Supporting Information

Efficient supramolecular artificial light-harvesting systems based on an AIE-active calix[4]arene derivative for cross-dehydrogenative Coupling reaction

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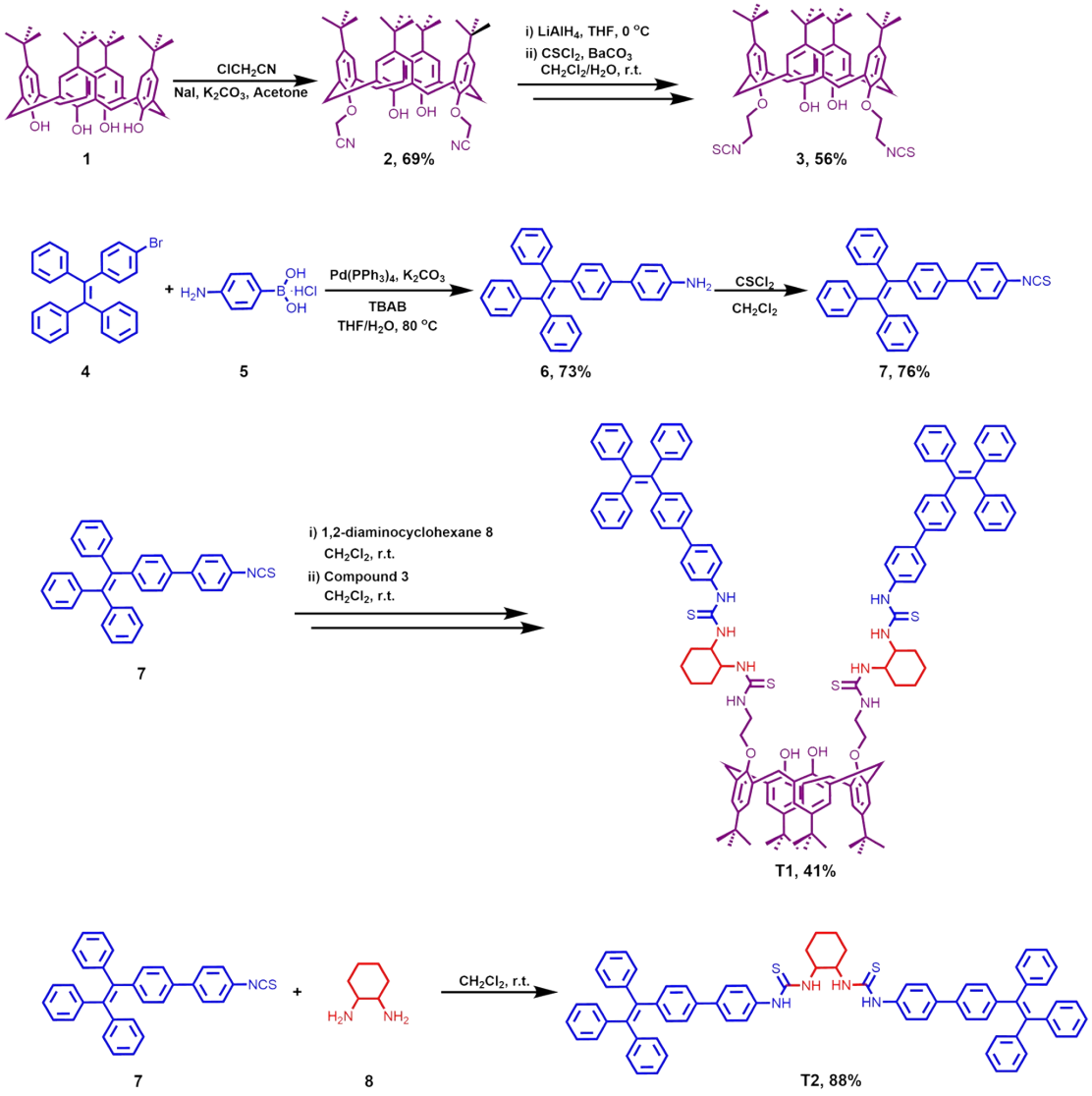
1. General information

Materials: All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received unless otherwise indicated.

Measurements: ^{1}H NMR and ^{13}C NMR spectra were obtained by an Agilent NMR Systems 400 MHz NMR Spectrometer at 298 K in $CDCl_3$ or DMSO-d_6. High-resolution mass spectra (HRMS) were measured by an AB SCIEX 4600 mass spectrometer. Absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrophotometer. Fluorescence spectra were collected on a HORIBA FLOUROMAX-4 fluorophotometer at 298 K. Dynamic light scattering (DLS) measurements were conducted using a Nanobrook Omni. The surface morphologies of the samples were analyzed using scanning electron microscope (SEM, FEI Quanta FEG 250). The luminescence lifetimes were measured on an Edinburgh FLS 1000 fluorescence spectrometer operating intime-correlated single-photon counting (TCSPC) mode.

2. General procedure for the synthesis of T1 and T2



Scheme S1. Synthetic route of **T1** and **T2**

Synthesis of 2[1]

To a two-neck 100 mL flask, p-tert-butyl calix[4]arene (1.0 g, 1.55 mmol) were dissolved in acetone (50 mL), followed by the sequential addition of K_2CO_3 (0.85 g, 6.2 mmol), NaI (0.92 g, 6.13 mmol), and $ClCH_2CN$ (0.4 mL, 5.3 mmol). Then, the reaction mixture was stirred and refluxed at 65 °C for 8 h. After cooling to room temperature, the brown transparent solution was filtered with diatomite, and the dichloromethane wash yielded a concentrated filtrate. Recrystallization with $CHCl_3/CH_3OH$ produced white crystals of compound **2**. (0.77 g, yield: 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (s, 4H), 6.73 (s, 4H), 4.81 (s, 4H), 4.22 (d, J = 13.6 Hz, 4H), 3.45 (d, J = 13.6 Hz, 4H), 1.33 (s, 18H), 0.88 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.85, 148.62, 148.49, 142.47, 131.77, 127.74, 126.11, 125.27, 115.06, 60.37, 33.93, 33.91, 31.65, 31.59, 30.79.

Synthesis of 3[1]

To a 250 mL two-necked bottle, dissolve compound **2** (1.45 g, 2.0 mmol) in THF (50 mL), slowly drop $LiAlH_4$ (1.0 M in THF, 12 mL) at 0 °C, and monitor the reaction process by TLC. After the reaction is completed, add 20% NaOH (0.5 mL) solution and H_2O (5 mL) until a white precipitate

is generated, filter out the white solid, and concentrate the filtrate to obtain a crude product. It can be directly used in the next step without purification. To a solution of crude product (1.47 g, 2.0 mmol) in CH_2Cl_2 (40 mL) was added thiophosgene (0.46 mL, 6.0 mmol), $BaCO_3$ (2.37 g, 12 mmol), and H_2O (9 mL). The reaction was stirred for 24 h at room temperature. After the reaction is completed, add CH_2Cl_2 (30 mL) and extract the system with H_2O (30 mL). The organic phase was dried and evaporated, and recrystallized with $CHCl_3/CH_3OH$ to obtain the white crystals of compound 3. (0.92 g, yield 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (s, 4H), 6.73 (s, 4H), 4.81 (s, 4H), 4.22 (d, J = 13.6 Hz, 4H), 3.45 (d, J = 13.6 Hz, 4H), 1.33 (s, 18H), 0.88 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.50, 149.22, 147.43, 141.69, 132.24, 127.59, 125.79, 125.18, 73.32, 45.04, 33.97, 33.85, 31.70, 31.69, 30.97.

Synthesis of 6[2]

Compound 4 (2.50 g, 6.0 mmol) and compound 5 (1.65 g, 12.0 mmol) were dissolved in pure THF (50 mL), and then TBAB (0.01 g) and K_2CO_3 (2.0 M, aq, 9 mL) were added. Under N_2, after stirring at room temperature for 0.5 h, $Pd(PPh_3)_4$ catalyst was added, heated to 80 ^{o}C and reflux for 24 h. After the reaction was completed, it was cooled to room temperature and extracted with EA. The organic phase was combined and concentrated. The crude product was purified by column chromatography (PE/EA, 5/1, v/v), and a pale yellow crystalline powder 6 (1.88 g, with a yield of 73%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.13-7.03 (m, 17 H), 6.71 (d, J = 8.4 Hz, 2H), 3.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.71, 143.89, 143.83, 141.61, 140.75, 140.71, 138.78, 131.67, 131.42, 131.35, 131.32, 130.99, 127.70, 127.68, 127.61, 127.58, 126.37, 126.30, 125.29, 115.32.

Synthesis of 7

Compound **6** (0.42 g, 1.0 mmol) was dissolved in 10 mL of dichloromethane, followed by the addition of triethylamine (0.42 mL, 3.0 mmol) and thiophosgene (0.15 mL, 2.0 mmol) at 0 ^{o}C. Under N_2, stirring at room temperature for 4 h. Quenching with water, extraction with methylene chloride, washing with saturated saline solution, and combining the organic layers were followed by drying over anhydrous Na_2SO_4. The crude product was purified via column chromatography (PE/EA = 50:1, v/v) to afford compound 7 as a yellow powder (0.35 g, yield: 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.2 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.13-7.03 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.59, 143.55, 143.46, 141.45, 140.24, 139.71, 137.22, 135.53, 131.93, 131.35, 131.30, 131.28, 130.03, 127.82, 127.79, 127.73, 127.64, 126.57, 126.55, 126.50, 126.05, 126.01. ESI$^+$ HRMS m/z calcd for $C_{33}H_{23}NS$ 465.1551 $[M+H]^+$, found 465.1559.

Synthesis of T1.

Under a nitrogen atmosphere, the dichloromethane solution (30 mL) of compound **7** (5.0 mmol, 2.33 g) was slowly added through a constant pressure drop funnel to a three-necked round-bottom flask containing 1,2-cyclohexanediamine (5.0 mmol, 0.57 g, dissolved in 10 mL of dichloromethane). Stir the reaction mixture at room temperature for 4 hours. Subsequently, the dichloromethane solution (30 mL) of compound **3** (2.4 mmol, 1.95 g) was injected into the reaction system using a syringe, and the reaction continued for 12 hours. After the reaction was completed, the solvent was removed under reduced pressure, and the crude product was purified by gradient elution using a silica gel column (PE/EA, 6/1-3/1, v/v). The target product **T1** is a yellow solid powder (1.93 g, yield: 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.64 (s, 2H), 8.47 (s, 2H), 7.71-7.65 (m, 6H), 7.48 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.37 (d, J = 8.0 Hz, 4H), 7.15-7.12 (m, 17H), 7.07-7.05 (m, 6H), 7.02-6.97 (m, 17H), 4.21-4.17 (m, 6H), 4.05 (s, 8H), 3.38 (d, J = 12.8 Hz,

2H), 2.11-1.99 (m, 6H), 1.62 (s, 6H), 1.24-1.16 (m, 26H), 1.05 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.54, 149.70, 149.24, 147.15, 143.19, 143.17, 143.10, 141.92, 141.56, 140.66, 140.10, 138.43, 137.40, 134.76, 133.18, 133.10, 131.25, 130.71, 130.63, 127.83, 127.78, 127.74, 127.59, 126.54, 126.47, 125.71, 125.37, 125.22, 122.89, 74.13, 57.08, 43.06, 33.87, 33.53, 31.44, 31.32, 31.23, 31.19, 30.88, 30.80, 24.31. ESI$^+$ HRMS m/z calcd for $C_{128}H_{136}N_8O_4S_4$ 1976.9567 $[M+Na]^+$, found 1999.9456.

Synthesis of T2

Compound **7** (0.93 g, 2.0 mmol) and compound **8** (0.12 g, 1.0 mmol) were respectively dissolved in dichloromethane (15 mL). Subsequently, under a nitrogen atmosphere, the dichloromethane solution of compound **8** was slowly dropwise added to the dichloromethane solution of compound **7**, and the reaction was carried out at room temperature for 8 hours. After the reaction was completed, the crude product was purified by silica gel column chromatography (PE/EA, 2/1, V/V). Yellow crystalline powder **T2** (0.92 g, yield 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.65 (s, 2H), 7.79 (s, 2H), 7.50-7.42 (m, 8H), 7.37 (d, J = 8.0 Hz, 4H),7.13-7.11 (m, 18H), 7.01-6.96 (m, 16H), 4.30 (s, 2H), 2.16 (s, 2H), 1.68 (s, 2H), 1.26 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.68, 143.20, 143.15, 143.12, 141.91, 140.65, 140.10, 138.56, 137.37, 134.70, 131.25, 130.70, 130.62, 127.86, 127.80, 127.76, 126.58, 126.54, 125.38, 122.90, 56.81, 31.55, 24.31. ESI$^+$ HRMS m/z calcd for $C_{72}H_{60}N_4S_2$ 1044.4259 $[M+H]^+$, found 1045.4326.

3. Characteristic spectra

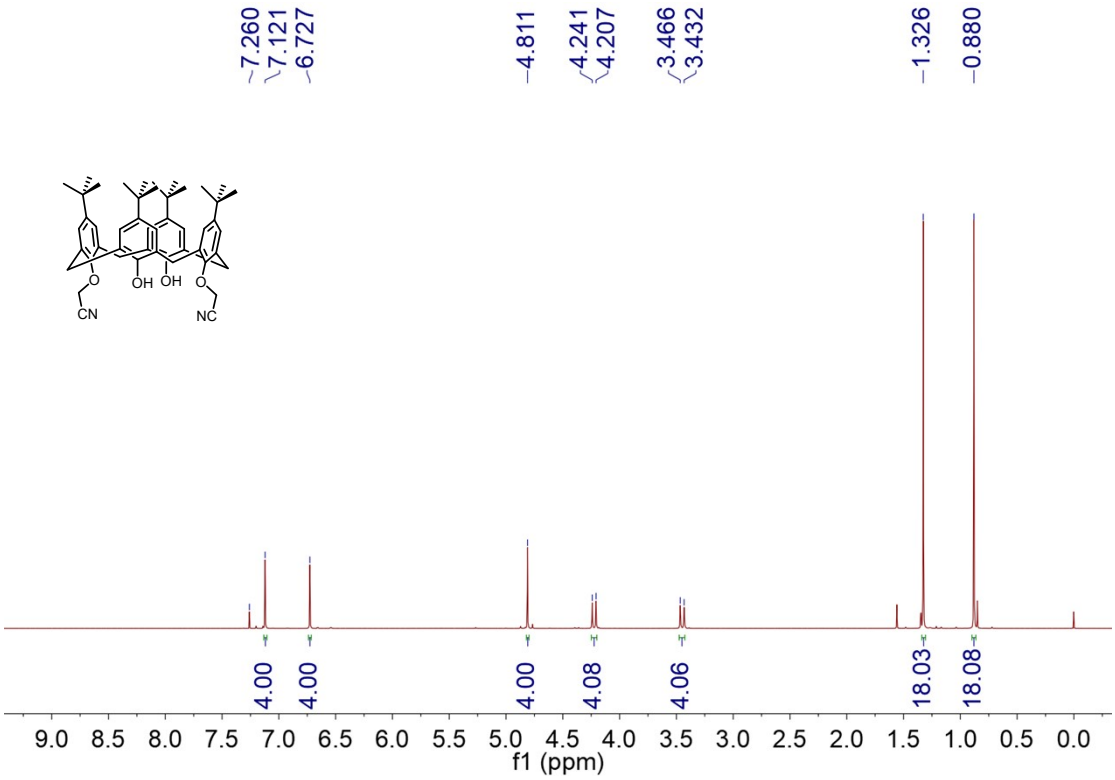


Fig. S1 ^{1}H NMR spectra of **2** (in $CDCl_3$).

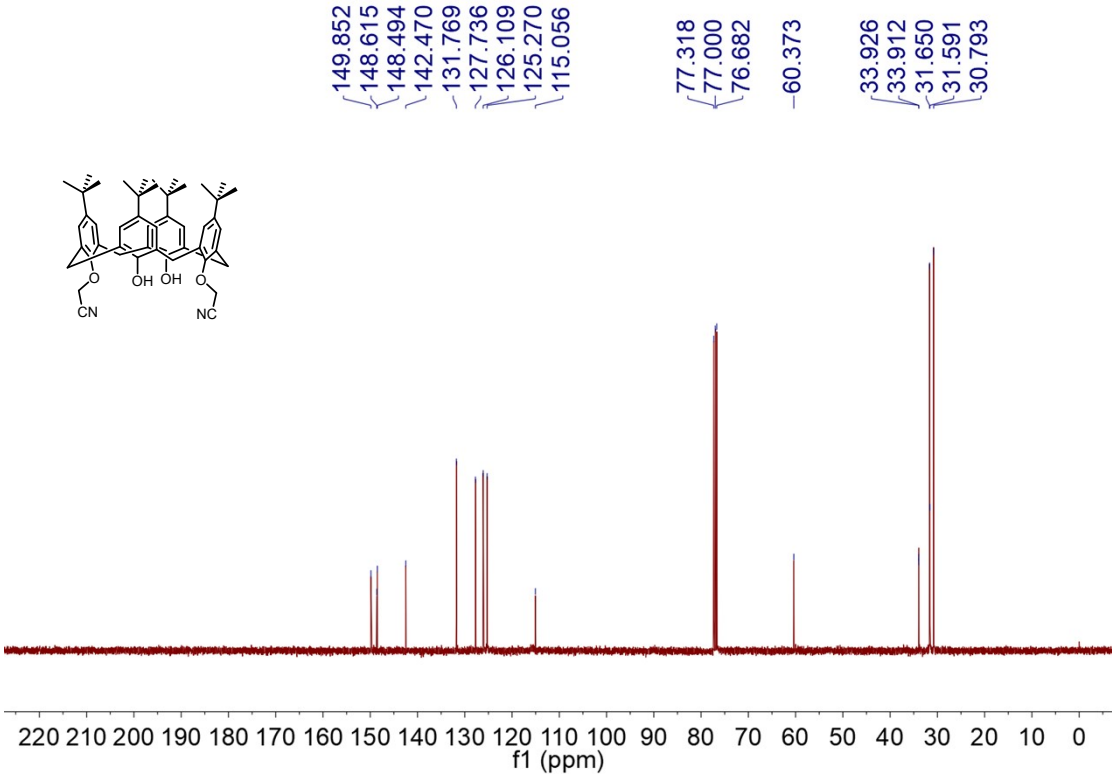


Fig. S2 ^{13}C NMR spectra of **2** (in $CDCl_3$).

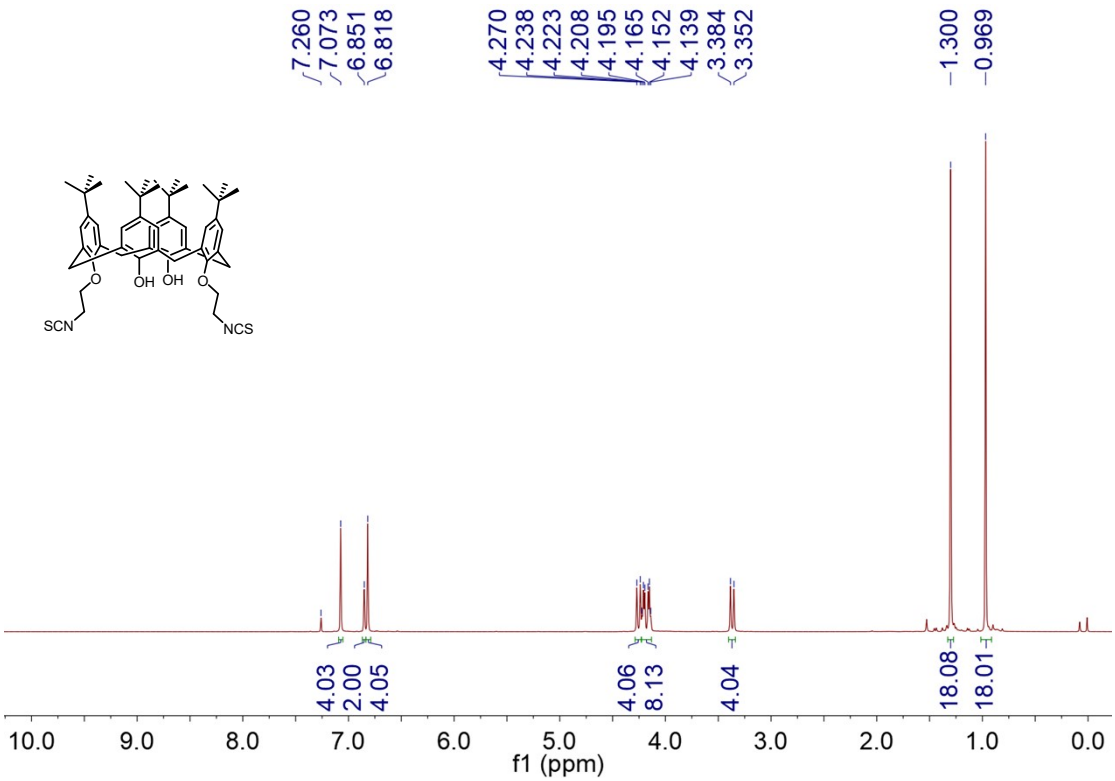


Fig. S3 ^{1}H NMR spectra of **3** (in $CDCl_3$).

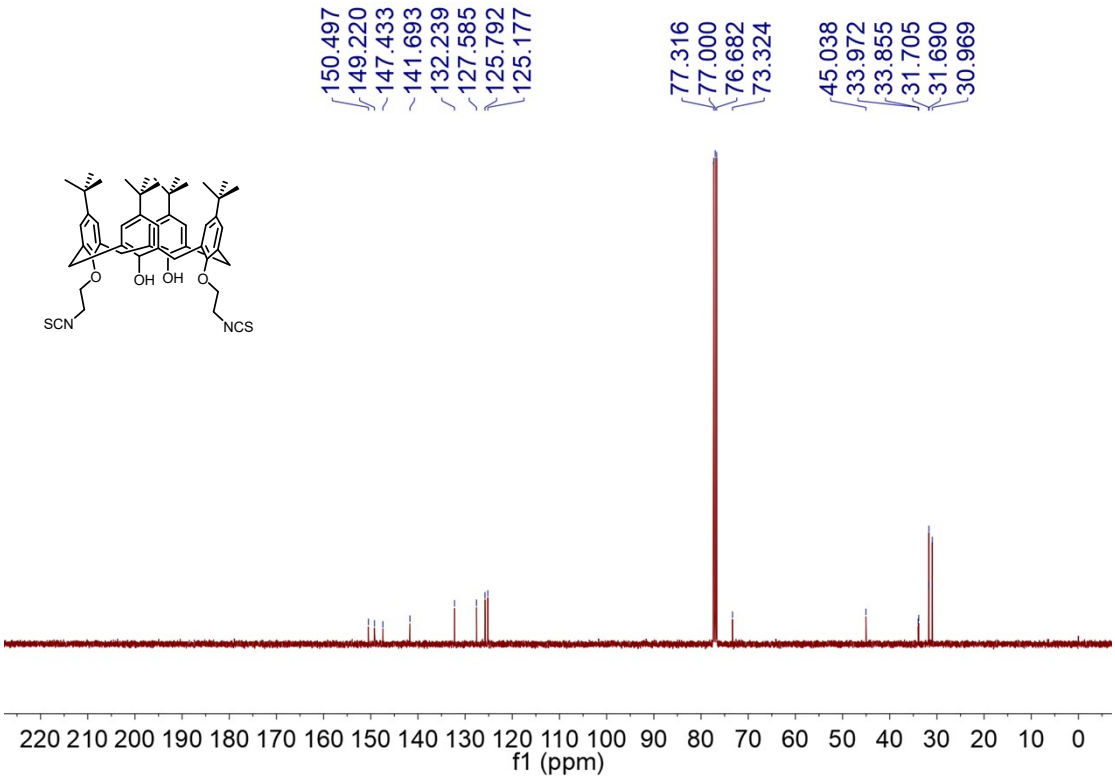


Fig. S4 ^{13}C NMR spectra of **3** (in $CDCl_3$).

