

Nickel-Catalyzed Reductive 1,1-Diarylation of Unactivated Alkenes with Aryl Iodides

Zhengwen Wang,[†] Zhou Jin[†] and Bingwei Zhou^{*}

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310014, China.

E-mail: zhoubw@zjut.edu.cn

[†]These authors contributed equally to this work.

Table of Contents

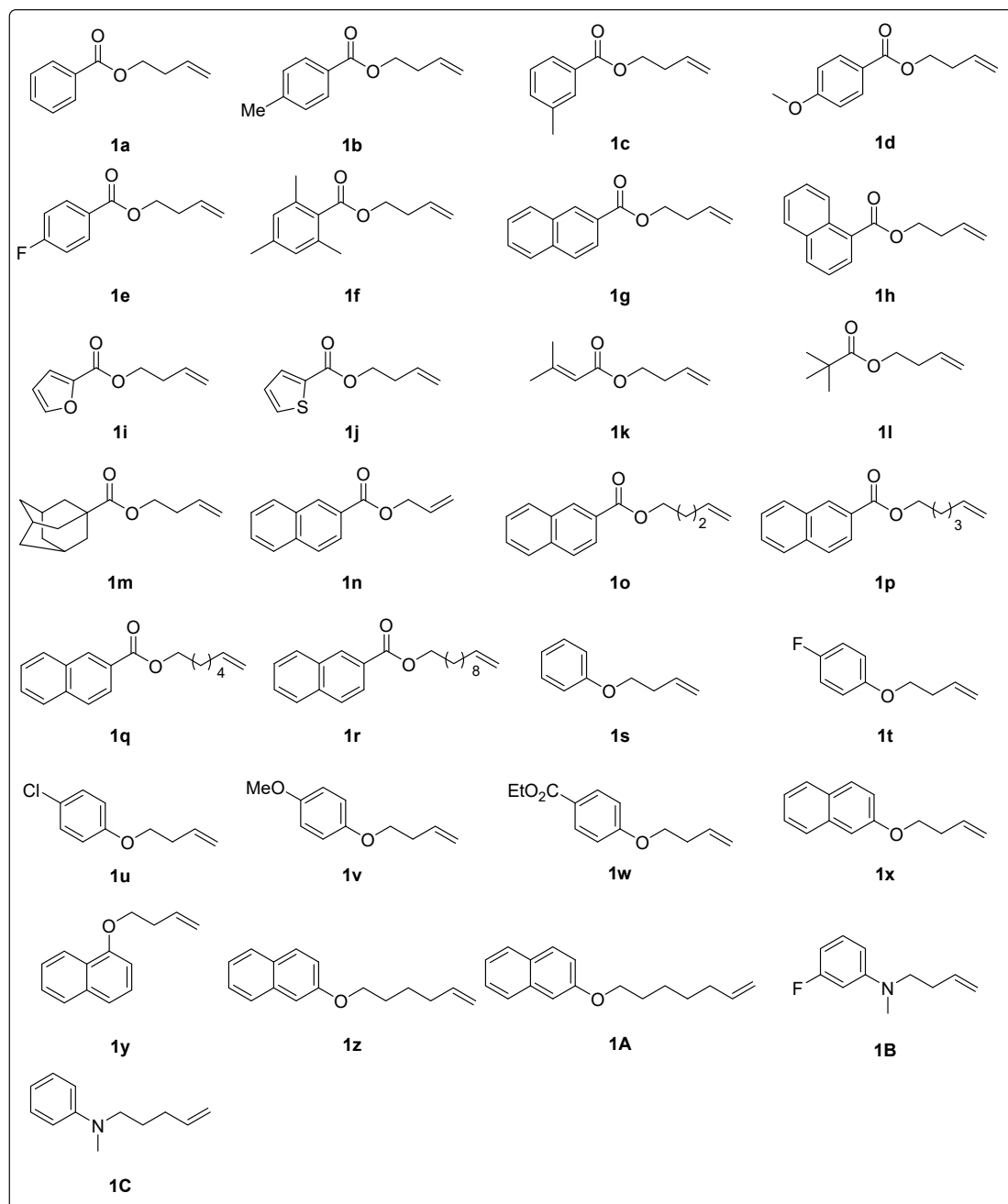
1.	General Information	S2
2.	Substrate Preparation	S3
3.	Nickel-Catalyzed 1,1-Diarylation of Alkenes with Aryl Iodides	S5
	3.1 Optimization of reaction conditions	S5
	3.2 Experimental details and characterization of products	S6
	3.3 The reaction of alkene with iodobenzene using L2 as ligand	S20
4.	Mechanistic Studies	S21
	4.1 Radical scavenging experiment	S21
	4.2 Deuterium-labelling experiment	S21
	4.3 The reaction of 4b with 2a	S25
	4.4 The model reaction by adding D ₂ O	S25
5.	References	S27
6.	¹ H, ¹³ C and ¹⁹ F NMR Spectra	S28

1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. (*Cautions: the 25-mL SYNTHWARE Schlenk tube usually could withstand 5 atm. And for safety concern, all the reactions should be conducted in the explosion-proof fume hood.*) Solvents were purified and dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

The ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 400 or 500 AV spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. Coupling constant (J) was reported in hertz unit (Hz). The high resolution mass spectra (HRMS) were recorded on an Agilent 6210 LC/TOF spectrometer.

2. Substrate Preparation



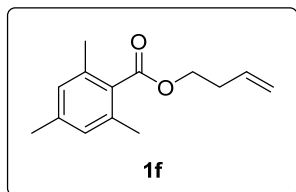
General procedure for the synthesis of esters:



A mixture of the corresponding acid (10.0 mmol), alkyl bromide (1.2 equiv.), and potassium carbonate (1.2 equiv.) in 10 ml of anhydrous DMF was stirred at 70 °C overnight. Then the reaction mixture was diluted with EtOAc (10×3 mL), washed with H₂O (20 mL), saturated NaHCO₃ (10 mL) and brine (10 mL) sequentially. The organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent under

reduced pressure, the crude product was purified by column chromatography on silica gel to give the product.^[1]

but-3-en-1-yl 2,4,6-trimethylbenzoate (**1f**)



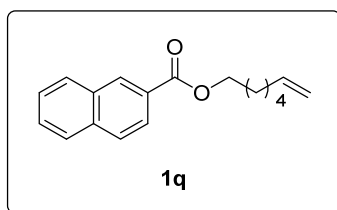
Yield: 93%, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.84 (s, 2H), 5.90 – 5.78 (m, 1H), 5.18 – 5.08 (m, 2H), 4.39 – 4.34 (m, 2H), 2.53 – 2.47 (m, 2H), 2.29 (d, *J* = 2.8 Hz, 6H), 2.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 169.9, 139.0, 134.9, 133.9, 130.9, 128.2, 117.2, 63.7, 33.0, 20.9, 19.6.

HRMS(ESI) Calculated for C₁₄H₁₈NaO₂⁺ ([M+Na]⁺): 241.11990, found: 241.11973.

hept-6-en-1-yl 2-naphthoate (**1q**)



Yield: 86%, colorless oil.

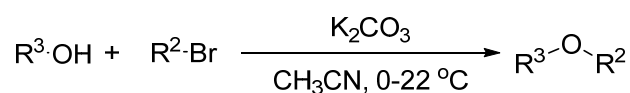
¹H NMR (400 MHz, CDCl₃) δ 8.59 (s, 1H), 8.08 – 8.02 (m, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.48 (m, 2H), 5.85 – 5.76 (m, 1H), 5.05 –

4.94 (m, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 2.08 (d, *J* = 6.4 Hz, 2H), 1.82 – 1.76 (m, 2H), 1.50 – 1.46 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 166.6, 138.5, 135.3, 132.4, 130.8, 129.2, 128.0, 127.9, 127.6, 126.4, 125.1, 114.4, 65.0, 33.5, 28.5, 28.4, 25.4.

HRMS(ESI) Calculated for C₁₈H₂₀NaO₂⁺ ([M+Na]⁺): 291.13555, found: 291.13538.

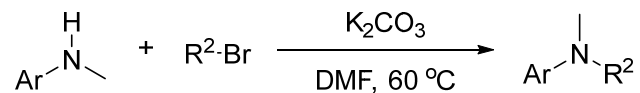
General procedure for the synthesis of ethers:



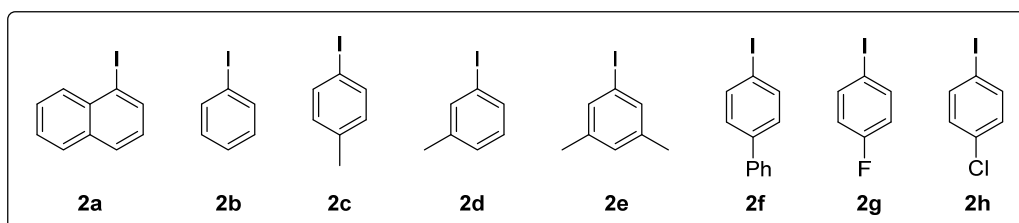
To a solution of aromatic alcohol (2.0 mmol) and K₂CO₃ (5.0 mmol) in CH₃CN (8.0 mL) was added alkyl bromide (4.0 mmol) and the mixture was refluxed for 12 h. It was then cooled to 22 °C and the solvent was removed in vacuo. The residue was partitioned between CH₂Cl₂ and water and the aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layer were washed with water (10 mL),

dried and concentrated in vacuo. The residue was purified by silica gel flash chromatography to provide the corresponding product. [2]

General procedure for the synthesis of amines:



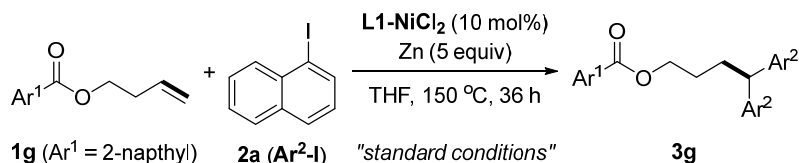
In a 100 mL round bottom flask, N-methyl aniline (10.0 mmol), dimethyl formamide (15 mL), potassium carbonate (25.0 mmol) and alkyl bromide (15.0 mmol) were added and stirred at 60 °C for four hours. The reaction mixture was quenched with ice water and extracted with ethyl acetate. Solvent was removed under reduced pressure. The crude product was purified by column chromatography (Eluent: Hexane) to give the pure product. [3]



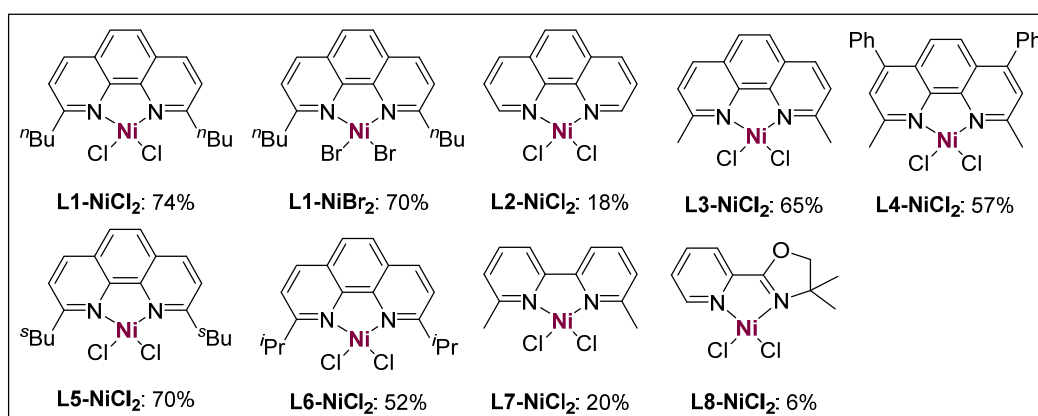
All of the aryl iodides are commercially available and used as received.

3. Nickel-Catalyzed Hydrosilylation/Cyclization of 1,7-Enynes

3.1 Optimization of reaction conditions^a

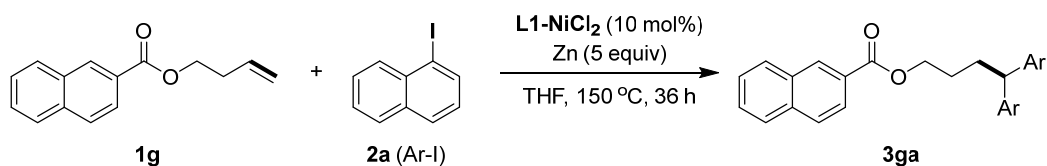


Entry	Derivation from standard conditions	Yield of 3ga
1	None	74%
2	NiCl ₂ , L1 instead of L1-NiCl₂	72%
3	NiBr ₂ , L1 instead of L1-NiCl₂	70%
4	Ni(acac) ₂ , L1 instead of L1-NiCl₂	0
5	No L1-NiCl₂	0
6	L2-NiBr₂-L8-NiCl₂	See below
7	L1-NiCl₂ (20 mol%)	77%
8	Mn, Sn or Mg instead of Zn	0
9	No Zn	0
10	Toluene	0
11	Dioxane	Trace
12	DME	0
13	DMF	0
14	1g : 2a = 2 : 1	Trace
15	1g : 2a = 1 : 1	30%
16	1g : 2a = 1 : 2	38%
17	1g : 2a = 1 : 6	74%
18	At 120 °C	67%
19	At 80 °C	40%
20	At 40 °C	30%
21	For 12 h	55%
22	For 48 h	72%



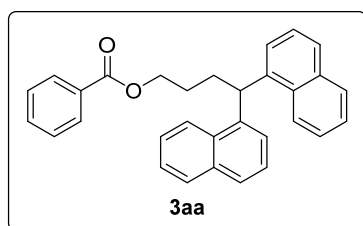
^aStandard reaction conditions: **1g** (0.2 mmol), **2a** (0.8 mmol), **L1-NiCl₂** (10 mol%), Zn (5 equiv), THF (1 mL), at 150 °C for 36 h.

3.2 Experimental details and characterization of products



To a 25-mL flame-dried Schlenk tube containing a stirring bar was added but-3-en-1-yl 2-naphthoate **1g** (0.2 mmol, 45.3 mg), 1-iodonaphthalene (0.8 mmol, 203.2 mg), **L1-NiCl₂** (10 mol%, 0.02 mmol, 8.5 mg), Zn (5 equiv, 1 mmol, 65 mg), THF (1 mL). The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product **3ga** in 74% yield.

4,4-di(naphthalen-1-yl)butyl benzoate (**3aa**)



Yield: 58% (49 mg), white solid, mp: 111-113 °C.

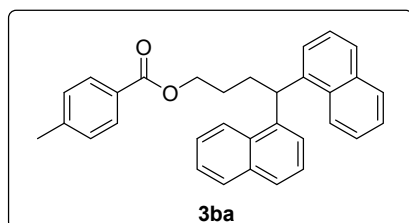
¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 –

7.36 (m, 10H), 5.63 (t, *J* = 7.4 Hz, 1H), 4.37 (t, *J* = 6.2 Hz, 2H), 2.47–2.41 (m, 2H), 2.03 – 1.96 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 166.6, 140.0, 134.1, 132.8, 131.8, 130.3, 129.5, 129.0, 128.3, 127.1, 126.3, 125.4, 125.4, 124.8, 123.1, 64.8, 40.8, 32.1, 27.6.

HRMS(ESI) Calculated for C₃₁H₂₆NaO₂⁺ ([M+Na]⁺): 453.18250, found: 453.18234.

4,4-di(naphthalen-1-yl)butyl 4-methylbenzoate (**3ba**)



Yield: 58% (51 mg), white solid, mp: 117-118 °C.

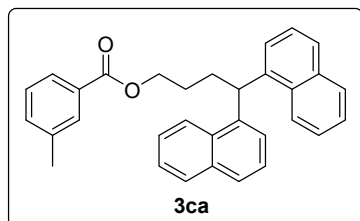
¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.86 – 7.83 (m, 2H), 7.74 – 7.69 (m, 2H), 7.46 – 7.35 (m, 8H), 7.22 – 7.18 (m, 2H), 5.63 (t, *J* = 7.4 Hz, 1H), 4.35 (t, *J* =

6.4 Hz, 2H), 2.47 – 2.40 (m, 2H), 2.38 (s, 3H), 2.03 – 1.95 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 143.5, 140.0, 134.1, 131.8, 129.6, 129.0, 129.0, 127.6, 127.1, 126.3, 125.4, 124.8, 123.2, 64.6, 40.8, 32.1, 27.6, 21.6.

HRMS(ESI) Calculated for $\text{C}_{32}\text{H}_{28}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 467.19815, found: 467.19803.

4,4-di(naphthalen-1-yl)butyl 3-methylbenzoate (3ca)



Yield: 62% (55 mg), white solid, mp: 111-113 °C.

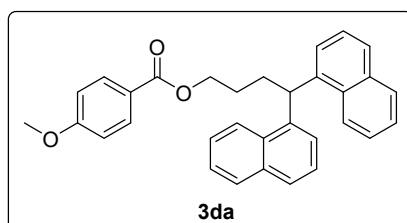
^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, J = 6.8 Hz, 2H), 7.86 – 7.81 (m, 4H), 7.74 – 7.71 (m, 2H), 7.46 – 7.42 (m, 2H), 7.41 – 7.34 (m, 7H), 7.29 (t, J = 5.0 Hz, 1H),

5.63 (t, J = 6.0 Hz, 1H), 4.37 (t, J = 5.2 Hz, 2H), 2.47 – 2.42 (m, 2H), 2.37 (s, 3H), 2.03 – 1.97 (m, 2H)..

^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 140.0, 138.1, 134.1, 133.6, 131.8, 130.1, 129.0, 128.2, 127.1, 126.7, 126.3, 125.4, 124.8, 123.2, 64.7, 40.8, 32.1, 27.6, 21.3.

HRMS(ESI) Calculated for $\text{C}_{32}\text{H}_{28}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 467.19815, found: 467.19803.

4,4-di(naphthalen-1-yl)butyl 4-methoxybenzoate (3da)



Yield: 41% (38 mg), white solid, mp: 111-113 °C.

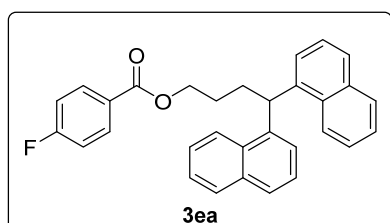
^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 7.6 Hz, 2H), 7.73 – 7.70 (m, 2H), 7.46 – 7.36 (m, 8H), 6.88 (d, J = 8.8 Hz, 2H), 5.63 (t, J = 7.4 Hz, 1H), 4.34 (t,

J = 6.1 Hz, 2H), 3.82 (s, 3H), 2.47 – 2.40 (m, 2H), 2.02 – 1.94 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 163.3, 140.1, 134.1, 131.8, 131.6, 129.0, 127.1, 126.3, 125.4, 124.8, 123.2, 122.7, 113.6, 64.5, 55.4, 40.8, 32.2, 27.6.

HRMS(ESI) Calculated for $\text{C}_{32}\text{H}_{28}\text{O}_3\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 483.19307, found: 483.19237.

4,4-di(naphthalen-1-yl)butyl 4-fluorobenzoate (3ea)



Yield: 63% (56 mg), white solid, mp: 127-129 °C.

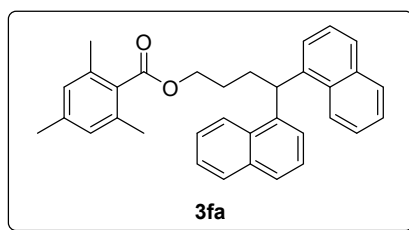
¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.5 Hz, 2H), 8.03 – 7.99 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.45 – 7.42 (m, 2H), 7.41 – 7.35 (m, 6H), 7.09 – 7.03 (m, 2H), 5.63 (t, *J* = 7.5 Hz, 1H), 4.36 (t, *J* = 6.5 Hz, 2H), 2.46 – 2.40 (m, 2H), 2.02 – 1.96 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 164.7 (¹*J*_{C-F} = 252.6 Hz), 165.6, 140.0, 134.2, 132.1 (³*J*_{C-F} = 9.3 Hz), 131.8, 129.1, 127.1, 126.5 (⁴*J*_{C-F} = 2.5 Hz), 126.3, 125.4, 125.4, 124.8, 123.1, 115.5 (²*J*_{C-F} = 21.8 Hz), 64.9, 40.8, 32.2, 27.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -105.7 (s).

HRMS(ESI) Calculated for C₃₁H₂₅O₂NaF⁺ ([M+Na]⁺): 471.17308, found: 471.17325.

4,4-di(naphthalen-1-yl)butyl 2,4,6-trimethylbenzoate (3fa)



Yield: 47% (44 mg), white solid, mp: 116-117 °C.

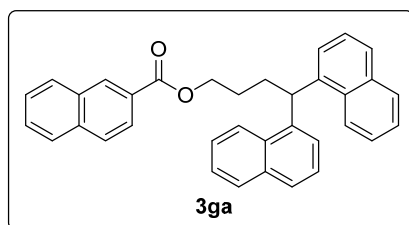
¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.44 – 7.40 (m, 1H), 7.39 – 7.32 (m, 6H), 6.81 (s, 2H), 5.59 (t, *J* = 7.5 Hz, 1H), 4.35 (t, *J* = 6.5 Hz,

2H), 2.42 – 2.36 (m, 2H), 2.26 – 2.22 (m, 9H), 1.97 – 1.91 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 170.1, 140.1, 139.2, 135.1, 134.1, 131.8, 131.0, 129.0, 128.4, 127.1, 126.3, 125.4, 124.8, 123.1, 64.8, 40.8, 32.5, 27.7, 21.1, 19.8.

HRMS(ESI) Calculated for C₃₄H₃₂O₂Na⁺ ([M+Na]⁺): 495.22945, found: 495.22931.

4,4-di(naphthalen-1-yl)butyl 2-naphthoate (3ga)



Yield: 74% (71mg), white solid, mp: 133-134 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.57 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 8.05 – 8.03 (m, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.82 (m, 4H), 7.72 – 7.69 (m, 2H), 7.56 – 7.52 (m, 1H), 7.51 – 7.47 (m, 1H), 7.43

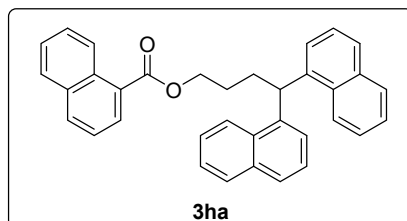
– 7.34 (m, 8H), 5.66 (t, *J* = 7.5 Hz, 1H), 4.43 (t, *J* = 6.3 Hz, 2H), 2.50 – 2.45 (m, 2H), 2.07 – 2.00 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 166.7, 140.0, 135.5, 134.2, 132.5, 131.8, 131.0, 129.3,

129.0, 128.2, 128.1, 127.7, 127.5, 127.1, 126.6, 126.3, 125.4, 125.2, 124.8, 123.1, 64.9, 40.8, 32.2, 27.6.

HRMS(ESI) Calculated for $C_{35}H_{28}O_2Na^+$ ($[M+Na]^+$): 503.19815 found: 503.19760.

4,4-di(naphthalen-1-yl)butyl 1-naphthoate (3ha)



Yield: 61% (59 mg), white solid, mp: 130-131 °C.

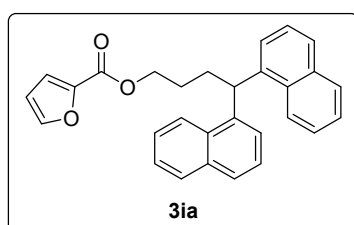
1H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, $J = 8.5$ Hz, 1H), 8.14 – 8.11 (m, 3H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.84 (t, $J = 7.5$ Hz, 3H), 7.72 – 7.69 (m, 2H), 7.57 –

7.53 (m, 1H), 7.51 – 7.47 (m, 1H), 7.44 – 7.39 (m, 3H), 7.38 – 7.33 (m, 6H), 5.65 (t, $J = 7.5$ Hz, 1H), 4.46 (t, $J = 6.3$ Hz, 2H), 2.50 – 2.45 (m, 2H), 2.08 – 2.01 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 140.0, 134.1, 133.8, 133.3, 131.8, 131.3, 130.1, 129.0, 128.5, 127.7, 127.2, 127.0, 126.3, 126.2, 125.8, 125.4, 124.8, 124.4, 123.1, 64.9, 40.9, 32.3, 27.7.

HRMS(ESI) Calculated for $C_{35}H_{28}O_2Na^+$ ($[M+Na]^+$): 503.19815 found: 503.19760.

4,4-di(naphthalen-1-yl)butyl furan-2-carboxylate (3ia)



Yield: 27% (23 mg), white solid, mp: 134-135 °C.

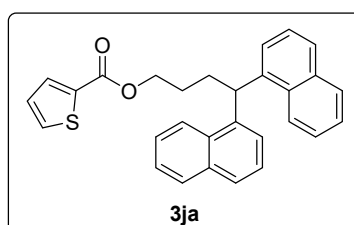
1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.0$ Hz, 2H), 7.86 – 7.84 (m, 2H), 7.73 – 7.70 (m, 2H), 7.55 (s, 1H), 7.46 – 7.35 (m, 8H), 7.13 (d, $J = 3.5$ Hz, 1H), 6.48 – 6.46 (m, 1H), 5.62 (t, $J = 7.5$ Hz, 1H), 4.36 (t, $J = 6.5$

Hz, 2H), 2.43 – 2.38 (m, 2H), 2.00 – 1.94 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 146.2, 144.7, 140.0, 134.1, 131.8, 129.0, 127.1, 126.3, 125.4, 124.8, 123.2, 117.8, 111.8, 64.8, 40.8, 32.0, 27.5.

HRMS(ESI) Calculated for $C_{29}H_{24}O_3Na^+$ ($[M+Na]^+$): 443.16177, found: 443.16129.

4,4-di(naphthalen-1-yl)butyl thiophene-2-carboxylate (3ja)



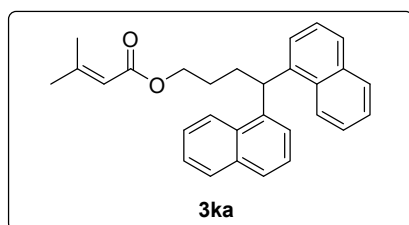
Yield: 65% (57 mg), white solid, mp: 126-128 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.87 – 7.83 (m, 2H), 7.78 – 7.76 (m, 1H), 7.75 – 7.69 (m, 2H), 7.53 – 7.51 (m, 1H), 7.46 – 7.35 (m, 8H), 7.08 – 7.05 (m, 1H), 5.62 (t, *J* = 7.4 Hz, 1H), 4.34 (t, *J* = 6.2 Hz, 2H), 2.45 – 2.39 (m, 2H), 2.01 – 1.93 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 162.3, 140.0, 134.1, 133.8, 133.4, 132.3, 131.8, 129.0, 127.70, 127.1, 126.3, 125.4, 124.8, 123.2, 64.9, 40.8, 32.0, 27.6.

HRMS(ESI) Calculated for C₂₉H₂₄O₂SNa⁺ ([M+Na]⁺): 459.13892, found: 459.13846.

4,4-di(naphthalen-1-yl)butyl 3-methylbut-2-enoate (3ka)



Yield: 22% (18 mg), white solid, mp: 117-118 °C.

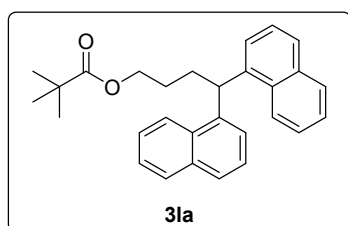
¹H NMR (500 MHz, CDCl₃) δ 8.13 – 8.10 (m, 2H), 7.86 – 7.82 (m, 2H), 7.71 – 7.69 (m, 2H), 7.45 – 7.39 (m, 4H), 7.38 – 7.33 (m, 4H), 5.66 – 5.64 (m, 1H), 5.59 (t, *J* = 7.5 Hz, 1H), 4.14 (t, *J* = 6.5 Hz,

2H), 2.37 – 2.32 (m, 2H), 2.13 (d, *J* = 1.0 Hz, 3H), 1.89 – 1.83 (m, 5H).

¹³C NMR (125 MHz, CDCl₃) δ 166.7, 156.6, 140.1, 134.1, 131.8, 129.0, 127.0, 126.2, 125.4, 125.4, 124.8, 123.2, 116.0, 63.4, 40.7, 32.2, 27.5, 27.3, 20.2.

HRMS(ESI) Calculated for C₂₉H₂₈O₂Na⁺ ([M+Na]⁺): 431.19815, found: 431.19785.

4,4-di(naphthalen-1-yl)butyl pivalate (3la)



Yield: 48% (39 mg), white solid, mp: 138-140 °C.

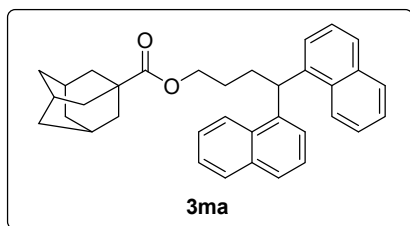
¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.87 – 7.84 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.33 (m, 8H), 5.57 (t, *J* = 7.2 Hz, 1H), 4.12 (t, *J* = 6.2 Hz, 2H), 2.38 – 2.31 (m, 2H), 1.90 – 1.82 (m, 2H), 1.18 (s,

9H).

¹³C NMR (100 MHz, CDCl₃) δ 178.6, 140.1, 134.2, 131.8, 129.0, 127.1, 126.3, 125.4, 125.4, 124.8, 123.2, 64.2, 41.0, 38.7, 32.1, 27.7, 27.2.

HRMS(ESI) Calculated for C₂₉H₃₀O₂Na⁺ ([M+Na]⁺): 433.21380, found: 433.21378.

4,4-di(naphthalen-1-yl)butyl (3r,5r,7r)-adamantane-1-carboxylate (3ma)



Yield: 42% (41 mg), white solid, mp: 152-154°C.

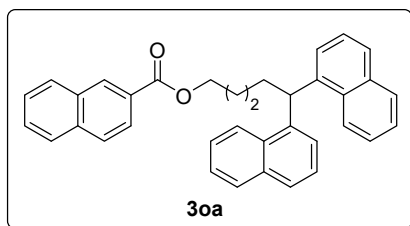
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.12 – 8.09 (m, 2H), 7.87 – 7.84 (m, 2H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.47 – 7.33 (m, 8H), 5.57 (t, $J = 7.4$ Hz, 1H), 4.11 (t, $J =$

6.2 Hz, 2H), 2.38 – 2.31 (m, 2H), 1.99 (s, 3H), 1.89 – 1.81 (m, 8H), 1.74 – 1.65 (m, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 177.7, 140.1, 134.1, 131.8, 129.0, 127.0, 126.3, 125.4, 125.4, 124.8, 123.2, 63.9, 41.0, 40.7, 38.9, 36.5, 32.1, 27.9, 27.7.

HRMS(ESI) Calculated for $\text{C}_{35}\text{H}_{36}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 511.26075, found: 511.26050.

5,5-di(naphthalen-1-yl)butyl 2-naphthoate (3oa)



Yield: 64% (63 mg), white solid, mp: 135-137 °C.

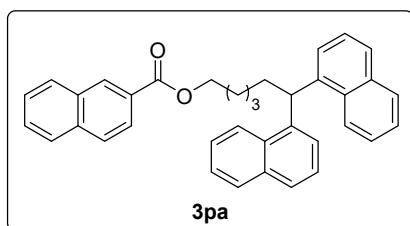
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.52 (s, 1H), 8.15 – 8.11 (m, 2H), 8.00 – 7.97 (m, 1H), 7.88 – 7.80 (m, 5H), 7.70 – 7.67 (m, 2H), 7.57 – 7.53 (m, 1H), 7.52

– 7.48 (m, 1H), 7.43 – 7.39 (m, 4H), 7.35 (t, $J = 6.5$ Hz, 4H), 5.58 (t, $J = 7.2$ Hz, 1H), 4.34 (t, $J = 6.7$ Hz, 2H), 2.38 – 2.32 (m, 2H), 1.91 – 1.87 (m, 2H), 1.73 – 1.69 (m, 2H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 166.7, 140.4, 135.4, 134.1, 132.4, 131.8, 130.9, 129.3, 129.0, 128.1, 128.0, 127.7, 127.6, 126.9, 126.5, 126.2, 125.4, 125.4, 125.2, 124.7, 123.2, 64.7, 41.2, 35.6, 28.8, 24.9.

HRMS(ESI) Calculated for $\text{C}_{36}\text{H}_{30}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 517.21380, found: 517.21362.

6,6-di(naphthalen-1-yl)butyl 2-naphthoate (3pa)



Yield: 50% (51 mg), white solid, mp: 128-131°C.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.56 (s, 1H), 8.14 – 8.11 (m, 2H), 8.03 – 8.00 (m, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.84 – 7.78 (m, 4H), 7.70 – 7.66 (m, 2H),

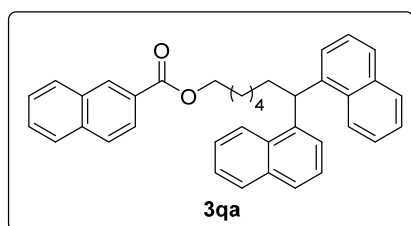
7.54 – 7.50 (m, 1H), 7.48 – 7.44 (m, 1H), 7.42 – 7.38 (m, 4H), 7.36 – 7.33 (m, 4H),

5.56 (t, $J = 7.3$ Hz, 1H), 4.32 (t, $J = 6.7$ Hz, 2H), 2.31 – 2.25 (m, 2H), 1.79 – 1.73 (m, 2H), 1.63 – 1.51 (m, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 140.4, 135.4, 134.1, 132.4, 131.8, 130.9, 129.3, 129.0, 128.1, 128.0, 127.7, 127.6, 126.9, 126.5, 126.2, 125.4, 125.4, 125.2, 124.7, 123.2, 64.7, 41.2, 35.6, 28.8, 24.9.

HRMS(ESI) Calculated for $\text{C}_{37}\text{H}_{32}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 531.22945, found: 531.22894.

7,7-di(naphthalen-1-yl)butyl 2-naphthoate (3qa)



Yield: 46% (48 mg), white solid, mp: 130-131 °C.

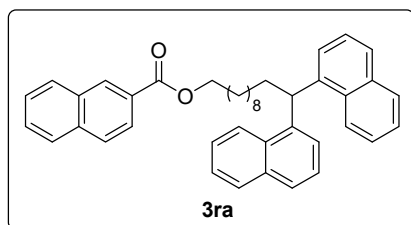
^1H NMR (500 MHz, CDCl_3) δ 8.56 (s, 1H), 8.14 – 8.11 (m, 2H), 8.04 – 8.01 (m, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.79 – 7.76 (m, 2H), 7.76 – 7.72 (m, 2H),

7.66 – 7.63 (m, 2H), 7.47 – 7.43 (m, 1H), 7.42 – 7.35 (m, 5H), 7.35 – 7.31 (m, 4H), 5.54 (t, $J = 7.2$ Hz, 1H), 4.28 (t, $J = 6.7$ Hz, 2H), 2.26 – 2.21 (m, 2H), 1.73 – 1.67 (m, 2H), 1.53 – 1.48 (m, 2H), 1.41 – 1.39 (m, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 166.6, 140.6, 135.3, 134.0, 132.4, 131.8, 130.8, 129.2, 128.9, 128.0, 127.6, 127.6, 126.8, 126.4, 126.1, 125.3, 125.2, 125.1, 124.7, 124.7, 123.2, 65.0, 41.2, 35.9, 29.4, 28.6, 28.3, 25.9.

HRMS(ESI) Calculated for $\text{C}_{38}\text{H}_{34}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 545.24510, found: 545.24438.

11,11-di(naphthalen-1-yl)butyl 2-naphthoate (3ra)



Yield: 40% (46 mg), white solid, mp: 134-136 °C.

^1H NMR (500 MHz, CDCl_3) δ 8.60 (s, 1H), 8.13 – 8.11 (m, 2H), 8.07 – 8.04 (m, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.88 – 7.84 (m, 5H), 7.71 (d, $J = 8.0$ Hz,

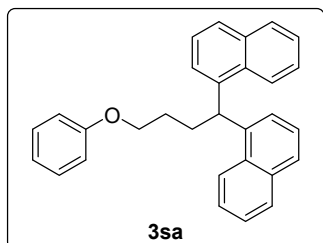
2H), 7.59 – 7.55 (m, 1H), 7.54 – 7.50 (m, 1H), 7.45 – 7.42 (m, 3H), 7.40 – 7.36 (m, 2H), 7.33 (d, $J = 6.5$ Hz, 2H), 5.53 (t, $J = 7.3$ Hz, 1H), 4.36 (t, $J = 6.7$ Hz, 2H), 2.26 – 2.21 (m, 2H), 1.82 – 1.76 (m, 2H), 1.52 – 1.48 (m, 2H), 1.46 – 1.42 (m, 2H), 1.37 – 1.28 (m, 4H), 1.26 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 166.8, 140.8, 135.5, 134.1, 132.5, 131.9, 130.9, 129.3,

129.0, 128.1, 128.1, 127.7, 126.8, 126.6, 126.1, 125.4, 125.3, 125.3, 124.8, 123.3, 65.3, 41.3, 36.0, 29.8, 29.5, 29.5, 29.3, 28.7, 28.5, 26.0.

HRMS(ESI) Calculated for $C_{42}H_{42}O_2Na^+$ ($[M+Na]^+$): 601.30770, found: 601.30682.

1,1'-(4-phenoxybutane-1,1-diyl)dinaphthalene (3sa)



Yield: 61% (49 mg), white solid, mp: 106-108°C.

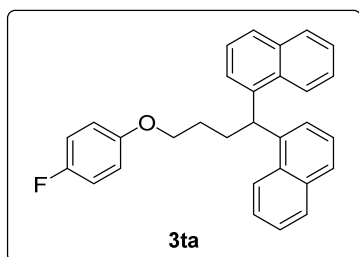
1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.0$ Hz, 2H), 7.82 – 7.80 (m, 2H), 7.69 – 7.66 (m, 2H), 7.41 – 7.31 (m, 8H), 7.25 – 7.21 (m, 2H), 6.90 (t, $J = 7.3$ Hz, 1H), 6.85 (d, $J = 8.0$ Hz, 2H), 5.63 (t, $J = 7.5$ Hz, 1H), 3.93 (t, $J = 6.0$

Hz, 2H), 2.46 – 2.41 (m, 2H), 1.98 – 1.93 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 140.2, 134.1, 131.8, 129.4, 129.0, 127.0, 126.2, 125.4, 125.4, 124.9, 123.3, 120.6, 114.5, 67.3, 40.7, 32.1, 27.9.

HRMS(ESI) Calculated for $C_{30}H_{25}O^-$ ($[M-H]^-$): 401.19109, found: 401.19092.

1,1'-(4-(4-fluorophenoxy)butane-1,1-diyl)dinaphthalene (3ta)



Yield: 69% (58 mg), white solid, mp: 98-99 °C.

1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, $J = 8.0$ Hz, 2H), 7.83 – 7.80 (m, 2H), 7.70 – 7.67 (m, 2H), 7.43 – 7.33 (m, 8H), 6.94 – 6.89 (m, 2H), 6.77 – 6.73 (m, 2H), 5.62 (t, $J = 7.5$ Hz, 1H), 3.88 (t, $J = 6.0$ Hz, 2H), 2.45 – 2.40

(m, 2H), 1.96 – 1.90 (m, 2H).

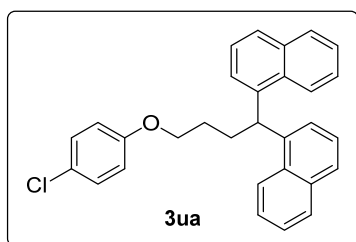
^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2 ($^1J_{C-F} = 236.6$ Hz), 155.0 ($^4J_{C-F} = 2.0$ Hz), 140.2, 134.1, 131.8, 129.0, 127.0, 126.3, 125.4, 124.9, 123.2, 115.7 ($^2J_{C-F} = 22.9$ Hz), 115.4 ($^3J_{C-F} = 7.8$ Hz), 68.0, 40.7, 32.1, 27.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -124.2(s).

HRMS(ESI) Calculated for $C_{30}H_{24}OF^-$ ($[M-H]^-$): 419.18167, found: 419.18170.

1,1'-(4-(4-chlorophenoxy)butane-1,1-diyl)dinaphthalene (3ua)

Yield: 67% (58 mg), white solid, mp: 122-124 °C.

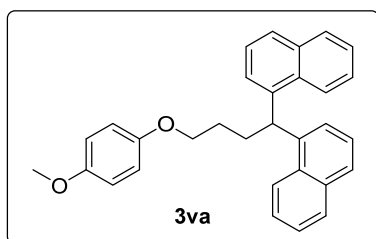


¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.85 – 7.82 (m, 2H), 7.71 – 7.68 (m, 2H), 7.44 – 7.38 (m, 4H), 7.38 – 7.34 (m, 4H), 7.20 – 7.17 (m, 2H), 6.77 – 6.74 (m, 2H), 5.62 (t, *J* = 7.5 Hz, 1H), 3.91 (t, *J* = 6.0 Hz, 2H), 2.46 – 2.40 (m, 2H), 1.98 – 1.92 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 157.5, 140.2, 134.1, 131.8, 129.3, 129.0, 127.0, 126.3, 125.4, 124.9, 123.2, 115.7, 67.8, 40.7, 32.1, 27.8.

HRMS(ESI) Calculated for C₃₀H₂₄OCl⁻ ([M-H]⁻): 435.15212, found: 435.15210.

1,1'-(4-(4-methoxyphenoxy)butane-1,1'-diyl)dinaphthalene (3va)



Yield: 41% (36 mg), white solid, mp: 101-102 °C.

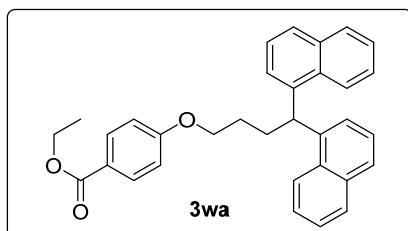
¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.81 – 7.78 (m, 2H), 7.68 – 7.65 (m, 2H), 7.40 – 7.30 (m, 8H), 6.77 (s, 4H), 5.62 (t, *J* = 7.5 Hz, 1H), 3.86 (t, *J* = 6.0 Hz, 2H), 3.68 (s, 3H), 2.45 – 2.39 (m,

2H), 1.94 – 1.88 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 153.7, 153.1, 140.3, 134.1, 131.8, 128.9, 126.9, 126.2, 125.4, 125.3, 124.8, 123.3, 115.4, 114.6, 68.0, 55.6, 40.6, 32.1, 27.9.

HRMS(ESI) Calculated for C₃₁H₂₇O₂⁻ ([M-H]⁻): 431.20165, found: 431.20166.

ethyl 4-(4,4-di(naphthalen-1-yl)butoxy)benzoate (3wa)



Yield: 42% (40 mg), white solid, mp: 125-126 °C.

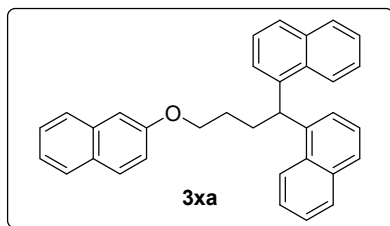
¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.0 Hz, 2H), 8.00 – 7.96 (m, 2H), 7.86 – 7.83 (m, 2H), 7.73 – 7.70 (m, 2H), 7.45 – 7.35 (m, 8H), 6.88 – 6.85 (m,

2H), 5.63 (t, *J* = 7.5 Hz, 1H), 4.36 – 4.31 (m, 2H), 4.01 (t, *J* = 6.0 Hz, 2H), 2.48 – 2.43 (m, 2H), 2.03 – 1.96 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 166.4, 162.6, 140.1, 134.1, 131.8, 131.5, 129.0, 127.0, 126.3, 125.4, 124.8, 123.2, 122.8, 114.0, 67.7, 60.6, 40.6, 32.0, 27.8, 14.4.

HRMS(ESI) Calculated for C₃₆H₃₀O₃⁻ ([M-H]⁻): 509.28411, found: 509.28434.

1,1'-(4-(naphthalen-2-yloxy)butane-1,1-diyl)dinaphthalene (3xa)



Yield: 52% (47 mg), white solid, mp: 150-153 °C.

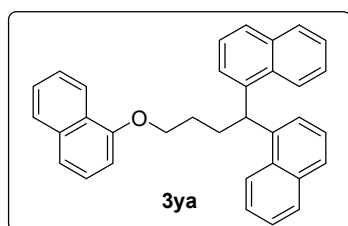
¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 8.5 Hz, 2H), 7.86 – 7.84 (m, 2H), 7.77 – 7.70 (m, 4H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.46 – 7.37 (m, 9H), 7.33 – 7.29

(m, 1H), 7.17 – 7.14 (m, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 5.68 (t, *J* = 7.3 Hz, 1H), 4.11 (t, *J* = 6.0 Hz, 2H), 2.54 – 2.49 (m, 2H), 2.09 – 2.03 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 156.9, 140.2, 134.6, 134.2, 131.9, 129.4, 129.0, 128.9, 127.6, 127.0, 126.7, 126.3, 125.4, 125.4, 124.9, 123.5, 123.3, 119.0, 106.6, 67.5, 40.6, 32.2, 27.8.

HRMS(ESI) Calculated for C₃₄H₂₇O⁺ ([M-H]⁺): 451.20674, found: 451.20694.

