Supporting Information

Co-catalyzed Ring-opening Addition of Azabenzonorbornadienes *via* C(sp^3)-H bond Activation of 8-Methylquinoline

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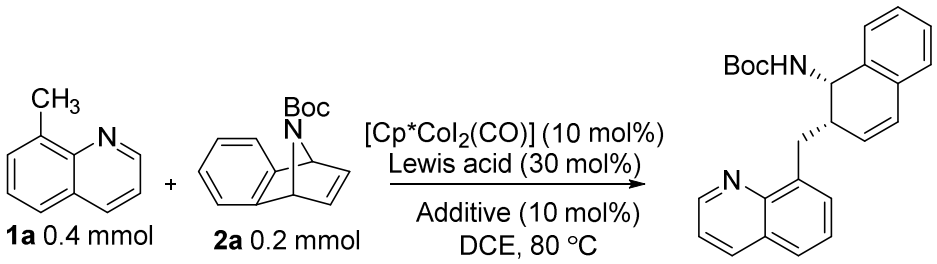
1. General information

The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox ((Mikrouna, Supper1220/750). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. $CDCl_3$ was used as solvent. Chemical shifts (δ) were reported in ppm with tetramethylsilane (TMS) as internal standard and *J* values were given in Hz. Melting points were measured on X-4 melting point apparatus and uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents. Anhydrous THF (Tetrahydrofuran), toluene, 1,4-dioxane were distilled from sodium benzophenone ketyl prior to use. Anhydrous DCE (dichloroethane), were distilled from calcium hydride. Commercially available reagents and solvents were used without further purification unless indicated otherwise.

2.Optimization table for the formation of 3aa[a,b]

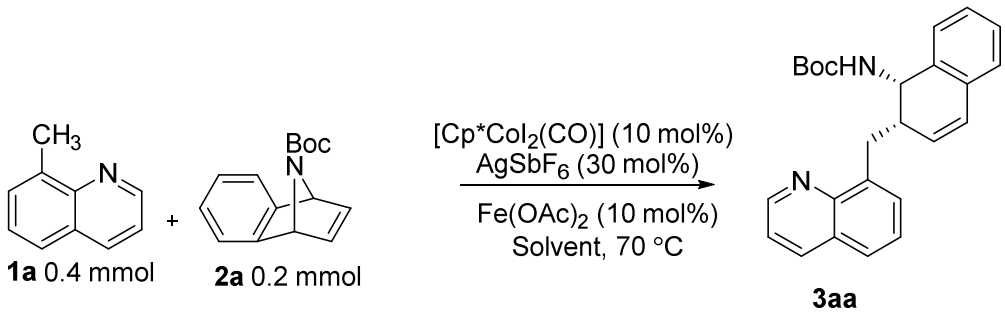


Entry	[M]	Ag	Additive	Solvent	Temp. (℃)	Time (h)	Yield (%)[b]
1	[Cp*CoI_2(CO)]	$AgSbF_6$	NaOAc	DCE	80	48	44
2	[Cp*CoI_2(CO)]	$AgPF_6$	NaOAc	DCE	80	48	35
3	[Cp*CoI_2(CO)]	$AgBF_4$	NaOAc	DCE	80	48	9
4	[Cp*CoI_2(CO)]	AgOTf	NaOAc	DCE	80	48	29
5	[Cp*CoI_2(CO)]	$AgNTf_2$	NaOAc	DCE	80	48	35

6	[Cp*CoI_2(CO)]	-	NaOAc	DCE	80	48	NR[c]
7	[Cp*CoI_2(CO)]	$AgSbF_6$	LiOAc	DCE	80	48	44
8	[Cp*CoI_2(CO)]	$AgSbF_6$	KOAc	DCE	80	48	NR
9	[Cp*CoI_2(CO)]	$AgSbF_6$	CsOAc	DCE	80	48	NR
10	[Cp*CoI_2(CO)]	$AgSbF_6$	AgOAc	DCE	80	48	14
11	**[Cp*CoI_2(CO)]**	**$AgSbF_6$**	**$Fe(OAc)_2$**	**DCE**	**80**	**48**	**54**
12	[Cp*CoI_2(CO)]	$AgSbF_6$	$Cu(OAc)_2$	DCE	80	48	18
13	[Cp*CoI_2(CO)]	$AgSbF_6$	$Zn(OAc)_2$	DCE	80	48	36
14	[Cp*CoI_2(CO)]	$AgSbF_6$	$PhI(OAc)_2$	DCE	80	48	ND
15	[Cp*CoI_2(CO)]	$AgSbF_6$	Ag_2CO_3	DCE	80	48	Trace
16	[Cp*CoI_2(CO)]	$AgSbF_6$	AcOH	DCE	80	48	Trace
17	[Cp*CoI_2(CO)]	$AgSbF_6$	PivOH	DCE	80	48	32
18	[Cp*CoI_2(CO)]	$AgSbF_6$	-	DCE	80	48	9
19[d]	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	DCE	80	48	50
20[e]	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	DCE	80	48	56
21[f]	**[Cp*CoI_2(CO)]**	**$AgSbF_6$**	**$Fe(OAc)_2$**	**DCE**	**80**	**48**	**57**

[a]reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), [Cp*CoI_2(CO)] (5 mol%), Lewis acid (30 mol%), Additive (0.2 mmol), DCE (2 mL) 80 °C under argon atmosphere. [b]Isolated yield. [c]NR = No Reaction. [d]Fe(OAc) (2 equiv). [e]Fe(OAc) (50 mol%). [f]Fe(OAc) (10 mol%).

3.Furhter optimization of reaction conditions[a,b]



1a 0.4 mmol + **2a** 0.2 mmol → **3aa**

Entry	[M]	Ag	Additive	Solvent	Temp. (℃)	Time (h)	Yield (%)[b]
1	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	Toluene	80	48	55
2	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	1,4-dioxane	80	48	25
3	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	THF	80	48	10
4	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	DCM	80	48	51
5	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	TFE	80	48	20
6	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	MTBE	80	48	16
7	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	PhCl	80	48	46
8	[Cp*CoI_2(CO)]	**$AgSbF_6$**	**$Fe(OAc)_2$**	**PhOMe**	**80**	**48**	**64**
9[c]	[Cp*CoI_2(CO)]	**$AgSbF_6$**	**$Fe(OAc)_2$**	**PhOMe**	**80**	**16**	**70**
10	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	PhOMe	60	48	70
11	**[Cp*CoI_2(CO)]**	**$AgSbF_6$**	**$Fe(OAc)_2$**	**PhOMe**	**70**	**24**	**78**
12	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	PhOMe	90	24	69
13[d]	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	PhOMe	70	24	30
14[e]	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	PhOMe	70	24	72
15[f]	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	PhOMe	70	24	71
16[g]	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	PhOMe	70	24	70
17[h]	**[Cp*CoI_2(CO)]**	**$AgSbF_6$**	**$Fe(OAc)_2$**	**PhOMe**	**70**	**18**	**87**
18[i]	[Cp*CoI_2(CO)]	$AgSbF_6$	$Fe(OAc)_2$	PhOMe	70	17	82

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), [Cp*CoI_2(CO)] (5 mol%), $AgSbF_6$ (30 mol%), $Fe(OAc)_2$ (10 mol%), Solvent (2mL) at 80 °C under argon atmosphere. [b]Isolated yields.

[c][Cp*CoI_2(CO)] (10 mol%). [d]$AgSbF_6$ (20 mol%). [e]$AgSbF_6$ (40 mol%). [f]PhOMe (1 mL). [g]PhOMe (3 mL). [h]**1a** (0.6 mmol). [i]**1a** (0.8 mmol).

4. General procedure

a) Typical procedure for the Ring-opening Addition of Azabenzonorbornadiene with 8-Methylquinoline:

Under argon atmosphere, [Cp*CoI_2(CO)] (9.8 mg, 0.02 mmol, 10 mol%), $Fe(OAc)_2$ (3.5 mg, 0.02 mmol, 10 mol%), $AgSbF_6$ (21.5 mg, 0.06 mmol, 30 mol%), 8-methylquinoline **1a** (0.6 mmol), Azabenzonorbornadiene **2a** (0.2 mmol), and PhOMe (2 mL) were added sequentially to a 25 mL Schlenk tube equipped with a magnetic stir bar. The reaction mixture was stirred at 70 ^oC under argon atmosphere with TLC monitoring until the complete consumption of **2a**. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give the ring-opening addition product **3aa** in 87% yield.

b) General procedure for the synthesis of substituted 8-methylquinolines:[1]

The substrates **1f**, **1m**, **1p**,[2] 8-methylquinoline-*d3*,[3] were prepared according to the literatures.

Glycerine (12 mmol) was added over a period of 0.5 h to a solution of substituted *o*-toluidine (10 mmol), NaI (0.13 mmol) and 80% H_2SO_4 (45 mmol) at 140 °C. The reaction mixture was allowed tostir at the same temperature for 24 h. Next the mixture was neutralized with 25% aq. NaOH solution and PH was adjusted to 9-10 and extracted with toluene (30 mL x 3). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel with hexane/ethyl acetate as eluant. All of yields were not optimized.

5. Reference

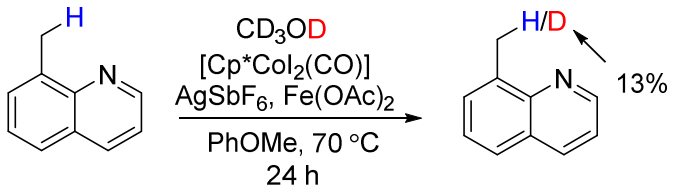
[1] C. O'Murchu, *Synthesis*, **1989**, *11*, 880.

[2] Evans, P.; Hogg, P.; Grigg, R.; Nurnabi, M.; Hinsley, J.; Sridharan, V.; Suganthan, S.;Korn, S.; Collard, S.; Muir, J. E. *Tetrahedron,* **2005**, *61*, 9696.

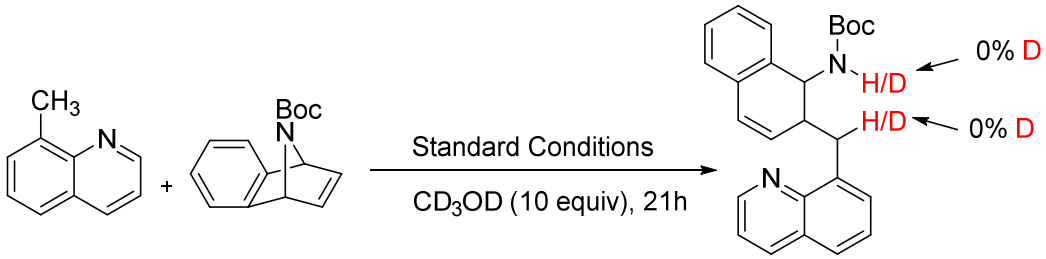
[3] Suggs, J.W.; Pearson, G. D. N. *J. Org. Chem.* **1980**, *45*, 1514.

6. Mechanistic Experiments

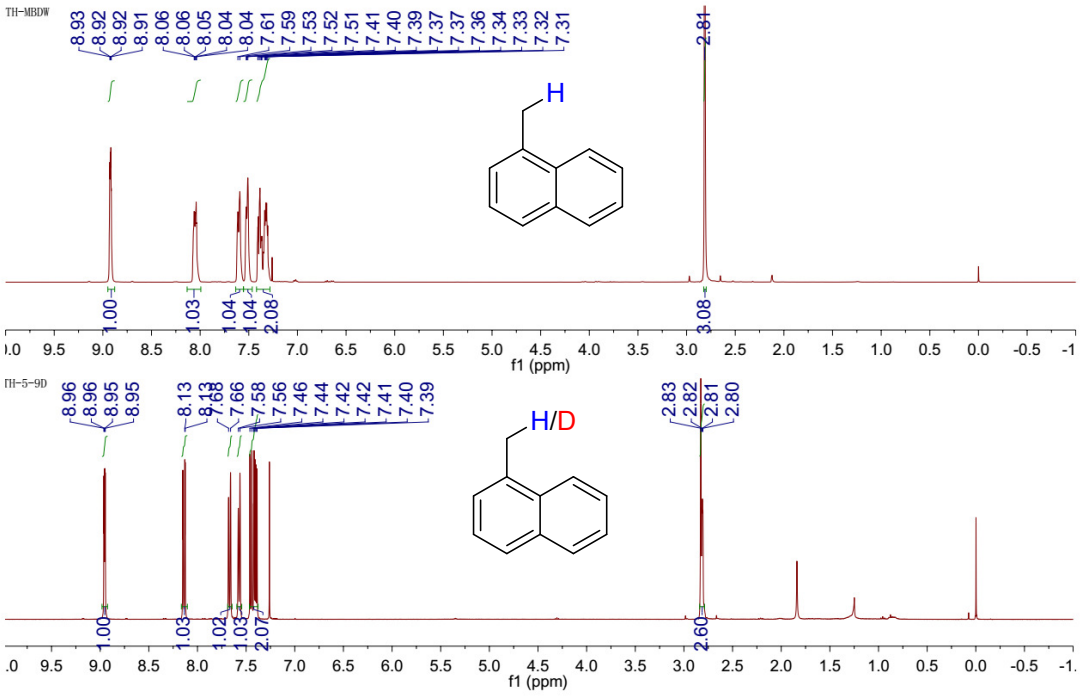
a) H/D exchange experiments:



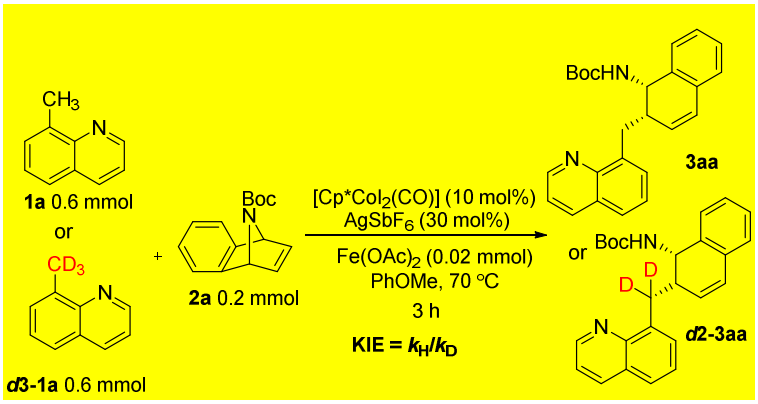
Procedures for the reaction without Azabenzonorbornadienes: Under argon atmosphere, [Cp*CoI_2(CO)] (9.8 mg, 0.02 mmol, 10 mol%), $Fe(OAc)_2$ (3.5 mg, 0.02 mmol, 10 mol%), $AgSbF_6$ (21.5 mg, 0.06 mmol, 30 mol%), 8-methylquinoline (0.2 mmol), CD_3OD (10 equiv.), and PhOMe (2 mL) were added sequentially to a 25 mL Schlenk tube equipped with a magnetic stir bar. The reaction was stirred at 70 ^oC for 24 h. Afterwards it was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. The recovered 8-methylquinoline was obtained by flash columnchromatography on silica gel (eluent: EtOAc/PE = 1:10).



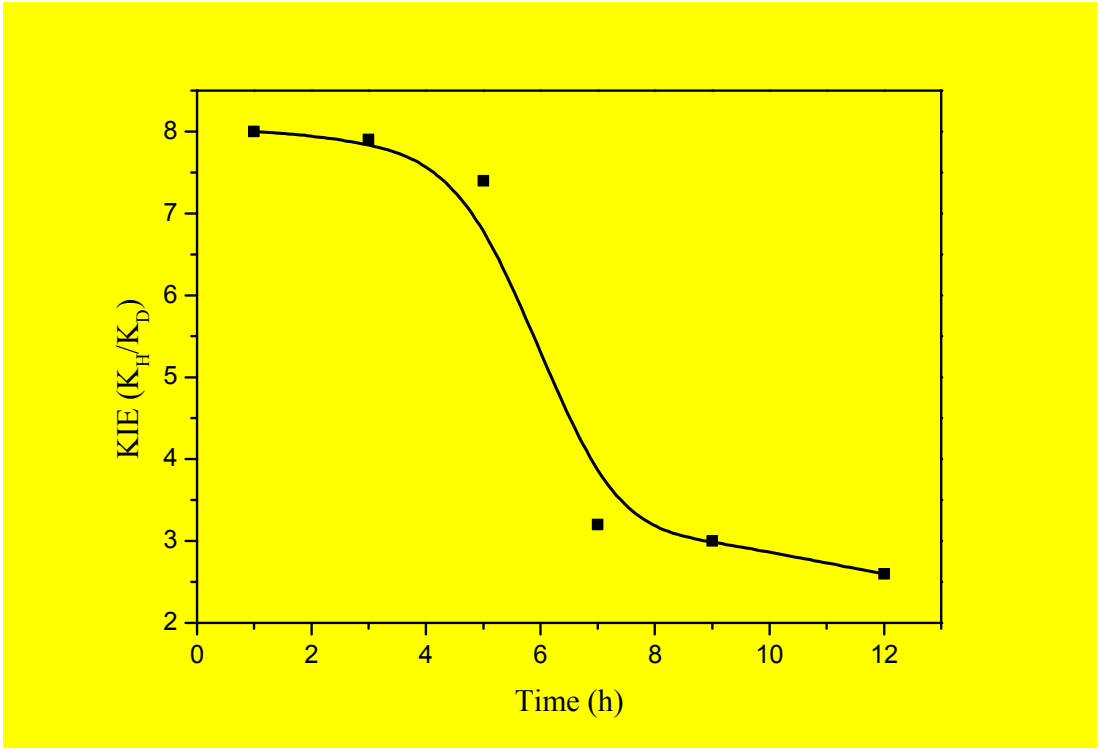
^{1}H NMR (400 MHz $CDCl_3$) spectra of H/D exchange experiments



b) Parallel Experiment

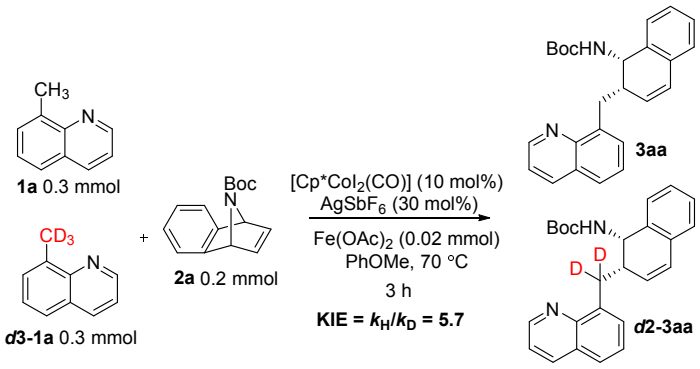


Time (h)	1	3	5	7	9	12
3aa	24%	63%	74%	76%	77%	79%
d2-3aa	3%	8%	10%	24%	26%	30%
KIE (K_H/K_D)	8	7.9	7.4	3.2	3.0	2.6



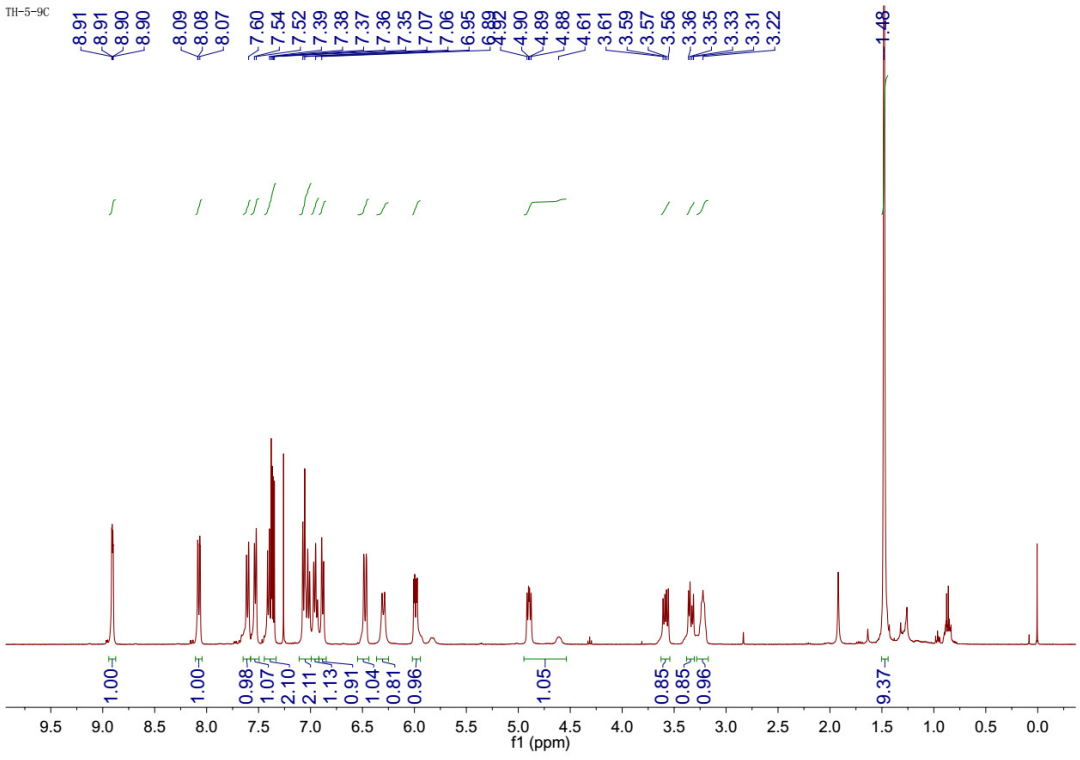
Under an argon atmosphere, in two 25 mL Schlenk test tubes equipped with a magnetic stir bar, sequentially weigh the azabenzonorbornene substrate (0.2 mmol) and [Cp*CoI_2(CO)] (0.02 mmol), $AgSbF_6$ (0.06 mmol) $Fe(OAc)_2$ (0.02 mmol), **1a** (0.6 mmol) or ***d3*-1a-** (0.6 mmol) were added to different test tubes with micro syringes, and labeled, and finally added 2 mL of anhydrous PhOMe solvent, plug it with a rubber stopper and send it out of the glove box, placed in a 70 °C oil bath and heated to react for 3 hours. The reaction mixture was cooled to room temperature, concentrated under reduced pressure and purified by silica gel column chromatography, the pure product obtained was weighed to calculate the yield, and measured KIE = 7.9.

c) Competitive Experiment:



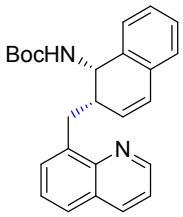
Under an argon atmosphere, in a 25 mL Schlenk tube equipped with a magnetic stirrer, weigh azabenzonorbornadiene **2a** (0.2 mmol), [Cp*CoI_2(CO)] (0.02 mmol), $AgSbF_6$ (0.06 mmol), $Fe(OAc)_2$ (0.02 mmol), then **1a** (0.3 mmol) and ***d3-1a*** (0.3 mmol) were added to the test tube with a micro syringe, and finally added 2 mL of anhydrous PhOMe solvent, plug the rubber stopper and taken out of the glove box, then put into an oil bath at 70 °C to heat the reaction for 3 hours. The reaction mixture was cooled to room temperature, concentrated under reduced pressure and purified by silica gel column chromatography. KIE = 5.7 was measured by ^{1}H NMR spectrum analysis of the product.

^{1}H NMR of product obtained from the KIE experiment for intermolecular competition.



