Supporting Information

C-H Silylation and Boronation Enabled by Alkyne Insertion/Vinyl to Aryl 1,5-Palladium Migration

Zhendong Cheng,[‡a] Weiwei Xu,[‡a] Xuliang Tan,[a] Zhengrui Zhou,[a] Liwei Zhou,*[ab] Yun Liang,*[a] and Yuan Yang*[a]

[a]Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, China.

[b]Hunan Provincial Key Laboratory of the TCM Agricultural Biogenomics, College of Pharmacy, Changsha Medical University, Changsha, Hunan 410219, China.

[‡]These authors contributed equally to this work.

E-mail: hnzhouliwei@126.com; yliang@hunnu.edu.cn; yuanyang@hunnu.edu.cn.

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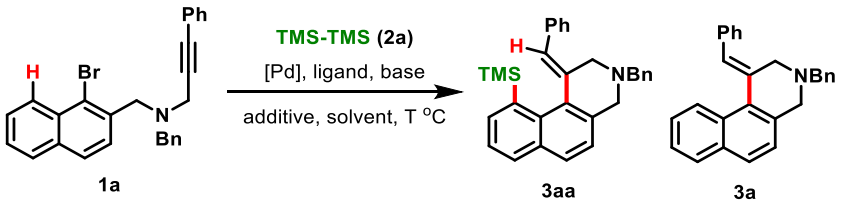
1 General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instruments or Avance-400 instruments (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26 ppm), ^{13}C NMR: $CDCl_3$ (77.00 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; dd, doublets of doublet; t, triplet, and m, multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC system coupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

2.Optimization of Reaction Parameters

2.1 Table S1. Optimization of reaction conditions for the synthesis of 3aa[a]

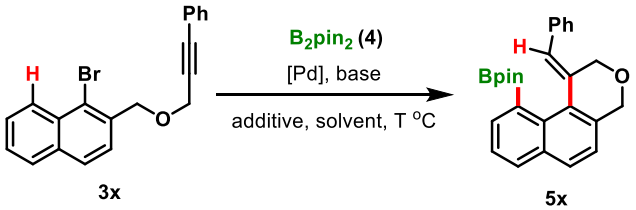


Entry	Catalyst	Ligand	Base	Solvent	Temperature /°C	Yield of **3aa** (%)[b]	Yield of **3a'** (%)[b]
1	$Pd(OAc)_2$	–	Cs_2CO_3	DMF	100	24	5
2	$Pd(dba)_2$	–	Cs_2CO_3	DMF	100	45	19
3	$PdCl_2$	–	Cs_2CO_3	DMF	100	29	20
4	$Pd(PPh_3)_4$	–	Cs_2CO_3	DMF	100	25	14
5	$Pd(PPh_3)_2Cl_2$	–	Cs_2CO_3	DMF	100	34	12
6	$Pd(dba)_2$	PPh_3	Cs_2CO_3	DMF	100	trace	23
7	$Pd(dba)_2$	PCy_3	Cs_2CO_3	DMF	100	trace	33

8	$Pd(dba)_2$	TFP	Cs_2CO_3	DMF	100	7	19
9	$Pd(dba)_2$	dppp	Cs_2CO_3	DMF	100	trace	29
10	$Pd(dba)_2$	dppf	Cs_2CO_3	DMF	100	trace	27
11	$Pd(dba)_2$	–	K_2CO_3	DMF	100	48	6
12	$Pd(dba)_2$	–	Na_2CO_3	DMF	100	40	7
13	$Pd(dba)_2$	–	KOAc	DMF	100	20	trace
14	$Pd(dba)_2$	–	K_2CO_3	DMAc	100	38	14
15	$Pd(dba)_2$	–	K_2CO_3	MeCN	100	14	23
16	$Pd(dba)_2$	–	K_2CO_3	Toluene	100	trace	trace
17	$Pd(dba)_2$	–	K_2CO_3	Dioxane	100	trace	27
18	$Pd(dba)_2$	–	K_2CO_3	DMF	90	42	14
29	$Pd(dba)_2$	–	K_2CO_3	DMF	110	50	10
20	$Pd(dba)_2$	–	K_2CO_3	DMF	120	47	12
21[c]	$Pd(dba)_2$	–	K_2CO_3	DMF	110	**70 (61)**[d]	**8**
22[e]	$Pd(dba)_2$	–	K_2CO_3	DMF	110	25	trace
23[f]	$Pd(dba)_2$	–	K_2CO_3	DMF	110	36	10
24[c,g]	$Pd(dba)_2$	–	K_2CO_3	DMF	110	45	9

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Pd catalyst (10 mol%), monodentate ligand (20 mol%) or bidentate ligand (10 mol%), base (1 equiv) and solvent (2 mL) under N_2 for 10 h. [b]Isolated yield. [c]TBAB (1 equiv) was added. [d]**1a** (1 mmol). [e]TBAI (1 equiv) was added. [f]TBAAc (1 equiv) was added. [g]Under air.

2.2 Table S2. Optimization of reaction conditions for the synthesis of 5x[a]



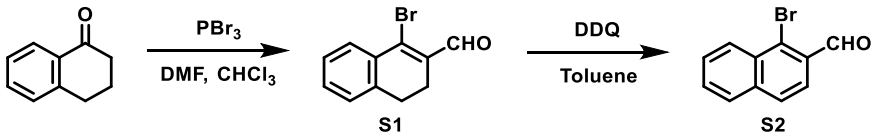
Entry	Catalyst	Base	Addtive	Temperature /°C	Solvent	Yield of **5x** (%)[b]
1	$Pd(dba)_2$	K_2CO_3	TBAB	110	DMSO	31
2	$PdCl_2$	K_2CO_3	TBAB	110	DMSO	21
3	$Pd(PPh_3)_2Cl_2$	K_2CO_3	TBAB	110	DMSO	58

4	$Pd(PPh_3)_2Cl_2$	K_2CO_3	TBAB	110	DMF	43
5	$Pd(PPh_3)_2Cl_2$	K_2CO_3	TBAB	110	Dioxane	22
6	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	TBAB	110	DMSO	43
7	$Pd(PPh_3)_2Cl_2$	Na_2CO_3	TBAB	110	DMSO	**68**
8	$Pd(PPh_3)_2Cl_2$	Li_2CO_3	TBAB	110	DMSO	32
9	$Pd(PPh_3)_2Cl_2$	KOAc	TBAB	110	DMSO	trace
10	$Pd(PPh_3)_2Cl_2$	Na_2CO_3	–	110	DMSO	59
11	$Pd(PPh_3)_2Cl_2$	Na_2CO_3	TBAI	110	DMSO	46
12	$Pd(PPh_3)_2Cl_2$	Na_2CO_3	TBAAc	110	DMSO	trace
13	$Pd(PPh_3)_2Cl_2$	Na_2CO_3	TBAB	100	DMSO	51
14	$Pd(PPh_3)_2Cl_2$	Na_2CO_3	TBAB	120	DMSO	57

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Pd catalyst (10 mol%), base (1 equiv) additive (1 equiv) and solvent (2 mL) under N_2 for 2 h. [b]Isolated yield.

3 Synthetic Methods of Starting Materials

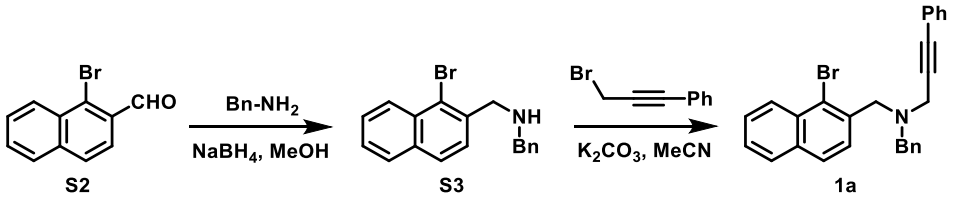
3.1 General procedure for the synthesis of substrates 1a-v and 1y[1-3]



To a mixture of DMF (160.0 mmol, 4.0 equiv, 12.4 mL) and chloroform (0.5 M) was added PBr_3 (108.0 mmol, 2.7 equiv, 10.2 mL) dropwise at 0 ºC, and the mixture was stirred for 1 h before the addition of ketones (40.0 mmol, 1.0 equiv, 5.3 mL). The resulting solution was stirred for 24-48 h at room temperature before it was poured into 100 mL ice water, neutralized with solid $NaHCO_3$ until pH = 7, and extracted with dichloromethane. The extract was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to give the compound **S1**.

To a solution of **S1** (10.0 mmol, 1.0 equiv, 2.4 g) in toluene (0.5 M) at room temperature was added DDQ (12.0 mmol, 1.2 equiv, 2.7 g), and the mixture was then

refluxed for 1-2 day. The mixture was cooled and filtered through Celite and washed with ethyl acetate. The filtrate was concentrated and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to provide 1-bromo-2-naphthaldehyde **S2**.

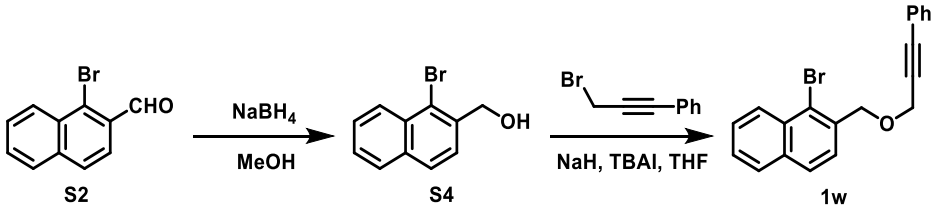


To a solution of **S2** (10.0 mmol, 1.0 equiv, 2.3 g) in MeOH (0.5 M) at 0 °C was added $BnNH_2$ (10.0 mmol, 1.0 equiv, 1.1 mL) slowly, and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was again cooled to 0 °C, and $NaBH_4$ (15.0 mmol, 1.5 equiv, 0.6 g) was added slowly in three portions. Then the resulting mixture was stirred at room temperature for 2 h, and the solvent was evaporated to 1/3 of its original volume under reduced pressure. The reaction was quenched with saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate for three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford **S3**.

To a solution of **S3** (10.0 mmol, 1.0 equiv, 3.3 g) in CH_3CN, K_2CO_3 (40.0 mmol, 4.0 equiv, 5.5 g) and (3-bromoprop-1-yn-1-yl) benzene (15.0 mmol, 1.5 equiv, 2.9 g) were added. After stirring at 80 °C in oil bath for 12 h, the cooled reaction mixture was then filtered through a pad of celite, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 30:1) to provide **1a**.

The procedures of **1b to 1v** and **1y** were similar to **1a**.

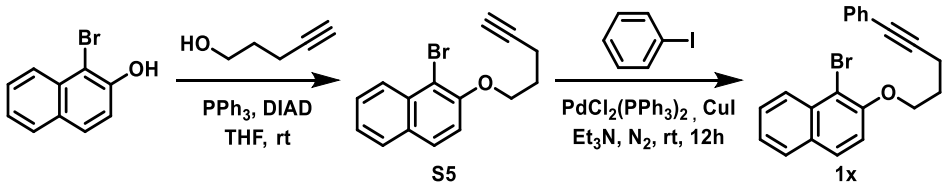
3.2 General procedure for the synthesis of substrates 1w[4]



To a solution of **S2** (10.0 mmol, 1.0 equiv, 2.3 g) in MeOH (0.5 M) was added $NaBH_4$ (15.0 mmol, 1.5 equiv, 0.6 g) in portions at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then quenched with a saturated aqueous solution of NH_4Cl. The resulting mixture was extracted with ethyl acetate and washed with brine. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The obtained residue was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford **S4**.

To a solution of **S4** (10.0 mmol, 1.0 equiv, 2.4 g) in THF (0.5 M) was added NaH (60%, 12.0 mmol, 1.2 equiv, 0.5 g) in portions at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then (3-bromoprop-1-yn-1-yl) benzene (15.0 mmol, 1.5 equiv, 2.9 g) was added dropwise over 10 min. The reaction mixture was warmed to room temperature and stirred for an additional 24 h before being quenched with water. The resulting mixture was extracted with EtOAc and washed with brine. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 50:1) to provide **1w**.

3.3 General procedure for the synthesis of substrates 1x[5]



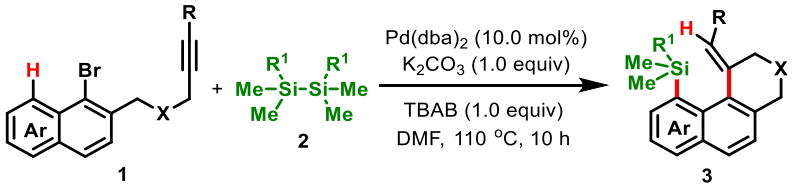
To a solution of 1-bromonaphthalen-2-ol (10.0 mmol, 1.0 equiv, 2.2 g), PPh_3 (12.0 mmol, 1.2 equiv, 3.2 g) and pent-4-yn-1-ol (10.0 mmol, 1.0 equiv, 0.8 g) in dry THF at 0 °C under nitrogen balloon was added DIAD (12.0 mmol, 1.2 equiv, 2.4 mL) slowly. The reaction mixture was warmed up to room temperature and further stirred overnight. After completion, the mixture was extracted with ethyl acetate, The

combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 50:1) to afford **S5**.

To a Schlenk tube under an N_2 atmosphere iodobenzene (6.0 mmol, 1.2 equiv, 1.2 g), $Pd(PPh_3)_2Cl_2$ (0.1 mmol, 2.0 mol%, 70.2 mg), CuI (0.2 mmol, 4.0 mol%, 38.1 mg), and Et_3N (0.5 M) were added at room temperature. The mixture was stirred for 5 min before **S5** (5.0 mmol, 1.0 equiv, 1.4 g) was added. The reaction was then stirred at room temperature for 12 h. The reaction mixture was filtered through a celite pad, and washed with ethyl acetate. The filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 50:1) to provide **1x**.

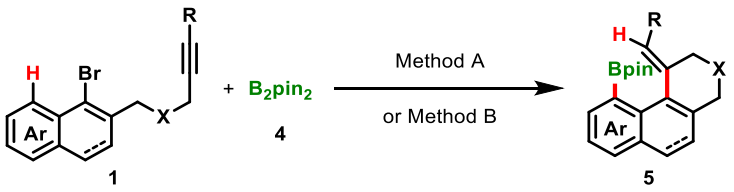
4 Typical Procedures

4.1 Typical procedure for the synthesis of 3



To a 25 mL Schlenk tube was added alkyne-tethered *α*-bromopenhthalene **1** (0.2 mmol, 1.0 equiv), disilane **2** (0.4 mmol, 2.0 equiv), $Pd(dba)_2$ (0.02 mmol, 10.0 mol%, 11.6 mg), K_2CO_3 (0.2 mmol, 1.0 equiv, 27.6 mg), TBAB (0.2 mmol, 1.0 equiv, 64.5 mg) and DMF (2 mL). Then the tube was charged with nitrogen and stirred at 110 °C (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (eluent: petroleum ether/EtOAc = 30:1) to provide the desired product **3**.

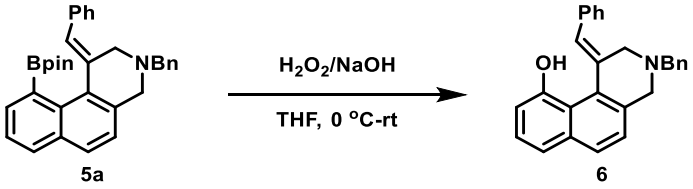
4.2 Typical procedure for the synthesis of 5



Method A: To a 25 mL Schlenk tube was added alkyne-tethered *α*-bromopenhthalene **1** (0.2 mmol, 1.0 equiv), bis(pinacolato)diboron **4** (0.4 mmol, 2.0 equiv, 101.6 mg), $Pd(dba)_2$ (0.02 mmol, 10.0 mol%, 11.6 mg), K_2CO_3 (0.2 mmol, 1.0 equiv, 27.6 mg), TBAB (0.2 mmol, 1.0 equiv, 64.5 mg) and DMF (2 mL). Then the tube was charged with nitrogen and stirred at 110 °C (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **5**.

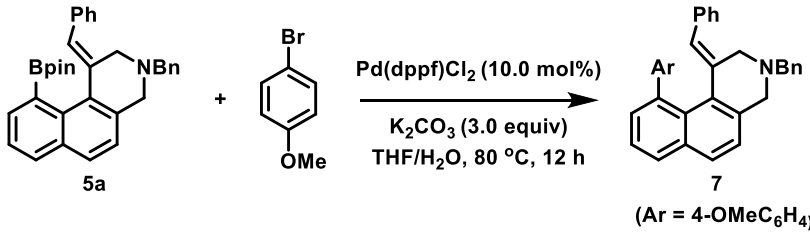
Method B: To a 25 mL Schlenk tube was added alkyne-tethered *α*-bromopenhthalene **1** (0.2 mmol, 1.0 equiv), bis(pinacolato)diboron **4** (0.4 mmol, 2.0 equiv, 101.6 mg), $Pd(PPh_3)_2Cl_2$ (0.02 mmol, 10.0 mol%, 14.0 mg), Na_2CO_3 (0.2 mmol, 1.0 equiv, 21.2 mg), TBAB (0.2 mmol, 1.0 equiv, 64.5 mg) and DMSO (2 mL). Then the tube was charged with nitrogen and stirred at 110 °C (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **5**.

5 Synthetic Transformations of 5a[6-7]



To an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar,

(*Z*)-3-benzyl-1-benzylidene-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline **5a** (0.2 mmol, 1.0 equiv, 97.5 mg) and THF (2.0 mL) were added under a nitrogen atmosphere, the reaction system was cooled to 0 °C, H_2O_2 (1.0 mL, 30% in H_2O) was added followed by NaOH (2.0 mL, 3.0 M in H_2O). The reaction mixture was allowed to warm to room temperature and was allowed to stir for 1 hours, then cooled to 0 °C and saturated aq. $Na_2S_2O_3$ was added dropwise. The reaction was then warmed to room temperature and the aqueous layer was extracted with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **6**.



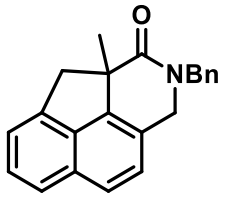
To an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar, (*Z*)-3-benzyl-1-benzylidene-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline **5a** (0.2 mmol, 1.0 equiv, 97.5 mg), 1-bromo-4-methoxybenzene (0.24 mmol, 1.2 equiv, 44.6 mg), Pd(dppf)Cl_2 (0.02 mmol, 10.0 mol%, 14.6 mg), K_2CO_3 (0.6 mmol, 3.0 equiv, 82.8 mg), THF (2.0 mL) and H_2O (0.5 mL) were added under a nitrogen atmosphere, the reaction mixture was then stirred at 80 °C for 12 h. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **7**.

6 Crystal Culture Procedure

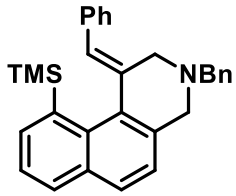
To a round-bottom flask (25 mL) was added (Z)-2-((3-benzyl-10-(trimethylsilyl)-3,4-dihydrobenzo[*f*]isoquinolin-1(2*H*)-ylidene)methyl)benzonitrile **3oa** (10.0 mg). Dichloromethane (1 mL) were added slowly to make it dissolve completely. Then petroleum ether (5 mL) was added. Finally, the round-bottom flask was sealed with a

rubber stopper, and connected the air with a syringe needle. Putting the flask in a dry and ventilated place to make the organic solvent volatilize slowly. After a few days, the crystal of **3oa** were separated out.

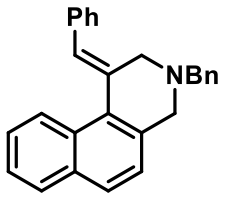
7 Characterization Data



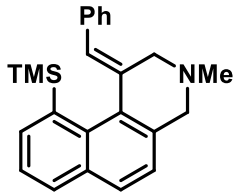
2-benzyl-3a-methyl-2,3,3a,4-tetrahydro-1H-indeno[2,1,7-*def*]isoquinolin-1-one (3A): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); light yellow oil, isolated yield 62% (38.8 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.49-7.45 (m, 1H), 7.34 (d, *J* = 6.5 Hz, 1H), 7.31-7.27 (m, 2H), 7.26-7.20 (m, 4H), 4.90-4.81 (m, 2H), 4.68 (d, *J* = 14.5 Hz, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 3.93 (d, J = 17.0 Hz, 1H), 3.43 (d, *J* = 17.0 Hz, 1H), 1.54 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.9, 145.2, 142.3, 137.3, 135.1, 130.3, 128.7, 128.6, 127.7, 127.4, 124.2, 123.6, 123.4, 122.5, 121.1, 50.9, 50.6, 49.7, 42.6, 25.6; **HRMS (ESI)** m/z calcd for $C_{22}H_{20}NO^+$ $(M+H)^+$ 314.1539, found 314.1538.



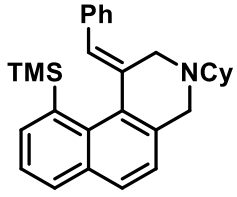
(*Z*)-3-benzyl-1-benzylidene-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3aa): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown oil, isolated yield 70% (60.7 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.47-7.41 (m, 3H), 7.38-7.31 (m, 5H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.48 (s, 1H), 4.32 (d, *J* = 15.0 Hz, 1H), 3.92 (d, *J* = 15.0 Hz, 1H), 3.85 (s, 2H), 3.79 (d, *J* = 15.0 Hz, 1H), 3.54 (d, *J* = 14.5 Hz, 1H), 0.25 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.8, 138.4, 137.7, 137.5, 135.9, 135.51, 135.50, 134.6, 134.1, 131.1, 129.2, 129.1, 128.8, 128.3, 128.2, 127.7, 127.1, 126.6, 123.9, 123.6, 61.4, 56.8, 55.9, 1.9; **HRMS (ESI)** m/z calcd for $C_{30}H_{32}NSi^+$ $(M+H)^+$ 434.2299, found 434.2292.



(*Z*)-3-benzyl-1-benzylidene-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3a): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); yellow solid, mp: 105.1-106.6 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.57-7.51 (m, 2H), 7.46-7.41 (m, 2H), 7.40-7.33 (m, 8H), 7.25 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 4.00 (s, 2H), 3.92 (s, 2H), 3.76 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.1, 137.2, 133.8, 133.7, 132.4, 131.5, 130.3, 129.1, 129.0, 128.5, 128.21, 128.19, 127.2, 127.0, 126.8, 126.0, 125.5, 125.1, 124.6, 61.2, 55.6, 53.9; **HRMS (ESI)** m/z calcd for $C_{27}H_{20}N^+$ $(M+H)^+$ 362.1903, found 362.1912.

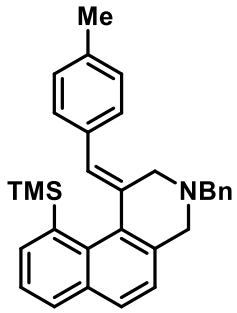


(*Z*)-1-benzylidene-3-methyl-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ba): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); light yellow solid, isolated yield 56% (40.0 mg); mp: 103.5-105.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.42-7.38 (m, 2H), 7.30-7.26 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.49 (s, 1H), 4.37 (d, *J* = 15.0 Hz, 1H), 3.85 (d, *J* = 14.5 Hz, 1H), 3.66 (d, *J* = 15.0 Hz, 1H), 3.45 (d, *J* = 14.5 Hz, 1H), 2.61 (s, 3H), 0.27 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.7, 137.44, 137.35, 136.0, 135.4, 134.9, 134.6, 134.1, 131.1, 129.22, 129.19, 128.3, 127.8, 126.7, 123.9, 123.5, 58.9, 58.1, 45.0, 1.9; **HRMS (ESI)** m/z calcd for $C_{24}H_{28}NSi^+$ $(M+H)^+$ 358.1986, found 358.1978.

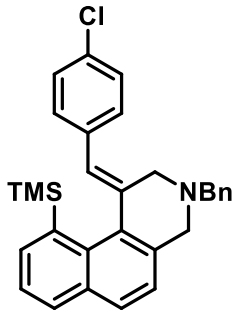


(*Z*)-1-benzylidene-3-cyclohexyl-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoq

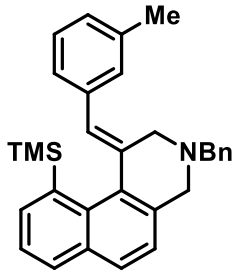
uinoline (3ca): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); light yellow solid, isolated yield 62% (52.7 mg); mp: 99.5-101.2 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.45-7.39 (m, 3H), 7.30-7.27 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.48 (s, 1H), 4.37 (d, *J* = 14.5 Hz, 1H), 4.00 (d, *J* = 14.5 Hz, 1H), 3.92 (d, *J* = 14.5 Hz, 1H), 3.58 (d, *J* = 14.5 Hz, 1H), 2.64-2.57 (m, 1H), 2.12 (d, *J* = 12.0 Hz, 1H), 1.99 (d, *J* = 11.5 Hz, 1H), 1.88 (t, *J* = 11.5 Hz, 2H), 1.70 (d, *J* = 12.5 Hz, 1H), 1.46-1.30 (m, 5H), 0.26 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.7, 138.5, 137.6, 136.5, 135.9, 135.4, 134.7, 134.1, 130.6, 129.22, 129.17, 128.3, 127.7, 126.5, 123.7, 123.6, 62.1, 52.7, 29.9, 29.0, 26.2, 25.7, 25.6, 2.0; **HRMS (ESI)** m/z calcd for $C_{29}H_{36}NSi^+$ $(M+H)^+$ 426.2612, found 426.2597.



(*Z*)-3-benzyl-1-(4-methylbenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo [*f*]isoquinoline (3ea): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown oil, isolated yield 48% (42.9 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.5 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.43-7.38 (m, 3H), 7.36-7.28 (m, 3H), 7.14 (d, *J* = 8.0Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.41 (s, 1H), 4.28 (d, *J* = 15.0 Hz, 1H), 3.87 (d, *J* = 14.5 Hz, 1H), 3.81 (s, 2H), 3.73 (d, *J* = 15.5 Hz, 1H), 3.48 (d, *J* = 15.0 Hz, 1H), 2.36 (s, 3H), 0.22 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.8, 138.4, 136.9, 136.4, 135.8, 135.7, 135.4, 134.7, 134.6, 134.1, 131.2, 129.2, 129.1, 129.0, 128.9, 128.3, 127.5, 127.1, 123.9, 123.5, 61.4, 57.0, 55.9, 21.2, 1.9; **HRMS (ESI)** m/z calcd for $C_{31}H_{34}NSi^+$ $(M+H)^+$ 448.2455, found 448.2442.

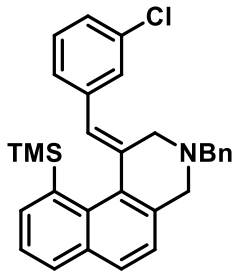


(*Z*)-3-benzyl-1-(4-chlorobenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3fa): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown oil, isolated yield 66% (61.7 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 6.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.36-7.28 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.41 (s, 1H), 4.22 (d, *J* = 15.0 Hz, 1H), 3.91 (d, *J* = 14.5 Hz, 1H), 3.82 (s, 2H), 3.70 (d, *J* = 15.0 Hz, 1H), 3.54 (d, *J* = 14.5 Hz, 1H), 0.22 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.6, 138.3, 138.1, 136.0, 135.9, 135.5, 135.1, 134.5, 134.0, 132.3, 130.3, 129.7, 129.2, 128.8, 128.4, 128.3, 127.9, 127.2, 124.0, 123.6, 61.4, 56.5, 56.0, 1.9; **HRMS (ESI)** m/z calcd for $C_{30}H_{31}ClNSi^+$ $(M+H)^+$ 468.1909, found 468.1893.

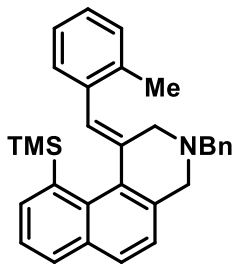


(*Z*)-3-benzyl-1-(3-methylbenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ga): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown oil, isolated yield 61% (54.6 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 6.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.47-7.42 (m, 3H), 7.40-7.33 (m, 3H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.46 (s, 1H), 4.31 (d, *J* = 15.0 Hz, 1H), 3.93 (d, *J* = 15.0 Hz, 1H), 3.90-3.82 (m, 2H), 3.79 (d, *J* = 15.5 Hz, 1H), 3.54 (d, *J* = 15.0 Hz, 1H), 2.37 (s, 3H), 0.27 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.8, 138.3, 137.7, 137.48, 137.46, 135.9, 135.6, 135.4, 134.6, 134.1,

131.3, 130.0, 129.1, 128.9, 128.2, 128.1, 127.6, 127.4, 127.1, 126.2, 123.9, 123.6, 61.4, 56.9, 55.9, 21.5, 1.9; **HRMS (ESI)** m/z calcd for $C_{31}H_{34}NSi^+$ $(M+H)^+$ 448.2455, found 448.2442.

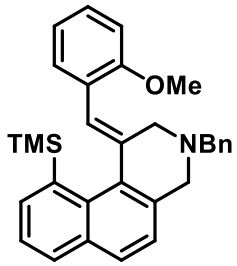


(*Z*)-3-benzyl-1-(3-chlorobenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ha): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown solid, isolated yield 78% (72.9 mg); mp: 63.5-64.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.5 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.45-7.42 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.36-7.32 (m, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.20 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 4.28 (d, *J* = 15.0 Hz, 1H), 3.95 (d, *J* = 15.0 Hz, 1H), 3.86 (s, 2H), 3.76 (d, *J* = 15.0 Hz, 1H), 3.57 (d, *J* = 15.0 Hz, 1H), 0.27 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.2, 139.1, 138.5, 138.0, 136.1, 135.7, 134.9, 134.5, 134.1, 134.0, 129.43, 129.42, 129.2, 128.9, 128.3, 128.1, 127.20, 127.19, 126.5, 124.0, 123.6, 61.4, 56.5, 55.9, 1.9; **HRMS (ESI)** m/z calcd for $C_{30}H_{31}ClNSi^+$ $(M+H)^+$ 468.1909, found 468.1881.

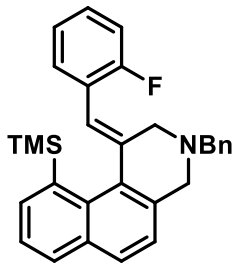


(*Z*)-3-benzyl-1-(2-methylbenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ia): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown oil, isolated yield 68% (60.8 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.5 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.30-7.17 (m, 2H), 7.25-7.21 (m, 3H), 7.20-7.15 (m, 2H),

7.14-7.10 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 4.15 (d, *J* = 14.5 Hz, 1H), 3.89 (d, *J* = 14.5 Hz, 1H), 3.73 (d, *J* = 14.5 Hz, 1H), 3.67 (s, 2H), 3.53 (d, *J* = 15.0 Hz, 1H), 1.98 (s, 3H), 0.23 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.5, 138.3, 136.9, 136.1, 135.9, 135.1, 134.9, 134.6, 134.0, 130.1, 129.4, 129.1, 128.8, 128.7, 128.2, 127.8, 127.0, 126.9, 125.3, 123.85, 123.80, 60.9, 56.0, 55.7, 20.3, 1.9; **HRMS (ESI)** m/z calcd for $C_{31}H_{34}NSi^+$ $(M+H)^+$ 448.2455, found 448.2443.

