

Synthesis of amidines via iron-catalyzed dearomative amination of β -naphthols with oxadiazolones

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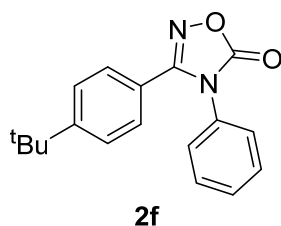
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I. General Information

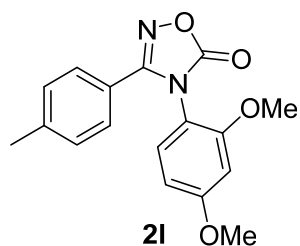
All manipulations were maintained under an atmosphere of nitrogen unless otherwise stated. Commercially available reagents were used without further purification. Solvents were pre-dried over activated 4 Å molecular sieves and were refluxed over sodium-benzophenone (toluene, tetrahydrofuran), phosphorus pentoxide (chloroform) or calcium hydride (dichloromethane, dichloroethane, acetonitrile) under an nitrogen atmosphere and collected by distillation. Column chromatography was performed on silica gel (200-300 mesh). ¹H NMR spectra were recorded on a 400 MHz NMR spectrometer and ¹³C NMR spectra were recorded on a 101 MHz NMR spectrometer. Infrared spectra were prepared as KBr pellets and were recorded on a Varian Excalibur 3100 series FT-IR spectrometer. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry.

II. Preparation of the Substrates

1a^[1], **1b**^[1], **1c**^[1], **1e**^[1], **1f**^[1], **1g**^[1], **1h**^[1], **1j**^[1], **1l**^[1], **1m**^[1], **1o**^[2], **1d**^[2], **1i**^[2], **1k**^[2] and **1n**^[2] were prepared according to the published procedures. The synthesis of substituted oxadiazolones **2** was accomplished following the reported procedures.^[3, 4, 5, 6]



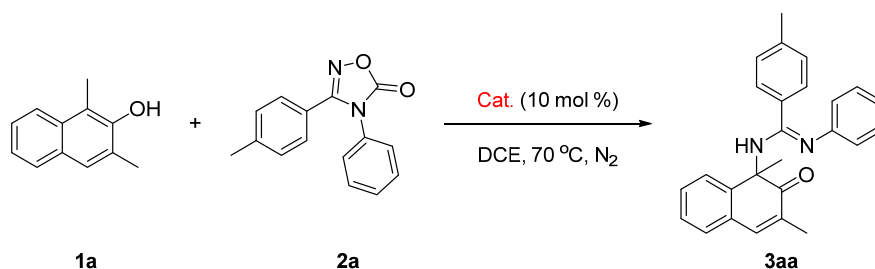
3-(4-(tert-butyl)phenyl)-4-phenyl-1,2,4-oxadiazol-5(4H)-one (2f); white solid; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 3H), 7.35 – 7.32 (m, 2H), 7.27 – 7.21 (m, 4H), 1.26 (s, 9H); ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 158.4, 157.4, 155.5, 132.1, 129.8, 129.5, 127.8, 127.0, 125.9, 120.0, 35.0, 31.0; HRMS (ESI, *m/z*): calcd for C₁₈H₁₉N₂O₂⁺ [M+H]⁺: 295.1441; found: 295.1446.



4-(2,4-dimethoxyphenyl)-3-(p-tolyl)-1,2,4-oxadiazol-5(4H)-one (21); white solid; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.8$ Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 2H), 6.54 (dt, $J = 8.8, 2$ Hz, 1H), 6.47 (s, 1H), 3.82 (s, 3H), 3.61 (s, 3H), 2.33 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 162.2, 158.9, 158.6, 156.0, 142.0, 129.9, 129.4, 127.2, 120.9, 113.5, 105.3, 99.7, 55.7, 55.6, 21.4; HRMS (ESI, m/z): calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_4^+$ $[\text{M}+\text{H}]^+$: 313.1183; found: 313.1180.

III. Optimization of Reaction Conditions

Table S1. Optimization of the Reaction Conditions (Metal Salts) for the Synthesis of Product **3aa**

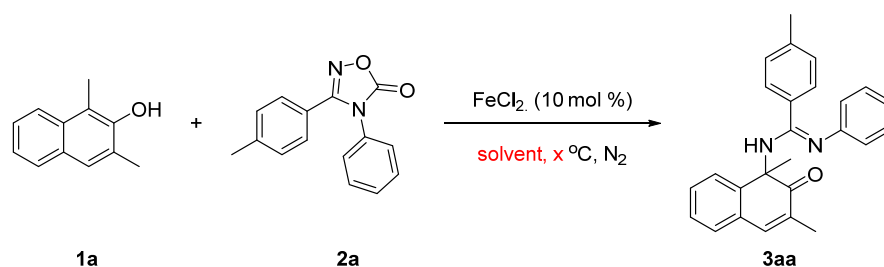


Entry	catalyst	Time (h)	yield ^b (%)
1	FeCl_2	16	62
2	$\text{Cu}(\text{OTf})_2$	16	NR ^c
3	$[\text{Ru}(\text{p-Cymene})\text{Cl}_2]_2$	16	NR ^c
4	CoCl_2	16	NR ^c
5	$\text{Ni}(\text{OAc})_2$	16	NR ^c
6	$[\text{Rh}(1,5\text{-cod})\text{Cl}]_2$	16	NR ^c
7	$[\text{IrCp}^*\text{Cl}_2]_2$	16	trace
8	$\text{Pd}(\text{OAc})_2$	16	NR ^c
9	$\text{Zn}(\text{OTf})_2$	16	NR ^c

10	Mn(OTf) ₂	16	NR ^c
11	FeBr ₂	16	50
12	FeF ₂	16	trace
13	FeI ₂	16	28
14	Fe(ClO ₄) ₂ •H ₂ O	16	16
15	Fe(OAc) ₂	16	NR ^c
16	FeCl ₃	16	29
17	FeF ₃	16	20
18	FeBr ₃	16	18
19	Fe(OTf) ₃	16	NR ^c

^a Reaction condition: **1a** (0.2 mmol), **2a** (1.1 equiv), Cat. (10 mol %), DCE (3mL), 70 °C, N₂ atmosphere. ^b Isolated yield. ^c No Reaction. DCE = 1,2dichloroethane.

Table S2. Optimization of the Reaction Conditions (solvent, temperature and time) for the Synthesis of Product **3aa**

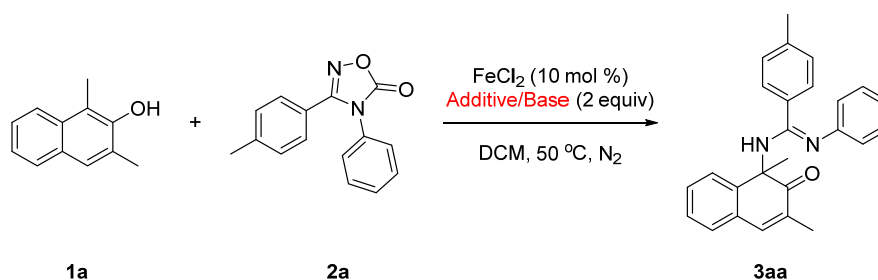


Entry	solvent	Temp (°C)	Time (h)	yield ^b (%)
1	DCM	50	16	62
2	MeCN	70	16	34
3	PhCl	70	16	49
4	CHCl ₃	60	16	31
5	CCl ₄	70	16	NR ^c
6	Toluene	70	16	45
7	1,4-Dioxane	70	16	trace
8	DCM	40	16	12
9	DCM	rt	16	NR ^c

10	DCM	50	36	63
11	DCM	50	48	65

^a Reaction condition: **1a** (0.2 mmol), **2a** (1.1 equiv), FeCl₂ (10 mol%), solvent (3 mL), N₂ atmosphere. ^b Isolated yield. ^c No Reaction. DCM= Dichloromethane.

Table S3. Optimization of the Reaction Conditions (additive or base) for the Synthesis of Product **3aa**

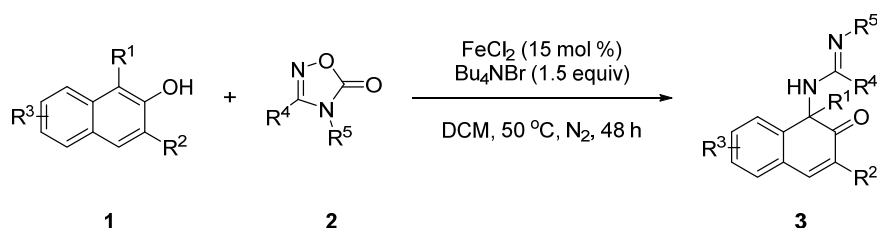


Entry	solvent	Additive/base	Time (h)	yield ^b (%)
1	DCM	Bu ₄ NCl	48	74
2	DCM	Bu ₄ NBr	48	78
3	DCM	Bu ₄ NI	48	76
4	DCM	LiCl	48	22
5	DCM	LiBr	48	23
6	DCM	KBr	48	21
7	DCM	NaI	48	trace
8	DCM	K ₂ CO ₃	48	64
9	DCM	CsCO ₃	48	62
10 ^c	DCM	Bu ₄ NBr	48	92
11 ^{c,d}	DCM	Bu ₄ NBr	48	60
12 ^{c,e}	DCM	Bu ₄ NBr	48	76
13^{c,f}	DCM	Bu₄NBr	48	92
14 ^{g,f}	DCM	Bu ₄ NBr	48	85

^a Reaction condition: **1a** (0.2 mmol), **2a** (1.1 equiv), FeCl₂ (10 mol %), solvent (3 mL), N₂ atmosphere. ^b Isolated yield. ^c 15 mol % of FeCl₂ was used. ^d 4 equiv of Bu₄NBr was used. ^e 10 mol % of Bu₄NBr was used. ^f 1.5 equiv of Bu₄NBr was used. ^g 12 mol % of FeCl₂ was used.

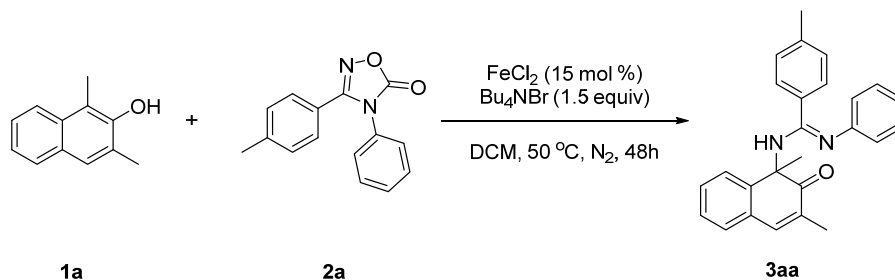
IV. General Procedure for Catalytic Reaction.

General Procedure:

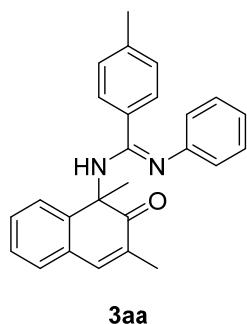


To a 20 mL over-dried and sealed flask were added **1** (0.2 mmol), **2** (0.22 mmol), FeCl₂ (15 mol %, 0.03 mmol), ⁿBu₄NBr (0.3 mmol) and anhydrous CH₂Cl₂ (3 mL) under N₂ atmosphere. The mixture was stirred at 50 °C for 48 hours as monitoring by TLC. Upon completion, the crude product was purified by column chromatography via silica gel to afford the desired product **3**.

The procedure for gram Scale:

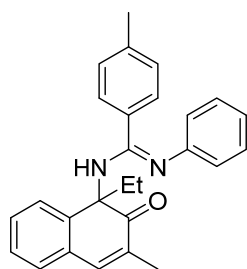


To a 100 mL over-dried and sealed flask were added **1a** (3.5 mmol), **2a** (3.9 mmol), FeCl₂ (15 mol %, 67 mg), ⁿBu₄NBr (5.3 mmol) and anhydrous CH₂Cl₂ (50 mL) under N₂ atmosphere. The solution was stirred at 50 °C for 48 hours as monitoring by TLC. Upon completion, the crude product was purified by column chromatography via silica gel to afford the desired product **3aa** (2.9 mmol, 1.10 g, 83% yield).



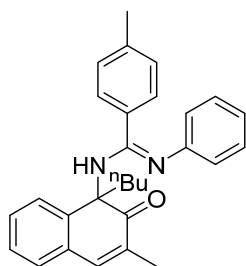
(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-N'-phenylbenzimidamide (3aa); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; TLC: R_f = 0.2 (PE/EA=10 : 1, UV); white solid

(m.p.: 293-295 °C); 92% yield (70 mg, 0.19 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.35-7.31 (m, 1H), 7.21 (d, *J* = 4.4 Hz, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.17 (d, *J* = 8.0 Hz, 2H), 5.52 (br, 1H), 2.28 (s, 3H), 2.10 (s, 3H), 1.44 (s, 3H). **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 200.7, 153.6, 149.7, 146.2, 140.2, 139.5, 132.4, 130.9, 130.2, 129.0, 128.7, 128.6, 128.4, 128.1, 126.6, 123.9, 122.3, 121.3, 61.8, 29.1, 21.5, 16.2. **IR ν (neat, cm⁻¹):** 3297, 2920, 2848, 2360, 1624, 1594, 1489, 823; **HRMS (ESI, m/z):** calcd for C₂₆H₂₅N₂O⁺ [M+H]⁺: 381.1961; found: 381.1961.



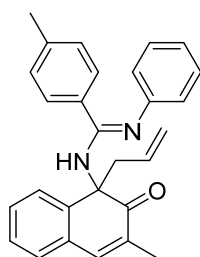
3ba

(*E*)-*N*-(1-ethyl-3-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-*N'*-phenylbenzimidamide (3ba); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC:** *R_f* = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 301-303 °C); 91% yield (72 mg, 0.18 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.14 (m, 5H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.16 (d, *J* = 7.6 Hz, 2H), 5.47 (s, 1H), 2.28 (s, 3H), 2.08 (s, 3H), 2.02 – 1.93 (m, 1H), 1.90 – 1.80 (m, 1H), 0.63 (t, *J* = 7.2 Hz, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 201.0, 153.5, 149.7, 144.4, 140.2, 139.4, 134.0, 131.8, 131.0, 129.0, 128.6, 128.4, 128.08, 128.05, 126.6, 124.5, 122.3, 121.2, 64.9, 36.7, 21.5, 16.0, 7.4; **IR ν (neat, cm⁻¹):** 3321, 2920, 2357, 2334, 1654, 1592, 1499, 502; **HRMS (ESI, m/z):** calcd for C₂₇H₂₇N₂O⁺ [M+H]⁺: 395.2118; found: 395.2117.



3ca

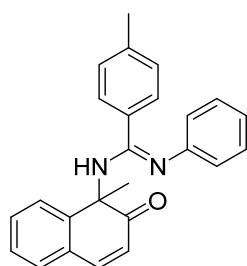
(E)-N-(1-butyl-3-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-N'-phenylbenzimidamide (3ca); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EAc=10 : 1, UV); white solid (m.p.: 286-289 °C); 89% yield (75 mg, 0.18 mmol); **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ 7.62 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 6.8 Hz, 1H), 7.23 – 7.13(m, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 7.6 Hz, 2H), 6.68 (t, J = 7.6 Hz, 1H), 6.15 (d, J = 7.6Hz, 2H), 5.47 (br, 1H), 2.28 (s, 3H), 2.08 (s, 3H), 1.92 (td, J = 12.4, 4.4 Hz, 1H), 1.78 (td, J = 12, 4.8 Hz, 1H), 1.18 - 1.01 (m, 3H), 0.96 – 0.86 (m, 1H), 0.74 (t, J = 6.4 Hz, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 201.0, 153.4, 149.7, 144.8, 140.0, 139.4, 133.8, 131.7, 131.0, 129.0, 128.6, 128.4, 128.1, 126.6, 124.4, 122.3, 121.2, 64.5, 43.5, 24.6, 23.0, 21.5, 16.1, 13.9; **IR ν (neat, cm^{-1})**: 3317, 2955, 2920, 2860, 2334, 1657, 1594, 1512, 1275, 827, 696, 587, 509; **HRMS (ESI, m/z)**: calcd for $\text{C}_{29}\text{H}_{31}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 423.2431; found: 423.2430.



3da

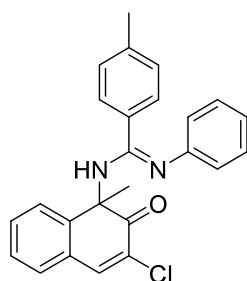
(E)-N-(1-allyl-3-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-N'-phenylbenzimidamide (3da); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EAc=10 : 1, UV); white solid (m.p.: 275-277 °C); 87% yield (71 mg, 0.18 mmol); **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ 7.63 (d, J = 8.0 Hz, 1H), 7.33 (td, J = 6.8, 2.0 Hz, 1H), 7.24 – 7.15(m, 5H), 7.03

(d, $J = 8.0$ Hz, 2H), 6.88 (t, $J = 7.6$ Hz, 2H), 6.68 (t, $J = 7.2$ Hz, 1H), 6.17 (d, $J = 7.6$ Hz, 2H), 5.59–5.48 (m, 2H), 5.06 (s, 1H), 5.02 (d, $J = 8.0$ Hz, 1H), 2.52 (d, $J = 7.2$ Hz, 2H), 2.29 (s, 3H), 2.07 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 200.0, 153.4, 149.7, 144.4, 140.2, 139.4, 133.2, 131.04, 131.00, 129.0, 128.6, 128.4, 128.3, 128.1, 126.7, 124.5, 122.2, 121.3, 120.1, 64.4, 46.4, 21.5, 16.1; IR ν (neat, cm^{-1}): 3347, 2915, 2848, 2364, 2342, 1656, 1630, 1591, 1482, 818, 665; HRMS (ESI, m/z): calcd for $\text{C}_{28}\text{H}_{27}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 407.2118; found: 407.2117.



3ea

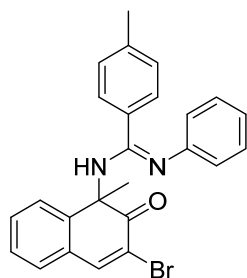
(*E*)-4-methyl-*N*-(1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-*N'*-phenylbenzimidamide (3ea); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 5:1; TLC: $R_f = 0.4$ (PE/EA=2 : 1, UV); white solid (m.p.: 298-301 °C); 53% yield (39 mg, 0.11 mmol); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, $J = 7.6$ Hz, 1H), 7.42 – 7.37 (m, 1H), 7.26 – 7.19 (m, 5H), 7.03 (d, $J = 7.6$ Hz, 2H), 6.94 (t, $J = 7.6$ Hz, 2H), 6.80 – 6.76 (m, 1H), 6.35 (s, 2H), 6.22 (s, 1H), 2.28 (s, 3H), 1.50 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 200.7, 155.0, 146.3, 141.7, 139.8, 129.8, 129.7, 129.0, 128.8, 128.2, 126.8, 125.2, 124.8, 123.2, 122.2, 63.6, 27.8, 21.5; IR ν (neat, cm^{-1}): 3295, 2922, 2850, 2359, 1666, 1592, 1482, 823; HRMS (ESI, m/z): calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 367.1805; found: 367.1804.



3fa

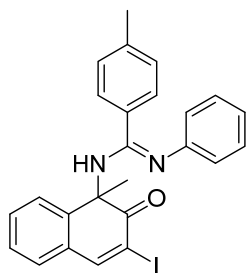
(*E*)-*N*-(3-chloro-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-*N'*-phenylbenzimidamide (3fa); reaction temperature: 50 °C; reaction time: 48 h;

petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); yellow solid (m.p.: 316-318 °C); 88% yield (71 mg, 0.18 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.73 (d, J = 8.0 Hz, 1H), 7.54 (s, 1H), 7.41 (td, J = 6.8, 2 Hz, 1H), 7.25 – 7.21(m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.93 (t, J = 7.6 Hz, 2H), 6.76 (t, 7.2 Hz, 1H), 6.28 (d, J = 7.6Hz, 2H), 5.58 (br, 1H), 2.29 (s, 3H), 1.52 (s, 3H); **¹³C{¹H} NMR (101 MHz, DMSO-*d*6)** δ 191.8, 153.8, 149.3, 146.7, 140.0, 139.0, 130.0, 129.7, 129.2, 128.70, 128.68, 128.56, 128.1, 126.8, 124.2, 122.0, 121.0, 63.1, 27.6, 20.8; **IR ν (neat, cm⁻¹)**: 3357, 3318, 2920, 2850, 2359, 2341, 1674, 1593, 1486, 925, 739; **HRMS (ESI, m/z)**: calcd for C₂₅H₂₂ClN₂O⁺ [M+H]⁺: 401.1415; found: 401.1416.



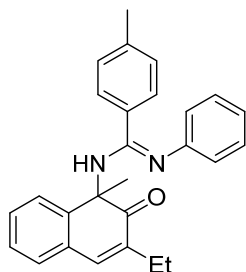
3ga

(*E*)-*N*-(3-bromo-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-*N'*-phenylbenzimidamide (3ga); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); yellow solid (m.p.: 315-317 °C); 90% yield (80 mg, 0.18 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.82 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.26 – 7.22 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 7.6 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 6.26 (d, J = 7.6 Hz, 2H), 5.64 (br, 1H), 2.29 (s, 3H), 1.51 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 193.7, 153.8, 148.7, 146.2, 144.7, 139.8, 130.2, 130.1, 129.6, 129.0, 128.9, 128.6, 128.2, 127.1, 124.4, 122.5, 122.2, 121.9, 63.5, 28.5, 21.5; **IR ν (neat, cm⁻¹)**: 3355, 2920, 2843, 2356, 2339, 1674, 1591, 1483, 824, 695; **HRMS (ESI, m/z)**: calcd for C₂₅H₂₂BrN₂O⁺ [M+H]⁺: 445.0910; found: 445.0909.



3ha

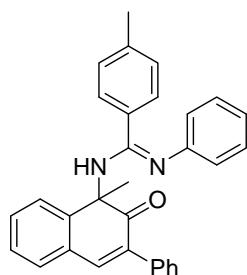
(E)-N-(3-iodo-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-N'-phenylbenzimidamide (3ha); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); yellow solid (m.p.: 324-326 °C); 92% yield (91 mg, 0.18 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 8.14 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.43 (td, J = 7.2, 2.0 Hz, 1H), 7.26 – 7.21(m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.91 (t, J = 7.6 Hz, 2H), 6.73 (t, J = 7.6 Hz, 1H), 6.23 (d, J = 7.6 Hz, 2H), 5.62 (br, 1H), 2.29 (s, 3H), 1.49 (s, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 194.7, 153.7, 152.5, 148.9, 146.9, 139.8, 130.8, 130.4, 130.2, 129.0, 128.8, 128.7, 128.2, 126.9, 124.3, 122.4, 121.8, 101.7, 62.1, 28.8, 21.5; **IR ν (neat, cm^{-1})**: 3351, 2920, 2845, 2339, 1661, 1631, 1589, 1482, 824, 665; **HRMS (ESI, m/z)**: calcd for $\text{C}_{25}\text{H}_{22}\text{IN}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 493.0771; found: 493.0771.



3ia

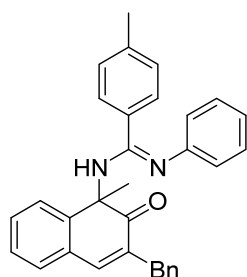
(E)-N-(3-ethyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-N'-phenylbenzimidamide (3ia); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 300-304 °C); 85% yield (67 mg, 0.17 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.68 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 6.4 Hz, 1H), 7.26 – 7.17 (m, 5H), 7.04 (d, J = 8.0 Hz, 2H), 6.88 (t, J = 7.6 Hz, 2H), 6.68 (t, J = 7.2 Hz, 1H), 6.17 (d, J = 8.0 Hz, 2H), 5.53 (br, 1H), 2.52 (q, J = 7.6 Hz, 2H), 2.29 (s, 3H), 1.44 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 200.2, 153.6, 149.9, 146.1, 139.4,

138.6, 137.9, 130.9, 130.2, 128.9, 128.71, 128.65, 128.6, 128.0, 126.6, 123.8, 122.2, 121.2, 61.9, 29.0, 22.8, 21.4, 13.1; **IR** ν (neat, cm^{-1}): 3353, 3304, 2920, 2850, 1656, 1630, 1593, 1484, 1379, 821, 509; **HRMS (ESI, m/z)**: calcd for $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 395.2118; found: 395.2117.



3ja

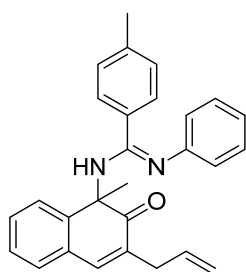
(E)-4-methyl-N-(1-methyl-2-oxo-3-phenyl-1,2-dihydronaphthalen-1-yl)-N'-phenylbenzimidamide (3ja); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); yellow solid (m.p.: 276-279 °C); 95% yield (84 mg, 0.19 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.75 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.51 (s, 1H), 7.48 – 7.34 (m, 5H), 7.26 (t, J = 9.2 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.6 Hz, 2H), 6.88 (t, J = 7.6 Hz, 2H), 6.69 (t, J = 7.2 Hz, 1H), 6.20 (d, J = 7.6 Hz, 2H), 5.64 (s, 1H), 2.29 (s, 3H), 1.55 (s, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 198.9, 153.7, 149.7, 146.7, 141.6, 139.5, 136.6, 135.5, 130.8, 129.9, 129.62, 129.60, 129.04, 128.98, 128.7, 128.2, 128.1, 127.9, 126.8, 123.9, 122.2, 121.3, 62.5, 29.0, 21.5; **IR** ν (neat, cm^{-1}): 3359, 3321, 2920, 2848, 2357, 1662, 1628, 1591, 1487, 825, 695; **HRMS (ESI, m/z)**: calcd for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 443.2118; found: 443.2117.



3ka

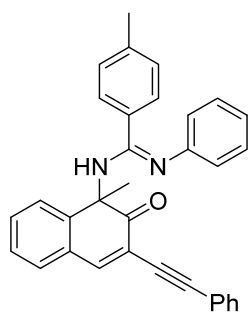
(E)-N-(3-benzyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-N'-phenylbenzimidamide (3ka); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); white solid

(m.p.: 302-305 °C); 89% yield (81 mg, 0.18 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.26 – 7.16 (m, 9H), 7.04 (t, *J* = 10.0 Hz, 3H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.10 (d, *J* = 7.6 Hz, 2H), 5.51 (br, 1H), 3.84 (s, 2H), 2.28 (s, 3H), 1.43 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 199.9, 153.5, 149.7, 146.3, 141.0, 139.8, 139.5, 135.6, 130.8, 129.9, 129.3, 129.1, 129.0, 128.7, 128.5, 128.1, 126.6, 126.1, 123.8, 122.3, 121.3, 62.1, 35.6, 29.0, 21.5; **IR ν (neat, cm⁻¹):** 3359, 3316, 2920, 2848, 2360, 2341, 1661, 1653, 1486, 821, 418; **HRMS (ESI, m/z):** calcd for C₃₂H₂₉N₂O⁺ [M+H]⁺: 457.2274; found: 457.2271.



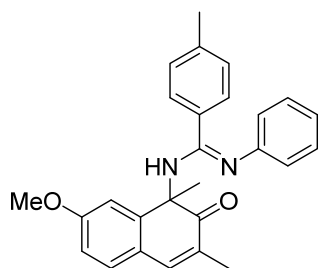
3a

(*E*)-*N*-(3-allyl-1-methyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-*N'*-phenylbenzimidamide (3a); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC:** *R_f* = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 276-279 °C); 77% yield (63 mg, 0.15 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 6.0 Hz, 1H), 7.26 – 7.17 (m, 5H), 7.03 (d, *J* = 8 Hz, 2H), 6.89 (t, *J* = 7.6 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 2H), 6.03 – 5.93 (m, 1H), 5.58 (br, 1H), 5.19 – 5.10 (m, 2H), 3.31 – 3.20 (m, 2H), 2.29 (s, 3H), 1.45 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 198.7, 153.7, 149.5, 146.1, 140.1, 139.5, 135.8, 134.4, 130.7, 129.9, 129.0, 128.9, 128.8, 128.7, 128.1, 126.7, 123.9, 122.4, 121.4, 116.8, 62.1, 33.6, 28.9, 21.4; **IR ν (neat, cm⁻¹):** 3299, 2921, 2845, 2341, 1659, 1629, 1483, 1442, 823, 421; **HRMS (ESI, m/z):** calcd for C₂₈H₂₇N₂O⁺ [M+H]⁺: 407.2118; found: 407.2119.



3ma

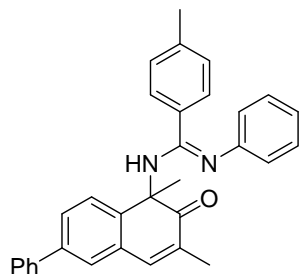
(E)-4-methyl-N-(1-methyl-2-oxo-3-(phenylethynyl)-1,2-dihydronaphthalen-1-yl)-N'-phenylbenzimidamide (3ma); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 5:1; **TLC**: R_f = 0.2 (PE/EA=5 : 1, UV); yellow solid (m.p.: 231-234 °C); 76% yield (71 mg, 0.15 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.79 (d, J = 8.0 Hz, 1H), 7.52 – 7.32 (m, 9H), 7.25 – 7.22 (m, 3H), 7.05 – 7.00(m, 4H), 6.92 (br, 1H), 6.63 (br, 1H), 2.27 (s, 3H), 1.61 (s, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 145.1, 139.8, 131.9, 130.3, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 127.0, 125.9, 124.1, 122.9, 120.2, 95.1, 85.7, 66.7, 29.8, 21.5; **IR ν (neat, cm^{-1})**: 3349, 3061, 2923, 2853, 2360, 2340, 1664, 1630, 1593, 1489, 1366, 1156, 824,, 519; **HRMS (ESI, m/z)**: calcd for $\text{C}_{33}\text{H}_{27}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 467.2118; found: 467.2117.



3na

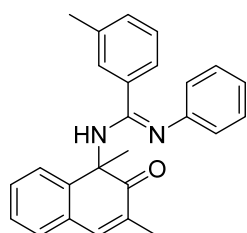
(E)-N-(7-methoxy-1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methyl-N'-phenylbenzimidamide (3na); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 319-322 °C); 85% yield (70 mg, 0.17 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.25 (s, 1H), 7.17(t, J = 6.8 Hz, 4H), 7.04 (d, J = 7.6 Hz, 2H), 6.90 (t, J = 7.6 Hz, 2H), 6.76 – 6.70 (m, 2H), 6.22 (d, J = 7.6 Hz, 2H), 5.52 (br, 1H), 3.86 (s, 3H), 2.28 (s, 3H), 2.07 (s, 3H), 1.43 (s, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 200.8, 160.5, 153.6, 149.7, 148.5, 140.2, 139.4, 130.9, 129.9, 129.8, 128.9, 128.6, 128.1, 123.6,

122.3, 121.3, 111.3, 110.4, 62.0, 55.4, 29.4, 21.4, 16.1; **IR** ν (neat, cm^{-1}): 3356, 3299, 2920, 2850, 2362, 1631, 1628, 1594, 1493, 1425, 1207, 823, 509; **HRMS (ESI, m/z)**: calcd for $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 411.2067; found:411.2067.



3oa

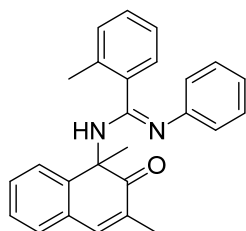
(E)-N-(1,3-dimethyl-2-oxo-6-phenyl-1,2-dihydronaphthalen-1-yl)-4-methyl-N'-phenylbenzimidamide (3oa); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 285-288 °C); 78% yield (71 mg, 0.16 mmol); **$^1\text{H NMR}$ (400 MHz, Chloroform-*d*)** δ 7.75 (d, J =8.0 Hz, 1H), 7.61 – 7.57 (t, J = 8.0 Hz, 3H), 7.44 (t, J = 8.4 Hz, 3H), 7.35 (t, J = 7.6 Hz, 1H), 7.28 (s, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.90 (t, J = 7.6 Hz, 2H), 6.70 (t, J = 7.6 Hz, 1H), 6.22 (d, J = 7.6 Hz, 2H), 5.56 (s, 1H), 2.29 (s, 3H), 2.13 (s, 3H), 1.48 (s, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 200.4, 153.7, 149.6, 145.1, 140.6, 140.0, 139.51, 139.46, 132.8, 130.8, 130.5, 129.0, 128.9, 128.7, 128.1, 127.4, 127.1, 127.0, 124.5, 122.4, 121.4, 61.7, 29.0, 21.4, 16.3; **IR** ν (neat, cm^{-1}): 3349, 3054, 2923, 2854, 2237, 1666, 1630, 1592, 1483, 1367, 1115, 824, 696, 518; **HRMS (ESI, m/z)**: calcd for $\text{C}_{32}\text{H}_{29}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 457.2274; found: 457.2275.



3ab

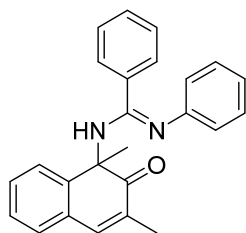
(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-3-methyl-N'-phenylbenzimidamide (3ab); reaction temperature: 50 °C; reaction time: 48 h;

petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 295-298 °C); 82% yield (62 mg, 0.16 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.68 (d, J = 7.6 Hz, 1H), 7.36 – 7.26 (m, 1H), 7.22 (d, J = 4.4 Hz, 3H), 7.18 – 7.05 (m, 3H), 7.01 (s, 1H), 6.88 (t, J = 7.6 Hz, 2H), 6.68 (t, J = 7.2 Hz, 1H), 6.18 (d, J = 7.6 Hz, 2H), 5.52 (br, 1H), 2.26 (s, 3H), 2.10 (s, 3H), 1.45 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 200.5, 153.7, 149.5, 146.2, 140.2, 138.0, 133.7, 132.4, 130.12, 130.09, 129.1, 128.7, 128.4, 128.1, 128.0, 126.6, 125.8, 123.9, 122.3, 121.4, 61.9, 29.0, 21.4, 16.2; **IR ν (neat, cm⁻¹)**: 3298, 2920, 2850, 2359, 1659, 1630, 1589, 1482, 793; **HRMS (ESI, m/z)**: calcd for C₂₆H₂₅N₂O⁺ [M+H]⁺: 381.1961; found: 381.1962.



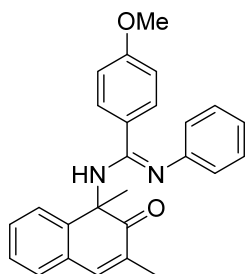
3ac

(*E*)-*N*-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-2-methyl-*N'*-phenylbenzimidamide (3ac); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 5:1; **TLC**: R_f = 0.2 (PE/EA=5 : 1, UV); yellow oil; 96% yield (73 mg, 0.19 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.69 (d, J = 7.6 Hz, 1H), 7.43 – 7.26 (m, 5H), 7.22 – 7.10 (m, 2H), 7.03 (d, J = 7.6 Hz, 1H), 6.84 (t, J = 7.6 Hz, 2H), 6.66 (t, J = 7.2 Hz, 1H), 6.16 (d, J = 8.0 Hz, 2H), 5.43 (s, 1H), 2.12 (s, 6H), 1.43 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 200.8, 154.1, 149.1, 146.3, 140.3, 136.0, 134.1, 132.4, 130.2, 130.1, 129.6, 129.0, 128.7, 128.4, 127.8, 126.6, 125.4, 124.0, 122.1, 121.6, 61.6, 29.0, 19.5, 16.3; **IR ν (neat, cm⁻¹)**: 3360, 2922, 2848, 2359, 2341, 1661, 1630, 1593, 1485, 695; **HRMS (ESI, m/z)**: calcd for C₂₆H₂₅N₂O⁺ [M+H]⁺: 381.1961; found: 381.1959.



3ad

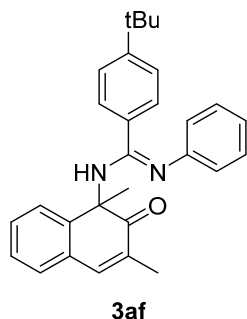
(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-N'-phenylbenzimidamide (3ad); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 275-279 °C); 83% yield (61 mg, 0.17 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.69 (d, J = 7.6 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.32 – 7.26 (m, 4H), 7.24 – 7.19 (m, 3H), 6.88 (t, J = 7.6 Hz, 2H), 6.69 (t, J = 7.6 Hz, 1H), 6.18 (d, J = 7.6 Hz, 2H), 5.57 (br, 1H), 2.11 (s, 3H), 1.45 (s, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 200.7, 153.6, 149.5, 146.1, 140.2, 133.8, 132.4, 130.1, 129.4, 128.74, 128.69, 128.4, 128.3, 128.1, 126.6, 123.9, 122.3, 121.4, 61.8, 29.1, 16.2; **IR ν (neat, cm^{-1})**: 3339, 2985, 2922, 2848, 1661, 1632, 1592, 1484, 1260, 750, 698; **HRMS (ESI, m/z)**: calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 367.1805; found: 367.1804.



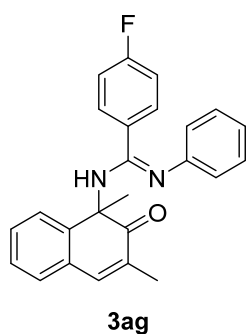
3ae

(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methoxy-N'-phenylbenzimidamide (3ae); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); yellow solid (m.p.: 276-278 °C); 87% yield (69 mg, 0.17 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.68 (d, J = 7.6 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.26 – 7.12 (m, 5H), 6.90 (t, J = 7.6 Hz, 2H), 6.80 – 6.62 (m, 3H), 6.37 – 6.09 (m, 2H), 5.56 (s, 1H), 3.75 (s, 3H), 2.09 (s, 3H), 1.44 (s, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 200.2, 160.4, 153.4, 149.6, 146.1, 140.0, 132.4, 130.3, 130.1, 128.7, 128.4, 128.1, 126.6, 125.8, 123.9, 122.4,

121.4, 113.6, 61.9, 55.3, 28.9, 16.2; **IR** ν (neat, cm^{-1}): 3358, 2917, 2848, 2362, 1664, 1631, 1589, 1482, 1437, 1172, 1028, 833, 514; **HRMS (ESI, m/z)**: calcd for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 397.1911; found: 397.1912.

