

Supporting Information

Tandem Rh(II)-catalyzed 1,3-acyloxy migration/intermolecular [2+2] cycloaddition of electronically deficient propargylic esters with alkenes and alkynes

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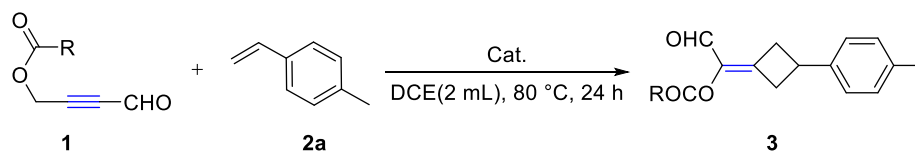
1. General information

All reactions were carried out under an inert atmosphere of dry N₂ in Schlenk tube. Tetrahydrofuran and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and dichloroethane were distilled from CaH₂ prior to use. All other reagents and solvents were used as received from commercial sources, unless specified otherwise, or prepared. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on Bruker AVANCE 400 MHz or 500 MHz, ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ¹⁹F NMR chemical shifts were determined relative to CFCl₃ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Melting points were determined using a hot stage apparatus. HRMS (EI) and HRMS (ESI) were determined on Waters Micromass GCT Premier, Agilent Technologies 6224 TOF LC/MS, and APEX III 7.0 TESLA FTMS spectrometers, respectively.

2. Optimization of reaction conditions

2.1 Condition screening of propargylic esters and alkenes

Table S1

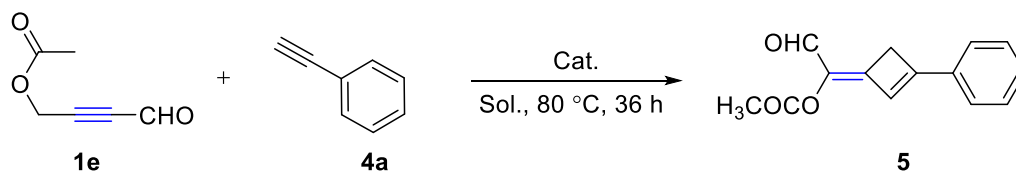


Entry	R	Cat. (mol%)	2 (eq)	Yield ^a
1	-OCH ₃ (1a)	Rh ₂ (OPiv) ₄ (5)	5.0 eq	73%
2	-OCH ₃ (1a)	PtCl ₂ (5)	5.0 eq	N.D.
3	-OCH ₃ (1a)	PPh ₃ AuCl/AgOTf (5)	5.0 eq	N.D.
4 ^b	-OCH ₃ (1a)	Rh ₂ (OPiv) ₄ (5)	5.0 eq	trace
5	-OBn (1b)	Rh ₂ (OPiv) ₄ (5)	5.0 eq	82%
6	- ^t Bu (1c)	Rh ₂ (OPiv) ₄ (5)	5.0 eq	80%
7	-Ph (1d)	Rh ₂ (OPiv) ₄ (5)	5.0 eq	74%
8	-CH ₃ (1e)	Rh ₂ (OPiv) ₄ (5)	5.0 eq	94%
9	-CH ₃ (1e)	Rh ₂ (OPiv) ₄ (1)	5.0 eq	84%
10 ^c	-CH ₃ (1e)	Rh ₂ (OPiv) ₄ (1)	5.0 eq	97%
11 ^c	-CH ₃ (1e)	Rh ₂ (OPiv) ₄ (1)	2.0 eq	95% (82%) ^d

Reaction condition: the reactions were stirred with **1** (0.2 mmol), **2a** and catalyst in 2 mL DCE at 80 °C for 24 h; Yields were based on ¹H NMR analysis with 4-Nitrotoluene as internal standard.^a NMR yield. ^b60 °C. ^creaction time :48 h. ^disolated yield. DCE: 1,2-dichloroethane

2.2 Condition screening of propargylic esters and alkynes

Table S2



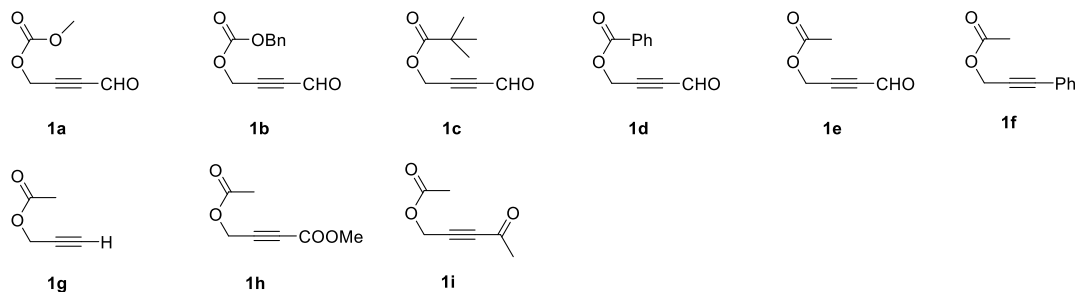
Entry	Cat.(mol%)	Sol.(mL)	1e/4a (eq)	Yield
1	Rh ₂ (OPiv) ₄ (1)	DCE(1.0)	4a (2.0 eq)	55%
2	PPh ₃ AuCl/AgOTf (5)	DCE(1.0)	4a (2.0 eq)	N.D.
3	PtCl ₂ (5)	DCE(1.0)	4a (2.0 eq)	N.D.
4	Rh ₂ (OPiv) ₄ (1)	Toluene(1.0)	4a (2.0 eq)	36%
5	Rh ₂ (OPiv) ₄ (1)	CH ₃ CN(1.0)	4a (2.0 eq)	trace
6	Rh ₂ (OPiv) ₄ (1)	PhCF ₃ (1.0)	4a (2.0 eq)	trace
7	Rh ₂ (OPiv) ₄ (1)	DCE(0.7)	4a (2.0 eq)	55%
8	Rh ₂ (OPiv) ₄ (1)	DCE(0.5)	4a (2.0 eq)	34%
9 ^a	Rh ₂ (OPiv) ₄ (1)	DCE(0.7)	4a (2.0 eq)	28%
10	Rh ₂ (OPiv) ₄ (1)	DCE(1.0)	4a (5.0 eq)	trace
11 ^b	Rh ₂ (OPiv) ₄ (1)	DCE(1.0)	1e (5.0 eq)	56% (55%) ^c
12 ^b	Rh ₂ (OPiv) ₄ (1)	DCE(3.0)	1e (5.0 eq)	71% (62%) ^c
13 ^b	Rh ₂ (OPiv) ₄ (1)	DCE(3.0)	1e (4.0 eq)	60%
14 ^b	Rh ₂ (OPiv) ₄ (1)	DCE(3.0)	1e (2.0 eq)	49%

Table 2. Condition screening of propargylic esters and alkynes. Reaction condition: the reactions were stirred with **1e** (0.2 mmol), **4a** and catalyst in DCE at 80 °C for 36 h; Yields were based on ¹H NMR analysis with 4-Nitrotoluene as internal standard. ^a Reaction temperature is 60 °C. ^b The reactions were stirred with **1e**, **4a** (0.2 mmol) and catalyst in DCE at 80 °C for 72 h. ^c Isolated yield. DCE: 1,2-dichloroethane

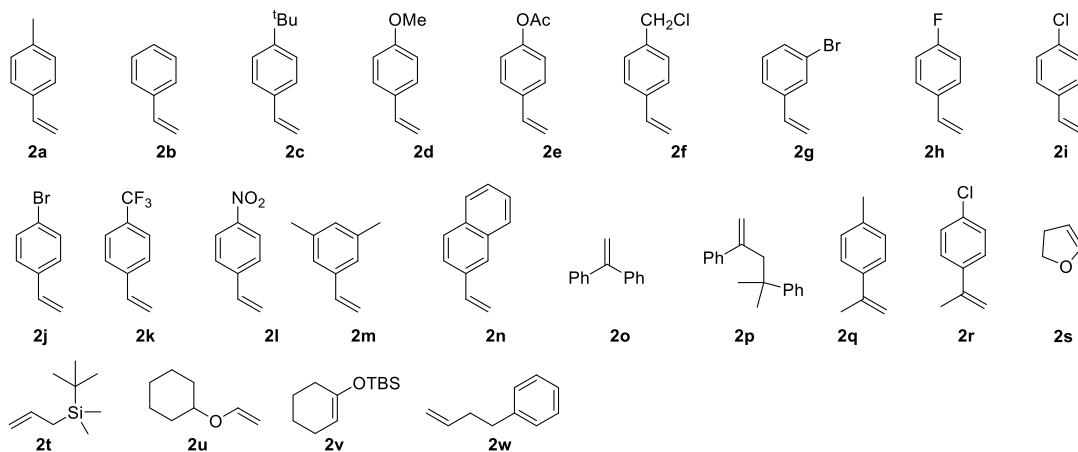
3. Preparation of the substrates

The related substrates are listed below

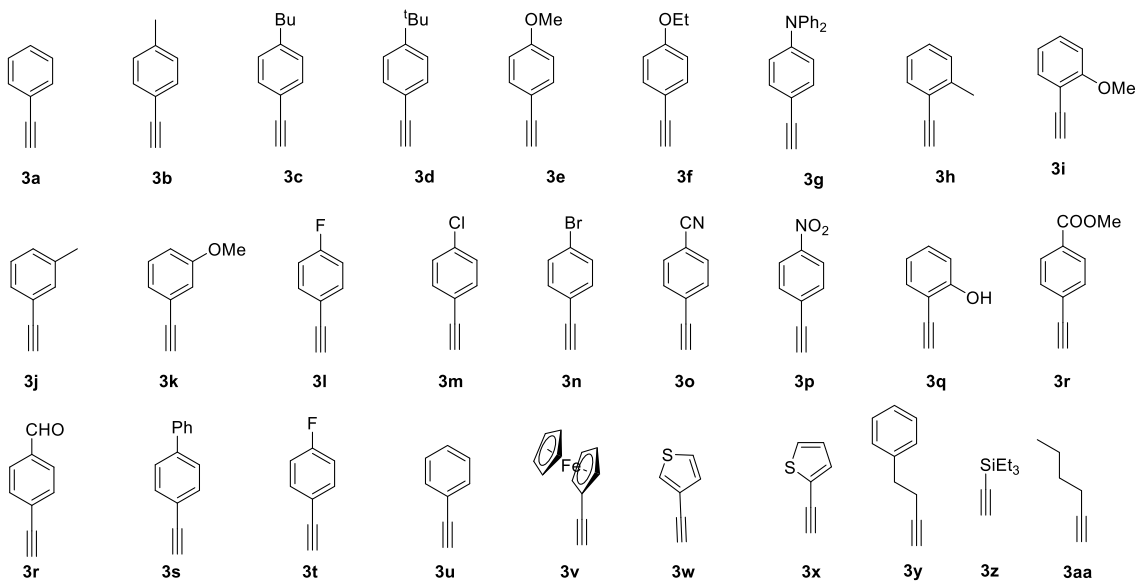
The substrates of propargylic esters



The substrates of styrenes

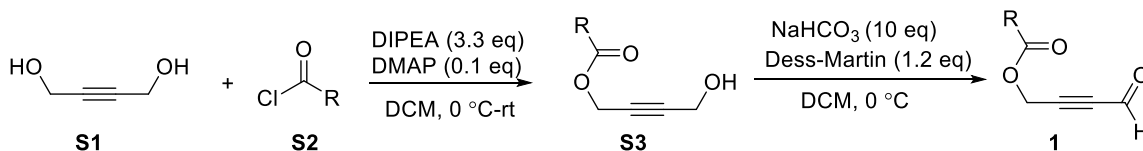


The substrates of phenylacetylenes



3.1 General procedure for preparation of propargylic esters

General Procedure A¹:

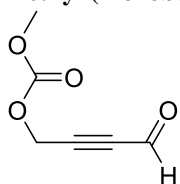


To a stirred solution of but-2-yne-1,4-diol **S1** (30 mmol, 3.0 equiv) in DCM (100 mL) maintained at 0 °C, *N,N*-diisopropylethylamine (33 mmol, 3.3 equiv) and 4-dimethylaminopyridine (1 mmol, 0.1 equiv) was added. Then, acyl chloride **S2** (10 mmol, 1.0 equiv) was slowly added over 15 min at the same temperature. The reaction mixture was warmed to room temperature and then stirred for additional 4 h monitored by TLC (SiO₂, petroleum ether/ethyl acetate = 3:1). After completed, the reaction was diluted with DCM and quenched with water (30 mL). The layers were separated and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford the desired product **S3**.

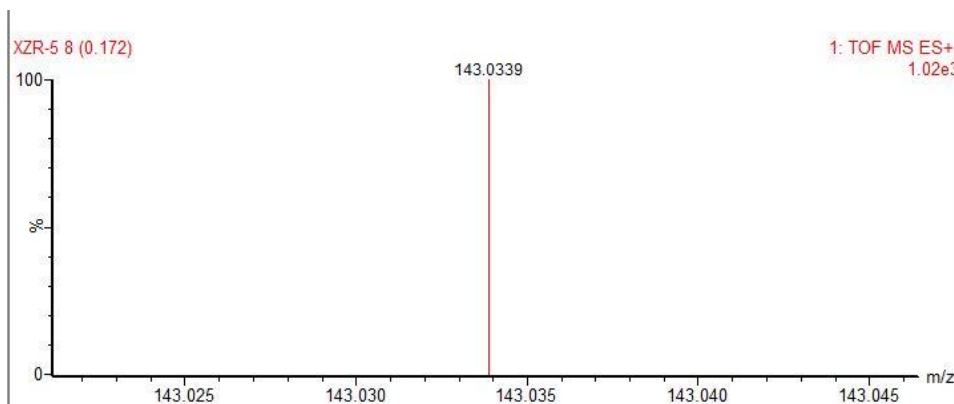
To the solution of **S3** (5 mmol, 1.0 equiv) in 10 mL DCM at 0 °C, NaHCO₃ (50 mmol, 10.0 eq) and DMP (6.0 mmol, 1.2 equiv) was added and the mixture was stirred at room temperature for about 30 min. After the complete consumption of **S3** determined by TLC, the reaction mixture was then quenched with sat. aqueous Na₂S₂O₃. The organic layer was separated. The aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layers were washed with brine (50 mL), dried upon anhydrous Na₂SO₄, filtered and concentrated. The resulting residue was flash chromatographed (PE: EA = 20:1) on silica gel to afford the product **1**.

The substrates such as **1a**, **1b**, **1c**, **1d**, **1e** were synthesized according to General procedure A.

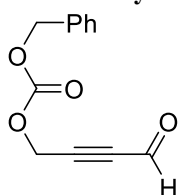
Methyl (4-oxobut-2-yn-1-yl) carbonate (**1a**)



Yellow liquid, purified by chromatography (PE/EA = 20/1, R_f = 0.5); ¹H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 4.93 (s, 2H), 3.86 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 175.80, 154.92, 88.65, 85.57, 55.49, 54.63. HRMS (ESI) [M+H]⁺ calculated for C₆H₇O₄⁺: 143.0339, found: 143.0339.

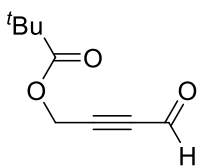


4-oxobut-2-yn-1-yl 2-phenylacetate (**1b**)

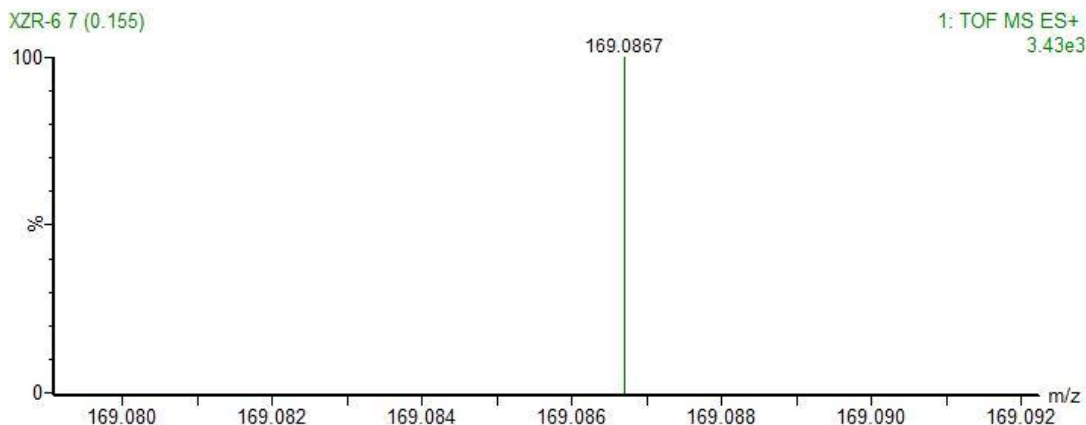


Yellow liquid, purified by chromatography (PE/EA = 20/1, R_f = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.73 – 7.18 (m, 5H), 5.20 (s, 2H), 4.90 (s, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 175.85, 154.31, 134.62, 128.84, 128.71, 128.46, 88.67, 85.67, 70.52, 54.69.

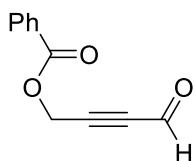
4-oxobut-2-yn-1-yl pivalate (1c)



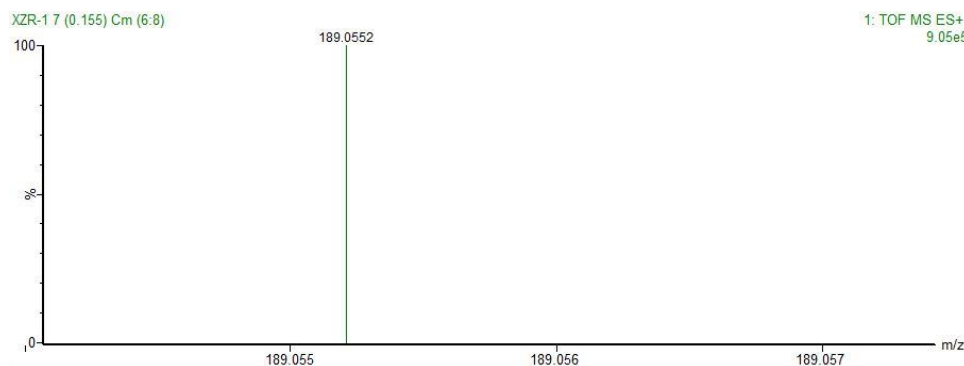
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 4.86 (s, 2H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.28, 175.99, 89.87, 84.83, 51.30, 38.68, 26.90. HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_9\text{H}_{13}\text{O}_3^+$: 168.0859, found: 169.0867.



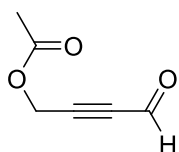
4-oxobut-2-yn-1-yl benzoate (1d)



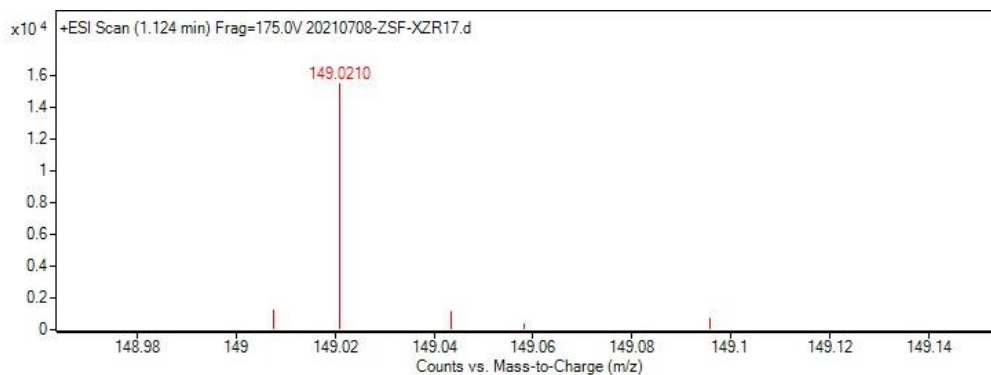
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.12 – 8.00 (m, 2H), 7.71 – 7.55 (m, 1H), 7.47 (t, J = 7.8 Hz, 2H), 5.10 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.01, 165.53, 133.70, 129.89, 128.84, 128.58, 89.68, 85.26, 51.84. HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_9\text{O}_3^+$: 189.0546, found 189.0552.



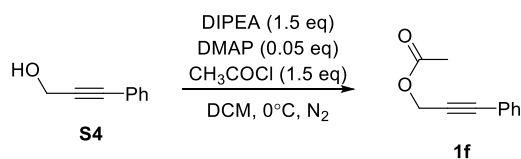
4-oxobut-2-yn-1-yl acetate (1e)



Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 7.27 (s, 1H), 4.86 (s, 2H), 2.14 (d, J = 1.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.90, 169.85, 89.56, 85.08, 51.30, 20.48. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_6\text{H}_6\text{O}_3\text{Na}^+$: 149.0209, found 149.0210.

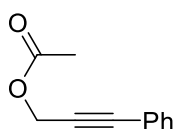


General Procedure B²:



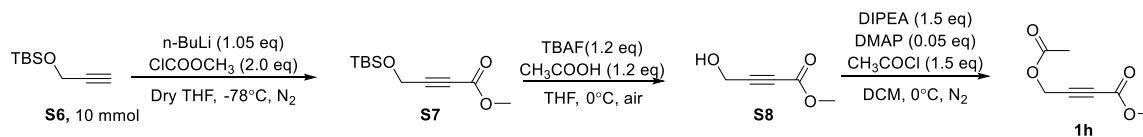
To a stirred solution of propargyl alcohol **S4** (500 mg, 3.8 mmol, 1.0 equiv) in DCM (10 mL) maintained at 0 °C, *N,N*-diisopropylethylamine (4.56 mmol, 1.2 equiv) and 4-dimethylaminopyridine (0.38 mmol, 0.1 equiv) was added. Then, acetyl chloride (4.56 mmol, 1.2 equiv) was slowly added over 15 min at the same temperature. The reaction mixture was warmed to room temperature and then stirred for additional 2 h monitored by TLC (SiO₂, petroleum ether/ethyl acetate 100:1). After completed, the reaction was diluted with DCM (30 mL) and quenched with water (5 mL). The layers were separated and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford the desired alkylylic ester **1f** in 84% yield (556 mg).

3-phenylprop-2-yn-1-yl acetate(1f)²



Known compounds, Yellow liquid, purified by chromatography (PE/EA = 20/1, R_f = 0.5); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.45 (m, 2H), 7.38 – 7.30 (m, 3H), 4.93 (s, 2H), 2.15 (s, 3H).

General Procedure C³:



Under N₂ atmosphere, the solution of *n*-BuLi (10.5 mmol, 1.05 equiv) in hexane (1.6 mol/L) was added dropwise into the solution of **S6** (10mmol, 1.0 equiv) in anhydrous THF at -78 °C over 10 minutes. The resulting mixture was stirred at -78°C for 1 h. Methyl chloroformate (20 mmol, 2.0 equiv) was added dropwise via a syringe. Stirring was continued for 1.5 hours at -78 °C and the reaction was allowed to warm to room temperature monitored by TLC (SiO₂, petroleum ether/ethyl acetate 100:1). After completed, the reaction mixture was then quenched with sat. aqueous NH₄Cl. The organic layer was separated. The aqueous layer was extracted with diethyl ether (2 x 20 mL). The combined organic layers were washed with brine (50

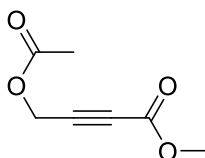
mL), dried upon anhydrous Na₂SO₄, filtered and concentrated. The residue was purified through silica gel flash column chromatography (eluent: EtOAc and hexanes) to yield the desired compound **S7** in 69% yield.

To the solution of **S7** (1.1 g, 4.83 mmol, 1.0 equiv) in 2 mL THF, acetic acid (1.2 equiv) and TBAF (1.2 equiv) was added and the mixture was stirred at room temperature overnight. After the complete consumption of **S7** determined by TLC, the reaction mixture was filtered through silica gel and the filtrate was concentrated by rotary evaporator. The resulting residue was flash chromatographed (PE: EA = 5:1) on silica gel to afford the product **S8** in 50% yield.

To a stirred solution of propargyl alcohol **S8** (239 mg, 2.1 mmol, 1.0 equiv) in DCM (10 mL) maintained at 0 °C, N,N-diisopropylethylamine (3.15 mmol, 1.5 equiv) and 4-dimethylaminopyridine (0.105 mmol, 0.05 equiv) was added. Then, acetyl chloride (3.15 mmol, 1.5 equiv) was slowly added over 15 min at the same temperature. The reaction mixture was warmed to room temperature and then stirred for additional 2 h monitored by TLC (SiO₂, petroleum ether/ethyl acetate 100:1). After completed, the reaction was diluted with DCM (30 mL) and quenched with water (5 mL). The layers were separated and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 5:1) to afford the desired alkynylic ester **1h** in 99% yield (324 mg).

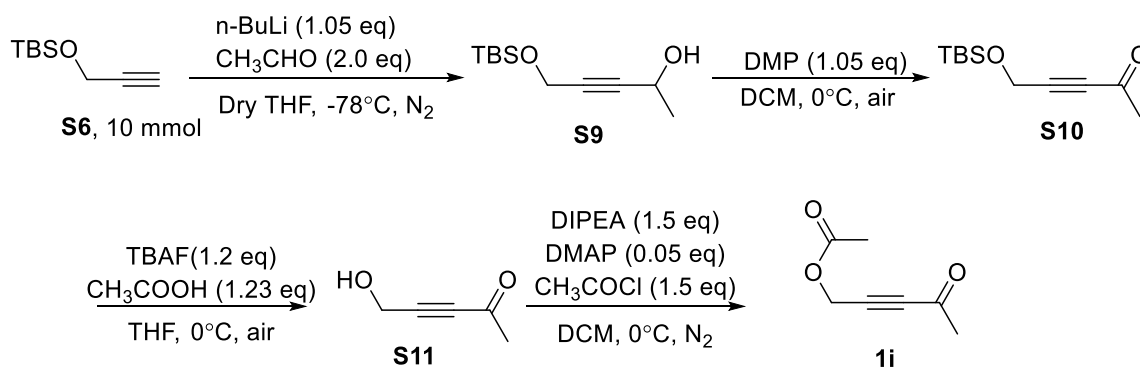
The substrates such as **1h** were synthesized according to General procedure C

Methyl 4-acetoxybut-2-ynoate (**1h**)³



Known compounds, Yellow liquid, purified by chromatography (PE/EA = 5/1, R_f = 0.5); ¹H NMR (400 MHz, Chloroform-*d*) δ 4.80 (s, 2H), 3.81 (s, 3H), 2.13 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.87, 153.27, 81.28, 52.91, 51.23, 20.52.

General Procedure D⁴:



Under N₂ atmosphere, the solution of n-BuLi (10.5 mmol, 1.05 equiv) in hexane (1.6 mol/L) was added dropwise into the solution of **S6** (10 mmol, 1.0 equiv) in anhydrous THF at -78 °C over 10 minutes. The resulting mixture was stirred at -78 °C for 1 h. Acetaldehyde (20 mmol, 2.0 equiv) was added dropwise via a syringe. Stirring was continued for 1.5 hours at -78 °C and the reaction was allowed to warm to room temperature monitored by TLC (SiO₂, petroleum ether/ethyl acetate 100:1). After completed, the reaction mixture was then quenched with sat. aqueous NH₄Cl. The organic layer was separated. The aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were washed with brine (50 mL), dried upon anhydrous Na₂SO₄, filtered and concentrated. The residue was purified through silica gel flash column chromatography (eluent: EtOAc and hexanes) to yield the desired compound **S9** in 83% yield.

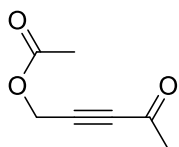
To the solution of **S9** (8.3 mmol, 1.0 equiv) in 10 mL DCM at 0 °C, DMP (8.7 mmol, 1.05 equiv) was added and the mixture was stirred at room temperature for about 30 min. After the complete consumption of **S9** determined by TLC, the reaction mixture was filtered through silica gel and the filtrate was concentrated by rotary evaporator. The resulting residue was flash chromatographed (PE: EA = 20:1) on silica gel to afford the product **S10** in 67% yield.

To the solution of **S10** (1.42 g, 6.7 mmol, 1.0 equiv) in 2 mL THF, acetic acid (1.2 equiv) and TBAF (1.2 equiv) was added and the mixture was stirred at room temperature at overnight. After the complete consumption of **S7** determined by TLC, the reaction mixture was filtered through silica gel and the filtrate was concentrated by rotary evaporator. The resulting residue was flash chromatographed (PE: EA = 5:1) on silica gel to afford the product **S11** in 66% yield.

To a stirred solution of propargyl alcohol **S11** (6.6 mmol, 1.0 equiv) in DCM (30 mL) maintained at 0 °C, *N,N*-diisopropylethylamine (9.9 mmol, 1.5 equiv) and 4-dimethylaminopyridine (0.33 mmol, 0.05 equiv) was added. Then, acetyl chloride (9.9 mmol, 1.5 equiv) was slowly added over 15 min at the same temperature. The reaction mixture was warmed to room temperature and then stirred for additional 2 h monitored by TLC (SiO₂, petroleum ether/ethyl acetate 100:1). After completed, the reaction was diluted with DCM (30 mL) and quenched with water (5 mL). The layers were separated and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to afford the desired alkynylic ester **1i** in 99% yield (914 mg).

The substrates such as **1i** were synthesized according to General procedure **C**.

4-oxopent-2-yn-1-yl acetate (**1i**)⁴

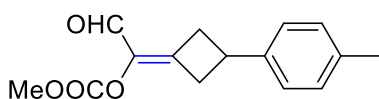


Known compounds, Yellow liquid, purified by chromatography (PE/EA = 10/1, R_f = 0.7); ¹H NMR (500 MHz, Chloroform-*d*) δ 4.75 (s, 2H), 2.29 (s, 3H), 2.06 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 183.58, 169.85, 85.26, 84.87, 51.34, 32.39, 20.48.

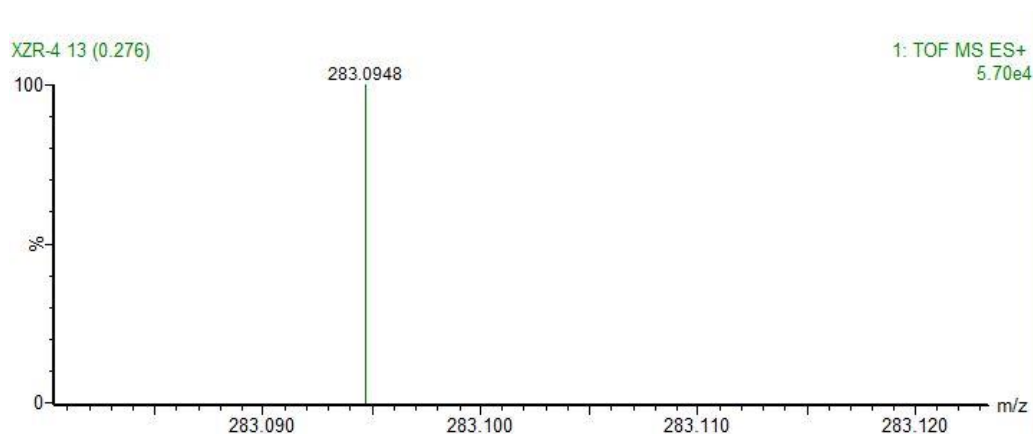
4. General procedure for tandem Rh(II)-catalyzed 1,3-acyl migration/[2 + 2] cycloaddition of propargylic esters with alkenes

To a 1,2-dichloroethane solution of **1** (0.2 mmol, 2.0 mL) in Schlenk tube with a magnetic bar was added Rh₂(OPiv)₄ (0.002 mmol, 1 mol%, 1.3 mg) with various styrene derivatives **2** (2.0 equiv) at 30 °C under N₂. The sealed tube was then stirred at 80 °C under nitrogen atmosphere for 48 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **3**.

Methyl (2-oxo-1-(3-(*p*-tolyl)cyclobutylidene)ethyl) carbonate (**3aa**)



Yellow liquid, 23.3 mg, 62%, purified by chromatography (PE/EA = 10/1, R_f = 0.4); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 7.15 (d, *J* = 9.3 Hz, 4H), 3.87 (s, 3H), 3.80 – 3.60 (m, 2H), 3.37 (ddt, *J* = 17.6, 8.4, 3.7 Hz, 1H), 3.28 (ddd, *J* = 16.6, 7.5, 3.5 Hz, 1H), 3.08 (ddd, *J* = 17.9, 7.6, 3.3 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.66, 153.55, 153.17, 140.18, 139.82, 136.57, 129.39, 126.19, 55.74, 37.58, 36.51, 35.18, 21.04. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₆O₄Na⁺: 283.0941, found 283.0948.

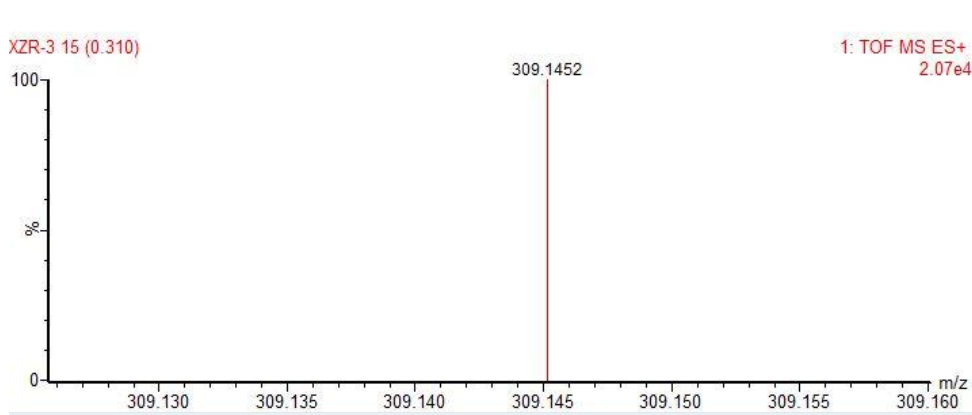


2-oxo-1-(3-(p-tolyl)cyclobutylidene)ethyl benzoate(3ba)

O=C(Oc1ccccc1)C(=O)C=C2C(C=C2)c3ccc(C)cc3 Yellow liquid, 31.3 mg, 51%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 9.60 (s, 1H), 8.13 (dd, $J = 8.3, 1.4$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.20 – 7.12 (m, 4H), 3.81 – 3.68 (m, 2H), 3.41 – 3.28 (m, 2H), 3.14 – 2.99 (m, 1H), 2.34 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 182.04, 164.03, 153.85, 140.38, 139.83, 136.48, 133.75, 130.34, 129.38, 128.69, 128.57, 126.24, 37.85, 36.78, 35.23, 21.06.

2-oxo-1-(3-(p-tolyl)cyclobutylidene)ethyl pivalate(3ca)

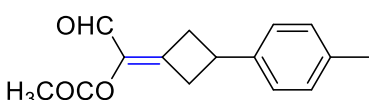
O=C(OCC(C)(C)C)C(=O)C=C2C(C=C2)c3ccc(C)cc3 Yellow liquid, 38.9 mg, 68%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 7.16 (s, 4H), 3.81 – 3.51 (m, 2H), 3.32 – 3.18 (m, 2H), 3.00 (ddd, $J = 18.8, 7.6, 3.3$ Hz, 1H), 2.34 (s, 3H), 1.31 (s, 9H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 181.90, 176.05, 152.80, 140.44, 139.87, 136.44, 129.35, 126.21, 39.07, 37.49, 36.56, 35.22, 27.19, 21.04. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{Na}^+$: 309.1461, found 309.1452.



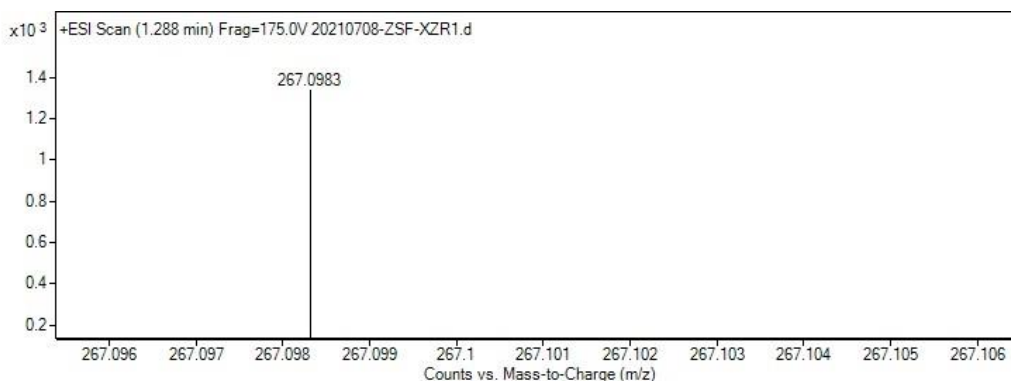
Benzyl (2-oxo-1-(3-(p-tolyl)cyclobutylidene)ethyl) carbonate (3da)

O=C(OCC1=CC=CC=C1)C(=O)C=C2C(C=C2)c3ccc(C)cc3 Yellow liquid, 46.4 mg, 69%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 9.51 (s, 1H), 7.45 – 7.33 (m, 6H), 7.16 (s, 4H), 5.24 (s, 2H), 3.79 – 3.50 (m, 2H), 3.31 (dddd, $J = 30.3, 16.5, 8.0, 3.8$ Hz, 1H), 3.05 (ddd, $J = 17.9, 7.5, 3.2$ Hz, 1H), 2.34 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 181.64, 153.48, 152.55, 140.18, 139.84, 136.55, 134.61, 129.37, 128.74, 128.67, 128.35, 126.19, 70.71, 37.60, 36.53, 35.17, 21.03.

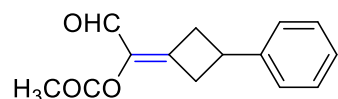
2-oxo-1-(3-(p-tolyl)cyclobutylidene)ethyl acetate(3ea)



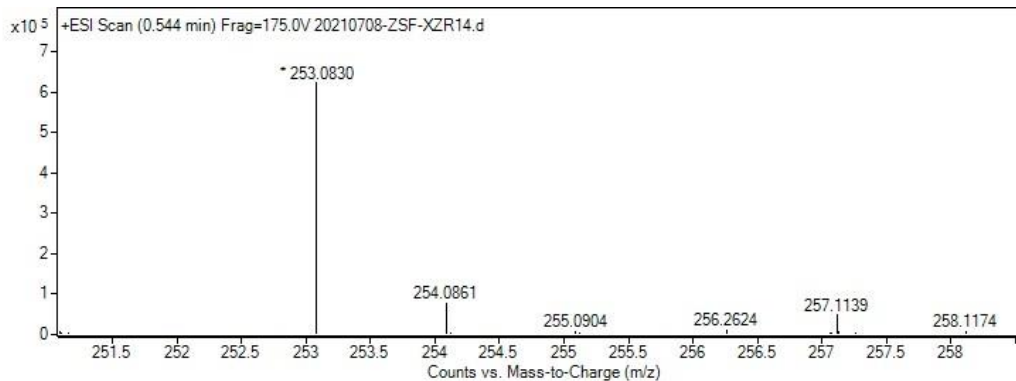
Yellow liquid, 40 mg, 82%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 7.16 (s, 4H), 3.85 – 3.48 (m, 2H), 3.29 (dddd, J = 16.6, 10.5, 7.3, 3.5 Hz, 2H), 3.03 (ddd, J = 17.8, 7.3, 3.1 Hz, 1H), 2.34 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.87, 168.27, 153.67, 140.32, 139.78, 136.52, 129.37, 126.20, 37.74, 36.60, 35.14, 21.04, 20.26. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{Na}^+$: 267.0991, found 267.0983.



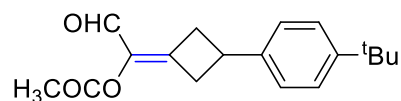
2-oxo-1-(3-phenylcyclobutylidene)ethyl acetate (3eb)



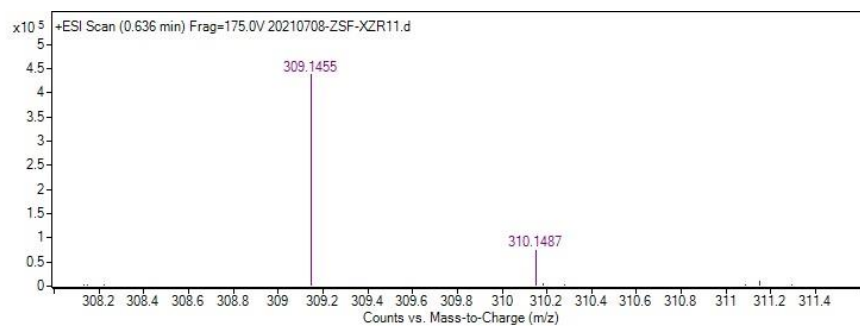
Yellow liquid, 35.4 mg, 77%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 7.39 – 7.32 (m, 2H), 7.30 – 7.25 (m, 3H), 3.78 (p, J = 8.0 Hz, 1H), 3.73 – 3.65 (m, 1H), 3.49 – 3.22 (m, 2H), 3.06 (ddd, J = 17.1, 7.3, 3.2 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.86, 168.26, 153.36, 143.30, 139.81, 128.72, 126.87, 126.29, 37.59, 36.47, 35.44, 20.25. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Na}^+$: 253.0835, found 253.0830.



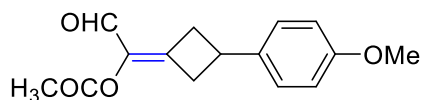
1-(3-(4-(tert-butyl)phenyl)cyclobutylidene)-2-oxoethyl acetate(3ec)



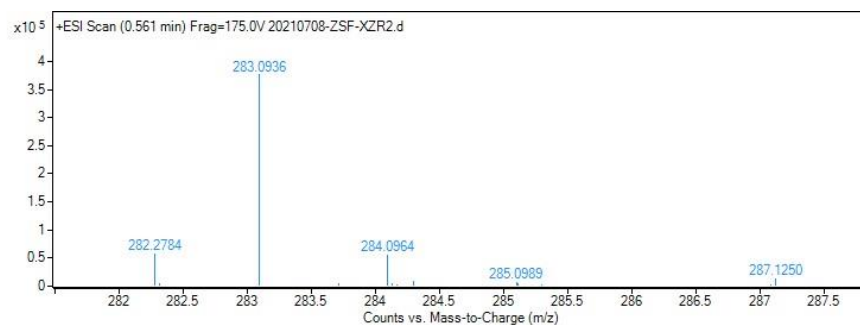
Yellow liquid, 20.2 mg, 36%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 3.80 – 3.60 (m, 2H), 3.34 – 3.24 (m, 2H), 3.13 – 2.99 (m, 1H), 2.24 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.89, 168.26, 153.71, 149.87, 140.28, 139.78, 126.04, 125.60, 54.72, 37.69, 36.56, 35.08, 34.49, 31.35, 20.23. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{Na}^+$: 309.1461, found 309.1455.



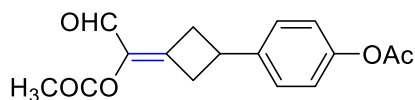
1-(3-(4-methoxyphenyl)cyclobutylidene)-2-oxoethyl acetate(3ed)



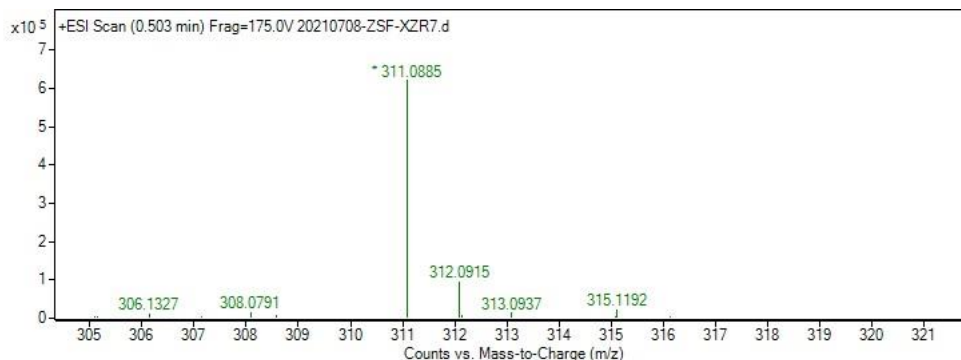
Yellow liquid, 36.4 mg, 70%, purified by chromatography (PE/EA = 5/1, R_f = 0.4); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.49 (s, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.76 – 3.63 (m, 2H), 3.36 – 3.22 (m, 2H), 3.05 – 2.96 (m, 1H), 2.24 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.92, 168.29, 158.50, 153.71, 139.78, 135.45, 127.35, 114.10, 55.34, 37.91, 36.77, 34.85, 20.23. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₆O₄Na⁺ : 283.0941, found 283.0936.



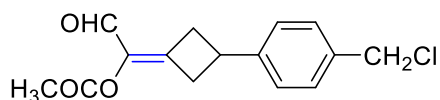
4-(3-(1-acetoxy-2-oxoethylidene)cyclobutyl)phenyl acetate(3ee)



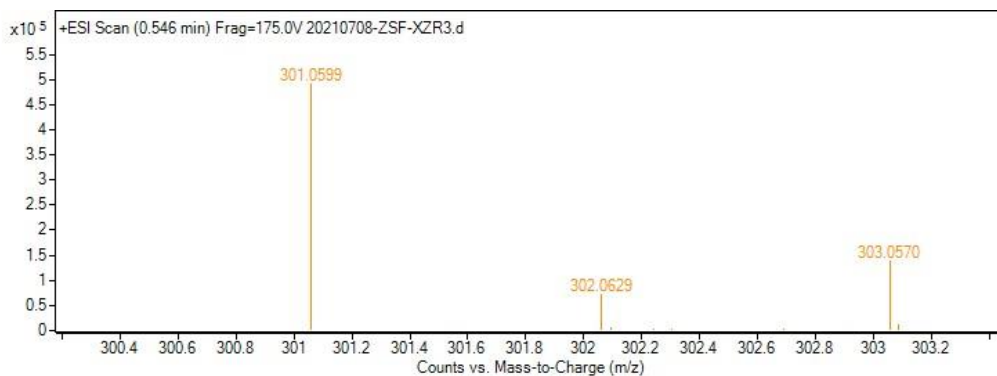
Yellow liquid, 38.0 mg, 66%, purified by chromatography (PE/EA = 10/1, R_f = 0.4); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.49 (s, 1H), 7.39 – 7.23 (m, 2H), 7.20 – 6.99 (m, 2H), 3.91 – 3.53 (m, 2H), 3.31 (dddt, *J* = 17.1, 14.8, 7.5, 3.6 Hz, 2H), 3.03 (ddd, *J* = 17.6, 7.5, 3.3 Hz, 1H), 2.30 (s, 3H), 2.24 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.87, 169.61, 168.25, 149.44, 140.88, 139.83, 127.38, 121.82, 37.70, 36.57, 35.00, 21.10, 20.23. HRMS (ESI) [M+Na]⁺ calculated for C₁₆H₁₆O₅Na⁺ : 331.0890, found 331.0885.



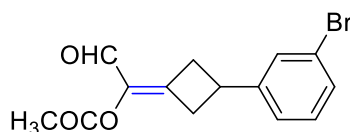
1-(3-(4-(chloromethyl)phenyl)cyclobutylidene)-2-oxoethyl acetate(3ef)



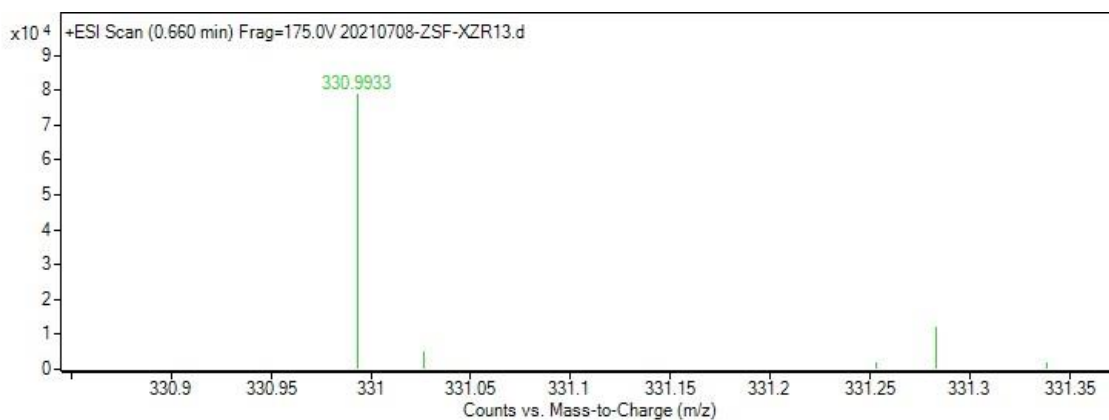
Yellow liquid, 33.4 mg, 60%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.58 (s, 2H), 3.85 – 3.64 (m, 2H), 3.38 – 3.17 (m, 2H), 3.04 (ddd, *J* = 17.7, 7.5, 3.4 Hz, 1H), 2.25 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.87, 168.23, 152.83, 143.65, 139.84, 129.00, 126.74, 45.91, 37.54, 36.44, 35.20, 20.24. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₅ClO₃Na⁺ : 301.0602, found 301.0599.



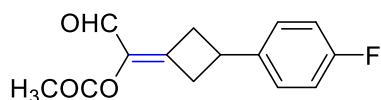
1-(3-(3-bromophenyl)cyclobutylidene)-2-oxoethyl acetate (3eg)



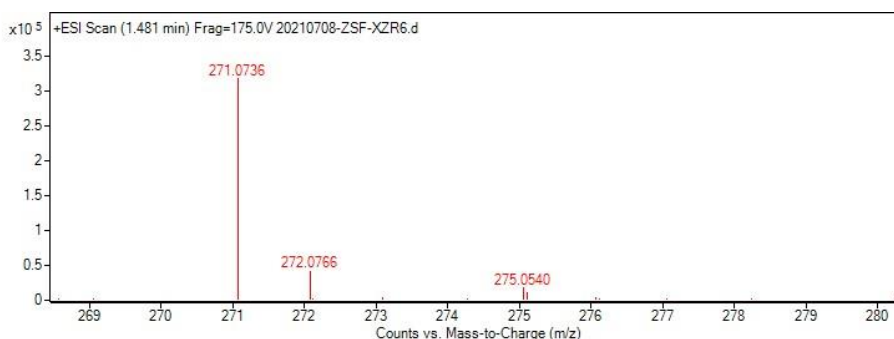
Yellow solid, M.P: 104-105 °C, 29.0 mg, 47%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.49 (s, 1H), 7.41 (t, *J* = 1.8 Hz, 1H), 7.39 (dt, *J* = 7.3, 1.8 Hz, 1H), 7.25 – 7.18 (m, 2H), 3.79 – 3.65 (m, 2H), 3.47 – 3.24 (m, 2H), 3.16 – 2.97 (m, 1H), 2.25 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.83, 168.21, 152.12, 145.61, 139.88, 130.30, 129.98, 129.58, 124.91, 122.82, 37.39, 36.32, 35.08, 20.23. HRMS (ESI) [M+Na]⁺ calculated for C₁₄H₁₃BrO₃Na⁺ : 330.9940, found 330.9935.



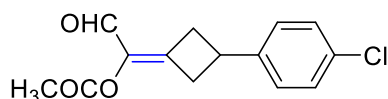
1-(3-(4-fluorophenyl)cyclobutylidene)-2-oxoethyl acetate(3eh)



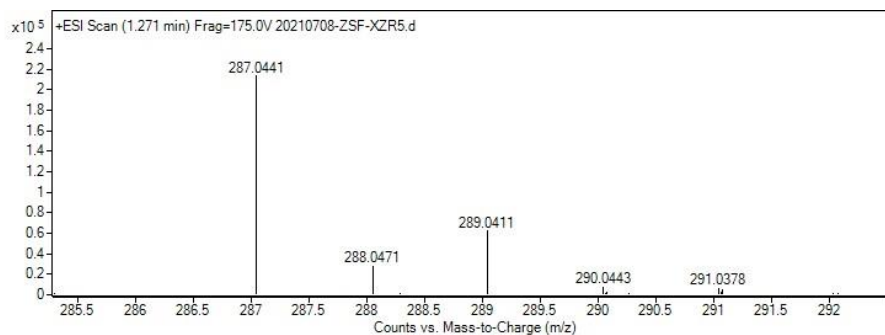
Yellow liquid, 32.3mg, 65%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 0H), 7.24 (dd, J = 8.5, 5.4 Hz, 1H), 7.04 (dd, J = 9.6, 7.7 Hz, 1H), 3.81 – 3.60 (m, 1H), 3.30 (dddd, J = 23.8, 16.3, 7.8, 3.8 Hz, 1H), 3.01 (ddd, J = 17.9, 7.3, 3.1 Hz, 0H), 2.25 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.85, 168.25, 161.71 (d, J = 245.2 Hz), 152.70, 139.84, 139.03 (d, J = 3.5 Hz), 127.82 (d, J = 8.1 Hz), 115.52 (d, J = 21.4 Hz), 37.75, 36.66, 34.85, 20.23. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -115.88. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{13}\text{FO}_3\text{Na}^+$: 271.0741, found 271.0736.



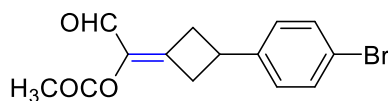
1-(3-(4-chlorophenyl)cyclobutylidene)-2-oxoethyl acetate (3ei)



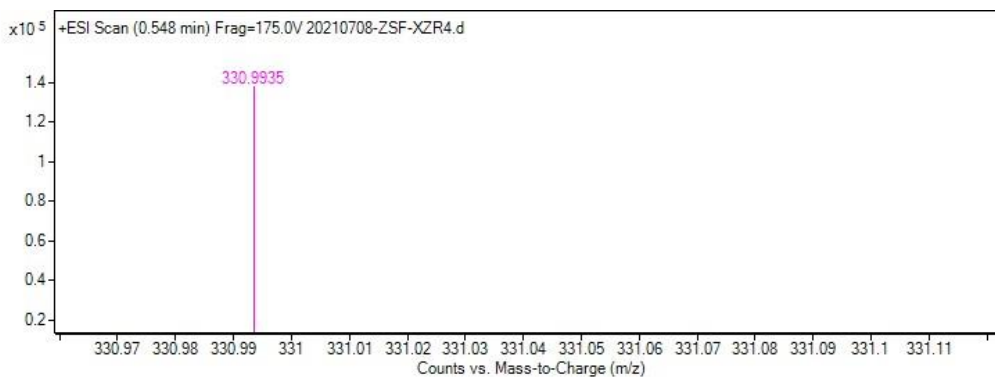
Yellow liquid, 35.4 mg, 67%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.49 (s, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 3.81 – 3.59 (m, 2H), 3.30 (dddd, J = 26.2, 16.0, 7.5, 3.5 Hz, 2H), 3.01 (ddd, J = 17.6, 7.2, 2.9 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.88, 168.29, 152.64, 141.78, 139.85, 132.60, 128.83, 127.72, 37.57, 36.47, 34.91, 20.27. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{13}\text{ClO}_3\text{Na}^+$: 287.0445, found 287.0441.



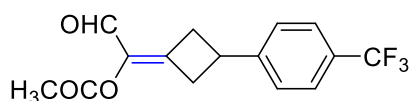
1-(3-(4-bromophenyl)cyclobutylidene)-2-oxoethyl acetate (3ej)



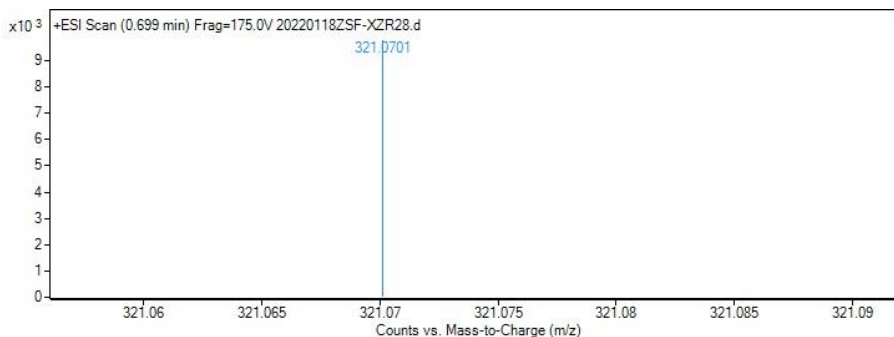
Yellow solid, M.P.: 109-110 °C 49.9 mg, 81%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.49 (s, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 3.78 – 3.65 (m, 2H), 3.30 (dddd, J = 28.5, 16.5, 7.1, 3.0 Hz, 1H), 3.01 (dq, J = 17.7, 3.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.85, 168.24, 152.41, 142.29, 139.86, 131.79, 128.08, 120.64, 37.49, 36.40, 34.99, 20.24. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{13}\text{BrO}_3\text{Na}^+$: 330.9940, found 330.9935.



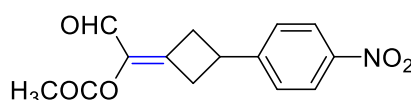
2-oxo-1-(3-(4-(trifluoromethyl)phenyl)cyclobutylidene)ethyl acetate (3ek)



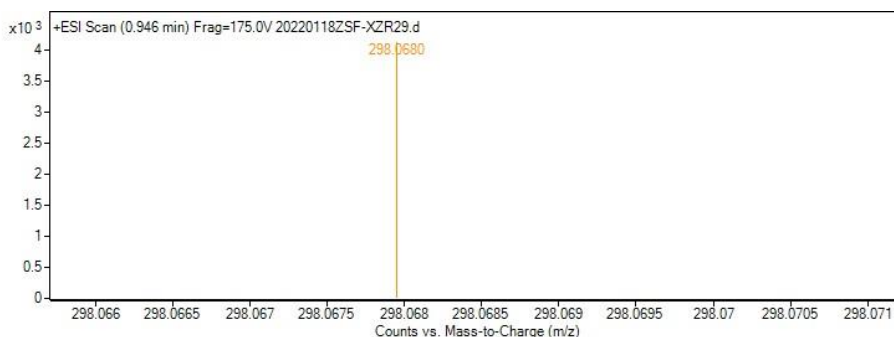
Yellow liquid, 24.5 mg, 41%, purified by chromatography (PE/EA = 5/1, Rf = 0.6); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.51 (s, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 3.98 – 3.81 (m, 1H), 3.74 (ddt, J = 16.3, 8.8, 3.7 Hz, 1H), 3.45 (ddt, J = 17.8, 8.7, 3.5 Hz, 1H), 3.34 (ddd, J = 16.9, 7.5, 3.5 Hz, 1H), 3.12 (ddd, J = 17.9, 7.6, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.72, 153.12, 151.91, 147.11, 139.91, 129.08, 126.95, 126.70, 125.70 (q, J = 3.7 Hz), 55.81, 37.17, 36.21, 35.26. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.50. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{O}_3\text{Na}^+$: 321.0709, found 321.0701.



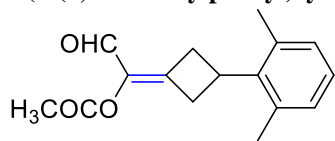
1-(3-(4-nitrophenyl)cyclobutylidene)-2-oxoethyl acetate (3el)



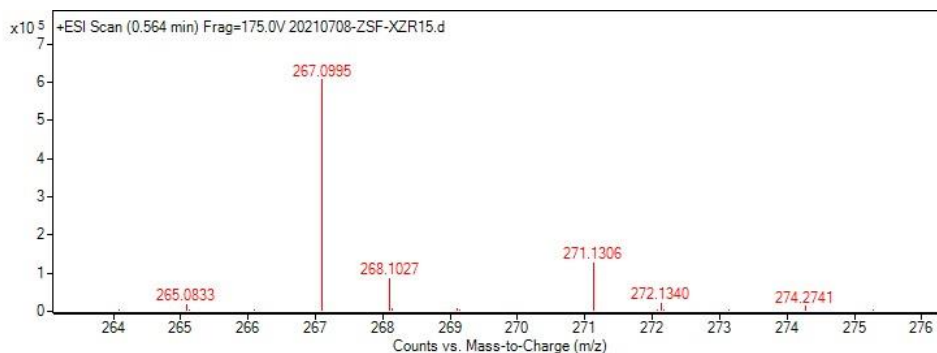
Reddish brown liquid, 19.3 mg, 35%, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 8.28 – 8.18 (m, 2H), 7.53 – 7.38 (m, 2H), 3.90 (p, J = 8.1 Hz, 1H), 3.78 (ddt, J = 16.6, 8.7, 3.2 Hz, 1H), 3.47 – 3.30 (m, 2H), 3.08 (ddd, J = 17.8, 7.5, 3.5 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.85, 168.21, 150.70, 146.93, 139.99, 127.26, 124.04, 37.27, 36.30, 35.33, 20.22. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{13}\text{NO}_5\text{Na}^+$: 298.06822, found 298.0680.



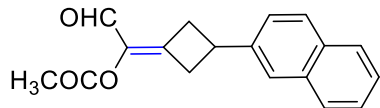
1-(3-(2,6-dimethylphenyl)cyclobutylidene)-2-oxoethyl acetate(3em)



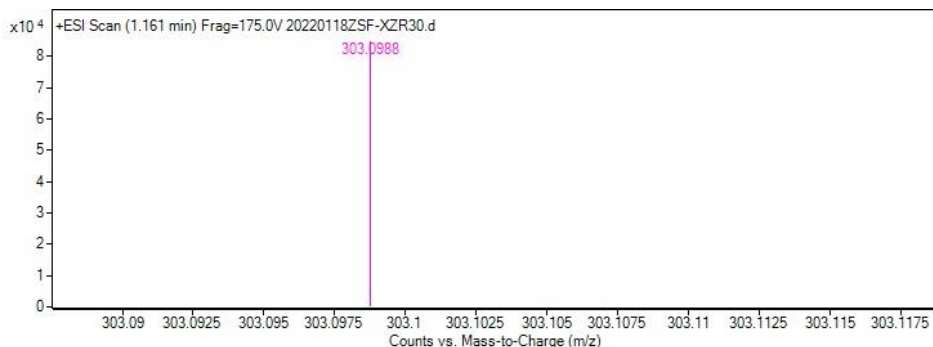
Yellow liquid, 20.2 mg, 36%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.51 (s, 1H), 7.10 – 7.02 (m, 2H), 6.98 (dd, J = 7.7, 1.9 Hz, 1H), 3.87 (p, J = 8.4 Hz, 1H), 3.74 – 3.60 (m, 1H), 3.36 – 3.23 (m, 2H), 3.07 (ddd, J = 18.3, 8.3, 3.4 Hz, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.91, 168.29, 153.43, 140.27, 139.65, 135.70, 132.64, 130.36, 127.39, 125.65, 36.43, 35.24, 33.09, 21.16, 20.25, 19.14. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{Na}^+$: 267.0991, found 267.0995.



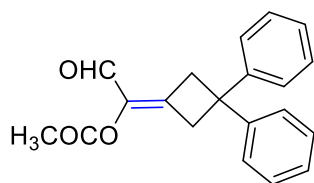
1-(3-(naphthalen-2-yl)cyclobutylidene)-2-oxoethyl acetate(3en)



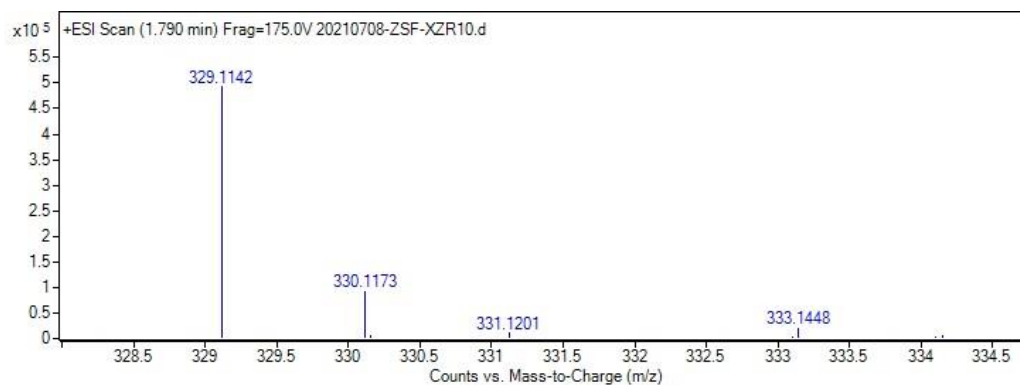
Yellow liquid, 20.2 mg, 36%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.53 (s, 1H), 7.95 – 7.77 (m, 4H), 7.69 (d, J = 1.8 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.41 (dd, J = 8.4, 1.9 Hz, 1H), 3.94 (p, J = 8.2 Hz, 1H), 3.76 (ddt, J = 15.5, 8.7, 3.6 Hz, 1H), 3.47 – 3.34 (m, 2H), 3.16 (ddd, J = 18.5, 7.7, 3.6 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.90, 168.28, 153.27, 140.59, 139.90, 133.37, 132.40, 128.63, 127.69, 127.66, 126.41, 125.82, 124.70, 124.61, 37.52, 36.39, 35.62, 20.27. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Na}^+$: 303.0991, found 303.0988.



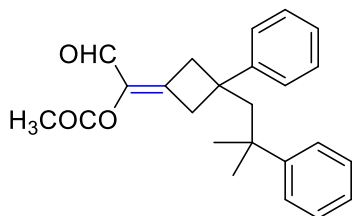
1-(3,3-diphenylcyclobutylidene)-2-oxoethyl acetate(3eo)



Yellow liquid, 39.2 mg, 64%, purified by chromatography (PE/EA = 10/1, Rf = 0.4); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 7.31 (d, J = 7.5 Hz, 4H), 7.28 – 7.23 (m, 4H), 7.21 (s, 2H), 3.96 (s, 2H), 3.65 (s, 2H), 2.24 (s, 3H). ^1H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 7.31 (d, J = 7.5 Hz, 4H), 7.28 – 7.23 (m, 4H), 7.21 (s, 2H), 3.96 (s, 2H), 3.65 (s, 2H), 2.24 (s, 3H). HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{20}\text{H}_{18}\text{O}_3\text{Na}^+$: 329.1148, found 329.1142.

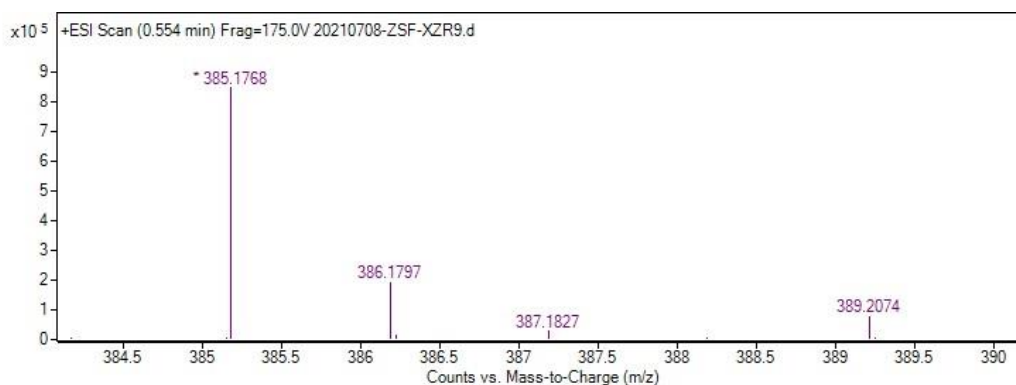


1-(3-(2-methyl-2-phenylpropyl)-3-phenylcyclobutylidene)-2-oxoethyl acetate (3ep)

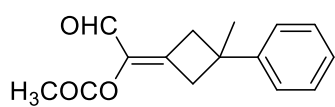


Yellow liquid, 43.5 mg, 60%, purified by chromatography (PE/EA = 10/1, R_f = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.25 (s, 1H), 7.29 – 7.19 (m, 8H), 7.19 – 7.12 (m, 2H), 7.12 – 7.05 (m, 2H), 3.22 (dd, *J* = 16.5, 3.1 Hz, 1H), 3.04 – 2.89 (m, 2H), 2.67 (dt, *J* = 17.0, 3.4 Hz, 1H), 2.37 (d, *J* = 4.8 Hz, 2H), 2.19 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.84, 168.15, 153.18, 148.19, 146.60, 140.05, 128.21, 128.07, 126.31, 126.21, 126.17, 125.77, 55.71, 44.13, 43.15, 41.23, 38.63, 30.03, 29.49, 20.22. HRMS (ESI) [M+Na]⁺ calculated for C₂₄H₂₆O₃Na⁺ : 385.1774, found

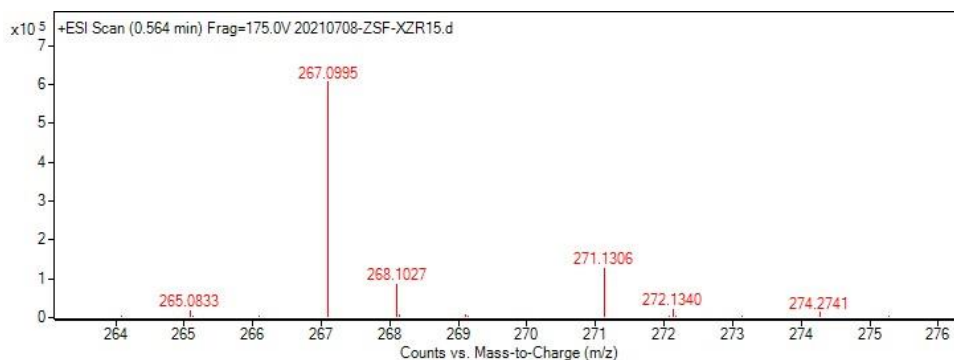
385.1768.



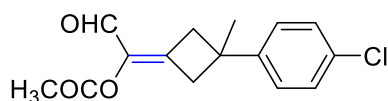
1-(3-methyl-3-phenylcyclobutylidene)-2-oxoethyl acetate(3eq)



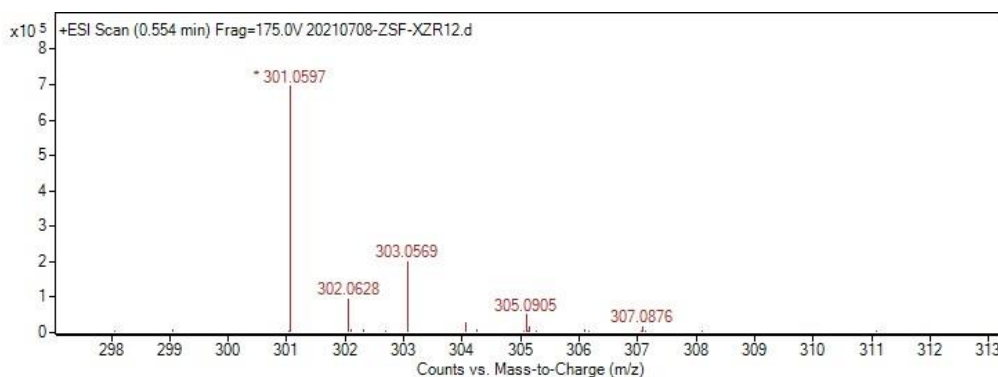
Yellow liquid, 36.2 mg, 74%, purified by chromatography (PE/EA = 10/1, R_f = 0.5); ¹H NMR (400 MHz, Chloroform-*d*) δ 9.52 (s, 1H), 7.43 – 7.34 (m, 2H), 7.26 (ddt, *J* = 8.9, 3.7, 1.7 Hz, 3H), 3.57 (dd, *J* = 16.1, 3.3 Hz, 1H), 3.41 – 3.23 (m, 2H), 2.99 (dt, *J* = 16.6, 3.4 Hz, 1H), 2.27 (s, 3H), 1.59 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 181.96, 168.19, 152.39, 148.51, 140.83, 128.59, 126.26, 124.82, 42.85, 41.65, 40.36, 30.61, 20.25. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₆O₃Na⁺ : 267.0991, found 267.0995.



