Supporting Information

for

Direct synthesis of ring-fused quinolines and pyridines catalyzed by NN_HY-ligated manganese complexes (Y = NR_2 or SR)

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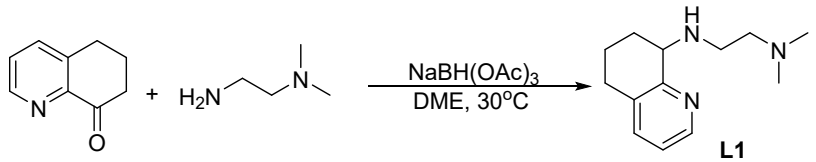
1 General Considerations

All manipulations and their complexes were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and distilled under nitrogen prior to use. All the liquid and solid substrates were used directly without further purification. Other reagents were purchased from Aldrich, Acros or local suppliers. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 NMR and Bruker AV-500 NMR spectrometers. Chemical shift values shown in the ^{1}H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (J) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, and br s = broad singlet. Elemental analysis was carried out with a Vario EL III CHN microanalyzer. Single-crystal X-ray diffraction studies were conducted on a Rigaku Sealed Tube CCD (Saturn 724+) diffractometer with graphite-mono chromated Mo-Kα radiation (λ = 0.71073 Å) or Cu Kα (λ = 1.54184) at 173(2) K and the cell parameters obtained by global refinement of the positions of all collected reflections. GC was performed using Agilent 6820 instrument using a HP-5 column: injector temp. 300 °C, detector temp. 300 °C, column temp. 120 °C, withdraw time 2 min, then 20 °C /min to 240 °C keeping for 5 min, then 20 °C /min to 300 °C, withdraw time for 5 min. The detection of H_2 by GC was performed using a FuLi 9790II instrument (TCD detector) using a column packed with 5 Å molecular sieves (60 – 80 mesh, SS/0.3 mm × 10.2 mm × 3 m), N_2 was used as the carrier gas: injector temp. 120 °C, detector temp. 120 °C, column temp. 80 °C, withdraw time 10 min.

2 Synthesis and characterization of ligands and manganese(I) complexes

2.1. Synthesis of 8-(2-YCH_2CH_2)$NHC_9H_{10}N$ [Y = R_2N, NN_HN (L1 – L3); EtS, NN_HS (L4)] [1]

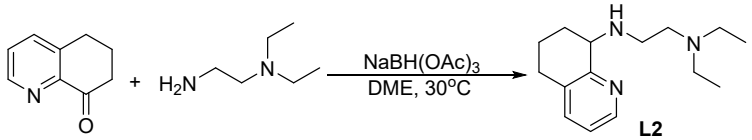
2.1.1 Preparation of N^1,N^1-dimethyl-N^2-(5,6,7,8-tetrahydroquinolin-8-yl)ethane-1,2-diamine (THQ^{Me2}, **L1**)



Similar to our previous work,[1] a mixture of 5,6,7-trihydroquinolin-8-one (2.94 g, 20 mmol), *N*,*N*-dimethylethane-1,2-diamine (2.12 g, 24 mmol, 1.2 eq.) and sodium triacetoxyborohydride (6.33 g, 30 mol, 1.5 eq.) were loaded in a 250 mL flask followed by 1,2-dichloroethane (100 mL). The reaction mixture was stirred at 30 °C for 12 h. An aqueous saturated solution of $NaHCO_3$ (100 mL) was added

to quench the reaction (pH > 8) and the mixture extracted with ethyl acetate (3 × 30 mL). The combined organic phases were dried over sodium sulfate and concentrated, the residue was purified by silica gel column chromatography (dichloromethane/methanol = 500/1 to 100/1) to give **L1** as a yellow oil (3.12 g, 71%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.37 – 8.32 (m, 1H), 7.35 – 7.30 (m, 1H), 7.02 (dd, *J* = 7.7, 4.7 Hz, 1H), 3.77 (dd, *J* = 7.6, 5.3 Hz, 1H), 3.32 (br, 1H, N*H*), 2.80 (q, *J* = 6.5 Hz, 3H), 2.69 (dt, *J* = 16.6, 5.5 Hz, 1H), 2.47 (td, *J* = 6.3, 2.3 Hz, 2H), 2.22 (s, 6H), 2.13 – 2.07 (m, 1H), 2.00 – 1.93 (m, 1H), 1.80 – 1.74 (m, 1H), 1.73 – 1.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.36, 146.73, 136.85, 132.39, 121.88, 59.43, 57.85, 45.63, 45.50, 44.99, 28.83, 28.56, 19.53.

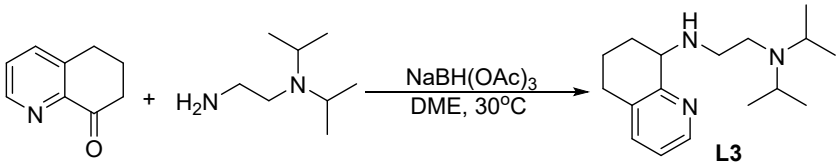
2.1.2 Preparation of N^1,N^1-diethyl-N^2-(5,6,7,8-tetrahydroquinolin-8-yl)ethane-1,2-diamine (THQ^{Et2}, **L2**)



Using a similar procedure and molar ratios to that described for **L1**, **L2** was obtained as a yellow oil (3.24 g, 65%). ^{1}H NMR ($CDCl_3$,500 MHz) δ 8.36 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.02 (dd, *J* = 7.7, 4.7 Hz, 1H), 3.77 (dd, *J* = 7.7, 5.4 Hz, 1H), 3.30 (br, 1H, N*H*), 2.84 – 2.75 (m, 3H), 2.70 (dt, *J* = 16.2, 5.2 Hz, 1H), 2.64 – 2.60 (m, 2H), 2.54 (qd, *J* = 7.1, 1.4 Hz, 4H), 2.15 – 2.10 (m, 1H), 2.01 – 1.94 (m, 1H), 1.80 – 1.66 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 6H);^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.51, 146.77, 136.97, 132.52, 122.00, 57.83, 52.30, 46.88, 44.38, 28.72, 28.18, 19.77, 11.38.

L2 can be further purified by adding an aqueous 10 w% HCl solution (10 mL) and the water then removed under reduced pressure to give **L2**·HCl a pale-yellow solid (4.45 g, 62%). ^{1}H NMR (D_2O, 400 MHz) δ 8.54 (d, *J* = 5.2 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.71 (ddt, *J* = 7.8, 5.1, 2.6 Hz, 1H), 4.58 (d, *J* = 5.7 Hz, 1H), 3.64 – 3.45 (m, 4H), 3.33 – 3.26 (m, 4H), 3.07 – 2.87 (m, 2H), 2.30 (d, *J* = 11.8 Hz, 1H), 2.10 (s, 1H), 2.03 – 1.89 (m, 2H), 1.28 (t, *J* = 7.3 Hz, 6H).

2.1.3 Preparation of N^1,N^1-diisopropyl-N^2-(5,6,7,8-tetrahydroquinolin-8-yl)ethane-1,2-diamine (THQ^{Et2}, **L3**)



Using a similar procedure and molar ratios to that described for **L1**, **L3** was obtained as a yellow oil (4.45 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 4.8 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.03 (dd, *J* = 7.7, 4.8 Hz, 1H), 3.76 (t, *J* = 6.4 Hz, 1H), 3.00 (p, *J* = 6.5 Hz, 2H), 2.82 – 2.69 (m, 4H), 2.61 (dd, *J* = 6.9, 5.2 Hz, 2H), 2.13 (dd, *J* = 11.3, 6.0 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.75 (tdd, *J* = 10.2, 7.1, 3.6 Hz, 2H), 1.00 (d, *J* = 6.5 Hz, 12H).

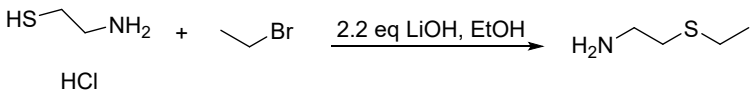
L3 can be further purified by adding an aqueous 10 w% HCl solution (10 mL) and the water then removed under reduced pressure to give **L3**·HCl as a pale-yellow solid (5.95 g, 77%). ^{1}H NMR (400 MHz, D_2O) δ 8.56 (dd, *J* = 5.6, 1.5 Hz, 1H), 8.20 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.77 (dd, *J* = 8.1, 5.5 Hz, 1H), 4.69 (d, *J* = 4.6 Hz, 1H), 3.73 -3.67 (m, 2H), 3.65 – 3.58 (m, 1H), 3.50 (dt, *J* = 11.2, 7.4 Hz, 1H),

3.41 (dd, J = 9.0, 7.2 Hz, 2H), 3.00 (dt, J = 18.2, 5.2 Hz, 1H), 2.87 (dt, J = 17.9, 7.6 Hz, 1H), 2.19 (dtt, J = 29.8, 9.8, 4.8 Hz, 2H), 1.97 – 1.83 (m, 2H), 1.30 – 1.21 (m, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.07, 146.93, 137.26, 132.41, 122.46, 58.15, 47.95, 47.02, 44.06, 28.59, 21.58, 20.54, 19.67.

2.1.4 Preparation of *N*-(2-(ethylthio)ethyl)-5,6,7,8-tetrahydroquinolin-8-amine (**L4**)

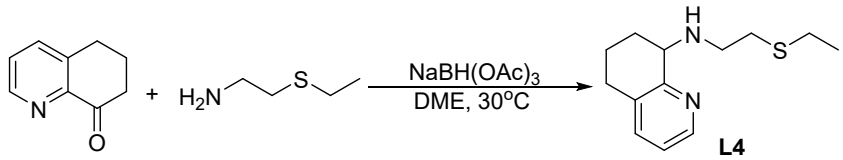
L4 was prepared in two steps as follows.

i) Synthesis of 2-(ethylthio)ethan-1-amine[2]



Under a nitrogen atmosphere, a suspension of 2-aminoethanethiol hydrochloride (11.3 g, 100 mmol), NaOH (4.0 g, 100 mmol) and LiOH (4.6 g, 200 mmol) in EtOH (120 mL) and H_2O (30 mL) was stirred for 10 min at 0 °C. Bromoethane (11.8 g, 110 mmol) was then added dropwise to the mixture over a period of 30 min at 0 °C. After stirring for 24 h at 35 °C the reaction mixture was cooled to room temperature and the ethanol removed under reduced pressure. The residue was treated with water (80 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic phases were dried over Na_2SO_4 and following filtration, the solvent was removed under reduced pressure yielding 2-(ethylthio)ethan-1-amine as a yellow oil (6.5 g, 61%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.74 (t, J = 7.0 Hz, 2H), 2.58 (d, J = 7.3 Hz, 1H), 2.51 (dd, J = 9.8, 4.9 Hz, 1H), 1.17 (t, J = 7.4 Hz, 4H).

(ii) Synthesis of **L4**

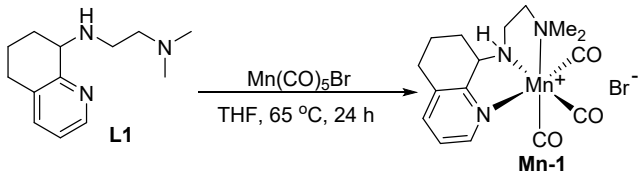


By employing a similar procedure and molar ratios to that described for the synthesis **L1** but with 2-(ethylthio)ethan-1-amine as the amine, **L4** was obtained as a yellow oil (3.85 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 4.2 Hz, 1H), 7.32 (t, J = 6.5 Hz, 1H), 7.01 (dt, J = 7.8, 5.1 Hz, 1H), 3.80 – 3.70 (m, 1H), 3.02 (br, 1H, N*H*), 2.90 (td, J = 6.8, 3.6 Hz, 2H), 2.77 – 2.66 (m, 4H), 2.55 – 2.48 (m, 3H), 2.13 – 2.05 (m, 1H), 1.99 – 1.91 (m, 1H), 1.77 – 1.65 (m, 2H), 1.21 (dd, J = 7.5, 5.5 Hz, 3H);^{13}C NMR (100 MHz, DMSO-d_6) δ 157.82, 146.91, 137.25, 132.35, 122.34, 57.58, 31.82, 29.05, 28.67, 25.39, 19.50, 15.36

2.2 Synthesis of [(*fac*-NN_HN)Mn(CO)$_3$]Br (Mn-1 – Mn-3) and [(*fac*-NN_HS)Mn(CO)$_3$]Br (Mn-4)

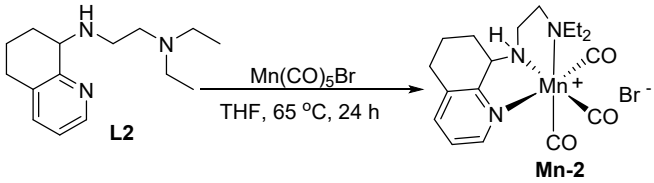
Preparative details for [(8-(2-YCH$_2$CH$_2$)NHC$_9$H$_{10}$N)MnBr(CO)$_3$]Br (Y = R$_2$N, RS)

a) Y = Me_2N, **Mn-1**[3]



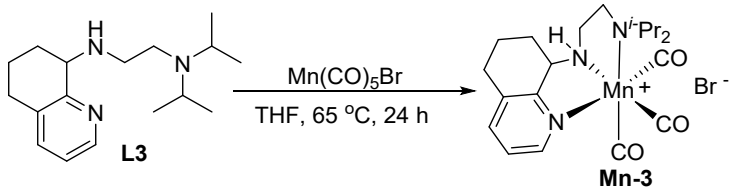
To a 25 mL Schlenk flask maintained under nitrogen, a solution of **L1** (THQ-NNN^{Me2}, 219 mg, 1 mmol) in THF (5 mL) was added followed by an orange solution of $Mn(CO)_5Br$ (275 mg, 1 mmol) in THF (10 mL). The reaction mixture was then stirred and heated at 65 °C for 24 h. Once cooled to room temperature the mixture was concentrated under reduced pressure. The solid residue was washed with Et_2O (10 mL) and then dried to give **Mn-1** as a pale-yellow solid (375 mg, 85%). Single crystals of **Mn-1** were obtained by layering a saturated solution of the complex in dichloromethane with diethyl ether. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (s, 1H, N*H*), 7.89 (d, J = 7.2 Hz, 1H), 7.61 – 7.48 (m, 1H), 7.39 – 7.23 (m, 1H), 4.35 (d, J = 9.6 Hz, 1H), 3.05 – 2.75 (m, 6H), 2.59 (d, J = 11.6 Hz, 1H), 2.44-2.42 (m, 1H), 2.14 (d, J = 15.6 Hz, 2H), 1.93 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ 219.64, 219.26, 218.98, 158.68, 152.46, 140.24, 136.87, 125.81, 64.81, 62.97, 57.00, 49.03, 43.62, 27.42, 26.68, 21.14; IR (ATR, cm^{-1}, KBr): 1753 (s, ν_{CO}), 1779 (s, ν_{CO}), 1898 (s, ν_{CO}). Anal. Calcd for [$C_{16}H_{21}BrMnN_3O_3$ (Mw: 438.20)]: C, 43.86; H, 4.83; N, 9.59. Found: C, 43.90; H, 4.96; N, 9.54%

b) Y = Et_2N **Mn-2**



Using a similar procedure and molar ratios to that described for **Mn-1**, **Mn-2** was isolated as a yellow powder (412 mg, 89%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (br, 1H), 7.91 (s, 1H), 7.56 (s, 1H), 7.19 (s, 1H), 4.40 (s, 1H), 3.29 (s, 4H), 2.85 (s, 4H), 2.04 – 2.00 (m, 4H), 1.43 (s, 1H), 1.30 (br, 3H), 1.16 (s, 1H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.73, 149.59, 138.32, 135.70, 123.55, 62.77, 56.44, 53.50, 44.57, 41.62, 28.10, 27.04, 21.46, 9.31, 9.20. CO not observed. IR (ATR, cm^{-1}, KBr): 1905 (s, ν_{CO}), 1936 (s, ν_{CO}), 2025 (s, ν_{CO}). Anal. Calcd for [$C_{18}H_{25}BrMnN_3O_3$ (Mw: 466.26)]: C, 46.37; H, 5.40; N, 9.01; Found: C, 46.46; H, 5.51; N, 8.92%

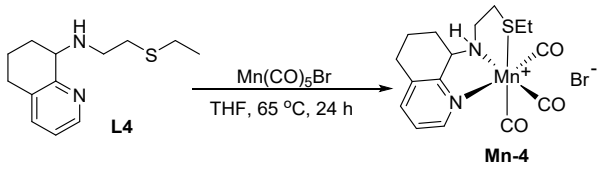
c) Y = i-Pr_2N **Mn-3**



Using a similar procedure and molar ratios to that described for **Mn1**, **Mn-3** was isolated as a yellow powder (425 mg, 85%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.78 (br, 1H), 7.76 (d, J = 2.2 Hz, 1H), 7.53 – 7.37 (m, 1H), 4.31 – 4.13 (m, 1H), 3.41 (d, J = 34.6 Hz, 1H), 3.21 (s, 1H), 2.97 (d, J = 6.8 Hz, 2H), 2.93 – 2.71 (m, 4H), 2.02 (s, 1H), 1.79 (s, 1H), 1.64 (s, 2H), 1.02 (s, 12H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.02, 151.90, 139.41, 139.15, 135.36, 134.99, 125.16, 64.73, 53.72, 48.33, 47.74, 43.23, 43.23, 43.05, 43.05, 28.12, 27.26, 26.15, 22.32, 21.59, 21.01, 20.07. CO not observed. IR

(ATR, cm^{-1}, KBr): 1812 (s, ν_{CO}), 1843 (s, ν_{CO}), 1934 (s, ν_{CO}). Anal. Calcd for [$C_{20}H_{29}BrMnN_3O_3$ (Mw: 494.31)]: C, 48.60; H, 5.91; N, 8.50; Found: C, 48.65; H, 5.97; N, 8.44%

d) Y = EtS **Mn-4**[4]



Using a similar procedure and molar ratios to that described for **Mn-1**, **Mn-4** was isolated as a pale-green powder (395 mg, 87%). Single crystals of **Mn-4** were obtained by layering a saturated solution of the complex in dichloromethane with diethyl ether. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.65 (d, J = 1.5 Hz, 1H), 7.83 (d, J = 6.1 Hz, 1H), 7.50 (d, J = 4.6 Hz, 1H), 4.38 (s, 1H), 3.15 – 3.00 (m, 2H), 2.89 (d, J = 8.3 Hz, 1H), 2.83 – 2.60 (m, 4H), 2.09 (s, 1H), 2.04 – 1.74 (m, 4H), 1.72 – 1.56 (m, 1H), 1.36-1.19 (m, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 217.45 (C=O), 211.06 (C=O), 211.00 (C=O), 159.10, 151.69, 140.28, 135.76, 125.97, 63.83, 46.09, 33.02, 31.30, 27.14, 26.19, 21.01, 13.66. IR (ATR, cm^{-1}, KBr): 1917 (s, ν_{CO}), 1947 (s, ν_{CO}), 2027 (s, ν_{CO}). Anal. Calcd for [$C_{16}H_{20}BrMnSN_2O_3$ (Mw: 455.25)]: C, 42.21; H, 4.43; N, 6.15; Found: C, 42.23; H, 4.51; N, 6.08%

2.3 The ^{1}H and ^{13}C NMR spectra for L1 - L4 and Mn-1 – Mn-4

Figure S1 The ^{1}H and ^{13}C NMR spectra for **L1** in $CDCl_3$

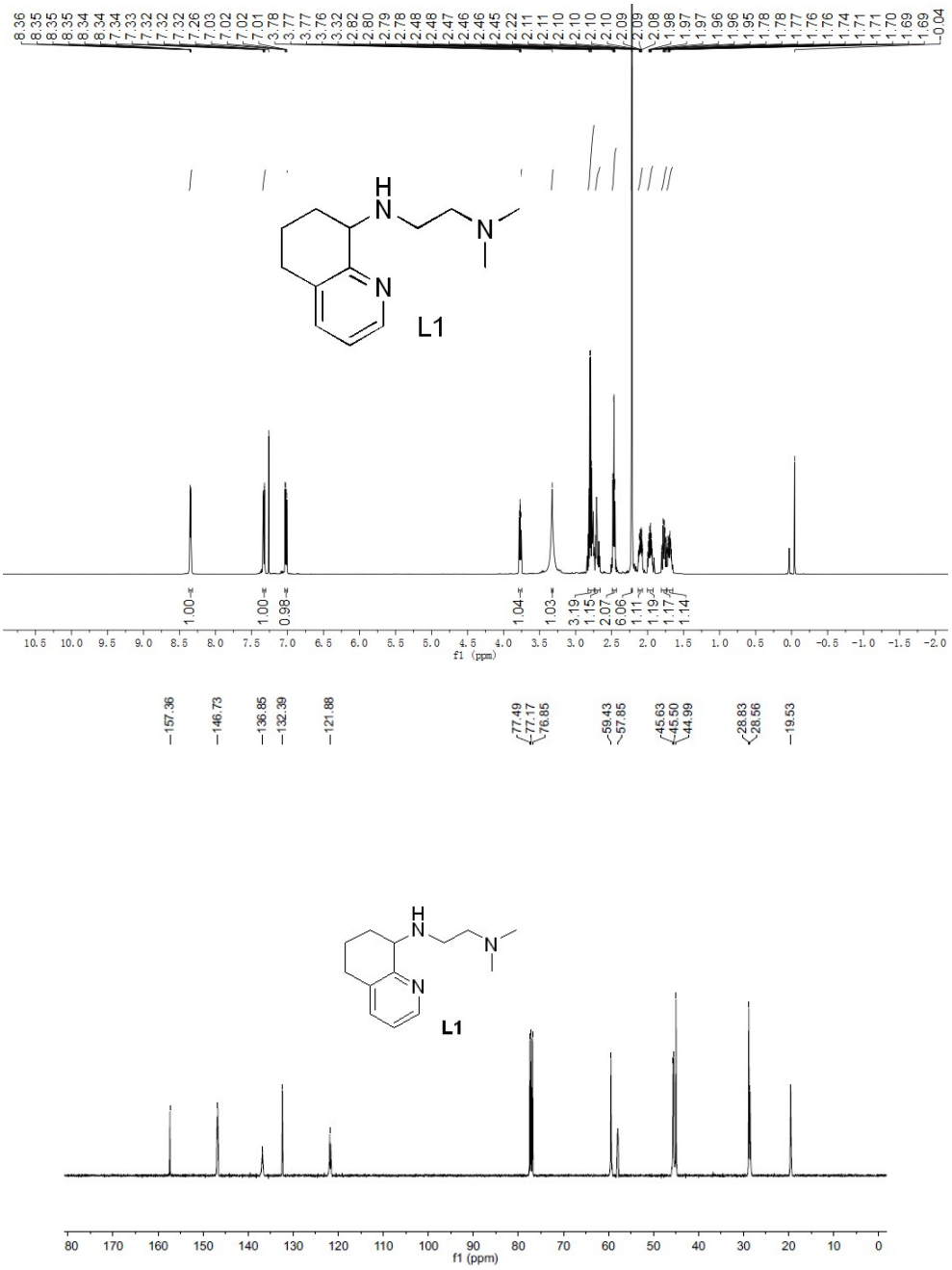


Figure S2 The ^{1}H and ^{13}C NMR spectra for **L2** in $CDCl_3$

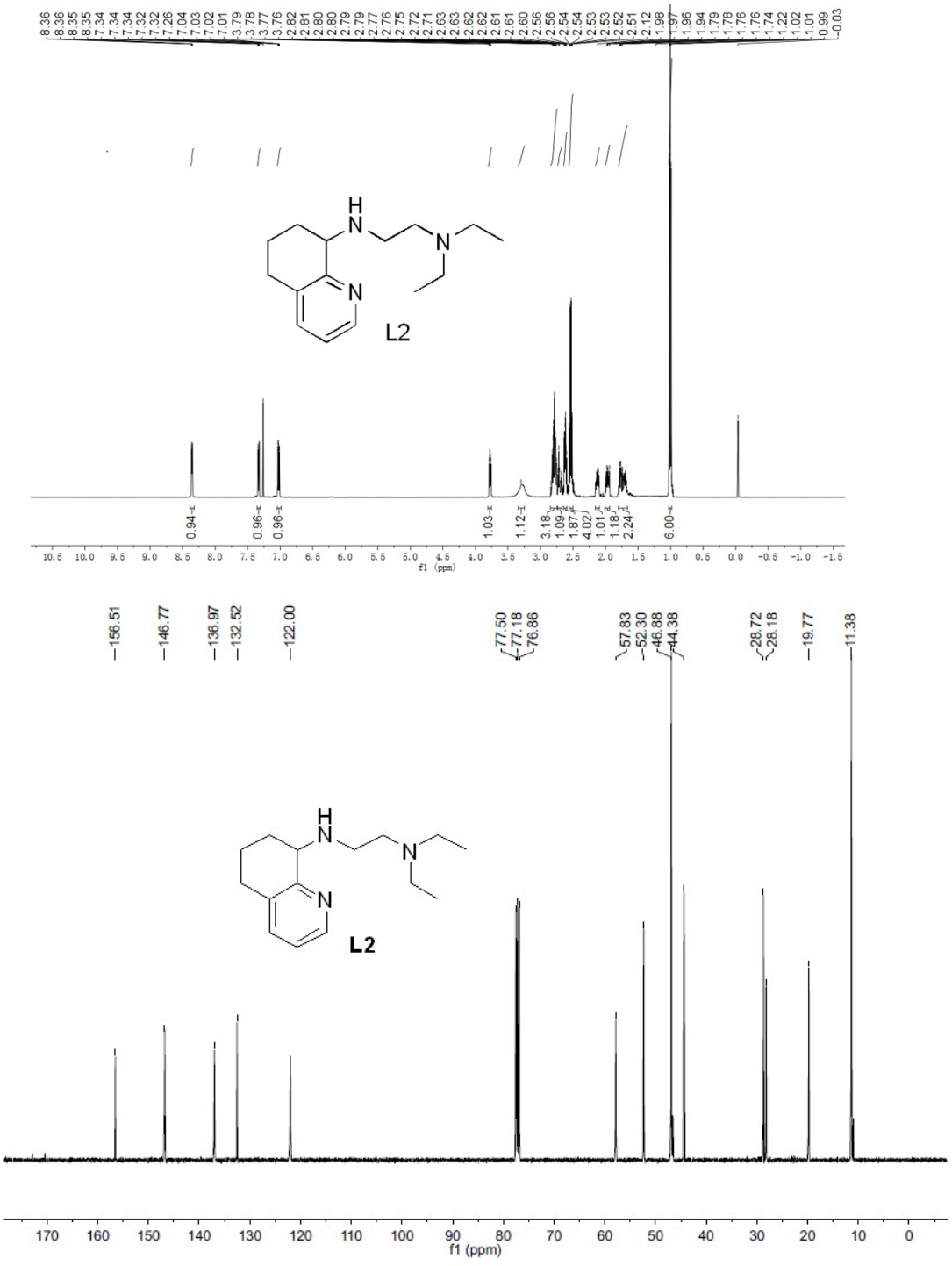


Figure S3 ^{1}H NMR spectrum of **L2**·HCl in D_2O

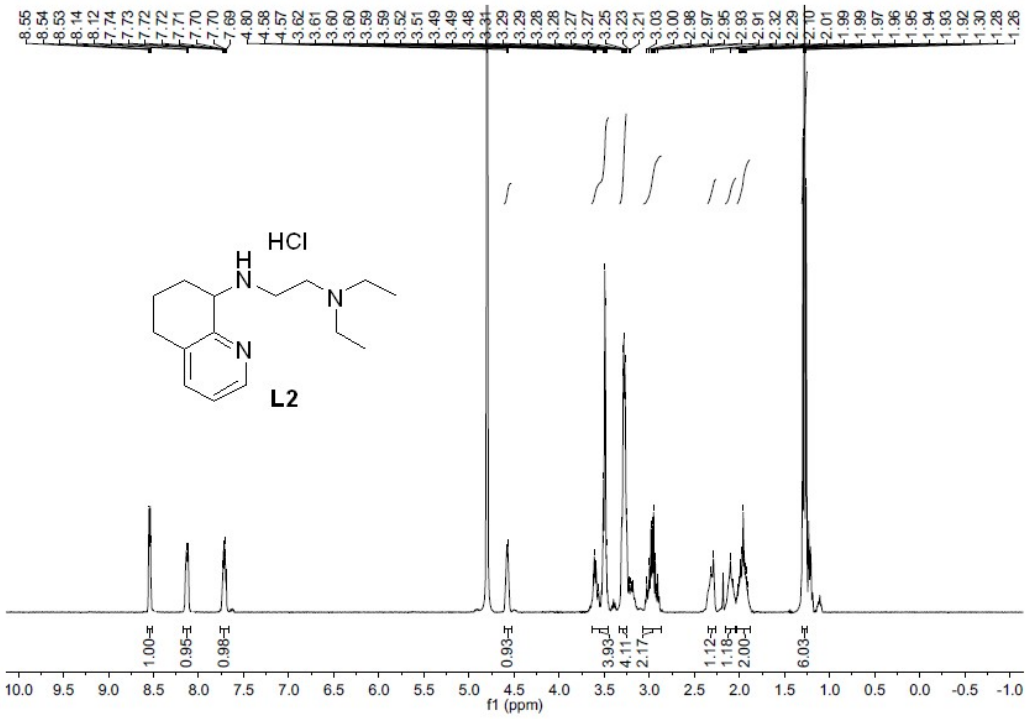


Figure S4 ^{1}H NMR spectrum of **L3** in $CDCl_3$

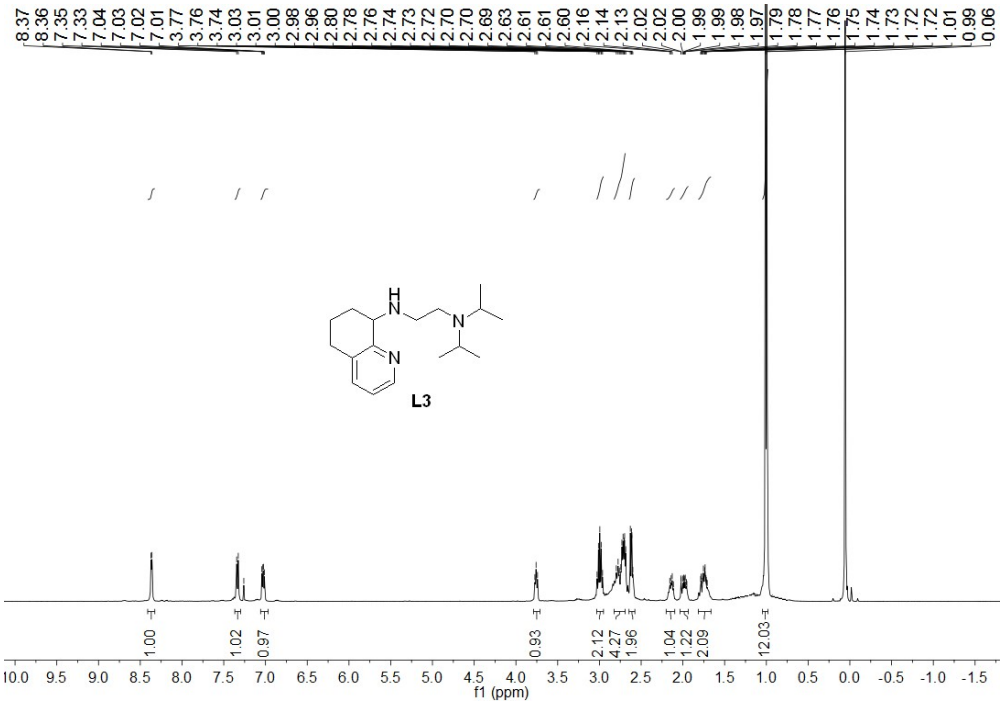


Figure S5 ^{1}H and ^{13}C NMR spectra of **L3**·HCl in DMSO-d_6

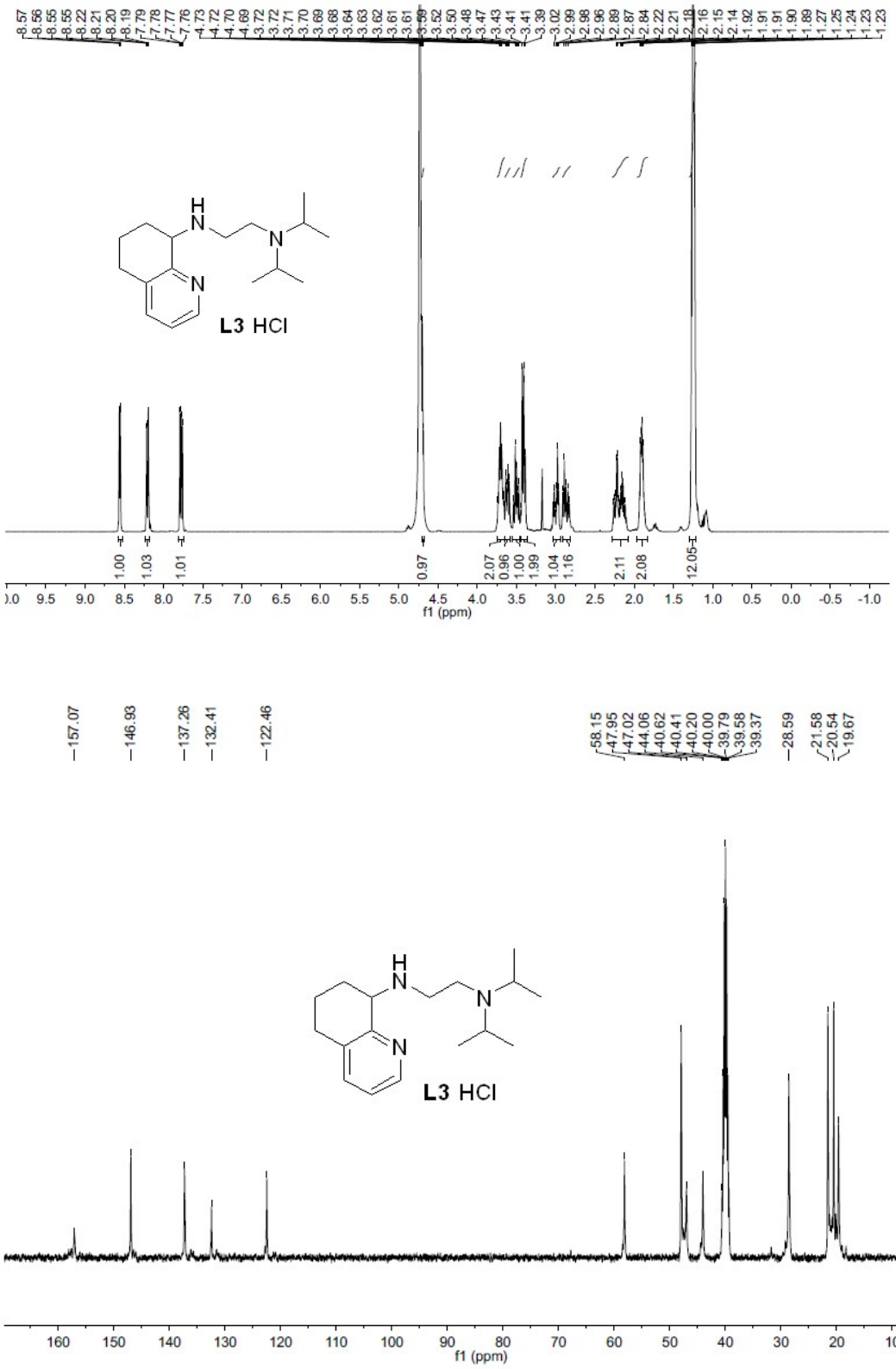


Figure S6 ^{1}H NMR spectrum of 2-(ethylthio)ethan-1-amine in DMSO-d_6

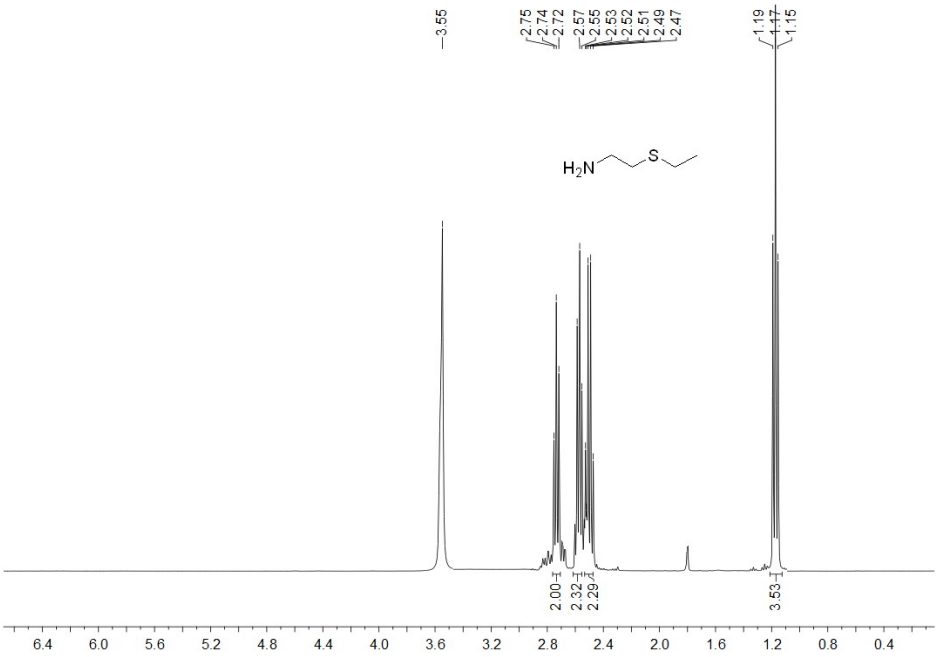
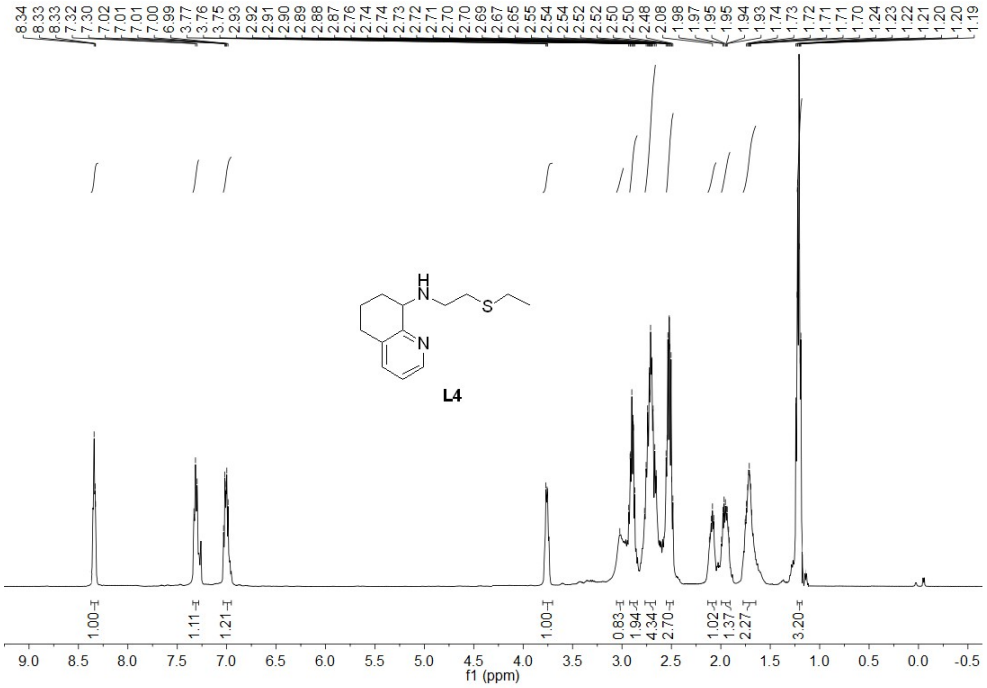


Figure S7 ^{1}H and ^{13}C NMR spectra of **L4** in DMSO-d_6



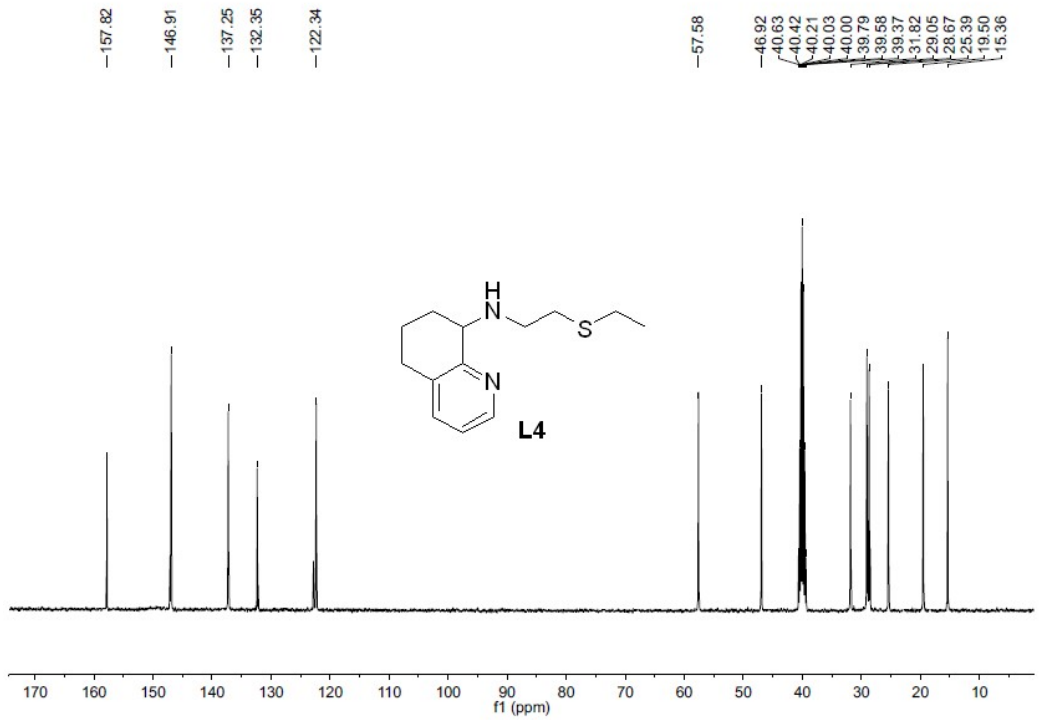
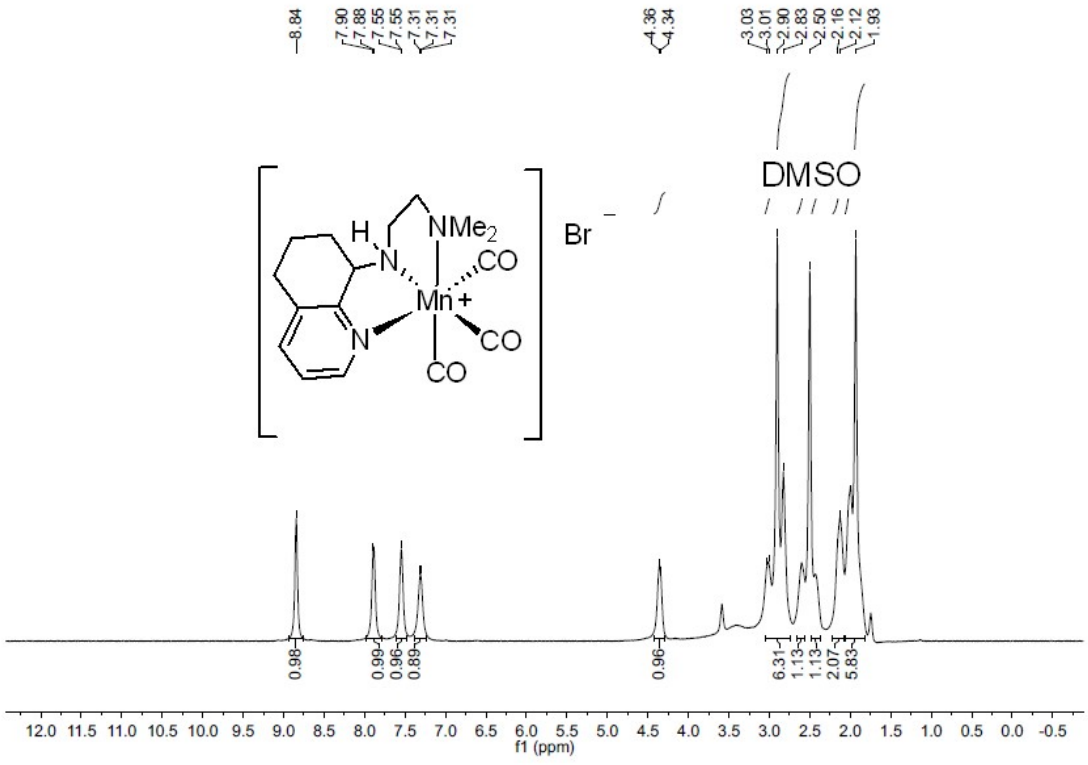


Figure S8 ^{1}H and ^{13}C NMR spectra of **Mn-1** in DMSO-d_6



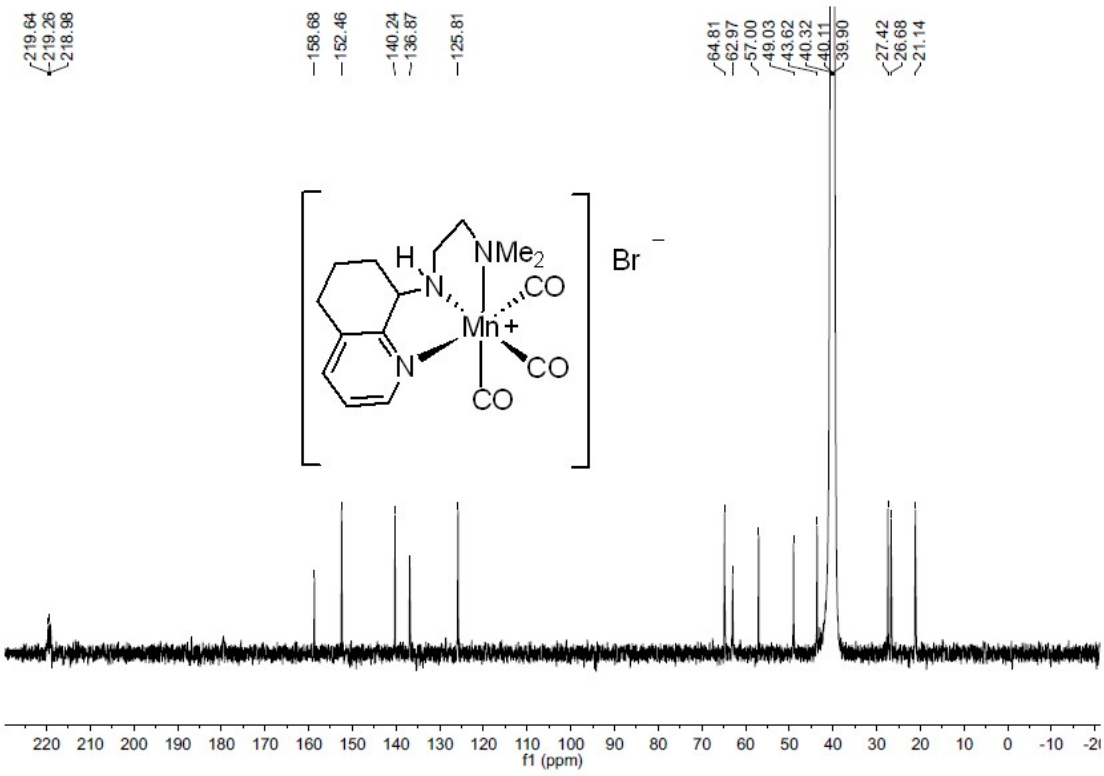
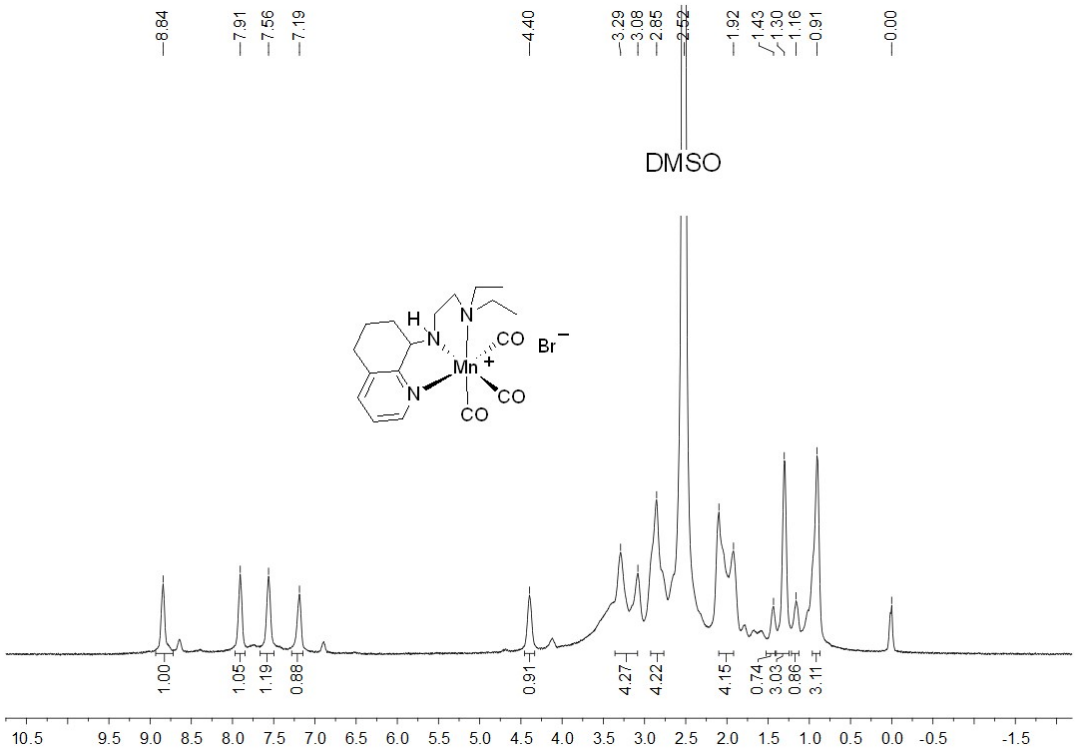


Figure S9 ^{1}H and ^{13}C NMR spectra of **Mn-2** in DMSO-d_6



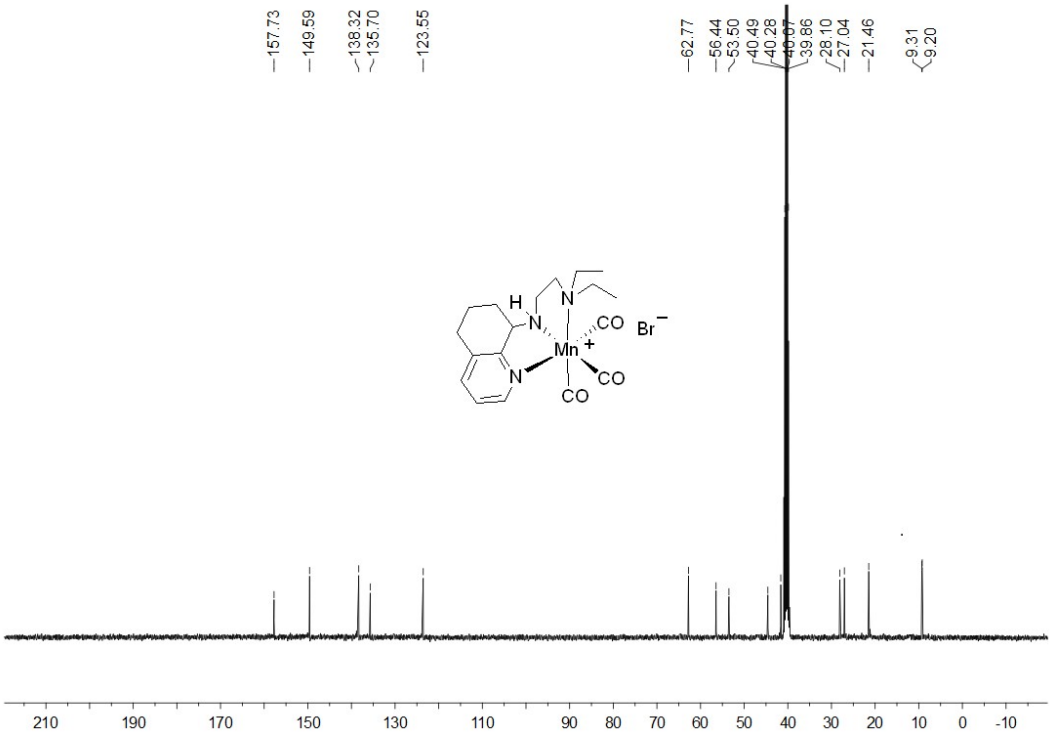
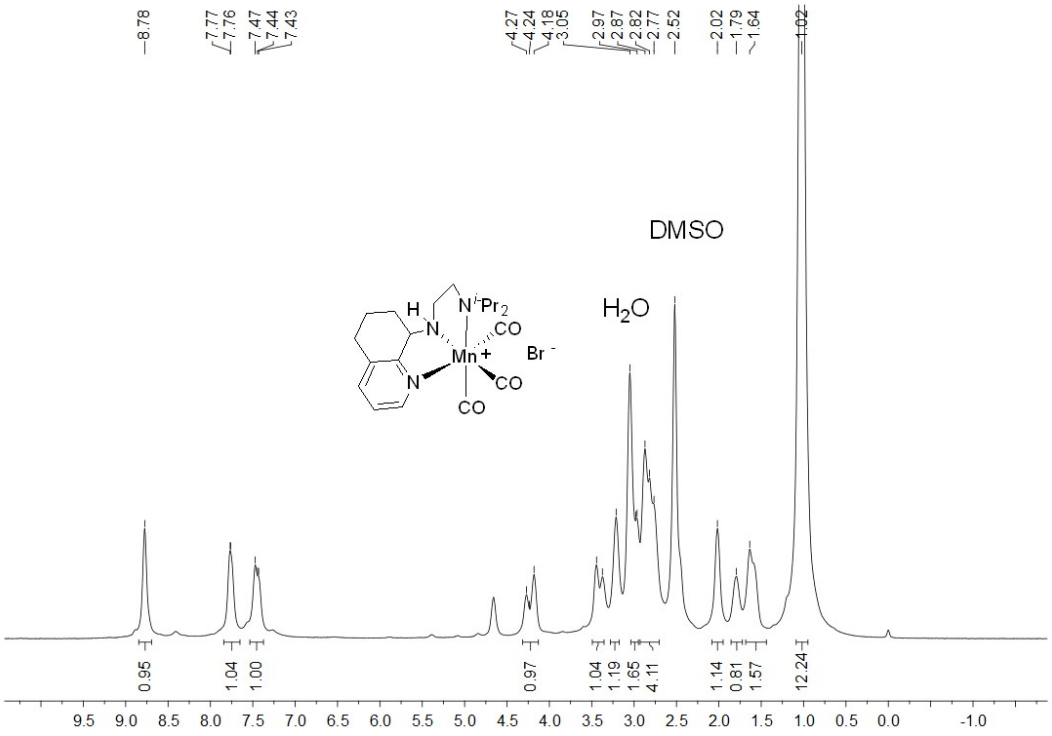


Figure S10 ^{1}H and ^{13}C NMR spectra of **Mn-3** in DMSO-d_6



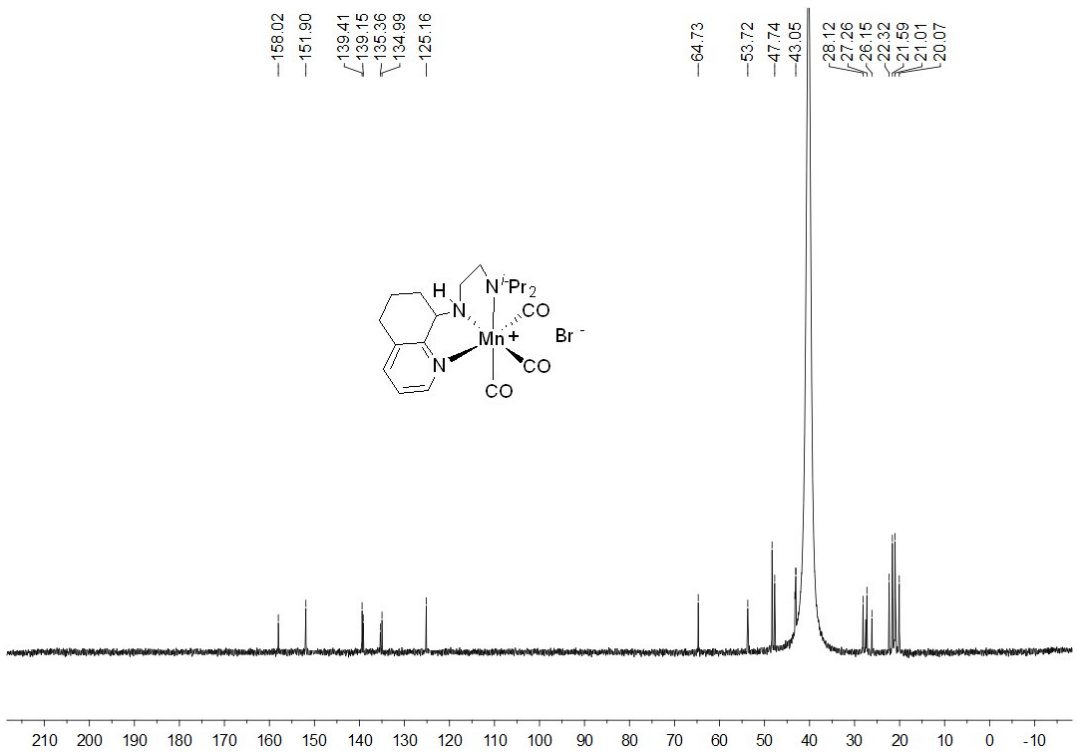
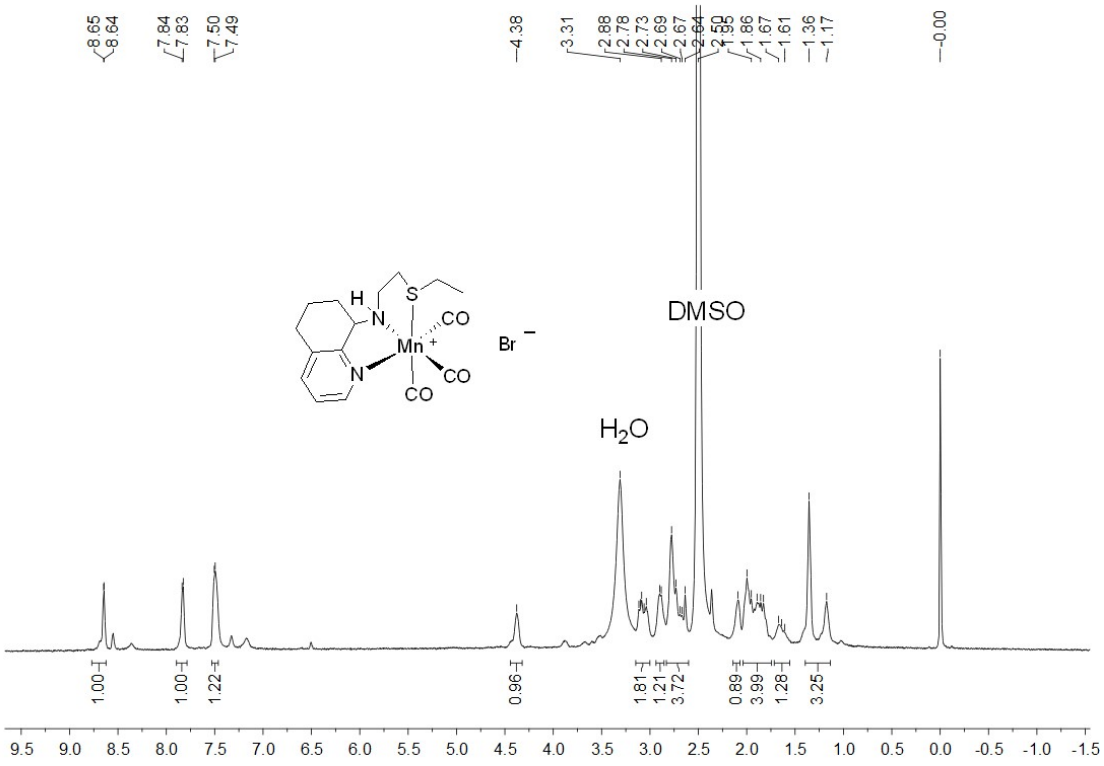
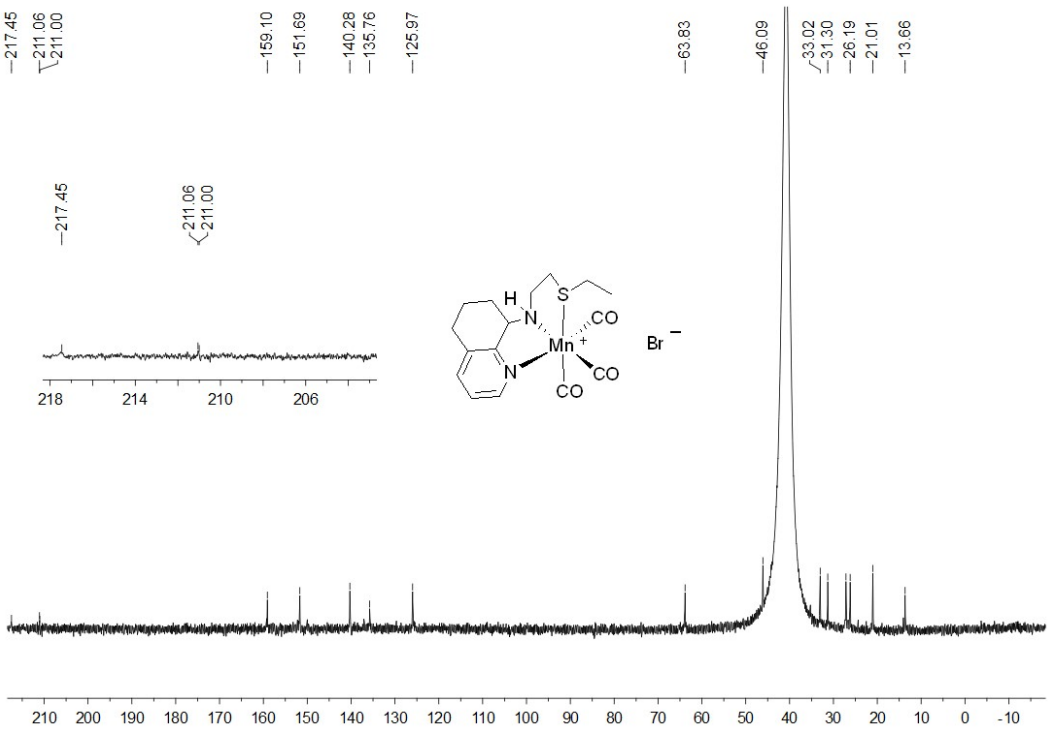


Figure S11 ^{1}H and ^{13}C NMR spectra of **Mn-4** in DMSO-d_6

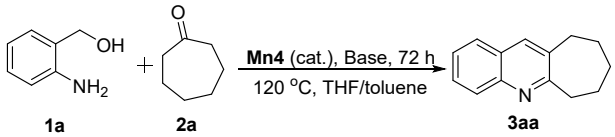




3 Manganese catalyzed synthesis of quinolines and pyridines by the reaction of an amino alcohol with a ketone or alcohol

3.1 General Procedure for the coupling cyclization of 2-aminobenzyl alcohol (**1a**) with cycloheptanone (**2a**) to give 7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline (**3aa**). Under a nitrogen atmosphere, a 25 mL dried Schlenk tube was charged with 2-aminobenzyl alcohol (**1a**, 0.5 – 2.0 mmol), cycloheptanone (**2a**, 0.5 – 4.0 mmol) or cycloheptanol (0.5 – 4.0 mmol), the manganese complex (1.0 – 50.0 μmol, **Mn1** - **Mn5**, 0.05 - 5.0 mol%), the desired amount of base (*t*-BuOK, *t*-BuONa, *i*-PrONa, NaOMe KOH, NaOH, Cs_2CO_3 LiOH, $Ca(OH)_2$, K_2CO_3, Na_2CO_3, quinoline, pyridine or pyrrole) (0.5 – 4.0 mmol) and the solvent (THF/toluene, 1,4-dioxane, diglyme, 2-methoxyethanol, DMF, MeCN, 2-butanol, isoamyl alcohol, N-methylaniline, N,N-dimethylaniline, CCl_4, quinoline, pyrrole) to be used (0 – 5 mL). The mixture was heated to the desired temperature (bath temperature, 40 – 120 °C) and the contents stirred. After the desired reaction time (3 – 48 h), the mixture was cooled to room temperature and the pressure slowly released. The reaction mixture was filtered through a plug of silica gel and then analyzed by GC. The crude product was purified by flash chromatography.

