

Supplementary Information

Intermolecular Diastereoselective Annulation of Azaarenes into Fused N-heterocycles by Ru(II) Reductive Catalysis

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General information

All the obtained products were characterized by melting points (m.p.), $^1\text{H-NMR}$, $^{13}\text{C-NMR}$. Melting points (m.p.) were performed using a Büchi AG M-565. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and NOESY spectra were obtained on Bruker-400 or Bruker-500 and referenced to 7.26 ppm for chloroform solvent or 2.54 ppm for dimethyl sulfoxide solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m). Analytical HPLC was run with an Agilent 1260 Infinity, equipped with a Daicel CHIRALPAK IA (4.6 mm \times 250 mm) and a Agilent LC1260 II DAD-G7115A detector. The high resolution mass spectrums were recorded on a Bruker maXis impact mass spectrometer. X-Ray diffraction data of one these crystals were collected on a Bruker SMART diffractometer. And the structures were solved by direct methods SHELXS-2014.

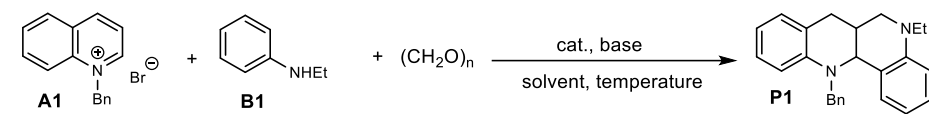
All the reagents were purchased from *Bide Pharmatech Ltd.* and *Energy Chemical*. All solvents were purchased from *Greagent* (Shanghai Titansci incorporated company) and used without further purification. All reactions were heated by metal sand bath (WATTCAS, LAB-500, <https://www.wattcas.com>). Column chromatography was performed on silica gel (200-300 mesh). Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254).

Noteworthy, the employed N-heteroarenes are named **A'**, the N-heteroarenium salts are named **A**, the anilines are named **B**, and the obtained products are named **P**.

Supplementary Methods

Optimization of reaction conditions

Supplementary Table 1. Optimization of reaction conditions^a



Entry	Catalyst	Base	Solvent	T (°C)	Yields of P1 ^b
1	Ru ₃ (CO) ₁₂ /Xantphos	Mg(OMe) ₂	methanol	65	0
2	RuHCl(CO)(PPh ₃) ₃	Mg(OMe) ₂	methanol	65	0
3	Co ₂ (CO) ₈	Mg(OMe) ₂	methanol	65	0
4	FeCl ₃	Mg(OMe) ₂	methanol	65	0
5	MnBr(CO) ₅ /Xantphos	Mg(OMe) ₂	methanol	65	0
6	NiCl ₂ (PPh) ₂	Mg(OMe) ₂	methanol	65	0
7	[Ru(<i>p</i> -cymene)Cl ₂] ₂	<i>t</i> -BuONa	methanol	65	0
8	[Ru(<i>p</i> -cymene)Cl ₂] ₂	NaOH	methanol	65	0
9	[Ru(<i>p</i> -cymene)Cl ₂] ₂	CsCO ₃	methanol	65	0
10	[Ru(<i>p</i> -cymene)Cl ₂] ₂	Et ₃ N	methanol	65	0
11	[Ru(<i>p</i> -cymene)Cl ₂] ₂	MgCl ₂	methanol	65	0
12	[Ru(<i>p</i> -cymene)Cl ₂] ₂	NaOTf	methanol	65	0

^a Unless otherwise stated, the reaction in MeOH (1 mL) was performed with **A1** (0.2 mmol), **B1** (0.2 mmol), cat. (1 mol %), base (0.75 eq), (CH₂O)_n (10 eq) at 65 °C for 18 h under N₂ protection.

^b NMR yield by using anisole as the internal standard.

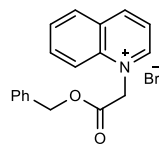
Substrate preparation

Synthesis of N-heteroareanium Bromide Salts

Method 1: Synthesis of compound **A1**: quinoline (3 mmol), benzyl bromide (6 mmol) and acetone (5 mL) were introduced in a flask (50 mL). The resulting mixture was then stirred at room temperature for 24 h. Then, the solvent was removed. The reaction mixture was washed with small amount of diethyl ether and finally dried under vacuum to get the salt **A1**.

Method 2: Synthesis of compound **A16**: quinoline (3 mmol), (2-bromoethyl)benzene (3 mmol) and toluene (3 mL) were introduced in a flask (50 mL). The resulting mixture was stirred at 110 °C for 24 h. Then, the solvent was removed. The reaction mixture was washed with small amount of diethyl ether and finally dried under vacuum to get the salt **A16**.

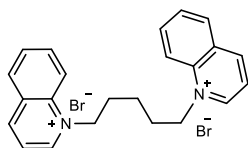
(1) 1-(2-(benzyloxy)-2-oxoethyl)quinolin-1-ium bromide (**A19**)



Method 1; Yellow solid; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.68 (d, *J* = 4.0 Hz, 1H), 9.47 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 9.0 Hz, 1H), 8.37 – 8.23 (m, 2H), 8.08 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.30 (m, 5H), 6.33 (s, 2H), 5.26 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 166.6, 151.7, 149.6, 138.7,

136.6, 135.4, 131.2, 130.6, 129.8, 129.0, 128.9, 128.6, 122.6, 119.4, 68.1, 57.9. HRMS (ESI): Calcd. for $C_{18}H_{16}BrNO_2$ $[M-Br]^+$: 278.1181; found: 278.1173.

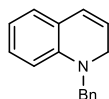
(2) ethene,1,1'-(propane-1,3-diyl)bis(quinolin-1-ium) bromide (**A21**)



Method 1; Black solid; 1H NMR (500 MHz, $DMSO-d_6$) δ 9.77 (d, $J = 5.2$ Hz, 1H), 9.37 (d, $J = 8.4$ Hz, 1H), 8.69 (d, $J = 9.0$ Hz, 1H), 8.58 – 8.52 (m, 1H), 8.33 – 8.22 (m, 3H), 8.08 (t, $J = 7.6$ Hz, 1H), 5.16 (t, $J = 7.6$ Hz, 3H), 2.19 – 2.03 (m, 3H), 1.59-1.63 (m, 1H). ^{13}C NMR (101 MHz, $DMSO-d_6$) δ 150.2, 147.8, 137.8, 136.2, 131.2, 130.3, 130.1, 122.7, 122.6, 119.6, 57.4, 29.3, 23.1. HRMS (ESI): Calcd. for $C_{23}H_{25}Br_2N_2$ $[M-Br+H]^+$: 329.2018; found: 329.2012.

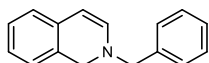
Preparation of intermediates

(1) Synthesis of 1-benzyl-1,2-dihydroquinoline (int-1)



To a suspension of 1-benzylquinolin-1-ium bromide **A1** (3.0 mmol) in 25 mL of THF was slowly added lithium aluminium hydride (3.0 mmol) at room temperature. The reaction was stirred at room temperature for 20 min, then slowly quenched with 0.1 mL of water and stirred for an additional 10 min. To the reaction was added 0.2 mL 10 % sodium hydroxide solution and stirred at room temperature for an additional 10 min. The reaction was added 5% Na_2CO_3 solution and the resulting mixture was extracting with ethyl acetate, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum to give the unstable crude 1-benzyl-1,2-dihydroquinoline as a yellow oil. 1H NMR (400 MHz, $CHCl_3-d$) δ 7.51 – 7.38 (m, 5H), 7.12 (d, $J = 8.0$ Hz, 1H), 7.02 (d, $J = 5.8$ Hz, 1H), 6.74 (t, $J = 7.4$ Hz, 1H), 6.61 (d, $J = 8.2$ Hz, 1H), 6.50 (d, $J = 2.2$ Hz, 1H), 5.78 (dt, $J = 9.9, 3.8$ Hz, 1H), 4.50 (s, 2H), 4.33 (dd, $J = 3.8, 2.0$ Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 137.6, 129.3, 128.8, 127.4, 127.2, 127.1, 126.7, 122.1, 121.9, 117.0, 110.2, 53.8, 50.6. HRMS (ESI): Calcd. for $C_{16}H_{16}N$ $[M+H]^+$: 222.1277; found: 222.1276.

(2) Synthesis of 2-benzyl-1,2-dihydroisoquinoline (int-6)



The synthetic procedure of **int-6** is similar to that of **int-1** described above. Yellow oil; 1H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 4H), 7.22 (td, $J = 6.6, 6.1, 2.6$ Hz, 1H), 7.03 (t, $J = 7.7$ Hz, 1H), 6.89 (td, $J = 7.4, 1.2$ Hz, 1H), 6.82 (d, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 7.4$ Hz, 1H), 6.17 (d, $J = 7.4$ Hz, 1H), 5.26 (d, $J = 7.4$ Hz, 1H), 4.13 (s, 2H), 4.03 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 137.4, 134.0, 128.8, 128.3, 127.7, 127.7, 125.7, 124.9, 122.9, 98.3, 59.4, 51.1.

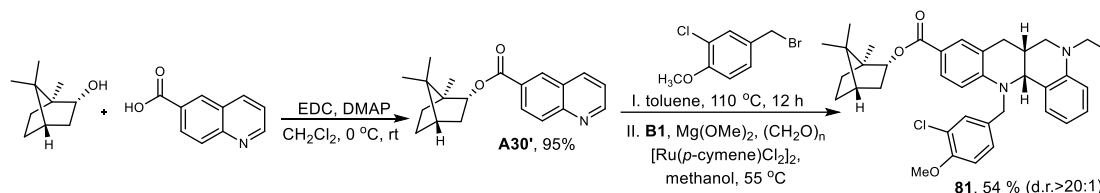
Typical procedure for the synthesis of product P1

Under N_2 atmosphere, $[Ru(p\text{-cymene})Cl_2]_2$ (1 mol %), 1-benzylquinolin-1-ium bromide **A1** (0.2 mmol), N-ethylaniline **B1** (0.2 mmol), $Mg(OMe)_2$ (0.75 eq, 12.9 mg), $(CH_2O)_n$ (10.0 eq, 60

mg) and methanol (1 mL) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed and the resulting mixture was stirred at 55 °C for 18 h. After cooling down to room temperature, the mixture was extracted with ethyl acetate, washed with 5% Na₂CO₃ solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give 12-benzyl-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine **P1**.

Synthetic Utility

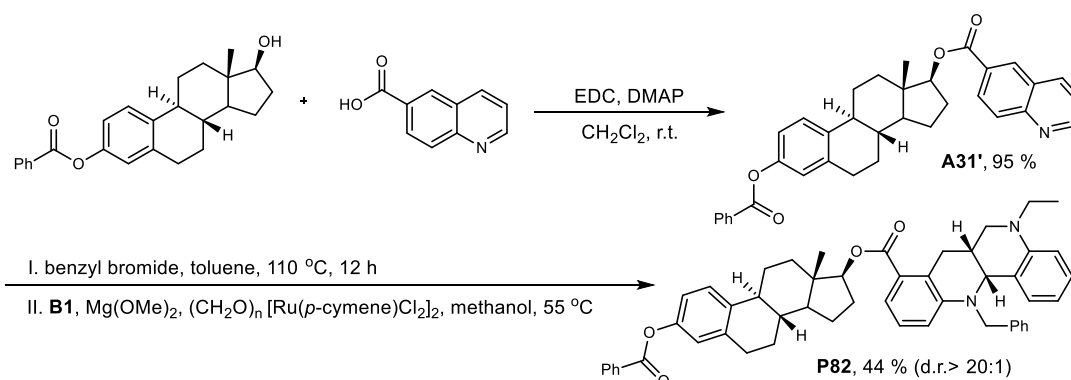
Synthesis of Compound P81



To a suspension of quinoline-6-carboxylic acid (1 mmol) in CH₂Cl₂ was added DMAP (4-(dimethylamino)-pyridine, 2 mmol) in one portion at room temperature. The reaction mixture was stirred for 10 min at room temperature. N-(3-(Dimethylamino)propyl)-N'-ethylcarbodiimide hydrochloride (EDC, 1 mmol) was added at 0 °C. Then the resultant suspension was stirred for 10 min at 0 °C. A solution of (-)-Bomeol (0.8 mmol) in CH₂Cl₂ was added at 0 °C. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 16 h. The solution was diluted by the addition of saturated aqueous NH₄Cl solution and CH₂Cl₂ at room temperature. The organic phase was dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give a white solid **A30'** (234.8 mg, 95% yield).¹

Under N₂ atmosphere, **A30'** (0.2 mmol), 4-(bromomethyl)-2-chloro-1-methoxybenzene (0.2 mmol), and toluene (1.0 mL) were introduced in a Schlenk tube, successively. The Schlenk tube was closed and the resulting mixture was stirred at 110 °C for 12 h. Then the solvent was removed and to the reaction were added [Ru(*p*-cymene)Cl₂]₂ (1 mol%), N-ethylaniline **B1** (0.2 mmol), Mg(OMe)₂ (75 mol%), paraformaldehyde (10 eq) and methanol (1 mL). The reaction was performed at 55 °C for 18 h. After cooling down to room temperature, the resulting mixture was extracting with CH₂Cl₂, washed with 5% Na₂CO₃ solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give **P81** (54% yield).

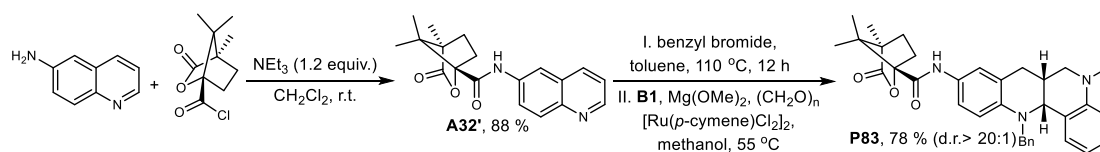
Synthesis of Compound P82



To a suspension of quinoline-6-carboxylic acid (1 mmol) in CH_2Cl_2 was added DMAP (4-(dimethylamino)-pyridine, 2 mmol) in one portion at room temperature. The reaction mixture was stirred for 10 min at room temperature. *N*-(3-(Dimethylamino)propyl)-*N'*-ethylcarbodiimide hydrochloride (EDC, 1 mmol) was added at 0 °C. Then the resultant suspension was stirred for 10 min at 0 °C. A solution of 1-Adamantanol (0.8 mmol) in CH_2Cl_2 was added at 0 °C. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 16 h. The solution was diluted by the addition of saturated aqueous NH_4Cl solution and CH_2Cl_2 at room temperature. The organic phase was dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give a white solid **A31'** (235.6 mg, 91% yield).¹

Under N_2 atmosphere, **A31'** (0.2 mmol), benzyl bromide (0.2 mmol), and toluene (1.0 mL) were introduced in a Schlenk tube, successively. The Schlenk tube was closed and the resulting mixture was stirred at 110 °C for 12 h. Then the solvent was removed and to the reaction were added $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (1 mol%), *N*-ethylaniline **A50** (0.2 mmol), $\text{Mg}(\text{OMe})_2$ (75 mol%), Paraformaldehyde (10 equiv) and methanol (1 mL). The reaction was performed at 55 °C for 18 h. After cooling down to room temperature, the resulting mixture was extracting with CH_2Cl_2 , washed with 5% Na_2CO_3 solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give **P82** (44% yield).

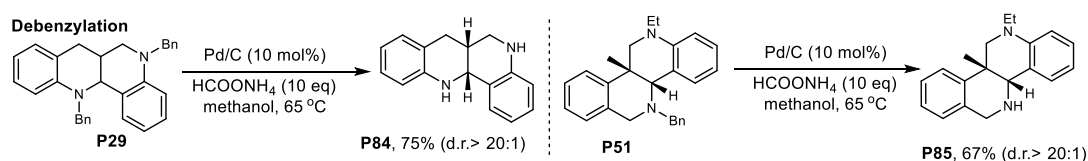
Synthesis of Compound P83



To a solution of 6-aminoquinoline (10 mmol, 1.44 g) in anhydrous CH_2Cl_2 was added triethylamine (12 mmol, 1.21 g) and (-)-1*S*,4*R*-Camphanoyl chloride (11 mmol, 2.38 g) at 0 °C. The reaction mixture was stirred at room temperature until the reaction was completed (monitored by TLC). Water (50 mL) was added to the mixture and extracted with CH_2Cl_2 (30 mL). The organic phase was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **A32'** (88% yield).²

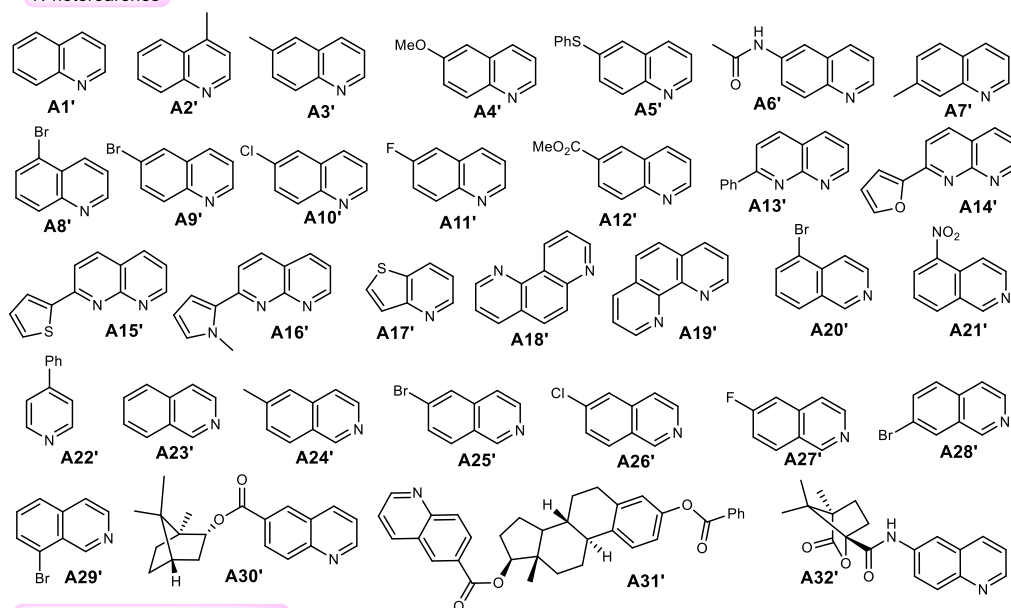
Under N_2 atmosphere, **A32'** (0.2 mmol), benzyl bromide (0.2 mmol), and toluene (1.0 mL) were introduced in a Schlenk tube, successively. The Schlenk tube was closed and the resulting mixture was stirred at 110 °C for 12 h. Then the solvent was removed and to the reaction were added $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (1 mol%), *N*-ethylaniline (0.2 mmol), $\text{Mg}(\text{OMe})_2$ (75 mol%), paraformaldehyde (10 equiv) and toluene (1 mL) The reaction was performed at 55 °C for 18 h. After cooling down to room temperature, the resulting mixture was extracting with CH_2Cl_2 , washed with 5% Na_2CO_3 solution, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give **P83** (78% yield).

Debenzylation of compounds P29 and P51

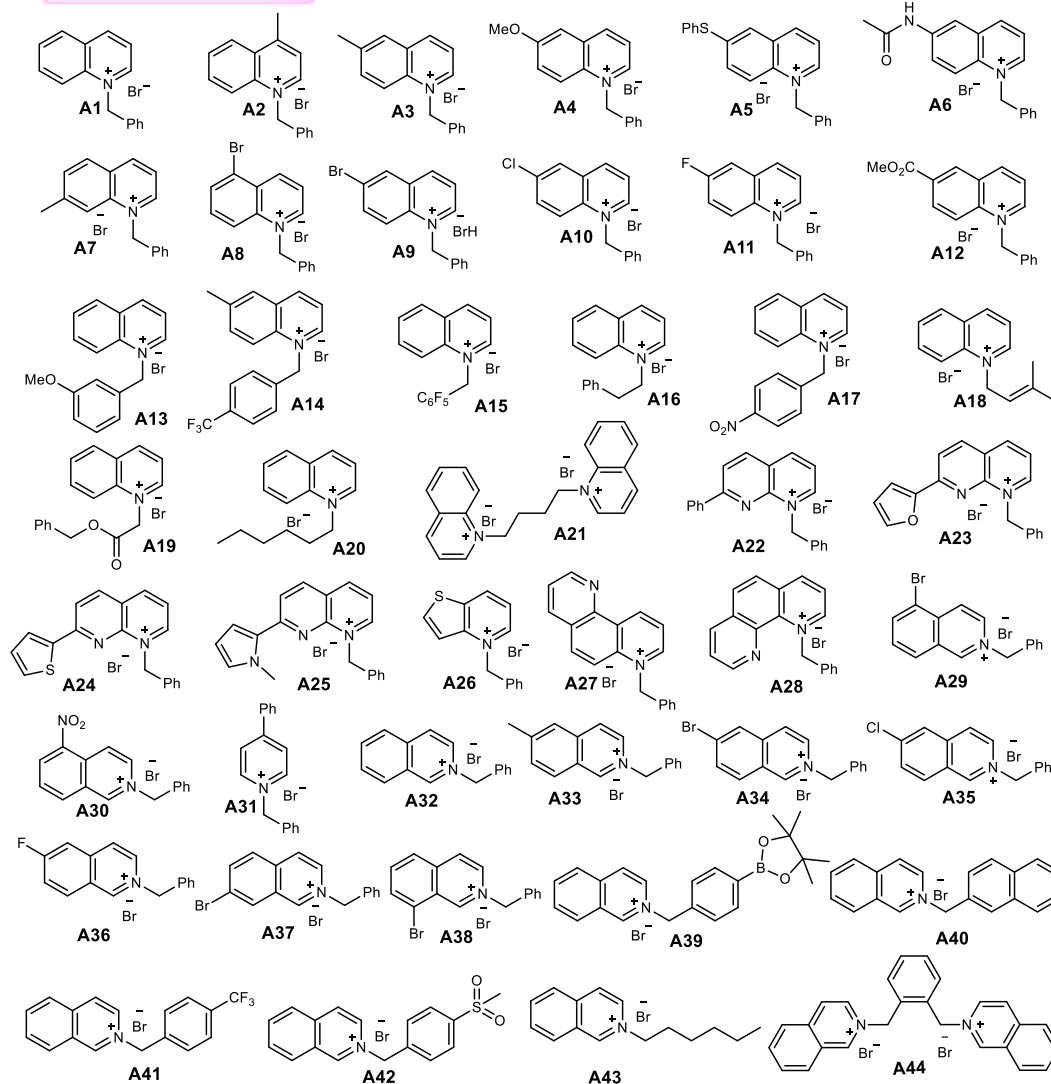


Under N₂ atmosphere, 10 mol % Pd/C, **P29** (0.2 mmol, 83.2 g), HCOONH₄ (2 mmol, 136 mg), and methanol (0.5 mL) were introduced in a Schlenk tube, successively. Then the Schlenk tube was closed and the resulting mixture was stirred at 65 °C for 12 h. After cooling down to room temperature, the resulting mixture was extracting with ethyl acetate, washed with H₂O, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give **P84** (74% yield). Similarly, compound **P51** underwent N-debenzylation under the same reaction conditions to afforded **P85** in 67% yield.

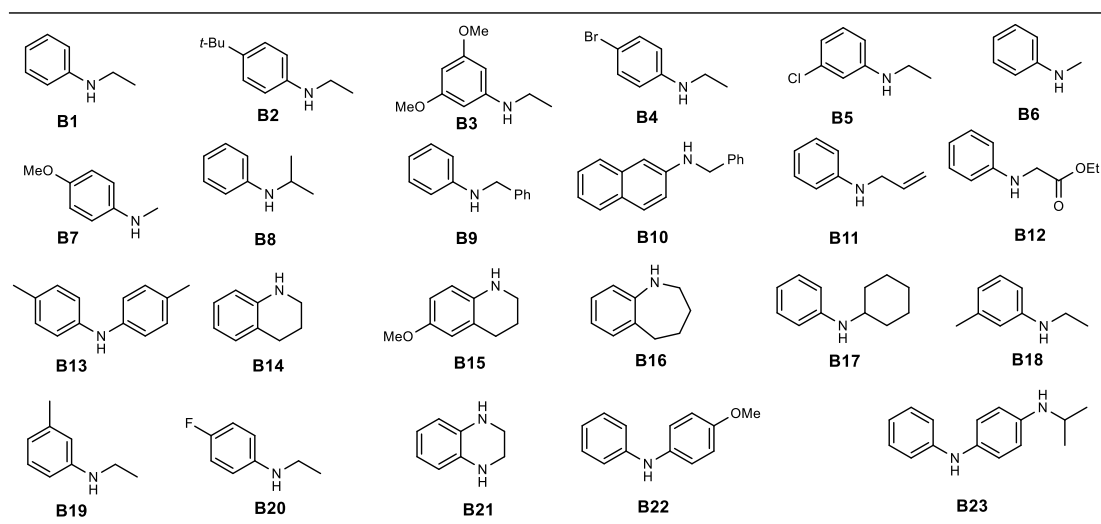
N-heteroarenes



N-heteroarene Bromide Salts



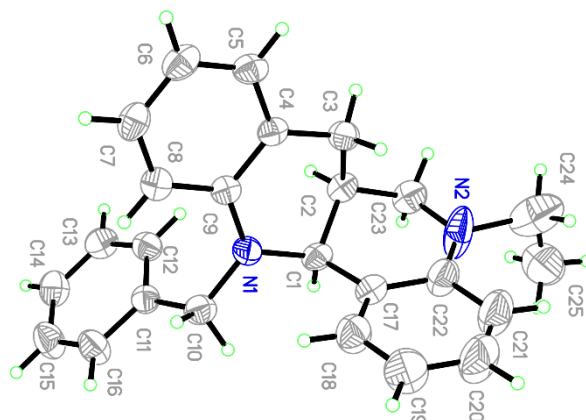
Supplementary Fig. 1. Substrates employed for the reaction.



Supplementary Fig. 2. Substrate N-substituted aniline **B** employed for the reaction.

Supplementary Discussion

(1) Single crystal X-ray diffraction data of **P1**



Supplementary Fig. 3 Molecular structure of **P1** (CCDC 2051637) is displayed with thermal ellipsoids set at 30% probability.

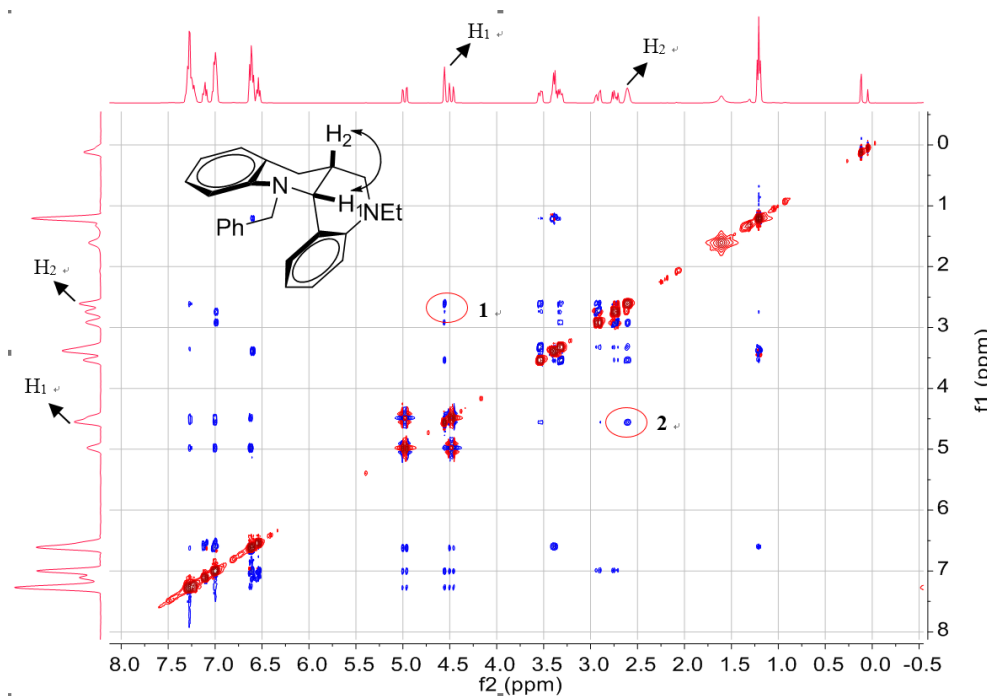
Yellow block-like single crystals of **P1** were grown by layering a THF solution with n-hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a Bruker APEX-II CCD. The measurements were performed with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 293 (2) K, using the phi and omega scans to a maximum θ value of 29.275° . The data were refined by full-matrix least-squares techniques on F^2 with SHELXL-2014. And the structures were solved by direct methods SHELXL-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. An ORTEP representation of the structure is shown below.

Supplementary Table 2. Crystal data and structure refinement for P1.

Identification code	P1	
Empirical formula	C ₂₅ H ₂₆ N ₂	
Formula weight	354.48	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 12.8508(19) Å	α = 90°.
	b = 14.337(3) Å	β = 90°.
	c = 21.517(5) Å	γ = 90°.
Volume	3964.4(13) Å ³	
Z	8	
Density (calculated)	1.188 Mg/m ³	
Absorption coefficient	0.069 mm ⁻¹	
F(000)	1520	
Crystal size	0.220 x 0.200 x 0.180 mm ³	
Theta range for data collection	3.415 to 29.275°.	
Index ranges	-17 ≤ h ≤ 11, -17 ≤ k ≤ 19, -27 ≤ l ≤ 27	
Reflections collected	19084	
Independent reflections	9204 [R(int) = 0.0465]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9204 / 233 / 543	
Goodness-of-fit on F ²	0.965	
Final R indices [I > 2σ(I)]	R1 = 0.0640, wR2 = 0.1025	
R indices (all data)	R1 = 0.1826, wR2 = 0.1425	
Absolute structure parameter	-1.6(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.154 and -0.177 e.Å ⁻³	

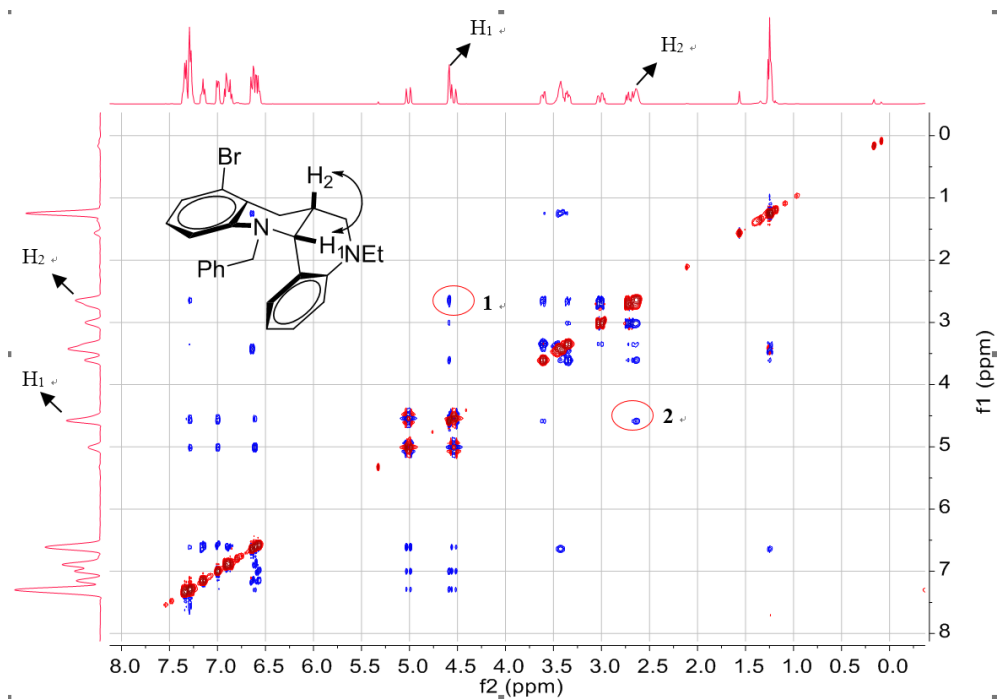
(2) NOESY spectra of partial obtained compounds

NOESY spectrum of P1



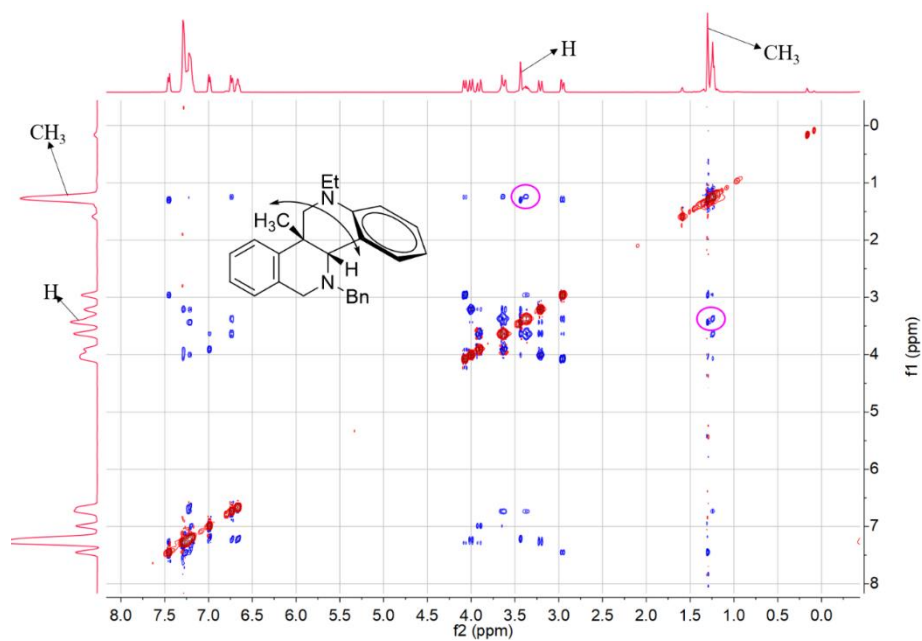
Supplementary Fig. 4. NOESY spectrum of compound P1.

NOESY spectrum of P8



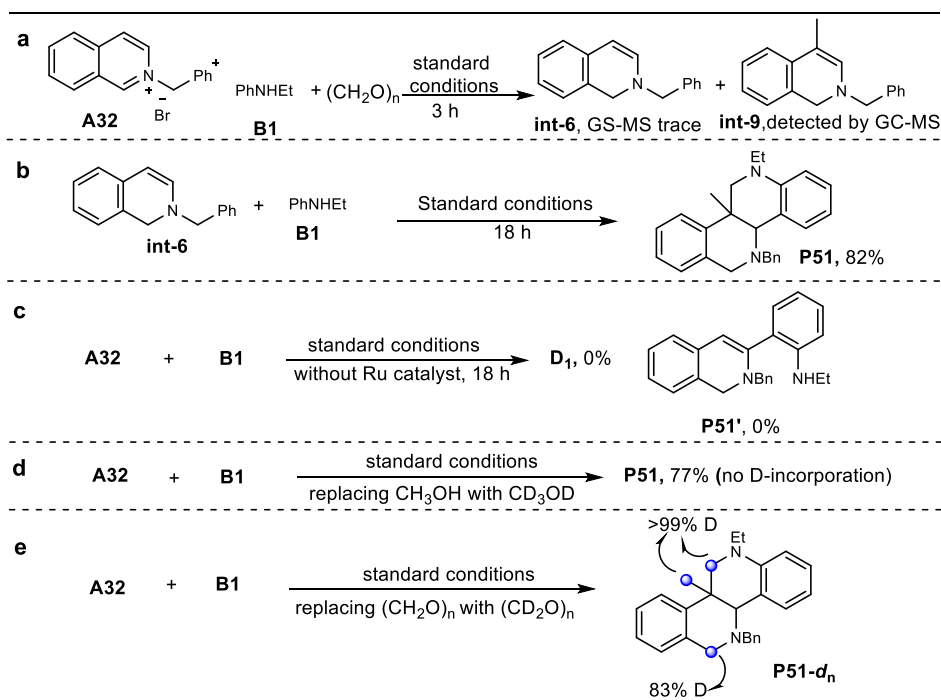
Supplementary Fig. 5 NOESY spectrum of compound P8.

NOESY spectrum of P51

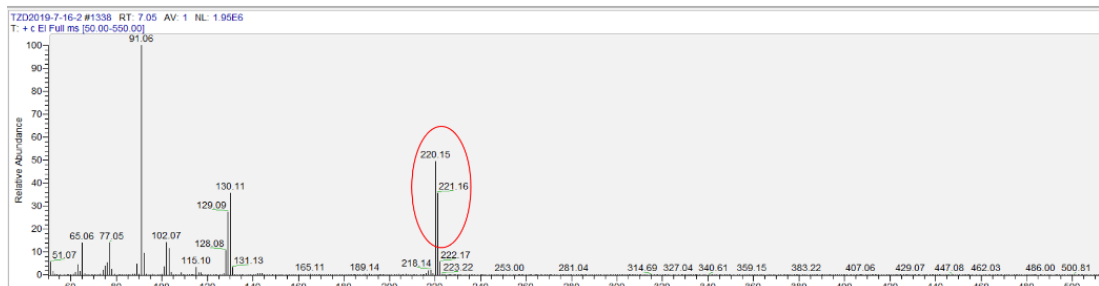
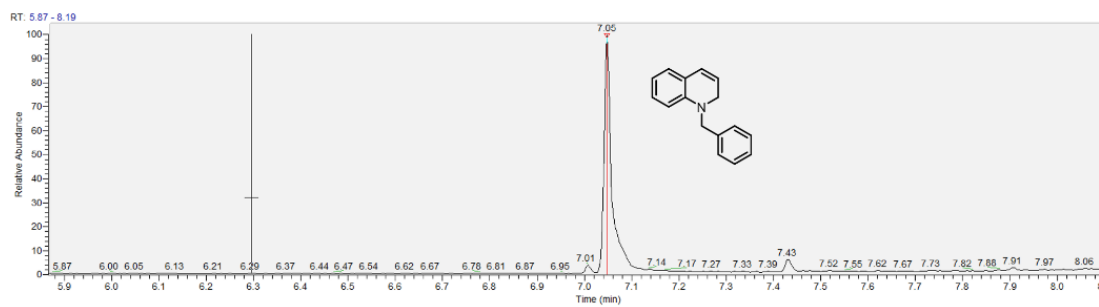


Supplementary Fig. 6 NOESY spectrum of compound P51.

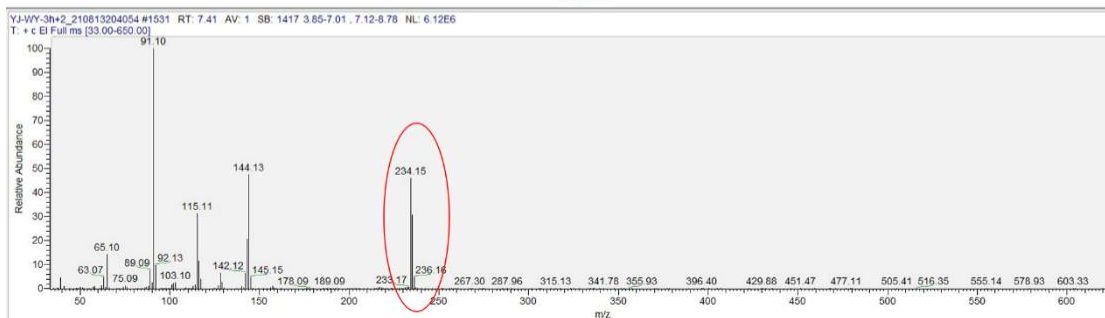
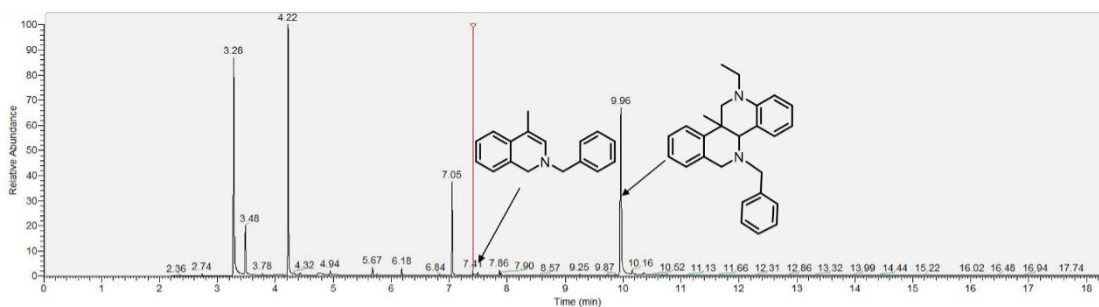
(3) Control experiments



Supplementary Fig. 7 Supplementary control experiments.

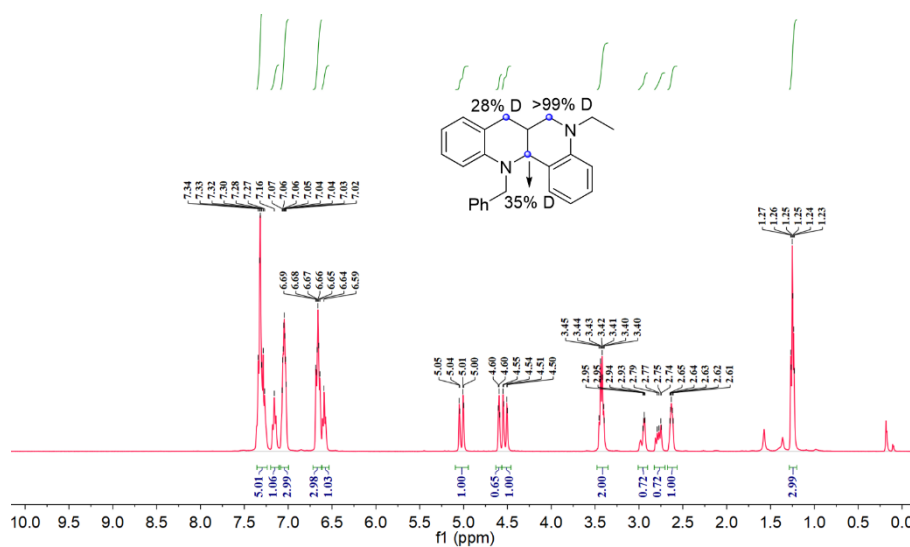


Supplementary Fig. 8 GC-MS spectrum of int-1.

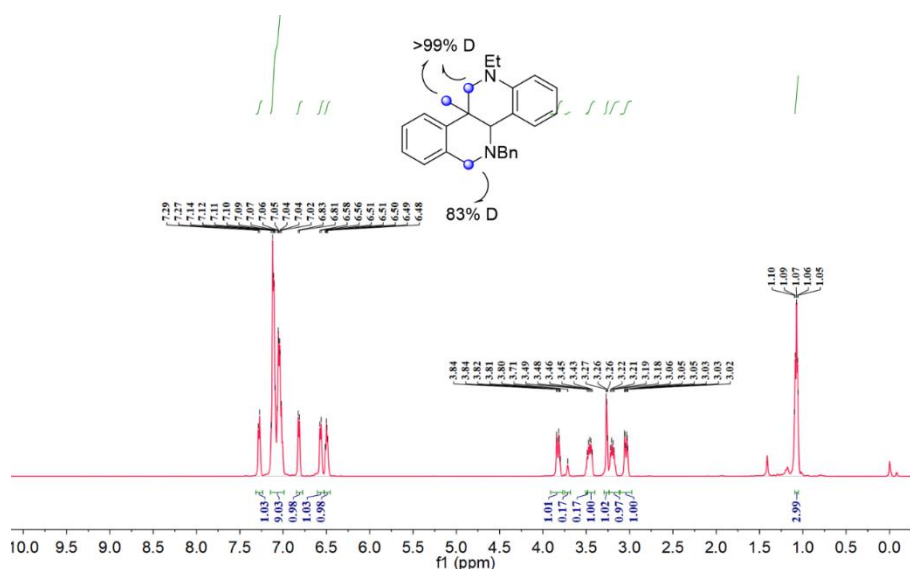


Supplementary Fig. 9 GC-MS spectrum of int-9.

(4) Deuterium Experiments



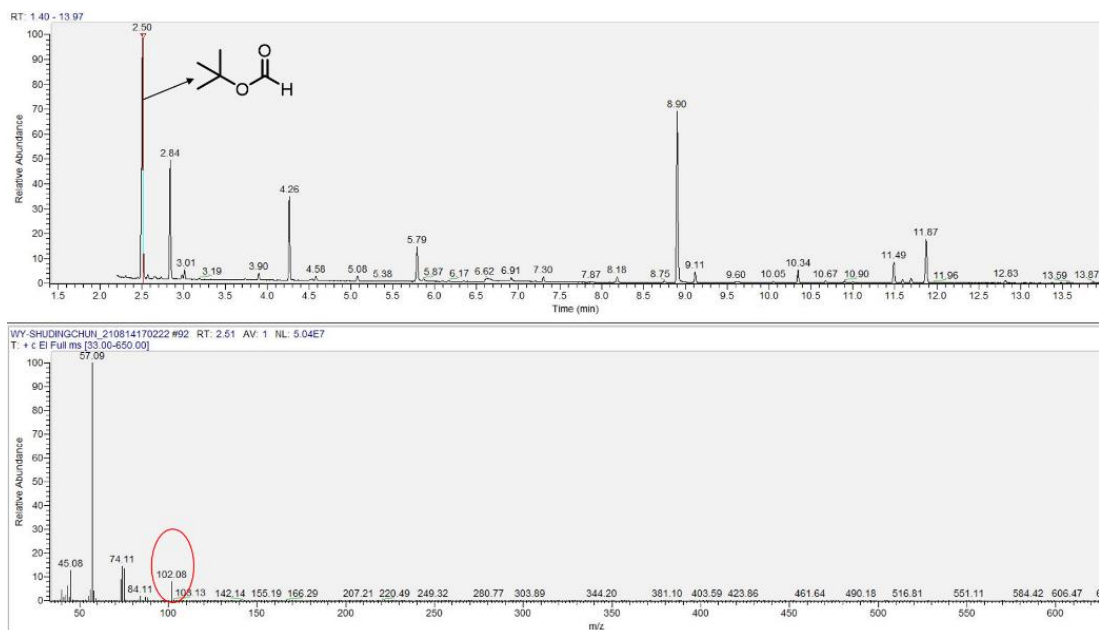
Supplementary Fig. 10 ¹H-NMR spectrum of P1-d_n.



Supplementary Fig. 11 ¹H-NMR spectrum of P51-d_n.

(5) Detection of the ester products by GC-MS

By replacing MeOH with *t*-BuOH as the solvent, the GC-MS analysis of the model reaction shows the formation of *t*-butyl formate, which is formed via the addition of alcohol to formaldehyde followed by a base-mediated anion exchange with the ruthenium catalyst and Ru-catalyzed β -hydride elimination. Meanwhile, such a process generates the reductive species [HRu^{II}X], which is involved in the reductive annulation reaction.

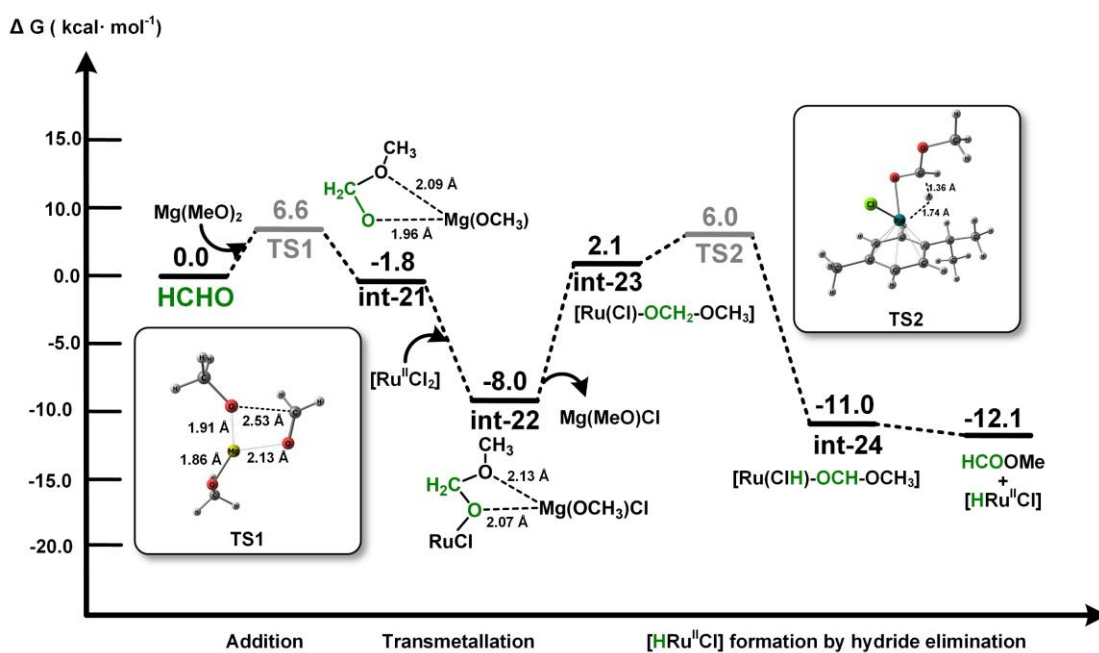


Supplementary Fig. 12 GC-MS analysis of the model reaction by replacing MeOH with *t*-BuOH as the solvent.

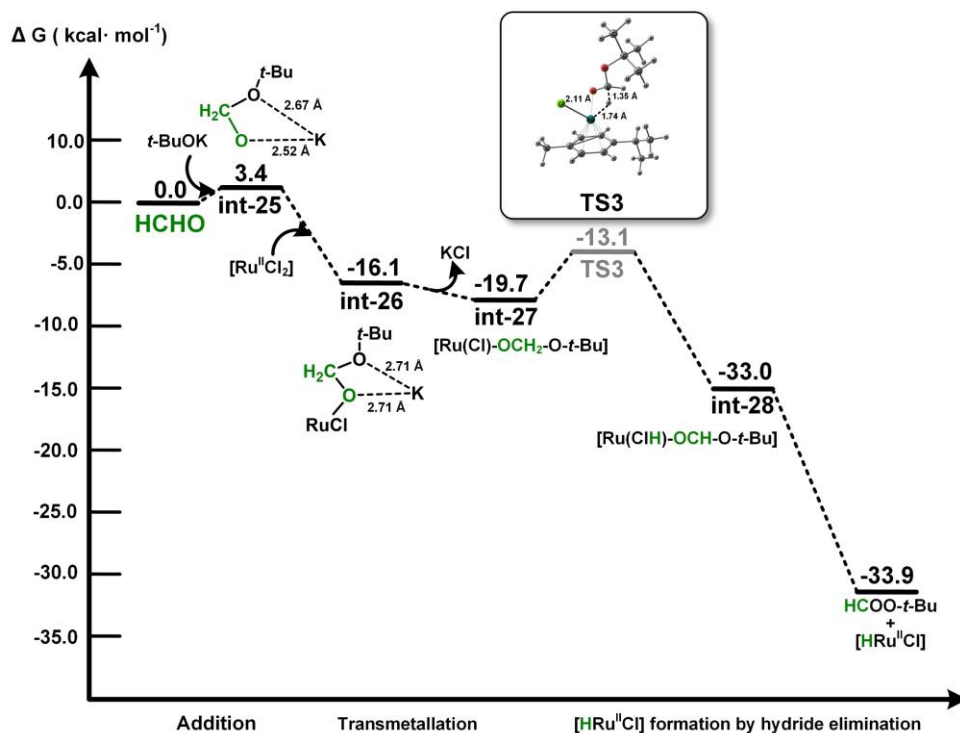
(6) Computational Details

All calculations were carried out using the Gaussian 16 C.01 program package.³ The geometry optimizations were performed using hybrid B3LYP exchange correlation⁴⁻⁶. The LanL2DZ basis set pseudopotential⁷ was used for Ru atom. The 6-311G(d, p) basis set⁸⁻¹⁰ was used for remaining atoms. Vibrational frequency calculations were performed to characterize the nature of each stationary point and to make the zero-point energy (ZPE) corrections. The synchronous transit-guided quasi-Newton (QSTN) method, implemented with the Gaussian keyword QST3¹¹ was performed to locate the transition states. The minimum energy path (MEP) was constructed by intrinsic reaction coordinate (IRC) theory for each reaction channel¹². A tight convergence (10^{-12} au) criterion was employed, and the solvent CH₃OH was considered using the IEF-PCM solvent model¹³.

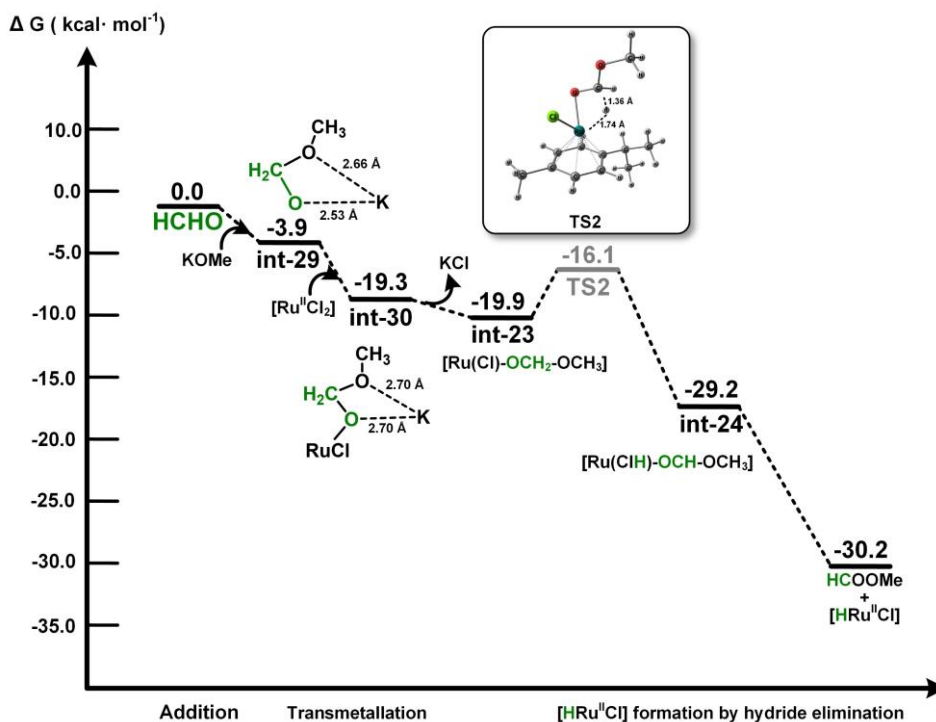
Potential energy surface for the formation of $[\text{Ru}^{\text{II}}\text{HCl}]$ employing different bases:



Supplementary Fig. 13 Potential energy surface for the formation of $[\text{Ru}^{\text{II}}\text{HCl}]$ employing $\text{Mg}(\text{OMe})_2$ as the base (free energies in kcal·mol⁻¹). The process from int-22 to int-23 is referred to the transmetalation step.



Supplementary Fig. 14 Potential energy surface for the formation of $[\text{Ru}^{\text{II}}\text{HCl}]$ employing *t*-BuOK as the base (free energies in kcal·mol⁻¹). The process from int-26 to int-27 is referred to the transmetalation step.

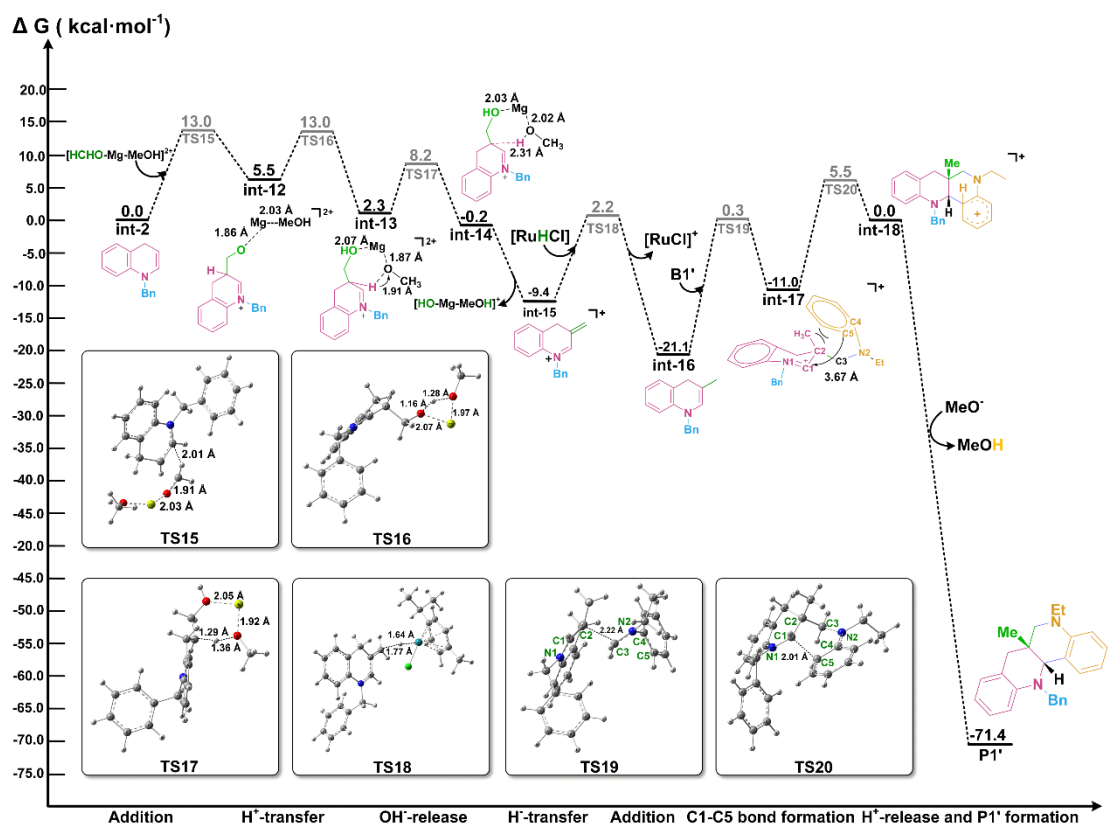


Supplementary Fig. 15 Potential energy surface for the formation of $[\text{Ru}^{\text{II}}\text{HCl}]$ employing KOMe as the base (free energies in kcal·mol⁻¹). The process from int-29 to int-30 is referred to the transmetalation step.

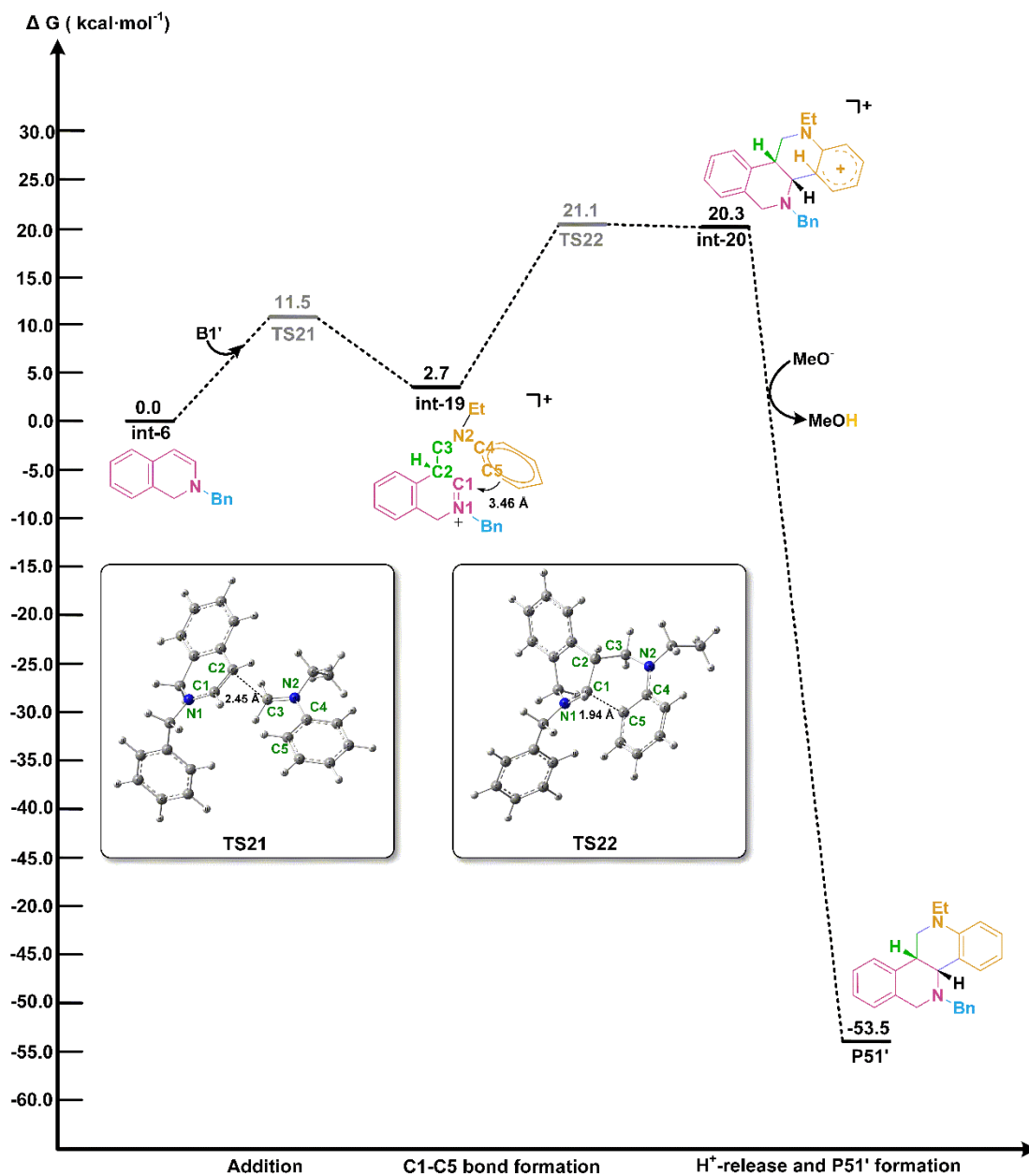
To understand the origin of generating different products **P1** and **P51**, the formation of β -methylated product **P1'** from **int-2** has also been investigated by means of the same DFT calculations. Similar to the processes for the formation product **P51** (see Fig. 8b in the manuscript), the calculated highest barrier for **P1'** generation is 21.4 kcal·mol⁻¹ (Supplementary Fig.16), which is corresponding to transition state **TS19** (**int-16** → **int-17**), higher than any barrier of the favorable pathway toward the generation of product **P1** (Fig. 8a, **int-2** → **int-3a** → **int-4** → **P1**).

As for the formation of product **P51'** (Supplementary Fig. 17), the reaction pathway is similar with the generation of compound **P1** (see Fig. 8a in the manuscript). Herein, we also calculated the most favorable pathway: the addition of **int-6** to **B1'**, C1-C5 bond formation, and H⁺-release and **P51'** formation. As shown in Fig. S14, despite the absence of a methyl unit in **int-19** (vs. **int-10a**), the associated barrier is still significant ($\Delta G^\ddagger = 18.3$ kcal·mol⁻¹, **TS22**), higher than any transition states calculated in Fig. 8b.

Based on the above-described calculation results, it supports that the generation of product **P1'** and **P51'** is disfavored under the same reaction conditions. All in one, the enamine intermediates arising from hydride transfer to the azaarenium salts play a critical role in determining the product structures.



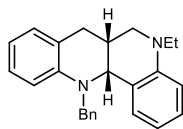
Supplementary Fig. 16 Potential energy surface for the process of int-2 to P1' (free energies in kcal·mol⁻¹).



Supplementary Fig. 17 Potential energy surface for the process of int-6 to P51' (free energies in kcal·mol⁻¹).

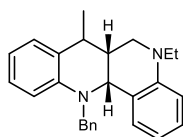
Analytic data of the obtained compounds

(1) (6a-*cis*)-12-benzyl-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (P1)



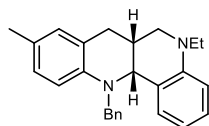
Brown solid; m.p. : 110-112 °C, (64.4 mg, 91% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.13 (m, 5H), 7.05 (t, *J* = 6.9 Hz, 1H), 6.99 – 6.88 (m, 3H), 6.60 – 6.53 (m, 3H), 6.49 (t, *J* = 7.3 Hz, 1H), 4.92 (d, *J* = 17.2 Hz, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.42 (d, *J* = 17.2 Hz, 1H), 3.47 (dd, *J* = 11.6, 5.0 Hz, 1H), 3.33 (q, *J* = 7.2 Hz, 2H), 3.26 (dd, *J* = 11.6, 6.2 Hz, 1H), 2.86 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.68 (dd, *J* = 16.3, 8.4 Hz, 1H), 2.61 – 2.49 (m, 1H), 1.15 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.8, 143.7, 139.5, 129.6, 128.8, 128.6, 128.5, 127.2, 126.6, 126.6, 121.9, 120.8, 116.4, 115.2, 112.3, 110.2, 58.5, 53.8, 50.5, 44.7, 30.0, 29.7, 11.1. HRMS (ESI): Calcd. for C₂₅H₂₇N₂ [M+H]⁺: 355.2169; found: 355.2172.

(2) (6a-*cis*)-12-benzyl-5-ethyl-7-methyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (P2)



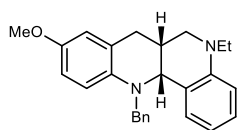
Yellow solid; m.p. : 146-148 °C, (52.3 mg, 71% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.16 (m, 2H), 7.15 – 7.12 (m, 1H), 7.11 – 7.06 (m, 4H), 7.01 – 6.93 (m, 1H), 6.91 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.64 (td, *J* = 7.3, 1.2 Hz, 1H), 6.56 – 6.51 (m, 2H), 6.44 (td, *J* = 7.3, 1.2 Hz, 1H), 4.75 (d, *J* = 17.4 Hz, 1H), 4.50 (d, *J* = 2.8 Hz, 1H), 4.26 (d, *J* = 17.4 Hz, 1H), 3.42 – 3.26 (m, 3H), 3.15 (dd, *J* = 11.3, 5.2 Hz, 1H), 2.79 (dd, *J* = 7.2, 3.0 Hz, 1H), 2.24 – 2.16 (m, 1H), 1.41 (d, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 144.4, 143.3, 139.9, 131.2, 129.5, 129.4, 128.3, 127.3, 126.4, 126.2, 125.8, 120.8, 116.5, 114.4, 113.0, 110.3, 54.0, 51.1, 48.9, 44.6, 36.7, 33.5, 24.5, 11.2. HRMS (ESI): Calcd. for C₂₆H₂₉N₂ [M+H]⁺: 369.2325; found: 369.2321.

(3) (6a-*cis*)-12-benzyl-5-ethyl-9-methyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (P3)



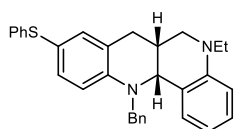
Yellow solid; m.p. : 113-115 °C, (68.4 mg, 93% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.19 – 7.11 (m, 4H), 7.09 – 7.03 (m, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.69 (s, 1H), 6.68 (s, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 6.42 – 6.36 (m, 2H), 4.79 (d, *J* = 17.0 Hz, 1H), 4.38 (d, *J* = 3.4 Hz, 1H), 4.31 (d, *J* = 17.0 Hz, 1H), 3.37 (dd, *J* = 11.6, 5.0 Hz, 1H), 3.21-3.24 (m, 2H), 3.19 (dd, *J* = 11.4, 6.4 Hz, 1H), 2.77 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.57 (dd, *J* = 16.4, 8.2 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.08 (s, 3H), 1.06 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.7, 140.3, 138.7, 129.2, 127.8, 127.5, 127.3, 126.6, 125.5, 125.4, 124.3, 120.9, 119.7, 114.0, 111.4, 109.1, 57.3, 52.8, 49.4, 43.6, 28.9, 28.5, 19.2, 10.0. HRMS (ESI): Calcd. for C₂₆H₂₉N₂ [M+H]⁺: 369.2325; found: 369.2320.

(4) (6a-*cis*)-12-benzyl-5-ethyl-9-methoxy-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6] naphthyridine (**P4**)



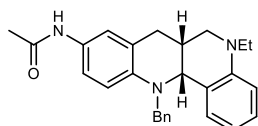
Brown solid; m.p. : 129-131 °C, (49.1 mg, 64% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 5.4 Hz, 4H), 7.17 (q, *J* = 5.6, 4.6 Hz, 1H), 7.06 (t, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.59 – 6.51 (m, 4H), 6.48 (t, *J* = 7.4 Hz, 1H), 4.82 (d, *J* = 17.0 Hz, 1H), 4.42 (d, *J* = 3.4 Hz, 1H), 4.38 (d, *J* = 16.8 Hz, 1H), 3.67 (s, 3H), 3.46 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.34 (q, *J* = 7.0, 3.6 Hz, 2H), 3.29 (dd, *J* = 11.6, 6.2 Hz, 1H), 2.87 (dd, *J* = 16.6, 5.6 Hz, 1H), 2.67 (dd, *J* = 16.6, 8.2 Hz, 1H), 2.57 – 2.49 (m, 1H), 1.15 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 151.2, 143.8, 140.0, 138.1, 128.9, 128.5, 128.4, 126.7, 126.6, 122.5, 121.9, 115.3, 115.1, 114.1, 112.6, 110.1, 58.2, 55.6, 54.7, 50.5, 44.7, 29.7, 29.6, 11.1. HRMS (ESI): Calcd. for C₂₆H₂₉N₂O [M+H]⁺: 385.2274; found: 385.2269.

(5) (6a-*cis*)-12-benzyl-5-ethyl-9-(phenylthio)-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6] naphthyridine (**P5**)



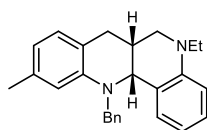
Brown solid; m.p. : 130-132 °C, (62.8 mg, 68% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.15 (m, 2H), 7.14 – 7.05 (m, 5H), 7.05 – 6.93 (m, 6H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.51 – 6.41 (m, 3H), 4.87 (d, *J* = 17.2 Hz, 1H), 4.46 (d, *J* = 3.4 Hz, 1H), 4.38 (d, *J* = 17.2 Hz, 1H), 3.42 (dd, *J* = 11.8, 5.0 Hz, 1H), 3.25 (q, *J* = 7.2 Hz, 2H), 3.14 (dd, *J* = 11.6, 5.8 Hz, 1H), 2.72 (dd, *J* = 16.4, 5.2 Hz, 1H), 2.63 – 2.53 (m, 1H), 2.52 – 2.33 (m, 1H), 1.07 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.0, 142.5, 138.9, 137.7, 134.9, 132.9, 127.7, 127.5, 127.5, 126.1, 125.8, 125.4, 124.0, 120.9, 120.3, 116.3, 114.1, 111.8, 109.2, 57.6, 52.8, 49.3, 43.6, 28.7, 28.4, 10.0. HRMS (ESI): Calcd. for C₃₁H₃₁N₂S [M+H]⁺: 463.2202; found: 463.2193.

(6) N-((6a-*cis*)-12-benzyl-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridin-9-yl)-acetamide (**P6**)



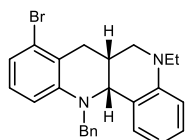
Orange solid; m.p. : 121-123 °C, (74.8 mg, 91% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.15 (m, 6H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.92 (t, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 8.2 Hz, 1H), 6.50 – 6.44 (m, 2H), 4.87 (d, *J* = 17.0 Hz, 1H), 4.46 (d, *J* = 3.4 Hz, 1H), 4.39 (d, *J* = 17.0 Hz, 1H), 3.44 (dd, *J* = 11.6, 5.0 Hz, 1H), 3.32 (q, *J* = 7.2 Hz, 2H), 3.23 (dd, *J* = 11.6, 6.2 Hz, 1H), 2.81 (dd, *J* = 16.6, 5.6 Hz, 1H), 2.64 (dd, *J* = 16.6, 8.4 Hz, 1H), 2.53 – 2.47 (m, 1H), 2.02 (s, 3H), 1.14 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 168.3, 143.7, 140.9, 139.4, 128.8, 128.6, 128.5, 127.2, 126.7, 126.6, 122.8, 121.7, 121.3, 120.3, 115.1, 112.5, 110.2, 58.4, 54.0, 50.4, 44.6, 29.8, 29.6, 24.2, 11.0. HRMS (ESI): Calcd. for C₂₇H₃₀N₃O [M+H]⁺: 412.2383; found: 412.2375.

(7) (6a-*cis*)-12-benzyl-5-ethyl-10-methyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P7**)



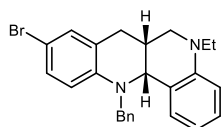
Yellow solid; m.p. : 111-113 °C, (59.6 mg, 81% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.06 (m, 5H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 1H), 6.40 (t, *J* = 7.5 Hz, 1H), 6.37 – 6.31 (m, 2H), 4.84 (d, *J* = 17.2 Hz, 1H), 4.38 (d, *J* = 3.2 Hz, 1H), 4.33 (d, *J* = 17.0 Hz, 1H), 3.37 (dd, *J* = 11.6, 5.0 Hz, 1H), 3.24 (q, *J* = 7.4 Hz, 2H), 3.17 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.74 (dd, *J* = 16.4, 5.2 Hz, 1H), 2.55 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.47 – 2.37 (m, 1H), 2.08 (s, 3H), 1.06 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.7, 142.5, 138.5, 135.6, 128.4, 127.7, 127.4, 127.3, 125.5, 125.5, 120.8, 116.8, 116.2, 114.0, 111.8, 109.0, 57.2, 52.6, 49.4, 43.5, 29.0, 28.3, 20.6, 10.0. HRMS (ESI): Calcd. for C₂₆H₂₉N₂ [M+H]⁺: 369.2325; found: 369.2315.

(8) (6a-*cis*)-12-benzyl-8-bromo-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6] naphthyridine (**P8**)



Brown solid; m.p. : 125-127 °C, (34.64 mg, 40% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.26 (m, 5H), 7.20 – 7.09 (m, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.69 – 6.55 (m, 3H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.60 (d, *J* = 3.4 Hz, 1H), 4.55 (d, *J* = 17.2 Hz, 1H), 3.62 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.44 (q, *J* = 7.2 Hz, 2H), 3.36 (dd, *J* = 11.8, 5.4 Hz, 1H), 3.03 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.72 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.68 – 2.58 (m, 1H), 1.26 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 144.0, 142.6, 137.8, 127.7, 127.5, 127.3, 126.8, 125.8, 125.4, 125.0, 120.2, 119.4, 114.2, 110.3, 109.3, 57.3, 53.5, 49.5, 43.6, 29.3, 28.8, 10.0. HRMS (ESI): Calcd. for C₂₅H₂₆BrN₂ [M+H]⁺: 433.1274; found: 433.1268.

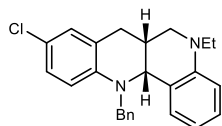
(9) (6a-*cis*)-12-benzyl-9-bromo-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P9**)



Brown solid; m.p. : 139-141 °C, (38.1 mg, 44% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.22 (m, 2H), 7.21 – 7.16 (m, 3H), 7.10 – 7.05 (m, 1H), 7.04 – 6.98 (m, 2H), 6.92 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 6.50 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 8.6 Hz, 1H), 4.89 (d, *J* = 17.2 Hz, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.42 (d, *J* = 17.2 Hz, 1H), 3.50 (dd, *J* = 11.2, 5.0 Hz, 1H), 3.33 (q, *J* = 7.0 Hz, 2H), 3.23 (dd, *J* = 11.6, 5.8 Hz, 1H), 2.81 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.66 (dd, *J* = 16.6, 8.8 Hz, 1H), 2.57 – 2.50 (m, 1H), 1.16 (t, *J* = 5.0, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.6, 142.6, 138.8, 131.9, 129.8, 128.7, 128.6, 128.5, 126.8, 126.4, 123.1, 121.3, 115.2, 113.8, 110.3,

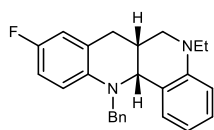
108.1, 58.5, 54.0, 50.3, 44.6, 29.7, 29.4, 11.0. HRMS (ESI): Calcd. for C₂₅H₂₆BrN₂ [M+H]⁺: 433.1274; found: 433.1269.

(10) (6a-*cis*)-12-benzyl-9-chloro-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P10**)



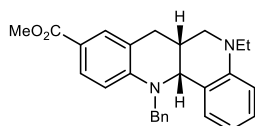
Yellow solid; m.p. : 138-140 °C, (31.0 mg, 40% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.16 (m, 2H), 7.14 – 7.09 (m, 3H), 7.00 – 6.89 (m, 1H), 6.87 – 6.79 (m, 3H), 6.51 – 6.47 (m, 1H), 6.46 – 6.35 (m, 2H), 4.83 (d, *J* = 17.2 Hz, 1H), 4.43 (d, *J* = 3.6 Hz, 1H), 4.36 (d, *J* = 17.2 Hz, 1H), 3.43 (dd, *J* = 11.6, 5.0 Hz, 1H), 3.27 (q, *J* = 7.0 Hz, 2H), 3.16 (dd, *J* = 11.6, 5.8 Hz, 1H), 2.74 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.59 (dd, *J* = 16.6, 8.8 Hz, 1H), 2.51 – 2.38 (m, 1H), 1.08 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.6, 142.1, 138.9, 129.1, 128.7, 128.6, 126.9, 126.8, 126.5, 122.6, 121.4, 120.9, 115.2, 113.4, 110.3, 58.5, 54.1, 50.4, 44.6, 29.7, 29.4, 11.0. HRMS (ESI): Calcd. for C₂₅H₂₆ClN₂ [M+H]⁺: 389.1779; found: 389.1772.

(11) (6a-*cis*)-12-benzyl-5-ethyl-9-fluoro-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P11**)



Brown solid; m.p. : 81-83 °C, (46.2 mg, 62% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.16 (m, 5H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.52 – 6.41 (m, 2H), 4.87 (d, *J* = 17.0 Hz, 1H), 4.47 (d, *J* = 3.2 Hz, 1H), 4.42 (d, *J* = 17.0 Hz, 1H), 3.50 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.35 (q, *J* = 7.2 Hz, 2H), 3.26 (dd, *J* = 11.6, 5.8 Hz, 1H), 2.83 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.67 (dd, *J* = 16.8, 8.6 Hz, 1H), 2.59 – 2.49 (m, 1H), 1.11 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 156.0, 154.2, 143.7, 140.0, 139.4, 128.7, 128.5, 127.7 (d, *J* = 237.0 Hz), 126.6, 122.5 (d, *J* = 6.4 Hz), 121.6, 115.8 (d, *J* = 22.68 Hz), 115.2, 113.4 (d, *J* = 21.42 Hz), 113.4 (d, *J* = 7.56 Hz), 110.2, 58.4, 54.7, 50.5, 44.7, 29.6, 29.5, 11.1. ¹⁹F NMR (471 MHz, CDCl₃) δ -129.45(s). HRMS (ESI): Calcd. for C₂₅H₂₆FN₂ [M+H]⁺: 373.2075; found: 373.2068.

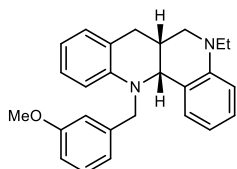
(12) methyl((6a-*cis*)-12-benzyl-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine)-9-carboxylate (**P12**)



Yellow solid; m.p. : 151-153 °C, (49.4 mg, 60% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.66 (s, 1H), 7.64 (s, 1H), 7.30 – 7.14 (m, 5H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 9.4 Hz, 2H), 6.53 – 6.50 (m, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 4.58 (d, *J* = 4.6 Hz, 1H), 4.51 (d, *J* = 17.2 Hz, 1H), 3.80 (s, 3H), 3.52 (dd, *J* = 12.0, 5.0 Hz, 1H), 3.34 – 3.30 (m, 2H), 3.22 (dd, *J* = 11.8, 5.8 Hz, 1H), 2.87 (dd, *J* = 16.4, 5.2 Hz, 1H), 2.72 (dd, *J* = 16.4, 9.0 Hz, 1H), 2.60 – 2.51 (m, 1H), 1.16

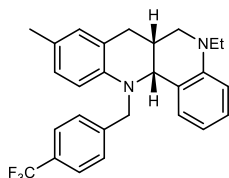
(t, $J = 5.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.4, 147.5, 143.6, 138.1, 131.3, 129.5, 128.9, 128.7, 128.4, 127.0, 126.4, 121.0, 120.1, 117.4, 115.3, 111.0, 110.4, 58.8, 53.7, 51.5, 50.2, 44.6, 29.7, 29.5, 11.0. HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 413.2224; found: 413.2216.