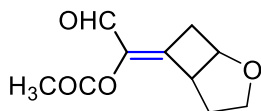
1-(3-(4-chlorophenyl)-3-methylcyclobutylidene)-2-oxoethyl acetate (3er)



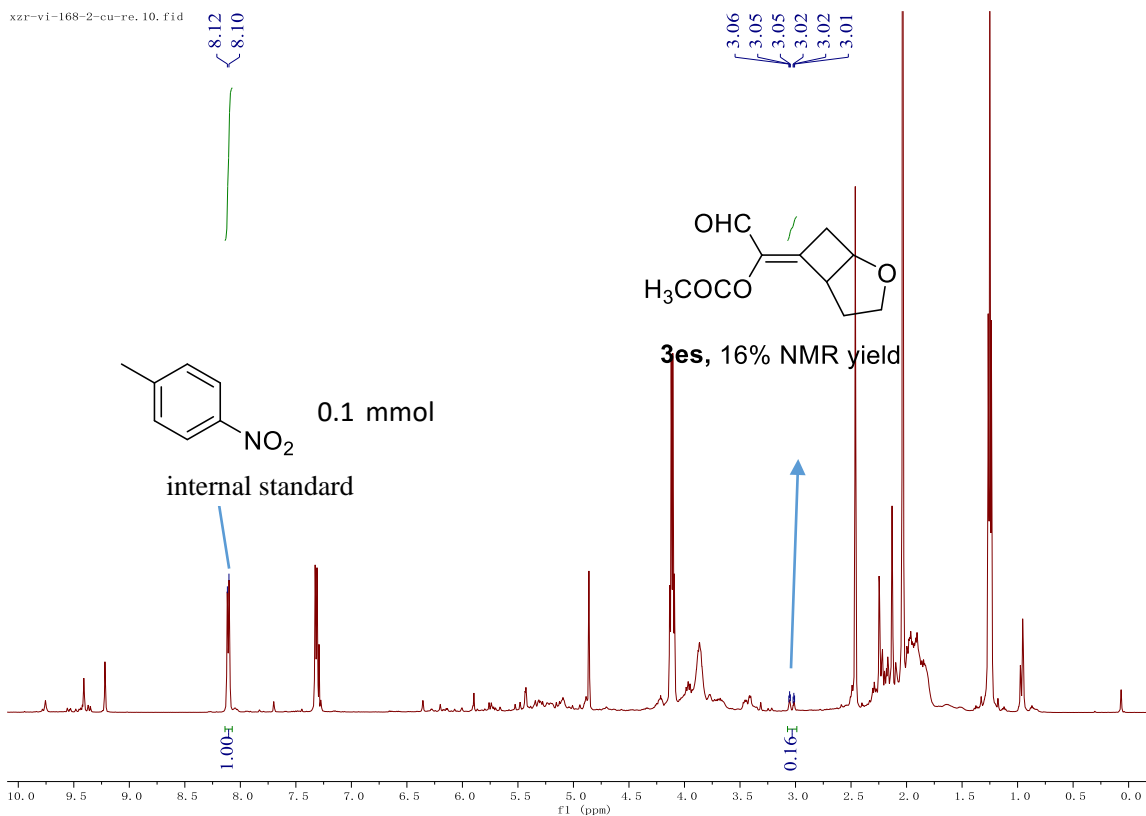
Yellow liquid, 38.4 mg, 69%, purified by chromatography (PE/EA = 10/1, R_f = 0.4); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.48 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 3.50 (dd, *J* = 16.4, 3.4 Hz, 1H), 3.32 (dt, *J* = 16.4, 3.5 Hz, 1H), 3.22 (dd, *J* = 17.2, 3.4 Hz, 1H), 2.96 (dt, *J* = 17.2, 3.5 Hz, 1H), 2.24 (s, 3H), 1.54 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.92, 168.17, 151.37, 146.95, 140.86, 132.08, 128.70, 126.34, 42.81, 41.65, 30.45, 20.23. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₅ClO₃Na⁺: 301.0602, found 301.0597.



(Z)-1-(2-oxabicyclo[3.2.0]heptan-6-ylidene)-2-oxoethyl acetate (3es)

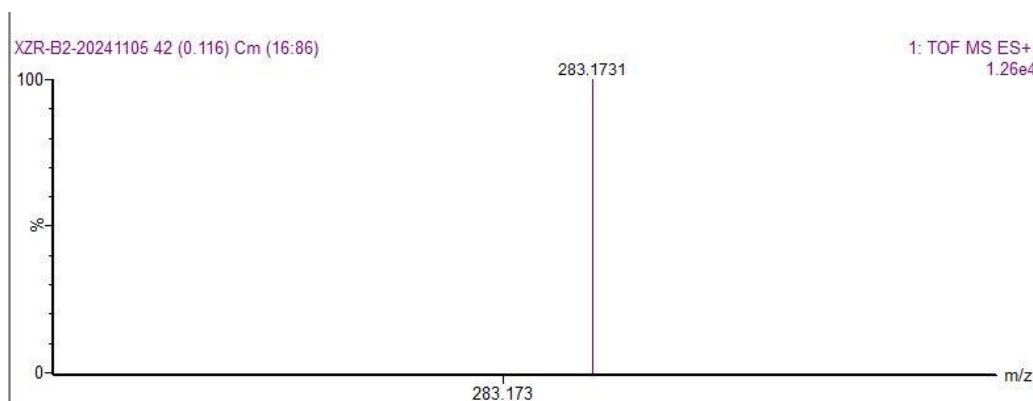


Yellow liquid, 6.3 mg, 16% (NMR yield with 4-nitrotoluene as internal standard. Note: **3es** was unstable during purification with silica gel.), purified by chromatography (PE/EA = 10/1, R_f = 0.4); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.41 (s, 1H), 4.87 (td, *J* = 6.0, 2.8 Hz, 1H), 4.24 – 4.15 (m, 1H), 3.97 – 3.92 (m, 1H), 3.77 (td, *J* = 4.6, 2.2 Hz, 1H), 3.43 (ddd, *J* = 18.9, 6.3, 2.8 Hz, 1H), 3.02 (ddd, *J* = 18.9, 3.9, 2.8 Hz, 1H), 2.25 (s, 3H), 1.99 – 1.95 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 182.02, 168.36, 153.53, 140.65, 75.22, 67.28, 48.22, 34.40, 29.87, 20.21.

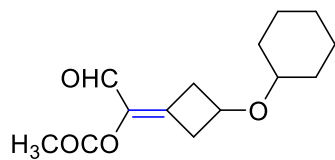


1-(3-((tert-butyldimethylsilyl)methyl)cyclobutylidene)-2-oxoethyl acetate (**3et**)

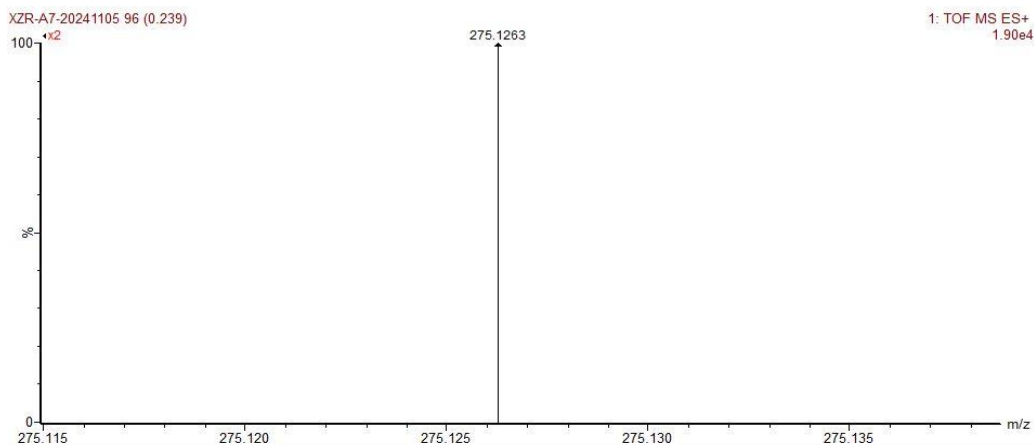
Colorless liquid, 22.3 mg, 40%, purified by chromatography (PE/EA = 20/1, R_f = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.47 (s, 1H), 3.45 (ddt, *J* = 15.9, 7.7, 3.7 Hz, 1H), 3.08 (ddt, *J* = 17.4, 7.7, 3.7 Hz, 1H), 2.81 (ddd, *J* = 16.6, 7.2, 3.6 Hz, 1H), 2.67 (dt, *J* = 15.3, 7.6 Hz, 1H), 2.53 (ddd, *J* = 17.5, 7.2, 3.6 Hz, 1H), 2.27 (s, 3H), 0.95 (dd, *J* = 7.7, 3.6 Hz, 2H), 0.91 (s, 9H), -0.00 (d, *J* = 1.9 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 181.85, 168.27, 155.11, 139.37, 39.23, 37.86, 28.51, 26.39, 21.03, 20.24, 16.38, -5.67, -5.70. HRMS (ESI) [M+H]⁺ calculated for C₁₅H₂₇ClO₃Si⁺: 283.1724, found 283.1731.



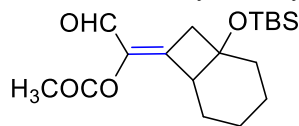
1-(3-(cyclohexyloxy)cyclobutylidene)-2-oxoethyl acetate (**3eu**)



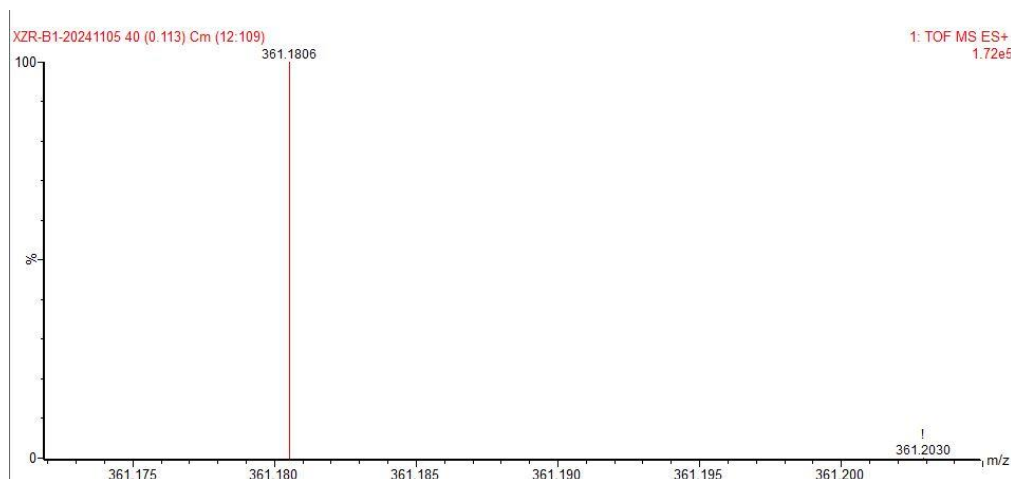
Colorless liquid, 10 mg, 20%, purified by chromatography (PE/EA = 15/1, Rf = 0.5); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 4.20 (p, J = 6.4 Hz, 1H), 3.51 – 3.38 (m, 1H), 3.24 (tt, J = 9.3, 3.9 Hz, 1H), 3.06 (dddt, J = 14.8, 8.9, 5.8, 3.2 Hz, 2H), 2.82 (ddd, J = 17.4, 6.1, 3.2 Hz, 1H), 2.16 (s, 3H), 1.87 – 1.61 (m, 6H), 1.61 – 1.40 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.97, 168.20, 149.40, 140.59, 66.71, 40.10, 38.52, 32.68, 32.66, 29.71, 25.61, 24.14, 20.24. . HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{20}\text{O}_4\text{Na}^+$: 275.1254, found 275.1263.



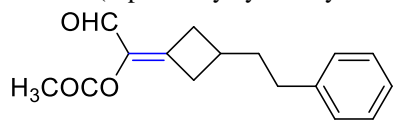
(E)-1-(1-((tert-butyldimethylsilyl)oxy)bicyclo[4.2.0]octan-7-ylidene)-2-oxoethyl acetate (**3ew**)



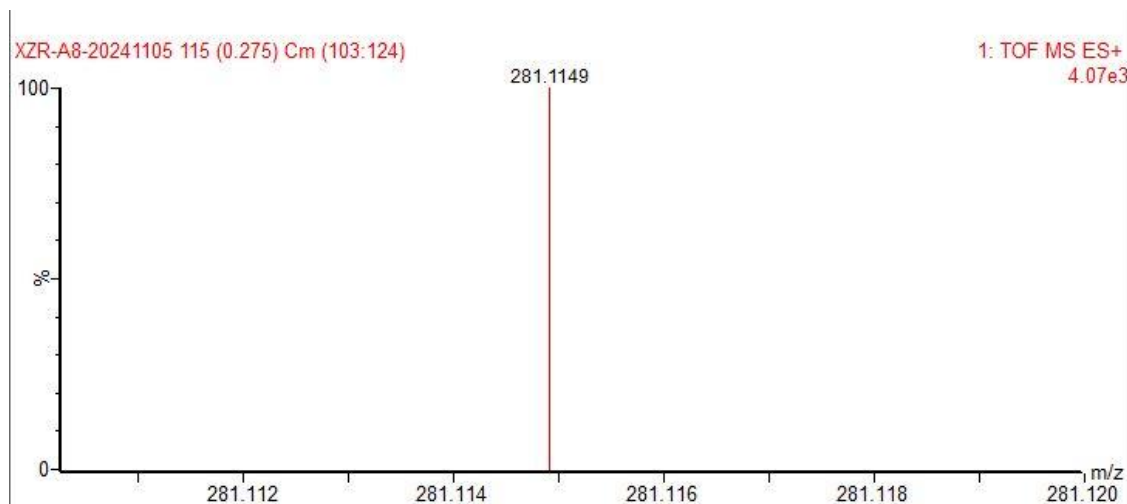
Colorless liquid, 14.2 mg, 21%, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^1H NMR (500 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 3.17 – 3.07 (m, 1H), 3.00 (dd, J = 14.9, 2.1 Hz, 1H), 2.88 (d, J = 14.9 Hz, 1H), 2.11 (s, 3H), 1.89 – 1.82 (m, 1H), 1.74 (dd, J = 14.3, 3.6 Hz, 1H), 1.59 – 1.29 (m, 6H), 0.77 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 182.42, 168.42, 152.22, 141.06, 70.26, 53.37, 44.08, 36.62, 25.61, 22.08, 21.67, 20.33, 20.25, 17.80, -2.84, -2.96. . HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{30}\text{O}_4\text{SiNa}^+$: 361.1805, found 361.1806.



2-oxo-1-(3-phenethylcyclobutylidene)ethyl acetate (**3ex**)



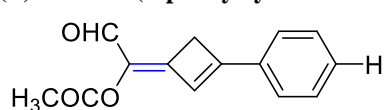
Colorless liquid, 5.2 mg, 10%, purified by chromatography (PE/EA = 20/1, R_f = 0.5); ¹H NMR (400 MHz, Chloroform-*d*) δ 9.45 (s, 1H), 7.31 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.20 – 7.14 (m, 2H), 3.35 (ddd, *J* = 17.1, 4.8, 3.0 Hz, 1H), 3.00 (dt, *J* = 9.4, 3.3 Hz, 1H), 2.82 (ddd, *J* = 16.9, 6.4, 3.9 Hz, 1H), 2.69 – 2.59 (m, 2H), 2.59 – 2.46 (m, 2H), 2.24 (s, 3H), 1.91 (q, *J* = 7.3 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.84, 168.25, 155.06, 141.43, 139.82, 128.47, 128.36, 126.03, 37.90, 35.64, 34.27, 33.47, 30.82, 29.72. HRMS (ESI) [M+Na]⁺ calculated for C₁₆H₁₈O₃Na⁺ : 281.1148, found 281.1149.



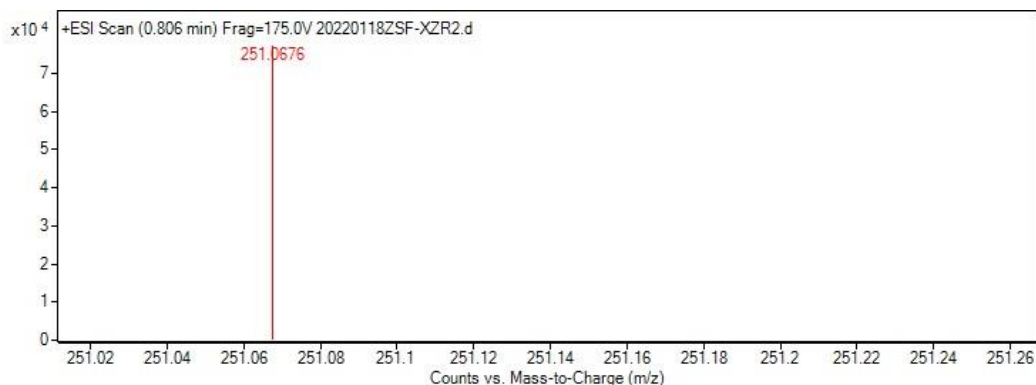
5. General procedure for tandem Rh(II)-catalyzed 1,3-acyloxy migration/[2 + 2] cycloaddition of propargylic esters with alkynes

To a 1,2-dichloroethane solution of **1** (1.0 mmol, 5.0 equiv, 3.0 mL) in Schlenk tube with a magnetic bar was added Rh₂(OPiv)₄ (0.002 mmol, 1 mol%, 1.3 mg) with various styrene derivatives **2** (0.2 mmol, 1.0 equiv) at 30 °C under N₂. The sealed tube was then stirred at 80 °C under nitrogen atmosphere for 36 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **5**.

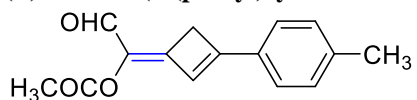
(*Z*)-2-oxo-1-(3-phenylcyclobut-2-en-1-ylidene)ethyl acetate (**5ea**)



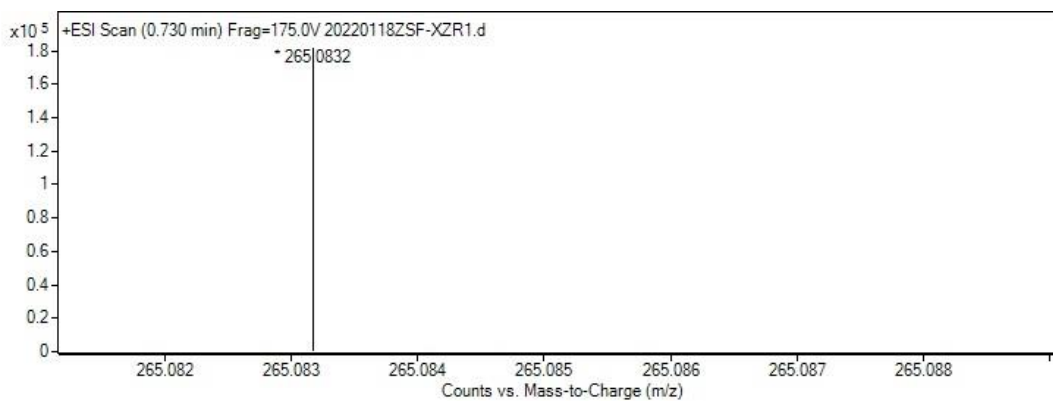
Yellow liquid, 28.3 mg, 62%, purified by chromatography (PE/EA = 10/1, R_f = 0.5); ¹H NMR (400 MHz, Chloroform-*d*) δ 9.46 (s, 1H), 7.58 – 7.54 (m, 2H), 7.49 – 7.45 (m, 3H), 6.77 (s, 1H), 3.77 – 3.65 (m, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 181.88, 168.64, 159.45, 146.85, 132.91, 131.97, 131.25, 128.96, 126.89, 125.45, 34.00, 20.39. HRMS (ESI) [M+Na]⁺ calculated for C₁₄H₁₂O₃Na⁺ : 251.0678, found 251.0676.



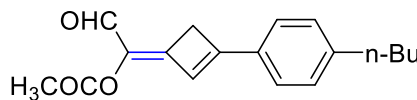
(Z)-2-oxo-1-(3-(p-tolyl)cyclobut-2-en-1-ylidene)ethyl acetate (5eb)



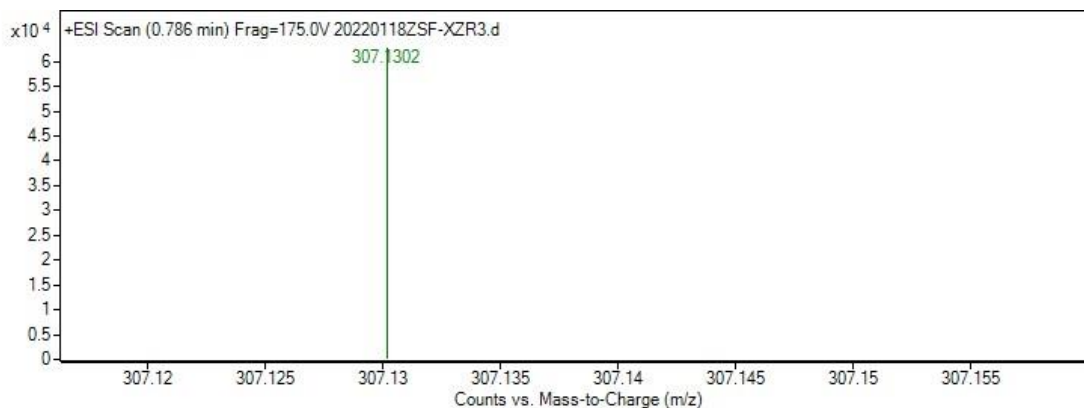
Yellow liquid, 42.1 mg, 87%, purified by chromatography (PE/EA = 10/1, R_f = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.41 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.68 (s, 1H), 3.63 (s, 2H), 2.40 (s, 3H), 2.29 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.77, 168.64, 159.69, 147.30, 142.05, 132.68, 129.70, 129.33, 126.95, 124.46, 33.99, 21.74, 20.37. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₄O₃Na⁺ : 265.0835, found 265.0832.



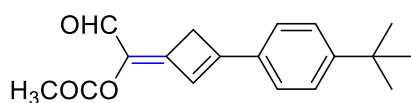
(Z)-1-(3-(4-butylphenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate (5ec)



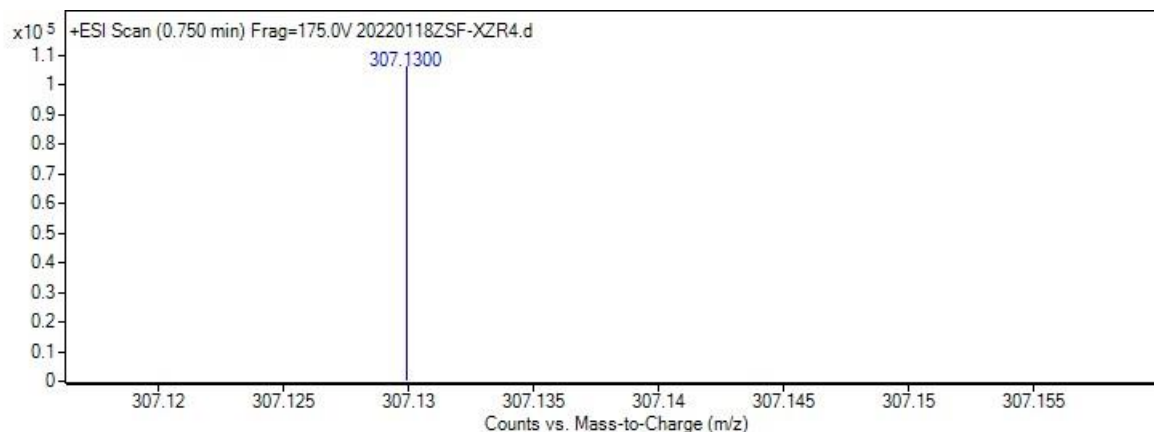
Yellow liquid, 49.4 mg, 87%, purified by chromatography (PE/EA = 10/1, R_f = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.42 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 1H), 3.64 (s, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.29 (s, 3H), 1.65 – 1.57 (m, 2H), 1.36 (q, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.76, 168.64, 159.73, 147.33, 147.06, 132.67, 129.52, 129.07, 126.99, 124.46, 35.79, 34.00, 33.31, 22.31, 20.37, 13.89. HRMS (ESI) [M+Na]⁺ calculated for C₁₈H₂₀O₃Na⁺ : 307.1304, found 307.1302.



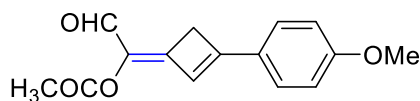
(Z)-1-(3-(4-(tert-butyl)phenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5ed)



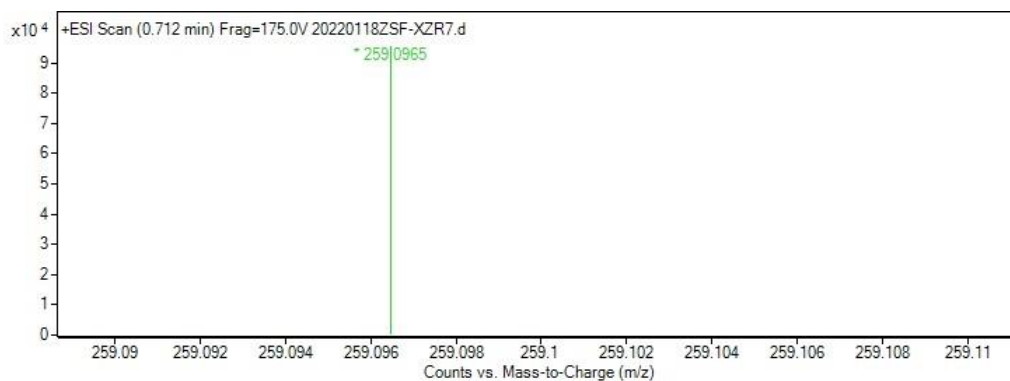
Yellow liquid, 44.3 mg, 78%, purified by chromatography (PE/EA = 10/1, R_f = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.42 (s, 1H), 7.48 (s, 5H), 6.70 (s, 1H), 3.65 (s, 2H), 2.30 (s, 3H), 1.34 (s, 9H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.81, 168.66, 159.64, 155.14, 147.38, 132.69, 129.28, 126.86, 125.96, 124.61, 35.15, 34.02, 31.11, 20.39. HRMS (ESI) [M+Na]⁺ calculated for C₁₈H₂₀O₃Na⁺ : 307.1304, found 307.1300.



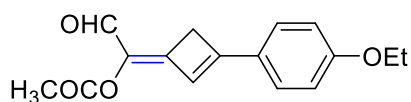
(Z)-1-(3-(4-methoxyphenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate (5ee)



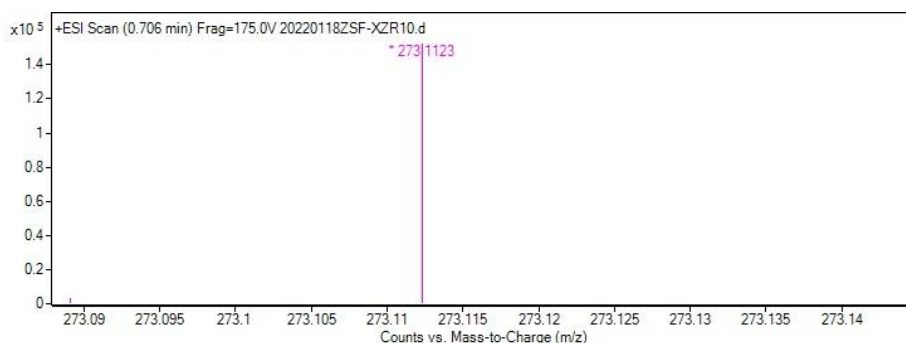
Yellow liquid, 44.9 mg, 87%, purified by chromatography (PE/EA = 5/1, R_f = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.39 (d, *J* = 1.9 Hz, 1H), 7.51 – 7.44 (m, 2H), 6.99 – 6.93 (m, 2H), 6.60 (d, *J* = 1.5 Hz, 1H), 3.86 (d, *J* = 1.7 Hz, 3H), 3.64 – 3.59 (m, 2H), 2.29 (d, *J* = 1.4 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.62, 168.67, 162.26, 159.50, 147.61, 132.34, 128.91, 124.87, 123.04, 114.49, 55.50, 34.01, 20.38. HRMS (ESI) [M+H]⁺ calculated for C₁₅H₁₅O₄⁺ : 259.0964, found 259.0965.



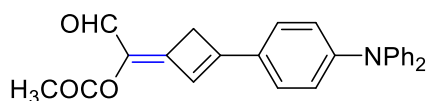
(Z)-1-(3-(4-ethoxyphenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5ef)



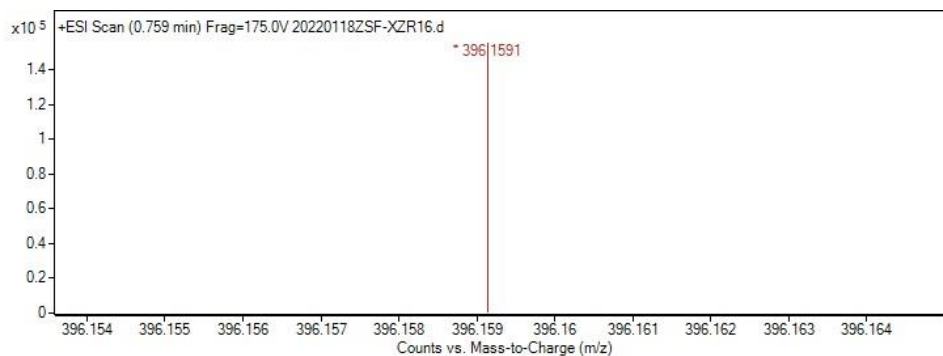
Yellow liquid, M.P: 97-98 °C, 49.5 mg, 91%, purified by chromatography (PE/EA = 5/1, Rf = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.39 (s, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.61 (s, 2H), 2.29 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.61, 168.67, 161.69, 159.61, 147.70, 132.30, 128.93, 124.67, 122.89, 114.93, 63.81, 34.00, 20.37, 14.66. HRMS (ESI) [M+H]⁺ calculated for C₁₆H₁₇O₄⁺ : 273.1121, found 273.1123.



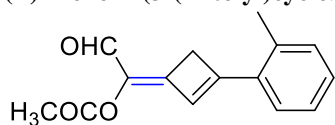
(Z)-1-(3-(4-(diphenylamino)phenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5eg)



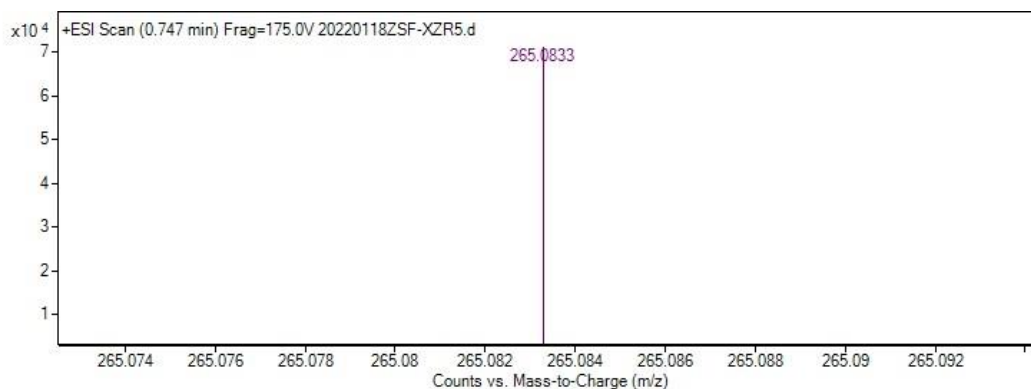
Yellow solid, M.P: 115-116 °C, 48.2 mg, 61%, purified by chromatography (PE/EA = 3/1, Rf = 0.4); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.38 (s, 1H), 7.39 – 7.29 (m, 6H), 7.18 – 7.10 (m, 6H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.56 (s, 1H), 3.60 (s, 2H), 2.28 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.48, 168.71, 159.42, 150.81, 147.95, 146.47, 132.24, 129.65, 128.35, 125.85, 124.66, 124.47, 122.61, 120.67, 34.01, 20.42. HRMS (ESI) [M+H]⁺ calculated for C₂₆H₂₂NO₃⁺ : 396.1593, found 396.1591.



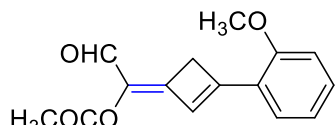
(Z)-2-oxo-1-(3-(m-tolyl)cyclobut-2-en-1-ylidene)ethyl acetate(5eh)



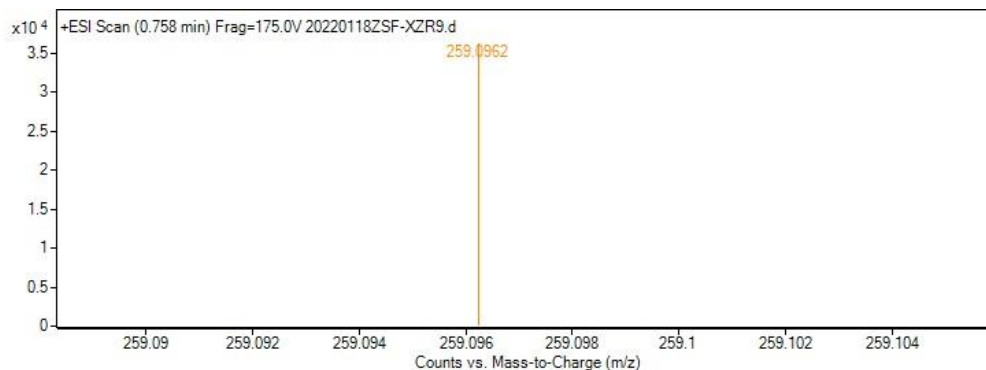
Yellow liquid, 35.3 mg, 73%, purified by chromatography (PE/EA = 10/1, Rf = 0.5). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.43 (s, 1H), 7.35 – 7.32 (m, 3H), 7.29 – 7.25 (m, 1H), 6.72 (s, 1H), 3.65 (s, 2H), 2.40 (s, 3H), 2.30 (s, 3H). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.43 (s, 1H), 7.35 – 7.32 (m, 3H), 7.29 – 7.25 (m, 1H), 6.72 (s, 1H), 3.65 (s, 2H), 2.40 (s, 3H), 2.30 (s, 3H). HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₄O₃Na⁺ : 265.0835, found 265.0833.



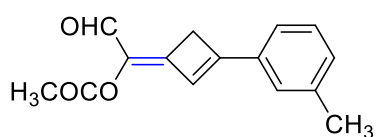
(Z)-1-(3-(3-methoxyphenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5ei)



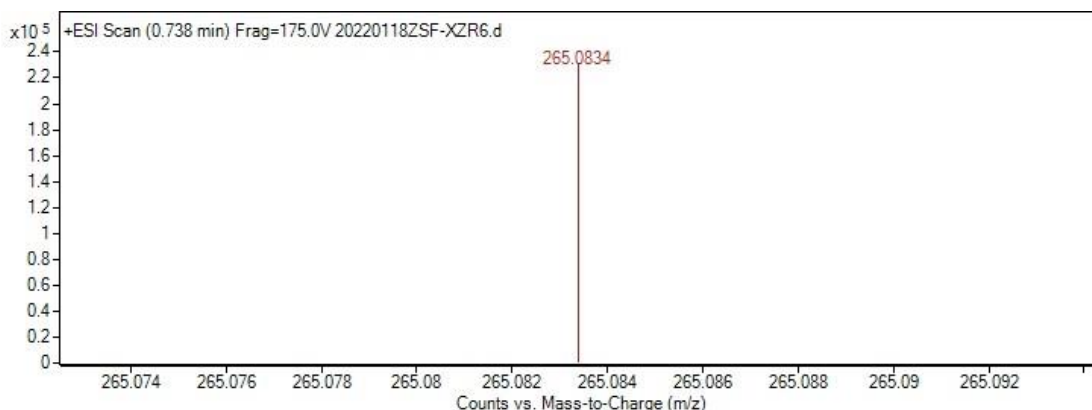
Yellow solid, M.P: 95-96 °C, 50.0 mg, 97%, purified by chromatography (PE/EA = 5/1, Rf = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.40 (d, *J* = 1.9 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.31 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 1.6 Hz, 1H), 3.92 (d, *J* = 1.9 Hz, 3H), 3.65 – 3.62 (m, 2H), 2.30 (d, *J* = 1.5 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.78, 168.66, 159.89, 156.22, 148.84, 132.84, 132.49, 129.39, 129.07, 121.06, 120.64, 110.89, 55.41, 34.89, 20.40. HRMS (ESI) [M+H]⁺ calculated for C₁₅H₁₅O₄⁺ : 259.0965, found 259.0962.



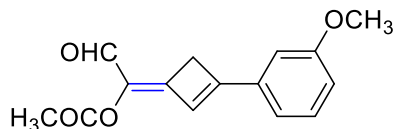
(Z)-2-oxo-1-(3-(m-tolyl)cyclobut-2-en-1-ylidene)ethyl acetate(5ej)



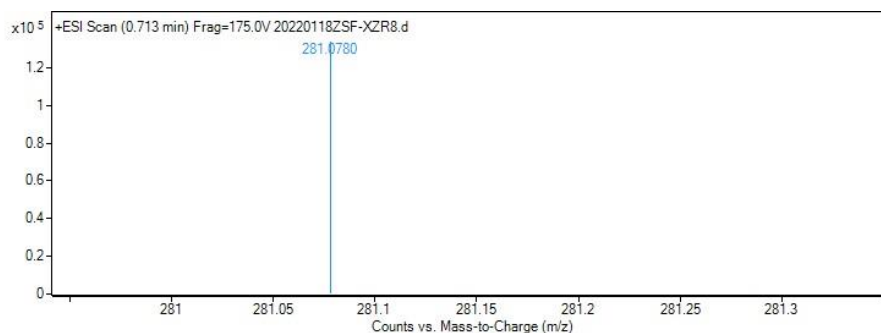
Yellow liquid, 29.0 mg, 60%, purified by chromatography (PE/EA = 10/1, Rf = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.43 (s, 1H), 7.34 (d, *J* = 2.8 Hz, 3H), 6.72 (s, 1H), 3.65 (s, 2H), 2.40 (s, 3H), 2.30 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.83, 168.63, 159.74, 147.05, 138.70, 132.82, 132.15, 131.92, 128.84, 127.45, 125.26, 124.10, 34.01, 21.29, 20.37. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₄O₃Na⁺ : 265.0835, found 265.0834.



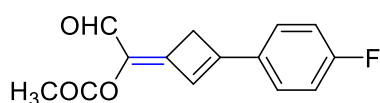
(Z)-1-(3-(3-methoxyphenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5ek)



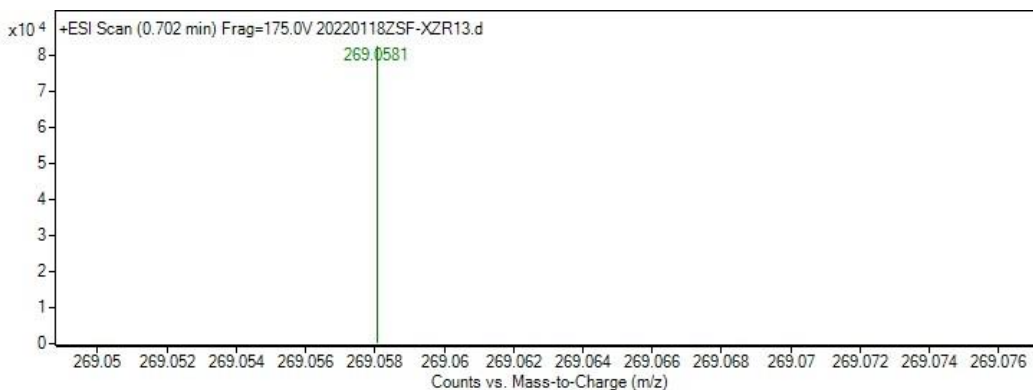
Yellow solid, M.P: 93-94 °C, 41.3mg, 80%, purified by chromatography (PE/EA = 5/1, Rf = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.42 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.03 – 6.98 (m, 2H), 3.84 (s, 3H), 3.64 (s, 2H), 2.29 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.87, 168.61, 159.92, 159.36, 146.76, 133.23, 132.95, 130.02, 125.74, 119.51, 117.14, 111.76, 55.38, 34.04, 20.36. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₄O₄Na⁺ : 281.0784, found 281.0780.



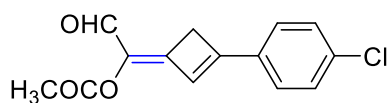
(Z)-1-(3-(4-fluorophenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5el)



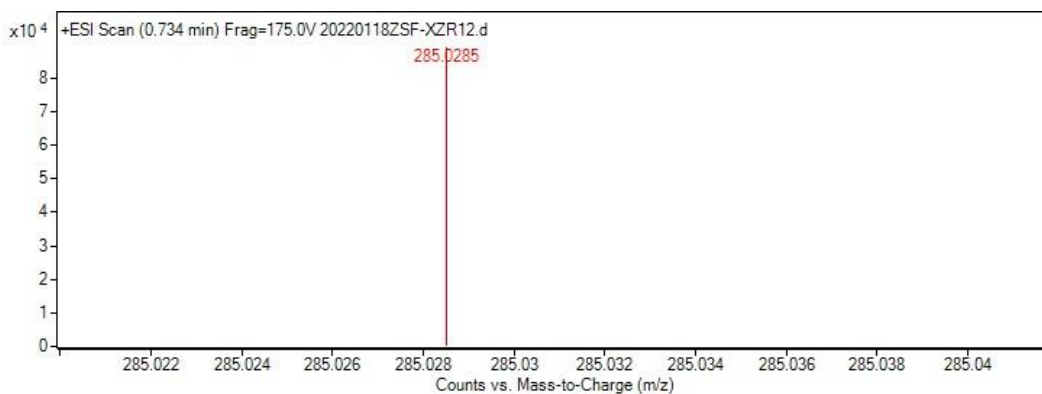
Yellow solid, M.P: 125-126 °C, 26.0 mg, 53%, purified by chromatography (PE/EA = 10/1, Rf = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.43 (s, 1H), 7.63 – 7.45 (m, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.69 (s, 1H), 3.66 (s, 2H), 2.30 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.82, 168.61, 164.40 (d, *J* = 253.9 Hz), 158.10, 146.41, 132.90, 129.05 (d, *J* = 8.9 Hz), 128.45 (d, *J* = 3.3 Hz), 125.01 (d, *J* = 2.3 Hz), 116.31 (d, *J* = 22.2 Hz), 34.07, 20.36. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -106.89. HRMS (ESI) [M+Na]⁺ calculated for C₁₄H₁₁FO₃Na⁺ : 269.0584, found 269.0581.



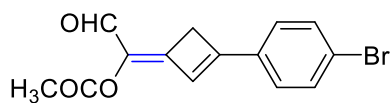
(Z)-1-(3-(4-chlorophenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5em)



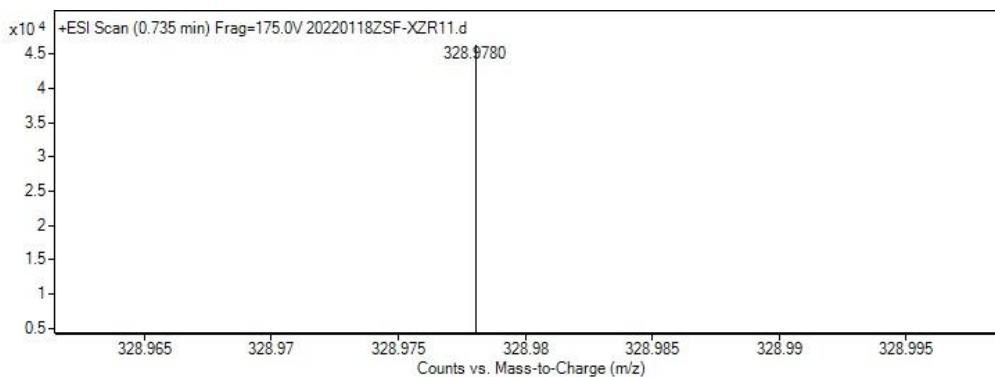
Yellow solid, M.P: 96-97 °C, 40.0 mg, 61%, purified by chromatography (PE/EA = 10/1, R_f = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 6.36 (s, 1H), 4.55 (s, 4H), 4.20 (s, 5H), 3.56 (s, 2H), 2.28 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.84, 168.58, 157.81, 146.15, 137.29, 133.11, 130.46, 129.33, 128.05, 125.95, 34.00, 20.36. HRMS (ESI) [M+Na]⁺ calculated for C₁₄H₁₁ClO₃Na⁺ : 285.0289, found 285.0285.



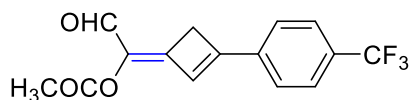
(Z)-1-(3-(4-bromophenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5en)



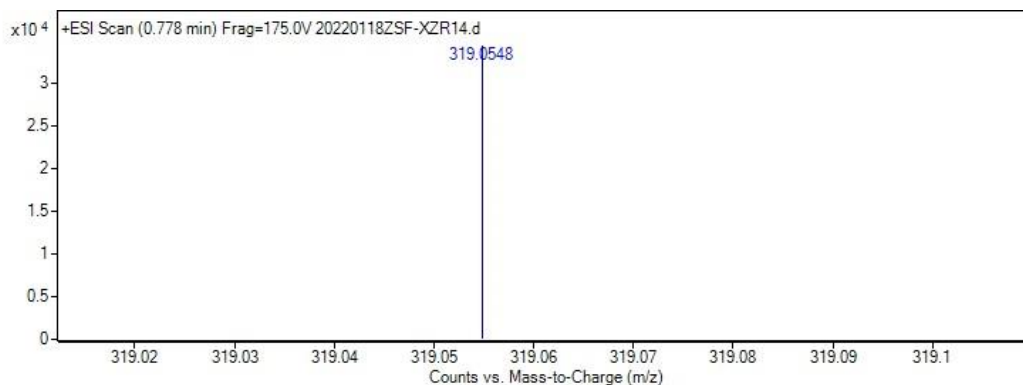
Yellow solid, M.P: 90-91 °C, 54.5 mg, 89%, purified by chromatography (PE/EA = 10/1, R_f = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.43 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.75 (s, 1H), 3.66 (s, 2H), 2.30 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.85, 168.55, 157.85, 146.10, 133.14, 132.28, 130.85, 128.19, 126.10, 125.73, 33.96, 20.36. HRMS (ESI) [M+Na]⁺ calculated for C₁₄H₁₁BrO₃Na⁺ : 328.9784, found 328.9780.



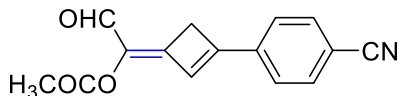
(Z)-2-oxo-1-(3-(4-(trifluoromethyl)phenyl)cyclobut-2-en-1-ylidene)ethyl acetate(5eo)



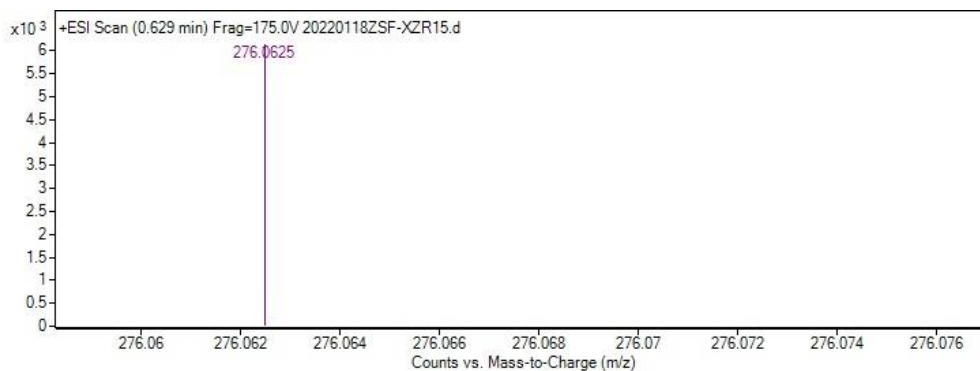
Yellow solid, M.P: 160-161 °C, 26.1 mg, 44%, purified by chromatography (PE/EA = 10/1, Rf = 0.5); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.47 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 6.86 (s, 1H), 3.72 (s, 2H), 2.31 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.91, 168.52, 157.00, 145.38, 135.09, 133.57, 127.79, 126.93, 126.25, 125.96 (q, *J* = 3.8 Hz), 34.05, 20.35. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -62.99. . HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₁F₃O₃Na⁺ : 319.0552, found 319.0548.



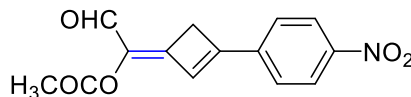
(Z)-1-(3-(4-cyanophenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5ep)



Yellow liquid, 22.3 mg, 44%, purified by chromatography (PE/EA = 5/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.47 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 6.89 (s, 1H), 3.72 (s, 2H), 2.31 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.98, 168.51, 156.18, 144.84, 135.79, 133.85, 132.69, 128.89, 127.04, 118.20, 113.94, 34.01, 20.36. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₁NO₃Na⁺ : 276.0631, found 276.0625.

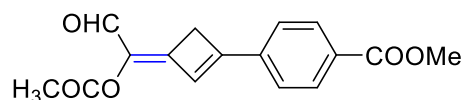


(Z)-1-(3-(4-nitrophenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate (5eq)

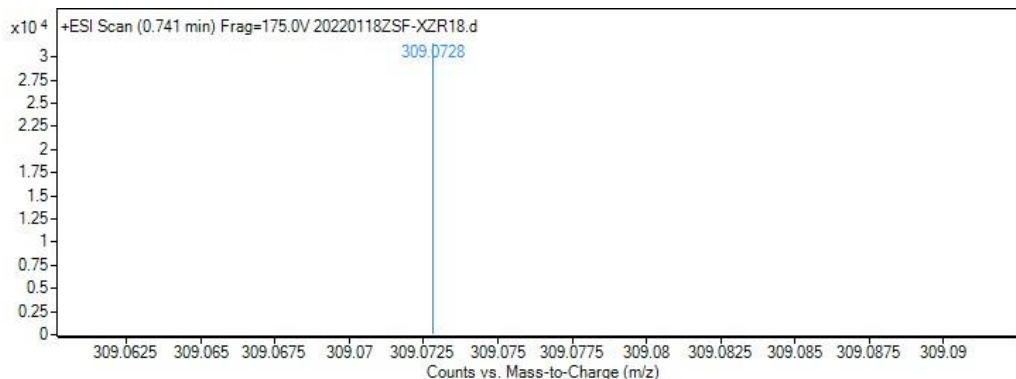


Yellow liquid, 33.9 mg, 62%, purified by chromatography (PE/EA = 5/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.41 (s, 1H), 8.23 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 1H), 3.68 (s, 2H), 2.24 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 182.02, 168.50, 155.70, 148.68, 144.67, 137.55, 133.98, 129.53, 127.39, 124.29, 34.14, 20.34.

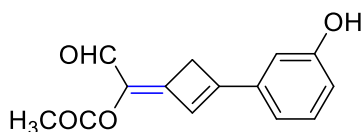
Methyl (Z)-4-(3-(1-acetoxy-2-oxoethylidene)cyclobut-1-en-1-yl)benzoate (5er)



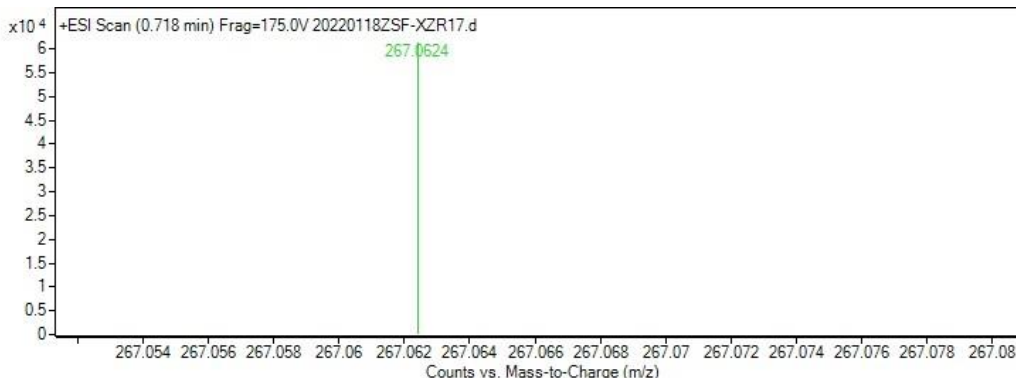
Yellow solid, M.P: 95-96 °C, 40.1mg, 70%, purified by chromatography (PE/EA = 5/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.46 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 6.85 (s, 1H), 3.95 (s, 3H), 3.71 (s, 2H), 2.31 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.96, 168.55, 166.24, 157.63, 145.82, 135.77, 133.47, 131.93, 130.11, 127.75, 126.64, 52.40, 34.04, 20.35. HRMS (ESI) [M+Na]⁺ calculated for C₁₆H₁₄O₅Na⁺ : 309.0733, found 309.0728.



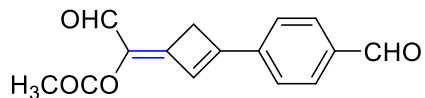
(Z)-1-(3-(3-hydroxyphenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate (5es)



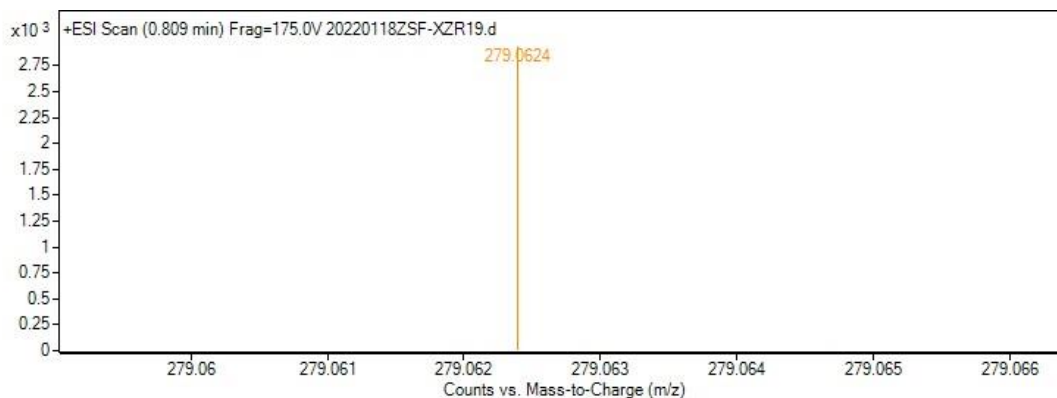
Yellow solid, M.P: 118-119 °C, 29.8 mg, 61%, purified by chromatography (PE/EA = 3/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 7.30 – 7.25 (m, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.94 (dd, *J* = 6.2, 2.8 Hz, 2H), 6.66 (s, 1H), 3.48 (s, 2H), 2.31 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 182.24, 169.40, 159.99, 156.64, 147.87, 133.14, 132.73, 130.12, 125.44, 119.31, 118.87, 113.45, 33.92, 20.43. HRMS (ESI) [M+Na]⁺ calculated for C₁₄H₁₂O₄Na⁺ : 267.0628, found 267.0624.



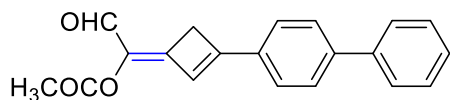
(Z)-1-(3-(4-formylphenyl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate (5et)



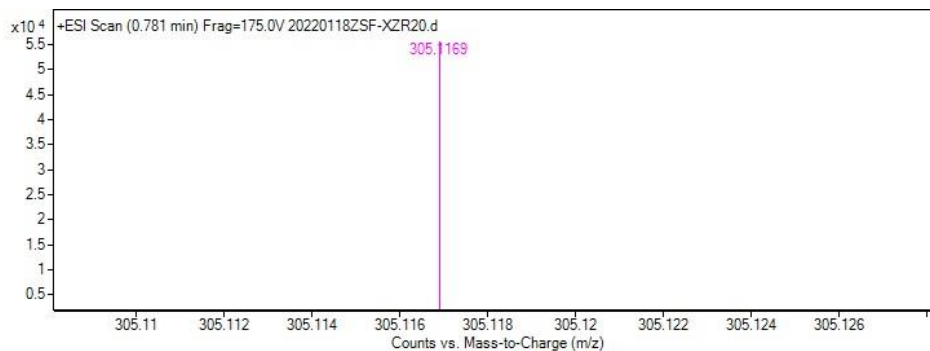
Yellow solid, M.P: 148-149 °C, 33.3 mg, 65%, purified by chromatography (PE/EA = 5/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 10.06 (s, 1H), 9.47 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 6.90 (s, 1H), 3.74 (s, 2H), 2.31 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 191.25, 181.98, 168.53, 157.11, 145.40, 137.45, 137.10, 133.68, 130.16, 128.57, 127.21, 34.09, 20.36. HRMS (ESI) [M+Na]⁺ calculated for C₁₅H₁₂O₄Na⁺ : 279.0628, found 279.0624.



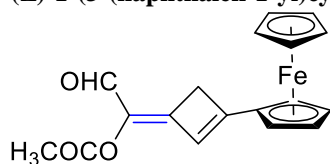
(Z)-1-(3-((1,1'-biphenyl)-4-yl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate (5eu)



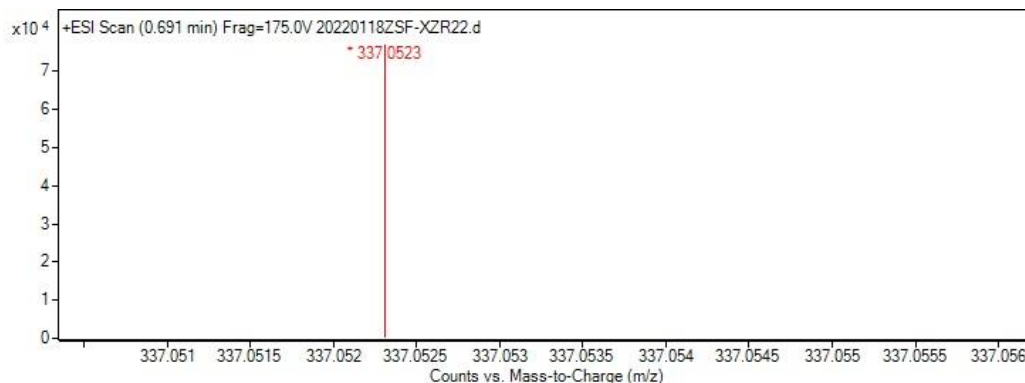
Yellow solid, M.P: 156-157 °C, 35.9 mg, 59%, purified by chromatography (PE/EA = 10/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.36 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.53 (dd, *J* = 14.1, 7.9 Hz, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 1H), 6.68 (s, 1H), 3.60 (s, 2H), 2.23 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.88, 168.69, 159.09, 147.04, 143.96, 139.87, 132.88, 130.82, 129.02, 128.20, 127.58, 127.46, 127.10, 125.40, 34.06, 20.41. HRMS (ESI) [M+H]⁺ calculated for C₂₀H₁₇O₃⁺ : 305.1172, found 305.1169.



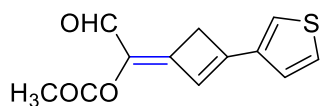
(Z)-1-(3-(naphthalen-1-yl)cyclobut-2-en-1-ylidene)-2-oxoethyl acetate(5ev)



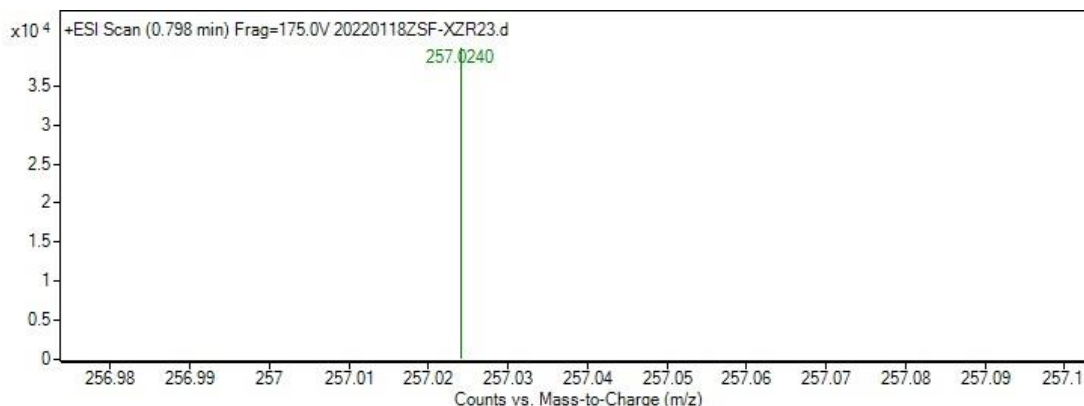
Red solid, M.P: 115-116 °C, 34.3 mg, 51%, purified by chromatography (PE/EA = 10/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 6.36 (s, 1H), 4.55 (s, 4H), 4.20 (s, 5H), 3.56 (s, 2H), 2.28 (s, 3H). ¹H NMR (500 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 6.36 (s, 1H), 4.55 (s, 4H), 4.20 (s, 5H), 3.56 (s, 2H), 2.28 (s, 3H). HRMS (ESI) [M+H]⁺ calculated for C₁₈H₁₇FeO₃⁺ : 337.0522, found 337.0523.



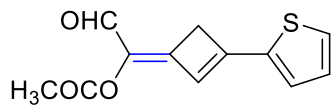
(Z)-2-oxo-1-(3-(thiophen-3-yl)cyclobut-2-en-1-ylidene)ethyl acetate (5ew)



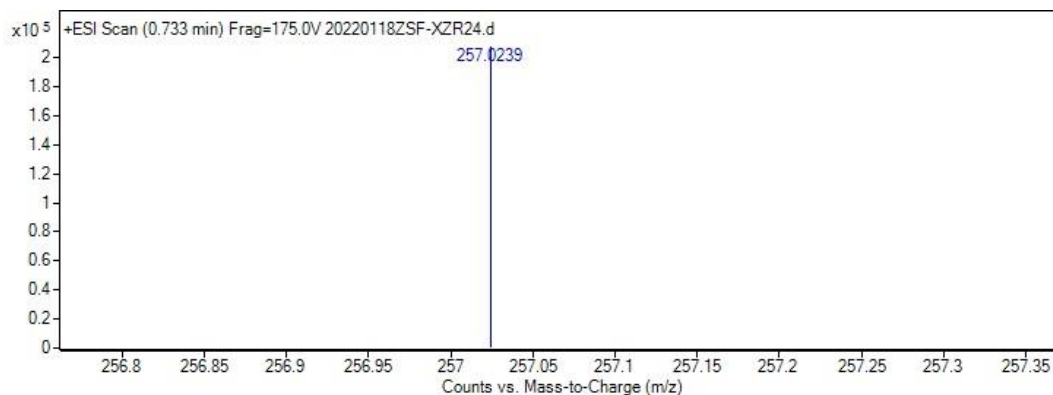
Yellow solid, M.P: 150-151 °C, 43.1 mg, 92%, purified by chromatography (PE/EA = 10/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.40 (s, 1H), 7.59 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.40 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.31 – 7.26 (m, 1H), 6.50 (s, 1H), 3.64 (s, 2H), 2.29 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.73, 168.60, 153.75, 147.80, 135.36, 132.97, 127.97, 127.45, 125.55, 124.32, 34.78, 20.36. HRMS (ESI) [M+Na]⁺ calculated for C₁₂H₁₀O₃SNa⁺ : 257.0243, found 257.0240.



(Z)-2-oxo-1-(3-(thiophen-2-yl)cyclobut-2-en-1-ylidene)ethyl acetate (5ex)

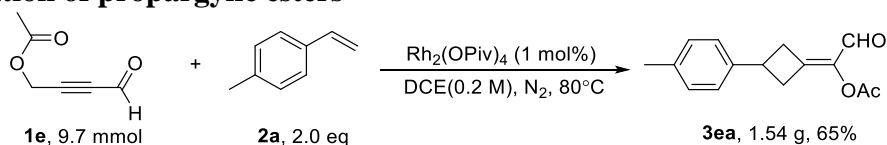


Yellow solid, M.P: 150-151 °C, 41.2 mg, 88%, purified by chromatography (PE/EA = 10/1, Rf = 0.6); ¹H NMR (500 MHz, Chloroform-*d*) δ 9.38 (s, 1H), 7.57 (d, *J* = 5.0 Hz, 1H), 7.32 (d, *J* = 3.7 Hz, 1H), 7.13 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.50 (s, 1H), 3.68 (s, 2H), 2.28 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 181.59, 168.57, 152.00, 147.39, 136.17, 132.95, 131.37, 129.96, 128.62, 123.74, 35.39, 20.34. HRMS (ESI) [M+Na]⁺ calculated for C₁₂H₁₀O₃SNa⁺ : 257.0243, found 257.0239.



6. Gram-scale reaction and synthetic applications

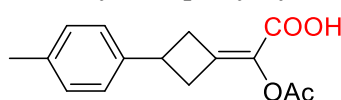
6.1 Gram-scale reaction of tandem Rh(II)-catalyzed 1,3-acyl migration/[2 + 2] cycloaddition of propargylic esters



Procedure for gram-scale reaction: To a 1,2-dichloroethane solution of **1e** (9.7 mmol, 30 mL) in Schlenk tube with a magnetic bar was added $\text{Rh}_2(\text{OPiv})_4$ (0.097 mmol, 1 mol%, 59.2 mg) with 4-methylstyrene **2a** (2.0 equiv) at 30°C under N_2 . The sealed tube was then stirred at 80°C under nitrogen atmosphere for 96 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 30:1) to afford the desired product **3ea** (1.54 g, 65%).

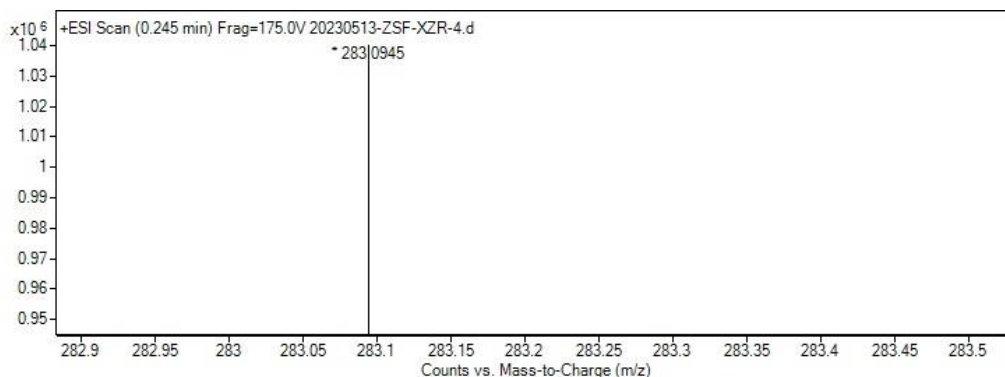
6.2 The derivatization of alkylidenecyclobutanes:

2-acetoxy-2-(3-(p-tolyl)cyclobutylidene)acetic acid (**6a**)⁵

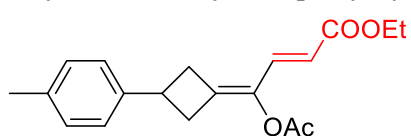


The substrates **3e** (48.8 mg, 0.2 mmol) was dissolved in tBuOH (1.5 mL) and H_2O (0.5 mL) at rt, NaClO_2 (0.6 mmol, 3.0 equiv), KH_2PO_4 (0.8 mmol, 4.0 equiv) and 2-methylbut-2-ene (2 mmol, 10.0 equiv) was added into the solution and then stirred for overnight monitored by TLC (SiO_2 , dichloromethane / MeOH = 20:1). After completed, the reaction was diluted with DCM and quenched with water (30 mL). The layers were separated and the aqueous phase was extracted with DCM (3×5 mL). The combined organic layers were washed with brine (3 mL), dried over anhydrous Na_2SO_4 , filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum dichloromethane / MeOH = 20:1) to afford the desired product **6a**. (Yellow solid, 28.1 mg, 54%).

Purified by chromatography (DCM / MeOH = 20:1, R_f = 0.5). Colorless solid, M.P: $89-90^\circ\text{C}$. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.07 (s, 4H), 3.55 (p, J = 8.9 Hz, 2H), 3.25 – 3.05 (m, 2H), 2.88 – 2.72 (m, 1H), 2.26 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.95, 167.09, 150.48, 141.05, 136.14, 130.67, 129.25, 126.26, 39.29, 37.10, 34.74, 21.03, 20.30. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{16}\text{O}_4\text{Na}^+$: 283.0941, found 283.0945.



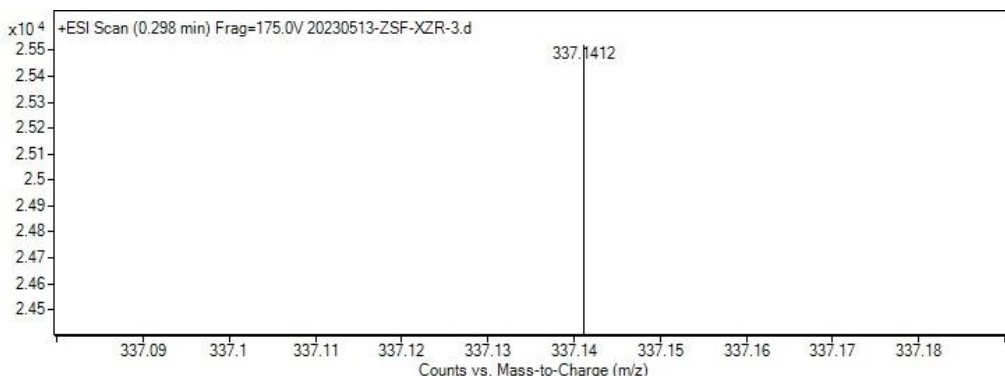
Ethyl (E)-4-acetoxy-4-(3-(p-tolyl)cyclobutylidene)but-2-enoate (**6b**)



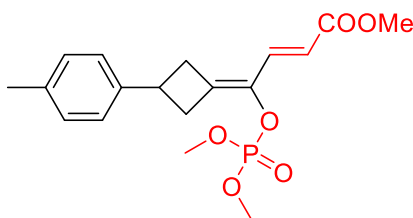
Under N_2 atmosphere, the substrates **3e** (48.8 mg, 0.2 mmol) was dissolved THF at 0°C , NaH (0.2 mmol, 1.0 eq) was added into the solution and then stirred for 30 min. Then, $\text{Ph}_3\text{P}=\text{CHCOOEt}$ was added into the solution and stirred for 2 h and monitored by TLC (SiO_2 , petroleum ether/ethyl acetate = 3:1). After completed, the reaction was quenched with water (30 mL) and diluted with EA. The layers were separated and the aqueous phase was extracted with EA (3×2 mL). The combined organic layers were washed with brine (3 mL), dried over anhydrous Na_2SO_4 , filtrated and concentrated under reduced pressure. The residue was purified by silica

gel chromatography (petroleum ether/ethyl acetate = 3:1) to afford the desired product **6b**. (Yellow liquid, 62.3 mg, 99%).

Purified by chromatography (PE /EA = 3:1, Rf = 0.5). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 15.5 Hz, 1H), 7.14 (d, *J* = 3.6 Hz, 4H), 5.75 (d, *J* = 15.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.60 (p, *J* = 8.1 Hz, 1H), 3.40 (ddt, *J* = 15.4, 8.7, 3.1 Hz, 1H), 3.07 (dddd, *J* = 27.5, 16.5, 8.1, 3.4 Hz, 2H), 2.82 (ddd, *J* = 17.4, 7.6, 3.7 Hz, 1H), 2.32 (s, 3H), 2.22 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 167.98, 166.77, 141.21, 140.17, 137.66, 136.10, 134.61, 129.23, 126.30, 115.44, 60.51, 36.91, 36.70, 34.31, 21.03, 20.43, 14.32. HRMS (ESI) [M+Na]⁺ calculated for C₁₉H₂₂O₄Na⁺: 337.1410, found 337.1412.



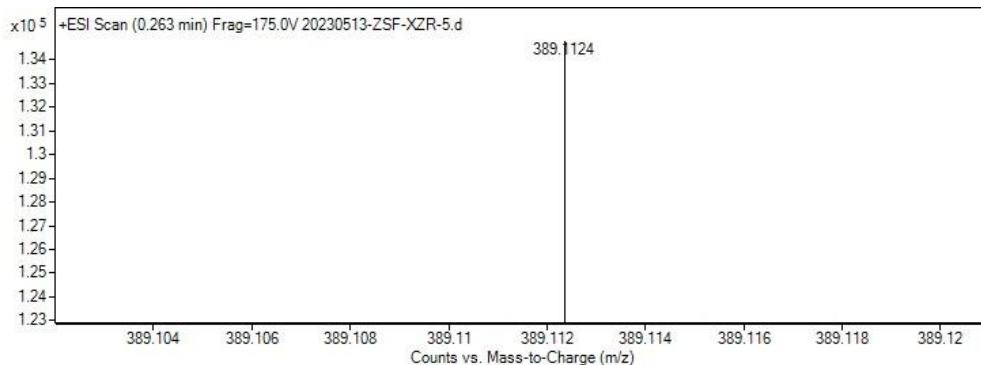
Methyl (E)-4-((dimethoxyphosphoryl)oxy)-4-(3-(p-tolyl)cyclobutylidene)but-2-enoate (**6c**)⁶



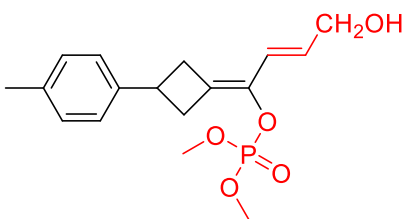
Under N₂ atmosphere, the substrates **3e** (48.8 mg, 0.2 mmol) was dissolved THF at 0 °C, NaH (0.2 mmol, 1.0 eq) was added into the solution and then stirred for 30 min. Then, (MeO)₂P(O)CH₂COOMe was dropwise into the solution and stirred for 2 h and monitored by TLC (SiO₂, petroleum ether/ethyl acetate = 3:1). After completed, the reaction was quenched with water (30 mL) and diluted with EA. The layers were separated and the aqueous phase was extracted with EA (3 × 2 mL). The

combined organic layers were washed with brine (3 mL), dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1) to afford the desired product **6d**. (Yellow liquid, 43.9 mg, 60%).