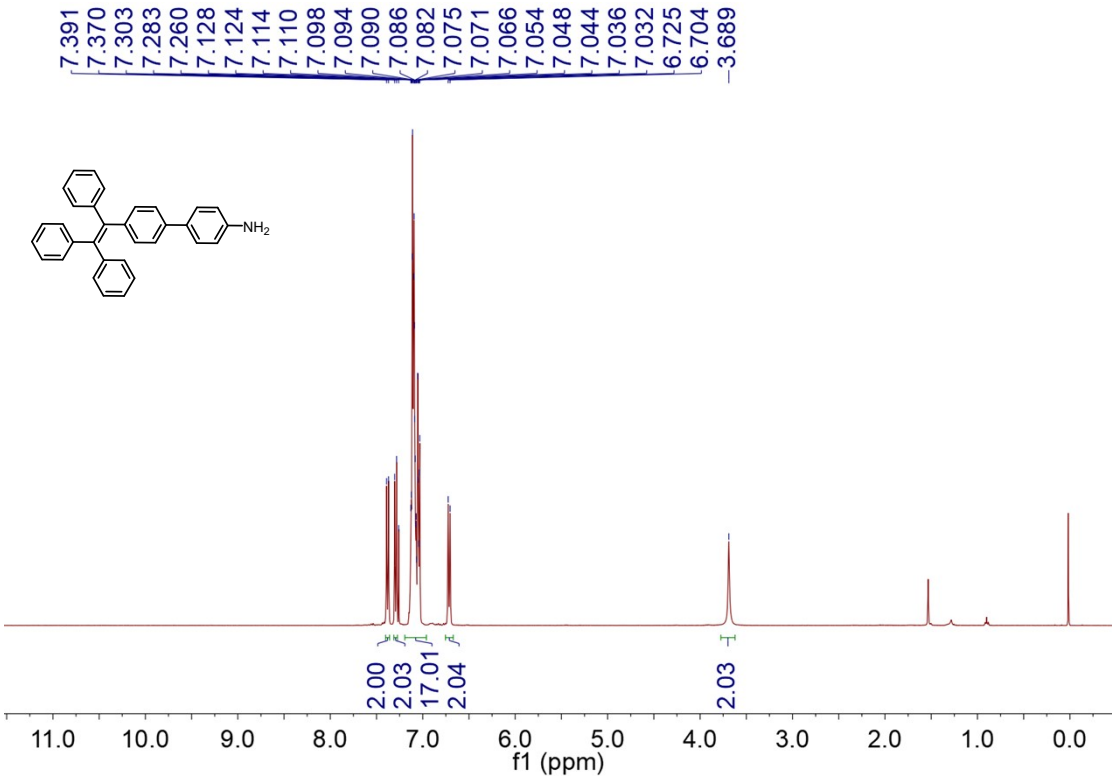


Fig. S5 ^{1}H NMR spectra of **6** (in $CDCl_3$).

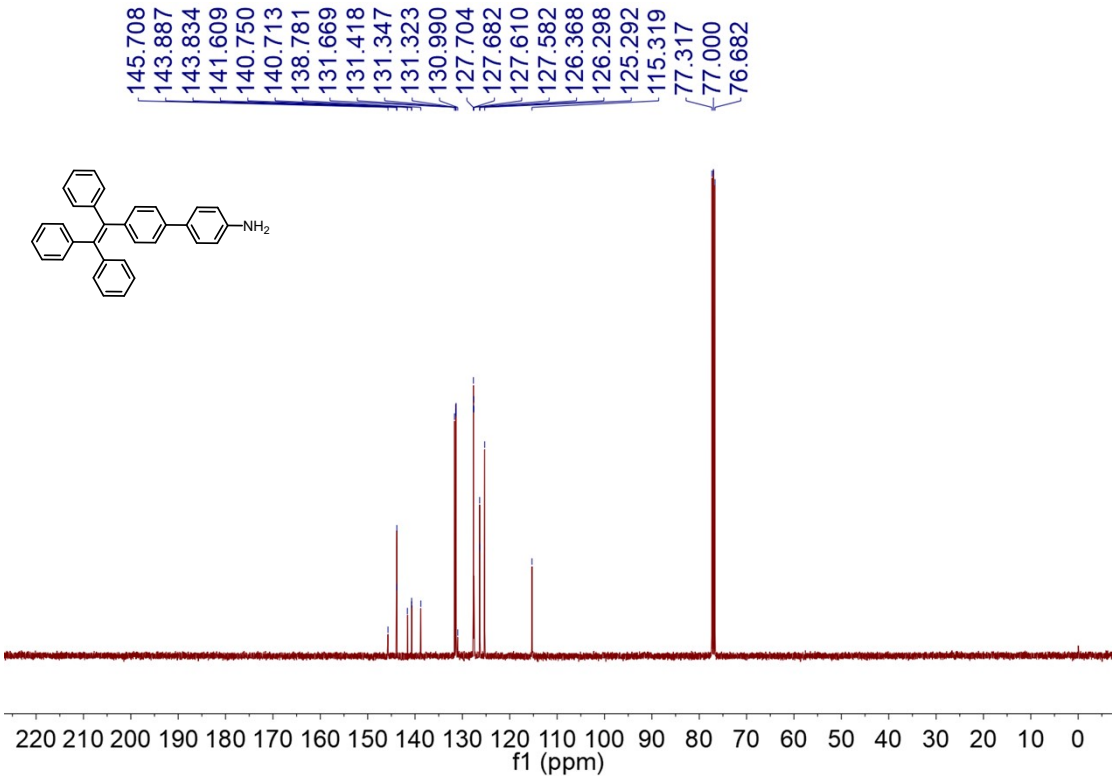


Fig. S6 ^{13}C NMR spectra of **6** (in $CDCl_3$).

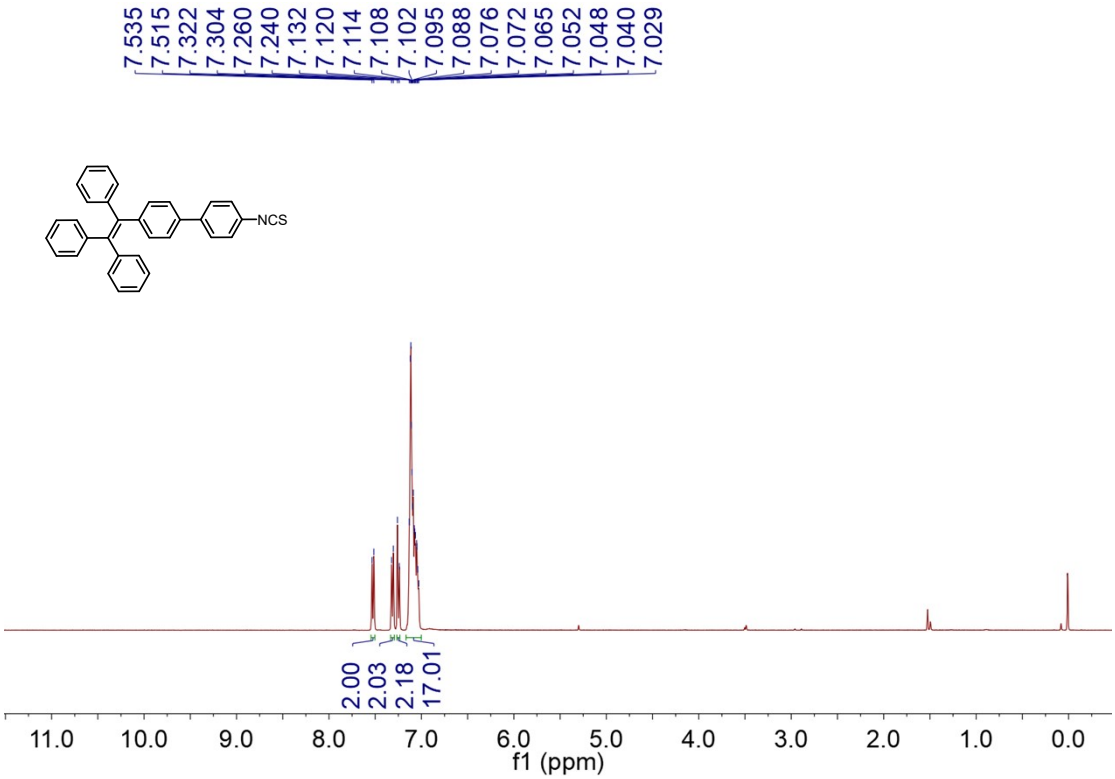


Fig. S7 ^{1}H NMR spectra of **7** (in $CDCl_3$).

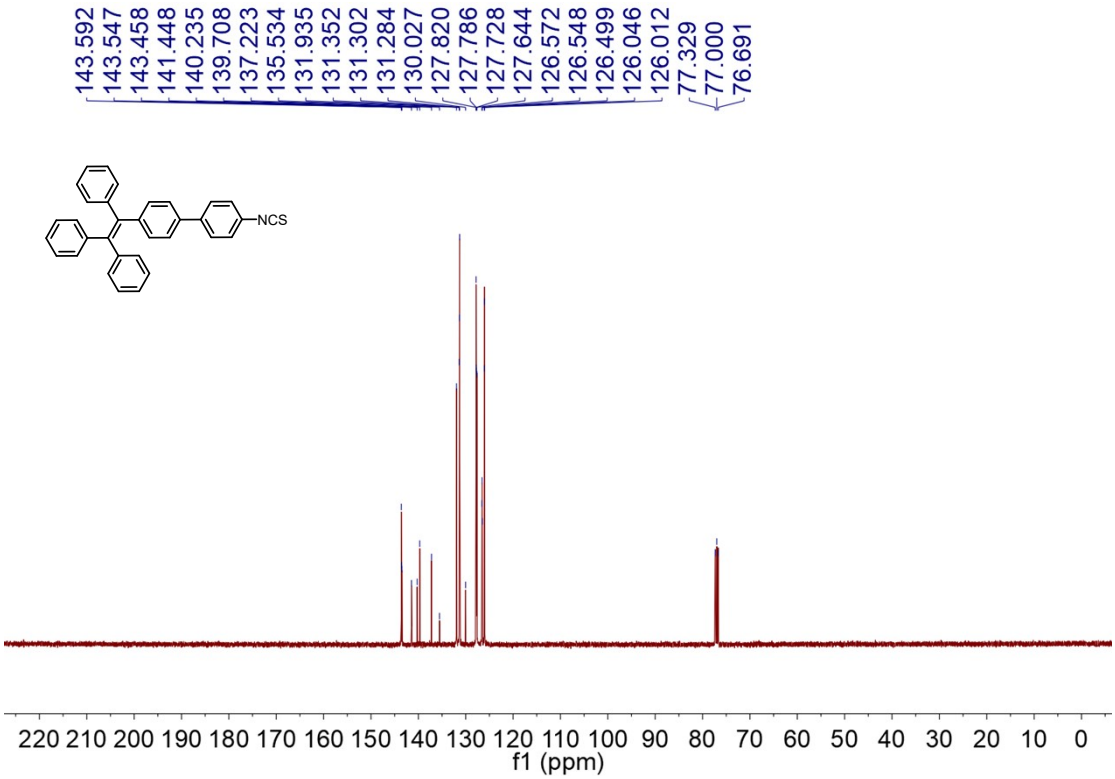


Fig. S8 ^{13}C NMR spectra of **7** (in $CDCl_3$).

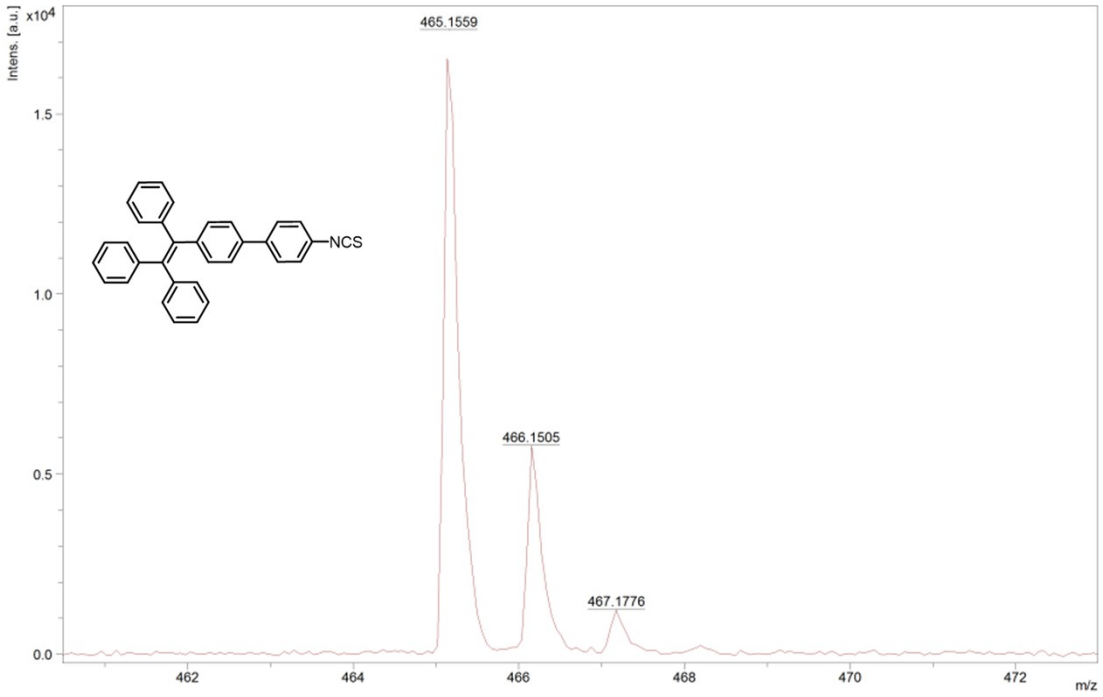


Fig. S9 HRMS spectrum of **7**

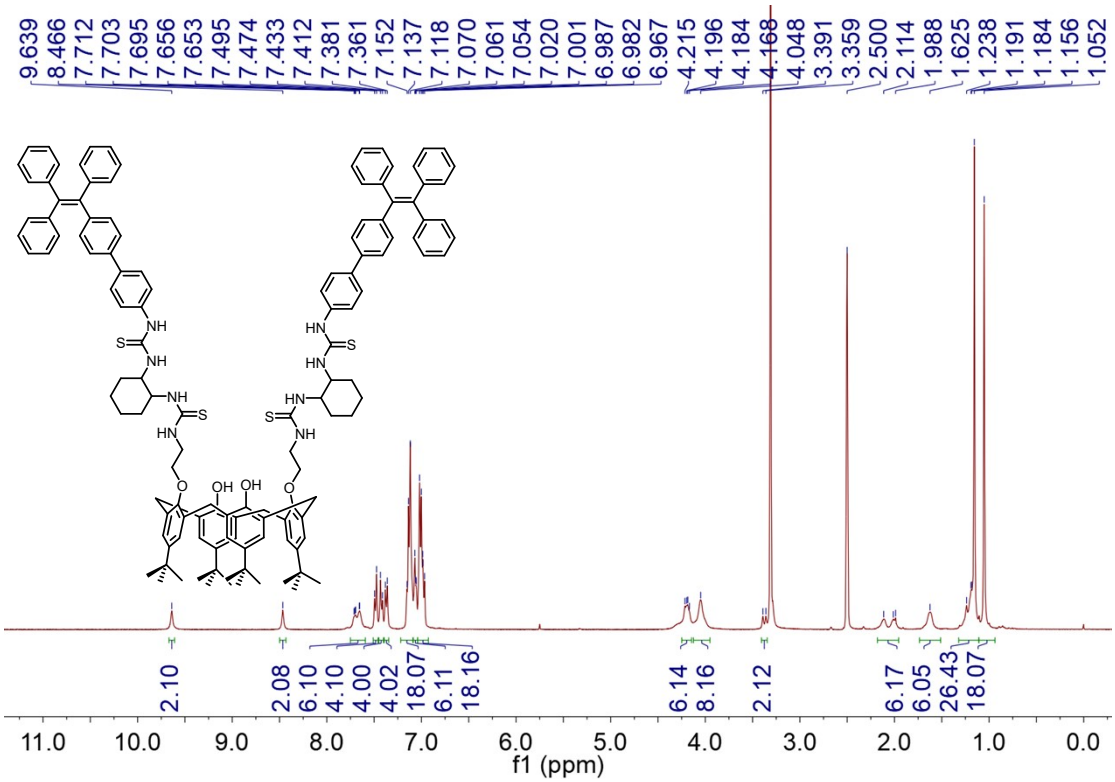


Fig. S10 ^{1}H NMR spectra of **T1** (DMSO-d_6).

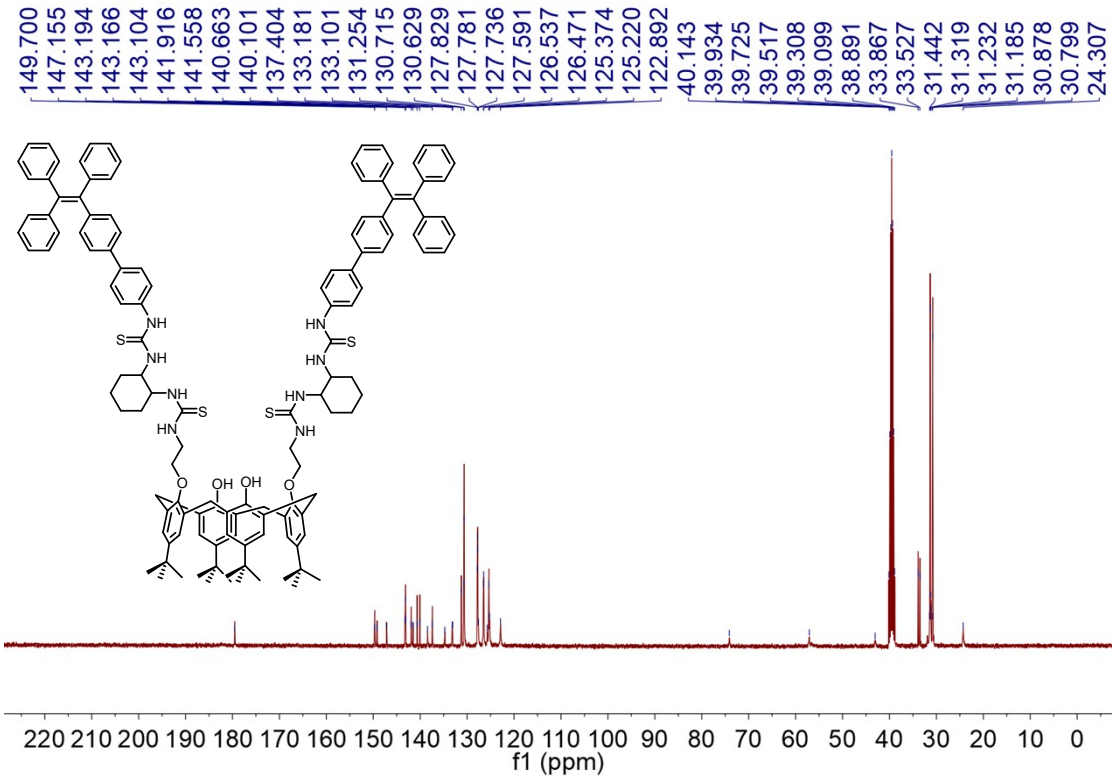


Fig. S11 ^{13}C NMR spectra of **T1** (DMSO-d_6).

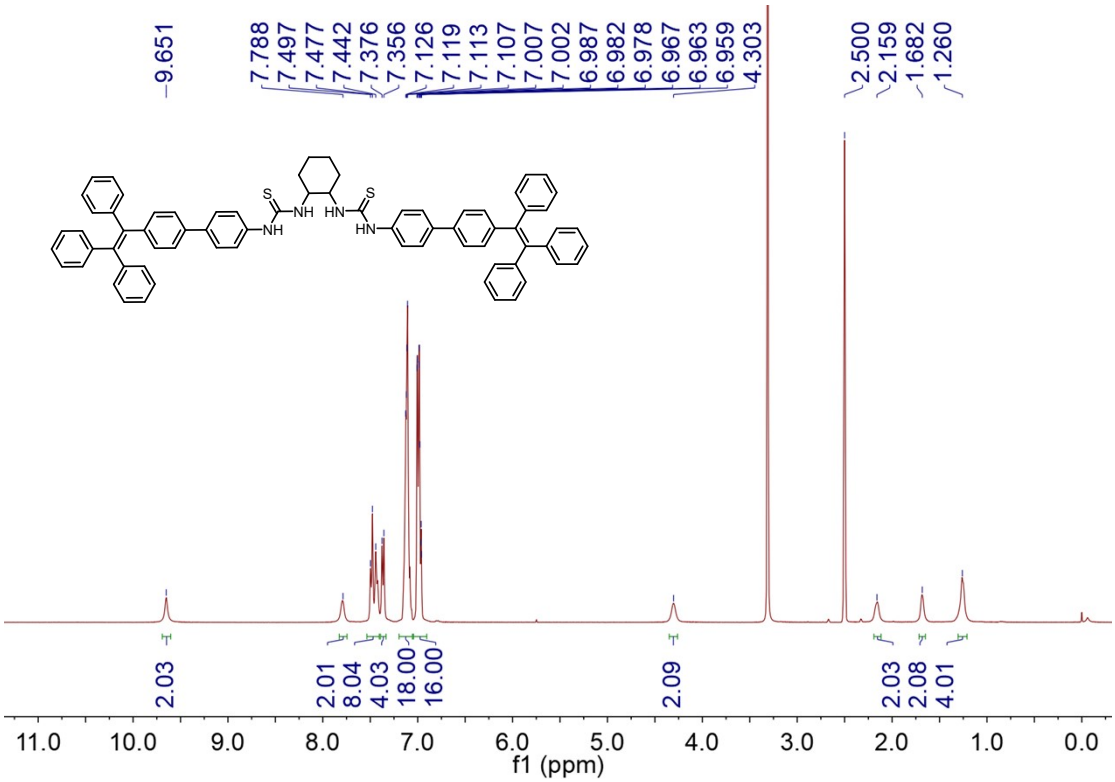


Fig. S12 ^{1}H NMR spectra of **T2** (DMSO-d_6).

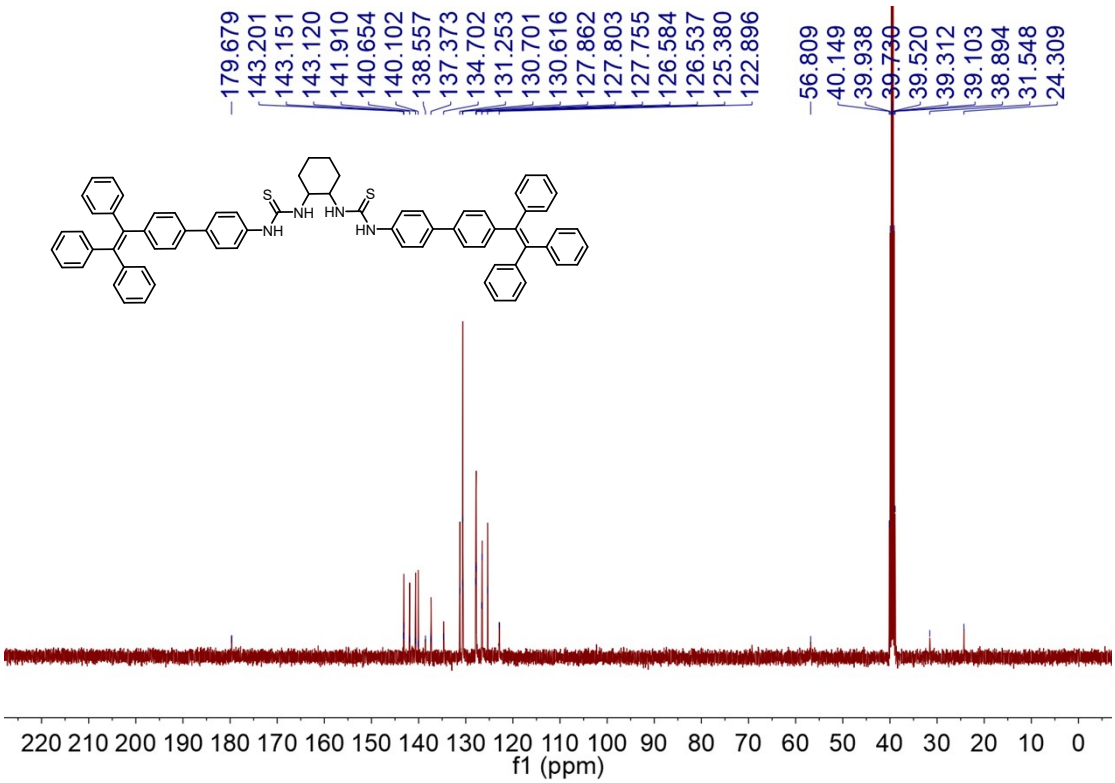


Fig. S13 ^{13}C NMR spectra of **T2** (DMSO-d_6).