(13) (6a-*cis*)-5-ethyl-12-(3-methoxybenzyl)-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P13**)



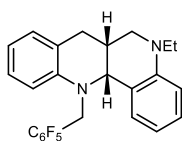
Black solid; m.p. : 79-81 °C, (72.3 mg, 94% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.19 – 7.12 (m, 1H), 7.06 (t, $J = 7.8$ Hz, 1H), 6.98 – 6.88 (m, 3H), 6.81 (d, $J = 7.6$ Hz, 1H), 6.76 (s, 1H), 6.71 (d, $J = 8.2$ Hz, 1H), 6.59 – 6.52 (m, 3H), 6.49 (t, $J = 7.3$ Hz, 1H), 4.88 (d, $J = 17.2$ Hz, 1H), 4.49 (d, $J = 3.4$ Hz, 1H), 4.40 (d, $J = 17.2$ Hz, 1H), 3.71 (s, 3H), 3.47 (dd, $J = 11.6, 5.0$ Hz, 1H), 3.32 (q, $J = 7.6$ Hz, 2H), 3.25 (dd, $J = 11.6, 6.2$ Hz, 1H), 2.85 (dd, $J = 16.4, 5.4$ Hz, 1H), 2.67 (dd, $J = 16.4, 8.4$ Hz, 1H), 2.58 – 2.49 (m, 1H), 1.15 (t, $J = 5.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.9, 143.8, 143.7, 141.4, 129.6, 129.5, 128.8, 128.6, 127.2, 121.9, 120.9, 118.9, 116.44, 115.2, 112.4, 112.4, 111.8, 110.2, 58.5, 55.2, 53.9, 50.5, 44.7, 30.0, 29.7, 11.1. HRMS (ESI): Calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 385.2274; found: 385.2266.

(14) (6a-*cis*)-5-ethyl-9-methyl-12-(4-(trifluoromethyl)benzyl)-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P14**)



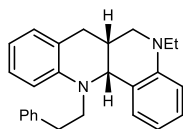
White solid; m.p. : 112-114 °C, (83.7 mg, 96% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.97 (m, 1H), 6.84 (d, $J = 7.4$ Hz, 1H), 6.76 – 6.66 (m, 2H), 6.46 (d, $J = 8.4$ Hz, 1H), 6.39 (t, $J = 7.4$ Hz, 1H), 6.29 (d, $J = 8.2$ Hz, 1H), 4.77 (d, $J = 17.4$ Hz, 1H), 4.35 (d, $J = 3.0$ Hz, 1H), 4.30 (d, $J = 17.4$ Hz, 1H), 3.36 – 3.19 (m, 4H), 2.88 (dd, $J = 16.6, 5.6$ Hz, 1H), 2.58 (dd, $J = 16.6, 6.8$ Hz, 1H), 2.49 – 2.43 (m, 1H), 2.09 (s, 3H), 1.07 (t, $J = 5.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.5, 143.9, 141.3, 130.5, 129.4, 129.0, 128.8 (q, $J = 32.76$ Hz), 127.9, 126.8, 126.0, 125.4 (q, $J = 3.78$ Hz), 124.4 (q, $J = 272.16$ Hz), 121.5, 120.9, 115.0, 112.5, 110.3, 58.6, 53.1, 50.0, 44.6, 30.2, 29.8, 20.3, 11.1. ^{19}F NMR (471 MHz, CDCl_3) δ -62.19. HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{28}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 437.2199; found: 437.2194.

(15) (6a-*cis*)-5-ethyl-12-((perfluorophenyl)methyl)-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P15**)



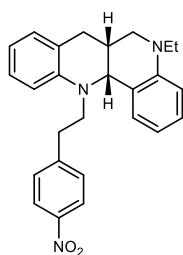
Black solid; m.p. : 56-58 °C, (55.9 mg, 63% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.04 (q, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.71 – 6.60 (m, 1H), 6.54 – 6.45 (m, 2H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.59 (d, *J* = 3.8 Hz, 1H), 4.51 (d, *J* = 16.0 Hz, 1H), 3.65 (dd, *J* = 11.8, 4.4 Hz, 1H), 3.39 – 3.26 (m, 2H), 3.18 (dd, *J* = 11.8, 4.0 Hz, 1H), 2.74 – 2.60 (m, 2H), 2.53 – 2.44 (m, 1H), 1.16 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 146.5-144.5 (m), 143.5, 142.1, 141.4-136.4 (m), 129.9, 128.4, 127.6, 127.0, 122.5, 121.4, 117.7, 115.3, 112.9-112.7 (m), 112.4, 109.9, 59.2, 51.1, 45.0, 44.7, 28.5, 28.3, 10.9. ¹⁹F NMR (471 MHz, CDCl₃) δ -142.4 (dd, *J* = 23.6, 8.0 Hz), -155.5 (t, *J* = 20.9 Hz), -162.1 (td, *J* = 22.2, 8.4 Hz). HRMS (ESI): Calcd. for C₂₅H₂₂F₅N₂ [M+H]⁺: 445.1698; found: 445.1688.

(16) (6a-*cis*)-5-ethyl-12-phenethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P16**)



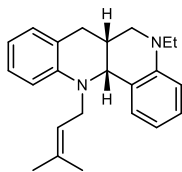
Black oil; (62.6 mg, 85% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.15 (m, 2H), 7.12 – 7.07 (m, 1H), 7.06 – 6.97 (m, 4H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.54 – 6.41 (m, 3H), 4.16 (d, *J* = 3.6 Hz, 1H), 3.92 – 3.80 (m, 1H), 3.34 (dd, *J* = 15.6, 8.0 Hz, 1H), 3.28 (dd, *J* = 12.3, 5.6 Hz, 1H), 3.22 (q, *J* = 7.2 Hz, 2H), 3.06 (dd, *J* = 11.6, 5.8 Hz, 1H), 2.85 – 2.76 (m, 1H), 2.71 – 2.61 (m, 2H), 2.52 (dd, *J* = 16.3, 8.8 Hz, 1H), 2.23 – 2.16 (m, 1H), 1.04 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.6, 142.9, 139.8, 129.8, 129.0, 128.7, 128.6, 128.5, 127.3, 126.2, 122.1, 121.0, 115.8, 115.2, 111.1, 110.1, 58.4, 52.3, 50.4, 44.7, 33.7, 29.6, 29.4, 11.0. HRMS (ESI): Calcd. for C₂₆H₂₉N₂ [M+H]⁺: 369.2320; found: 369.2320.

(17) (6a-*cis*)-5-ethyl-12-(4-nitrophenethyl)-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P17**)



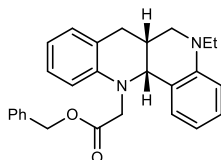
Brown solid; m.p. : 105-107 °C, (67.7 mg, 82% yield); ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.12 (t, *J* = 8.1 Hz, 2H), 7.01 – 6.91 (m, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.59 – 6.52 (m, 2H), 4.21 (d, *J* = 3.4 Hz, 1H), 3.90 (t, *J* = 12.4 Hz, 1H), 3.41 (dt, *J* = 15.8, 8.4 Hz, 1H), 3.35 – 3.26 (m, 3H), 3.17 (dd, *J* = 12.0, 7.0 Hz, 1H), 3.02 – 2.92 (m, 1H), 2.84 (dd, *J* = 16.6, 5.2 Hz, 1H), 2.78 – 2.69 (m, 1H), 2.61 (dd, *J* = 16.5, 7.8 Hz, 1H), 2.33 – 2.26 (m, 1H), 1.12 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 147.7, 146.6, 143.8, 142.7, 130.0, 129.8, 129.0, 129.0, 127.4, 123.7, 121.5, 121.0, 116.4, 115.0, 111.1, 110.3, 58.5, 51.4, 49.9, 44.6, 33.9, 29.7, 29.6, 11.0. HRMS (ESI): Calcd. for C₂₆H₂₈N₃O₂ [M+H]⁺: 414.2176; found: 414.2167.

(18) (6a-*cis*)-5-ethyl-12-(3-methylbut-2-en-1-yl)-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P18**)



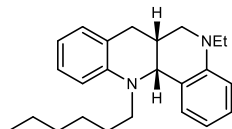
Black oil; (47.1 mg, 71% yield); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.04 – 6.90 (m, 3H), 6.83 (d, $J = 7.4$ Hz, 1H), 6.58 (d, $J = 8.4$ Hz, 1H), 6.54 – 6.40 (m, 3H), 5.20 – 5.10 (m, 1H), 4.32 (d, $J = 3.6$ Hz, 1H), 4.15 (dd, $J = 16.8, 5.6$ Hz, 1H), 3.74 (dd, $J = 16.7, 6.4$ Hz, 1H), 3.40 (dd, $J = 11.6, 4.8$ Hz, 1H), 3.25 (q, $J = 7.2$ Hz, 2H), 3.13 (dd, $J = 11.5, 5.9$ Hz, 1H), 2.70 (dd, $J = 16.5, 5.5$ Hz, 1H), 2.55 (dd, $J = 16.5, 9.0$ Hz, 1H), 2.34 – 2.29 (m, 1H), 1.61 (s, 3H), 1.56 (s, 3H), 1.07 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.6, 142.5, 132.9, 128.5, 128.0, 127.3, 126.0, 121.3, 120.7, 120.3, 114.9, 114.1, 111.1, 109.0, 56.4, 49.4, 47.1, 43.6, 28.6, 28.5, 24.7, 17.0, 9.9. HRMS (ESI): Calcd. for $\text{C}_{23}\text{H}_{29}\text{N}_2$ $[\text{M}+\text{H}]^+$: 333.2325; found: 333.2317.

(19) Benzyl 2-((6a-*cis*)-5-ethyl-5,6a,7,12a-tetrahydrodibenzo[b,h][1,6]naphthyridin-12(6H)-yl)acetate (**P19**)



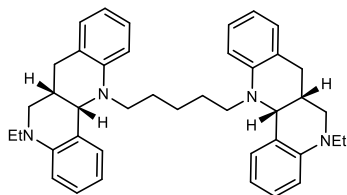
Yellow solid; m.p. : 67-69 °C, (18.2 mg, 22% yield); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 – 7.29 (m, 3H), 7.28 – 7.22 (m, 2H), 7.12 (t, $J = 7.8$ Hz, 1H), 7.03 (t, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 7.4$ Hz, 1H), 6.90 – 6.72 (m, 1H), 6.59 (d, $J = 8.4$ Hz, 1H), 6.50 – 6.45 (m, 2H), 5.13 (s, 2H), 4.52 (d, $J = 3.8$ Hz, 1H), 4.20 (d, $J = 18.4$ Hz, 1H), 3.88 (d, $J = 18.4$ Hz, 1H), 3.33 – 3.25 (m, 3H), 3.21 (dd, $J = 11.4, 5.2$ Hz, 1H), 3.08 (dd, $J = 16.6, 5.8$ Hz, 1H), 2.65 (dd, $J = 16.6, 4.8$ Hz, 1H), 2.54 – 2.46 (m, 1H), 1.10 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.6, 144.0, 143.3, 135.9, 130.3, 129.8, 129.3, 128.6, 128.2, 128.2, 127.3, 121.1, 120.7, 117.4, 114.8, 111.5, 110.6, 66.5, 57.6, 49.6, 49.0, 44.7, 30.0, 29.8, 11.0. HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 413.2224; found: 413.2214.

(20) (6a-*cis*)-5-ethyl-12-hexyl-5,6,6a,7,12,12a-hexahydrodibenzo[b,h][1,6]naphthyridine (**P20**)



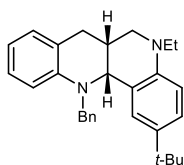
Black oil; (40.4 mg, 58% yield); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.04 – 6.95 (m, 2H), 6.90 (d, $J = 7.6$ Hz, 1H), 6.81 (d, $J = 7.4$ Hz, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 6.50 – 6.38 (m, 3H), 4.31 (d, $J = 4.0$ Hz, 1H), 3.69 – 3.54 (m, 1H), 3.48 (dd, $J = 11.6, 4.6$ Hz, 1H), 3.26 (p, $J = 7.1$ Hz, 2H), 3.13 – 3.04 (m, 2H), 2.63 (dd, $J = 16.4, 5.2$ Hz, 1H), 2.54 (dd, $J = 16.4, 9.4$ Hz, 1H), 2.36 – 2.27 (m, 1H), 1.57 – 1.45 (m, 2H), 1.24 – 1.15 (m, 6H), 1.08 (t, $J = 7.1$ Hz, 3H), 0.81 (t, $J = 5.8$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 143.6, 143.3, 129.6, 128.4, 128.3, 127.1, 122.5, 121.0, 115.5, 115.3, 111.3, 110.1, 58.3, 51.0, 50.9, 44.7, 31.7, 29.5, 29.4, 27.1, 26.8, 22.7, 14.1, 11.0. HRMS (ESI): Calcd. for $\text{C}_{24}\text{H}_{33}\text{N}_2$ $[\text{M}+\text{H}]^+$: 349.2638; found: 349.2634.

(21) 1-((6a-*cis*)-5-ethyl-5,6a,7,12a-tetrahydrodibenzo[*b,h*][1,6]naphthyridin-12(6H)-yl)-5-((6a-*cis*)-5-ethyl-5,6a,7,12a-tetrahydrodibenzo[*b,h*][1,6]naphthyridin-12(6H)-yl)pentane (**P21**)



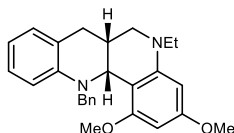
Brown solid, m.p. : 67-69 °C (84.6 mg, 71% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.05 (q, *J* = 7.2 Hz, 4H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 7.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.58 – 6.45 (m, 6H), 4.34 (d, *J* = 3.4 Hz, 2H), 3.75 – 3.63 (m, 2H), 3.52 (td, *J* = 11.7, 4.6 Hz, 2H), 3.39 – 3.25 (m, 4H), 3.14 (dq, *J* = 14.6, 8.0, 7.2 Hz, 4H), 2.74 – 2.66 (m, 2H), 2.60 (dd, *J* = 16.4, 9.6 Hz, 2H), 2.43 – 2.30 (m, 2H), 1.66 – 1.53 (m, 4H), 1.35 – 1.23 (m, 2H), 1.20 – 1.08 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 143.6, 143.2, 129.7, 128.3, 128.3, 127.1, 122.4, 121.0, 115.6, 115.2, 111.3, 110.1, 58.3, 50.8, 44.7, 29.5, 29.4, 29.4, 27.2, 24.7, 24.7, 11.0. HRMS (ESI): Calcd. for C₄₁H₄₉N₄ [M+H]⁺: 597.3952; found: 597.3941.

(22) (6a-*cis*)-12-benzyl-2-(tert-butyl)-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P22**)



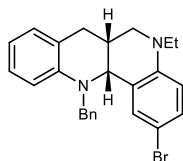
White solid; m.p. : 102-104 °C, (59.9 mg, 73% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.24 (m, 2H), 7.21 (d, *J* = 7.2 Hz, 3H), 7.12 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.67 – 6.58 (m, 2H), 6.54 (d, *J* = 8.6 Hz, 1H), 4.85 (d, *J* = 17.4 Hz, 1H), 4.56 (d, *J* = 3.2 Hz, 1H), 4.40 (d, *J* = 17.4 Hz, 1H), 3.42 – 3.27 (m, 4H), 3.07 (dd, *J* = 16.6, 5.6 Hz, 1H), 2.76 (dd, *J* = 16.6, 6.4 Hz, 1H), 2.63 – 2.53 (m, 1H), 1.21 – 1.14 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 144.0, 141.6, 139.5, 137.3, 129.5, 128.3, 127.2, 126.7, 126.6, 126.4, 125.5, 120.9, 120.7, 116.3, 112.5, 109.8, 58.2, 52.8, 49.8, 44.7, 33.5, 31.5, 30.0, 11.2, 1.1. HRMS (ESI): Calcd. for C₂₉H₃₅N₂ [M+H]⁺: 411.2795; found: 411.2787.

(23) (6a-*cis*)-12-benzyl-5-ethyl-1,3-dimethoxy-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P23**)



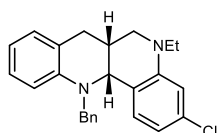
Brown solid; m.p. : 87-89 °C, (65.4 mg, 79% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.22 (m, 5H), 7.09 – 7.03 (m, 2H), 6.72 – 6.64 (m, 2H), 6.56 (s, 1H), 6.29 (s, 1H), 4.92 (d, *J* = 17.2 Hz, 1H), 4.55 (d, *J* = 3.2 Hz, 1H), 4.47 (d, *J* = 17.4 Hz, 1H), 3.91 (s, 3H), 3.67 (s, 3H), 3.48 – 3.29 (m, 4H), 3.08 (dd, *J* = 16.6, 5.8 Hz, 1H), 2.81 (dd, *J* = 16.6, 6.8 Hz, 1H), 2.66 – 2.55 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 143.9, 139.6, 139.5, 138.9, 129.6, 128.5, 127.3, 126.7, 126.6, 120.8, 116.5, 114.9, 113.5, 112.6, 96.5, 57.6, 56.9, 56.0, 53.1, 50.0, 45.3, 30.3, 29.9, 11.3. HRMS (ESI): Calcd. for C₂₇H₃₁N₂O₂ [M+H]⁺: 415.2380; found: 415.2373.

(24) (6a-*cis*)-12-benzyl-2-bromo-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P24**)



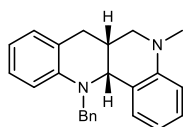
White solid; m.p. : 134-136 °C, (27.6 mg, 32% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.23 (m, 5H), 7.17 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.11 – 6.96 (m, 3H), 6.73 – 6.63 (m, 2H), 6.45 (d, *J* = 8.8 Hz, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 4.60 – 4.41 (m, 2H), 3.56 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.36 (q, *J* = 7.2 Hz, 2H), 3.29 (dd, *J* = 11.6, 5.4 Hz, 1H), 2.87 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.73 (dd, *J* = 16.3, 9.2 Hz, 1H), 2.60 – 2.51 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 142.6, 139.1, 131.1, 130.9, 129.6, 128.6, 127.3, 126.8, 126.6, 124.1, 120.7, 116.7, 112.5, 111.8, 106.8, 58.2, 54.3, 50.7, 44.7, 29.5, 29.4, 10.9. HRMS (ESI): Calcd. for C₂₅H₂₆BrN₂ [M+H]⁺: 433.1274; found: 433.1267.

(25) (6a-*cis*)-12-benzyl-3-chloro-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P25**)



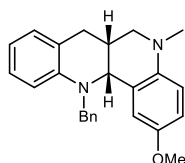
Black solid; m.p. : 90-92 °C, (34.9 mg, 45% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.21 (m, 5H), 7.06 – 6.97 (m, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.68 – 6.61 (m, 2H), 6.55 (d, *J* = 1.9 Hz, 1H), 6.50 (dd, *J* = 8.0, 1.8 Hz, 1H), 4.95 (d, *J* = 17.0 Hz, 1H), 4.50 (d, *J* = 3.4 Hz, 1H), 4.46 (d, *J* = 17.2 Hz, 1H), 3.53 (dd, *J* = 11.7, 4.9 Hz, 1H), 3.42 – 3.28 (m, 3H), 2.93 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.72 (dd, *J* = 16.4, 8.6 Hz, 1H), 2.62 – 2.48 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.7, 143.4, 139.2, 134.3, 129.7, 129.6, 128.5, 127.3, 126.7, 126.5, 120.7, 120.2, 116.7, 114.8, 112.6, 109.8, 57.9, 53.9, 50.3, 44.7, 29.5, 29.3, 10.9. HRMS (ESI): Calcd. for C₂₅H₂₆ClN₂ [M+H]⁺: 389.1779; found: 389.1766.

(26) (6a-*cis*)-12-benzyl-5-methyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P26**)



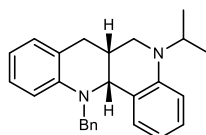
Brown solid; m.p. : 121-123 °C, (48.3 mg, 71% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.14 (m, 5H), 7.12 – 7.05 (m, 1H), 7.00 – 6.90 (m, 3H), 6.61 – 6.50 (m, 4H), 4.93 (dd, *J* = 17.1, 4.2 Hz, 1H), 4.51 (d, *J* = 7.4 Hz, 1H), 4.45 (dd, *J* = 17.1, 4.2 Hz, 1H), 3.50 (dd, *J* = 8.2, 5.6 Hz, 1H), 3.15 (dd, *J* = 11.1, 4.4 Hz, 1H), 2.88 (s, 3H), 2.84 – 2.73 (m, 1H), 2.68 – 2.55 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 145.2, 143.7, 139.4, 129.6, 128.5, 128.0, 127.3, 126.7, 126.6, 122.9, 120.8, 116.3, 116.0, 112.1, 110.6, 58.4, 53.9, 53.7, 38.2, 30.6, 30.2. HRMS (ESI): Calcd. for C₂₄H₂₅N₂ [M+H]⁺: 341.2012; found: 341.2010.

(27) (6a-*cis*)-12-benzyl-2-methoxy-5-methyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P27**)



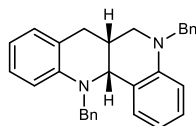
White solid; m.p. : 91-93 °C, (59.9 mg, 81% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.73 – 6.57 (m, 4H), 5.07 (d, *J* = 17.2 Hz, 1H), 4.59 (s, 1H), 4.55 (s, 1H), 3.73 (s, 3H), 3.59 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.05 (dd, *J* = 11.2, 3.8 Hz, 1H), 2.92 (s, 3H), 2.80 (d, *J* = 14.4 Hz, 1H), 2.75 – 2.61 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 151.44, 143.67, 139.93, 139.16, 129.43, 128.61, 127.29, 126.80, 126.62, 125.75, 121.00, 116.31, 114.47, 112.68, 111.93, 111.72, 58.55, 55.74, 54.67, 54.43, 38.71, 31.02, 30.45. HRMS (ESI): Calcd. for C₂₅H₂₇N₂O [M+H]⁺: 371.2118; found: 371.2111.

(28) (6a-*cis*)-12-benzyl-5-isopropyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P28**)



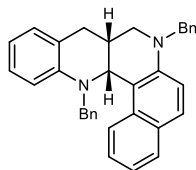
Yellow solid; m.p. : 116-118 °C, (63.3 mg, 86% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.24 (m, 5H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.09 – 7.00 (m, 3H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.71 – 6.64 (m, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.58 (d, *J* = 3.2 Hz, 1H), 4.53 (d, *J* = 17.2 Hz, 1H), 4.21 (p, *J* = 6.8 Hz, 1H), 3.47 (dd, *J* = 11.5, 5.4 Hz, 1H), 3.30 (dd, *J* = 11.5, 6.2 Hz, 1H), 2.95 (dd, *J* = 16.2, 5.4 Hz, 1H), 2.74 (dd, *J* = 16.2, 8.2 Hz, 1H), 2.68 – 2.57 (m, 1H), 1.33 (d, *J* = 6.8 Hz, 3H), 1.29 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.3, 143.8, 139.6, 129.7, 128.9, 128.7, 128.5, 127.2, 126.7, 126.6, 122.4, 120.8, 116.4, 115.0, 112.3, 110.5, 58.6, 53.7, 46.9, 42.8, 29.9, 29.8, 19.2, 18.7. HRMS (ESI): Calcd. for C₂₆H₂₉N₂ [M+H]⁺: 369.2325; found: 369.2316.

(29) (6a-*cis*)-5,12-dibenzyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P29**)



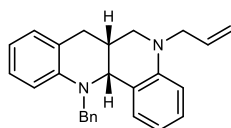
Brown solid; m.p. : 115-117 °C, (63.2 mg, 76% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.24 (m, 10H), 7.12 – 6.98 (m, 4H), 6.74 – 6.52 (m, 4H), 5.03 (dd, *J* = 17.2, 2.2 Hz, 1H), 4.67 (d, *J* = 5.4 Hz, 1H), 4.63 – 4.48 (m, 3H), 3.62 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.44 (dd, *J* = 11.5, 6.2 Hz, 1H), 2.98 (dd, *J* = 16.5, 5.4 Hz, 1H), 2.85 (dd, *J* = 16.3, 8.4 Hz, 1H), 2.70 (dd, *J* = 8.8, 2.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.6, 143.7, 139.5, 138.6, 129.7, 128.8, 128.7, 128.6, 127.3, 127.1, 126.7, 126.7, 126.6, 122.0, 120.8, 116.5, 116.0, 112.4, 111.1, 58.5, 54.5, 53.8, 51.6, 30.5, 29.8. HRMS (ESI): Calcd. for C₃₀H₂₉N₂ [M+H]⁺: 417.2325; found: 417.2317.

(30) (8a-*cis*)-7,14-dibenzyl-7,8,8a,9,14,14a-hexahydrobenzo[*b*]naphtho[2,1-*h*][1,6]naphthyridine (P30)



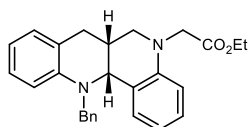
Brown solid; m.p. : 111-113 °C, (40.0 mg, 43% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 9.2 Hz, 1H), 7.36 – 7.21 (m, 6H), 7.15 – 7.02 (m, 5H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 2H), 6.87 (d, *J* = 9.2 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.34 (s, 1H), 4.74 (d, *J* = 17.4 Hz, 1H), 4.42 (d, *J* = 17.4 Hz, 2H), 4.21 (d, *J* = 17.0 Hz, 1H), 3.69 (t, *J* = 12.2 Hz, 1H), 3.46 (dd, *J* = 16.9, 6.4 Hz, 1H), 3.30 (dd, *J* = 11.2, 5.5 Hz, 1H), 2.74 (d, *J* = 17.0 Hz, 1H), 2.69 – 2.60 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 144.7, 143.2, 141.1, 138.4, 134.1, 130.0, 129.7, 128.8, 128.6, 128.0, 127.3, 127.1, 126.8, 126.5, 126.4, 126.2, 126.0, 121.0, 120.9, 120.2, 116.7, 114.9, 113.4, 110.7, 54.6, 52.0, 50.3, 48.6, 31.2, 30.9. HRMS (ESI): Calcd. for C₃₄H₃₁N₂ [M+H]⁺: 467.2482; found: 467.2480.

(31) (6a-*cis*)-5-allyl-12-benzyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (P31)



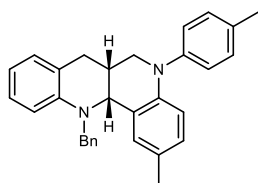
Brown solid; m.p. : 85-87 °C, (63.0 mg, 86% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.20 (m, 5H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.06 – 6.97 (m, 3H), 6.65 (d, *J* = 7.8 Hz, 2H), 6.62 – 6.55 (m, 2H), 5.96 – 5.83 (m, 1H), 5.26 (dd, *J* = 11.4, 1.8 Hz, 1H), 5.23 – 5.21 (m, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 4.60 (d, *J* = 3.4 Hz, 1H), 4.51 (d, *J* = 17.2 Hz, 1H), 3.94 (d, *J* = 4.9 Hz, 2H), 3.55 (dd, *J* = 11.4, 5.2 Hz, 1H), 3.36 (dd, *J* = 11.4, 6.0 Hz, 1H), 2.95 (dd, *J* = 16.2, 5.4 Hz, 1H), 2.77 (dd, *J* = 16.3, 8.4 Hz, 1H), 2.69 – 2.60 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 144.1, 143.7, 139.4, 133.2, 129.6, 128.6, 128.5, 127.2, 126.6, 126.6, 121.9, 120.7, 116.4, 116.2, 115.6, 112.3, 110.8, 58.4, 53.7, 53.0, 51.0, 30.3, 29.8. HRMS (ESI): Calcd. for C₂₆H₂₇N₂ [M+H]⁺: 367.2169; found: 367.2162.

(32) ethyl 2-((6a-*cis*)-12-benzyl-6a,7,12,12a-tetrahydrodibenzo[*b,h*][1,6]naphthyridin-5(6H)-yl)-acetate (P32)



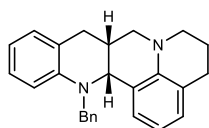
Brown solid; m.p. : 113-115 °C, (41.2 mg, 50% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.21 (m, 5H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.05 – 6.95 (m, 3H), 6.70 – 6.56 (m, 3H), 6.41 (d, *J* = 8.2 Hz, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 4.61 (d, *J* = 3.4 Hz, 1H), 4.53 (d, *J* = 17.2 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.03 (d, *J* = 4.0 Hz, 2H), 3.70 (dd, *J* = 11.0, 5.2 Hz, 1H), 3.43 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.03 – 2.78 (m, 2H), 2.72 – 2.63 (m, 1H), 1.32 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 143.6, 143.5, 139.3, 129.6, 128.6, 128.5, 128.4, 127.2, 126.7, 126.6, 122.4, 120.9, 116.7, 116.4, 112.2, 110.1, 61.0, 58.3, 54.2, 52.4, 52.2, 30.2, 29.5, 14.3. HRMS (ESI): Calcd. for C₂₇H₂₉N₂O₂ [M+H]⁺: 413.2224; found: 413.2218.

(33) (6a-*cis*)-12-benzyl-2-methyl-5-(*p*-tolyl)-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthayridine (**P33**)



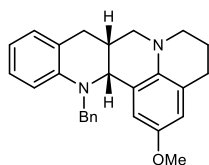
Yellow solid; m.p. : 149-151 °C, (41.3 mg, 48% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.14 (m, 4H), 7.14 – 7.09 (m, 1H), 7.07 – 7.00 (m, 4H), 6.93 – 6.85 (m, 2H), 6.77 (s, 1H), 6.70 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 4.94 (d, *J* = 17.2 Hz, 1H), 4.49 (d, *J* = 3.0 Hz, 1H), 4.42 (d, *J* = 17.2 Hz, 1H), 3.77 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.44 (dd, *J* = 11.4, 5.2 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.71 – 2.61 (m, 2H), 2.25 (s, 3H), 2.10 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 144.9, 144.0, 141.1, 139.4, 132.8, 130.0, 129.5, 129.0, 128.6, 128.5, 127.4, 127.3, 126.7, 126.5, 125.3, 123.4, 120.8, 116.4, 116.1, 112.2, 58.5, 54.0, 52.3, 32.0, 30.2, 20.9, 20.7. HRMS (ESI): Calcd. for C₃₁H₃₁N₂ [M+H]⁺: 431.2482; found: 431.2482.

(34) (8a-*cis*)-14-benzyl-5,6,8a,9,14,14a-hexahydro-4H,8H-benzo[*b*]quinolino[1,8-*gh*][1,6]naphthayridine (**P34**)



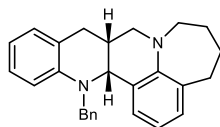
Black solid; m.p. : 99-101 °C, (51.2 mg, 70% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.24 (m, 5H), 7.13 – 7.02 (m, 2H), 6.91 (t, *J* = 7.2 Hz, 2H), 6.68 (t, *J* = 7.4 Hz, 2H), 6.52 (t, *J* = 7.4 Hz, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 4.60 (d, *J* = 3.4 Hz, 1H), 4.53 (d, *J* = 17.2 Hz, 1H), 3.51 (dd, *J* = 11.6, 5.4 Hz, 1H), 3.39 – 3.20 (m, 3H), 3.00 (dd, *J* = 16.2, 5.2 Hz, 1H), 2.89 – 2.74 (m, 3H), 2.72 – 2.62 (m, 1H), 2.08 – 1.95 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.8, 141.0, 139.7, 129.6, 128.5, 128.2, 127.3, 126.7, 126.6, 126.6, 121.4, 120.9, 120.8, 116.3, 114.8, 112.2, 58.4, 53.7, 52.2, 49.8, 30.1, 30.0, 27.8, 21.9. HRMS (ESI): Calcd. for C₂₆H₂₇N₂ [M+H]⁺: 367.2169; found: 367.2169.

(35) (8a-*cis*)-14-benzyl-2-methoxy-5,6,8a,9,14,14a-hexahydro-4H,8H-benzo[*b*]quinolino[1,8-*gh*][1,6]naphthayridine (**P35**)



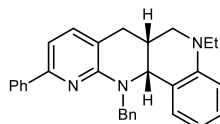
Brown solid; m.p. : 97-99 °C, (55.6 mg, 70% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.22 (m, 4H), 7.20 – 7.16 (m, 1H), 6.99 – 6.91 (m, 2H), 6.61 – 6.54 (m, 2H), 6.44 (d, *J* = 11.2 Hz, 2H), 4.95 (d, *J* = 17.0 Hz, 1H), 4.50 – 4.41 (m, 2H), 3.62 (s, 3H), 3.41 (dd, *J* = 11.4, 5.6 Hz, 1H), 3.19 (dt, *J* = 11.3, 5.8 Hz, 1H), 3.10 – 3.01 (m, 2H), 2.86 – 2.66 (m, 4H), 2.62 – 2.54 (m, 1H), 1.99 – 1.88 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 150.3, 143.6, 139.4, 135.5, 129.4, 128.5, 127.1, 126.7, 126.6, 123.1, 122.8, 121.1, 116.3, 113.5, 112.4, 112.2, 58.5, 55.7, 54.3, 53.1, 49.9, 30.2, 30.1, 27.9, 22.1. HRMS (ESI): Calcd. for C₂₇H₂₉N₂O [M+H]⁺: 397.2274; found: 397.2275.

(36) (9a-*cis*)-15-benzyl-4,5,6,7,9a,10,15,15a-octahydro-9H-azepino[3,2,1-*ij*]quinolino[3,2-*c*]quinoline (**P36**)



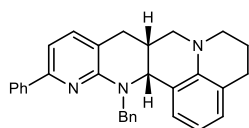
Brown solid; m.p. : 66-68 °C, (35.7 mg, 47% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.20 (m, 5H), 7.09 – 7.02 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.69 – 6.61 (m, 3H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.60 – 4.44 (m, 2H), 3.49 – 3.40 (m, 2H), 3.36 (dd, *J* = 11.1, 6.6 Hz, 1H), 3.28 – 3.20 (m, 1H), 3.04 – 2.95 (m, 1H), 2.92 – 2.79 (m, 2H), 2.76 – 2.63 (m, 2H), 1.97 – 1.75 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 144.2, 139.7, 130.9, 130.7, 129.6, 128.5, 127.2, 126.8, 126.6, 126.5, 126.4, 120.8, 117.9, 116.4, 112.3, 58.8, 54.6, 54.1, 53.1, 34.0, 32.5, 30.2, 27.8, 25.6. HRMS (ESI): Calcd. for C₂₇H₂₉N₂ [M+H]⁺: 381.2325; found: 381.2317.

(37) (6a-*cis*)-12-benzyl-5-ethyl-10-phenyl-5,6,6a,7,12,12a-hexahydrobenzo[*h*]pyrido[2,3-*b*][1,6]naphthyridine (**P37**)



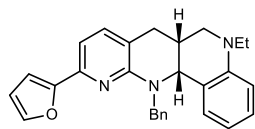
Yellow solid; m.p. : 156-158 °C, (53.4 mg, 62% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.87 – 7.84 (m, 2H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.23 – 7.14 (m, 5H), 7.13 – 7.05 (m, 2H), 7.03 – 6.96 (m, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.48 – 6.42 (m, 2H), 6.05 (d, *J* = 15.4 Hz, 1H), 4.51 (d, *J* = 3.8 Hz, 1H), 4.30 (d, *J* = 15.6 Hz, 1H), 3.41 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.23 – 3.12 (m, 2H), 3.02 (dd, *J* = 11.7, 4.6 Hz, 1H), 2.67 – 2.47 (m, 2H), 2.39 – 2.24 (m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 154.0, 153.2, 143.5, 140.4, 140.1, 137.2, 128.6, 128.4, 128.3, 128.1, 127.6, 126.6, 126.5, 121.6, 115.5, 114.4, 110.3, 108.6, 56.6, 50.8, 50.6, 44.7, 29.6, 28.9, 11.0. HRMS (ESI): Calcd. for C₃₀H₃₀N₃ [M+H]⁺: 432.2434; found: 432.2428.

(38) (8a-*cis*)-14-benzyl-12-phenyl-5,6,8a,9,14,14a-hexahydro-4H,8H-pyrido[2,3-*b*]quinolino[1,8-*gh*][1,6]naphthyridine (**P38**)



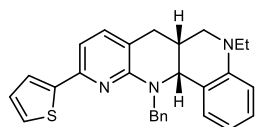
Red solid; m.p. : 131-133 °C, (44.3 mg, 50% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.13 (m, 7H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.45 (t, *J* = 7.4 Hz, 1H), 6.08 – 5.96 (m, 1H), 4.57 (d, *J* = 3.8 Hz, 1H), 4.43 (d, *J* = 15.6 Hz, 1H), 3.39 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.18 (td, *J* = 11.3, 6.7, 4.7 Hz, 1H), 3.04 (td, *J* = 16.6, 11.5, 4.8 Hz, 2H), 2.75 – 2.68 (m, 2H), 2.69 – 2.62 (m, 2H), 2.44 – 2.37 (m, 1H), 1.93 – 1.80 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 154.1, 153.2, 140.8, 140.5, 140.1, 137.1, 128.4, 128.3, 128.2, 128.1, 127.6, 126.5, 126.1, 121.4, 120.5, 115.1, 114.4, 108.5, 56.5, 52.3, 50.5, 49.8, 29.6, 29.3, 27.7, 21.8. HRMS (ESI): Calcd. for C₃₁H₃₀N₃ [M+H]⁺: 444.2434; found: 444.2433.

(39) (6a-*cis*)-12-benzyl-5-ethyl-10-(furan-2-yl)-5,6,6a,7,12,12a-hexahydrobenzo[*h*]pyrido[2,3-*b*][1,6]naphthyridine (**P39**)



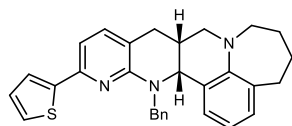
Black solid; m.p. : 136-138 °C, (48.8 mg, 58% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.40 (s, 1H), 7.31 – 7.16 (m, 5H), 7.14 – 7.01 (m, 3H), 6.91 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.86 – 6.80 (m, 1H), 6.58 – 6.51 (m, 2H), 6.42 (s, 1H), 6.03 (d, *J* = 15.4 Hz, 1H), 4.58 (d, *J* = 3.6 Hz, 1H), 4.33 (d, *J* = 15.4 Hz, 1H), 3.49 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.37 – 3.20 (m, *J* = 7.2 Hz, 2H), 3.10 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.71 – 2.57 (m, 2H), 2.41 – 2.29 (m, 1H), 1.19 – 1.08 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 155.1, 153.9, 145.7, 143.5, 142.2, 140.3, 136.9, 128.5, 128.3, 128.1, 127.7, 126.6, 121.5, 115.4, 114.6, 111.7, 110.2, 107.1, 107.0, 56.5, 50.8, 50.5, 44.6, 29.5, 29.0, 11.0. HRMS (ESI): Calcd. for C₂₈H₂₈N₃O [M+H]⁺: 422.2227; found: 422.2218.

(40) (6a-*cis*)-12-benzyl-5-ethyl-10-(thiophen-2-yl)-5,6,6a,7,12,12a-hexahydrobenzo[*h*]pyrido[2,3-*b*][1,6]naphthyridine (**P40**)



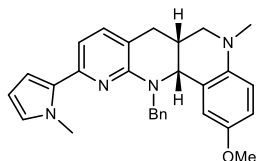
Black solid; m.p. : 81-83 °C, (63.8 mg, 73% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.44 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.29 – 7.14 (m, 4H), 7.13 – 7.02 (m, 3H), 7.01 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.59 – 6.49 (m, 2H), 6.02 (s, 1H), 4.60 (d, *J* = 3.8 Hz, 1H), 4.35 (d, *J* = 15.4 Hz, 1H), 3.51 (dd, *J* = 11.7, 4.8 Hz, 1H), 3.35 – 3.18 (m, *J* = 7.4 Hz, 2H), 3.10 (dd, *J* = 11.7, 4.4 Hz, 1H), 2.64 (dd, *J* = 8.2, 3.6 Hz, 2H), 2.44 – 2.29 (m, 1H), 1.11 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.6, 148.6, 146.7, 143.5, 140.2, 137.0, 128.5, 128.3, 127.8, 127.63, 126.6, 126.1, 123.1, 121.5, 115.5, 114.3, 110.2, 107.0, 56.6, 50.9, 50.6, 44.6, 29.5, 28.8, 11.0. HRMS (ESI): Calcd. for C₂₈H₂₈N₃S [M+H]⁺: 438.1998; found: 438.1988.

(41) (9a-*cis*)-15-benzyl-13-(thiophen-2-yl)-4,5,6,7,9a,10,15,15a-octahydro-9H-azepino[3',2',1':8,1]quinolino[4,3-*b*][1,8]naphthyridine (**P41**)



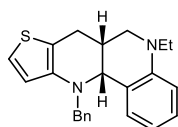
Brown solid; m.p. : 92-94 °C, (61.2 mg, 66% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, *J* = 3.4 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.16 – 7.11 (m, 3H), 7.09 (d, *J* = 2.8 Hz, 1H), 6.99 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.85 – 6.73 (m, 3H), 6.56 – 6.50 (m, 1H), 5.80 (s, 1H), 4.42 (d, *J* = 3.6 Hz, 1H), 4.38 – 4.28 (m, 1H), 3.29 – 3.13 (m, 2H), 3.08 – 3.01 (m, 1H), 2.97 – 2.85 (m, 1H), 2.78 – 2.55 (m, 3H), 2.50 – 2.42 (m, 1H), 2.38 – 2.32 (m, 1H), 1.78 – 1.55 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 154.1, 148.6, 146.7, 145.6, 140.4, 137.0, 130.9, 130.6, 128.2, 127.9, 127.6, 126.5, 126.2, 126.1, 125.9, 123.1, 118.1, 114.3, 107.0, 57.1, 54.3, 54.0, 50.3, 33.9, 32.2, 29.3, 27.7, 25.6. HRMS (ESI): Calcd. for C₃₀H₃₀N₃S [M+H]⁺: 464.2155; found: 464.2154.

(42) (6a-*cis*)-12-benzyl-2-methoxy-5-methyl-10-(1-methyl-1H-pyrrol-2-yl)-5,6,6a,7,12,12a-hexahydrobenzo[*h*]pyrido[2,3-*b*][1,6]naphthyridine (**P42**)



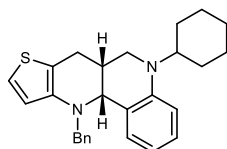
Brown solid; m.p. : 92-95 °C, (46.8 mg, 52% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.21 (m, 4H), 7.21 – 7.16 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.72 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.68 (d, *J* = 3.0 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.53 (d, *J* = 8.8 Hz, 1H), 6.47 (dt, *J* = 3.1, 1.4 Hz, 1H), 6.11 – 6.07 (m, 1H), 6.01 (d, *J* = 16.0 Hz, 1H), 4.54 (d, *J* = 3.4 Hz, 1H), 4.32 (d, *J* = 16.2 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.49 (dd, *J* = 11.2, 5.4 Hz, 1H), 2.86 (dd, *J* = 11.2, 3.0 Hz, 1H), 2.81 (s, 3H), 2.63 – 2.52 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.4, 151.7, 149.2, 139.8, 139.7, 136.8, 133.1, 128.3, 126.9, 126.5, 125.5, 125.3, 113.8, 112.8, 112.1, 111.9, 110.0, 109.5, 107.1, 56.7, 55.8, 54.5, 51.0, 38.7, 36.9, 31.0, 30.0. HRMS (ESI): Calcd. for C₂₉H₃₁N₄O [M+H]⁺: 451.2492; found: 451.2490.

(43) (6a-*cis*)-11-benzyl-5-ethyl-5,6,6a,7,11,11a-hexahydrobenzo[*h*]thieno[3,2-*b*][1,6]naphthyridine (**P43**)



Brown solid; m.p. : 127-129 °C, (36.1 mg, 50% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.08 (m, 5H), 7.01 – 6.95 (m, 2H), 6.87 (d, *J* = 5.4 Hz, 1H), 6.52 (d, *J* = 5.4 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 1H), 6.41 (t, *J* = 7.3 Hz, 1H), 4.53 (d, *J* = 16.2 Hz, 1H), 4.19 (d, *J* = 3.2 Hz, 1H), 4.15 (d, *J* = 16.2 Hz, 1H), 3.35 – 3.18 (m, 4H), 2.90 – 2.84 (m, 1H), 2.52 (dd, *J* = 16.4, 6.2 Hz, 1H), 2.43 – 2.34 (m, 1H), 1.08 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 144.0, 142.7, 140.3, 129.2, 128.7, 128.4, 127.24, 126.7, 121.4, 121.0, 119.2, 114.7, 112.4, 110.0, 57.2, 49.9, 46.8, 44.7, 25.0, 11.0, 1.0. HRMS (ESI): Calcd. for C₂₃H₂₅N₂S [M+H]⁺: 361.1733; found: 361.1729.

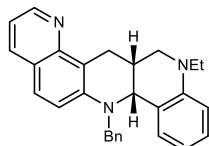
(44) (6a-*cis*)-11-benzyl-5-cyclohexyl-5,6,6a,7,11,11a-hexahydrobenzo[*h*]thieno[3,2-*b*][1,6]naphthyridine (**P44**)



Brown solid; m.p. : 87-89 °C, (51.3 mg, 62% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.24 (m, 4H), 7.22 (d, *J* = 5.3, 3.8 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.97 (d, *J* = 5.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 5.4 Hz, 1H), 6.51 (t, *J* = 7.3 Hz, 1H), 4.64 (d, *J* = 16.2 Hz, 1H), 4.30 – 4.19 (m, 2H), 3.64 (td, *J* = 12.8, 12.0, 6.6 Hz, 1H), 3.41 – 3.20 (m, 2H), 2.97 (dd, *J* = 16.5, 6.0 Hz, 1H), 2.59 (dd, *J* = 16.3, 5.6 Hz, 1H), 2.51 – 2.41 (m, 1H), 1.98 – 1.79 (m, 4H), 1.74 (d, *J* = 13.2 Hz, 1H), 1.62 – 1.49 (m, 2H), 1.47 – 1.36 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.3, 142.9, 140.5, 129.1, 128.8, 128.3, 127.2, 126.6, 121.3, 121.3, 119.2, 114.3, 113.2, 110.2, 57.4, 56.1, 43.6, 30.1, 29.5,

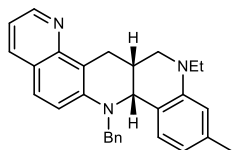
29.3, 26.3, 26.2, 26.1, 26.0, 25.2. HRMS (ESI): Calcd. for C₂₇H₃₁N₂S [M+H]⁺: 415.2202; found: 415.2200

(45) (7a-*cis*)-7-benzyl-12-ethyl-7,7a,12,13,13a,14-hexahydroquinolino[4,3-*j*][1,7]phenanthroline (P45)



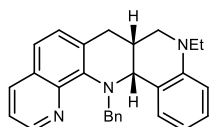
Brown solid; m.p. : 125-127 °C, (59.9 mg, 74% yield); ¹H NMR (500 MHz, CDCl₃) δ 8.74 (dd, *J* = 4.3, 1.8 Hz, 1H), 7.85 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.42 (d, *J* = 9.2 Hz, 1H), 7.28 (s, 2H), 7.27 (s, 2H), 7.24 – 7.18 (m, 1H), 7.10 (d, *J* = 9.2 Hz, 1H), 7.06 – 7.01 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 8.8 Hz, 1H), 6.46 (t, *J* = 7.4 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 4.64 – 4.53 (m, 2H), 3.59 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.52 (dd, *J* = 17.4, 5.8 Hz, 1H), 3.41 – 3.25 (m, 3H), 3.09 (dd, *J* = 17.4, 9.4 Hz, 1H), 2.70 – 2.58 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 149.7, 147.8, 143.9, 143.9, 139.1, 135.8, 128.7, 128.6, 128.0, 127.0, 126.6, 126.6, 121.4, 121.1, 117.0, 116.3, 115.0, 114.2, 110.2, 58.6, 54.7, 50.9, 44.8, 29.1, 24.5, 11.1. HRMS (ESI): Calcd. for C₂₈H₂₈N₃ [M+H]⁺: 406.2278; found: 406.2268.

(46) (7a-*cis*)-7-benzyl-12-ethyl-10-methyl-7,7a,12,13,13a,14-hexahydroquinolino[4,3-*j*][1,7]phenanthroline (P46)



Yellow solid; m.p. : 111-113 °C, (55.3 mg, 66% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.79 (dd, *J* = 4.3, 1.8 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.28 – 7.22 (m, 1H), 7.14 (d, *J* = 9.2 Hz, 1H), 7.10 (dd, *J* = 8.1, 4.4 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.41 (s, 1H), 6.33 (d, *J* = 7.6 Hz, 1H), 5.16 (d, *J* = 17.2 Hz, 1H), 4.70 – 4.57 (m, 2H), 3.62 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.55 (dd, *J* = 17.5, 6.0 Hz, 1H), 3.45 – 3.34 (m, 3H), 3.14 (dd, *J* = 17.5, 9.0 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.25 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 149.6, 147.8, 143.8, 143.8, 139.2, 138.3, 135.8, 128.6, 128.0, 126.9, 126.6, 126.5, 121.3, 118.3, 116.9, 116.3, 115.8, 114.2, 110.9, 58.4, 54.6, 50.9, 44.8, 29.1, 24.4, 21.7, 11.2. HRMS (ESI): Calcd. for C₂₉H₃₀N₃ [M+H]⁺: 420.2434; found: 420.2430.

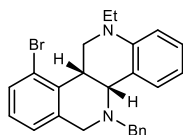
(47) (7a-*cis*)-14-benzyl-9-ethyl-7,7a,8,9,13b,14-hexahydroquinolino[4,3-*b*][1,10]phenanthroline (P47)



Brown solid; m.p. : 146-148 °C, (68.8 mg, 85% yield); ¹H NMR (500 MHz, CDCl₃) δ 8.89 (d, *J* = 5.8 Hz, 1H), 7.96 (d, *J* = 9.8 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.32 (m, 2H), 7.30 – 7.16 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 7.18 Hz, 1H), 6.40 (d, *J* = 8.2 Hz, 1H), 6.34 (t, *J* = 7.4 Hz, 1H), 5.26 (d, *J* = 14.4 Hz, 1H), 4.46 (d, *J* = 14.4 Hz, 1H), 4.33 (d, *J* = 4.2

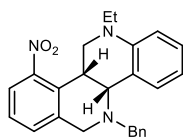
Hz, 1H), 3.64 (dd, $J = 11.8, 3.8$ Hz, 1H), 3.34 (dd, $J = 14.8, 7.2$ Hz, 1H), 3.24 (dd, $J = 14.8, 7.4$ Hz, 1H), 3.19 (d, $J = 11.6$ Hz, 1H), 2.81 – 2.66 (m, 2H), 2.48 – 2.37 (m, 1H), 1.11 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.9, 143.8, 143.7, 141.5, 140.9, 136.1, 129.1, 128.9, 128.3, 128.2, 127.8, 127.7, 127.4, 127.1, 121.7, 120.3, 120.2, 115.6, 109.2, 60.0, 55.5, 51.9, 44.9, 28.3, 23.5, 11.0. HRMS (ESI): Calcd. for $\text{C}_{28}\text{H}_{28}\text{N}_3$ $[\text{M}+\text{H}]^+$: 406.2278; found: 406.2267.

(48) (*cis*)-5-benzyl-10-bromo-12-ethyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P48**)



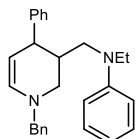
Brown solid; m.p. : 93-95 °C, (51.8 mg, 60% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 7.8$ Hz, 1H), 7.36 – 7.20 (m, 6H), 7.14 (dd, $J = 7.4, 1.8$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.79 (d, $J = 8.2$ Hz, 1H), 6.65 (t, $J = 7.2$ Hz, 1H), 4.27 – 4.11 (m, 1H), 3.95 (ddd, $J = 13.2, 8.6, 2.8$ Hz, 2H), 3.69 – 3.55 (m, 2H), 3.52 – 3.35 (m, 4H), 3.15 (dd, $J = 13.2, 1.8$ Hz, 1H), 1.28 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.6, 140.4, 138.1, 135.9, 133.4, 130.5, 129.6, 128.3, 128.2, 127.8, 126.7, 125.8, 124.6, 119.1, 114.3, 111.1, 61.4, 57.6, 55.5, 49.0, 45.0, 38.8, 11.2. HRMS (ESI): Calcd. for $\text{C}_{25}\text{H}_{26}\text{BrN}_2$ $[\text{M}+\text{H}]^+$: 433.1274; found: 433.1271.

(49) (*cis*)-5-benzyl-12-ethyl-10-nitro-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P49**)



Yellow solid; m.p. : 94-96 °C, (39.1 mg, 49% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 1H), 7.31 – 7.16 (m, 8H), 7.10 (dd, $J = 7.4, 1.6$ Hz, 1H), 6.74 (d, $J = 8.2$ Hz, 1H), 6.60 (td, $J = 7.2, 1.0$ Hz, 1H), 4.13 (d, $J = 13.2$ Hz, 1H), 4.07 – 3.99 (m, 2H), 3.86 – 3.76 (m, 1H), 3.65 (t, $J = 1.6$ Hz, 1H), 3.60-3.51 (m, 2H), 3.43-3.34 (m, 2H), 3.11 (d, $J = 16$ Hz, 1H), 1.23 (t, $J = 8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.0, 144.4, 140.0, 139.0, 133.0, 131.7, 131.6, 129.6, 128.4, 128.2, 126.9, 126.8, 122.9, 118.6, 114.3, 111.1, 60.8, 57.7, 55.4, 50.4, 45.0, 35.1, 11.1. HRMS (ESI): Calcd. for $\text{C}_{25}\text{H}_{26}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 400.2020; found: 400.2018.

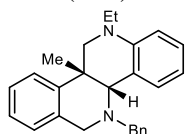
(50) (*cis*)-1-benzyl-6-ethyl-4-phenyl-1,4,4a,5,6,10b-hexahydrobenzo[*h*][1,6]naphthyridine (**P50**)



Yellowish oil (25.0 mg, 49% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.40 (m, 2H), 7.37 – 7.32 (m, 6H), 7.29 – 7.25 (m, 2H), 7.14 – 7.10 (m, 2H), 6.65 (d, $J = 8.0$ Hz, 2H), 6.58 (t, $J = 7.2$ Hz, 1H), 5.88 (dd, $J = 4.7, 2.3$ Hz, 1H), 3.67 (d, $J = 12.7$ Hz, 1H), 3.53 – 3.48 (m, 2H), 3.38 (dd, $J = 17.2, 4.6$ Hz, 1H), 3.23 (dq, $J = 14.0, 6.9$ Hz, 1H), 3.11 (dd, $J = 14.2, 3.5$ Hz, 1H), 3.05 (d, $J = 11.4$ Hz, 2H), 2.95 (dq, $J = 14.2, 6.9$ Hz, 1H), 2.86 – 2.82 (m, 1H), 2.39 (dd, $J = 11.5, 3.8$ Hz, 1H), 0.96 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.1, 140.9, 138.6, 138.1, 129.4, 129.1, 128.5, 128.3,

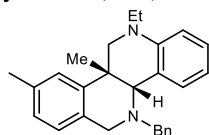
127.3, 127.2, 126.1, 124.8, 115.3, 112.1, 62.9, 53.7, 52.3, 51.6, 44.9, 37.4, 11.5. HRMS (ESI): Calcd. for $C_{27}H_{31}N_2$ $[M+H]^+$: 383.2482; found: 383.2476.

(51) (*cis*)-5-benzyl-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P51**)



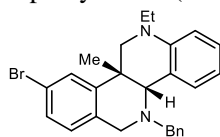
Brown solid; m.p. : 140-142 °C, (61.1mg, 83% yield); 1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, $J = 7.8$ Hz, 1H), 7.32 – 7.24 (m, 5H), 7.23 – 7.13 (m, 4H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.72 (d, $J = 8.4$ Hz, 1H), 6.65 (t, $J = 7.2$ Hz, 1H), 4.06 (d, $J = 11.2$ Hz, 1H), 3.98 (d, $J = 13.4$ Hz, 1H), 3.89 (d, $J = 15.4$ Hz, 1H), 3.67 – 3.57 (m, 2H), 3.42 (s, 1H), 3.35 (dt, $J = 14.4, 7.2$ Hz, 1H), 3.19 (d, $J = 13.4$ Hz, 1H), 2.94 (dd, $J = 11.0, 1.4$ Hz, 1H), 1.28 (s, 3H), 1.23 (t, $J = 12.0, 4.0$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 141.4, 140.8, 135.0, 133.9, 129.1, 128.3, 128.1, 126.5, 126.5, 126.4, 126.3, 126.1, 118.8, 114.3, 110.5, 68.0, 58.0, 57.1, 55.6, 44.8, 36.6, 22.7, 11.0. HRMS (ESI): Calcd. for $C_{26}H_{29}N_2$ $[M+H]^+$: 369.2325; found: 369.2323.

(52) (*cis*)-5-benzyl-12-ethyl-9,10b-dimethyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P52**)



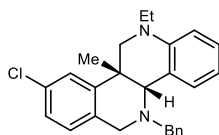
Brown solid; m.p. : 115-117 °C, (53.4 mg, 70% yield); 1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.12 (m, 8H), 6.99 (d, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 7.6$ Hz, 1H), 6.70 (d, $J = 8.2$ Hz, 1H), 6.63 (t, $J = 7.2$ Hz, 1H), 4.03 (d, $J = 11.2$ Hz, 1H), 3.95 (d, $J = 13.4$ Hz, 1H), 3.84 (d, $J = 15.2$ Hz, 1H), 3.66 – 3.51 (m, 2H), 3.43 – 3.28 (m, 2H), 3.17 (d, $J = 13.2$ Hz, 1H), 2.93 (d, $J = 11.4$ Hz, 1H), 2.38 (s, 3H), 1.26 (s, 3H), 1.21 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 141.2, 140.9, 135.6, 133.9, 131.9, 129.0, 128.3, 128.0, 127.0, 126.9, 126.5, 126.4, 118.9, 114.3, 110.4, 68.0, 57.9, 57.1, 55.4, 44.8, 36.5, 22.7, 21.4, 11.0. HRMS (ESI): Calcd. for $C_{27}H_{31}N_2$ $[M+H]^+$: 383.2482; found: 383.2478.

(53) (*cis*)-5-benzyl-9-bromo-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P53**)



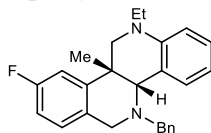
Brown solid; m.p. : 94-96 °C, 58.9 mg, 66% yield); 1H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, $J = 2.4$ Hz, 1H), 7.15 – 7.09 (m, 5H), 7.08 – 6.98 (m, 3H), 6.69 (d, $J = 8.2$ Hz, 1H), 6.57 (dd, $J = 8.2, 2.4$ Hz, 1H), 6.51 (td, $J = 7.2, 2.6$ Hz, 1H), 3.88 – 3.81 (m, 2H), 3.69 (dd, $J = 15.4, 2.8$ Hz, 1H), 3.50 – 3.42 (m, 1H), 3.38 (dd, $J = 15.4, 2.6$ Hz, 1H), 3.25 – 3.18 (m, 2H), 3.06 (dd, $J = 13.4, 2.6$ Hz, 1H), 2.78 (dt, $J = 11.2, 1.8$ Hz, 1H), 1.12 (d, $J = 2.4$ Hz, 3H), 1.08 (td, $J = 7.0, 2.2$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 143.6, 140.5, 134.0, 133.8, 129.5, 129.2, 129.2, 128.3, 128.2, 128.2, 126.7, 119.9, 118.4, 114.5, 110.6, 67.6, 57.9, 56.9, 55.0, 44.8, 36.9, 22.8, 11.1. HRMS (ESI): Calcd. for $C_{26}H_{28}BrN_2$ $[M+H]^+$: 447.1430; found: 447.1429.

(54) (*cis*)-5-benzyl-9-chloro-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P54**)



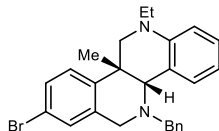
Yellow solid; m.p. : 96-98 °C, (59.5 mg, 74% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.42 (t, $J = 2.2$ Hz, 1H), 7.28 (t, $J = 3.0$ Hz, 4H), 7.25 – 7.18 (m, 3H), 7.15 (dt, $J = 8.2, 2.0$ Hz, 1H), 6.90 (d, $J = 8.2$ Hz, 1H), 6.76 – 6.71 (m, 1H), 6.67 (td, $J = 7.5, 2.2$ Hz, 1H), 4.08 – 3.94 (m, 2H), 3.87 (dd, $J = 15.4, 2.2$ Hz, 1H), 3.67 – 3.52 (m, 2H), 3.44 – 3.33 (m, 2H), 3.22 (dd, $J = 13.4, 2.2$ Hz, 1H), 2.94 (dt, $J = 11.4, 1.8$ Hz, 1H), 1.28 (d, $J = 2.0$ Hz, 3H), 1.24 (td, $J = 7.2, 2.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.6, 143.4, 140.6, 133.8, 133.5, 131.9, 129.3, 128.3, 128.2, 127.9, 126.7, 126.6, 126.3, 118.5, 114.6, 110.6, 67.6, 58.0, 56.9, 55.0, 44.9, 36.9, 22.8, 11.1. HRMS (ESI): Calcd. for $\text{C}_{26}\text{H}_{28}\text{ClN}_2$ $[\text{M}+\text{H}]^+$: 403.1936; found: 403.1935.

(55) (*cis*)-5-benzyl-12-ethyl-9-fluoro-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P55**)



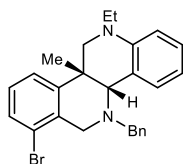
Brown solid; m.p. : 81-83 °C, (50.2 mg, 65% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.18 (m, 7H), 7.13 (dt, $J = 10.6, 2.2$ Hz, 1H), 6.96 – 6.83 (m, 2H), 6.73 (d, $J = 8.2$ Hz, 1H), 6.66 (t, $J = 7.2$ Hz, 1H), 4.07 – 3.94 (m, 2H), 3.86 (d, $J = 15.2$ Hz, 1H), 3.69 – 3.51 (m, 2H), 3.43 – 3.30 (m, 2H), 3.21 (dd, $J = 13.2, 1.6$ Hz, 1H), 2.94 (t, $J = 10.6$ Hz, 1H), 1.26 (dd, $J = 5.8, 1.6$ Hz, 3H), 1.23 (dd, $J = 7.2, 1.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.7, 160.3, 143.6, 143.5, 140.6, 133.8, 130.6, 130.5, 129.2, 128.3, 128.1, 127.9, 127.8, 126.6, 118.5, 114.5, 113.4, 113.2, 113.1, 112.9, 110.6, 67.6, 57.9, 56.9, 54.9, 44.9, 36.9, 22.8, 11.0. ^{19}F NMR (376 MHz, CDCl_3) δ -116.3. HRMS (ESI): Calcd. for $\text{C}_{26}\text{H}_{28}\text{FN}_2$ $[\text{M}+\text{H}]^+$: 387.2231; found: 387.2229.

(56) (*cis*)-5-benzyl-8-bromo-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P56**)



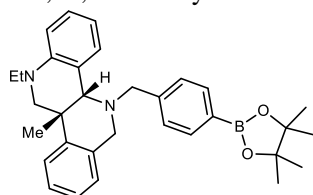
Black solid; m.p. : 74-76 °C, (53.5 mg, 60% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.29 (dd, $J = 8.4, 2.2$ Hz, 1H), 7.24 – 7.17 (m, 5H), 7.17 – 7.09 (m, 3H), 7.05 (d, $J = 2.0$ Hz, 1H), 6.65 (d, $J = 8.2$ Hz, 1H), 6.59 (tt, $J = 7.2, 1.4$ Hz, 1H), 3.97 – 3.85 (m, 2H), 3.81 – 3.67 (m, 1H), 3.63 – 3.45 (m, 2H), 3.33 (d, $J = 1.6$ Hz, 1H), 3.32 – 3.22 (m, 1H), 3.13 (dd, $J = 13.2, 1.6$ Hz, 1H), 2.84 (dd, $J = 11.0, 1.6$ Hz, 1H), 1.18 (d, $J = 1.6$ Hz, 3H), 1.15 (td, $J = 7.0, 1.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.6, 140.5, 140.4, 137.4, 133.8, 129.4, 129.3, 129.2, 128.3, 128.3, 128.2, 126.7, 119.9, 118.5, 114.6, 110.6, 67.7, 57.9, 56.9, 54.9, 44.9, 36.5, 22.8, 11.0. HRMS (ESI): Calcd. for $\text{C}_{26}\text{H}_{28}\text{BrN}_2$ $[\text{M}+\text{H}]^+$: 447.1430; found: 447.1425.

(57) (*cis*)-5-benzyl-7-bromo-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P57**)



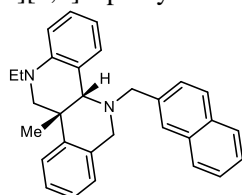
Yellow solid; m.p. : 117-119 °C, (74.0 mg, 83% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.39 (m, 2H), 7.28 (d, $J = 3.6$ Hz, 4H), 7.23 (dd, $J = 10.0, 5.6$ Hz, 3H), 7.14 (t, $J = 7.8$ Hz, 1H), 6.77 – 6.63 (m, 2H), 4.05 (dd, $J = 18.2, 11.8$ Hz, 3H), 3.62 (dq, $J = 14.2, 7.0$ Hz, 1H), 3.53 – 3.41 (m, 2H), 3.37 (dd, $J = 14.6, 7.2$ Hz, 1H), 3.31 (d, $J = 13.4$ Hz, 1H), 2.97 (dd, $J = 11.2, 1.4$ Hz, 1H), 1.28 (s, 3H), 1.24 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.2, 143.6, 140.4, 134.6, 133.7, 130.3, 129.2, 128.4, 128.1, 127.5, 126.6, 125.7, 122.7, 118.6, 114.6, 110.5, 67.2, 58.0, 56.9, 56.4, 44.9, 37.1, 23.1, 11.1. HRMS (ESI): Calcd. for $\text{C}_{26}\text{H}_{28}\text{BrN}_2$ $[\text{M}+\text{H}]^+$: 447.1430; found: 447.1429.

(58) (*cis*)-12-ethyl-10b-methyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P58**)



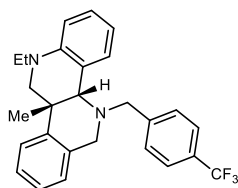
Yellow solid; m.p. : 76-78 °C, (63.2 mg, 64% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.29 – 7.14 (m, 9H), 6.95 (d, $J = 7.4$ Hz, 1H), 6.69 (d, $J = 8.2$ Hz, 1H), 6.62 (td, $J = 7.2, 1.1$ Hz, 1H), 4.03 (d, $J = 11.0$ Hz, 1H), 3.95 (d, $J = 13.2$ Hz, 1H), 3.86 (d, $J = 15.4$ Hz, 1H), 3.68 – 3.53 (m, 2H), 3.41 – 3.27 (m, 2H), 3.16 (d, $J = 13.2$ Hz, 1H), 2.96 – 2.82 (m, 1H), 1.25 (s, 3H), 1.20 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.3, 143.6, 141.4, 134.9, 134.6, 133.9, 129.1, 127.8, 126.5, 126.3, 126.3, 126.1, 118.8, 114.3, 110.5, 83.7, 67.9, 58.1, 57.1, 55.7, 44.8, 36.6, 24.9, 22.6, 11.0. HRMS (ESI): Calcd. for $\text{C}_{32}\text{H}_{40}\text{BN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 495.3177; found: 495.3183.

(59) (*cis*)-12-ethyl-10b-methyl-5-(naphthalen-2-ylmethyl)-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P59**)



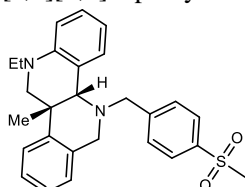
Brown solid; m.p. : 129-131 °C, (72.7 mg, 87% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.63 (dq, $J = 8.8, 5.2, 4.2$ Hz, 2H), 7.57 – 7.49 (m, 2H), 7.32 – 7.19 (m, 4H), 7.06 (tdd, $J = 10.9, 5.2, 2.7$ Hz, 3H), 6.98 (td, $J = 7.6, 3.3$ Hz, 1H), 6.74 (dd, $J = 7.6, 3.2$ Hz, 1H), 6.60 – 6.43 (m, 2H), 3.95 (tt, $J = 9.0, 4.2$ Hz, 2H), 3.73 (dt, $J = 15.5, 4.4$ Hz, 1H), 3.47 (ddd, $J = 11.0, 7.6, 3.5$ Hz, 2H), 3.31 – 3.24 (m, 1H), 3.20 – 3.06 (m, 2H), 2.86 – 2.65 (m, 1H), 1.17 – 1.11 (m, 3H), 1.08 (td, $J = 7.1, 3.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.7, 141.5, 138.4, 135.0, 134.0, 133.4, 132.7, 129.3, 127.8, 127.7, 127.7, 127.0, 126.8, 126.5, 126.4, 126.4, 126.2, 125.9, 125.4, 118.9, 114.5, 110.6, 68.1, 58.3, 57.2, 55.8, 44.9, 36.7, 22.8, 11.1. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{31}\text{N}_2$ $[\text{M}+\text{H}]^+$: 419.2482; found: 419.2477.

(60) (*cis*)-12-ethyl-10b-methyl-5-(4-(trifluoromethyl)benzyl)-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P60**)



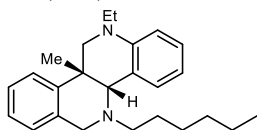
Brown solid; m.p. : 91-93 °C, (74.1 mg, 85% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, $J = 18.8, 7.8$ Hz, 3H), 7.38 (d, $J = 7.8$ Hz, 2H), 7.32 – 7.25 (m, 1H), 7.23 – 7.11 (m, 3H), 7.01 (d, $J = 7.6$ Hz, 1H), 6.68 (td, $J = 9.4, 9.0, 6.8$ Hz, 2H), 4.13 – 3.95 (m, 2H), 3.88 (dd, $J = 15.2, 2.2$ Hz, 1H), 3.71 (d, $J = 15.2$ Hz, 1H), 3.67 – 3.53 (m, 1H), 3.45 (s, 1H), 3.40 – 3.26 (m, 2H), 2.98 (dt, $J = 11.2, 1.8$ Hz, 1H), 1.30 (d, $J = 2.0$ Hz, 3H), 1.23 (td, $J = 7.0, 2.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.1, 143.6, 141.3, 134.6, 133.8, 129.3, 128.5, 126.5, 126.4, 126.3, 125.0, 124.9, 118.4, 114.4, 110.4, 68.0, 57.5, 57.1, 56.1, 44.8, 36.6, 22.7, 11.1. ^{19}F NMR (376 MHz, CDCl_3) δ -62.20, -62.21, -62.23. HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{28}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 437.2199; found: 437.2198.

(61) (*cis*)-12-ethyl-10b-methyl-5-(4-(methylsulfonyl)benzyl)-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P61**)



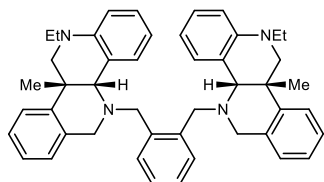
Brown solid; m.p. : 114-116 °C, (63.3 mg, 71% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.43 (t, $J = 8.7$ Hz, 3H), 7.33 – 7.23 (m, 1H), 7.17 (dt, $J = 14.2, 7.0$ Hz, 3H), 7.00 (d, $J = 7.6$ Hz, 1H), 6.62 (t, $J = 7.6$ Hz, 2H), 4.02 (dd, $J = 12.6, 6.3$ Hz, 2H), 3.86 (d, $J = 15.0$ Hz, 1H), 3.75 (d, $J = 15.2$ Hz, 1H), 3.56 (dq, $J = 14.2, 7.0$ Hz, 1H), 3.46 – 3.27 (m, 3H), 3.03 (s, 3H), 2.96 (d, $J = 11.2$ Hz, 1H), 1.26 (s, 3H), 1.19 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.7, 143.6, 141.2, 138.4, 134.4, 133.7, 129.4, 129.0, 127.0, 126.6, 126.5, 126.4, 126.3, 118.3, 114.4, 110.2, 68.0, 57.5, 57.0, 56.4, 44.8, 44.6, 36.5, 22.6, 11.1. HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 447.2101; found: 447.2099.

(62) (*cis*)-12-ethyl-5-hexyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P62**)



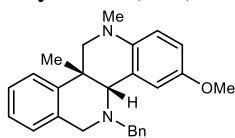
Yellow solid; m.p. : 77-79 °C, (47.8 mg, 66% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.27 (dt, $J = 7.5, 2.1$ Hz, 1H), 7.12 – 7.07 (m, 3H), 6.99 – 6.95 (m, 2H), 6.56 – 6.54 (m, 1H), 6.50 – 6.46 (m, 1H), 3.97 – 3.94 (m, 1H), 3.74 (dd, $J = 11.1, 3.0$ Hz, 1H), 3.50 (dd, $J = 15.3, 2.7$ Hz, 1H), 3.43 – 3.35 (m, 1H), 3.23 – 3.15 (m, 1H), 2.75 – 2.72 (m, 1H), 2.56 – 2.50 (m, 1H), 2.11 – 2.04 (m, 1H), 1.22 – 1.17 (m, 1H), 1.11 – 0.92 (m, 12H), 0.73 – 0.69 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.7, 141.5, 135.3, 133.8, 128.8, 126.4, 126.3, 126.2, 126.1, 119.1, 114.1, 110.1, 68.1, 56.9, 55.6, 53.0, 44.8, 36.4, 31.6, 27.8, 26.7, 22.7, 22.7, 14.1, 11.0. HRMS (ESI): Calcd. for $\text{C}_{25}\text{H}_{35}\text{N}_2$ $[\text{M}+\text{H}]^+$: 363.5589; found: 363.5451.

(63) 1-(((*cis*)-12-ethyl-10b-methyl-6,10b,11,12-tetrahydrodibenzo[*c,h*][1,6]naphthyridin-5(4b*H*)-yl)methyl)-2-(((*cis*)-12-ethyl-10b-methyl-6,10b,11,12-tetrahydrodibenzo[*c,h*][1,6]naphthyridin-5(4b*H*)-yl)methyl)benzene (**P63**)



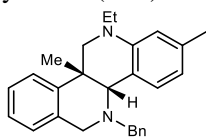
Yellow solid; m.p. : 133-135 °C, (55.3 mg, 42% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.27 (dd, $J = 7.5, 3.6$ Hz, 2H), 7.10 (t, $J = 8.3$ Hz, 2H), 7.06 – 6.89 (m, 10H), 6.74 (ddd, $J = 17.1, 7.6, 2.6$ Hz, 2H), 6.54 (dt, $J = 7.6, 3.5$ Hz, 2H), 6.47 (tt, $J = 7.1, 3.3$ Hz, 2H), 3.89 – 3.59 (m, 6H), 3.47 – 3.32 (m, 4H), 3.26 – 3.09 (m, 4H), 2.97 (td, $J = 12.6, 3.4$ Hz, 2H), 2.75 (ddd, $J = 21.8, 11.2, 2.9$ Hz, 2H), 1.11 (t, $J = 3.7$ Hz, 6H), 1.04 (td, $J = 7.1, 2.7$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.7, 141.4, 141.4, 140.5, 140.3, 135.1, 135.1, 133.9, 133.8, 129.1, 128.6, 128.1, 127.9, 127.8, 126.5, 126.5, 126.4, 126.3, 126.2, 126.2, 126.1, 118.9, 114.3, 110.4, 110.4, 68.0, 68.0, 58.0, 58.0, 57.1, 55.7, 55.7, 44.8, 44.8, 36.6, 22.7, 22.7, 11.1. HRMS (ESI): Calcd. for $\text{C}_{46}\text{H}_{51}\text{N}_4$ $[\text{M}+\text{H}]^+$: 658.3887; found: 658.3896.

(64) (*cis*)-5-benzyl-3-methoxy-10b,12-dimethyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P64**)



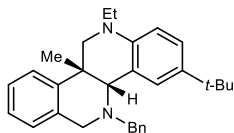
Brown solid; m.p. : 128-130 °C, (49.9 mg, 65% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.30 (d, $J = 7.8$ Hz, 1H), 7.16 – 7.07 (m, 6H), 7.03 (d, $J = 7.5$ Hz, 1H), 6.84 (d, $J = 7.6$ Hz, 1H), 6.78 (t, $J = 2.3$ Hz, 1H), 6.72 (dt, $J = 9.0, 2.1$ Hz, 1H), 6.53 (d, $J = 8.8$ Hz, 1H), 3.82 (d, $J = 13.3$ Hz, 1H), 3.72 (d, $J = 12.3$ Hz, 5H), 3.53 (d, $J = 15.4$ Hz, 1H), 3.37 (s, 1H), 3.20 (d, $J = 13.3$ Hz, 1H), 2.87 (s, 4H), 1.23 – 1.16 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.3, 141.3, 140.7, 140.4, 134.8, 128.3, 128.1, 126.6, 126.5, 126.4, 126.1, 120.6, 118.8, 114.8, 112.0, 67.7, 60.0, 57.6, 56.0, 54.9, 39.3, 37.2, 23.6. HRMS (ESI): Calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 385.2274; found: 385.2271.

(65) (*cis*)-5-benzyl-12-ethyl-2,10b-dimethyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P65**)



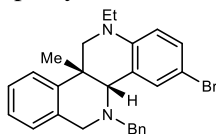
Brown solid; m.p. : 110-112 °C, (61.1 mg, 80% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.28 (dd, $J = 7.9, 3.2$ Hz, 1H), 7.11 (qq, $J = 6.0, 3.5, 3.0$ Hz, 5H), 7.06 – 6.97 (m, 2H), 6.92 (dd, $J = 7.6, 3.8$ Hz, 1H), 6.81 (dd, $J = 7.7, 2.8$ Hz, 1H), 6.44 – 6.29 (m, 2H), 3.87 (td, $J = 13.8, 12.6, 4.0$ Hz, 2H), 3.73 (dd, $J = 15.4, 3.8$ Hz, 1H), 3.46 (ddt, $J = 16.0, 14.1, 5.2$ Hz, 2H), 3.28 – 3.13 (m, 2H), 3.02 (dd, $J = 13.4, 3.7$ Hz, 1H), 2.77 (dt, $J = 11.2, 2.4$ Hz, 1H), 2.20 (d, $J = 3.7$ Hz, 3H), 1.13 (d, $J = 3.8$ Hz, 3H), 1.07 (dt, $J = 7.0, 3.9$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.5, 141.6, 140.9, 138.8, 135.1, 133.8, 128.4, 128.1, 126.5, 126.5, 126.4, 126.3, 126.1, 116.1, 115.5, 111.1, 67.7, 58.0, 57.1, 55.6, 44.8, 36.7, 22.8, 21.9, 11.1. HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{31}\text{N}_2$ $[\text{M}+\text{H}]^+$: 383.2482; found: 383.2481.

(66) (*cis*)-5-benzyl-3-(tert-butyl)-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P66**)



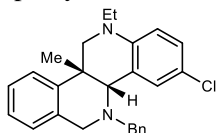
Brown solid; m.p. : 131-133 °C, (67.8 mg, 80% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.15 (m, 9H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.73 – 6.59 (m, 1H), 4.03 – 3.86 (m, 3H), 3.72 – 3.57 (m, 2H), 3.46 (s, 1H), 3.33 (dq, *J* = 14.4, 7.0 Hz, 1H), 3.25 (dd, *J* = 13.2, 1.6 Hz, 1H), 2.94 (d, *J* = 11.0 Hz, 1H), 1.38 (d, *J* = 1.8 Hz, 9H), 1.31 (d, *J* = 1.6 Hz, 3H), 1.22 (td, *J* = 7.0, 1.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 141.7, 141.4, 141.0, 137.1, 135.0, 130.7, 128.4, 128.1, 126.5, 126.5, 126.4, 126.3, 126.1, 125.7, 118.5, 110.1, 68.1, 57.6, 57.1, 55.4, 44.9, 36.8, 33.6, 31.7, 23.2, 11.1. HRMS (ESI): Calcd. for C₃₀H₃₇N₂ [M+H]⁺: 425.2951; found: 425.2950.

(67) (*cis*)-5-benzyl-3-bromo-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P67**)



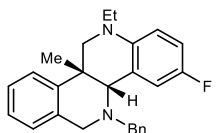
Brown solid; m.p. : 95-97 °C, (49.1 mg, 55% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.16 – 6.98 (m, 9H), 6.83 (d, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 8.2 Hz, 1H), 6.53 – 6.46 (m, 1H), 3.91 (d, *J* = 11.2 Hz, 1H), 3.84 (d, *J* = 13.4 Hz, 1H), 3.75 (d, *J* = 15.4 Hz, 1H), 3.48 (dq, *J* = 14.2, 6.7 Hz, 2H), 3.28 (d, *J* = 1.4 Hz, 1H), 3.20 (dt, *J* = 14.2, 7.0 Hz, 1H), 3.05 (d, *J* = 13.2 Hz, 1H), 2.80 (dd, *J* = 11.2, 1.3 Hz, 1H), 1.14 (s, 3H), 1.08 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.7, 141.4, 140.8, 135.0, 133.9, 129.1, 128.3, 128.1, 126.5, 126.5, 126.4, 126.3, 126.1, 118.8, 114.3, 110.5, 68.0, 58.0, 57.1, 55.6, 44.8, 36.6, 22.7, 11.0. HRMS (ESI): Calcd. for C₂₆H₂₈BrN₂ [M+H]⁺: 447.1430; found: 447.1429.

