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 164.3, 141.1, 139.6, 136.3, 134.8, 134.7, 130.7, 130.6, 130.5, 129.8, 127.9, 127.8, 126.0, 125.7, 125.6, 123.8, 122.0, 120.4, 118.8, 110.8, 105.8, 28.1, 8.5.	
	LRMS (ESI): <i>m/z</i> = 357 [M+H].	
	HRMS (ESI): Calcd for C ₂₃ H ₁₈ ClN ₂ : 357.1159. Found 357.1159.	
	IR (neat, cm ⁻¹): 1612, 1565, 1484, 1456, 1363, 1212, 840, 756.	

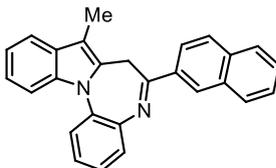
3ga	56%	Pale yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.87 – 7.81 (m, 1H), 7.74 – 7.69 (m, 1H), 7.59 – 7.51 (m, 2H), 7.47 (dd, <i>J</i> = 8.1, 1.2 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.25 – 7.15 (m, 4H), 4.33 (d, <i>J</i> = 13.8 Hz, 1H), 3.66 (d, <i>J</i> = 14.0 Hz, 1H), 2.14 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 168.3, 140.8, 139.3, 136.3, 134.7, 131.6, 130.6, 130.2, 129.8, 127.9, 127.1, 126.3, 125.7, 123.8, 122.0, 120.3, 118.9, 110.7, 106.6, 32.2, 8.1.	
	LRMS (ESI): <i>m/z</i> = 379 [M+Na].	
	HRMS (ESI): Calcd for C ₂₃ H ₁₇ ClN ₂ Na: 379.0978. Found 379.0977.	
	IR (neat, cm ⁻¹): 1616, 1566, 1486, 1455, 1364, 1213, 834, 754.	

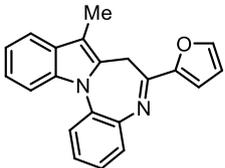
3ha	22%	Yellow oil.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 – 7.79 (m, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.55 – 7.47 (m, 2H), 7.42 – 7.33 (m, 2H), 7.26 – 7.17 (m, 3H), 7.13 (d, J = 8.2 Hz, 1H), 4.30 (d, J = 13.9 Hz, 1H), 3.64 (d, J = 13.9 Hz, 1H), 2.15 (s, 3H).	
	$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.2, 140.6, 137.8, 136.0, 134.7, 132.5, 131.2, 130.6, 130.2, 129.7, 127.9, 127.5, 126.5, 125.8, 123.8, 122.1, 120.4, 119.0, 110.7, 106.7, 32.0, 8.1.	
	LRMS (ESI): m/z = 391 [M+H].	
	HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{17}\text{Cl}_2\text{N}_2$: 391.0769. Found 391.0768.	
	IR (neat, cm^{-1}): 1616, 1583, 1486, 1456, 1364, 1013, 814, 741.	

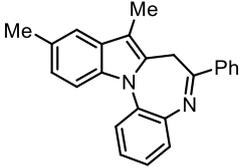
3ia	63%	Pale yellow solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.15 (d, J = 8.6 Hz, 2H), 7.83 (dd, J = 7.7, 1.7 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.70 – 7.66 (m, 1H), 7.61 – 7.56 (m, 1H), 7.54 (dd, J = 7.6, 1.9 Hz, 1H), 7.43 – 7.31 (m, 2H), 7.25 – 7.15 (m, 2H), 4.54 (d, J = 14.0 Hz, 1H), 3.49 (d, J = 13.9 Hz, 1H), 2.41 (s, 3H).	
	$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.3, 141.1, 141.0, 136.2, 134.7, 132.3 (q, J = 32.7 Hz), 130.6, 130.5, 127.92, 127.88, 126.2, 125.8, 125.6 (q, J = 3.8 Hz), 123.9 (q, J = 272.3 Hz), 123.8, 122.1, 120.4, 118.9, 110.8, 105.9, 28.1, 8.5.	
	$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -65.0.	
	LRMS (ESI): m/z = 391 [M+H].	
	HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{N}_2$: 391.1422. Found 391.1420.	
IR (neat, cm^{-1}): 1483, 1456, 1315, 1120, 754.		

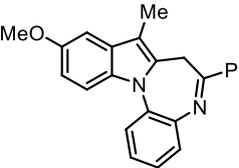
3ja	20%	Yellow solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.13 (d, J = 8.5 Hz, 2H), 7.87 – 7.79 (m, 1H), 7.75 (d, J = 8.5 Hz, 2H), 7.68 (dd, J = 8.3, 1.2 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.55 – 7.49 (m, 1H), 7.43 – 7.31 (m, 2H), 7.25 – 7.15 (m, 2H), 4.51 (d, J = 14.0 Hz, 1H), 3.49 (d, J = 14.0 Hz, 1H), 2.41 (s, 3H).	
	$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.7, 141.7, 140.9, 136.1, 134.7, 132.4, 130.6, 130.5, 128.1, 127.9, 126.5, 125.8, 123.9, 122.2, 120.5, 118.9, 118.4, 114.1, 110.8, 106.0, 28.0, 8.5.	
	LRMS (ESI): m/z = 348 [M+H].	
	HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{18}\text{N}_3$: 348.1501. Found 348.1504.	
IR (neat, cm^{-1}): 2228, 1614, 1558, 1484, 1456, 1363, 743.		

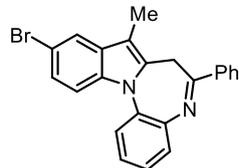
3ka	68%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.14 (d, <i>J</i> = 8.5 Hz, 2H), 7.84 (dd, <i>J</i> = 7.9, 1.6 Hz, 1H), 7.70 (d, <i>J</i> = 8.3 Hz, 3H), 7.68 – 7.62 (m, 2H), 7.57 (td, <i>J</i> = 7.9, 1.7 Hz, 2H), 7.47 (t, <i>J</i> = 7.6 Hz, 2H), 7.39 (td, <i>J</i> = 7.6, 1.6 Hz, 2H), 7.33 (td, <i>J</i> = 7.6, 1.7 Hz, 1H), 7.25 – 7.15 (m, 2H), 4.62 (d, <i>J</i> = 13.8 Hz, 1H), 3.48 (d, <i>J</i> = 13.8 Hz, 1H), 2.44 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 165.2, 143.5, 141.6, 140.1, 136.6, 136.5, 134.7, 130.7, 130.5, 128.9, 128.2, 127.9, 127.8, 127.3, 127.1, 125.7, 125.6, 123.8, 121.9, 120.2, 118.8, 110.8, 105.7, 28.0, 8.5.	
	LRMS (ESI): <i>m/z</i> = 399 [M+H].	
	HRMS (ESI): Calcd for C ₂₉ H ₂₃ N ₂ : 391.1861. Found 391.1862.	
	IR (neat, cm ⁻¹): 1602, 1484, 1455, 755.	

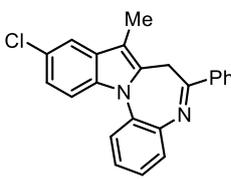
3la	54%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.48 (s, 1H), 8.22 (dd, <i>J</i> = 8.7, 1.8 Hz, 1H), 8.00 – 7.93 (m, 1H), 7.93 – 7.81 (m, 3H), 7.74 – 7.66 (m, 1H), 7.62 – 7.51 (m, 4H), 7.40 (td, <i>J</i> = 7.6, 1.6 Hz, 1H), 7.33 (td, <i>J</i> = 7.6, 1.7 Hz, 1H), 7.24 – 7.13 (m, 2H), 4.75 (d, <i>J</i> = 13.8 Hz, 1H), 3.53 (d, <i>J</i> = 13.9 Hz, 1H), 2.47 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 165.5, 141.6, 136.7, 135.1, 134.7, 134.5, 132.9, 130.7, 130.5, 129.0, 128.4, 128.1, 127.9, 127.7, 127.5, 126.5, 125.7, 124.6, 123.8, 121.9, 120.2, 118.8, 110.8, 105.7, 28.1, 8.5.	
	LRMS (ESI): <i>m/z</i> = 373 [M+H].	
	HRMS (ESI): Calcd for C ₂₇ H ₂₁ N ₂ : 373.1705. Found 373.1704.	
	IR (neat, cm ⁻¹): 1606, 1484, 1456, 1363, 741.	

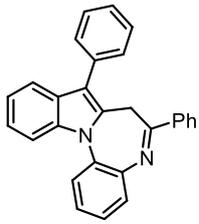
3ma	29%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.80 (dd, <i>J</i> = 7.8, 1.7 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.61 (dd, <i>J</i> = 1.8, 0.7 Hz, 1H), 7.55 (td, <i>J</i> = 7.7, 1.5 Hz, 2H), 7.36 (td, <i>J</i> = 7.6, 1.7 Hz, 1H), 7.31 (td, <i>J</i> = 7.6, 1.8 Hz, 1H), 7.24 – 7.12 (m, 3H), 6.55 (dd, <i>J</i> = 3.5, 1.8 Hz, 1H), 4.44 (d, <i>J</i> = 13.9 Hz, 1H), 3.42 (d, <i>J</i> = 13.9 Hz, 1H), 2.38 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 155.8, 151.9, 145.8, 141.1, 136.2, 134.7, 130.6, 128.1, 125.8, 125.7, 124.0, 122.0, 120.3, 118.8, 114.5, 112.3, 110.7, 106.1, 27.7, 8.1.	
	LRMS (ESI): <i>m/z</i> = 335 [M+Na].	
	HRMS (ESI): Calcd for C ₂₁ H ₁₆ N ₂ ONa: 335.1160. Found 335.1159.	
	IR (neat, cm ⁻¹): 1609, 1479, 1455, 1363, 742.	

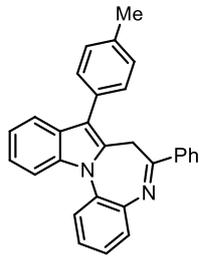
3ab	79%	Pale yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.09 – 8.00 (m, 2H), 7.80 (dd, <i>J</i> = 7.8, 1.6 Hz, 1H), 7.57 (d, <i>J</i> = 8.4 Hz, 1H), 7.53 (dd, <i>J</i> = 7.8, 1.8 Hz, 1H), 7.46 (dd, <i>J</i> = 4.8, 2.2 Hz, 3H), 7.40 – 7.27 (m, 3H), 7.03 (dd, <i>J</i> = 8.4, 1.7 Hz, 1H), 4.55 (d, <i>J</i> = 13.8 Hz, 1H), 3.43 (d, <i>J</i> = 13.8 Hz, 1H), 2.48 (s, 3H), 2.38 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 165.6, 141.4, 137.8, 136.7, 133.0, 130.9, 130.8, 130.7, 129.6, 128.6, 127.8, 127.6, 125.6, 125.4, 123.6, 123.3, 118.5, 110.5, 105.2, 28.1, 21.4, 8.5.	
	LRMS (ESI): <i>m/z</i> = 337 [M+H].	
	HRMS (ESI): Calcd for C ₂₄ H ₂₁ N ₂ : 337.1705. Found 337.1708.	
	IR (neat, cm ⁻¹): 1598, 1486, 1457, 757.	

3ac	44%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.09 – 8.01 (m, 2H), 7.78 (dd, <i>J</i> = 8.0, 1.5 Hz, 1H), 7.57 (d, <i>J</i> = 8.8 Hz, 1H), 7.53 (dd, <i>J</i> = 7.8, 1.7 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.35 (td, <i>J</i> = 7.6, 1.7 Hz, 1H), 7.30 (td, <i>J</i> = 7.6, 1.8 Hz, 1H), 6.99 (d, <i>J</i> = 2.5 Hz, 1H), 6.84 (dd, <i>J</i> = 8.9, 2.5 Hz, 1H), 4.55 (d, <i>J</i> = 13.9 Hz, 1H), 3.88 (s, 3H), 3.40 (d, <i>J</i> = 13.9 Hz, 1H), 2.38 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 165.4, 154.5, 141.3, 137.8, 137.2, 131.3, 130.8, 130.7, 129.8, 128.6, 127.9, 127.6, 125.7, 125.4, 123.5, 111.7, 111.4, 105.4, 100.9, 55.9, 28.2, 8.6.	
	LRMS (ESI): <i>m/z</i> = 353 [M+H].	
	HRMS (ESI): Calcd for C ₂₄ H ₂₁ N ₂ O: 353.1654. Found 353.1656.	
	IR (neat, cm ⁻¹): 1598, 1484, 1457, 757.	

3ad	60%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.08 – 8.00 (m, 2H), 7.73 (dd, <i>J</i> = 8.0, 1.6 Hz, 1H), 7.67 (d, <i>J</i> = 1.9 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.50 – 7.44 (m, 3H), 7.38 (td, <i>J</i> = 7.6, 1.5 Hz, 1H), 7.31 (td, <i>J</i> = 7.7, 1.7 Hz, 1H), 7.29 – 7.24 (m, 1H), 4.56 (d, <i>J</i> = 13.8 Hz, 1H), 3.42 (d, <i>J</i> = 13.9 Hz, 1H), 2.36 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 165.5, 141.5, 137.7, 137.5, 133.3, 132.4, 131.0, 130.1, 128.7, 127.9, 127.6, 126.0, 125.8, 124.6, 123.6, 121.4, 113.4, 112.2, 105.3, 28.0, 8.4.	
	LRMS (ESI): <i>m/z</i> = 401 [M+H].	
	HRMS (ESI): Calcd for C ₂₃ H ₁₈ BrN ₂ : 401.0653. Found 401.0653.	
	IR (neat, cm ⁻¹): 1609, 1485, 1456, 756.	