Purified by chromatography (PE /EA = 3:1, Rf = 0.2). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.21 – 7.10 (m, 5H), 6.05 (d, *J* = 15.4 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.76 (s, 3H), 3.60 (p, *J* = 8.2 Hz, 1H), 3.39 (dddd, *J* = 34.1, 17.7, 9.8, 4.3 Hz, 2H), 3.04 (tdt, *J* = 16.1, 7.7, 3.9 Hz, 2H), 2.33 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 167.32, 141.16, 138.60, 138.56, 137.35, 137.29, 136.09, 134.86, 134.84, 129.21, 126.29, 115.96, 54.94, 54.89, 51.71, 37.29, 36.77, 34.19, 21.02. ³¹P NMR (202 MHz, Chloroform-*d*) δ -2.93. HRMS (ESI) [M+Na]⁺ calculated for C₁₈H₂₃O₆PNa⁺: 389.1124, found 389.1124.



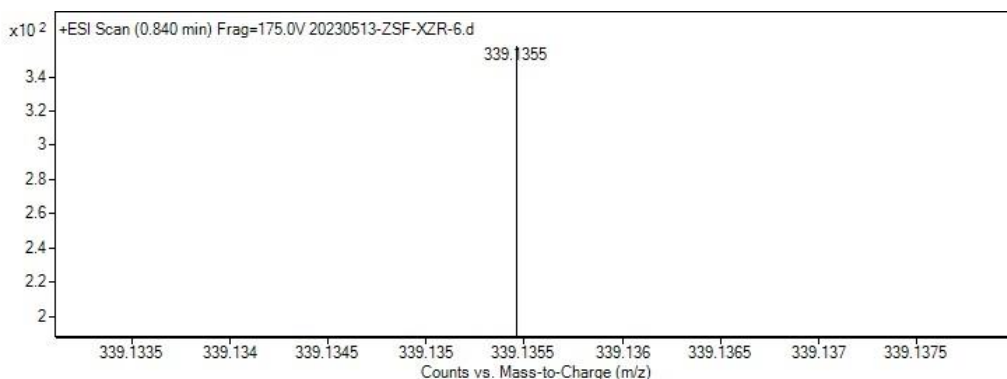
(E)-4-hydroxy-1-(3-(p-tolyl)cyclobutylidene)but-2-en-1-yl dimethyl phosphate (6d)



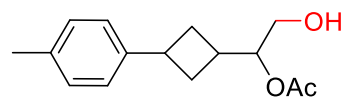
Under N₂ atmosphere, the substrates **3e** (48.8 mg, 0.2 mmol) was dissolved THF at 0 °C, NaH(0.2 mmol, 1.0 eq) was added into the solution and then stirred for 30 min. Then, (MeO)₂P(O)CH₂COOMe was dropwise into the solution and stirred for 2 h and monitored by TLC (SiO₂, petroleum ether/ethyl acetate = 3:1). After completed, the reaction was quenched with water (30 mL) and diluted with EA. The layers were separated and the aqueous phase was extracted with EA (3 × 2 mL). The combined organic layers were washed with brine (3 mL), dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1) to afford the desired product **6c**. (Yellow liquid, 43.9 mg, 60%).

The substrates **6c** (0.12 mmol, 1.0 equiv) was dissolved in toluene (1.0 mL) at 0 °C, LiAlH₄ (1.2 equiv) was added into the solution and then stirred for 2 h monitored by TLC (SiO₂, petroleum ether/ethyl acetate = 1:1). After completed, the reaction was quenched with water (1 mL) and diluted with EA. The layers were separated and the aqueous phase was extracted with EA (3 × 3 mL). The combined organic layers were washed with brine (3 mL), dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 1:1) to afford the desired product **6d**. (Yellow liquid, 20.3 mg, 55%).

Purified by chromatography (PE /EA = 1:1, R_f = 0.3). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.08 (m, 4H), 6.07 (d, *J* = 15.6 Hz, 1H), 5.95 (dt, *J* = 15.6, 5.4 Hz, 1H), 4.18 (d, *J* = 5.4 Hz, 2H), 3.77 (d, *J* = 2.7 Hz, 4H), 3.75 (d, *J* = 2.7 Hz, 4H), 3.48 (p, *J* = 8.2 Hz, 1H), 3.31 – 3.21 (m, 1H), 3.20 – 3.10 (m, 1H), 2.87 (ddt, *J* = 19.9, 12.1, 3.8 Hz, 2H), 2.26 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 141.85, 137.69 (d, *J* = 8.8 Hz), 135.88, 129.15, 127.71 (d, *J* = 5.7 Hz), 126.32, 121.48 (d, *J* = 3.0 Hz), 62.93, 54.84, 54.78, 36.47, 36.13, 34.46, 21.03. HRMS (ESI) [M+H]⁺ calculated for C₁₇H₂₄O₅P⁺: 339.1356, found 339.1355.



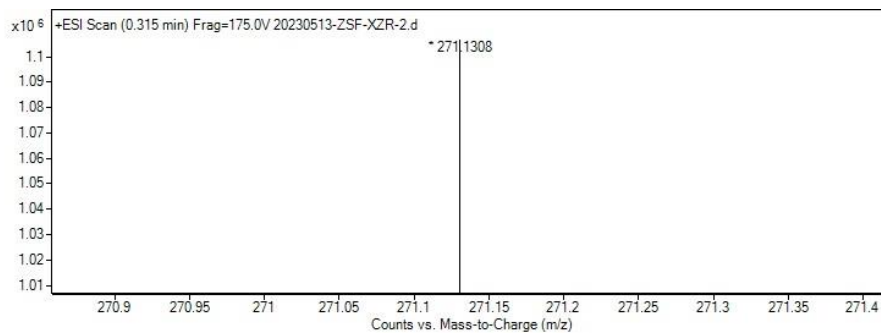
2-hydroxy-1-(3-(p-tolyl)cyclobutyl)ethyl acetate (6e)



The substrates **3ea** (0.2 mmol, 1.0 equiv) was dissolved in CH₃OH (2.0 mL) at 0 °C, NaBH₄ (3.0 equiv) was added into the solution and then stirred for overnight monitored by TLC (SiO₂, petroleum ether/ethyl acetate = 5:1). After completed, the reaction was quenched with water (2 mL) and diluted with EA. The layers were separated and the aqueous phase was extracted with EA (3 × 3 mL). The combined organic layers were washed with brine (3 mL), dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to afford the desired product **6e**. (Colorless liquid, 35.2 mg, 71%).

Purified by chromatography (PE /EA = 5:1, R_f = 0.5). Four isomers determined by the ¹³C NMR of **6e**, but the dr value of **6e** was difficult to determine. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.09 – 6.98 (m, 4H), 4.83 (td, *J* = 7.0, 3.1 Hz, 1H), 4.22 – 3.98 (m, 1H), 3.94 – 3.82 (m, 1H), 3.73 – 3.52 (m, 1H), 3.52 – 3.22 (m, 1H), 2.43 – 2.27 (m, 3H), 2.24 (d, *J* = 5.0 Hz, 3H), 2.03 (d, *J* = 8.5 Hz, 3H), 1.99 – 1.75 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 171.84, 171.78, 171.42, 171.37, 142.91, 142.64, 142.35, 142.10, 135.52, 135.47,

135.39, 129.07, 128.99, 128.97, 126.29, 126.24, 78.62, 78.56, 73.57, 73.09, 67.16, 66.96, 63.38, 63.16, 35.93, 35.83, 35.74, 33.64, 33.57, 32.26, 32.14, 32.00, 31.74, 31.55, 31.44, 30.98, 30.93, 30.73, 30.40, 21.23, 21.17, 21.02, 20.94. HRMS (ESI) $[M+Na]^+$ calculated for $C_{15}H_{20}O_3Na^+$: 271.1304, found 271.1308.



7. General procedure for mechanism experiments

7.1 Intermediate exploration test

To a deuterium chloroform solution of **1e** (0.2 mmol, 2.0 mL) in Schlenk tube with a magnetic bar was added $\text{Rh}_2(\text{OPiv})_4$ (0.002 mmol, 1 mol%, 1.3 mg) with 4-methylstyrene **2a** (0.4 mmol, 2.0 equiv) at 30 °C under N_2 . The sealed tube was then stirred at 80 °C under nitrogen atmosphere for 0 min, 1 h, 2 h, 3 h, 4 h, 5 h, 12 h, 24 h, 32 h and 46 h. Absorbing 500 μL mixture in the nuclear magnetoscope and doing NMR analysis. As shown below, the ^1H -NMR of different time periods is showed.

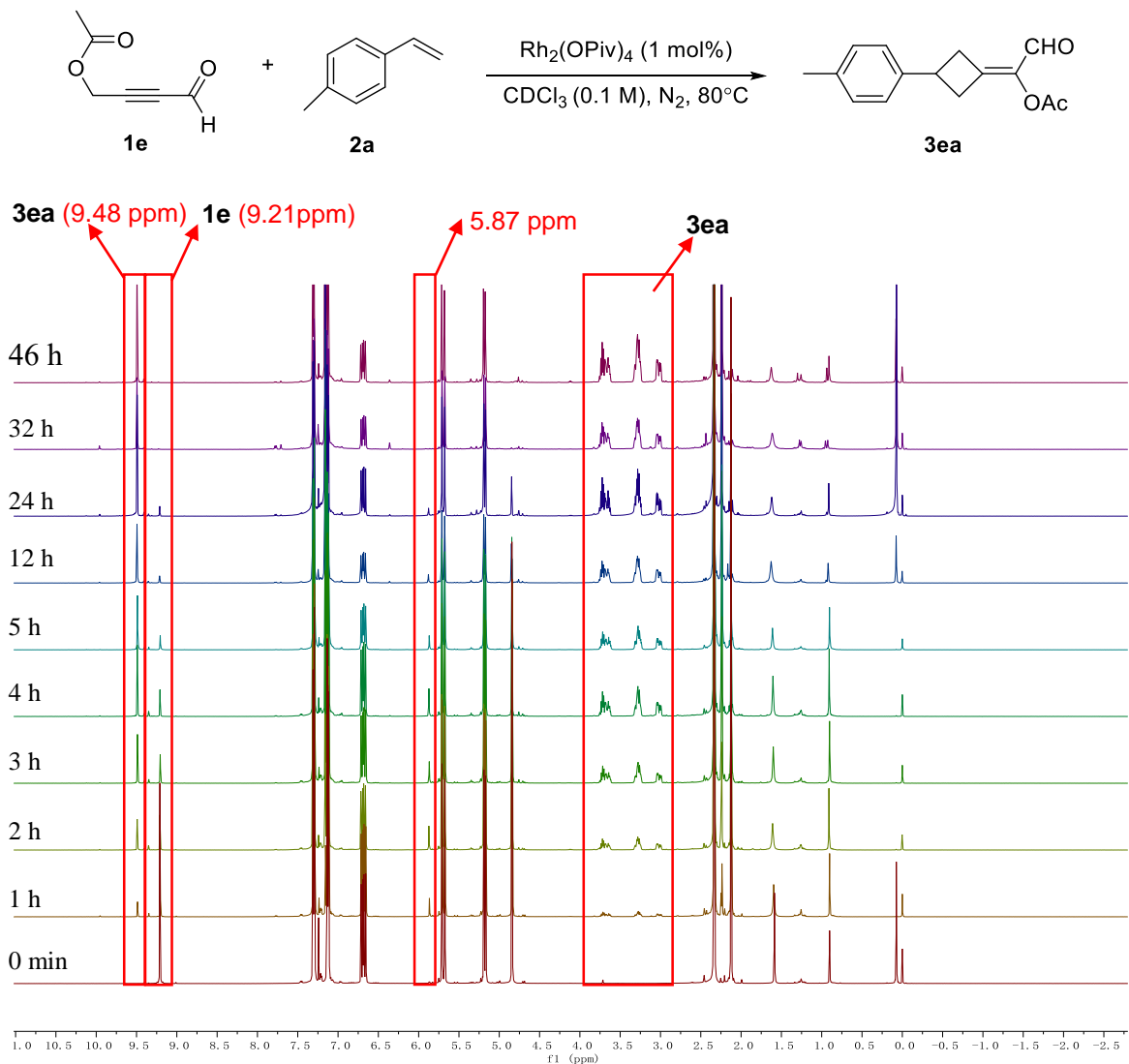


Figure S1. Intermediate experiments monitoring through real-time ^1H -NMR study

As shown below, the ^{13}C -NMR of the combined reaction mixture contained 5.87 ppm chemical shift was presented.

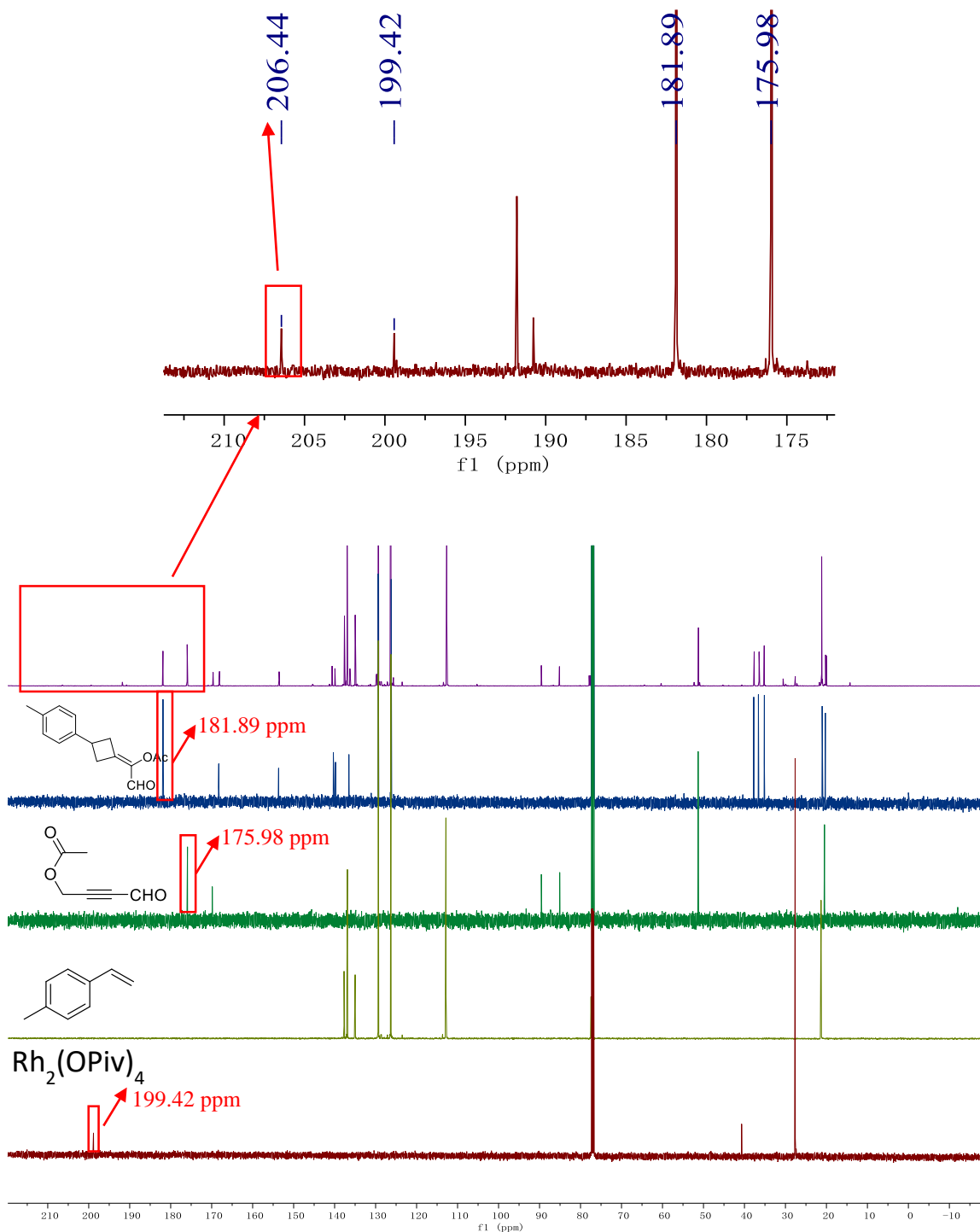


Figure S2. The ^{13}C -NMR of the combined reaction mixture contained 5.87 ppm chemical shift

To a deuterium chloroform solution of **1e** (0.2 mmol, 2.0 mL) in Schlenk tube with a magnetic bar was added $\text{Rh}_2(\text{OPiv})_4$ (0.002 mmol, 1 mol%, 1.3 mg) at 30 °C under N_2 . The sealed tube was then stirred at 30 °C under nitrogen atmosphere for 48 h. Absorbing 500 μL mixture in the nuclear magnetoscope and doing NMR analysis. As shown below, the nuclear magnetic spectrum is presented.

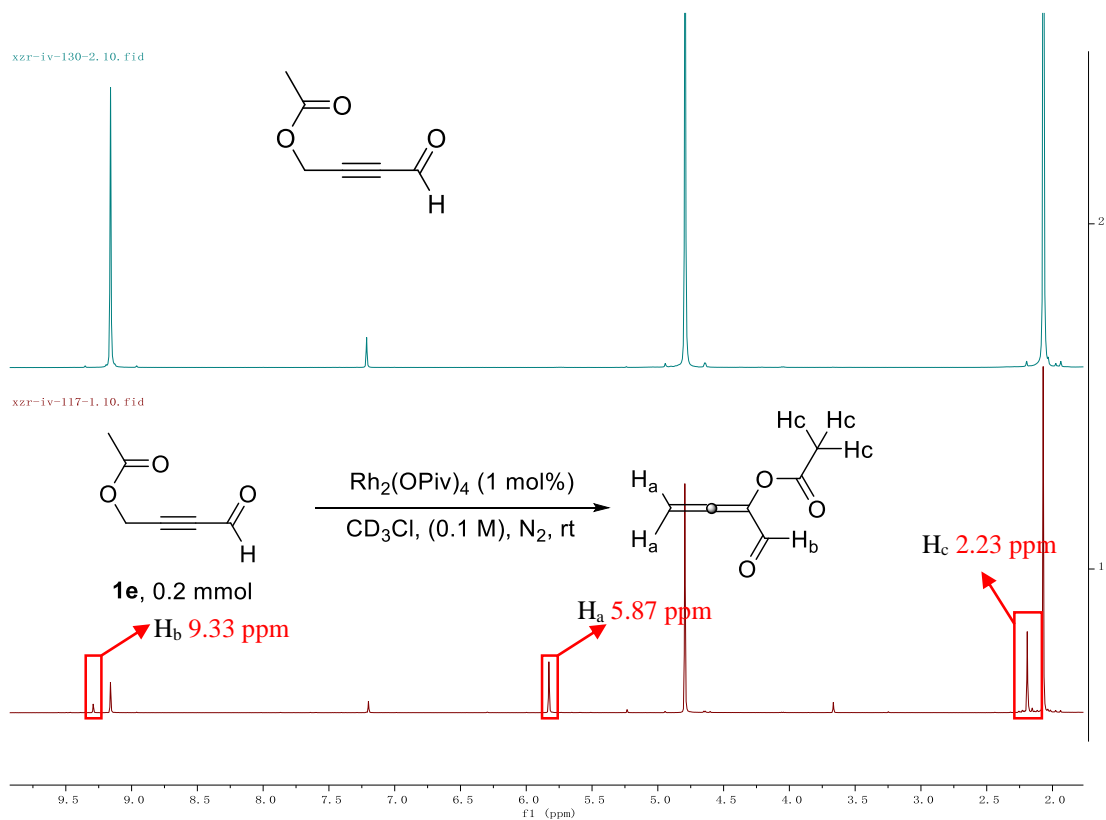
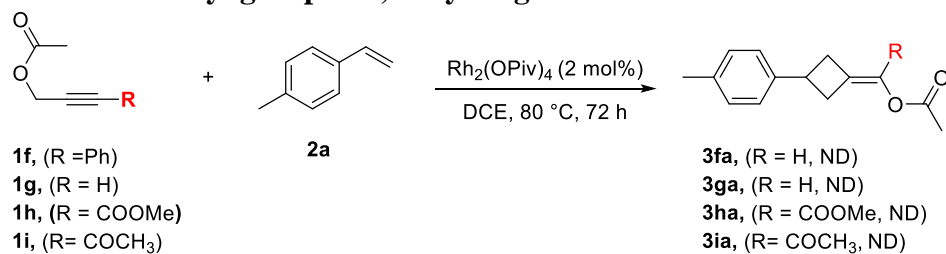


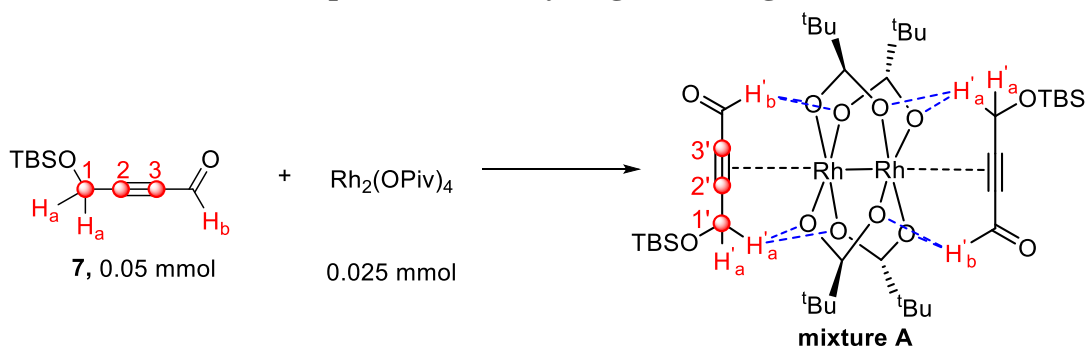
Figure S3. Intermediate preparation experiments

7.2 The effect of foemyl group of 1,3-acyl migration



To a 1,2-dichloroethane solution of **1** (0.15 mmol, 1.5 mL) in Schlenk tube with a magnetic bar was added Rh₂(OPiv)₄ (0.003 mmol, 2 mol%, 1.8 mg) with 4-methylstyrene **2a** (5.0 equiv) at 30 °C under N₂. The sealed tube was then stirred at 80 °C under nitrogen atmosphere for 72 h. The mixture was then detected by GCMS and ¹H-NMR.

7.3 The evidence of Cooperative weak hydrogen bonding interactions



To deuterated chloroform (1.0 mL) solution of **7** (0.05 mmol, 4.9 mg) in Schlenk tube with a magnetic bar was added $\text{Rh}_2(\text{OPiv})_4$ (0.025 mmol, 15.25 mg) at rt under N_2 . The sealed tube was then stirred at rt under nitrogen atmosphere for 15 min. Then, the mixture **A** was identified by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$.

Table S3. The NMR comparison between **7** and **mixture A**.

Selected corresponding ^1H NMR data (ppm)				
7	H_b (9.24)	H_a (4.51)	^tBu (0.92)	CH_3 (0.14)
mixture A	H'_b (9.21)	H'_a (4.65)	$^t\text{Bu}'$ (0.96)	CH_3' (0.20)
Deviation	-0.03	0.14	0.04	0.06

Selected corresponding ^{13}C NMR data (ppm)							
7	CHO(176.40)	C2(94.84)	C3(84.19)	C1(51.52)	25.68	18.22	-5.27
mixture A	CHO(177.21)	C2'(93.92)	C3'(83.62)	C1'(52.24)	25.74	18.29	-5.19
Deviation	0.81	-0.92	-0.57	0.72	0.06	0.07	0.08

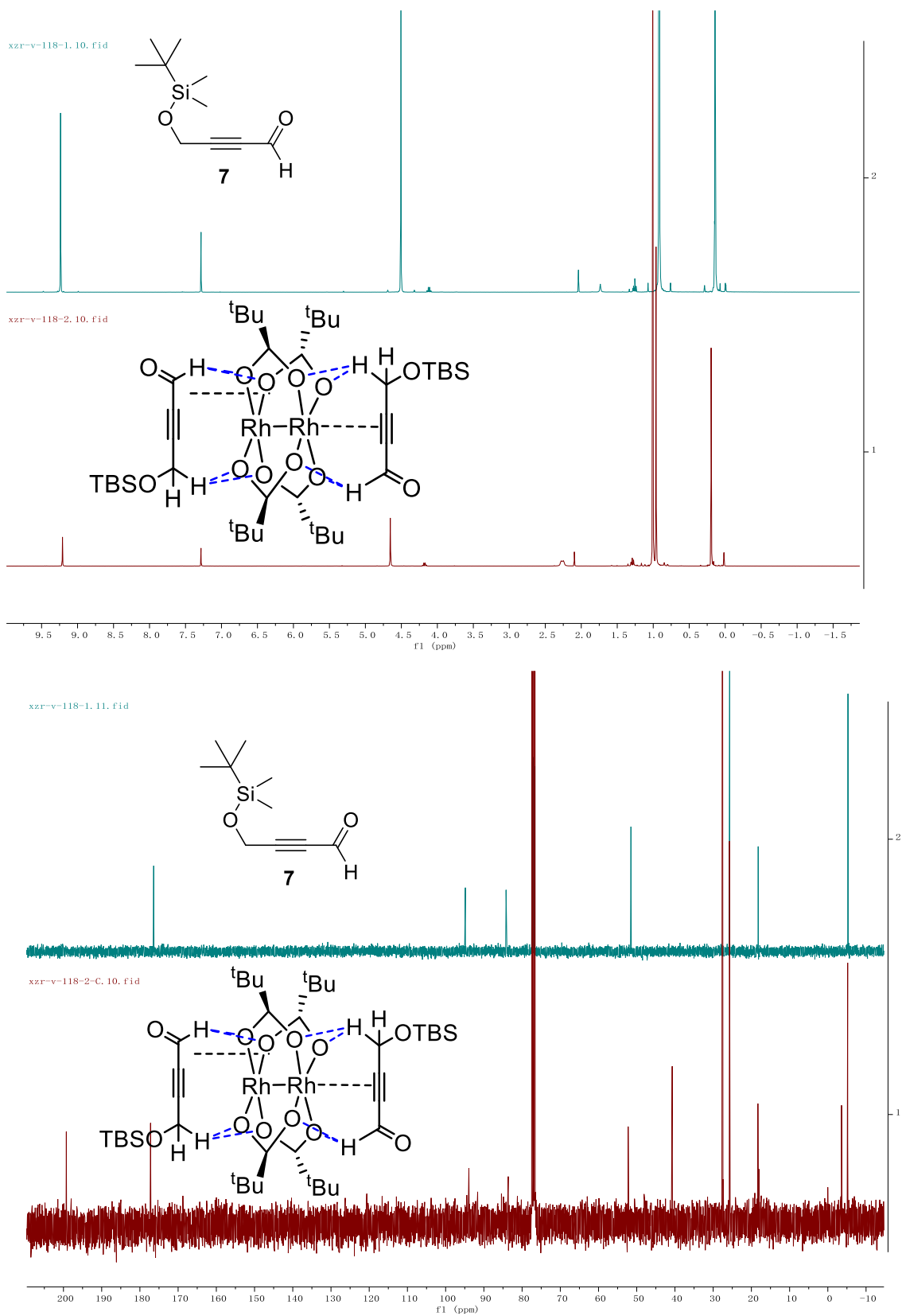
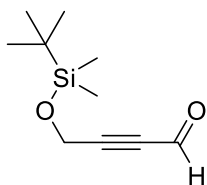
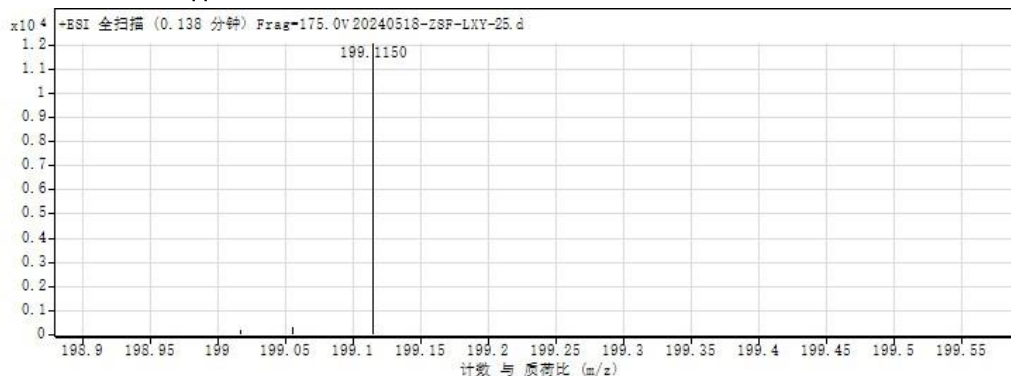


Figure S4. The stacked NMR figures of **7** and **mixture A**. (up for ^1H NMR, down for ^{13}C NMR)

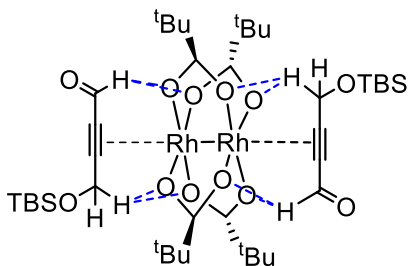
4-((tert-butyl dimethylsilyl)oxy)but-2-ynal (7)



Yellow liquid, purified by chromatograph (PE/EA = 20/1). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 4.51 (s, 2H), 0.92 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.40, 94.84, 84.19, 51.52, 25.68, 18.22, -5.27. HRMS (ESI) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_6\text{H}_7\text{O}_4^+$: 199.1149, found 199.1150.



mixture A



^1H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 4.65 (s, 2H), 1.01 (s, 18H), 0.96 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.26, 177.21, 93.92, 83.62, 52.24, 40.72, 27.59, 25.74, 18.29, -5.19.

8.references

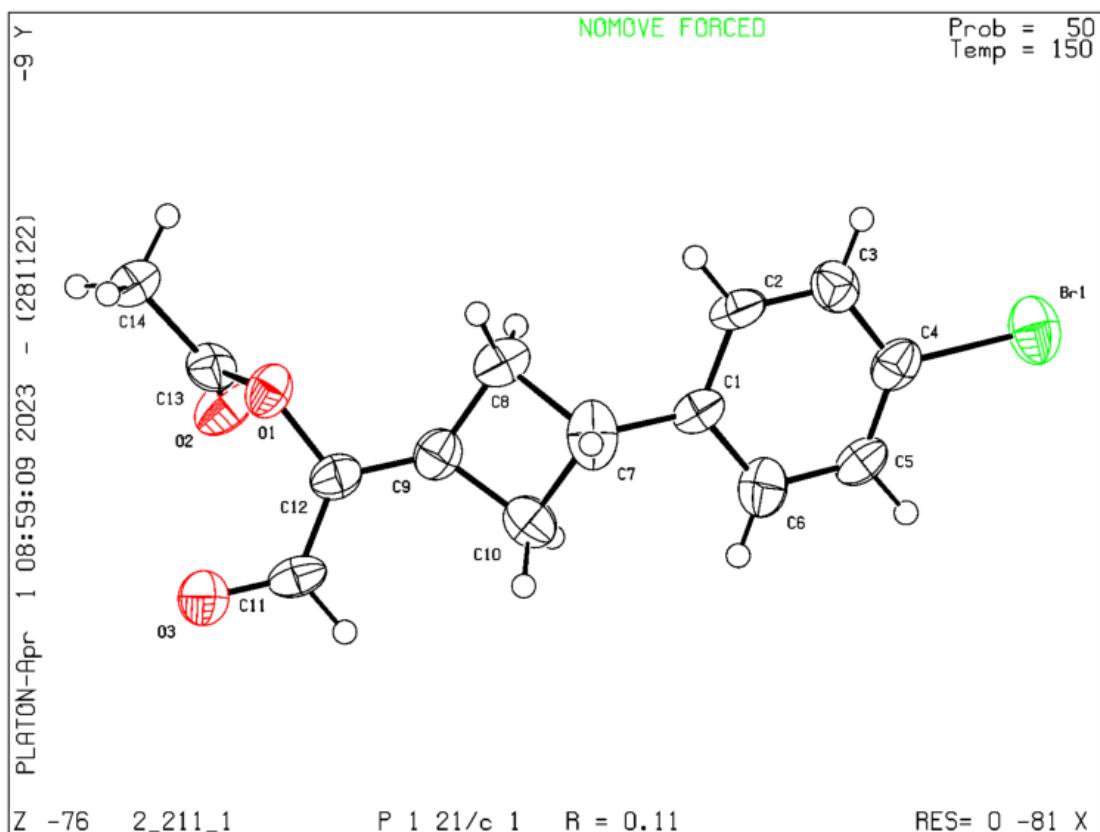
1. Y. Zhou, L. Wang, S. Li, S. Ma, P.J. Walsh, Q. Bian, F. Li, M. Wang and J. Zhong, *Synlett*, 2020, **31**, 60.
2. C. Tsukano, S. Yamamoto and Y. Takemoto, *Chem. Pharm. Bull.*, 2015, **63**, 710.
3. G. Zhang and L. Zhang, *J. Am. Chem. Soc.*, 2008, **130**, 12598.
4. U. Wong and R.J. Cox, *Angew. Chem. Int. Ed.*, 2007, **46**, 4926.
5. T. Takemoto, K. Yasuda and S.V. Ley, *Synlett*, 2001, **2001**, 1555.
6. V. Zullo and A. Iuliano, *Eur. J. Org. Chem.*, 2018, **2019**, 1377.

9. The X-ray diffraction analysis

9.1 Crystal data and structure refinement for 3ej (CCDC 2335728).

Single crystal of **3ej** was grown from slow evaporation of DCM/PE solvent. A suitable crystal was selected and measured on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection.

Datablock 2_211_1 - ellipsoid plot



Ellipsoid plot of the crystal structure of 3ej (Prob = 50, Temp = 150 K)

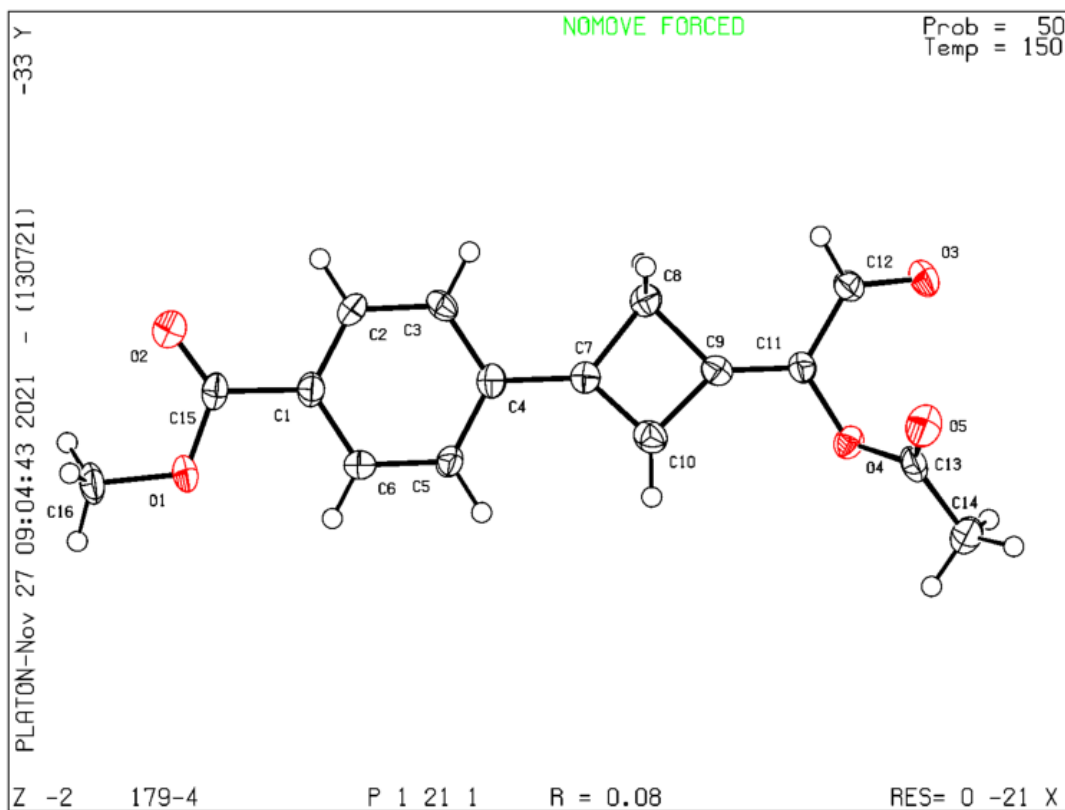
Identification code	XZR-2-211-1
Empirical formula	C ₁₄ H ₁₃ BrO ₃
Formula weight	309.15
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	6.5459(6)
b/Å	7.4134(4)
c/Å	27.118(3)
α/°	90
β/°	96.115(9)
γ/°	90
Volume/Å ³	1308.48(19)
Z	4

$\rho_{\text{calc}}/\text{cm}^3$	1.569
μ/mm^{-1}	4.273
F(000)	624.0
Crystal size/ mm^3	$0.13 \times 0.12 \times 0.08$
Radiation	Cu K α ($\lambda = 1.54184$)
2θ range for data collection/ $^\circ$	6.556 to 133.136
Index ranges	$-7 \leq h \leq 7, -8 \leq k \leq 8, -3 \leq l \leq 32$
Reflections collected	2308
Independent reflections	2308 [$R_{\text{int}} = ?$, $R_{\text{sigma}} = 0.1447$]
Data/restraints/parameters	2308/0/165
Goodness-of-fit on F^2	2.595
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1337$, $wR_2 = 0.3452$
Final R indexes [all data]	$R_1 = 0.1451$, $wR_2 = 0.3523$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	3.42/-1.54

9.2 Crystal data and structure refinement for 5er (CCDC 2335731).

Single crystal of **5er** was grown from slow evaporation of DCM/PE solvent. A suitable crystal was selected and measured on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection.

Datablock 179-4 - ellipsoid plot



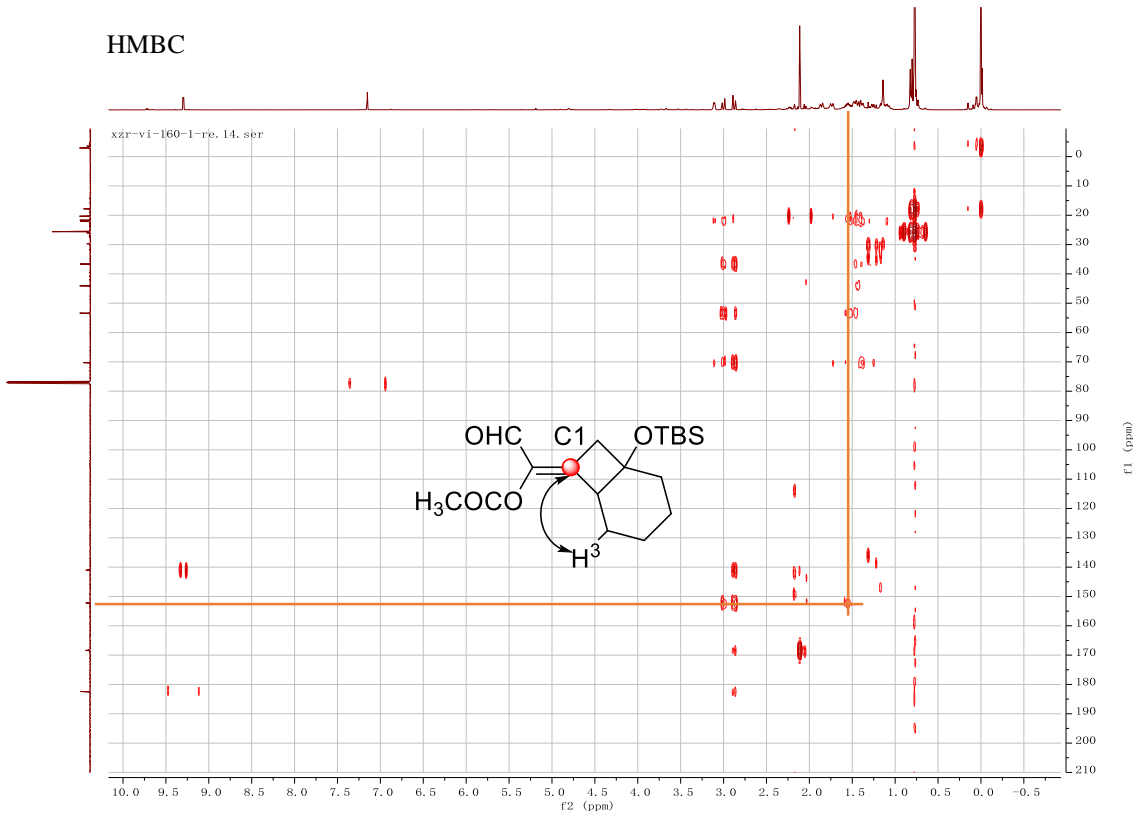
Ellipsoid plot of the crystal structure of 5er (Prob = 50, Temp = 150 K)

Identification code	179-4
Empirical formula	C ₁₆ H ₁₄ O ₅
Formula weight	286.27
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	6.7856(4)
b/Å	6.0442(4)
c/Å	16.6292(9)
α/°	90
β/°	92.683(5)
γ/°	90
Volume/Å ³	681.27(7)
Z	2
ρ _{calc} /cm ³	1.396
μ/mm ⁻¹	0.871
F(000)	300.0
Crystal size/mm ³	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	5.32 to 146.87
Index ranges	-5 ≤ h ≤ 8, -6 ≤ k ≤ 7, -20 ≤ l ≤ 19
Reflections collected	2502
Independent reflections	1897 [R _{int} = 0.0449, R _{sigma} = 0.0340]
Data/restraints/parameters	1897/1/193
Goodness-of-fit on F ²	1.141
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0834, wR ₂ = 0.2455
Final R indexes [all data]	R ₁ = 0.0853, wR ₂ = 0.2464
Largest diff. peak/hole / e Å ⁻³	0.53/-0.36
Flack parameter	-0.1(3)

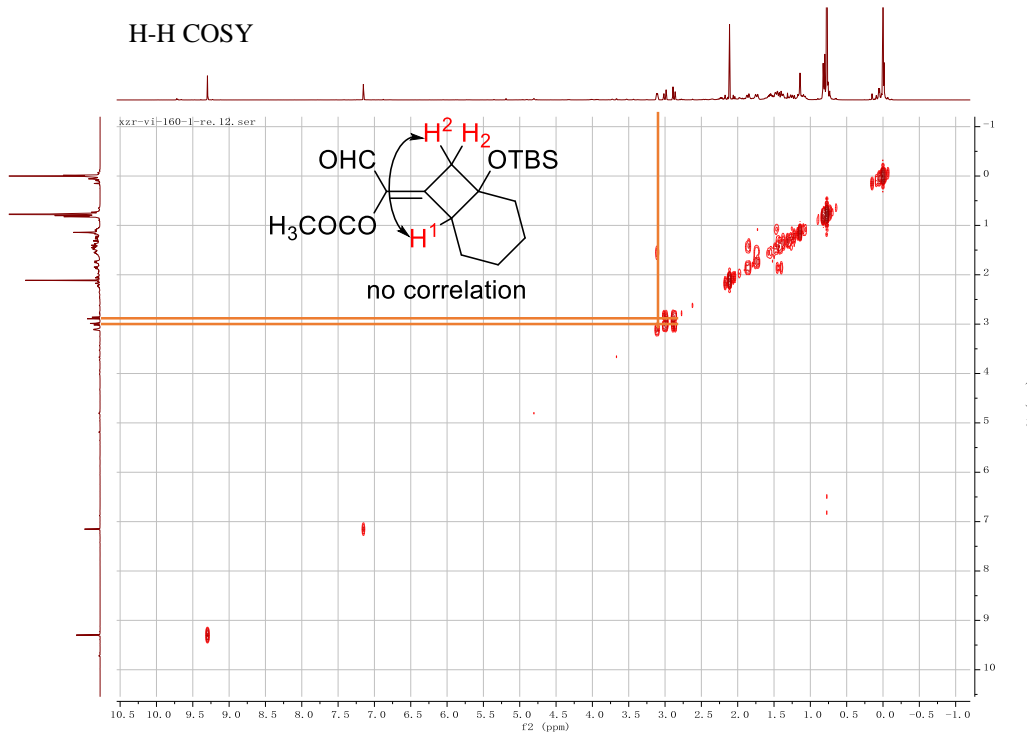
10. The NMR bidimensional study on compound 3ev

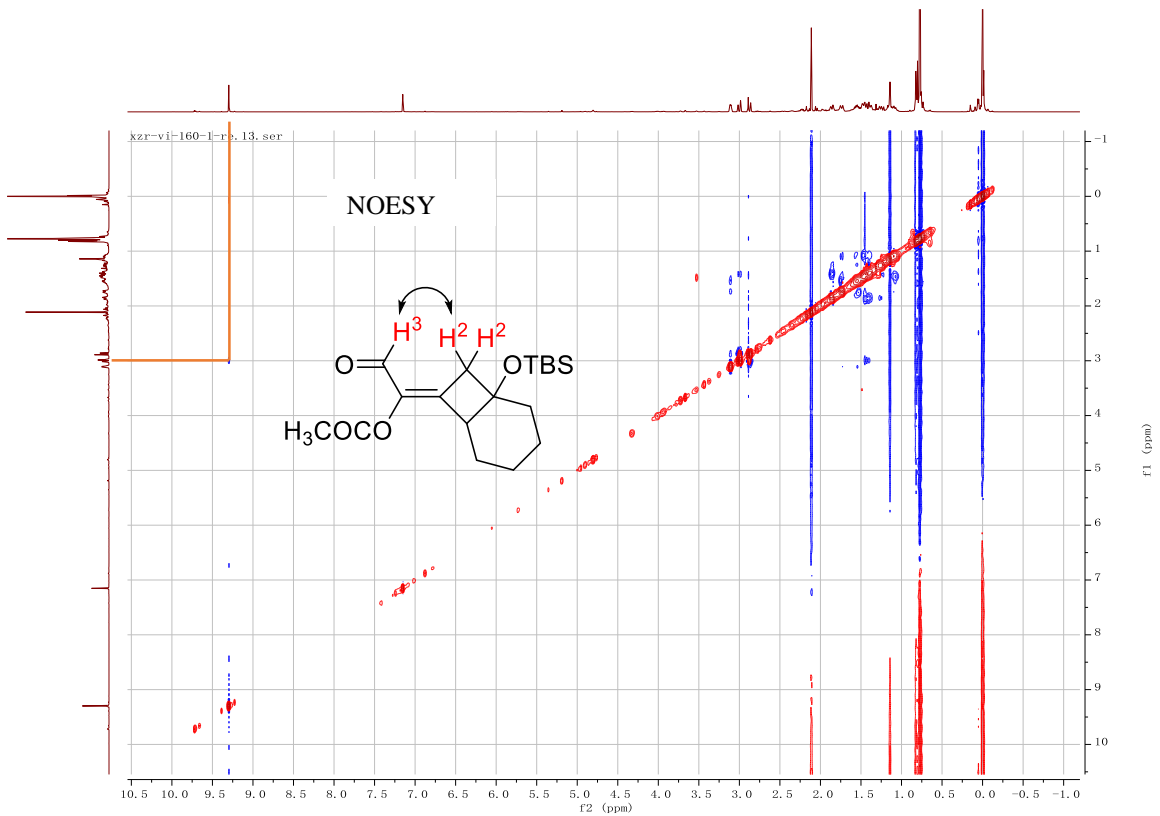
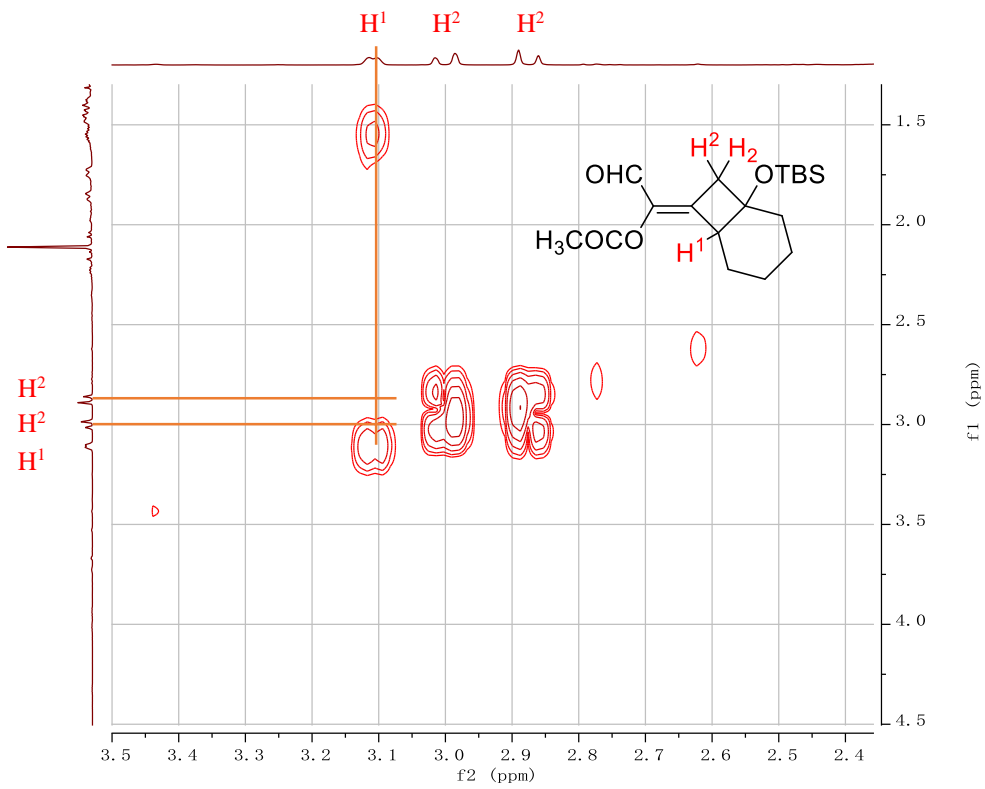
Based on the ¹H-¹H COSY and HMBC study on compound **3ev**, there was correlation between the C1 and H³ in HMBC study. Meanwhile, there was no correlation between the H¹ and H² in ¹H-¹H COSY. Therefore, the head-to-tail product was determined.

HMBC

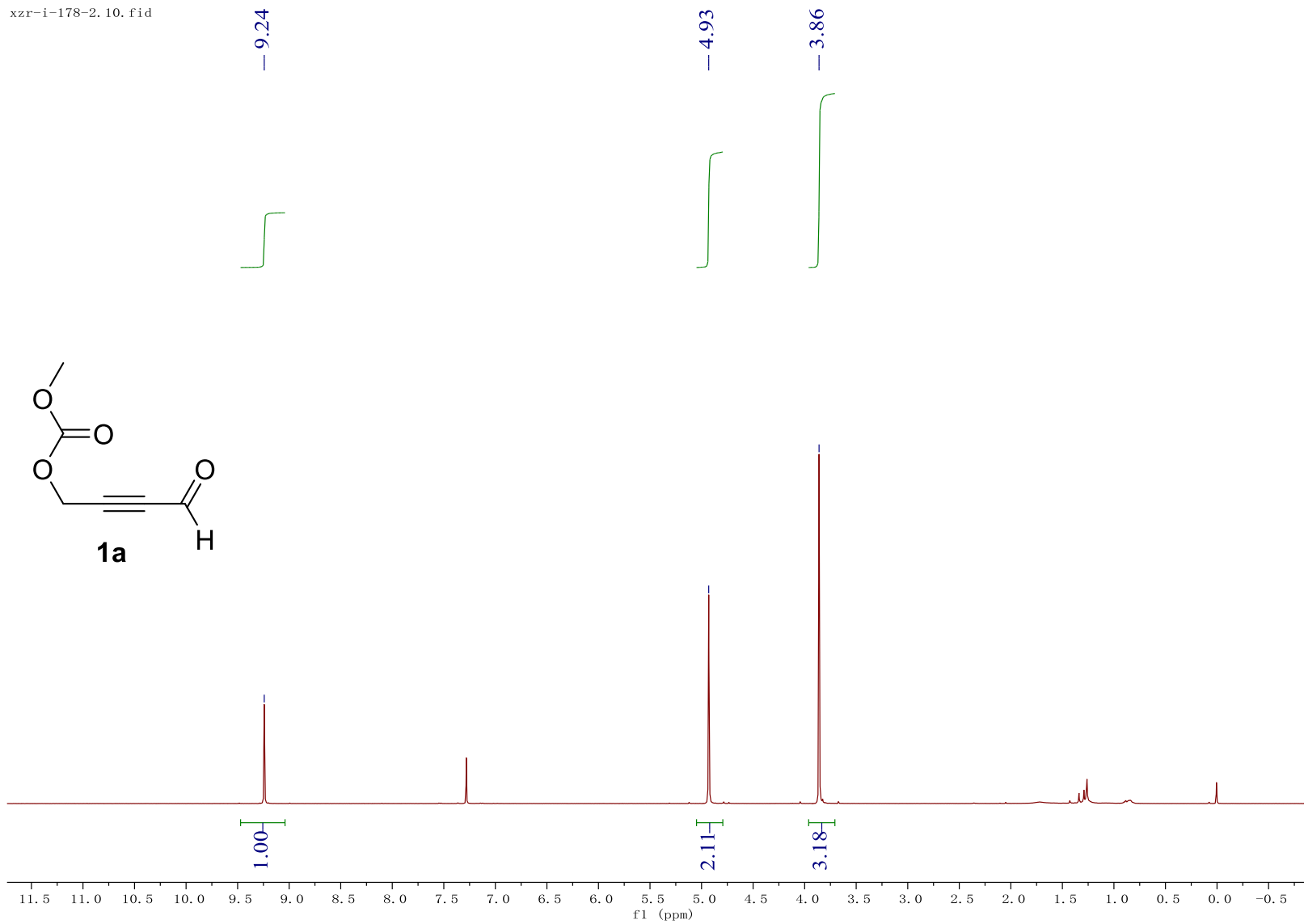


H-H COSY





xzr-i-178-2.10.fid



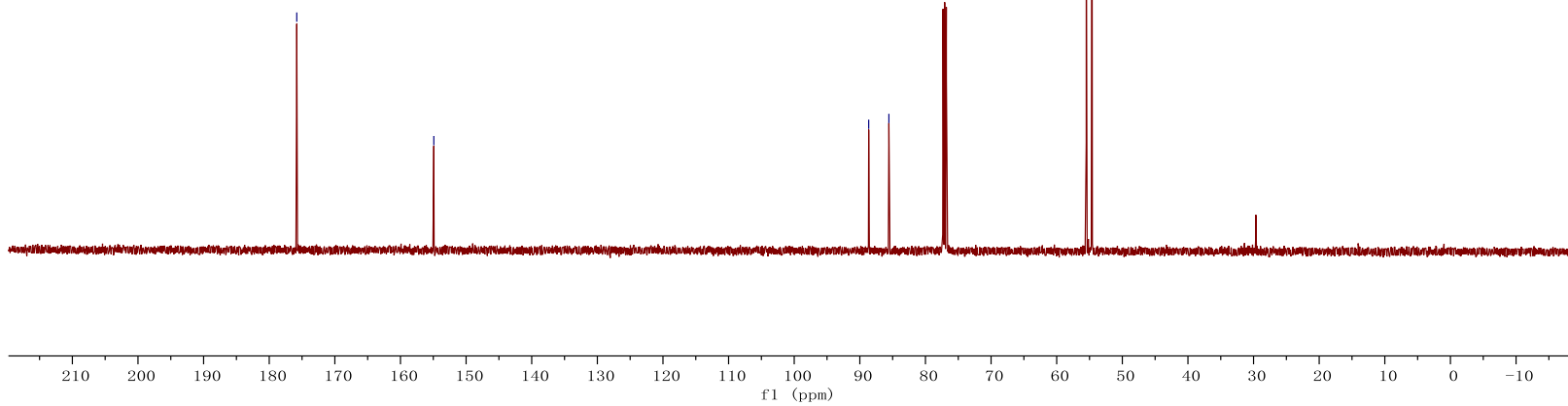
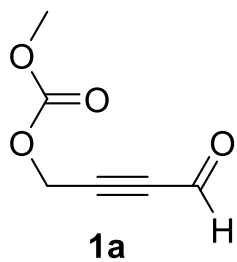
xzr-i-154-1.11.fid

— 175.80

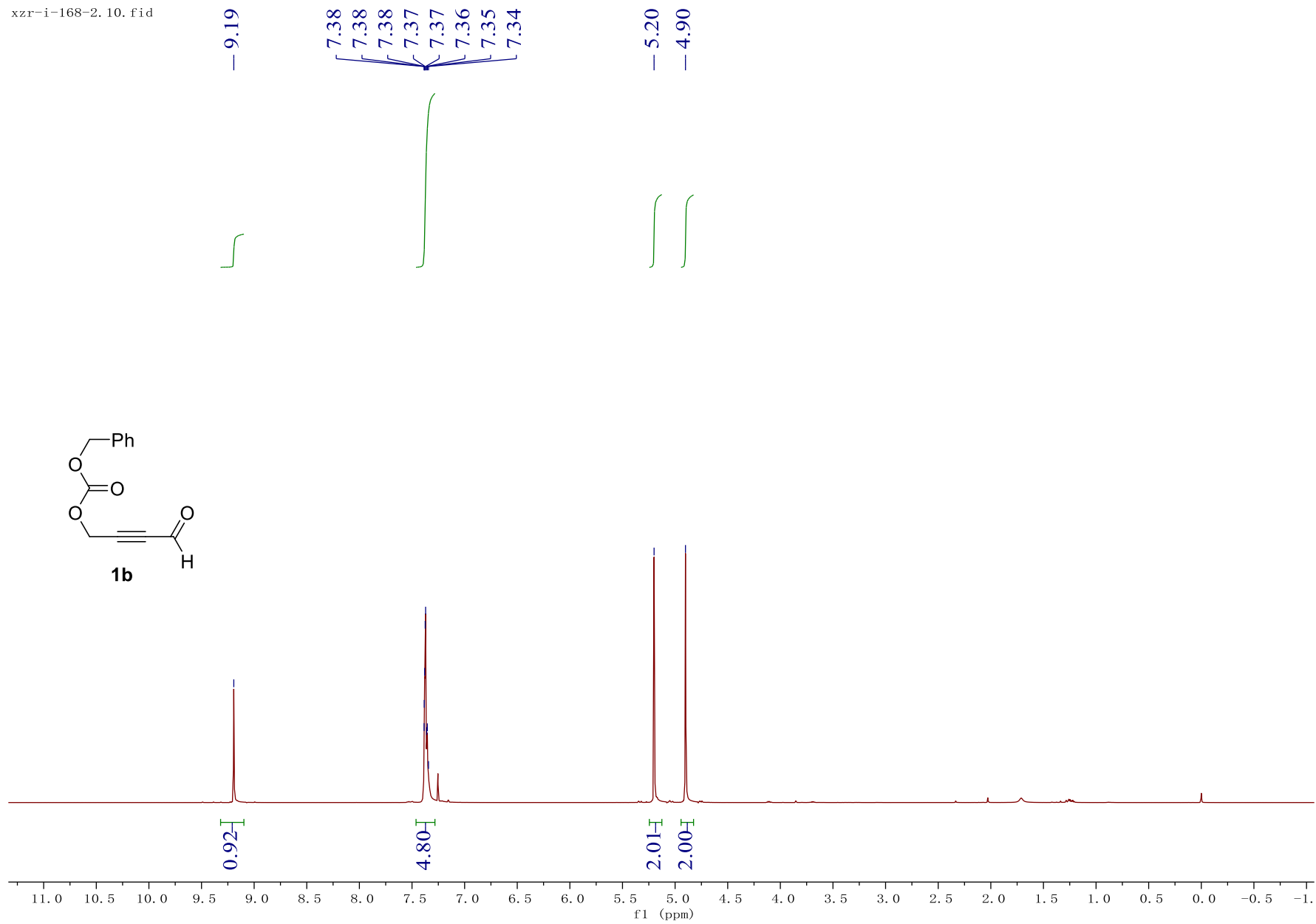
— 154.92

~ 88.65
~ 85.57

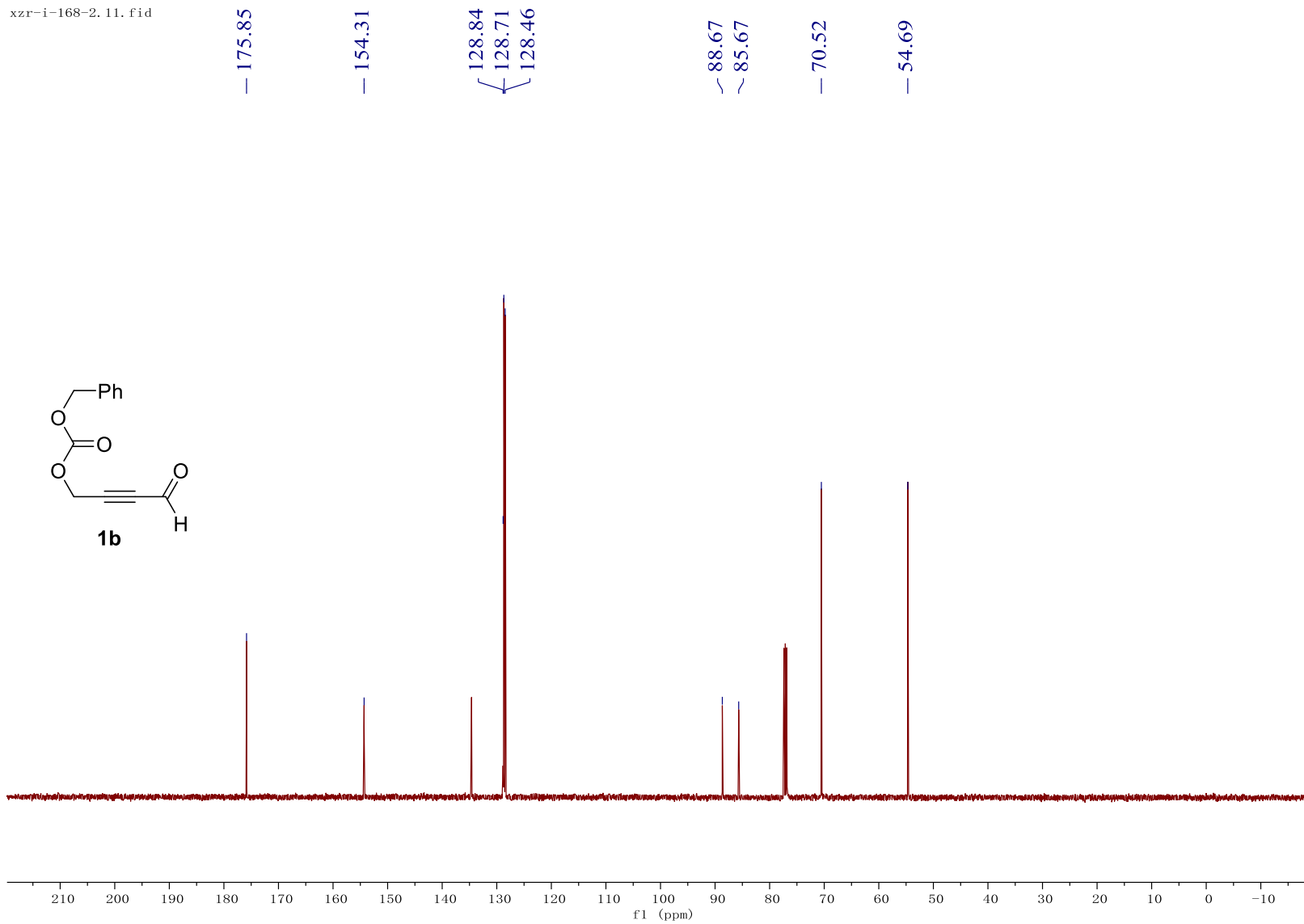
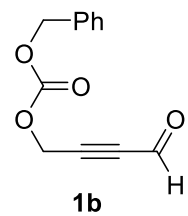
~ 55.49
~ 54.63



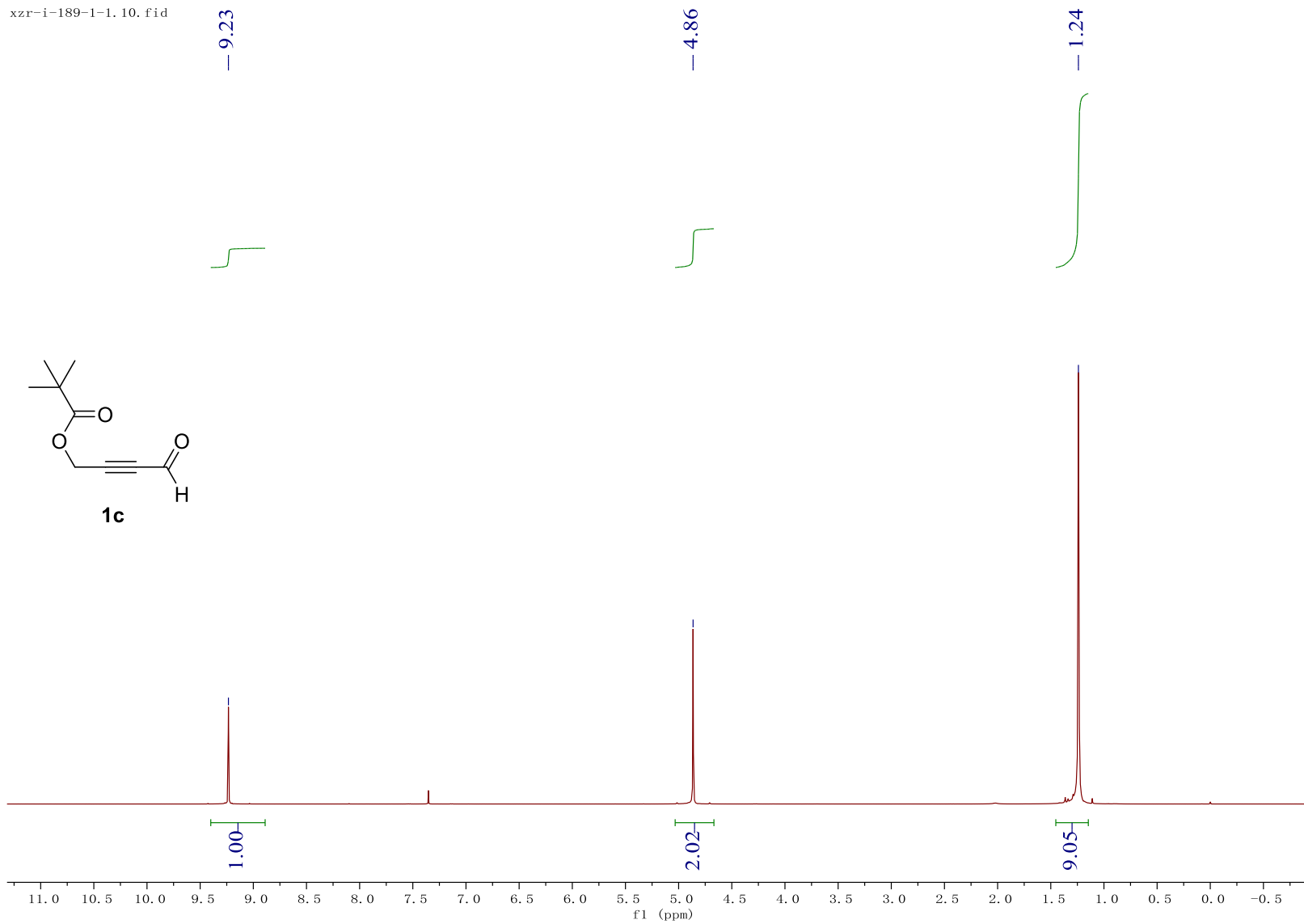
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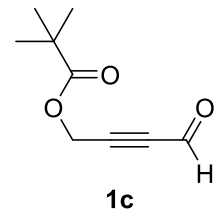
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xzr-i-189-1-1.10.fid



XZR-I-189-1-1-C. 10. fid



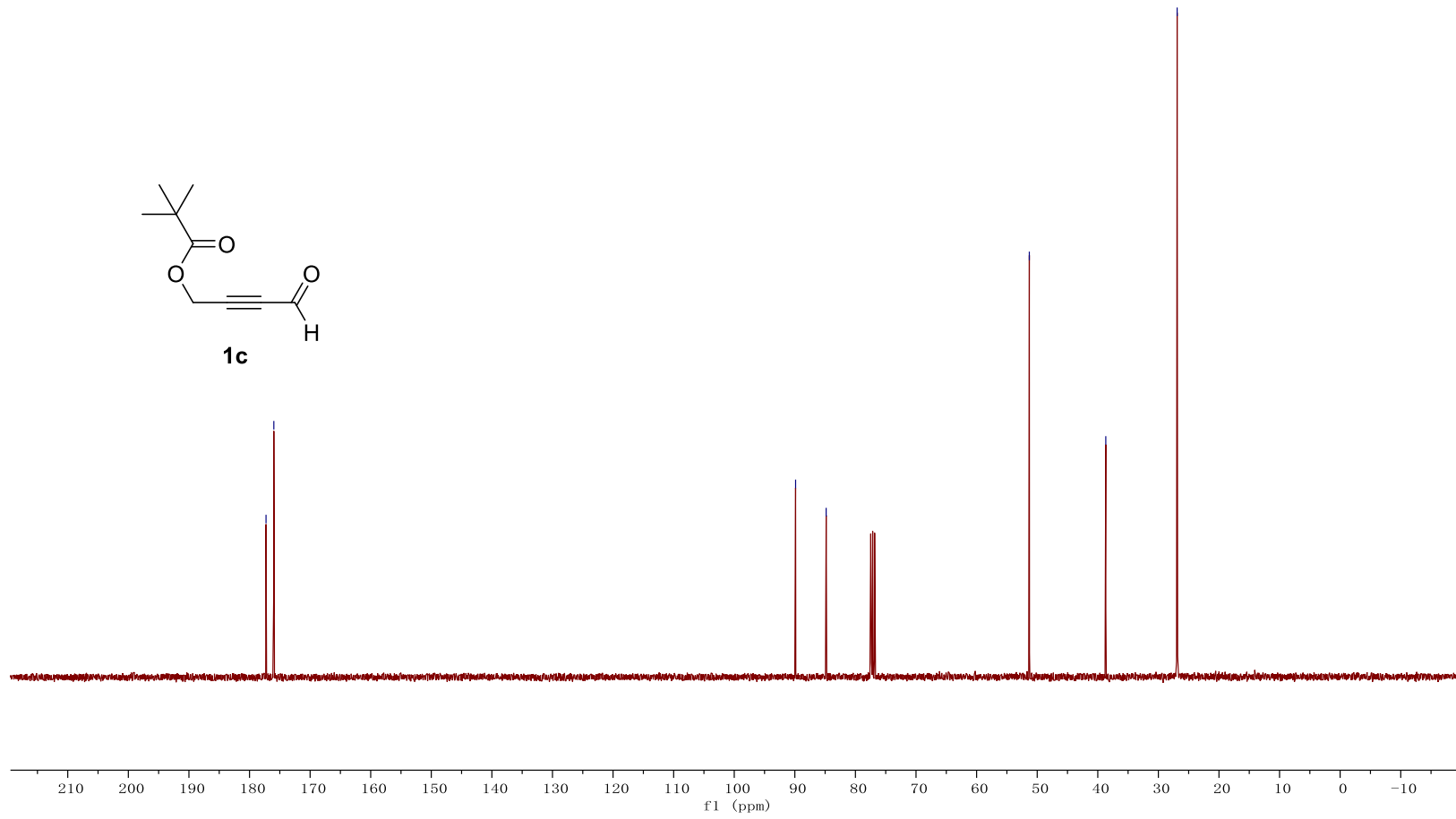
177.28
175.99

89.87
84.83

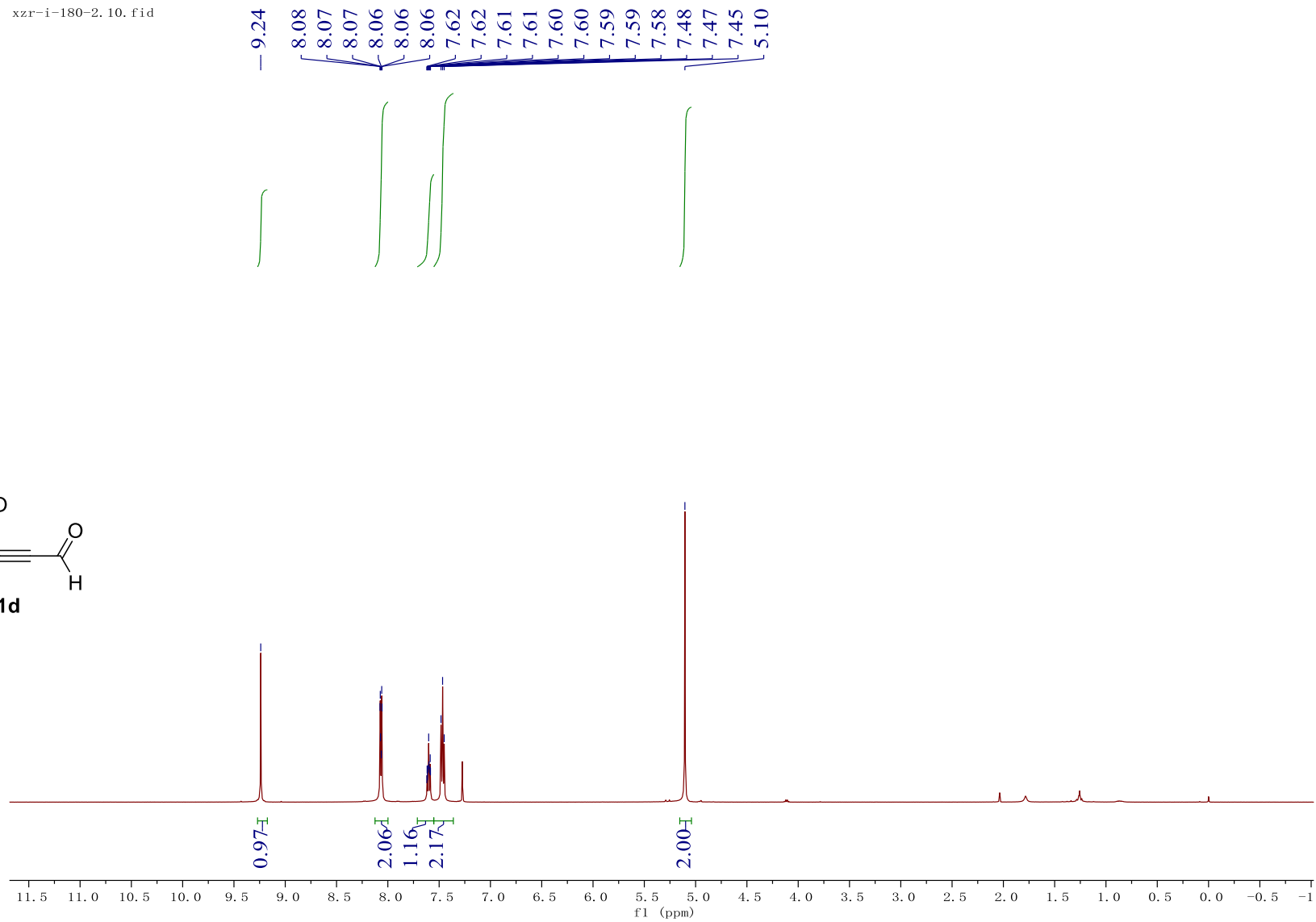
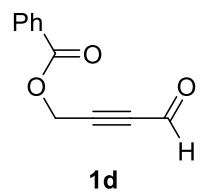
51.30