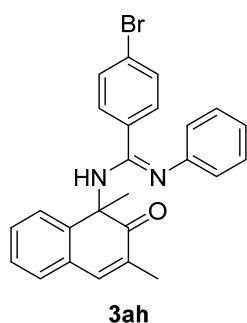


(E)-4-(tert-butyl)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-N'-phenylbenzimidamide (3af); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: $R_f = 0.2$ (PE/EA=10 : 1, UV); white solid (m.p.: 276-279 °C); 98% yield (83 mg, 0.19 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.67 (d, $J = 8.0$ Hz, 1H), 7.35 – 7.31 (m, 1H), 7.28 – 7.13 (m, 7H), 6.89 (t, $J = 7.6$ Hz, 2H), 6.70 (t, $J = 7.6$ Hz, 1H), 6.19 (d, $J = 7.6$ Hz, 2H), 5.54 (s, 1H), 2.10 (s, 3H), 1.44 (s, 3H), 1.26 (s, 9H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 200.8, 153.4, 152.6, 149.7, 146.3, 140.2, 132.5, 130.8, 130.2, 128.7, 128.5, 128.4, 128.1, 126.6, 125.2, 123.9, 122.2, 121.3, 61.8, 34.8, 31.3, 29.1, 16.2; **IR** ν (neat, cm^{-1}): 3328, 2962, 2848, 2362, 1662, 1623, 1592, 1485, 1437, 1126, 841, 695; **HRMS (ESI, m/z)**: calcd for $\text{C}_{29}\text{H}_{31}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 423.2431; found: 423.2432.



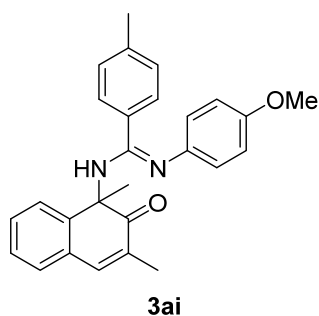
(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-fluoro-N'-phenylbenzimidamide (3ag); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: $R_f = 0.2$ (PE/EA=10 : 1, UV); white solid (m.p.: 298-302 °C); 86% yield (66 mg, 0.17 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.66 (d, $J = 7.6$ Hz, 1H), 7.36 – 7.32 (m, 1H), 7.28 -7.25 (m, 2H), 7.24 – 7.17 (m,

3H), 6.91 (dd, $J = 18.4, 8.8$ Hz, 4H), 6.70 (t, $J = 7.6$ Hz, 1H), 6.16 (d, $J = 8.0$ Hz, 2H), 5.51 (s, 1H), 2.10 (s, 3H), 1.45 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 200.5, 163.2 (d, $J = 250.7$ Hz) 152.7, 149.3, 146.0, 140.3, 132.4, 130.8 (d, $J = 8.4$ Hz), 130.1, 129.8, 128.8, 128.5, 128.2, 126.7, 123.8, 122.2, 121.7, 115.4 (d, $J = 21.6$ Hz), 62.0, 29.1, 16.2; IR ν (neat, cm^{-1}): 3344, 2921, 2848, 1663, 1631, 1592, 1483, 1152, 841, 507; HRMS (ESI, m/z): calcd for $\text{C}_{25}\text{H}_{22}\text{FN}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 385.1711; found: 385.1711.

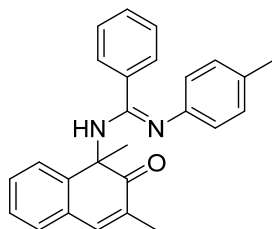


(*E*)-4-bromo-*N*-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-*N'*-

phenylbenzimidamide (3ah); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; TLC: $R_f = 0.2$ (PE/EA=10 : 1, UV); white solid (m.p.: 299-302 °C); 77% yield (69 mg, 0.15 mmol); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, $J = 7.6$ Hz, 1H), 7.38 – 7.32 (m, 3H), 7.26 – 7.21 (m, 3H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.90 (t, $J = 7.6$ Hz, 2H), 6.71 (t, $J = 7.6$ Hz, 1H), 6.15 (d, $J = 8.0$ Hz, 2H), 5.51 (s, 1H), 2.10 (s, 3H), 1.45 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 200.7, 152.6, 149.1, 145.9, 140.4, 132.7, 132.4, 131.6, 130.3, 130.1, 128.8, 128.5, 128.3, 126.7, 123.8, 122.1, 121.8, 62.0, 29.1, 16.2; IR ν (neat, cm^{-1}): 3284, 3060, 2922, 2850, 2357, 2334, 1649, 1628, 1587, 1483, 1442, 1175, 1113, 827, 694; HRMS (ESI, m/z): calcd for $\text{C}_{25}\text{H}_{22}\text{BrN}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 445.0910; found: 445.0911.

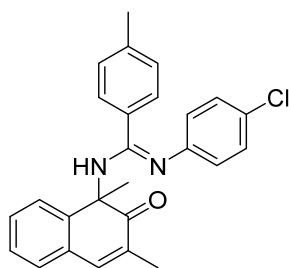


(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-N'-(4-methoxyphenyl)-4-methylbenzimidamide (3ai); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); yellow solid (m.p.: 251-254 °C); 82% yield (67 mg, 0.16 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.68 (d, J = 7.6 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.24 – 7.09 (m, 5H), 7.04 (d, J = 7.6 Hz, 2H), 6.46 (d, J = 8.4 Hz, 2H), 6.14 (s, 2H), 5.29 (br, 1H), 3.61 (s, 3H), 2.29 (s, 3H), 2.07 (s, 3H), 1.43 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 199.4, 154.7, 154.0, 146.1, 142.5, 139.4, 132.4, 130.7, 130.1, 129.0, 128.71, 128.66, 128.2, 126.6, 124.1, 123.3, 113.5, 62.1, 55.3, 28.6, 21.4, 16.3; **IR ν (neat, cm⁻¹)**: 3349, 2920, 2848, 2357, 2334, 1661, 1632, 1502, 1237, 1177, 1118, 1030, 830, 694; **HRMS (ESI, m/z)**: calcd for C₂₇H₂₇N₂O₂⁺ [M+H]⁺: 411.2067; found: 411.2065.



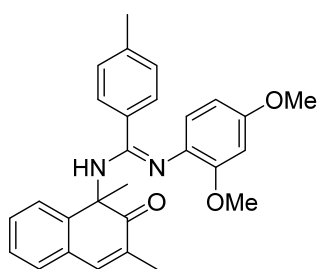
3aj

(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-N'-(p-tolyl)benzimidamide (3aj); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 273-275 °C); 91% yield (69 mg, 0.18 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.68 (d, J = 7.6 Hz, 1H), 7.37 – 7.26 (m, 5H), 7.24 – 7.20 (m, 4H), 6.68 (d, J = 8.0 Hz, 2H), 6.07 (d, J = 7.6 Hz, 2H), 5.51 (br, 1H), 2.09 (s, 6H), 1.44 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 200.6, 153.4, 146.7, 146.2, 140.1, 134.0, 132.5, 130.7, 130.2, 129.4, 128.74, 128.71, 128.4, 128.3, 126.6, 123.9, 122.1, 61.9, 29.0, 20.8, 16.3; **IR ν (neat, cm⁻¹)**: 3334, 2919, 2848, 2282, 1659, 1621, 1598, 1527, 1504, 1443, 1331, 1031, 830, 501; **HRMS (ESI, m/z)**: calcd for C₂₆H₂₅N₂O⁺ [M+H]⁺: 381.1961; found: 381.1961.



3ak

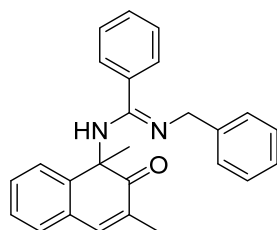
(E)-N'-(4-chlorophenyl)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methylbenzimidamide (3ak); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 15:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); white solid (m.p.: 279-282 °C); 86% yield (74 mg, 0.17 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.64 (d, J = 7.6 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.26 – 7.21 (m, 3H), 7.15 (d, J = 7.6 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 6.07 (d, J = 8.0 Hz, 2H), 5.58 (s, 1H), 2.30 (s, 3H), 2.09 (s, 3H), 1.44 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 200.6, 154.1, 148.3, 146.1, 140.2, 139.7, 132.4, 130.4, 130.1, 129.1, 128.8, 128.6, 128.4, 128.1, 126.6, 126.3, 123.7, 123.4, 61.8, 29.0, 21.4, 16.1; **IR ν (neat, cm⁻¹)**: 3349, 2987, 2920, 2848, 2359, 2342, 1666, 1628, 1581, 1483, 1275, 1260, 1083, 836, 750; **HRMS (ESI, m/z)**: calcd for C₂₆H₂₄ClN₂O⁺ [M+H]⁺: 415.1572; found: 415.1571.



3al

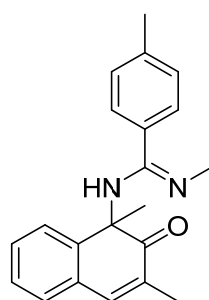
(E)-N'-(2,4-dimethoxyphenyl)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-4-methylbenzimidamide (3al); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; **TLC**: R_f = 0.2 (PE/EA=10 : 1, UV); yellow solid (m.p.: 251-254 °C); 91% yield (80 mg, 0.18 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.73 (d, J = 8.0 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.21 – 7.12 (m, 4H), 6.98 (d, J = 8.0 Hz, 2H), 6.20 (s, 3H), 3.64 (s, 3H), 3.30 (s, 3H), 2.25 (s, 3H), 1.96 (s, 3H), 1.49 (s, 3H); **¹³C{¹H} NMR (101 MHz, DMSO-*d*6)** δ 199.0, 154.9, 152.0, 146.7, 138.5, 131.8, 129.8,

128.2, 128.1, 127.4, 126.1, 124.3, 104.8, 100.5, 61.6, 55.6, 54.9, 27.8, 20.8, 16.2; **IR ν (neat, cm^{-1}):** 3366, 3007, 2920, 2848, 2362, 2334, 1634, 1499, 1469, 1275, 1260, 1207, 1157, 1035, 824, 504; **HRMS (ESI, m/z):** calcd for $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 441.2173; found: 441.2172.



3am

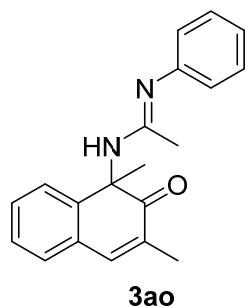
(*E*)-*N'*-benzyl-*N*-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)benzimidamide (3am); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; **TLC:** R_f = 0.2 (PE/EA=10 : 1, UV); yellow oil; 81% yield (62 mg, 0.16 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.70 (d, J = 7.6 Hz, 1H), 7.37 – 7.34 (m, 6H), 7.30 – 7.22 (m, 3H), 7.03 (s, 3H), 6.57 (s, 2H), 4.19 (d, J = 16.4 Hz, 1H), 3.99 (d, J = 16.4 Hz, 1H), 1.98 (s, 3H), 1.43 (s, 3H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)** δ 202.4, 156.7, 146.3, 142.0, 138.9, 133.6, 132.3, 130.2, 129.4, 128.8, 128.5, 128.1, 127.82, 127.75, 126.6, 126.5, 125.6, 124.6, 63.0, 52.7, 28.6, 16.5; **IR ν (neat, cm^{-1}):** 3349, 3059, 2986, 2920, 2848, 1648, 1599, 1494, 1443, 1293, 1260, 1027, 948, 751; **HRMS (ESI, m/z):** calcd for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 381.1961; found:381.1962.



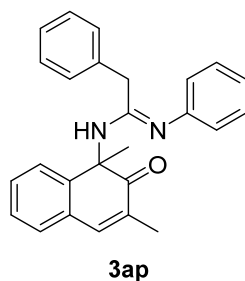
3an

(*E*)-*N*-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-*N'*,4-dimethylbenzimidamide (3an); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 5:1; **TLC:** R_f = 0.2 (PE/EA=2 : 1, UV); yellow oil; 39% yield (25 mg, 0.08 mmol); **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.69 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.26 – 7.14 (m, 5H), 7.00 (d, J = 7.6 Hz, 1H), 6.51 (s,

1H), 2.79 (s, 3H), 2.35 (s, 3H), 2.14 (s, 3H), 1.53 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 203.2, 164.0, 142.7, 140.1, 131.9, 130.1, 129.0, 128.6, 128.0, 127.2, 126.8, 125.9, 71.5, 30.7, 23.7, 21.5, 18.6; IR ν (neat, cm^{-1}): 3349, 3052, 2924, 2359, 1661, 1616, 1586, 1514, 1442, 1375, 1118, 1019, 951, 825, 579; HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 319.1805; found: 319.1805.



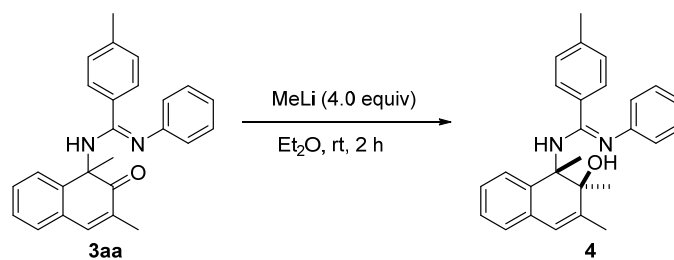
(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-N'-phenylacetimidamide (3ao); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; TLC: R_f = 0.2 (PE/EA=5 : 1, UV); white solid (m.p.: 255-257 °C); 82% yield (50 mg, 0.16 mmol); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.15 (s, 1H), 7.06 (t, J = 7.6 Hz, 2H), 6.84 (t, J = 7.2 Hz, 1H), 6.30 (d, J = 8.0 Hz, 2H), 5.29 (br, 1H), 2.00 (s, 3H), 1.78 (s, 3H), 1.42 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 199.0, 152.4, 149.9, 146.1, 139.8, 132.1, 130.0, 128.6, 128.5, 128.2, 126.5, 124.1, 122.0, 121.8, 61.8, 28.8, 16.28, 16.25; IR ν (neat, cm^{-1}): 3348, 2919, 2848, 2359, 1667, 1646, 1628, 1589, 1509, 1484, 1374, 1260, 1083, 836, 796; HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$: 305.1648; found: 305.1649.



(E)-N-(1,3-dimethyl-2-oxo-1,2-dihydronaphthalen-1-yl)-N',2-diphenylacetimidamide (3ap); reaction temperature: 50 °C; reaction time: 48 h; petroleum ether/ethylacetate = 10:1; TLC: R_f = 0.2 (PE/EA=5 : 1, UV); white solid

(m.p.: 231-234 °C); 66% yield (50 mg, 0.13 mmol); **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.38 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.28 (m, 3H), 7.24 – 7.21 (m, 4H), 7.17 (s, 1H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.31 (d, *J* = 7.6 Hz, 2H), 5.12 (s, 1H), 3.49 (q, *J* = 15.6 Hz, 2H), 2.02 (s, 3H), 1.28 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 200.6, 152.4, 149.9, 146.2, 140.1, 136.3, 132.2, 130.2, 129.2, 128.9, 128.53, 128.47, 128.2, 127.0, 126.5, 123.9, 122.0, 121.6, 61.3, 35.8, 28.7, 16.2; **IR ν (neat, cm⁻¹):** 3349, 3048, 2919, 2850, 2341, 1659, 1641, 1592, 1589, 1509, 1483, 1031, 901, 668; **HRMS (ESI, m/z):** calcd for C₂₆H₂₅N₂O⁺ [M+H]⁺: 381.1961; found: 381.1959.

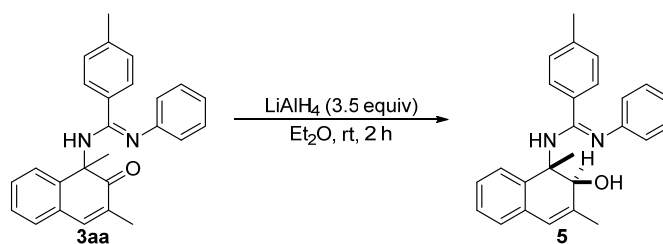
V. Further Transformations



Compound **4** was prepared according to the reported procedures^[7].

To a solution of **3aa** (0.2 mmol, 76 mg) in anhydrous diethyl ether (5 mL), methyl lithium (0.27 mL, 3 M in Et₂O, 0.8 mmol, 4.0 equiv) was added at 0 °C. The reaction was then stirred at room temperature for 2 h. The reaction was quenched with water and extracted with ethyl acetate for three times. The combined organic extracts were dried over MgSO₄ and concentrated in a vacuum. The crude product was purified by column chromatography (petroleum ether/ethylacetate = 10:1) to give **4**. Yield: 89%, 71 mg; White solid, m.p. 231-234 °C; **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.93 (s, 1H), 7.57 – 7.52 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 3.6 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 2H), 7.03 – 7.00 (m, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.06 (s, 1H), 5.39 (s, 1H), 2.33 (s, 3H), 2.05 (s, 3H), 1.83 (s, 3H), 1.31 (s, 3H); **¹³C{¹H} NMR (101 MHz, Chloroform-*d*)** δ 159.1, 148.0, 145.8, 141.9, 140.4, 133.0, 132.2, 129.4, 129.0, 128.5, 127.9, 127.2, 126.5, 123.5, 122.6, 122.3, 120.0, 78.9, 68.1, 23.9, 21.5, 21.3, 18.1; **HRMS (ESI, m/z):** calcd for C₂₆H₂₇N₂O⁺ [M+H]⁺:

397.2274; found: 397.2279.

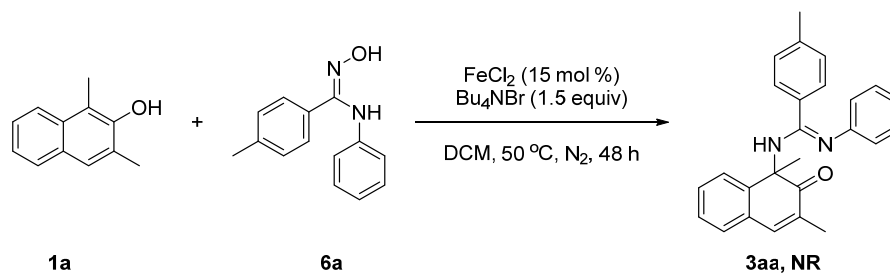


Compound **5** was prepared according to the reported procedures^[8].

To a solution of **3aa** (0.4 mmol, 152 mg) in anhydrous diethyl ether (5 mL), LiAlH₄ (1.4 mmol, 53.1 mg) was added slowly at 0 °C. The suspension was stirred at room temperature for 2 h. Then the mixture was quenched with water and was extracted with ethyl acetate for three times. The combined organic extracts were dried over MgSO₄ and concentrated in a vacuum. The crude product was purified by column chromatography (petroleum ether/ethylacetate = 10:1) to give **5**. Yield: 37%, 57 mg; White solid, m.p. 226-228 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 1H), 7.28 (s, 1H), 7.23 (dd, *J* = 6.0, 3.1 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.05 (m, 4H), 7.02 (t, *J* = 4.2 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 3H), 6.13 (s, 1H), 5.39 (s, 1H), 5.11 (s, 1H), 2.32 (s, 3H), 2.06 (s, 3H), 1.77 (s, 3H); ¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 158.8, 148.3, 140.9, 140.8, 140.2, 133.0, 132.0, 129.3, 129.0, 128.5, 128.0, 127.2, 126.4, 123.4, 123.3, 122.1, 121.3, 79.2, 65.1, 21.4, 20.1, 19.1; HRMS (ESI, *m/z*): calcd for C₂₆H₂₇N₂O⁺ [M+H]⁺: 383.2118; found: 383.2127.

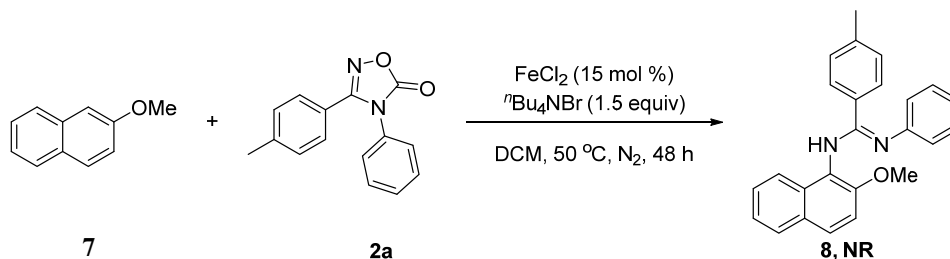
VI. Mechanistic Experiments

(a) Control Experiments



To a 20 mL over-dried and sealed flask were added **1a** (0.1 mmol), **6a** (0.11 mmol), FeCl₂ (0.015 mmol), ⁿBu₄NBr (0.15 mmol) and anhydrous CH₂Cl₂ (2 ml) under N₂

atmosphere. After stirring at 50 °C for 48 hours, the reaction did not work monitored by TLC.

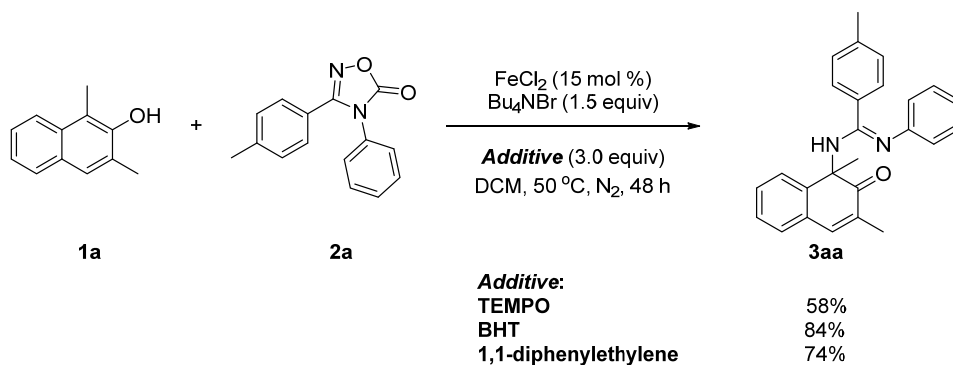


To a 20 mL over-dried and sealed flask were added **7** (0.1 mmol), **2a** (0.11 mmol), FeCl₂ (15 mol %, 0.015 mmol), ^tBu₄NBr (0.15 mmol) and anhydrous CH₂Cl₂ (2 mL) under N₂ atmosphere. After stirring at 50 °C for 48 hours, the reaction did not work monitored by TLC.



To a 20 mL over-dried and sealed flask were added **1a** (0.1 mmol), **9** (0.11 mmol), FeCl₂ (15 mol %, 0.015 mmol), ^tBu₄NBr (0.15 mmol) and anhydrous CH₂Cl₂ (2 mL) under N₂ atmosphere. After stirring at 50 °C for 48 hours, the reaction mixture was purified by column chromatography via silica gel to afford the product **10** (0.023 mmol, 7.1 mg, 23% yield). **1,3-dimethylnaphthalen-2-yl p-tolylcarbamate (10)**, oil; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8Hz, 1H), 7.77 (d, *J* = 12Hz, 1H), 7.57 (s, 1H), 7.50 - 7.42 (m, 2H), 7.37 (d, *J* = 8Hz, 2H), 7.14 (d, *J* = 8Hz, 2H), 7.08 (brs, 1H), 2.56 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H).

(b) Radical inhibition reactions



To a 20 mL over-dried and sealed flask were added **1a** (0.1 mmol), **2a** (0.11 mmol), FeCl_2 (15 mol %, 0.015 mmol), Bu_4NBr (0.15 mmol), radical scavenger (3 equiv, 0.3 mmol) and anhydrous CH_2Cl_2 (3 ml) under N_2 atmosphere. The solution was stirred at 50 °C for 48 hours as monitoring by TLC. Upon completion, the crude product was purified by column chromatography via silica gel to afford the desired product **3aa**.

VII. Crystallographic Data

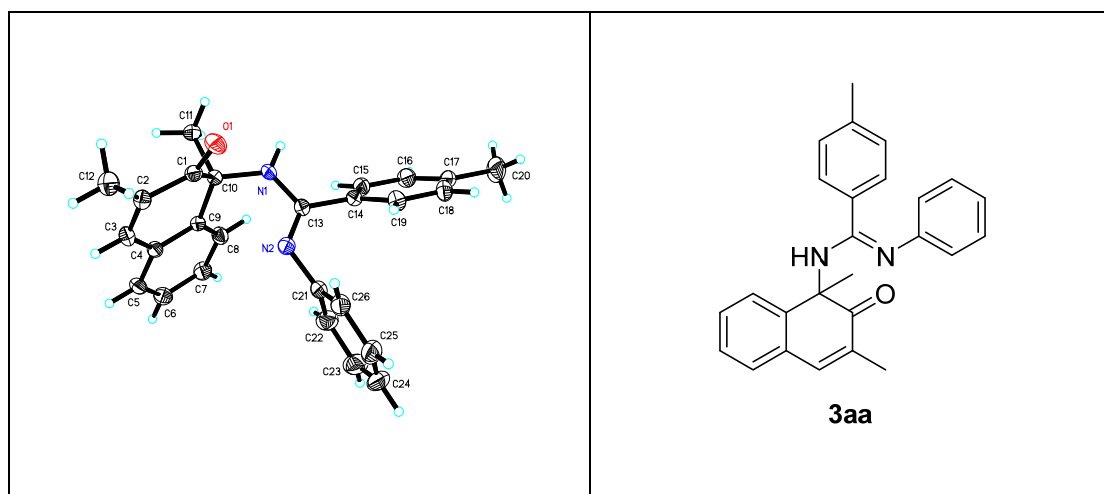


Table S4. Crystal data and structure refinement for **3aa**

Identification code	mo_ddz20013_0m	
Empirical formula	C ₂₆ H ₂₄ N ₂ O	
Formula weight	380.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.6708(10) Å	$\alpha = 90^\circ$.
	b = 6.6613(5) Å	$\beta = 108.489(2)^\circ$.
	c = 12.8991(11) Å	$\gamma = 90^\circ$.

Volume	1032.54(14) Å ³
Z	2
Density (calculated)	1.224 Mg/m ³
Absorption coefficient	0.075 mm ⁻¹
F(000)	404
Crystal size	0.200 x 0.120 x 0.090 mm ³
Theta range for data collection	2.727 to 25.991°.
Index ranges	-15<=h<=15, -8<=k<=8, -15<=l<=13
Reflections collected	9850
Independent reflections	4023 [R(int) = 0.0270]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6347
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4023 / 1 / 266
Goodness-of-fit on F ²	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.0928
R indices (all data)	R1 = 0.0579, wR2 = 0.1035
Absolute structure parameter	-0.1(9)
Extinction coefficient	0.038(5)
Largest diff. peak and hole	0.165 and -0.153 e.Å ⁻³

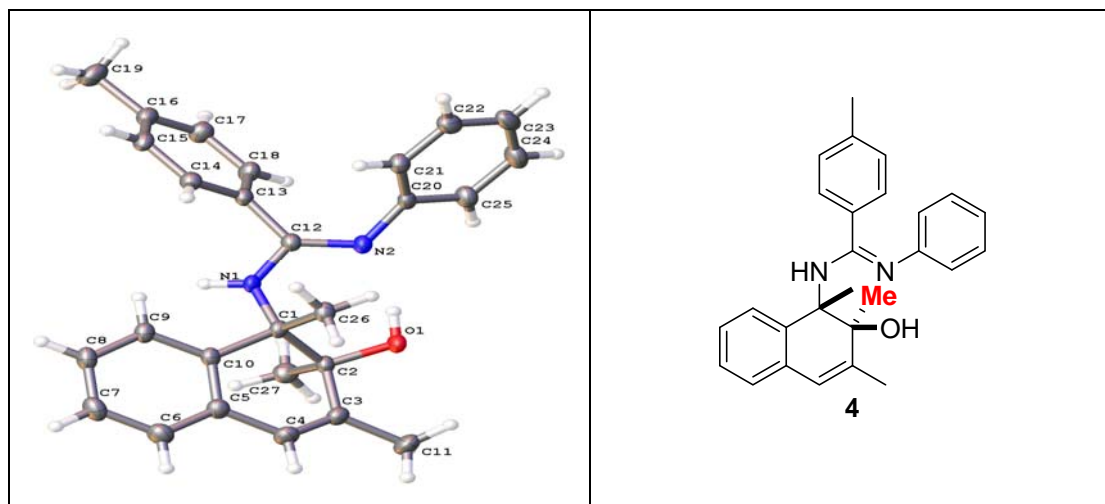


Table S5. Crystal data and structure refinement for **4**

Identification code	210512fyh_1_0m
Empirical formula	C ₂₇ H ₂₈ N ₂ O
Formula weight	396.51
Temperature	193.0 K
Wavelength	1.34139 Å

Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5678(8) Å	α = 99.125(3)°.
	b = 10.2437(8) Å	β = 106.904(3)°.
	c = 12.1688(9) Å	γ = 96.828(3)°.
Volume	1109.37(15) Å ³	
Z	2	
Density (calculated)	1.187 Mg/m ³	
Absorption coefficient	0.359 mm ⁻¹	
F(000)	424	
Crystal size	0.07 x 0.06 x 0.05 mm ³	
Theta range for data collection	3.862 to 54.923°.	
Index ranges	-11 ≤ h ≤ 11, -9 ≤ k ≤ 12, -14 ≤ l ≤ 14	
Reflections collected	11819	
Independent reflections	4093 [R(int) = 0.0433]	
Completeness to theta = 53.594°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5667	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4093 / 0 / 276	
Goodness-of-fit on F ²	1.059	
Final R indices [I > 2σ(I)]	R1 = 0.0577, wR2 = 0.1591	
R indices (all data)	R1 = 0.0660, wR2 = 0.1695	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.269 and -0.263 e.Å ⁻³	

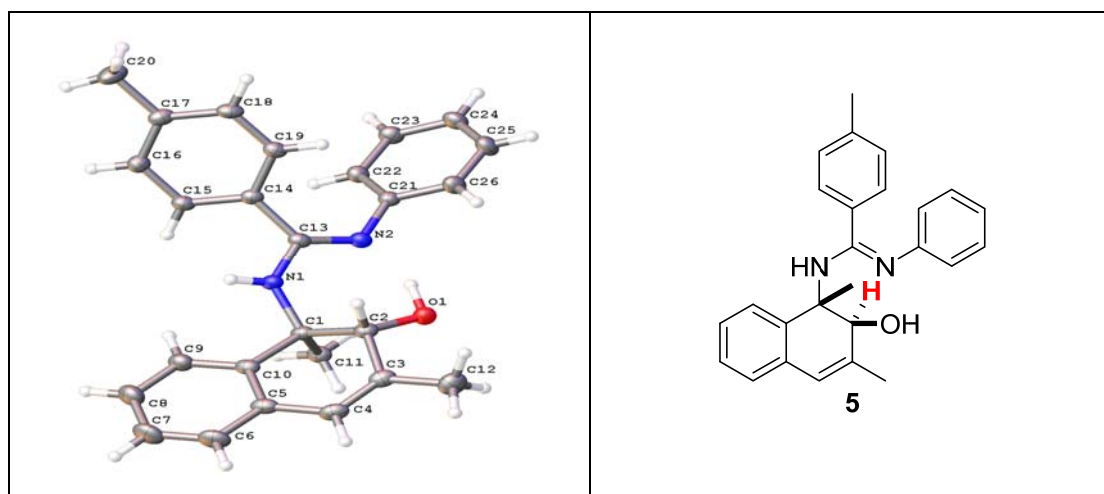


Table S6. Crystal data and structure refinement for **5**

Identification code 210512fyh_2

Empirical formula	C ₂₆ H ₂₆ N ₂ O	
Formula weight	382.49	
Temperature	192.99 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 19.3797(3) Å	α = 90°.
	b = 10.5232(2) Å	β = 90°.
	c = 20.7635(3) Å	γ = 90°.
Volume	4234.44(12) Å ³	
Z	8	
Density (calculated)	1.200 Mg/m ³	
Absorption coefficient	0.365 mm ⁻¹	
F(000)	1632	
Crystal size	0.09 x 0.07 x 0.05 mm ³	
Theta range for data collection	3.704 to 54.959°.	
Index ranges	-23 ≤ h ≤ 23, -11 ≤ k ≤ 12, -25 ≤ l ≤ 25	
Reflections collected	43616	
Independent reflections	4018 [R(int) = 0.0406]	
Completeness to theta = 53.594°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.6413	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4018 / 0 / 269	
Goodness-of-fit on F ²	1.045	
Final R indices [I > 2σ(I)]	R1 = 0.0398, wR2 = 0.0995	
R indices (all data)	R1 = 0.0475, wR2 = 0.1055	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.272 and -0.252 e.Å ⁻³	

VIII. References

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- [8] D. Yang, L. Wang, F. Han, D. Li, D. Zhao and R. Wang, Intermolecular Enantioselective Dearomatization Reaction of β -Naphthol Using meso-Aziridine: A Bifunctional In Situ Generated Magnesium Catalyst, *Angew. Chem., Int. Ed.*, 2015, **54**, 2185-2189.
- [9] [9]. Shou-Guo Wang.; Qin Yin.; Chun-Xiang Zhuo.; Shu-Li You., *Angew. Chem. Int. Ed.* **2015**, **54**, 647 –65

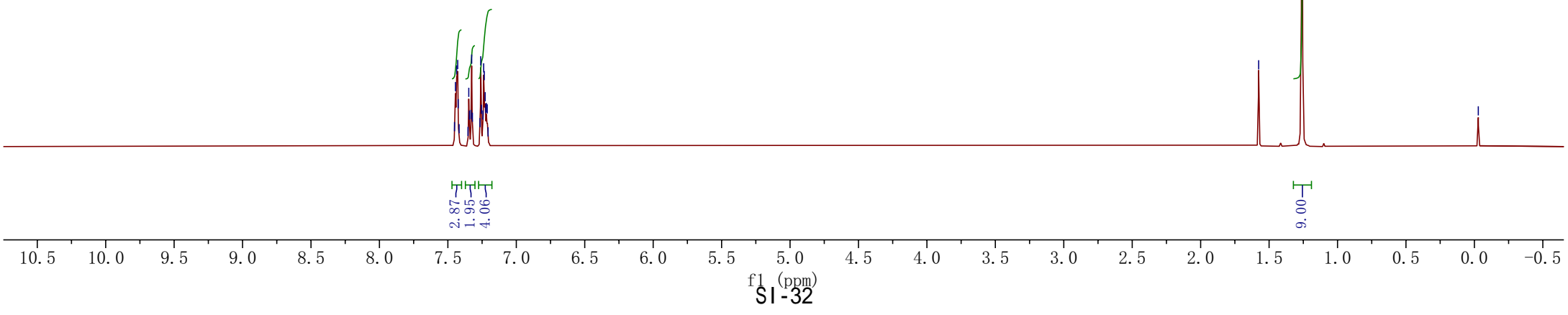
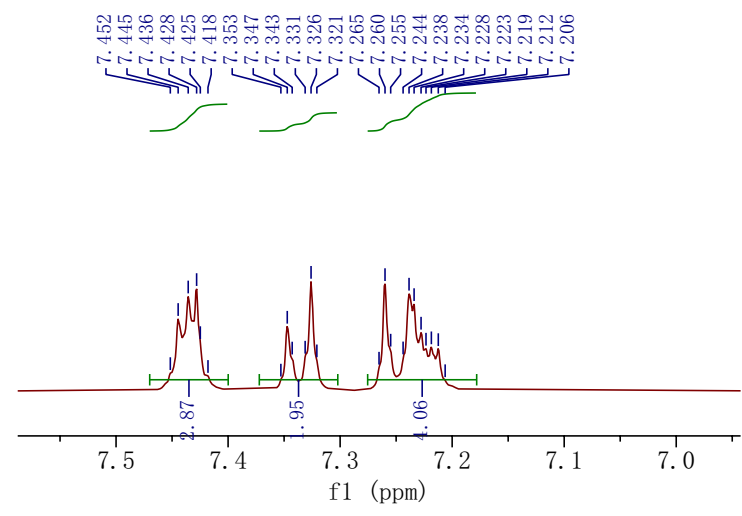
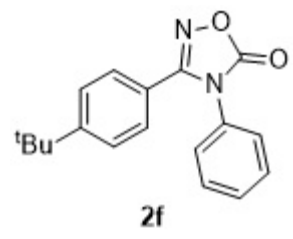
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7.228
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7.219
7.212
7.206

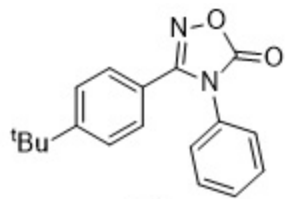
— 1.576

— 1.260

— 0.029

IX. NMR Spectra of New Compounds (¹H NMR, ¹³C NMR)





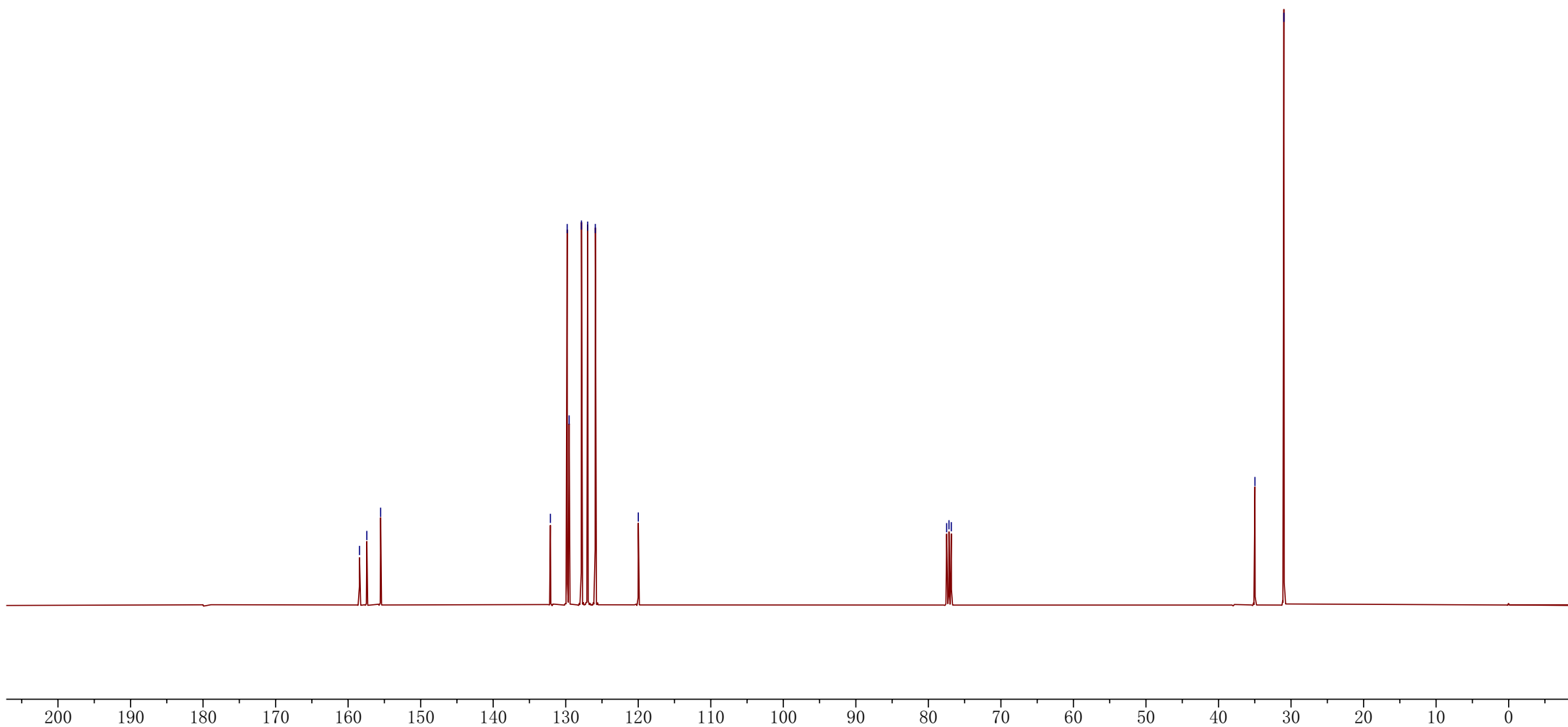
2f

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157.422
155.515

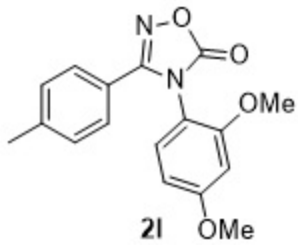
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129.527
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125.923
119.991