(68) (*cis*)-5-benzyl-3-chloro-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P68**)



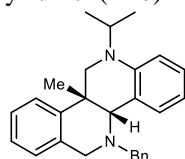
Brown solid; m.p. : 85-87 °C, (50.6 mg, 63% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.28 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.04 (m, 6H), 7.05 – 6.98 (m, 1H), 6.83 (td, *J* = 8.1, 7.1, 2.7 Hz, 2H), 6.77 (ddt, *J* = 11.6, 5.4, 2.8 Hz, 1H), 6.46 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.89 – 3.80 (m, 2H), 3.74 (dd, *J* = 15.5, 3.6 Hz, 1H), 3.54 – 3.36 (m, 2H), 3.25 (d, *J* = 3.5 Hz, 1H), 3.20 – 3.05 (m, 2H), 2.83 – 2.64 (m, 1H), 1.15 – 1.10 (m, 3H), 1.05 (ddt, *J* = 7.1, 4.7, 2.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 141.1, 140.4, 140.3, 134.8, 128.3, 128.2, 126.7, 126.5, 126.4, 126.3, 126.2, 120.0, 120.0, 119.5, 119.3, 115.7, 115.5, 111.2, 111.2, 67.8, 57.9, 57.0, 55.3, 45.2, 36.7, 23.0, 10.8. HRMS (ESI): Calcd. for C₂₆H₂₈ClN₂ [M+H]⁺: 403.1936; found: 403.1935.

(69) (*cis*)-5-benzyl-12-ethyl-3-fluoro-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P69**)



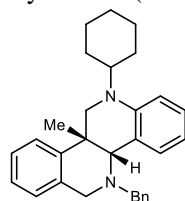
Brown solid; m.p. : 83-85 °C, (48.6 mg, 63% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.27 (dd, *J* = 7.9, 3.3 Hz, 1H), 7.08 (dt, *J* = 44.1, 4.0 Hz, 8H), 6.98 (ddd, *J* = 9.0, 4.3, 2.4 Hz, 1H), 6.83 (dd, *J* = 7.6, 2.6 Hz, 1H), 6.46 (dd, *J* = 8.9, 3.2 Hz, 1H), 3.88 (dd, *J* = 11.2, 3.7 Hz, 1H), 3.82 (dd, *J* = 13.3, 3.8 Hz, 1H), 3.75 (dd, *J* = 15.5, 3.7 Hz, 1H), 3.53 – 3.35 (m, 2H), 3.23 – 3.13 (m, 2H), 3.09 (dd, *J* = 13.2, 3.7 Hz, 1H), 2.78 (dq, *J* = 8.9, 3.1, 2.4 Hz, 1H), 1.11 (d, *J* = 3.6 Hz, 3H), 1.06 (td, *J* = 7.0, 3.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.3, 140.9, 140.4, 134.8, 132.9, 128.8, 128.4, 128.1, 126.6, 126.5, 126.4, 126.3, 120.4, 118.7, 111.6, 67.7, 58.0, 57.0, 55.7, 45.0, 36.5, 22.7, 10.9. ¹⁹F NMR (471 MHz, CDCl₃) δ -131.5. HRMS (ESI): Calcd. for C₂₆H₂₈FN₂ [M+H]⁺: 387.2231; found: 387.2230.

(70) (*cis*)-5-benzyl-12-isopropyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphth yridine (**P70**)



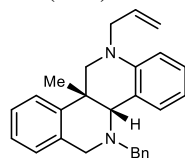
Brown solid; m.p. : 111-113 °C, (58.8 mg, 77% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.48 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.35 – 7.13 (m, 9H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 4.32 (p, *J* = 6.6 Hz, 1H), 4.04 (d, *J* = 13.4 Hz, 1H), 3.93 (d, *J* = 15.2 Hz, 1H), 3.80 (d, *J* = 11.2 Hz, 1H), 3.64 (d, *J* = 15.4 Hz, 1H), 3.44 (d, *J* = 1.4 Hz, 1H), 3.23 (d, *J* = 13.2 Hz, 1H), 3.04 (dd, *J* = 11.2, 1.4 Hz, 1H), 1.34 (d, *J* = 6.6 Hz, 3H), 1.30 – 1.25 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 144.3, 141.8, 140.8, 135.1, 134.0, 129.2, 128.4, 128.1, 126.5, 126.5, 126.5, 126.3, 126.2, 119.2, 114.2, 110.5, 68.1, 58.0, 55.6, 49.1, 46.5, 36.2, 22.6, 19.6, 19.0. HRMS (ESI): Calcd. for C₂₇H₃₁N₂ [M+H]⁺: 383.2482; found: 383.2480.

(71) (*cis*)-5-benzyl-12-cyclohexyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphth yridine (**P71**)



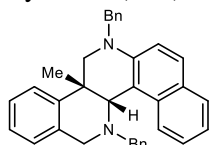
Brown solid; m.p. : 126-128 °C, (65.0 mg, 77% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.29 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.16 – 6.98 (m, 9H), 6.82 (dd, *J* = 7.7, 2.5 Hz, 1H), 6.63 (dd, *J* = 8.5, 3.1 Hz, 1H), 6.47 (dt, *J* = 8.0, 4.5 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.78 – 3.69 (m, 1H), 3.67 – 3.57 (m, 2H), 3.45 (dd, *J* = 15.4, 3.1 Hz, 1H), 3.25 (d, *J* = 3.1 Hz, 1H), 3.10 – 3.00 (m, 1H), 2.91 (dt, *J* = 11.2, 2.3 Hz, 1H), 1.84 – 1.70 (m, 4H), 1.64 – 1.58 (m, 1H), 1.50 – 1.27 (m, 4H), 1.08 (d, *J* = 3.0 Hz, 3H), 1.04 (d, *J* = 3.5 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 144.2, 141.8, 140.9, 135.1, 134.0, 129.1, 128.4, 128.1, 126.5, 126.5, 126.4, 126.3, 126.1, 119.1, 114.0, 110.4, 68.1, 58.1, 55.8, 55.6, 50.6, 36.3, 30.0, 29.7, 26.4, 26.3, 26.1, 22.6. HRMS (ESI): Calcd. for C₃₀H₃₅N₂ [M+H]⁺: 423.2795; found: 423.2794.

(72) (*cis*)-12-allyl-5-benzyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphth yridine (**P72**)



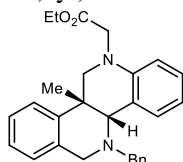
Yellow solid; m.p. : 89-91 °C, (60.8 mg, 80% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.13 (m, 9H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.66 (dt, *J* = 7.4, 3.2 Hz, 2H), 5.89 (ddt, *J* = 17.2, 9.8, 4.8 Hz, 1H), 5.35 – 5.09 (m, 2H), 4.14 – 3.82 (m, 5H), 3.61 (d, *J* = 15.4 Hz, 1H), 3.44 (s, 1H), 3.21 (d, *J* = 13.4 Hz, 1H), 2.98 (dd, *J* = 11.2, 1.6 Hz, 1H), 1.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.1, 141.3, 140.7, 134.9, 133.7, 133.2, 129.1, 128.3, 128.1, 126.5, 126.4, 126.4, 126.3, 126.1, 118.7, 116.0, 114.8, 111.0, 68.0, 58.0, 57.8, 55.7, 53.3, 36.9, 36.6, 22.9. HRMS (ESI): Calcd. for C₂₇H₂₉N₂ [M+H]⁺: 381.2325; found: 381.2323.

(73) (*cis*)-6,13-dibenzyl-14a-methyl-5,6,6a,13,14,14a-hexahydrobenzo[*c*]naphtho[1,2-*h*][1,6]naphthyridine (**P73**)



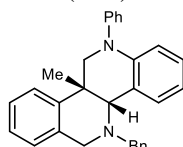
Brown solid; m.p. : 123-125 °C, (73.9 mg, 77% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.94 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.56 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.48 (dd, *J* = 9.1, 4.3 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.26 (dd, *J* = 8.1, 4.0 Hz, 1H), 7.23 – 6.93 (m, 14H), 6.87 (dd, *J* = 7.8, 3.8 Hz, 1H), 4.74 (dd, *J* = 17.4, 4.1 Hz, 1H), 4.52 (dd, *J* = 17.3, 3.9 Hz, 1H), 4.26 (d, *J* = 5.1 Hz, 1H), 4.09 (dd, *J* = 11.4, 5.2 Hz, 1H), 3.92 – 3.78 (m, 2H), 3.63 (dd, *J* = 13.8, 5.7 Hz, 1H), 3.31 (dd, *J* = 13.7, 5.4 Hz, 1H), 3.07 – 2.96 (m, 1H), 1.19 (d, *J* = 4.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.3, 141.8, 141.2, 138.8, 135.7, 135.1, 129.7, 128.8, 128.7, 128.2, 128.1, 127.1, 127.0, 126.7, 126.7, 126.6, 126.5, 126.4, 126.3, 122.3, 121.2, 114.8, 108.9, 61.0, 58.0, 56.3, 55.2, 55.2, 36.6, 23.2. HRMS (ESI): Calcd. for C₃₅H₃₃N₂ [M+H]⁺: 481.2638; found: 481.2637.

(74) ethyl2-((*cis*)-5-benzyl-10b-methyl-5,6,10b,11-tetrahydrodibenzo[*c,h*][1,6]naphthyridin-12(4*bH*)-yl)acetate (**P74**)



Yellow solid; m.p. : 131-133 °C, (34.9 mg, 41% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.37 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.28 – 7.10 (m, 9H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.67 (td, *J* = 7.3, 1.1 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 4.23 – 4.07 (m, 4H), 3.97 (d, *J* = 17.9 Hz, 1H), 3.90 (d, *J* = 13.3 Hz, 1H), 3.83 (d, *J* = 15.4 Hz, 1H), 3.58 (d, *J* = 15.4 Hz, 1H), 3.45 (s, 1H), 3.20 (d, *J* = 13.3 Hz, 1H), 3.01 (dd, *J* = 10.8, 1.5 Hz, 1H), 1.27 (s, 3H), 1.21 (td, *J* = 7.1, 1.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.9, 143.6, 141.0, 140.7, 134.9, 133.7, 129.2, 128.4, 128.0, 126.5, 126.3, 126.3, 126.2, 119.2, 115.8, 110.0, 67.7, 60.9, 58.9, 57.8, 55.4, 52.8, 36.9, 23.0, 14.3. HRMS (ESI): Calcd. for C₂₈H₃₁N₂O₂ [M+H]⁺: 427.2380; found: 427.2376.

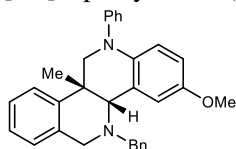
(75) (*cis*)-5-benzyl-10b-methyl-12-phenyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P75**)



Brown solid; m.p. : 107-109 °C, (41.6 mg, 50% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.35 (dt, *J* = 15.5, 7.8 Hz, 3H), 7.29 – 7.21 (m, 7H), 7.20 – 7.13 (m, 3H), 7.10 (td, *J* = 7.3, 1.2 Hz, 1H), 7.00

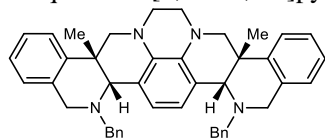
(ddd, $J = 8.7, 7.2, 1.5$ Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.71 (t, $J = 7.4$ Hz, 1H), 6.67 (d, $J = 8.3$ Hz, 1H), 4.21 (d, $J = 11.4$ Hz, 1H), 4.03 (d, $J = 13.3$ Hz, 1H), 3.86 (d, $J = 15.4$ Hz, 1H), 3.64 (d, $J = 15.4$ Hz, 1H), 3.56 (s, 1H), 3.40 (dd, $J = 11.4, 1.4$ Hz, 1H), 3.32 (d, $J = 13.3$ Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.8, 143.8, 140.8, 140.7, 133.5, 129.6, 128.4, 128.2, 126.6, 126.5, 126.4, 126.4, 126.3, 126.2, 124.8, 120.2, 116.8, 114.5, 67.5, 59.7, 57.8, 55.0, 37.6, 23.2. HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{29}\text{N}_2$ $[\text{M}+\text{H}]^+$: 417.2325; found: 417.2324.

(76) (*cis*)-5-benzyl-12-(4-methoxyphenyl)-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P76**)



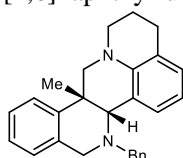
Brown solid; m.p. : 93-95 °C, (44.6 mg, 50% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 2H), 7.18 – 7.13 (m, 3H), 7.12 – 7.04 (m, 4H), 7.01 (dd, $J = 8.0, 6.8$ Hz, 1H), 6.92 – 6.82 (m, 4H), 6.61 – 6.54 (m, 1H), 6.42 – 6.38 (m, 1H), 4.21 – 4.06 (m, 1H), 3.96 (d, $J = 13.4$ Hz, 1H), 3.78 (d, $J = 15.5$ Hz, 1H), 3.74 (s, 3H), 3.55 (d, $J = 15.4$ Hz, 1H), 3.45 (s, 1H), 3.27 – 3.14 (m, 2H), 1.29 (d, $J = 1.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 157.3, 144.6, 140.9, 140.8, 140.5, 134.9, 133.6, 128.5, 128.5, 128.3, 128.2, 126.6, 126.5, 126.4, 126.3, 126.1, 119.2, 116.0, 115.0, 113.7, 67.6, 60.1, 57.9, 55.5, 55.3, 37.3, 23.0. HRMS (ESI): Calcd. for $\text{C}_{31}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 447.2431; found: 447.2430.

(77) (*cis,cis*)-16,19-dibenzyl-4b,10a-dimethyl-4b,5,7,8,10,10a,15,16,16a,18b,19,20-dodecahydroisoquinolino[4,3-*c*:3',4'-*i*]pyrazino[1,2,3,4-*lmn*][1,10]phenanthroline (**P77**)



Brown solid; m.p. : 116-118 °C, (51.5 mg, 41% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.28 (dd, $J = 7.9, 2.9$ Hz, 2H), 7.14 (ddt, $J = 28.0, 22.9, 6.9$ Hz, 12H), 7.05 – 6.98 (m, 2H), 6.83 (d, $J = 7.7$ Hz, 2H), 6.48 (d, $J = 3.7$ Hz, 2H), 3.90 (dd, $J = 13.6, 3.5$ Hz, 2H), 3.80 – 3.63 (m, 4H), 3.57 – 3.38 (m, 4H), 3.27 (d, $J = 3.4$ Hz, 2H), 3.24 – 3.06 (m, 4H), 2.74 (d, $J = 10.8$ Hz, 2H), 1.17 (d, $J = 3.5$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.73, 141.19, 135.12, 130.42, 128.39, 128.07, 126.53, 126.47, 126.35, 125.98, 121.17, 116.61, 67.17, 58.59, 57.38, 55.40, 47.32, 36.72, 23.55. HRMS (ESI): Calcd. for $\text{C}_{44}\text{H}_{45}\text{N}_4$ $[\text{M}+\text{H}]^+$: 629.3639; found: 629.3639.

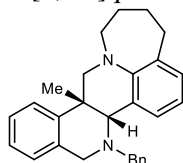
(78) (*cis*)-6-benzyl-14a-methyl-6,6a,11,12,14,14a-hexahydro-5*H*,10*H*-benzo[*c*]quinolino[1,8-*gh*][1,6]naphthyridine (**P78**)



Brown solid; m.p. : 121-123 °C, (64.6 mg, 85% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.44 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.28 (dd, $J = 8.0, 2.8$ Hz, 5H), 7.22 – 7.13 (m, 2H), 7.06 (dd, $J = 7.6, 1.4$ Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.91 (dd, $J = 7.2, 1.6$ Hz, 1H), 6.56 (t, $J = 7.4$ Hz, 1H), 3.99 (d, $J = 13.4$ Hz, 1H), 3.95 – 3.82 (m, 2H), 3.66 (d, $J = 15.4$ Hz, 1H), 3.46 (d, $J = 1.4$ Hz, 1H), 3.39 – 3.17 (m, 3H), 2.91 (dd, $J = 11.2, 1.6$ Hz, 1H), 2.86 – 2.70 (m, 2H), 2.14 – 2.05 (m, 1H), 2.01 – 1.88 (m, 1H),

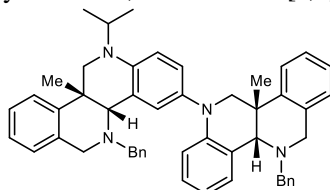
1.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.6, 141.4, 141.0, 135.1, 131.4, 128.4, 128.3, 128.0, 126.5, 126.4, 126.3, 126.0, 121.2, 117.6, 114.1, 67.8, 58.6, 57.7, 55.5, 49.7, 36.6, 28.0, 23.2, 21.8. HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{29}\text{N}_2$ $[\text{M}+\text{H}]^+$: 381.2325; found: 381.2324.

(79) (*cis*)-6-benzyl-15a-methyl-6,6a,10,11,12,13,15,15a-octahydro-5*H*-azepino[3,2,1-*ij*]isoquinolino[4,3-*c*]quinoline (**P79**)



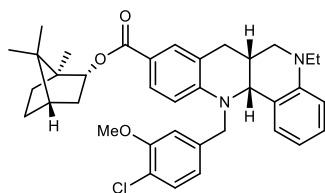
Black solid; m.p. : 140-142 °C, (48.9 mg, 62% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 8.0 Hz, 1H), 7.29 – 7.20 (m, 6H), 7.15 (td, J = 7.4, 1.2 Hz, 1H), 7.09 (dd, J = 7.4, 1.6 Hz, 1H), 7.02 (dd, J = 7.4, 1.6 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.72 (t, J = 7.4 Hz, 1H), 4.04 (d, J = 13.2 Hz, 1H), 3.91 – 3.76 (m, 2H), 3.60 (d, J = 15.6 Hz, 1H), 3.47 (d, J = 1.6 Hz, 1H), 3.34 – 3.11 (m, 4H), 2.84 – 2.70 (m, 2H), 1.87 – 1.73 (m, 3H), 1.65 – 1.59 (m, 1H), 1.21 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.0, 141.5, 140.8, 134.8, 131.7, 131.2, 130.8, 128.4, 128.1, 126.6, 126.5, 126.4, 126.3, 126.0, 123.3, 117.7, 68.3, 62.2, 58.0, 56.6, 55.3, 38.4, 35.2, 29.3, 25.6, 23.1. HRMS (ESI): Calcd. for $\text{C}_{28}\text{H}_{31}\text{N}_2$ $[\text{M}+\text{H}]^+$: 395.2482; found: 395.2480.

(80) (*cis,cis*)-5,5'-dibenzyl-12-isopropyl-10*b*,10'*b*-dimethyl-4*b*,4'*b*,5,5',6,10*b*,10'*b*,11,11',12-decahydro-6'*H*-3,12'-bidibenzo[*c,h*][1,6]naphthyridine (**P80**)



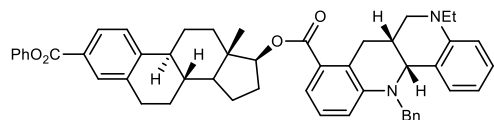
Brown solid; m.p. : 118-120 °C, (87.8 mg, 62% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.40 (dd, J = 8.0, 2.4 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.28 – 7.13 (m, 12H), 7.10 – 7.01 (m, 3H), 6.93 (p, J = 8.0, 7.4 Hz, 3H), 6.76 (dd, J = 7.9, 3.9 Hz, 1H), 6.62 (t, J = 7.5 Hz, 1H), 6.48 (td, J = 7.6, 2.9 Hz, 1H), 4.26 – 4.17 (m, 2H), 4.12 – 3.94 (m, 2H), 3.90 – 3.77 (m, 2H), 3.74 – 3.61 (m, 2H), 3.59 – 3.49 (m, 2H), 3.39 – 3.25 (m, 3H), 3.20 (ddd, J = 12.9, 9.6, 2.8 Hz, 1H), 2.98 (d, J = 11.3 Hz, 1H), 1.39 (d, J = 2.8 Hz, 3H), 1.28 (dd, J = 6.4, 2.9 Hz, 3H), 1.21 (q, J = 2.9 Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.3, 142.3, 141.7, 141.1, 141.0, 140.9, 140.8, 140.7, 135.0, 134.4, 134.3, 133.5, 132.8, 132.7, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 126.6, 126.6, 126.5, 126.4, 126.3, 126.3, 126.3, 126.2, 126.1, 120.4, 118.8, 118.6, 115.4, 115.3, 113.7, 113.5, 111.4, 111.4, 67.9, 67.8, 67.7, 60.4, 60.1, 57.9, 57.7, 57.5, 55.4, 55.4, 55.3, 49.0, 46.7, 37.3, 37.2, 36.2, 23.2, 23.2, 22.8, 19.7, 18.8. HRMS (ESI): Calcd. for $\text{C}_{51}\text{H}_{53}\text{N}_4$ $[\text{M}+\text{H}]^+$: 721.4265; found: 721.4264.

(81) (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl-(6*a-cis*)-12-(3-chloro-4-methoxybenzyl)-5-ethyl-5,6,6*a*,7,12,12*a*-hexahydrodibenzo[*b,h*][1,6]naphthyridine-9-carboxylate (**P81**)



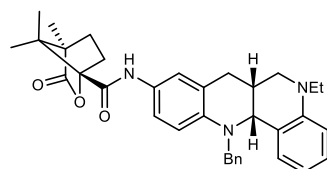
Brown solid; m.p. : 101-103 °C, (64.6 mg, 54% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.70 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 2.2 Hz, 1H), 7.10 – 7.04 (m, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.58 – 6.48 (m, 3H), 5.03 (d, *J* = 15.2 Hz, 1H), 4.90 (d, *J* = 17.0 Hz, 1H), 4.55 (d, *J* = 3.4 Hz, 1H), 4.39 (d, *J* = 17.0 Hz, 1H), 3.84 (s, 3H), 3.54 – 3.48 (m, 1H), 3.40 – 3.28 (m, *J* = 7.3 Hz, 2H), 3.23 (dd, *J* = 11.7, 6.4 Hz, 1H), 2.94 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.74 (dd, *J* = 16.4, 8.2 Hz, 1H), 2.60 – 2.52 (m, 1H), 2.45 – 2.35 (m, 1H), 2.13 – 2.05 (m, 1H), 1.80 – 1.73 (m, 1H), 1.68 (t, *J* = 4.6 Hz, 1H), 1.39 – 1.22 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.09 – 1.01 (m, 1H), 0.93 (s, 3H), 0.88 (s, 3H), 0.86 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.1, 153.9, 147.2, 143.7, 131.6, 131.2, 129.5, 129.1, 128.1, 125.6, 122.7, 120.8, 120.1, 118.5, 115.2, 112.2, 111.1, 110.4, 79.5, 58.9, 56.2, 52.7, 49.9, 49.0, 47.8, 45.1, 44.6, 37.0, 29.9, 29.7, 29.6, 28.1, 27.5, 19.8, 19.0, 13.6, 11.0. HRMS (ESI): Calcd. for C₃₇H₄₄ClN₂O₃ [M+H]⁺: 599.3035; found: 599.3028.

(82) (8R,9S,13S,17S)-3-(benzoyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl (6a-cis)-12-benzyl-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine-8-carboxylate (**P82**)



Yellow solid; m.p. : 105-107 °C, (66.6 mg, 44% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 7.8 Hz, 2H), 7.77 – 7.65 (m, 3H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.27 – 7.24 (m, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.04 – 6.98 (m, 3H), 6.69 – 6.54 (m, 3H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.99 – 4.90 (m, 1H), 4.66 – 4.54 (m, 2H), 3.62 – 3.55 (m, 1H), 3.40 (q, *J* = 8.0 Hz, 2H), 3.32 – 3.24 (m, 1H), 3.04 – 2.87 (m, 3H), 2.85 – 2.74 (m, 1H), 2.68 – 2.59 (m, 1H), 2.40 – 2.23 (m, 3H), 1.99 (t, *J* = 11.4 Hz, 2H), 1.88 – 1.79 (m, 1H), 1.75 – 1.33 (m, 7H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.99 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 165.5, 148.7, 147.4, 143.5, 138.3, 138.2, 138.1, 133.5, 131.3, 130.2, 129.8, 129.5, 128.9, 128.7, 128.6, 128.3, 127.0, 126.6, 126.4, 121.7, 121.1, 120.1, 118.7, 118.0, 115.4, 111.1, 110.4, 82.3, 59.0, 53.9, 50.3, 49.9, 44.7, 44.1, 43.3, 38.3, 37.0, 29.8, 29.6, 29.5, 27.9, 27.1, 26.2, 23.5, 12.5, 11.1. HRMS (ESI): Calcd. for C₅₁H₅₃N₂O₄ [M+H]⁺: 757.4000; found: 757.3983.

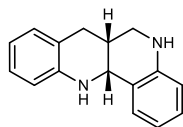
(83) (1S,4R)-N-(((6a-cis)-12-benzyl-5-ethyl-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridin-9-yl)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxamide (**P83**)



Yellow solid; m.p. : 88-90 °C, (85.7 mg, 78% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.89 (s, 1H), 7.30 – 7.14 (m, 6H), 7.09 – 7.01 (m, 2H), 6.93 (d, *J* = 9.6 Hz, 1H), 6.57 – 6.44 (m, 3H), 4.91 (d, *J* = 17.2 Hz, 1H), 4.49 (d, *J* = 3.4 Hz, 1H), 4.42 (d, *J* = 17.2 Hz, 1H), 3.56 – 3.41 (m, 1H), 3.37 – 3.30 (m, 2H), 3.25 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.92 – 2.81 (m, 1H), 2.72 – 2.64 (m, 1H), 2.61 – 2.48 (m, 2H), 2.01 – 1.86 (m, 2H), 1.74 – 1.61 (m, 1H), 1.17 – 1.11 (m, 9H), 0.93 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 178.2, 164.6, 143.7, 141.2, 139.2, 128.7, 128.5, 126.7, 126.6, 126.2, 122.1, 121.6,

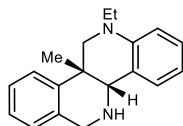
121.4, 119.7, 115.2, 112.5, 110.3, 92.6, 58.5, 55.5, 54.2, 54.0, 50.4, 44.6, 30.5, 29.8, 29.6, 29.2, 16.8, 16.6, 11.1, 9.8. HRMS (ESI): Calcd. for C₃₅H₄₀N₃O₃ [M+H]⁺: 550.3064; found: 550.3058.

(84) (6a-*cis*)-5,6,6a,7,12,12a-hexahydrodibenzo[*b,h*][1,6]naphthyridine (**P84**)

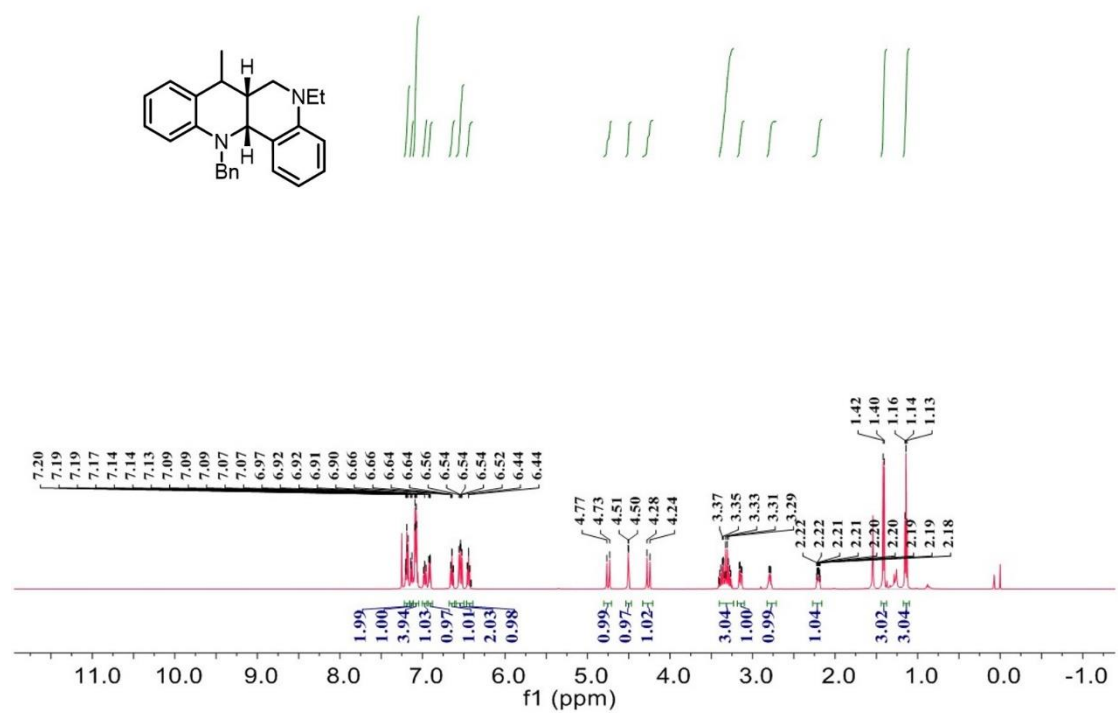


Yellow solid; m.p. : 128-130 °C, (35.4 mg, 75% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.12 (m, 2H), 7.07 – 7.00 (m, 2H), 6.74 – 6.66 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 4.41 (d, *J* = 3.0 Hz, 1H), 4.02 (s, 1H), 3.86 (s, 1H), 3.37 (t, *J* = 11.4 Hz, 1H), 3.24 (dd, *J* = 16.8, 6.2 Hz, 1H), 3.16 (dd, *J* = 11.3, 4.2 Hz, 1H), 2.69 (dd, *J* = 16.9, 2.6 Hz, 1H), 2.50 – 2.40 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.8, 141.8, 129.5, 129.3, 129.0, 127.1, 122.1, 118.6, 117.1, 116.6, 114.1, 113.8, 50.6, 41.9, 29.8, 29.1. HRMS (ESI): Calcd. for C₁₆H₁₇N₂ [M+H]⁺: 237.1386; found: 237.1382.

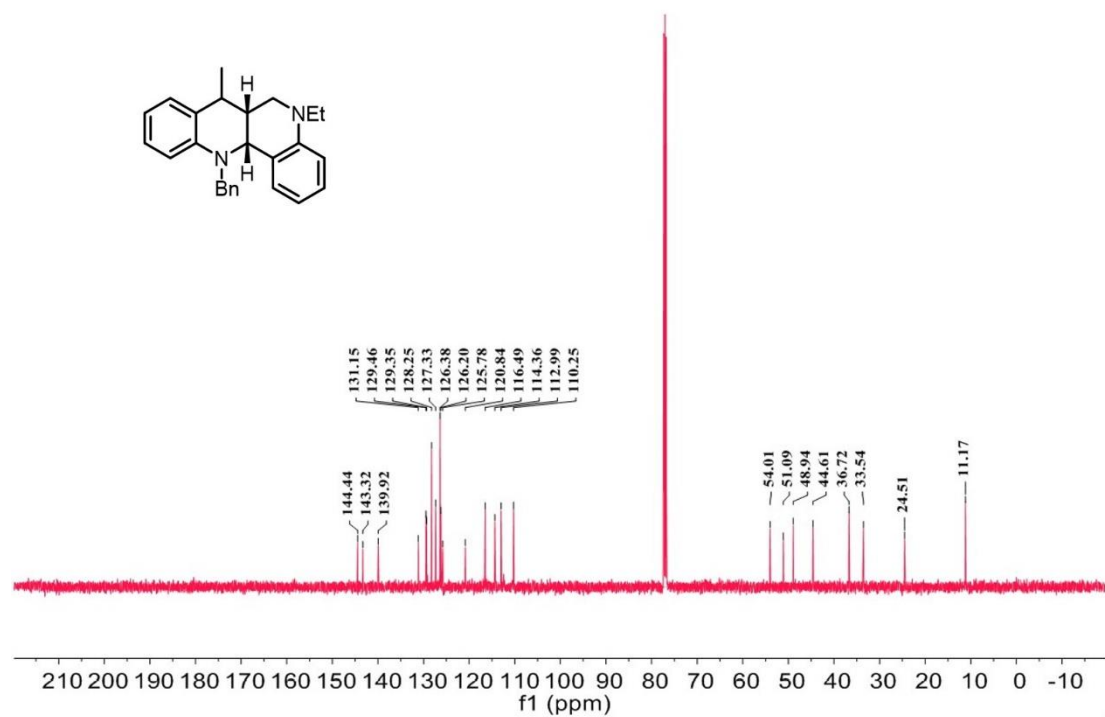
(85) (*cis*)-12-ethyl-10b-methyl-4b,5,6,10b,11,12-hexahydrodibenzo[*c,h*][1,6]naphthyridine (**P85**)



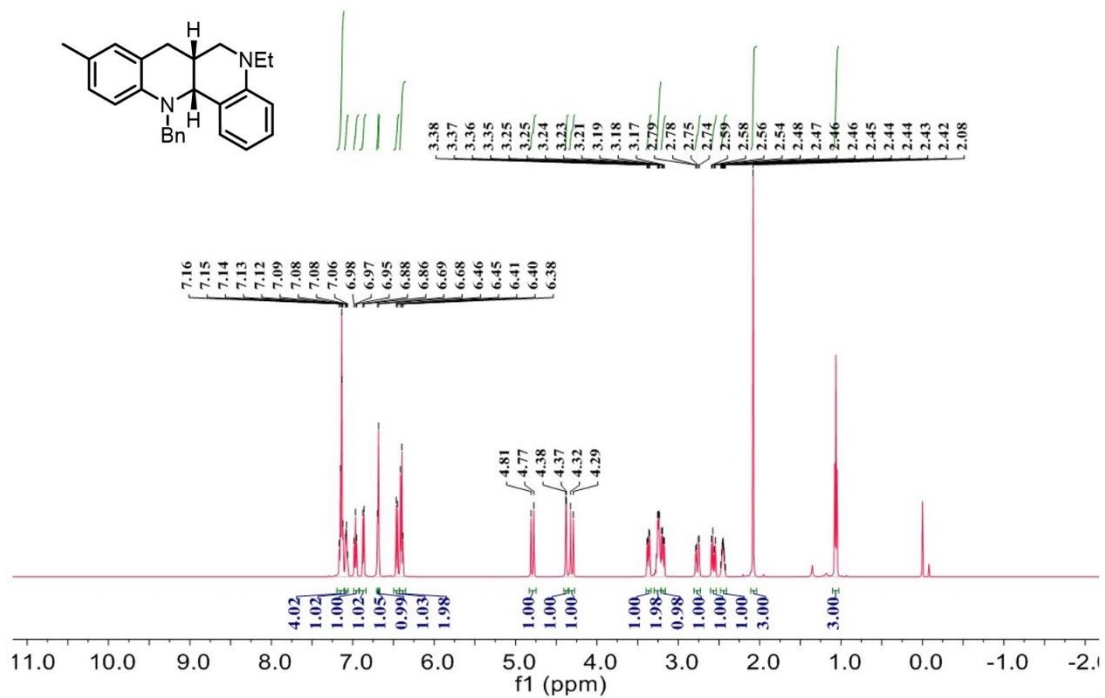
Brown solid; m.p. : 119-121 °C, (37.2 mg, 67% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 7.5 Hz, 1H), 7.18 – 7.11 (m, 2H), 7.07 (td, *J* = 7.7, 2.2 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.60 – 6.54 (m, 2H), 4.19 (d, *J* = 15.2 Hz, 1H), 3.93 (d, *J* = 15.5 Hz, 1H), 3.55 – 3.36 (m, 3H), 3.22 (dq, *J* = 14.3, 7.1, 1.9 Hz, 1H), 2.78 (dt, *J* = 11.6, 1.9 Hz, 1H), 1.14 (d, *J* = 2.3 Hz, 3H), 1.06 (td, *J* = 7.1, 2.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.5, 141.2, 135.9, 131.6, 128.7, 126.8, 126.6, 126.2, 126.1, 122.5, 115.8, 110.6, 61.4, 55.9, 49.1, 45.3, 35.1, 22.7, 11.1. HRMS (ESI): Calcd. for C₁₉H₂₃N₂ [M+H]⁺: 279.1856; found: 279.1854.



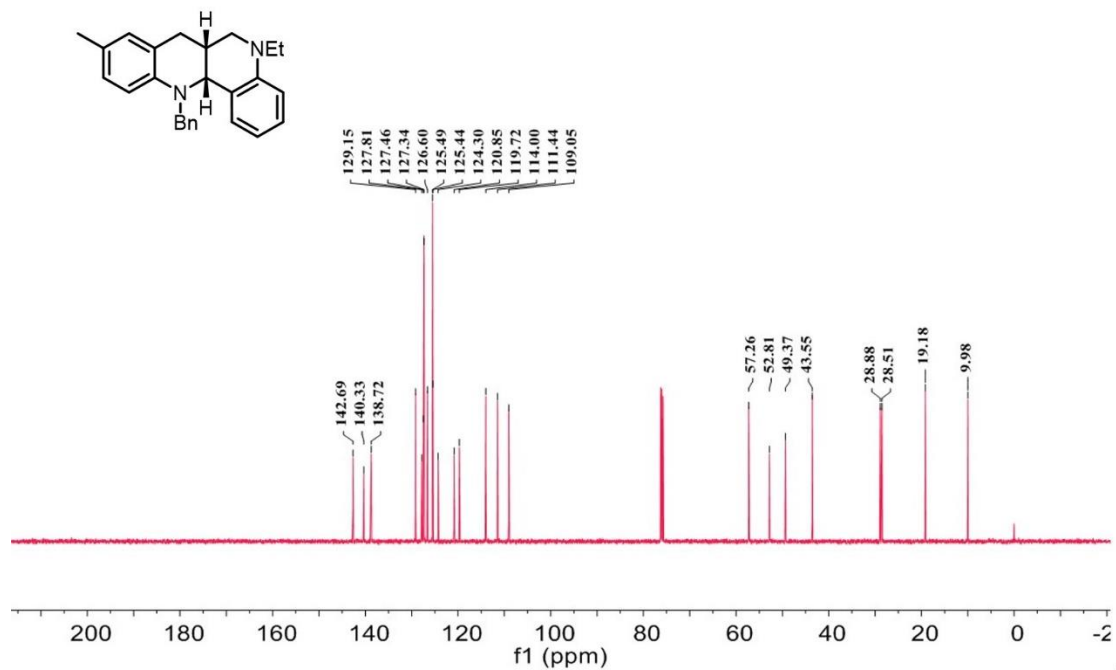
Supplementary Fig. 20 ¹H-NMR spectrum of P2



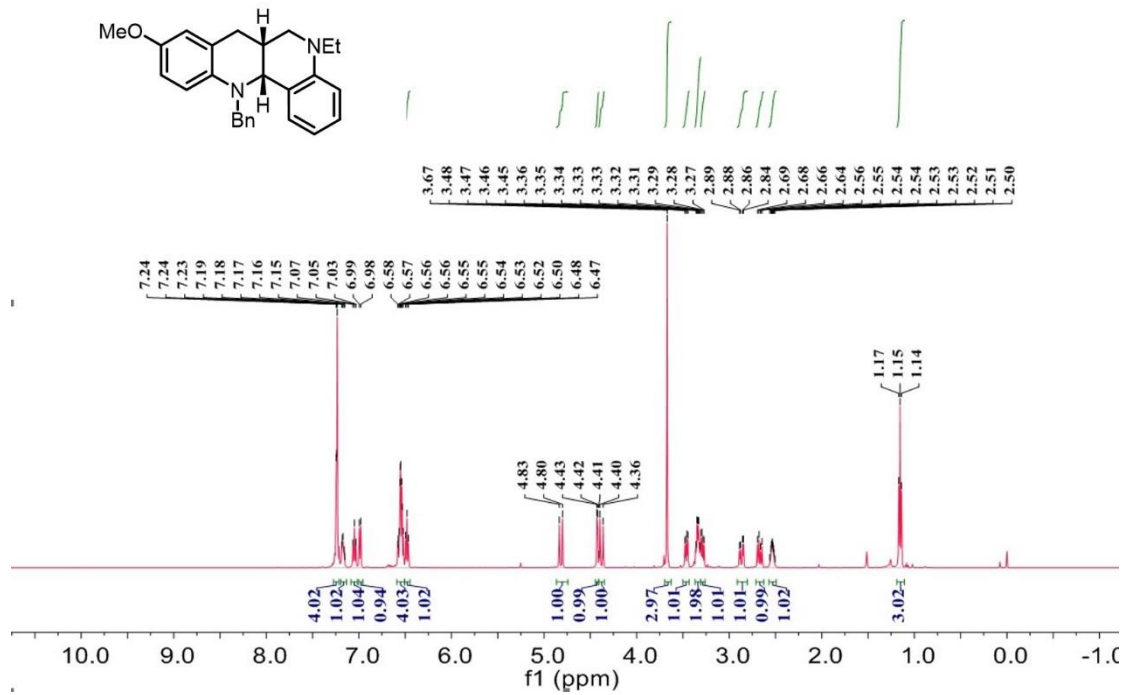
Supplementary Fig. 21 ¹³C-NMR spectrum of P2



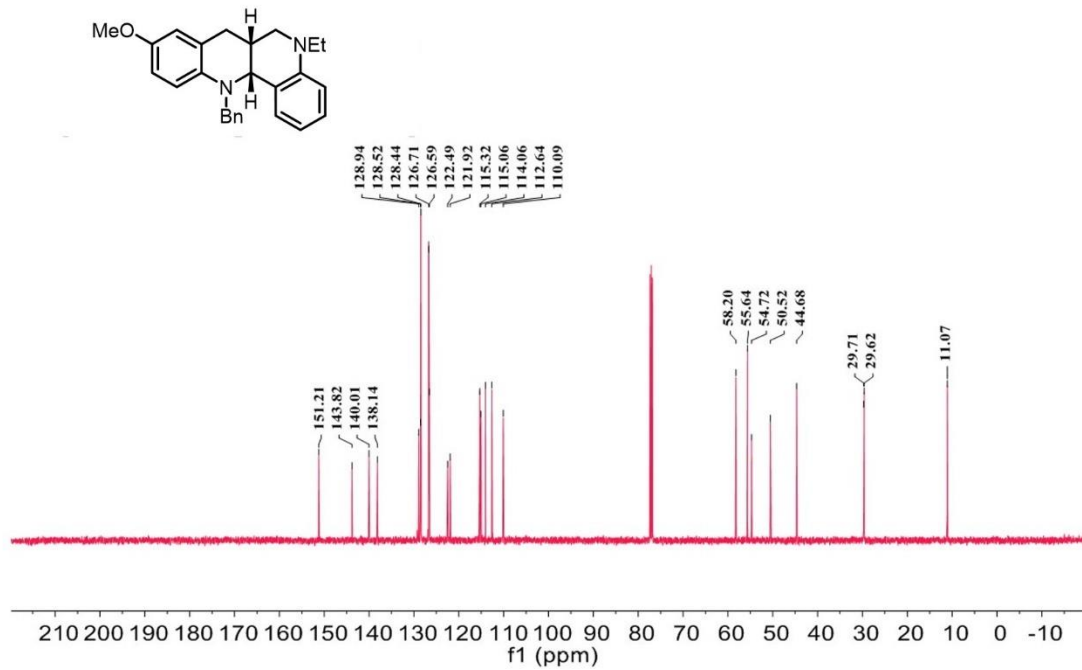
Supplementary Fig. 22 ¹H-NMR spectrum of P3



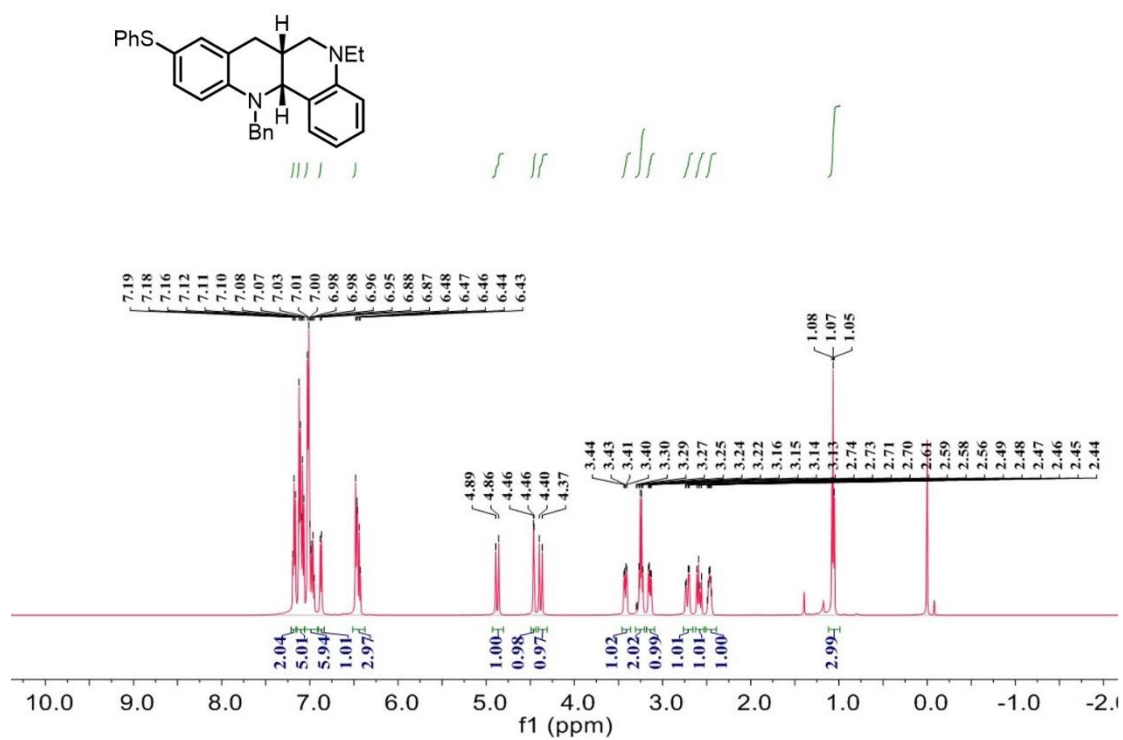
Supplementary Fig. 23 ¹³C-NMR spectrum of P3



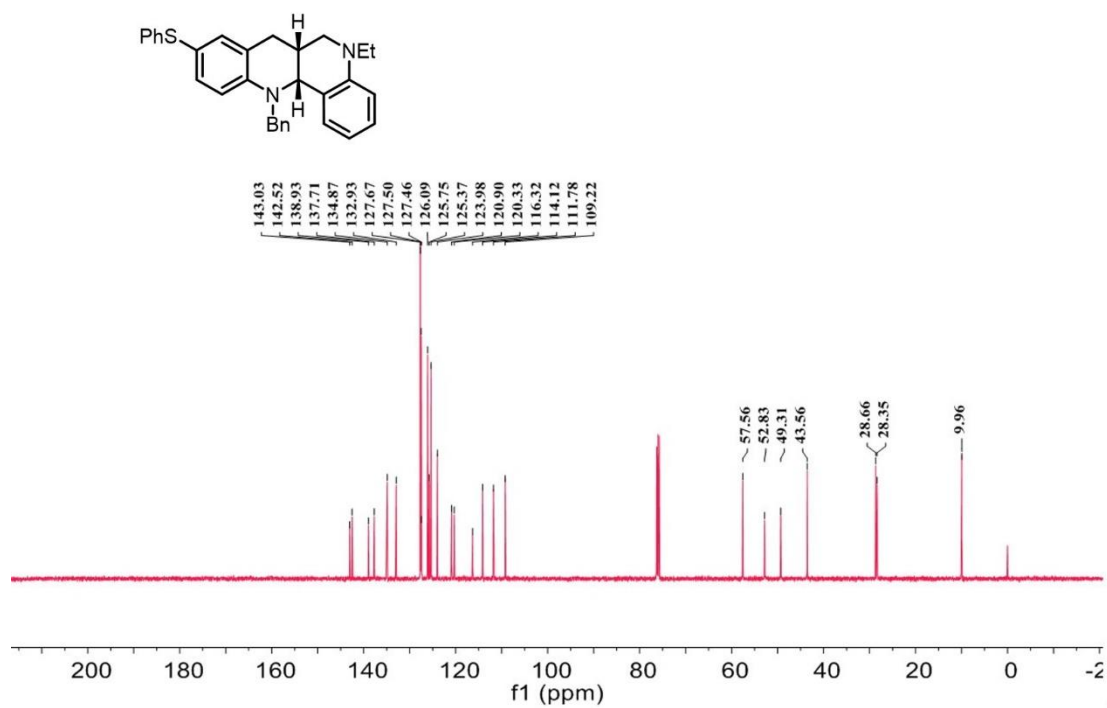
Supplementary Fig. 24 ¹H-NMR spectrum of P4



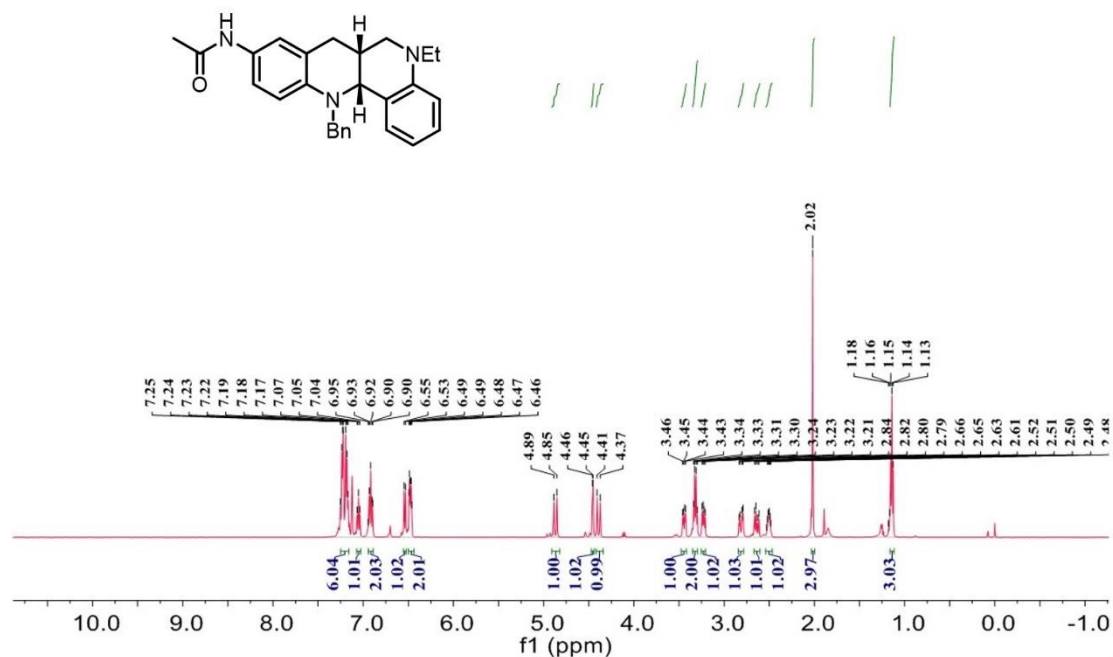
Supplementary Fig. 25 ¹³C-NMR spectrum of P4



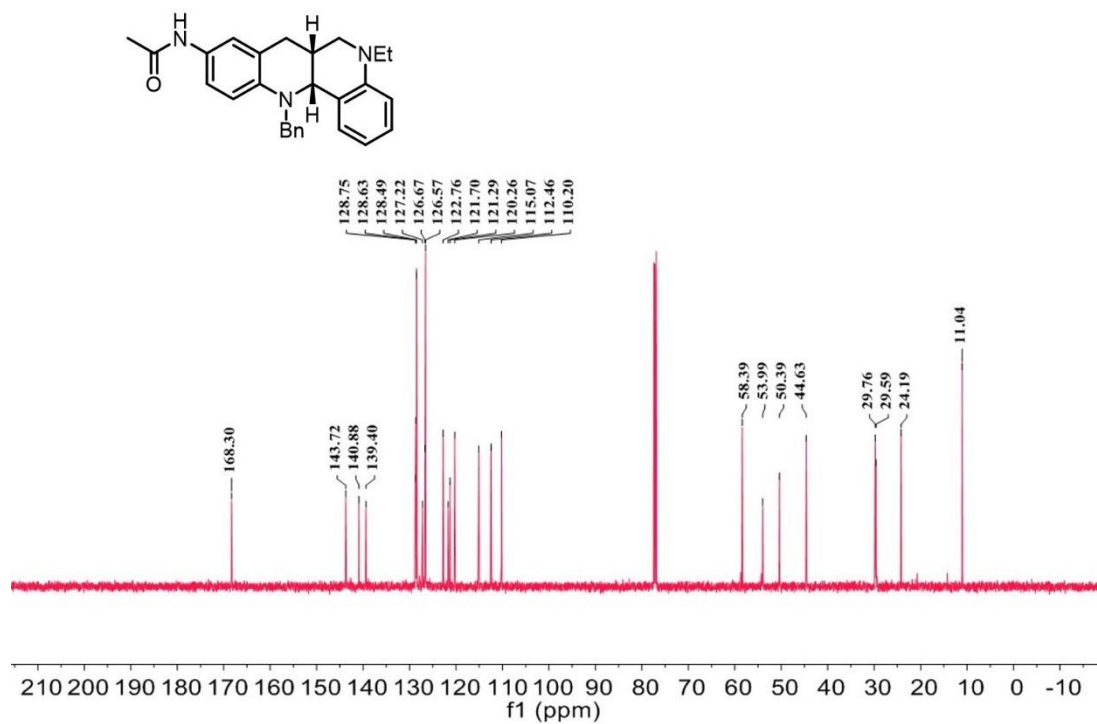
Supplementary Fig. 26 ¹H-NMR spectrum of P5



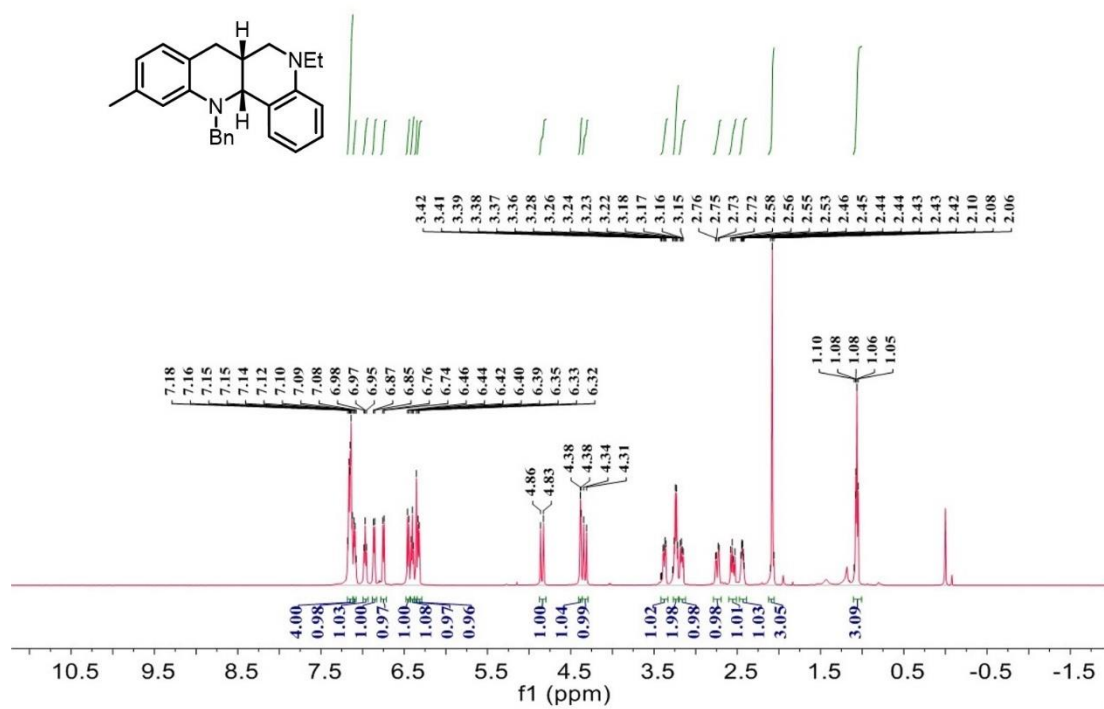
Supplementary Fig. 27 ¹³C-NMR spectrum of P5



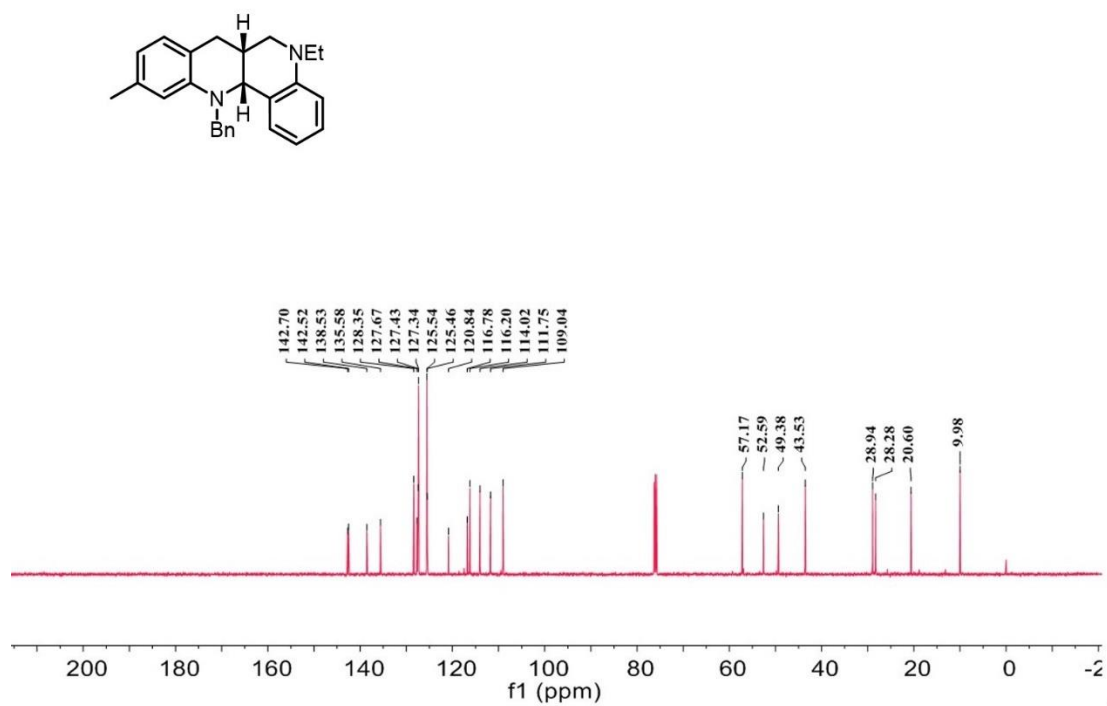
Supplementary Fig. 28 ¹H-NMR spectrum of P6



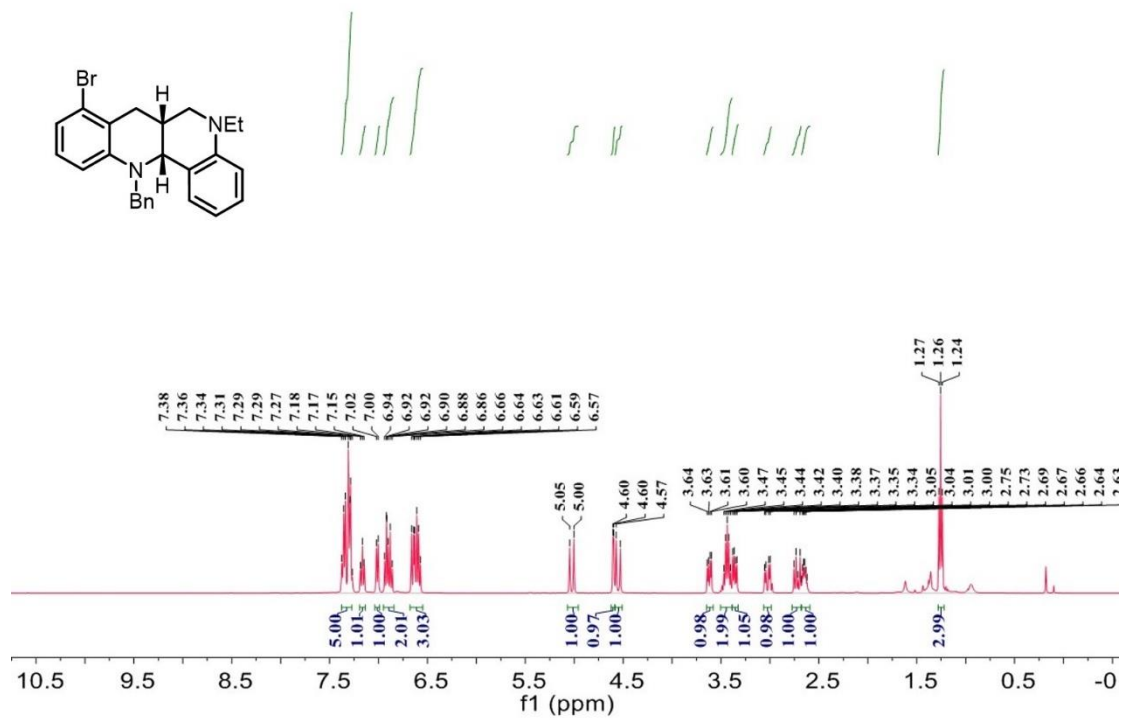
Supplementary Fig. 29 ¹³C-NMR spectrum of P6



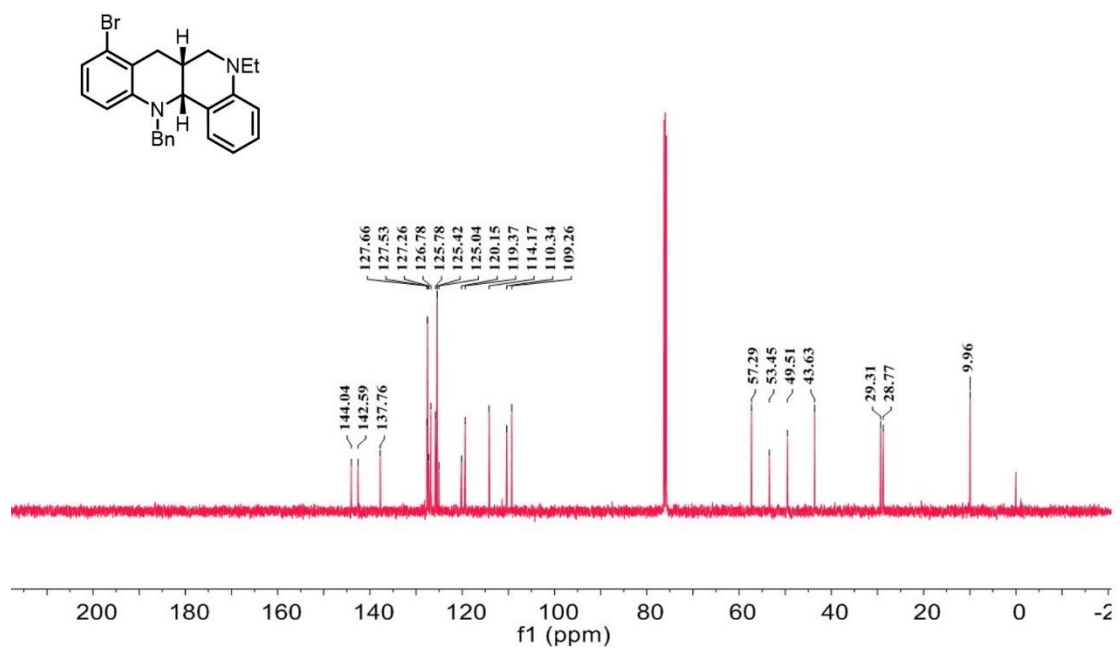
Supplementary Fig. 30 ¹H-NMR spectrum of P7



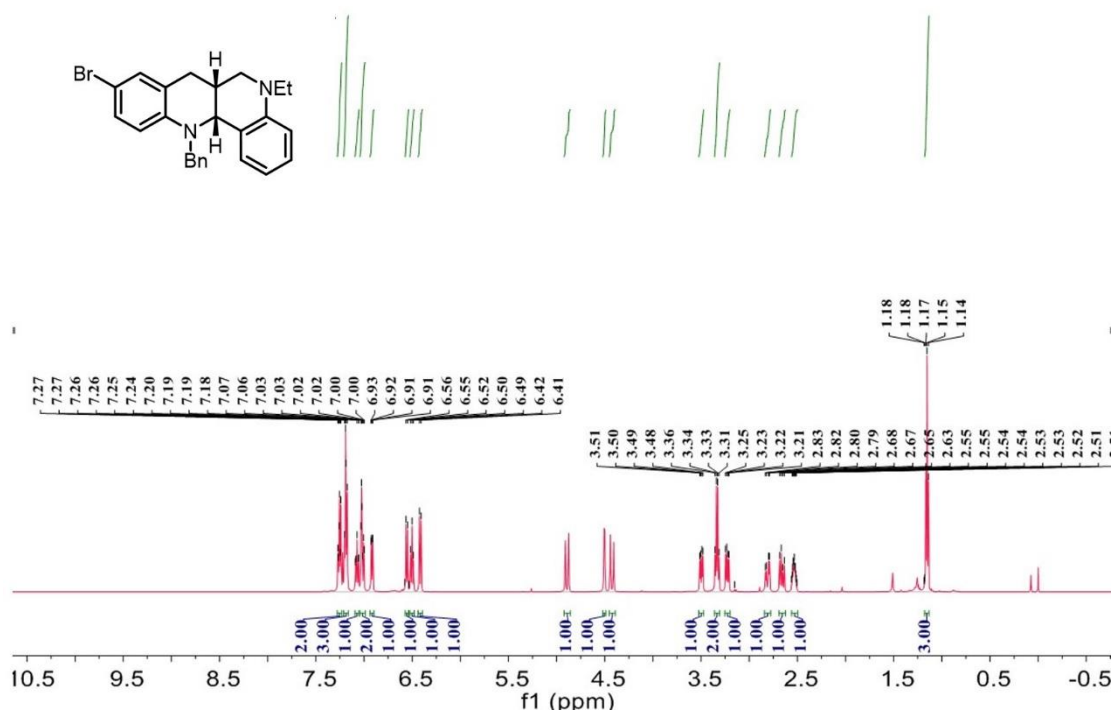
Supplementary Fig. 31 ¹³C-NMR spectrum of P7



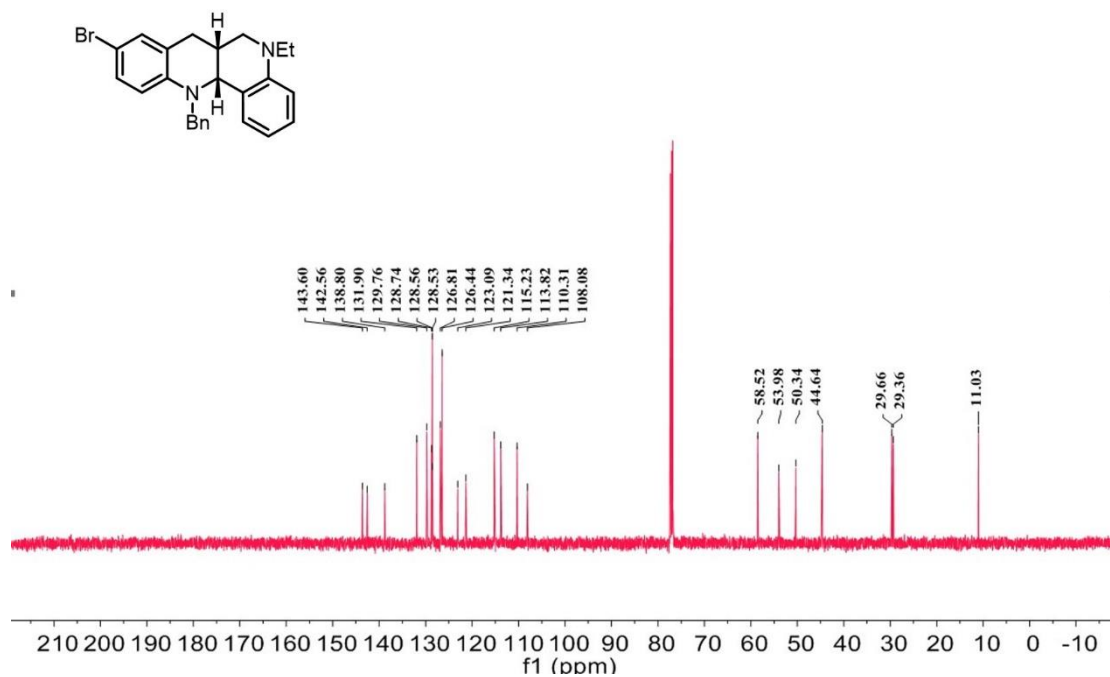
Supplementary Fig. 32 ¹H-NMR spectrum of P8



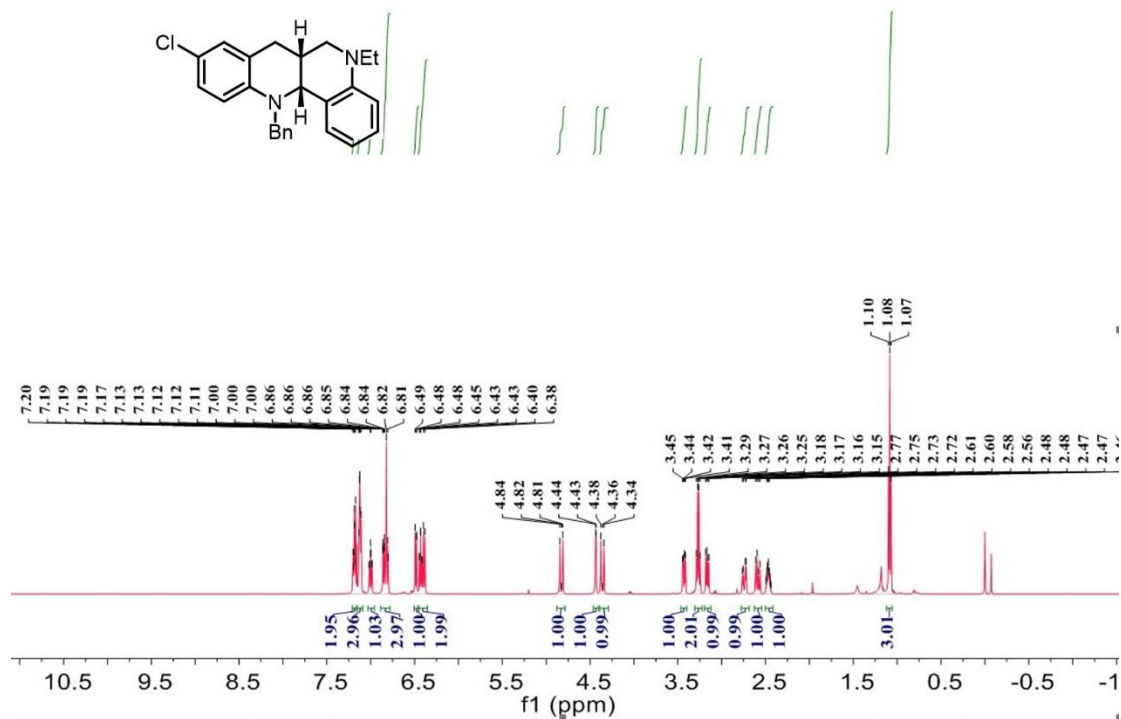
Supplementary Fig. 33 ¹³C-NMR spectrum of P8



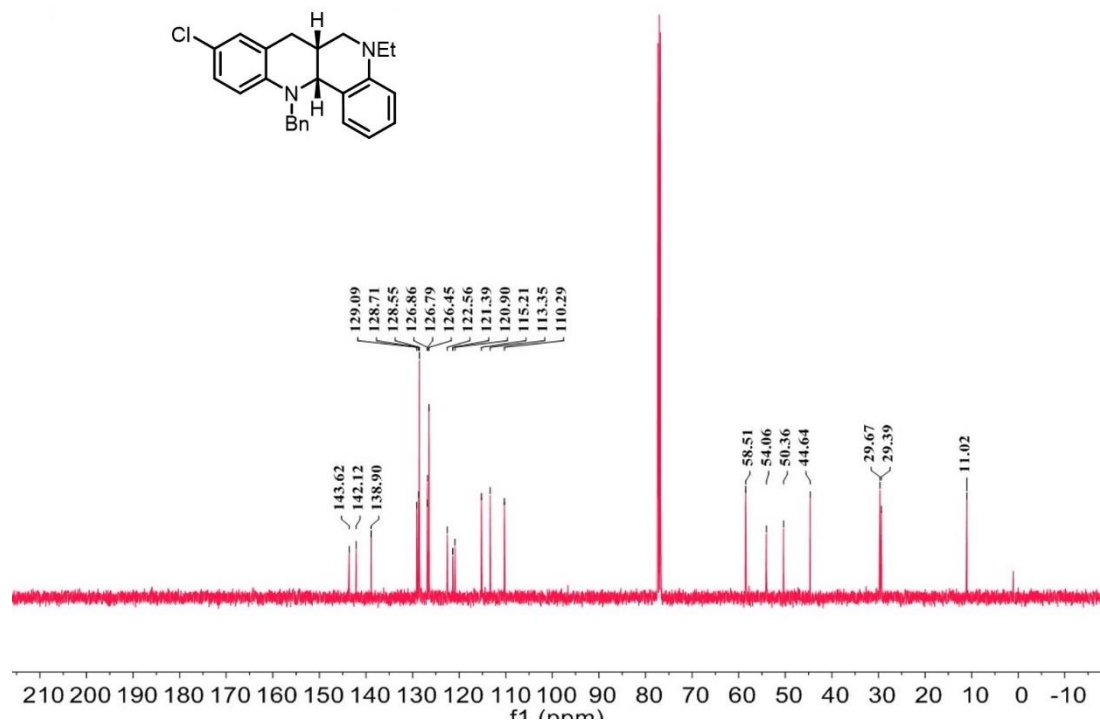
Supplementary Fig. 34 ¹H-NMR spectrum of P9



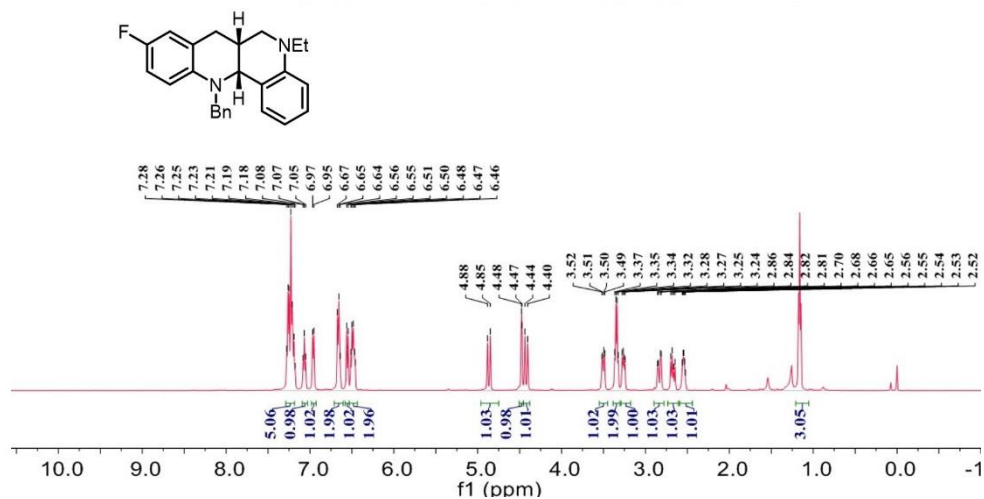
Supplementary Fig. 35 ¹³C-NMR spectrum of P9



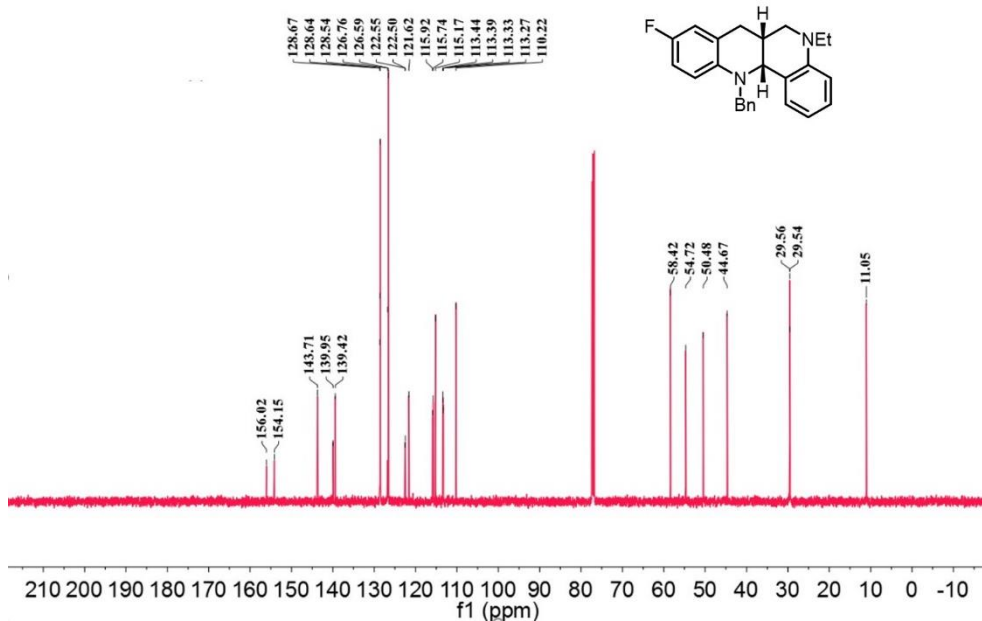
Supplementary Fig. 36 ¹H-NMR spectrum of P10



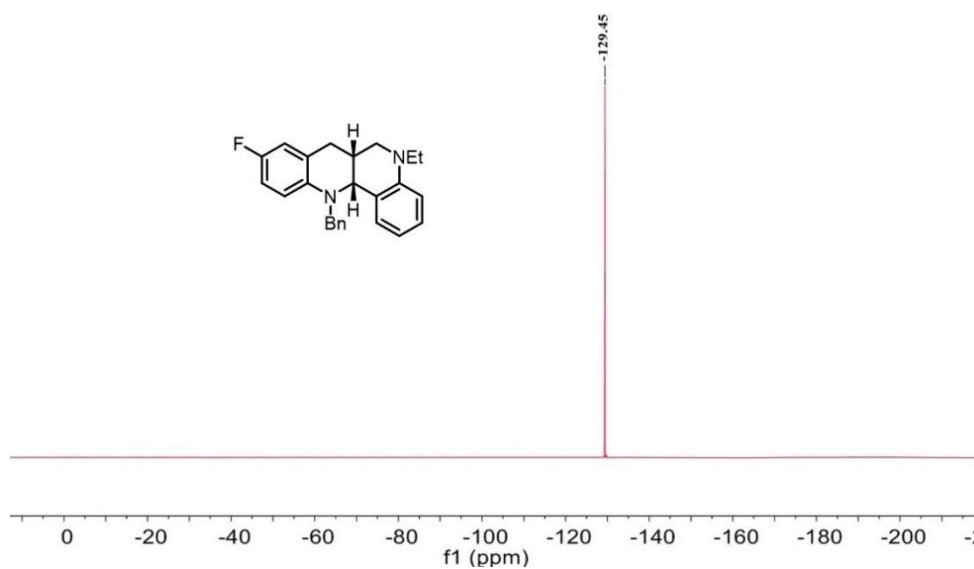
Supplementary Fig. 37 ¹³C-NMR spectrum of P10



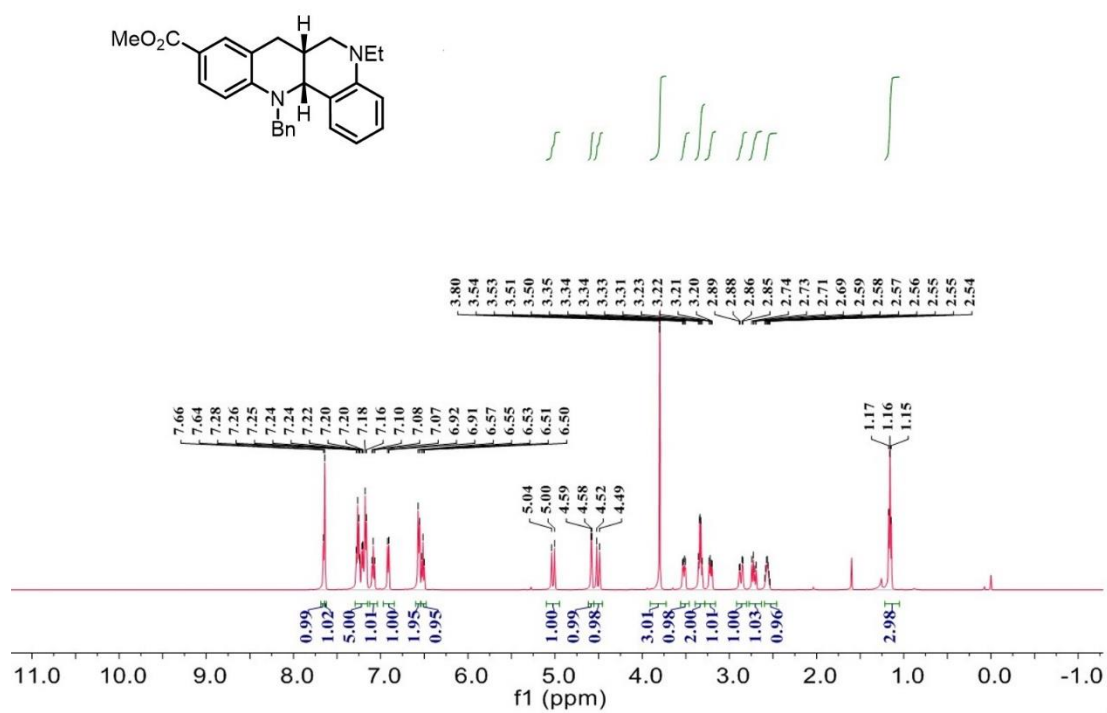
Supplementary Fig. 38 ¹H-NMR spectrum of P11