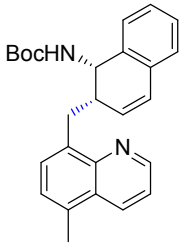
7. Characterization Data of Products

***tert*-butyl (2-(quinolin-8-ylmethyl)-1,2-dihydronaphthalen-1-yl)carbamate (3aa)**



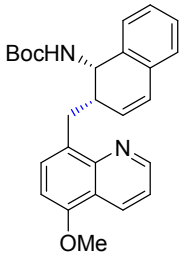
White solid (67.3 mg, 87%), M. p. = 138-140 □. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.0, 1.5 Hz, 1H), 8.05 (dd, J = 8.2, 1.5 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 6.8 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.34 (dd, J = 8.2, 4.2 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 7.2 Hz, 1H), 6.48 (d, J = 9.5 Hz, 1H), 6.37 (d, J = 9.8 Hz, 1H), 6.00 (dd, J = 9.6, 3.9 Hz, 1H), 4.96 (dd, J = 9.6, 6.0 Hz, 1H), 3.60 (dd, J = 13.2, 7.1 Hz, 1H), 3.37 (dd, J = 13.2, 5.9 Hz, 1H), 3.25 (s, 1H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.0, 146.8, 137.7, 136.5, 136.2, 132.9, 131.0, 130.6, 128.3, 128.0, 127.3, 127.2, 126.5, 126.0, 125.8, 125.7, 120.8, 78.9, 51.1, 39.6, 31.2, 28.5. HRMS(EI): m/z calculated for $C_{25}H_{26}N_2O_2$ $[M]^+$: 386.1994, found: 386.2000.

***tert*-butyl (2-((5-methylquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ba)**



Colorless oily liquid (74.5 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 2.7 Hz, 1H), 8.14 (dd, J = 8.5, 1.4 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.28 (dd, J = 8.5, 4.1 Hz, 1H), 7.12 (d, J = 7.1 Hz, 1H), 7.01 – 6.91 (m, 2H), 6.87 (t, J = 7.3 Hz, 1H), 6.80 (d, J = 7.2 Hz, 1H), 6.37 (d, J = 9.4 Hz, 1H), 6.10 (d, J = 9.6 Hz, 1H), 5.88 (dd, J = 9.5, 3.6 Hz, 1H), 4.79 (dd, J = 9.4, 5.9 Hz, 1H), 3.43 (dd, J = 13.1, 7.1 Hz, 1H), 3.23 (dd, J = 13.1, 6.1 Hz, 1H), 3.12 (s, 1H), 2.50 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 148.6, 147.2, 136.4, 135.8, 133.0, 132.9, 131.3, 130.3, 127.9, 127.7, 127.3, 127.1, 126.6, 125.9, 120.4, 79.0, 51.2, 39.8, 31.3, 28.6, 18.6. HRMS(ESI): m/z calculated for $C_{26}H_{28}N_2NaO_2$ $[M+Na]^+$: 423.2049, found: 423.2046.

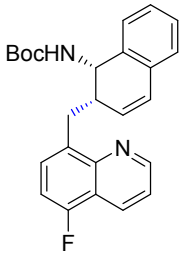
***tert*-butyl (2-((5-methoxyquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ca)**



White solid (72.5 mg, 87%), M. p. = 78-80 □. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 4.1, 1.6 Hz, 1H), 8.51 (dd, J = 8.4, 1.6 Hz, 1H), 7.42 (d, J = 7.9 Hz, 1H), 7.34 (dd, J = 8.4, 4.2 Hz, 1H), 7.06 (dd, J = 15.9, 7.4 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 7.3 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 6.48 (d,

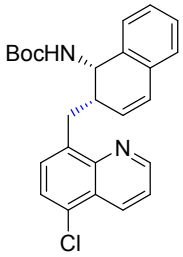
J = 9.6 Hz, 1H), 6.21 (d, *J* = 9.8 Hz, 1H), 5.99 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.88 (dd, *J* = 9.8, 5.7 Hz, 1H), 3.95 (s, 3H), 3.49 (dd, *J* = 13.2, 6.8 Hz, 1H), 3.25 (dd, *J* = 13.1, 6.3 Hz, 1H), 3.19 (d, *J* = 5.6 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 154.0, 149.4, 147.4, 136.4, 133.0, 131.4, 131.1, 130.3, 129.4, 127.9, 127.3, 127.2, 125.9, 125.8, 120.9, 119.9, 79.0, 55.7, 51.1, 39.7, 30.9, 28.6. HRMS(ESI): m/z calculated for $C_{26}H_{28}N_2NaO_3$ $[M+Na]^+$: 439.1998, found: 439.1995.

***tert*-butyl (2-((5-fluoroquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate(3da)**



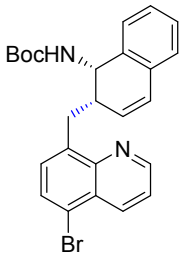
White solid (53.4 mg, 66%), M. p. = 138-140 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.34 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.10 – 6.99 (m, 3H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 9.4 Hz, 1H), 6.21 (d, *J* = 9.9 Hz, 1H), 5.96 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.88 (dd, *J* = 9.9, 5.7 Hz, 1H), 3.56 (dd, *J* = 12.8, 6.4 Hz, 1H), 3.30 – 3.15 (m, 2H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 155.9, 155.4, 149.9, 147.1, 136.1, 133.5, 132.9, 130.8, 129.8, 128.2, 127.3, 125.9, 125.7, 120.9, 119.0, 109.5, 79.1, 50.9, 39.6, 30.9, 28.6. HRMS(ESI): m/z calculated for $C_{25}H_{25}FN_2NaO_2$ $[M+Na]^+$: 427.1798, found: 427.1793.

***tert*-butyl (2-((5-chloroquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ea)**



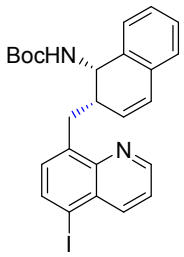
White solid (58.1 mg, 69%), M. p. = 150-152 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.0, 1.4 Hz, 1H), 8.49 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.45 (dt, *J* = 9.0, 6.0 Hz, 3H), 7.07 – 6.98 (m, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 9.5 Hz, 1H), 6.13 (d, *J* = 9.9 Hz, 1H), 5.95 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.88 (dd, *J* = 9.9, 5.9 Hz, 1H), 3.55 (dd, *J* = 13.1, 6.9 Hz, 1H), 3.27 (dd, *J* = 13.1, 6.2 Hz, 1H), 3.20 (d, *J* = 5.8 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.6, 147.4, 137.2, 136.1, 133.4, 132.9, 130.7, 130.3, 129.6, 128.3, 127.4, 127.3, 126.2, 126.1, 125.9, 125.7, 121.63, 8.16, 50.9, 39.7, 31.1, 28.6. HRMS(ESI): m/z calculated for $C_{25}H_{25}ClN_2NaO_2$ $[M+Na]^+$: 443.1502, found: 443.1507.

***tert*-butyl (2-((5-bromoquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3fa)**



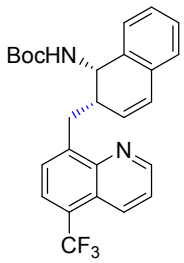
White solid (63.3 mg, 69%), M. p. = 150-152 □. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.0, 1.3 Hz, 1H), 8.46 (dd, J = 8.5, 1.5 Hz, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.46 (dd, J = 8.5, 4.2 Hz, 1H), 7.38 (d, J = 7.7 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.94 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 7.4 Hz, 1H), 6.51 – 6.44 (m, 1H), 6.11 (d, J = 10.0 Hz, 1H), 5.95 (dd, J = 9.6, 3.9 Hz, 1H), 4.89 (dd, J = 9.9, 5.8 Hz, 1H), 3.55 (dd, J = 13.1, 6.9 Hz, 1H), 3.28 (dd, J = 13.1, 6.2 Hz, 1H), 3.21 (d, J = 5.8 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149. 7, 147.6, 138.0, 136.1, 136.00, 132.8, 130.9, 130.7, 129.8, 128.3, 127.5, 127.4, 127.2, 125.9, 125.7, 122.0, 120.2, 79.2, 51.0, 39.6, 31.2, 28.6. HRMS(ESI): m/z calculated for $C_{25}H_{25}BrN_2NaO_2$ $[M+Na]^+$: 487.0997, found: 487.0992.

***tert*-butyl (2-((5-iodoquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ga)**



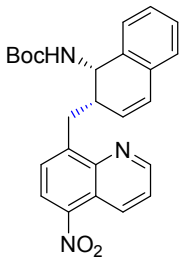
White solid (68.7 mg, 67%), M. p. = 154-156 □. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dd, J = 4.0, 1.3 Hz, 1H), 8.29 (dd, J = 8.5, 1.5 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.42 (dd, J = 8.5, 4.2 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.03 (dd, J = 12.4, 6.8 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 7.4 Hz, 1H), 6.47 (d, J = 9.6 Hz, 1H), 6.10 (d, J = 9.9 Hz, 1H), 5.94 (dd, J = 9.6, 3.9 Hz, 1H), 4.88 (dd, J = 9.9, 5.8 Hz, 1H), 3.54 (dd, J = 13.1, 6.9 Hz, 1H), 3.28 (dd, J = 13.1, 6.2 Hz, 1H), 3.20 (d, J = 5.8 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.87, 149.82, 147.42, 140.88, 139.05, 137.21, 136.05, 132.85, 131.70, 130.73, 129.95, 128.27, 127.43, 127.22, 125.93, 125.66, 122.55, 96.70, 79.18, 50.99, 39.60, 31.11, 28.59. HRMS(ESI): m/z calculated for $C_{25}H_{25}IN_2NaO_2$ $[M+Na]^+$: 535.0858, found: 535.0852.

***tert*-butyl (2-((5-(trifluoromethyl)quinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ha)**



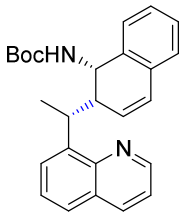
White solid (69.9 mg, 67%), M. p. = 139-141 □. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 – 8.95 (m, 1H), 8.41 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.49 (dd, J = 8.7, 4.1 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.91 (t, J = 7.1 Hz, 1H), 6.85 (d, J = 7.4 Hz, 1H), 6.49 (d, J = 9.6 Hz, 1H), 6.20 (d, J = 10.0 Hz, 1H), 5.97 (dd, J = 9.6, 4.1 Hz, 1H), 4.91 (dd, J = 10.0, 5.9 Hz, 1H), 3.66 (dd, J = 13.0, 6.7 Hz, 1H), 3.31 (dd, J = 13.0, 6.1 Hz, 1H), 3.27 – 3.16 (m, 1H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.6, 147.0, 143.1, 135.9, 133.0, 132.8 – 132.6, 130.5, 129.0, 128.5, 127.4 (d, J = 11.2 Hz), 125.9, 125.7, 125.4, 124.9, 124.6 (d, J = 5.7 Hz), 124.3, 122.9, 122.1, 79.3, 51.0, 39.6, 31.5, 28.6. HRMS(ESI): m/z calculated for $C_{26}H_{25}F_3N_2NaO_2$ $[M+Na]^+$: 477.1766, found: 477.1765.

***tert*-butyl (2-((5-nitroquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ia)**



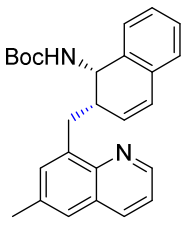
White solid (38.8 mg, 45%), M. p. = 183-185 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (dd, J = 4.0, 1.4 Hz, 1H), 8.96 (dd, J = 8.8, 1.5 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.62 – 7.60 (m, 1H), 7.60 – 7.57 (m, 1H), 7.01 (dd, J = 7.8, 6.8 Hz, 1H), 6.96 (d, J = 7.1 Hz, 1H), 6.90 (td, J = 7.4, 1.2 Hz, 1H), 6.84 (d, J = 7.4 Hz, 1H), 6.50 (d, J = 9.6 Hz, 1H), 6.10 (d, J = 10.1 Hz, 1H), 5.95 (dd, J = 9.6, 4.0 Hz, 1H), 4.88 (dd, J = 10.1, 5.9 Hz, 1H), 3.70 (dd, J = 12.8, 6.7 Hz, 1H), 3.33 (dd, J = 12.9, 6.3 Hz, 1H), 3.27 – 3.20 (m, 1H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 150., 146.5, 146.4, 144.2, 135.8, 132.7, 132.6, 130.1, 128.8, 128.7, 127.6, 127.4, 126.0, 125.4, 124.2, 123.7, 121.1, 79.4, 50.8, 39.7, 31.9, 28.6. HRMS(ESI): m/z calculated for $C_{25}H_{25}N_3NaO_4$ $[M+Na]^+$: 454.1743, found: 454.1741.

***tert*-butyl (2-(1-(quinolin-8-yl)ethyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ja)**



Colorless oily liquid (20 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.1, 1.8 Hz, 1H), 8.15 (dd, J = 8.3, 1.8 Hz, 1H), 7.72 (dd, J = 7.9, 1.4 Hz, 1H), 7.61 (dd, J = 7.1, 1.2 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.37 (dd, J = 8.2, 4.1 Hz, 1H), 7.24 – 7.08 (m, 4H), 6.66 (dd, J = 9.7, 2.4 Hz, 1H), 6.17 (dd, J = 9.7, 3.0 Hz, 1H), 5.27 (d, J = 7.6 Hz, 1H), 4.58 (s, 1H), 4.46 (s, 1H), 3.26 (s, 1H), 1.44 (d, J = 4.8 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 149.2, 146.4, 144.46, 137.0, 136.7, 132.9, 129.6, 128.8, 128.6, 127.7, 127.3, 127.0, 126.6, 126.3, 126.2, 120.9, 78.6, 50.4, 43.7, 28.2, 19.9. HRMS(ESI): m/z calculated for $C_{26}H_{28}N_2NaO_2$ $[M+Na]^+$: 423.2049, found: 423.2050.

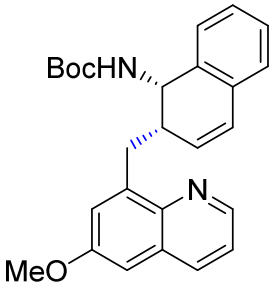
***tert*-butyl (2-((6-methylquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ka)**



White solid (73.6 mg, 92%), M. p. = 134-136 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 2.7 Hz, 1H), 7.98 (dd, J = 8.2, 1.7 Hz, 1H), 7.37 (d, J = 2.7 Hz, 2H), 7.31 (dd, J = 8.2, 4.2 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 7.05 (t, J = 7.2 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.49 (dd, J = 9.6, 1.8 Hz, 1H), 6.25 (d, J = 9.6 Hz, 1H), 6.00 (dd, J = 9.5, 3.6 Hz, 1H), 4.88 (dd, J = 9.4, 5.9 Hz, 1H), 3.56 (dd, J = 13.0, 6.9 Hz, 1H), 3.31 (dd, J = 13.0, 6.3 Hz, 1H), 3.23 (s, 1H), 2.48 (s, 3H), 1.49 (s, 9H).

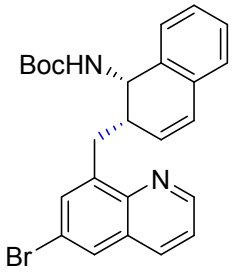
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 148.2, 145.6, 137.4, 136.435, 135.8, 135.8, 133.0, 131.2, 128.5, 128.0, 127.4, 127.3, 126.0, 125.8, 125.4, 120.9, 79.0, 51.1, 39.8, 31.2, 28.6, 21.7. HRMS(ESI): m/z calculated for $C_{26}H_{28}N_2NaO_2$ $[M+Na]^+$: 423.2049, found: 423.2044.

***tert*-butyl (2-((6-methoxyquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3la)**



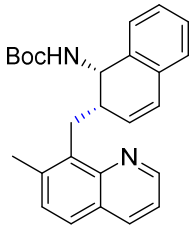
Colorless oily liquid (80 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, J = 4.1, 1.5 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.30 (dd, J = 8.2, 4.2 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.12 – 7.00 (m, 2H), 6.96 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 7.3 Hz, 1H), 6.86 (d, J = 2.1 Hz, 1H), 6.49 (d, J = 9.5 Hz, 1H), 6.29 (d, J = 9.6 Hz, 1H), 5.98 (dd, J = 9.5, 3.8 Hz, 1H), 4.92 (dd, J = 9.5, 6.0 Hz, 1H), 3.88 (s, 3H), 3.50 (dd, J = 13.1, 7.3 Hz, 1H), 3.31 (dd, J = 13.2, 5.7 Hz, 1H), 3.21 (s, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 156.0, 146.6, 143.3, 139.6, 136.3, 135.3, 133.0, 131.0, 129.6, 128.1, 127.4, 127.3, 125.8, 123.2, 121.3, 104.0, 79.1, 55.5, 51.2, 39.6, 31.7, 28.6. HRMS(ESI): m/z calculated for $C_{26}H_{28}N_2NaO_3$ $[M+Na]^+$: 439.1998, found: 439.1994.

***tert*-butyl (2-((6-bromoquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3ma)**



White solid (67 mg, 72%), M. p. = 85-87 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 4.0, 1.5 Hz, 1H), 7.94 (dd, J = 8.3, 1.4 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.59 (d, J = 1.9 Hz, 1H), 7.36 (dd, J = 8.3, 4.2 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.90 (dd, J = 11.0, 7.1 Hz, 2H), 6.51 (d, J = 9.5 Hz, 1H), 6.27 (d, J = 9.9 Hz, 1H), 5.96 (dd, J = 9.5, 3.6 Hz, 1H), 4.91 (dd, J = 9.9, 5.4 Hz, 1H), 3.56 (td, J = 8.9, 3.7 Hz, 1H), 3.32 – 3.12 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.3, 145.5, 140.0, 136.0, 135.6, 133.8, 132.9, 130.4, 129.3, 128.4, 127.4, 127.3, 125.9, 125.5, 121.7, 120.0, 79.2, 50.9, 39.5, 30.8, 28.6. HRMS(ESI): m/z calculated for $C_{25}H_{25}BrN_2NaO_2$ $[M+Na]^+$: 487.0997, found: 487.0987.

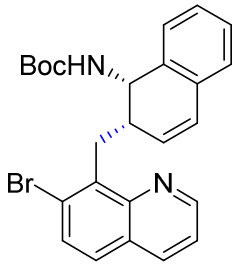
***tert*-butyl (2-((7-methylquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3na)**



Colorless oily liquid (36 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 4.2, 1.8 Hz, 1H), 8.07 (dd, J = 8.2, 1.7 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.17 (dd, J = 5.5, 3.2 Hz, 2H), 7.01 (dd, J = 5.6, 3.1 Hz, 1H), 6.43 (dd, J = 9.6, 1.5 Hz, 2H), 5.99 (dd, J = 9.5, 3.9 Hz, 1H), 4.97 (dd, J

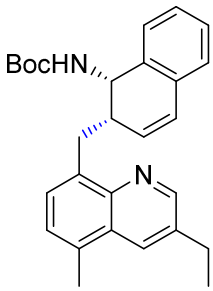
= 8.6, 6.0 Hz, 1H), 3.62 (dd, *J* = 13.5, 5.0 Hz, 1H), 3.40 (dd, *J* = 13.4, 8.1 Hz, 1H), 3.06 (s, 1H), 2.54 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 149.2, 147.2, 138.0, 136.4, 133.2, 131.9, 130.0, 127.6, 127.5, 127.3, 126.9, 126.4 126.1, 125.8, 120.2, 79.0, 52.5, 39.9, 28.6, 26.9, 20.9. HRMS(ESI): m/z calculated for $C_{26}H_{28}N_2NaO_2$ $[M+Na]^+$: 423.2049, found: 423.2044.

***tert*-butyl (2-((7-bromoquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3oa)**



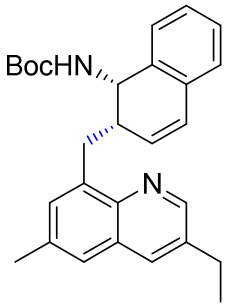
White solid (57.7 mg, 62%), M. p. = 89-91 □. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.08 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.20 – 7.14 (m, 2H), 7.00 (dd, *J* = 5.9, 2.8 Hz, 1H), 6.42 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.02 (dd, *J* = 8.9, 4.1 Hz, 2H), 5.05 (dd, *J* = 9.1, 5.8 Hz, 1H), 3.75 (dd, *J* = 13.0, 4.9 Hz, 1H), 3.70 – 3.56 (m, 1H), 3.24 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 150.1, 147.6, 138.9, 136.6, 136.1, 133.0, 131.3, 131.1, 127.6, 127.5, 127.4, 127.3, 127.2, 126.8, 126.7, 126.1, 121.3, 79.0, 52.1, 39.7, 30.4, 28.5. HRMS(ESI): m/z calculated for $C_{25}H_{25}BrN_2NaO_2$ $[M+Na]^+$: 487.0997, found: 487.0988.

***tert*-butyl (2-((3-ethyl-5-methylquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate(3pa)**



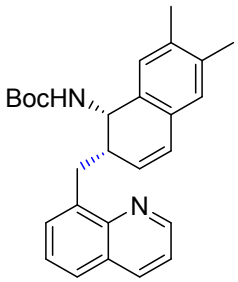
Colorless oily liquid (48 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 1.7 Hz, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.1 Hz, 1H), 7.00 (td, *J* = 7.4, 1.3 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 9.5 Hz, 1H), 6.18 (d, *J* = 9.4 Hz, 1H), 5.99 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.89 (dd, *J* = 9.2, 5.9 Hz, 1H), 3.48 (dd, *J* = 13.1, 7.3 Hz, 1H), 3.36 (dd, *J* = 13.2, 6.1 Hz, 1H), 3.22 (s, 1H), 2.85 (q, *J* = 7.6 Hz, 2H), 2.60 (s, 3H), 1.48 (s, 9H), 1.37 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.9, 145.6, 136.4, 135.9, 135.7, 133.0, 132.5, 131.4, 130.5, 129.3, 127.8, 127.6, 127.3, 127.2, 126.6, 126.1, 125.9, 79.0, 51.3, 39.8, 31.4, 28.6, 26.6, 18.6, 15.7. HRMS(ESI): m/z calculated for $C_{28}H_{32}N_2NaO_2$ $[M+Na]^+$: 451.2362, found: 451.2360.

***tert*-butyl (2-((3-ethyl-6-methylquinolin-8-yl)methyl)-1,2-dihydronaphthalen-1-yl)carbamate (3qa)**



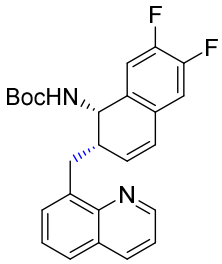
Colorless oily liquid (59 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 1.7 Hz, 1H), 7.75 (d, J = 2.2 Hz, 1H), 7.32 (d, J = 7.1 Hz, 2H), 7.13 (d, J = 7.4 Hz, 1H), 7.11 – 7.04 (m, 1H), 7.00 (td, J = 7.4, 1.4 Hz, 1H), 6.93 (d, J = 7.3 Hz, 1H), 6.49 (dd, J = 9.6, 1.8 Hz, 1H), 6.20 (d, J = 9.6 Hz, 1H), 5.99 (dd, J = 9.5, 3.6 Hz, 1H), 4.87 (dd, J = 9.5, 5.8 Hz, 1H), 3.50 (dd, J = 13.1, 7.2 Hz, 1H), 3.33 (dd, J = 13.1, 6.3 Hz, 1H), 3.22 (s, 1H), 2.80 (q, J = 7.6 Hz, 2H), 2.47 (s, 3H), 1.48 (s, 9H), 1.34 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.7, 144.1, 137.2, 136.4, 136.3, 135.8, 133.3, 133.0, 132.0, 131.3, 128.5, 127.9, 127.4, 127.3, 126.1, 125.9, 125.0, 79.0, 51.2, 39.8, 31.3, 28.6, 26.3, 21.7, 15.4. HRMS(ESI): m/z calculated for $C_{28}H_{32}N_2NaO_2$ $[M+Na]^+$: 451.2362, found: 451.2361.