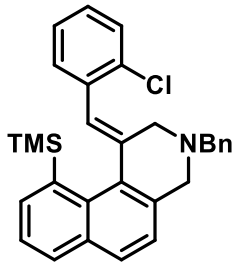


(*Z*)-3-benzyl-1-(2-methoxybenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahydroben zo[*f*]isoquinoline (3ja): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); light yellow oil, isolated yield 52% (48.2 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.41-7.37 (m, 2H), 7.36-7.24 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.68 (s, 1H), 4.28 (d, *J* = 15.0 Hz, 1H), 3.94 (d, *J* = 15.0 Hz, 1H), 3.84-3.74 (m, 2H), 3.70 (d, *J* = 15.0 Hz, 1H), 3.66 (s, 3H), 3.58 (d, *J* = 14.5 Hz, 1H), 0.27 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.9, 138.8, 138.5, 137.0, 135.8, 135.7, 135.1, 134.9, 134.1, 129.7, 129.1, 128.9, 128.2, 128.1, 127.6, 127.0, 126.4, 123.8, 123.7, 119.8, 110.4, 61.1, 56.4, 55.9, 54.9, 1.8; **HRMS (ESI)** m/z calcd for $C_{31}H_{34}NOSi^+$ $(M+H)^+$ 464.2404, found 464.2396.

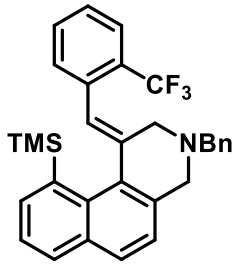


(*Z*)-3-benzyl-1-(2-fluorobenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ka): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown oil, isolated yield 84% (75.8 mg); **^{1}H NMR** (500 MHz,

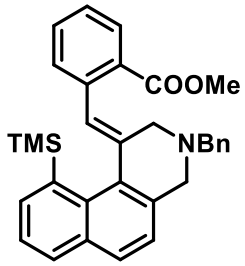
$CDCl_3$) δ 7.85 (d, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.41-7.37 (m, 2H), 7.36-7.26 (m, 5H), 7.17-7.13 (m, 2H), 7.06 (t, *J* = 9.0 Hz, 1H), 6.59 (s, 1H), 4.26 (d, *J* = 15.0 Hz, 1H), 3.96 (d, *J* = 15.0 Hz, 1H), 3.81 (s, 2H), 3.71 (d, *J* = 15.0 Hz, 1H), 3.61 (d, *J* = 14.5 Hz, 1H), 0.28 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.9 (d, *J* = 247.3 Hz), 139.1, 138.5, 138.3, 136.1, 135.3, 135.0, 134.7, 134.0, 130.0 (d, *J* = 2.6 Hz), 129.2, 128.8, 128.4 (d, *J* = 8.3 Hz), 128.2, 128.1, 127.1, 125.3 (d, *J* = 13.1 Hz), 124.0, 123.7, 123.3 (d, *J* = 3.9 Hz), 115.6 (d, *J* = 22.5 Hz), 61.1, 56.2 (d, *J* = 1.9 Hz), 55.8, 1.8; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -113.32; **HRMS (ESI)** m/z calcd for $C_{30}H_{31}FNSi^+$ $(M+H)^+$ 452.2204, found 452.2198.



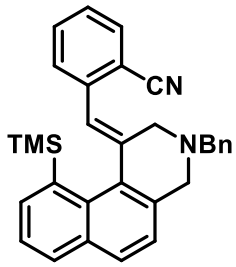
(*Z*)-3-benzyl-1-(2-chlorobenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3la): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown oil, isolated yield 82% (76.6 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38-7.33 (m, 4H), 7.32-7.26 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 4.22 (d, *J* = 15.0 Hz, 1H), 3.99 (d, *J* = 15.0 Hz, 1H), 3.78-3.71 (m, 3H), 3.62 (d, *J* = 15.0 Hz, 1H), 0.26 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.4, 138.3, 138.2, 136.1, 135.3, 134.6, 134.1, 134.0, 130.0, 129.7, 129.2, 128.7, 128.3, 128.2, 127.9, 127.5, 127.0, 126.2, 124.0, 123.7, 60.7, 55.7, 55.6, 1.9; **HRMS (ESI)** m/z calcd for $C_{30}H_{31}ClNSi^+$ $(M+H)^+$ 468.1909, found 468.1900.



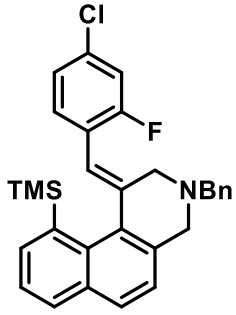
(*Z*)-3-benzyl-1-(2-(trifluoromethyl)benzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrah ydrobenzo[*f*]isoquinoline (3ma): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown solid, isolated yield 91% (91.2 mg); mp: 141.7-143.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.0 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.52-7.46 (m, 2H), 7.39-7.29 (m, 6H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.85 (s, 1H), 4.22 (d, *J* = 15.0 Hz, 1H), 4.04 (d, *J* = 15.0 Hz, 1H), 3.78-3.73 (m, 3H), 3.66 (d, *J* = 15.0 Hz, 1H), 0.34 (s, 9H); **^{13}C NMR** (125 MHz, CDCl3) δ 139.2, 138.4, 137.8, 136.2, 135.9 (d, *J* = 1.4 Hz), 135.2, 134.5, 134.3, 133.9, 131.1, 130.4, 129.3, 128.6, 128.5, 128.3 (d, *J* = 31.4 Hz), 128.2, 127.0, 126.6, 126.5, 126.0 (q, *J* = 5.6 Hz), 124.0, 123.9 (d, *J* = 272.4 Hz), 123.8, 60.6, 55.8, 55.4, 1.9; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -60.41; **HRMS (ESI)** m/z calcd for $C_{31}H_{31}F_3NSi^+$ $(M+H)^+$ 502.2172, found 502.2162.



methyl(*Z*)-2-((3-benzyl-10-(trimethylsilyl)-3,4-dihydrobenzo[*f*]isoquinolin-1(2H)-ylidene)methyl)benzoate (3na): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); reddish-brown oil, isolated yield 87% (85.5 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 6.5 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34-7.28 (m, 6H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 4.18 (d, *J* = 14.5 Hz, 1H), 4.01 (d, *J* = 16.0 Hz, 1H), 3.77-3.69 (m, 3H), 3.65 (d, *J* = 14.5 Hz, 1H), 3.59 (s, 3H), 0.30 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.4, 138.4, 138.2, 138.1, 137.0, 135.9, 135.0, 134.8, 134.6, 133.9, 131.1, 130.6, 130.1, 130.0, 129.8, 129.2, 128.7, 128.14, 128.08, 126.9, 126.5, 123.8, 123.7, 60.7, 55.8, 55.4, 51.7, 1.9; **HRMS (ESI)** m/z calcd for $C_{32}H_{34}NO_2Si^+$ $(M+H)^+$ 492.2353, found 492.2340.

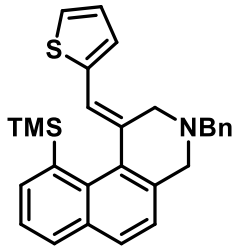


(*Z*)-2-((3-benzyl-10-(trimethylsilyl)-3,4-dihydrobenzo[*f*]isoquinolin-1(2H)-ylidene)methyl)benzonitrile (3oa): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); reddish-brown solid, isolated yield 88% (80.7 mg); mp: 182.7-184.3 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49-7.45 (m, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.33-7.30 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 4.30 (d, *J* = 15.0 Hz, 1H), 4.01 (d, *J* = 15.0 Hz, 1H), 3.89-3.78 (m, 2H), 3.74 (d, *J* = 15.0 Hz, 1H), 3.64 (d, *J* = 15.0 Hz, 1H), 0.26 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.6, 140.5, 138.1, 137.7, 136.5, 135.9, 134.6, 134.1, 133.5, 132.2, 129.4, 129.0, 128.8, 128.7, 128.3, 127.1, 126.7, 126.2, 124.3, 123.5, 117.7, 112.4, 60.9, 56.0, 55.8, 1.9; **HRMS (ESI)** m/z calcd for $C_{31}H_{31}N_2Si^+$ $(M+H)^+$ 459.2251, found 459.2238.

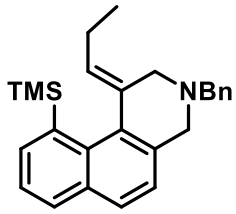


(*Z*)-3-benzyl-1-(4-chloro-2-fluorobenzylidene)-10-(trimethylsilyl)-1,2,3,4-tetrahyd robenzo[*f*]isoquinoline (3pa): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown oil, isolated yield 79% (76.7 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 6.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38-7.35 (m, 2H), 7.34-7.29 (m, 3H), 7.19-7.11 (m, 3H), 7.08 (d, *J* = 10.0 Hz, 1H), 6.49 (s, 1H), 4.15 (d, *J* = 14.5 Hz, 1H), 3.96 (d, *J* = 15.0 Hz, 1H), 3.79 (s, 2H), 3.62 (d, *J* = 14.5 Hz, 2H), 0.24 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.6 (d, *J* = 250.5 Hz), 139.8, 138.3, 138.1, 136.2, 135.4, 134.6 (d, *J*

= 9.1 Hz), 134.0, 133.1 (d, *J* = 10.5 Hz), 130.5, 130.4, 129.2, 128.8, 128.4, 128.3, 127.1, 124.13, 124.10 (d, *J* = 19.4 Hz), 124.07, 124.0, 123.7, 122.1 (d, *J* = 3.4 Hz), 116.4 (d, *J* = 26.0 Hz), 61.2, 56.0, 55.9 (d, *J* = 2.0 Hz), 1.8; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -110.73; **HRMS (ESI)** m/z calcd for $C_{30}H_{30}ClFNSi^+$ $(M+H)^+$ 486.1815, found 486.1777.

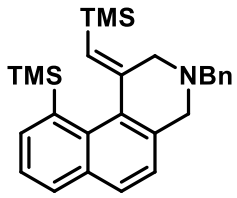


(*Z*)-3-benzyl-1-(thiophen-2-ylmethylene)-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3qa): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); reddish-brown oil, isolated yield 24% (21.1 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.34-7.31 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.08-7.04 (m, 1H), 6.88 (d, *J* = 3.5 Hz, 1H), 6.69 (s, 1H), 4.21 (d, *J* = 15.5 Hz, 1H), 3.98-3.87 (m, 3H), 3.62 (d, *J* = 16.0 Hz, 1H), 3.48 (d, *J* = 14.5 Hz, 1H), 0.20 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.8, 138.9, 138.1, 136.3, 136.0, 135.8, 134.9, 134.3, 134.1, 129.0, 128.9, 128.3, 127.8, 127.5, 127.3, 127.2, 126.1, 124.0, 123.4, 122.6, 61.7, 58.0, 56.3, 1.8; **HRMS (ESI)** m/z calcd for $C_{28}H_{30}NSSi^+$ $(M+H)^+$ 440.1863, found 440.1846.

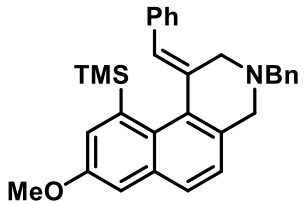


(*Z*)-3-benzyl-1-propylidene-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ra): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 50:1); light yellow oil, isolated yield 63% (48.5 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.45-7.40 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.56 (m,

1H), 3.96-3.84 (m, 3H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.64 (d, *J* = 14.5 Hz, 1H), 3.46 (d, *J* = 14.0 Hz, 1H), 2.28-2.18 (m, 1H), 2.14-2.05 (m, 1H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.33 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.7, 138.5, 135.4, 135.2, 134.8, 134.2, 133.8, 133.7, 132.4, 128.83, 128.80, 128.3, 127.1, 126.8, 123.7, 123.5, 61.9, 57.0, 55.2, 21.4, 13.3, 2.0; **HRMS (ESI)** m/z calcd for $C_{26}H_{32}NSi^+$ $(M+H)^+$ 386.2299, found 386.2283.

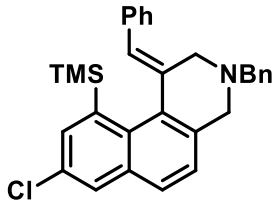


(*Z*)-3-benzyl-10-(trimethylsilyl)-1-((trimethylsilyl)methylene)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3sa): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 50:1); light yellow solid, isolated yield 72% (61.8 mg); mp: 103.1-104.8 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 6.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.47-7.42 (m, 3H), 7.39-7.36 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 5.85 (s, 1H), 3.94-3.85 (m, 3H), 3.81 (d, *J* = 12.5 Hz, 1H), 3.76 (d, *J* = 14.5 Hz, 1H), 3.65 (d, *J* = 13.5 Hz, 1H), 0.38 (s, 9H), 0.20 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.8, 138.6, 137.9, 135.9, 135.7, 133.9, 133.61, 133.55, 130.2, 129.3, 128.9, 128.3, 128.0, 127.3, 123.9, 123.7, 62.4, 58.8, 56.8, 2.3, -0.1; **HRMS (ESI)** m/z calcd for $C_{27}H_{36}NSi_2^+$ $(M+H)^+$ 430.2381, found 430.2382.

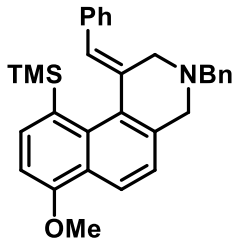


(*Z*)-3-benzyl-1-benzylidene-8-methoxy-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ta): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); reddish-brown solid, isolated yield 59% (54.7 mg); mp: 139.3-142.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.40-7.32 (m, 4H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14-7.11 (m, 2H), 6.48 (s, 1H), 4.33 (d, *J* = 15.0 Hz, 1H), 4.00 (s, 3H), 3.91 (d,

J = 14.5 Hz, 1H), 3.86 (s, 2H), 3.80 (d, *J* = 15.5 Hz, 1H), 3.53 (d, *J* = 14.5 Hz, 1H), 0.28 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.5, 141.2, 138.3, 137.8, 137.5, 135.7, 135.5, 133.4, 131.2, 130.0, 129.2, 128.8, 128.4, 128.24, 128.22, 127.1, 126.6, 126.5, 124.0, 106.8, 61.4, 56.8, 55.7, 55.1, 1.9; **HRMS (ESI)** m/z calcd for $C_{31}H_{34}NOSi^+$ $(M+H)^+$ 464.2404, found 464.2413.

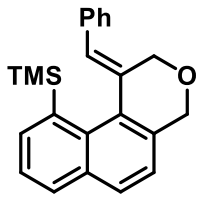


(*Z*)-3-benzyl-1-benzylidene-8-chloro-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ua): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); reddish-brown solid, isolated yield 52% (48.6 mg); mp: 157.5-158.9 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.70 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.44-7.40 (m, 2H), 7.38-7.32 (m, 5H), 7.29-7.24 (m, 1H), 7.20 (d, *J* = 7.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.41 (s, 1H), 4.31 (d, *J* = 15.0 Hz, 1H), 3.90 (d, *J* = 15.0 Hz, 1H), 3.84 (s, 2H), 3.76 (d, *J* = 15.0 Hz, 1H), 3.51 (d, *J* = 15.0 Hz, 1H), 0.26 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.2, 138.2, 137.5, 137.23, 137.18, 136.0, 135.9, 135.8, 135.0, 133.0, 131.7, 130.0, 129.2, 128.8, 128.3, 127.4, 127.2, 126.8, 126.7, 124.6, 61.4, 56.8, 55.8, 1.8; **HRMS (ESI)** m/z calcd for $C_{30}H_{31}ClNSi^+$ $(M+H)^+$ 468.1909, found 468.1915.

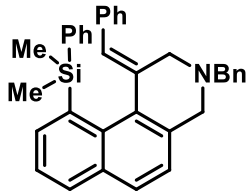


(*Z*)-3-benzyl-1-benzylidene-7-methoxy-10-(trimethylsilyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3va): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark brown oil, isolated yield 49% (45.4 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.39-7.32 (m, 5H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.47 (s, 1H), 4.32 (d, *J* = 15.0 Hz, 1H), 4.07 (s, 3H),

3.92 (d, J = 14.5 Hz, 1H), 3.85 (s, 2H), 3.78 (d, J = 15.0 Hz, 1H), 3.53 (d, J = 14.5 Hz, 1H), 0.24 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.9, 138.4, 137.62, 137.59, 136.4, 136.0, 135.8, 135.3, 131.7, 129.24, 129.19, 128.8, 128.3, 128.2, 127.1, 126.53, 126.51, 122.9, 120.9, 102.4, 61.4, 56.9, 55.9, 55.5, 2.1; **HRMS (ESI)** m/z calcd for $C_{31}H_{34}NOSi^+$ $(M+H)^+$ 464.2404, found 464.2414.

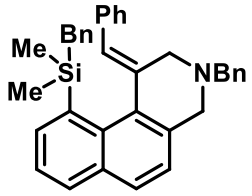


(*Z*)-(1-benzylidene-1,4-dihydro-2H-benzo[*f*]isochromen-10-yl)trimethylsilane (3wa): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 100:1); light yellow solid, isolated yield 38% (26.2 mg); mp: 173.7-174.8 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 7.17-7.13 (m, 3H), 6.45 (s, 1H), 5.27 (d, J = 13.5 Hz, 1H), 4.85 (d, J = 14.5 Hz, 1H), 4.80 (d, J = 14.5 Hz, 1H), 4.38 (d, J = 14.0 Hz, 1H), 0.21 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.6, 137.1, 136.8, 136.6, 136.5, 134.54, 134.49, 133.7, 130.7, 129.5, 129.2, 128.4, 128.0, 127.0, 124.2, 121.5, 69.3, 68.6, 1.9; **HRMS (ESI)** m/z calcd for $C_{23}H_{25}NSi^+$ $(M+H)^+$ 345.1669, found 345.1663.

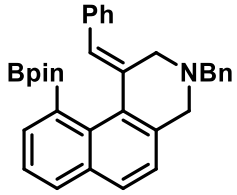


(*Z*)-3-benzyl-1-benzylidene-10-(dimethyl(phenyl)silyl)-1,2,3,4-tetrahydrobenzo[*f*] isoquinoline (3ab): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 20:1); dark green oil, isolated yield 47% (46.6 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, J = 6.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.46-7.39 (m, 2H), 7.30-7.27 (m, 4H), 7.25-7.11 (m, 8H), 7.05 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 7.0 Hz, 2H), 6.25 (s, 1H), 3.69 (d, J = 14.5 Hz, 1H), 3.57 (d, J = 13.0 Hz, 1H), 3.46 (d, J = 13.0 Hz, 1H), 3.38 (d, J = 15.0 Hz, 1H), 3.25 (d, J = 14.5 Hz, 1H), 2.95 (d, J = 14.5 Hz, 1H), 0.42 (s, 3H), 0.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ

140.2, 138.5, 137.9, 137.5, 137.2, 135.9, 135.7, 134.7, 134.2, 133.8, 133.1, 131.1, 129.8, 129.3, 128.9, 128.3, 128.2, 127.9, 127.60, 127.57, 127.0, 126.3, 123.9, 123.8, 61.0, 55.7, 55.1, 2.3, 0.1; **HRMS (ESI)** m/z calcd for $C_{35}H_{34}NSi^+$ $(M+H)^+$ 496.2455, found 496.2452.

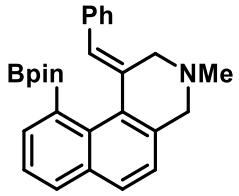


(*Z*)-3-benzyl-10-(benzyldimethylsilyl)-1-benzylidene-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (3ac): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 50:1); yellow oil, isolated yield 71% (72.3 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.49-7.45 (m, 3H), 7.44-7.36 (m, 5H), 7.33-7.29 (m, 3H), 7.23-7.17 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 2H), 6.65 (s, 1H), 4.43 (d, *J* = 15.5 Hz, 1H), 3.97 (d, *J* = 14.5 Hz, 1H), 3.90 (s, 2H), 3.86 (d, *J* = 15.0 Hz, 1H), 3.58 (d, *J* = 14.5 Hz, 1H), 2.43-2.32 (m, 2H), 0.32 (s, 3H), 0.21 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.3, 138.2, 138.0, 137.3, 137.0, 136.5, 135.7, 135.4, 134.8, 134.2, 130.9, 129.3, 129.2, 128.8, 128.5, 128.4, 128.3, 127.9, 127.8, 127.1, 126.8, 123.83, 123.80, 123.6, 61.4, 57.0, 55.9, 27.1, 0.3, -1.0; **HRMS (ESI)** m/z calcd for $C_{36}H_{36}NSi^+$ $(M+H)^+$ 510.2612, found 510.2615.

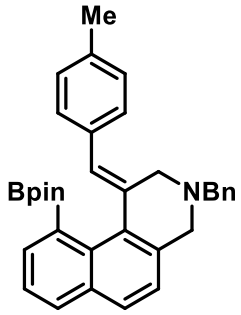


(*Z*)-3-benzyl-1-benzylidene-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5a): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark red solid, isolated yield 73% (71.1 mg, Method A), and 72% (70.2 mg, Method B); mp: 176.2-177.6 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 6.5 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.41-7.35 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.27-7.22 (m, 4H), 7.19-7.14 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.72 (s, 1H), 3.98 (s, 2H), 3.81 (s, 4H), 1.10 (s, 6H), 1.03 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.3, 137.8, 137.1,

135.3, 134.2, 134.0, 133.0, 132.8, 130.2, 129.7, 129.4, 128.7, 128.3, 128.1, 127.2, 127.0, 126.6, 124.5, 124.2, 83.5, 61.3, 56.2, 55.1, 25.6, 24.5; **HRMS (ESI)** m/z calcd for $C_{33}H_{35}BNO_2^+$ $(M+H)^+$ 488.2755, found 488.2762.

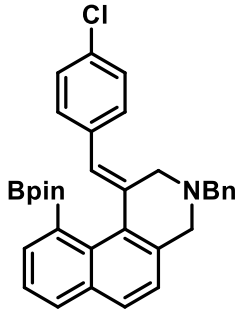


(*Z*)-1-benzylidene-3-methyl-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5b): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 5:1); dark red solid, isolated yield 75% (61.7 mg, Method A) and 79% (65.0 mg, Method B); mp: 75.6-78.2 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 6.5 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.34-7.30 (m, 3H), 7.27 (t, *J* = 7.0 Hz, 2H), 7.17-7.12 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 4.05-3.72 (m, 2H), 3.69-3.49 (m, 2H), 2.53 (s, 3H), 1.12 (s, 6H), 0.95 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.8, 137.1, 134.8, 134.7, 134.0, 133.1, 133.0, 130.2, 129.8, 128.6, 128.2, 127.0, 126.7, 124.5, 124.0, 83.5, 58.0, 57.9, 44.9, 25.5, 24.6; **HRMS (ESI)** m/z calcd for $C_{27}H_{31}BNO_2^+$ $(M+H)^+$ 412.2442, found 412.2451.

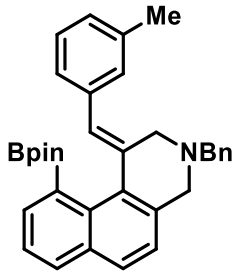


(*Z*)-3-benzyl-1-(4-methylbenzylidene)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5e): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark red solid, isolated yield 86% (86.2 mg, Method A); mp: 201.4-202.7 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 6.5 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.40-7.34 (m, 3H), 7.33-7.28 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.69 (s, 1H), 3.96 (s, 2H), 3.80 (s, 4H), 2.31 (s, 3H),

1.11 (s, 6H), 1.03 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.4, 136.9, 136.4, 135.4, 134.3, 134.1, 134.0, 133.0, 132.7, 130.1, 129.7, 129.4, 128.8, 128.7, 128.3, 127.2, 126.8, 124.5, 124.2, 83.5, 61.3, 56.2, 55.3, 25.6, 24.5, 21.2; **HRMS (ESI)** m/z calcd for $C_{34}H_{37}BNO_2^+$ $(M+H)^+$ 502.2912, found 502.2919.

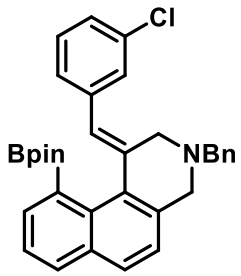


(*Z*)-3-benzyl-1-(4-chlorobenzylidene)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5f): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark red solid, isolated yield 83% (86.5 mg, Method A); mp: 208.7-210.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.41-7.35 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.20-7.11 (m, 5H), 6.68 (s, 1H), 3.97-3.76 (m, 6H), 1.07 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.5, 138.1, 135.5, 135.0, 134.1, 133.9, 132.8, 132.3, 130.8, 130.2, 129.4, 128.4, 128.2, 127.33, 127.29, 127.25, 124.6, 124.2, 83.6, 61.5, 56.5, 54.5, 25.6, 24.4; **HRMS (ESI)** m/z calcd for $C_{33}H_{34}BClNO_2^+$ $(M+H)^+$ 522.2366, found 522.2376.

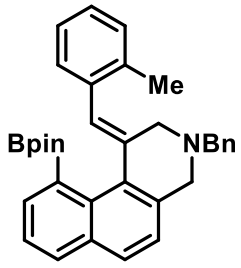


(*Z*)-3-benzyl-1-(3-methylbenzylidene)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5g): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark red solid, isolated yield 83% (83.2 mg, Method A); mp: 174.4-177.2 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 6.5 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.41-7.34 (m, 3H), 7.32-7.28 (m, 1H), 7.15-7.10 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 1H),

6.99 (d, J = 7.5 Hz, 1H), 6.69 (s, 1H), 3.97 (d, J = 12.5 Hz, 2H), 3.81 (s, 4H), 2.29 (s, 3H), 1.11 (s, 6H), 1.04 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.3, 137.7, 137.5, 137.0, 135.4, 134.1, 134.0, 133.0, 132.8, 130.9, 130.1, 129.4, 128.8, 128.3, 127.9, 127.4, 127.2, 127.0, 126.4, 124.5, 124.2, 83.5, 61.4, 56.1, 55.3, 25.6, 24.5, 21.4; **HRMS (ESI)** m/z calcd for $C_{34}H_{37}BNO_2^+$ $(M+H)^+$ 502.2912, found 502.2916.

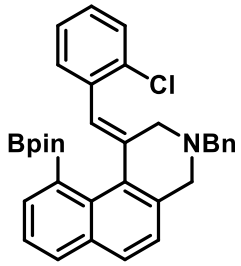


(*Z*)-3-benzyl-1-(3-chlorobenzylidene)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5h): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark red solid, isolated yield 90% (93.8 mg, Method A); mp: 171.4-173.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 6.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 2H), 7.42-7.35 (m, 4H), 7.33-7.29 (m, 1H), 7.15-7.10 (m, 3H), 7.07 (d, J = 6.0 Hz, 1H), 6.67 (s, 1H), 3.96-3.77 (m, 6H), 1.09 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.4, 138.8, 138.0, 134.8, 134.3, 134.0, 133.9, 133.0, 132.9, 130.2, 129.6, 129.4, 129.3, 128.4, 127.42, 127.39, 127.3, 127.0, 126.6, 124.6, 124.2, 83.6, 61.5, 56.2, 54.8, 25.6, 24.4; **HRMS (ESI)** m/z calcd for $C_{33}H_{34}BClNO_2^+$ $(M+H)^+$ 522.2366, found 522.2375.

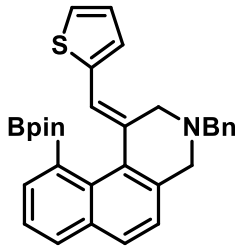


(*Z*)-3-benzyl-1-(2-methylbenzylidene)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5i): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark red solid, isolated yield 78% (78.2 mg, Method A), and 75% (75.2 mg, Method B); mp: 173.4-174.8 °C; **^{1}H NMR** (500 MHz,

$CDCl_3$) δ 7.80 (t, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.39-7.36 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30-7.26 (m, 1H), 7.13-7.08 (m, 4H), 6.83 (s, 1H), 4.02 (s, 2H), 3.80-3.73 (m, 4H), 2.20 (s, 3H), 1.09 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.3, 137.8, 137.7, 136.0, 135.4, 134.3, 134.0, 133.6, 133.3, 130.4, 130.3, 129.3, 128.5, 128.2, 127.1, 126.9, 126.8, 126.0, 125.1, 124.5, 124.2, 83.4, 61.2, 55.6, 55.4, 25.1, 20.5; **HRMS (ESI)** m/z calcd for $C_{34}H_{37}BNO_2^+$ $(M+H)^+$ 502.2912, found 502.2916.

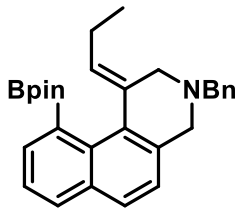


(*Z*)-3-benzyl-1-(2-chlorobenzylidene)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5l): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark red solid, isolated yield 67% (69.8 mg, Method A), and 77% (80.3 mg, Method B); mp: 192.9-194.4 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.43-7.38 (m, 4H), 7.35-7.31 (m, 3H), 7.30-7.27 (m, 1H), 7.16-7.09 (m, 3H), 6.95 (s, 1H), 4.00 (s, 2H), 3.83-3.75 (m, 4H), 1.11 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.9, 138.3, 135.5, 134.6, 134.2, 134.0, 133.3, 130.5, 129.8, 129.7, 129.3, 128.2, 127.7, 127.4, 127.1, 125.8, 124.6, 124.3, 124.1, 83.3, 61.0, 55.6, 54.9, 25.1; **HRMS (ESI)** m/z calcd for $C_{33}H_{34}BClNO_2^+$ $(M+H)^+$ 522.2366, found 522.2374.

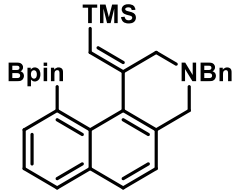


(*Z*)-3-benzyl-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-2-ylmethylene)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5q): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 5:1); yellow solid, isolated yield 30% (29.6

mg, Method A), and 41% (40.4 mg, Method B); mp: 109.6-112.6 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 6.5 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31-7.27 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.02-6.97 (m, 3H), 4.03 (d, *J* = 16.0 Hz, 1H), 3.93-3.85 (m, 2H), 3.83-3.77 (m, 2H), 3.63 (d, *J* = 15.0 Hz, 1H), 1.07 (s, 6H), 0.97 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.6, 138.2, 135.2, 134.9, 134.4, 134.1, 133.0, 132.8, 130.2, 129.3, 128.5, 128.3, 127.2, 127.1, 127.0, 126.3, 124.6, 124.2, 121.5, 83.5, 60.9, 56.3, 56.0, 25.6, 24.5; **HRMS (ESI)** m/z calcd for $C_{31}H_{33}BNO_2S^+$ $(M+H)^+$ 494.2320, found 494.2325.

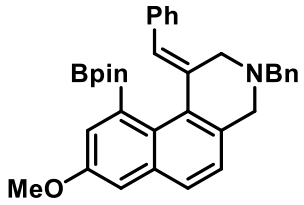


(*Z*)-3-benzyl-1-propylidene-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5r): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); red solid, isolated yield 70% (61.5 mg, Method A), and 87% (76.4 mg, Method B); mp: 73.5-75.4 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 6.5 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.36-7.31 (m, 3H), 7.29-7.25 (m, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 5.77 (t, *J* = 7.5 Hz, 1H), 3.89-3.71 (m, 4H), 3.60 (s, 2H), 2.24-2.04 (m, 2H), 1.27 (s, 12H), 0.96 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.6, 134.6, 134.2, 133.7, 133.0, 132.4, 132.2, 131.7, 129.7, 129.0, 128.2, 127.0, 126.2, 124.4, 124.3, 83.5, 61.2, 56.0, 52.9, 25.8, 24.2, 21.8, 13.6; **HRMS (ESI)** m/z calcd for $C_{29}H_{35}BNO_2^+$ $(M+H)^+$ 440.2755, found 440.2763.