1,1'-(4-(naphthalen-1-yloxy)butane-1,1-diyl)dinaphthalene (3ya)



Yield: 63% (57 mg), white solid, mp: 148-151 °C.

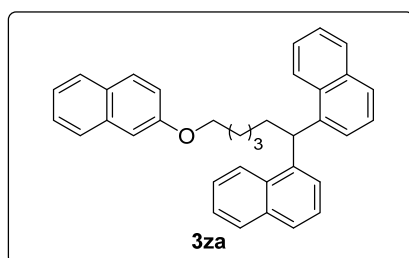
¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.22

(m, 12H), 6.60 (d, *J* = 7.5 Hz, 1H), 5.66 (t, *J* = 7.5 Hz, 1H), 4.00 (t, *J* = 5.8 Hz, 2H), 2.54 – 2.48 (m, 2H), 2.07 – 2.00 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 154.6, 140.2, 134.5, 134.1, 131.8, 129.0, 127.4, 127.0, 126.3, 126.2, 125.9, 125.6, 125.4, 125.1, 124.9, 123.2, 122.1, 120.1, 104.4, 67.4, 40.7, 32.2, 28.0.

HRMS(ESI) Calculated for C₃₄H₂₇O⁺ ([M-H]⁺): 451.20674, found: 451.20694.

1,1'-(5-(naphthalen-2-yloxy)butane-1,1-diyl)dinaphthalene (3za)



Yield: 30% (29 mg), white solid, mp: 152-156 °C.

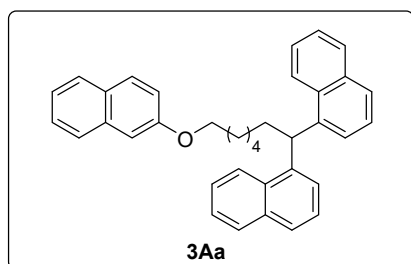
¹H NMR (500 MHz, CDCl₃) δ 8.15 – 8.12 (m, 2H), 7.84 – 7.82 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.66 (m, 4H), 7.44 – 7.37 (m, 5H), 7.36 – 7.33 (m,

4H), 7.31 – 7.27 (m, 1H), 7.10 – 7.05 (m, 2H), 5.56 (t, $J = 7.3$ Hz, 1H), 3.98 (t, $J = 6.5$ Hz, 2H), 2.31 – 2.26 (m, 2H), 1.82 – 1.76 (m, 2H), 1.59 – 1.57 (m, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 157.0, 140.6, 134.6, 134.1, 131.9, 129.3, 129.0, 128.9, 127.6, 126.9, 126.7, 126.2, 126.2, 125.4, 125.3, 124.8, 123.4, 123.3, 119.0, 106.6, 67.8, 41.2, 36.0, 29.1, 28.3, 26.4.

HRMS(ESI) Calculated for $\text{C}_{36}\text{H}_{31}\text{O}^-$ ($[\text{M}-\text{H}]^-$): 479.23804, found: 479.23825.

1,1'-(6-(naphthalen-2-yloxy)butane-1,1-diyl)dinaphthalene (3Aa)



Yield: 27% (27 mg), white solid, mp: 147-150°C.

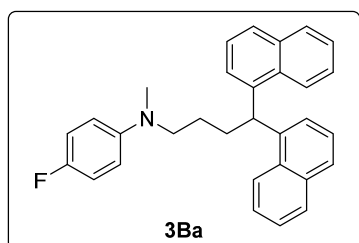
^1H NMR (500 MHz, CDCl_3) δ 8.13 – 8.10 (m, 2H), 7.82 – 7.78 (m, 2H), 7.71 – 7.64 (m, 5H), 7.40 – 7.36 (m, 5H), 7.34 – 7.32 (m, 4H), 7.28 – 7.24 (m, 1H), 7.10 – 7.07 (m, 1H), 7.04 (d, $J = 2.5$ Hz, 1H),

5.54 (t, $J = 7.0$ Hz, 1H), 3.93 (t, $J = 6.5$ Hz, 2H), 2.27 – 2.22 (m, 2H), 1.75 – 1.72 (m, 2H), 1.54 – 1.50 (m, 2H), 1.44 – 1.41 (m, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 157.0, 140.7, 134.6, 134.1, 131.9, 129.3, 129.0, 128.9, 127.6, 126.8, 126.6, 126.2, 126.1, 125.4, 125.3, 124.7, 123.4, 123.3, 119.0, 106.5, 67.8, 41.3, 36.0, 29.6, 29.2, 28.5, 26.0.

HRMS(ESI) Calculated for $\text{C}_{37}\text{H}_{33}\text{O}^-$ ($[\text{M}-\text{H}]^-$): 493.25901, found: 493.25925.

N-(4,4-di(naphthalen-1-yl)butyl)-4-fluoro-N-methylaniline (3Ba)



Purified by silica gel column chromatography as yellow oil (42 mg, 46% yield).

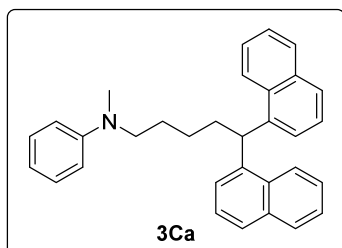
^1H NMR (500 MHz, CDCl_3) δ 8.08 (d, $J = 8.0$ Hz, 2H), 7.85 – 7.82 (m, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.45 – 7.38 (m, 4H), 7.36 – 7.29 (m, 4H), 6.88 – 6.83 (m, 2H),

6.55 – 6.52 (m, 2H), 5.55 (t, $J = 7.3$ Hz, 1H), 3.26 (t, $J = 7.3$ Hz, 2H), 2.77 (s, 3H), 2.30 – 2.25 (m, 2H), 1.81 – 1.74 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 155.3 ($^1J_{\text{C-F}} = 234.3$ Hz), 146.3, 140.2, 134.1, 131.8, 129.0, 127.0, 126.3, 125.4, 124.8, 123.2, 115.4 ($^2J_{\text{C-F}} = 21.6$ Hz), 113.8, 113.7, 53.3, 41.0, 38.9, 33.2, 25.6.

HRMS(ESI) Calculated for $\text{C}_{31}\text{H}_{29}\text{NF}^+$ ($[\text{M}+\text{H}]^+$): 434.22785, found: 434.22754.

N-(6,6-di(naphthalen-1-yl)hexyl)-N-methylaniline (3Ca)



Purified by silica gel column chromatography as yellow oil (34 mg, 38% yield).

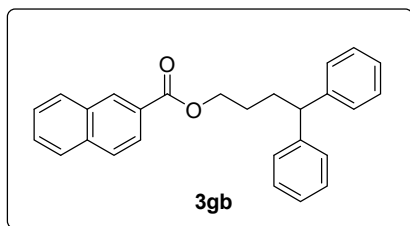
^1H NMR (500 MHz, CDCl_3) δ 8.12 – 8.10 (m, 2H), 7.86 – 7.83 (m, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.46 – 7.40 (m, 4H), 7.39 – 7.32 (m, 4H), 7.21 – 7.17 (m, 2H), 6.67 –

6.62 (m, 3H), 5.54 (t, $J = 7.3$ Hz, 1H), 3.25 – 3.22 (m, 2H), 2.82 (s, 3H), 2.30 – 2.25 (m, 2H), 1.68 – 1.61 (m, 2H), 1.56 – 1.49 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 149.3, 140.5, 134.1, 131.8, 129.1, 129.0, 126.9, 126.2, 125.4, 125.4, 124.8, 123.2, 115.9, 112.1, 52.7, 41.3, 38.2, 36.0, 26.9, 26.1.

HRMS(ESI) Calculated for $\text{C}_{33}\text{H}_{34}\text{N}^+$ ($[\text{M}+\text{H}]^+$): 444.26858, found: 444.26852.

4,4-diphenylbutyl 2-naphthoate (3gb)



Yield: 44% (33 mg), white solid, mp: 86-87 °C.

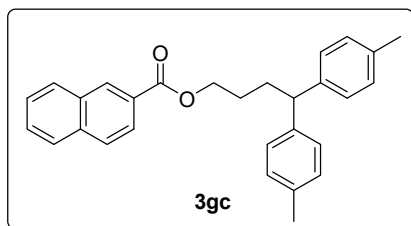
^1H NMR (500 MHz, CDCl_3) δ 8.58 (s, 1H), 8.05 – 8.02 (m, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.5$ Hz, 2H), 7.60 – 7.51 (m, 2H), 7.29 – 7.27 (m,

8H), 7.20 – 7.16 (m, 2H), 4.39 (t, $J = 6.5$ Hz, 2H), 3.98 (t, $J = 8.0$ Hz, 1H), 2.27 – 2.22 (m, 2H), 1.83 – 1.77 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 166.8, 144.6, 135.5, 132.4, 131.0, 129.3, 128.5, 128.2, 128.1, 127.8, 127.7, 127.6, 126.6, 126.3, 125.2, 65.0, 51.0, 32.0, 27.3.

HRMS(ESI) Calculated for $\text{C}_{27}\text{H}_{24}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 403.16685, found: 403.16617.

4,4-di-p-tolylbutyl 2-naphthoate (3gc)



Yield: 36% (29 mg), white solid, mp: 87-88 °C.

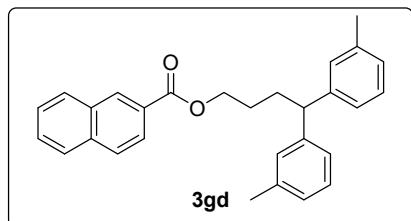
¹H NMR (500 MHz, CDCl₃) δ 8.57 (s, 1H), 8.05 – 8.02 (m, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.15 (d, *J* = 8.0

Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 4H), 4.37 (t, *J* = 6.8 Hz, 2H), 3.91 (t, *J* = 7.8 Hz, 1H), 2.28 (s, 6H), 2.23 – 2.17 (m, 2H), 1.82 – 1.75 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 166.7, 141.9, 135.6, 135.5, 132.5, 130.9, 129.3, 129.2, 128.1, 128.0, 127.7, 127.6, 127.5, 126.6, 125.2, 65.0, 50.1, 32.1, 27.4, 20.9.

HRMS(ESI) Calculated for C₂₉H₂₈O₂Na⁺ ([M+Na]⁺): 431.19815, found: 431.19763.

4,4-di-m-tolylbutyl 2-naphthoate (3gd)



Yield: 38% (31 mg), white solid, mp: 86-88 °C.

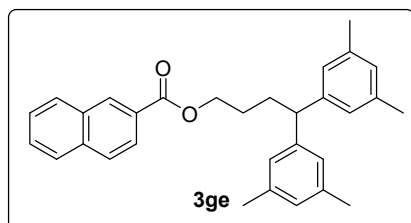
¹H NMR (500 MHz, CDCl₃) δ 8.58 (s, 1H), 8.06 – 8.03 (m, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.17 (t, *J* = 7.8

Hz, 2H), 7.08 (d, *J* = 7.0 Hz, 4H), 6.98 (d, *J* = 7.5 Hz, 2H), 4.38 (t, *J* = 6.5 Hz, 2H), 3.89 (t, *J* = 8.0 Hz, 1H), 2.30 (s, 6H), 2.24 – 2.19 (m, 2H), 1.82 – 1.75 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 166.7, 144.7, 138.0, 135.5, 132.5, 130.9, 129.3, 128.6, 128.4, 128.1, 128.0, 127.7, 127.0, 126.6, 125.2, 124.7, 65.0, 50.9, 32.0, 27.4, 21.5.

HRMS(ESI) Calculated for C₂₉H₂₈O₂Na⁺ ([M+Na]⁺): 431.19815, found: 431.19763.

4,4-bis(3,5-dimethylphenyl)butyl 2-naphthoate (3ge)



Yield: 40% (35 mg), white solid, mp: 90-91 °C.

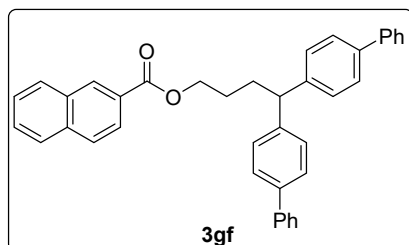
¹H NMR (500 MHz, CDCl₃) δ 8.58 (s, 1H), 8.06 – 8.03 (m, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.85 – 7.82 (m, 2H), 7.54 – 7.49 (m, 2H), 6.89 (s, 4H), 6.80 (s,

2H), 4.38 (t, *J* = 6.5 Hz, 2H), 3.81 (t, *J* = 7.8 Hz, 1H), 2.26 (s, 12H), 2.22 – 2.16 (m, 2H), 1.80 – 1.76 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 166.7, 144.7, 137.8, 135.4, 132.4, 130.9, 129.2, 128.1, 128.0, 127.8, 127.7, 127.6, 126.5, 125.5, 125.2, 65.0, 50.8, 32.0, 27.4, 21.3.

HRMS(ESI) Calculated for $C_{31}H_{32}O_2Na^+$ ($[M+Na]^+$): 459.22945, found: 459.22885.

4,4-di([1,1'-biphenyl]-4-yl)butyl 2-naphthoate (3gf)



Yield: 48% (51 mg), white solid, mp: 128-129 °C.

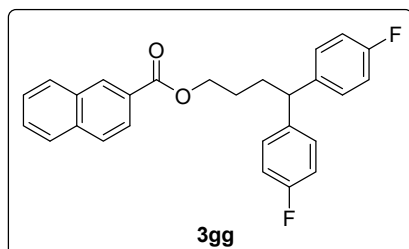
1H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.07 – 8.04 (m, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.5$ Hz, 2H), 7.58 – 7.52 (m, 10H), 7.43 – 7.37 (m, 8H), 7.31 (t, $J = 7.3$ Hz, 2H), 4.43 (t, $J = 6.5$ Hz,

2H), 4.08 (t, $J = 7.8$ Hz, 1H), 2.35 – 2.29 (m, 2H), 1.91 – 1.84 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 143.7, 140.9, 139.3, 135.5, 132.5, 131.0, 129.3, 128.7, 128.2, 128.1, 127.8, 127.6, 127.3, 127.1, 127.0, 126.6, 125.2, 65.0, 50.4, 32.1, 27.4.

HRMS(ESI) Calculated for $C_{39}H_{32}O_2Na^+$ ($[M+Na]^+$): 555.22945, found: 555.22864.

4,4-bis(4-fluorophenyl)butyl 2-naphthoate (3gg)



Yield: 41% (34 mg), white solid, mp: 78-79 °C.

1H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.05 – 8.02 (m, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.5$ Hz, 2H), 7.61 – 7.53 (m, 2H), 7.21 – 7.17 (m, 4H), 7.00 – 6.96 (m, 4H), 4.39 (t, $J = 6.5$ Hz, 2H),

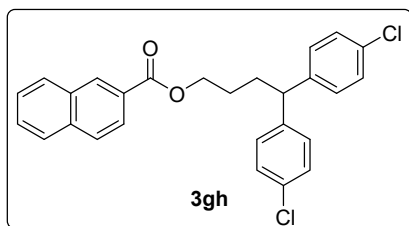
3.96 (t, $J = 8.0$ Hz, 1H), 2.21 – 2.15 (m, 2H), 1.81 – 1.74 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 161.4 ($^1J_{C-F} = 243.1$ Hz), 140.2 ($^4J_{C-F} = 2.8$ Hz), 135.5, 132.5, 131.0, 129.3, 129.1 ($^3J_{C-F} = 7.5$ Hz), 128.3, 128.2, 127.8, 127.5, 126.7, 125.2, 115.4 ($^2J_{C-F} = 21.0$ Hz), 64.8, 49.4, 32.3, 27.3.

HRMS(ESI) Calculated for $C_{27}H_{22}O_2F_2Na^+$ ($[M+Na]^+$): 439.14801, found: 439.14746.

4,4-bis(4-chlorophenyl)butyl 2-naphthoate (3gh)

Yield: 37% (33 mg), white solid, mp: 86-87°C.



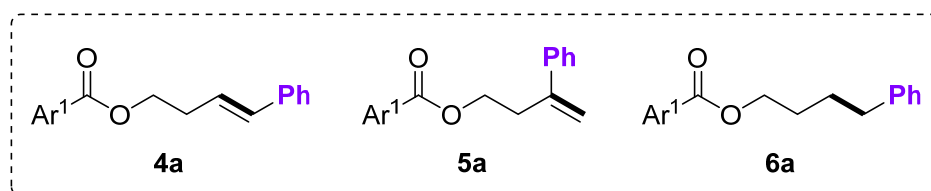
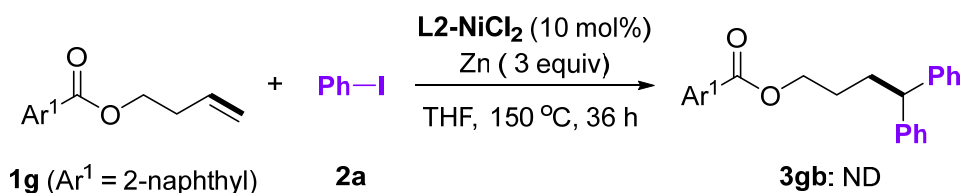
^1H NMR (500 MHz, CDCl_3) δ 8.57 (s, 1H), 8.04 – 8.02 (m, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.5$ Hz, 2H), 7.59 – 7.54 (m, 2H), 7.27 – 7.24 (m, 4H), 7.16 – 7.13 (m, 4H), 4.38 (t, $J = 6.5$ Hz, 2H),

3.93 (t, $J = 7.8$ Hz, 1H), 2.20 – 2.14 (m, 2H), 1.80 – 1.73 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 142.6, 135.5, 132.5, 132.3, 131.0, 129.0, 128.8, 128.3, 128.2, 127.8, 127.5, 127.4, 126.7, 125.1, 64.7, 49.7, 31.9, 27.2.

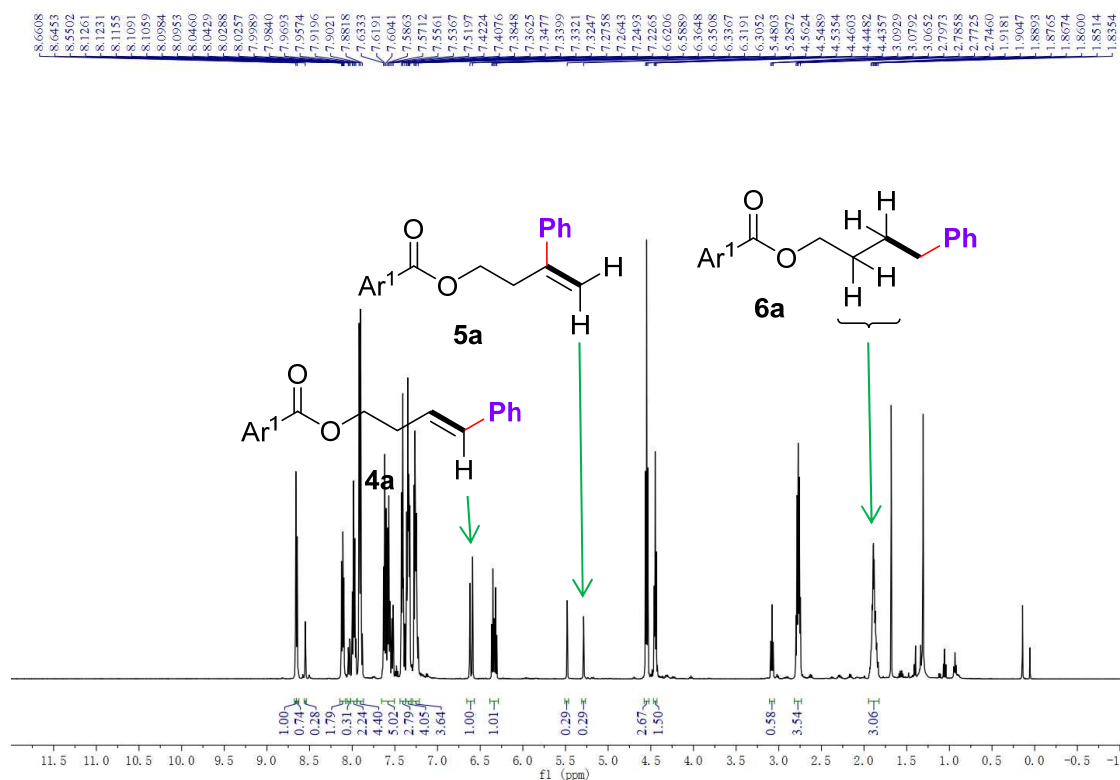
HRMS(ESI) Calculated for $\text{C}_{27}\text{H}_{22}\text{O}_2\text{Cl}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$): 471.08891, found: 471.08908.

3.3 The reaction of alkene with iodobenzene using L2 as ligand



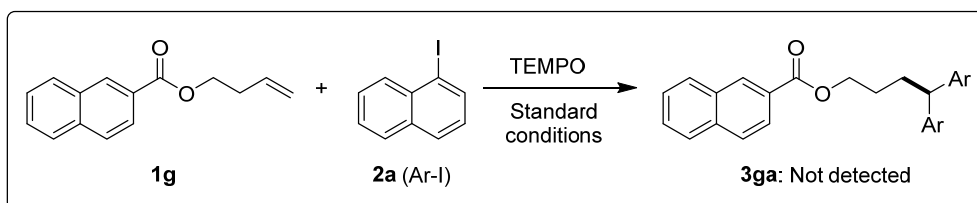
an inseparable mixture (**4a** : **5a** : **6a** = 1 : 0.29 : 0.75)

To a 25-mL flame-dried Schlenk tube containing a stirring bar was added but-3-en-1-yl 2-naphthoate (0.2 mmol, 45.3 mg), iodobenzene (0.6mmol, 122.4 mg), **L2-NiCl₂** (10 mol%, 0.02 mmol, 8.5mg), Zn (3 equiv, 0.6 mmol, 39 mg), THF (1 mL). The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the inseparable mixture (12.1 mg). The ratio of each component was determined by ^1H NMR analysis.



4. Mechanistic Studies

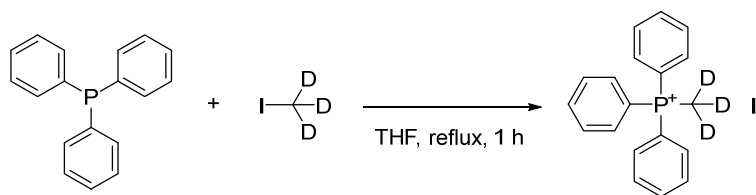
4.1 Radical scavenging experiment



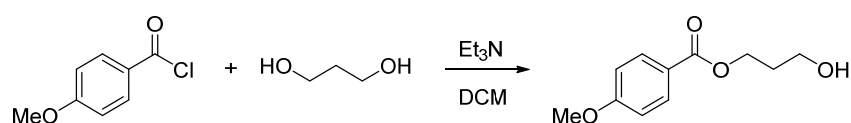
Experimental procedure:

To a 25-mL flame-dried Schlenk tube containing a stirring bar was added but-3-en-1-yl-4-methoxybenzoate **1g** (0.2 mmol, 45.3 mg), 1-iodonaphthalene **2a** (0.8mmol, 203.2 mg), TEMPO (2equiv, 0.4mmol, 62.5mg), **L1-NiCl₂** (10 mol%, 0.02 mmol, 8.5 mg), Zn (5 equiv, 1 mmol, 65 mg), THF (1 mL). The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was monitored by TLC analysis. No any product was detected and the starting material was recovered.

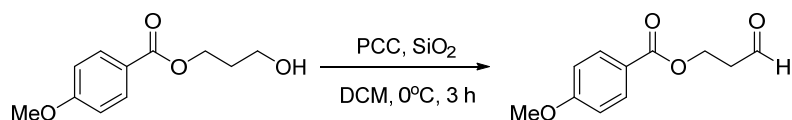
4.2 Deuterium-labelling experiment



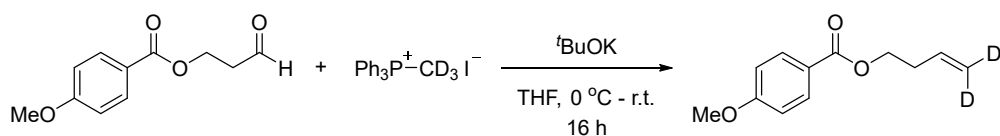
Add CD₃I (1.74g, 12.0 mmol, 1.2 equiv, 99% D) dropwise to a dry THF (10 mL) solution of triphenylphosphine (2.65 g, 10 mmol, 1 equiv). The mixture was heated to reflux for 1 h. After the reaction is complete, the mixture is cooled to room temperature and filtered. The precipitate was washed with xylene and dried under high vacuum to obtain methyl-*d*₃-triphenylphosphine in 98% yield (3.98 g).^[4]



To a solution of 1,3-propanediol (4.5 g, 60 mmol) and trimethylamine (4.0 g, 40 mmol) in DCM (40 mL) at 0 °C was added *p*-methoxybenzoyl chloride (3.5 g, 20 mmol) slowly. The ice-bath was removed and the reaction was warmed to room temperature and stirred for further 12 h. After the completion, water (50 mL) was added to the reaction mixture and extracted with DCM (3 × 10 mL). The combined organic extracts are washed with saline, dried with anhydrous Na₂SO₄, filtered and concentrated in vacuum. The residue was purified by column chromatography to give 3-hydroxypropyl 4-methoxybenzoate as colorless oil (3.49 g, 81% yield).^[5]

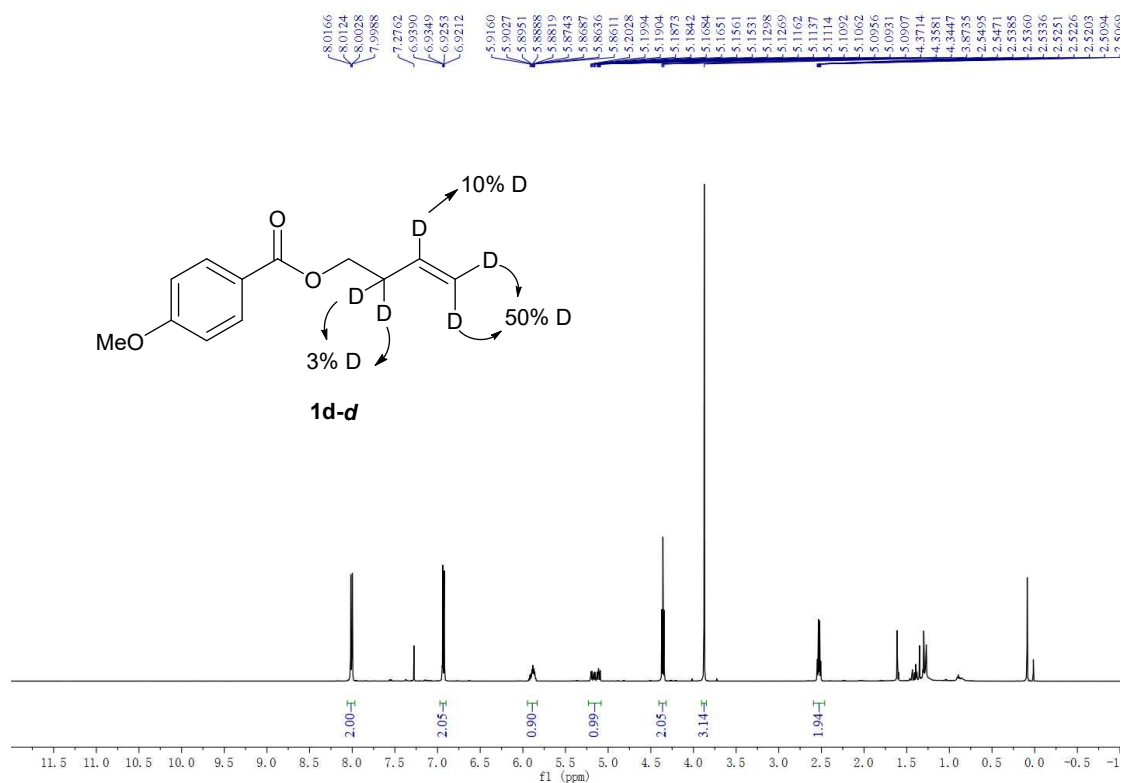


To a solution of 3-hydroxypropyl 4-methoxybenzoate (3.4 g, 16 mmol) in dichloromethane (10 mL) was added pyridine chlorochromate (6.92 g, 32 mmol.) at 0 °C. SiO₂ (2.5 g) was then added to reaction mixture and the reaction was for 3 h. The reaction mixture was filtered through a short pad of silica gel. The filtrate was condensed and purified by column chromatography to give colorless oil (2.56 g, 76%).^[6]

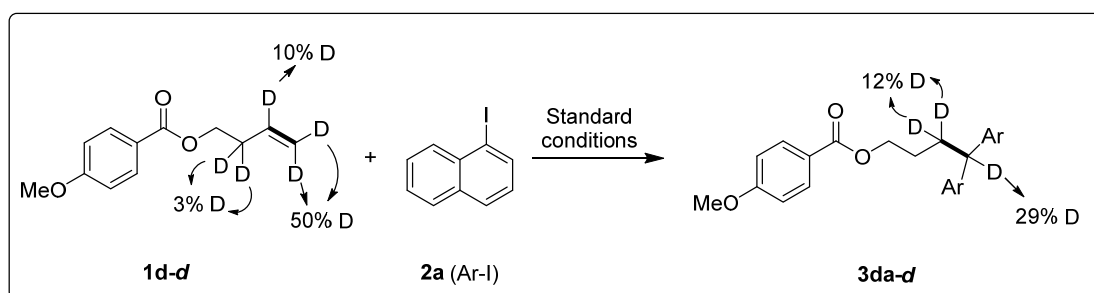


To a solution of methyl-*d*₃-triphenylphosphonium iodide (5.88 g, 14.4 mmol) in THF

(3 mL) was added t BuOK (2.04 g, 18 mmol), resulting in a bright yellow suspension. After stirring for 30 minutes, 3-oxopropyl 4-methoxybenzoate (2.52 g, 12 mmol) was then added slowly. After stirring for 3 h, the reaction was quenched with water (10 mL) and extracted with DCM (3×10 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The product was obtained by column chromatography (PE/EA = 20 : 1) in 32% yield as colorless oil. [7]



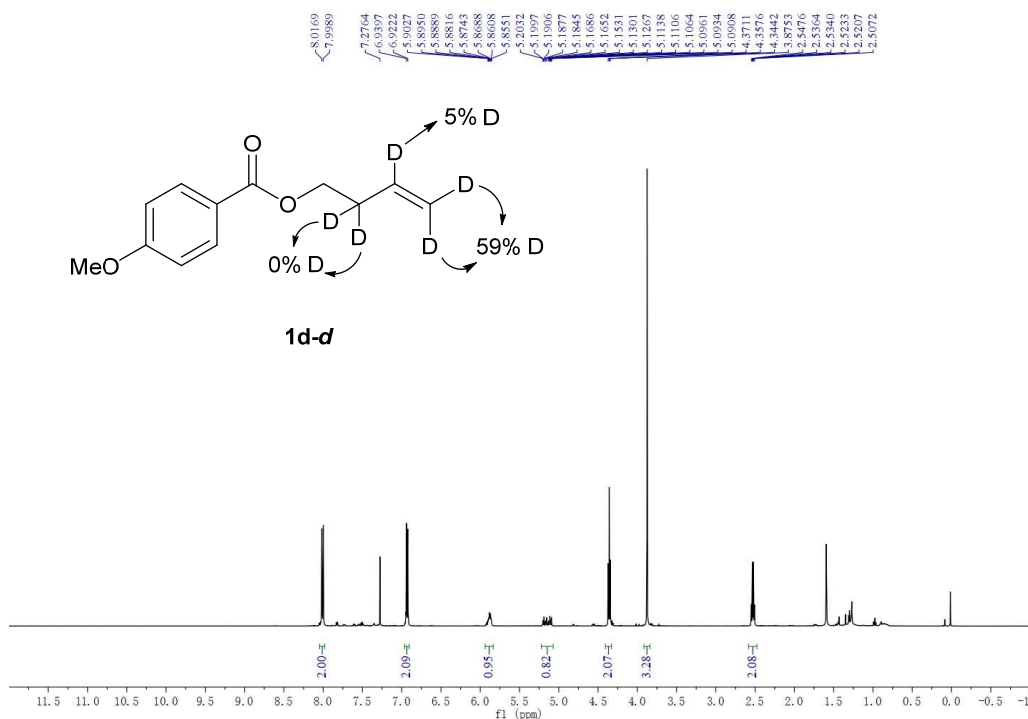
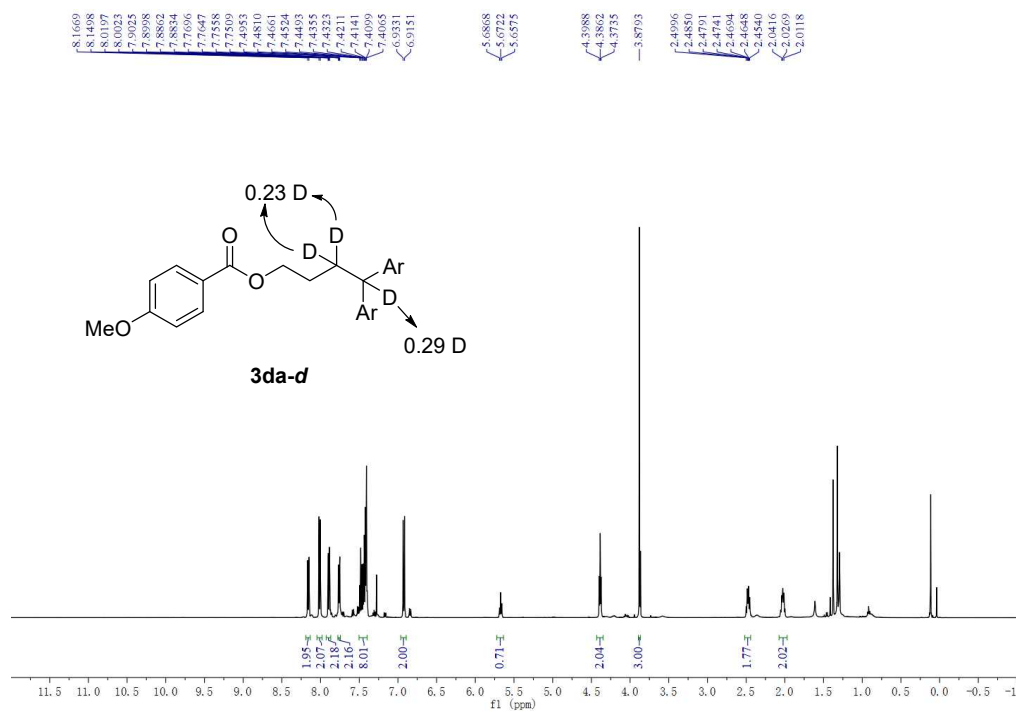
The reaction of **2d-d** with 1-iodonaphthalene **2a**



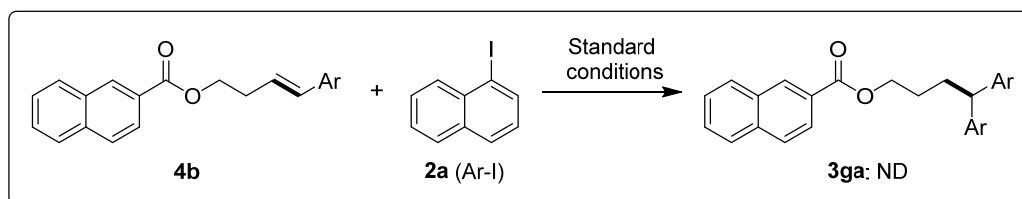
Experimental procedure:

To a 25-mL flame-dried Schlenk tube containing a stirring bar was added but-3-en-1-yl-4,4-d₂ 4-methoxybenzoate (0.2 mmol, 45.3 mg), 1-iodonaphthalene

(0.6mmol, 203.2mg), **L1-NiCl₂** (10 mol%, 0.02 mmol, 8.5 mg), Zn (1 mmol, 65 mg), tetrahydrofuran (1 mL). The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product in 36% yield.



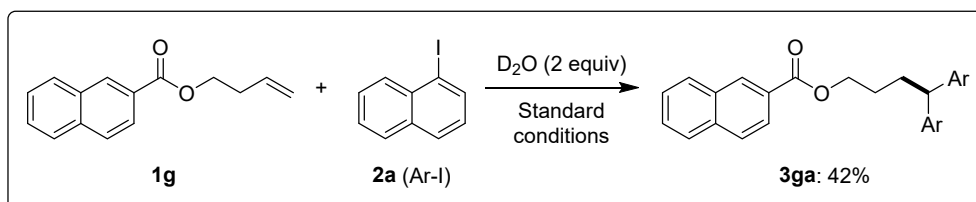
4.3 The reaction of 4b with 2a



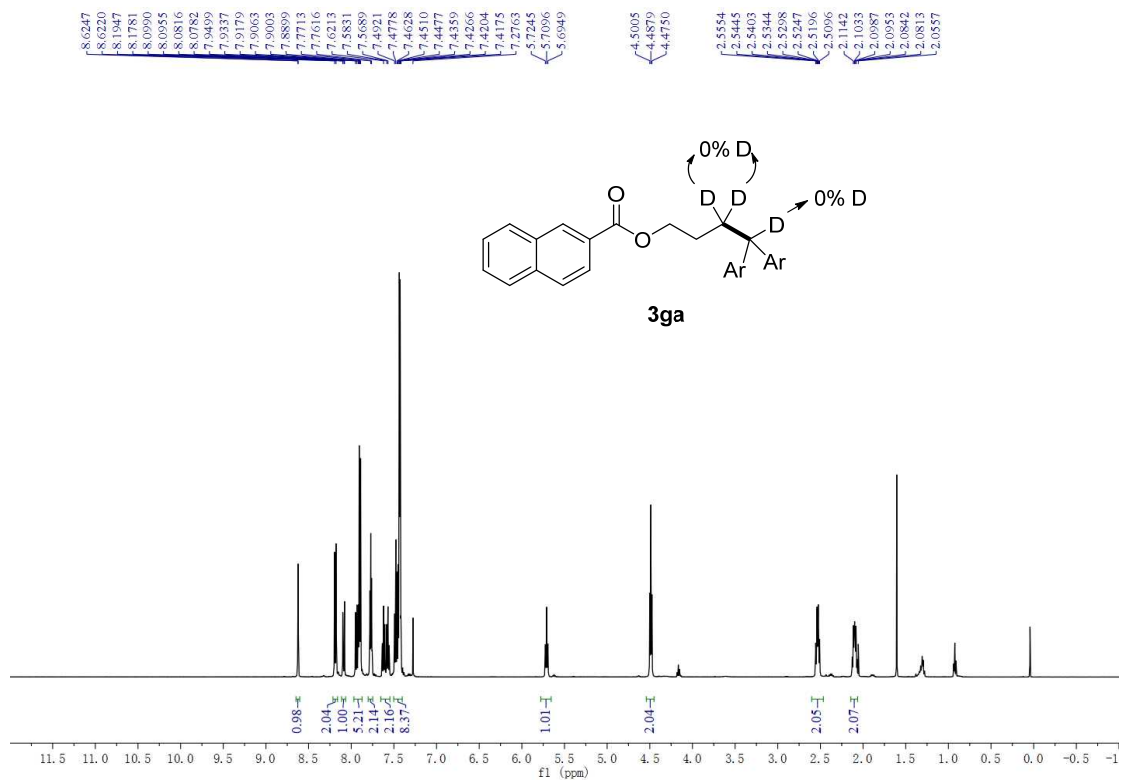
Experimental procedure:

To a 25-mL flame-dried Schlenk tube containing a stirring bar was added but-4-(naphthalen-1-yl)but-3-en-1-yl 2-naphthoate (0.2 mmol, 70.5 mg), 1-iodonaphthalene (0.6mmol, 152.4 mg), **L1-NiCl₂** (10 mol%, 0.02 mmol, 8.5 mg), Zn (1 mmol, 65 mg), THF (1 mL). The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was monitored by TLC analysis and no any product was detected.

4.4 The model reaction by adding D₂O



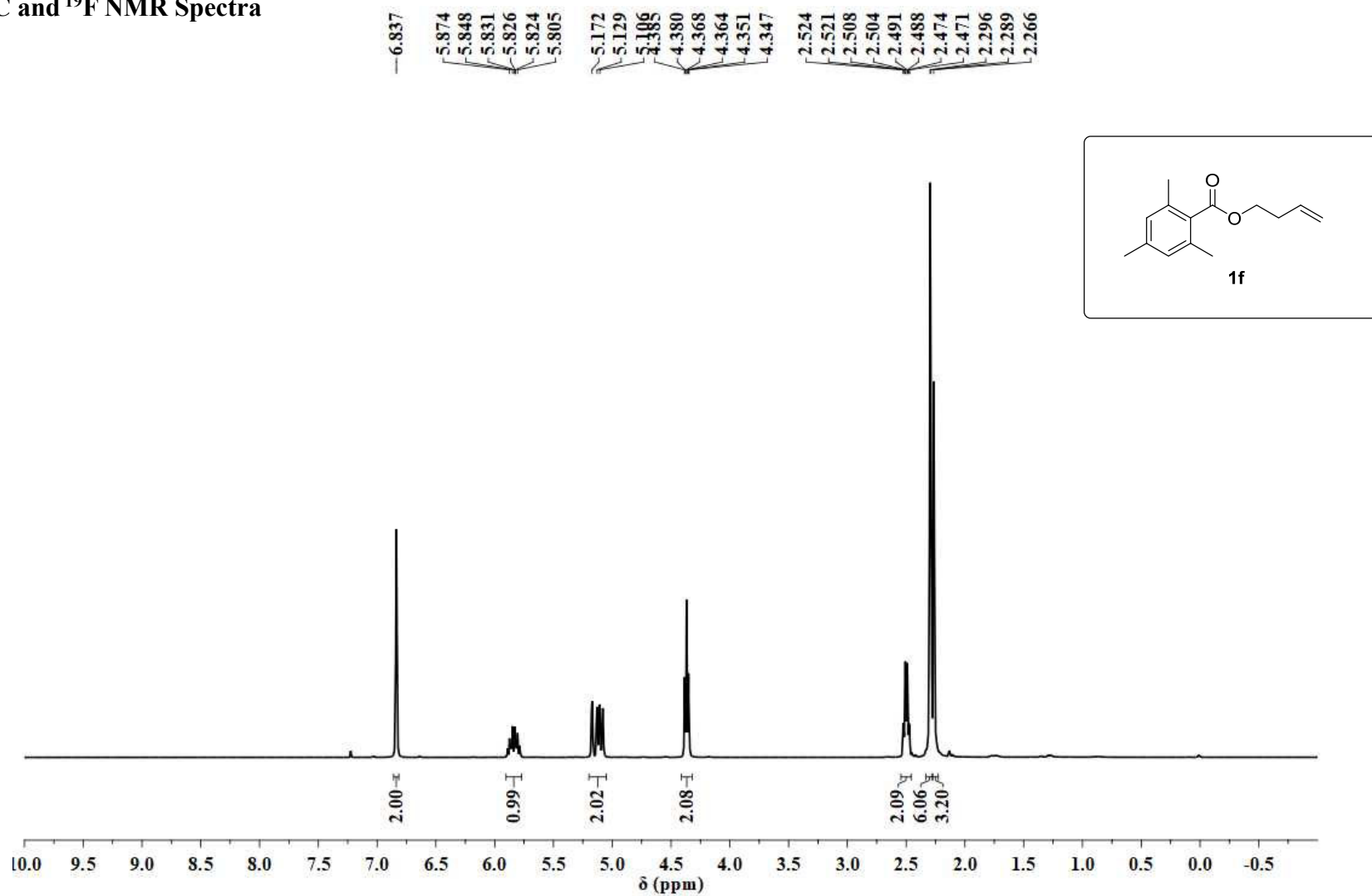
To a 25 ml flame-dried Schlenk tube containing a stirring bar was added but-3-en-1-yl 2-naphthoate (0.2 mmol, 45.3 mg), 1-iodonaphthalene (0.8 mmol, 203.2 mg), D₂O (0.4 mmol, 8 mg), **L1-NiCl₂** (10 mol%, 0.02 mmol, 8.5 mg), Zn (5 equiv, 1 mmol, 65 mg), THF (1 mL). The tube was sealed and stirred at 150 °C for 36 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product in 42% yield (40.3 mg).