3ae	61%	Pale yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.08 – 8.01 (m, 2H), 7.74 (dd, <i>J</i> = 7.9, 1.5 Hz, 1H), 7.57 (d, <i>J</i> = 8.8 Hz, 1H), 7.53 (dd, <i>J</i> = 7.9, 1.7 Hz, 1H), 7.51 (d, <i>J</i> = 2.1 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.38 (td, <i>J</i> = 7.9, 1.5 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.14 (dd, <i>J</i> = 8.7, 2.1 Hz, 1H), 4.56 (d, <i>J</i> = 13.8 Hz, 1H), 3.42 (d, <i>J</i> = 13.9 Hz, 1H), 2.37 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 165.5, 141.5, 137.9, 137.5, 133.0, 131.8, 131.0, 130.2, 128.7, 127.9, 127.6, 126.0, 125.84, 125.81, 123.6, 122.0, 118.3, 111.8, 105.4, 28.1, 8.4.	
	LRMS (ESI): <i>m/z</i> = 357 [M+H].	
	HRMS (ESI): Calcd for C ₂₃ H ₁₈ ClN ₂ : 357.1159. Found 357.1160.	
	IR (neat, cm ⁻¹): 1610, 1485, 1457, 1213, 757.	

3af	81%	Pale yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.91 (dd, <i>J</i> = 7.9, 1.6 Hz, 1H), 7.75 (d, <i>J</i> = 8.2 Hz, 1H), 7.71 – 7.64 (m, 3H), 7.56 (dd, <i>J</i> = 7.9, 1.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.32 (m, 6H), 7.32 – 7.21 (m, 3H), 7.21 – 7.15 (m, 1H), 4.66 (d, <i>J</i> = 13.7 Hz, 1H), 3.48 (d, <i>J</i> = 13.7 Hz, 1H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 166.0, 141.9, 137.2, 136.5, 134.8, 133.9, 130.8, 130.1, 129.9, 129.2, 128.7, 128.4, 127.9, 127.8, 126.7, 126.2, 125.7, 124.0, 122.3, 121.1, 119.5, 113.7, 111.0, 28.4.	
	LRMS (ESI): <i>m/z</i> = 385 [M+H].	
	HRMS (ESI): Calcd for C ₂₈ H ₂₁ N ₂ : 385.1705. Found 385.1704.	
	IR (neat, cm ⁻¹): 1610, 1482, 1455, 1372, 757.	

3ag	84%	Yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 7.86 (dd, <i>J</i> = 7.8, 1.6 Hz, 1H), 7.71 (d, <i>J</i> = 8.2 Hz, 2H), 7.67 (d, <i>J</i> = 7.4 Hz, 3H), 7.63 (d, <i>J</i> = 7.8 Hz, 1H), 7.52 (dd, <i>J</i> = 7.9, 1.5 Hz, 2H), 7.41 – 7.23 (m, 4H), 7.23 – 7.17 (m, 2H), 7.17 – 7.11 (m, 2H), 4.61 (d, <i>J</i> = 13.7 Hz, 1H), 3.43 (d, <i>J</i> = 13.7 Hz, 1H), 2.43 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 166.1, 141.8, 137.3, 136.4, 136.3, 134.8, 130.8, 130.1, 129.8, 129.4, 129.3, 128.4, 127.9, 127.8, 126.1, 125.7, 124.0, 122.3, 121.0, 119.5, 113.6, 110.9, 28.5, 21.3.	
	LRMS (ESI): <i>m/z</i> = 399 [M+H].	
	HRMS (ESI): Calcd for C ₂₉ H ₂₃ N ₂ : 399.1861. Found 399.1861.	
	IR (neat, cm ⁻¹): 1610, 1483, 1455, 1372, 757.	

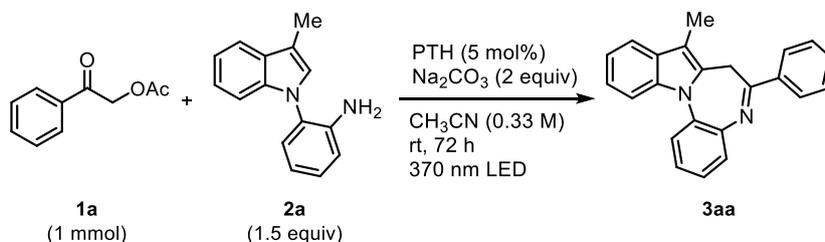
3ah	89%	Yellow solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.75 (d, $J = 8.3$ Hz, 1H), 7.73 – 7.69 (m, 2H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.56 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.45 – 7.37 (m, 2H), 7.37 – 7.28 (m, 5H), 7.28 – 7.21 (m, 1H), 7.18 (t, $J = 7.1$ Hz, 1H), 7.04 (d, $J = 8.6$ Hz, 2H), 4.63 (d, $J = 13.6$ Hz, 1H), 3.92 (s, 3H), 3.48 (d, $J = 13.7$ Hz, 1H).	
	$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.1, 158.5, 141.8, 137.3, 136.3, 134.7, 131.1, 130.8, 130.1, 129.5, 128.4, 127.9, 127.8, 126.11, 126.08, 125.7, 124.0, 122.2, 120.9, 119.4, 114.2, 113.3, 110.9, 55.4, 28.5.	
	LRMS (ESI): $m/z = 415$ [M+H].	
	HRMS (ESI): Calcd for $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}$: 415.1810. Found 415.1807.	
	IR (neat, cm^{-1}): 1510, 1483, 1455, 1245, 759.	

3ai	55%	Pale yellow solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 – 8.00 (m, 2H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.64 (s, 1H), 7.56 (d, $J = 7.7$ Hz, 1H), 7.50 – 7.39 (m, 4H), 7.25 – 7.14 (m, 3H), 4.56 (d, $J = 13.7$ Hz, 1H), 3.43 (d, $J = 13.7$ Hz, 1H), 2.46 (s, 3H), 2.41 (s, 3H).	
	$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.1, 139.1, 137.9, 136.6, 135.7, 134.6, 130.7, 130.3, 128.6, 127.7, 127.6, 126.6, 123.9, 121.8, 120.2, 118.7, 110.8, 105.5, 28.1, 21.2, 8.5.	
	LRMS (ESI): $m/z = 337$ [M+H].	
	HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2$: 337.1705. Found 337.1704.	
	IR (neat, cm^{-1}): 1612, 1458, 1361, 741.	

3aj	45%	Pale yellow solid.
	$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05 – 7.98 (m, 2H), 7.72 (dd, $J = 6.9, 2.0$ Hz, 1H), 7.56 (dd, $J = 6.9, 2.0$ Hz, 1H), 7.49 – 7.42 (m, 4H), 7.36 (d, $J = 2.8$ Hz, 1H), 7.24 – 7.15 (m, 2H), 6.95 (dd, $J = 8.8, 2.8$ Hz, 1H), 4.56 (d, $J = 13.7$ Hz, 1H), 3.88 (s, 3H), 3.45 (d, $J = 13.7$ Hz, 1H), 2.40 (s, 3H).	
	$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.3, 157.3, 138.0, 136.5, 135.2, 134.5, 131.4, 130.8, 130.6, 129.2, 128.6, 127.5, 121.9, 120.3, 118.8, 112.1, 110.7, 108.4, 105.6, 55.7, 28.0, 8.5.	
	LRMS (ESI): $m/z = 353$ [M+H].	
	HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}$: 353.1654. Found 353.1653.	
	IR (neat, cm^{-1}): 1609, 1496, 1262, 1199, 757.	

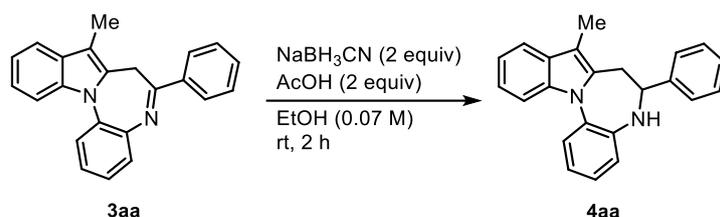
3ak	56%	Pale yellow solid.
	¹ H NMR (400 MHz, CDCl ₃) δ 8.06 – 8.00 (m, 2H), 7.81 (d, <i>J</i> = 2.2 Hz, 1H), 7.67 (d, <i>J</i> = 8.3 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.48 – 7.43 (m, 4H), 7.32 (dd, <i>J</i> = 8.3, 2.2 Hz, 1H), 7.25 – 7.16 (m, 2H), 4.58 (d, <i>J</i> = 13.8 Hz, 1H), 3.43 (d, <i>J</i> = 13.9 Hz, 1H), 2.40 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃) δ 166.1, 140.1, 137.5, 136.2, 134.5, 131.4, 131.1, 130.8, 130.7, 129.1, 128.7, 127.6, 125.8, 123.5, 122.3, 120.7, 118.9, 110.6, 106.4, 28.1, 8.5.	
	LRMS (ESI): <i>m/z</i> = 357 [M+H].	
	HRMS (ESI): Calcd for C ₂₃ H ₁₇ ClN ₂ : 357.1159. Found 357.1158.	
	IR (neat, cm ⁻¹): 1609, 1476, 1457, 757, 689.	

3.6. 1 mmol scale experiment



In a dried Schlenk tube, **1a** (178.2 mg, 1.0 mmol), **2a** (333.4 mg, 1.5 mmol), PTH (13.8 mg, 0.05 mmol) and sodium carbonate (212.0 mg, 2.0 mmol) were mixed in CH₃CN (3 mL), and degassed 4 times by freeze-pump-thaw. The mixture was irradiated with 370 nm LED for 72 h. After irradiation, water was added to the mixture and the mixture was extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by flash column chromatography (SiO₂, hexane/ethyl acetate) to give **3aa** (226.0 mg, 0.70 mmol) in 70%.

3.7. Reduction of 3aa



In a dried test tube, **3aa** (32.2 mg, 0.10 mmol) and sodium cyanoborohydride (12.6 mg, 0.20 mmol) were mixed in EtOH (1.5 mL). The mixture was cooled to 0 °C, and acetic acid (11.4 μ L, 0.20 mmol) was added to the mixture dropwise at 0 °C. After stirred at room temperature for 2 h, the solvent was removed *in vacuo* by rotary evaporator. Water was added and extracted with CH₂Cl₂ for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by recrystallization from a mixture of hexane and ethyl acetate to give **4aa** (20.0 mg, 0.062 mmol) in 62%.

4aa	62%	White crystal.
	¹ H NMR (400 MHz, DMSO- <i>d</i> ₆ , 140 °C) δ 7.55 (d, <i>J</i> = 7.8 Hz, 1H), 7.50 (d, <i>J</i> = 7.9 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.28 – 7.22 (m, 5H), 7.22 – 7.17 (m, 2H), 7.15 – 7.04 (m, 3H), 5.03 (s, 1H), 4.88 (q, <i>J</i> = 5.0, 5.0, 4.9 Hz, 1H), 3.18 (dd, <i>J</i> = 14.7, 5.1 Hz, 1H), 2.98 (dd, <i>J</i> = 14.8, 5.4 Hz, 1H), 1.88 (s, 3H).	
	¹³ C NMR (101 MHz, CDCl ₃ , 55 °C) δ 146.2 – 143.3 (brm), 141.5 – 138.7 (brm), 135.5, 133.6 – 130.7 (brm), 129.5, 128.4, 127.6, 126.5, 124.5, 123.0, 122.5, 121.6, 119.8, 118.6, 110.2, 108.8 – 105.7 (brm), 65.5, 30.7, 8.1.	
	LRMS (ESI): <i>m/z</i> = 325 [M+H].	
	HRMS (ESI): Calcd for C ₂₃ H ₂₁ N ₂ : 325.1705. Found 325.1706.	
	IR (neat, cm ⁻¹): 3436, 1507, 1457, 1365, 751.	

3.8. Conformational change of 4aa

When the ^1H NMR spectrum of **4aa** in CDCl_3 was recorded at room temperature, the aromatic region showed broad peaks. In addition, broad singlets for H^b (5.0 ppm and 4.8 ppm) and for methyl group (2.4 ppm and 1.7 ppm) were also observed, indicating an equilibrium mixture of two conformers in 1:0.8 ratio (Figure S1b). In order to investigate conformational change of **4aa**, we studied variable temperature NMR experiments. We observed clear signals corresponding to the two conformers at $-30\text{ }^\circ\text{C}$ and the two conformers converged to single conformer by gradually raising the temperature (Figure S1). After optimization, we found that the measurement of ^1H NMR spectra in $\text{DMSO}-d_6$ at $140\text{ }^\circ\text{C}$ was best conditions to obtain signals of single conformer (Page S57). The conformational change was also observed in the ^{13}C NMR spectra in CDCl_3 by raising the temperature (Figure S2). However, the aromatic region showed broad signals and the ^{13}C NMR spectra in $\text{DMSO}-d_6$ at high temperature became complicated. Further investigations of the structures and the NMR experiments of **4aa** are under way in our laboratory.

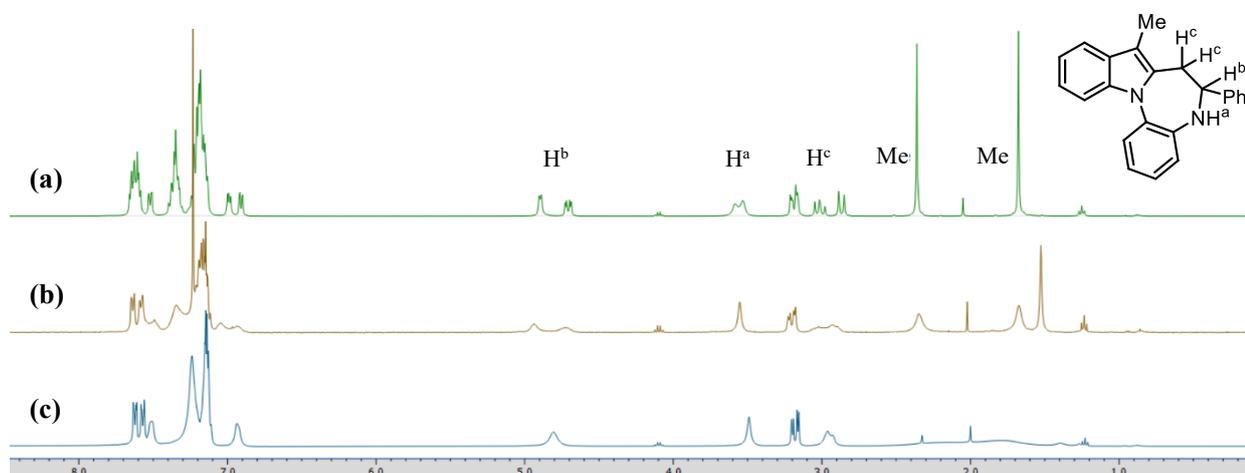


Figure S1. ^1H NMR spectra of **4aa** in CDCl_3 . (a) $-30\text{ }^\circ\text{C}$. (b) room temperature. (c) $55\text{ }^\circ\text{C}$.