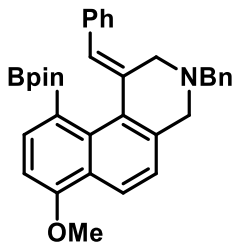


(*Z*)-3-benzyl-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-((trimethylsilyl) methylene)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5s): column chromatoghraphy

(silica gel; petroleum ether/ethyl acetate, 10:1); yellow solid, isolated yield 39% (37.7 mg, Method A); mp: 179.7-181.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 6.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.41-7.36 (m, 3H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 5.90 (s, 1H), 3.88-3.84 (m, 1H), 3.82-3.78 (m, 4H), 3.65 (d, *J* = 13.5 Hz, 1H), 1.33 (s, 6H), 1.32 (s, 6H), 0.11 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.2, 138.2, 136.1, 133.7, 132.9, 132.8, 132.7, 130.1, 129.4, 129.1, 128.3, 127.2, 127.0, 124.5, 124.4, 83.6, 61.7, 57.5, 56.1, 25.6, 24.5, 0.4; **HRMS (ESI)** m/z calcd for $C_{30}H_{39}BNO_2Si^+$ $(M+H)^+$ 484.2838, found 484.2847.

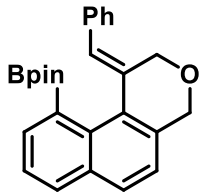


(*Z*)-3-benzyl-1-benzylidene-8-methoxy-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5t): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); red solid, isolated yield 81% (83.8 mg, Method A), and 90% (93.1 mg, Method B); mp: 156.1-157.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.27-7.22 (m, 4H), 7.16 (t, *J* = 6.5 Hz, 1H), 7.11-7.07 (m, 2H), 6.69 (s, 1H), 3.98-3.90 (m, 5H), 3.79 (s, 4H), 1.09 (s, 6H), 1.01 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.2, 138.3, 138.0, 137.0, 135.5, 135.4, 132.1, 129.7, 129.4, 128.7, 128.4, 128.3, 128.1, 127.2, 126.6, 125.9, 125.2, 124.7, 107.8, 83.6, 61.4, 56.1, 55.3, 55.1, 25.6, 24.4; **HRMS (ESI)** m/z calcd for $C_{34}H_{37}BNO_3^+$ $(M+H)^+$ 518.2861, found 518.2873.

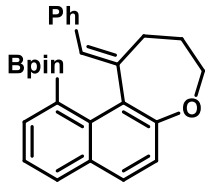


(*Z*)-3-benzyl-1-benzylidene-7-methoxy-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborola

n-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (5v): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); red solid, isolated yield 64% (66.2 mg, Method A), and 77% (79.6 mg, Method B); mp: 81.6-82.7 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.26-7.22 (m, 4H), 7.17-7.11 (m, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 4.01-3.95 (m, 5H), 3.85-3.77 (m, 4H), 1.09 (s, 6H), 1.02 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.1, 138.4, 138.1, 137.2, 135.2, 134.8, 134.3, 133.7, 129.6, 129.4, 128.9, 128.3, 128.0, 127.2, 126.5, 126.4, 123.6, 120.6, 102.5, 83.2, 61.3, 56.2, 55.5, 55.1, 25.5, 24.6; **HRMS (ESI)** m/z calcd for $C_{34}H_{37}BNO_3^+$ $(M+H)^+$ 518.2861, found 518.2869.

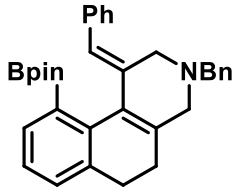


(*Z*)-2-(1-benzylidene-1,4-dihydro-2*H*-benzo[*f*]isochromen-10-yl)-4,4,5,5-tetramet hyl-1,3,2-dioxaborolane (5w): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 50:1); red oil, isolated yield 26% (20.7 mg, Method A), and 68% (54.2 mg, Method B); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 6.5 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.35-7.29 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 6.82 (s, 1H), 4.42 (s, 2H), 3.33 (s, 2H), 1.11 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.8, 137.4, 134.0, 133.8, 133.0, 130.4, 130.2, 129.4, 128.8, 128.2, 126.9, 126.6, 123.1, 122.8, 117.7, 83.5, 67.3, 31.4, 25.1; **HRMS (ESI)** m/z calcd for $C_{26}H_{28}BNO_3^+$ $(M+H)^+$ 399.2126, found 399.2125.

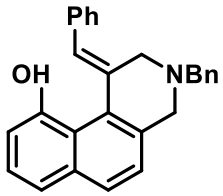


(*E*)-2-(1-benzylidene-1,2,3,4-tetrahydronaphtho[2,1-*b*]oxepin-11-yl)-4,4,5,5-tetra methyl-1,3,2-dioxaborolane (5x): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 30:1); light yellow oil, isolated yield 13% (10.7 mg, Method A), and 44% (36.3 mg, Method B); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz,

1H), 7.80 (d, *J* = 6.5 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.45-7.39 (m, 3H), 7.32-7.26 (m, 2H), 6.39 (s, 1H), 4.69 (d, *J* = 11.0 Hz, 1H), 4.01 (t, *J* = 11.0 Hz, 1H), 3.39 (d, *J* = 13.5 Hz, 1H), 2.62 (t, *J* = 11.5 Hz, 1H), 2.46-2.35 (m, 1H), 2.31-2.22 (m, 1H), 1.15 (s, 6H), 1.11 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.1, 141.4, 137.0, 135.7, 133.7, 133.4, 133.3, 131.6, 130.1, 129.3, 129.0, 128.1, 127.0, 123.4, 121.5, 83.7, 73.0, 30.8, 30.4, 25.6, 24.6; **HRMS (ESI)** m/z calcd for $C_{27}H_{30}BNO_3^+$ $(M+H)^+$ 413.2283 , found 413.2286.

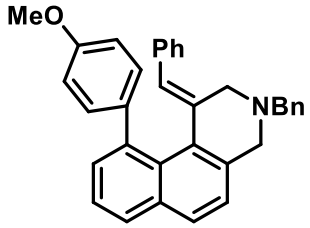


(*Z*)-3-benzyl-1-benzylidene-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4,5,6-hexahydrobenzo[*f*]isoquinoline (5y): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 10:1); dark red solid, isolated yield 43% (42.1 mg, Method A), and 61% (59.7 mg, Method B); mp: 176.7-177.5 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54-7.49 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.39-7.36 (m, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.22-7.18 (m, 5H), 7.16-7.12 (m, 1H), 6.66 (s, 1H), 3.98 (d, *J* = 13.0 Hz, 1H), 3.86 (d, *J* = 12.5 Hz, 1H), 3.73 (d, *J* = 12.0 Hz, 1H), 3.58 (d, *J* = 17.0 Hz, 1H), 3.49-3.38 (m, 2H), 2.90-2.75 (m, 1H), 2.65 (d, *J* = 14.5 Hz, 1H), 2.40 (t, *J* = 16.0 Hz, 1H), 2.06 (d, *J* = 14.0 Hz, 1H), 1.20 (s, 6H), 1.12 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.1, 137.9, 137.7, 137.1, 136.7, 135.6, 132.8, 131.7, 129.6, 129.4, 129.1, 128.3, 127.8, 127.2, 126.1, 125.5, 121.9, 83.6, 62.1, 57.4, 53.1, 29.0, 27.4, 25.6, 24.0; **HRMS (ESI)** m/z calcd for $C_{33}H_{36}BNO_2$ (M) 489.2839, found 489.2852.



(*Z*)-3-benzyl-1-benzylidene-1,2,3,4-tetrahydrobenzo[*f*]isoquinolin-10-ol (6): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 5:1); light yellow solid, isolated yield 85% (64.1 mg); mp: 193.5-195.3 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.36-7.30

(m, 7H), 7.26-7.22 (m, 3H), 7.13 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.88 (s, 1H), 6.52 (s, 1H), 4.03 (s, 2H), 3.72 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.1, 137.9, 137.3, 135.8, 135.6, 135.2, 131.7, 130.0, 129.2, 129.1, 128.5, 128.41, 128.38, 127.6, 127.3, 126.3, 124.1, 121.1, 119.4, 112.9, 61.4, 55.5, 54.8; **HRMS (ESI)** m/z calcd for $C_{27}H_{24}NO^+$ $(M+H)^+$ 378.1852, found 378.1850.



(*Z*)-3-benzyl-1-benzylidene-10-(4-methoxyphenyl)-1,2,3,4-tetrahydrobenzo[*f*]isoquinoline (7): column chromatoghraphy (silica gel; petroleum ether/ethyl acetate, 5:1); red oil, isolated yield 73% (68.2 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H), 7.34-7.25 (m, 6H), 7.19 (d, J = 8.0 Hz, 1H), 7.15-6.93 (m, 4H), 6.84-6.55 (m, 4H), 5.82 (s, 1H), 3.79-3.66 (m, 7H), 3.60-3.51 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.0, 139.5, 138.5, 138.1, 137.8, 137.0, 135.2, 134.4, 133.7, 132.1, 129.9, 129.2, 128.9, 128.6, 128.3, 127.6, 127.4, 127.1, 126.9, 126.3, 124.8, 124.1, 61.1, 55.2, 55.1, 54.2; **HRMS (ESI)** m/z calcd for $C_{34}H_{30}NO^+$ $(M+H)^+$ 468.2322, found 468.2322.

8.The X-ray single-crystal diffraction analysis of 3oa

Single crystal of **3oa** was obtained by diffusion of petroleum ether into CH_2Cl_2 solution. A suitable crystal of **3oa** was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex[2], the structure was solved with the olex[2].solve[3] structure solution program using Charge Flipping and refined with the ShelXL[4] refinement package using Least Squares minimisation.

Crystallographic data for **3oa** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-2190128.

Table S3. Crystallographic data details of **3oa**

CCDC deposition No.	2190128
Empirical formula	$C_{31}H_{30}N_2Si$
Formula weight	458.66
Temperature	293 K
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a=13.9229(6) Å alpha=90 °
	b=13.3923(5) Å beta=102.886(5) °
	c=28.3795(14) Å gamma=90 °
Volume	5158.4(4) $Å^3$
Z; Calculated density	8; 1.181 g/cm^3
Absorption coefficient	0.950 mm^{-1}
F(000)	1952.0
Crystal size	0.5 x 0.5 x 0.05 mm^3
Theta range for data collection	6.39 to 133.2°
Index ranges	$-16 \leq h \leq 16$ $-15 \leq k \leq 15$, $-33 \leq l \leq 33$
Reflections collected / unique	17398 / 9064 [Rint= 0.0799, Rsigma= 0.0908]
Data / restraints / parameters	9064 / 0 / 619
Goodness-of-fit on F2	1.014
Final R indices [I>=2sigma(I)]	R1 = 0.1016, wR2 = 0.2706
R indices (all data)	R1 = 0.1259, wR2 = 0.3072
Largest diff. peak/hole	0.69/-0.72 $e.Å^{-3}$

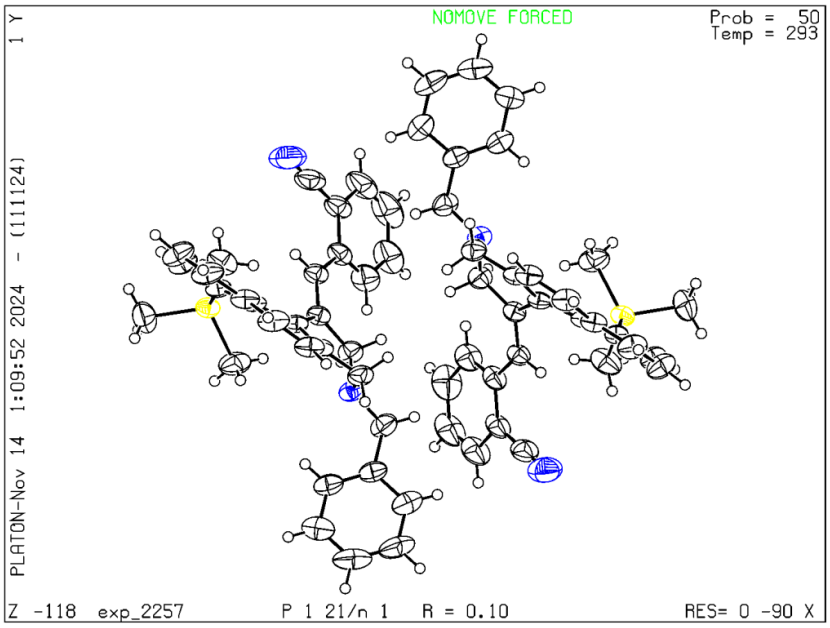


Fig. S1 X-ray structure of **3oa**

9.References

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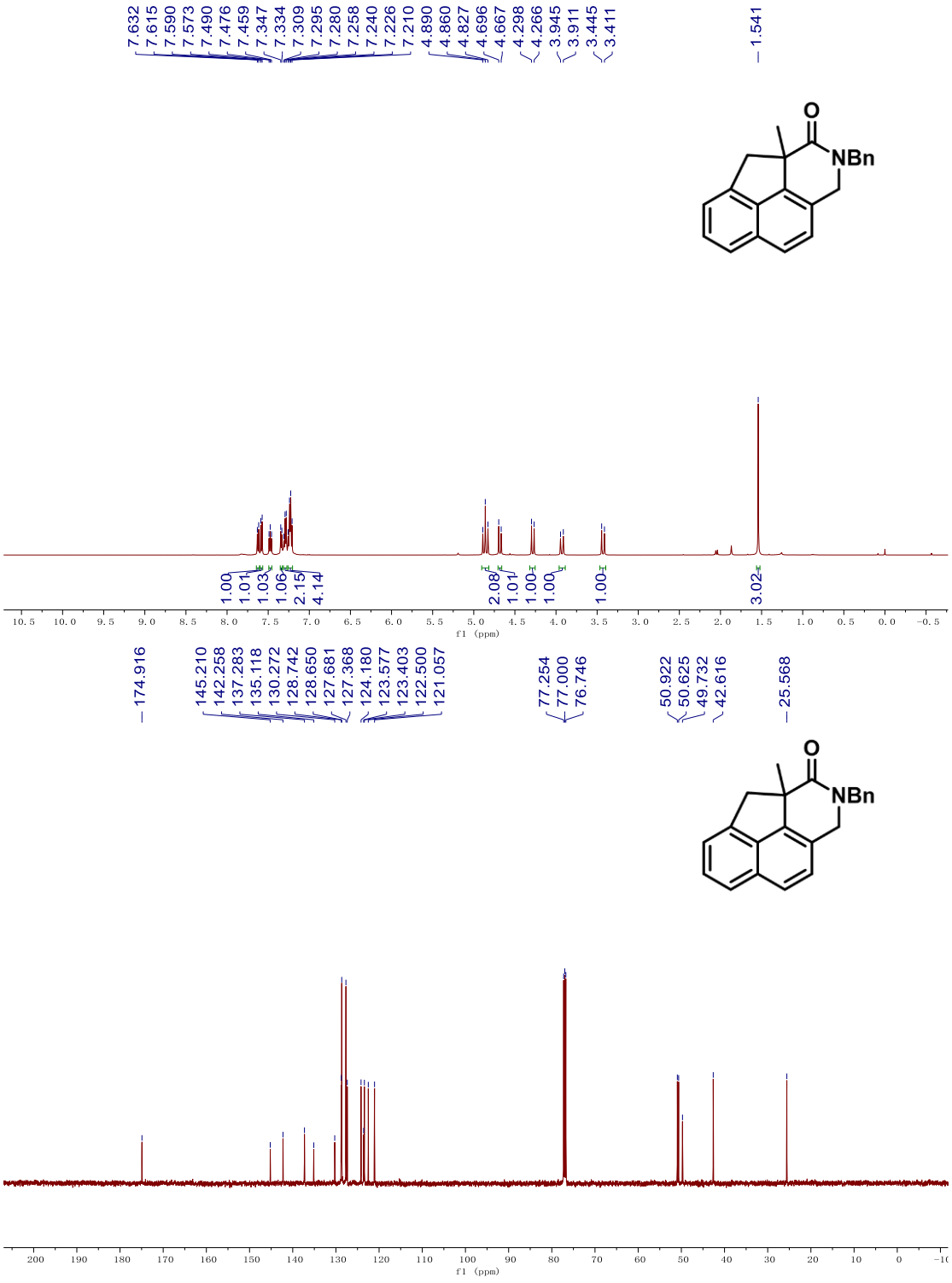
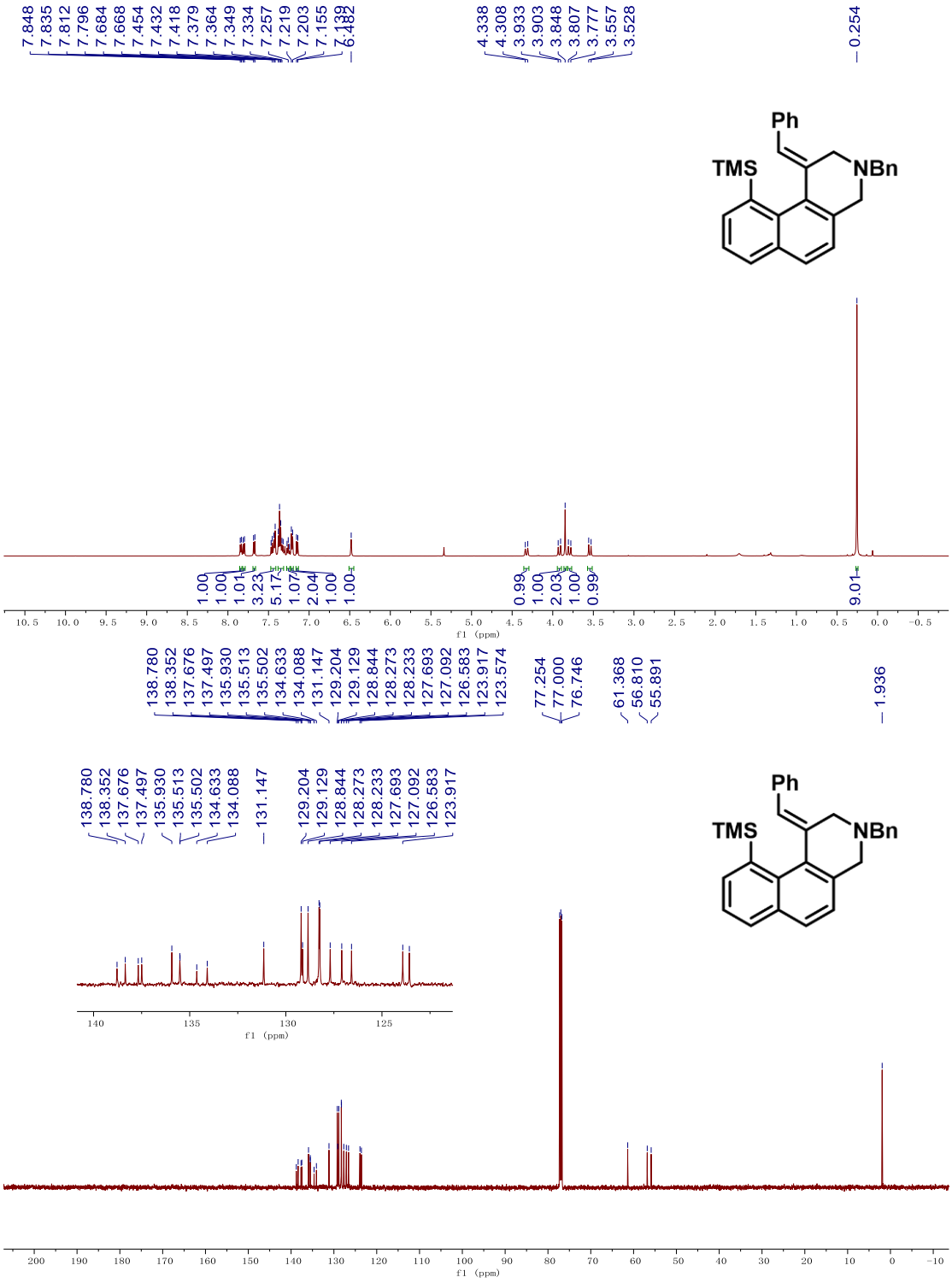
10 NMR Spectra of Substrates and Products

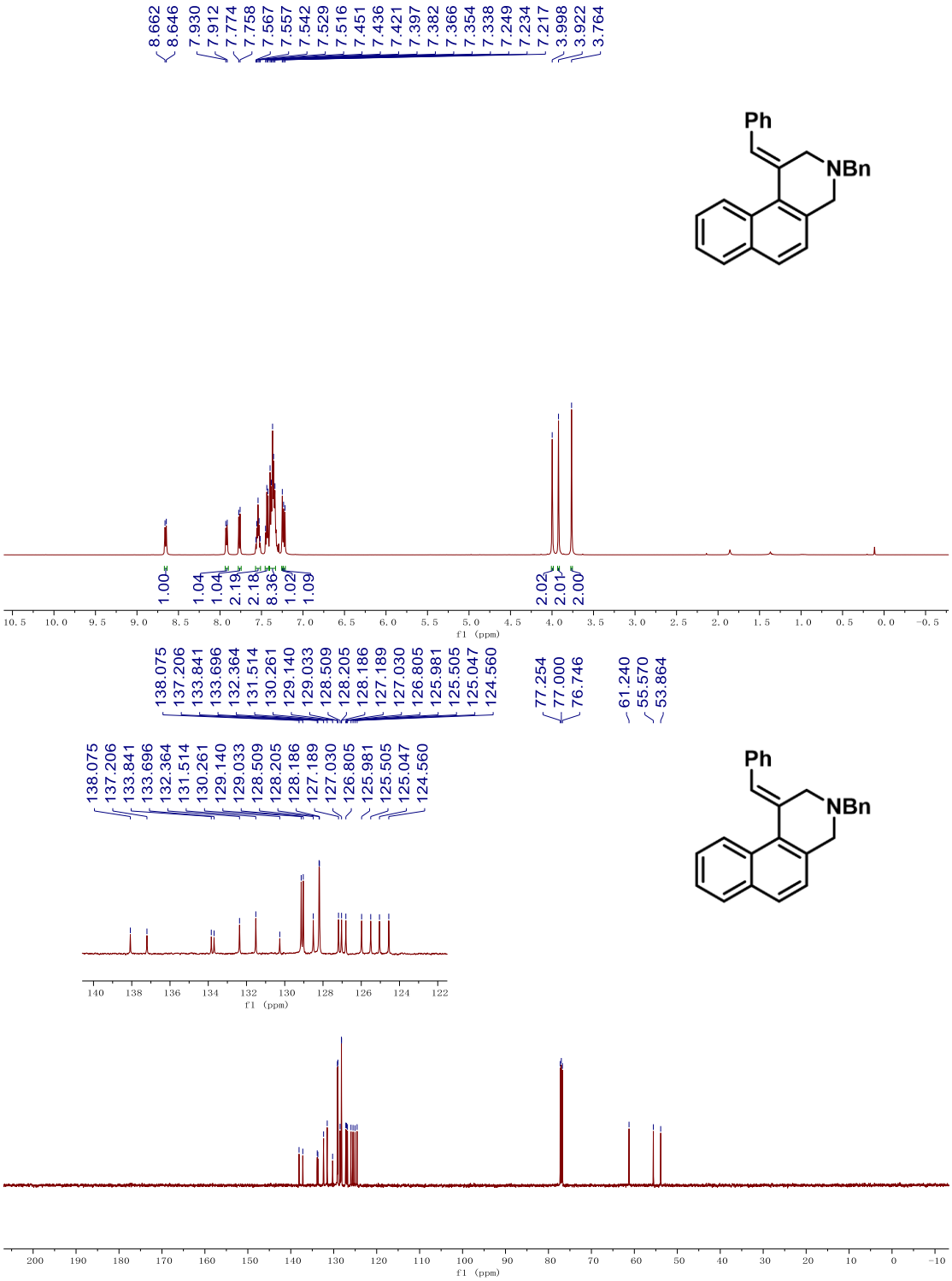
^{1}H NMR of **3A** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3A** (125 MHz, $CDCl_3$)



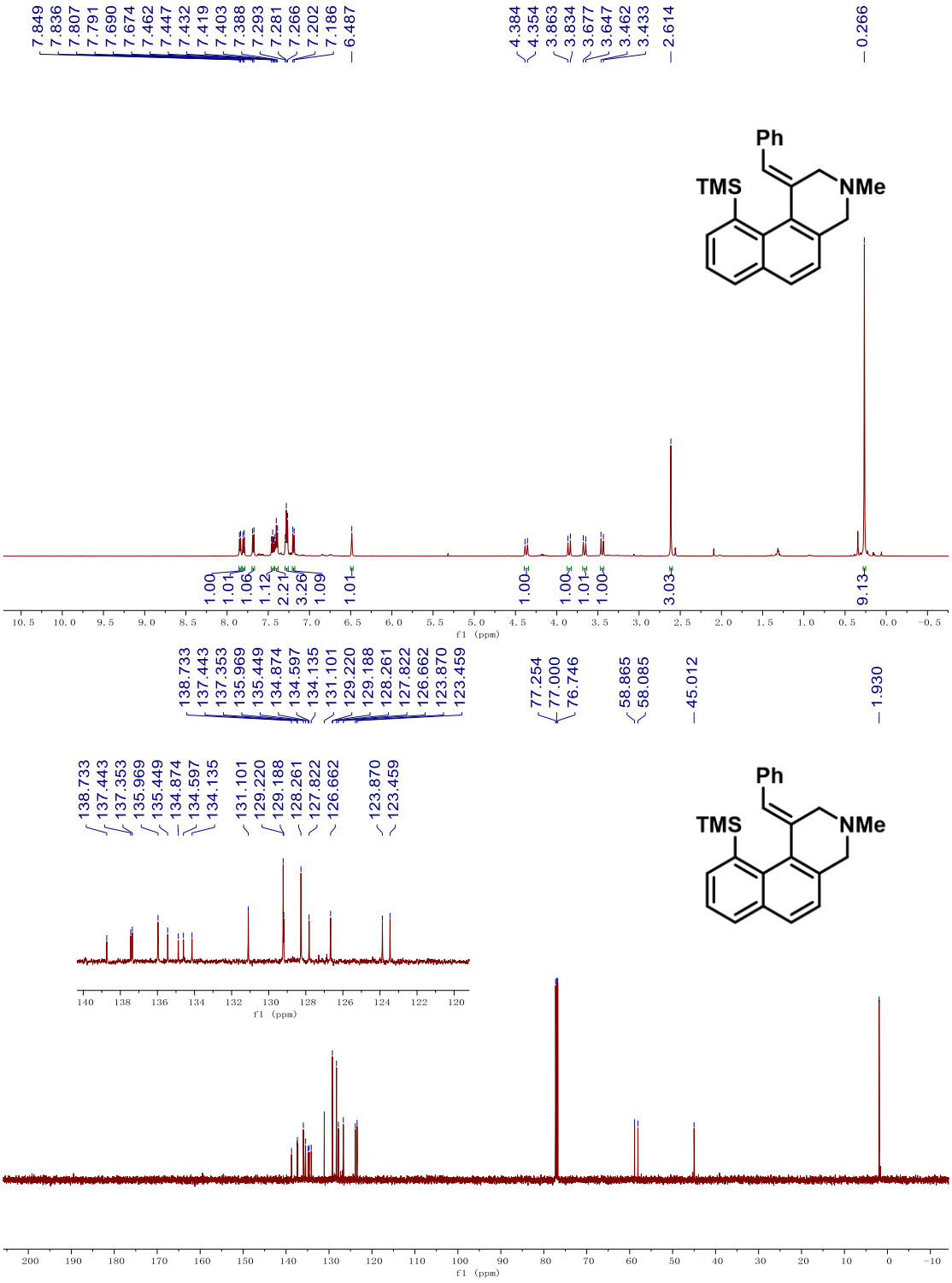
^{1}H NMR of **3aa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3aa** (125 MHz, $CDCl_3$)



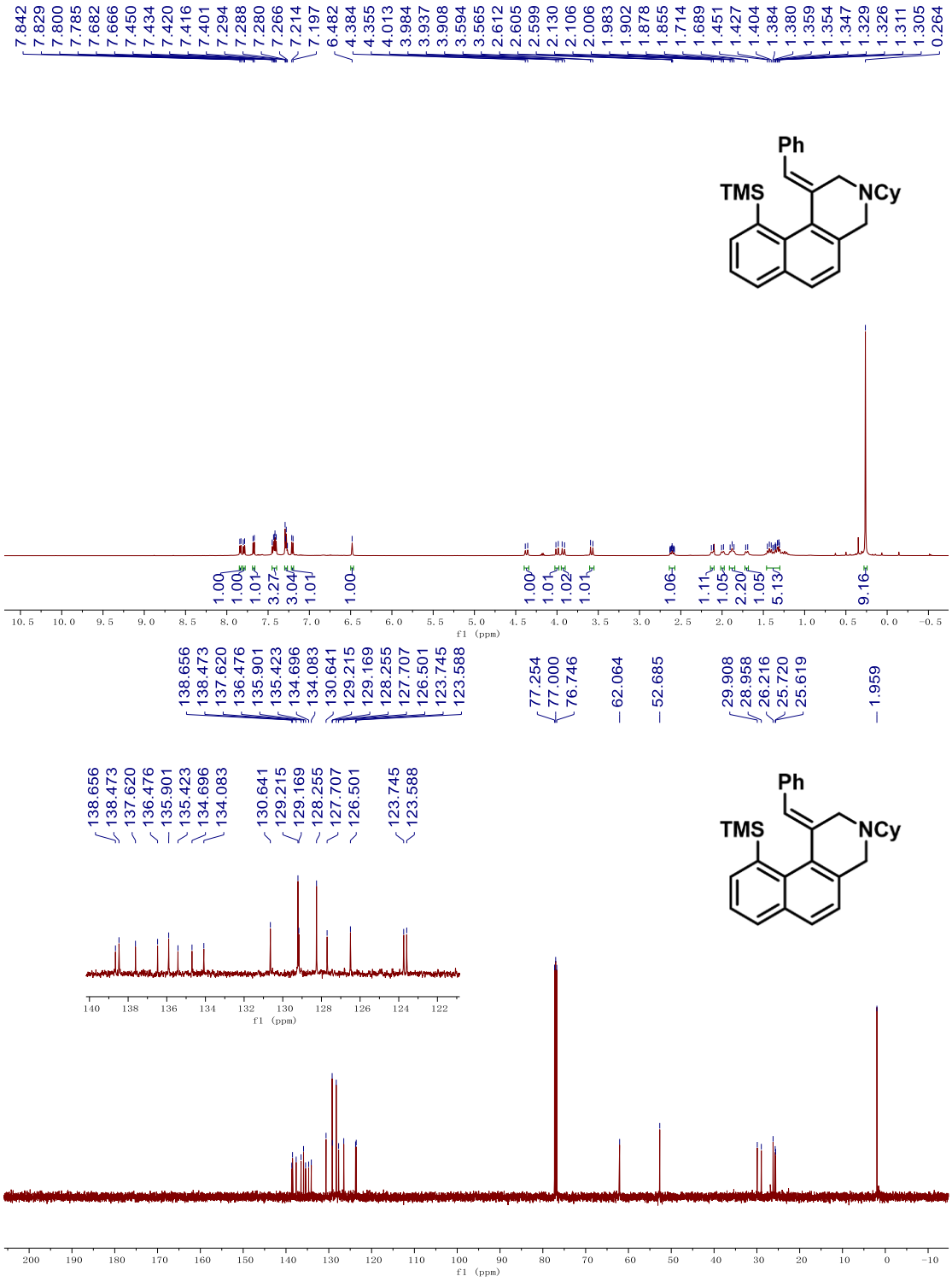
^{1}H NMR of **3a** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3a** (125 MHz, $CDCl_3$)