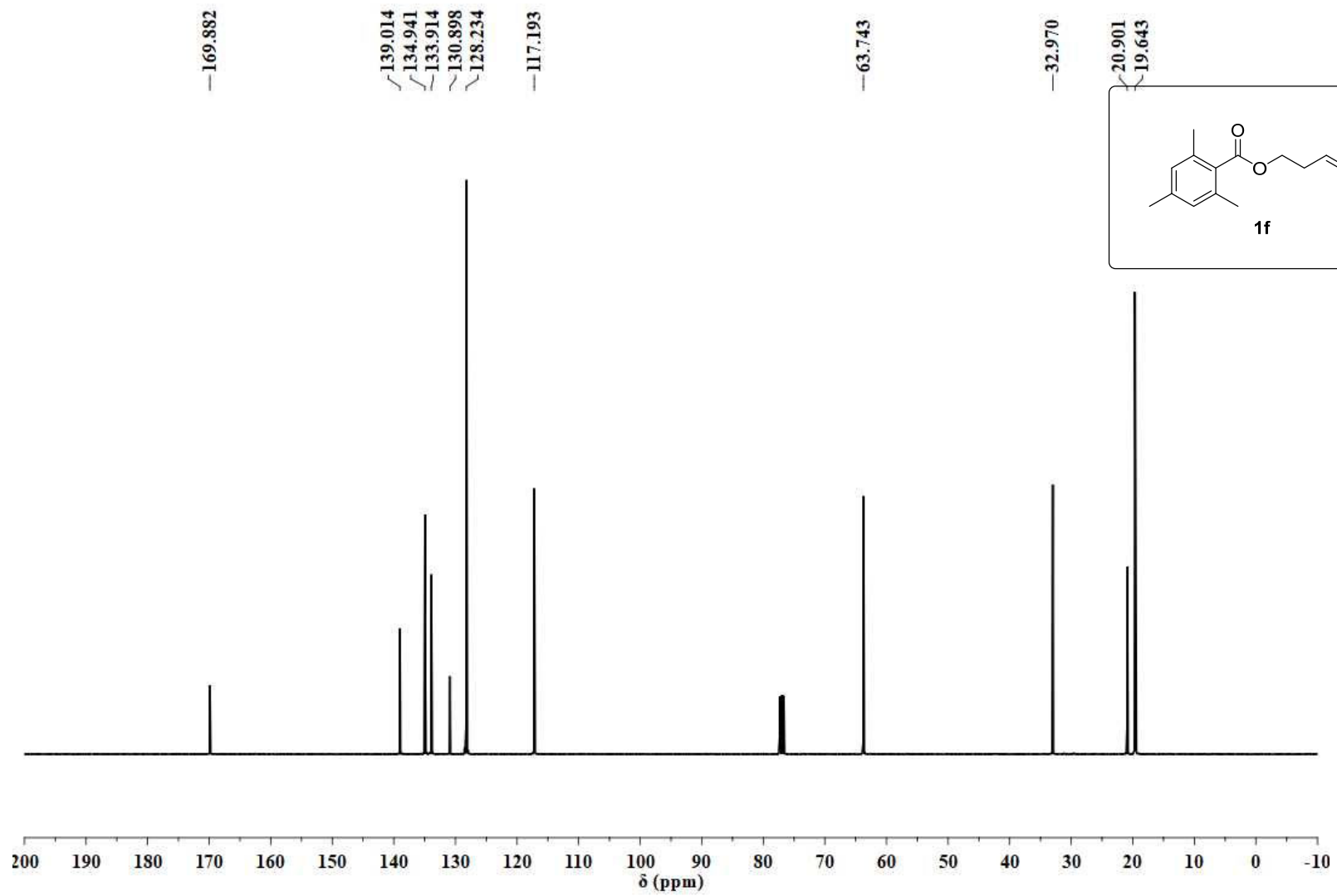


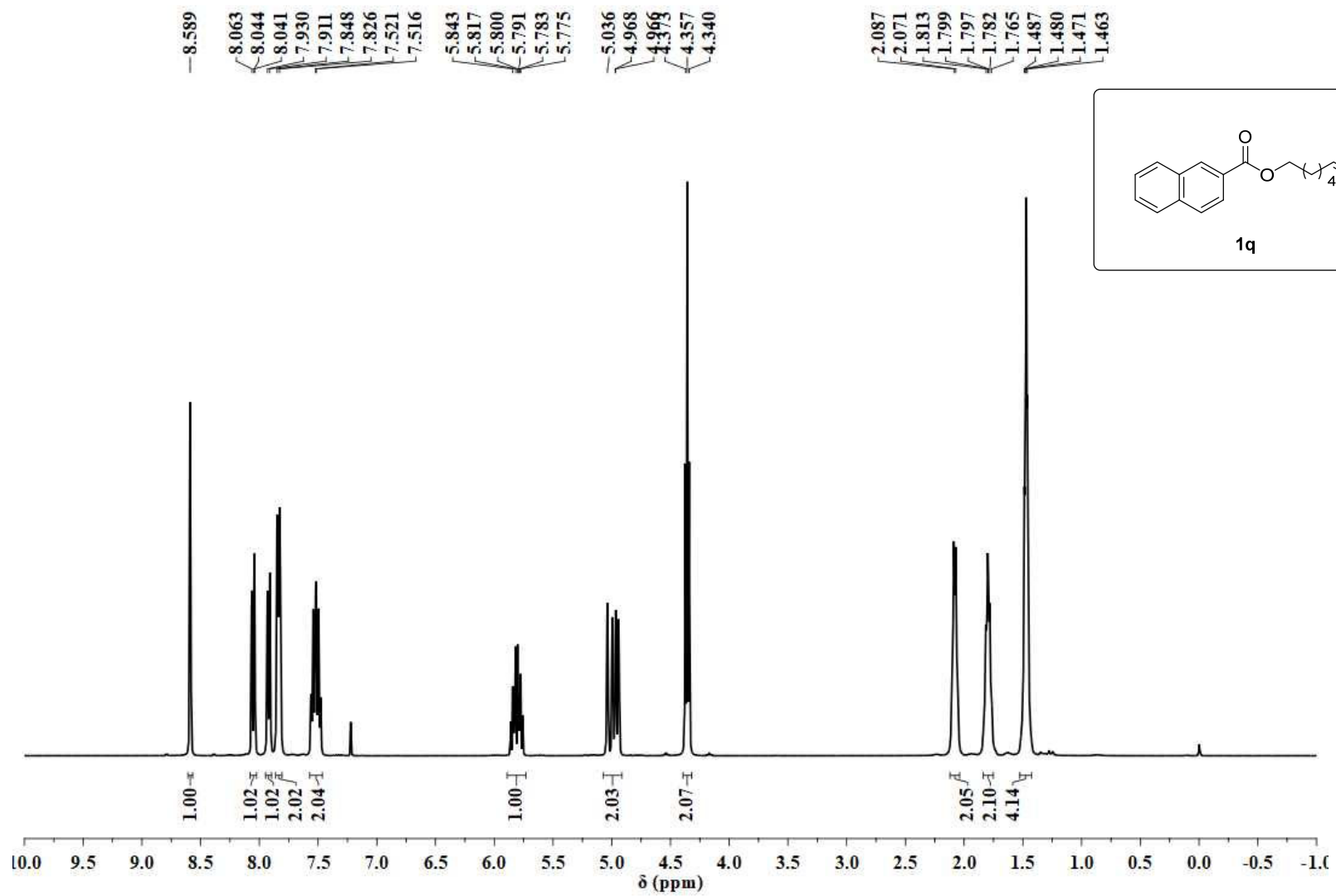
5. References

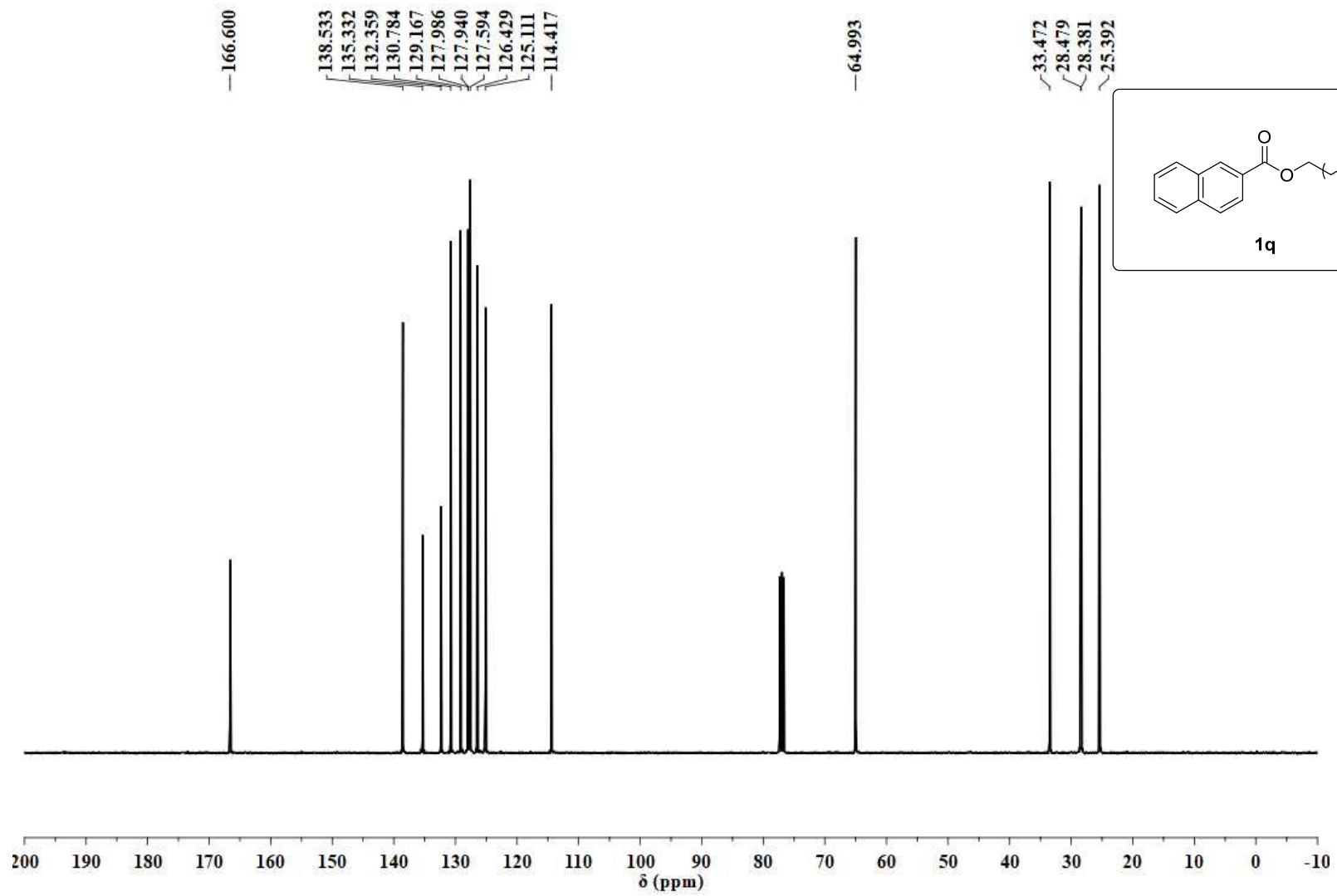
- [1] P.-W. Sun, Z. Zhang, X. Wang, L. Li, Y. Li and Z. Li, *Chin. J. Chem*, **2022**, *40*, 1066-1072.
- [2] C. Meng, H. Niu, J. Ning, W. Wu and J. Yi, Nickel-Catalyzed Removal of Alkene Protecting Group of Phenols, Alcohols via Chain Walking Process. *Molecules*, **2020**, *25*, 602.
- [3] G. Perumal, M. Kandasamy, B. Ganesan, K. Govindan, H. Sathya, M.-Y. Hung, G. C. Senadi, Y.-C. Wu and W. Y. Lin, Visible light-induced N-methyl activation of unsymmetric tertiary amines. *Tetrahedron*, **2021**, *80*, 131891.
- [4] F. Belitz, A.-K. Seitz, J. F. Goebel, Z. Hu and L. J. Gooßen, Ru-Catalyzed C–H Arylation of Acrylic Acids with Aryl Bromides. *Org Lett*, **2022**, *24*, 3466-3470.
- [5] X. Wu, F. A. Cruz, A. Lu and V. M. Dong, Tandem Catalysis: Transforming Alcohols to Alkenes by Oxidative Dehydroxylation. *J Am Chem Soc*, **2018**, *140*, 10126-10130.
- [6] W. Zhang, Z. Wang, G. Lin, Y. Xue, M. Wu, P. Tang and F. Chen, Stereoselective Total Syntheses of C18-Oxo Eburnamine-Vincamine Alkaloids. *Org. Lett.* **2022**, *24*, 2409-2413.
- [7] L. A. Evans, N. Fey, J. N. Harvey, D. Hose, G. C. Lloyd-Jones, P. Murray, A. G. Orpen, R. Osborne, G. J. J. Owen-Smith and M. Purdie, Counterintuitive Kinetics in Tsuji-Trost Allylation: Ion-Pair Partitioning and Implications for Asymmetric Catalysis. *J. Am. Chem. Soc.*, **2008**, *130*, 14471-14473.