Table S1 Screening of base[a]



1a 2a 3aa

Run	Base	Conv. (%)[b]	GC yield of **3aa** (%)[b]	Sel. of **3aa** (%)[b]
1	*t*-BuOK	76	75	98
2	*t*-BuONa	56	55	98
3	*i*-PrONa	41	31	75
4	EtONa	33	28	85
5	MeONa	62	61	98
6	KOH	89	85	95
7	NaOH	72	70	97
8	$CsCO_3$	77	66	86
9	LiOH	2	1	55
10	$Ca(OH)_2$	45	25	55
11	K_2CO_3	10	5	50
12	Na_2CO_3	11	8	72
13	Pyridine	50	nr	--
14	Pyrrole	60	nr	--
15[c]	KOH+*t*-BuOK	98	95	97
16[cd]	KOH+*t*-BuOK	99	98	99
17[cde]	KOH+*t*-BuOK	99	97	98
18[cdef]	KOH+*t*-BuOK	99	75	48

[a] Reaction conditions: 0.5 mmol of 2-aminobenzyl alcohol (**1a**), 1.0 mmol of cycloheptanone (**2a**), 10 μmol of **Mn**-**4**, 1.0 mmol of base, 4 mL of toluene and 1 mL of THF, 120 °C, 72 h, under N_2;

[b] The conversion (with reference to **1a**) and yield were determined by GC with mesitylene as an internal standard. The selectivity of **3aa** (with reference to all products formed from **1a**) was determined by GC analysis. Note: the by-products were reaction intermediates such as **8**, **9** and **10**;

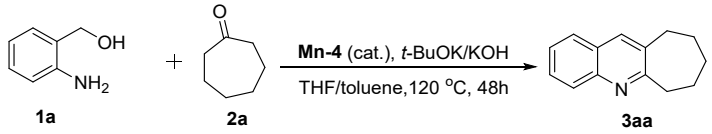
[c] 1.0 mmol of KOH and 1.0 mmol of *t*-BuOK;

[d] 2 mL of toluene and 0.5 mL of THF, 120 °C;

[e] 48 h;

[f] In the absence of **Mn-4**.

Table S2 Screening of the ratio of *t*-BuOK and KOH[a]

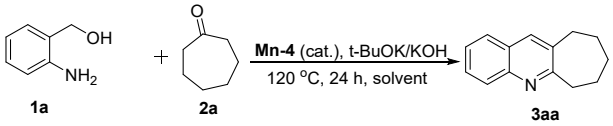


1a 2a 3aa

Run	*t*-BuOK (X mmol)	KOH (Y mmol)	Conv. (%)[b]	GC yield of **3aa** (%)[b]	Sel. of **3aa** (%)[b]
1	1.00	1.00	99	97	98
2	0.50	0.50	98	90	91
3	0.25	0.50	94	88	93
4	0.25	0.25	91	82	90
5	0.25	0.50	91	80	88
6[c]	1.00	1.00	99	96	97
7[c]	0.50	0.50	84	75	89

[a] Reaction conditions: 0.5 mmol of 2-aminobenzyl alcohol (**1a**), 1.0 mmol of cycloheptanone (**2a**), 10 μmol of **Mn-4**, 2 mL of toluene and 0.5 mL of THF, 120 °C, 48 h, under N_2;
[b] The conversion (with reference to **1a**) and yield were determined by GC with mesitylene as an internal standard. The selectivity of **3aa** (with reference to all products formed from **1a**) was determined by GC analysis. Note: the by-products were reaction intermediates such as **8**, **9** and **10**;
[c] 24 h.

Table S3 Screening of reaction solvents[a]

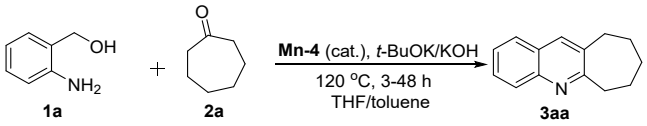


Run	Solvent	Conv. (%)[b]	**3aa** (%)[b]	Sel. of **3aa** (%)[b]
1	THF/toluene	99	96	97
2	1,4-dioxane	96	94	96
3	diglyme	97	91	93
4	2-methoxyethanol	86	85	98
5	DMF	28	22	78
6	DMSO	90	66	73
7	MeCN	25	<1	--
8	2-butanol	95	41	43
9	3-methyl-1-butanol	88	52	59
10	*N*-methylaniline	92	89	96
11	*N*,*N*-dimethylaniline	85	80	94
12	CCl_4	95	68	71
13	quinoline	82	73	89
14	pyrrole	89	52	58

[a] Reaction conditions: 0.5 mmol of 2-aminobenzyl alcohol (**1a**), 1.0 mmol of cycloheptanone (**2a**), 10 μmol of **Mn-4**, 1.0 mmol of *t*-BuOK and 1.0 mmol KOH, 2 mL of toluene and 0.5 mL of THF, 120 °C, 24 h, under N_2;

[b] The conversion (with reference to **1a**) and yield were determined by GC with mesitylene as an internal standard. The selectivity of **3aa** (with reference to all products formed from **1a**) was determined by GC analysis. Note: the by-products were reaction intermediates such as **8**, **9** and **10**.

Table S4 Screening of reaction times[a]

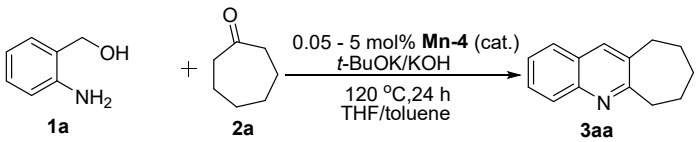


Run	Time (h)	Conv. (%)[b]	GC yield of **3aa** (%)[b]	Sel. of **3aa** (%)[b]
1	3	66	59	89
2	6	72	64	88
3	9	78	68	87
4	12	85	75	88
5	24	99	96	97
6	48	99	97	98

[a] Reaction conditions: 0.5 mmol of 2-aminobenzyl alcohol (**1a**), 1.0 mmol of cycloheptanone (**2a**), 10 μmol of **Mn-4**, 1.0 mmol of *t*-BuOK, 1.0 mmol of KOH, 2 mL of toluene and 0.5 mL of THF, 120 °C, 3 - 48 h, under N_2;

[b] The conversion (with reference to **1a**) and yield were determined by GC with mesitylene as an internal standard. The selectivity of **3aa** (with reference to all products formed from **1a**) was determined by GC analysis. Note: the byproducts were reaction intermediates such as **8**, **9** and **10**.

Table S5 Screening of catalyst loading[a]

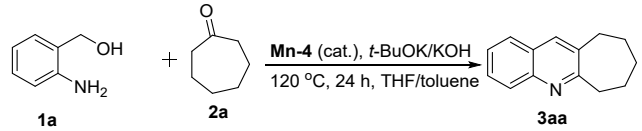


Run	S:C	**Mn-4** (mol%)	Conv. (%)[b]	GC yield of **3aa** (%)[b]
1	20	5.0	100	98
2	50	2.0	99	96
3	100	1.0	99	95
4	400	0.25	99	90
5	1000	0.10	75	68
6	2000	0.05	54	42

[a] Reaction conditions: 0.5 - 2.0 mmol of 2-aminobenzyl alcohol (**1a**), 1.0 - 4.0 mmol of cycloheptanone (**2a**), 1.0 - 4.0 mmol of *t*-BuOK, 1.0 - 4.0 mmol of KOH, 1.0 - 10 μmol of **Mn-4**, 2 - 4 mL of toluene and 0.5 - 1 mL of THF, 120 °C, 24 h, S:C = the substrate to catalyst molar ratio, under N_2;

[b] The conversion (with reference to **1a**) and yield were determined by GC with mesitylene as an internal standard.

Table S6 Screening of equivalents of cycloheptanone (**2a**) with respect to **1a**[a]



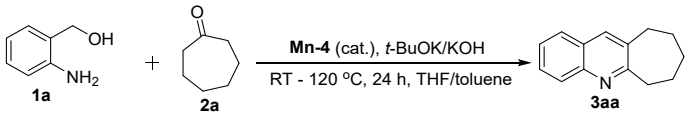
1a **2a** **3aa**

Run	**2a** (mmol)	Conv. (%)[b]	GC yield of **3aa** (%)[b]
1	0.50 (1.0 eq.)	70	66
2	0.75 (1.5 eq.)	95	90
3	1.00 (2.0 eq.)	99	95
4	1.50 (3.0 eq.)	89	85

[a] Reaction conditions: 0.5 mmol of 2-aminobenzyl alcohol (**1a**), 0.5 - 1.5 mmol of cycloheptanone (**2a**), 1.0 mmol of *t*-BuOK, 1.0 mmol of KOH, 5.0 μmol of **Mn-4**, 2 mL of toluene and 0.5 mL of THF, 120 °C, 24 h, under N_2;

[b] The conversion (with reference to **1a**) and yield were determined by GC with mesitylene as an internal standard.

Table S7 Screening of reaction temperature.[a]



1a **2a** **3aa**

Run	T (°C)	Conv. (%)[b]	GC yield of **3aa** (%)[b]
1	20	12	9
2	40	25	20
3	60	35	31
4	80	80	69
5	100	90	85
6	120	99	95
7[c]	120	99	95

[a] Reaction conditions: 0.5 mmol of 2-aminobenzyl alcohol (**1a**), 1.0 mmol of cycloheptanone (**2a**), 1.0 mmol of *t*-BuOK, 1.0 mmol of KOH, 5.0 μmol of **Mn-4**, 2.0 mL of toluene and 0.5 mL of THF, 20 - 120 °C, 24 h, under N_2;

[b] The conversion (with reference to **1a**) and yield were determined by GC with mesitylene as an internal standard;

[c] 1 mmol of **1a**, 2.0 mmol of **2a**, 2.0 mmol of *t*-BuOK, 2.0 mmol of KOH, 10 μmol of **Mn-4**, 4.0 mL of toluene and 1.0 mL of THF, 120 °C, 24 h.

3.2 General experimental procedures for the synthesis of the 2-substituted or 2,3-substituted quinolines (3aa – 3av)

Reaction conditions A

This procedure makes use of a ketone as the reaction partner.

Under a nitrogen atmosphere, a dry 25 mL Schlenk tube was loaded with firstly 2-aminobenzyl alcohol (**1a**, 1.0 mmol), *t*-BuOK (2.0 mmol), KOH (2.0 mmol), **Mn-4** (10.0 μmol) and the corresponding ketone (**2a** -

2v, 2.0 mmol) and then toluene (4 mL) and THF (1 mL) added. After sealing the Schlenk tube, the reaction mixture was stirred and heated at 120 °C for 24 h. Once cooled to room temperature, the reaction mixture was treated with ethyl acetate (5 mL) and then concentrated under reduced pressure. The residue was purified by flash column chromatography using a gradient of petroleum ether and ethyl acetate (eluent system) to afford the pure product (**3aa** – **3av**).

Reaction conditions B

This procedure makes use of a secondary alcohol as the reaction partner.

Under a nitrogen atmosphere, a dry 25 mL Schlenk tube was loaded firstly with 2-aminobenzyl alcohol (**1a**, 1.0 mmol), *t*-BuOK (2.0 mmol), KOH (2.0 mmol), **Mn-4** (50.0 μmol) and the corresponding secondary alcohol (**2a'** - **2v'**, 2.0 mmol) and then toluene (4 mL) and THF (1 mL) added. After sealing the Schlenk tube, the reaction mixture was stirred and heated at 120 °C for 48 h. Once cooled to room temperature, the reaction mixture was treated with ethyl acetate (5 mL) and then concentrated under reduced pressure. The residue was purified by flash column chromatography using a gradient of petroleum ether and ethyl acetate (eluent system) to afford the pure product (**3aa** – **3av**).

3.3 General experimental procedure for the synthesis of 2,3,4-substituted or 2,3,6-substituted quinolines (3)

Under a nitrogen atmosphere, a dry 25 mL Schlenk tube was loaded firstly with the aryl γ-amino alcohol (**1b** - **1e**, 1.0 mmol), *t*-BuOK (2.0 mmol), KOH (2.0 mmol), **Mn-4** (10 μmol) and the ketone (2.0 mmol) and then toluene (4 mL) and THF (1 mL) added. After sealing the Schlenk tube, the reaction mixture was stirred and heated at 120 °C for 24 h. Once cooled to room temperature, the reaction mixture was treated with ethyl acetate (5 mL) then concentrated under reduced pressure. The residue was purified by flash column chromatography using a gradient of petroleum ether and ethyl acetate (eluent system) to afford the pure products.

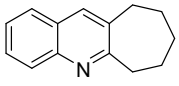
3.4 General experimental procedure for the synthesis of 2,3-substituted or 2,3,6-substituted pyridines (4)

Under a nitrogen atmosphere, a dry 25 mL Schlenk tube was loaded with the γ-amino alcohol (**1f** - **1h**, 1.0 mmol), *t*-BuOK (2.0 mmol), KOH (2.0 mmol), **Mn-4** (10 μmol) and the ketone (2.0 mmol) and then toluene (4.0 mL) and THF (1 mL) added. After sealing the Schlenk tube the reaction mixture was stirred and heated at 120 °C for 24 h. Once cooled to room temperature, the reaction mixture was treated with ethyl acetate (5 mL) and then concentrated under reduced pressure. The residue was purified by flash column chromatography using a gradient of petroleum ether and ethyl acetate (eluent system) to afford the pure product.

4. Characterization data for the products[1b,4b,5-11]

In sub-sections 4.1 to 4.22, '&' refers to the isolated yield of the product using conditions in method A while 'Φ' refers to the isolated yield of the product using conditions in method B (see section 3.2).

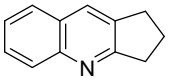
4.1. 7,8,9,10-Tetrahydro-6H-cyclohepta[*b*]quinoline (**3aa**)[1b,9,10a]



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200:1 to 10:1. Pale-yellow solid (&91% and Φ72%, &180 mg and Φ141 mg). Mp: 62–63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ

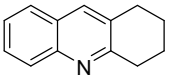
8.01 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.49 – 7.40 (m, 1H), 3.24 – 3.18 (m, 2H), 2.94 (dd, *J* = 6.5, 4.4 Hz, 2H), 1.89 (d, *J* = 5.3 Hz, 2H), 1.84 – 1.70 (m, 4H). NMR ($CDCl_3$, 125 MHz) δ 164.70, 146.28, 136.52, 134.57, 128.48, 128.46, 127.38, 126.81, 125.74, 40.10, 35.47, 32.26, 28.88, 27.04.

4.2. 2,3-Dihydro-1H-cyclopenta[*b*]quinoline (3ab)[1b]



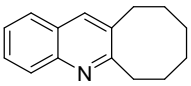
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 10/1. Pale-yellow oil (&56% and Φ36%, &94 mg and Φ60 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.77 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 3.09 (t, *J* = 7.5 Hz, 2H), 2.98 (t, *J* = 7.1 Hz, 2H), 2.13 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.76, 146.27, 134.57, 129.35, 127.33, 127.30, 126.38, 126.31, 124.46, 33.44, 29.40, 22.55.

4.3 1,2,3,4-Tetrahydroacridine (3ac)[5a,8a,9]



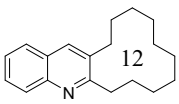
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 100/1 to 10/1. Pale-yellow solid (&76% and Φ51%, &140 mg and Φ93 mg). Mp: 51–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.78 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.42 (dd, *J* = 11.1, 3.9 Hz, 1H), 3.13 (t, *J* = 6.5 Hz, 2H), 2.96 (t, *J* = 6.3 Hz, 2H), 2.04 – 1.94 (m, 2H), 1.93 – 1.83 (m, 2H); ^{13}CNMR ($CDCl_3$, 125 MHz) δ 159.33, 146.65, 134.95, 130.97, 128.47, 128.32, 127.22, 126.69, 125.52, 33.61, 29.28, 23.25, 22.93.

4.4 6,7,8,9,10,11-Hexahydrocycloocta[*b*]quinoline (3ad)[1b,7a]



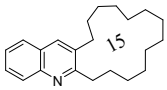
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 10/1. Pale-yellow solid (&92% and Φ75%, &194 mg and Φ150 mg). Mp: 72–73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 3.17 – 3.12 (m, 2H), 2.96 – 2.92 (m, 2H), 1.87 (dd, *J* = 9.9, 7.2 Hz, 2H), 1.76 (d, *J* = 1.9 Hz, 2H), 1.41 – 1.37 (m, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.11, 145.93, 134.06, 133.93, 127.45, 127.33, 126.57, 125.80, 124.48, 34.21, 31.65, 31.01, 29.93, 25.00, 24.86.

4.5 6,7,8,9,10,11,12,13,14,15-Decahydrocyclododeca[*b*]quinoline (3ae)[10a]



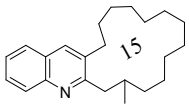
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 15/1. Pale-yellow solid (&81% and Φ65%, &216 mg and Φ173 mg). Mp: 88–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.88 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 3.02 (t, *J* = 7.7 Hz, 2H), 2.82 (t, *J* = 7.8 Hz, 2H), 1.94 (d, *J* = 11.7 Hz, 2H), 1.78 (d, *J* = 13.4 Hz, 2H), 1.58 – 1.41 (m, 12H).^{13}C NMR (100 MHz, $CDCl_3$) δ 161.62, 145.54, 134.72, 133.79, 127.35, 126.11, 125.76, 124.48, 31.67, 28.71, 28.62, 27.45, 25.68, 25.44, 24.99, 24.41, 22.06, 21.97.

4.6. 7,8,9,10,11,12,13,14,15,16,17,18-Dodecahydro-6H-cyclopentadeca[*b*]quinoline (3af)[10d]



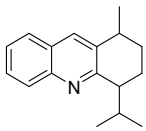
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow solid (&64% and Φ42%, &210 mg and Φ129 mg). Mp: 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.68 (s, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 2.92 – 2.80 (m, 2H), 2.70 – 2.57 (m, 2H), 1.80 – 1.68 (m, 2H), 1.63 – 1.55 (m, 2H), 1.51 – 1.18 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.86, 146.15, 134.84, 133.90, 128.02, 126.93, 126.44, 125.15, 35.47, 34.89, 32.01, 28.93, 27.89, 27.03, 26.79, 26.50, 26.45, 26.27, 26.24, 25.64, 25.20, 22.90.

4.7. 7-Methyl-7,8,9,10,11,12,13,14,15,16,17,18-dodecahydro-6H-cyclopentadeca[*b*]quinoline (3ag)



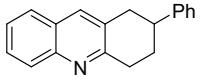
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow oil (&74% and Φ46%, &240 mg and Φ148 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.83 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.45 – 7.38 (m, 1H), 3.22 (dd, *J* = 13.3, 4.8 Hz, 1H), 2.78 (t, *J* = 8.2 Hz, 2H), 2.67 (dd, *J* = 13.3, 10.0 Hz, 1H), 2.19 – 2.06 (m, 1H), 1.87 – 1.75 (m, 1H), 1.72 – 1.65 (m, 1H), 1.63 – 1.56 (m, 1H), 1.49 – 1.31 (m, 17H), 0.92 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.24, 145.10, 133.71, 133.52, 127.55, 127.21, 126.23, 125.75, 124.50, 42.63, 35.12, 30.53, 30.35, 27.40, 26.35, 25.49, 25.39, 25.37, 24.95, 24.89, 24.61, 24.00, 18.33.

4.8. 4-Isopropyl-1-methyl-1,2,3,4-tetrahydroacridine (3ah)[7a]



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (&71% and Φ48%, &170 mg and Φ114 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 1H), 7.81 (s, 1H), 7.64 (t, *J* = 8.4 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.38 – 7.32 (m, 1H), 3.05 –2.99 (m, 1H), 2.91 –2.84 (m, 1H), 2.01 – 1.92 (m, 1H), 1.84 –1.78 (m, 1H), 1.70-1.63 (m, 1H), 1.31 (dd, *J* = 18.5, 7.0 Hz, 3H), 1.19 (d, *J* = 13.6 Hz, 2H), 1.01 (dd, *J* = 22.7, 6.9 Hz, 3H), 0.63 (dd, *J* = 41.2, 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.59, 136.04, 135.72, 133.32, 131.48, 127.53, 126.03, 125.81, 124.43, 45.88, 32.24, 31.80, 30.25, 27.50, 22.06, 20.68, 20.16, 19.98.

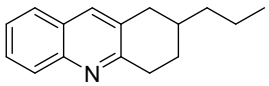
4.9. 2-Phenyl-1,2,3,4-tetrahydroacridine (3ai)[7b]



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 15/1. Pale-yellow solid (&78% and Φ51%, &202 mg and Φ132 mg). Mp: 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.75 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.22 (m, 4H), 7.21 – 7.15 (m, 1H), 3.31 – 3.23 (m, 1H), 3.22 – 3.12 (m, 2H), 3.04 (d, *J* = 11.0 Hz, 2H), 2.29 – 2.22 (m, 1H), 2.15 – 2.01 (m, 1H), 1.32 – 1.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.71, 147.00,

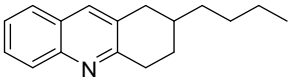
145.93, 135.44, 130.61, 129.06, 128.91, 128.57, 127.40, 127.25, 127.10, 126.79, 126.03, 40.67, 37.64, 33.86, 30.71.

4.10. 2-Propyl-1,2,3,4-tetrahydroacridine (3aj)[7c]



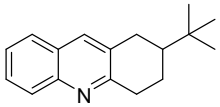
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 15/1. Pale-yellow solid (&73% and Φ39%, &165 mg and Φ88 mg). Mp: 54 –55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.83 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 3.31 – 3.22 (m, 1H), 3.15-3.04 (m, 2H), 2.61 (dd, *J* = 16.4, 10.6 Hz, 1H), 2.18 – 2.07 (m, 1H), 1.90 – 1.82 (m, 1H), 1.65–1.55 (m, 1H), 1.51 – 1.36 (m, 4H), 0.96 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.29, 146.66, 135.00, 130.61, 128.46, 128.28, 127.17, 126.88, 125.49, 38.39, 35.90, 33.71, 33.07, 29.37, 20.12, 14.34.

4.11. 2-Butyl-1,2,3,4-tetrahydroacridine (3ak)



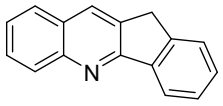
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 15/1. Pale-yellow solid (&72% and Φ40%, &175 mg and Φ95mg). Mp: 59–60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.79 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 3.26 – 3.18 (m, 1H), 3.12 – 3.02 (m, 2H), 2.59 (dd, *J* = 16.3, 10.7 Hz, 1H), 1.84 – 1.67 (m, 2H), 1.60 – 1.53 (m, 1H), 1.35 – 1.26 (m, 6H), 0.90 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.08, 146.50, 134.93, 130.46, 128.36, 128.13, 127.09, 126.79, 125.39, 36.07, 35.82, 33.91, 32.91, 32.06, 29.27, 26.64, 22.64, 14.07.

4.12. 2-(tert-Butyl)-1,2,3,4-tetrahydroacridine (3al)



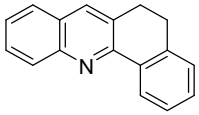
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 15/1. Pale-yellow solid (&58% and Φ38%, &142 mg and Φ91 mg). Mp: 85–86 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.79 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 3.31 – 3.23 (m, 1H), 3.08 – 2.98 (m, 2H), 2.70 (dd, *J* = 16.0, 11.5 Hz, 1H), 2.20 – 2.12 (m, 1H), 1.60 – 1.51 (m, 2H), 0.99 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.36, 146.58, 135.23, 131.22, 128.45, 128.27, 127.17, 126.85, 125.48, 44.62, 34.33, 32.54, 30.78, 27.27, 24.58.

4.13. 11*H*-Indeno[1,2-*b*]quinoline (3am)[5a]



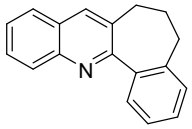
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 10/1. Pale-yellow oil (&52% and Φ32%, &115 mg and Φ70 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.9 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.07 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.60 (dd, *J* = 12.6, 5.5 Hz, 2H), 7.51 (d, *J* = 6.7 Hz, 1H), 7.43 – 7.39 (m, 2H), 3.93 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.63, 146.98, 144.04, 139.29, 133.55, 130.12, 128.93, 128.04, 127.78, 126.73, 126.48, 124.63, 124.41, 121.04, 32.96.

4.14. 5,6-Dihydrobenzo[*c*]acridine (3an)[5a,6.8a]



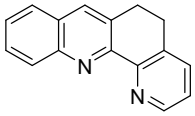
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 5/1. White solid (&82% and Φ61%, &190 mg and Φ140 mg). Mp: 62–63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.1 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.93 (d, *J* = 7.0 Hz, 1H), 2.53 (d, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.19, 146.10, 138.91, 138.08, 133.60, 132.11, 128.16, 127.92, 127.71, 127.27, 126.61, 125.91, 125.82, 125.55, 125.14, 124.85, 29.72, 29.36.

4.15. 6,7-Dihydro-5*H*-benzo[6,7]cyclohepta[1,2-*b*]quinoline (3ao)[6]



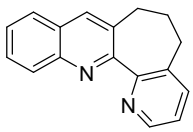
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 5/1. White solid (&79% and Φ65%, &194 mg and Φ159 mg). Mp: 66–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.2 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.65 (s, 1H), 7.49 (dd, *J* = 20.3, 7.9 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 2.83 (dd, *J* = 31.5, 6.1 Hz, 4H), 1.14 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.18, 147.46, 139.24, 134.55, 133.52, 130.38, 129.52, 129.25, 128.47, 127.80, 127.70, 127.15, 126.80, 125.93, 125.87, 29.62, 28.61, 28.20.

4.16. 5,6-Dihydrobenzo[*b*][1,10]phenanthroline (3ap)[6]



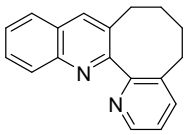
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 3/1. Purple solid (&73% and Φ48%, &170 mg and Φ111 mg). Mp: 89–90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.35 (d, *J* = 6.9 Hz, 1H), 7.93 (d, *J* = 6.3 Hz, 1H), 7.72 (d, *J* = 6.5 Hz, 1H), 7.66-7.62 (m, 1H), 7.58-7.54 (m, 1H), 7.51 – 7.44 (m, 1H), 7.24 (d, *J* = 4.3 Hz, 1H), 3.12 (d, *J* = 5.5 Hz, 2H), 3.00 (d, *J* = 5.6 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.76, 151.18, 150.58, 148.21, 146.80, 135.13, 133.21, 130.40, 129.35, 127.84, 125.82, 125.76, 122.92, 121.39, 27.01, 26.64.

4.17. 6,7-Dihydro-5H-pyrido[3',2':6,7]cyclohepta[1,2-*b*]quinoline (3aq)[6]



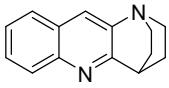
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 3/1. Brown solid (&59% and Φ34%, &146 mg and Φ83 mg), Mp: 132–134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.8, 1.3 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 7.91 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.50 (d, *J* = 1.1 Hz, 1H), 7.45 (dd, *J* = 11.1, 3.8 Hz, 1H), 7.22 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.61 (t, *J* = 7.0 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.17 – 2.11 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.31, 156.82, 148.62, 147.49, 136.61, 135.12, 135.10, 132.69, 130.12, 128.89, 126.86, 123.64, 118.21, 117.84, 31.20, 29.87, 29.55.

4.18. 5,6,7,8-Tetrahydropyrido[3',2':7,8]cycloocta[1,2-*b*]quinoline (3ar)[6]



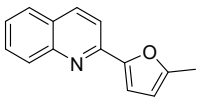
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 3/1. Pale-yellow solid (&69% and Φ37%, &180 mg and Φ98 mg), Mp: 163–164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.0 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.01 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.89 (dd, *J* = 13.8, 7.9 Hz, 1H), 2.70 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.35 – 2.28 (m, 1H), 2.19 (dd, *J* = 17.0, 8.2 Hz, 2H), 2.13 – 2.04 (m, 1H), 1.67 – 1.51 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.69, 155.98, 147.40, 146.58, 137.40, 136.02, 129.49, 128.77, 128.21, 126.65, 126.52, 123.73, 117.65, 115.59, 31.34, 31.24, 30.52, 29.04.

4.19. 3,4-dihydro-2H-1,4-ethanobenzo[*b*][1,5]naphthyridine (3as)



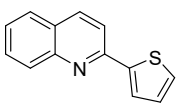
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 3/1. White solid (&76% and Φ41%, &160 mg and Φ86 mg). Mp: 121–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 3.41 (s, 1H), 3.31 – 3.23 (m, 2H), 2.79 (td, *J* = 12.0, 4.7 Hz, 2H), 2.06 (d, *J* = 10.9 Hz, 2H), 1.79 (d, *J* = 10.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.85, 146.54, 143.43, 128.74, 128.62, 128.57, 128.02, 127.72, 125.69, 49.57, 34.18, 27.56.

4.20. 2-(5-methylfuran-2-yl)quinoline (3at)



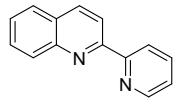
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 5/1. White solid (&69% and Φ33%, &144 mg and Φ68 mg). Mp: 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.75 (t, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.12 (s, 1H), 6.18 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.51, 151.04, 148.10, 147.03, 135.44, 128.66, 128.16, 126.46, 125.87, 124.80, 116.24, 110.50, 107.60, 12.99.

4.21. 2-(Thiophen-2-yl)quinoline (3au)[5,7a,8a]



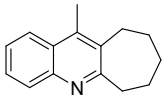
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 10/1. Brown solid (&72% and Φ41%, &158 mg and Φ86 mg). Mp: 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, *J* = 7.8 Hz, 2H), 7.74 (dt, *J* = 19.9, 8.2 Hz, 4H), 7.53 – 7.44 (m, 2H), 7.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.25, 147.03, 144.32, 135.53, 128.73, 128.18, 127.51, 127.01, 126.41, 126.10, 125.02, 124.78, 116.56.

4.22. 2-(pyridin-2-yl)quinoline (3av)[5,7a]



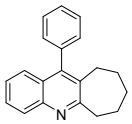
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 5/1. White solid ($^{\&}$87% and $^{\Phi}$57%, $^{\&}$180 mg and $^{\Phi}$117 mg). Mp: 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 3.7 Hz, 1H), 8.66 (d, *J* = 7.9 Hz, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 9.4 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.24, 155.07, 148.08, 146.84, 135.86, 135.72, 128.74, 128.48, 127.16, 126.55, 125.67, 122.95, 120.75, 117.87.

4.23.11-Methyl-7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline (3ba)[1b]



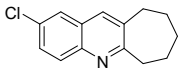
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow solid (85%, 180 mg). Mp: 104–105 °C; ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 7.97 (ddd, *J* = 8.1, 6.3, 1.4 Hz, 2H), 7.60 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.48 (ddd, *J* = 8.4, 4.9, 1.4 Hz, 1H), 3.26 – 3.18 (m, 2H), 3.04 – 2.98 (m, 2H), 2.63 (d, *J* = 2.4 Hz, 3H), 1.87 (q, *J* = 5.3 Hz, 2H), 1.79 (t, *J* = 5.2 Hz, 2H), 1.71 (t, *J* = 5.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm: 164.44, 145.72, 139.10, 134.21, 129.27, 127.91, 127.22, 125.49, 123.84, 40.00, 31.82, 29.35, 27.83, 27.02, 14.17

4.24. 11-Phenyl-7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline (3ca)[8b]



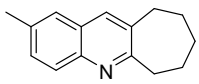
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 500/1 to 10/1. Pale-yellow solid (60%, 162 mg). Mp: 126–127 °C. ^{1}H NMR ($CDCl_3$,400 MHz) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.51 (qd, *J* = 7.9, 7.3, 4.3 Hz, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.24 (dd, *J* = 7.8, 6.0 Hz, 2H), 3.33 (d, *J* = 5.4 Hz, 2H), 2.75 – 2.69 (m, 2H), 1.92 – 1.81 (m, 4H), 1.62 (t, *J* = 5.5 Hz, 2H); ^{13}C (125 MHz, $CDCl_3$) δ 164.76, 145.86, 145.48, 137.67, 133.81, 129.46, 128.62, 128.44, 128.19, 127.64, 126.95, 126.35, 125.58, 40.17, 31.93, 30.70, 28.53, 27.07.

4.25. 2-Chloro-7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline (3da)



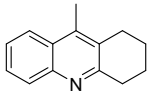
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 100/1 to 20/1, pale-yellow solid (90%, 210 mg). Mp: 121–122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 1H), 7.64 (s, 1H), 7.62 (s, 1H), 7.51 (dd, *J* = 8.9, 1.2 Hz, 1H), 3.18 – 3.13 (m, 2H), 2.91 – 2.85 (m, 2H), 1.86 (d, *J* = 5.1 Hz, 2H), 1.79 – 1.66 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.01, 144.57, 137.54, 133.54, 131.29, 130.07, 129.24, 127.98, 125.48, 77.35, 77.10, 76.84, 39.99, 35.39, 32.15, 28.72, 26.90.

4.26. 2-Methyl-7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline (3ea)



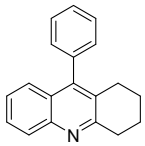
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow solid (87%, 185 mg). Mp: 99–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.72 (s, 1H), 7.47 (s, 1H), 7.46 – 7.43 (m, 1H), 3.23 – 3.17 (m, 2H), 2.93 (dd, *J* = 6.6, 4.5 Hz, 2H), 2.50 (s, 3H), 1.89 (dd, *J* = 11.0, 5.6 Hz, 2H), 1.82 – 1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.68, 144.76, 136.45, 135.44, 134.06, 130.68, 128.11, 127.38, 125.76, 39.97, 35.49, 32.27, 28.90, 27.07, 21.53.

4.27. 9-Methyl-1,2,3,4-tetrahydroacridine (3bc)[1a]



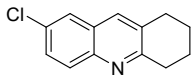
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Yellow oil (64%, 126 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.44 – 7.39 (m, 1H), 3.10 (t, *J* = 6.0 Hz, 2H), 2.84 (t, *J* = 5.8 Hz, 2H), 2.49 (s, 3H), 1.93 – 1.87 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.45, 144.85, 140.14, 127.91, 127.58, 127.01, 125.86, 124.16, 122.22, 33.43, 25.99, 22.14, 21.71, 12.40.

4.28. 9-Phenyl-1,2,3,4-tetrahydroacridine (3cc)



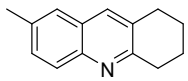
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Yellow solid (69%, 180 mg). Mp: 75–77 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.25 – 7.22 (m, 2H), 3.21 (t, *J* = 6.6 Hz, 2H), 2.61 (t, *J* = 6.5 Hz, 2H), 2.00 – 1.93 (m, 2H), 1.83 – 1.75 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.09, 146.64, 146.25, 137.14, 129.13, 128.65, 128.44, 128.41, 128.30, 128.18, 127.79, 126.71, 126.60, 125.81, 125.46, 34.14, 28.09, 23.05, 22.93.

4.29. 7-Chloro-1,2,3,4-tetrahydroacridine (3dc)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow solid (73%, 160 mg). Mp: 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.62 (s, 1H), 7.58 (s, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 3.03 (t, *J* = 6.2 Hz, 2H), 2.89 (t, *J* = 5.8 Hz, 2H), 1.91 (d, *J* = 5.8 Hz, 2H), 1.82 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.74, 144.93, 133.98, 132.05, 131.09, 129.92, 129.36, 127.76, 125.49, 33.50, 29.25, 23.09, 22.76.

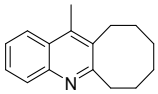
4.30. 7-Methyl-1,2,3,4-tetrahydroacridine (3ec)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow solid (71%, 140 mg). Mp: 52 – 53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.0 Hz, 1H), 7.68 (s, 1H), 7.42 (d, *J* = 7.1 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H), 2.93 (t, *J* = 6.0 Hz, 2H), 2.48 (s, 3H), 2.00 – 1.93 (m, 2H), 1.87 (dd, *J* = 10.3, 5.0 Hz, 2H);^{13}C NMR (125 MHz, $CDCl_3$) δ 158.19, 145.11, 135.16, 134.42, 130.81,

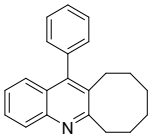
127.85, 127.23, 125.70, 33.36, 29.24, 23.25, 22.93, 21.50.

4.31 12-Methyl-6,7,8,9,10,11-hexahydrocycloocta[*b*]quinoline (3bd)[1b]



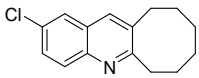
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow solid (80%, 180 mg). Mp: 105 – 106 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 8.08-8.04 (m, 1H), 7.97-7.94 (m, 1H), 7.62-7.60 (t, 1H), 7.50-7.48 (t, 1H), 3.23-3.20 (t, 2H), 3.06-3.03 (t, 2H), 2.66 (s, 3H), 1.90-1.87 (m, 2H), 1.76-1.72 (m, 2H), 1.52-1.47 (m, 4H). ^{13}CNMR ($CDCl_3$, 125 MHz) δ ppm:162.94, 145.71, 140.91, 132.05, 128.82, 128.23, 127.33, 125.56, 123.56, 36.63, 34.78, 31.29, 29.87, 27.44, 27.21, 14.15.

4.32 12-Phenyl-6,7,8,9,10,11-hexahydrocycloocta[*b*]quinoline (3cd)



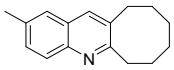
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow solid (66%, 192 mg). Mp: 109 – 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 1H), 7.60 (ddd, J = 8.3, 6.7, 1.5 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.34 – 7.28 (m, 1H), 7.26 – 7.19 (m, 3H), 3.28 – 3.20 (m, 2H), 2.77 (dd, J = 7.3, 5.2 Hz, 2H), 1.95 (td, J = 8.5, 7.5, 4.6 Hz, 2H), 1.54 – 1.44 (m, 4H), 1.38 (q, J = 5.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.41, 146.70, 146.29, 137.61, 131.91, 129.31, 128.41, 128.34, 127.70, 127.28, 126.18, 125.48, 36.22, 31.29, 31.20, 28.14, 26.70, 25.83.

4.33 2-Chloro-6,7,8,9,10,11-hexahydrocycloocta[*b*]quinoline (3dd)



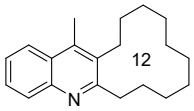
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow solid (85%, 210 mg). Mp: 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.9 Hz, 1H), 7.72 (s, 1H), 7.67 (s, 1H), 7.53 (d, J = 8.9 Hz, 1H), 3.17 – 3.09 (m, 2H), 2.96 – 2.88 (m, 2H), 1.89-1.86 (m, 2H), 1.79-1.74 (m, 2H), 1.42-1.38 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.62, 145.29, 136.22, 134.02, 131.15, 130.13, 129.25, 128.20, 125.51, 35.24, 32.64, 32.04, 30.91, 26.02, 25.87.

4.34 2-Methyl-6,7,8,9,10,11-hexahydrocycloocta[*b*]quinoline (3ed)



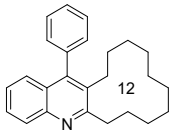
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 15/1. Pale-yellow solid (65%, 150 mg). Mp: 84 – 85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.5 Hz, 1H), 7.74 (s, 1H), 7.49 – 7.42 (m, 2H), 3.17 – 3.11 (m, 2H), 2.95 – 2.89 (m, 2H), 2.50 (s, 3H), 1.90 -1.80 (m, 2H), 1.78-1.71 (m, 2H), 1.42-1.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.16, 145.49, 135.25, 135.07, 134.46, 130.69, 128.15, 127.64, 125.73, 35.17, 32.74, 32.06, 31.01, 26.07, 25.91, 21.53.

4.35. 16-Methyl-6,7,8,9,10,11,12,13,14,15-decahydrocyclododeca[*b*]quinoline (3be)



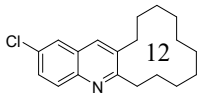
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow solid (57%, 160 mg). Mp: 102 – 103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.63 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.51 – 7.46 (m, 1H), 3.11 – 3.03 (m, 4H), 2.98 – 2.92 (m, 2H), 2.68 (s, 3H), 2.00 – 1.92 (m, 2H), 1.73 (ddd, *J* = 14.3, 10.0, 7.1 Hz, 2H), 1.63 (t, *J* = 7.6 Hz, 6H), 1.56 – 1.48 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.28, 146.74, 144.62, 132.36, 130.13, 129.76, 129.38, 129.24, 129.09, 128.06, 127.09, 125.87, 125.40, 123.56, 123.50, 121.05, 117.25, 34.38, 28.55, 27.97, 27.90, 27.44, 27.35, 26.77, 22.99, 22.66, 14.53.

4.36. 16-Phenyl-6,7,8,9,10,11,12,13,14,15-decahydrocyclododeca[*b*]quinoline (3ce)



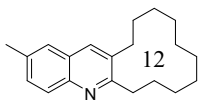
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 15/1. Pale-yellow solid (70%, 242 mg). Mp: 131 – 132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.61 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.34 – 7.29 (m, 1H), 7.29 – 7.26 (m, 2H), 7.22 (dd, *J* = 8.4, 0.9 Hz, 1H), 3.14 – 3.09 (m, 2H), 2.70 – 2.65 (m, 2H), 2.11 – 2.04 (m, 2H), 1.67 (dd, *J* = 11.0, 6.7 Hz, 2H), 1.64 – 1.59 (m, 2H), 1.54 – 1.48 (m, 6H), 1.36 – 1.27 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.65, 147.30, 146.08, 137.81, 132.16, 129.42, 128.41, 128.28, 127.63, 126.91, 126.14, 125.43, 33.87, 28.91, 28.58, 28.38, 28.08, 27.82, 27.14, 26.95, 23.30, 22.87.

4.37. 2-Chloro-6,7,8,9,10,11,12,13,14,15-decahydrocyclododeca[*b*]quinoline (3de)



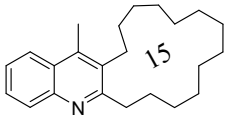
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 25/1. Pale-yellow solid (69%, 210 mg). Mp: 113 – 114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 1H), 7.80 (s, 1H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.53 (dd, *J* = 9.0, 2.3 Hz, 1H), 3.04 – 2.99 (m, 2H), 2.85 – 2.79 (m, 2H), 1.99 – 1.92 (m, 2H), 1.79 (ddd, *J* = 14.0, 10.0, 6.9 Hz, 2H), 1.54 (dd, *J* = 14.2, 6.2 Hz, 4H), 1.49 (dd, *J* = 11.9, 6.4 Hz, 4H), 1.42 (d, *J* = 3.1 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.10, 144.88, 135.95, 134.85, 131.15, 130.02, 129.31, 127.75, 125.45, 32.67, 29.69, 28.38, 26.70, 26.45, 25.99, 25.44, 23.16, 23.09.

4.38. 2-Methyl-6,7,8,9,10,11,12,13,14,15-decahydrocyclododeca[*b*]quinoline (3ee)



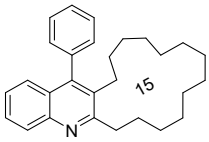
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 15/1. Pale-yellow solid (57%, 160 mg). Mp: 99–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.47 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 3.02 (t, *J* = 7.8 Hz, 2H), 2.85 – 2.79 (m, 2H), 2.50 (s, 3H), 2.00 – 1.93 (m, 2H), 1.83 – 1.76 (m, 2H), 1.55 (dd, *J* = 13.1, 6.2 Hz, 4H), 1.49 (dd, *J* = 12.1, 6.4 Hz, 4H), 1.42 (d, *J* = 3.0 Hz, 4H);^{13}C NMR (100 MHz, $CDCl_3$) δ 160.58, 144.04, 134.22, 133.74, 129.71, 126.95, 126.14, 124.61, 31.54, 28.71, 28.64, 27.48, 25.70, 25.47, 25.03, 24.43, 22.09, 22.01, 20.48.

4.39 19-Methyl-7,8,9,10,11,12,13,14,15,16,17,18-dodecahydro-6H-cyclopentadeca[*b*]quinoline (3bf)



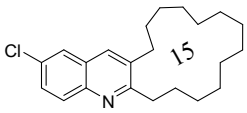
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow solid (51%, 164 mg). Mp: 108 – 110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 3.02 – 2.96 (m, 2H), 2.83 – 2.77 (m, 2H), 2.62 (s, 3H), 1.88 – 1.81 (m, 2H), 1.57 – 1.53 (m, 2H), 1.49 – 1.45 (m, 4H), 1.38 – 1.33 (m, 14H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.64, 144.88, 139.73, 131.09, 128.08, 126.81, 126.05, 124.24, 122.32, 116.21, 35.51, 28.33, 27.38, 27.12, 26.75, 26.64, 26.10, 25.40, 25.25, 24.95, 24.37, 24.27, 22.19, 13.03.

4.40 19-Phenyl-7,8,9,10,11,12,13,14,15,16,17,18-dodecahydro-6H-cyclopentadeca[*b*]quinoline (3cf)



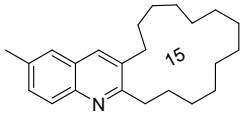
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 20/1. Pale-yellow solid (54%, 210 mg). Mp: 121 – 122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.58 – 7.50 (m, 3H), 7.35 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.32 – 7.26 (m, 3H), 3.14 – 3.07 (m, 2H), 2.62 – 2.56 (m, 2H), 2.04 – 1.95 (m, 2H), 1.71 (d, *J* = 6.6 Hz, 2H), 1.55-1.51 (m, 4H), 1.43 – 1.33 (m, 14H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.30, 137.70, 132.13, 129.28, 128.34, 127.67, 127.01, 126.20, 125.48, 35.99, 30.00, 29.71, 29.19, 28.19, 27.81, 27.70, 26.85, 26.60, 26.31, 26.09, 25.49, 25.39, 23.47.

4.41 2-Chloro-7,8,9,10,11,12,13,14,15,16,17,18-dodecahydro-6H-cyclopentadeca[*b*]quinoline (3df)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 25/1. Pale-yellow solid (70%, 240 mg). Mp: 117 – 118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.9 Hz, 1H), 7.78 (s, 1H), 7.69 (s, 1H), 7.55 (dd, *J* = 8.9, 2.1 Hz, 1H), 3.01 – 2.95 (m, 2H), 2.83 – 2.77 (m, 2H), 1.87 – 1.79 (m, 2H), 1.77 – 1.70 (m, 2H), 1.62 – 1.55 (m, 4H), 1.49 – 1.44 (m, 4H), 1.39-1.34 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.76, 144.83, 135.49, 134.28, 131.15, 130.04, 129.24, 127.89, 125.49, 77.30, 77.04, 76.79, 35.78, 32.40, 29.24, 28.10, 27.54, 27.41, 26.86, 26.82, 26.80, 26.61, 26.05, 25.92, 25.68, 25.63, 23.13.

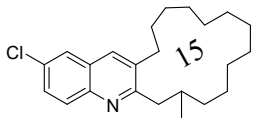
4.42 2-Methyl -7,8,9,10,11,12,13,14,15,16,17,18-dodecahydro-6H-cyclopentadeca[*b*]quinoline (3ef)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow solid (55%, 190 mg). Mp: 116–117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.46 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 2.96 (dd, *J* = 10.0, 6.8 Hz, 2H), 2.80 – 2.74 (m, 2H), 2.50 (s, 3H), 1.85 – 1.78 (m, 2H), 1.75 – 1.69 (m, 2H), 1.60 – 1.53 (m, 4H), 1.47 – 1.42 (m, 4H), 1.35 (d, *J* = 3.3 Hz, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.28, 145.18, 135.10, 134.59, 134.23, 130.55, 128.16, 127.31,

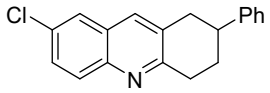
125.70, 35.83, 32.46, 29.36, 28.26, 27.58, 27.45, 26.90, 26.87, 26.63, 26.06, 25.92, 25.65, 25.60, 21.49.

4.43 2-Chloro-7-methyl-7,8,9,10,11,12,13,14,15,16,17,18-dodecahydro-6H-cyclopentadeca[*b*]quinoline (3dg)



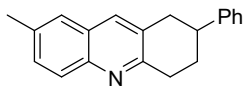
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow solid (42%, 162 mg). Mp: 125–126 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 1H), 7.69 (s, 1H), 7.63 (s, 1H), 7.49 (dd, *J* = 8.9, 2.3 Hz, 1H), 3.17 (dd, *J* = 13.4, 4.7 Hz, 1H), 2.73 (t, *J* = 8.1 Hz, 2H), 2.62 (dd, *J* = 13.4, 10.0 Hz, 1H), 2.08 (dd, *J* = 9.0, 5.2 Hz, 1H), 1.80 – 1.71 (m, 1H), 1.68 – 1.60 (m, 1H), 1.58 – 1.52 (m, 1H), 1.48 (dd, *J* = 12.8, 6.5 Hz, 1H), 1.44 – 1.25 (m, 16H), 0.90 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.60, 143.47, 134.53, 132.59, 130.04, 129.26, 127.99, 126.80, 124.39, 42.49, 35.10, 30.51, 30.30, 27.28, 26.29, 25.47, 25.41, 25.37, 24.90, 24.65, 23.97, 18.39.

4.44 7-Chloro-2-phenyl-1,2,3,4-tetrahydroacridine (3di)



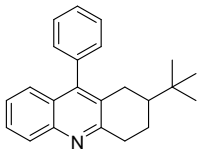
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 25/1. Pale-yellow solid (61%, 178 mg). Mp: 94 – 96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 1H), 7.75 (s, 1H), 7.71 (s, 1H), 7.57 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.31 (m, 2H), 7.28 (dd, *J* = 9.4, 2.2 Hz, 1H), 3.33-3.31 (m, 1H), 3.29 – 3.22 (m, 2H), 3.13 (d, *J* = 10.7 Hz, 2H), 2.38 – 2.32 (m, 1H), 2.21 – 2.13 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.76, 144.34, 144.02, 132.93, 130.27, 130.14, 128.93, 128.46, 127.58, 126.56, 125.69, 125.49, 124.47, 39.15, 36.20, 32.48, 29.23.

4.45 7-Methyl-2-phenyl-1,2,3,4-tetrahydroacridine (3ei)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 25/1. Pale-yellow solid (76%, 205 mg). Mp: 85 – 87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 3.5 Hz, 1H), 7.49 (s, 1H), 7.33 – 7.27 (m, 4H), 7.22 – 7.19 (m, 2H), 3.70 (td, *J* = 10.8, 5.4 Hz, 1H), 3.30 – 3.20 (m, 2H), 3.17 – 3.09 (m, 2H), 2.52 (s, 3H), 1.97 – 1.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.42, 145.79, 145.39, 135.45, 134.61, 131.16, 130.30, 128.67, 128.41, 128.00, 126.88, 126.84, 126.53, 37.40, 36.06, 33.47, 30.52.

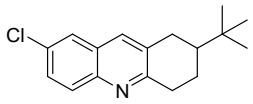
4.46. 2-(tert-Butyl)-9-phenyl-1,2,3,4-tetrahydroacridine (3cl)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow solid (50%, 160 mg). Mp: 102 – 103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.5 Hz,

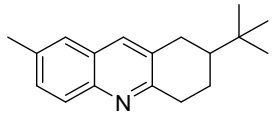
1H), 7.61 (dd, *J* = 11.8, 3.8 Hz, 1H), 7.53 (dd, *J* = 10.6, 5.1 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 3.3 Hz, 2H), 7.25 – 7.21 (m, 2H), 3.36 (d, *J* = 16.9 Hz, 1H), 3.14 (ddd, *J* = 17.4, 11.4, 5.6 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.32 (dd, *J* = 16.7, 11.6 Hz, 1H), 2.18 – 2.11 (m, 1H), 1.58 – 1.47 (m, 2H), 0.85 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.27, 146.83, 146.13, 137.01, 129.17, 128.93, 128.85, 128.75, 128.66, 128.60, 128.40, 128.24, 127.78, 126.69, 125.83, 125.40, 44.73, 34.79, 32.59, 29.33, 27.15, 24.16.

4.47 2-(tert-Butyl)-7-chloro-1,2,3,4-tetrahydroacridine (3dl)



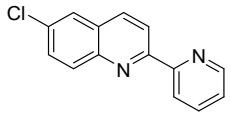
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow solid (78%, 216 mg). Mp: 86 – 87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.7 Hz, 1H), 7.74 (s, 1H), 7.67 (s, 1H), 7.53 (dd, *J* = 9.0, 2.2 Hz, 1H), 3.07 – 2.98 (m, 2H), 2.72 (dd, *J* = 15.9, 11.4 Hz, 1H), 2.21 – 2.14 (m, 1H), 1.78 (d, *J* = 11.7 Hz, 1H), 1.60 – 1.54 (m, 2H), 1.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.82, 143.86, 133.26, 131.37, 130.05, 128.86, 128.33, 126.72, 124.44, 43.49, 35.09, 33.22, 31.53, 29.78, 26.22, 24.59, 23.44.

4.48 2-(tert-Butyl)-7-methyl-1,2,3,4-tetrahydroacridine (3el)



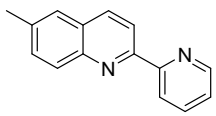
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow solid (83%, 210 mg). Mp: 81 – 82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 7.26 (d, *J* = 10.0 Hz, 2H), 2.86 (ddd, *J* = 31.0, 18.4, 11.0 Hz, 2H), 2.50 (dd, *J* = 15.7, 11.7 Hz, 1H), 2.33 (s, 3H), 1.88 (d, *J* = 10.5 Hz, 1H), 1.61 (d, *J* = 11.0 Hz, 1H), 1.41 – 1.32 (m, 2H), 1.12 (d, *J* = 13.6 Hz, 1H), 0.85 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.11, 143.99, 133.97, 133.62, 129.98, 129.69, 126.75, 126.12, 124.58, 35.02, 32.96, 31.41, 29.66, 26.59, 26.19, 24.61, 23.49, 20.42.

4.49 6-Chloro-2-(pyridin-2-yl)quinoline (3dv)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 100/1 to 10/1, Pale-yellow solid (72%, 175 mg). Mp:121 – 122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.7 Hz, 1H), 8.64 (d, *J* = 7.9 Hz, 1H), 8.52 (d, *J* = 8.6 Hz, 1H), 8.19 (dd, *J* = 8.6, 2.6 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.61 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.37 – 7.32 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.25, 155.06, 148.11, 148.07, 135.82, 135.80, 135.66, 134.68, 130.31, 129.34, 128.76, 128.44, 126.52, 125.64, 125.20, 123.09, 122.91, 120.73, 120.67, 118.71, 117.87.

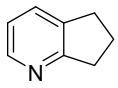
4.50 6-Methyl -2-(pyridin-2-yl)quinoline (3ev)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 100/1 to 10/1. Pale-yellow solid (70%, 155 mg). Mp: 115 – 116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.2 Hz,

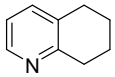
1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.51 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.82 (td, *J* = 7.7, 1.7 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.30 (ddd, *J* = 7.4, 4.8, 0.9 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.50, 155.34, 149.13, 146.53, 136.87, 136.69, 136.09, 131.85, 129.51, 128.29, 126.51, 123.84, 121.69, 118.95, 21.64.

4.51 6,7-Dihydro-5H-cyclopenta[*b*]pyridine (4fb, n = 0)[1a,10a]



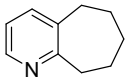
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 500/1 to 60/1. Pale-yellow oil (37%, 45 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.22 (s, 1H), 7.37 – 7.35 (d, *J* = 10 Hz, 1H), 6.91 – 6.89 (d, *J* = 10 Hz, 1H), 2.93 – 2.90 (t, *J* = 7.5 Hz, 2H), 2.83 – 2.80 (t, *J* = 7.5 Hz,2H), 2.03 – 1.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.54, 147.33, 136.90, 132.04, 120.94, 34.19, 30.72, 23.07.

4.52 5,6,7,8-Tetrahydroquinoline (4fc, n = 1)[1a,10a]



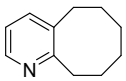
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 500/1 to 40/1. Pale-yellow oil (38%, 51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.16 – 7.09 (m, 1H), 3.05 (t, *J* = 6.3 Hz, 2H), 2.88 (t, *J* = 6.1 Hz, 2H), 2.07 – 1.98 (m, 2H), 1.97 – 1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.71, 145.33, 138.07, 133.15, 121.26, 31.64, 28.59, 22.69, 22.44.

4.53 6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine (4fa, n = 2)[1a,10a,10c,11]



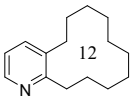
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 500/1 to 40/1. Pale-yellow oil (44%, 65 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.15 (m, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.01 – 6.89 (m, 1H), 3.04 – 2.92 (m, 2H), 2.77 – 2.66 (m, 2H), 1.81 (d, *J* = 4.1 Hz, 2H), 1.62 (d, *J* = 4.5 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.20, 146.01, 138.16, 136.46, 121.17, 39.34, 35.31, 32.49, 27.90, 26.43.

4.54 5,6,7,8,9,10-Hexahydrocycloocta[*b*]pyridine (4fd, n = 3)[1a]



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow oil (42%, 68 mg). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 – 8.36 (d, *J* = 5.0 Hz, 1H), 7.42 – 7.40 (d, *J* = 5.0, 1H), 7.10 – 7.07 (m, 1H), 3.00 – 2.98 (m, 2H), 2.78 – 2.76 (m, 2H), 1.59 – 1.57 (m, 4H), 1.38 – 1.37 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.86, 154.78, 137.43, 134.78, 128.63, 128.52, 128.43, 126.92, 118.47, 32.53, 32.18, 31.64, 30.79, 26.09, 25.93.