***tert*-butyl (6,7-dimethyl-2-(quinolin-8-ylmethyl)-1,2-dihydronaphthalen-1-yl)carbamate (4ab)**



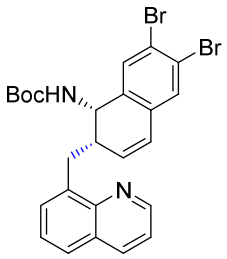
White solid (42.3 mg, 51%), M. p. = 105-107 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 – 8.87 (m, 1H), 8.09 (dd, J = 8.2, 1.5 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 6.9 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.36 (dd, J = 8.2, 4.2 Hz, 1H), 6.92 (s, 1H), 6.72 (s, 1H), 6.42 (d, J = 9.4 Hz, 1H), 5.96 – 5.80 (m, 2H), 4.80 (dd, J = 9.8, 5.6 Hz, 1H), 3.53 (dd, J = 13.1, 7.6 Hz, 1H), 3.41 (dd, J = 13.1, 6.5 Hz, 1H), 3.22 (s, 1H), 2.14 (s, 3H), 2.12 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 149.2, 147.00, 138.2, 136.5, 135.77, 135.4, 133.8, 130.6, 130.6, 130.1, 128.4, 127.7, 127.4, 126.5, 126.2, 120.8, 79.00, 50.8, 40.1, 31.6, 28.6, 19. 7, 19.4. HRMS(ESI): m/z calculated for $C_{27}H_{30}N_2NaO_2$ $[M+Na]^+$: 437.2205, found: 437.2203.

***tert*-butyl (6,7-difluoro-2-(quinolin-8-ylmethyl)-1,2-dihydronaphthalen-1-yl)carbamate (4ac)**



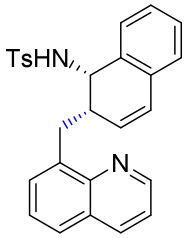
White solid (38 mg, 45%), M. p. = 120-122 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.0, 1.5 Hz, 1H), 8.06 (dd, J = 8.2, 1.4 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 6.7 Hz, 1H), 7.38 (dd, J = 8.2, 4.2 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 9.7 Hz, 1H), 6.63 (dd, J = 10.8, 8.1 Hz, 1H), 6.50 (dd, J = 10.6, 7.8 Hz, 1H), 6.33 (d, J = 9.7 Hz, 1H), 6.08 (dd, J = 9.6, 4.3 Hz, 1H), 4.89 (dd, J = 9.3, 6.1 Hz, 1H), 3.69 (dd, J = 15.1, 7.6 Hz, 1H), 3.21 – 3.02 (m, 2H), 1.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.1 (d, J = 12.8 Hz), 149.0, 147.6 (d, J = 12.8 Hz), 146.6, 136.9, 136.7, 133.1, 131.5, 130.9, 129.8, 128.1, 126.7, 125.9, 121.0, 114.4 – 113.5, 79.4, 50.4, 39.0, 30.4, 28.6. HRMS(ESI): m/z calculated for $C_{25}H_{24}F_2N_2NaO_2$ $[M+Na]^+$: 445.1704, found: 4445.1703.

***tert*-butyl (6,7-dibromo-2-(quinolin-8-ylmethyl)-1,2-dihydronaphthalen-1-yl)carbamate (4ad)**



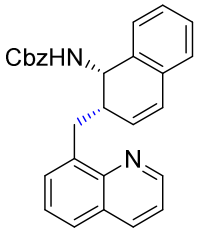
White solid (38.1 mg, 35%), M. p. = 101-103 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 9.6 Hz, 1H), 6.93 (s, 1H), 6.84 (s, 1H), 6.31 (d, J = 9.6 Hz, 1H), 6.14 (dd, J = 9.5, 5.0 Hz, 1H), 4.97 – 4.83 (m, 1H), 3.73 (dd, J = 13.3, 5.7 Hz, 1H), 3.19 – 2.95 (m, 2H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.20, 149.00, 146.58, 136.86, 136.78, 136.25, 133.94, 132.82, 130.89, 129.70, 129.27, 128.12, 126.74, 126.67, 125.85, 122.30, 121.16, 79.44, 50.46, 39.17, 30.12, 28.62. HRMS(ESI): m/z calculated for $C_{25}H_{24}Br_2N_2NaO_2$ $[M+Na]^+$: 565.0102, found: 565.0086.

4-methyl-*N*-(2-(quinolin-8-ylmethyl)-1,2-dihydronaphthalen-1-yl)benzenesulfonamide(4ae)



White solid (52.7 mg, 60%), M. p. = 98-100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.3, 1.8 Hz, 1H), 8.42 (d, J = 9.0 Hz, 1H), 7.93 (dd, J = 8.3, 1.8 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.39 (dd, J = 8.2, 1.4 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.22 – 7.15 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 7.8 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 6.57 – 6.49 (m, 2H), 6.31 (d, J = 9.6 Hz, 1H), 5.91 (dd, J = 9.6, 5.5 Hz, 1H), 4.57 (dd, J = 9.1, 6.6 Hz, 1H), 3.46 (dd, J = 13.8, 5.9 Hz, 1H), 2.96 (dd, J = 13.8, 4.1 Hz, 1H), 2.76 – 2.62 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 146.2, 142.8, 139.1, 137.1, 136.4, 134.5, 133.1, 131.1, 130.2, 129.6, 128.6, 128.1, 127.0, 126.9, 126.8, 126.7, 125.9, 125.3, 124.5, 121.0, 54.8, 39.6, 30.5, 21.6. HRMS(ESI): m/z calculated for $C_{27}H_{24}N_2NaO_2S$ $[M+Na]^+$: 463.1456, found: 463.1449.

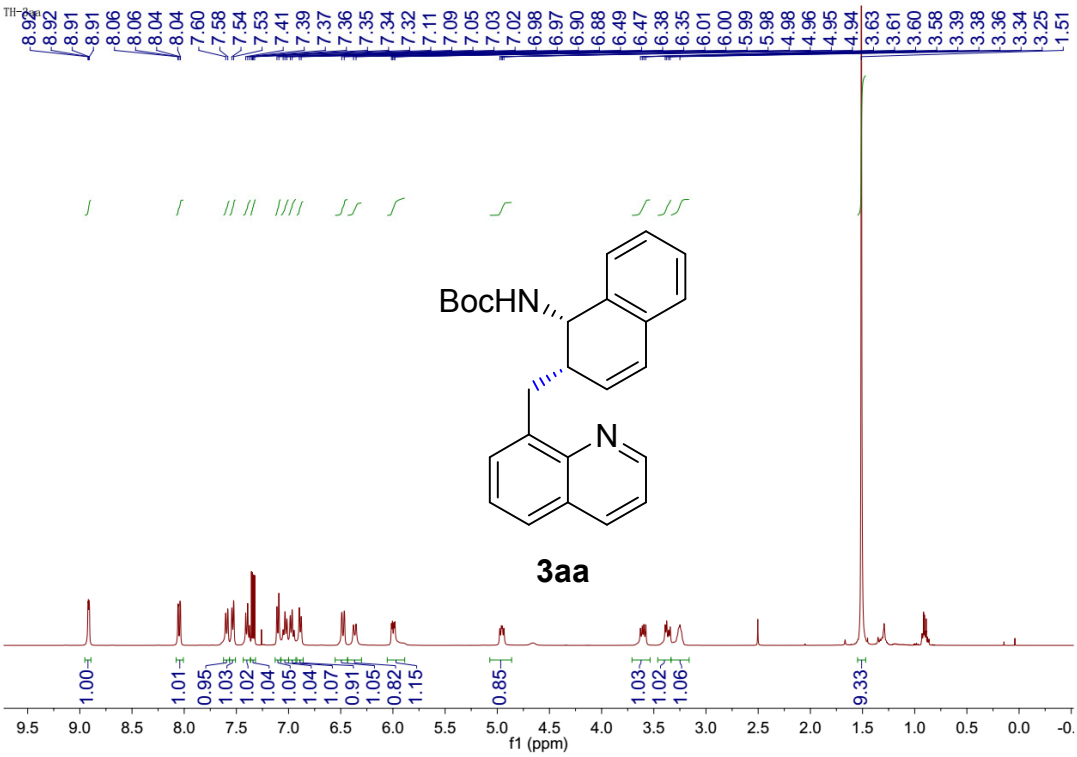
benzyl (2-(quinolin-8-ylmethyl)-1,2-dihydronaphthalen-1-yl)carbamate (4af)

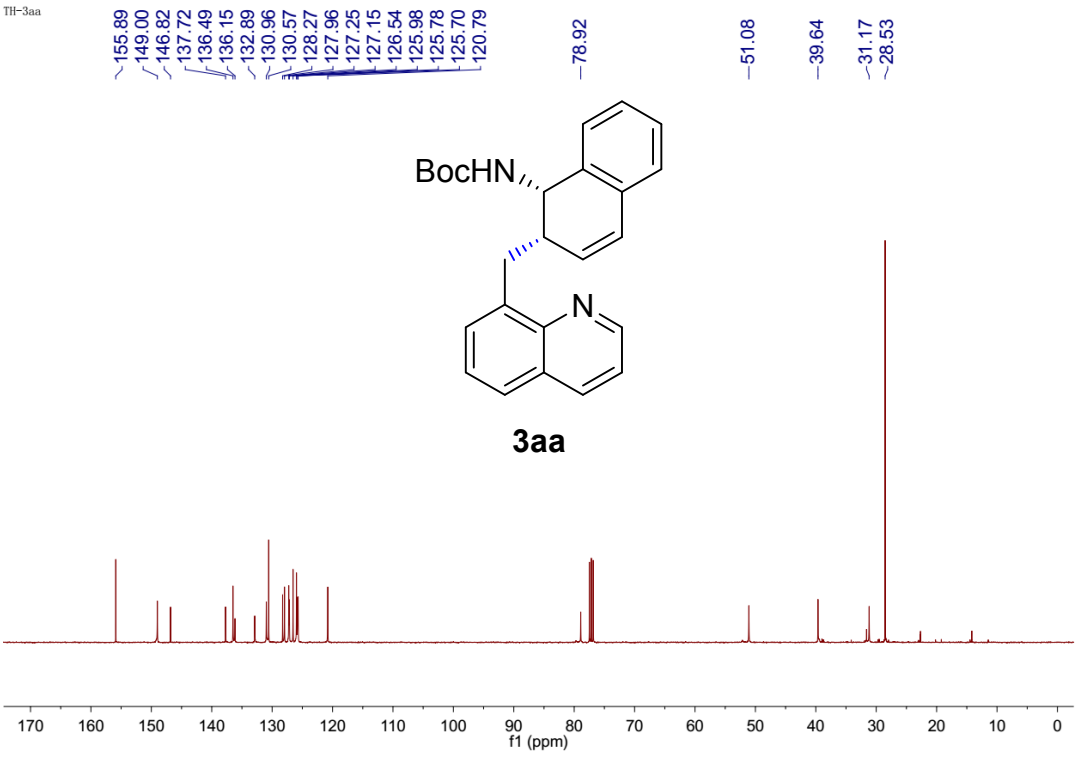


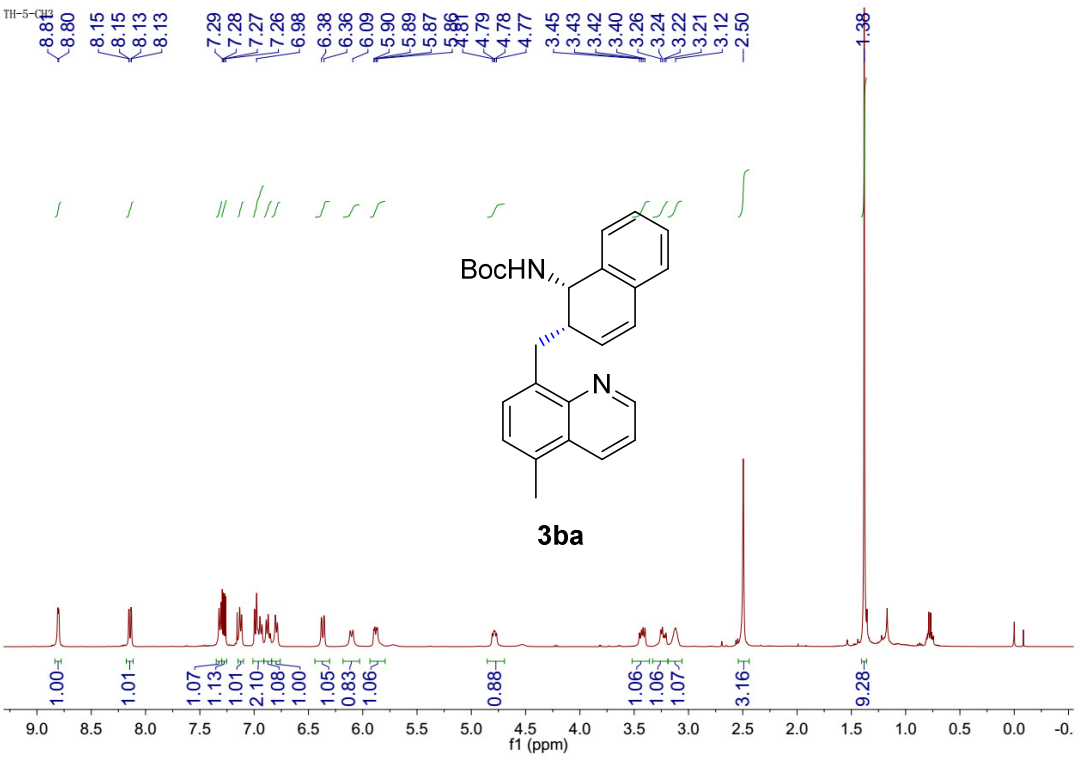
Colorless oily liquid (52.1 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.04 (d, J = 6.5 Hz, 1H), 7.57 (d, J = 6.8 Hz, 1H), 7.47 (d, J = 5.7 Hz, 1H), 7.37 (dd, J = 17.3, 11.5 Hz, 7H), 7.09 – 6.95 (m,

2H), 6.95 – 6.80 (m, 2H), 6.74 (d, J = 7.9 Hz, 1H), 6.46 (d, J = 8.2 Hz, 1H), 6.05 – 5.84 (m, 1H), 5.15 (q, J = 12.3 Hz, 2H), 4.97 (s, 1H), 3.65 – 3.54 (m, 1H), 3.37 – 3.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 149.1, 146.9, 137.5, 137.0, 136.6, 135.8, 132.9, 130.7, 128.6, 128.3, 128.3, 128.2, 128.1, 127.4, 126.7, 126.1, 125.9, 125.7, 120.9, 66.7, 51.8, 39.7, 31.6. HRMS(ESI): m/z calculated for $C_{28}H_{24}N_2NaO_2$ $[M+Na]^+$: 443.1736, found: 443.1734.

8. NMR spectra


8.93
8.92
8.91
8.91
8.06
8.06
8.04
8.04
7.60
7.58
7.54
7.53
7.41
7.39
7.37
7.36
7.35
7.34
7.32
7.11
7.09
7.05
7.03
7.02
6.98
6.97
6.90
6.88
6.49
6.47
6.38
6.35
6.01
6.00
5.99
5.98
4.98
4.96
4.95
4.94
3.63
3.61
3.60
3.58
3.39
3.38
3.36
3.34
3.25
1.51
BocHN
N
3aa
1.00
1.01
0.95
1.03
1.02
1.04
1.05
1.04
1.07
0.91
1.05
0.82
1.15
0.85
1.03
1.02
1.06
9.33
f1 (ppm)


155.89
149.00
146.82
137.72
136.49
136.15
132.89
130.96
130.57
128.27
127.96
127.25
127.15
126.54
125.98
125.78
125.70
120.79
78.92
51.08
39.64
31.17
28.53
BocHN
N
3aa
f1 (ppm)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8.80
8.15
8.15
8.13
8.13
7.29
7.28
7.27
7.26
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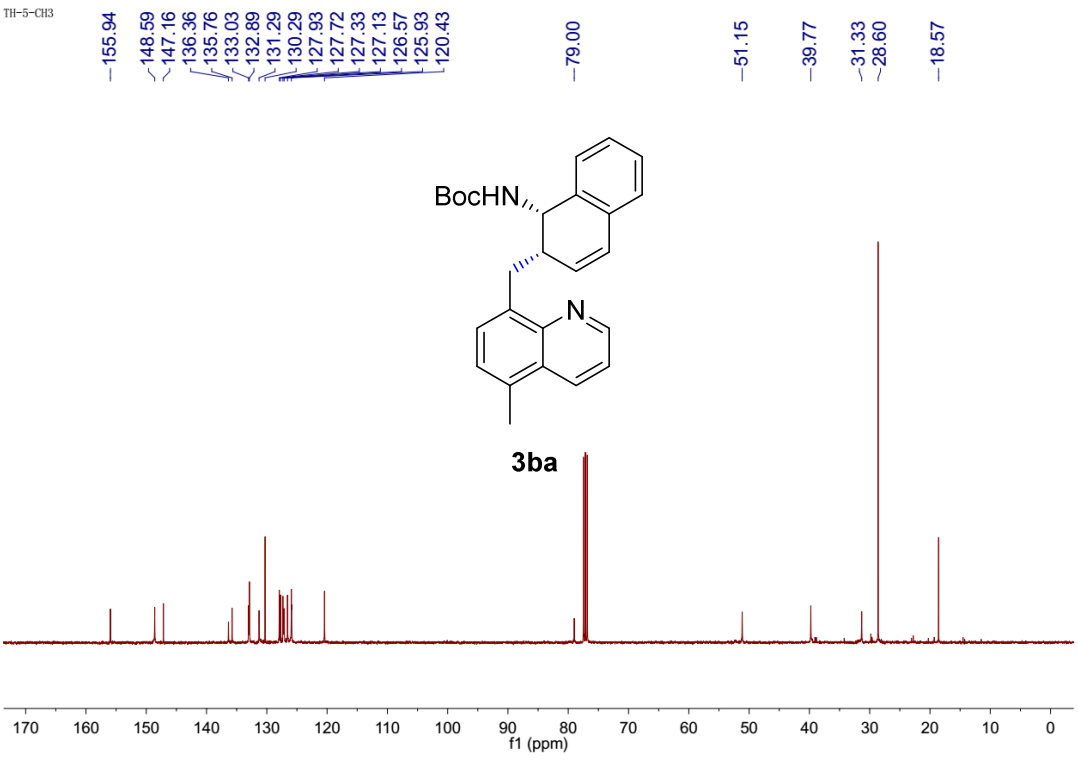
6.38
6.36
6.09
5.90
5.89
5.87
4.81
4.79
4.78
4.77
3.45
3.43
3.42
3.40
3.26
3.24
3.22
3.21
3.12
2.50
1.38
BocHN
N
3ba
1.00
1.01
1.07
1.13
1.01
2.10
1.08
1.00
1.05
0.83
1.06
0.88
1.06
1.06
1.07
3.16
9.28
f1 (ppm)