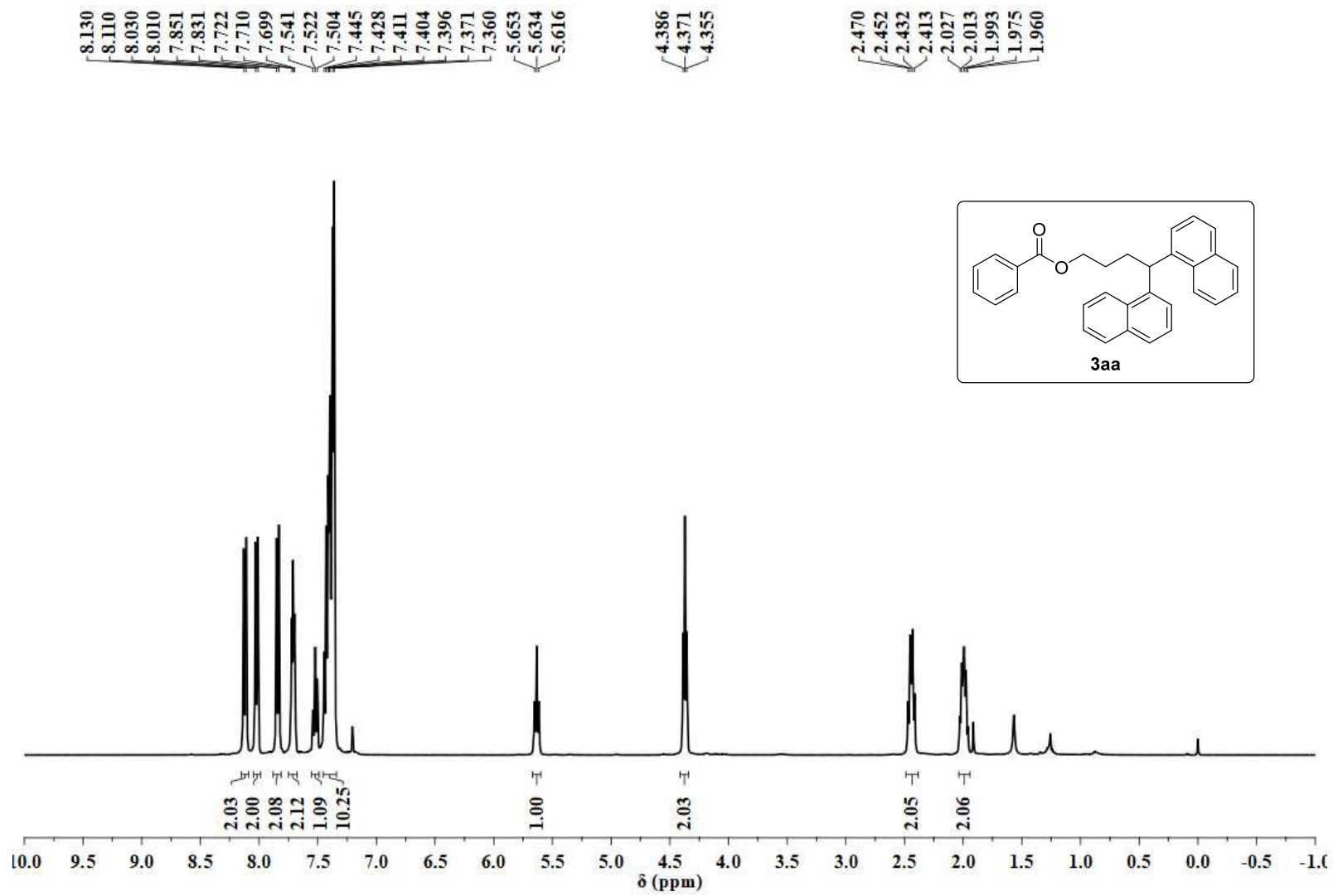
6. ^1H , ^{13}C and ^{19}F NMR Spectra

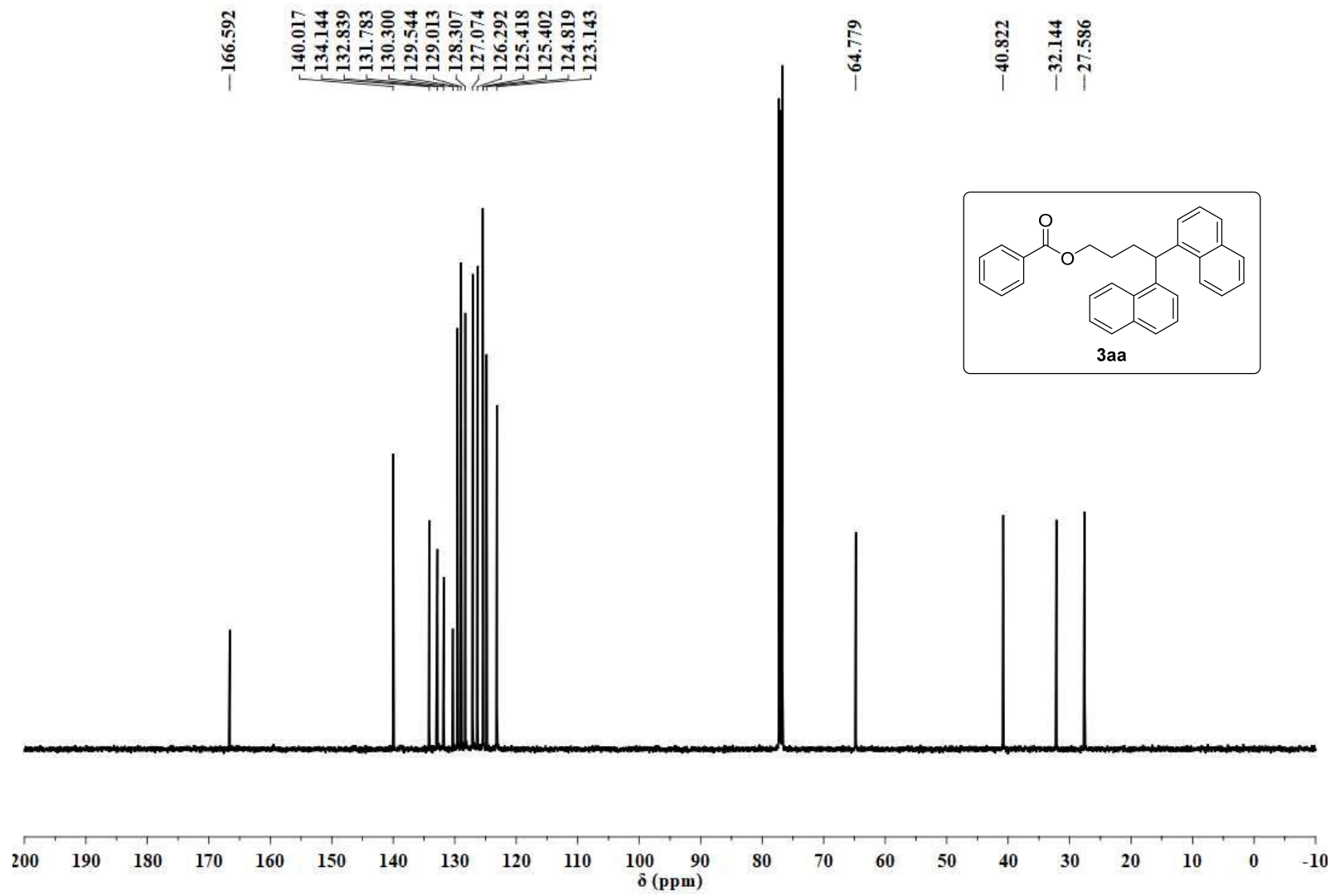


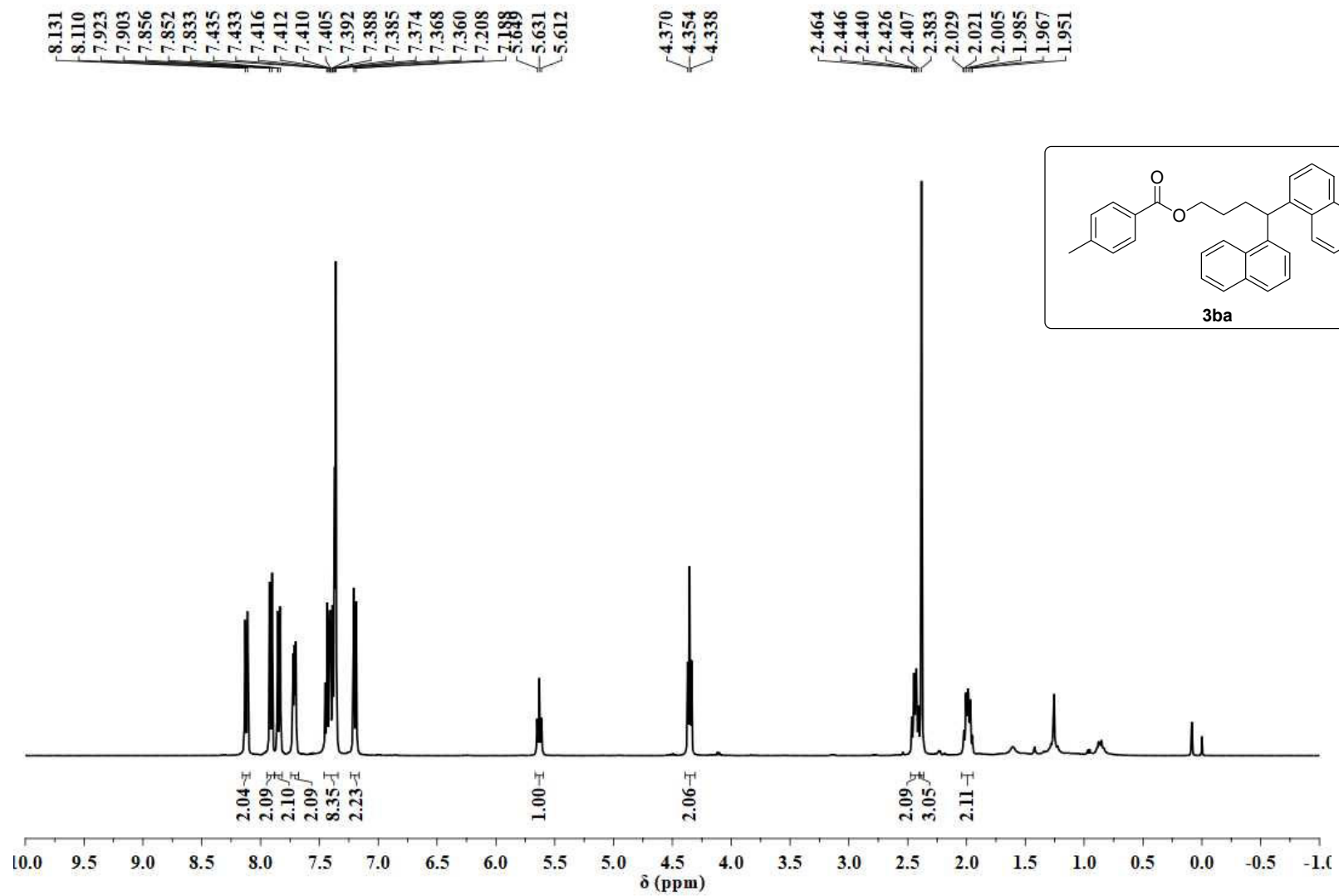


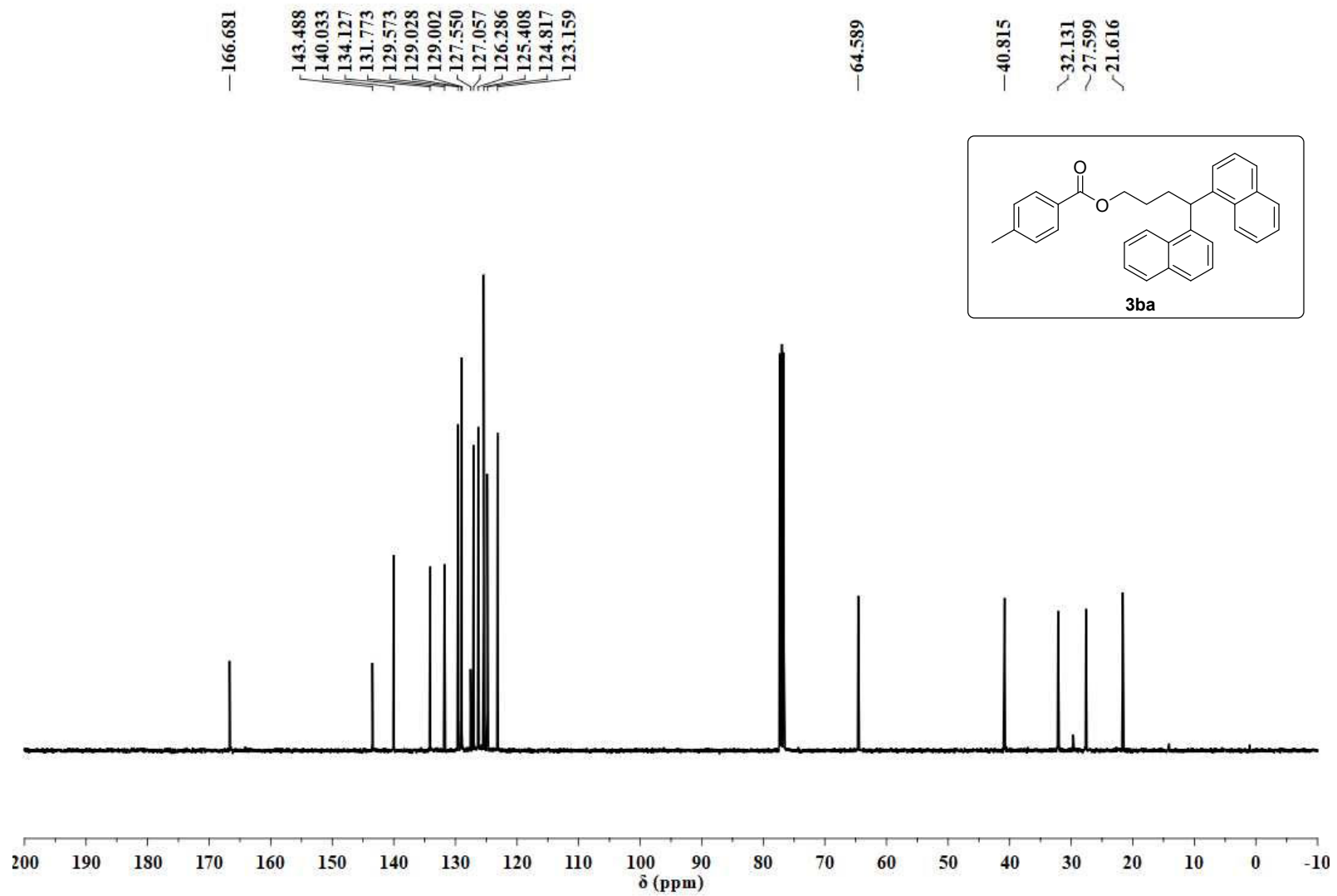


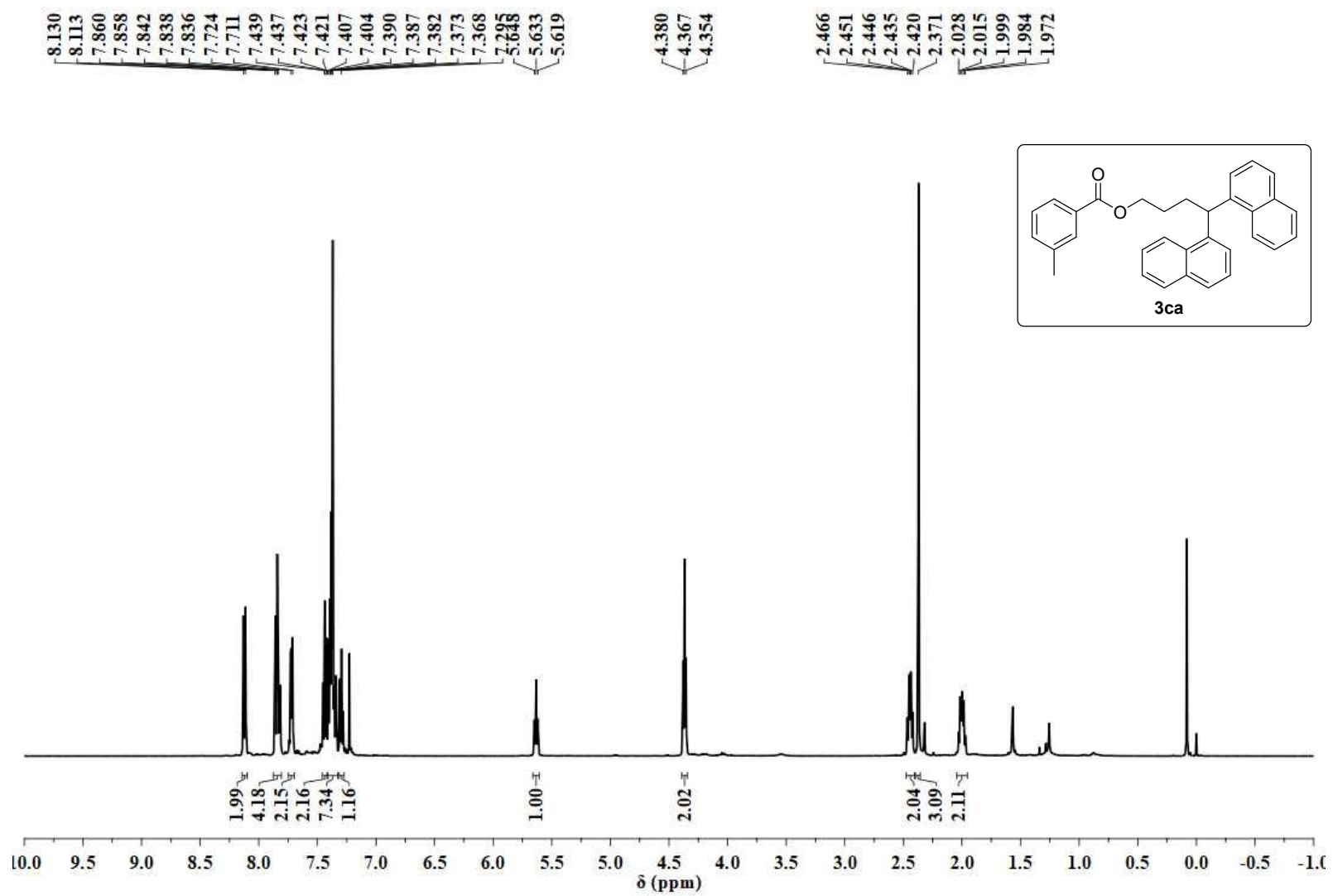


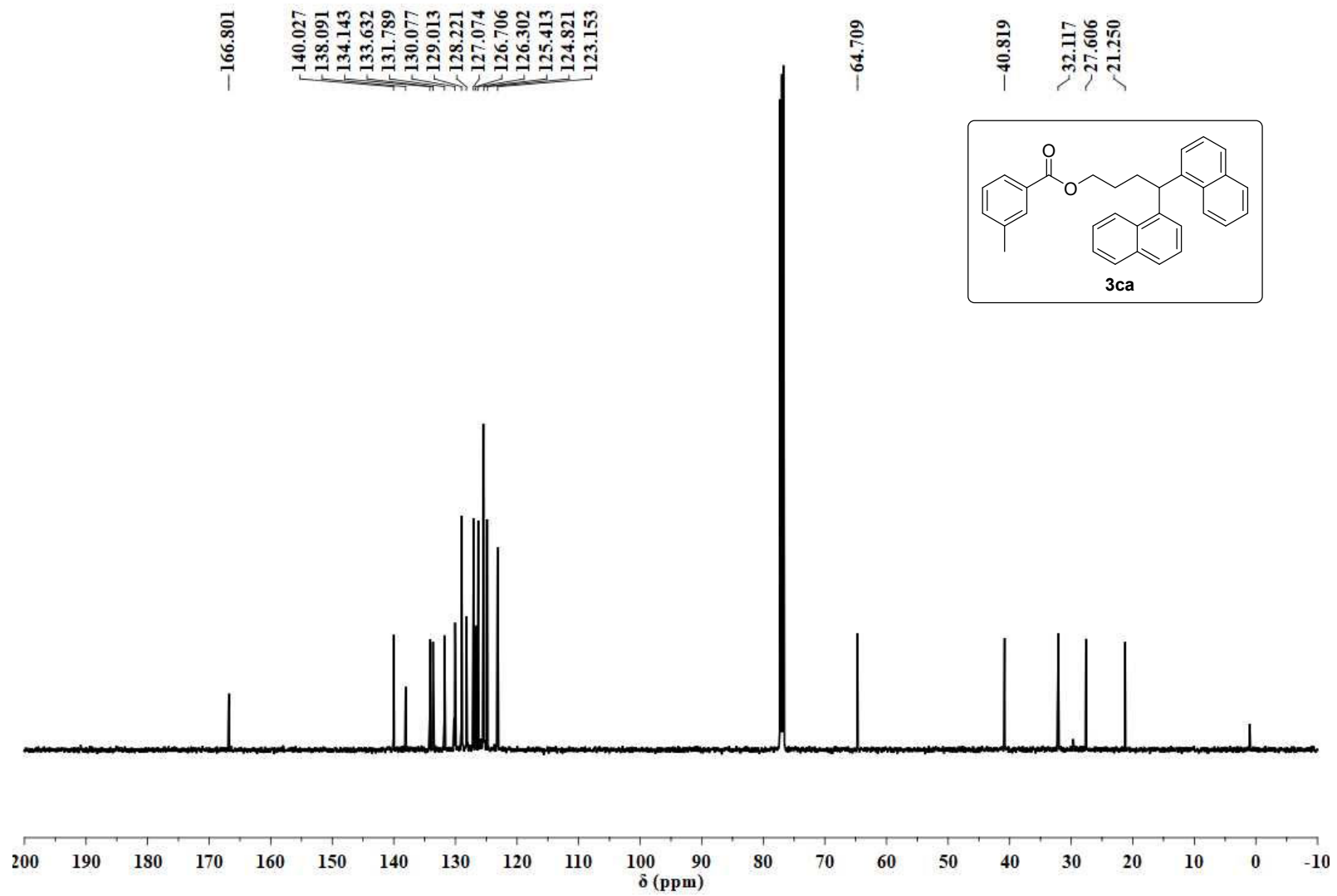


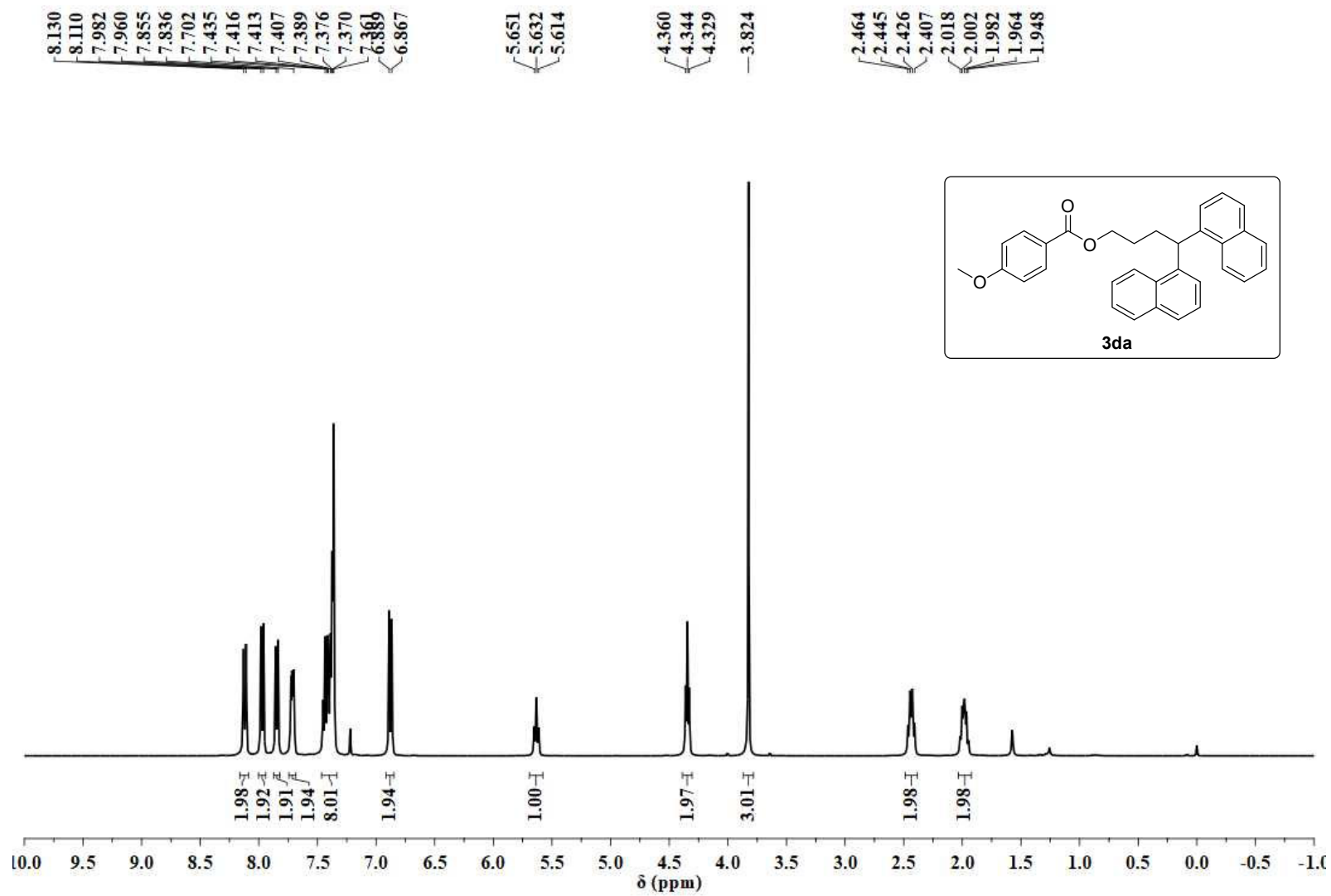


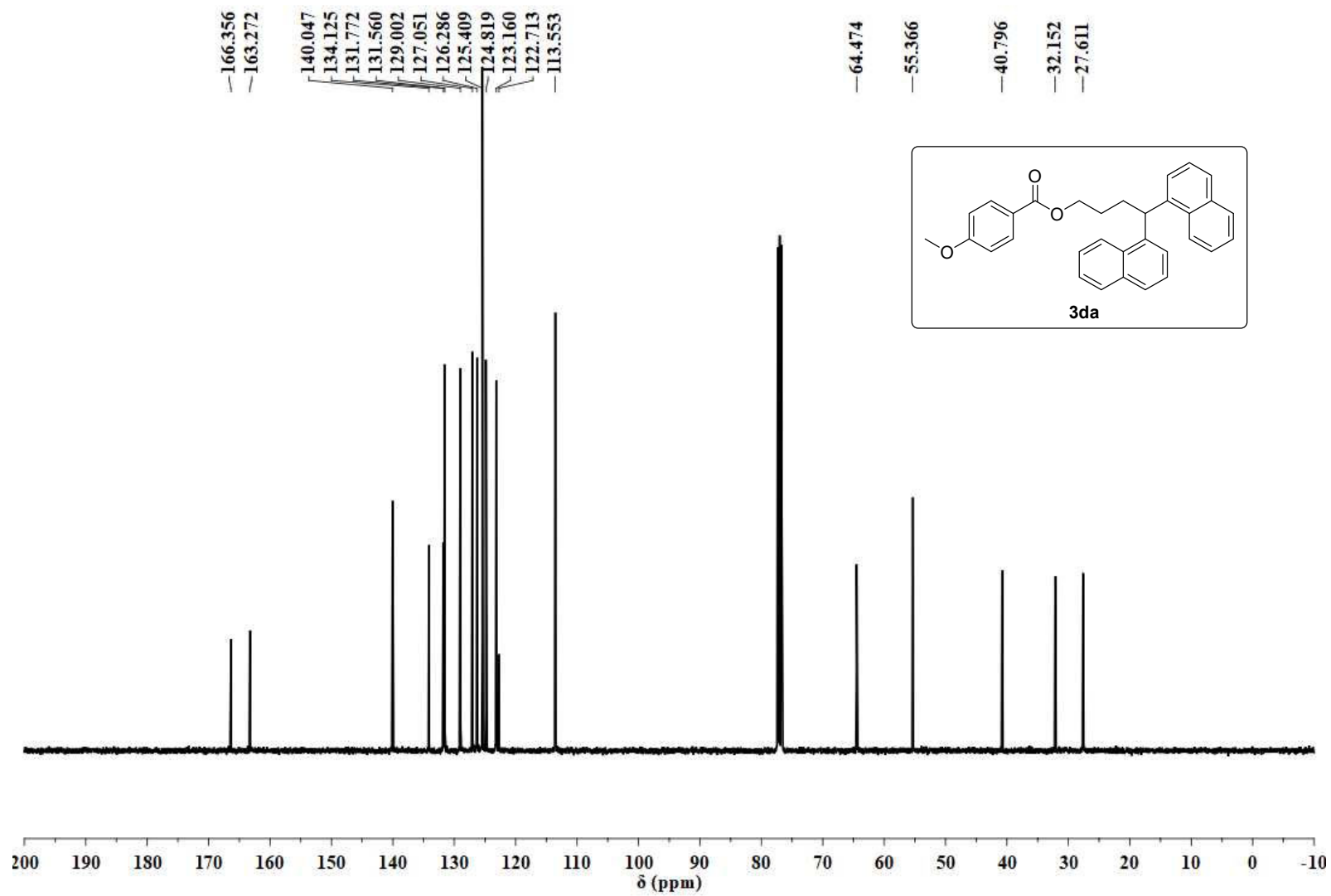


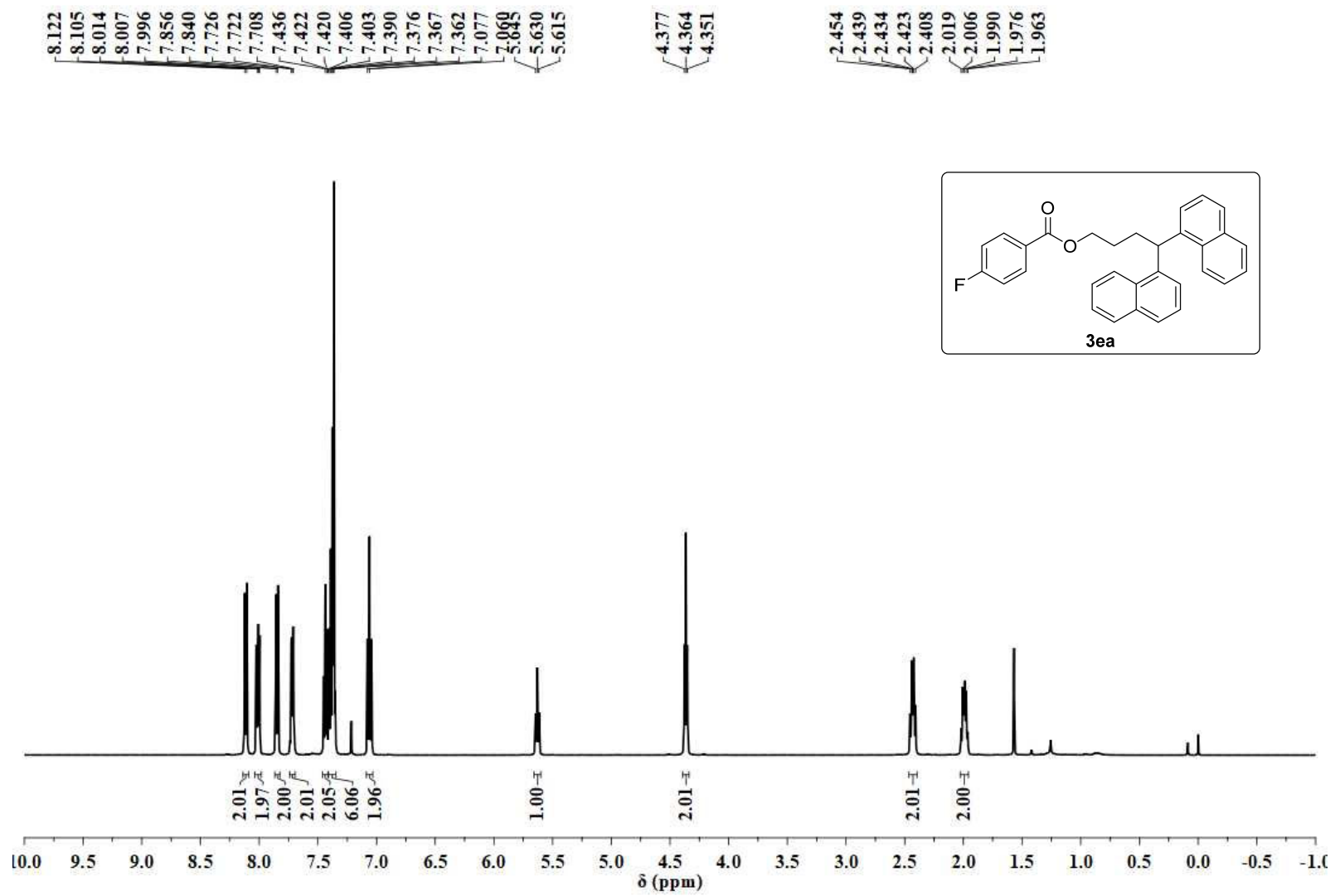


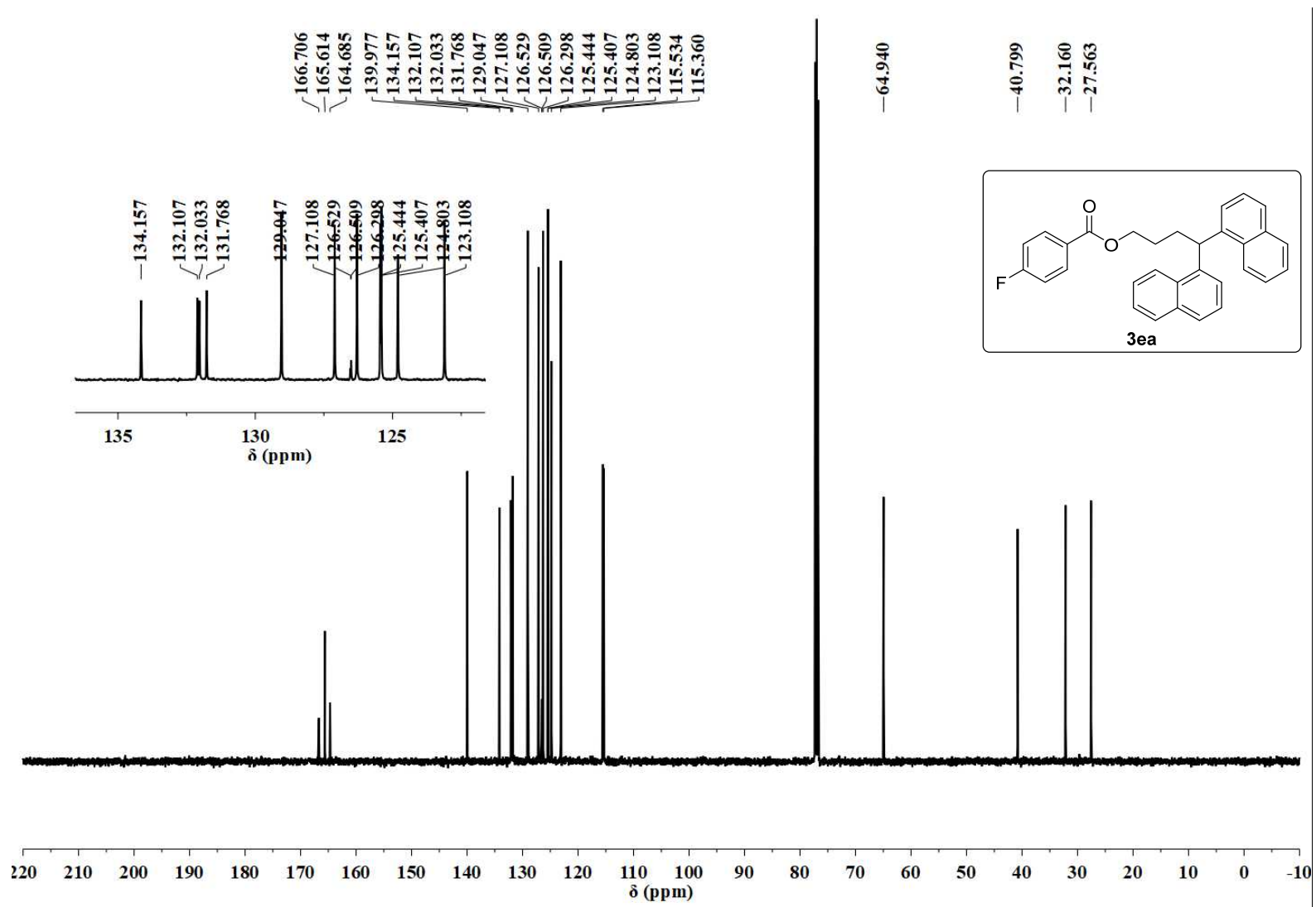


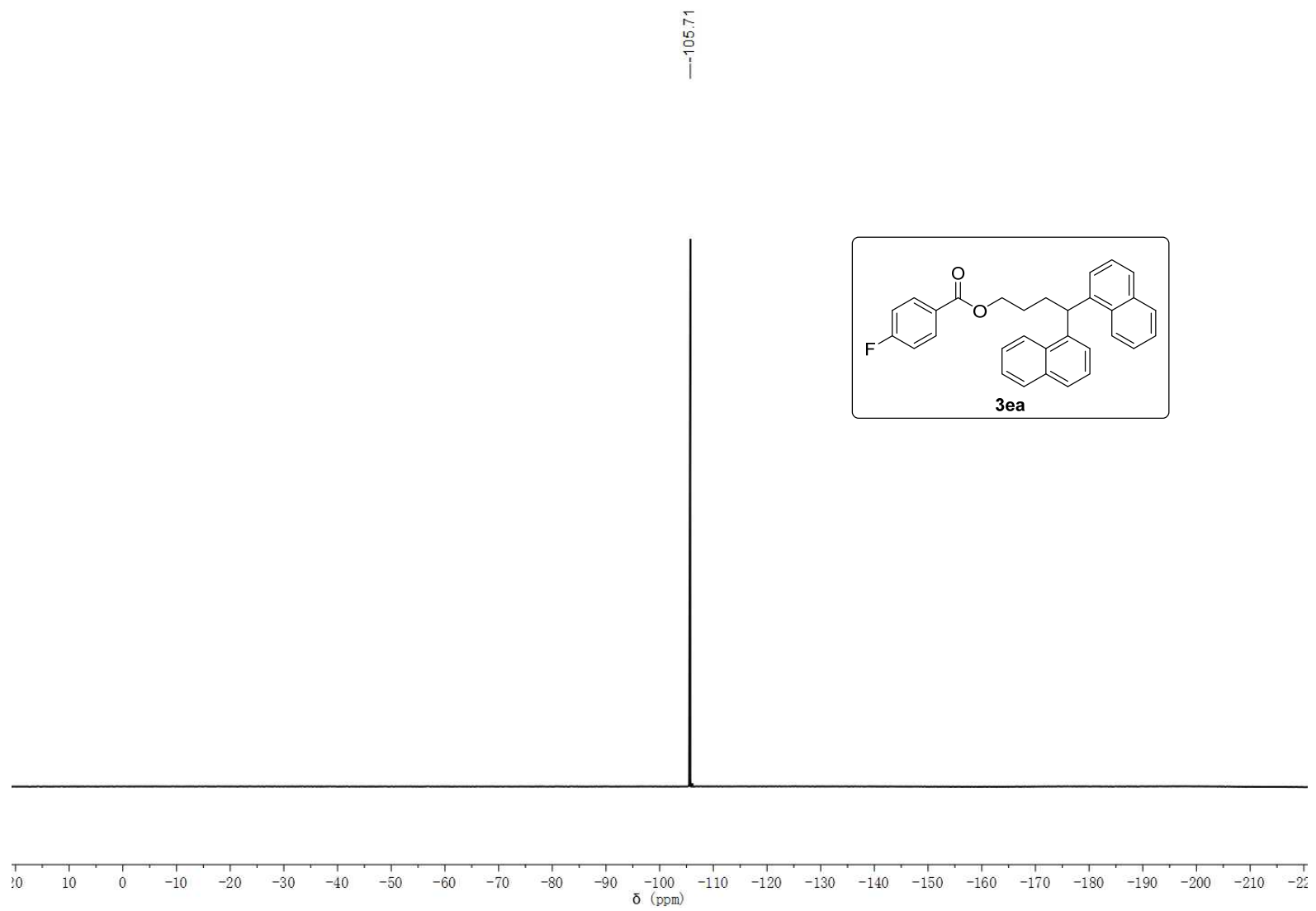


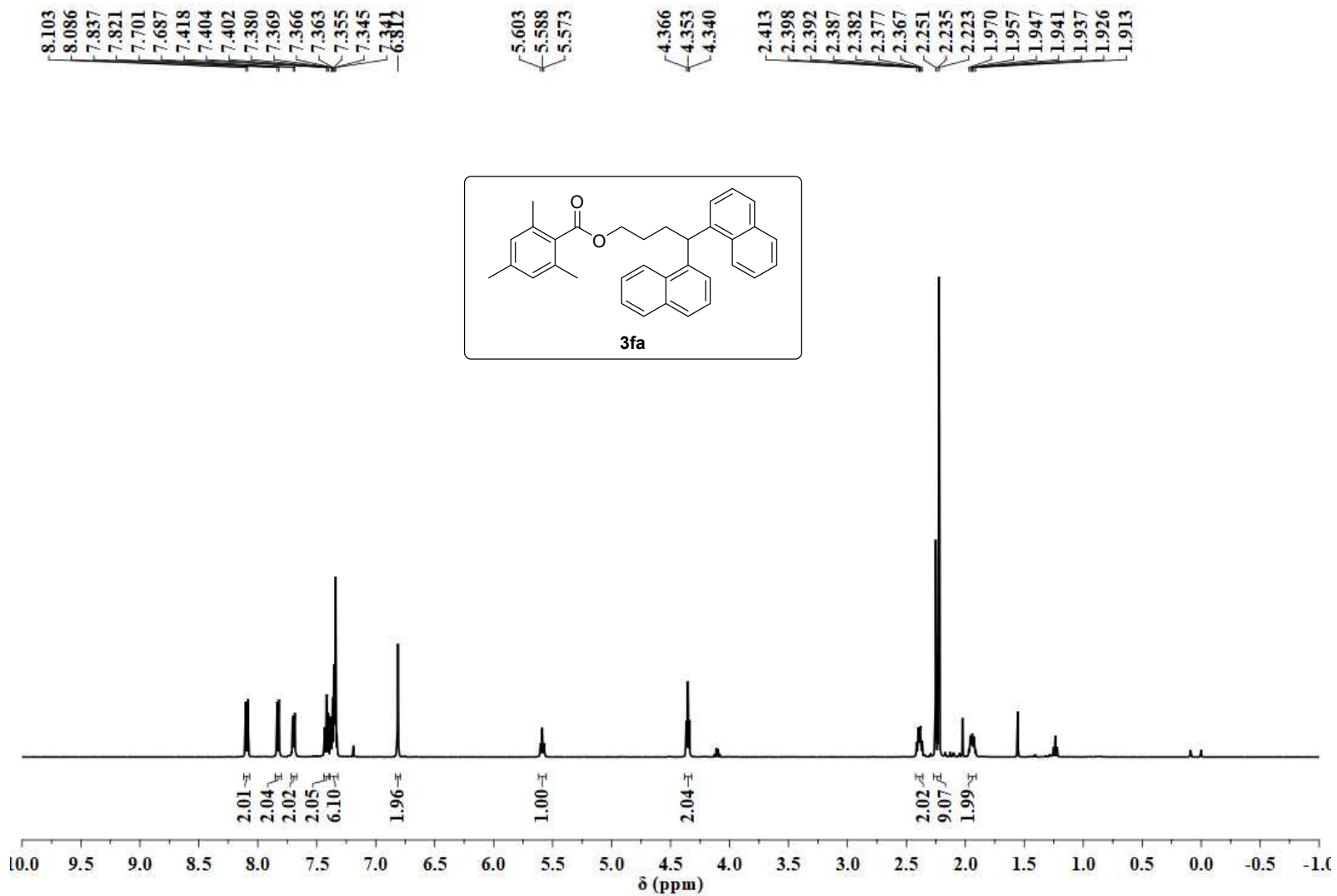


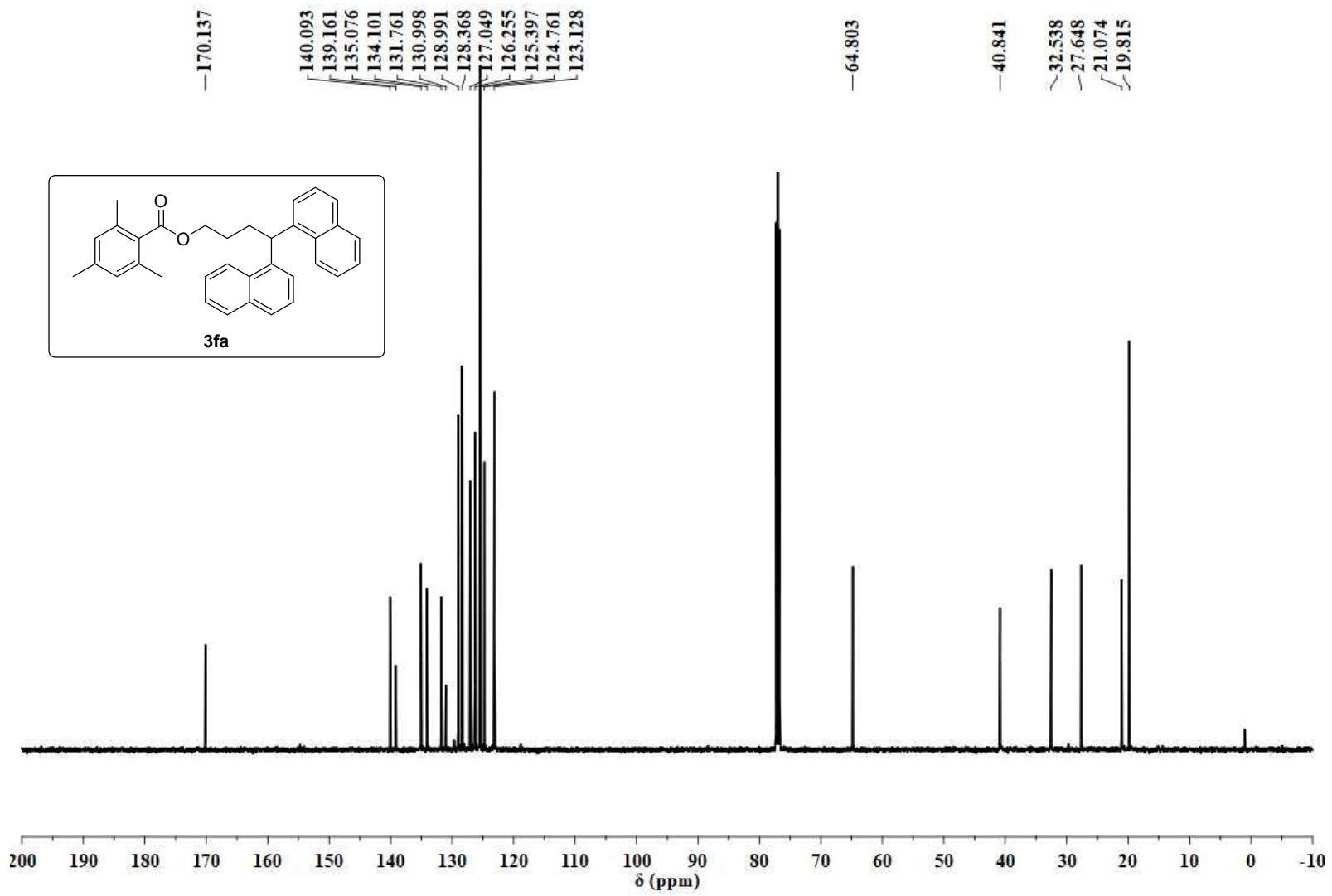