4. Photophysical spectra

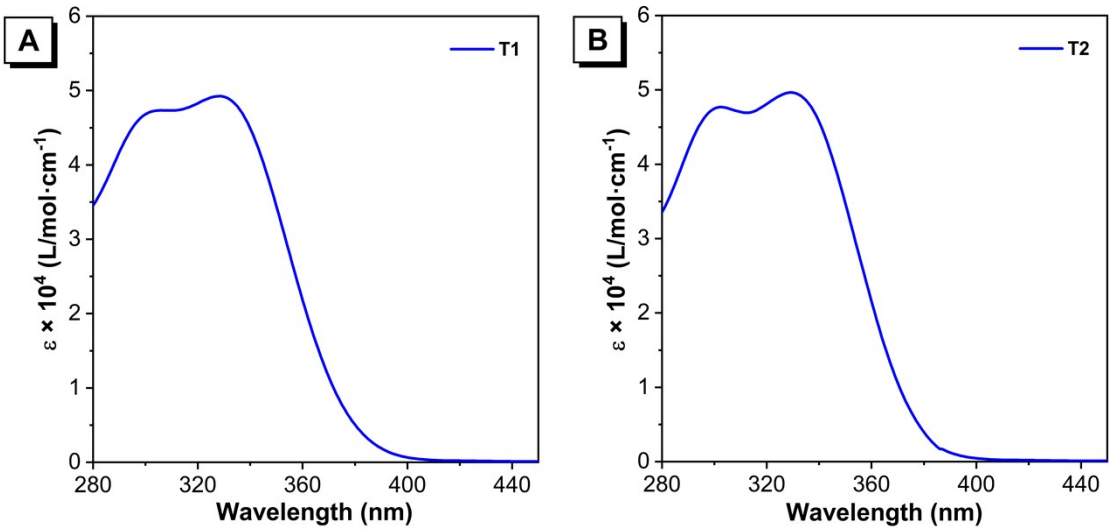


Fig. S14 (A) Absorption spectra of **T1** in THF, [**T1**] = 1×10^{-5} M, λ_{max} = 330 nm, ex/em slits 2/2 nm. (B) Absorption spectra of **T2** in THF, [**T2**] = 1×10^{-5} M, λ_{max} = 330 nm, ex/em slits 2/2 nm.

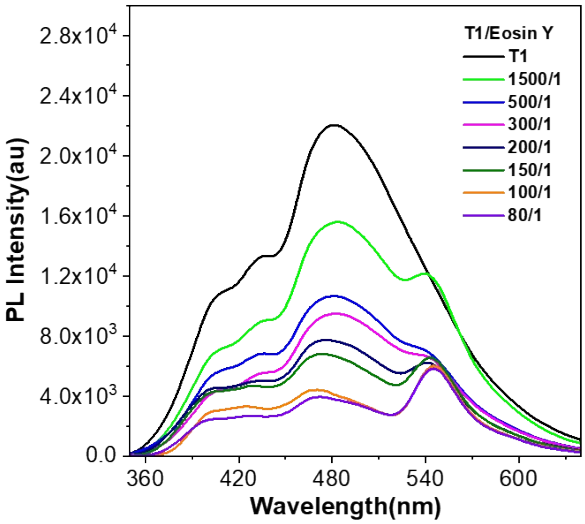


Fig. S15 PL spectra of **T1** in THF-water (v/v = 1:4) with different concentrations of **Eosin Y** (λ_{ex} = 330 nm), ex/em slits 1/1 nm.

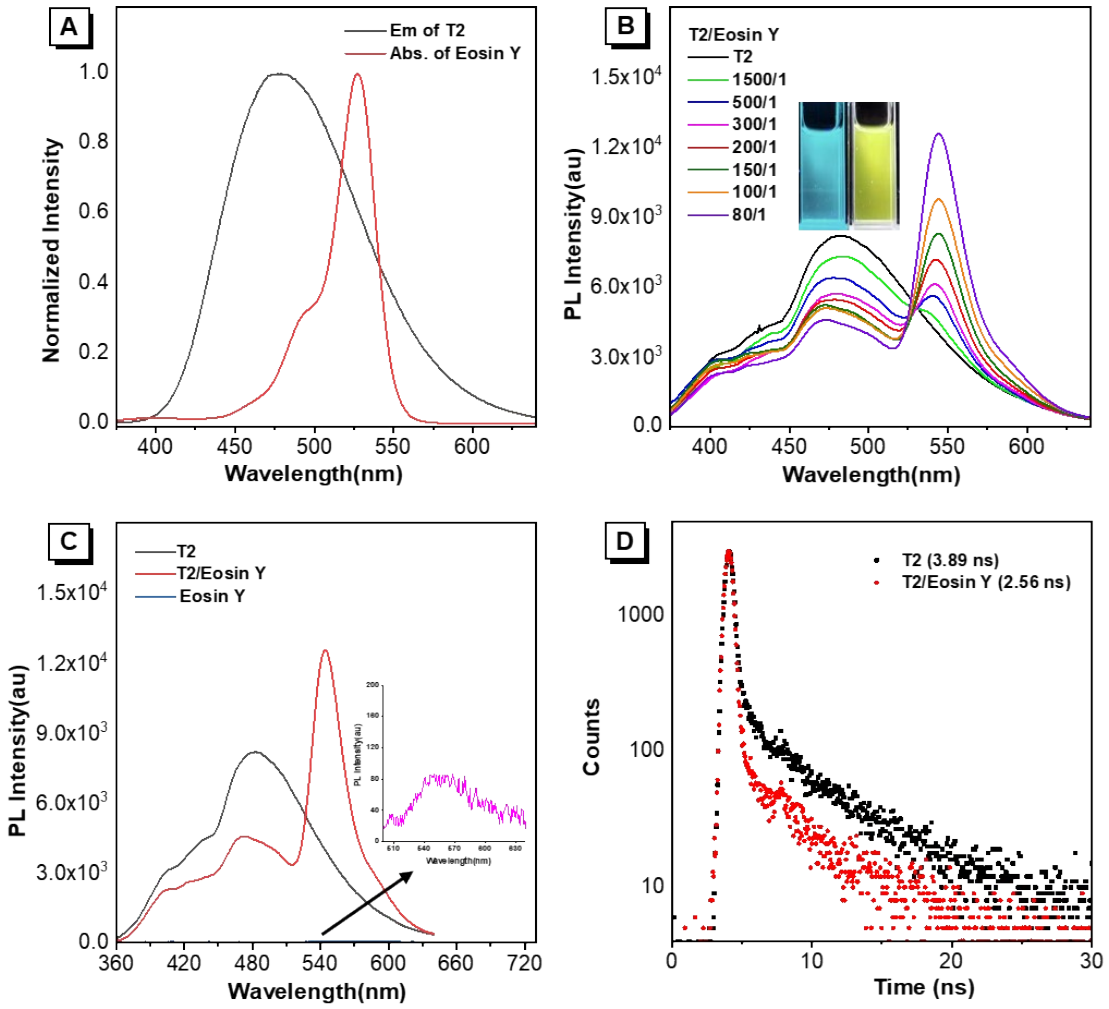


Fig. S16 (A) Normalized PL spectrum of **T2** (λ_{em} = 480 nm) and absorption profile of **Eosin Y** (λ_{ex} = 520 nm), ex/em slits 1/1 nm. (B) PL spectra of **T2** in CH_2Cl_2-CH_3OH (v/v = 1:4) with different concentrations of **Eosin Y** (λ_{ex} = 330 nm), ex/em slits 1/1 nm. (C) A representative case showing the calculation principle of Φ_{ET} and AE. inset: Fluorescence spectra of **Eosin Y** (λ_{ex} = 330 nm) in CH_2Cl_2-CH_3OH (v/v = 1:4), ex/em slits 1/1 nm. (D) Fluorescence decay profiles of **T2** assembly (black dot), and **T2/Eosin Y** assemblies (red dot) (λ_{em} = 480nm), ex/em slits 1/1 nm.

5. Energy transfer efficiency (Φ_{ET}) and antenna effect (AE) calculation

(1) Energy transfer efficiency (Φ_{ET}), is the ability to transfer energy from donor to acceptor, that is, the ratio of the fluorescence intensity of the donor in the absence of and presence of the acceptor (I_D and I_{DA}). Φ_{ET} was calculated using Equation **S1**:

$$\boldsymbol{\Phi_{ET} = 1\text{-}I_{DA}/I_D}$$

Where I_{DA} and I_D are the fluorescence intensities at 480 nm of **T1**/**Eosin Y** and **T1** respectively when excited at 330 nm.

Where I_{DA} and I_D are the fluorescence intensities at 480 nm of **T2**/**Eosin Y** and **T2** respectively when excited at 330 nm.

(2) Antenna effect (AE), is the ability of the acceptor to harvest energy from the donor. AE was calculated using Equation **S2**:

$$\mathbf{AE = (I_{DA,330}\text{-}I_{D,330})/I_{DA,480}}$$

Where $\mathbf{I_{DA,330}}$ is the fluorescence intensity at Maximum emission wavelength nm of **T1**/**Eosin Y** when indirect excitation of the acceptor at 330 nm, $\mathbf{I_{D,330}}$ is the fluorescence intensity at Maximum emission wavelength of **T1** which is normalized with **T1**/**Eosin Y** at 545 nm. $\mathbf{I_{DA,480}}$ is the fluorescence intensity at Maximum emission wavelength of **T1**/**Eosin Y** when direct excitation of the acceptor at 330 nm.

$$\mathbf{AE = (I_{DA,330}\text{-}I_{D,330})/I_{DA,480}}$$

Where $\mathbf{I_{DA,330}}$ is the fluorescence intensity at Maximum emission wavelength nm of **T2**/**Eosin Y** when indirect excitation of the acceptor at 330 nm, $I_{D,330}$ is the fluorescence intensity at Maximum emission wavelength of **T2** which is normalized with **T2**/**Eosin Y** at 545 nm. $I_{DA,480}$ is the fluorescence intensity at Maximum emission wavelength of **T2**/**Eosin Y** when direct excitation of the acceptor at 330 nm.

Table S1 Fluorescence lifetimes of **T1** and **T1**/**Eosin Y** in CH_2Cl_2–CH_3OH (1/4, v/v)

T1:Eosin Y	τ_1	τ_2	α_1	α_2	τ_{ave}	χ^2
1500:0	0.7287	6.3701	13.26%	86.74%	5.62	1.1138
80:1	0.2059	4.4282	23.82%	76.18%	3.42	1.0407

Table S2 Energy transfer efficiency and antenna effect of **T1**/**Eosin Y**.

Sample (**T1:Eosin Y**)	**Concentration, Respectively** (**T1/Eosin Y**)	Φ_{ET} **(%)**	**AE**
1500:1	5×10^{-5} M, 3.33×10^{-8} M	21.1	1.15
500:1	5×10^{-5} M, 1×10^{-7} M	34.9	1.15
300:1	5×10^{-5} M, 1.67×10^{-7} M	42.2	1.60
200:1	5×10^{-5} M, 2.5×10^{-7} M	44.2	2.28
150:1	5×10^{-5} M, 3.33×10^{-7} M	47.3	2.30
100:1	5×10^{-5} M, 5×10^{-7} M	47.9	2.82
80:1	5×10^{-5} M, 6.25×10^{-7} M	57.1	2.18

Table S3 Fluorescence lifetimes of **T2** and **T2**/**Eosin Y** in CH_2Cl_2–CH_3OH (1/4, v/v)

T2:Eosin Y	τ_1	τ_2	α_1	α_2	τ_{ave}	χ^2
1500:0	0.3189	4.5470	15.33%	84.67%	3.90	1.0573
80:1	0.1940	4.8717	49.43%	50.57%	2.56	1.1424

Table S4 Energy transfer efficiency and antenna effect of **T2**/**Eosin Y**.

Sample (**T2:Eosin Y**)	**Concentration, Respectively** (**T2**, **Eosin Y**)	Φ_{ET} **(%)**	**AE**
1500:1	1×10^{-5} M, 5×10^{-8} M	10.9	2.36
500:1	1×10^{-5} M, 1×10^{-7} M	22.1	1.72
300:1	1×10^{-5} M, 1.5×10^{-7} M	30.3	2.96
200:1	1×10^{-5} M, 2×10^{-7} M	33.5	2.31
150:1	1×10^{-5} M, 2.5×10^{-7} M	37.8	2.46
100:1	1×10^{-5} M, 3×10^{-7} M	38.7	1.72
80:1	1×10^{-5} M, 4×10^{-7} M	45.4	2.27

6. SEM、DLS and EDX

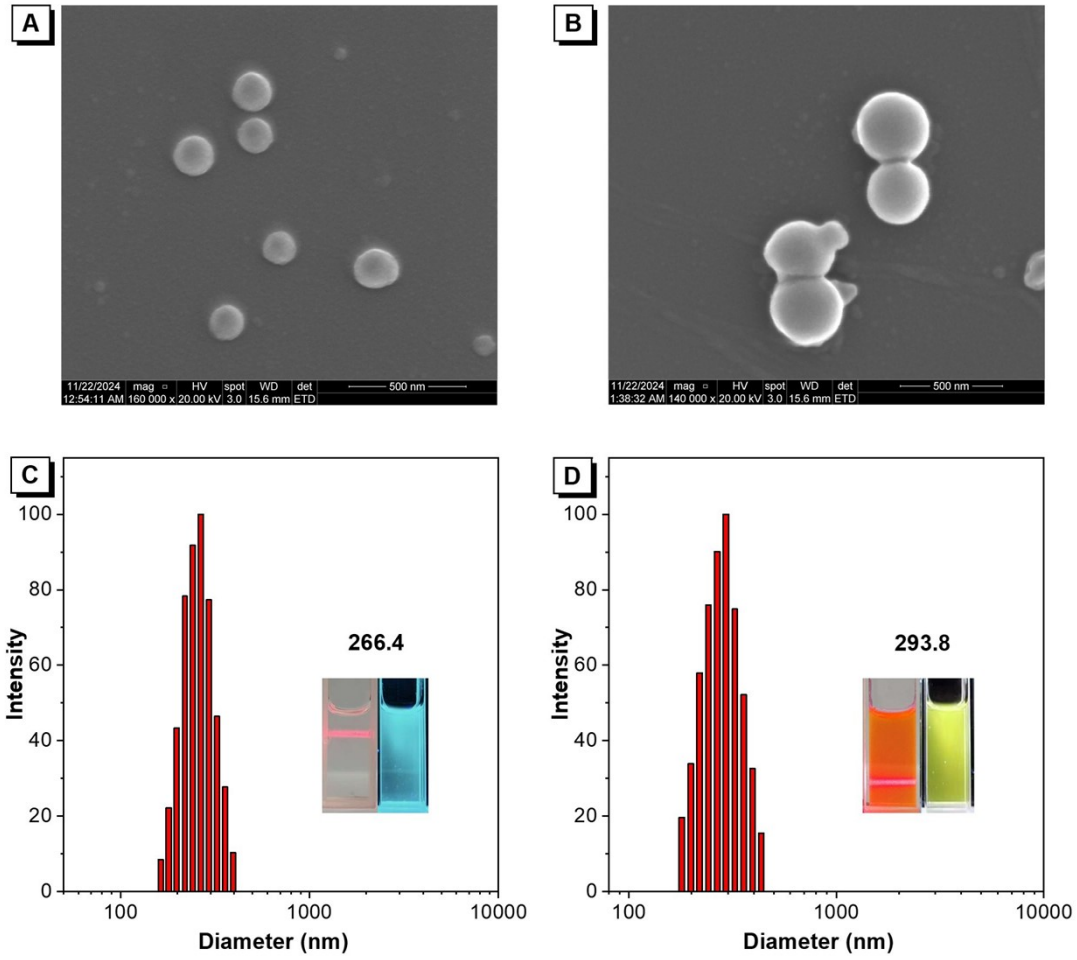


Fig. S17 SEM images: (A) **T2** nanoparticles, (B) **T2/Eosin Y** (80:1, molar ratio). DLS data: (C) **T2** nanoparticles, inset: Tyndall effect and fluorescence photograph of **T2**. (D) **T2/Eosin Y** (80:1, molar ratio), inset: Tyndall effect and fluorescence photograph of **T2/Eosin Y** (80:1, molar ratio). [**T2**] = 5×10^{-5} M, [**Eosin Y**] = 6.25×10^{-7} M, respectively.

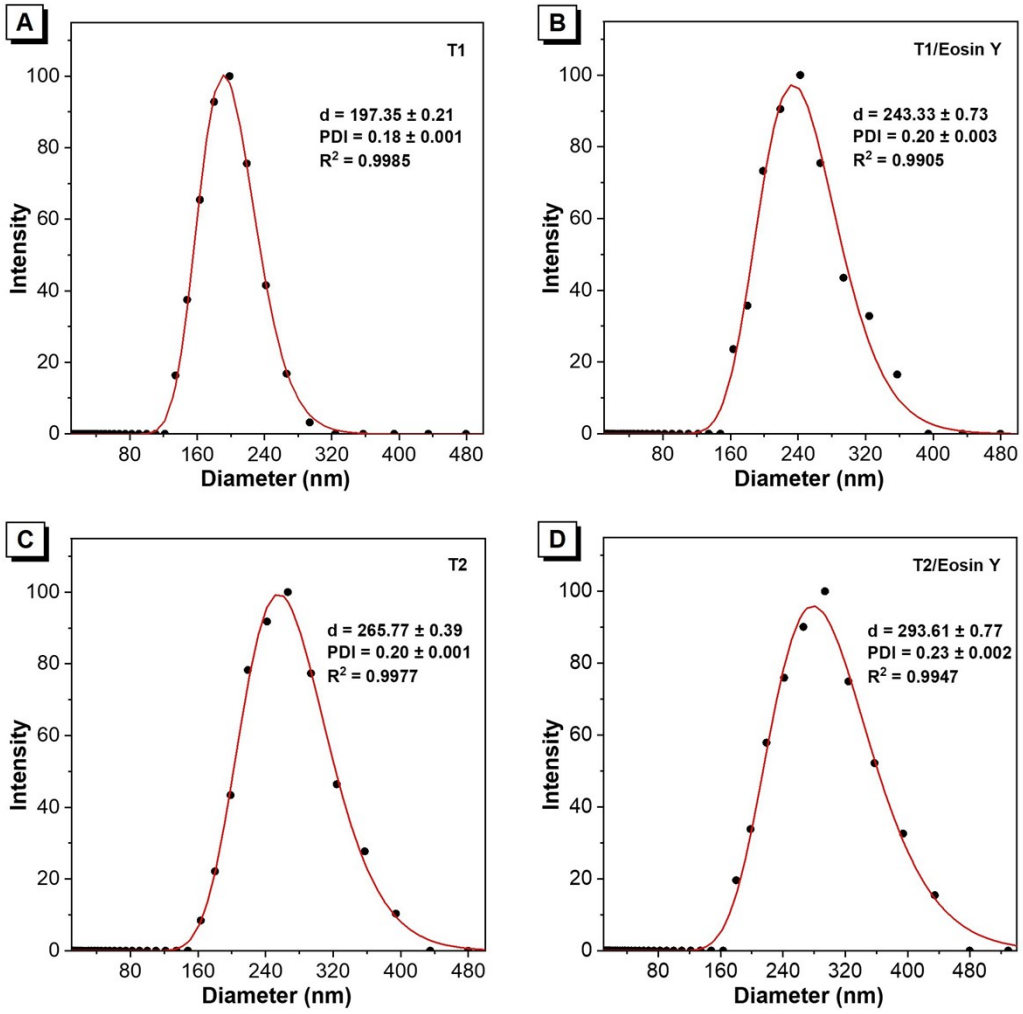


Fig. S18 Fitting curve of normal distribution of DLS data

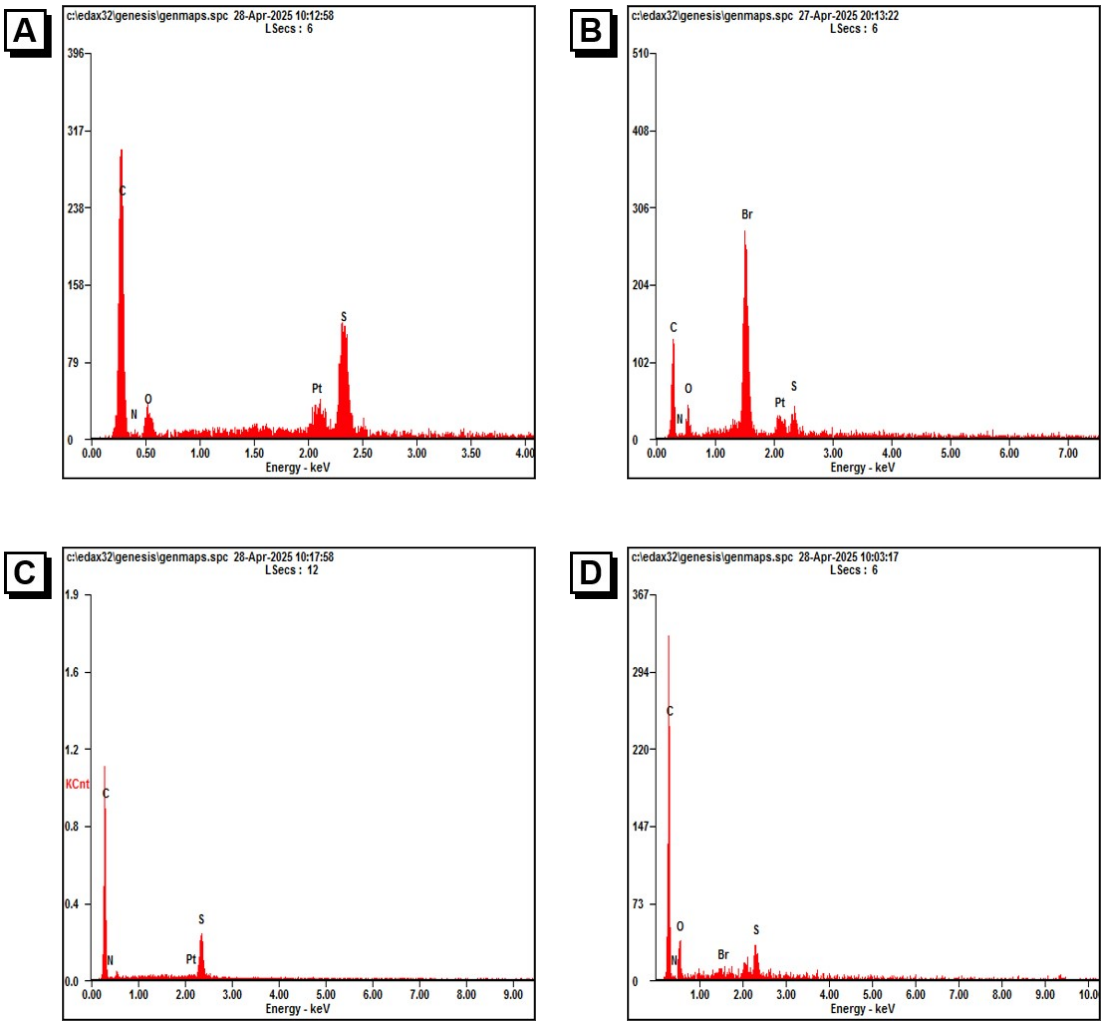


Fig. S19 (A-D) EDX elemental mapping images of T1, T1/Eosin Y, T2, and T2/Eosin Y, respectively.

