Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cp*Rh(III)-catalyzed and solvent-controlled tunable [4+1]/[4+3] annulation for the divergent assembly of dihydrobenzo[*cd*]indoles and dihydronaphtho[1,8-*bc*]azepines

Zhuo-Zhuo Zhang,*[a] Ya Li [b] and Bing-Feng Shi*[b]

[a]School of Food and Biological Engineering, Chengdu University, Chengdu 610106 (China)

[b]Department of Chemistry, Zhejiang University, Hangzhou 310027 (China)

Supporting Information

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1. General Information

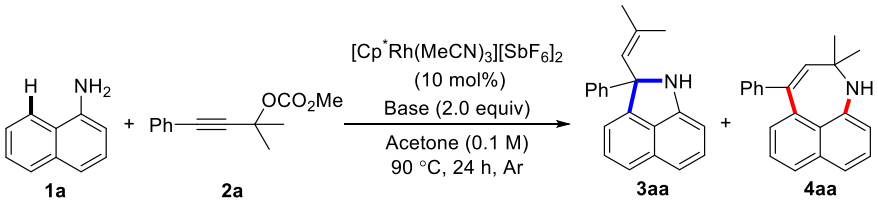
NMR spectra were recorded on a Bruke Avance operating for ^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz, using TMS as internal standard. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument using EI ionization and ESI ionization. The Crystal data of the products were collected on a Bruker D8 Venture.

All commercially available chemicals were used as received without further purification, unless otherwise stated. Catalytic reactions were carried out in Schlenk flasks under Ar atmosphere using pre-dried glassware. Free 1-naphthylamine **1** were obtained from Bide Pharmatech Ltd. $AgSbF_6$ were obtained from Energy. LiOAc, NaOAc, and $Cu(OAc)_2$ were obtained from Aladdin. $[Cp^*Rh(MeCN)_3][SbF_6]_2$ were prepared according to the literature.[S1] **2** was known compounds and prepared according to the literature.[S2]

2. Experiment Details and Characterization Date

2.1 Optimization of Reaction Conditions.

Table S1. Optimization of Bases.[a]

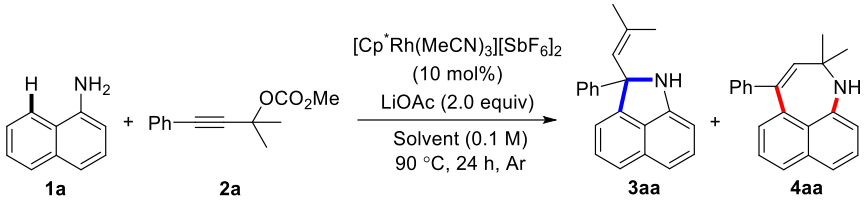


1a 2a 3aa 4aa

entry	base	solvent	yield (%)	
			3aa	4aa
1	NaOAc	Aectone	30[b]	0
2	KOAc	Aectone	24	0
3	CsOAc	Aectone	trace	0
4	LiOAc	Aectone	46	0
5	$Cu(OAc)_2$	Aectone	5	0
6	$Zn(OAc)_2$	Aectone	trace	0

[a] Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (10 mol%), Base (2.0 equiv.), Acetone (1.0 mL), 90 °C, 24 h under Ar atmosphere. ^1H NMR yield using 1,3,5-Trimethoxybenzene as internal standard. [b] Isolated yield.

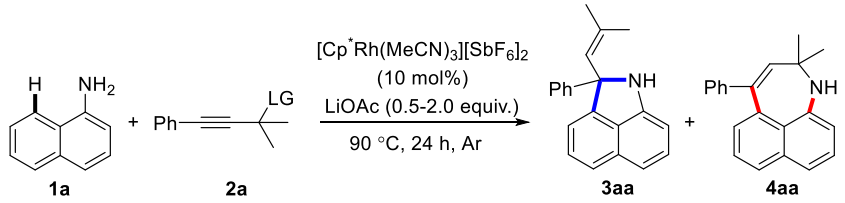
Table S2. Optimization of Solvents.[a]



entry	base	Solvent	yield (%)	
			3aa	4aa
1	LiOAc	PhCl	trace	trace
2	LiOAc	$PhCF_3$	14	trace
3	LiOAc	DCE	trace	10
4	LiOAc	Dioxane	trace	0
5	LiOAc	MTBE	40	0
6	LiOAc	THF	44	trace
7	LiOAc	EtOAc	36	0
8	LiOAc	MeCN	37	8
9	LiOAc	DMF	0	trace
10	LiOAc	Aectone/MeCN (9:1, v/v)	56	4
11	LiOAc	THF/MeCN (9:1, v/v)	61	0
12	LiOAc	EtOAc/MeCN (9:1, v/v)	63	0
13	**LiOAc**	**MTBE/MeCN (9:1, v/v)**	**75 (72)[b]**	**0**
14	LiOAc	$PhCF_3$/MeCN (9:1, v/v)	27	15
15	LiOAc	DCE/MeCN (9:1, v/v)	20	40
16	LiOAc	DCE/MeCN (9:1, v/v)	23	55
17	LiOAc	DCE/MeCN (8:2, v/v)	15	58
18	LiOAc	DCE/MeCN (7:3, v/v)	14	65
19	LiOAc (1.0 equiv)	DCE/MeCN (7:3, v/v)	13	70
20	**LiOAc (0.5 equiv.)**	**DCE/MeCN (7:3, v/v)**	**10**	**72 (68)[b]**

[a] Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (10 mol%), LiOAc (0.5-2.0 equiv.), solvent (1.0 mL), 90 °C, 24 h under Ar atmosphere. ^1H NMR yield using 1,3,5-Trimethoxybenzene as internal standard. [b] Isolated yield.

Table S3. Optimization of Leaving Groups.[a]

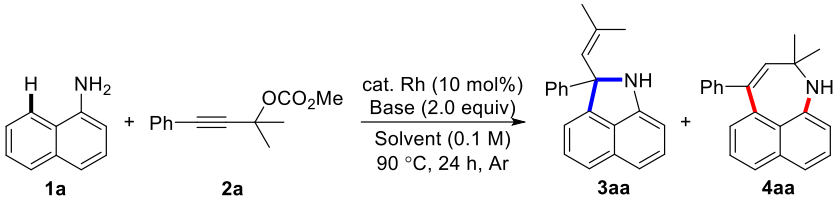


1a 2a 3aa 4aa

entry	leaving group (LG)	base	solvent	yield (%) 3aa	yield (%) 4aa
1	OH	LiOAc (2.0 equiv)	MTBE/MeCN (9:1, v/v)	0	0
2	OH	LiOAc (0.5 equiv)	DCE/MeCN (7:3, v/v)	0	0
3	OAc	LiOAc (2.0 equiv)	MTBE/MeCN (9:1, v/v)	38	trace
4	OAc	LiOAc (0.5 equiv)	DCE/MeCN (7:3, v/v)	trace	23
5	OBoc	LiOAc (2.0 equiv)	MTBE/MeCN (9:1, v/v)	31	trace
6	OBoc	LiOAc (0.5 equiv)	DCE/MeCN (7:3, v/v)	trace	14

[a] Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (10 mol%), LiOAc (0.5-2.0 equiv.), solvent (1.0 mL), 90 °C, 24 h under Ar atmosphere. ^1H NMR yield using 1,3,5-Trimethoxybenzene as internal standard.

Table S4. Optimization of Catalysts.[a]

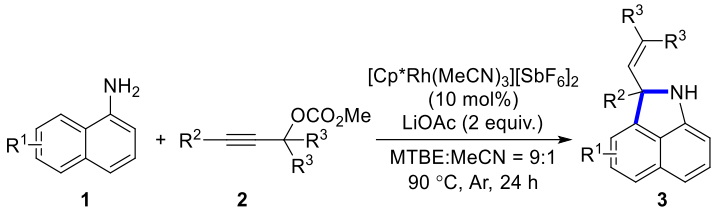


entry	catalyst	base	solvent	yield (%)	
				3aa	4aa
1	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	---	MTBE/MeCN (9:1, v/v)	0	0
2	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	---	DCE/MeCN (7:3, v/v)	0	0
3	$[Cp^*RhCl_2] + AgSbF_6$	LiOAc (2.0 equiv.)	MTBE/MeCN (9:1, v/v)	trace	0
4	$[Cp^*RhCl_2] + AgSbF_6$	LiOAc (0.5 equiv.)	DCE/MeCN (7:3, v/v)	0	trace
5	$[Cp^*Ir(MeCN)_3][SbF_6]_2$	LiOAc (2.0 equiv.)	MTBE/MeCN (9:1, v/v)	24	0
6	$[Cp^*Ir(MeCN)_3][SbF_6]_2$	LiOAc (0.5 equiv.)	DCE/MeCN (7:3, v/v)	0	22
7	$[Cp^*Co(MeCN)_3][SbF_6]_2$	LiOAc (2.0 equiv.)	MTBE/MeCN (9:1, v/v)	0	0
8	$[Cp^*Co(MeCN)_3][SbF_6]_2$	LiOAc (0.5 equiv.)	DCE/MeCN (7:3, v/v)	0	0
9	$[Cp^*Rh(OAc)_2]$	LiOAc (2.0 equiv.)	MTBE/MeCN (9:1, v/v)	0	0
10	$[Cp^*Rh(OAc)_2]$	LiOAc (0.5 equiv.)	DCE/MeCN (7:3, v/v)	0	0
11	$[Cp^*Rh(OAc)_2] + AgSbF_6$	LiOAc (2.0 equiv.)	MTBE/MeCN (9:1, v/v)	49	0
12	$[Cp^*Rh(OAc)_2] + AgSbF_6$	LiOAc (0.5 equiv.)	DCE/MeCN (7:3, v/v)	24	16
13	---	LiOAc (2.0 equiv.)	MTBE/MeCN (9:1, v/v)	0	0
14	---	LiOAc (0.5 equiv.)	DCE/MeCN (7:3, v/v)	0	0

[a] Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), [Rh] (10 mol%), LiOAc (0.5-2.0 equiv.), solvent (1.0 mL), 90 °C, 24 h under Ar atmosphere. ^{1}H NMR yield using 1,3,5-Trimethoxybenzene as internal standard.

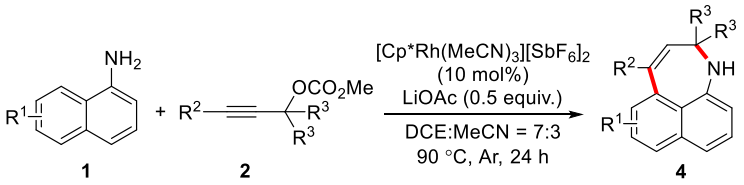
2.2 General Procedure for Cp*Rh(III)-Catalyzed and Solvent-Controlled Tunable [4+1]/[4+3] Annulation of free 1-Naphthylamines

The Synthesis of 3:



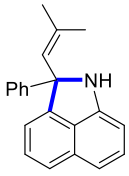
General Procedure A: To a 20 mL Schlenk tube was added free 1-naphthylamine **1** (0.12 mmol), propargyl carbonate **2** (0.1 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 10 mol%), LiOAc (13.2 mg, 0.2 mmol), MTBE (0.9 mL) and MeCN (0.1 mL), the tube was sealed up with a cap and evacuated then refilled with Ar and kept stirring at 90 °C (aluminum heat transfer block) for 24 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC using Hexane/EtOAc or Hexane/Acetone as the eluent to afford the desired product **3**.

The Synthesis of 4:



General Procedure B: To a 20 mL Schlenk tube was added 1-naphthylamine **1** (0.12 mmol), propargyl carbonate **2** (0.1 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 10 mol%), LiOAc (3.3 mg, 0.05 mmol), DCE (0.7 mL) and MeCN (0.3 mL), the tube was sealed up with a cap and evacuated then refilled with Ar and kept stirring at 90 °C (aluminum heat transfer block) for 24 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC using Hexane/EtOAc or Hexane/Acetone as the eluent to afford the desired product **4**.

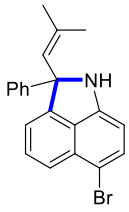
2-(2-methylprop-1-en-1-yl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3aa)



Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 15 : 1 to give **3aa** as yellow solid (20.5 mg, 72% yield) m.p.: 73-74 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (dd, *J* = 7.6, 5.0 Hz, 2H), 6.55 (d, *J* = 7.2 Hz, 1H), 5.99 (s, 1H), 5.03 (s, 1H), 1.81 (s, 3H), 1.45 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.8, 149.0, 147.1, 137.5, 132.0, 131.1, 129.8, 128.7, 128.6, 128.0, 126.9, 125.9, 122.9, 116.7, 113.7, 100.0, 73.5, 26.8, 20.0. **HRMS (ESI)**

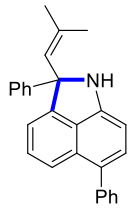
m/z: $[M+H]^+$ calc. for $C_{21}H_{20}N$ 286.1590; found: 286.1591.

6-bromo-2-(2-methylprop-1-en-1-yl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3ba)



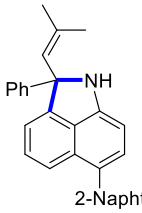
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ba** as yellow powder (16.3 mg, 45% yield). m.p.: 105-106 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.15 (d, *J* = 7.0 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 5.96 (t, *J* = 1.5 Hz, 1H), 5.05 (s, 1H), 1.81 (d, *J* = 1.5 Hz, 3H), 1.42 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.6, 149.0, 146.5, 138.1, 132.5, 131.1, 130.3, 129.8, 128.8, 127.1, 125.8, 122.4, 117.7, 105.8, 100.8, 74.0, 26.8, 20.0. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}Br$ 364.0695; found: 364.0694.

2-(2-methylprop-1-en-1-yl)-2,6-diphenyl-1,2-dihydrobenzo[*cd*]indole (3ca)



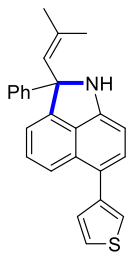
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ca** as yellow solid (28.9 mg, 80% yield). m.p.: 124-125 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.54 (m, 4H), 7.52 – 7.46 (m, 2H), 7.45 – 7.42 (m, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.25 – 7.21 (m, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 6.64 (d, *J* = 7.4 Hz, 1H), 6.03 (p, *J* = 1.5 Hz, 1H), 5.10 (s, 1H), 1.83 (d, *J* = 1.5 Hz, 3H), 1.50 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.5, 149.3, 147.0, 140.8, 137.5, 131.1, 130.6, 130.1, 129.7, 128.9, 128.7, 128.5, 128.1, 127.3, 126.9, 126.4, 126.0, 121.6, 116.9, 100.0, 73.7, 26.8, 20.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{27}H_{24}N$ 362.1903; found: 362.1901.

2-(2-methylprop-1-en-1-yl)-6-(naphthalen-2-yl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3da)



Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3da** as yellow oil (29.2 mg, 71% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 1.8 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.76 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.55 – 7.48 (m, 3H), 7.47 – 7.43 (m, 1H), 7.34 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 6.9 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.10 – 5.92 (m, 1H), 5.14 (s, 1H), 1.85 (d, *J* = 1.5 Hz, 3H), 1.51 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.6, 149.3, 147.0, 138.4, 137.6, 133.9, 132.4, 131.0, 131.0, 130.3, 129.0, 128.8, 128.5, 128.2, 128.1, 127.9, 127.9, 127.8, 127.1, 127.0, 126.2, 126.0, 125.6, 121.6, 117.1, 100.1, 73.8, 26.8, 20.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{31}H_{26}N$ 412.2060; found: 412.2058.

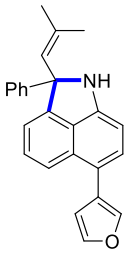
2-(2-methylprop-1-en-1-yl)-2-phenyl-6-(thiophen-3-yl)-1,2-dihydrobenzo[*cd*]indole (3ea)



Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ea** as brown solid (20.2 mg, 55% yield). m.p.: 121-123 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.50 – 7.43 (m, 1H), 7.46 – 7.39 (m, 2H), 7.37 (d, *J* = 4.0 Hz, 2H), 7.31 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.26 – 7.18 (m, 1H), 7.15 (d, *J* = 7.0 Hz, 1H), 6.59 (d, *J* = 7.4 Hz, 1H), 6.01 (t, *J* = 1.5 Hz, 1H), 5.09 (s, 1H), 1.82 (d, *J* = 1.4 Hz, 3H), 1.47 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.5, 149.3, 146.9, 141.4, 137.6, 131.0, 130.3, 130.2, 129.3, 129.0, 128.7, 128.1, 126.9, 125.9, 125.2, 121.9, 121.6, 121.4, 117.0, 99.9, 73.7, 26.8, 20.0. **HRMS (ESI)**

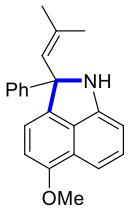
m/z: $[M+H]^+$ calc. for $C_{25}H_{22}NS$ 368.1467; found: 368.1465.

6-(furan-3-yl)-2-(2-methylprop-1-en-1-yl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3fa)



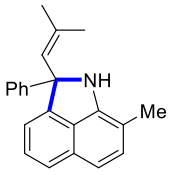
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3fa** as brown solid (18.6 mg, 53% yield). m.p.: 109-110 ºC.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 1.2 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.47 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 7.15 (d, *J* = 7.0 Hz, 1H), 6.77 – 6.70 (m, 1H), 6.58 (d, *J* = 7.4 Hz, 1H), 6.00 (p, *J* = 1.4 Hz, 1H), 5.08 (s, 1H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.46 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.4, 149.3, 146.9, 142.8, 139.3, 137.7, 130.9, 130.2, 129.9, 129.0, 128.8, 128.2, 127.0, 125.9, 124.8, 121.4, 117.5, 117.0, 111.8, 99.9, 73.7, 26.8, 20.0. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{25}H_{22}NO$ 351.1623; found: 351.1620.

5-methoxy-2-(2-methylprop-1-en-1-yl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3ga)



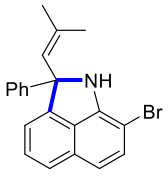
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ga** as yellow oil (17.6 mg, 56% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.46 (m, 2H), 7.33 (dd, *J* = 8.4, 6.5 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.22 – 7.17 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.56 (dd, *J* = 6.5, 1.2 Hz, 1H), 5.98 (p, *J* = 1.4 Hz, 1H), 4.98 (s, 1H), 3.95 (s, 3H), 1.80 (d, *J* = 1.6 Hz, 3H), 1.44 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.7, 149.2, 147.5, 140.9, 137.0, 131.5, 129.2, 129.0, 128.7, 126.7, 125.9, 123.7, 116.7, 109.2, 106.8, 100.8, 72.9, 55.8, 26.8, 19.9. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}NO$ 316.1696; found: 316.1696.

8-methyl-2-(2-methylprop-1-en-1-yl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3ha)



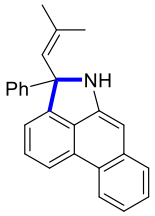
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ha** as yellow oil (23.0 mg, 77% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.50 (m, 3H), 7.38 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.30 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 6.01 (p, *J* = 1.4 Hz, 1H), 4.71 (s, 1H), 2.36 (s, 3H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.47 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.7, 147.3, 147.3, 137.2, 132.3, 131.5, 130.5, 128.7, 127.8, 127.6, 126.8, 126.0, 122.8, 116.7, 114.1, 109.8, 73.6, 26.9, 20.0, 16.4. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}N$ 300.1747; found: 300.1749.

8-bromo-2-(2-methylprop-1-en-1-yl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3ia)



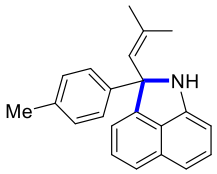
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ia** as yellow oil (15.6 mg, 43% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.48 (m, 3H), 7.42 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.31 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 5.95 (t, *J* = 1.5 Hz, 1H), 5.11 (s, 1H), 1.81 (d, *J* = 1.5 Hz, 3H), 1.43 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.9, 147.7, 146.3, 138.1, 132.2, 130.7, 130.2, 128.8, 128.7, 128.1, 127.1, 125.9, 123.2, 117.8, 115.3, 92.1, 73.7, 26.9, 19.9. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}BrN$ 364.0695; found: 364.0697.

4-(2-methylprop-1-en-1-yl)-4-phenyl-4,5-dihydrodibenzo[*cd,f*]indole (3ja)



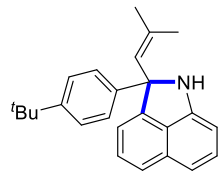
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ja** as yellow oil (18.1 mg, 54% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 – 8.39 (m, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.48 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.33 – 7.27 (m, 3H), 7.24 – 7.18 (m, 1H), 6.69 (s, 1H), 6.04 (p, *J* = 1.5 Hz, 1H), 5.08 (s, 1H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.44 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.1, 147.3, 147.1, 137.9, 136.9, 130.5, 129.2, 128.9, 128.8, 128.7, 127.1, 127.0, 127.0, 125.8, 124.9, 123.0, 122.2, 120.0, 119.3, 96.6, 73.4, 26.9, 19.9. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{25}H_{22}N$ 336.1747; found: 336.1746.

2-(2-methylprop-1-en-1-yl)-2-(p-tolyl)-1,2-dihydrobenzo[*cd*]indole (3ab)



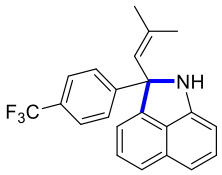
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ab** as yellow oil (15.8 mg, 53% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.37 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.10 (dd, *J* = 8.2, 5.8 Hz, 4H), 6.53 (d, *J* = 7.2 Hz, 1H), 6.10 – 5.85 (m, 1H), 5.00 (s, 1H), 2.30 (s, 3H), 1.79 (d, *J* = 1.6 Hz, 3H), 1.45 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.8, 149.2, 144.1, 137.3, 136.5, 132.1, 131.1, 129.8, 129.4, 128.6, 128.0, 125.9, 122.8, 116.6, 113.6, 99.9, 73.4, 26.8, 21.1, 20.0. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}N$ 300.1747; found: 300.1748.

2-(4-(tert-butyl)phenyl)-2-(2-methylprop-1-en-1-yl)-1,2-dihydrobenzo[*cd*]indole (3ac)



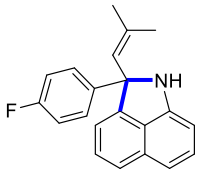
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ac** as yellow oil (16.4 mg, 48% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.34 – 7.25 (m, 3H), 7.11 (dd, *J* = 7.6, 6.2 Hz, 2H), 6.52 (d, *J* = 7.1 Hz, 1H), 5.97 (t, *J* = 1.4 Hz, 1H), 5.00 (s, 1H), 1.79 (d, *J* = 1.5 Hz, 3H), 1.43 (d, *J* = 1.3 Hz, 3H), 1.28 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.8, 149.7, 148.9, 144.0, 137.3, 132.0, 131.0, 129.8, 128.6, 128.2, 125.6, 125.6, 122.8, 116.8, 113.5, 99.9, 73.4, 34.5, 31.5, 27.0, 19.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{25}H_{28}N$ 342.2216; found: 342.2215.

2-(2-methylprop-1-en-1-yl)-2-(4-(trifluoromethyl)phenyl)-1,2-dihydrobenzo[*cd*]indole (3ad)



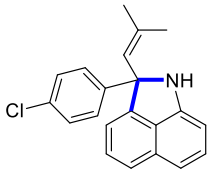
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ad** as yellow oil (24.7 mg, 70% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.58 (dd, *J* = 9.9, 8.2 Hz, 3H), 7.44 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.39 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.62 (d, *J* = 7.2 Hz, 1H), 6.00 (t, *J* = 1.5 Hz, 1H), 5.02 (s, 1H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.44 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.2, 149.7, 148.5, 138.4, 132.1, 130.7, 129.9, 129.0 (q, C–F, $2J_{C-F}$ = 32.3 Hz), 128.7, 127.7, 126.3, 125.7 (q, C–F, $3J_{C-F}$ = 3.9 Hz), 124.4 (q, C–F, $1J_{C-F}$ = 272.2 Hz), 123.3, 116.7, 114.2, 100.5, 73.1, 26.6, 20.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.2. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{19}F_3N$ 354.1464; found: 354.1462.

2-(4-fluorophenyl)-2-(2-methylprop-1-en-1-yl)-1,2-dihydrobenzo[*cd*]indole (3ae)



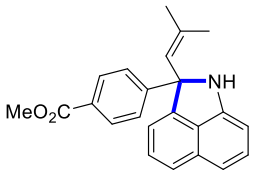
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ae** as yellow oil (20.6 mg, 68% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.43 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 7.0 Hz, 1H), 6.98 (t, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 7.2 Hz, 1H), 6.04 – 5.91 (m, 1H), 5.01 (s, 1H), 1.81 (d, *J* = 1.5 Hz, 3H), 1.46 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.8 (d, C–F, $1J_{C-F}$ = 246.4 Hz), 149.7, 149.0, 142.9 (d, C–F, $4J_{C-F}$ = 4.0 Hz), 137.7, 132.1, 131.0, 129.9, 128.6, 127.8, 127.7 (d, C–F, $3J_{C-F}$ = 7.2 Hz), 123.0, 116.6, 115.4 (d, C–F, $2J_{C-F}$ = 21.2 Hz), 113.9, 100.2, 73.0, 26.7, 20.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -116.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}FN$ 304.1496; found: 304.1498.

2-(4-chlorophenyl)-2-(2-methylprop-1-en-1-yl)-1,2-dihydrobenzo[*cd*]indole (3af)



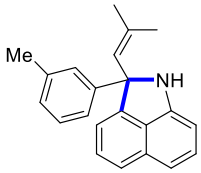
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3af** as yellow oil (20.4 mg, 64% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.42 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.35 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 7.1 Hz, 1H), 5.95 – 5.94 (m, 1H), 4.98 (s, 1H), 1.79 (d, *J* = 1.6 Hz, 3H), 1.44 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.7, 148.8, 145.8, 138.0, 132.7, 132.1, 130.8, 129.8, 128.8, 128.7, 127.7, 127.4, 123.1, 116.6, 114.0, 100.3, 73.0, 26.7, 20.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}ClN$ 320.1201; found: 320.1201.

methyl 4-(2-(2-methylprop-1-en-1-yl)-1,2-dihydrobenzo[cd]indol-2-yl)benzoate (3ag)



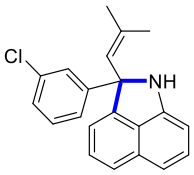
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 6 : 1 to give **3ag** as yellow oil (19.6 mg, 57% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 – 7.92 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 7.0 Hz, 1H), 6.59 (d, *J* = 7.2 Hz, 1H), 5.98 (t, *J* = 1.7 Hz, 1H), 5.02 (s, 1H), 3.88 (s, 3H), 1.80 (d, *J* = 1.4 Hz, 3H), 1.41 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.1, 152.3, 149.7, 148.5, 138.1, 132.1, 130.8, 130.1, 129.9, 128.7, 127.8, 126.0, 123.2, 116.7, 114.1, 100.4, 73.3, 52.2, 26.6, 20.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}ClN$ 344.1645; found: 344.1645.

2-(2-methylprop-1-en-1-yl)-2-(m-tolyl)-1,2-dihydrobenzo[*cd*]indole (3ah)



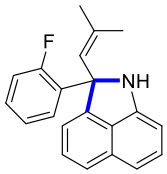
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ah** as yellow oil (16.4 mg, 55% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.35 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.23 – 7.16 (m, 1H), 7.12 (d, *J* = 3.8 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.55 (d, *J* = 7.1 Hz, 1H), 5.97 (p, *J* = 1.5 Hz, 1H), 5.01 (s, 1H), 2.30 (s, 3H), 1.80 (d, *J* = 1.4 Hz, 3H), 1.44 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.8, 149.0, 147.0, 138.3, 137.3, 132.0, 131.2, 129.8, 128.6, 128.6, 128.0, 127.7, 126.5, 123.1, 122.8, 116.7, 113.6, 99.9, 73.5, 26.8, 21.8, 19.9. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}N$ 300.1747; found: 300.1747.

2-(3-chlorophenyl)-2-(2-methylprop-1-en-1-yl)-1,2-dihydrobenzo[*cd*]indole (3ai)



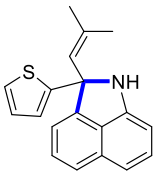
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ai** as yellow oil (20.7 mg, 65% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.54 (m, 2H), 7.46 – 7.40 (m, 2H), 7.36 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 6.9 Hz, 1H), 6.58 (d, *J* = 7.2 Hz, 1H), 6.07 – 5.88 (m, 1H), 4.98 (s, 1H), 1.80 (d, *J* = 1.5 Hz, 3H), 1.43 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.6, 149.4, 148.6, 138.2, 134.5, 132.1, 130.7, 130.0, 129.9, 128.6, 127.7, 127.0, 126.2, 124.2, 123.2, 116.7, 114.0, 100.4, 73.0, 26.7, 20.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}ClN$ 320.1201; found: 320.1203.

2-(2-fluorophenyl)-2-(2-methylprop-1-en-1-yl)-1,2-dihydrobenzo[*cd*]indole (3aj)



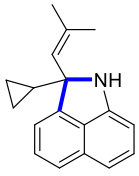
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3aj** as yellow oil (14.0 mg, 46% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.43 (td, *J* = 8.0, 1.8 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.33 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.13 – 7.06 (m, 2H), 7.00 (td, *J* = 7.5, 1.3 Hz, 1H), 6.51 (d, *J* = 7.1 Hz, 1H), 5.99 – 5.87 (m, 1H), 5.19 (s, 1H), 1.74 (s, 3H), 1.34 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.5 (d, C–F, $1J_{C-F}$ = 242.4 Hz), 149.0, 146.5, 135.6, (d, C–F, $4J_{C-F}$ = 2.0 Hz), 133.7 (d, C–F, $2J_{C-F}$ = 13.3 Hz), 132.1, 130.2 (d, C–F, $4J_{C-F}$ = 1.0 Hz), 129.8, 128.8 (d, C–F, $3J_{C-F}$ = 7.2 Hz), 128.5, 128.4, 128.2 (d, C–F, $4J_{C-F}$ = 4.0 Hz), 124.0 (d, C–F, $4J_{C-F}$ = 3.0 Hz), 123.4, 118.1 (d, C–F, $4J_{C-F}$ = 5.0 Hz), 116.5 (d, C–F, $2J_{C-F}$ = 20.2 Hz),113.5, 99.9, 71.6, 26.9, 18.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -110.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}FN$ 304.1496; found: 304.1498.

2-(2-methylprop-1-en-1-yl)-2-(thiophen-2-yl)-1,2-dihydrobenzo[*cd*]indole (3ak)



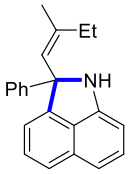
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ak** as yellow oil (11.9 mg, 41% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.39 – 7.31 (m, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.00 – 6.95 (m, 1H), 6.93 – 6.90 (m, 1H), 6.55 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.01 (q, *J* = 1.5 Hz, 1H), 5.14 (s, 1H), 1.79 (s, 3H), 1.53 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.0, 149.0, 148.4, 138.7, 132.0, 130.6, 129.8, 128.6, 127.6, 127.2, 124.6, 123.3, 123.1, 116.8, 114.1, 100.5, 71.0, 26.9, 19.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{19}H_{18}NS$ 292.1154; found: 292.1154.

2-cyclopropyl-2-(2-methylprop-1-en-1-yl)-1,2-dihydrobenzo[*cd*]indole (3al)



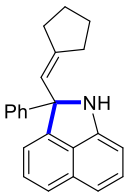
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3al** as yellow oil (9.2 mg, 37% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.43 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.07 (d, *J* = 1.9 Hz, 1H), 7.05 (d, *J* = 3.3 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 1H), 5.72 (p, *J* = 1.4 Hz, 1H), 4.41 (s, 1H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.39 – 1.30 (m, 1H), 1.20 (d, *J* = 1.2 Hz, 3H), 0.48 – 0.40 (m, 1H), 0.39 – 0.32 (m, 1H), 0.32 – 0.21 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.2, 147.9, 138.2, 131.8, 129.6, 129.3, 128.6, 128.3, 122.6, 115.9, 113.2, 99.6, 69.9, 27.3, 23.7, 19.0, 1.4, 0.5. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{18}H_{20}N$ 250.1590; found: 250.1591.

2-(2-methylbut-1-en-1-yl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3am)



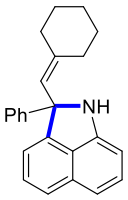
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3am** as yellow oil (12.9 mg, 43% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.49 (m, 3H), 7.42 (ddd, *J* = 8.2, 7.0, 1.5 Hz, 1H), 7.35 (td, *J* = 7.8, 7.1, 1.4 Hz, 1H), 7.29 (ddd, *J* = 7.9, 6.6, 1.4 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.11 (dd, *J* = 7.7, 4.0 Hz, 2H), 6.55 (d, *J* = 7.1 Hz, 1H), 5.97 (dd, *J* = 4.8, 1.7 Hz, 1H), 5.02 (s, 0.28H), 4.97 (s, 0.72H), 2.09 (qd, *J* = 7.5, 1.3 Hz, 0.6H), 1.92 – 1.83 (m, 1.4H), 1.79 (d, *J* = 1.5 Hz, 2.2H), 1.44 (d, *J* = 1.3 Hz, 0.8H), 1.05 (t, *J* = 7.4 Hz, 0.8H), 0.79 (t, *J* = 7.5 Hz, 2.2H). **^{13}C NMR (101 MHz, $CDCl_3$)** (Z) δ149.8, 149.2, 147.4, 142.5, 132.0, 131.0, 129.8, 128.6, 127.9, 126.9, 125.9, 122.9, 116.7, 113.7, 100.0, 73.5, 26.4, 23.3, 11.7. **^{13}C NMR (101 MHz, $CDCl_3$)** (E) δ 149.9, 149.1, 147.2, 142.9, 132.0, 131.0, 129.7, 128.7, 128.6, 127.9, 126.8, 125.9, 122.9, 116.7, 113.7, 100.0, 73.4, 33.3, 18.2, 12.9. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}N$ 300.1747; found: 300.1748.

2-(cyclopentylidenemethyl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3an)



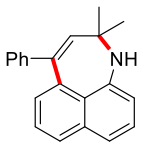
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3an** as yellow oil (12.8 mg, 41% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.44 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.25 – 7.19 (m, 1H), 7.12 (dd, *J* = 7.6, 6.0 Hz, 2H), 6.52 (d, *J* = 7.1 Hz, 1H), 6.14 – 6.00 (m, 1H), 4.98 (s, 1H), 2.47 – 2.25 (m, 2H), 1.98 – 1.74 (m, 2H), 1.61 – 1.48 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.7, 148.0, 147.9, 146.6, 132.0, 129.8, 128.7, 128.5, 128.2, 127.0, 126.2, 125.5, 122.9, 116.9, 113.4, 99.5, 74.1, 35.6, 29.8, 27.1, 25.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{22}N$ 312.1747; found: 312.1748.

2-(cyclohexylidenemethyl)-2-phenyl-1,2-dihydrobenzo[*cd*]indole (3ao)



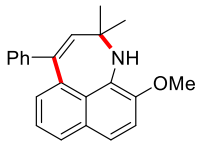
Prepared following General Procedure A and purified by flash chromatography in petroleum ether : ethyl acetate = 12 : 1 to give **3ao** as yellow oil (20.2 mg, 62% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 – 7.50 (m, 3H), 7.42 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.35 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.28 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.11 (t, *J* = 7.9 Hz, 2H), 6.55 (d, *J* = 7.1 Hz, 1H), 5.94 (s, 1H), 4.97 (s, 1H), 2.20 – 2.11 (m, 2H), 1.94 – 1.89 (m, 2H), 1.64 – 1.58 (m, 2H), 1.54 – 1.47 (m, 2H), 1.36 – 1.28 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9, 149.4, 147.3, 145.0, 132.0, 129.8, 128.7, 128.6, 128.5, 127.9, 126.8, 125.9, 122.9, 116.7, 113.7, 100.1, 73.3, 37.5, 30.8, 28.6, 26.9, 26.4. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{24}H_{24}N$ 326.1903; found: 326.1905.

2,2-dimethyl-4-phenyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4aa)



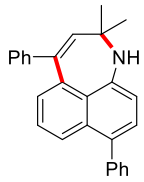
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4aa** as yellow oil (19.4 mg, 68% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.36 (dt, *J* = 8.1, 1.4 Hz, 2H), 7.33 (dt, *J* = 4.8, 1.7 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.72 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.14 (s, 1H), 4.07 (s, 1H), 1.43 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.4, 145.7, 142.6, 139.2, 136.3, 135.9, 130.0, 129.4, 129.1, 128.3, 126.8, 126.1, 124.8, 124.4, 121.1, 114.6, 53.6, 29.2. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{20}N$ 286.1590; found: 286.1589.

10-methoxy-2,2-dimethyl-4-phenyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4ba)



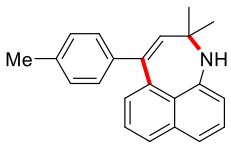
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ba** as yellow oil (22.7 mg, 72% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.35 (dd, *J* = 8.3, 4.9 Hz, 3H), 7.33 – 7.27 (m, 4H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.16 (s, 1H), 5.09 (s, 1H), 4.00 (s, 3H), 1.46 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 146.6, 144.6, 142.6, 138.8, 135.4, 133.6, 131.0, 130.1, 129.5, 129.1, 128.2, 126.7, 124.4, 122.7, 119.7, 112.6, 57.1, 53.3, 29.3. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}NO$ 316.1696; found: 316.1695.

2,2-dimethyl-4,8-diphenyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4ca)



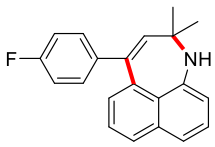
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ca** as yellow oil (7.2 mg, 20% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.43 – 7.32 (m, 2H), 7.30 (t, *J* = 8.5 Hz, 4H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.18 (s, 1H), 4.13 (s, 1H), 1.46 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 146.5, 145.2, 142.7, 142.1, 139.2, 136.1, 134.1, 132.6, 130.5, 129.9, 129.3, 128.2, 128.2, 127.5, 126.9, 126.7, 126.7, 124.6, 124.4, 113.9, 53.4, 29.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{27}H_{24}N$ 362.1903; found: 362.1899.

2,2-dimethyl-4-(p-tolyl)-1,2-dihydronaphtho[1,8-*bc*]azepine (4ab)



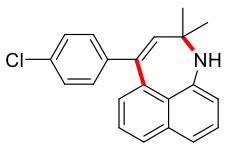
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ab** as yellow oil (16.0 mg, 54% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.66 – 7.62 (m, 1H), 7.35 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.13 (m, 5H), 7.02 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.71 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.12 (s, 1H), 4.06 (s, 1H), 2.39 (s, 3H), 1.42 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 143.5, 142.5, 138.8, 136.4, 136.3, 136.0, 129.9, 129.3, 129.1, 128.9, 126.1, 124.8, 124.4, 121.1, 114.6, 53.6, 29.2, 21.3. **HRMS (ESI)** m/z: $[M-H]^-$ calc. for $C_{22}H_{20}N$ 298.1600; found: 298.1593.

4-(4-fluorophenyl)-2,2-dimethyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4ac)



Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ac** as yellow oil (18.8 mg, 62% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.65 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.36 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.95 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.72 (dd, *J* = 7.3, 1.5 Hz, 1H), 6.12 (s, 1H), 4.06 (s, 1H), 1.42 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ162.0 (d, C–F, $1J_{C-F}$ = 246.4 Hz), 145.6, 142.3 (d, C–F, $4J_{C-F}$ = 4.0 Hz), 141.7, 139.3, 136.3, 135.8, 131.0 (d, C–F, $2J_{C-F}$ = 7.2 Hz), 129.8, 129.3, 126.2, 124.7, 124.3, 121.1, 115.1 (d, C–F, $2J_{C-F}$ = 21.2 Hz), 114.7, 53.5, 29.1. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -116.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}FN$ 304.1496; found: 304.1496.

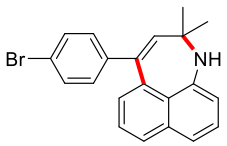
4-(4-chlorophenyl)-2,2-dimethyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4ad)



Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ad** as yellow oil (25.2 mg, 79% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.70 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.40 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.30 (t, *J* = 3.9 Hz, 1H), 7.26 (dt, *J* = 6.4,

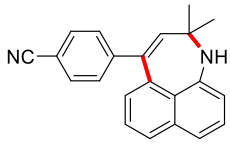
2.2 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 6.98 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.76 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.16 (s, 1H), 4.08 (s, 1H), 1.46 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.6, 144.8, 141.6, 139.5, 136.3, 135.5, 132.7, 130.8, 129.8, 129.4, 128.4, 126.2, 124.7, 124.3, 121.1, 114.7, 53.6, 29.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}ClN$ 320.1201; found: 320.1200.