38.68

26.90



xzr-i-180-2.10.fid



XZR-I-180-2-C.10.fid

— 176.01

— 165.53

133.70

129.89

128.84

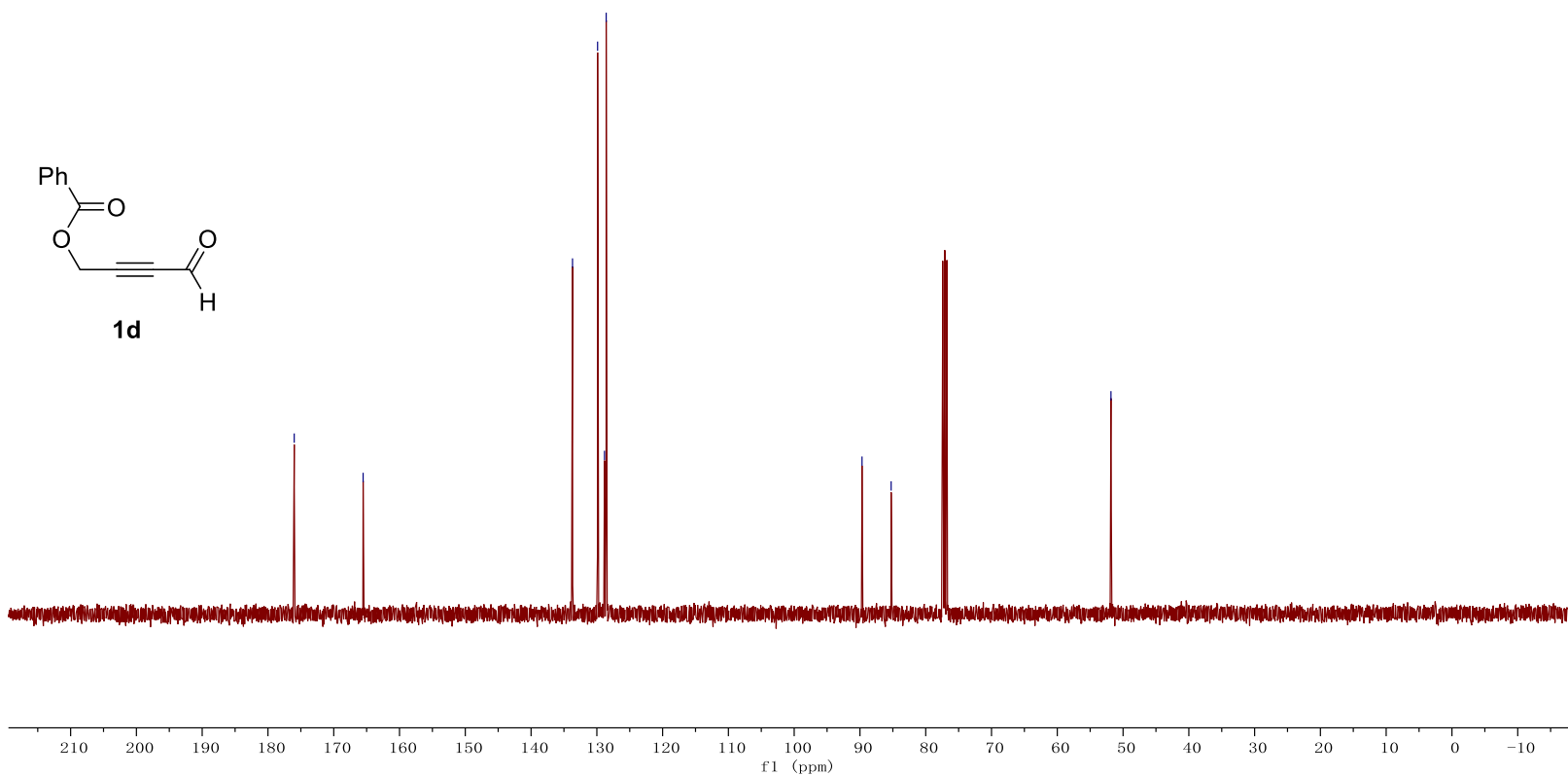
128.58

— 89.68

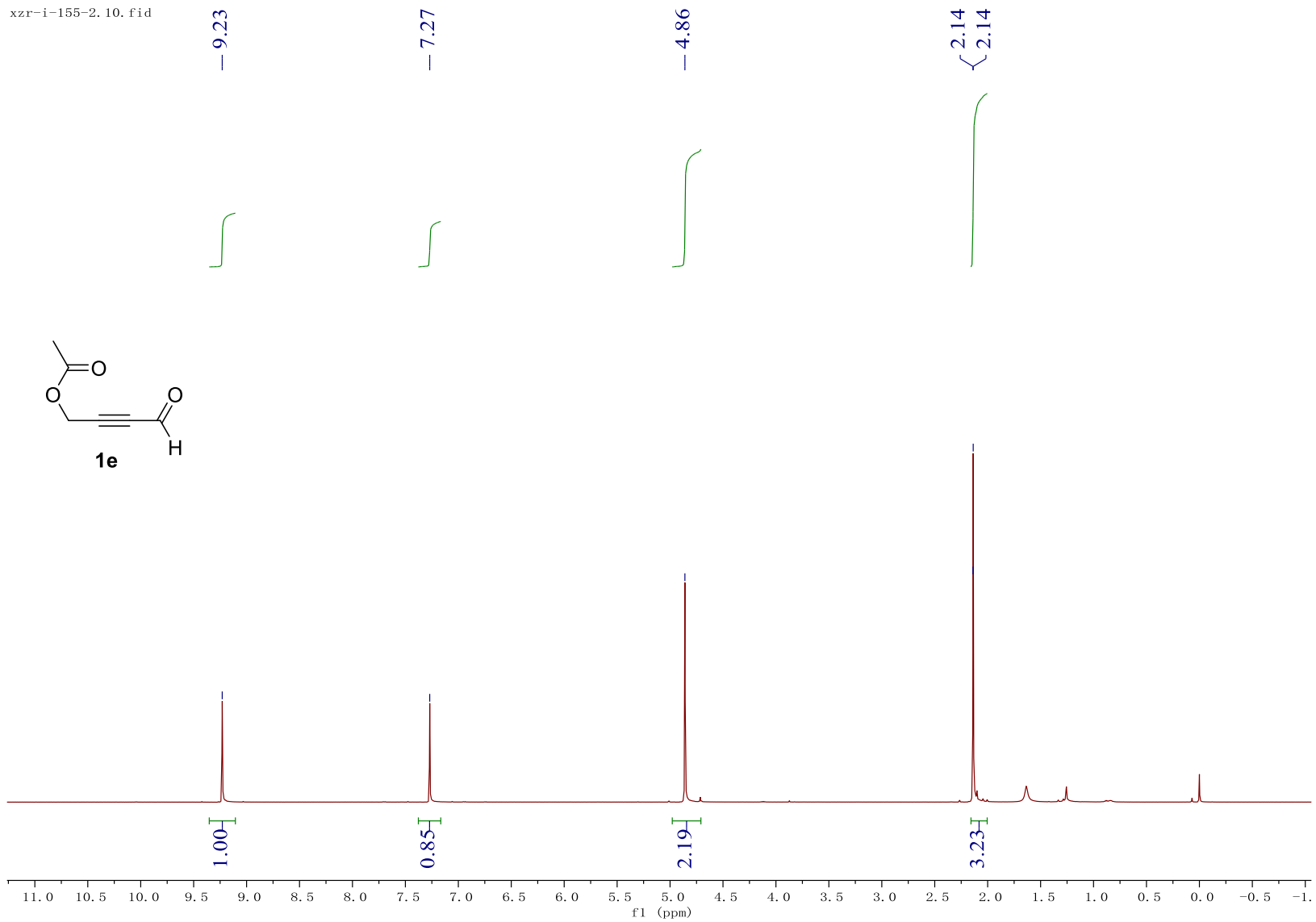
— 85.26

— 51.84

^{13}C NMR (101 MHz, Chloroform-*d*)



xzr-i-155-2.10.fid



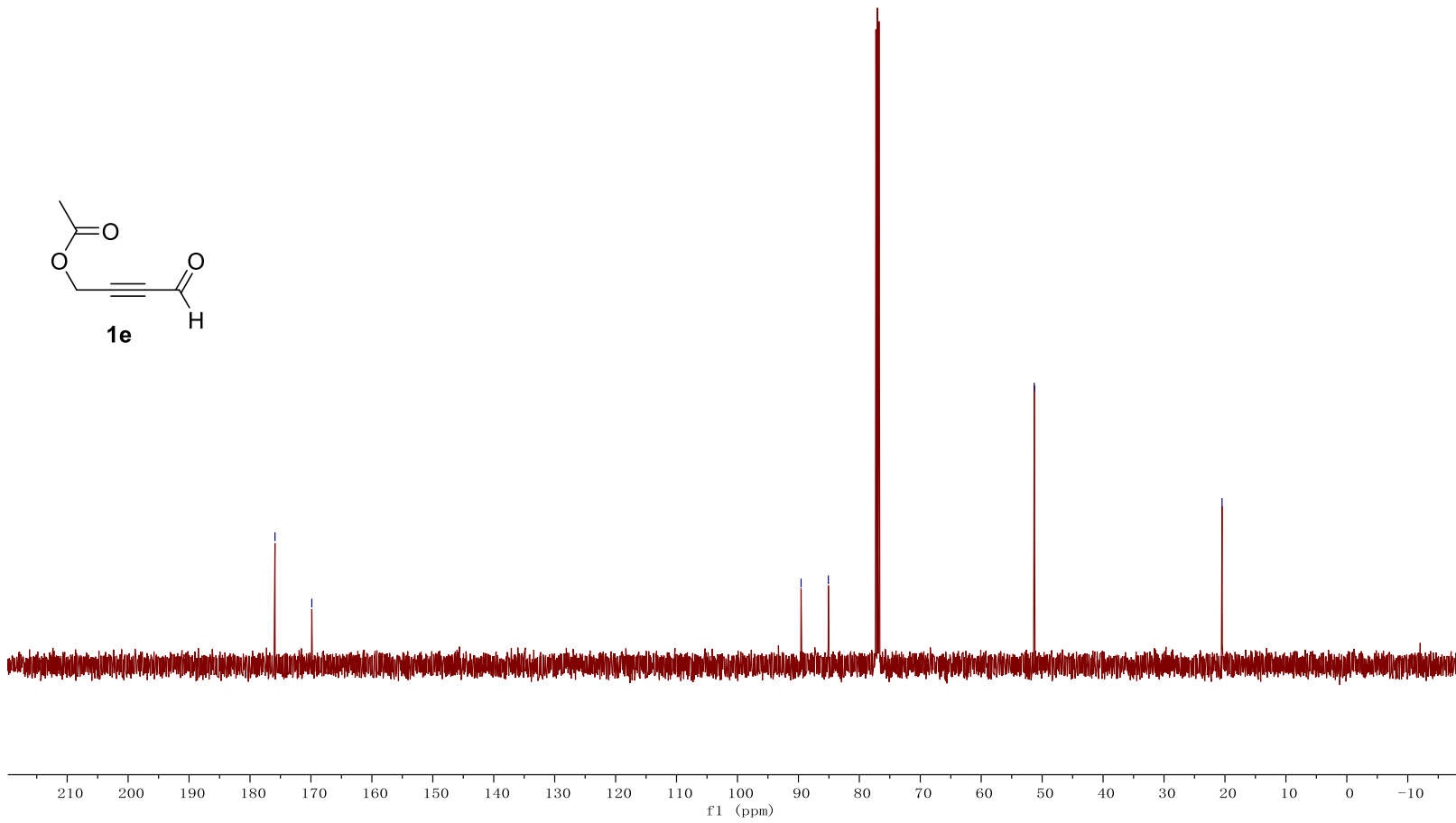
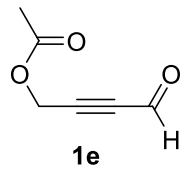
xzr-i-155-2.11.fid

— 175.90
— 169.85

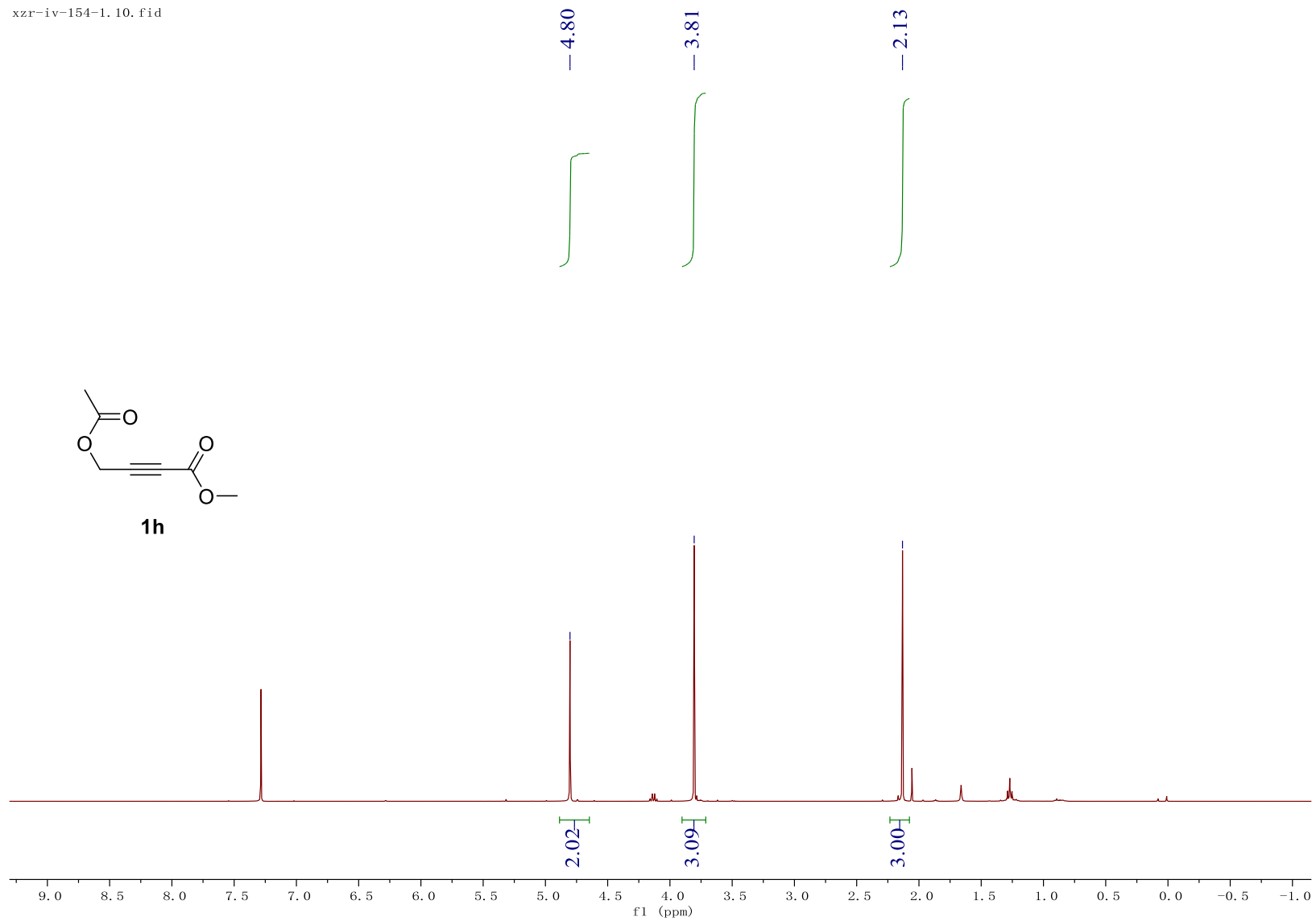
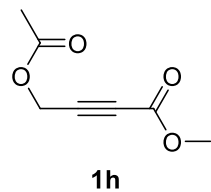
— 89.56
— 85.08

— 51.30

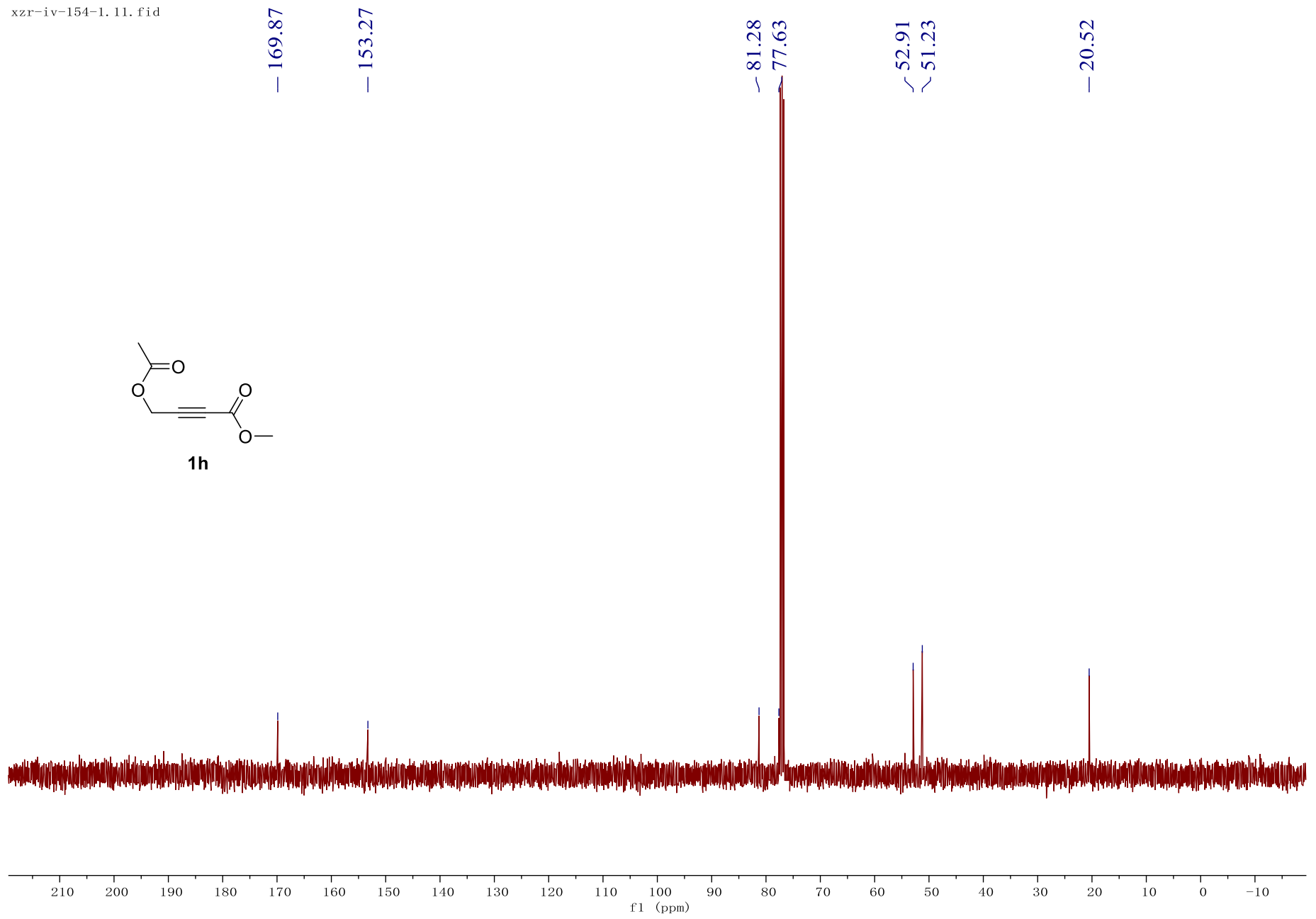
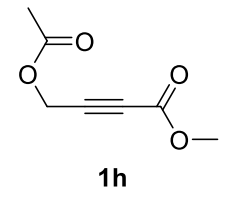
— 20.48



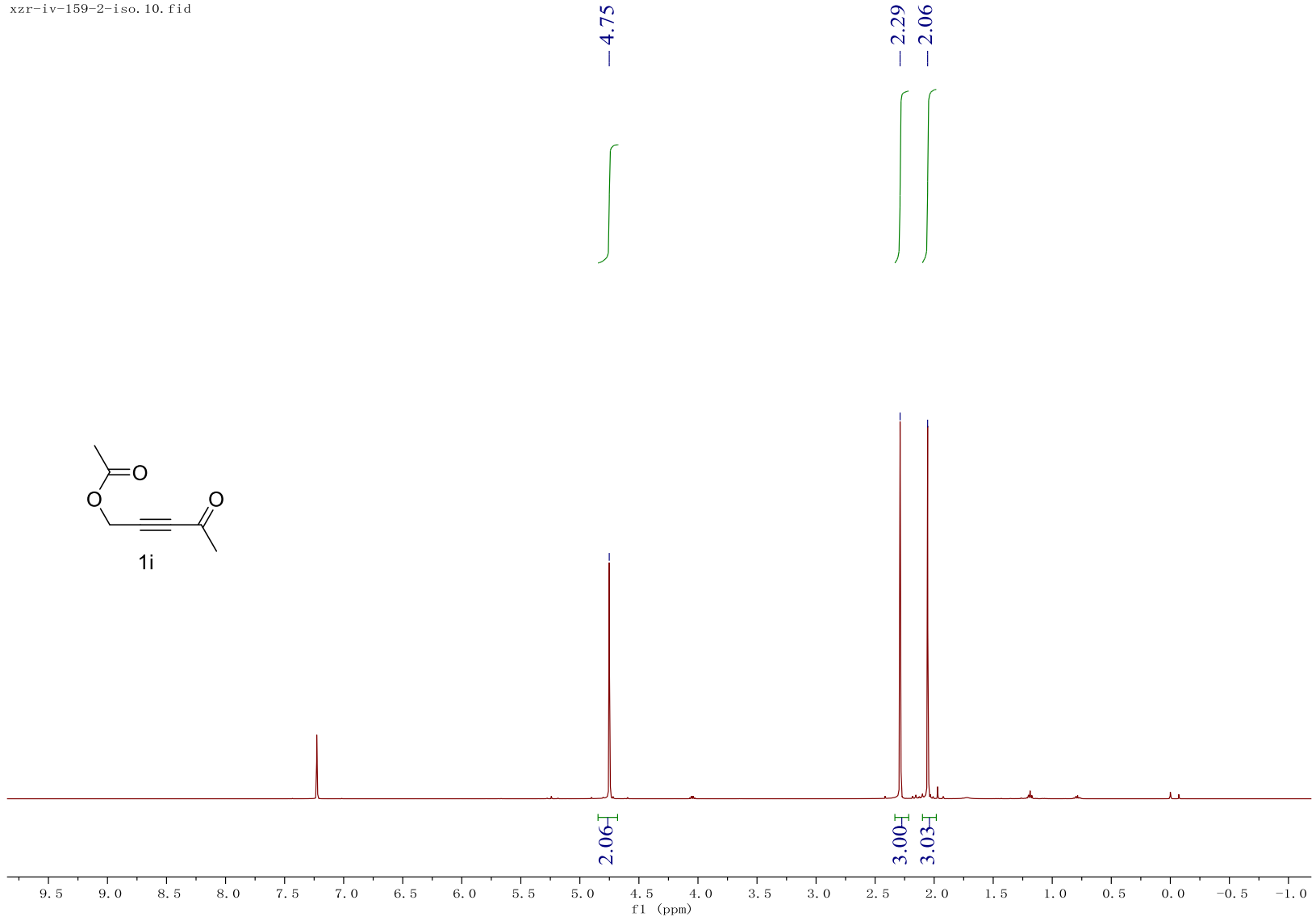
xzr-iv-154-1.10.fid



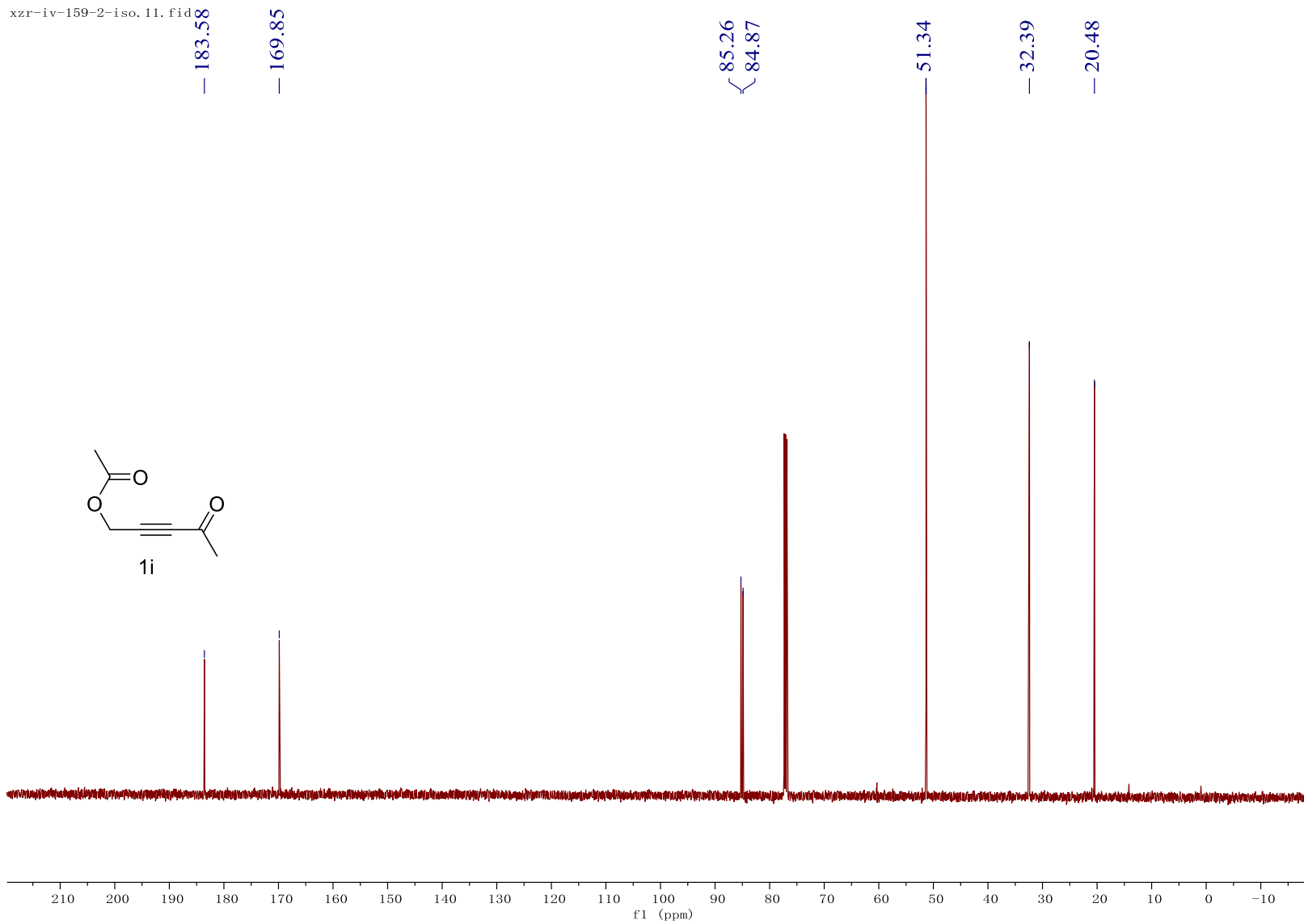
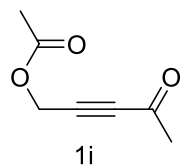
xzr-iv-154-1.11.fid



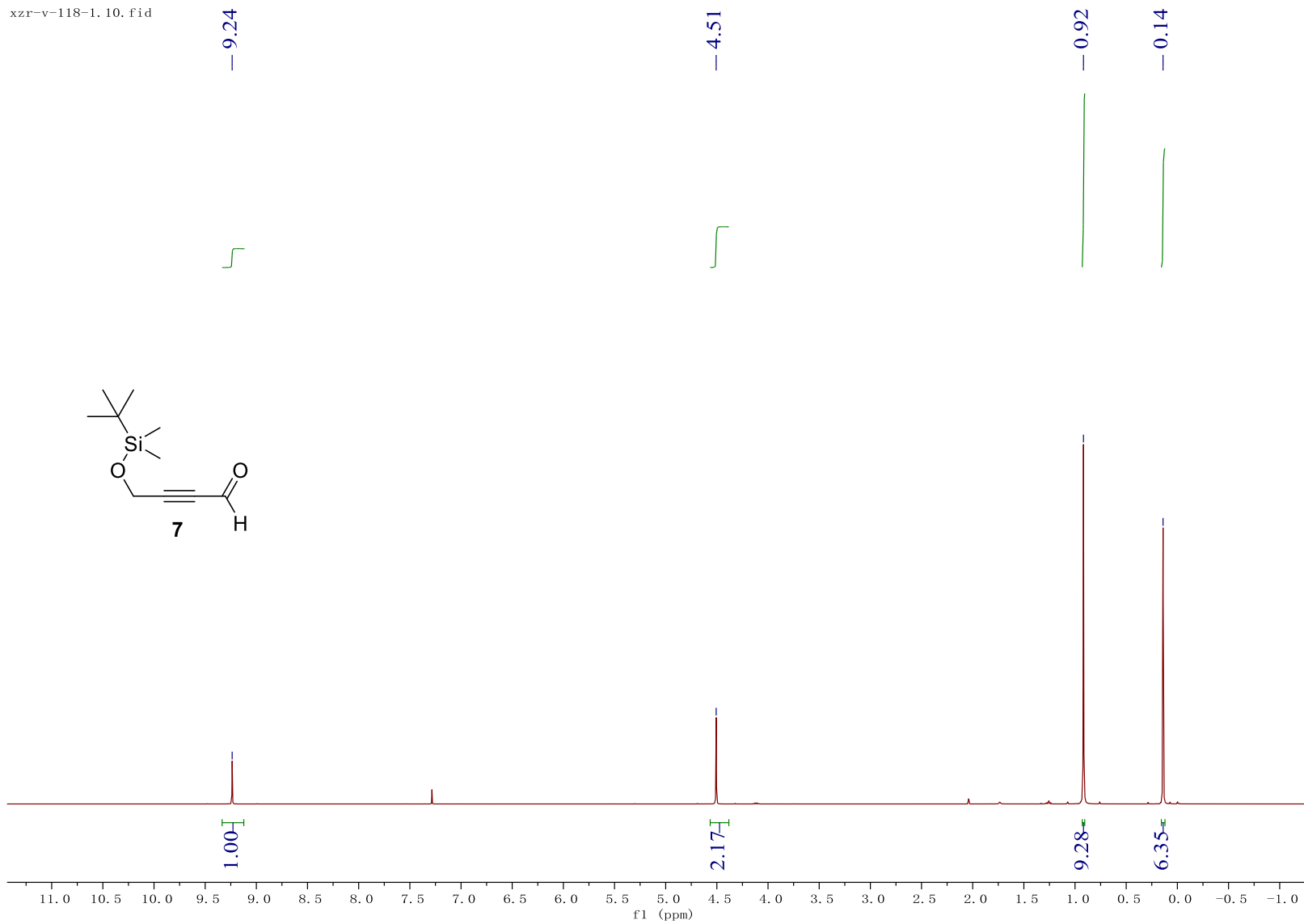
xzr-iv-159-2-iso.10.fid



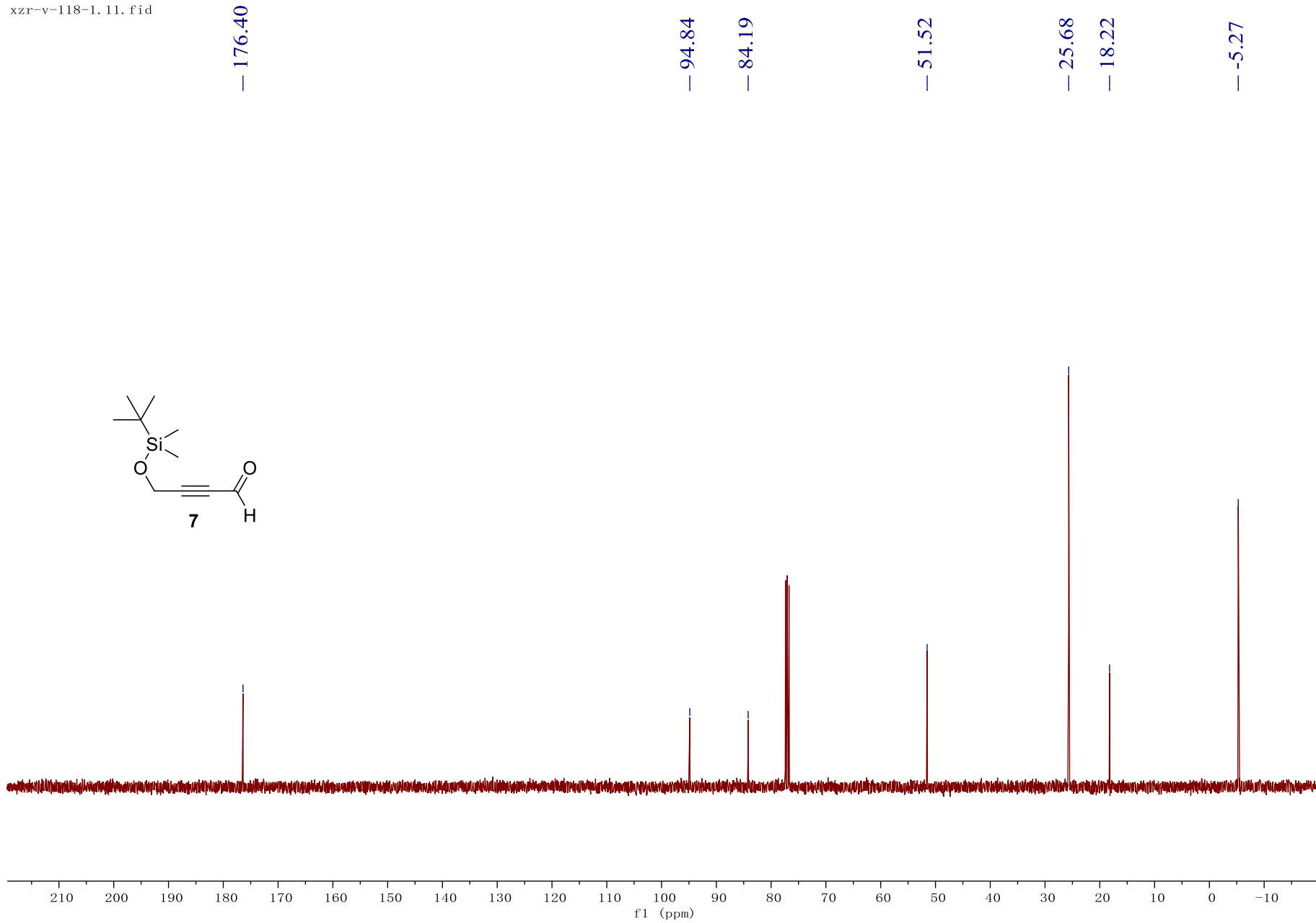
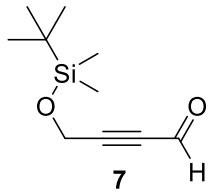
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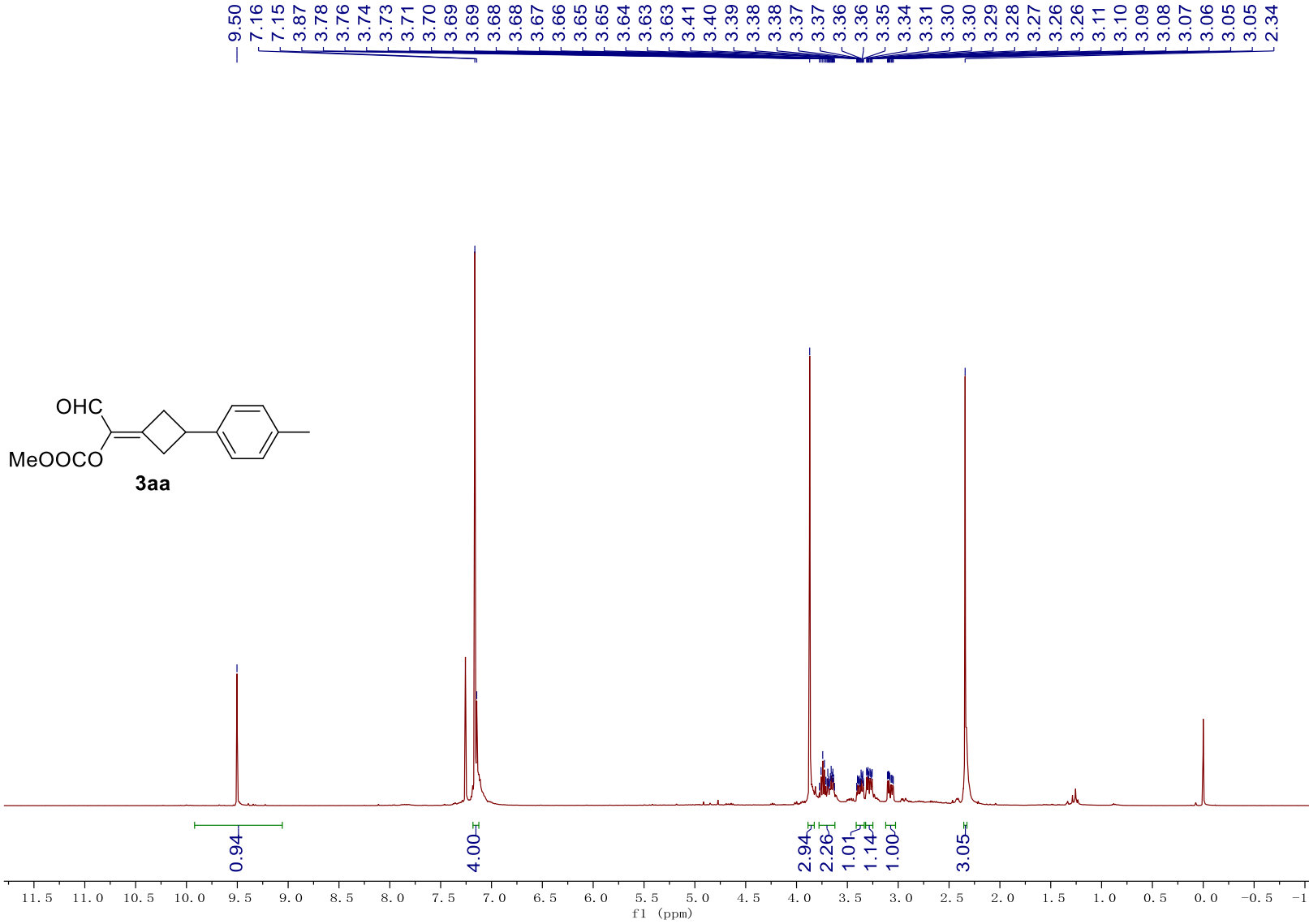
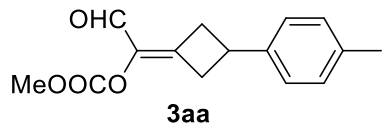


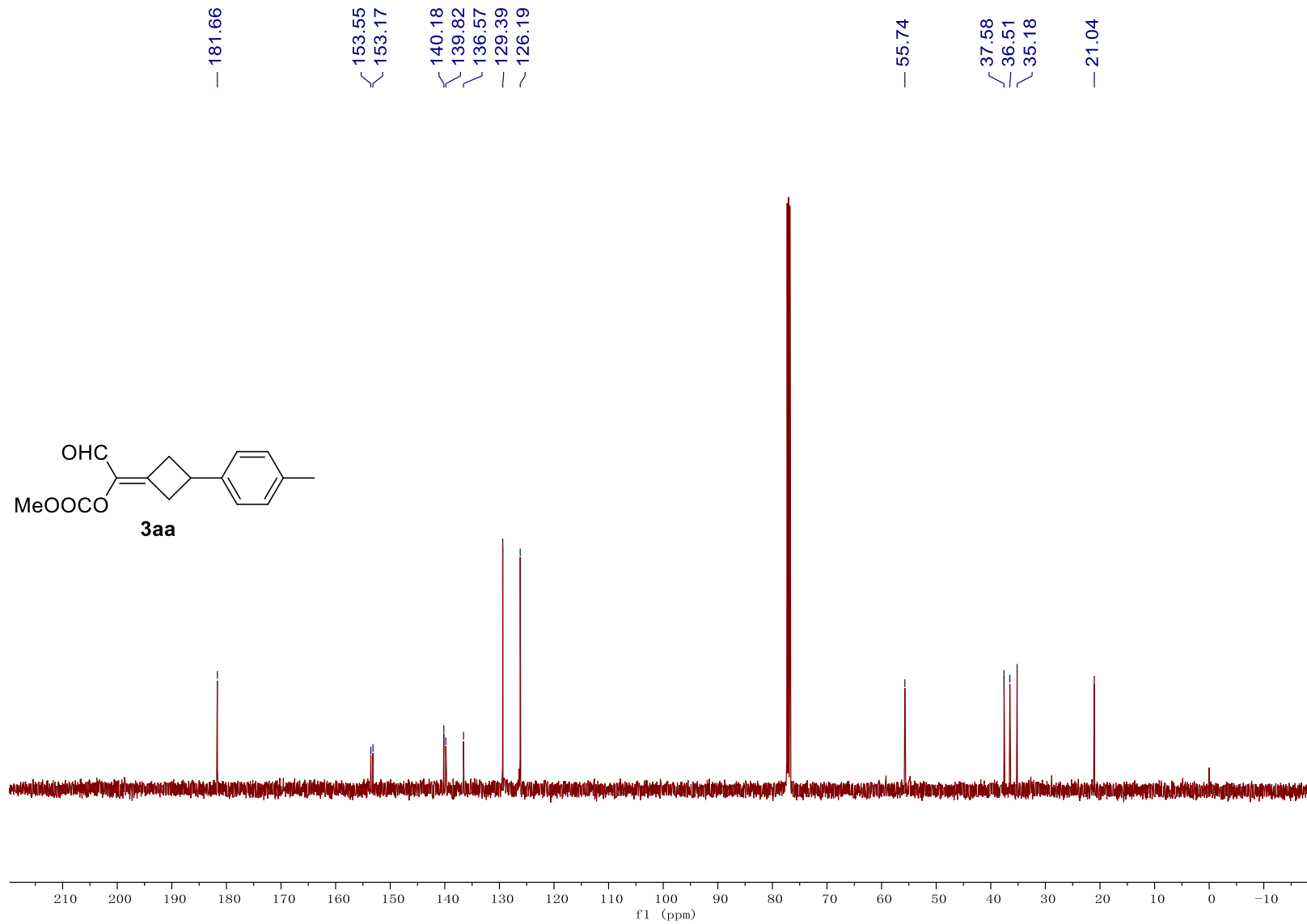
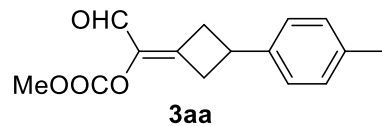
xzr-v-118-1.10.fid

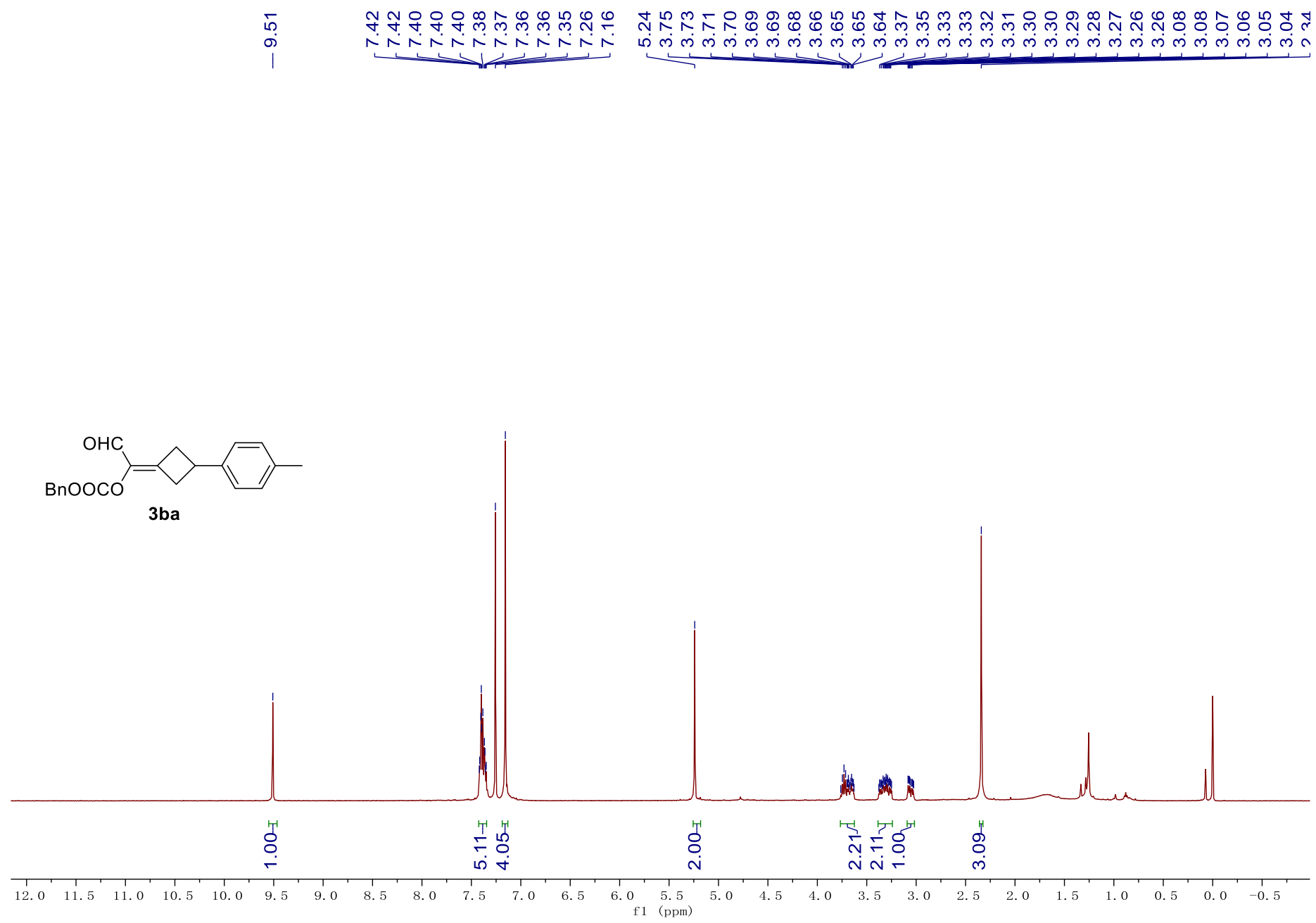
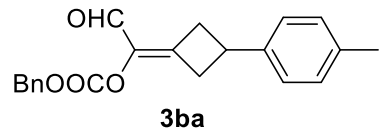


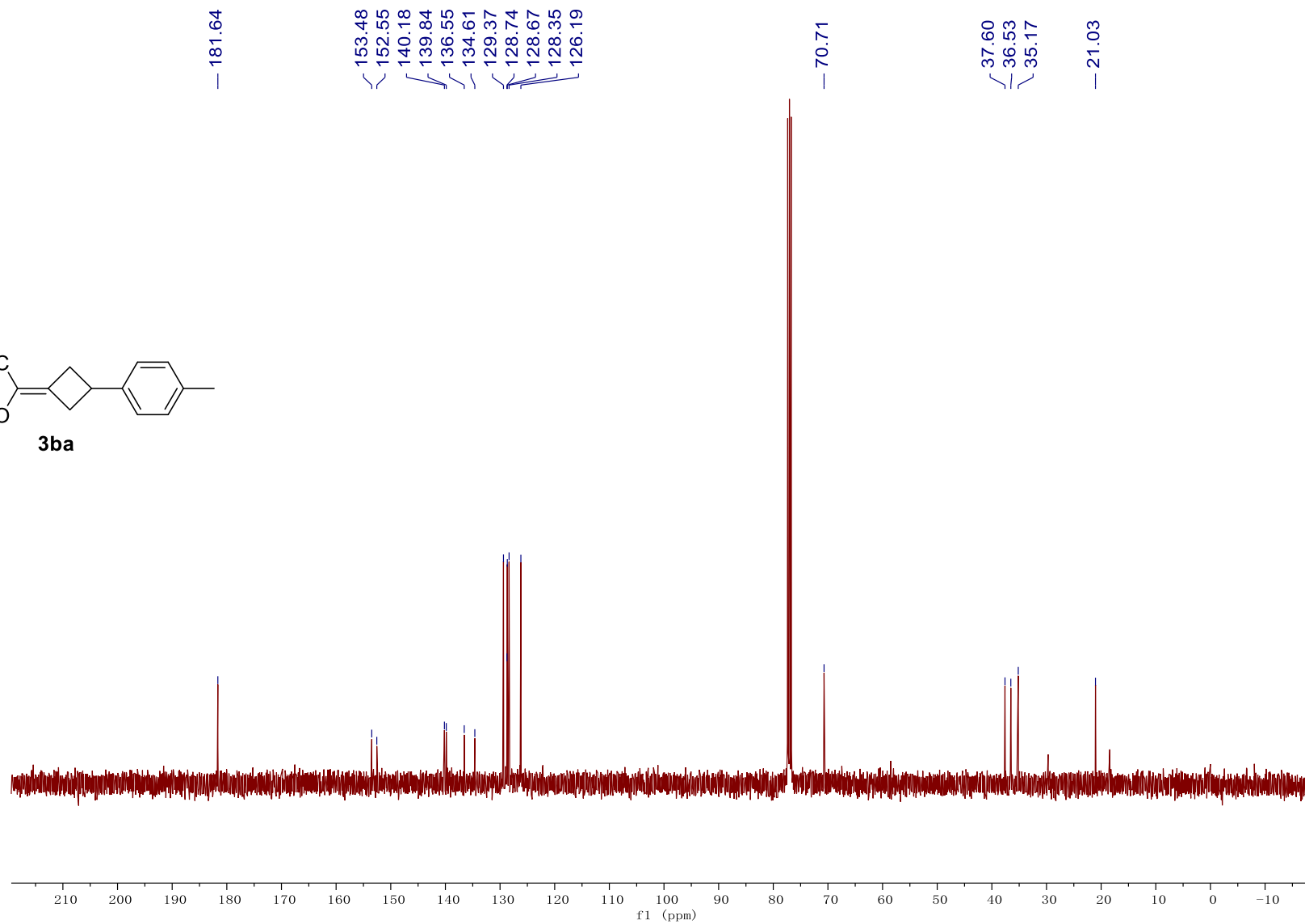
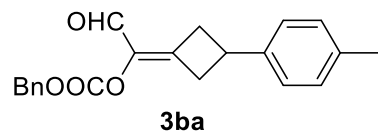
xzr-v-118-1. 11. fid

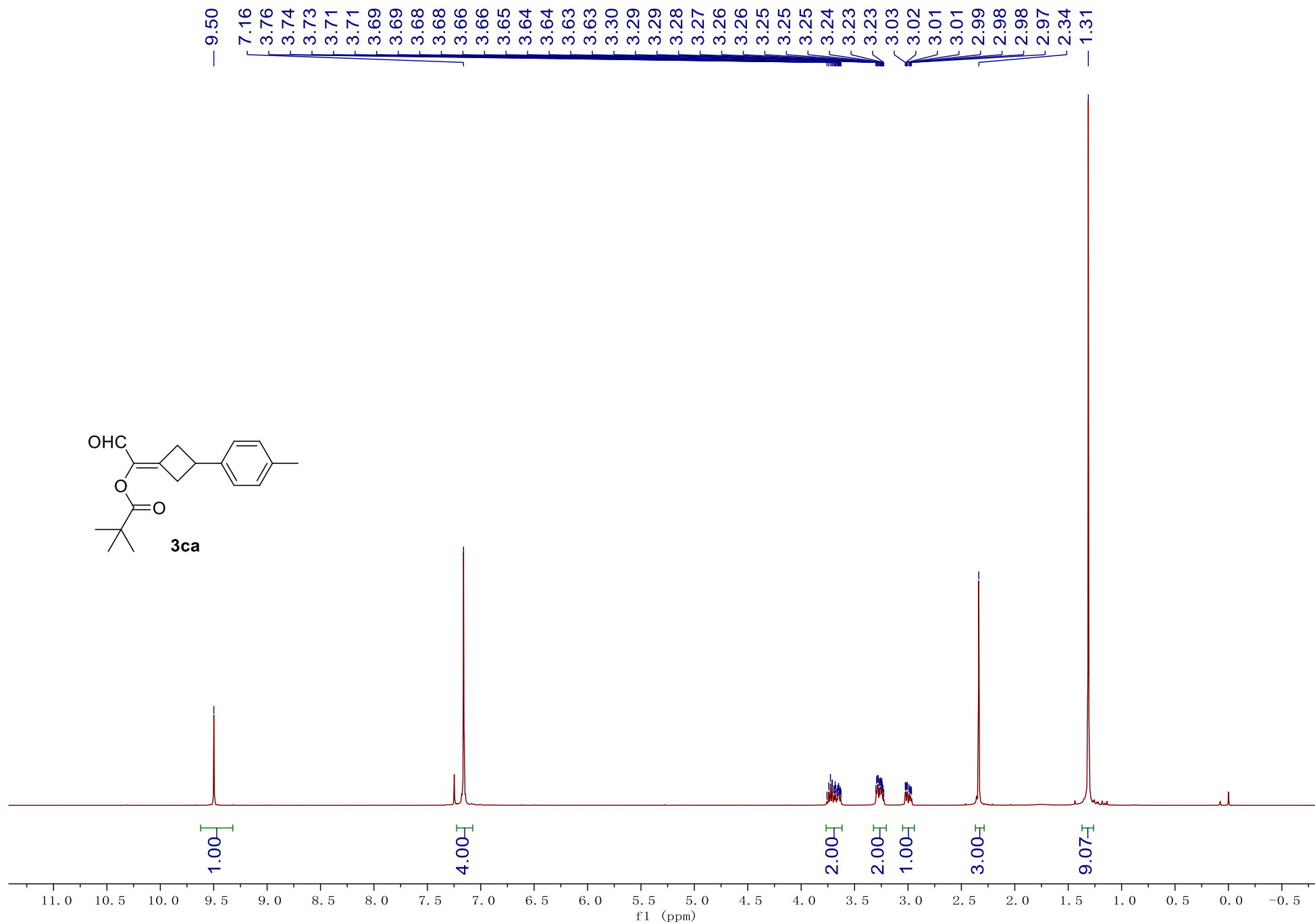


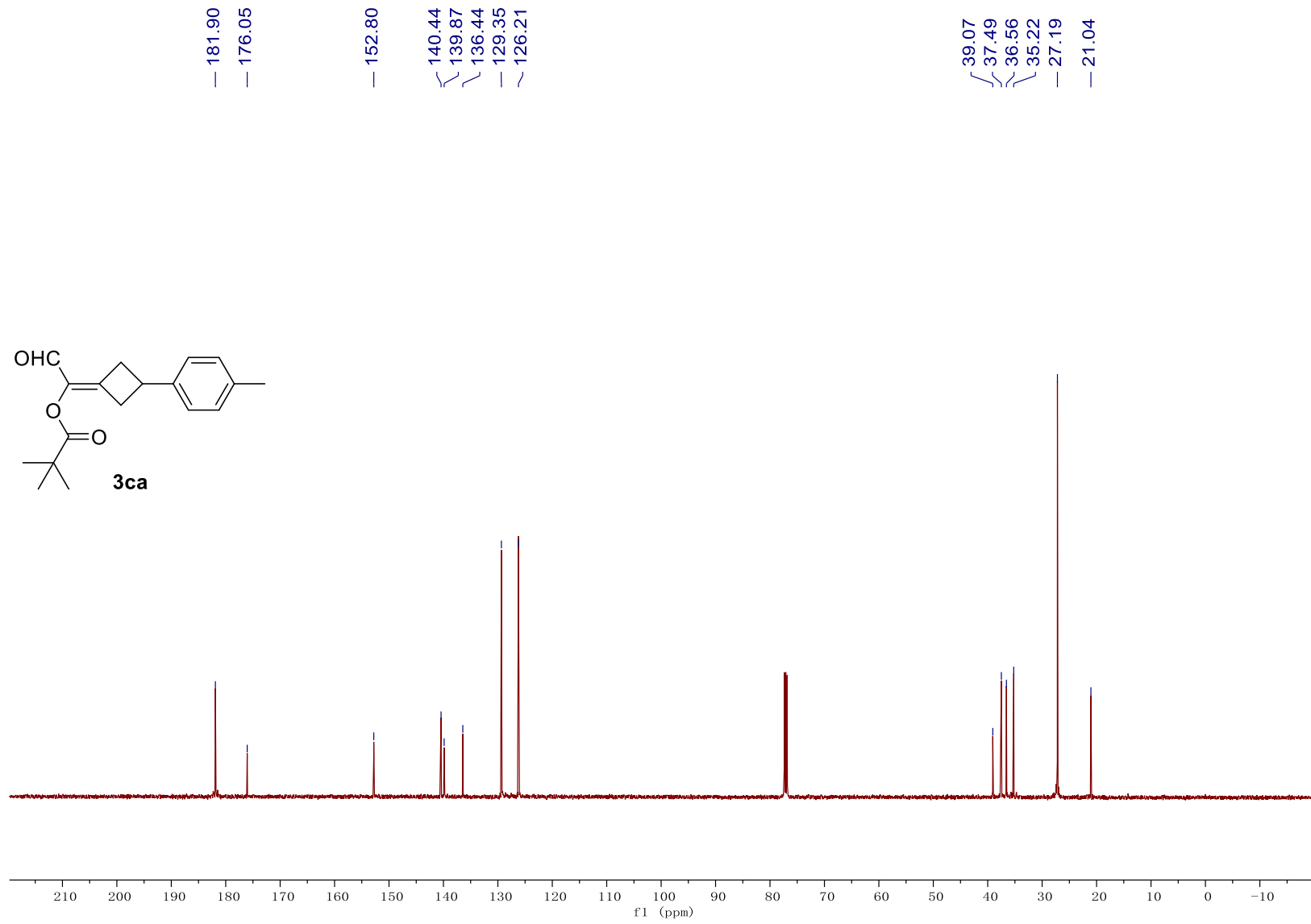
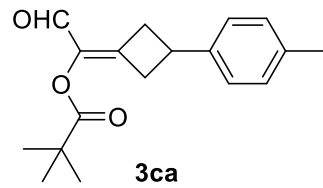


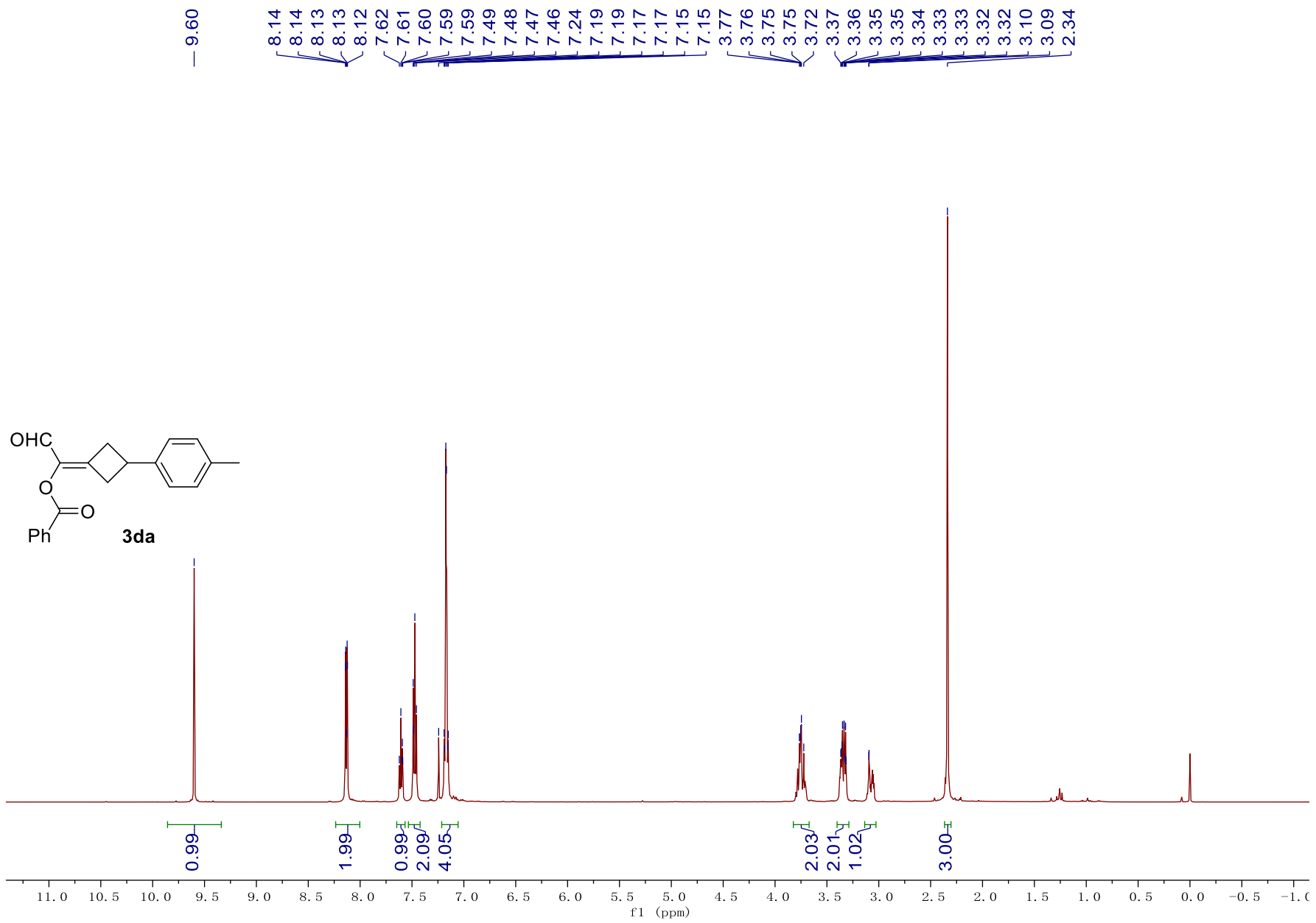
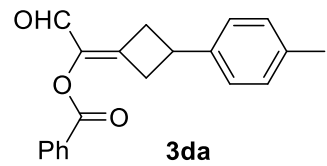


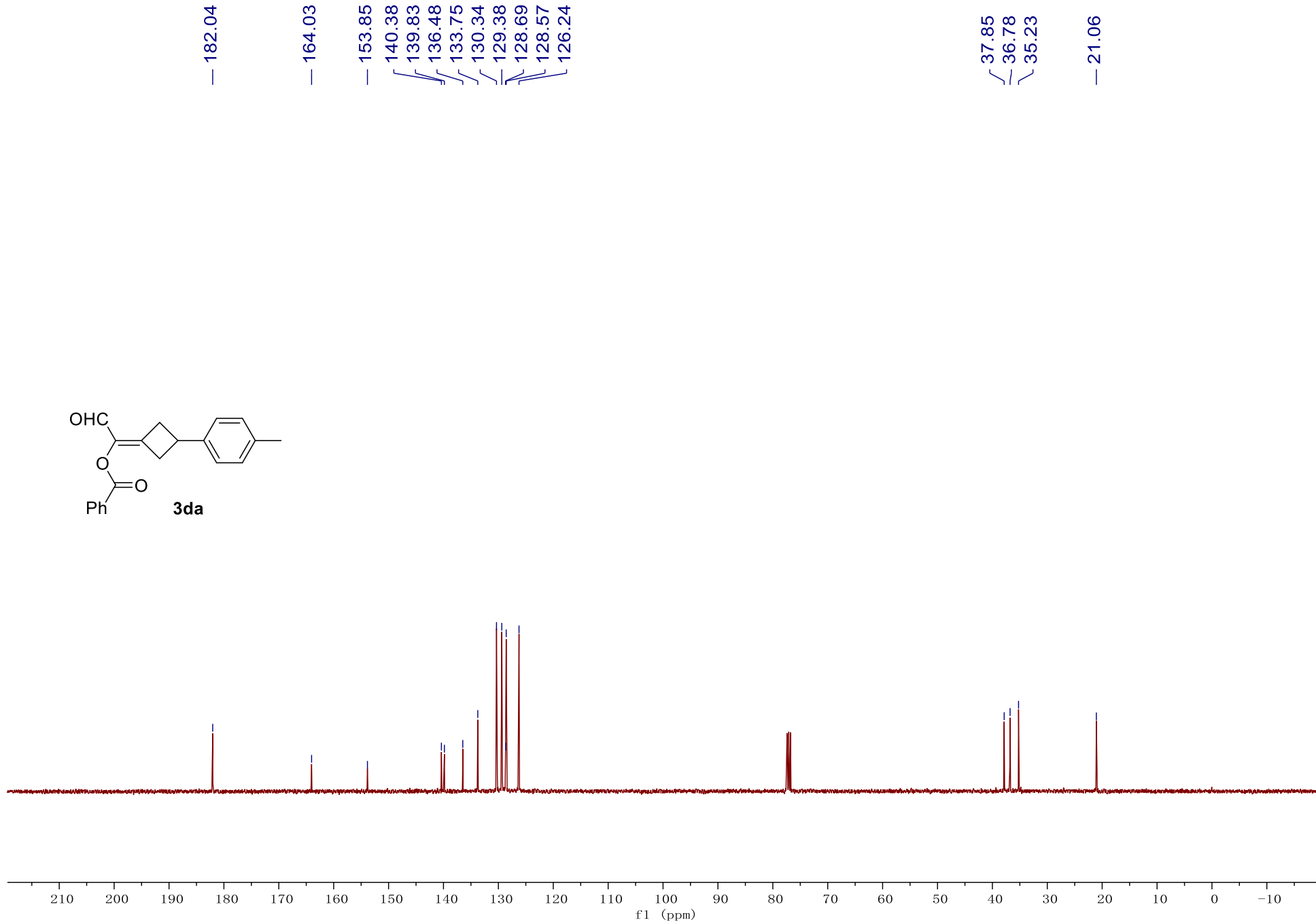
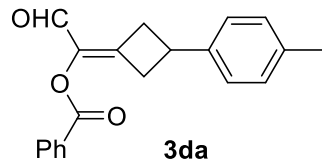


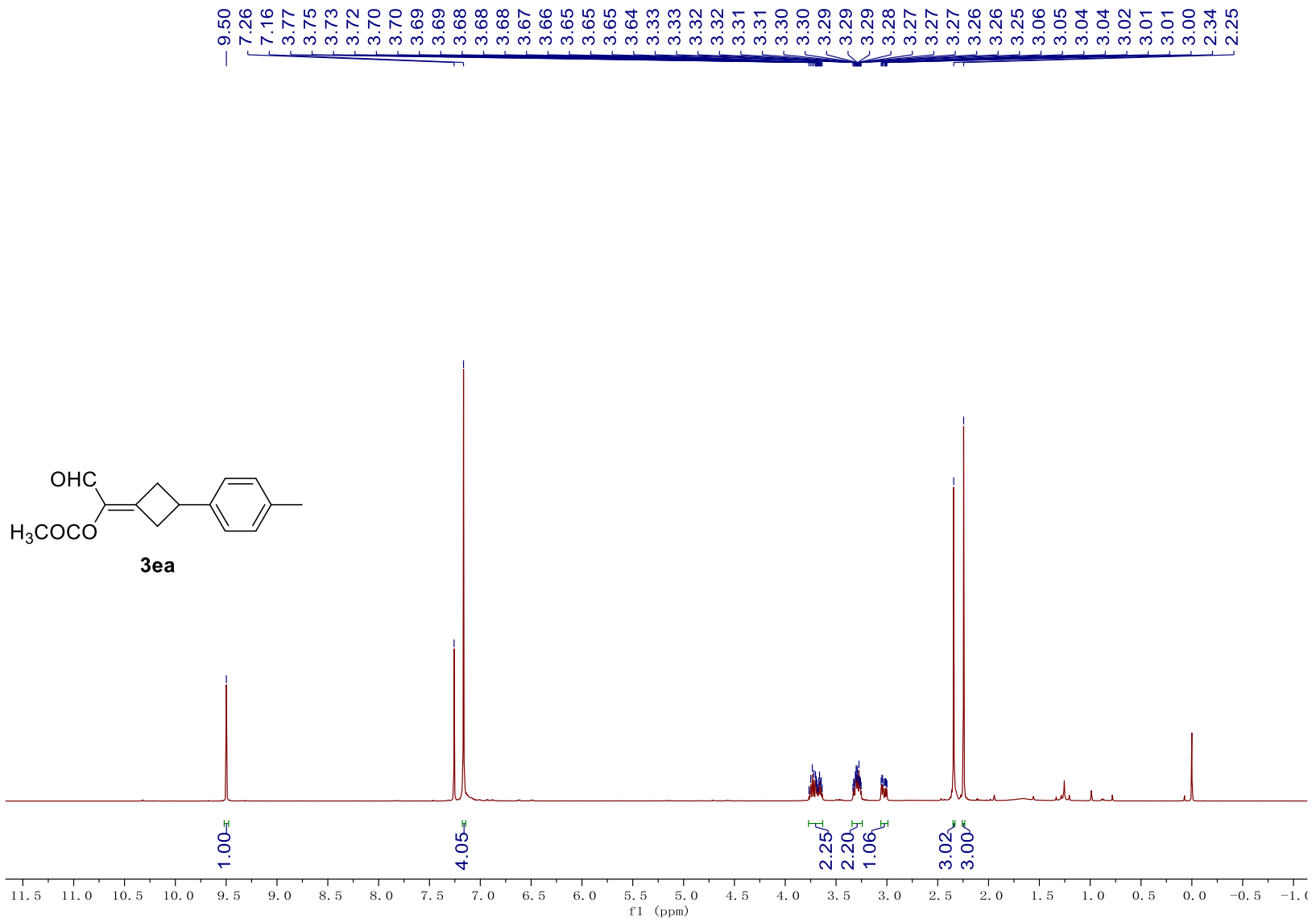


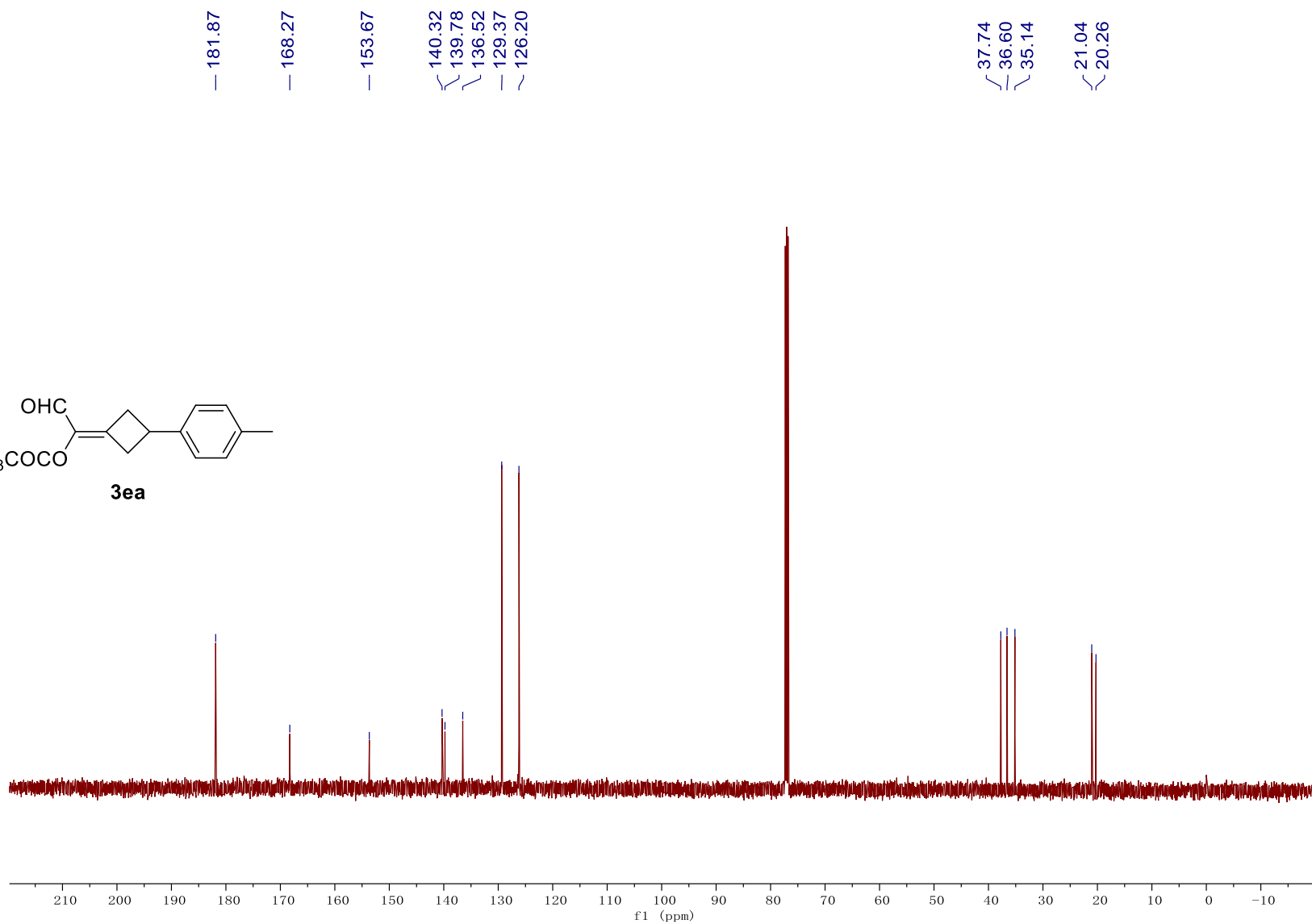
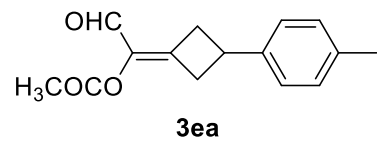