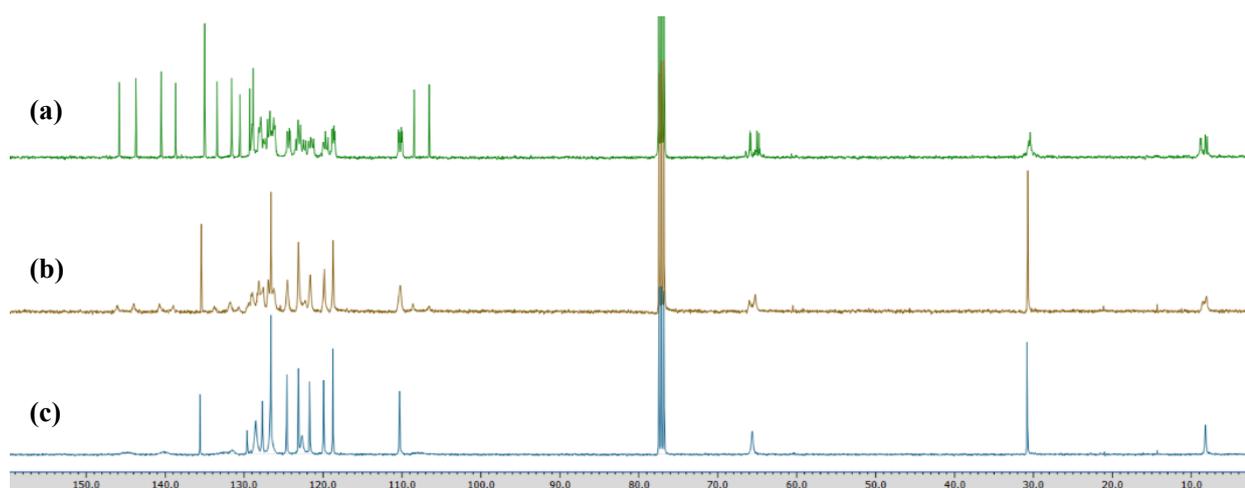
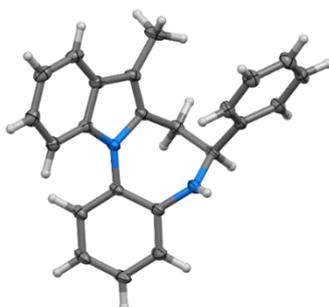


Figure S2. ^{13}C NMR spectra of **4aa** in CDCl_3 . (a) $-30\text{ }^\circ\text{C}$. (b) room temperature. (c) $55\text{ }^\circ\text{C}$.

3.9. X-Ray analysis of 4aa

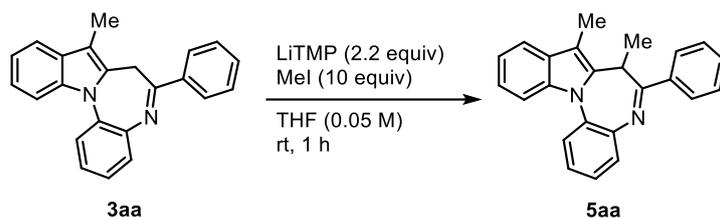
Single crystal of **4aa** for X-ray diffraction was obtained by recrystallization (hexane and ethyl acetate). Data collection was performed by XtaLAB mini II (Rigaku Co., Ltd.).

Table S4. Crystal data for 4aa



Empirical formula	C ₂₃ H ₂₀ N ₂	
Formula weight	324.41	
Temperature	100.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 11.0423(8) Å	<i>a</i> = 90°
	<i>b</i> = 15.3916(10) Å	<i>β</i> = 117.011(9)°
	<i>c</i> = 11.2723(8) Å	<i>γ</i> = 90°
Cell Volume	1706.8(2) Å ³	
<i>Z</i>	4	
<i>D</i> _{calc}	1.262 g/cm ³	
Absorption coefficient	0.074 mm ⁻¹	
<i>F</i> (000)	688	
Crystal size	0.11 x 0.09 x 0.06 mm ³	
Theta range for data collection	2.070 to 30.721°	
Index ranges	-15 ≤ <i>h</i> ≤ 15, -21 ≤ <i>k</i> ≤ 21, -16 ≤ <i>l</i> ≤ 13	
Reflections collected	16263	
Independent reflections	5054 [<i>R</i> _{int} = 0.0285]	
Max. and min. transmission	0.755 and 1.000	
data / restraints / parameters	5054 / 0 / 227	
Goodness-of-hit on <i>F</i> ²	1.035	
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> 1 = 0.0237, <i>wR</i> 2 = 0.0507	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0320, <i>wR</i> 2 = 0.0530	

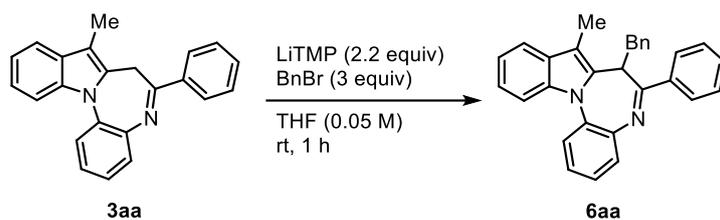
3.10. Methylation of 3aa



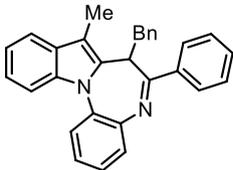
In a dried test tube, 1.51 M *n*-butyllithium (73 μ L, 0.11 mmol) was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (19.6 μ L, 0.115 mmol) in THF (0.5 mL) at -78 $^{\circ}$ C, and the mixture was stirred at 0 $^{\circ}$ C for 25 min. The mixture was cooled to -78 $^{\circ}$ C, and **3aa** (16.1 mg, 0.05 mmol) in THF (0.5 mL) was added dropwise. After the mixture was stirred at -78 $^{\circ}$ C for 30 min, iodomethane (31.1 μ L, 0.5 mmol) was added dropwise and the mixture was stirred at 25 $^{\circ}$ C for 1 h. Water was added to the mixture and extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by flash column chromatography (SiO_2 , hexane/ethyl acetate) to give **5aa** (12.7 mg, 0.038 mmol) in 75%.

5aa	75%	Yellow solid.
	^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.92 (m, 2H), 7.81 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.76 – 7.71 (m, 1H), 7.60 – 7.56 (m, 1H), 7.54 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.45 (dd, $J = 5.1, 2.0$ Hz, 3H), 7.34 (td, $J = 7.7, 1.6$ Hz, 1H), 7.29 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.25 – 7.16 (m, 2H), 5.02 (q, $J = 7.4$ Hz, 1H), 2.36 (s, 3H), 1.23 (d, $J = 7.4$ Hz, 3H).	
	^{13}C NMR (101 MHz, CDCl_3) δ 169.8, 141.2, 140.3, 139.5, 134.8, 130.5, 128.6, 127.5, 127.4, 125.6, 125.5, 123.4, 122.0, 120.3, 118.8, 110.9, 106.5, 34.8, 13.9, 8.2.	
	LRMS (ESI): $m/z = 337$ [$\text{M}+\text{H}$].	
	HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2$: 337.1705. Found 337.1708.	
	IR (neat, cm^{-1}): 1619, 1486, 1456, 1365, 1213, 753.	

3.11. Benzylation of 3aa

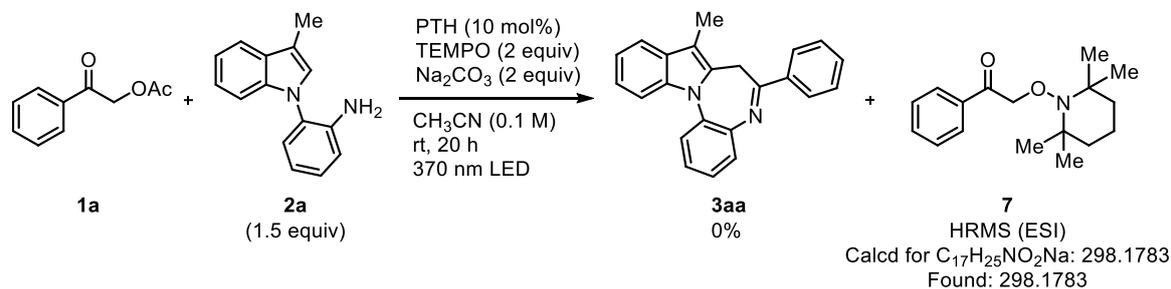


In a dried test tube, 1.51 M *n*-butyllithium (73 μ L, 0.11 mmol) was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (19.6 μ L, 0.115 mmol) in THF (0.5 mL) at -78 $^{\circ}$ C, and the mixture was stirred at 0 $^{\circ}$ C for 25 min. The mixture was cooled to -78 $^{\circ}$ C, and **3aa** (16.1 mg, 0.05 mmol) in THF (0.5 mL) was added dropwise. After the mixture was stirred at -78 $^{\circ}$ C for 30 min, benzyl bromide (17.8 μ L, 0.15 mmol) was added dropwise and the mixture was stirred at 25 $^{\circ}$ C for 1 h. Water was added to the mixture and extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo* by rotary evaporator. The crude mixture was purified by preparative TLC on SiO_2 (hexane/ethyl acetate) to give **6aa** (14.3 mg, 0.035 mmol) in 69%.

6aa	69%	Yellow powder.
	^1H NMR (400 MHz, CDCl_3) δ 7.91 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.77 (dd, $J = 8.2, 0.9$ Hz, 1H), 7.74 – 7.68 (m, 2H), 7.63 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.55 – 7.49 (m, 1H), 7.44 – 7.31 (m, 5H), 7.25 – 7.11 (m, 5H), 7.00 – 6.94 (m, 2H), 5.02 (t, $J = 8.1$ Hz, 1H), 2.89 (dd, $J = 13.5, 7.8$ Hz, 1H), 2.82 (dd, $J = 13.5, 8.5$ Hz, 1H), 2.07 (s, 3H).	
	^{13}C NMR (101 MHz, CDCl_3) δ 169.0, 141.4, 139.7, 138.9, 138.5, 134.9, 130.7, 130.5, 130.4, 128.7, 128.44, 128.41, 127.6, 127.4, 126.5, 125.84, 125.77, 123.4, 122.0, 120.3, 118.9, 111.0, 108.2, 43.9, 33.9, 7.8.	
	LRMS (ESI): $m/z = 413$ [M+H].	
	HRMS (ESI): Calcd for $\text{C}_{30}\text{H}_{25}\text{N}_2$: 413.2018. Found: 413.2020.	
	IR (neat, cm^{-1}): 1616, 1487, 1456, 1364, 1212, 742.	

4. Mechanistic study

4.1. Radical scavenging experiment



In a dried test tube, sodium carbonate (10.6 mg, 0.10 mmol) was dried up by heating gun under vacuum. **1a** (8.9 mg, 0.05 mmol), **2a** (16.7 mg, 0.075 mmol), TEMPO (15.6 mg, 0.10 mmol) and PTH (1.4 mg, 0.005 mmol) were mixed in CH_3CN (0.5 mL), and degassed 4 times by freeze-pump-thaw. The mixture was irradiated with 370 nm LED for 20 h. After irradiation, water was added to the mixture and extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo* by rotary evaporator. The corresponding product **3aa** was not observed in the crude mixture, and $[\text{7}^+\text{Na}]$ was detected by ESI-MS.

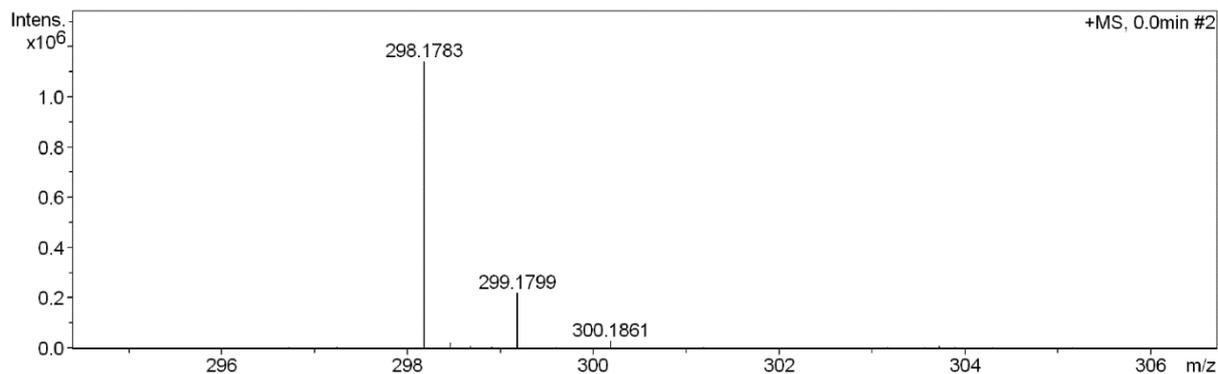


Figure S3. ESI-MS spectrum of **7**.

4.2. Stern–Volmer quenching experiment

In screw-capped quartz cell ($l = 1$ cm), various ratio of **1a** or **2a** were added to the PTH solution (1.9 mL, $c = 7.26 \times 10^{-4}$ M PTH in degassed DMF). Then emission spectra were measured by irradiation at 370 nm.