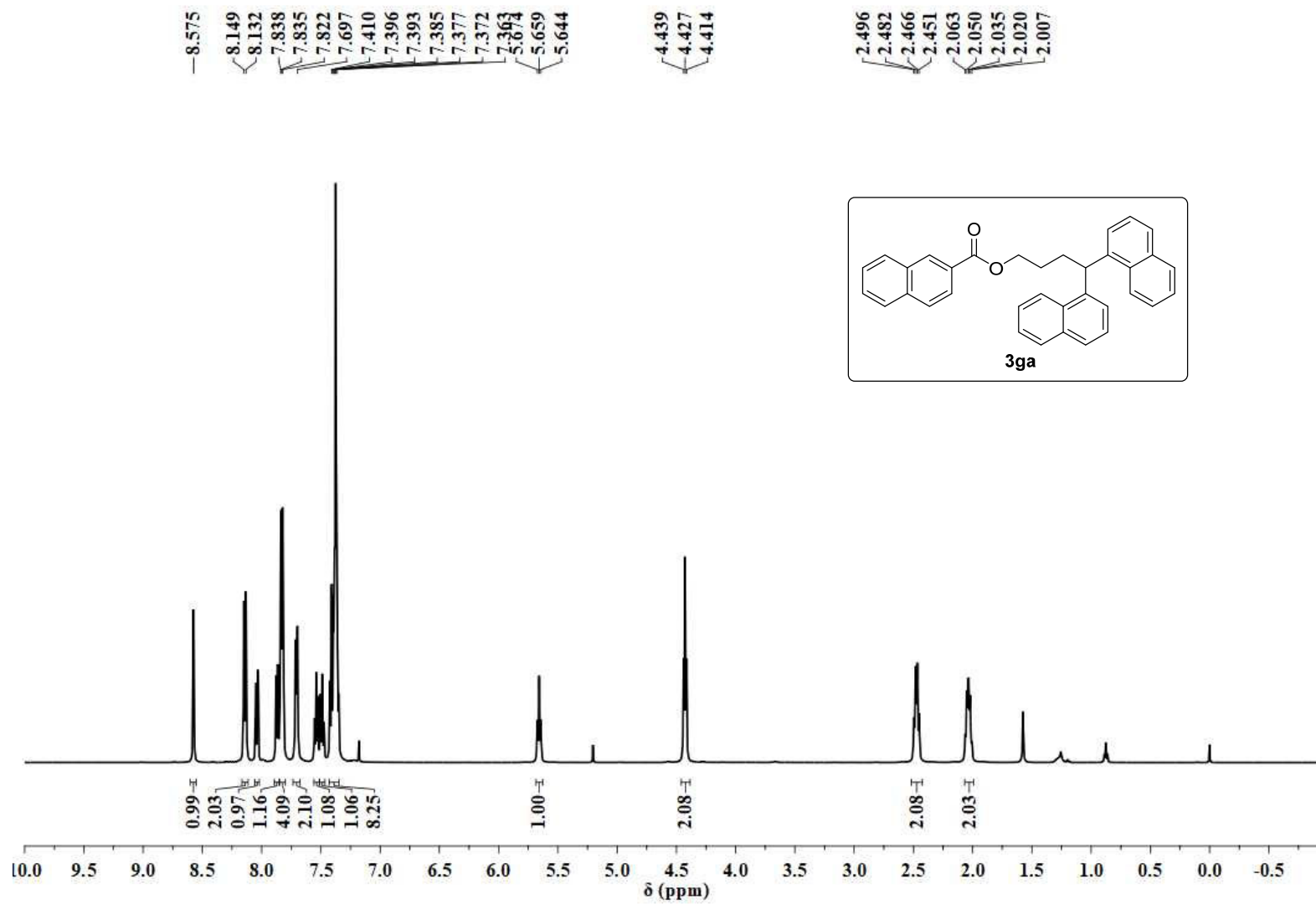


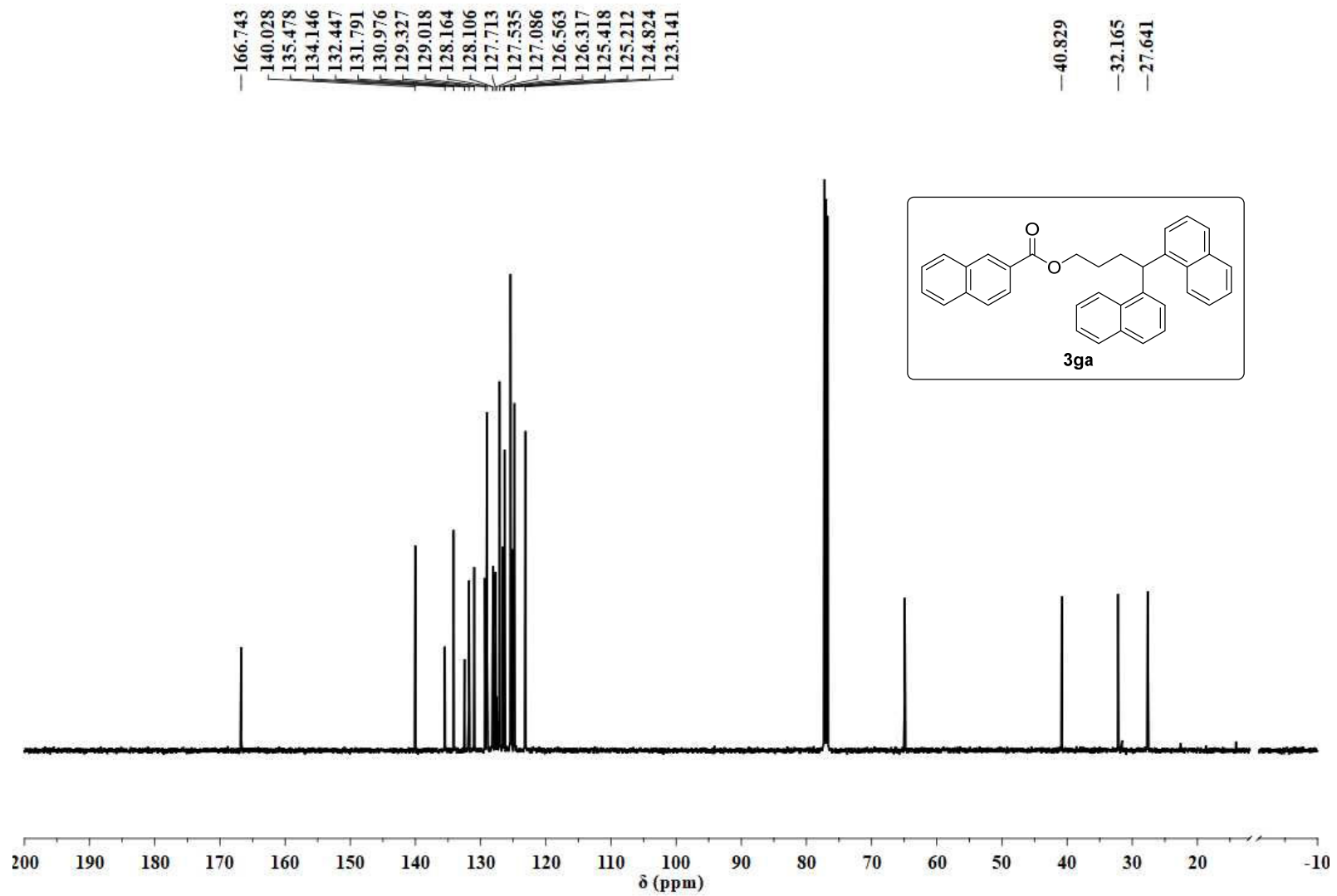


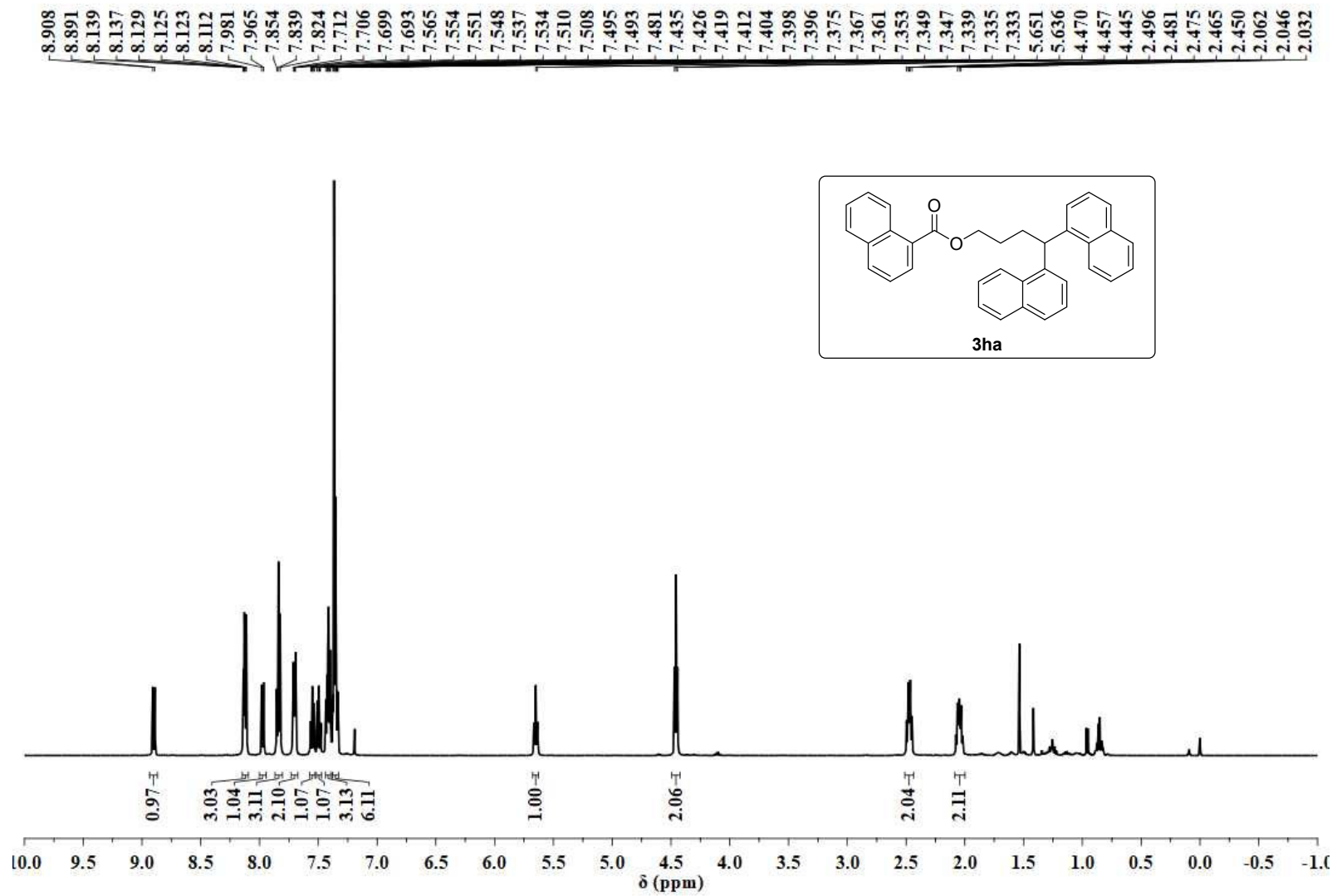


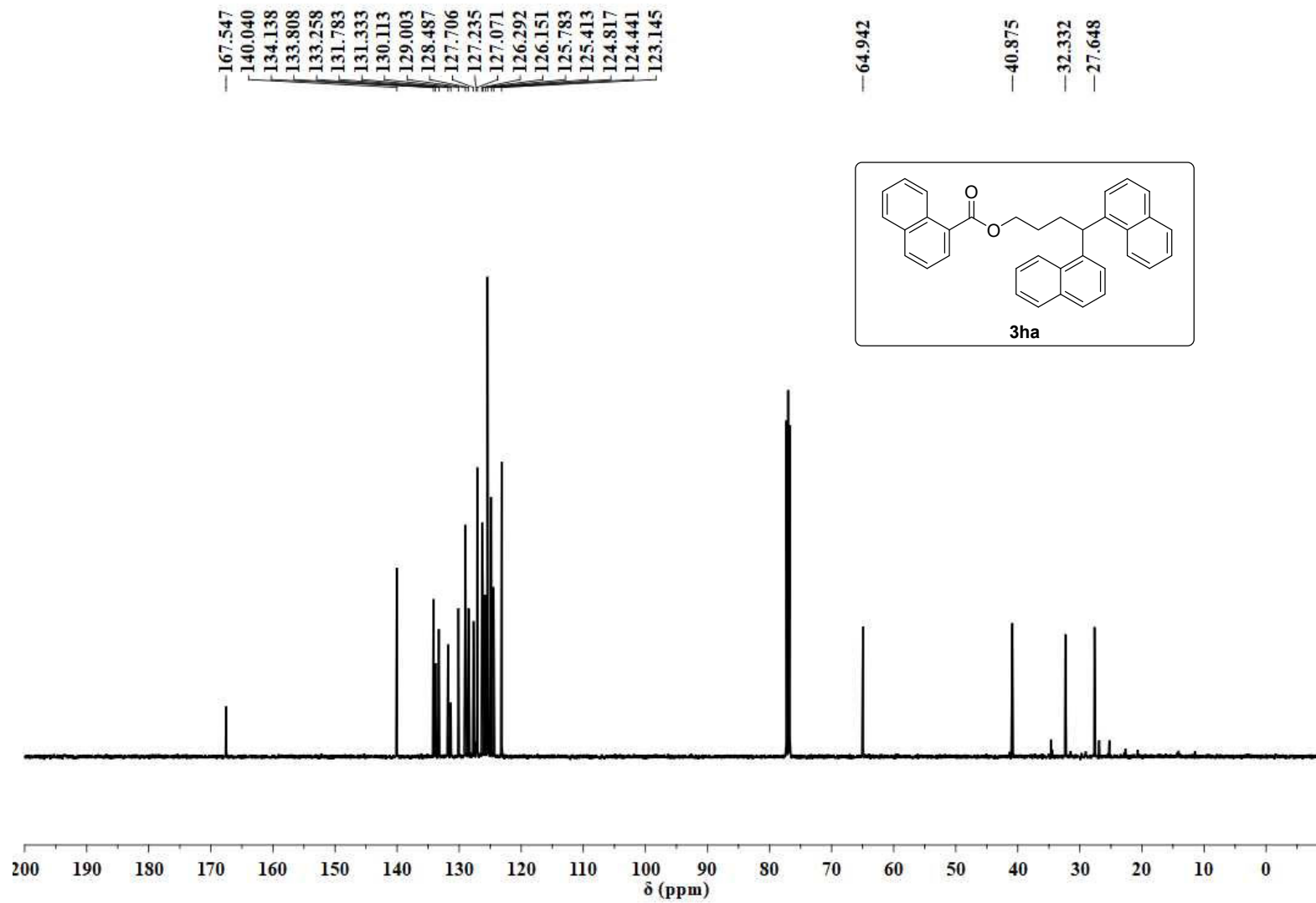


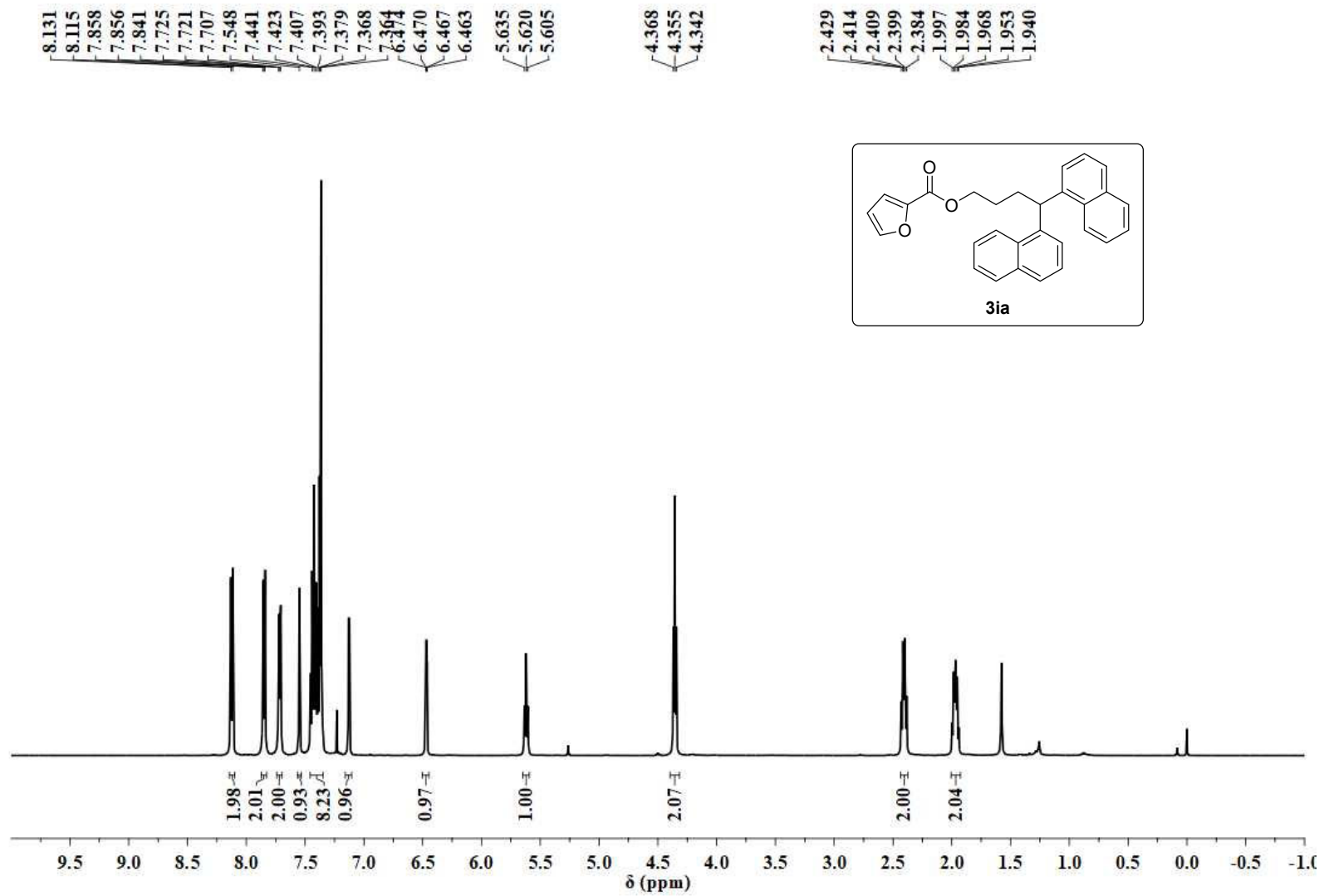


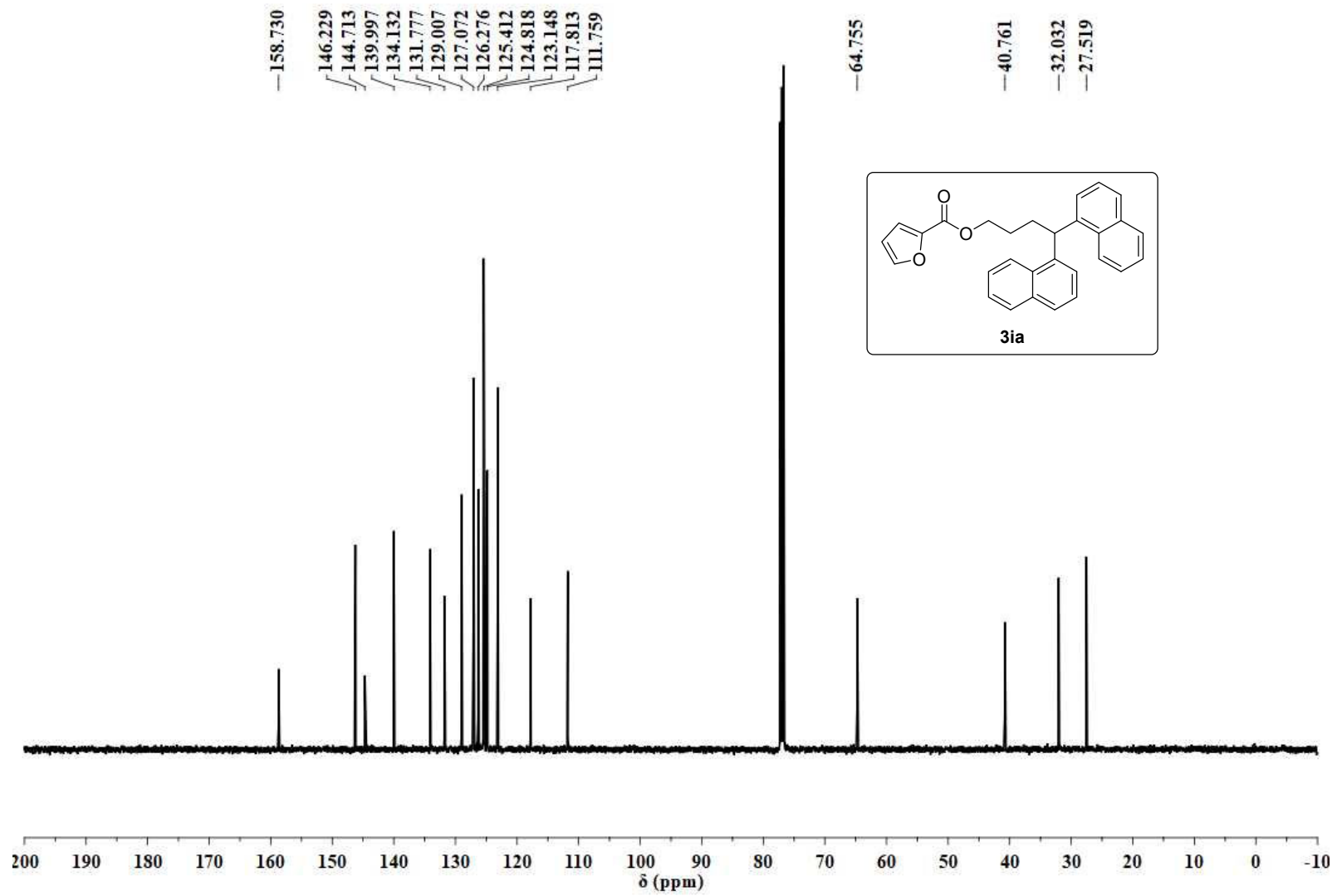


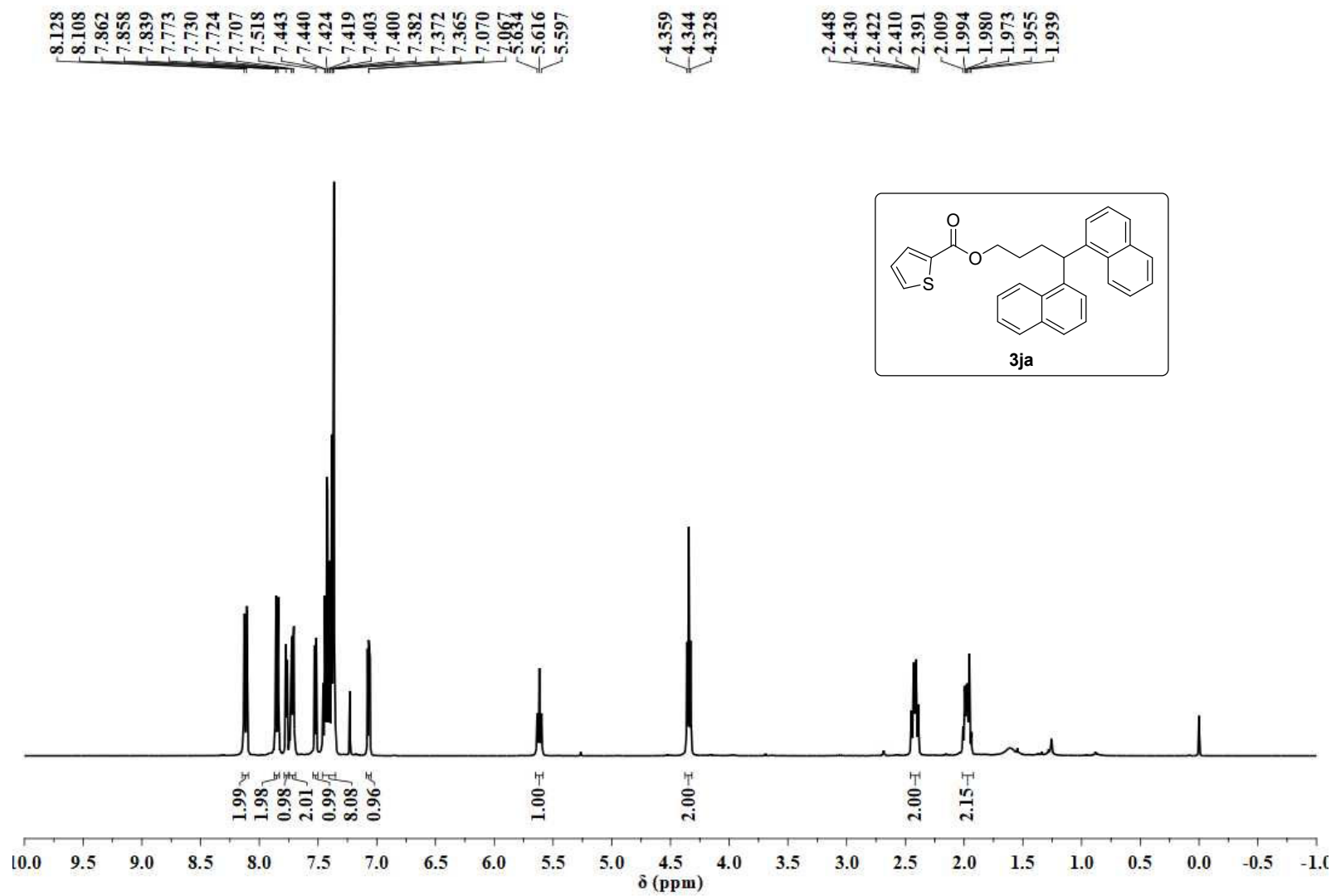


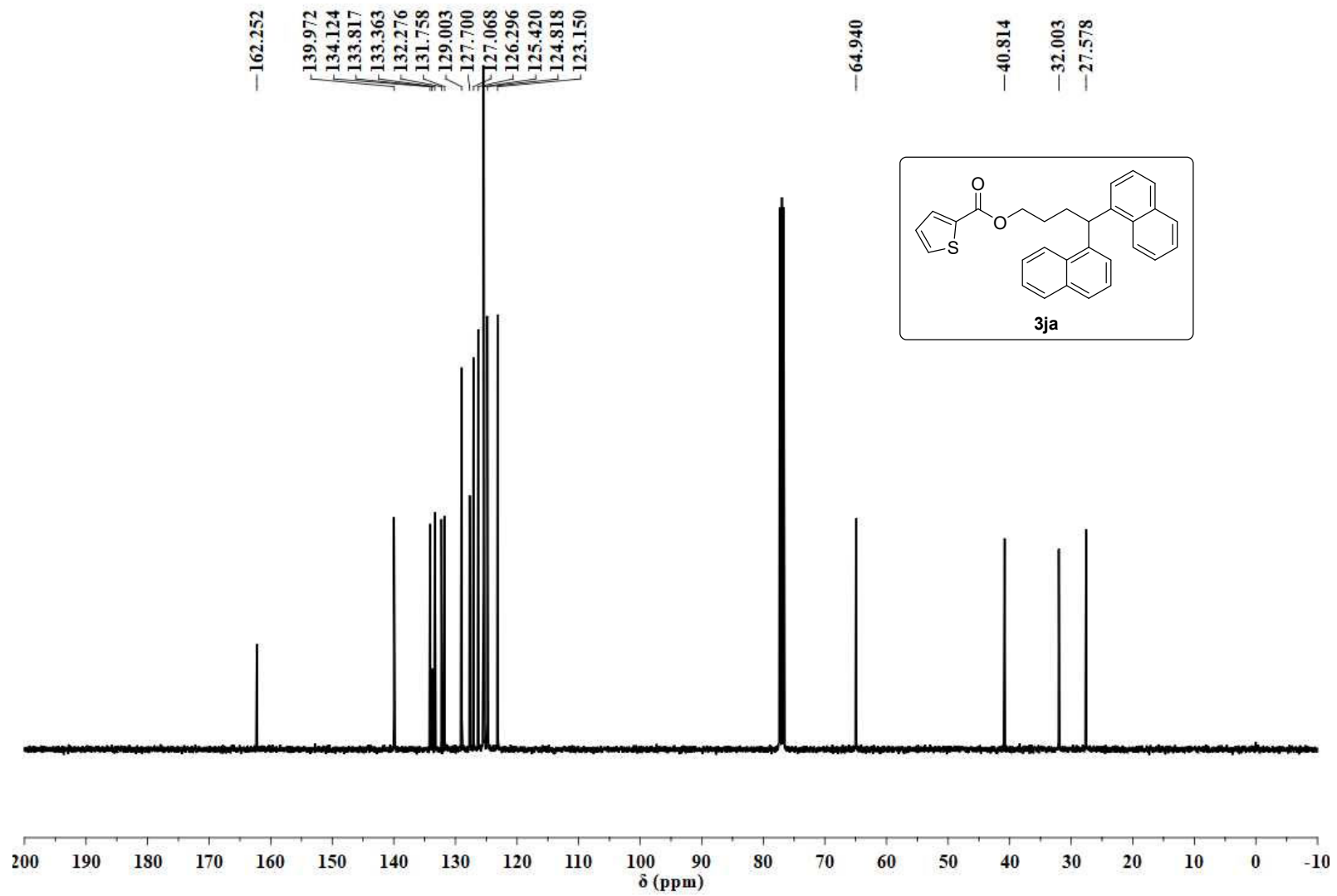


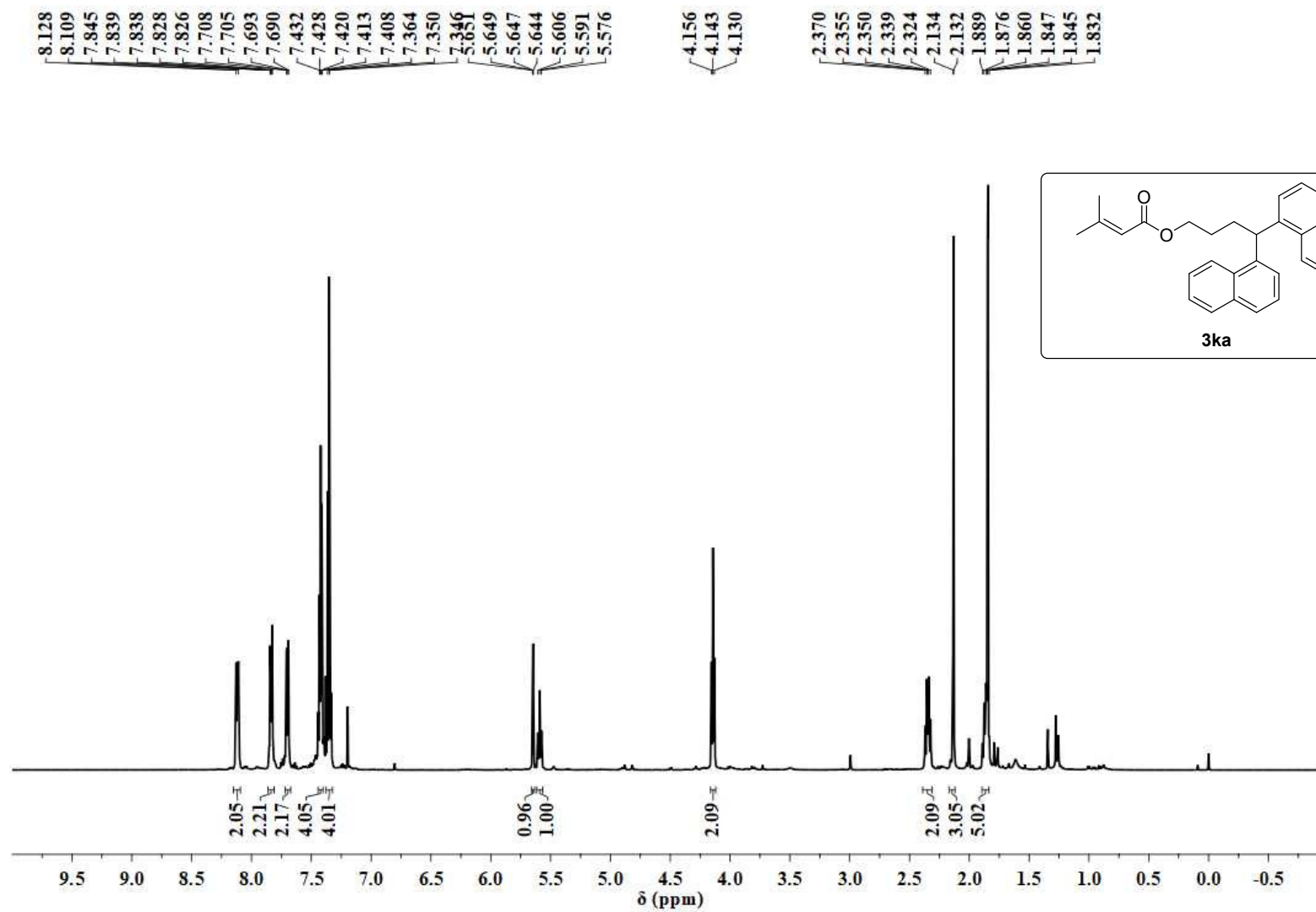


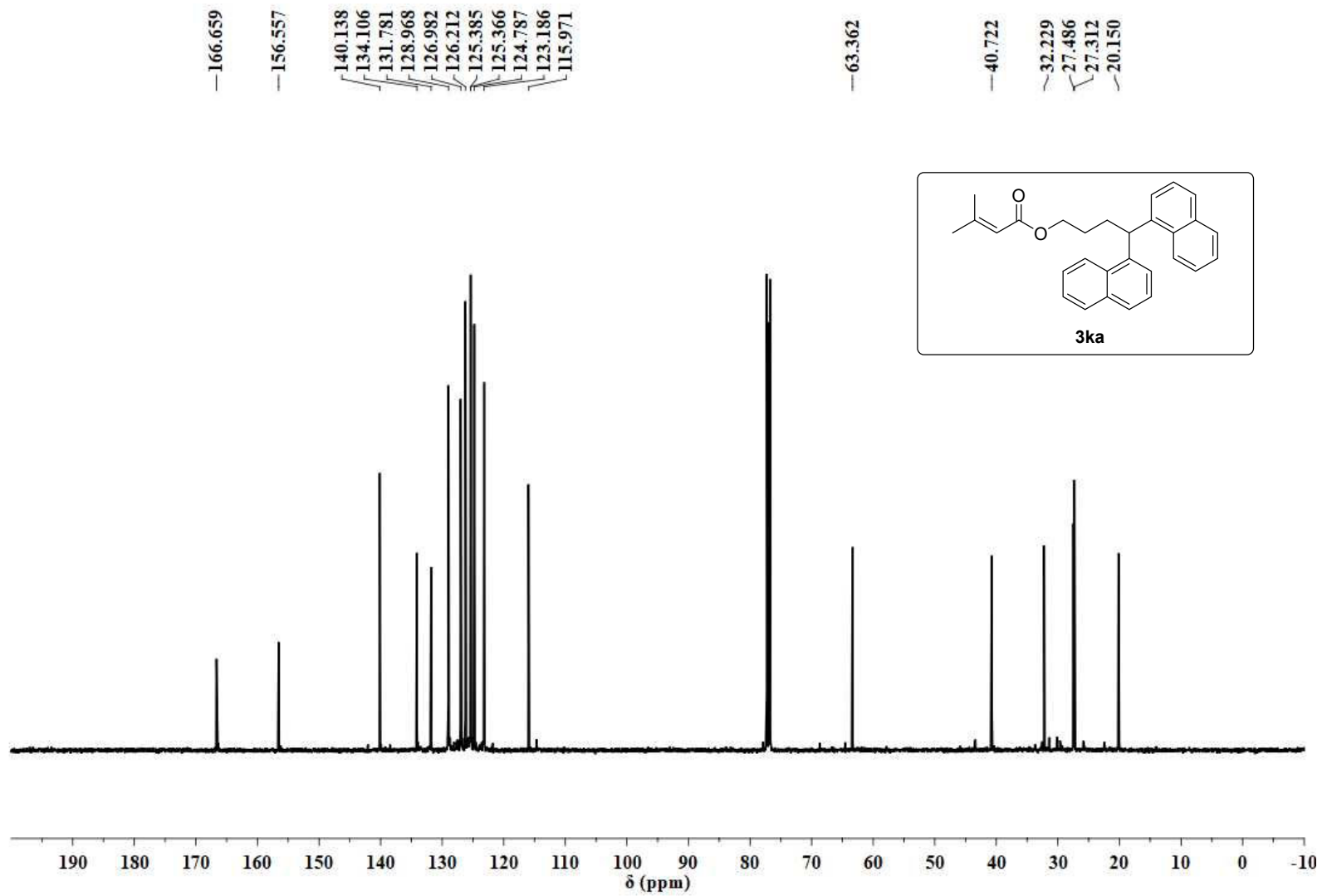


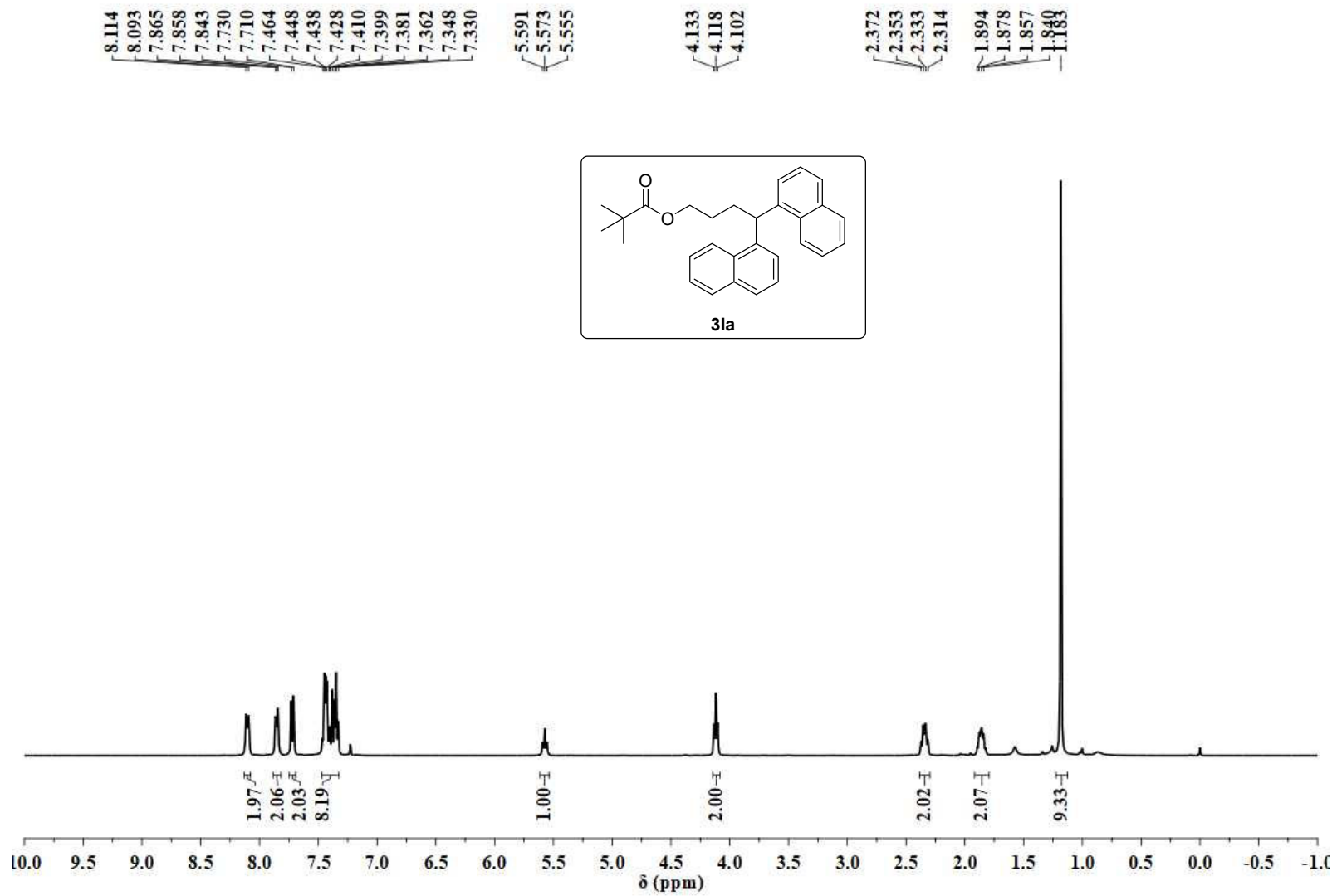


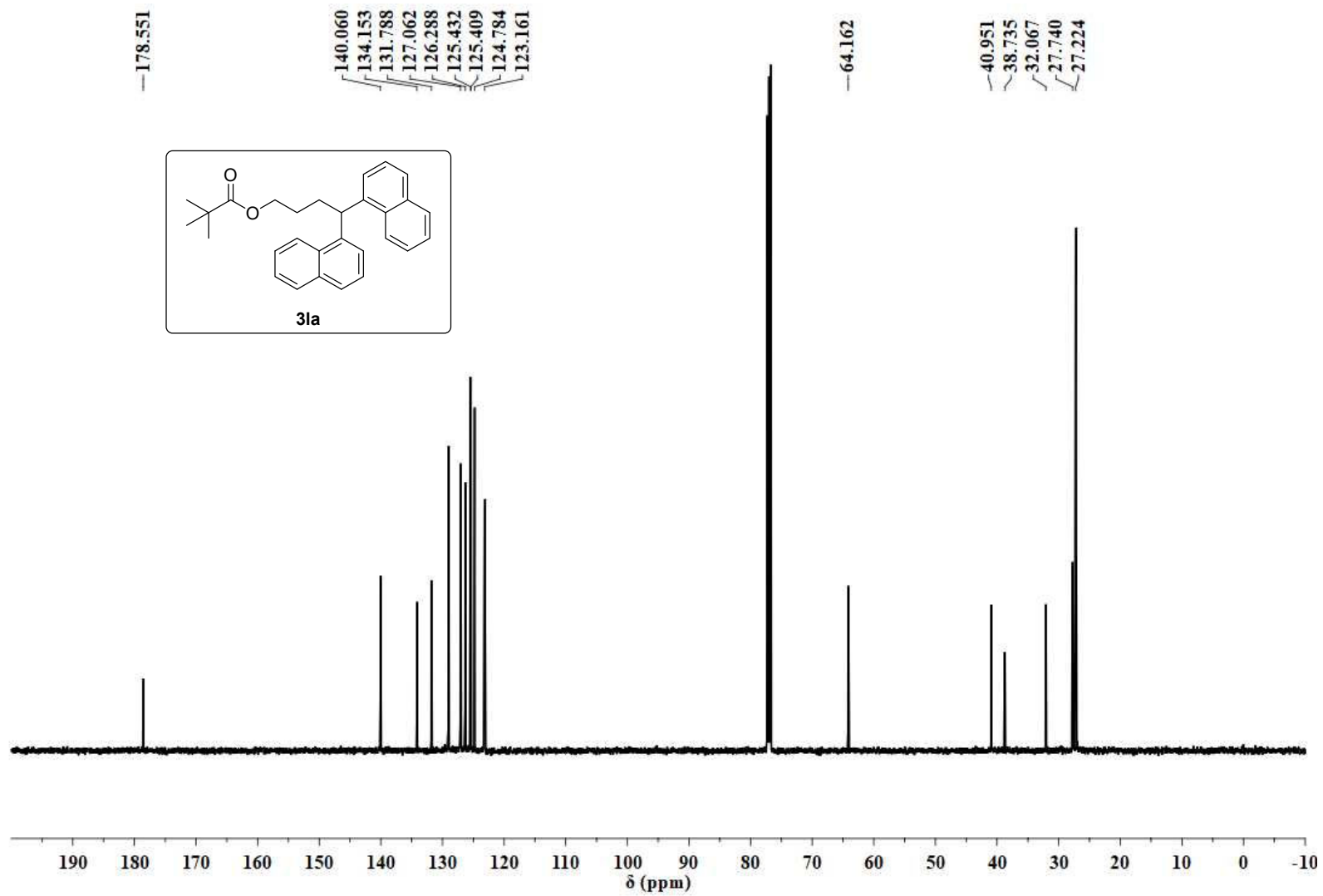


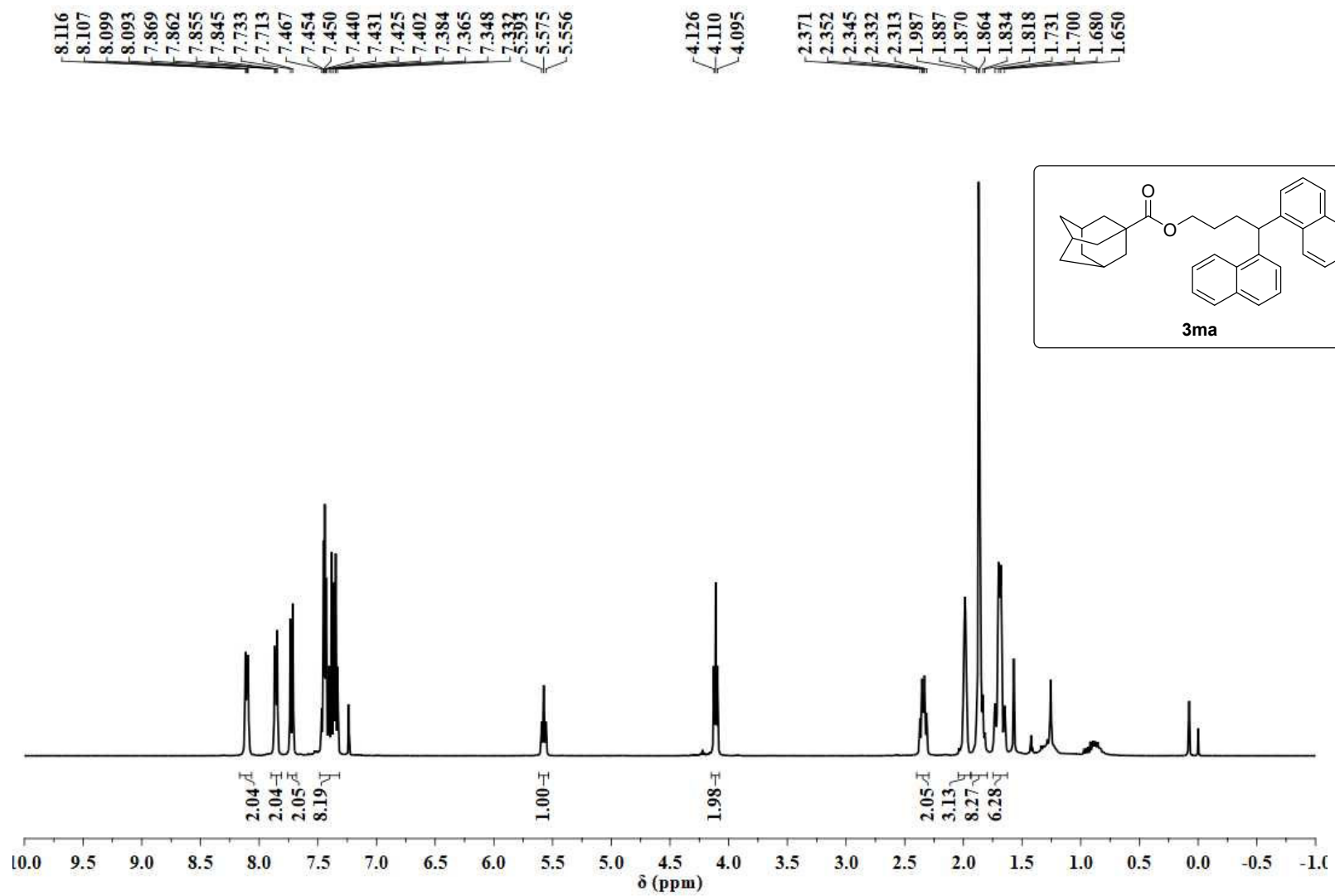


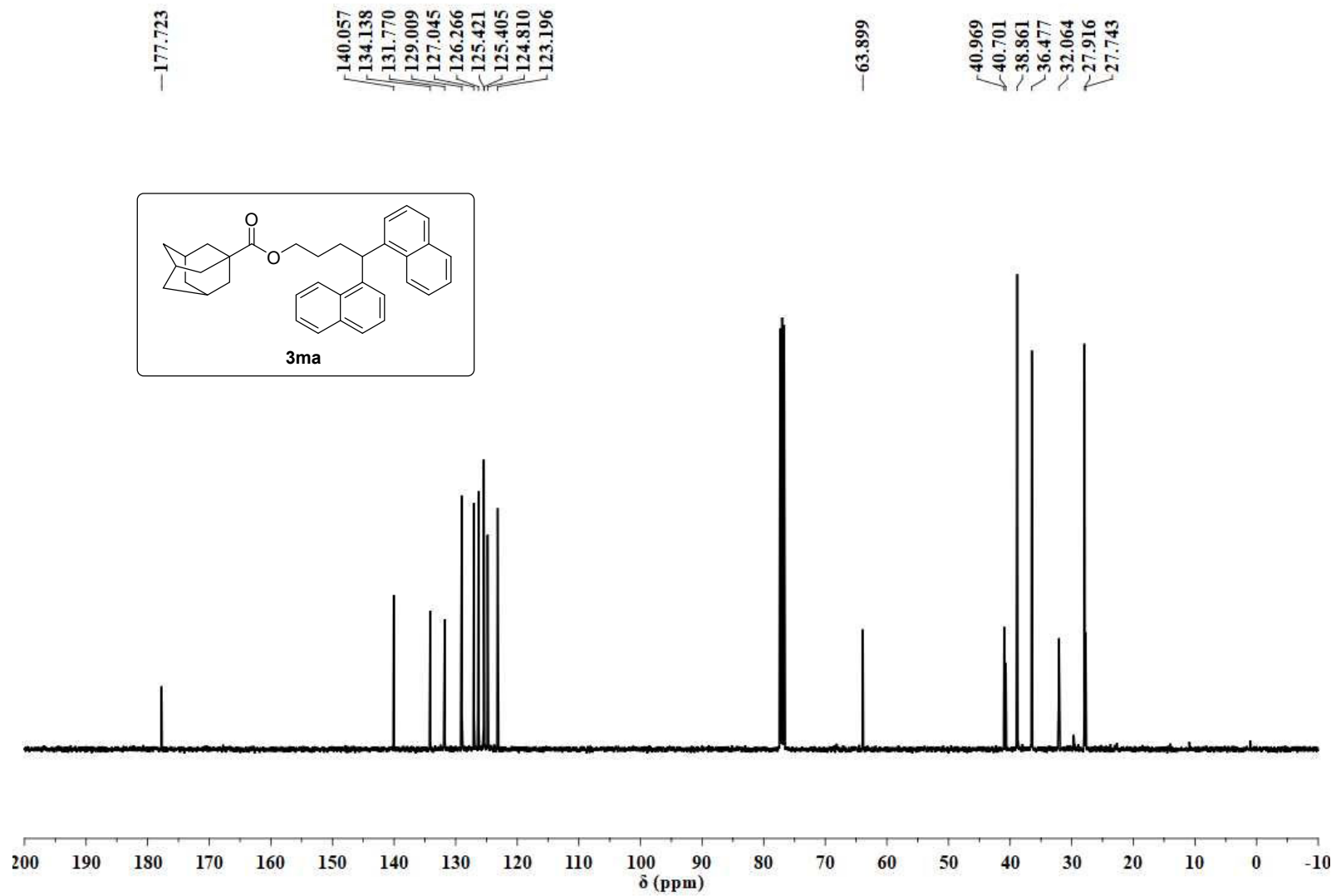