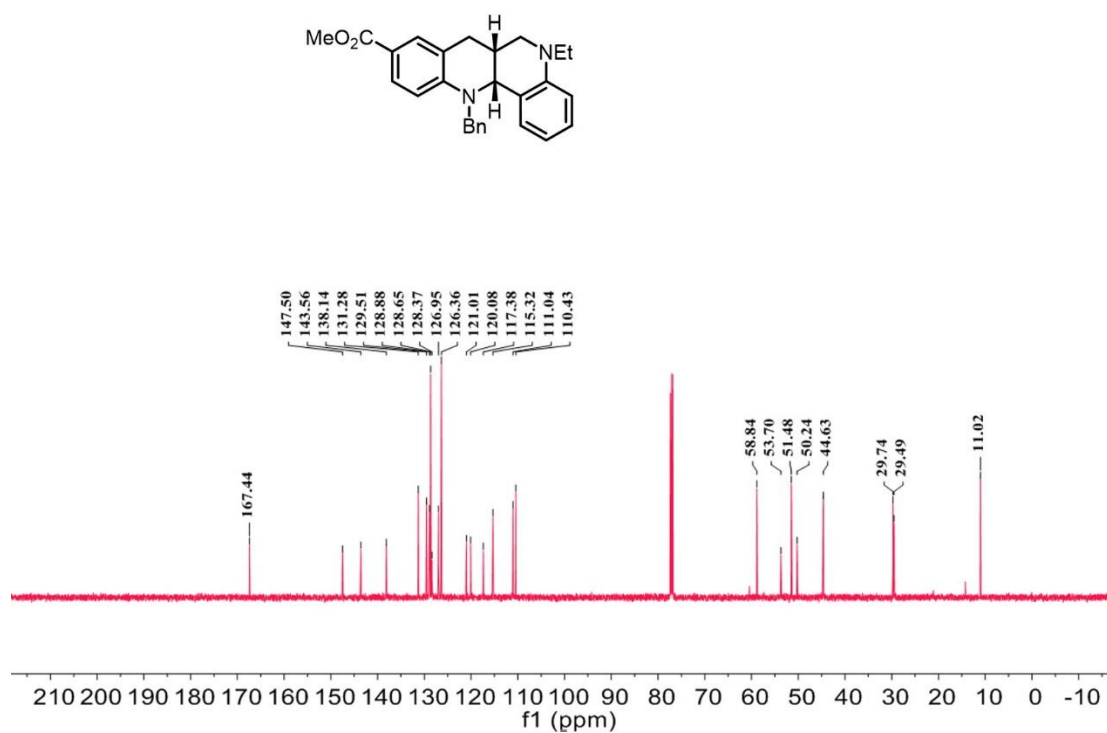
Supplementary Fig. 39 ¹³C-NMR spectrum of P11



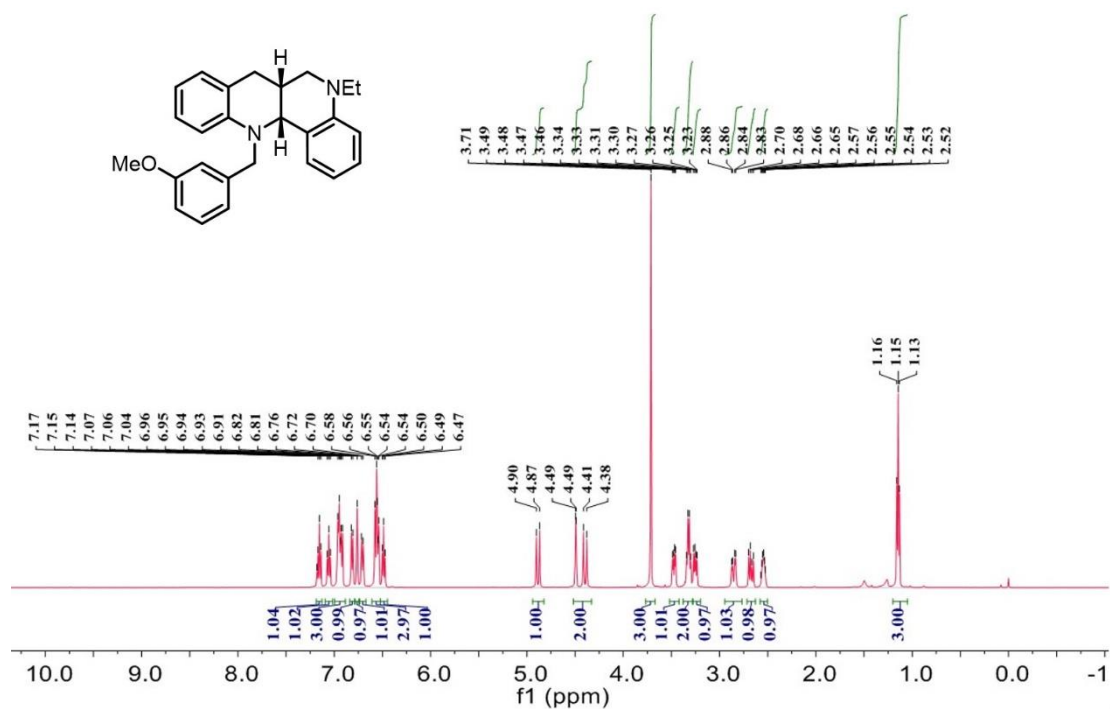
Supplementary Fig. 40 ¹⁹F-NMR spectrum of P11



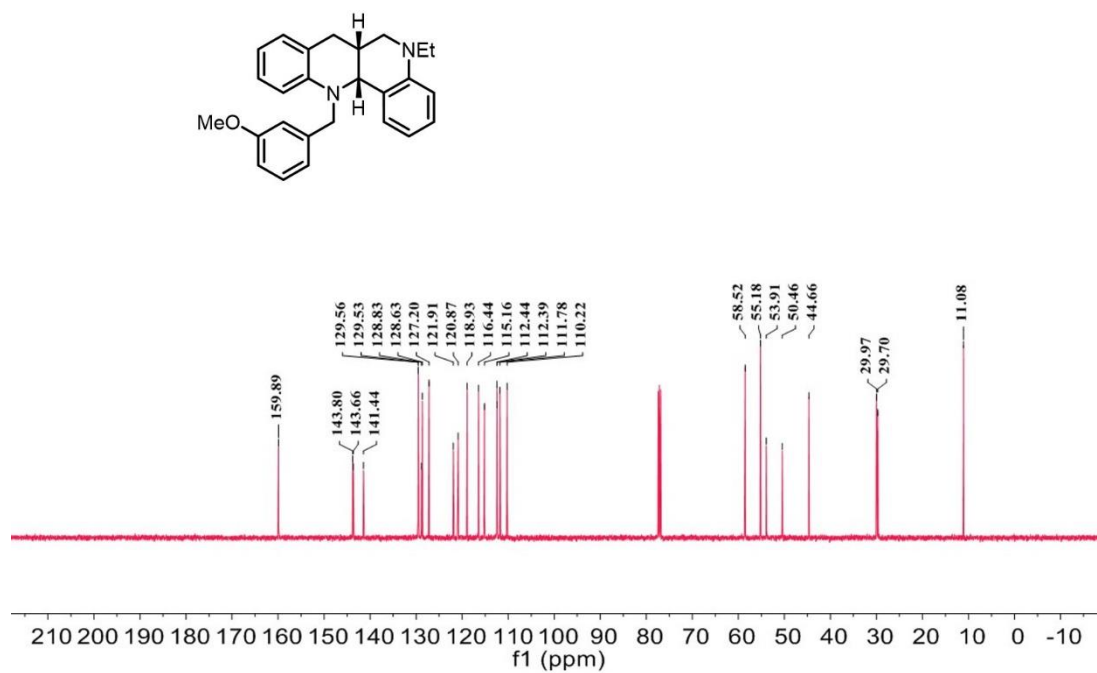
Supplementary Fig. 41 ^1H -NMR spectrum of P12



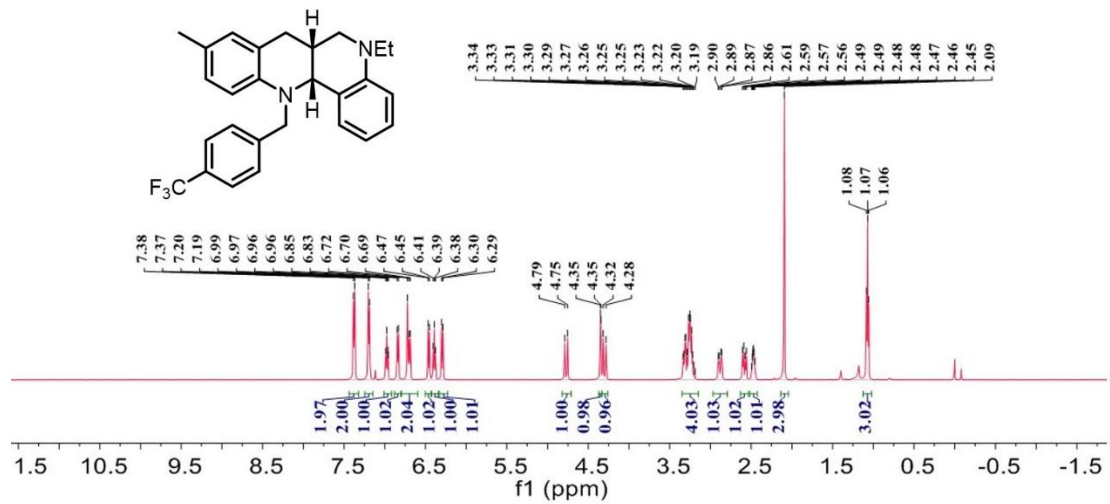
Supplementary Fig. 42 ^{13}C -NMR spectrum of P12



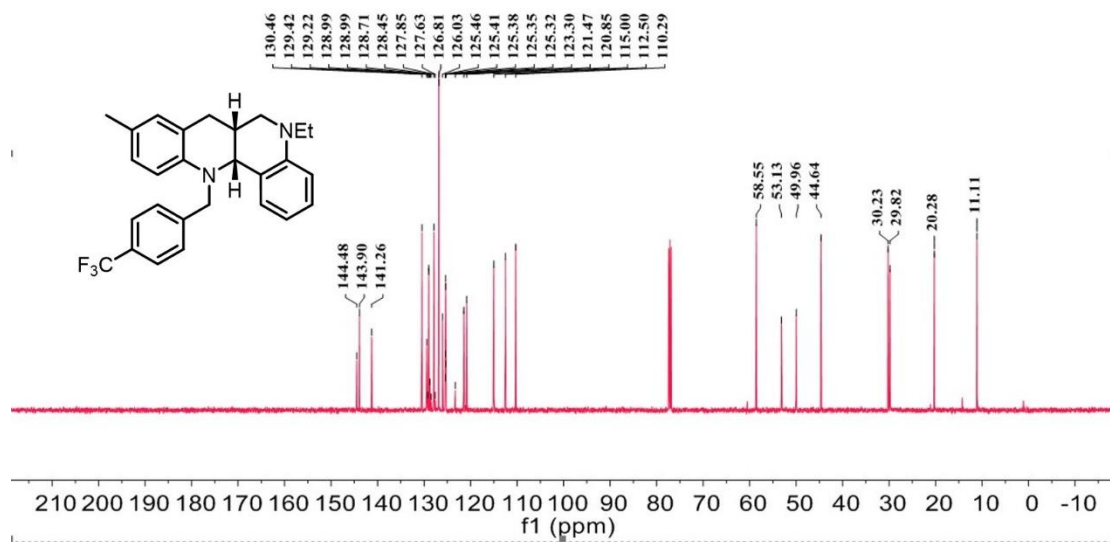
Supplementary Fig. 43 ¹H-NMR spectrum of P13



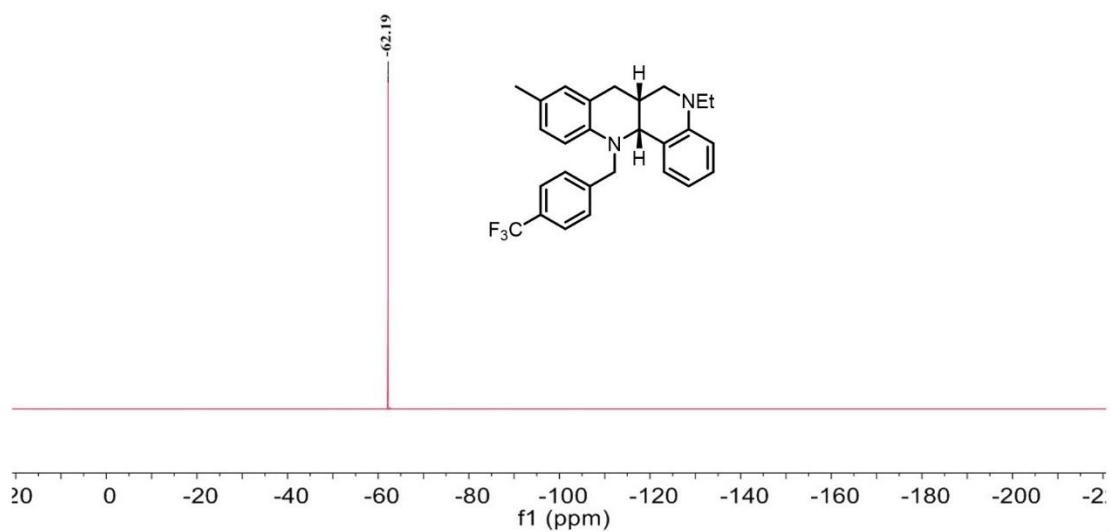
Supplementary Fig. 44 ¹³C-NMR spectrum of P13



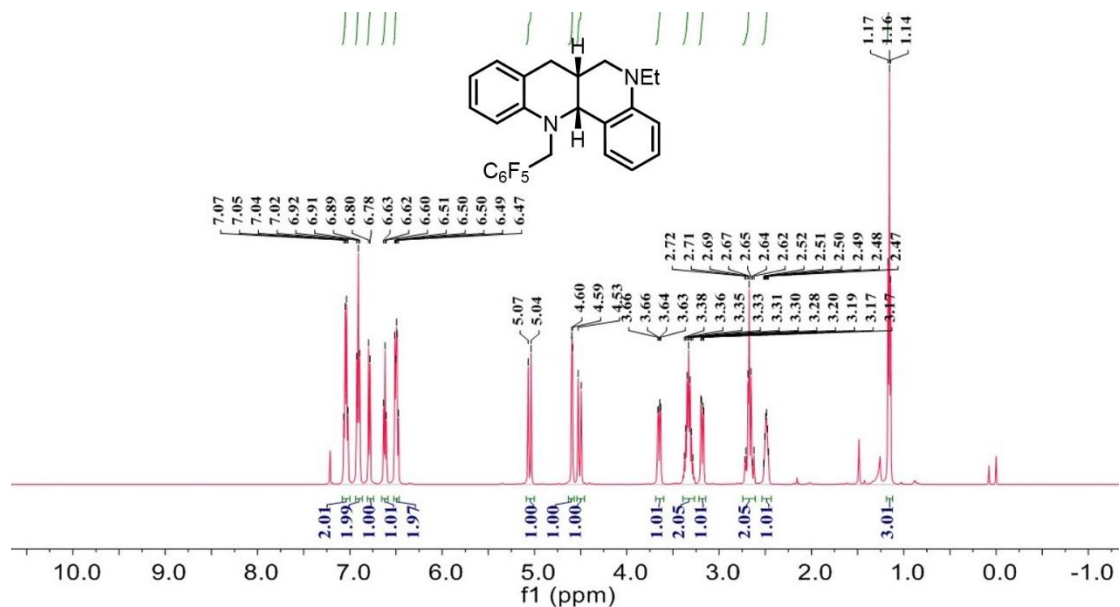
Supplementary Fig. 45 ¹H-NMR spectrum of P14



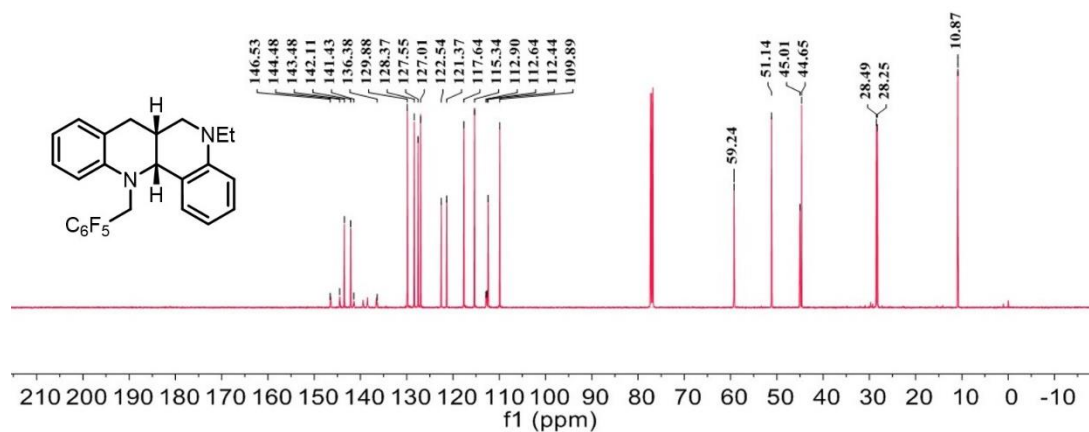
Supplementary Fig. 46 ¹³C-NMR spectrum of P14



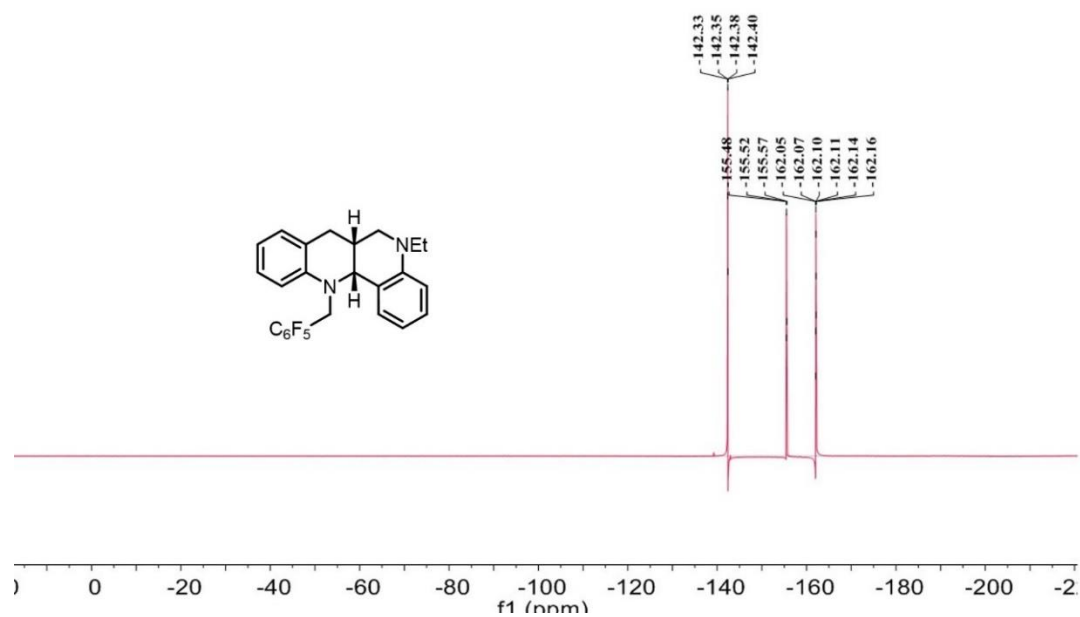
Supplementary Fig. 47 ¹⁹F-NMR spectrum of P14



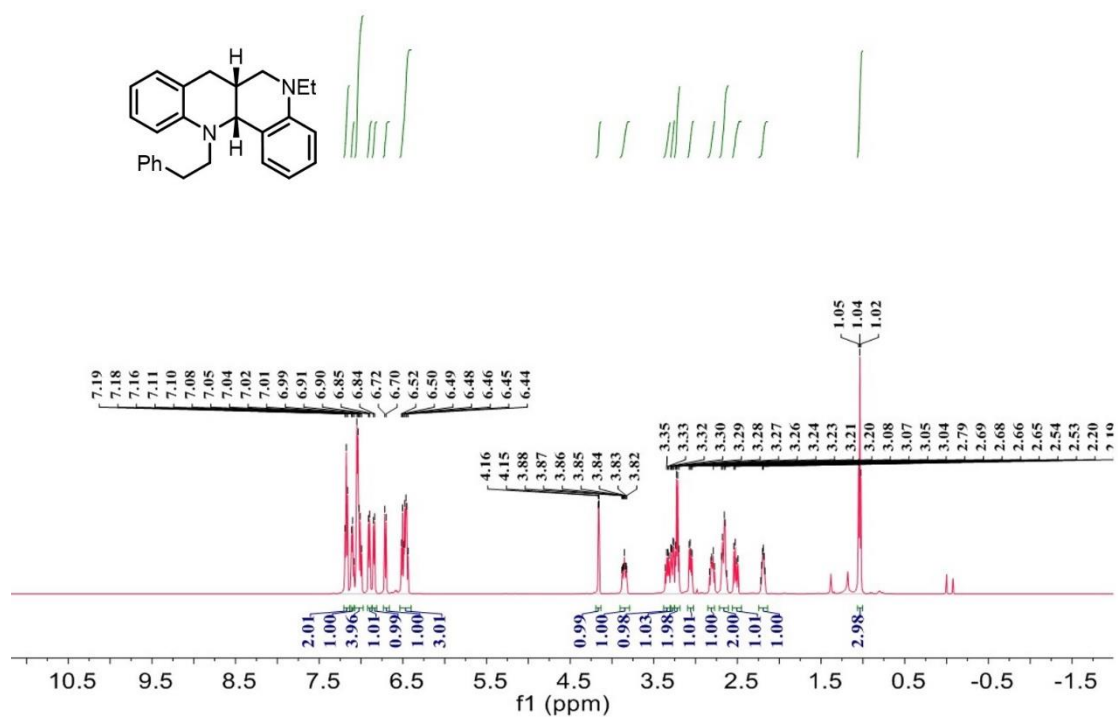
Supplementary Fig. 48 ^1H -NMR spectrum of P15



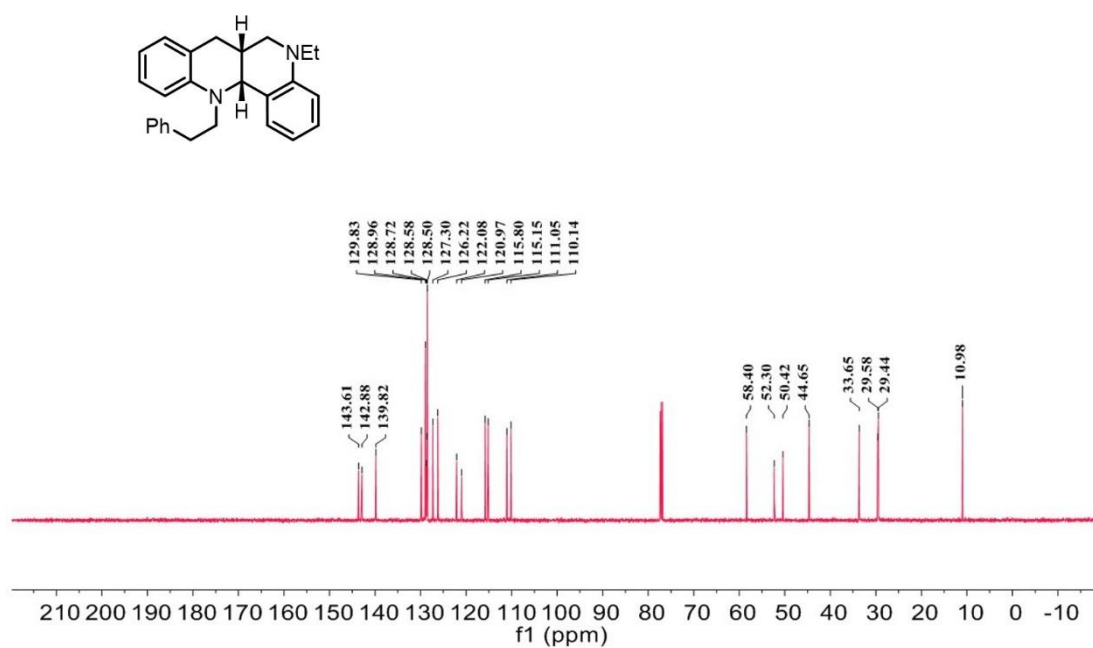
Supplementary Fig. 49 ^{13}C -NMR spectrum of P15



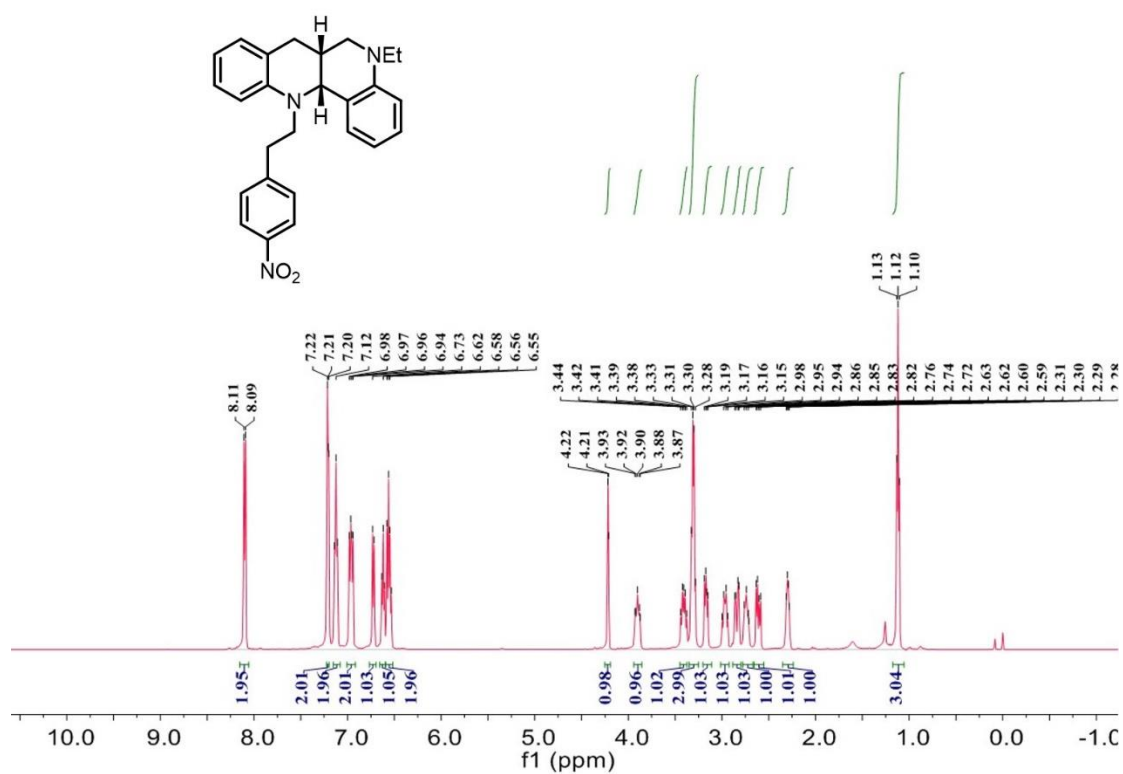
Supplementary Fig. 50 ^{19}F -NMR spectrum of P15



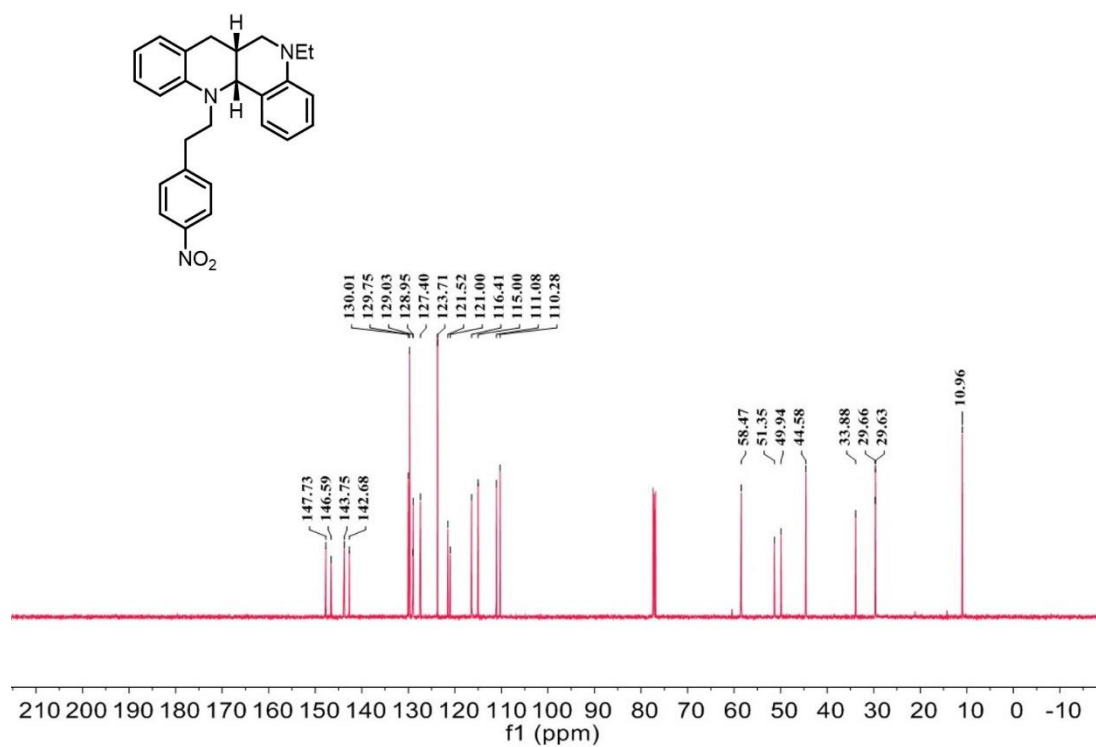
Supplementary Fig. 51 ¹H-NMR spectrum of P16



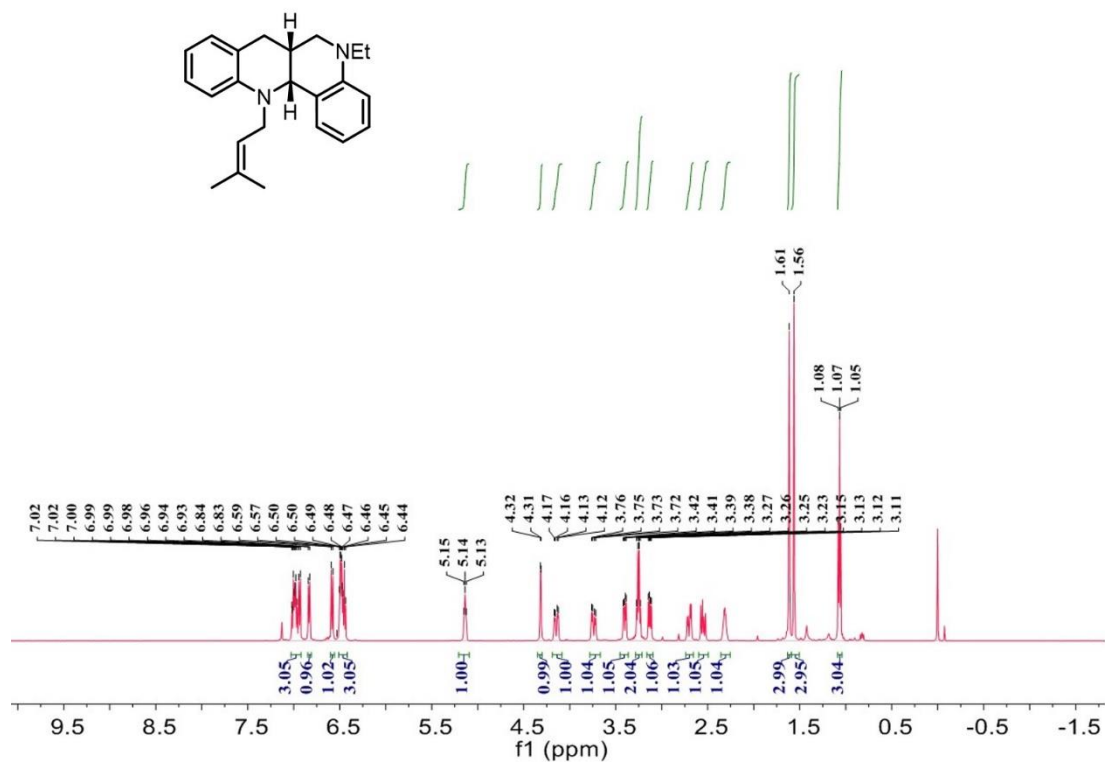
Supplementary Fig. 52 ¹³C-NMR spectrum of P16



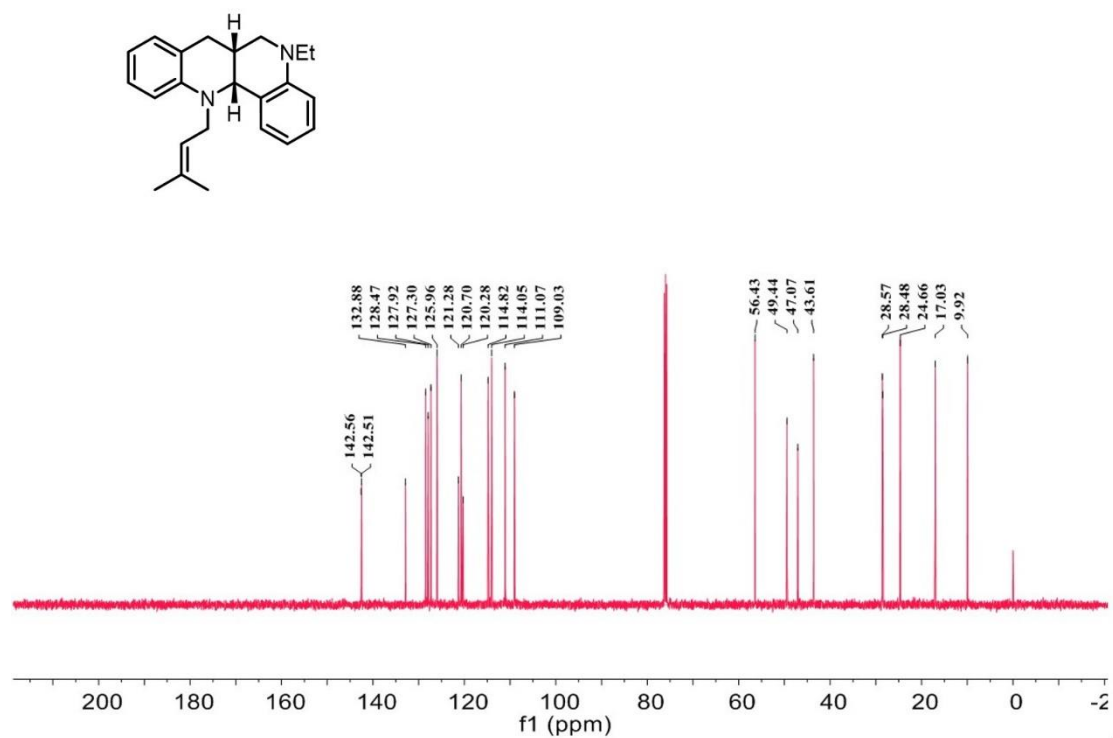
Supplementary Fig. 53 ¹H-NMR spectrum of P17



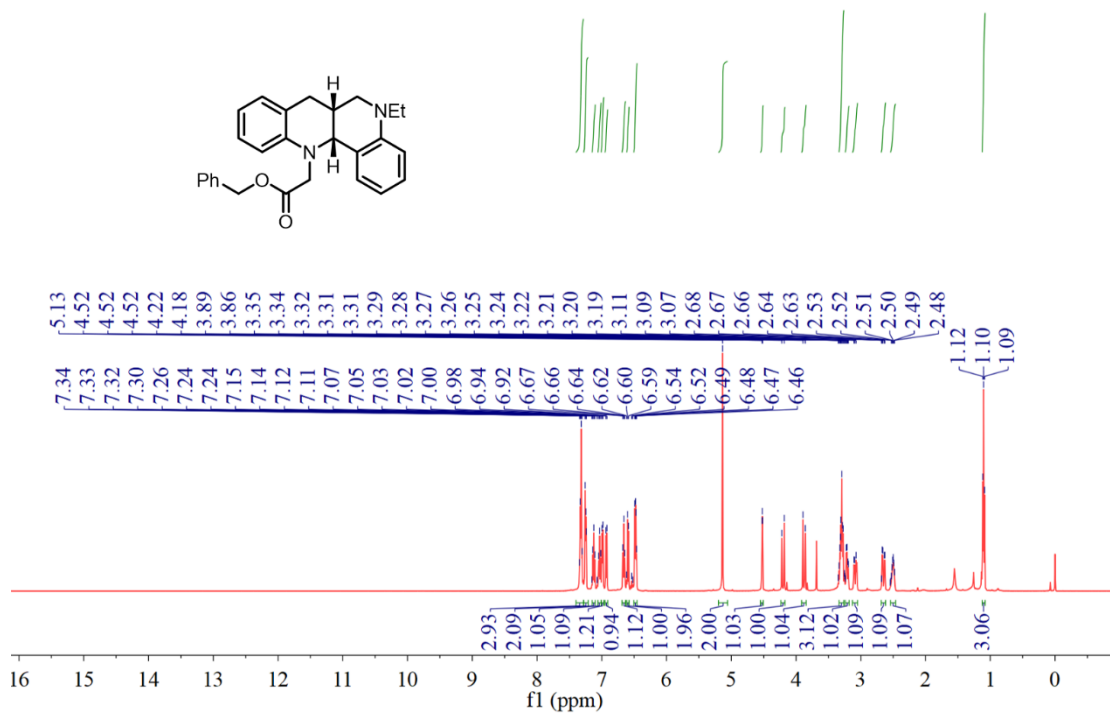
Supplementary Fig. 54 ¹³C-NMR spectrum of P17



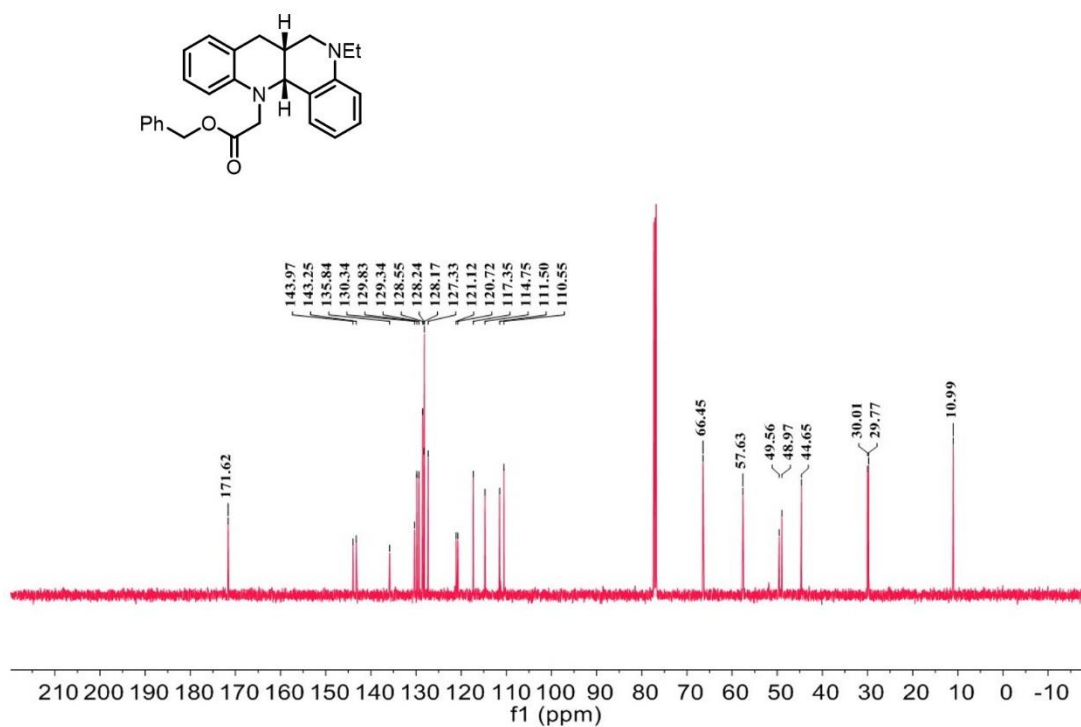
Supplementary Fig. 55 ¹H-NMR spectrum of P18



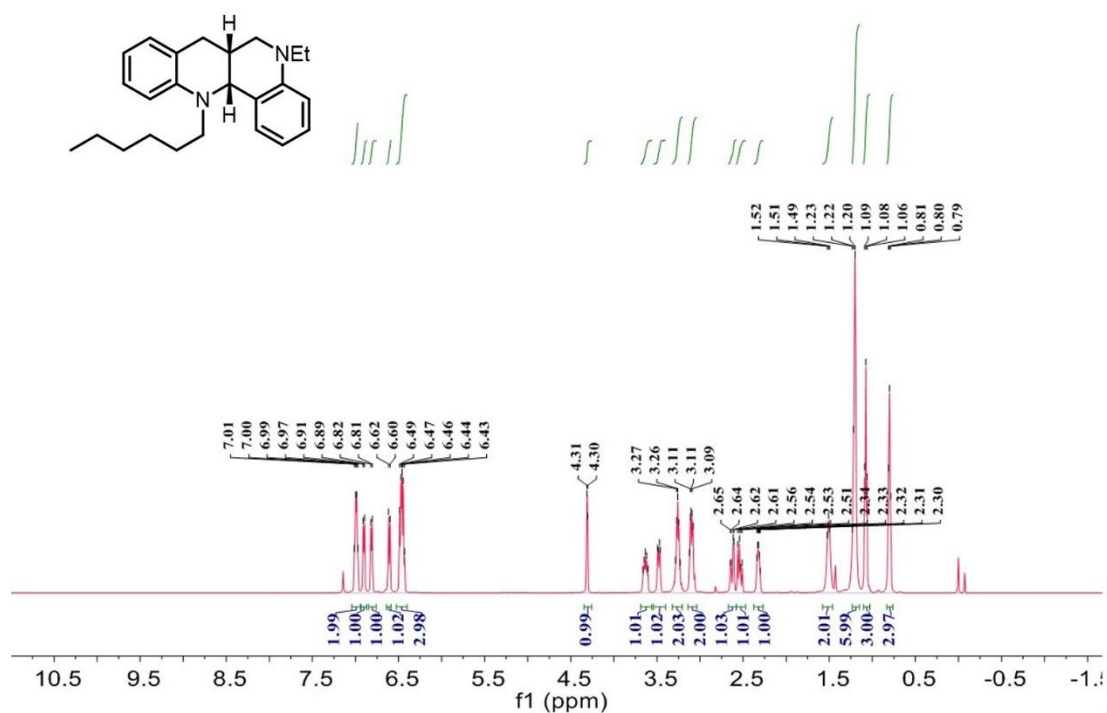
Supplementary Fig. 56 ¹³C-NMR spectrum of P18



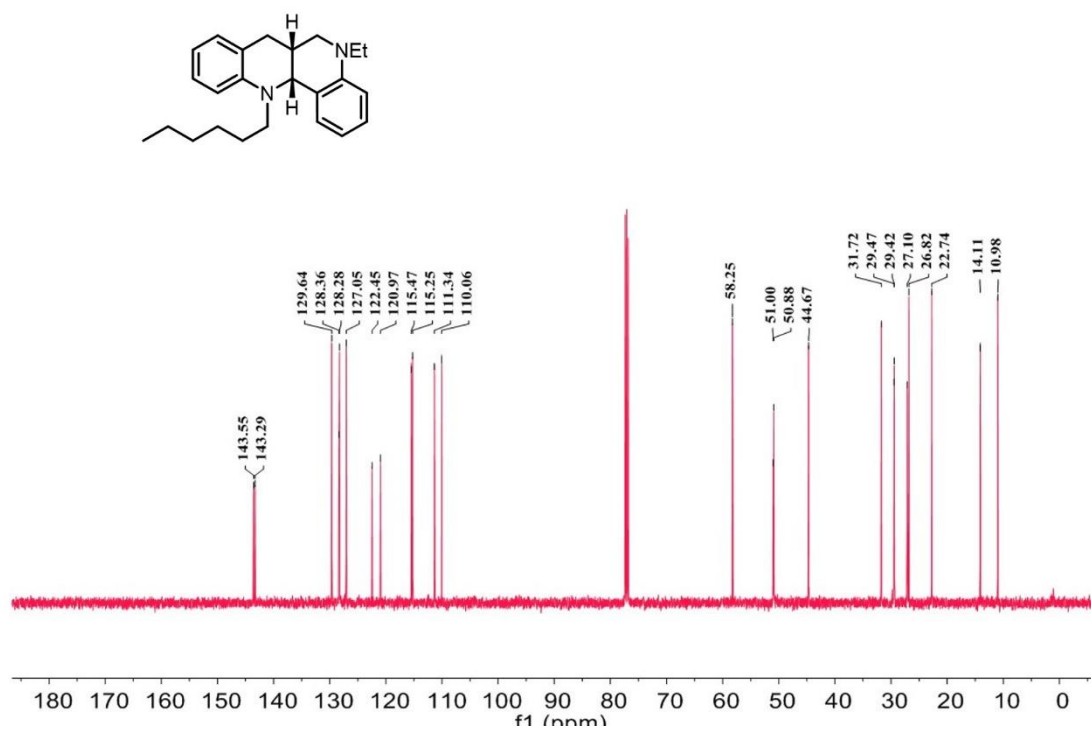
Supplementary Fig. 57 ¹H-NMR spectrum of P19



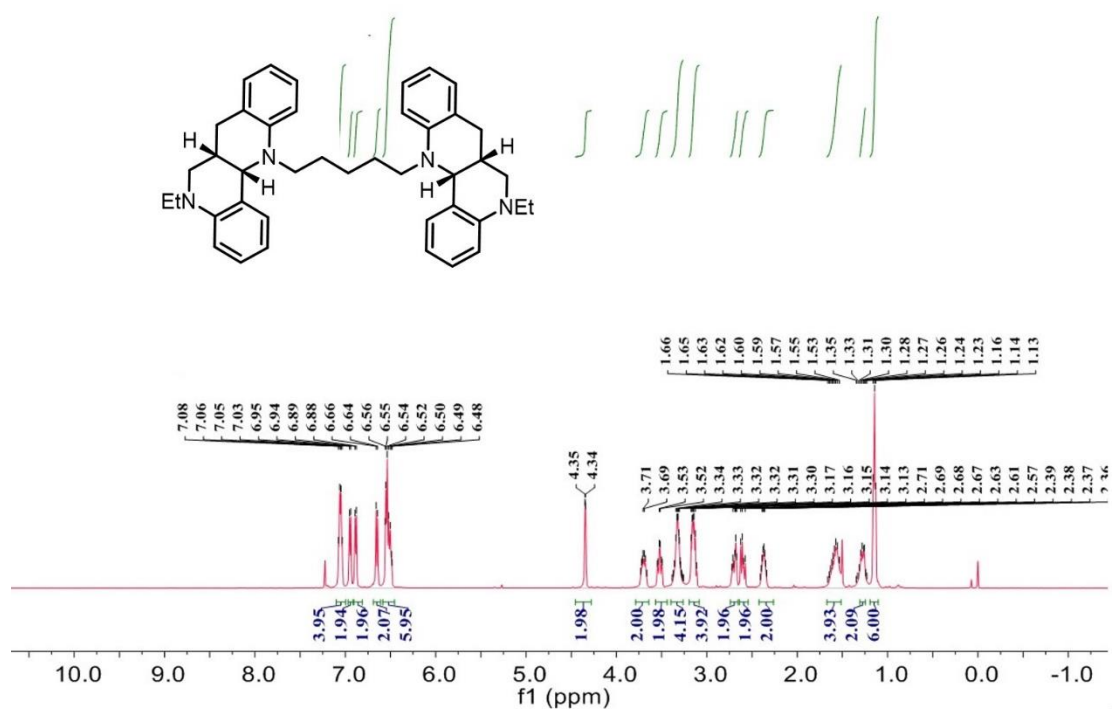
Supplementary Fig. 58 ¹³C-NMR spectrum of P19



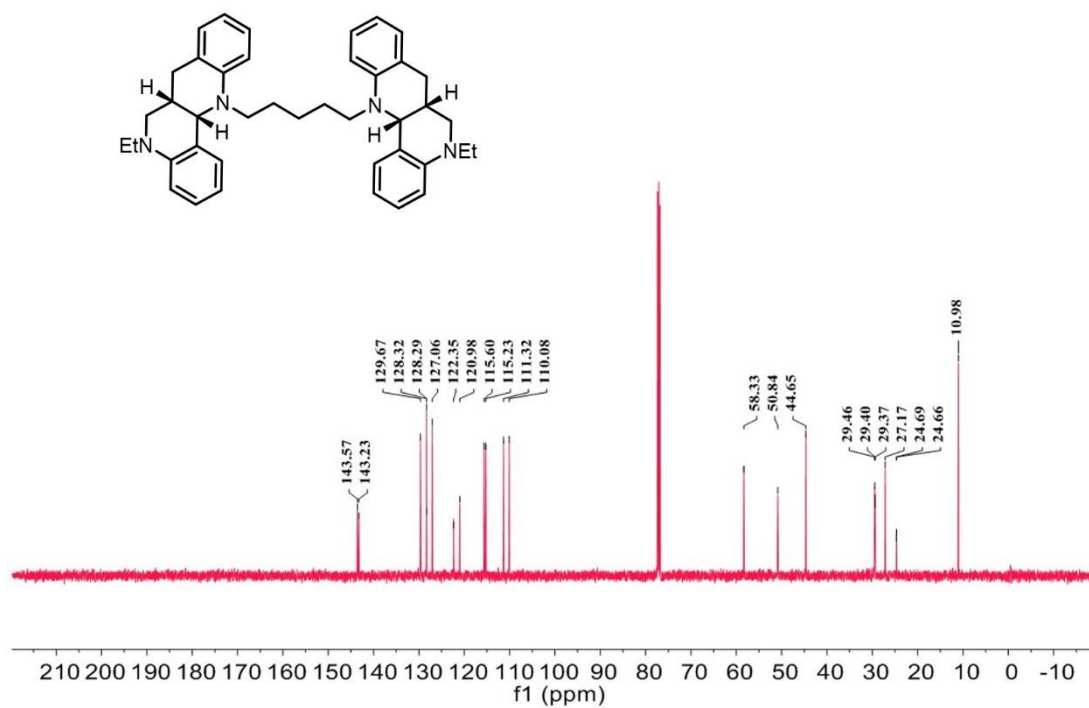
Supplementary Fig. 59 ¹H-NMR spectrum of P20



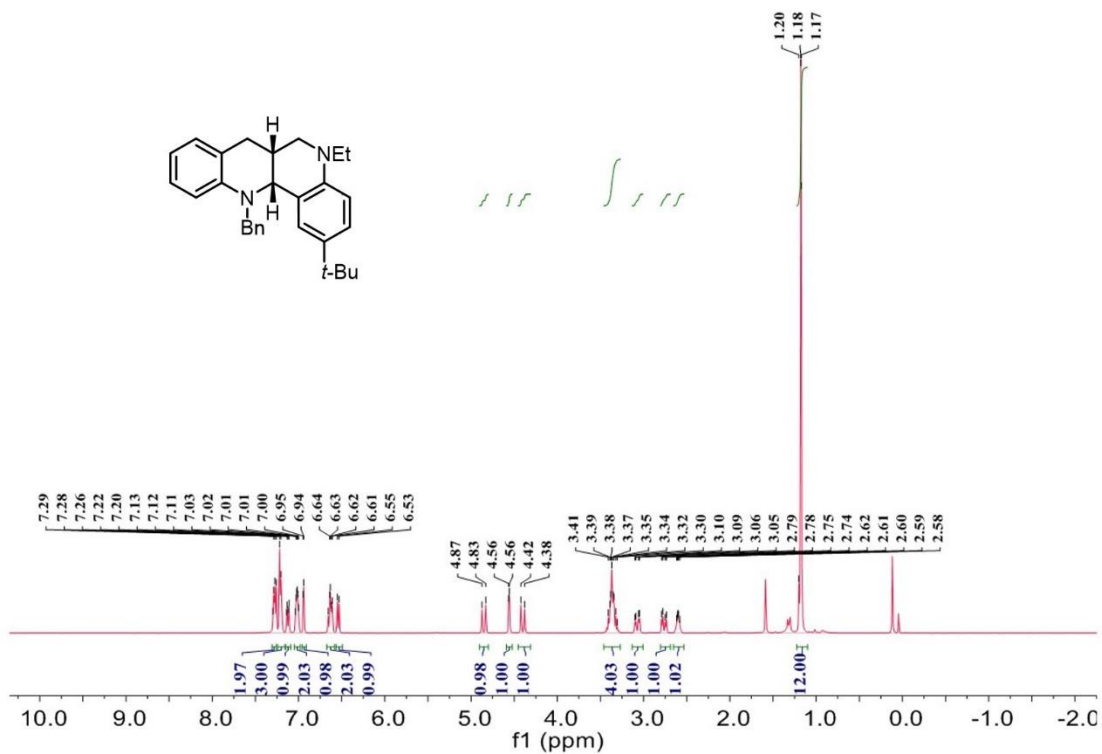
Supplementary Fig. 60 ¹³C-NMR spectrum of P20



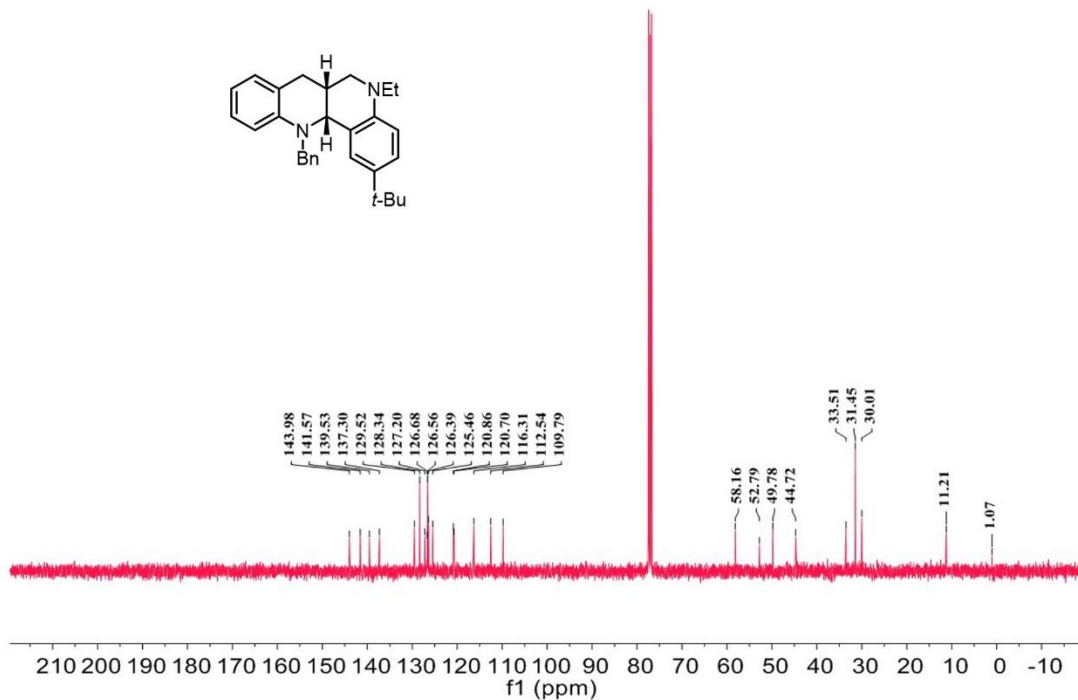
Supplementary Fig. 61 ¹H-NMR spectrum of P21



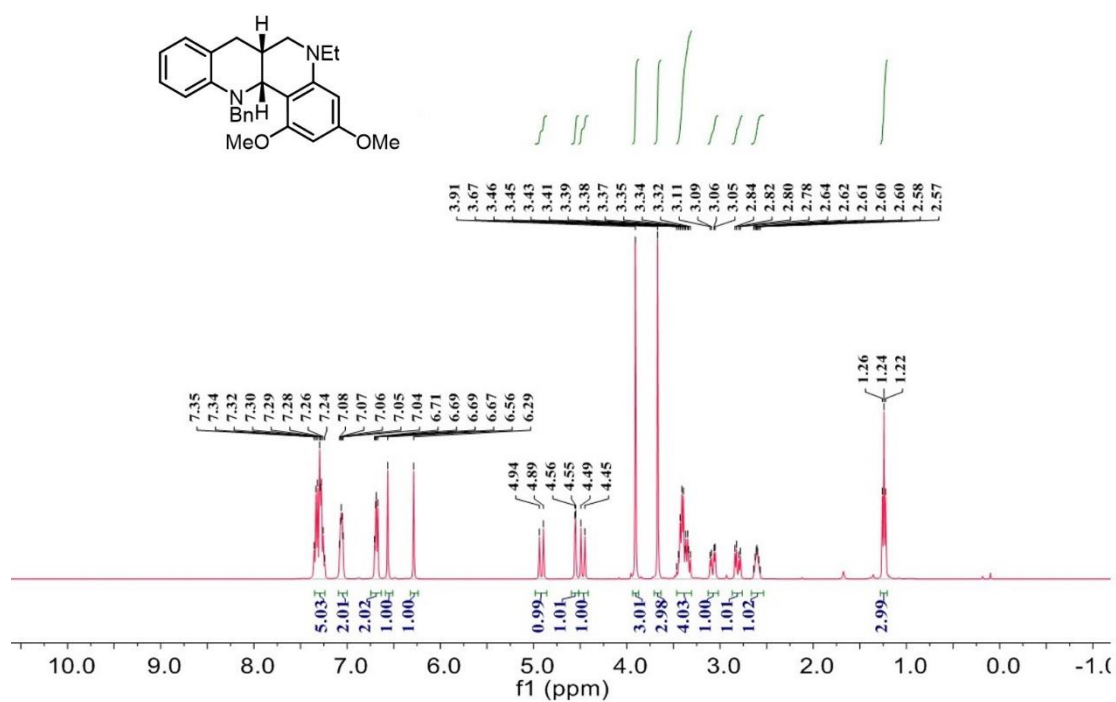
Supplementary Fig. 62 ¹³C-NMR spectrum of P21



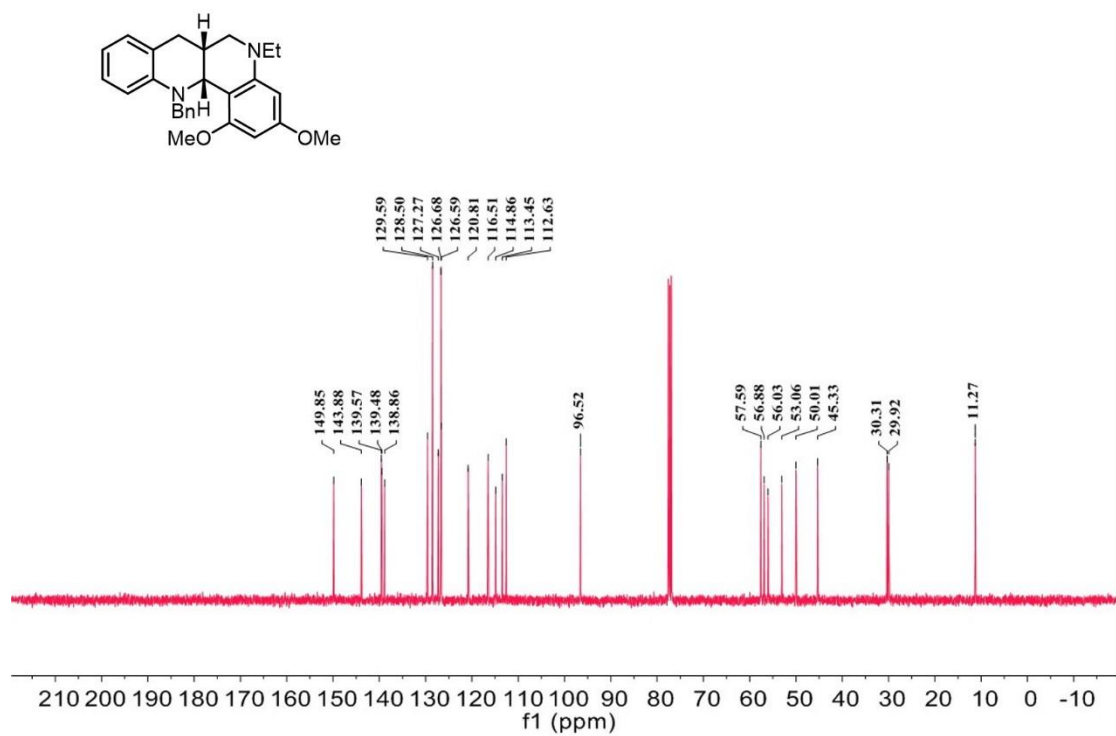
Supplementary Fig. 63 $^1\text{H-NMR}$ spectrum of P22



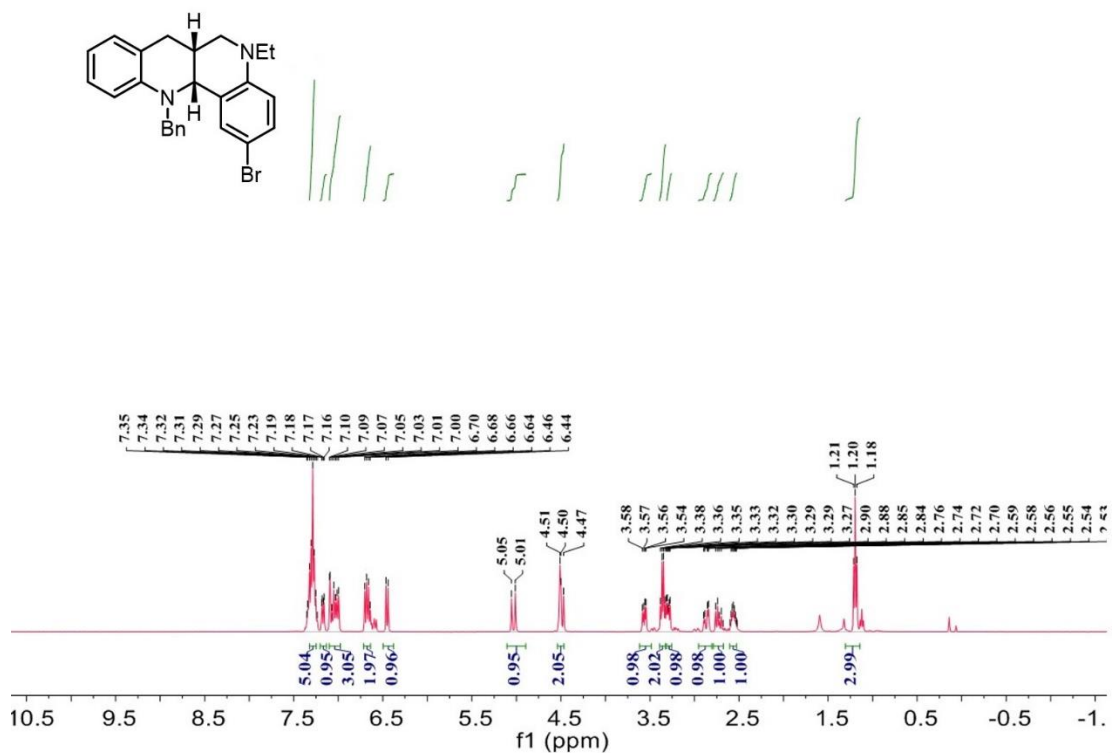
Supplementary Fig. 64 $^{13}\text{C-NMR}$ spectrum of P22



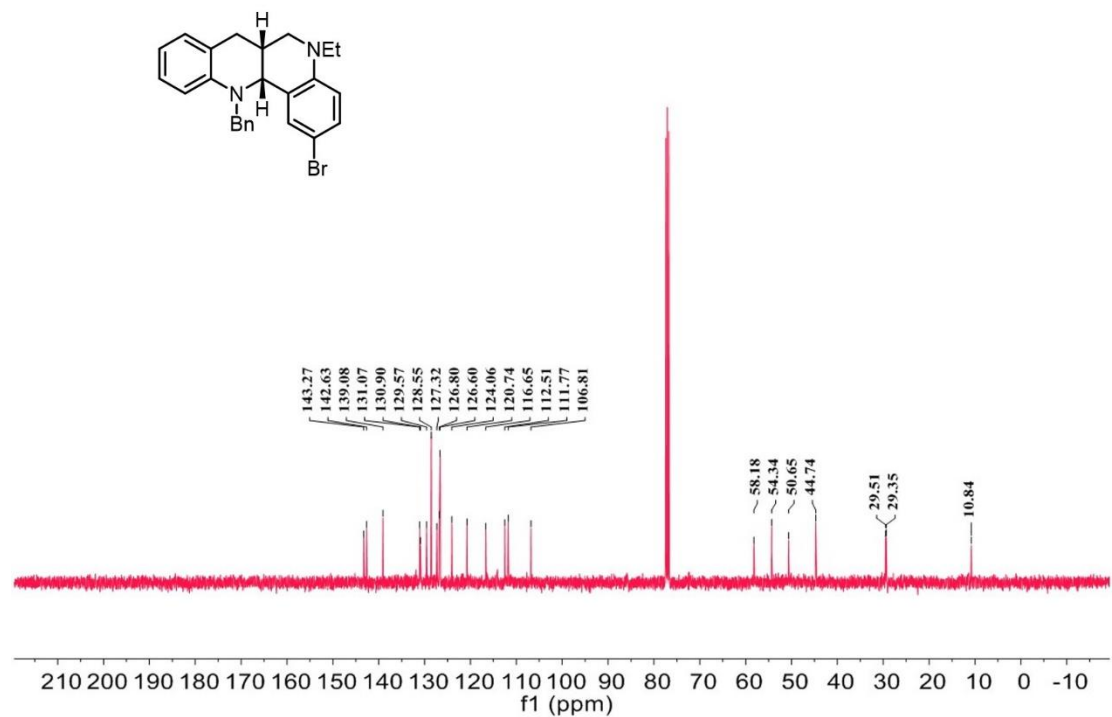
Supplementary Fig. 65 ¹H-NMR spectrum of P23



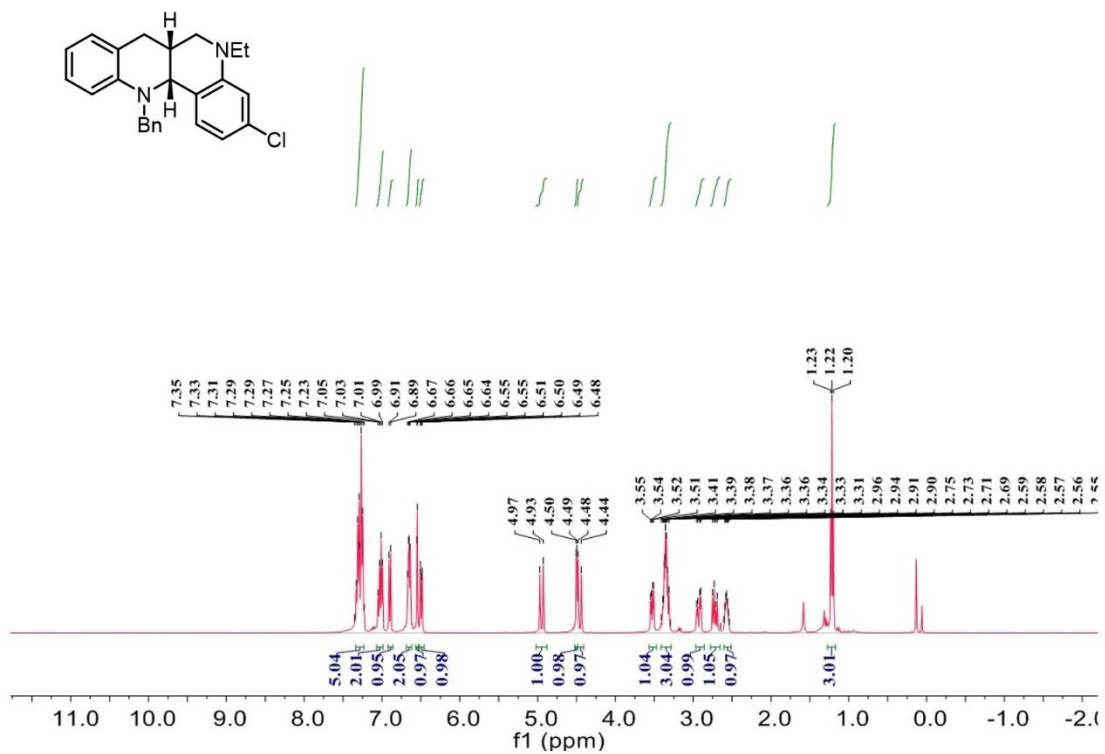
Supplementary Fig. 66 ¹³C-NMR spectrum of P23



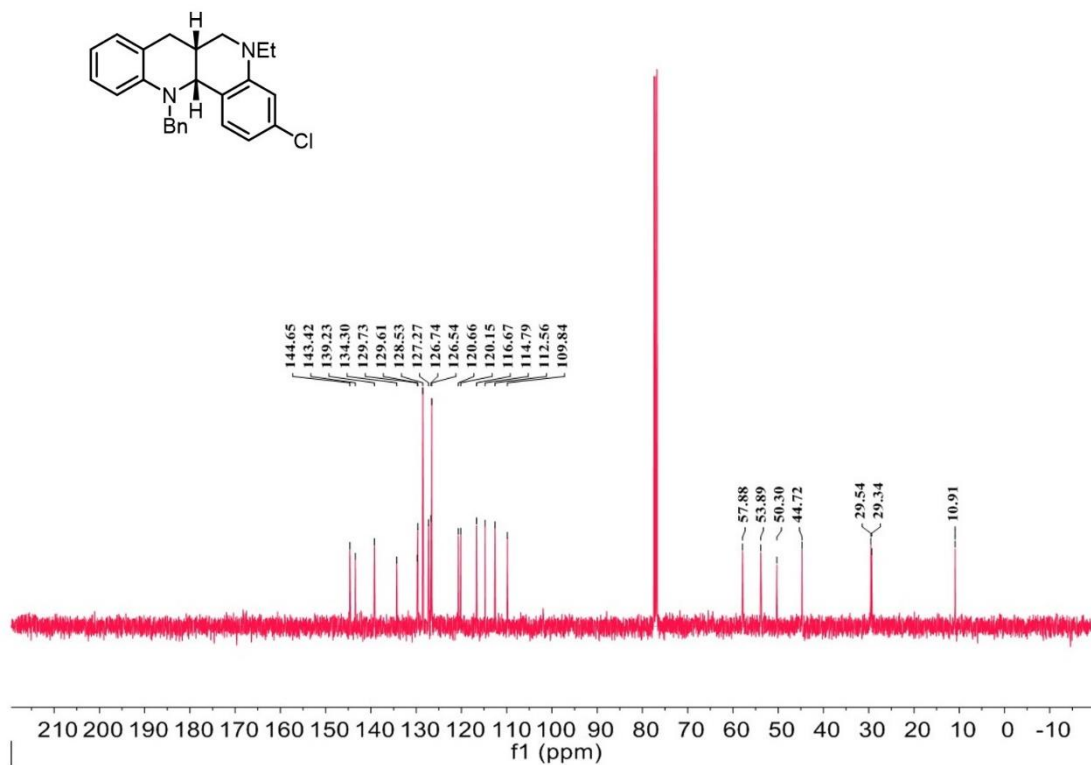
Supplementary Fig. 67 ¹H-NMR spectrum of P24



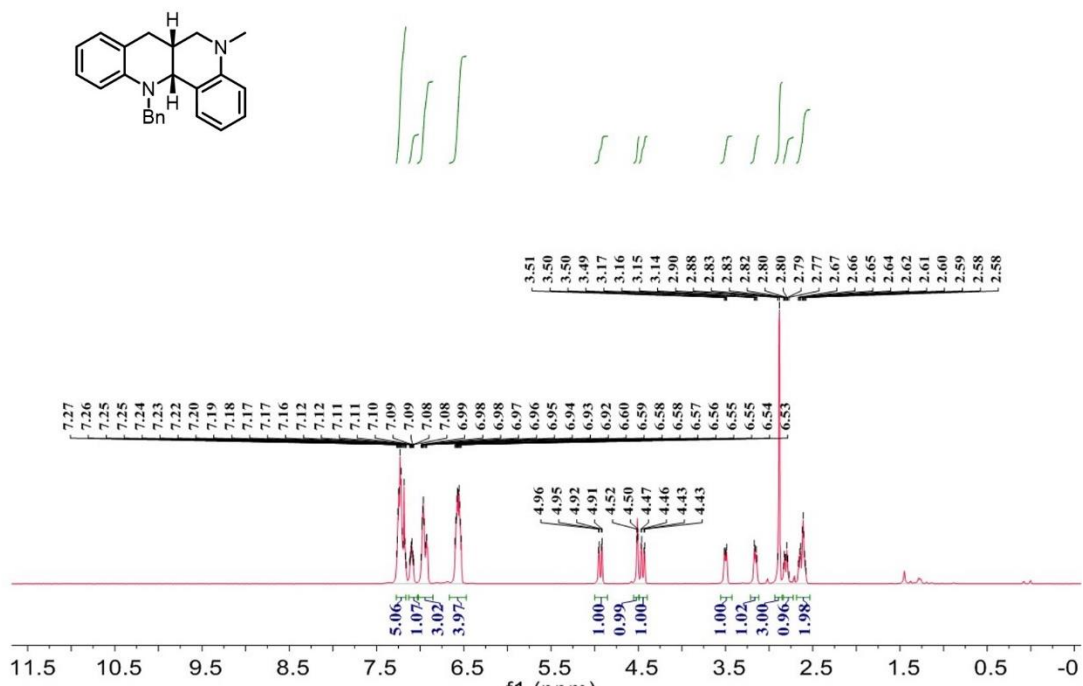
Supplementary Fig. 68 ¹³C-NMR spectrum of P24



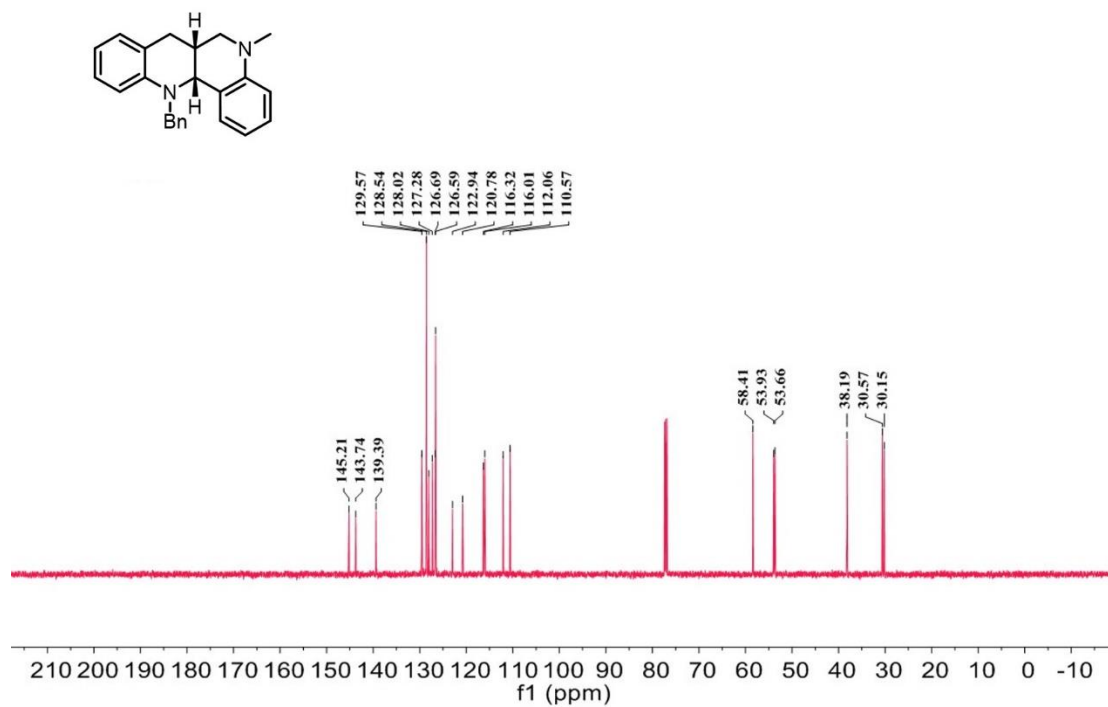
Supplementary Fig. 69 $^1\text{H-NMR}$ spectrum of P25



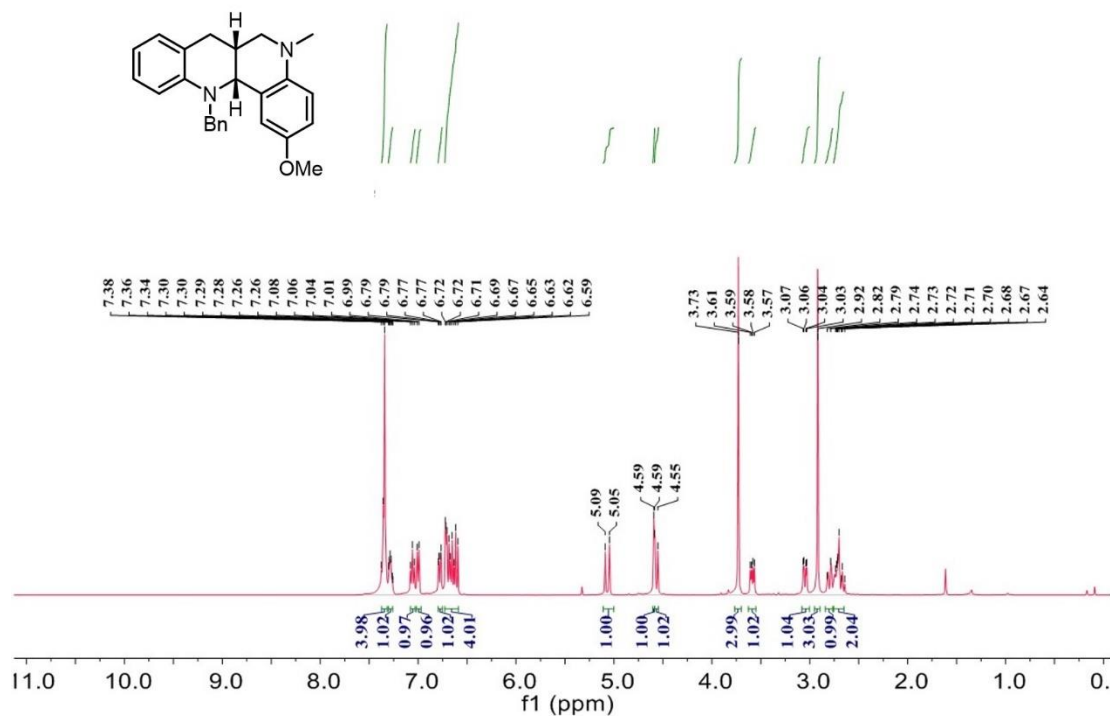
Supplementary Fig. 70 $^{13}\text{C-NMR}$ spectrum of P25