7. Photocatalysis

Synthesis of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline：

CuI (200 mg, 1.0 mmol), potassium phosphate (4.25 g, 20.0 mmol), 2-propanol (10 mL), ethylene glycol (1.11 mL), 1,2,3,4-tetrahydroisoquinoline (2.0 mL, 15.0 mmol), iodobenzene (1.12 mL, 10.0 mmol) were added to the reaction flask in turn, evacuated and replaced with nitrogen three times, and then reacted at 90 °C for 24 h. After the reaction, the mixture was cooled to room temperature and 25 mL of water were added. Then the mixture was extracted with ethyl acetate. The organic phases were combined, washed with brine, and dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure, and the pure yellow product was obtained by silica gel column chromatography.

General procedure for the cross-dehydrogenative coupling (CDC) reaction：

N-phenyl-1,2,3,4-tetrahydroisoquinoline or its derivatives (0.2 mmol, 1.0 equiv) and indole and its derivatives (0.3 mmol, 1.5 equiv) and photocatalyst (5.0 mol%) were dissolved in the CH_2Cl_2 (0.4 mL) and CH_3OH (1.6 mL), the mixture was irradiated by blue LEDs (460 nm, 30 W) at room temperature under the ambient air condition. Then the mixture was extracted with ethyl acetate, and the combined organic layer was dried with anhydrous $MgSO_4$. Then the organic solvent was concentrated in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the products.

Table S5. A comparative study of the CDC reactions between *N*-Phenyl-1,2,3,4-tetrahydroisoquinoline and indole under various solvent conditions.[a]

Entry	Photocatalyst	Solvent	Yield (%)
1	T1/Eosin Y = 20:1	Toluene	18
2	T1/Eosin Y = 20:1	DCE	32
3	T1/Eosin Y = 20:1	$CHCl_3$	53
4	T1/Eosin Y = 20:1	CH_2Cl_2	68
5	T1/Eosin Y = 20:1	EA	65
6	T1/Eosin Y = 20:1	THF	44
7	T1/Eosin Y = 20:1	Acetone	12
8	T1/Eosin Y = 20:1	CH_3OH	33
9	T1/Eosin Y = 20:1	DMF	NR
10	T1/Eosin Y = 20:1	CH_3CN	37
11	T1/Eosin Y = 20:1	DMSO	15

[a]Reaction conditions: *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (0.2 mmol, 1.0 equiv), indole (0.3 mmol, 1.5 equiv), photocatalyst (5.0 mol%), CH_2Cl_2 (0.4 mL), CH_3OH (1.6 mL), blue LEDs, room

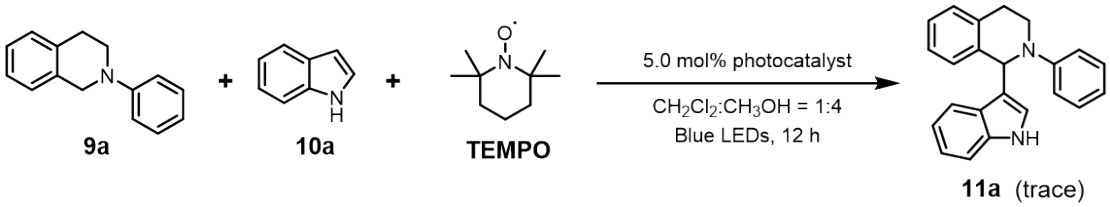
temperature, 12 h.

9. Mechanism study

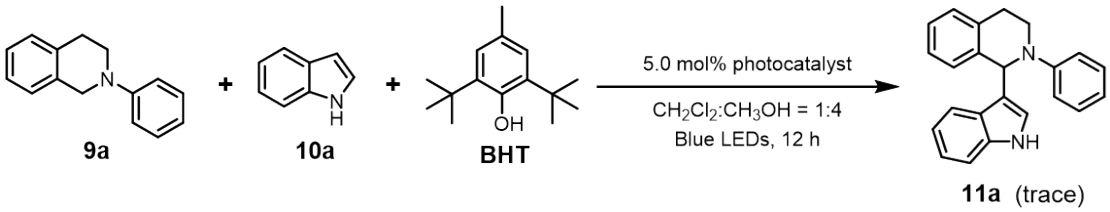
Table S6. Experiments on the mechanism of CDC reaction between *N*-phenyl-1,2,3,4-tetrahydroisoquinoline and indole.

Entry	Quencher	Role	Yield of 11a
1	TEMPO	Radical scavenger	trace
2	BHT	Radical scavenger	trace
3	9,10-Dimethylanthracene	$^1O_2$ scavenger	63
4	Benzoquinone	$O_2^{\bullet-}$ scavenger	trace

(1). Radical trapping experiments

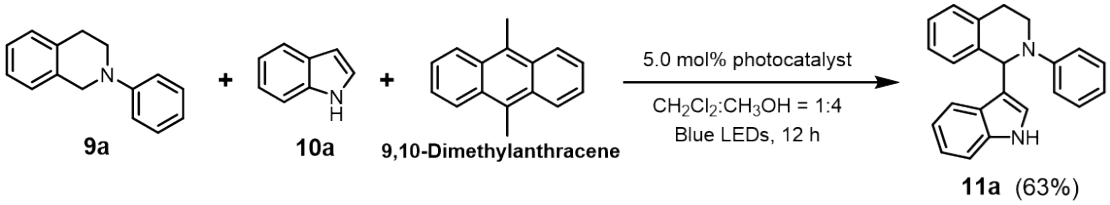


N-phenyl-1,2,3,4-tetrahydroisoquinoline (0.2 mmol, 1 equiv), indole (0.3 mmol, 1.5 equiv), photocatalyst (5.0 mol%) and TEMPO (0.6 mmol, 3.0 equiv) in CH_2Cl_2:CH_3OH = 1:4 (2.0 mL) was stirred under the irradiation of blue LEDs (460nm, 30 W) at room temperature for 12 h.

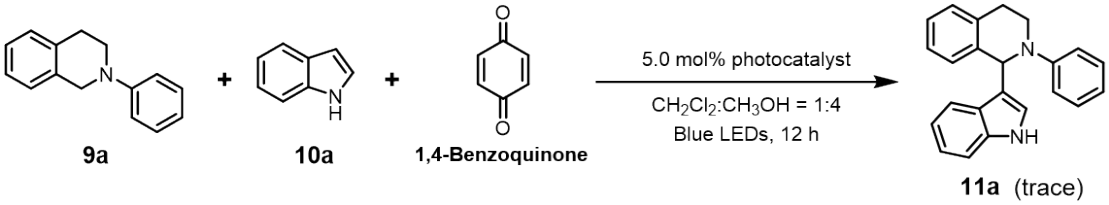


N-phenyl-1,2,3,4-tetrahydroisoquinoline (0.2 mmol, 1 equiv), indole (0.3 mmol, 1.5 equiv), photocatalyst (5.0 mol%) and BHT (0.6 mmol, 3.0 equiv) in CH_2Cl_2:CH_3OH=1:4 (2.0 mL) was stirred under the irradiation of blue LEDs (460nm, 30 W) at room temperature for 12 h.

(2). Experiments demonstrating the role of O_2

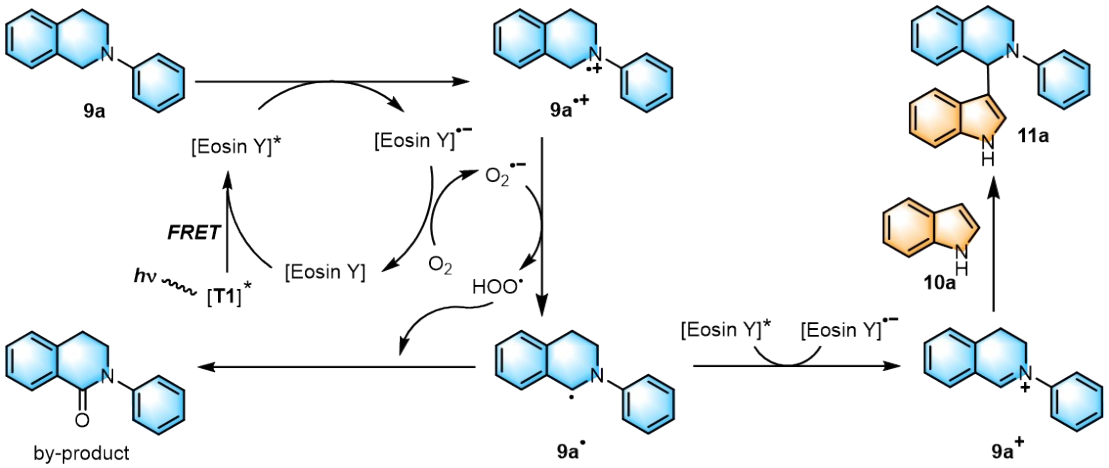


N-phenyl-1,2,3,4-tetrahydroisoquinoline (0.2 mmol, 1 equiv), indole (0.3 mmol, 1.5 equiv), photocatalyst (5.0 mol%) and 9,10-Dimethylanthracene (0.4 mmol, 2.0 equiv) in CH_2Cl_2:CH_3OH = 1:4 (2.0 mL) was stirred under the irradiation of blue LEDs (460nm, 30 W) at room temperature for 12 h.



N-phenyl-1,2,3,4-tetrahydroisoquinoline (0.2 mmol, 1.0 equiv), indole (0.3 mmol, 1.5 equiv), photocatalyst (5.0 mol%) and Benzoquinone (0.4 mmol, 2.0 equiv) in CH_2Cl_2:CH_3OH=1:4 (2.0 mL) was stirred under the irradiation of blue LEDs (460nm, 30 W) at room temperature for 12 h.

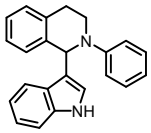
(3). Research on the reaction mechanism of aerobic CDC reaction.



Scheme S2 Proposed mechanism of the aerobic CDC reaction.

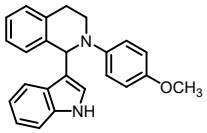
^{1}H NMR and ^{13}C NMR data of 11a-11q.

11a. 1-(1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



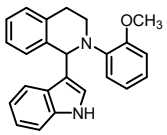
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (s, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.34-7.22 (m, 4H), 7.21-7.14 (m, 4H), 7.06-7.02 (m, 3H), 6.79 (t, J = 7.2 Hz, 1H), 6.64 (dd, J_1 = 2.4, J_2 = 1.2 Hz, 1H), 6.19 (s, 1H), 3.63 (dd, J_1 = 8.0, J_2 = 4.8 Hz, 2H), 3.12-3.04 (m, 1H), 2.85-2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.71, 137.32, 136.53, 135.53, 129.17, 128.79, 128.00, 126.63, 126.38, 125.66, 124.14, 122.07, 120.06, 119.58, 119.23, 118.03, 115.73, 111.00, 77.32, 77.00, 76.68, 56.57, 42.22, 26.55.

11b. 1-(1H-indol-3-yl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline



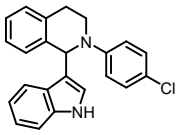
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.21-7.12 (m, 5H), 7.02-6.98 (m, 1H), 6.97-6.93 (m, 2H), 6.81-6.77 (m, 2H), 6.57 (d, J = 2.0 Hz, 1H), 5.97 (s, 1H), 3.75 (s, 3H), 3.59 (m, 2H), 3.08-3.00 (m, 1H), 2.83-2.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.25, 144.67, 137.48, 136.41, 135.35, 128.84, 128.17, 126.79, 126.42, 125.63, 124.28, 121.96, 120.23, 119.60, 119.51, 119.17, 114.36, 110.90, 57.89, 55.57, 43.76, 26.78.

11c. 1-(1H-indol-3-yl)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (s, 1H), 7.26-7.17 (m, 3H), 7.13-7.04 (m, 4H), 6.96-6.91 (m, 2H), 6.89-6.85 (m, 1H), 6.71-6.66 (m, 1H), 6.63-6.60 (m, 1H), 6.44 (d, J = 2.4 Hz, 1H), 6.16 (s, 1H), 3.91 (s, 3H), 3.53-3.46 (m, 1H), 3.42-3.37 (m, 1H), 3.18-3.09 (m, 1H), 2.91-2.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.17, 140.64, 138.16, 136.02, 134.95, 128.79, 128.49, 128.34, 127.47, 126.14, 125.48, 124.51, 122.73, 122.01, 121.59, 120.83, 120.21, 119.24, 111.60, 110.64, 56.40, 55.68, 42.97, 28.28.

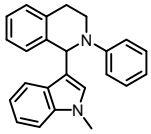
11d. 2-(4-chlorophenyl)-1-(1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.43 (dd, J_1 = 8.8, J_2 = 5.6 Hz, 1H), 7.28-7.27 (m, 1H), 7.25-7.14 (m, 5H), 7.03-6.98 (m, 3H), 6.82-6.72 (m, 2H), 6.60 (dd, J_1 = 2.4, J_2 = 1.2 Hz, 1H), 6.13 (s, 1H), 3.65-3.56 (m, 2H), 3.11-3.03 (m, 1H), 2.82-2.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)

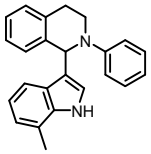
δ = 149.79, 136.96, 135.42, 134.88, 129.19, 128.89, 127.93, 127.44, 126.78, 125.77, 125.50, 125.32, 122.44, 119.59, 119.12, 118.67, 116.38, 111.97, 56.64, 42.51, 26.54.

11e. 1-(1-methyl-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



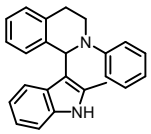
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (d, J = 8.0 Hz, 1H), 7.32-7.30 (m, 1H), 7.28-7.14 (m, 7H), 7.05-7.01 (m, 3H), 6.78 (t, J = 7.2 Hz, 1H), 6.51 (s, 1H), 6.19 (s,1H), 3.66 (s, 3H), 3.65-3.63 (m, 2H), 3.12-3.04 (m, 1H), 2.85-2.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.68, 137.54, 137.29, 135.53, 129.19, 128.78, 128.00, 126.78, 126.60, 125.66, 121.61, 120.11, 119.06, 117.88, 117.57, 115.53, 109.12, 56.52, 42.09, 32.71, 26.53.

11f. 1-(7-methyl-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



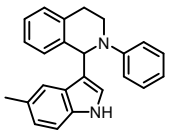
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (s, 1H), 7.41-7.37 (m, 1H), 7.28-7.26 (m, 1H), 7.24-7.20 (m, 2H), 7.18-7.12 (m, 3H), 7.00 (d, J = 7.6 Hz, 2H), 6.96-6.94 (m, 2H), 6.76 (t, J = 7.2 Hz, 1H), 6.60 (dd, J_1 = 2.4, J_2 = 0.8 Hz, 1H), 6.15 (s, 1H), 3.62-3.59 (m, 2H), 3.09-3.01 (m, 1H), 2.83-2.77 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.73, 137.41, 136.07, 135.51, 129.14, 128.73, 127.98, 126.60, 125.91, 125.66, 123.77, 122.59, 120.13, 119.80, 119.68, 117.97, 117.75, 115.69, 56.68, 42.26, 26.67, 16.54.

11g. 1-(2-methyl-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (s, 1H), 7.20-7.15 (m, 5H), 7.09-7.00 (m, 6H), 6.91 (t, J = 8.0 Hz, 1H), 6.84 (t, J = 7.2 Hz, 1H), 5.98 (s, 1H), 3.72-3.59 (m, 2H), 3.13-2.97 (m, 2H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.89, 137.94, 135.27, 134.84, 133.29, 128.77, 128.60, 128.19, 126.25, 126.02, 120.74, 120.13, 119.41, 119.40, 119.13, 113.36, 109.96, 57.06, 45.74, 27.86, 12.28.

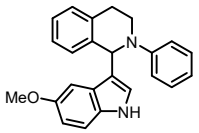
11h. 1-(5-methyl-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (s, 1H), 7.33 (s, 1H), 7.30-7.27 (m, 1H), 7.25-7.13 (m, 6H), 7.04 (d, J = 7.6 Hz, 2H), 6.99 (dd, J_1 = 8.4, J_2 = 1.6 Hz, 1H), 6.79 (t, J = 7.2 Hz, 1H), 6.58 (d, J = 2.4 Hz, 1H), 6.14 (s, 1H), 3.66-3.62 (m, 2H), 3.11-3.03 (m, 1H), 2.83-2.77 (m, 1H), 2.37 (s, 3H).

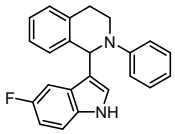
^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.01, 150.16, 137.66, 135.70, 131.73, 129.33, 128.92, 128.13, 127.06, 126.82, 125.81, 125.12, 118.85, 118.42, 116.33, 112.39, 111.78, 102.01, 77.48, 77.16, 76.84, 56.98, 55.81, 42.26, 27.08.

11i. 1-(5-methoxy-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



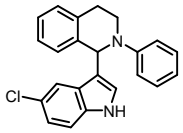
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (s, 1H), 7.30-7.23 (m, 3H), 7.22-7.16 (m, 4H), 7.04 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 2.4 Hz, 1H), 6.82-6.77 (m, 2H), 6.57 (dd, J_1 = 2.8, J_2 = 1.2 Hz, 1H), 6.16 (s, 1H), 3.67 (s, 3H), 3.62-3.59 (m, 2H), 3.12-3.04 (m, 1H), 2.86-2.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.31, 149.73, 137.35, 137.28, 135.46, 129.16, 128.76, 127.95, 126.60, 125.60, 123.00, 120.82, 120.63, 119.04, 118.04, 115.75, 109.42, 94.47, 56.66, 55.56, 42.14, 26.56.

11j. 1-(5-fluoro-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



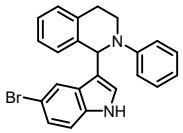
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (s, 1H), 7.28-7.13 (m, 8H), 7.02 (d, J = 8.0 Hz, 2H), 6.90 (td, J_1 = 8.8, J_2 = 2.4 Hz, 1H), 6.80 (t, J = 7.2 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 6.10 (s, 1H), 3.62-3.58 (m, 2H), 3.11-3.03 (m, 1H), 2.84-2.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.64 (d, J = 233 Hz), 149.76, 137.02, 135.47, 133.03, 129.20, 128.89, 127.93, 126.76, 125.83, 125.75, 119.36 (d, J = 4.6 Hz), 118.50, 116.17, 111.54 (d, J = 9.7 Hz), 110.49 (d, J = 26.3 Hz), 105.09 (d, J = 23.9 Hz), 56.68, 42.41, 26.59.

11k. 1-(5-chloro-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



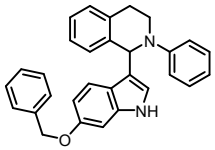
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.29-7.23 (m, 4H), 7.21-7.15 (m, 3H), 7.02 (d, J = 7.6 Hz, 2H), 6.98 (dd, J_1 = 8.4, J_2 = 1.6 Hz, 1H), 6.81 (t, J = 7.2 Hz, 1H), 6.61 (dd, J_1 = 2.4, J_2 = 1.2 Hz, 1H), 6.13 (s, 1H), 3.65-3.53 (m, 2H), 3.11-3.03 (m, 1H), 2.83-2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.75, 137.00, 136.88, 135.45, 129.21, 128.89, 128.01, 127.92, 126.78, 125.73, 125.03, 124.72, 121.02, 120.35, 119.42, 118.47, 116.14, 110.89, 56.60, 42.34, 26.60.

11l. 1-(5-bromo-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



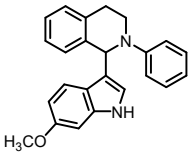
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.28-7.23 (m, 4H), 7.22-7.13 (m, 4H), 7.02 (d, J = 8.0 Hz, 2H), 6.90 (td, J_1 = 9.2, J_2 = 2.4 Hz, 1H), 6.80 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.10 (s, 1H), 3.67-3.55 (m, 2H), 3.11-3.03 (m, 1H), 2.84-2.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.82, 136.96, 135.41, 135.13, 129.19, 128.88, 128.10, 127.92, 126.80, 125.79, 125.34, 125.00, 122.67, 119.04, 118.75, 116.48, 112.97, 112.42, 56.68, 42.54, 26.58.

11m. 1-(6-(benzyloxy)-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



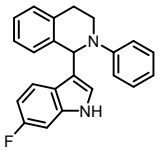
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.28-7.23 (m, 4H), 7.22-7.13 (m, 4H), 7.02 (d, J = 8.0 Hz, 2H), 6.90 (td, J_1 = 9.2, J_2 = 2.4 Hz, 1H), 6.80 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.10 (s, 1H), 3.67-3.55 (m, 2H), 3.11-3.03 (m, 1H), 2.84-2.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.50, 149.72, 137.36, 137.32, 137.20, 135.48, 129.17, 128.77, 128.51, 127.96, 127.79, 127.38, 126.61, 125.61, 123.13, 121.05, 120.67, 119.11, 118.03, 115.73, 110.13, 95.85, 77.32, 77.00, 76.68, 70.46, 56.63, 42.15, 26.53. ESI$^+$ HRMS m/z calcd for $C_{30}H_{26}N_2O$ 430.2045 $[M+H]^+$, found 431.2104.

11n. 1-(6-methoxy-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



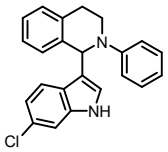
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (s, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.29-7.22 (m, 3H), 7.21-7.13 (m, 3H), 7.02 (d, J = 7.6 Hz, 2H), 6.80-6.75 (m, 2H), 6.69 (dd, J_1 = 8.8, J_2 = 2.4 Hz, 1H), 6.46 (d, J = 1.6 Hz, 1H), 6.13 (s, 1H), 3.79 (s, 3H), 3.62-3.59 (m, 2H), 3.10-3.02 (m, 1H), 2.82-2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.31, 149.73, 137.35, 137.28, 135.46, 129.16, 128.76, 127.95, 126.60, 125.60, 123.00, 120.82, 120.63, 119.04, 118.04, 115.75, 109.42, 94.47, 56.66, 55.56, 42.14, 26.56.

11o. 1-(6-fluoro-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



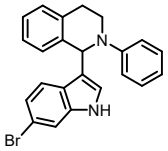
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (s, 1H), 7.44 (dd, J_1 = 8.8, J_2 = 5.6 Hz, 1H), 7.29-7.23 (m, 3H), 7.22-7.15 (m, 3H), 7.03 (d, J = 7.6 Hz, 2H), 6.98 (dd, J_1 = 9.6, J_2 = 2.4 Hz, 1H), 6.83-6.77 (m, 2H), 6.58 (dd, J_1 = 2.8, J_2 = 1.2 Hz, 1H), 6.14 (s, 1H), 3.67-3.55 (m, 2H), 3.12-3.04 (m, 1H), 2.83-2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.85 (d, J = 236.8 Hz), 149.73, 137.06, 136.47 (d, J =12.3 Hz), 135.48, 129.21, 128.89, 127.95, 126.74, 125.68, 124.42, 123.03, 120.90 (d, J = 10.0 Hz), 119.36, 118.36, 116.01, 108.35 (d, J = 24.1 Hz), 97.24 (d, J = 25.8 Hz), 56.58, 42.25, 26.50.

11p. 1-(6-chloro-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.28-7.15 (m, 7H), 7.11 (dd, J_1 = 8.8, J_2 = 2.4 Hz, 1H), 7.02 (d, J = 7.6 Hz, 2H), 6.82 (t, J = 7.2 Hz, 1H), 6.65 (d, J =2.4 Hz, 1H), 6.09 (s, 1H), 3.64-3.55 (m, 2H), 3.11-3.03 (m, 1H), 2.84-2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.79, 136.96, 135.42, 134.88, 129.19, 128.89, 127.93, 127.44, 126.78, 125.77, 125.50, 125.32, 122.44, 119.59, 119.12, 118.67, 116.38, 111.97, 56.64, 42.51, 26.54.

11q. 1-(6-bromo-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (s, 1H), 7.45 (d, J = 1.6 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H). 7.27-7.24 (m, 3H), 7.21-7.15 (m, 3H), 7.11 (dd, J_1 = 8.4, J_2 = 1.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.81 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 1.2 Hz, 1H), 6.12 (s, 1H), 3.65-3.53 (m, 2H), 3.11-3.03 (m, 1H), 2.83-2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.75, 137.30, 136.99, 135.44, 129.21, 128.89, 127.91, 126.79, 125.74, 125.34, 124.65, 122.92, 121.40, 119.46, 118.49, 116.16, 115.68, 113.89, 77.32, 77.00, 76.68, 56.59, 42.36, 26.62.