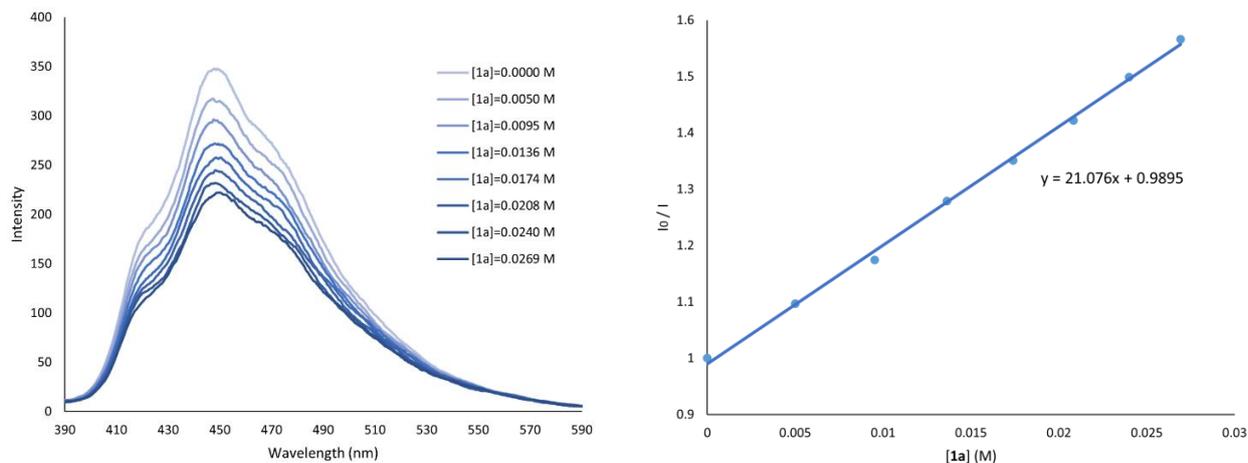


Figure S4. Emission spectra of PTH quenching by **1a** and Stern–Volmer plot.

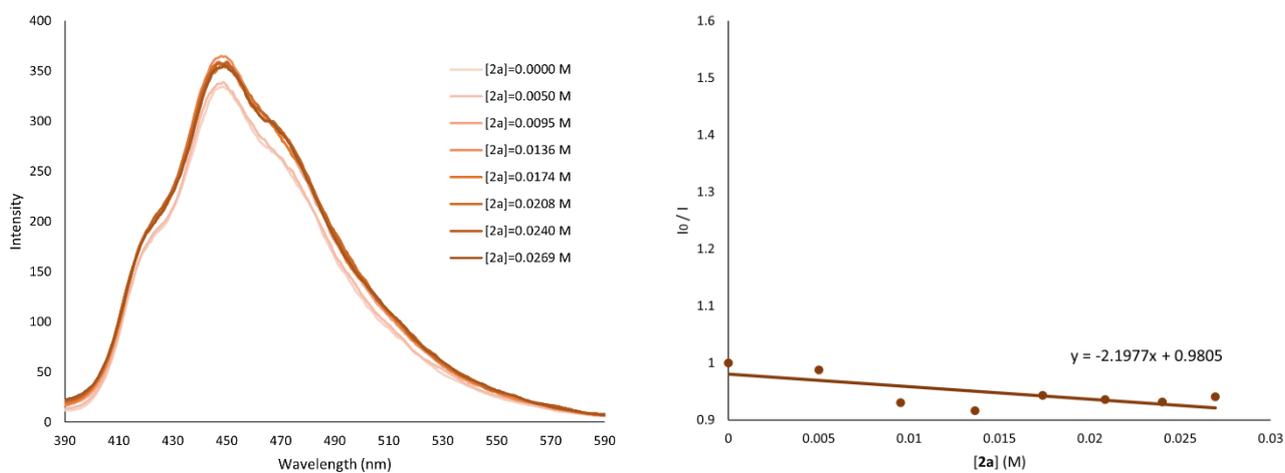


Figure S5. Emission spectra of PTH quenching by **2a** and Stern–Volmer plot.

4.3. Measurement of quantum yield

Quantum yield of the reaction was measured using UV light ($\lambda_{\max} = 370$ nm) for 1 h.

4.3.1. Measurement of photon flux

The photon flux of this UV light was determined by standard ferrioxalate actinometry. The ferrioxalate solution was prepared by $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ (1.20 g) dissolving in degassed 0.05 M H_2SO_4 aq. (16.3 mL). The buffered phenanthroline solution was prepared by 1,10-phenanthroline (50 mg) and sodium acetate (11.25 g) dissolving in degassed 0.5 M H_2SO_4 aq. (50 mL).

The ferrioxalate solution (2.0 mL) in the quartz cell ($l = 1$ cm) was irradiated for 0.94 s or 1.66 s, and the buffered phenanthroline solution (0.35 mL) was added. The non-irradiated ferrioxalate solution was also treated under the same conditions (as $t = 0$ sample). This mixture was left to stand for 1 h. The concentrations of $Fe(phen)_3^{2+}$ were measured by UV-Vis spectra (Figure S6a).

The conversion of Fe^{3+} into Fe^{2+} was calculated using:

$$mol Fe^{2+} = \frac{V \cdot \Delta A_{510\text{ nm}}}{l \cdot \epsilon}$$

[V : total volume of solution (0.00235 L), $\Delta A_{510\text{ nm}}$: difference in the absorbance at $\lambda = 510$ nm between irradiated and non-irradiated solutions, l : path length (1.0 cm), ϵ : molar absorptivity of $Fe(phen)_3^{2+}$ at 510 nm ($11000\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)].

The mol/s Fe^{2+} was calculated by the slope of the plotted line to $1.74 \times 10^{-7}\text{ mol} \cdot \text{s}^{-1}$ (Figure S6b).

The photon flux (I) was calculated using:

$$I = \frac{mol/s Fe^{2+}}{\Phi_{Fe}(1 - 10^{-A_{370\text{ nm}}})}$$

[Φ_{Fe} : quantum yield of the ferrioxalate actinometer for 0.15 M solution at 365 nm (1.21)^{S12}, $A_{450\text{ nm}}$: absorbance of the ferrioxalate solution at 370 nm (3.89)]

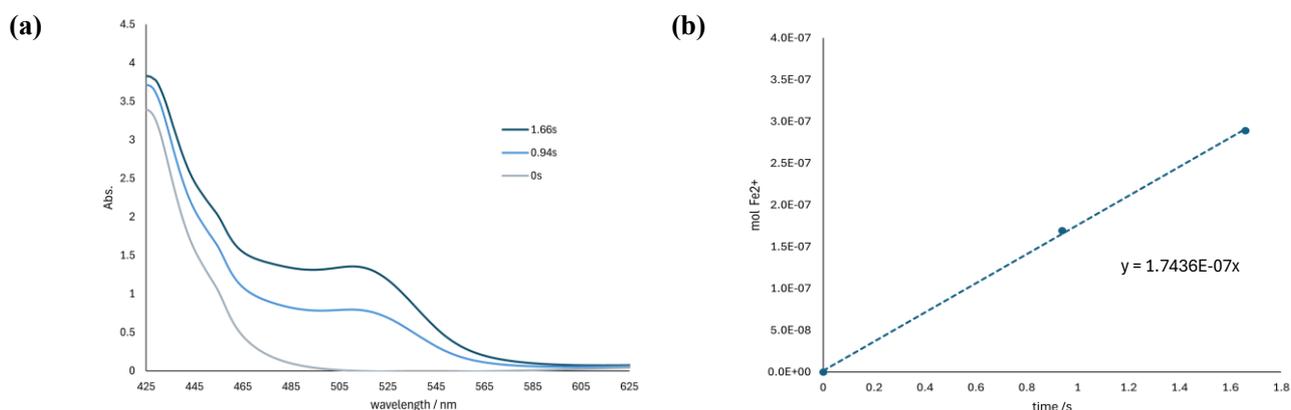
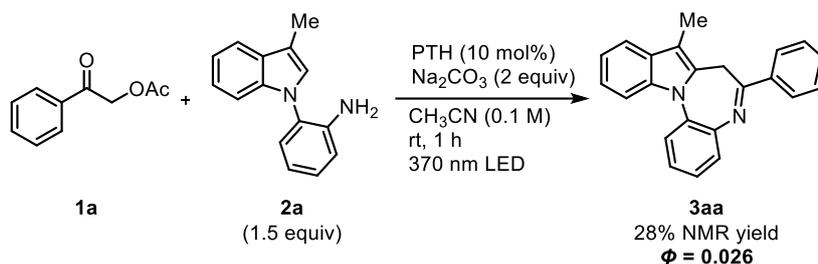


Figure S6. (a) UV-Vis spectra of generated $Fe(phen)_3^{2+}$. (b) The plot of moles of generated Fe^{2+} vs irradiation time.

4.3.2. Calculation of quantum yield



In a dried test tube, sodium carbonate (10.6 mg, 0.10 mmol) was dried up by heating gun under vacuum. **1a** (8.9 mg, 0.05 mmol), **2a** (16.7 mg, 0.075 mmol) and PTH (1.4 mg, 0.005 mmol) were mixed in CH₃CN (0.5 mL), and degassed 4 times by freeze-pump-thaw. The mixture was irradiated with 370 nm LED for 1 h. After irradiation, water was added to the mixture and extracted with ethyl acetate for 4 times. The combined organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* by rotary evaporator. **3aa** (0.0142 mmol) was obtained in 28% NMR yield (determined by ¹H NMR using 1,1,2-trichloroethane as an internal standard).

The quantum yield (Φ) was calculated using:

$$\Phi = \frac{\text{mol } \mathbf{3aa}}{I \cdot t \cdot (1 - 10^{-A})}$$

[I : photon flux of UV light (1.53×10^{-7} einstein \cdot s⁻¹), t : reaction time (3600 s), A : absorbance of reaction mixture at 370 nm (3.94)]

$$\Phi = \frac{1.42 \times 10^{-5}}{1.53 \times 10^{-7} \cdot 3600 \cdot (1 - 10^{-3.94})} = 0.026$$

4.4. Cyclic Voltammetry

All voltammograms were measured at room temperature using Ag/AgNO₃ reference electrode, a platinum (Pt) counter and working electrode. The conditions of the experiments were as follows: a CH₃CN solution of 50 mM tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) and a scan rate of 100 mV/s. In order to convert the potentials from Ag/AgNO₃ to Fc/Fc⁺ reference, ferrocene was measured under the above conditions in a CH₃CN solution, and -0.06 V was subtracted from the measured values. To convert the potentials from Fc/Fc⁺ to SCE reference, +0.38 V was added from the value according to the literature.^{S13}

The reduction potential of **1a** was determined to $E_{1/2} = -0.93$ V vs. SCE (Figure S7a) and the oxidation potential of **2a** was determined to $E_{p/2} = +0.93$ V vs. SCE (Figure S7b).

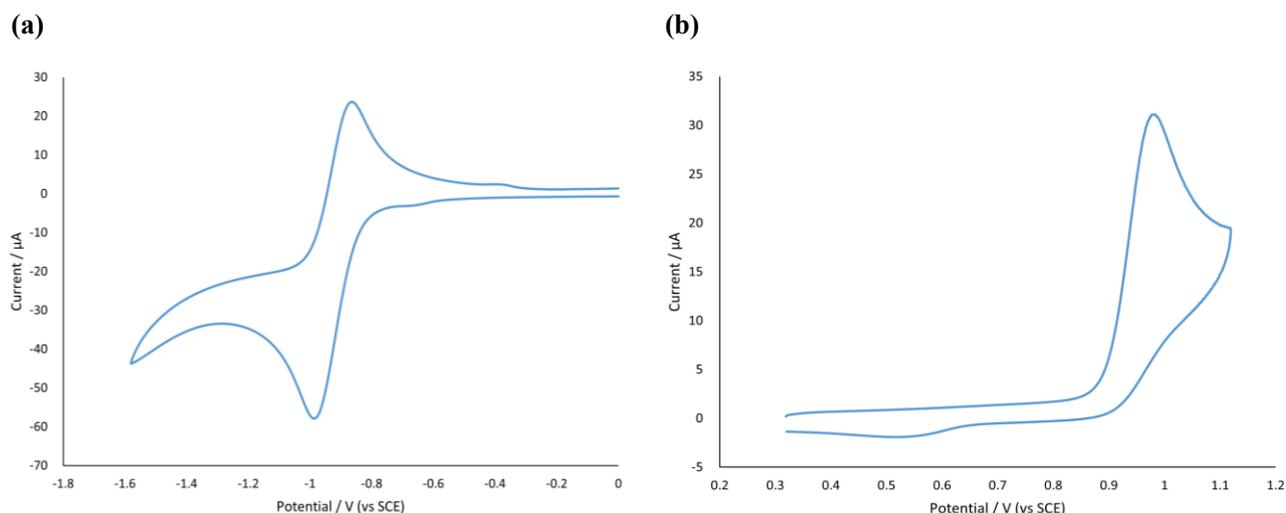


Figure S7. Cyclic voltammograms. (a) **1a**. (b) **2a**.

4.5. ^1H NMR study

In a 5 mm Wilmad[®] low pressure/vacuum NMR tube, **1a** (8.9 mg, 0.05 mmol), **2a** (16.7 mg, 0.075 mmol), PTH (1.4 mg, 0.005 mmol) and sodium carbonate (10.6 mg, 0.10 mmol) were mixed in CD_3CN (0.5 mL) and degassed 3 times by freeze-pump-thaw. After the initial measurement of ^1H NMR spectra, the tube was placed in a 40 °C oil bath and was heated for 2 h under dark conditions. Then, the ^1H NMR spectra was measured, and the tube was irradiated with 370 nm LED for 20 h. As a results, the formation of an imine intermediates with **1a** and **2a** was not observed under dark conditions, and conversion to desired product **3aa** occurred only under light-irradiation conditions. It suggests that the initiation of the reaction was single-electron reduction of **1a**.