4-(4-bromophenyl)-2,2-dimethyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4ae)



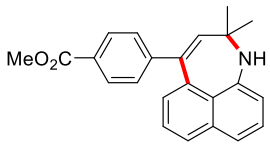
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ae** as yellow foam (9.4 mg, 26% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.35 (dd, *J* = 8.1, 1.4 Hz, 1H), δ 7.28 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.17 – 7.13 (m, 2H), 6.94 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.72 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.12 (s, 1H), 4.05 (s, 1H), 1.41 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.6, 145.3, 141.7, 139.5, 136.3, 135.4, 131.4, 131.1, 129.8, 129.4, 126.2, 124.7, 124.3, 121.1, 120.8, 114.7, 53.6, 29.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}BrN$ 364.0695; found: 364.0693.

4-(2,2-dimethyl-1,2-dihydronaphtho[1,8-*bc*]azepin-4-yl)benzonitrile (4af)



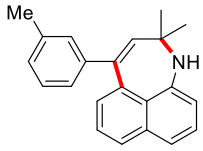
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 8 : 1 to give **4af** as yellow foam (15.5 mg, 50% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.41 – 7.35 (m, 3H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.83 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.74 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.15 (s, 1H), 4.06 (s, 1H), 1.43 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.1, 145.5, 141.6, 140.7, 136.3, 134.7, 132.2, 130.1, 129.7, 126.4, 124.7, 124.2, 121.2, 119.1, 114.9, 110.6, 53.7, 29.0. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{19}N_2$ 311.1543; found: 311.1543.

methyl 4-(2,2-dimethyl-1,2-dihydronaphtho[1,8-*bc*]azepin-4-yl)benzoate (4ag)



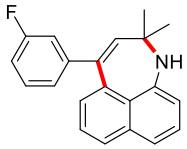
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 6 : 1 to give **4ag** as yellow foam (19.6 mg, 57% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 – 7.94 (m, 2H), 7.66 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.36 – 7.34 (m, 3H), 7.31 – 7.26 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.89 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.73 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.17 (s, 1H), 4.07 (s, 1H), 3.93 (s, 3H), 1.43 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 151.2, 145.6, 142.1, 140.0, 136.3, 135.2, 129.8, 129.7, 129.4, 128.6, 126.3, 124.7, 124.3, 121.2, 114.8, 53.7, 52.2, 29.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{22}NO_2$ 344.1645; found: 344.1644.

2,2-dimethyl-4-(m-tolyl)-1,2-dihydronaphtho[1,8-*bc*]azepine (4ah)



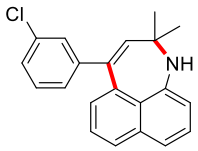
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ah** as yellow oil (15.2 mg, 51% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.36 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.15 – 7.07 (m, 3H), 7.01 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.72 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.13 (s, 1H), 4.06 (s, 1H), 2.36 (s, 3H), 1.43 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3, 145.8, 142.7, 139.0, 137.8, 136.3, 135.9, 130.2, 130.0, 129.1, 128.1, 127.5, 126.5, 126.1, 124.8, 124.4, 121.0, 114.6, 53.6, 29.2, 21.5. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}N$ 300.1747; found: 300.1745.

4-(3-fluorophenyl)-2,2-dimethyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4ai)



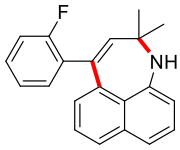
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ai** as yellow foam (18.8 mg, 62% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.66 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.36 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.10 – 6.95 (m, 4H), 6.73 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.15 (s, 1H), 4.05 (s, 1H), 1.42 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.8 (d, C–F, $1J_{C-F}$ = 246.4 Hz), 148.6 (d, C–F, $3J_{C-F}$ = 7.0 Hz), 145.6, 141.7, 139.7, 136.3, 135.3, 129.8, 129.7 (d, C–F, $3J_{C-F}$ = 8.1 Hz), 129.4, 126.2, 125.2, 124.8, 124.3, 121.1, 116.4 (d, C–F, $2J_{C-F}$ = 22.2 Hz), 114.7, 113.7 (d, C–F, $2J_{C-F}$ = 21.2 Hz), 53.6, 29.1. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -113.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}FN$ 304.1496; found: 304.1496.

4-(3-chlorophenyl)-2,2-dimethyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4aj)



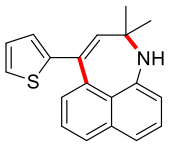
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4aj** as yellow foam (21.1 mg, 66% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.66 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.25 (d, *J* = 5.7 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.15 (dt, *J* = 6.7, 1.8 Hz, 1H), 6.95 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.73 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.14 (s, 1H), 4.05 (s, 1H), 1.52 – 1.27 (m, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 148.1, 145.6, 141.6, 139.9, 136.3, 135.2, 134.1, 129.9, 129.5, 129.5, 129.4, 127.7, 127.0, 126.2, 124.8, 124.3, 121.2, 114.8, 53.6, 29.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}ClN$ 320.1201; found: 320.1200.

4-(2-fluorophenyl)-2,2-dimethyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4ak)



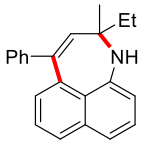
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4ak** as yellow oil (13.0 mg, 43% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.23 – 7.13 (m, 2H), 7.11 –7.06 (m, 1H), 6.95 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.74 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.15 (s, 1H), 4.04 (s, 1H), 1.43 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 160.1 (d, C–F, $1J_{C-F}$ = 247.4 Hz), 145.4, 141.0, 136.3, 136.0, 134.9, 133.1 (d, C–F, $3J_{C-F}$ = 16.2 Hz), 131.9 (d, C–F, $4J_{C-F}$ = 3.0 Hz), 129.3, 128.8 (d, C–F, $2J_{C-F}$ = 7.1Hz), 128.4, 126.1, 124.9, 124.2, 124.1 (d, C–F, $4J_{C-F}$ = 7.1 Hz), 121.4, 115.7 (d, C–F, $2J_{C-F}$ = 22.2 Hz), 115.0, 54.0, 29.1. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -114.5. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{19}FN$ 304.1496; found: 304.1496.

2,2-dimethyl-4-(thiophen-2-yl)-1,2-dihydronaphtho[1,8-*bc*]azepine (4al)



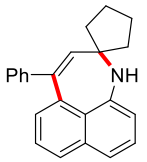
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4al** as brown oil (9.3 mg, 32% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.66 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.33 (dt, *J* = 7.5, 1.7 Hz, 2H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.24 – 7.21 (m, 2H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.94 (dd, *J* = 3.5, 1.3 Hz, 1H), 6.69 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.37 (s, 1H), 4.04 (s, 1H), 1.42 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 148.4, 145.7, 140.1, 136.2, 135.6, 135.5, 129.6, 129.5, 126.8, 126.4, 126.1, 124.7, 124.3, 123.9, 120.9, 114.4, 53.5, 28.9. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{19}H_{18}NS$ 292.1154; found: 292.1154.

2-ethyl-2-methyl-4-phenyl-1,2-dihydronaphtho[1,8-*bc*]azepine (4am)



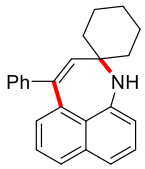
Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4am** as yellow oil (10.2 mg, 34% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.38 – 7.26 (m, 7H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.72 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.11 (s, 1H), 4.16 (s, 1H), 1.74 (q, *J* = 7.4Hz, 2H), 1.37 (s, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.6, 145.5, 142.8, 138.7, 136.3, 135.9, 129.9, 129.5, 129.1, 128.3, 126.8, 126.2, 124.8, 124.4, 120.9, 114.8, 56.3, 33.1, 26.6, 8.4. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}N$ 300.1747; found: 300.1744.

4-phenyl-1H-spiro[cyclopentane-1,2-naphtho[1,8-*bc*]azepine] (4an)



Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4an** as yellow oil (13.1 mg, 42% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.37 – 7.26 (m, 7H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.98 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.69 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.27 (s, 1H), 4.12 (s, 1H), 1.92 – 1.84 (m, 4H), 1.81 – 1.74 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3, 146.0, 143.5, 139.0, 136.4, 136.4, 129.8, 129.4, 129.0, 128.3, 126.8, 126.0, 124.8, 124.4, 121.0, 114.6, 64.9, 39.1, 23.0. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{22}N$ 312.1747; found: 312.1745.

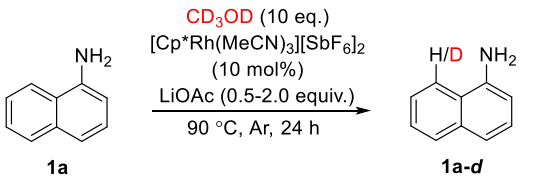
4-phenyl-1H-spiro[cyclohexane-1,2-naphtho[1,8-*bc*]azepine] (4ao)



Prepared following General Procedure B and purified by flash chromatography in petroleum ether : ethyl acetate = 10 : 1 to give **4an** as yellow oil (21.6 mg, 67% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.43 – 7.31 (m, 7H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.01 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.80 (dd, *J* = 7.2, 1.5 Hz, 1H), 6.17 (s, 1H), 4.32 (s, 1H), 1.93 – 1.87 (m, 2H), 1.68 – 1.54 (m, 8H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.7, 145.2, 142.7, 138.7, 136.2, 136.0, 129.9, 129.5, 129.1, 128.3, 126.8, 126.2, 124.8, 124.5, 120.8, 114.7, 55.2, 36.8, 25.8, 22.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{24}H_{24}N$ 324.1903; found: 324.1903.

2.3 General Procedure for Mechanistic Experiments.

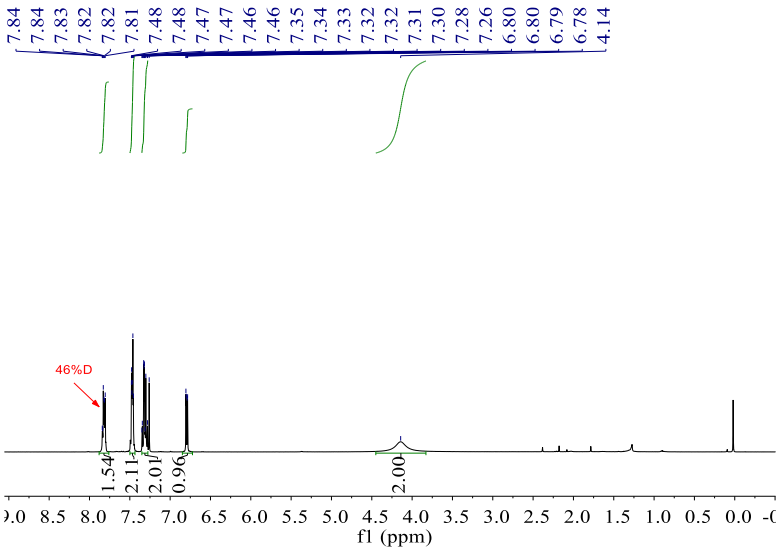
(a) Deuterium-Labeling Experiments without 2a



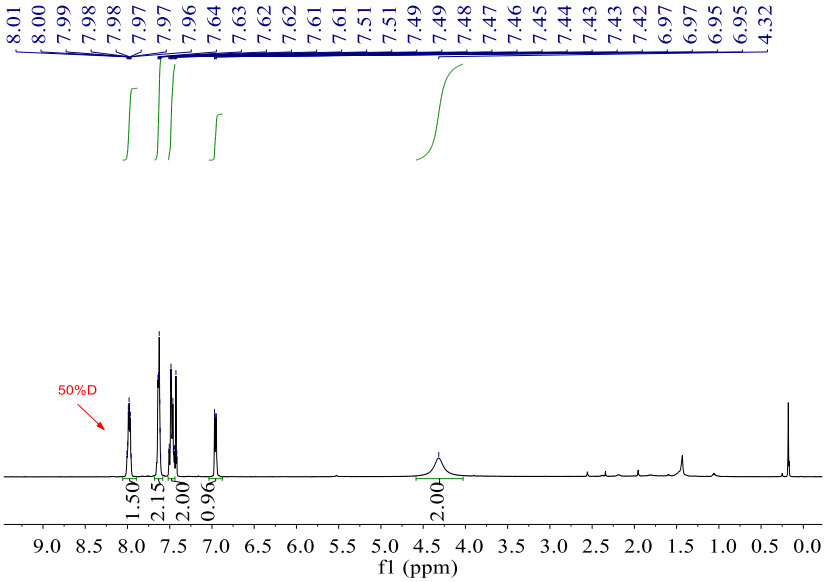
MTBE and MeCN as solvent : 46% deuteration
DCE and MeCN as solvent : 50% deuteration

The mixture of 1-naphthylamine **1a** (17.1 mg, 0.12 mmol) and CD_3OD (41 μL, 1.0 mmol) under standard conditions A or standard conditions B for 24 h. Afterwards, the mixture was purified by flash silica gel column chromatography to afford the product **1a-d**.

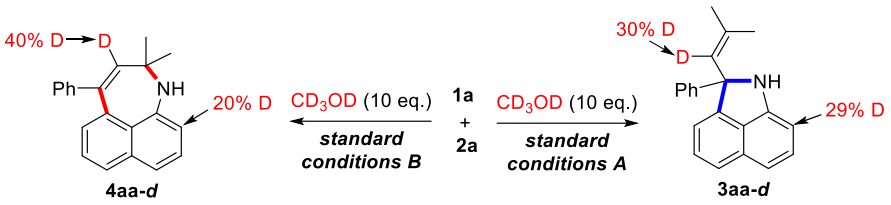
MTBE:MeCN = 0.9 mL:0.1 mL



DCE:MeCN = 0.7 mL:0.3 mL

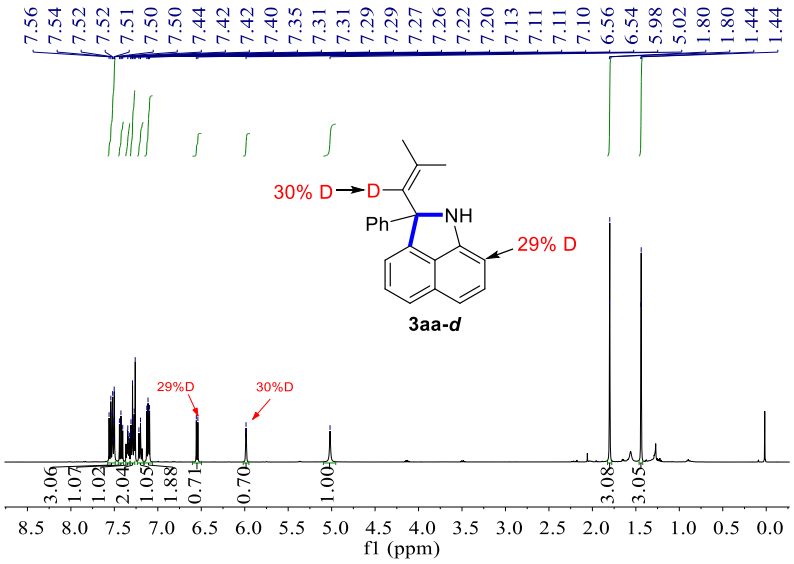


(b) Deuterium-Labeling Experiments with 2a

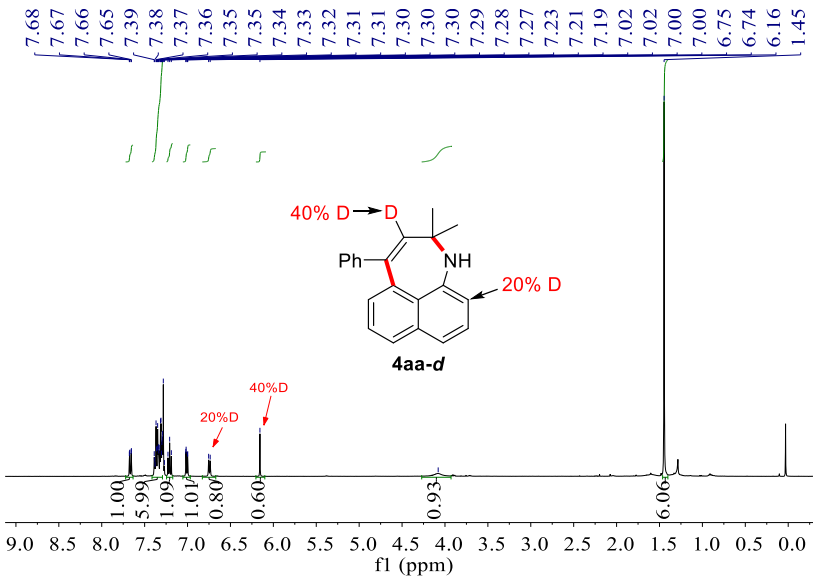


The mixture of 1-naphthylamine **1a** (17.1 mg, 0.12 mmol), propargyl carbonate **2a** (21.8 mg, 0.1 mmol) and CD_3OD (41 μL, 1.0 mmol) under standard conditions A or standard conditions B for 24 h. Afterwards, the mixture was purified by flash silica gel column chromatography to afford the product **3aa-d** or **4aa-d**.

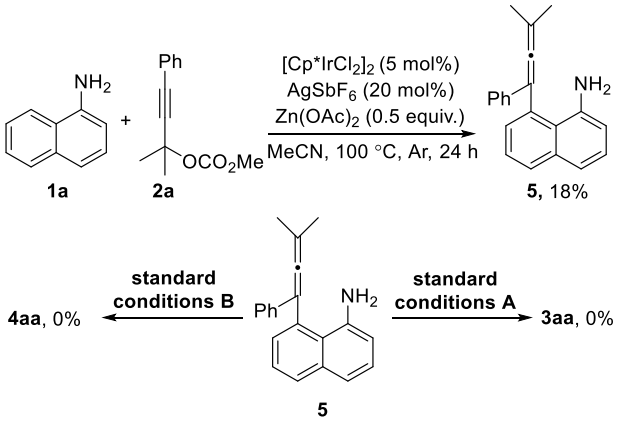
3aa-d



4aa-d



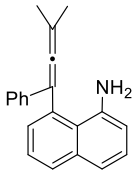
(c) Control Experiments



To six separated 20 mL Schlenk tubes were added 1-naphthylamine **1a** (34.3 mg, 0.24 mmol), propargyl carbonate **2a** (43.6 mg, 0.2 mmol), $[Cp^*IrCl_2]_2$ (8.0 mg, 5 mol%), $Zn(OAc)_2$ (18.2 mg, 0.1 mmol) and MeCN (2.0 mL), the tubes were sealed up with a cap and evacuated then refilled with Ar and kept stirring at 100 °C (aluminum heat transfer block) for 24 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC using Hexane/EtOAc or Hexane/Acetone as the eluent to afford the desired product **5**.

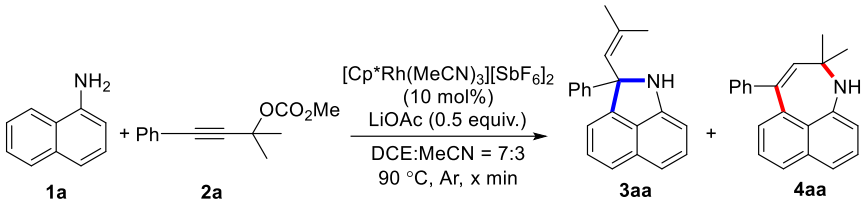
The mixture of **5** (0.1 mmol, 1.0 equiv) and $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 10 mol%) kept stirring for 24 h under standard conditions A or standard conditions B. When the reaction was completed, the mixture was purified by flash silica gel column chromatography to afford the desired products **3aa** or **4aa** in 0% yield.

8-(3-methyl-1-phenylbuta-1,2-dien-1-yl)naphthalen-1-amine (5)



Prepared following General Procedure C and purified by flash chromatography in petroleum ether : ethyl acetate = 6 : 1 to give **5** as yellow oil (61.5 mg, 18% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.00 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.96 – 7.87 (m, 1H), 7.59 – 7.52 (m, 1H), 7.51 – 7.46 (m, 1H), 7.36 (dd, *J* = 6.8, 2.6 Hz, 3H), 7.24 (dd, *J* = 5.1, 2.0 Hz, 3H), 6.75 (d, *J* = 7.9 Hz, 1H), 4.11 (s, 2H), 1.89 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.7, 132.5, 132.0, 131.6, 128.2, 127.6, 127.5, 125.2, 125.1, 124.5, 124.2, 122.9, 121.7, 109.0, 98.1, 81.6, 34.4, 31.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{20}N$ 286.1596; found: 286.1589.

(d) Rate of Reaction Experiments

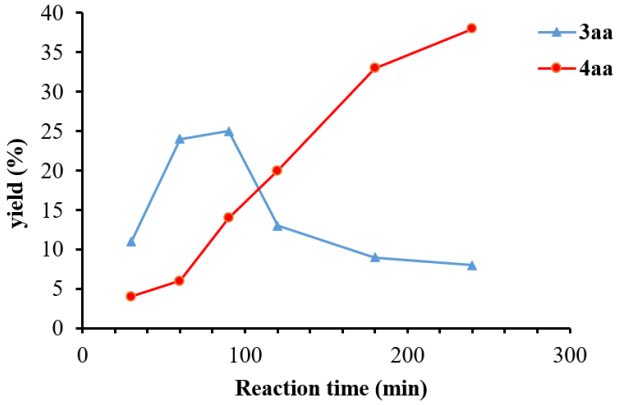


To a 20 mL Schlenk tube was added free 1-naphthylamine **1a** (0.12 mmol), propargyl carbonate **2a** (0.1 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 10 mol%), LiOAc (3.3 mg, 0.05 mmol), DCE (0.7 mL) and MeCN (0.3 mL), the tube was sealed up with a cap and evacuated then refilled with Ar and kept stirring at 90 °C (aluminum heat transfer block). Then immediately quenched with DCM, the ^{1}H NMR yields of desired product **4aa** and recovery of the **3aa** were determined by 1,3,5-Trimethoxybenzene as internal standard.

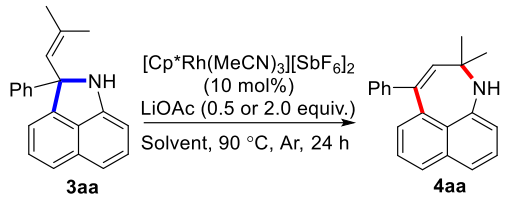
Table S5. Reaction rate of **4aa** under standard conditions B

entry	time (min)	yield (%)	
		3aa	4aa
1	30	11	4
2	60	24	6
3	90	25	14
4	120	13	20
5	180	9	33
6	240	8	38

Figure S1. Reaction rate under standard conditions B



(e) Control Experiments with Different Solvents



3aa **4aa**

In three separated oven-dried 20 mL Schlenk tubes were added **3aa** (28.5 mg, 0.10 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 10 mol%), LiOAc and different solvents (1.0 mL), the tubes were sealed up with a cap and evacuated then refilled with Ar and kept stirring at 90 °C (aluminum heat transfer block) for 24 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the ^{1}H NMR yield of desired product **4aa** and recovery of the **3aa** were determined by 1,3,5-Trimethoxybenzene as internal standard.

Table S6. Control experiments with different solvents

entry	[cat]	base	solvent	yield (%)[a]	
				3aa	4aa
1	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	LiOAc (2.0 equiv.)	MTBE/MeCN (9:1, v/v)	89	0
2	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	LiOAc (0.5 equiv.)	DCE/MeCN (7:3, v/v)	13	74
3	---	LiOAc (0.5 equiv.)	DCE/MeCN (7:3, v/v)	95	0

[a] ^{1}H NMR yield using 1,3,5-Trimethoxybenzene as internal standard.

3. X-Ray Crystallographic Data

A single crystal of **3aa** suitable for X-ray crystallography was obtained by crystallization via evaporation from its hexane/ethyl acetate solution.

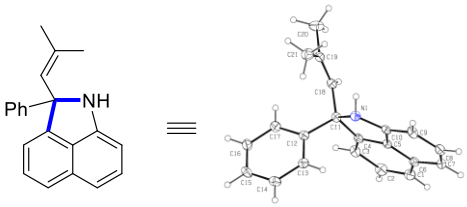


Table S5. Crystal data and structure refinement for **3aa**.

Bond precision	C–C = 0.0037 A	Wavelength = 0.71073	
Cell:	a = 7.7743(9)	b = 21.708(3)	c = 18.561(2)
	alpha = 90	beta = 96.518(4)	gamma = 90
Temperature:	170 K		
	Calculated	Reported	
Volume	3112.2 (7)	3112.2 (6)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	$C_{21}H_{19}N$	$C_{21}H_{19}N$	
Sum formula	$C_{21}H_{19}N$	$C_{21}H_{19}N$	
Mr	285.37	285.37	
Dx, g cm-3	1.218	1.218	
Z	8	8	
Mu (mm-1)	0.070	0.070	
F000	1216.0	1216.0	
F000’	1216.42		
h, k, 1max	9,27,23	9,27,23	
Nref	6418	6389	
Tmin, Tmax	0.996,0.999	0.630,0.745	
Tmin’	0.994		

Correction method= # Reported T Limits: Tmin = 0.630 Tmax = 0.745

AbsCorr = MULTI-SCAN

Data completeness = 0.995 Theta(max) = 26.443

R(reflections) = 0.0711(3724) wR2(reflections) = 0.2199(6389)

S = 1.029 Npar= 401

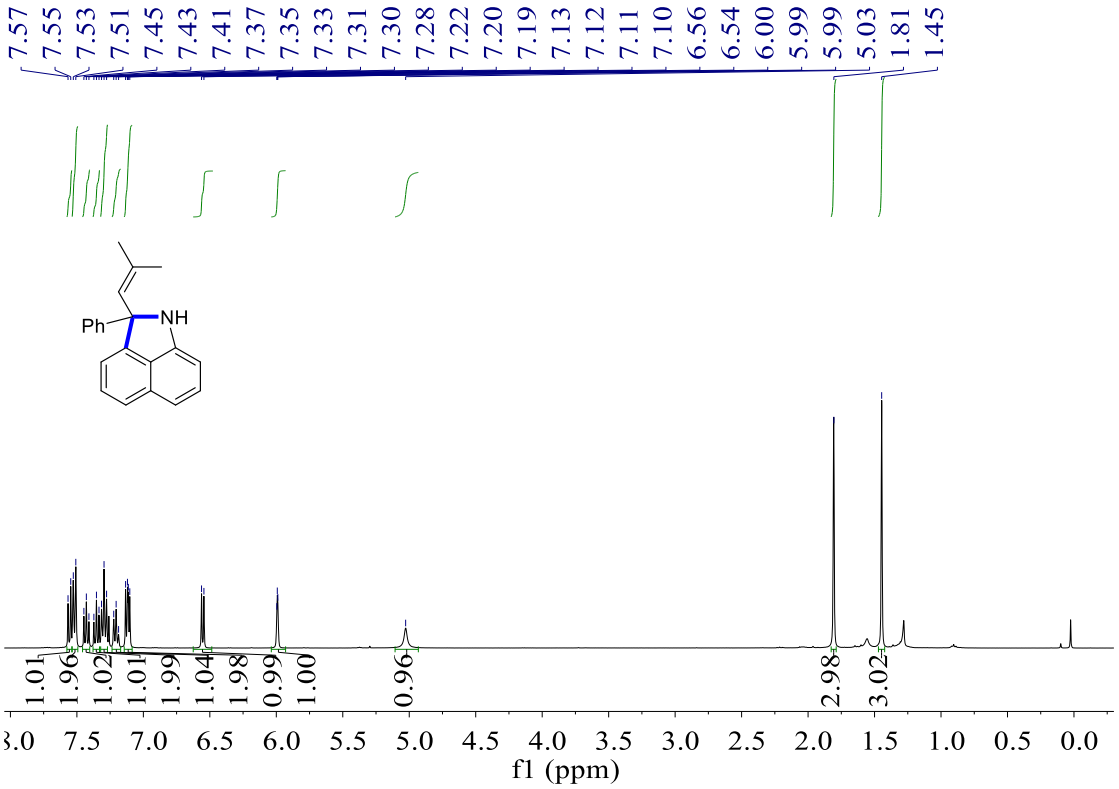
4. References

[1] M. P. Huestis, Rhodium(III)-Catalyzed C−H Functionalization of 1-(2H)-Phthalazinones at C8. *J. Org. Chem.* 2016, **81**, 12545-12552.

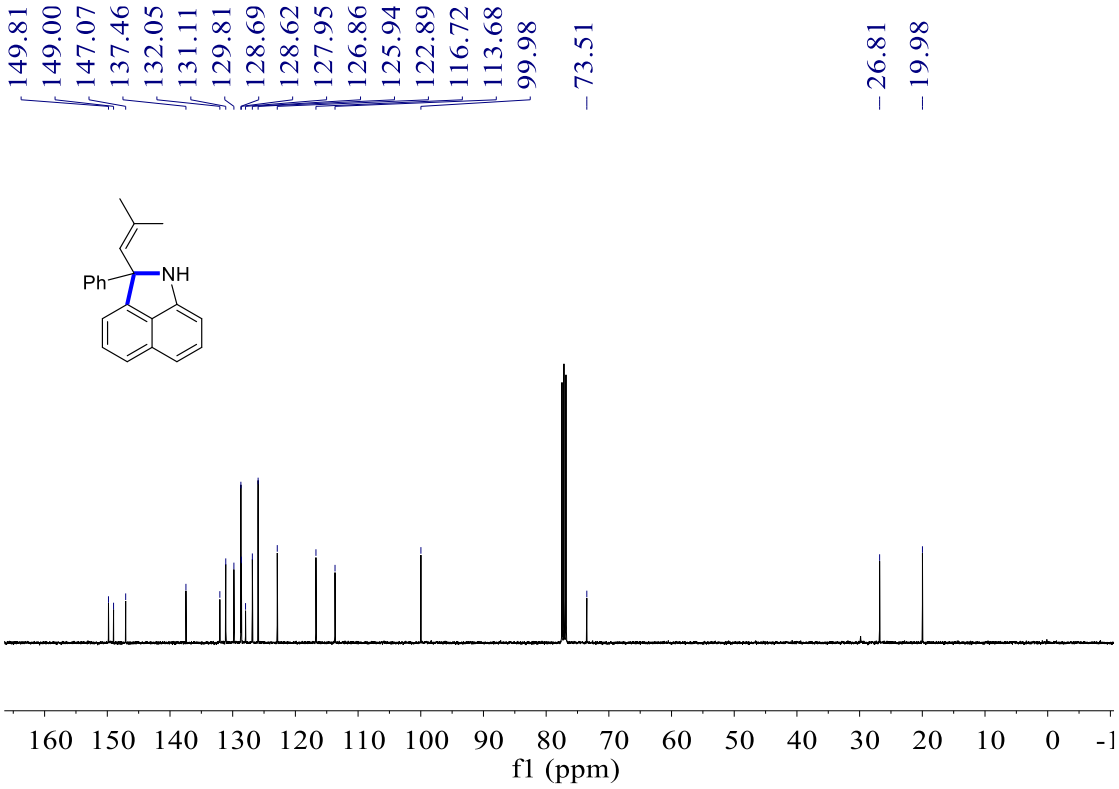
[2] Y. Li, H. Zou, J. Gong, J. Xiang, T. Luo, J. Quan, G. Wang and Z. Yang, Efficient Synthesis of Maleimides and Carbazoles via $Zn(OTf)_2$-Catalyzed Tandem Annulations of Isonitriles and Allenic Esters *Org. Lett.* 2007, **9**, 4057-4060.