[1]H-NMR, [13]C-NMR and HRMS spectra of 11a-11q

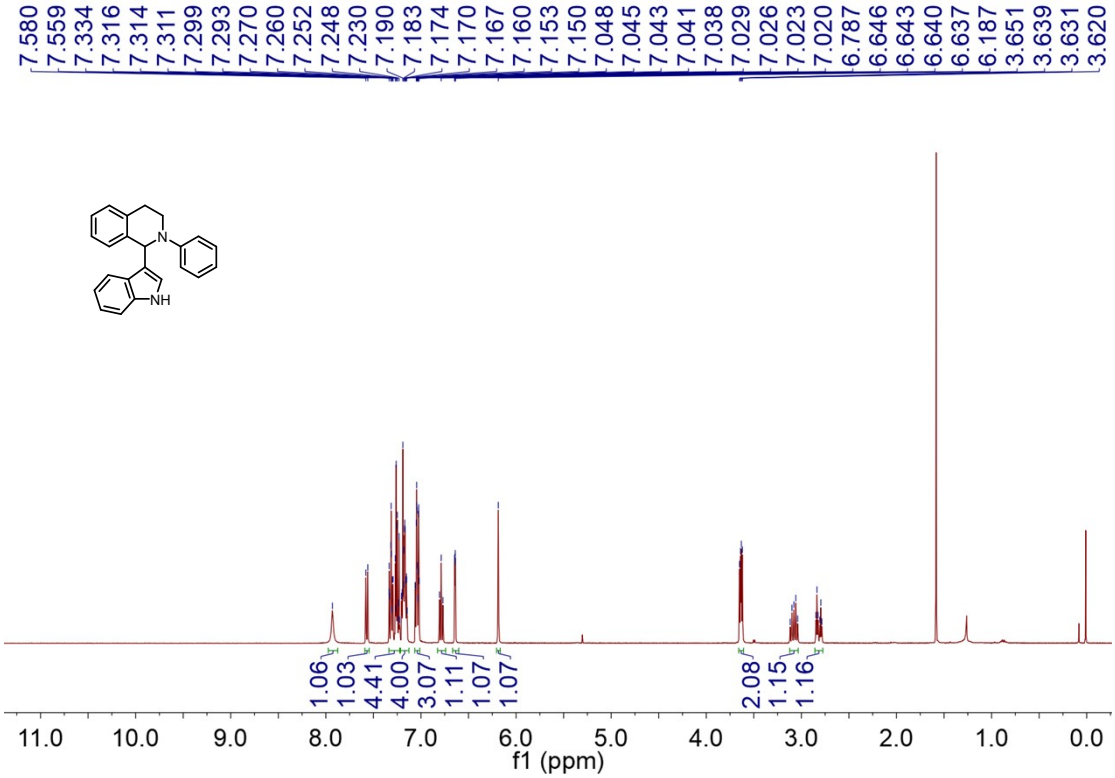


Fig. S20 [1]H NMR spectra of **11a** (in $CDCl_3$).

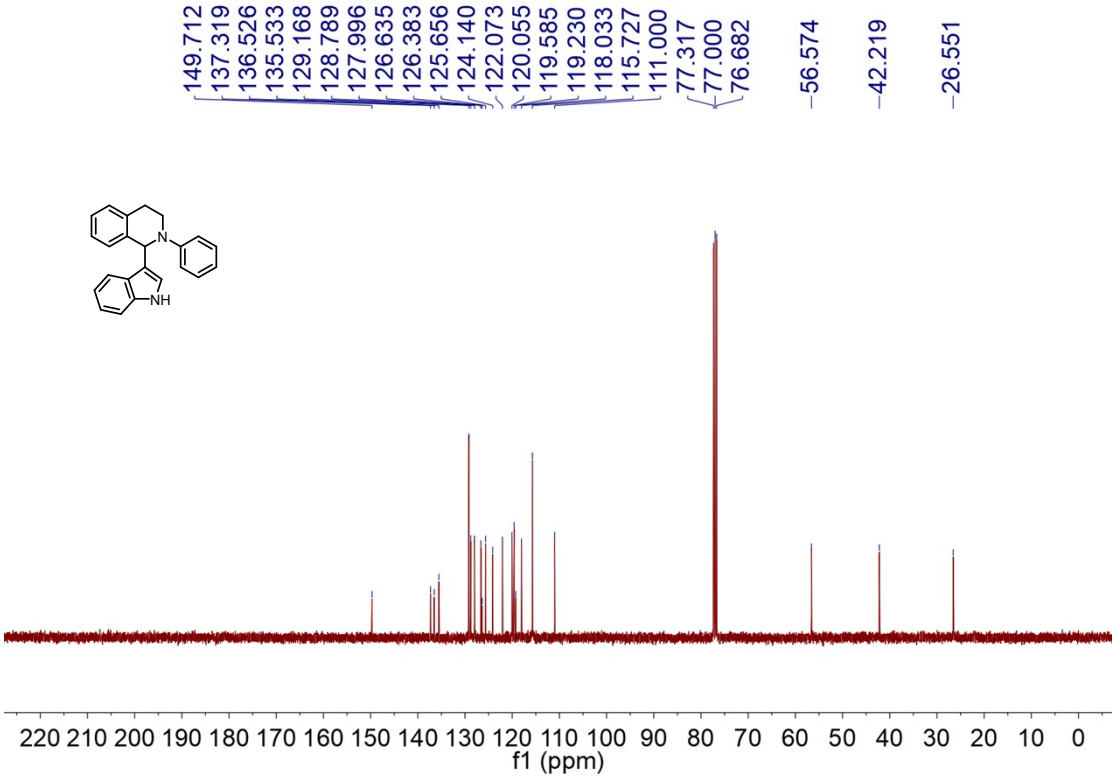


Fig. S21 [13]C NMR spectra of **11a** (in $CDCl_3$).

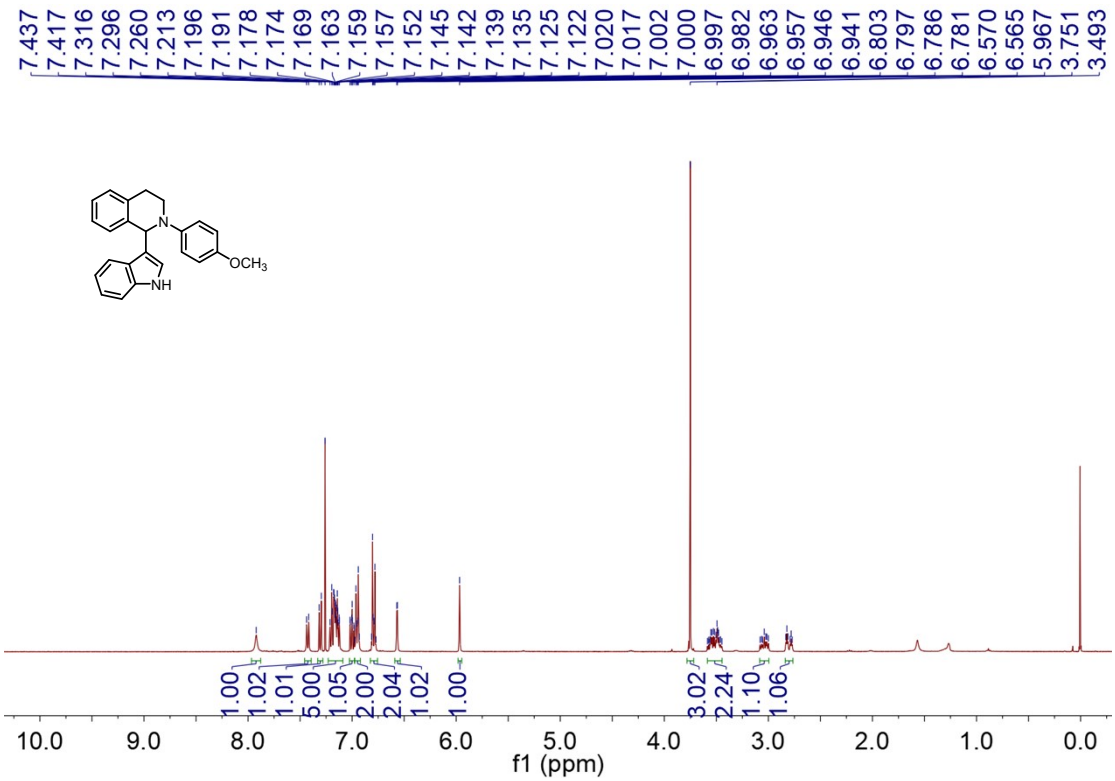


Fig. S22 ^{1}H NMR spectra of **11b** (in $CDCl_3$).

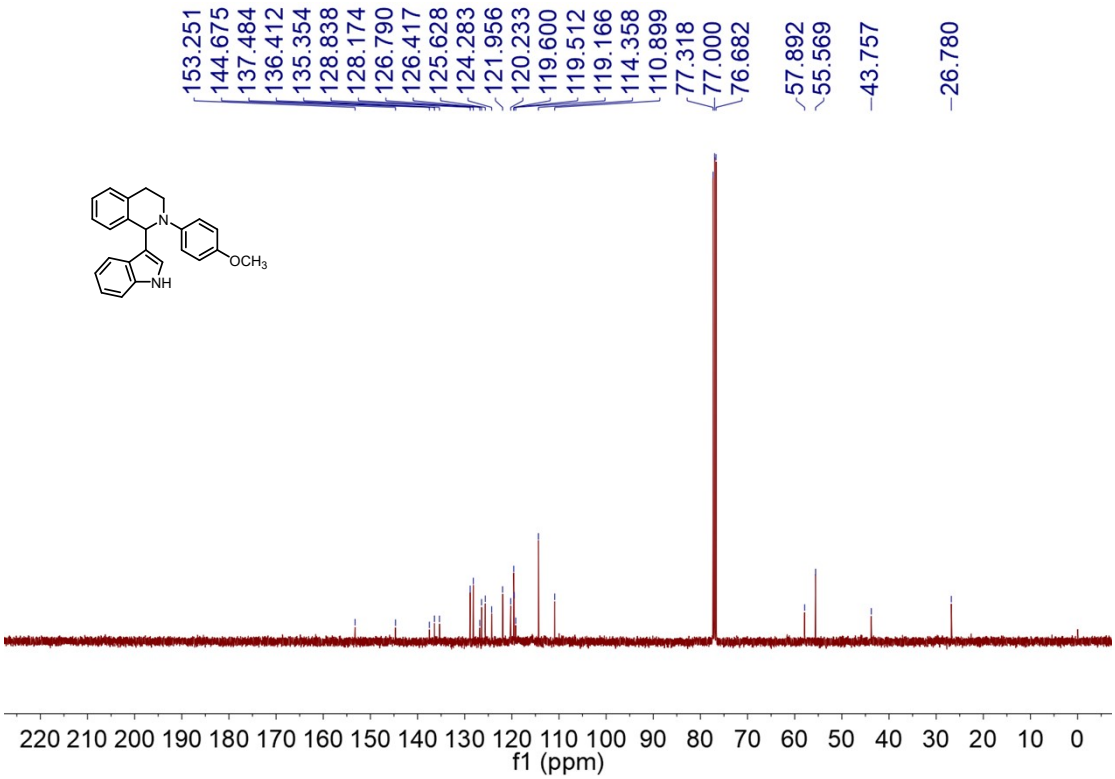


Fig. S23 ^{13}C NMR spectra of **11b** (in $CDCl_3$).

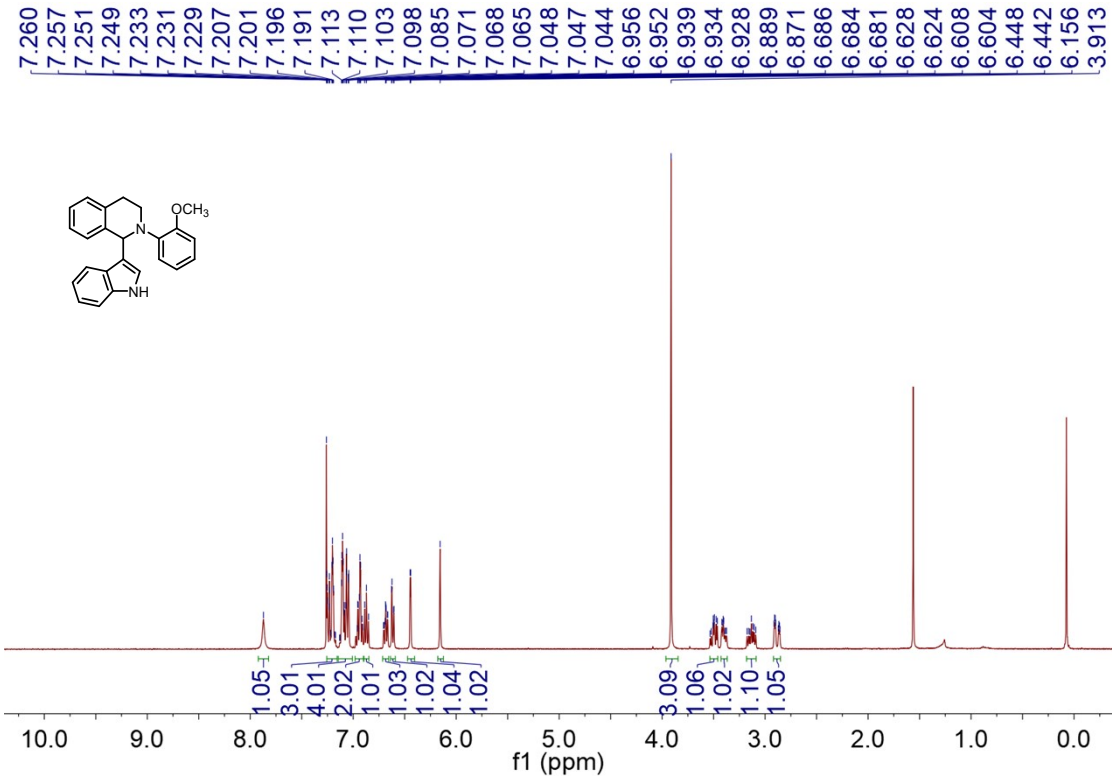


Fig. S24 ^{1}H NMR spectra of **11c** (in $CDCl_3$).

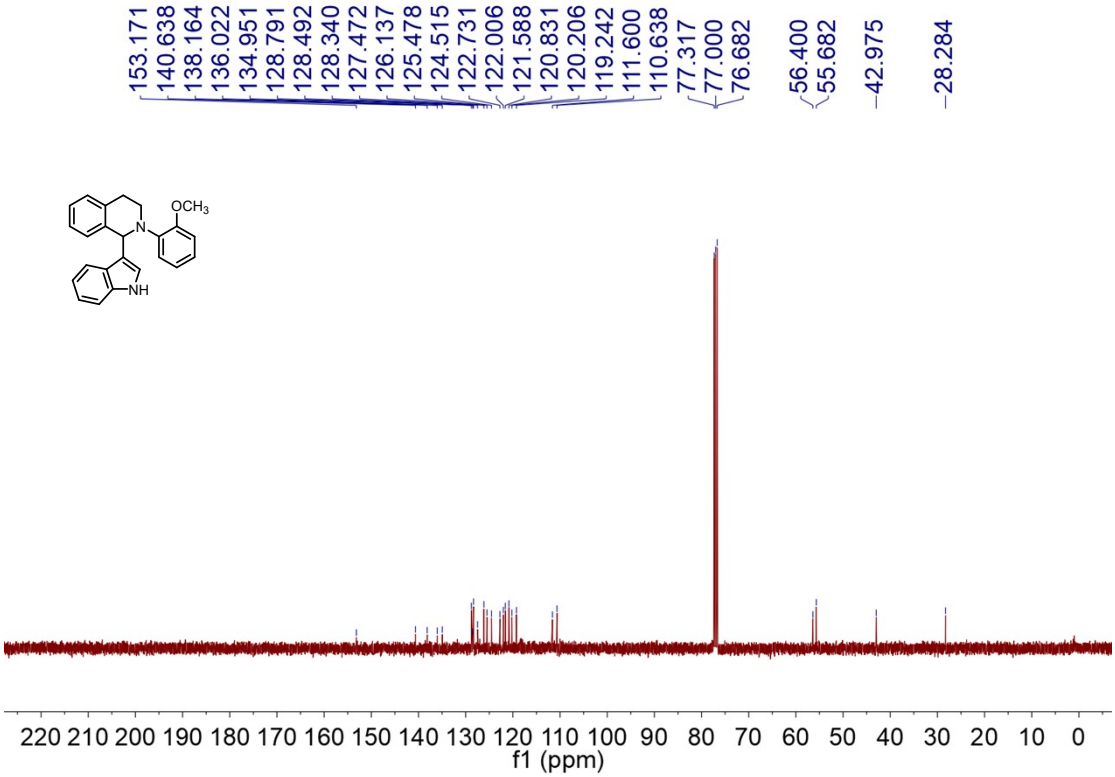


Fig. S25 ^{13}C NMR spectra of **11c** (in $CDCl_3$).

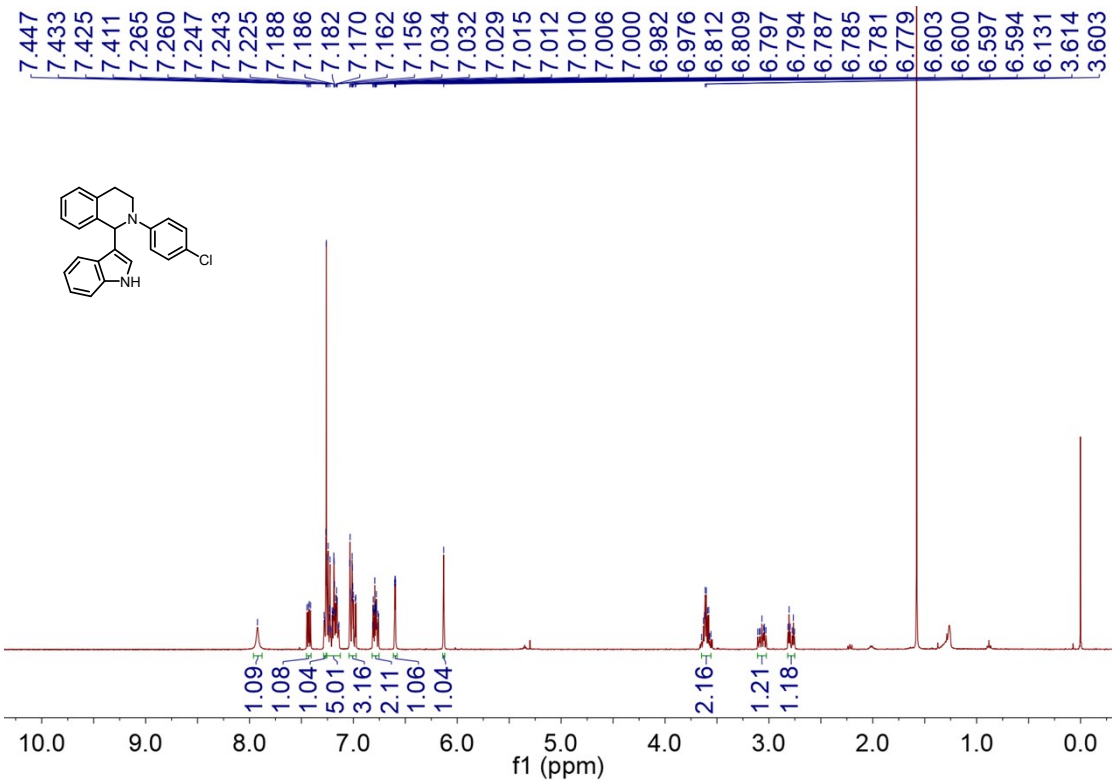


Fig. S26 ^{1}H NMR spectra of **11d** (in $CDCl_3$).

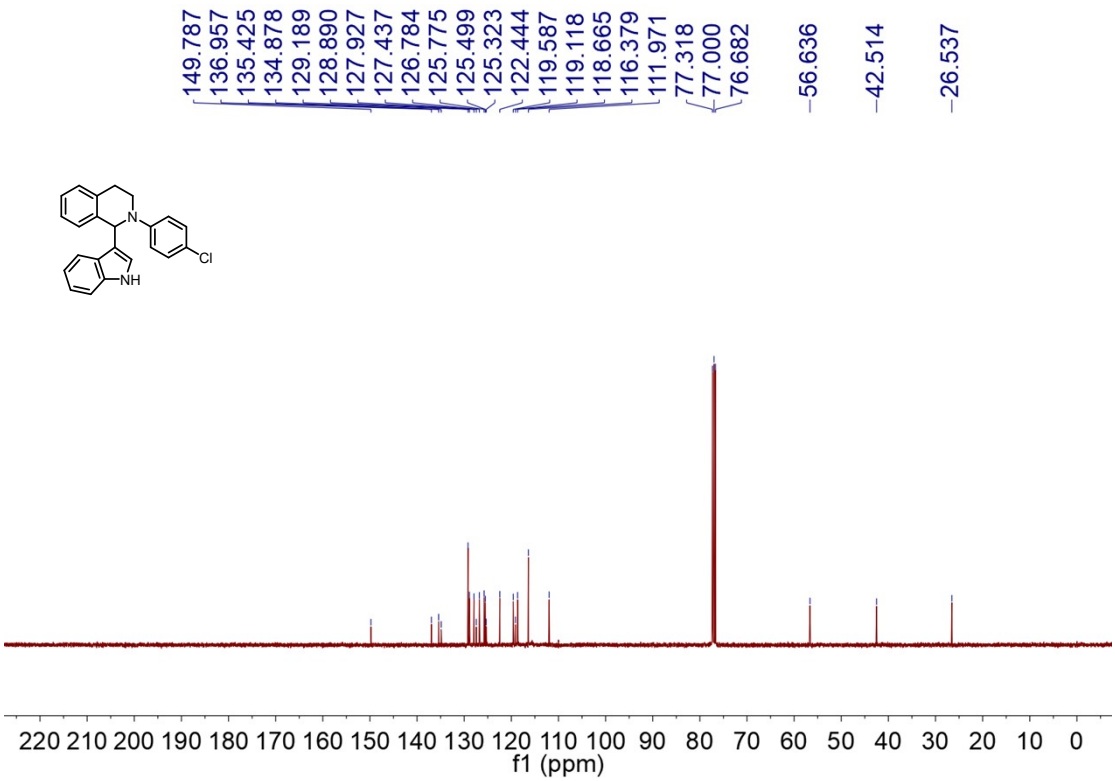


Fig. S27 ^{13}C NMR spectra of **11d** (in $CDCl_3$).