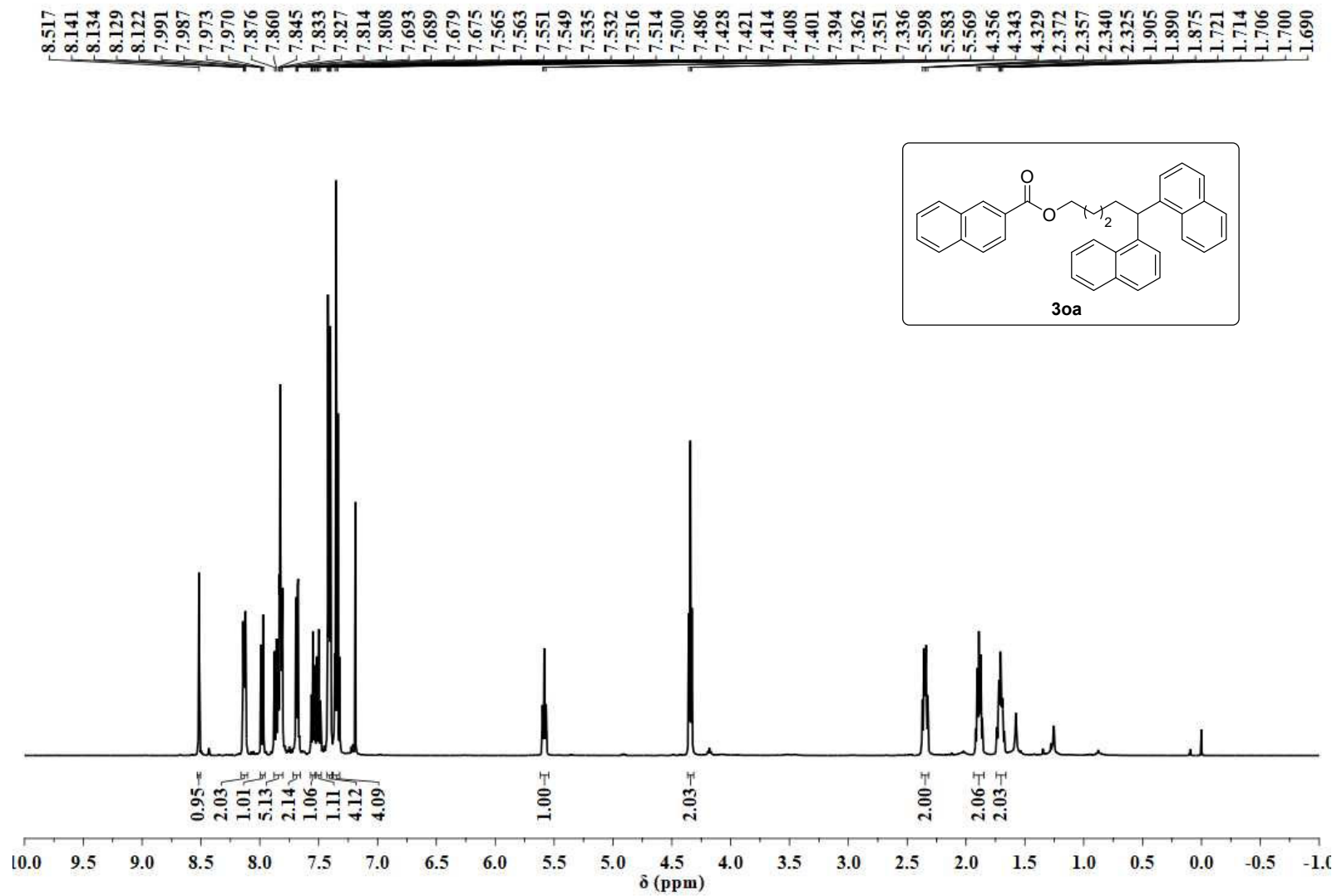


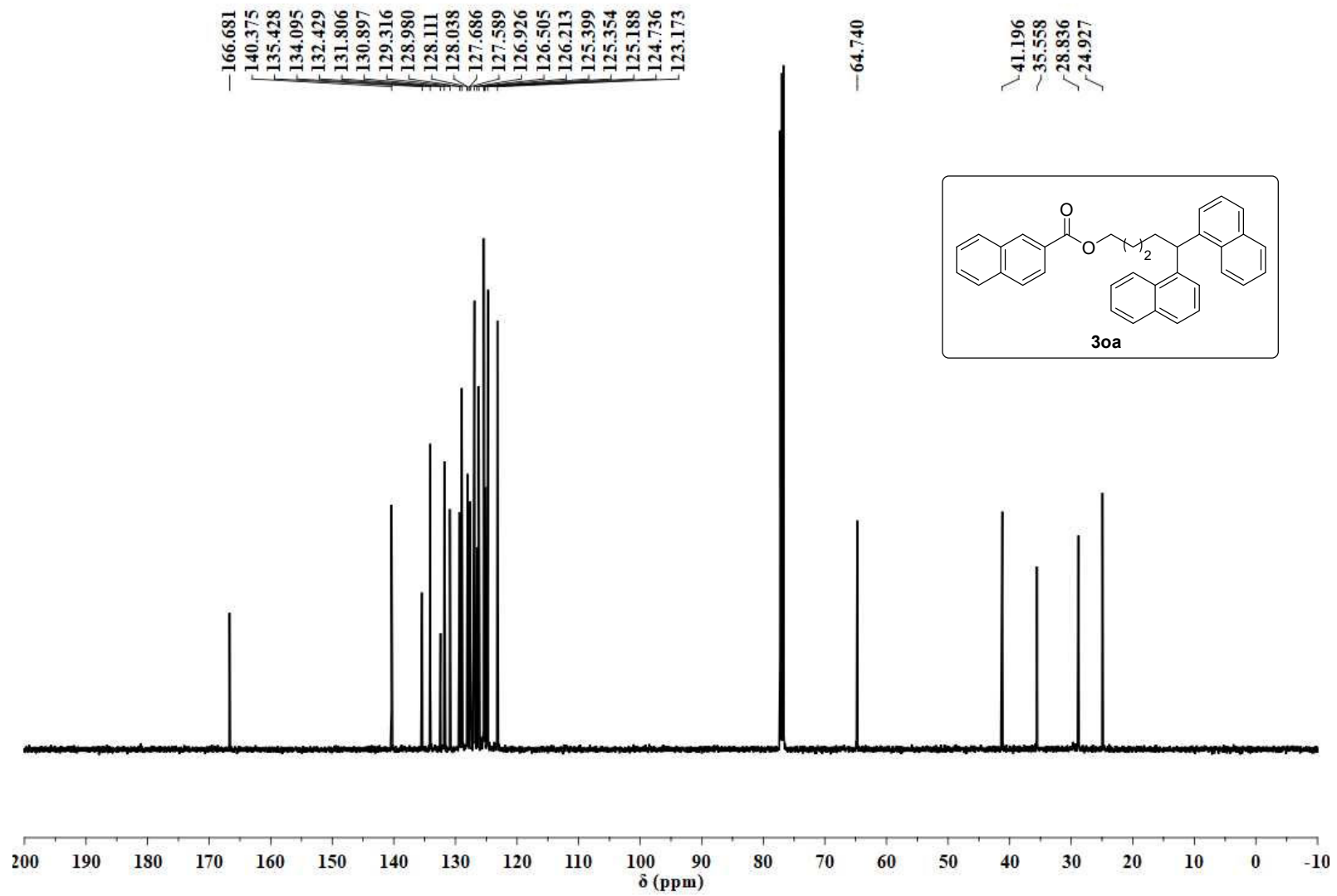


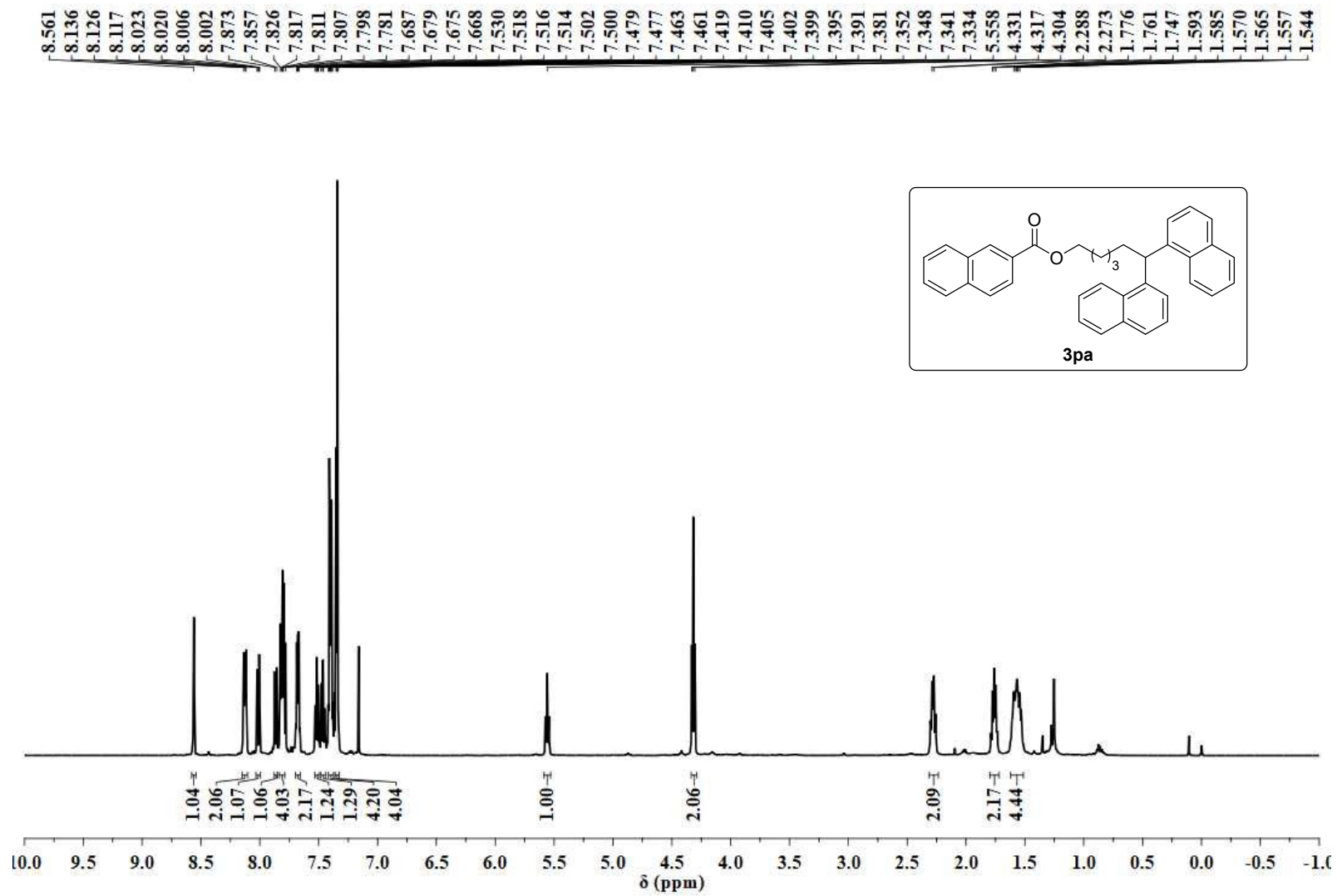


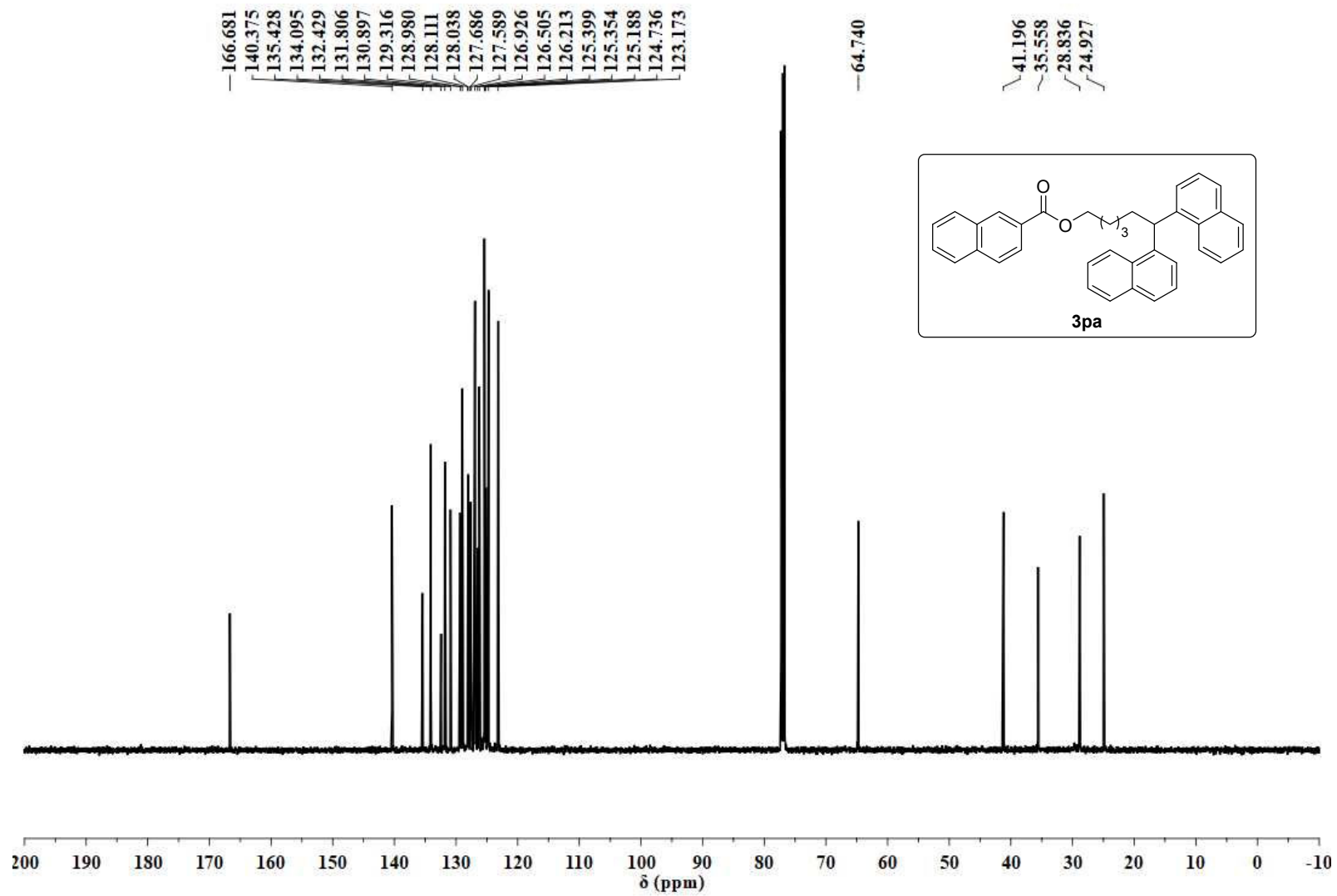


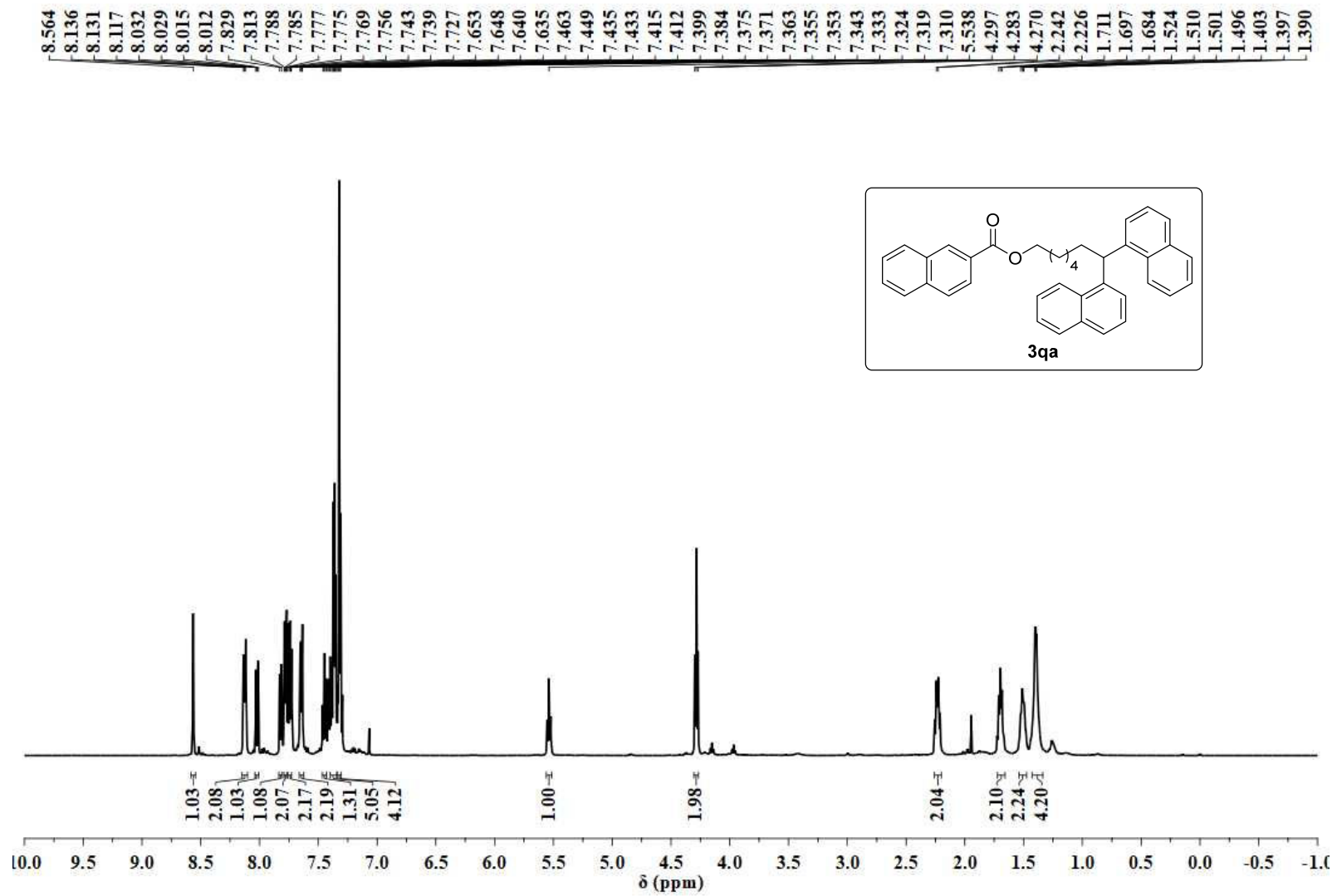


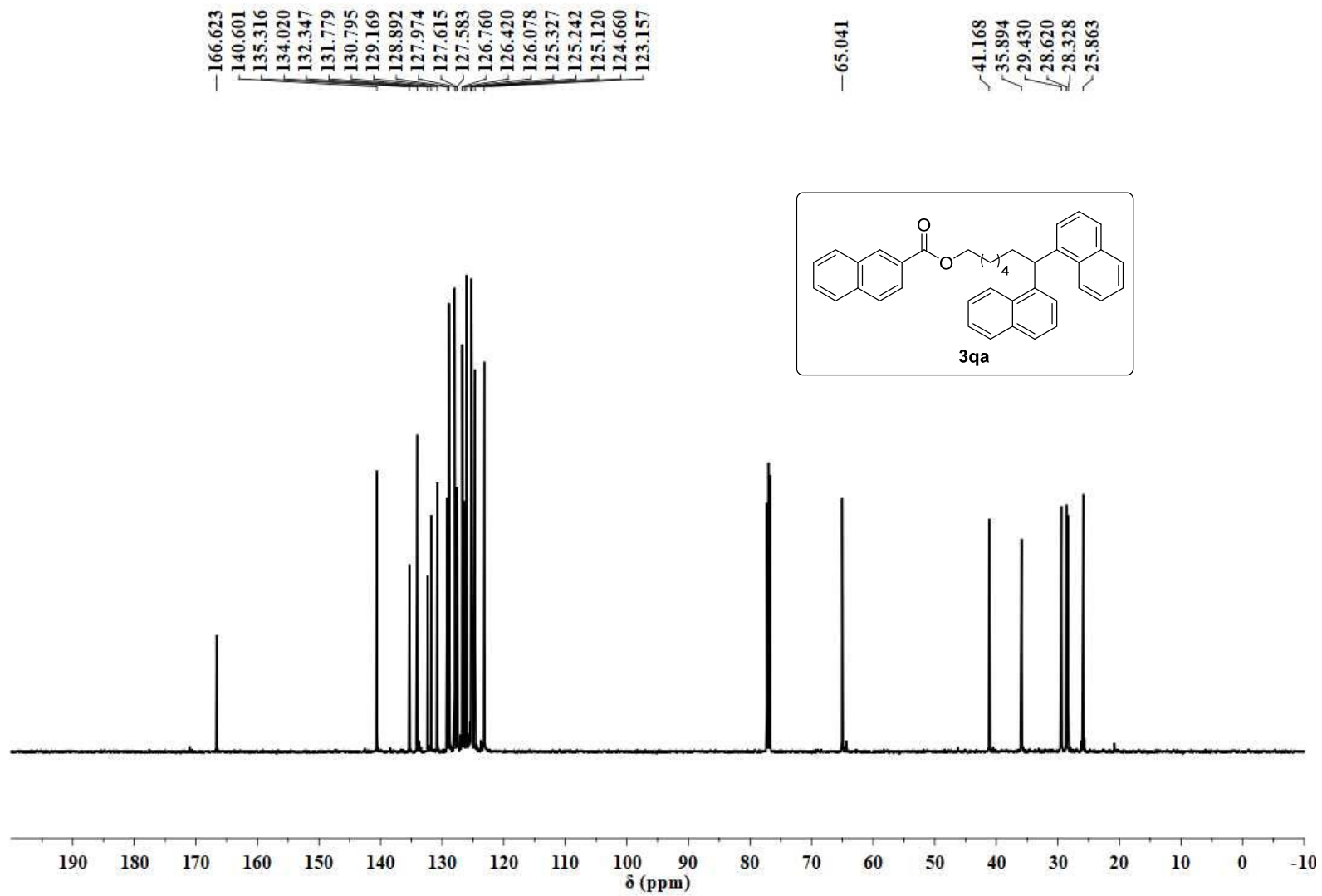


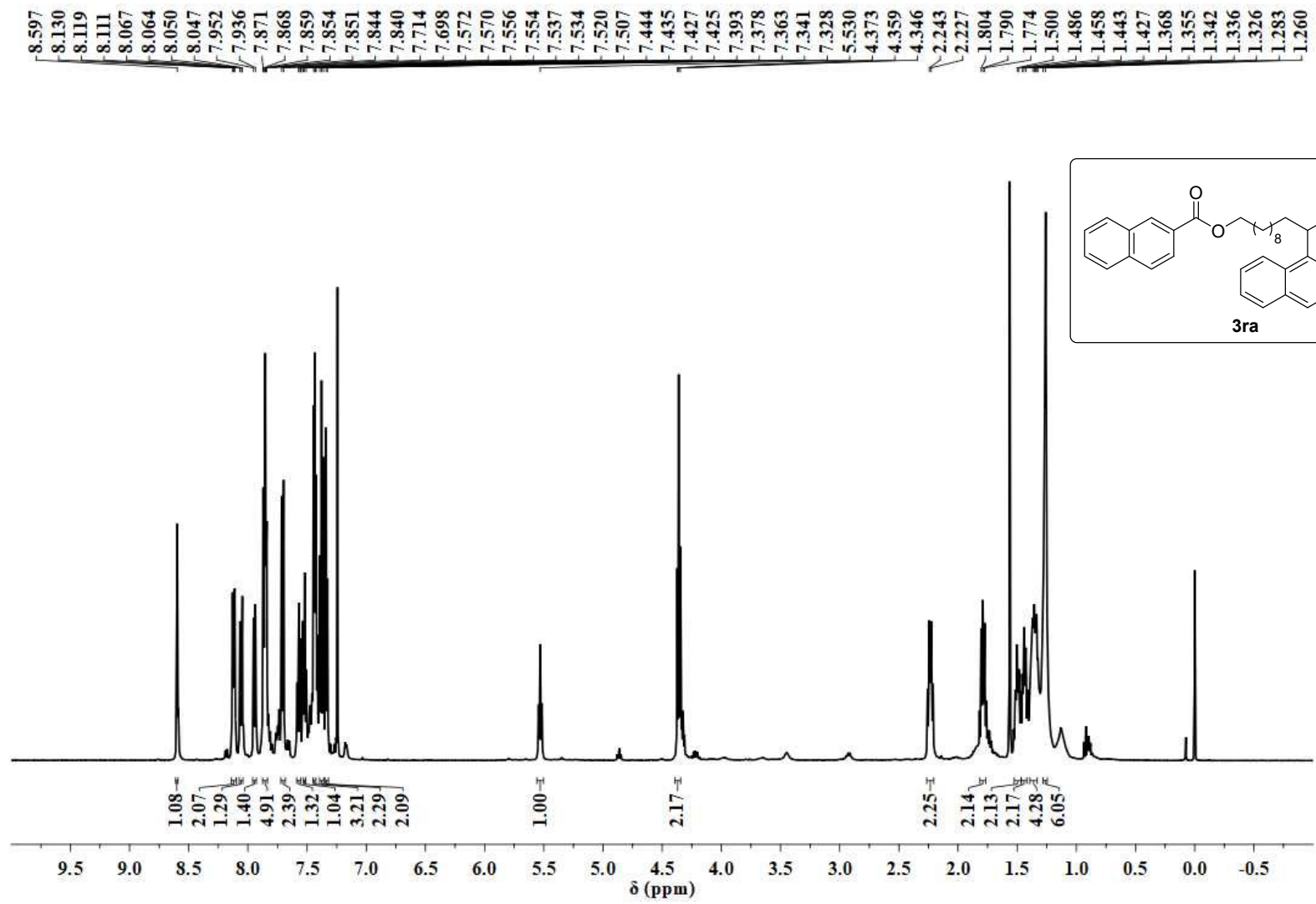


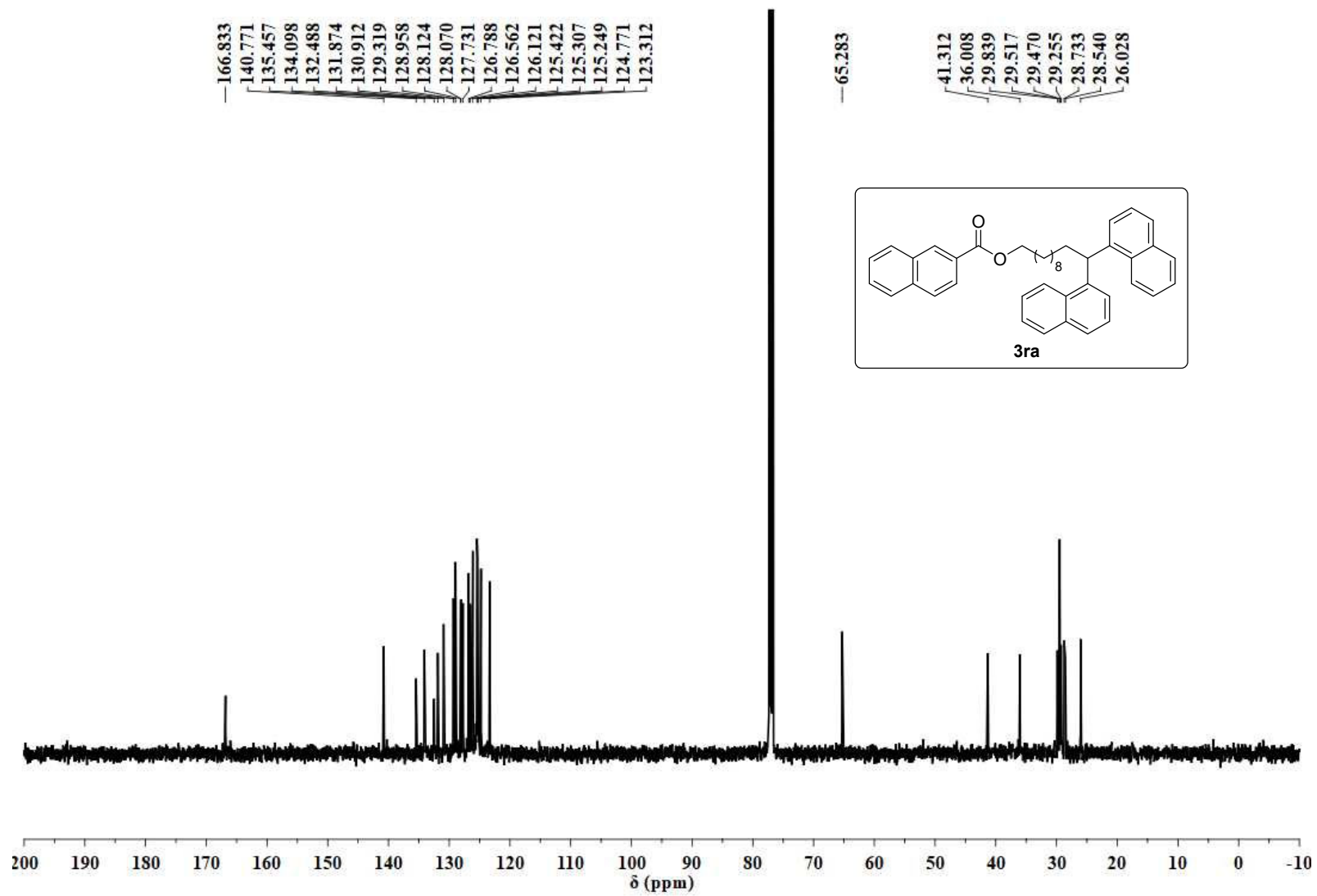


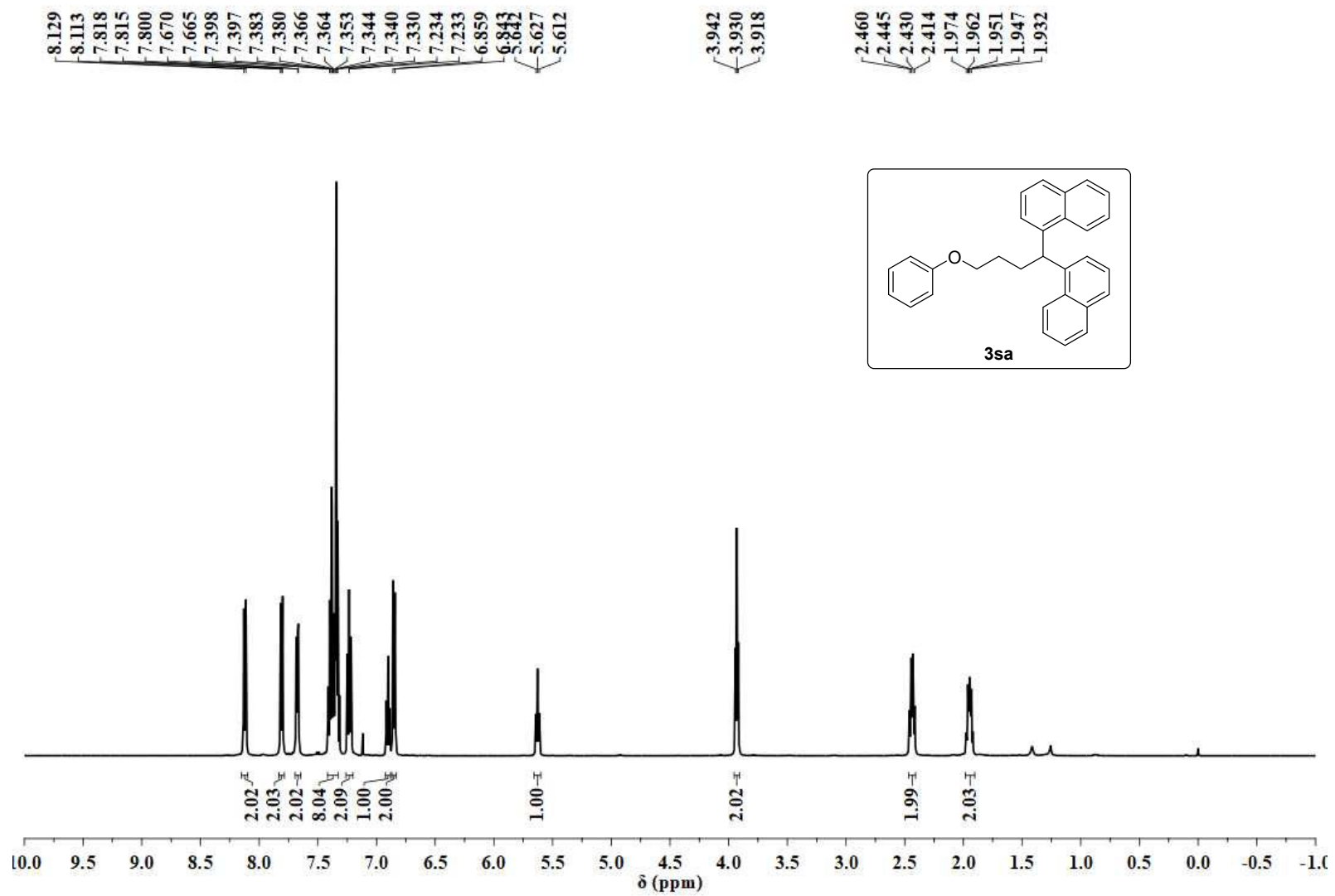


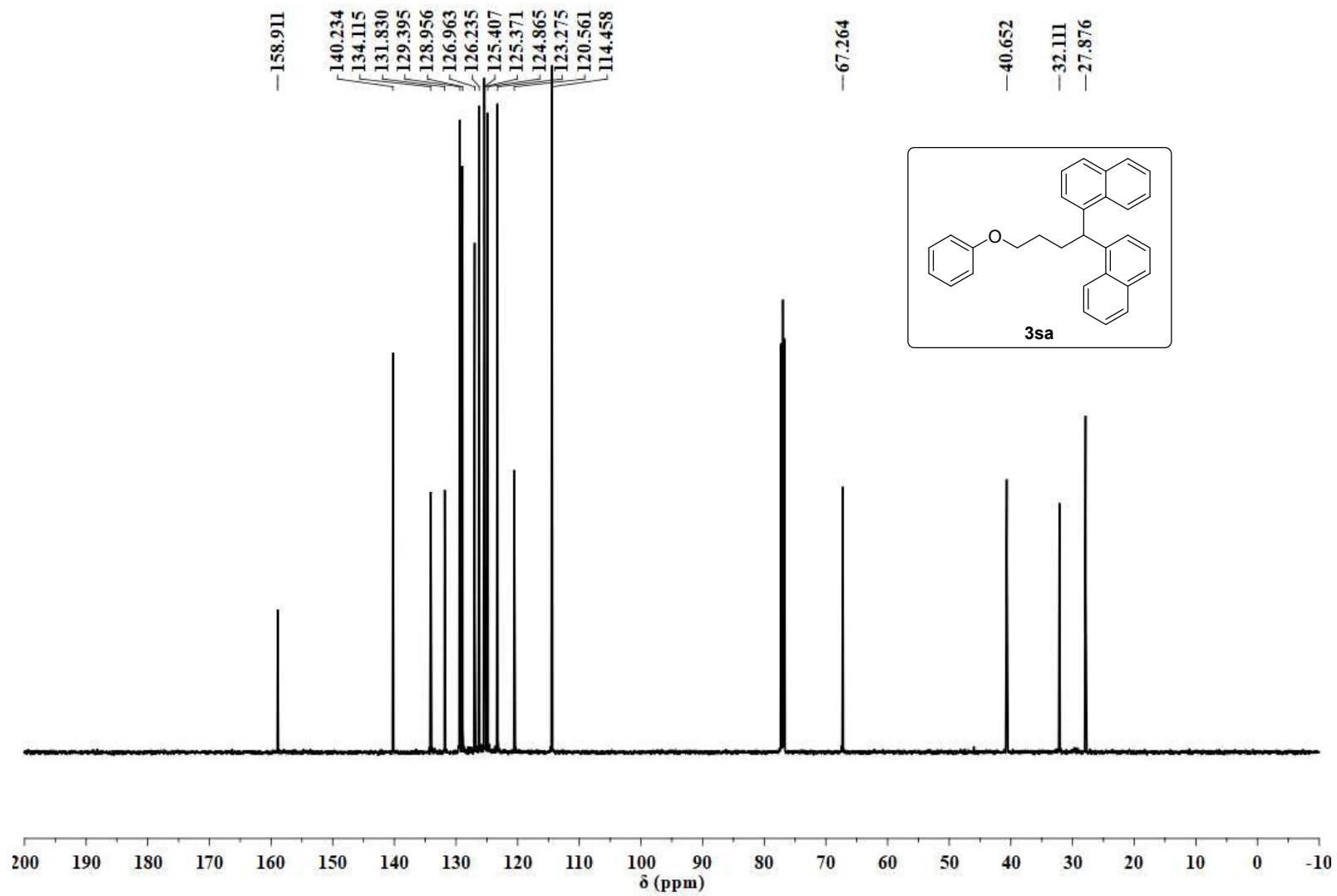


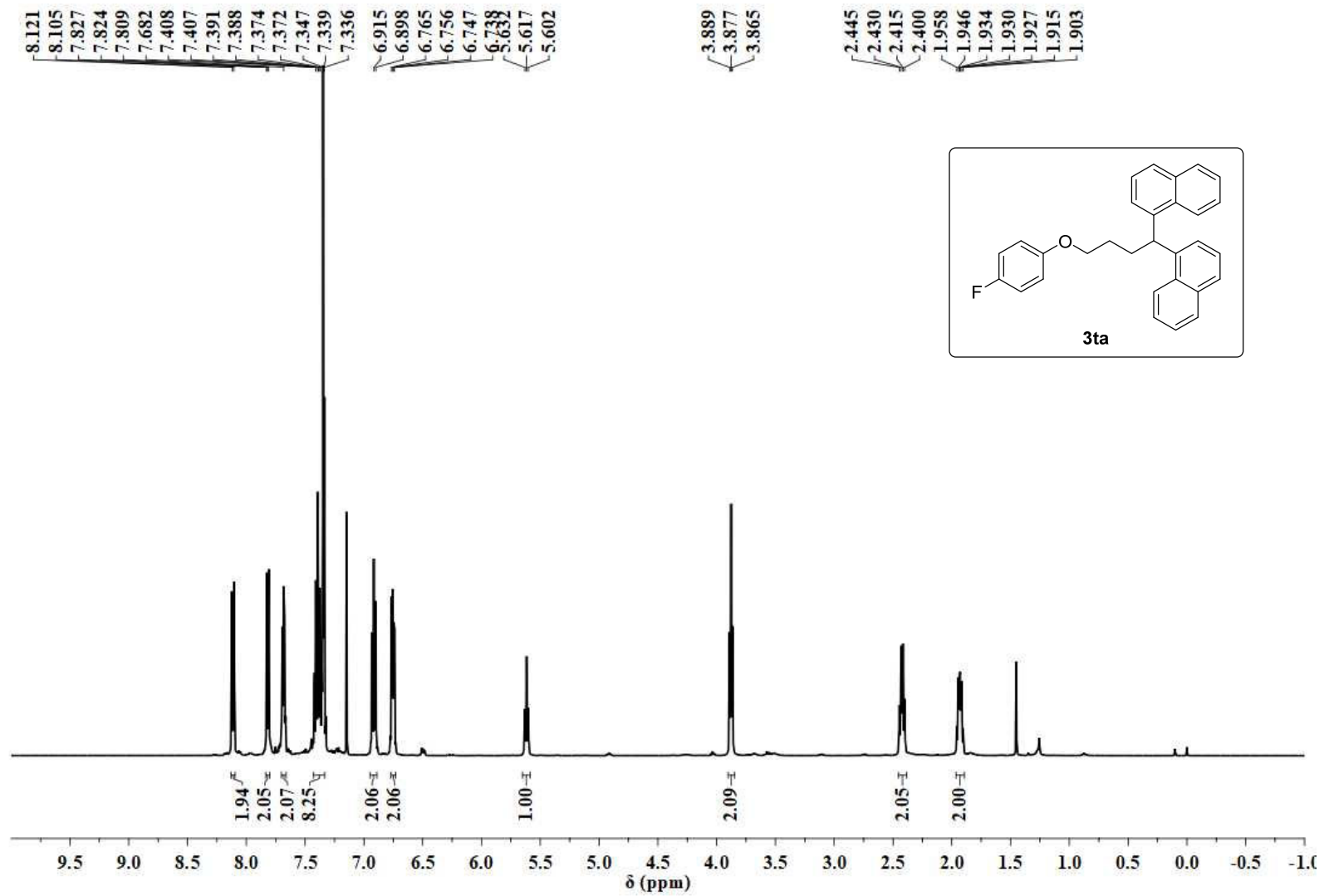


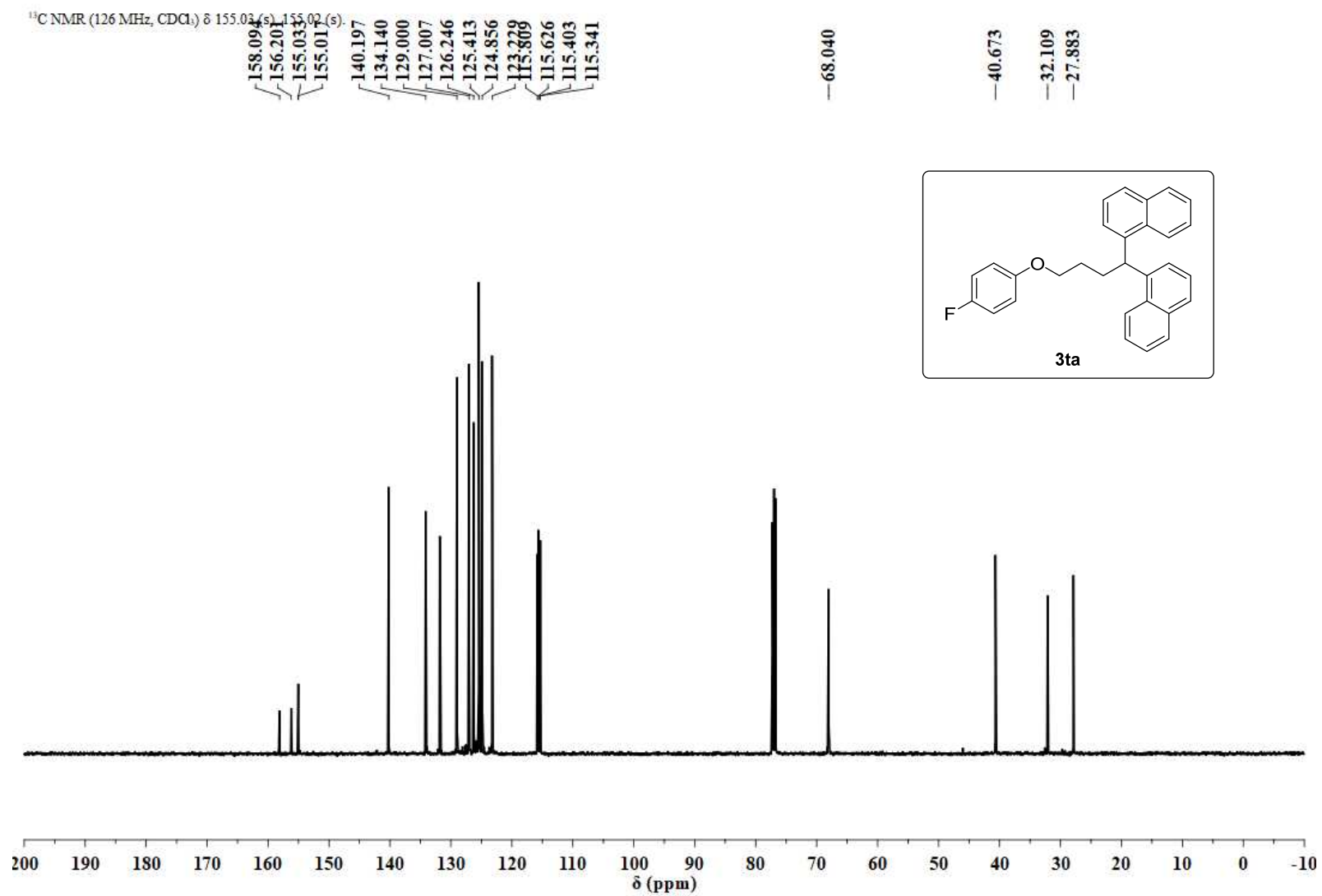


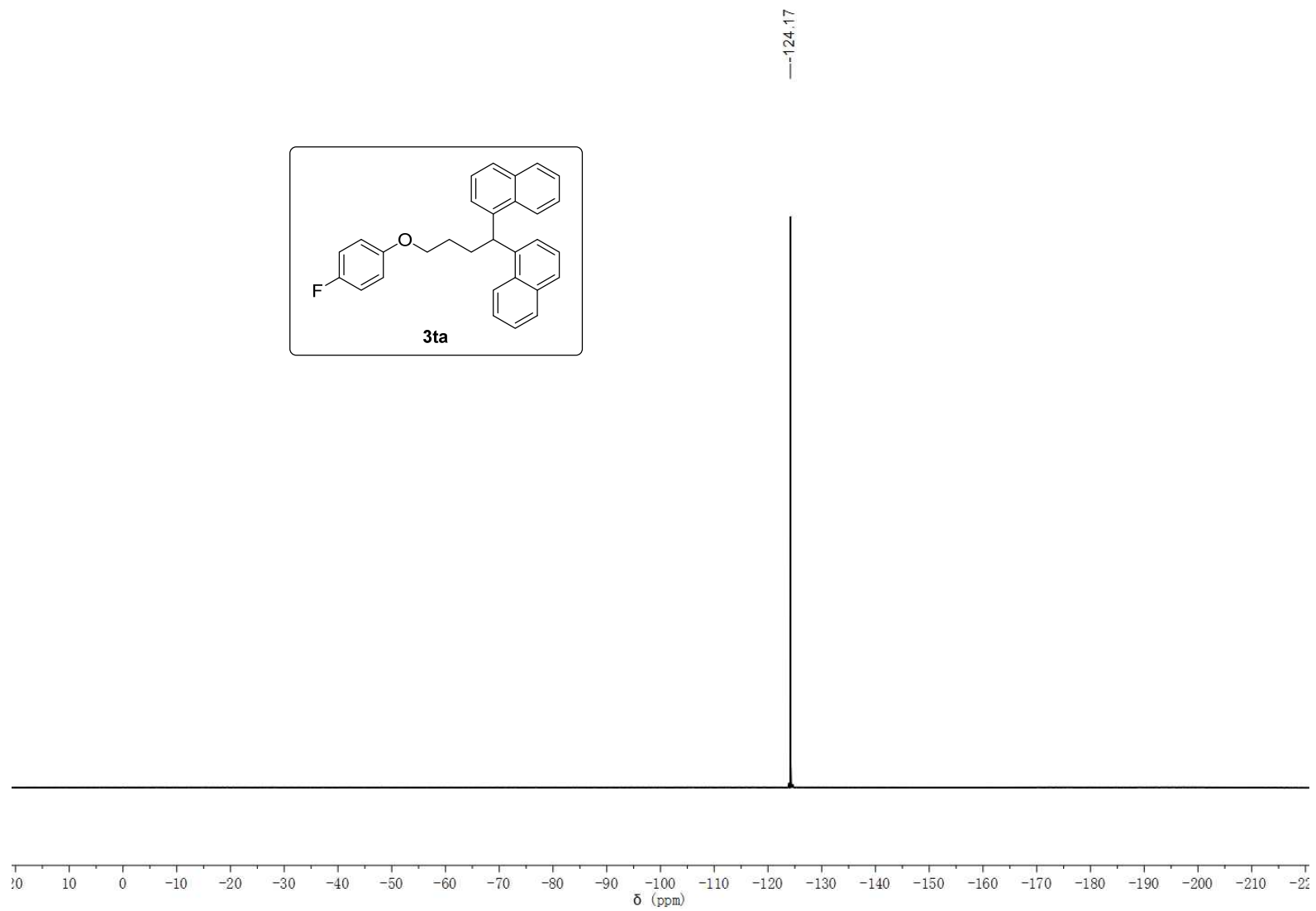
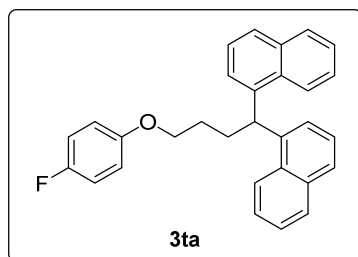