5. NMR Spectra

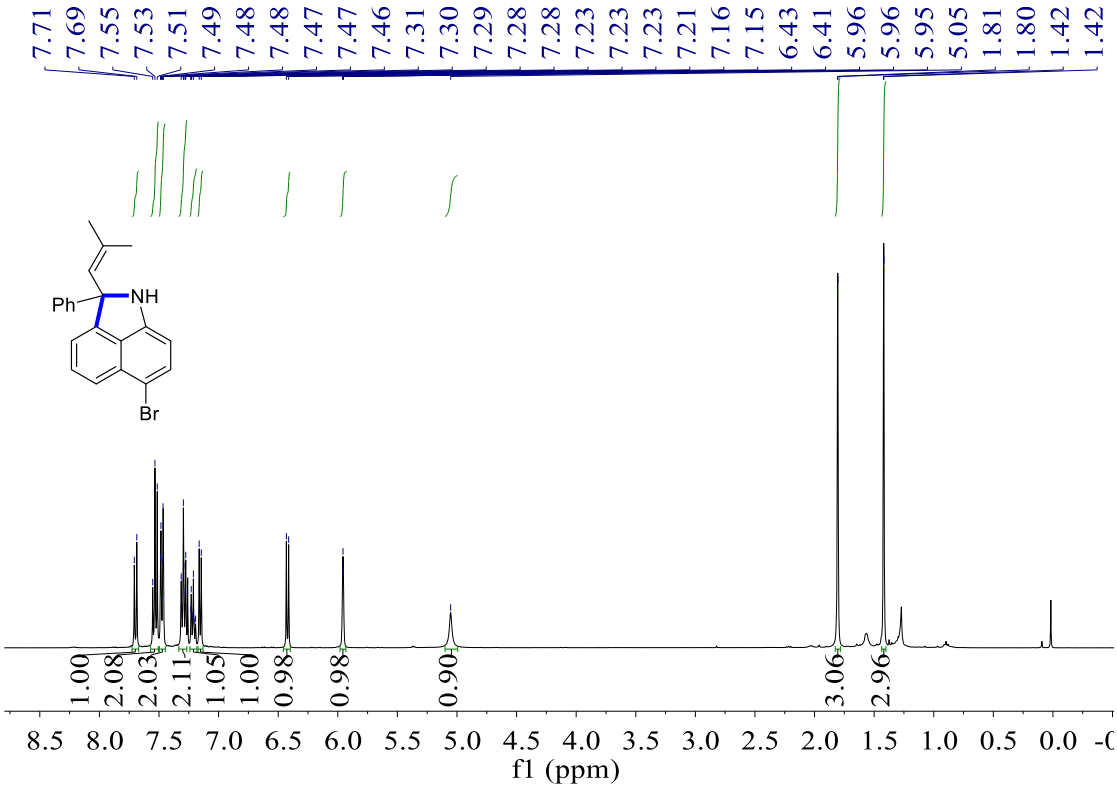
3aa, ^{1}H NMR, 400 MHz, $CDCl_3$



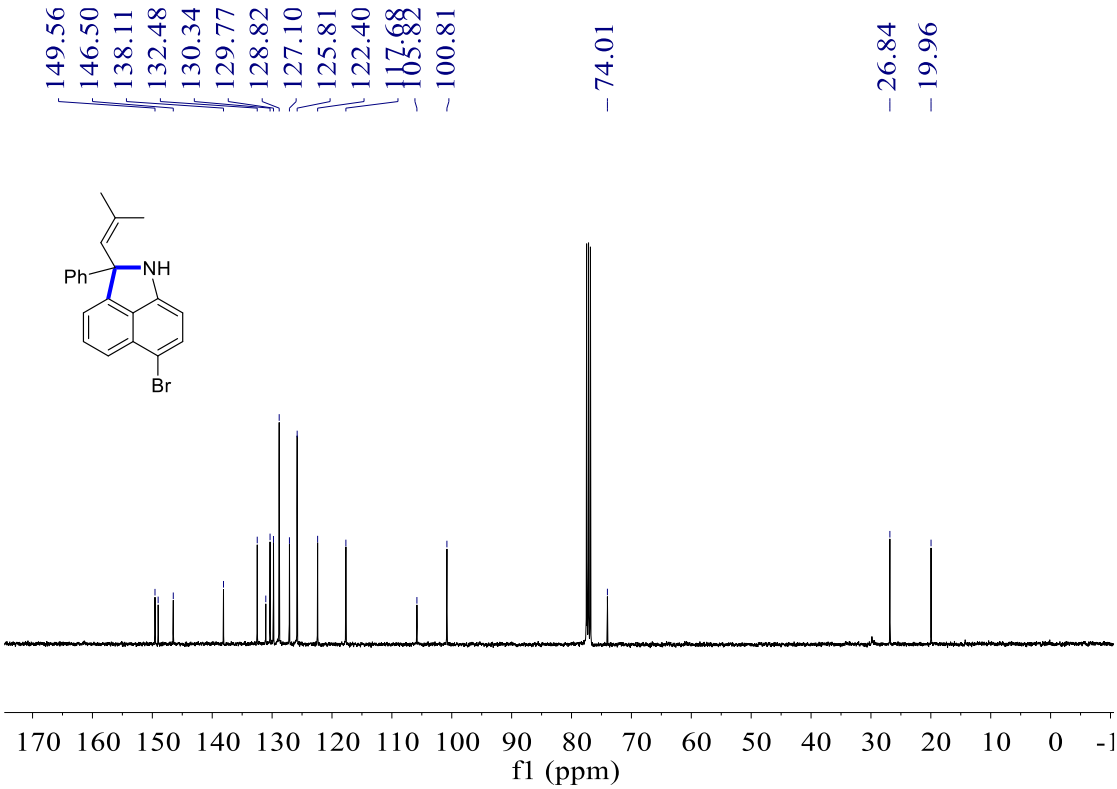
3aa,^{13}C NMR, 101 MHz, $CDCl_3$



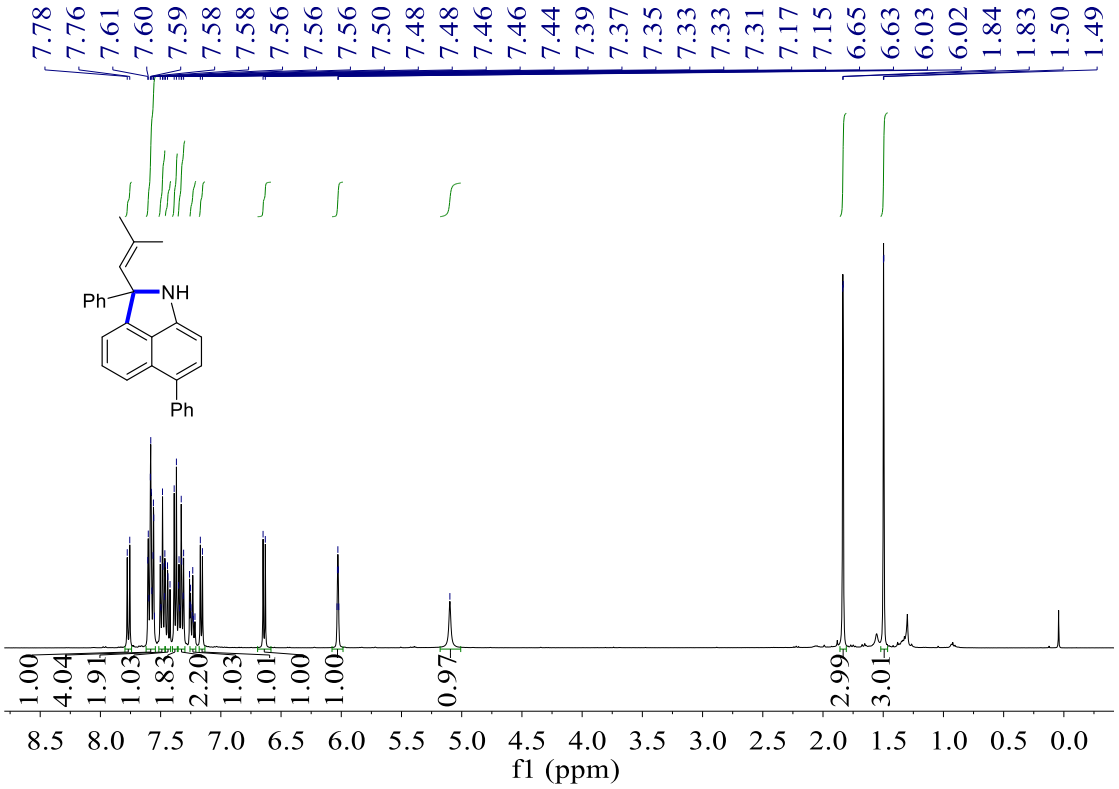
3ba, ^{1}H NMR, 400 MHz, $CDCl_3$



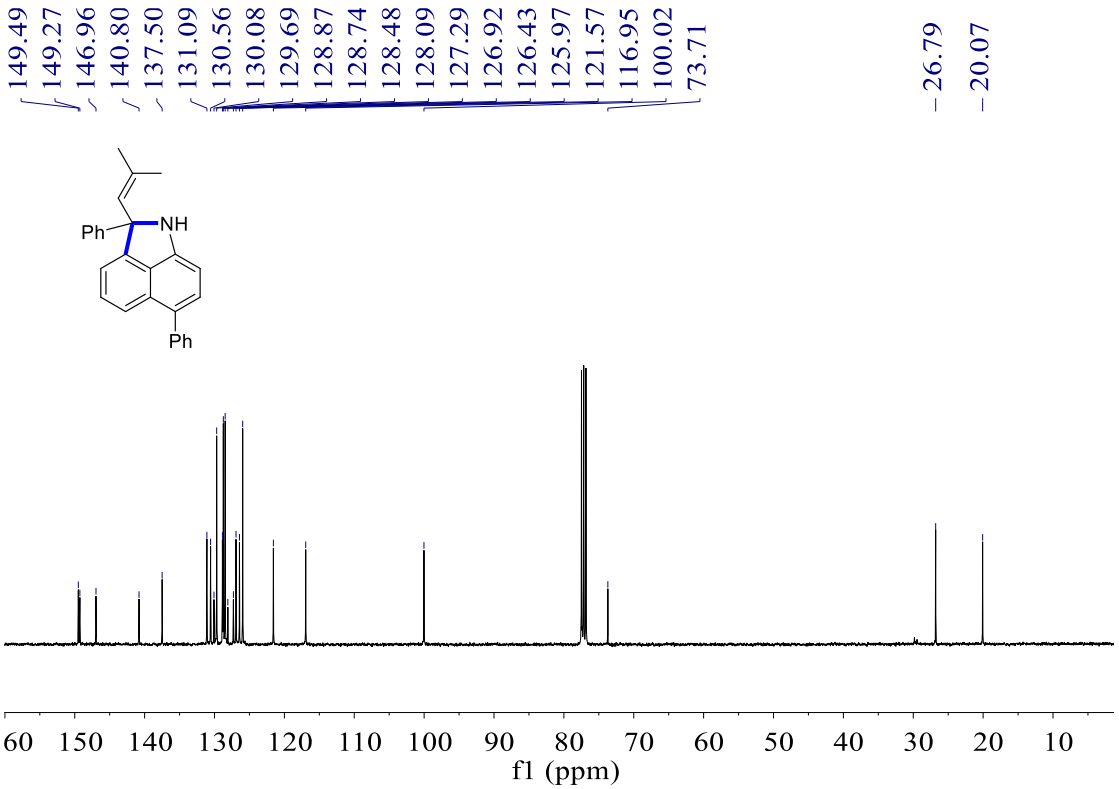
3ba,^{13}C NMR, 101 MHz, $CDCl_3$



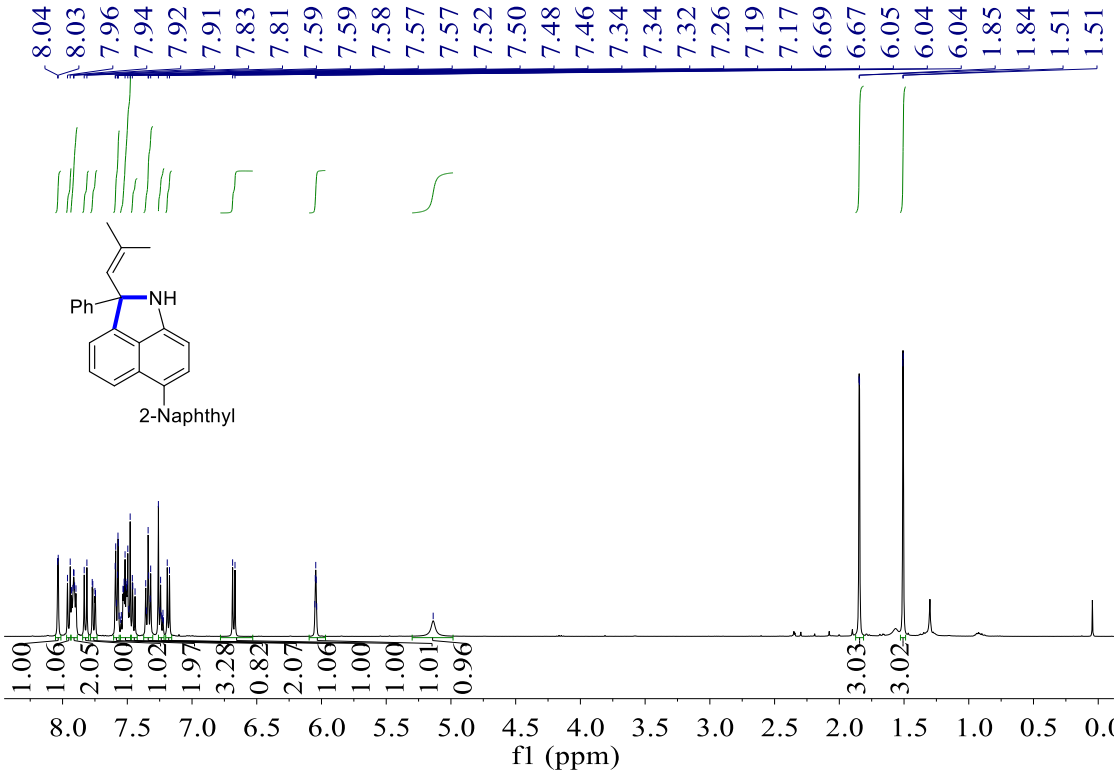
3ca, ^{1}H NMR, 400 MHz, $CDCl_3$



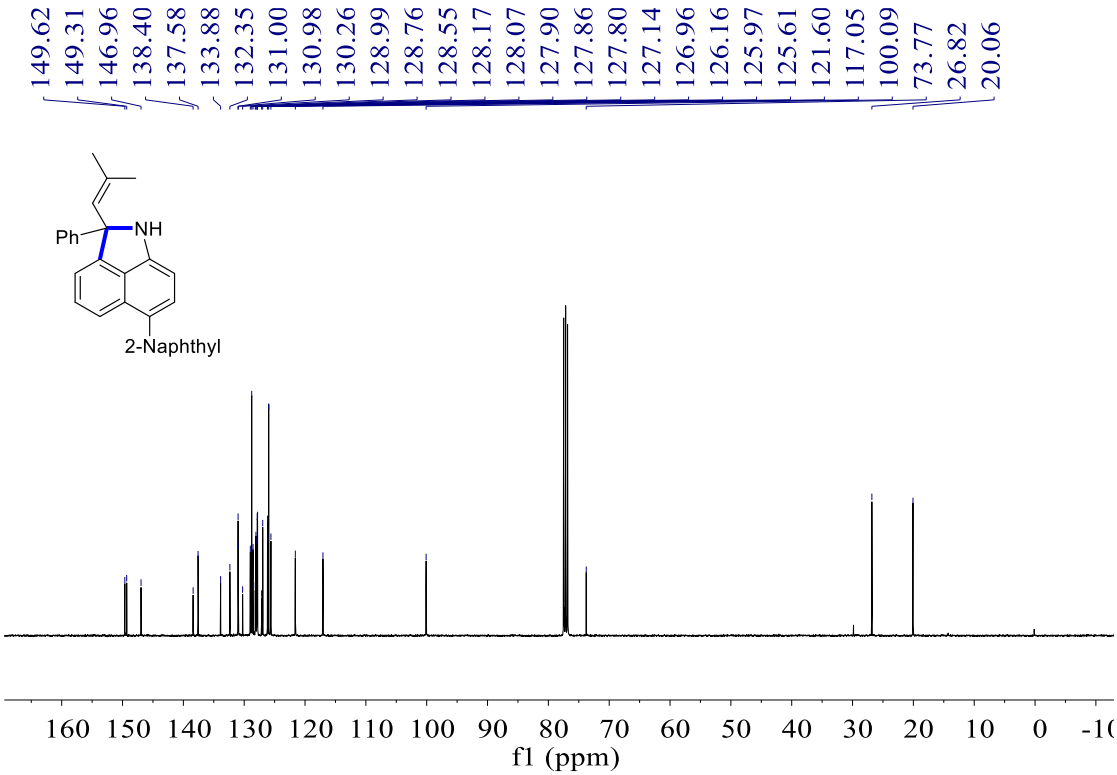
3ca,^{13}C NMR, 101 MHz, $CDCl_3$



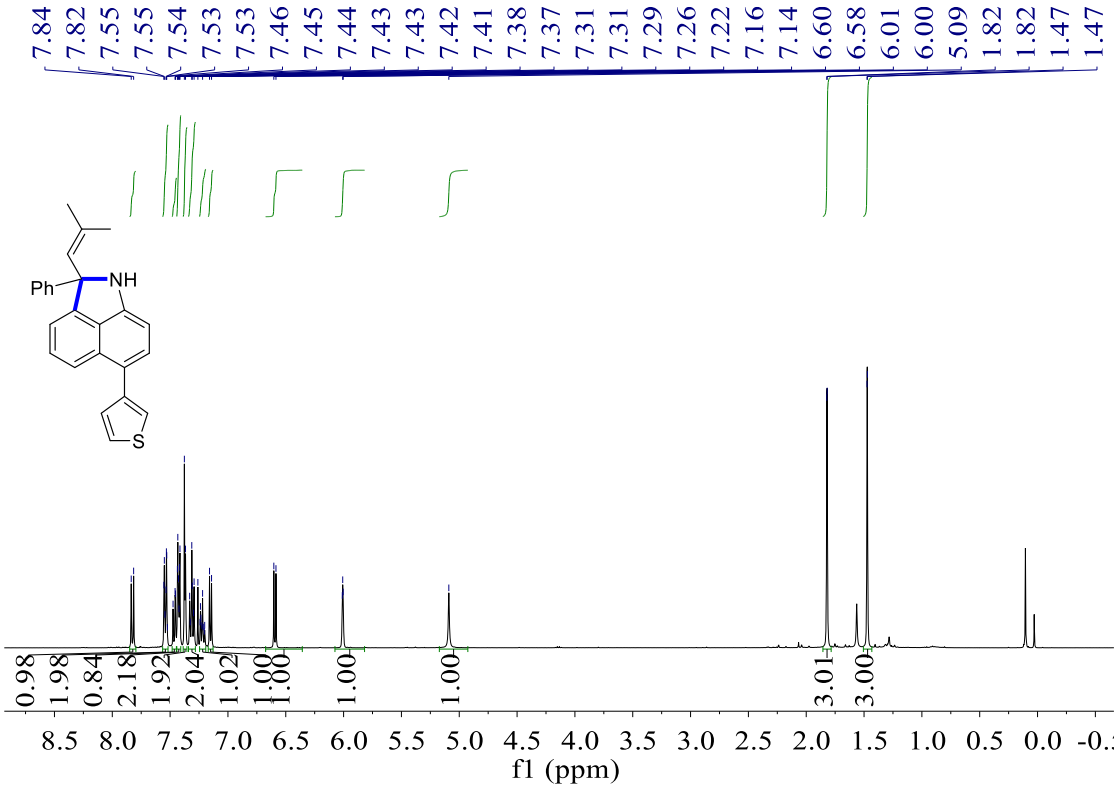
3da, ^{1}H NMR, 400 MHz, $CDCl_3$



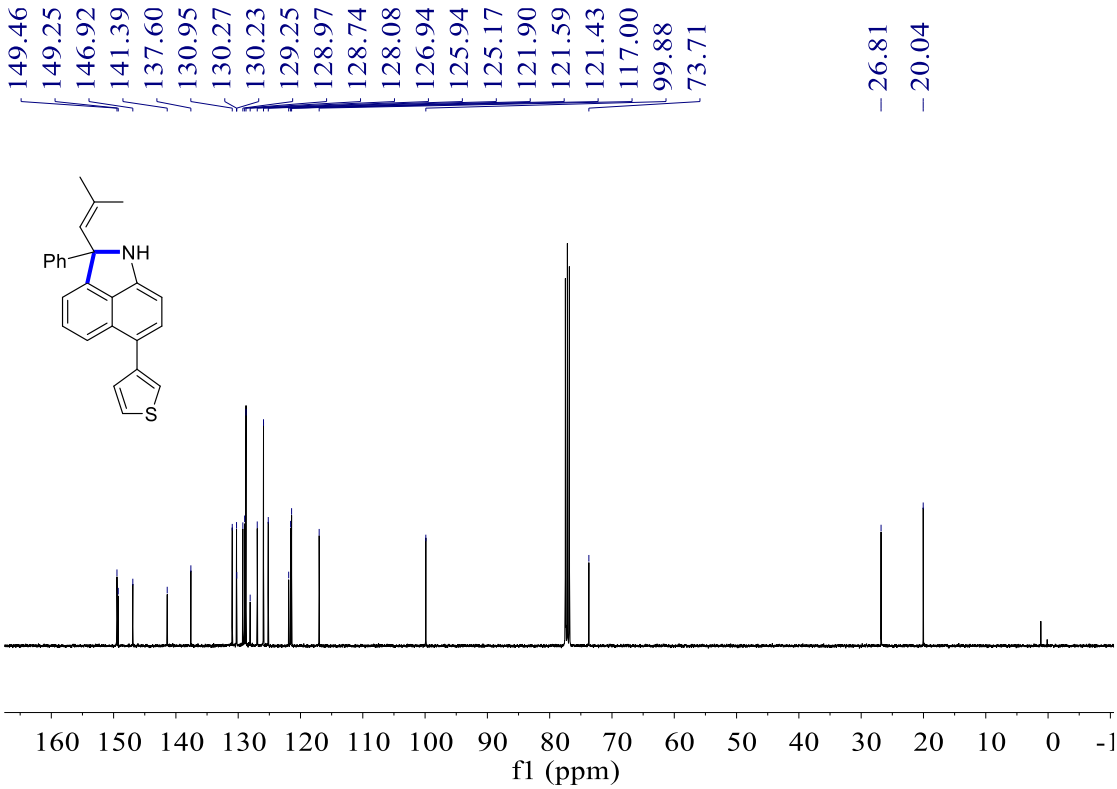
3da,^{13}C NMR, 101 MHz, $CDCl_3$



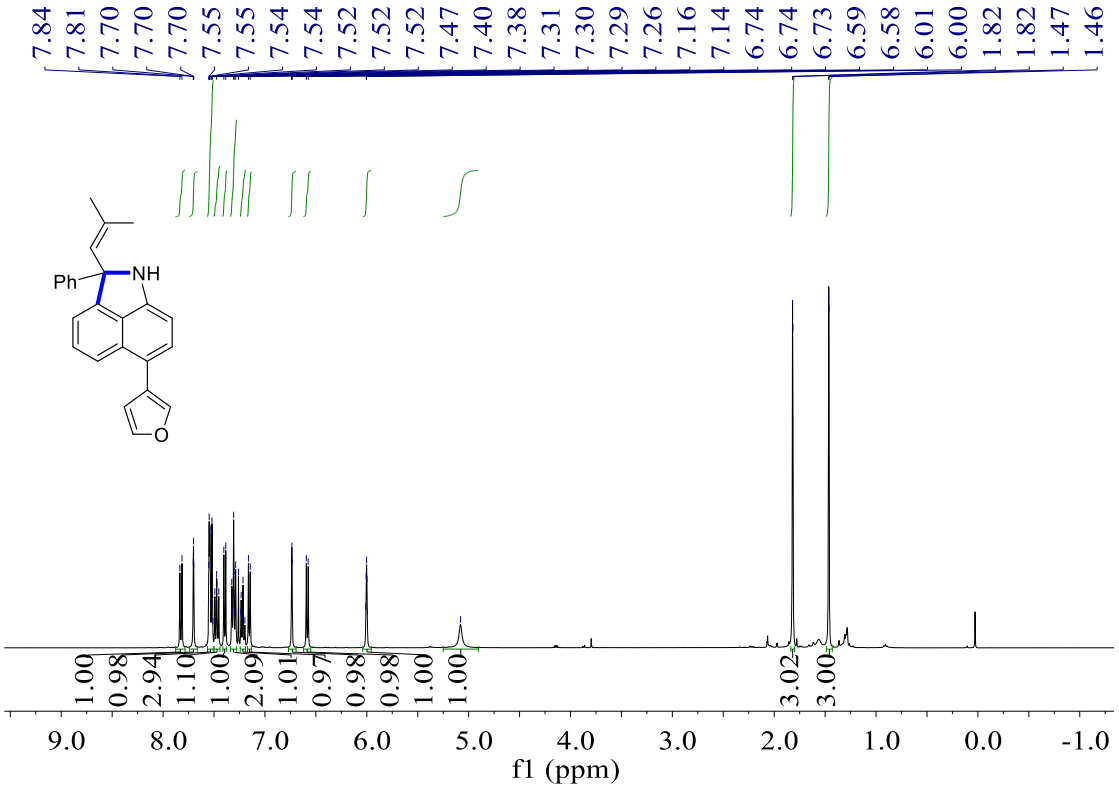
3ea, ^{1}H NMR, 400 MHz, $CDCl_3$



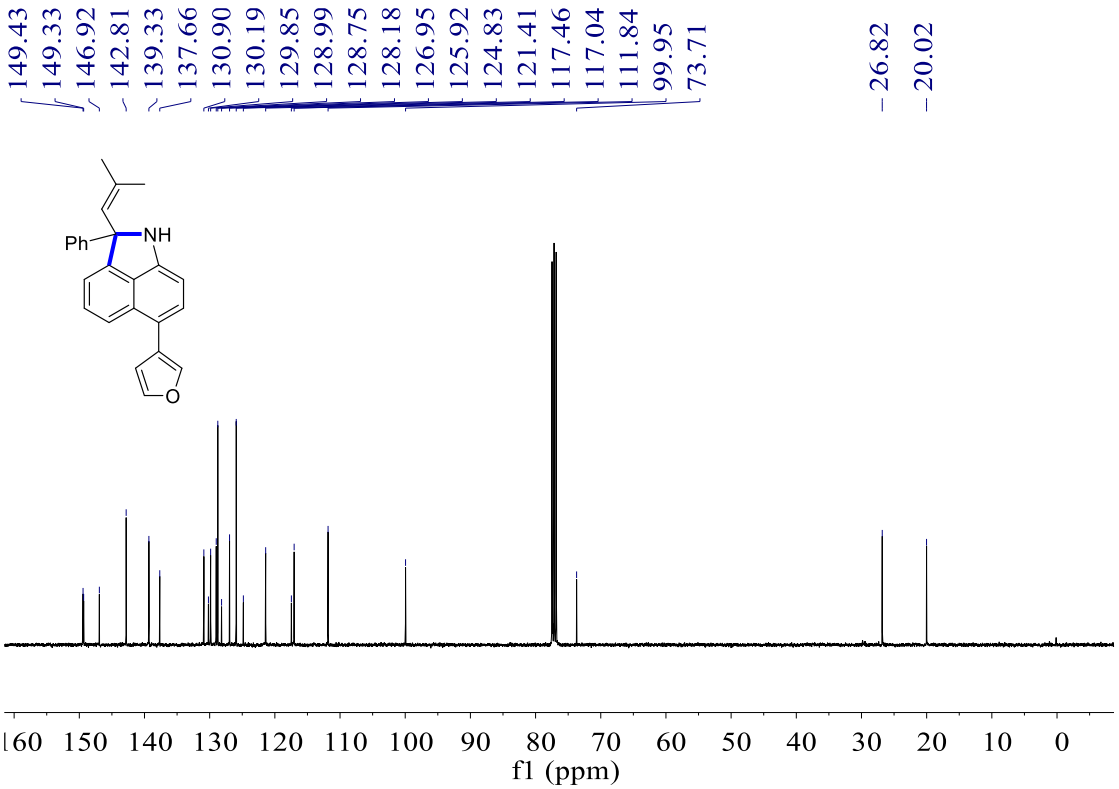
3ea, ^{13}C NMR, 101 MHz, $CDCl_3$



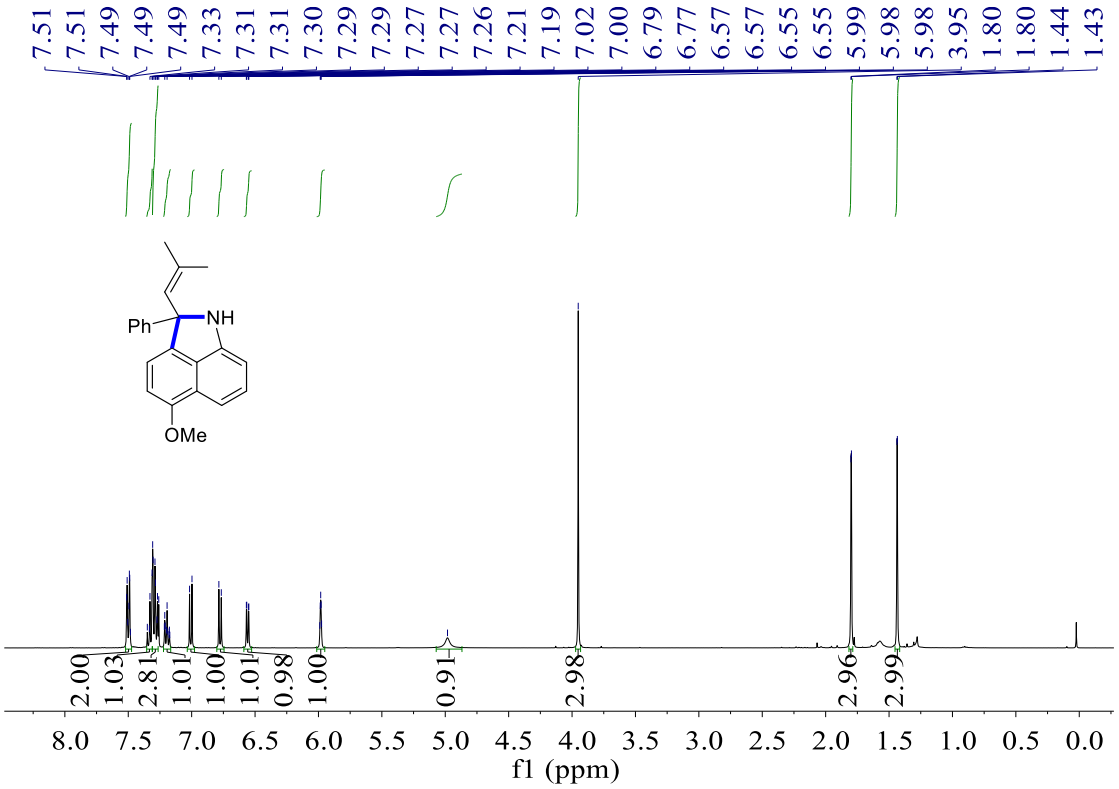
3fa, ^{1}H NMR, 400 MHz, $CDCl_3$



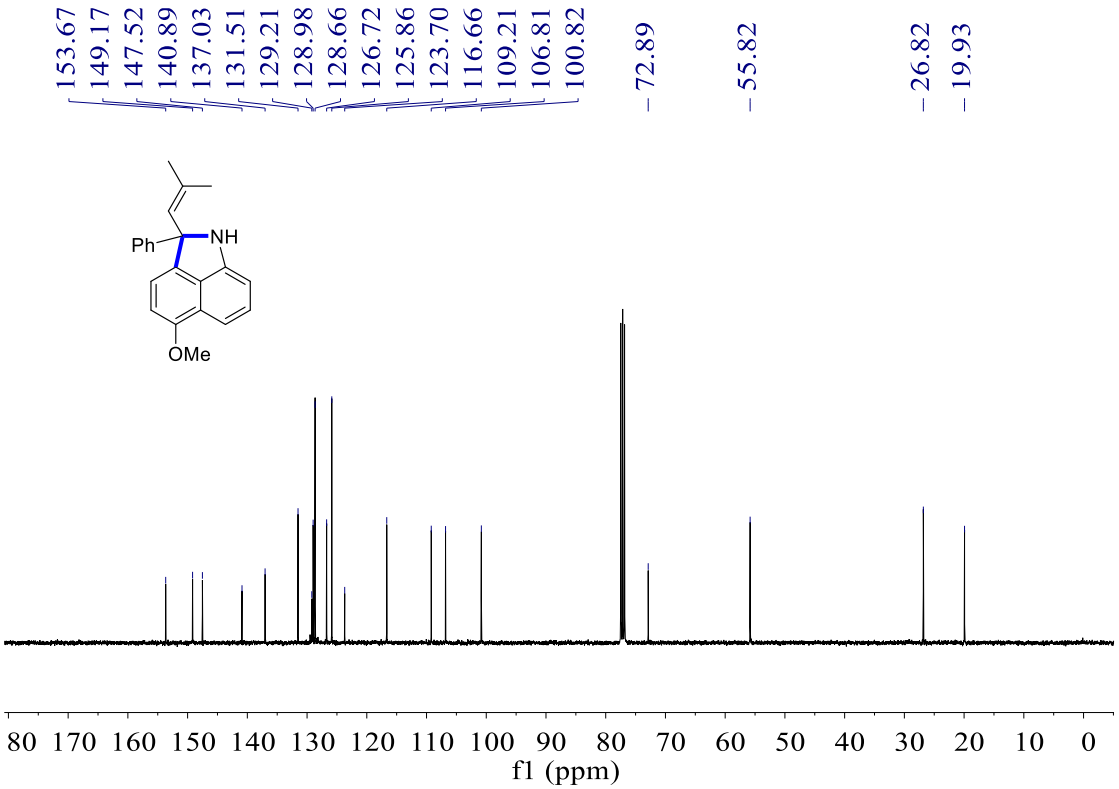
3fa, ^{13}C NMR, 101 MHz, $CDCl_3$



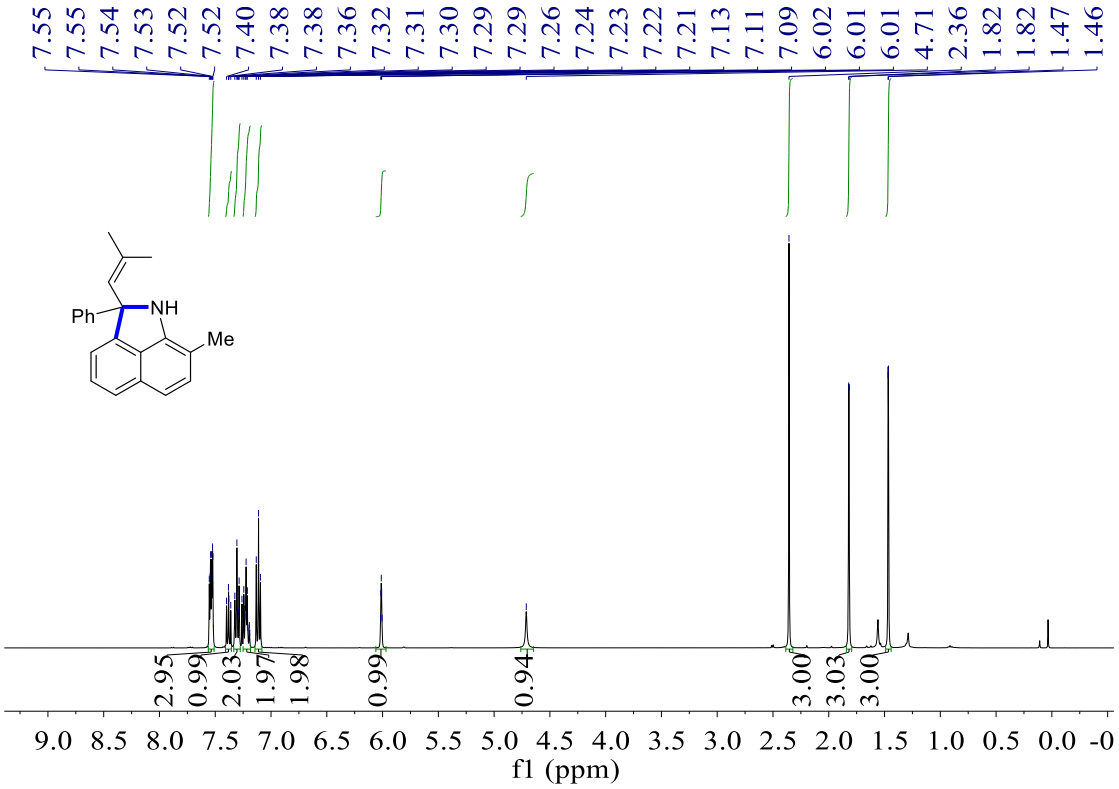
3ga, ^{1}H NMR, 400 MHz, $CDCl_3$



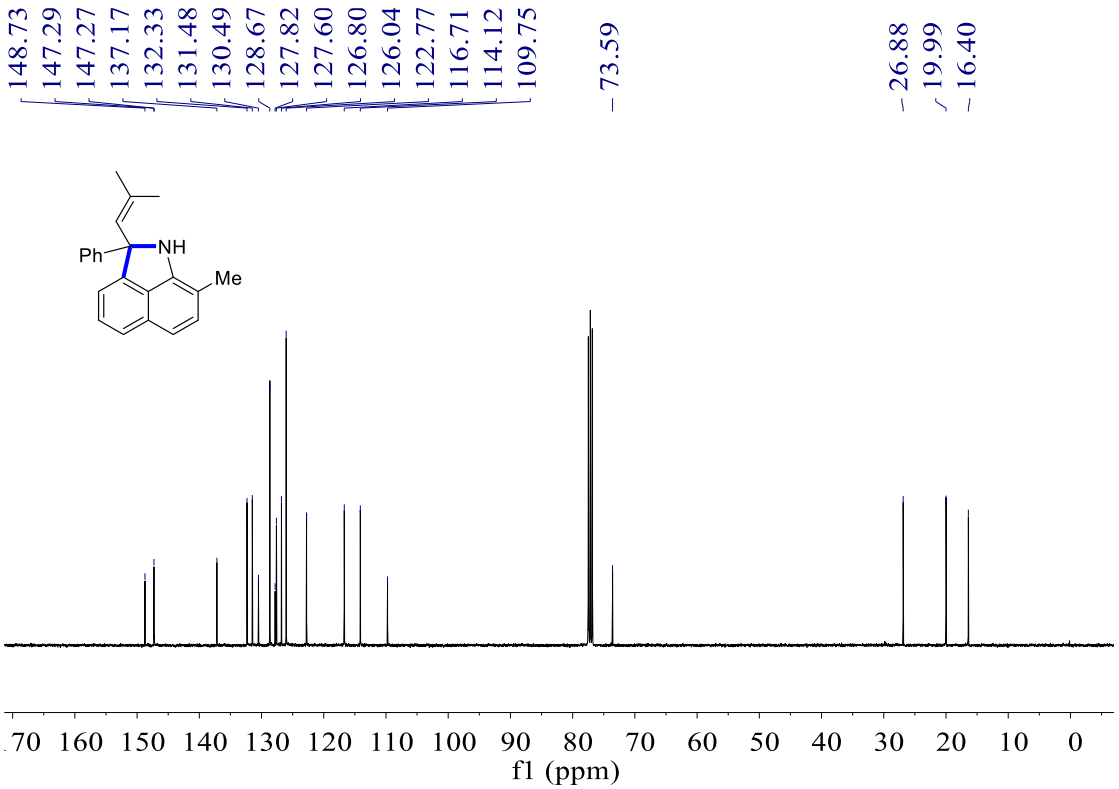
3ga, ^{13}C NMR, 101 MHz, $CDCl_3$



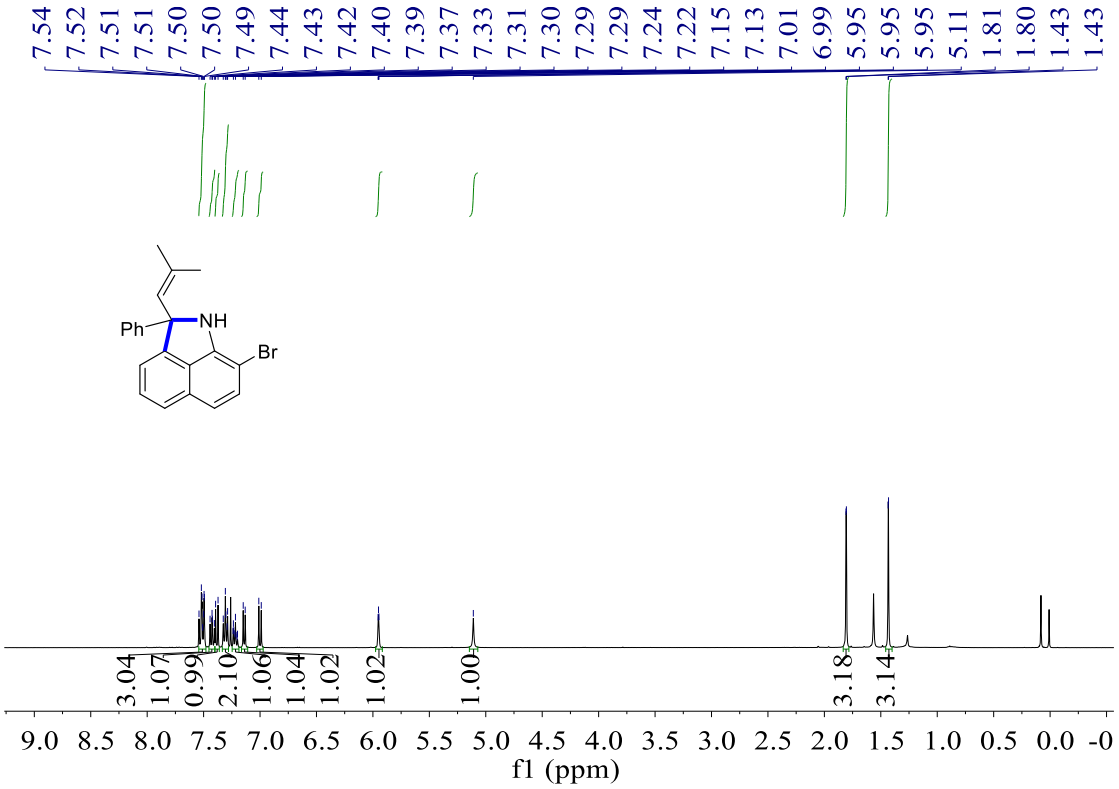
3ha, ^{1}H NMR, 400 MHz, $CDCl_3$



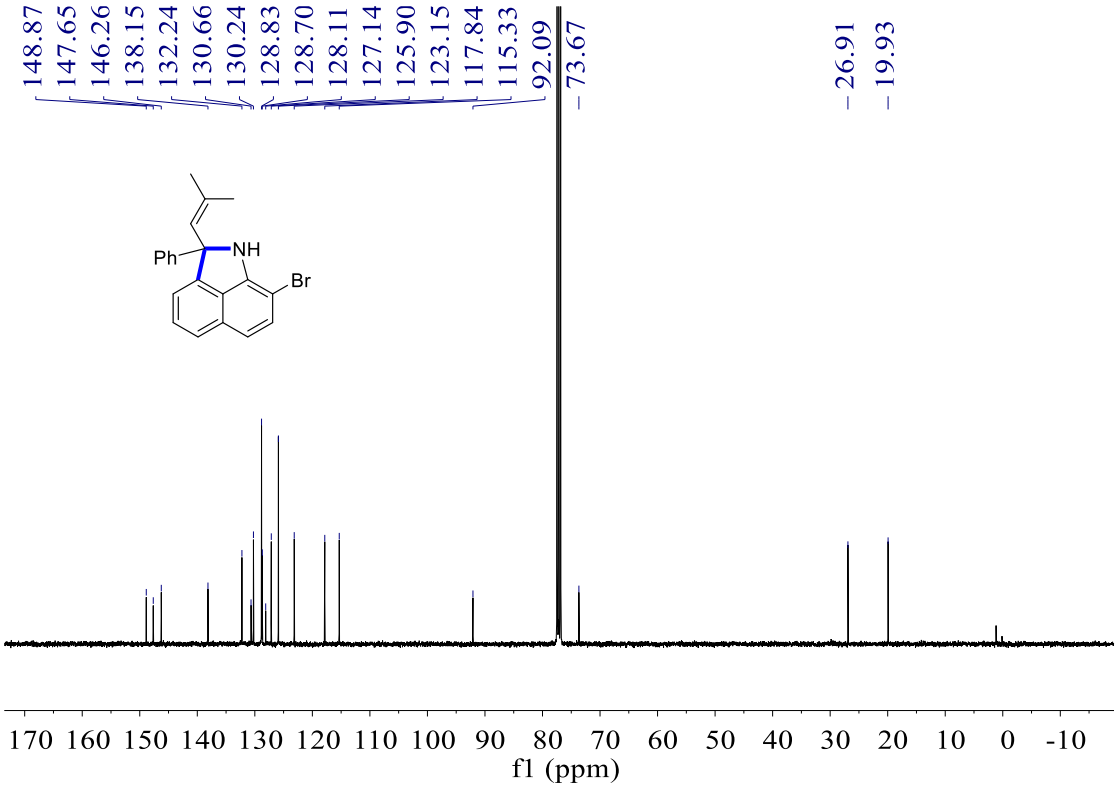
3ha, ^{13}C NMR, 101 MHz, $CDCl_3$



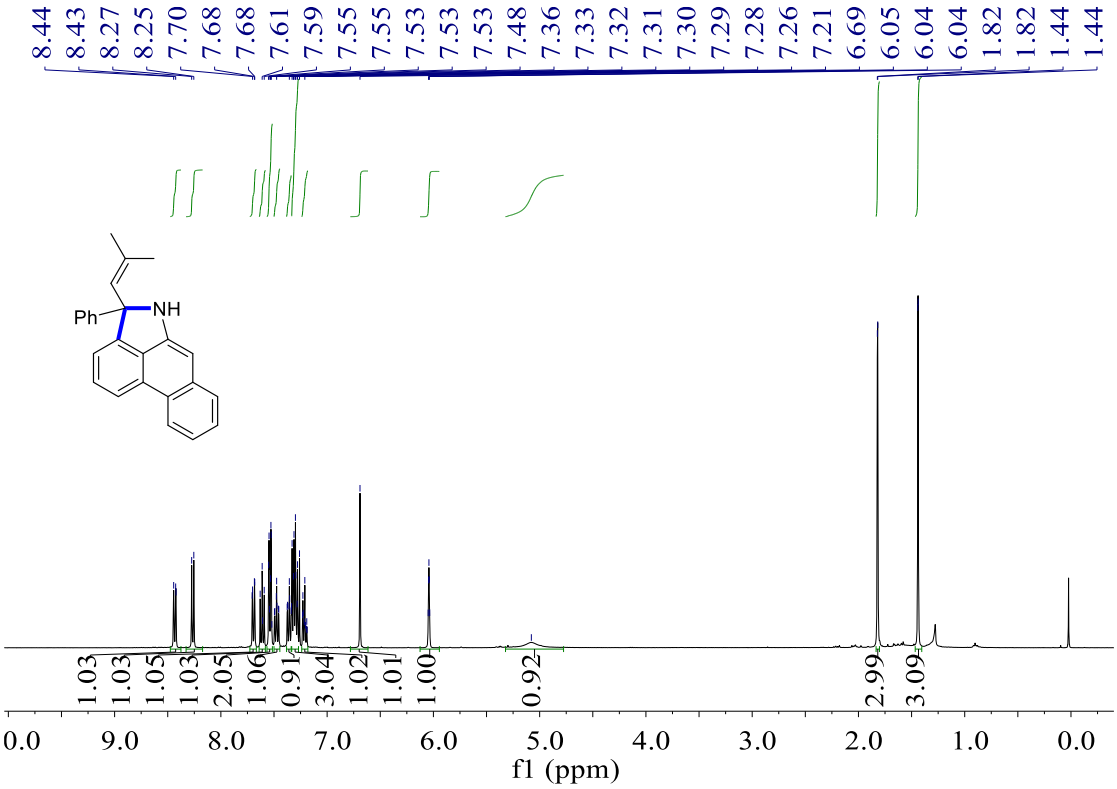