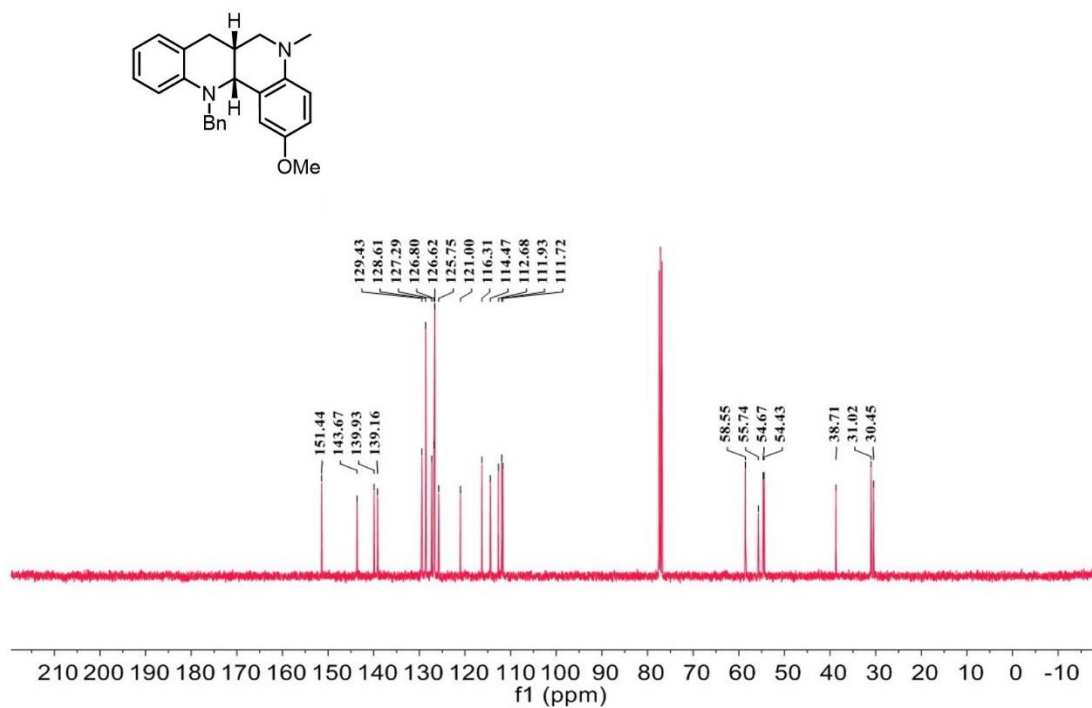
Supplementary Fig. 71 ¹H-NMR spectrum of P26



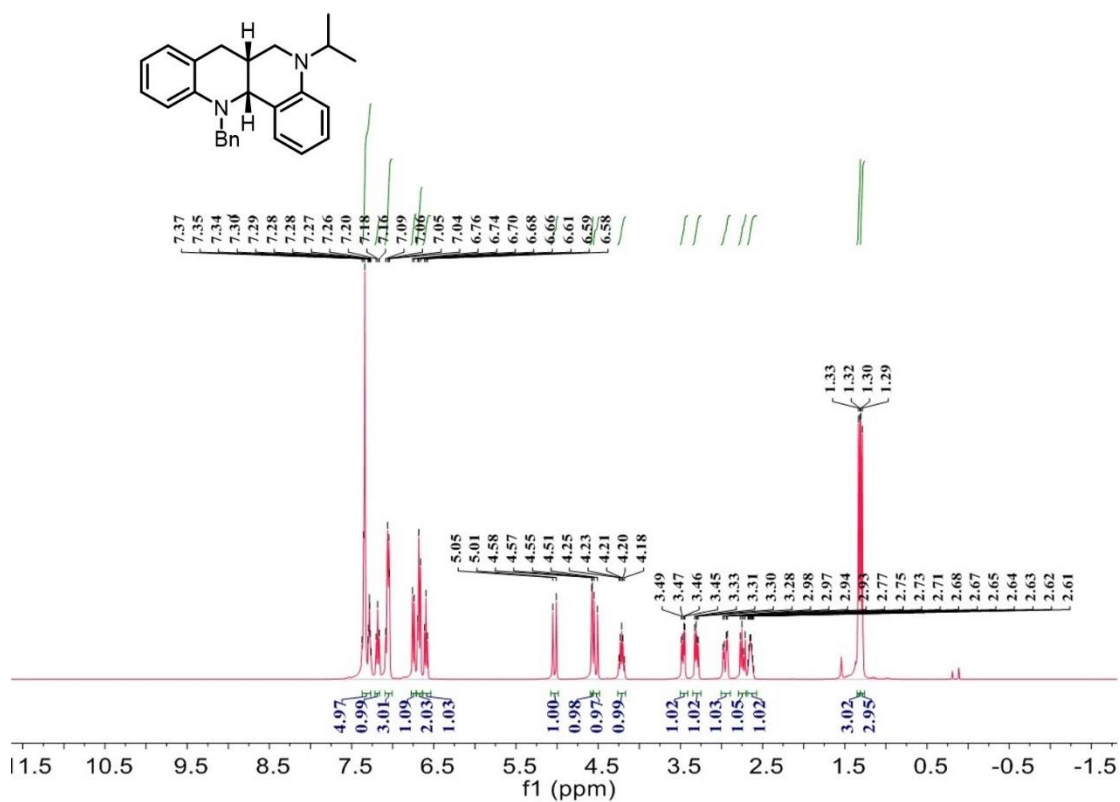
Supplementary Fig. 72 ¹³C-NMR spectrum of P26



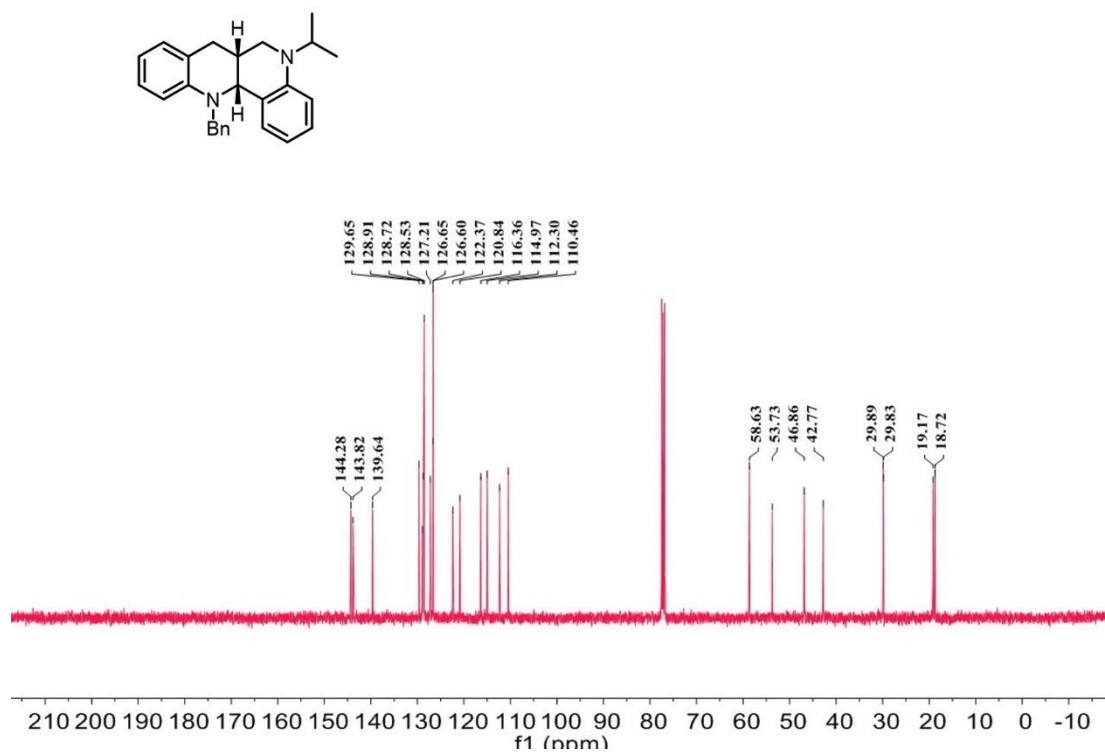
Supplementary Fig. 73 ¹H-NMR spectrum of P27



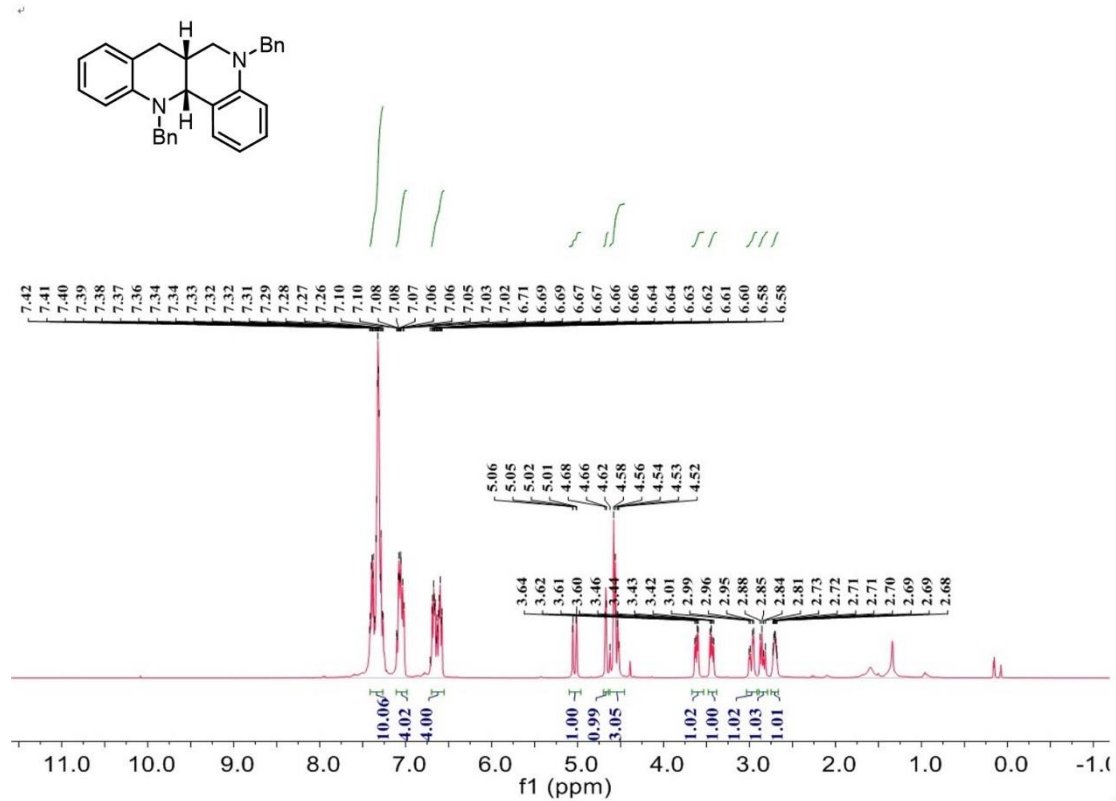
Supplementary Fig. 74 ¹³C-NMR spectrum of P27



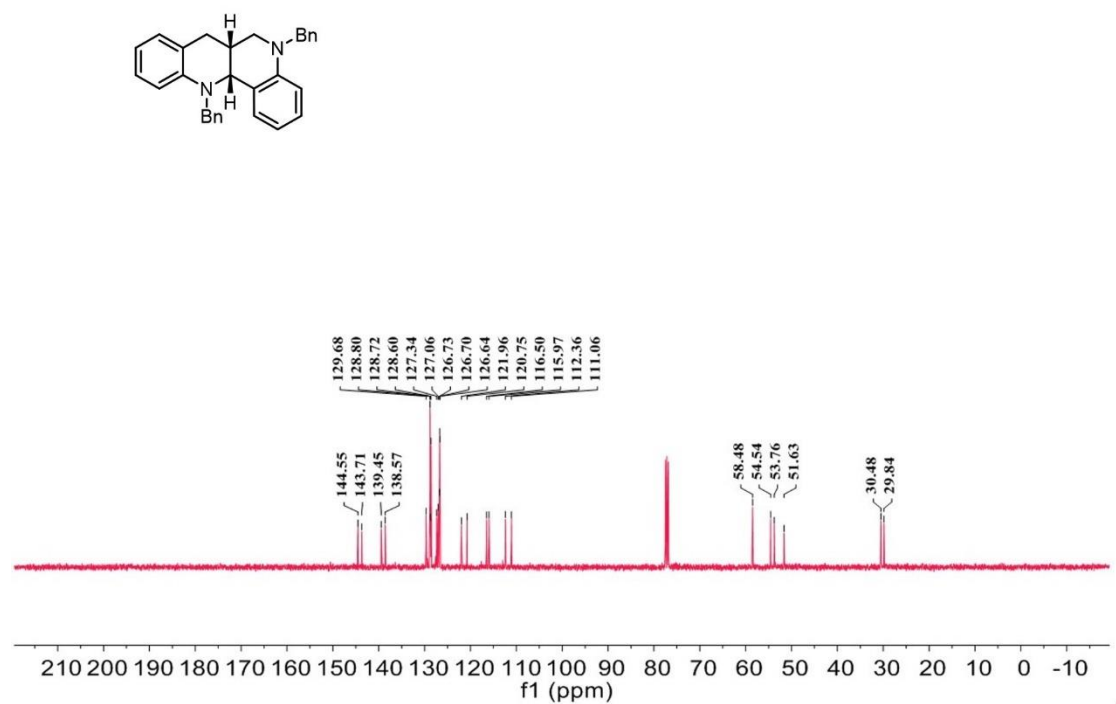
Supplementary Fig. 75 ¹H-NMR spectrum of P28



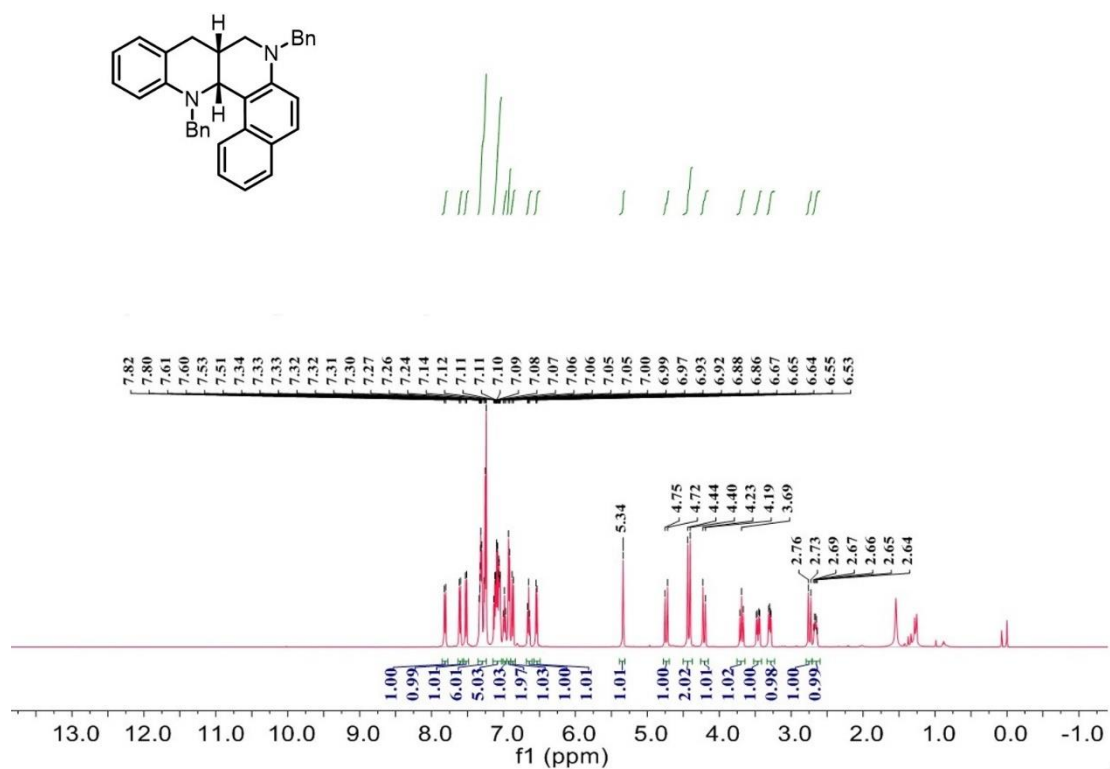
Supplementary Fig. 76 ¹³C-NMR spectrum of P28



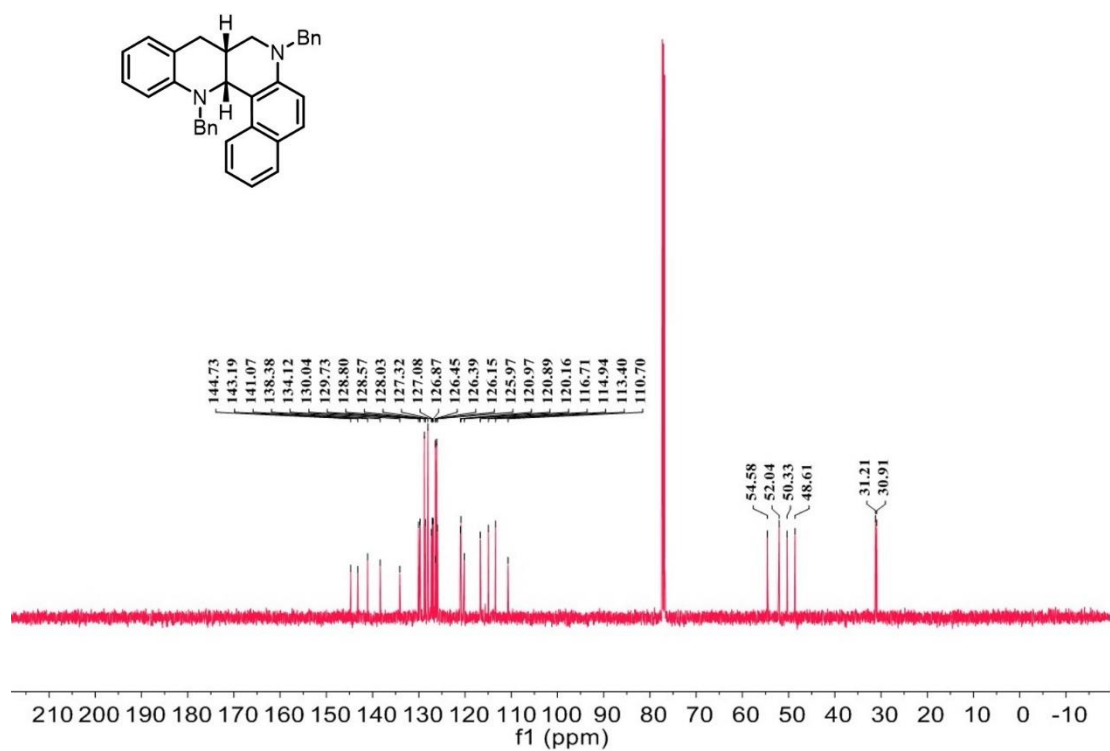
Supplementary Fig. 77 ¹H-NMR spectrum of P29



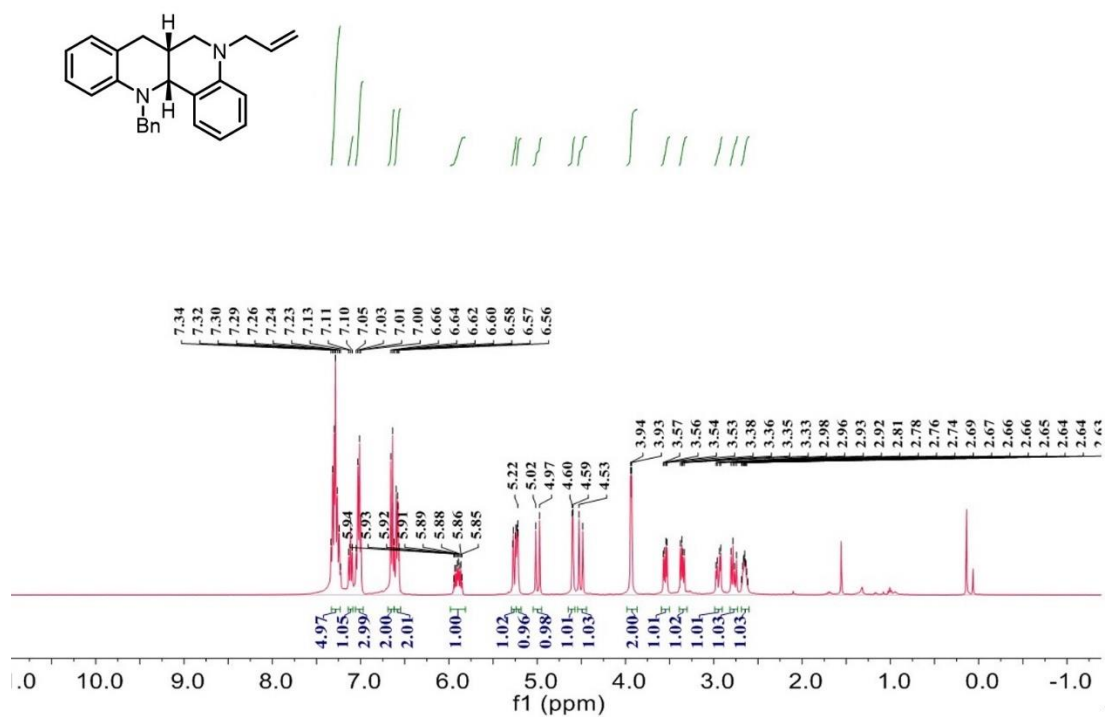
Supplementary Fig. 78 ¹³C-NMR spectrum of P29



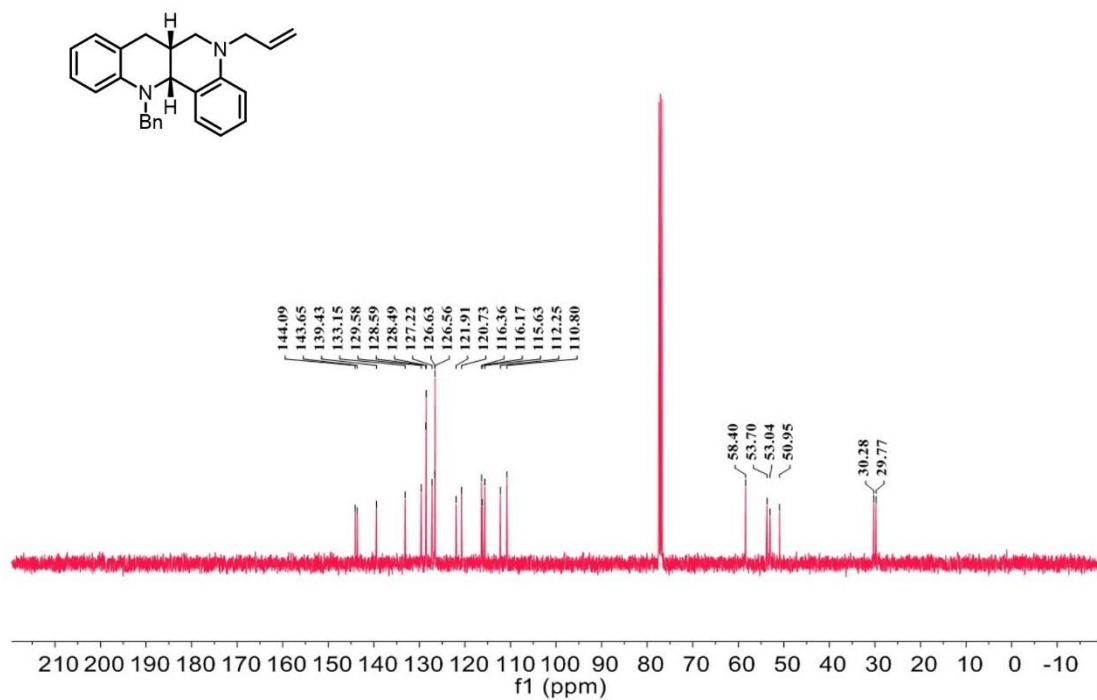
Supplementary Fig. 79 ¹H-NMR spectrum of P30



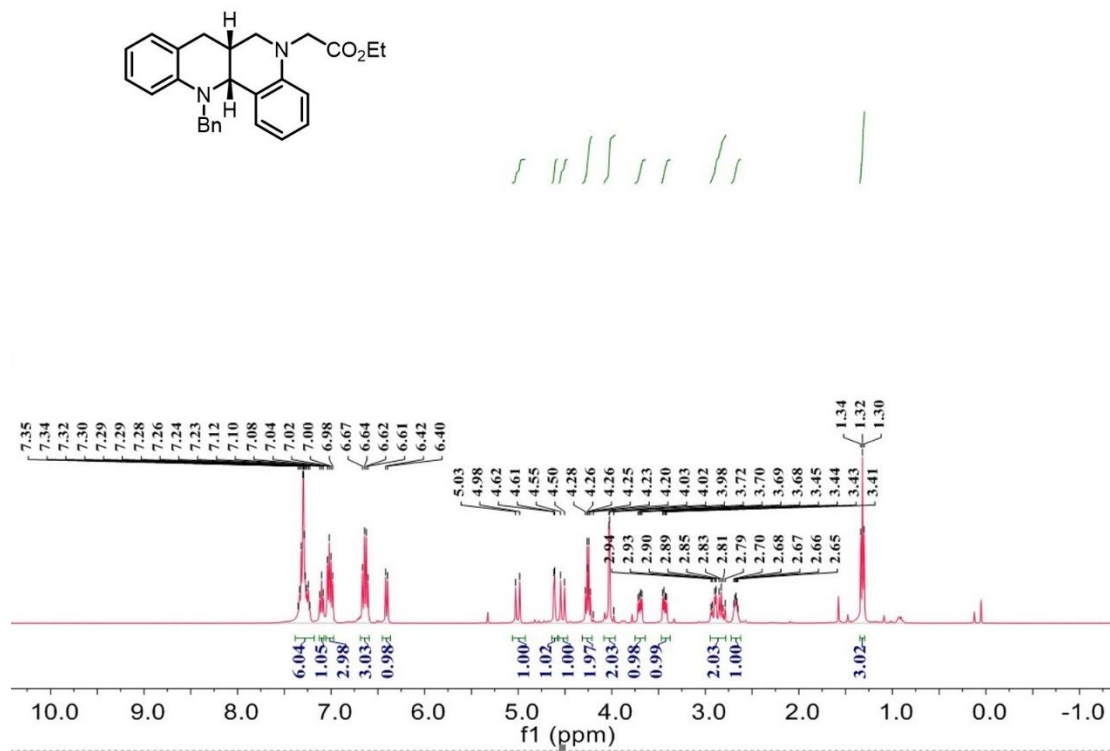
Supplementary Fig. 80 ¹³C-NMR spectrum of P30



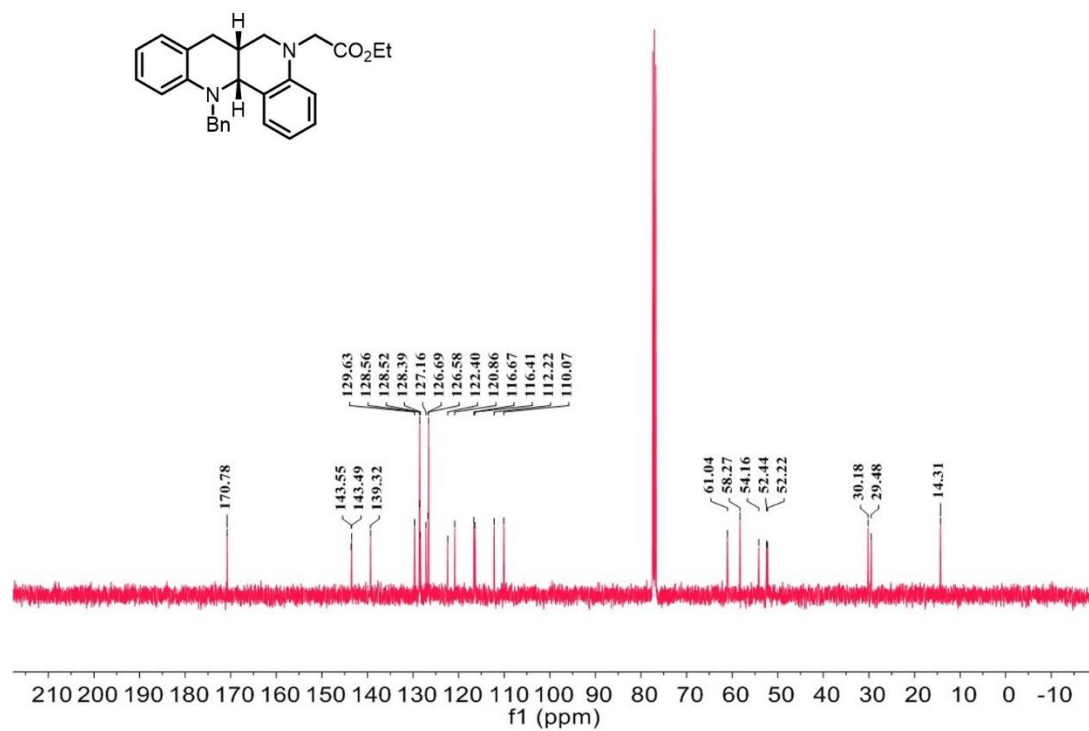
Supplementary Fig. 81 ¹H-NMR spectrum of P31



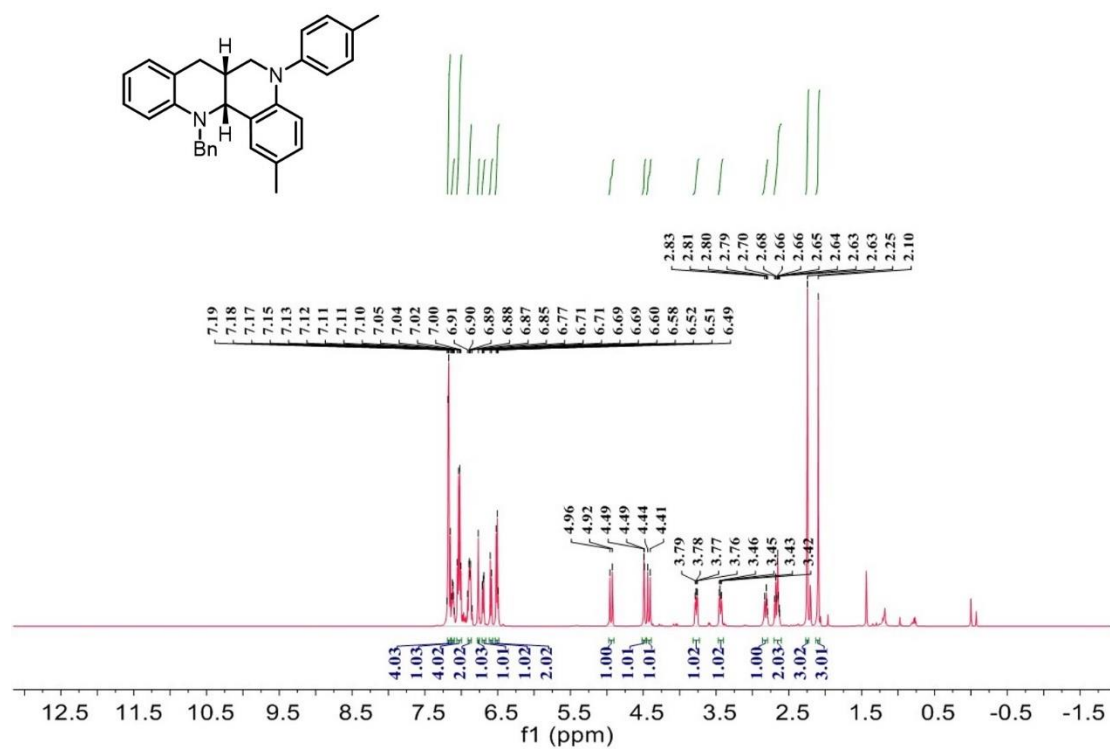
Supplementary Fig. 82 ¹³C-NMR spectrum of P31



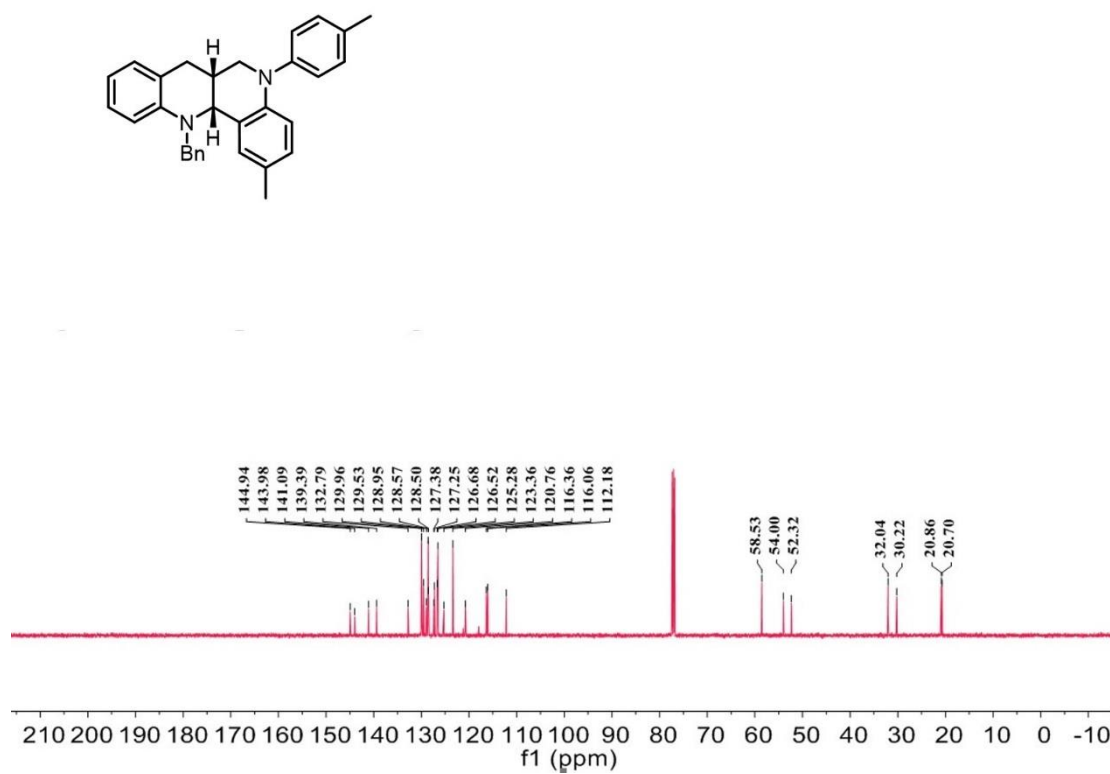
Supplementary Fig. 83 ¹H-NMR spectrum of P32



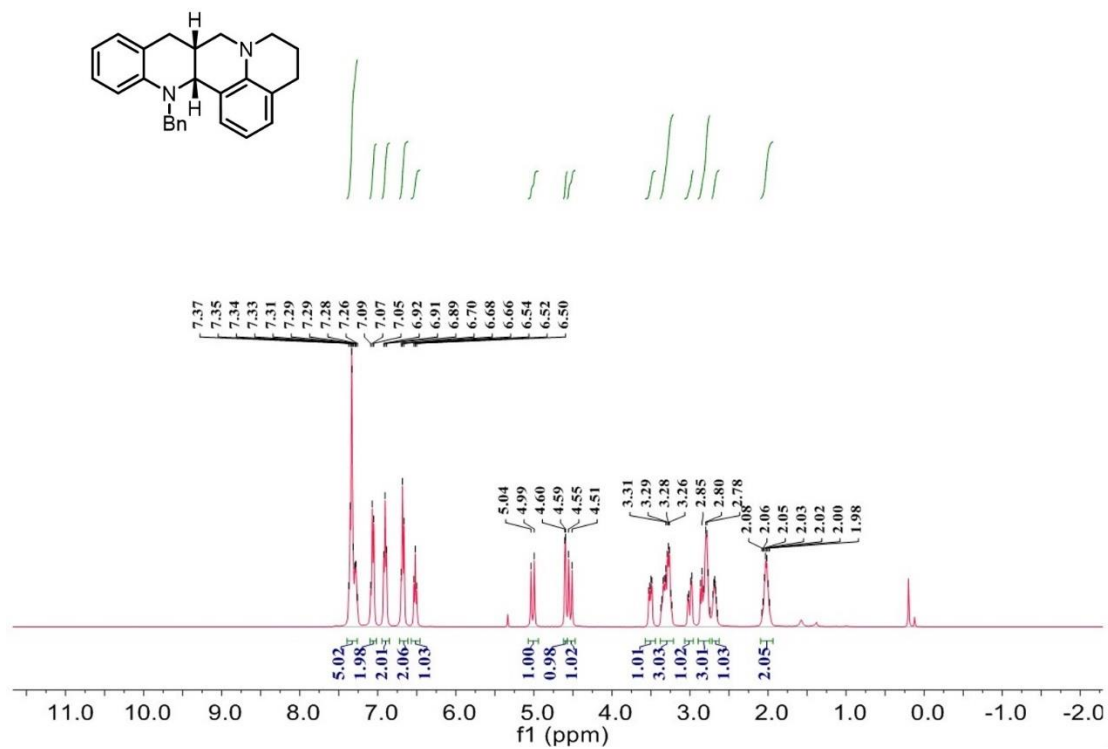
Supplementary Fig. 84 ¹³C-NMR spectrum of P32



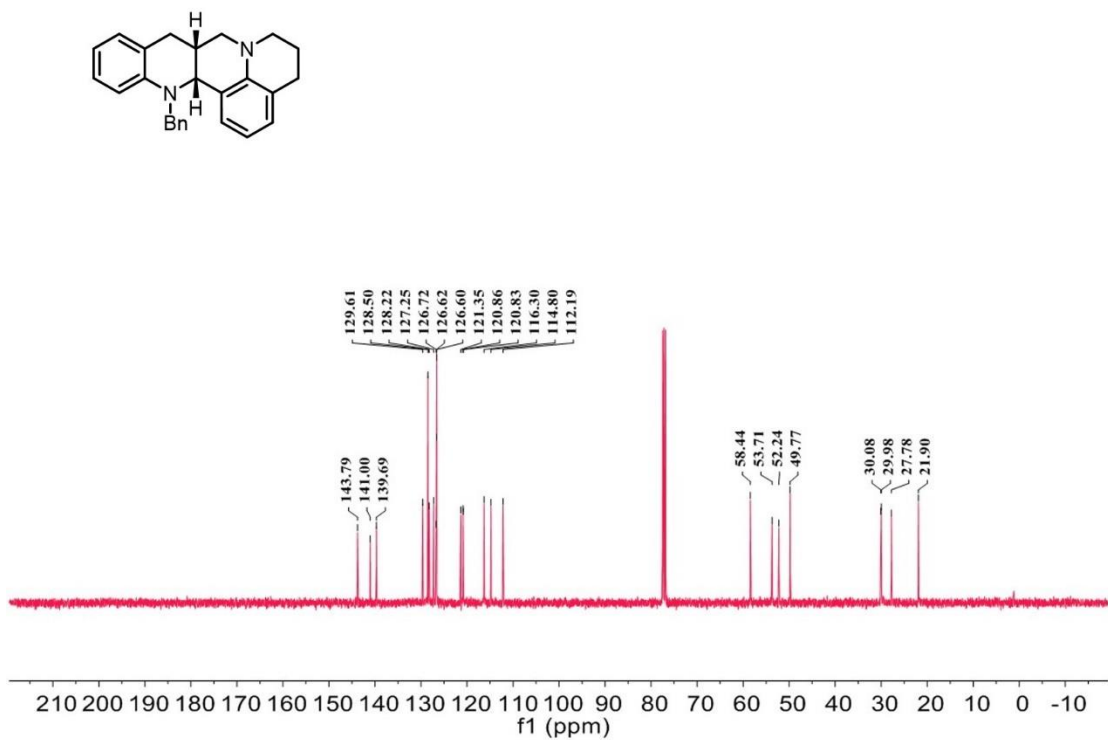
Supplementary Fig. 85 ¹H-NMR spectrum of P33



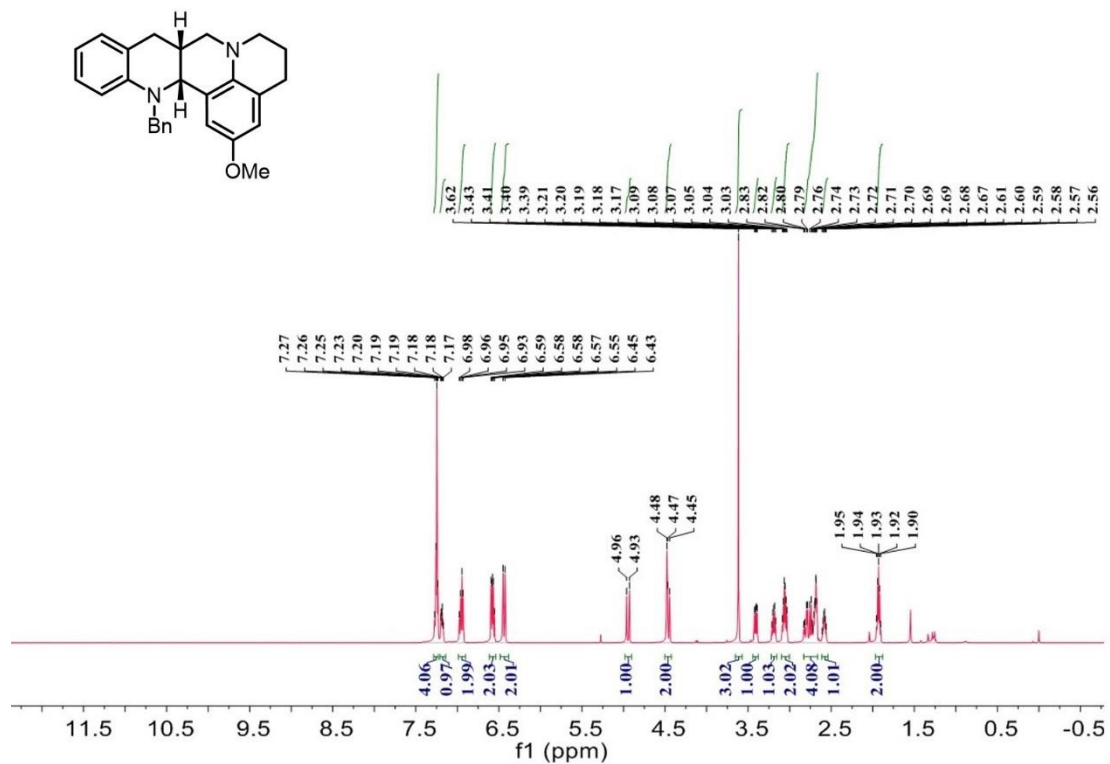
Supplementary Fig. 86 ¹³C-NMR spectrum of P33



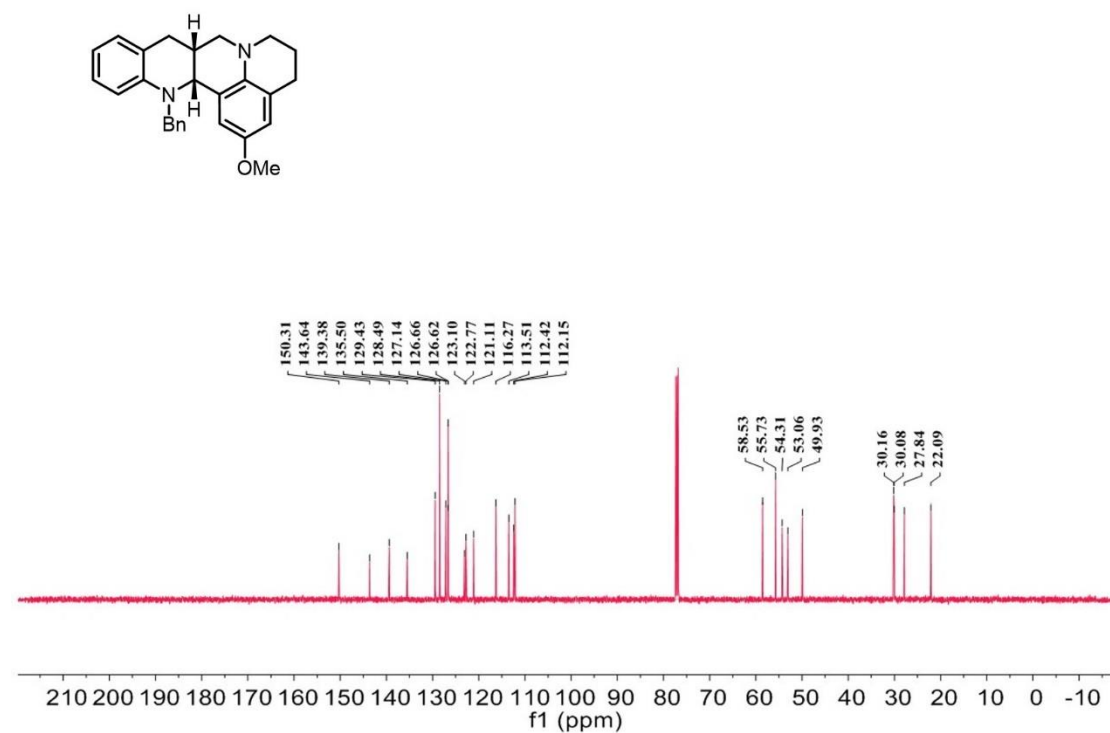
Supplementary Fig. 87 ¹H-NMR spectrum of P34



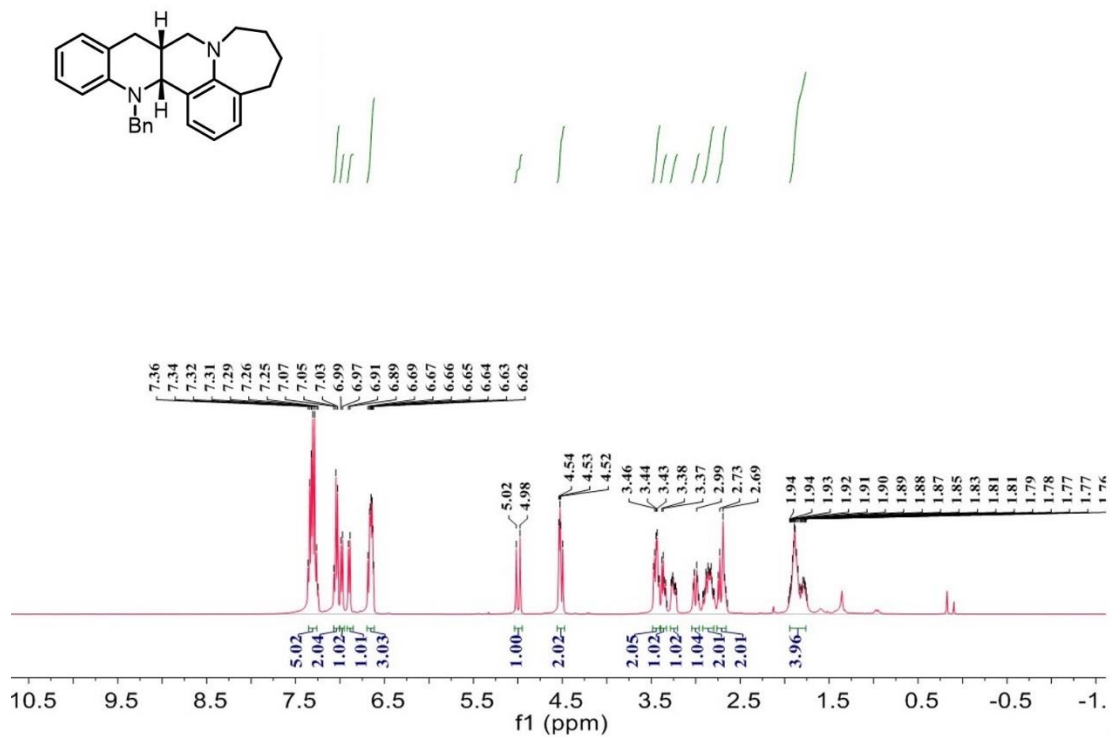
Supplementary Fig. 88 ¹³C-NMR spectrum of P34



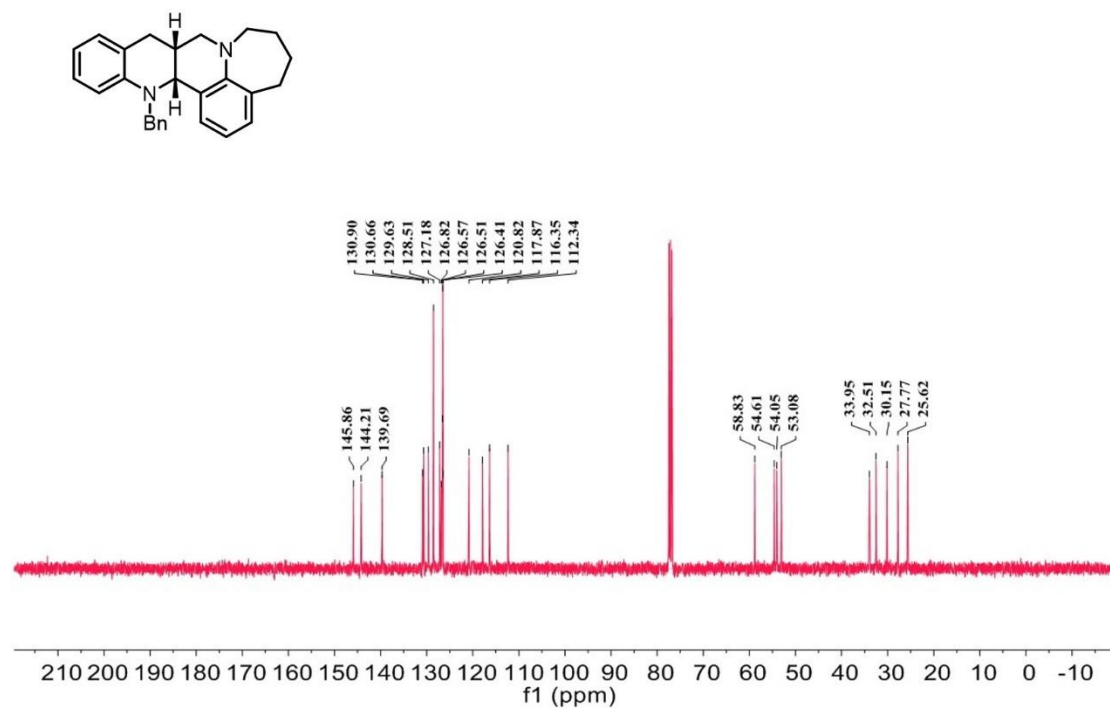
Supplementary Fig. 89 ¹H-NMR spectrum of P35



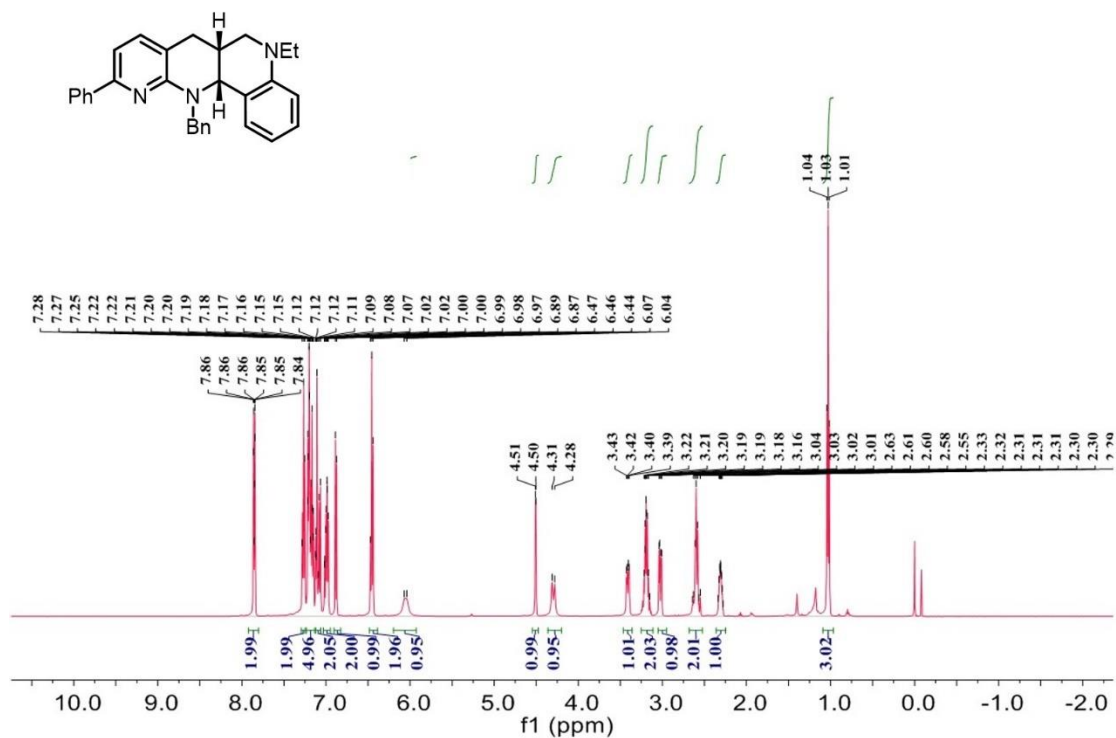
Supplementary Fig. 90 ¹³C-NMR spectrum of P35



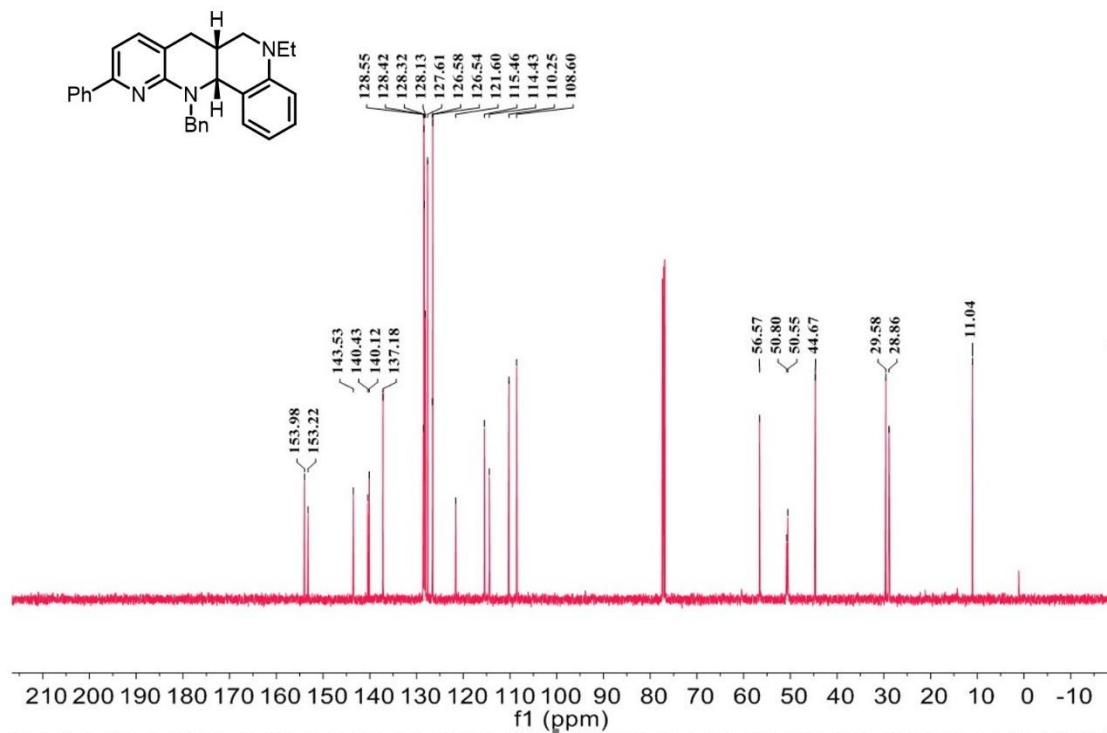
Supplementary Fig. 91 ¹H-NMR spectrum of P36



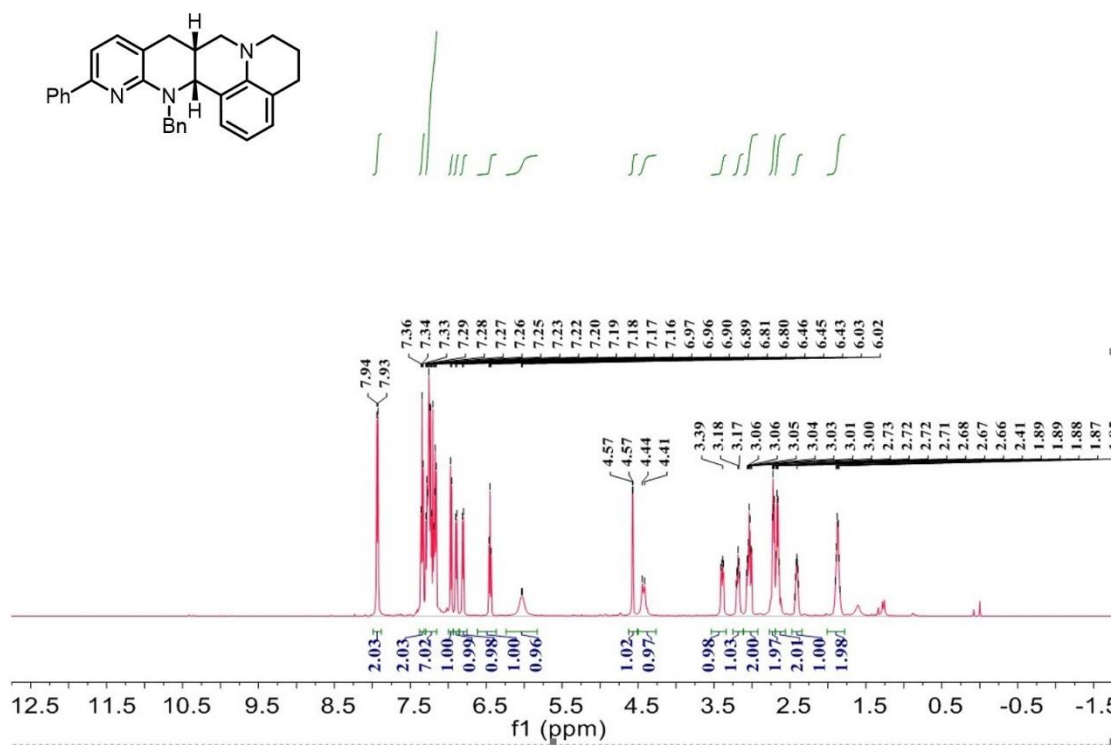
Supplementary Fig. 92 ¹³C-NMR spectrum of P36



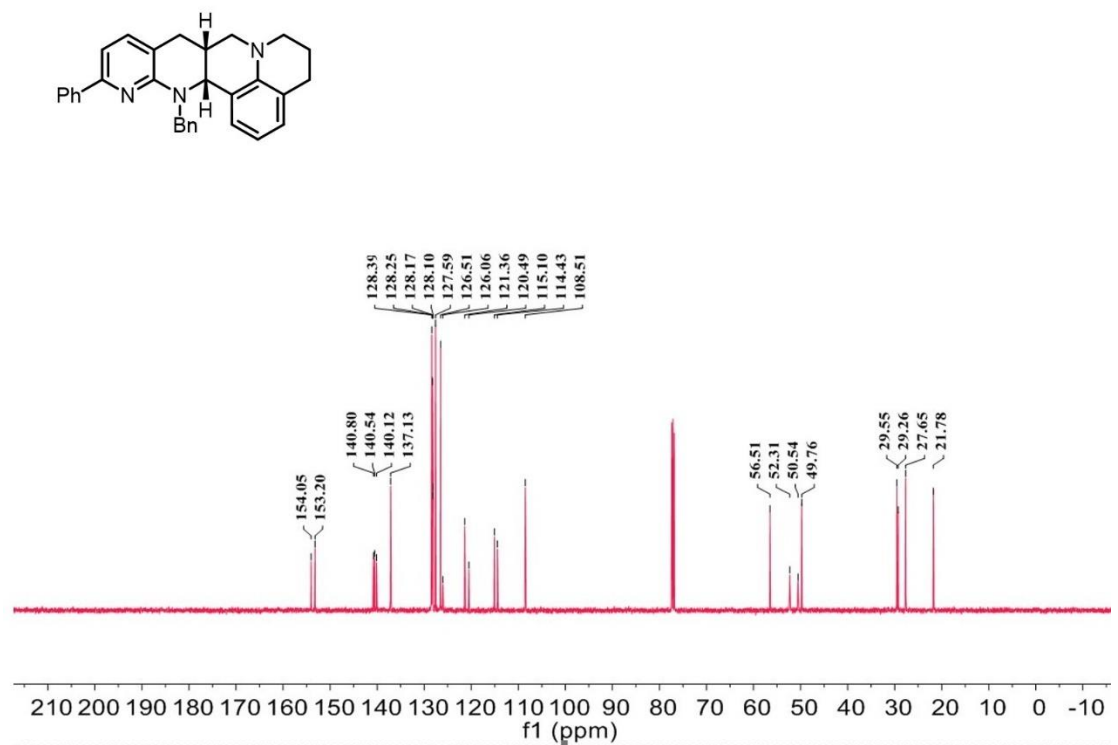
Supplementary Fig. 93 $^1\text{H-NMR}$ spectrum of P37



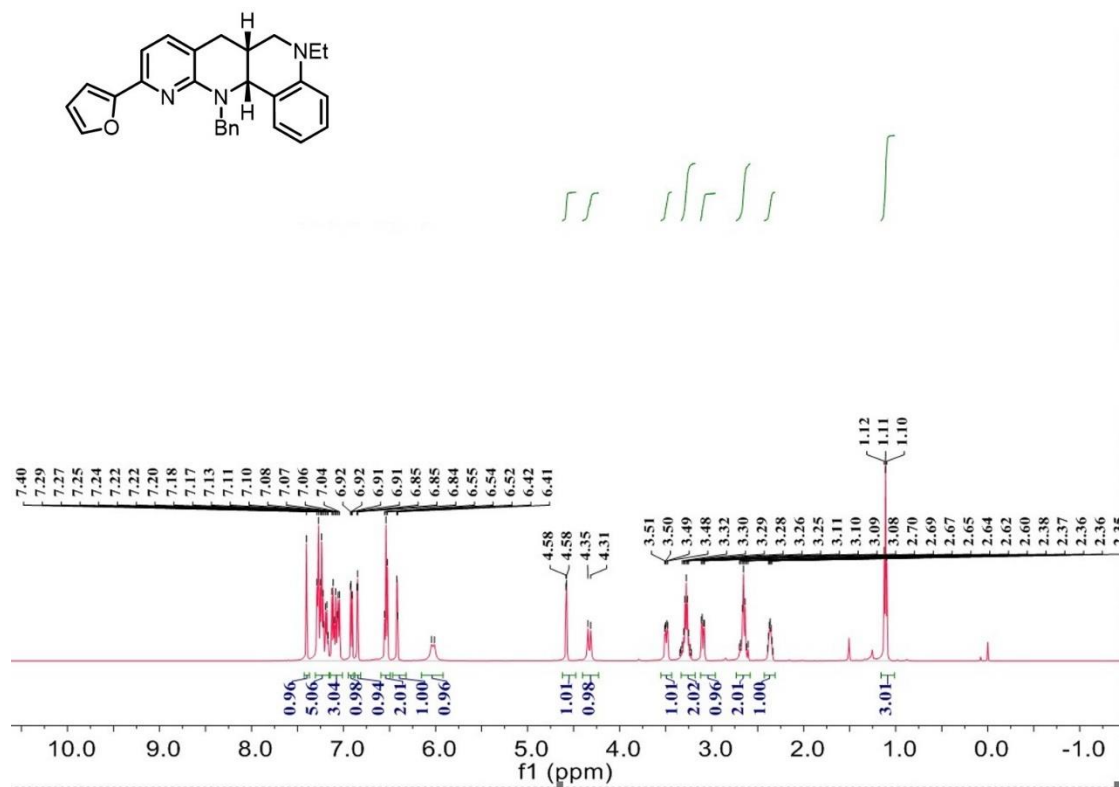
Supplementary Fig. 94 $^{13}\text{C-NMR}$ spectrum of P37



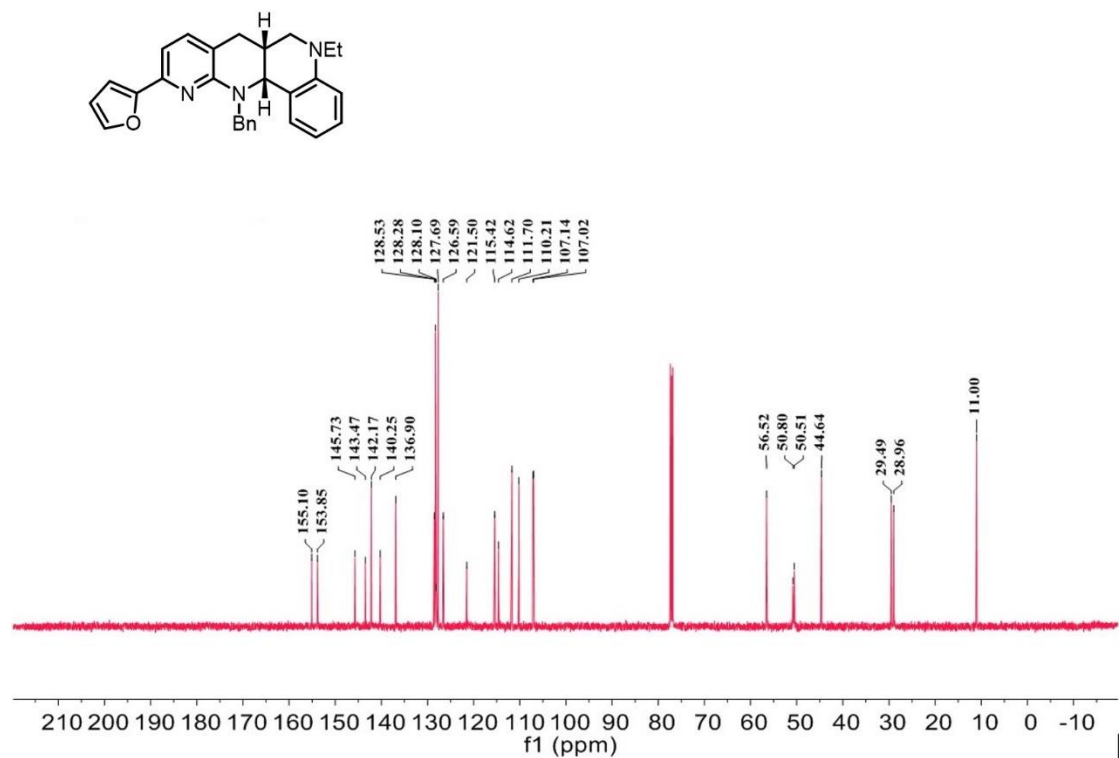
Supplementary Fig. 95 ¹H-NMR spectrum of P38



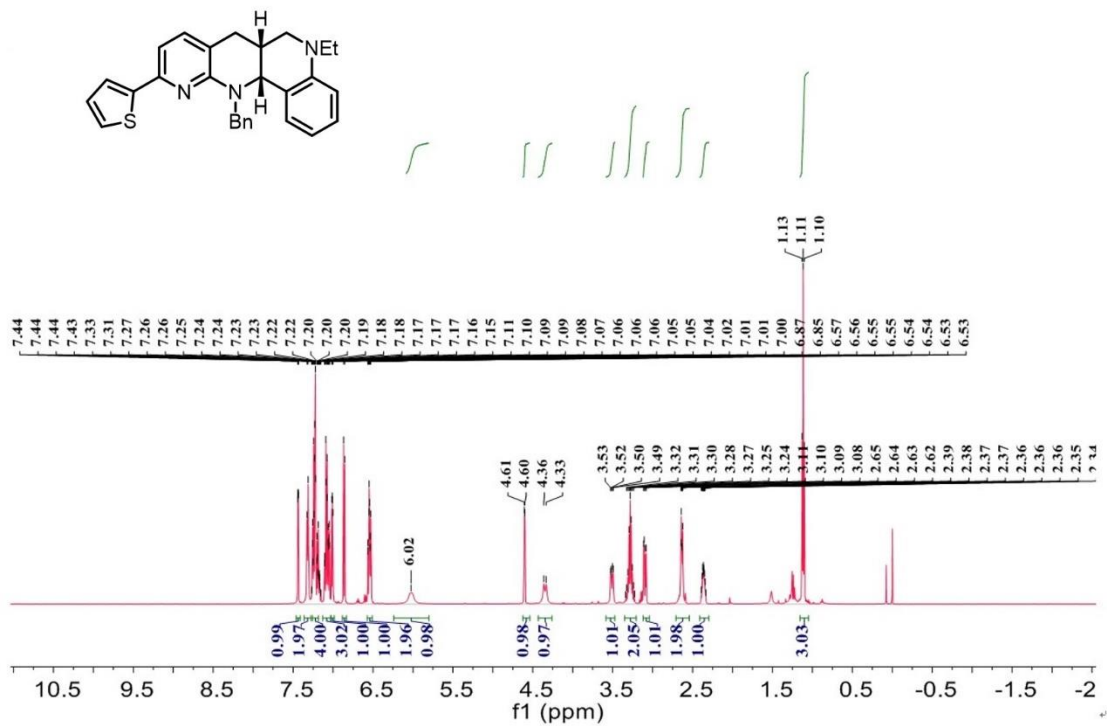
Supplementary Fig. 96 ¹³C-NMR spectrum of P38



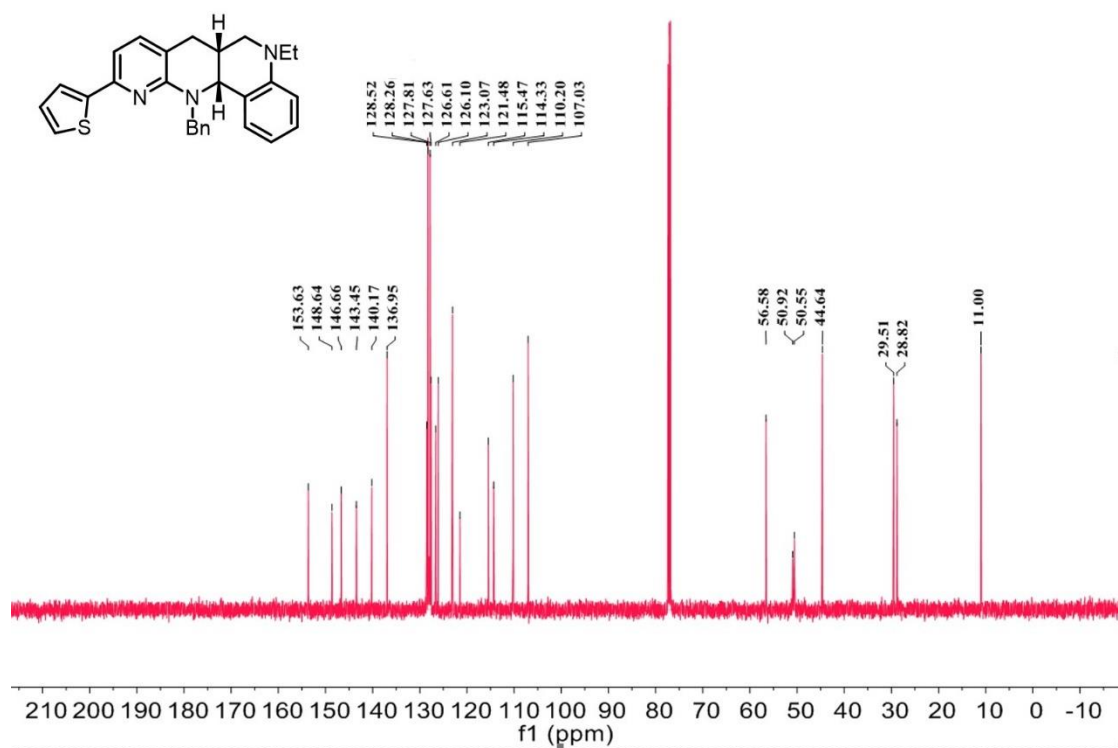
Supplementary Fig. 97 ¹H-NMR spectrum of P39



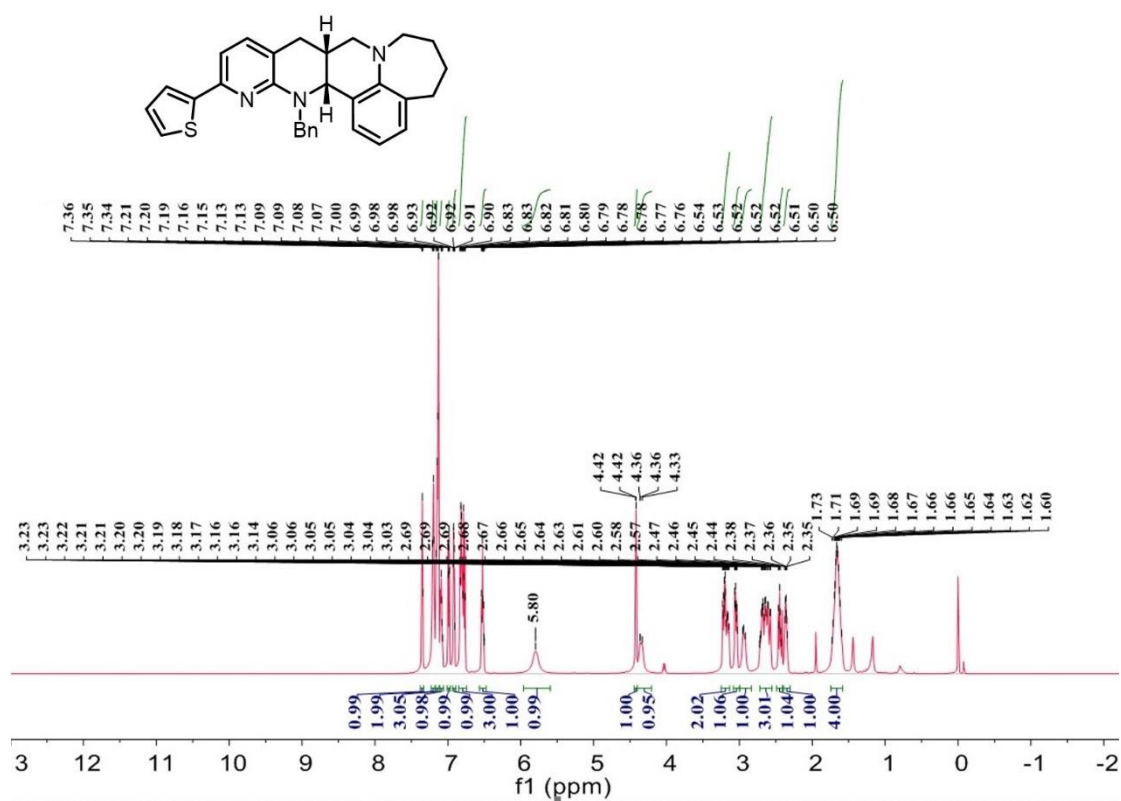
Supplementary Fig. 98 ¹³C-NMR spectrum of P39



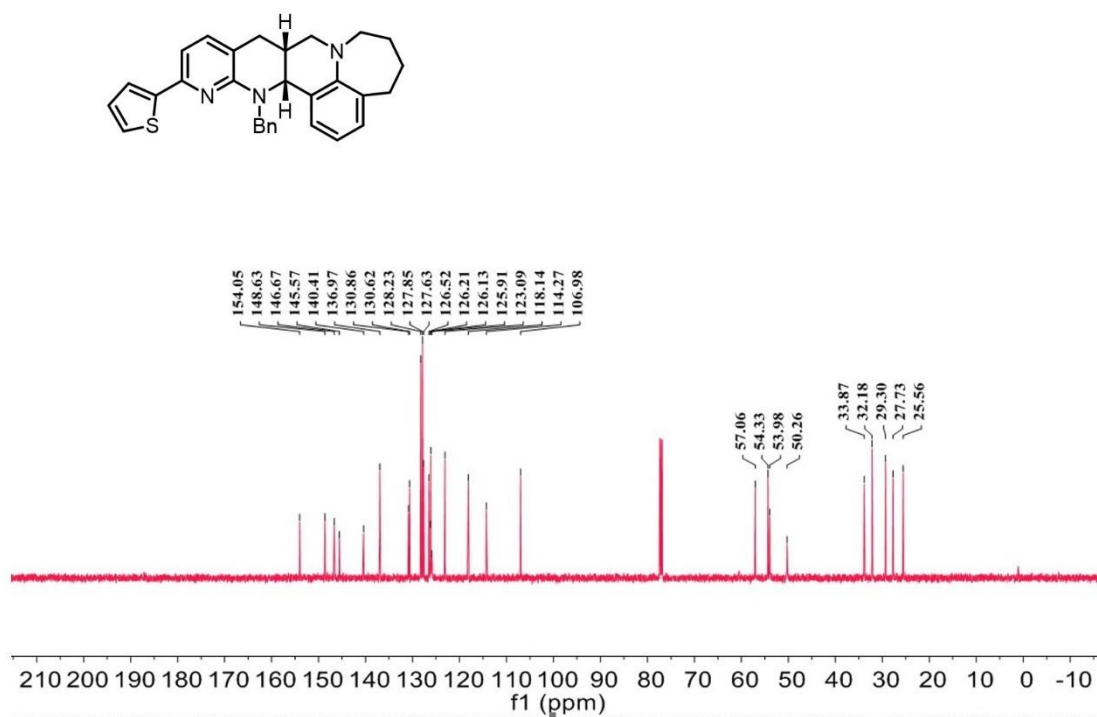
Supplementary Fig. 99 ¹H-NMR spectrum of P40



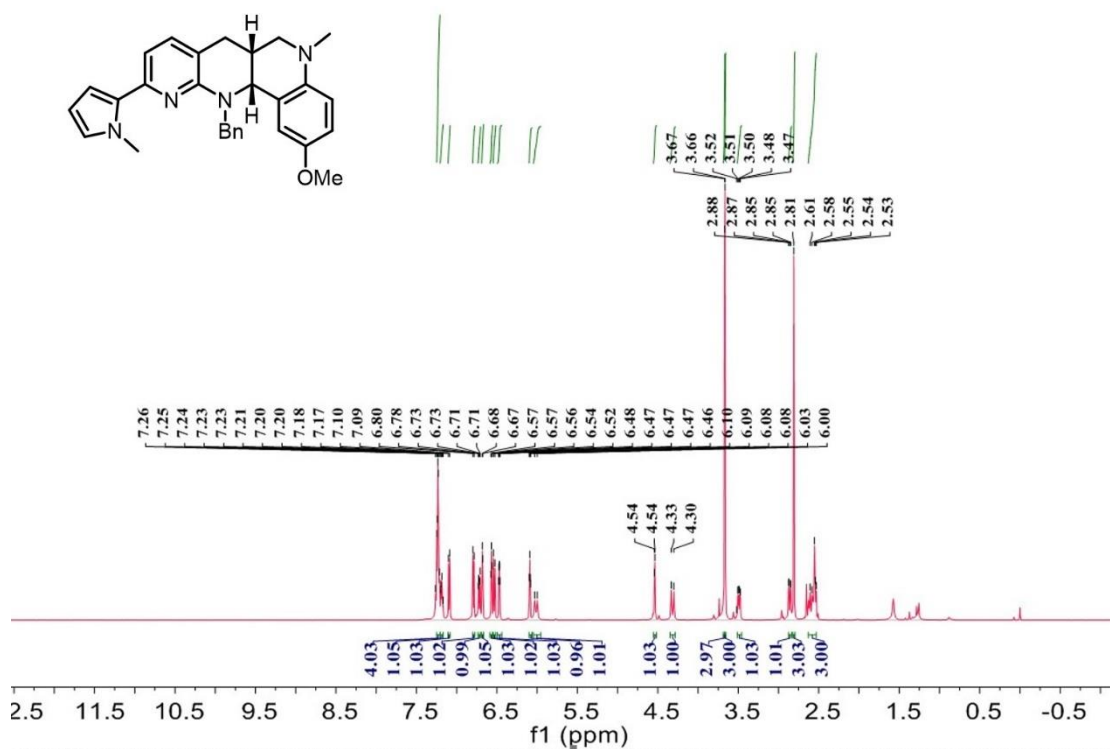
Supplementary Fig. 100 ¹³C-NMR spectrum of P40