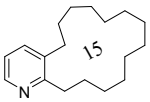
4.55 5,6,7,8,9,10,11,12,13,14-Decahydrocyclododeca[*b*]pyridine (4fe, n = 7)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 60/1. Pale-yellow oil (46%, 100 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.46 (dd, *J* =

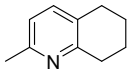
7.7, 1.4 Hz, 1H), 7.05 (dd, *J* = 7.7, 4.7 Hz, 1H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.69 – 2.65 (m, 2H), 1.88 (dd, *J* = 6.5, 5.1 Hz, 2H), 1.74 – 1.69 (m, 4H), 1.53 – 1.50 (m, 4H), 1.41 (dd, *J* = 5.9, 3.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.39, 145.55, 136.36, 135.12, 120.00, 41.56, 39.35, 34.04, 30.41, 28.68.

4.56 6,7,8,9,10,11,12,13,14,15,16,17-Dodecahydro-5H-cyclopentadeca[b]pyridine (4ff, n = 10)



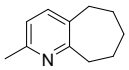
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (42%, 110 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.02 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.71 (dd, *J* = 12.0, 6.0 Hz, 2H), 2.80 – 2.75 (m, 2H), 2.61 – 2.56 (m, 2H), 1.74 – 1.70 (m, 2H), 1.56 (d, *J* = 7.4 Hz, 4H), 1.48 (dd, *J* = 6.4, 3.0 Hz, 4H), 1.42 – 1.36 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.45, 146.65, 137.12, 135.69, 121.10, 35.01, 32.45, 29.55, 28.31, 27.50, 27.12, 25.98, 25.49.

4.57 2-Methyl-5,6,7,8-tetrahydroquinoline (4gc, n = 1)[1a,10a]



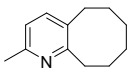
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (41%, 61 mg). ^{1}H NMR ($CDCl_3$, 500MHz) δ 7.23 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 2.89 (t, *J* = 6.5 Hz, 2H), 2.71 (t, *J* = 6.5 Hz, 2H), 2.49 (s, 3H), 1.9 –1.78 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.36, 154.97, 137.15, 128.94, 120.46, 32.46, 28.34, 24.03, 23.15, 22.78.

4.58 2-Methyl-6,7,8,9-tetrahydro-5H-cyclohepta[*b*]pyridine (4ga, n = 2)[1a,10a,10c]



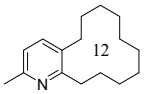
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (48%, 78 mg), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 3.05 – 2.99 (m, 2H), 2.78 – 2.71 (m, 2H), 2.50 (s, 3H), 1.87 (p, *J* = 5.9 Hz, 2H), 1.68 (dp, *J* = 22.6, 5.4 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.48, 154.39, 136.91, 134.81, 120.47, 39.40, 34.87, 32.55, 28.11, 26.58, 23.96.

4.59 2-Methyl-5,6,7,8,9,10-hexahydrocycloocta[*b*]pyridine (4gd, n = 3)[1a]



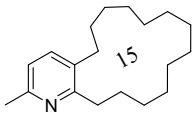
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (45%, 80 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 2.93 – 2.84 (m, 2H), 2.69 – 2.63 (m, 2H), 2.44 (s, 3H), 1.73 (m, 2H), 1.61 (d, *J* = 2.0 Hz, 2H), 1.32 (d, *J* = 2.6 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.94, 145.71, 140.91, 132.05, 128.82, 128.23, 127.33, 125.56, 123.56, 36.63, 34.78, 31.29, 29.87, 27.44, 27.21, 14.15.

4.60 2-Methyl-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[*b*]pyridine (4ge, n = 7)



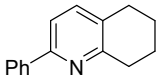
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (52%, 120 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.48 (s, 3H), 1.89 – 1.80 (m, 2H), 1.70 – 1.64 (m, 2H), 1.50 (d, *J* = 5.4 Hz, 4H), 1.42-1.32 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.59, 153.93, 136.53, 131.61, 119.57, 30.61, 28.36, 27.60, 27.38, 25.12, 24.96, 24.63, 24.05, 23.08, 21.91, 21.73.

4.61 2-Methyl-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-5H-cyclopentadeca[*b*]pyridine (4gf, n = 10)



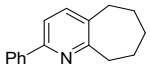
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (47%, 130 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 2.80 – 2.71 (m, 2H), 2.59 – 2.53 (m, 2H), 2.49 (s, 3H), 1.72 – 1.66 (m, 2H), 1.59 (dd, *J* = 9.7, 6.1 Hz, 2H), 1.54 – 1.47 (m, 4H), 1.44 – 1.38 (m, 6H), 1.36 – 1.31 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.64, 154.88, 137.63, 132.38, 125.50, 35.25, 32.06, 29.69, 28.67, 27.51, 27.46, 26.94, 26.91, 26.69, 26.11, 25.97, 25.46, 25.45.

4.62 2-Phenyl-5,6,7,8-tetrahydroquinoline (4hc, n = 1)[1a]



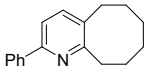
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (47%, 130 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.43 (m, 4H), 7.43 – 7.36 (m, 1H), 3.03 (t, *J* = 6.4 Hz, 1H), 2.80 (t, *J* = 6.3 Hz, 1H), 1.97 – 1.91 (m, 1H), 1.87 – 1.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.16, 153.59, 138.81, 136.40, 129.67, 127.56, 127.32, 125.79, 116.86, 31.78, 27.50, 22.17, 21.76.

4.63 2-Phenyl-6,7,8,9-tetrahydro-5H-cyclohepta[*b*]pyridine (4ha, n = 2)[1b,10a,11c]



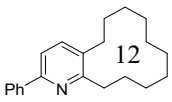
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 50/1. Pale-yellow oil (71%, 160 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.45 – 7.39 (m, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 3.15 – 3.10 (m, 2H), 2.79 (dd, *J* = 7.0, 4.1 Hz, 2H), 1.76 - 1.71 (m, 2H), 1.67 – 1.63 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.13, 154.03, 139.83, 137.19, 136.53, 128.61, 128.29, 126.78, 117.85, 39.76, 35.03, 32.61, 26.69, 21.49.

4.64 2-Phenyl-5,6,7,8,9,10-hexahydrocycloocta[*b*]pyridine (4hd, n = 3)[1b]



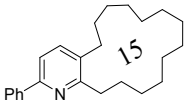
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 60/1. Pale-yellow oil (75%, 180 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.41 (m, 4H), 7.39 – 7.35 (m, 1H), 3.09 – 3.03 (m, 2H), 2.83 – 2.78 (m, 2H), 1.85 (dd, *J* = 4.4, 1.9 Hz, 2H), 1.72 (dd, *J* = 5.5, 2.3 Hz, 2H), 1.42 (dt, *J* = 5.7, 2.8 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.92, 154.87, 139.99, 137.19, 134.59, 128.62, 128.30, 126.83, 118.30, 34.94, 32.20, 30.80, 27.12, 25.93.

4.65 2-Phenyl-5,6,7,8,9,10,11,12,13,14-decahydrocyclododeca[*b*]pyridine (4he, n = 7)



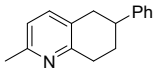
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale- yellow oil (56%, 165 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.46 (dt, *J* = 15.1, 9.1 Hz, 4H), 7.37 (d, *J* = 7.3 Hz, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.00 – 1.95 (m, 2H), 1.76 – 1.71 (m, 2H), 1.52 (dd, *J* = 10.2, 6.3 Hz, 4H), 1.40 (dd, *J* = 9.7, 6.9 Hz, 8H), 1.32 – 1.26 (m, 2H); ^{13}C NMR (125 MHz, CH_2Cl_2) δ 159.25, 153.17, 138.85, 136.81, 133.29, 127.52, 127.28, 125.71, 116.62, 30.51, 28.42, 27.65, 26.90, 25.03, 24.62, 24.14, 24.09, 22.03, 21.99.

4.66 2-Phenyl-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-5H-cyclopentadeca[*b*]pyridine (4hf, n = 10)



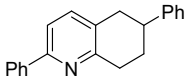
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 60/1. Pale-yellow oil (52%, 175 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.36 – 7.28 (m, 4H), 7.24 (t, *J* = 7.3 Hz, 1H), 2.79 – 2.72 (m, 2H), 2.54 – 2.47 (m, 2H), 1.77 – 1.70 (m, 2H), 1.56 – 1.51 (m, 2H), 1.48 – 1.44 (m, 2H), 1.40 (dd, *J* = 9.1, 4.3 Hz, 2H), 1.32 (d, *J* = 6.7 Hz, 4H), 1.24 (d, *J* = 2.6 Hz, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.06, 153.16, 138.86, 136.60, 132.97, 127.50, 127.21, 125.69, 116.66, 33.96, 31.12, 28.51, 27.07, 26.49, 26.41, 25.97, 25.87, 25.67, 25.02, 24.97, 24.61.

4.67 2-Methyl-6-phenyl-5,6,7,8-tetrahydroquinoline (4gi)



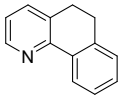
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow oil (42%, 95 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.27 (m, 3H), 7.25 – 7.23 (m, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.10 – 3.05 (m, 2H), 3.00 -2.97 (m, 2H), 2.93-2.87 (m, 1H), 2.53 (s, 3H), 2.25 – 2.21 (m, 1H), 2.07 – 1.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.61 (d, *J* = 28.8 Hz), 145.94, 137.15, 128.57, 128.45, 126.82, 126.40, 120.68, 40.32, 36.59, 32.75, 30.31, 24.14.

4.68 2,6-Diphenyl-5,6,7,8-tetrahydroquinoline (4hi)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 60/1. Pale-yellow solid (56%, 160 mg). Mp: 128 -129 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.48 (dt, *J* = 17.0, 8.7 Hz, 4H), 7.42 (d, *J* = 6.6 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 6.5 Hz, 1H), 3.25 – 3.13 (m, 2H), 3.11 – 3.04 (m, 2H), 3.03 – 2.97 (m, 1H), 2.31 – 2.27 (m, 1H), 2.15-2.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.62, 155.03, 145.96, 139.82, 137.45, 130.18, 128.75, 128.65, 128.58, 126.93, 126.90, 126.48, 118.07, 40.37, 36.80, 33.13, 30.41.

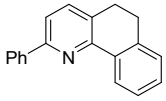
4.60 5,6-Dihydrobenzo[*h*]quinoline (4fn)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to

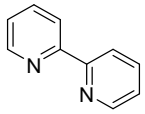
20/1. White solid (41%, 75 mg). Mp: 82 – 84 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.2, 4.2 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.31 – 7.25 (m, 2H), 7.13 (t, *J* = 5.9 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 2.88 – 2.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.54, 143.43, 137.05, 134.54, 133.49, 131.58, 130.82, 128.05, 126.74, 122.19, 121.16, 28.68.

4.70 2-Phenyl-5,6-dihydrobenzo[*h*]quinoline (4hn)[1b]



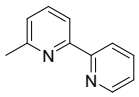
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 60/1. Pale-yellow solid (54%, 140 mg). Mp: 92 – 95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.40 (dt, *J* = 12.9, 4.5 Hz, 4H), 7.35 – 7.30 (m, 1H), 7.22 (t, *J* = 5.8 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 3.09 (ddd, *J* = 16.1, 10.2, 5.6 Hz, 1H), 2.90 – 2.83 (m, 1H), 2.26 – 2.19 (m, 1H), 2.17 – 2.07 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.15, 152.16, 139.79, 138.32, 135.00, 130.40, 128.74, 128.43, 127.65, 125.16, 124.91, 118.85, 30.81, 26.93.

4.71 2,2'-Bipyridine (4fv)



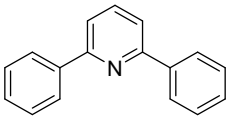
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 3/1. White solid (36%, 56 mg). Mp: 71 – 73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 2.6, 1.8 Hz, 2H), 8.38 (dd, *J* = 4.5, 3.4 Hz, 2H), 7.79 (d, *J* = 3.4 Hz, 2H), 7.31 – 7.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.05, 149.10, 136.80, 123.63, 120.98.

4.72 6-Methyl-2,2'-bipyridine (4gv)



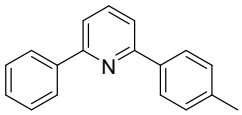
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 10/1. Pale-yellow oil (44%, 75 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (br, 1H), 8.41 – 8.35 (m, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.28 (dd, *J* = 7.4, 4.1 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.84 (*J* = 16.3 Hz), 155.56 (*J* = 14.3 Hz), 154.47 (*J* = 17.6 Hz), 148.07 (*J* = 9.2 Hz), 135.93 (*J* = 21.7 Hz), 123.22, 122. 120.23 (*J* = 15.8 Hz), 118.06, 117.08, 23.54 (*J* = 20.4 Hz).

4.73 2,6-Diphenylpyridine (4hw)[10a,10c,10d]



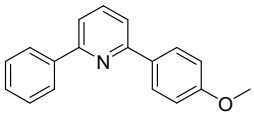
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow oil (55%, 127 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 4H), 7.70 – 7.63 (m, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.37 (m, 4H), 7.31 (dd, *J* = 9.4, 4.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.75, 138.44, 136.39, 127.91, 127.62, 127.56, 125.97, 125.93, 117.54.

4.74 2-Phenyl-6-(p-tolyl)pyridine (4hx)[10a,10c,10d]



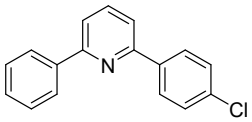
Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. White solid (58%, 142 mg). Mp: 125-127 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.6 Hz, 2H), 8.09 (d, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.75, 139.52, 138.86, 137.31, 136.66, 129.34, 128.83, 128.59, 126.91, 126.79, 118.24, 118.23, 21.23.

4.75 2-(4-Methoxyphenyl)-6-phenylpyridine (4hy)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. White solid (65%, 170 mg). Mp: 128-130 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.64 (dd, J = 7.7, 3.3 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.46, 155.58, 155.40, 138.50, 136.38, 131.04, 127.87, 127.61, 127.22, 125.93, 116.91, 116.84, 113.00, 54.30.

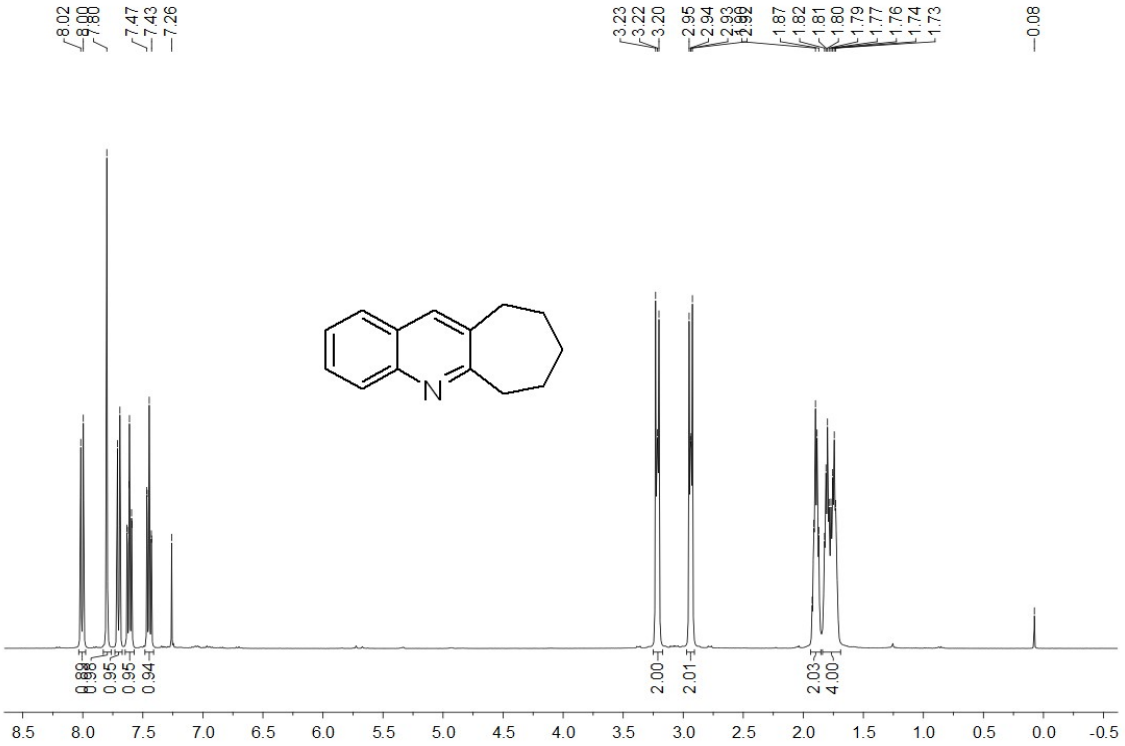
4.76. 2-(4-Chlorophenyl)-6-phenylpyridine (4hz)



Purification was carried out using flash chromatography with a gradient of petroleum ether/EtOAc from 200/1 to 40/1. Pale-yellow oil (37%, 98 mg). Mp: 125-127 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.07 (m, 4H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.64 (m, 2H), 7.53 – 7.43 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.16, 155.78, 139.48, 138.09, 135.27, 132.53, 131.11, 129.05, 128.44, 127.17, 119.10, 118.57.

5. ^{1}H NMR and ^{13}C NMR spectra for selected compounds

Figure S12. The ^{1}H and ^{13}C NMR spectra for **3aa**



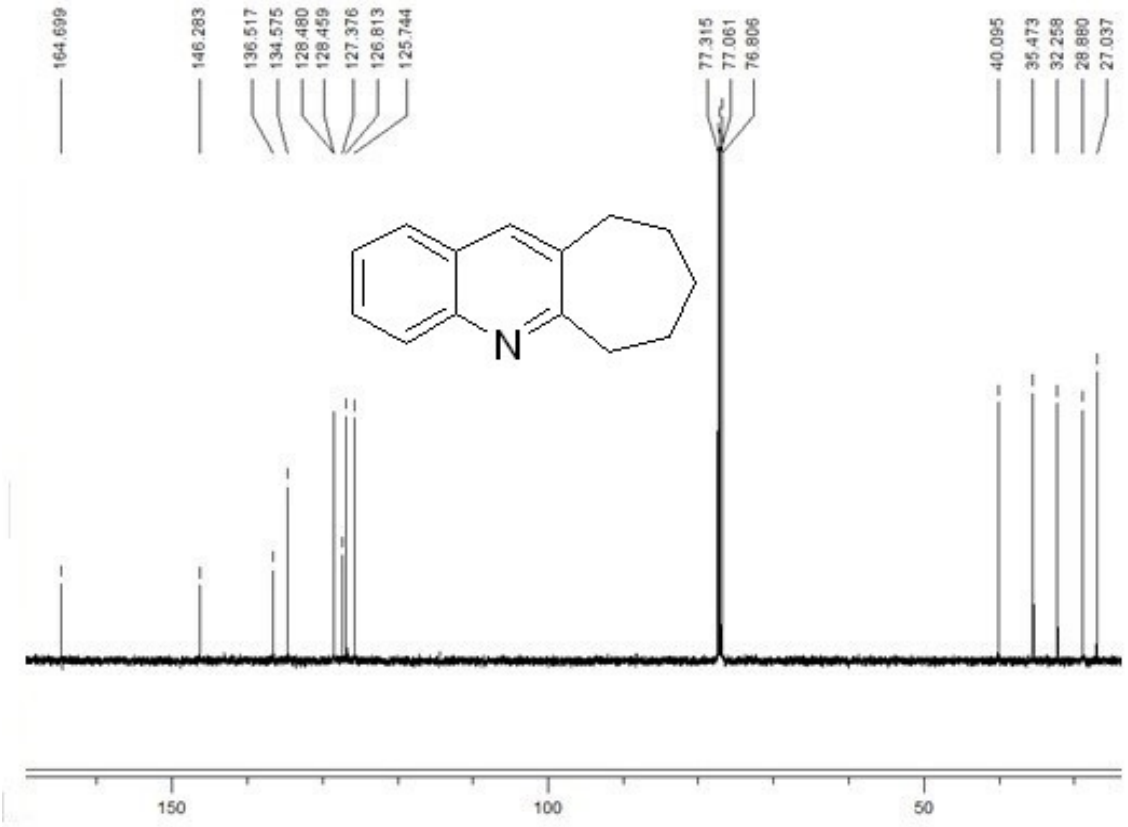


Figure S13. The ^{1}H and ^{13}C NMR spectra for **3ab**

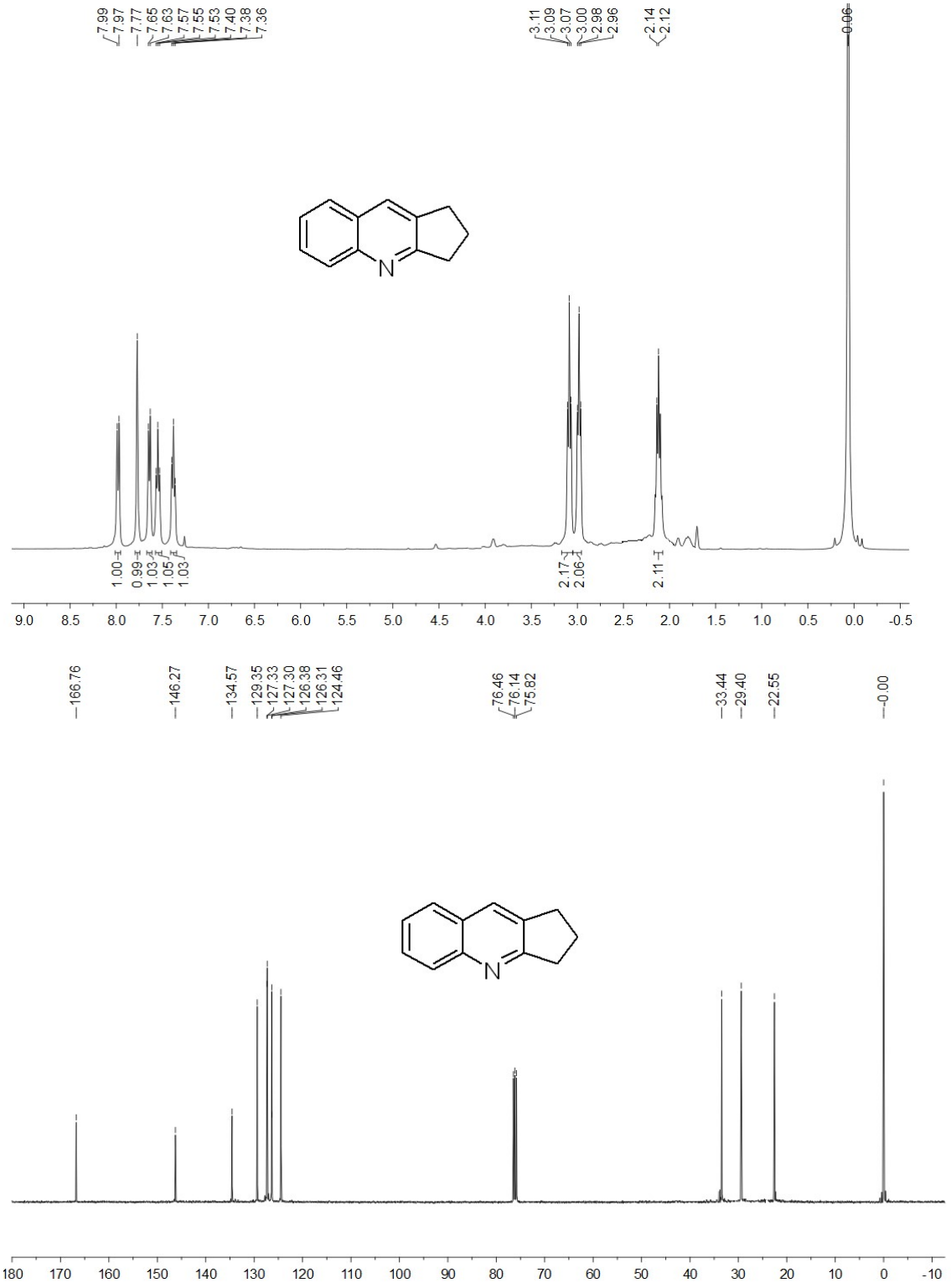


Figure S14. The ^{1}H and ^{13}C NMR spectra for **3ac**

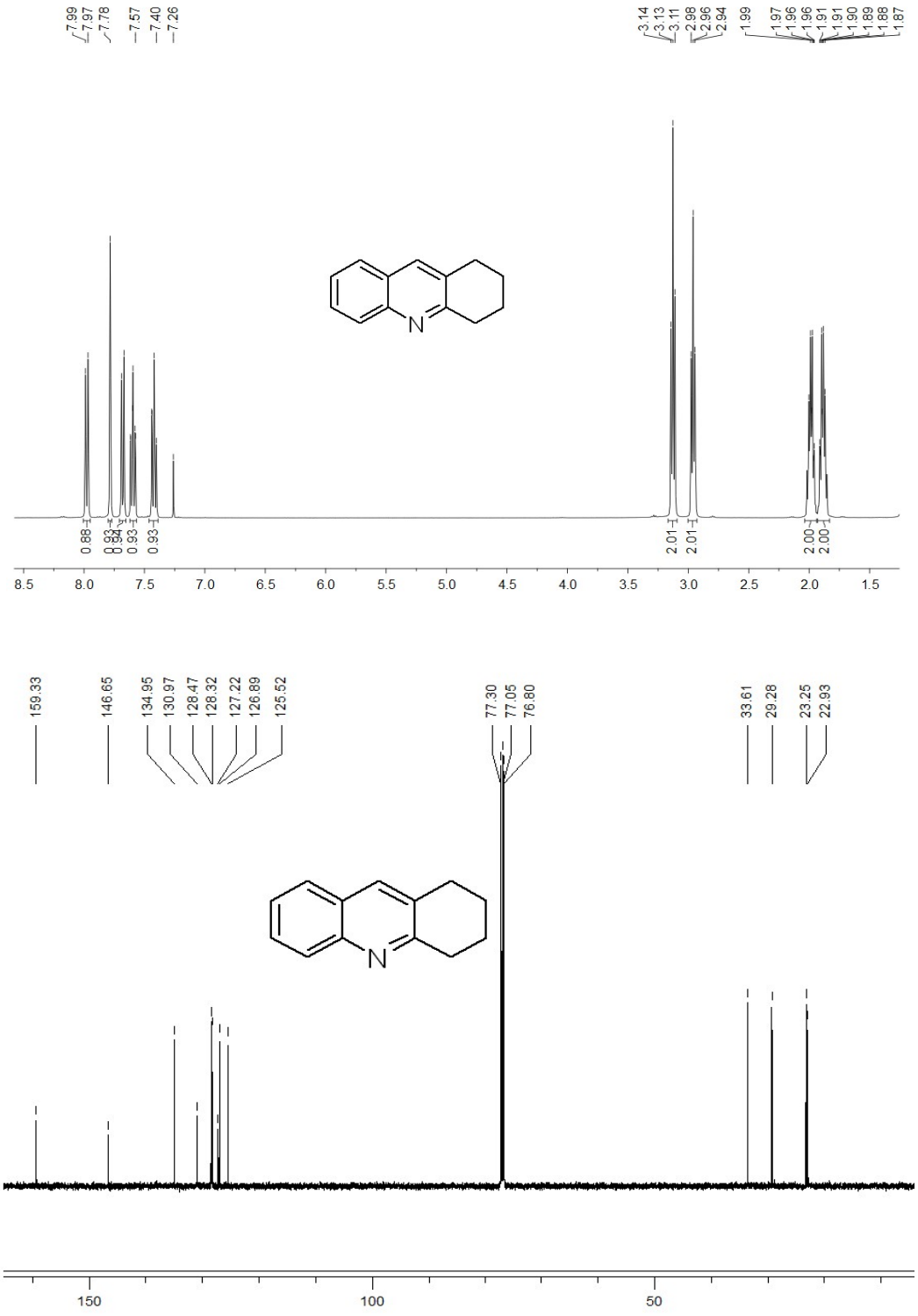


Figure S15. The ^{1}H and ^{13}C NMR spectra for **3ad**

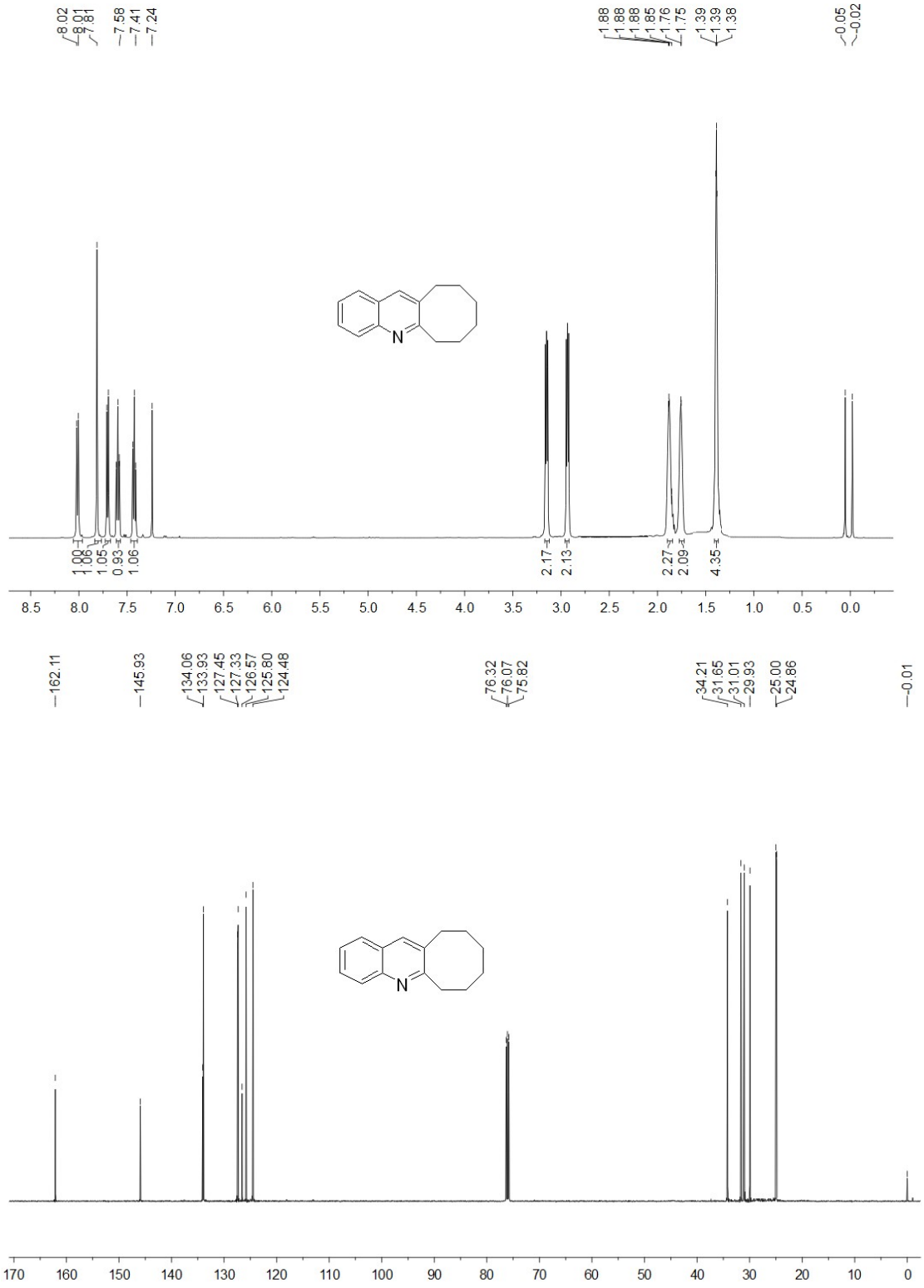


Figure S16. The ^{1}H and ^{13}C NMR spectra for **3ae**

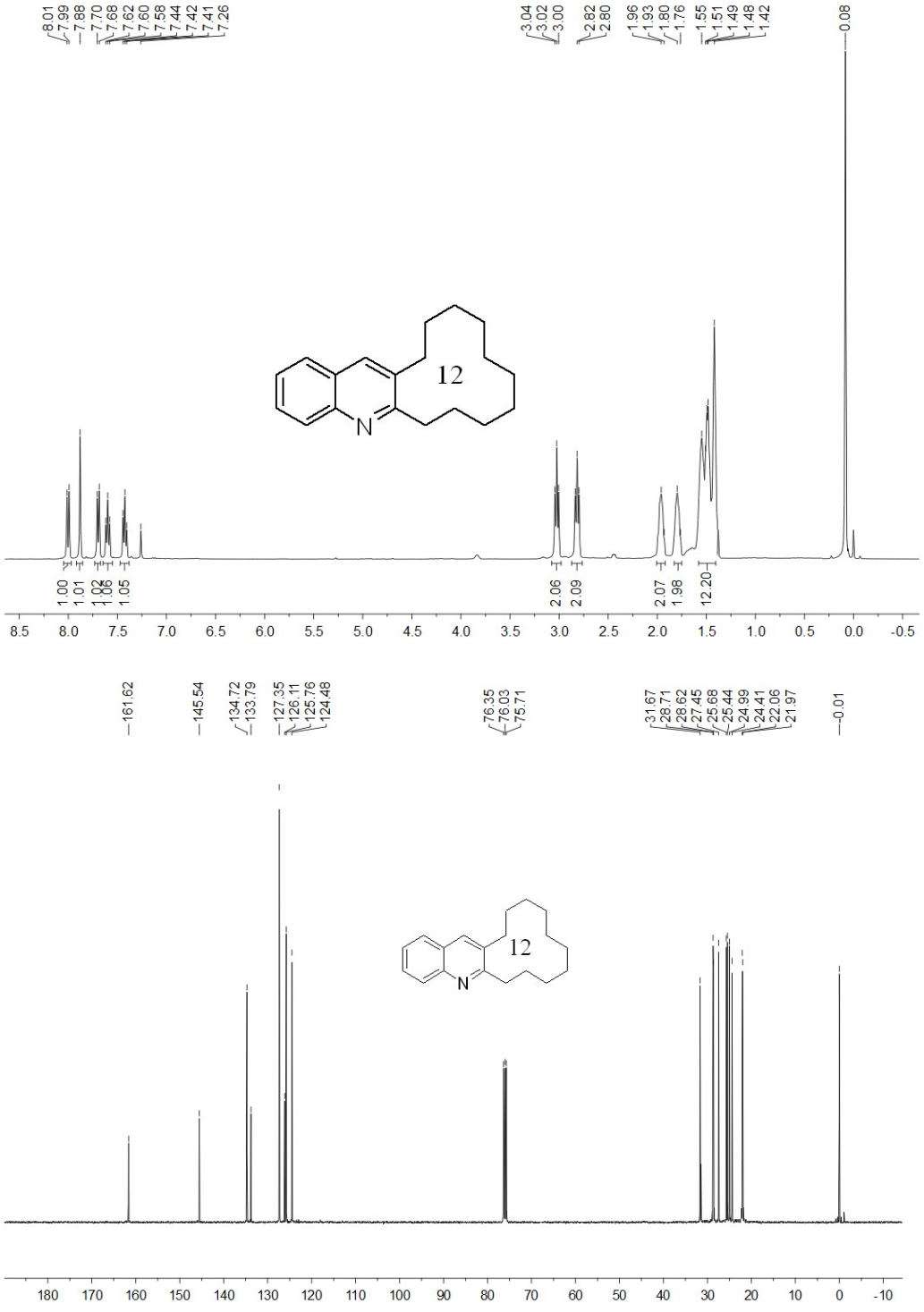


Figure S17. The ^{1}H and ^{13}C NMR spectra for **3af**

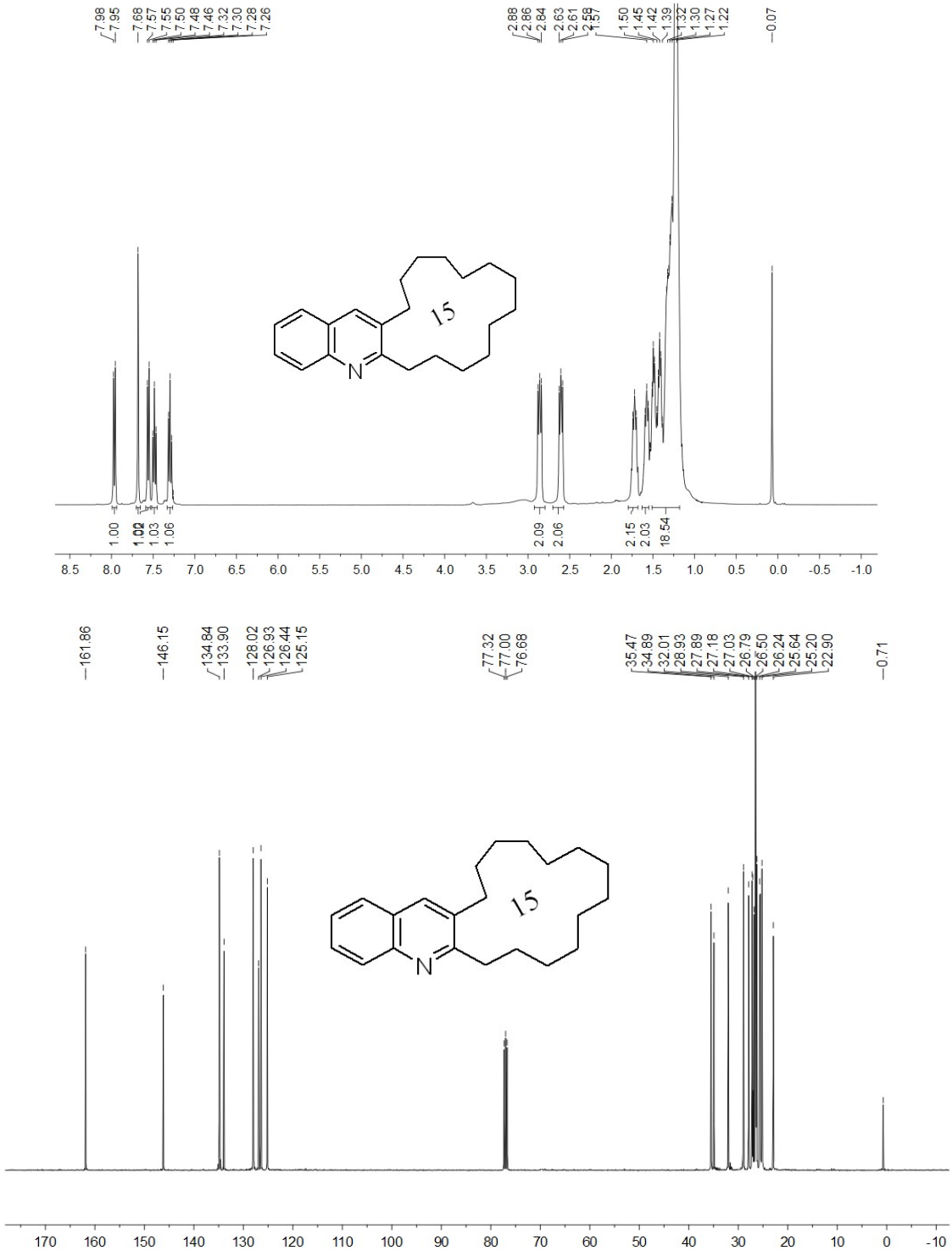


Figure S18. The ^{1}H and ^{13}C NMR spectra for **3ag**

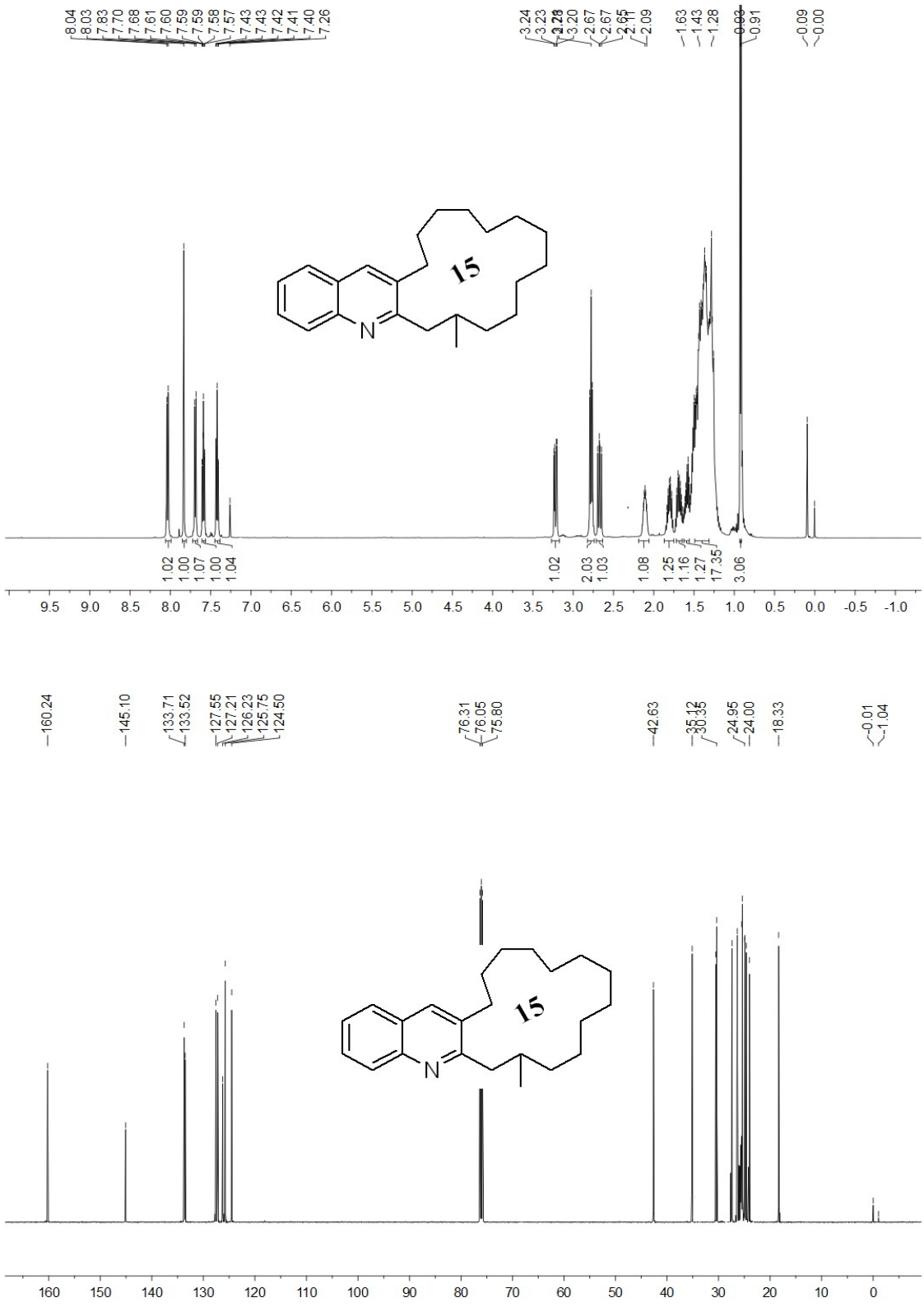


Figure S19. The ^{1}H and ^{13}C NMR spectra for **3ah**

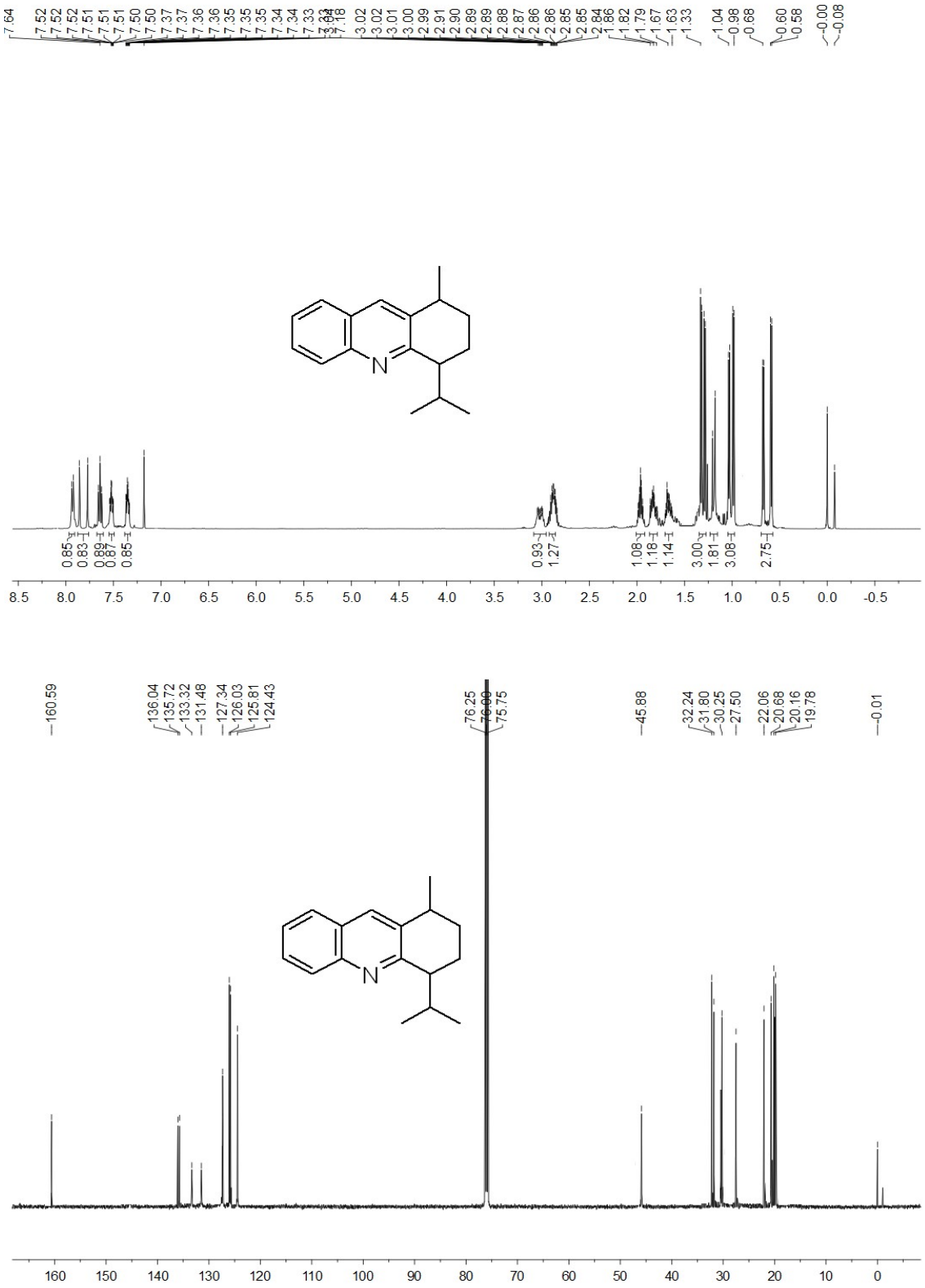


Figure S20. The ^{1}H and ^{13}C NMR spectra for **3ai**

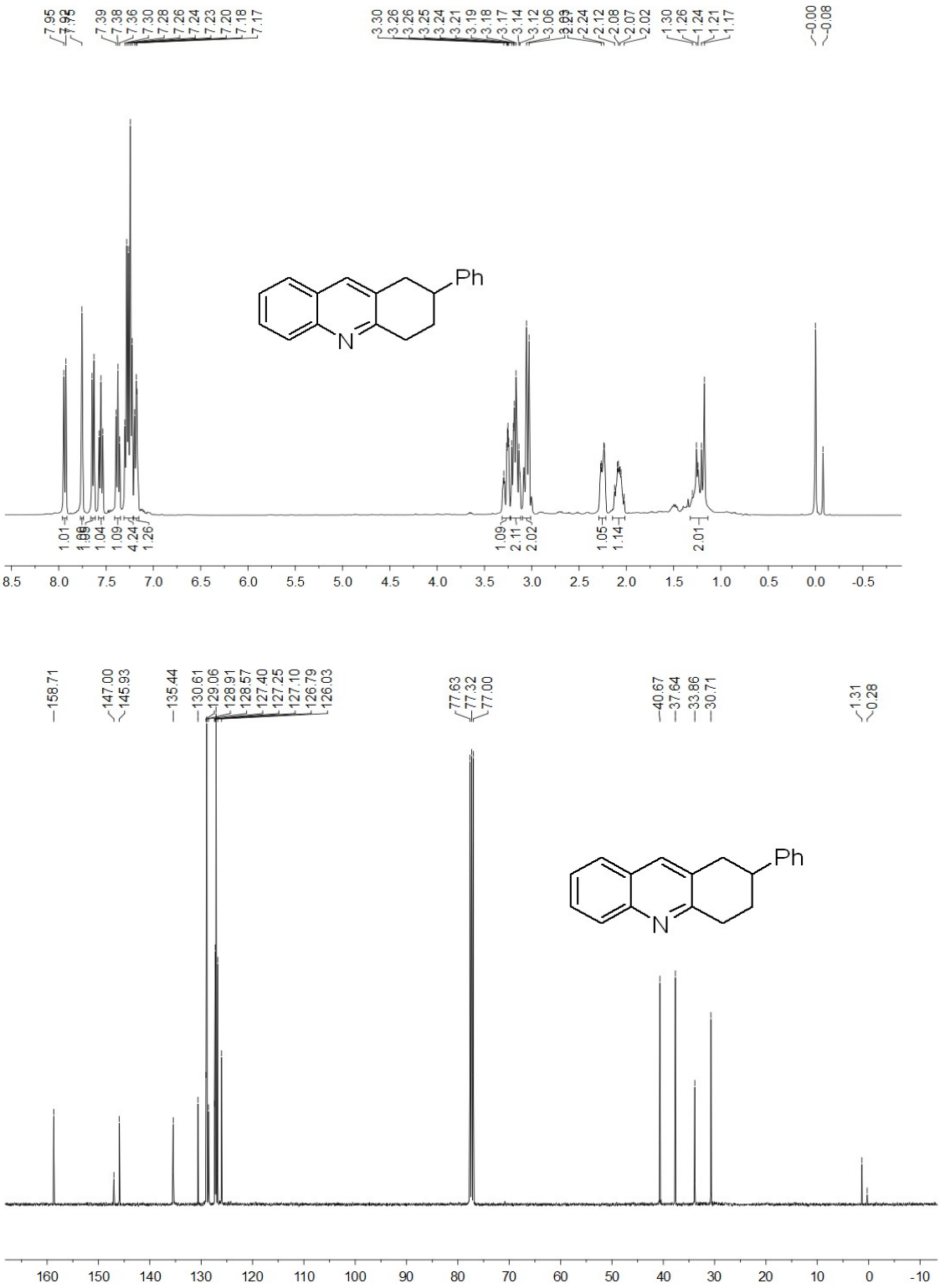


Figure S21. The ^{1}H and ^{13}C NMR spectra for **3aj**

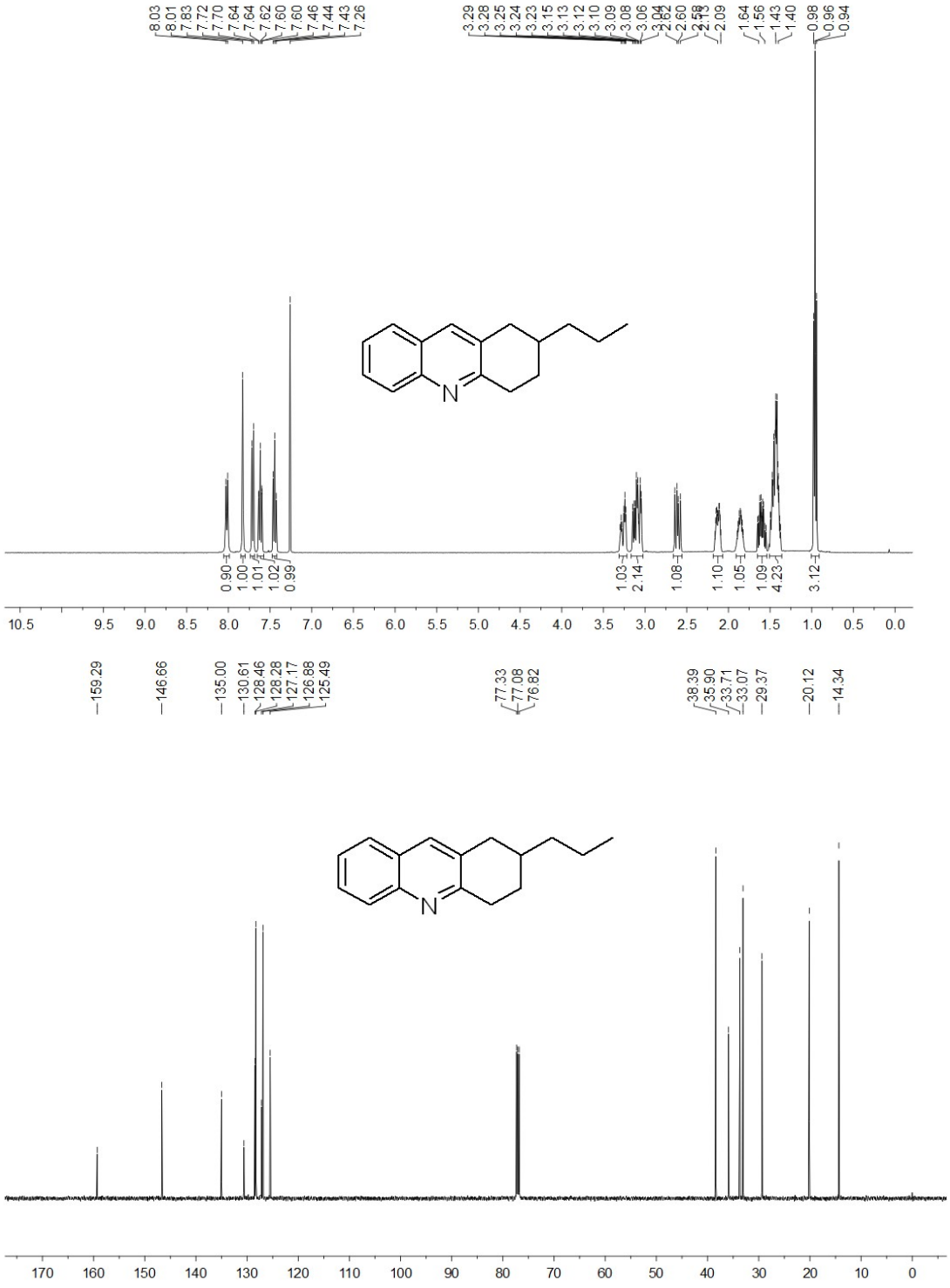


Figure S22. The ^{1}H and ^{13}C NMR spectra for **3ak**

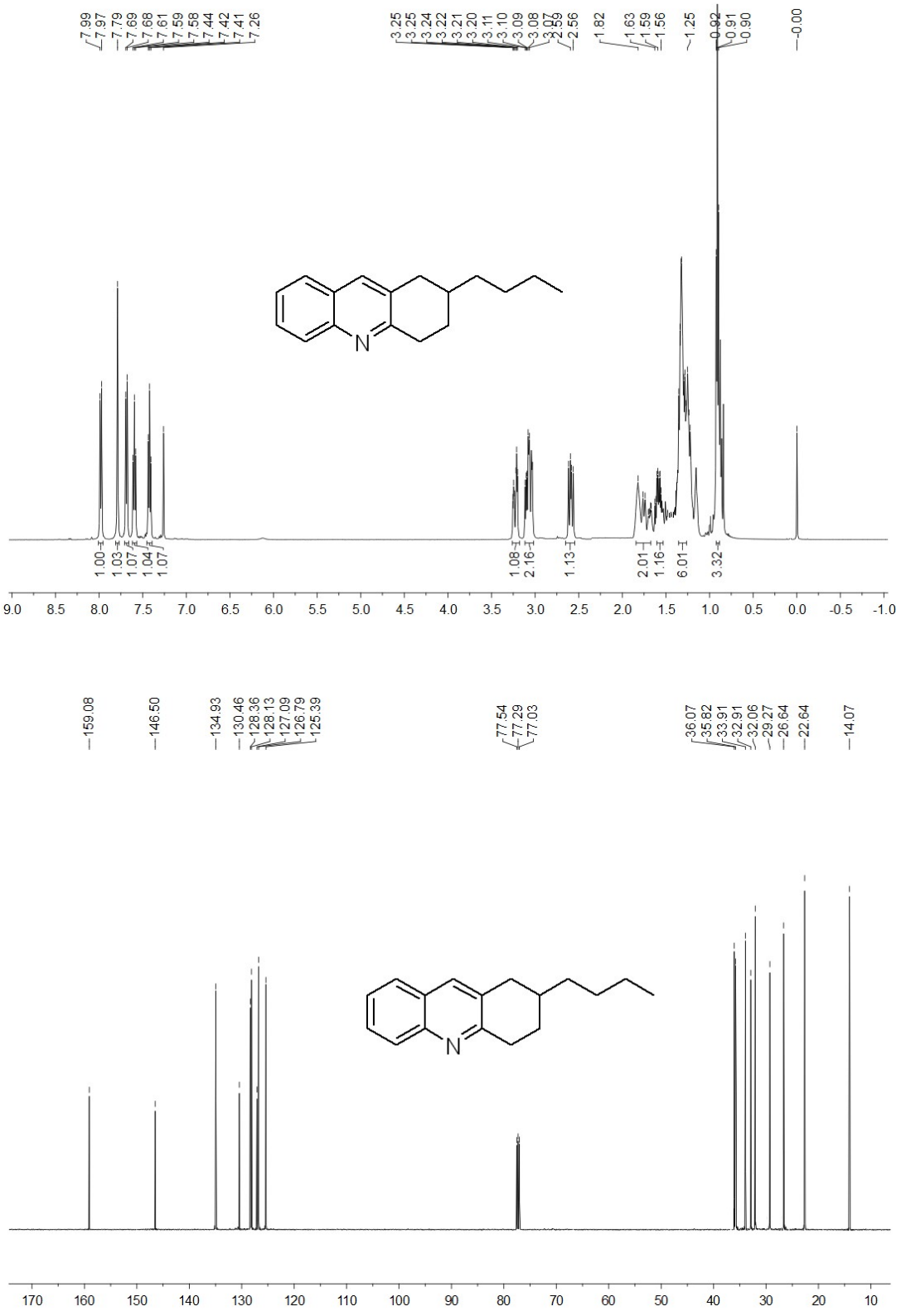


Figure S23. The ^{1}H and ^{13}C NMR spectra for **3al**

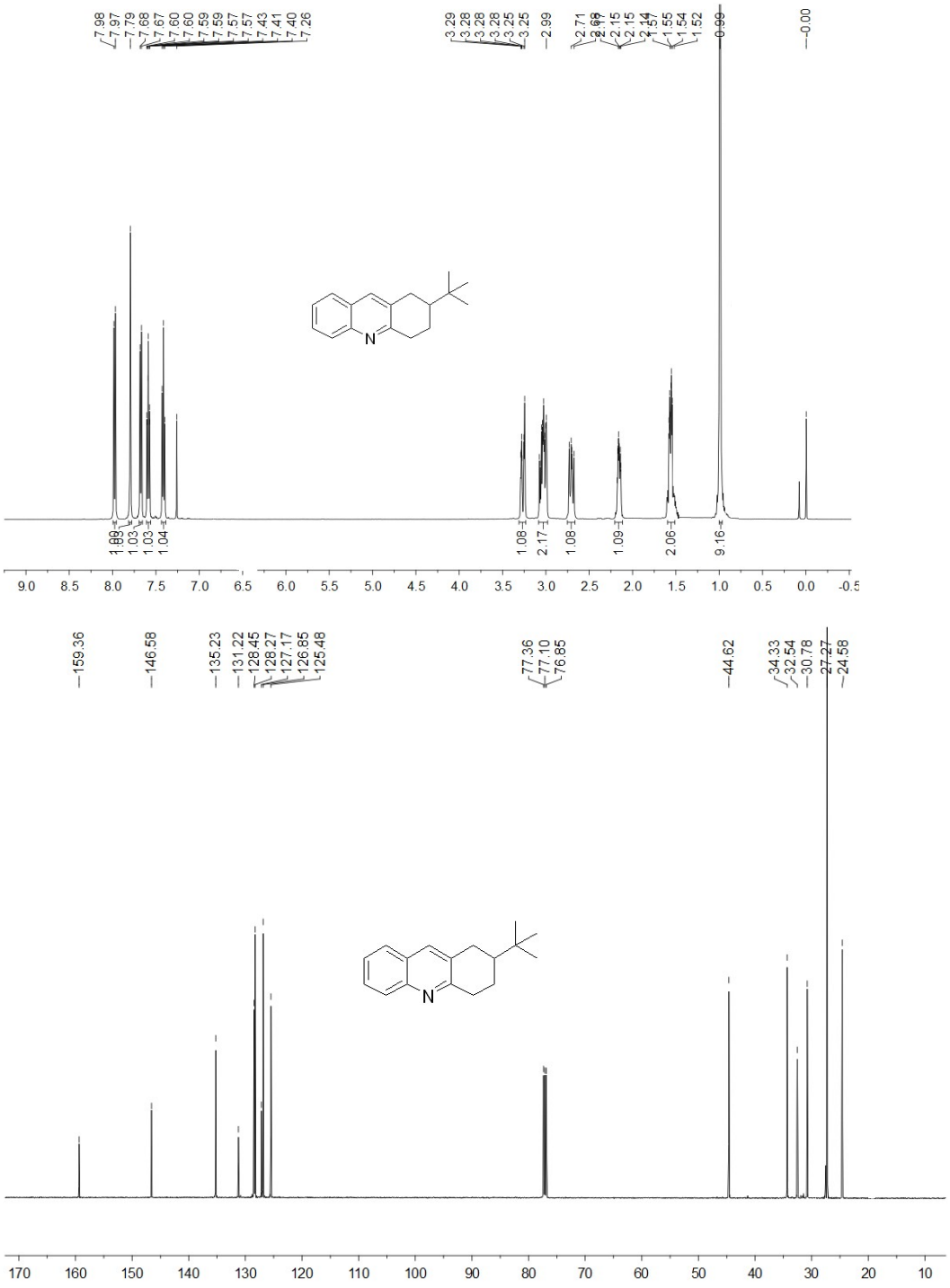


Figure S24. The ^{1}H and ^{13}C NMR spectra for **3am**

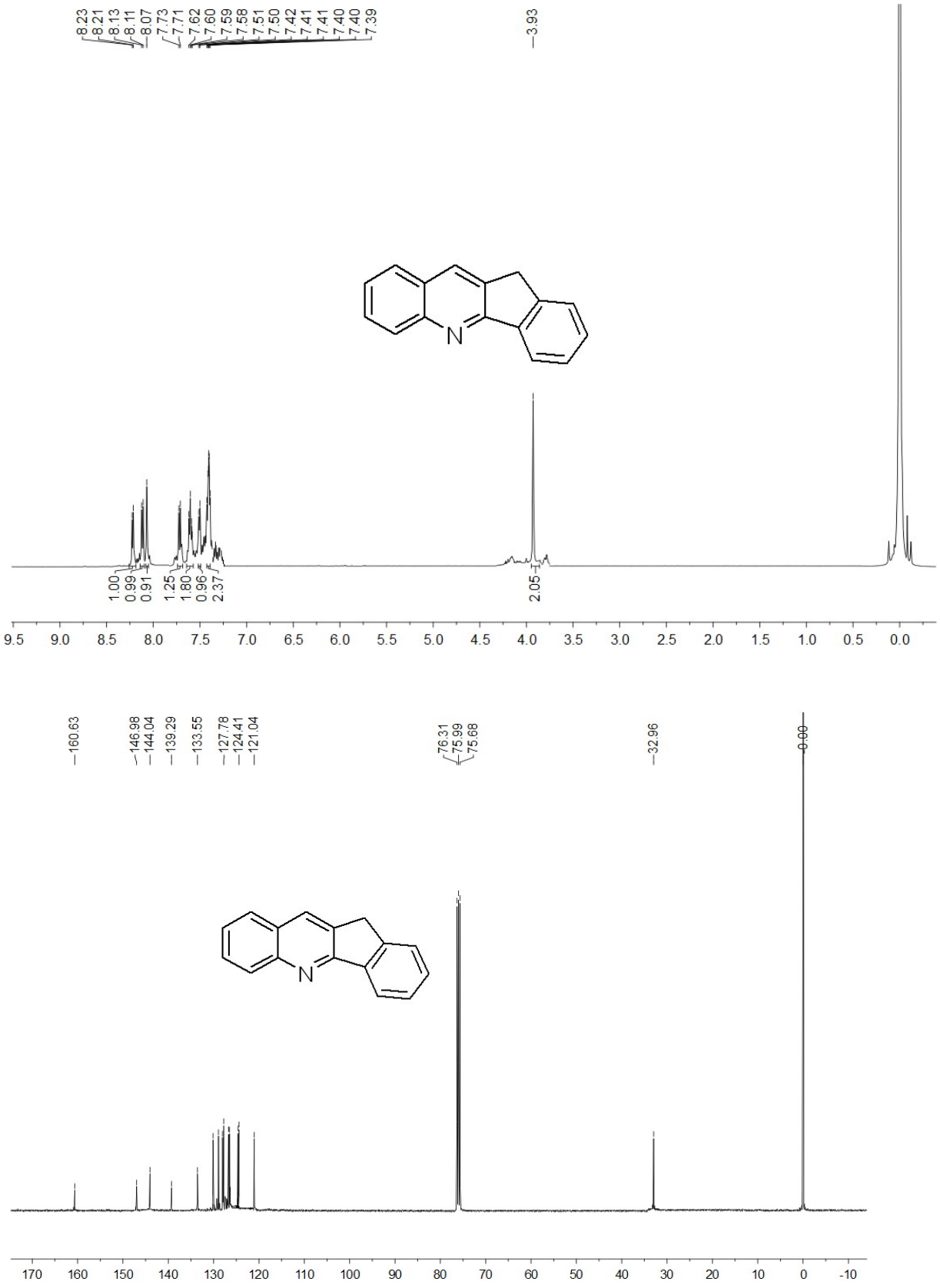
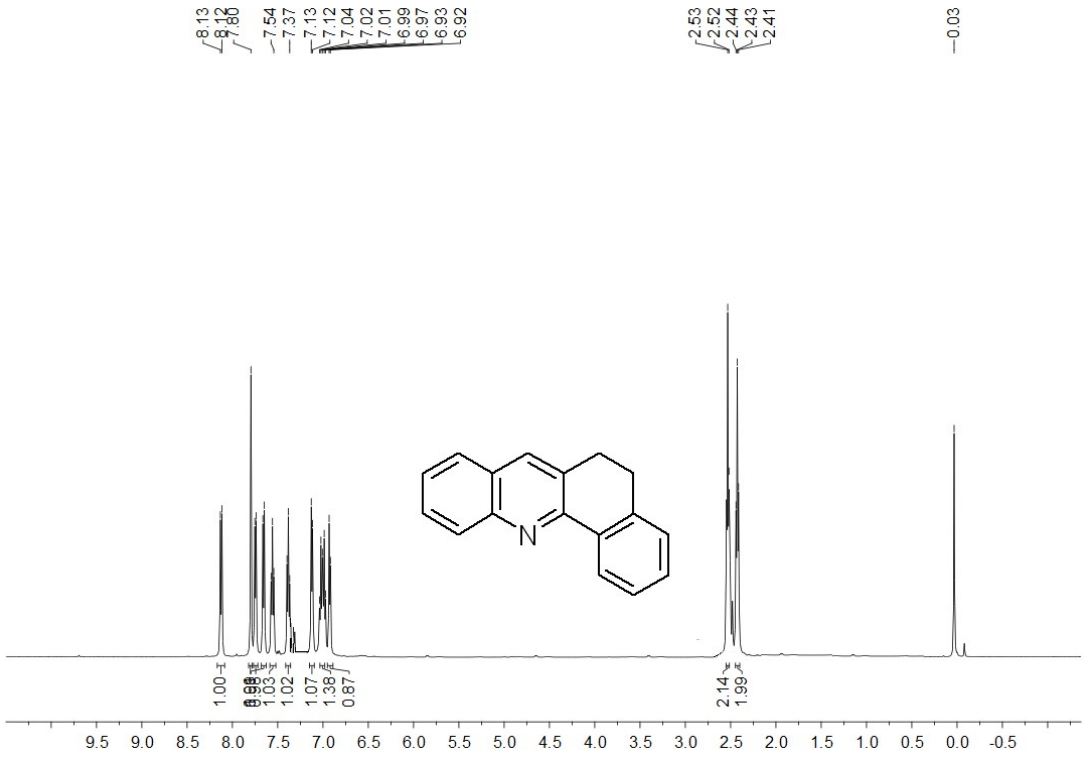