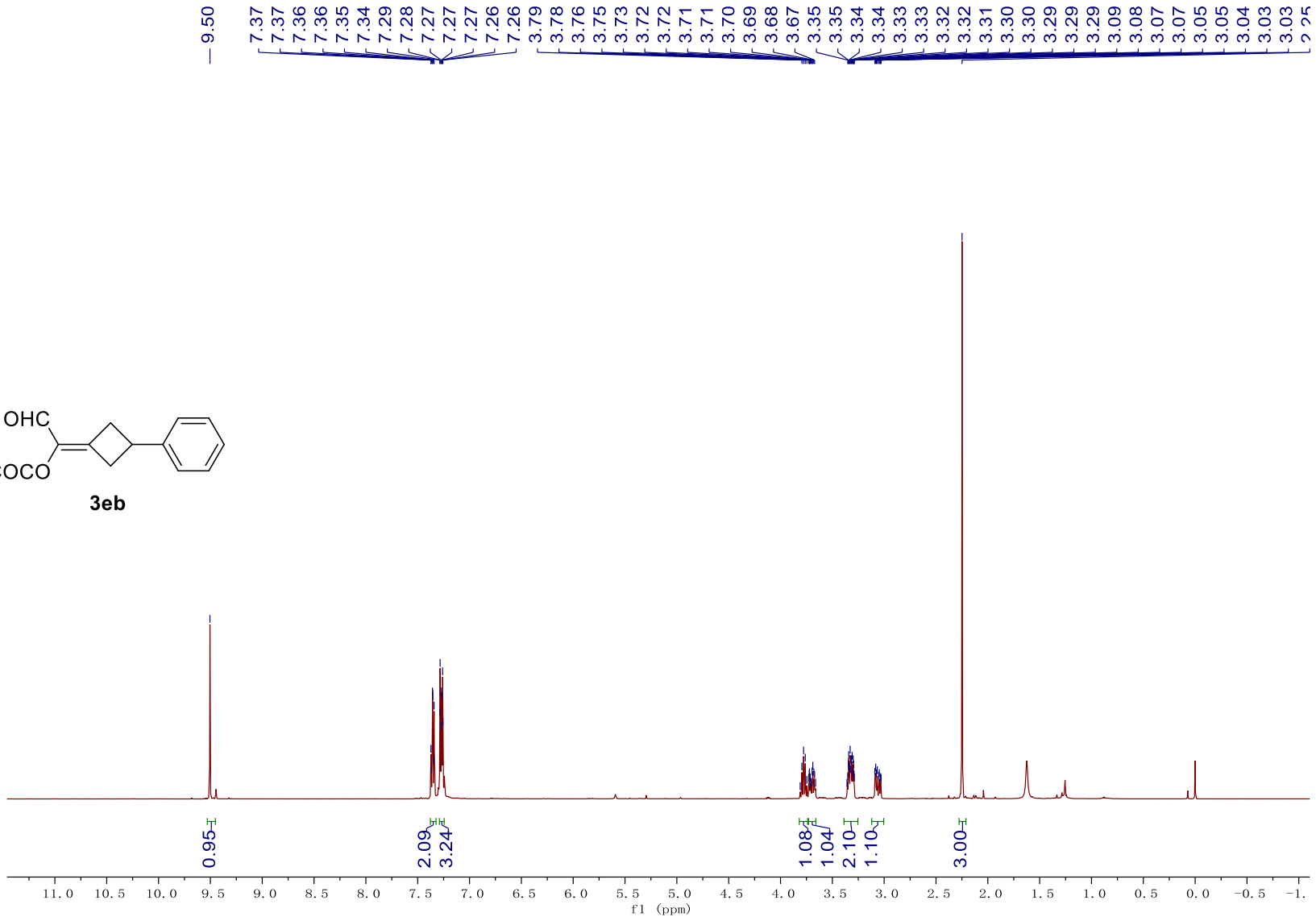
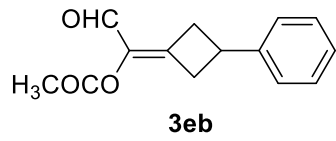


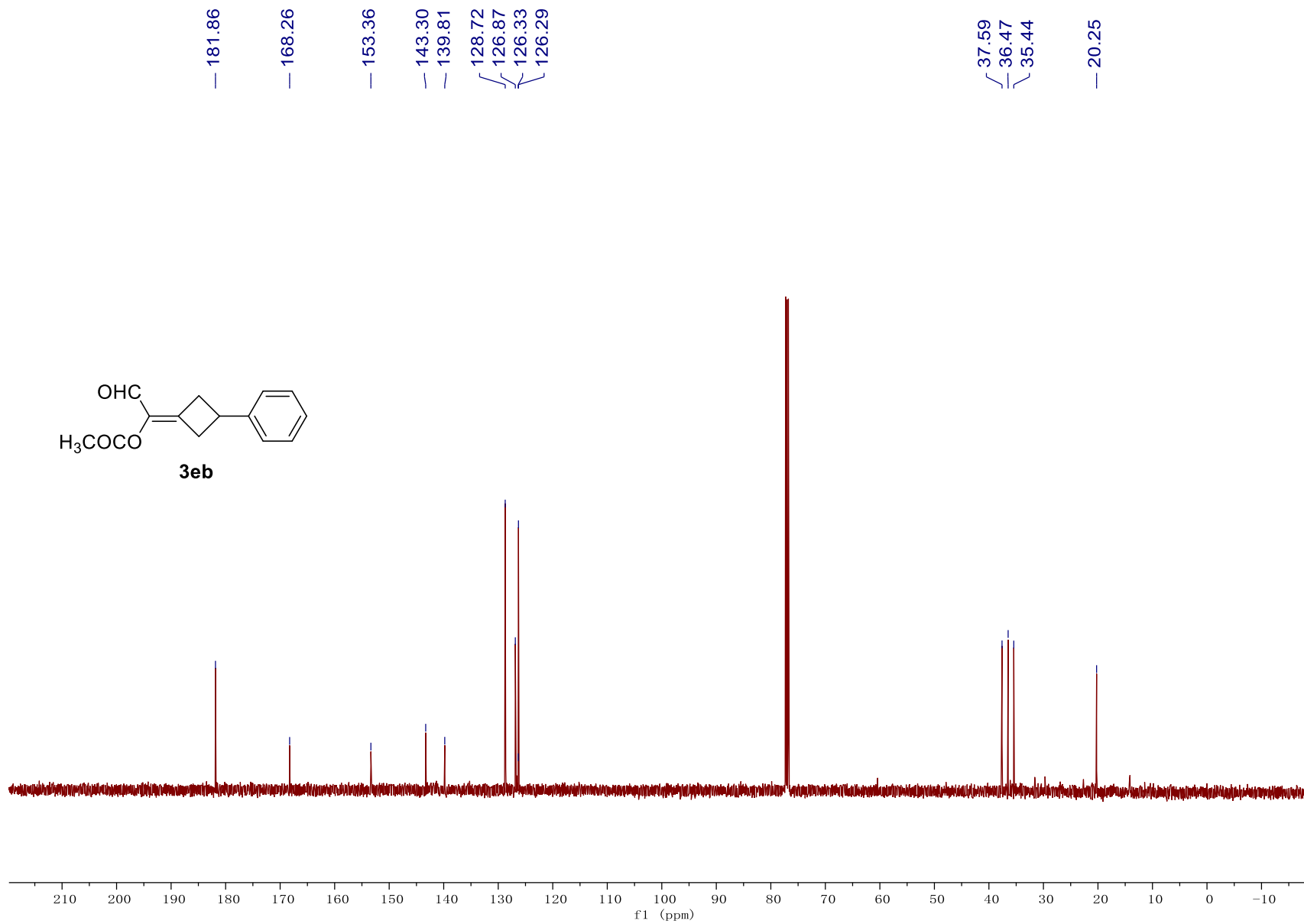
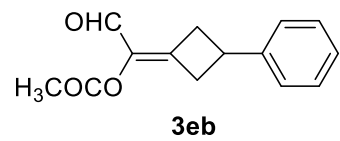


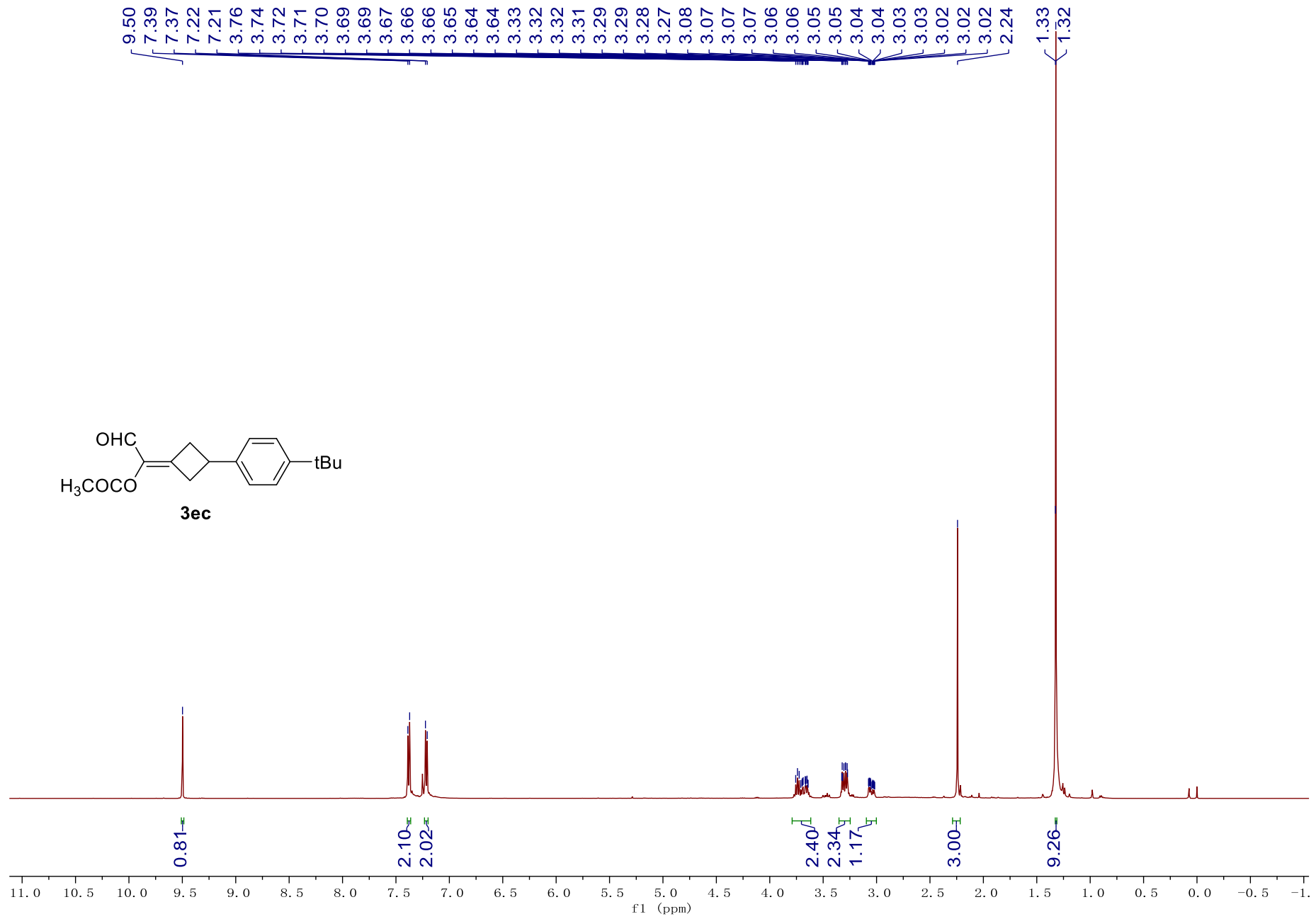


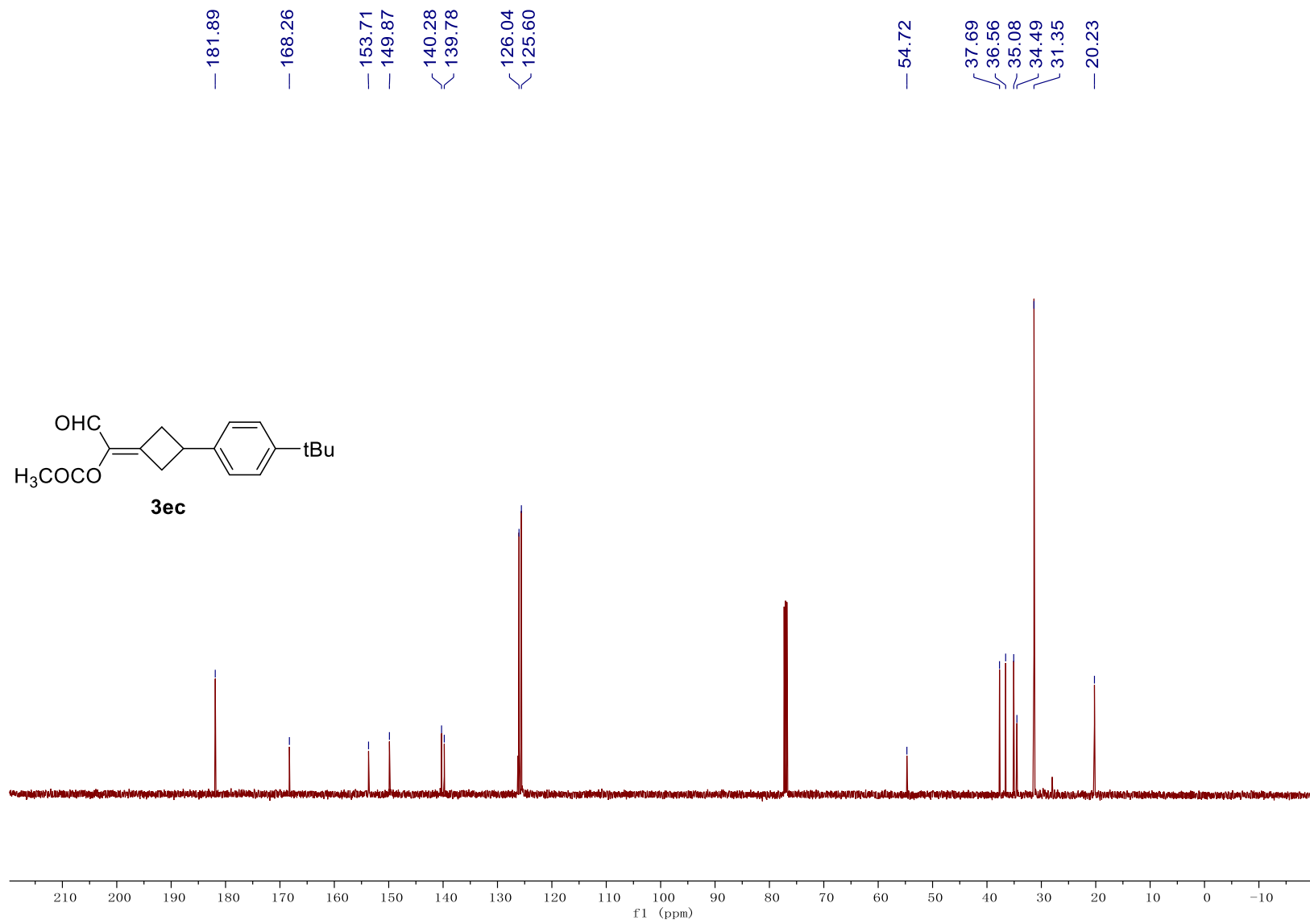
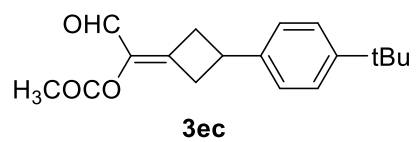


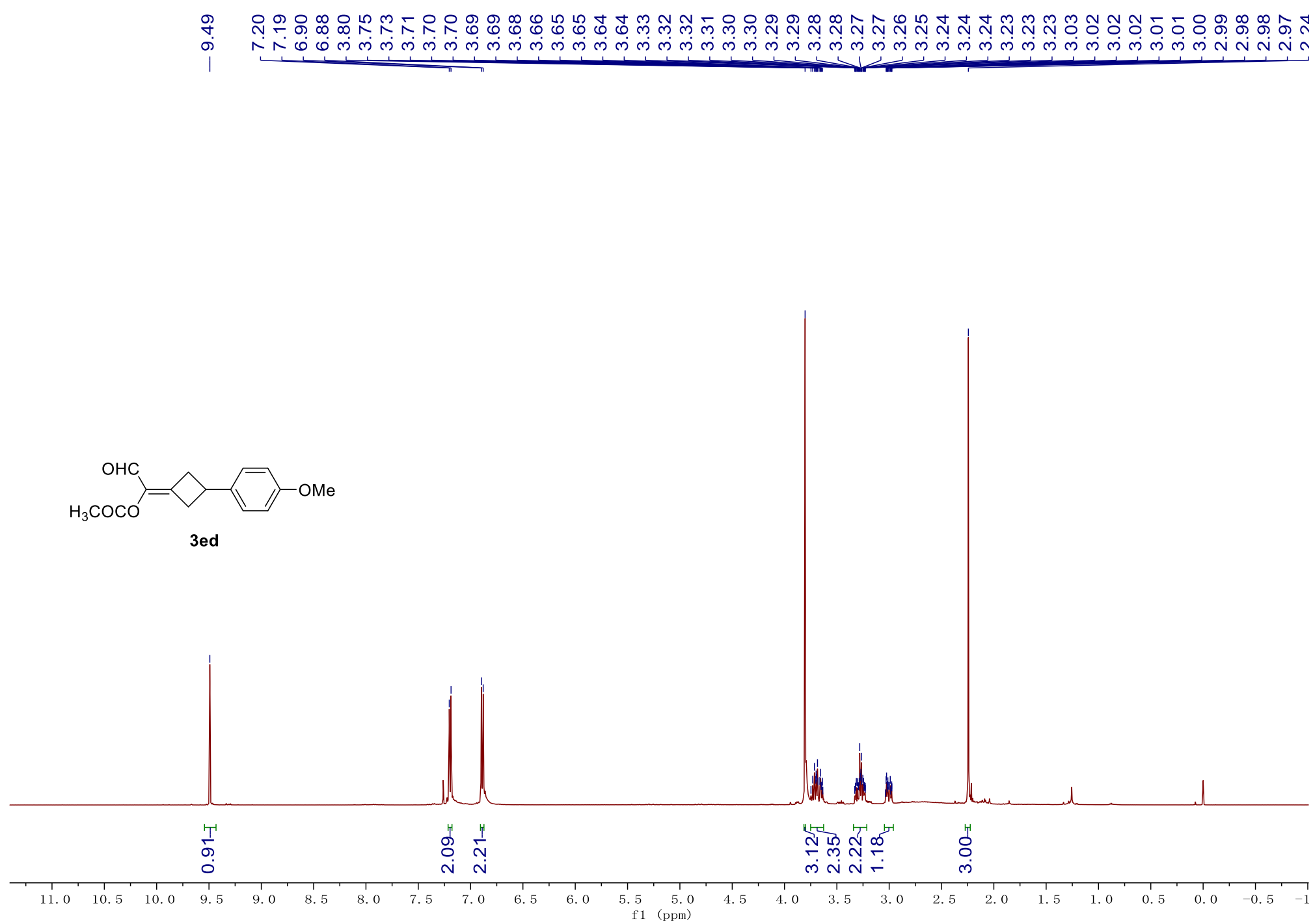
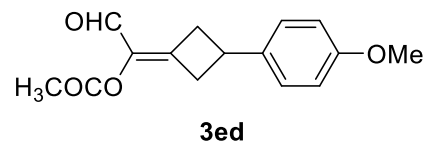


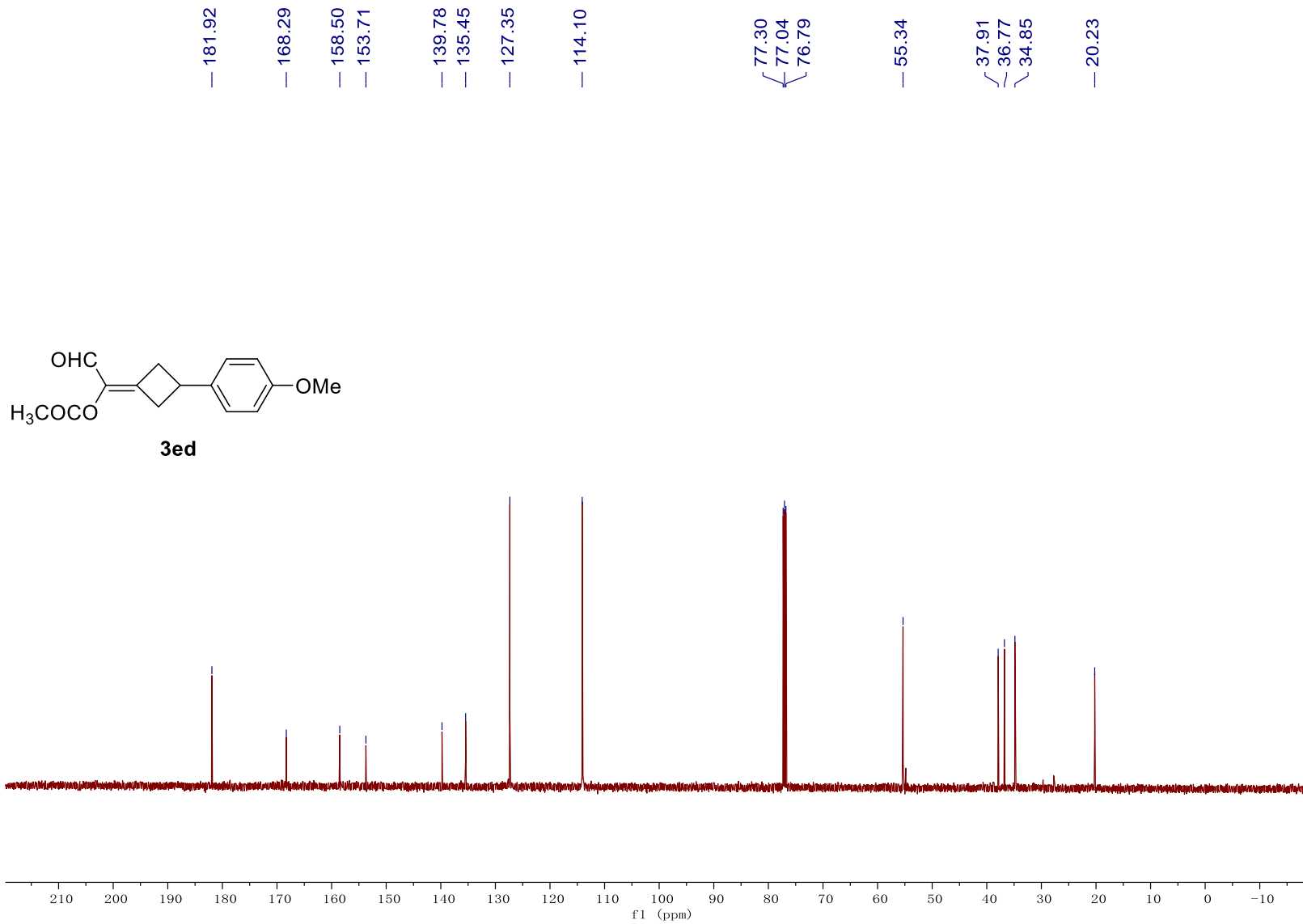


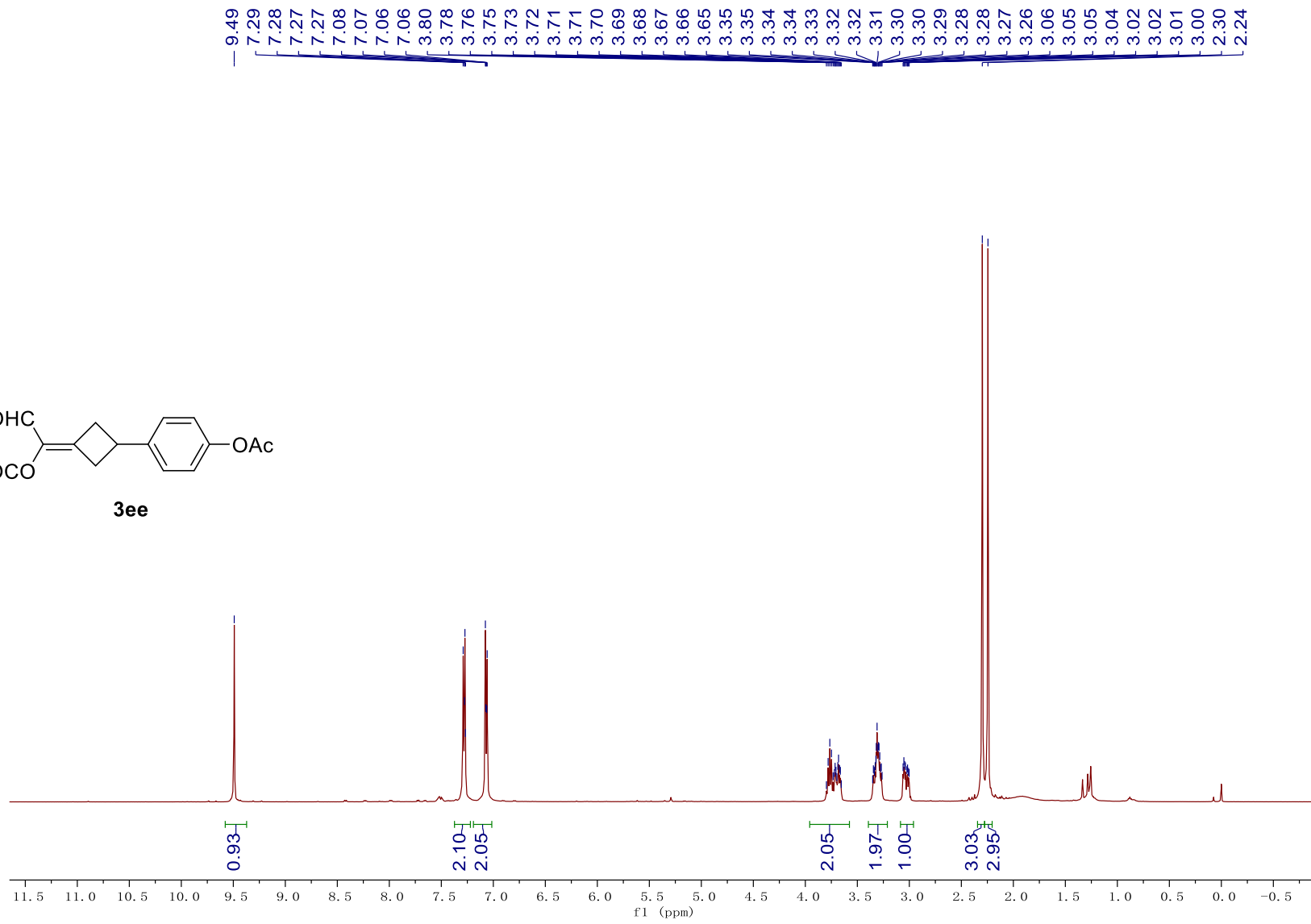
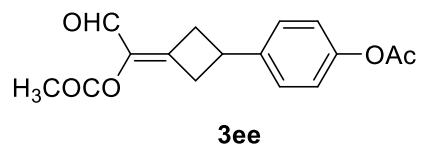


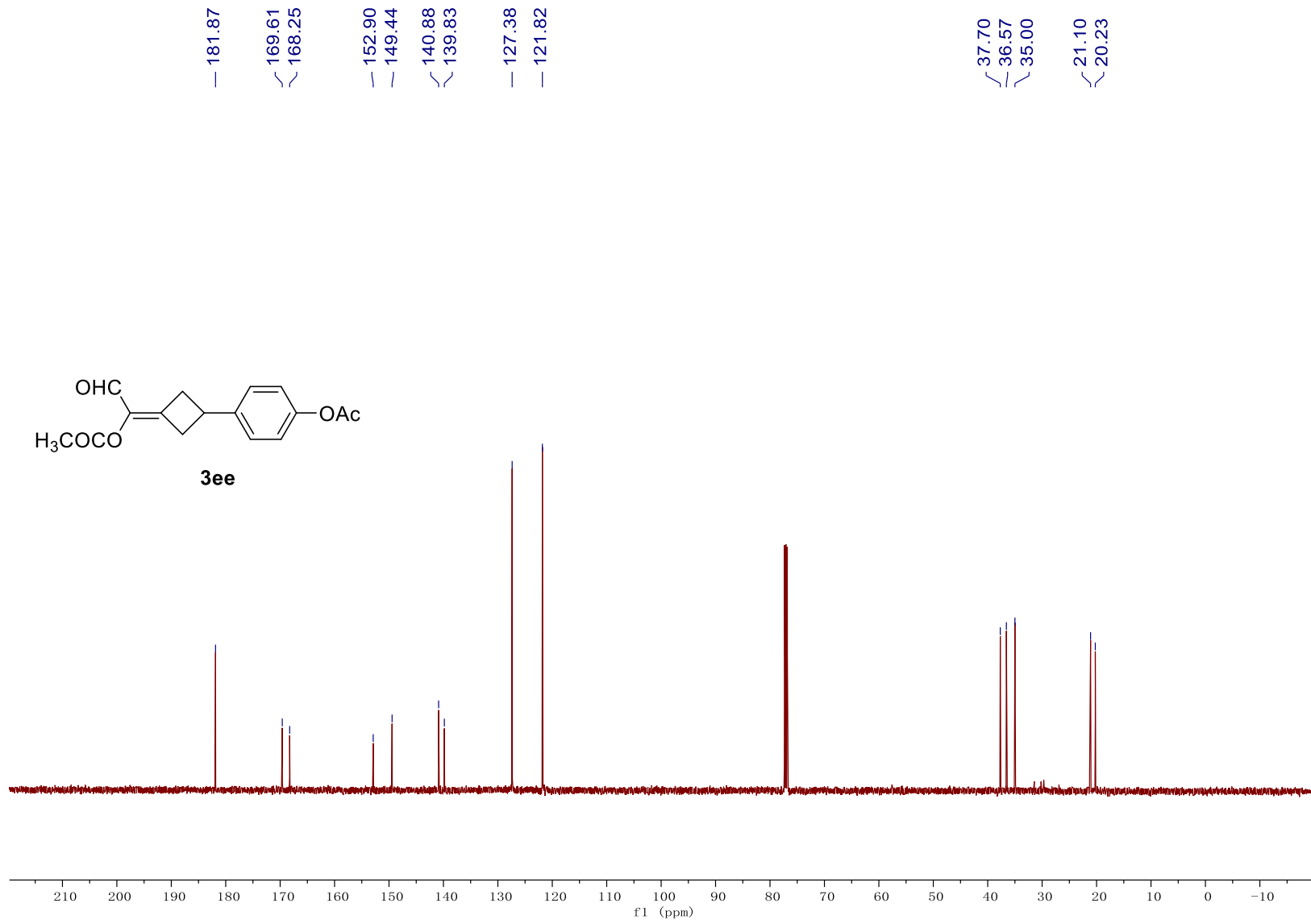


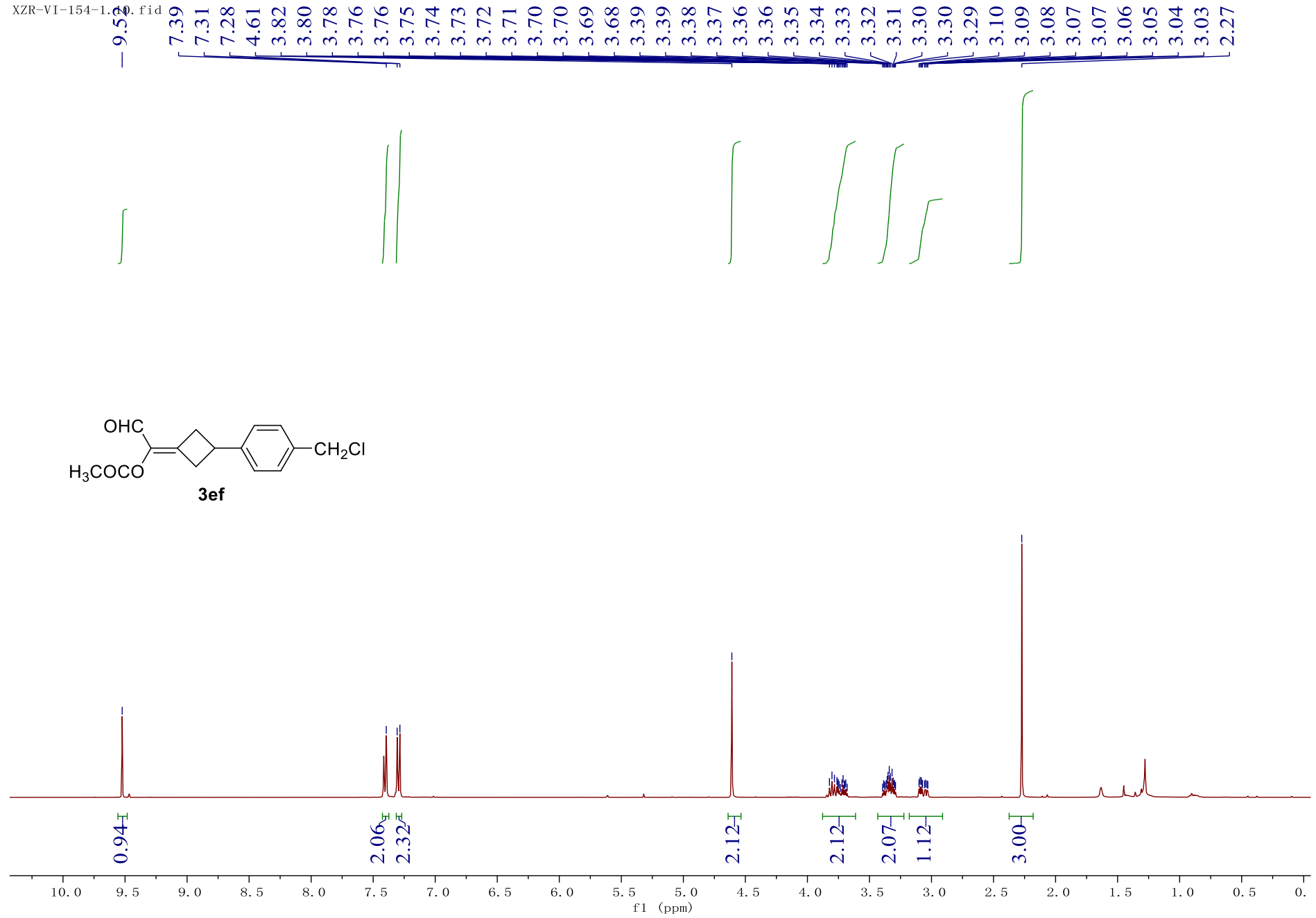


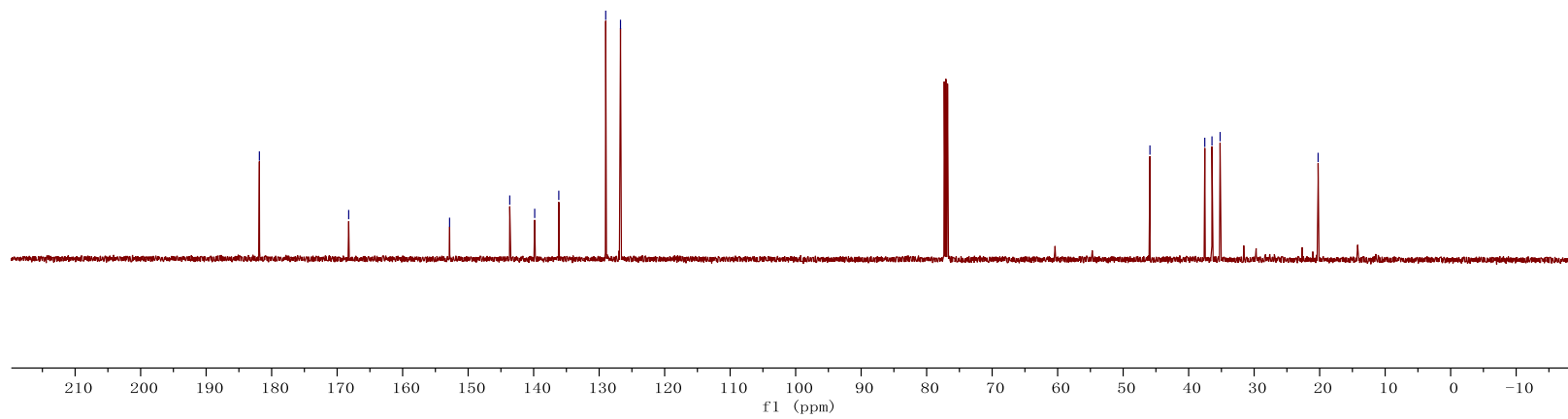
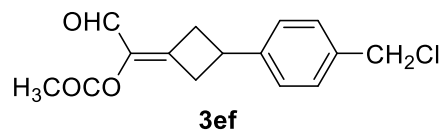


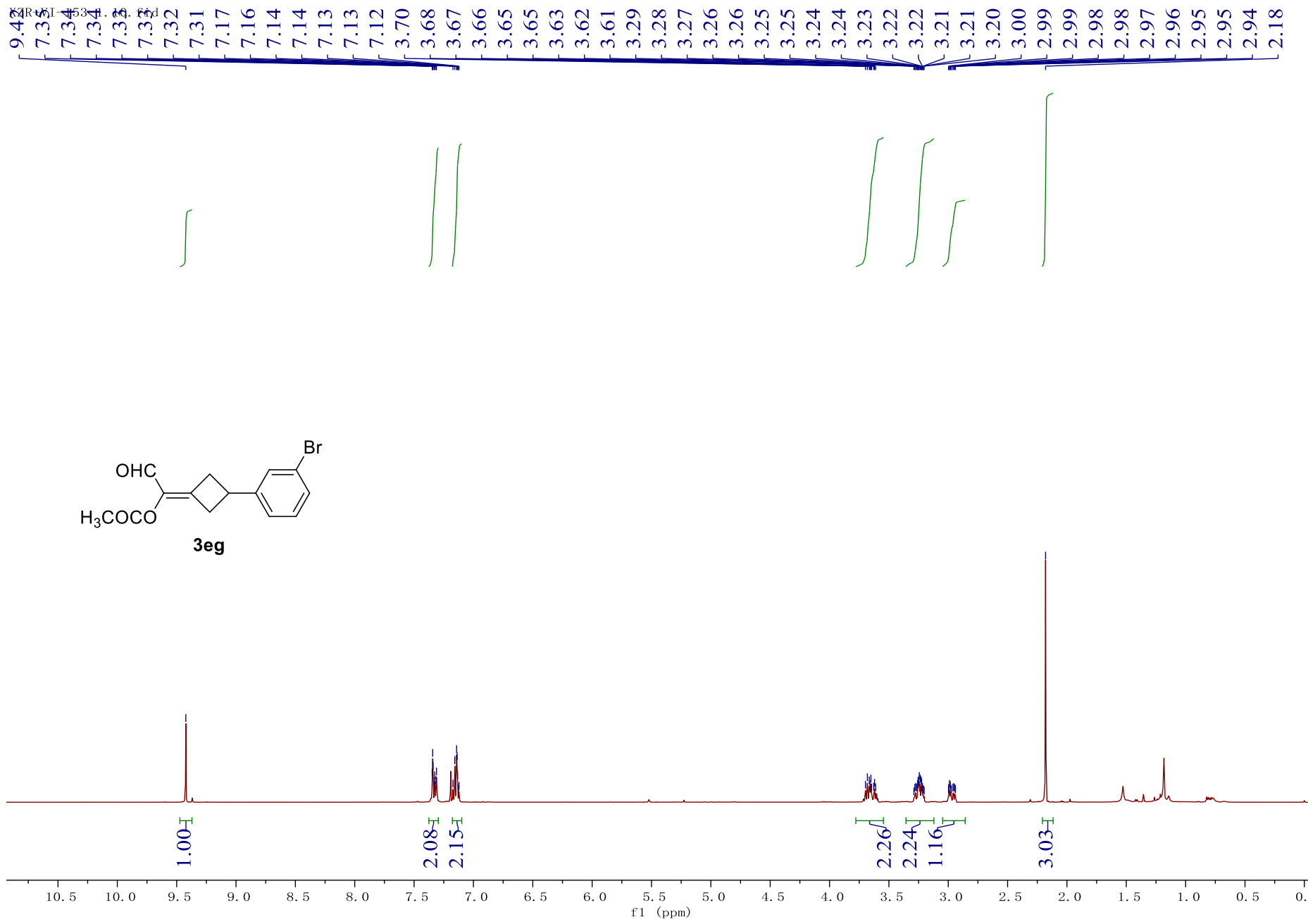


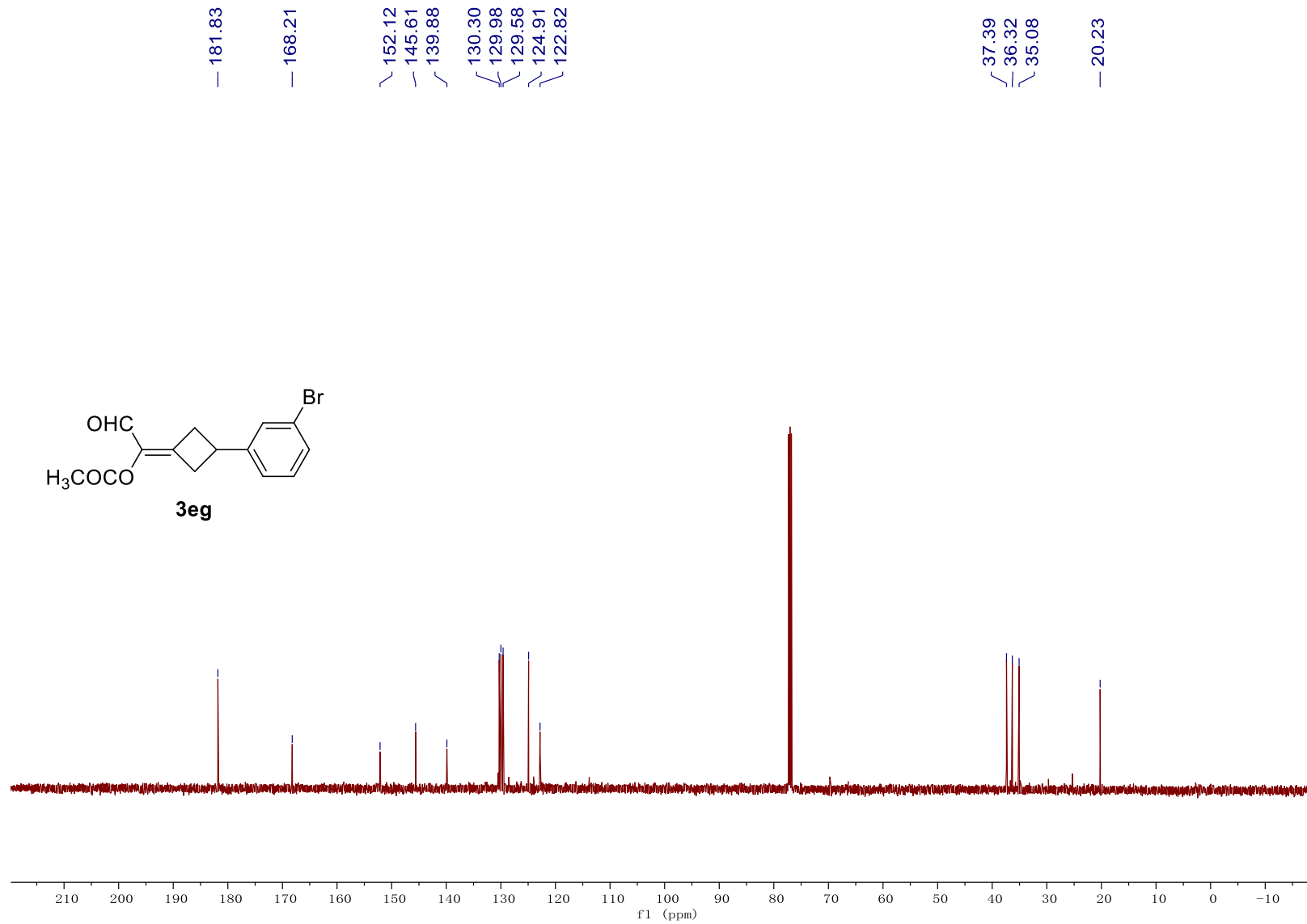


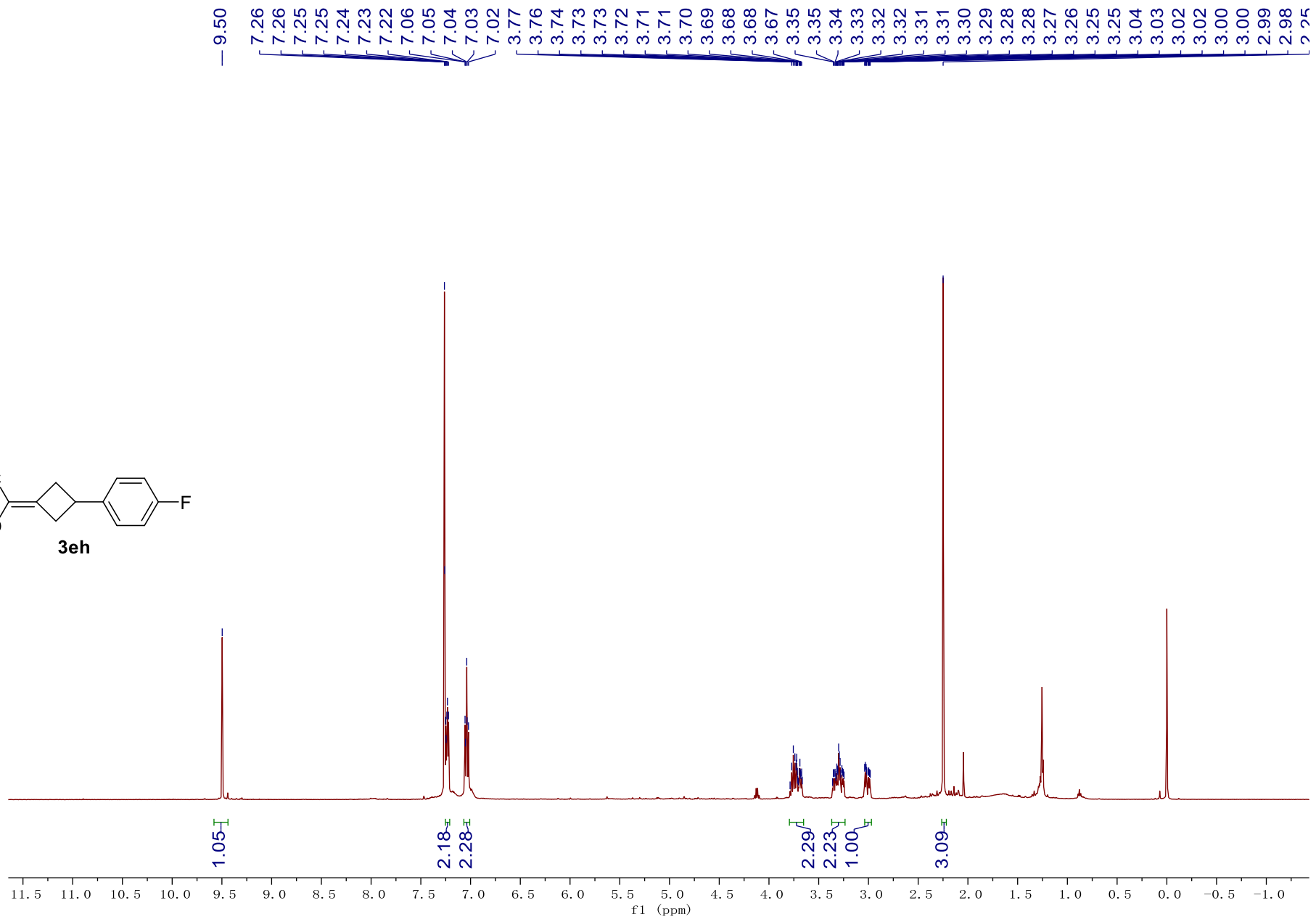
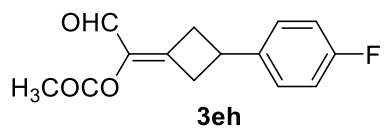


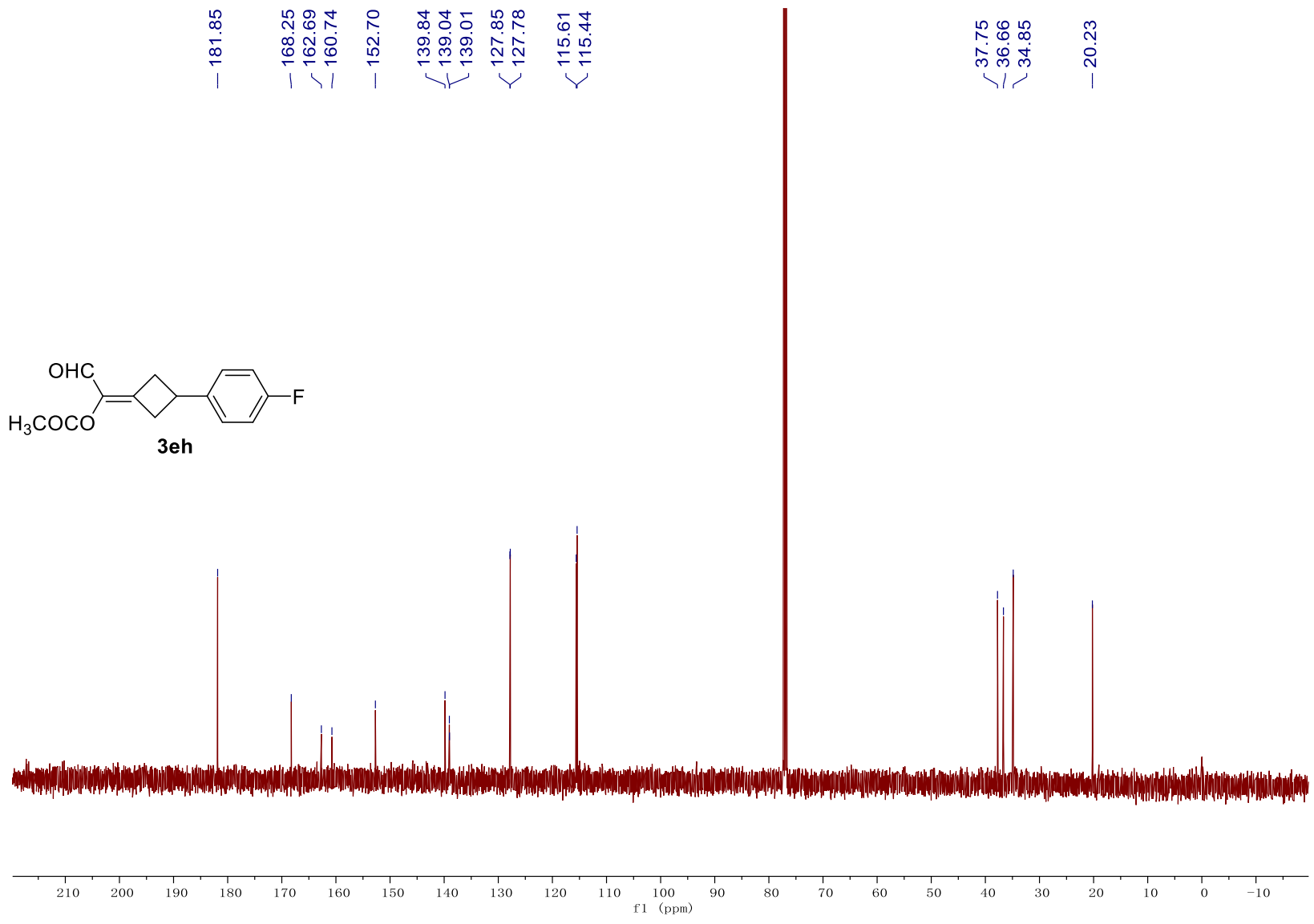
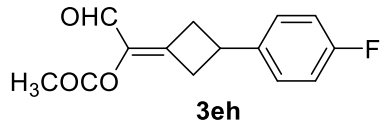


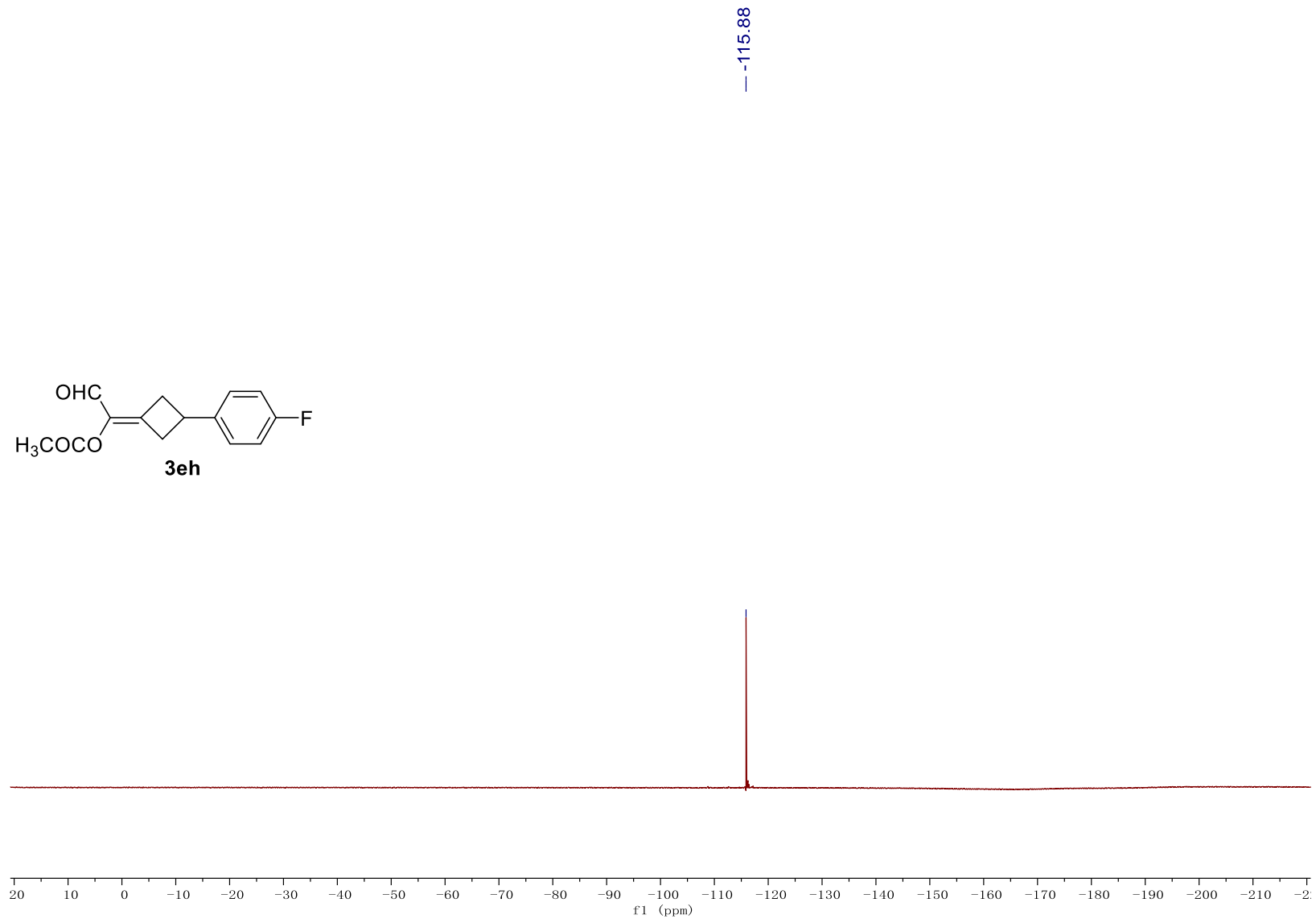
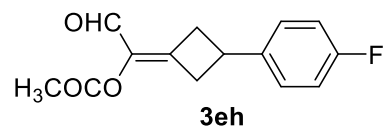


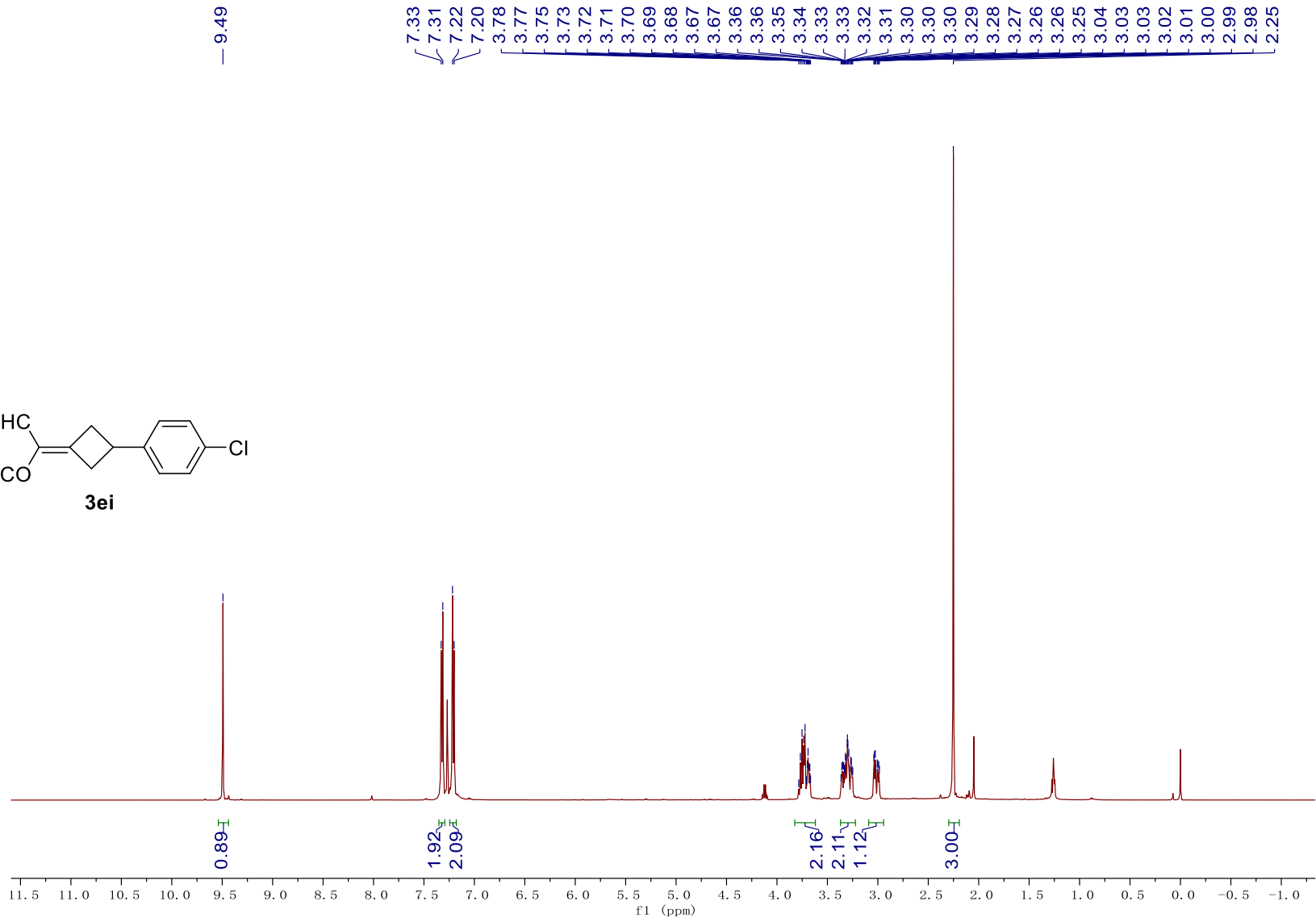
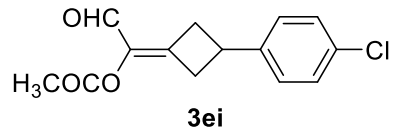


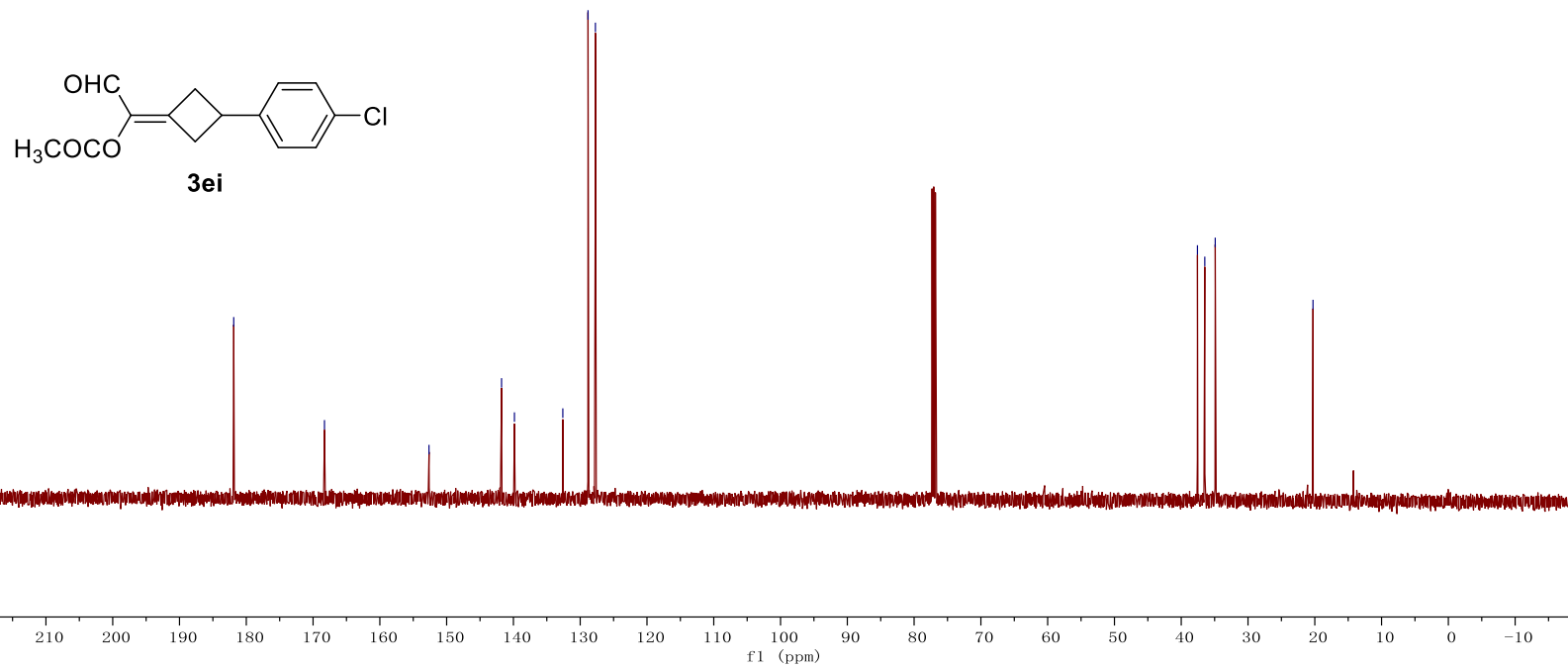


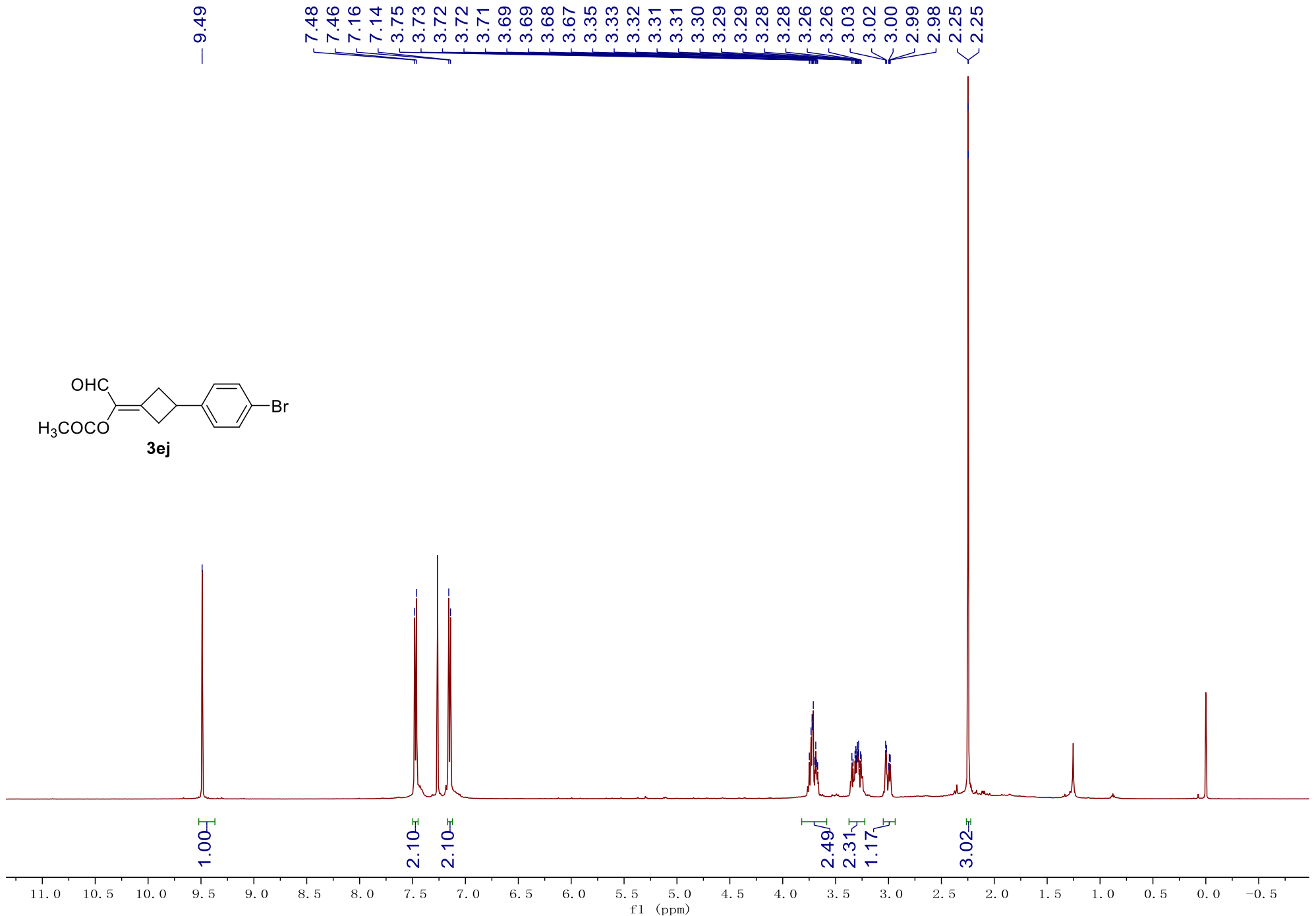
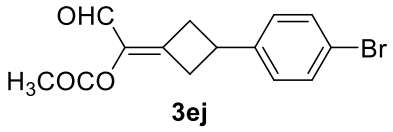












xzr-i-211-1.11.fid

— 181.85

— 168.24

— 152.41

~ 142.29

~ 139.86

~ 131.79

~ 128.08

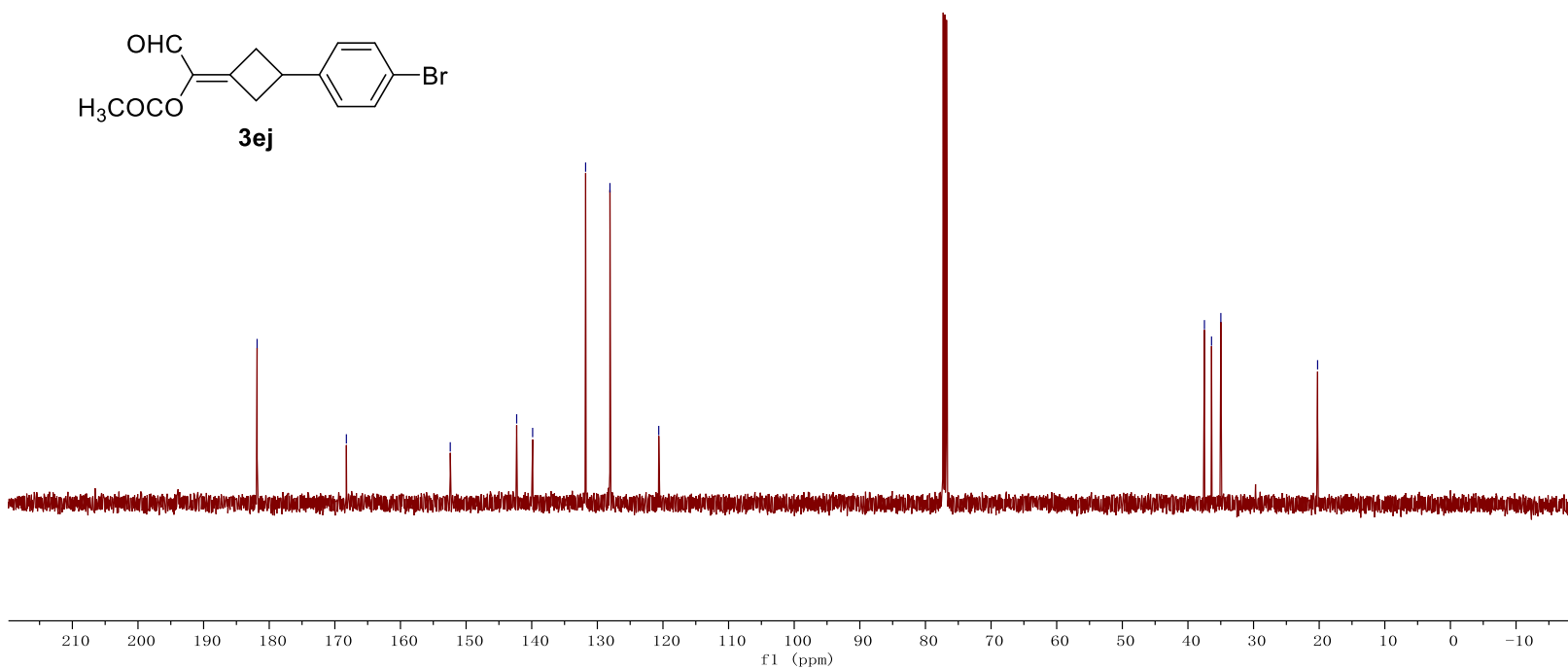
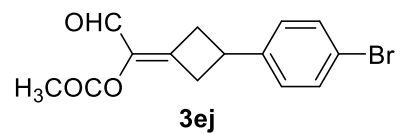
~ 120.64