77.479
77.160
76.842

34.977
30.983



f1 (ppm)
SI-33

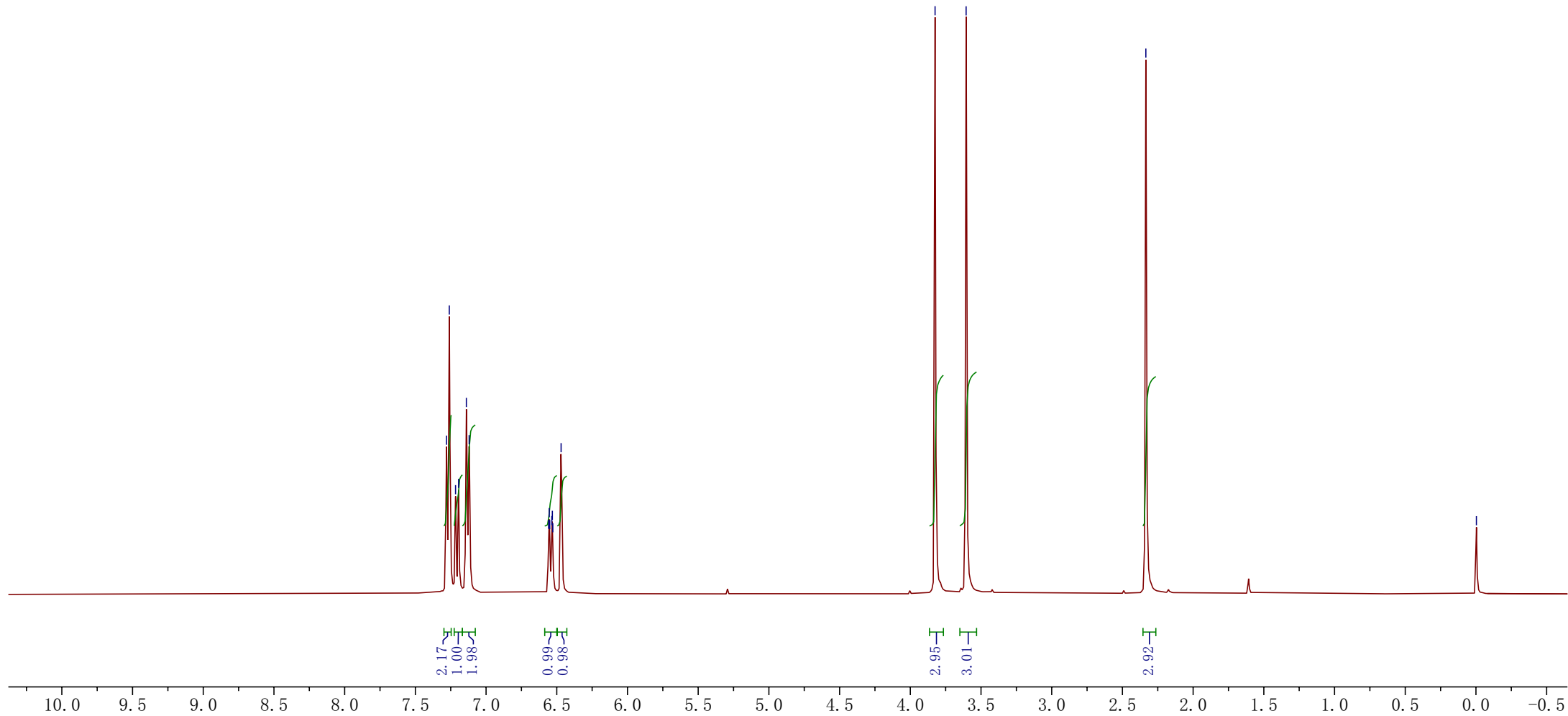


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6.535
6.531
6.528
6.469

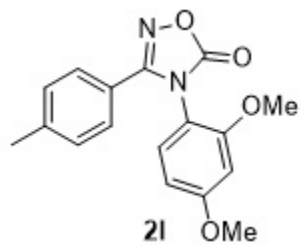
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2.334

0.003



f1 (ppm)
SI-34



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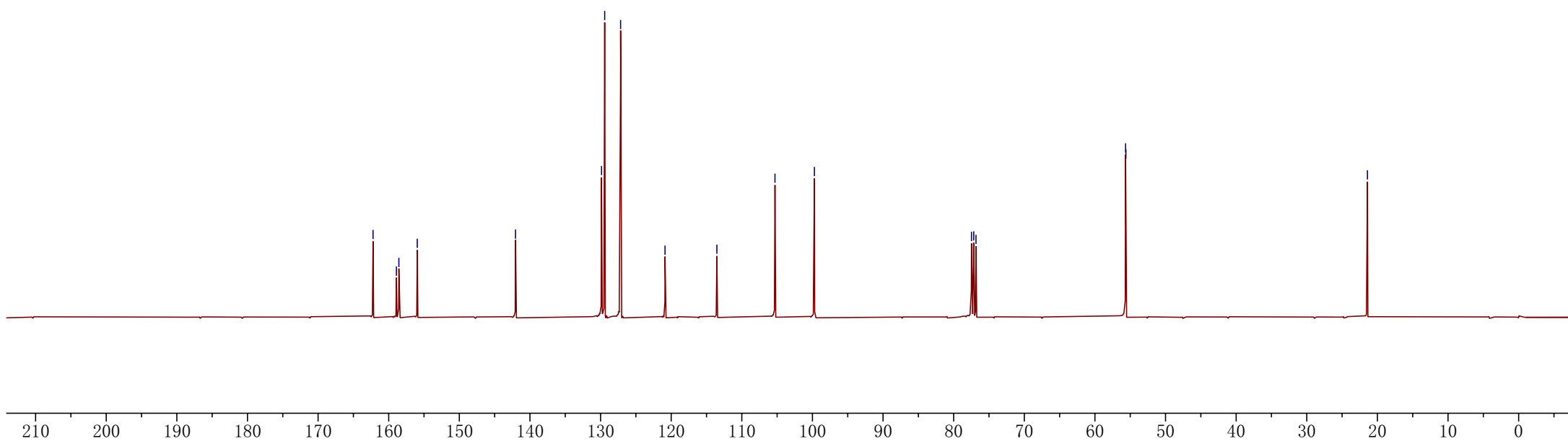
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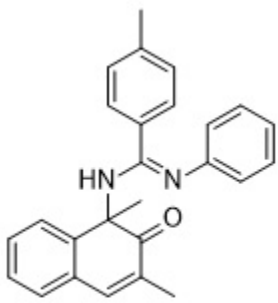
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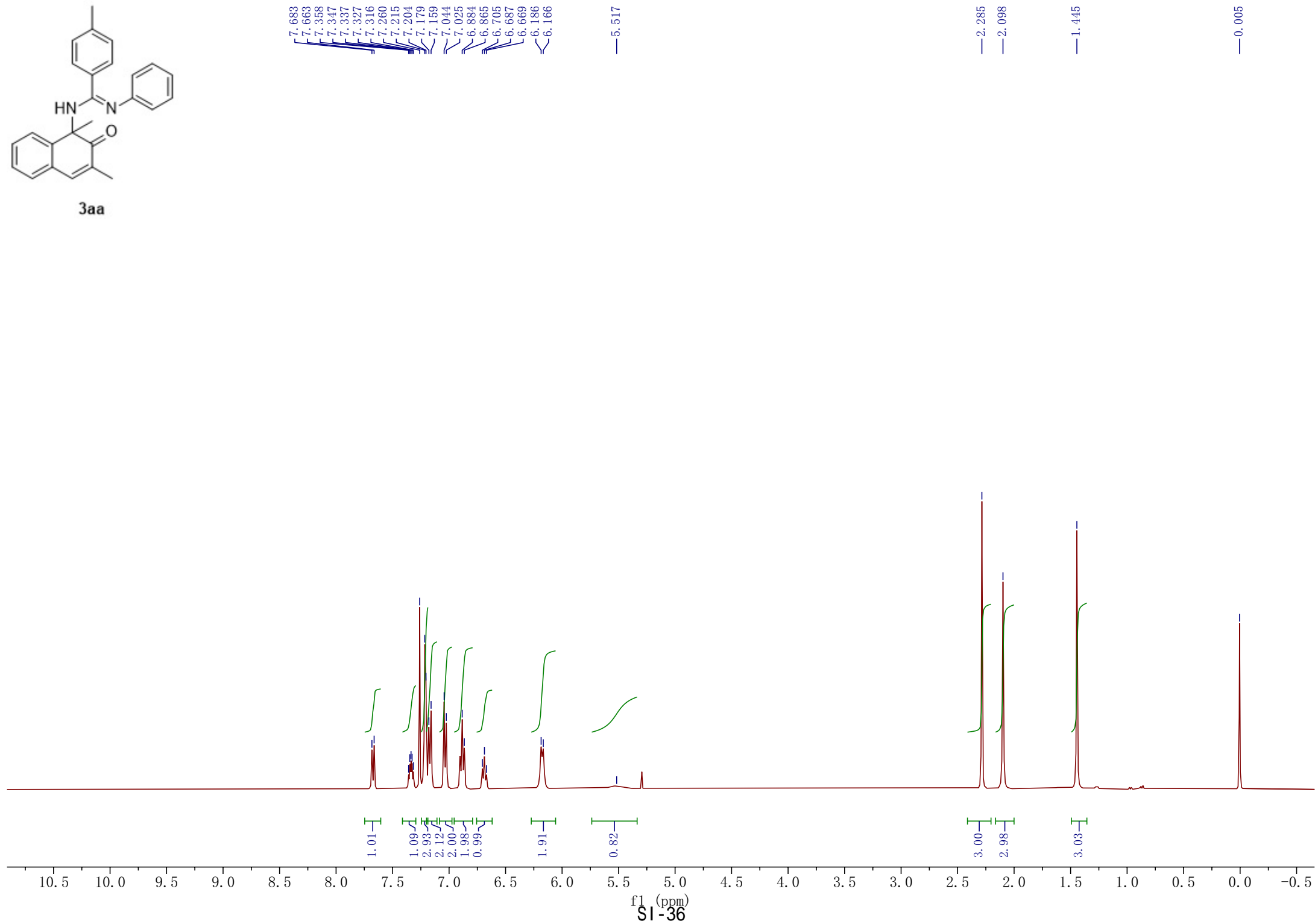
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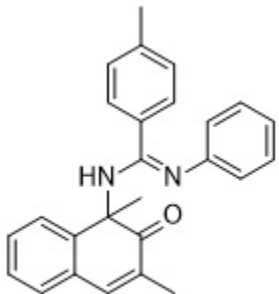


f1 (ppm)
SI-35

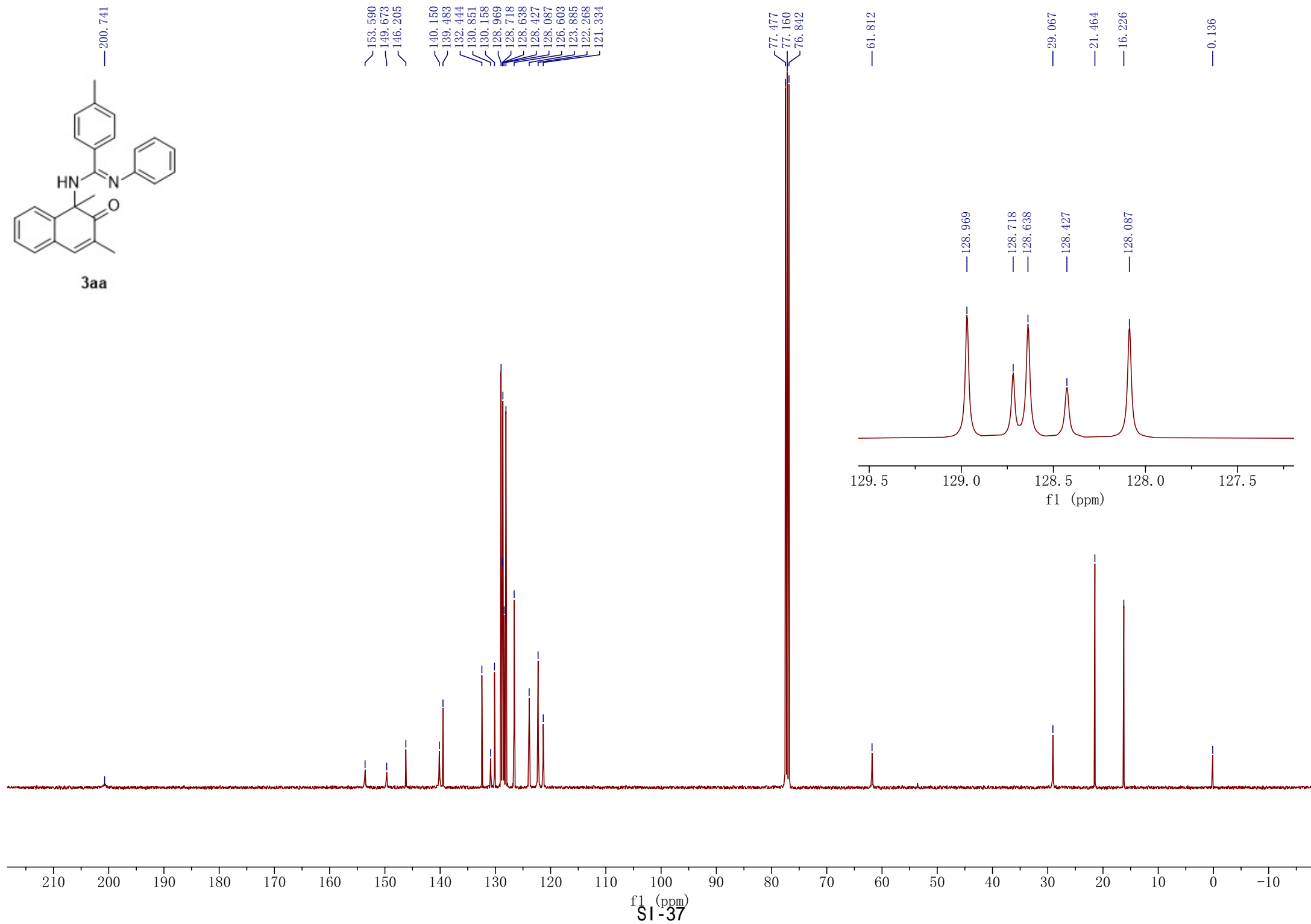


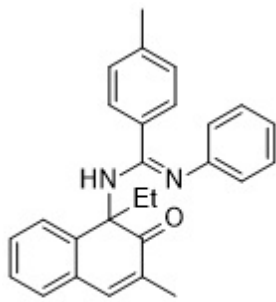
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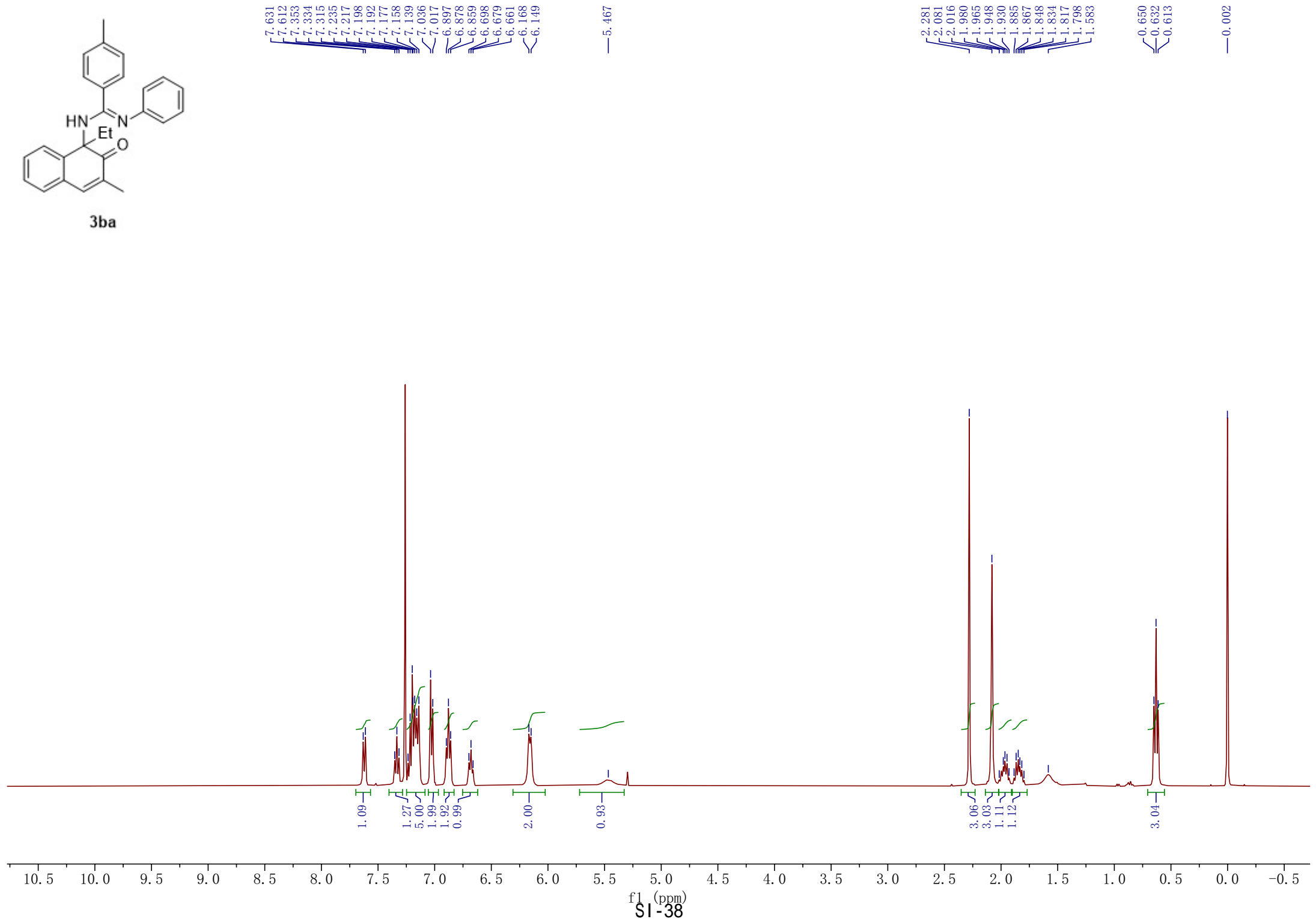


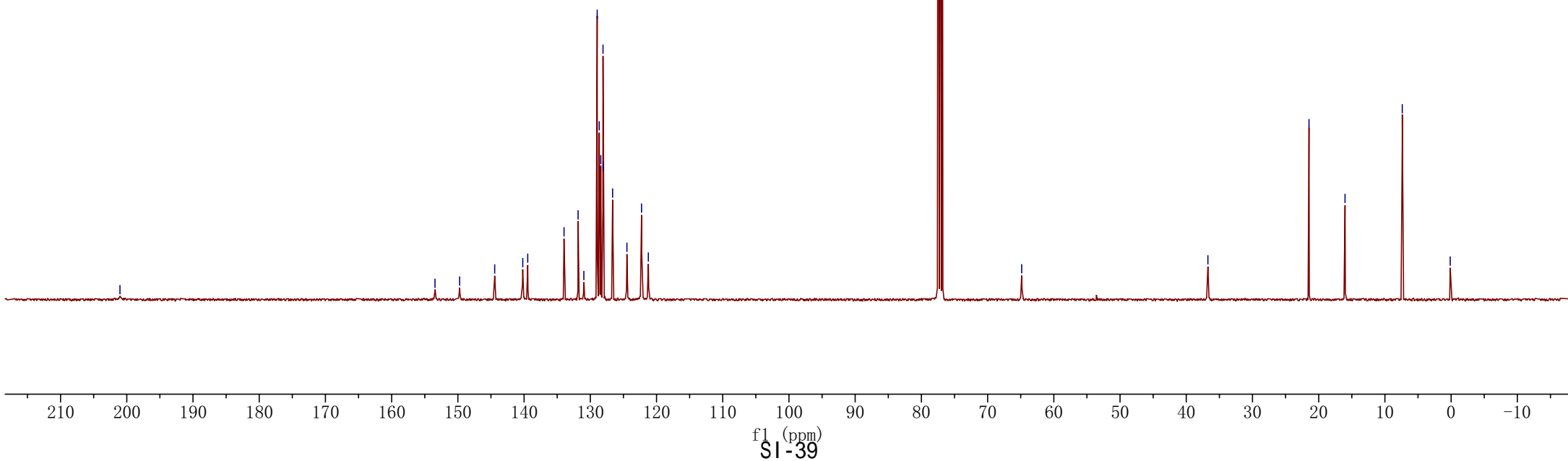
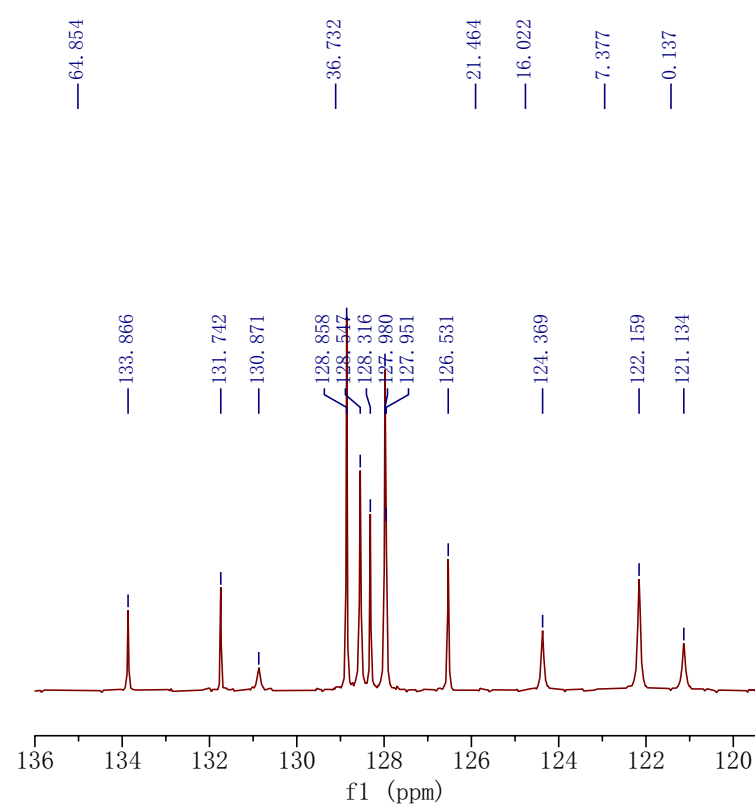
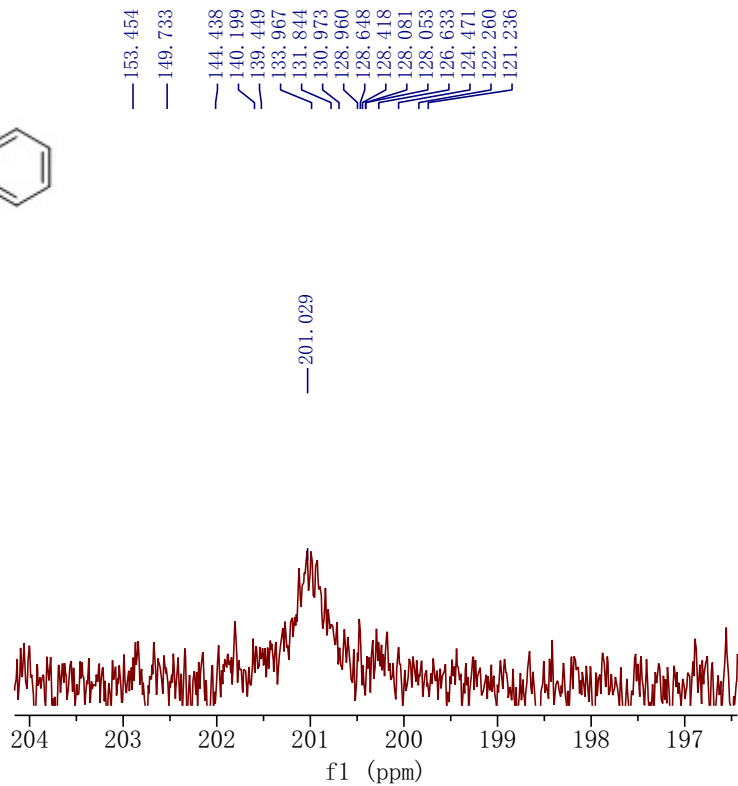
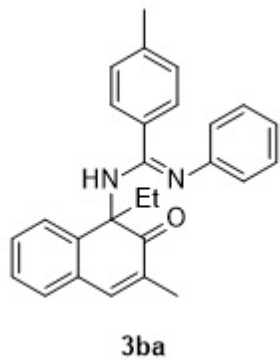
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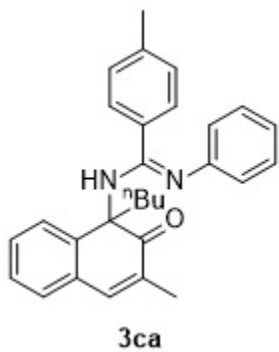




3ba



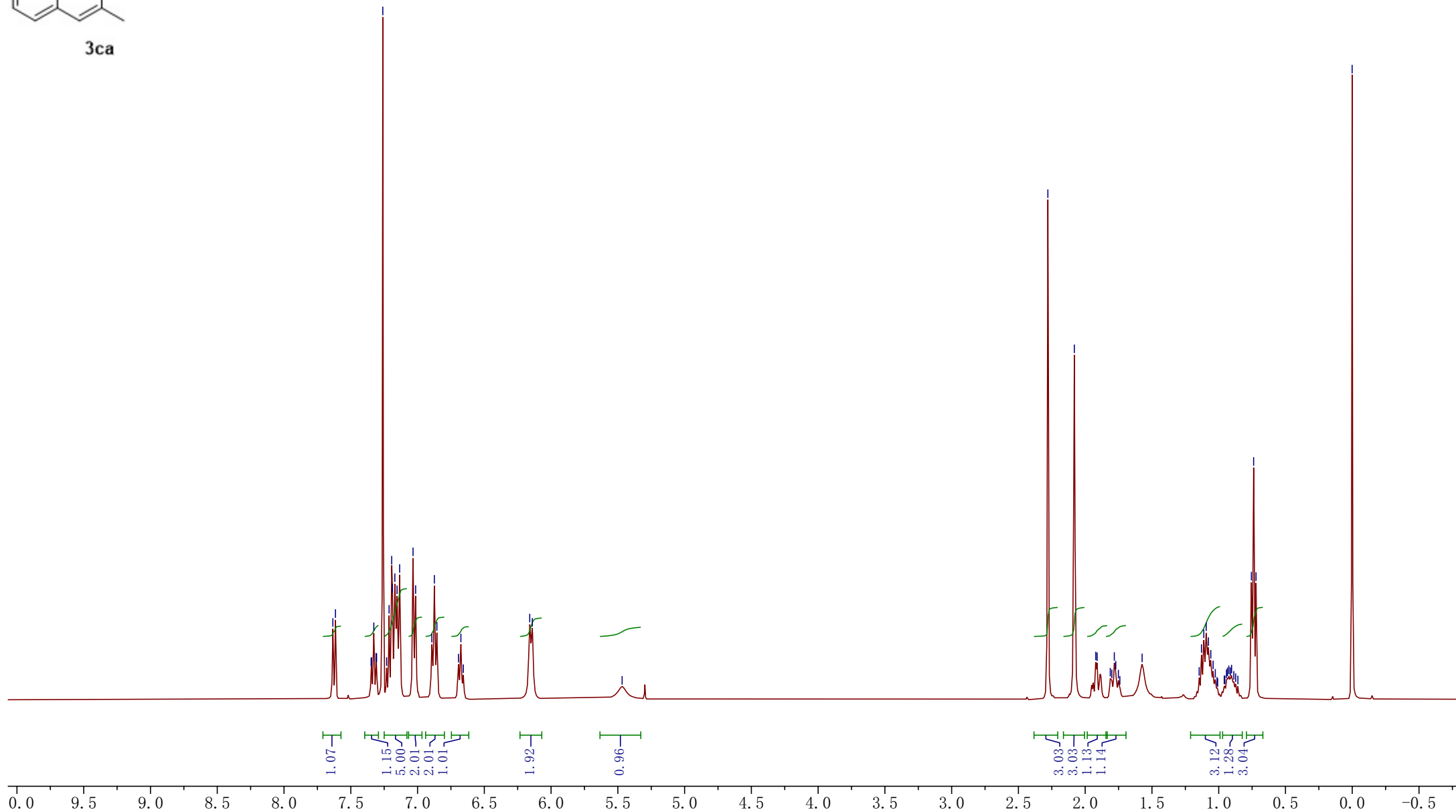




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6.141

5.468

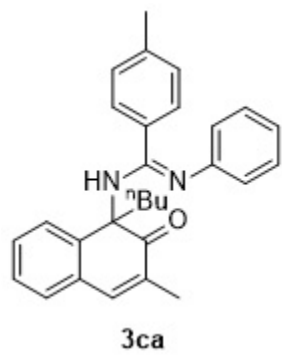
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1.129
1.112
1.094
1.077
1.059
1.042
1.026
1.013
1.008
0.959
0.954
0.942
0.934
0.924
0.913
0.904
0.887
0.873
0.856
0.755
0.739
0.720
0.001



f1 (ppm)

SI-40

— 201.000



— 153.380
— 149.726
— 144.782
— 140.144
— 139.426
— 133.785
— 131.675
— 130.978
— 128.952
— 128.631
— 128.392
— 128.066
— 126.582
— 124.434
— 122.255
— 121.221

— 77.477
— 77.160
— 76.843

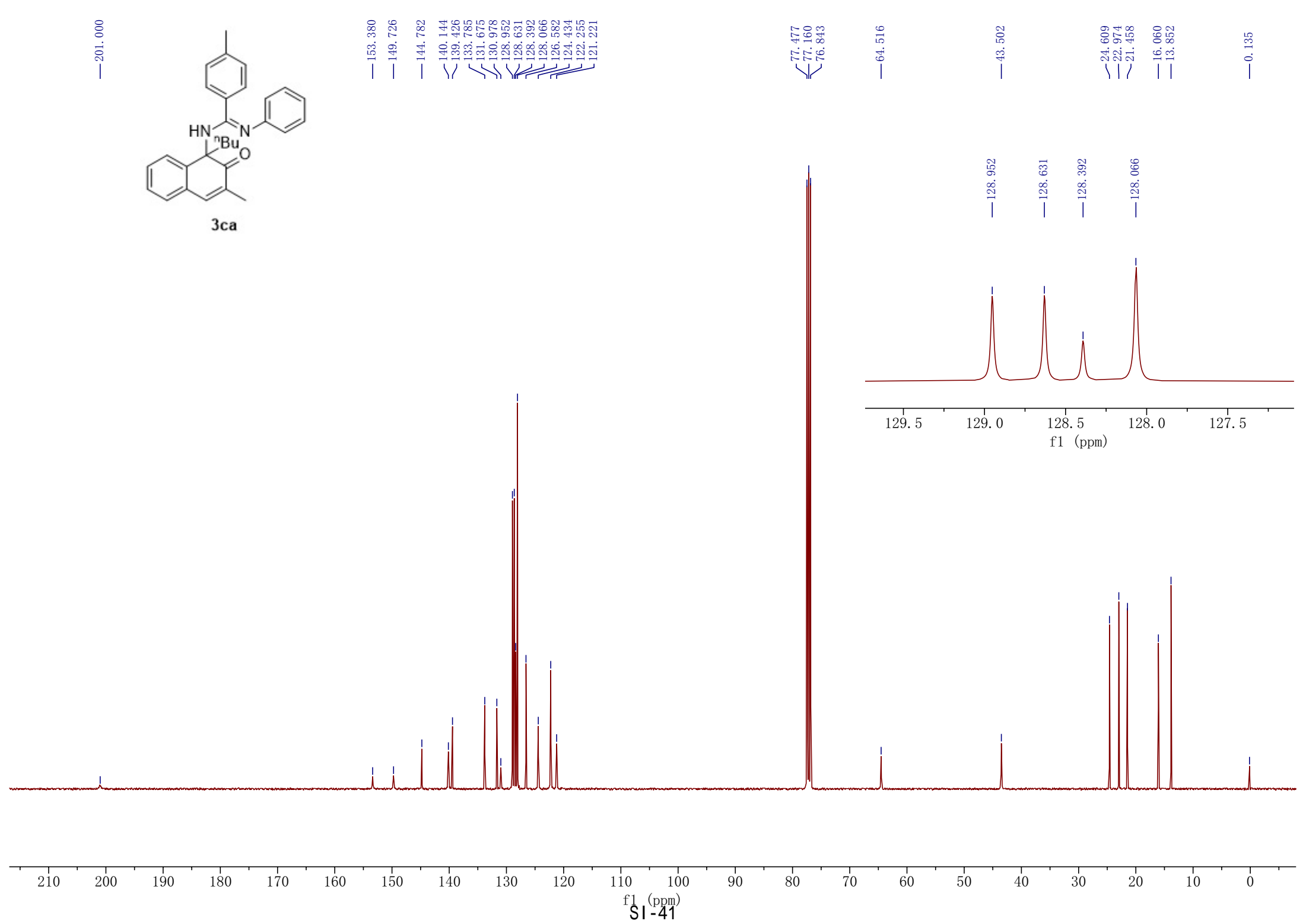
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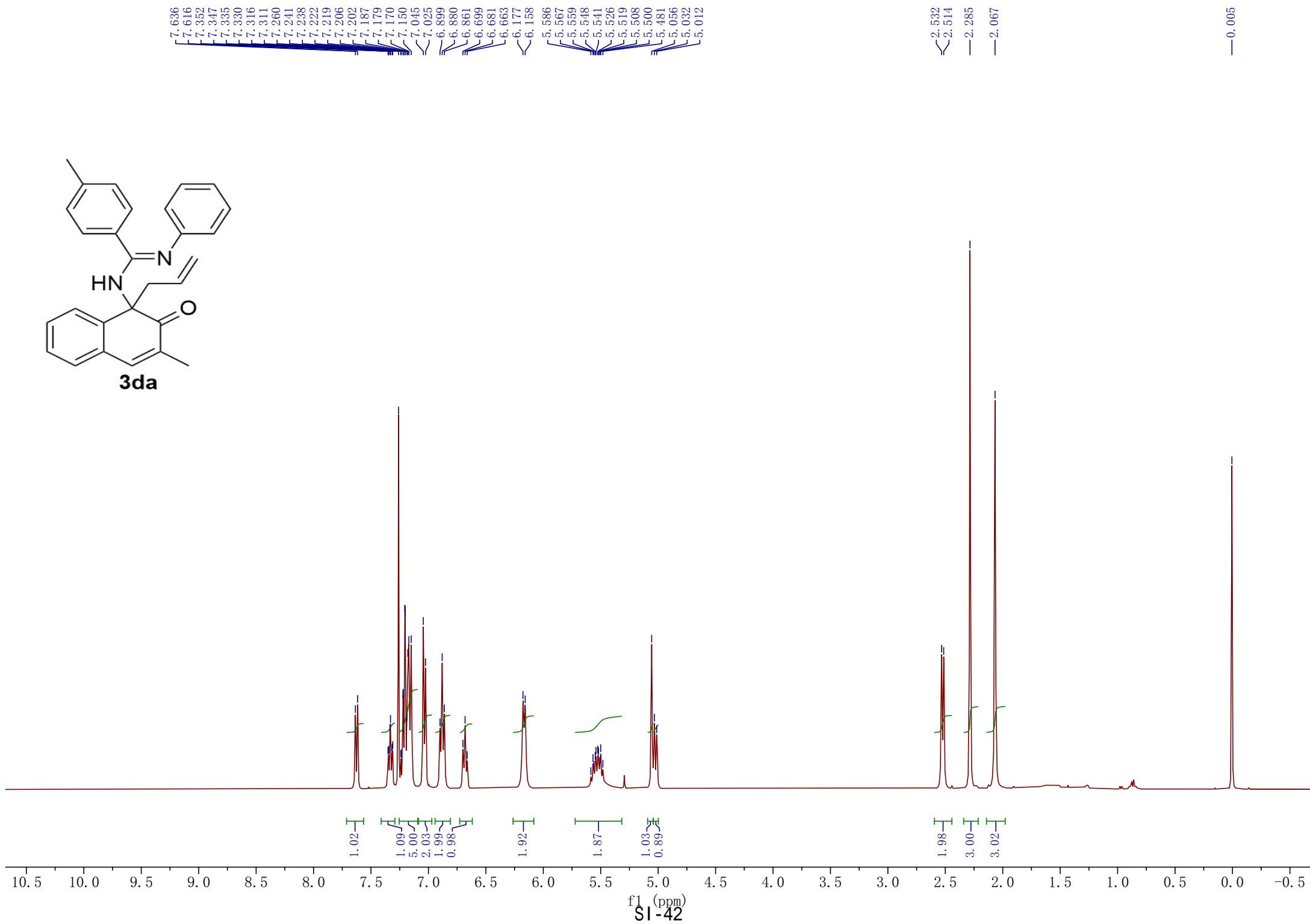
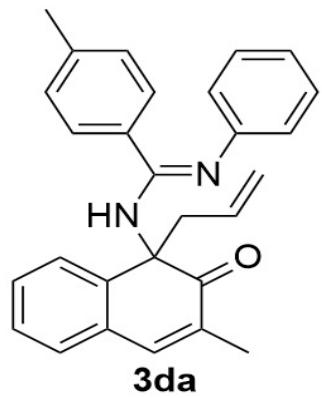
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— 24.609
— 22.974
— 21.458