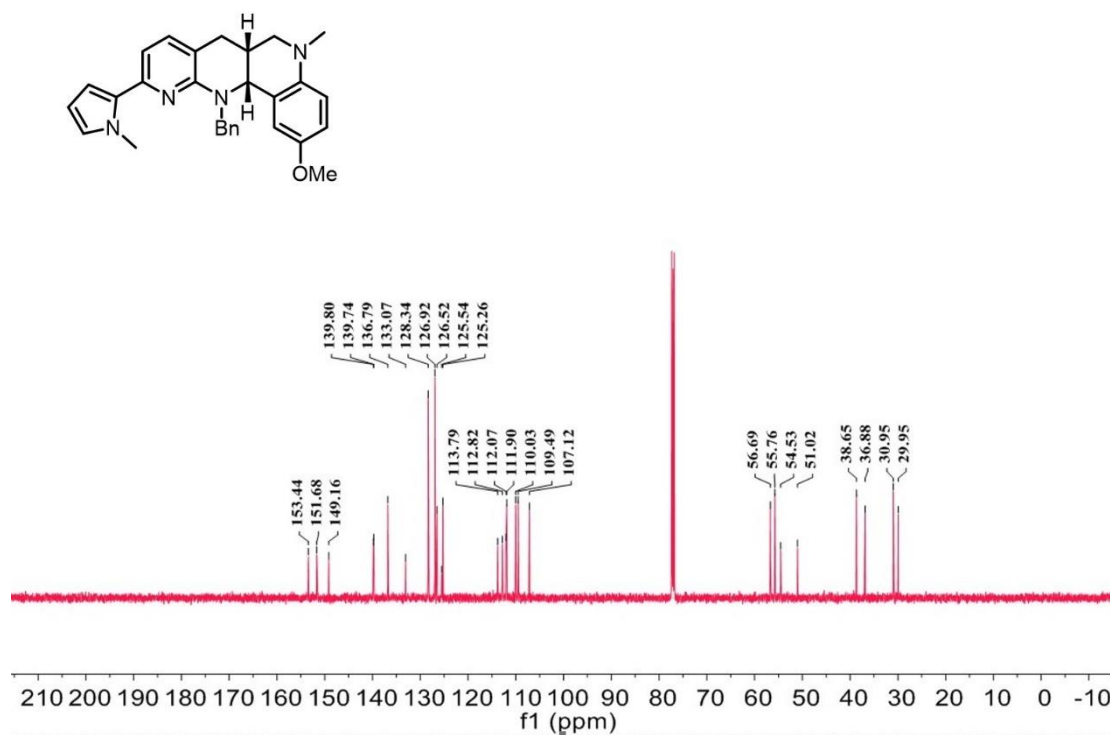
Supplementary Fig. 101 ¹H-NMR spectrum of P41



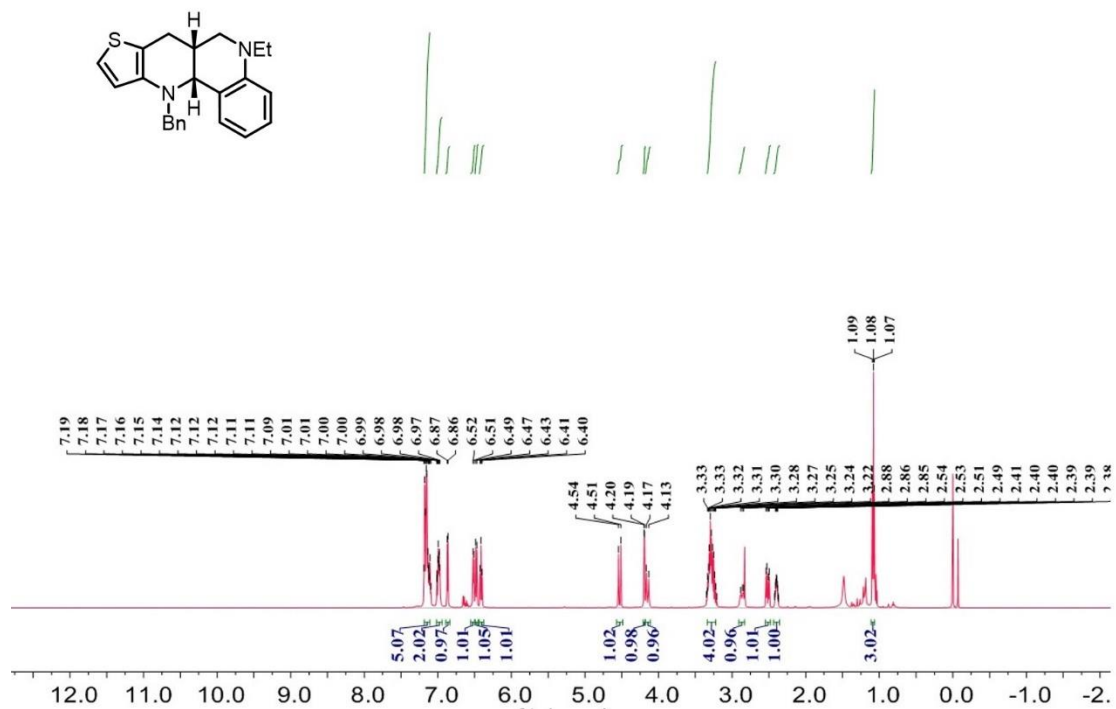
Supplementary Fig. 102 ¹³C-NMR spectrum of P41



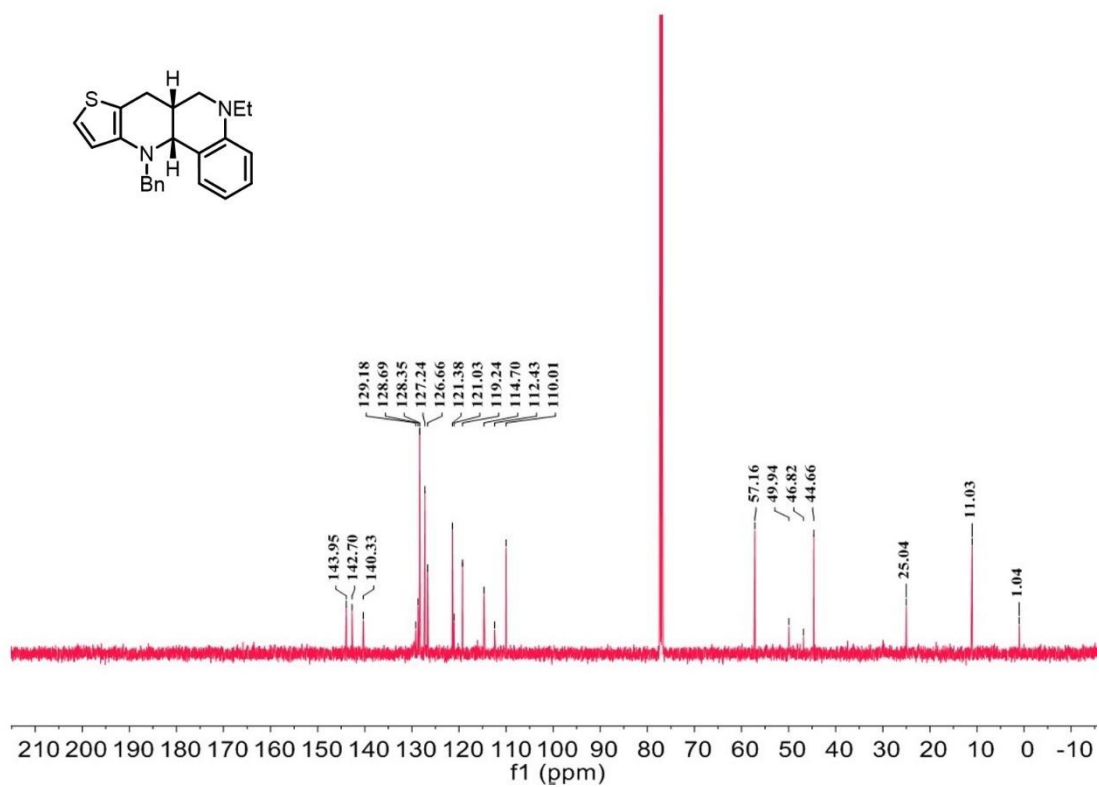
Supplementary Fig. 103 ¹H-NMR spectrum of P42



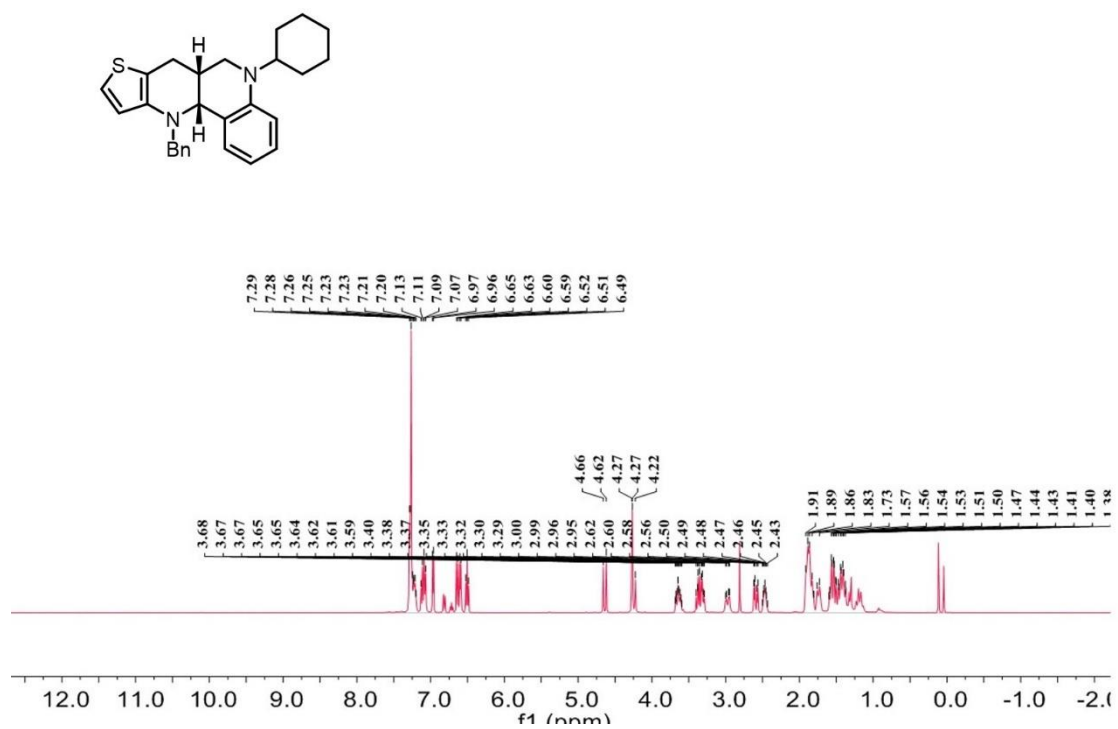
Supplementary Fig. 104 ¹³C-NMR spectrum of P42



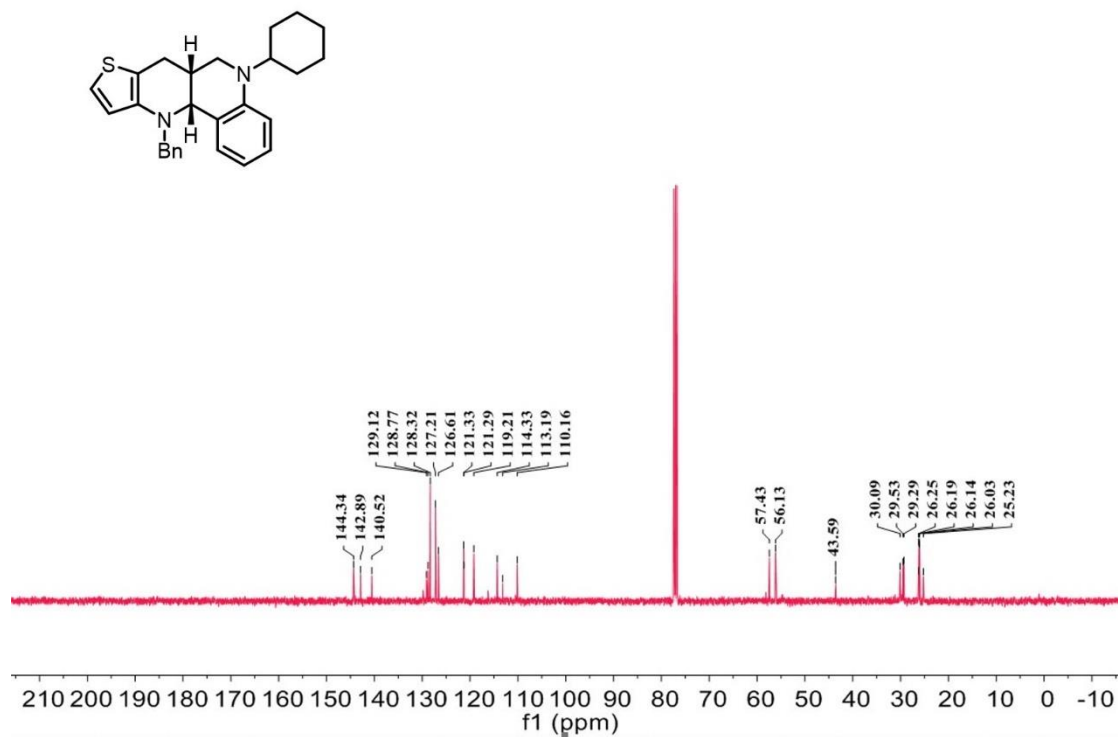
Supplementary Fig. 105 ¹H-NMR spectrum of P43



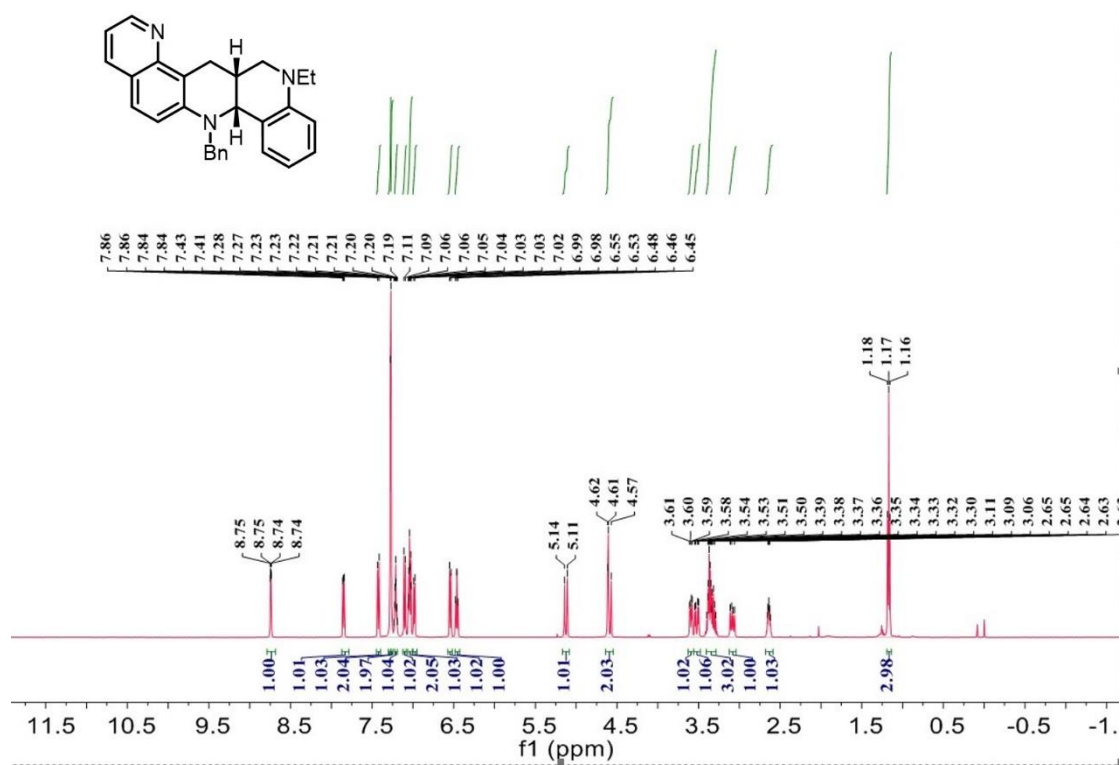
Supplementary Fig. 106 ¹³C-NMR spectrum of P43



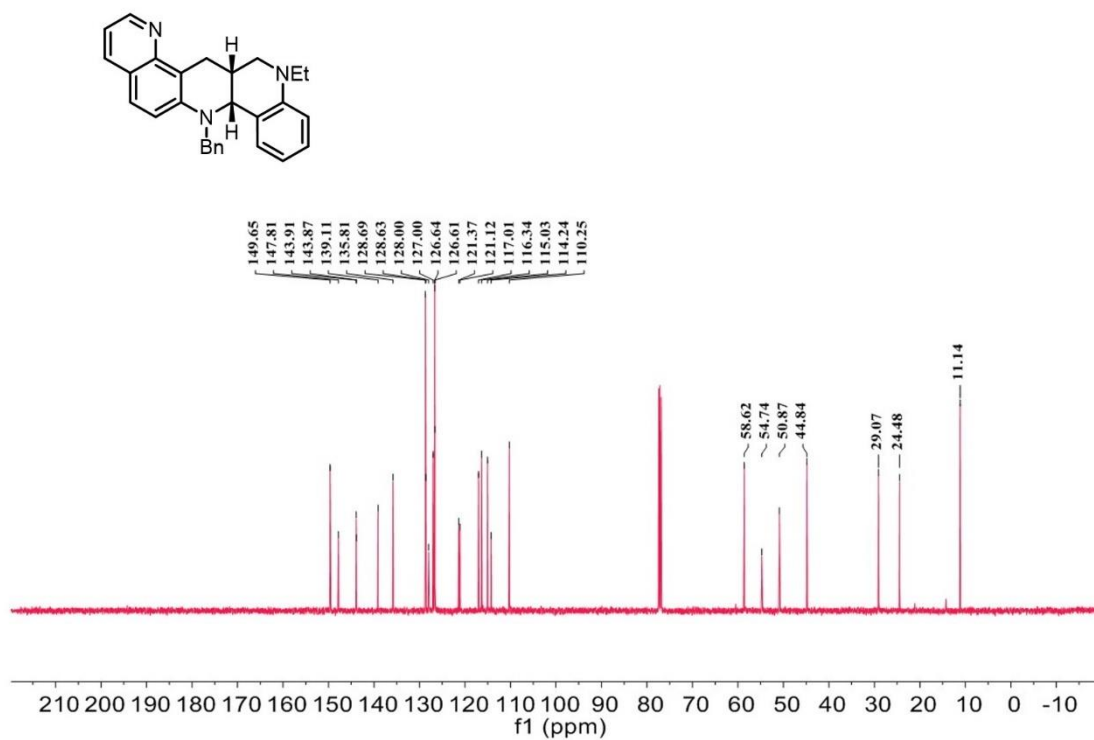
Supplementary Fig. 107 ¹H-NMR spectrum of P44



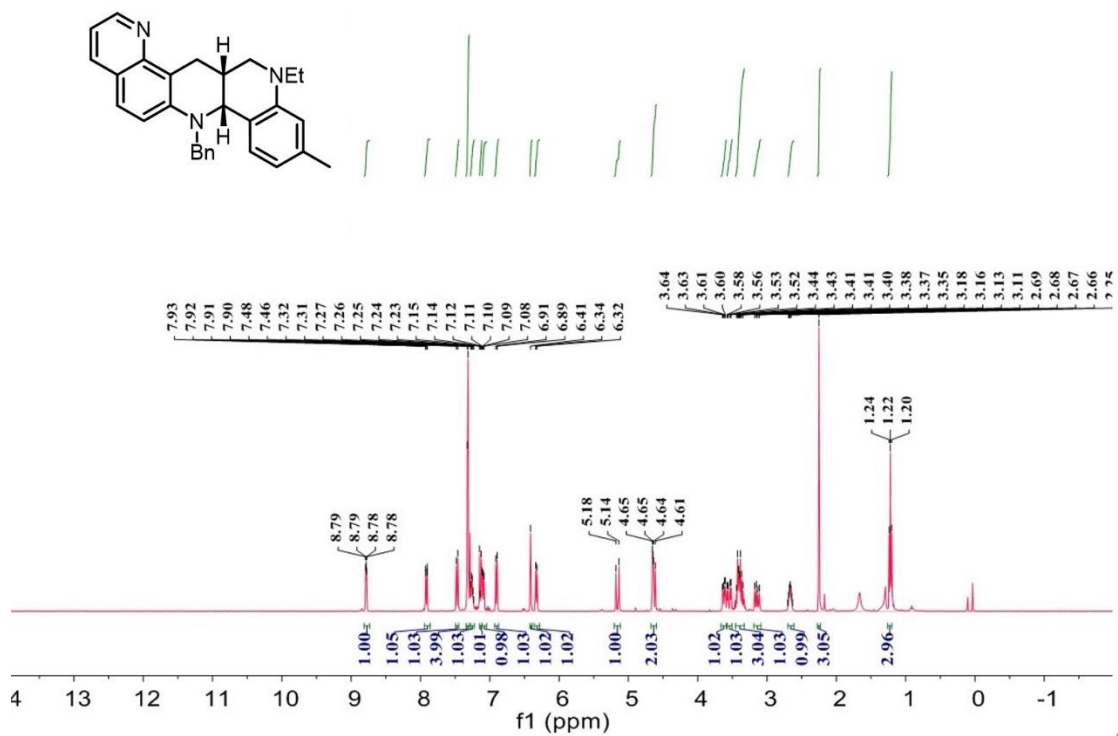
Supplementary Fig. 108 ¹³C-NMR spectrum of P44



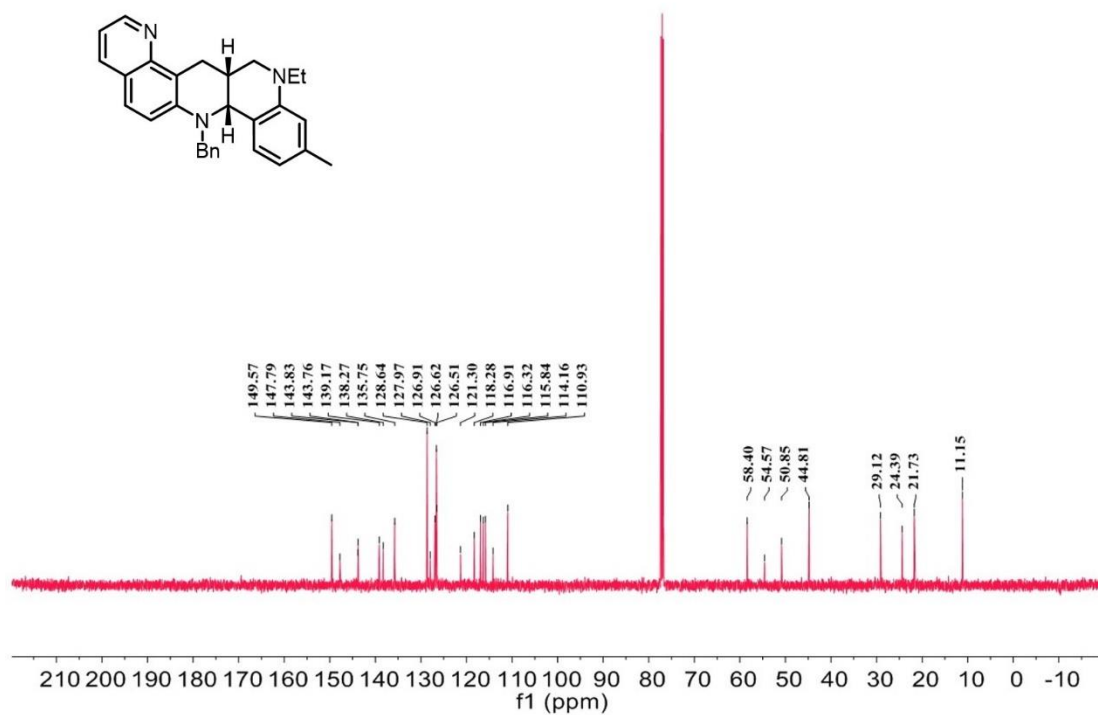
Supplementary Fig. 109 ¹H-NMR spectrum of P45



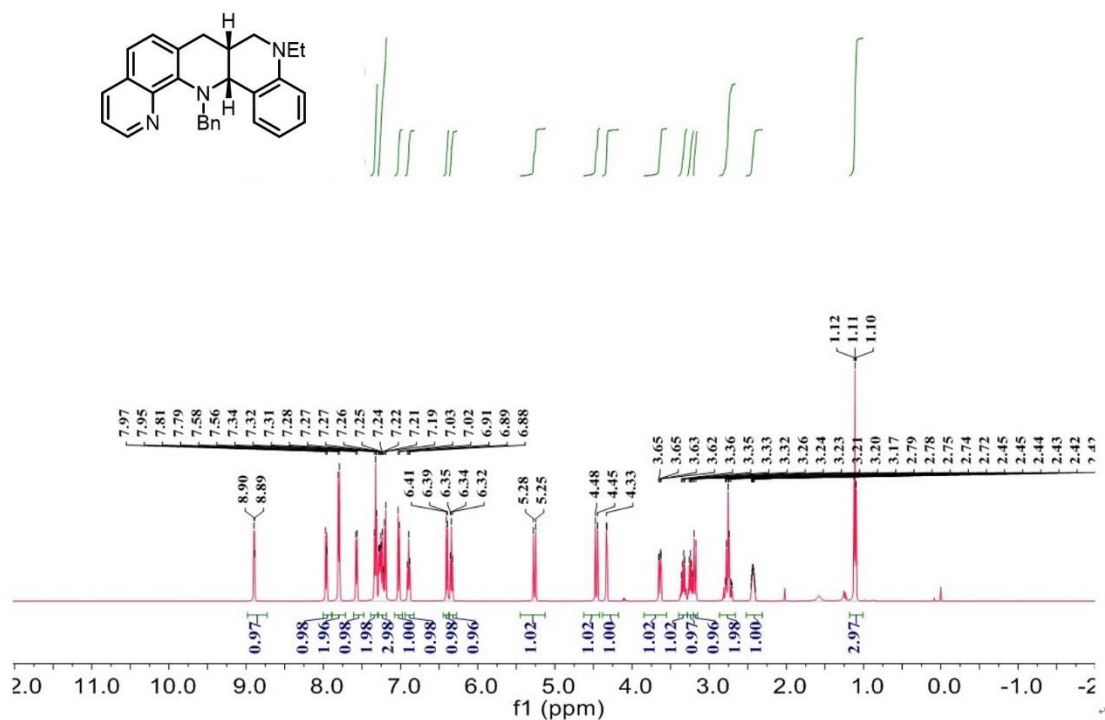
Supplementary Fig. 110 ¹³C-NMR spectrum of P45



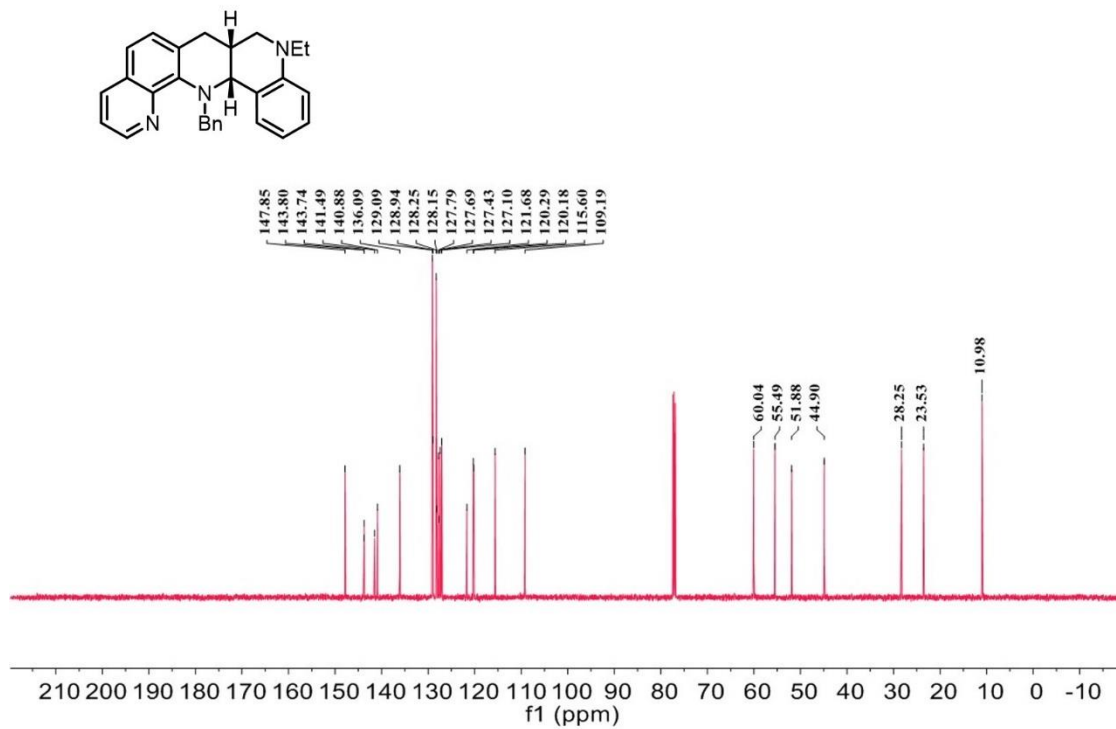
Supplementary Fig. 111 ¹H-NMR spectrum of P46



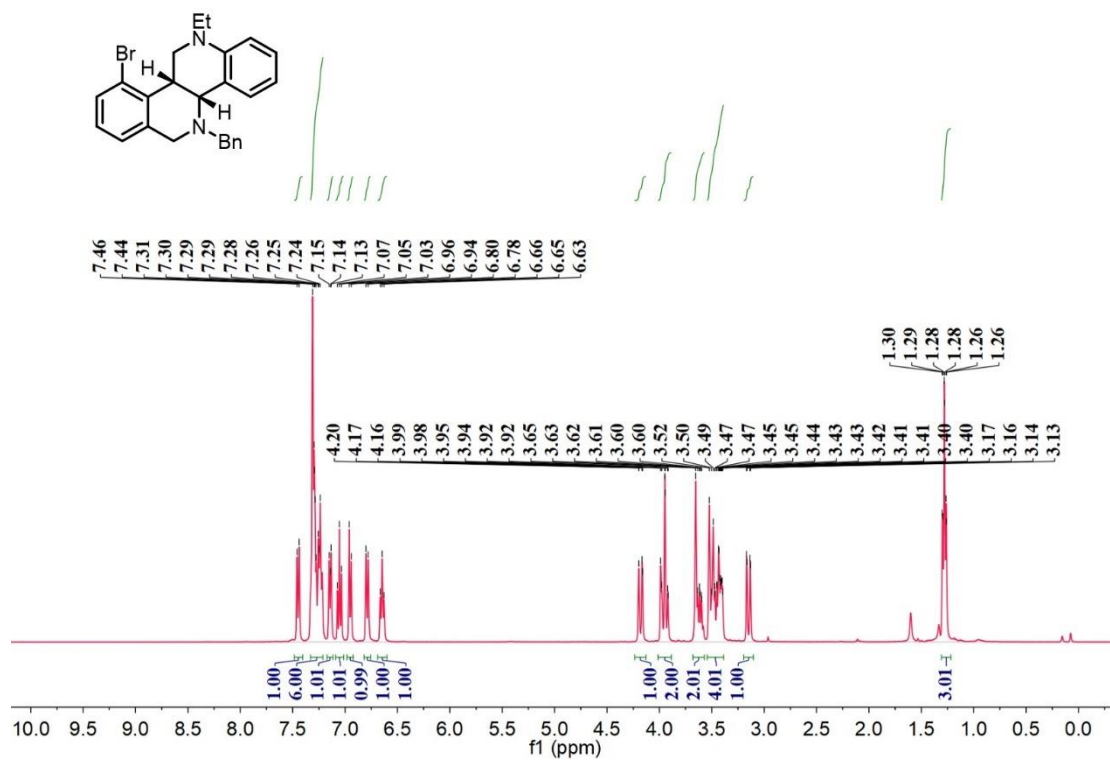
Supplementary Fig. 112 ¹³C-NMR spectrum of P46



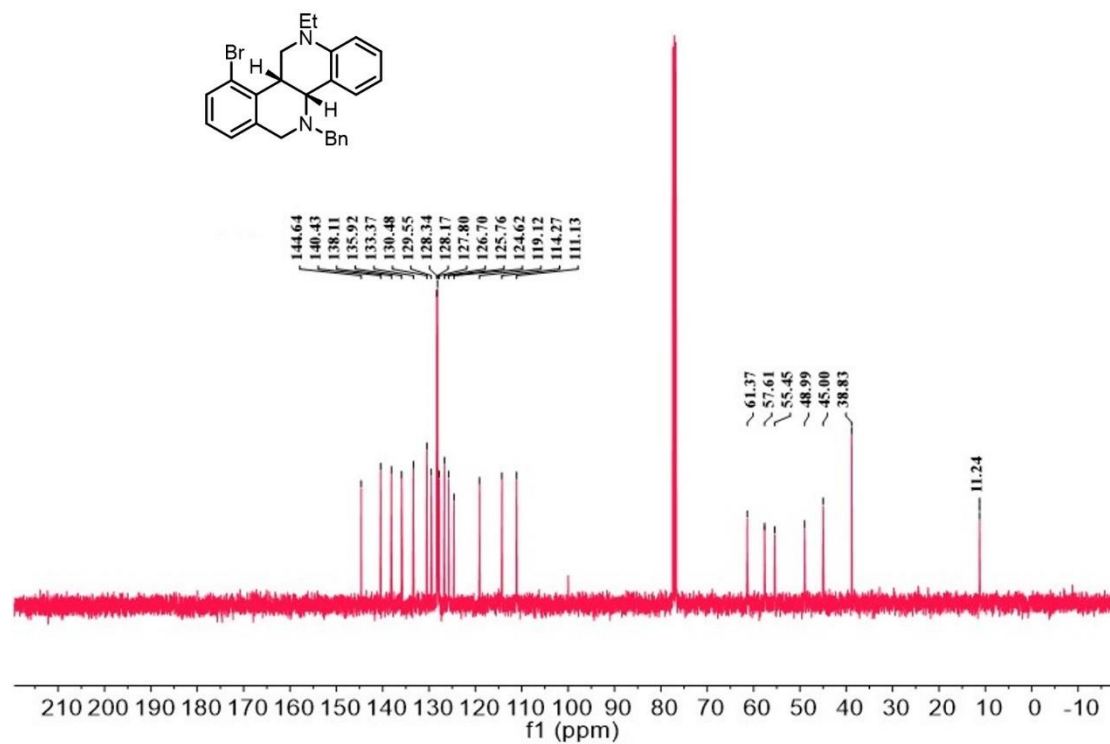
Supplementary Fig. 113 ¹H-NMR spectrum of P47



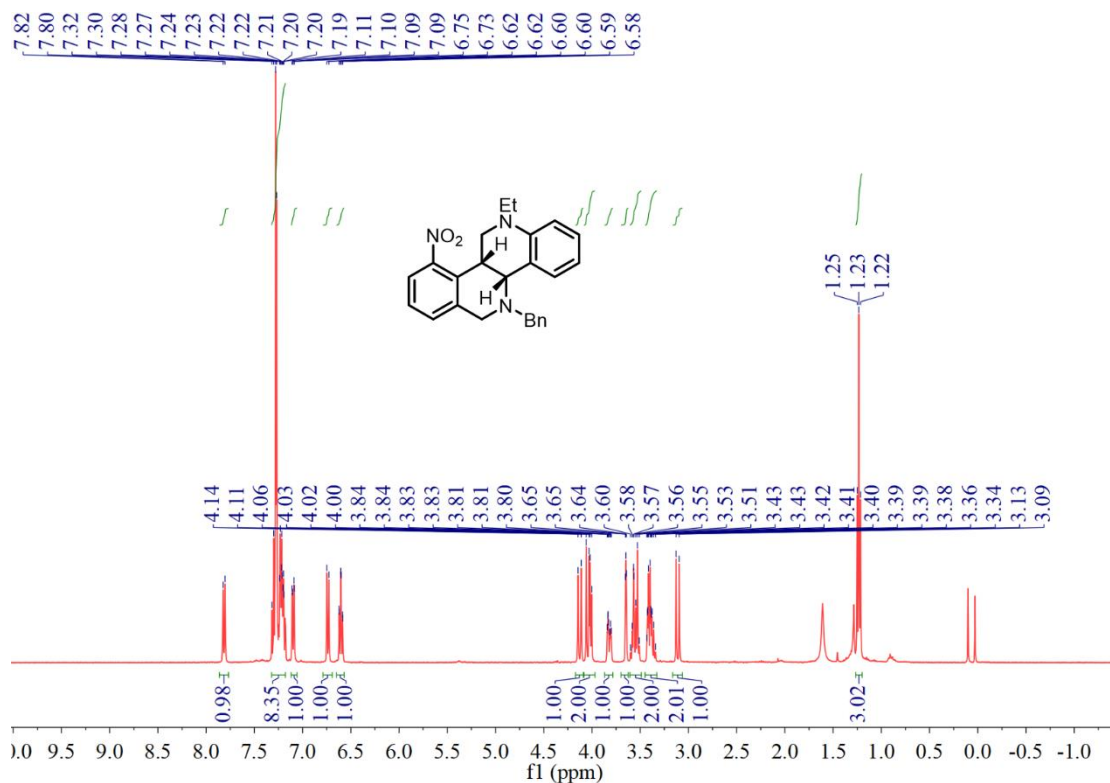
Supplementary Fig. 114 ¹³C-NMR spectrum of P47



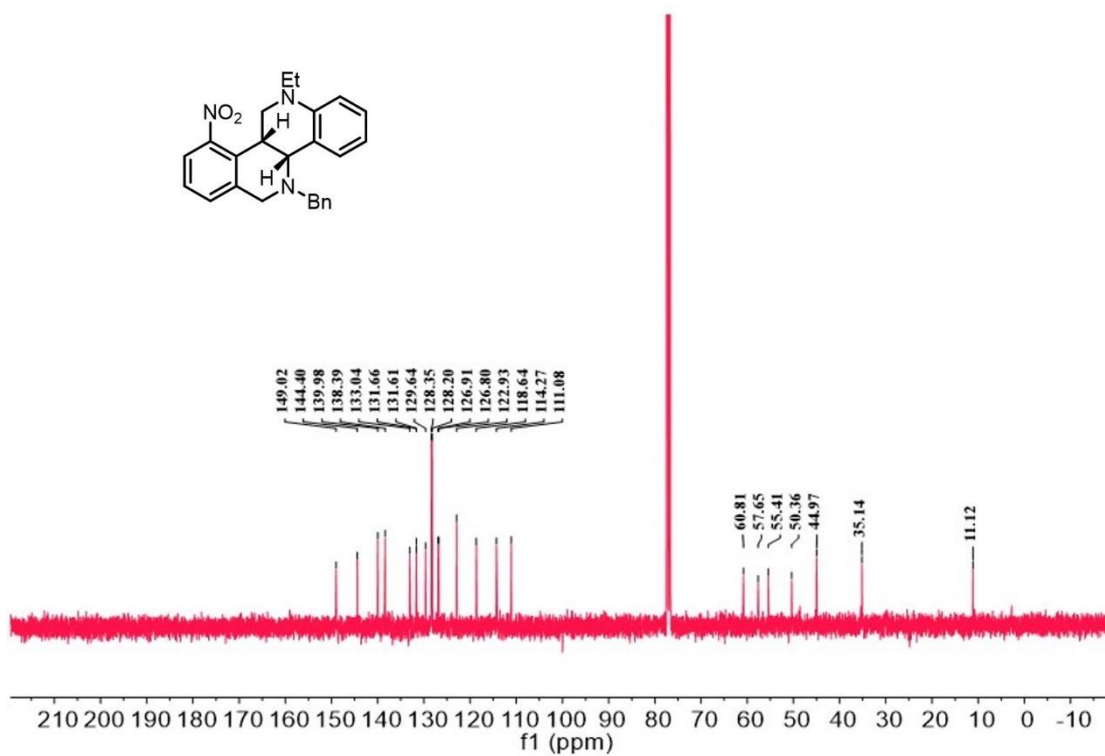
Supplementary Fig. 115 ¹H-NMR spectrum of P48



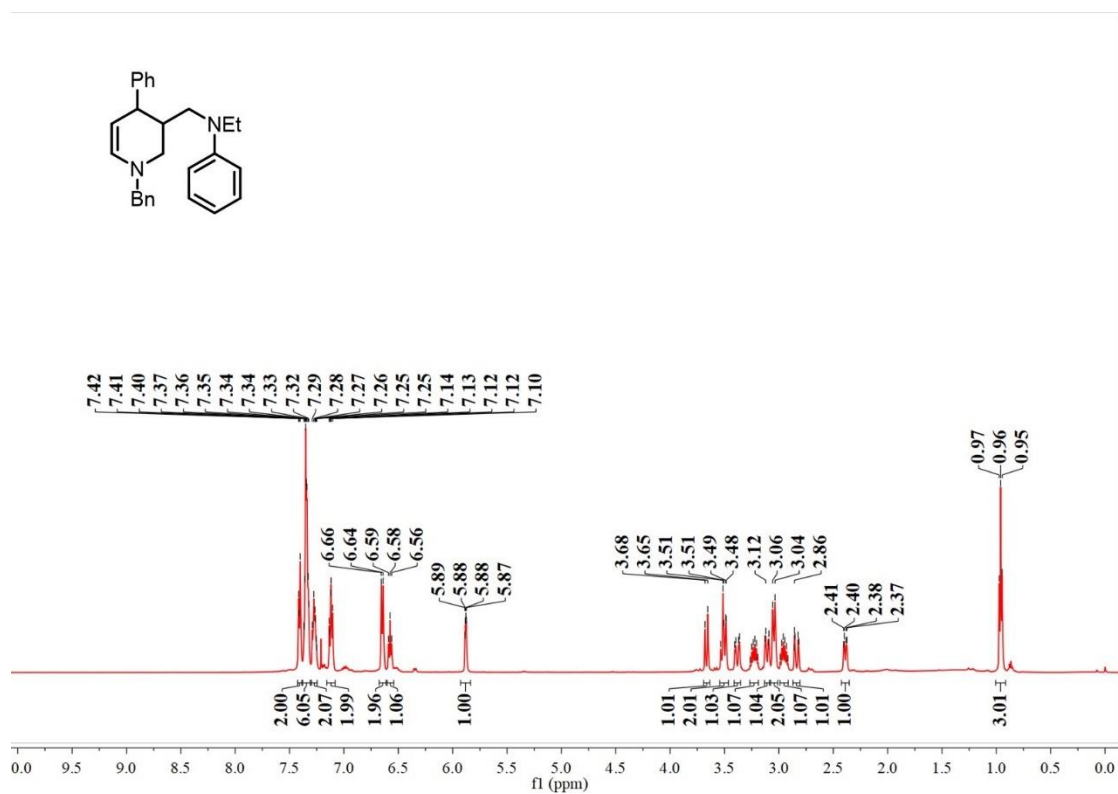
Supplementary Fig. 116 ¹³C-NMR spectrum of P48



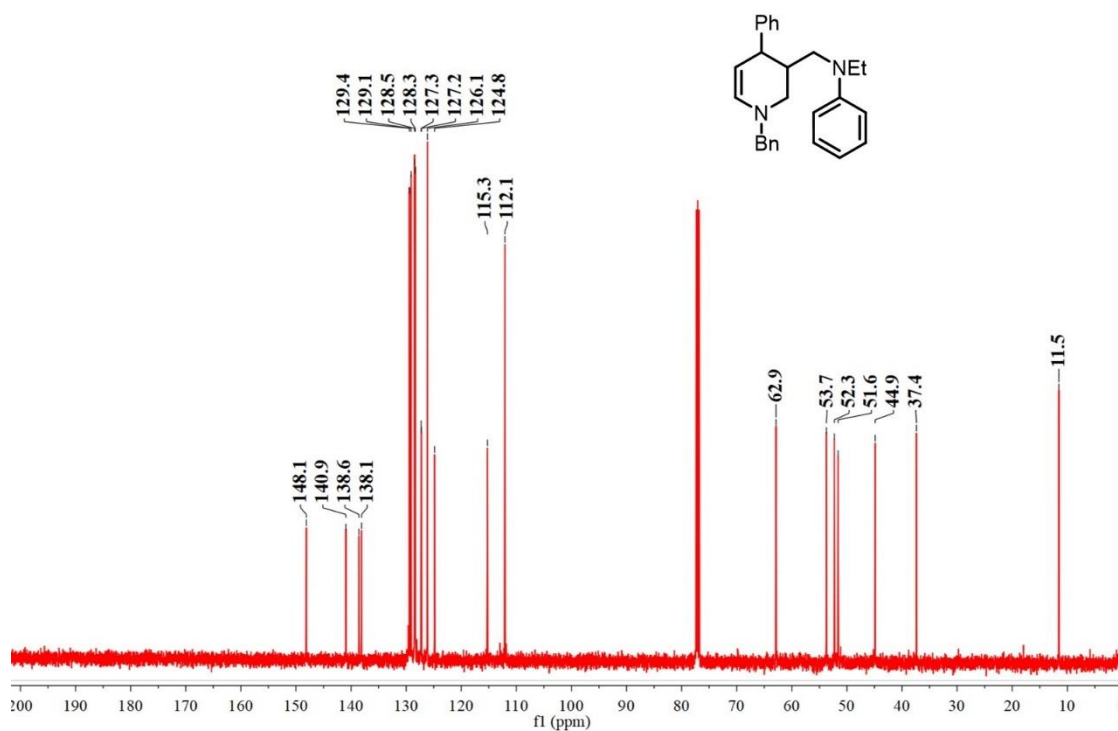
Supplementary Fig. 117 ¹H-NMR spectrum of P49



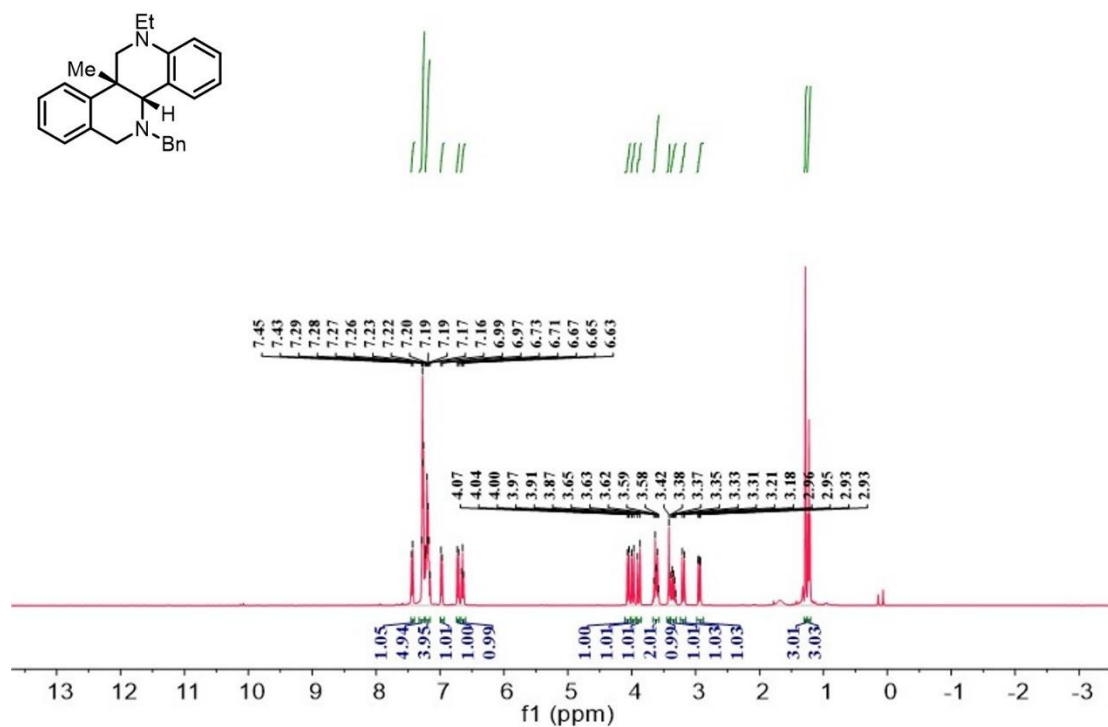
Supplementary Fig. 118 ¹³C-NMR spectrum of P49



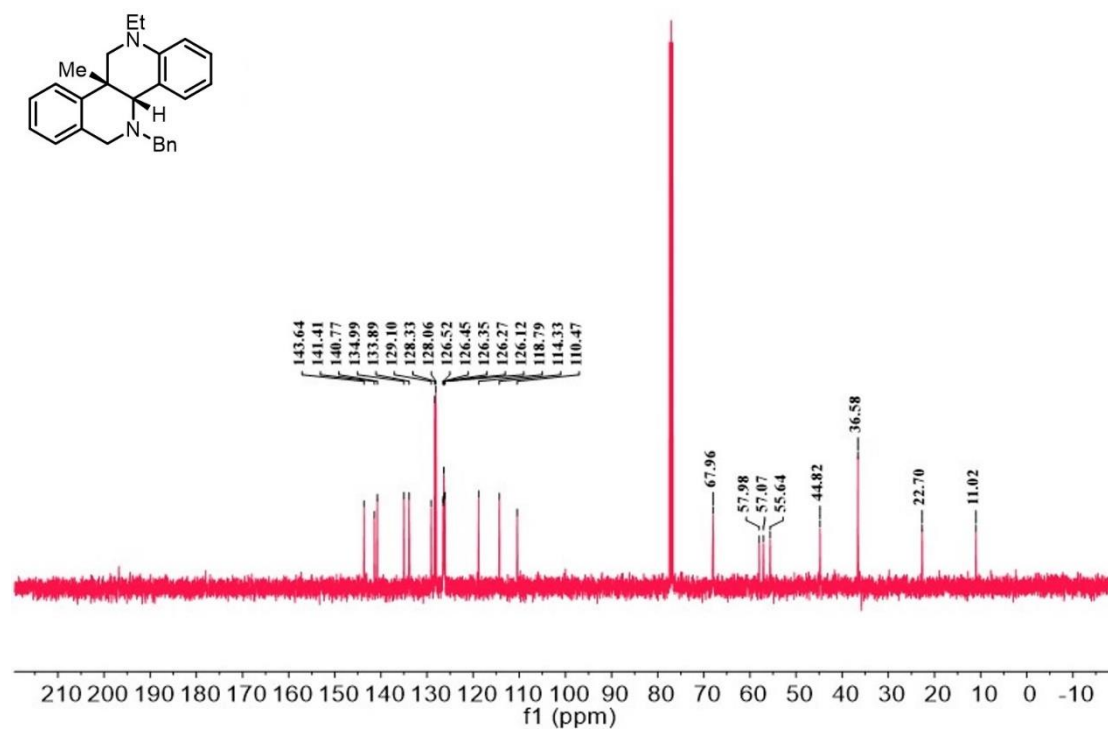
Supplementary Fig. 119 ¹H-NMR spectrum of P50



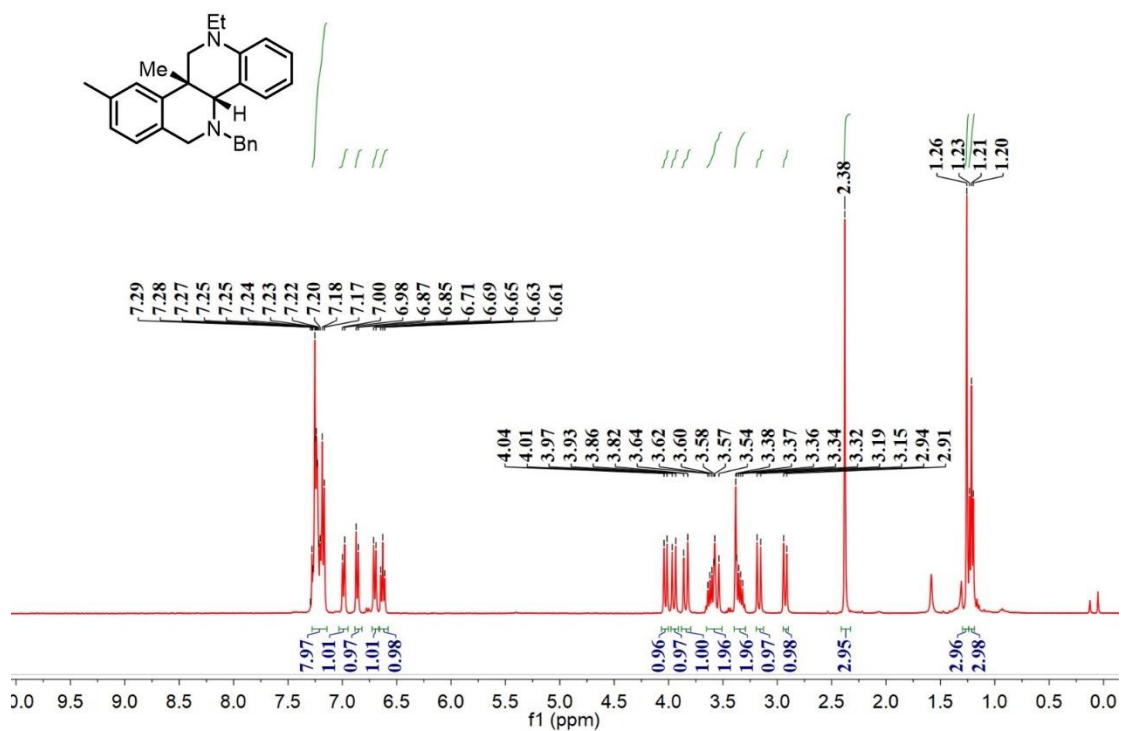
Supplementary Fig. 120 ¹³C-NMR spectrum of P50



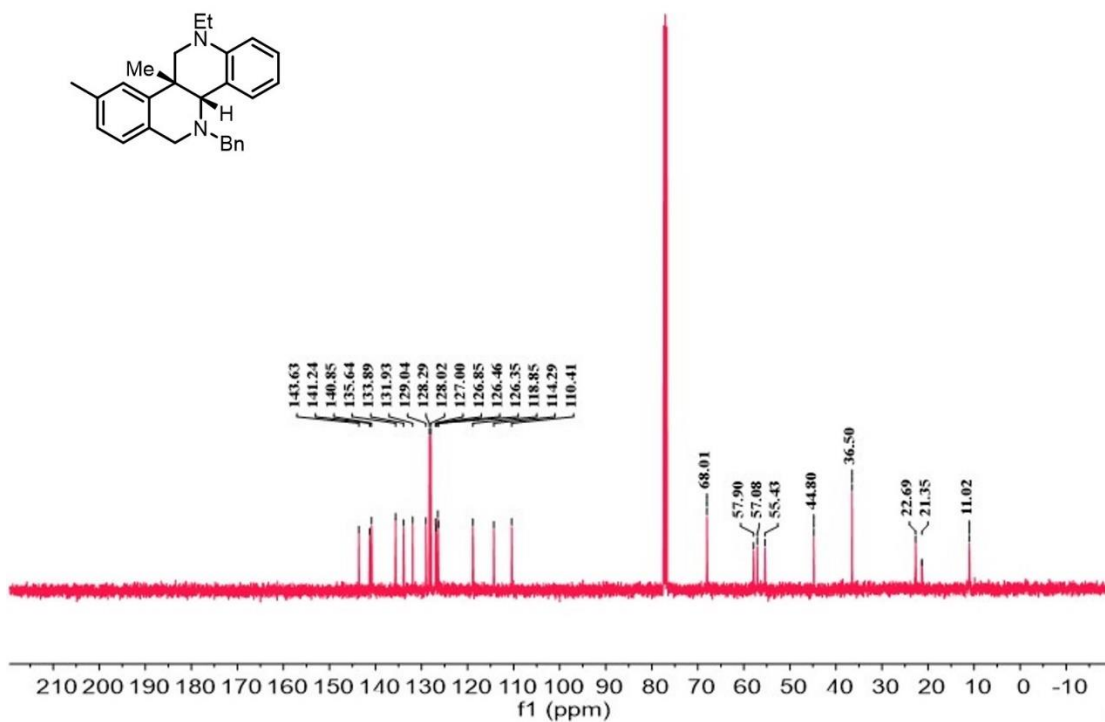
Supplementary Fig. 121 ¹H-NMR spectrum of P51



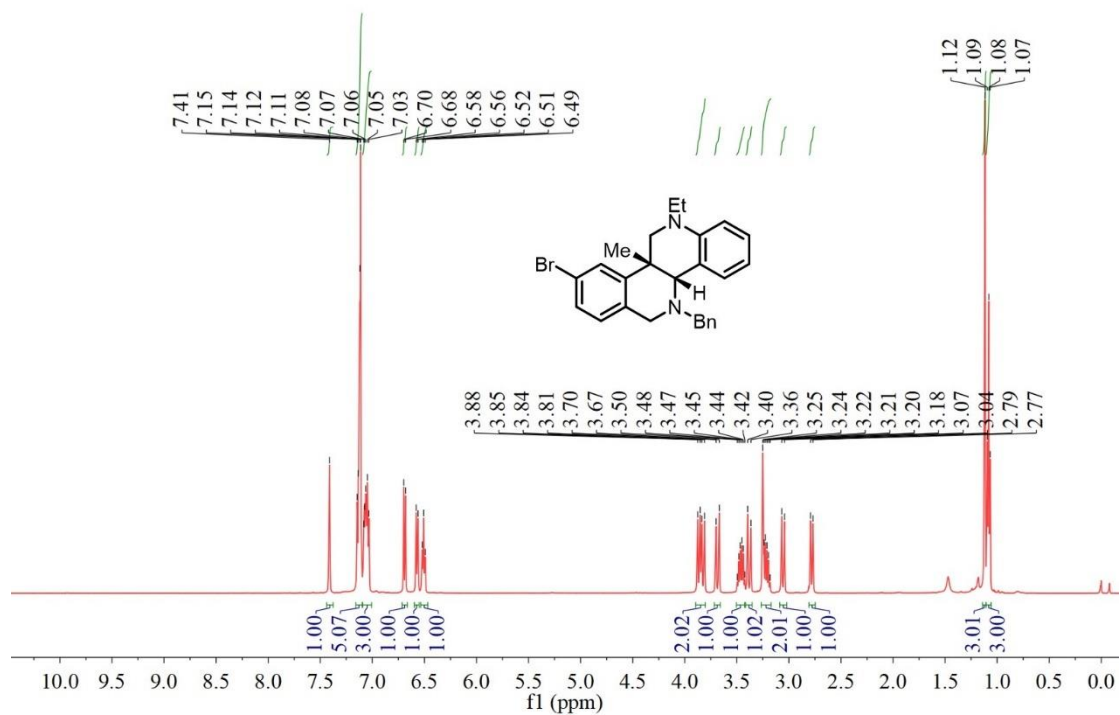
Supplementary Fig. 122 ¹³C-NMR spectrum of P51



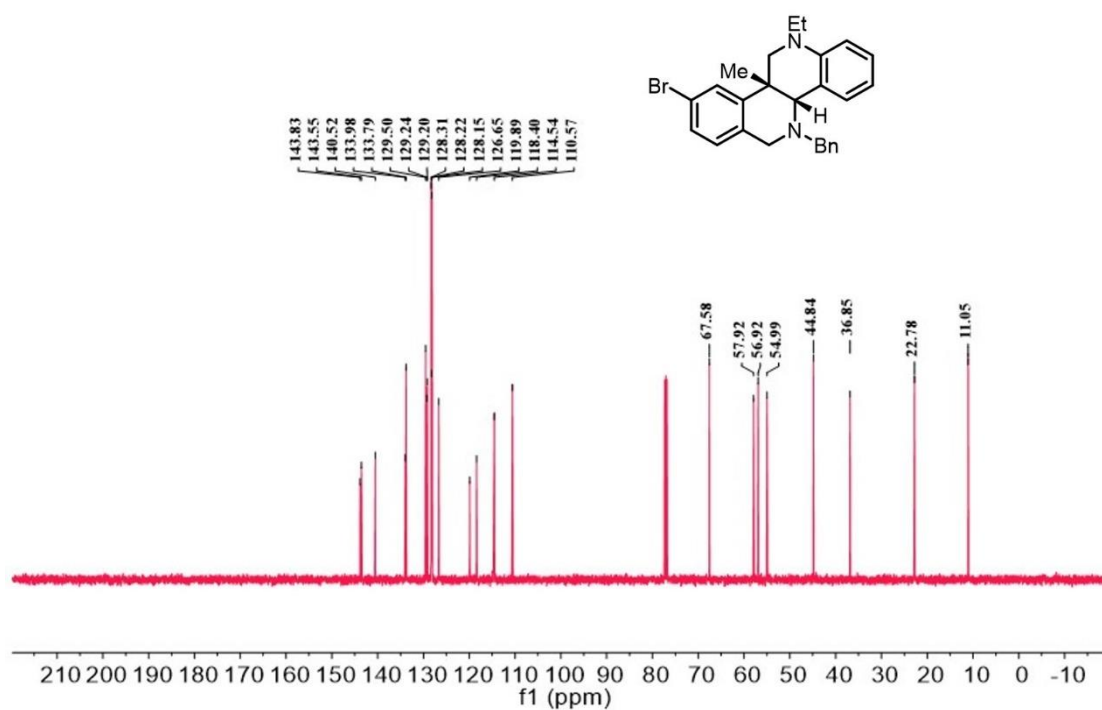
Supplementary Fig. 123 ¹H-NMR spectrum of P52



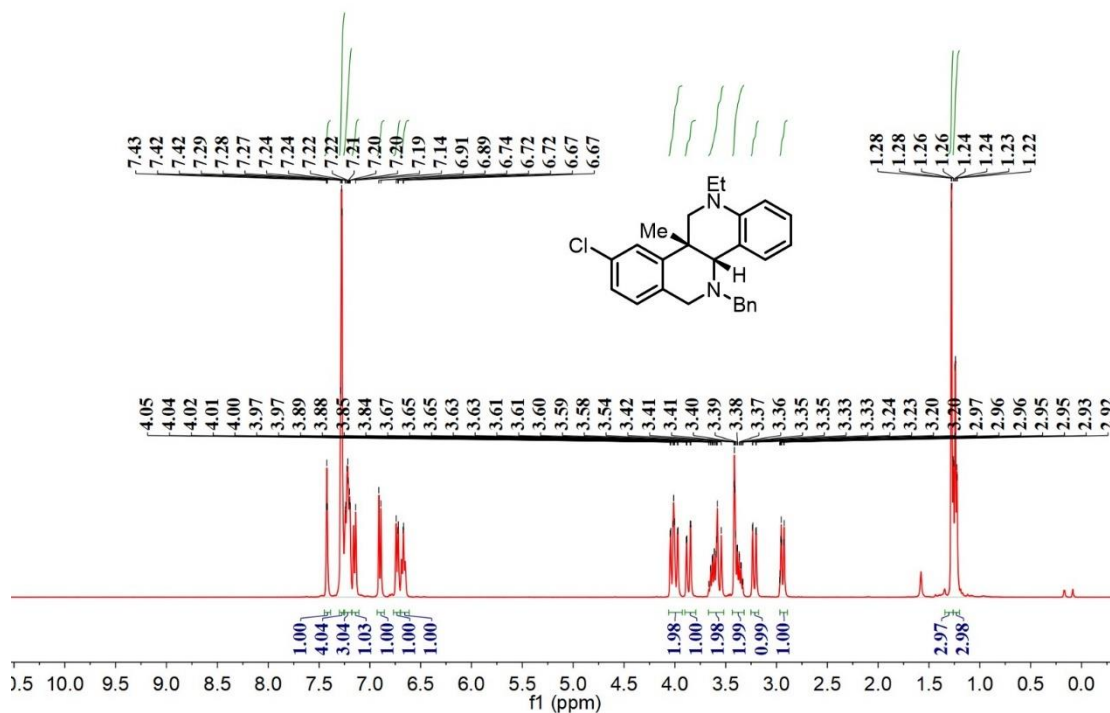
Supplementary Fig. 124 ¹³C-NMR spectrum of P52



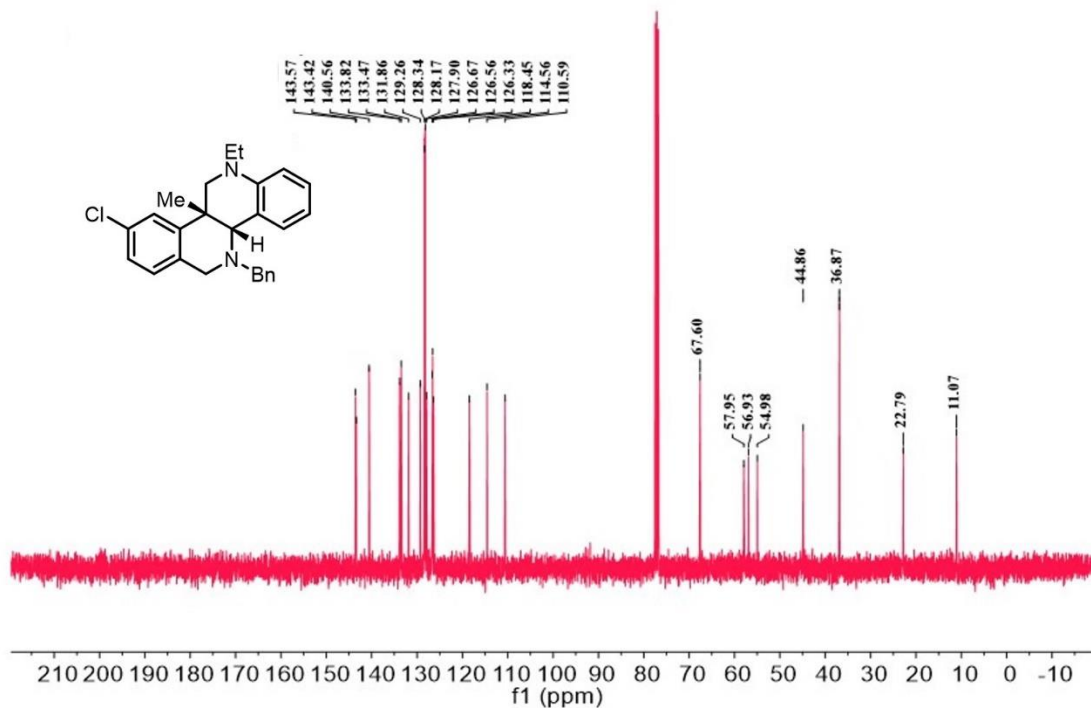
Supplementary Fig. 125 $^1\text{H-NMR}$ spectrum of P53



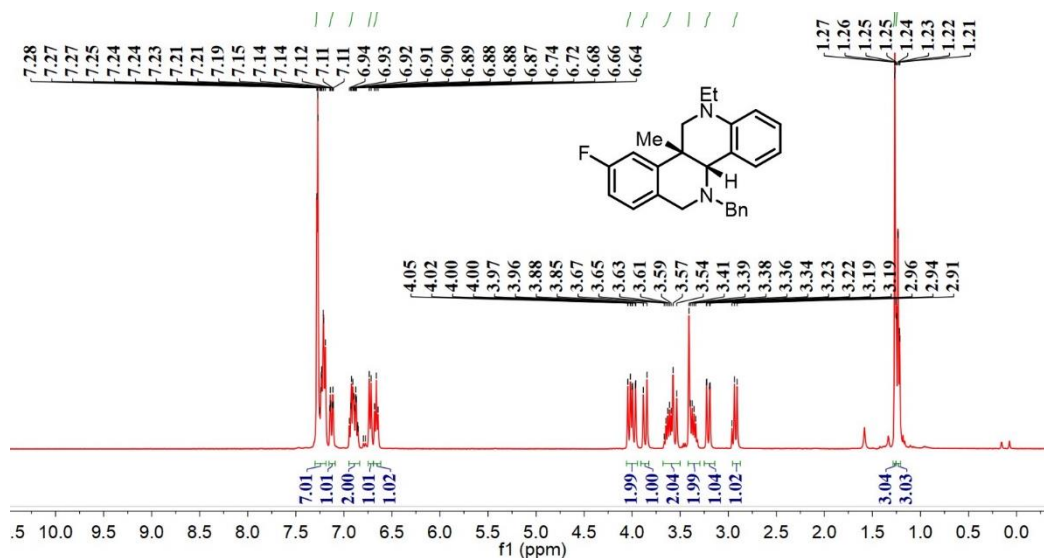
Supplementary Fig. 126 $^{13}\text{C-NMR}$ spectrum of P53



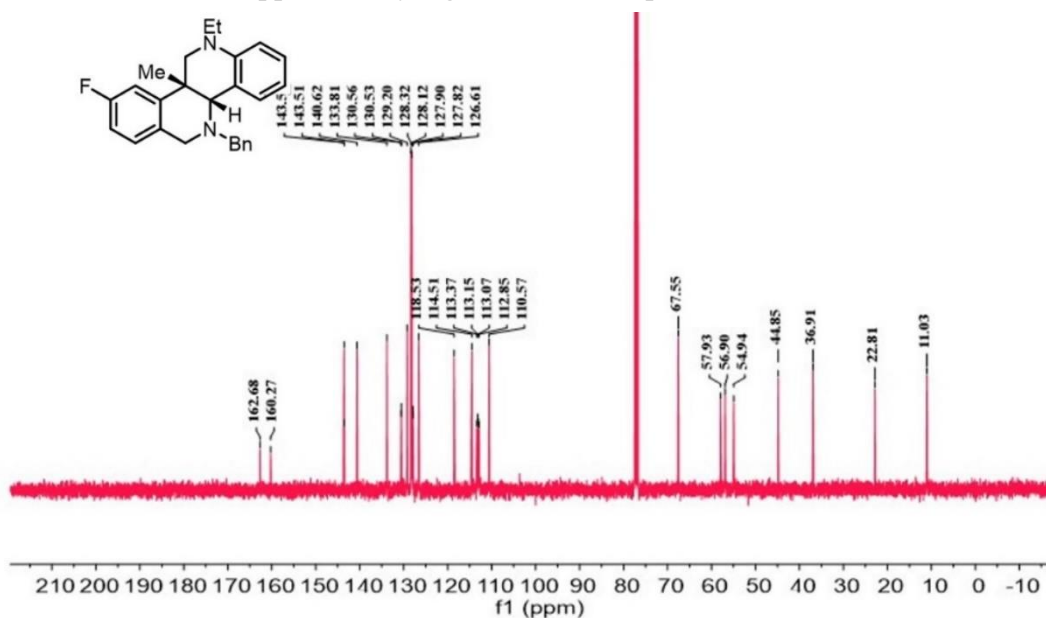
Supplementary Fig. 127 ¹H-NMR spectrum of P54



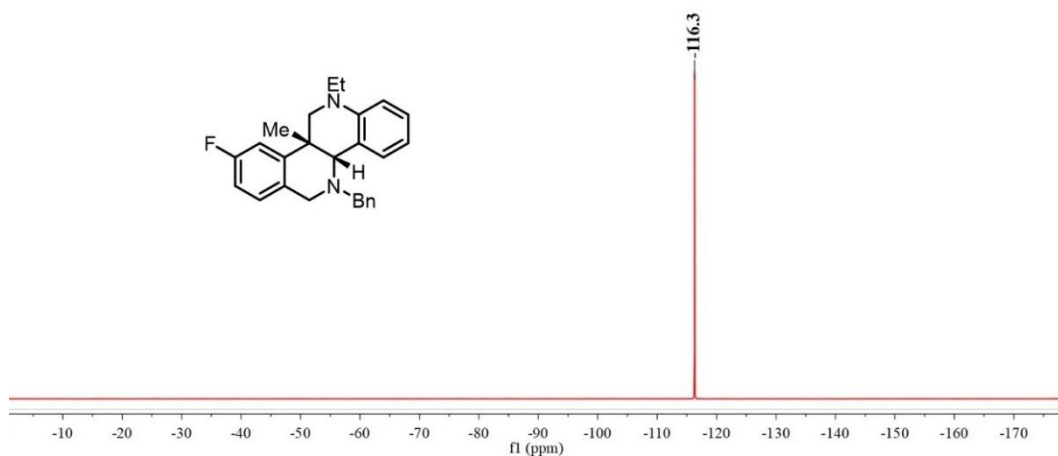
Supplementary Fig. 128 ¹³C-NMR spectrum of P54



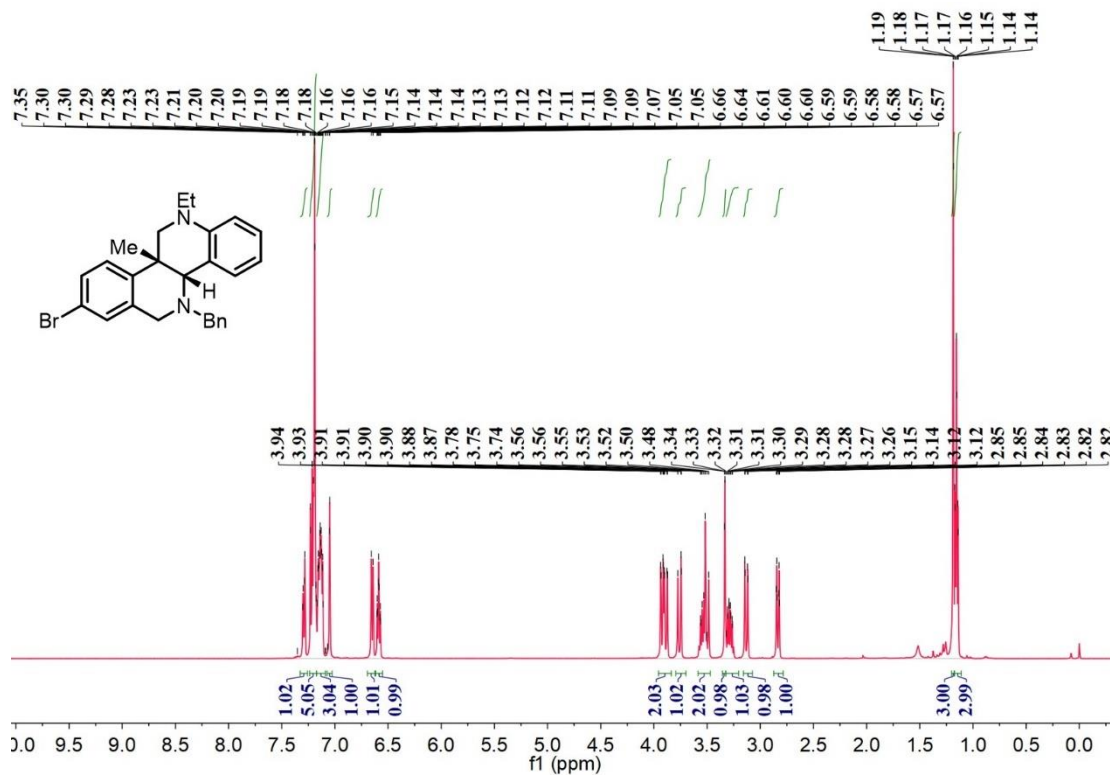
Supplementary Fig. 129 ¹H-NMR spectrum of P55



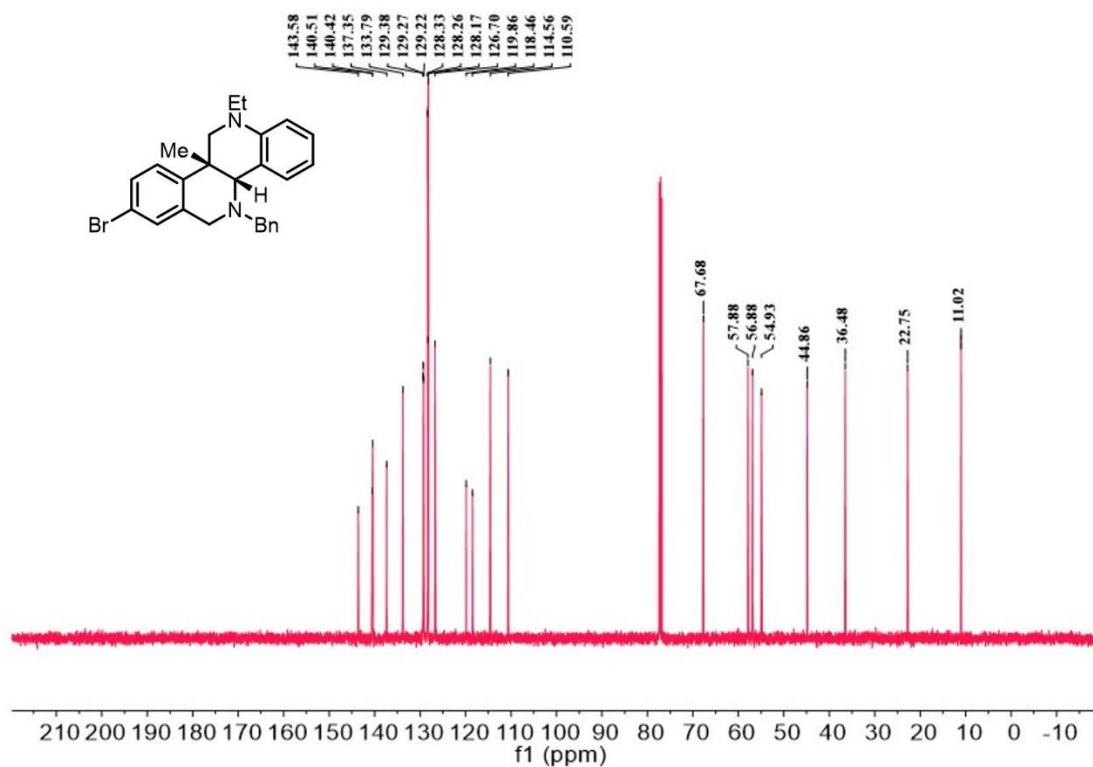
Supplementary Fig. 130 ¹³C-NMR spectrum of P55



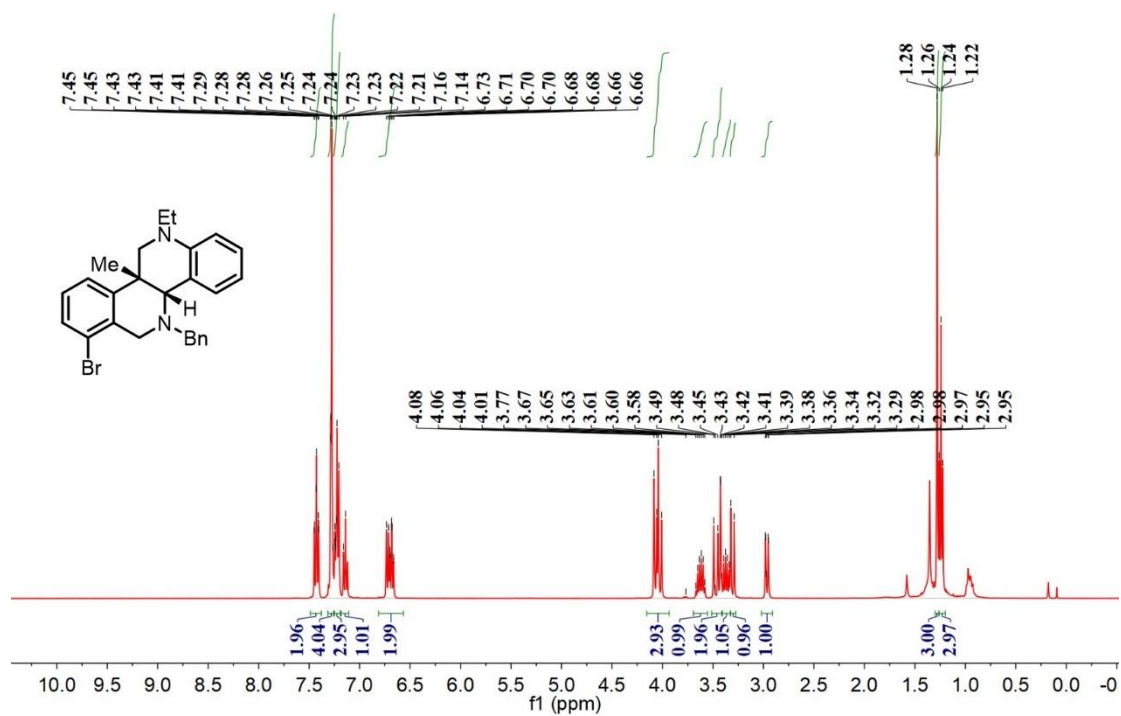
Supplementary Fig. 131 ¹⁹F-NMR spectrum of P55