TH-5-CH3
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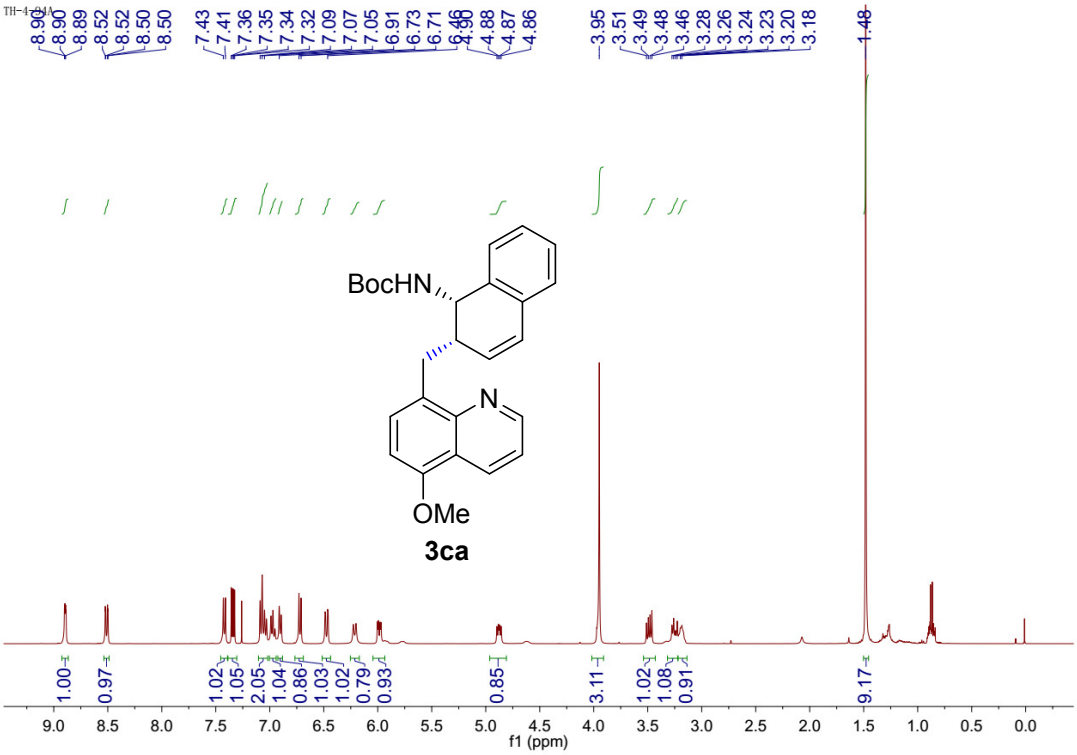
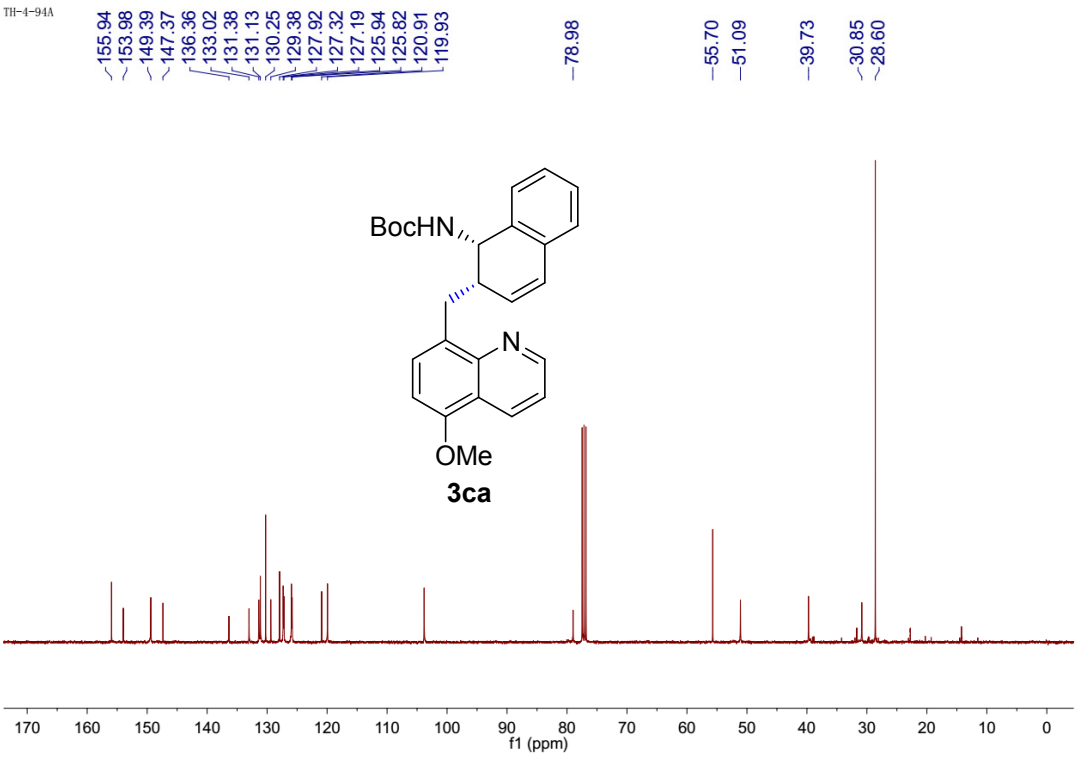
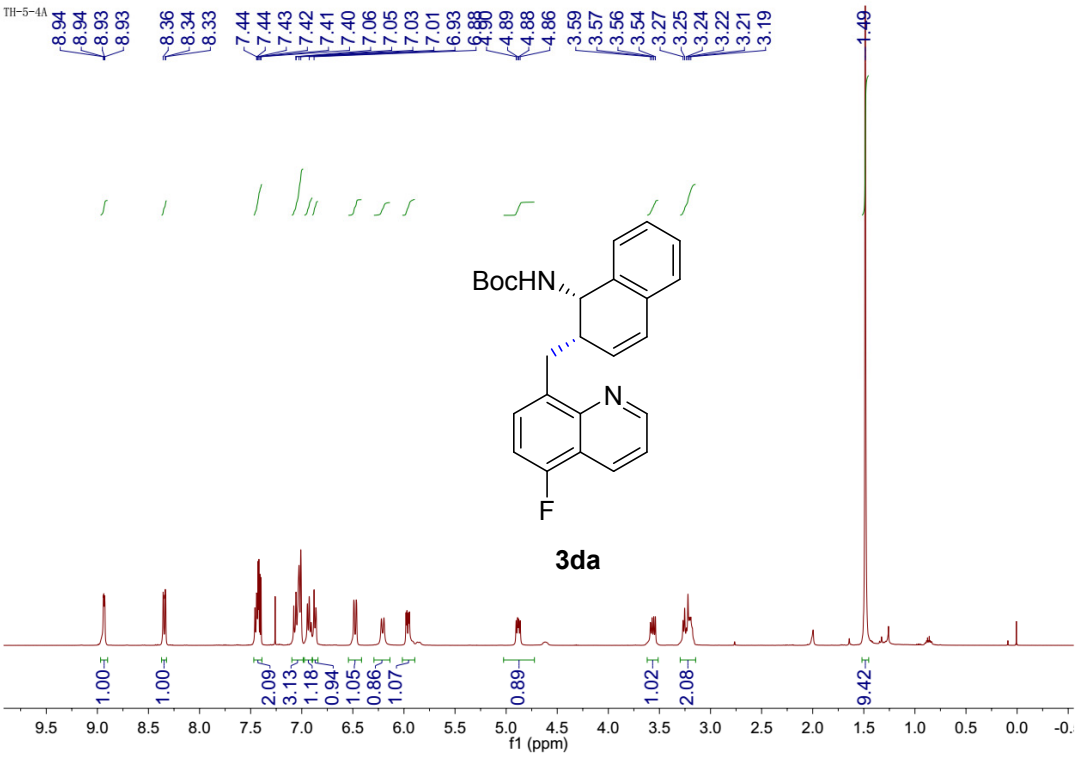
148.59
147.16
136.36
135.76
133.03
132.89
131.29
130.29
127.93
127.72
127.33
127.13
126.57
125.93
120.43
79.00
51.15
39.77
31.33
28.60
18.57
BocHN
N
3ba
f1 (ppm)


BocHN
N
OMe
3ca
f1 (ppm)


BocHN
N
OMe
3ca
f1 (ppm)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8.94
8.93
8.93
8.36
8.34
8.33
7.44
7.44
7.43
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7.41
7.40
7.06
7.05
7.03
7.01
6.93
4.89
4.88
4.86
3.59
3.57
3.56
3.54
3.27
3.25
3.24
3.22
3.21
3.19
1.49
BocHN
N
F
3da
1.00
1.00
2.09
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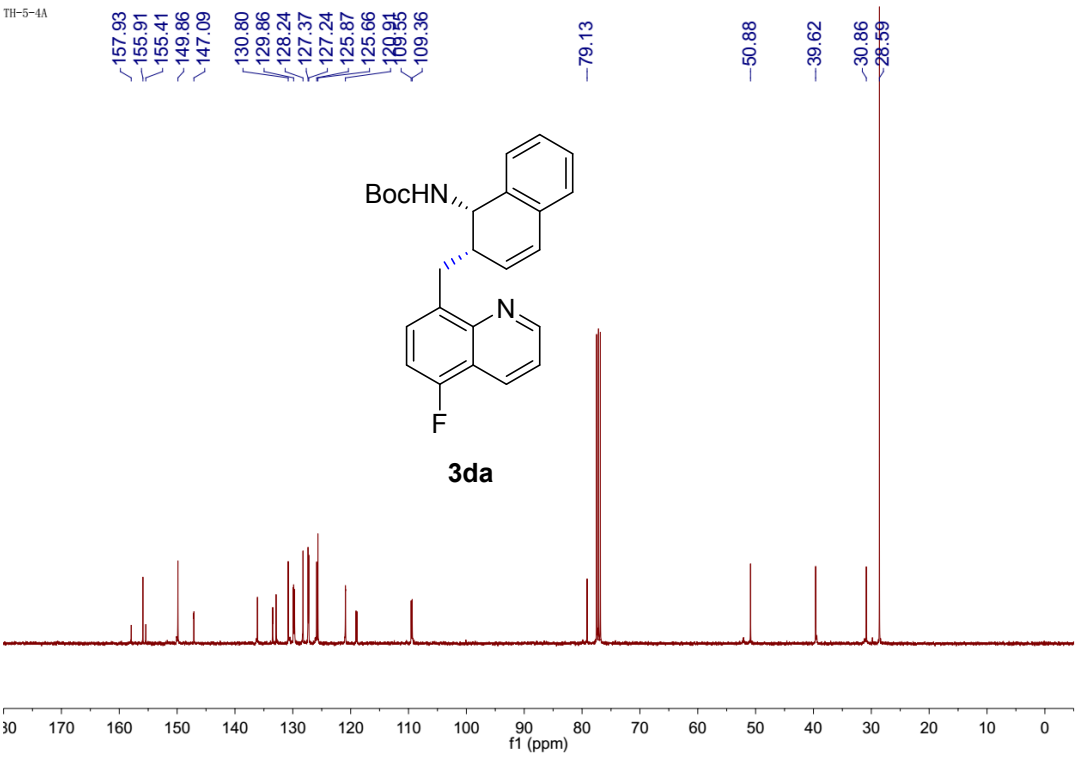
2.08
9.42
f1 (ppm)


TH-5-4A
157.93
155.91
155.41
149.86
147.09
130.80
129.86
128.24
127.37
127.24
125.87
125.66
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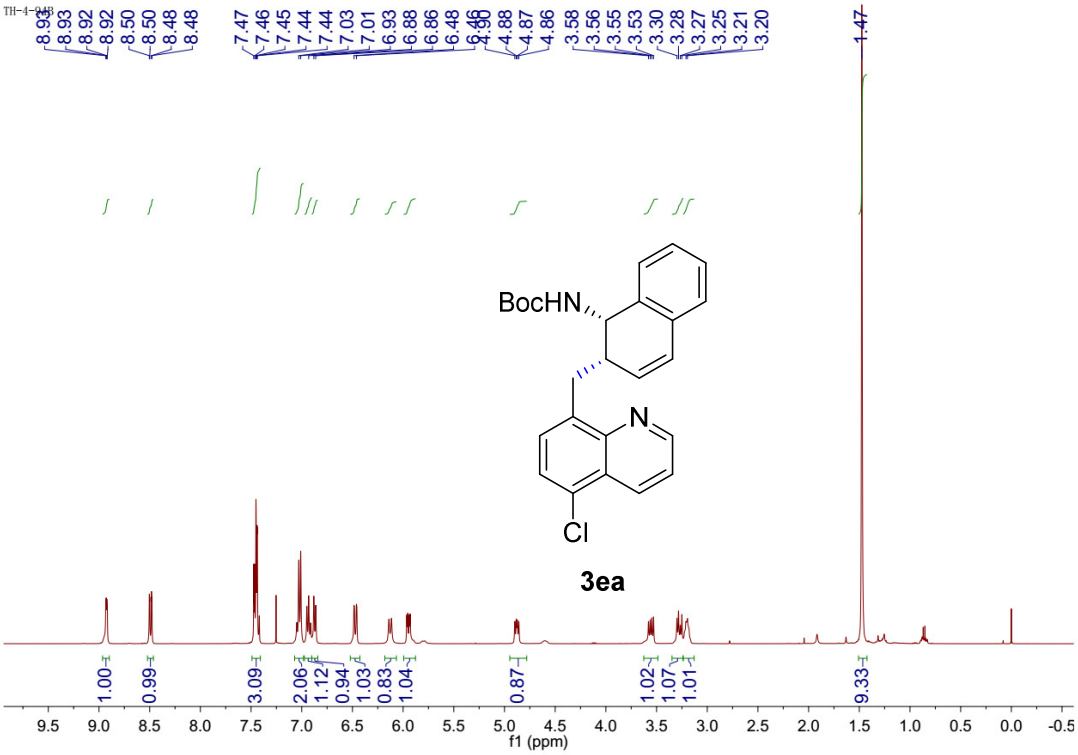
79.13
50.88
39.62
30.86
28.59
BocHN
N
F
3da
f1 (ppm)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8.92
8.92
8.50
8.50
8.48
8.48
7.47
7.46
7.45
7.44
7.44
7.03
7.01
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6.88
6.86
6.48
4.88
4.87
4.86
3.58
3.56
3.55
3.53
3.30
3.28
3.27
3.25
3.21
3.20
1.47
BocHN
N
Cl
3ea
1.00
0.99
3.09
2.06
1.12
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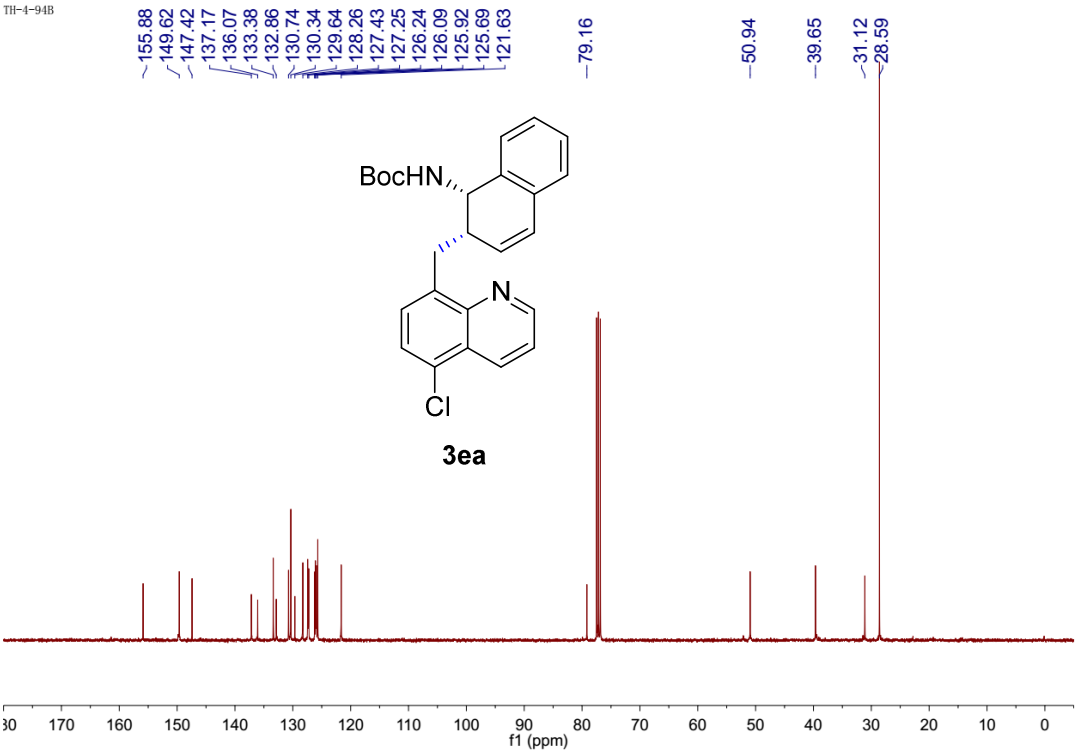
1.03
0.83
1.04
0.87
1.02
1.07
1.01
9.33
f1 (ppm)


TH-4-94B
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136.07
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132.86
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130.34
129.64
128.26
127.43
127.25
126.24
126.09
125.92
125.69
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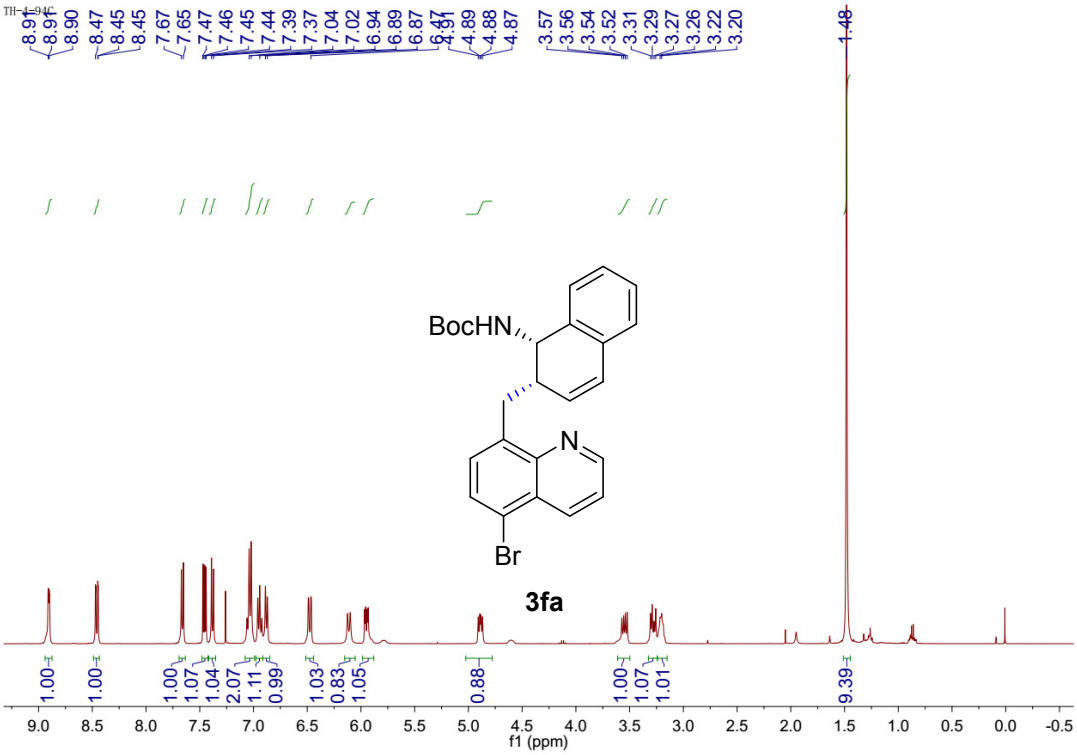
79.16
50.94
39.65
31.12
28.59
BocHN
N
Cl
3ea
f1 (ppm)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8.45
7.67
7.65
7.47
7.46
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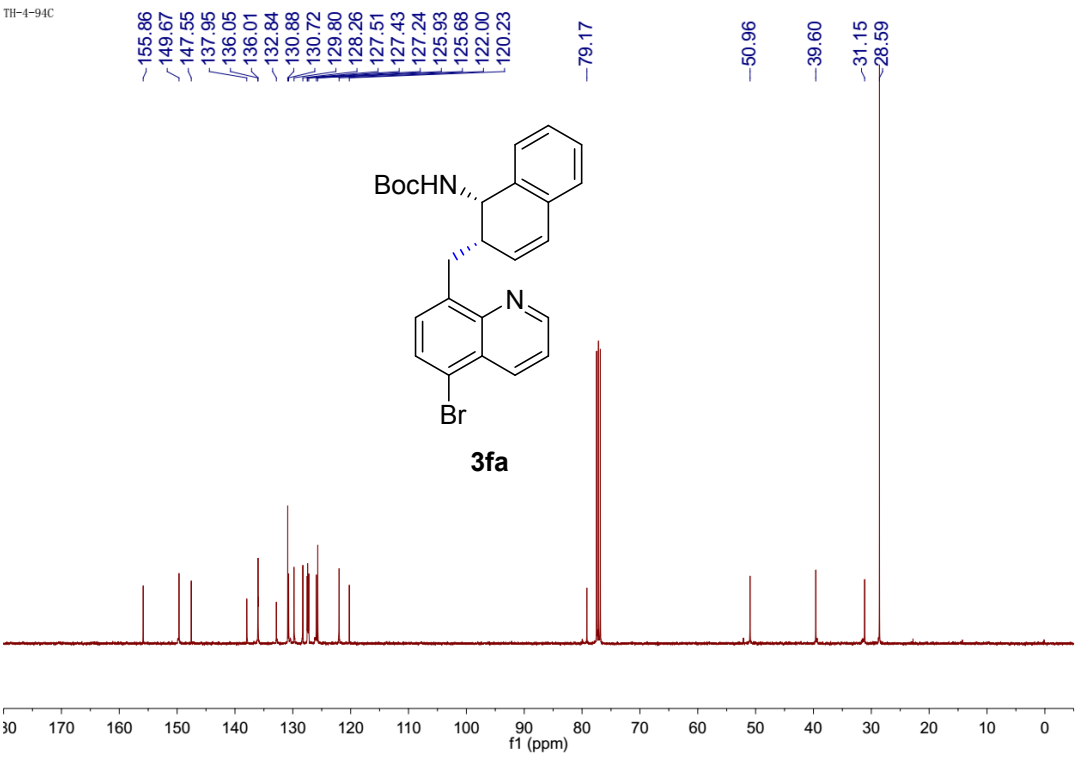
7.44
7.39
7.37
7.04
7.02
6.94
6.89
6.87
6.47
4.91
4.89
4.88
4.87
3.57
3.56
3.54
3.52
3.31
3.29
3.27
3.26
3.22
3.20
1.48
BocHN
N
Br
3fa
1.00
1.00
1.00
1.07
1.04
2.07
1.11
0.99
1.03
0.83
1.05
0.88
1.00
1.07
1.01
9.39
f1 (ppm)