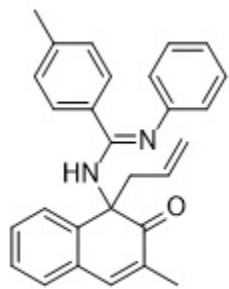
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— 13.852

— 0.135





— 199.980



3da

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— 149.744
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— 140.204
— 139.431
— 133.177
— 131.039
— 131.000
— 128.988
— 128.576
— 128.373
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— 126.722
— 124.533
— 122.214
— 121.264
— 120.072

77.478
77.160
76.843

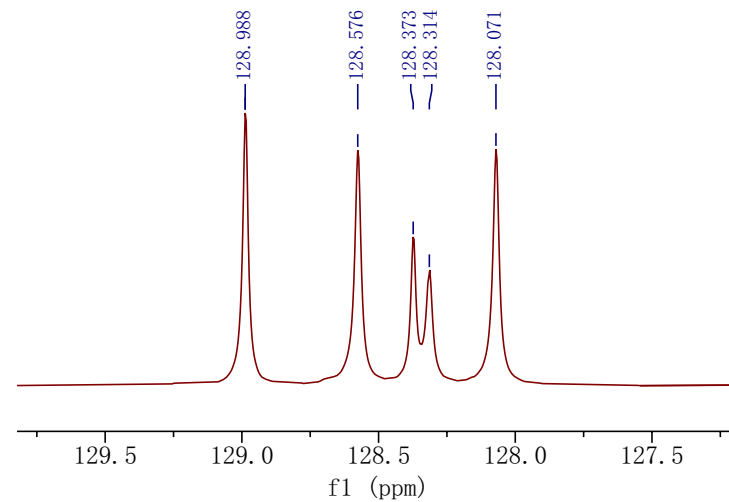
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— 46.427

— 21.450

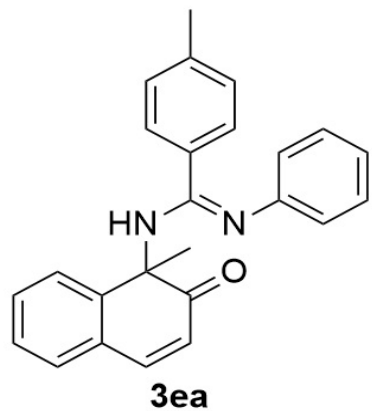
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— 0.132



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f1 (ppm)
SI-43



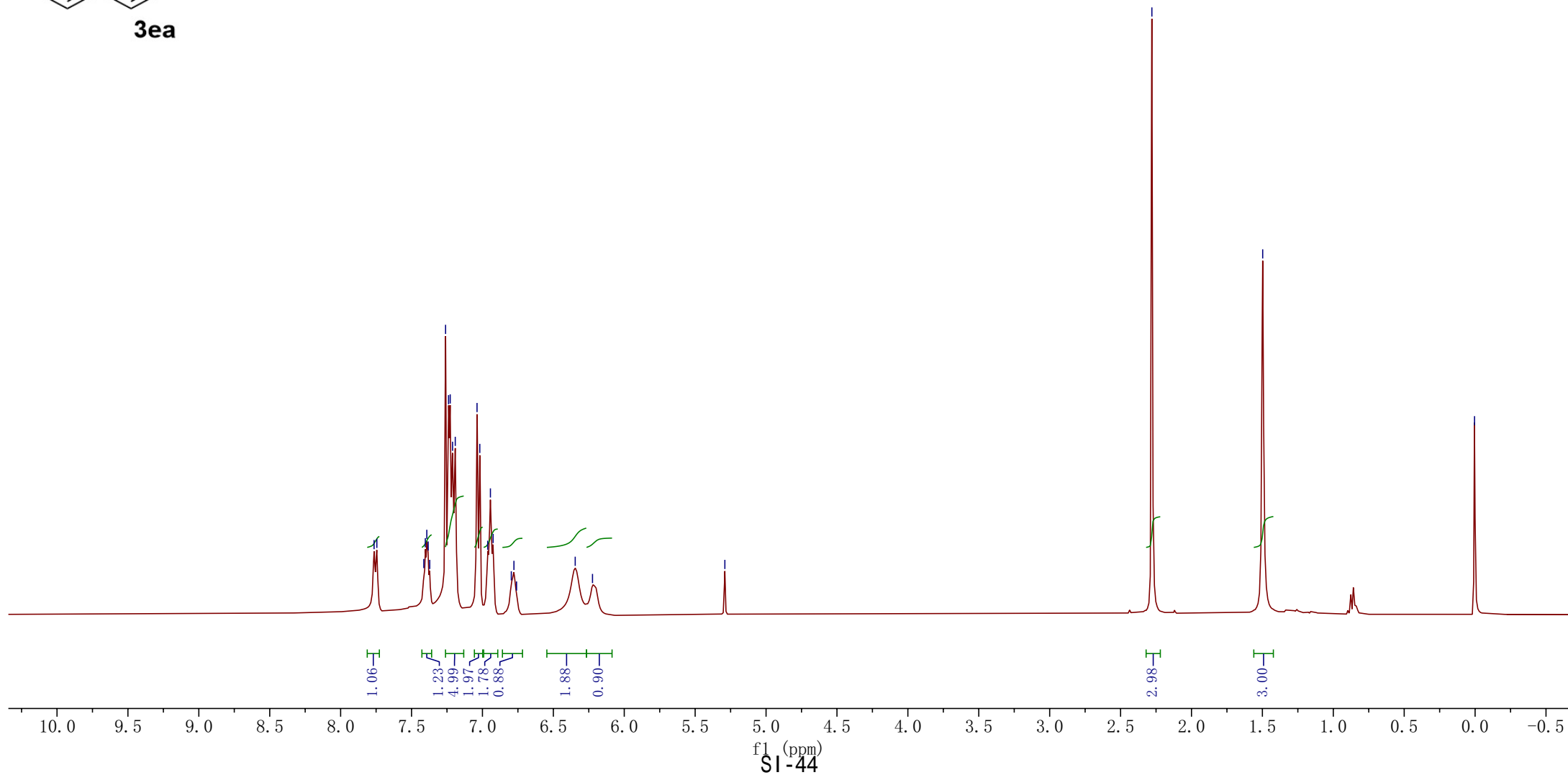
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6.346
6.224

5.291

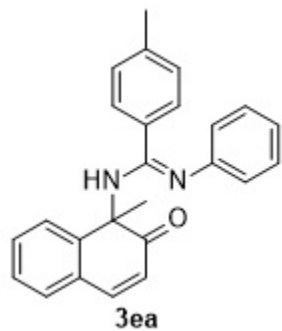
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1.498

0.004



—200.741



—155.025

—146.284

—141.699

—139.767

—129.776

—129.672

—128.956

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—128.224

—126.775

—125.220

—124.759

—123.152

—122.227

—77.478

—77.160

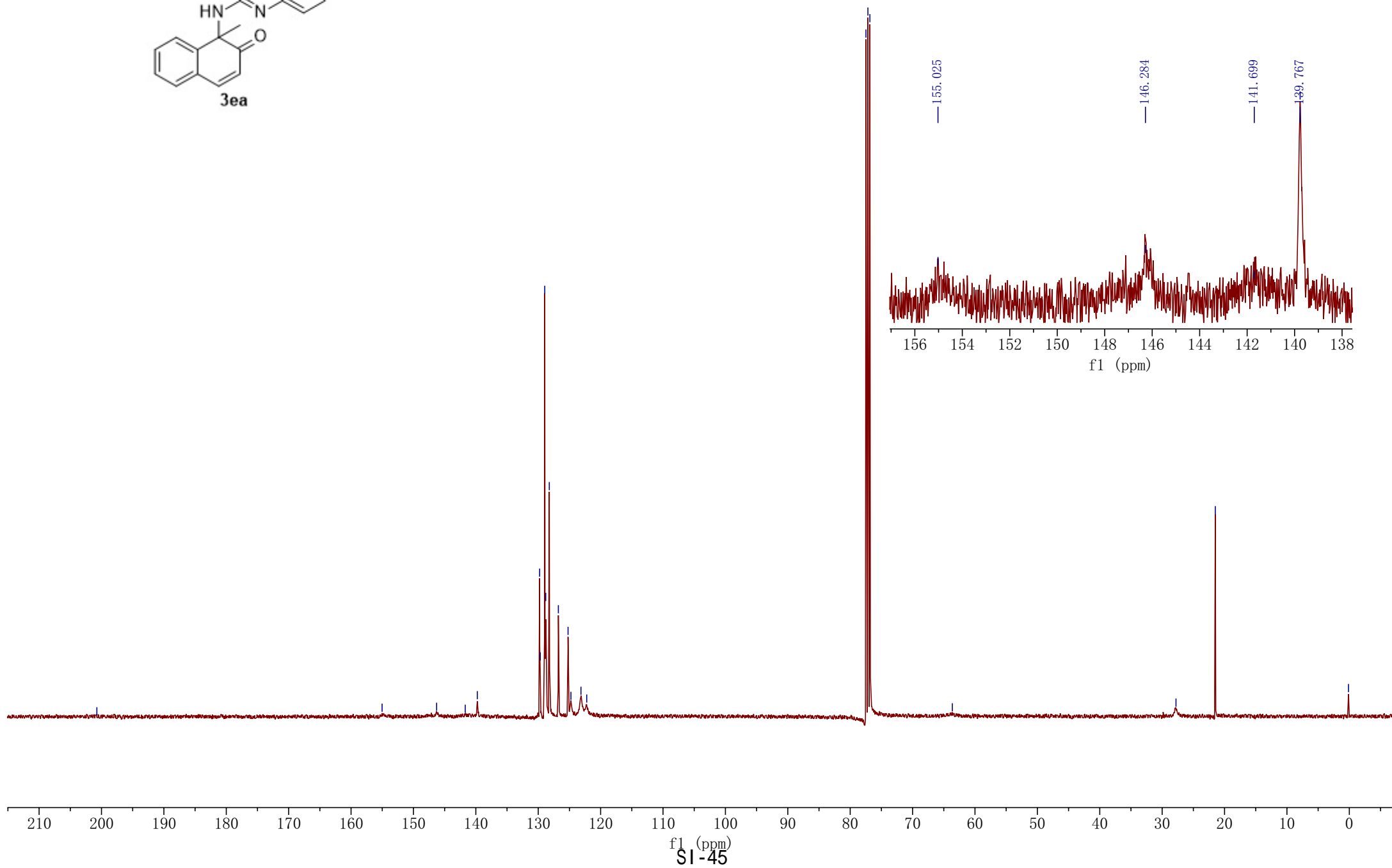
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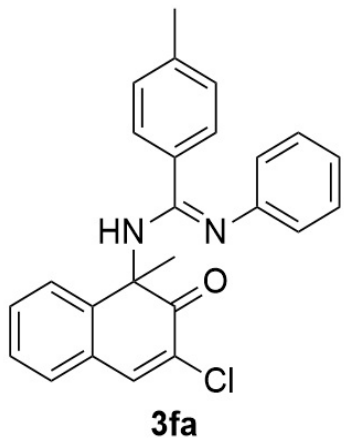
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—21.481

—0.132





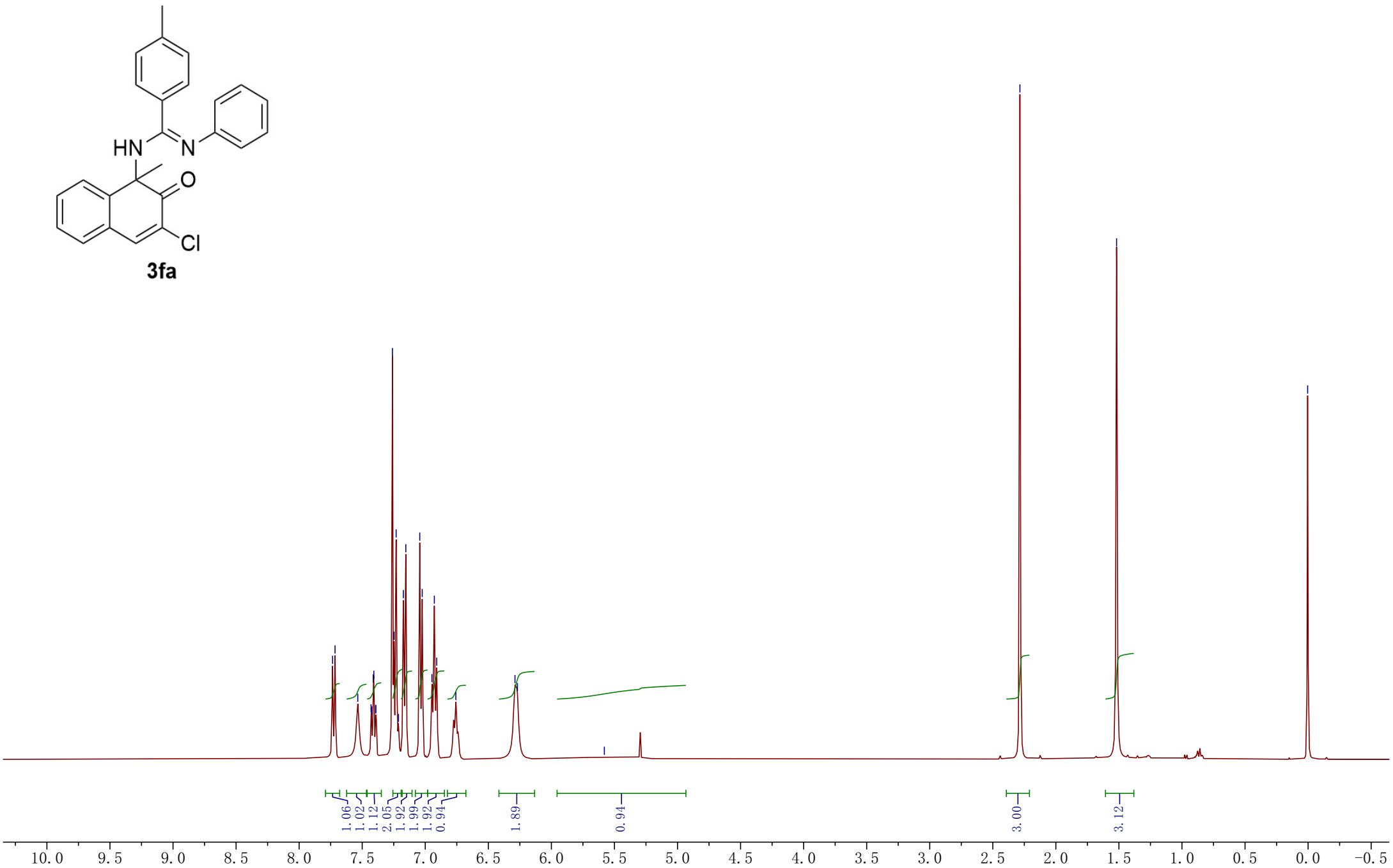
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6.928
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6.269

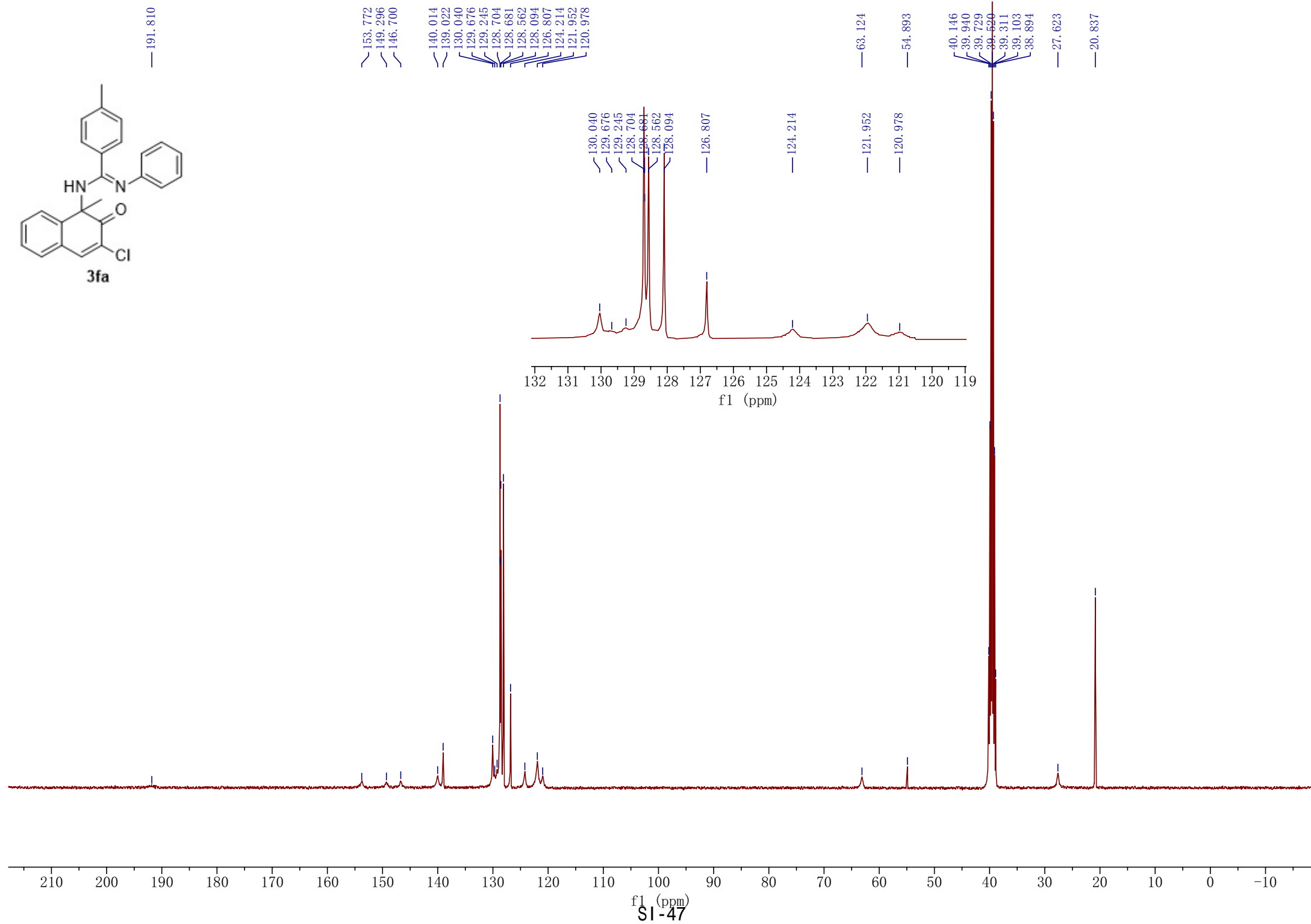
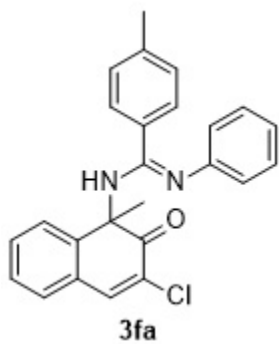
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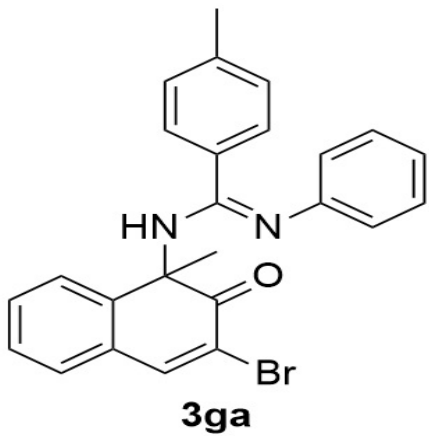
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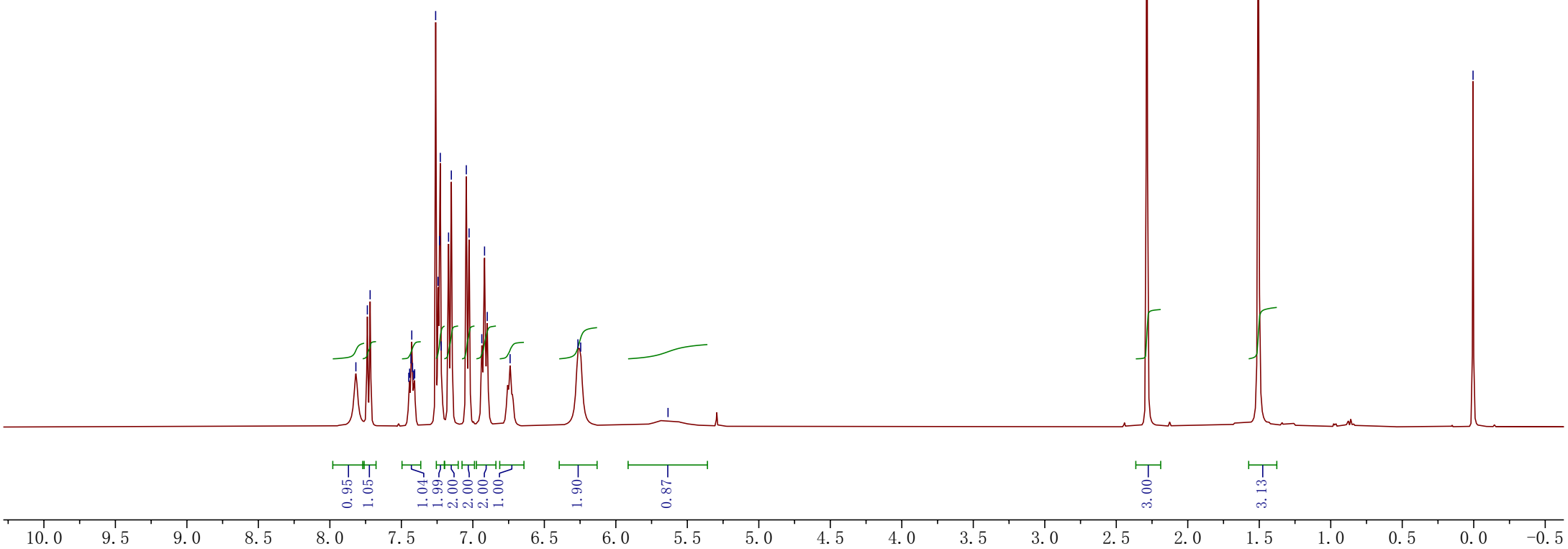
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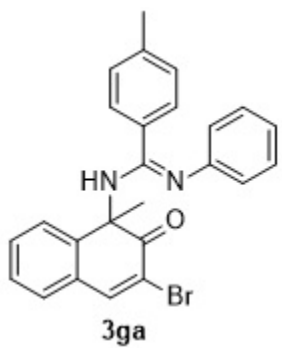
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127.084

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122.224

121.913

77.478

77.160

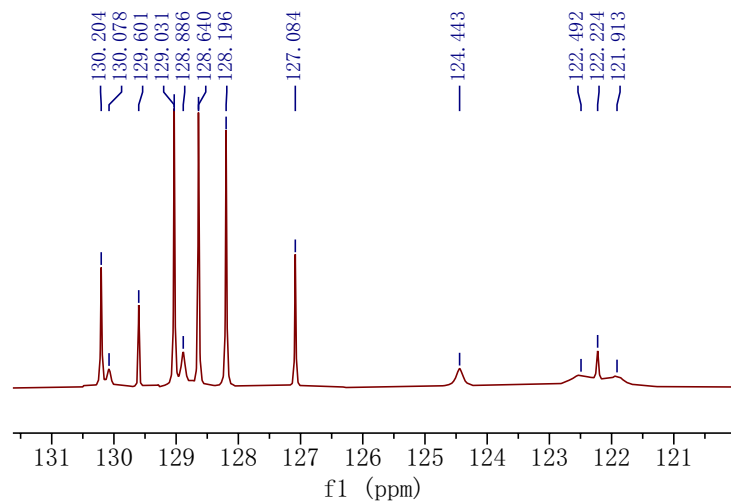
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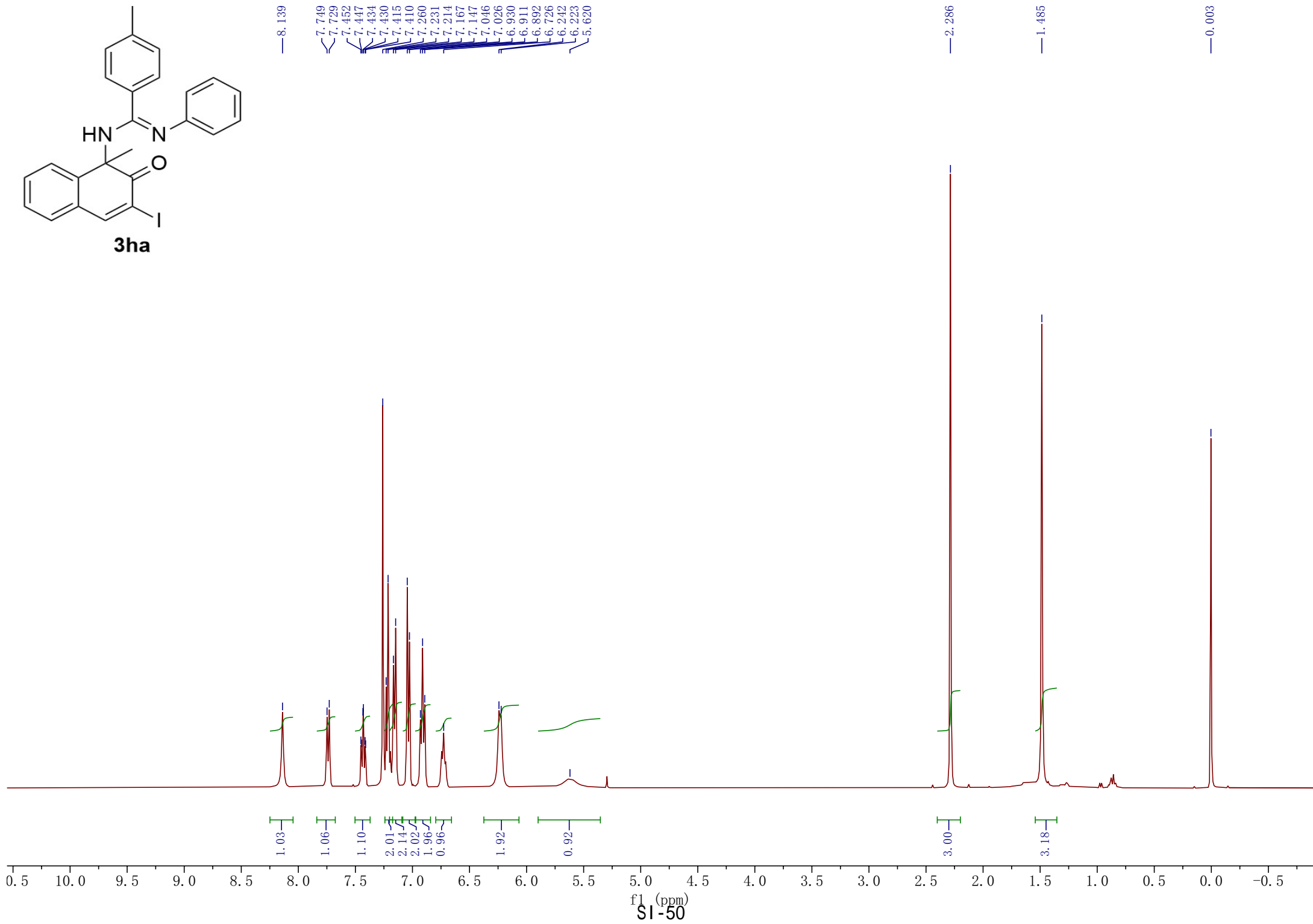
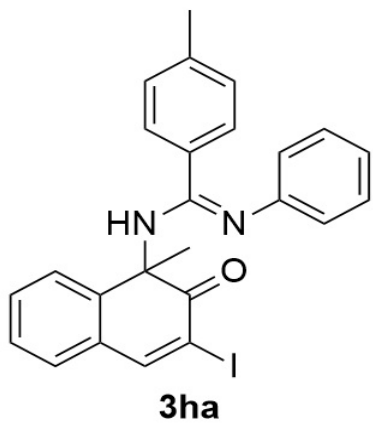
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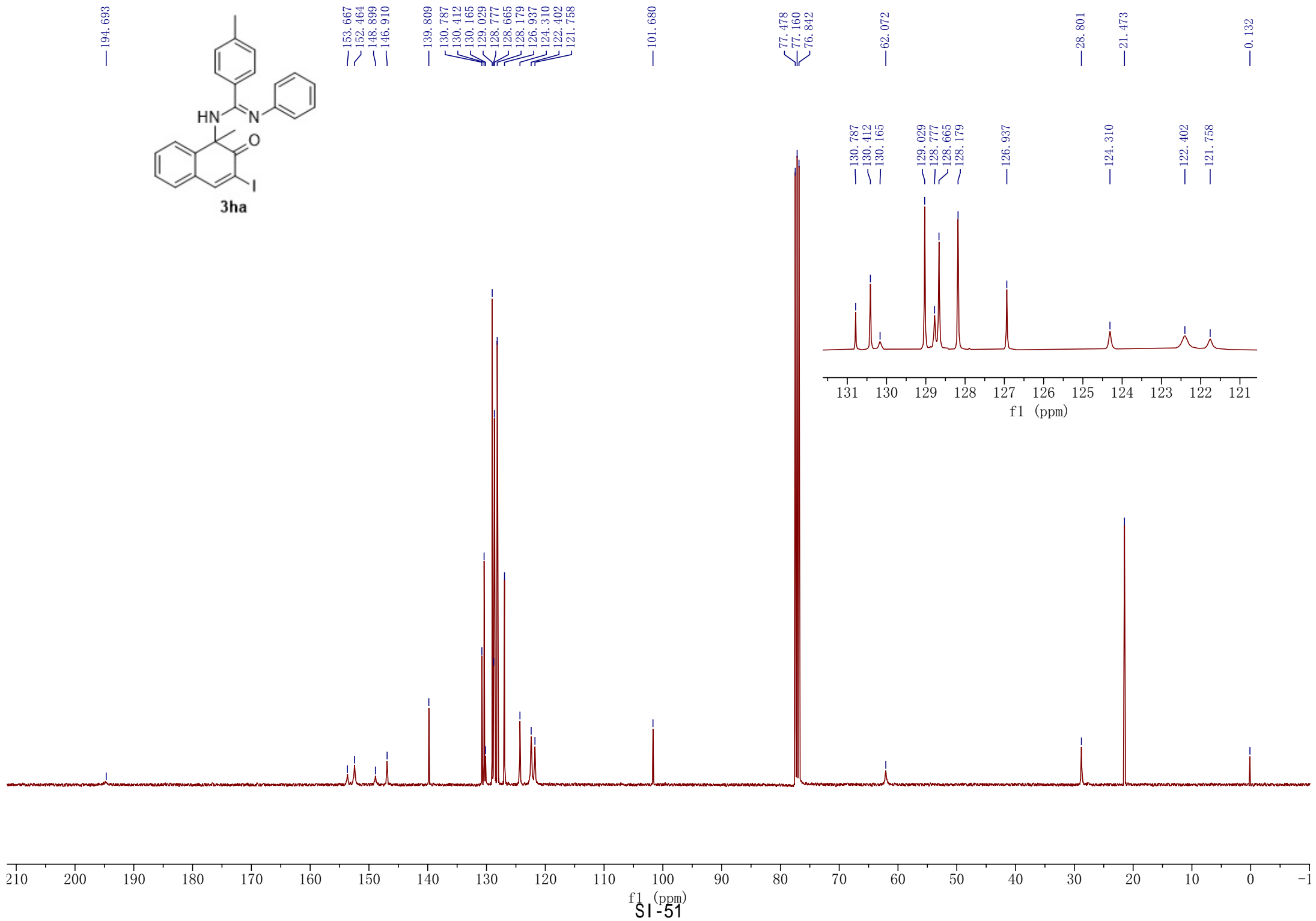
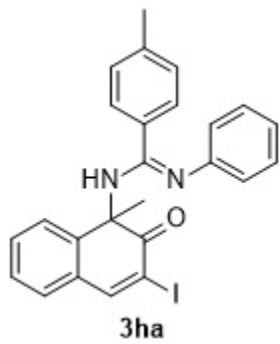
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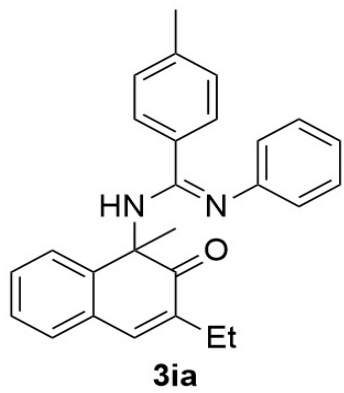


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f1 (ppm)
SI-49







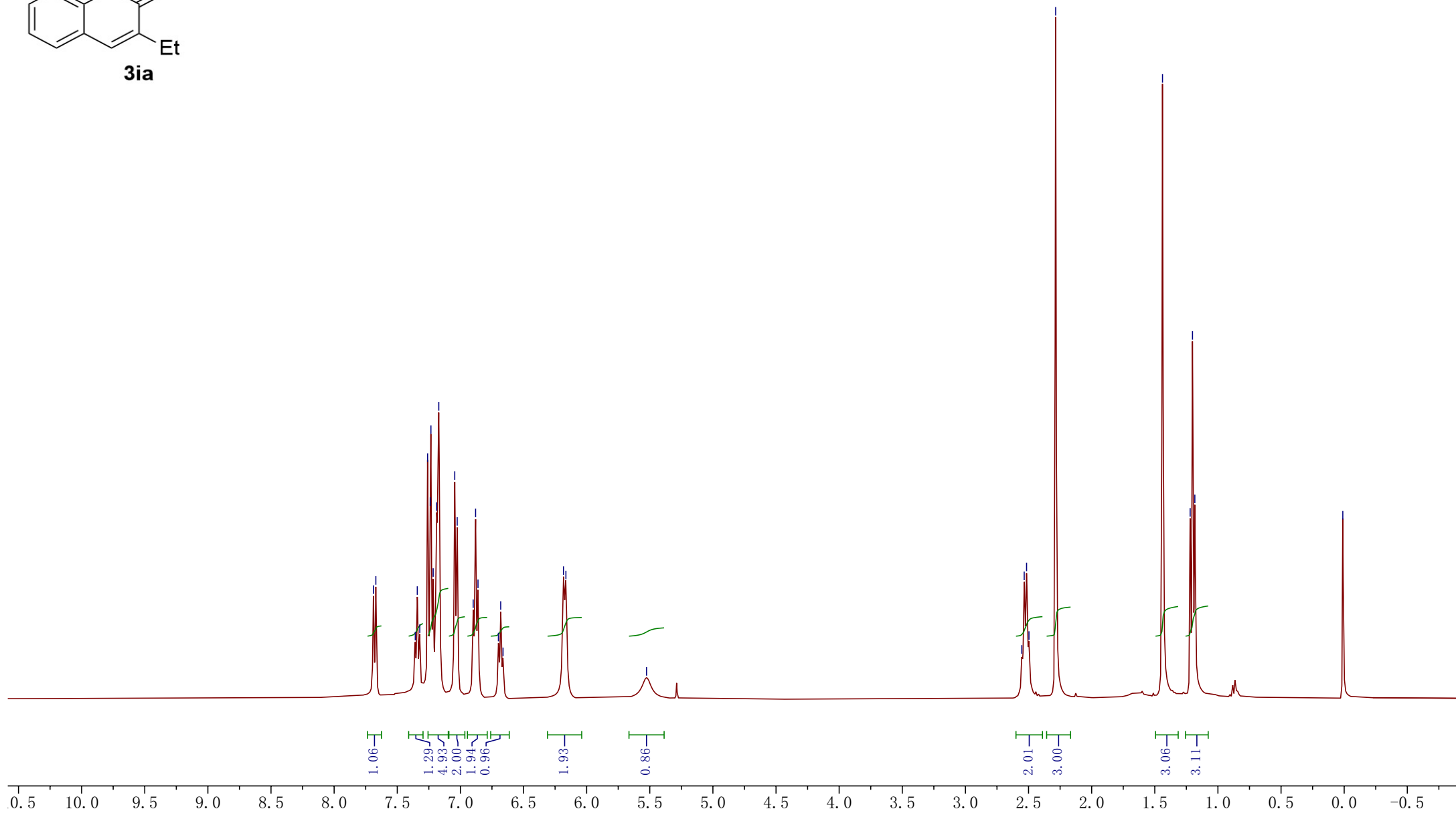
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6.681
6.662
6.184
6.164

5.525

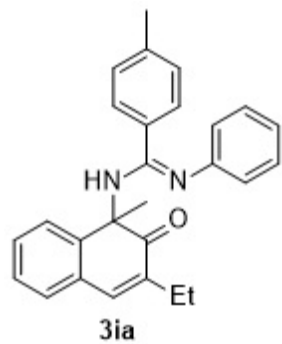
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2.285

1.439
1.220
1.201
1.183

0.011



— 200.220



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138.625
137.853
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130.154
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122.205
121.224