3ia, ^{1}H NMR, 400 MHz, $CDCl_3$



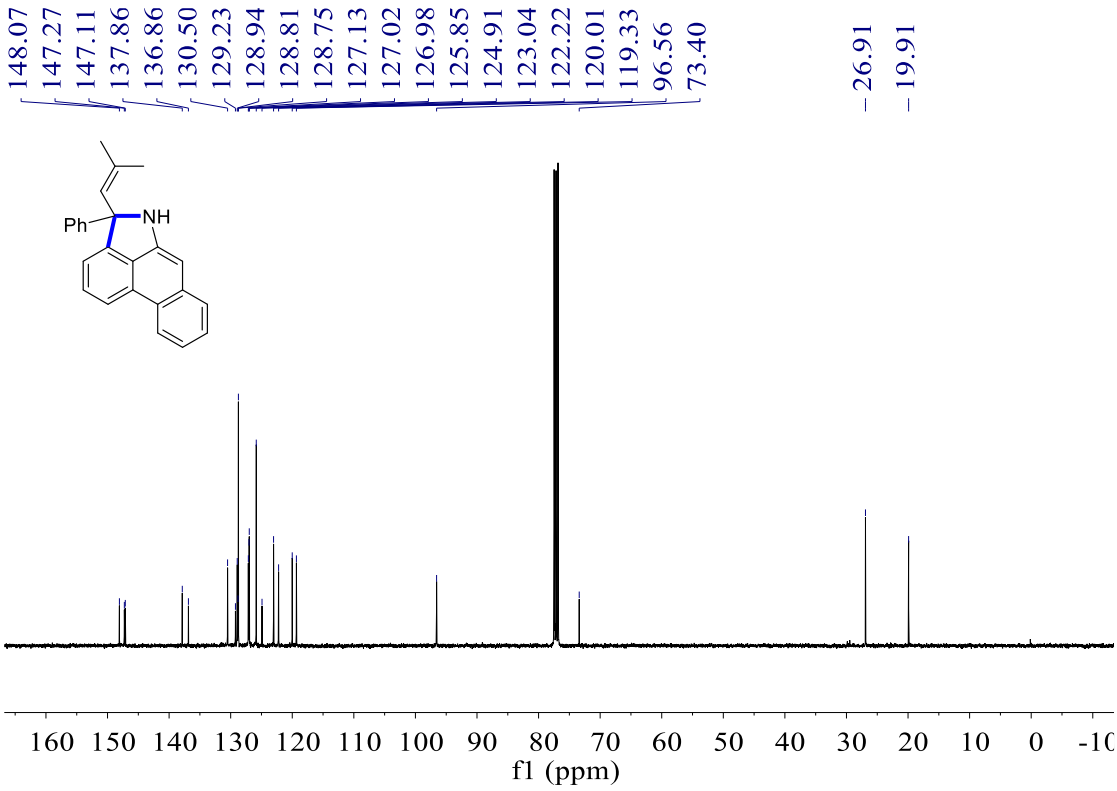
3ia, ^{13}C NMR, 101 MHz, $CDCl_3$



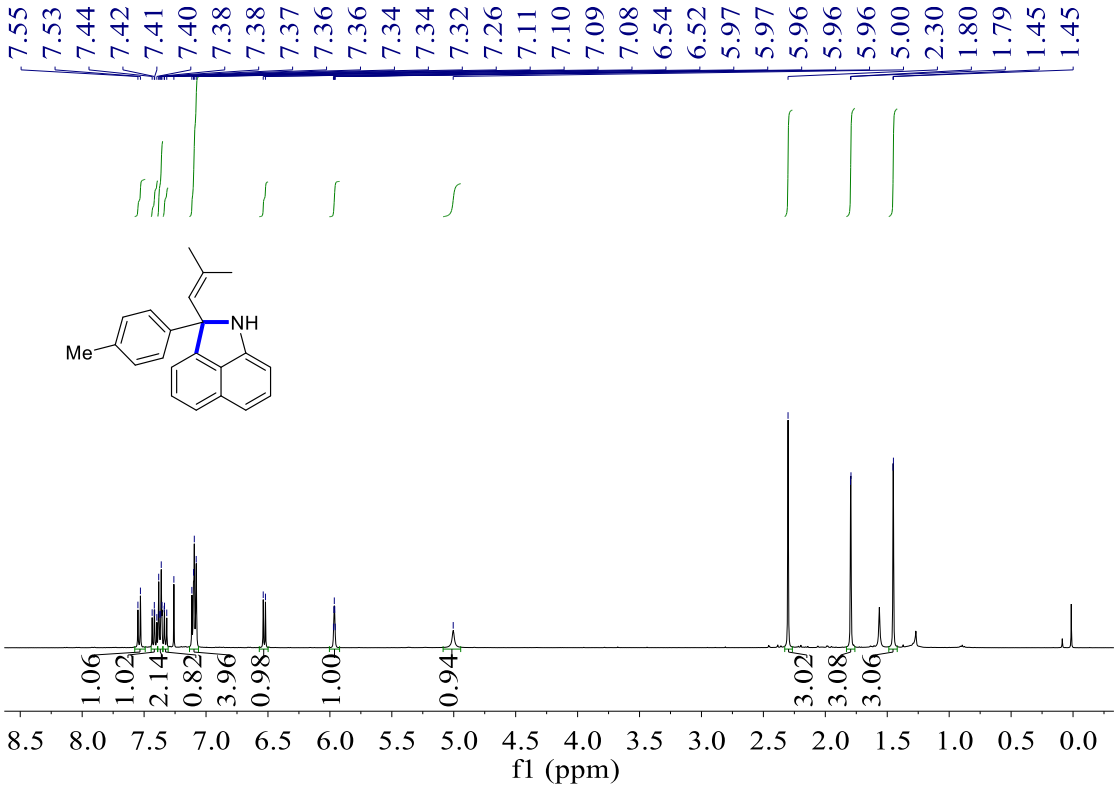
3ja, ^{1}H NMR, 400 MHz, $CDCl_3$



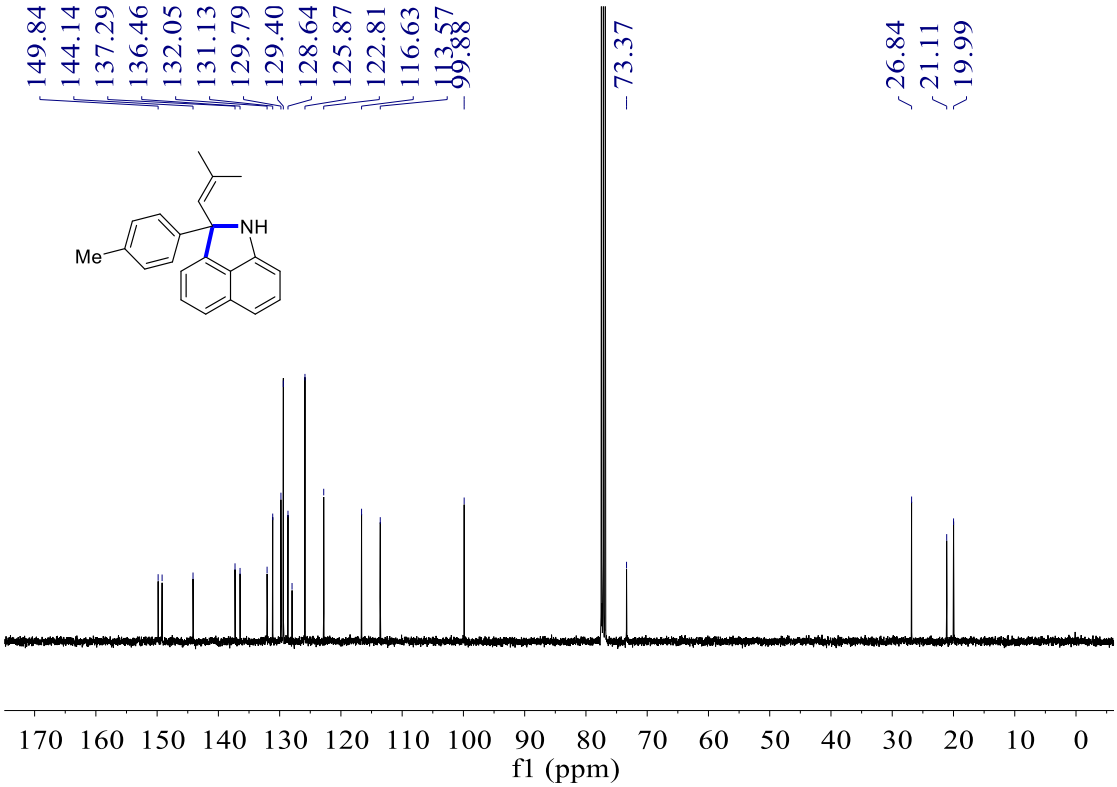
3ja, ^{13}C NMR, 101 MHz, $CDCl_3$



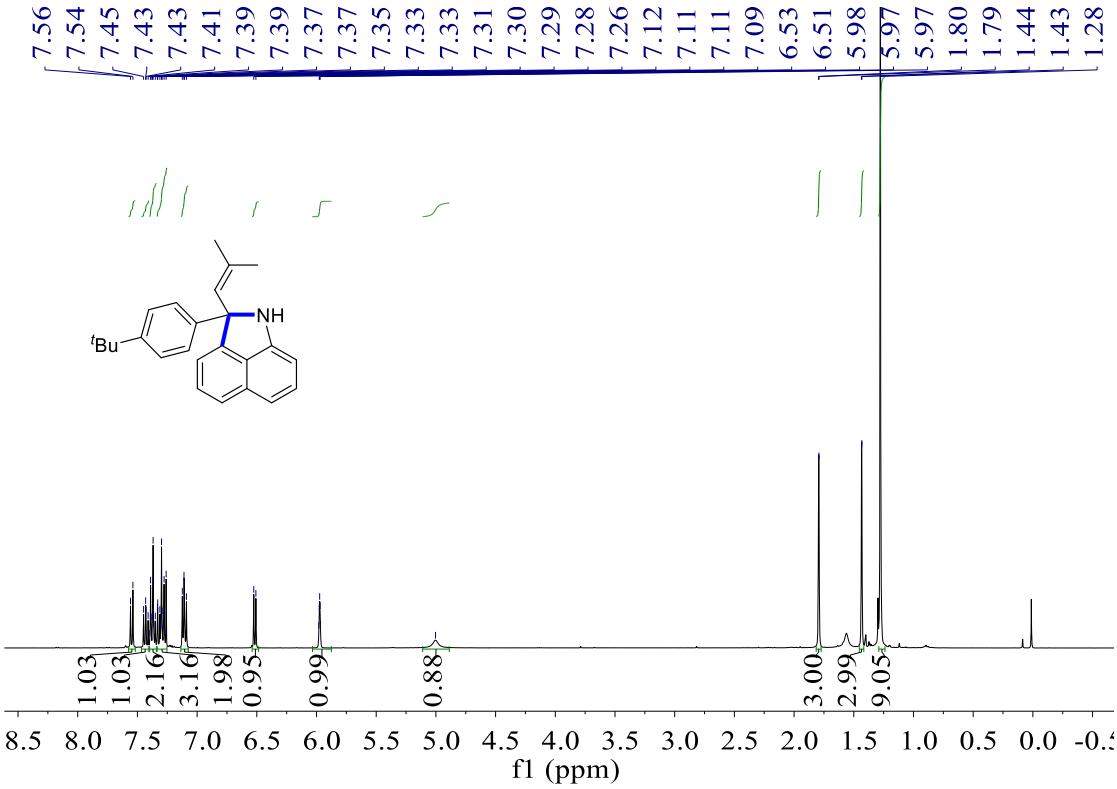
3ab, ^{1}H NMR, 400 MHz, $CDCl_3$



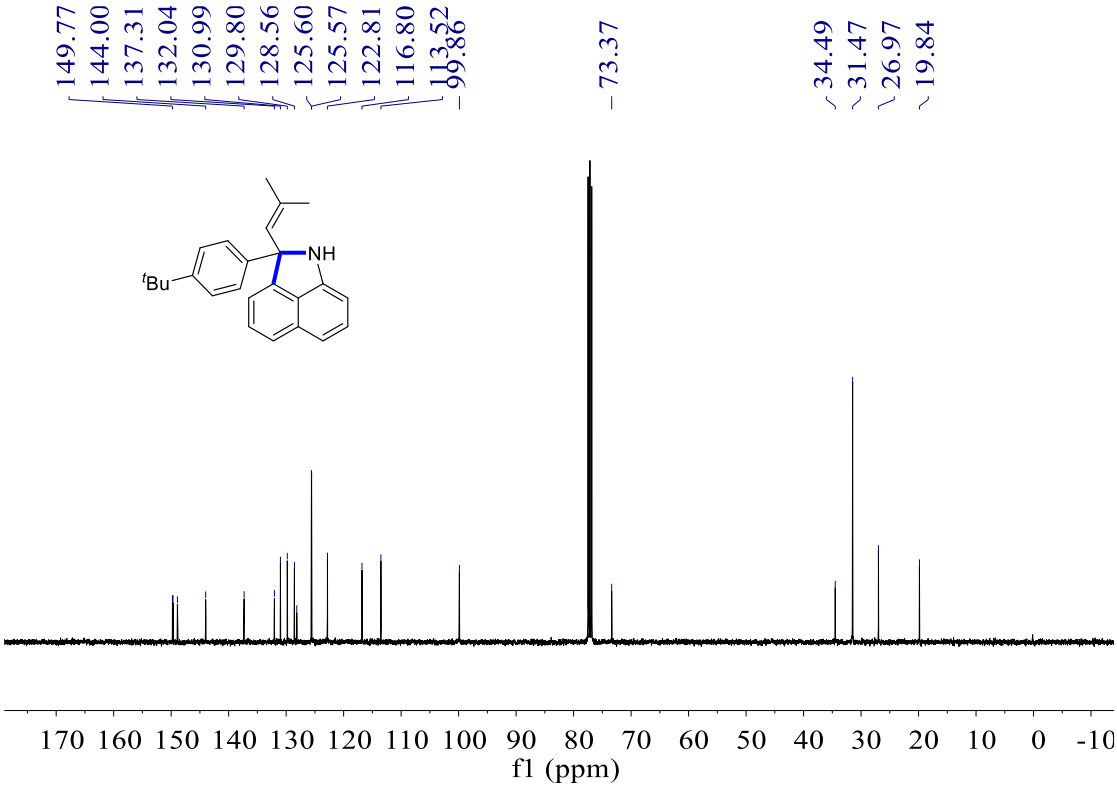
3ab, ^{13}C NMR, 101 MHz, $CDCl_3$



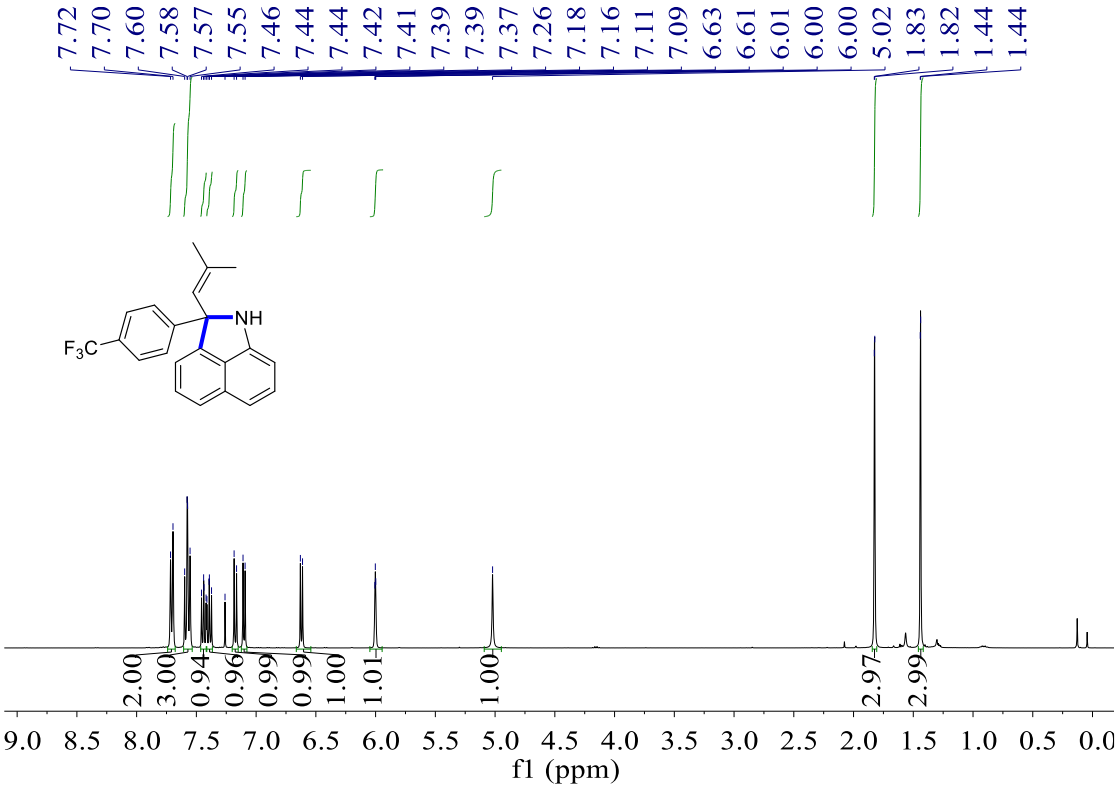
3ac, ^{1}H NMR, 400 MHz, $CDCl_3$



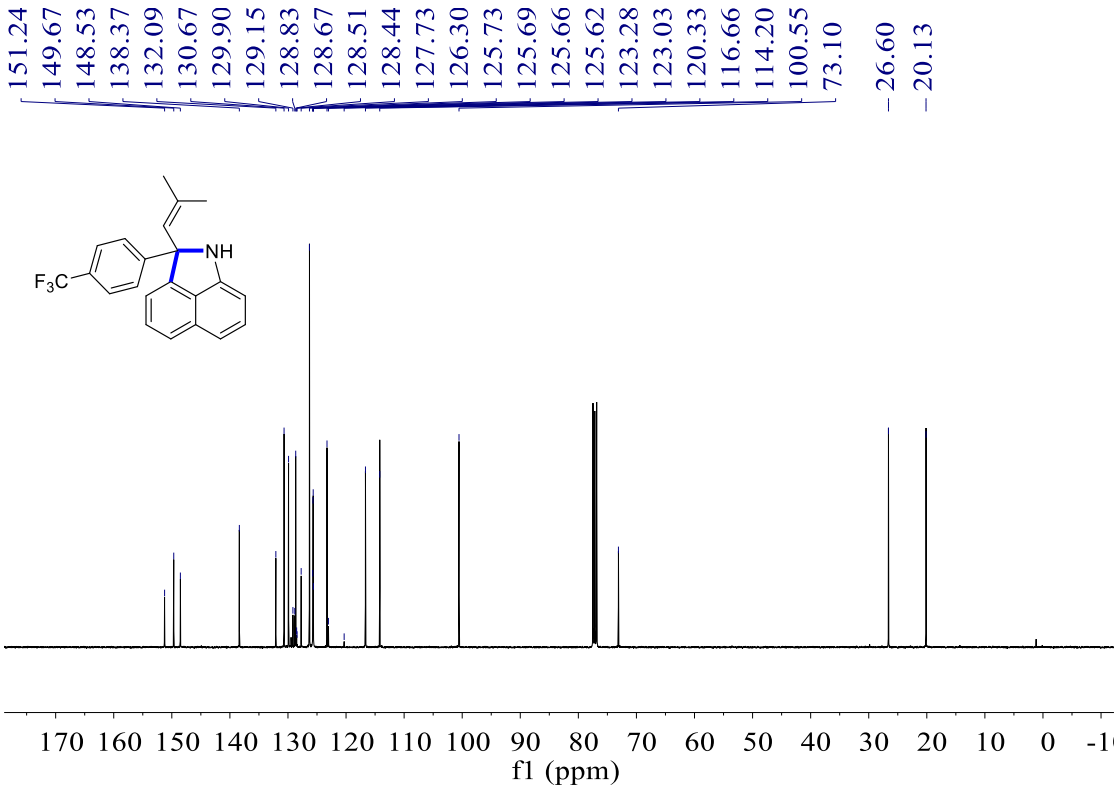
3ac, ^{13}C NMR, 101 MHz, $CDCl_3$



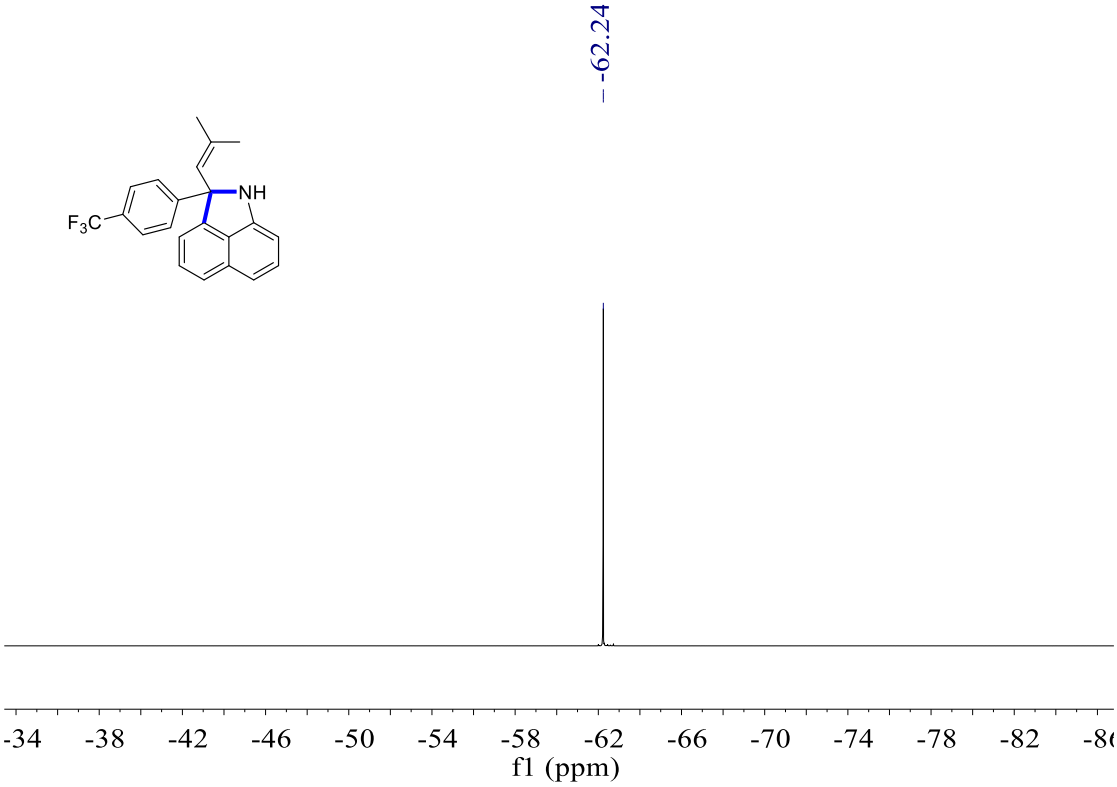
3ad, ^{1}H NMR, 400 MHz, $CDCl_3$



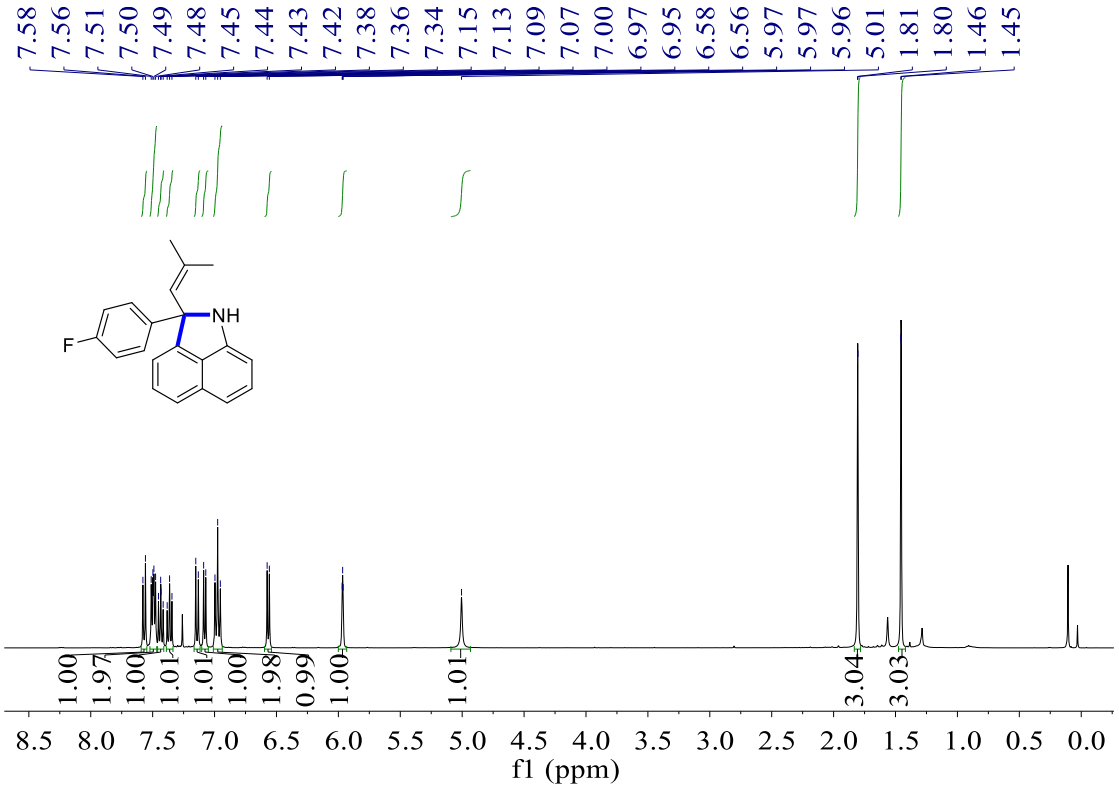
3ad, ^{13}C NMR, 101 MHz, $CDCl_3$



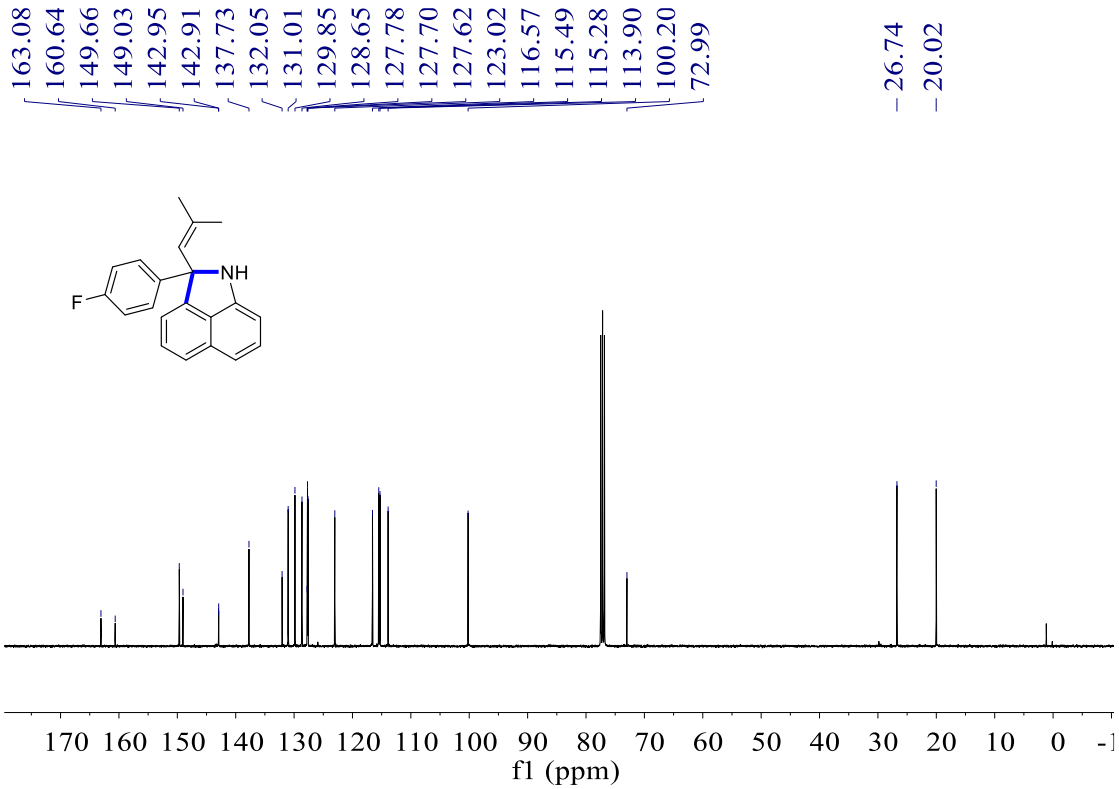
3ad, ^{19}F NMR, 376 MHz, $CDCl_3$



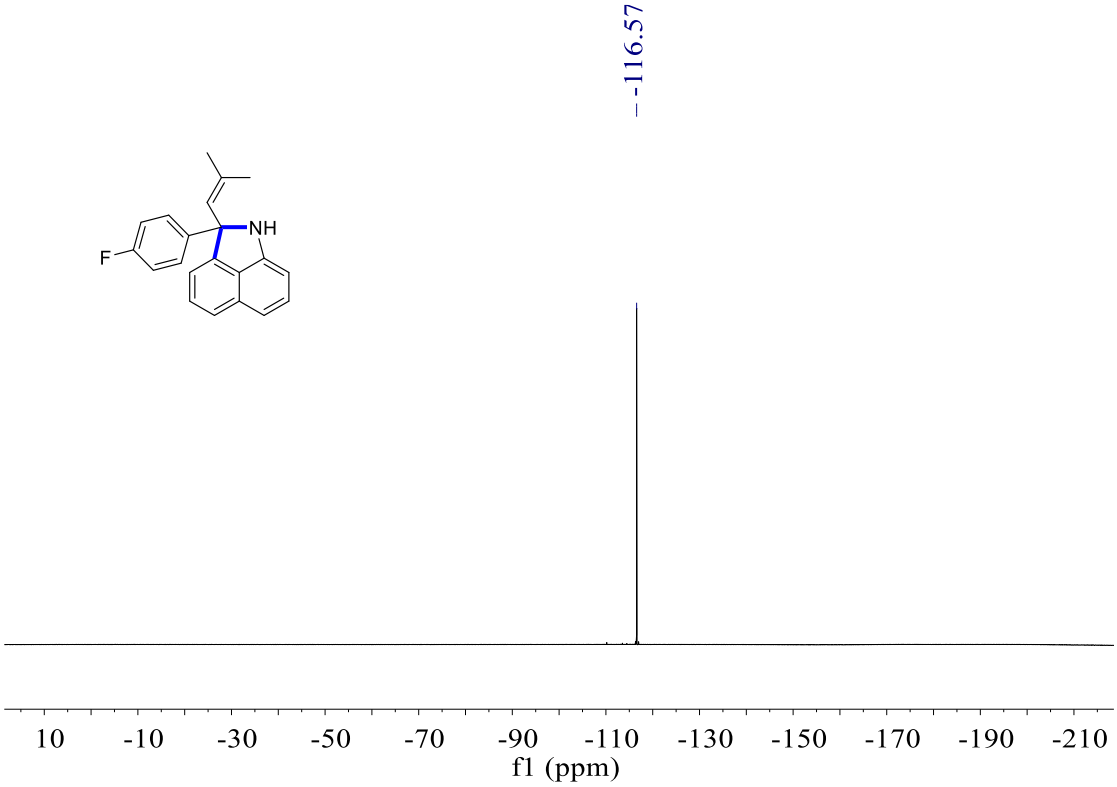
3ae, ^{1}H NMR, 400 MHz, $CDCl_3$



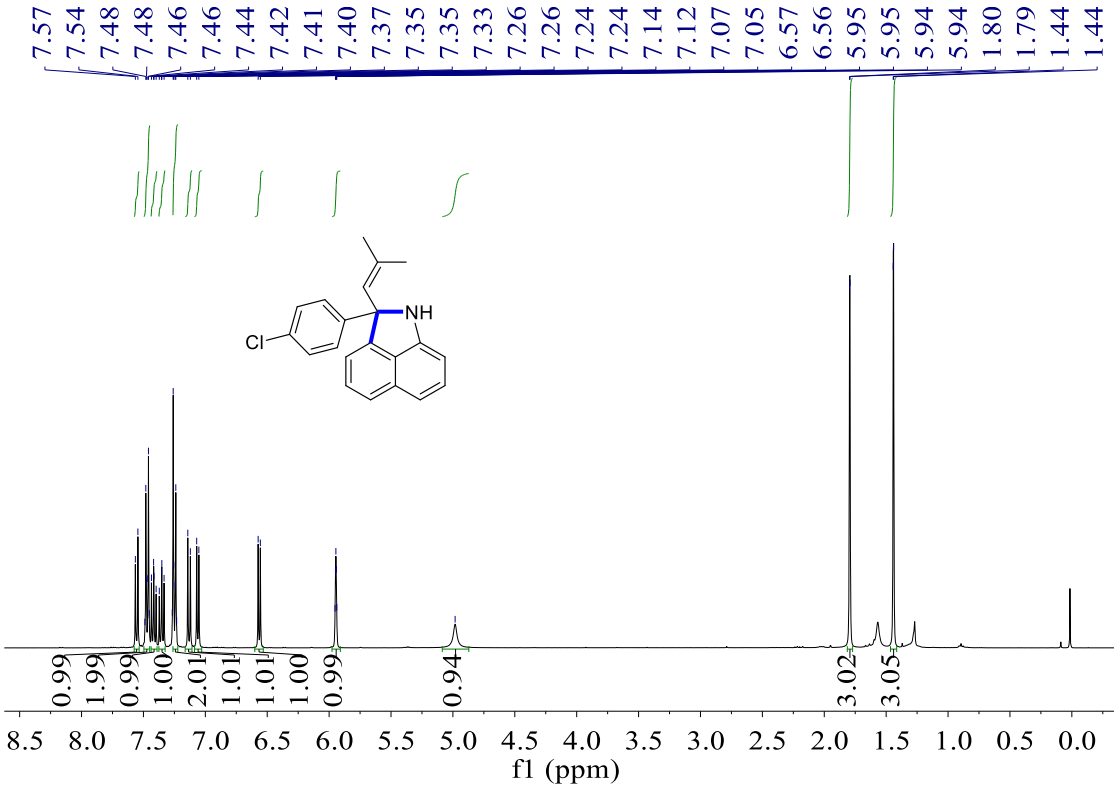
3ae, ^{13}C NMR, 101 MHz, $CDCl_3$



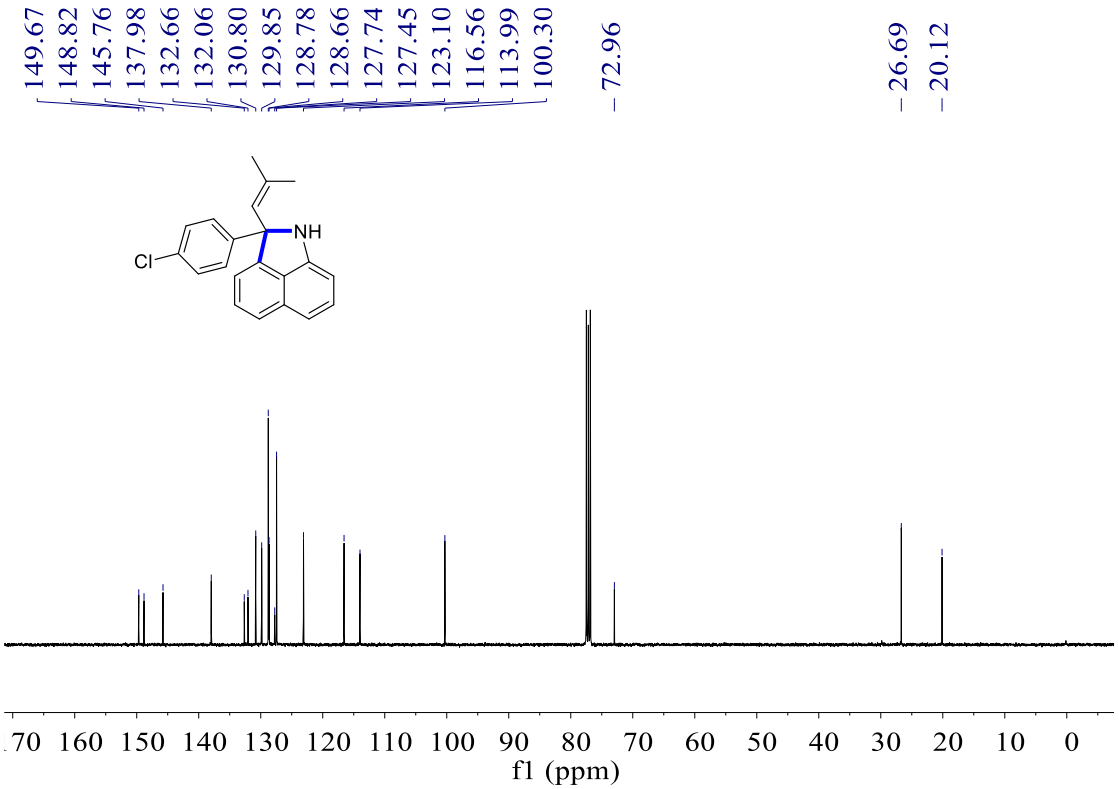
3ae, ^{19}F NMR, 376 MHz, $CDCl_3$



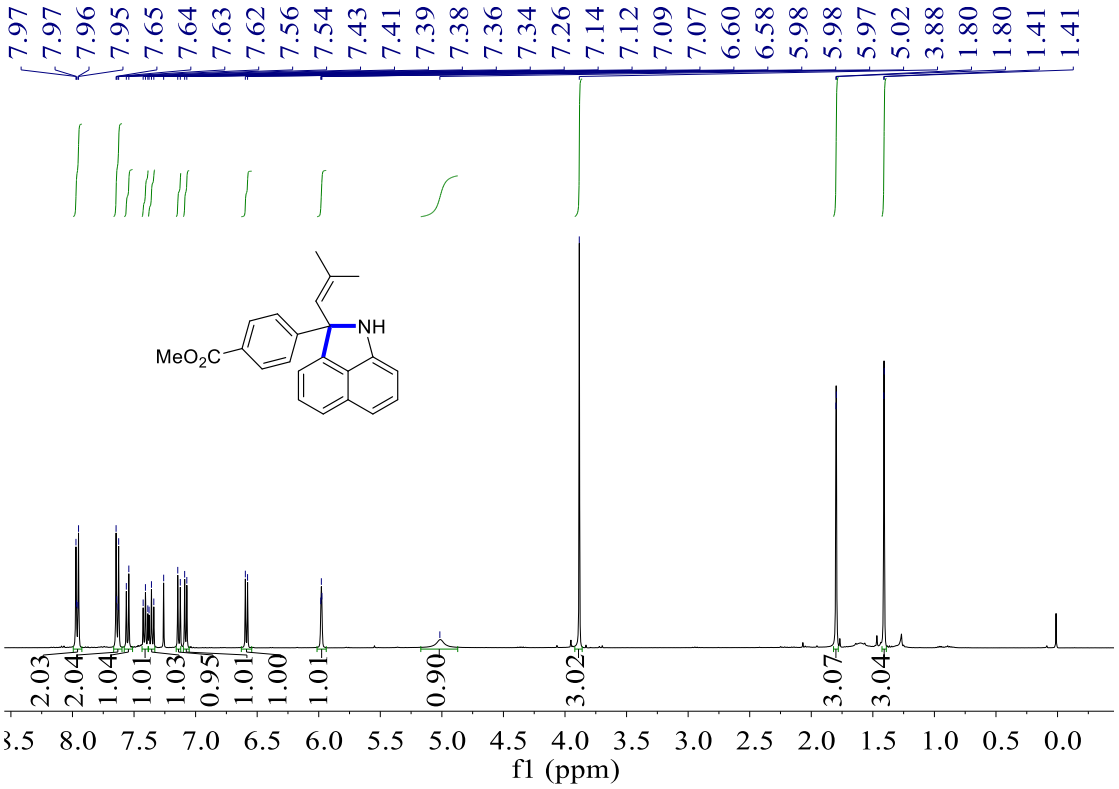
3af, ^{1}H NMR, 400 MHz, $CDCl_3$



3af, ^{13}C NMR, 101 MHz, $CDCl_3$



3ag, ^{1}H NMR, 400 MHz, $CDCl_3$



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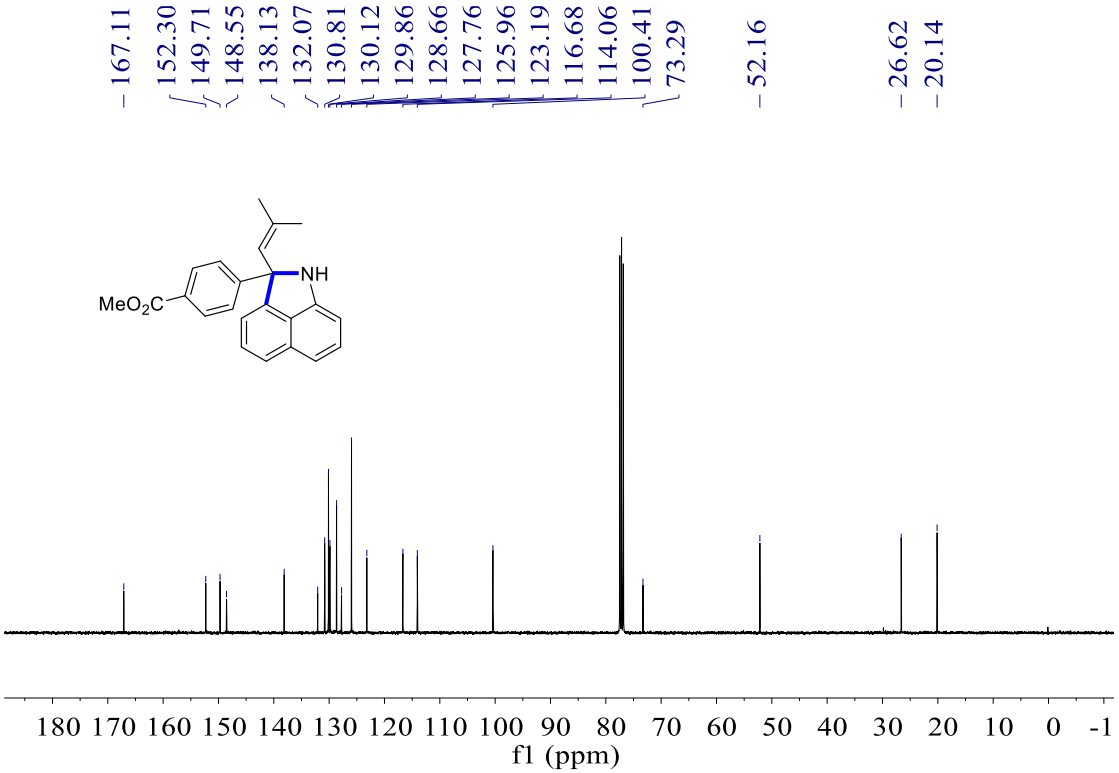