TH-4-94C
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149.67
147.55
137.95
136.05
136.01
132.84
130.88
130.72
129.80
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127.51
127.43
127.24
125.93
125.68
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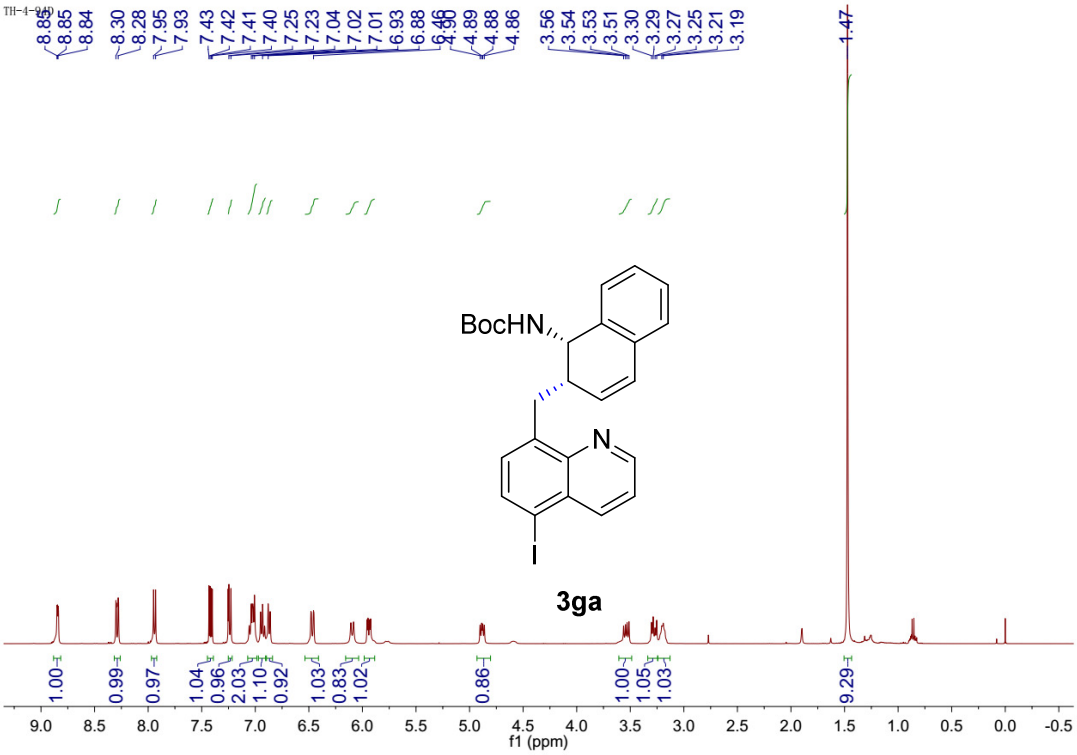
79.17
50.96
39.60
31.15
28.59
BocHN
N
Br
3fa
f1 (ppm)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8.28
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7.42
7.41
7.40
7.25
7.23
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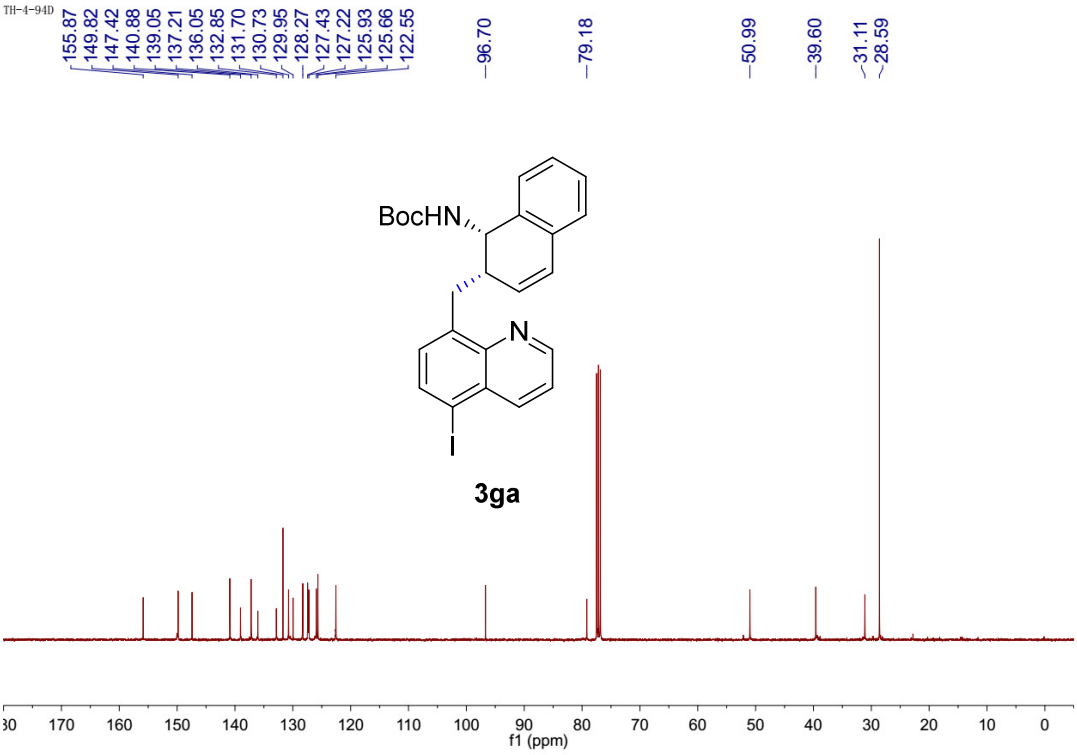
7.02
7.01
6.93
6.88
4.89
4.88
4.86
3.56
3.54
3.53
3.51
3.30
3.29
3.27
3.25
3.21
3.19
1.47
BocHN
N
I
3ga
1.00
0.99
0.97
1.04
0.96
2.03
1.10
0.92
1.03
0.83
1.02
0.86
1.00
1.05
1.03
9.29
f1 (ppm)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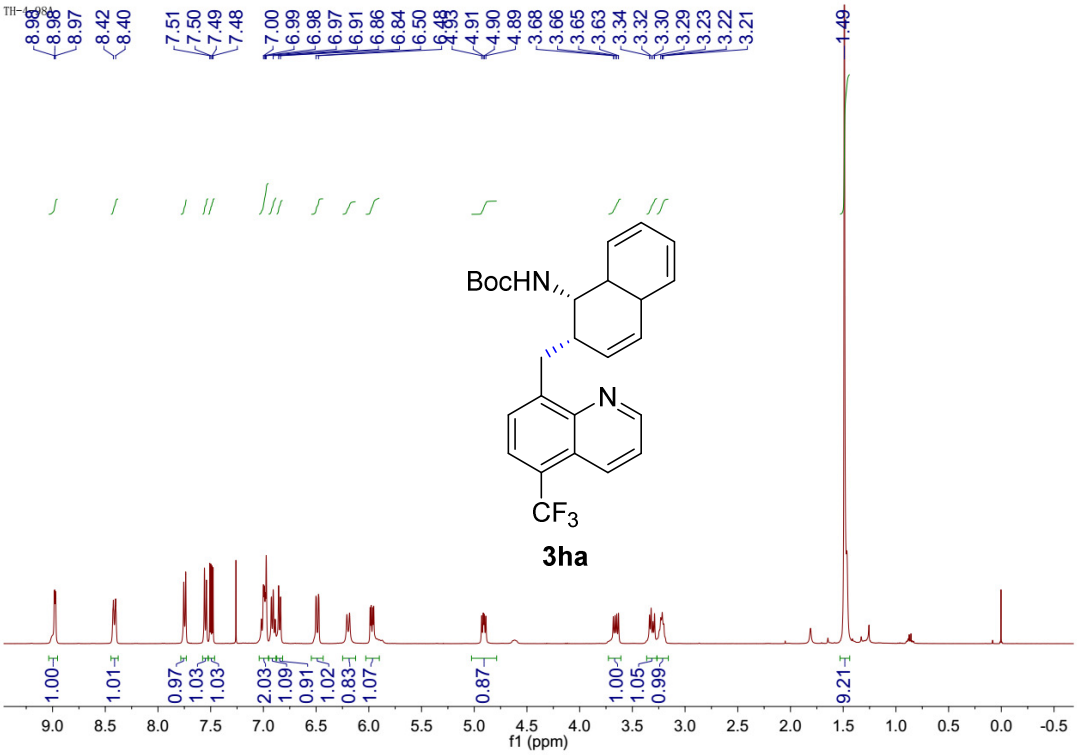
149.82
147.42
140.88
139.05
137.21
136.05
132.85
131.70
130.73
129.95
128.27
127.43
127.22
125.93
125.66
122.55
96.70
79.18
50.99
39.60
31.11
28.59
BocHN
N
I
3ga
f1 (ppm)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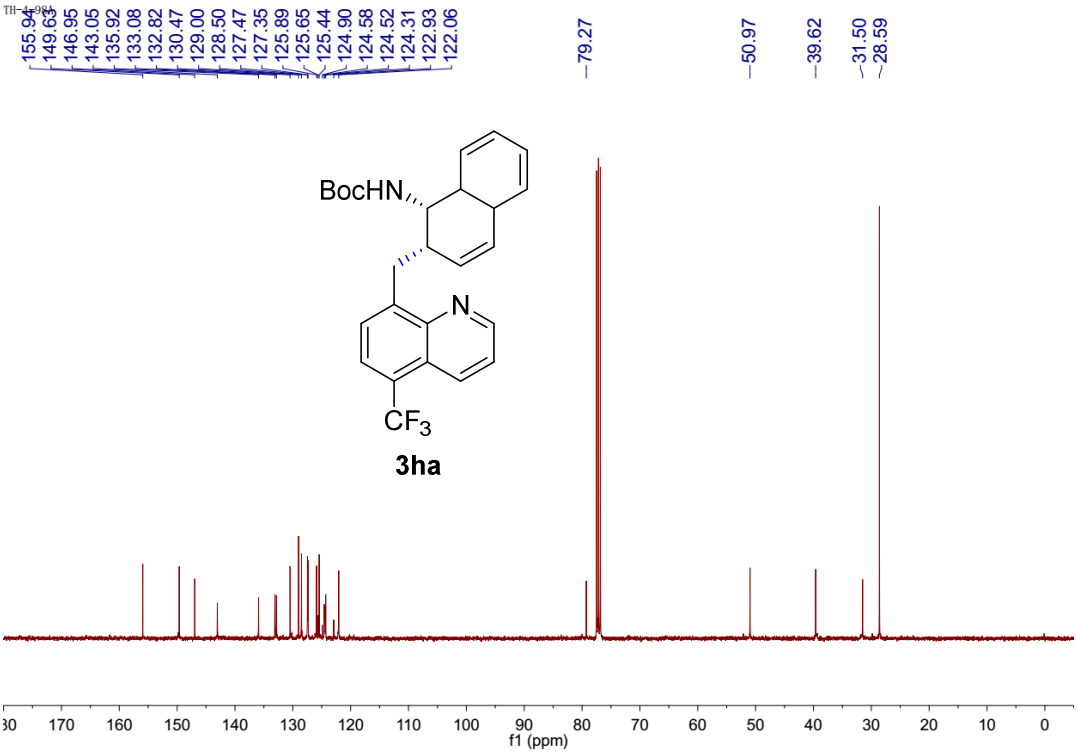
8.97
8.42
8.40
7.51
7.50
7.49
7.48
7.00
6.99
6.98
6.97
6.91
6.86
6.84
6.50
4.91
4.90
4.89
3.68
3.66
3.65
3.63
3.34
3.32
3.30
3.29
3.23
3.22
3.21
1.49
BocHN
N
CF3
3ha
1.00
1.01
0.97
1.03
1.03
2.03
1.09
0.91
1.02
0.83
1.07
0.87
1.00
1.05
0.99
9.21
f1 (ppm)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133.08
132.82
130.47
129.00
128.50
127.47
127.35
125.89
125.65
125.44
124.90
124.58
124.52
124.31
122.93
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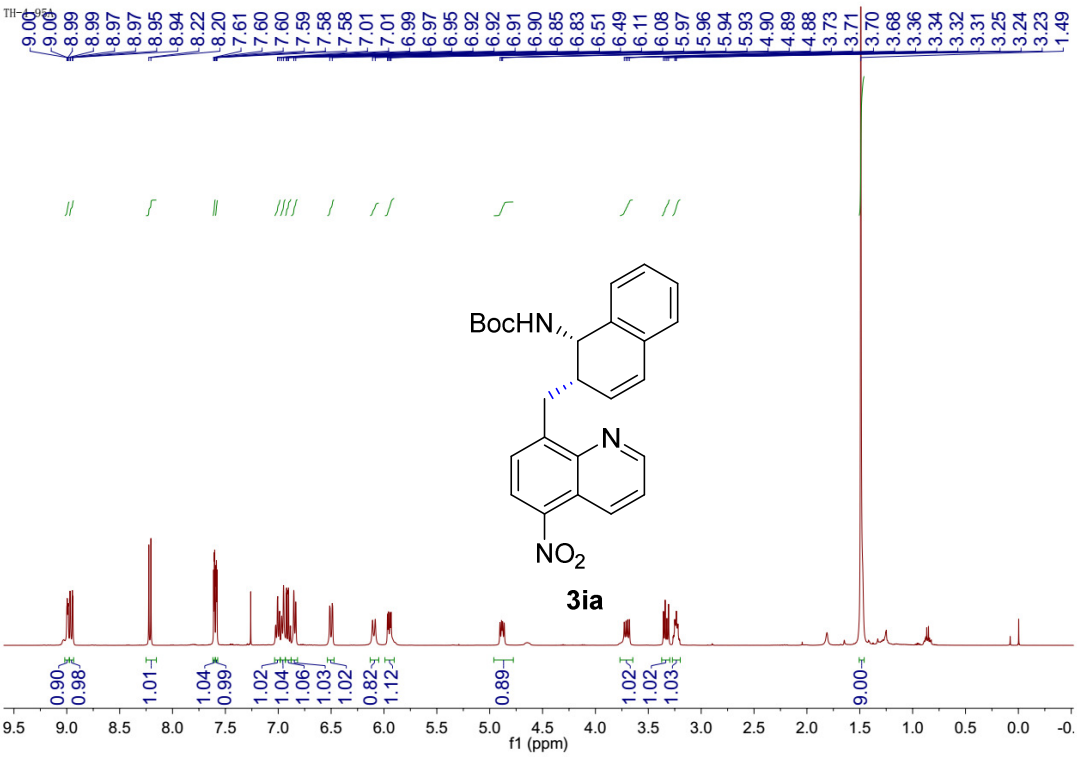
79.27
50.97
39.62
31.50
28.59
BocHN
N
CF3
3ha
f1 (ppm)


TH-4-95A
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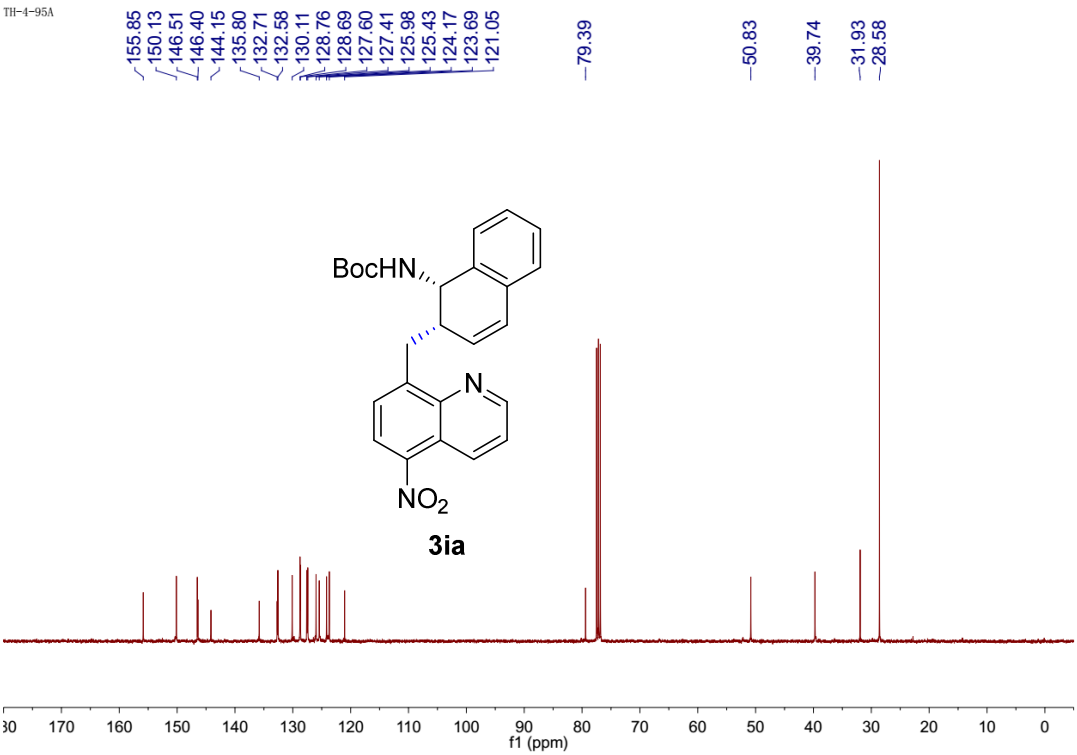
9.00
8.99
8.99
8.97
8.97
8.95
8.94
8.22
8.20
7.61
7.60
7.60
7.59
7.58
7.58
7.01
7.01
6.99
6.97
6.95
6.92
6.92
6.91
6.90
6.85
6.83
6.51
6.49
6.11
6.08
5.97
5.96
5.94
5.93
4.90
4.89
4.88
3.73
3.71
3.70
3.68
3.36
3.34
3.32
3.31
3.25
3.24
3.23
1.49
BocHN
N
NO2
3ia
0.90
0.98
1.01
1.04
0.99
1.02
1.04
1.06
1.03
1.02
0.82
1.12
0.89
1.02
1.02
1.03
9.00
f1 (ppm)


TH-4-95A
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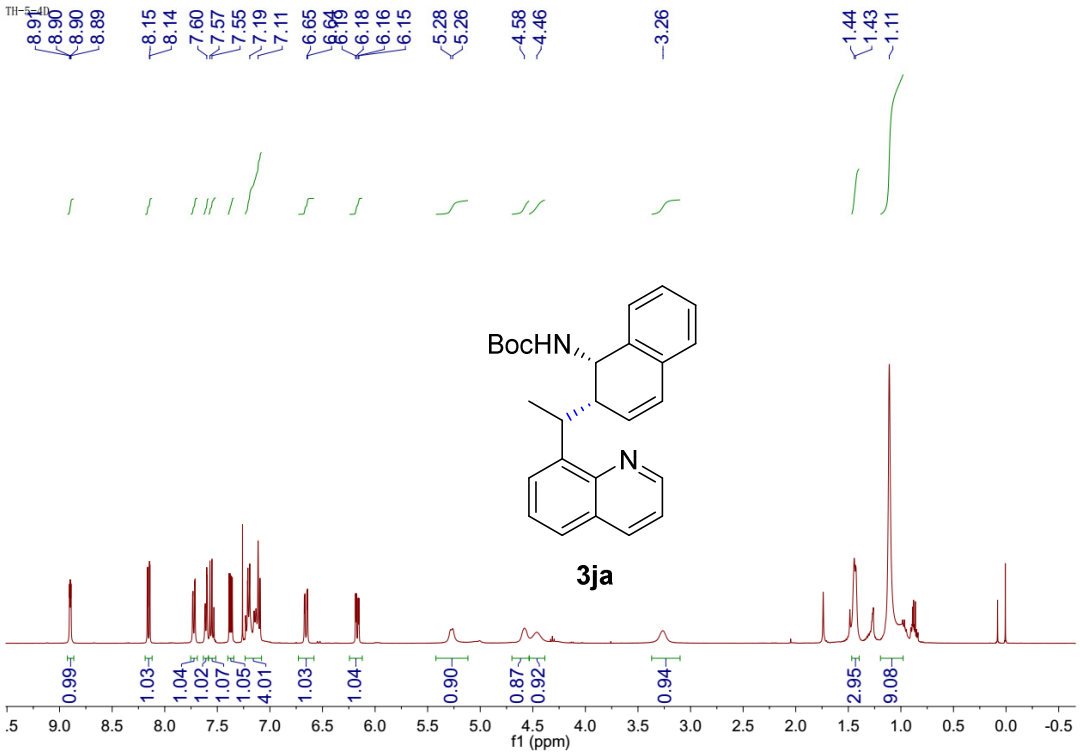
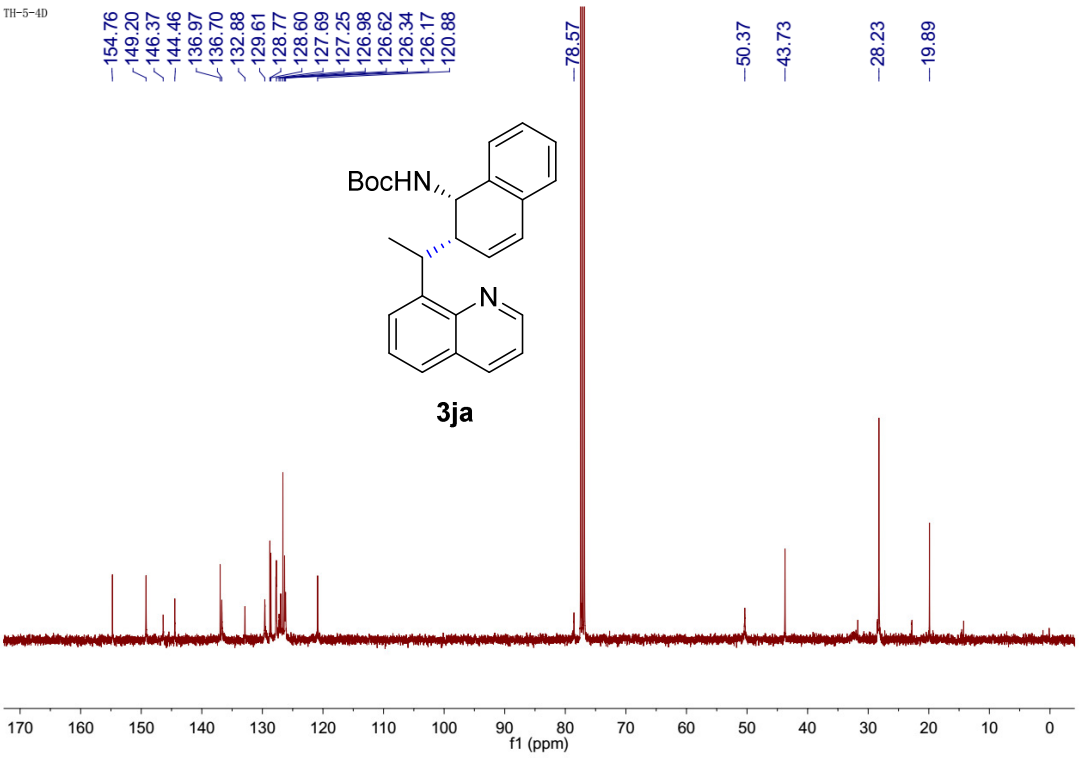
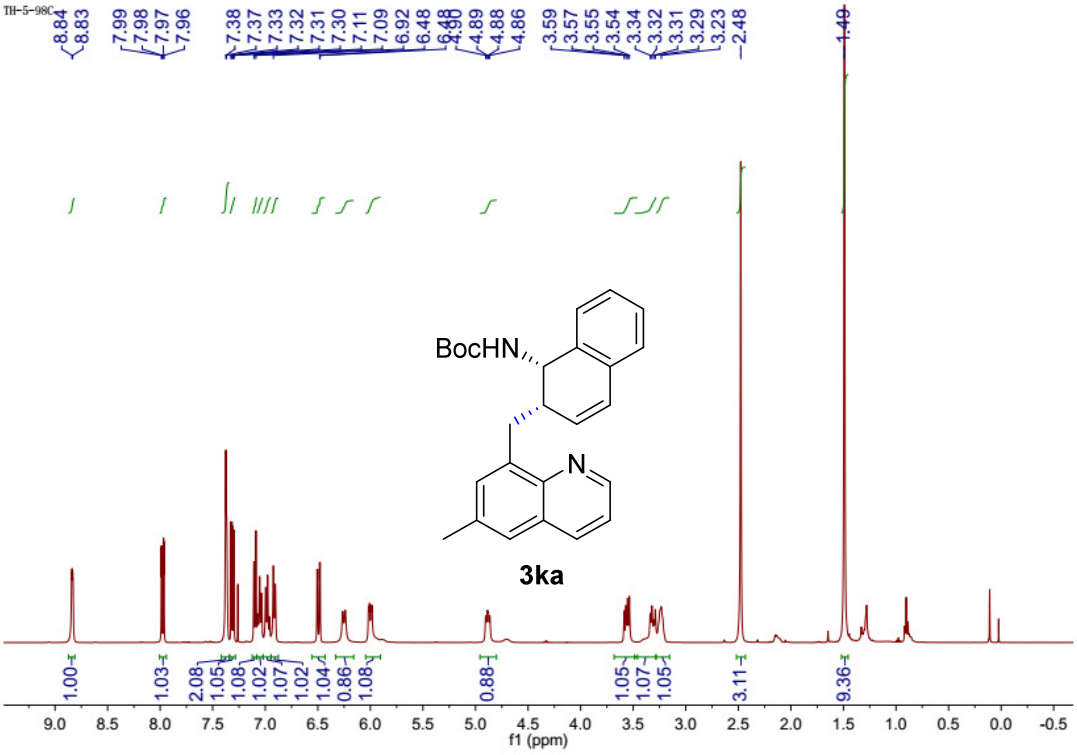
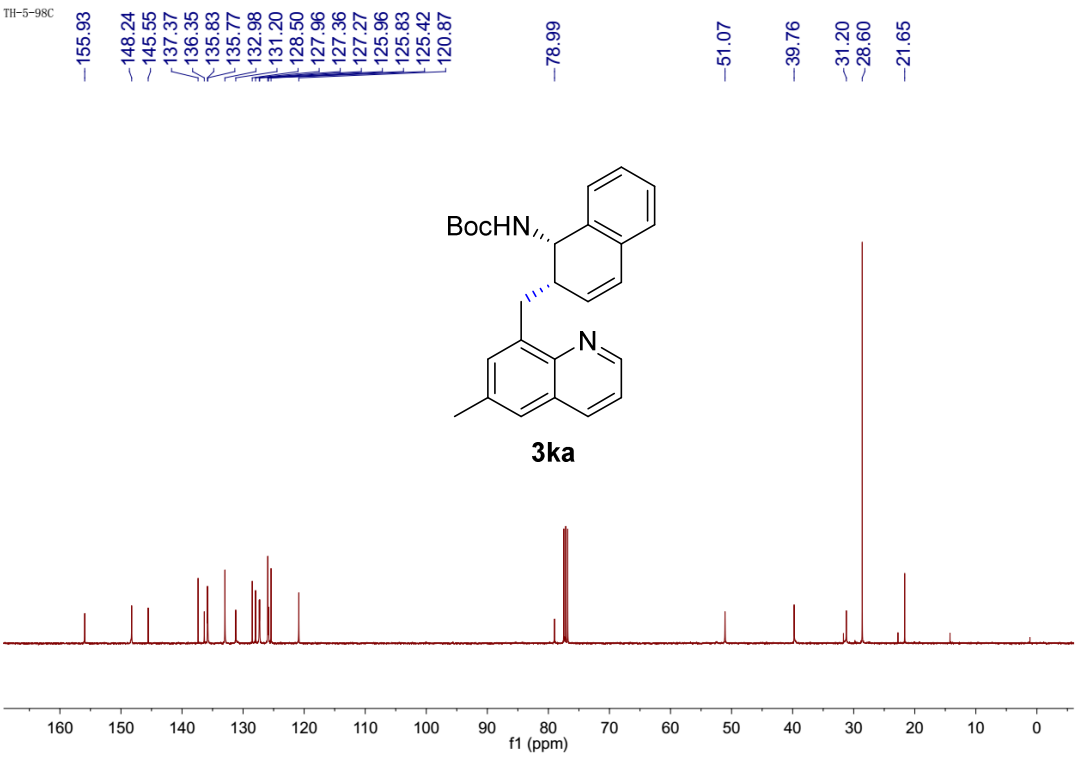
150.13
146.51
146.40
144.15
135.80
132.71
132.58
130.11
128.76
128.69
127.60
127.41
125.98
125.43
124.17
123.69
121.05
79.39
50.83
39.74
31.93
28.58
BocHN
N
NO2
3ia
f1 (ppm)