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77.161
76.843

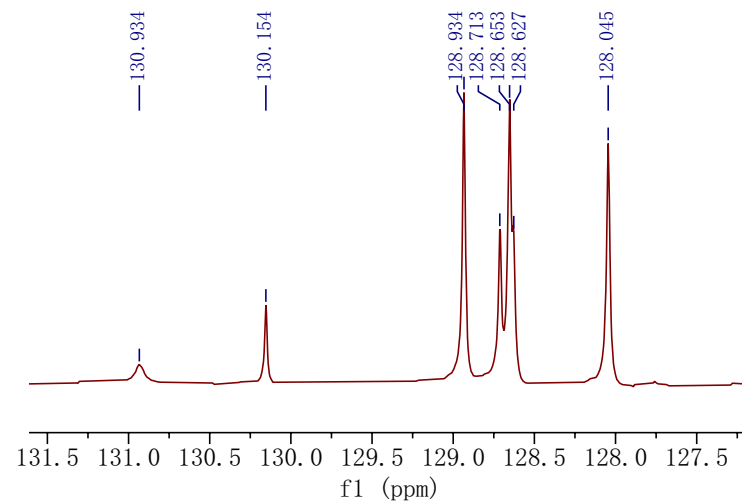
— 61.921

— 29.028

22.810
21.439

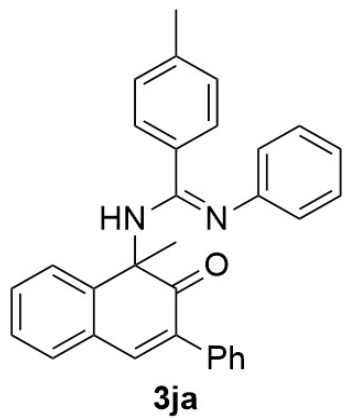
— 13.140

— 0.126



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)
SI-53



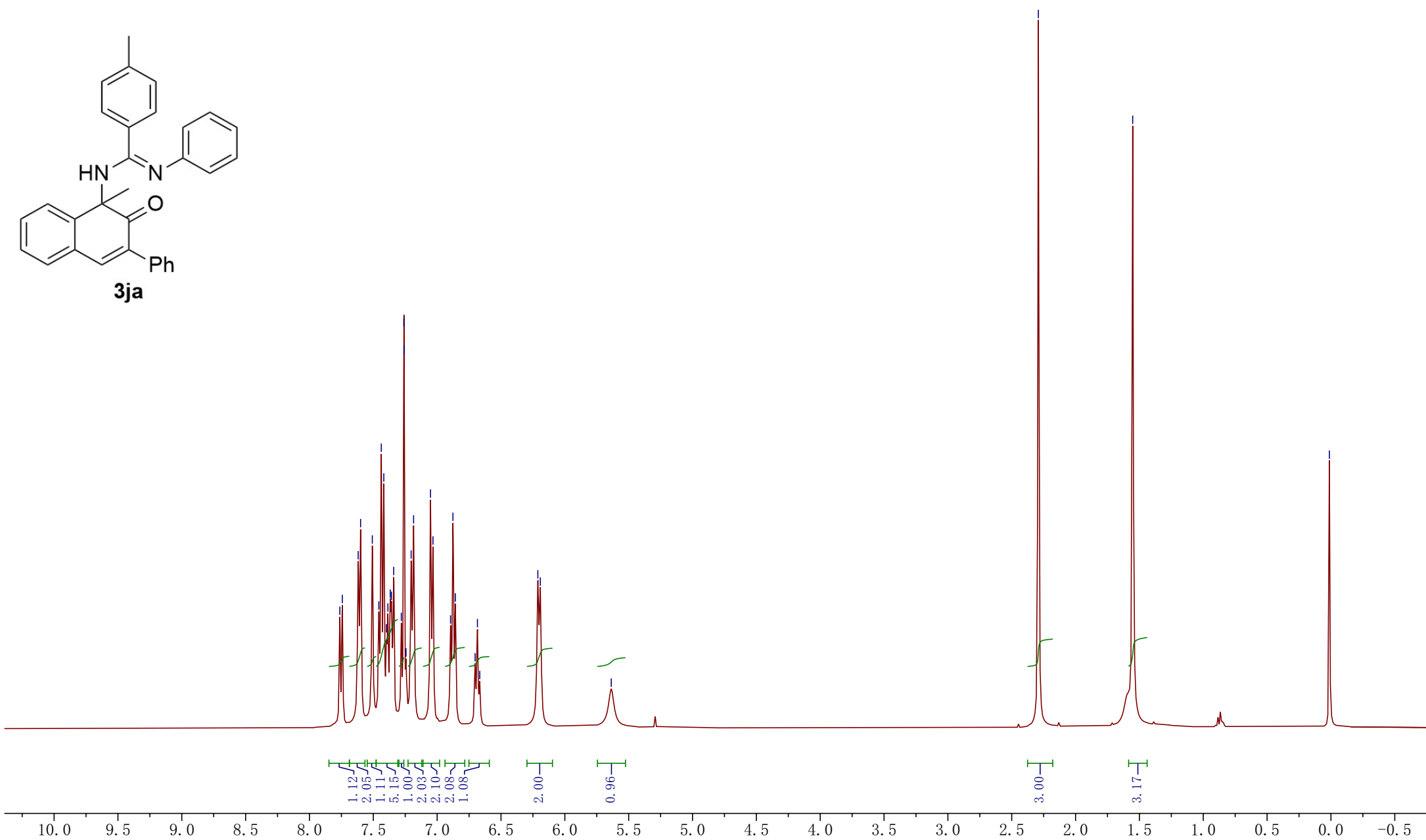
7.762
7.743
7.618
7.600
7.508
7.457
7.437
7.418
7.397
7.386
7.367
7.358
7.340
7.281
7.261
7.258
7.244
7.204
7.184
7.052
7.033
6.895
6.876
6.857
6.703
6.685
6.666
6.211
6.192

5.636

2.291

1.552

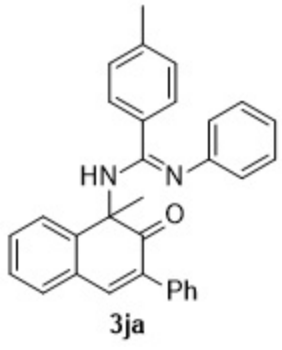
0.012



f1 (ppm)

SI-54

198.889



153.714
149.707
146.662
141.566
139.549
136.601
135.522
130.757
129.940
129.618
129.597
129.037
128.975
128.696
128.224
128.095
127.901
126.790
123.943
122.244
121.335

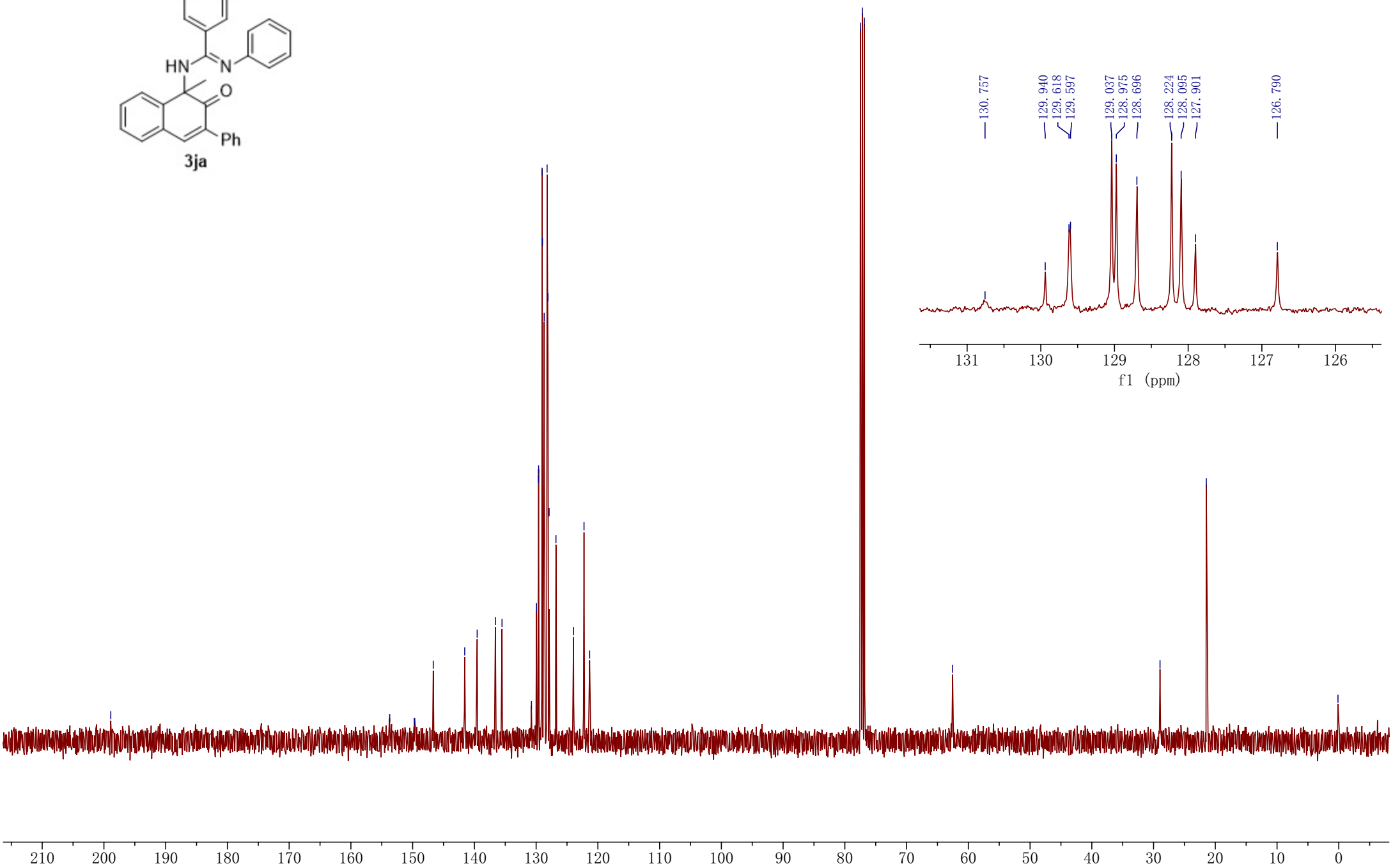
77.478
77.160
76.842

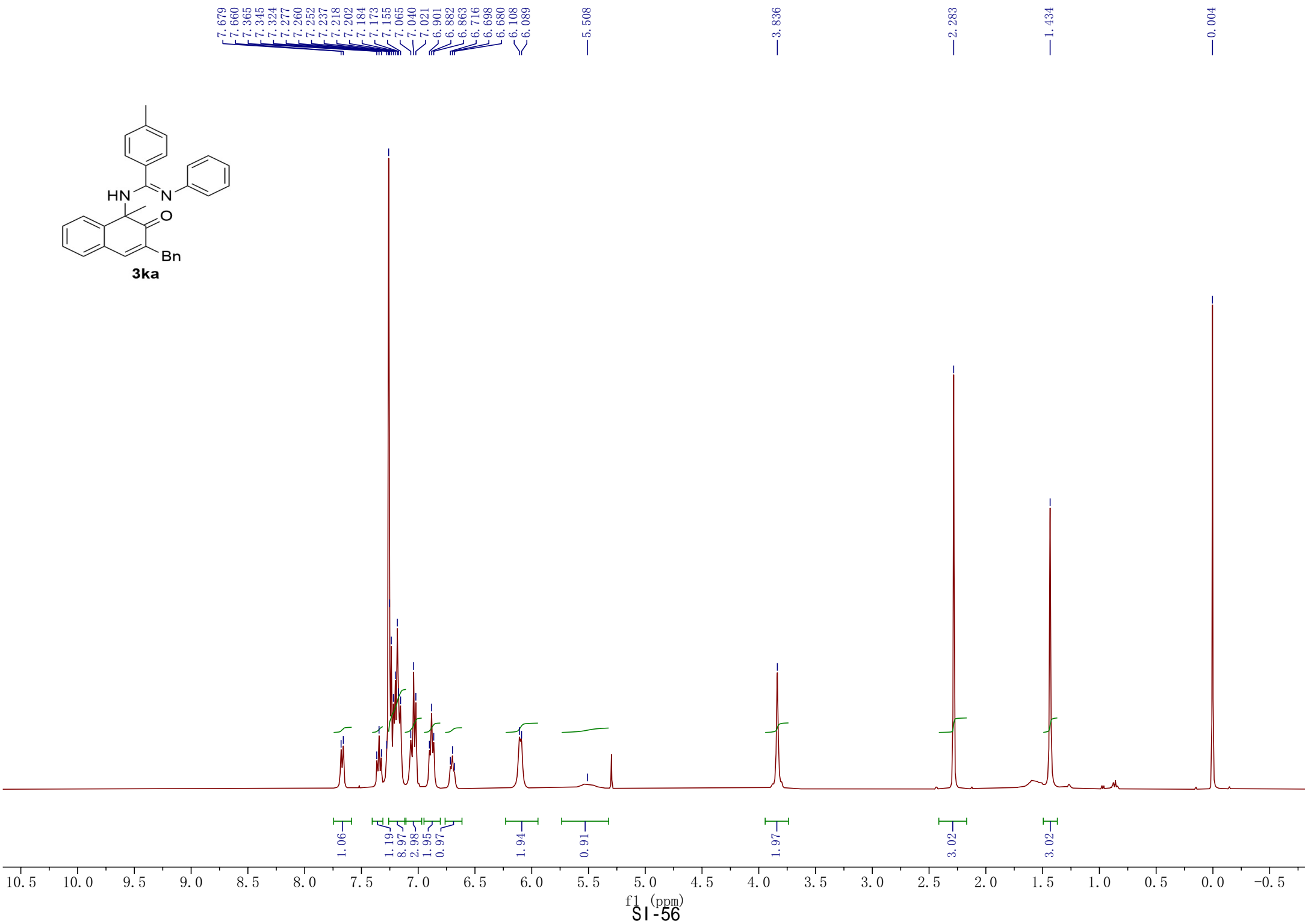
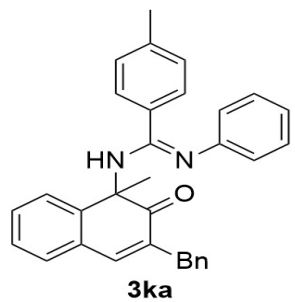
62.541

28.953

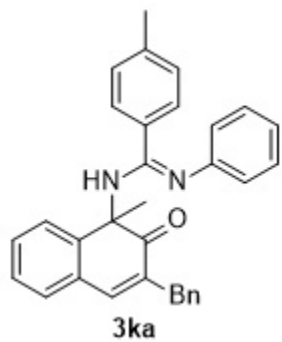
21.458

0.131





199.867



153.505
149.700
146.276
140.950
139.789
139.485
135.633
130.831
129.928
129.312
129.094
128.955
128.657
128.503
128.074
126.631
126.102
123.792
122.331
121.319

77.478
77.160
76.842

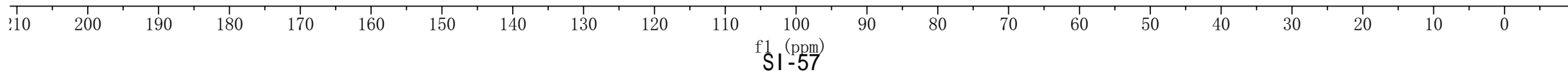
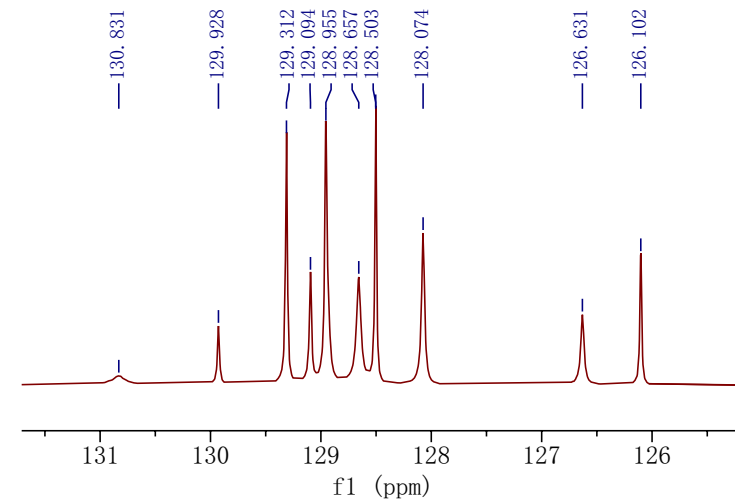
62.073

35.609

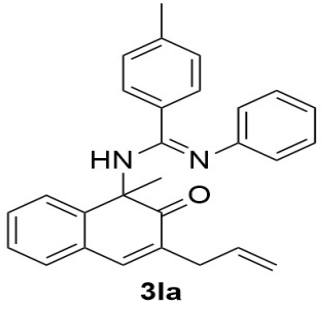
28.977

21.454

0.135



SI-57



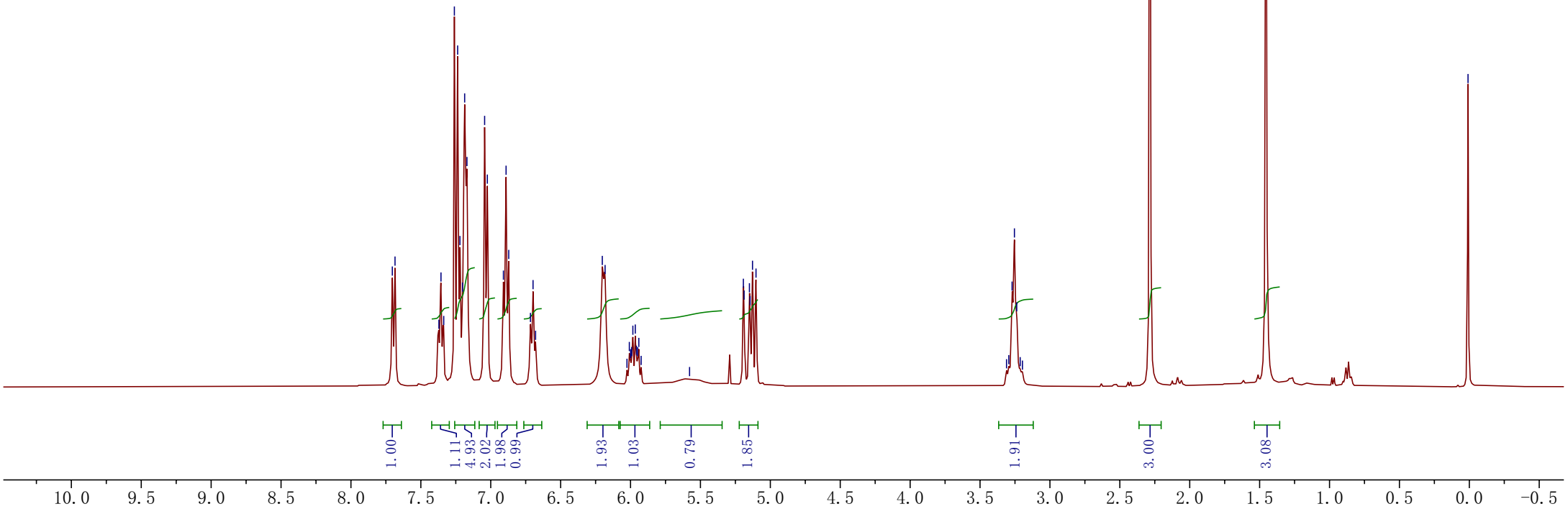
7.704
7.685
7.371
7.356
7.336
7.260
7.237
7.220
7.202
7.187
7.170
7.044
7.024
6.909
6.890
6.871
6.716
6.697
6.679
6.202
6.182
6.026
6.009
6.000
5.992
5.983
5.966
5.957
5.949
5.941
5.924
5.578
5.193
5.188
5.150
5.145
5.128
5.102

3.310
3.294
3.271
3.254
3.237
3.213
3.197

2.285

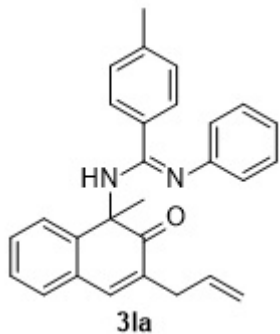
1.454

0.009



SI-58

198.679



153.725
149.498
146.115
140.051
139.538
135.796
134.354
130.662
129.942
129.014
128.945
128.794
128.685
128.071
126.663
123.875
122.363
121.425
116.776

77.477
77.160
76.842

62.110

33.615

28.894

21.446

130.662

129.942

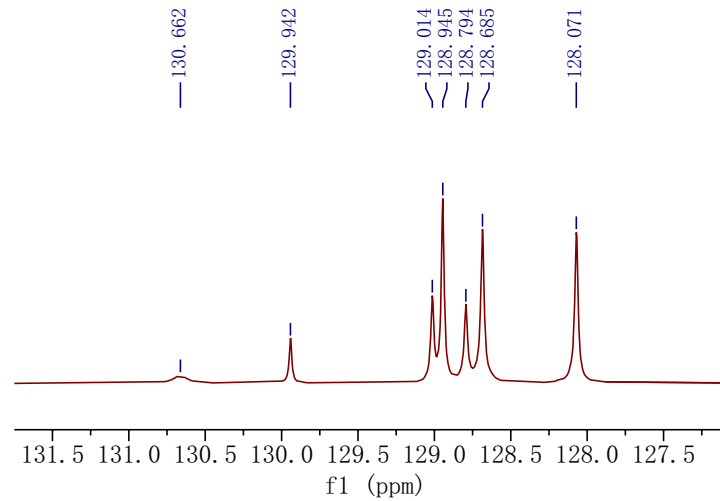
129.014

128.945

128.794

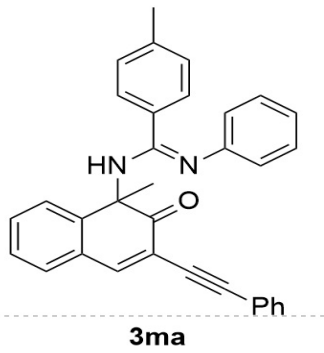
128.685

128.071

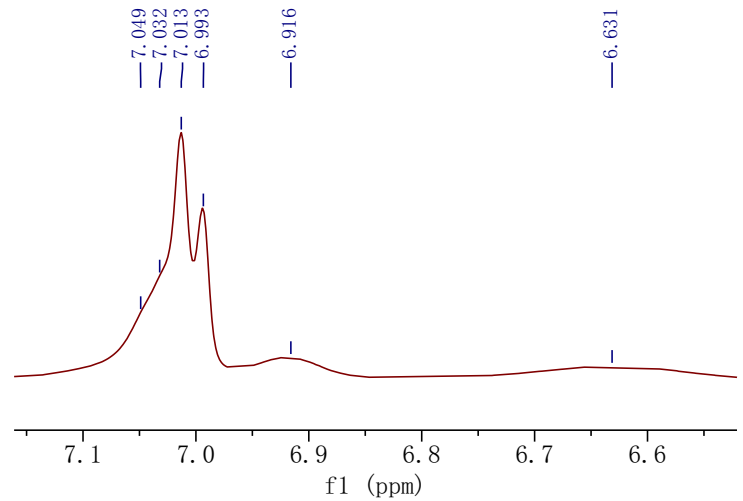


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)
SI-59

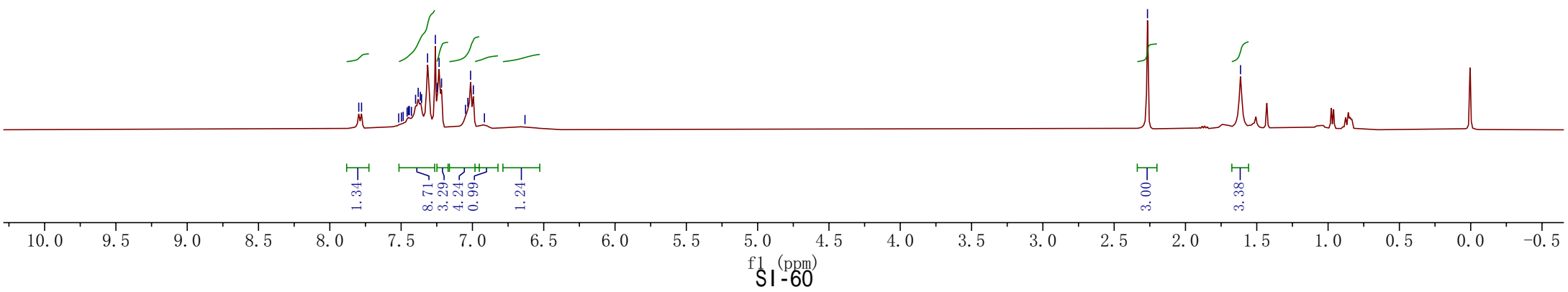


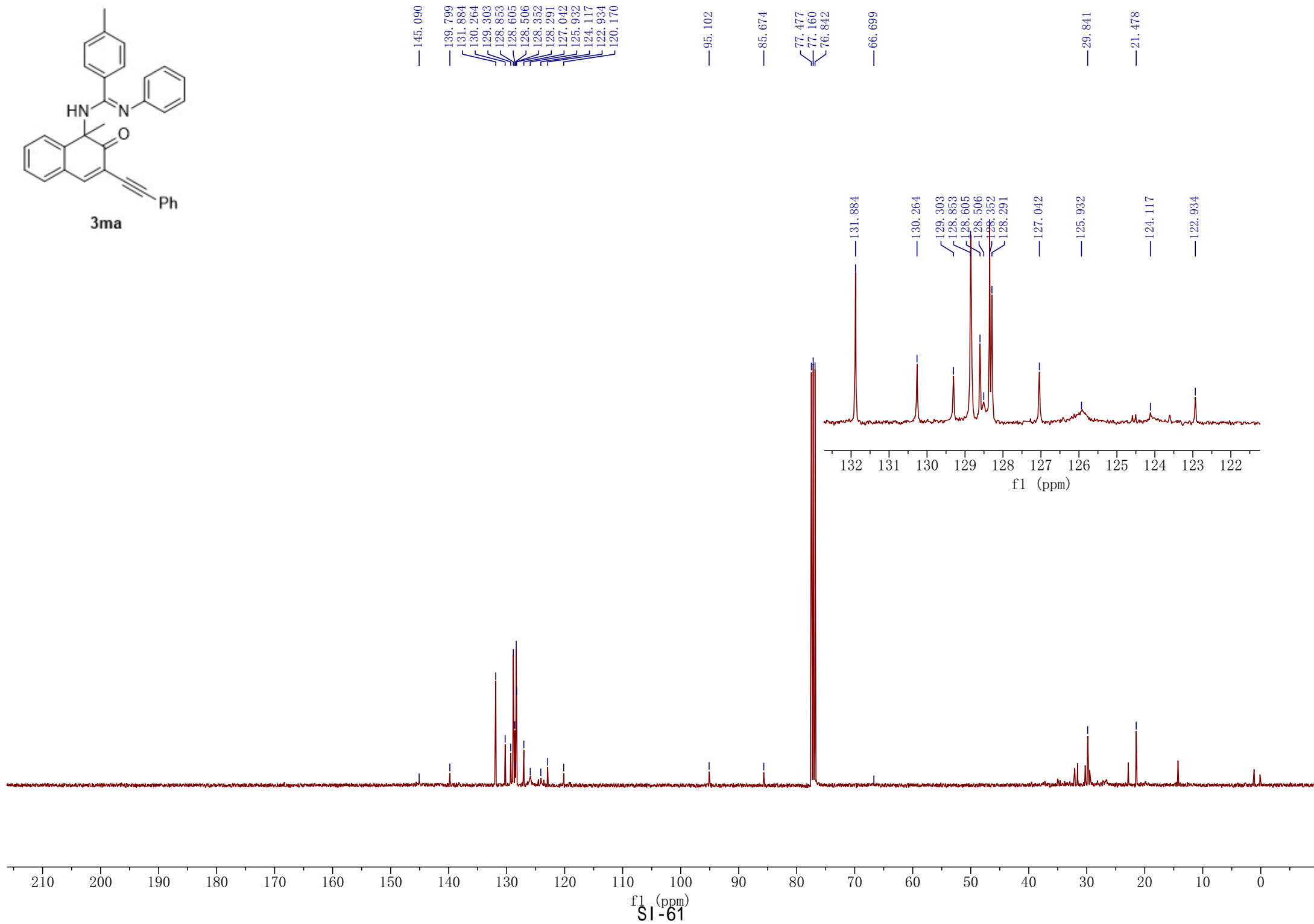
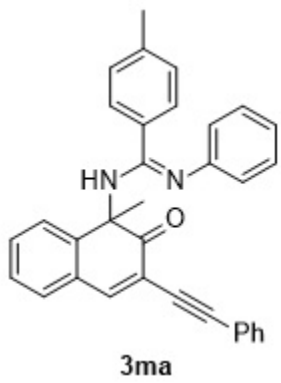
7.797
7.777
7.517
7.498
7.486
7.458
7.450
7.442
7.428
7.399
7.380
7.365
7.357
7.315
7.260
7.247
7.234
7.217
7.049
7.032
7.013
6.993
6.916
6.631

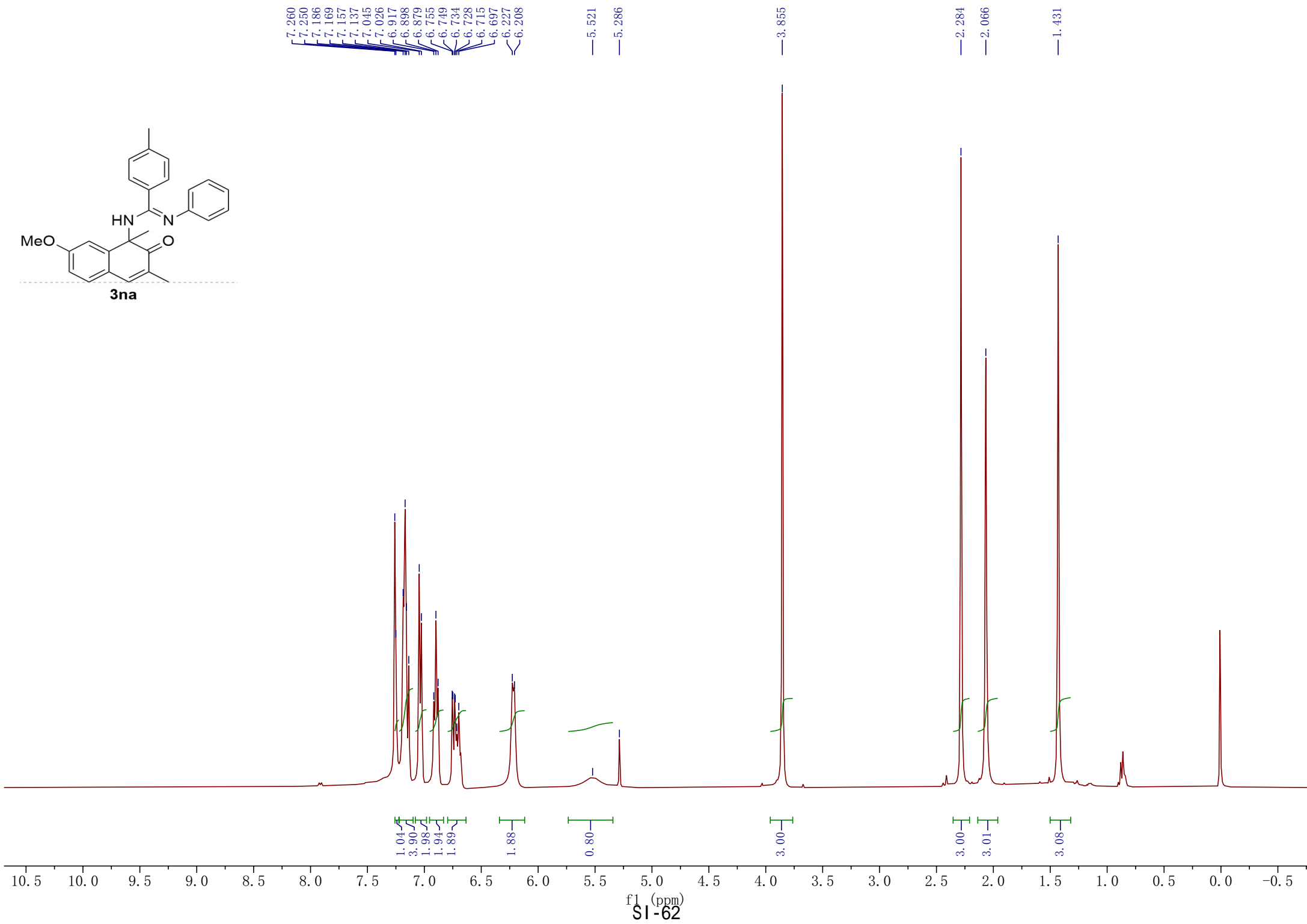
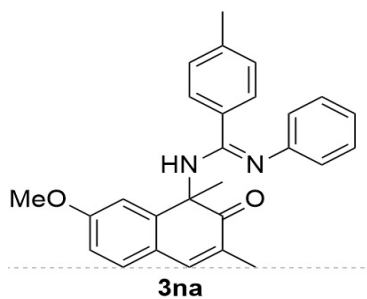


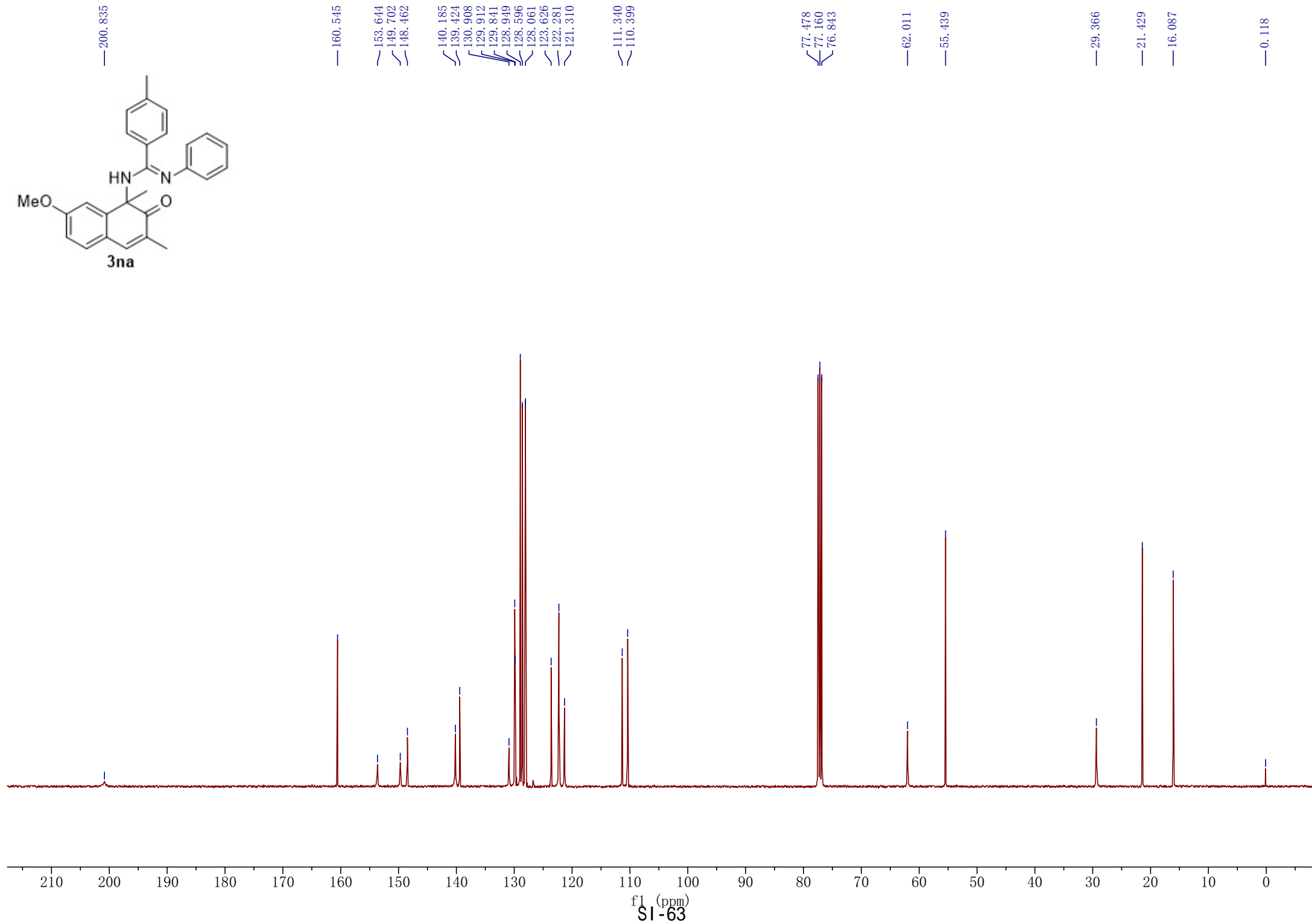
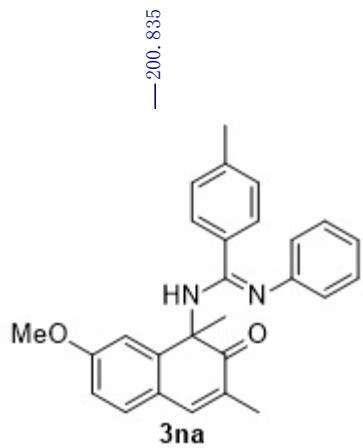
2.266