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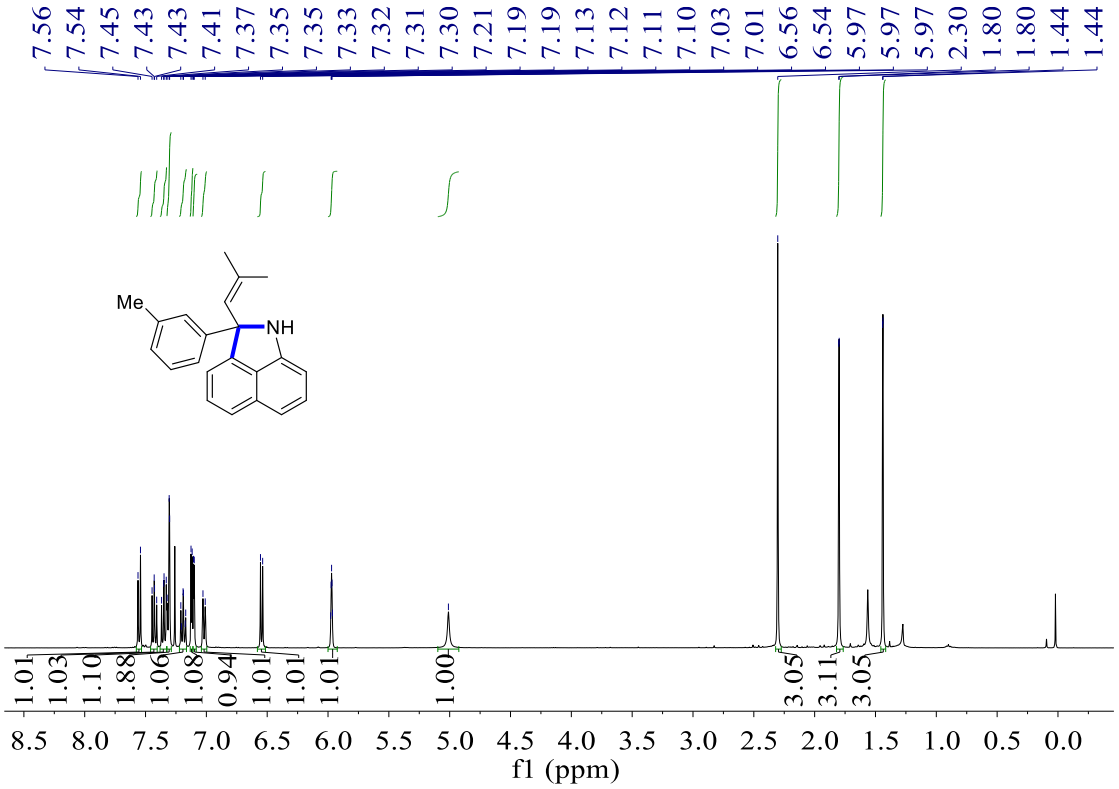

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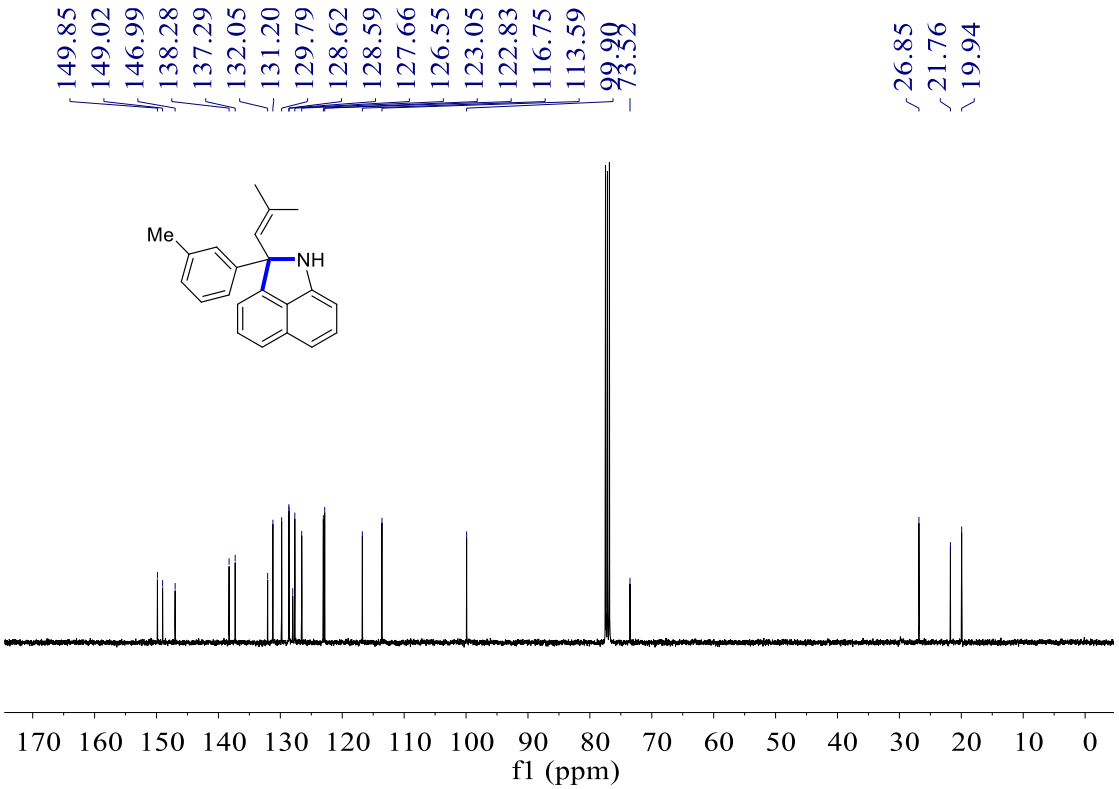
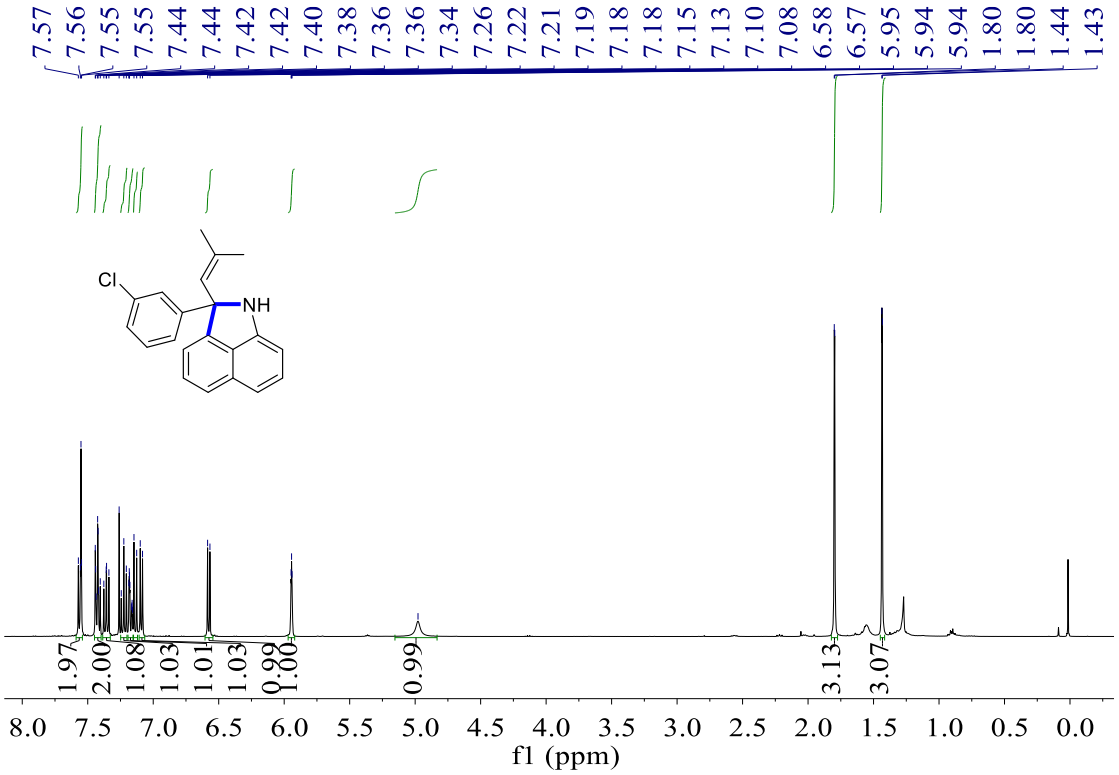
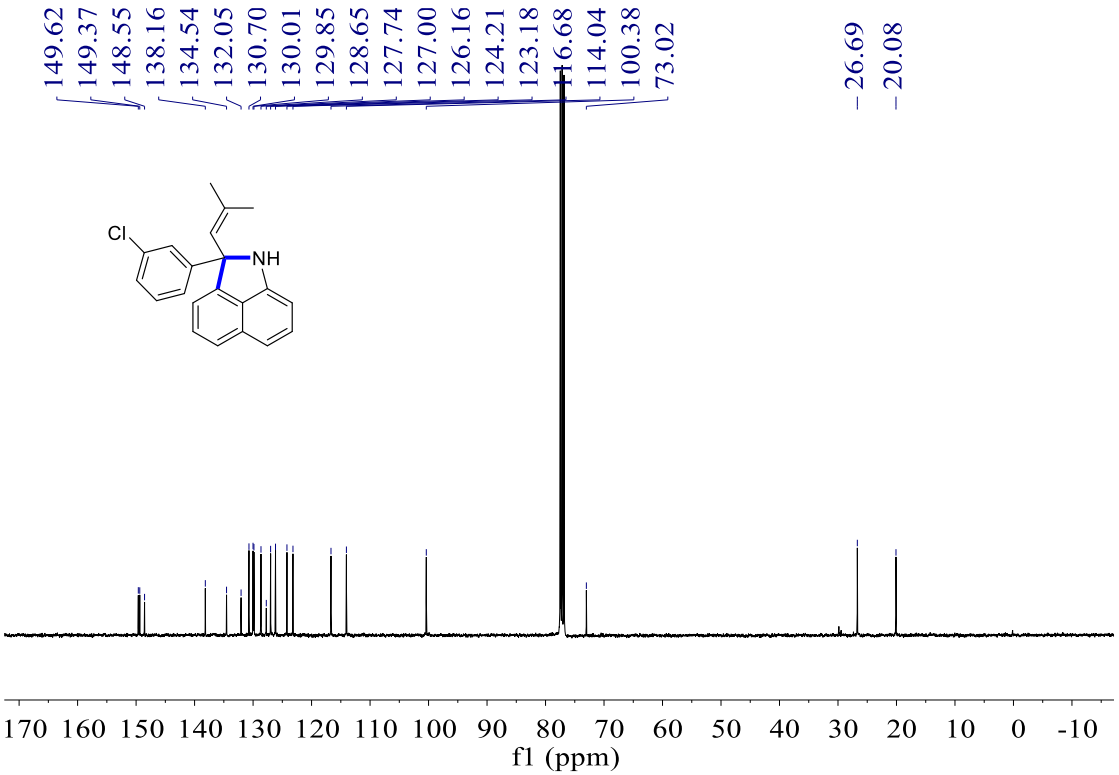