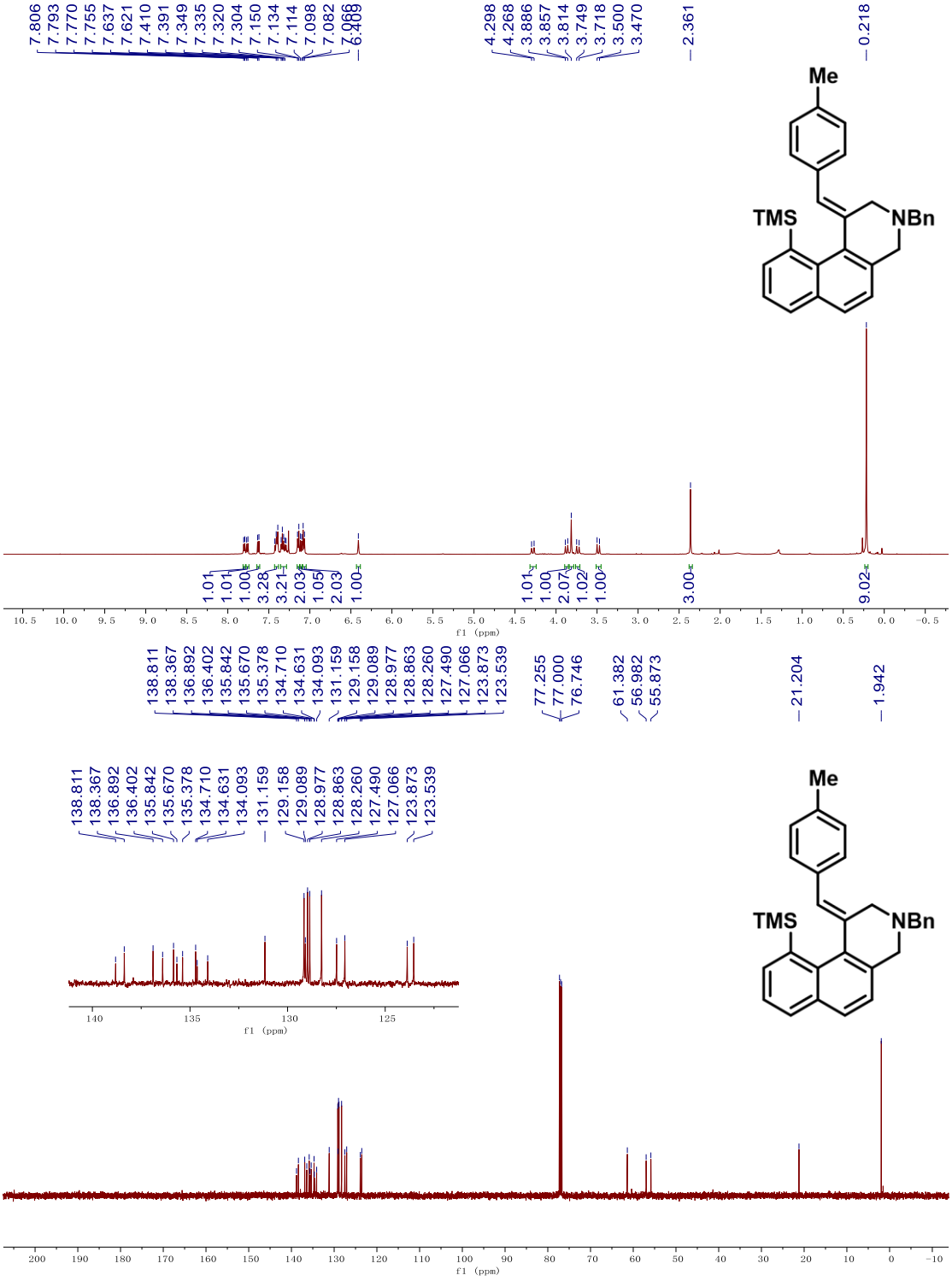
^{1}H NMR of **3ba** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ba** (125 MHz, $CDCl_3$)



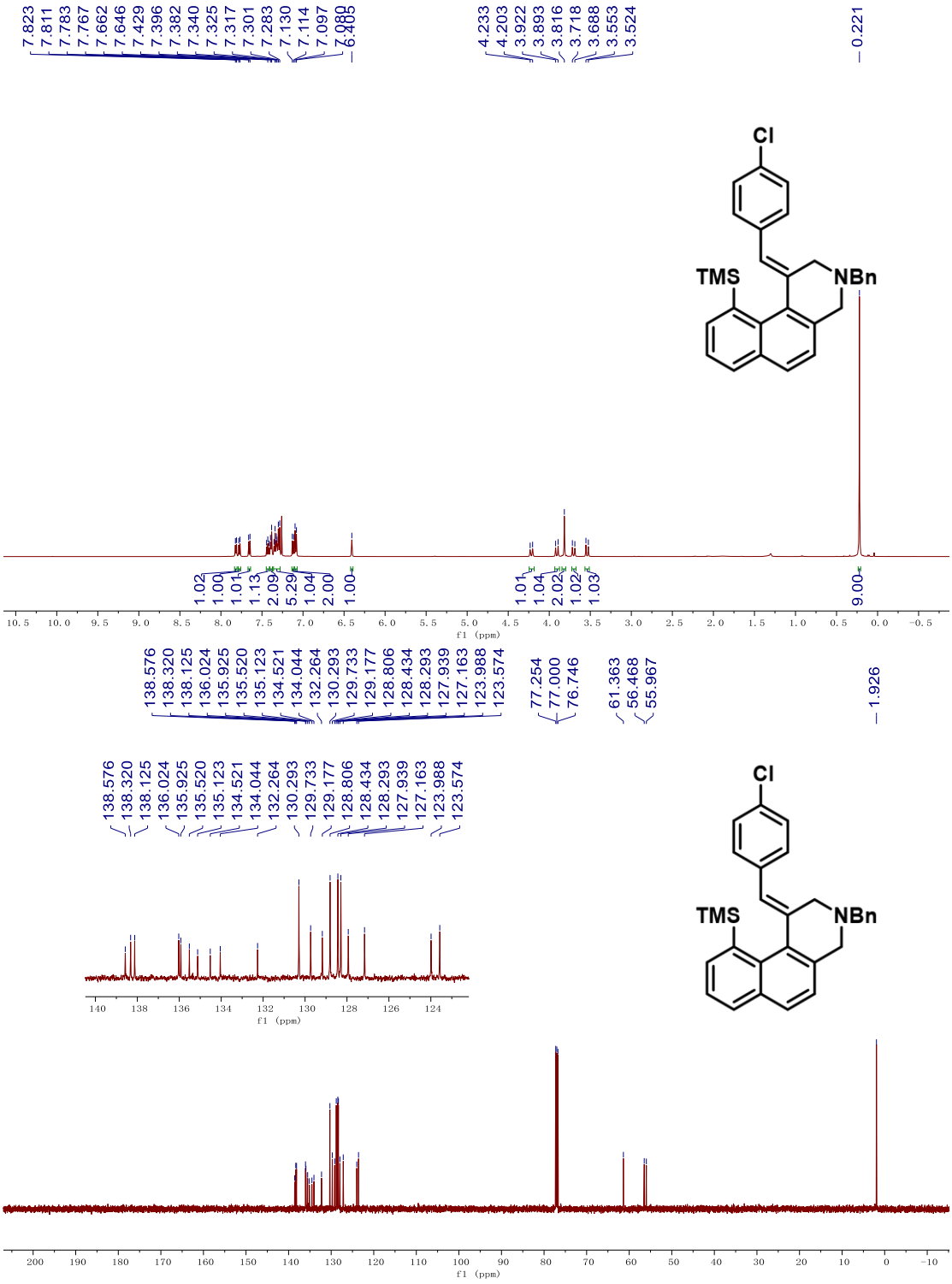
^{1}H NMR of **3ca** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ca** (125 MHz, $CDCl_3$)



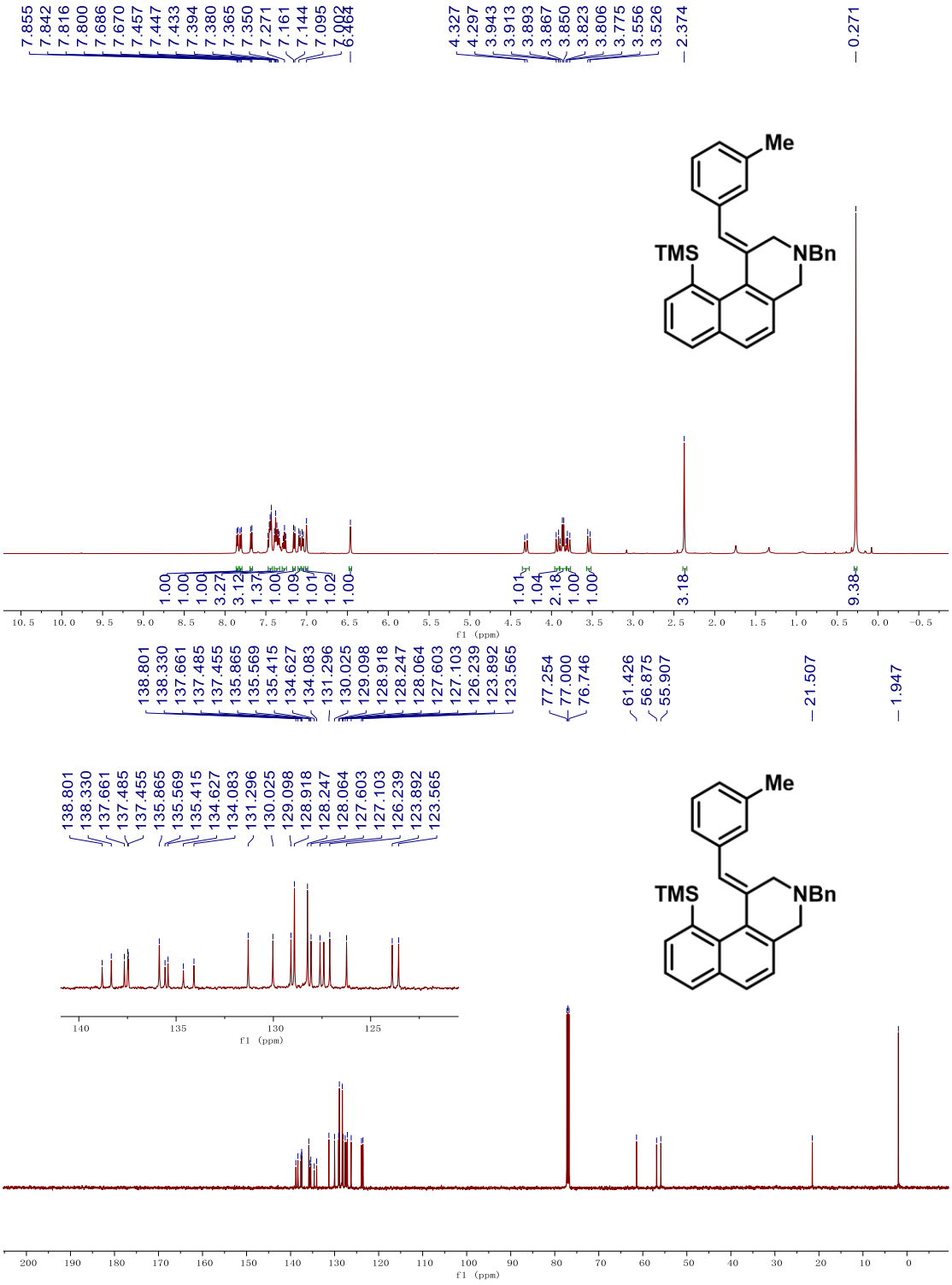
^{1}H NMR of **3ea** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ea** (125 MHz, $CDCl_3$)



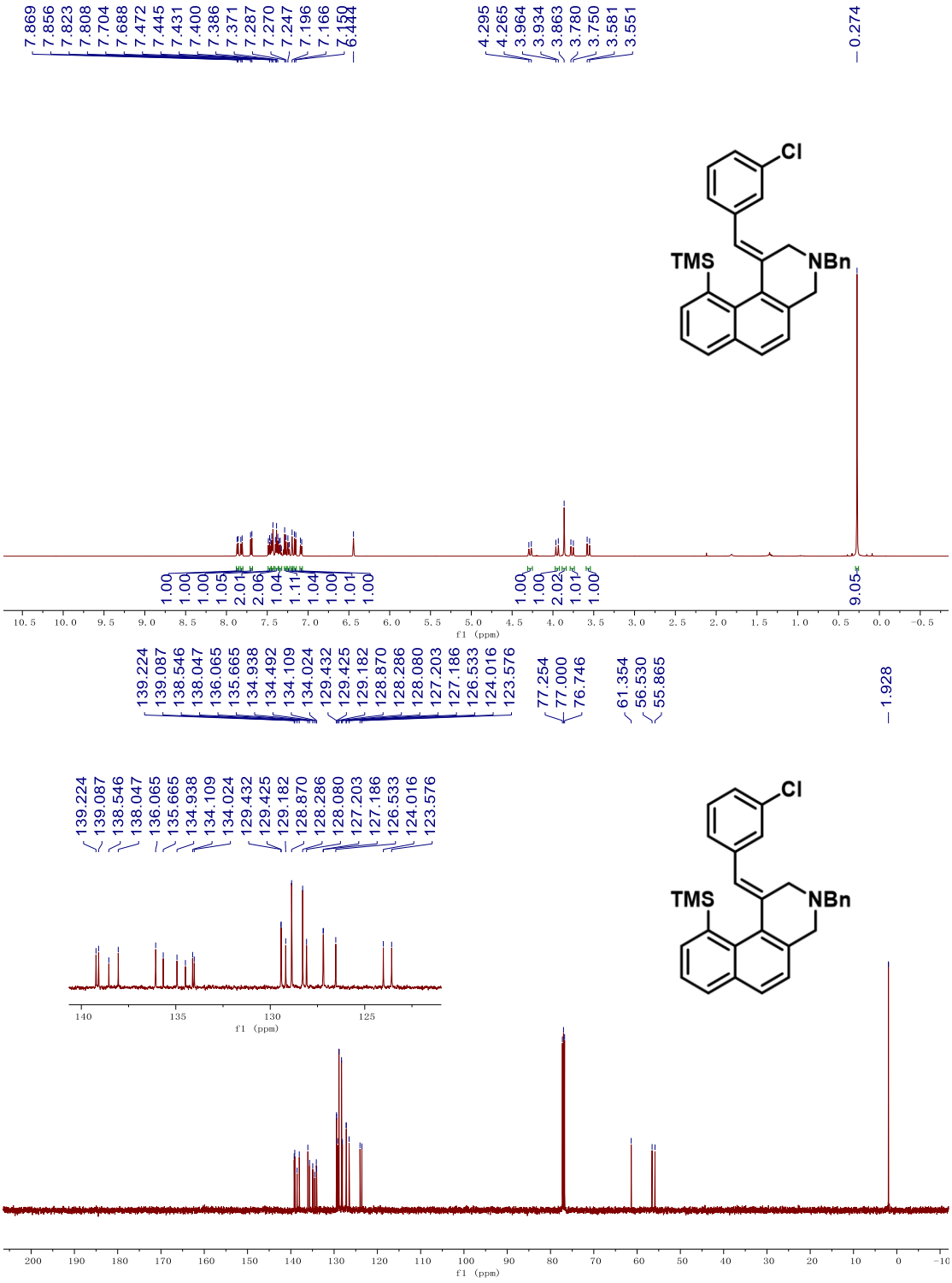
^{1}H NMR of **3fa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3fa** (125 MHz, $CDCl_3$)



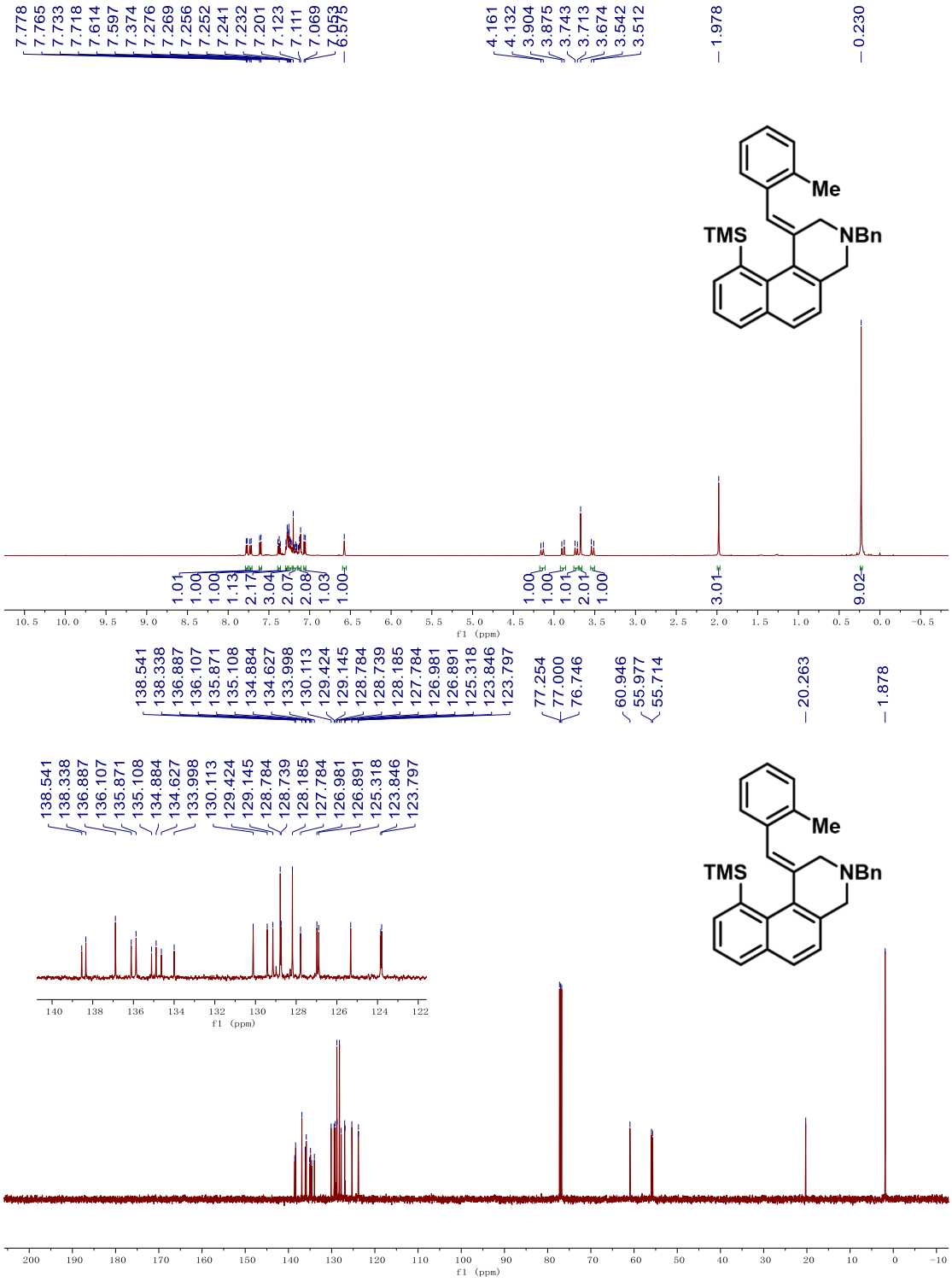
^{1}H NMR of **3ga** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ga** (125 MHz, $CDCl_3$)



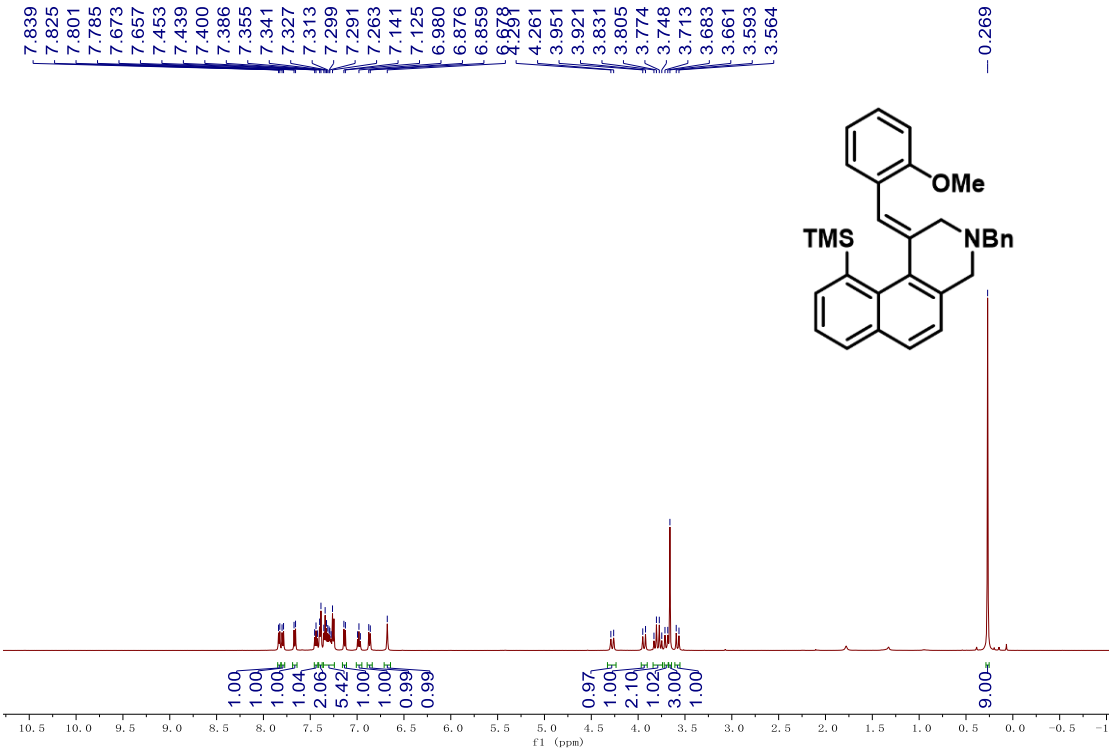
^{1}H NMR of **3ha** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ha** (125 MHz, $CDCl_3$)

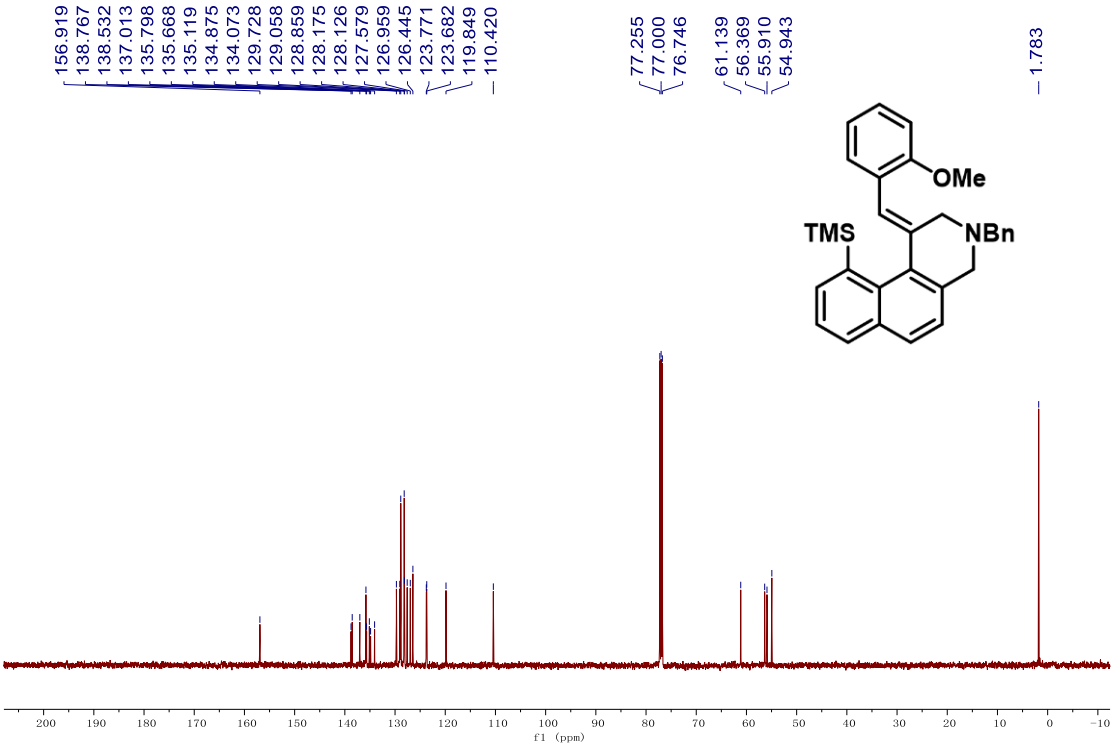


^{1}H NMR of **3ia** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ia** (125 MHz, $CDCl_3$)

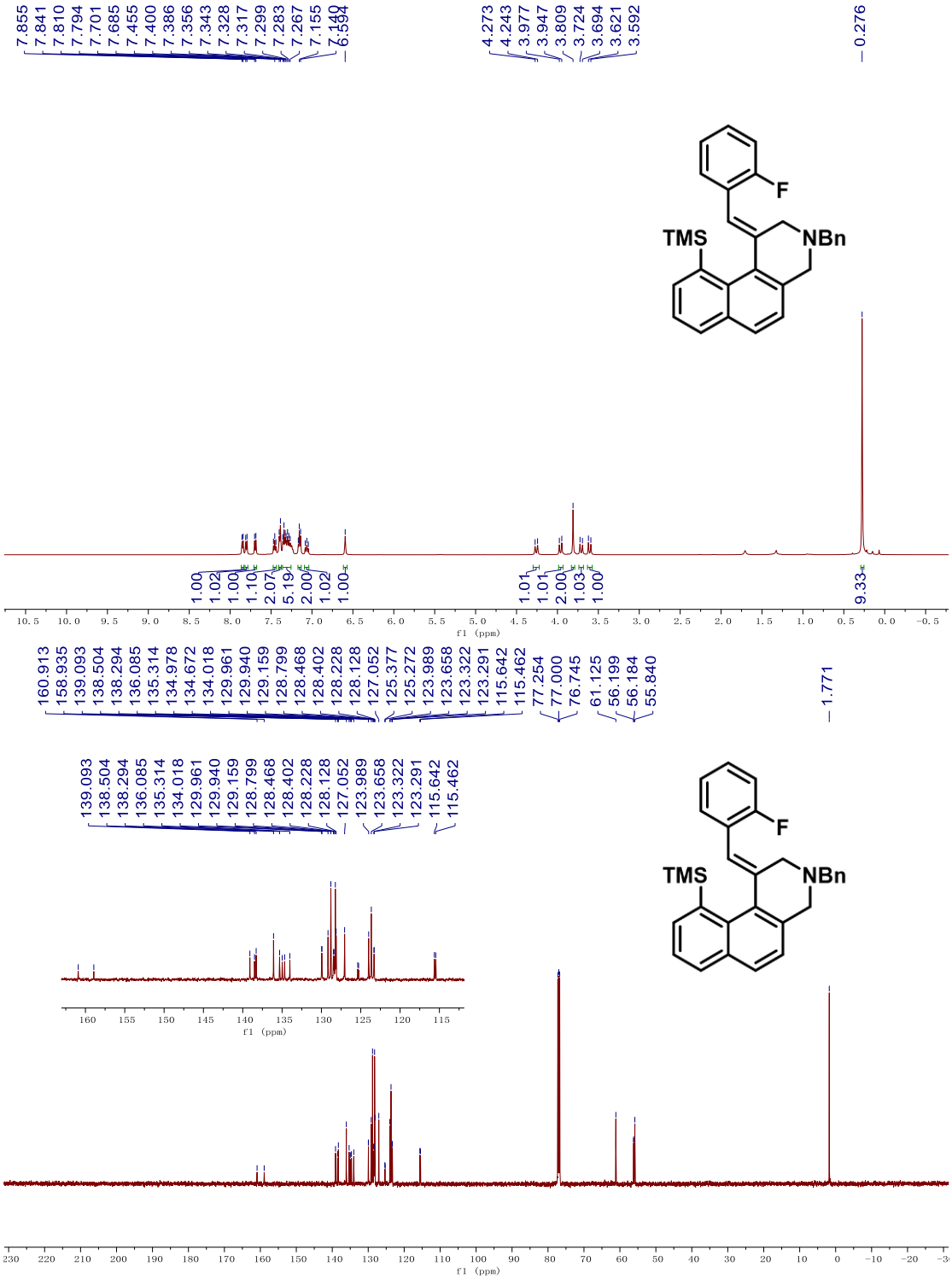


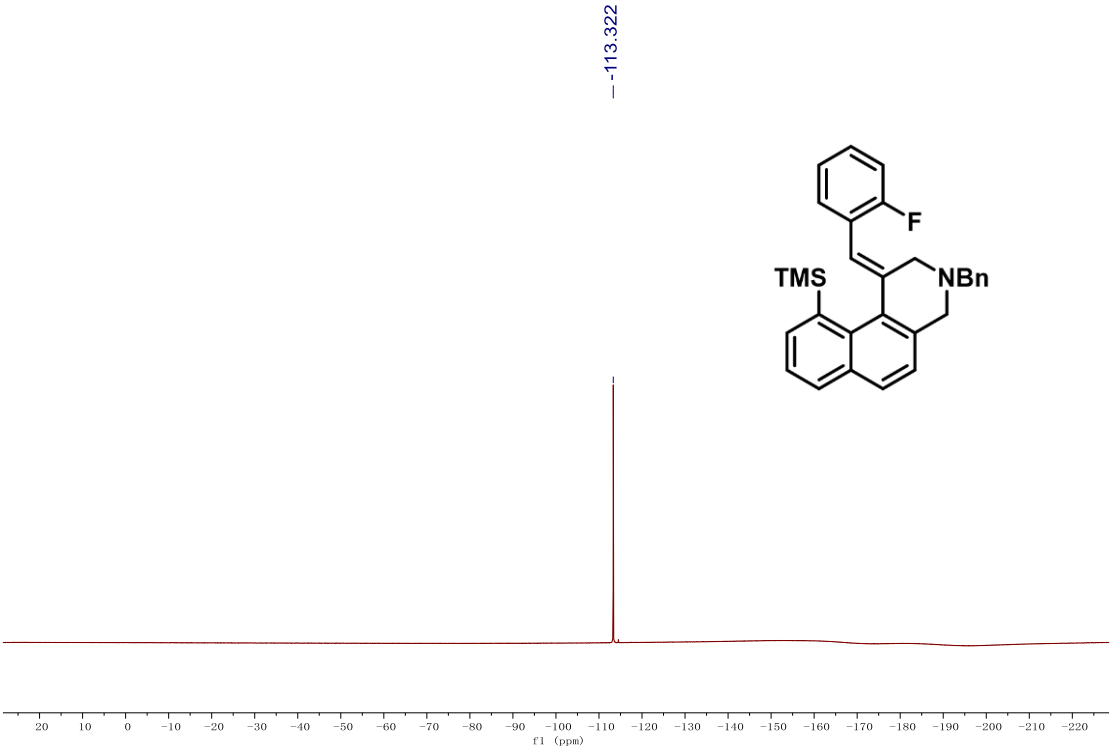
^{1}H NMR of **3ja** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ja** (125 MHz, $CDCl_3$)