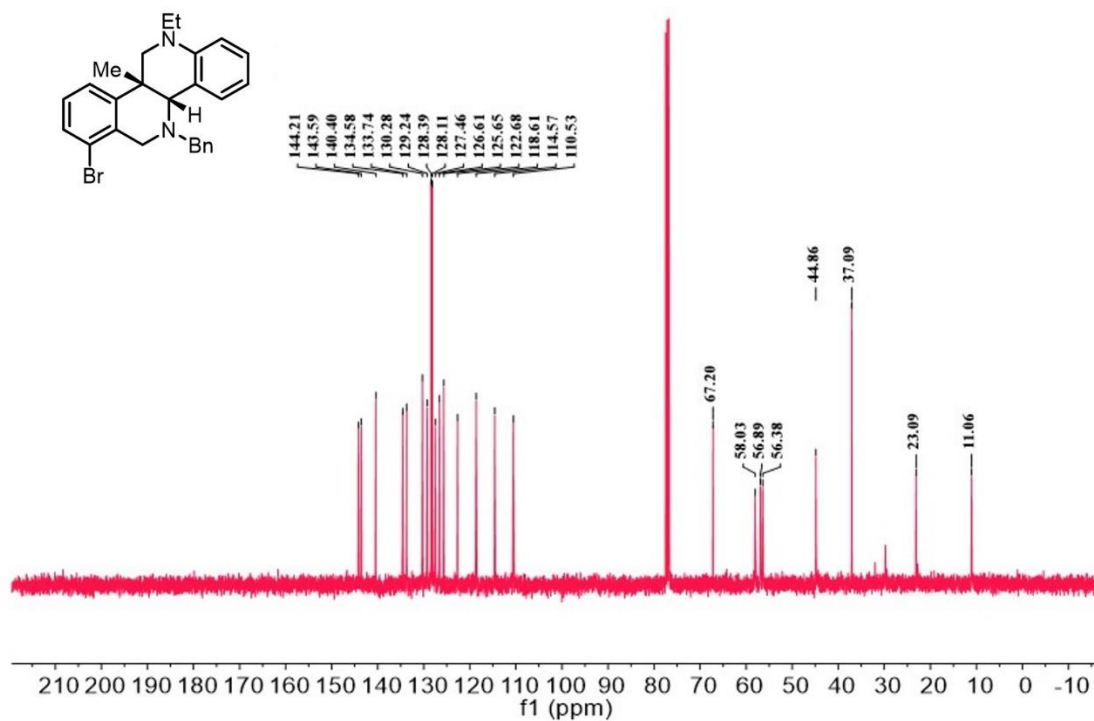
Supplementary Fig. 132 ¹H-NMR spectrum of P56



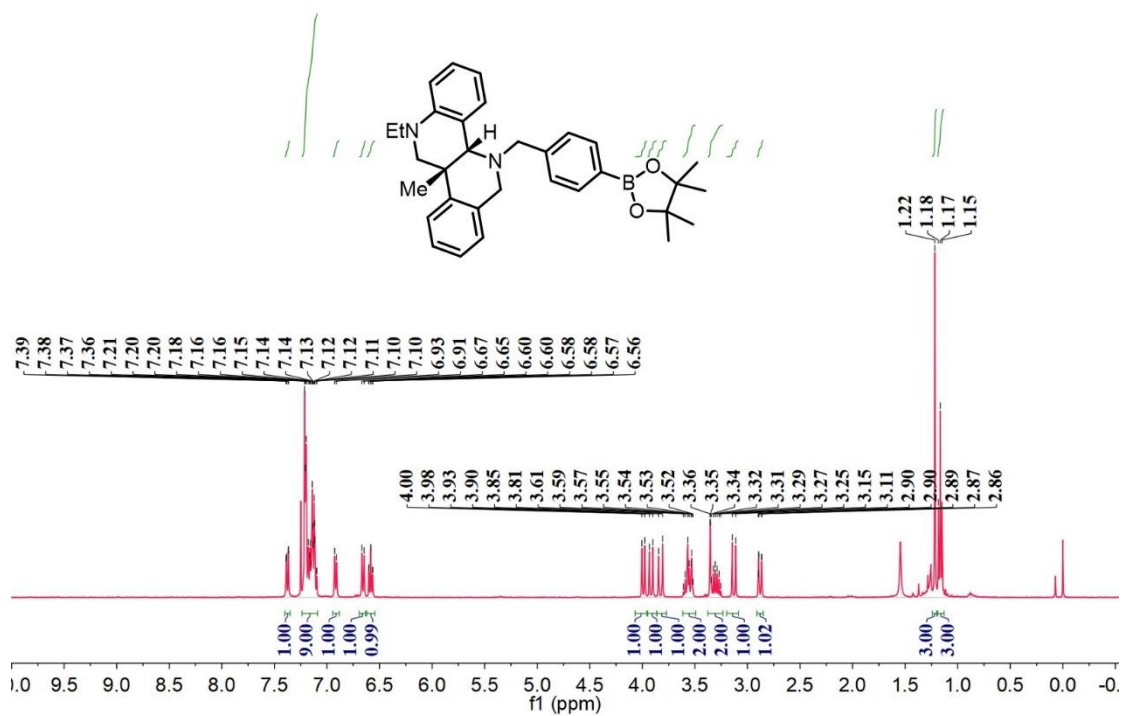
Supplementary Fig. 133 ¹³C-NMR spectrum of P56



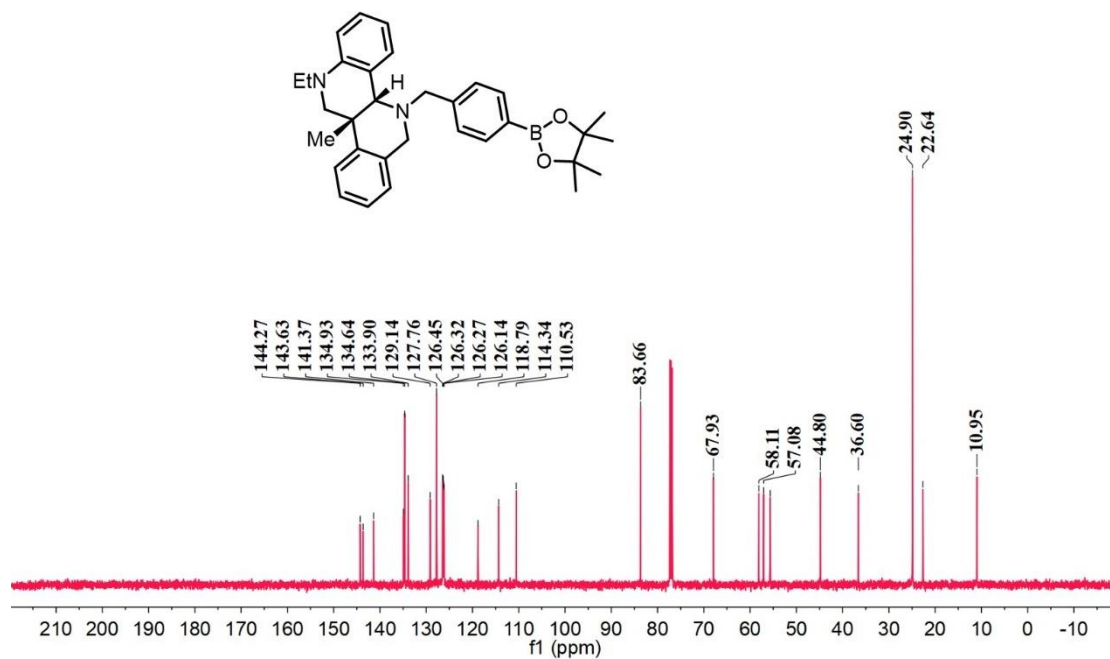
Supplementary Fig. 134 ¹H-NMR spectrum of P57



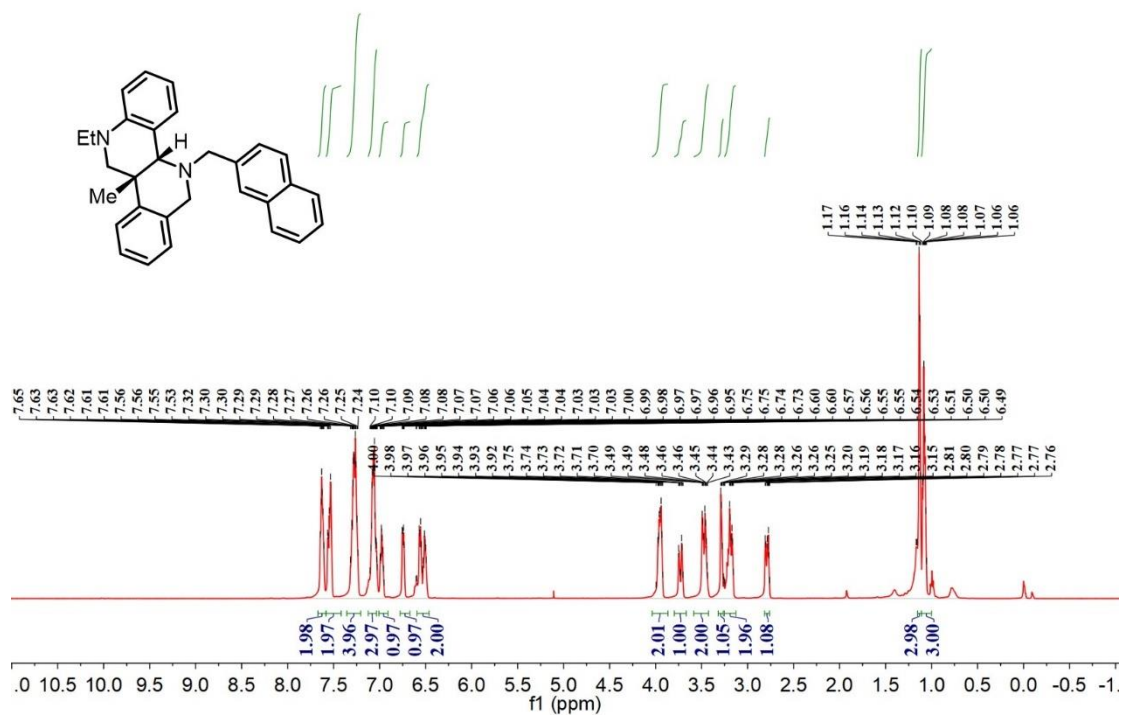
Supplementary Fig. 135 ¹³C-NMR spectrum of P57



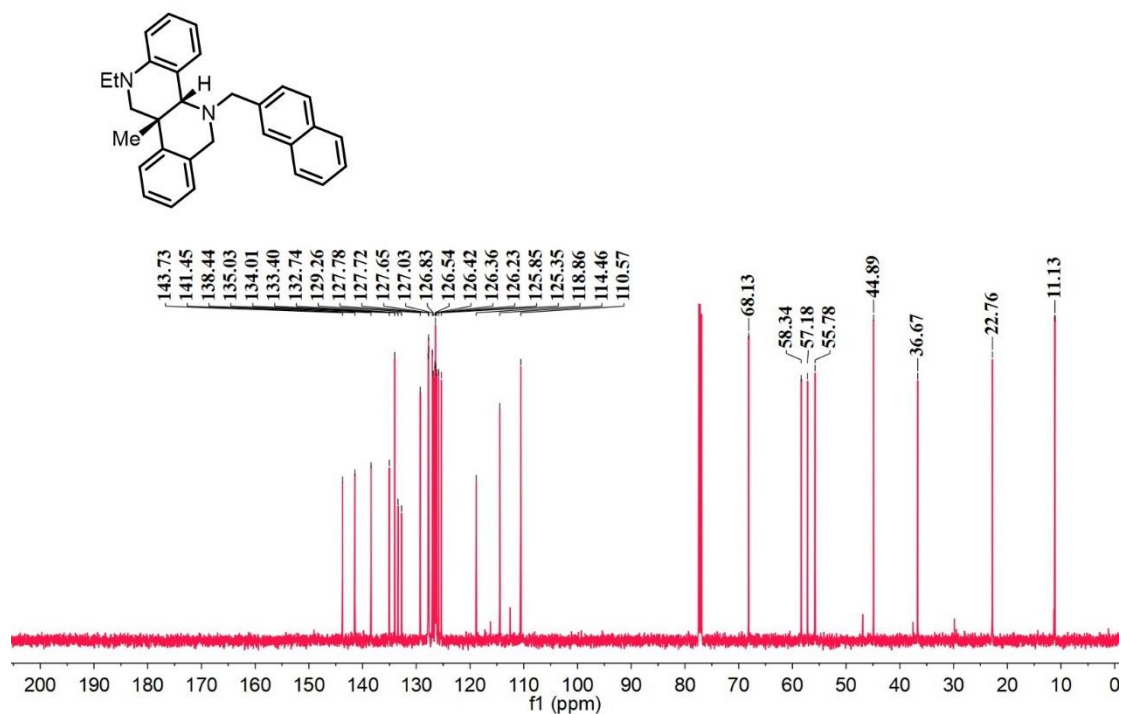
Supplementary Fig. 136 ¹H-NMR spectrum of P58



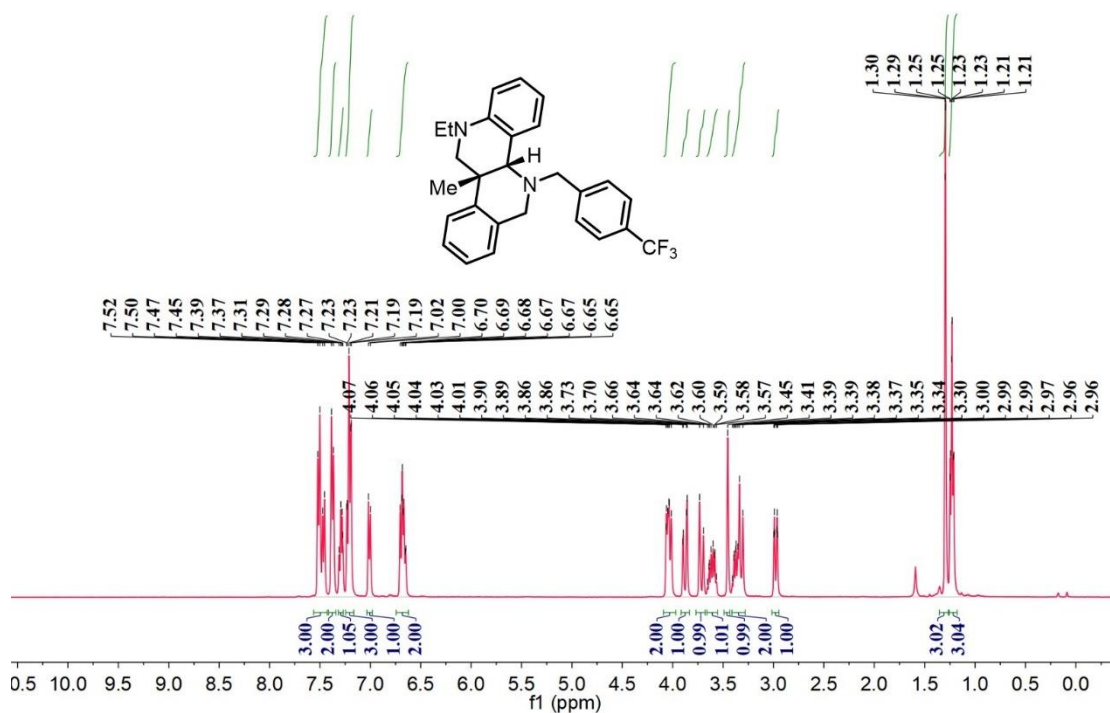
Supplementary Fig. 137 ¹³C-NMR spectrum of P58



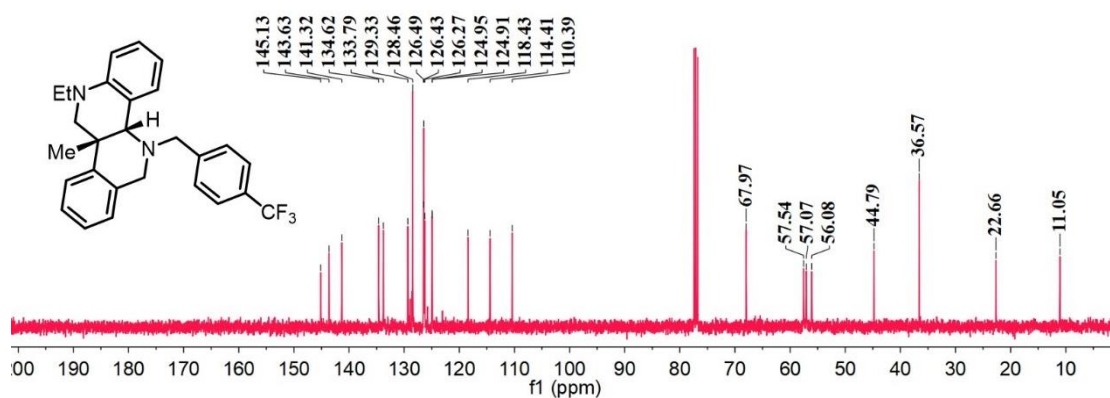
Supplementary Fig. 138 ¹H-NMR spectrum of P59



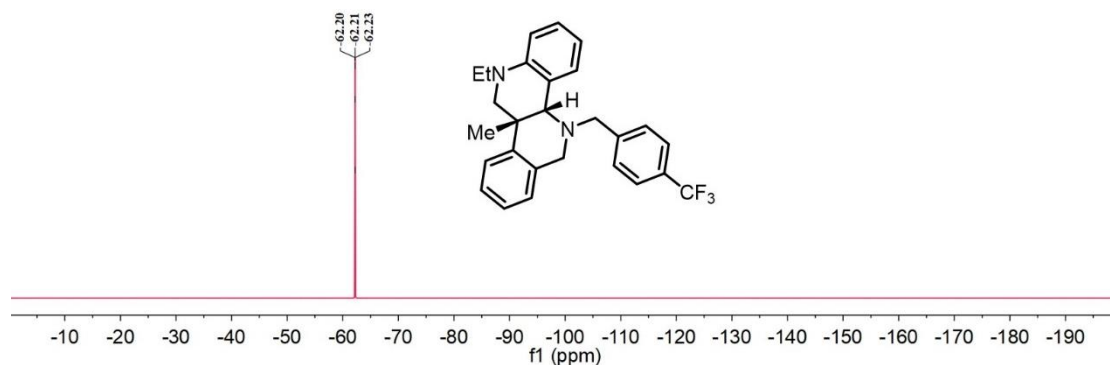
Supplementary Fig. 139 ¹³C-NMR spectrum of P59



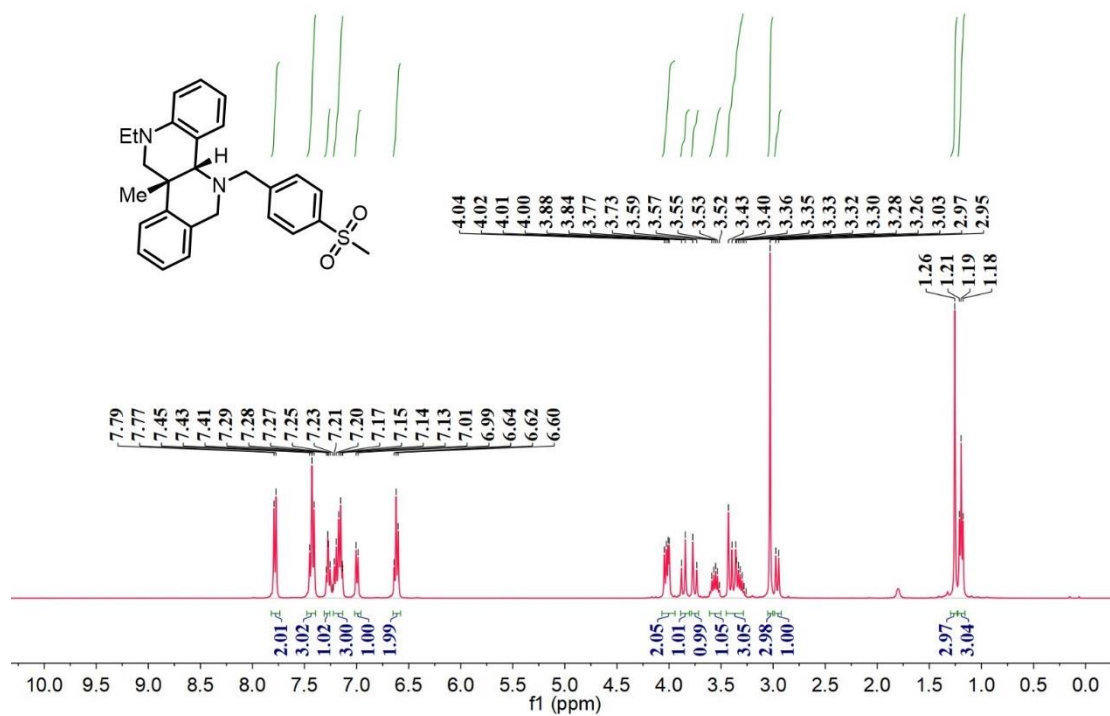
Supplementary Fig. 140 ¹H-NMR spectrum of P60



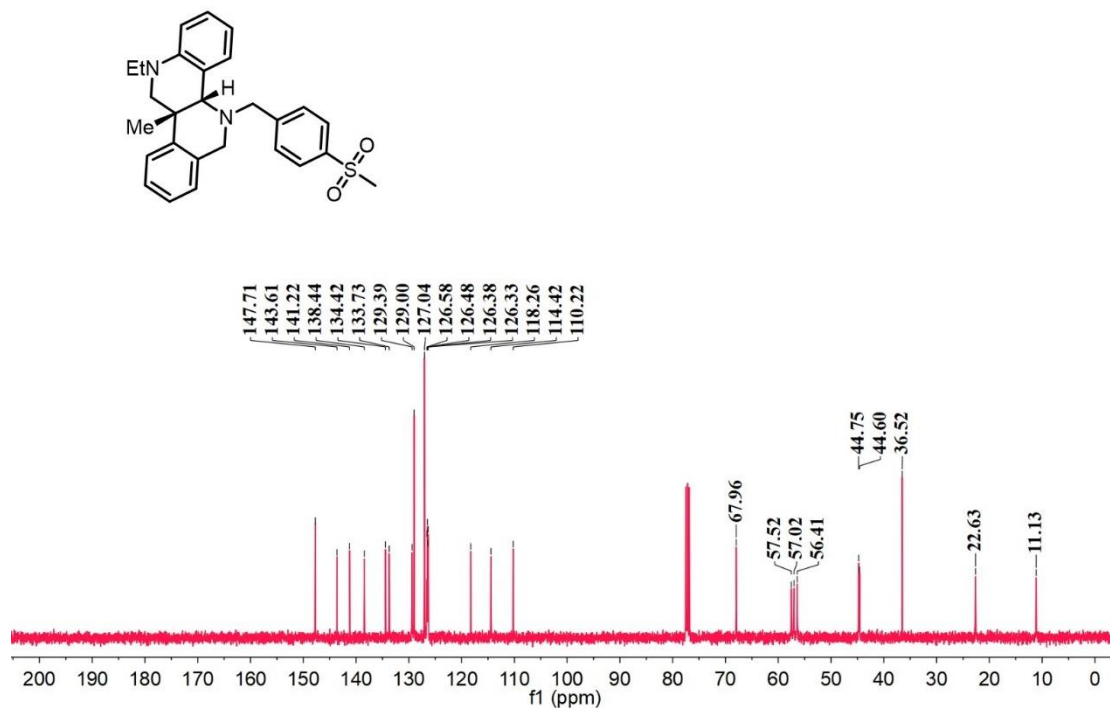
Supplementary Fig. 141 ¹³C-NMR spectrum of P60



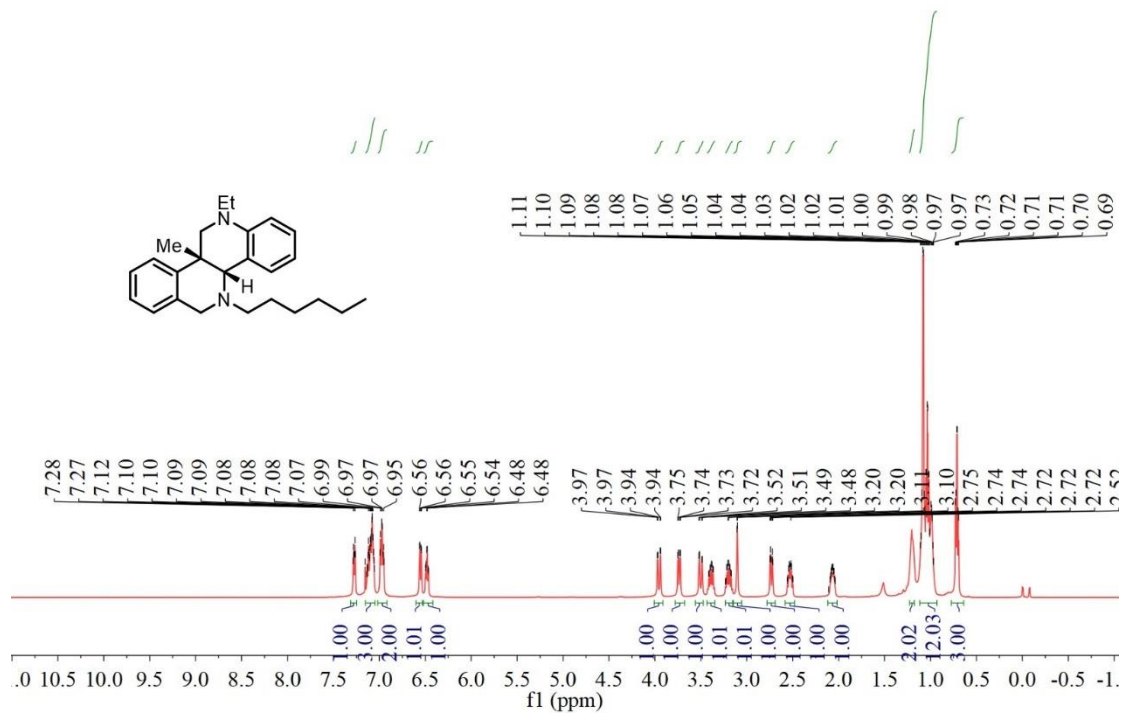
Supplementary Fig. 142 ¹⁹F-NMR spectrum of P60



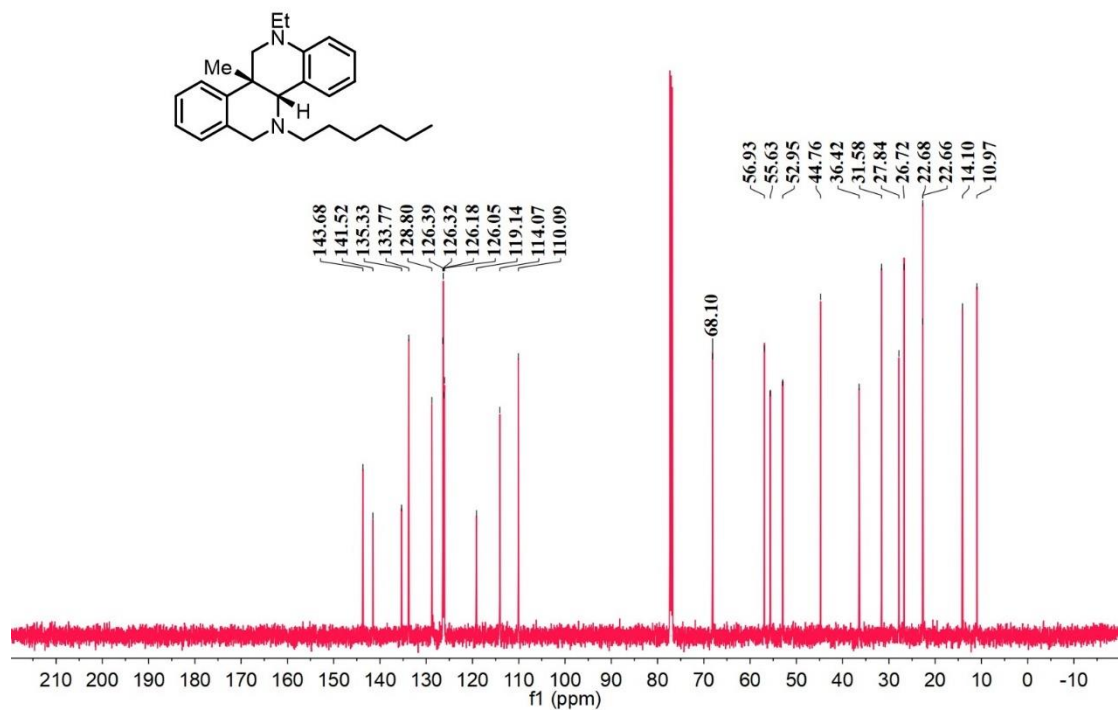
Supplementary Fig. 143 ¹H-NMR spectrum of P61



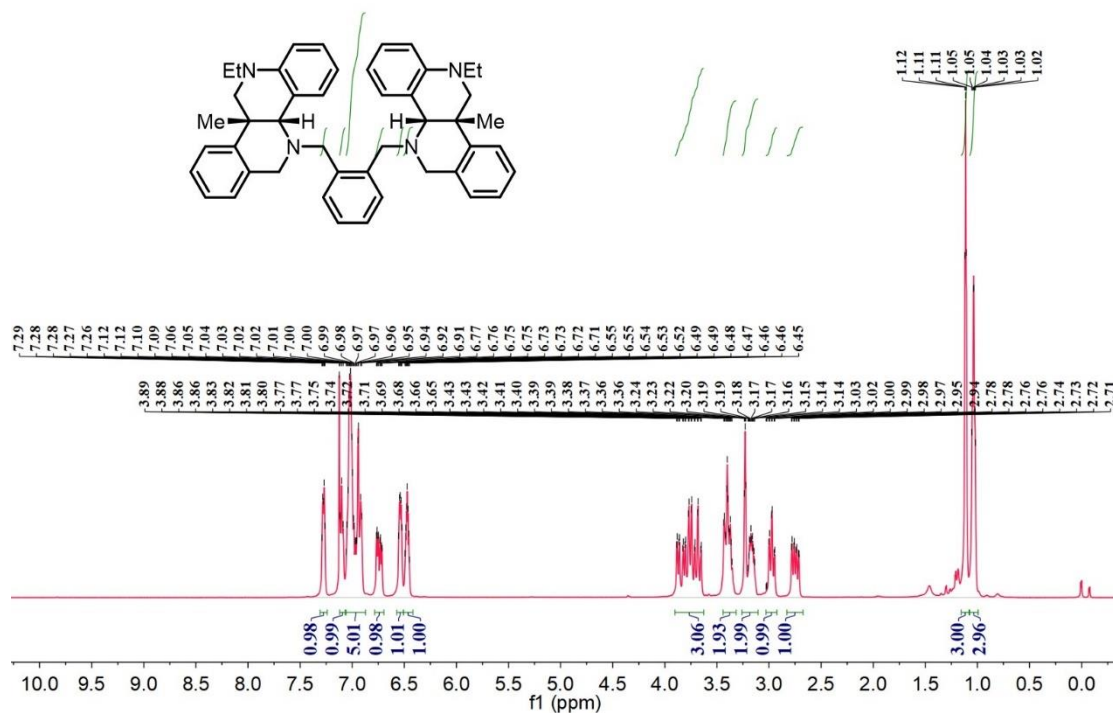
Supplementary Fig. 144 ¹³C-NMR spectrum of P61



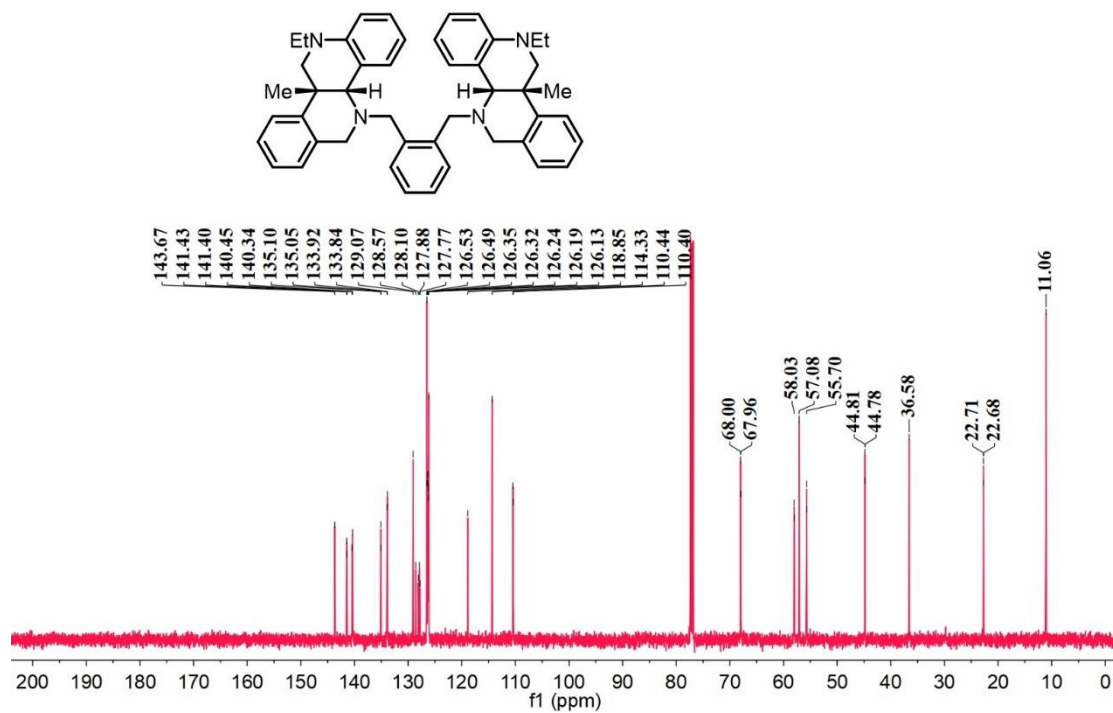
Supplementary Fig. 145 $^1\text{H-NMR}$ spectrum of P62



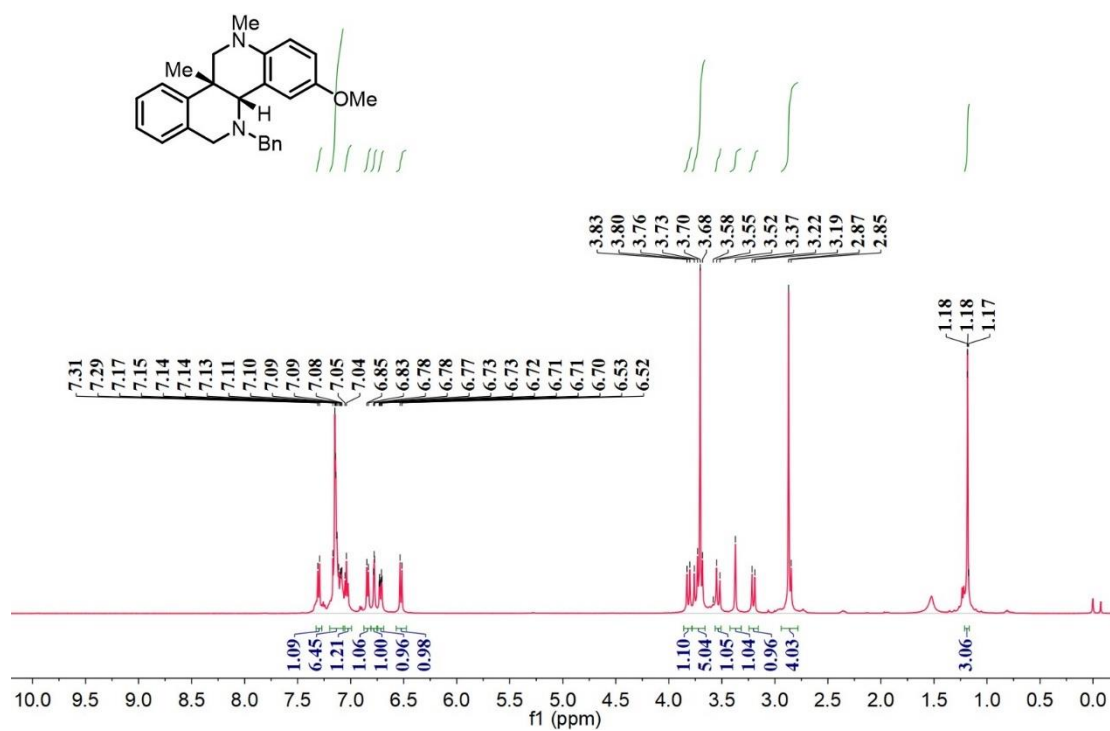
Supplementary Fig. 146 $^{13}\text{C-NMR}$ spectrum of P62



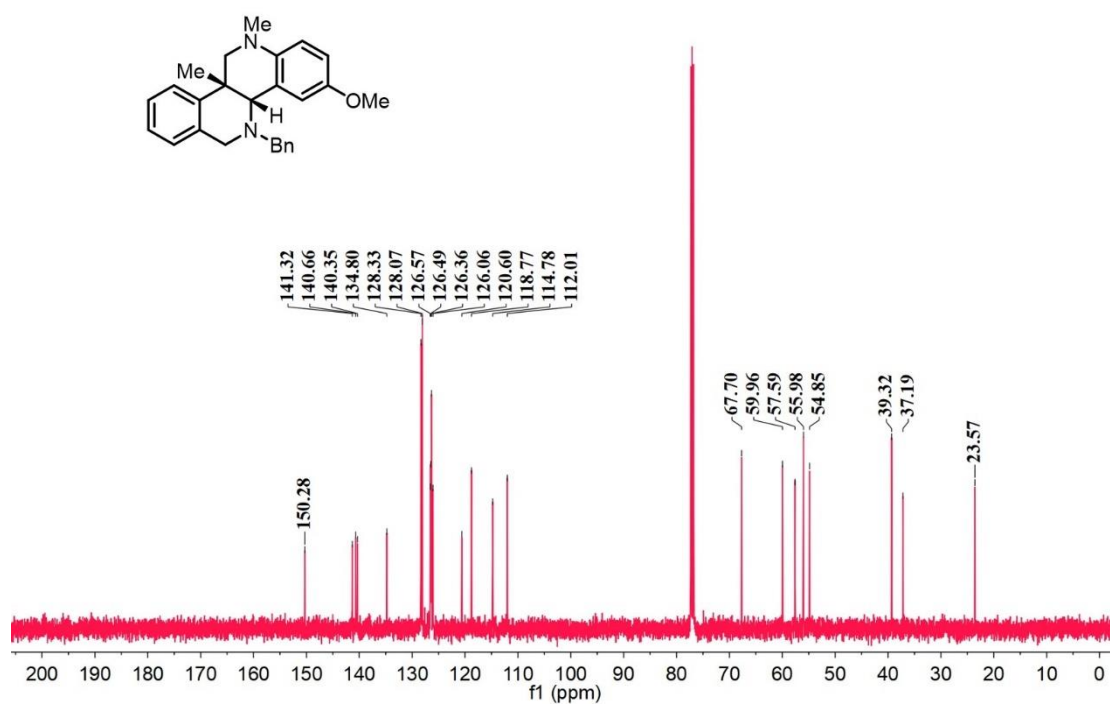
Supplementary Fig. 147 ¹H-NMR spectrum of P63



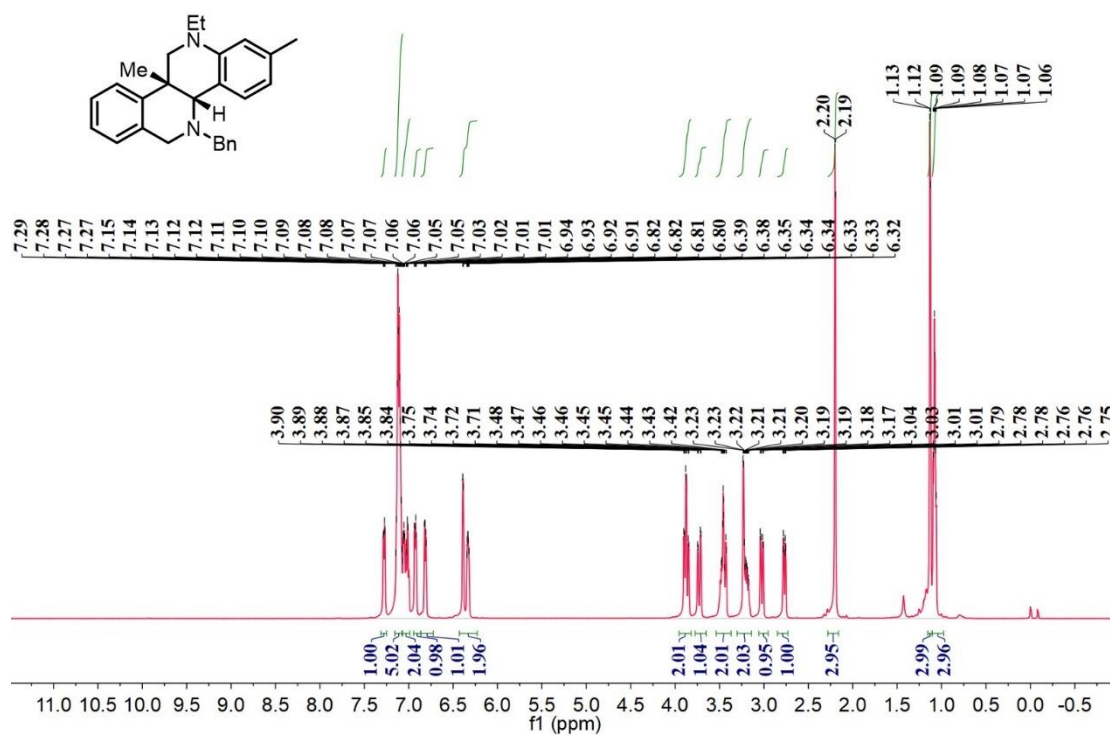
Supplementary Fig. 148 ¹³C-NMR spectrum of P63



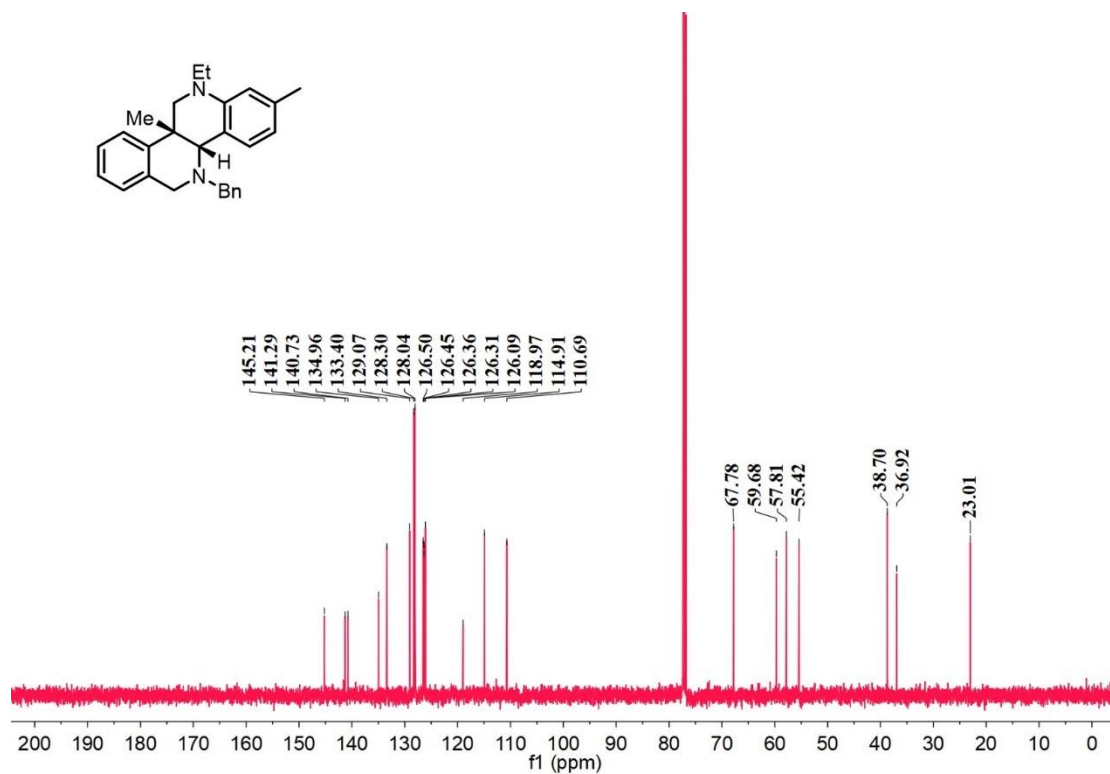
Supplementary Fig. 149 ¹H-NMR spectrum of P64



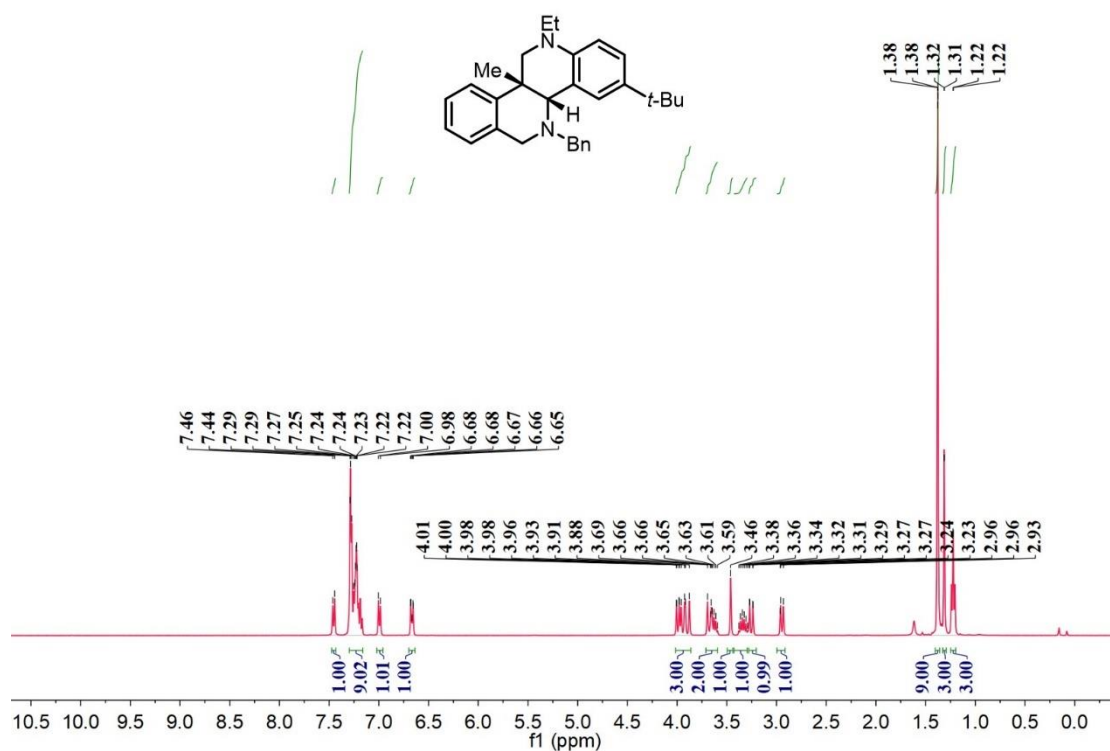
Supplementary Fig. 150 ¹³C-NMR spectrum of P64



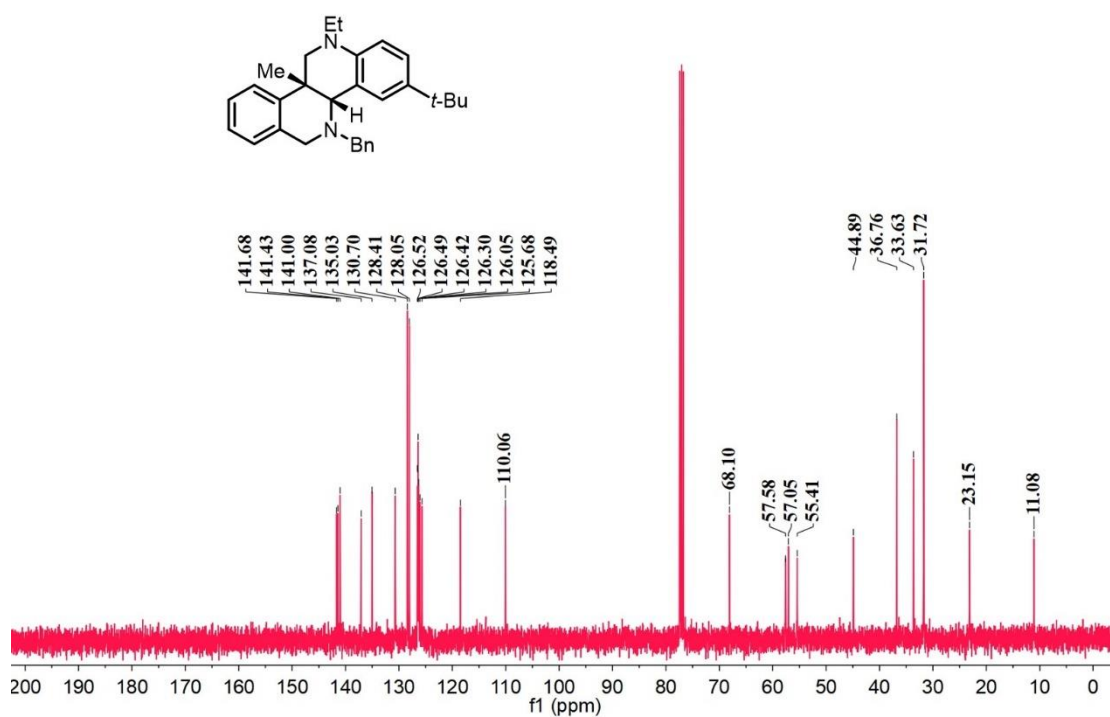
Supplementary Fig. 151 ¹H-NMR spectrum of P65



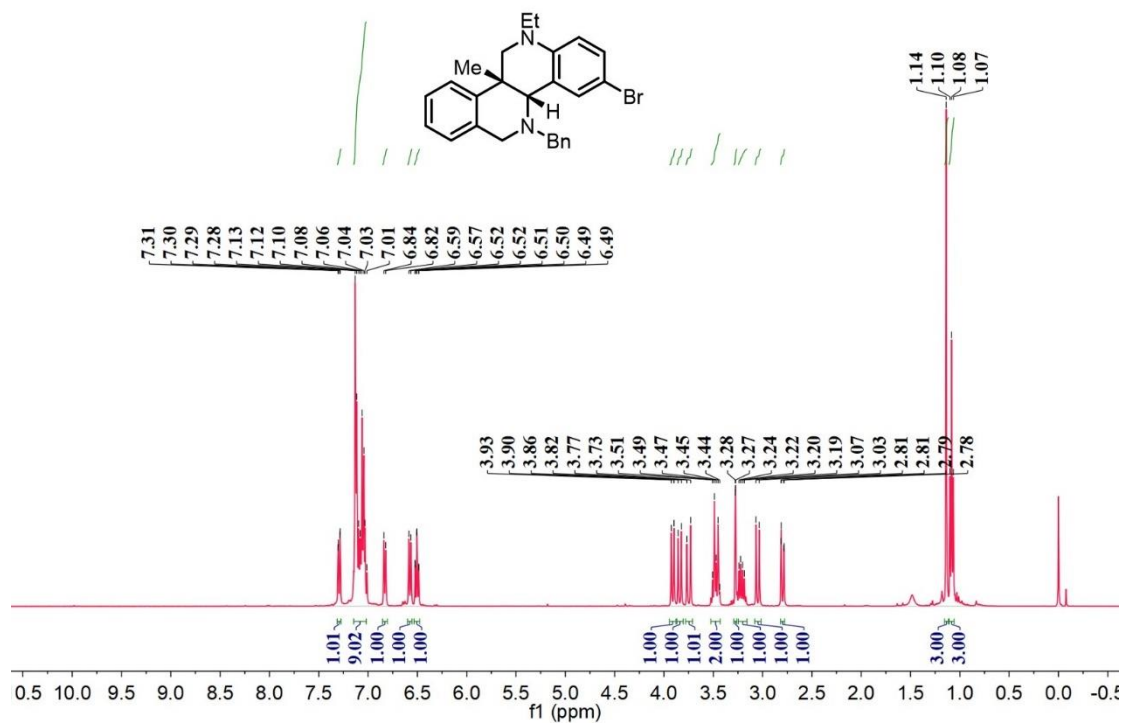
Supplementary Fig. 152 ¹³C-NMR spectrum of P65



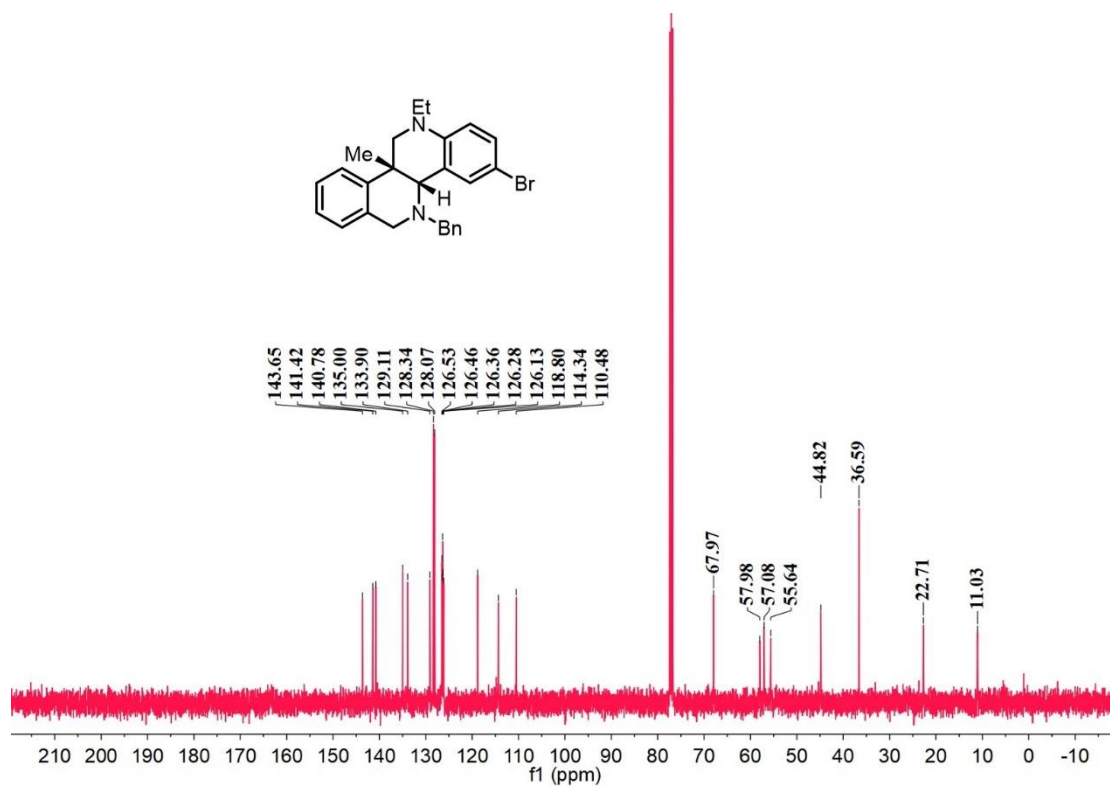
Supplementary Fig. 153 ¹H-NMR spectrum of P66



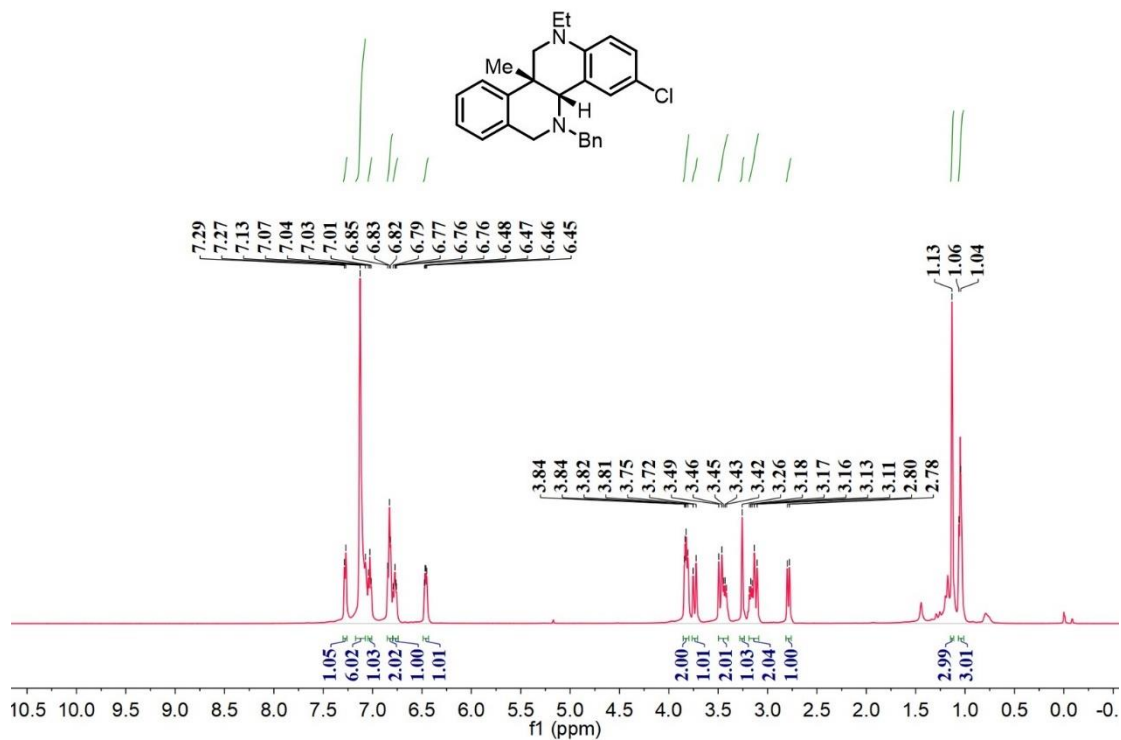
Supplementary Fig. 154 ¹³C-NMR spectrum of P66



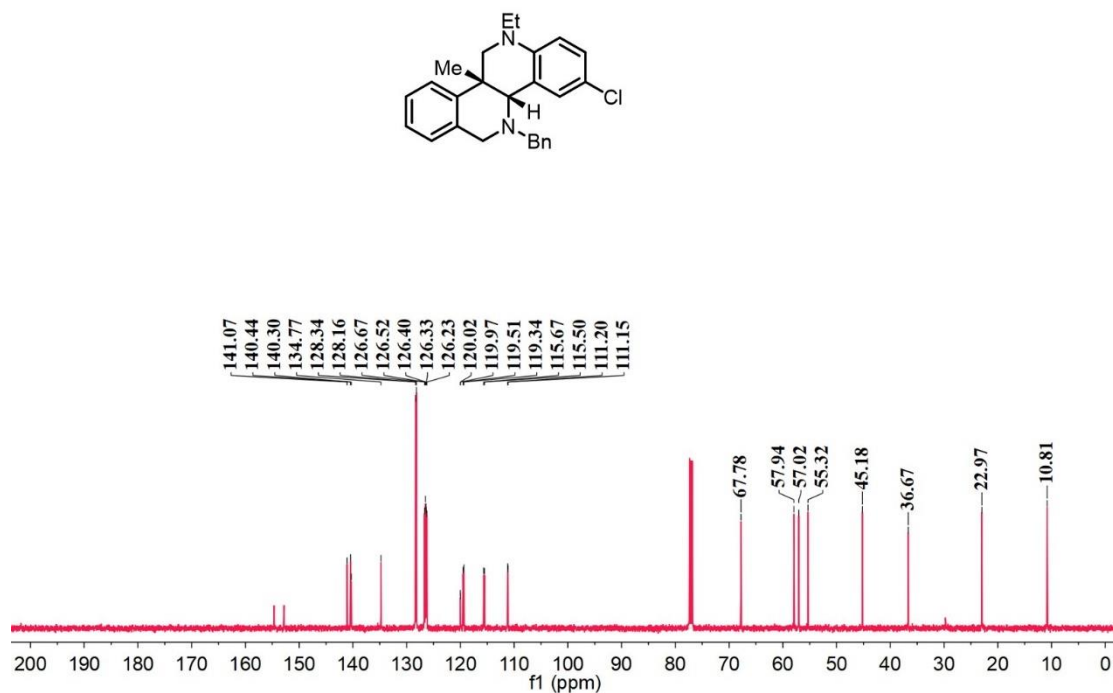
Supplementary Fig. 155 ¹H-NMR spectrum of P67



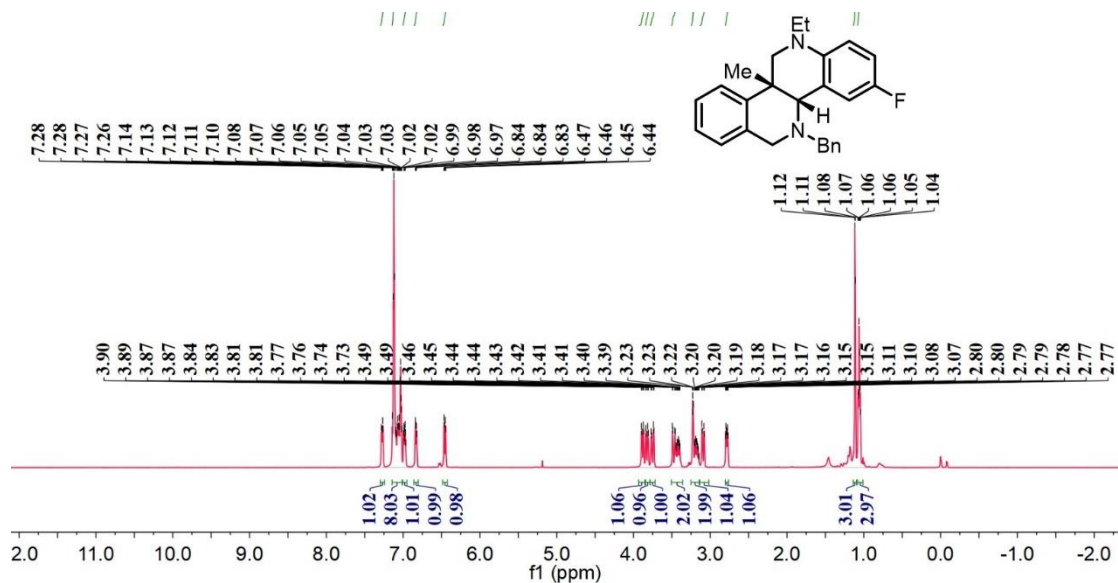
Supplementary Fig. 156 ¹³C-NMR spectrum of P67



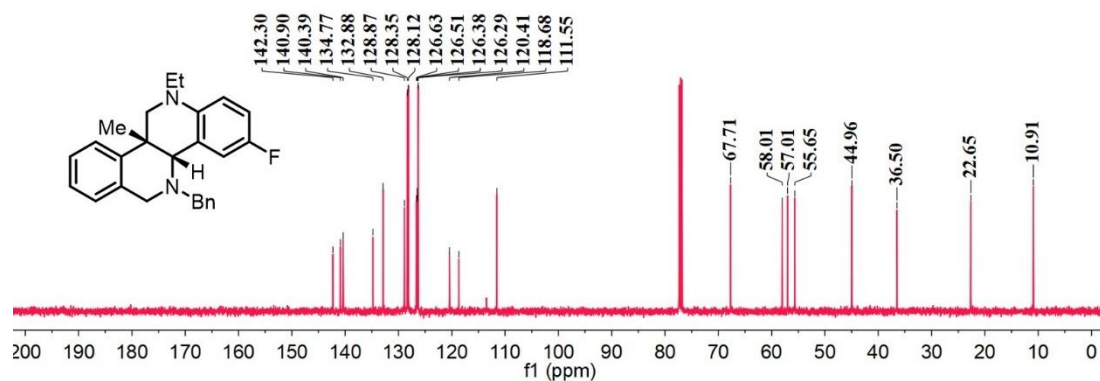
Supplementary Fig. 157 ¹H-NMR spectrum of P68



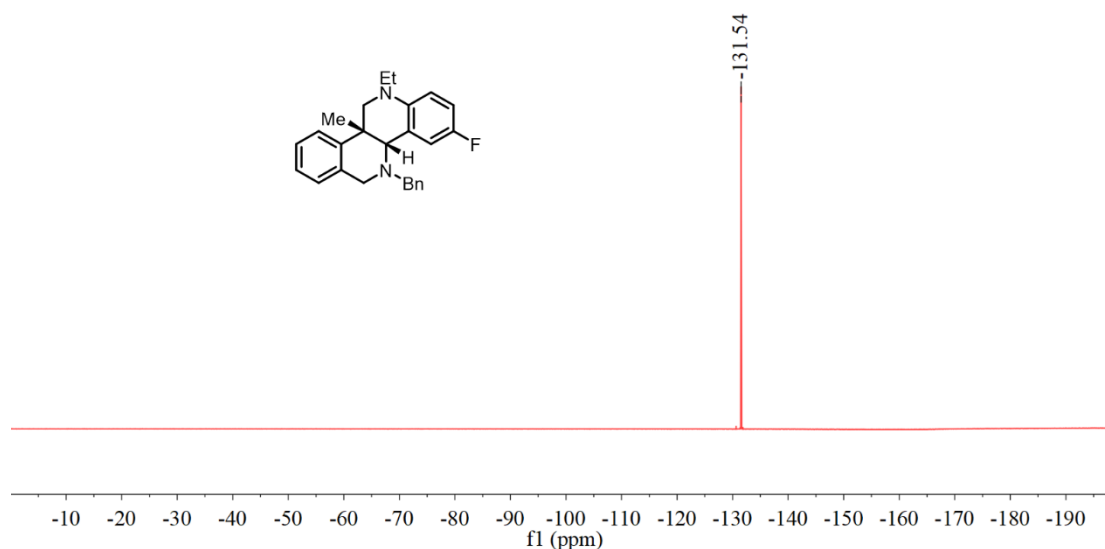
Supplementary Fig. 158 ¹³C-NMR spectrum of P68



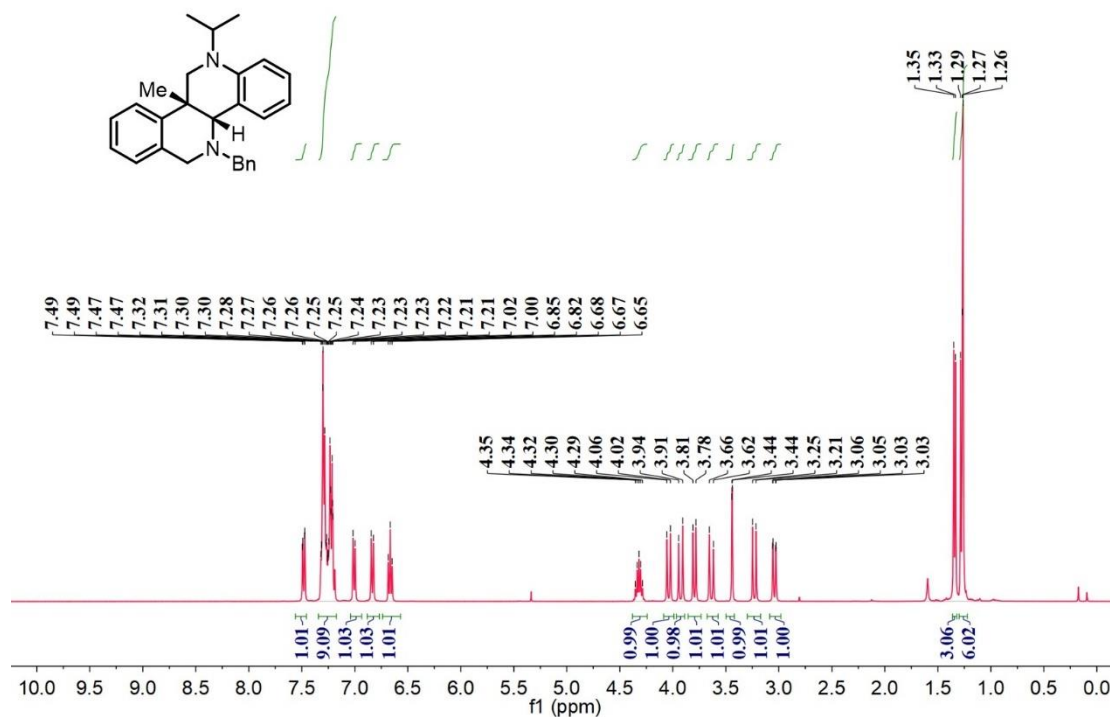
Supplementary Fig. 159 $^1\text{H-NMR}$ spectrum of P69



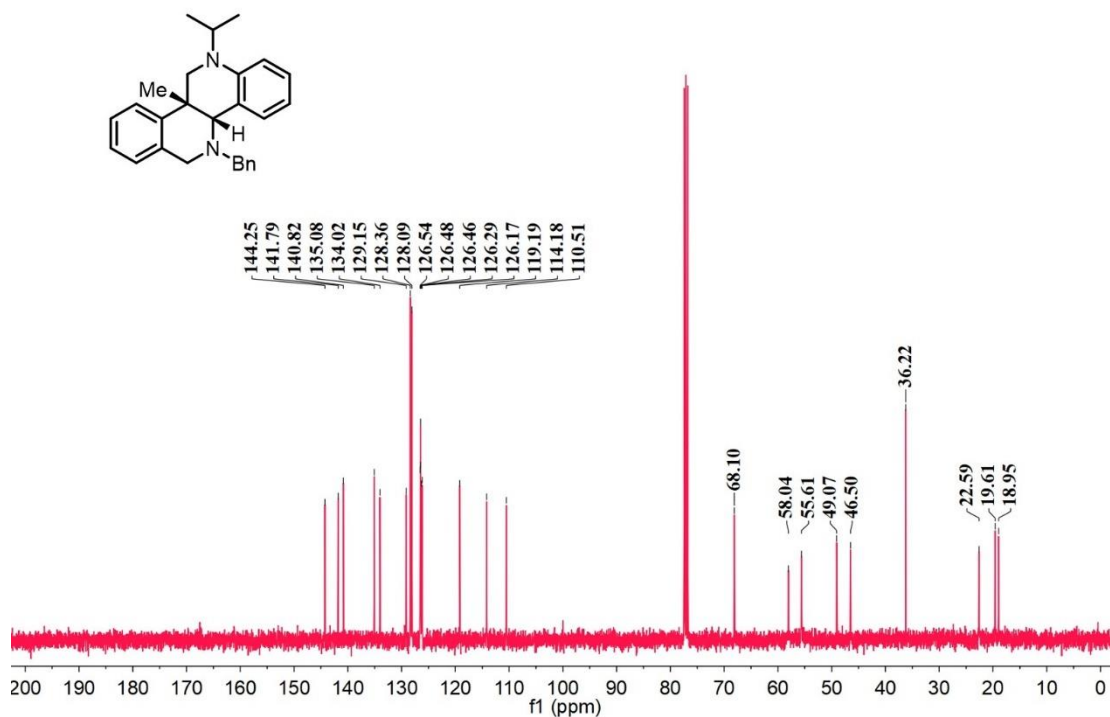
Supplementary Fig. 160 $^{13}\text{C-NMR}$ spectrum of P69



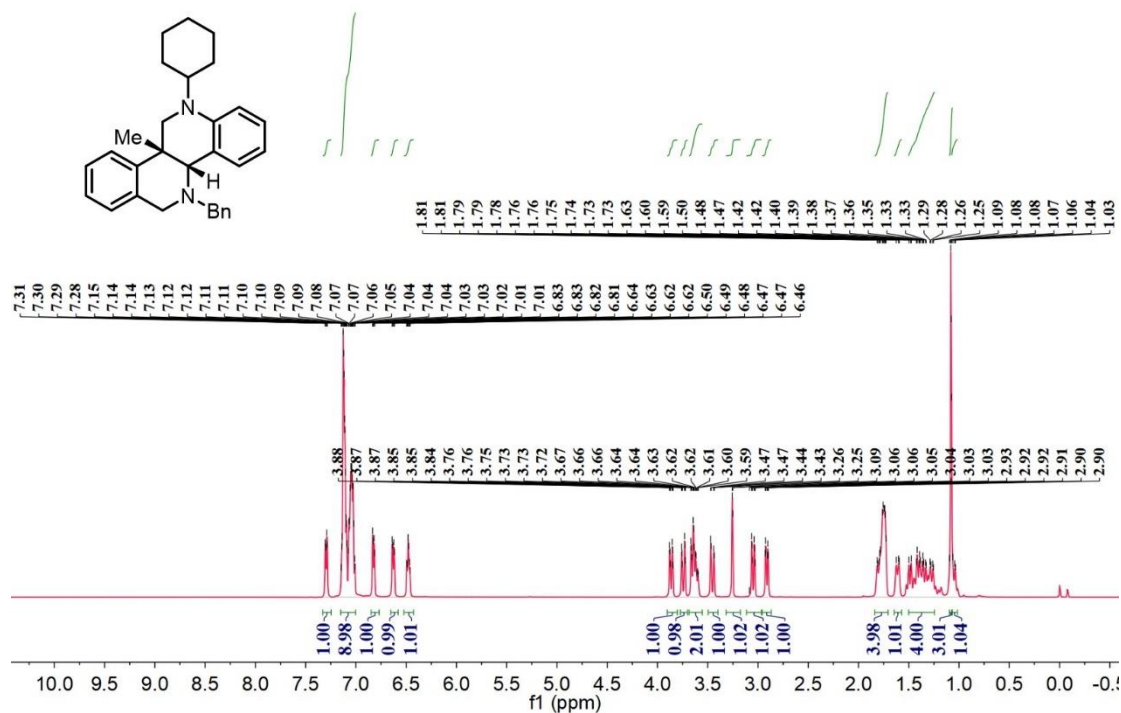
Supplementary Fig. 161 $^{19}\text{F-NMR}$ spectrum of P69



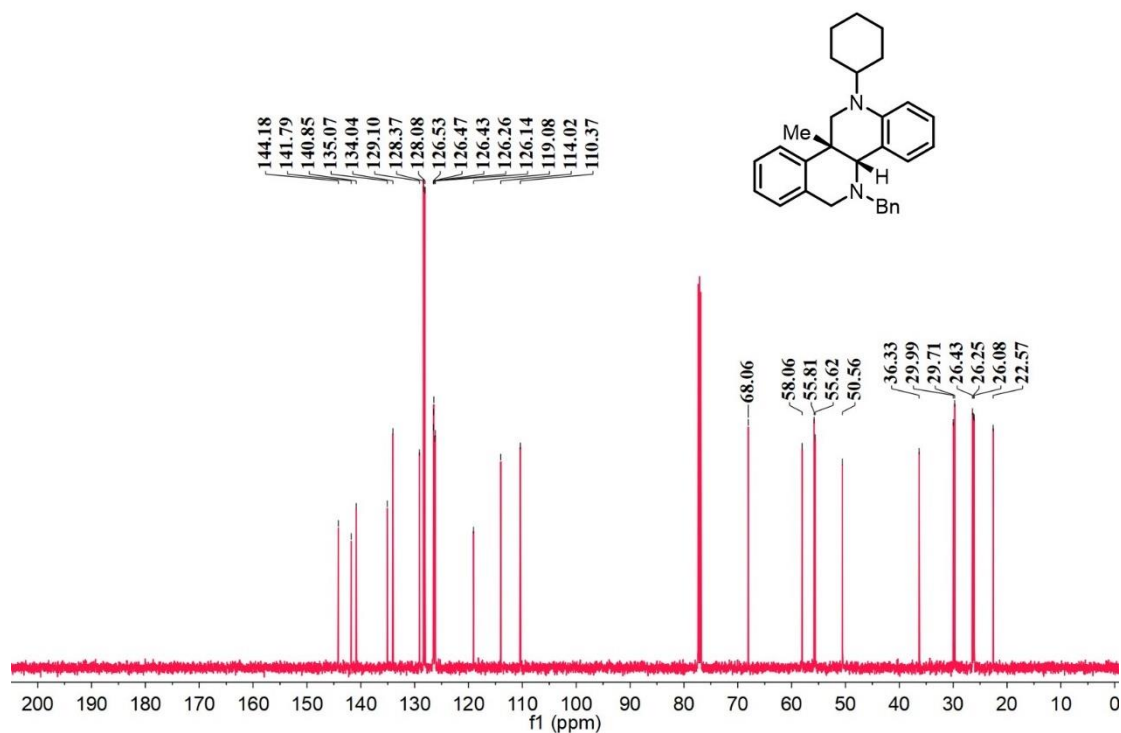
Supplementary Fig. 162 ¹H-NMR spectrum of P70



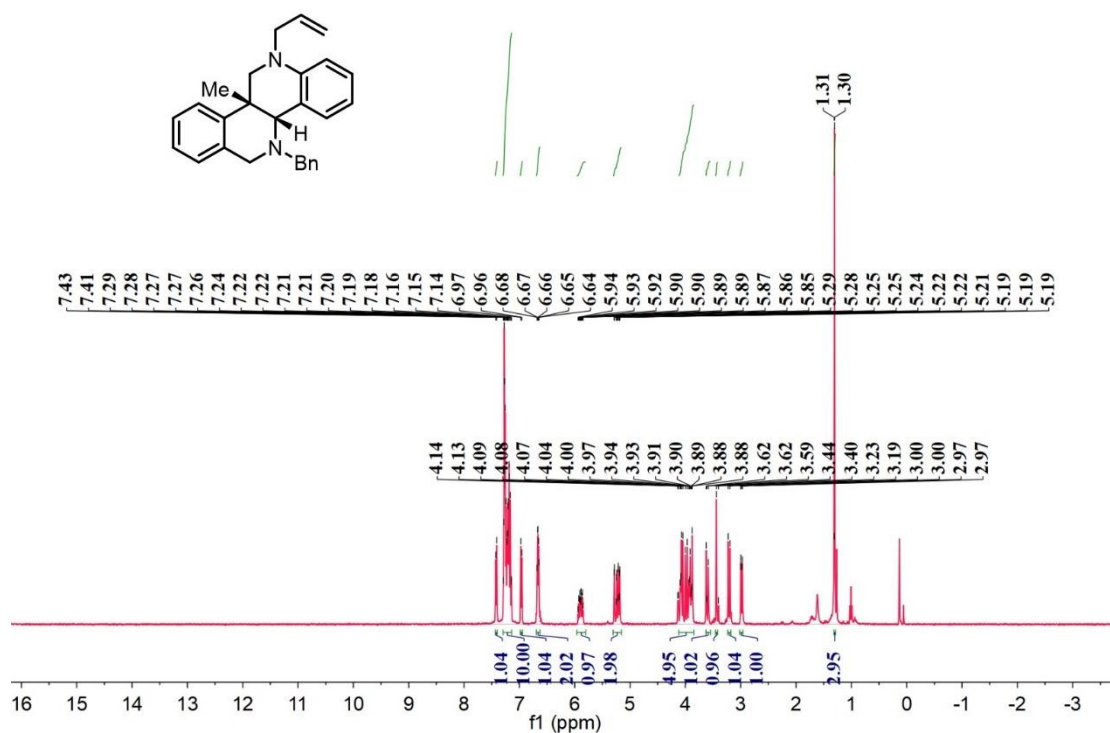
Supplementary Fig. 163 ¹³C-NMR spectrum of P70



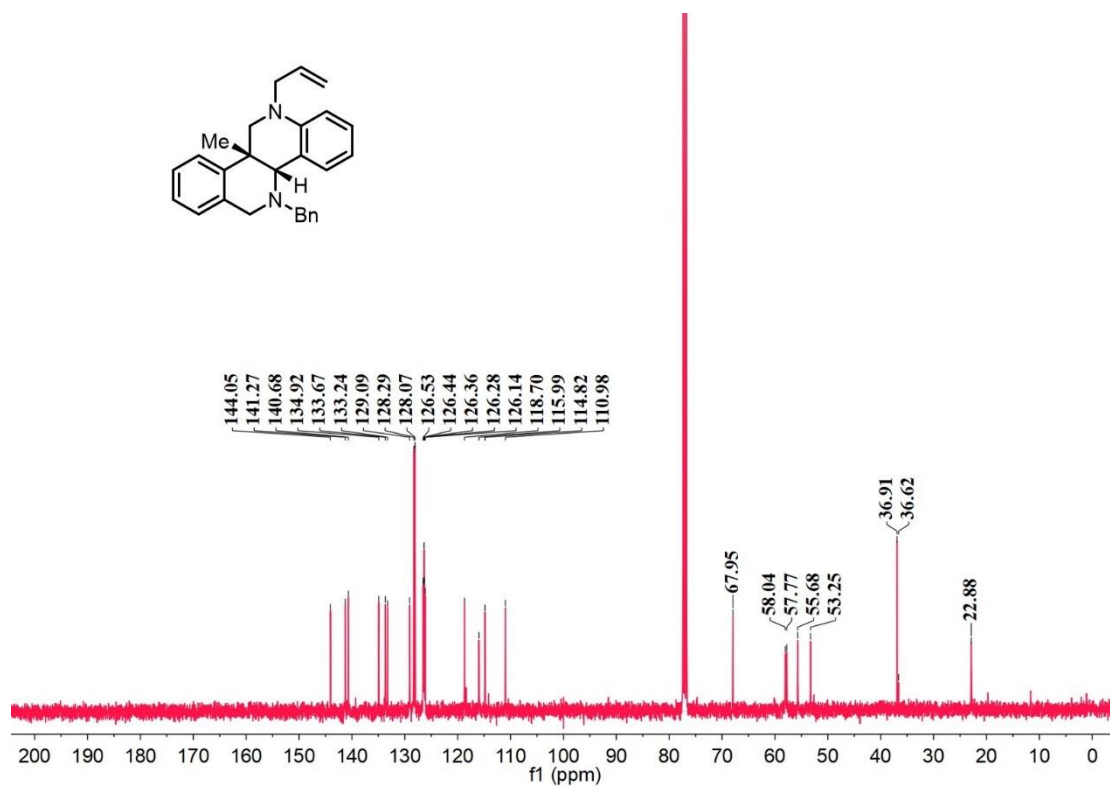
Supplementary Fig. 164 ¹H-NMR spectrum of P71