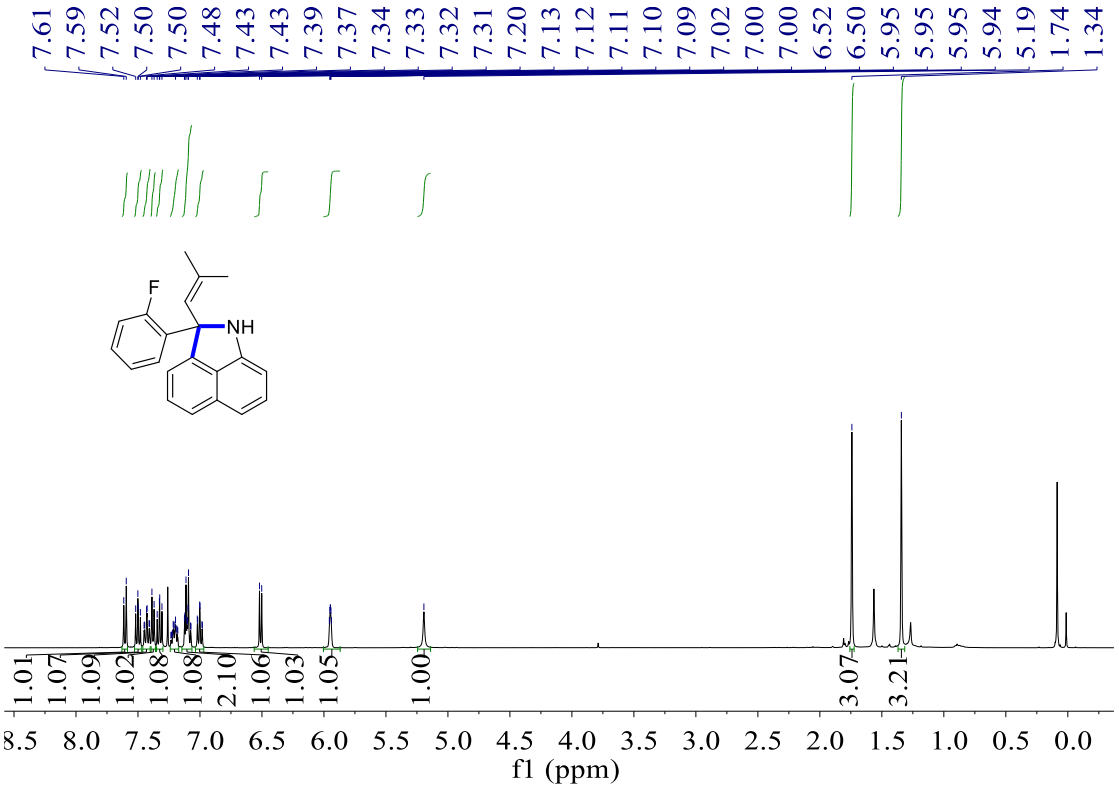
3ai, ^{1}H NMR, 400 MHz, $CDCl_3$



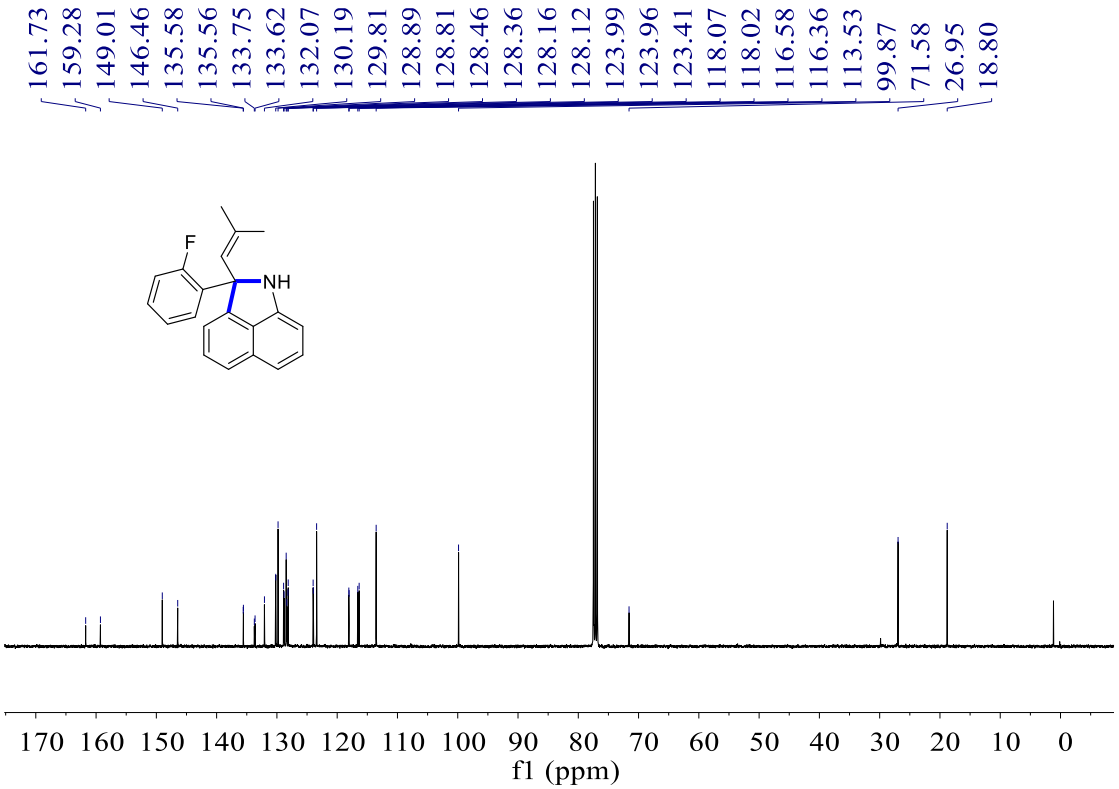
3ai, ^{13}C NMR, 101 MHz, $CDCl_3$



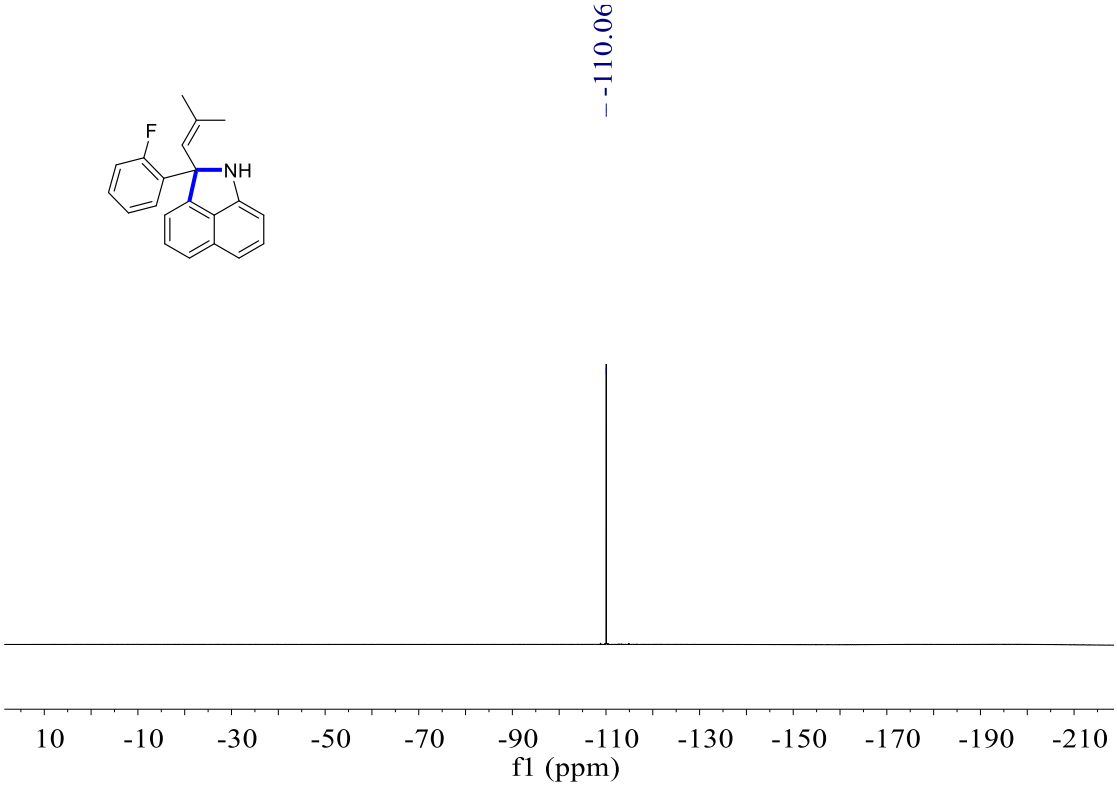
3aj, ^{1}H NMR, 400 MHz, $CDCl_3$



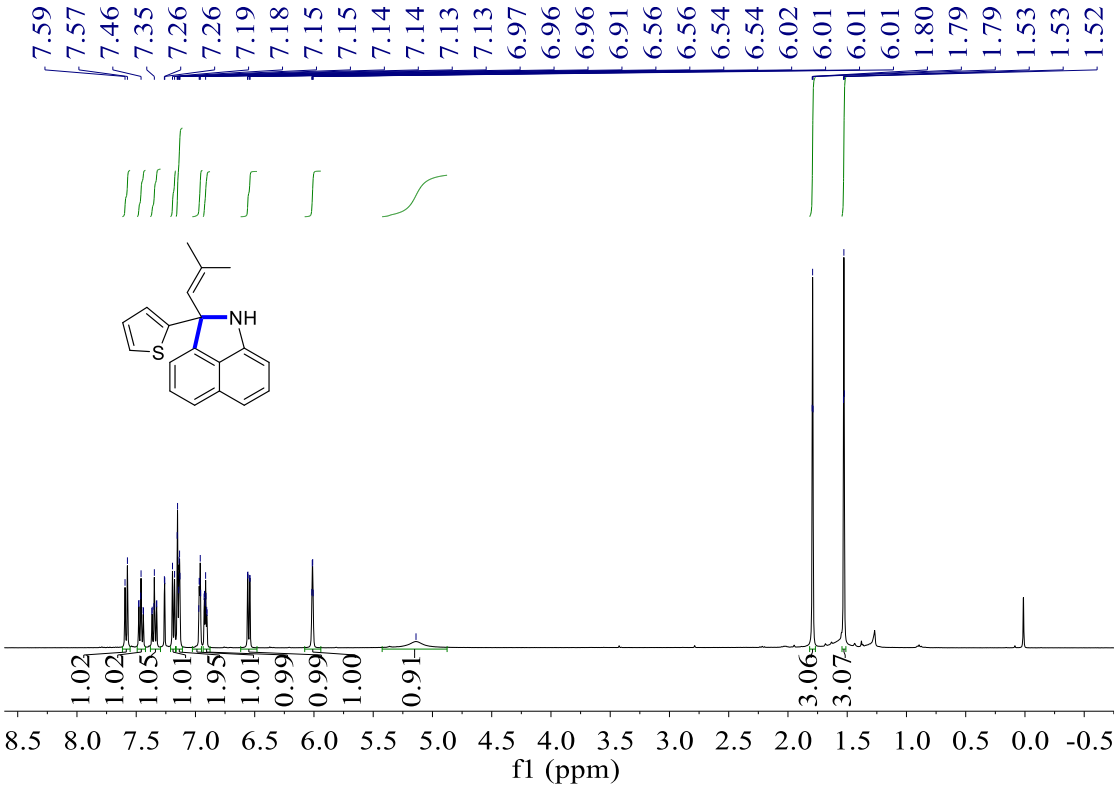
3aj, ^{13}C NMR, 101 MHz, $CDCl_3$



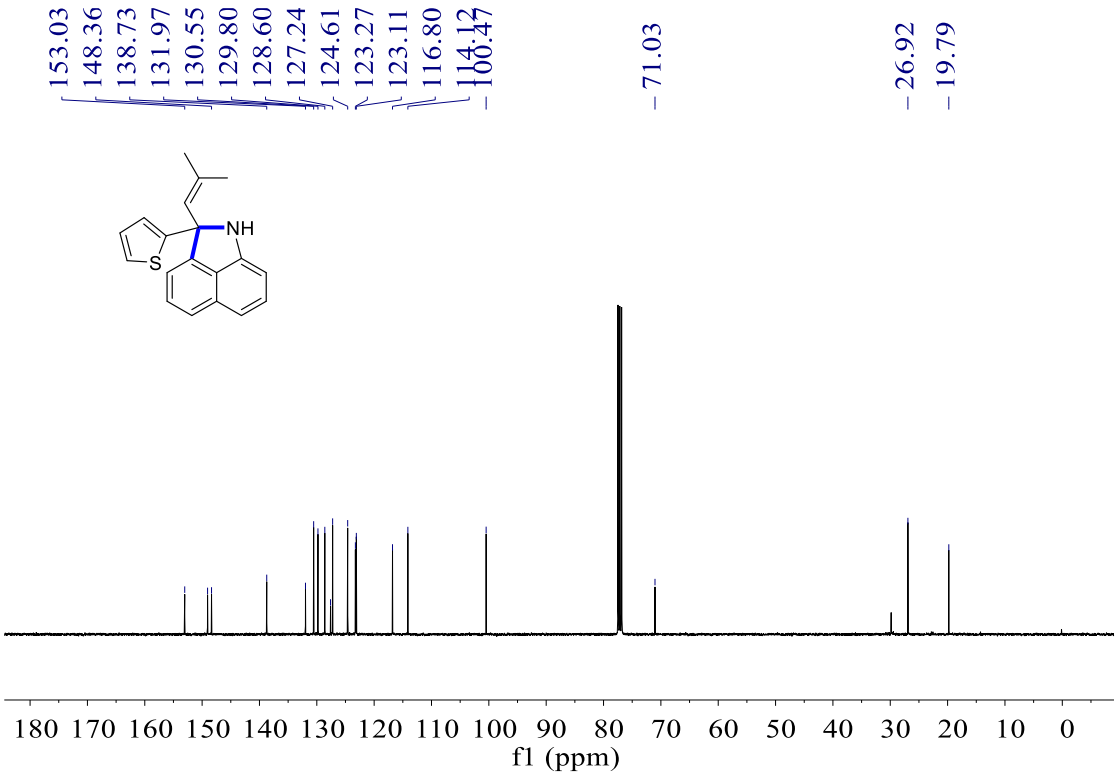
3aj, ^{19}F NMR, 376 MHz, $CDCl_3$



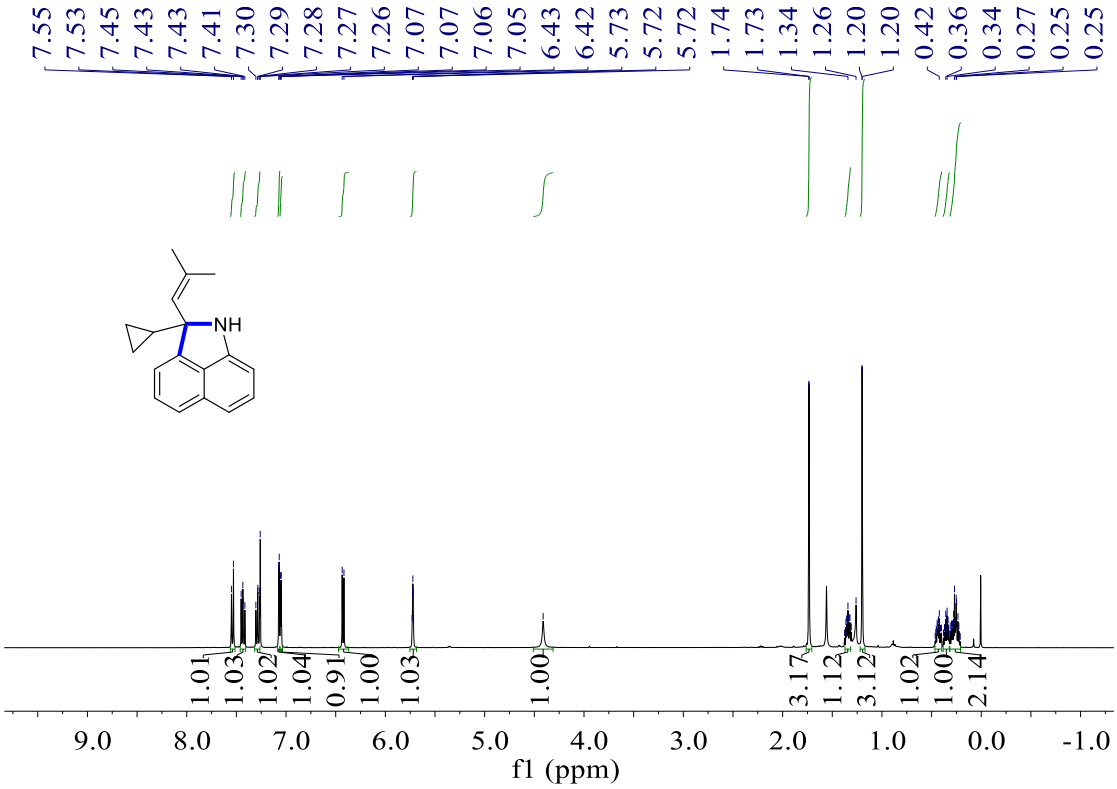
3ak, ^{1}H NMR, 400 MHz, $CDCl_3$



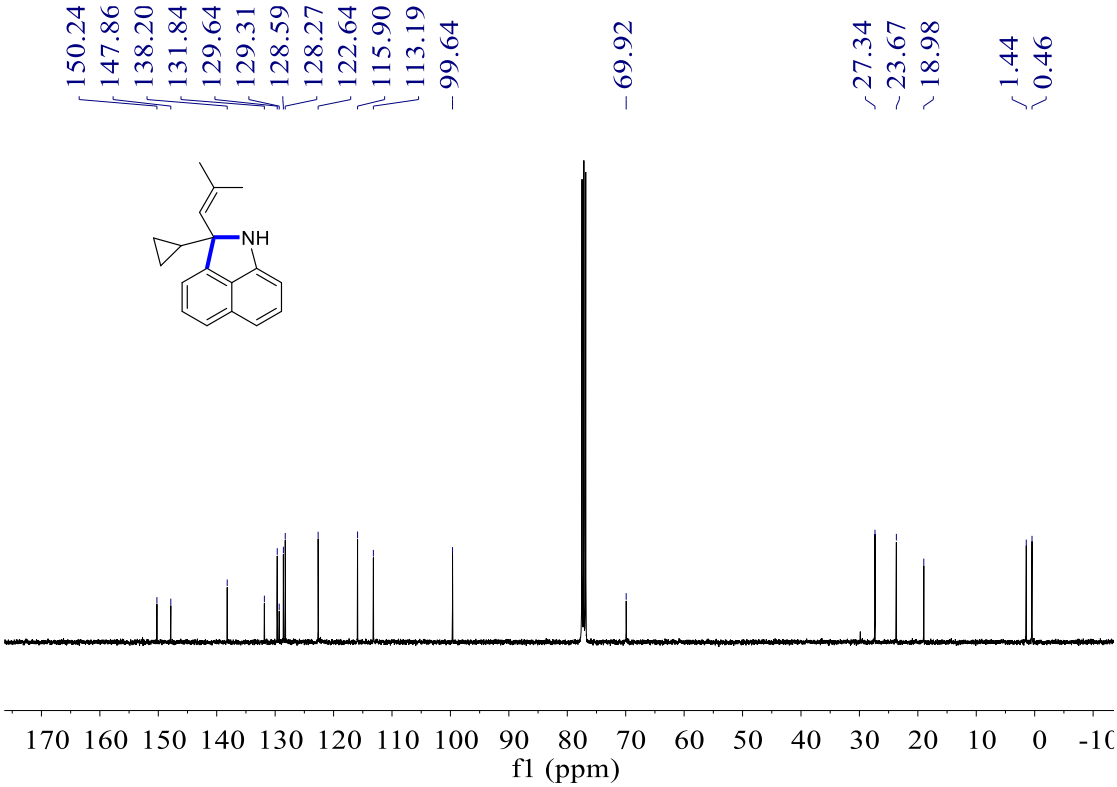
3ak, ^{13}C NMR, 101 MHz, $CDCl_3$



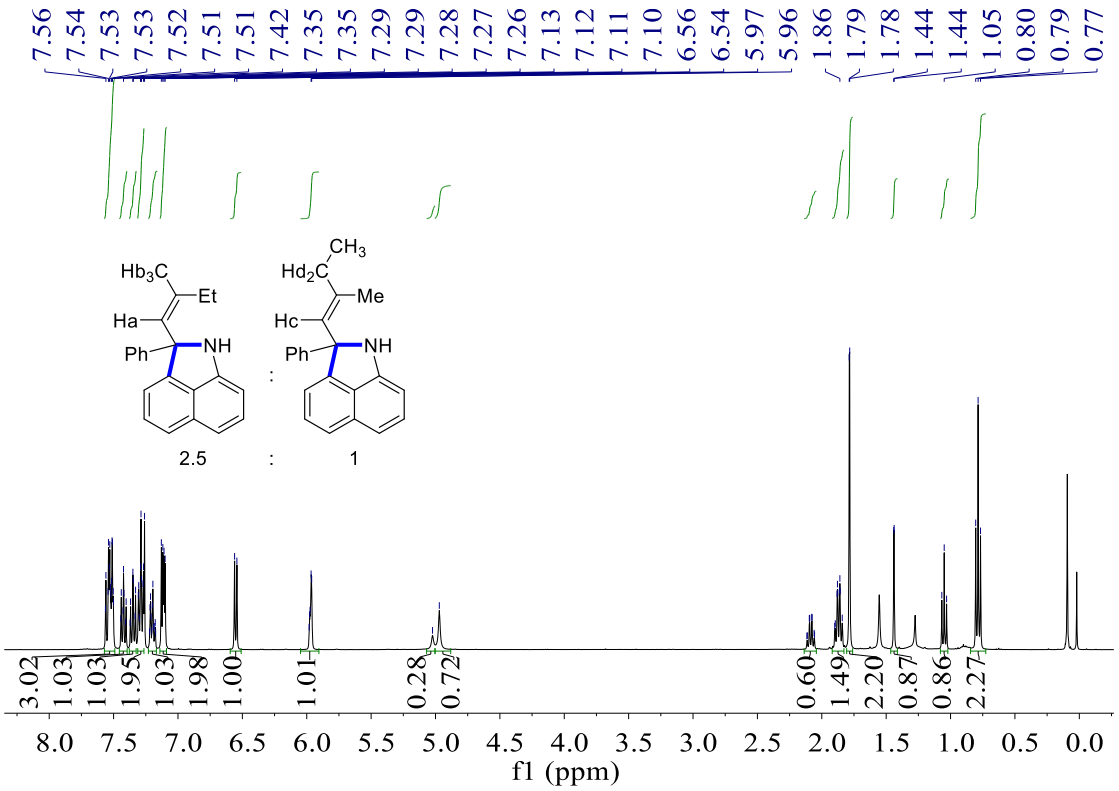
3al, ^{1}H NMR, 400 MHz, $CDCl_3$



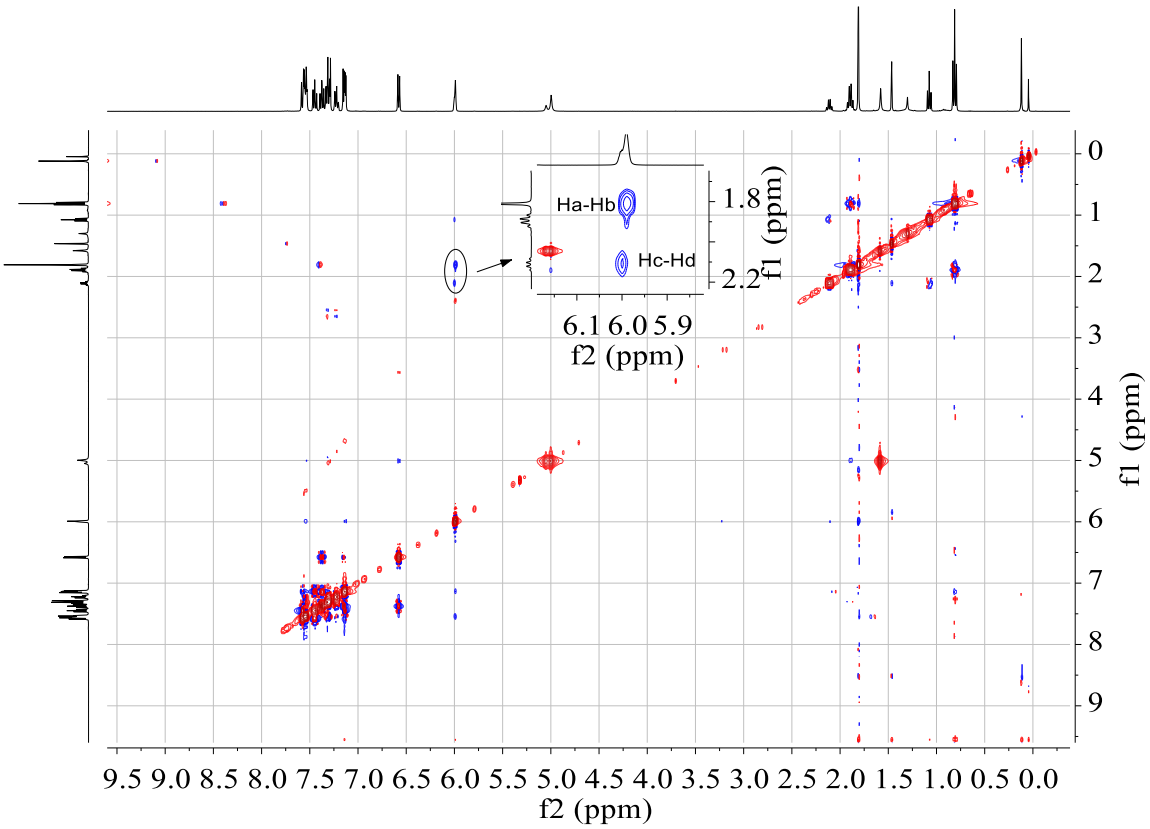
3al, ^{13}C NMR, 101 MHz, $CDCl_3$



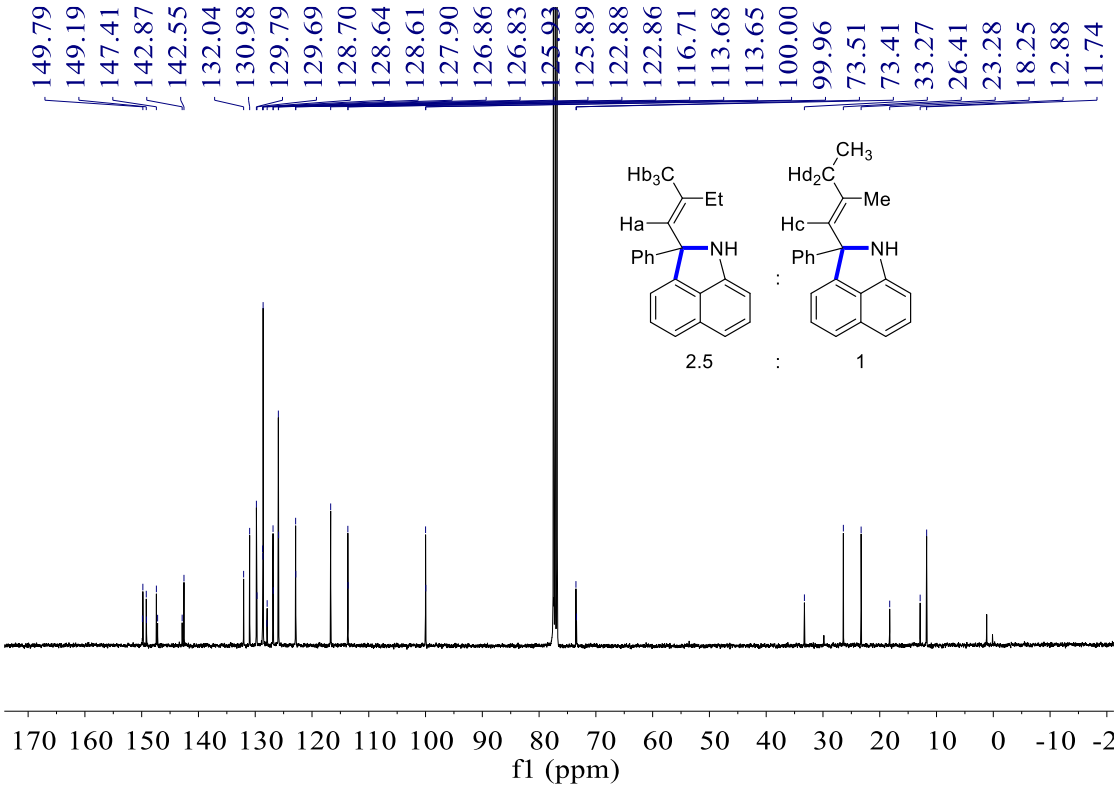
3am, ^{1}H NMR, 400 MHz, $CDCl_3$



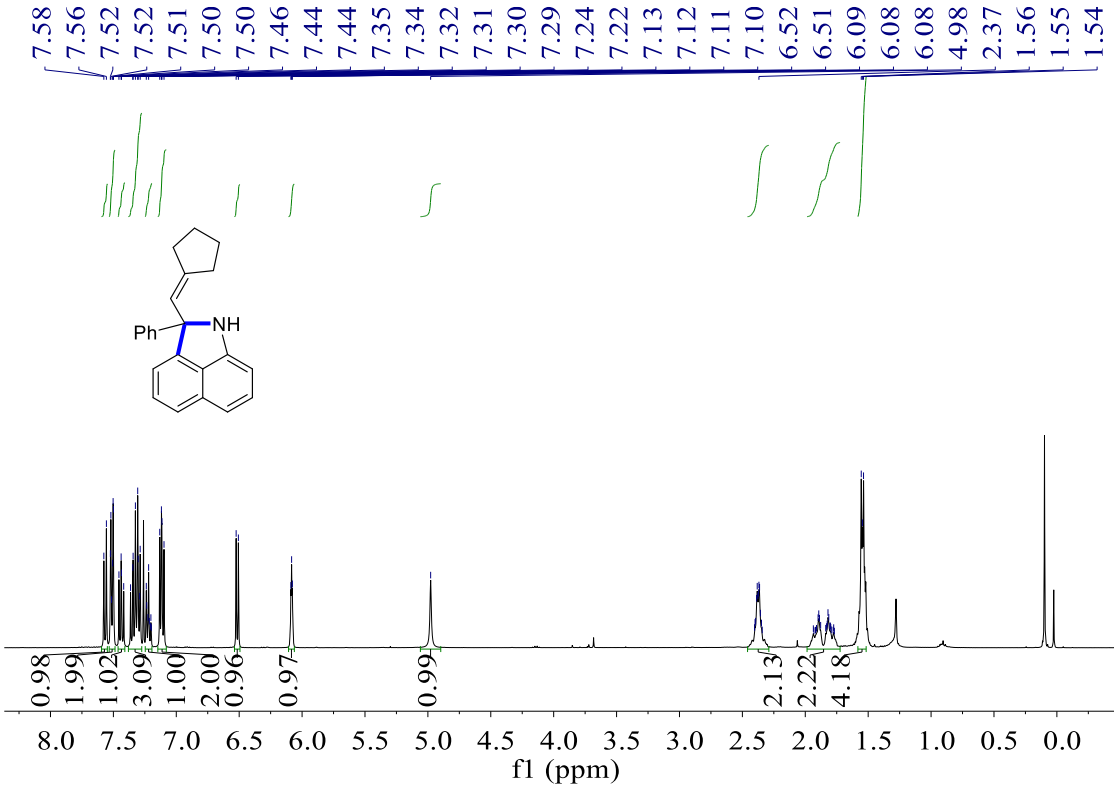
3am, NOESY



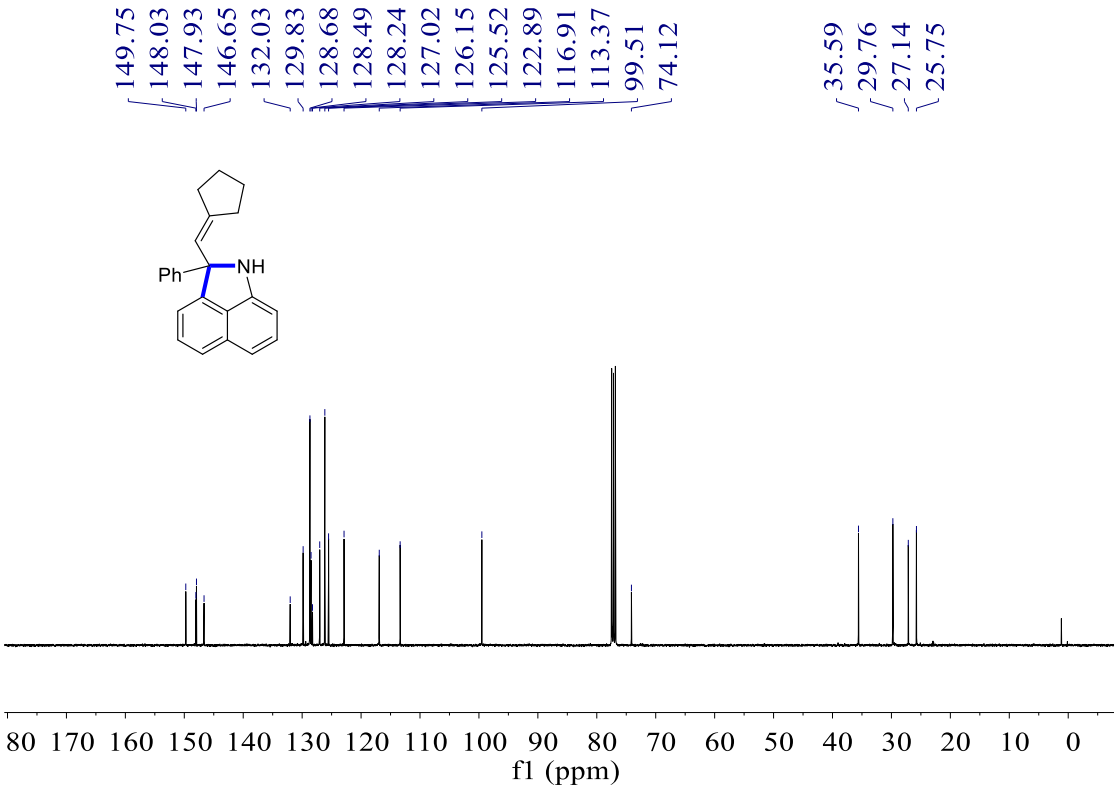
3am, ^{13}C NMR, 101 MHz, $CDCl_3$



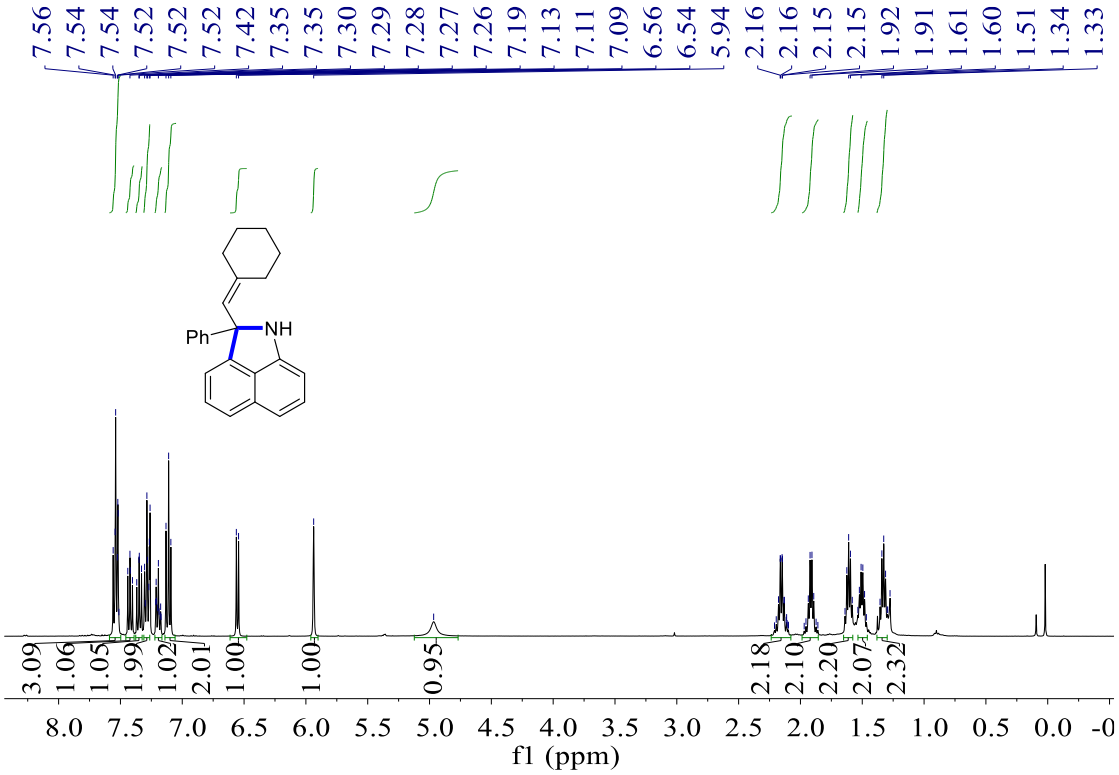
3an, ^{1}H NMR, 400 MHz, $CDCl_3$



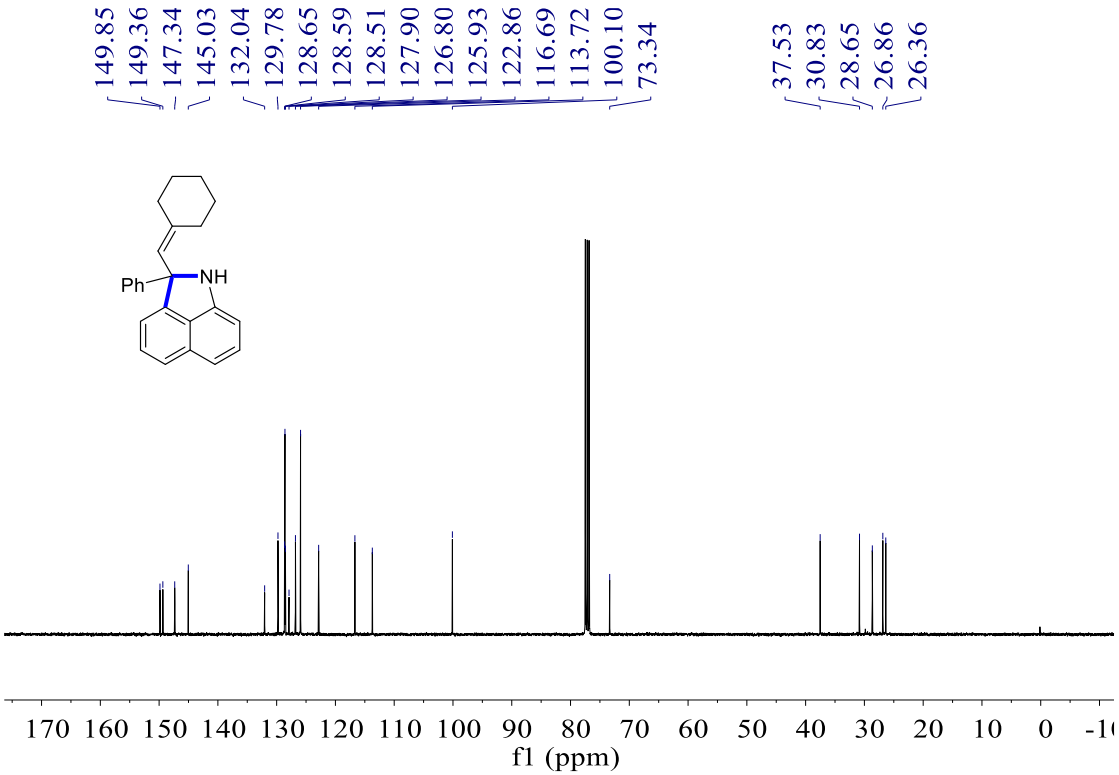
3an, ^{13}C NMR, 101 MHz, $CDCl_3$



3ao, ^{1}H NMR, 400 MHz, $CDCl_3$



3ao, ^{13}C NMR, 101 MHz, $CDCl_3$



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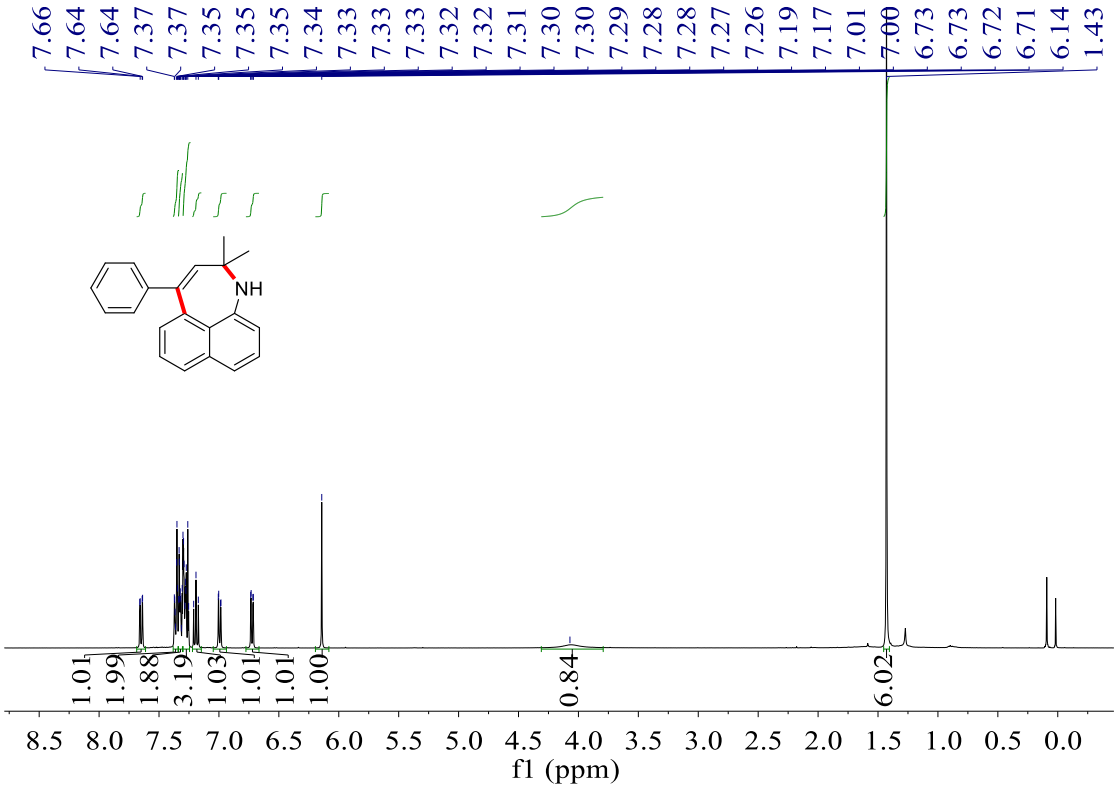
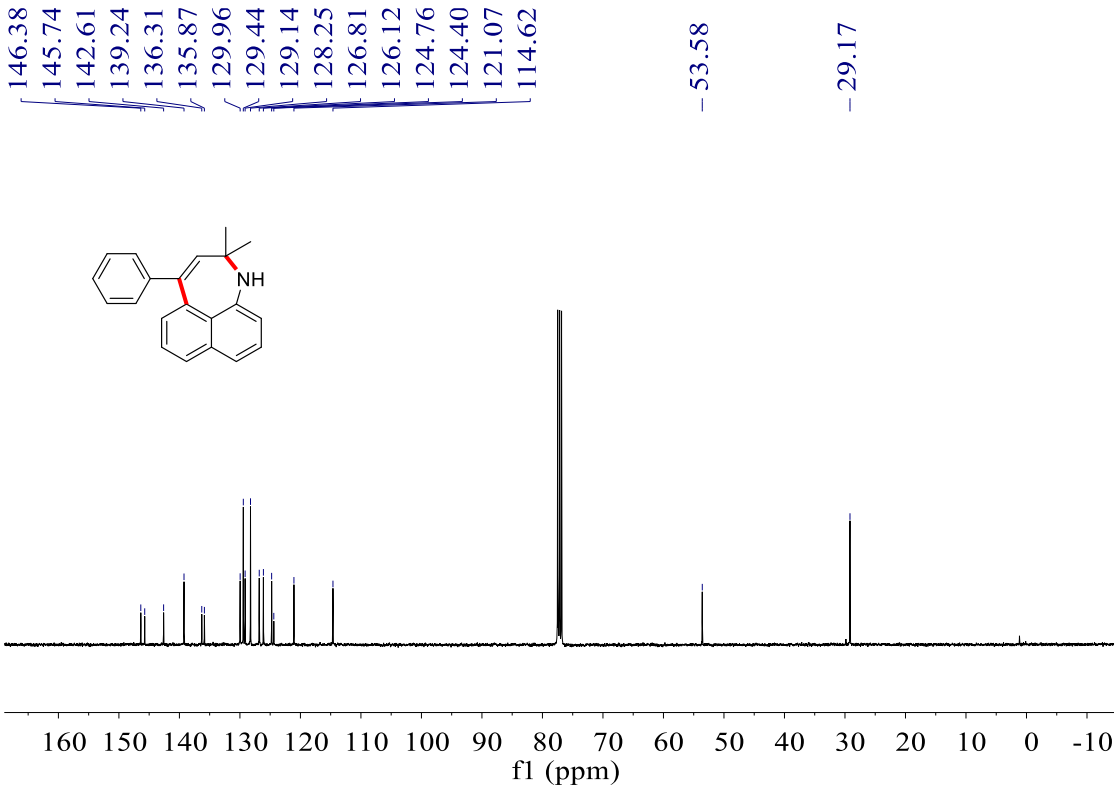
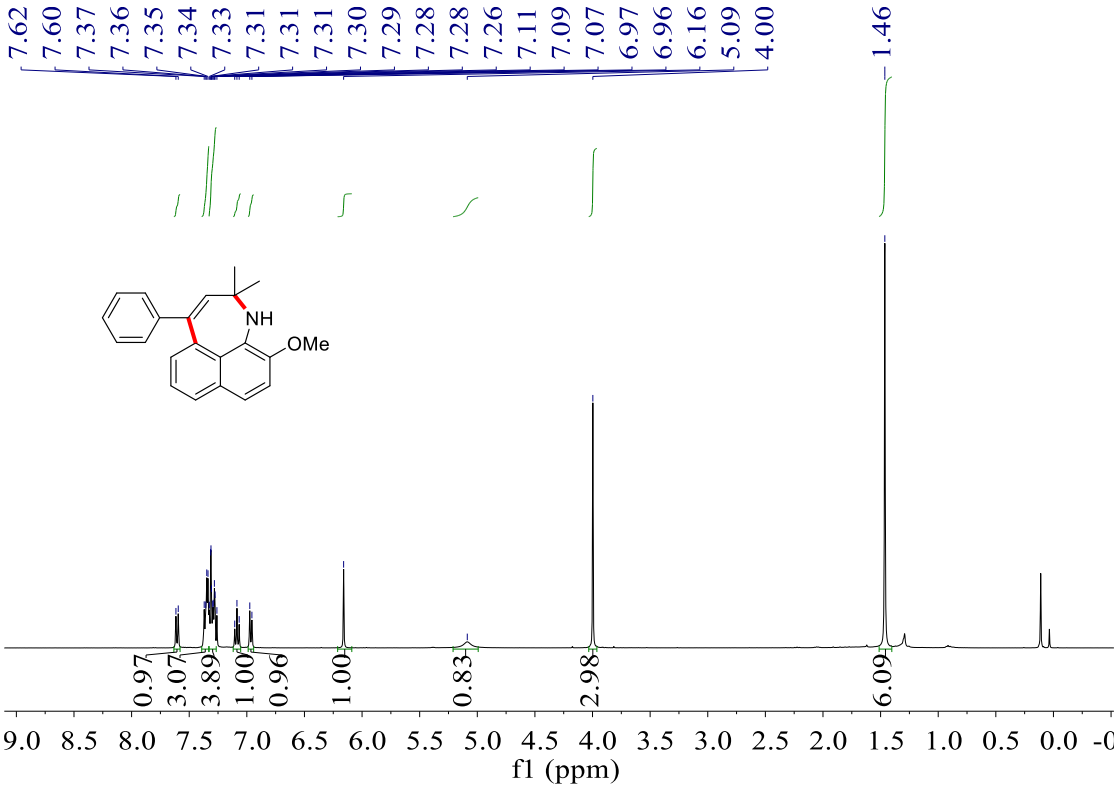