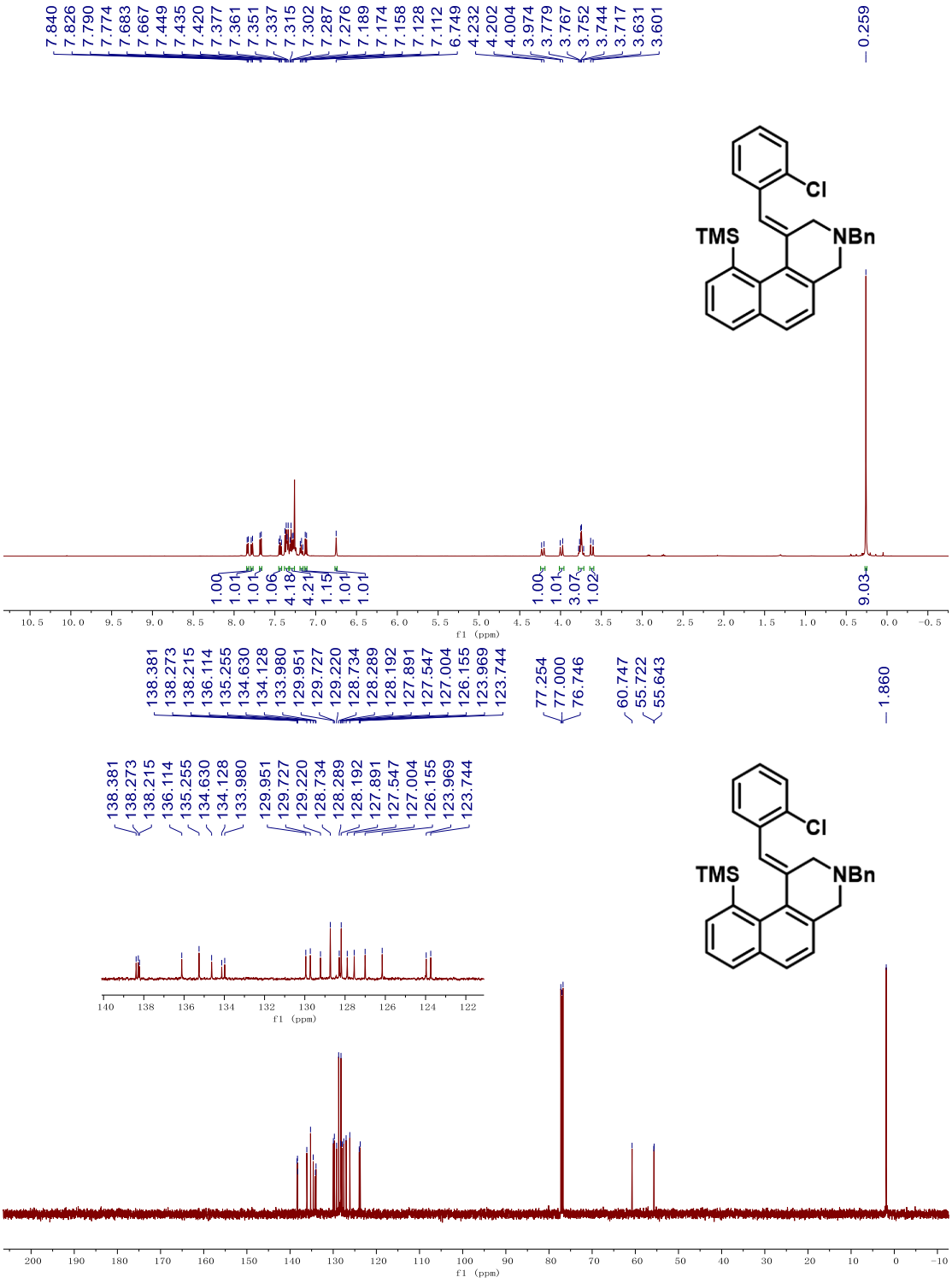


^{1}H NMR of **3ka** (500 MHz, $CDCl_3$), ^{13}C NMR of **3ka** (125 MHz, $CDCl_3$) and ^{19}F NMR **3ka** (470 MHz, $CDCl_3$)

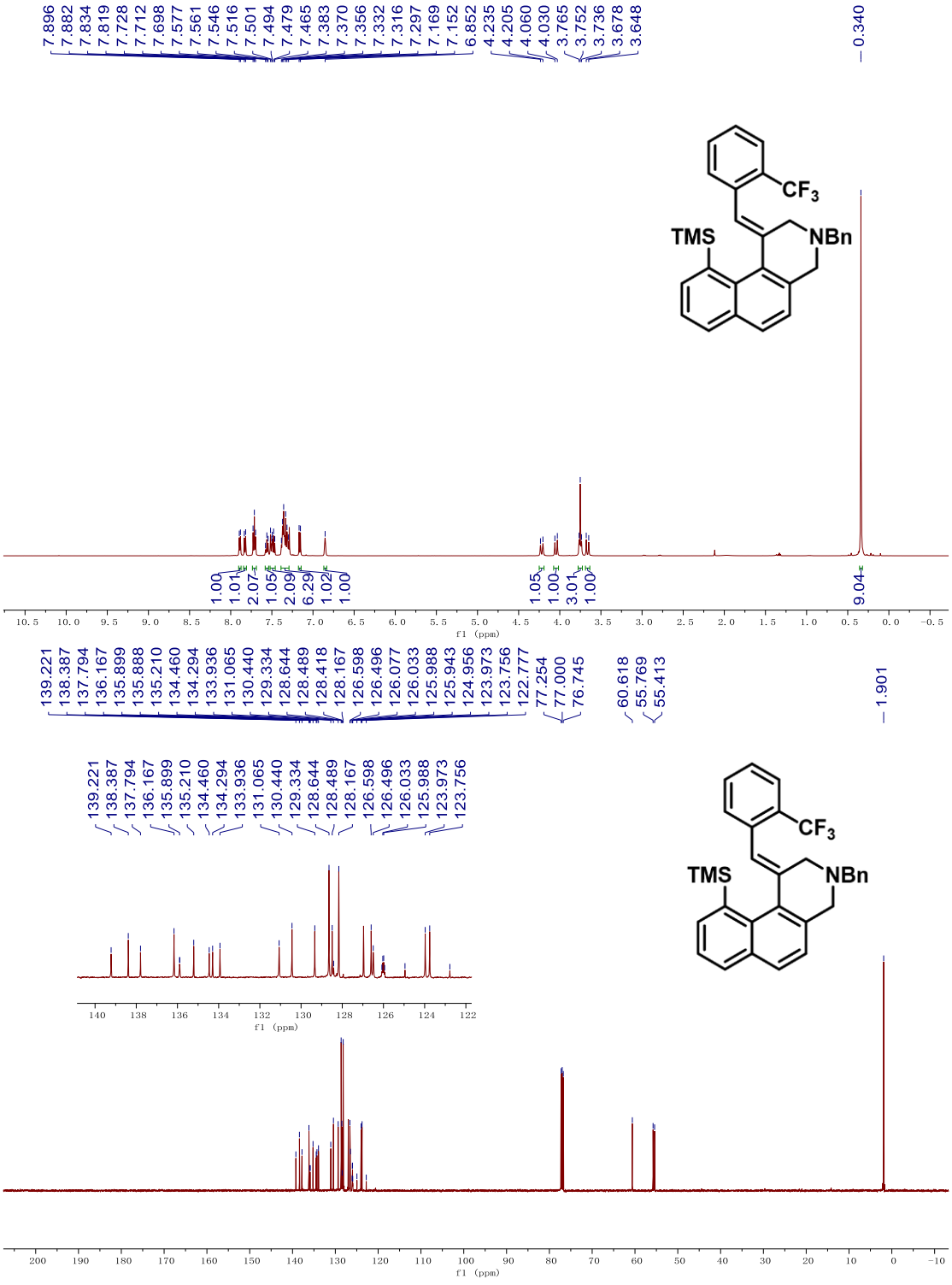


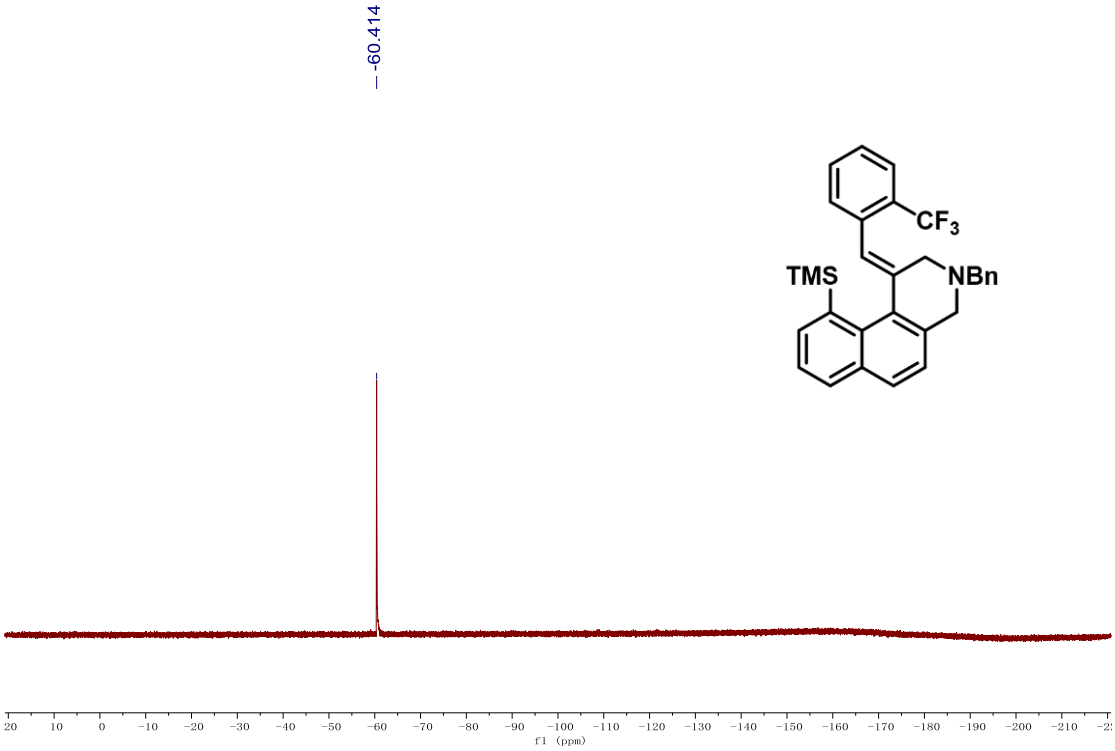

-113.322
F
TMS
NBn
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

^{1}H NMR of **3la** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3la** (125 MHz, $CDCl_3$)

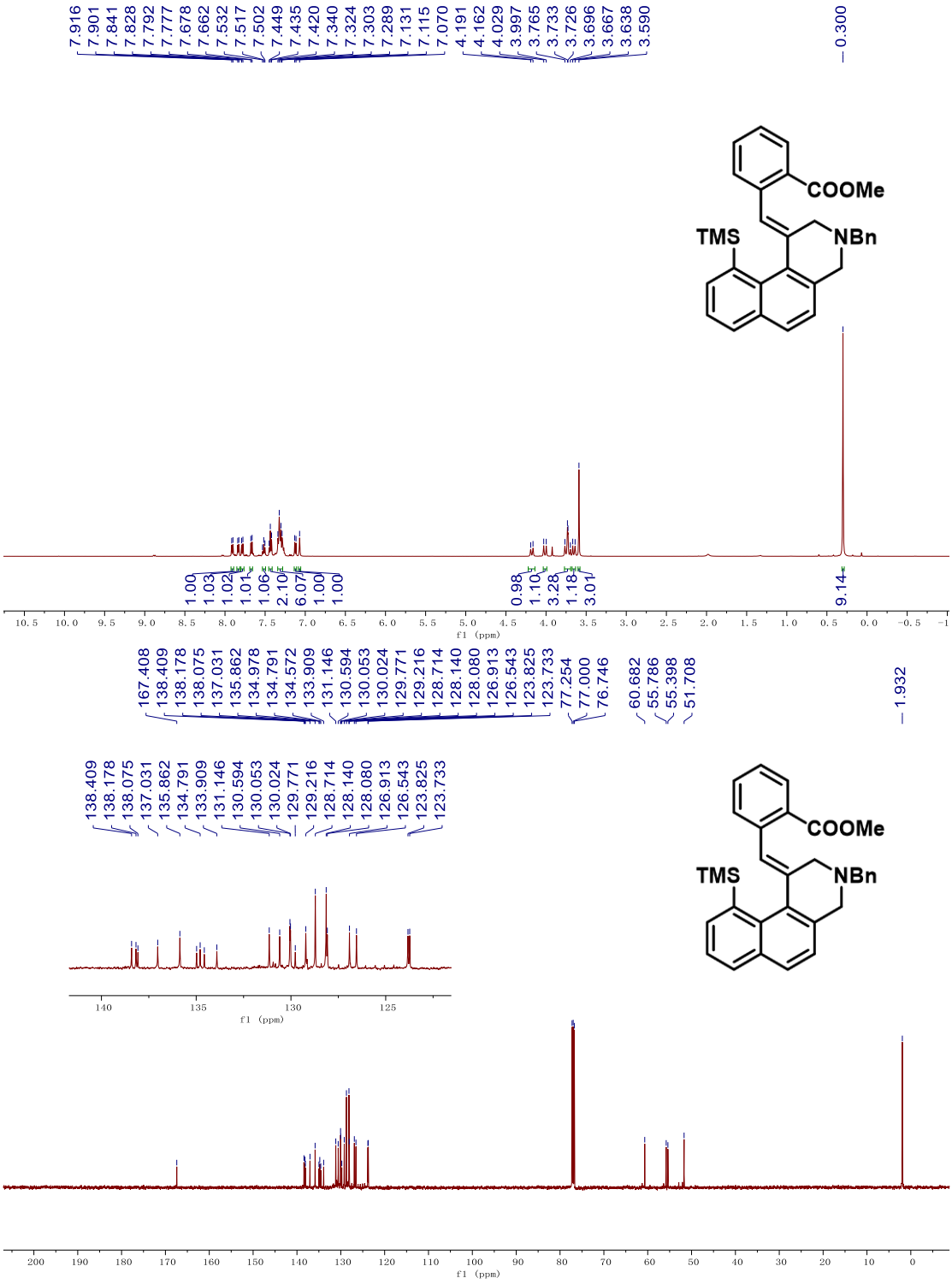


^{1}H NMR of **3ma** (500 MHz, $CDCl_3$), ^{13}C NMR of **3ma** (125 MHz, $CDCl_3$) and ^{19}F NMR **3ma** (470 MHz, $CDCl_3$)

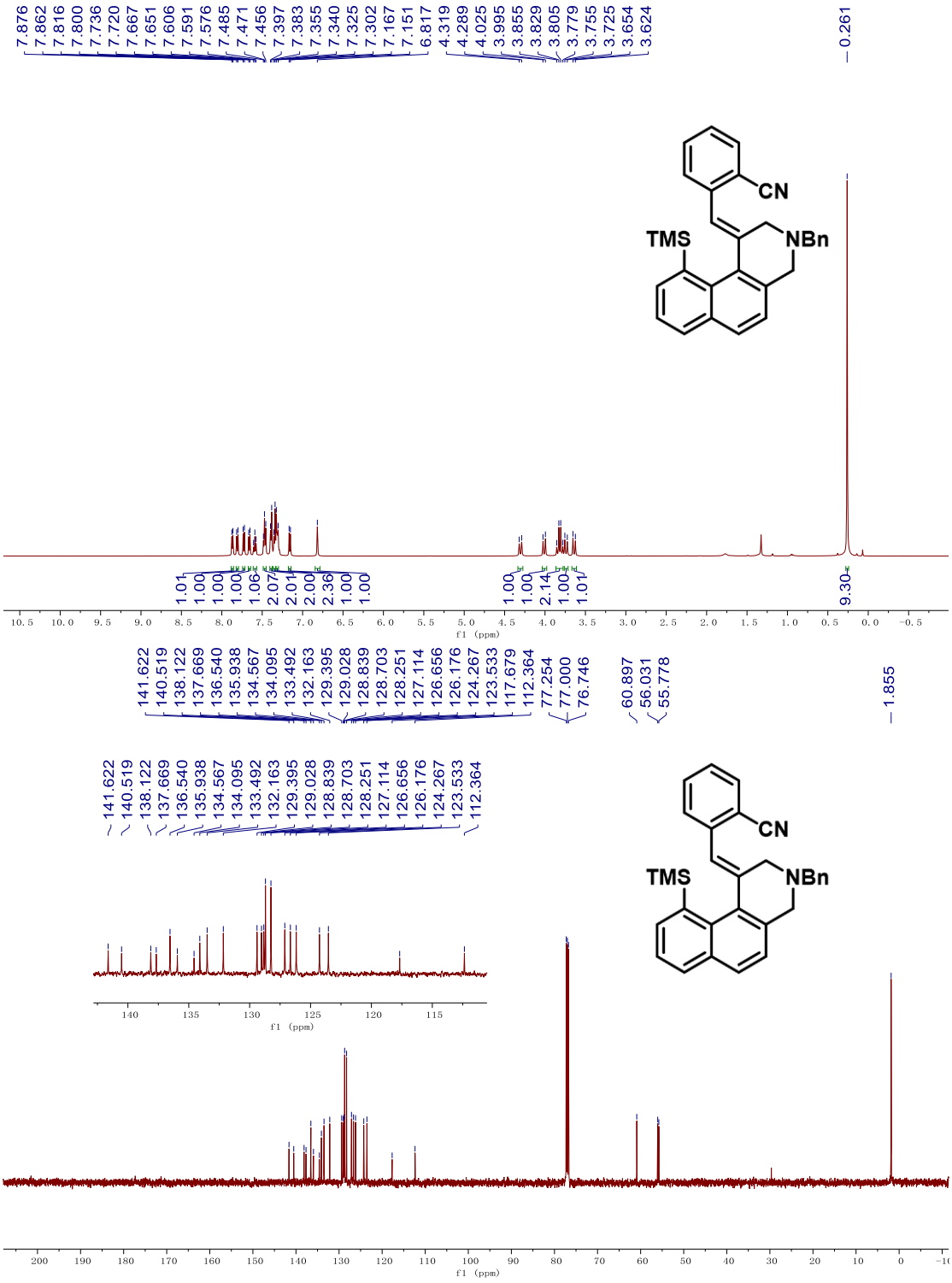



-60.414
CF3
TMS
NBn
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

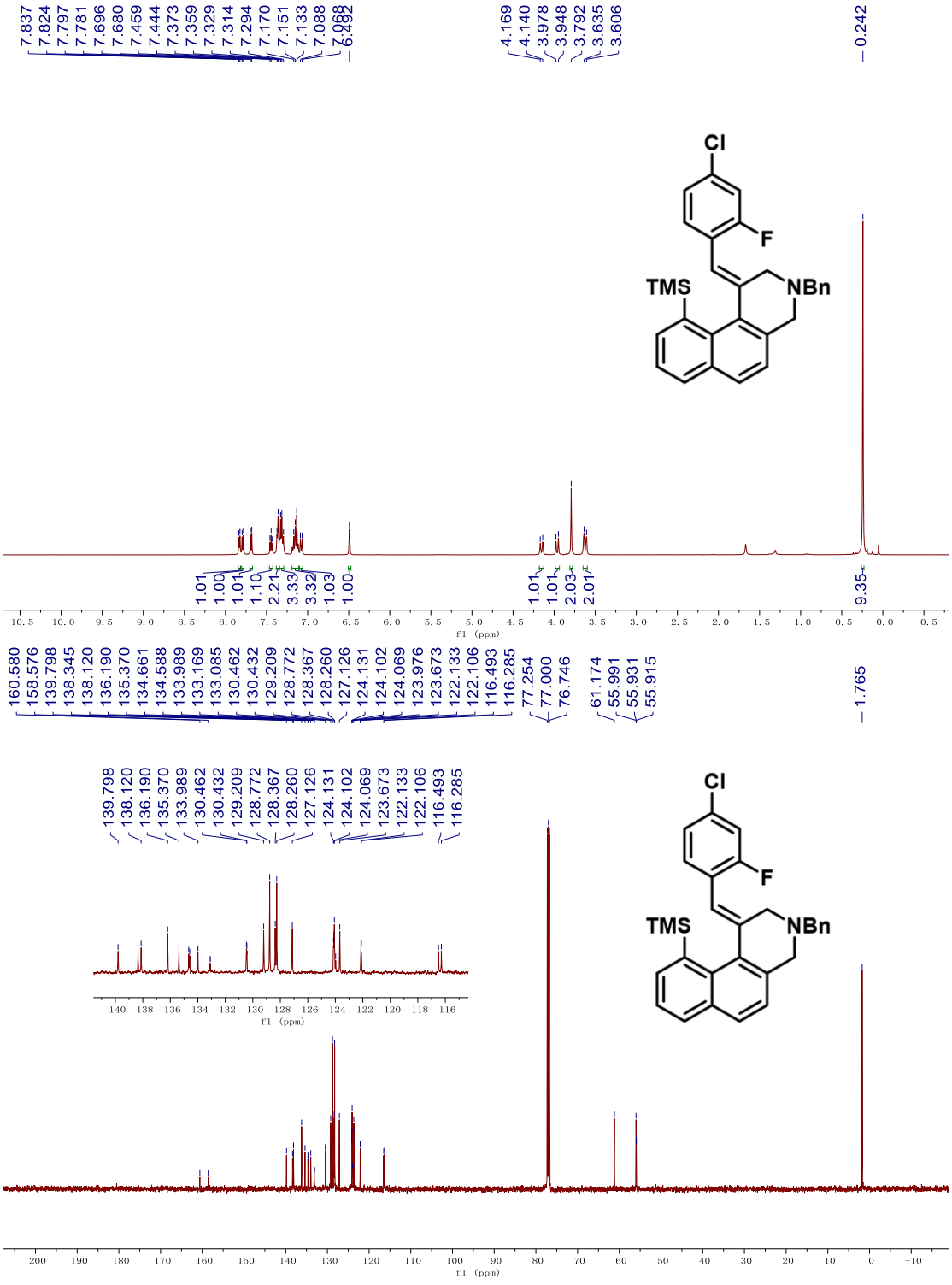
^{1}H NMR of **3na** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3na** (125 MHz, $CDCl_3$)

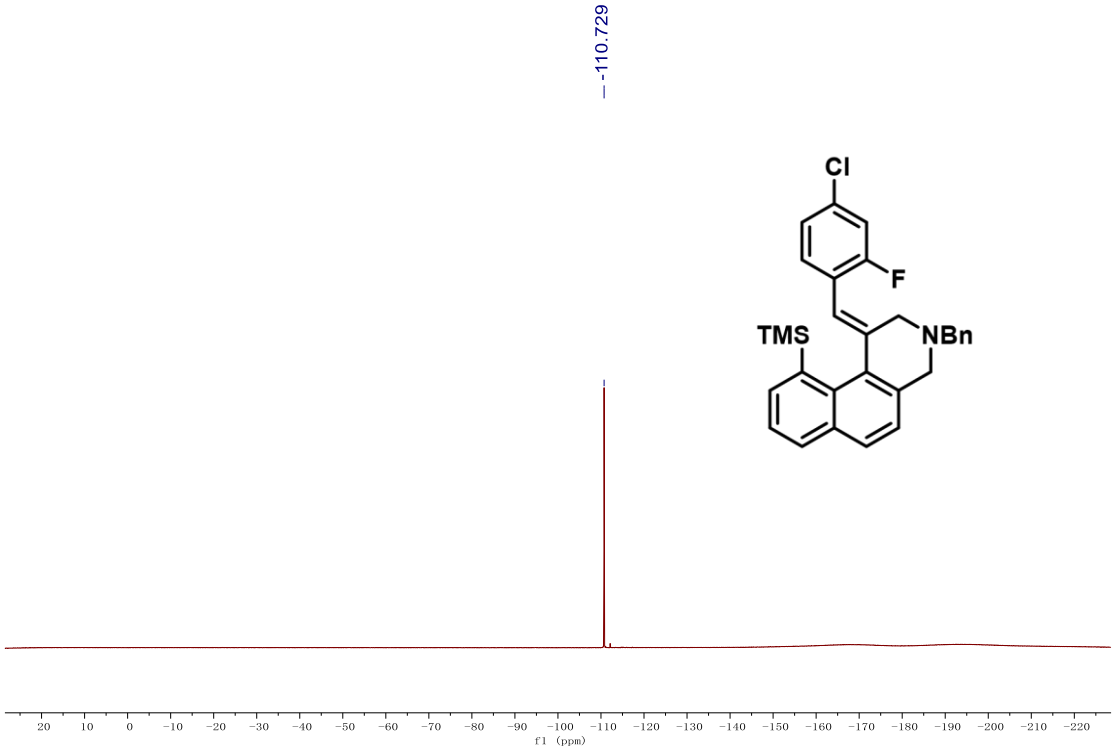


^{1}H NMR of **3oa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3oa** (125 MHz, $CDCl_3$)

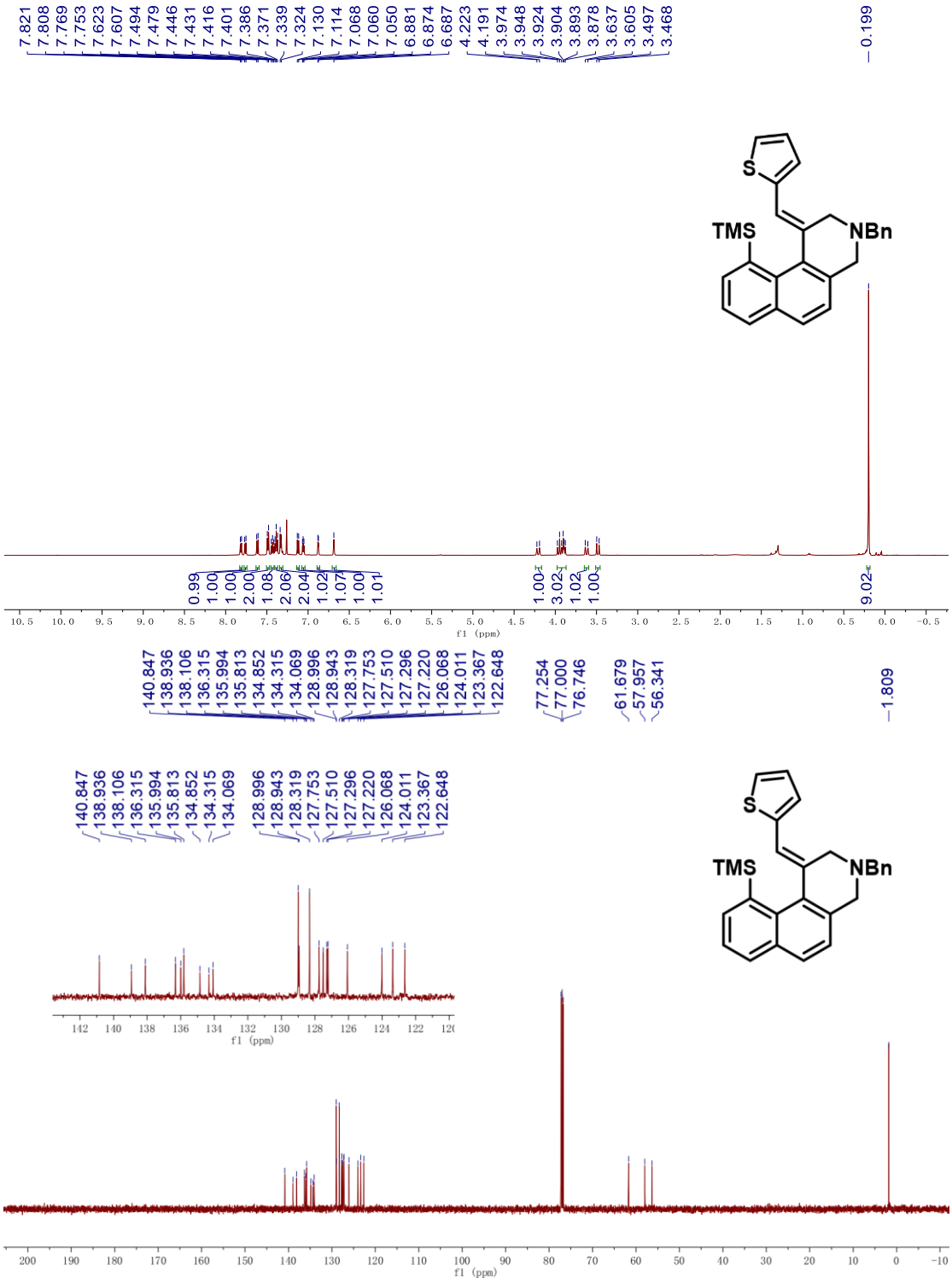


^{1}H NMR of **3pa** (500 MHz, $CDCl_3$), ^{13}C NMR of **3pa** (125 MHz, $CDCl_3$) and ^{19}F NMR **3pa** (470 MHz, $CDCl_3$)