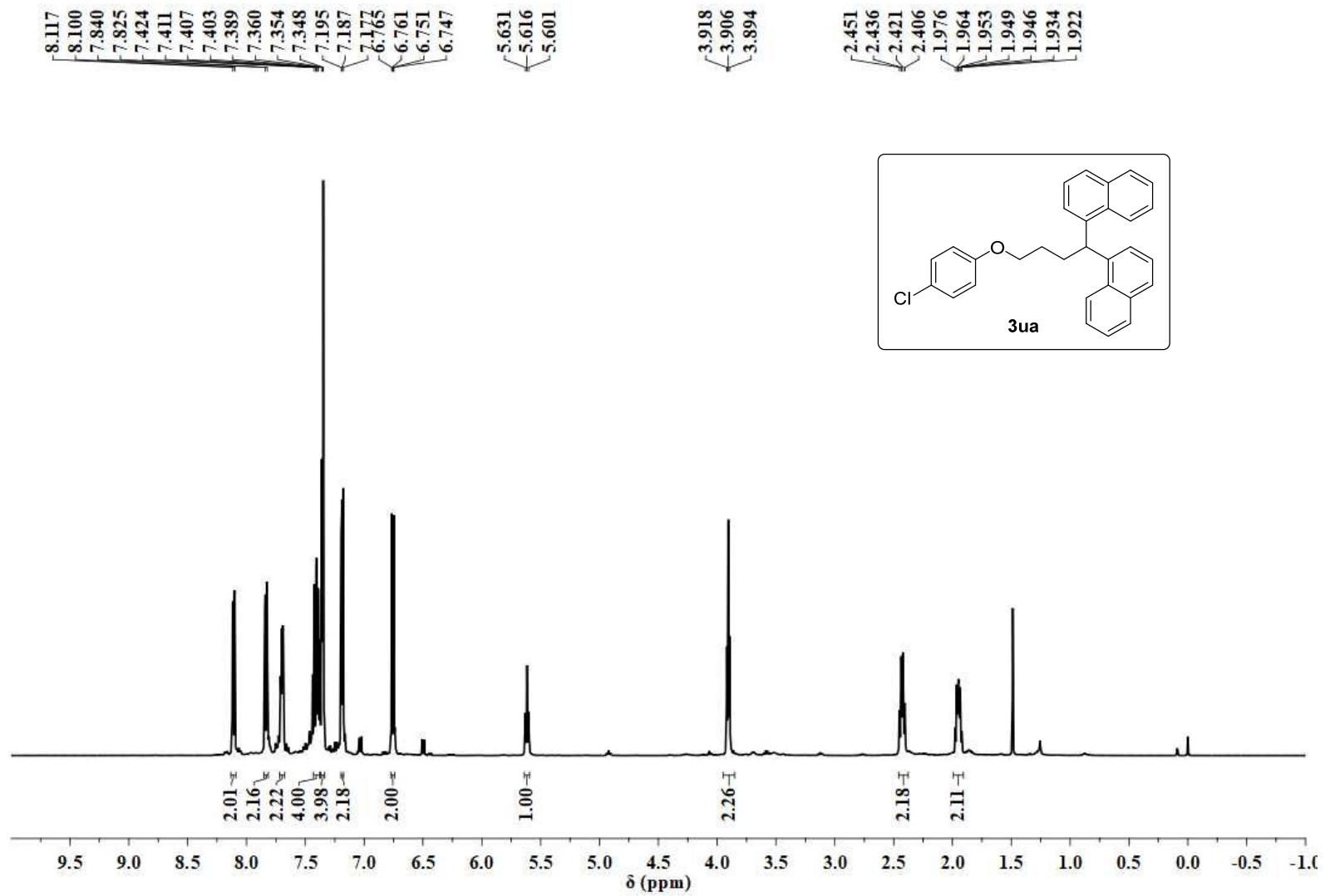


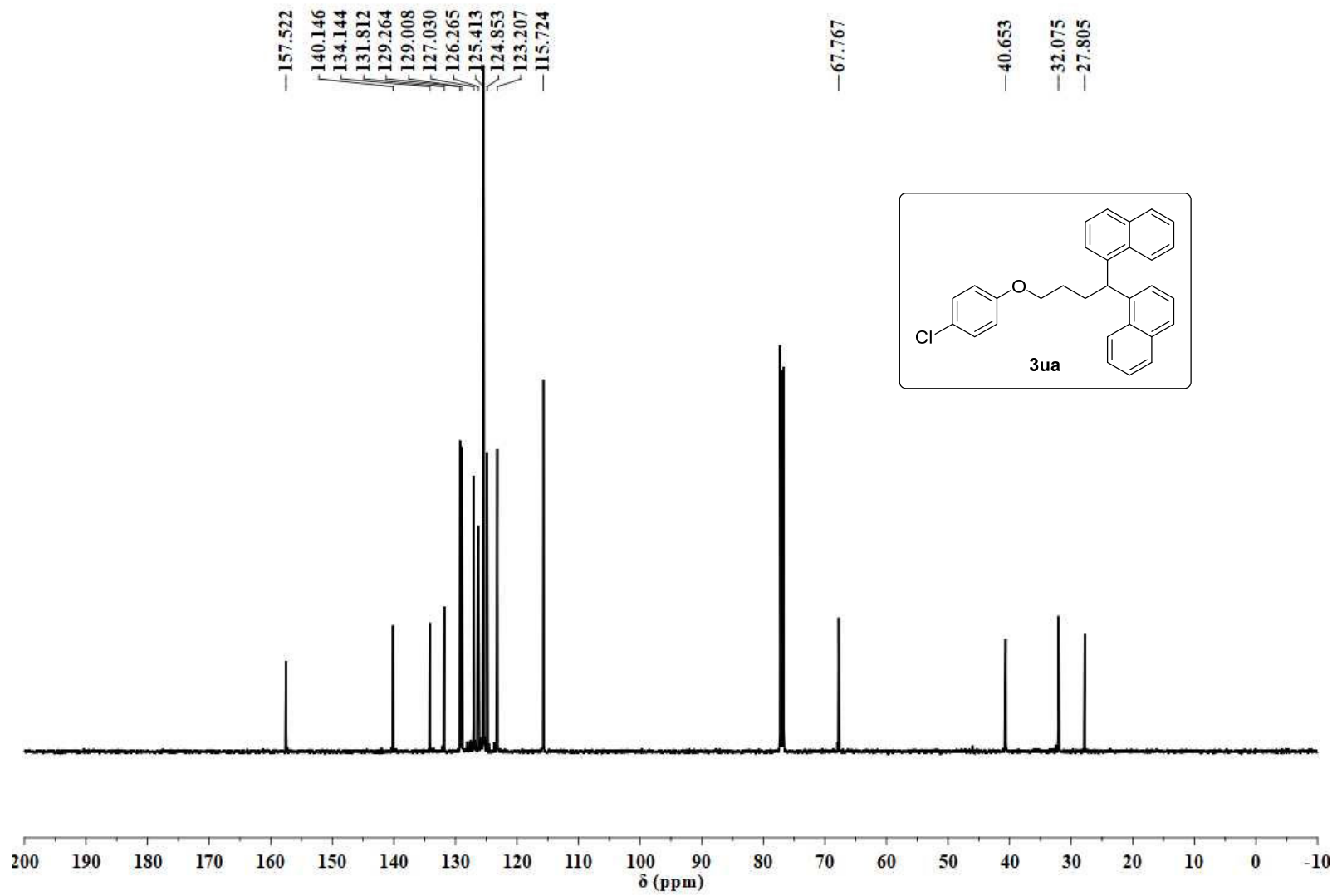


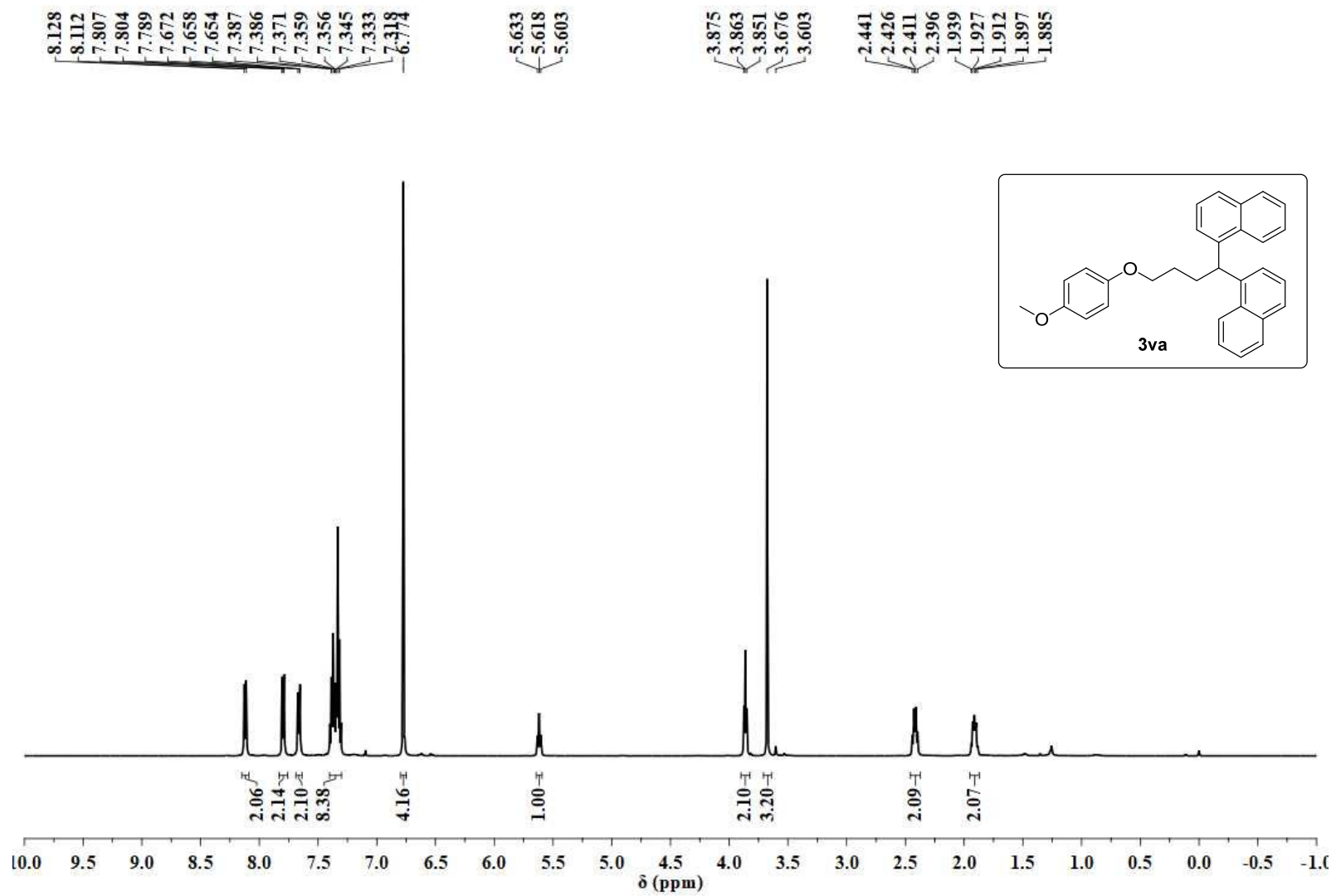


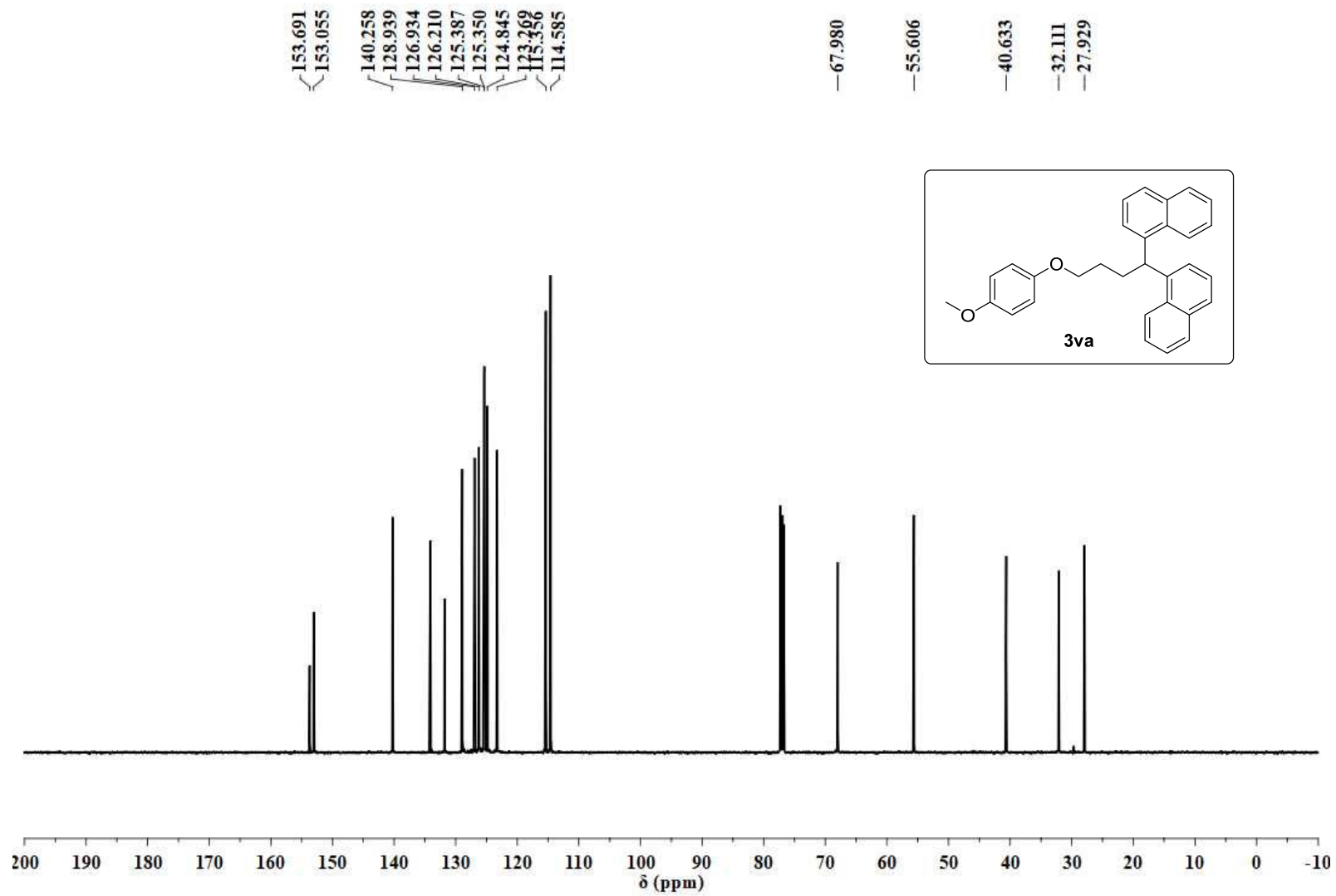


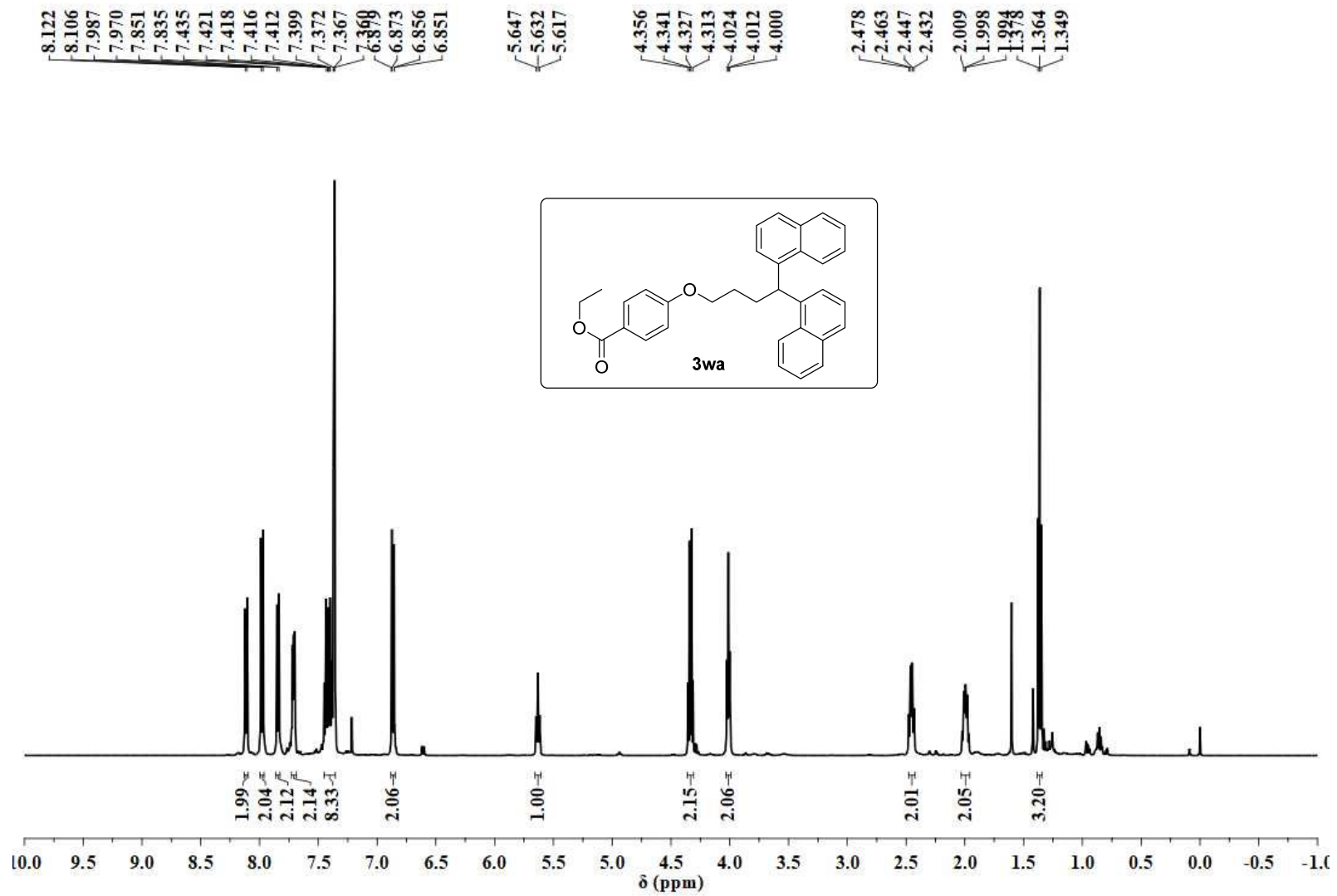


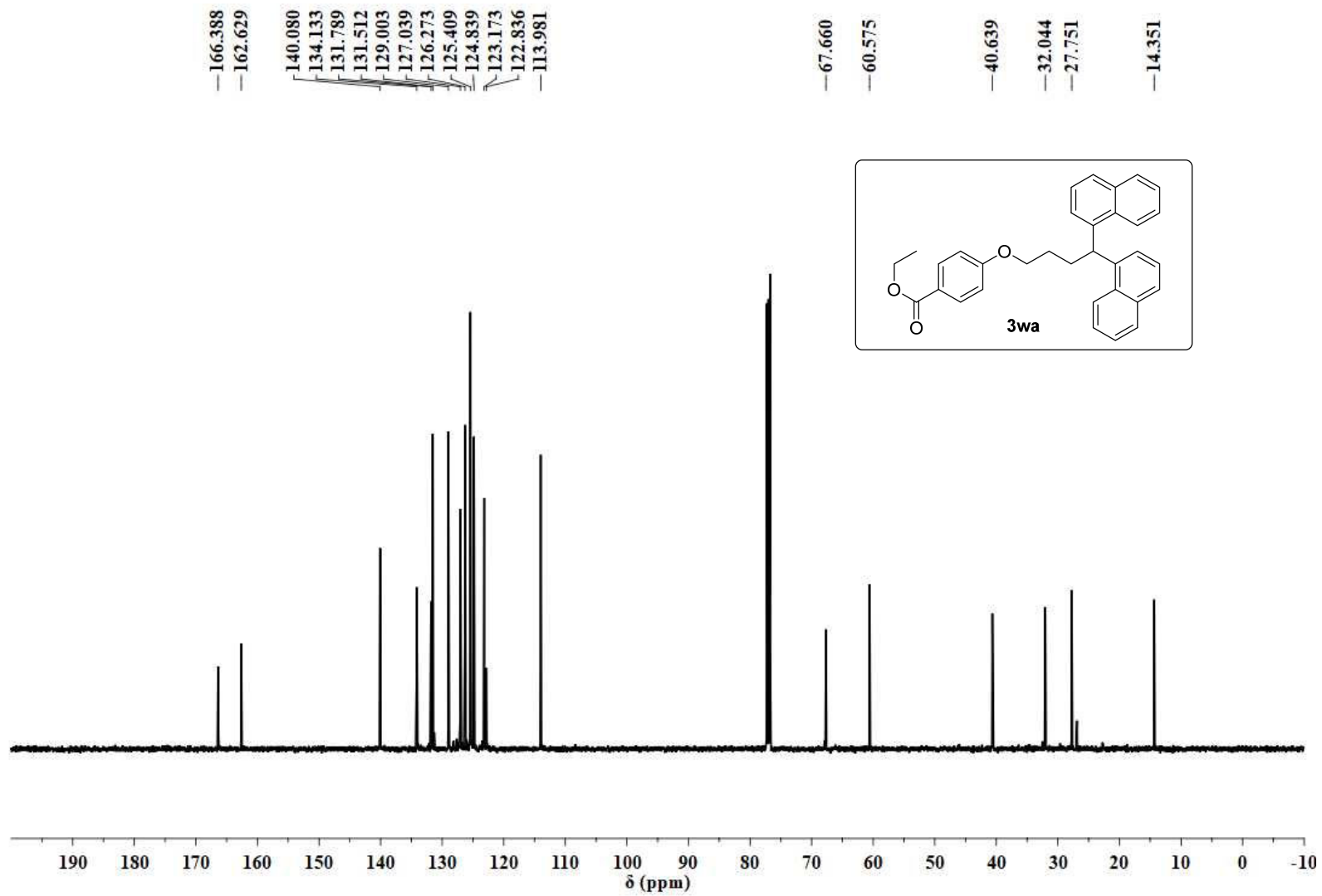


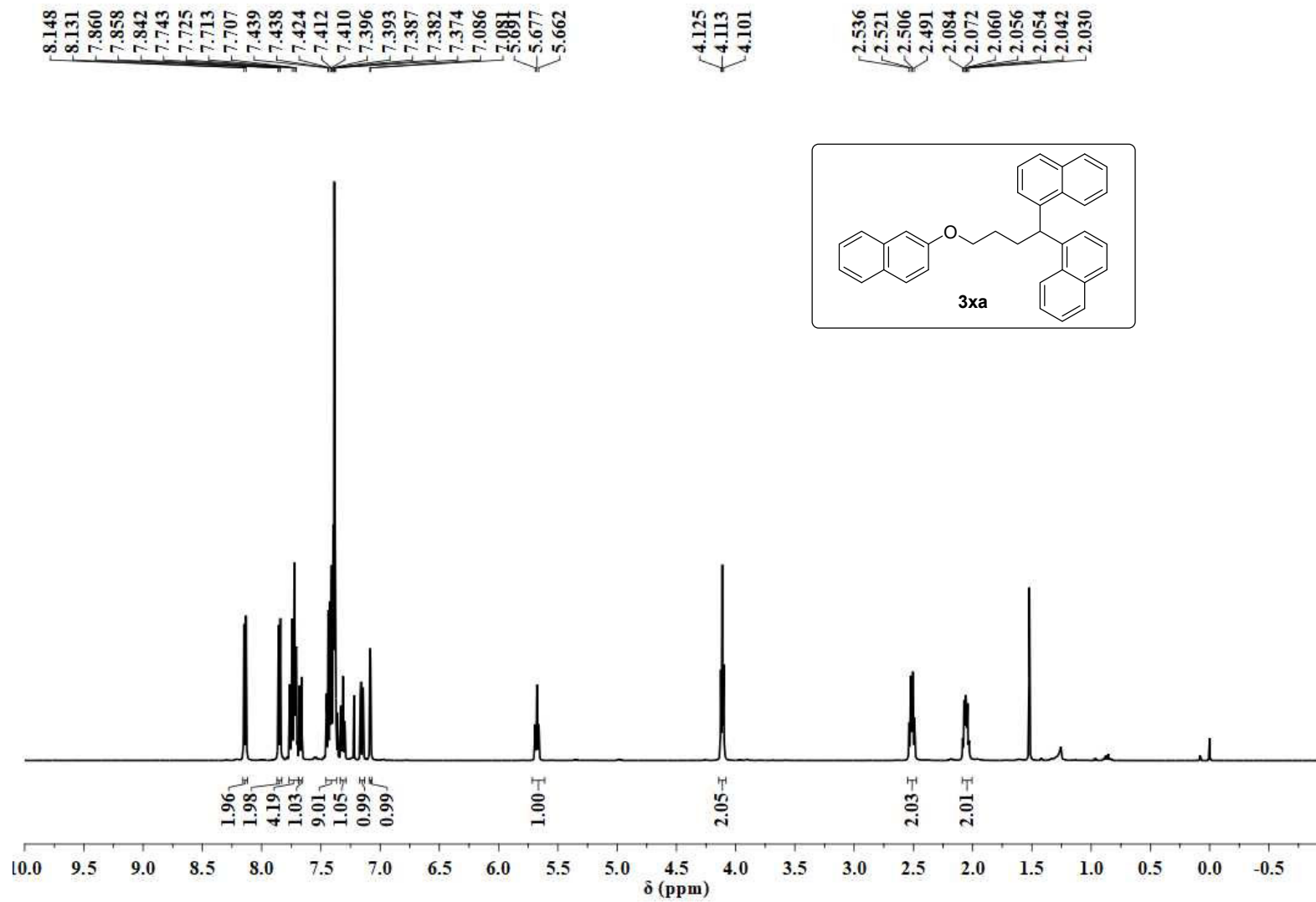


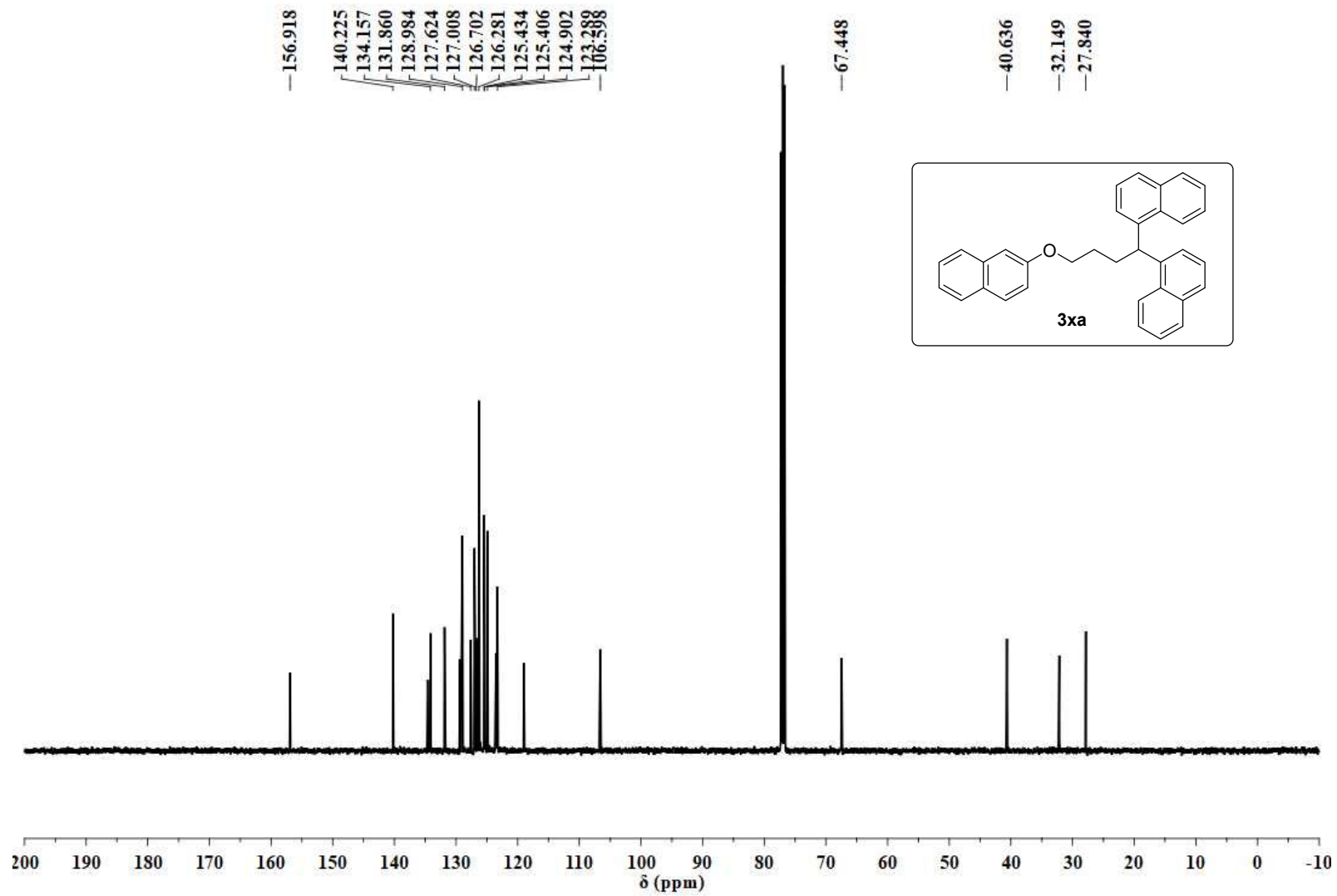


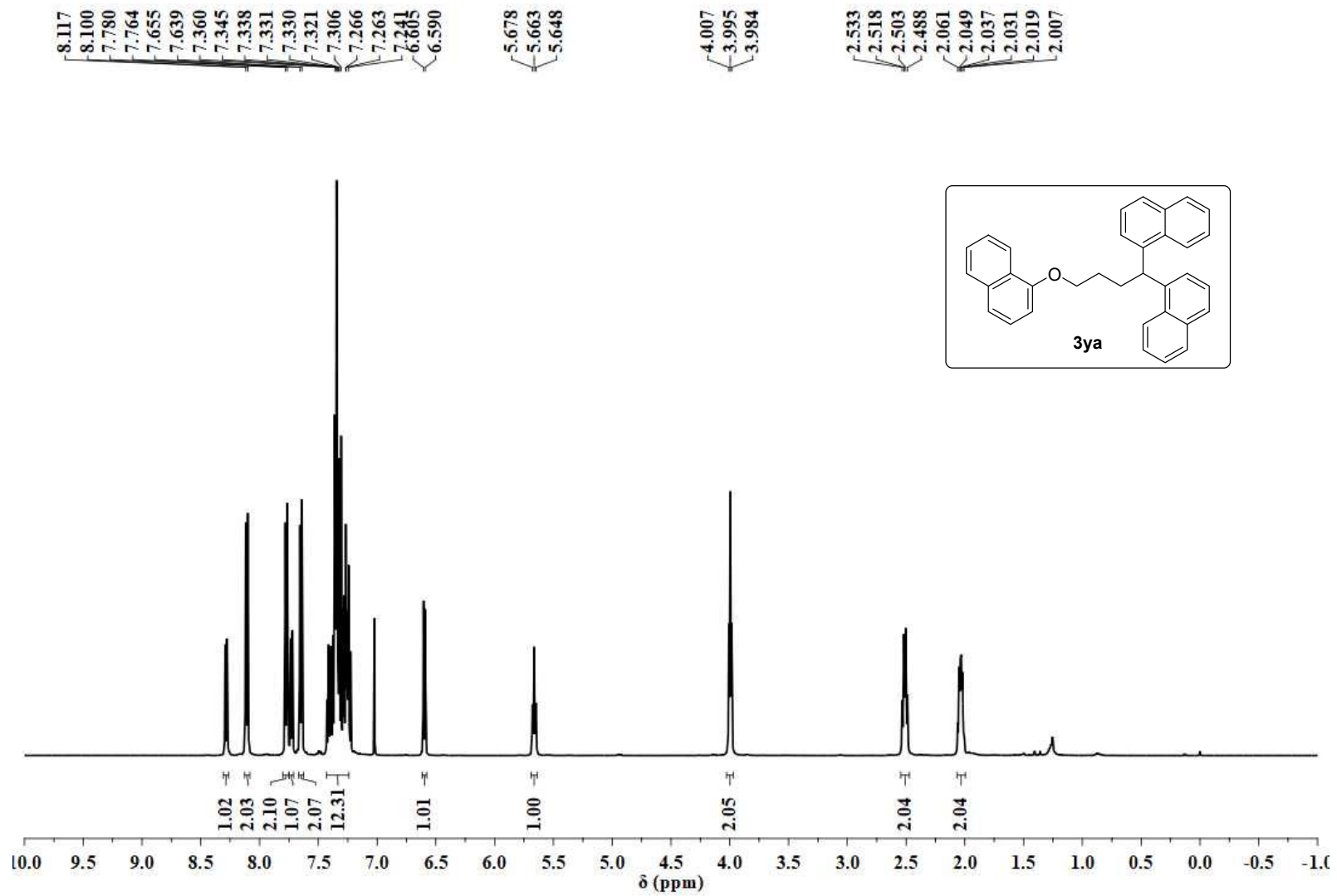


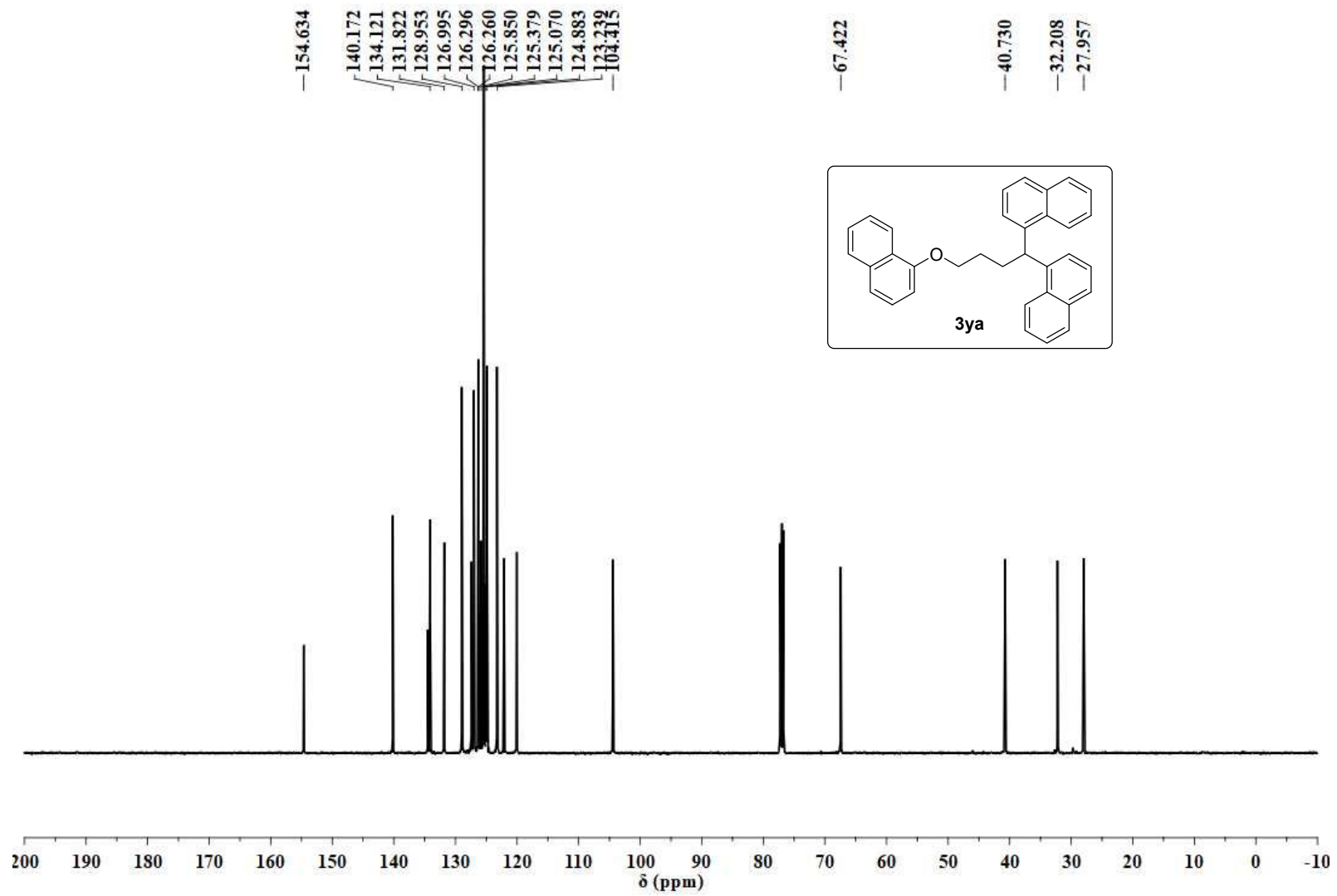


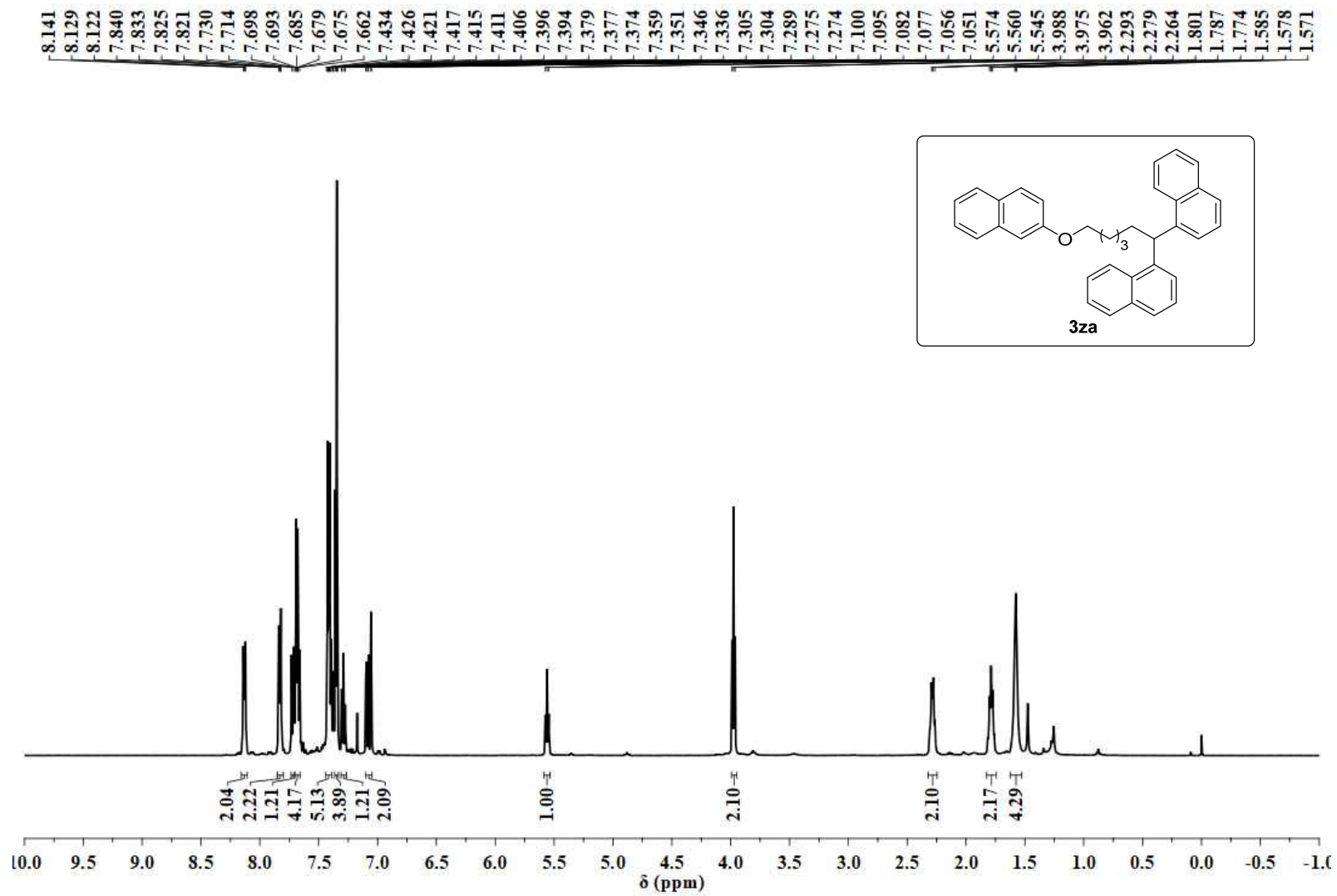


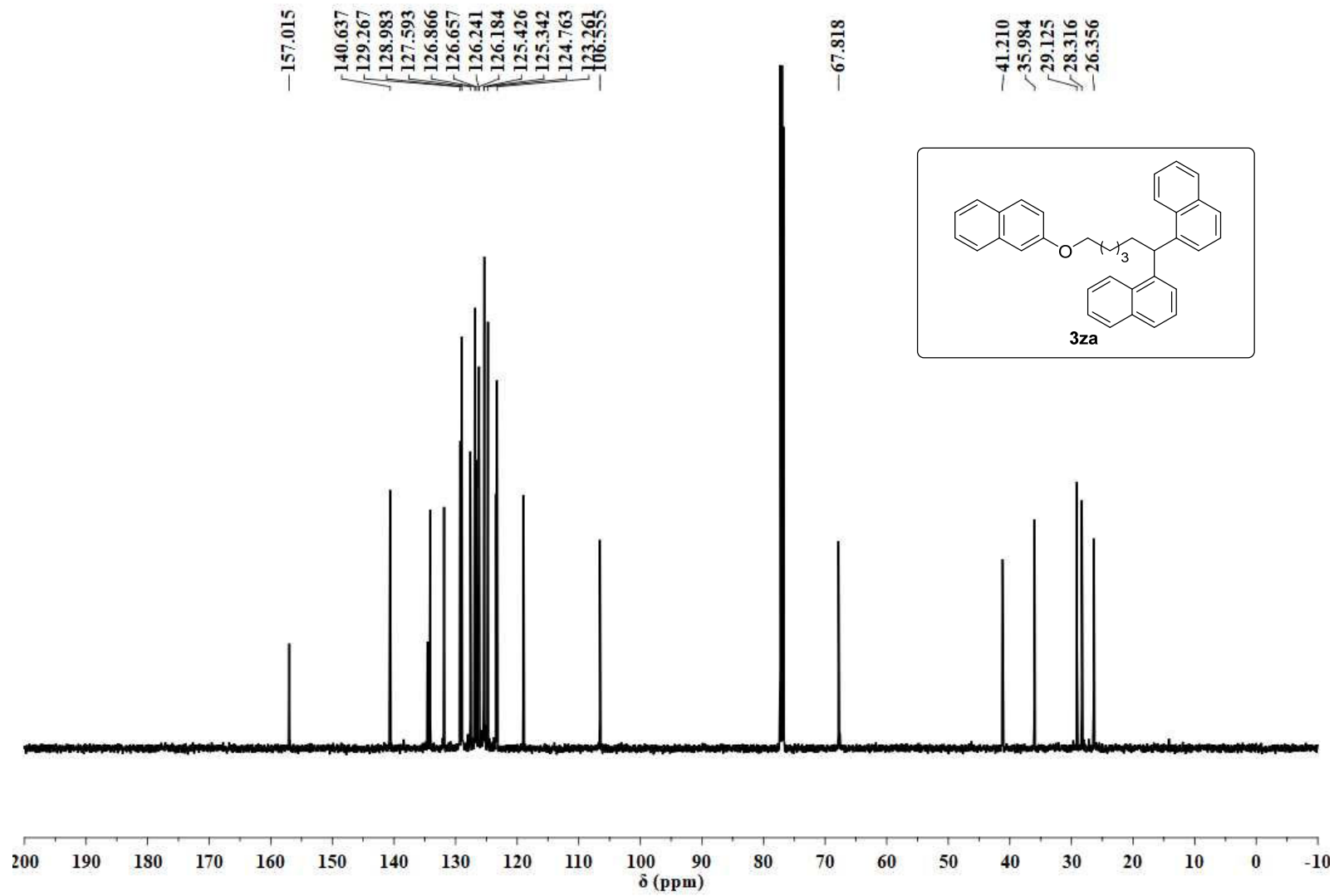


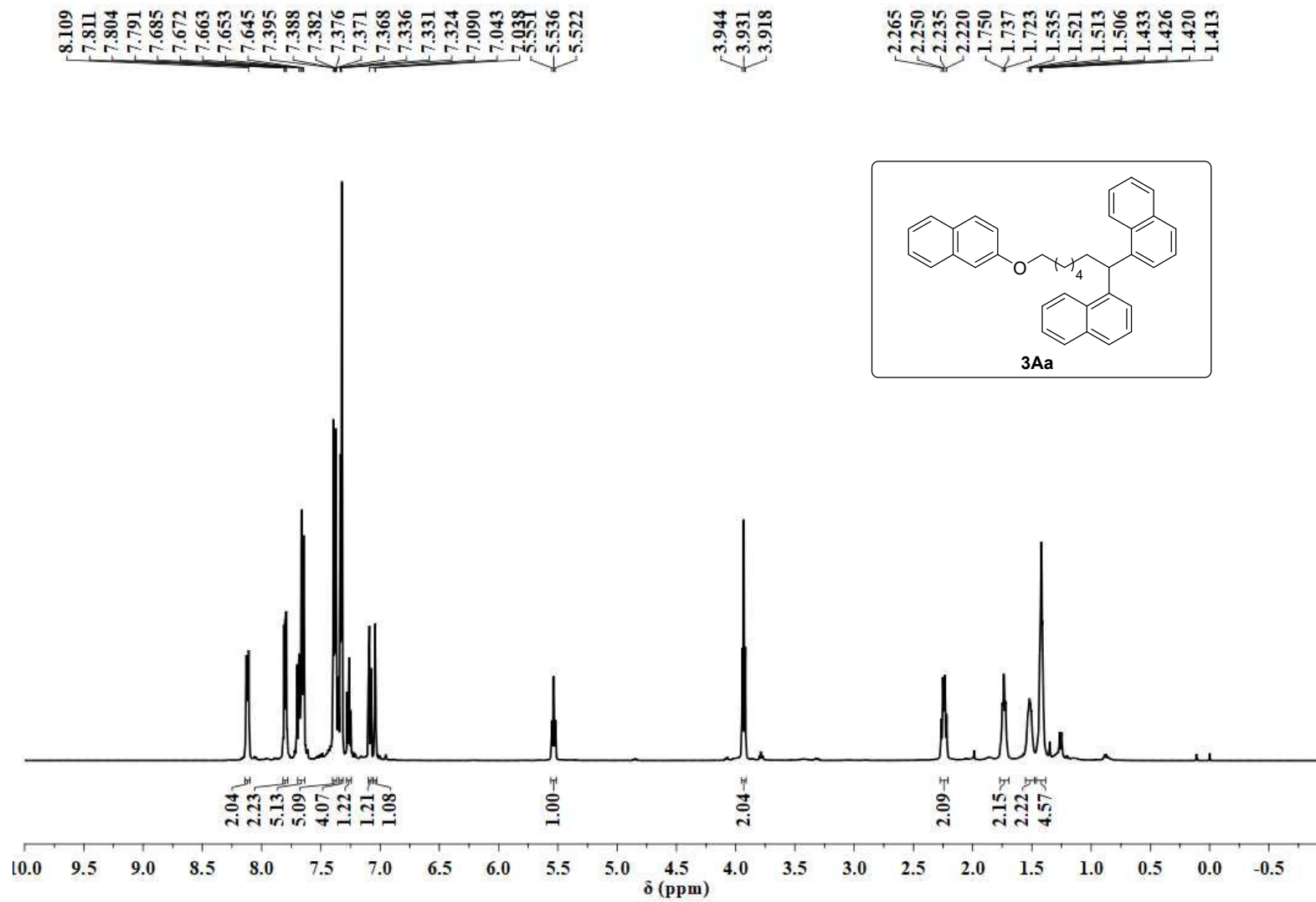


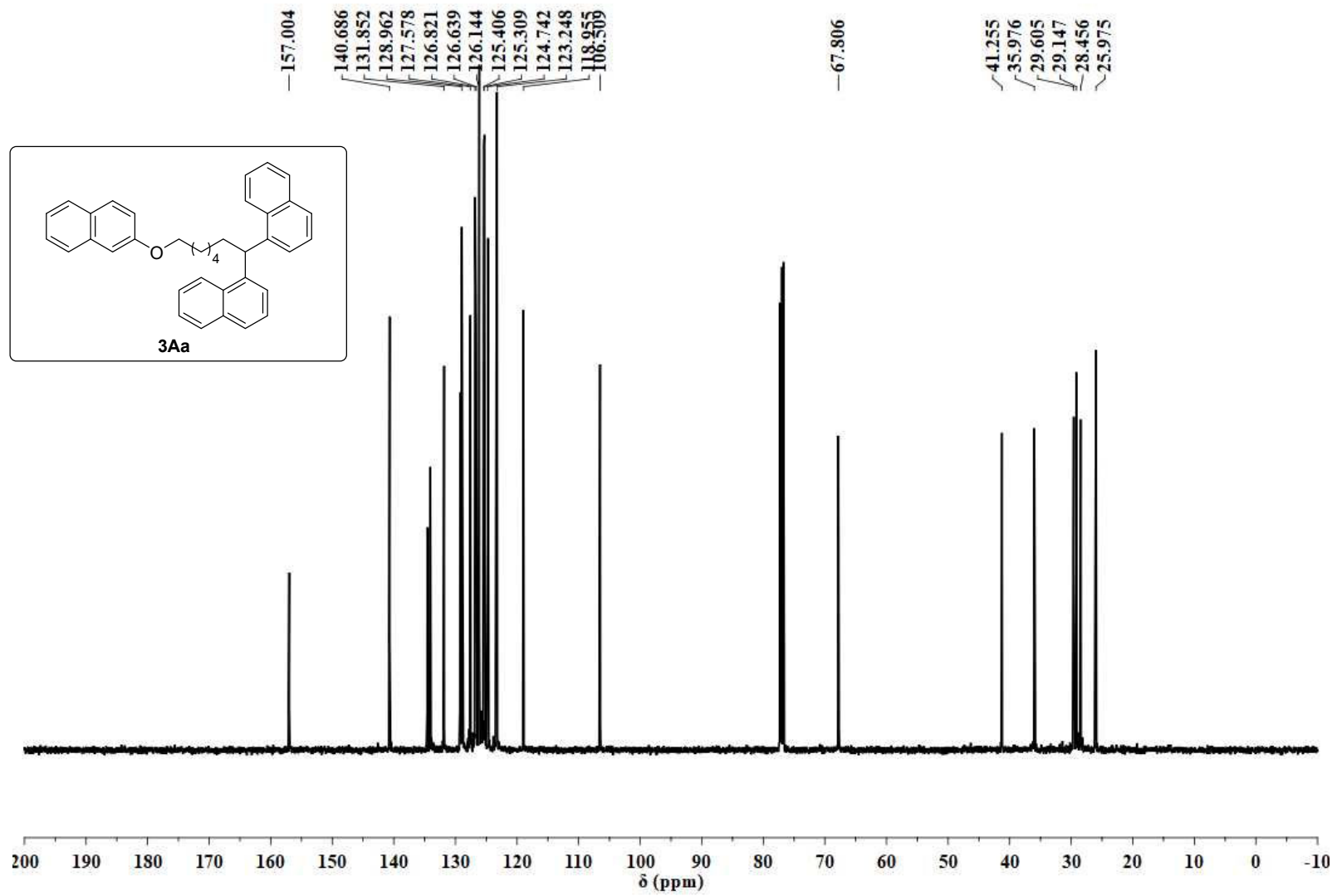


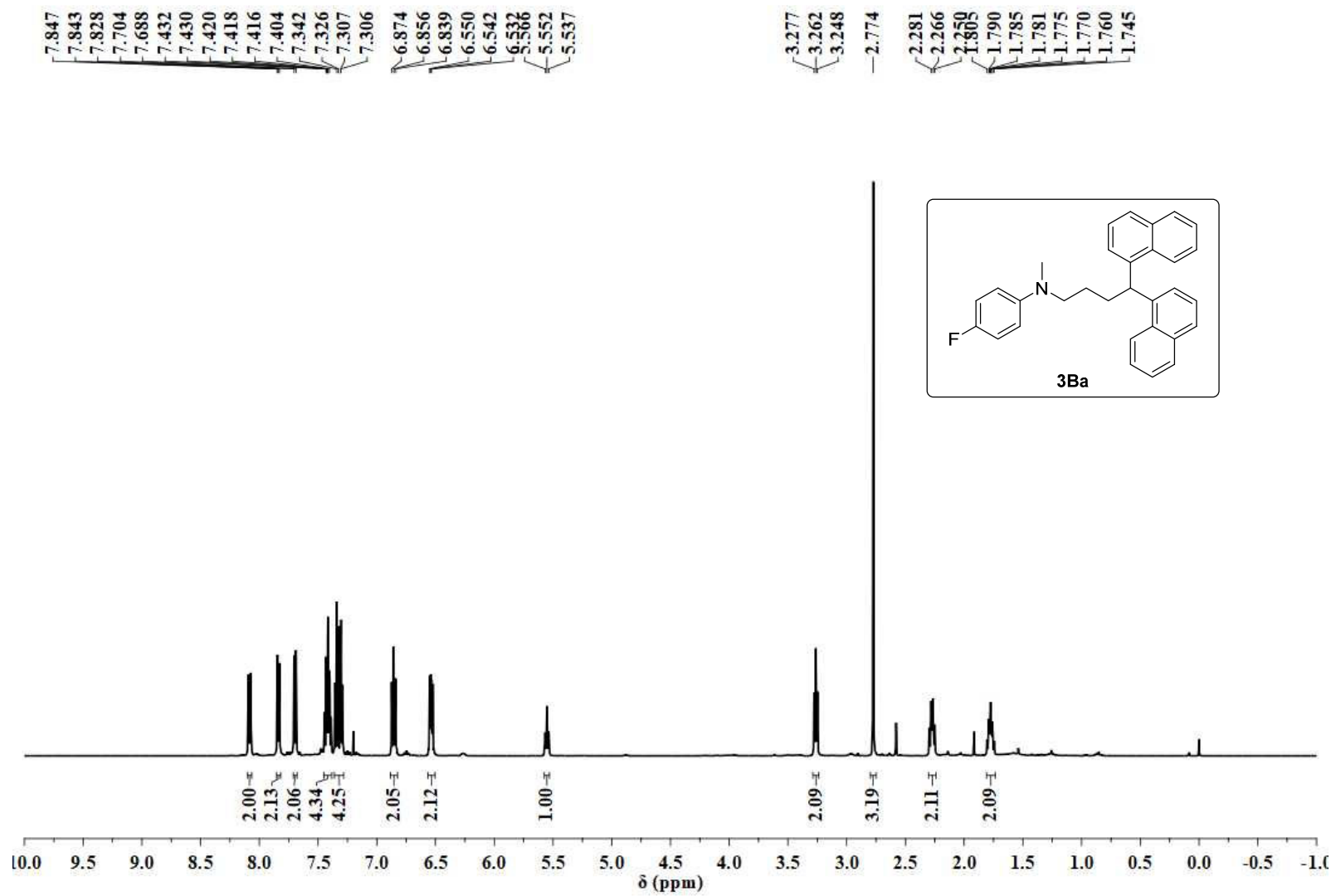