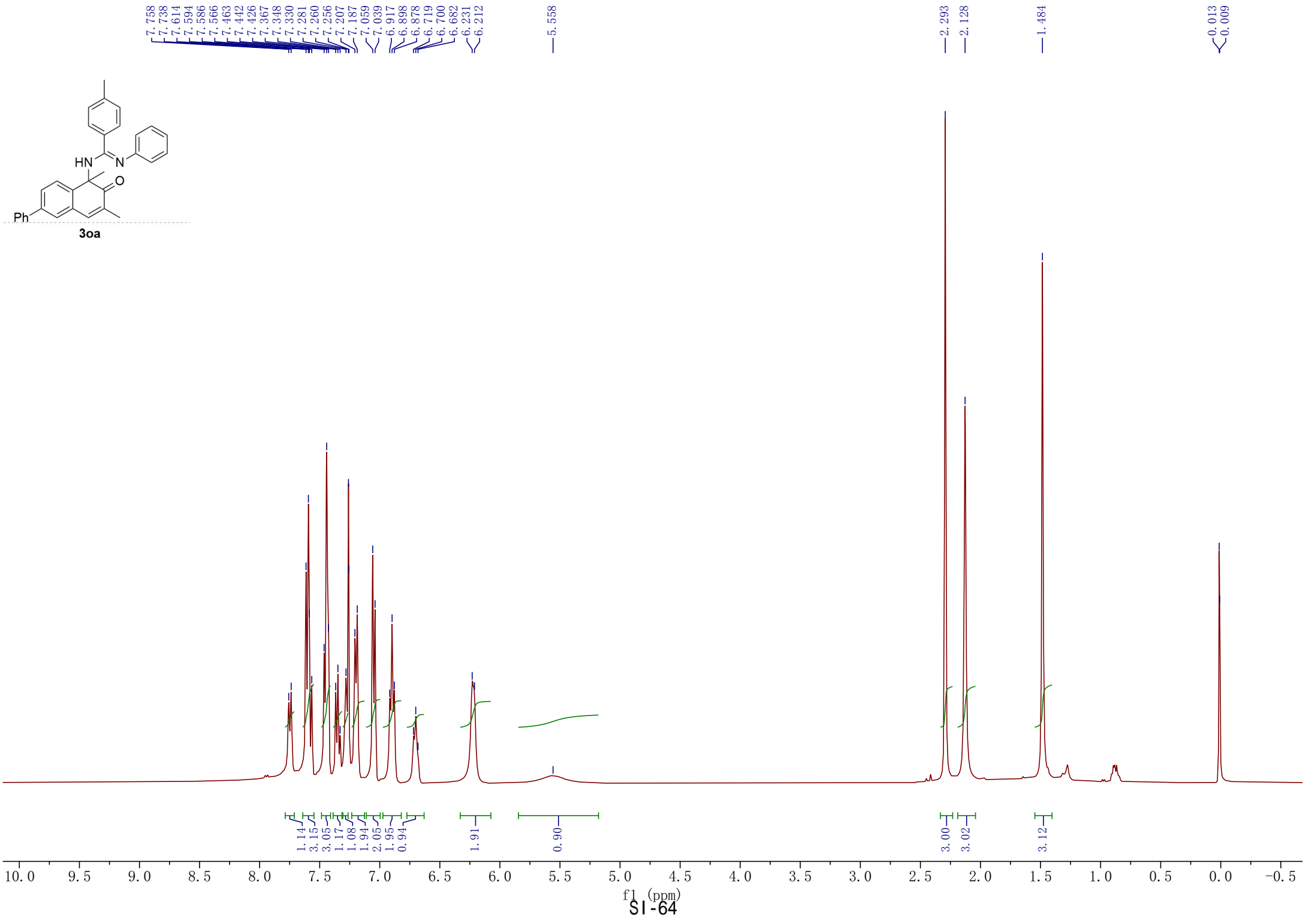
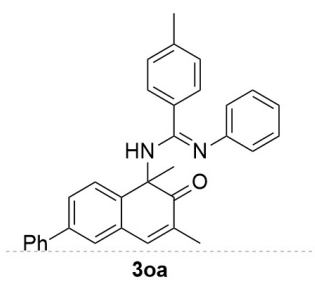
1.614

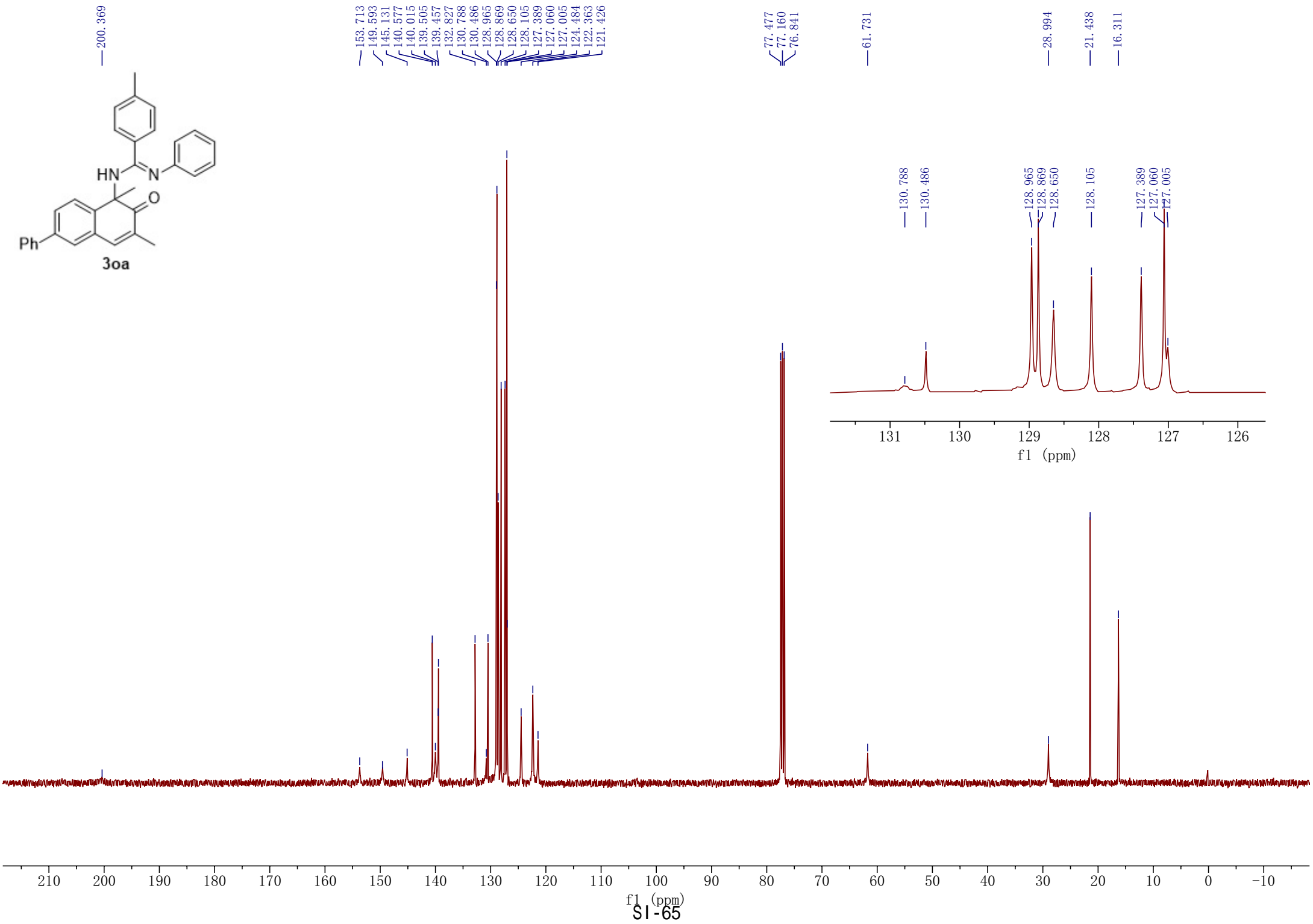
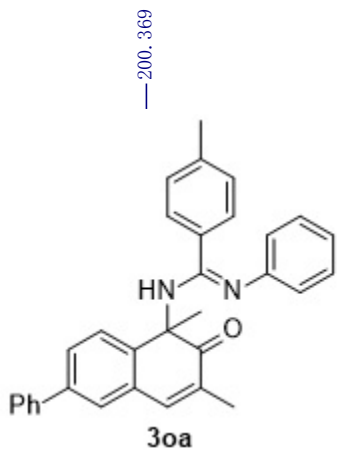


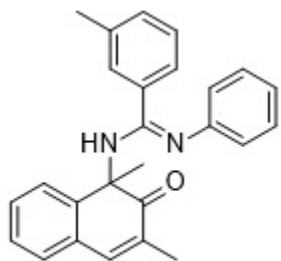












3ab

7.689
7.670
7.401
7.370
7.359
7.349
7.339
7.328
7.285
7.260
7.223
7.212
7.137
7.117
7.098
7.084
7.014
6.998
6.898
6.879
6.860
6.699
6.681
6.662
6.187
6.168

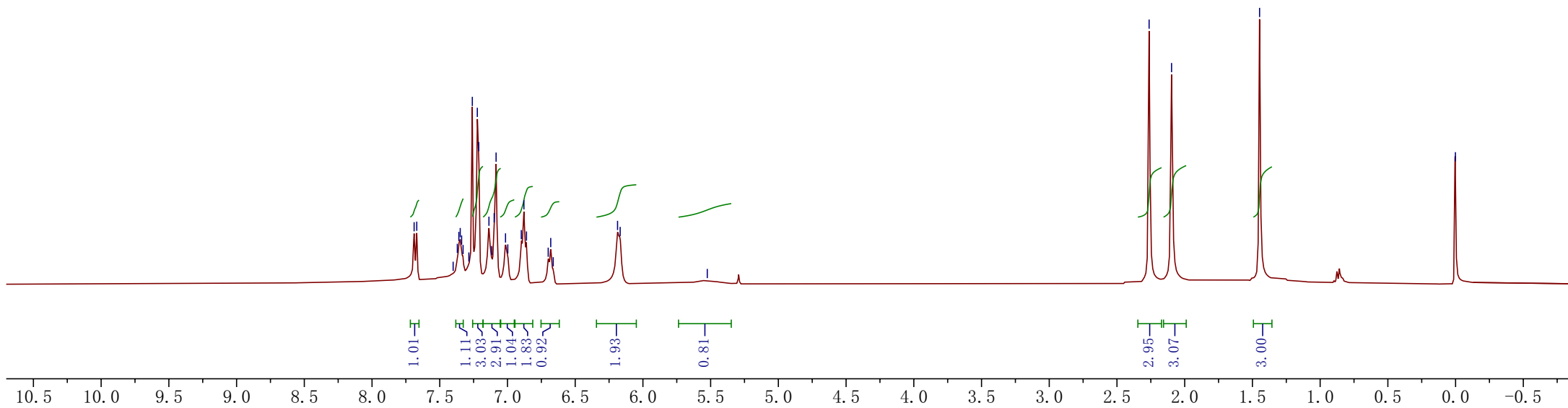
—5.525

—2.263

—2.097

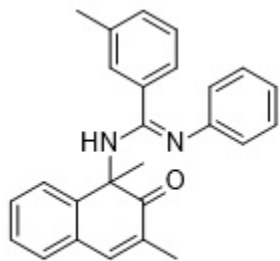
—1.447

—0.001



f1 (ppm)
SI-66

— 200.542



3ab

153.747
149.462
146.169
140.154
137.973
133.743
132.375
130.122
130.087
129.122
128.719
128.400
128.079
128.017
126.586
125.836
123.890
122.278
121.410

77.478
77.160
76.843

— 61.862

— 28.995

— 21.380

— 16.198

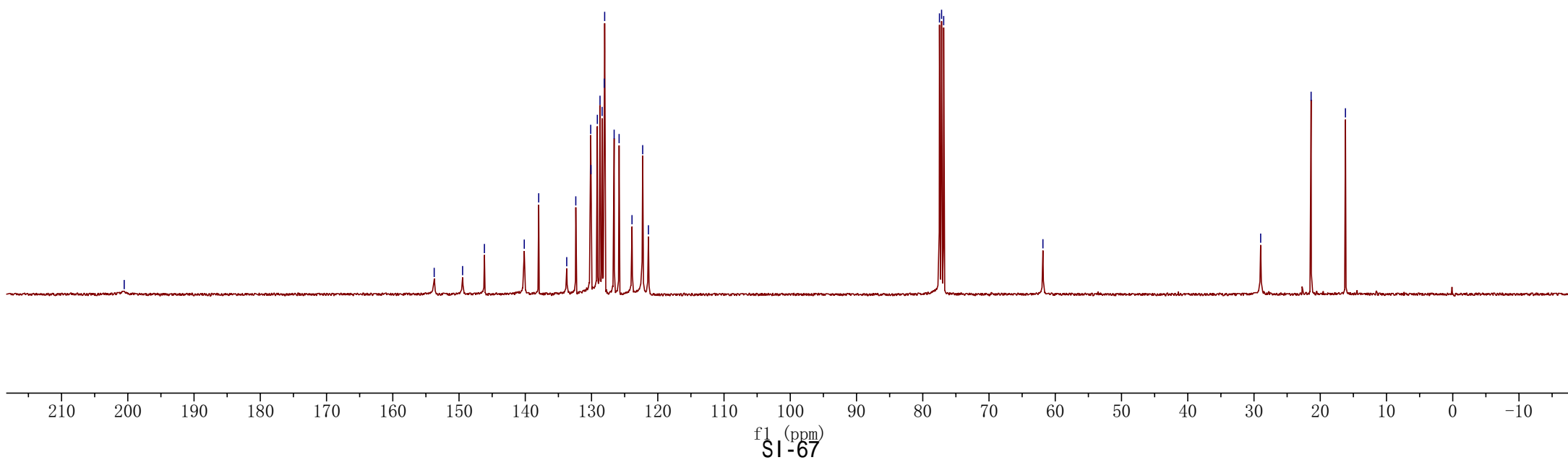
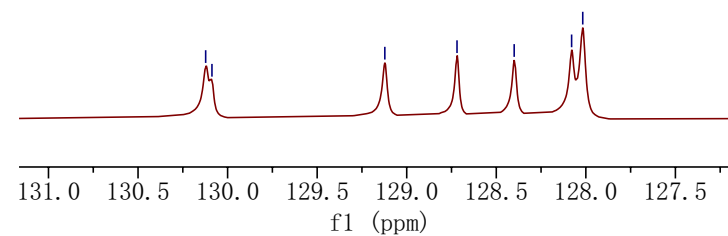
130.122
130.087

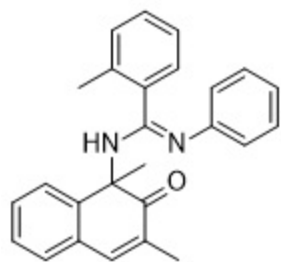
— 129.122

— 128.719

— 128.400

128.079
128.017





3ac

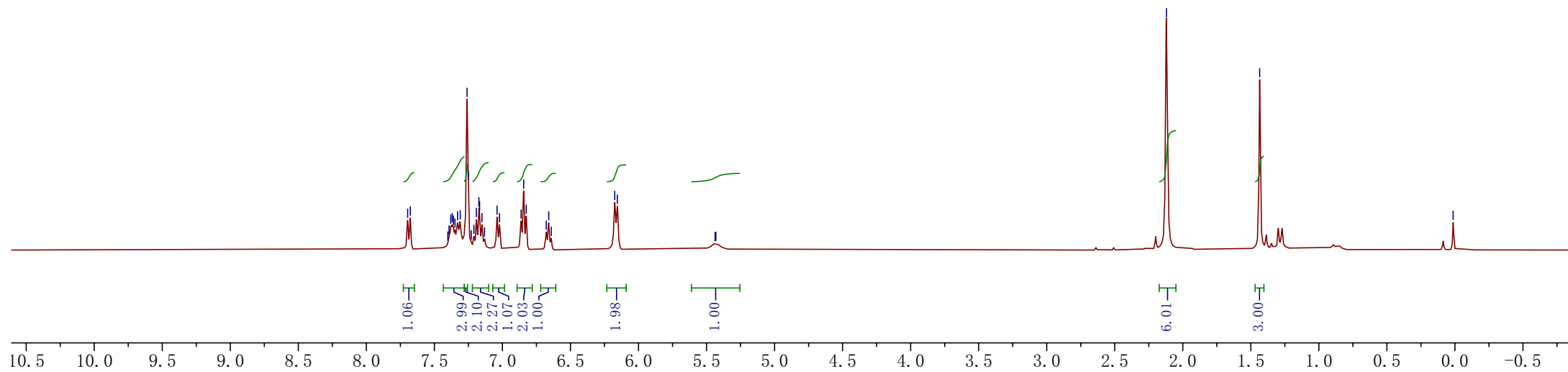
7.696
7.677
7.401
7.392
7.380
7.369
7.360
7.349
7.330
7.310
7.260
7.250
7.229
7.210
7.191
7.173
7.168
7.150
7.132
7.040
7.021
6.863
6.844
6.825
6.678
6.660
6.641
6.175
6.155

5.437
5.432

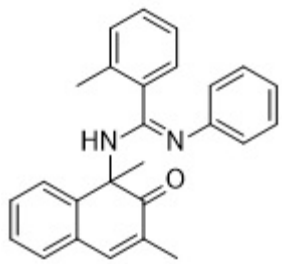
2.120

1.435

0.013



— 200.796



3ac

— 154.055

— 149.065

— 146.301

— 140.251

— 135.933

— 134.067

— 132.401

— 130.176

— 130.141

— 129.555

— 128.987

— 128.681

— 128.409

— 127.833

— 126.622

— 125.406

— 124.012

— 122.077

— 121.611

— 77.479

— 77.161

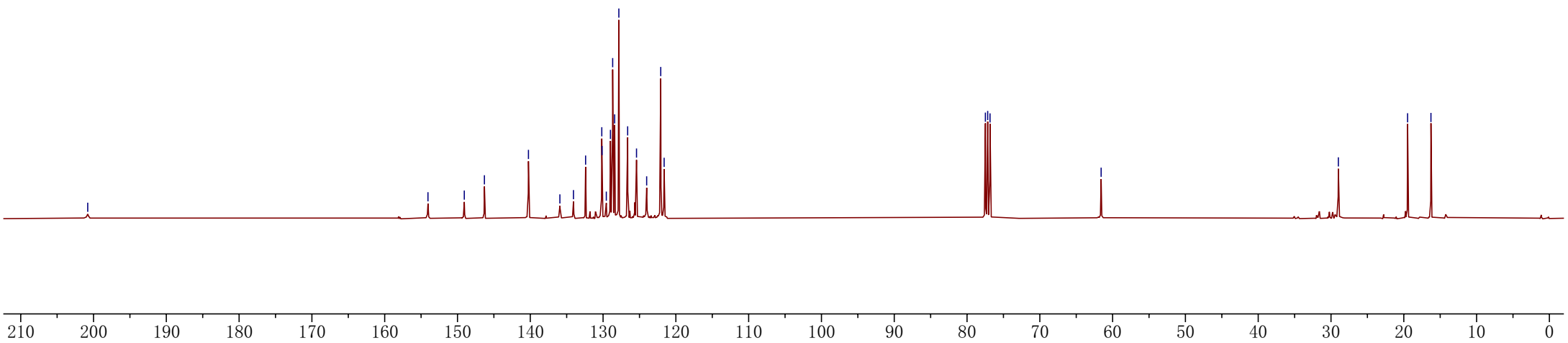
— 76.844

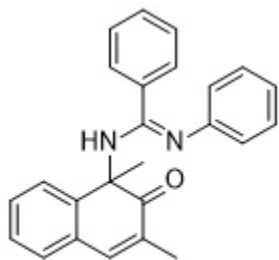
— 61.579

— 28.990

— 19.480

— 16.270





3ad

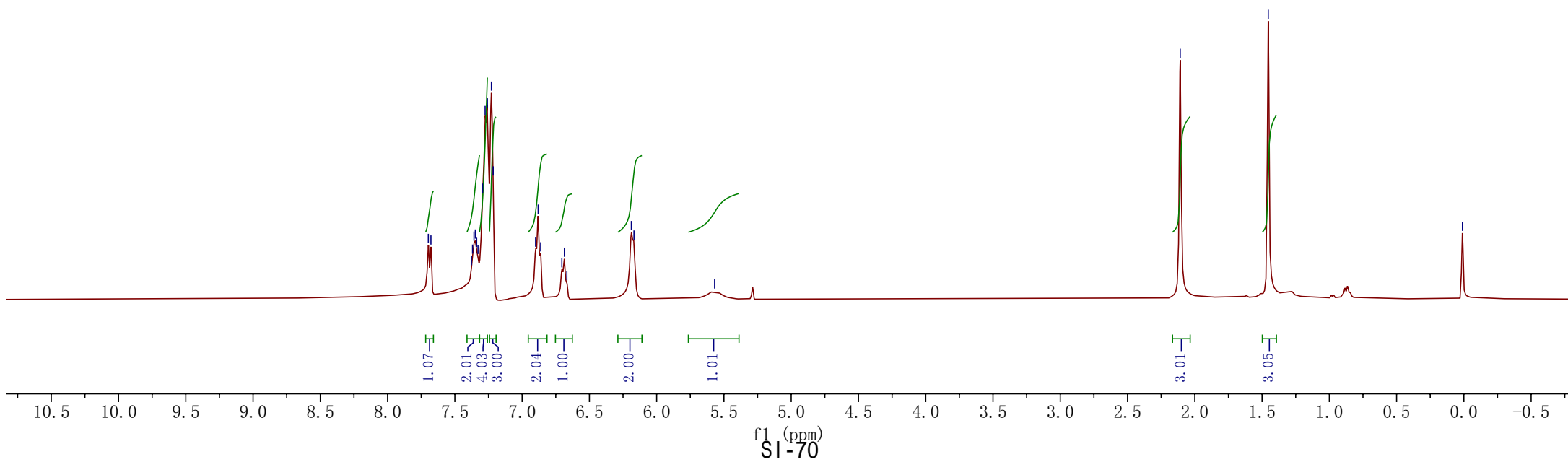
7.697
7.678
7.376
7.368
7.358
7.348
7.338
7.328
7.294
7.275
7.258
7.228
7.215
6.900
6.881
6.862
6.705
6.686
6.667
6.188
6.169

5.569

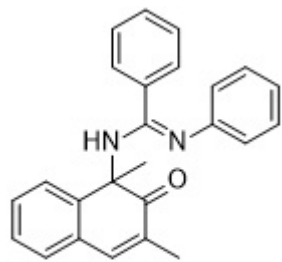
2.108

1.454

0.010



—200.706



3ad

153.575
149.490
146.146

140.238
133.827
132.410
130.131
129.411
128.738
128.686
128.448
128.271
128.075
126.631
123.852
122.261
121.427

77.477
77.160
76.842

—61.848

—29.060

—16.205

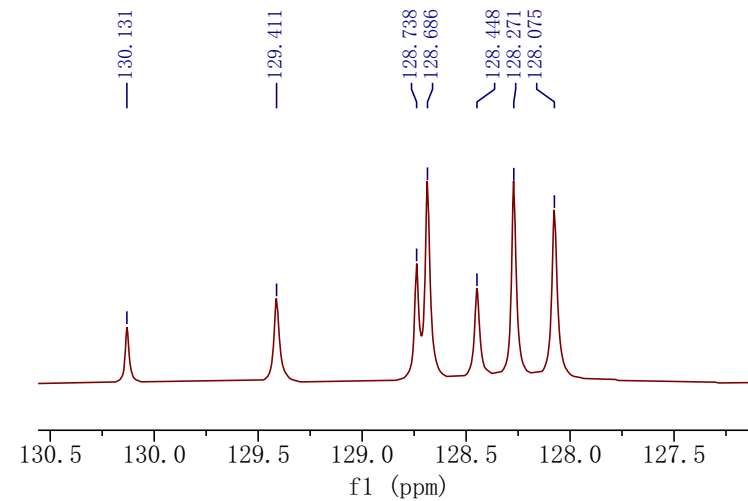
—0.129

—130.131

—129.411

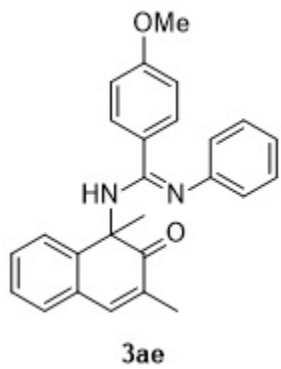
128.738
128.686

128.448
128.271
128.075



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)
SI-71



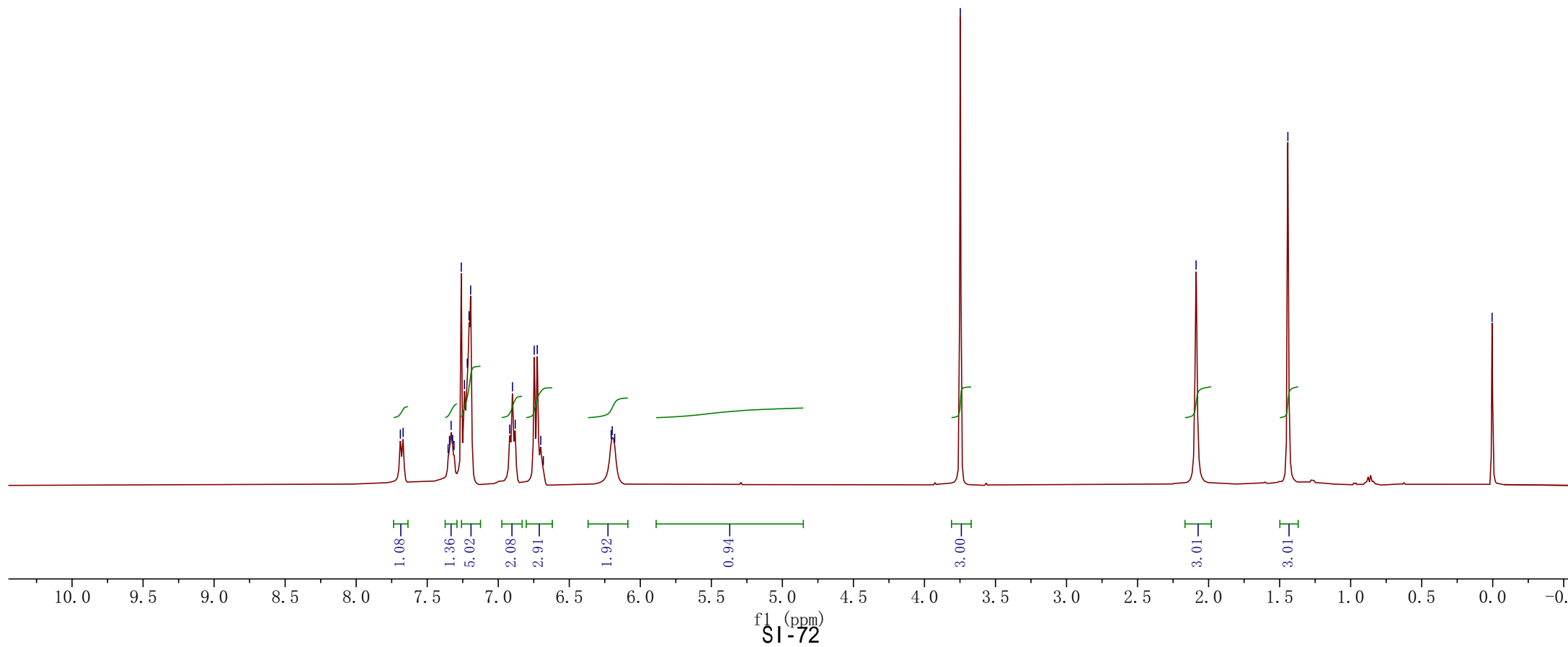
7.689
7.670
7.353
7.343
7.332
7.321
7.311
7.260
7.238
7.218
7.206
7.194
6.919
6.900
6.880
6.747
6.725
6.701
6.683
6.205
6.198
6.180

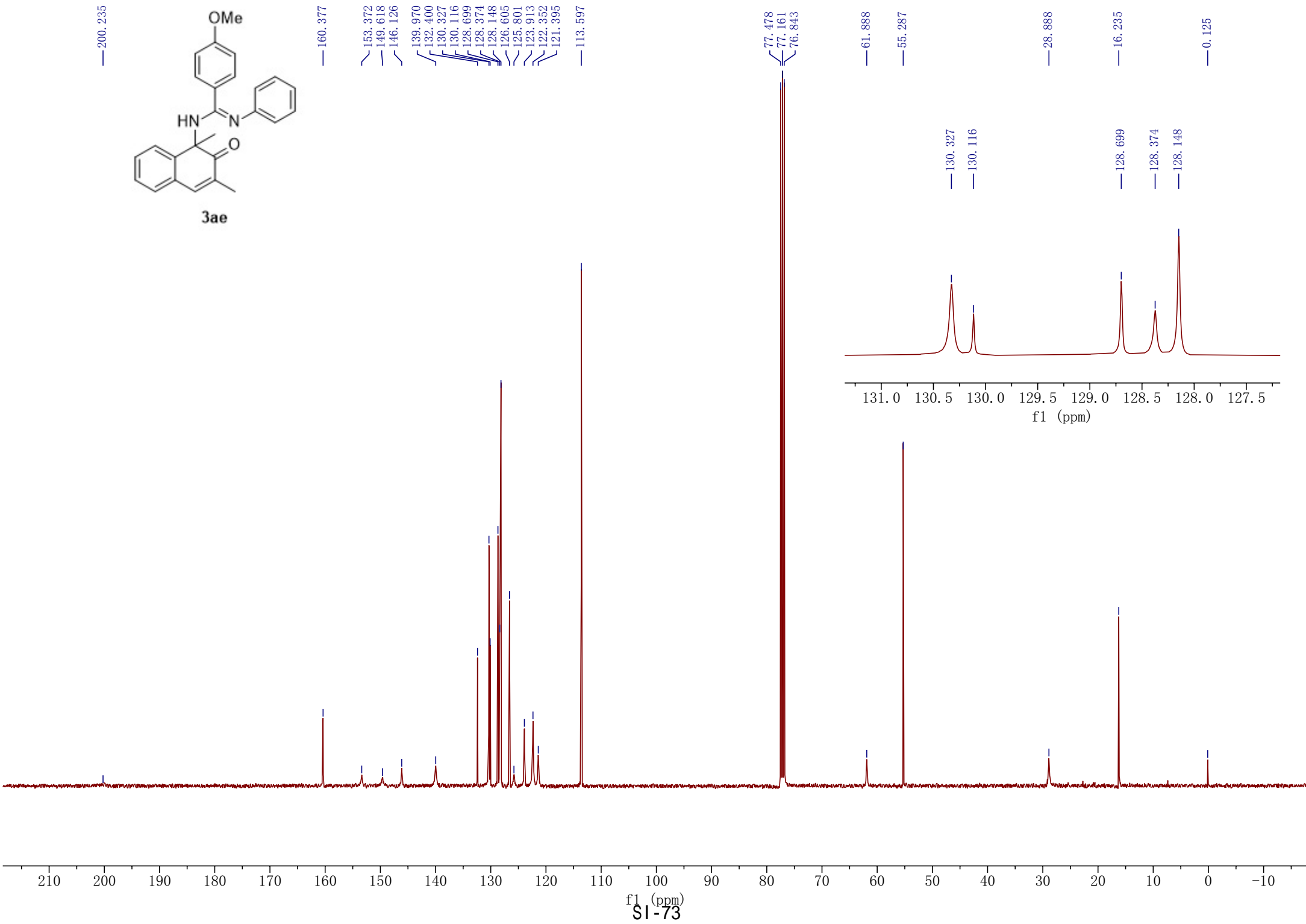
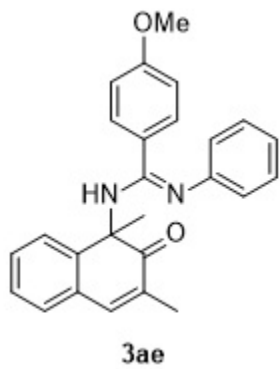
3.748

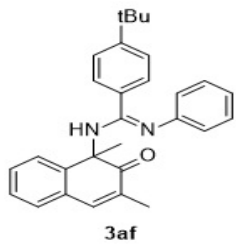
2.088

1.442

0.004







7.682
7.662
7.354
7.343
7.332
7.322
7.312
7.261
7.257
7.238
7.223
7.214
7.203
6.910
6.891
6.872
6.712
6.693

6.198
6.179

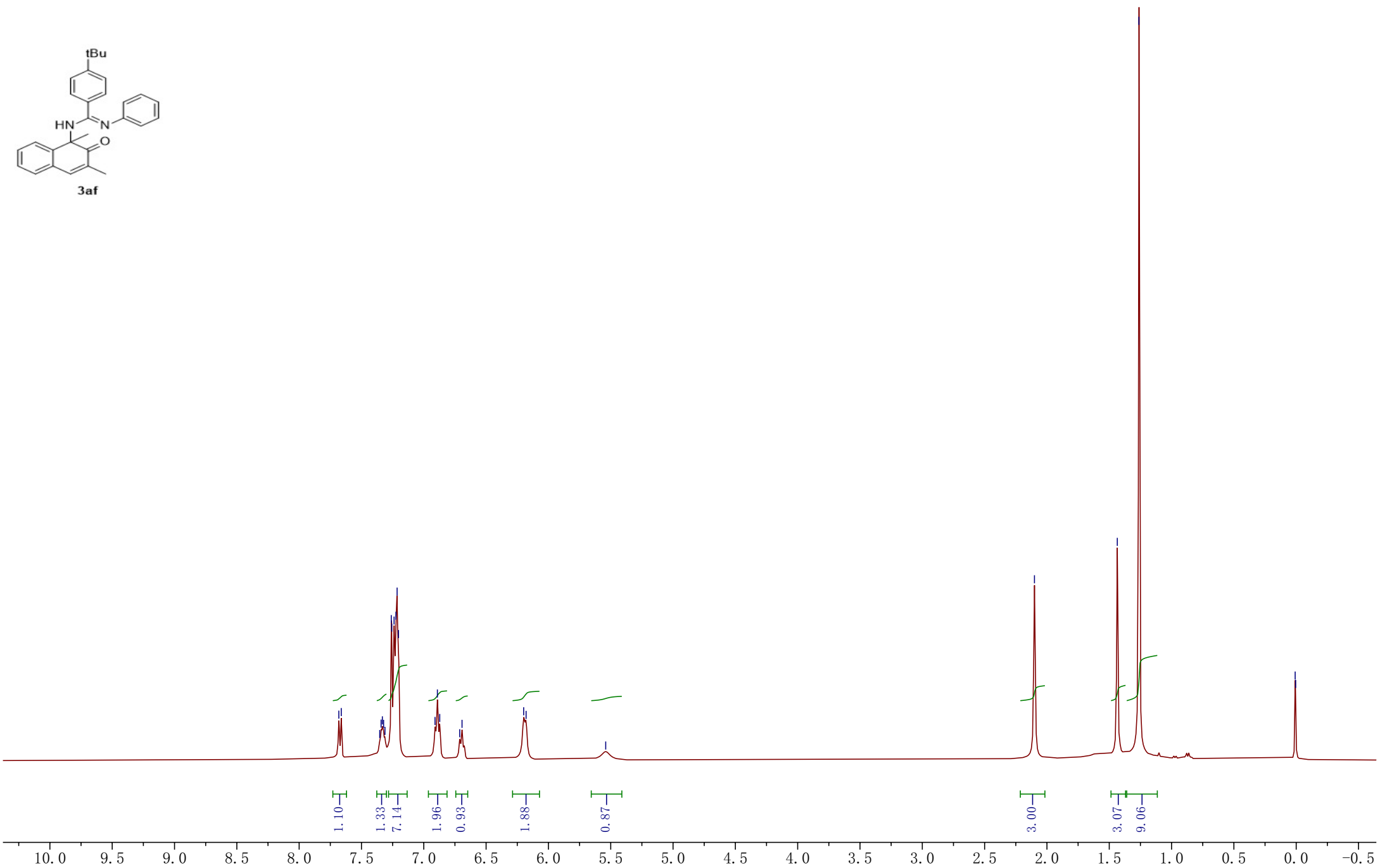
5.540

2.100

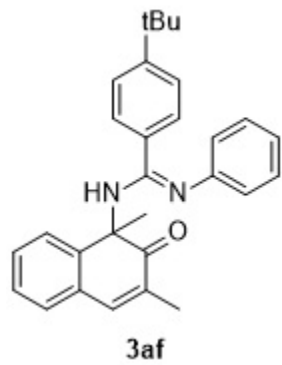
1.435

1.262

0.008
0.004



SI-74



— 200.788

153.382
152.606
149.660
146.275
140.158
132.460
130.828
130.182
128.705
128.478
128.417
128.095
126.597
125.199
123.888
122.245
121.273