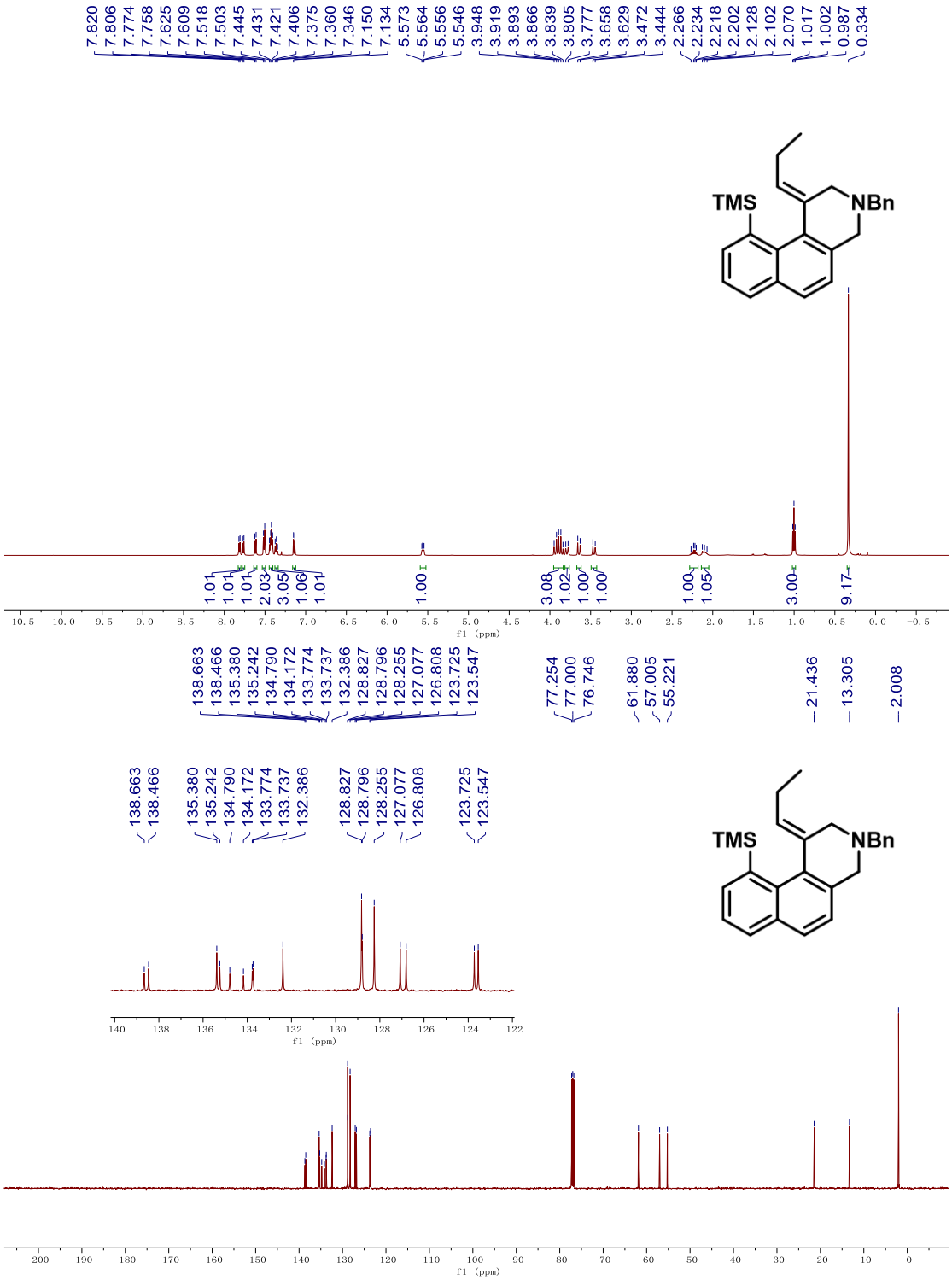



-110.729
Cl
F
TMS
NBn
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

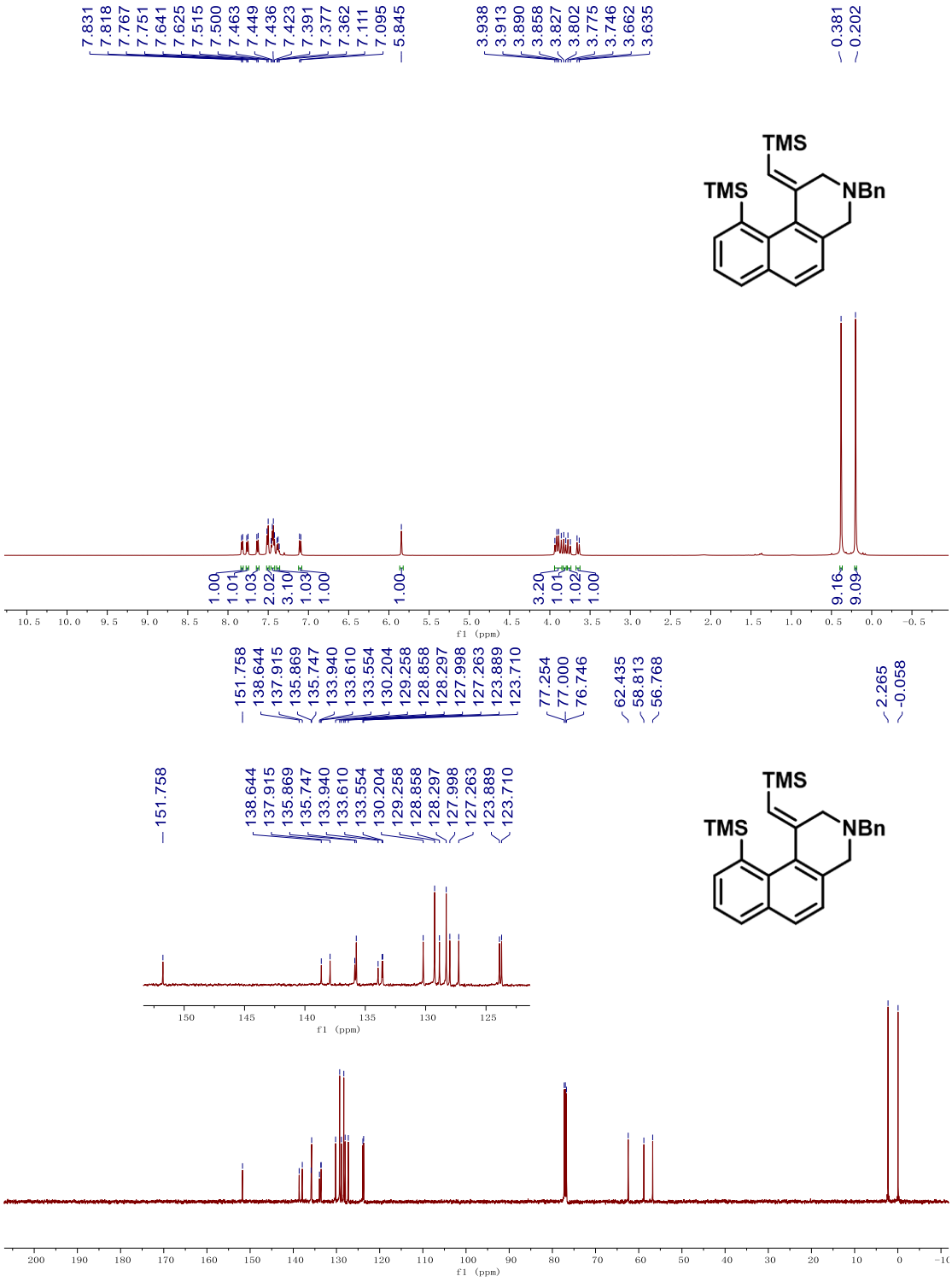
^{1}H NMR of **3qa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3qa** (125 MHz, $CDCl_3$)



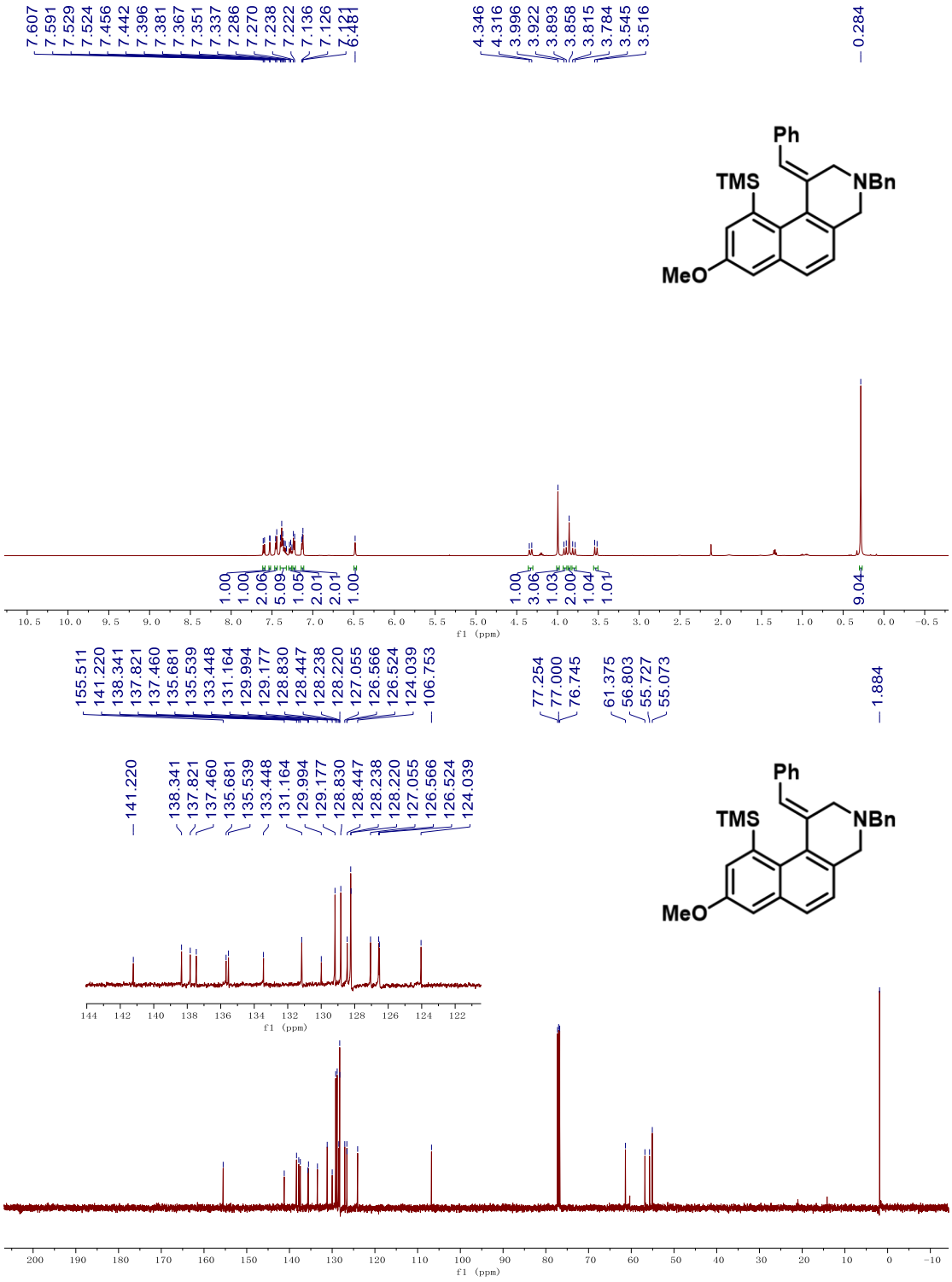
^{1}H NMR of **3ra** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ra** (125 MHz, $CDCl_3$)



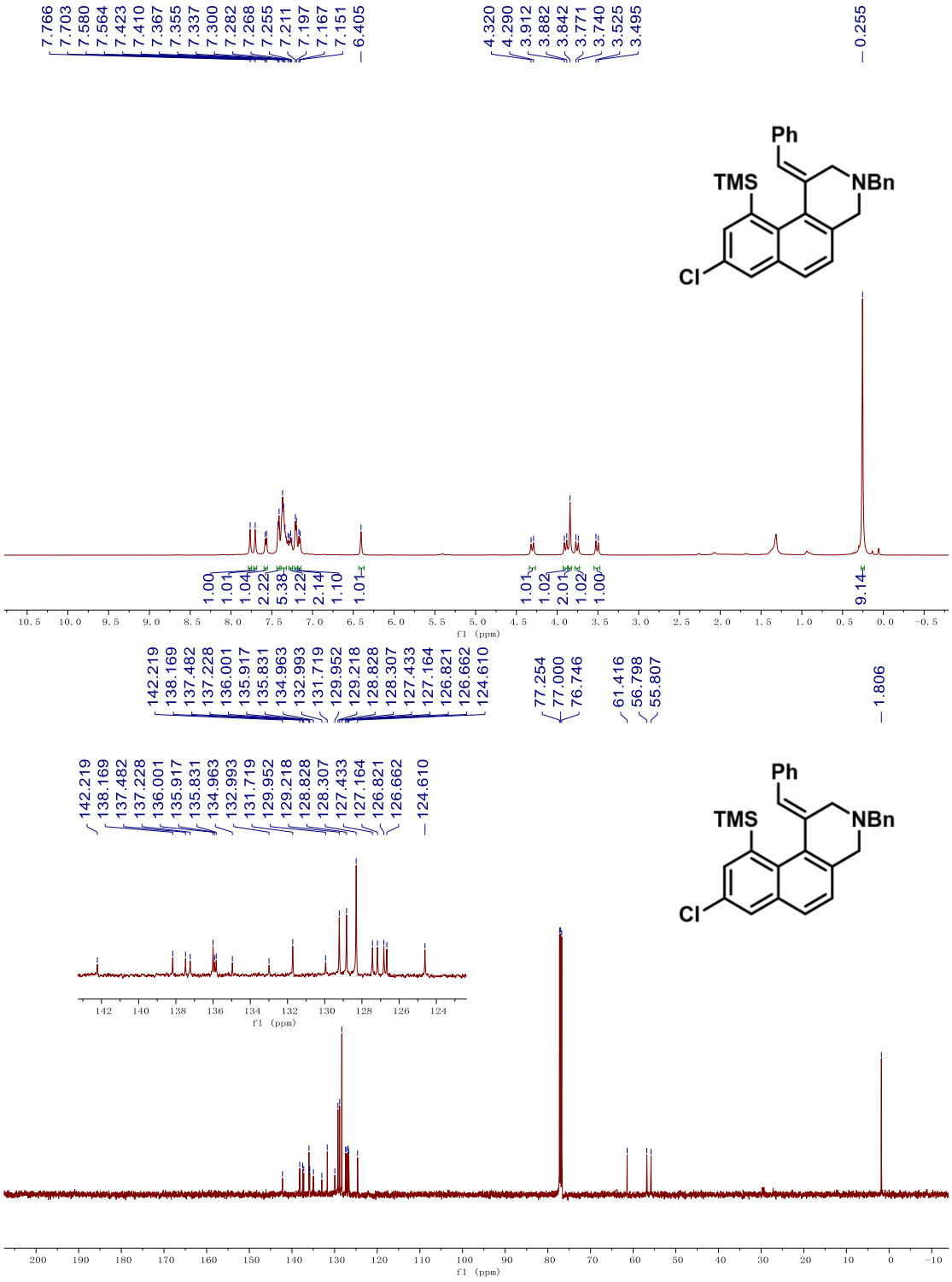
^{1}H NMR of **3sa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3sa** (125 MHz, $CDCl_3$)



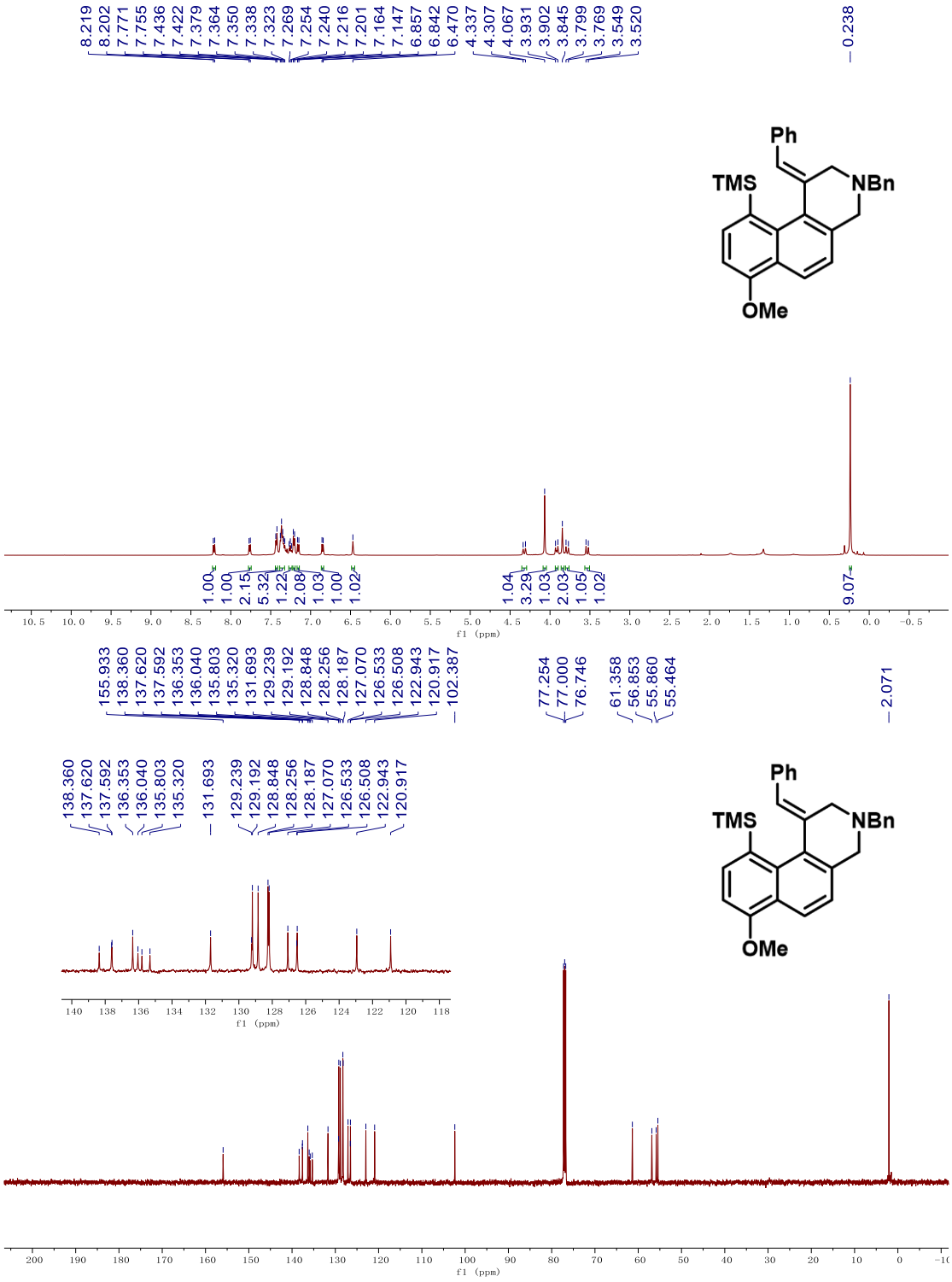
^{1}H NMR of **3ta** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ta** (125 MHz, $CDCl_3$)



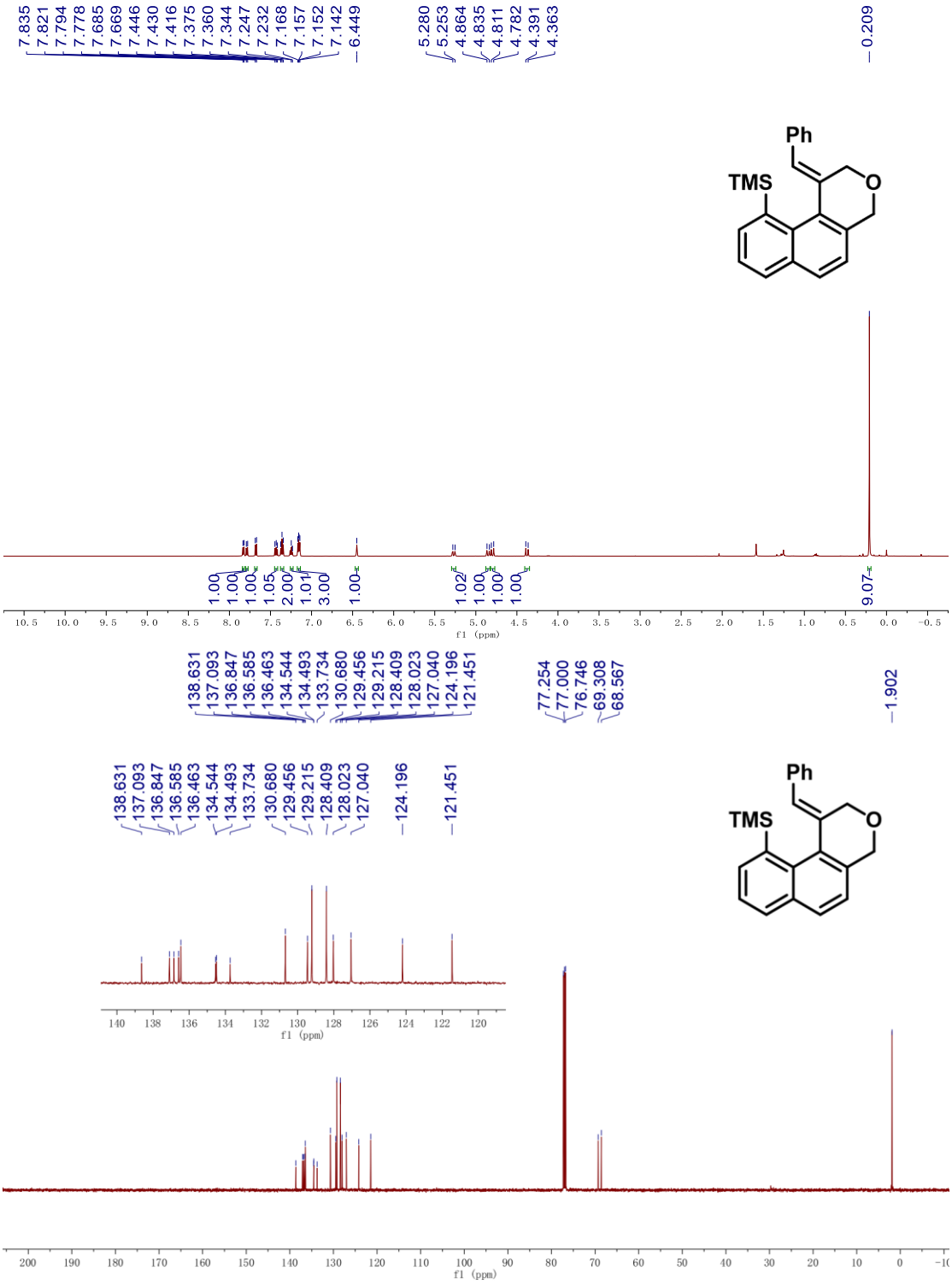
^{1}H NMR of **3ua** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ua** (125 MHz, $CDCl_3$)



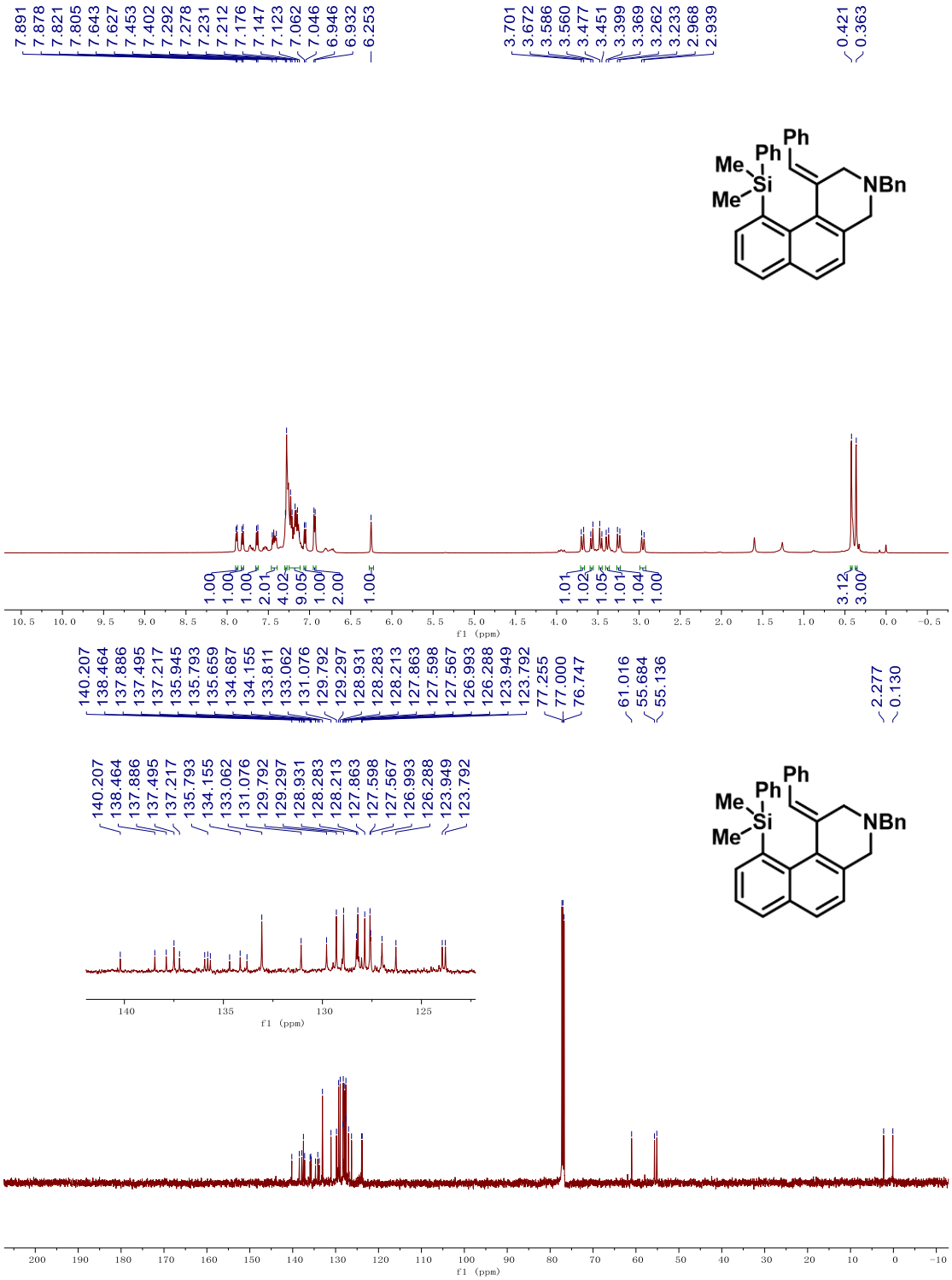
^{1}H NMR of **3va** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3va** (125 MHz, $CDCl_3$)



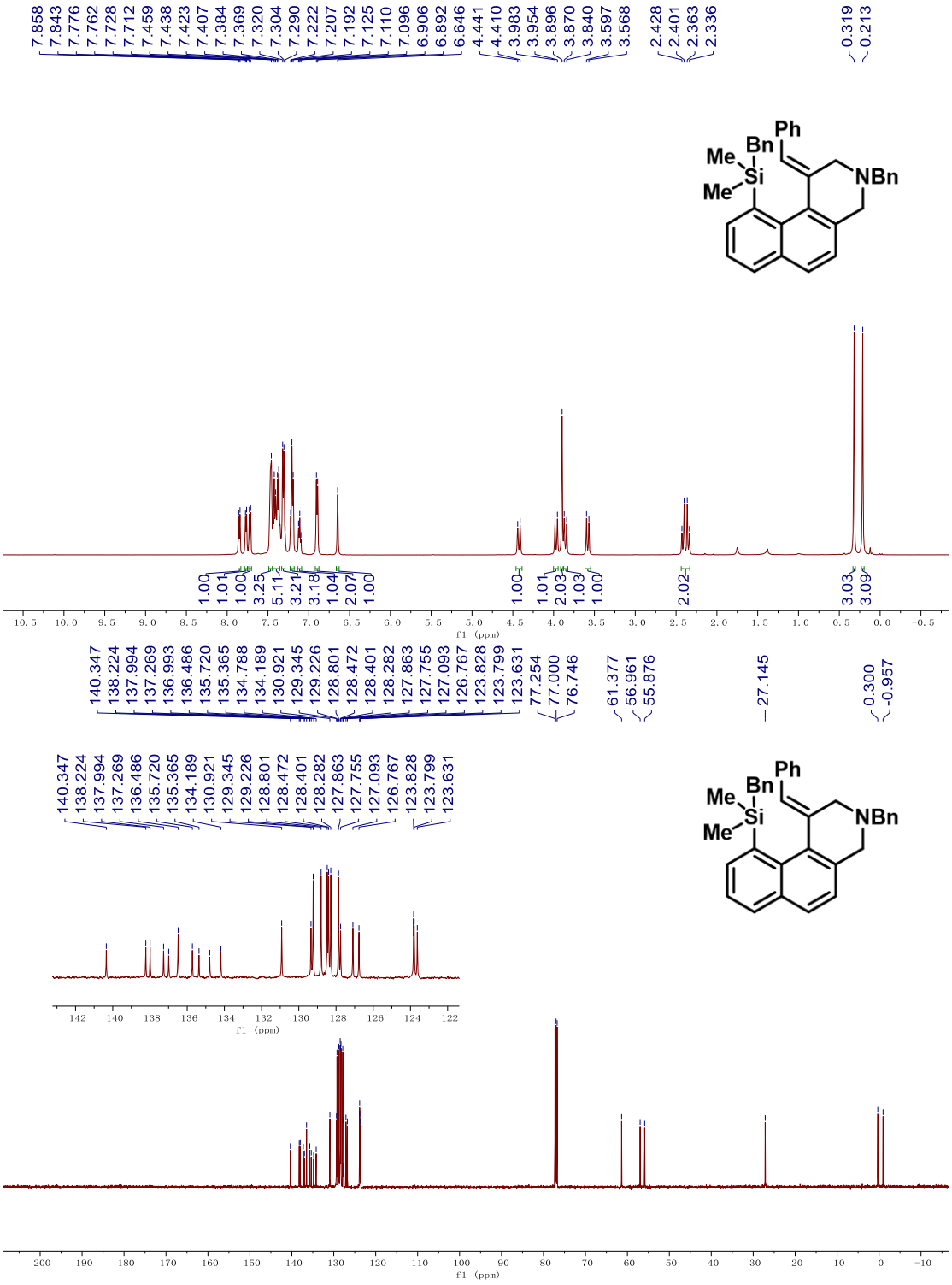
^{1}H NMR of **3wa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3wa** (125 MHz, $CDCl_3$)



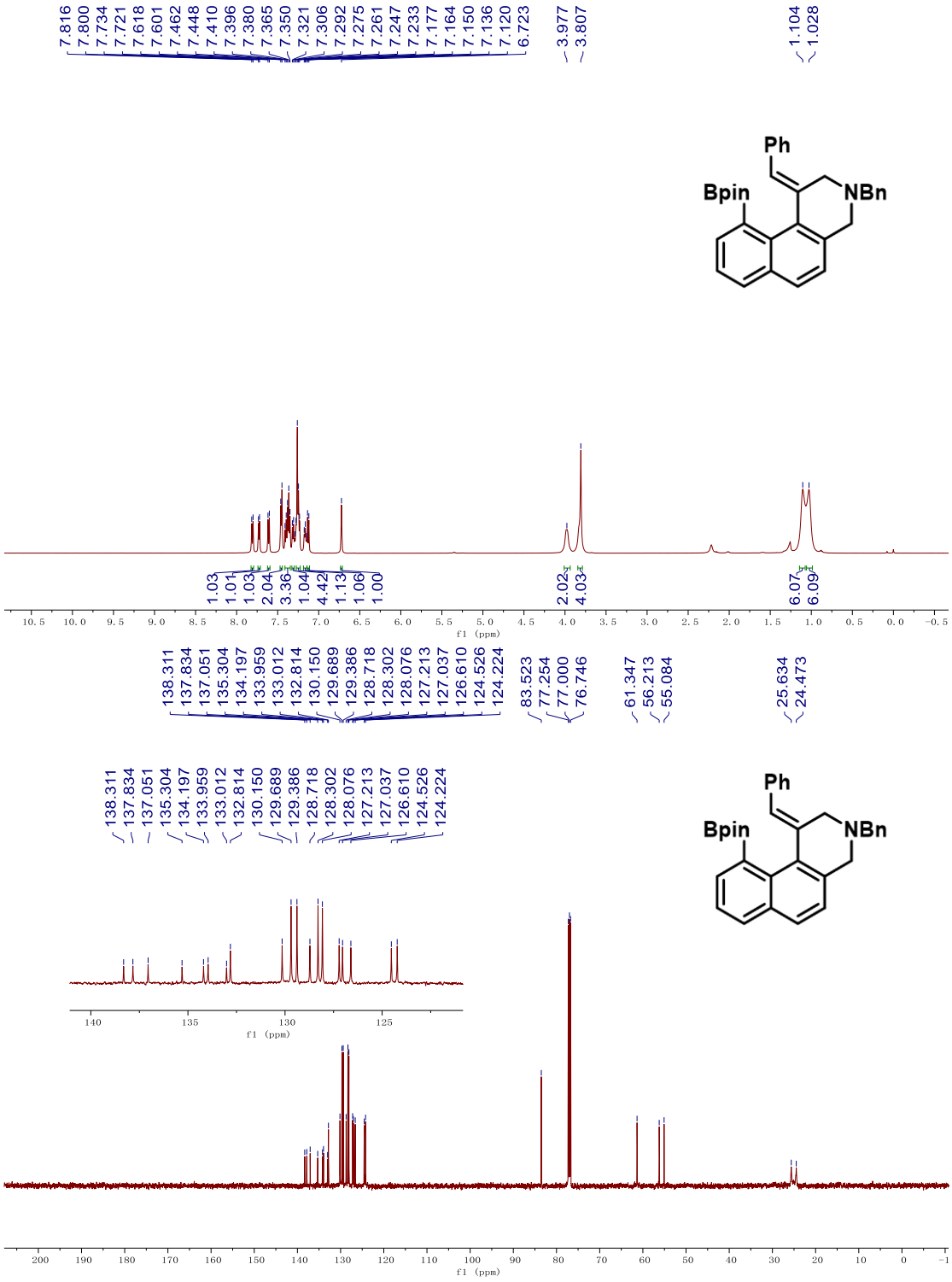
^{1}H NMR of **3ab** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ab** (125 MHz, $CDCl_3$)