TH-5-4D
8.91
8.90
8.90
8.89
8.15
8.14
7.60
7.57
7.55
7.19
7.11
6.65
6.64
6.18
6.16
6.15
5.28
5.26
4.58
4.46
3.26
1.44
1.43
1.11
BocHN
N
3ja
0.99
1.03
1.04
1.02
1.07
1.05
4.01
1.03
1.04
0.90
0.87
0.92
0.94
2.95
9.08
f1 (ppm)


TH-5-4D
154.76
149.20
146.37
144.46
136.97
136.70
132.88
129.61
128.77
128.60
127.69
127.25
126.98
126.62
126.34
126.17
120.88
78.57
50.37
43.73
28.23
19.89
BocHN
N
3ja
f1 (ppm)


TH-5-98C
8.84
8.83
7.99
7.98
7.97
7.96
7.38
7.37
7.33
7.32
7.31
7.30
7.11
7.09
6.92
6.48
4.89
4.88
4.86
3.59
3.57
3.55
3.54
3.34
3.32
3.31
3.29
3.23
2.48
1.49
BocHN
N
3ka
1.00
1.03
2.08
1.05
1.08
1.02
1.07
1.02
1.04
0.86
1.08
0.88
1.05
1.07
1.05
3.11
9.36
f1 (ppm)


TH-5-98C
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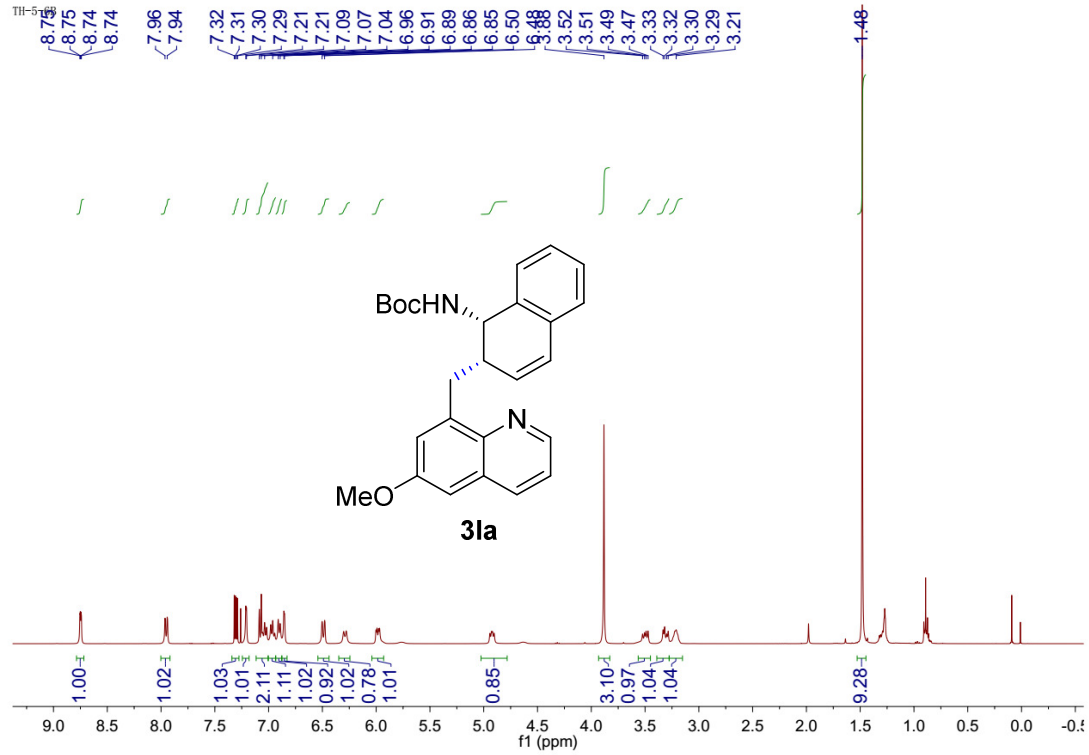
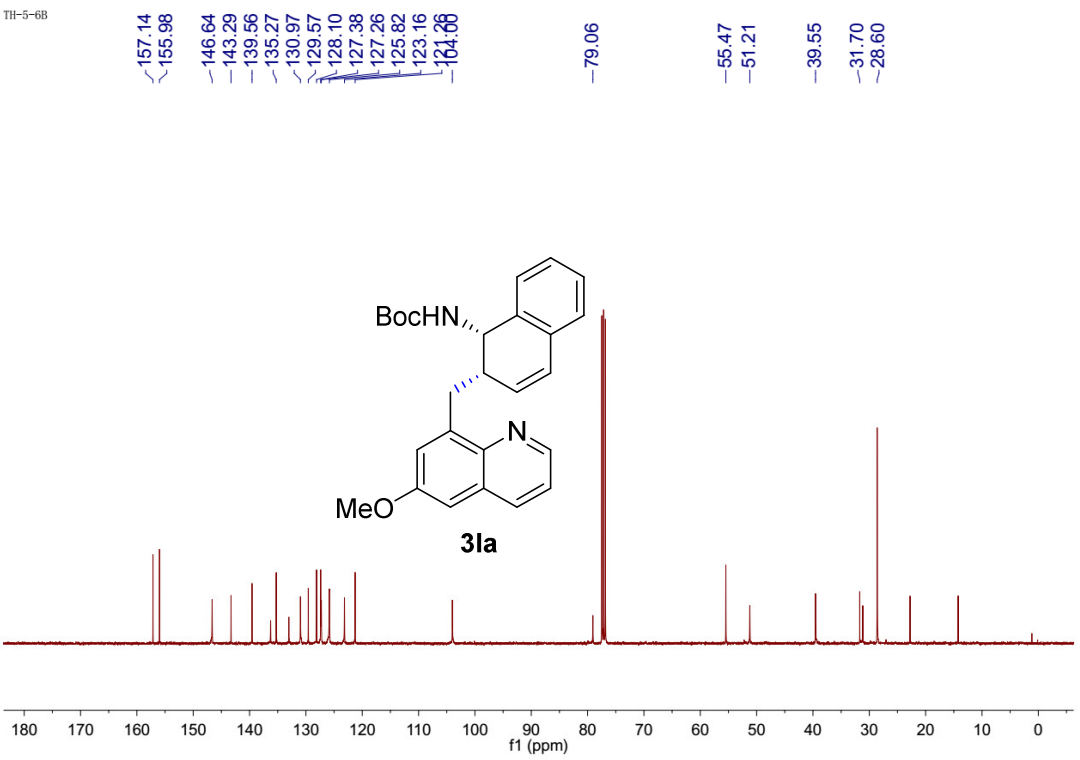
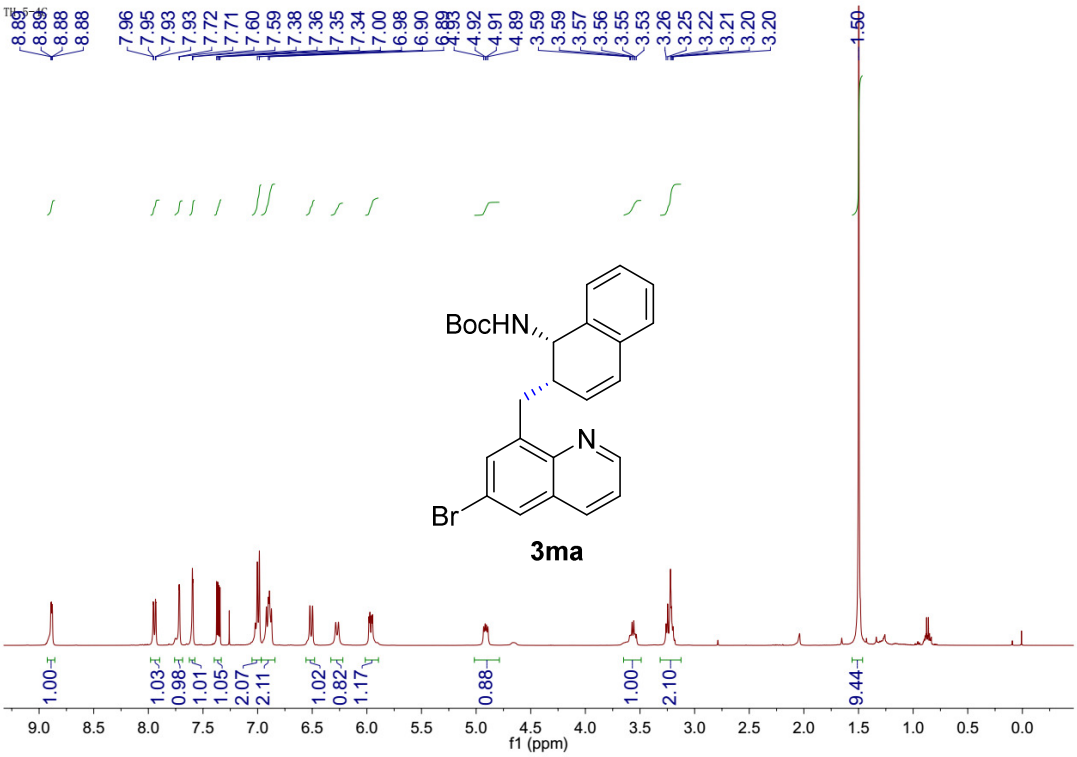
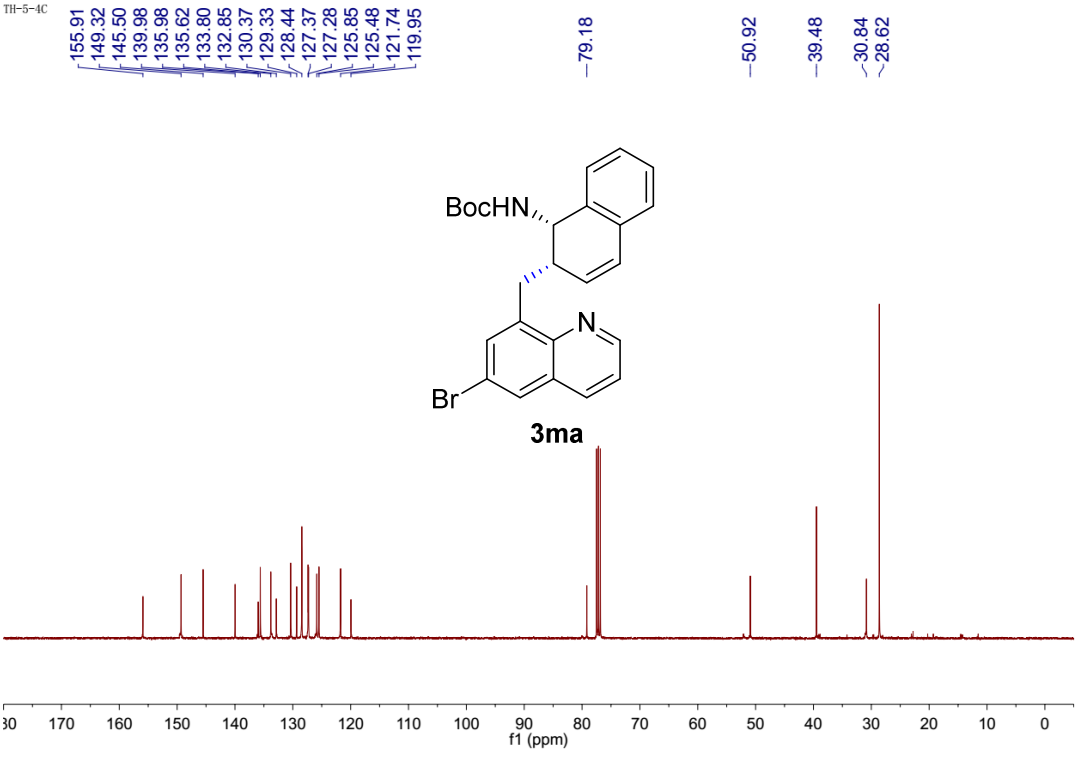
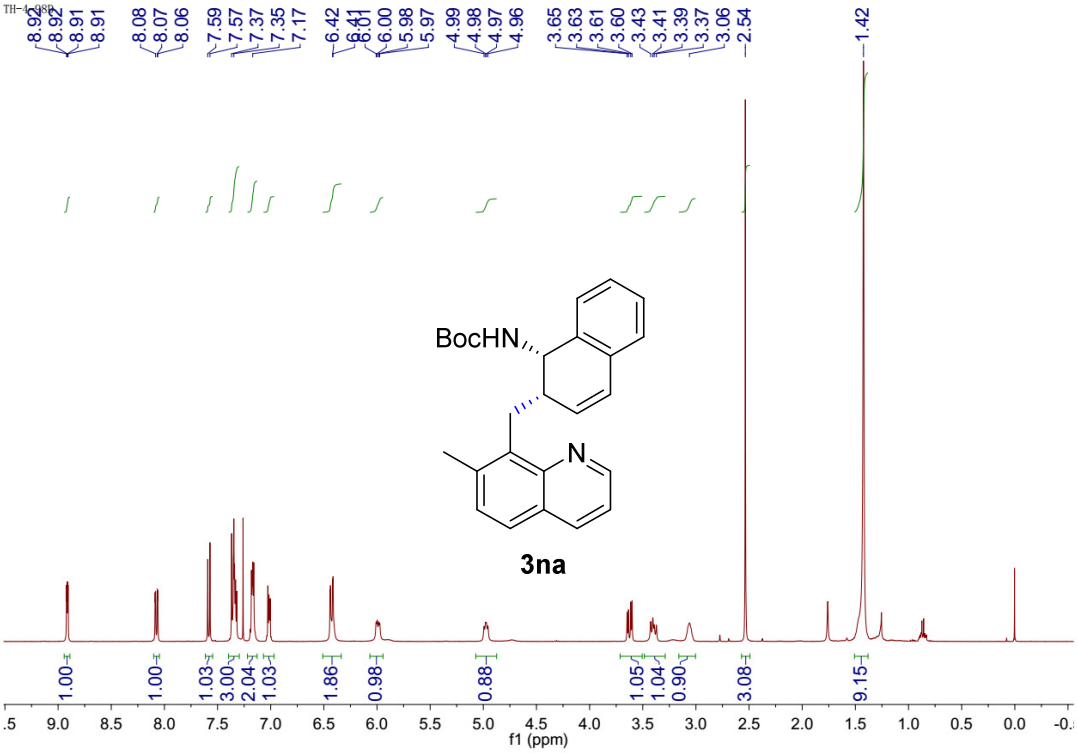
148.24
145.55
137.37
136.35
135.83
135.77
132.98
131.20
128.50
127.96
127.36
127.27
125.96
125.83
125.42
120.87
78.99
51.07
39.76
31.20
28.60
21.65
BocHN
N
3ka
f1 (ppm)

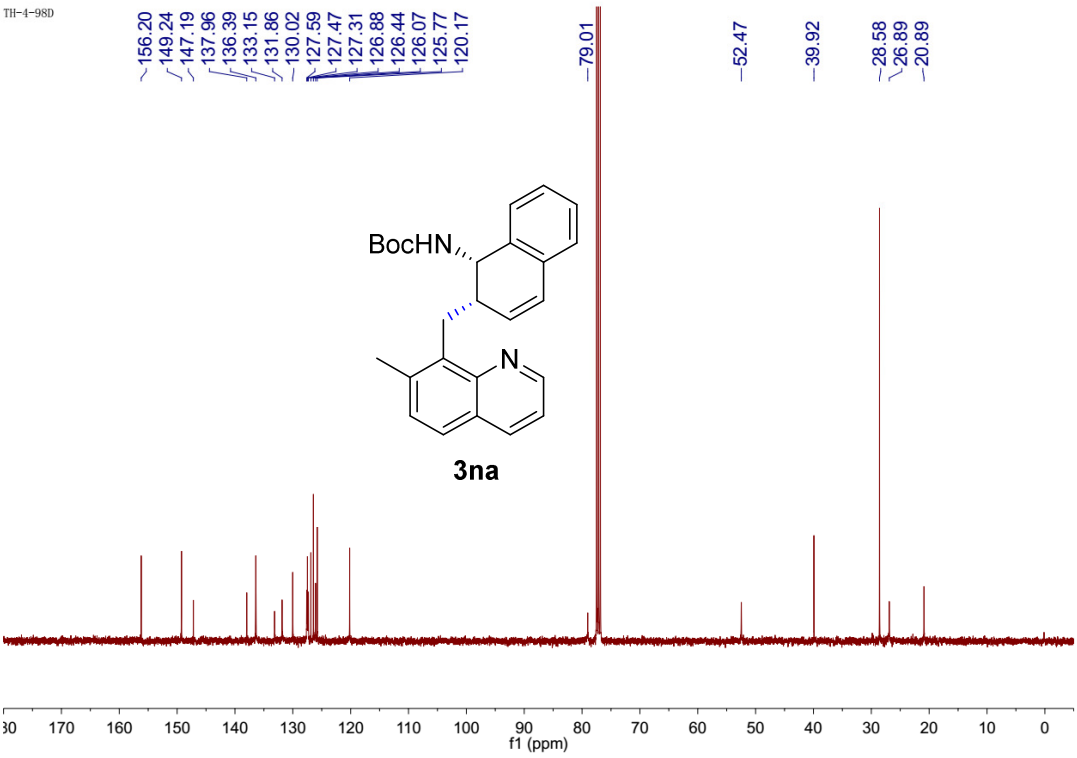

8.76
8.75
8.74
8.74
7.96
7.94
7.32
7.31
7.30
7.29
7.21
7.21
7.09
7.07
7.04
6.96
6.91
6.89
6.86
6.85
6.50
6.48
3.88
3.52
3.51
3.49
3.47
3.33
3.32
3.30
3.29
3.21
1.48
BocHN
N
MeO
3la
1.00
1.02
1.03
1.01
2.11
1.11
1.02
0.92
1.02
0.78
1.01
0.85
3.10
0.97
1.04
1.04
9.28
f1 (ppm)

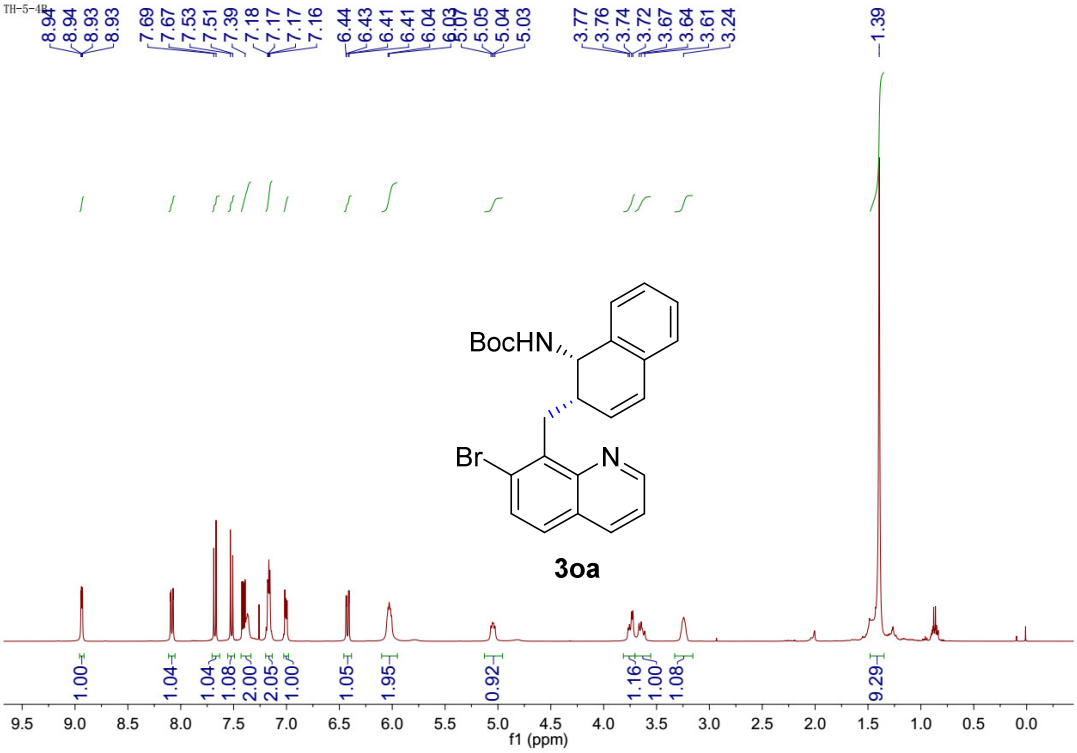

TH-5-6B
157.14
155.98
146.64
143.29
139.56
135.27
130.97
129.57
128.10
127.38
127.26
125.82
123.16
79.06
55.47
51.21
39.55
31.70
28.60
BocHN
N
MeO
3la
f1 (ppm)


BocHN
N
Br
3ma
f1 (ppm)


BocHN
N
Br
3ma
f1 (ppm)


8.93
8.92
8.91
8.91
8.08
8.07
8.06
7.59
7.57
7.37
7.35
7.17
6.42
6.41
6.01
6.00
5.98
5.97
4.99
4.98
4.97
4.96
3.65
3.63
3.61
3.60
3.43
3.41
3.39
3.37
3.06
2.54
1.42
BocHN
N
3na
1.00
1.00
1.03
3.00
2.04
1.03
1.86
0.98
0.88
1.05
1.04
0.90
3.08
9.15
f1 (ppm)


TH-4-98D
156.20
149.24
147.19
137.96
136.39
133.15
131.86
130.02
127.59
127.47
127.31
126.88
126.44
126.07
125.77
120.17
79.01
52.47
39.92
28.58
26.89
20.89
BocHN
N
3na
f1 (ppm)