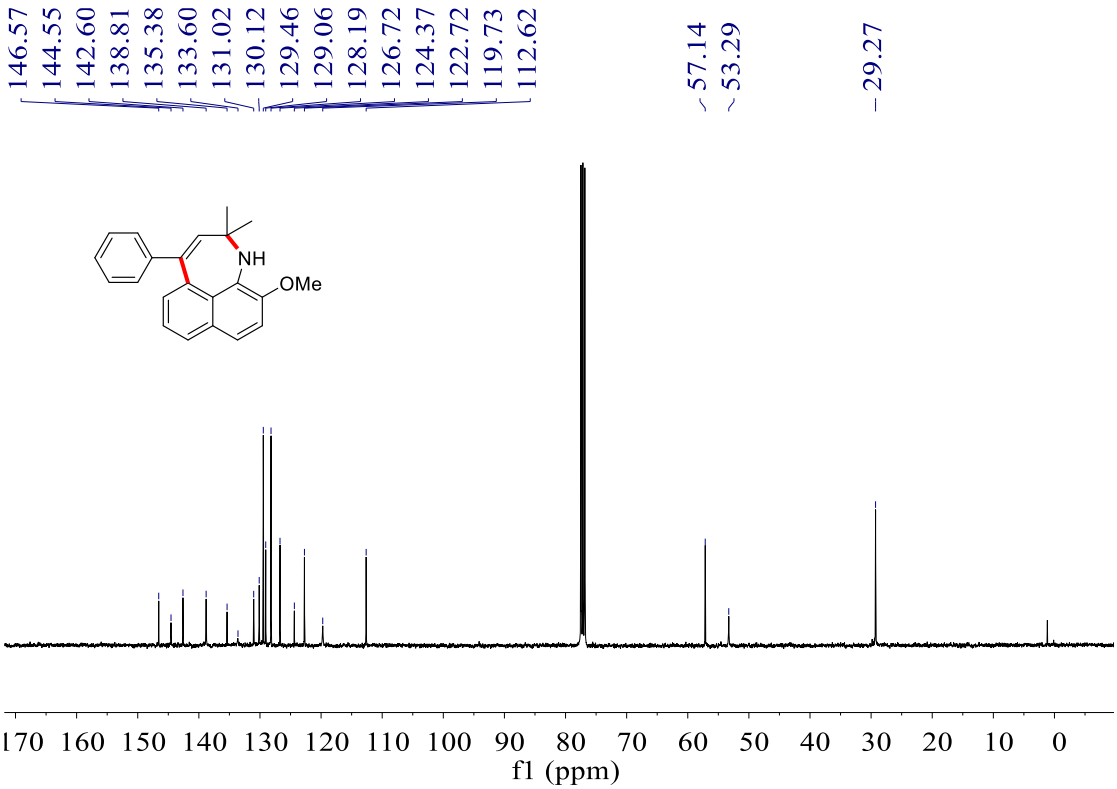
4aa, ^{13}C NMR, 101 MHz, $CDCl_3$



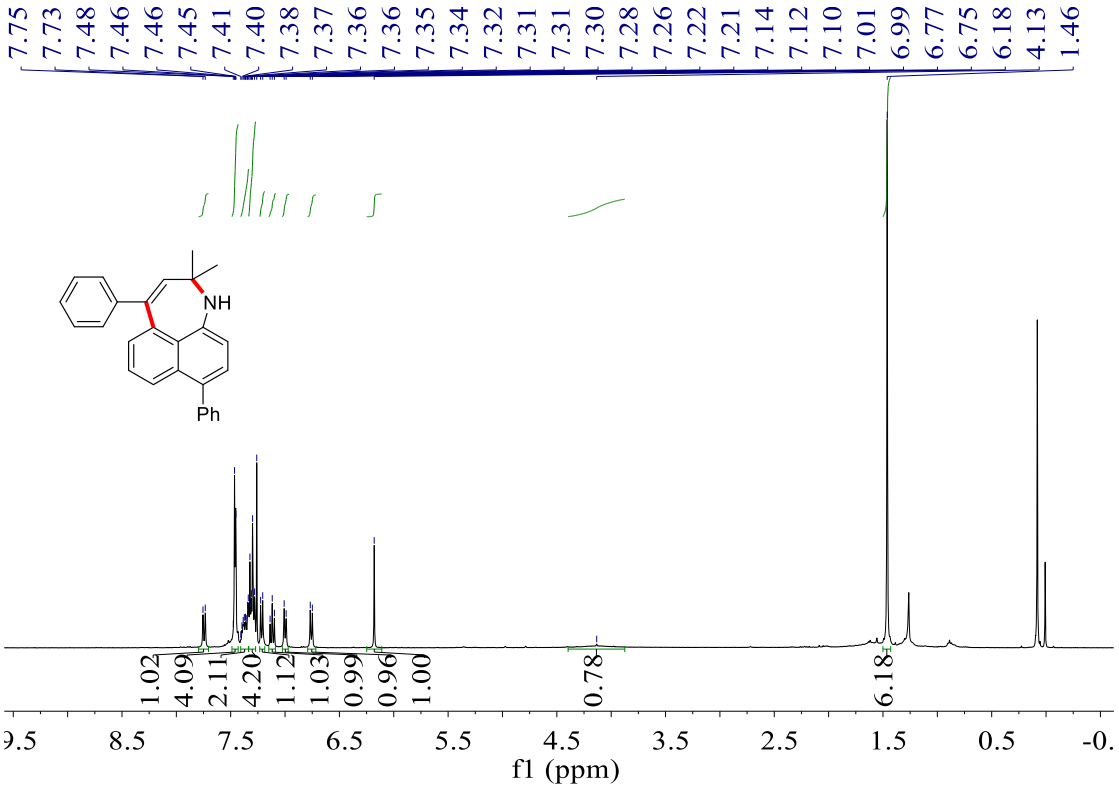
4ba, ^{1}H NMR, 400 MHz, $CDCl_3$



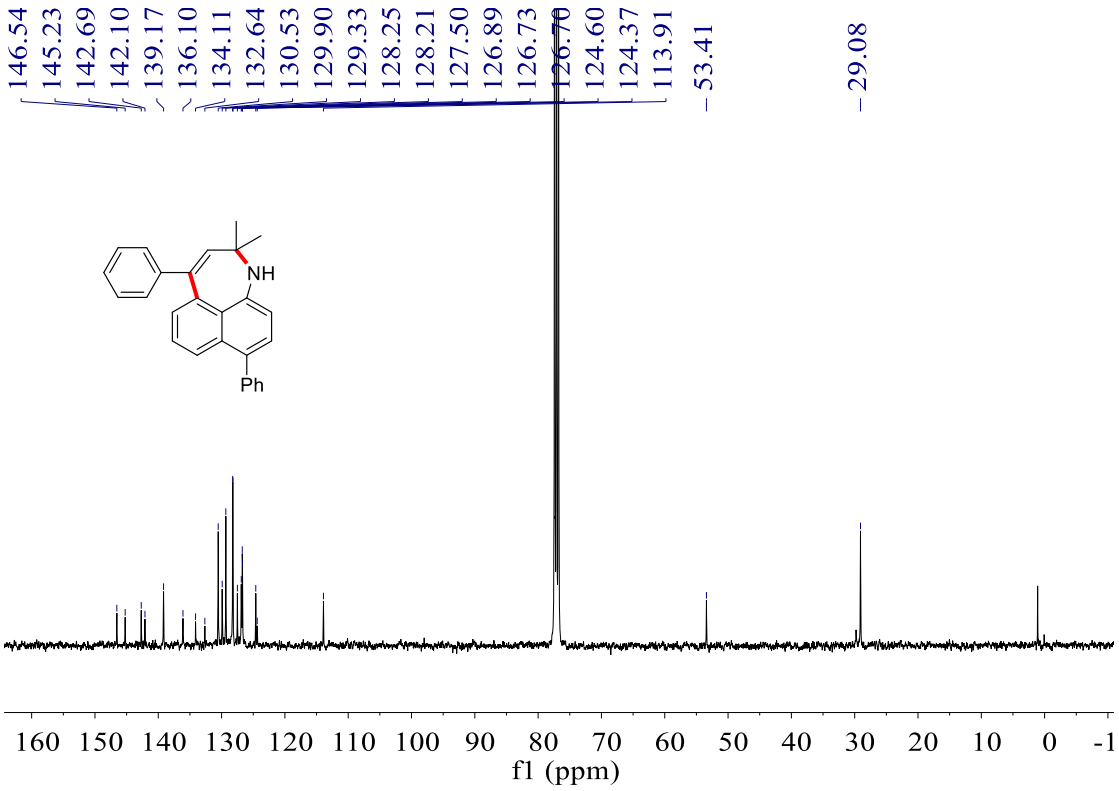
4ba, ^{13}C NMR, 101 MHz, $CDCl_3$



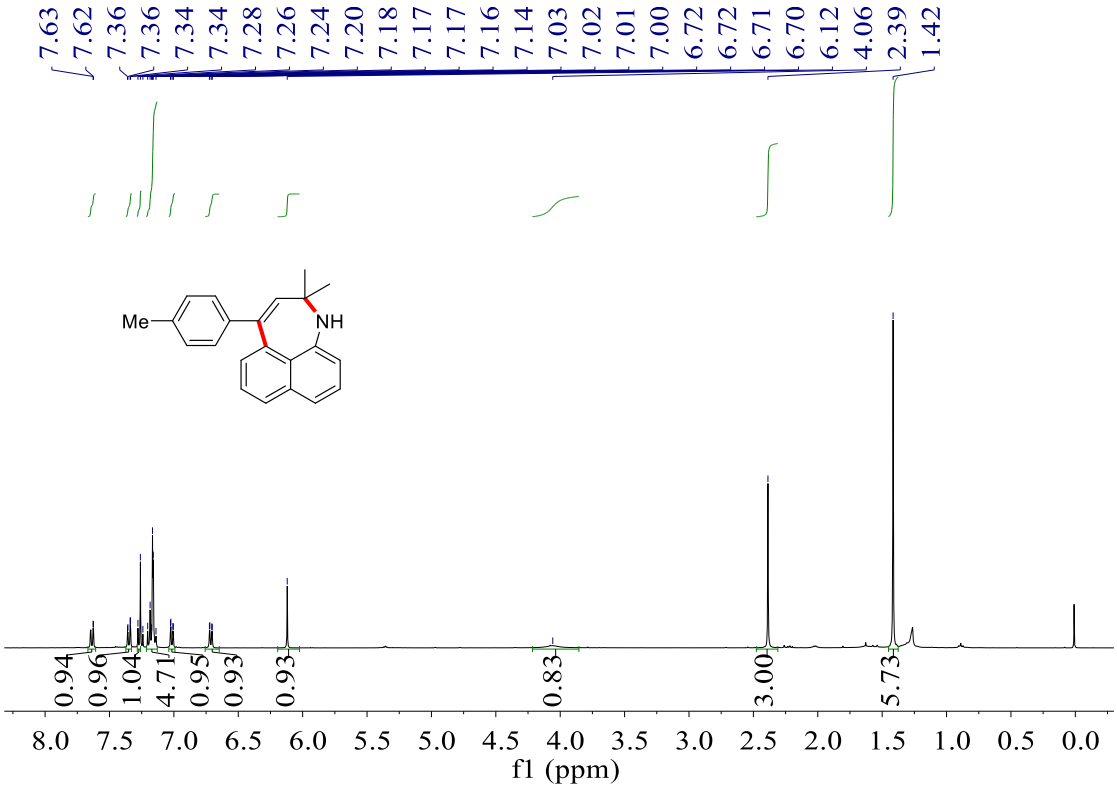
4ca, ^{1}H NMR, 400 MHz, $CDCl_3$



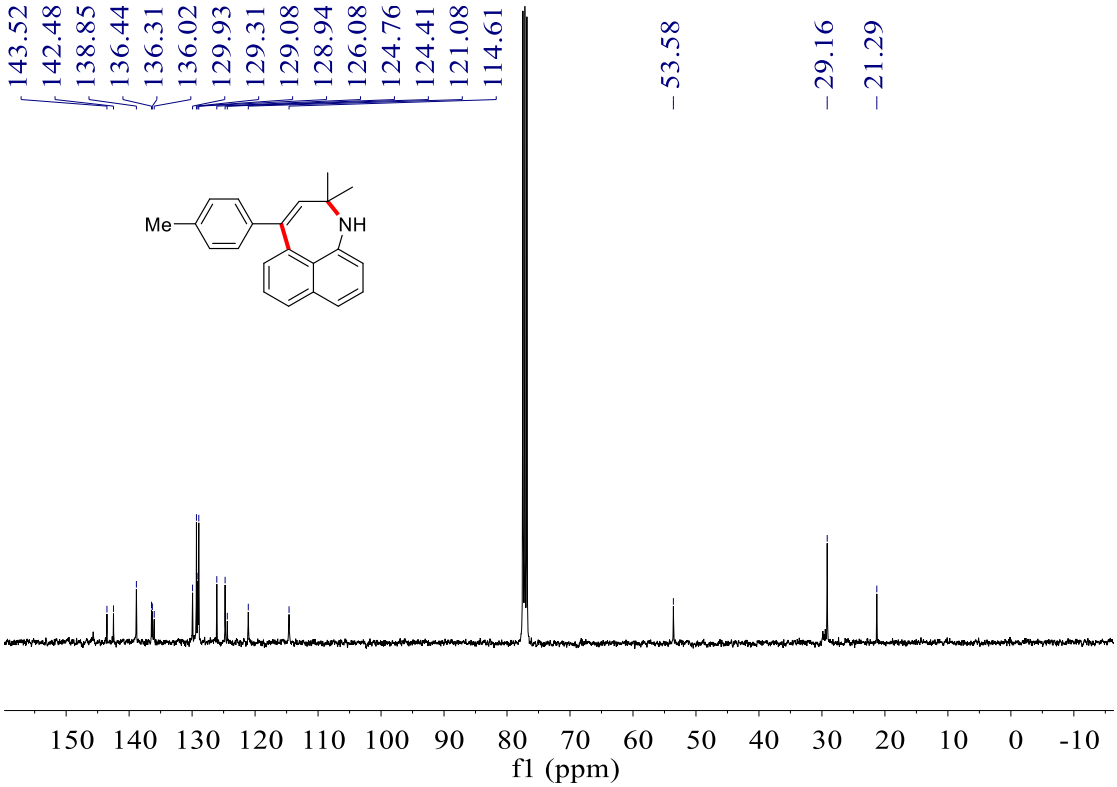
4ca, ^{13}C NMR, 101 MHz, $CDCl_3$



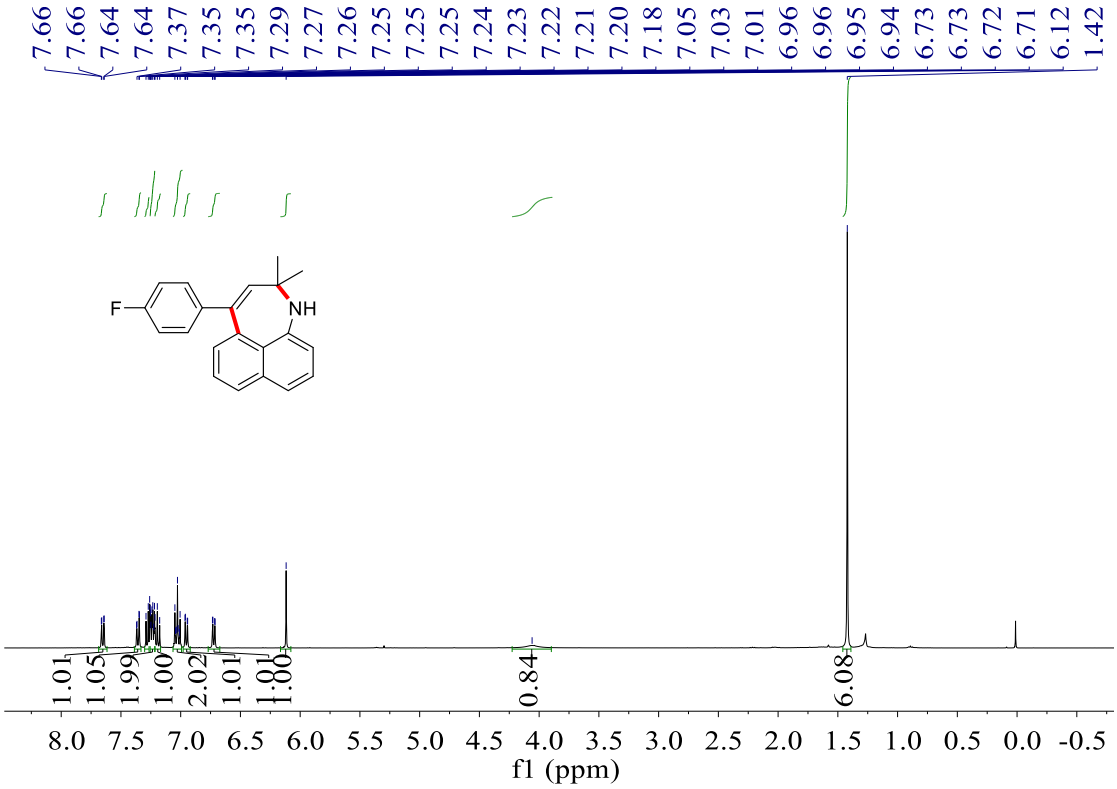
4ab, ^{1}H NMR, 400 MHz, $CDCl_3$



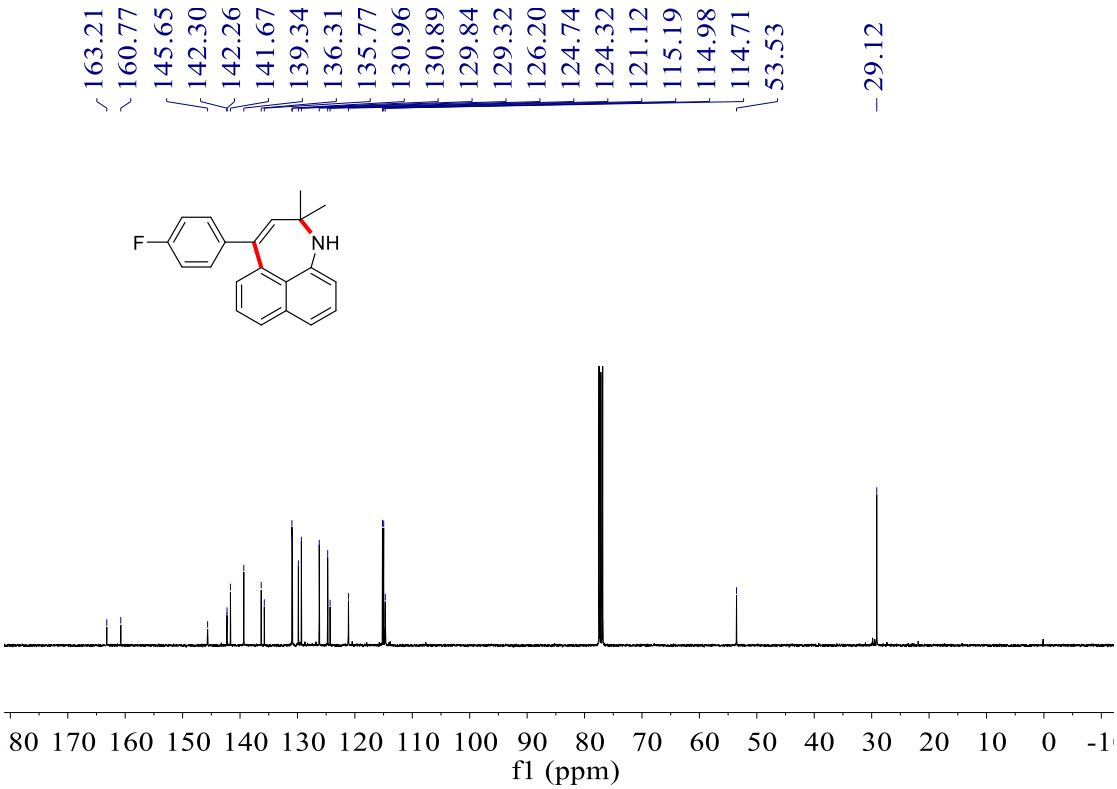
4ab, ^{13}C NMR, 101 MHz, $CDCl_3$



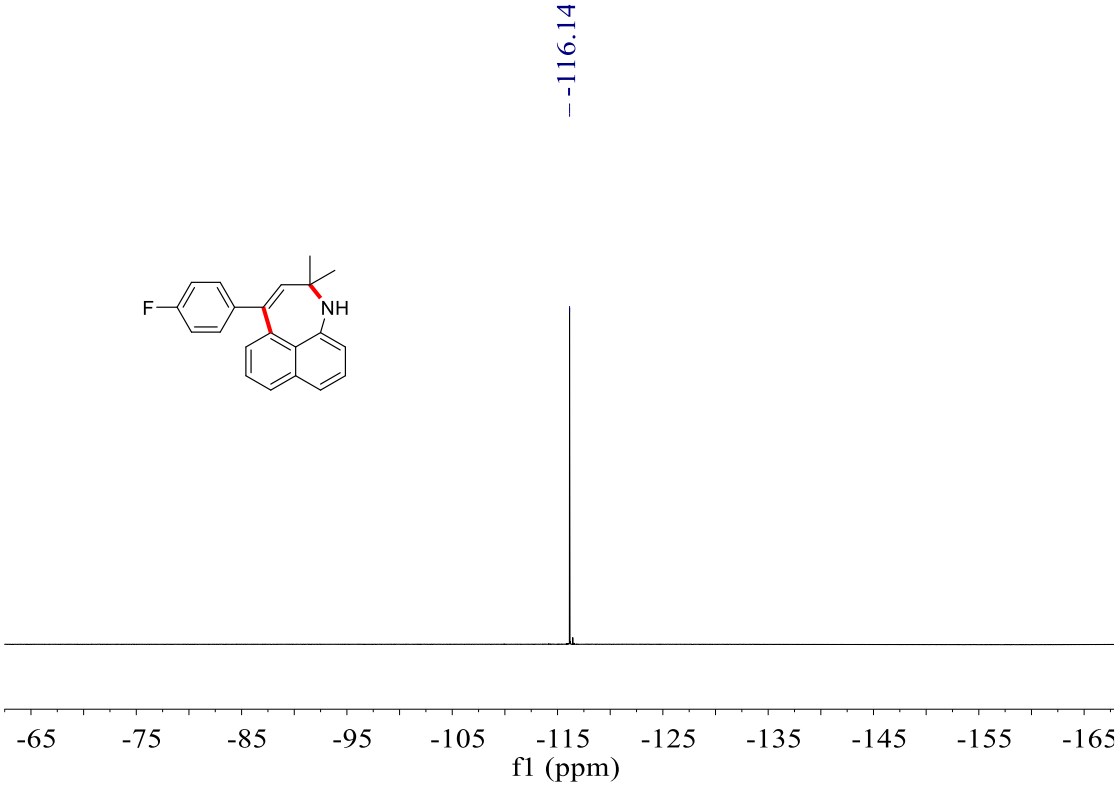
4ac, ^{1}H NMR, 400 MHz, $CDCl_3$



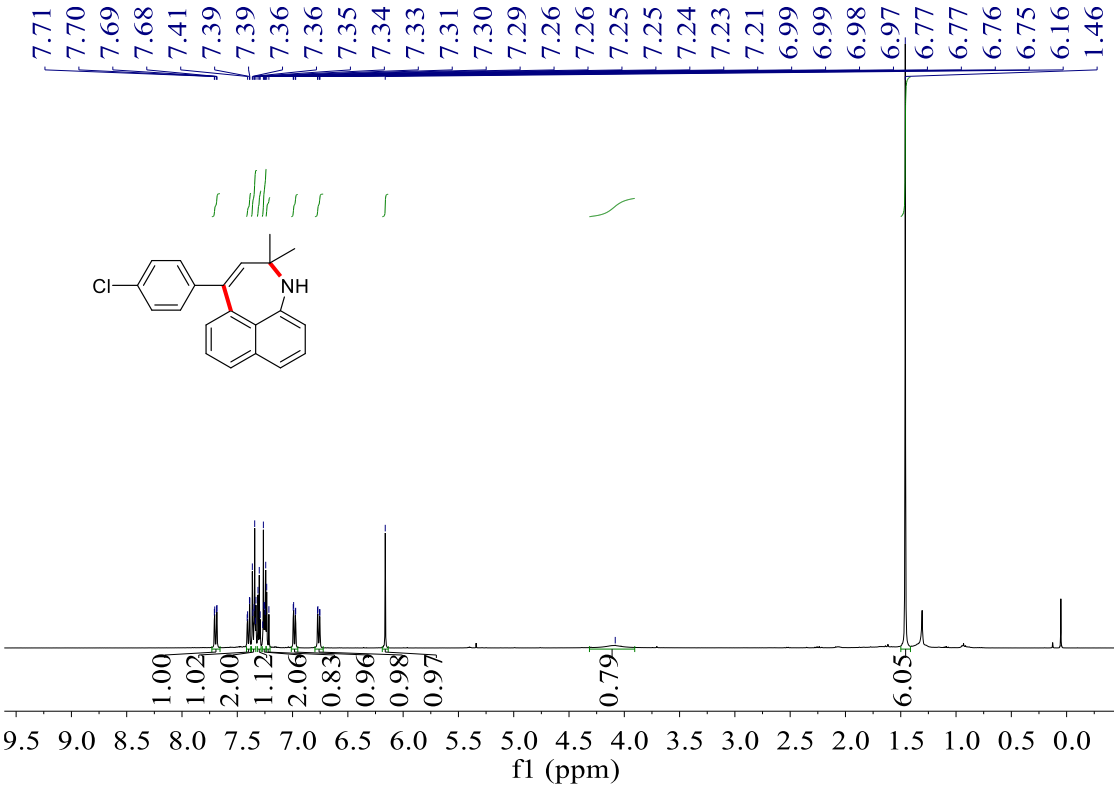
4ac, ^{13}C NMR, 101 MHz, $CDCl_3$



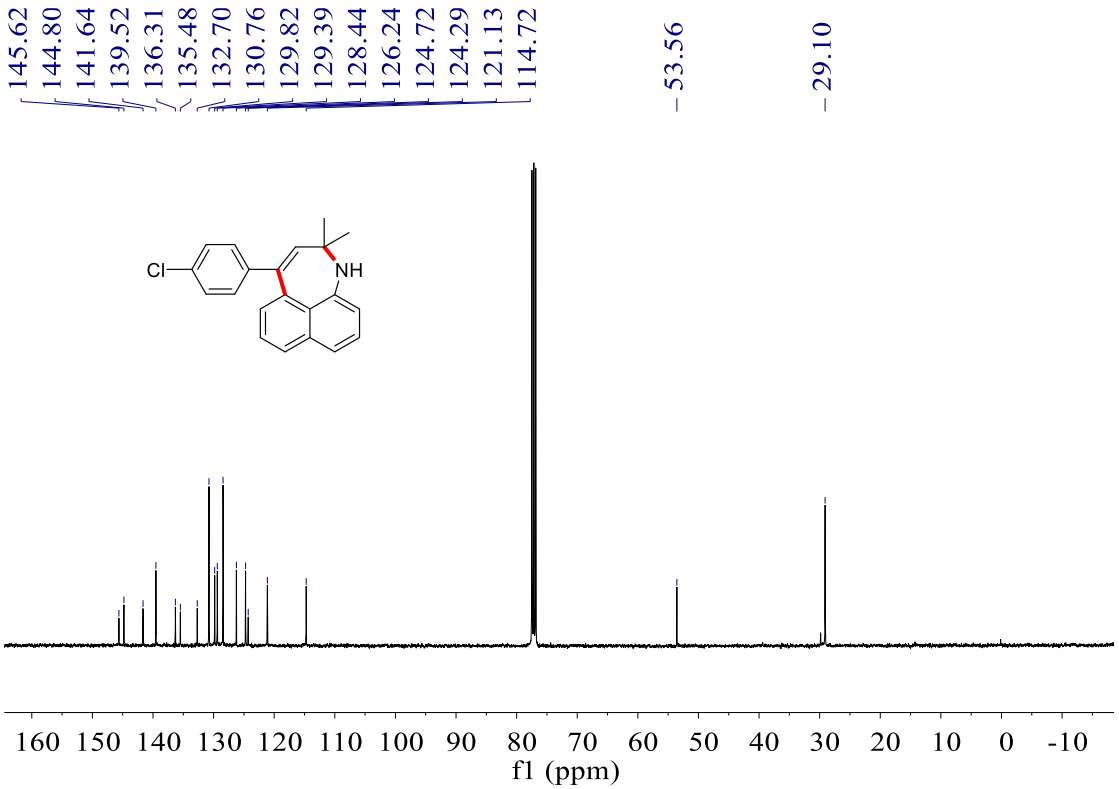
4ac, ^{19}F NMR, 376 MHz, $CDCl_3$



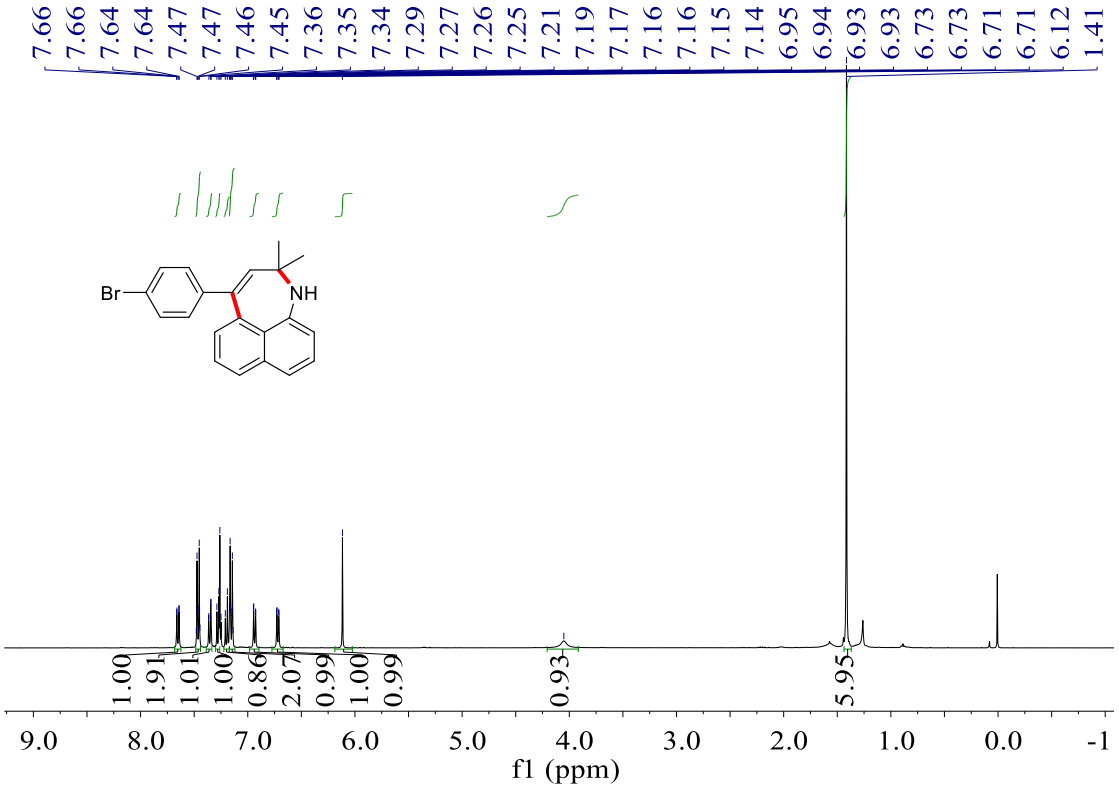
4ad, ^{1}H NMR, 400 MHz, $CDCl_3$



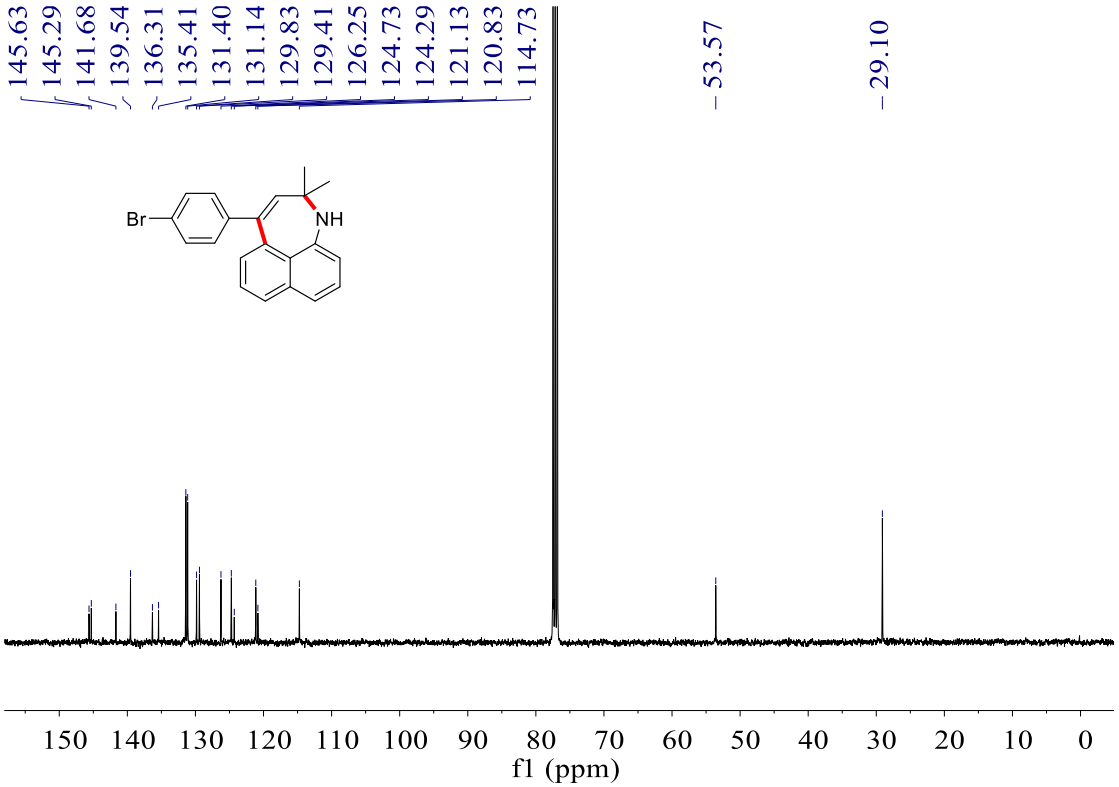
4ad, ^{13}C NMR, 101 MHz, $CDCl_3$



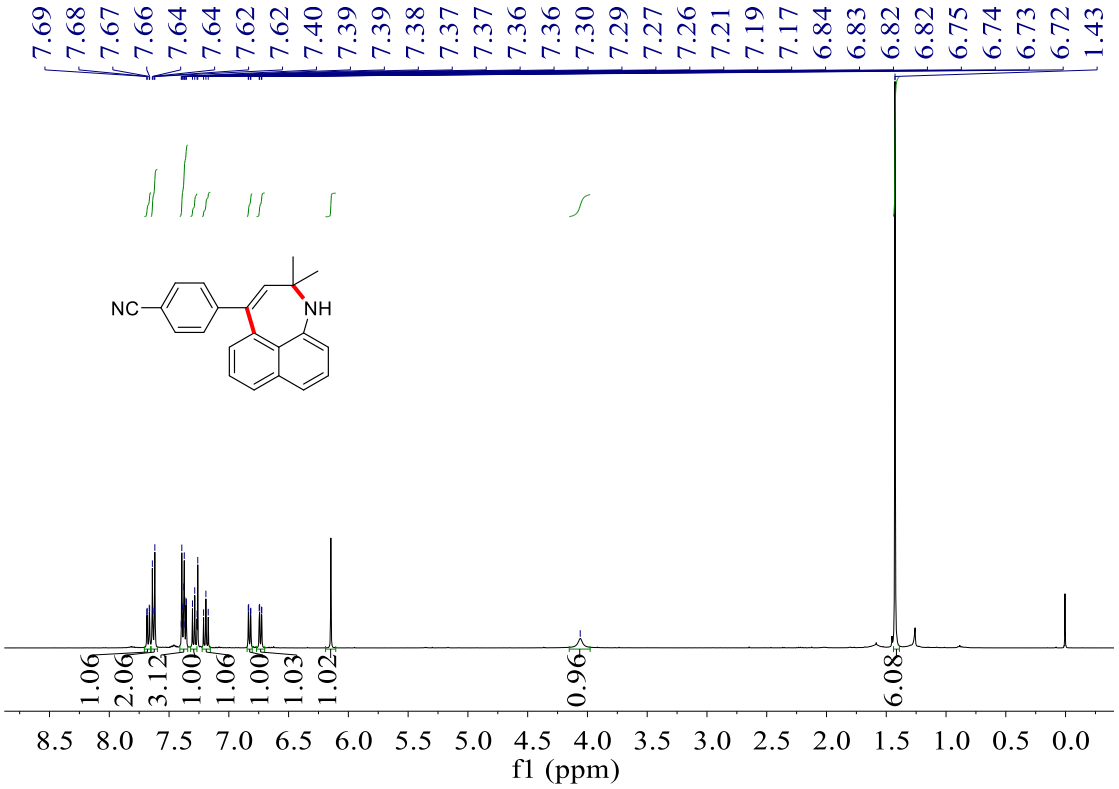
4ae, ^{1}H NMR, 400 MHz, $CDCl_3$



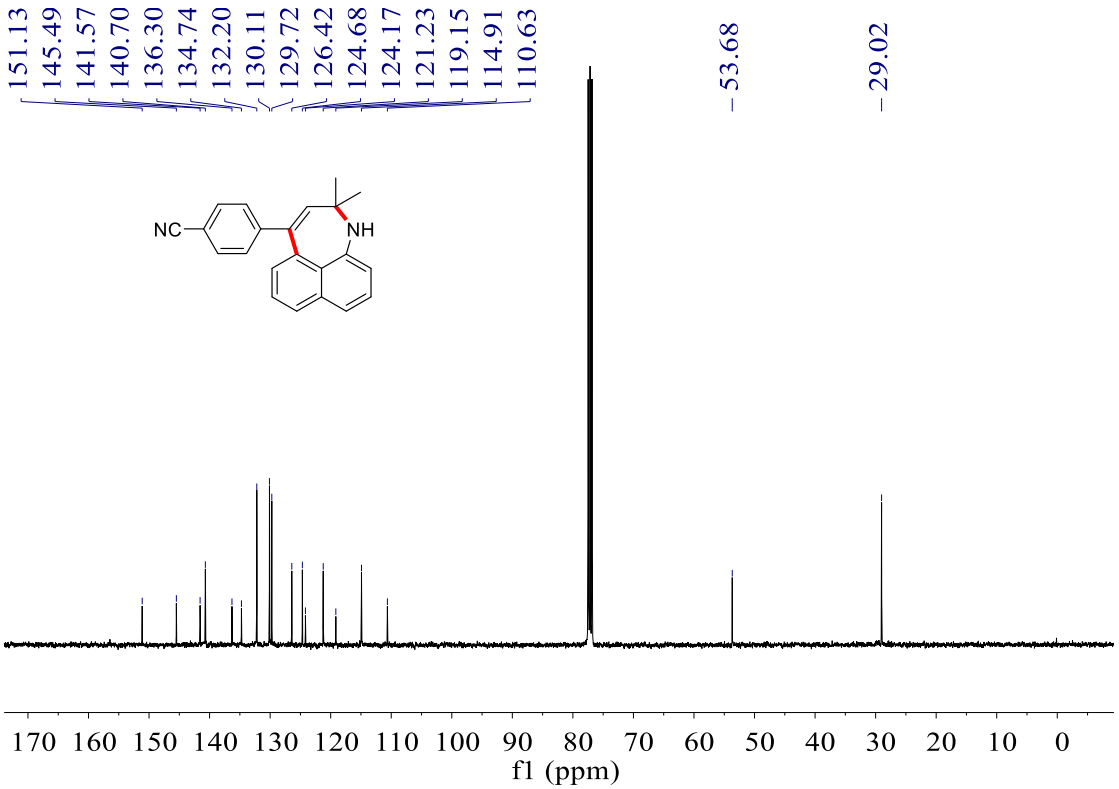
4ae, ^{13}C NMR, 101 MHz, $CDCl_3$



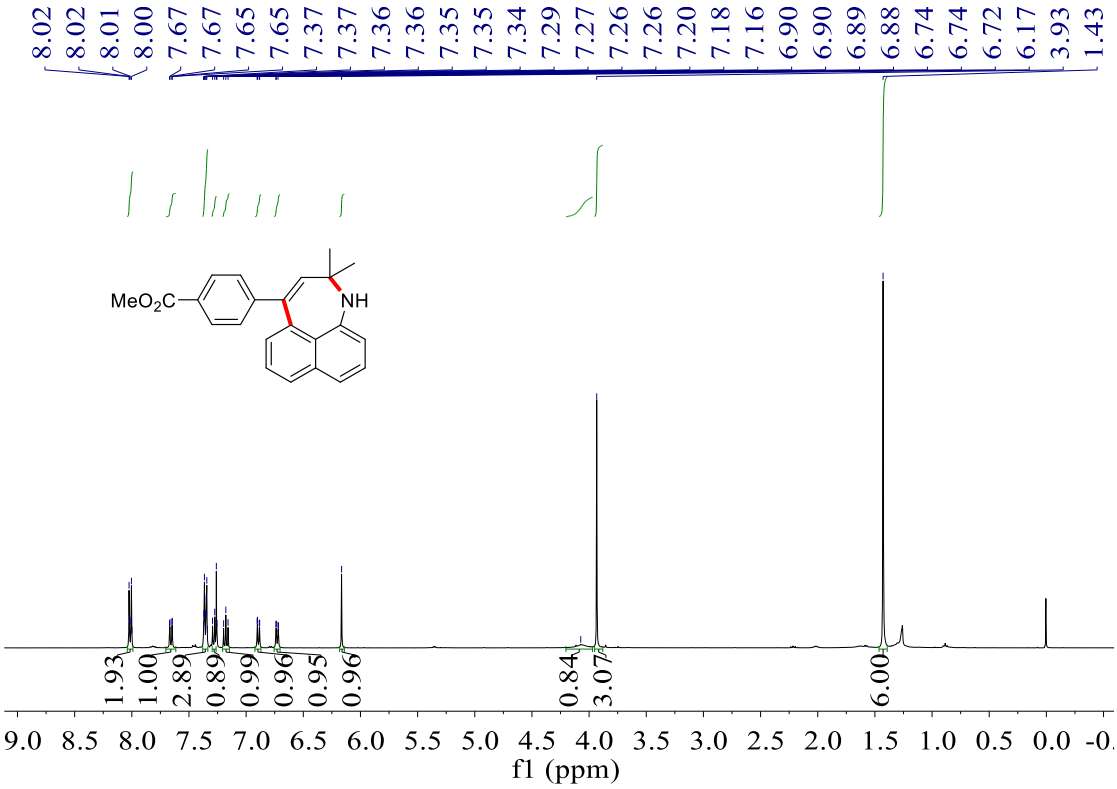
4af, ^{1}H NMR, 400 MHz, $CDCl_3$



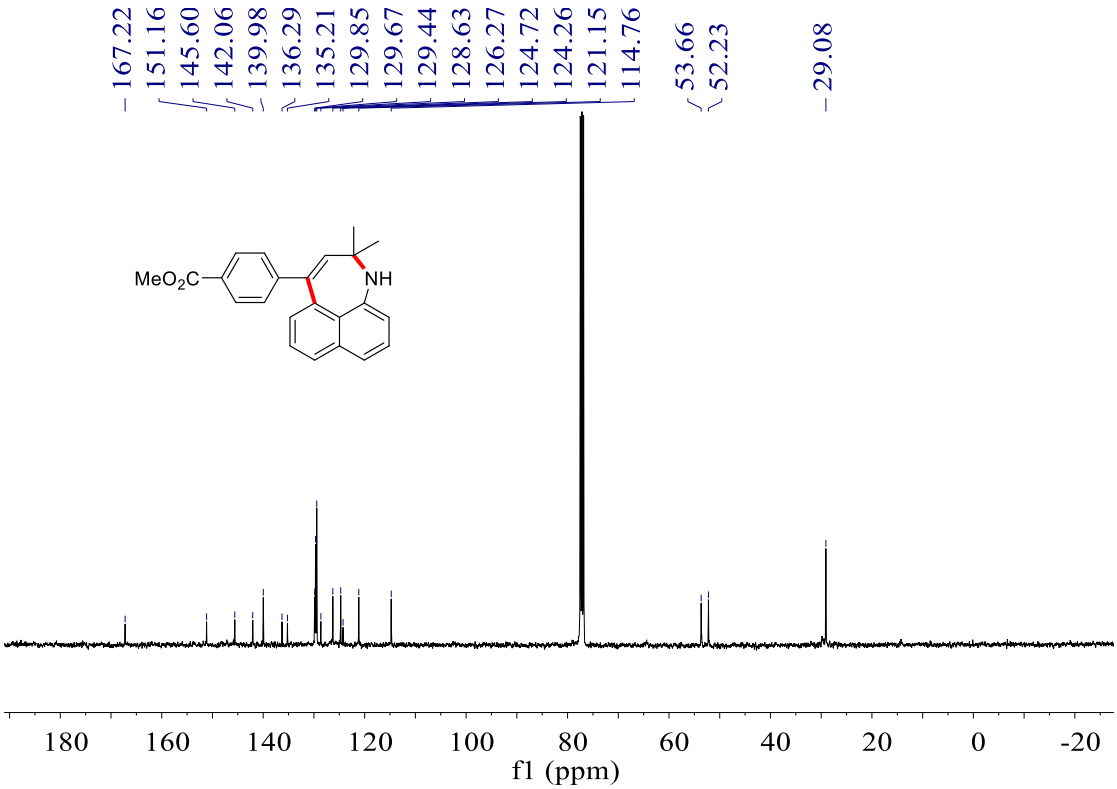
4af, ^{13}C NMR, 101 MHz, $CDCl_3$



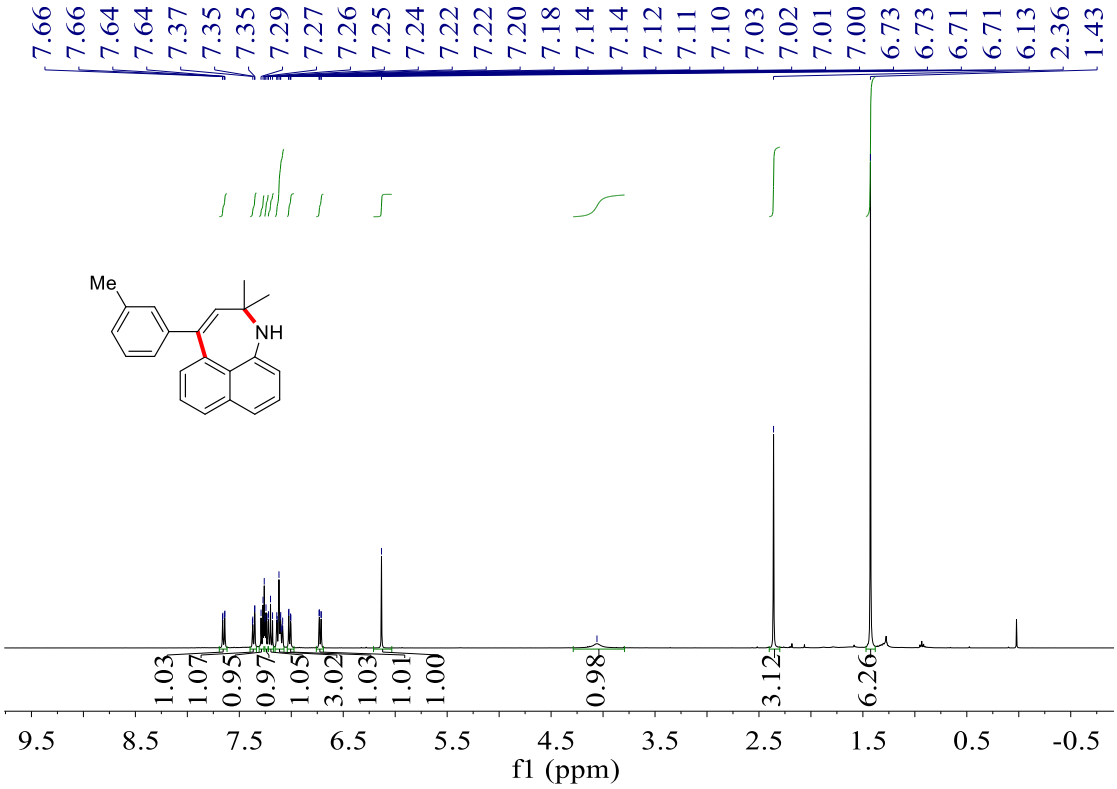
4ag, ^{1}H NMR, 400 MHz, $CDCl_3$



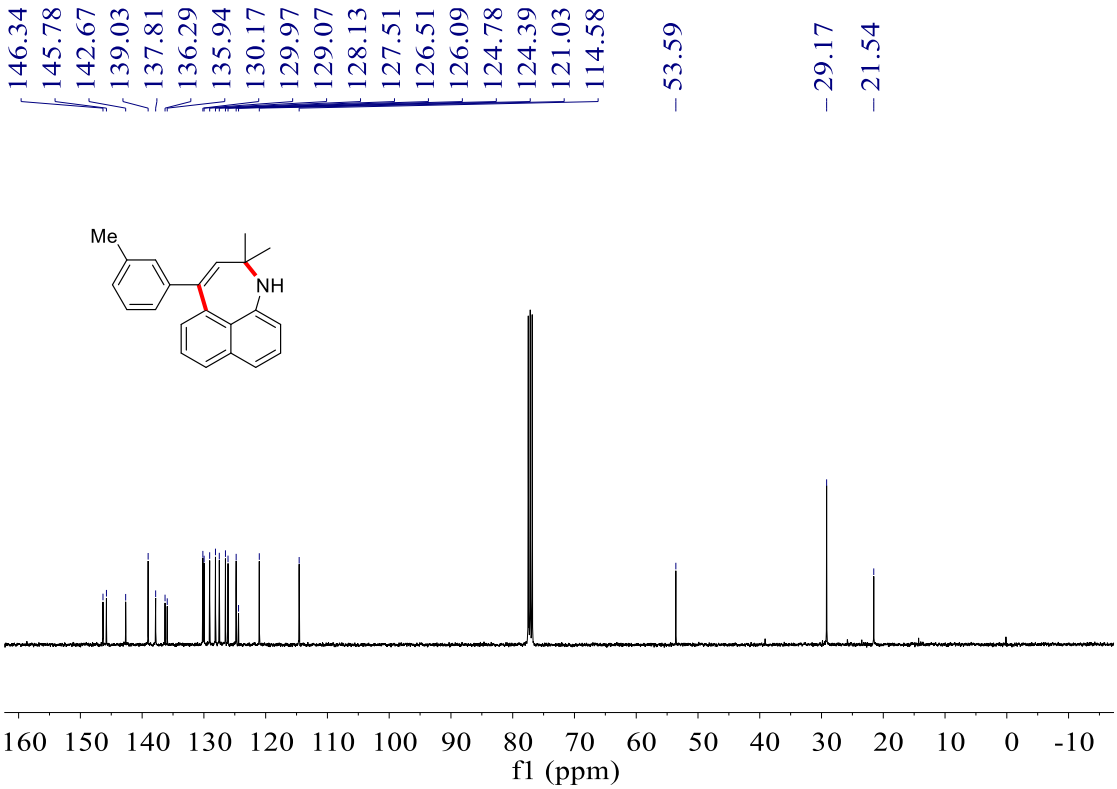
4ag, ^{13}C NMR, 101 MHz, $CDCl_3$