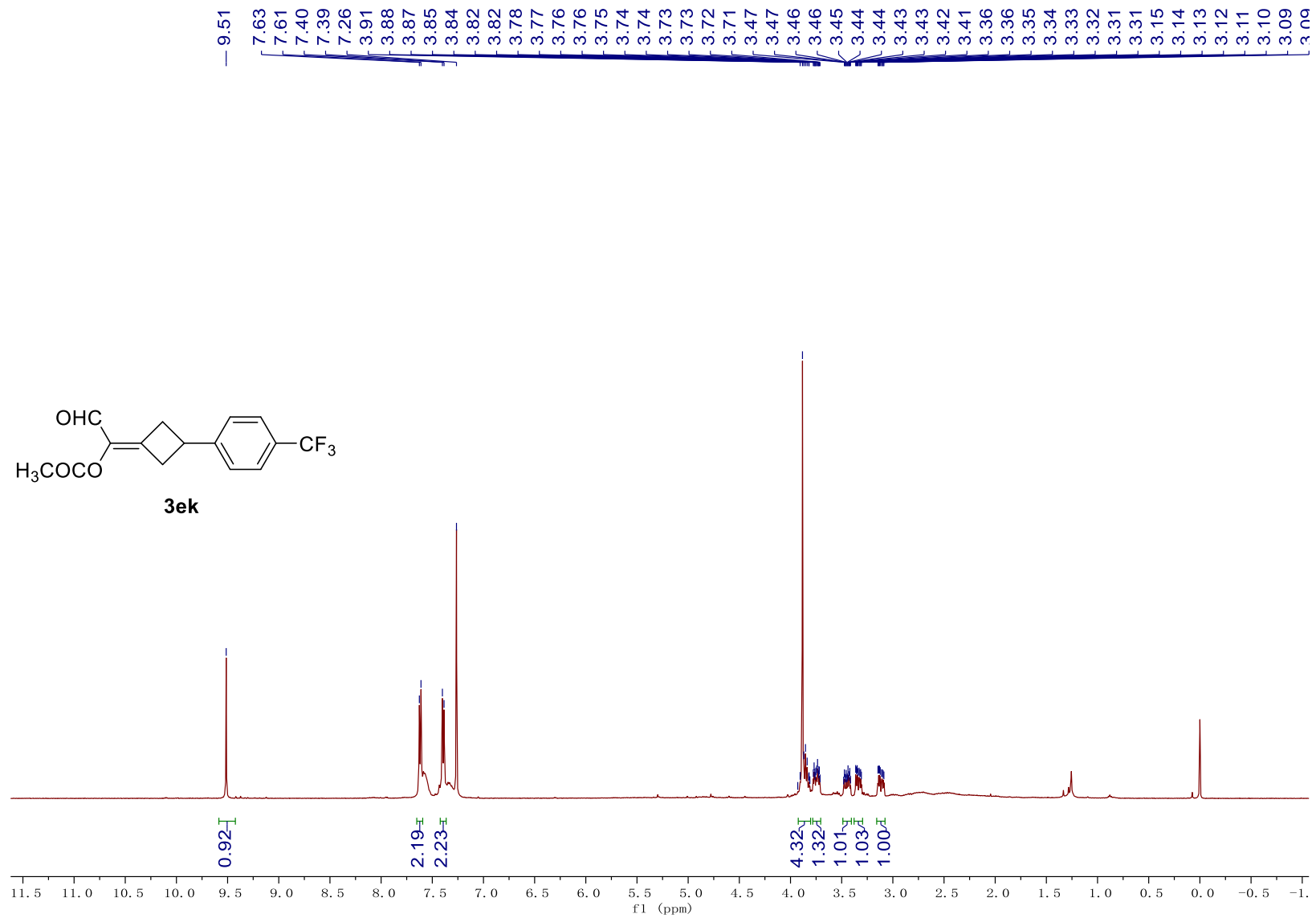
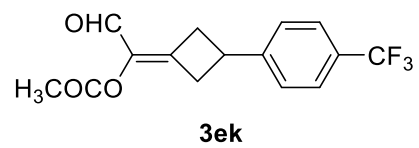
~ 37.49

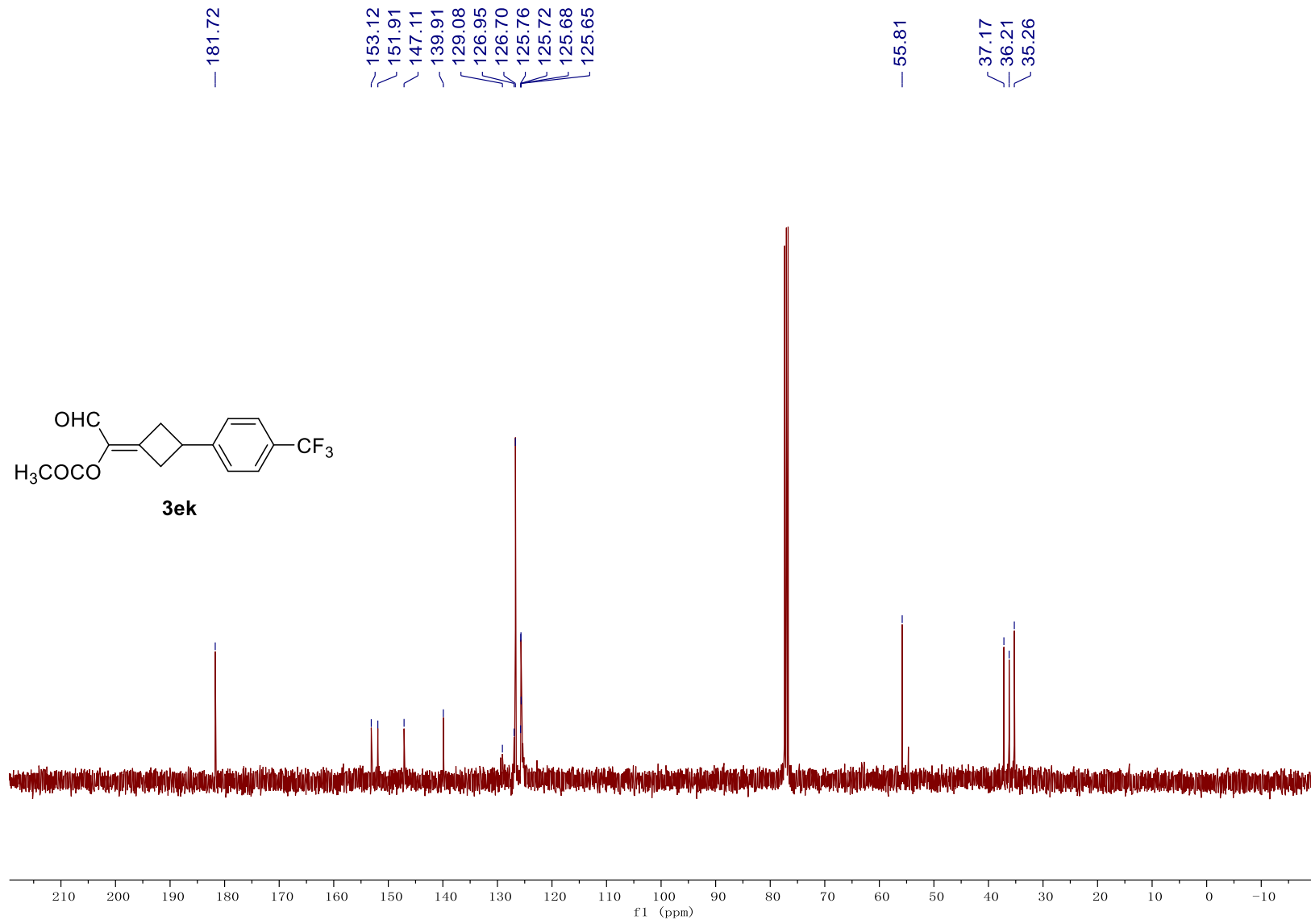
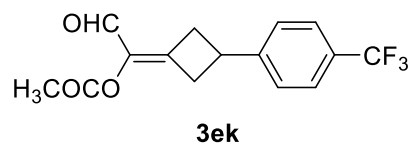
~ 36.40

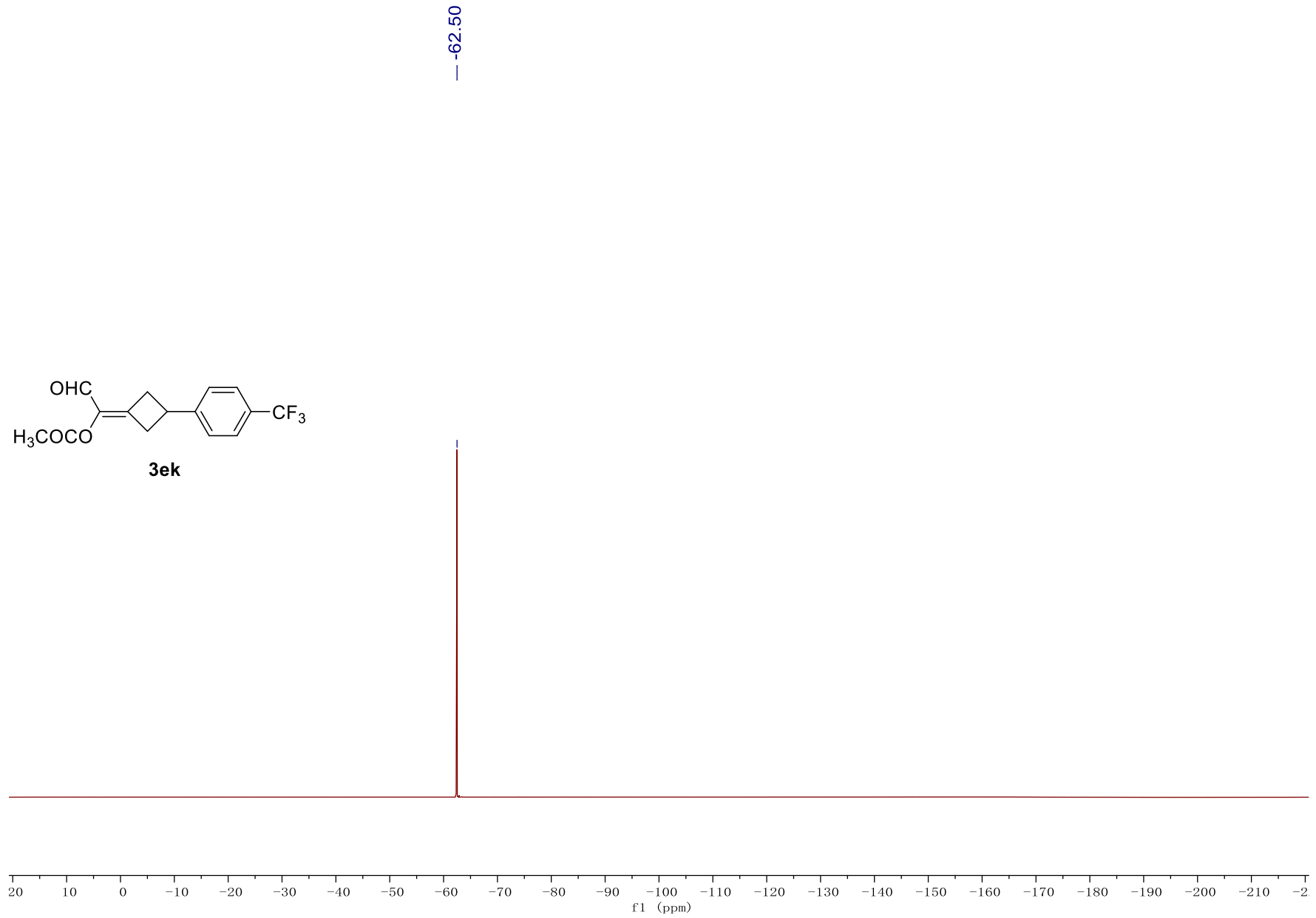
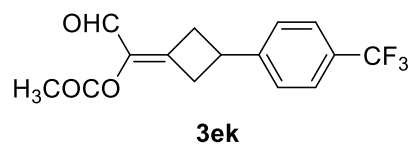
~ 34.99

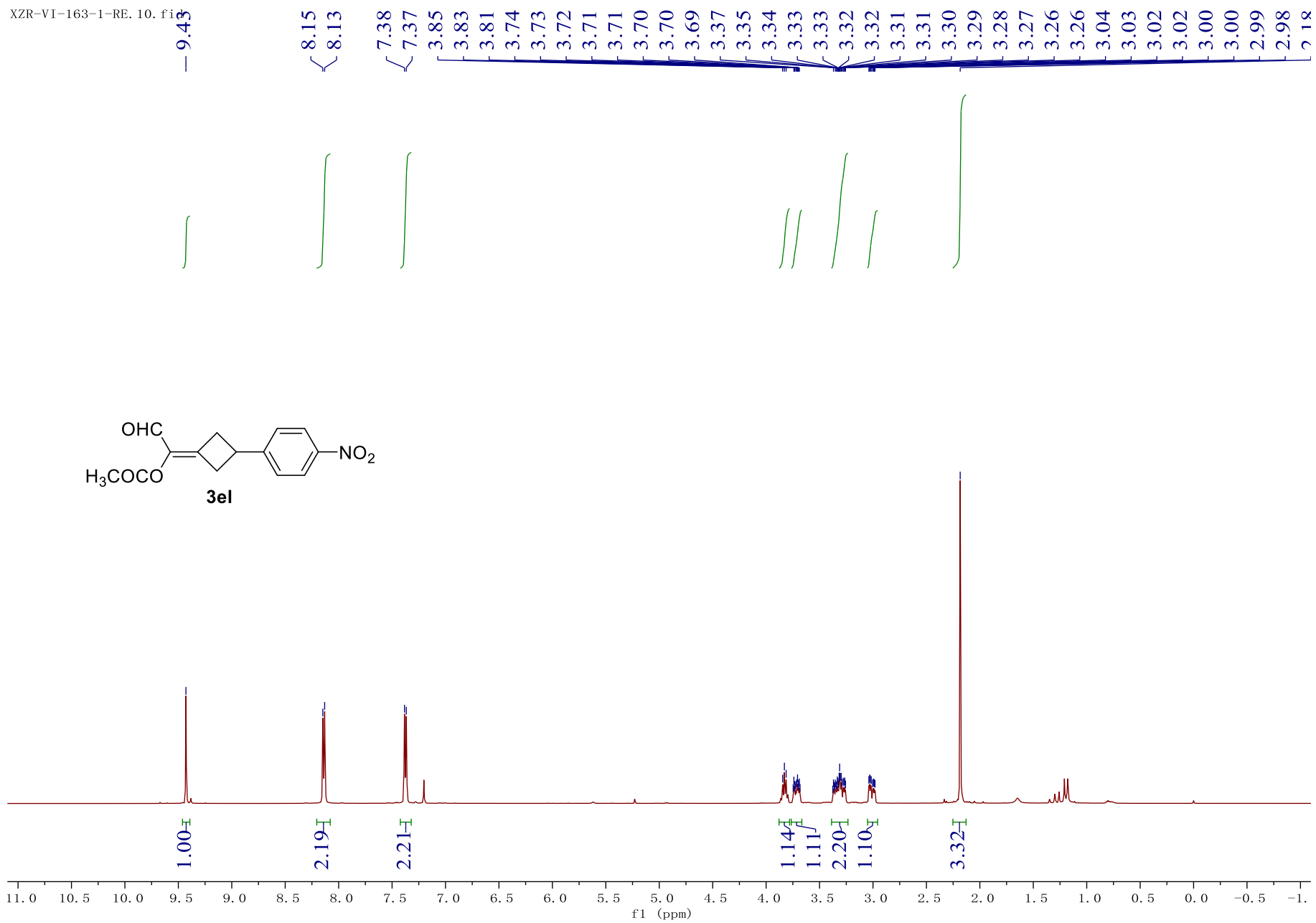
— 20.24



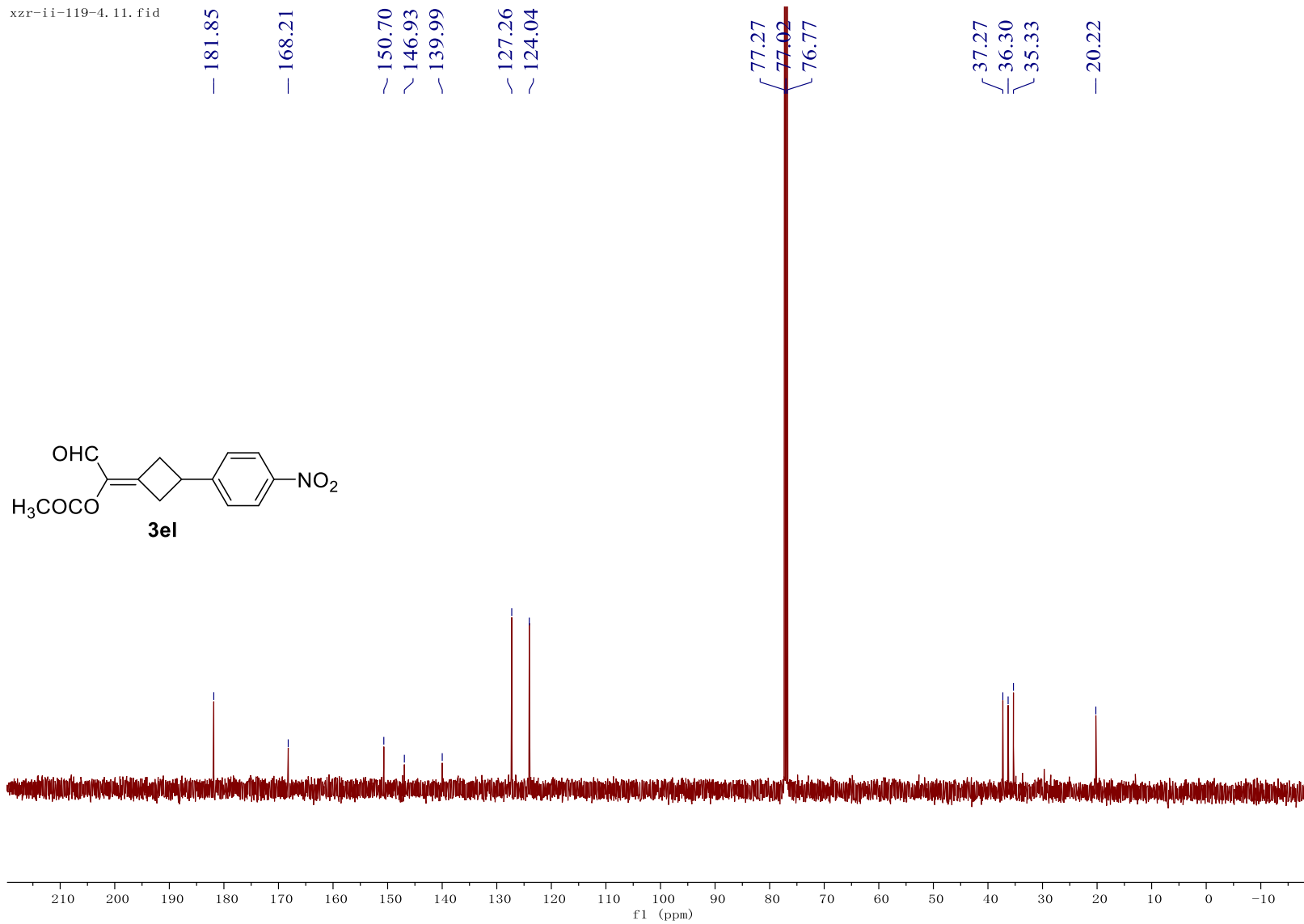


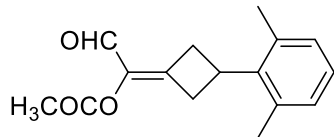




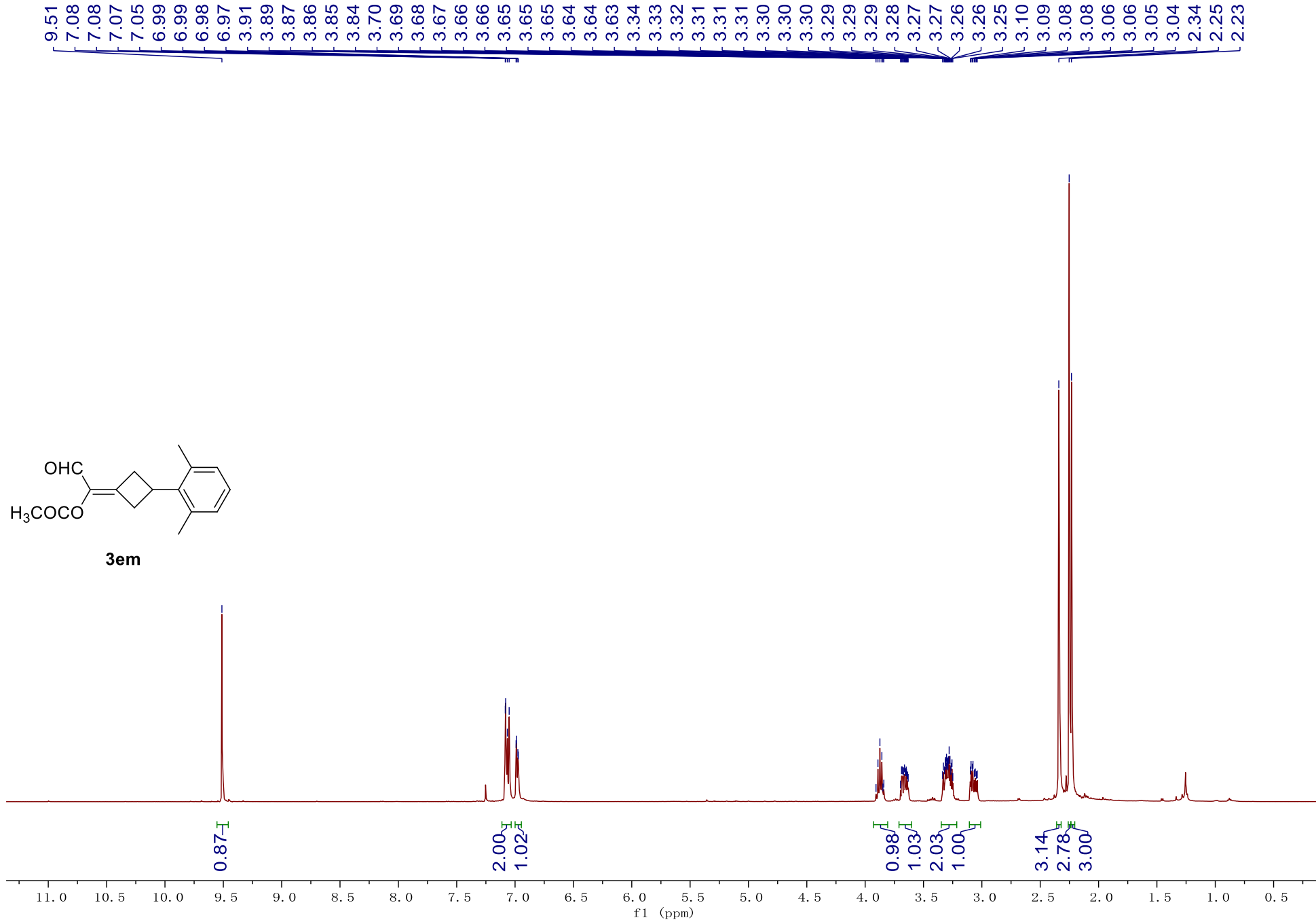


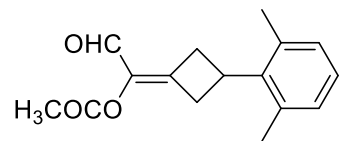
xzr-ii-119-4.11.fid



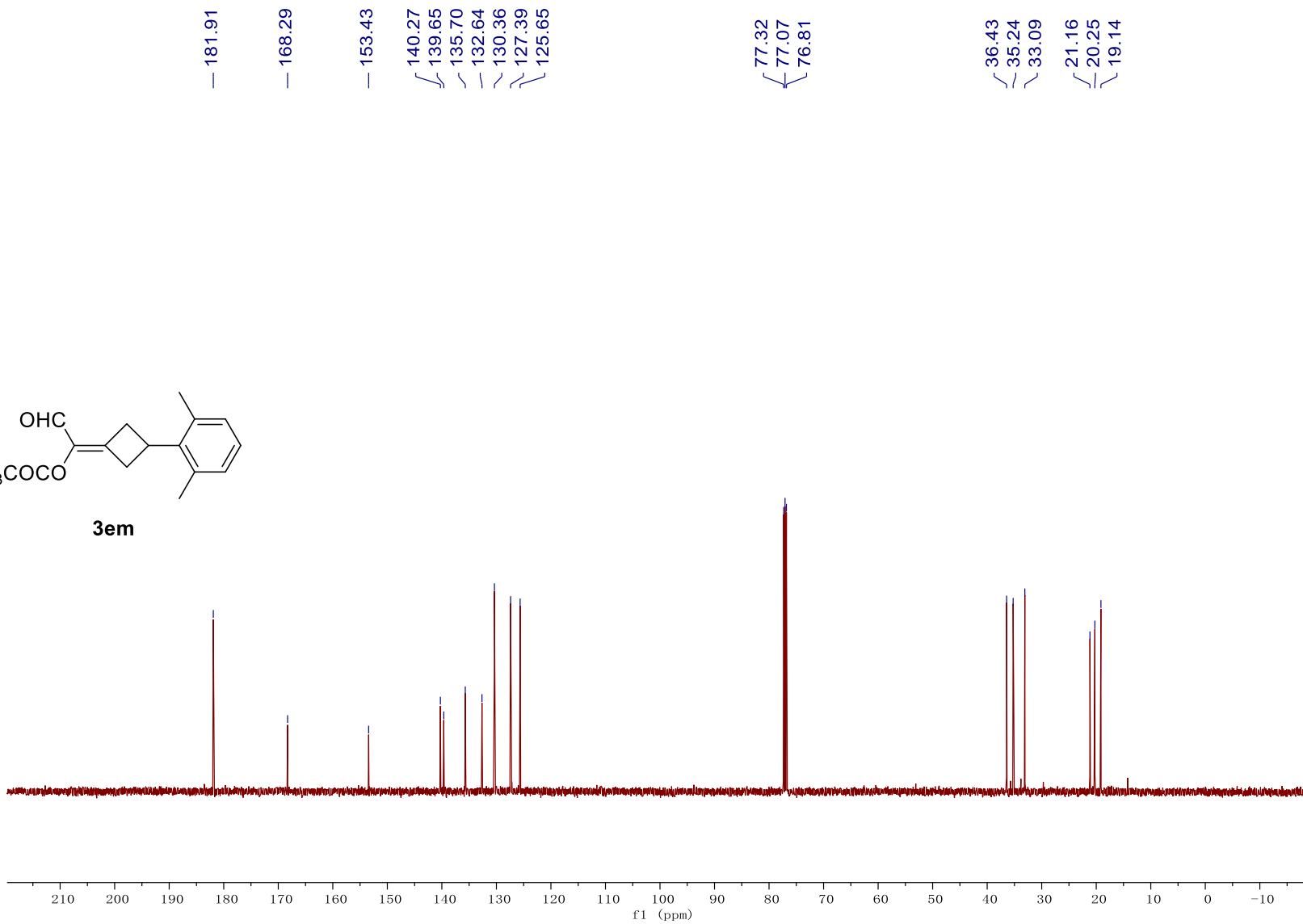


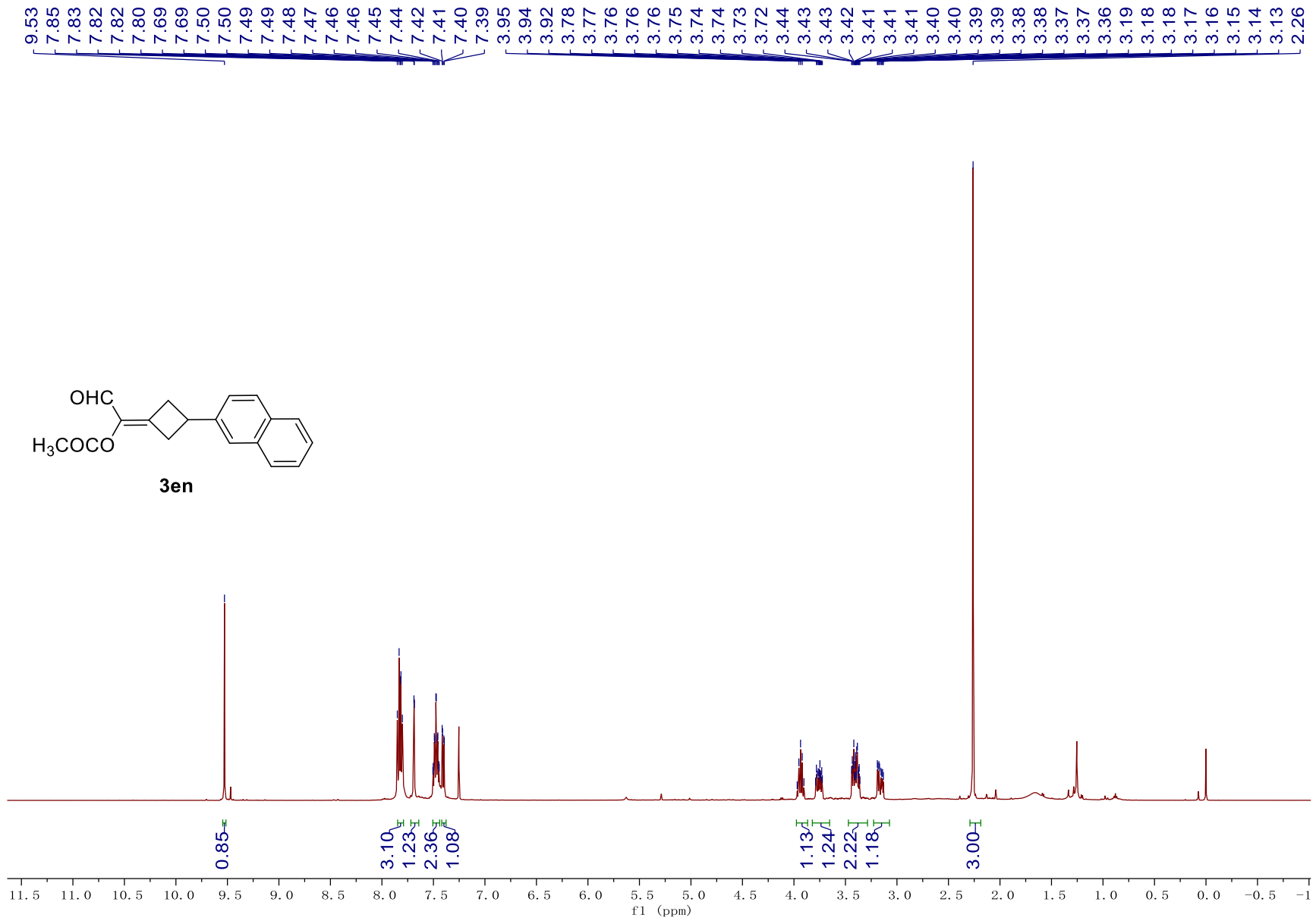
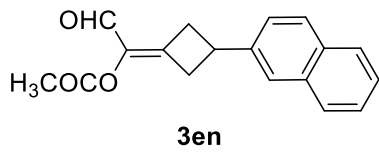
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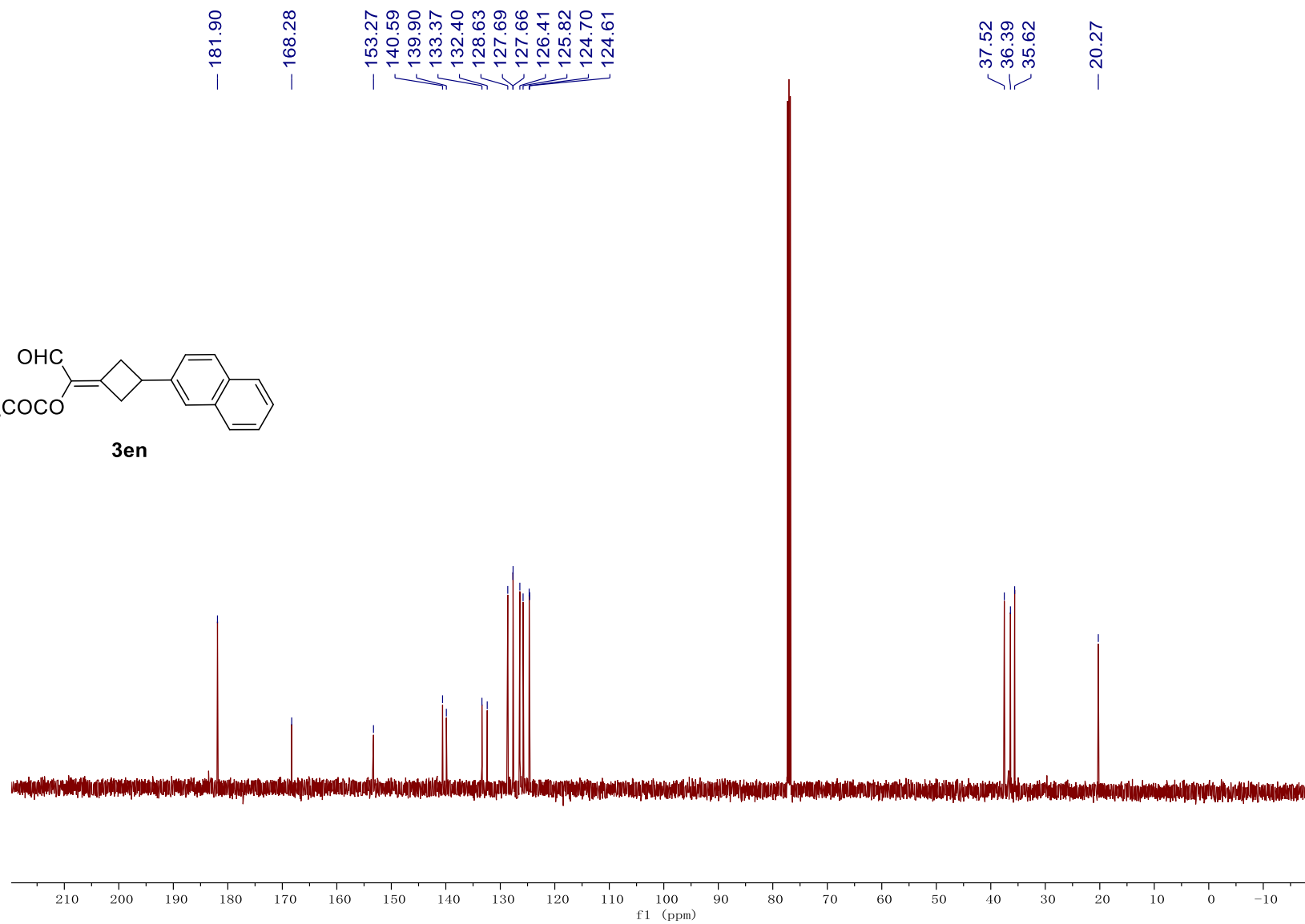
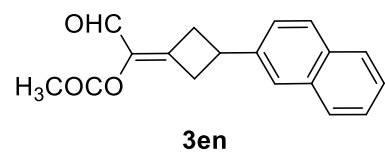


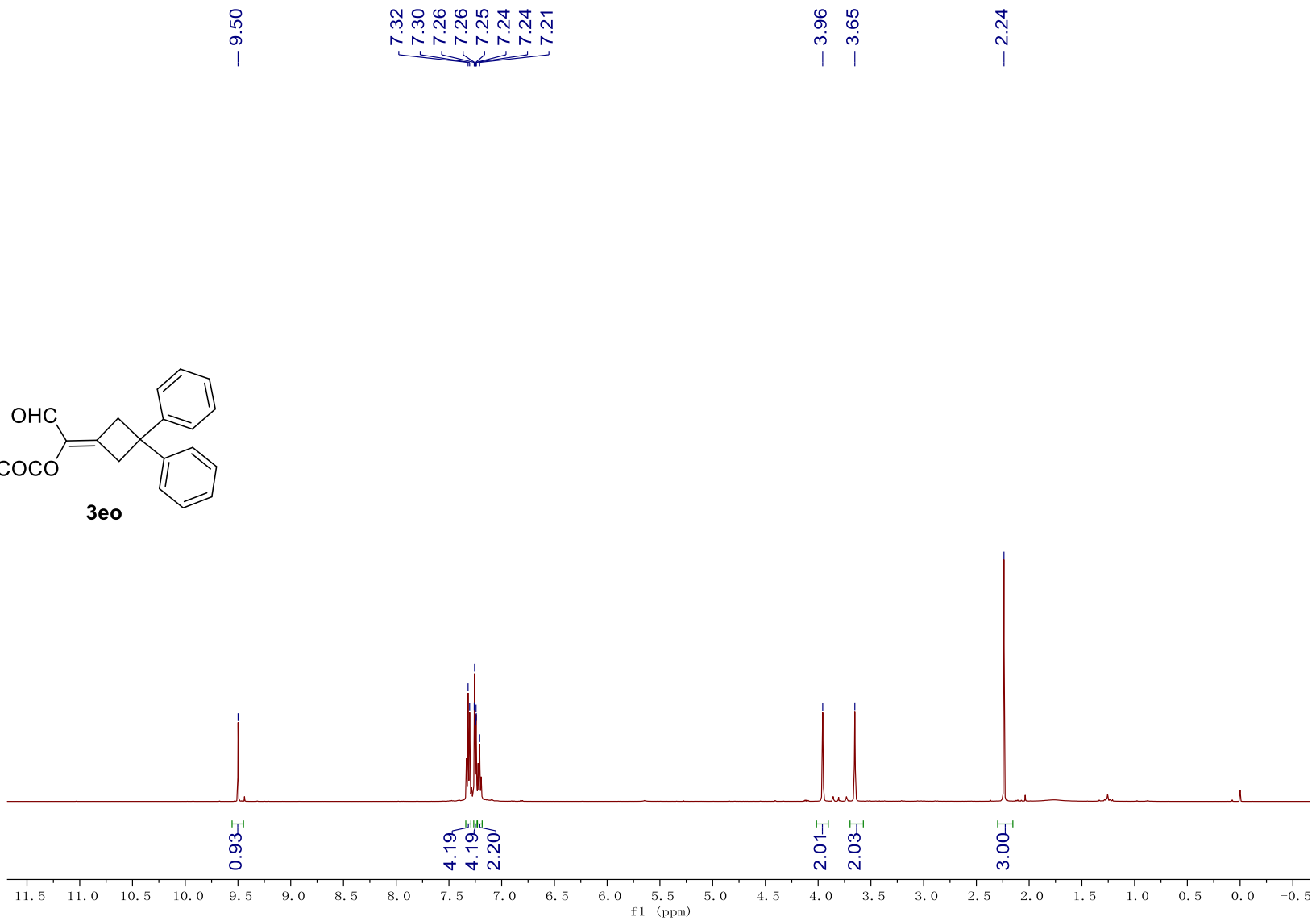
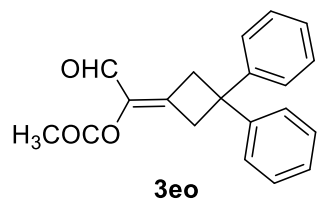


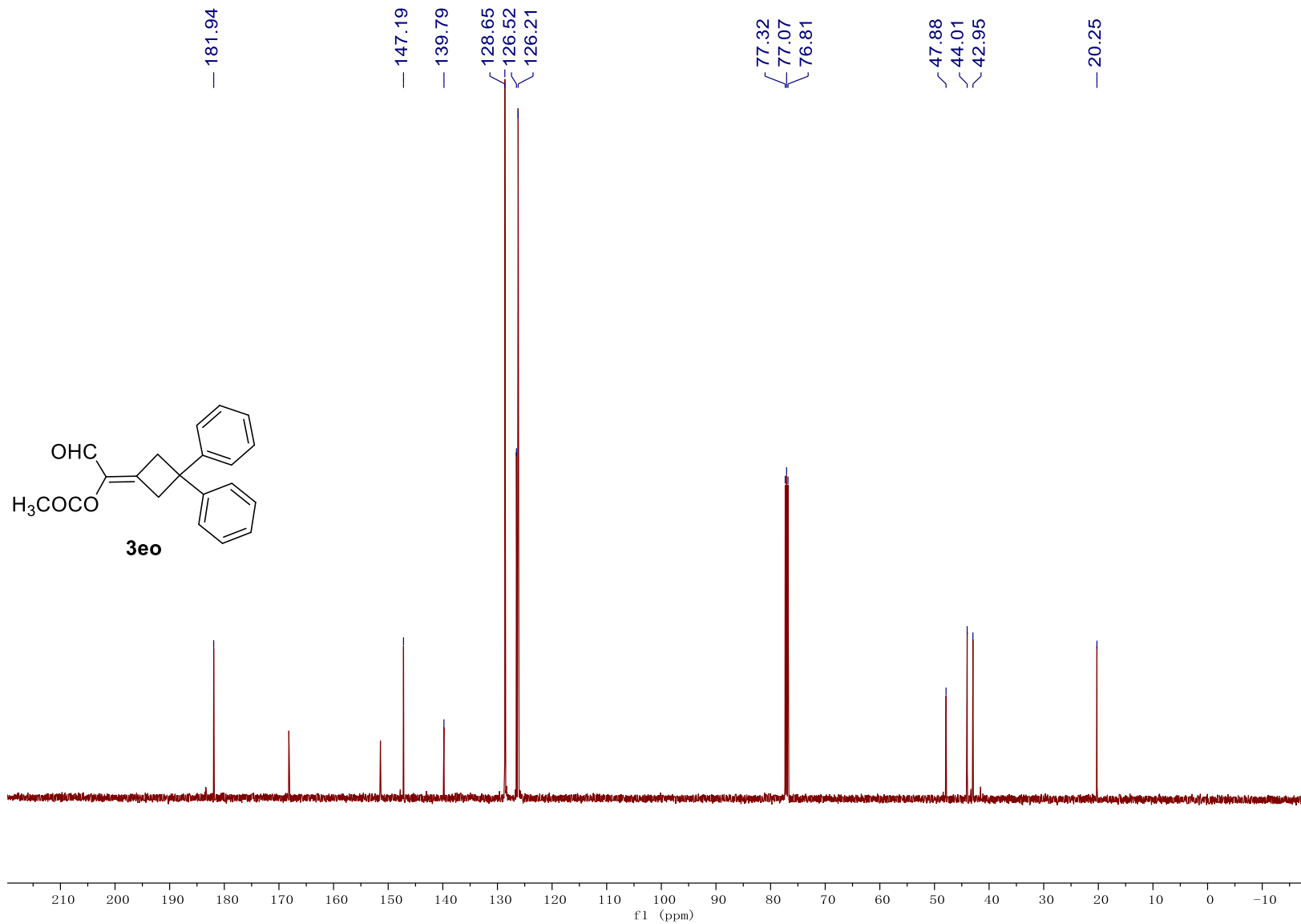
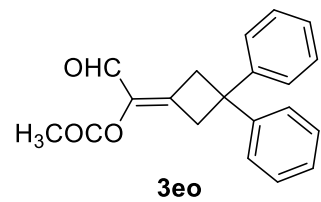
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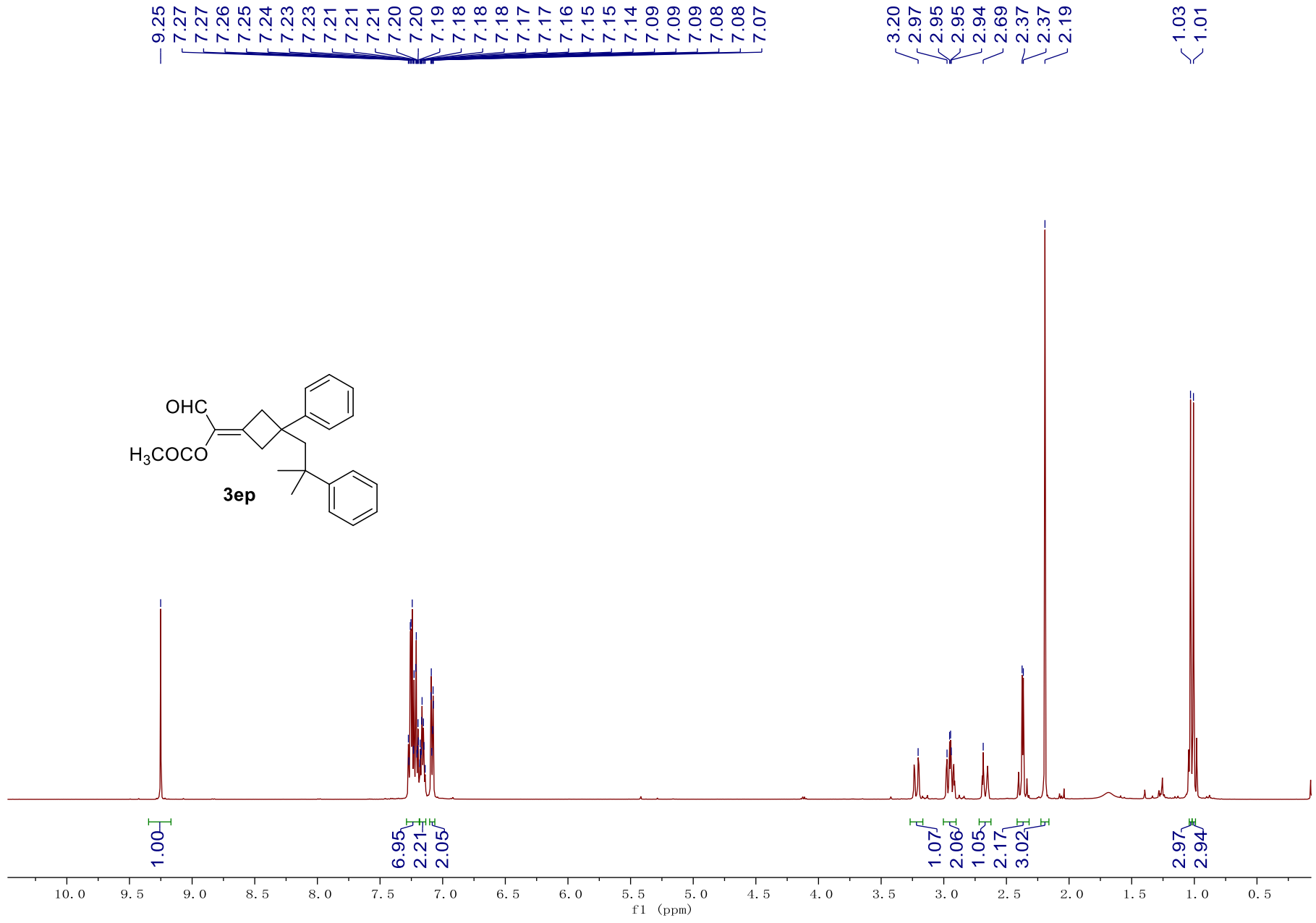
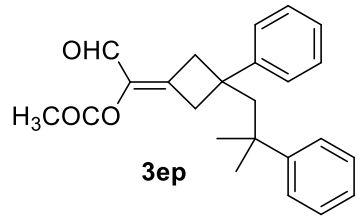


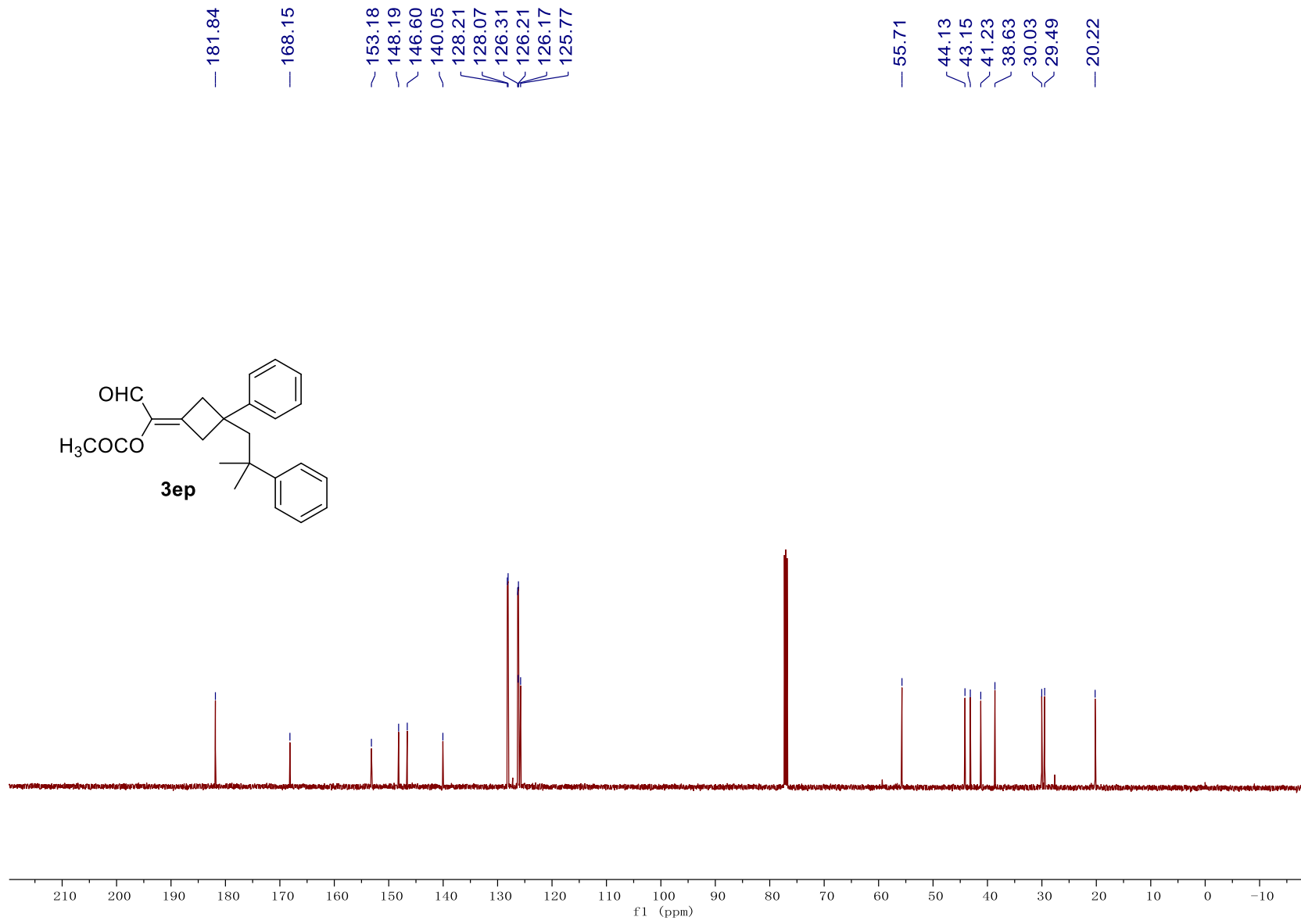
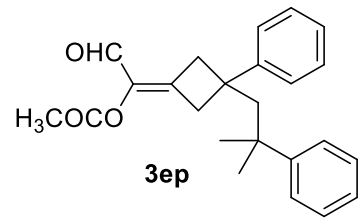


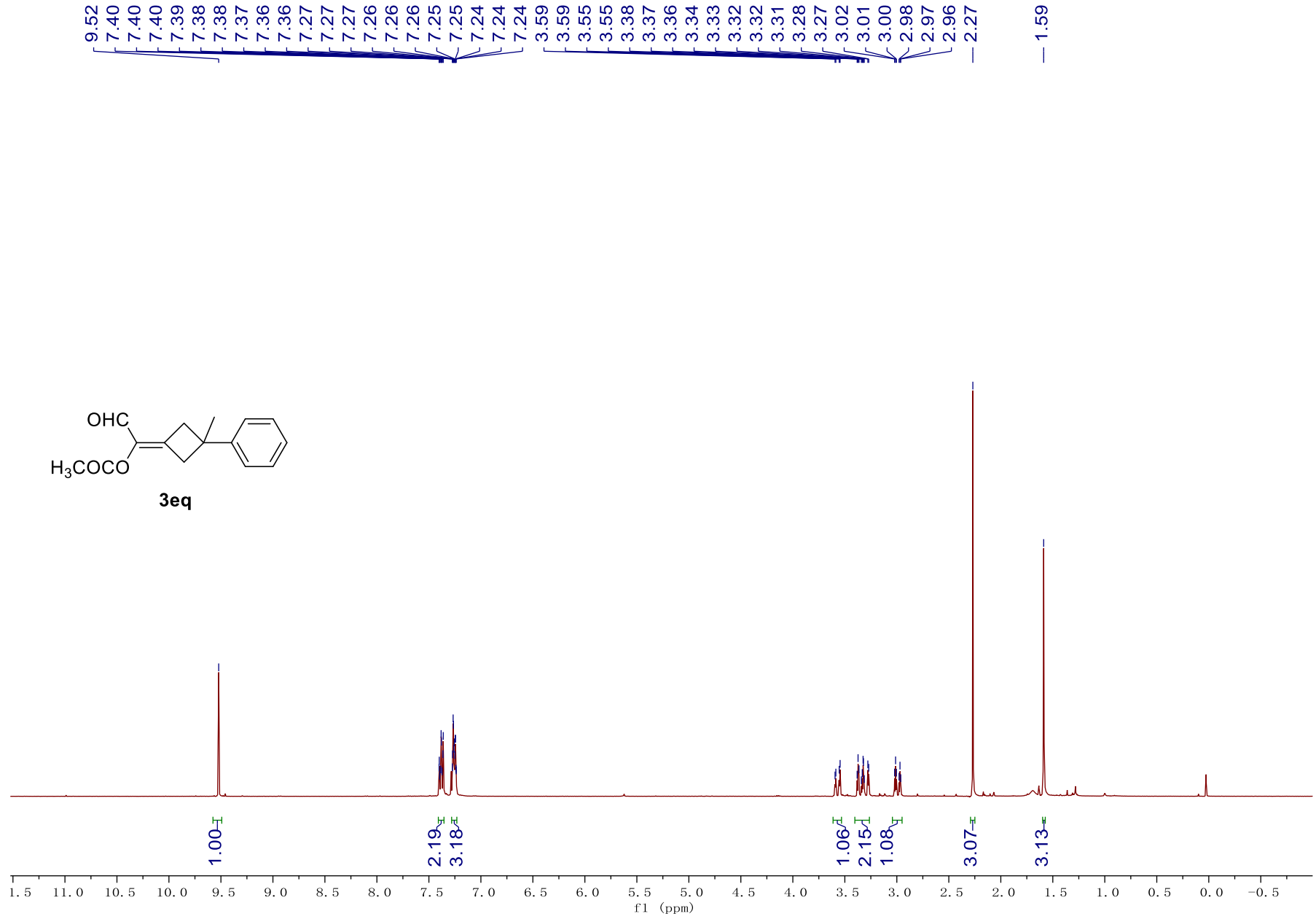
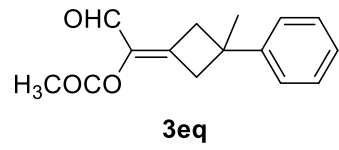


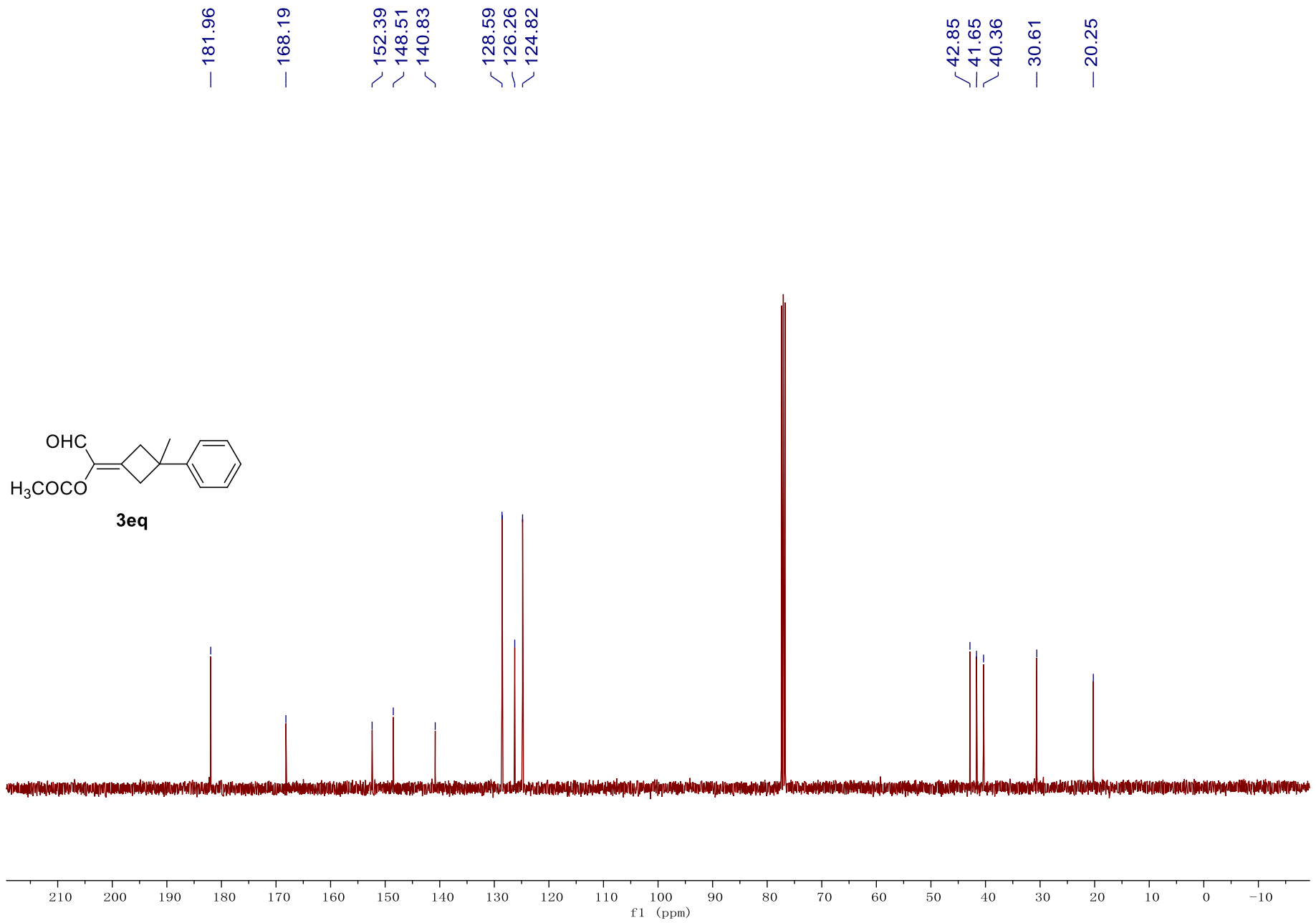
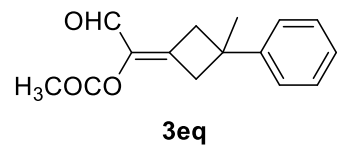




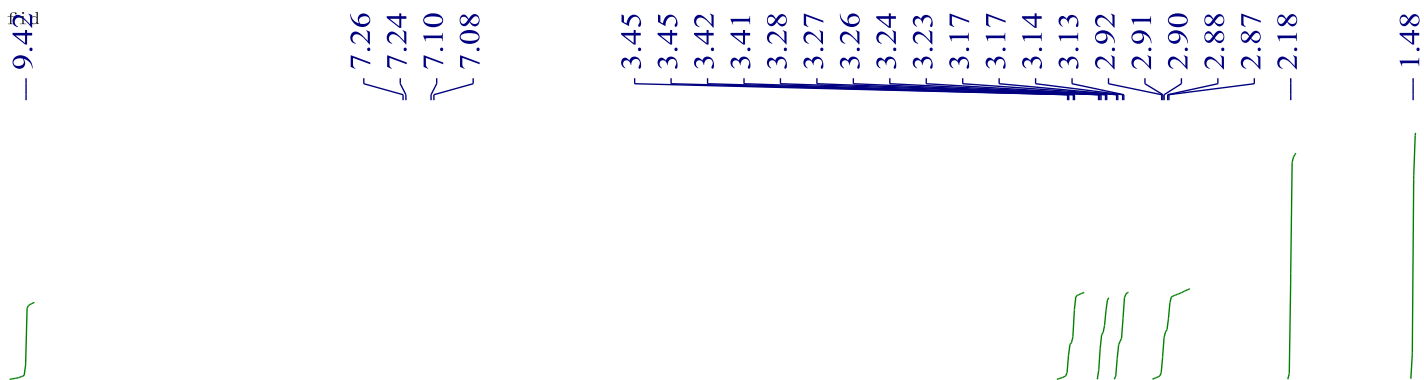
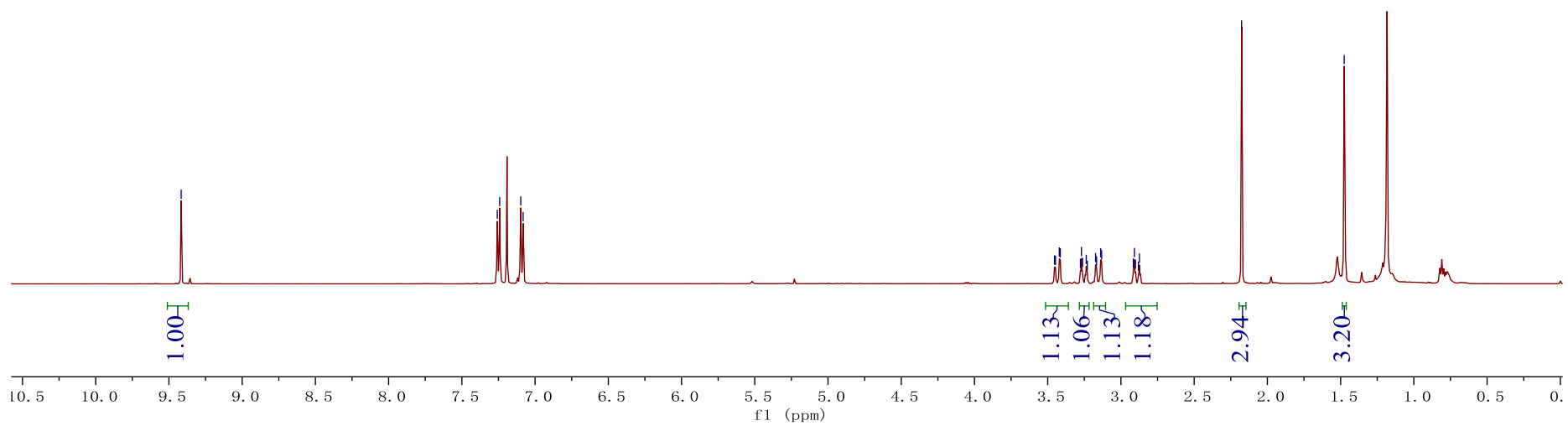
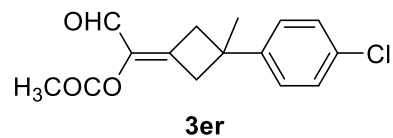


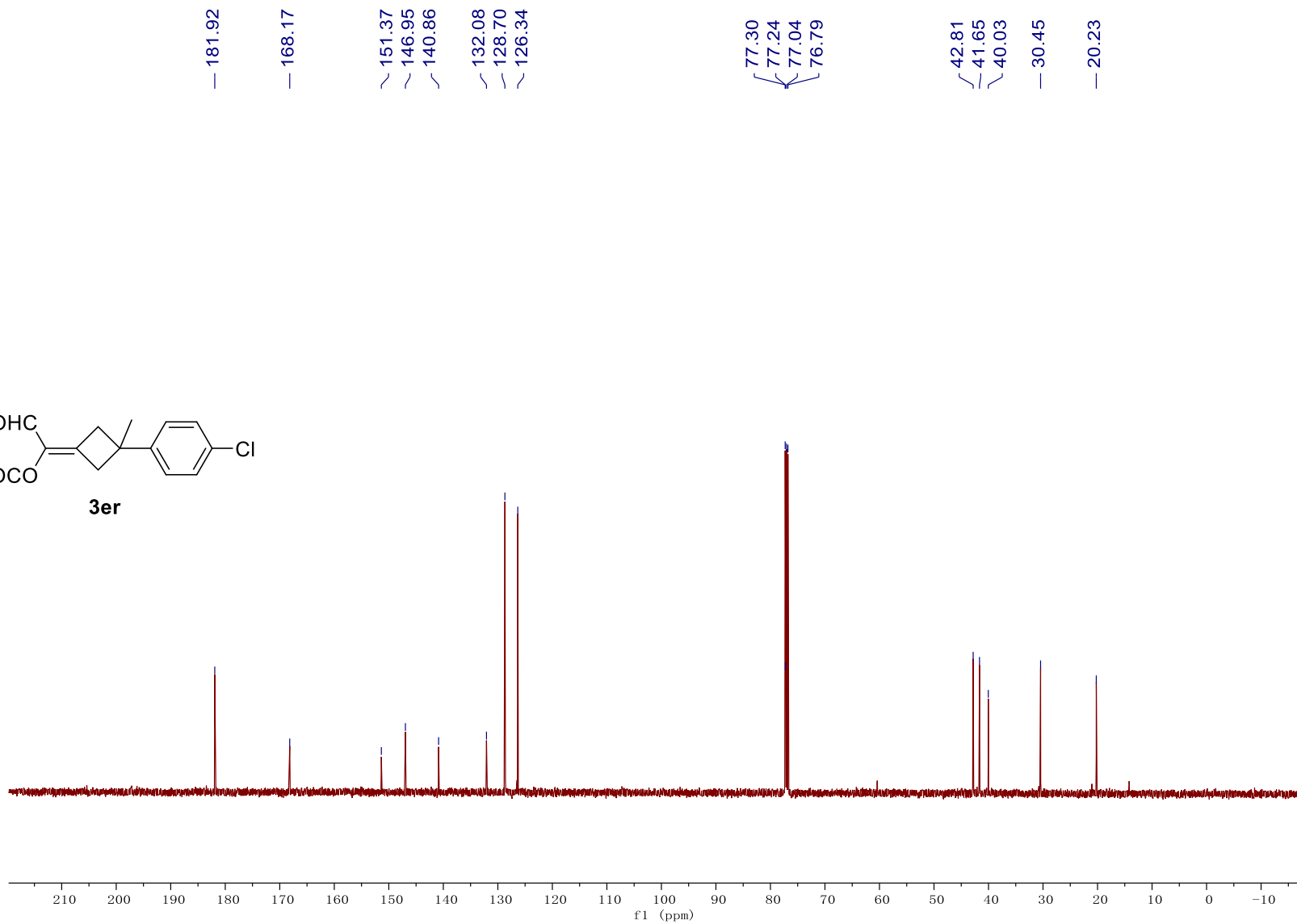
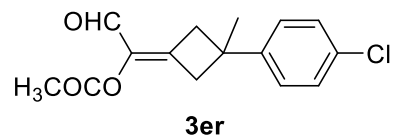


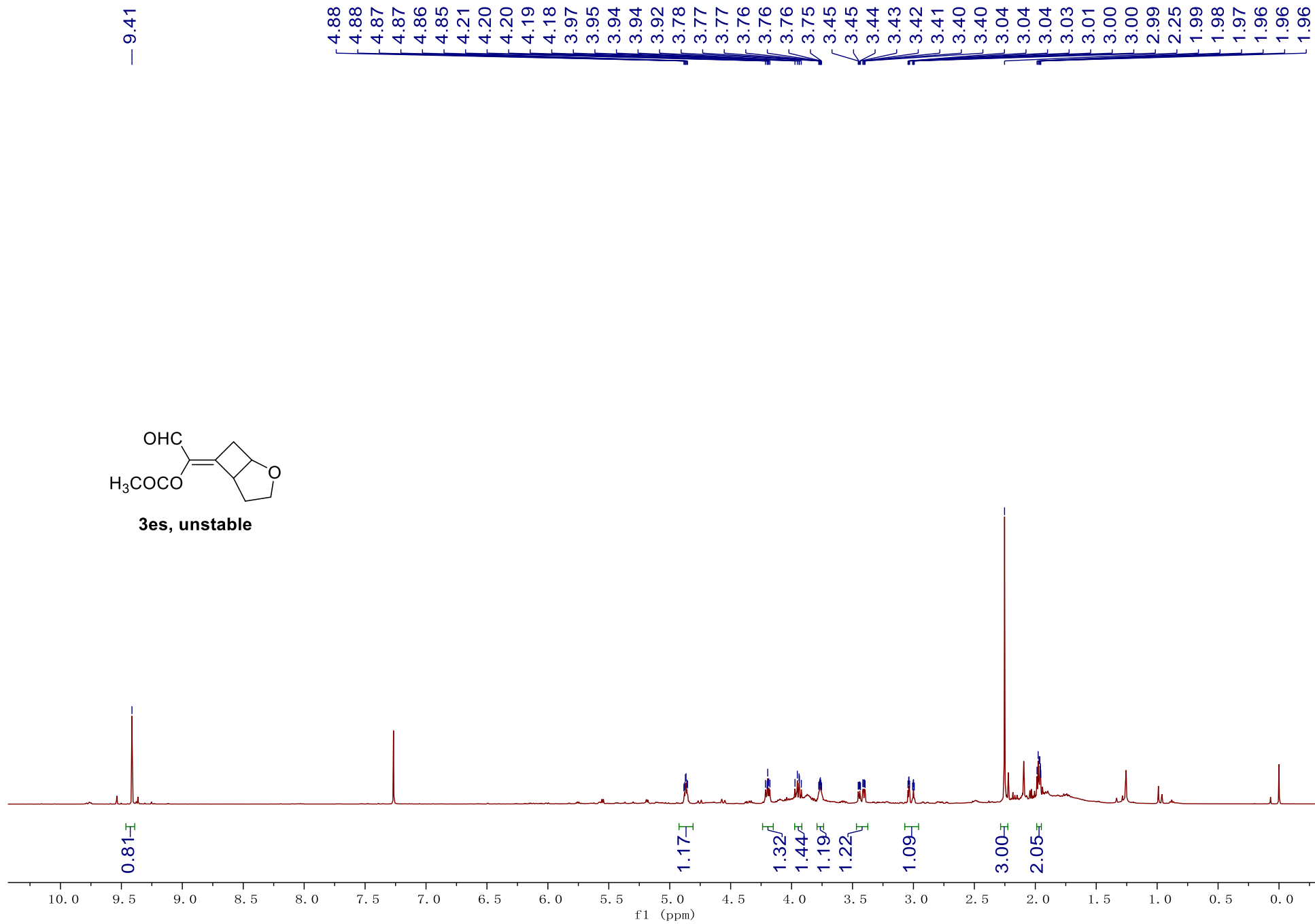
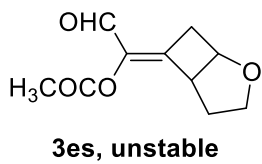