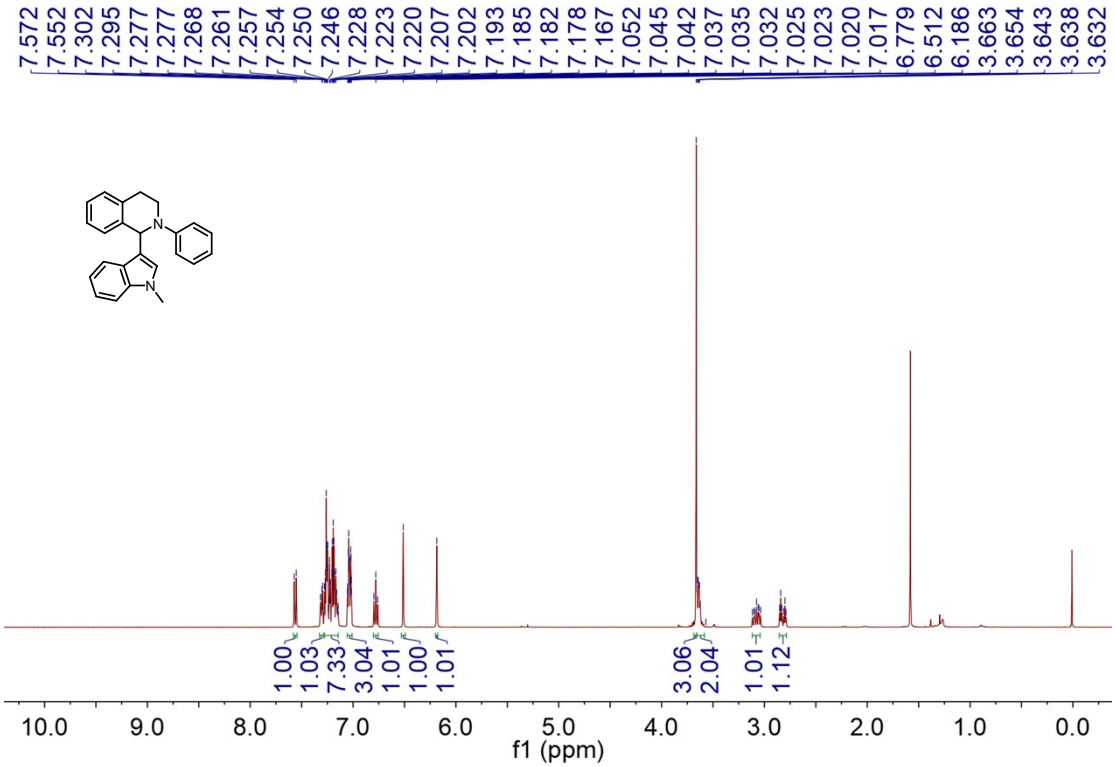


Fig. S28 ^{1}H NMR spectra of **11e** (in $CDCl_3$).

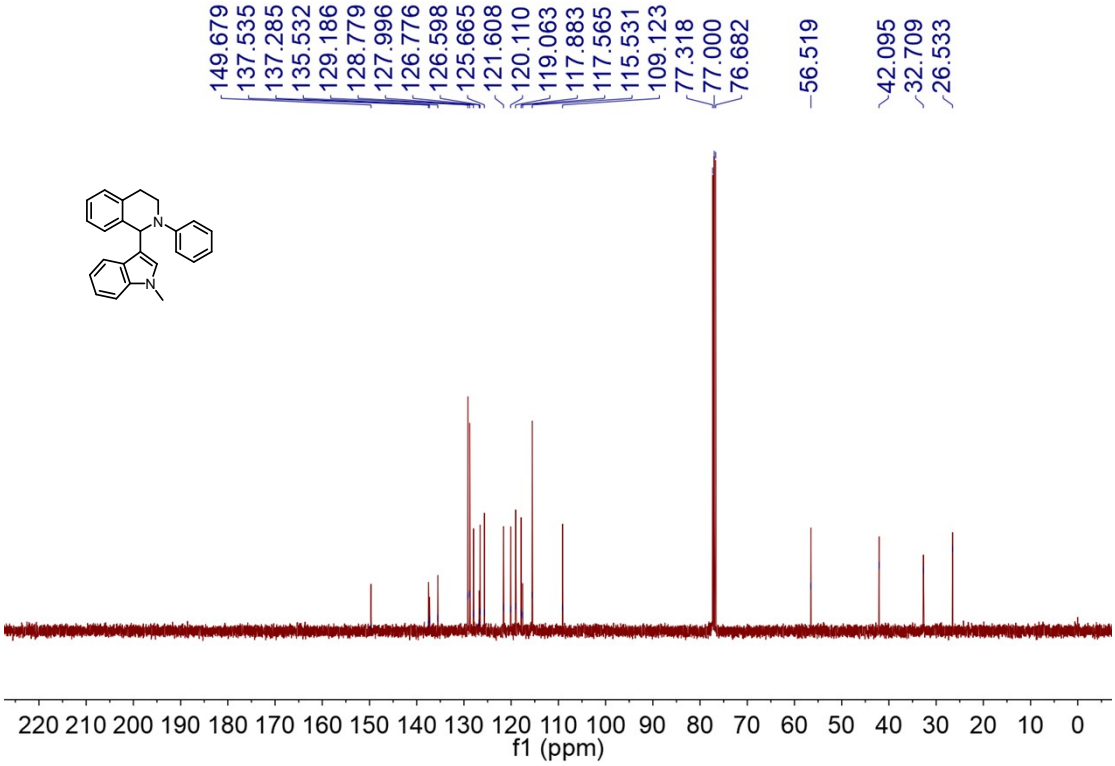


Fig. S29 ^{13}C NMR spectra of **11e** (in $CDCl_3$).

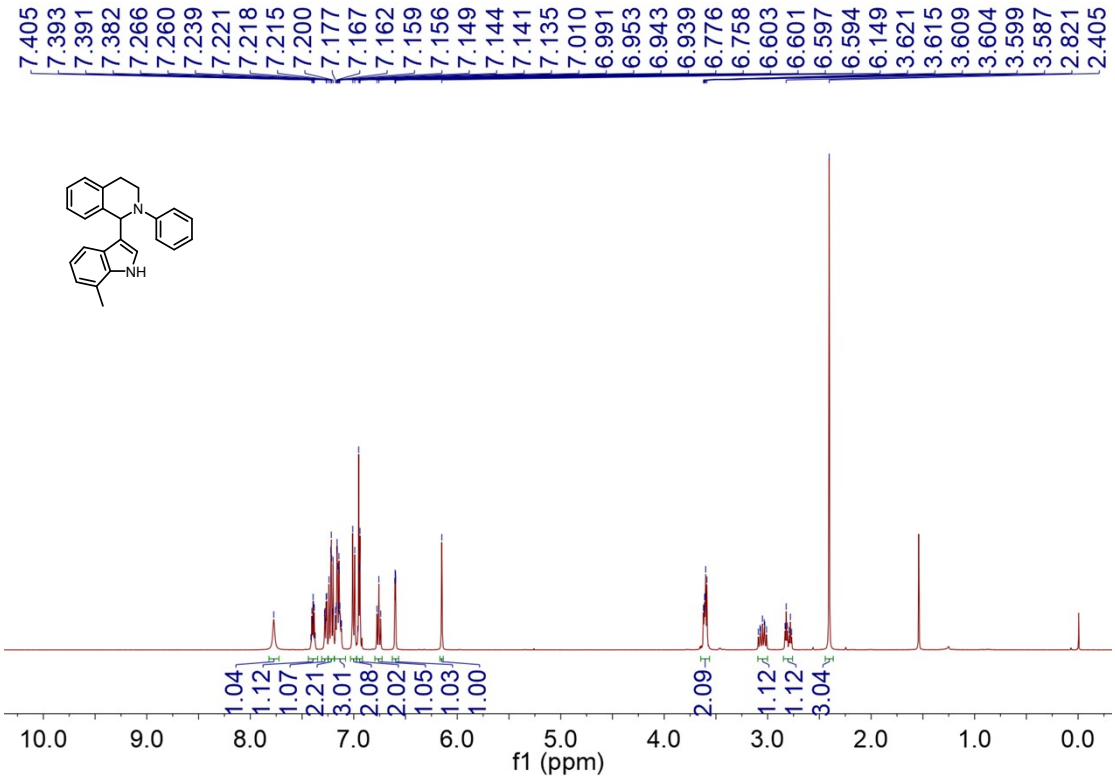


Fig. S30 ^{1}H NMR spectra of **11f** (in $CDCl_3$).

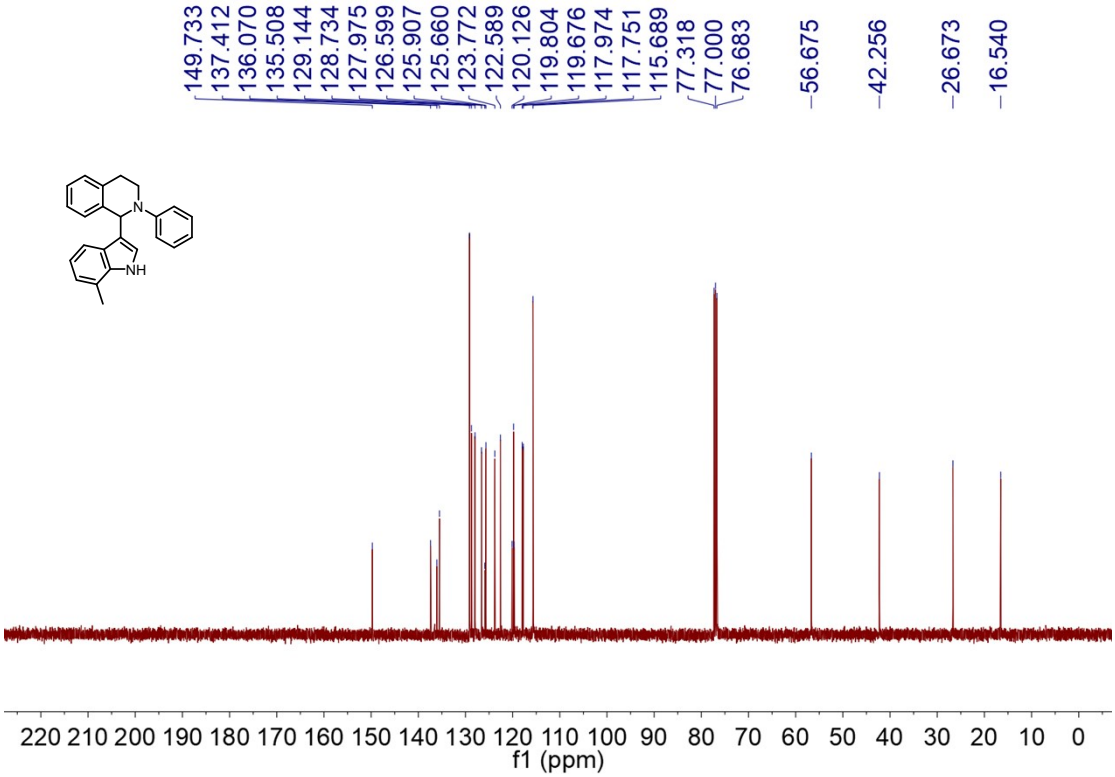


Fig. S31 ^{13}C NMR spectra of **11f** (in $CDCl_3$).

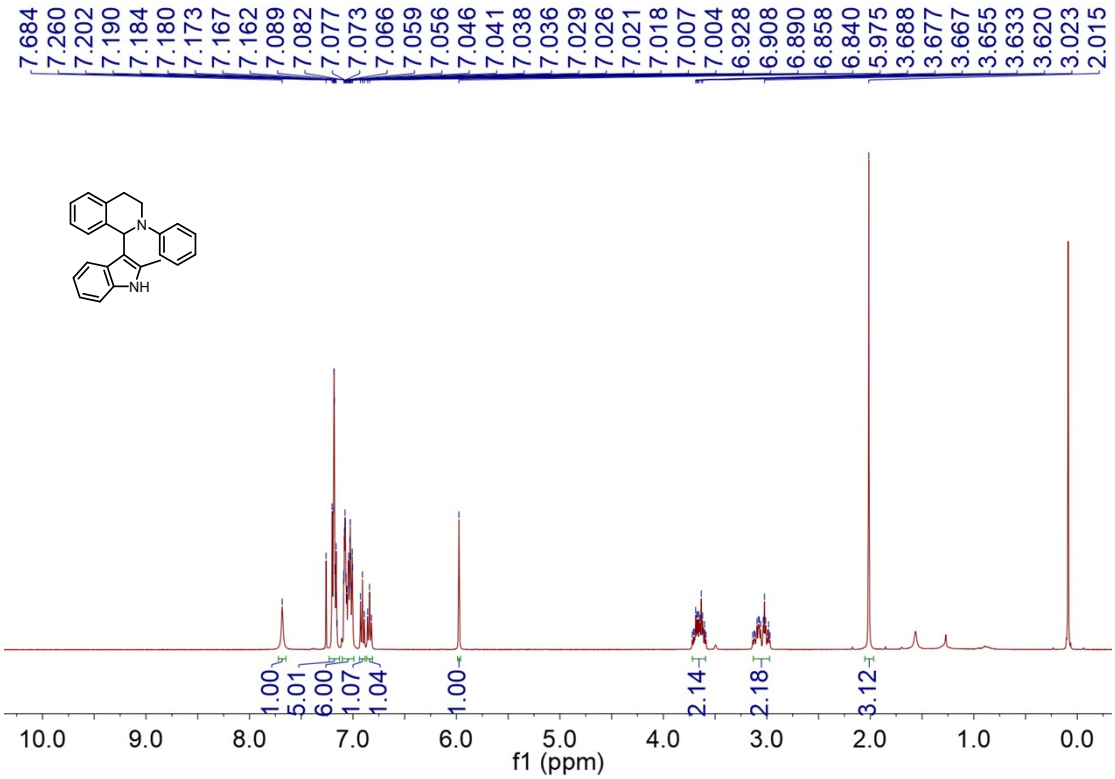


Fig. S32 ^{1}H NMR spectra of **11g** (in $CDCl_3$).

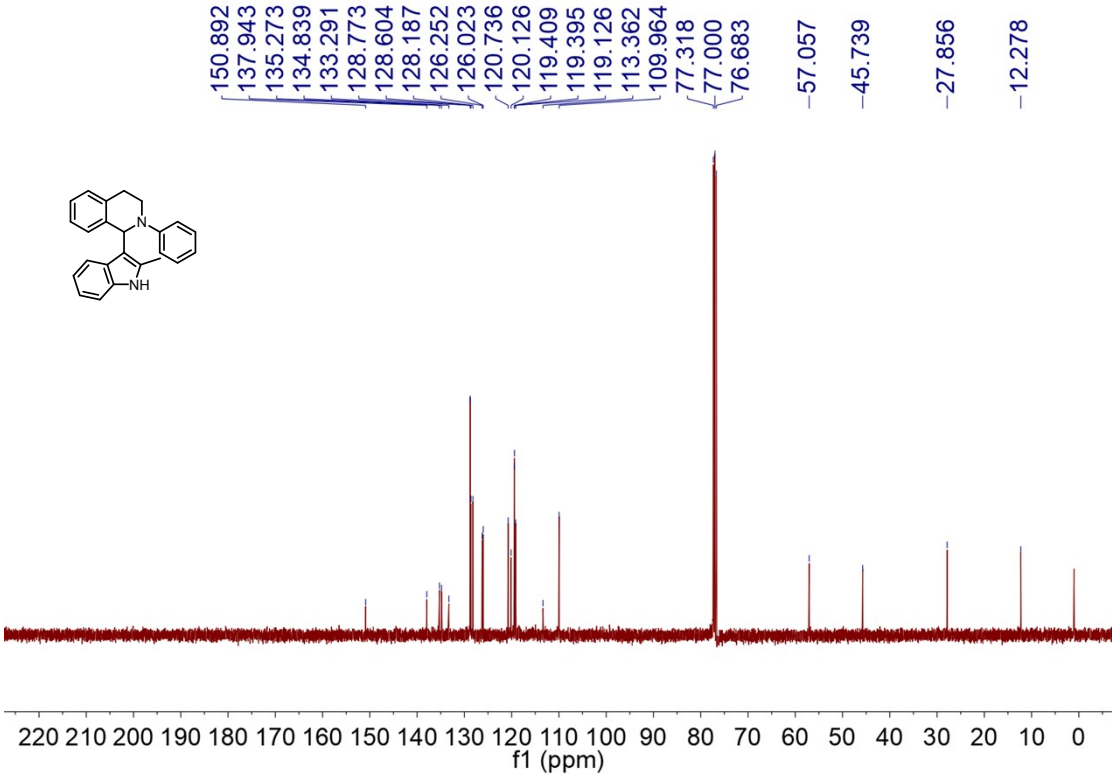


Fig. S33 ^{13}C NMR spectra of **11g** (in $CDCl_3$).

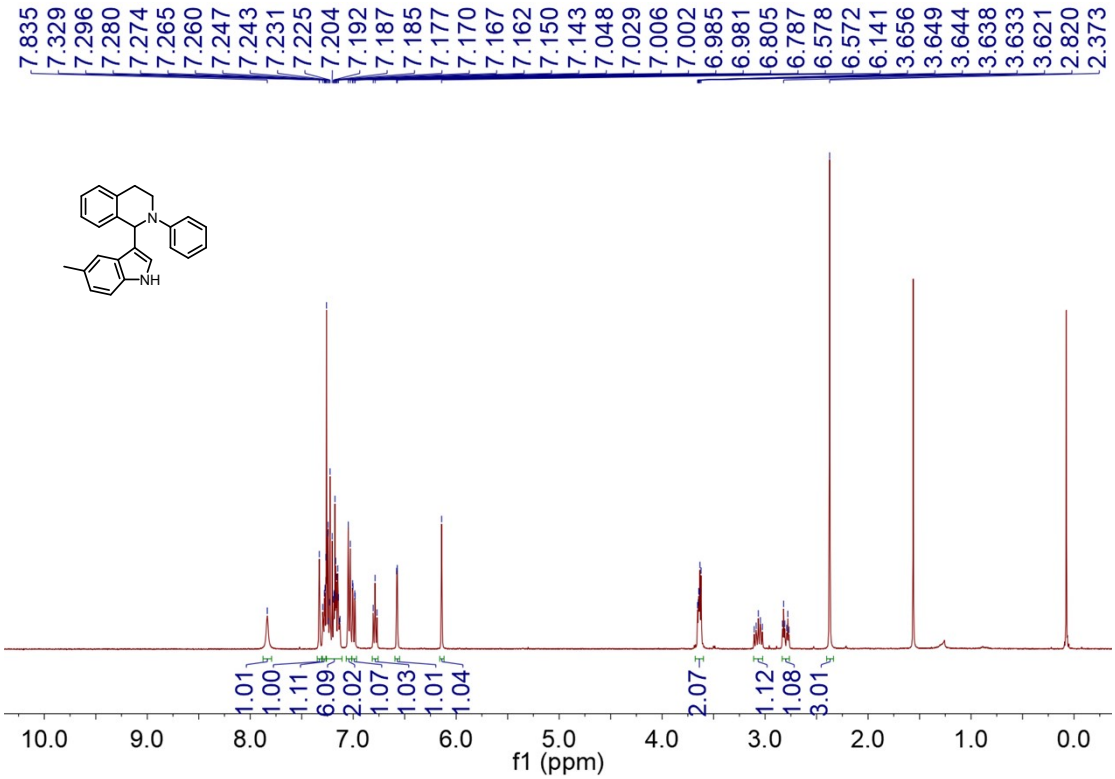


Fig. S34 ^{1}H NMR spectra of **11h** (in $CDCl_3$).

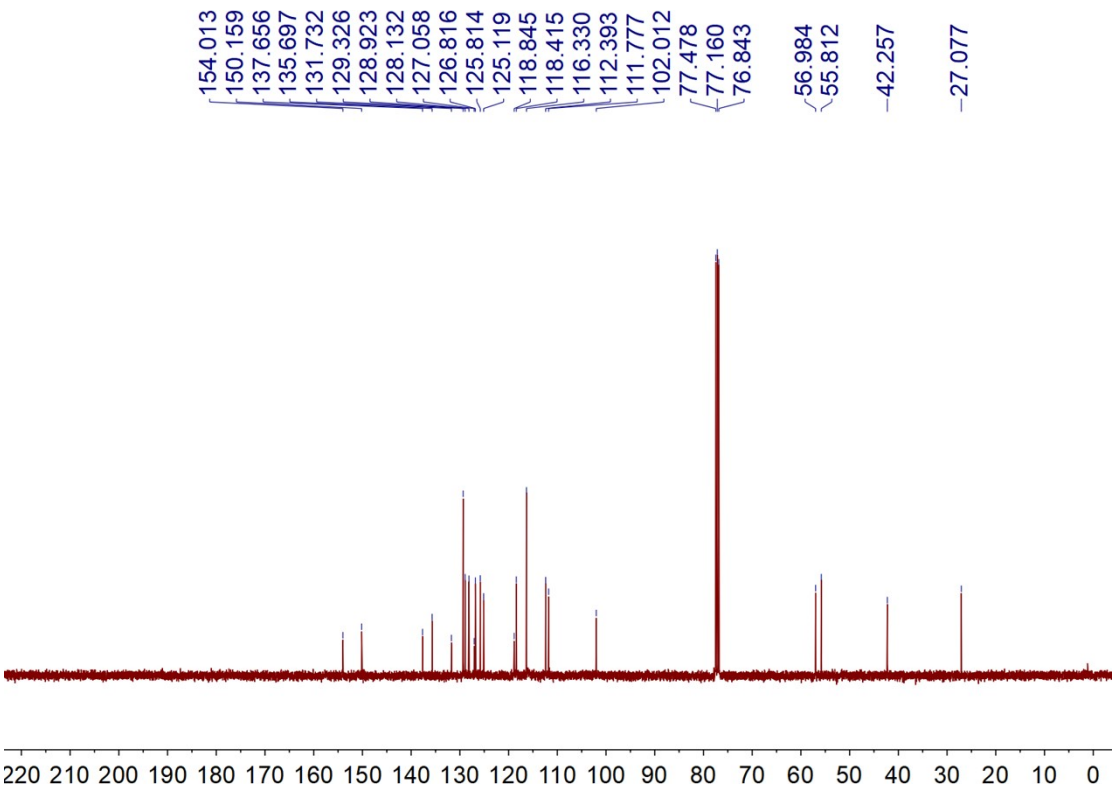


Fig. S35 ^{13}C NMR spectra of **11h** (in $CDCl_3$).

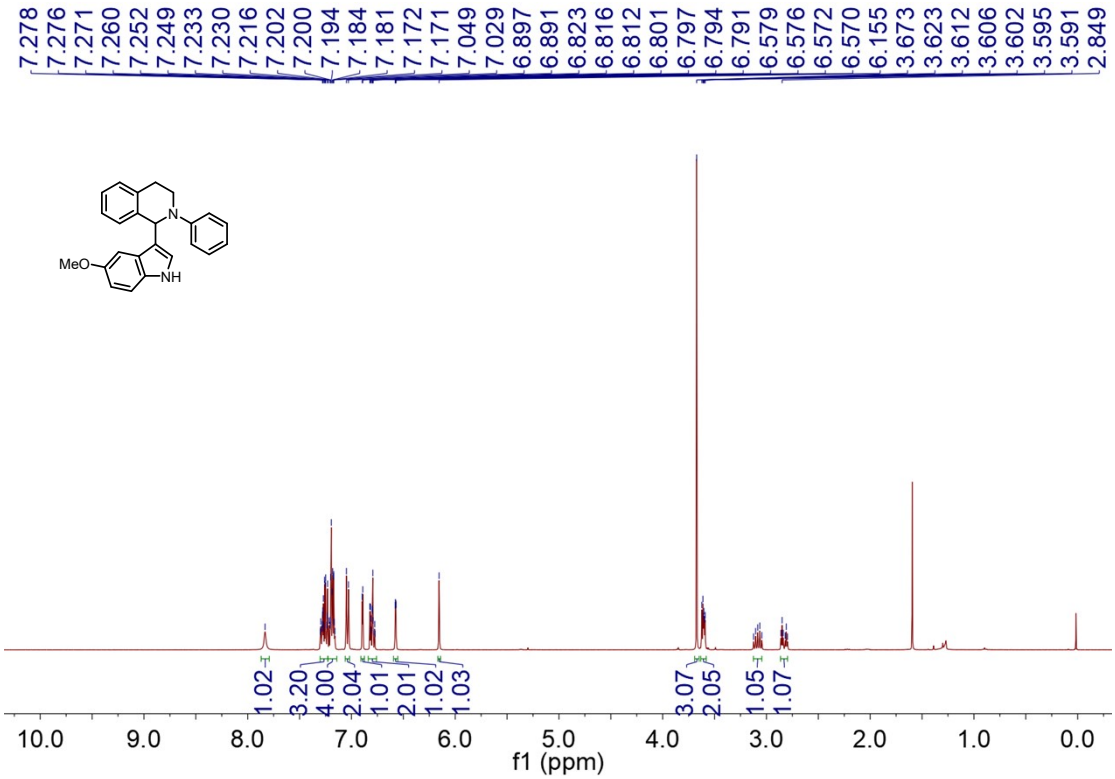


Fig. S36 ^{1}H NMR spectra of **11i** (in $CDCl_3$).