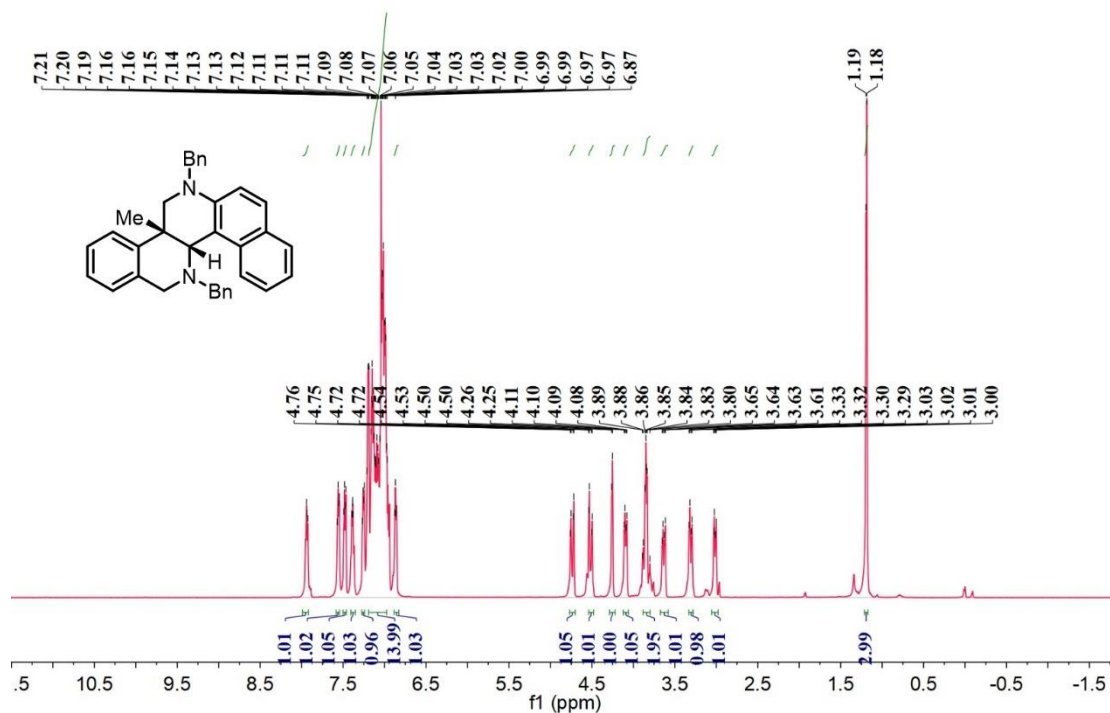
Supplementary Fig. 165 ¹³C-NMR spectrum of P71



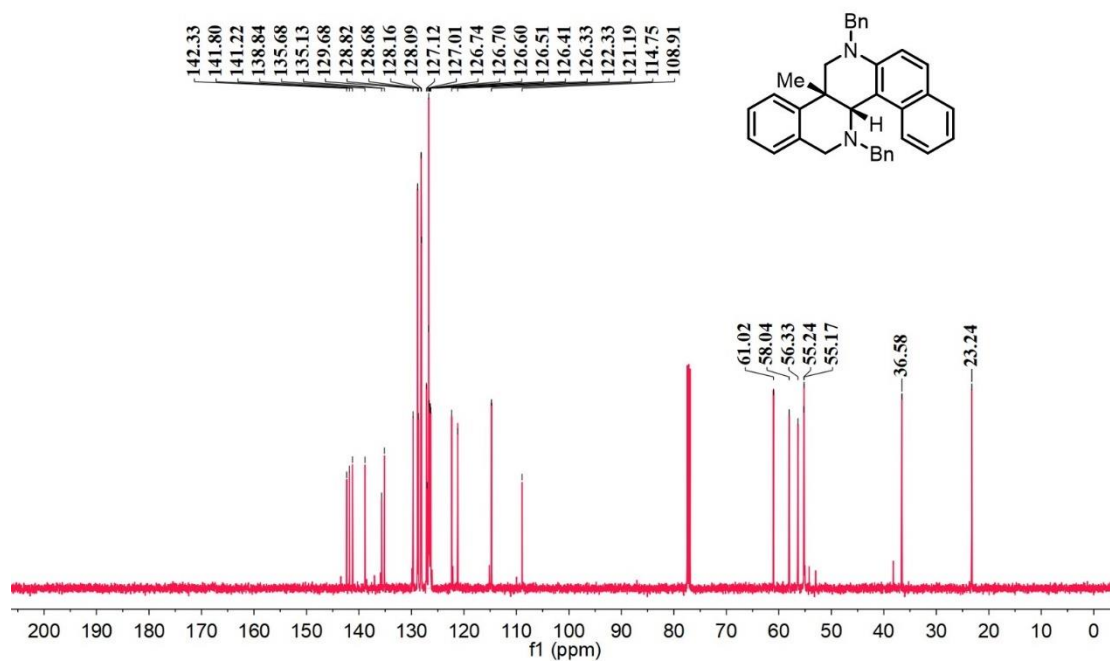
Supplementary Fig. 166 ¹H-NMR spectrum of P72



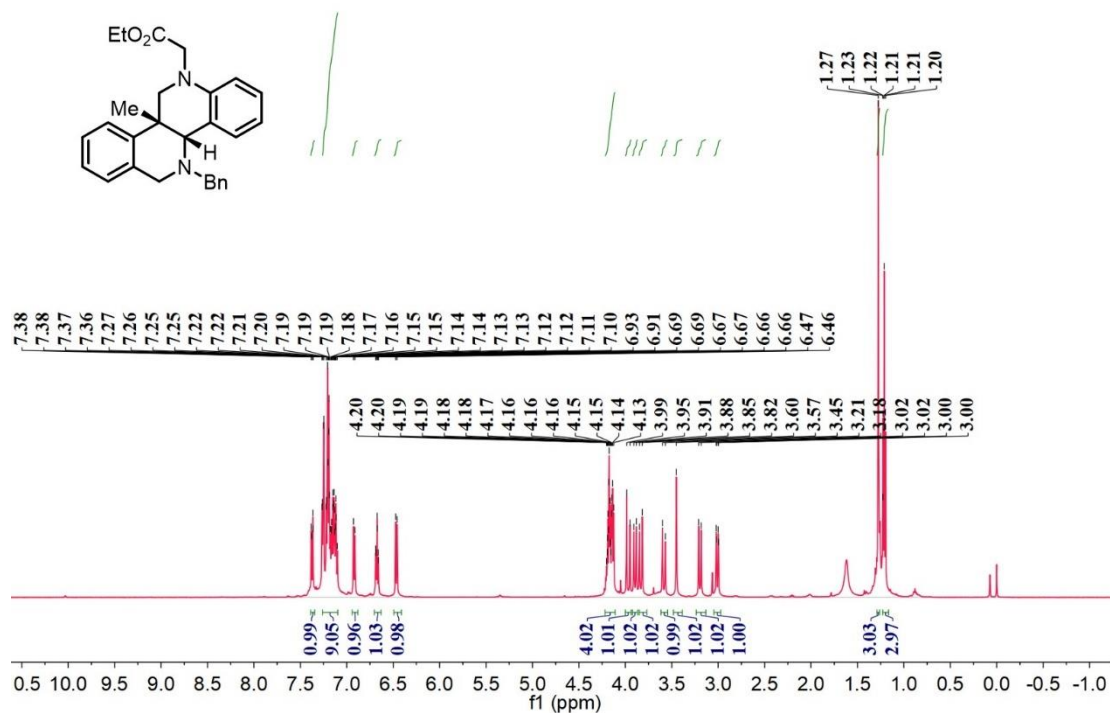
Supplementary Fig. 167 ¹³C-NMR spectrum of P72



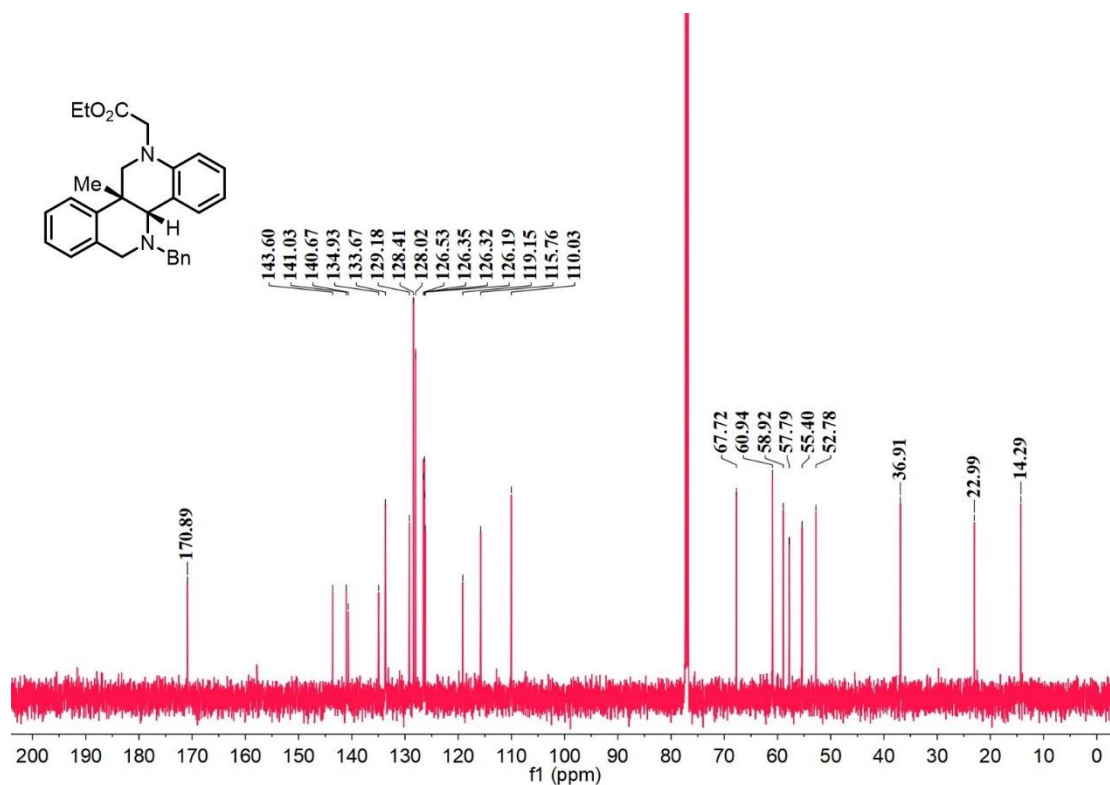
Supplementary Fig. 168 ¹H-NMR spectrum of P73



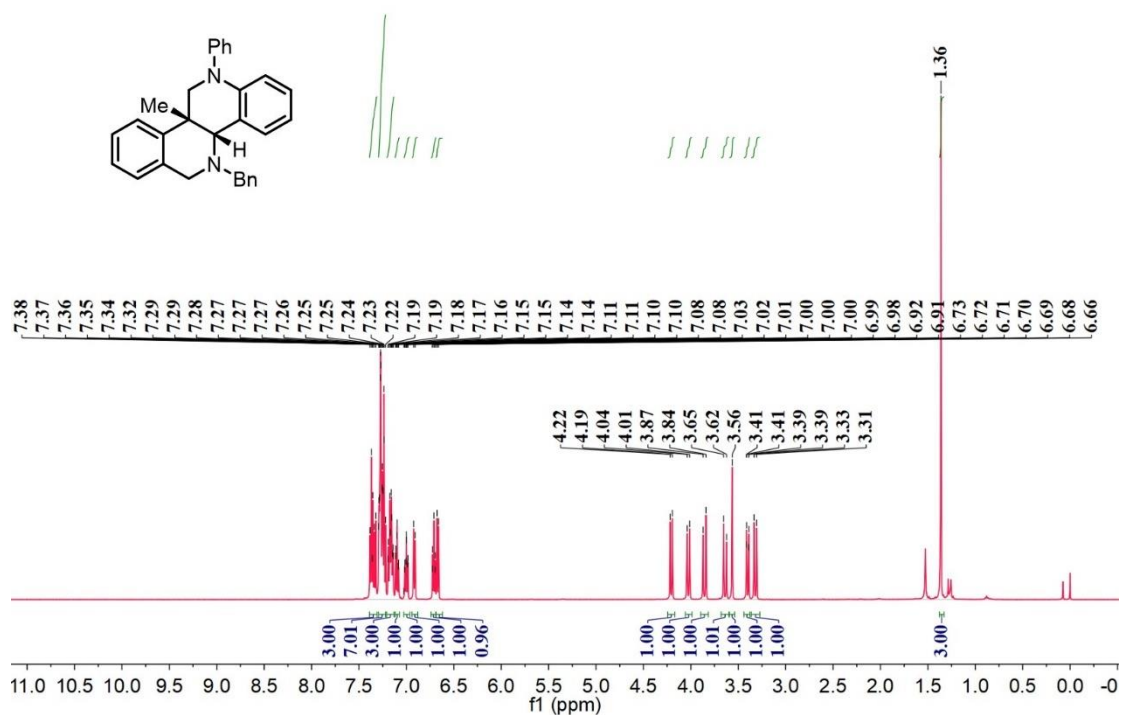
Supplementary Fig. 169 ¹³C-NMR spectrum of P73



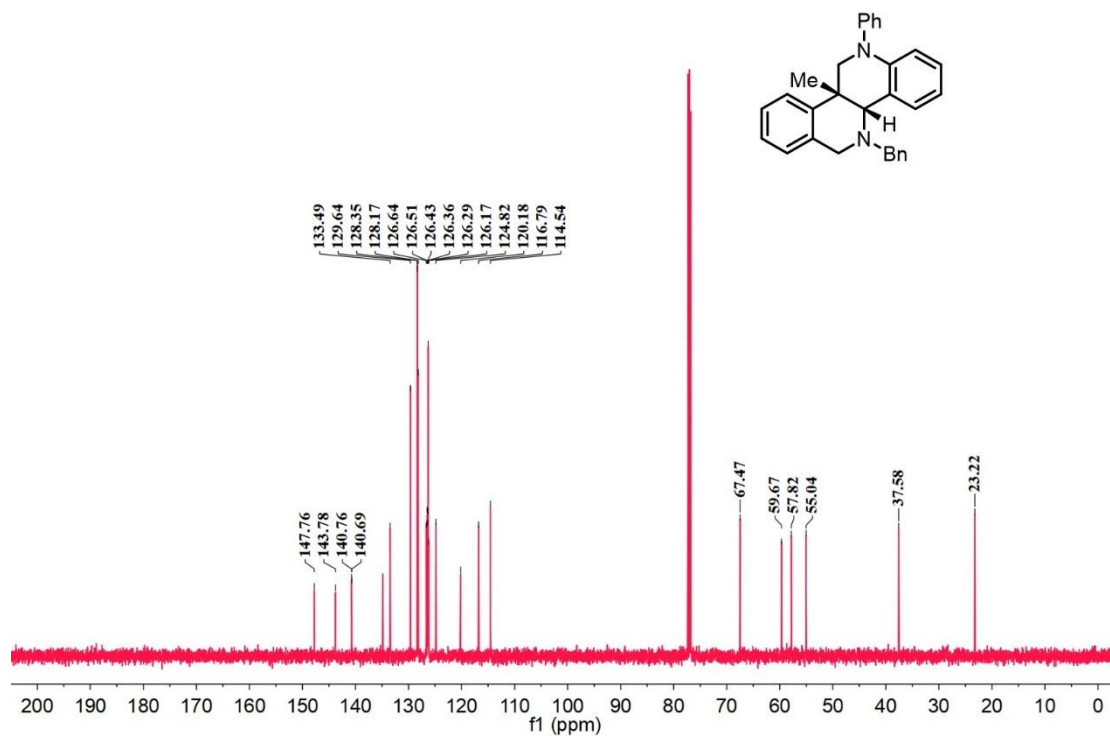
Supplementary Fig. 170 ¹H-NMR spectrum of P74



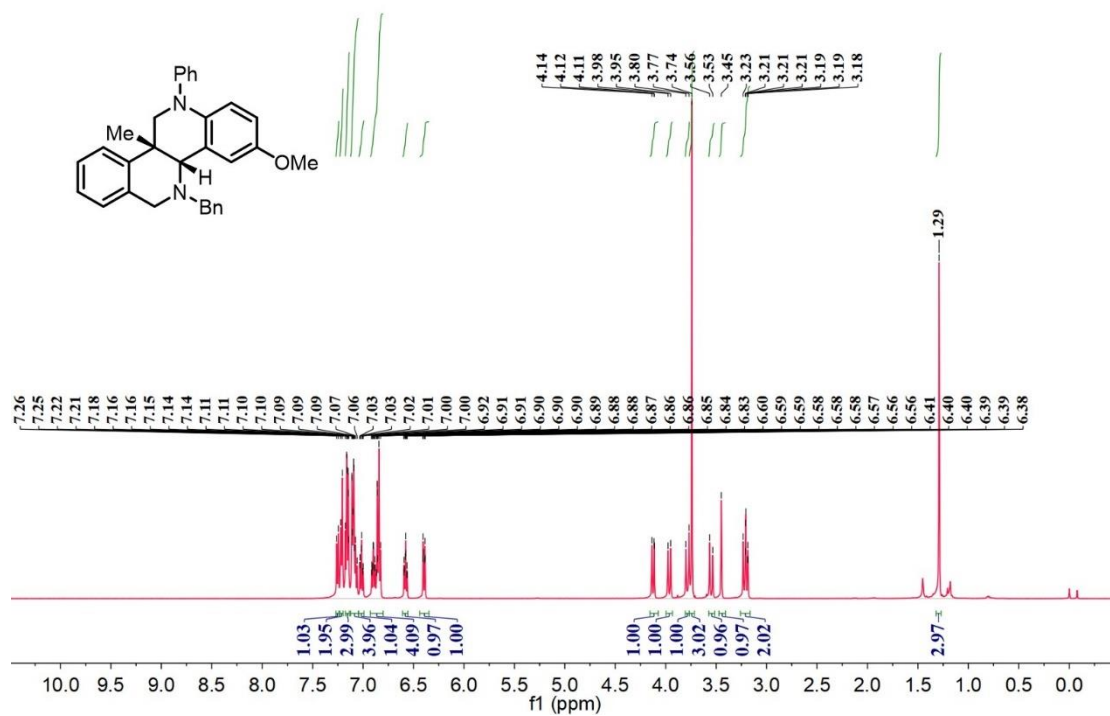
Supplementary Fig. 171 ¹³C-NMR spectrum of P74



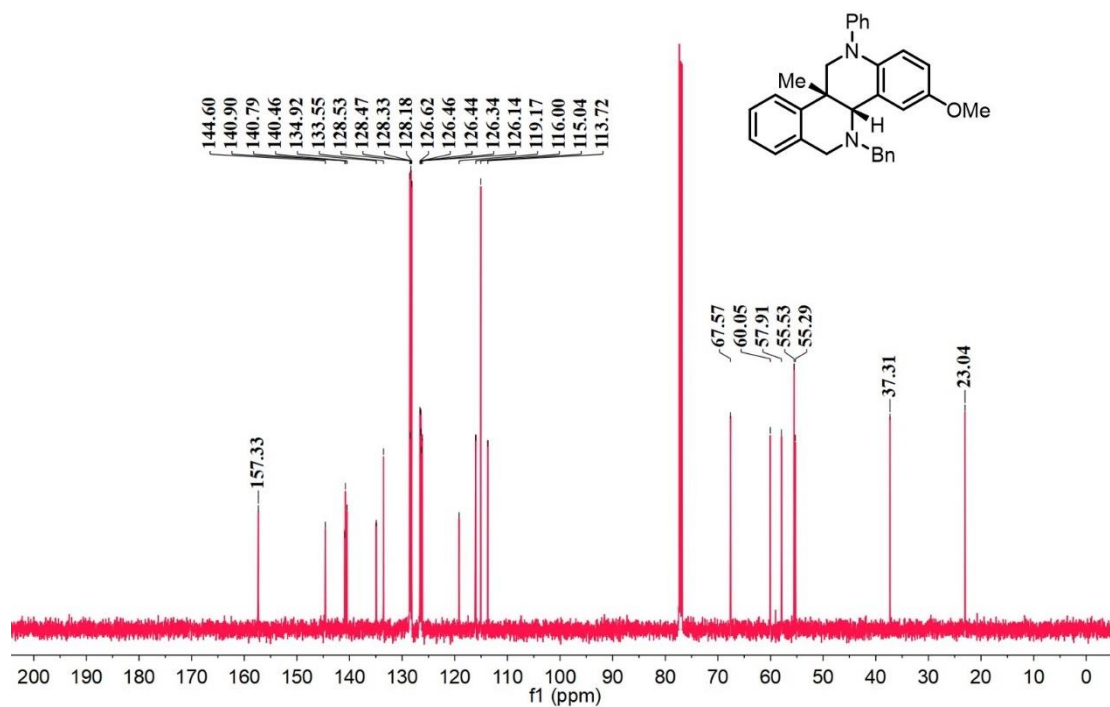
Supplementary Fig. 172 ¹H-NMR spectrum of P75



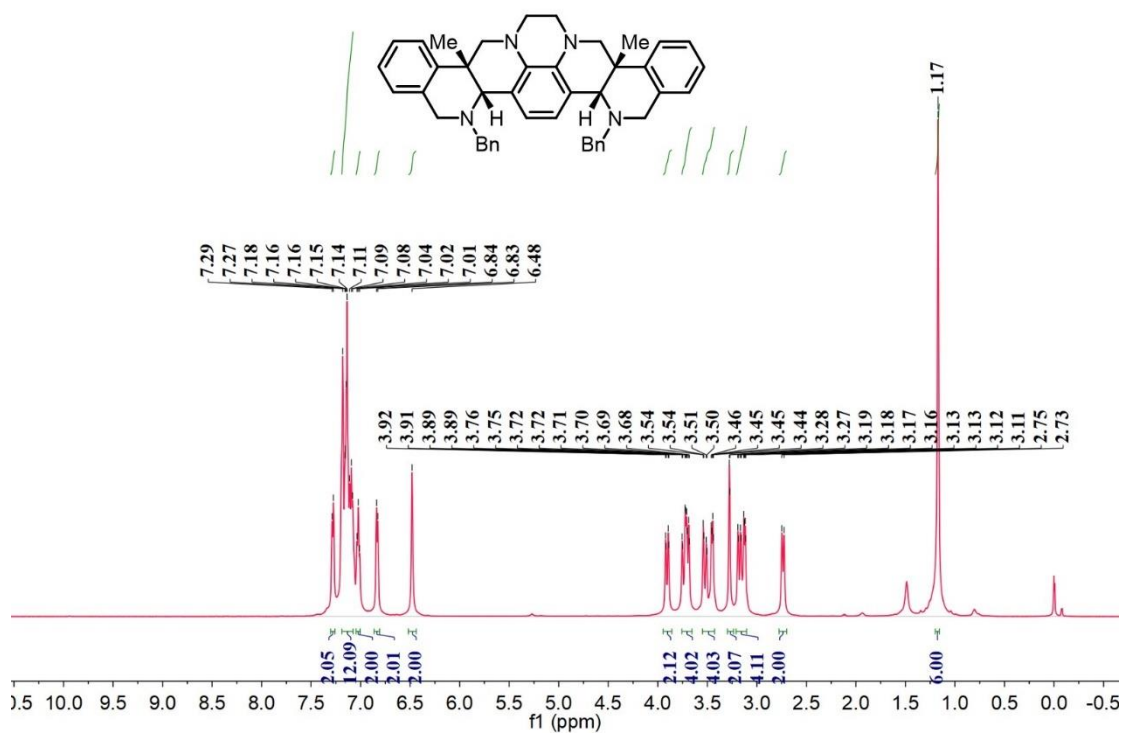
Supplementary Fig. 173 ¹³C-NMR spectrum of P75



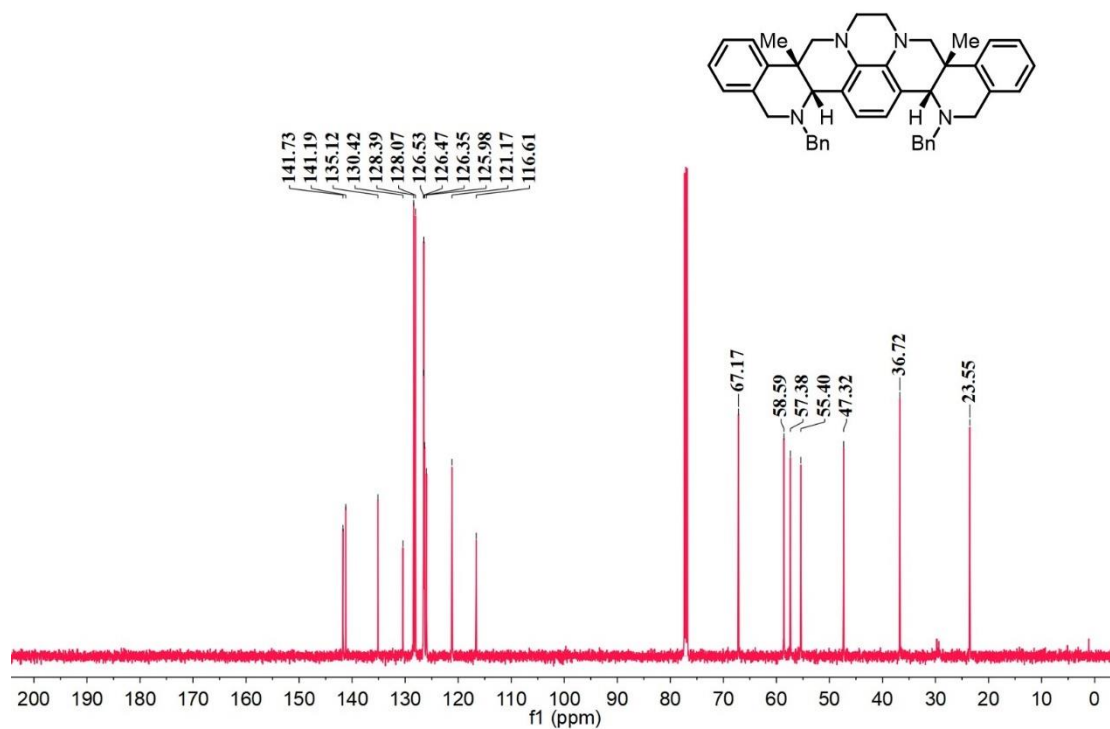
Supplementary Fig. 174 ¹H-NMR spectrum of P76



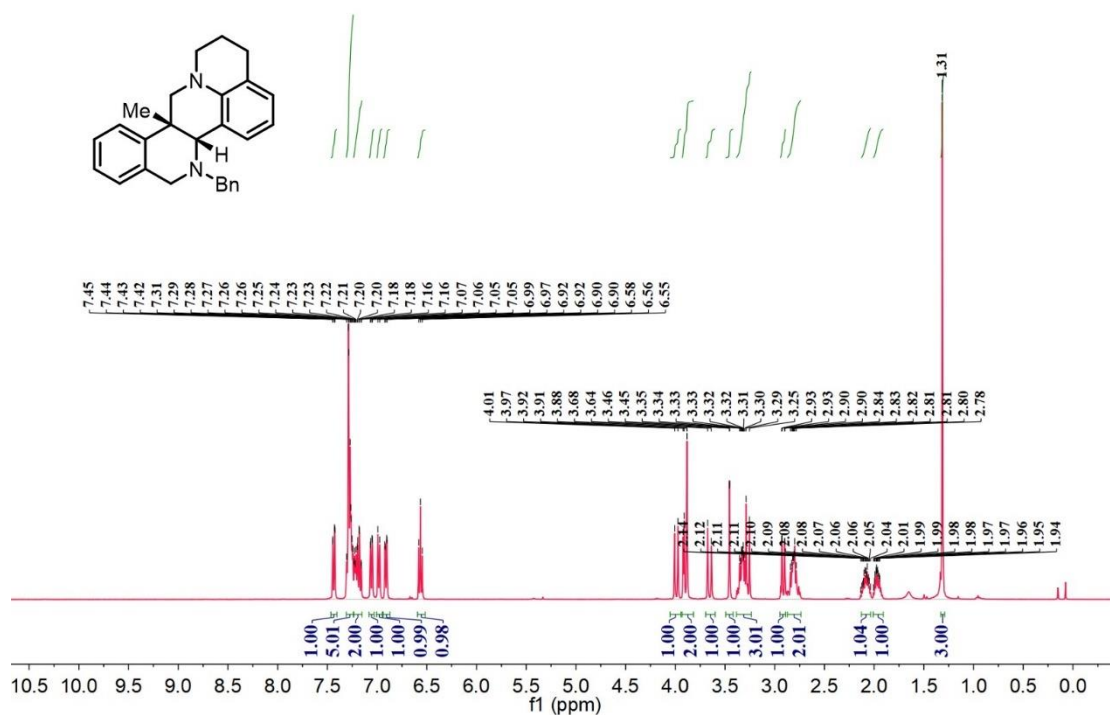
Supplementary Fig. 175 ¹³C-NMR spectrum of P76



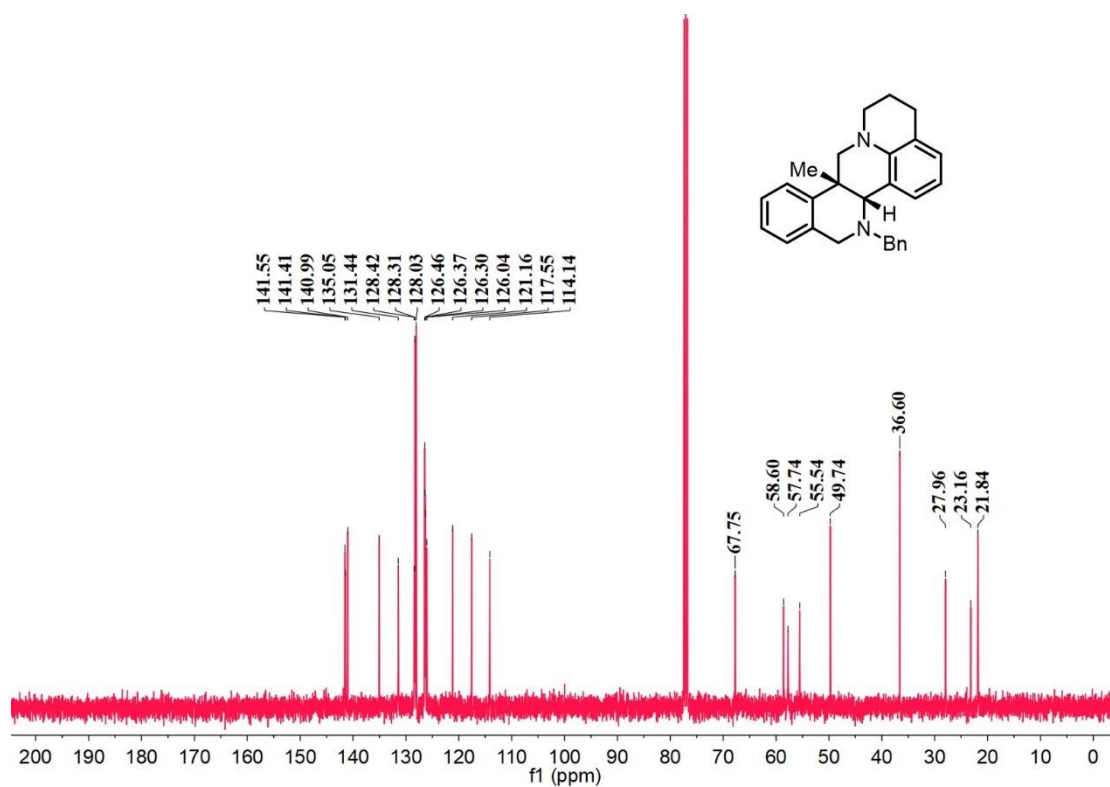
Supplementary Fig. 176 ¹H-NMR spectrum of P77



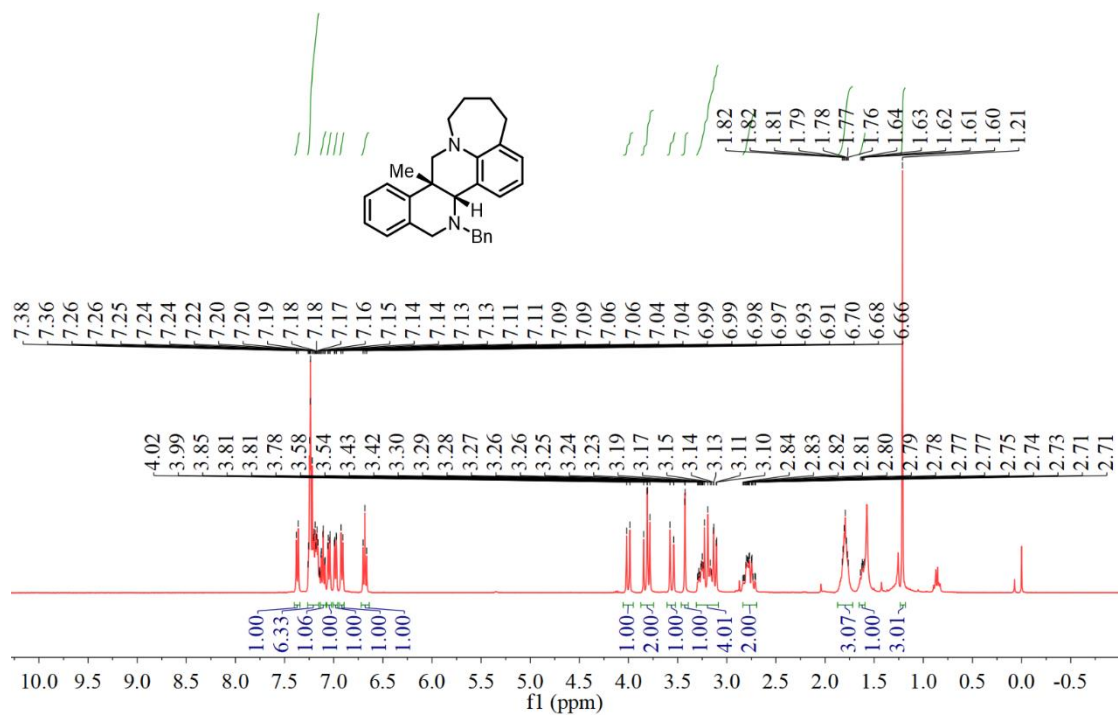
Supplementary Fig. 177 ¹³C-NMR spectrum of P77



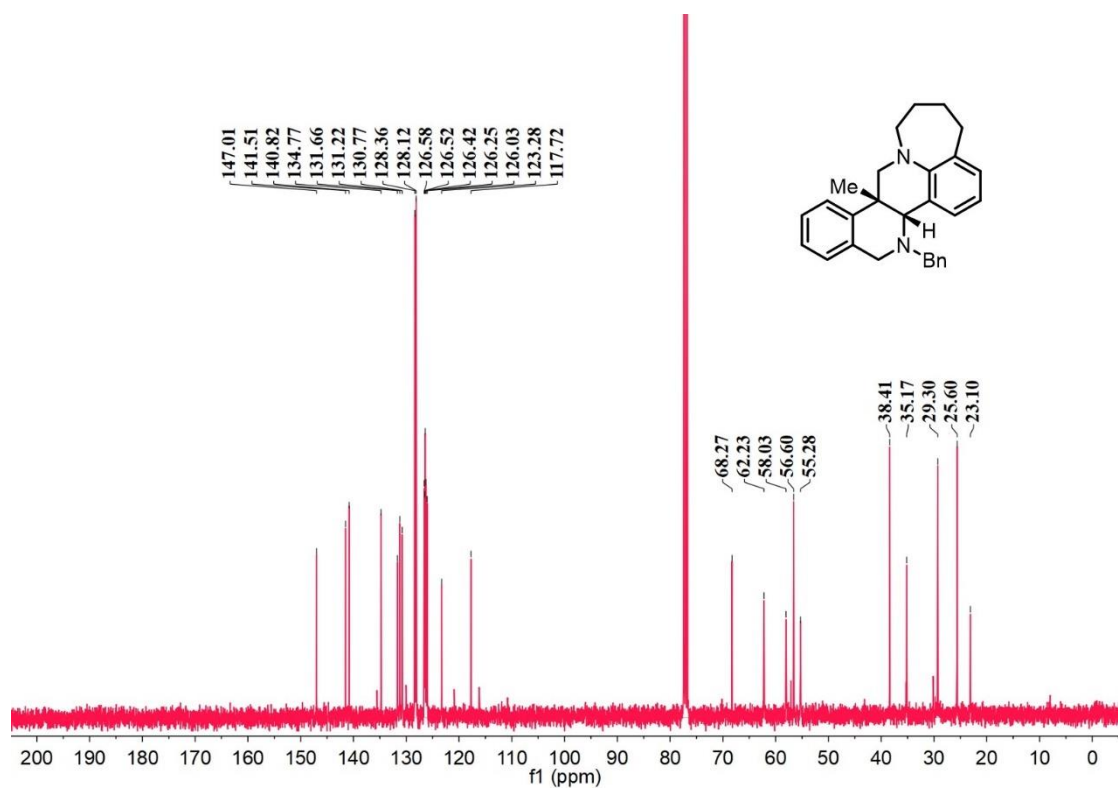
Supplementary Fig. 178 ¹H-NMR spectrum of P78



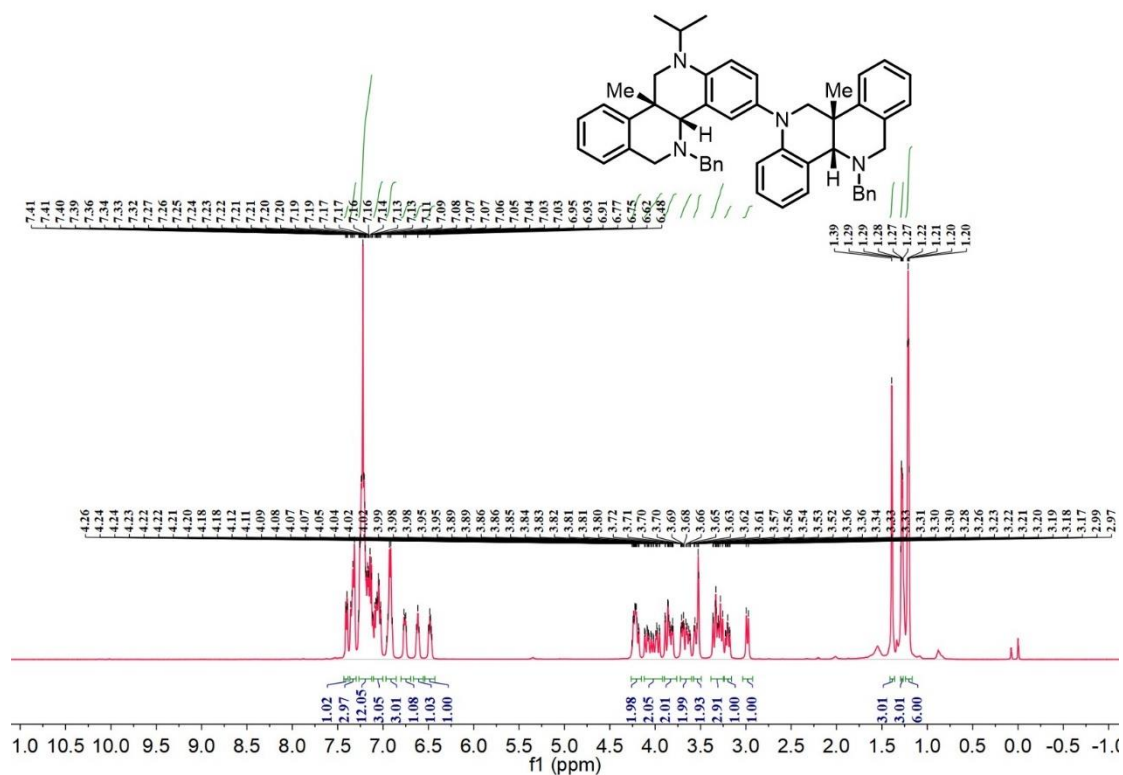
Supplementary Fig. 179 ¹³C-NMR spectrum of P78



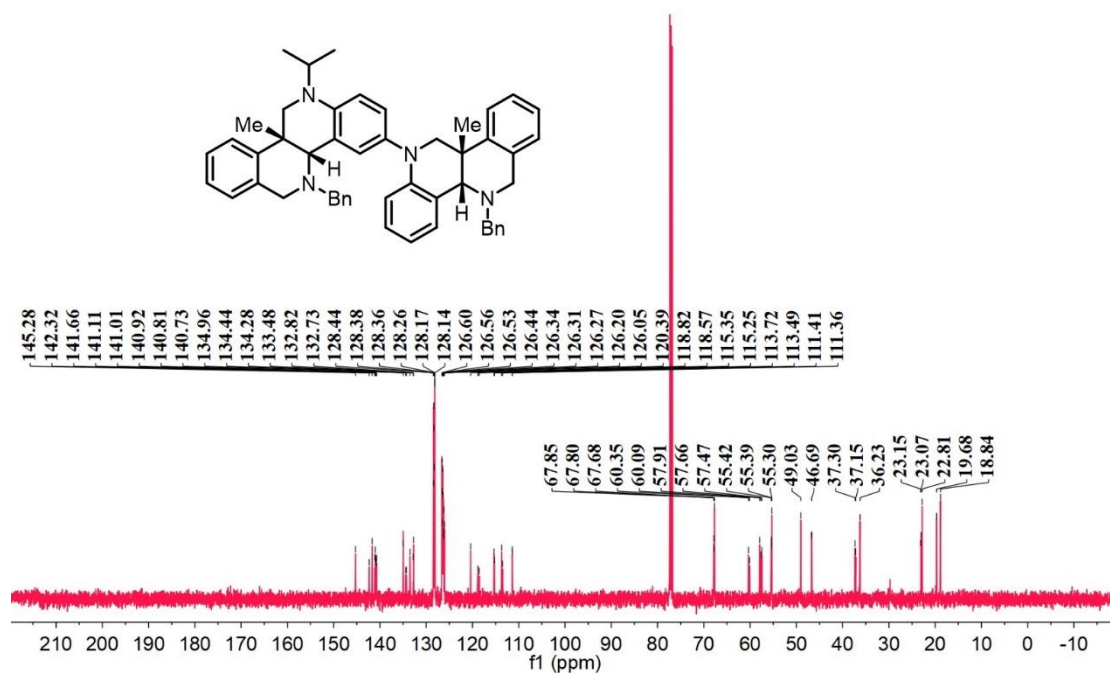
Supplementary Fig. 180 ¹H-NMR spectrum of P79



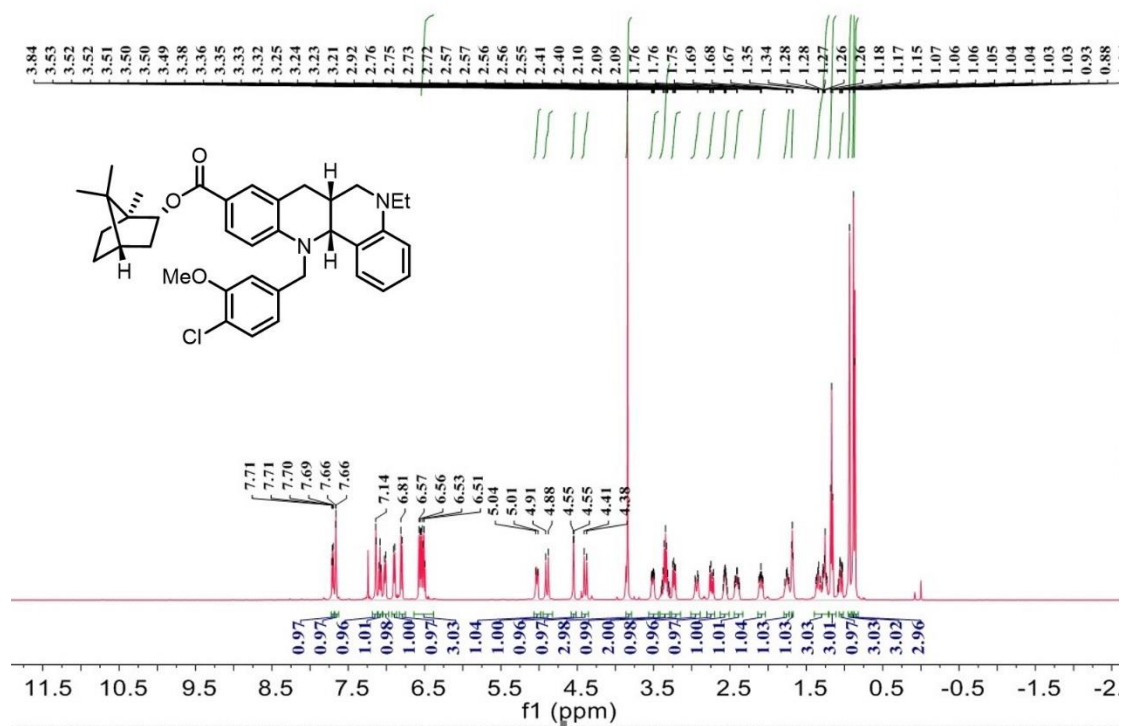
Supplementary Fig. 181 ¹³C-NMR spectrum of P79



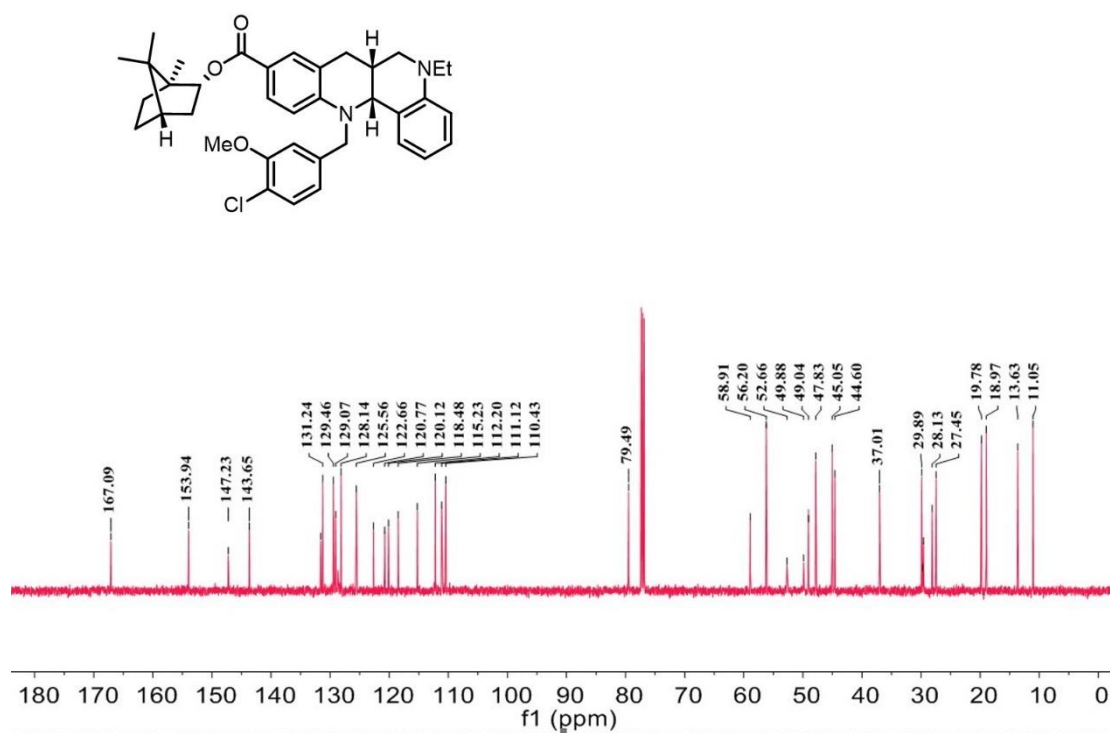
Supplementary Fig. 182 ¹H-NMR spectrum of P80



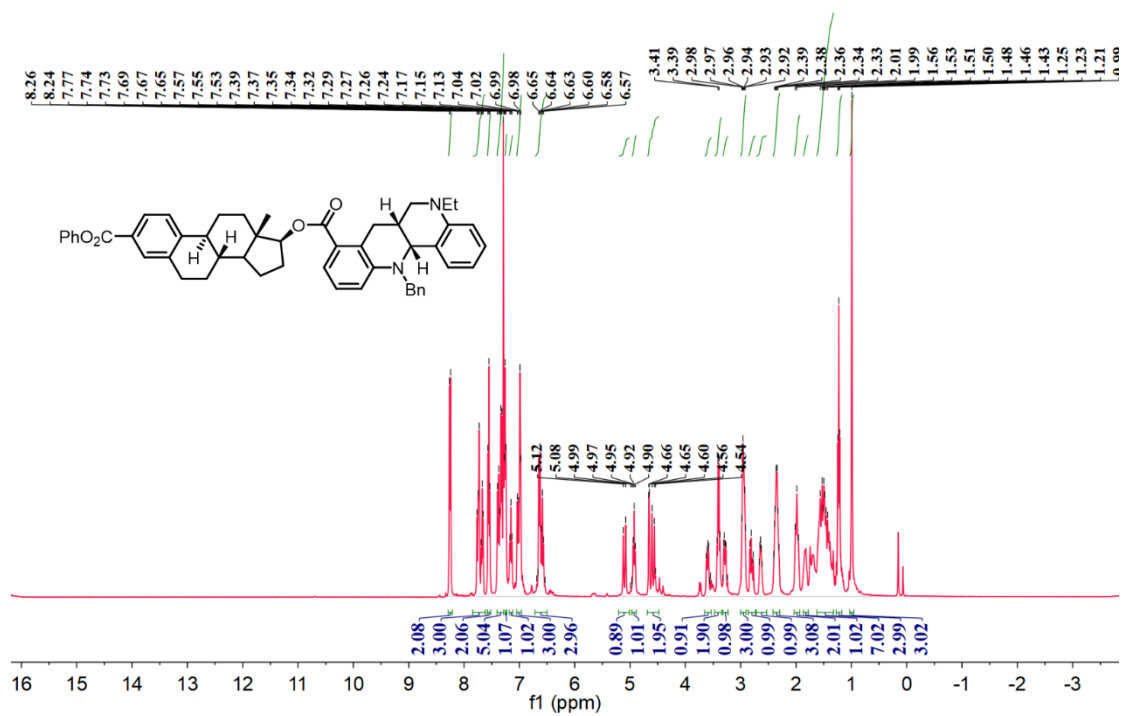
Supplementary Fig. 183 ¹³C-NMR spectrum of P80



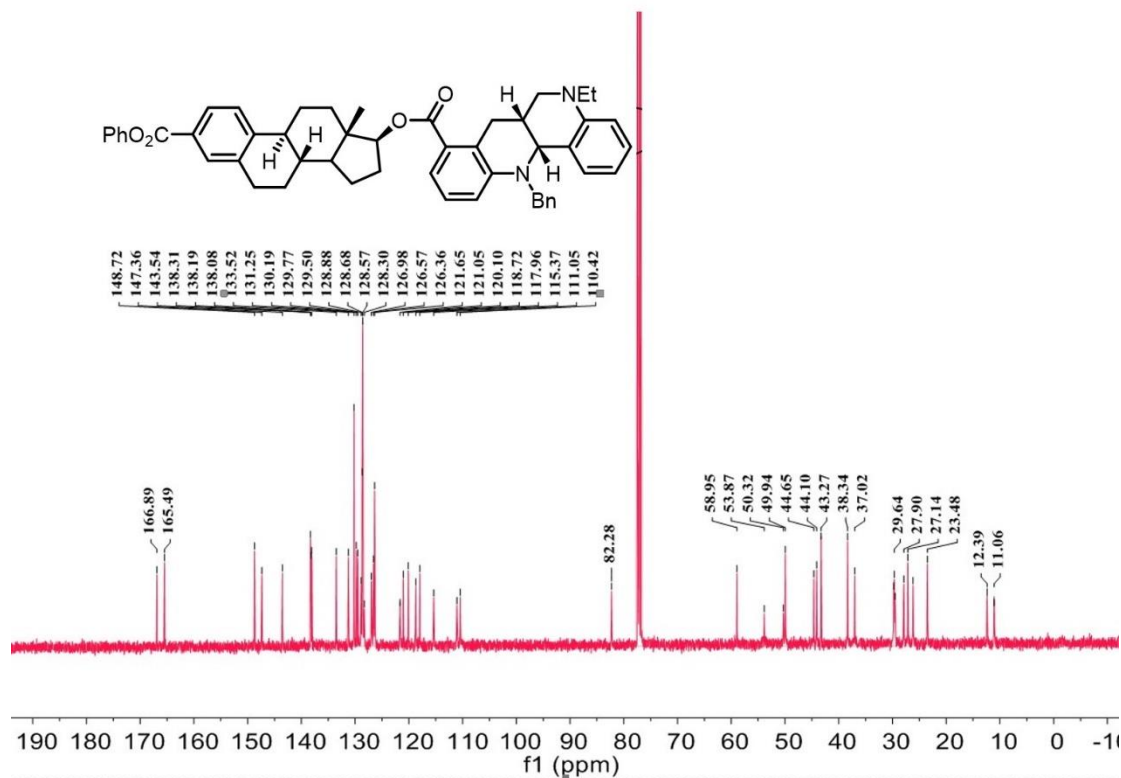
Supplementary Fig. 184 ¹H-NMR spectrum of P81



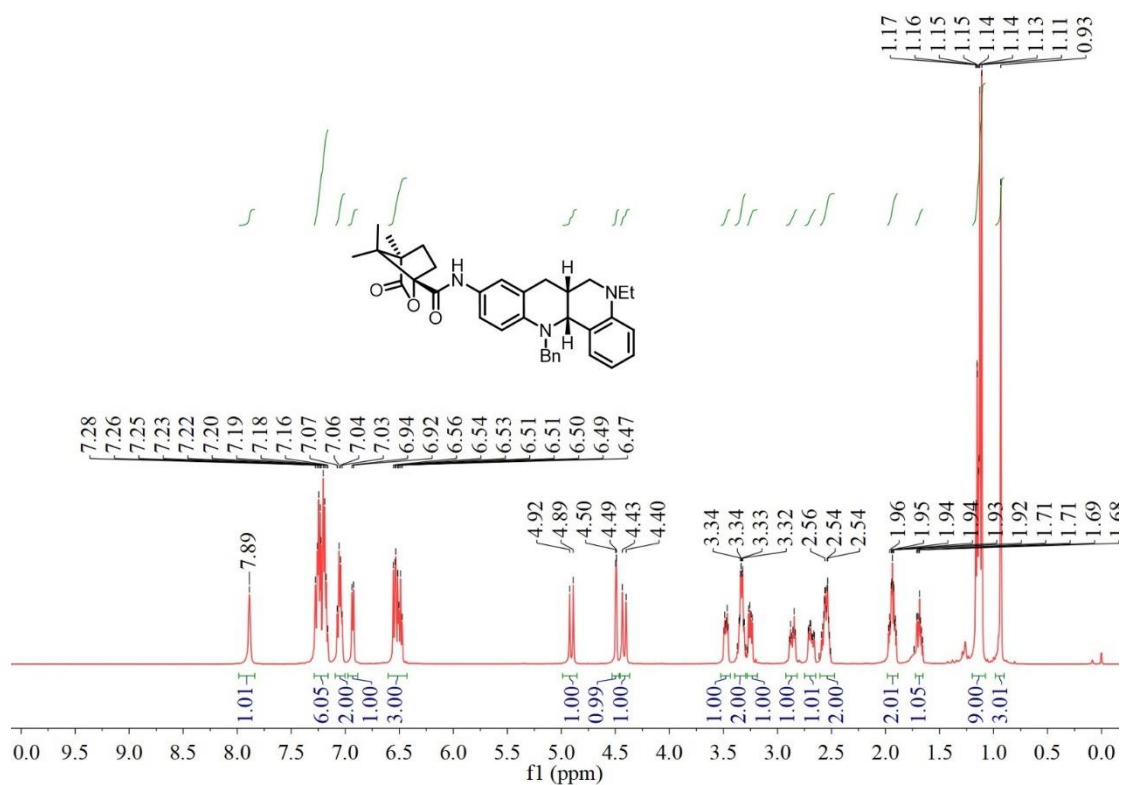
Supplementary Fig. 185 ¹³C-NMR spectrum of P81



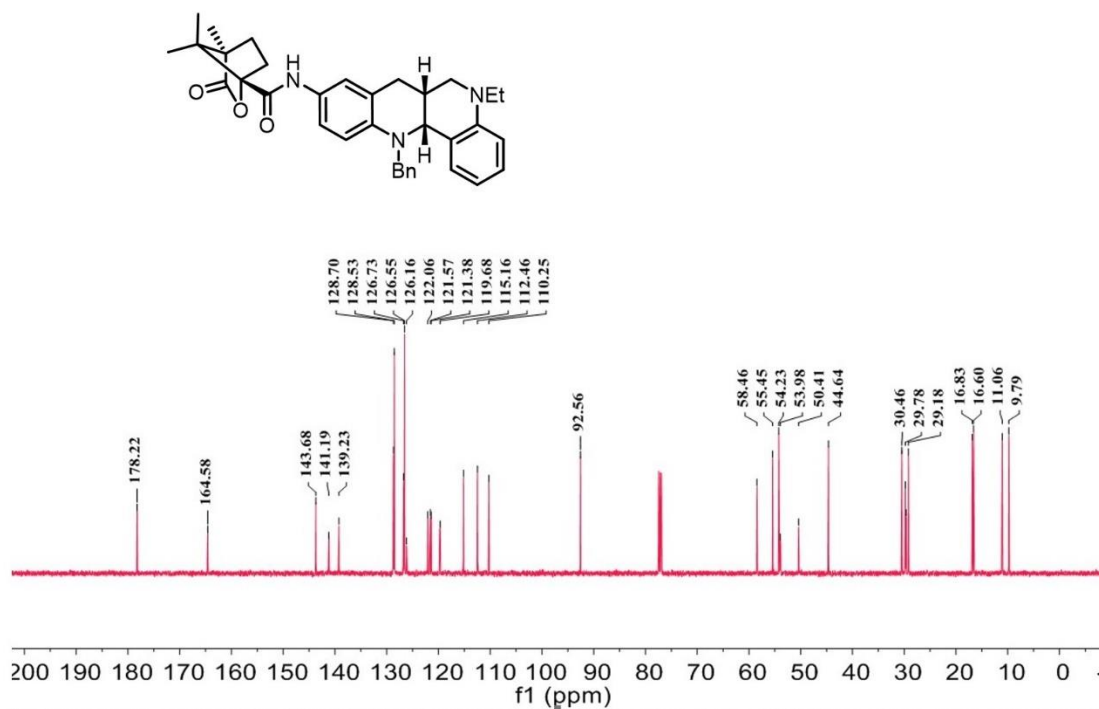
Supplementary Fig. 186 ¹H-NMR spectrum of P82



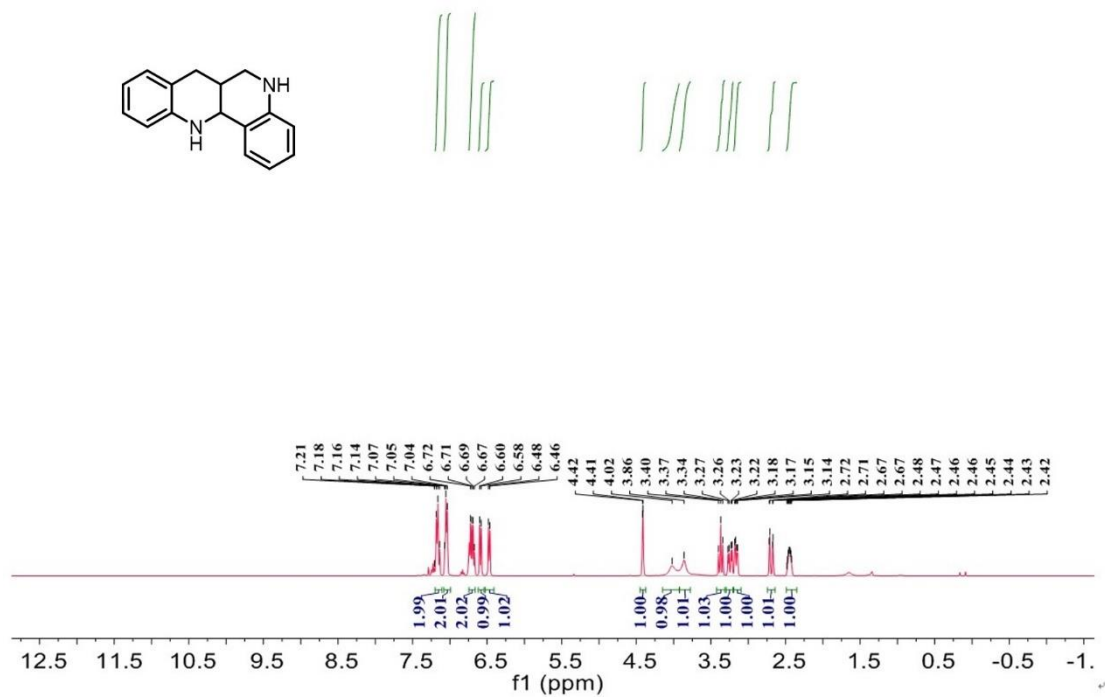
Supplementary Fig. 187 ¹³C-NMR spectrum of P82



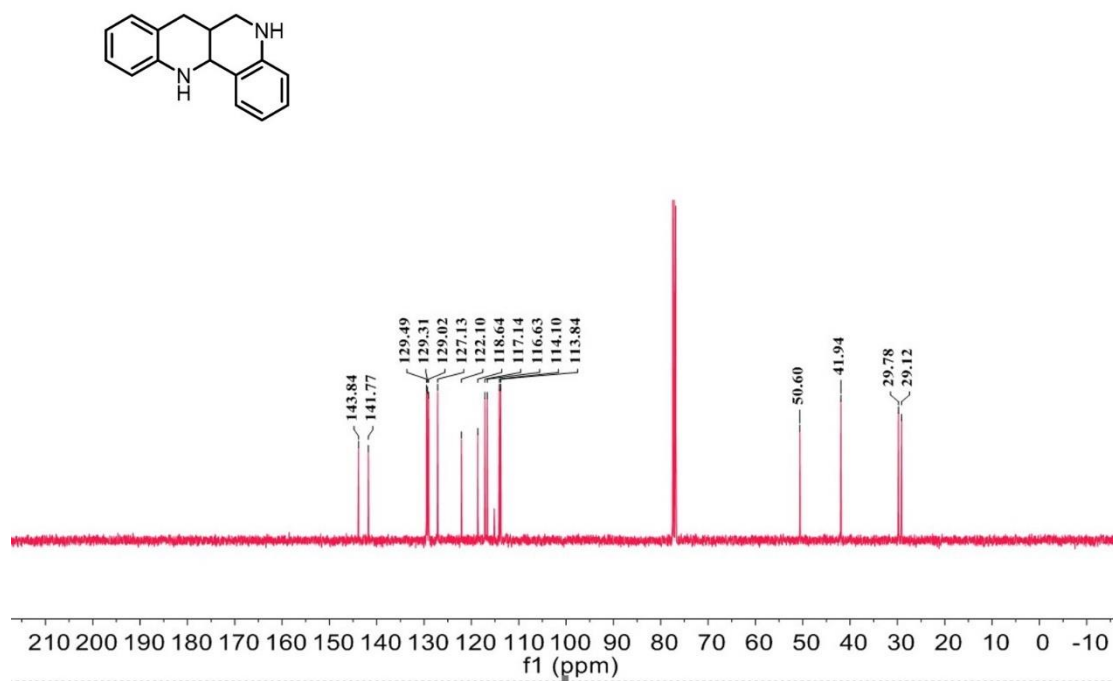
Supplementary Fig. 188 ¹H-NMR spectrum of P83



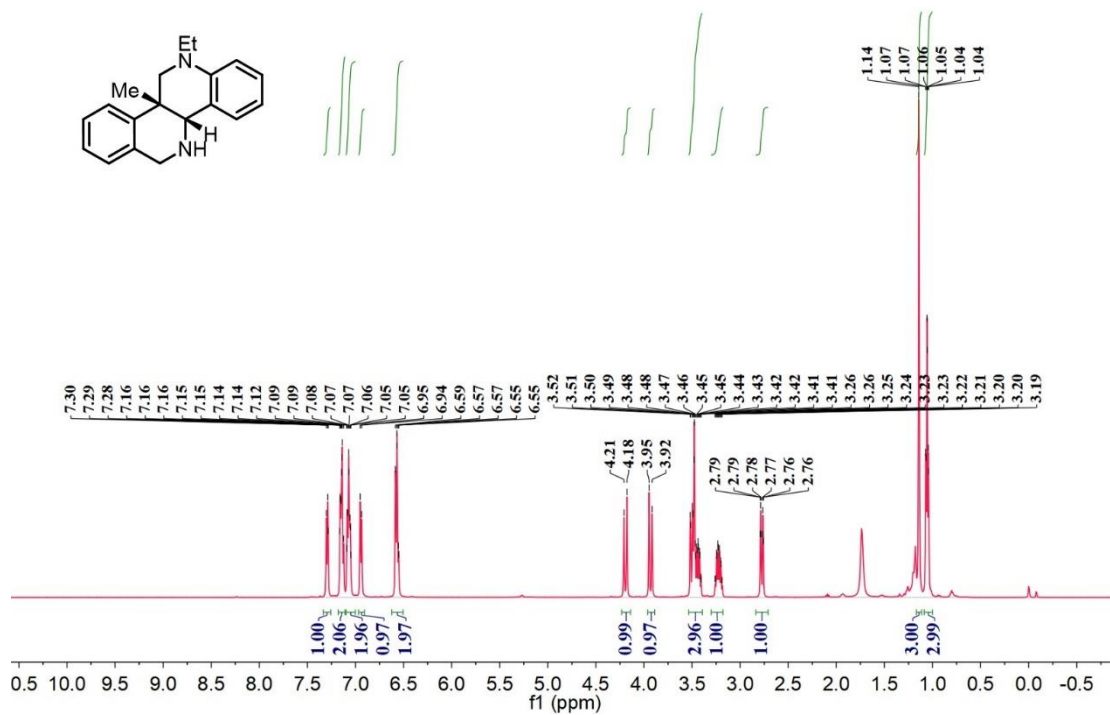
Supplementary Fig. 189 ¹³C-NMR spectrum of P83



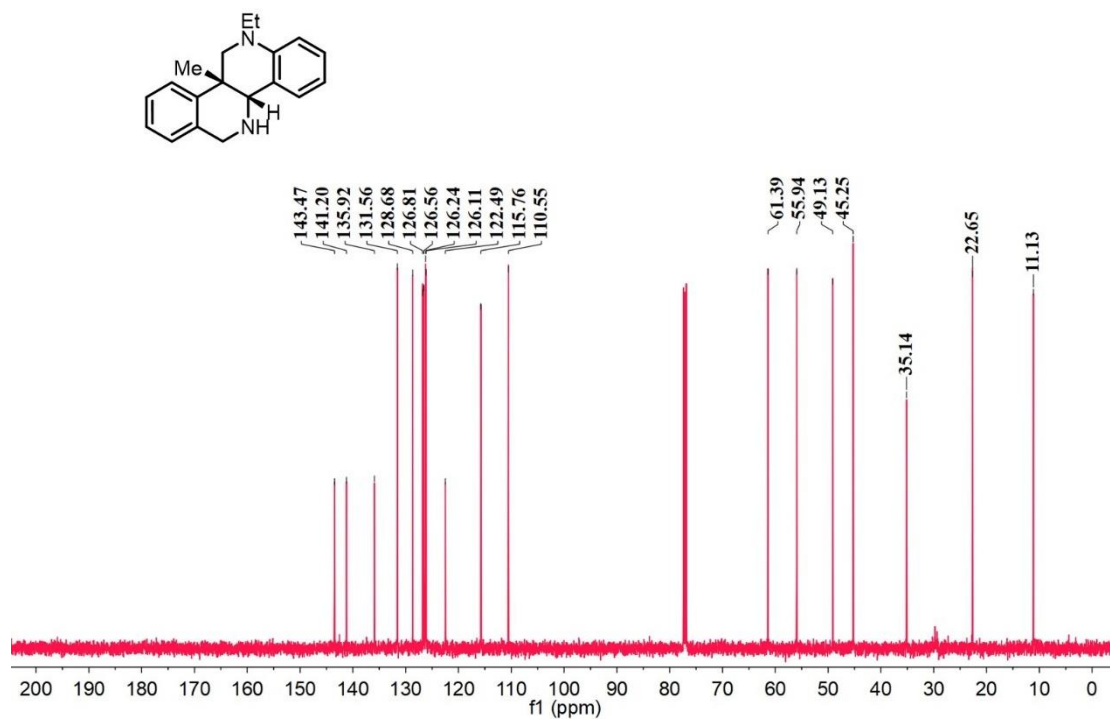
Supplementary Fig. 190 ¹H-NMR spectrum of P84



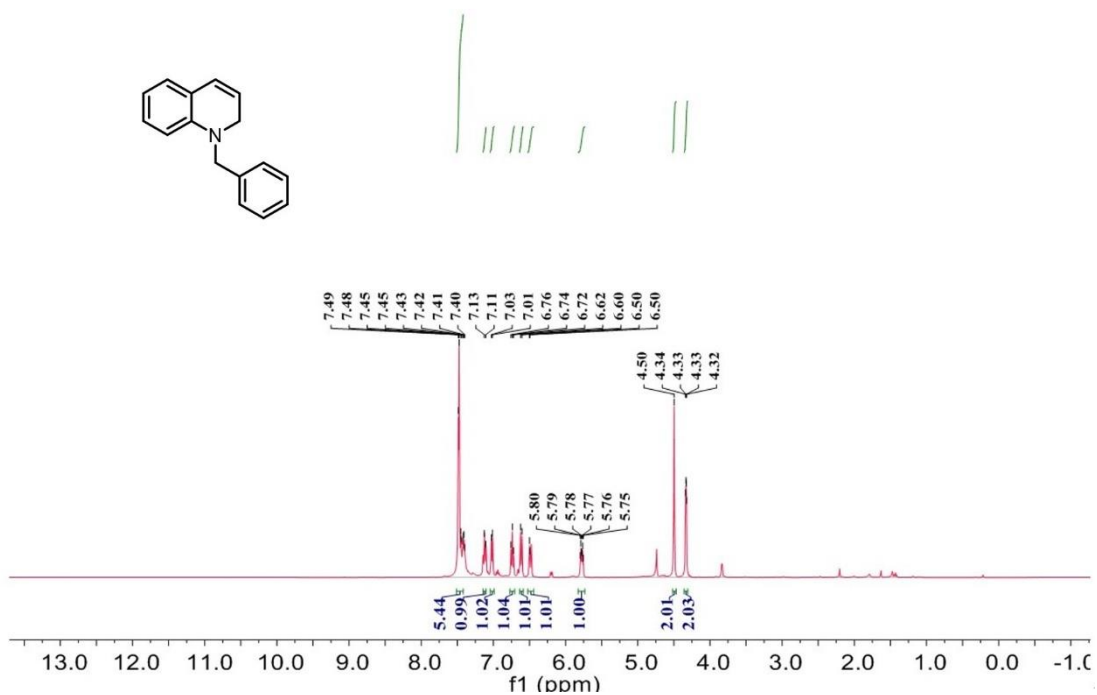
Supplementary Fig. 191 ¹³C-NMR spectrum of P84



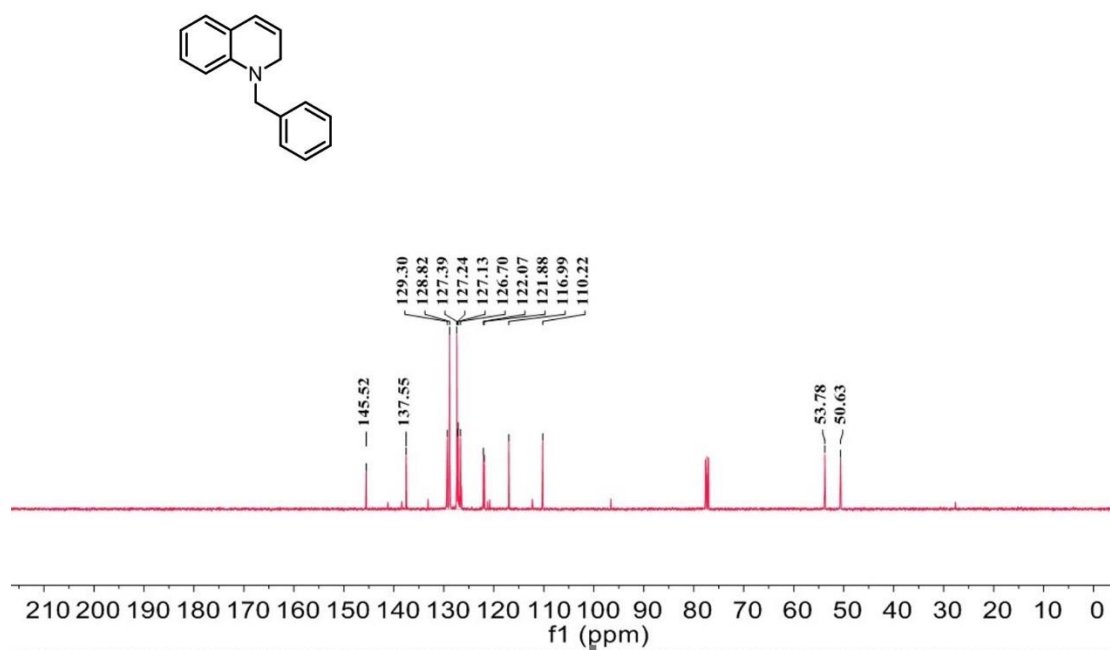
Supplementary Fig. 192 ¹H-NMR spectrum of P85



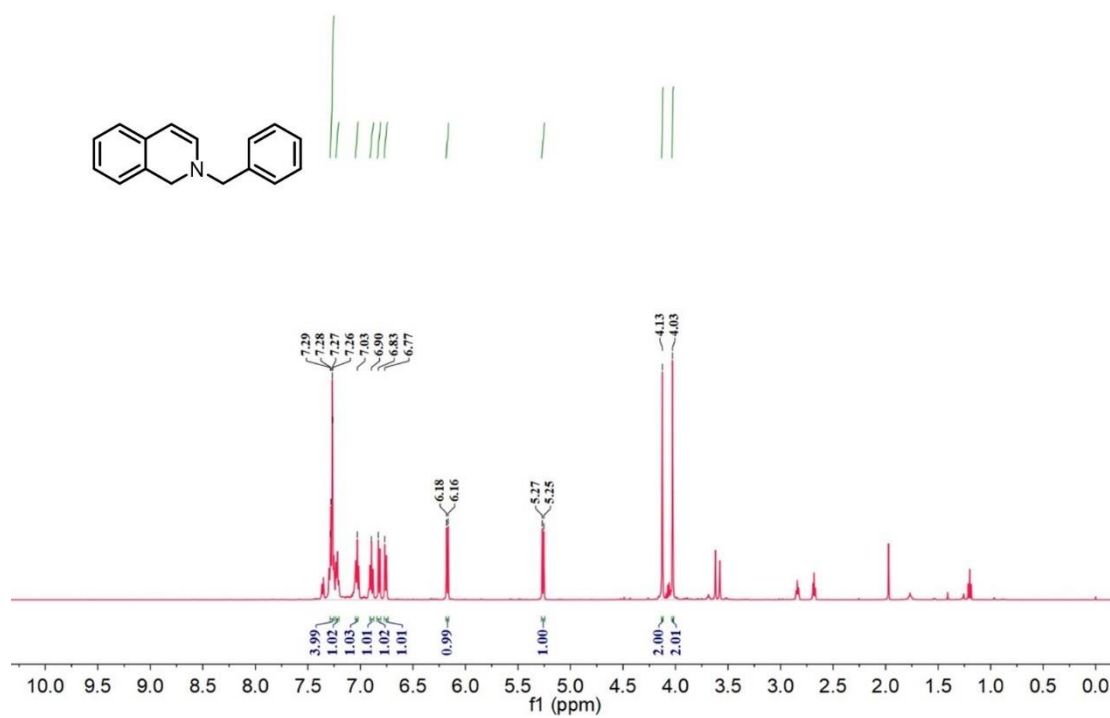
Supplementary Fig. 193 ¹³C-NMR spectrum of P85



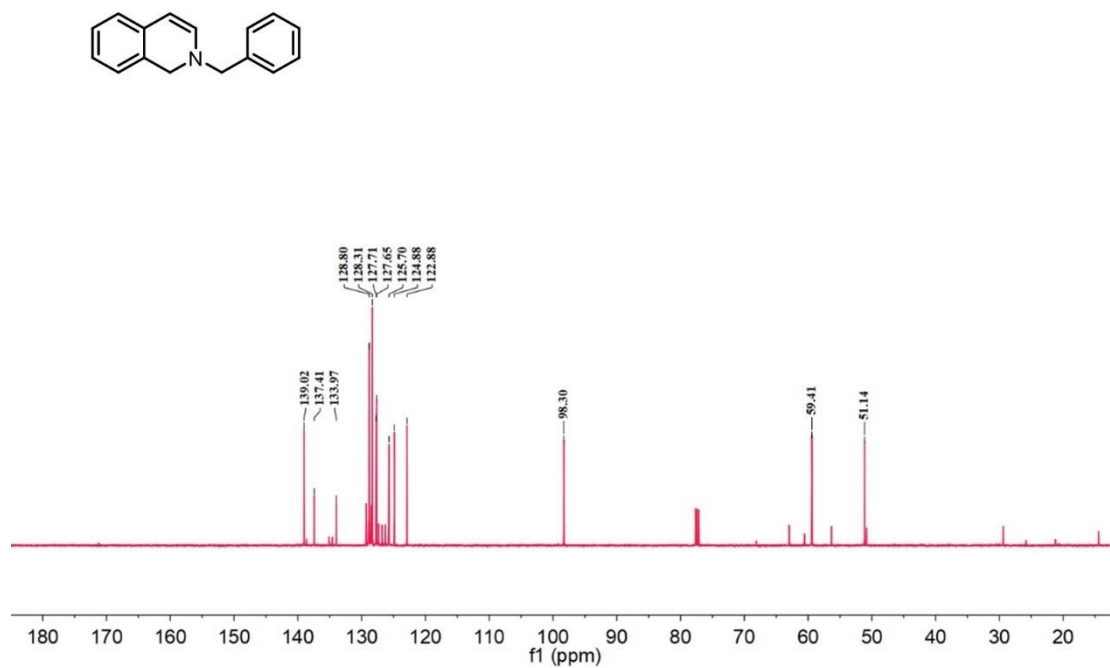
Supplementary Fig. 194 ¹H-NMR spectrum of int-1



Supplementary Fig. 195 ¹³C-NMR spectrum of int-1



Supplementary Fig. 196 ¹H-NMR spectrum of int-6



Supplementary Fig. 197 ¹³C-NMR spectrum of int-6

Supplementary References

- (1) Tan, Z. D.; Ci, C. G.; Yang, J.; Wu, Y.; Liang Cao, Jiang, H. F.; Zhang, M. Catalytic Conversion of N-Heteroaromatics to Functionalized Arylamines by Merging Hydrogen Transfer and Selective Coupling. *ACS Catal.* **10**, 5243–5249 (2020).
- (2) Yang, J.; Zhao, H.; Tan, Z. D.; Cao, L.; Jiang, H. F.; Ci, C. G.; Dixneuf, P. H.; Zhang, M. syn-Selective Construction of Fused Heterocycles by Catalytic Reductive Tandem Functionalization of N-Heteroarenes. *ACS Catal.* **11**, 9271–9278 (2021).
- (3) Frisch, M. J., et al. Gaussian 16; Gaussian, Inc., Wallingford, CT, 2016.
- (4) Lee, C.; Yang, C.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **37**, 785–789 (1988).
- (5) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993).
- (6) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. J. Phys. Chem.* **98**, 11623–11627 (1994).
- (7) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **82**, 270–283 (1985).
- (8) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **77**, 3654–3665 (1982).
- (9) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **56**, 2257–2261 (1972).
- (10) Hariharan, P. C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta.* **28**, 213–222 (1973).
- (11) Peng, C. Y.; Schlegel, H. B. Combining Synchronous Transit and Quasi-Newton Methods to Find Transition States. *Isr. J. Chem.* **33**, 449–454 (1993).
- (12) Hratchian, H. P.; Schlegel, H. B. Accurate reaction paths using a Hessian based predictor-corrector integrator. *J. Chem. Phys.* **120**, 9918–9924 (2004).
- (13) Cancès, E.; Mennucci, B.; Tomasi, J. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. *J. Chem. Phys.* **107**, 3032–3041 (1997).