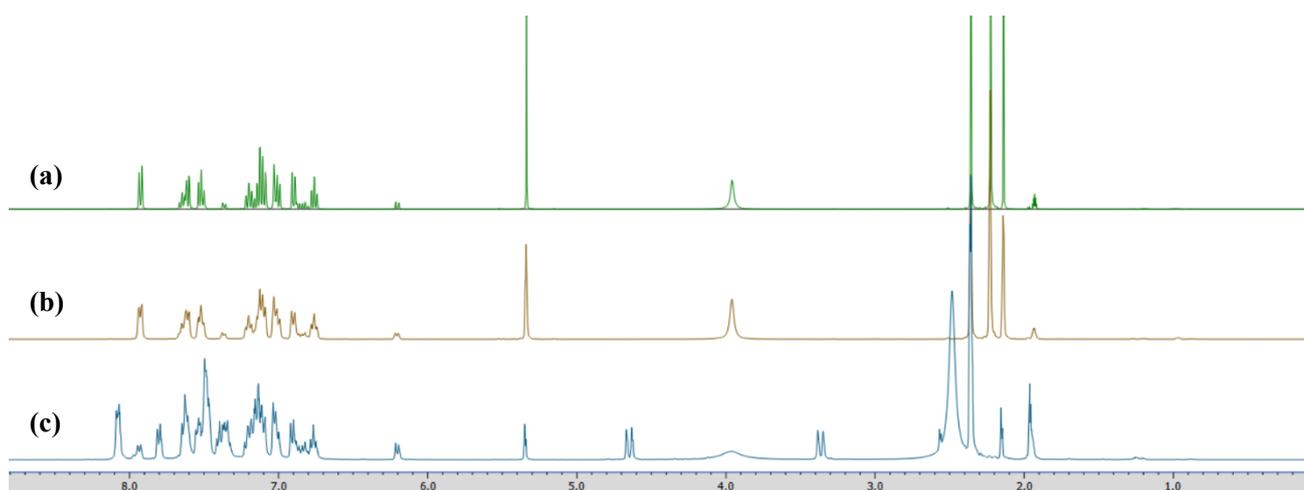


Figure S8. ^1H NMR study in CD_3CN . (a) 0 h. (b) after heating for 2 h under dark conditions. (c) after light irradiation for 20 h.

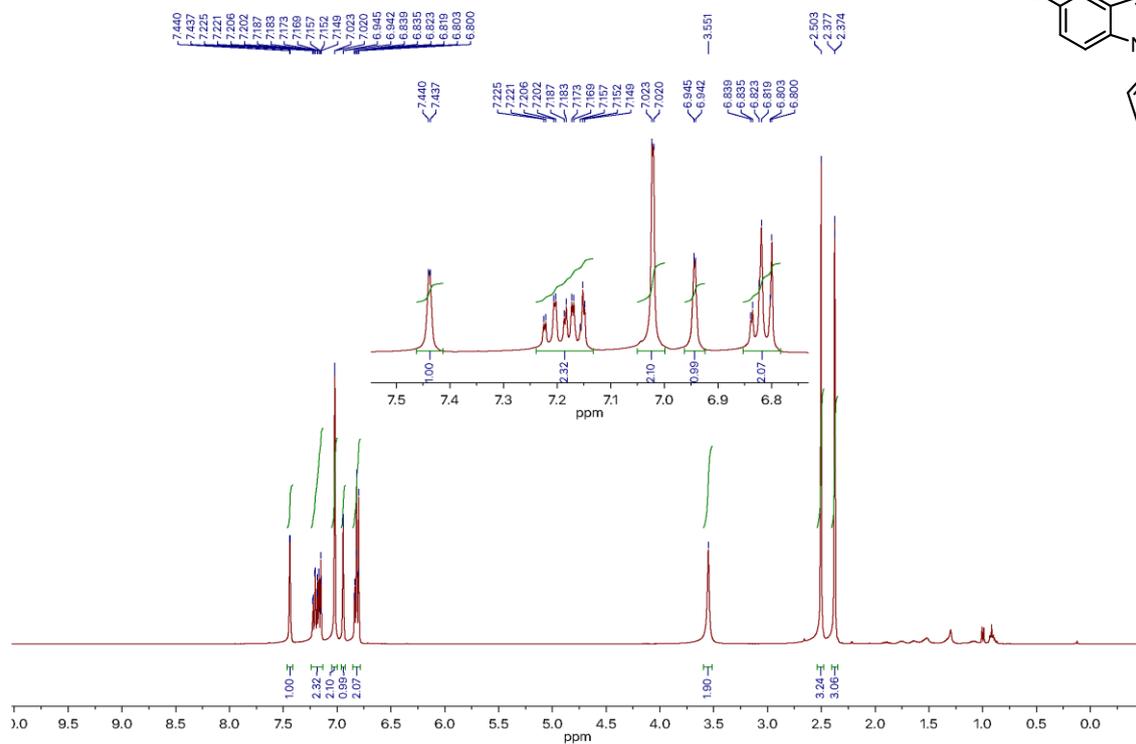
5. References

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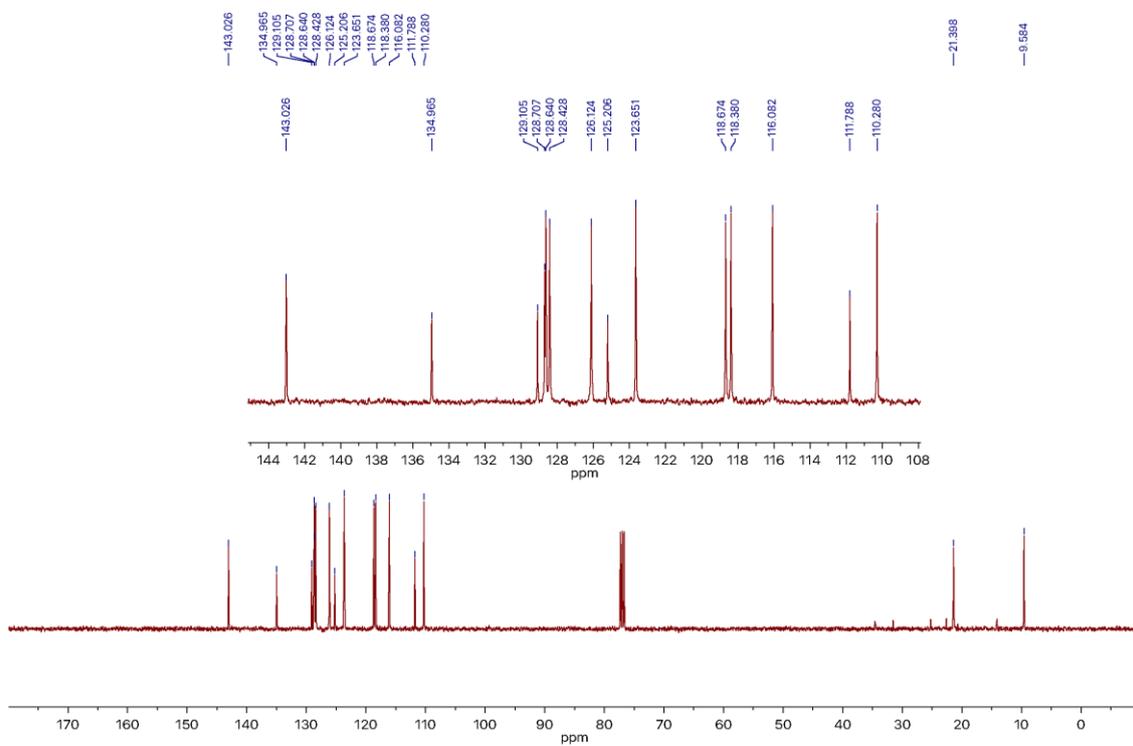
6. NMR spectra

2b

^1H NMR (400 MHz, CDCl_3)

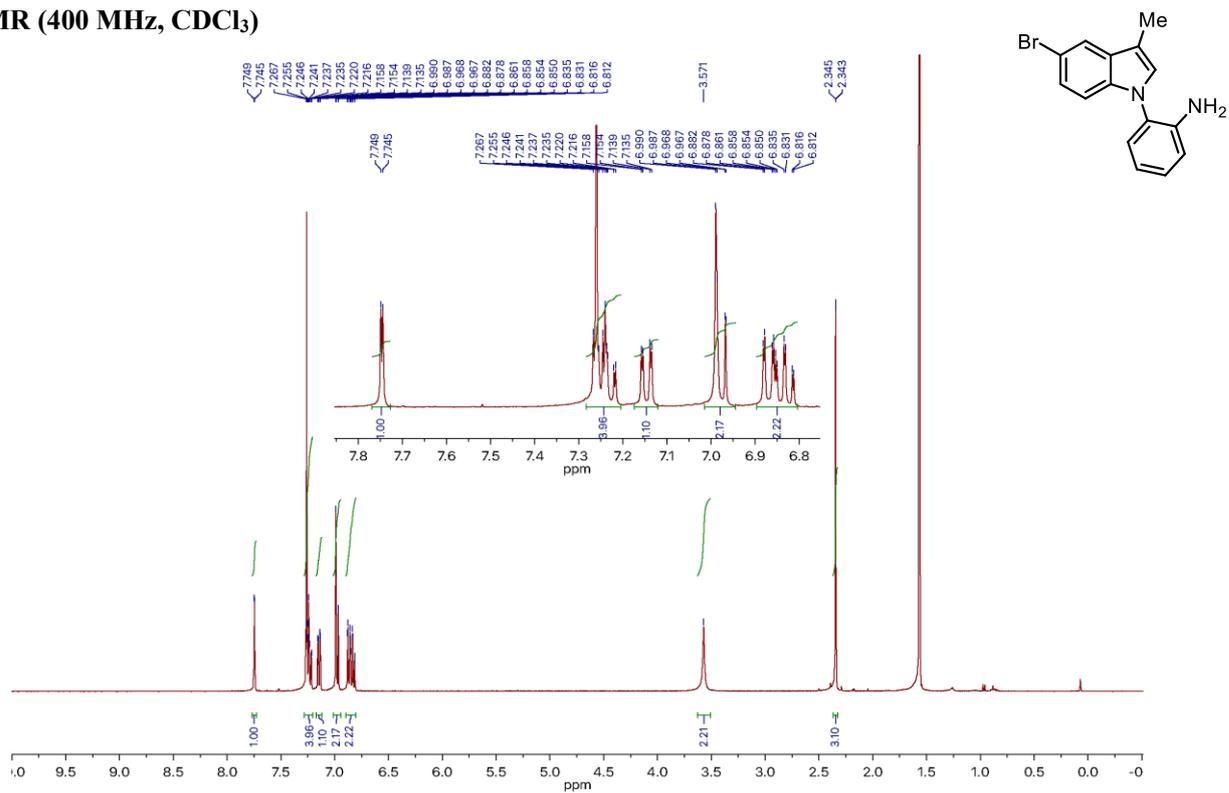


^{13}C NMR (101 MHz, CDCl_3)

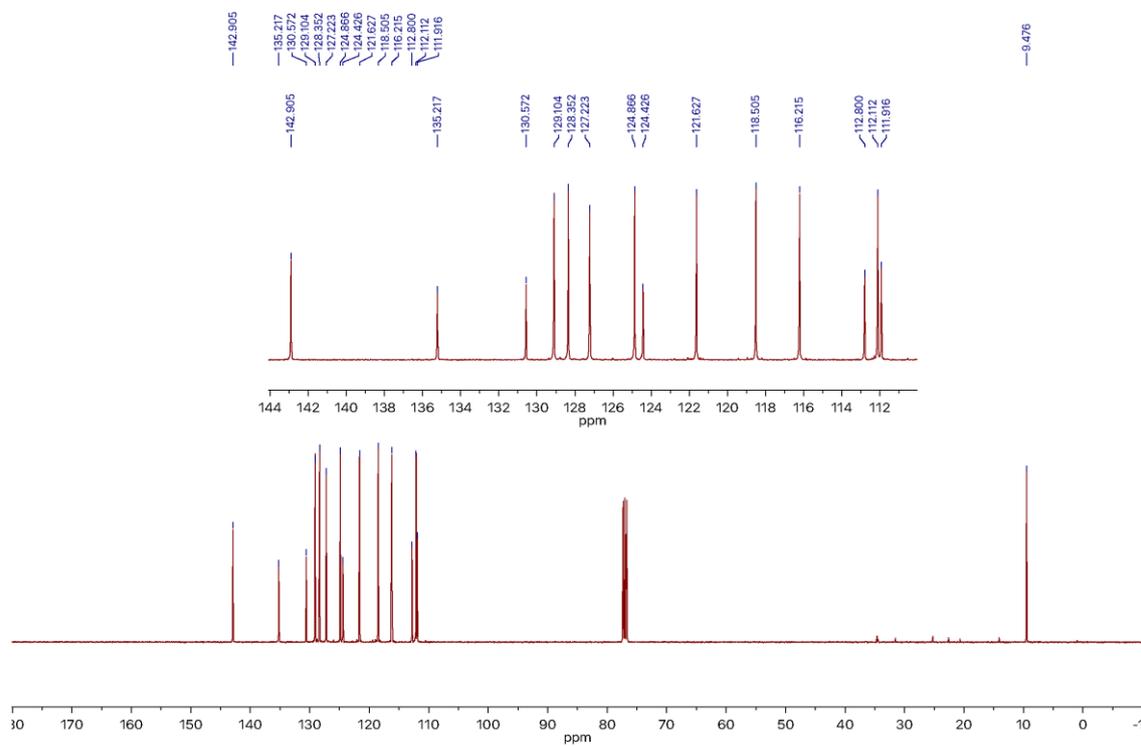


2d

¹H NMR (400 MHz, CDCl₃)