Figure S25. The ^{1}H and ^{13}C NMR spectra for **3an**



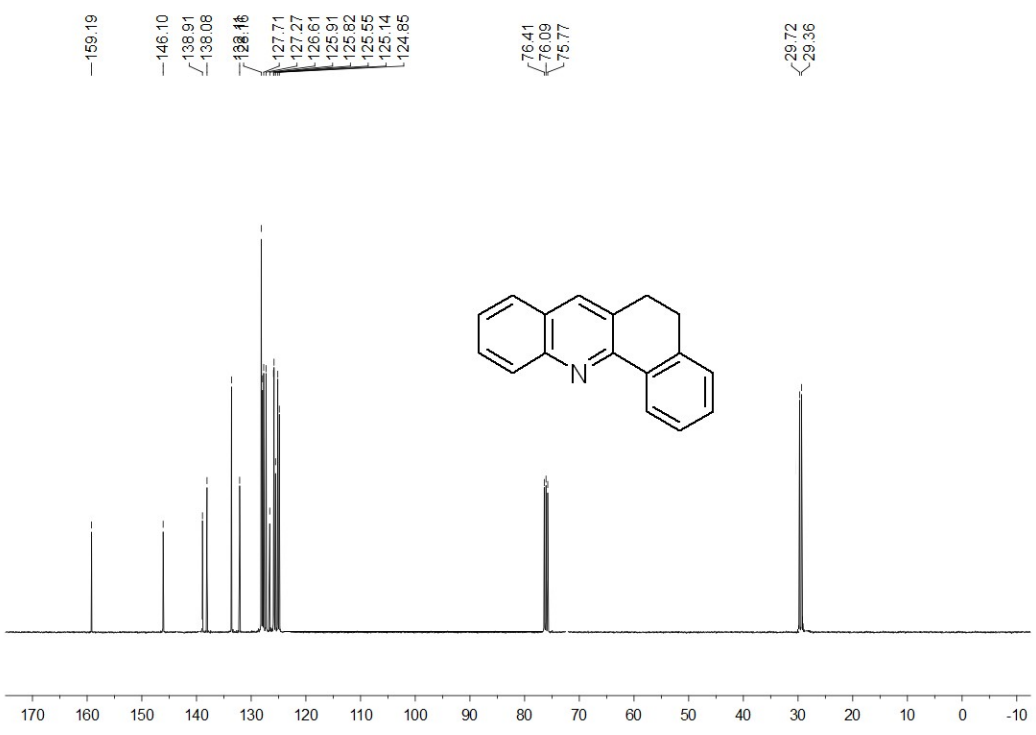


Figure S26. The ^{1}H and ^{13}C NMR spectra for **3ao**

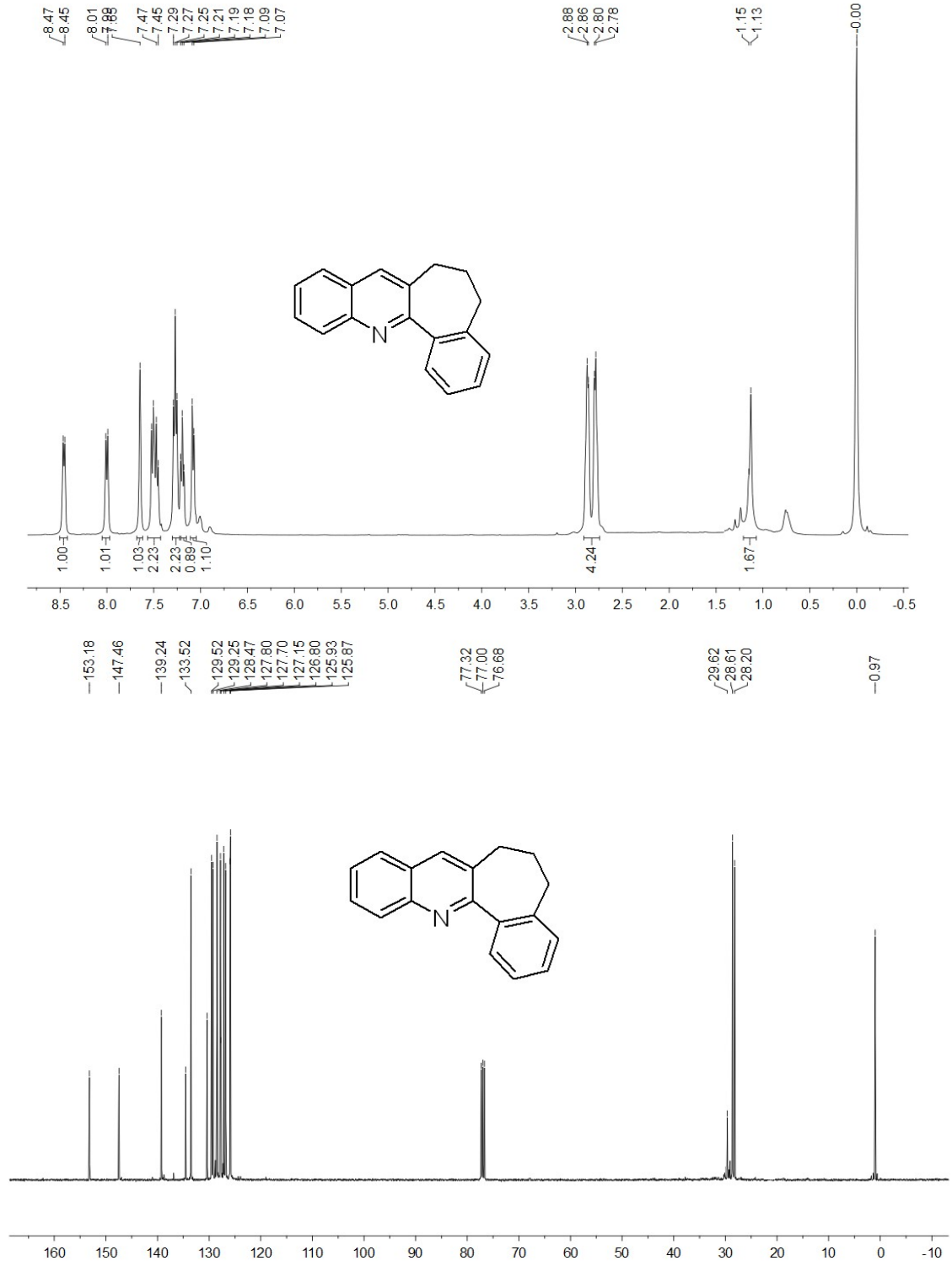


Figure S27. The ^{1}H and ^{13}C NMR spectra for **3ap**

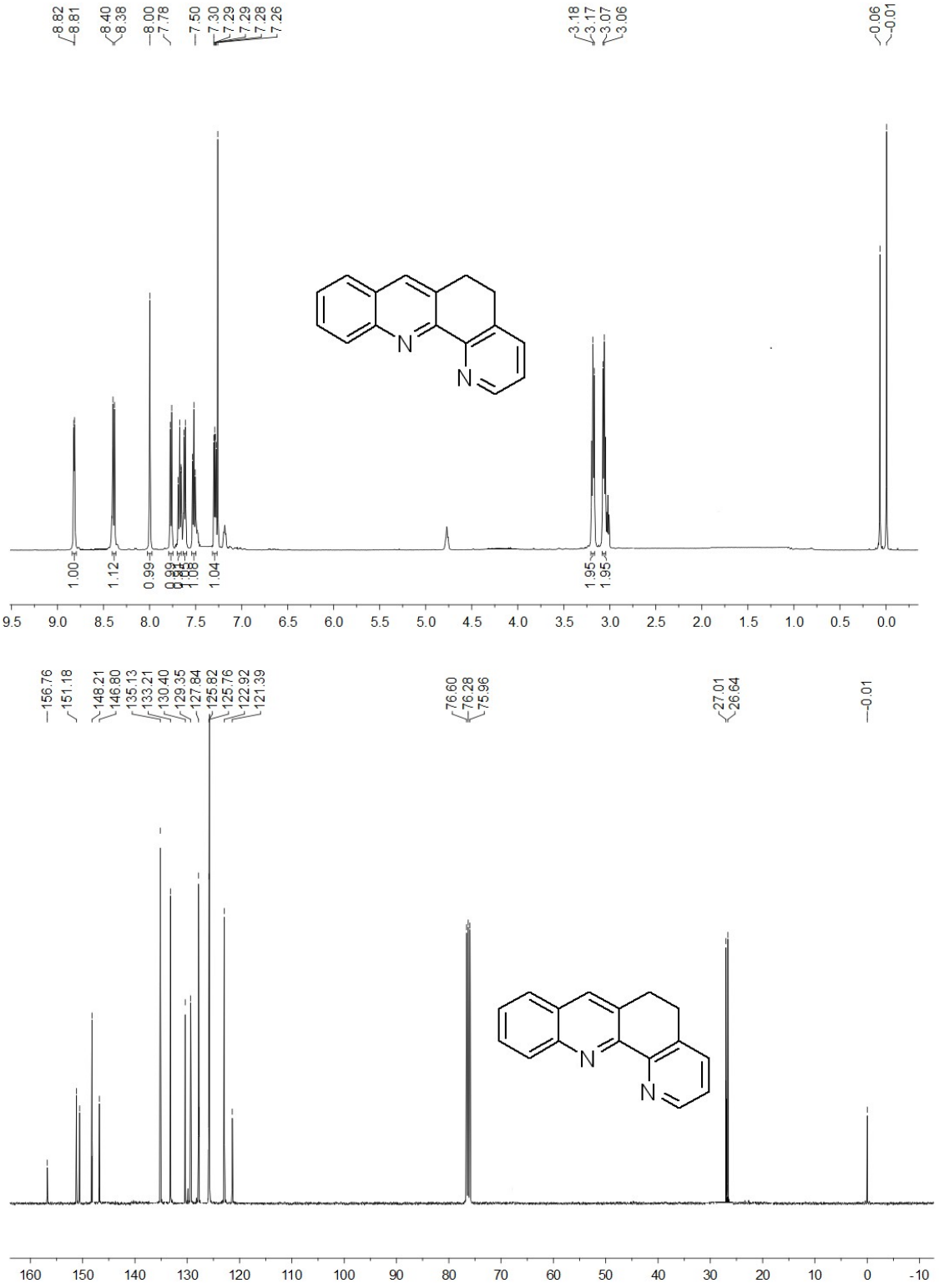
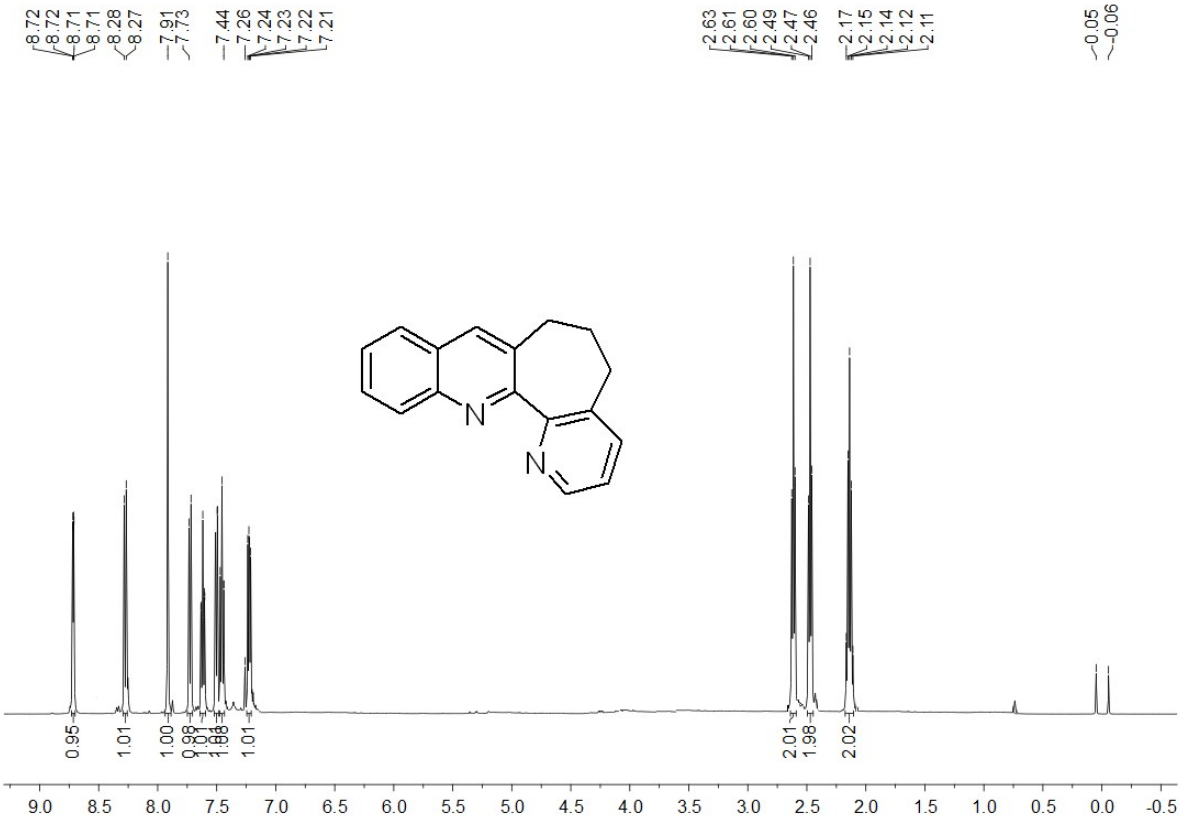