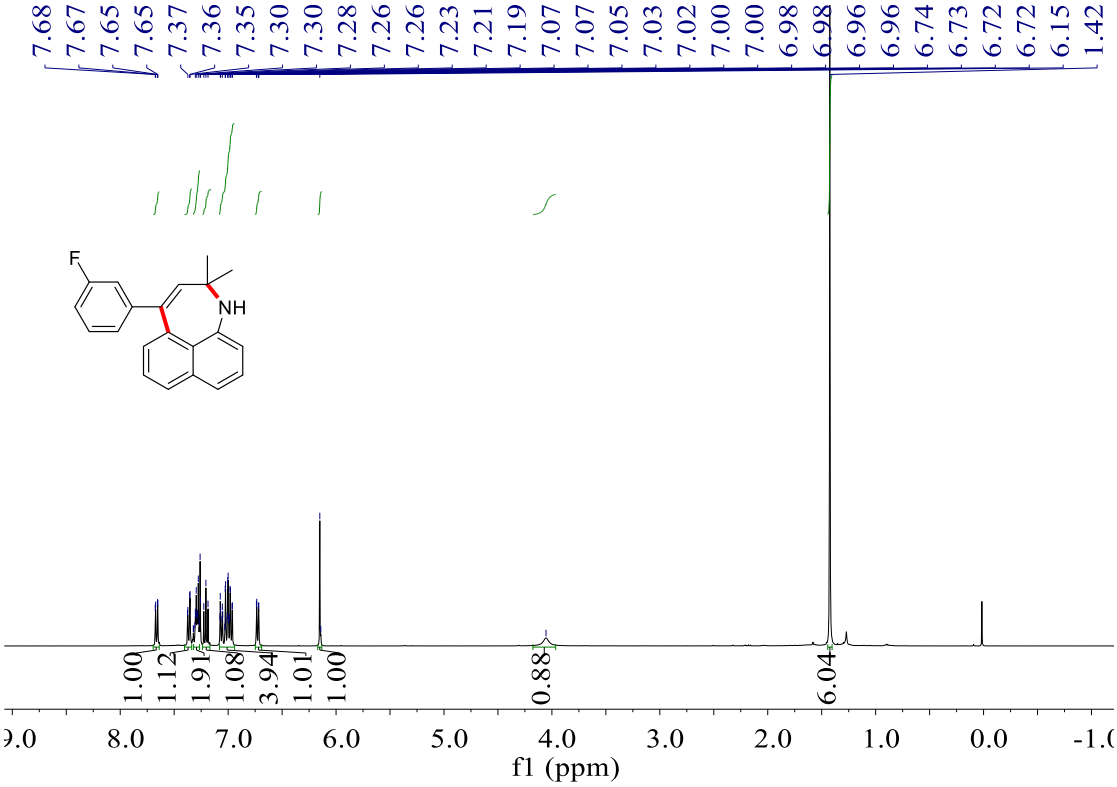
4ah, ^{1}H NMR, 400 MHz, $CDCl_3$



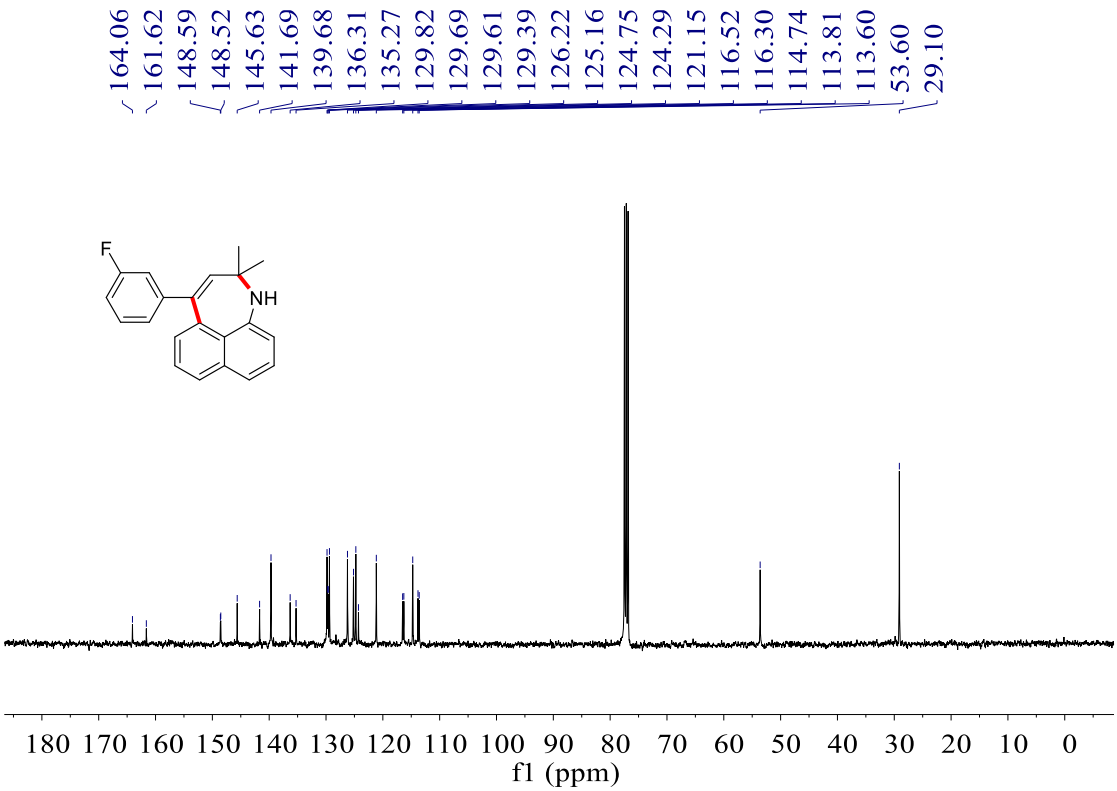
4ah, ^{13}C NMR, 101 MHz, $CDCl_3$



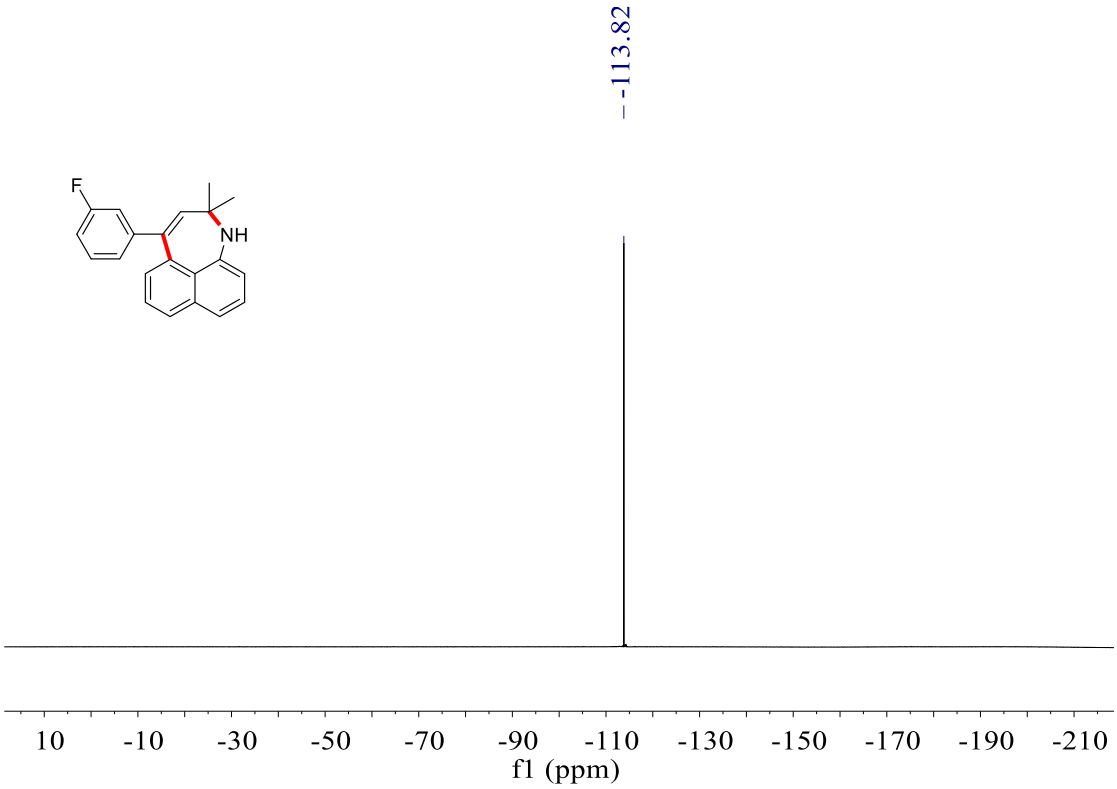
4ai, ^{1}H NMR, 400 MHz, $CDCl_3$



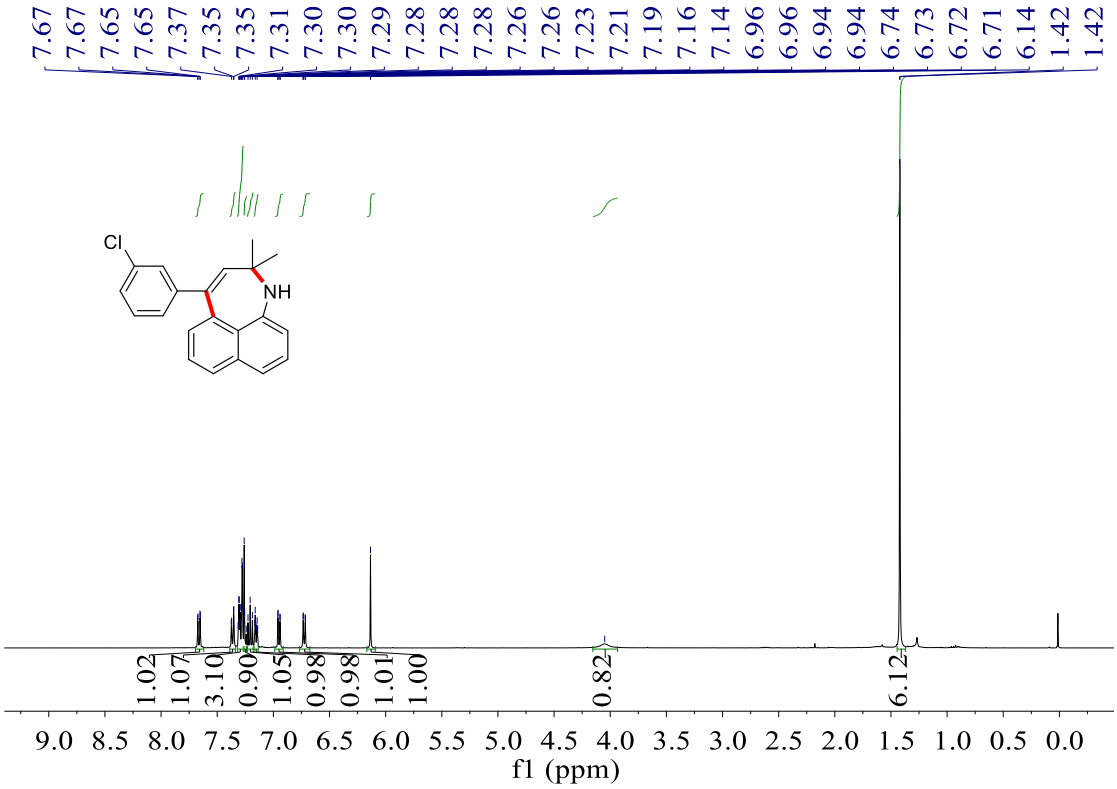
4ai, ^{13}C NMR, 101 MHz, $CDCl_3$



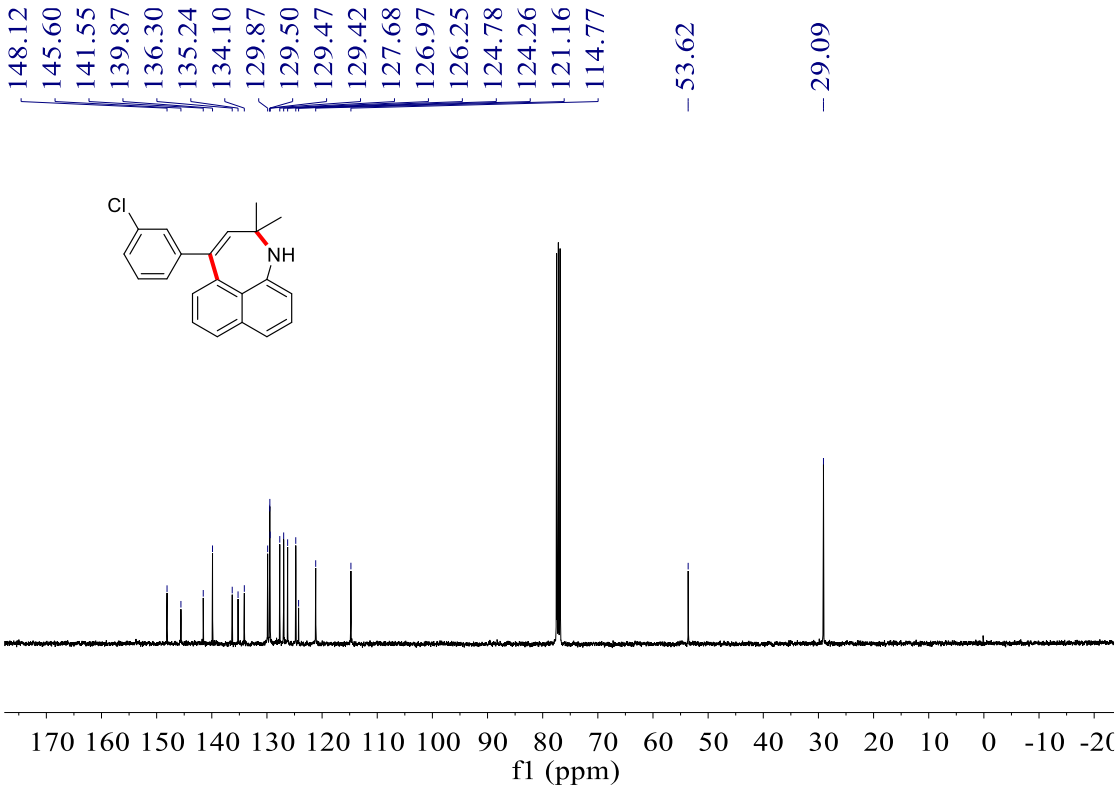
4ai, ^{19}F NMR, 376 MHz, $CDCl_3$



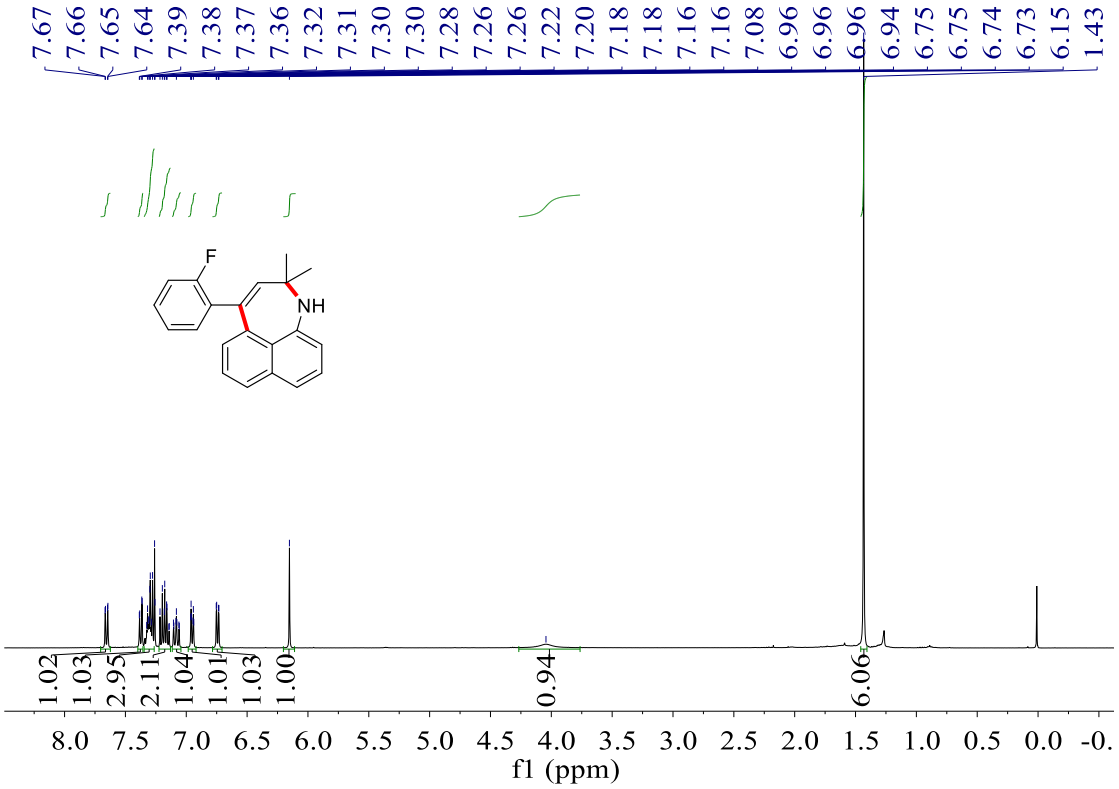
4aj, ^{1}H NMR, 400 MHz, $CDCl_3$



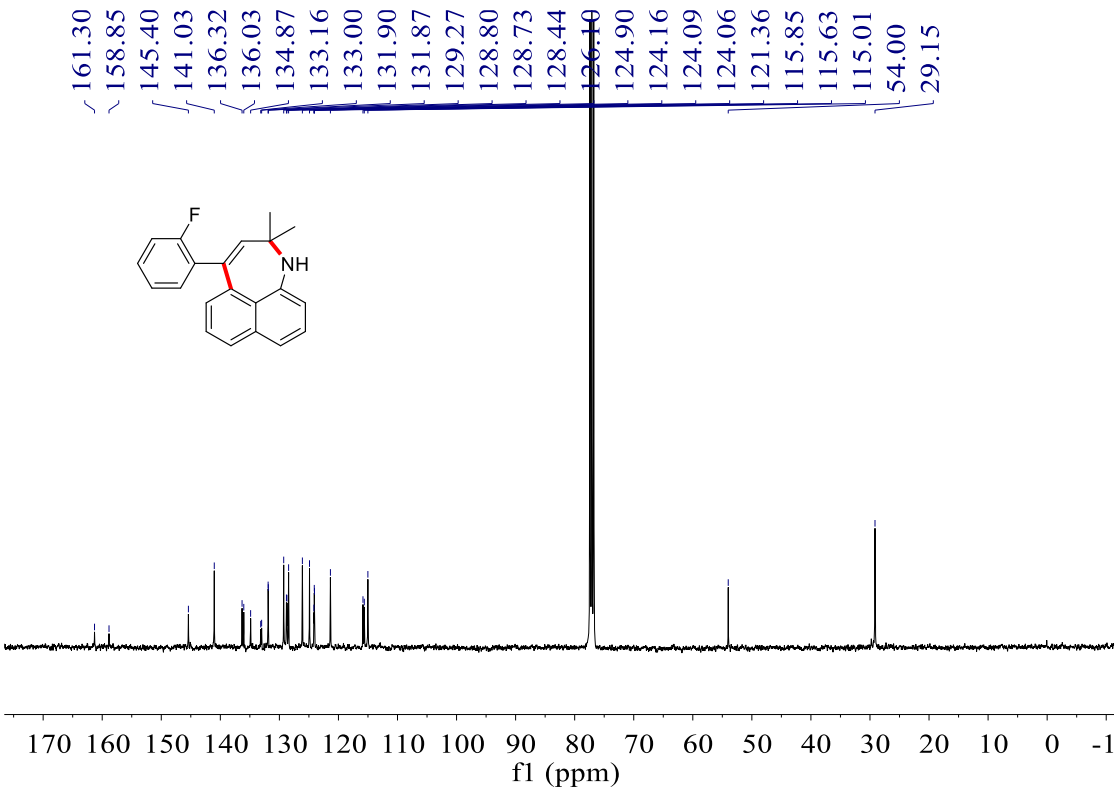
4aj, ^{13}C NMR, 101 MHz, $CDCl_3$



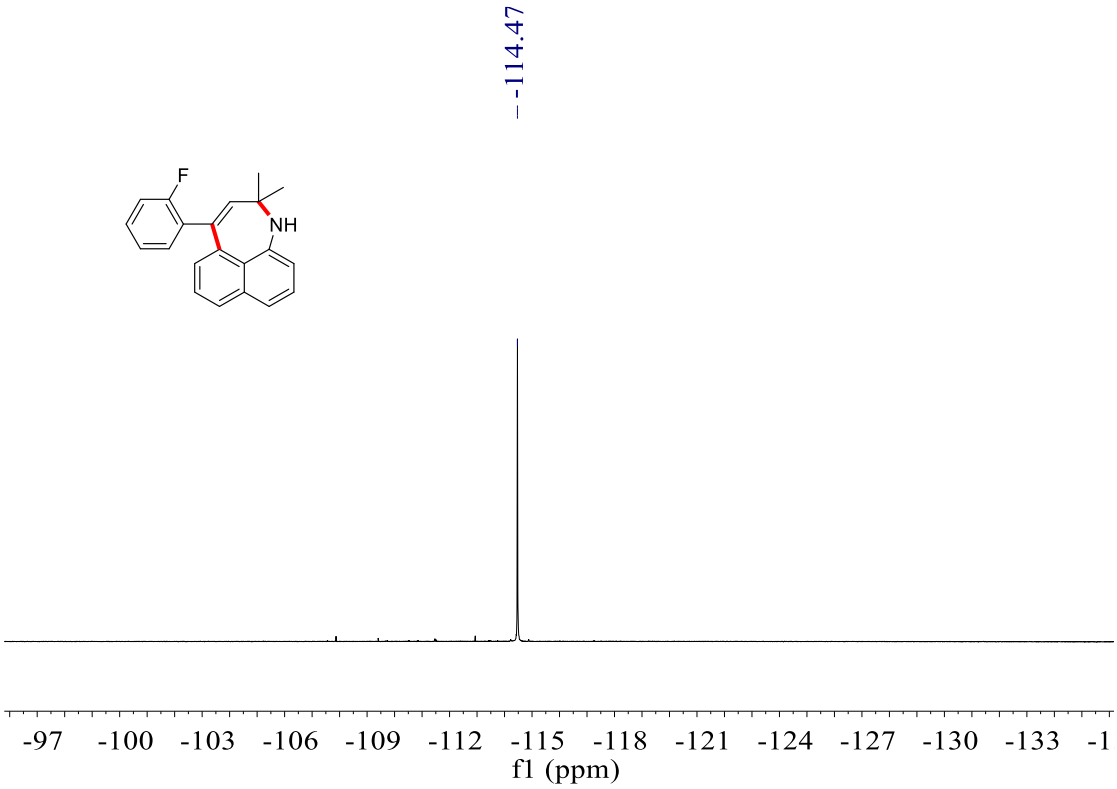
4ak, ^{1}H NMR, 400 MHz, $CDCl_3$



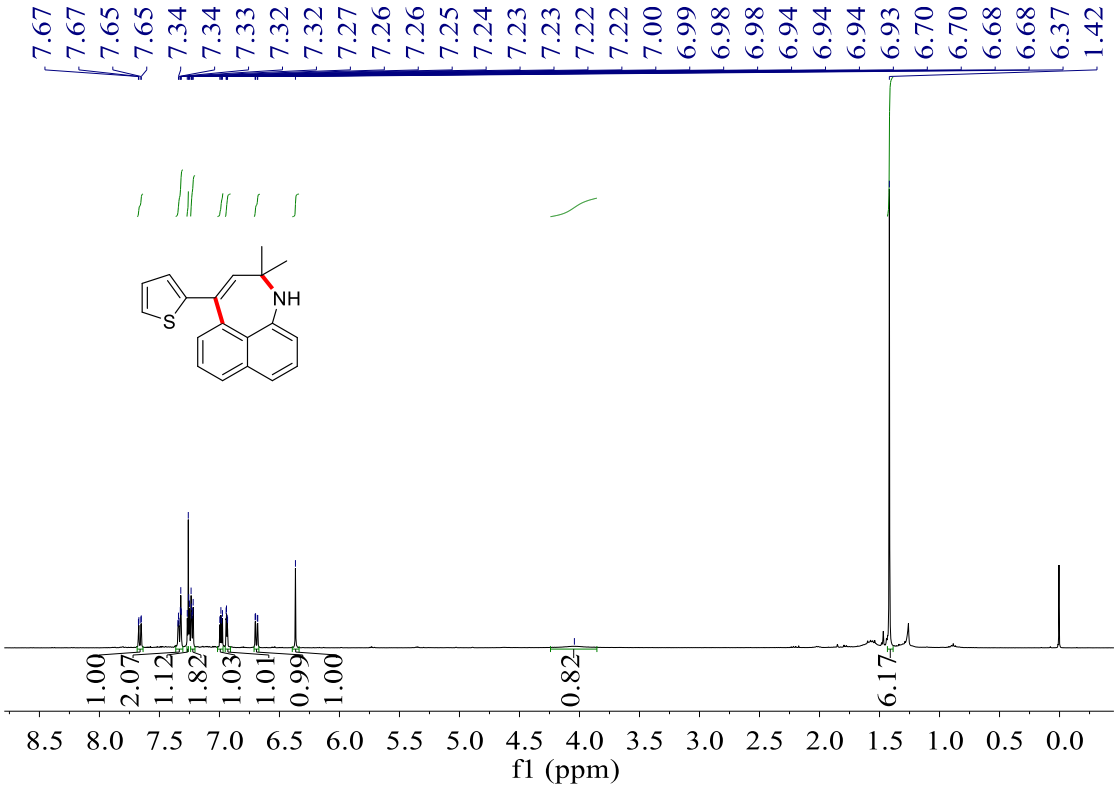
4ak, ^{13}C NMR, 101 MHz, $CDCl_3$



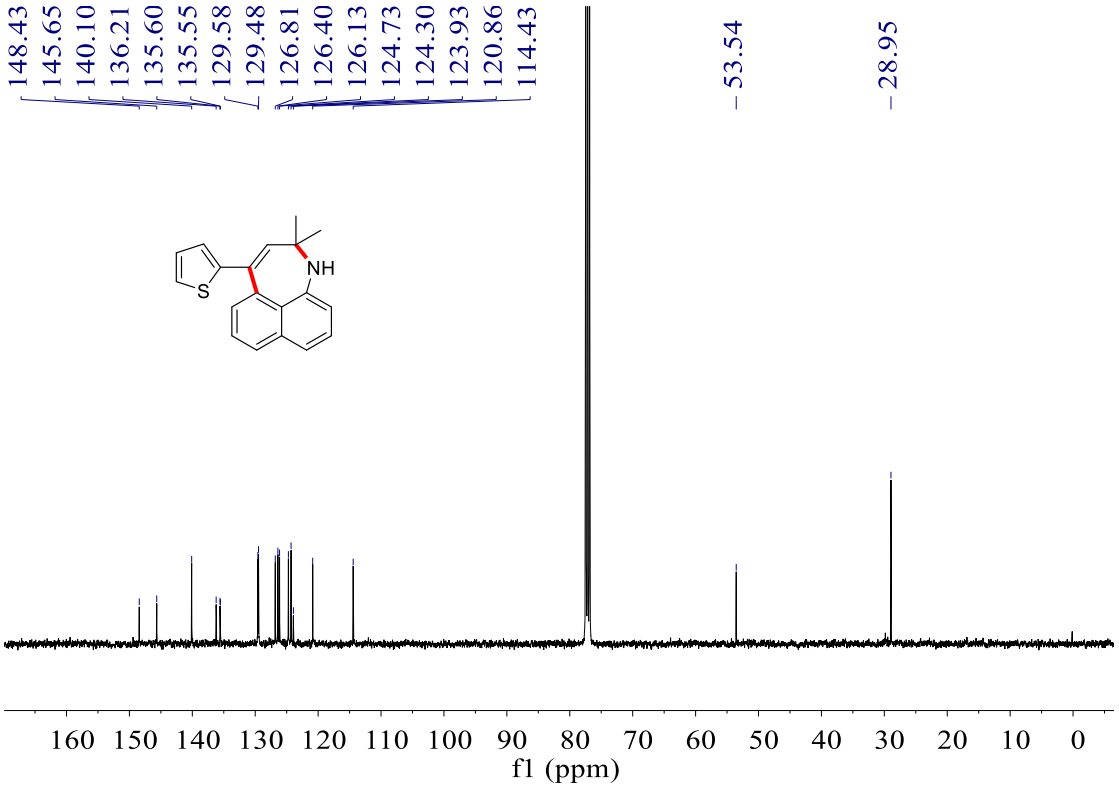
4ak, ^{19}F NMR, 376 MHz, $CDCl_3$



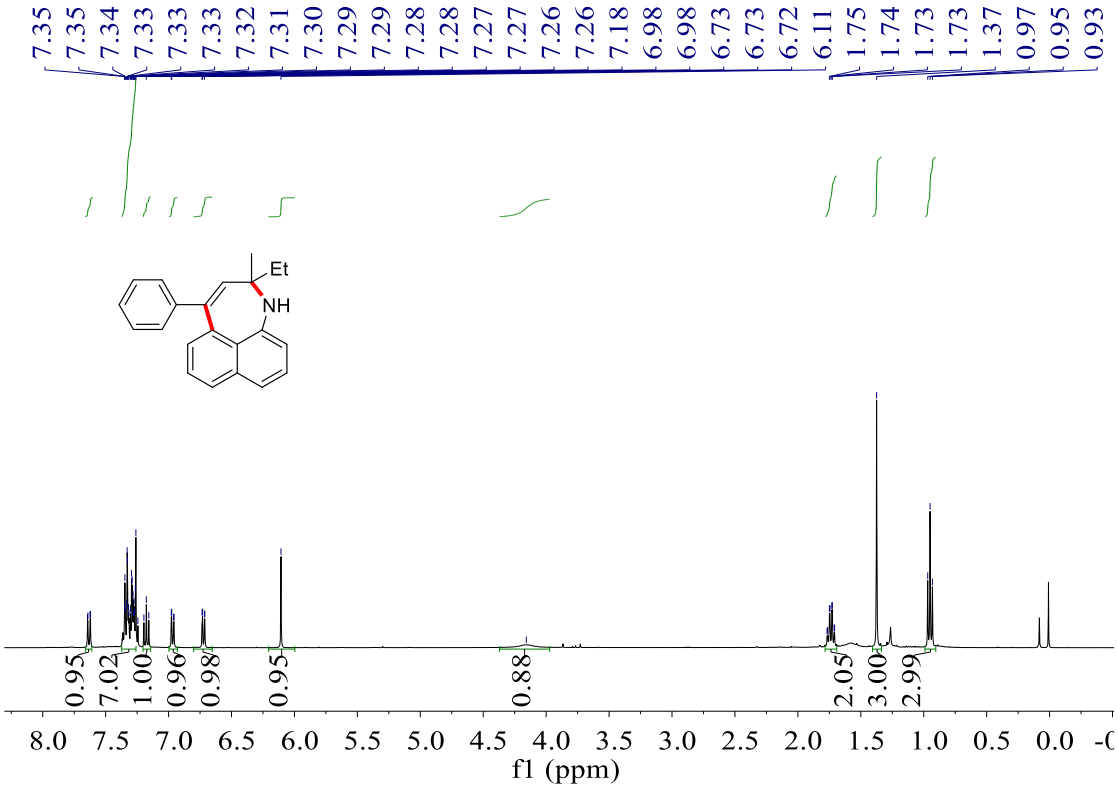
4al, ^{1}H NMR, 400 MHz, $CDCl_3$



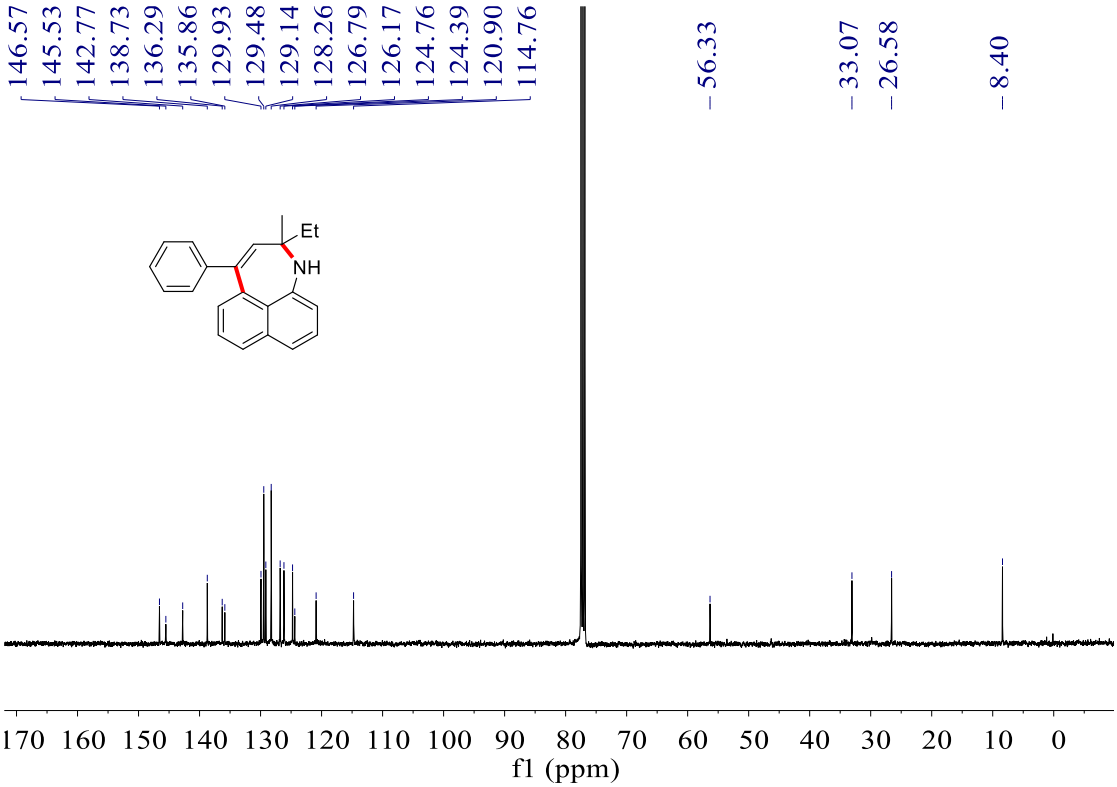
4al, ^{13}C NMR, 101 MHz, $CDCl_3$



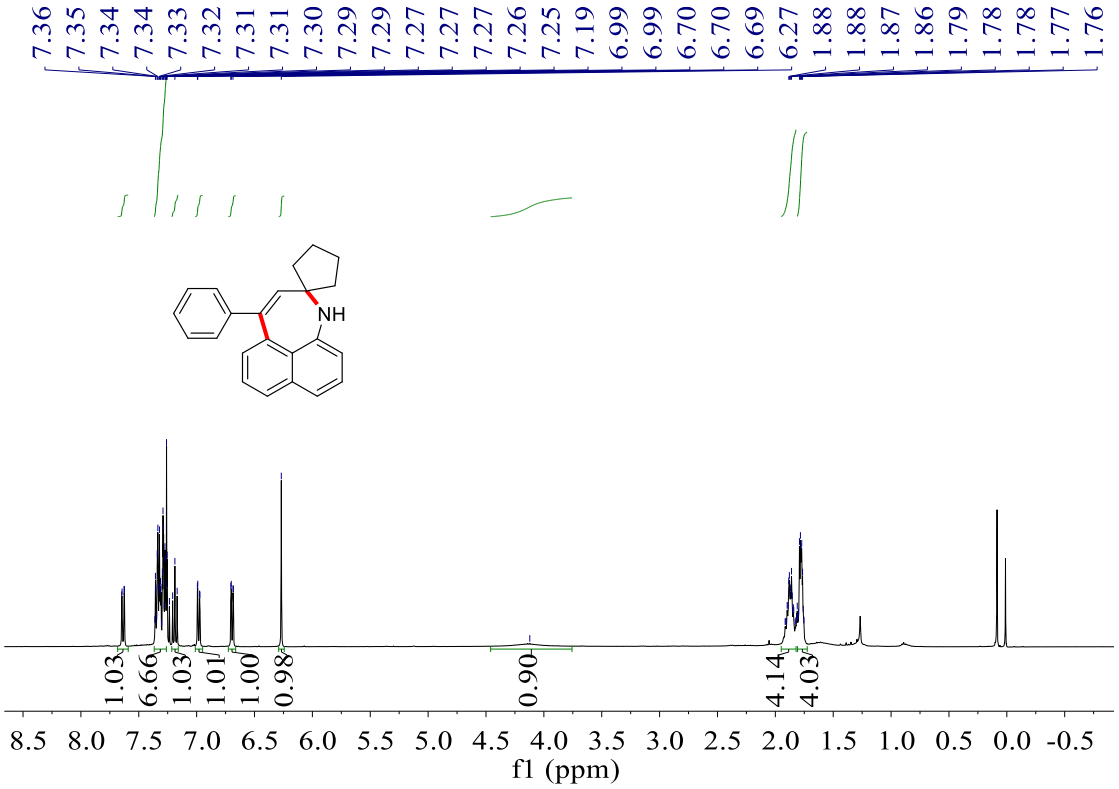
4am, ^{1}H NMR, 400 MHz, $CDCl_3$



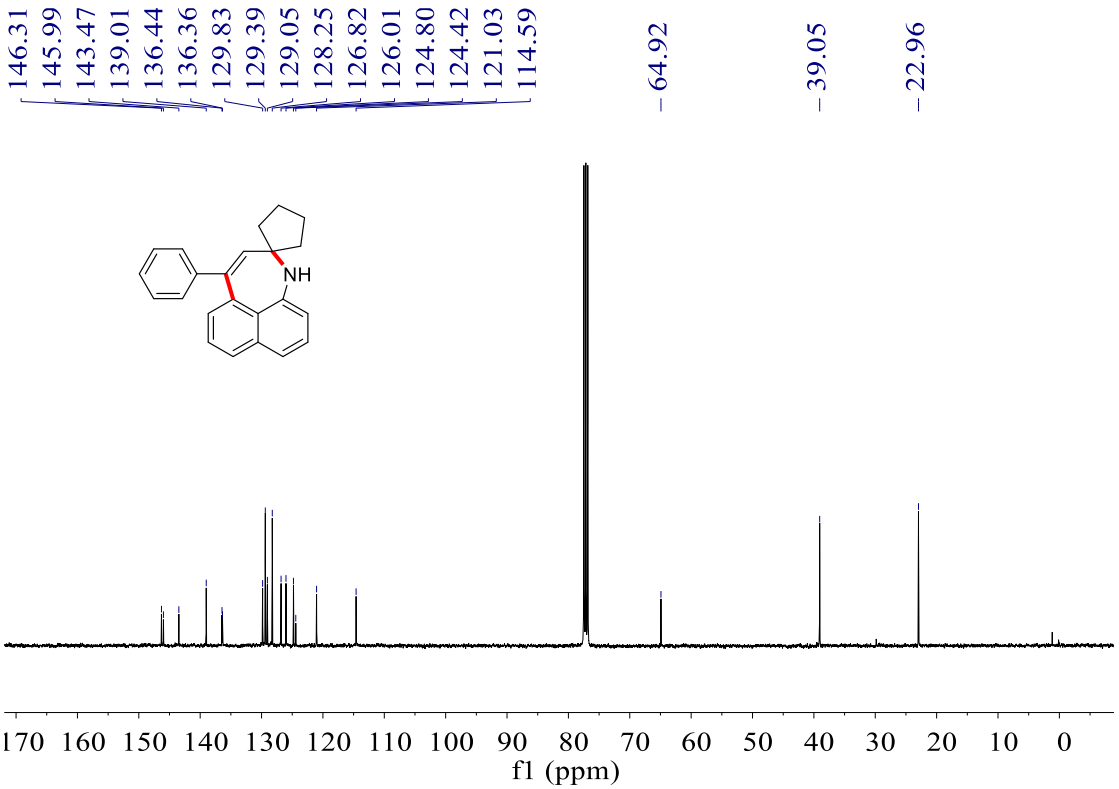
4am, ^{13}C NMR, 101 MHz, $CDCl_3$



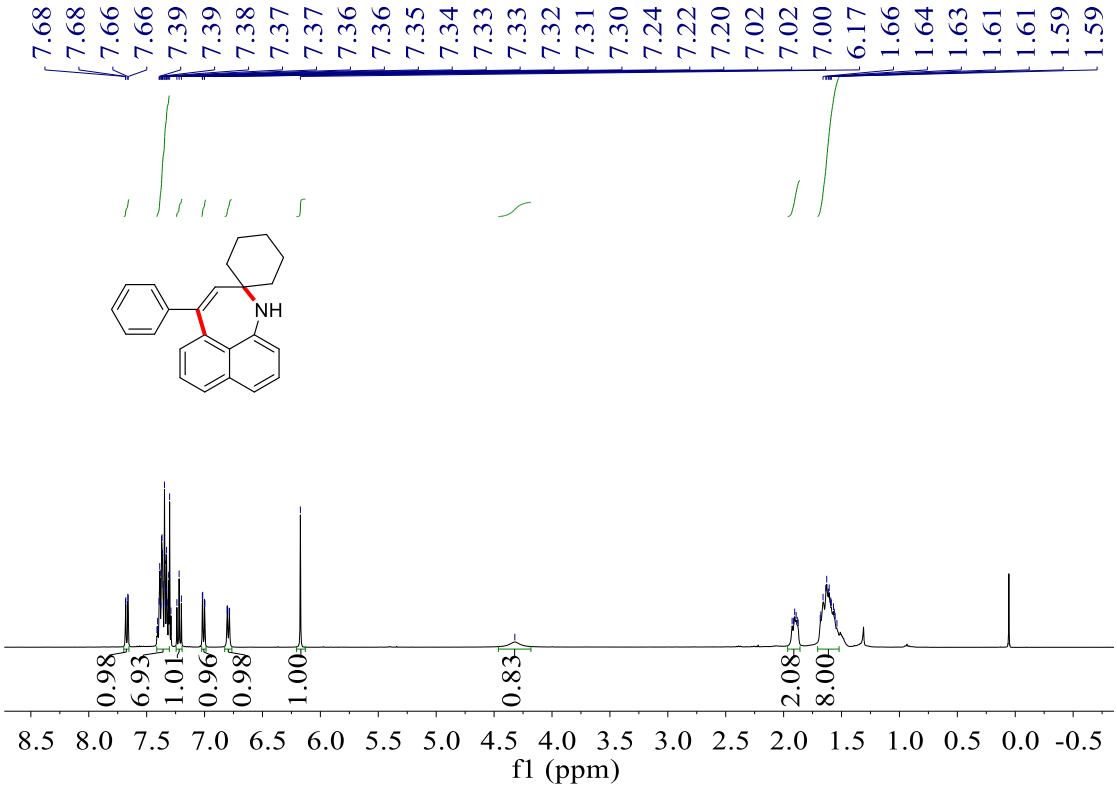
4an, ^{1}H NMR, 400 MHz, $CDCl_3$



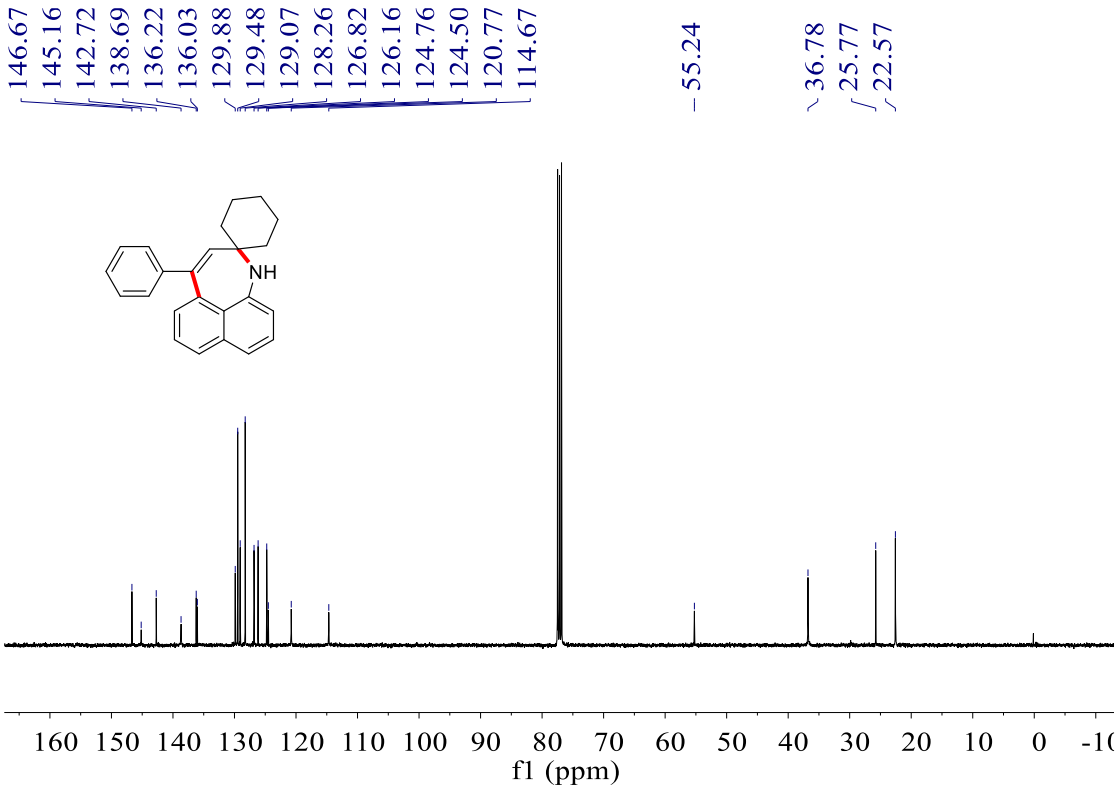
4an, ^{13}C NMR, 101 MHz, $CDCl_3$



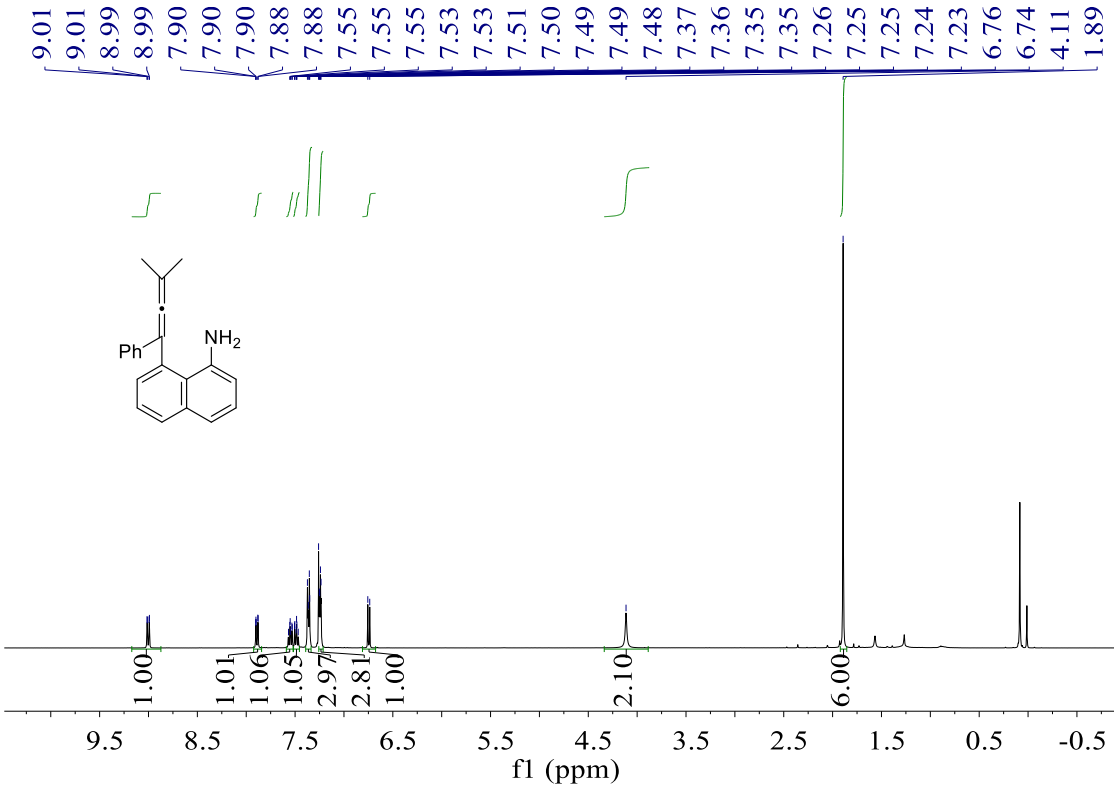
4ao, ^{1}H NMR, 400 MHz, $CDCl_3$



4ao, ^{13}C NMR, 101 MHz, $CDCl_3$



5, ^{1}H NMR, 400 MHz, $CDCl_3$



5, ^{13}C NMR, 101 MHz, $CDCl_3$