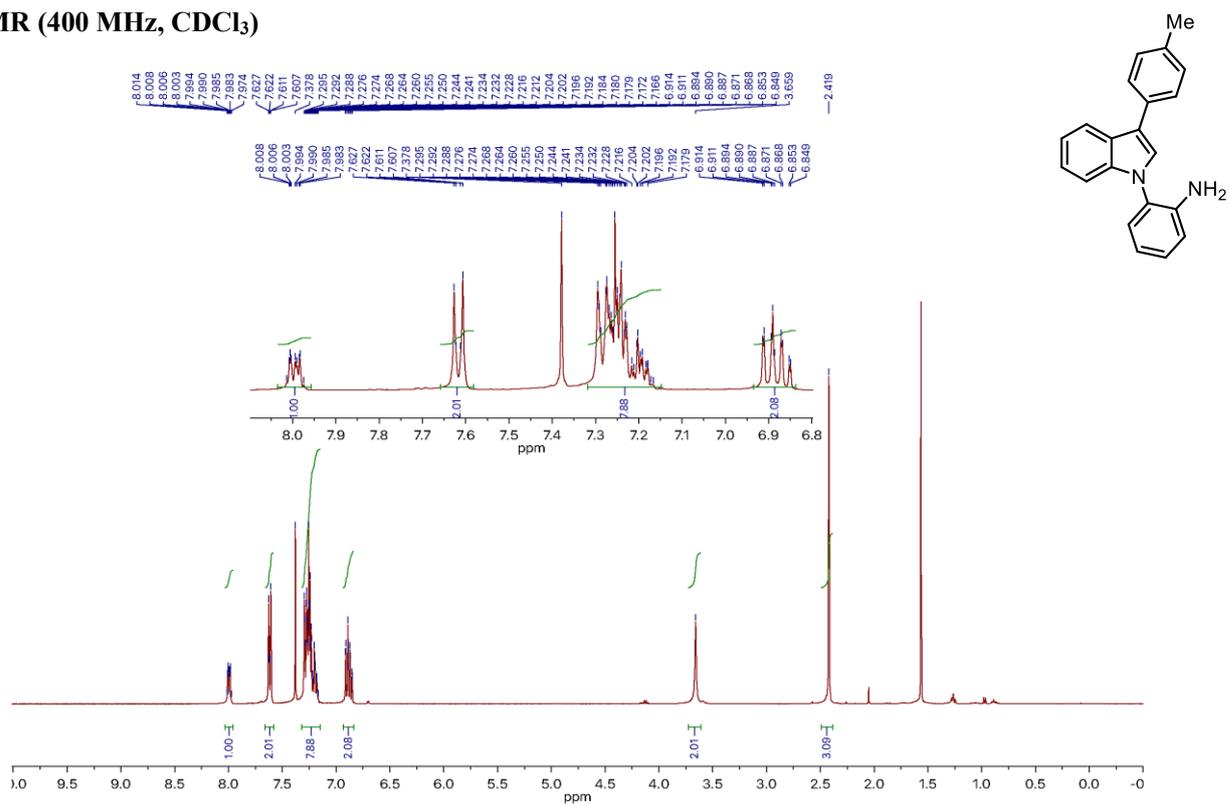


¹³C NMR (101 MHz, CDCl₃)



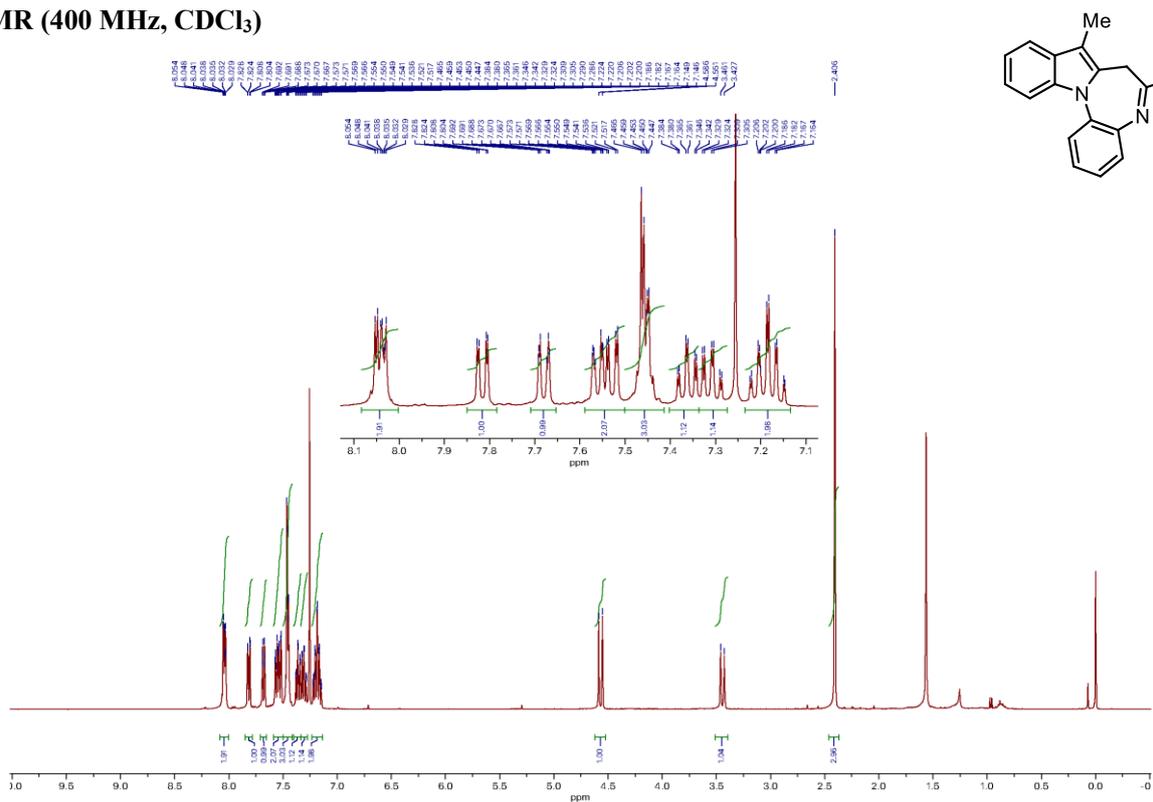
2g

¹H NMR (400 MHz, CDCl₃)

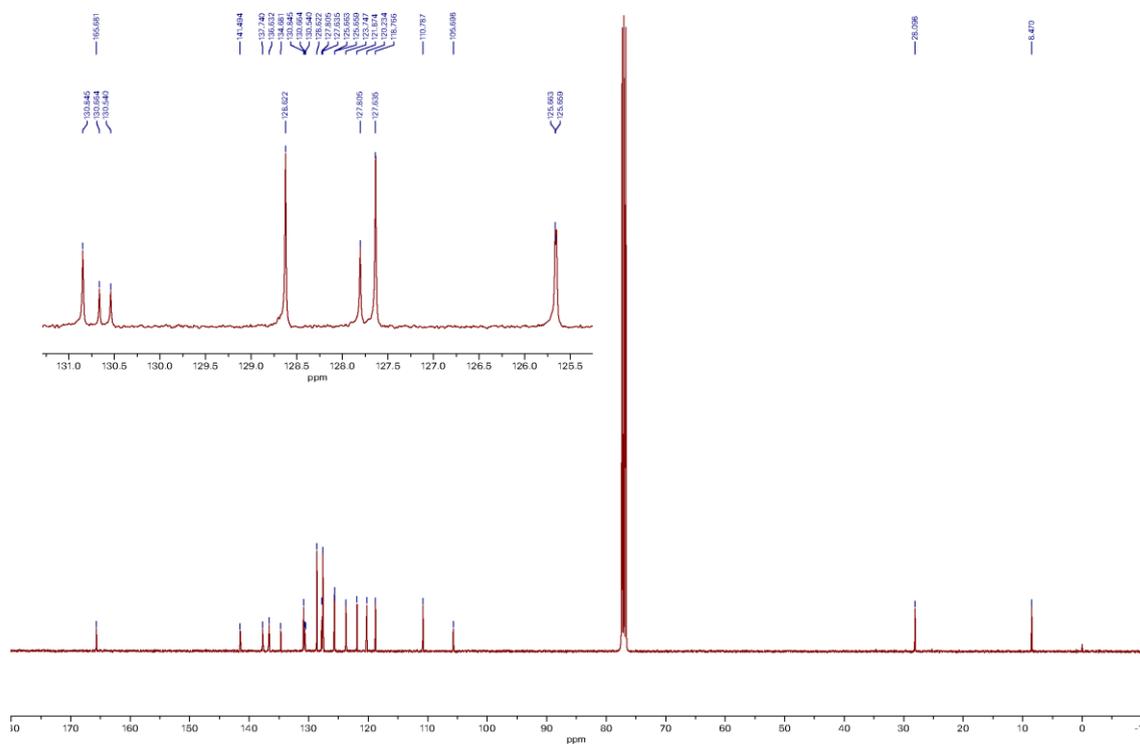


3aa

^1H NMR (400 MHz, CDCl_3)

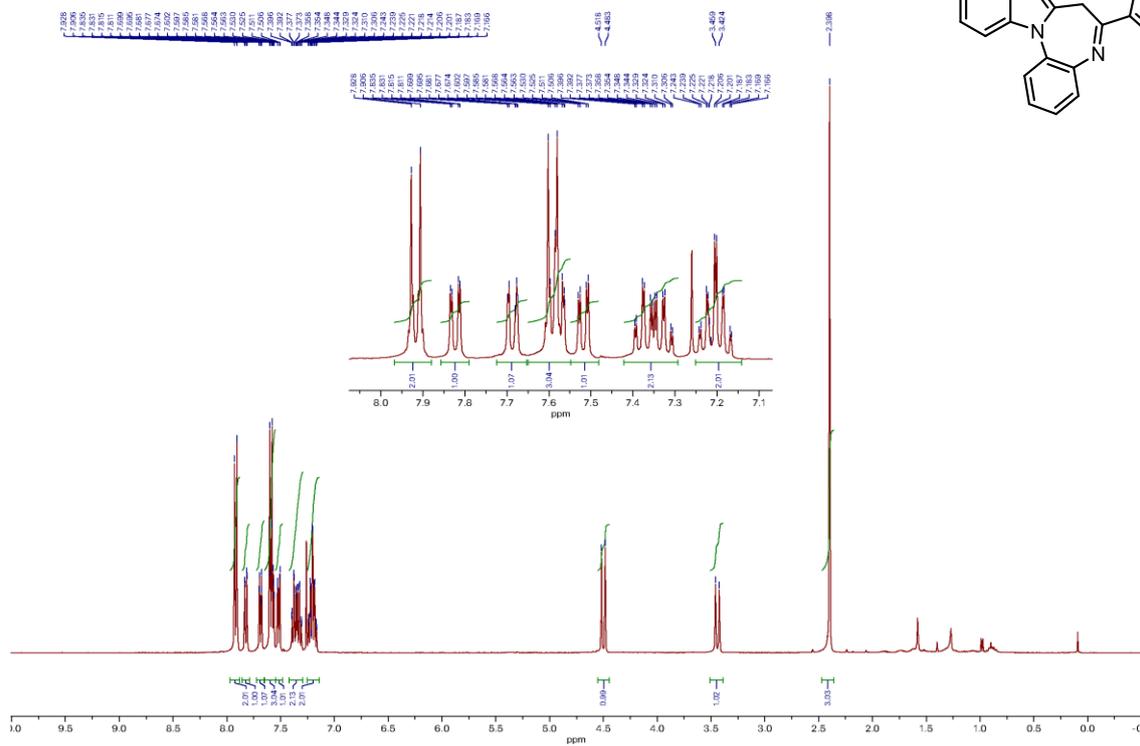


^{13}C NMR (101 MHz, CDCl_3)

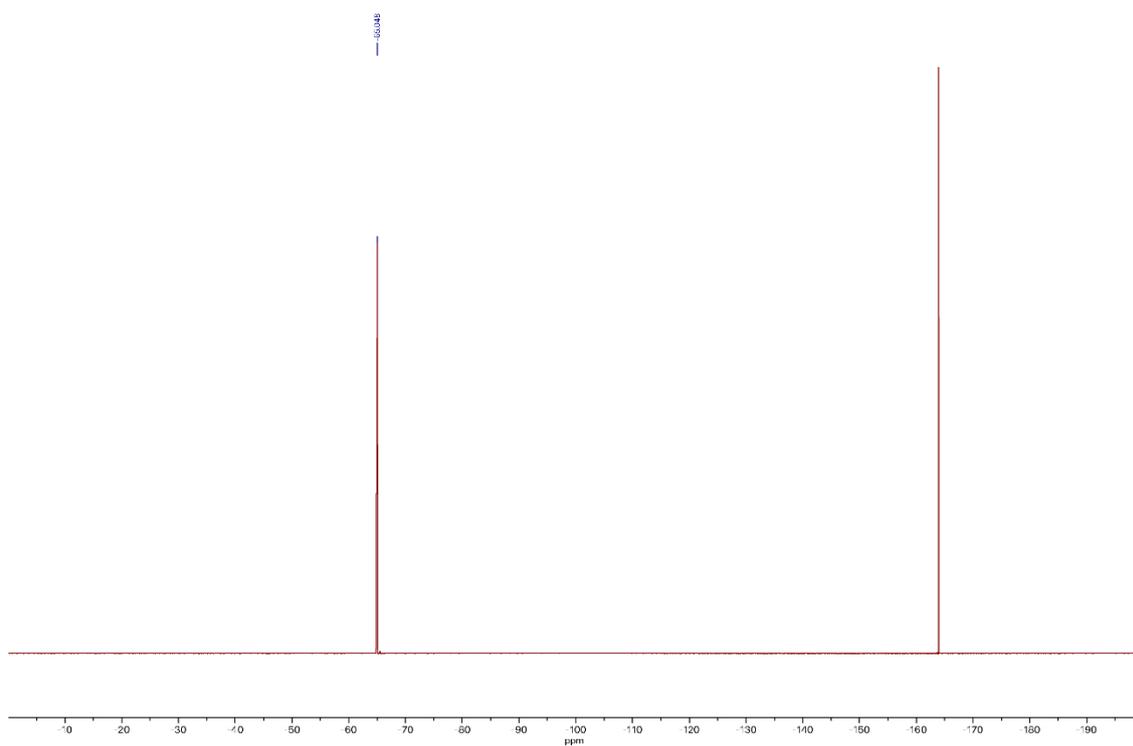


3da

^1H NMR (400 MHz, CDCl_3)