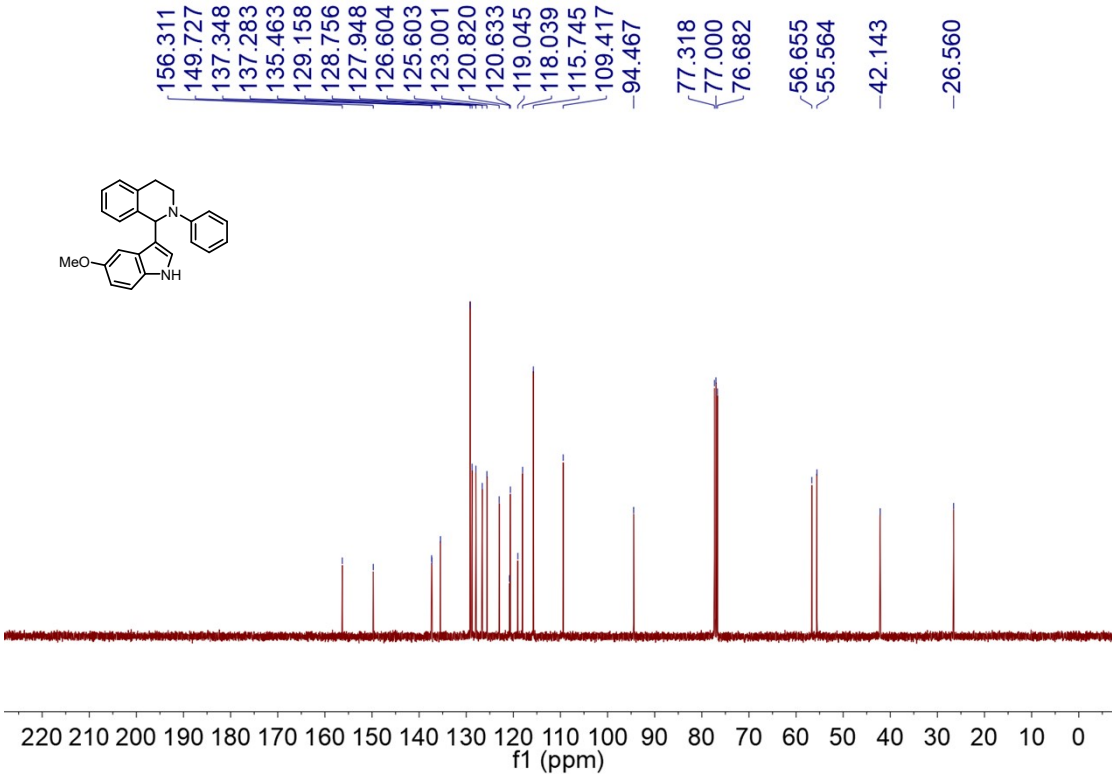


Fig. S37 ^{13}C NMR spectra of **11i** (in $CDCl_3$).

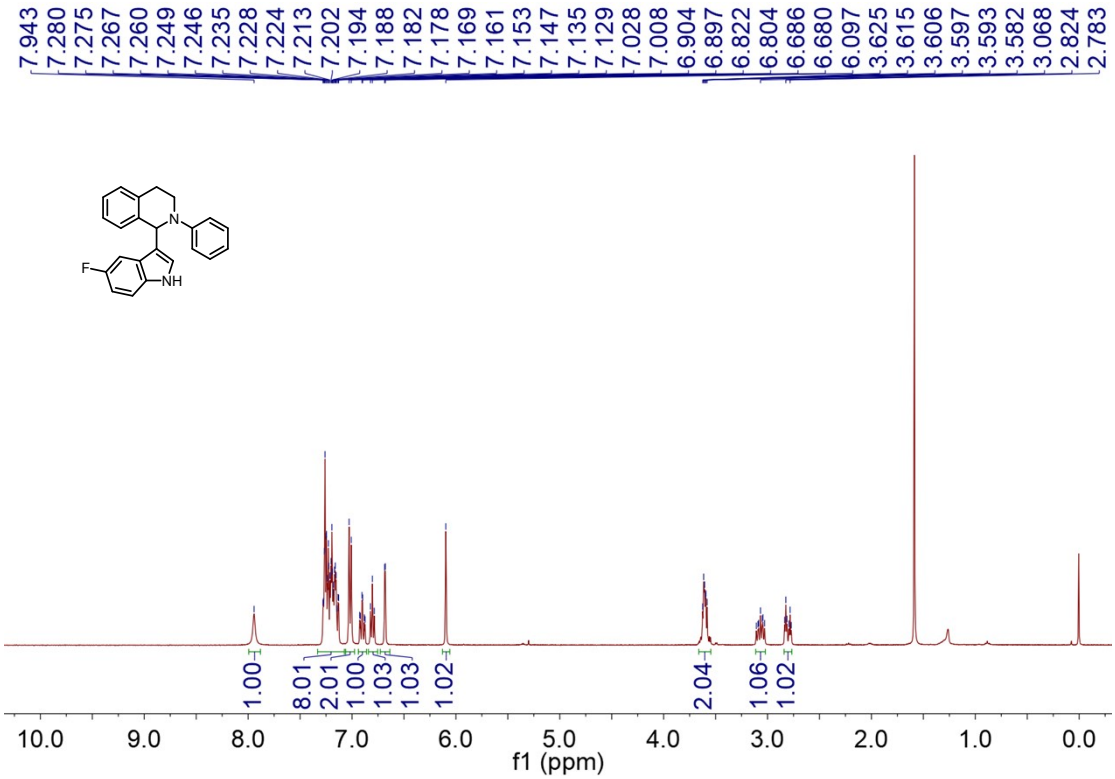


Fig. S38 ^{1}H NMR spectra of **11j** (in $CDCl_3$).

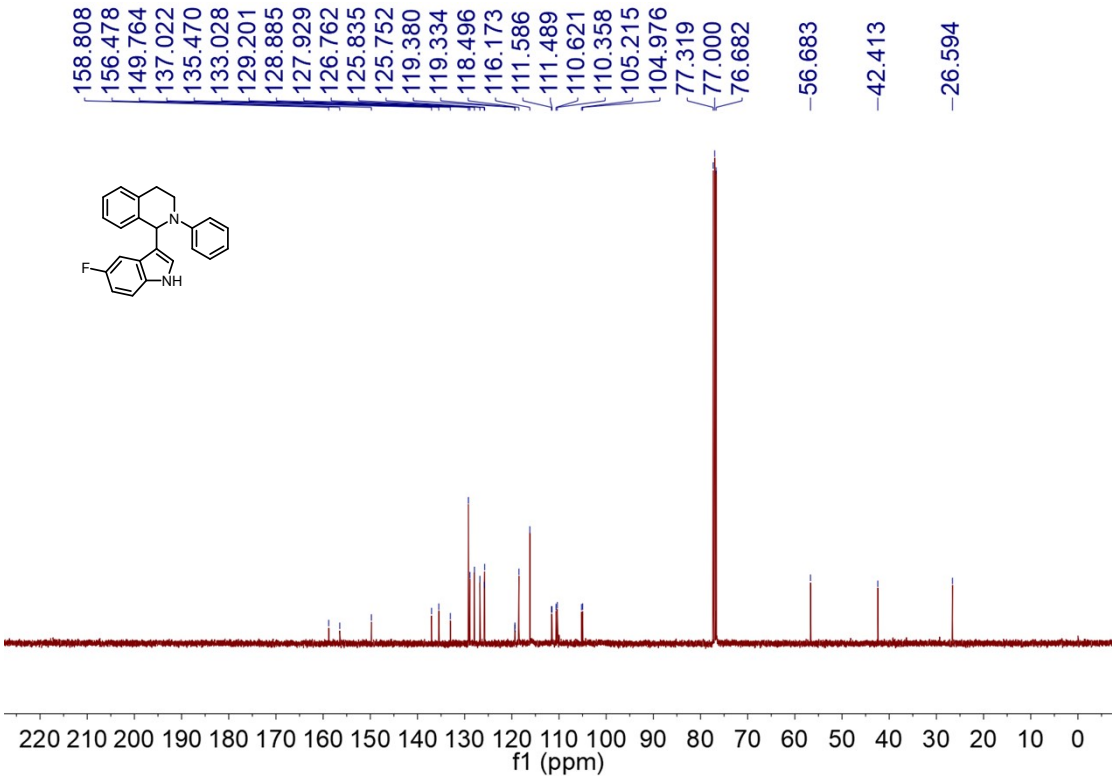


Fig. S39 ^{13}C NMR spectra of **11j** (in $CDCl_3$).

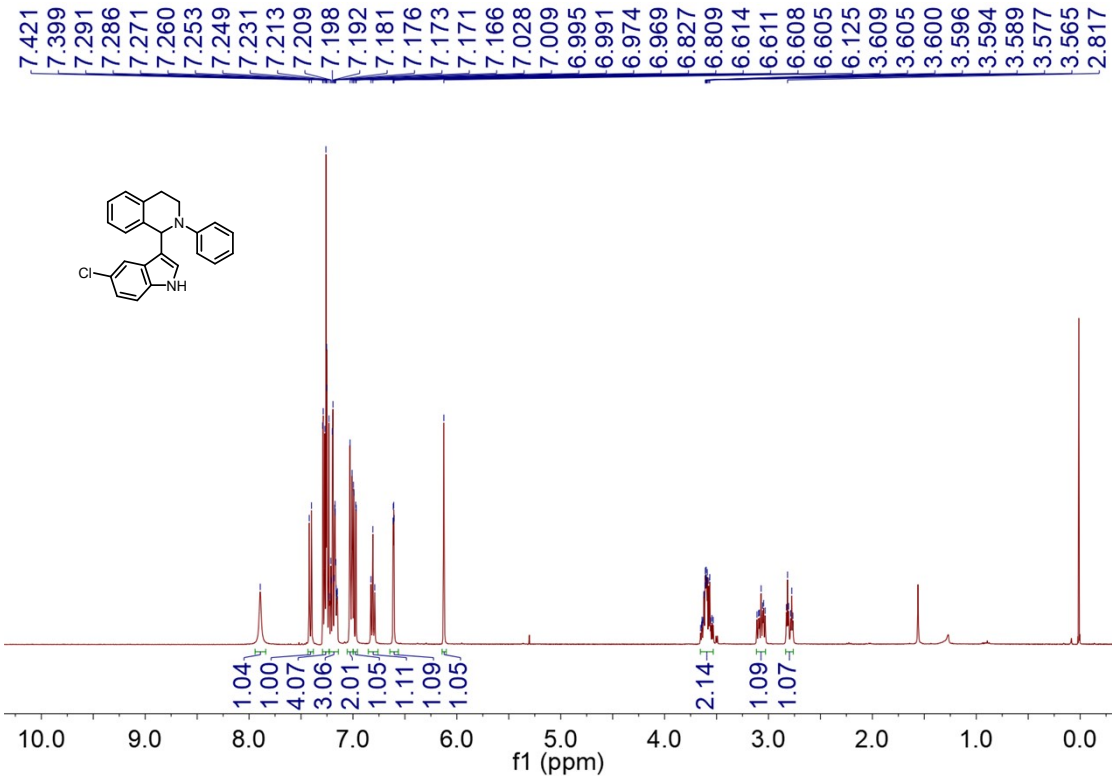


Fig. S40 ^{1}H NMR spectra of **11k** (in $CDCl_3$).

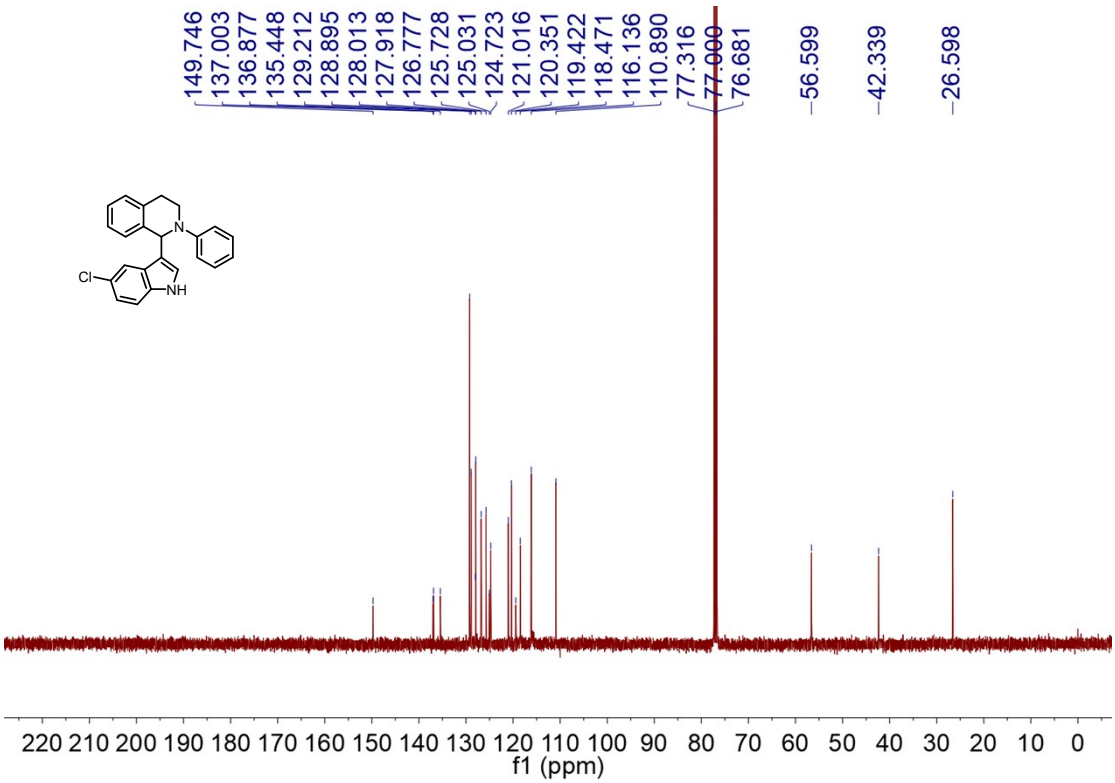


Fig. S41 ^{13}C NMR spectra of **11k** (in $CDCl_3$).

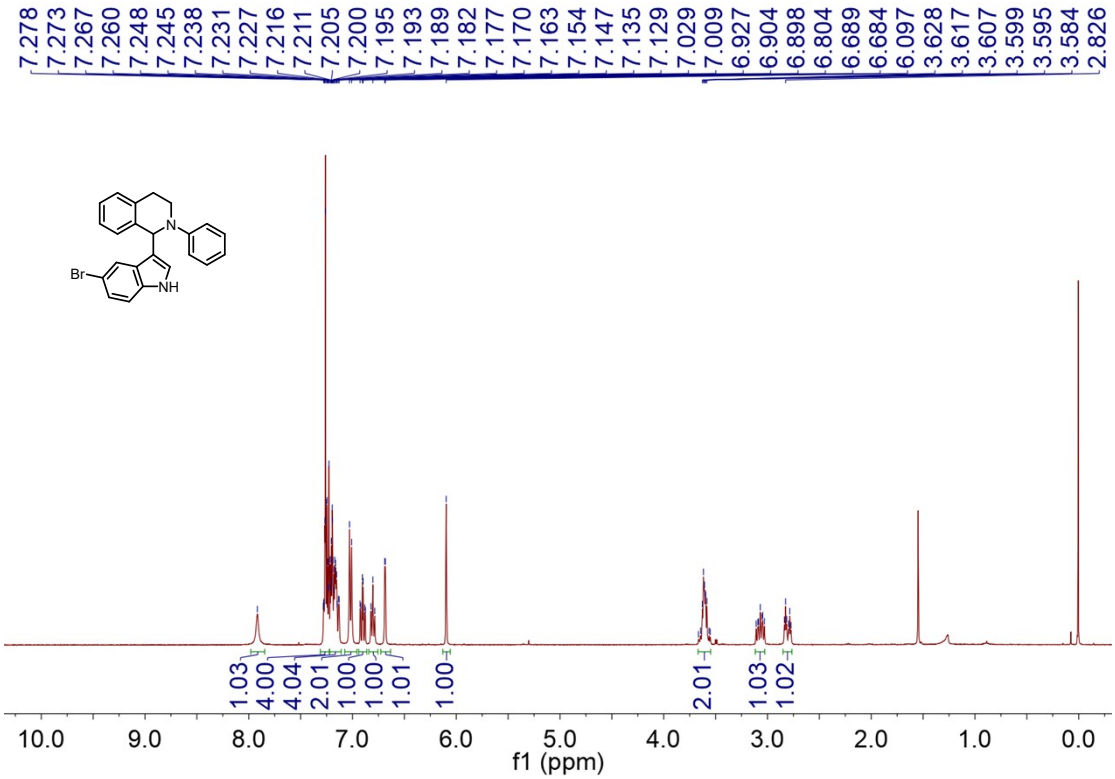


Fig. S42 ^{1}H NMR spectra of **11l** (in $CDCl_3$).

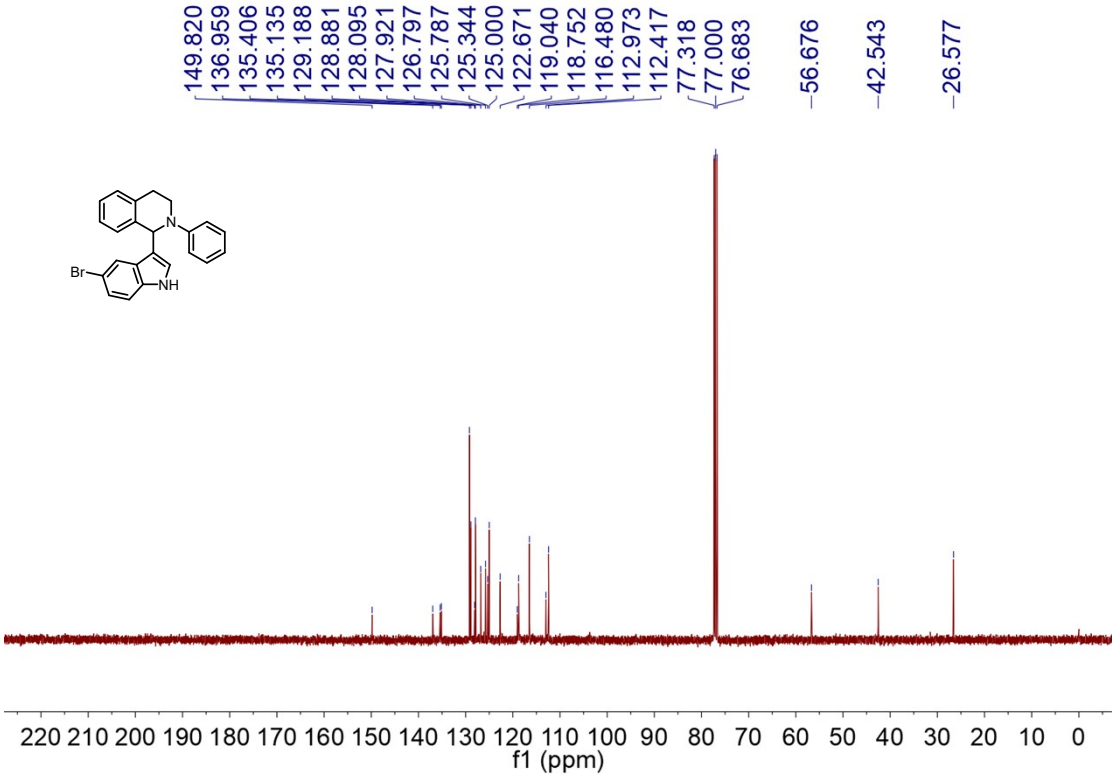


Fig. S43 ^{13}C NMR spectra of **11l** (in $CDCl_3$).

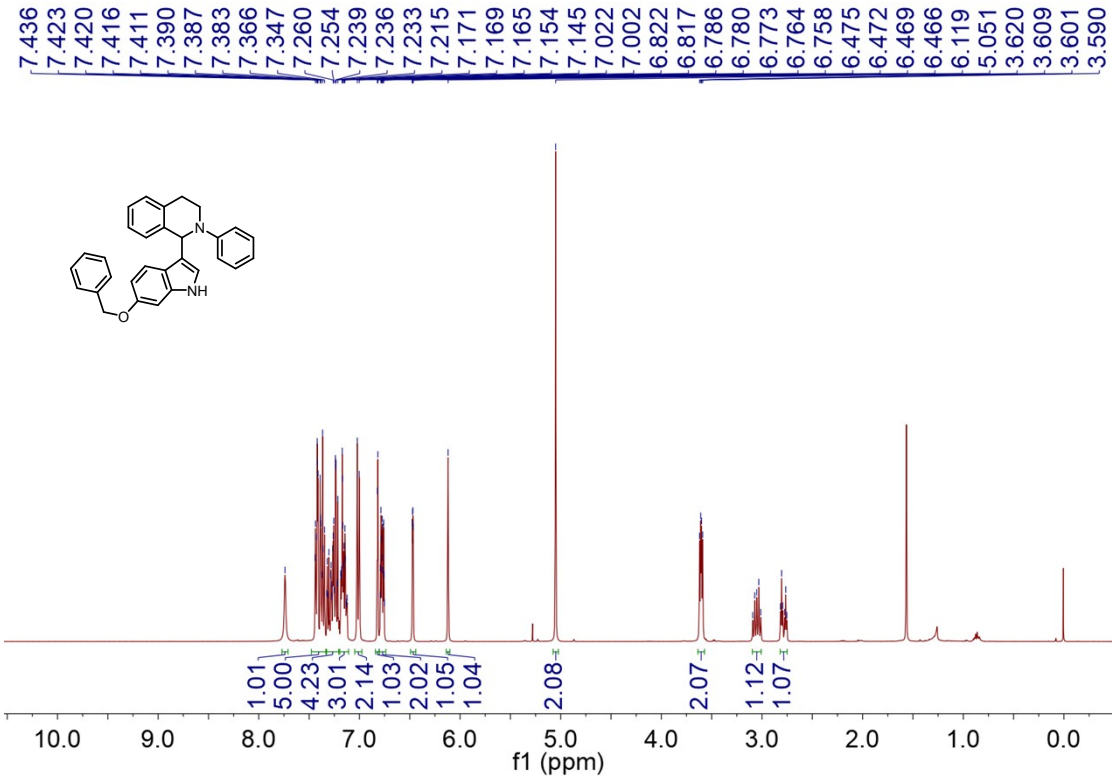


Fig. S44 ^{1}H NMR spectra of **11m** (in $CDCl_3$).

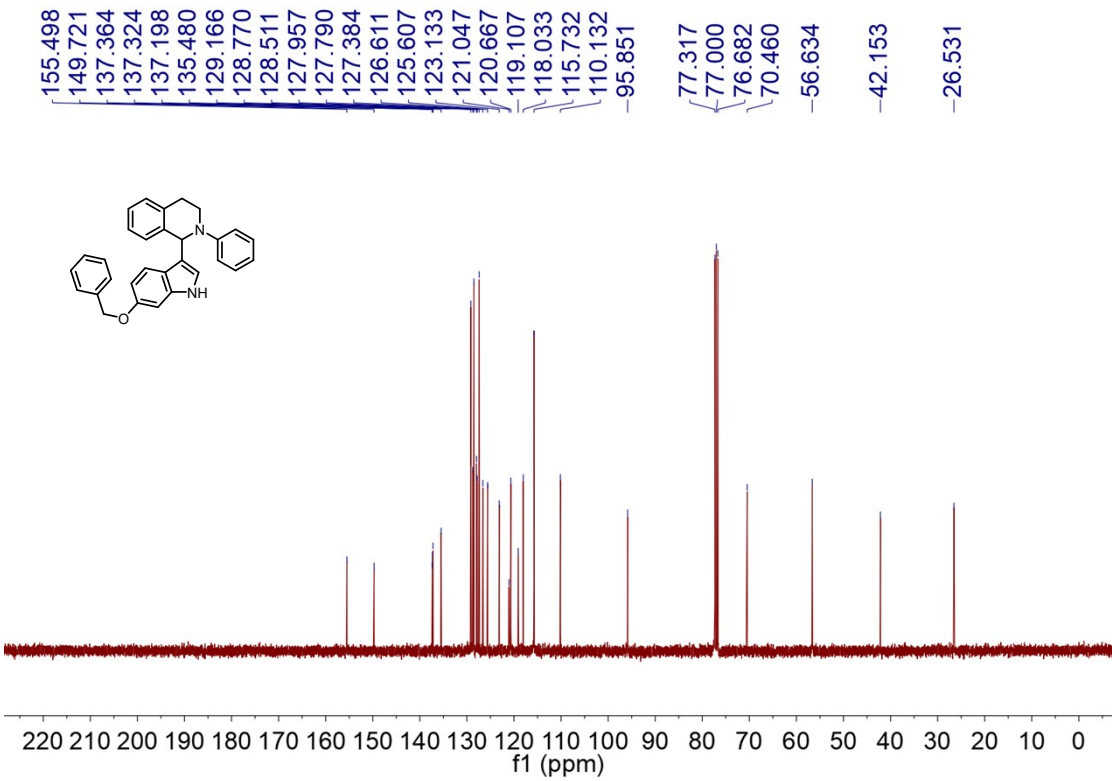


Fig. S45 ^{13}C NMR spectra of **11m** (in $CDCl_3$).