TH-5-4B
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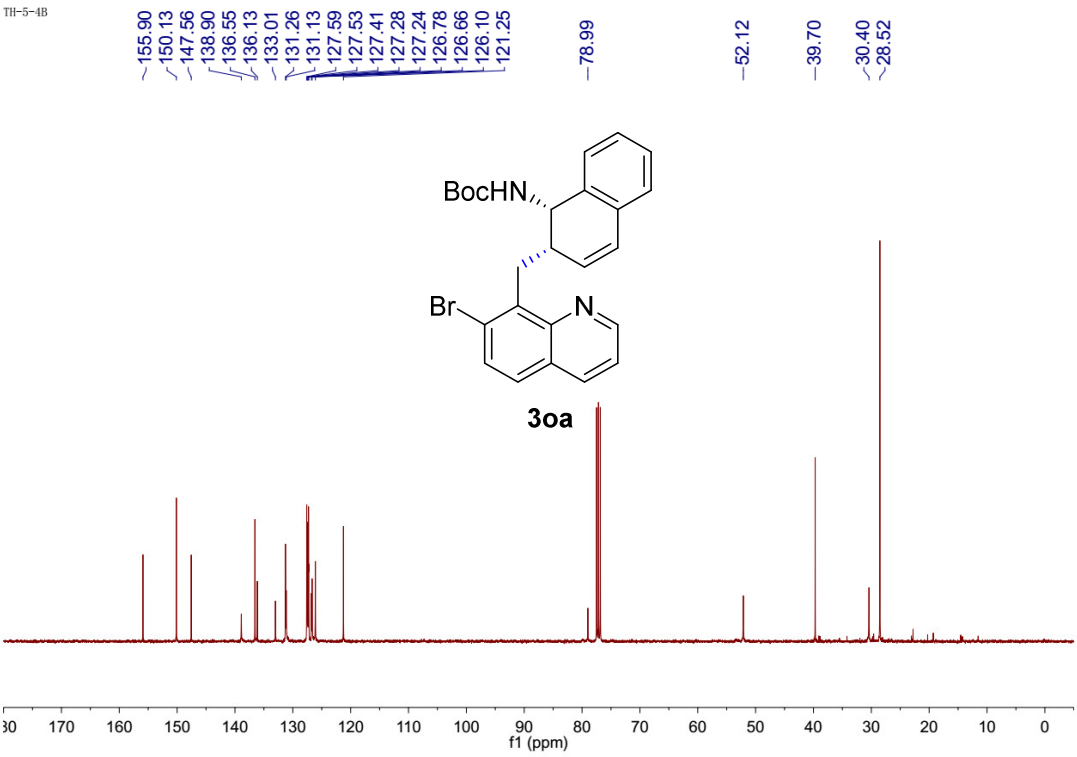
8.93
7.69
7.67
7.53
7.51
7.39
7.18
7.17
7.16
6.44
6.43
6.41
6.04
5.07
5.05
5.04
5.03
3.77
3.76
3.74
3.72
3.67
3.64
3.61
3.24
1.39
BocHN
Br
N
3oa
1.00
1.04
1.04
1.08
2.00
2.05
1.00
1.05
1.95
0.92
1.16
1.00
1.08
9.29
f1 (ppm)


TH-5-4B
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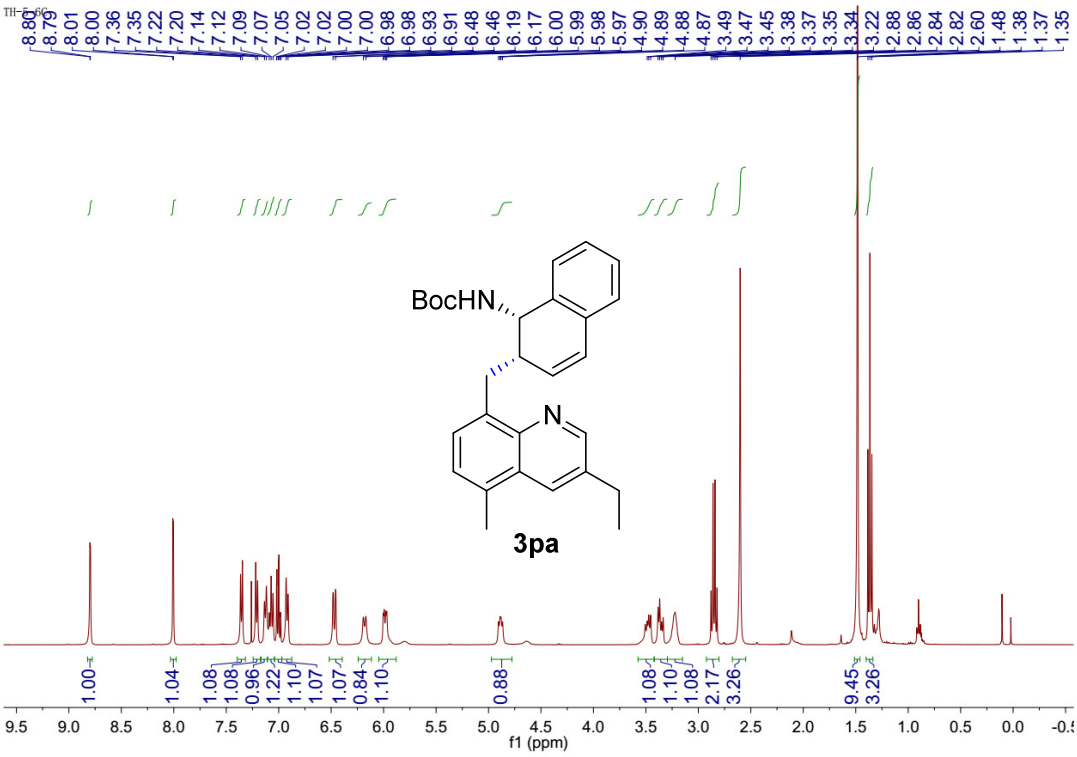
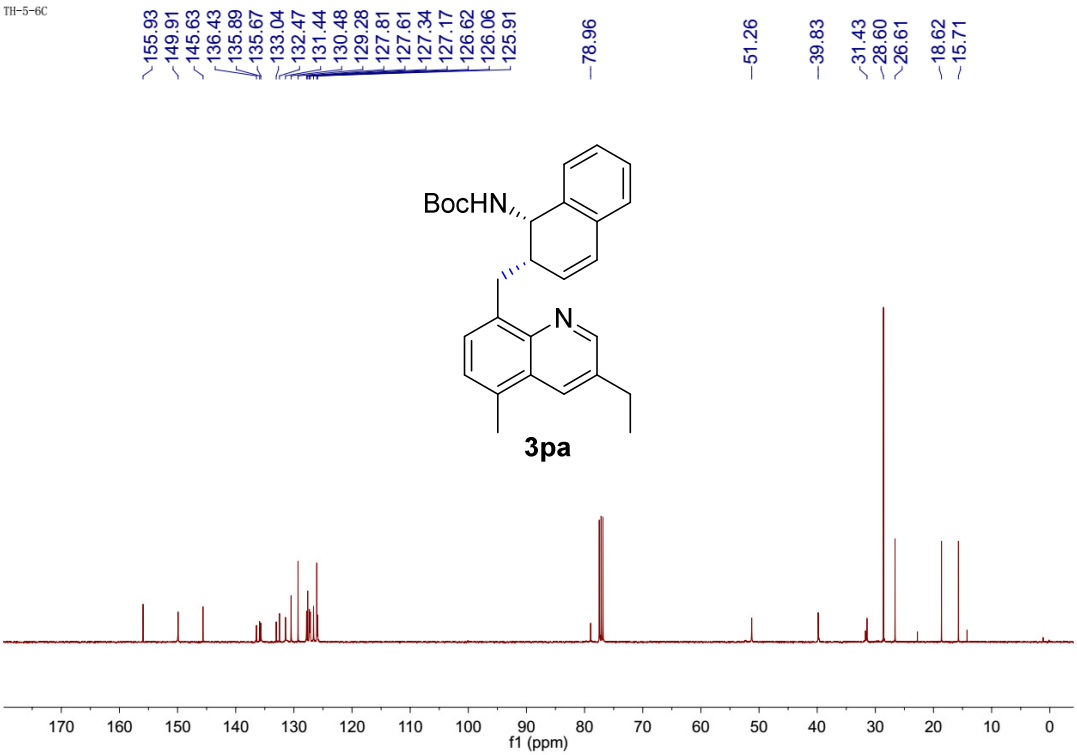
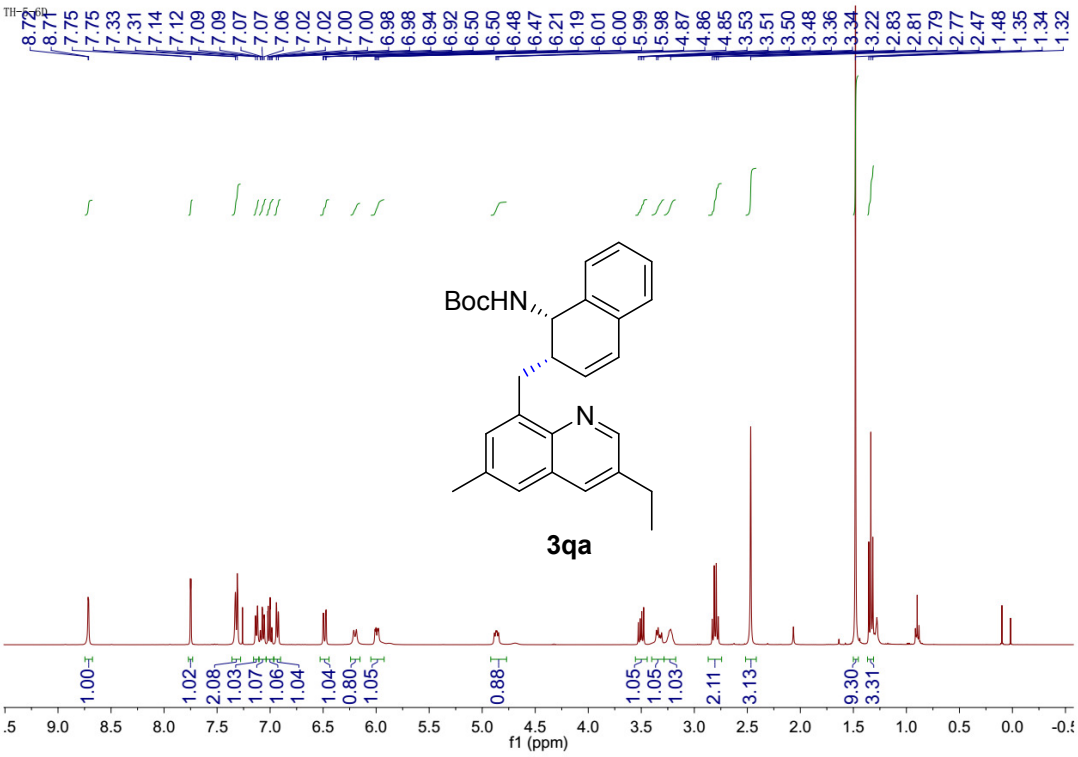
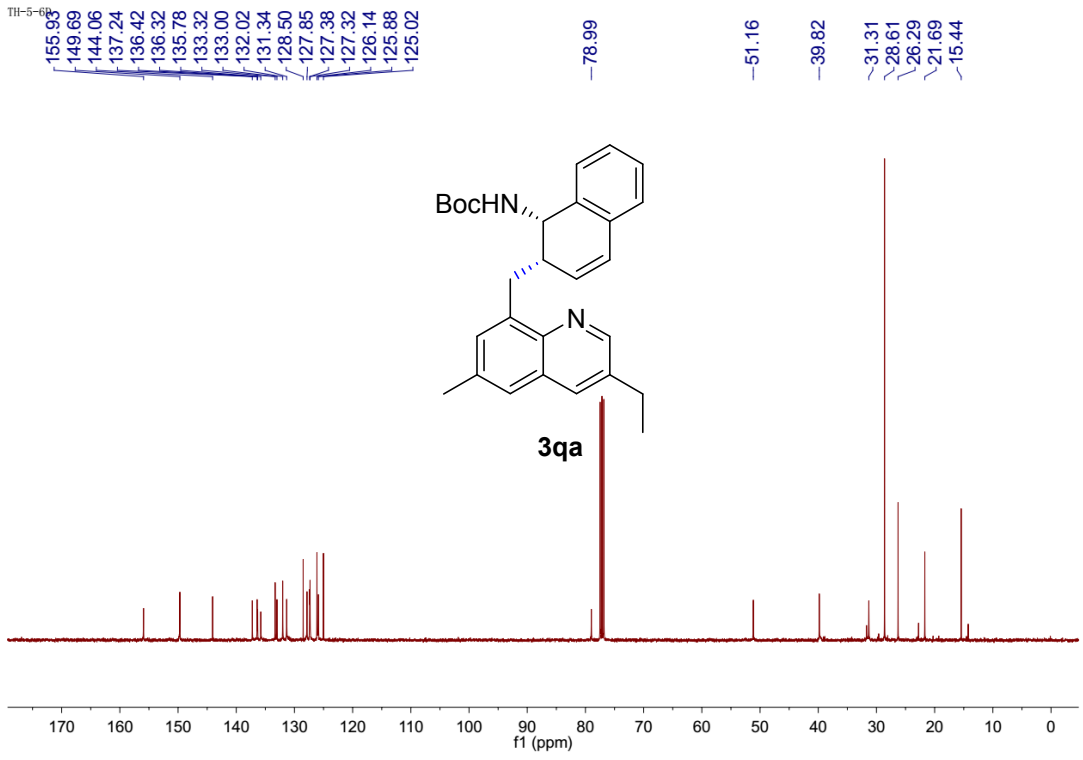
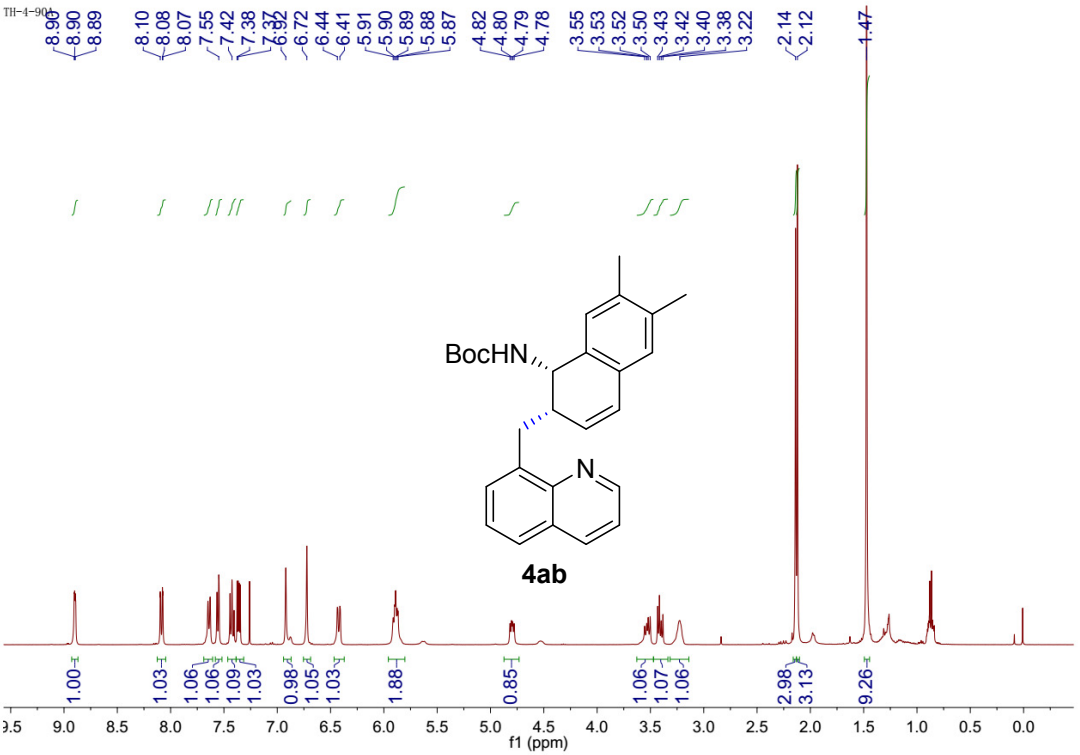
150.13
147.56
138.90
136.55
136.13
133.01
131.26
131.13
127.59
127.53
127.41
127.28
127.24
126.78
126.66
126.10
121.25
78.99
52.12
39.70
30.40
28.52
BocHN
Br
N
3oa
f1 (ppm)

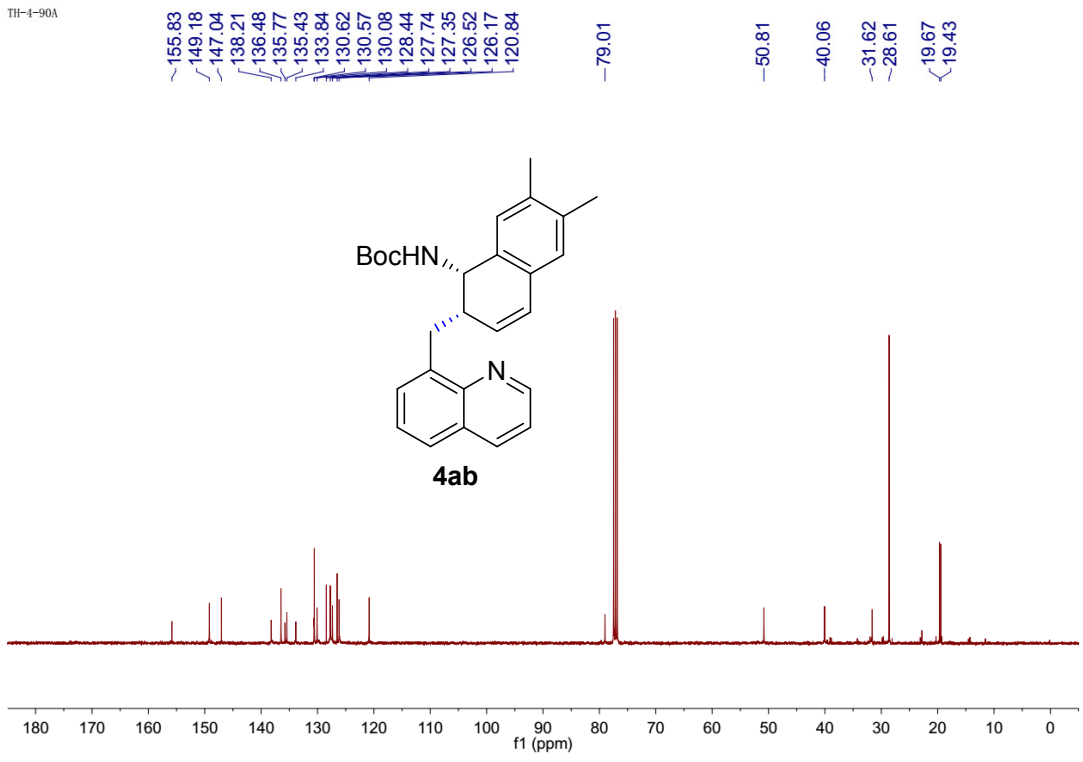

BocHN
N
3pa
f1 (ppm)

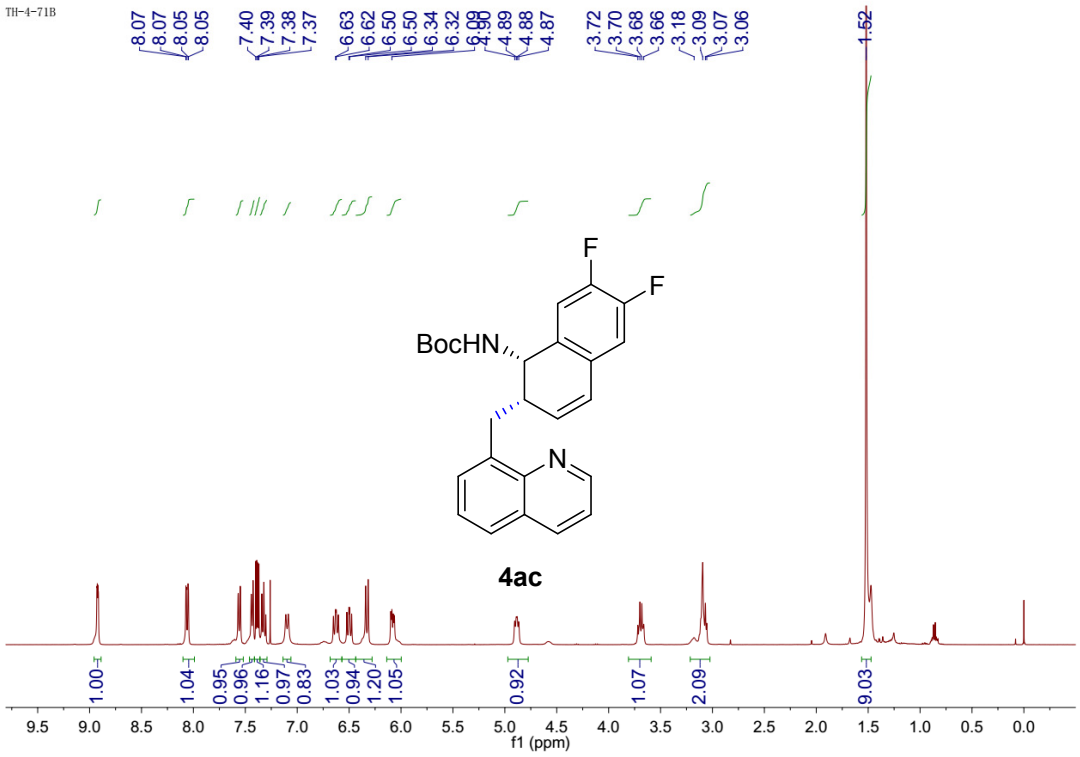

BocHN
N
3pa
f1 (ppm)

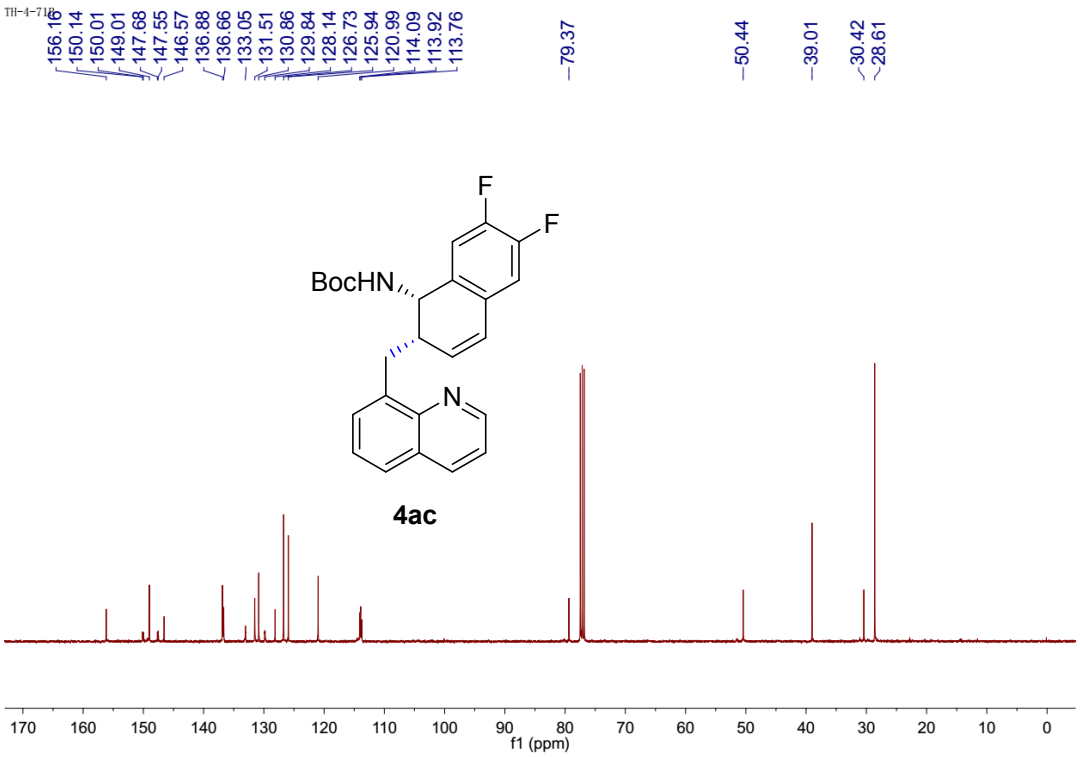

BocHN
N
3qa
f1 (ppm)