Figure S28. The ^{1}H and ^{13}C NMR spectra for **3aq**



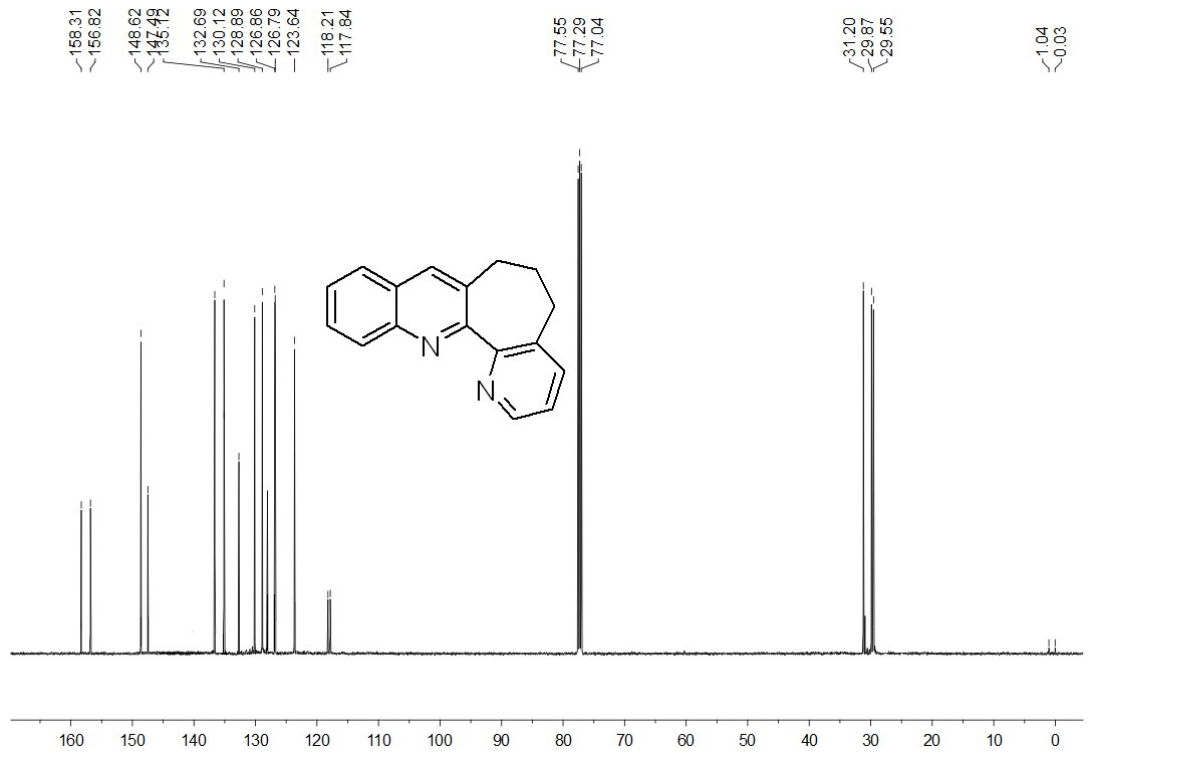


Figure S29. The ^{1}H and ^{13}C NMR spectra for **3ar**

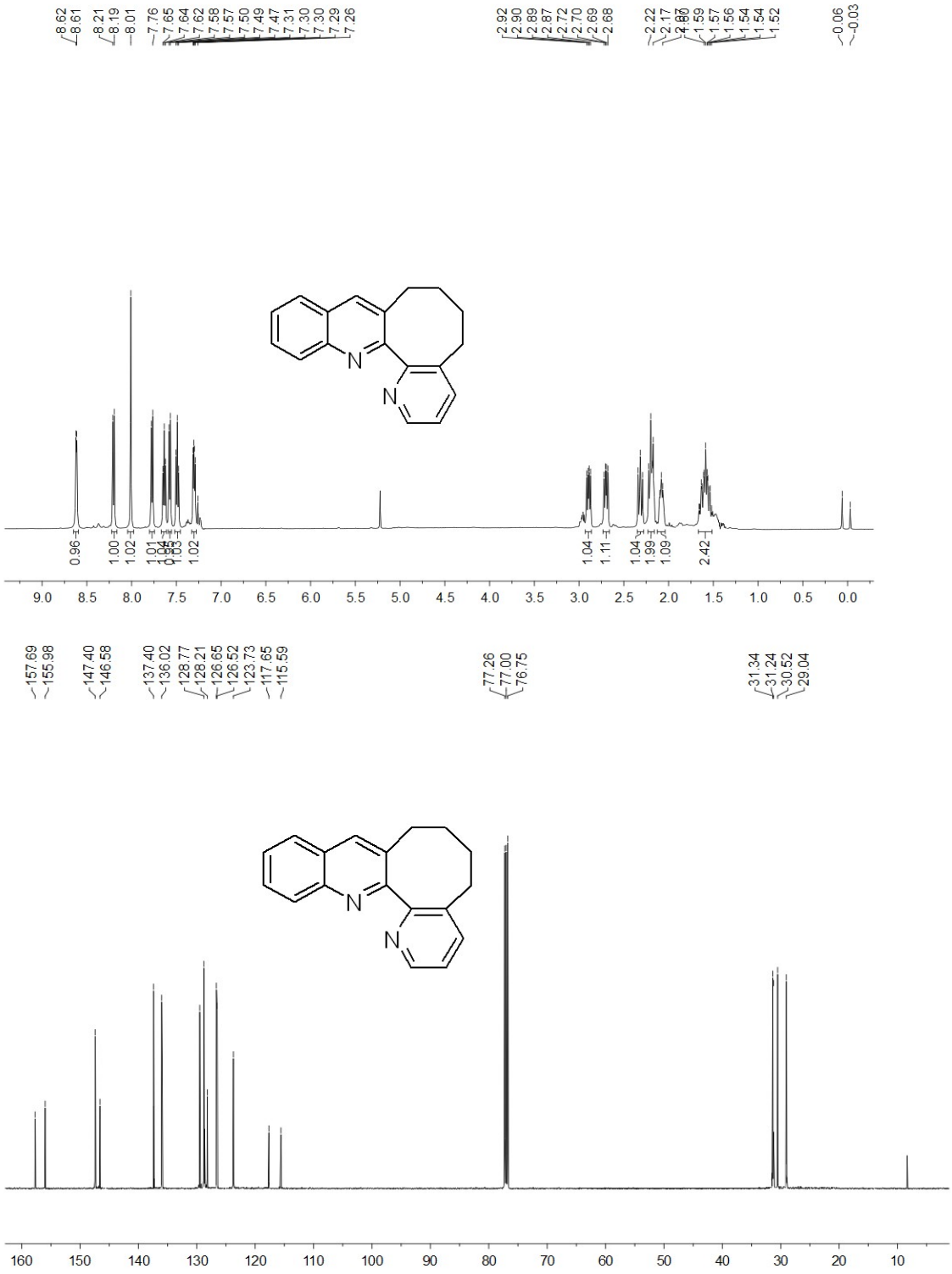


Figure S30. The ^{1}H and ^{13}C NMR spectra for **3as**

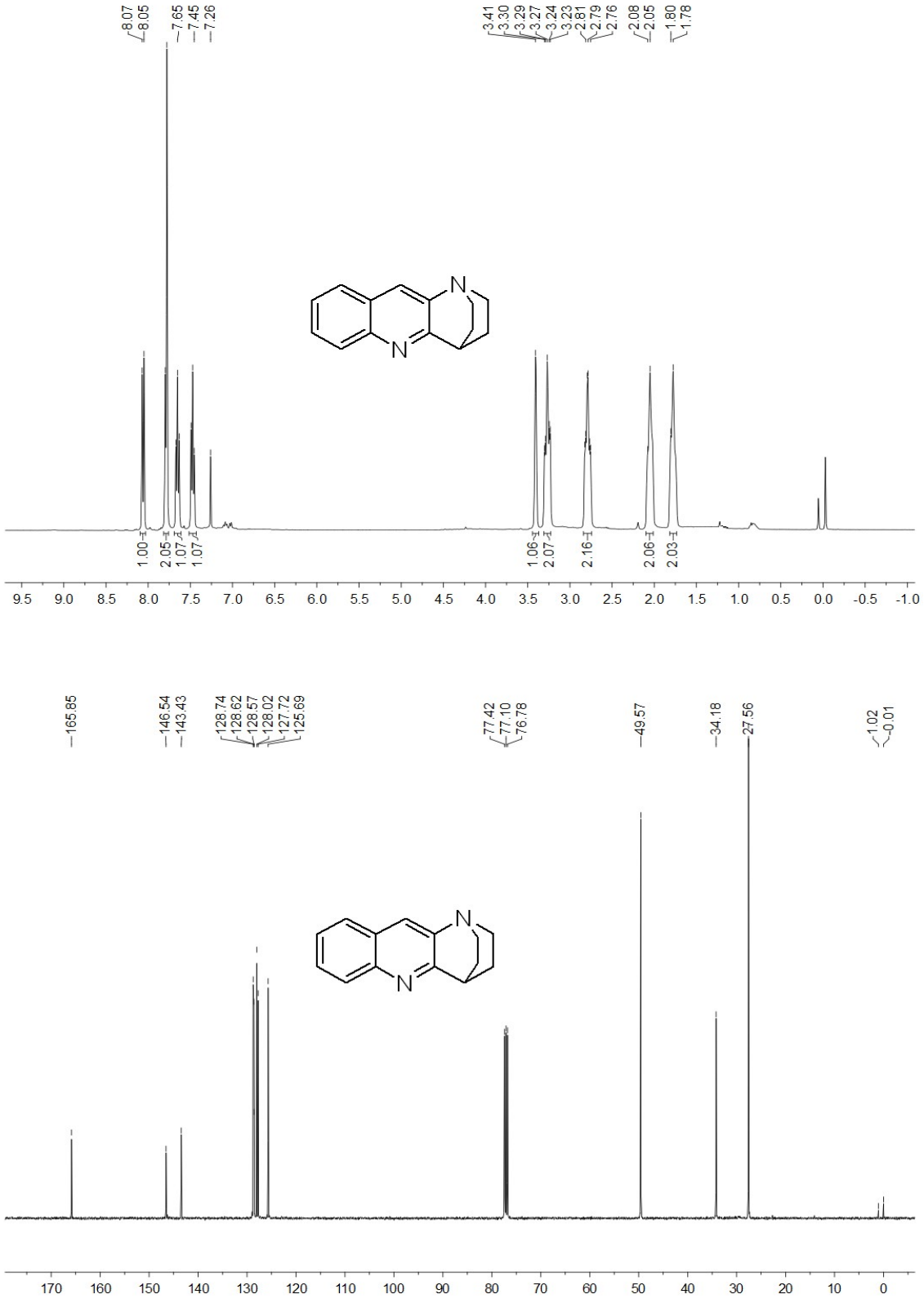


Figure S31. The ^{1}H and ^{13}C NMR spectra for **3at**

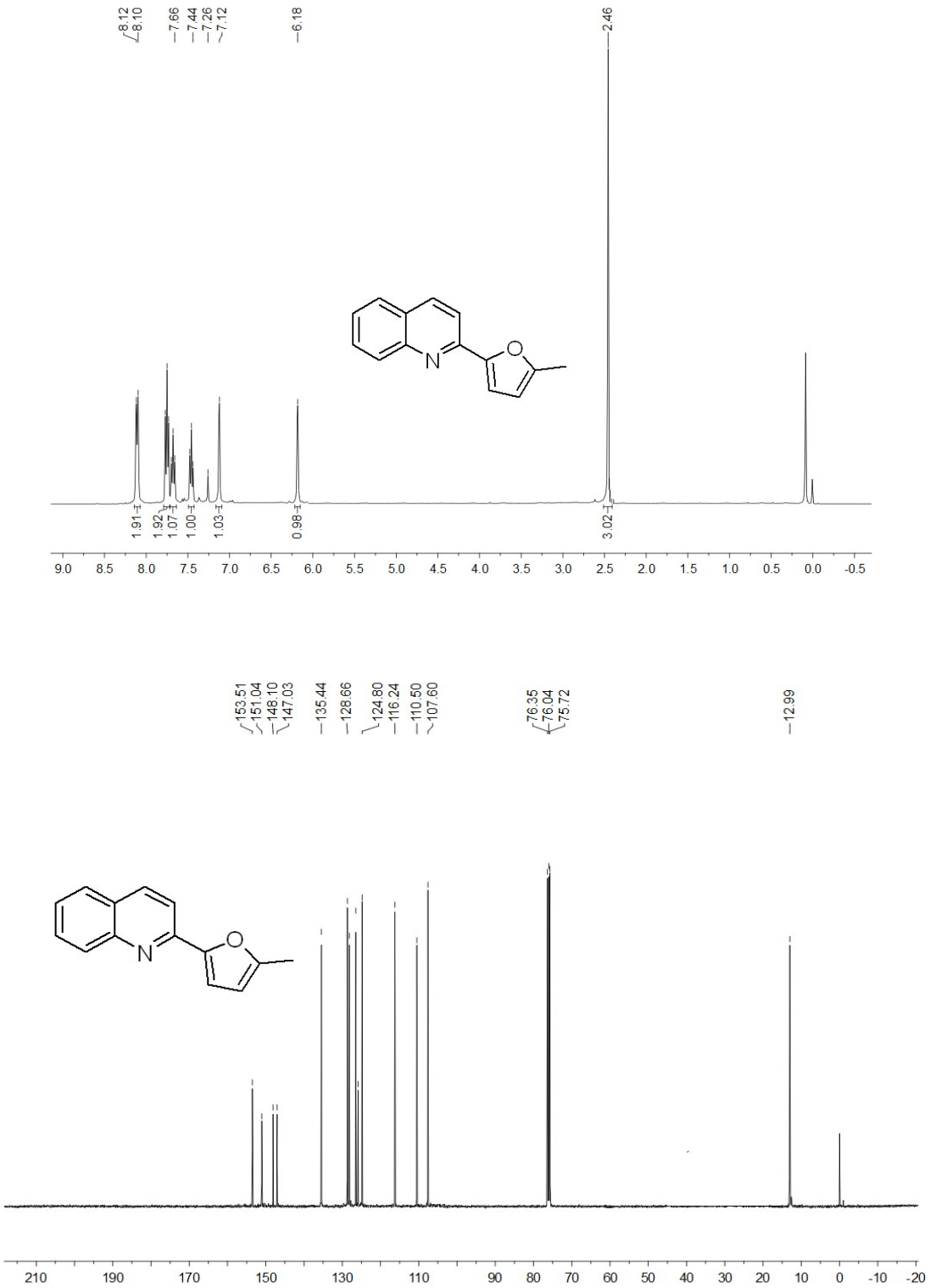


Figure S32. The ^{1}H and ^{13}C NMR spectra for **3au**

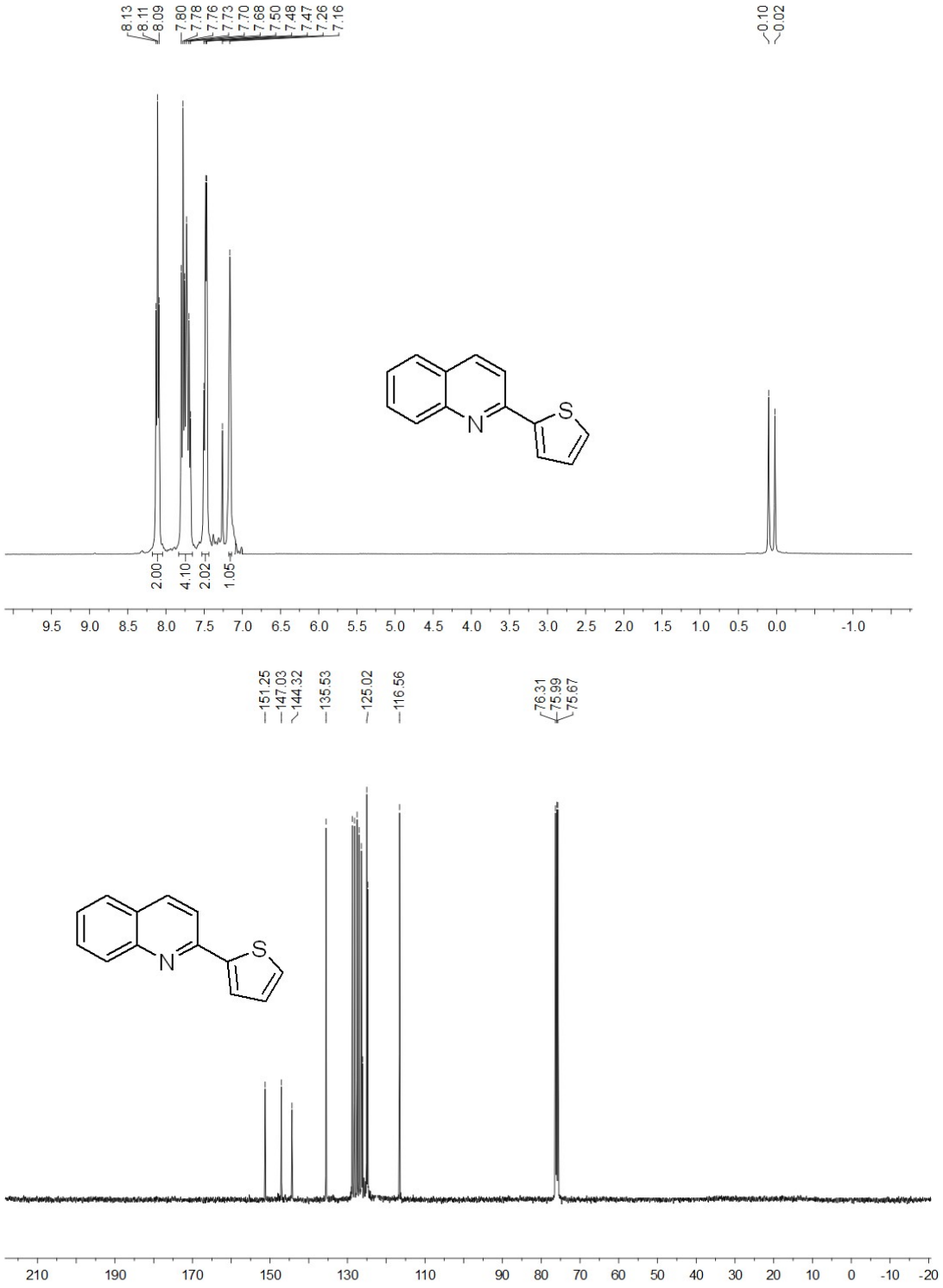


Figure S33. The ^{1}H and ^{13}C NMR spectra for **3av**

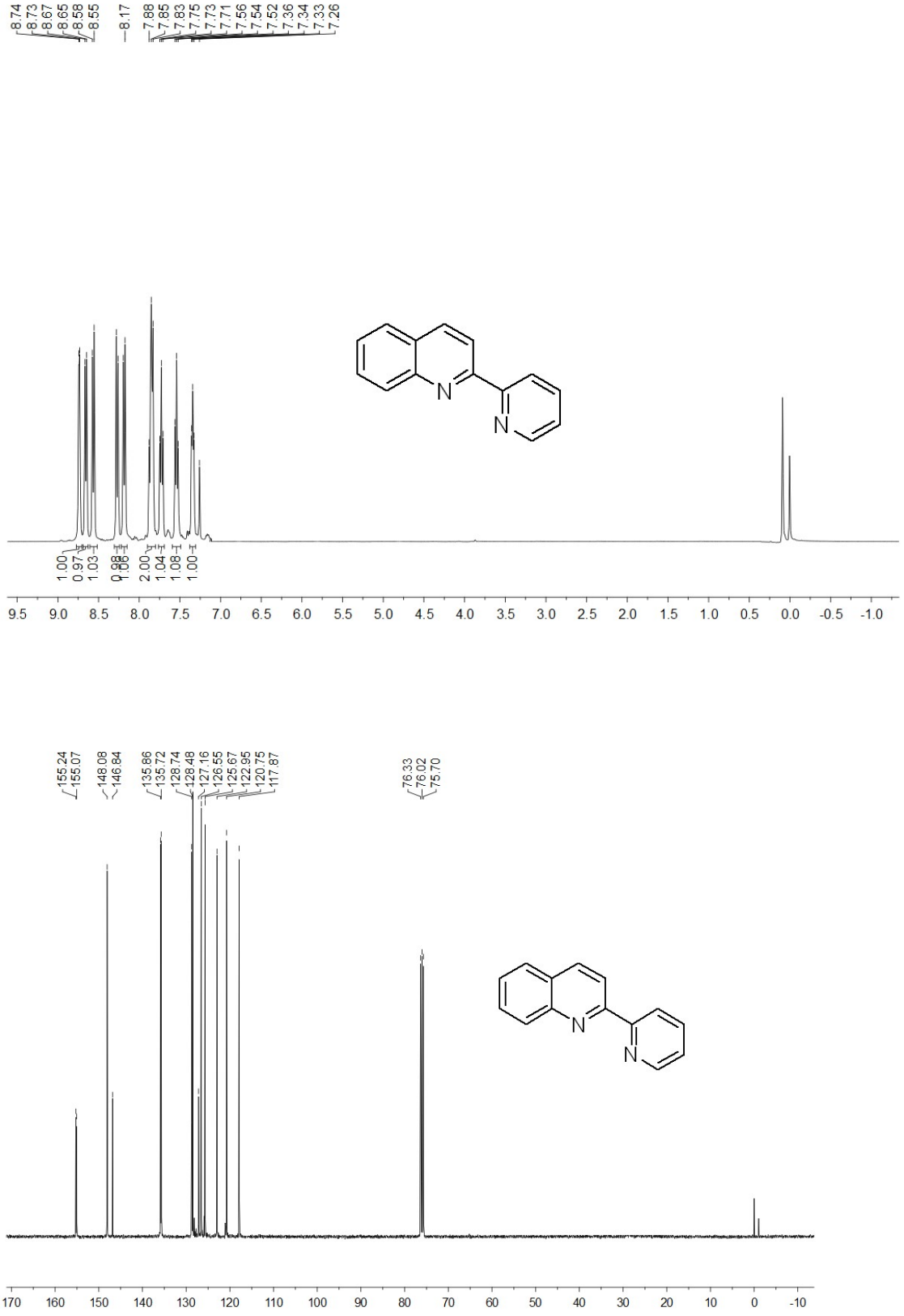


Figure S34. The ^{1}H and ^{13}C NMR spectra for **3ba**

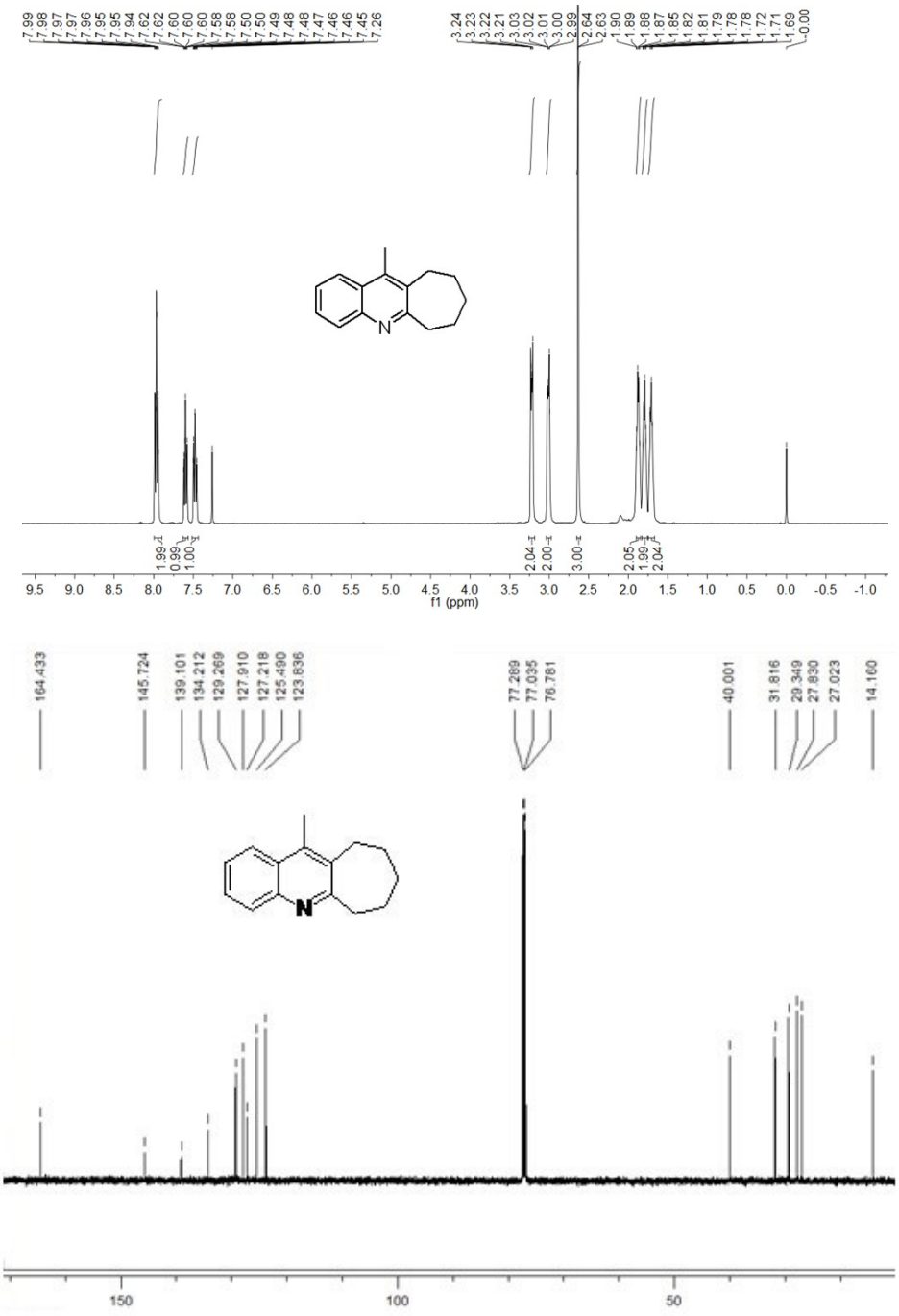


Figure S35. The ^{1}H and ^{13}C NMR spectra for **3ca**

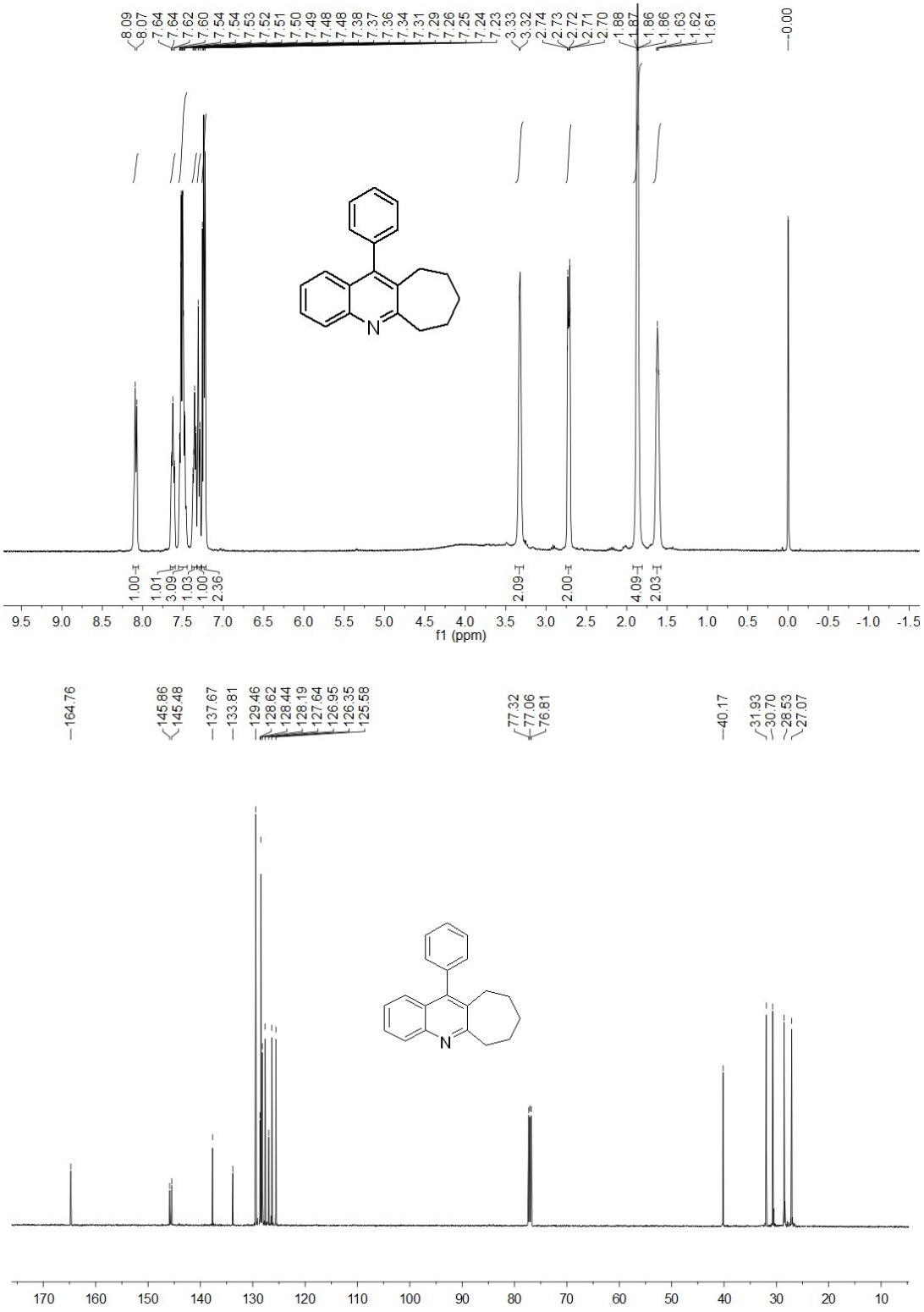


Figure S36. The ^{1}H and ^{13}C NMR spectra for **3da**

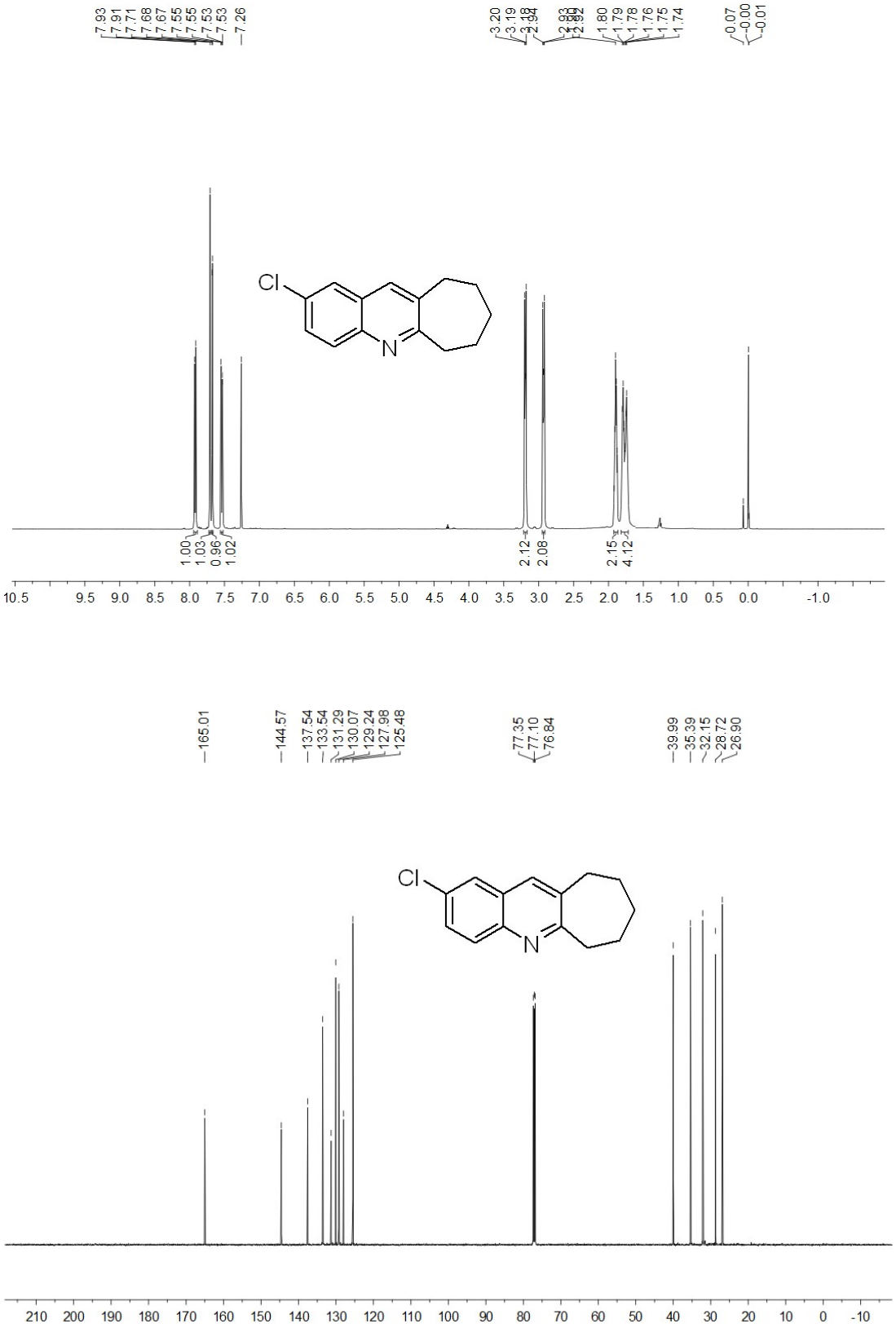


Figure S37. The ^{1}H and ^{13}C NMR spectra for **3ea**

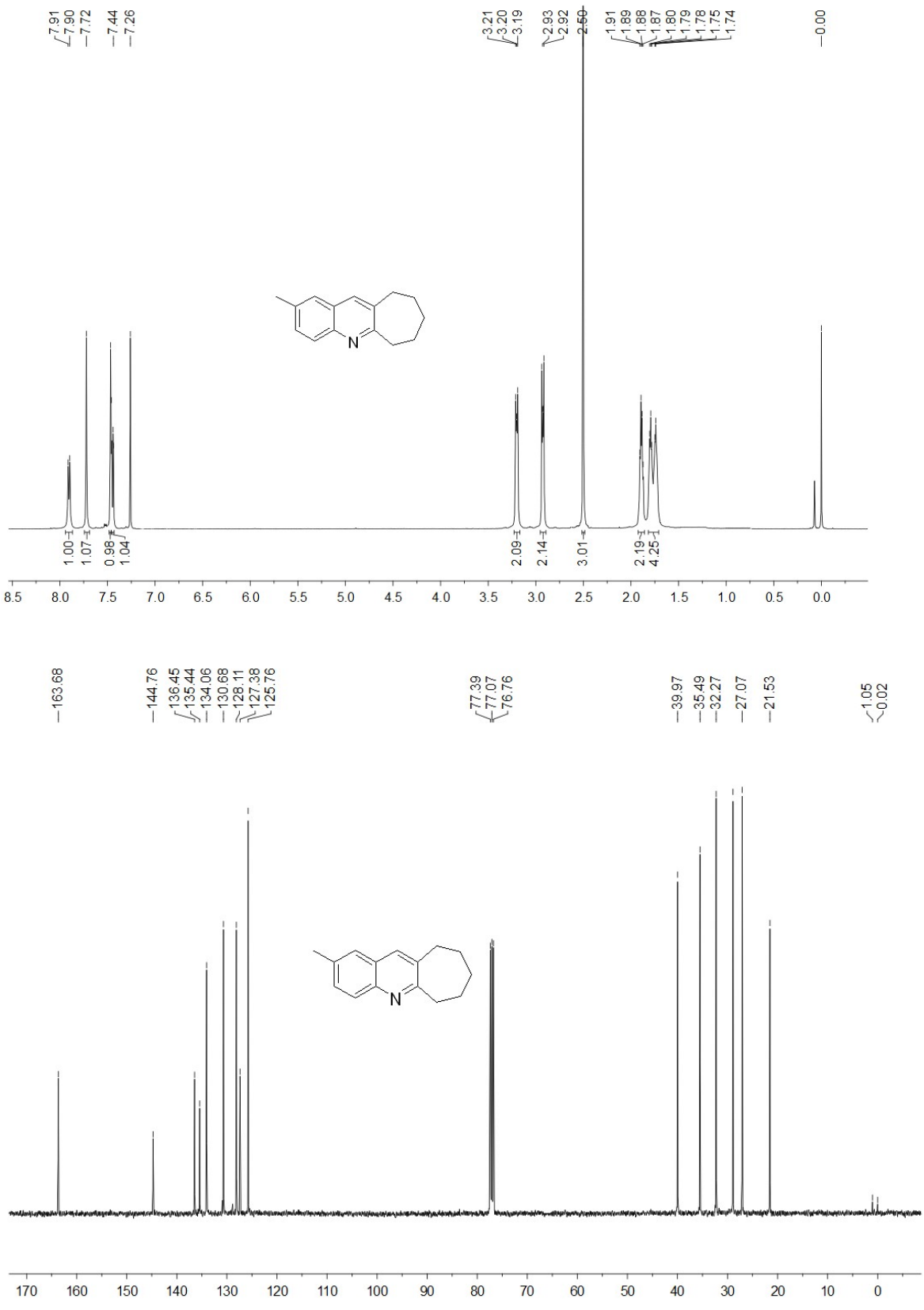


Figure S38. The ^{1}H and ^{13}C NMR spectra for **3bc**

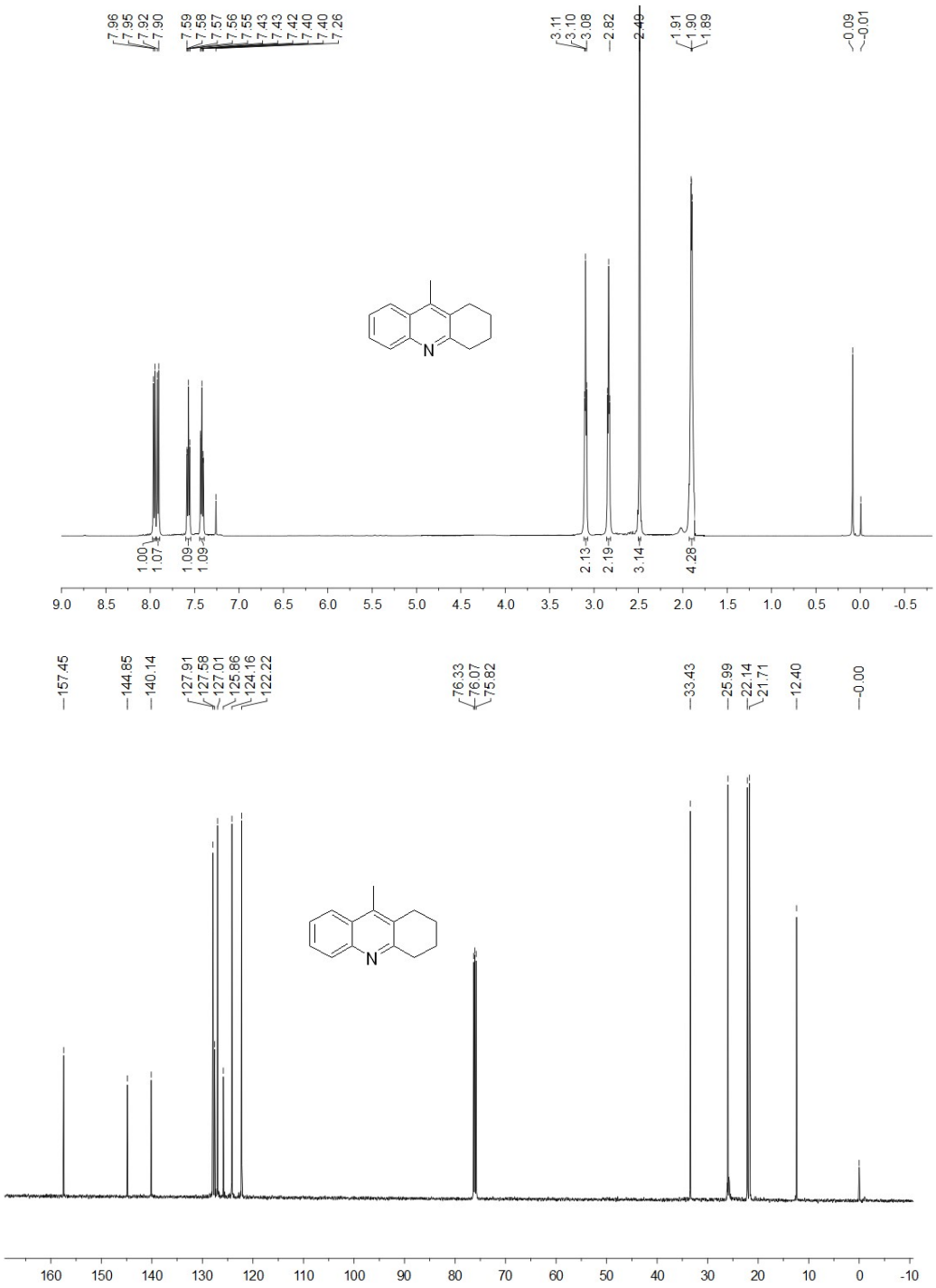


Figure S39. The ^{1}H and ^{13}C NMR spectra for **3cc**

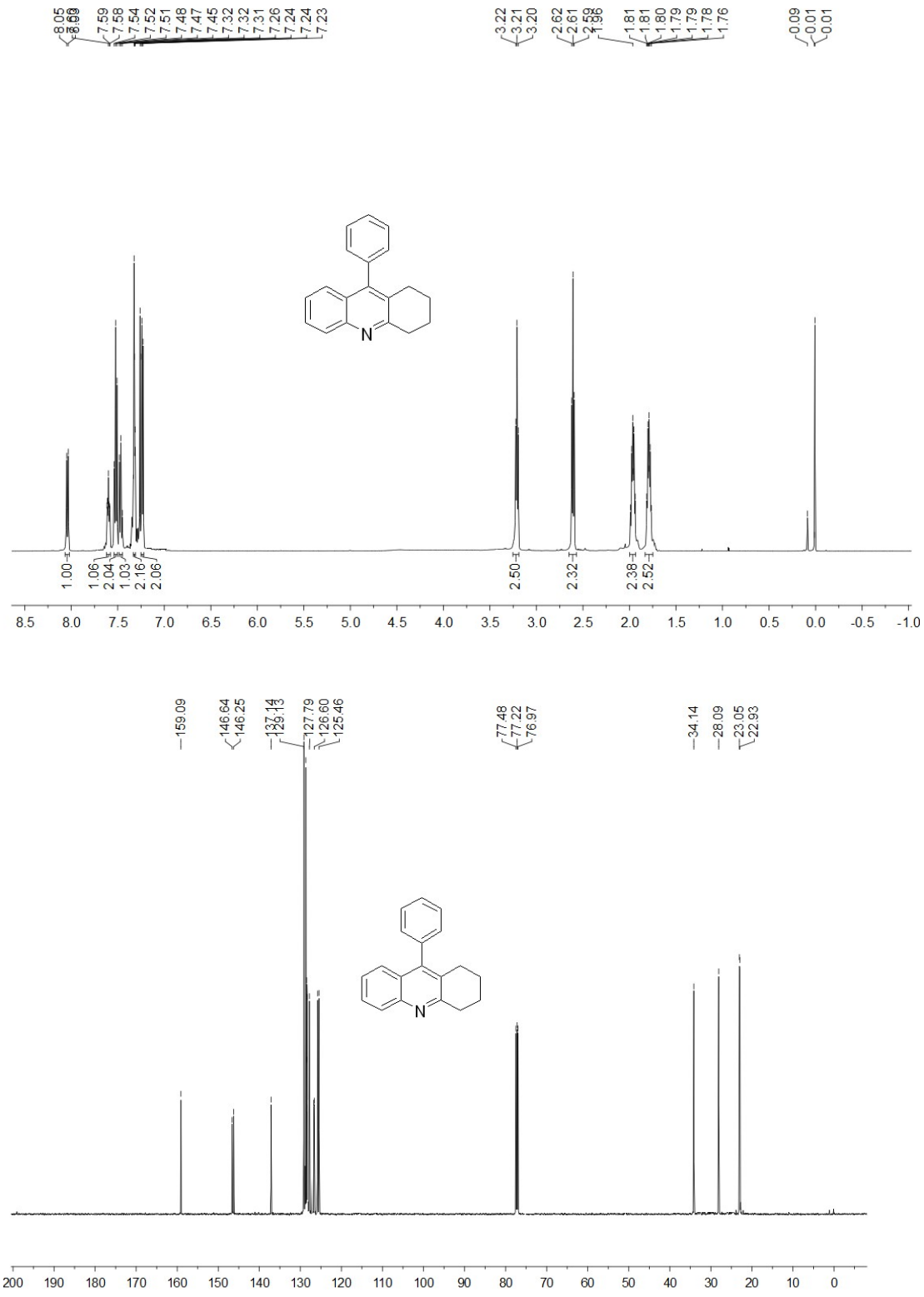


Figure S40. The ^{1}H and ^{13}C NMR spectra for **3dc**

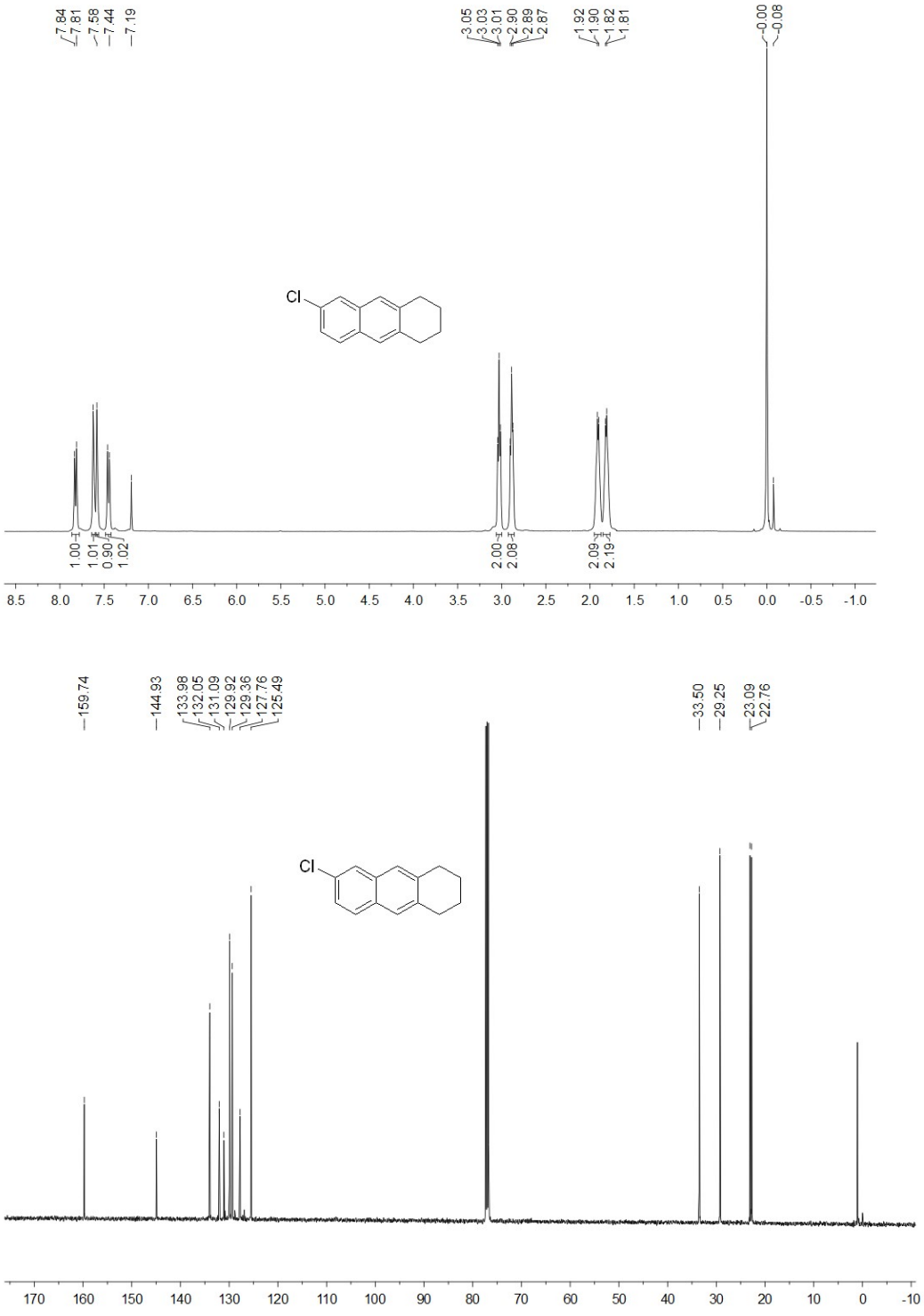


Figure S41. The ^{1}H and ^{13}C NMR spectra for **3ec**

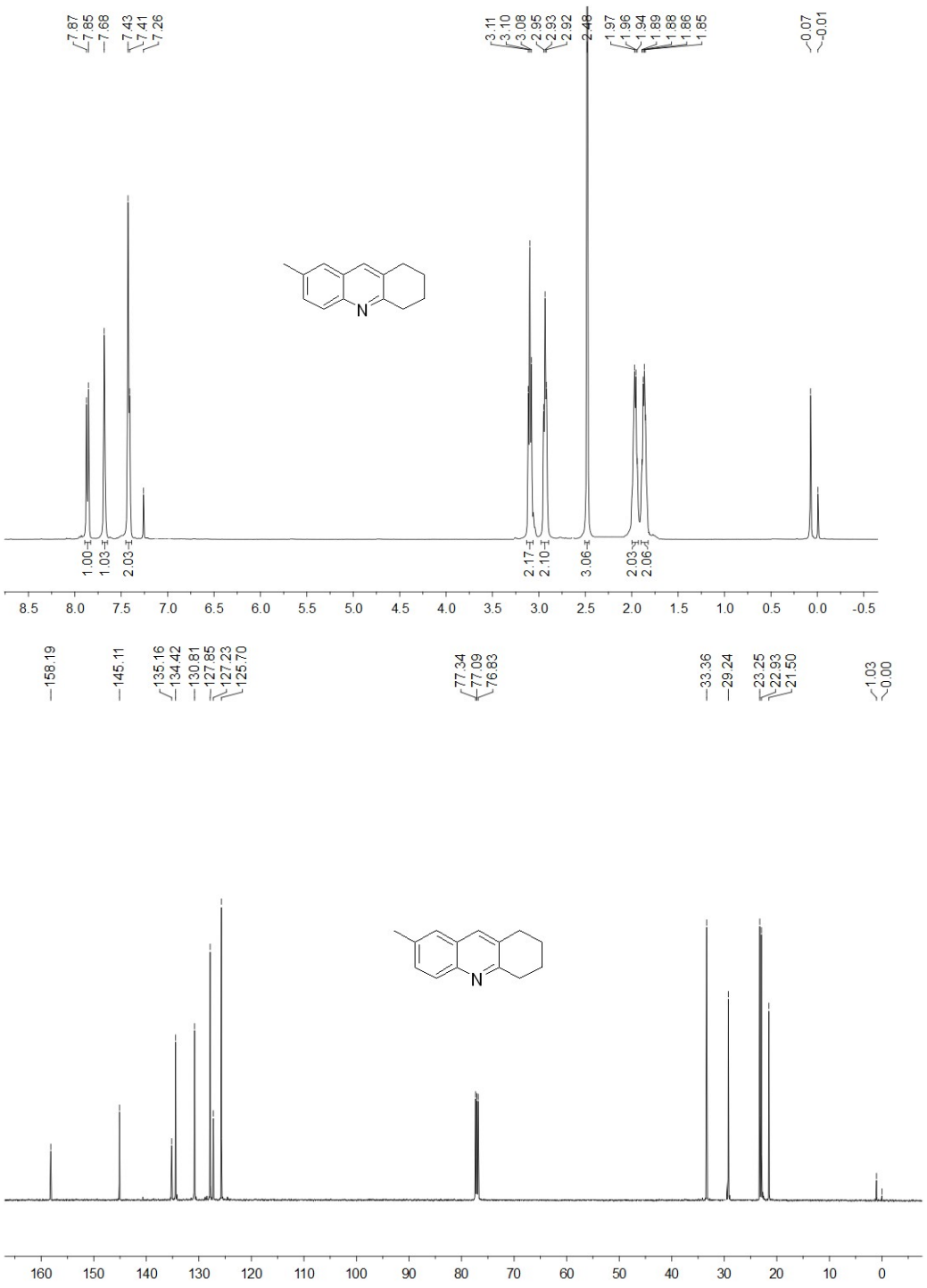


Figure S42. The ^{1}H and ^{13}C NMR spectra for **3bd**

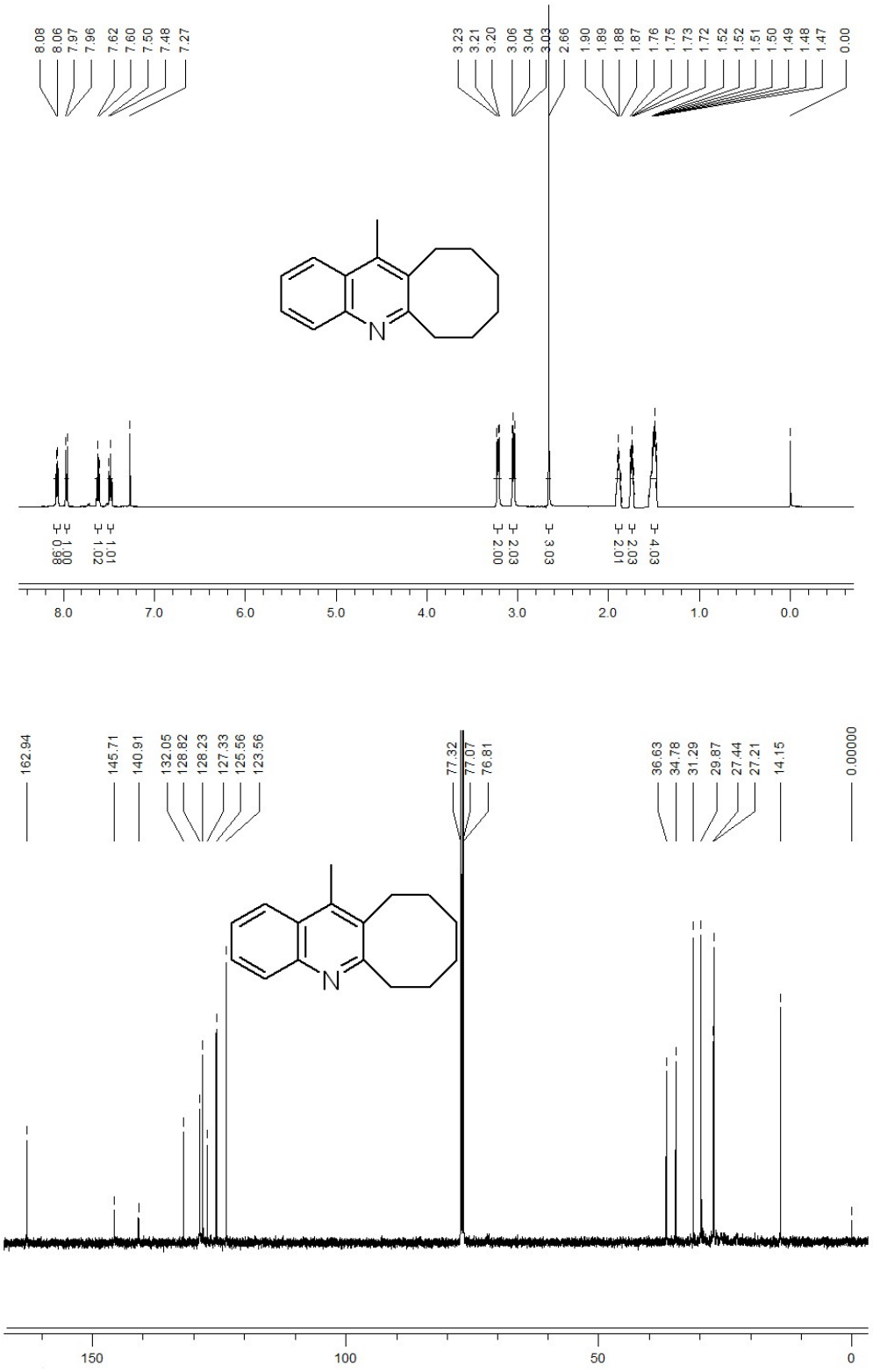
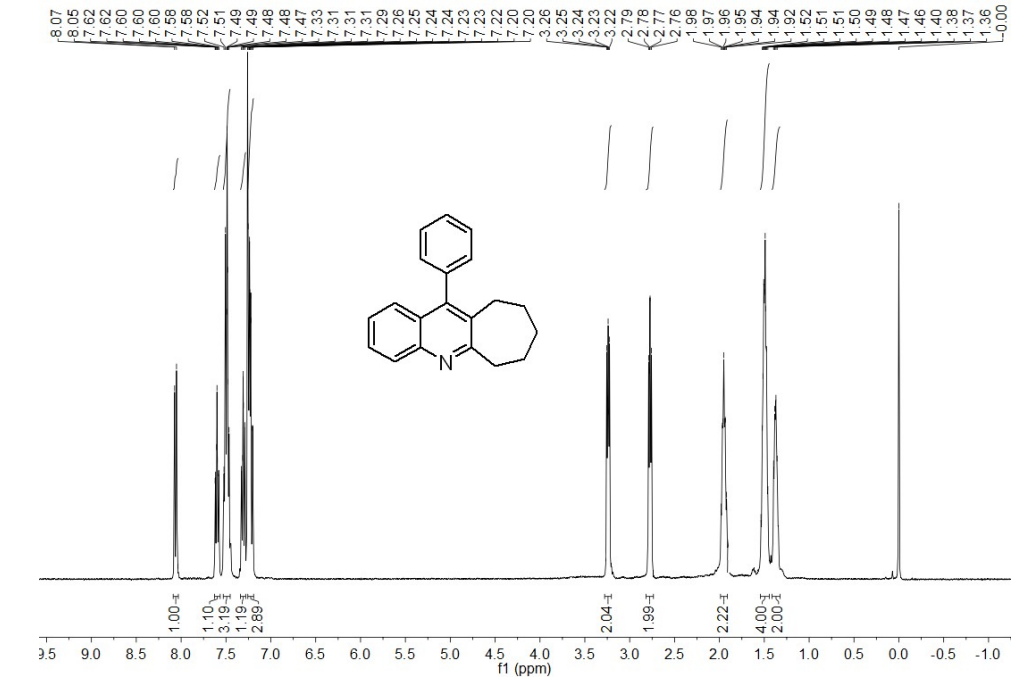


Figure S43. The ^{1}H and ^{13}C NMR spectra for **3cd**



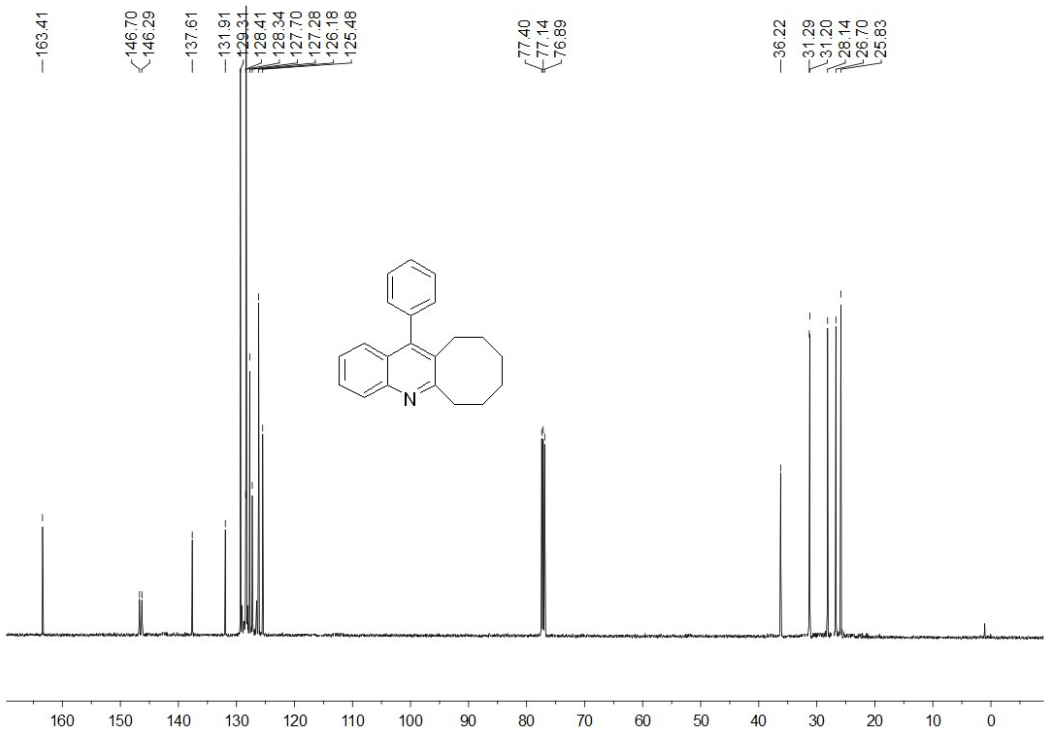


Figure S44. The ^{1}H and ^{13}C NMR spectra for **3dd**

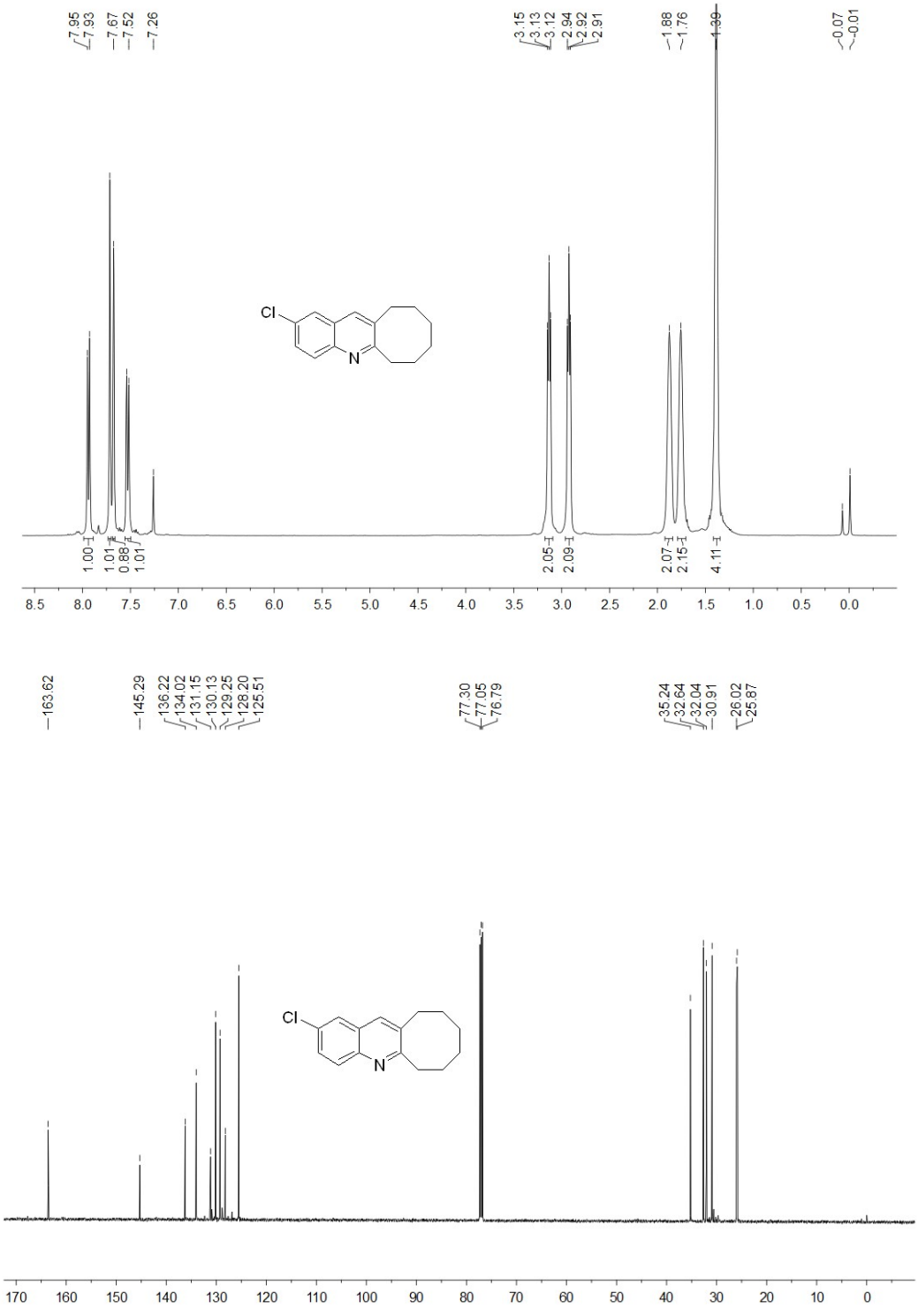


Figure S45. The ^{1}H and ^{13}C NMR spectra for **3ed**

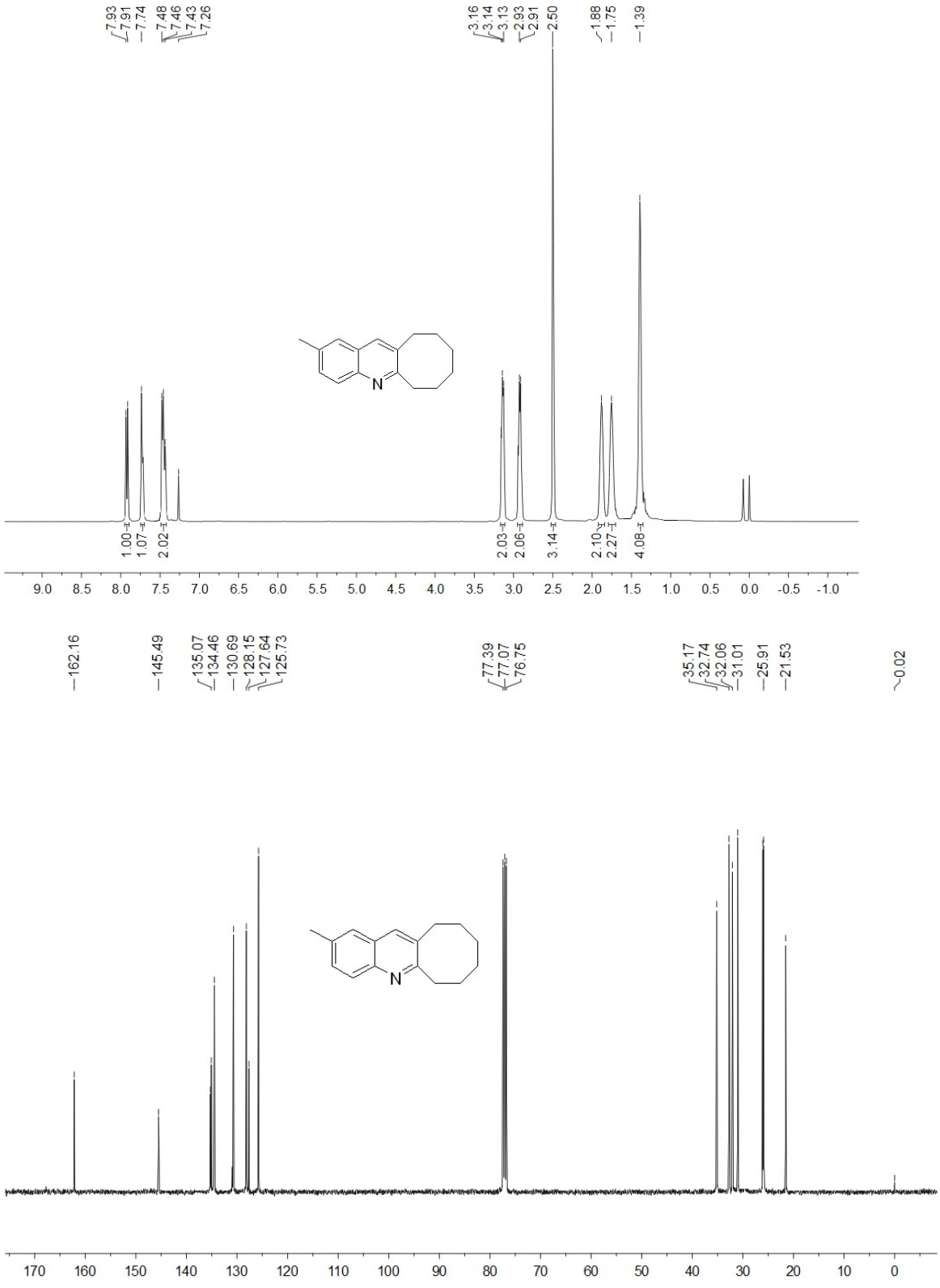


Figure S46. The ^{1}H and ^{13}C NMR spectra for **3be**

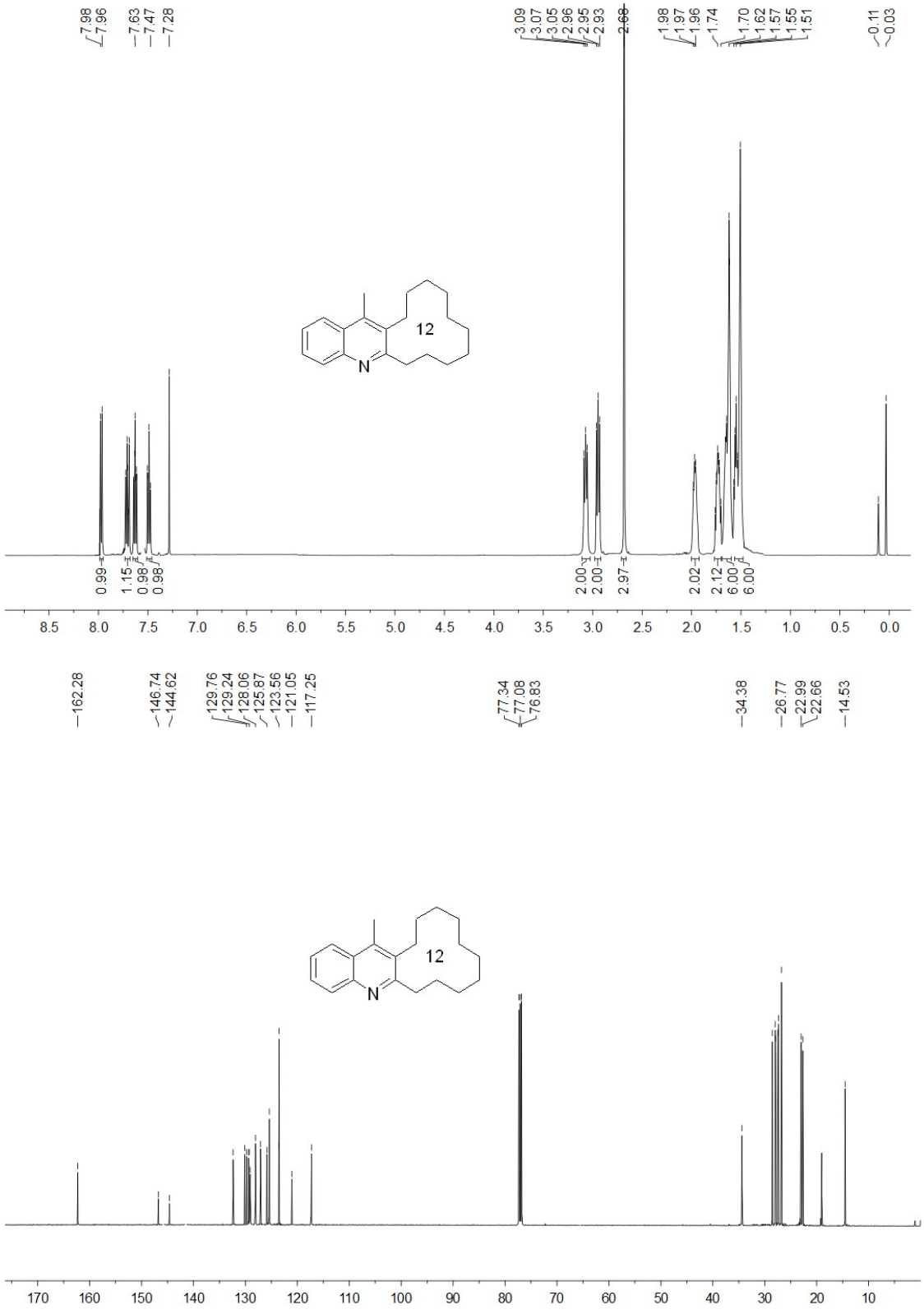


Figure S47. The ^{1}H and ^{13}C NMR spectra for **3ce**

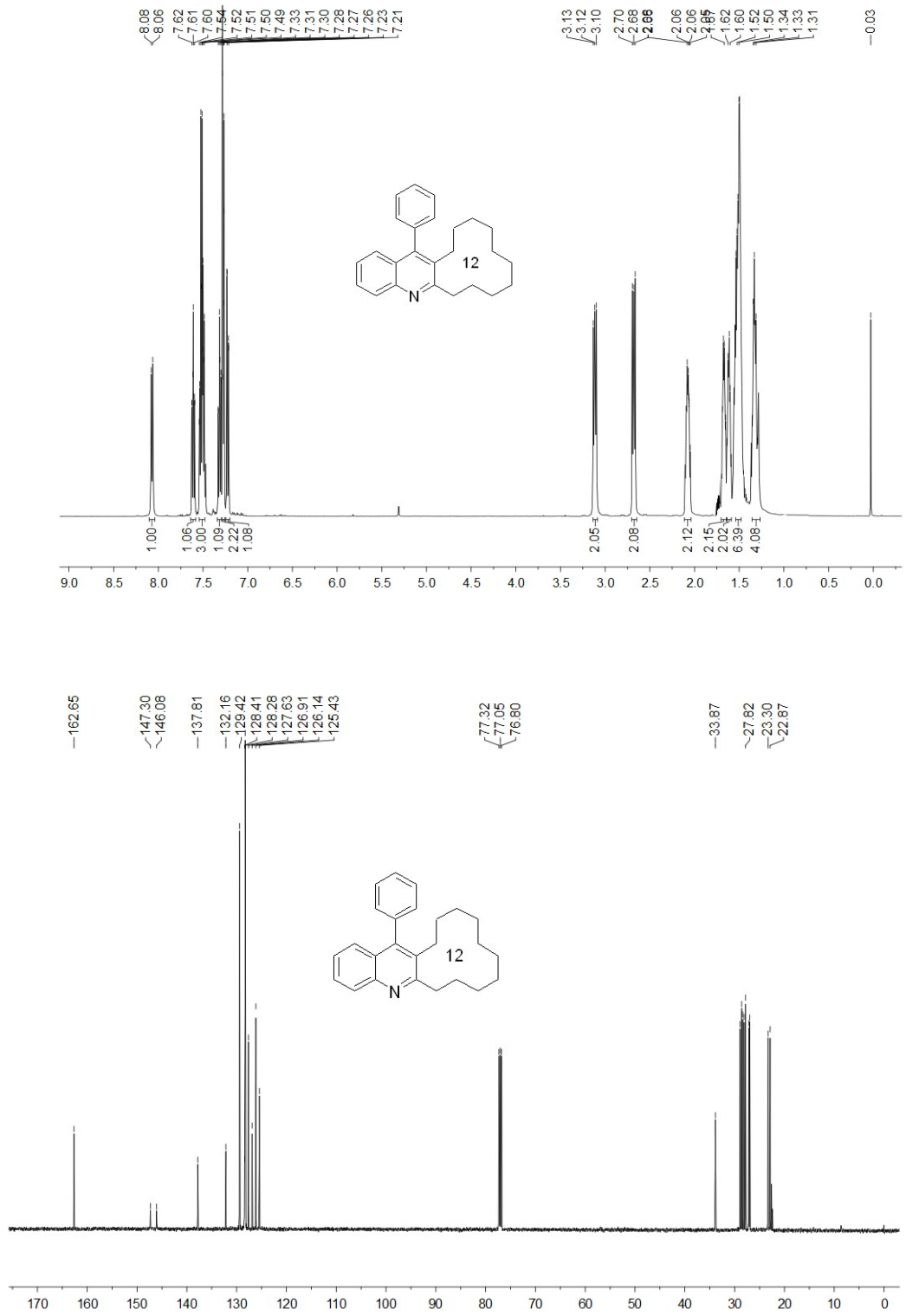


Figure S48. The ^{1}H and ^{13}C NMR spectra for **3de**

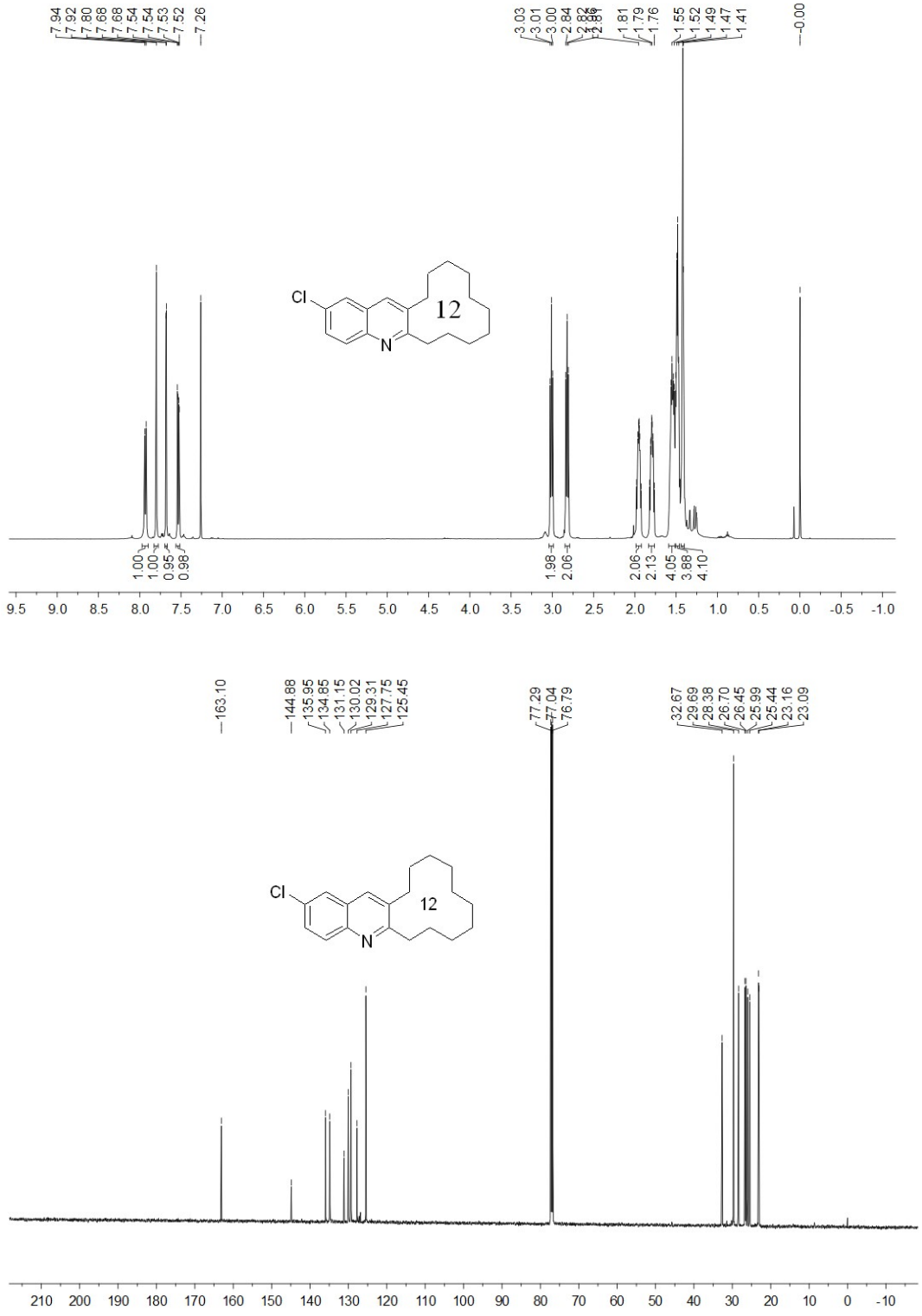


Figure S49. The ^{1}H and ^{13}C NMR spectra for **3ee**

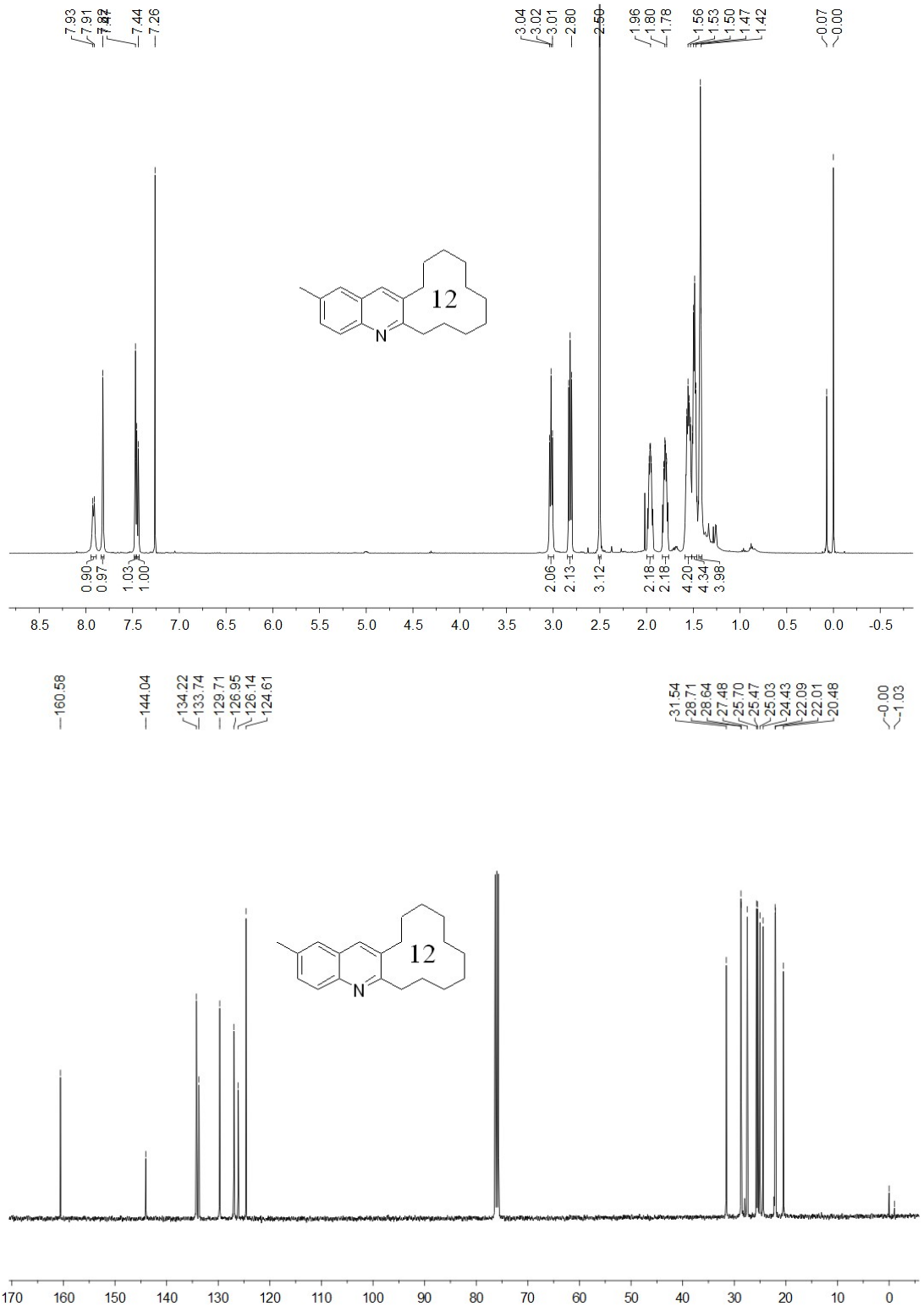


Figure S50. The ^{1}H and ^{13}C NMR spectra for **3ef**

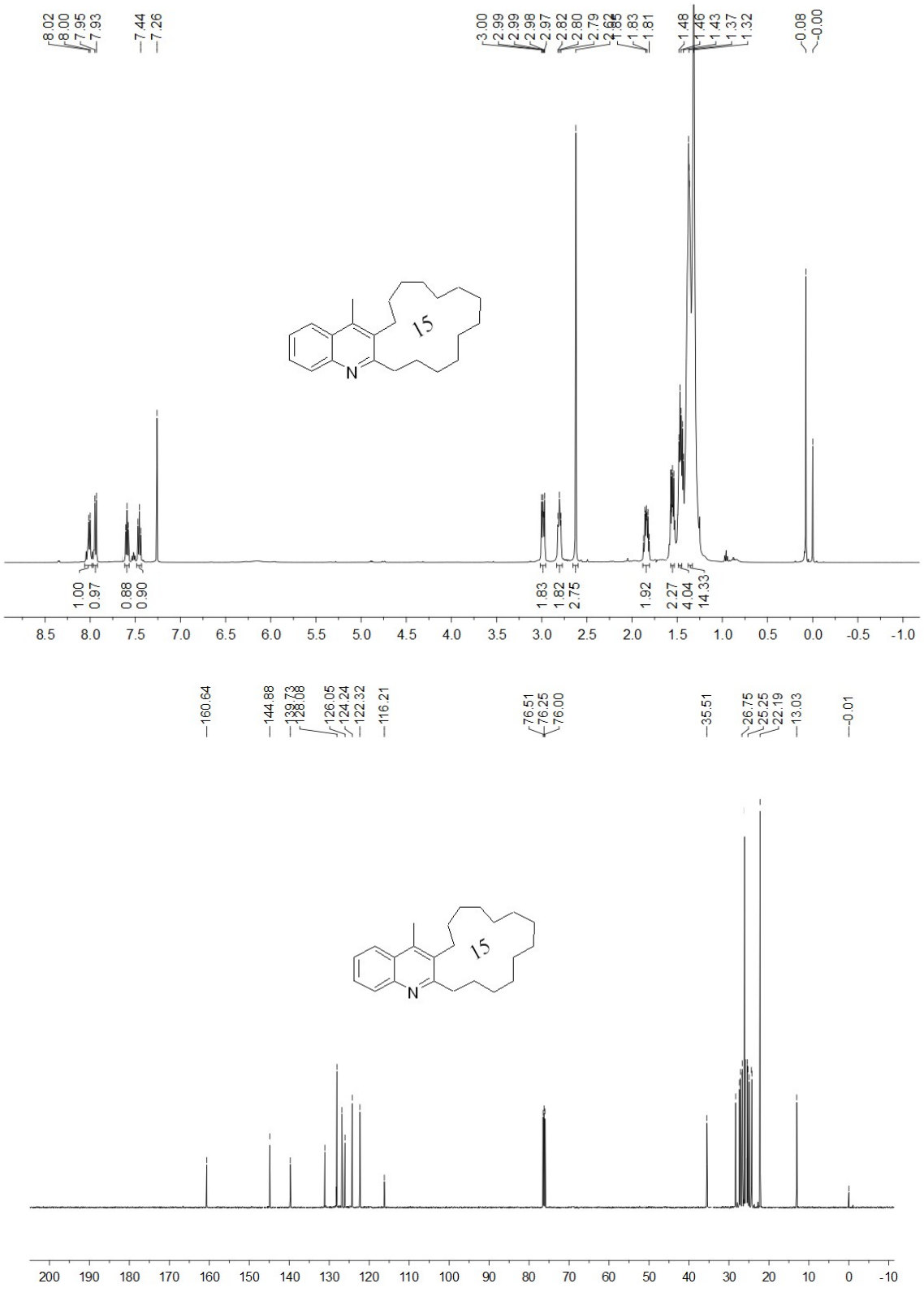


Figure S51. The ^{1}H and ^{13}C NMR spectra for **3cf**

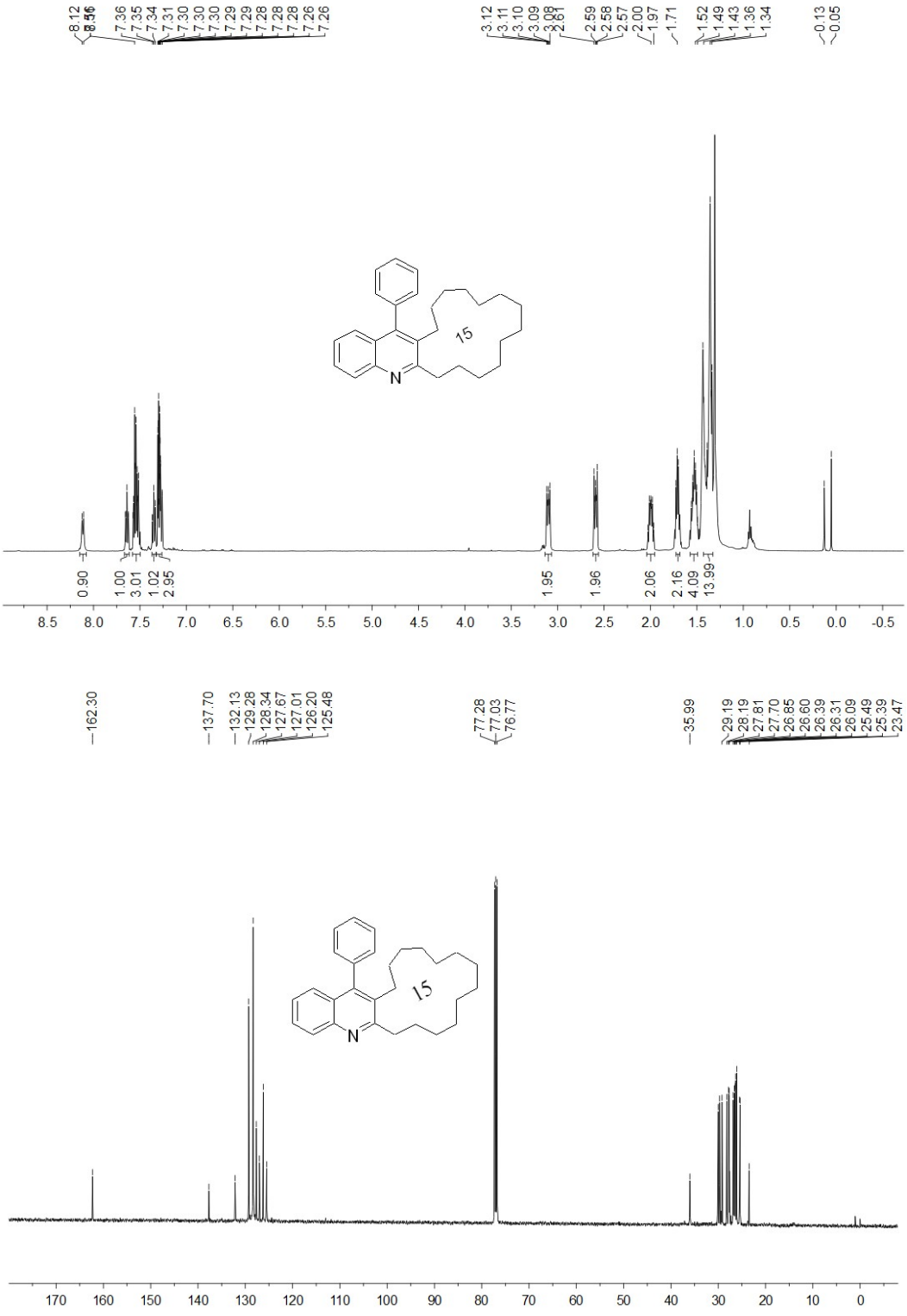


Figure S52. The ^{1}H and ^{13}C NMR spectra for **3df**

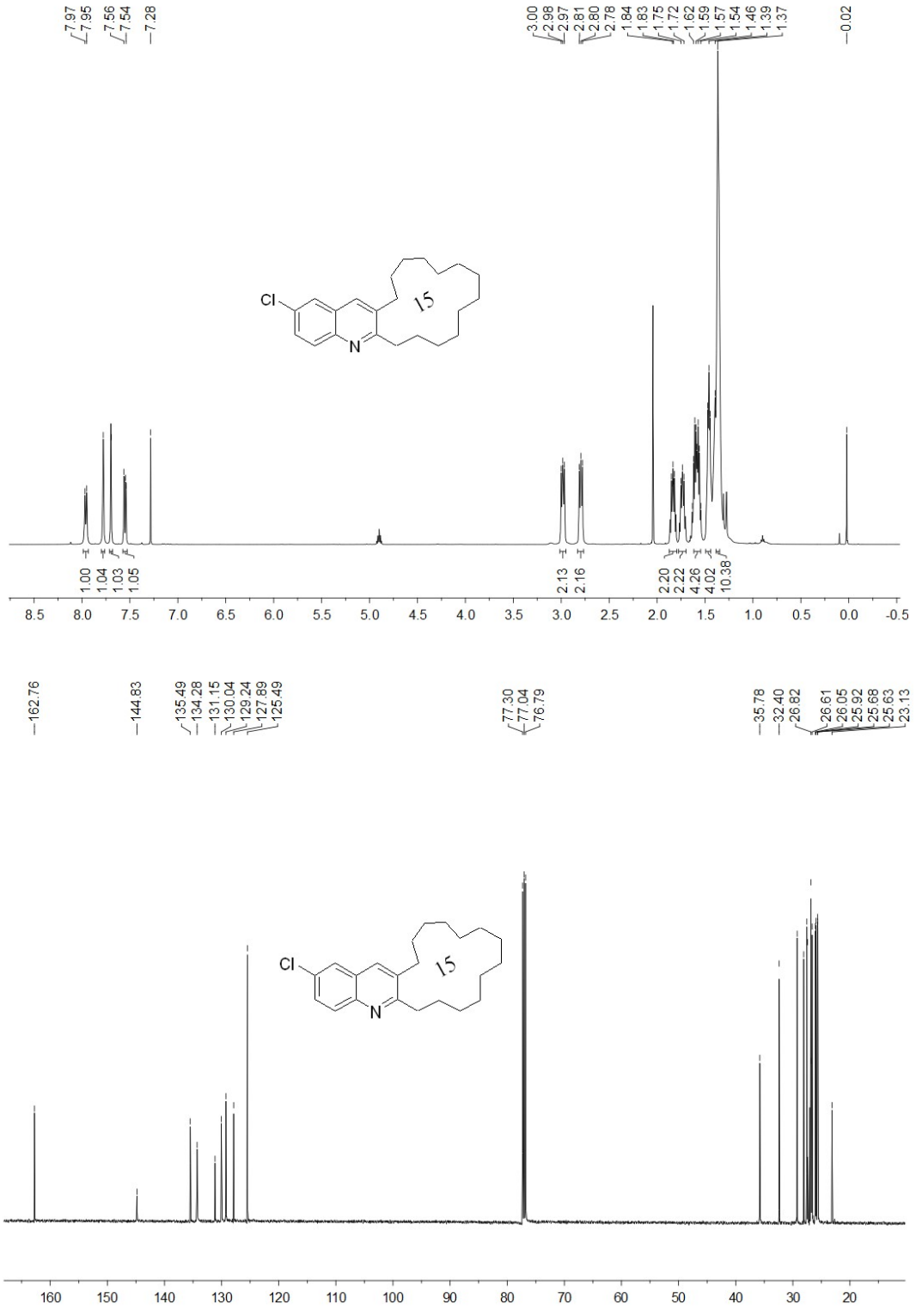
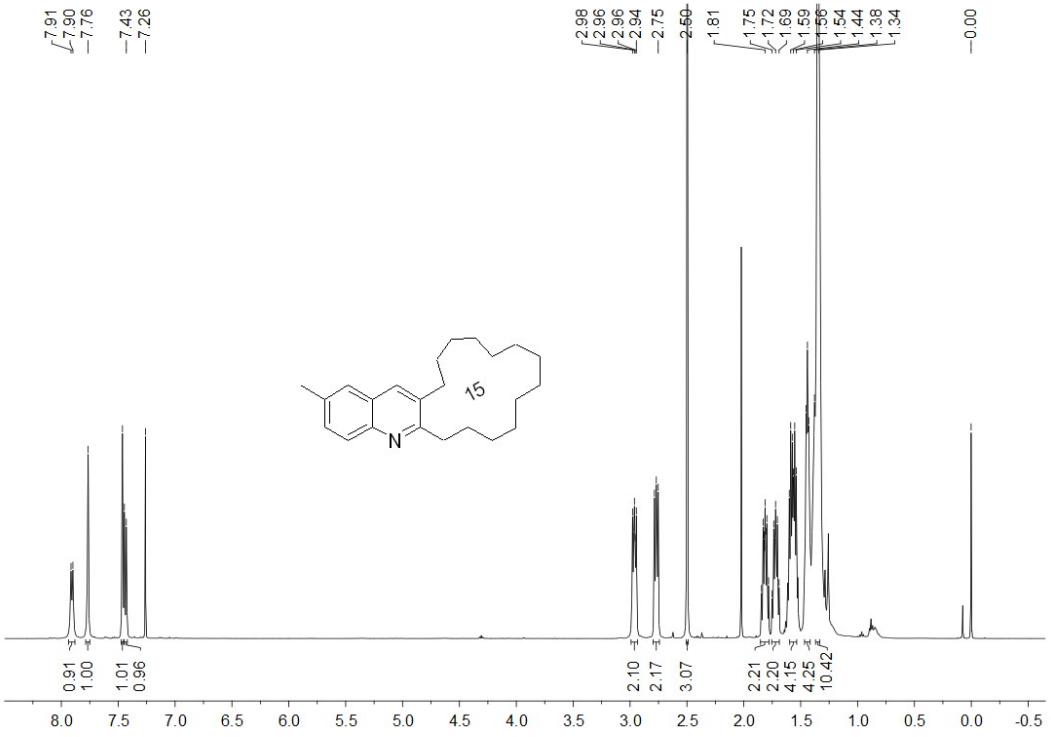


Figure S53. The ^{1}H and ^{13}C NMR spectra for 2-methyl-7,8,9,10,11,12,13,14,15,16,17,18-dodeca- hydro-6H-cyclopentadeca[b]quinoline (**3ef**).