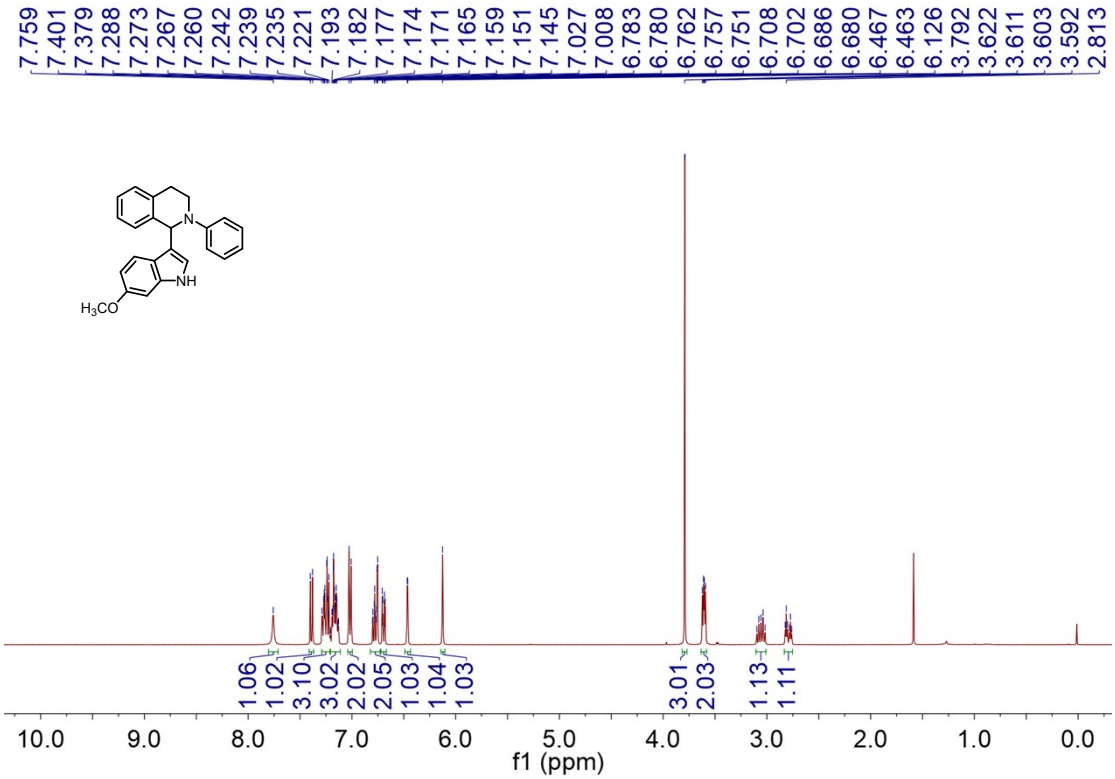


Fig. S46 ^{1}H NMR spectra of **11n** (in $CDCl_3$).

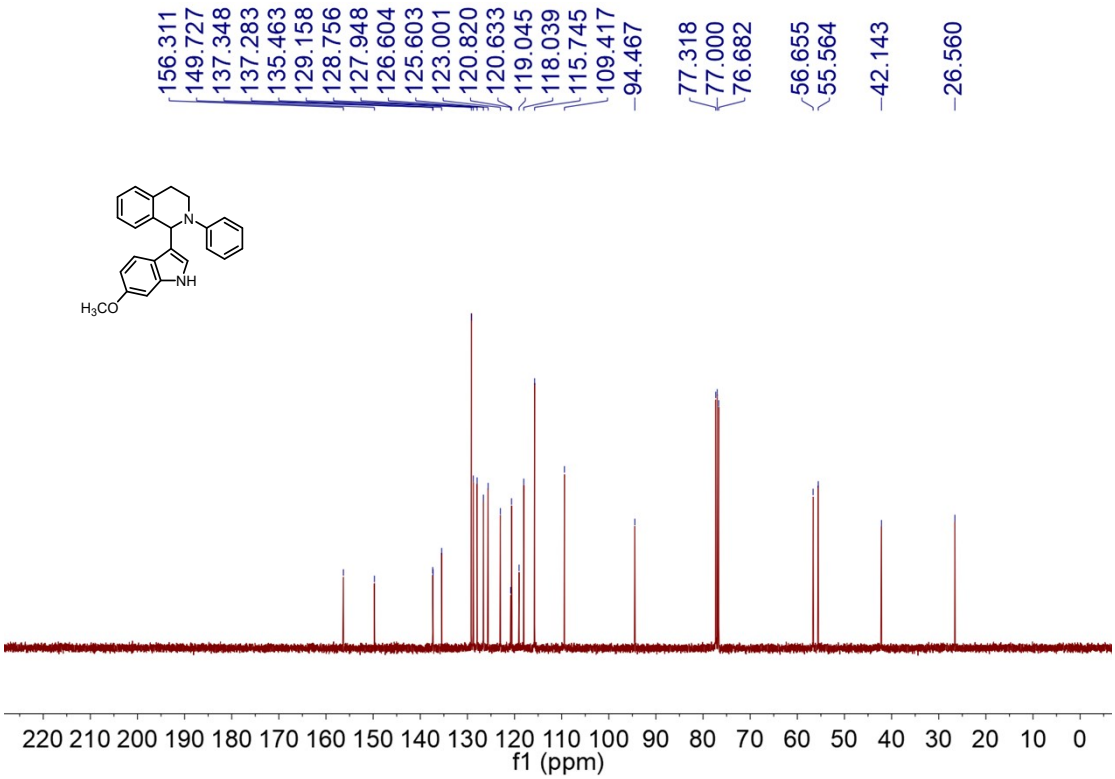


Fig. S47 ^{13}C NMR spectra of **11n** (in $CDCl_3$).

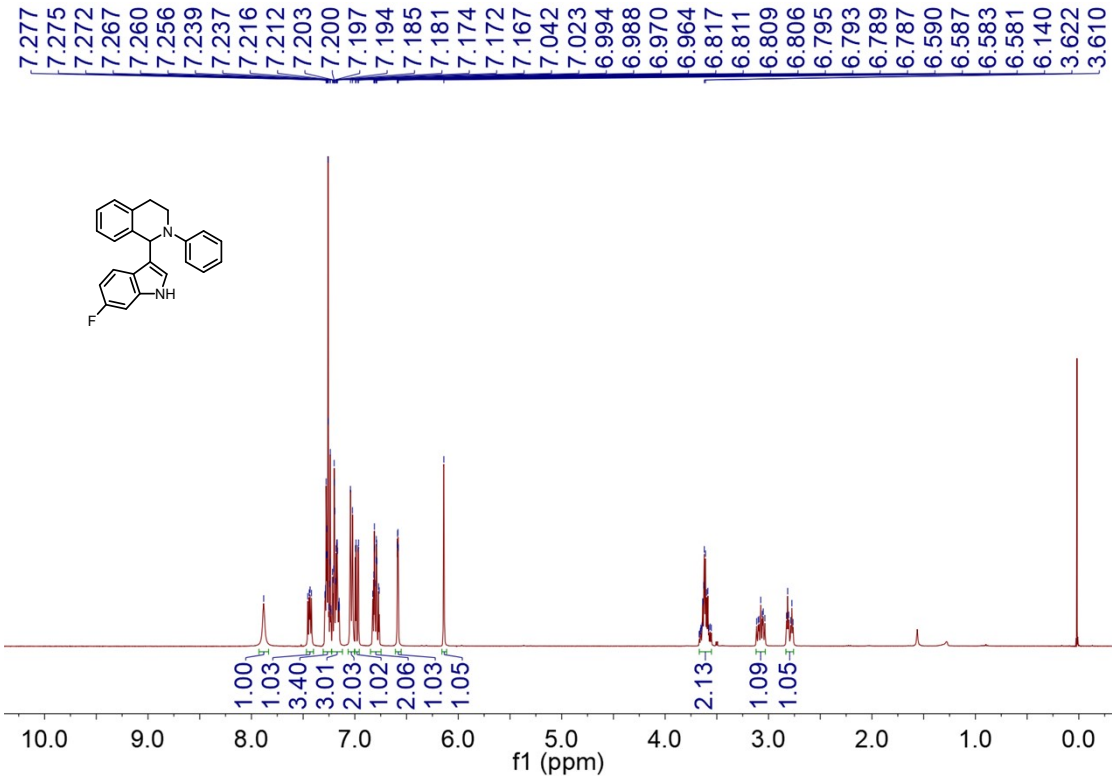


Fig. S48 ^{1}H NMR spectra of **11o** (in $CDCl_3$).

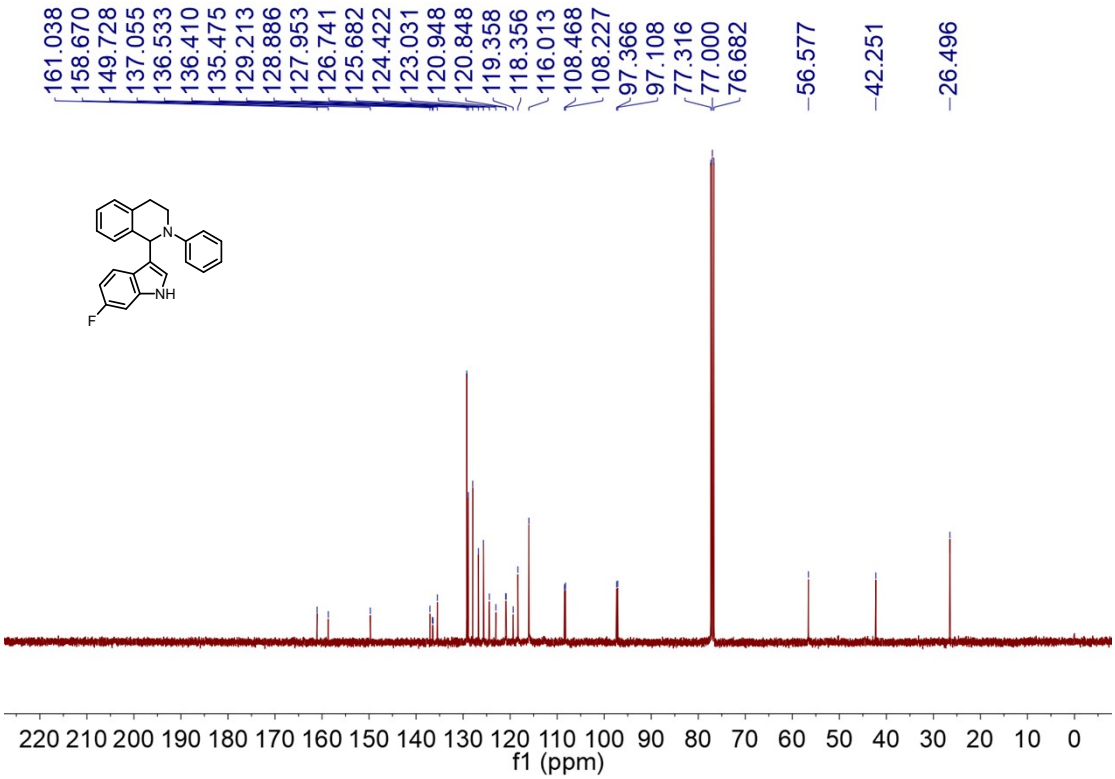


Fig. S49 ^{13}C NMR spectra of **11o** (in $CDCl_3$).

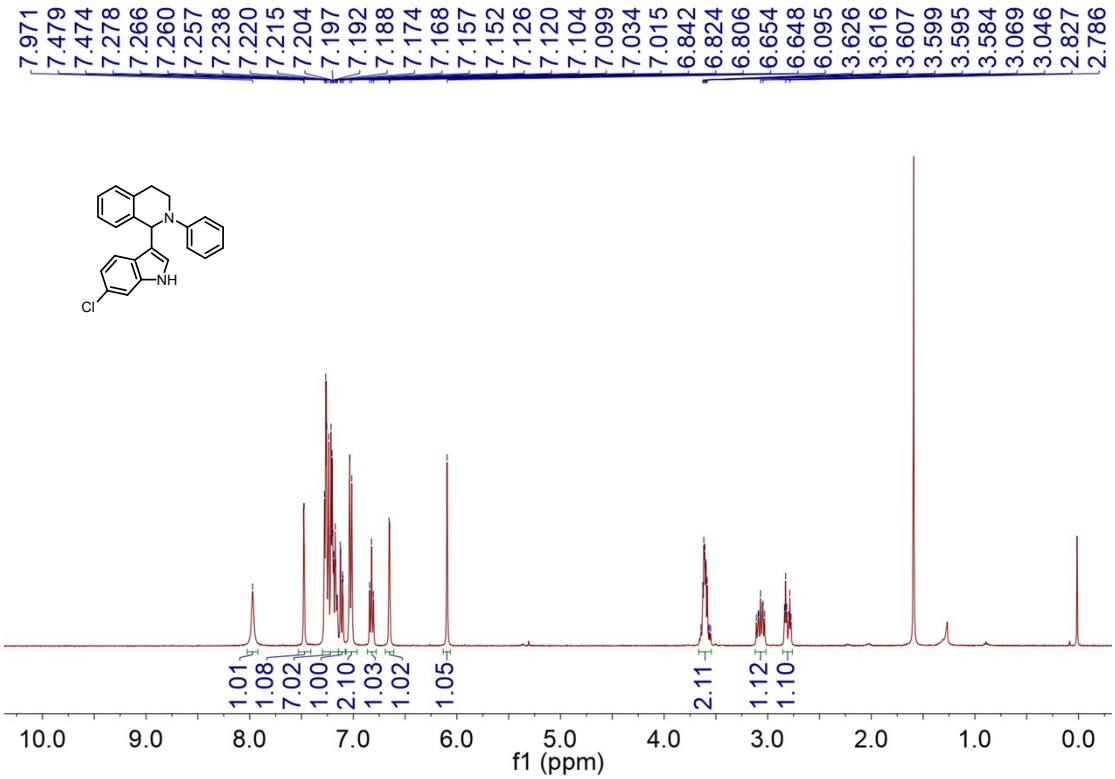


Fig. S50 ^{1}H NMR spectra of **11p** (in $CDCl_3$).

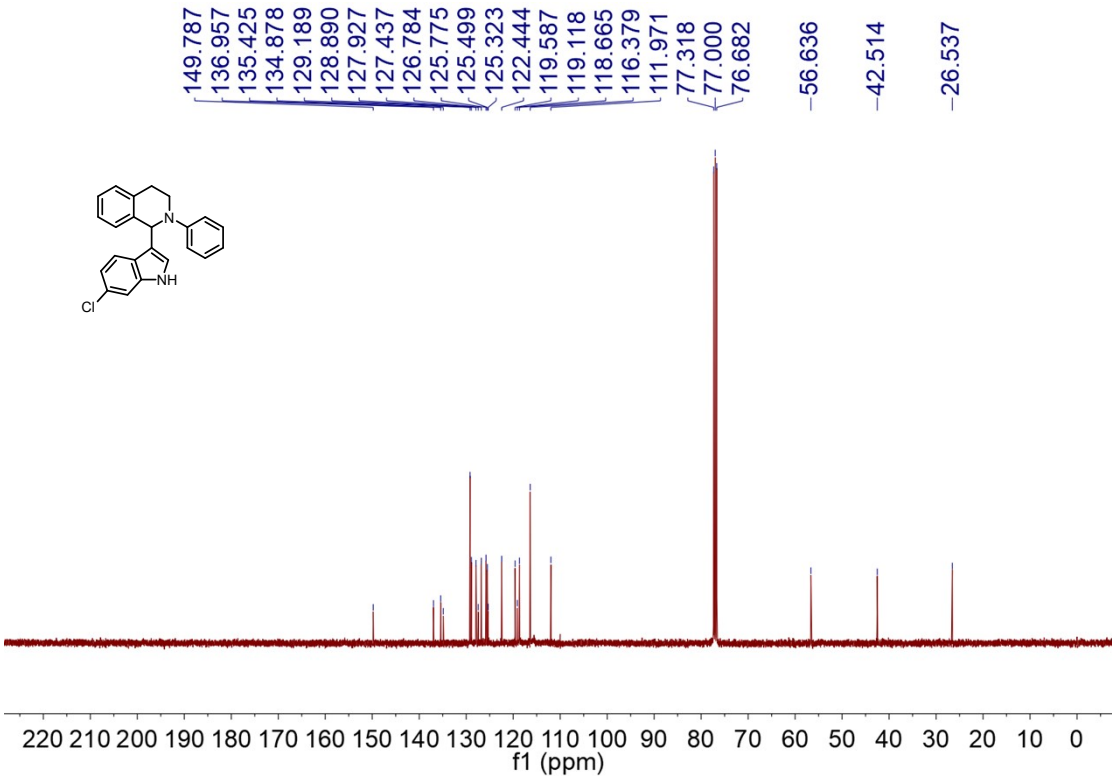


Fig. S51 ^{13}C NMR spectra of **11p** (in $CDCl_3$).

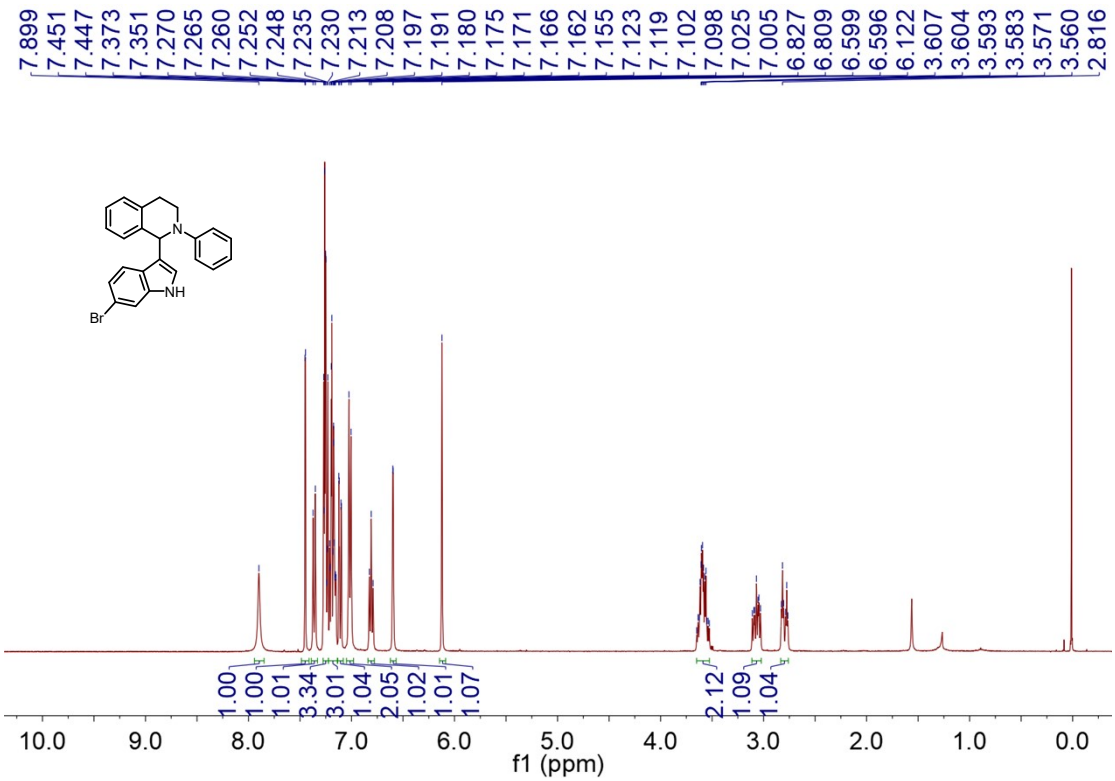


Fig. S52 ^{1}H NMR spectra of **11q** (in $CDCl_3$).

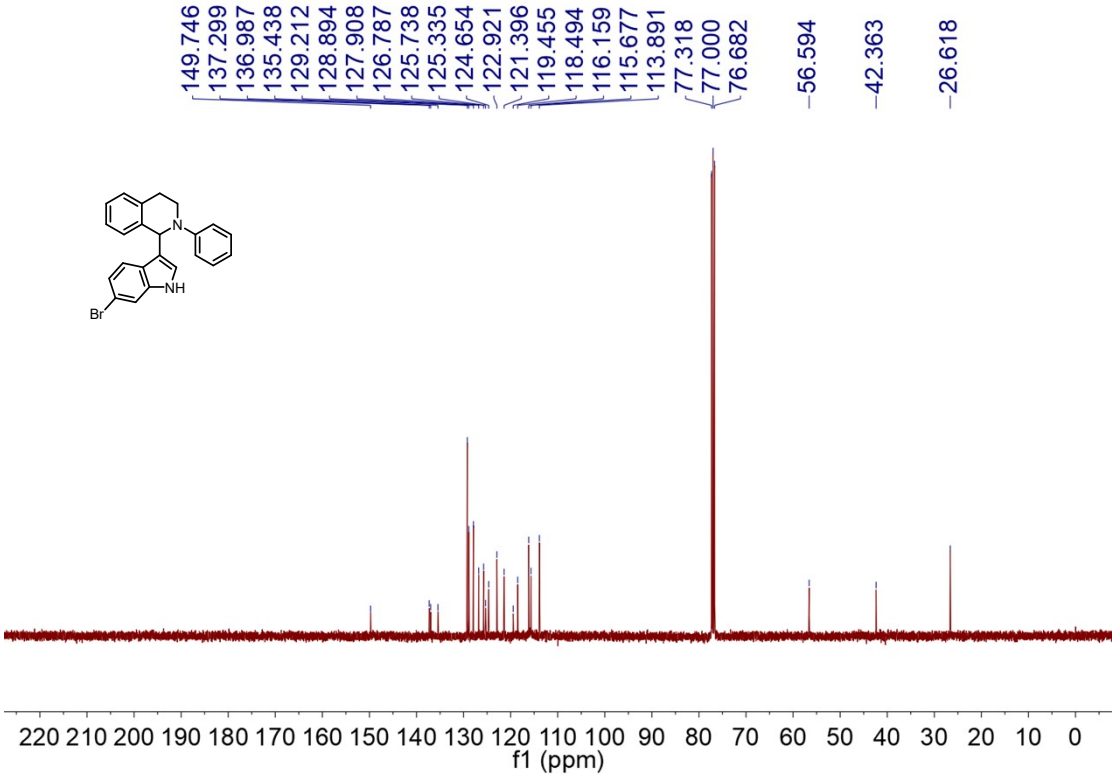


Fig. S53 ^{13}C NMR spectra of **11q** (in $CDCl_3$).

10. Reference:

[1] C. Quiroga-Campano, H. Gómez-Machuca, S. Moris, P. Jara, J. R. De la Fuente, H. Pessoa-Mahana, C. Jullian and C. Saitz, *J. Mol. Struct.*, 2017, **1141**, 133-141.

[2] M. Luo, X. Zhou, Z. Chi, S. Liu, Y. Zhang and J. Xu, *Dyes Pigm.,* 2014, **101**, 74-84.