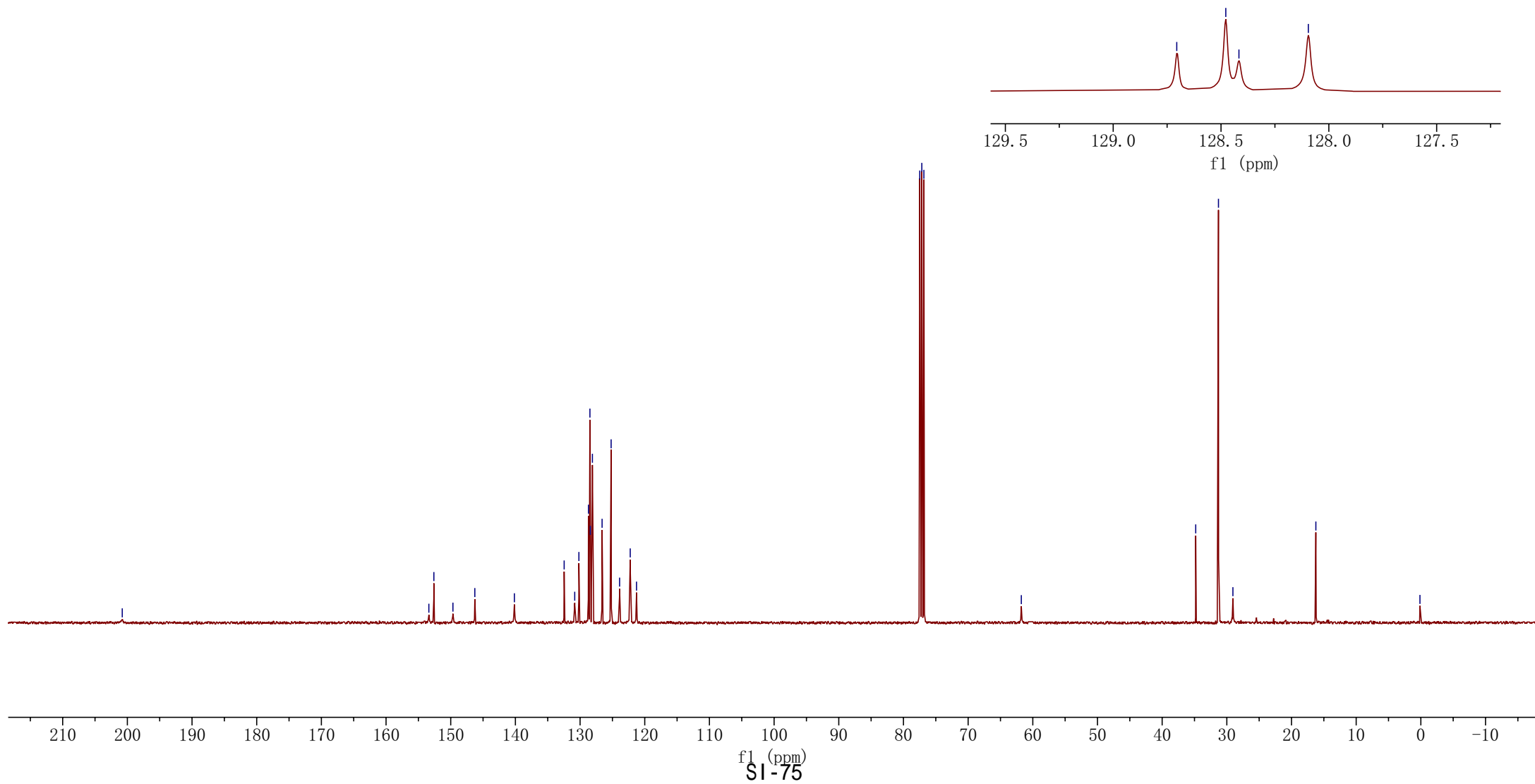
77.478
77.160
76.842

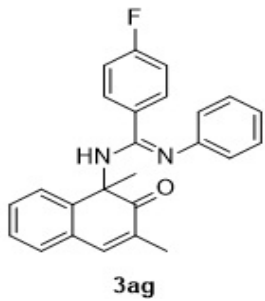
— 61.775

34.809
31.292
29.060

— 16.233

— 0.140





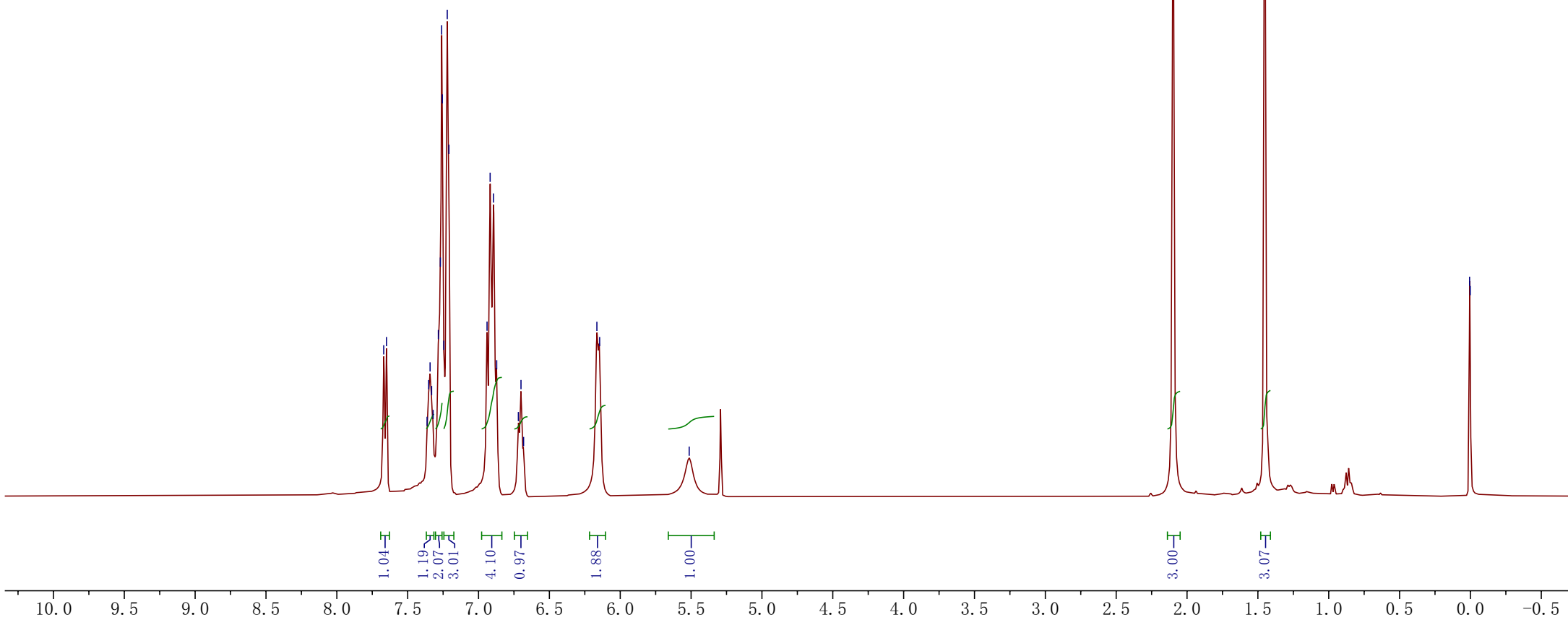
7.669
7.650
7.363
7.352
7.342
7.331
7.321
7.284
7.269
7.260
7.256
7.245
7.221
7.209
6.940
6.918
6.894
6.872
6.719
6.700
6.682
6.165
6.145

5.513

2.098

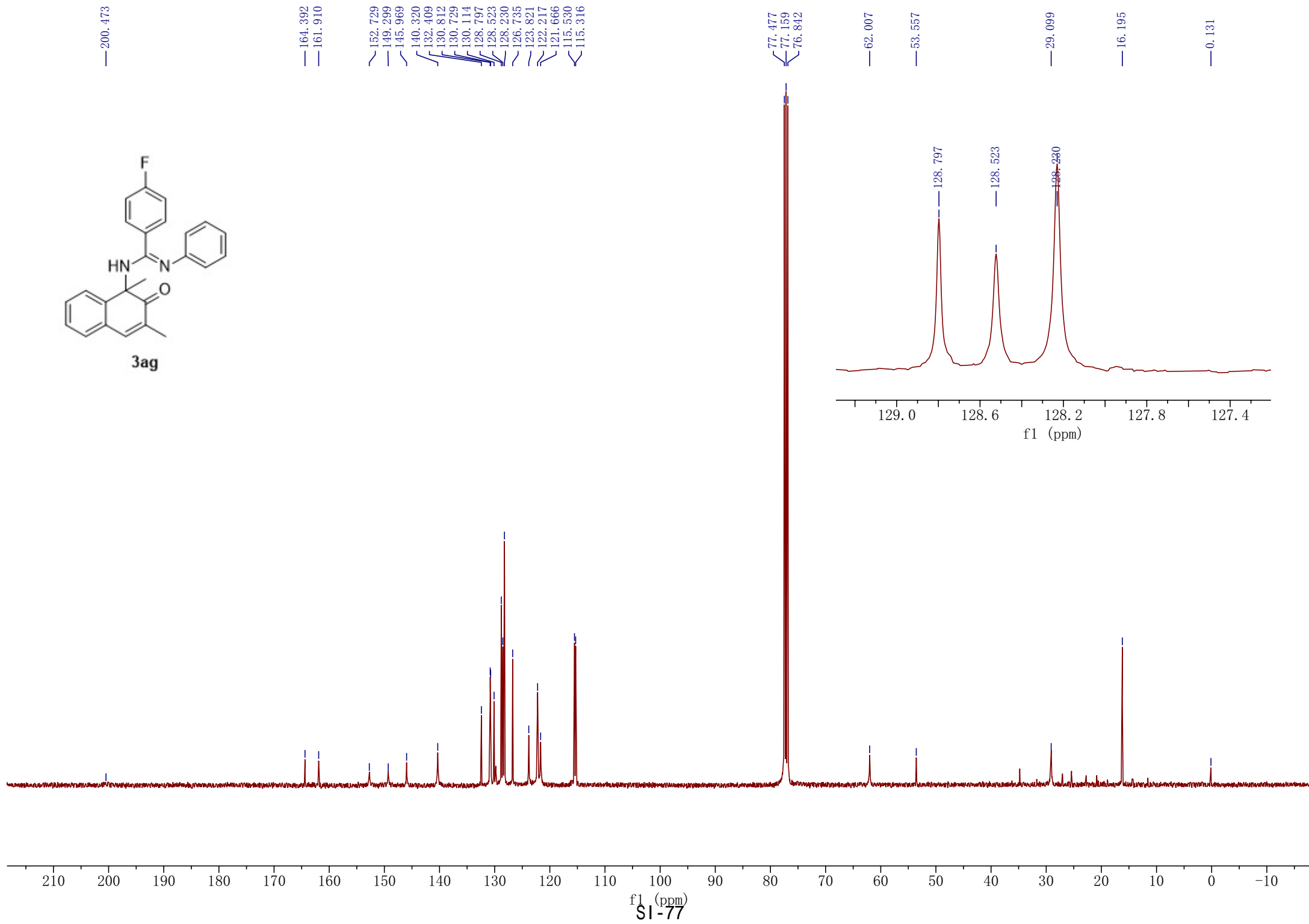
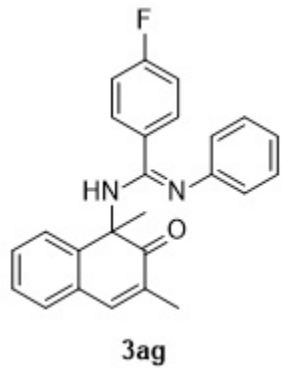
1.452

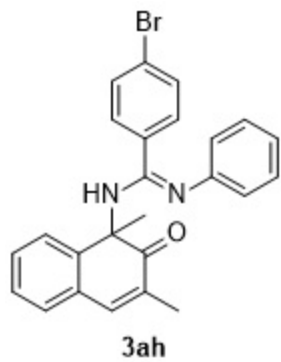
0.006
0.001



f1 (ppm)

SI-76





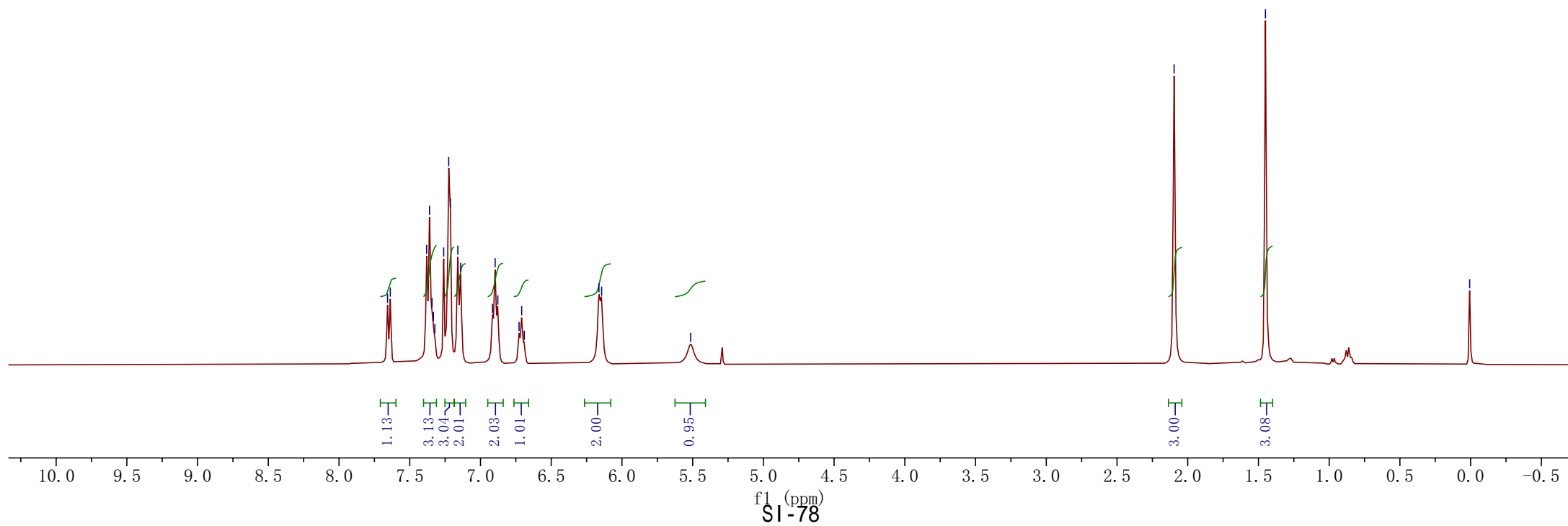
7.657
7.638
7.381
7.360
7.343
7.333
7.322
7.260
7.225
7.213
7.160
7.140
6.915
6.896
6.877
6.727
6.709
6.690
6.163
6.143

5.514

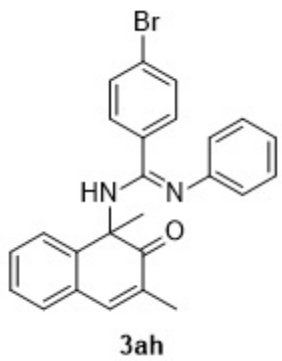
2.096

1.451

0.007



— 200.737



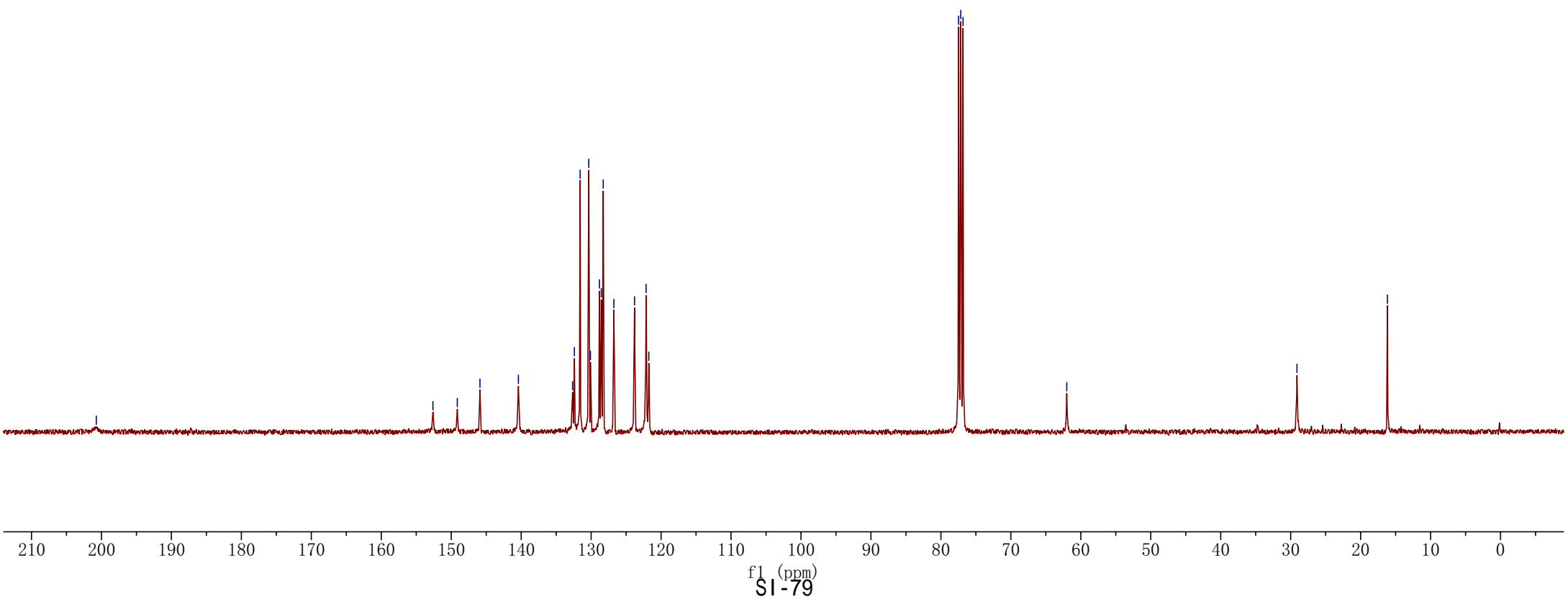
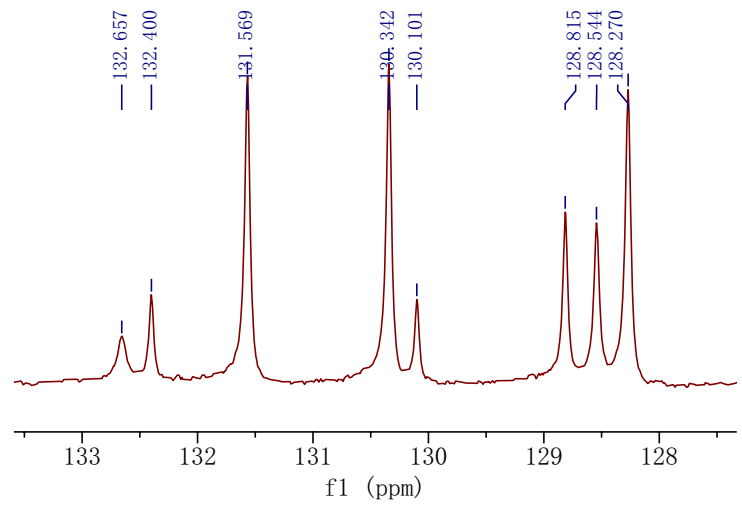
152.613
149.135
145.893
140.398
132.657
132.400
131.569
130.342
130.101
128.815
128.544
128.270
126.748
123.798
122.142
121.752

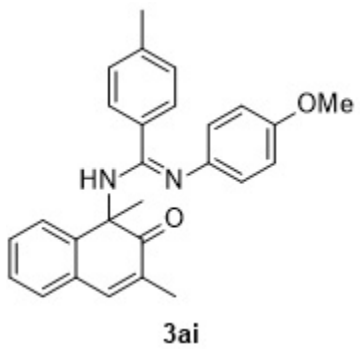
77.478
77.160
76.842

62.008

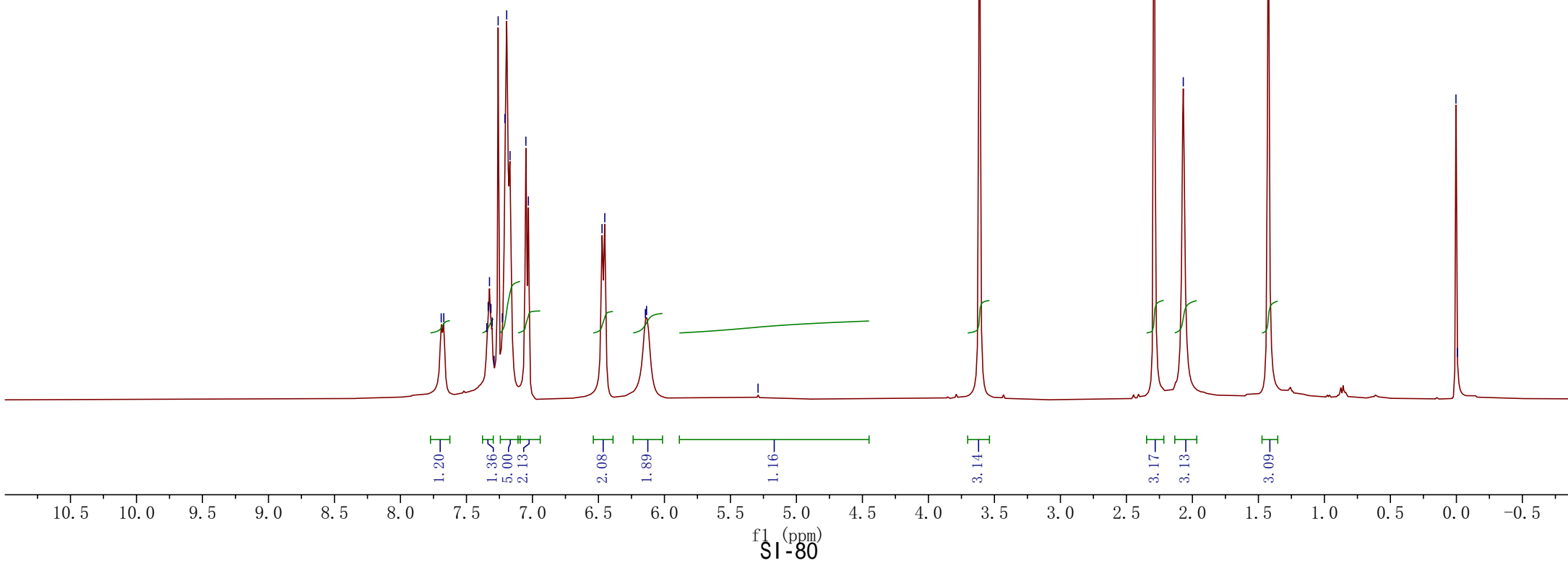
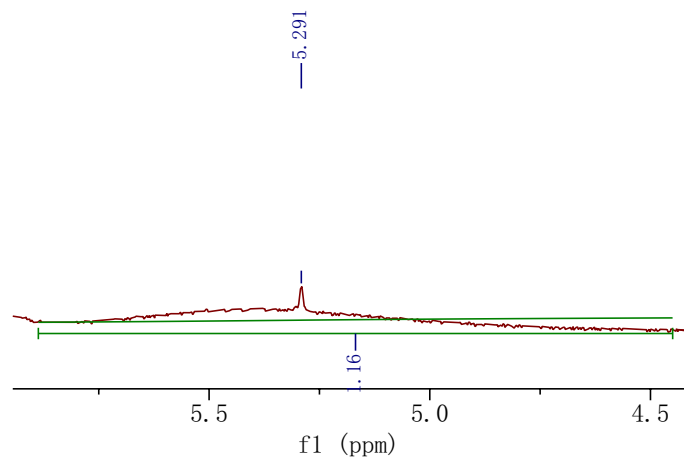
29.102

16.173

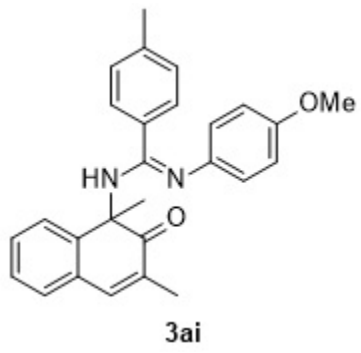




7.691
7.672
7.346
7.335
7.325
7.315
7.305
7.290
7.260
7.228
7.209
7.195
7.170
7.050
7.031
6.473
6.452
6.144
6.135
5.291
3.613
2.290
2.069
1.425
0.003
-0.008



199.382



154.713
153.965

146.070
142.476
139.442
132.422
130.739
130.108
128.952
128.708
128.657
128.216
126.573
124.060
123.317

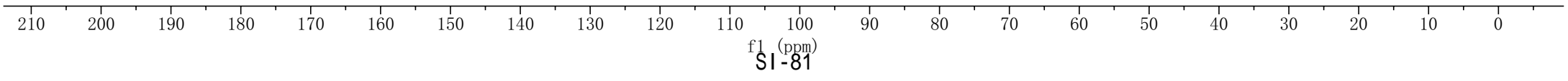
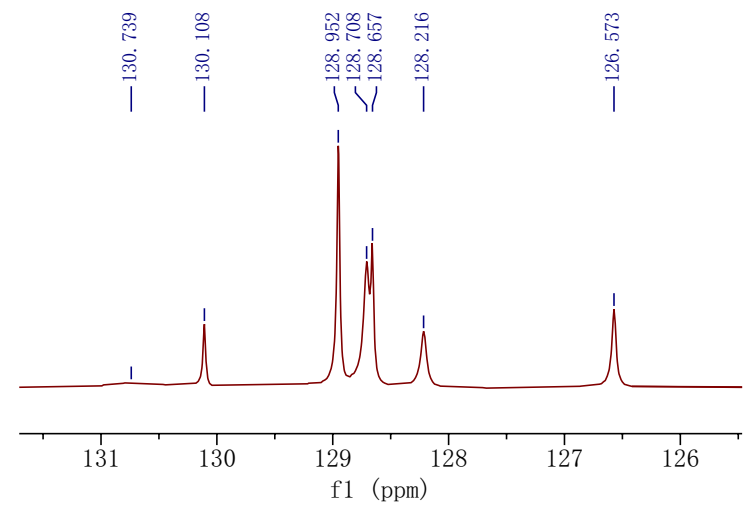
113.489

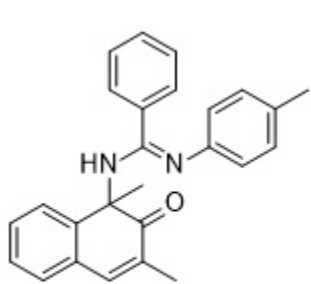
77.478
77.160
76.842

62.139
55.314

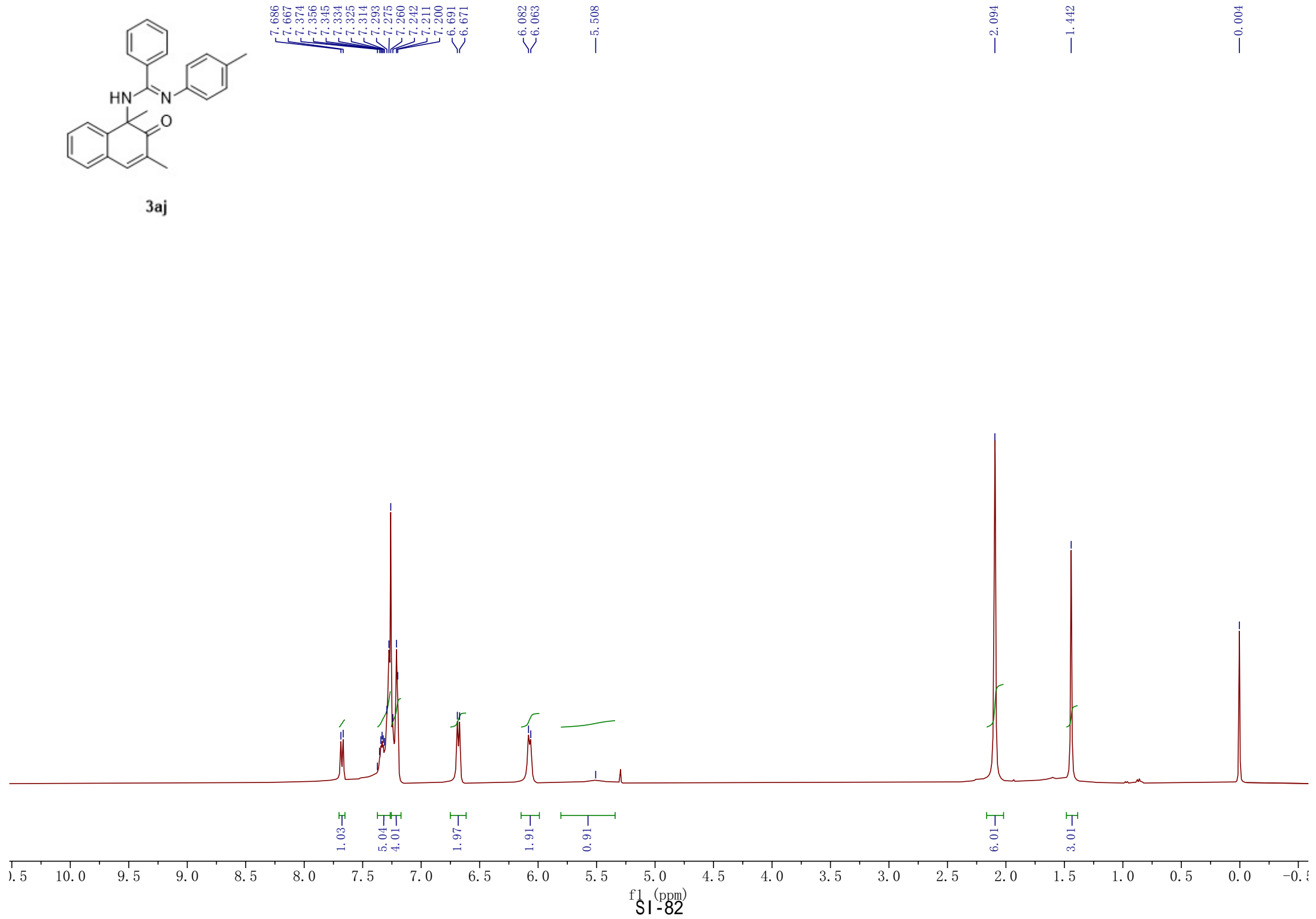
28.590
21.439
16.341

0.116

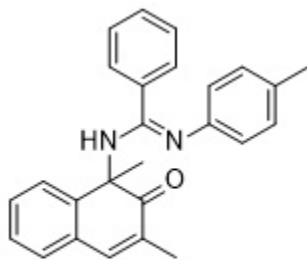




3aj



— 200.600



3aj

— 153.448

— 146.709

— 146.202

— 140.081

— 133.959

— 132.461

— 130.705

— 130.164

— 129.366

— 128.741

— 128.710

— 128.420

— 128.288

— 126.598

— 123.887

— 122.103

— 77.477

— 77.160

— 76.842

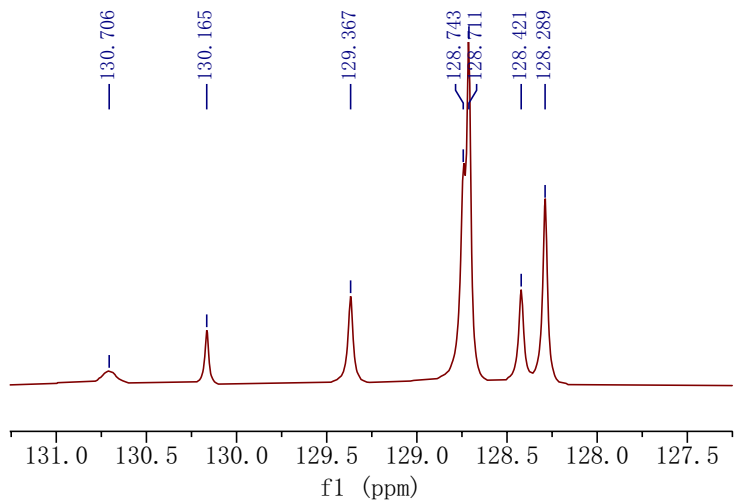
— 61.867

— 28.965

— 20.775

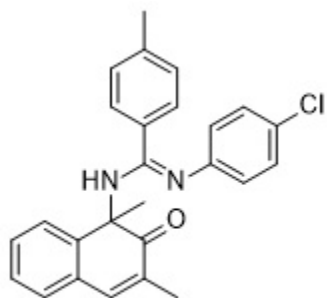
— 16.251

— 0.136



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)
SI-83



3ak

7.648
7.629
7.355
7.344
7.334
7.324
7.313
7.302
7.260
7.234
7.226
7.214
7.163
7.144
7.068
7.048
6.832
6.812
6.085
6.065

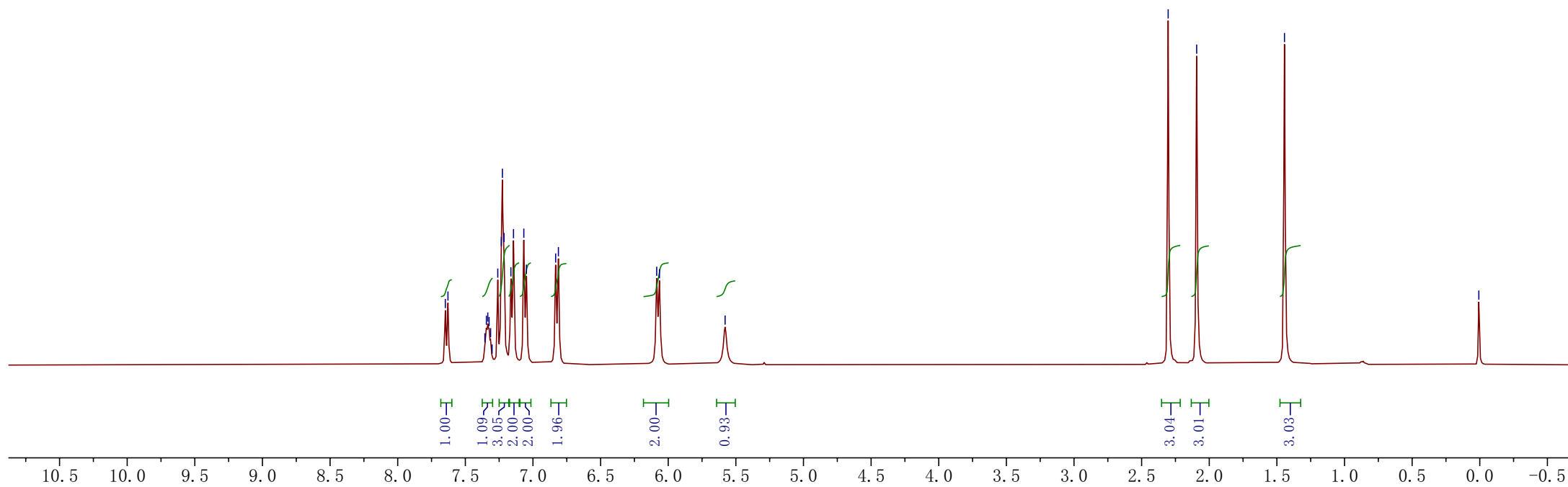
5.579

2.304

2.093

1.444

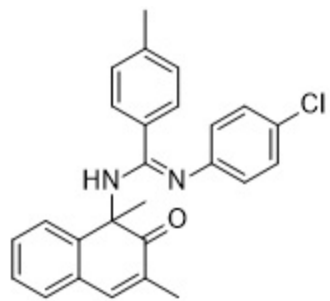
0.007



f1 (ppm)

SI-84

— 200.619



3ak

— 154.100

— 148.322

— 146.068

— 140.226

— 139.720

— 132.368

— 130.432

— 130.068

— 129.077

— 128.750

— 128.565

— 128.415

— 128.105

— 126.647

— 126.296

— 123.747

— 123.370

— 77.478

— 77.160

— 76.842

— 61.780

— 28.954

— 21.417

— 16.142

— 130.432

— 130.068

— 129.077

— 128.750

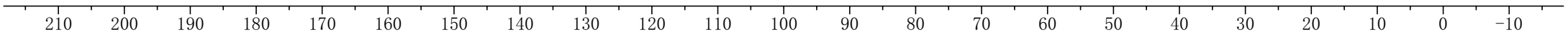
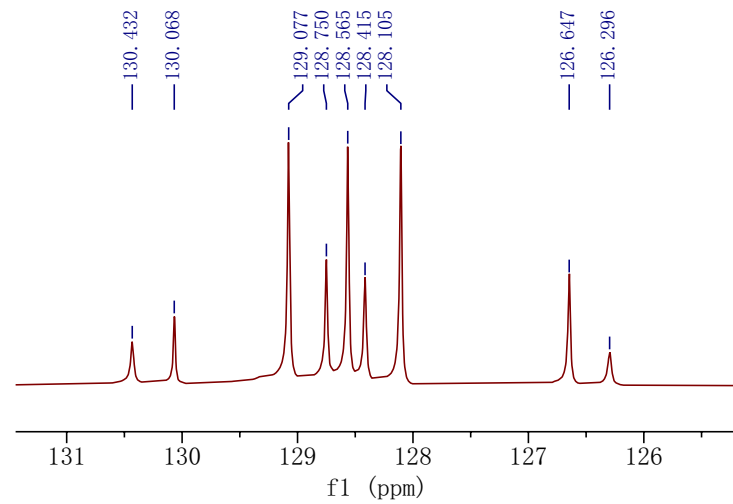
— 128.565

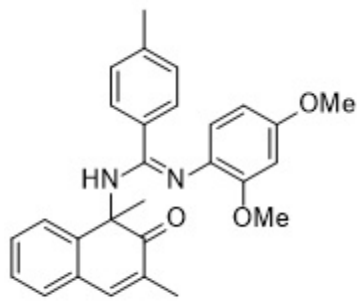
— 128.415

— 128.105

— 126.647

— 126.296





3al

7.739
7.719
7.312
7.292
7.260
7.210
7.196
7.180
7.161
7.120
6.992
6.972

6.198

5.290

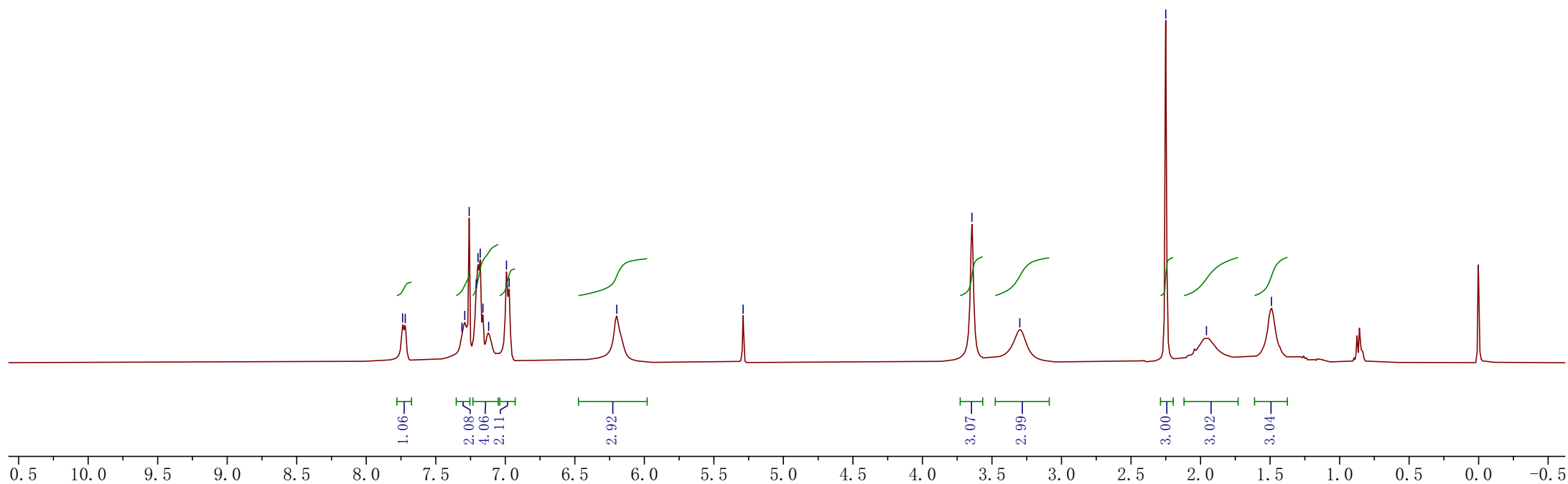
3.644

3.300

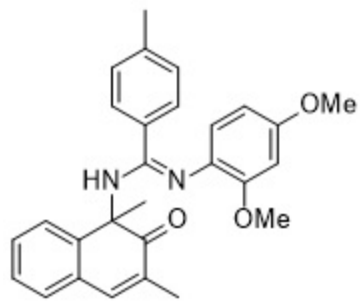
2.250

1.957

1.490



— 198.978



3al

— 154.933

— 151.982

— 146.723

— 138.476

— 131.794

— 129.837

— 128.206

— 128.057

— 127.448

— 126.139

— 124.279

— 104.822

— 100.532

— 61.555

— 55.630

— 54.940

— 40.147

— 39.937

— 39.730

— 39.524

— 39.312

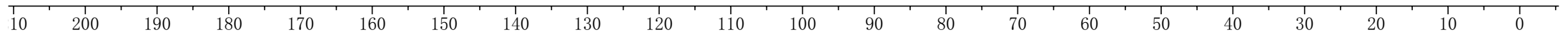
— 39.103

— 38.894

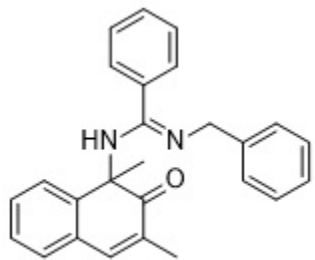
— 27.809

— 20.808

— 16.234



f1 (ppm)
SI-87



3am

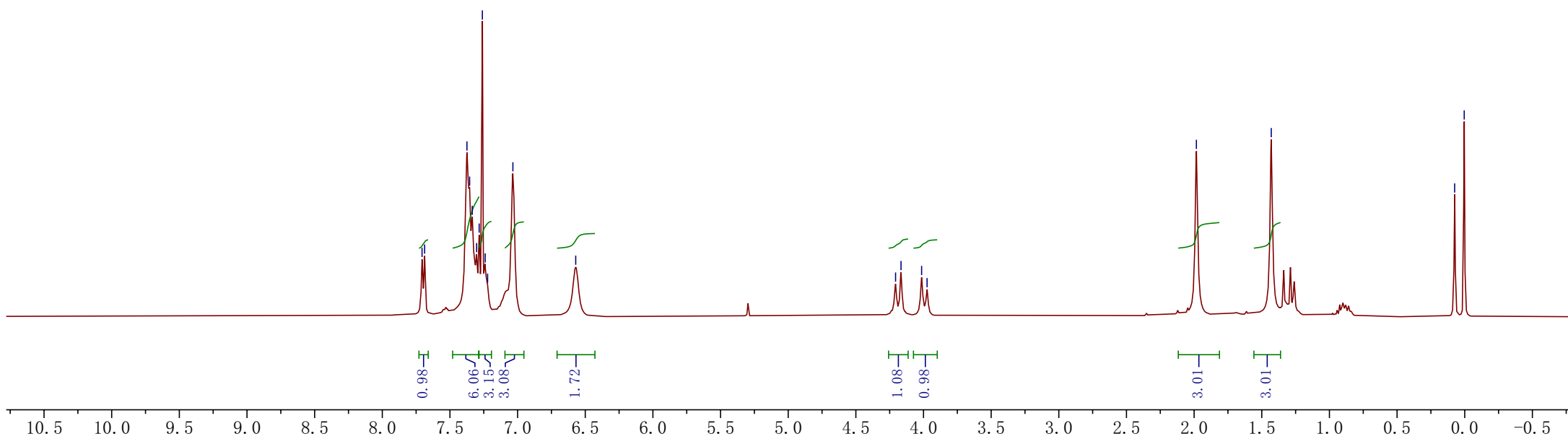
7.706
7.687
7.374
7.354
7.335
7.303
7.284
7.260
7.240
7.222
7.035
6.570