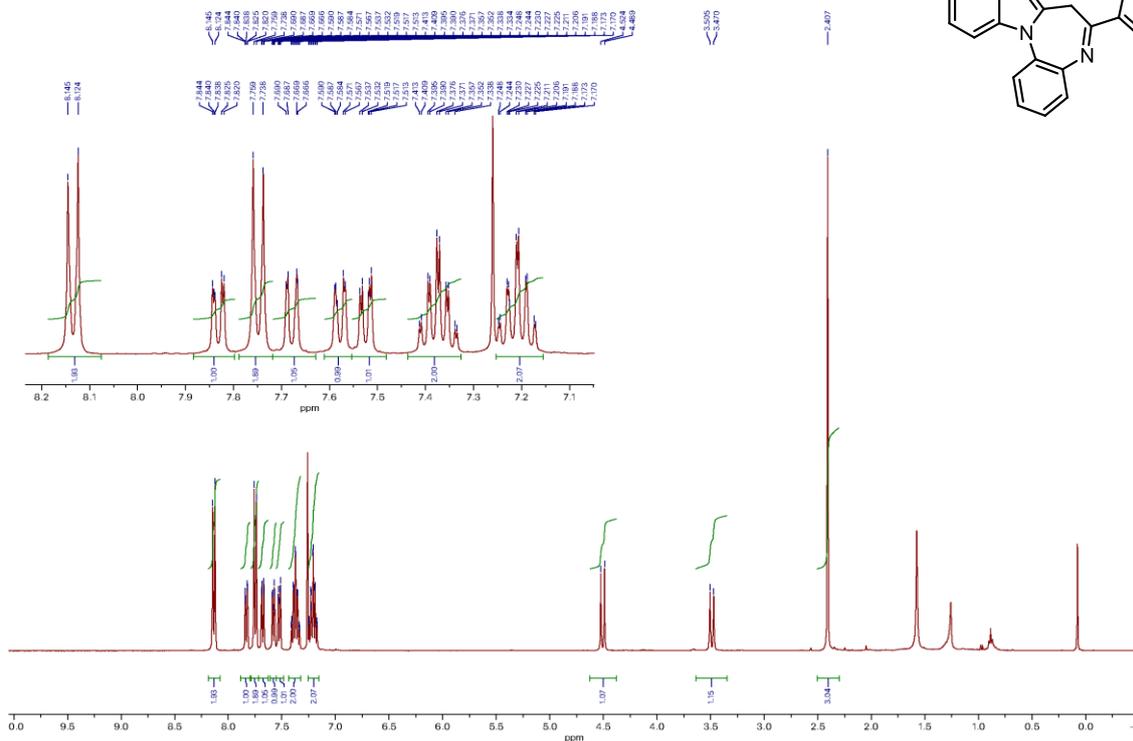


^{19}F NMR (376 MHz, CDCl_3)



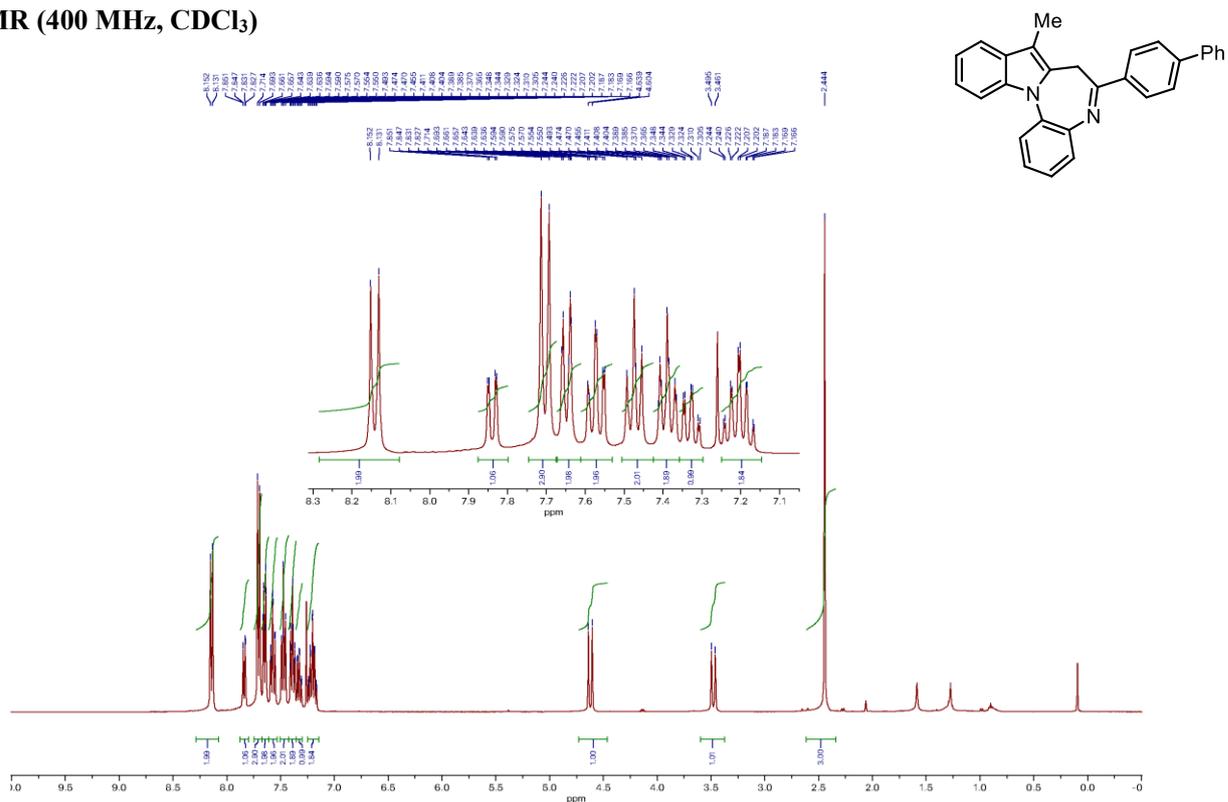
3ja

¹H NMR (400 MHz, CDCl₃)

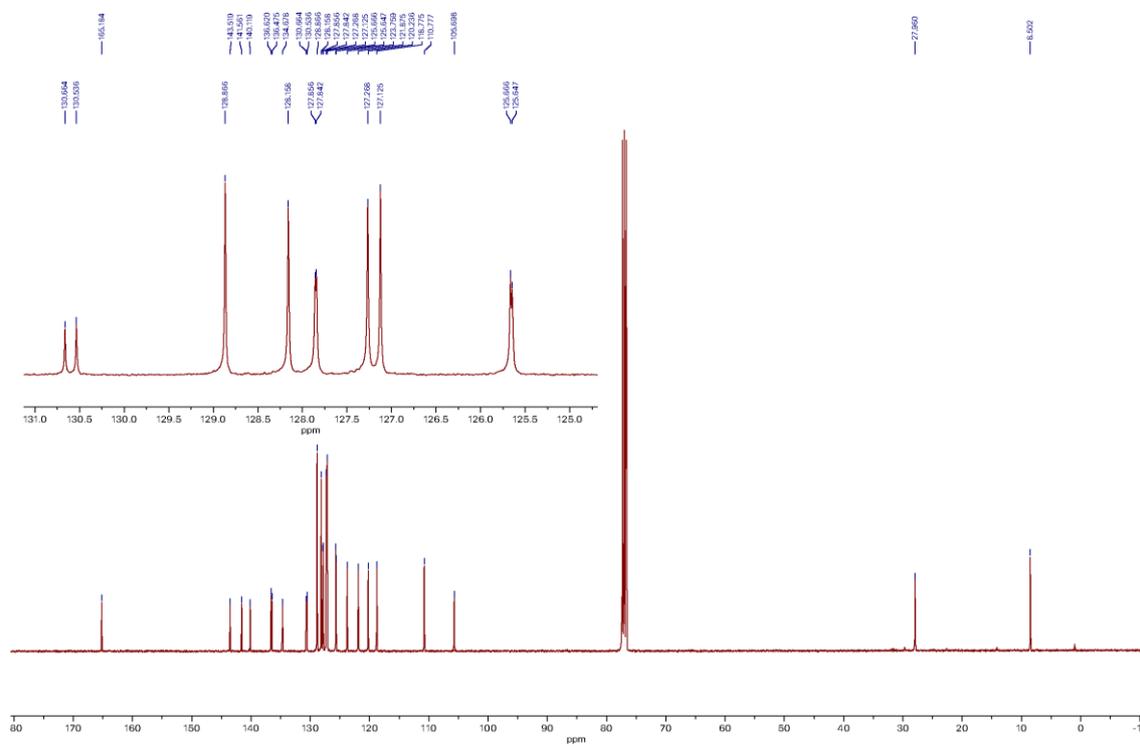


3ka

¹H NMR (400 MHz, CDCl₃)

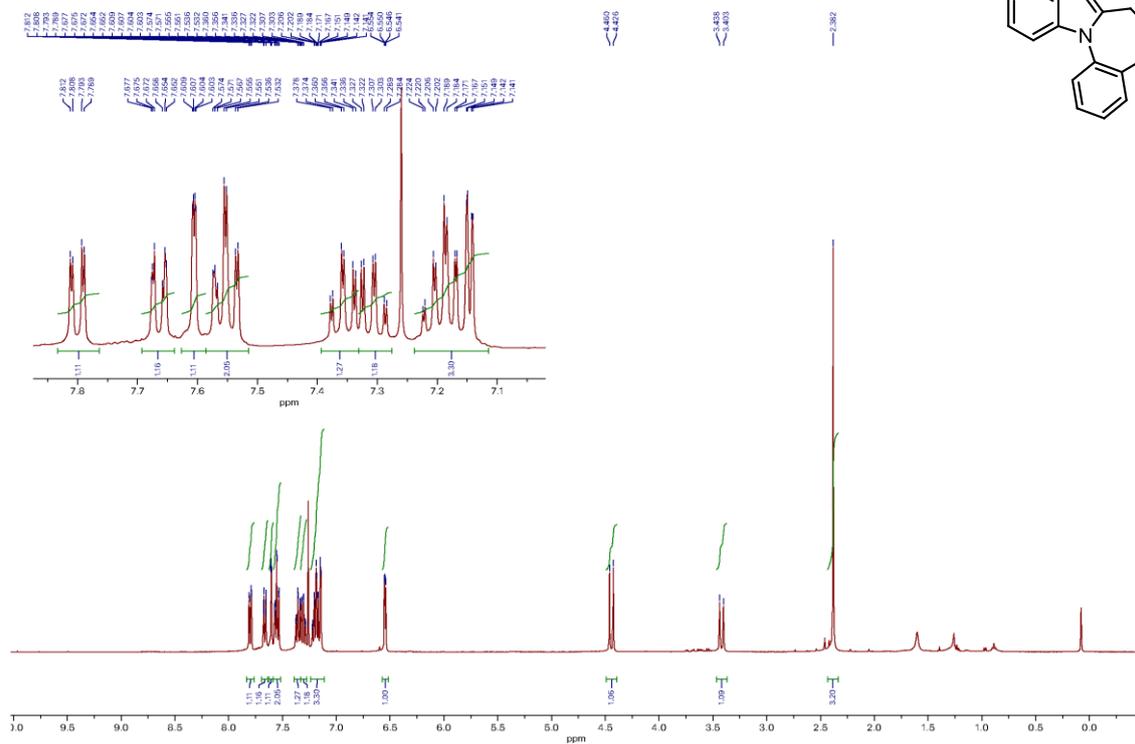


¹³C NMR (101 MHz, CDCl₃)



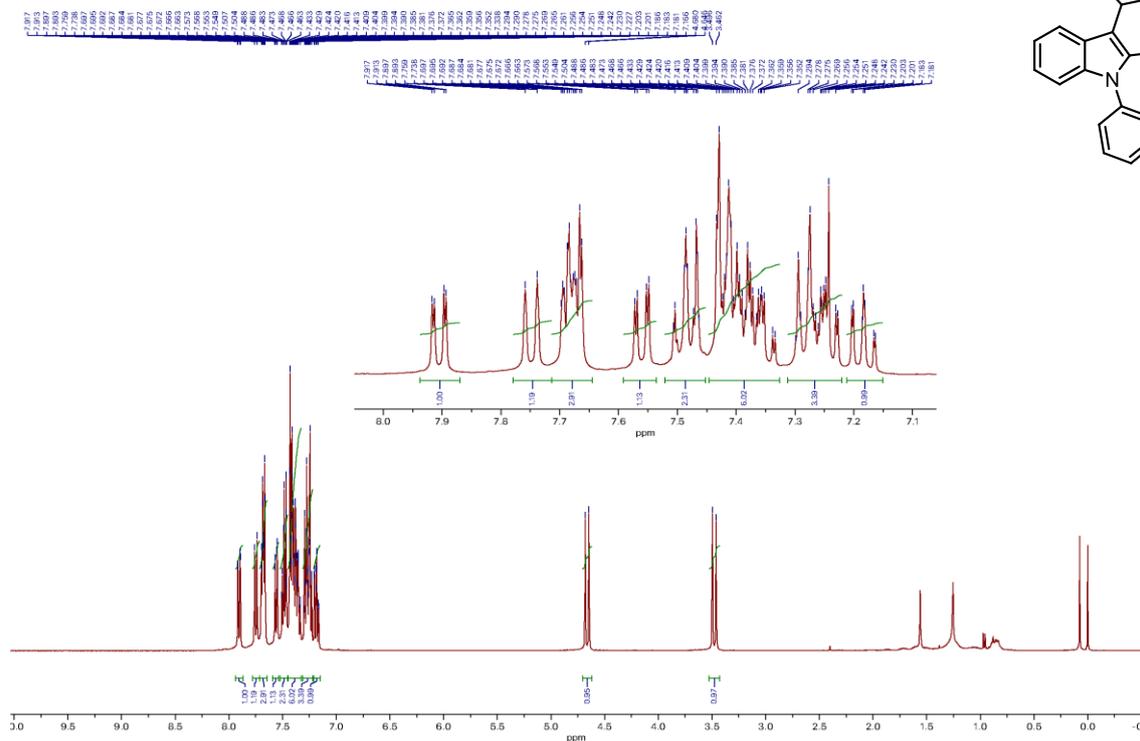
3ma

^1H NMR (400 MHz, CDCl_3)