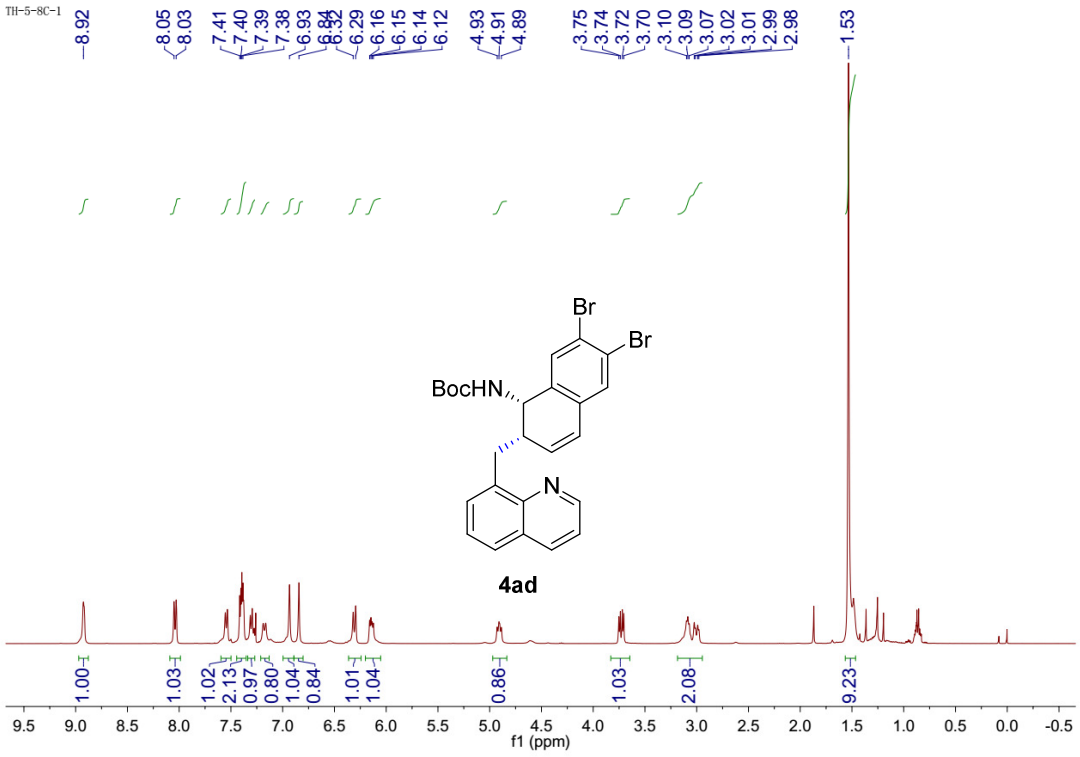

BocHN
N
3qa
f1 (ppm)


TH-4-90A
8.90
8.89
8.10
8.08
8.07
7.55
7.42
7.38
6.72
6.44
6.41
5.91
5.90
5.89
5.88
5.87
4.82
4.80
4.79
4.78
3.55
3.53
3.52
3.50
3.43
3.42
3.40
3.38
3.22
2.14
2.12
1.47
BocHN
N
4ab
1.00
1.03
1.06
1.06
1.09
1.03
0.98
1.05
1.03
1.88
0.85
1.06
1.07
1.06
2.98
3.13
9.26
f1 (ppm)


TH-4-90A
155.83
149.18
147.04
138.21
136.48
135.77
135.43
133.84
130.62
130.57
130.08
128.44
127.74
127.35
126.52
126.17
120.84
79.01
50.81
40.06
31.62
28.61
19.67
19.43
BocHN
N
4ab
f1 (ppm)


TH-4-71B
8.07
8.07
8.05
8.05
7.40
7.39
7.38
7.37
6.63
6.62
6.50
6.50
6.34
6.32
4.89
4.88
4.87
3.72
3.70
3.68
3.66
3.18
3.09
3.07
3.06
1.52
F
F
BocHN
N
4ac
1.00
1.04
0.95
0.96
1.16
0.97
0.83
1.03
0.94
1.20
1.05
0.92
1.07
2.09
9.03
f1 (ppm)


TH-4-71B
156.18
150.14
150.01
149.01
147.68
147.55
146.57
136.88
136.66
133.05
131.51
130.86
129.84
128.14
126.73
125.94
120.99
114.09
113.92
113.76
79.37
50.44
39.01
30.42
28.61
F
F
BocHN
N
4ac
f1 (ppm)


TH-5-8C-1
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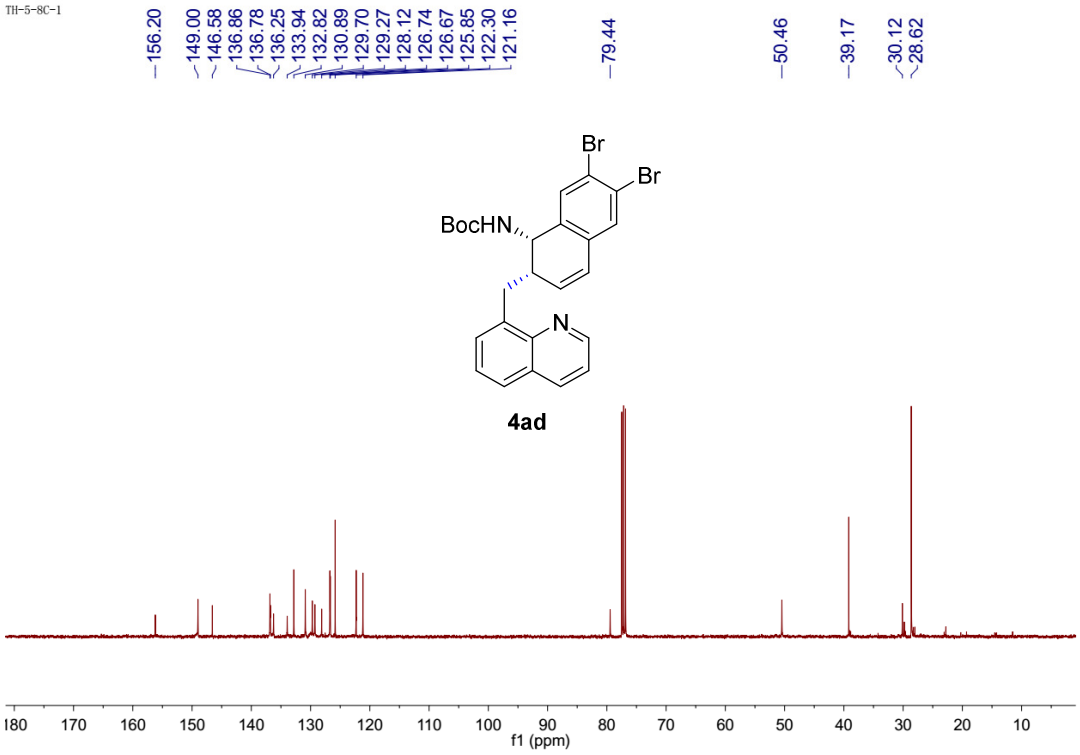
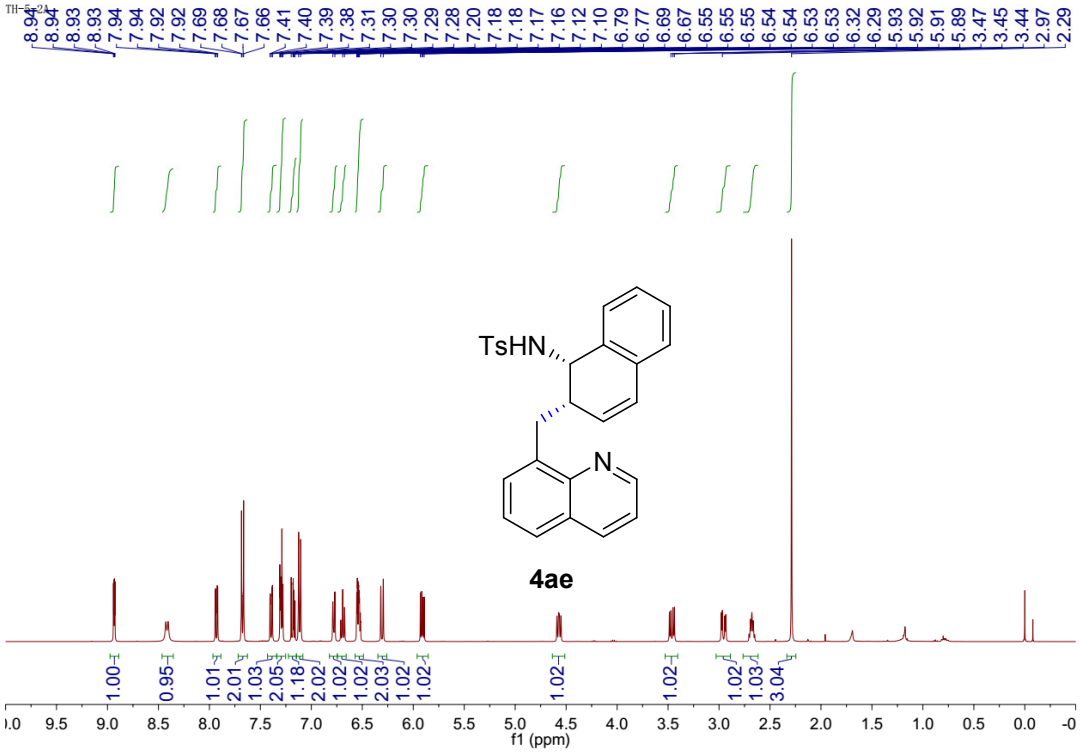
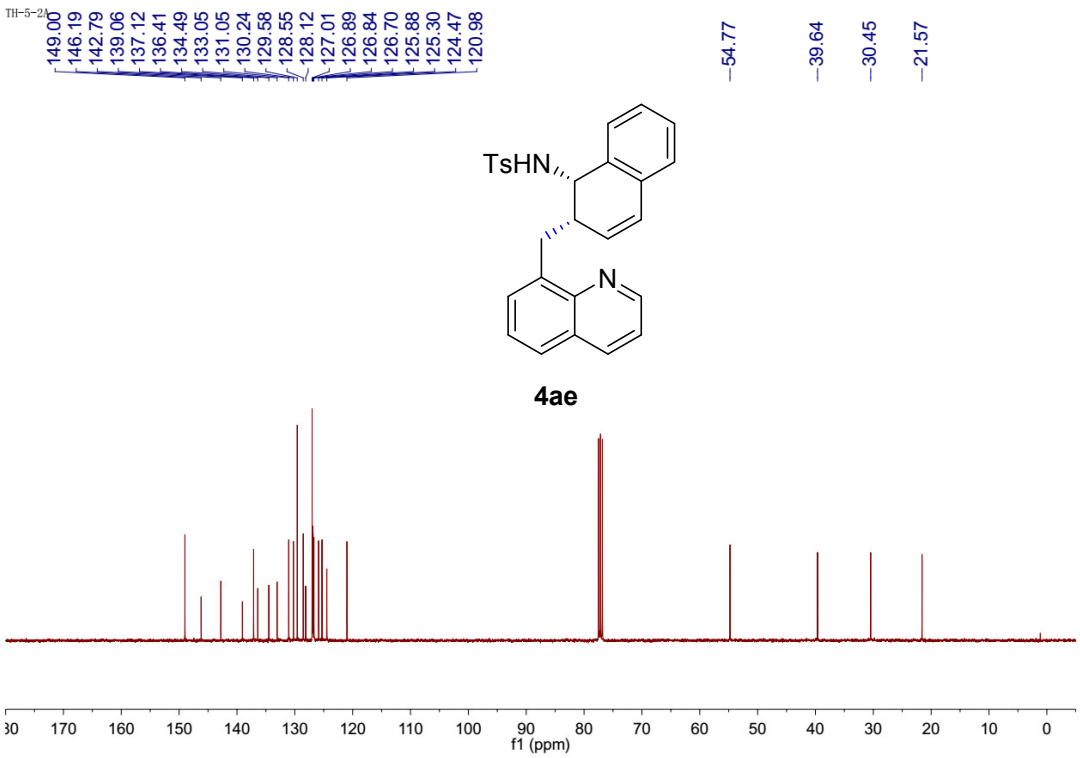
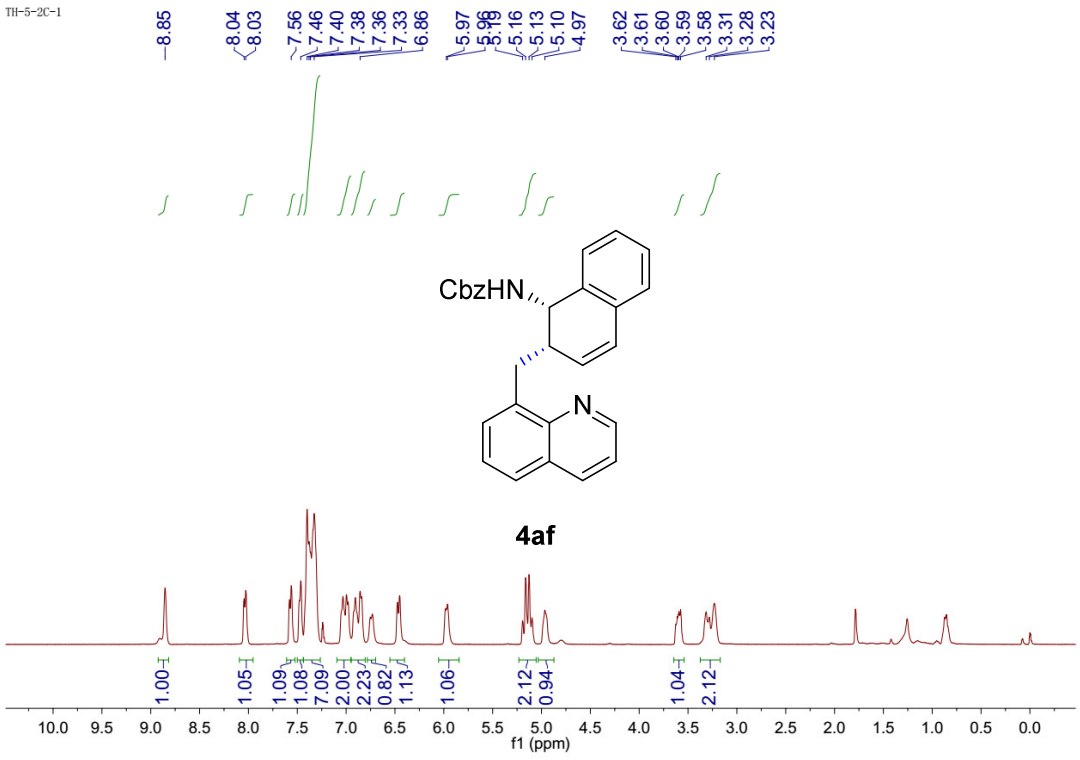
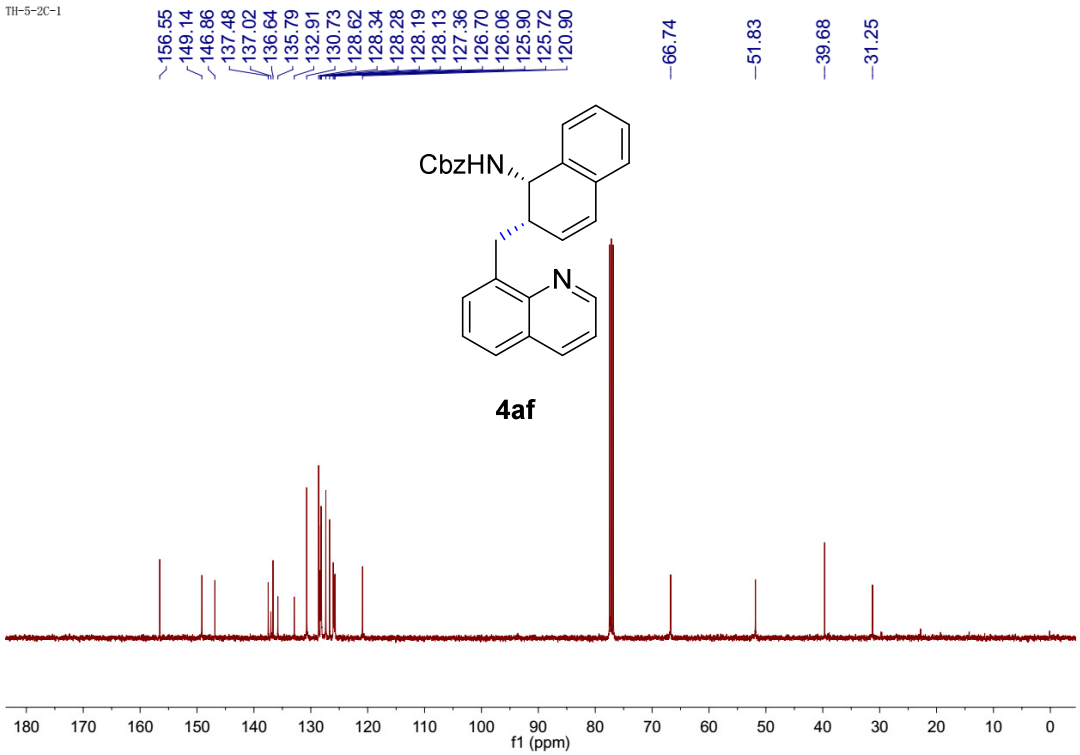
8.05
8.03
7.41
7.40
7.39
7.38
6.93
6.84
6.32
6.29
6.16
6.15
6.14
6.12
4.93
4.91
4.89
3.75
3.74
3.72
3.70
3.10
3.09
3.07
3.02
3.01
2.99
2.98
1.53
Br
Br
BocHN
N
4ad
1.00
1.03
1.02
2.13
0.97
0.80
1.04
0.84
1.01
1.04
0.86
1.03
2.08
9.23
f1 (ppm)


TH-5-8C-1
156.20
149.00
146.58
136.86
136.78
136.25
133.94
132.82
130.89
129.70
129.27
128.12
126.74
126.67
125.85
122.30
121.16
79.44
50.46
39.17
30.12
28.62
Br
Br
BocHN
N
4ad
f1 (ppm)


TsHN
N
4ae
f1 (ppm)

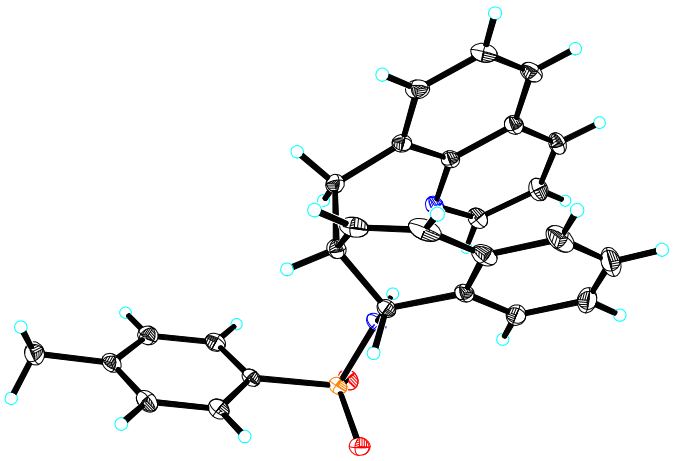

TsHN
N
4ae
f1 (ppm)


TH-5-2C-1
8.85
8.04
8.03
7.56
7.46
7.40
7.38
7.36
7.33
6.86
5.97
5.96
5.16
5.13
5.10
4.97
3.62
3.61
3.60
3.59
3.58
3.31
3.28
3.23
CbzHN
N
4af
1.00
1.05
1.09
1.08
7.09
2.00
2.23
0.82
1.13
1.06
2.12
0.94
1.04
2.12
f1 (ppm)


TH-5-2C-1
156.55
149.14
146.86
137.48
137.02
136.64
135.79
132.91
130.73
128.62
128.34
128.28
128.19
128.13
127.36
126.70
126.06
125.90
125.72
120.90
66.74
51.83
39.68
31.25
CbzHN
N
4af
f1 (ppm)

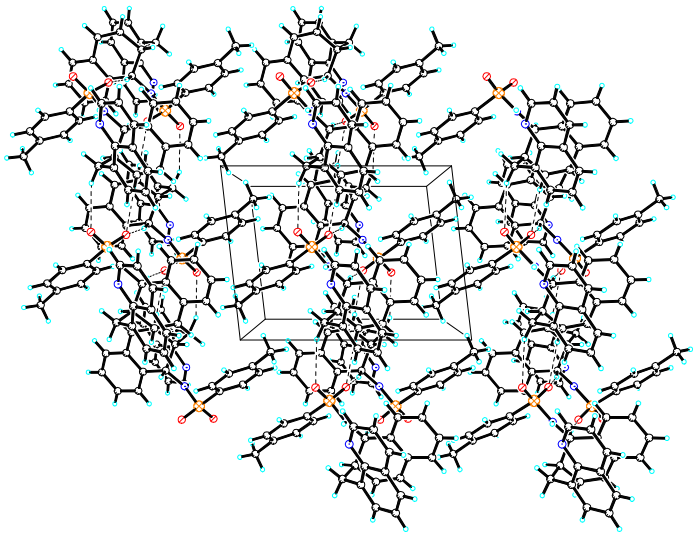
9: X-Ray Crystallography of Compound 4ae

Crystal data for qth1: $C_{27}H_{24}N_2O_2S$, M = 440.54, a = 8.1661(2) Å, b = 25.3026(5) Å, c = 10.7553(2) Å, α = 90°, β = 96.5120(10)°, γ = 90°, V = 2207.96(8) Å^3, T = 100.(2) K, space group $P121/n1$, Z = 4, μ(Cu Kα) = 1.516 mm^{-1}, 25622 reflections measured, 4363 independent reflections (R_{int} = 0.0373). The final R_1 values were 0.0354 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0923 ($I > 2\sigma(I)$). The final R_1 values were 0.0384 (all data). The final $wR(F^2)$ values were 0.0949 (all data). The goodness of fit on F^2 was 1.037.



View of a molecule of qth1 with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of qth1.

Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for qth1_0m.

Identification code	global	
Empirical formula	C27 H24 N2 O2 S	
Formula weight	440.54	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.1661(2) Å	α= 90°.
	b = 25.3026(5) Å	β= 96.5120(10)°.
	c = 10.7553(2) Å	γ = 90°.
Volume	2207.96(8) $Å^3$	
Z	4	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	1.516 mm^{-1}	
F(000)	928	
Crystal size	0.250 x 0.150 x 0.130 mm^3	
Theta range for data collection	3.49 to 72.44°.	
Index ranges	-9<=h<=10, -31<=k<=31, -13<=l<=12	
Reflections collected	25622	
Independent reflections	4363 [R(int) = 0.0373]	
Completeness to theta = 72.44°	99.7 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.83 and 0.57
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4363 / 0 / 290
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0923
R indices (all data)	R1 = 0.0384, wR2 = 0.0949
Largest diff. peak and hole	0.357 and -0.431 e.$Å^{-3}$