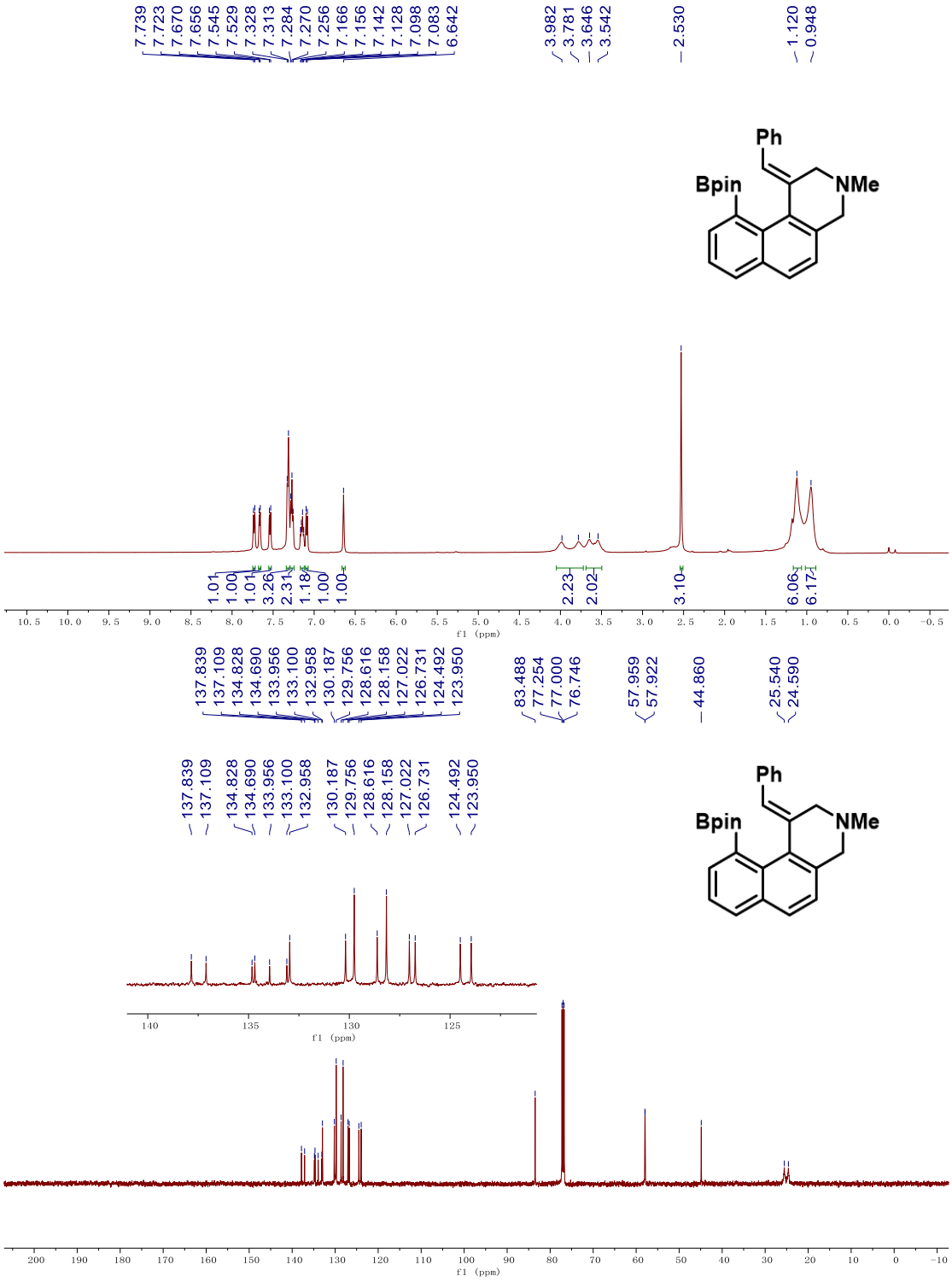
^{1}H NMR of **3ac** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ac** (125 MHz, $CDCl_3$)



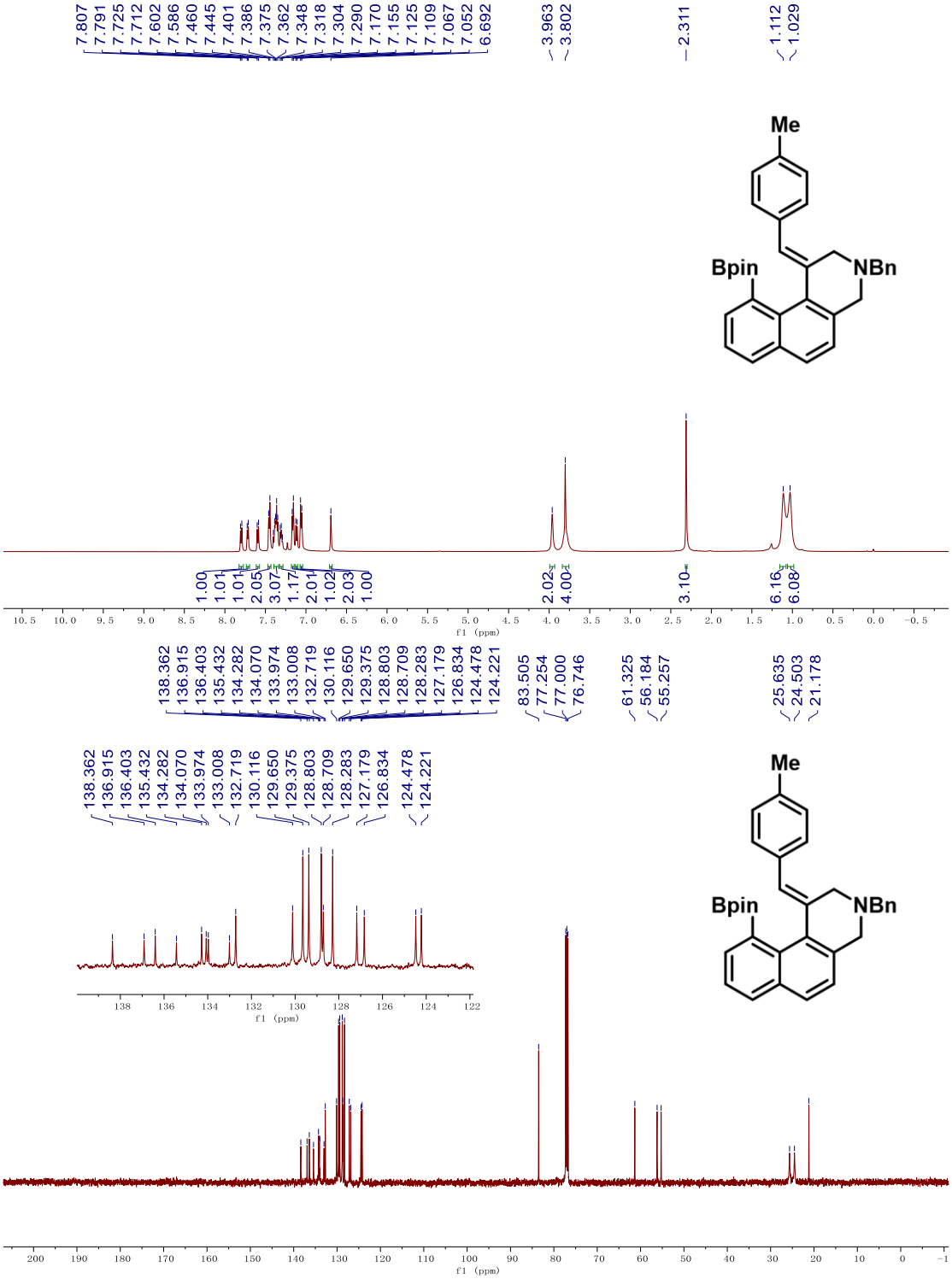
^{1}H NMR of **5a** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5a** (125 MHz, $CDCl_3$)



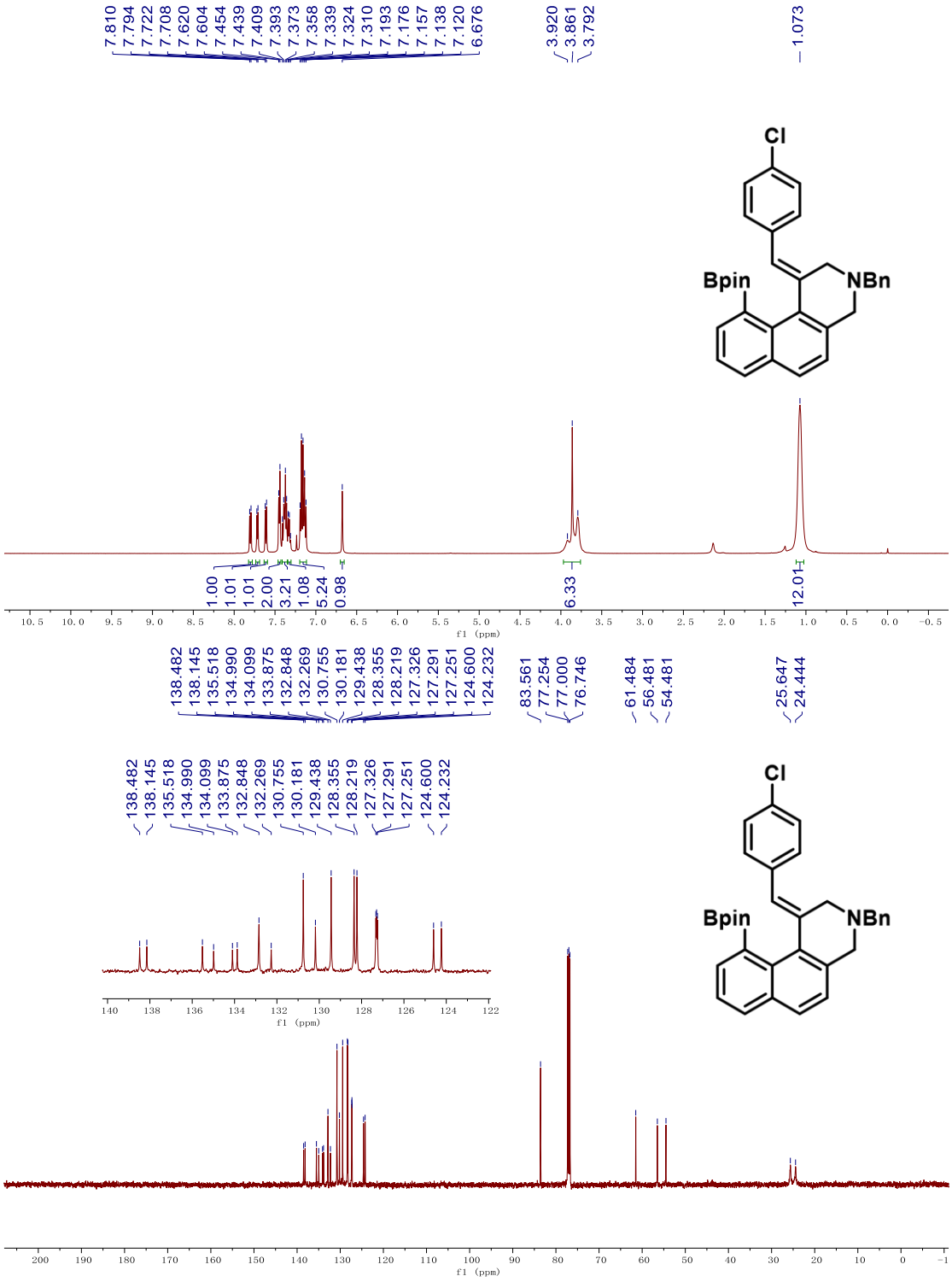
^{1}H NMR of **5b** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5b** (125 MHz, $CDCl_3$)



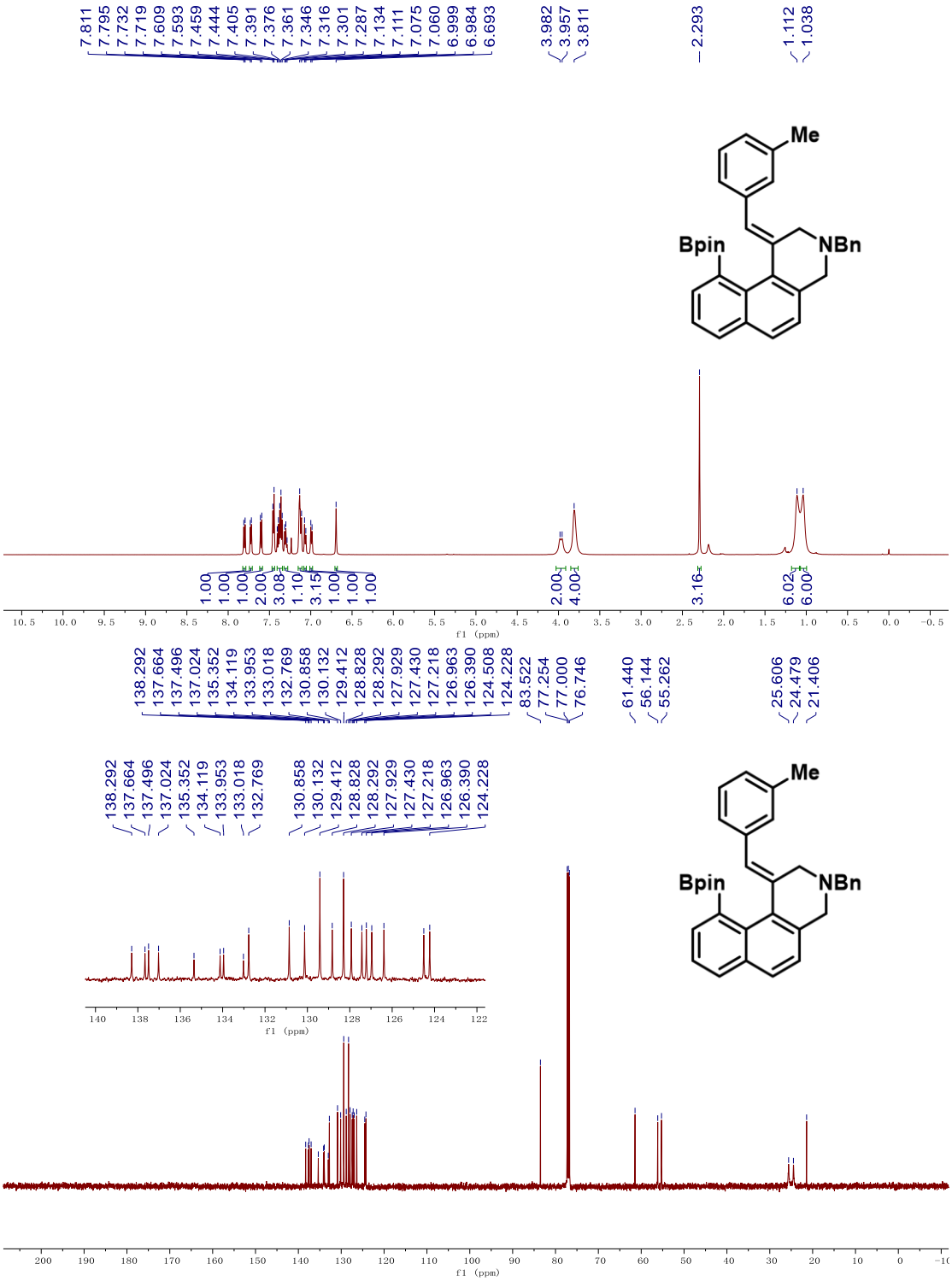
^{1}H NMR of **5e** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5e** (125 MHz, $CDCl_3$)



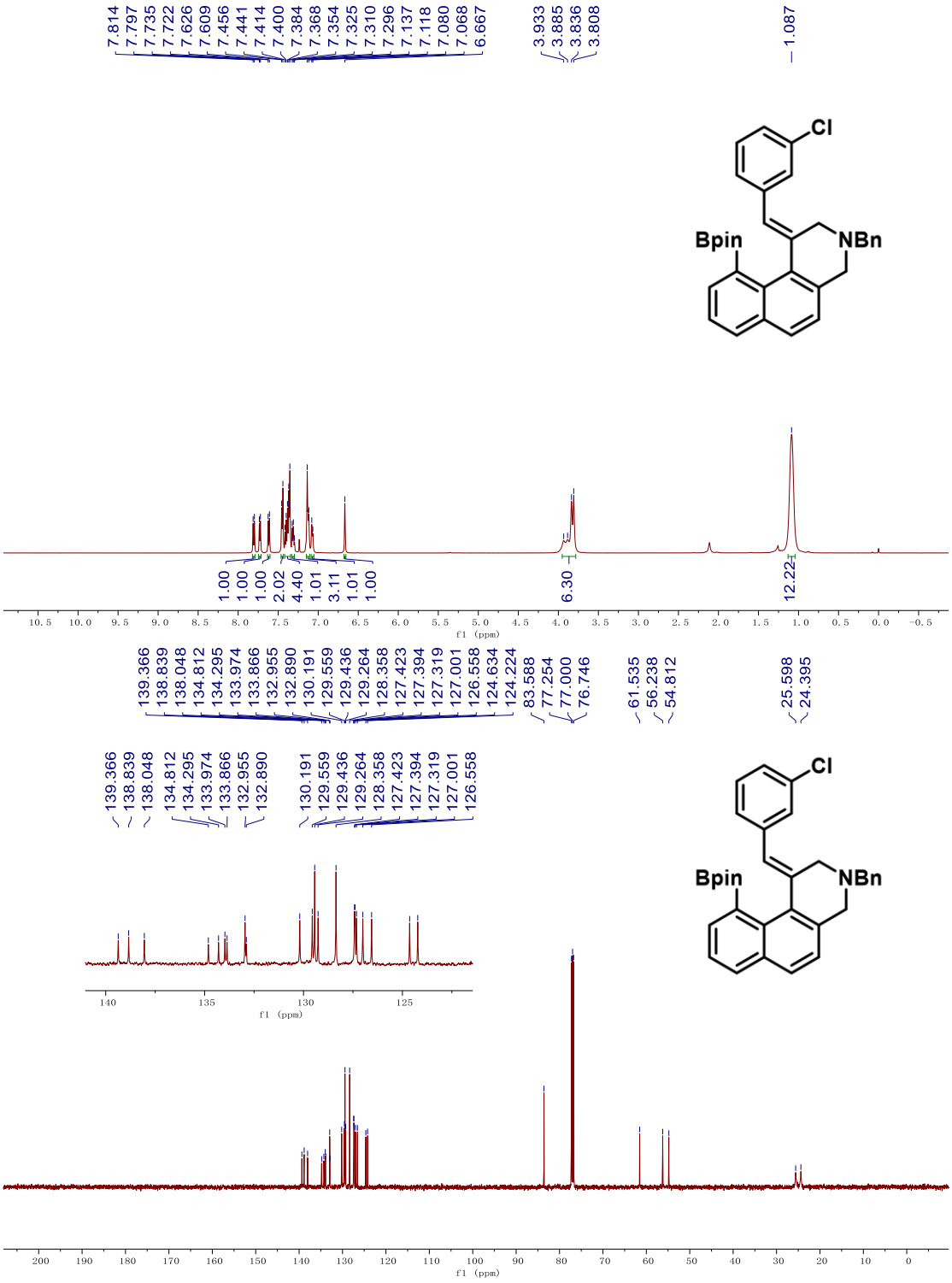
^{1}H NMR of **5f** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5f** (125 MHz, $CDCl_3$)



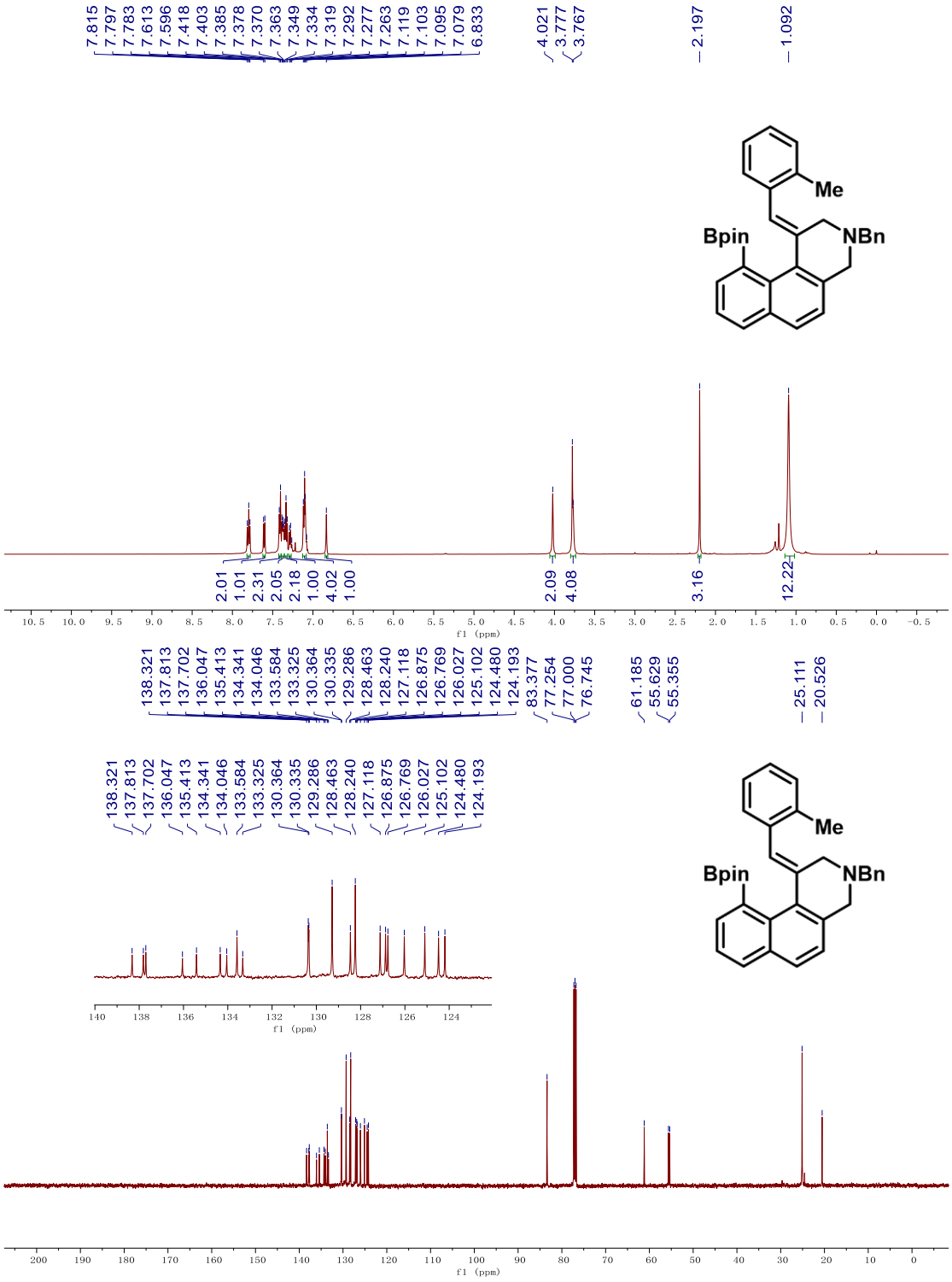
^{1}H NMR of **5g** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5g** (125 MHz, $CDCl_3$)



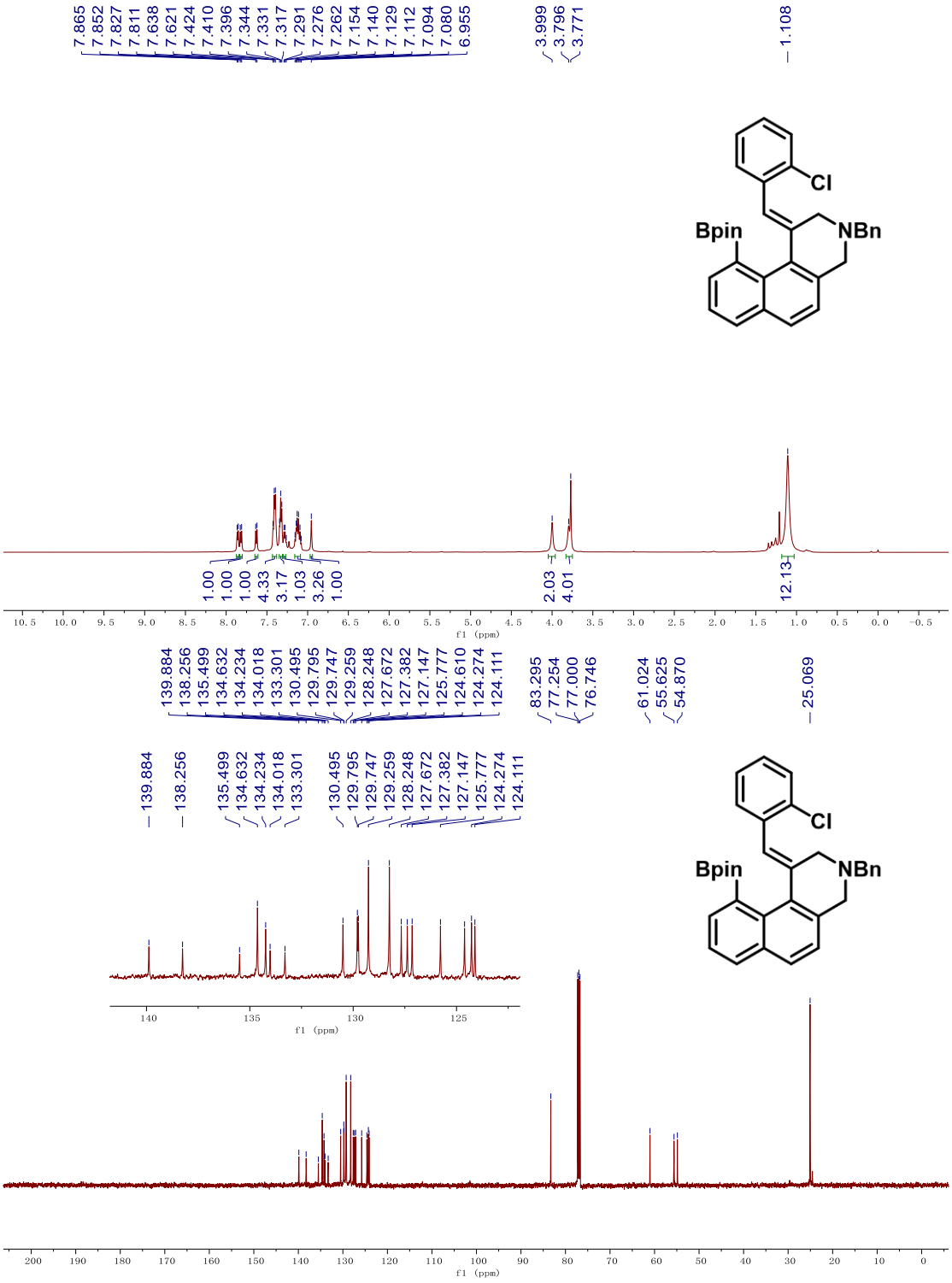
^{1}H NMR of **5h** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5h** (125 MHz, $CDCl_3$)



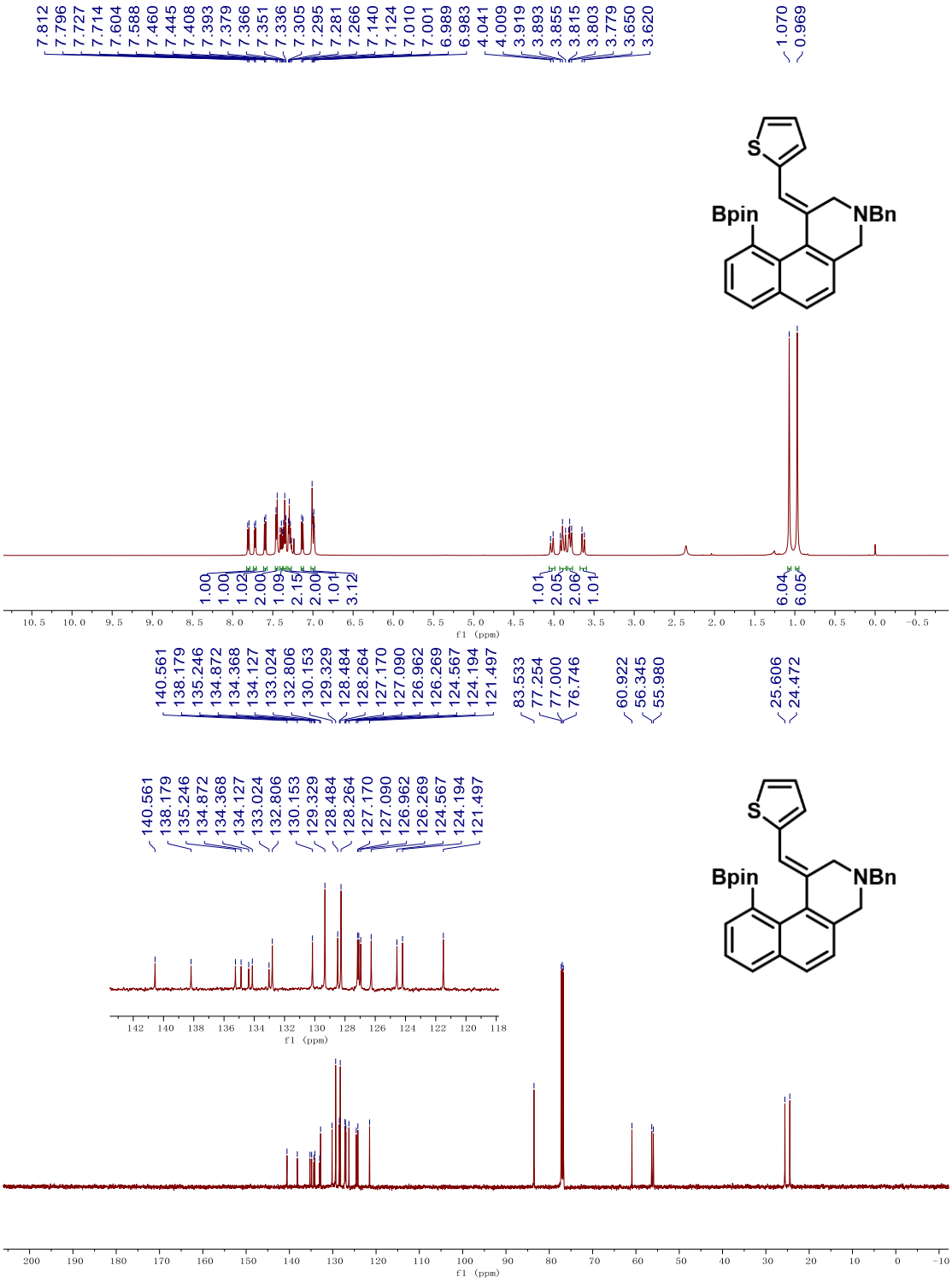
^{1}H NMR of **5i** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5i** (125 MHz, $CDCl_3$)