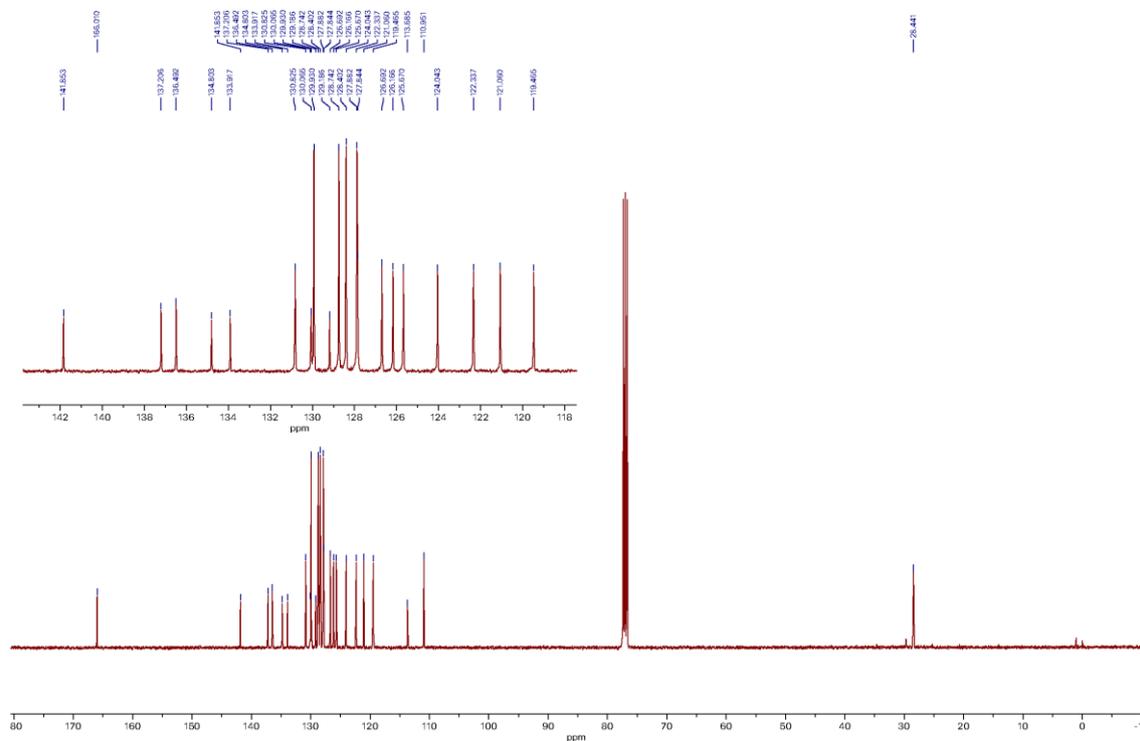


3af

¹H NMR (400 MHz, CDCl₃)

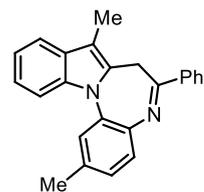
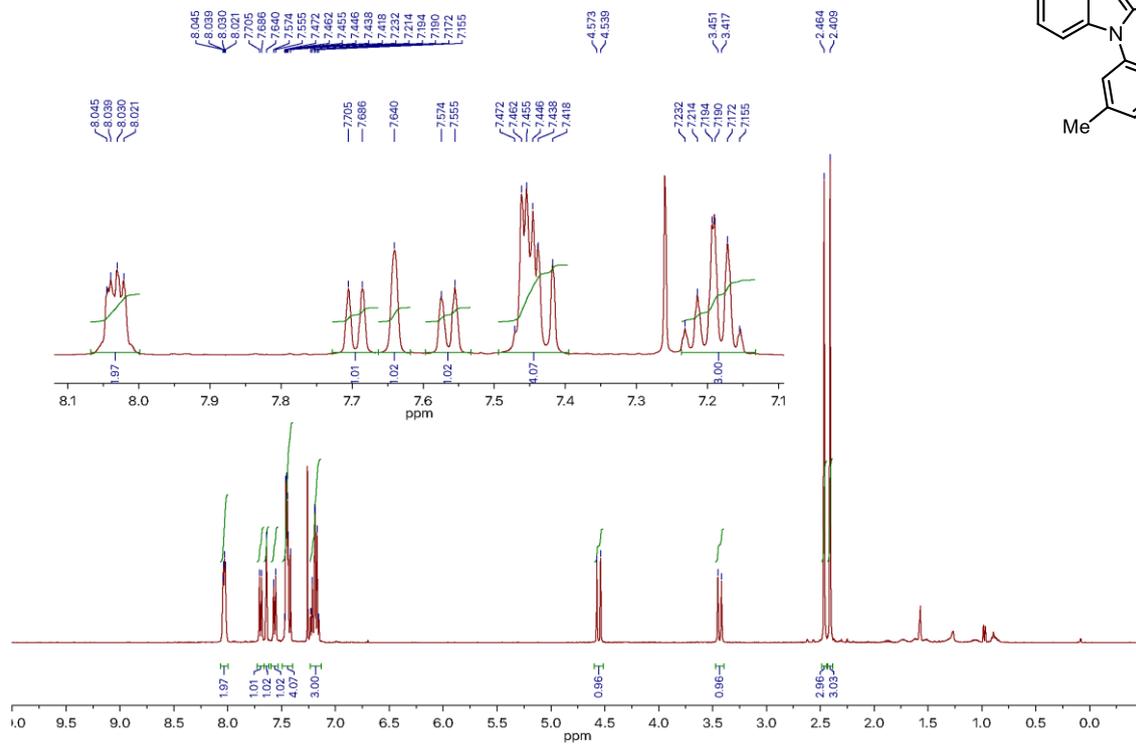


¹³C NMR (101 MHz, CDCl₃)

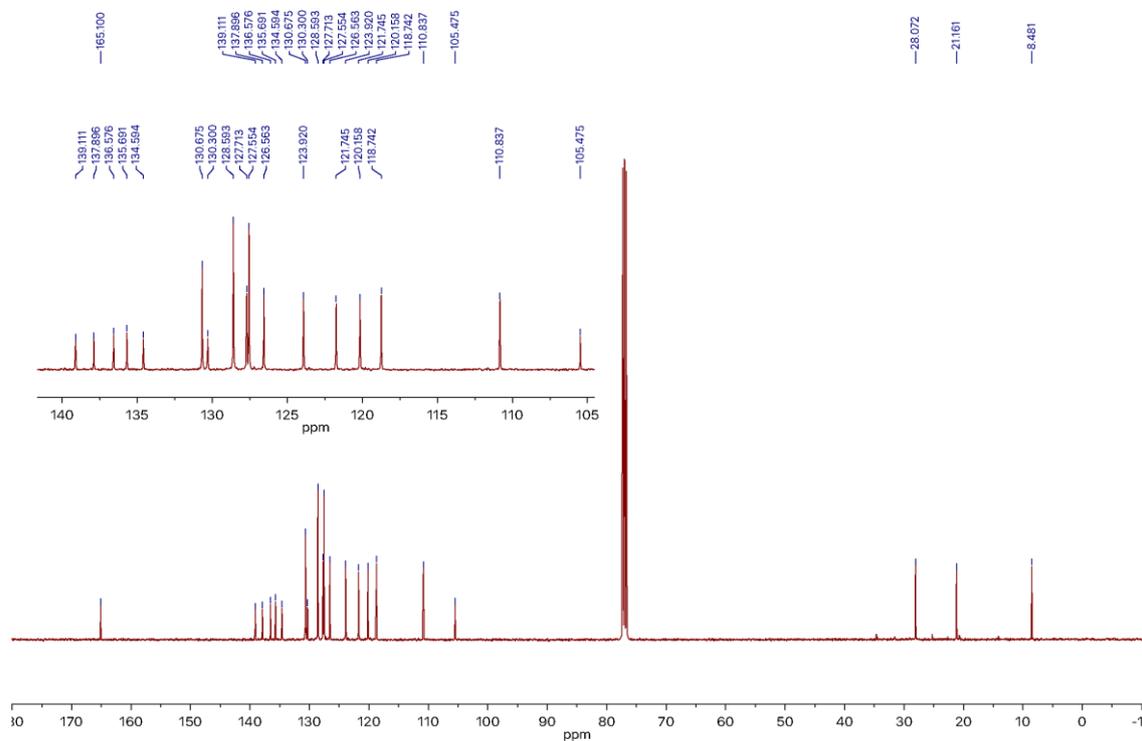


3ai

¹H NMR (400 MHz, CDCl₃)

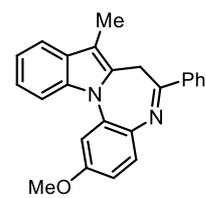
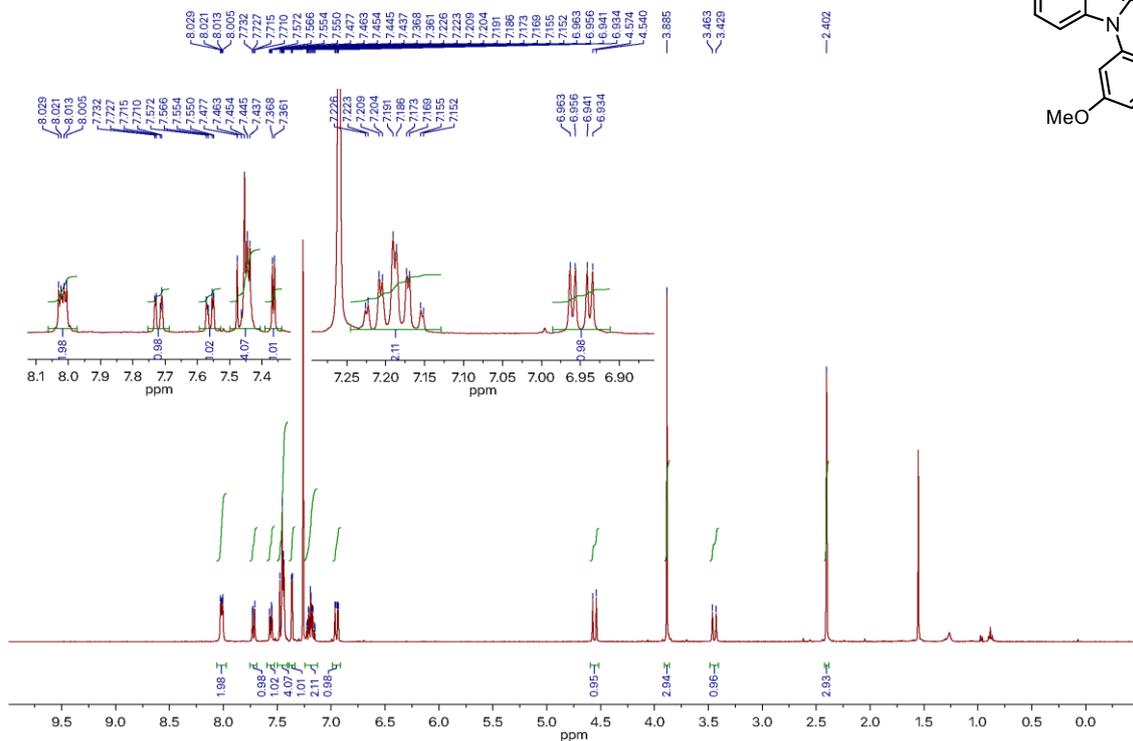


¹³C NMR (101 MHz, CDCl₃)

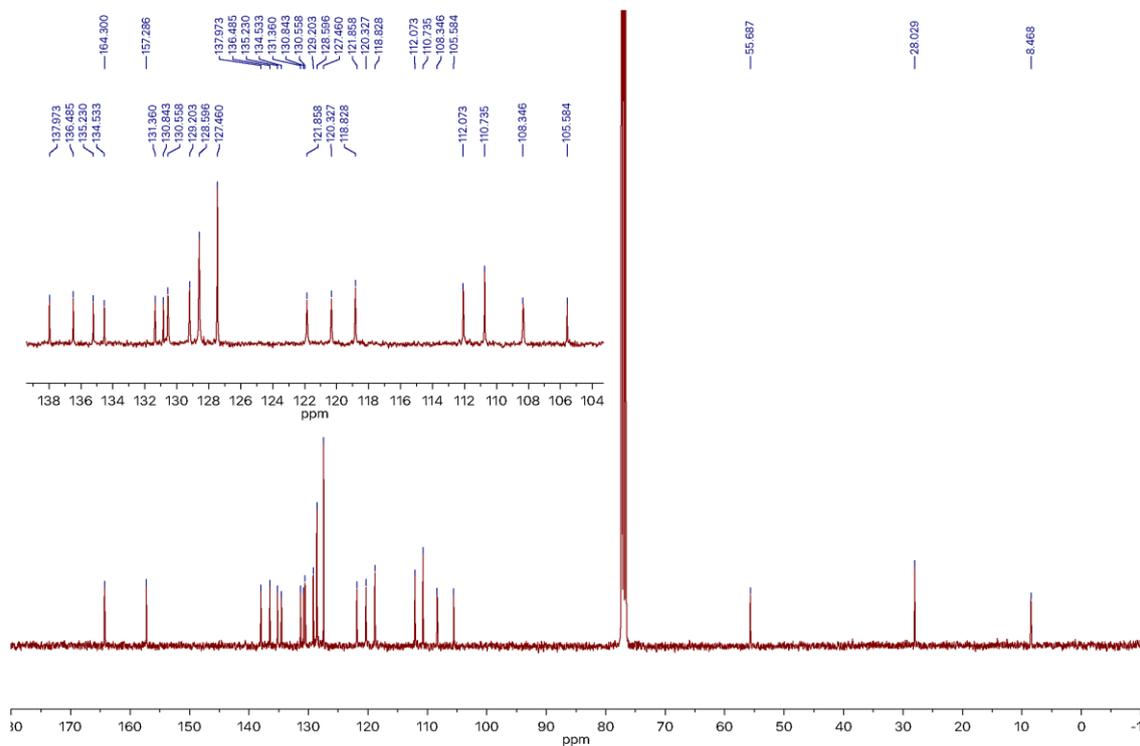


3aj

^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)



5aa

¹H NMR (400 MHz, CDCl₃)