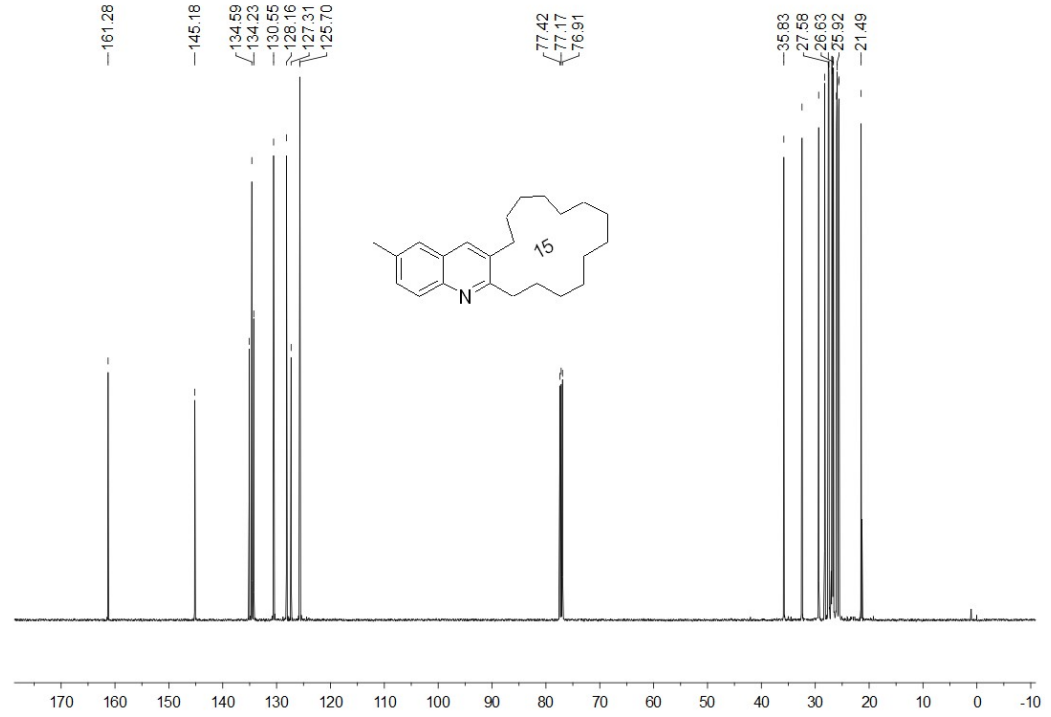


Figure S54. The ^{1}H and ^{13}C NMR spectra for **3dg**

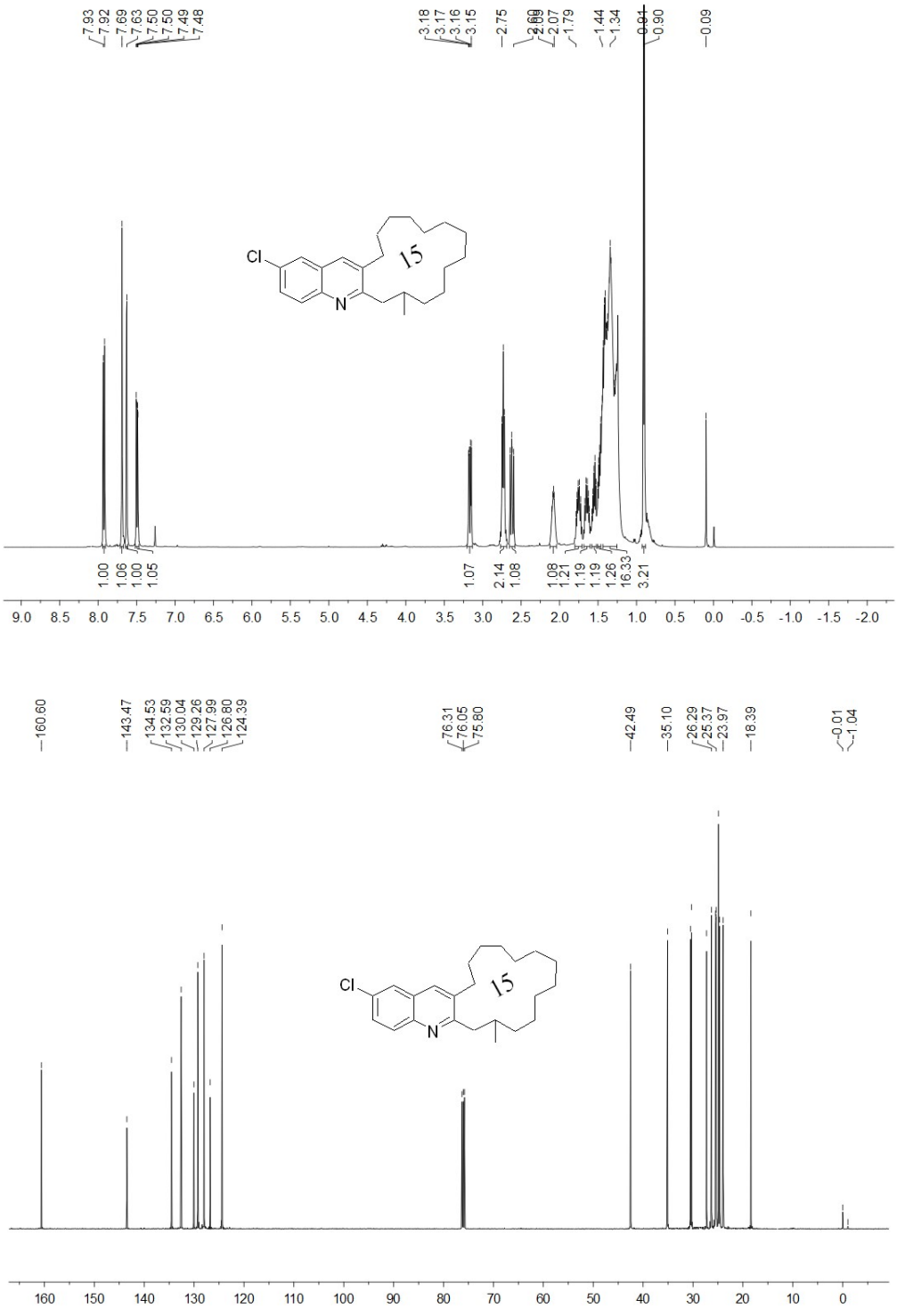


Figure S55. The ^{1}H and ^{13}C NMR spectra for **3di**

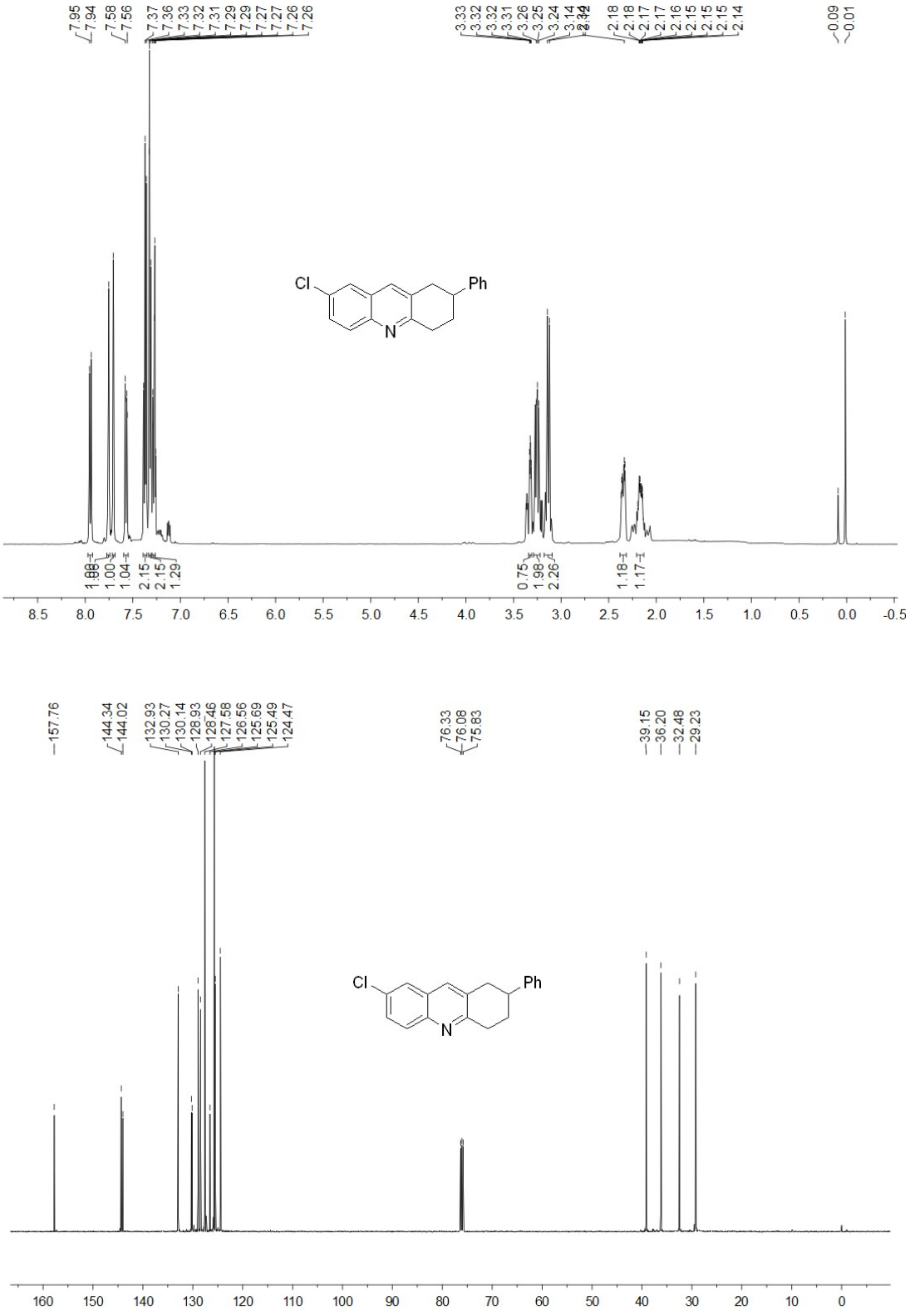


Figure S56. The ^{1}H and ^{13}C NMR spectra for **3ei**

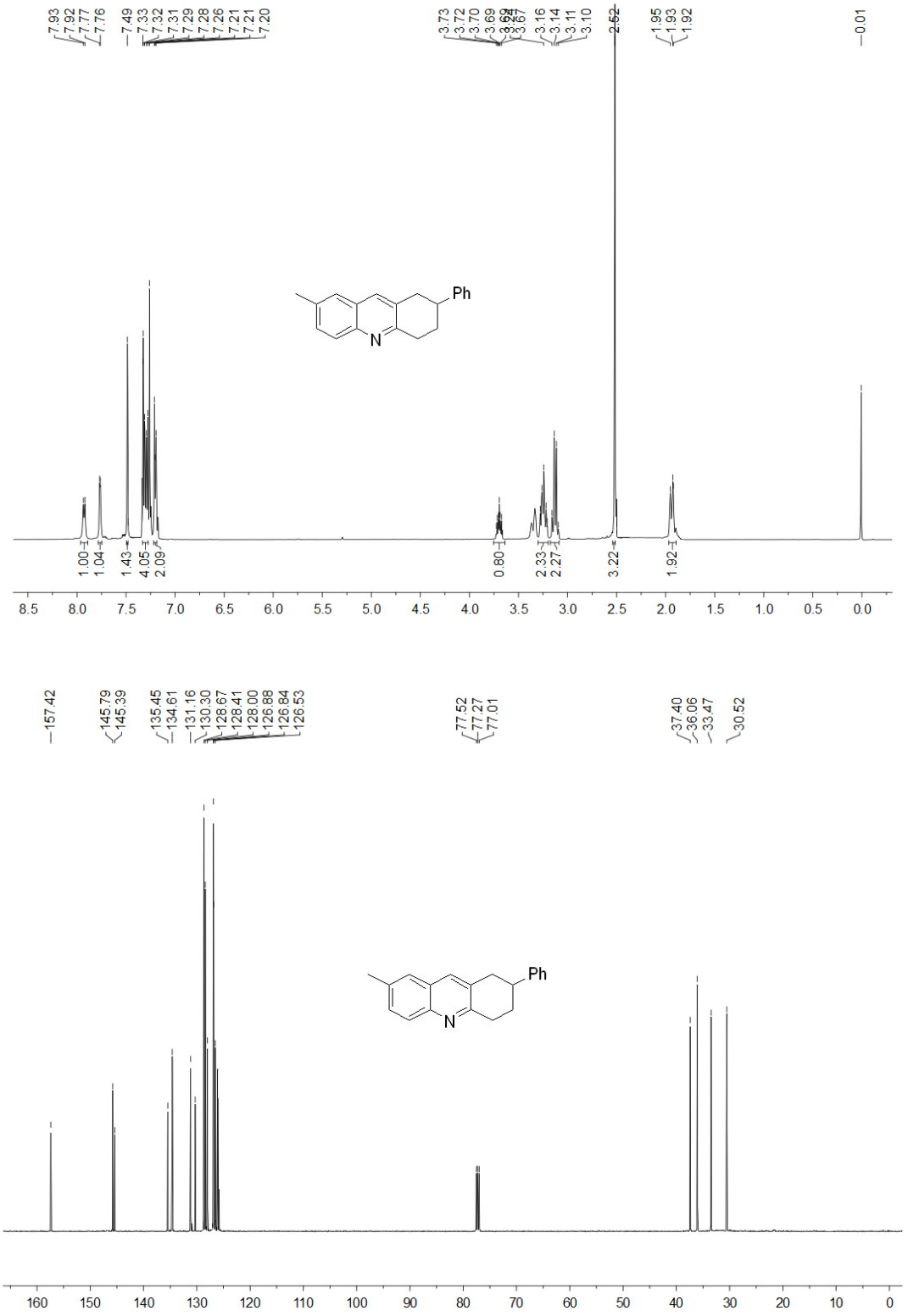


Figure S57. The ^{1}H and ^{13}C NMR spectra for **3cl**

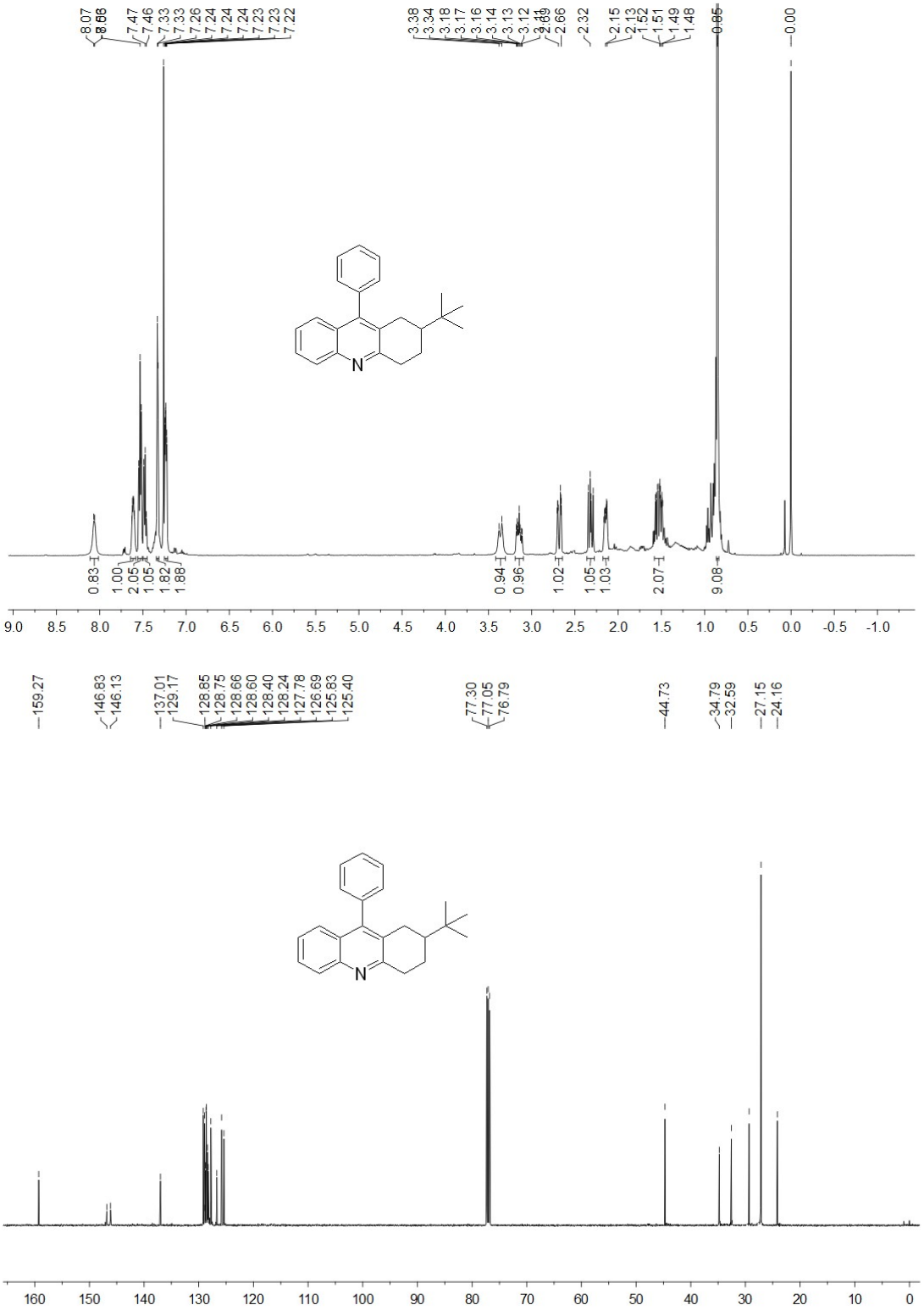


Figure S58. The ^{1}H and ^{13}C NMR spectra for **3dl**

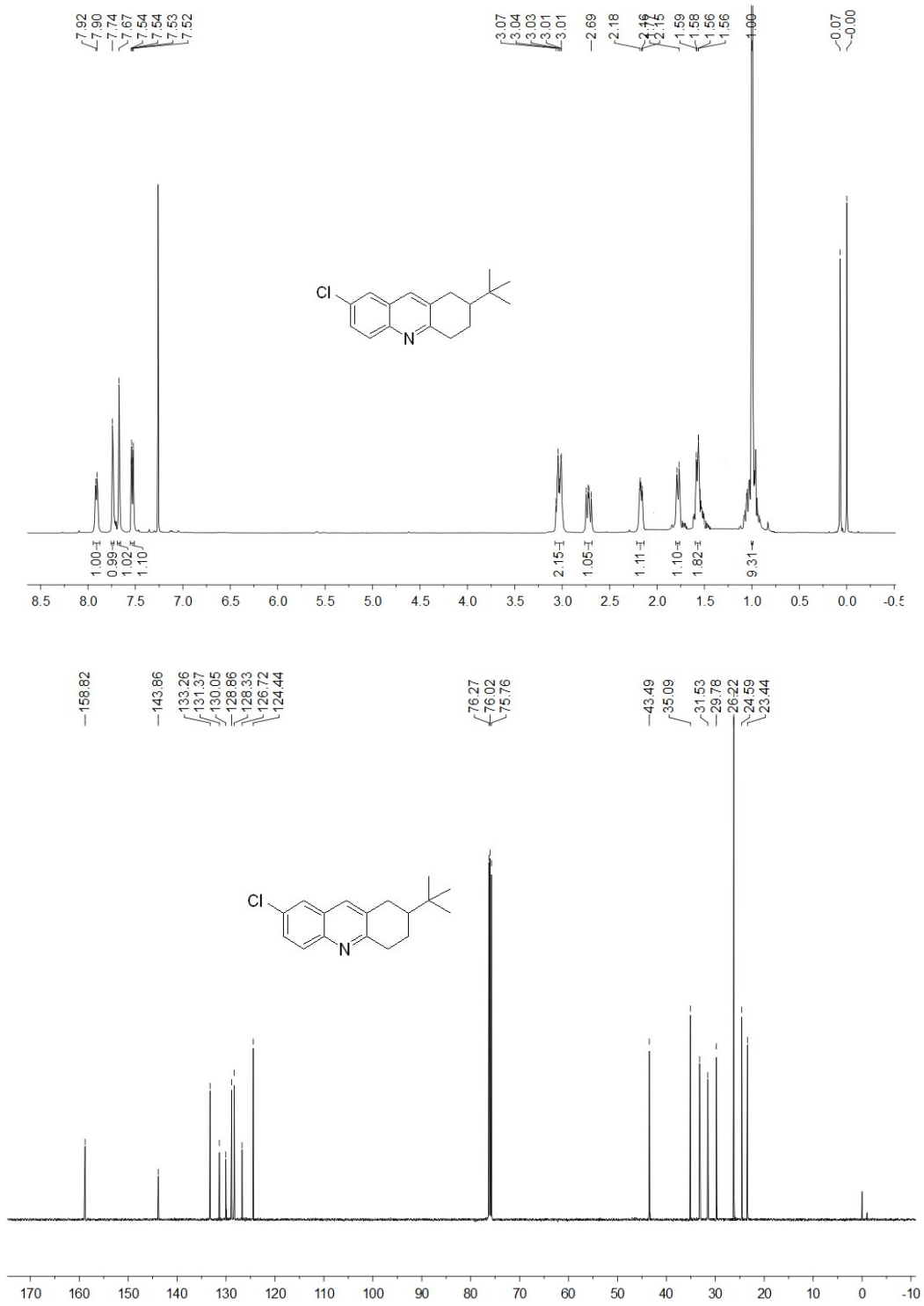


Figure S59. The ^{1}H and ^{13}C NMR spectra for **3el**

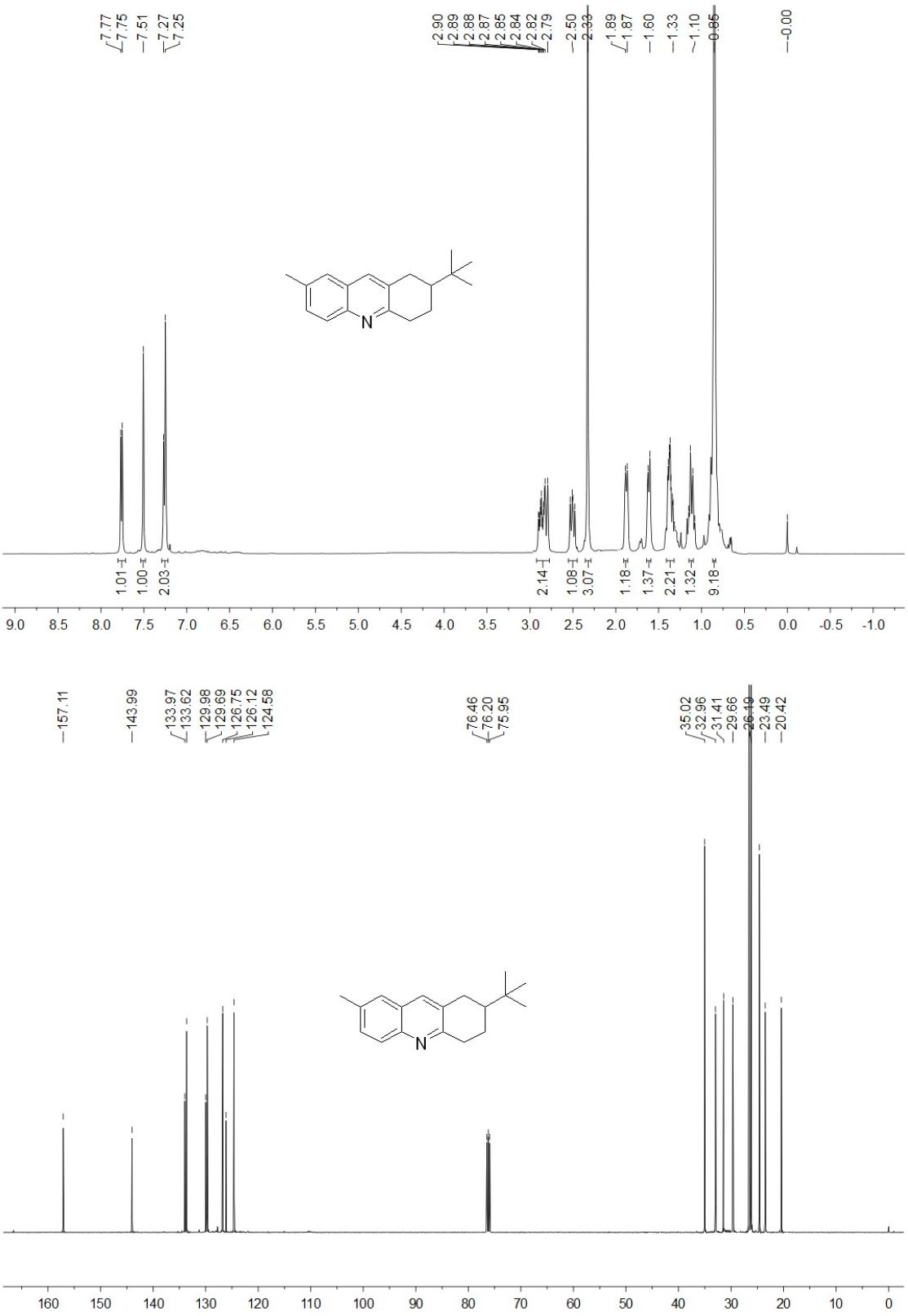


Figure S60. The ^{1}H and ^{13}C NMR spectra for **3dg**

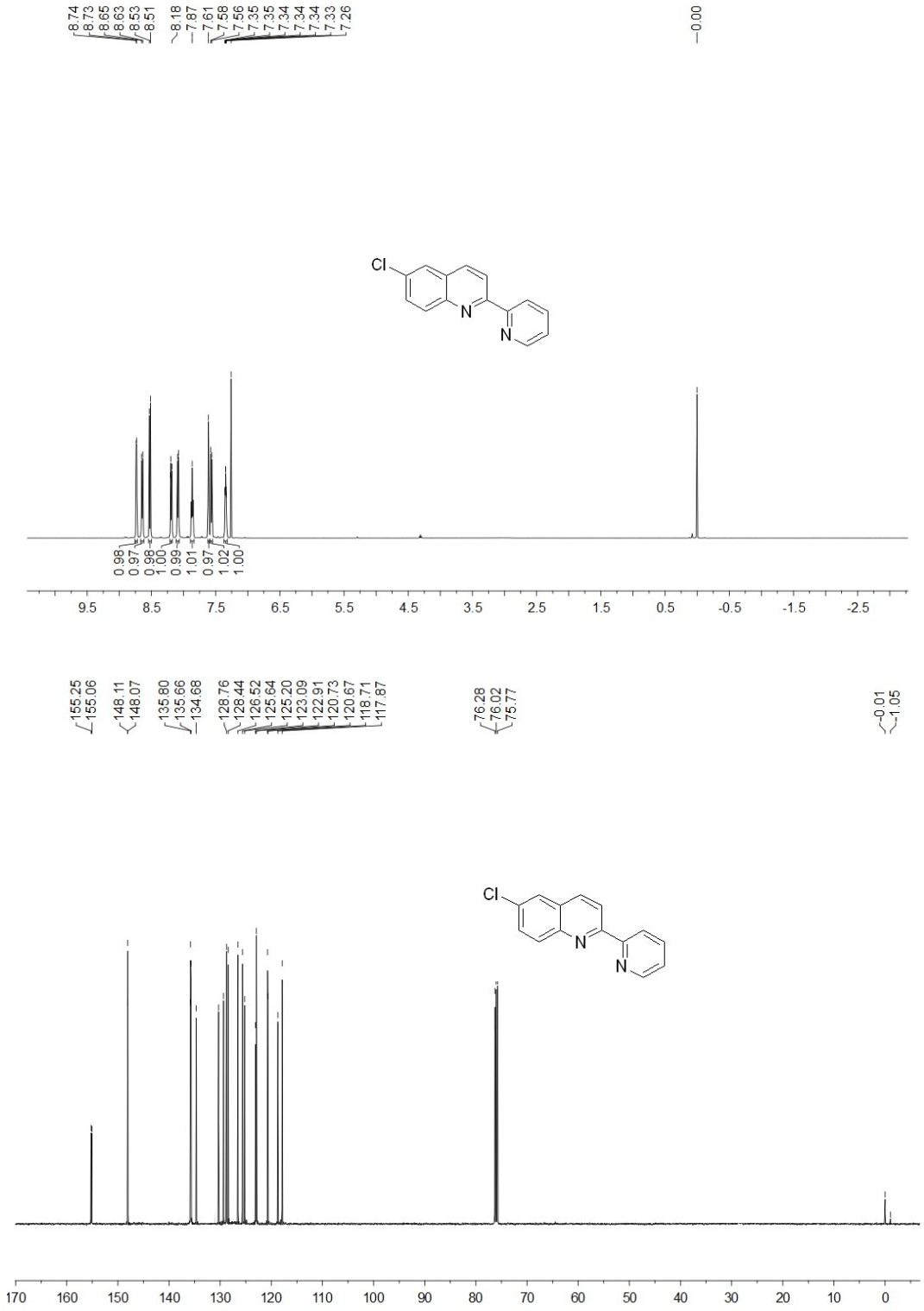


Figure S61. The ^{1}H and ^{13}C NMR spectra for **3dg**

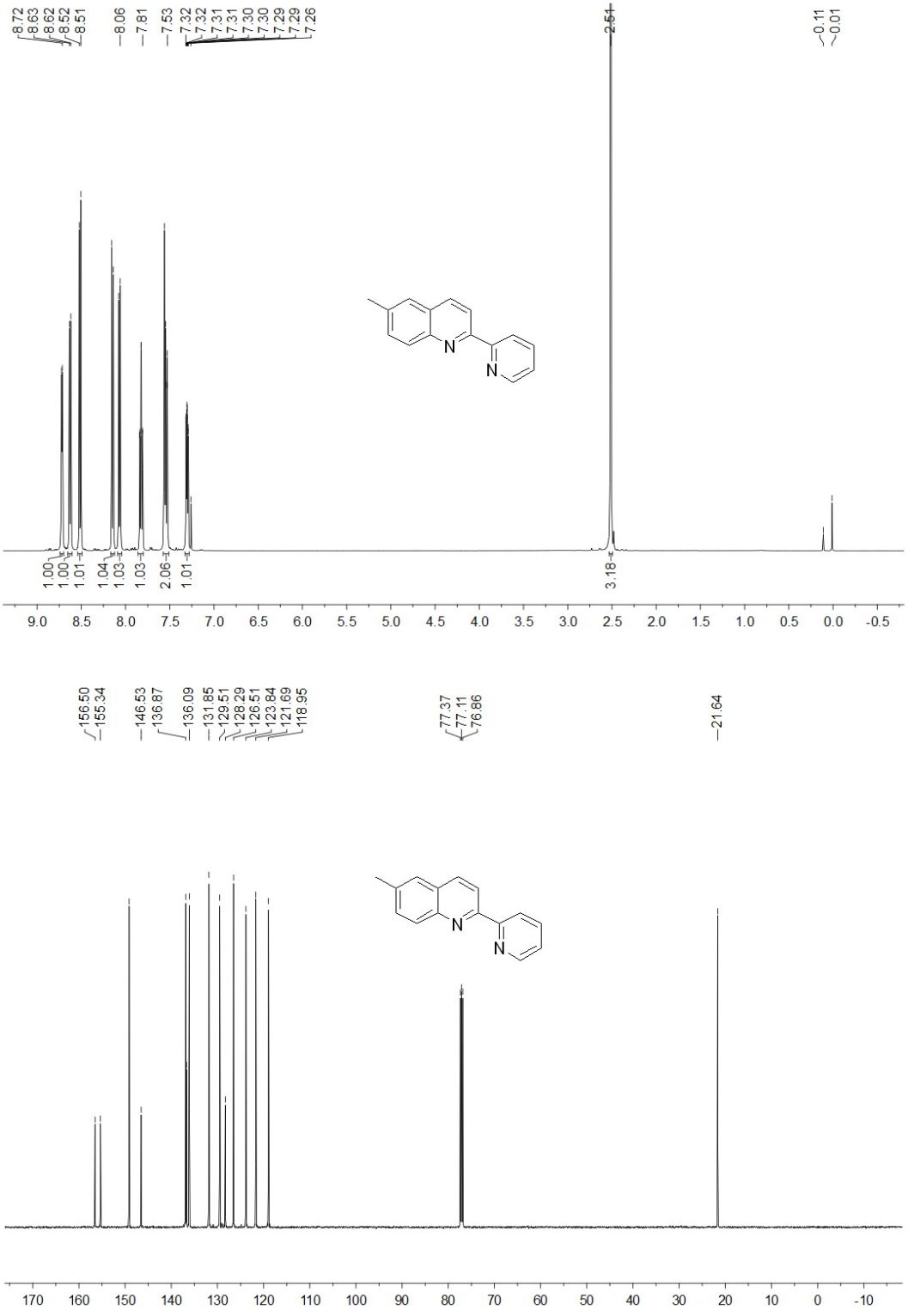


Figure S62. The ^{1}H and ^{13}C NMR spectra for **4fc** (n = 1)

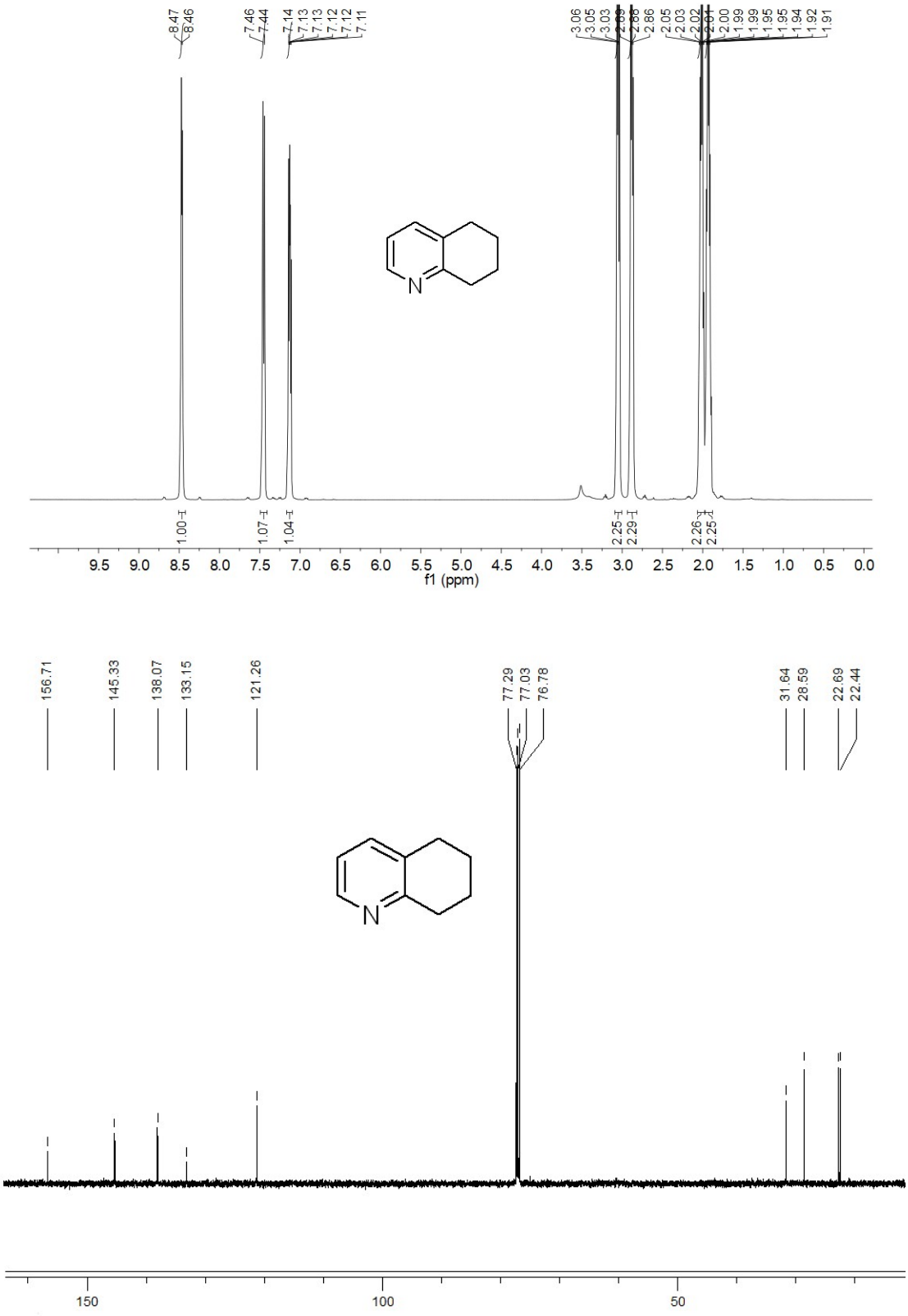


Figure S63. The ^{1}H and ^{13}C NMR spectra for **4fe** (n = 7)

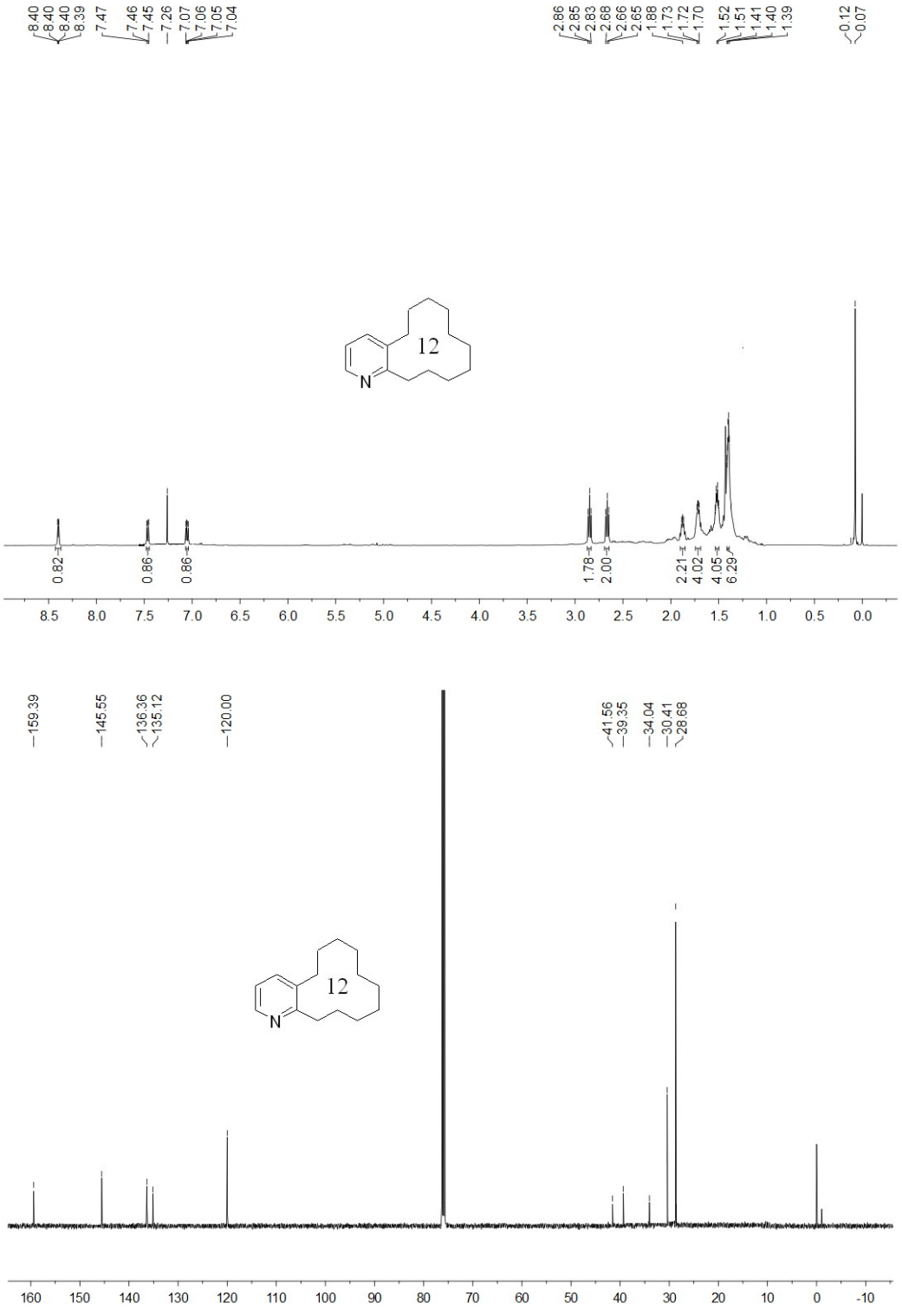


Figure S64. The ^{1}H and ^{13}C NMR spectra for **4ff** (n = 10)

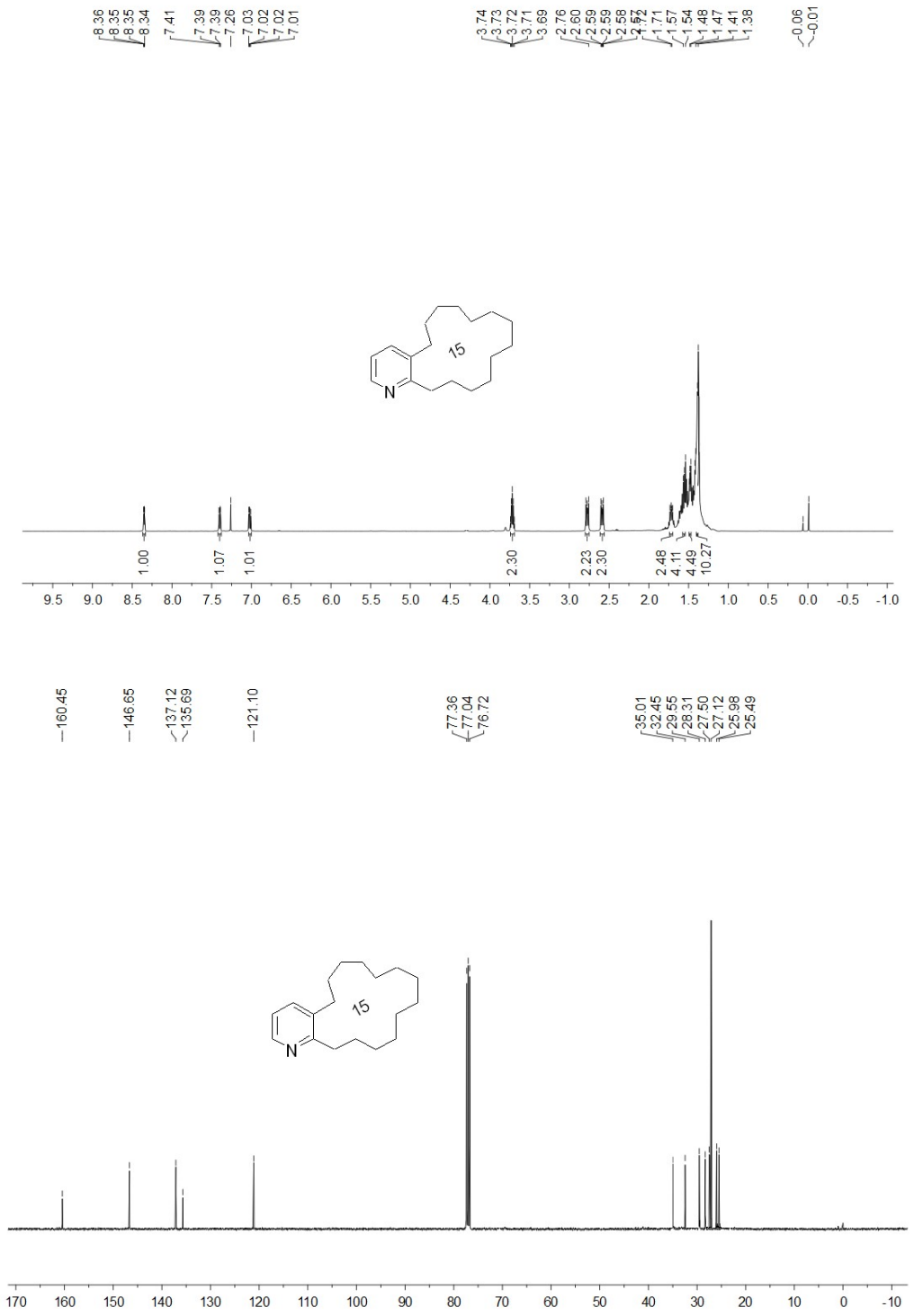


Figure S65. The ^{1}H and ^{13}C NMR spectra for **4ga** (n = 2)

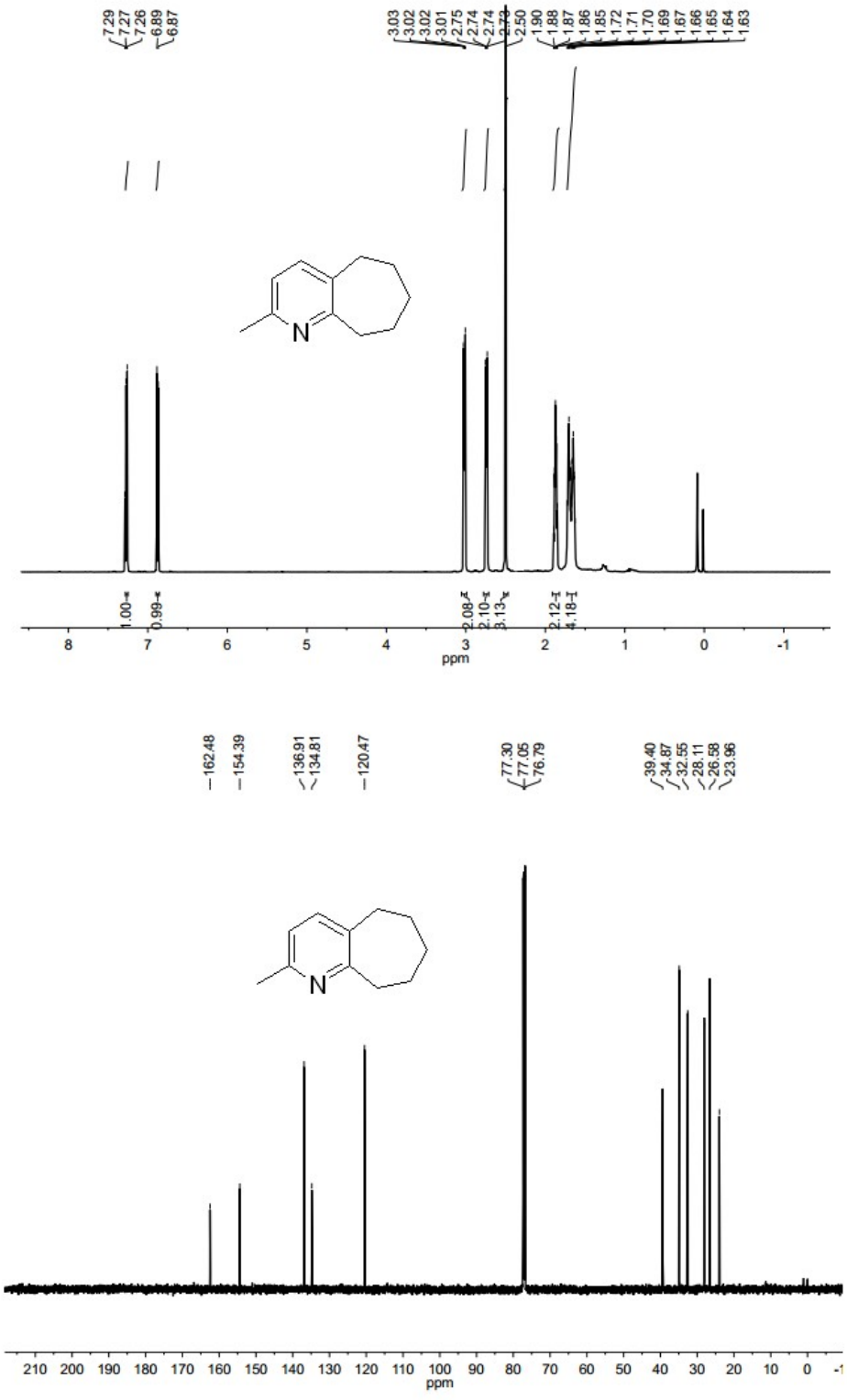


Figure S66. The ^{1}H and ^{13}C NMR spectra for **4gd** (n = 3)

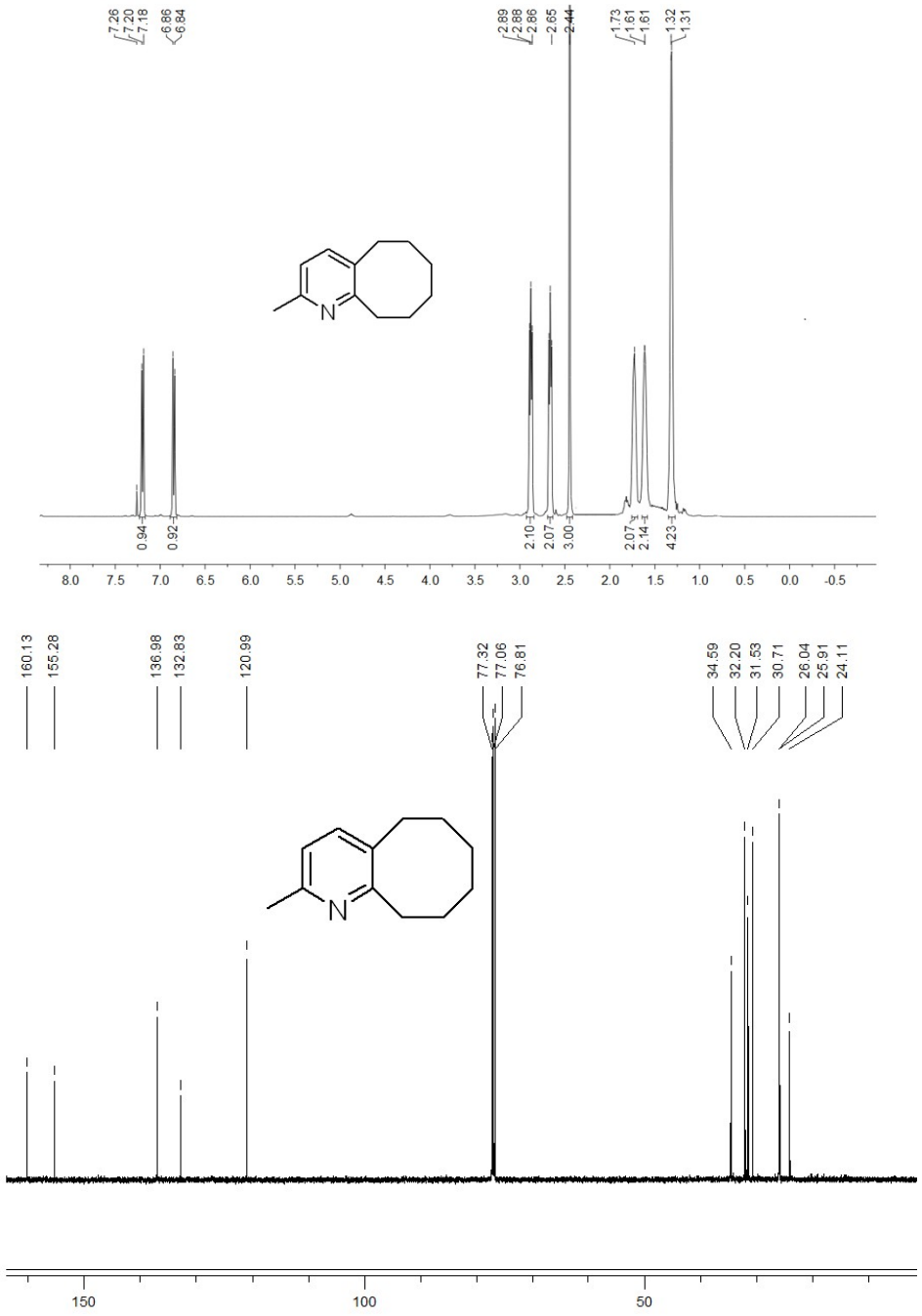


Figure S67. The ^{1}H and ^{13}C NMR spectra for **4ge** (n = 7)

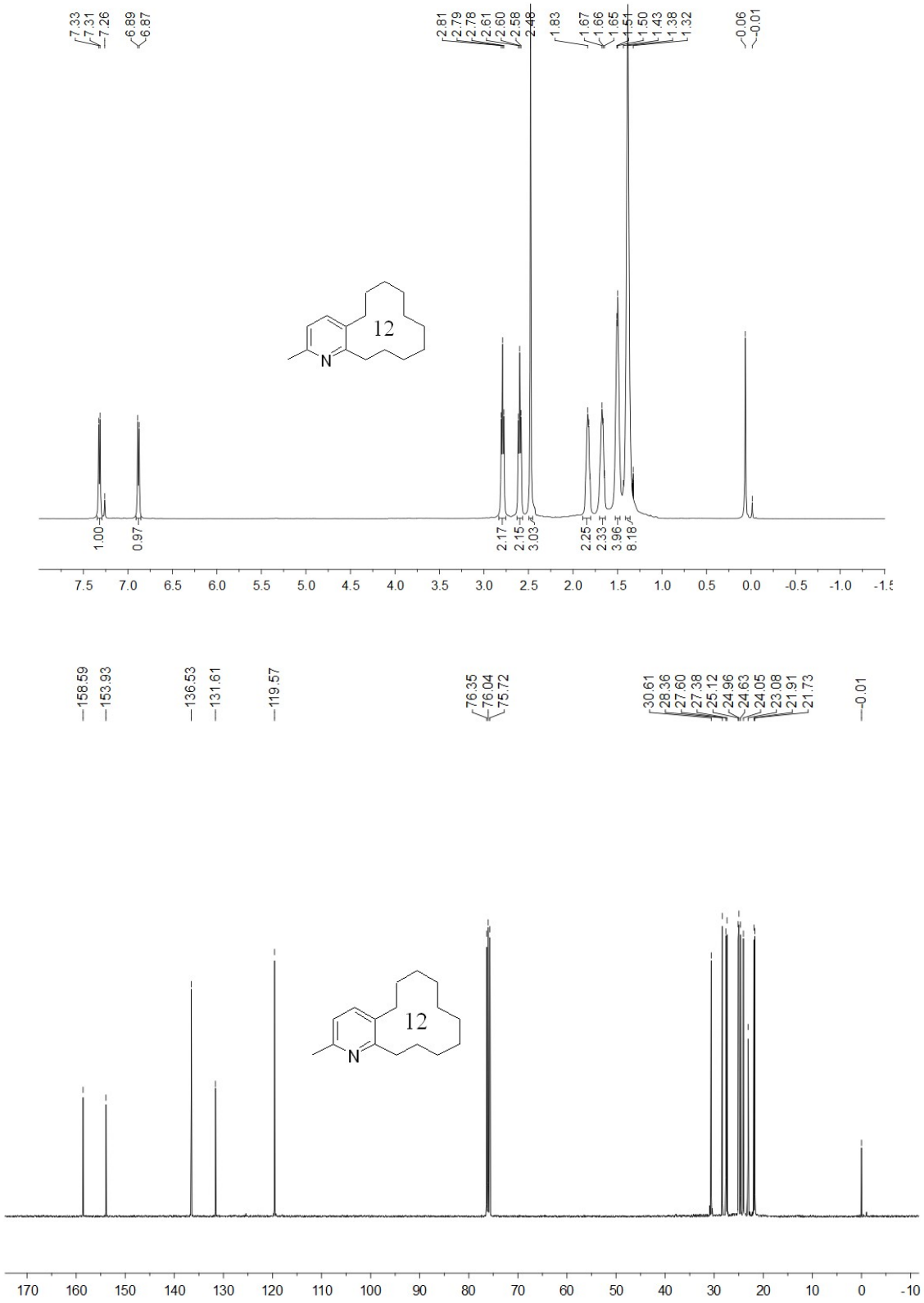


Figure S68. The ^{1}H and ^{13}C NMR spectra for **4gf** (n = 10)

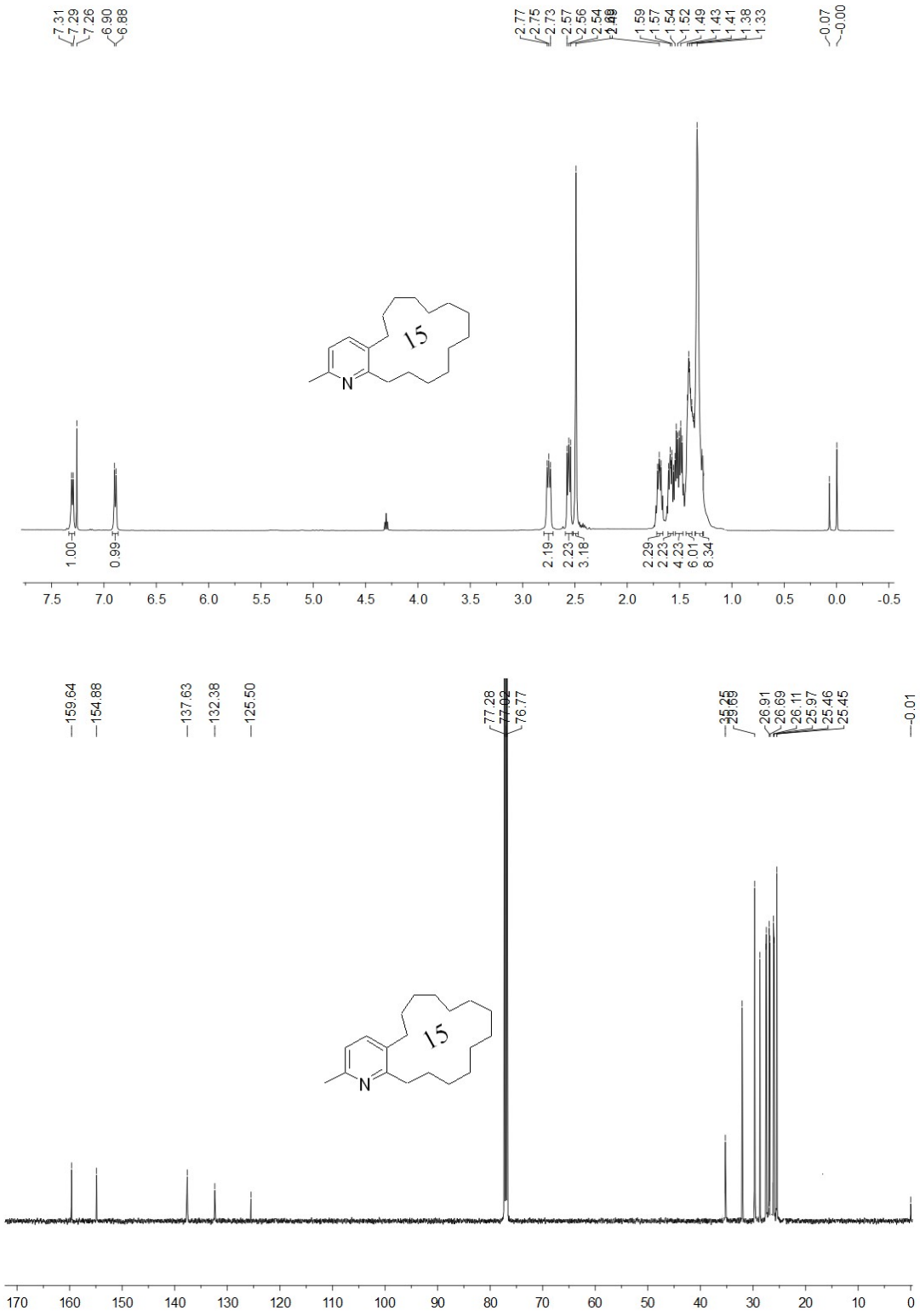


Figure S69. The ^{1}H and ^{13}C NMR spectra for **4hc** (n = 1)

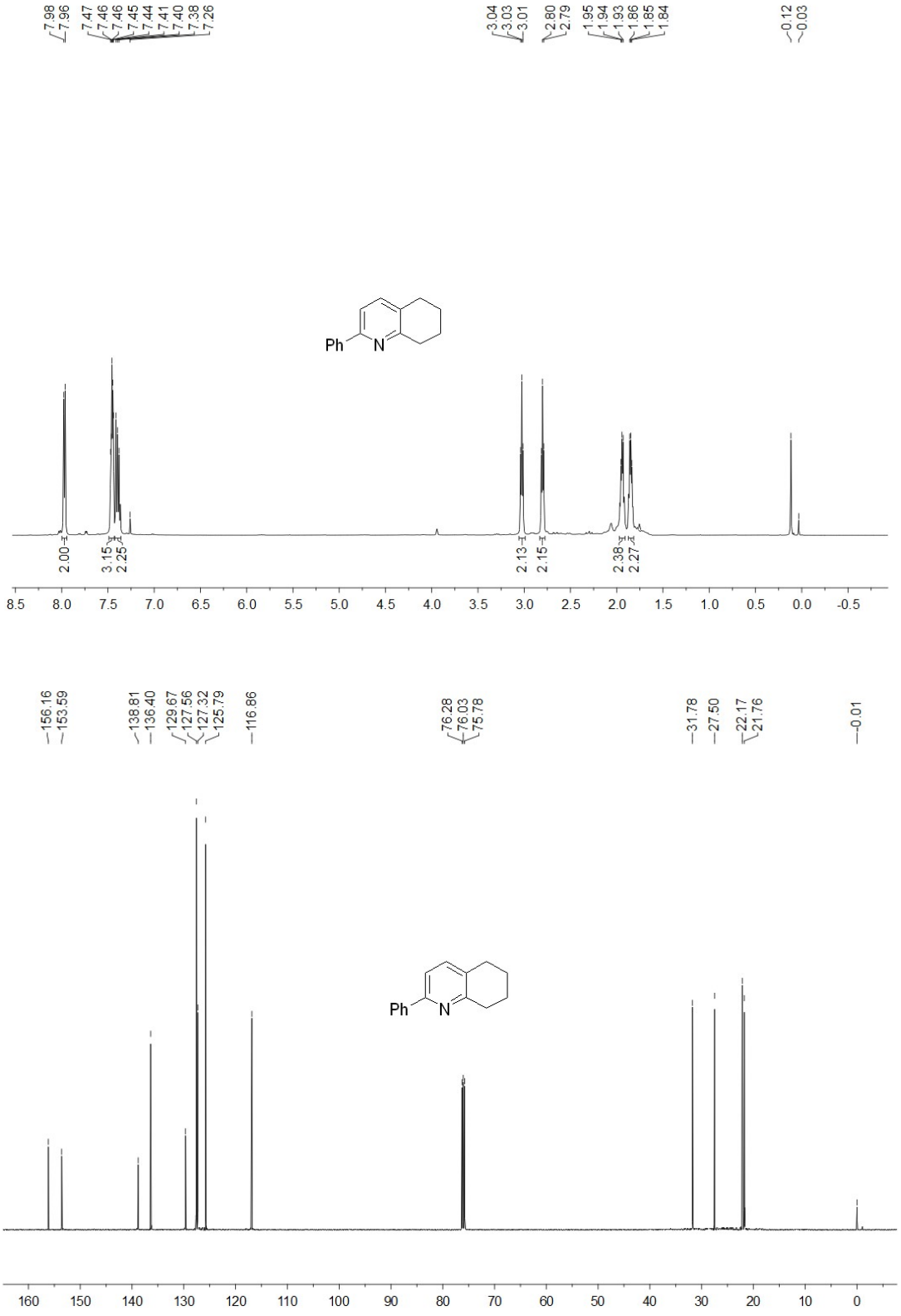


Figure S70. The ^{1}H and ^{13}C NMR spectra for **4hd** (n = 3)