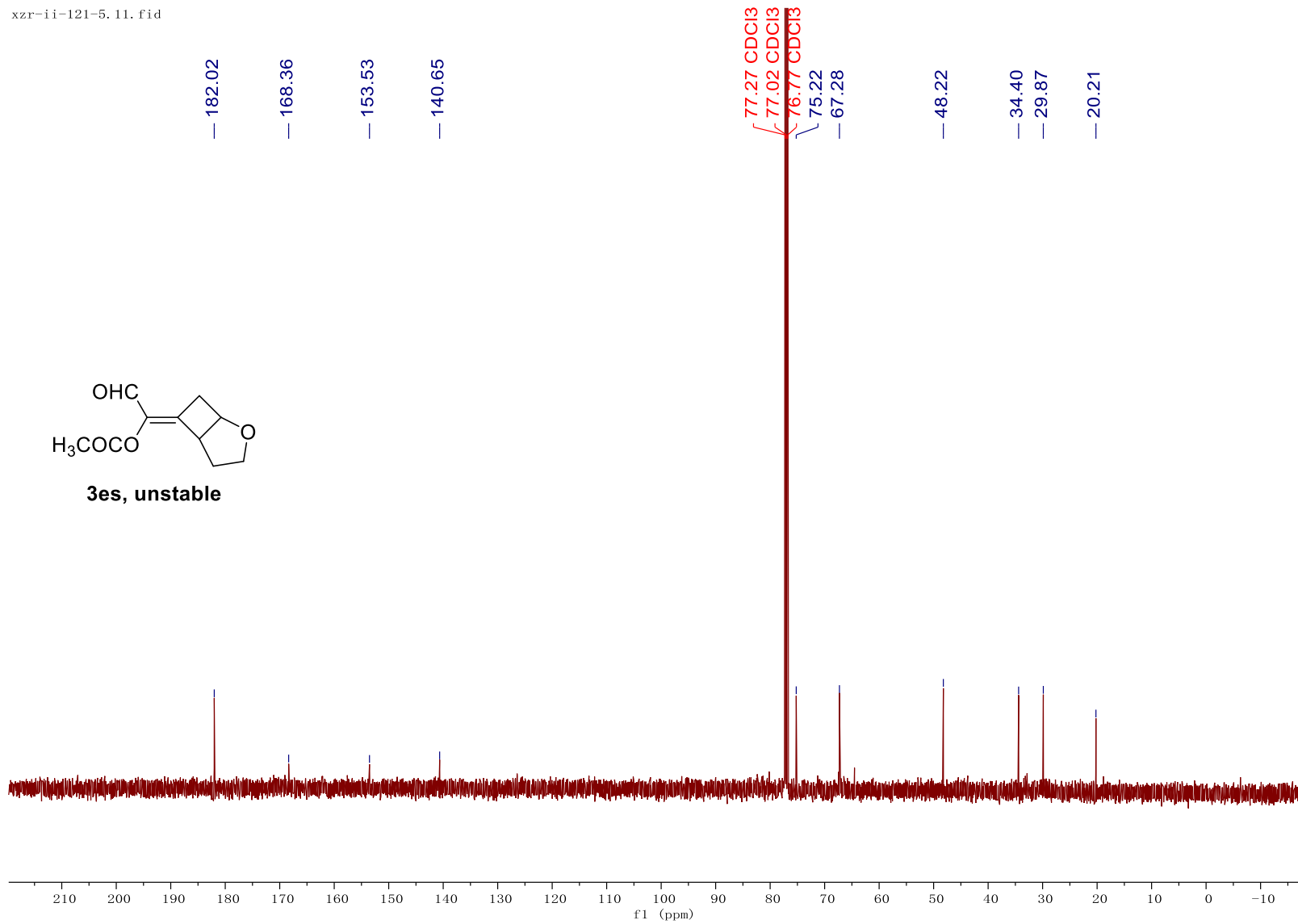
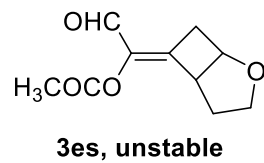
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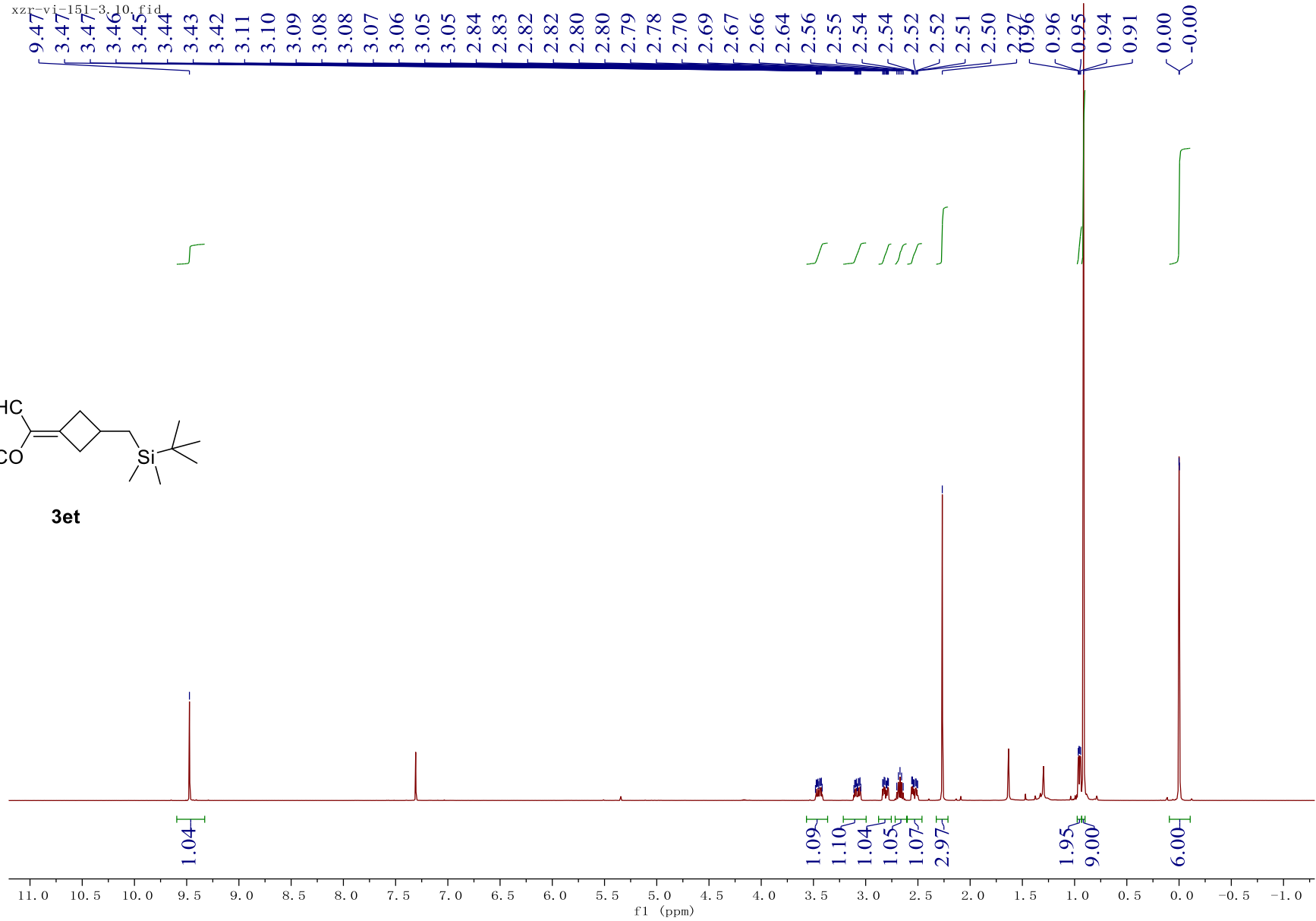
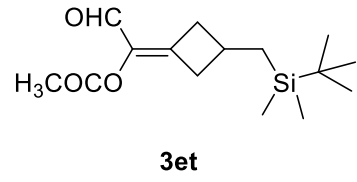




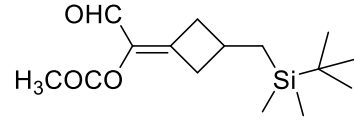


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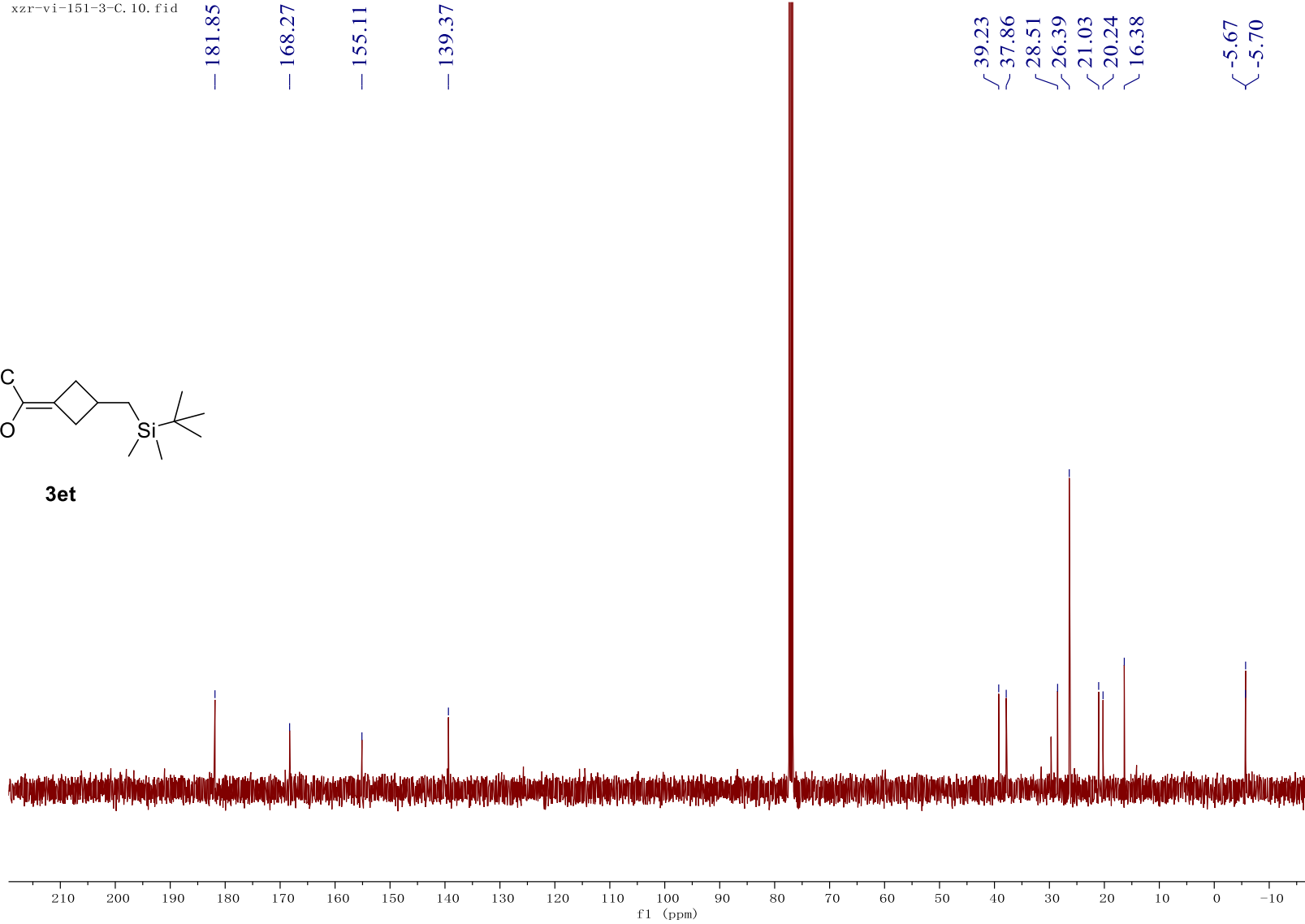


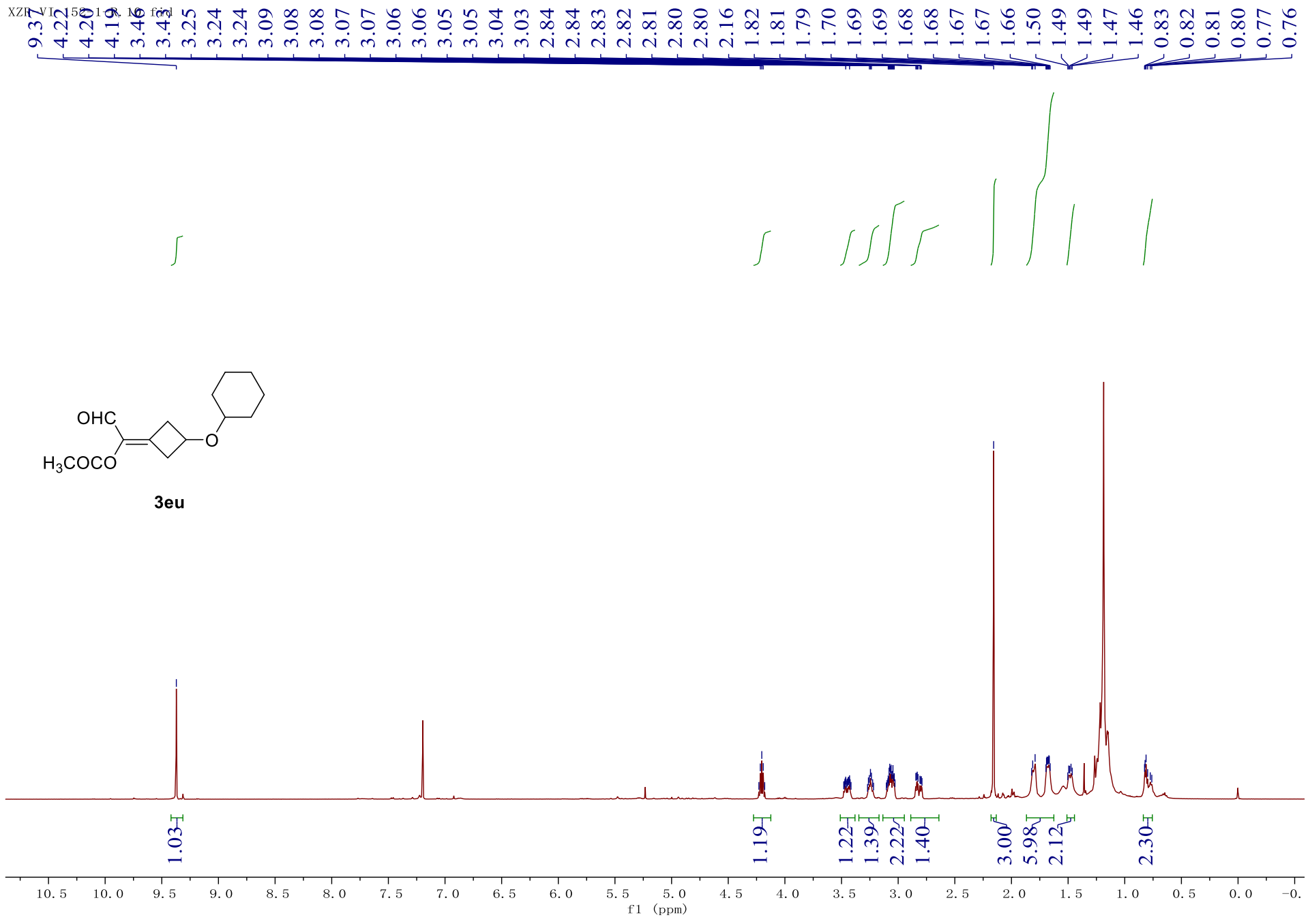


xzr-vi-151-3-C. 10. fid

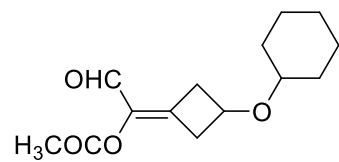


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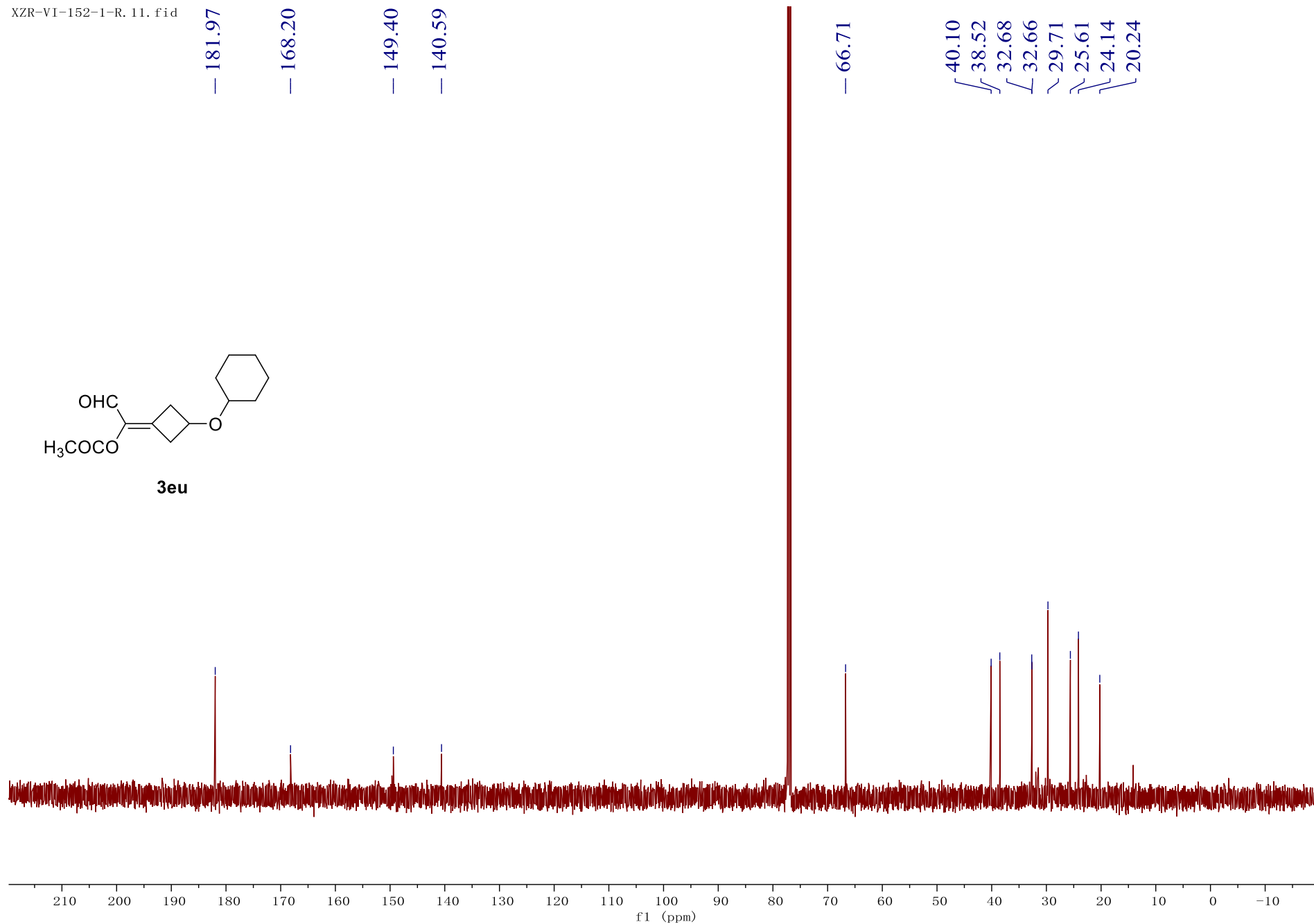




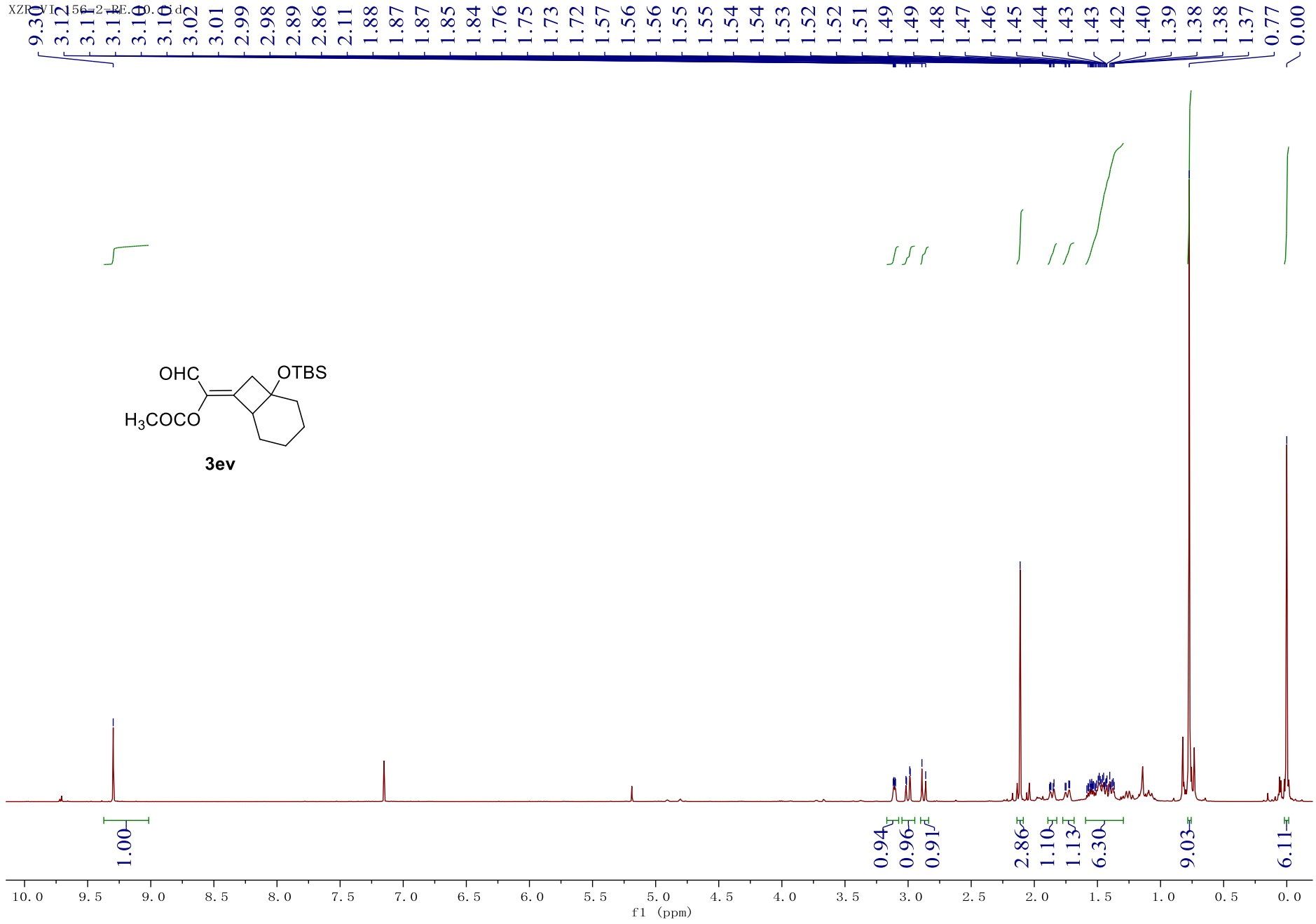
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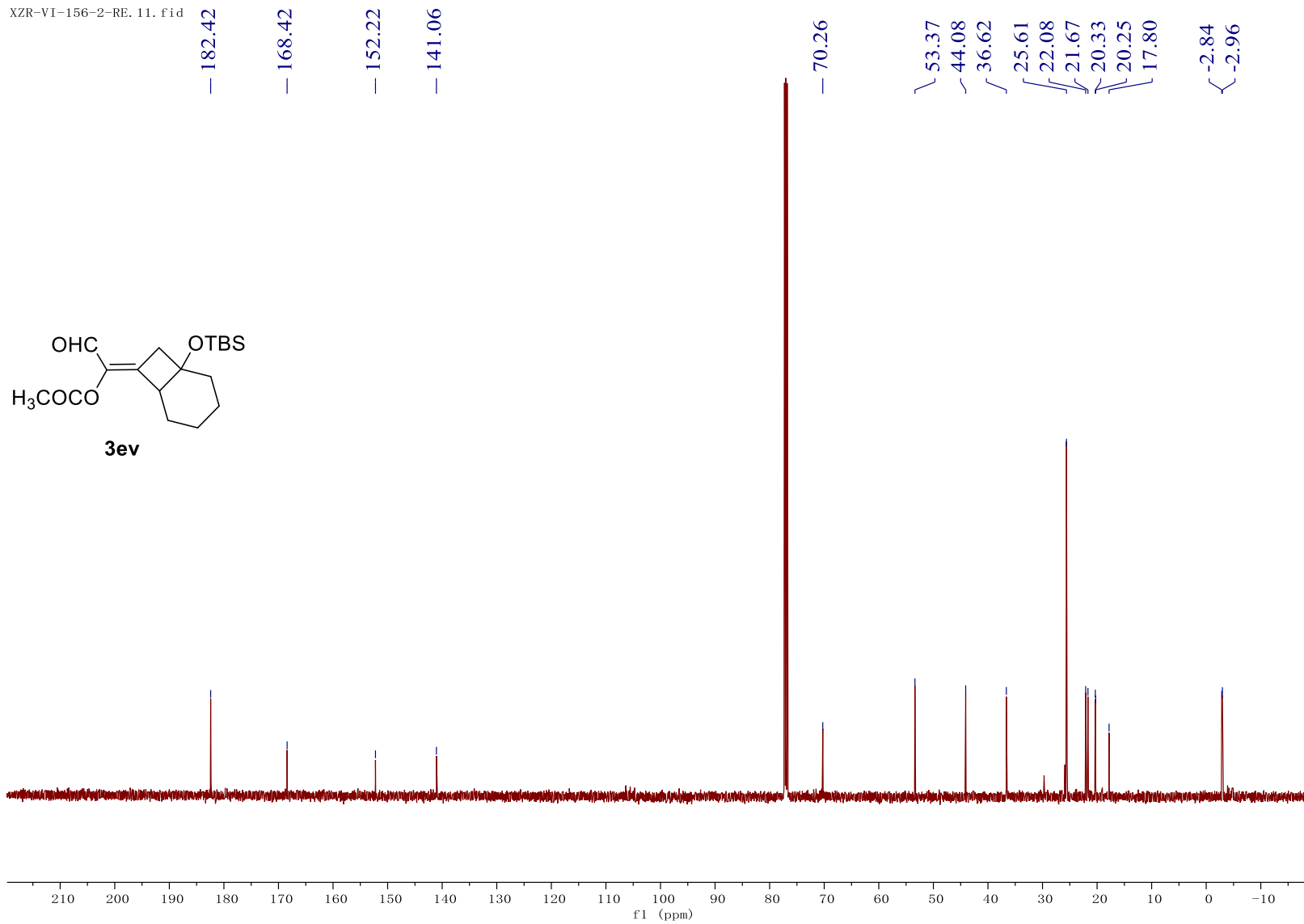
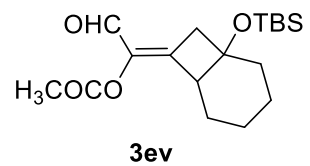
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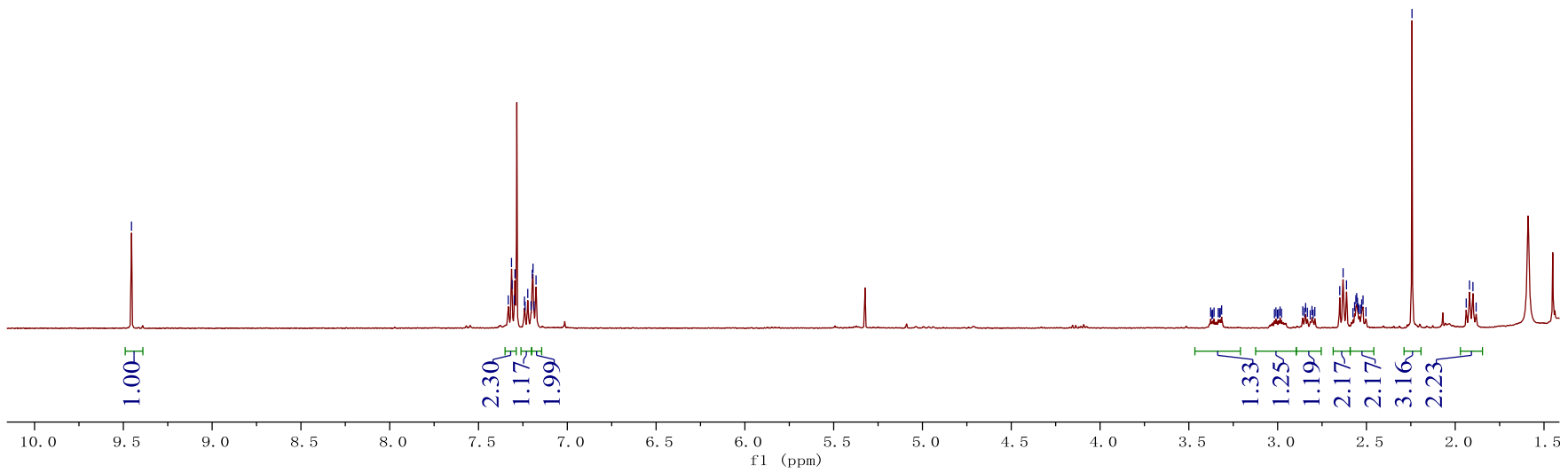
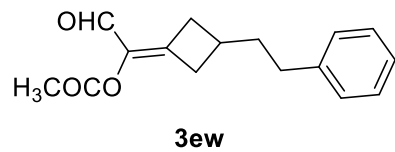


XZ12VT1562-PE.d

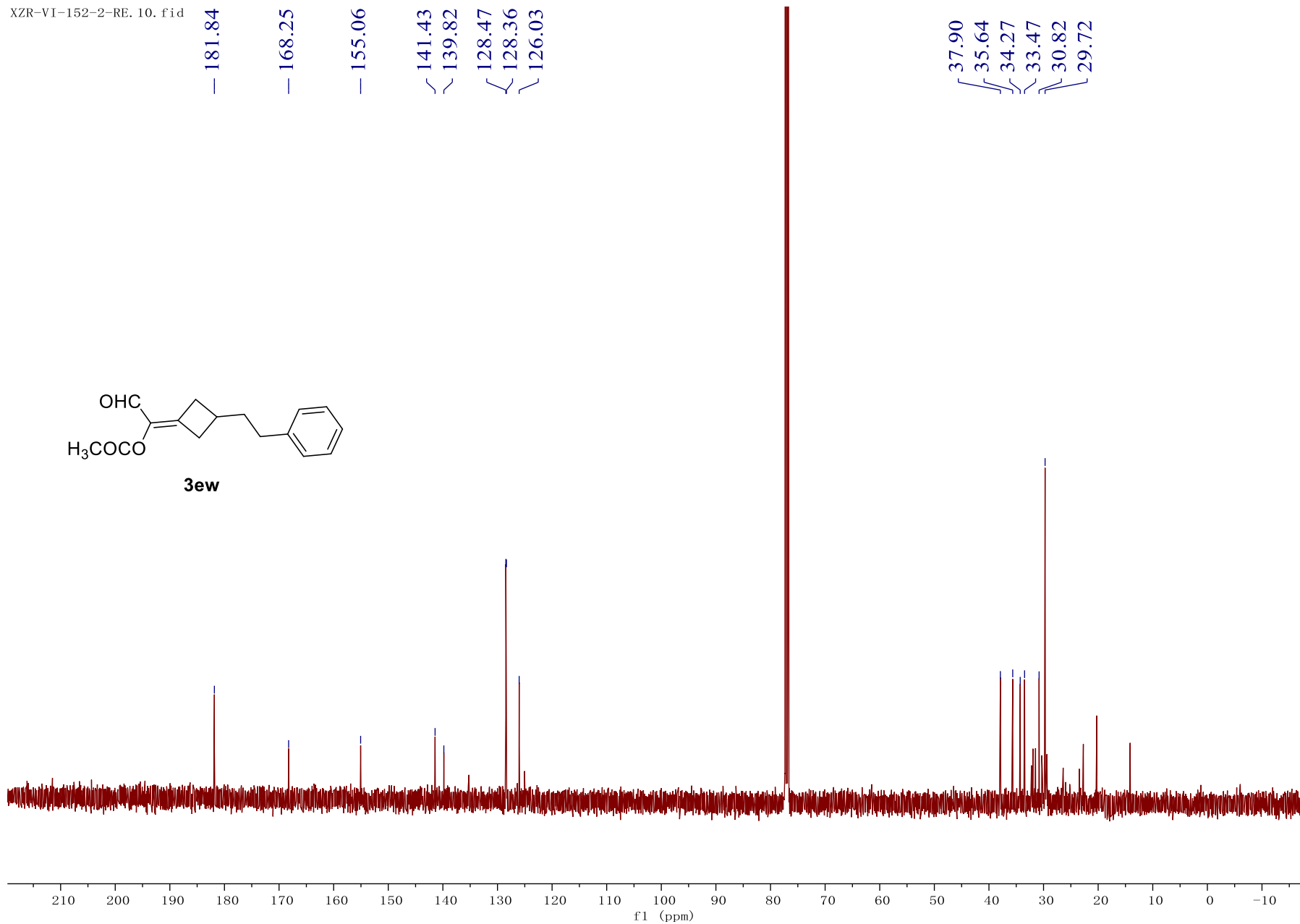


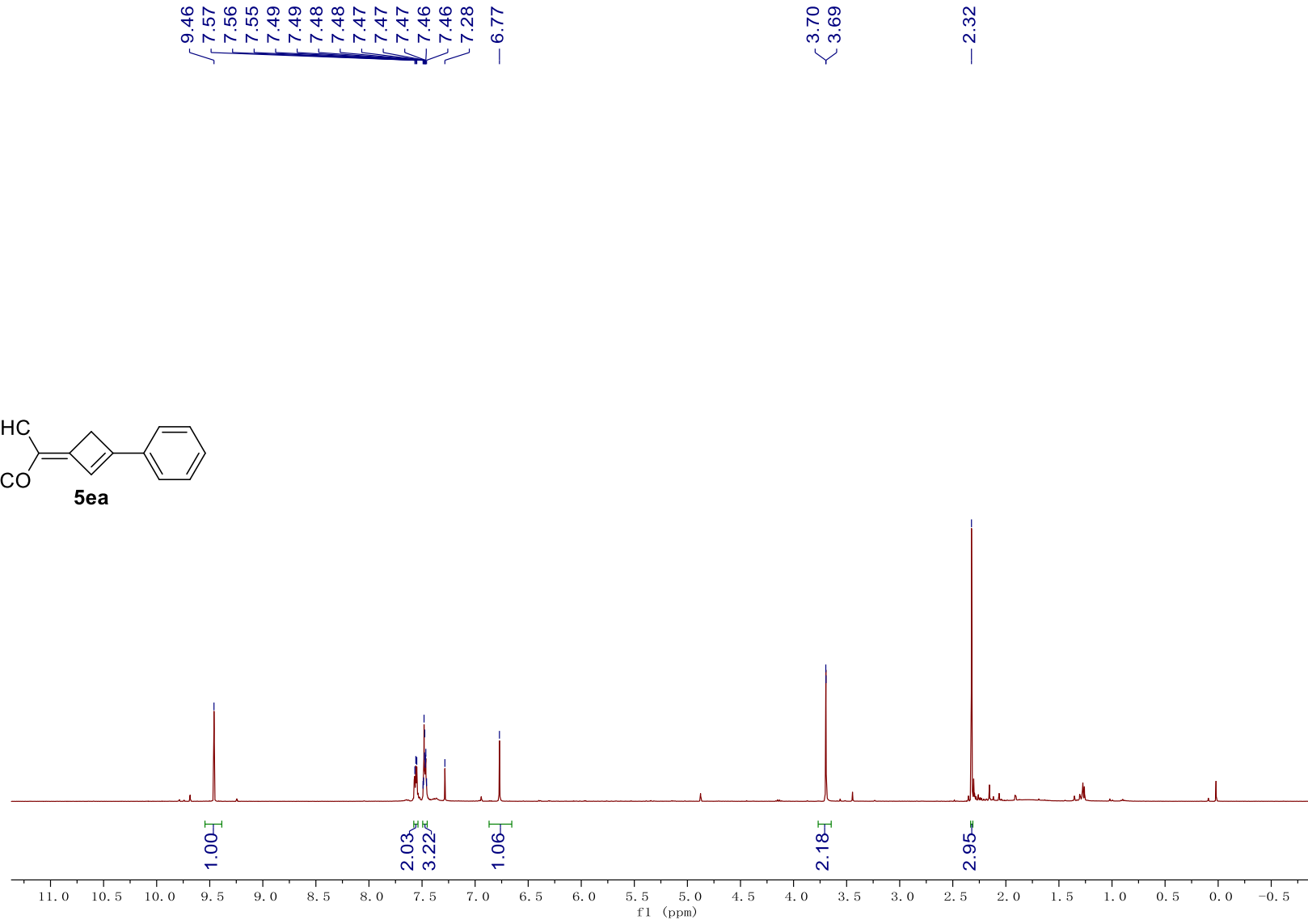
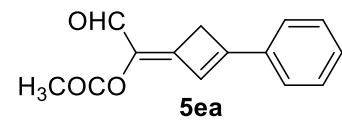
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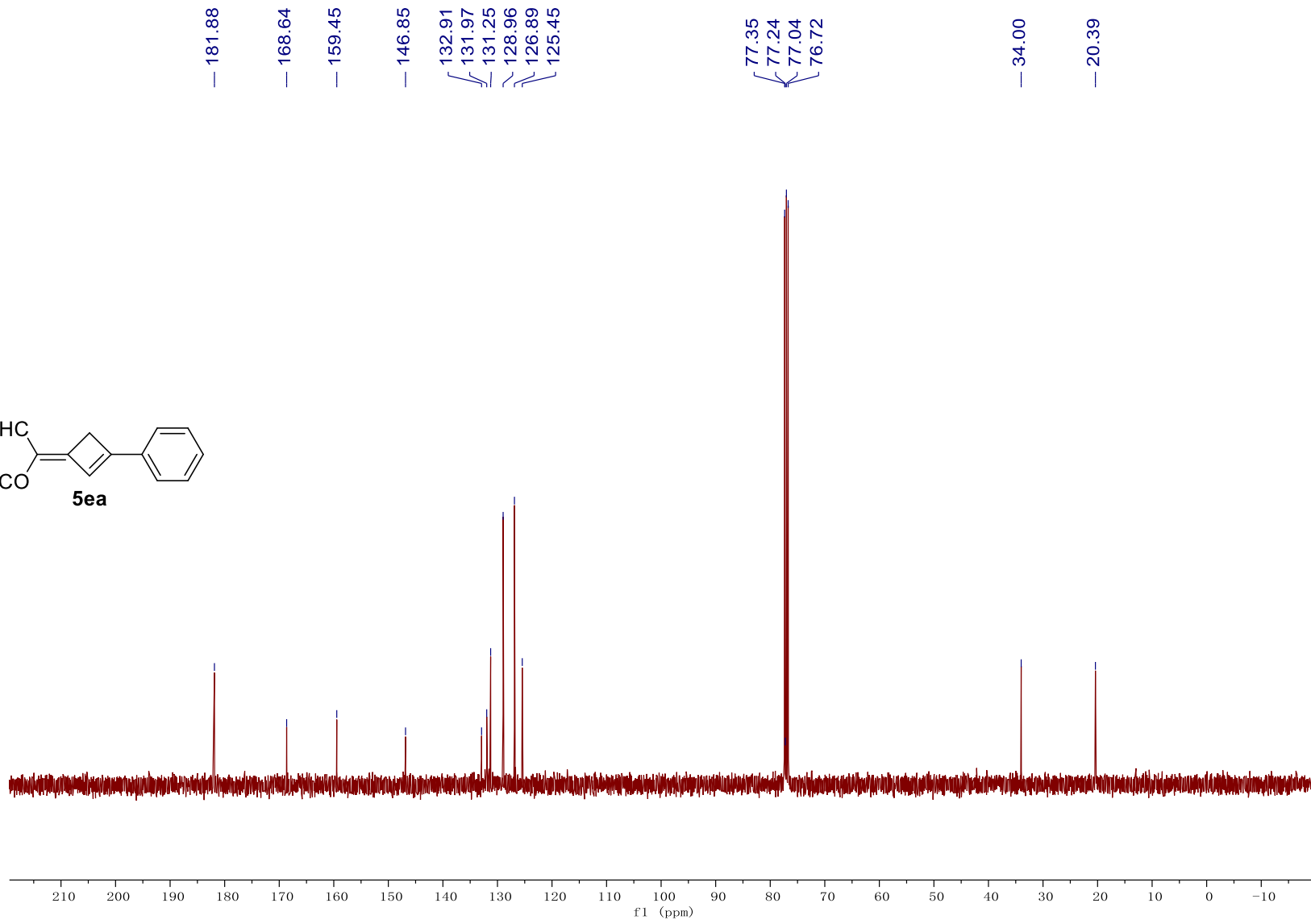
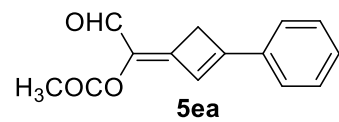


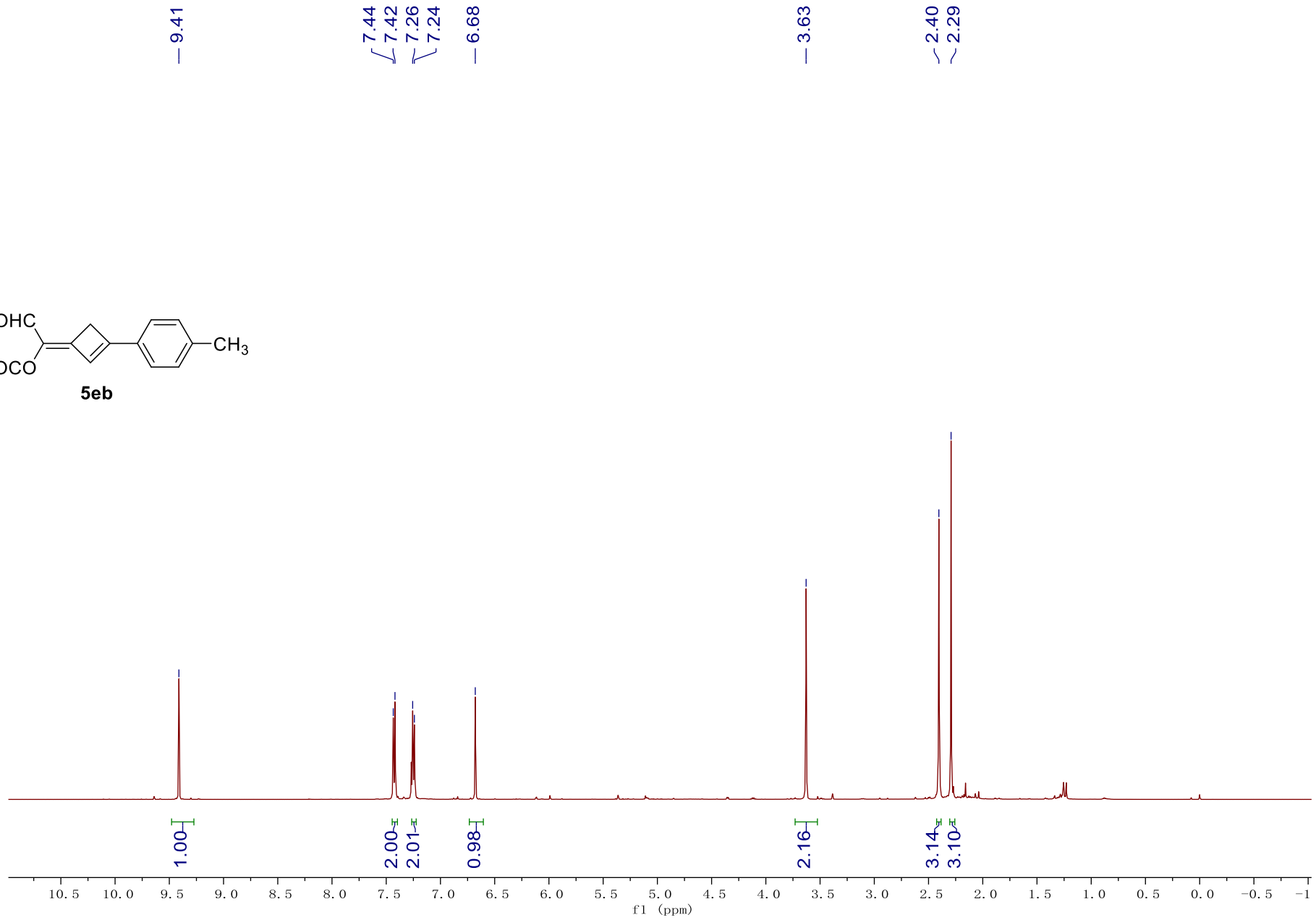
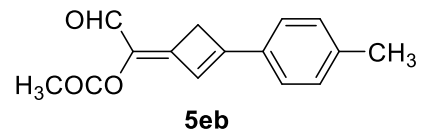


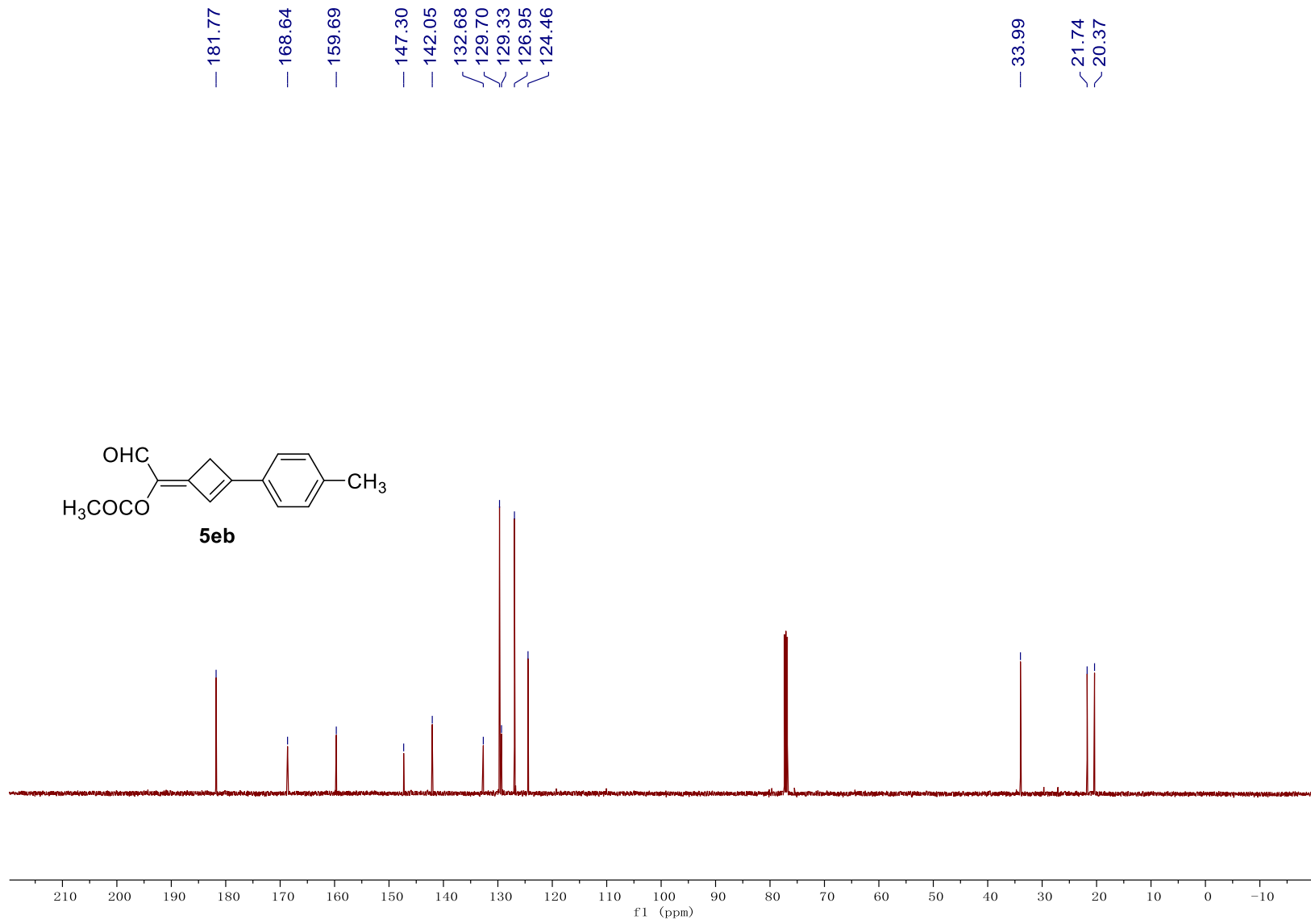
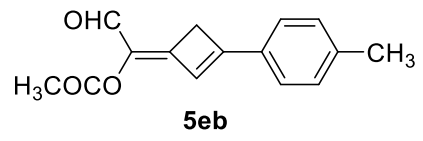
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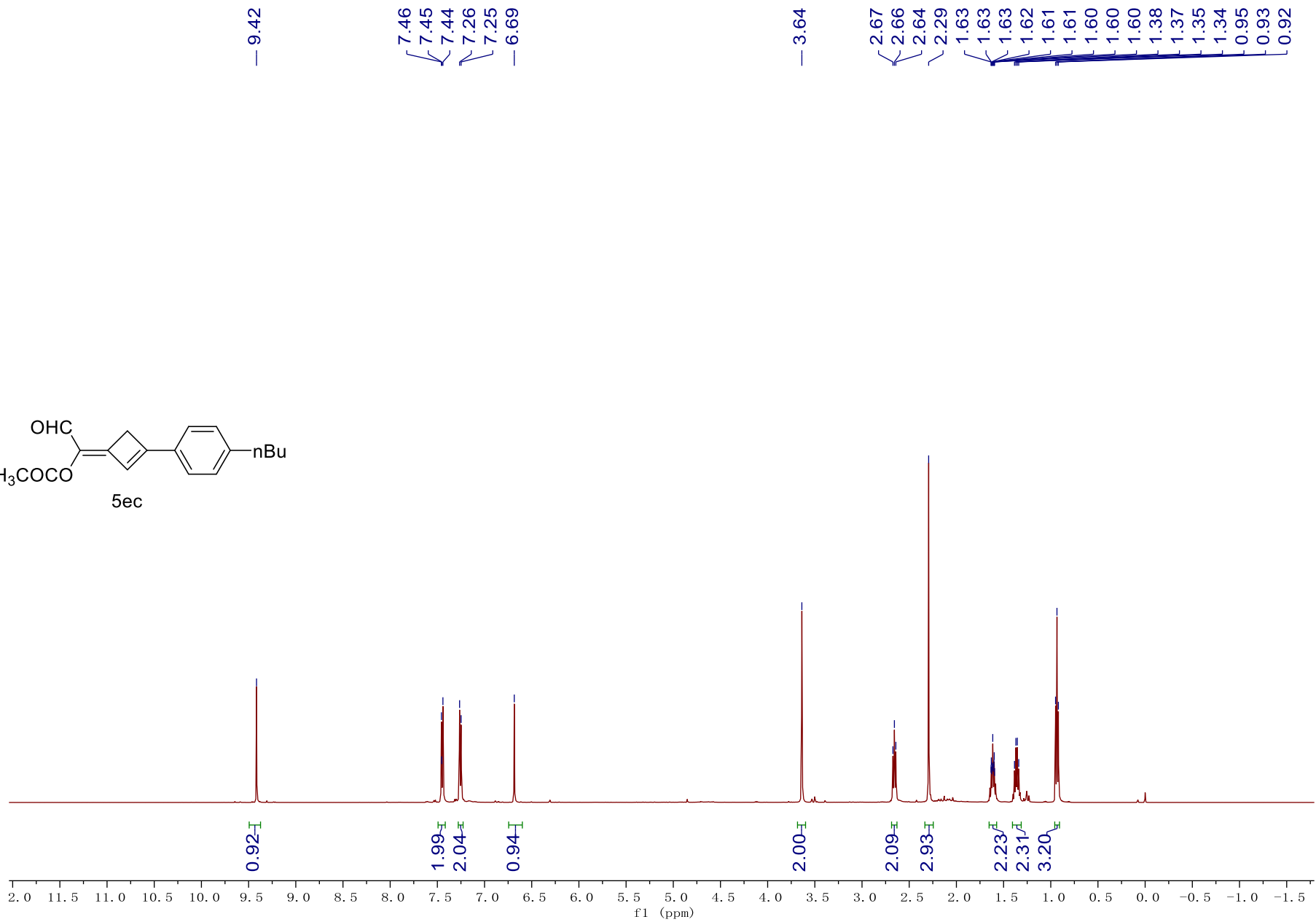
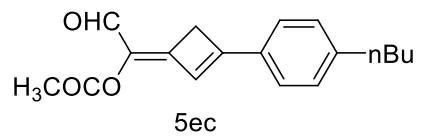


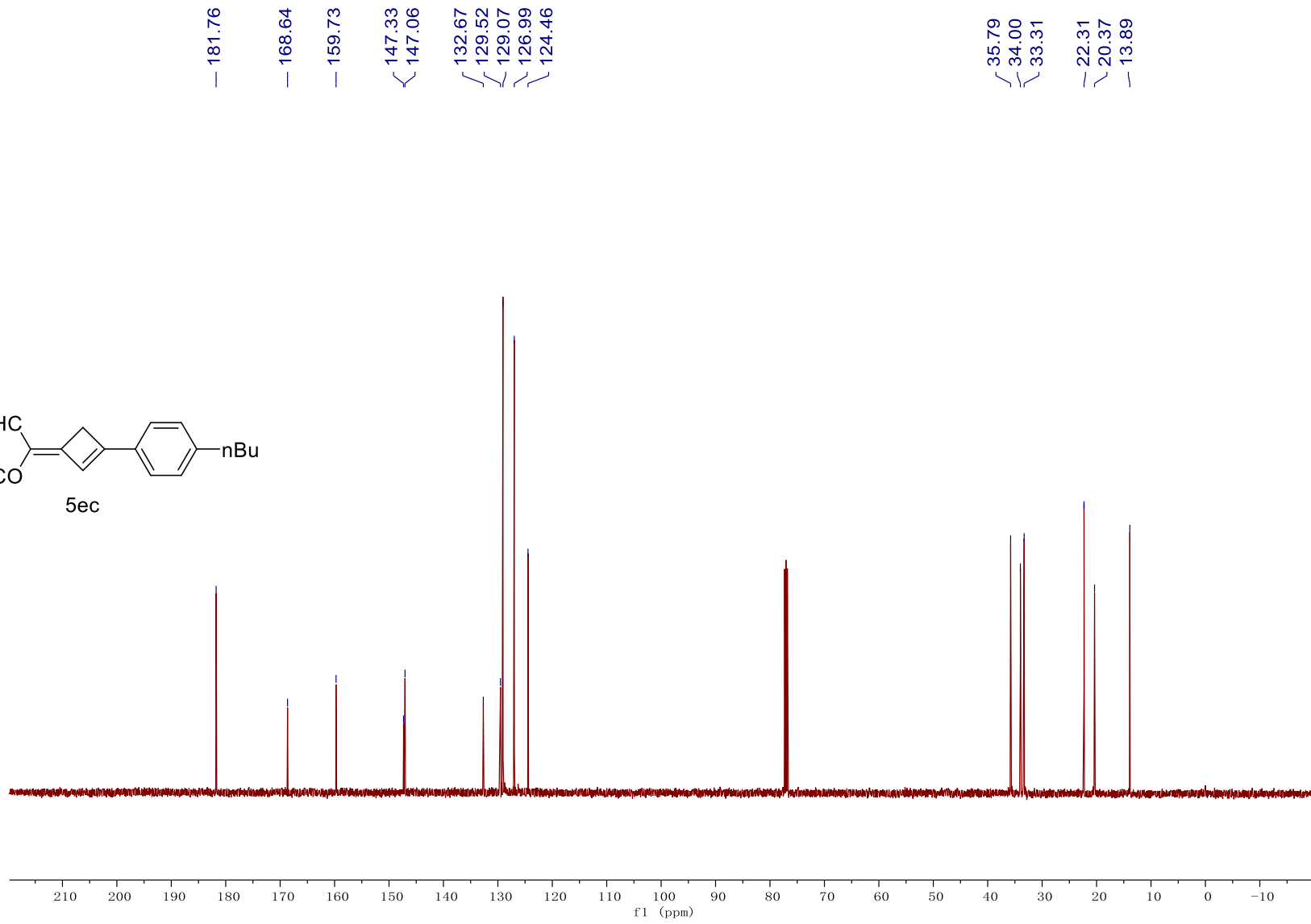
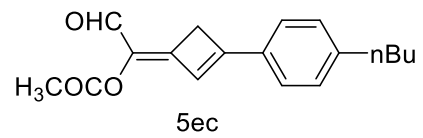


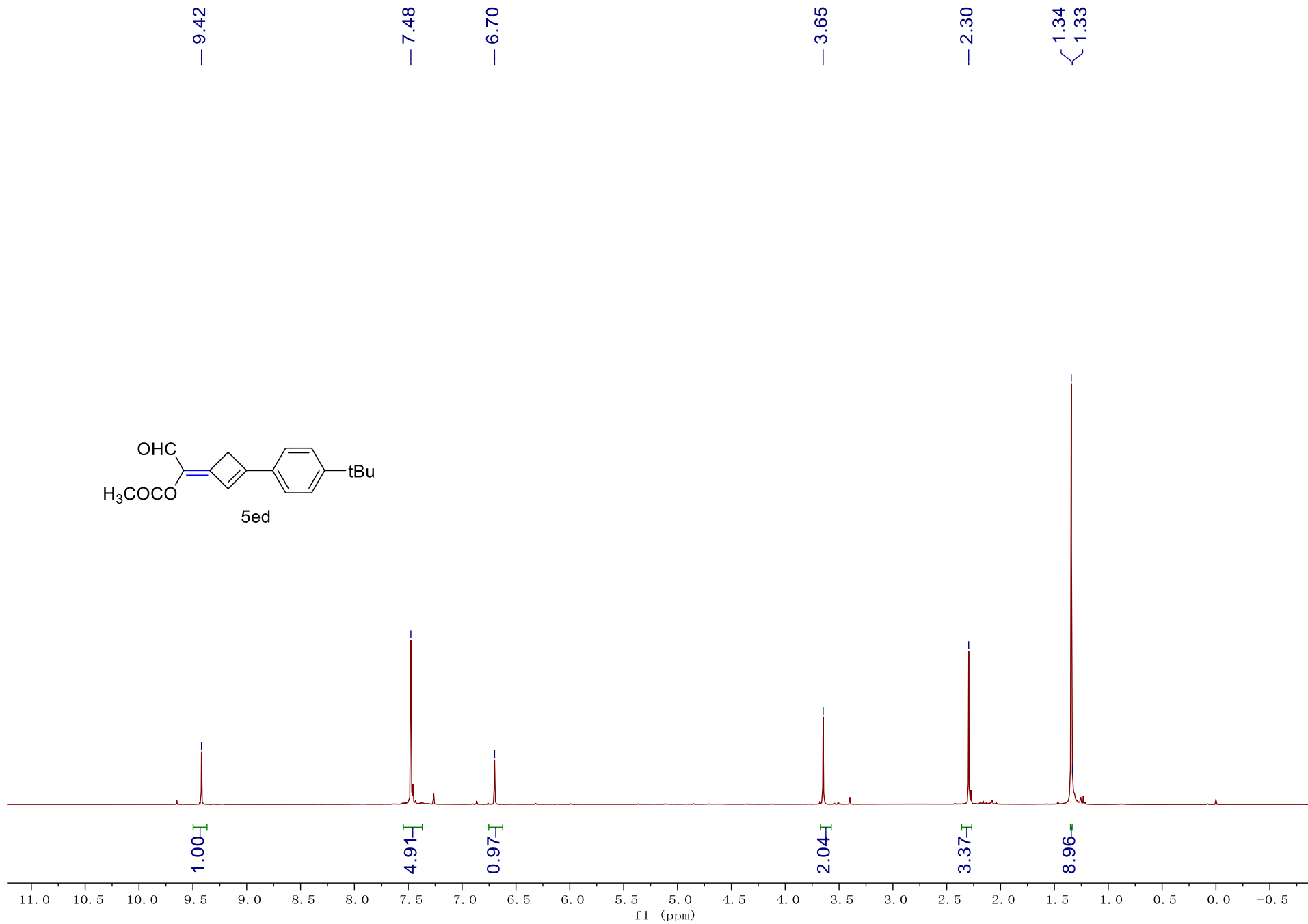
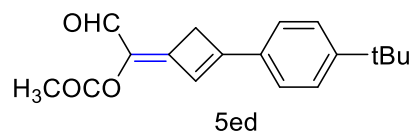


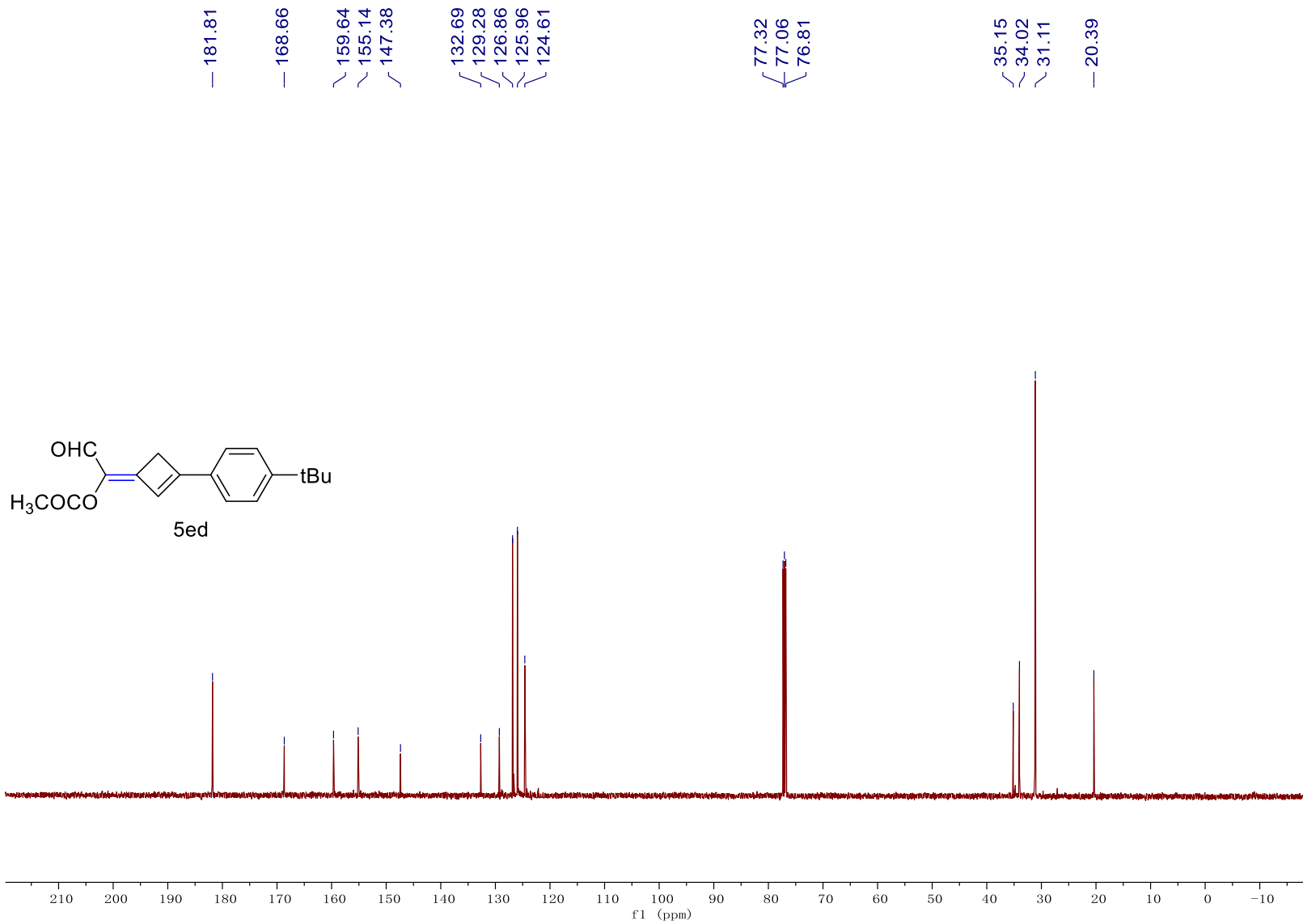


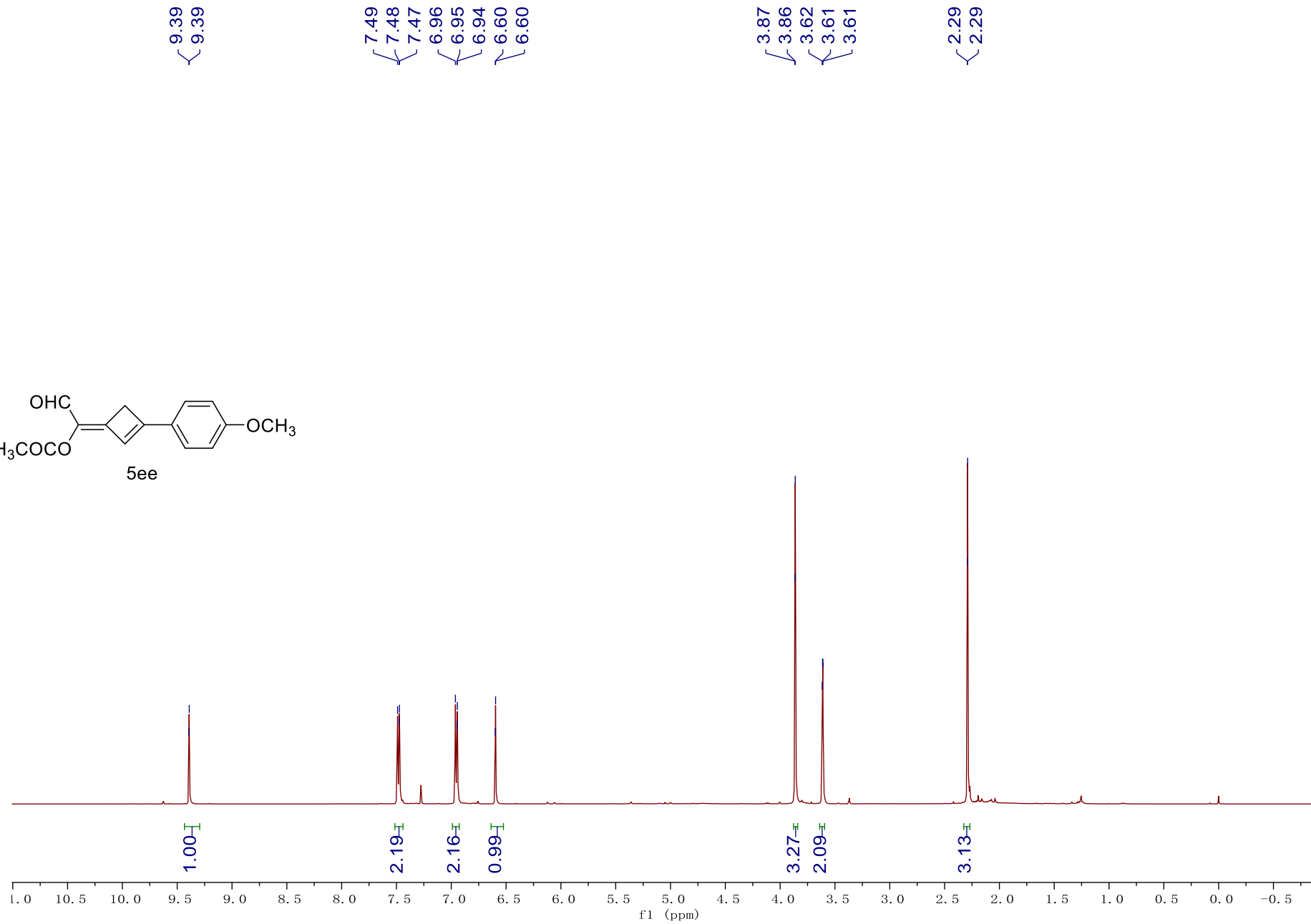
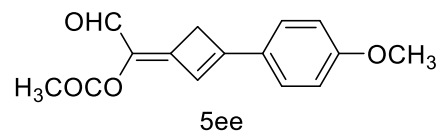


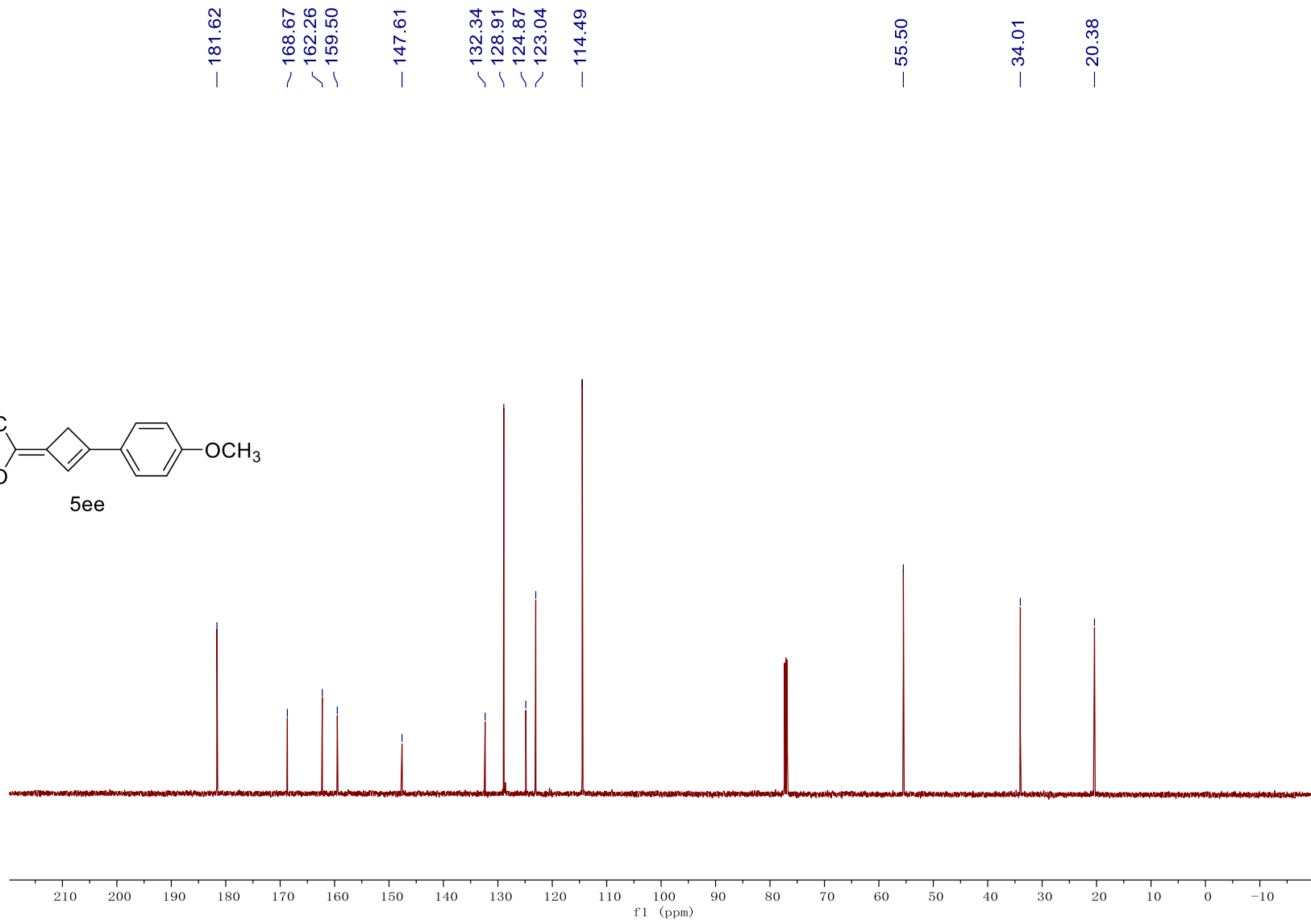
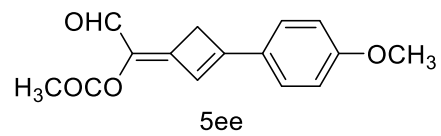