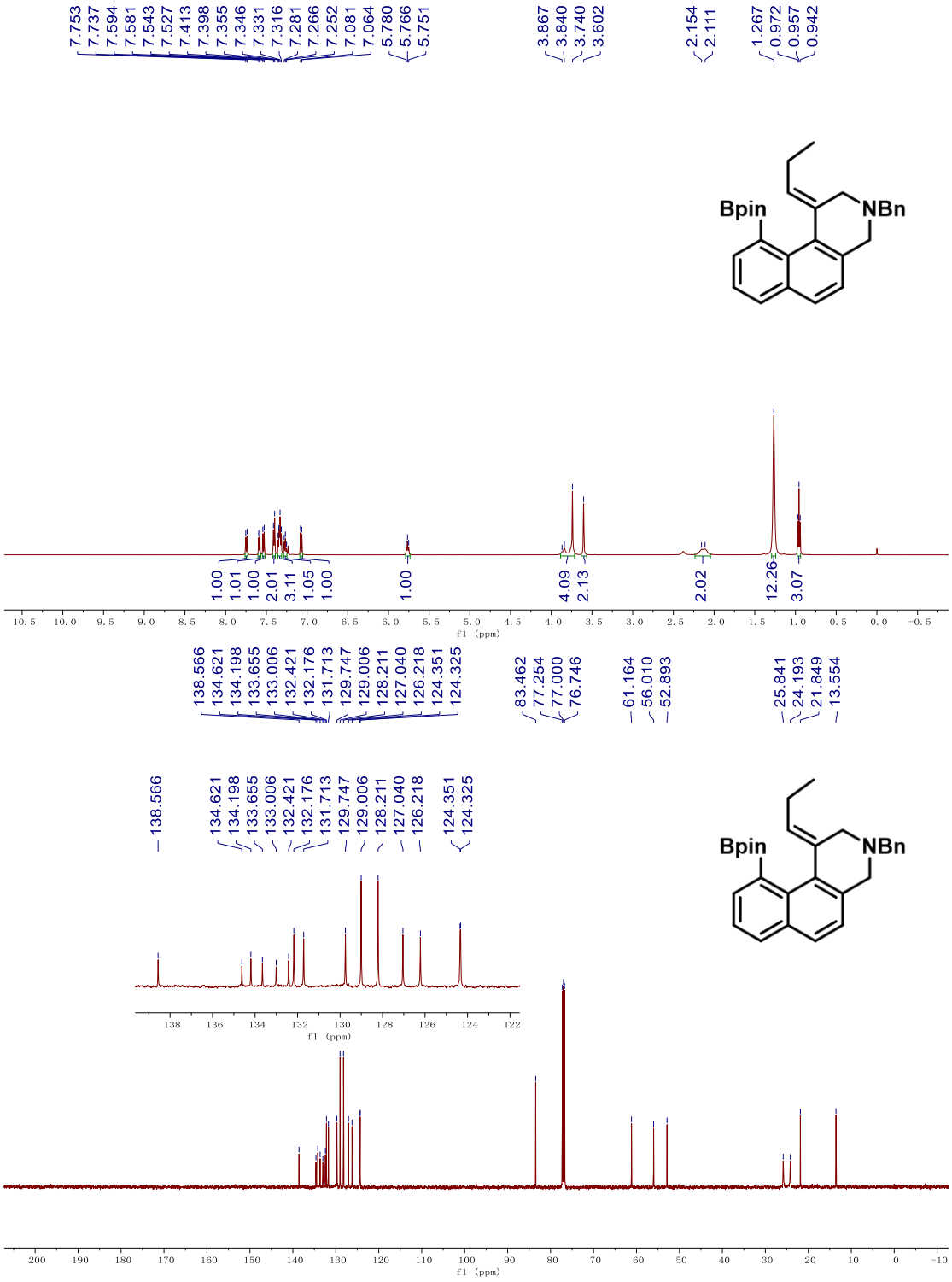
^{1}H NMR of **5l** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5l** (125 MHz, $CDCl_3$)



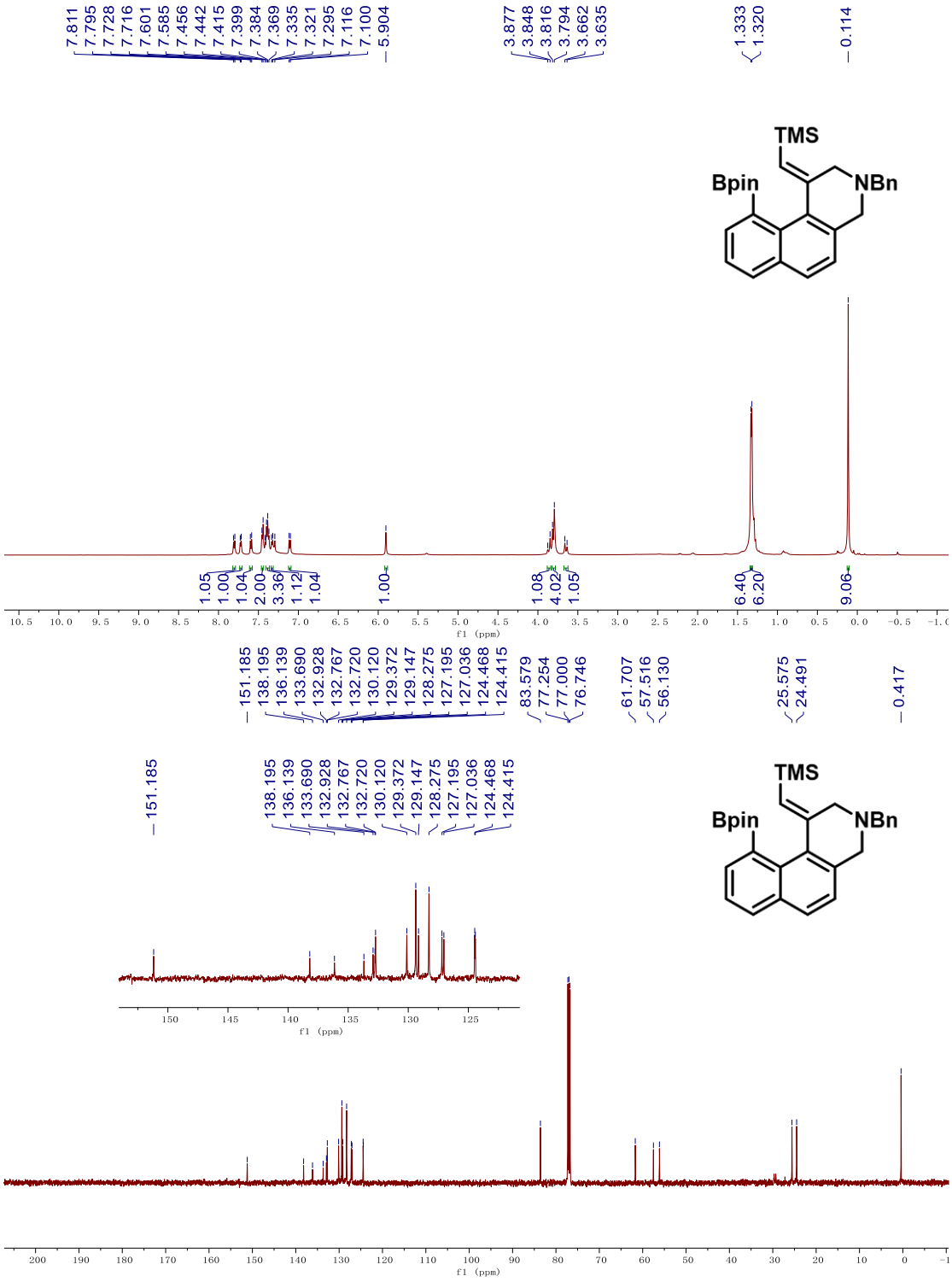
^{1}H NMR of **5q** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5q** (125 MHz, $CDCl_3$)



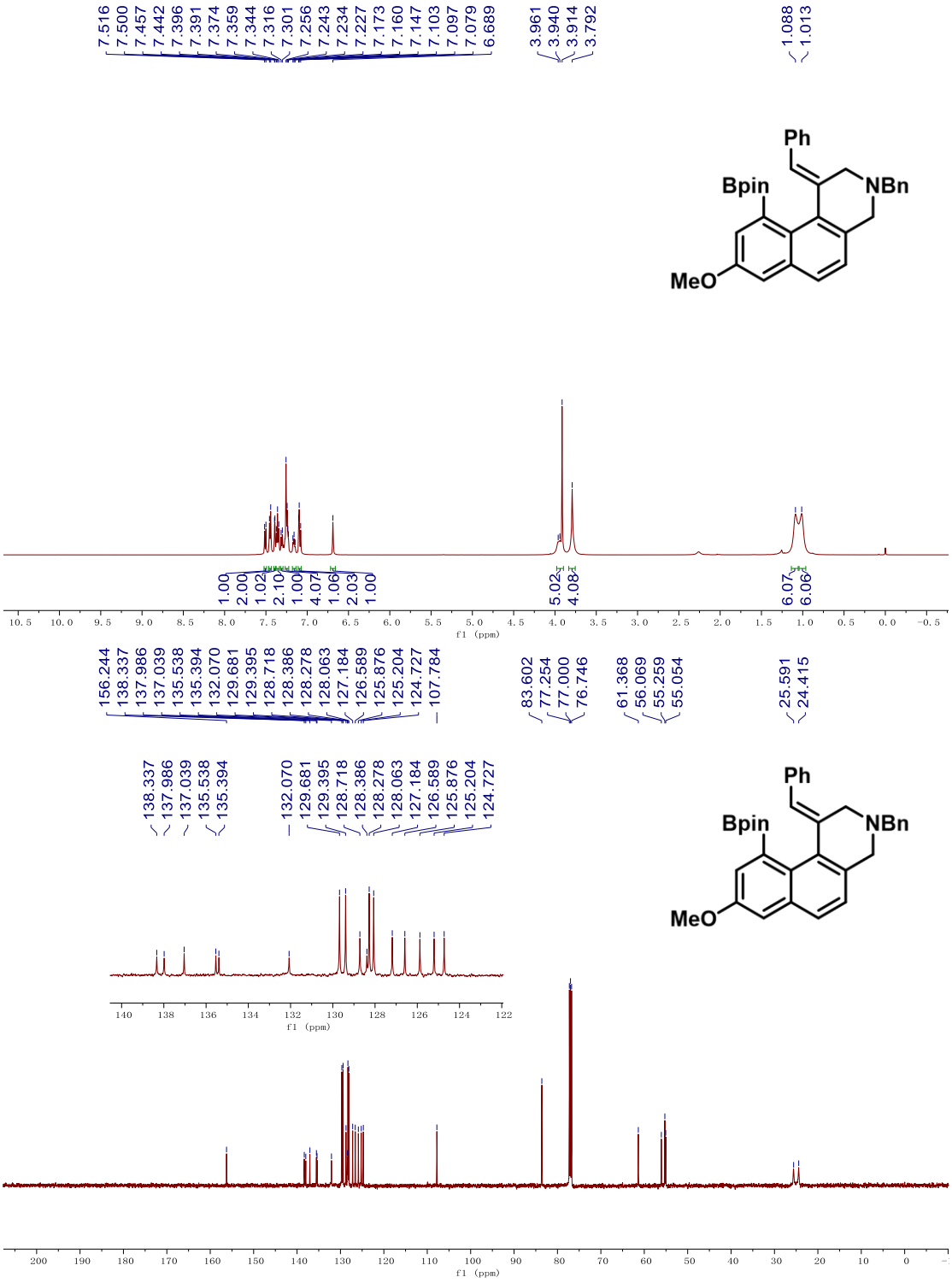
^{1}H NMR of **5r** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5r** (125 MHz, $CDCl_3$)



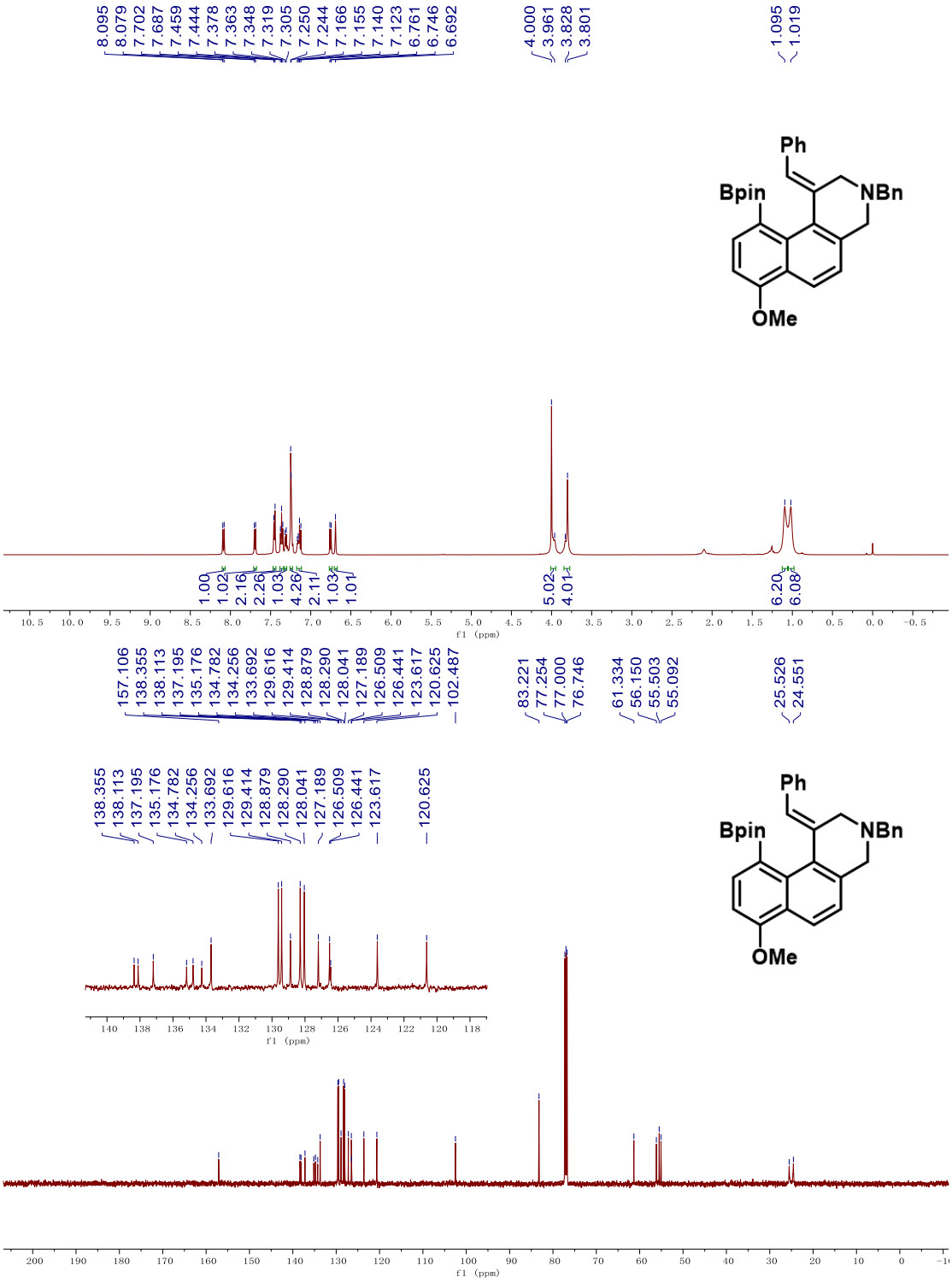
^{1}H NMR of **5s** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5s** (125 MHz, $CDCl_3$)



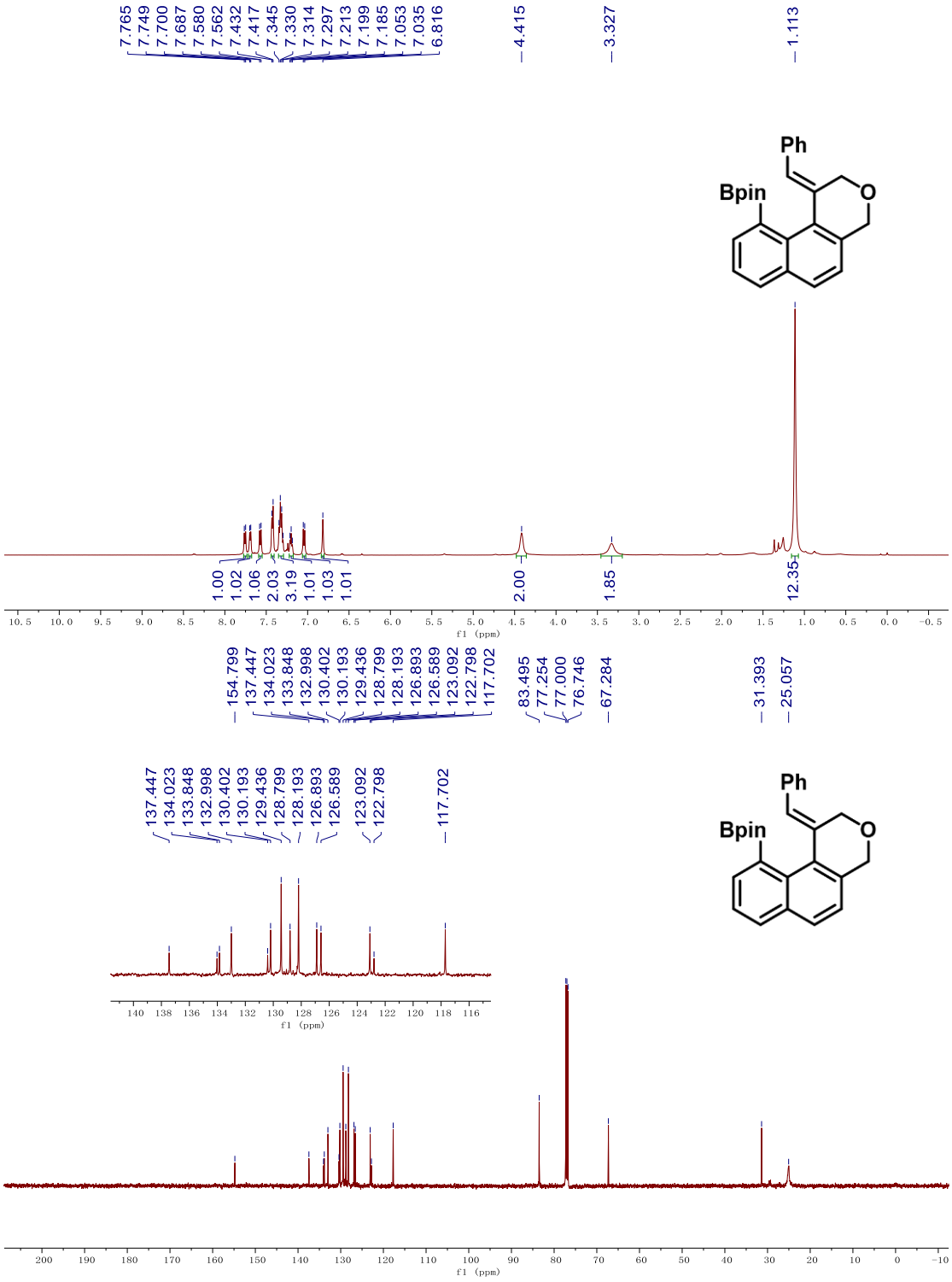
^{1}H NMR of **5t** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5t** (125 MHz, $CDCl_3$)



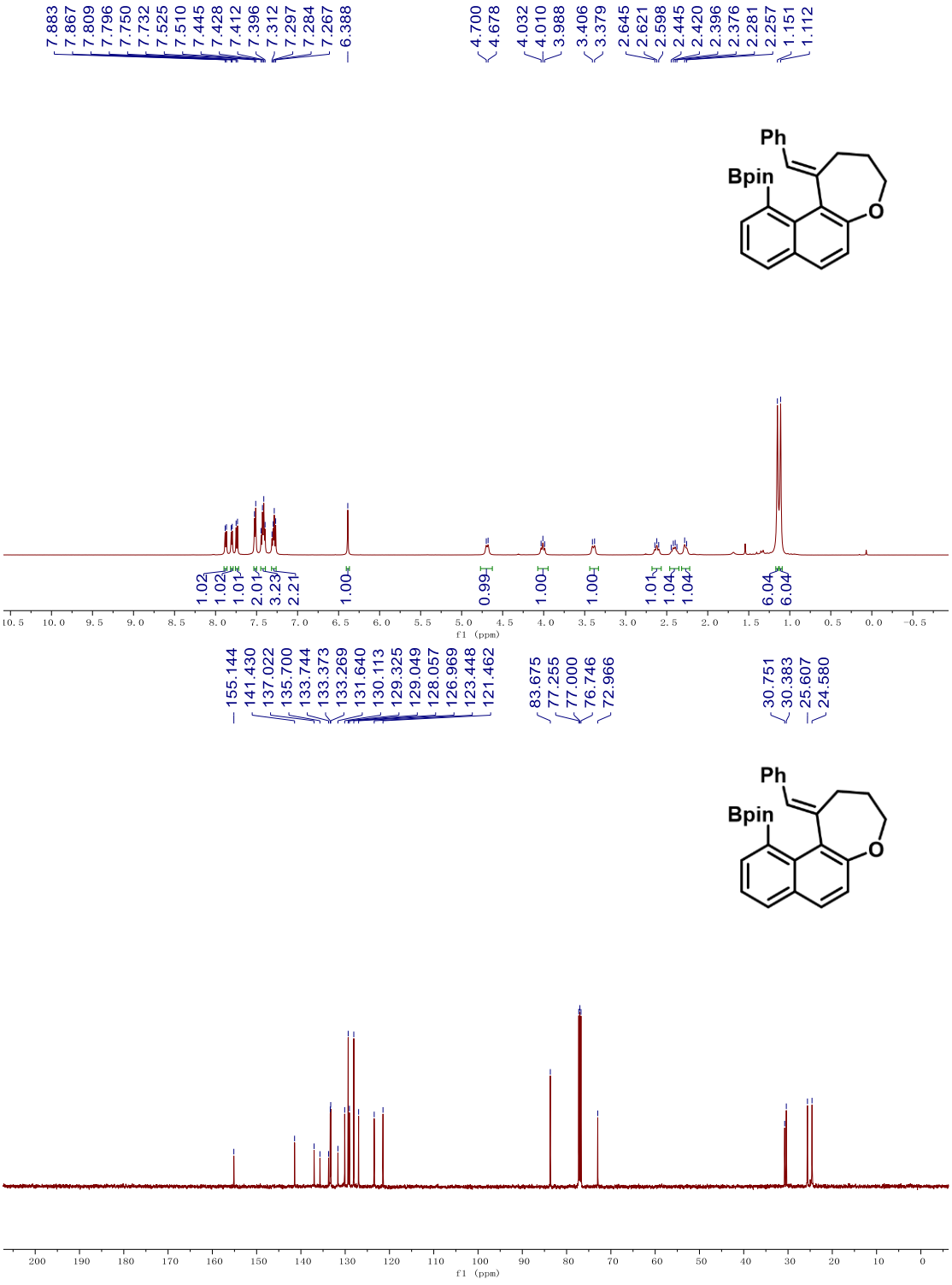
^{1}H NMR of **5v** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5v** (125 MHz, $CDCl_3$)



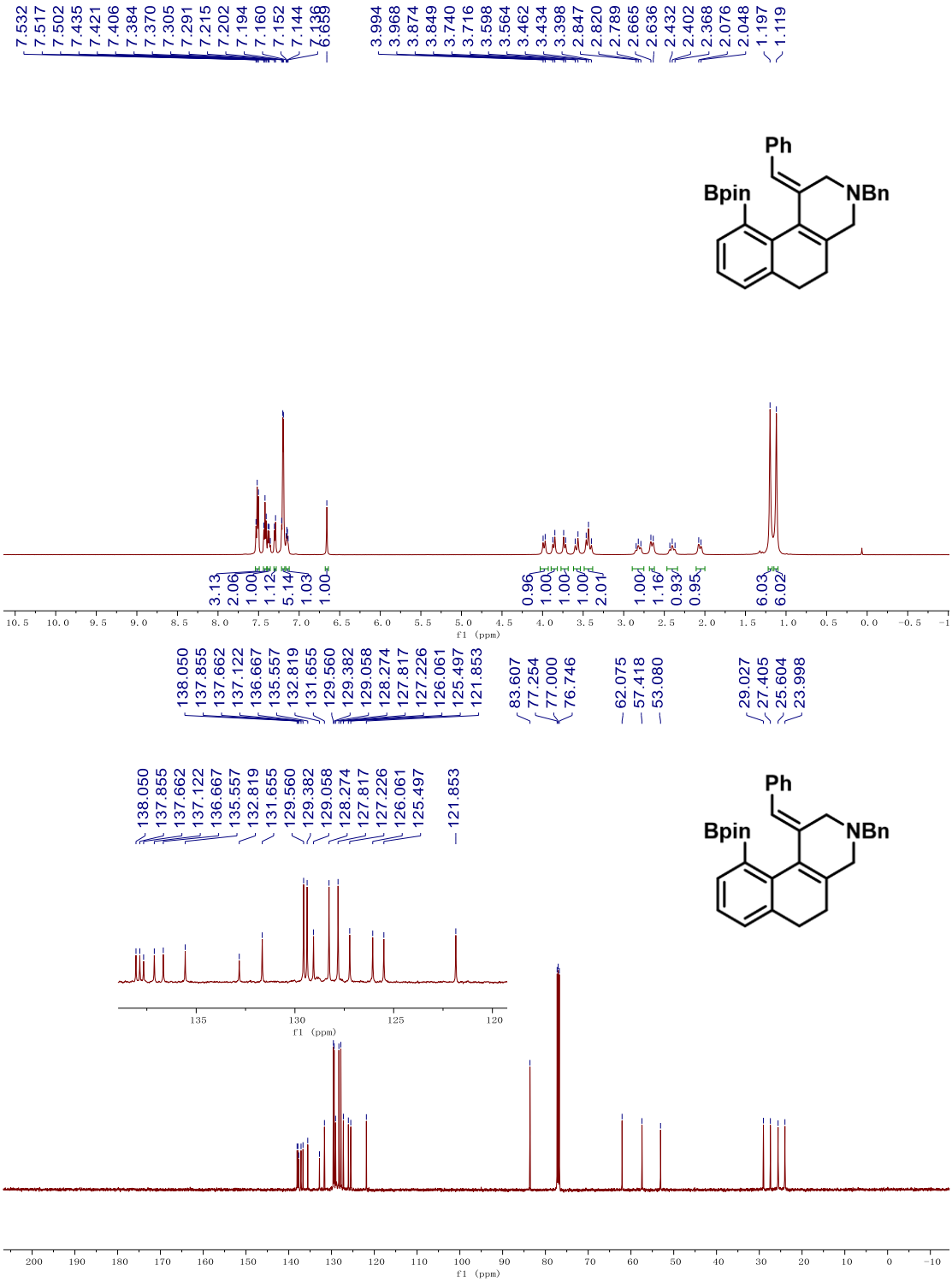
^{1}H NMR of **5w** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5w** (125 MHz, $CDCl_3$)



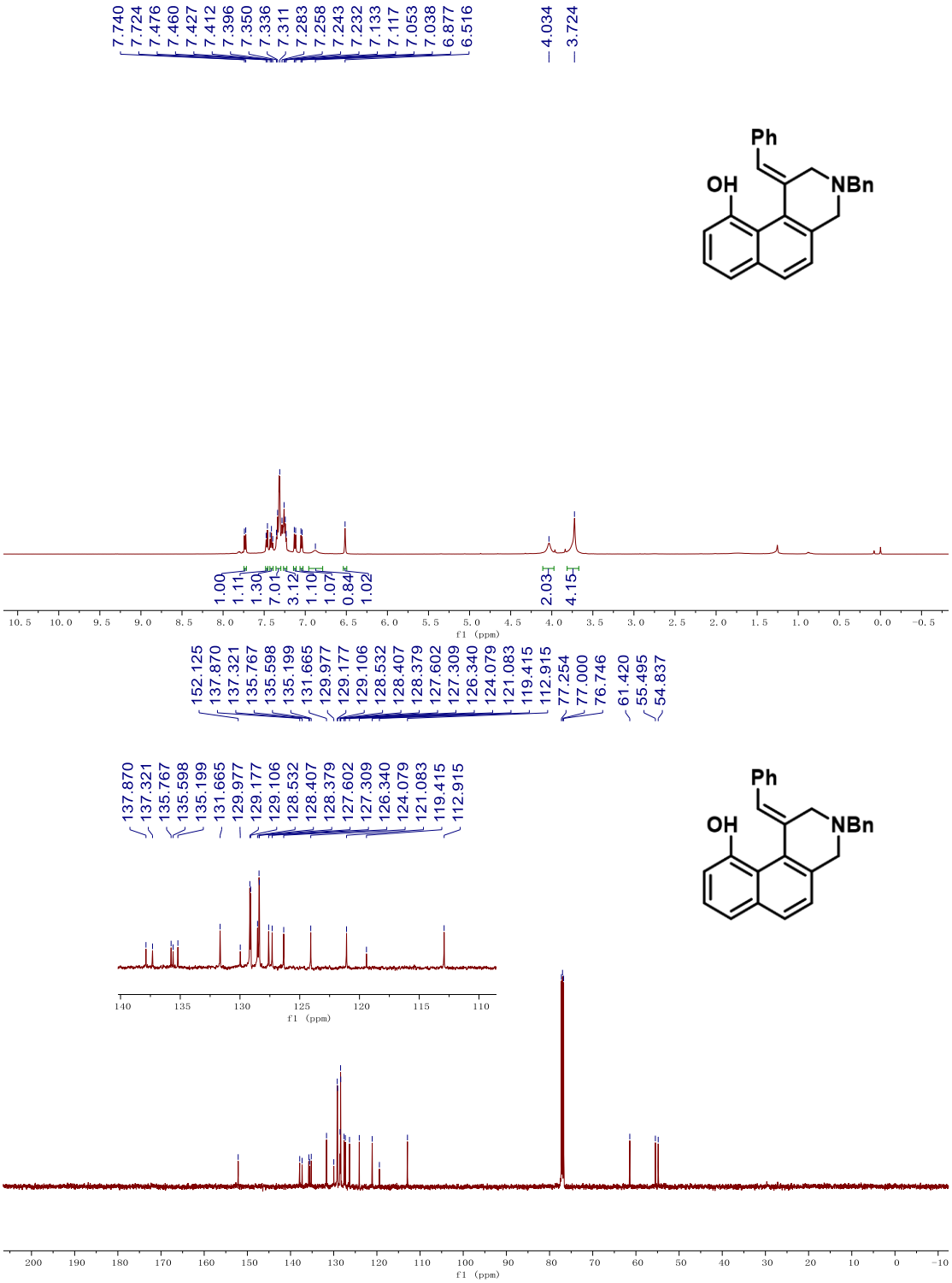
^{1}H NMR of **5x** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5x** (125 MHz, $CDCl_3$)



^{1}H NMR of **5y** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5y** (125 MHz, $CDCl_3$)



^{1}H NMR of **6** (500 MHz, $CDCl_3$) and ^{13}C NMR of **6** (125 MHz, $CDCl_3$)



^{1}H NMR of **7** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7** (125 MHz, $CDCl_3$)