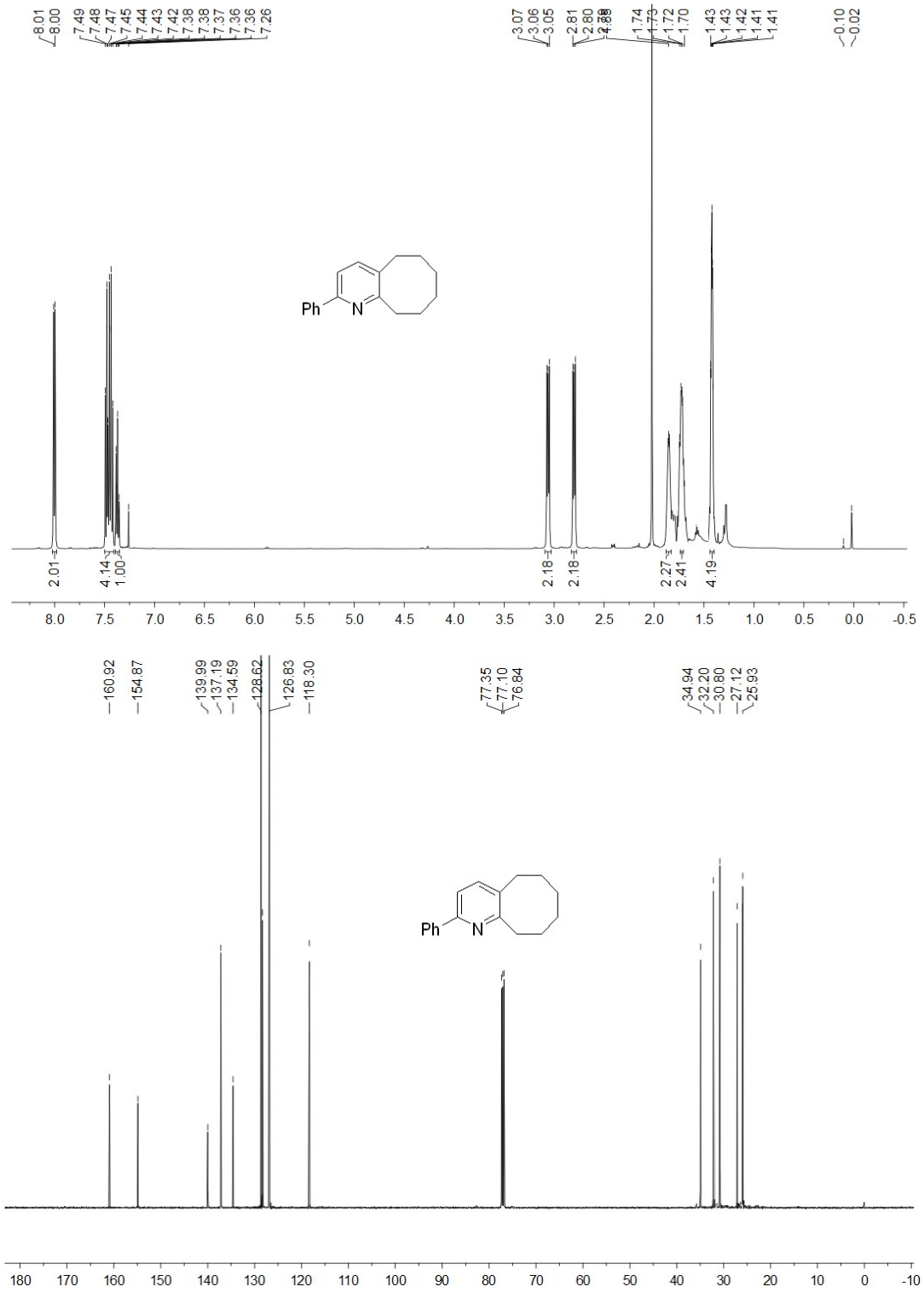


Figure S71. The ^{1}H and ^{13}C NMR spectra for **4hd** (n = 7)

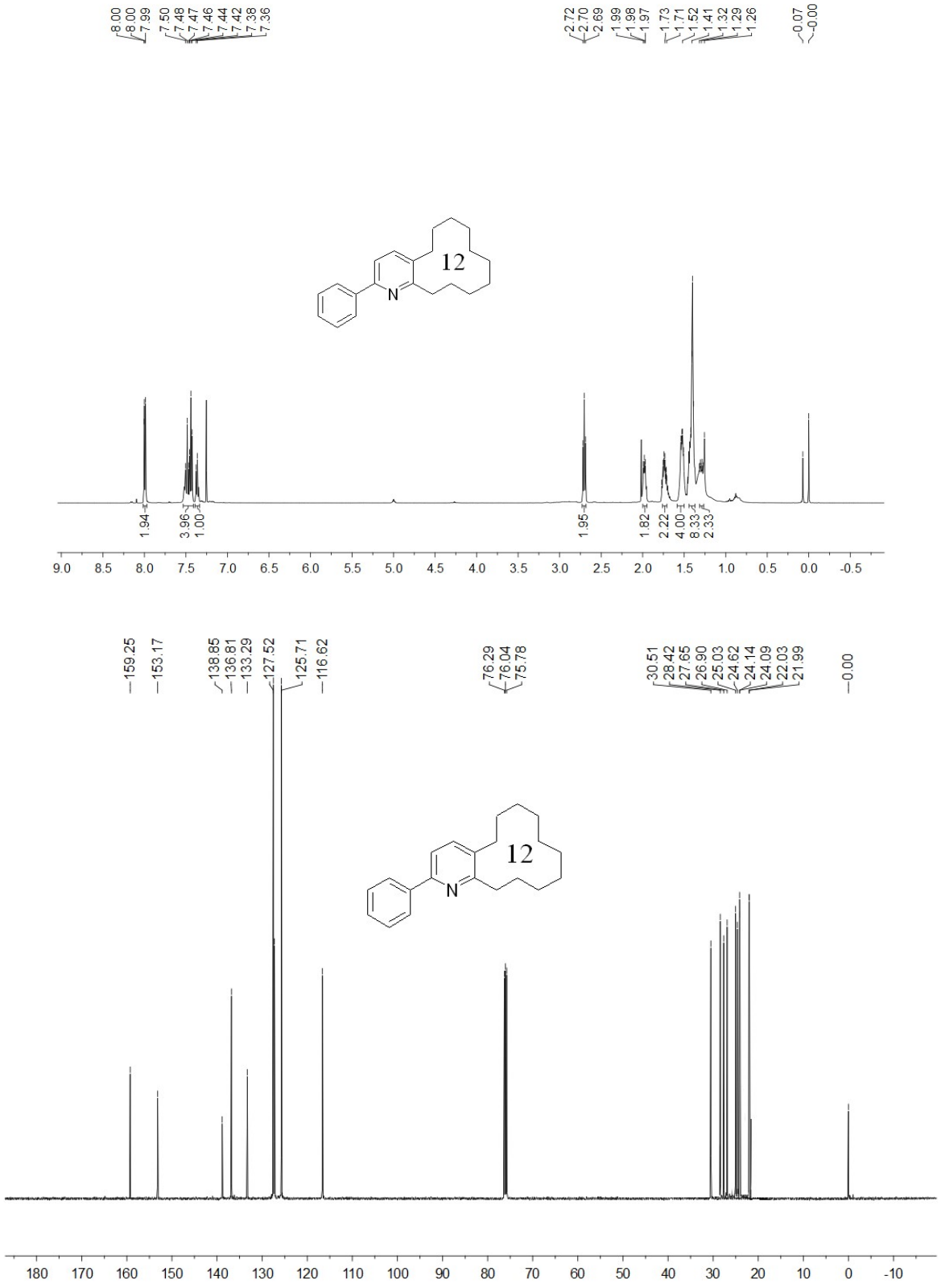


Figure S72. The ^{1}H and ^{13}C NMR spectra for **4hd** (n = 10)

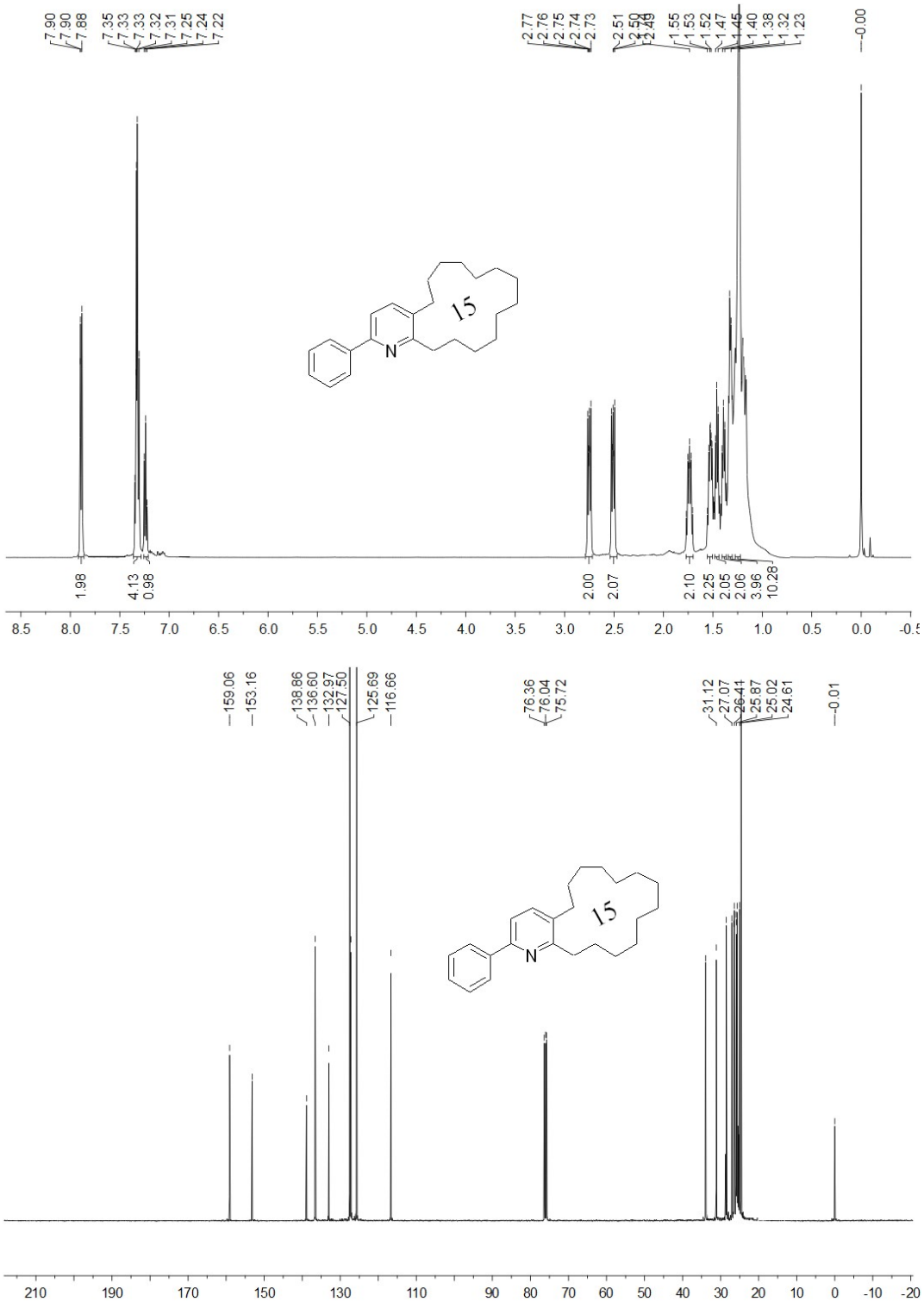


Figure S73. The ^{1}H and ^{13}C NMR spectra for **4gi**

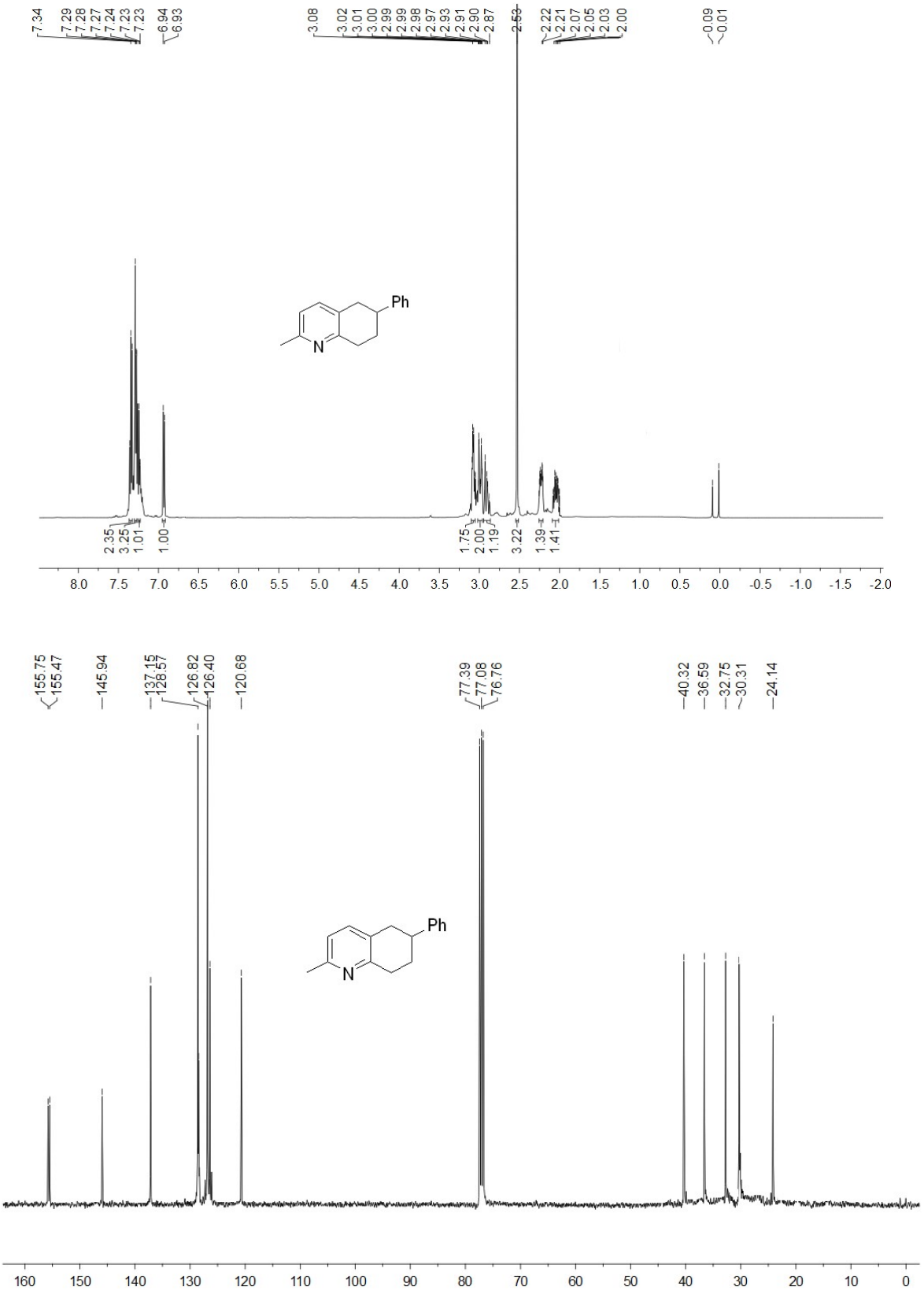


Figure S74. The ^{1}H and ^{13}C NMR spectra for **4hi**

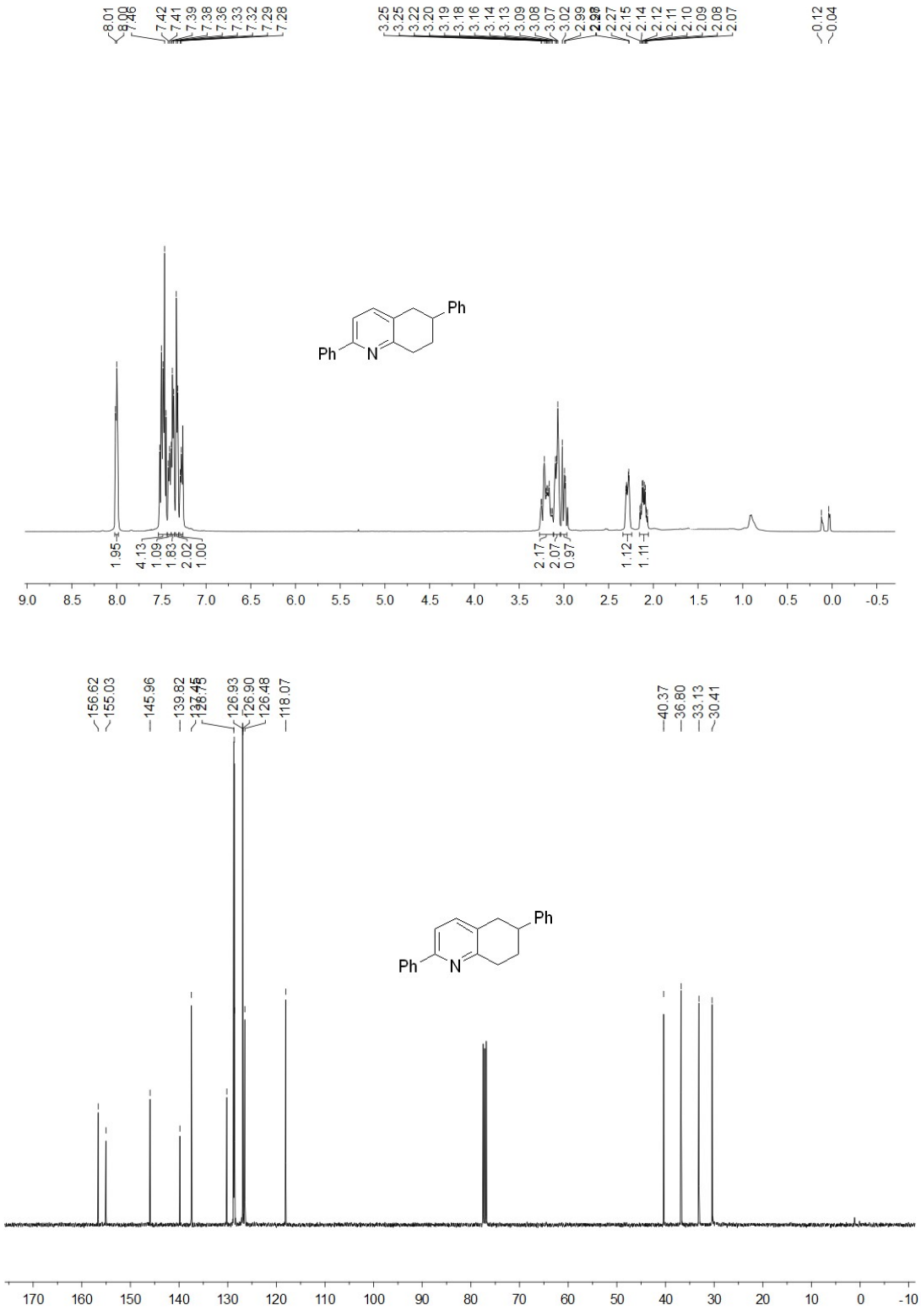


Figure S75. The ^{1}H and ^{13}C NMR spectra for **4fn**

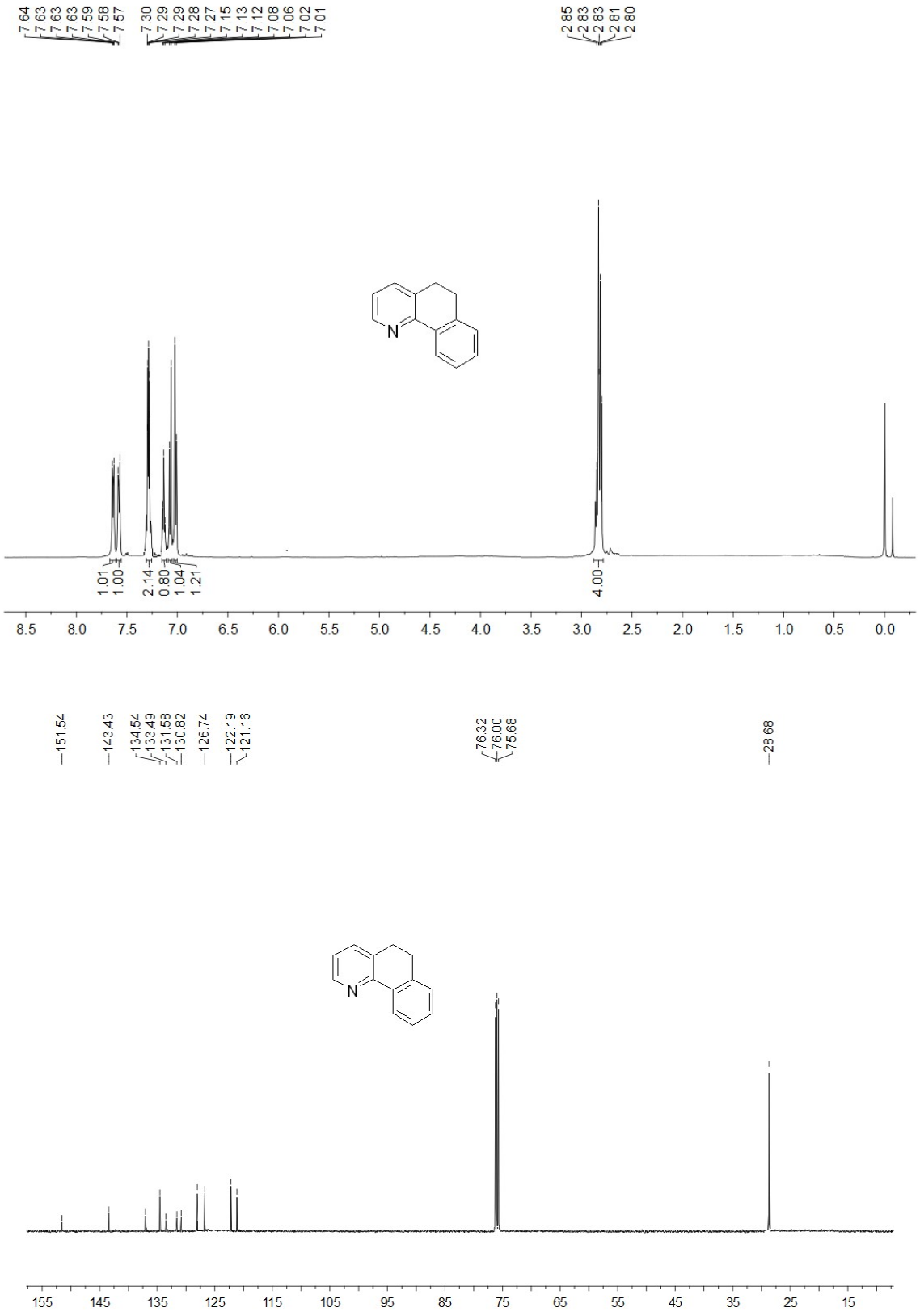


Figure S76. The ^{1}H and ^{13}C NMR spectra for **4hn**

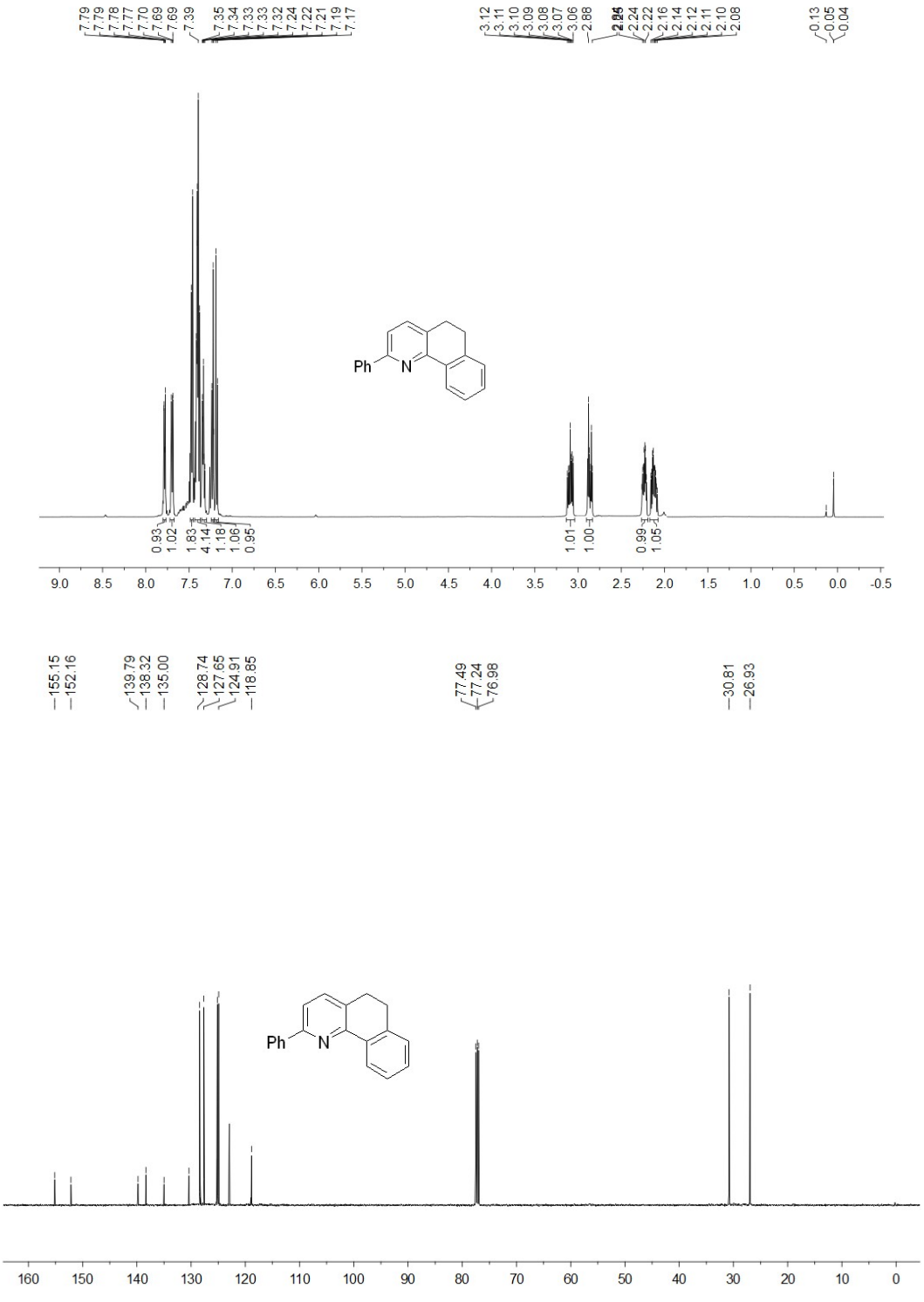


Figure S77. The ^{1}H and ^{13}C NMR spectra for **4fv**

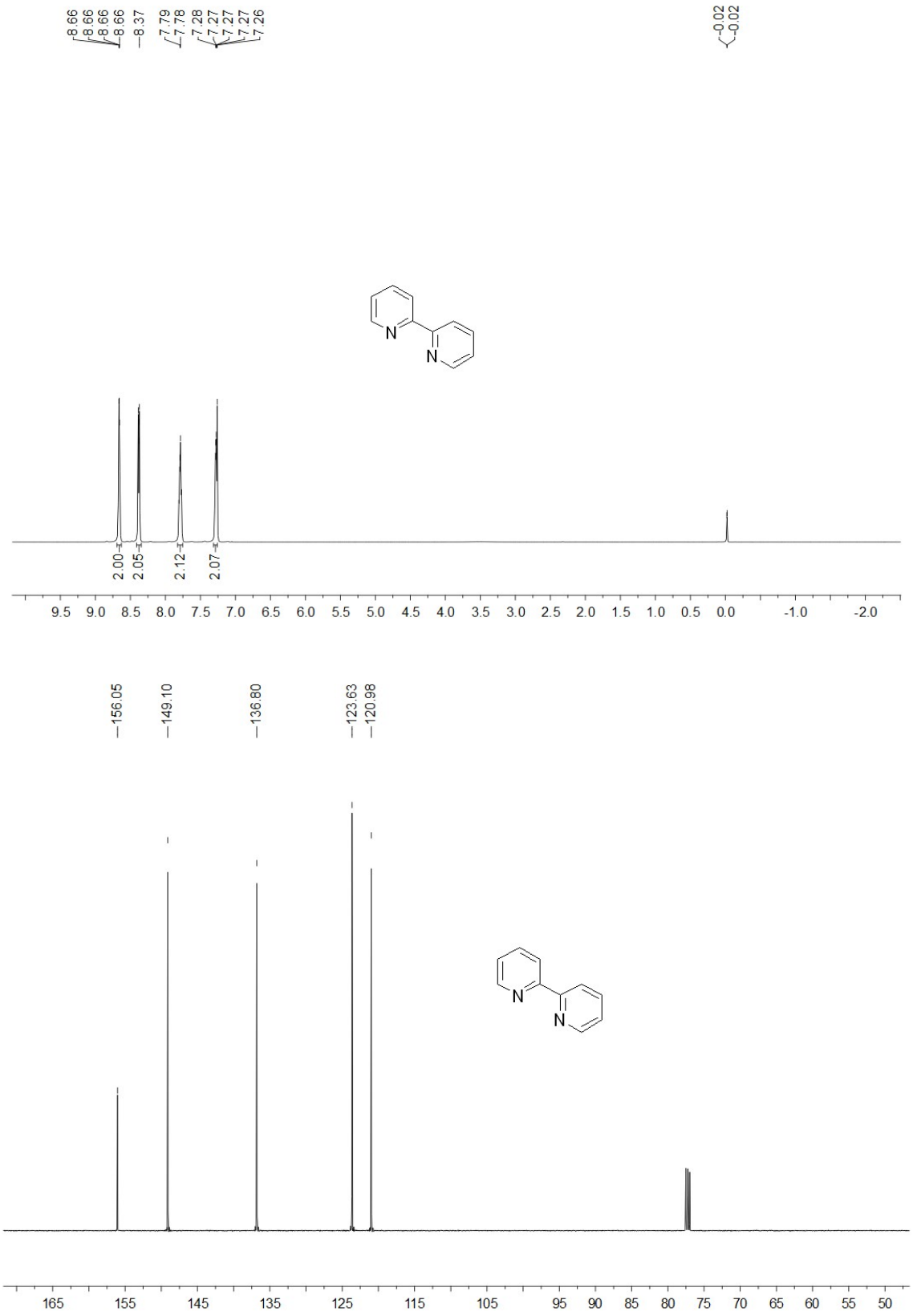
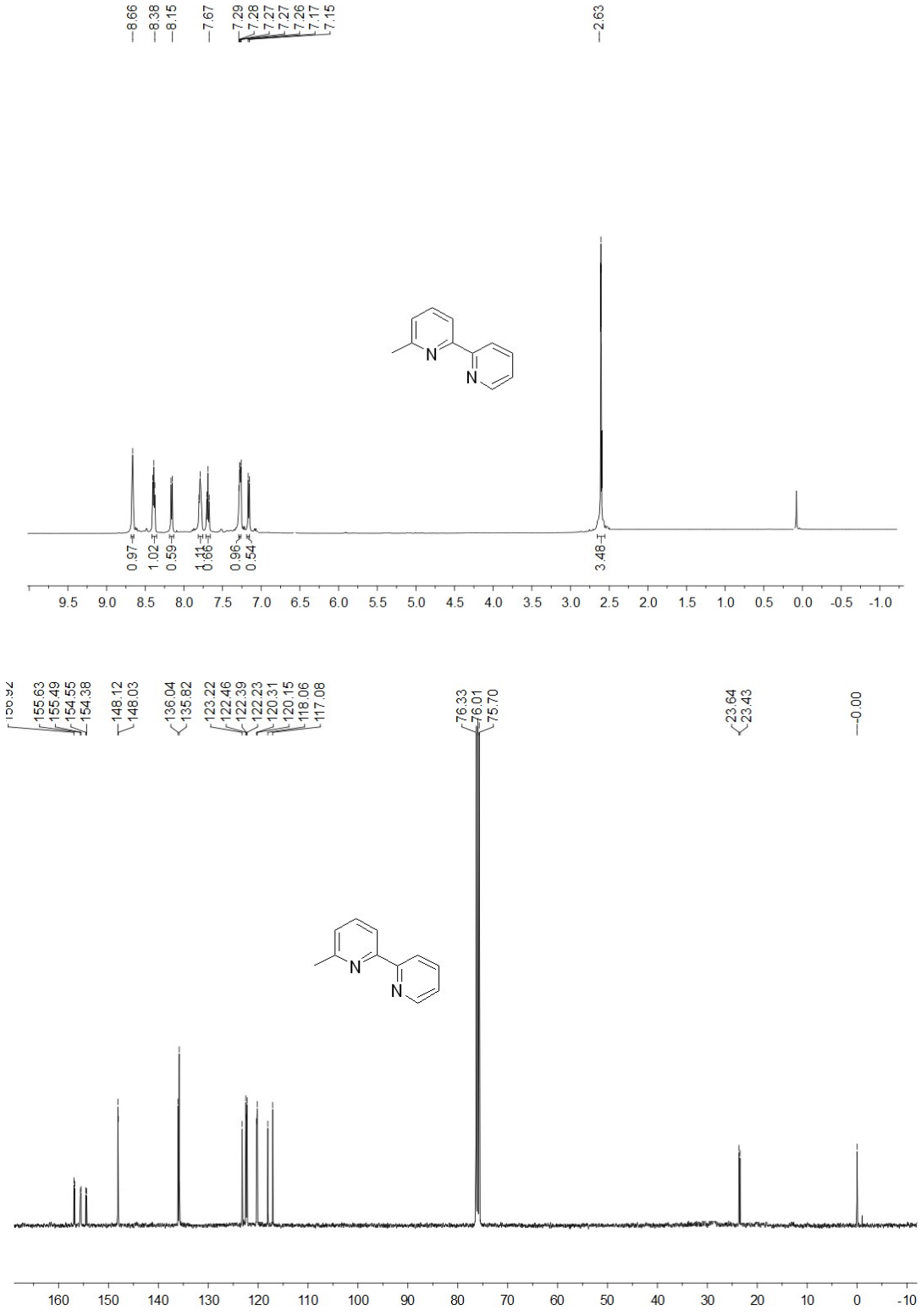


Figure S78. The ^{1}H and ^{13}C NMR spectra for **4gv**



Fgure S79. The ^{1}H and ^{13}C NMR spectra for **4hw**

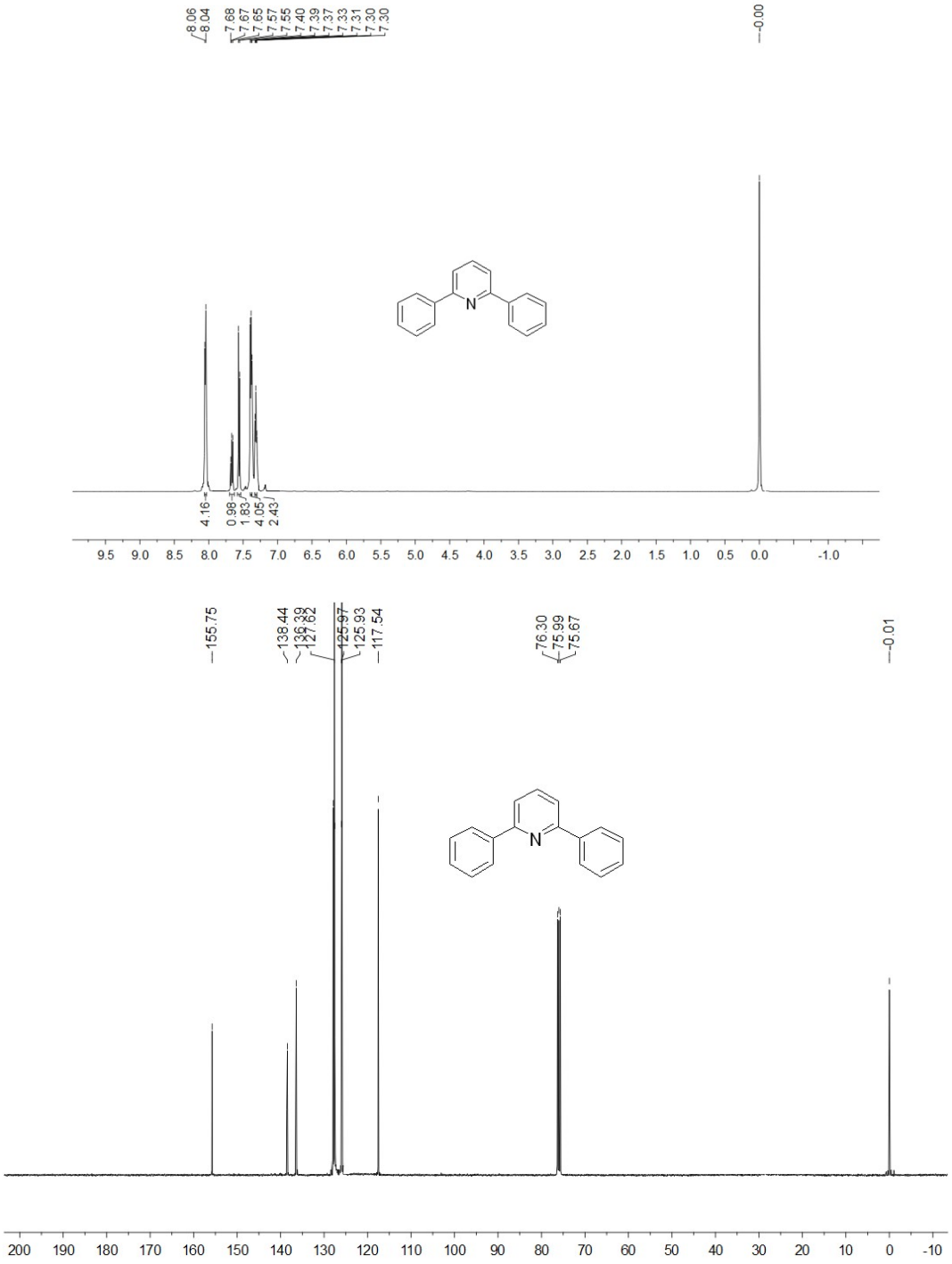


Figure S80. The ^{1}H and ^{13}C NMR spectra for **4hx**

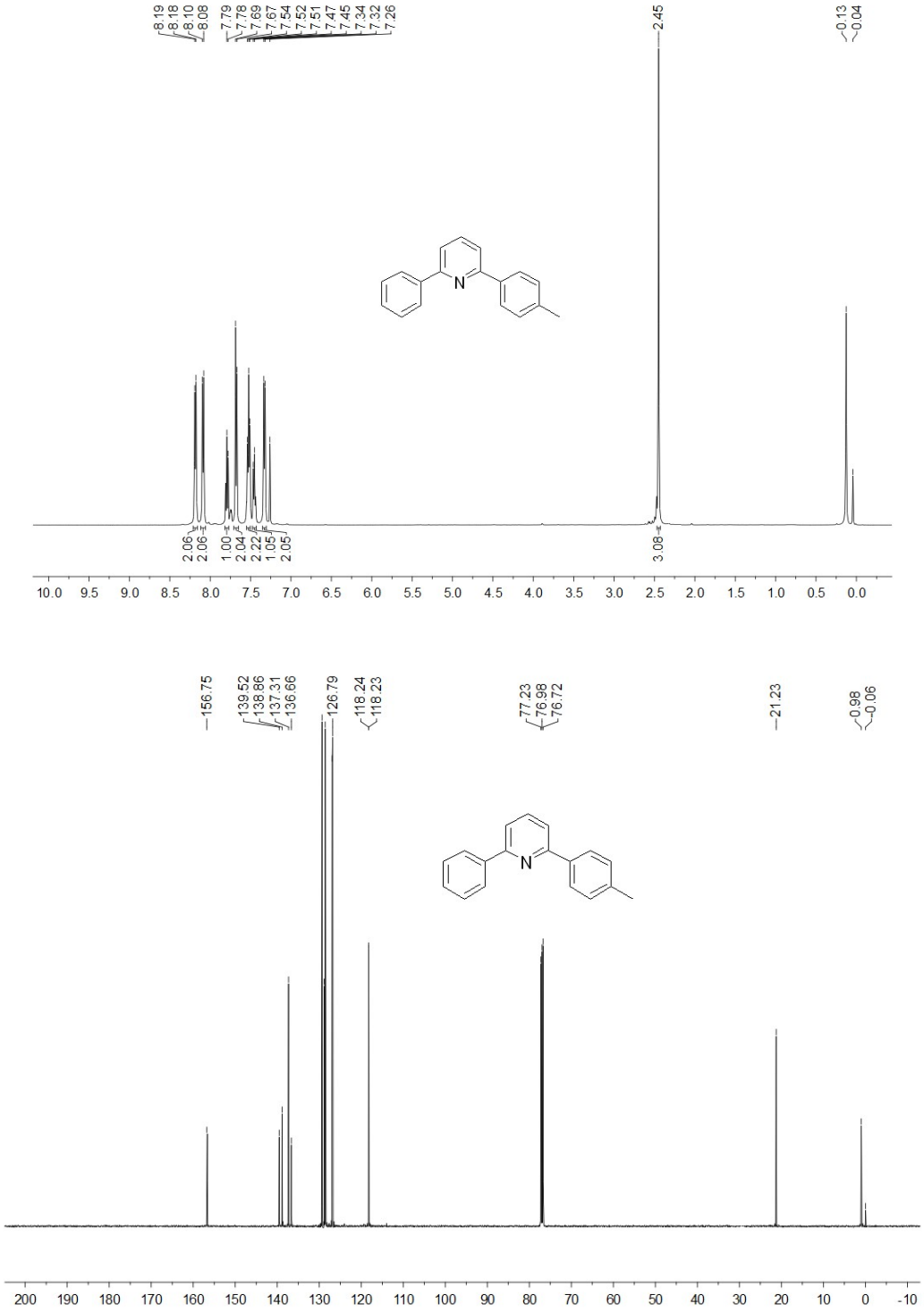


Figure S81. The ^{1}H and ^{13}C NMR spectra for **4hy**

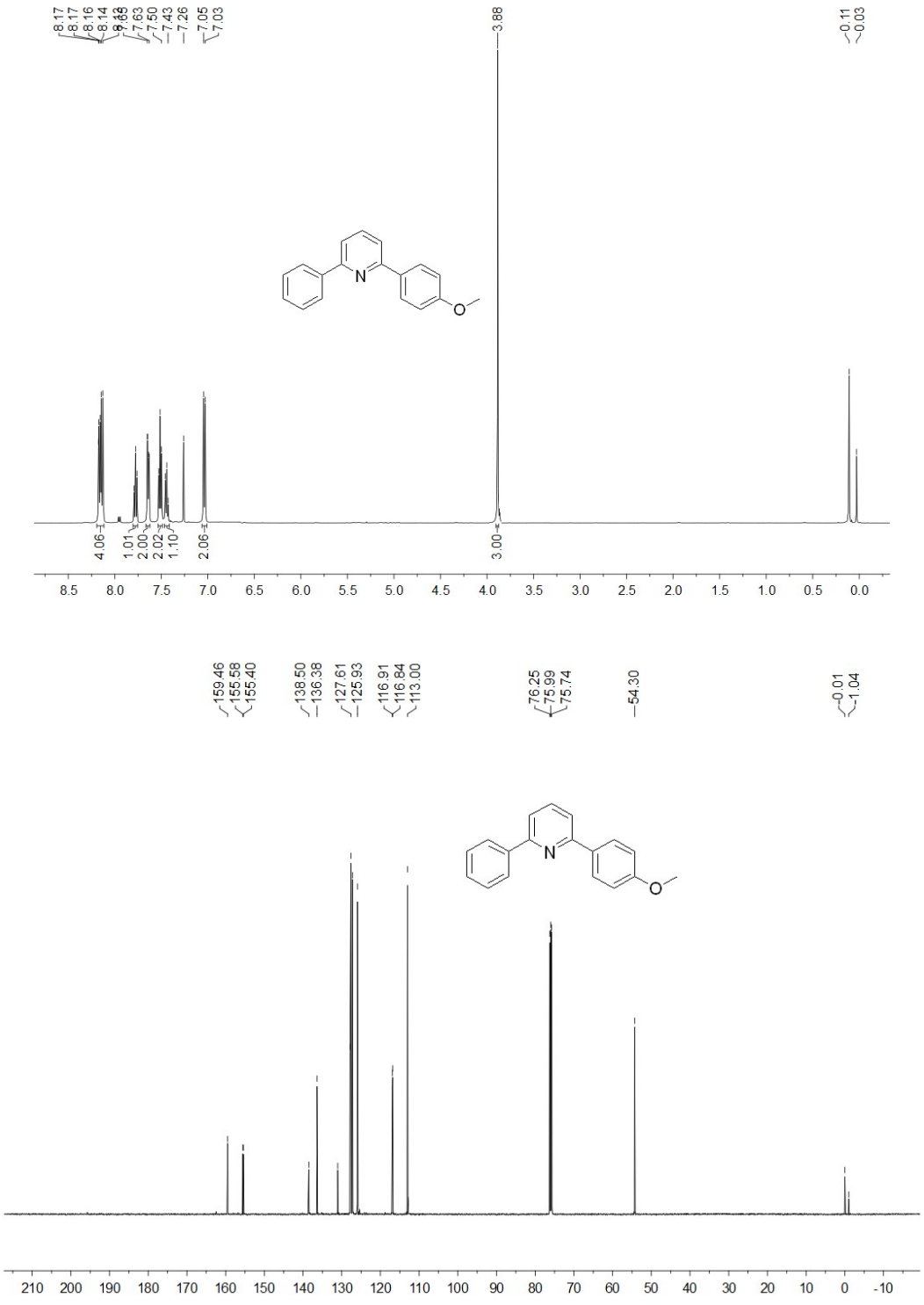
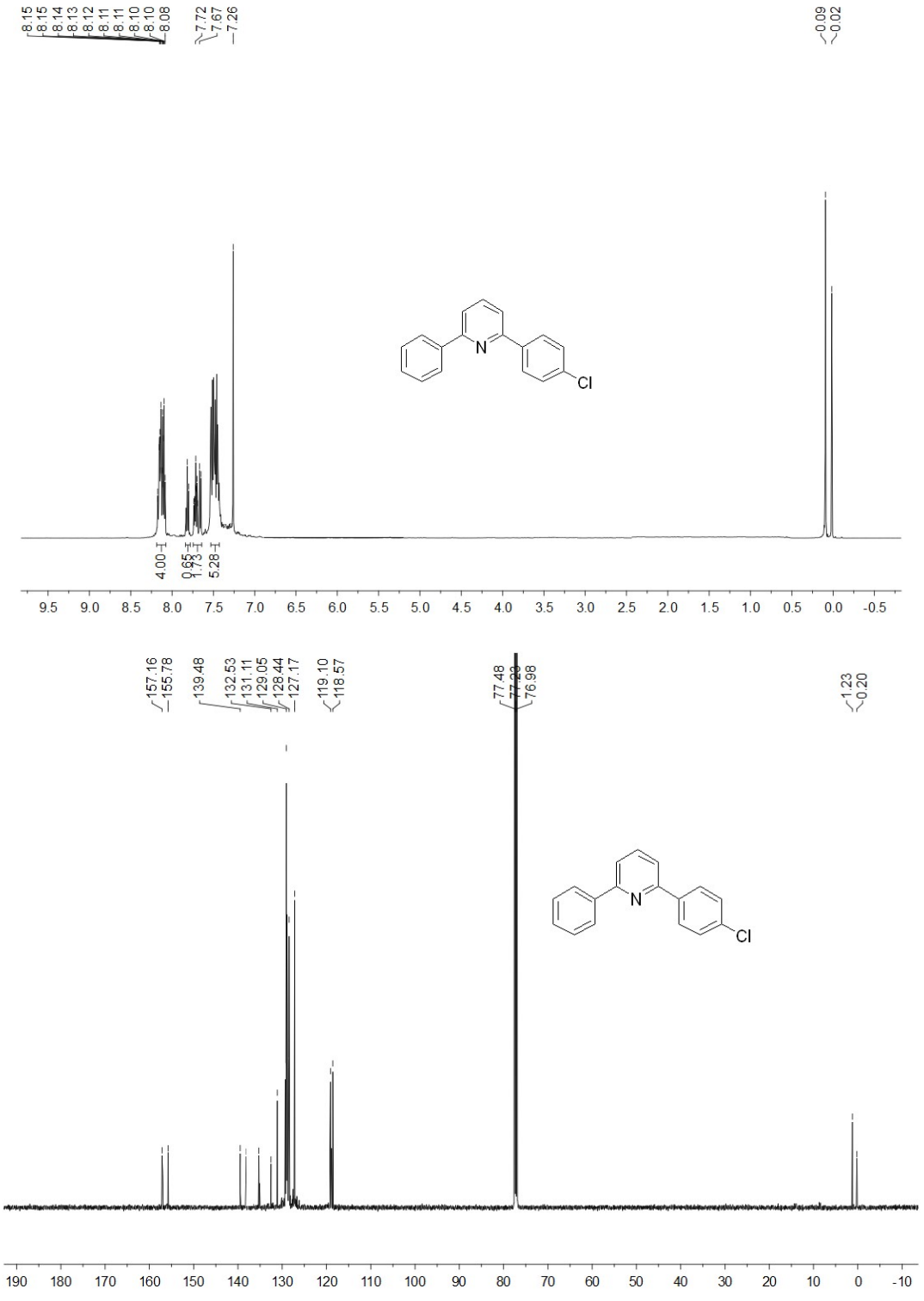
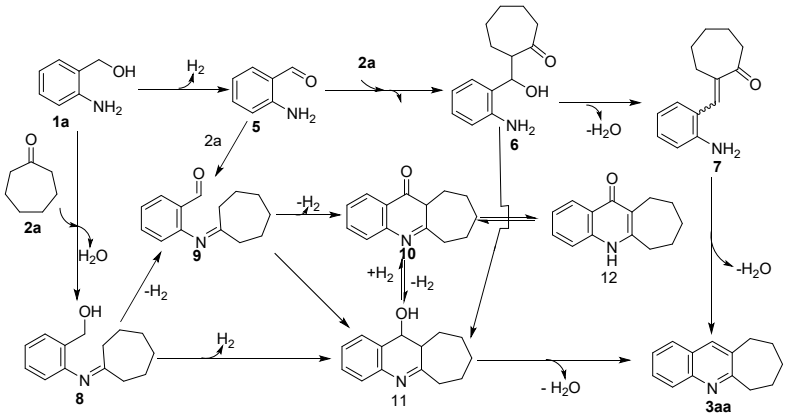


Figure S82. The ^{1}H and ^{13}C NMR spectra for **4hz**



6. Mechanistic studies

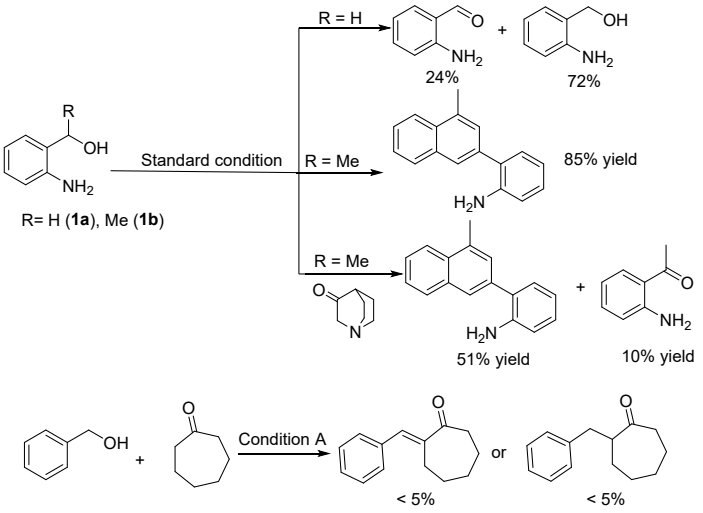


Scheme S1 Possible reaction pathways

6.1 Control experiments

Reactions which probe pathway A:

Scheme S2 Dehydrogenation of 2-aminobenzyl alcohols, **1a** and **1b**, and their self-condensation



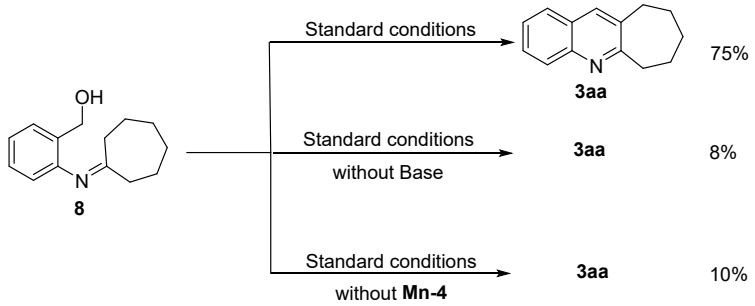
When 2-aminobenzyl alcohol (**1a**) or 1-(2-aminophenyl)ethanol (**1b**) was treated alone under the standard reactions conditions, we observed 24% of 2-aminobenzaldehyde and < 5% of aldol condensation product for **1a**, while 85% of the self-condensation product, 2-(4-methylquinolin-2-yl)benzenamine, was observed for **1b**.

When the reaction of 1-(2-aminophenyl)ethanol (**1b**) with quinuclidin-3-one was carried out, the side-product 2-(4-methylquinolin-2-yl)benzenamine (51%) and 2-aminoacetophenone (10%) were identified, no expected products were observed. 2-(4-methylquinolin-2-yl)aniline. Eluent: petroleum ether/ethyl acetate (40:1), Pale-yellow solid (85%, 141 mg). Mp: 114 – 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.67 (s, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 10.9, 8.1 Hz, 2H), 6.06 (br, 1H), 2.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.95, 147.44, 144.69, 130.15, 129.79, 129.38, 129.28, 125.90, 123.58, 121.10, 117.39, 117.28, 19.04.

When benzyl alcohol (1 mmol) and cycloheptanone (2 mmol) were treated under standard conditions A, only trace amounts 2-benzylidenecycloheptan-1-one or 2-benzylcycloheptan-1-one were observed.

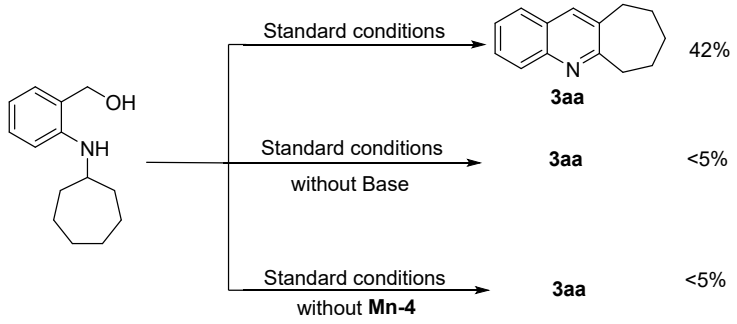
Reactions which probe pathway B

Scheme S3 Conversion of (2-(cycloheptylideneamino)phenyl)methanol (**8**) to **3aa**



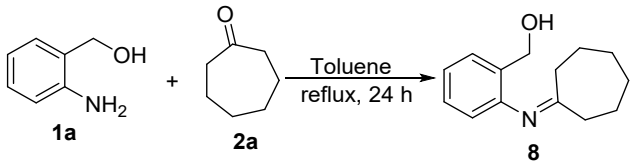
When imine **8** was treated under standard conditions, we observed 75% of **3aa**, while only 8% and 10% of **3aa** were formed in the absence of either base or catalyst, respectively.

Scheme S4 Conversion of (2-(cycloheptylamino)phenyl)methanol to **3aa**



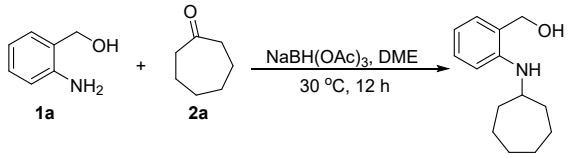
When (2-(cycloheptylamino)phenyl)methanol was treated under standard conditions, we observed only 42% of **3aa**, while only trace amounts of **3aa** were formed in the absence of either base or catalyst, respectively.

Scheme S5 Synthesis of **8**



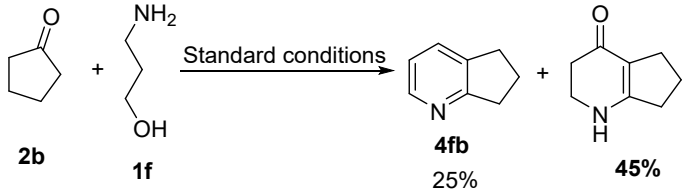
A mixture of **1a** (3.69 g, 30 mmol), **2a** (3.70 g, 33 mmol, 1.1 eq.) in freshly distilled toluene (120 mL) was placed in a 250 round-bottomed flask fitted with a Dean−Stark water separator and stirred at reflux for 24 h. After removal of a predetermined amount of water (~0.5 mL), the reaction was stopped and the solvent removed under reduced pressure to give a light off-white solid. Recrystallization from a mixture of toluene and petroleum ether (1:20) at 0 °C gave the product **8** as white crystals (5.12 g, 78%). Mp.: 91.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (q, J = 7.5 Hz, 1H), 6.93 (d, J = 7.4 Hz, 1H), 6.78 (d, J = 7.3 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 4.80 (s, 2H), 3.96 (br, 1H), 1.95 (dd, J = 13.9, 9.1 Hz, 2H), 1.80 (dd, J = 13.8, 9.8 Hz, 2H), 1.71 – 1.52 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.19, 127.14, 124.57, 120.94, 118.52, 116.90, 86.52, 61.33, 38.76, 29.56, 21.59.

Scheme S6 Synthesis of (2-(cycloheptylamino)phenyl)methanol



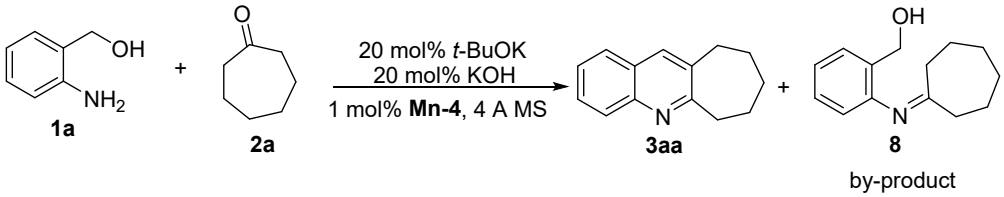
Similar to our previous work,[1] a mixture of **2a** (2.2 g, 20 mmol), **1a** (2.6 g, 22 mmol, 1.05 eq.) and sodium triacetoxyborohydride (6.33 g, 30 mol, 1.5 eq.) were loaded in a 250 mL flask followed by 1,2-dichloroethane (100 mL). The reaction mixture was stirred at 30 °C for 12 h. An aqueous saturated $NaHCO_3$ solution (100 mL) was added to quench the reaction (pH > 8). The mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic phases were dried over sodium sulfate and the solvent evaporated under reduced pressure yielding (2-(cycloheptyl-amino)phenyl)methanol as a yellow oil (3.6 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (td, *J* = 7.9, 1.5 Hz, 1H), 6.93 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.60 – 6.53 (m, 2H), 4.45 (s, 2H), 3.47 – 3.40 (m, 1H), 2.00 – 1.90 (m, 2H), 1.69 – 1.42 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.65, 129.43, 129.30, 124.79, 116.07, 111.61, 86.52, 64.47, 53.43, 34.84, 28.48, 24.57.

Scheme S7 Reactions which confirm by-product and intermediates

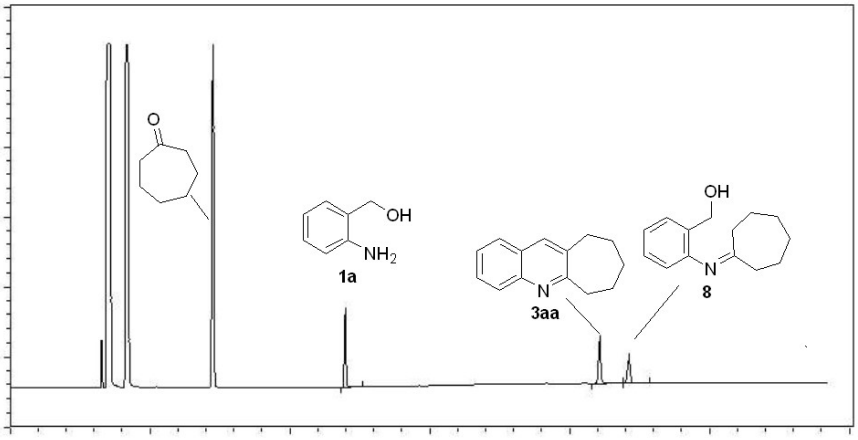


To establish direct evidence for the intermediates or by-products, a solution containing **1f** (2 mmol), **2b** (4 mmol), *t*-BuOK (4 mmol), KOH (4 mmol) and 1 mol% of **Mn-4** in a mixture of toluene (4 mL) and THF (1 mL) was heated to reflux for 12 h. We observed 25% (30 mg) of the expected product **4fb** and 45% (61 mg) of the byproduct. 1,2,3,5,6,7-hexahydro-4H-cyclopenta[b]pyridin-4-one. Eluent: petroleum ether/ethyl acetate (1:2), Pale-yellow solid (45%, 60 mg), Mp: 52-53 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.72 (br, 1H, NH), 2.19 (dd, *J* = 19.3, 8.0 Hz, 1H), 2.02 – 1.95 (m, 1H), 1.93 – 1.82 (m, 1H), 1.65-1.62 (m, 2H), 1.56 – 1.40 (m, 3H), 0.82 – 0.76 (m, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 207.41, 157.28, 127.50, 39.45, 33.14, 31.48, 28.68, 24.24.