4.207
4.166
4.014
3.974

1.983

1.430

0.074
0.004



0.98

6.06

3.15

3.08

1.72

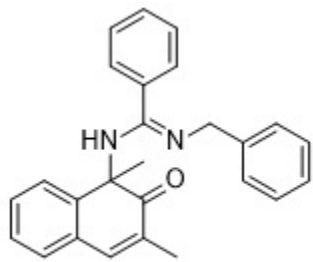
1.08

0.98

3.01

3.01

— 202.396



3am

— 156.737

— 146.279

— 141.953

— 138.924

— 133.622

— 132.299

— 130.238

— 129.410

— 128.846

— 128.518

— 128.139

— 127.820

— 127.753

— 126.625

— 126.504

— 125.603

— 124.574

— 77.478

— 77.160

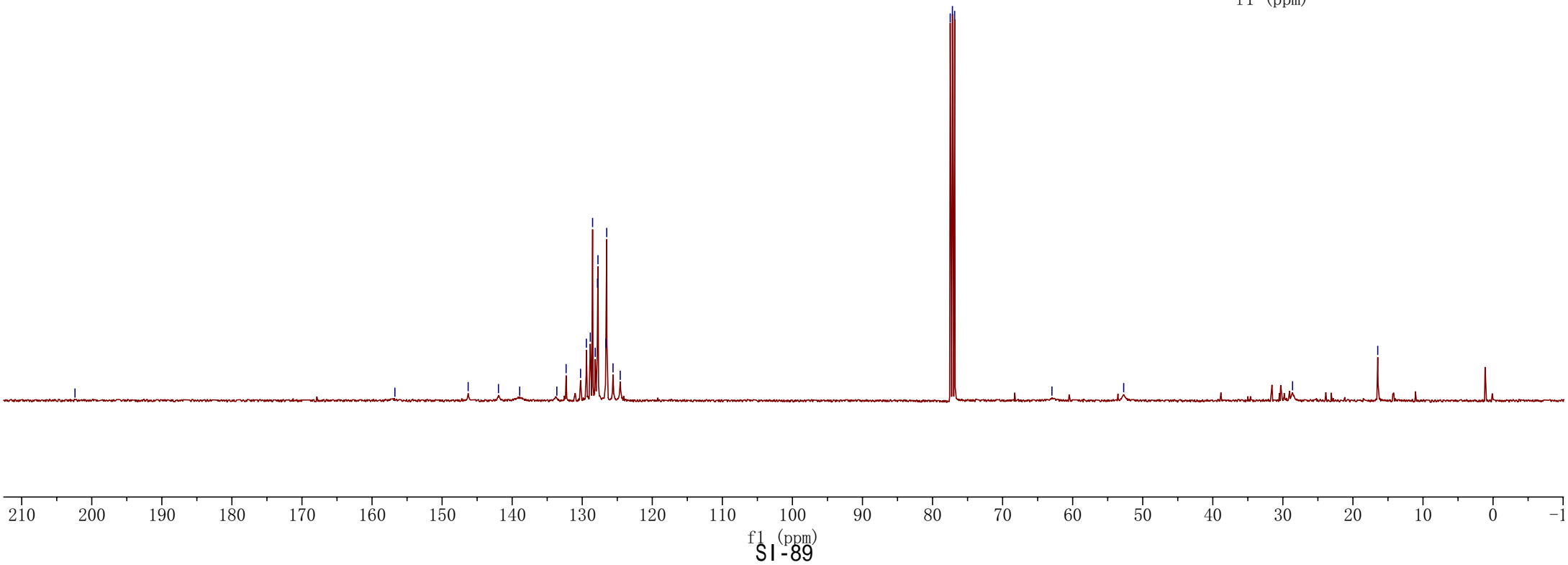
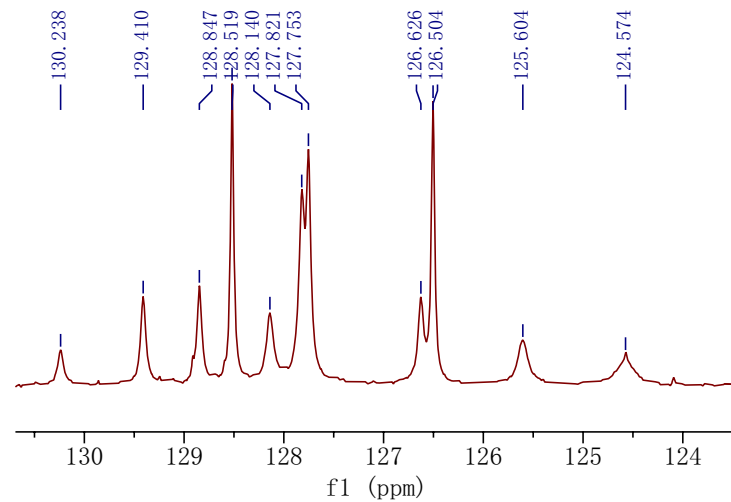
— 76.842

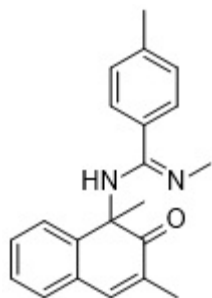
— 62.957

— 52.718

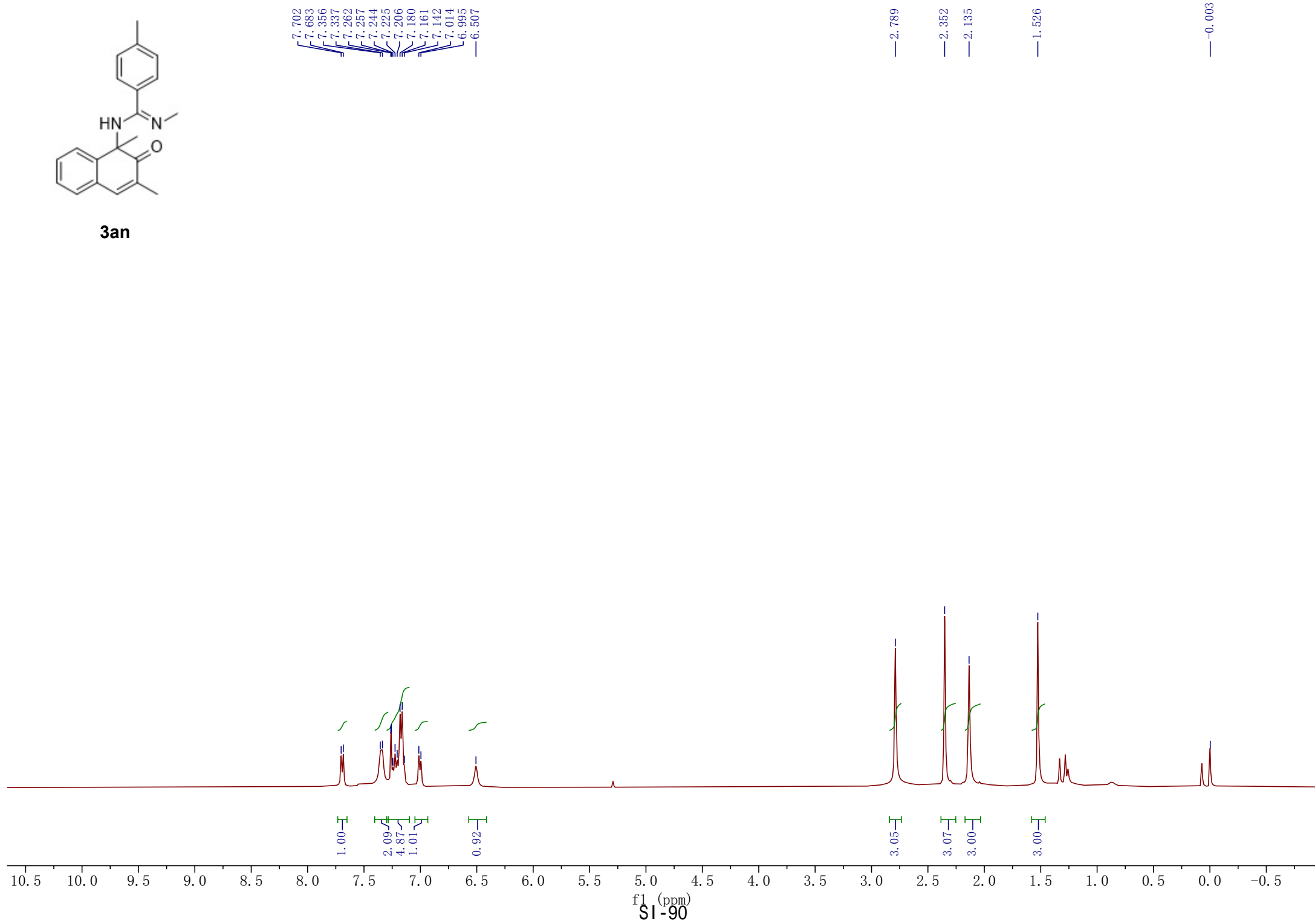
— 28.614

— 16.457

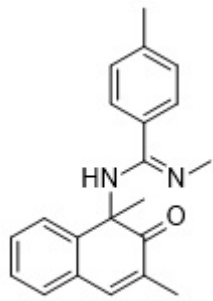




3an



— 203.222



3an

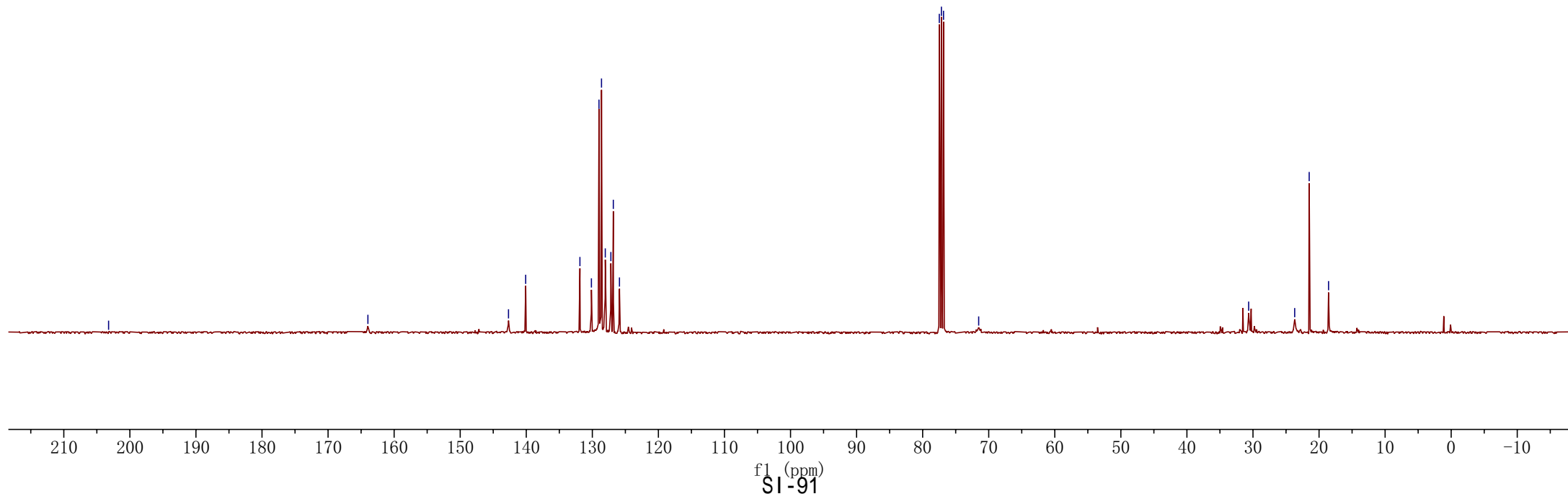
— 163.970

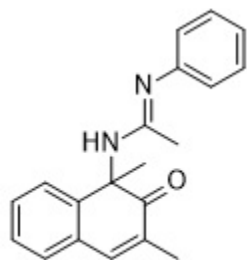
— 142.688
— 140.088
— 131.879
— 130.138
— 128.991
— 128.611
— 128.039
— 127.194
— 126.824
— 125.893

— 77.480
— 77.162
— 76.842
— 71.520

— 30.654

— 23.688
— 21.492
— 18.560





3ao

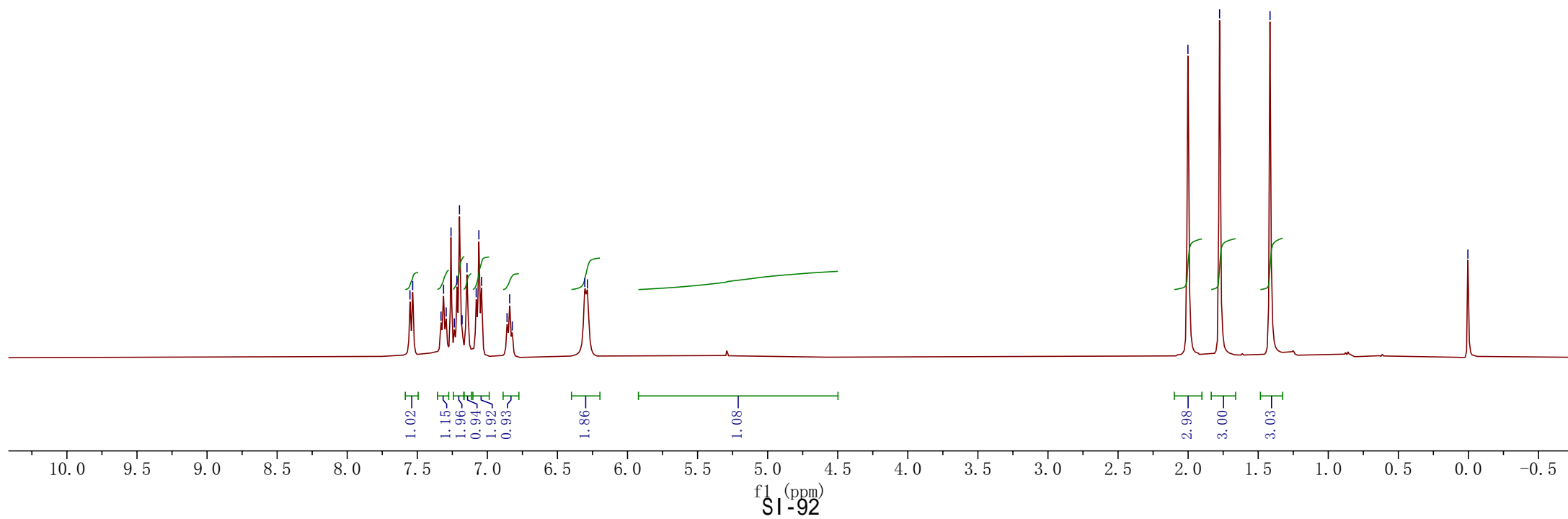
7.552
7.533
7.331
7.312
7.294
7.259
7.236
7.217
7.199
7.180
7.145
7.080
7.061
7.042
6.859
6.841
6.822
6.305
6.285

—2.001

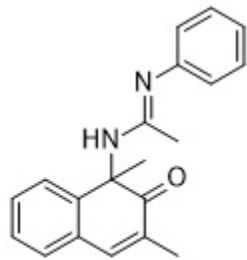
—1.776

—1.416

—0.004



— 199.031



3ao

• ao

~ 152.420
~ 149.888
~ 146.148
— 139.833
— 132.141
— 130.031
— 128.638
— 128.450
— 128.230
— 126.518
— 124.146
— 122.027
— 121.846

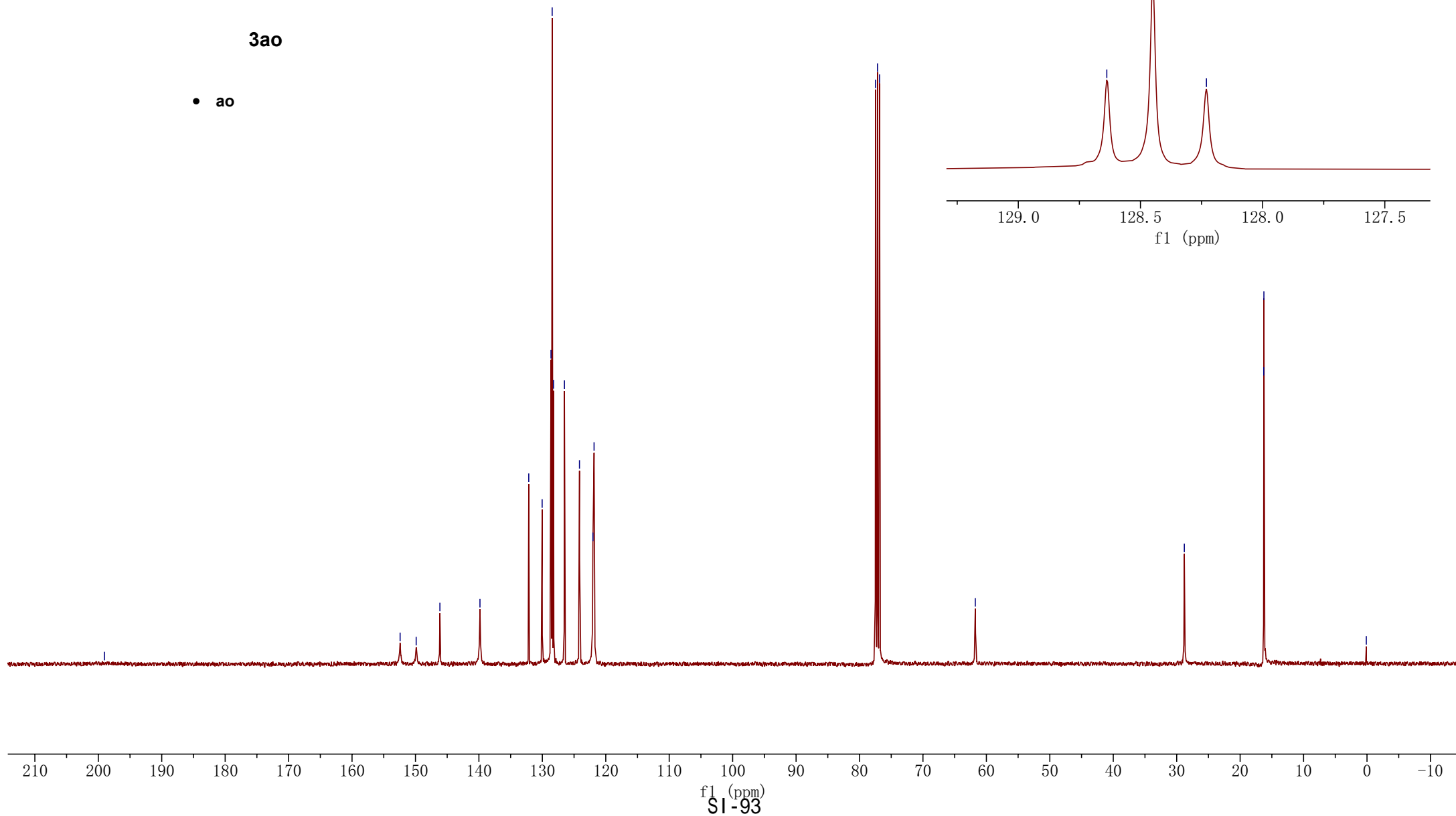
~ 77.478
~ 77.161
~ 76.843

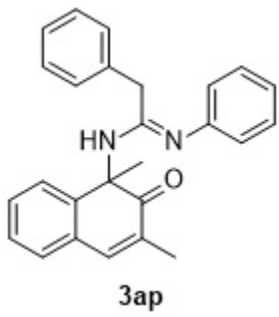
— 61.750

— 28.797

~ 16.279
~ 16.252

— 0.111





7.379
7.360
7.315
7.297
7.284
7.276
7.260
7.244
7.225
7.210
7.191
7.165
7.077
7.058
7.039
6.853
6.835
6.816
6.315
6.296

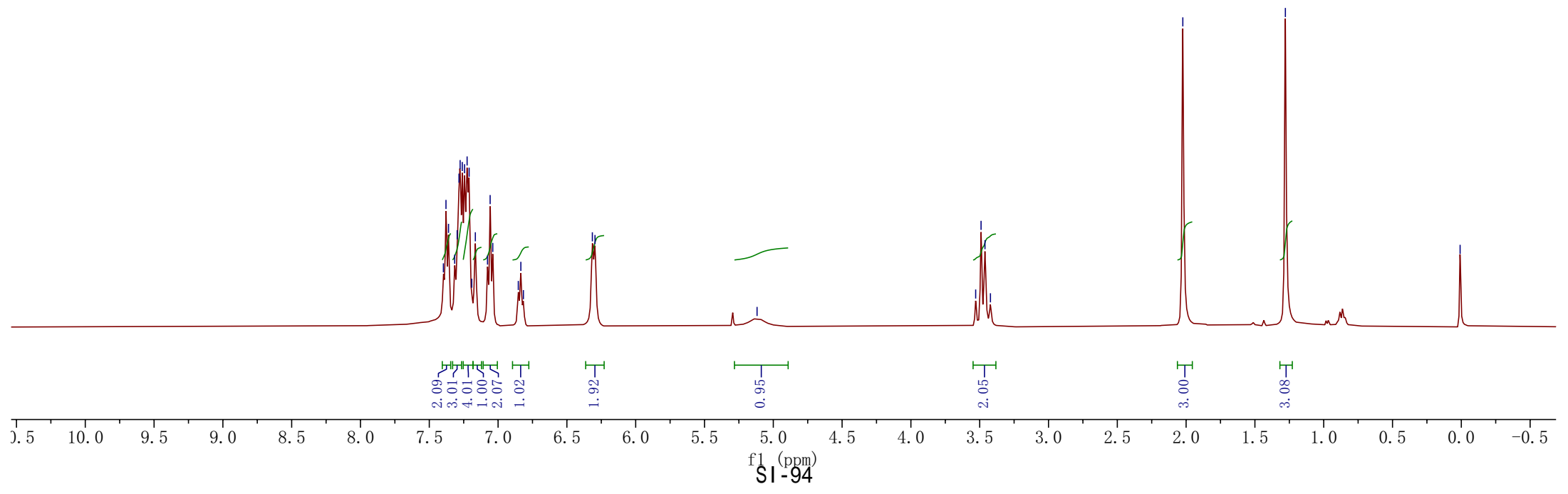
5.118

3.529
3.490
3.462
3.422

2.024

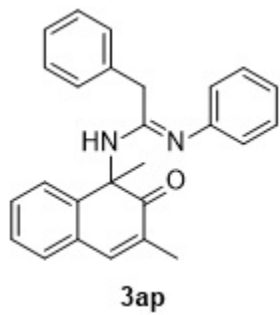
1.279

0.009



f1 (ppm)
SI-94

— 200.612



152.386
149.885
146.189
140.079
136.263
132.225
130.192
129.182
128.876
128.533
128.473
128.188
126.994
126.516
123.898
121.952
121.557

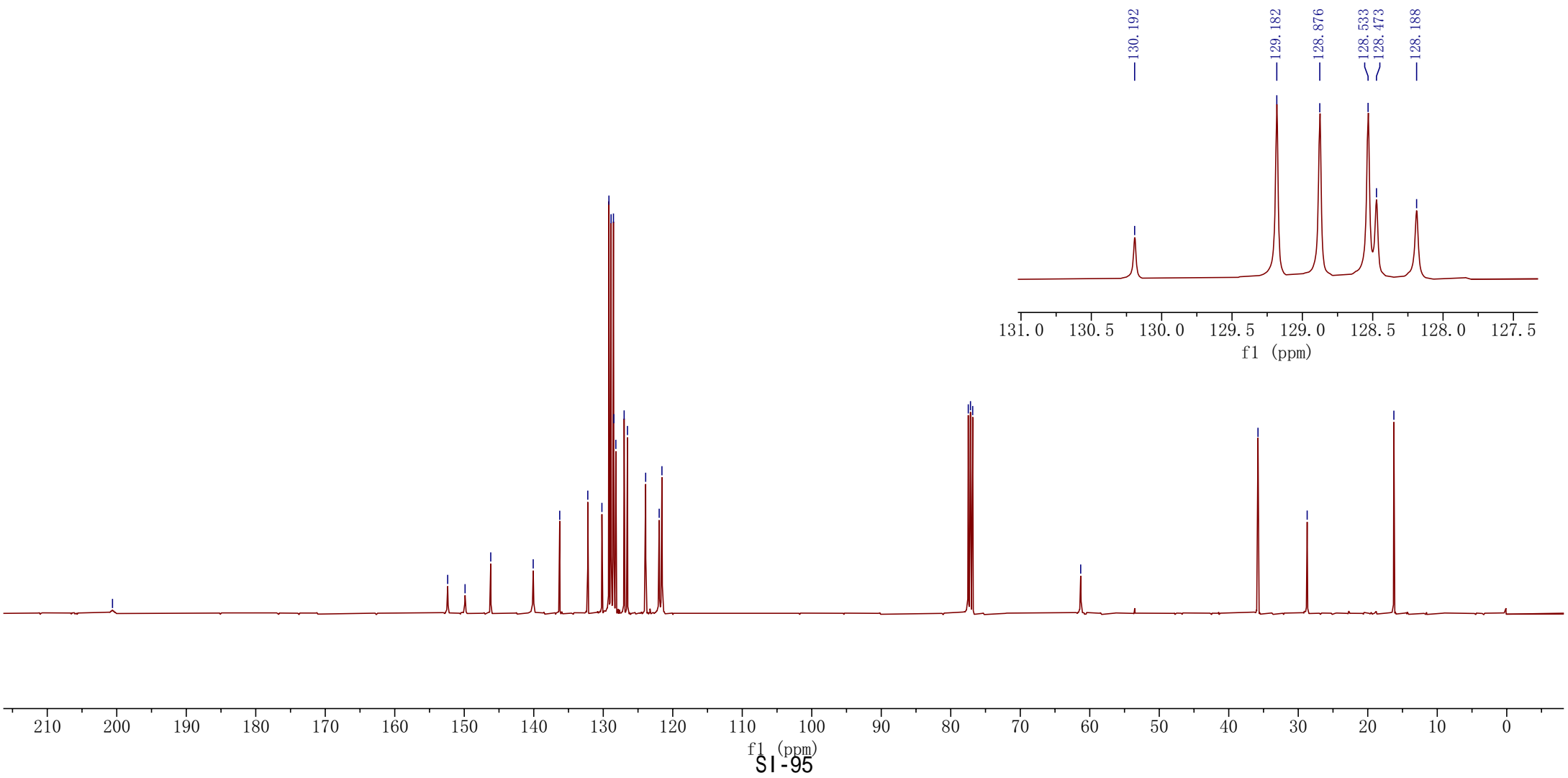
77.478
77.160
76.843

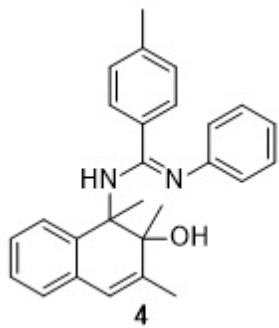
— 61.303

— 35.793

— 28.717

— 16.241





8.925
7.565
7.552
7.545
7.538
7.530
7.524
7.322
7.317
7.302
7.297
7.261
7.255
7.234
7.227
7.220
7.212
7.206
7.143
7.123
7.099
7.094
7.078
7.060
7.055
7.031
7.024
7.017
7.009
7.003
6.883
6.865
6.846
6.737
6.717
6.056

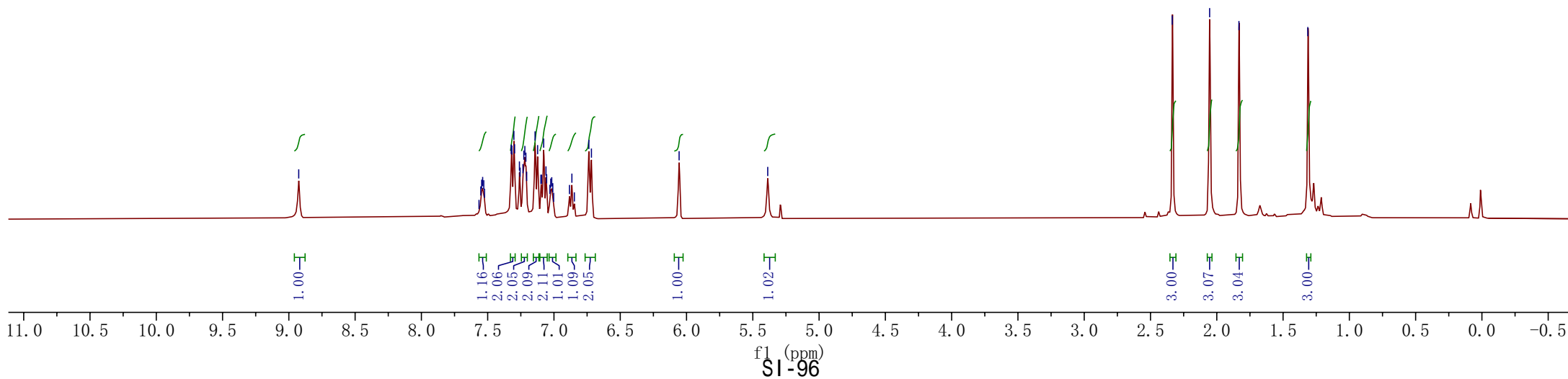
5.387

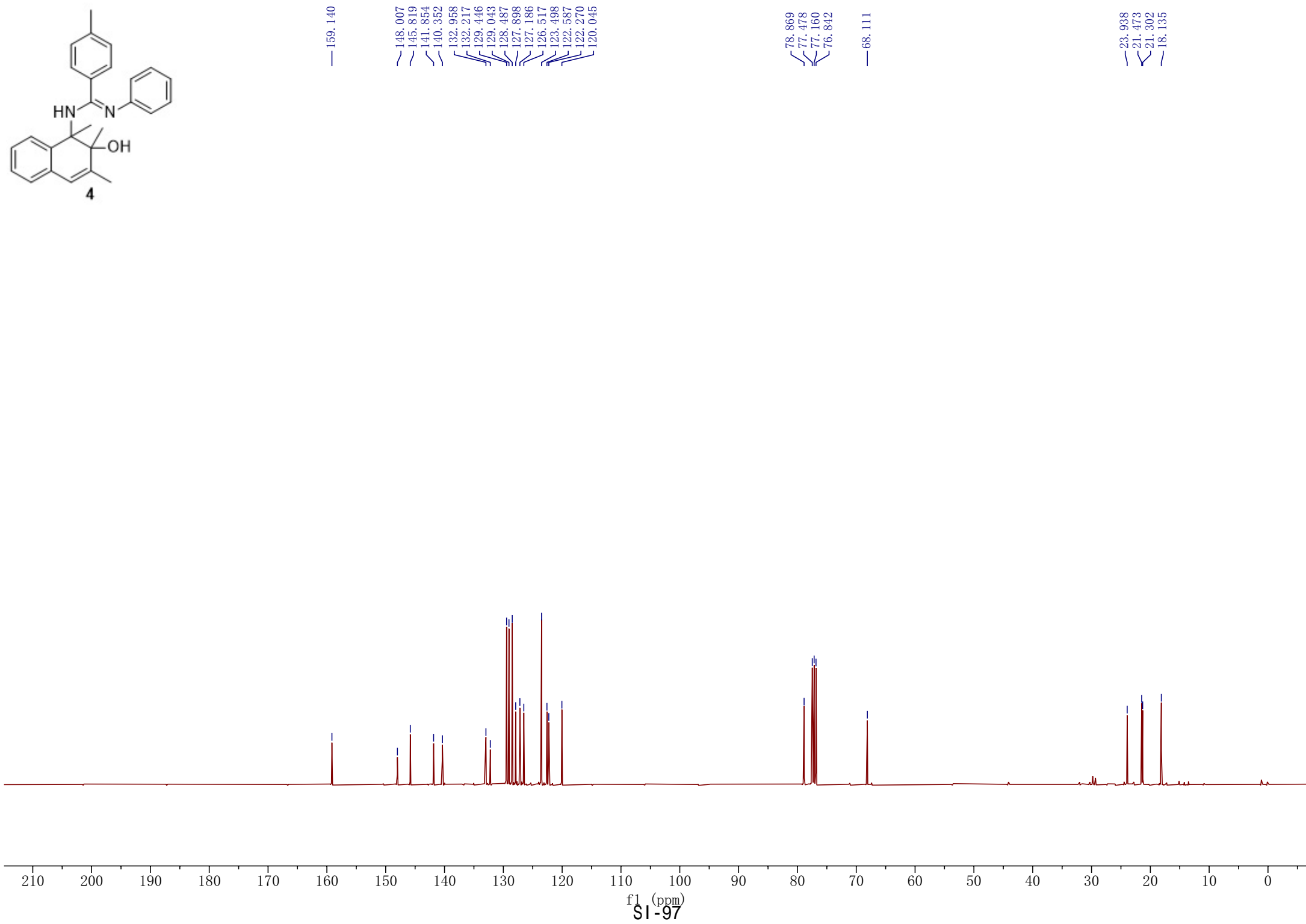
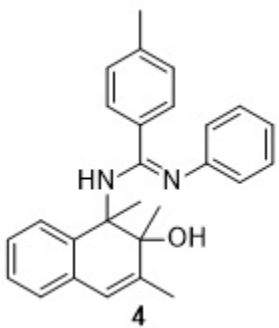
2.336

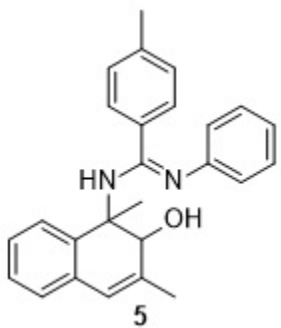
2.054

1.833

1.313



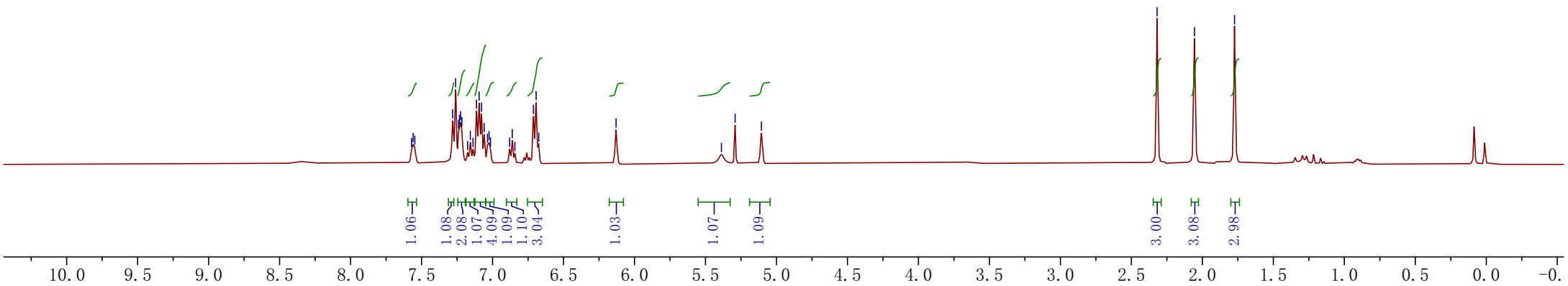




7.570
7.559
7.547
7.281
7.260
7.239
7.233
7.226
7.216
7.176
7.157
7.138
7.113
7.095
7.078
7.059
7.036
7.025
7.014
6.880
6.861
6.843
6.712
6.675
6.130

5.388
5.291
5.106

2.319
2.056
1.773



f1 (ppm)
SI-98