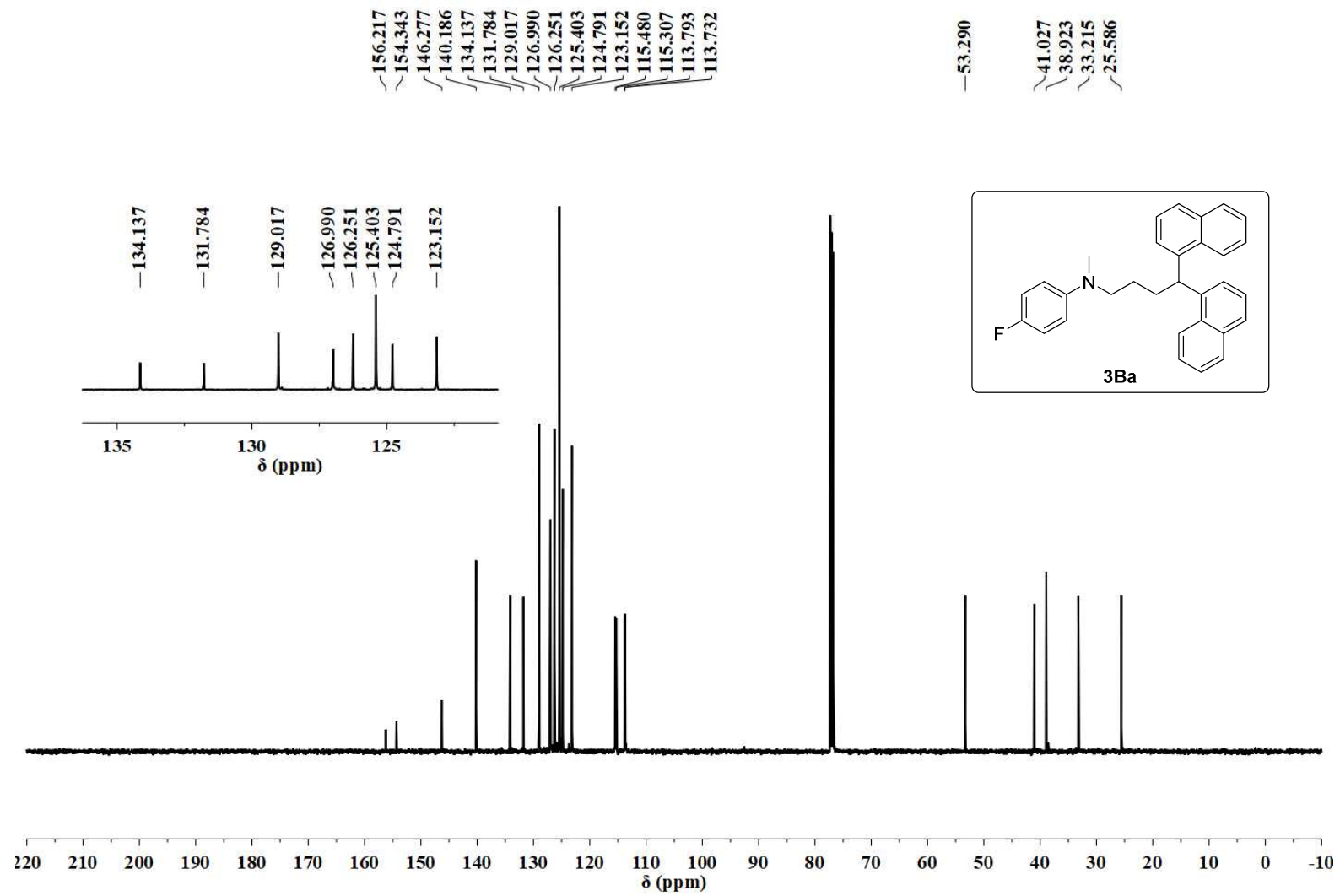


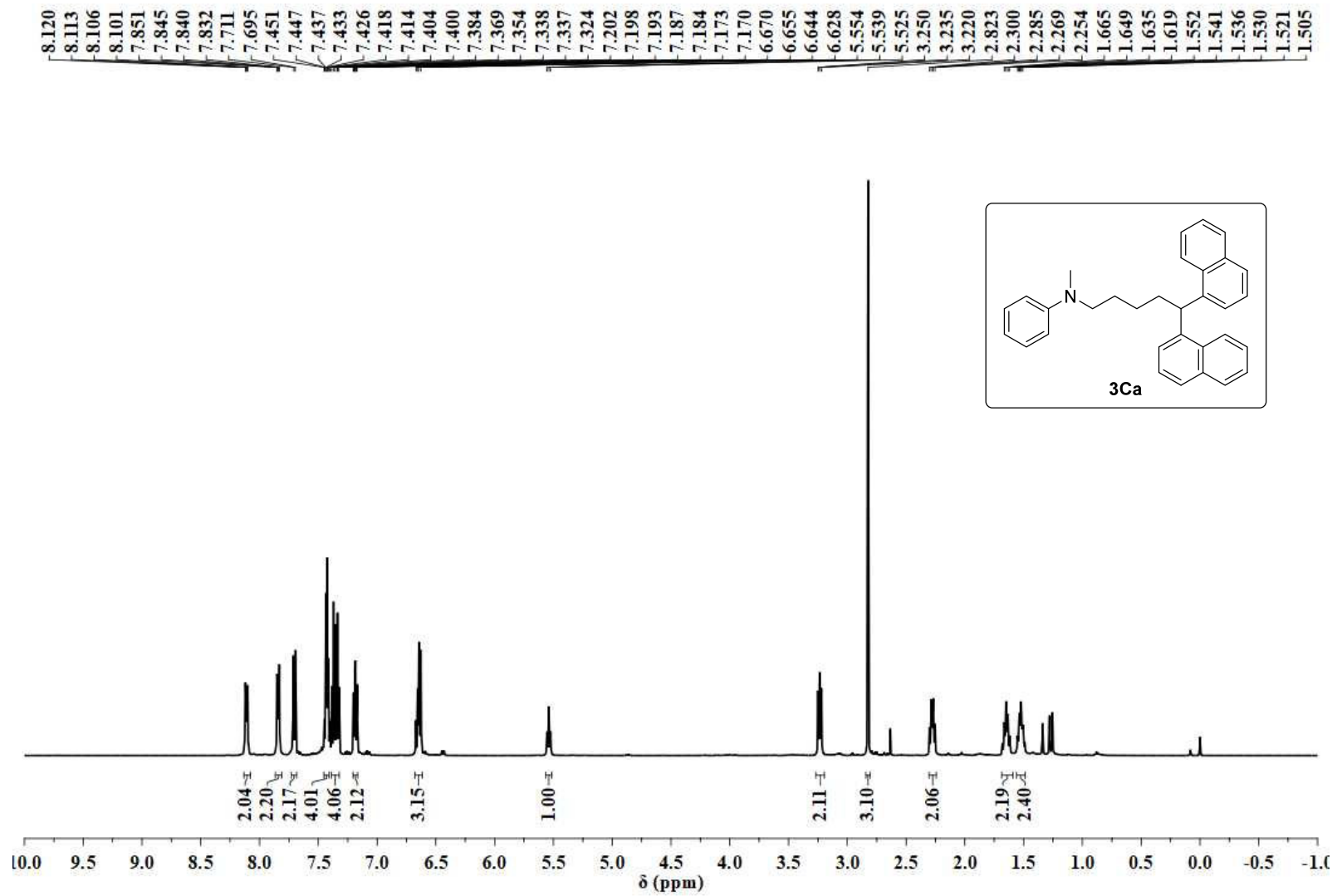


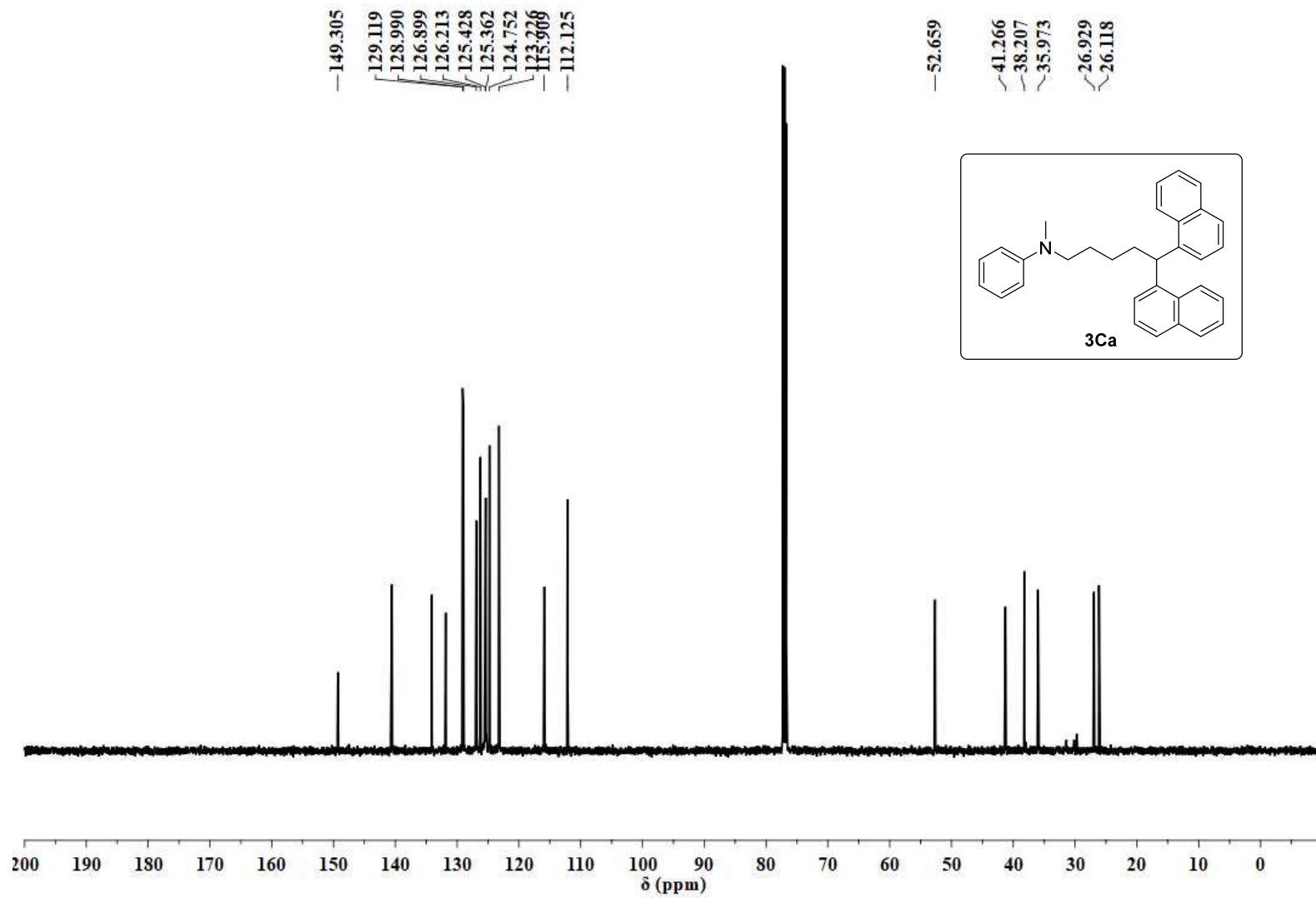


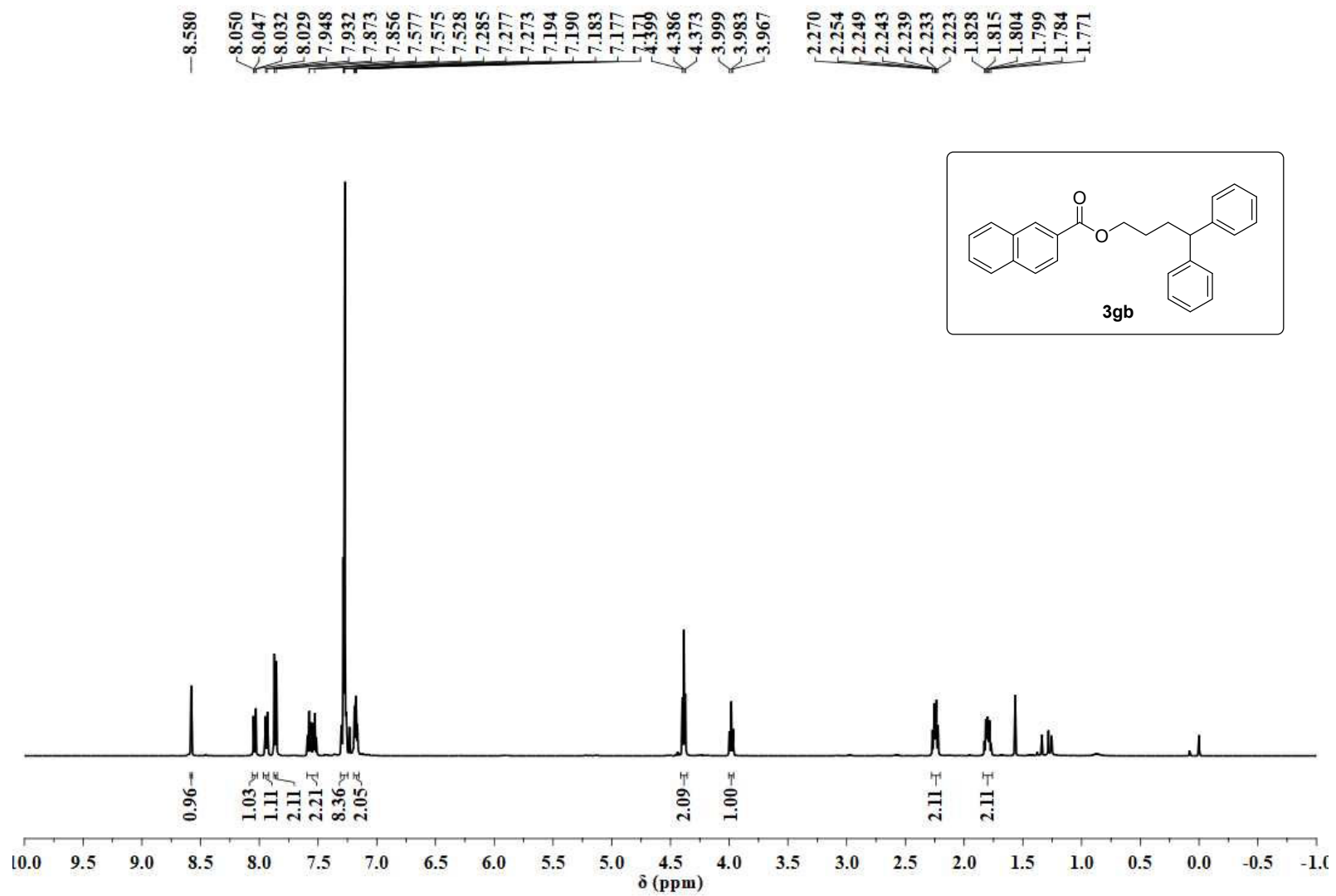


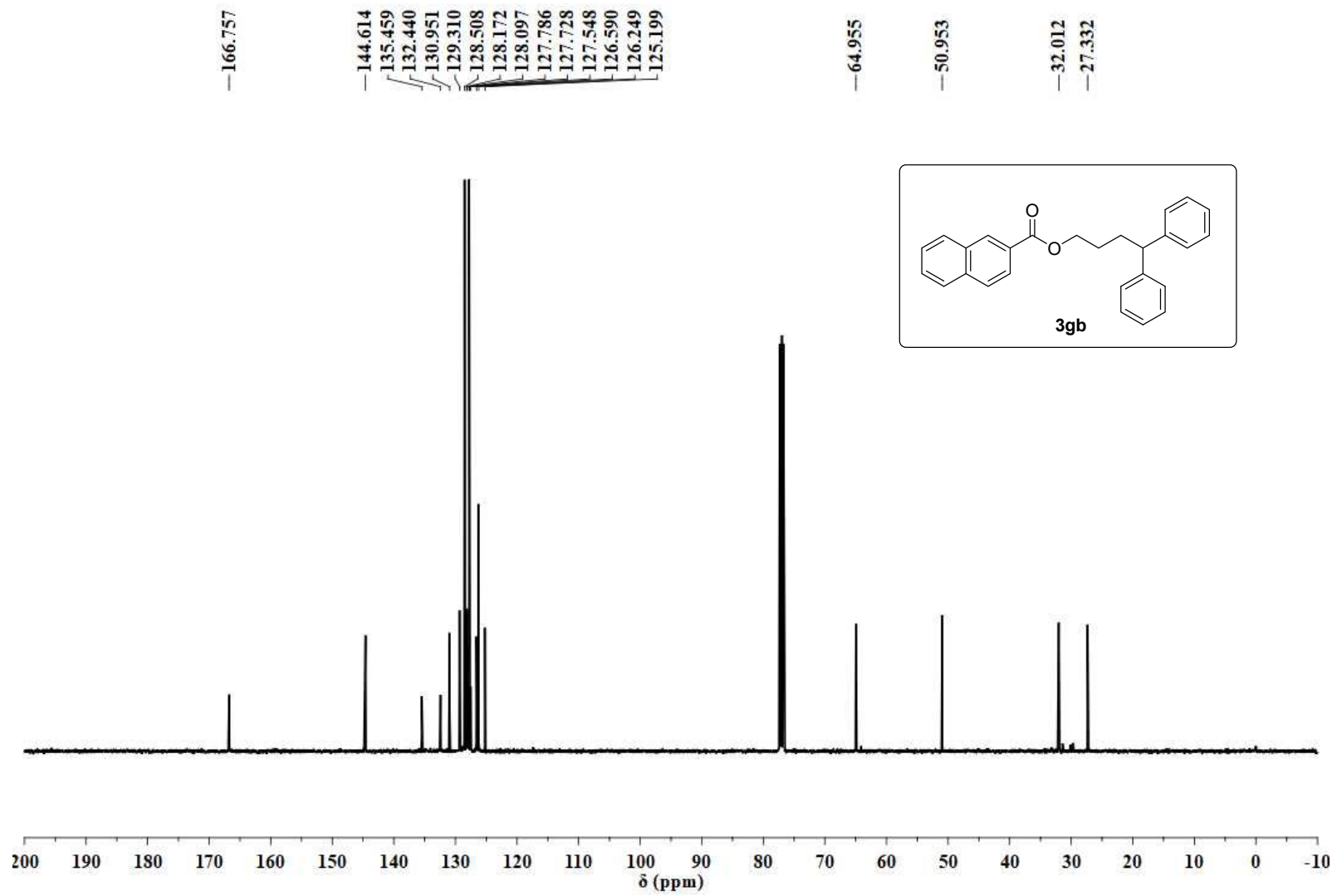


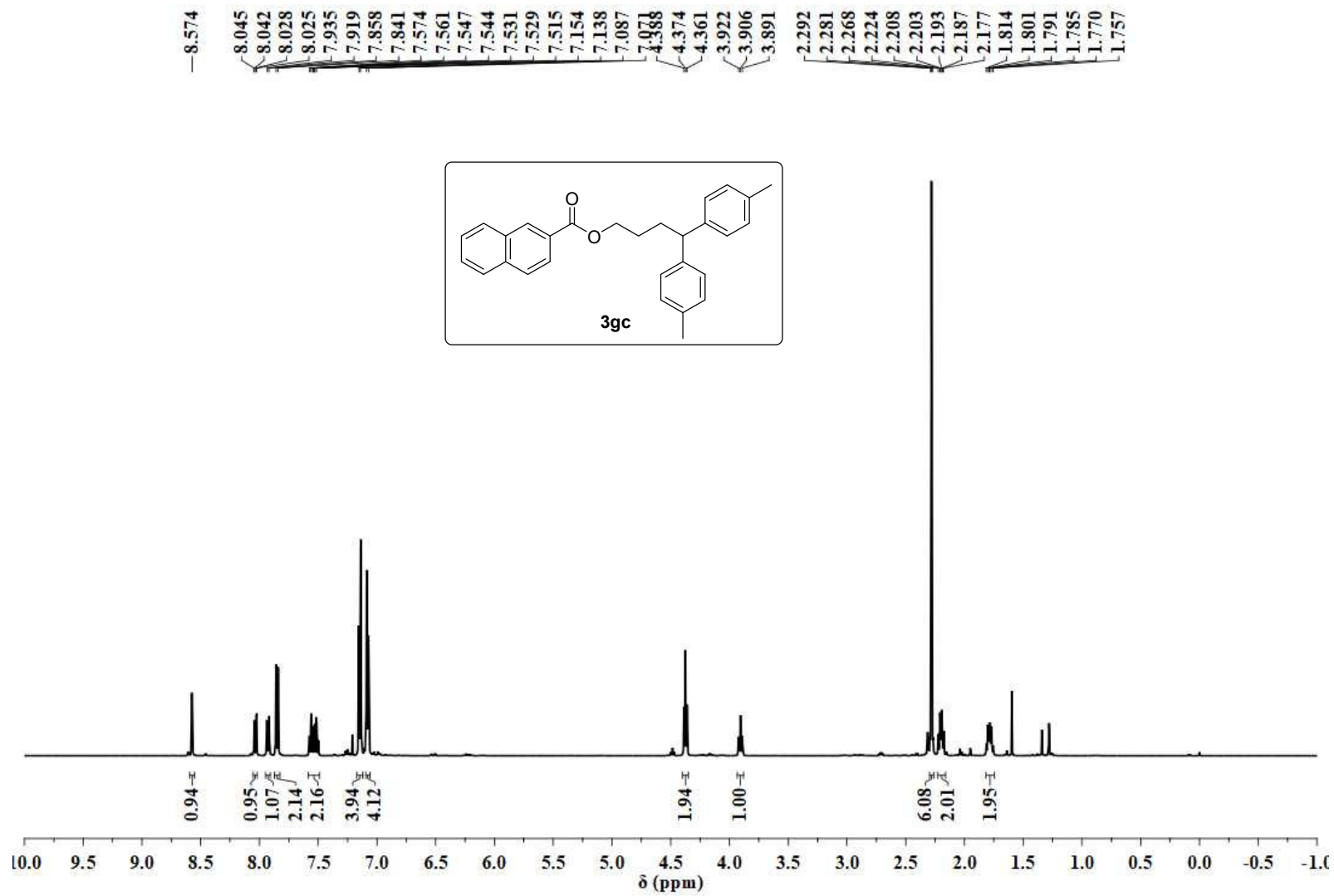


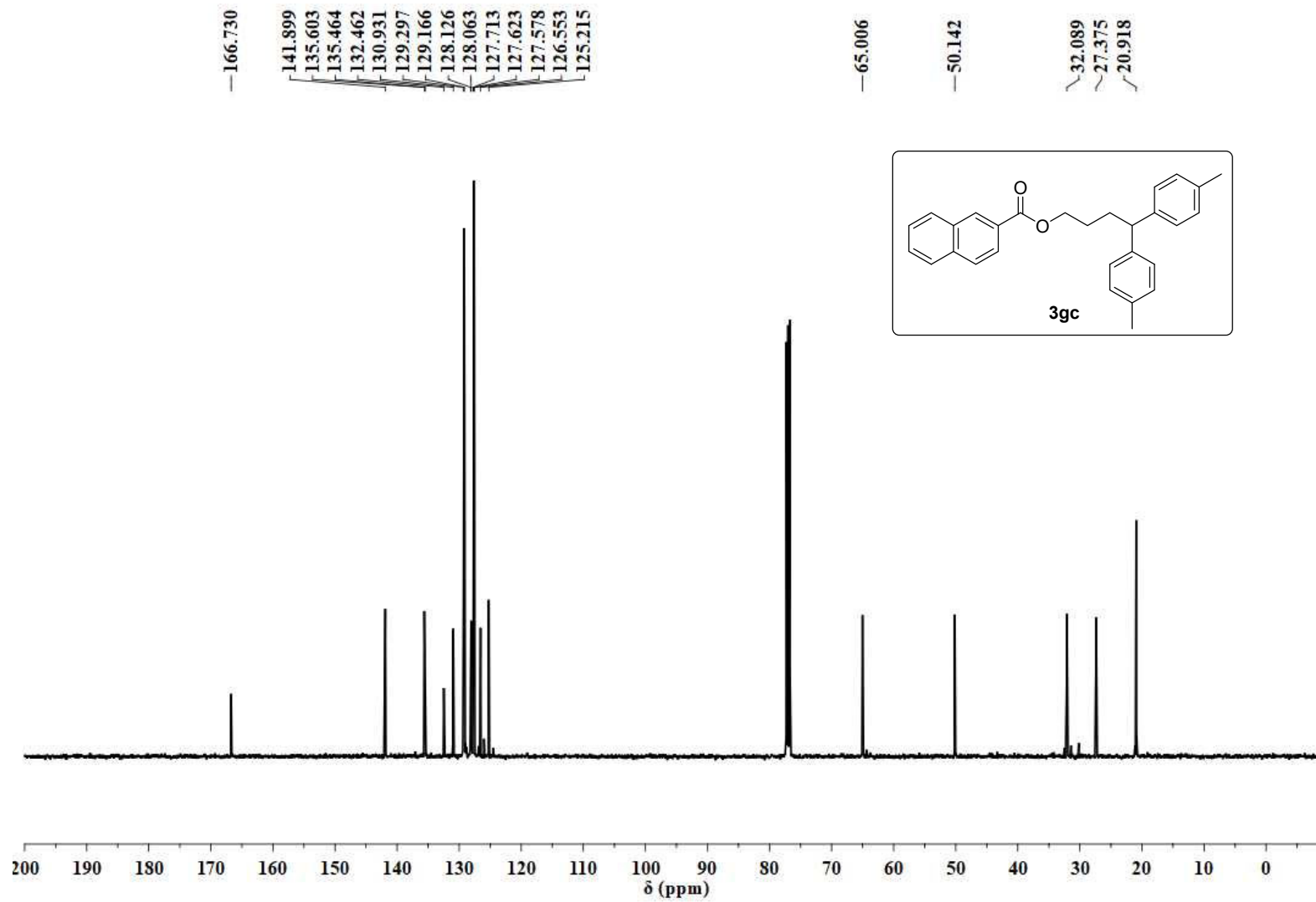


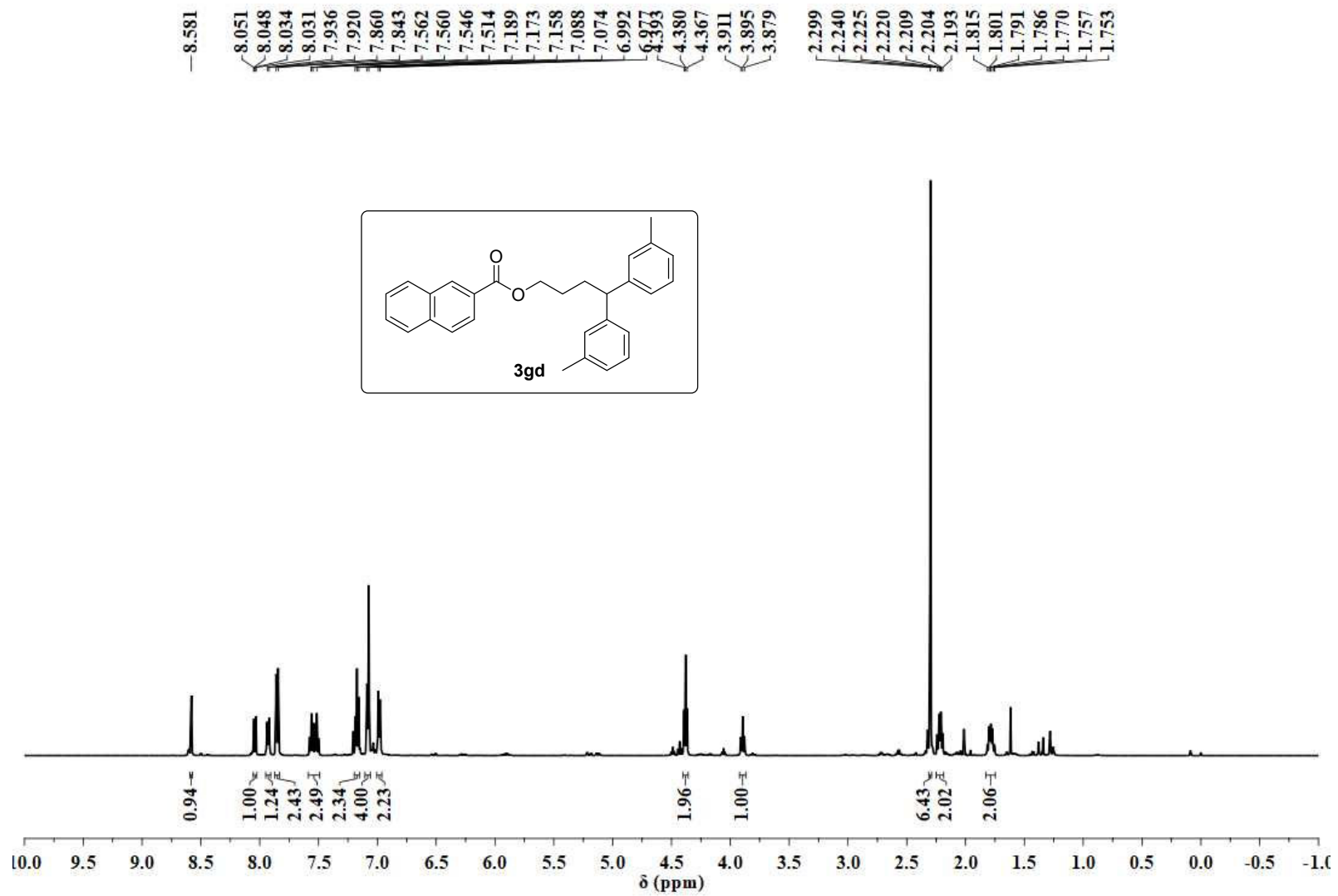


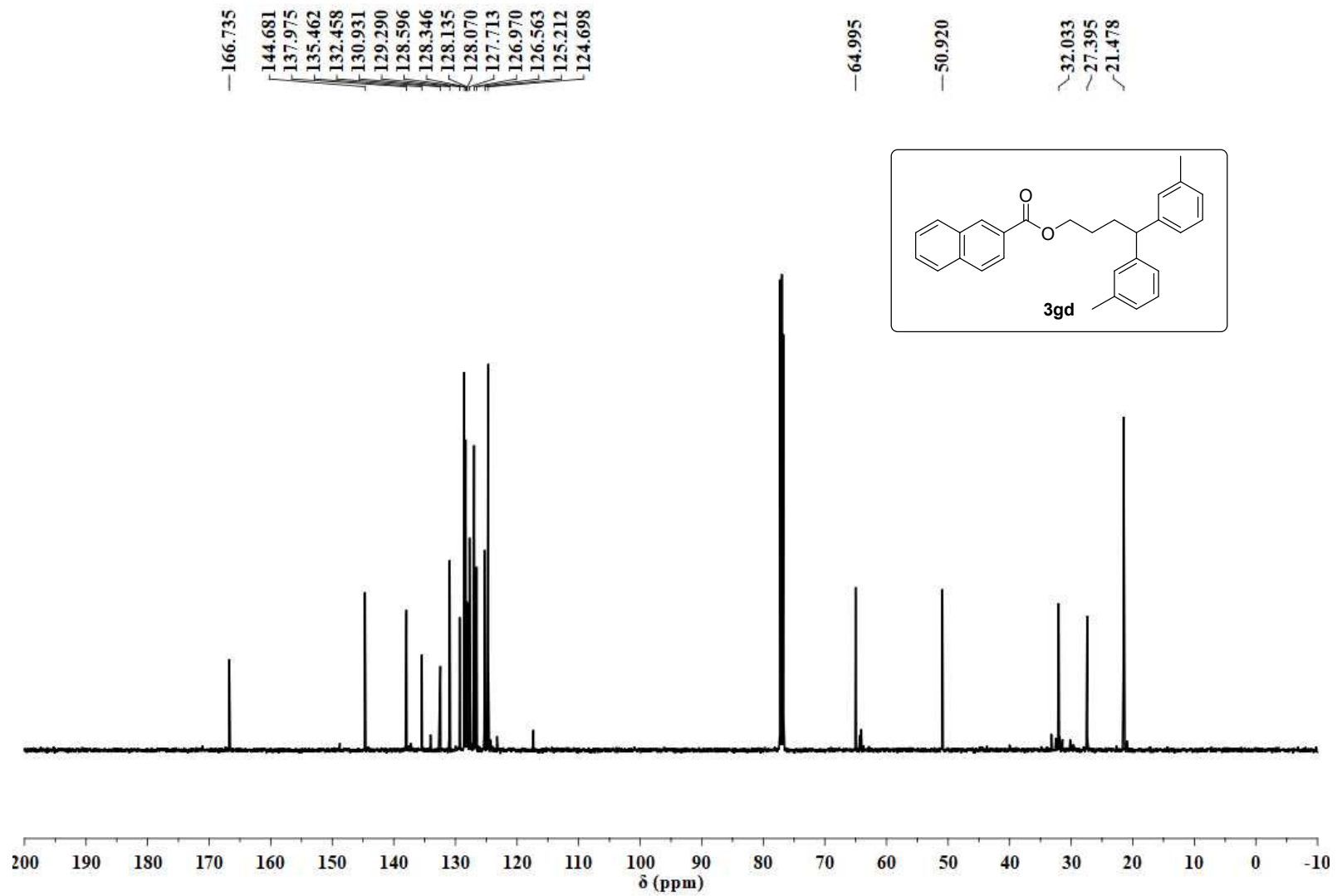


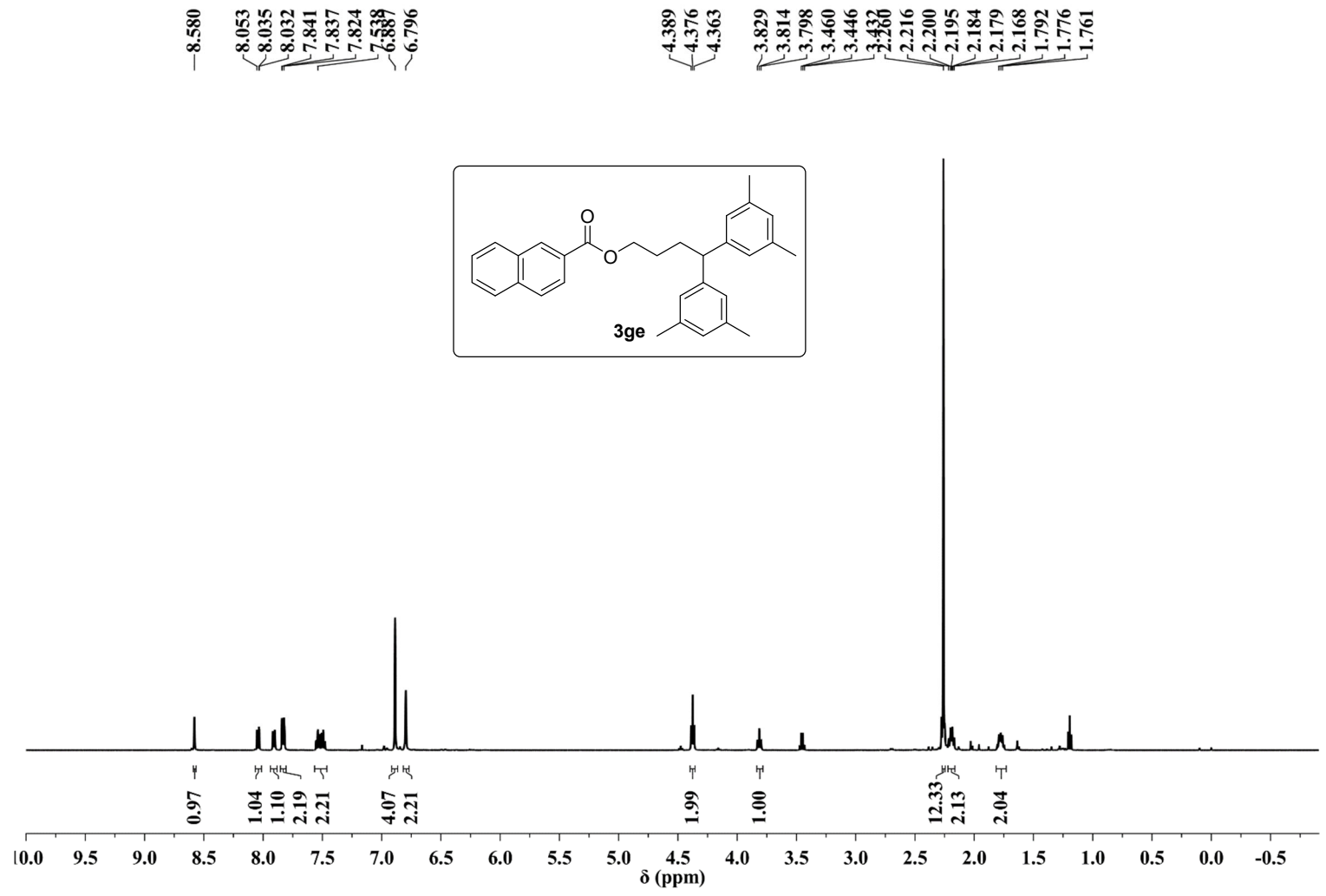


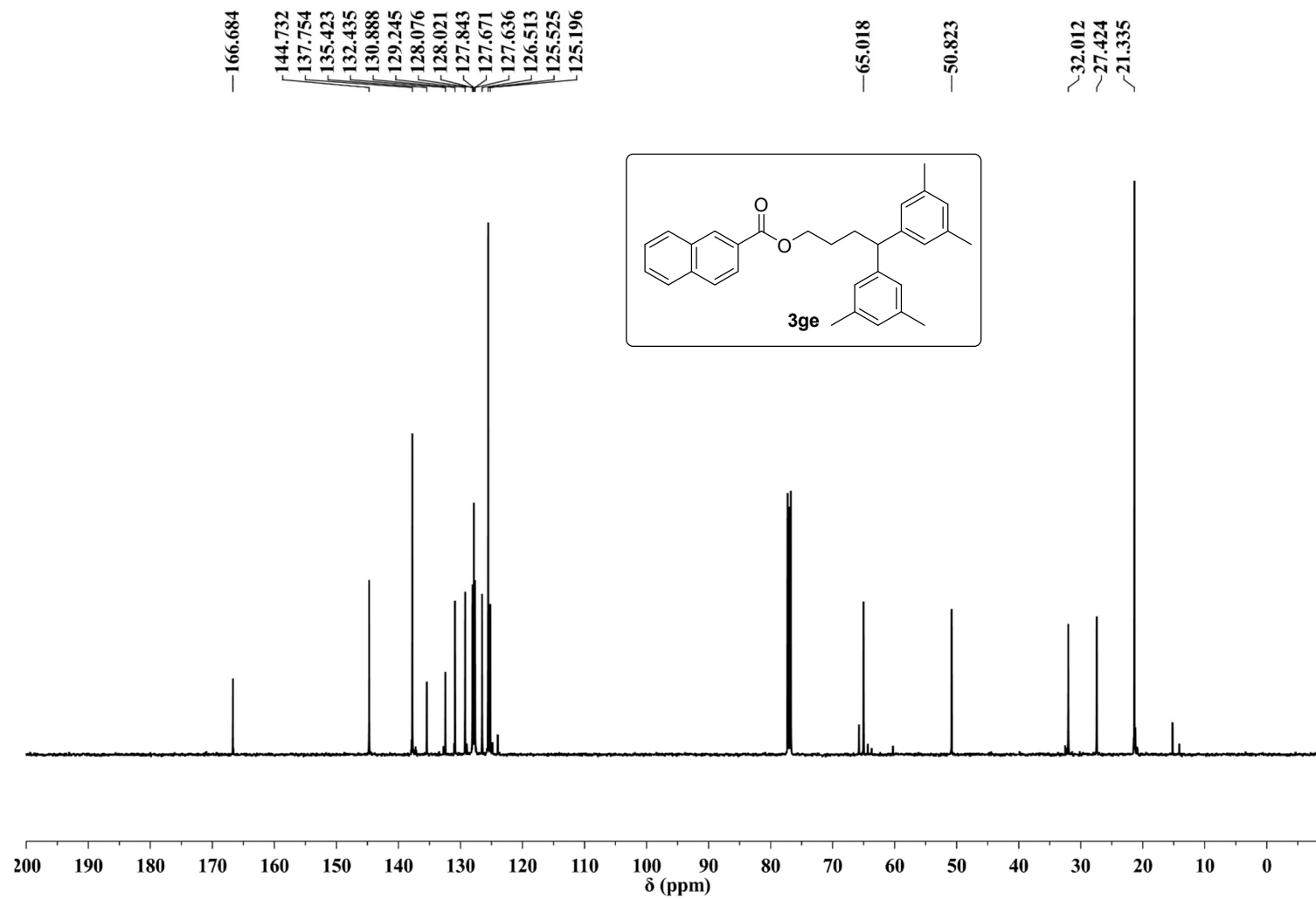


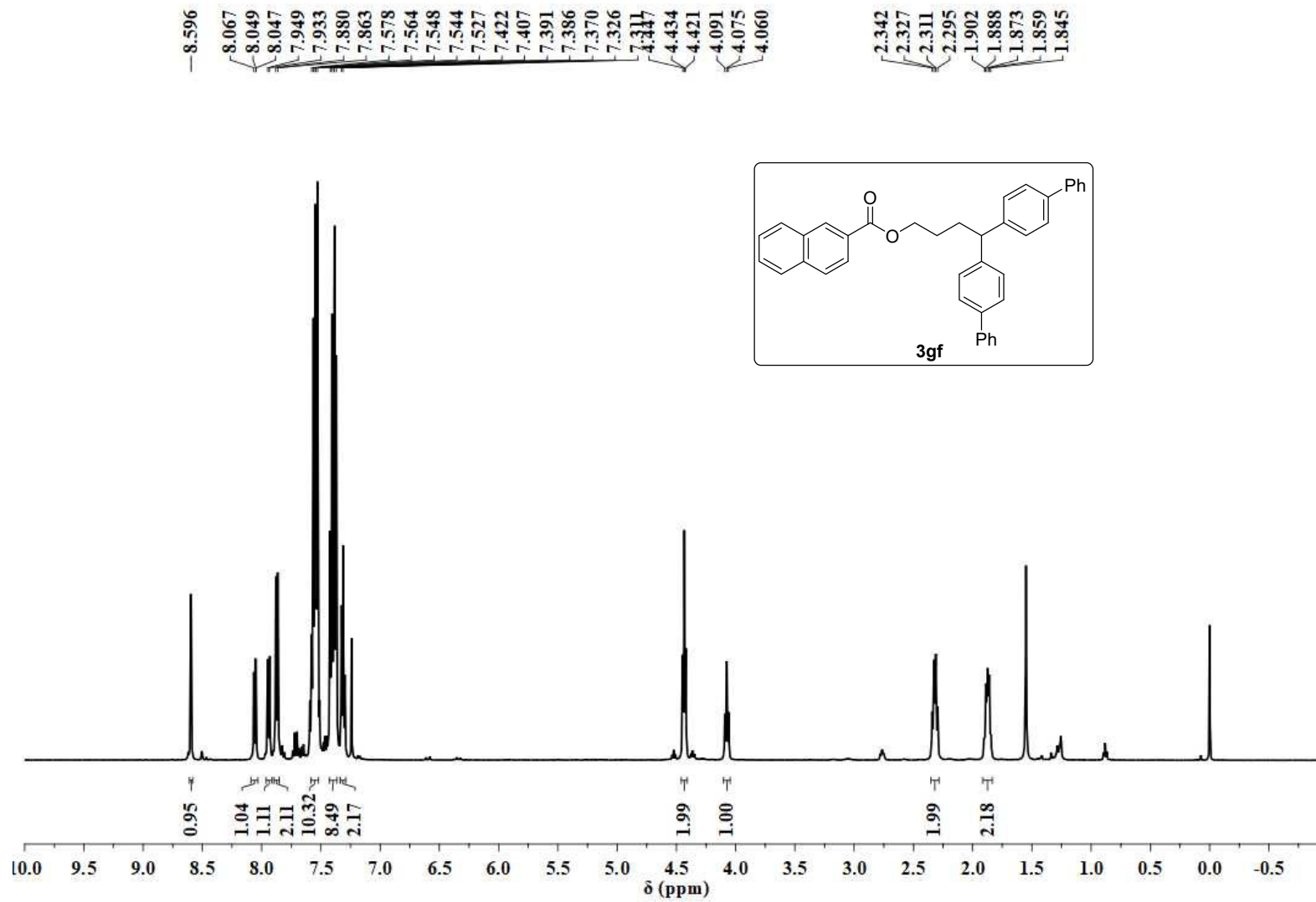


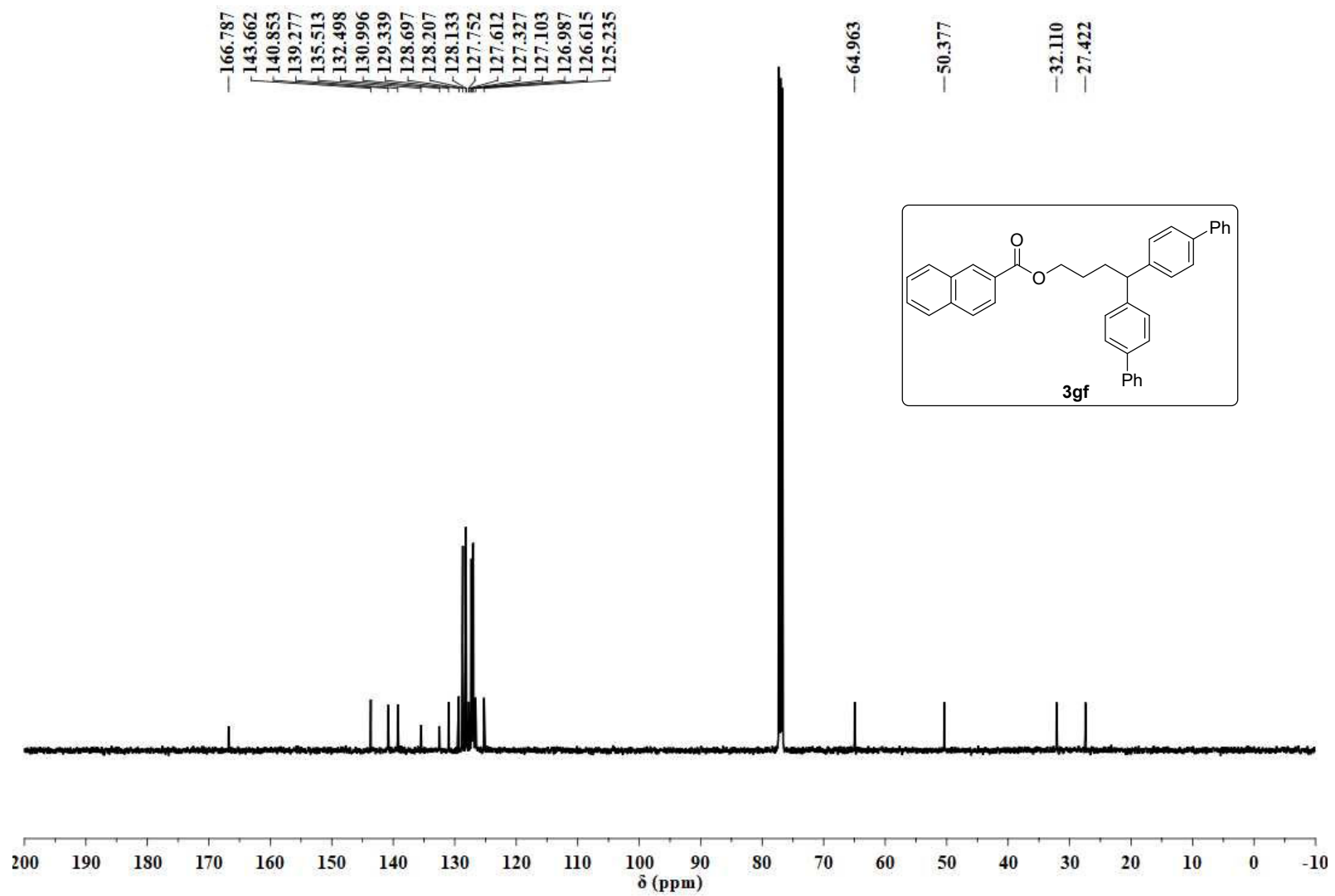




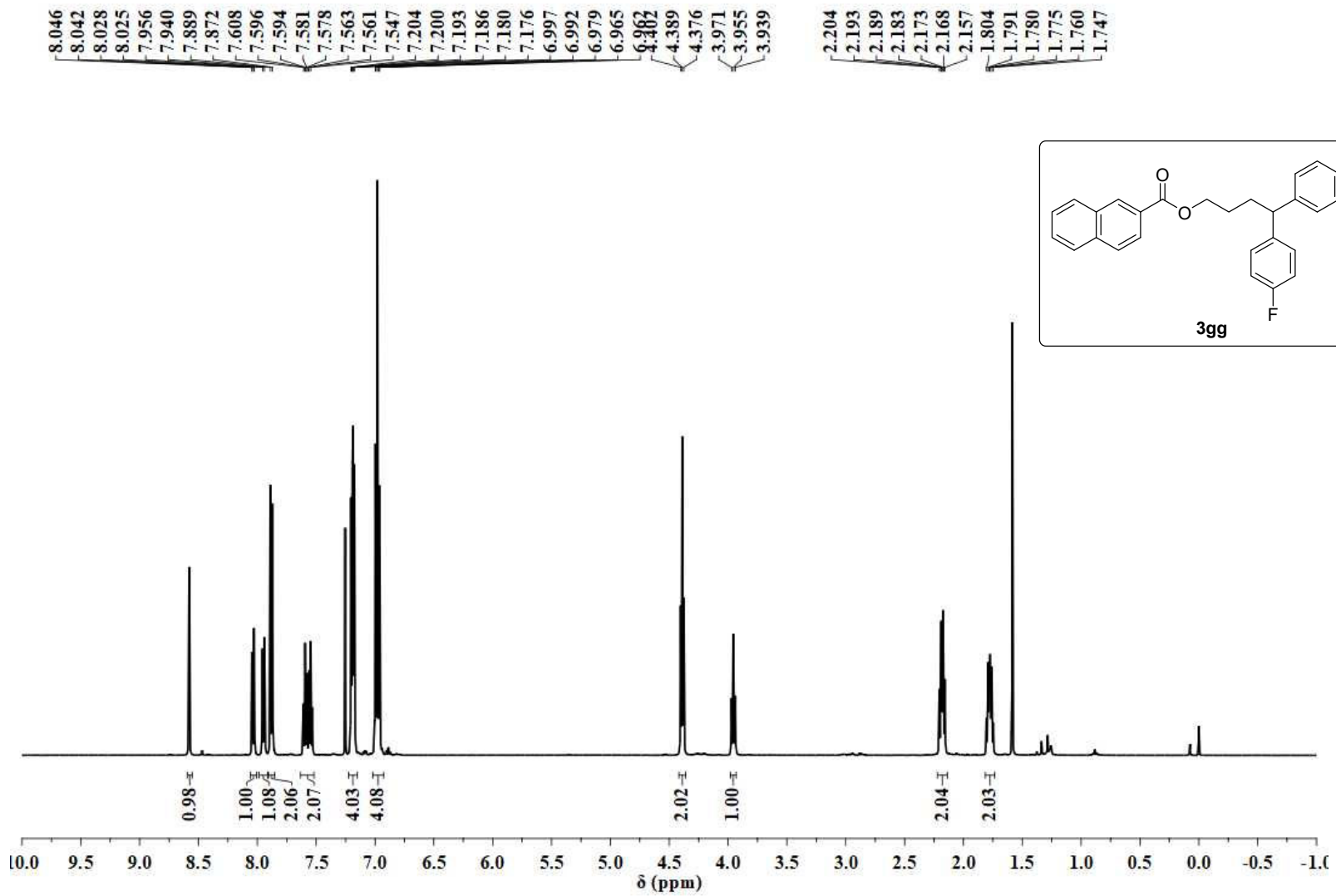


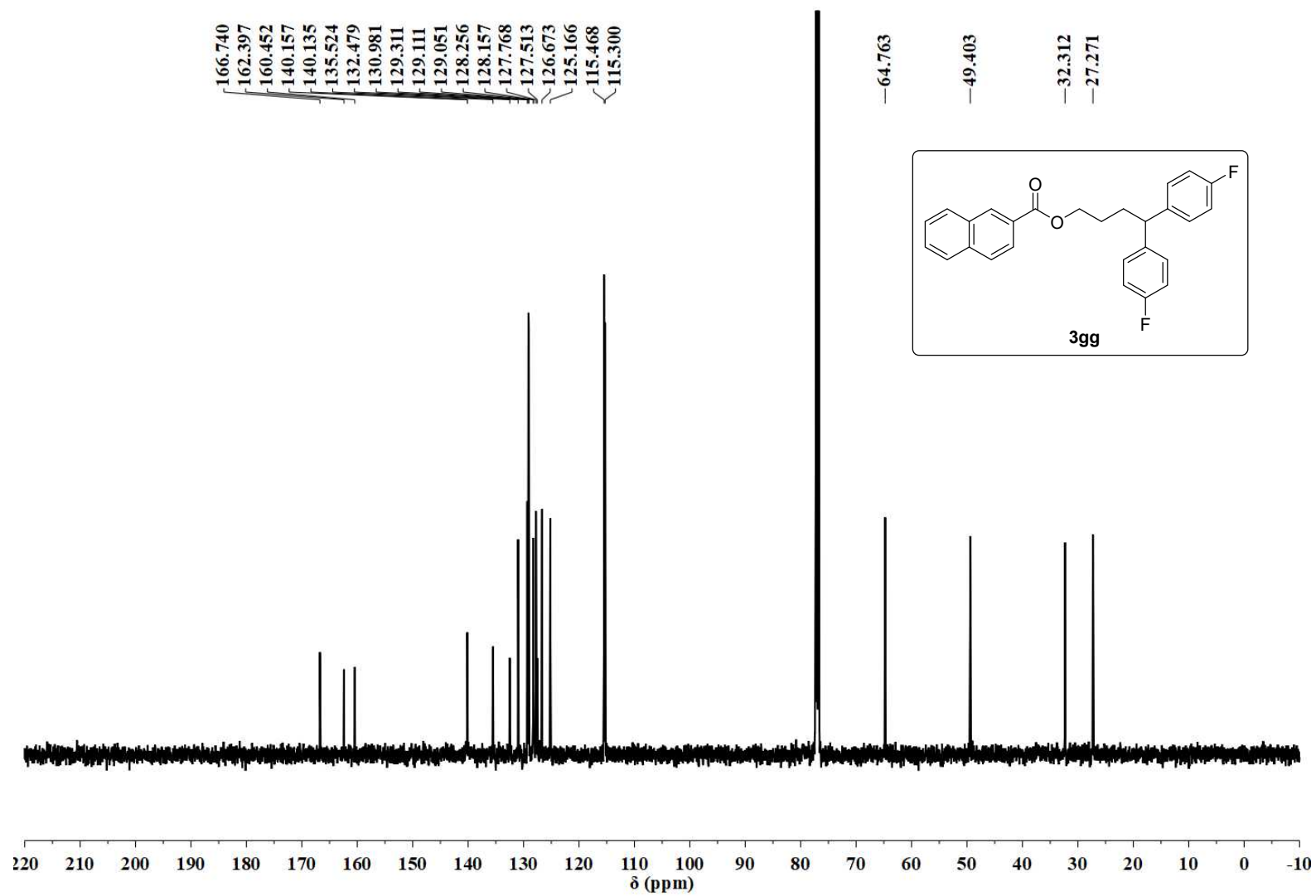






S100





S102