Scheme S8 Exploring 4 Å molecular sieves as water scavenger for the ADC reaction



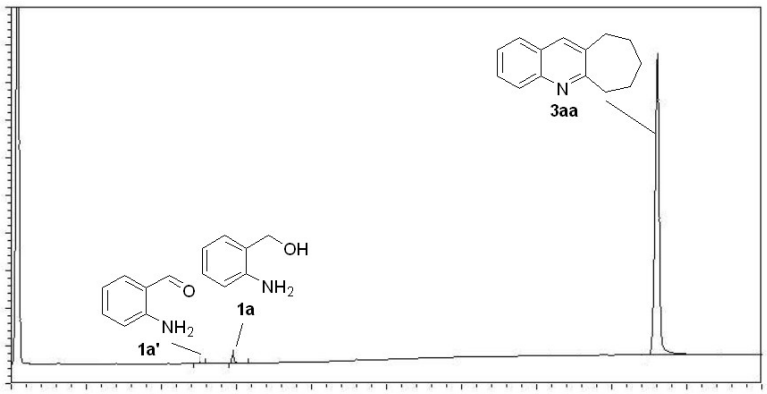
In an attempt to establish the role of base and water content in the ADC reaction,[13] a solution containing 2-aminobenzyl alcohol **1a** (2 mmol), cycloheptanone **2a** (4 mmol), *t*-BuOK (0.4 mmol), KOH (0.4 mmol), 4 Å molecular sieves (0.4 g) and 1 mol% of **Mn-4** in a mixture of toluene (4 mL) and THF (1 mL) was heated to reflux for 24 h (Fig. S84). We observed 59% conversion of **1a**, 34% GC-yield of **3aa** and 24% GC-yield of by-product (**8**). Upon addition of 1.8 equiv. of base (KOtBu and KOH), the ADC reaction (Fig. S85) was near-complete within 4 h. In this case, it was found that 98% conversion of **1a**, 97.5% GC-yield of **3aa** and 0.5% GC-yield of by-product (**8**).



Result

Peak	Name	Apex RT [min]	FWHM [min]	Height [uV]	Area [uV*s]	Area [%]	Content [%]	Type
1	1a	4.795	0.026	212825.4	371298.6	41.7788	41.7788	BB
2	3aa	8.432	0.036	122663.0	301193.2	33.8905	33.8905	VV
3	by-product	8.862	0.046	70575.8	216232.9	24.3307	24.3307	VB
			Sum:	406064.2	888724.7	100.0000	100.0000	

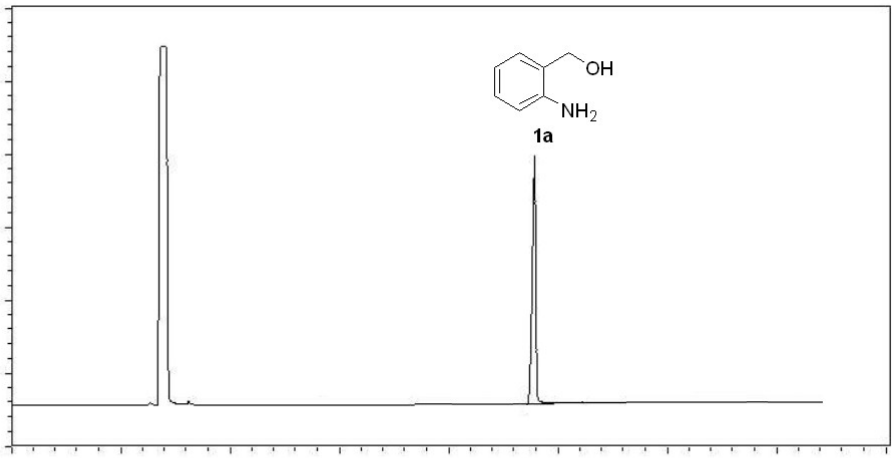
Figure S83 GC trace for the ADC reaction with 0.2 equiv. of base (Scheme S8)



Result

Peak	Name	Apex RT [min]	HWFM [min]	Height [uV]	Area [uV*s]	Area [%]	Content [%]	Type
1	1a'	4.487	0.025	3367.2	5477.7	0.4651	0.4651	BB
2	1a	4.779	0.025	13212.1	22975.9	1.9507	1.9507	BB
3	3aa	8.398	0.037	456489.7	1149394.5	97.5843	97.5843	BB
			Sum:	473069.0	1177848.1	100.0000	100.0000	

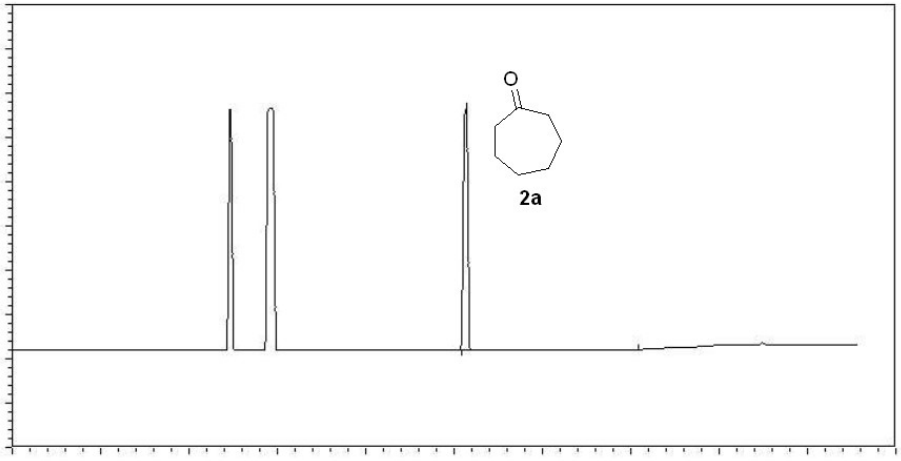
Figure S84 GC trace for the ADC reaction upon addition of 1.8 equiv. of base for 4 h (Scheme S8)



Result

Peak	Name	Apex RT [min]	HWFM [min]	Height [uV]	Area [uV*s]	Area [%]	Content [%]	Type
1	**1a**	4.787	0.034	663560.2	1510225.1	100.0000	100.0000	BB
			Sum:	663560.2	1510225.1	100.0000	100.0000	

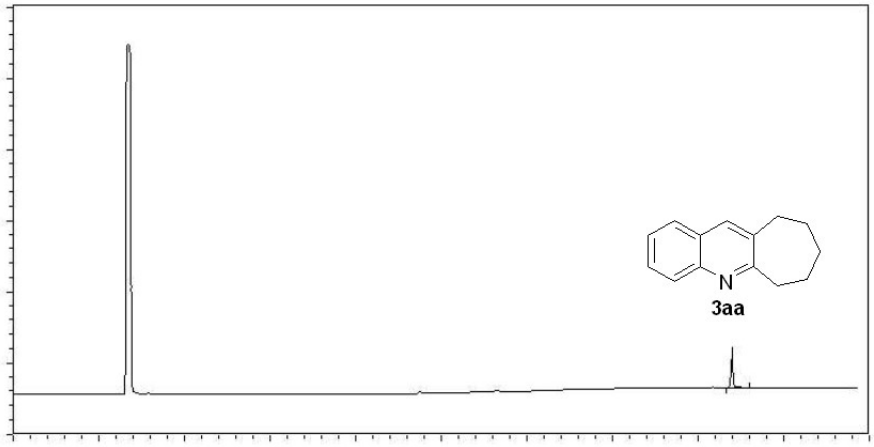
Figure S85 GC trace for **1a**



Result

Peak	Name	Apex RT [min]	HWFM [min]	Height [uV]	Area [uV*s]	Area [%]	Content [%]	Type
1	**2a**	2.886	0.033	1000000.0	1986795.7	100.0000	100.0000	BB
			Sum:	1000000.0	1986795.7	100.0000	100.0000	

Figure S86 GC trace for **2a**

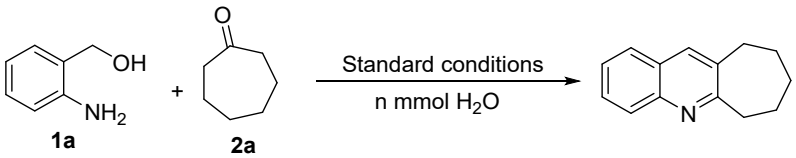


Result

Peak	Name	Apex RT [min]	HWFM [min]	Height [uV]	Area [uV*s]	Area [%]	Content [%]	Type
1	3aa	8.409	0.035	99042.1	233234.0	100.0000	100.0000	BB
			总计:	99042.1	233234.0	100.0000	100.0000	

Figure S87 GC trace for **3aa**

Table S9 The effect of H_2O on the ADC reaction[13]



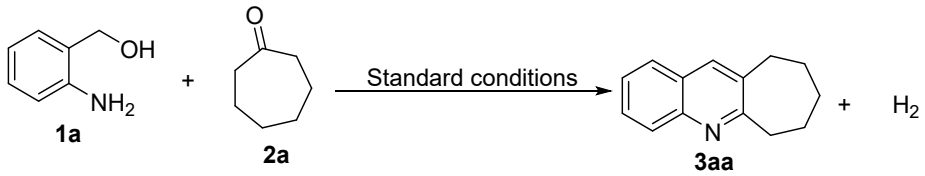
Run	n mmol of H_2O	Conv. (%)[b]	GC yield of **3aa** (%)[b]
1	0.5	99	95(92)
2	1.0	98	93
3	1.5	98	92
4	2.0	98	92
5	4.0	98	91(89)
6[c]	2.0	98	92

[a] Reaction conditions: 2.0 mmol of 2-aminobenzyl alcohol (**1a**), 4.0 mmol of cycloheptanone (**2a**), 4.0 mmol of *t*-BuOK, 4.0 mmol of KOH, 20 μmol of **Mn-4**, 0.5 - 4.0 mmol of H_2O, 4 mL of toluene and 1 mL of THF, 120 °C, 24 h under N_2;

[b] The conversion (with reference to **1a**) and yield were determined by GC with mesitylene as an internal standard, isolated yields in parentheses.

[c] 1.0 mmol of *t*-BuOK, 1.0 mmol of KOH was added to the mixture stirred for 20 h, then the addition 3.0 mmol of *t*-BuOK, 3.0 mmol of KOH was added for the 4 h.

Scheme S9 Detection of byproduct H_2 in the ADC reaction by GC



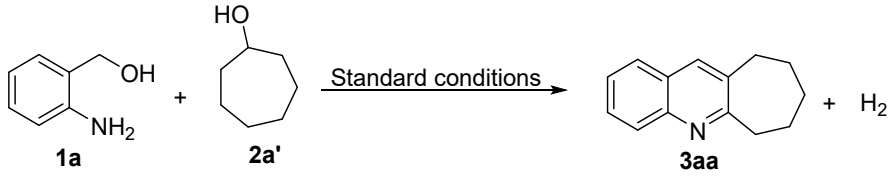
(a) Under conditions A (similar to Table 1, run 4)

A solution containing 2-aminobenzyl alcohol **1a** (1 mmol), cycloheptanone **2a** (2 mmol), t-BuOK (2 mmol), KOH (2 mmol) and 1 mol% of **Mn-4** in a mixture of toluene (2 mL) and THF (0.5 mL) was refluxed for 24 h. A 91% isolated yield of the expected product (**3aa**) was obtained. In addition, the liberated H_2 gas was collected in a 1000 mL Schlenk vessel and shown by GC to contain 19.22 mL (0.85 mmol) of H_2.

(b) Under conditions A (similar to Table 1, run 6)

A solution containing 2-aminobenzyl alcohol **1a** (1 mmol), cycloheptanone **2a** (2 mmol), t-BuOK (2 mmol) and KOH (2 mmol) in a mixture of toluene (2 mL) and THF (0.5 mL) was refluxed for 24 h. 30% isolated yield of the expected product, **3aa**, was obtained. The liberated H_2 gas was collected in a 1000 mL Schlenk vessel and shown by GC to contain 2.25 mL (0.1 mmol) of H_2

(c) Under conditions B (similar to Table 1, run 8)



A solution containing 2-aminobenzyl alcohol **1a** (1 mmol), cycloheptanol **2a'** (2 mmol), t-BuOK (2 mmol), KOH (2 mmol) and 5 mol% of **Mn-4** in a mixture of toluene (2 mL) and THF (0.5 mL) was refluxed for 48 h. 85% isolated yield of the expected product, **3aa**, was obtained. The liberated H_2 gas collected in 1000 mL Schlenk vessel was shown by GC to contain 38.15 mL (1.70 mmol) of H_2.

Analysis of the amount of H_2 generated in the ADC reaction

The amount of by-product H_2 produced for all cases is slightly less than their theoretical output, most notably when the reaction was run in the absence of **Mn-4**. Based on the previous literature,[3d] bases (such as *t*-BuOK) can promote hydrogen transfer. Therefore, the reaction mixtures were detected (reactions a and b) by GC using an Agilent polar column (HP-INNOWAX column). It was found that different amounts of cycloheptanol (Figs S93 and S94) are produced in these two cases. For the case involving an absence of **Mn-4** (b), t-BuOK and KOH also act as catalyst for the transfer hydrogenation.[3d] We confirmed that base-promoted hydrogen transfers for the dehydrogenation of 2-aminobenzyl alcohol (**1a**) to 2-aminobenzaldehyde in the presence of excess cycloheptanone, then afforded the stable **3aa** *via* condensation reaction.

Table S10 Standard volume of H_2 gas detected by GC

Entry[a]	H_2 (mL)	Area ()[b]
1	0	0
2	20	14332.0
3	60	43810.0
4	80	59579.0

[a] Standard solution: 0 - 80 mL of H_2 was injected into a 1000 mL Schlenk vessel - corresponding volume of nitrogen (1000 - 920 mL); [b] Peak area was detected by GC.

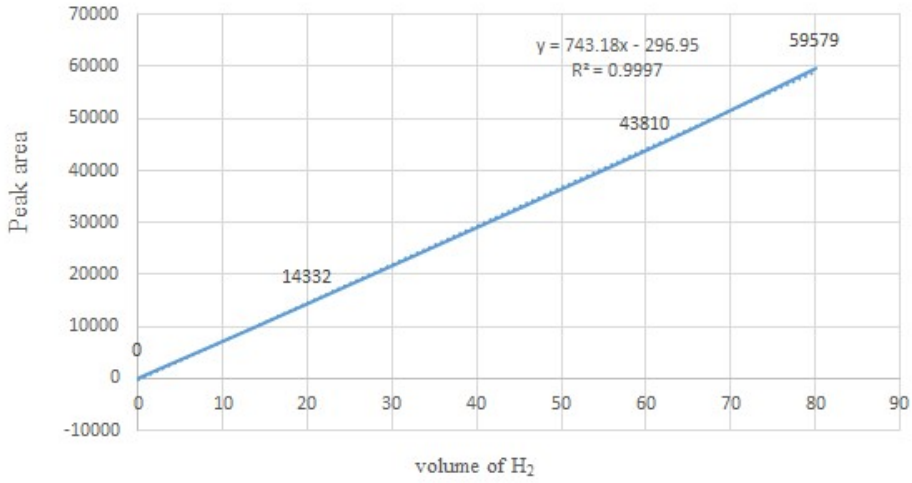
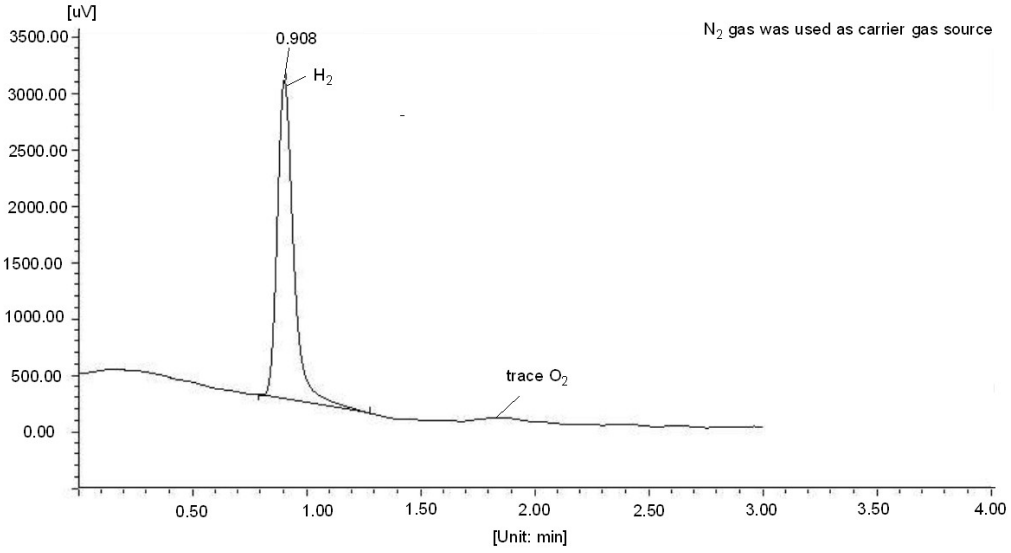


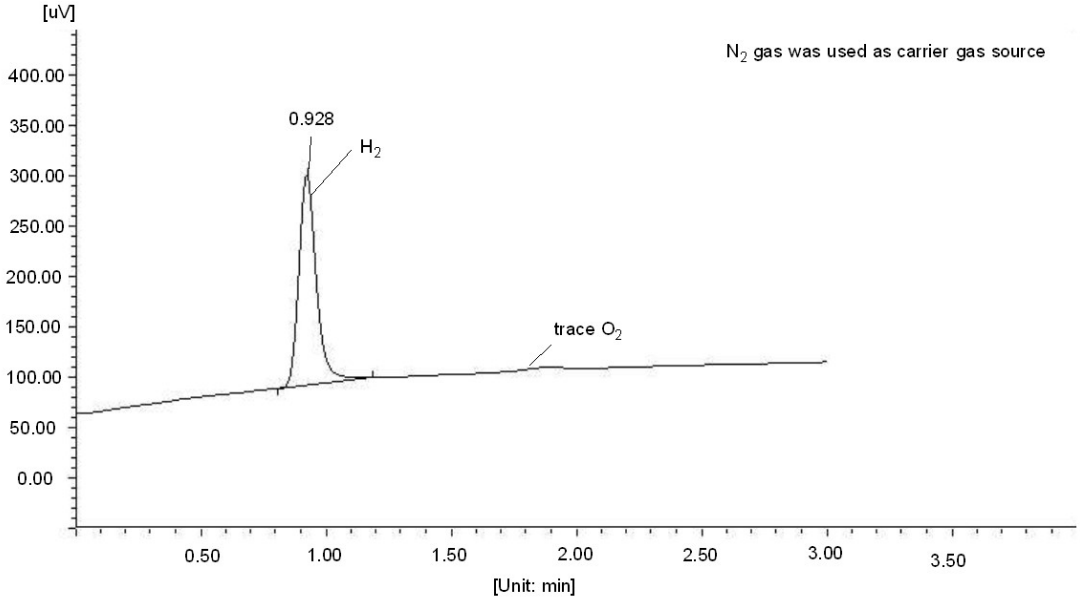
Figure S88 Standard volume plot of H_2



Result

Peak	Apex RT [min]	FWHM [min]	Height [uV]	Area [uV *s]	Area [%]	Content [%]
1	0.908	0.070	3310.7	13989.0	100.00	100.00
		Sum:	3310.7	13989.0	100.00	100.00

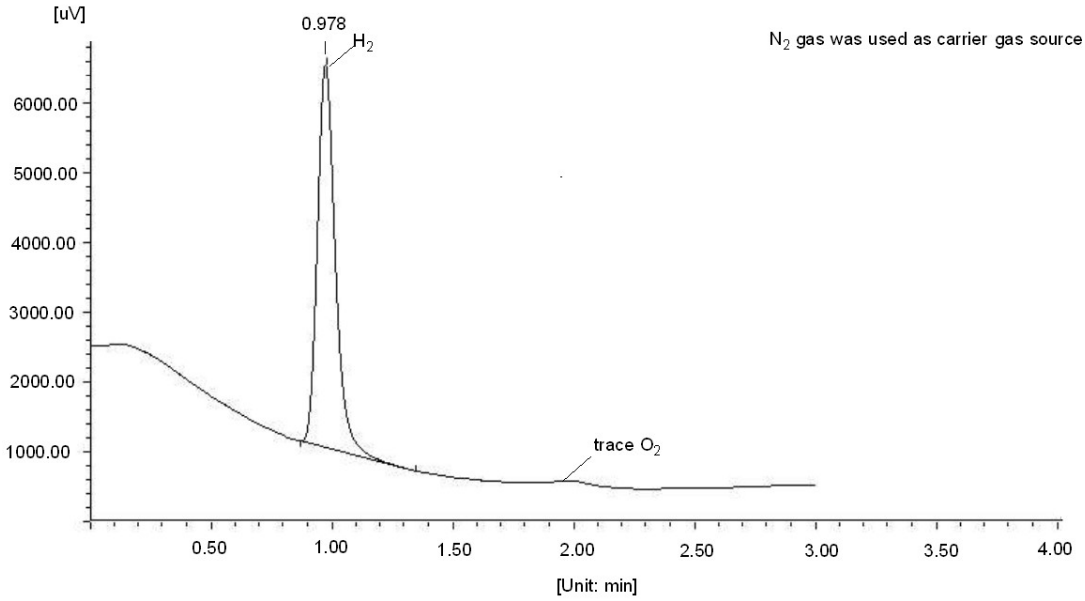
Figure S89 GC trace of the H_2 generated for the ADC reaction performed using conditions A (similar to Table 1, run 4); the retention time is 0.908 min.



Result

Peak	Apex RT [min]	FWHM [min]	Height [uV]	Area [Uv*s]	Area [%]	Content [%]
1	0.928	0.071	321.8	1379.8	100.00	100.00
		Sum:	321.8	1379.8	100.00	100.00

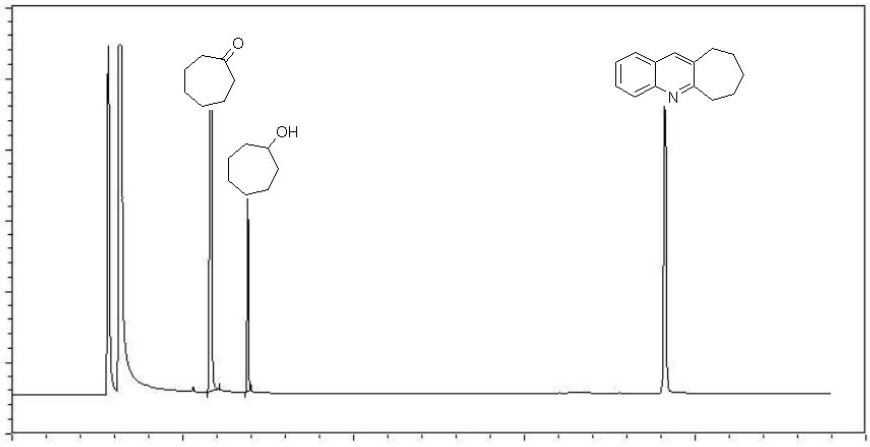
Figure S90 GC trace of the H_2 generated for the ADC reaction performed using conditions A (similar to Table 1, run 6); the retention time is 0.928 min.



Result

Peak	Apex RT [min]	FWHM [min]	Height [uV]	Area [uV *s]	Area [%]	Content [%]
1	0.978	0.075	6432.8	28056.5	100.00	100.00
		Sum:	6432.8	28056.5	100.00	100.00

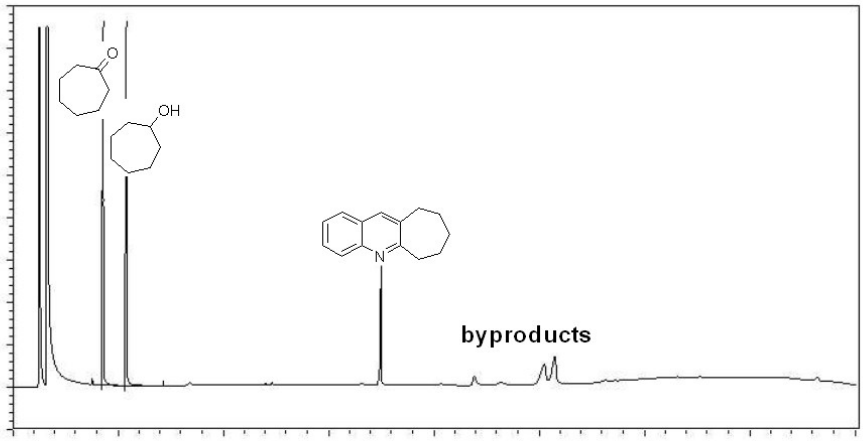
Figure S91 GC trace of the H_2 generated for the ADC reaction performed using conditions B (similar to Table 1, run 8); the retention time is 0.978 min.



Result

Peak	Name	RT [min]	HWFM [min]	Height [uV]	Area [uV*s]	Area [%]	Content [%]	Type
1	2a	3.507	0.049	977856.0	3047744.3	76.9559	76.9559	BB
2	2a'	4.155	0.025	552962.4	912635.2	23.0441	23.0441	BB
			总计:	1530818.4	3960379.5	100.0000	100.0000	

Figure S92 GC trace of the ADC reaction performed using conditions A (similar to Table 1, run 4); GC was performed using a Fuli 9790II instrument (FID detector) using an Agilent HP-INNOWAX column (30 m × 0.320 mm × 0.25 μm, Part number:19091N-113I)



Result

Peak	Name	RT [min]	PWHM [min]	Height [uV]	Area [uV*s]	Area [%]	Content [%]	Type
1	2a	3.495	0.036	981143.5	2282857.1	50.5910	50.5910	BB
2	2a'	4.149	0.034	982711.9	2229525.1	49.4090	49.4090	BB
			总计:	1963855.5	4512382.5	100.0000	100.0000	

Figure S93 GC trace of the ADC reaction performed using conditions A (similar to Table 1, run 6); GC was performed using a Fuli 9790II instrument (FID detector) using an Agilent HP-INNOWAX column (30 m × 0.320 mm × 0.25 μm, Part number:19091N-113I)

Based on a series of control experiments (Scheme S8) and GC experiments (Scheme S9), we believe that the current catalytic system follows an ADC mechanism rather than a radical mechanism. The reasons are as follows:

1. A coupling reaction that follows the ADC mechanism usually affords H_2 as a byproduct. In our case, H_2 gas was detected by GC and the amount measured using GC (TCD detector). By contrast, a reaction that proceeds *via* a radical mechanism does not generate H_2.

2. The base (such as *t*-BuOK and KOH) employed, mainly serves in the activation of the metal complex catalyst to produce the "active" catalyst and to assist in the regeneration of the active catalytic species from the inorganic product (Mn-alkoxide inhibition). It also acts as a catalyst for the transfer hydrogenation. Indeed, we have confirmed that the KOtBu promotes the hydrogen transfer for the dehydrogenation of 2-aminobenzyl alcohol (**1a**) to 2-aminobenzaldehyde in the presence of excess cycloheptanone, with a reasonable yield of cycloheptanol observed by GC (see Figs S93 and S94).

Overall, these experimental findings support this coupling reaction follows an ADC mechanism.

Figure S94 The ^{1}H and ^{13}C NMR spectra for 2-(4-methylquinolin-2-yl)aniline**.**

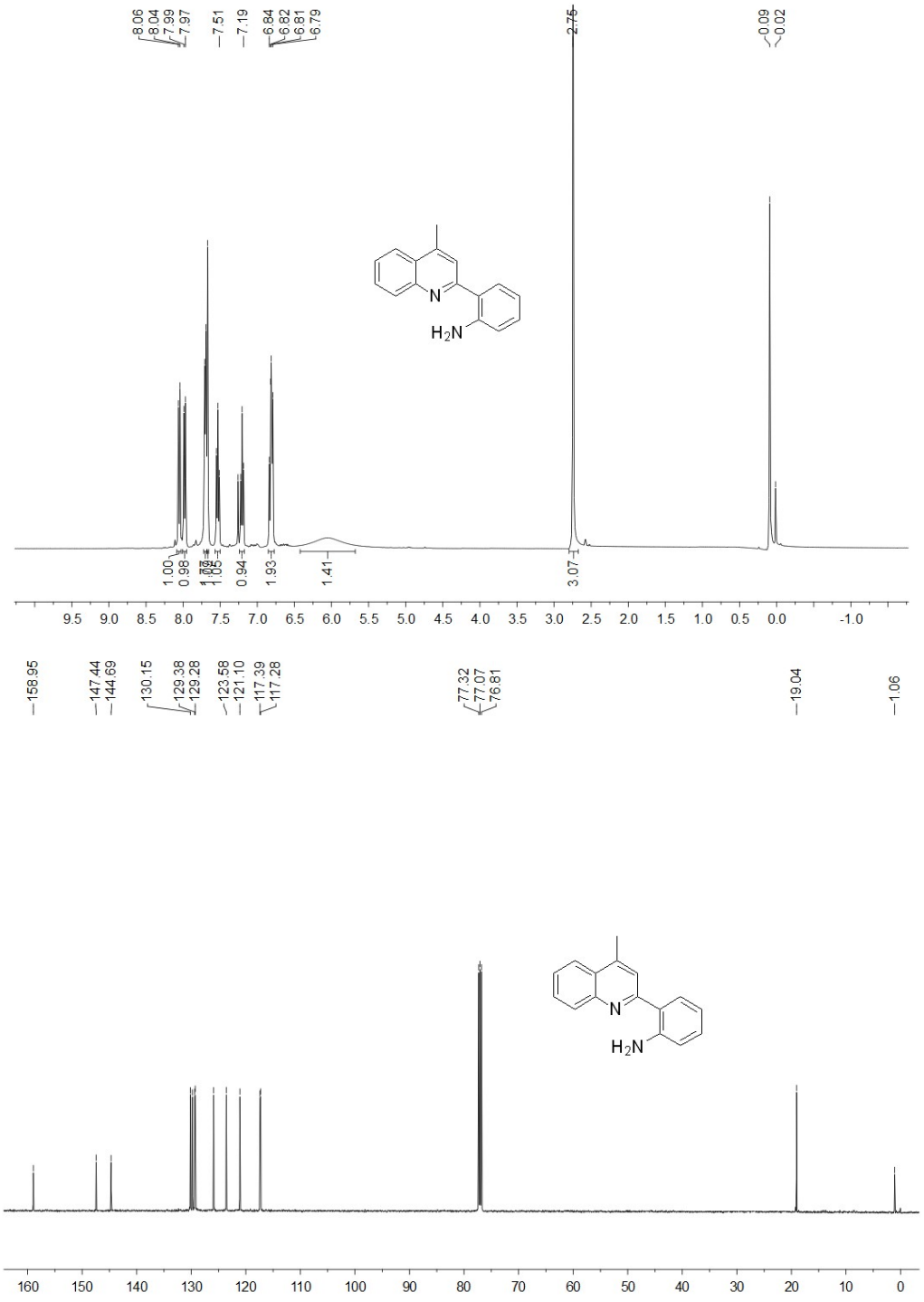


Figure S95 The ^{1}H and ^{13}C NMR spectra for (2-(cycloheptylideneamino)phenyl)methanol

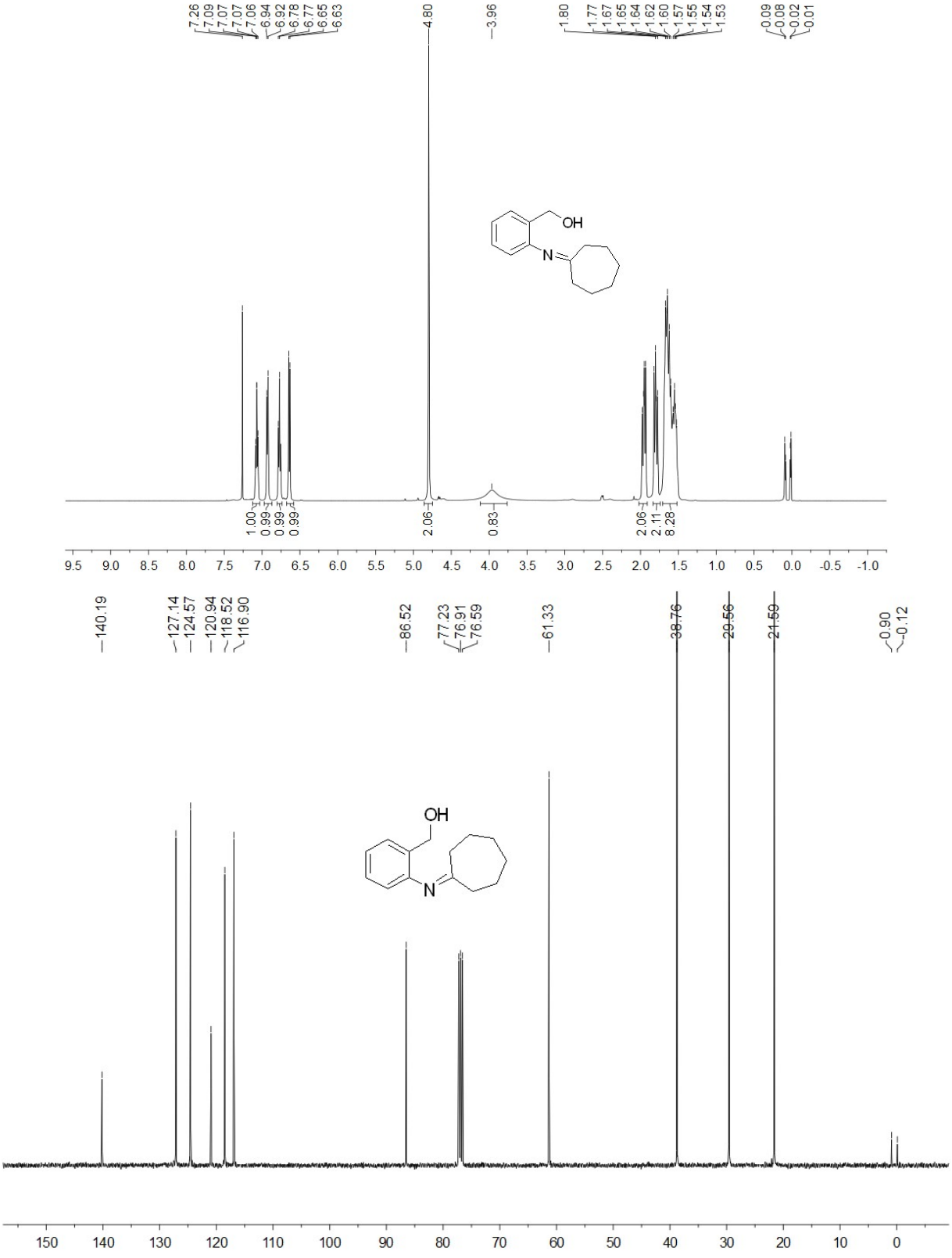


Figure S96 The ^{1}H and ^{13}C NMR spectra for (2-(cycloheptylamino)phenyl)methanol

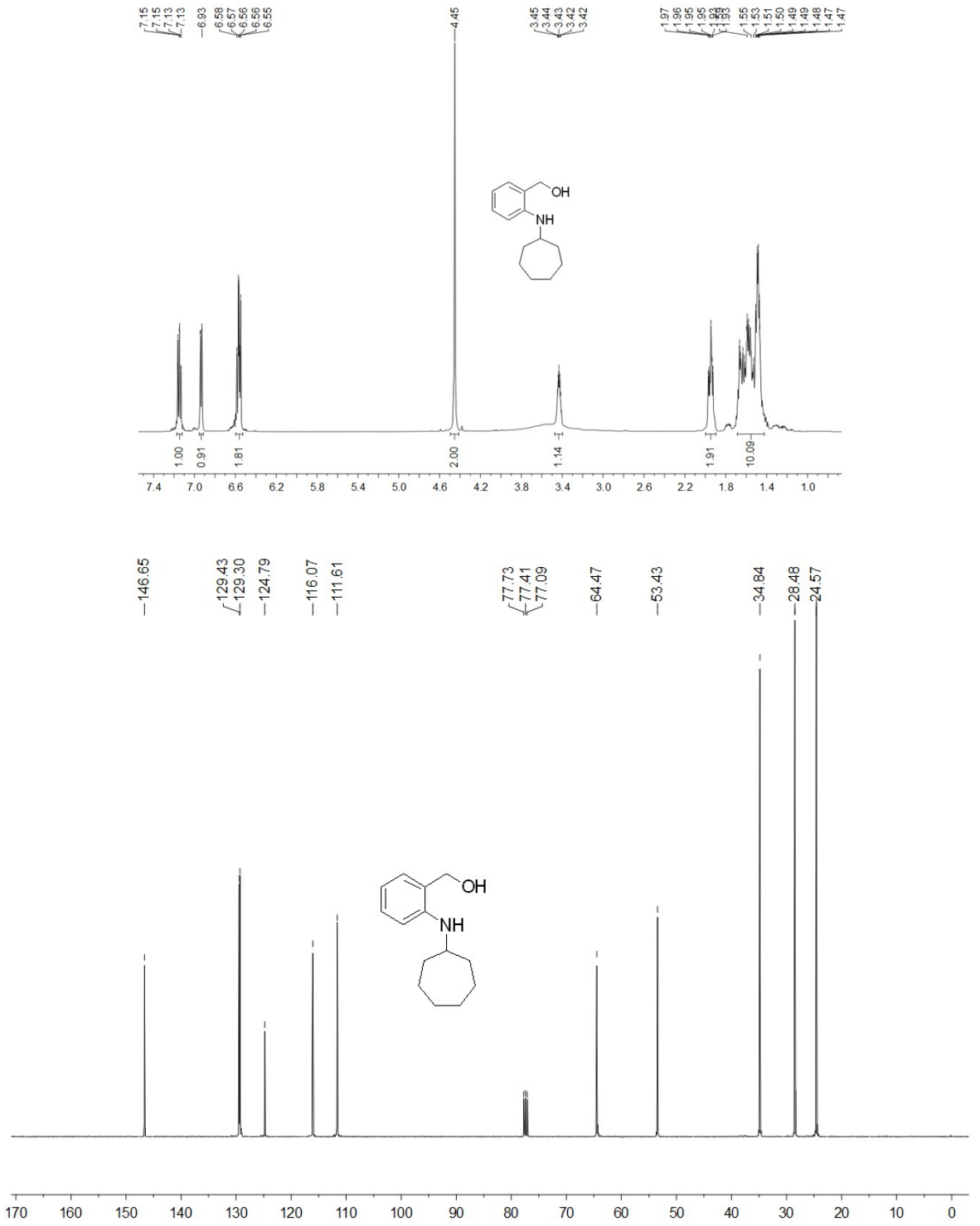
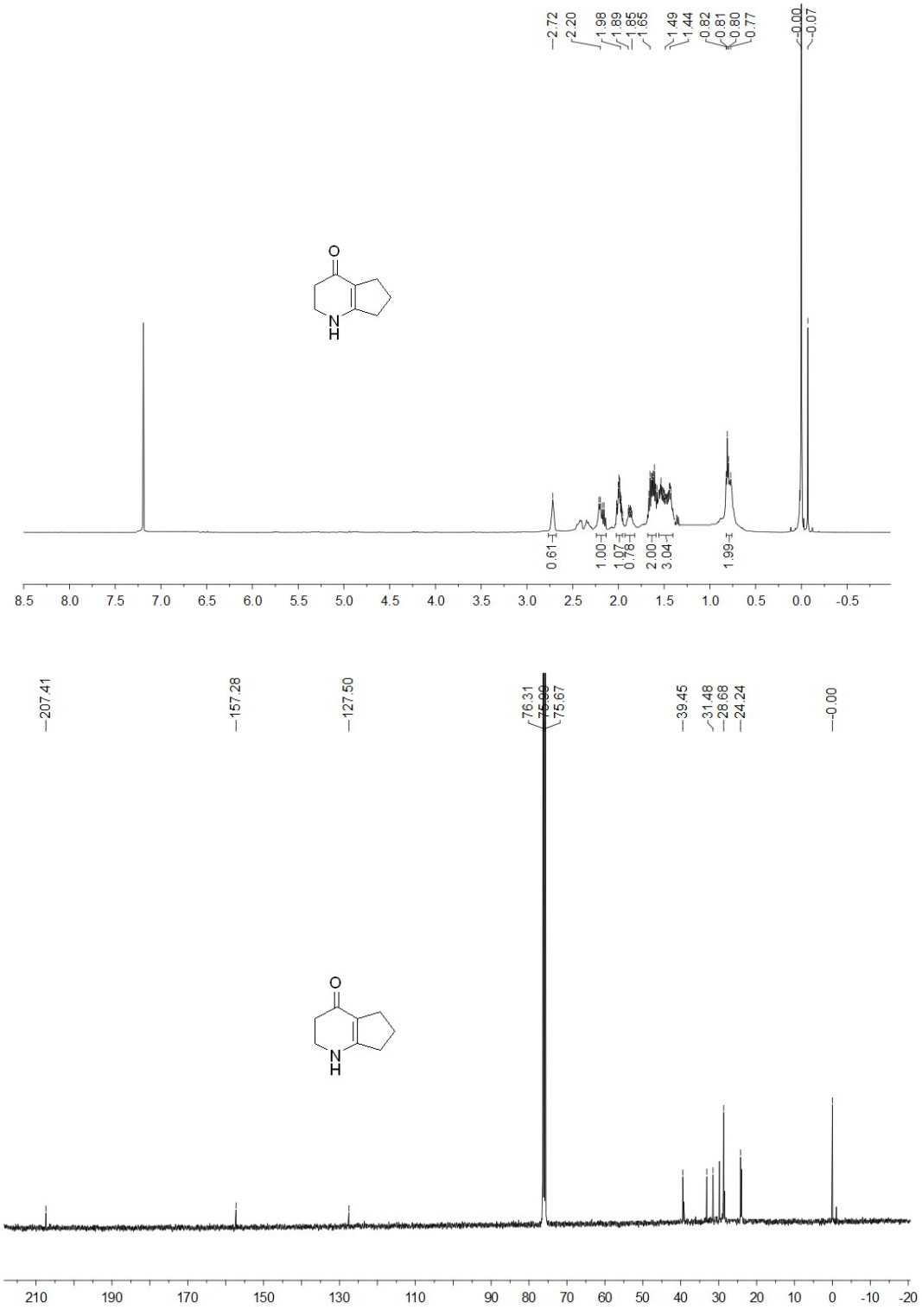
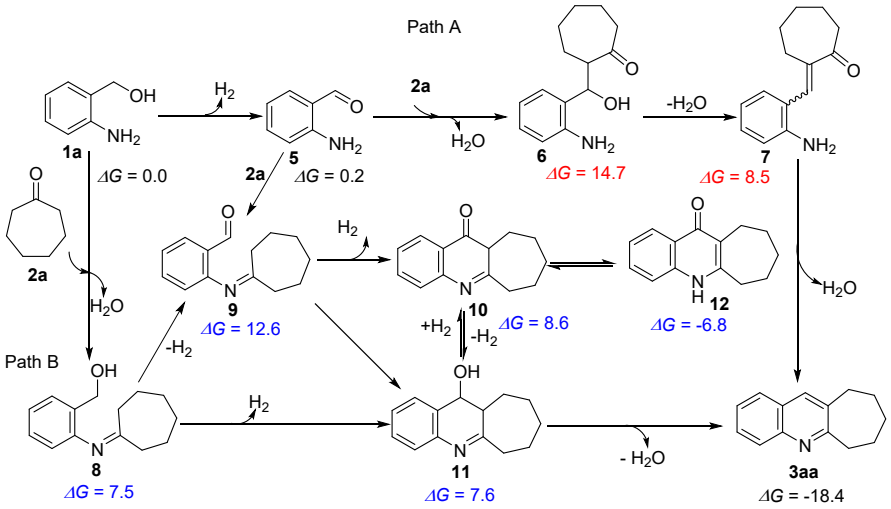


Figure S97 The ^{1}H and ^{13}C NMR spectra for 1,2,3,5,6,7-hexahydro-4H-cyclopenta[b]pyridin-4-one.



6.2 Computational details

All density functional calculations were performed using the Gaussian 09 suite of *ab initio* programs[14] for a hybrid meta-GGA level density functional M06[15] in conjunction with all-electron 6-31++G(d,p) basis set for all atoms.[16] All calculated structures were fully optimized in solvent using the integral equation formalism polarizable continuum model (IEFPCM)[17] with radii and cavity-dispersion-solvent-structure terms in Truhlar and co-workers' SMD solvation model[18] for the solvent effect correction of THF (ε = 7.4257). An ultrafine integration grid (99,590) was used for numerical integrations. Thermal corrections were calculated within the harmonic potential approximation on optimized structures under T = 298.15 K and 1 atm pressure.



Scheme S10 Plausible mechanism for the coupling cyclization of 2-aminobenzyl alcohol (**1a**) and cycloheptanone (**2a**) on the Basis of Calculated Relative Free Energies.

Absolute free energies (Hartree) and Cartesian coordinates (Ångström) of all structures optimized in the THF solvent.

1a

Gsolv= -401.769733

C	-1.880582	0.612229	-0.015542
C	-0.525000	0.963888	-0.002057
C	0.450499	-0.053987	0.014280
C	0.041625	-1.386009	0.025824
C	-1.309615	-1.731941	0.013564
C	-2.269956	-0.723192	-0.010961
H	-2.628643	1.405019	-0.030162
H	0.804343	-2.160920	0.038518
H	-1.605246	-2.778764	0.020885
H	-3.329486	-0.972511	-0.020981
C	1.899357	0.331591	0.003399
H	2.098171	0.974823	-0.872892
H	2.132123	0.937867	0.898585
O	2.711883	-0.823750	-0.027272
H	3.634713	-0.545679	-0.048032
N	-0.150458	2.305085	-0.069845

H	-0.894246	2.958074	0.147506
H	0.708442	2.561023	0.402625

2a

Gsolv= -348.830736

C	-1.645592	0.700400	-0.486776
C	-1.800457	-0.757148	-0.062707
C	-0.543026	-1.610185	-0.166444
C	-0.722566	1.524515	0.411986
C	0.637933	-1.128095	0.692863
C	0.759052	1.400162	0.079674
H	-1.282090	0.748691	-1.527316
H	-2.161981	-0.782843	0.978566
H	-0.219157	-1.675695	-1.217483
H	0.272616	-0.829878	1.686841
H	-0.904535	1.256980	1.464209
H	1.359809	1.952826	0.819131
H	-2.642363	1.162212	-0.491973
H	-2.586993	-1.225612	-0.670878
H	-0.785175	-2.636024	0.139874
H	-0.984670	2.587184	0.326805
H	1.364688	-1.938212	0.818977
H	0.979657	1.871473	-0.888445
C	1.358183	0.015102	0.030909
O	2.416129	-0.169950	-0.554417

3aa

Gsolv= -596.658050

C	3.974167	-0.763244	-0.270821
C	2.777293	-1.416901	-0.087186
C	1.579106	-0.681871	0.079707
C	1.631002	0.737751	0.055545
C	2.874593	1.386347	-0.134296
C	4.025238	0.649372	-0.294620
H	4.891147	-1.334741	-0.399199
H	2.719762	-2.503876	-0.066639
C	0.409780	1.430679	0.226491
H	2.901161	2.475588	-0.150075
H	4.979309	1.151459	-0.440127
C	-0.769547	0.749899	0.405431
C	-0.714242	-0.682542	0.412834
H	0.415689	2.522133	0.216270
N	0.408706	-1.358039	0.257341

C	-1.968088	-1.491004	0.582803
C	-2.976966	-1.325941	-0.560730
C	-3.834546	-0.069548	-0.474723
C	-3.077130	1.249331	-0.565214
C	-2.069555	1.485240	0.566396
H	-2.458211	-1.224356	1.533135
H	-2.440775	-1.352235	-1.522808
H	-4.393322	-0.090168	0.475739
H	-2.555694	1.317792	-1.533243
H	-1.663114	-2.540522	0.662152
H	-3.641023	-2.200813	-0.556915
H	-4.589285	-0.099797	-1.273229
H	-3.807258	2.070203	-0.549952
H	-1.843596	2.557485	0.629901
H	-2.542351	1.212715	1.523889

5

Gsolv= -400.598776

C	-1.296667	1.255623	0.000062
C	0.057640	0.856678	-0.000157
C	0.344127	-0.538169	-0.000035
C	-0.715606	-1.465273	-0.000053
C	-2.035457	-1.059979	-0.000088
C	-2.311295	0.317669	0.000076
H	-1.526907	2.320335	0.000281
H	-0.463615	-2.526168	-0.000082
H	-2.843415	-1.786681	-0.000134
H	-3.344816	0.659441	0.000239
O	2.730170	-0.388761	-0.000044
N	1.044688	1.784341	0.000065
H	0.816718	2.767881	-0.000432
H	2.012101	1.484477	-0.000118
C	1.696682	-1.055452	0.000160
H	1.759219	-2.166168	0.000349

6

Gsolv= -749.406527

C	4.051293	-0.184321	-0.188092
C	2.904059	0.617969	-0.101141
C	1.627361	0.006538	-0.108262
C	1.557910	-1.384029	-0.208837
C	2.700417	-2.177729	-0.299471
C	3.952042	-1.566149	-0.288953
H	5.028581	0.298386	-0.180552

H	0.586183	-1.873679	-0.228140
H	2.609862	-3.258733	-0.376817
H	4.857980	-2.165919	-0.355671
N	3.024943	2.001243	-0.078470
H	2.309137	2.474424	0.464385
H	3.957998	2.340781	0.121320
C	0.409495	0.899269	-0.081138
H	0.481899	1.559988	-0.967258
C	-0.940719	0.186447	-0.160960
C	-3.350972	0.665332	-0.982983
C	-1.327771	-0.576016	1.129923
C	-4.010202	-0.492647	-0.220906
C	-2.126162	-1.857019	0.894192
C	-3.196795	-1.784770	-0.197619
H	-0.912118	-0.514684	-1.008058
H	-3.134339	0.323567	-2.008354
H	-4.255086	-0.176188	0.804451
H	-1.892541	0.102769	1.786180
H	-2.600011	-2.138159	1.845497
H	-4.037482	1.516304	-1.055099
H	-0.415333	-0.809798	1.692111
H	-4.970842	-0.680106	-0.716581
H	-1.436272	-2.677681	0.647679
H	-3.875082	-2.637618	-0.064864
H	-2.736917	-1.927470	-1.188192
C	-2.058975	1.179486	-0.413458
O	-1.929145	2.364983	-0.123827
O	0.476451	1.722142	1.087507
H	-0.264548	2.343945	0.994039

7

Gsolv= -673.015737

C	4.013872	0.239704	0.109591
C	2.764136	0.878055	0.087214
C	1.595194	0.106479	-0.132645
C	1.732610	-1.278096	-0.321455
C	2.972759	-1.902642	-0.298490
C	4.116516	-1.131144	-0.079886
H	4.907092	0.839379	0.282629
H	0.841585	-1.864824	-0.538221
H	3.049935	-2.974655	-0.463389
H	5.097660	-1.601674	-0.058829
N	2.689251	2.250885	0.241921
H	1.844124	2.631186	0.647689

H	3.524947	2.697834	0.597803
C	0.305483	0.780765	-0.235860
H	0.314587	1.751697	-0.739990
C	-0.905044	0.375184	0.210220
C	-3.401527	0.888982	0.509363
C	-1.174408	-0.860886	1.021334
C	-4.009727	-0.425888	-0.036240
C	-1.952875	-1.946697	0.260745
C	-3.023786	-1.399738	-0.676786
H	-4.084544	1.725262	0.330238
H	-4.548281	-0.933290	0.776713
H	-1.750787	-0.573465	1.911821
H	-2.410913	-2.628356	0.992193
H	-3.261103	0.815318	1.596441
H	-0.233054	-1.276007	1.399663
H	-4.764464	-0.165957	-0.789250
H	-1.251871	-2.554139	-0.330603
H	-3.589327	-2.240695	-1.099963
H	-2.539404	-0.910262	-1.537182
C	-2.072177	1.259437	-0.103655
O	-1.967136	2.250669	-0.818989

8

Gsolv= -674.187938

C	2.158942	-1.429277	-0.852230
C	1.387592	-0.297316	-0.562064
C	1.894680	0.678912	0.318222
C	3.157340	0.487408	0.882050
C	3.922868	-0.640354	0.595463
C	3.414557	-1.600613	-0.277265
H	1.758780	-2.171421	-1.542036
H	3.540950	1.245779	1.564915
H	4.904229	-0.767190	1.047007
H	3.997002	-2.489127	-0.514075
C	1.111109	1.913507	0.641596
H	0.043195	1.672729	0.764261
H	1.468709	2.328643	1.597170
O	1.285527	2.862716	-0.406143
H	0.683911	3.600968	-0.248672
N	0.160933	-0.113379	-1.219473
C	-2.186926	-0.318929	-1.528257
C	-3.001479	0.828186	-0.912439
C	-3.824121	0.448552	0.311903
C	-0.932059	-0.594457	-0.752455

C	-3.037172	-0.125351	1.486399
C	-1.011380	-1.384426	0.530421
C	-2.377015	-1.475299	1.201583
H	-2.809825	-1.224142	-1.586310
H	-2.314303	1.655067	-0.667515
H	-4.585368	-0.289918	0.010556
H	-2.269476	0.596997	1.813343
H	-0.283234	-0.964505	1.240277
H	-1.888576	-0.048434	-2.547534
H	-3.679312	1.216867	-1.684004
H	-4.378057	1.336147	0.649048
H	-3.725367	-0.238046	2.335188
H	-0.641356	-2.398090	0.307416
H	-2.233005	-2.017429	2.145413
H	-3.061255	-2.096221	0.603446

9

Gsolv= -673.009286

C	1.967242	-1.766000	0.083862
C	1.270909	-0.612000	0.475874
C	1.901754	0.643181	0.330477
C	3.187882	0.716825	-0.226107
C	3.860503	-0.426623	-0.621853
C	3.240796	-1.671234	-0.458869
H	1.488175	-2.734960	0.214645
H	3.644539	1.699384	-0.329836
H	4.858768	-0.361072	-1.047349
H	3.760389	-2.578875	-0.760096
C	1.234380	1.868868	0.781977
H	0.281098	1.716849	1.331633
N	0.024035	-0.727765	1.090830
C	-1.167554	-0.938645	-1.054736
C	-1.511615	0.466677	-1.578536
C	-2.956562	0.897975	-1.362615
C	-1.064121	-0.937354	0.444586
C	-3.456655	0.853352	0.079947
C	-2.317098	-1.138403	1.247775
C	-3.596730	-0.562622	0.642273
H	-1.936781	-1.653849	-1.378603
H	-0.832292	1.196677	-1.110532
H	-3.614695	0.260537	-1.975645
H	-2.792745	1.449463	0.729573
H	-2.138541	-0.715011	2.244917
H	-0.213760	-1.260713	-1.488765

H	-1.290200	0.491955	-2.653504
H	-3.070603	1.918427	-1.753825
H	-4.436218	1.348807	0.115491
H	-2.439130	-2.223842	1.391312
H	-4.360131	-0.575798	1.430559
H	-3.977064	-1.224460	-0.150536
O	1.667770	2.997107	0.606303

10

Gsolv= -671.845091

C	-2.467488	-1.704501	-0.357629
C	-1.398845	-0.891063	0.035294
C	-1.624817	0.488575	0.216076
C	-2.899393	1.027449	0.014735
C	-3.947708	0.212785	-0.388500
C	-3.724982	-1.155738	-0.574943
H	-2.289041	-2.770858	-0.480840
H	-3.044320	2.095054	0.168406
H	-4.935484	0.634388	-0.558332
H	-4.545257	-1.799211	-0.886207
C	0.870447	0.712271	0.468958
C	1.390914	1.146483	-0.937368
C	2.897462	1.038488	-1.123451
C	0.868409	-0.788131	0.545304
C	3.502424	-0.345862	-0.914325
C	2.132524	-1.499110	0.924784
C	3.446171	-0.827160	0.534589
H	1.535943	1.147254	1.228125
H	0.866579	0.551315	-1.700898
H	3.391207	1.745005	-0.437453
H	3.001930	-1.078594	-1.569505
H	2.075122	-2.508195	0.495550
H	1.092315	2.192456	-1.086960
H	3.127508	1.386541	-2.139994
H	4.550393	-0.310862	-1.240695
H	2.104769	-1.634723	2.018214
H	4.245038	-1.557362	0.715597
H	3.661798	0.019433	1.204167
O	-0.621155	2.496343	0.986492
N	-0.166510	-1.510575	0.283479
C	-0.495732	1.334119	0.622233

11

Gsolv= -673.017229

C	-2.670399	-1.709962	0.153199
C	-1.561276	-0.913835	-0.140759
C	-1.695178	0.483337	-0.180382
C	-2.932445	1.062792	0.082465
C	-4.034242	0.263995	0.392219
C	-3.902689	-1.123132	0.427074
H	-2.543849	-2.791327	0.165849
H	-3.027086	2.145733	0.053514
H	-4.995477	0.727785	0.603814
H	-4.761081	-1.748514	0.663495
C	0.765011	0.591740	0.066145
C	2.052571	1.356549	-0.235972
C	3.235264	1.030453	0.675407
C	0.751012	-0.867886	-0.359029
C	3.967086	-0.266583	0.363492
C	2.027166	-1.581865	-0.680613
C	3.101327	-1.517280	0.413247
H	0.614881	0.594799	1.164659
H	2.332371	1.224712	-1.294114
H	2.877641	1.008654	1.717968
H	4.419464	-0.192971	-0.639221
H	2.446614	-1.165346	-1.611330
H	1.836611	2.425789	-0.110217
H	3.956474	1.857691	0.620165
H	4.802346	-0.378803	1.069105
H	1.757841	-2.622803	-0.892757
H	3.746924	-2.397614	0.298793
H	2.629856	-1.612835	1.404393
N	-0.340022	-1.549756	-0.428427
C	-0.469433	1.274269	-0.536816
H	-0.353820	1.273957	-1.639902
O	-0.639551	2.602648	-0.080253
H	-0.045791	3.182650	-0.571252

12

Gsolv= -671.869635

C	-2.753860	-1.612946	0.072625
C	-1.583699	-0.849272	-0.074092
C	-1.631689	0.554052	-0.026593
C	-2.874994	1.176650	0.171635
C	-4.029083	0.430205	0.316044
C	-3.962697	-0.972756	0.265825
H	-2.692173	-2.699535	0.032723
H	-2.896561	2.263775	0.206131

H	-4.986304	0.923598	0.467662
H	-4.869636	-1.562727	0.379928
C	0.822064	0.600198	-0.388206
C	2.112757	1.355543	-0.537848
C	3.127253	1.120559	0.585647
C	0.796984	-0.773235	-0.420195
C	3.886629	-0.197378	0.483893
C	2.028162	-1.609481	-0.591108
C	3.034567	-1.459215	0.556057
H	2.590689	1.113519	-1.501793
H	2.610775	1.183365	1.556681
H	4.444893	-0.208565	-0.467218
H	2.517751	-1.338050	-1.538845
H	1.854762	2.419537	-0.577443
H	3.860174	1.939708	0.572664
H	4.642474	-0.238594	1.280861
H	1.732548	-2.661999	-0.687492
H	3.701116	-2.331915	0.536912
H	2.497142	-1.500164	1.516356
O	-0.437621	2.593218	-0.129633
C	-0.402866	1.350986	-0.178808
N	-0.368826	-1.464686	-0.265771
H	-0.342067	-2.478350	-0.288927

H_2O

Gsolv= -76.400570

O	0.000000	0.000000	0.117212
H	0.000000	0.765440	-0.468848
H	0.000000	-0.765440	-0.468848

H_2

Gsolv= -1.170583

H	0.000000	0.000000	0.371621
H	0.000000	0.000000	-0.371621

7. X-ray structure determinations

Table S11 Crystal data and structure refinement for **Mn1** and **Mn4**

Identification code	**Mn1**	**Mn4**
Empirical formula	$C_{16}H_{23}BrMnN_3O_4$	$C_{16}H_{20}BrMnN_2O_3S$
CCDC No.	2085192	2085193
Formula weight	456.22	455.26
Temperature/K	169.99(11)	169.98(10)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	7.94037(15)	7.71788(15)
b/Å	10.1189(2)	10.1753(2)
c/Å	12.8889(3)	13.2154(2)
α/°	87.2665(19)	103.0666(16)
β/°	76.201(2)	101.3527(15)
γ/°	70.5516(19)	108.6668(17)
Volume/Å^3	947.76(4)	916.12(3)
Z	2	2
ρ_{calc}g/cm^3	1.5985	1.6503
μ/mm^{-1}	8.353	9.622
F(000)	462.8	459.3
Crystal size/mm^3	0.25 × 0.15 × 0.1	0.24 × 0.18 × 0.1
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.06 to 150.32°	9.66 to 150.46°
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -16 ≤ l ≤ 11	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -15 ≤ l ≤ 16
Reflections collected	10618	10617
Independent reflections	3755 [R_{int} = 0.0261, R_{sigma} = 0.0218]	3608 [R_{int} = 0.0251, R_{sigma} = 0.0209]
Data/restraints/parameters	3755/0/231	3608/0/218
Goodness-of-fit on F^2	1.028	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0892	R_1 = 0.0337, wR_2 = 0.0915
Final R indexes [all data]	R_1 = 0.0328, wR_2 = 0.0894	R_1 = 0.0341, wR_2 = 0.0919
Largest diff. peak/hole / e Å^{-3}	0.63/-0.56	0.74/-0.67

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