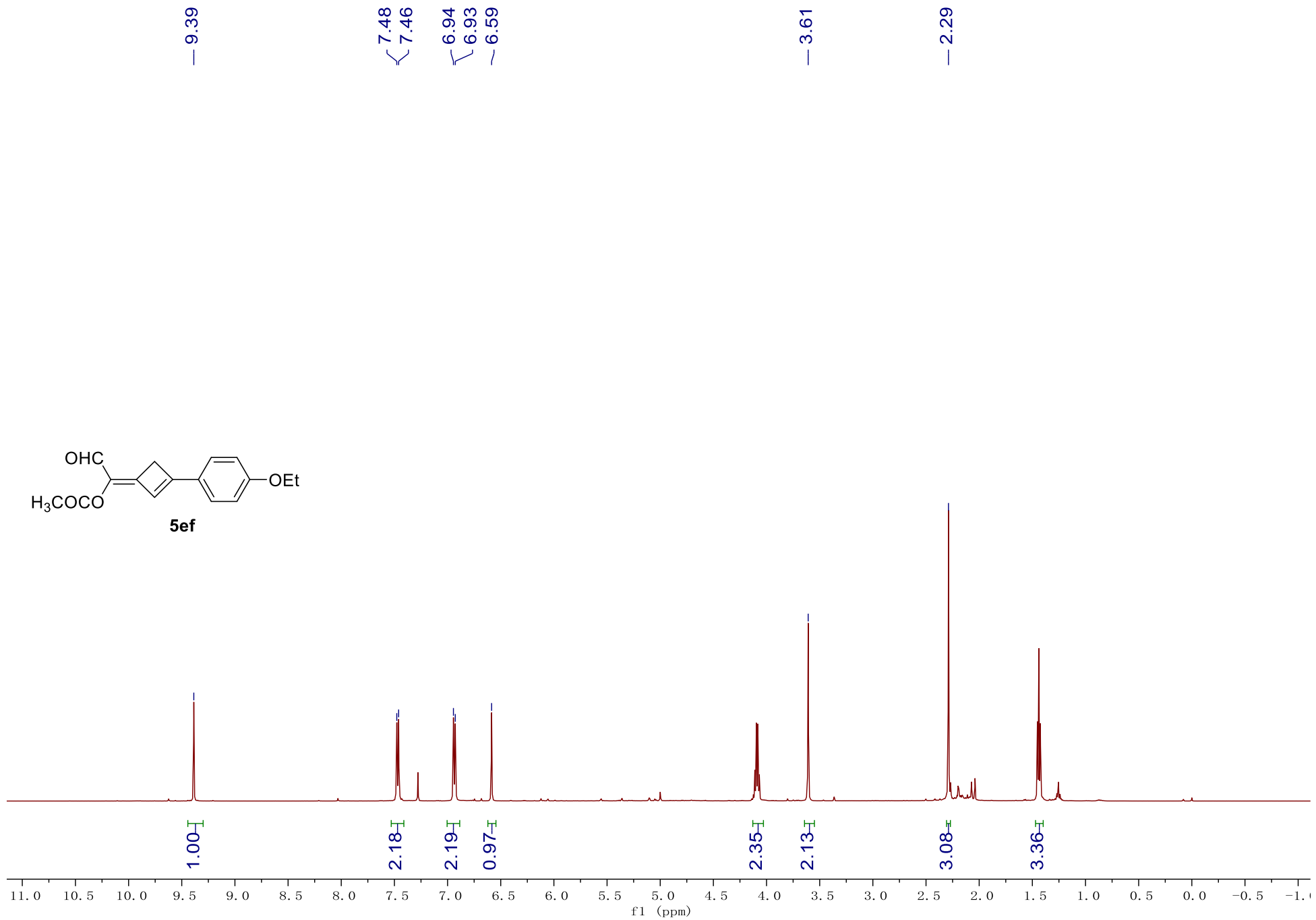
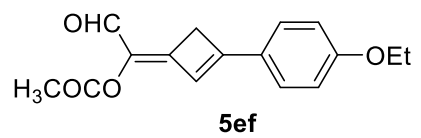


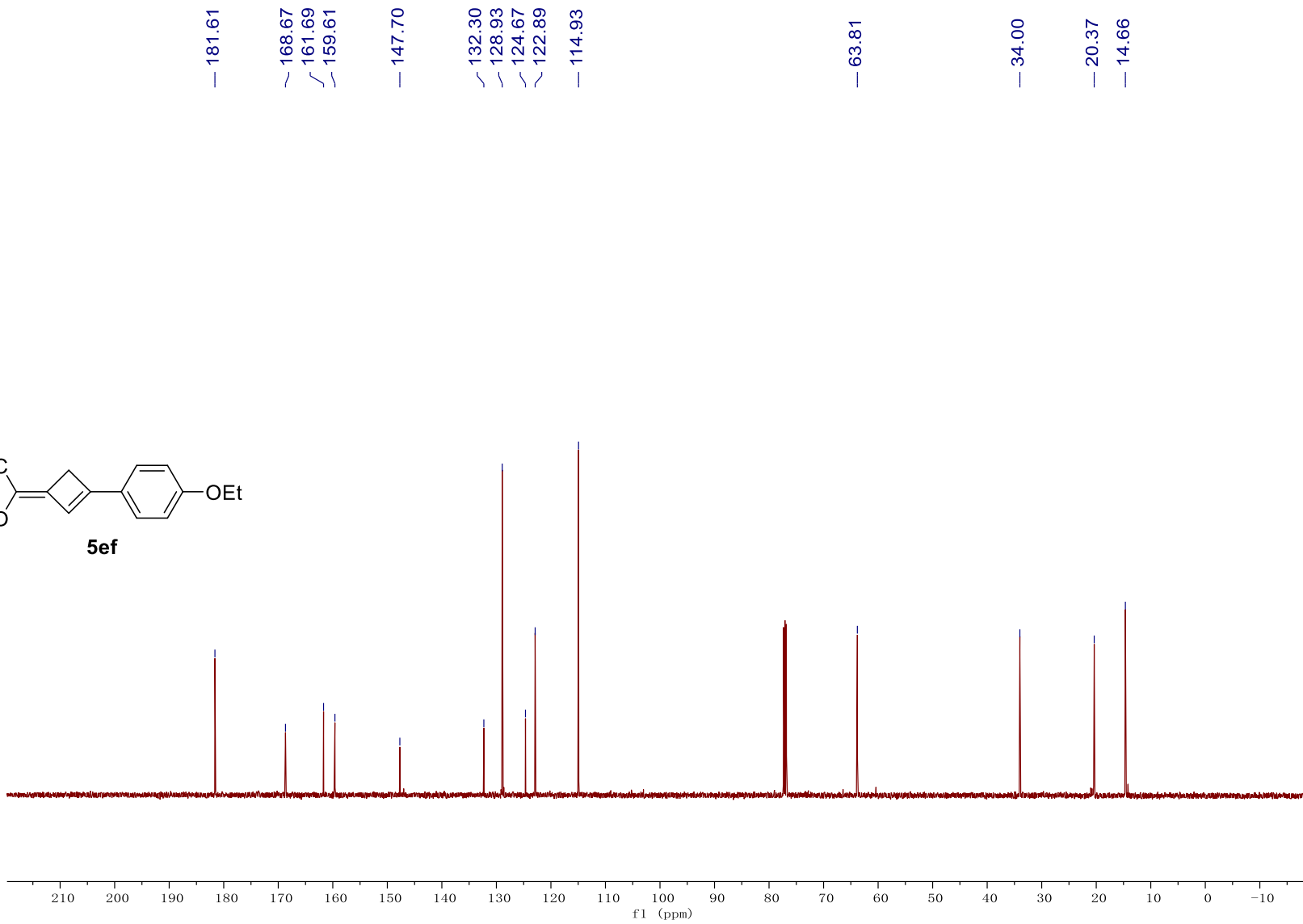
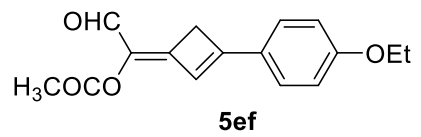


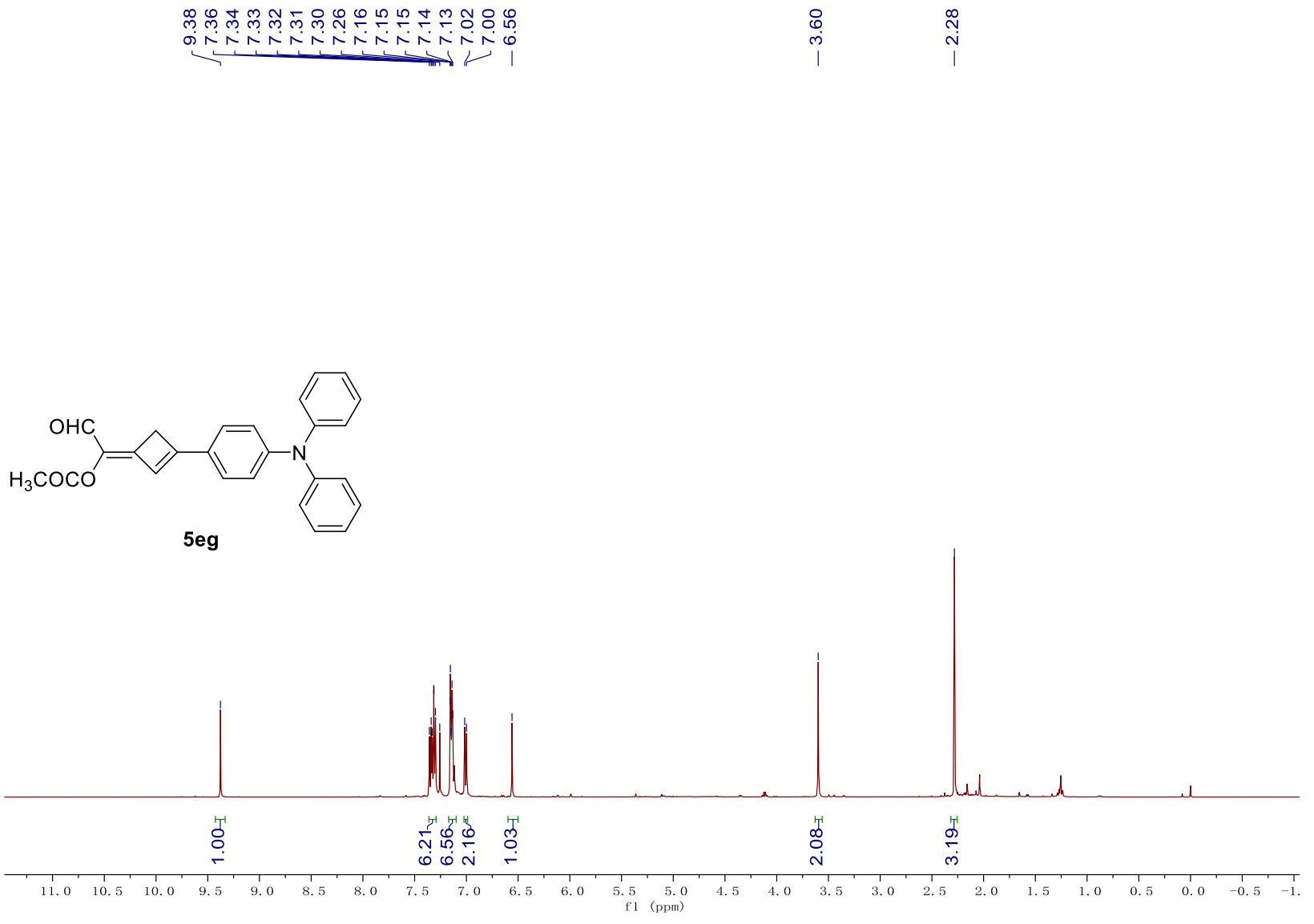
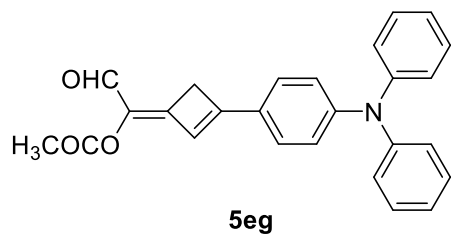


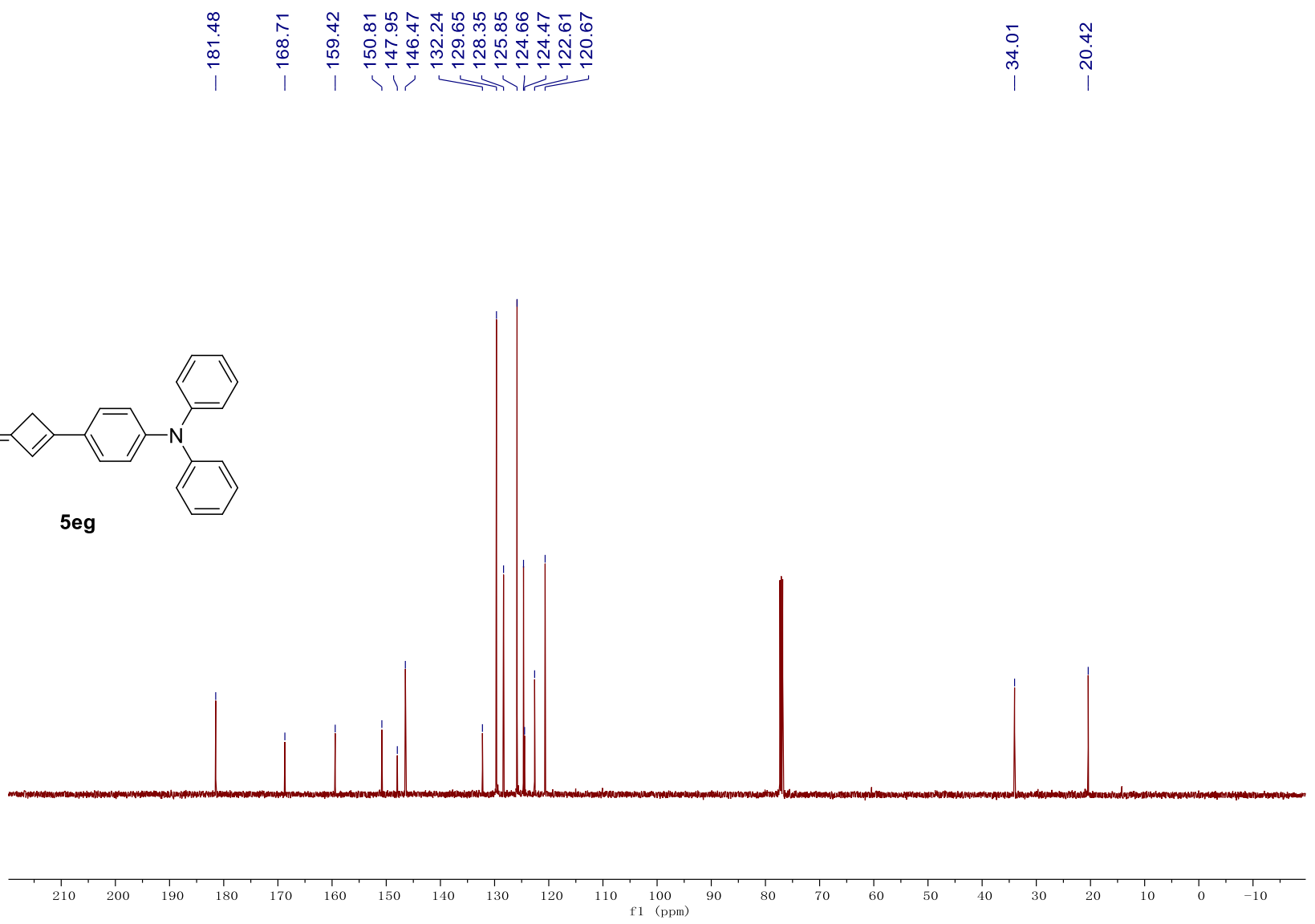
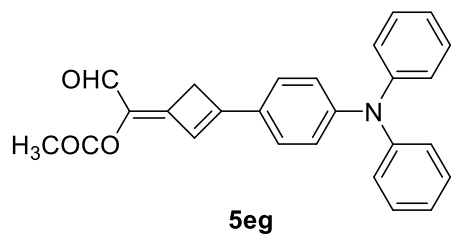


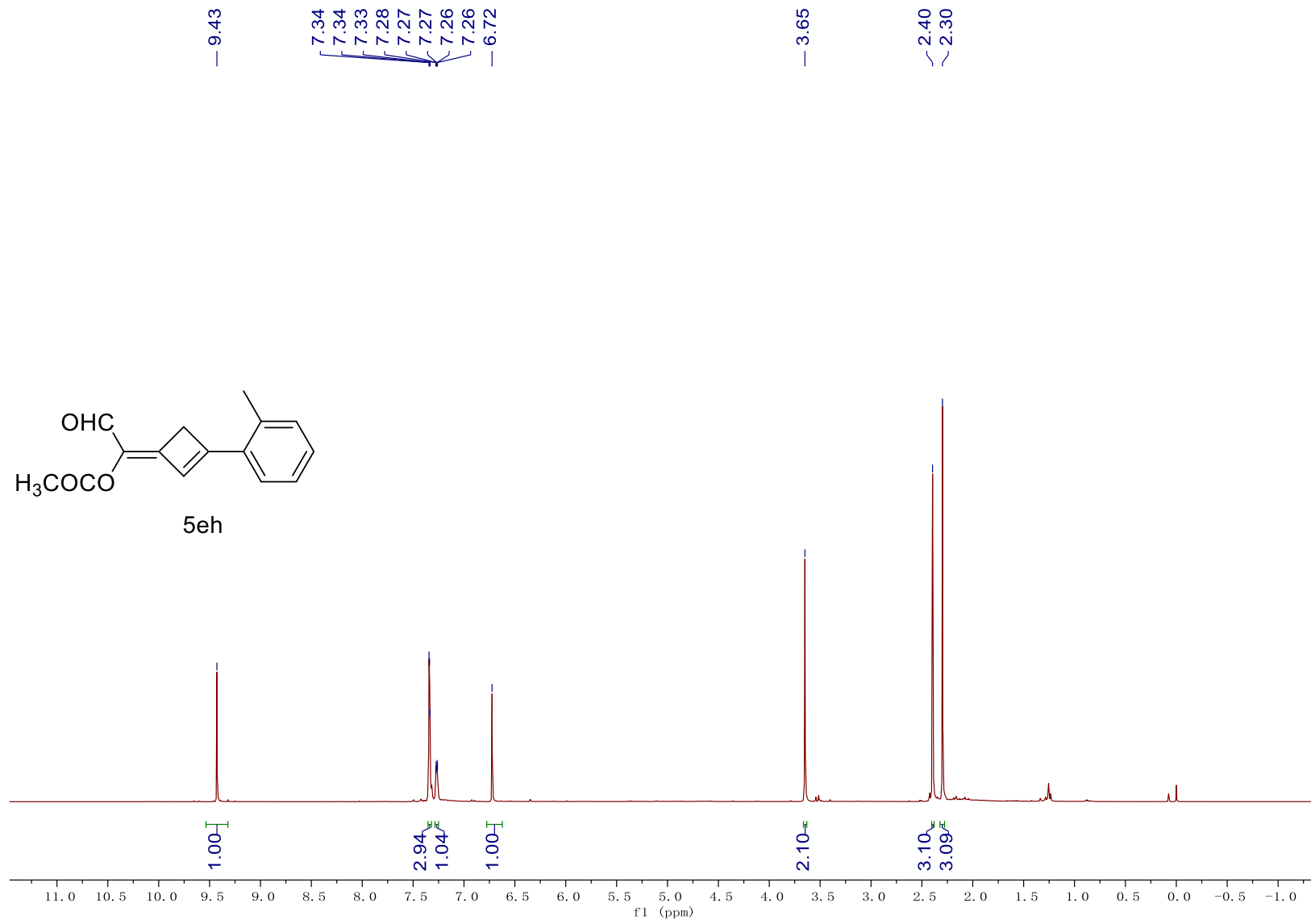
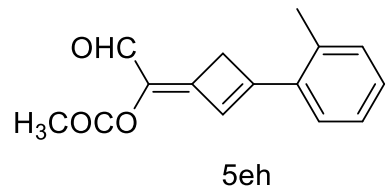


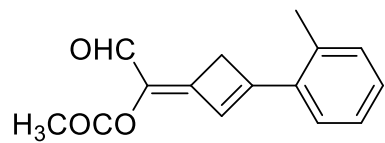




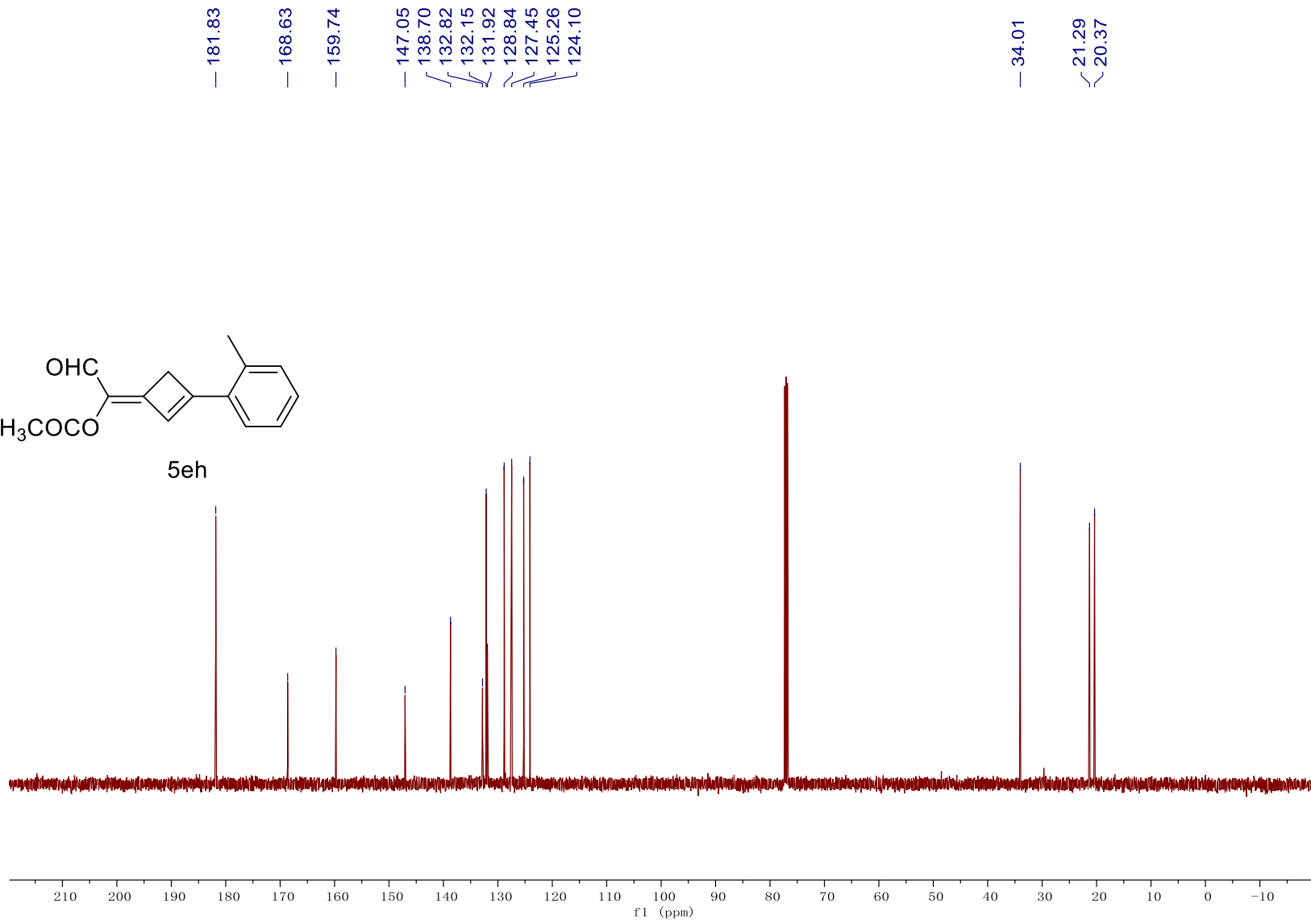


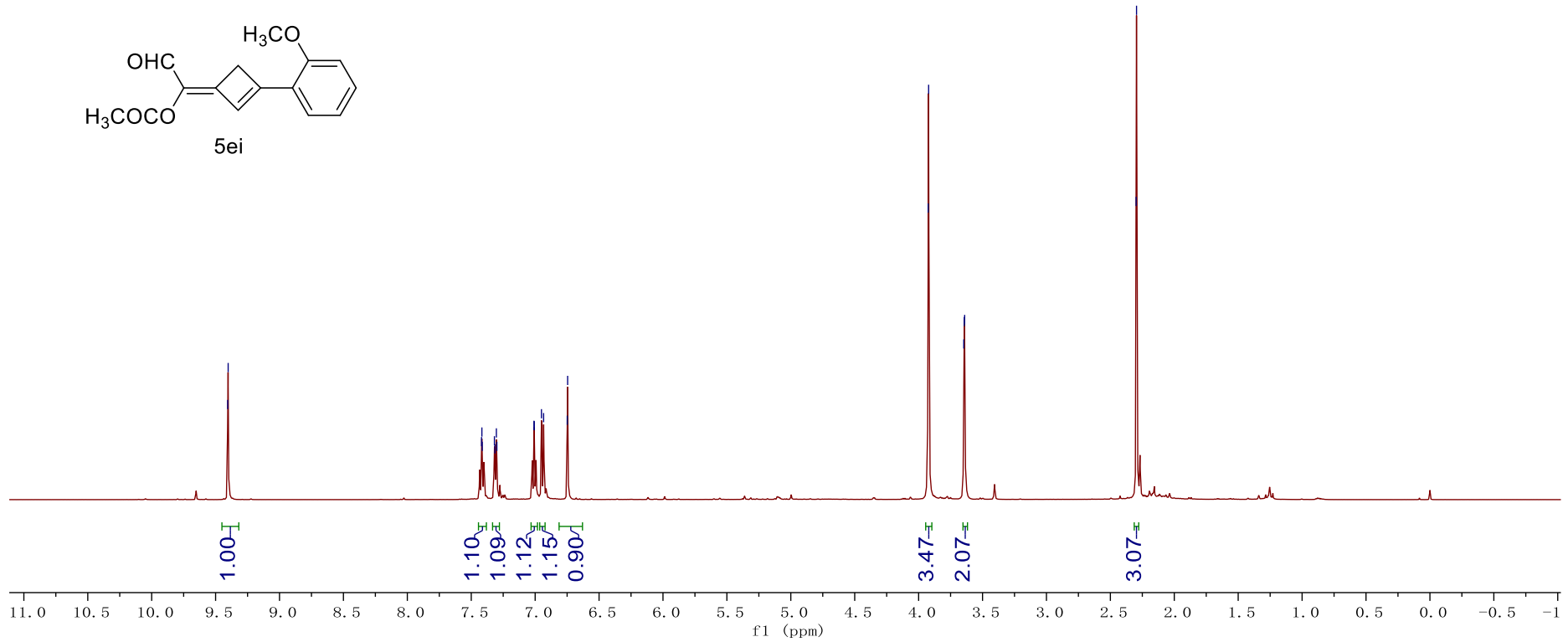
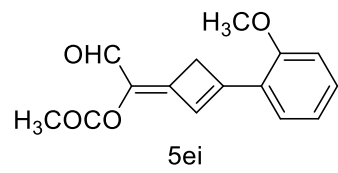


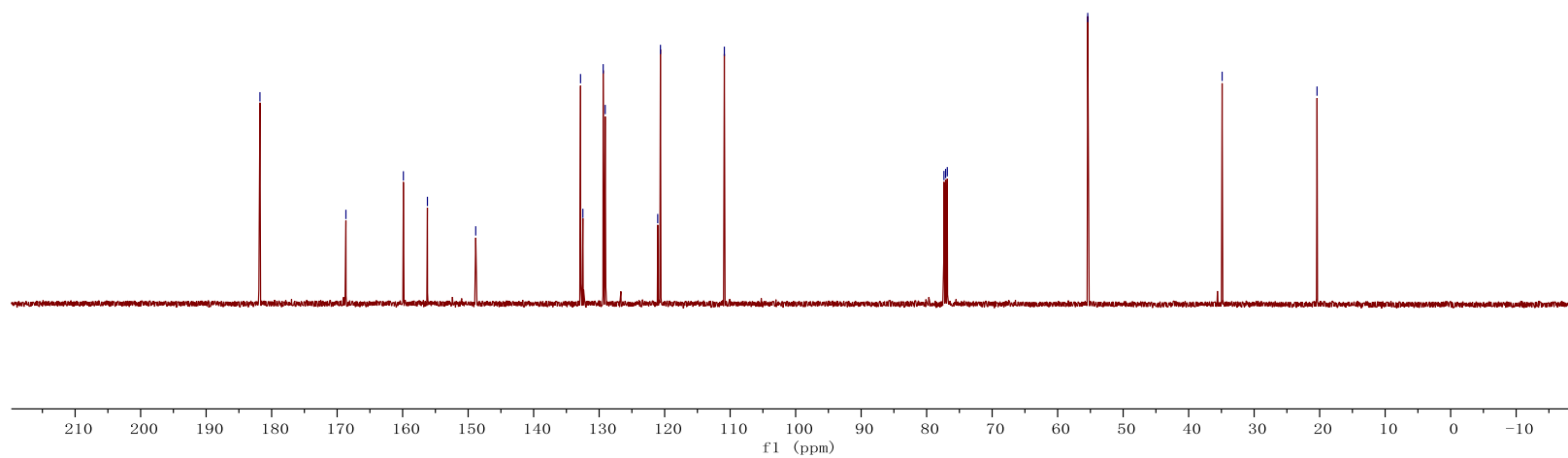
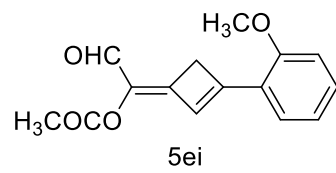




5eh







— 181.78

— 168.66

~ 159.89

~ 156.22

~ 148.84

132.84

132.49

129.39

129.07

121.06

120.64

— 110.89

77.36

77.11

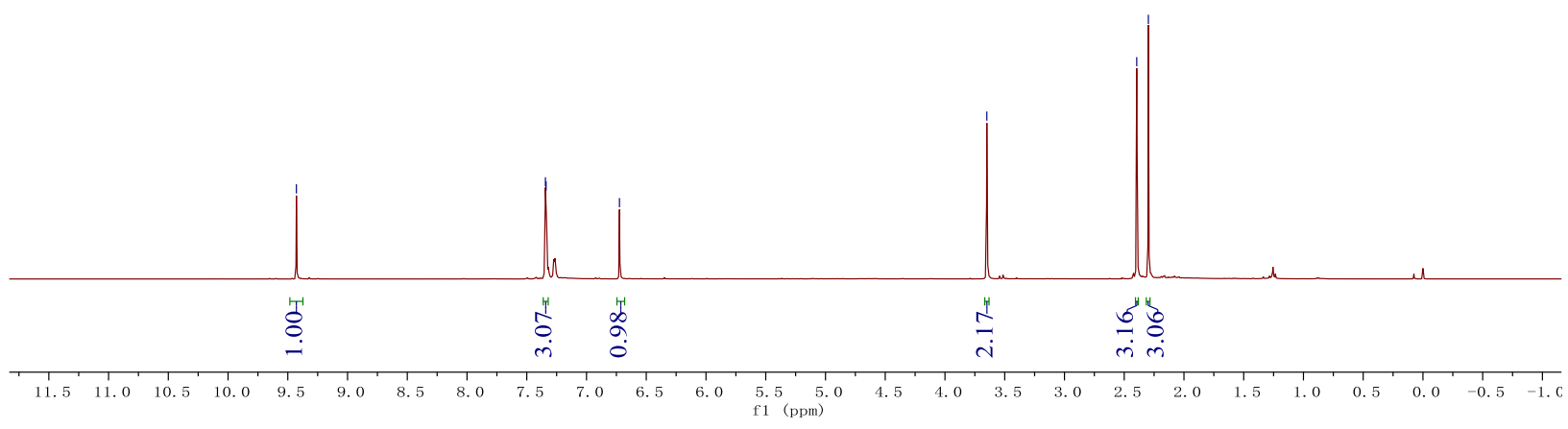
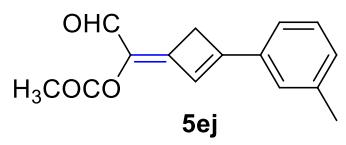
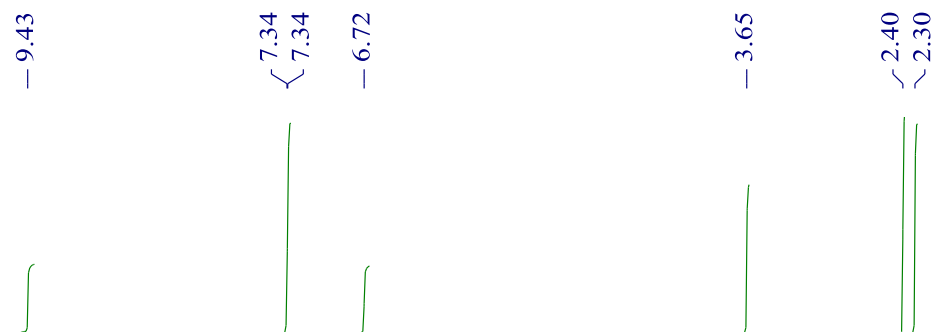
76.85

— 55.41

— 34.89

— 20.40

xzr-ii-164-2-iso. 22. fid



xzr-ii-164-2-iso.23.fid

— 181.83

— 168.63

— 159.74

147.05

138.70

132.82

132.15

131.92

128.84

127.45

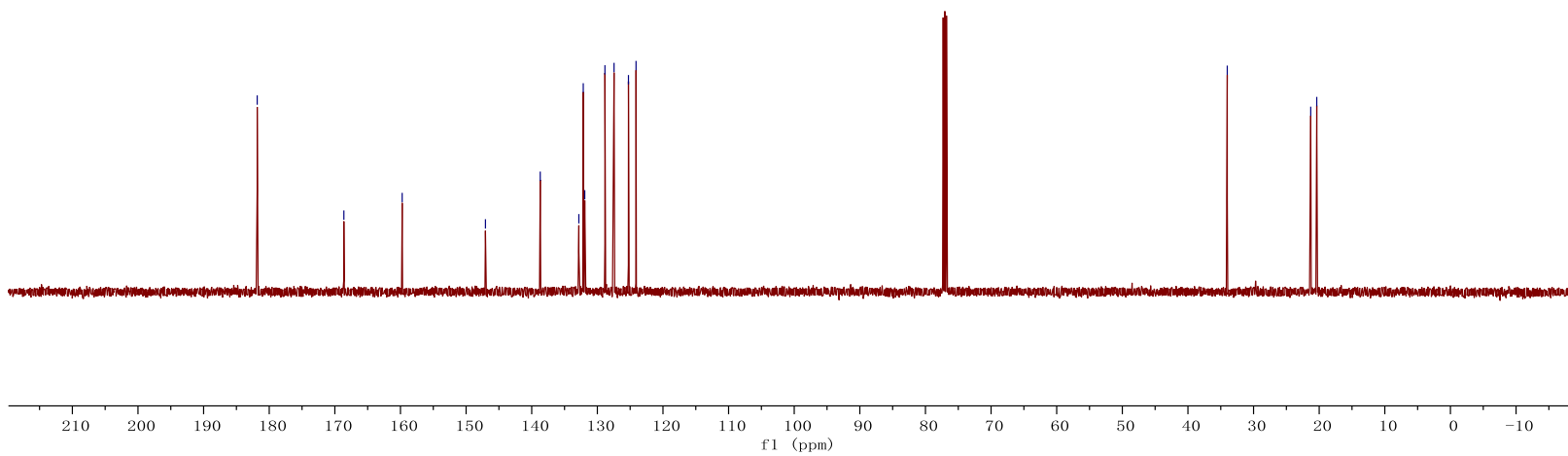
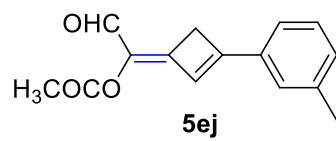
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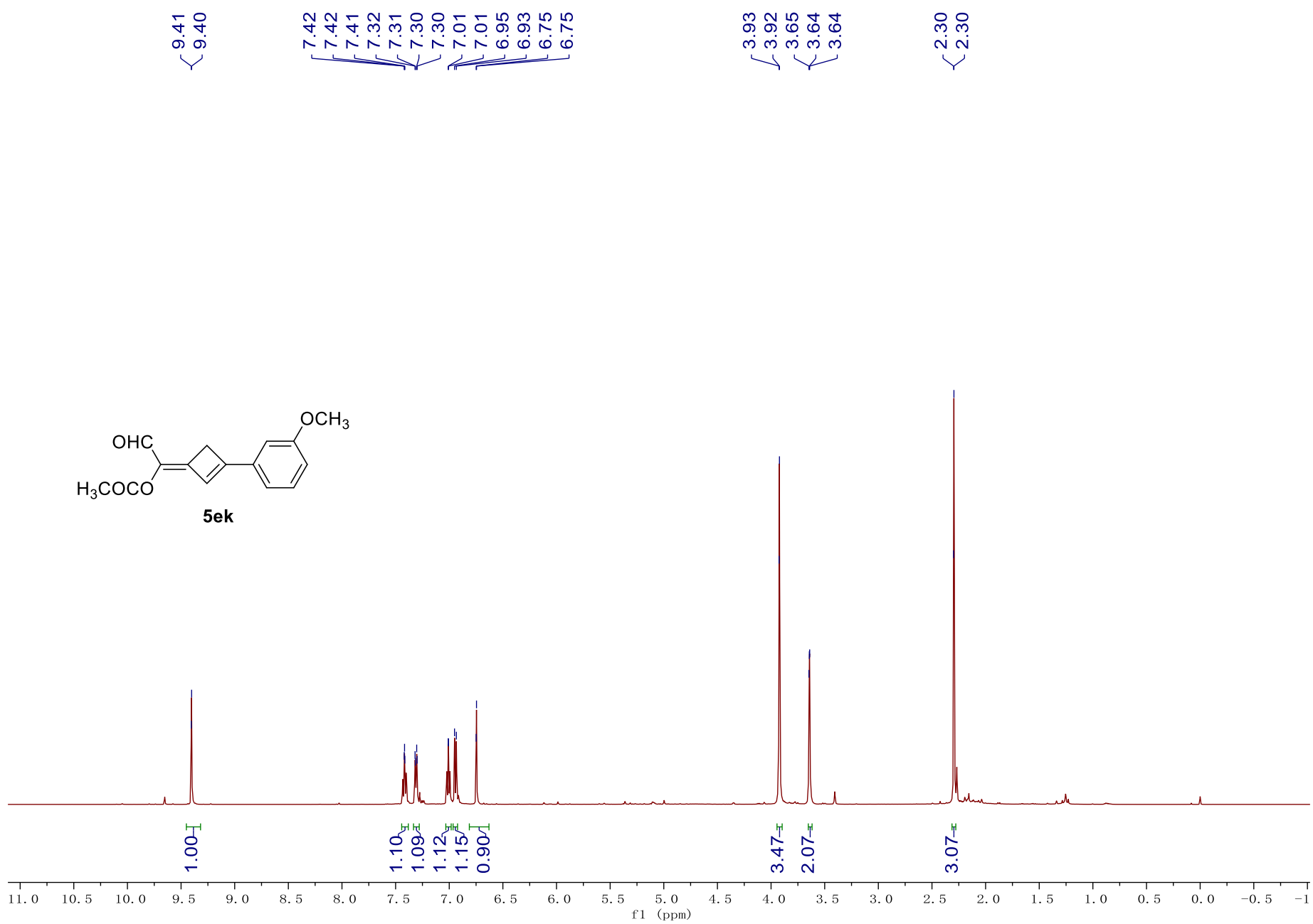
124.10

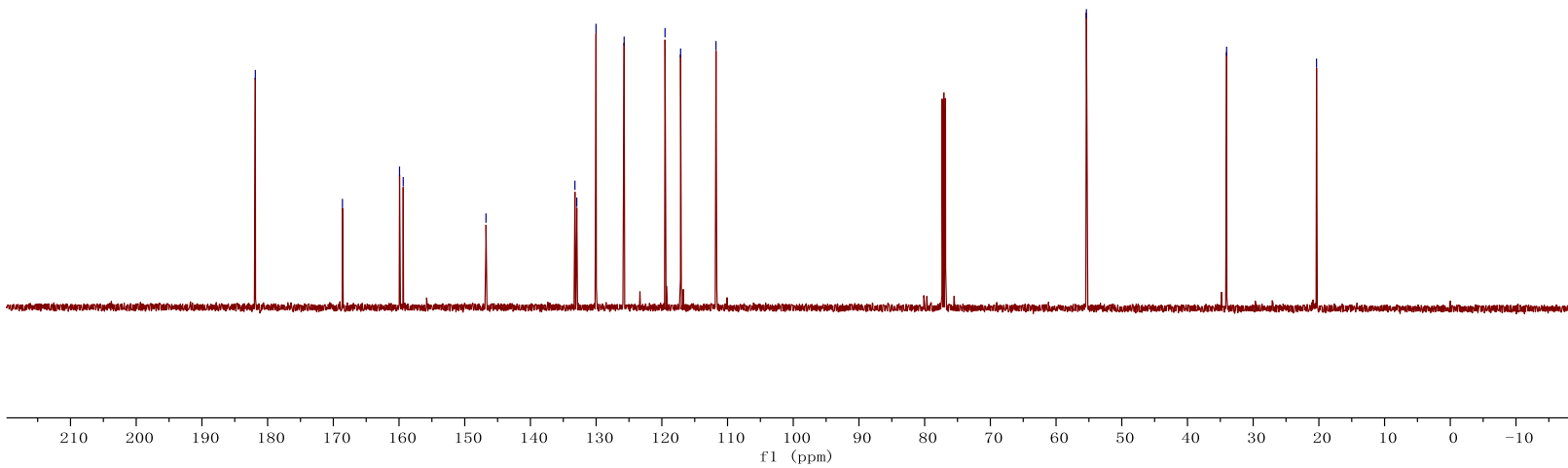
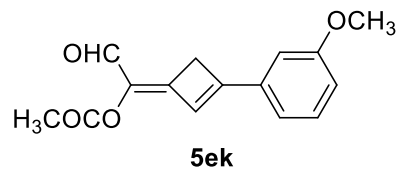
— 34.01

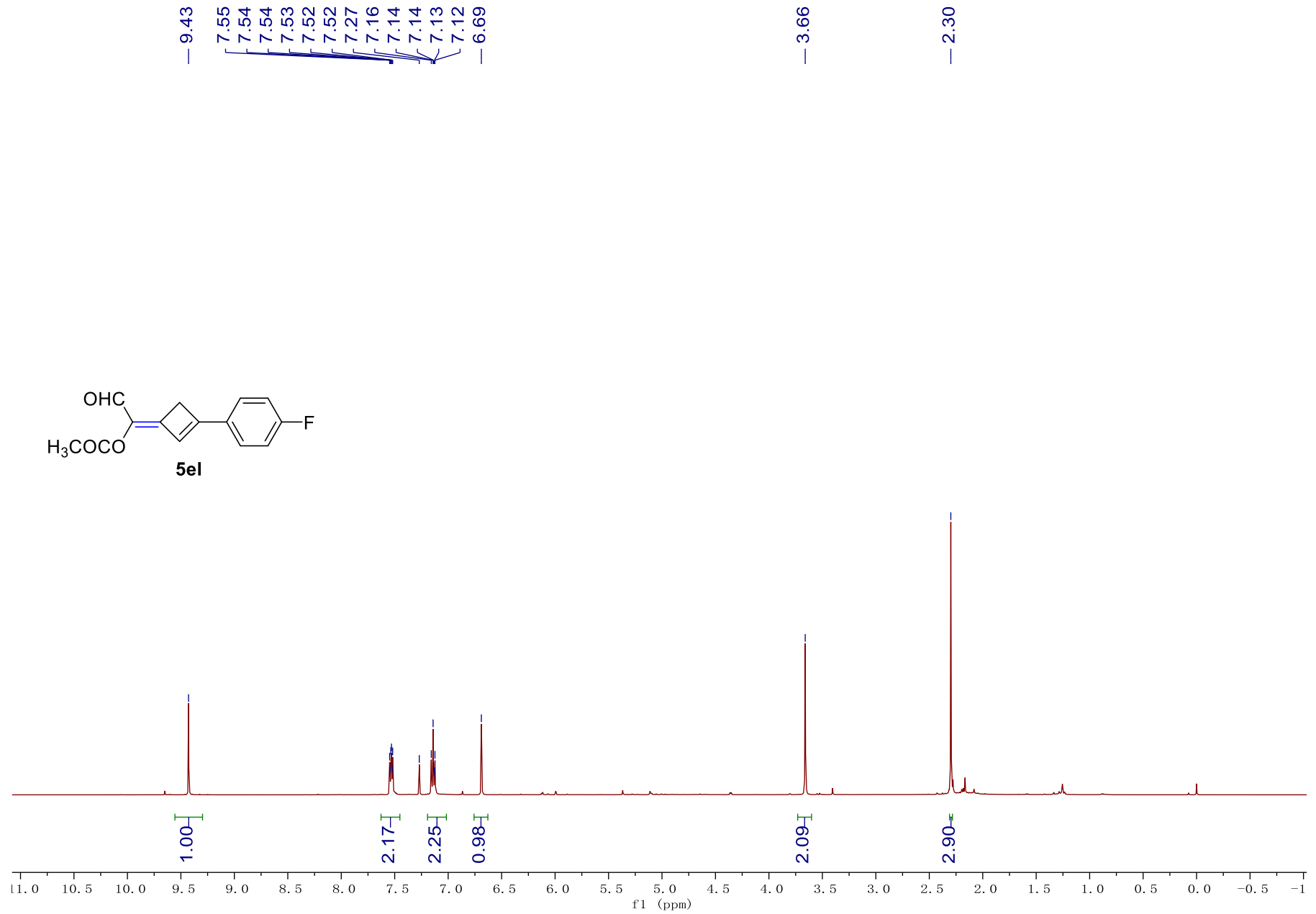
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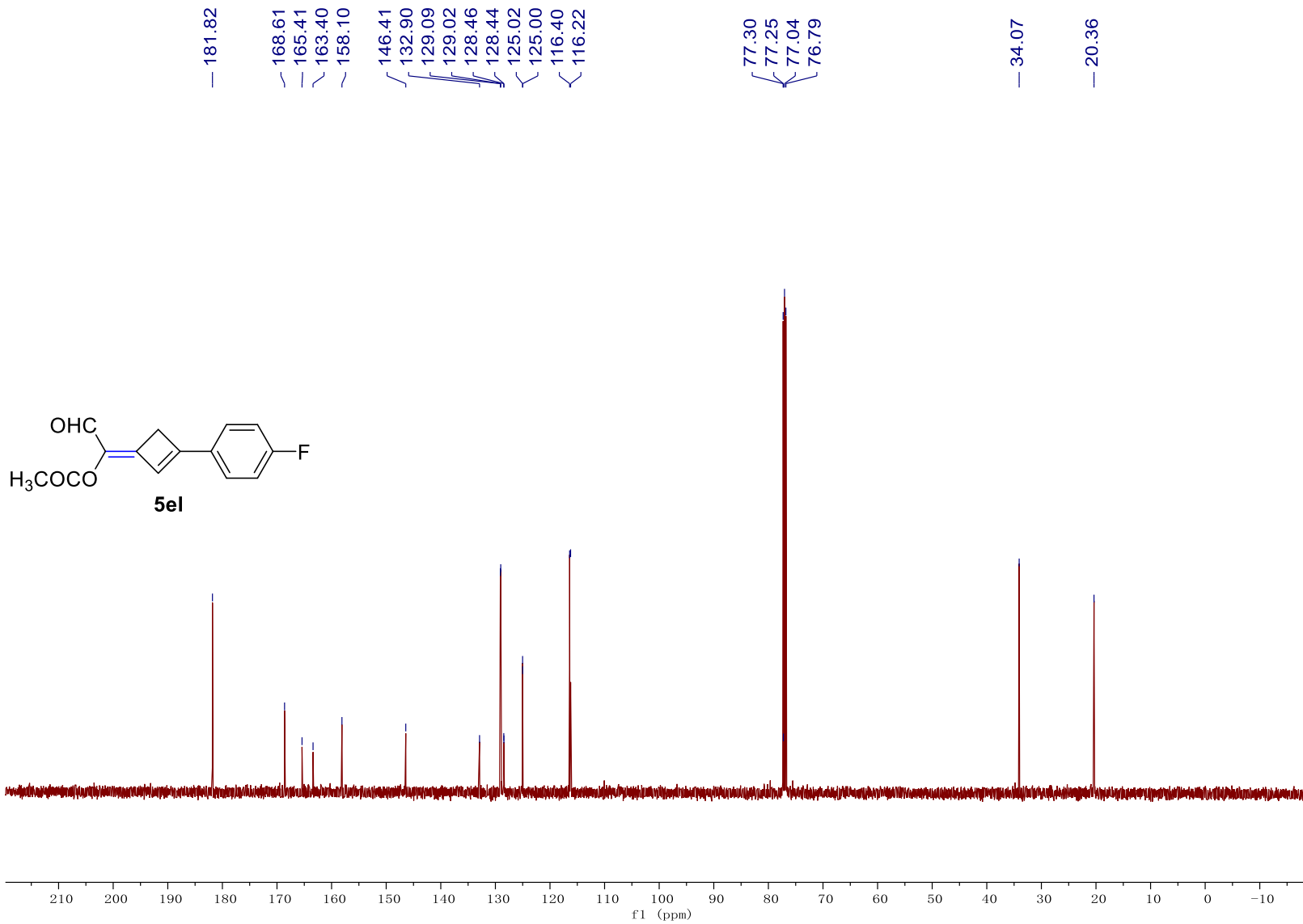
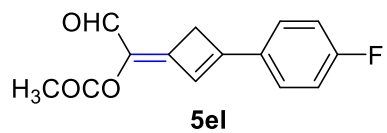
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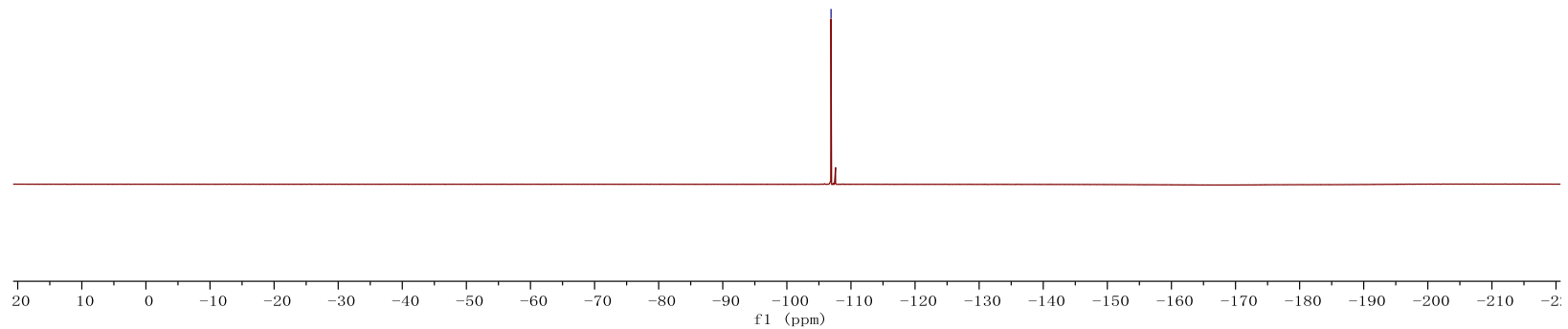
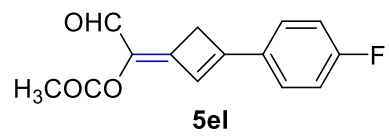


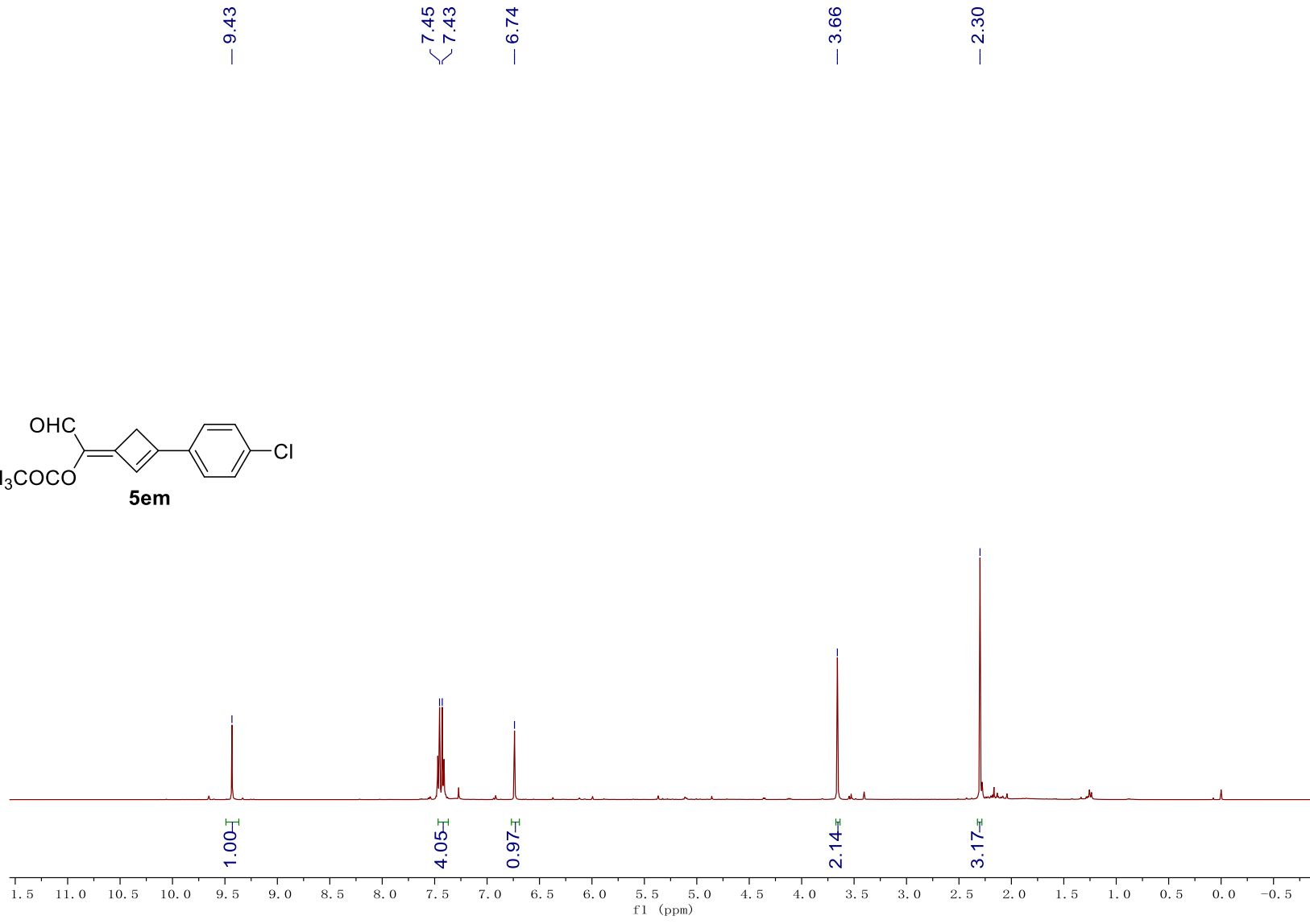
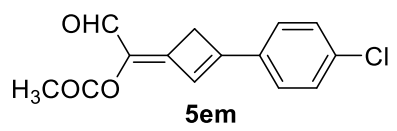


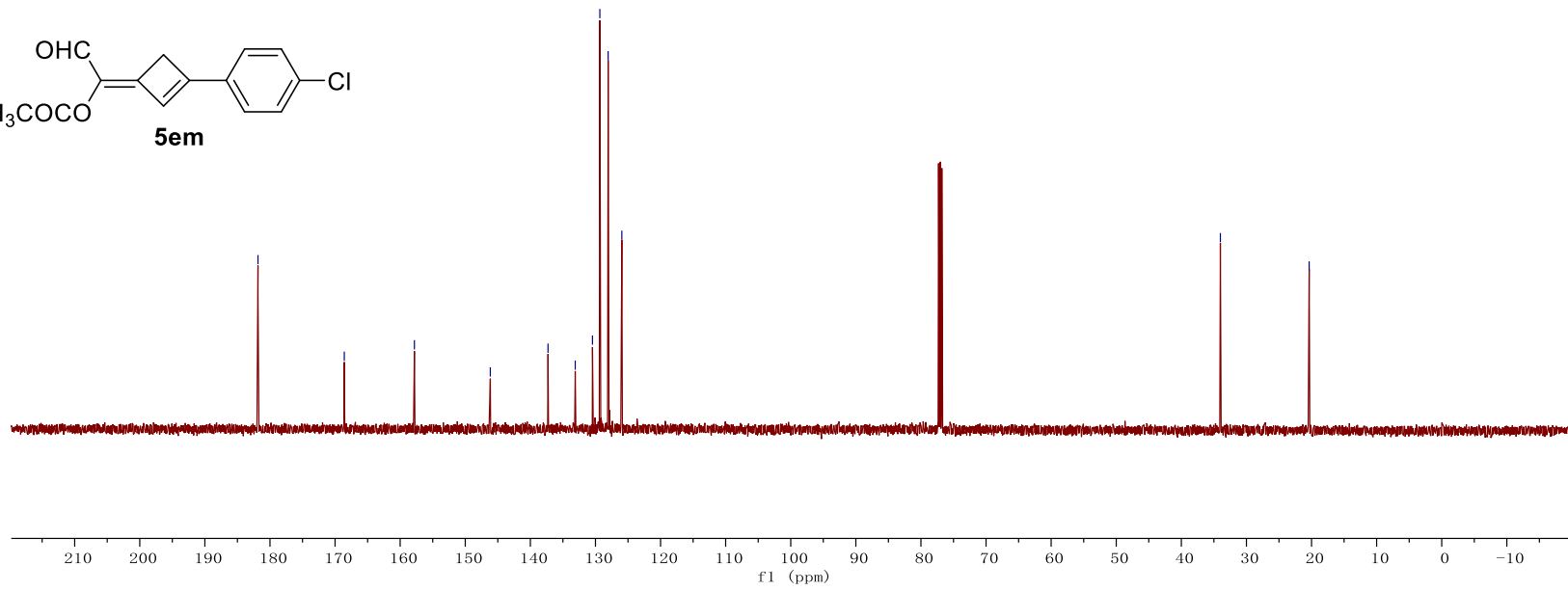
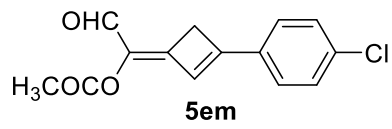


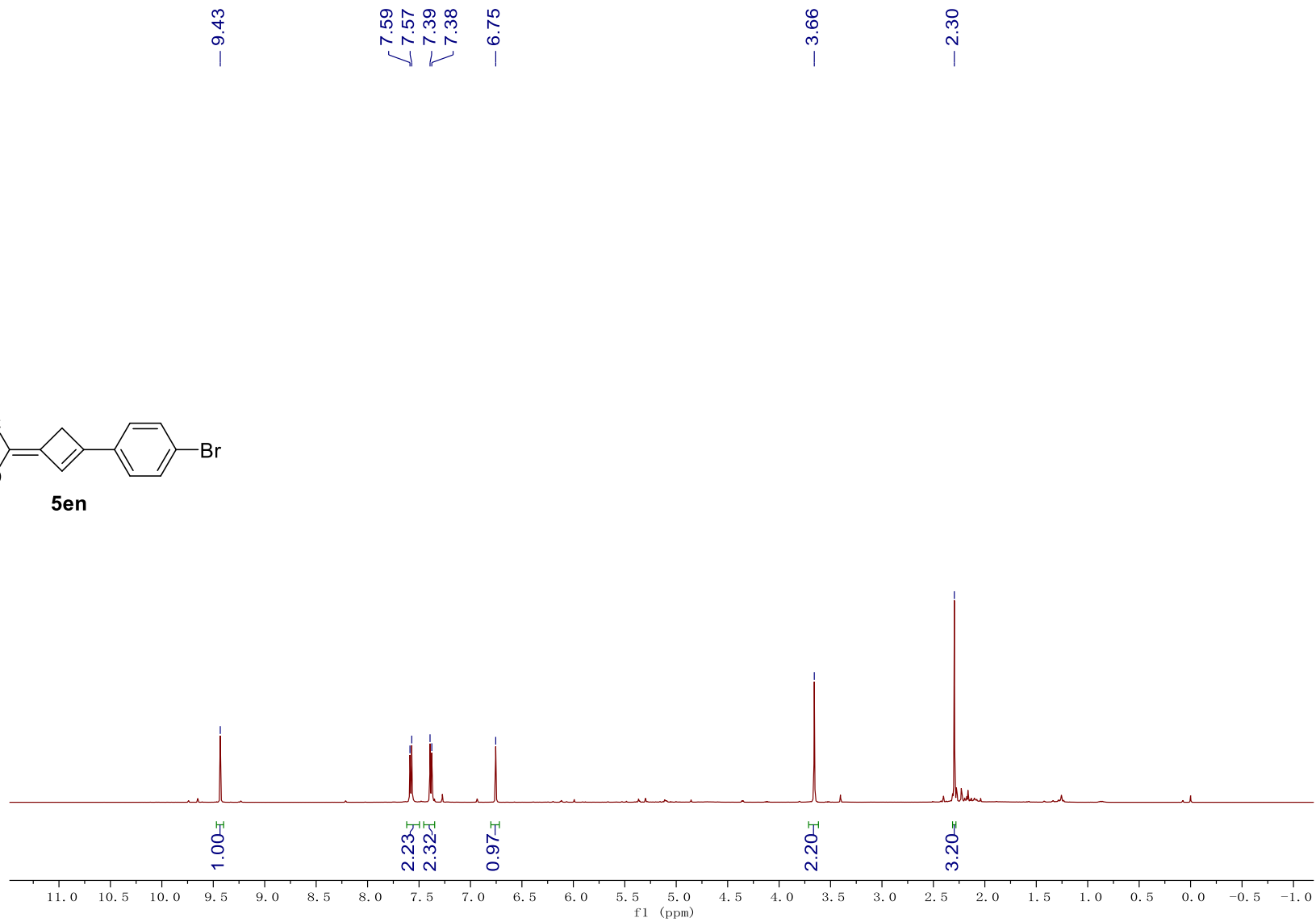
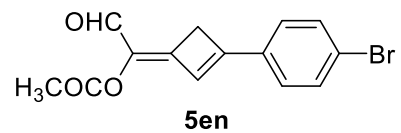


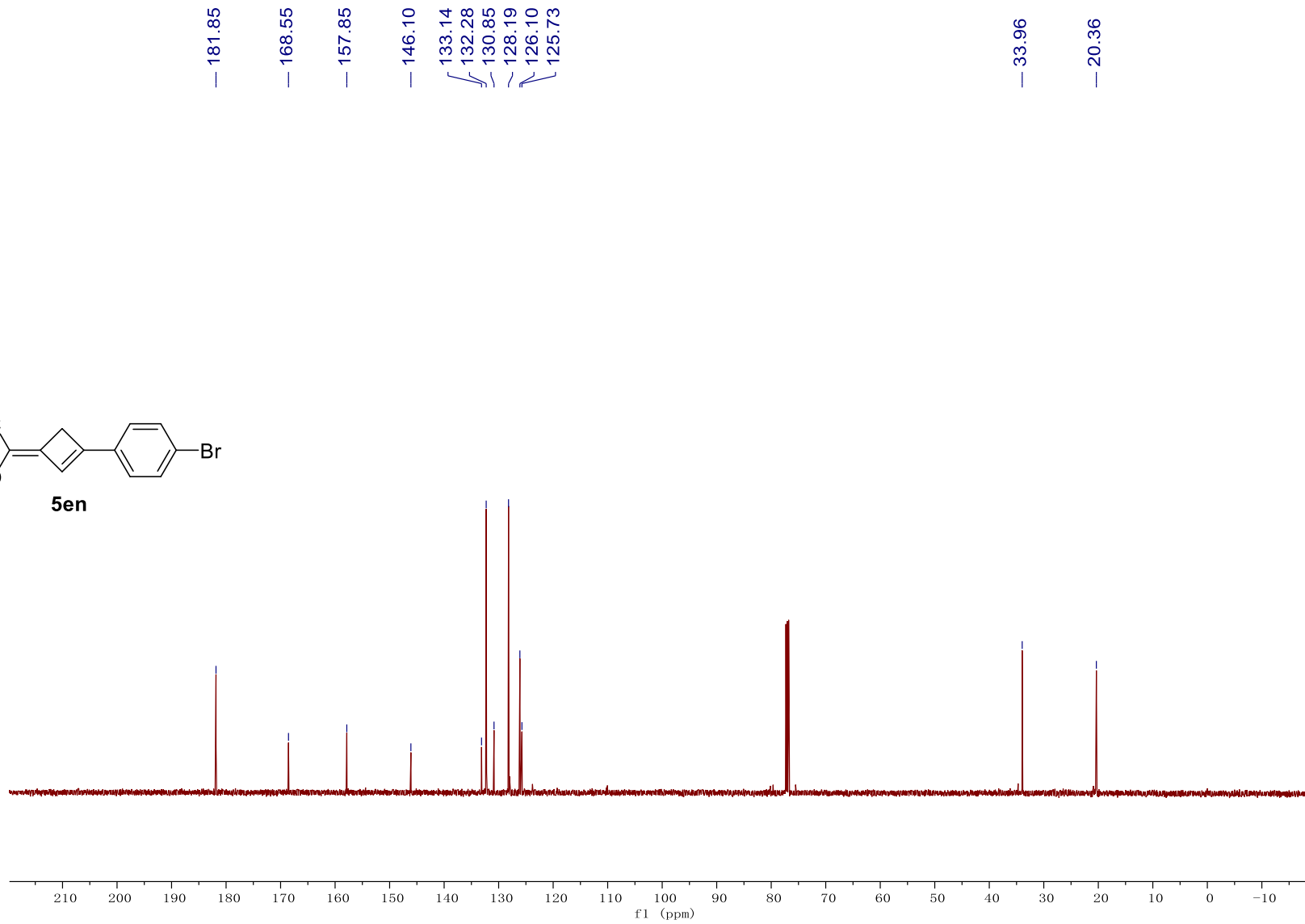
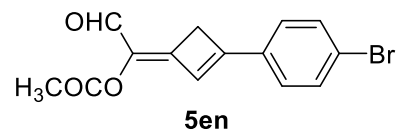


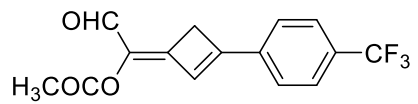




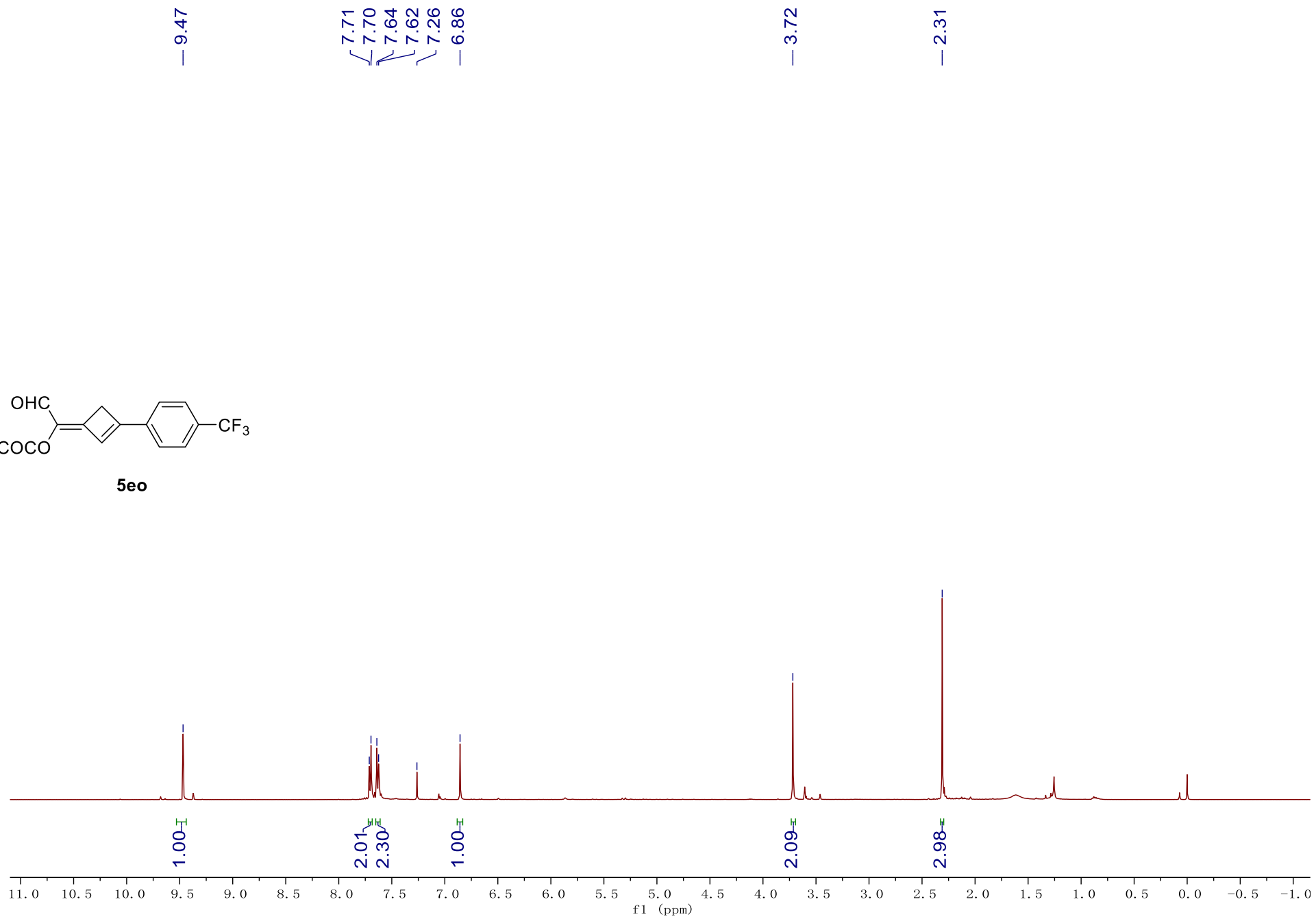


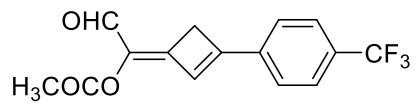




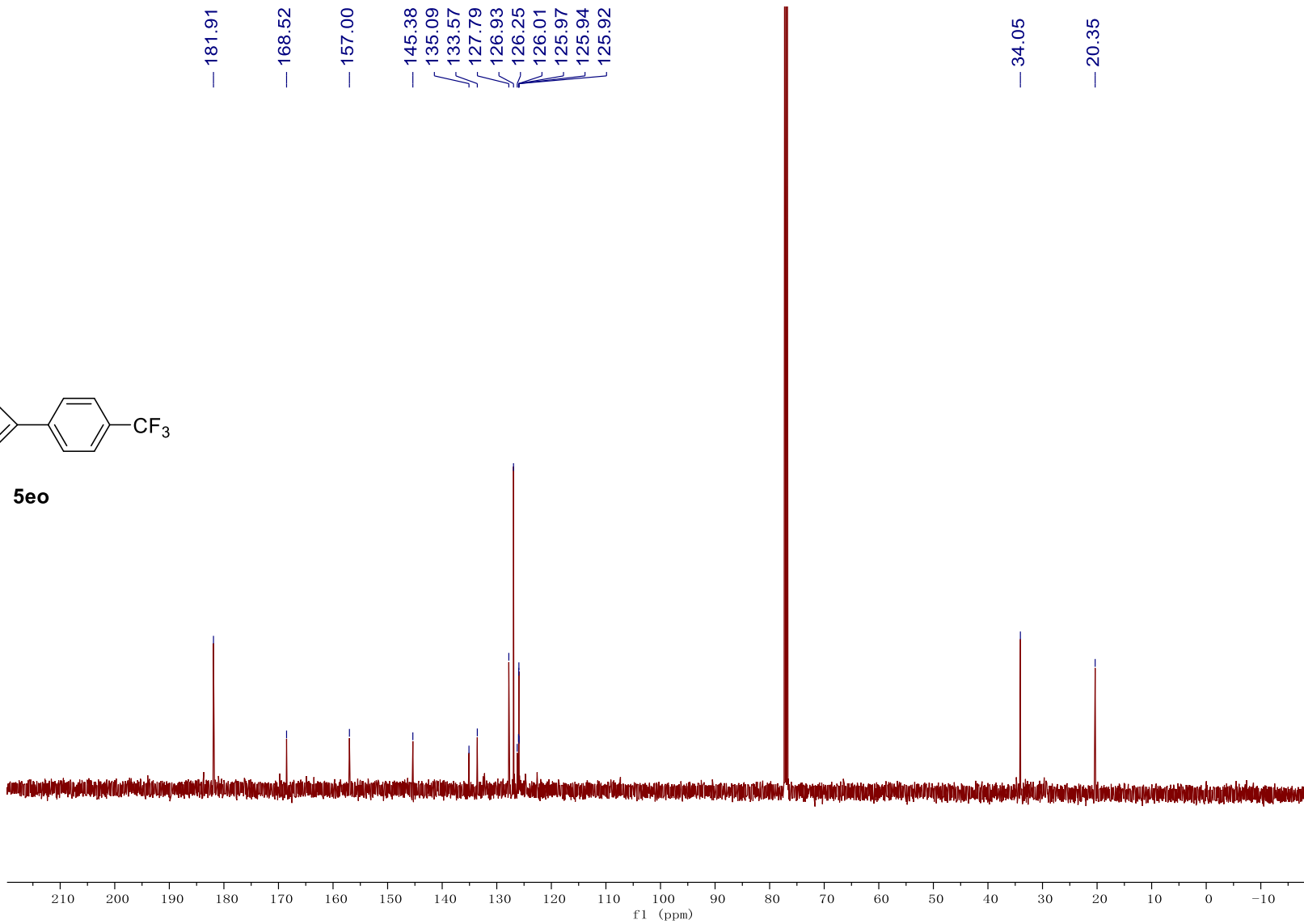


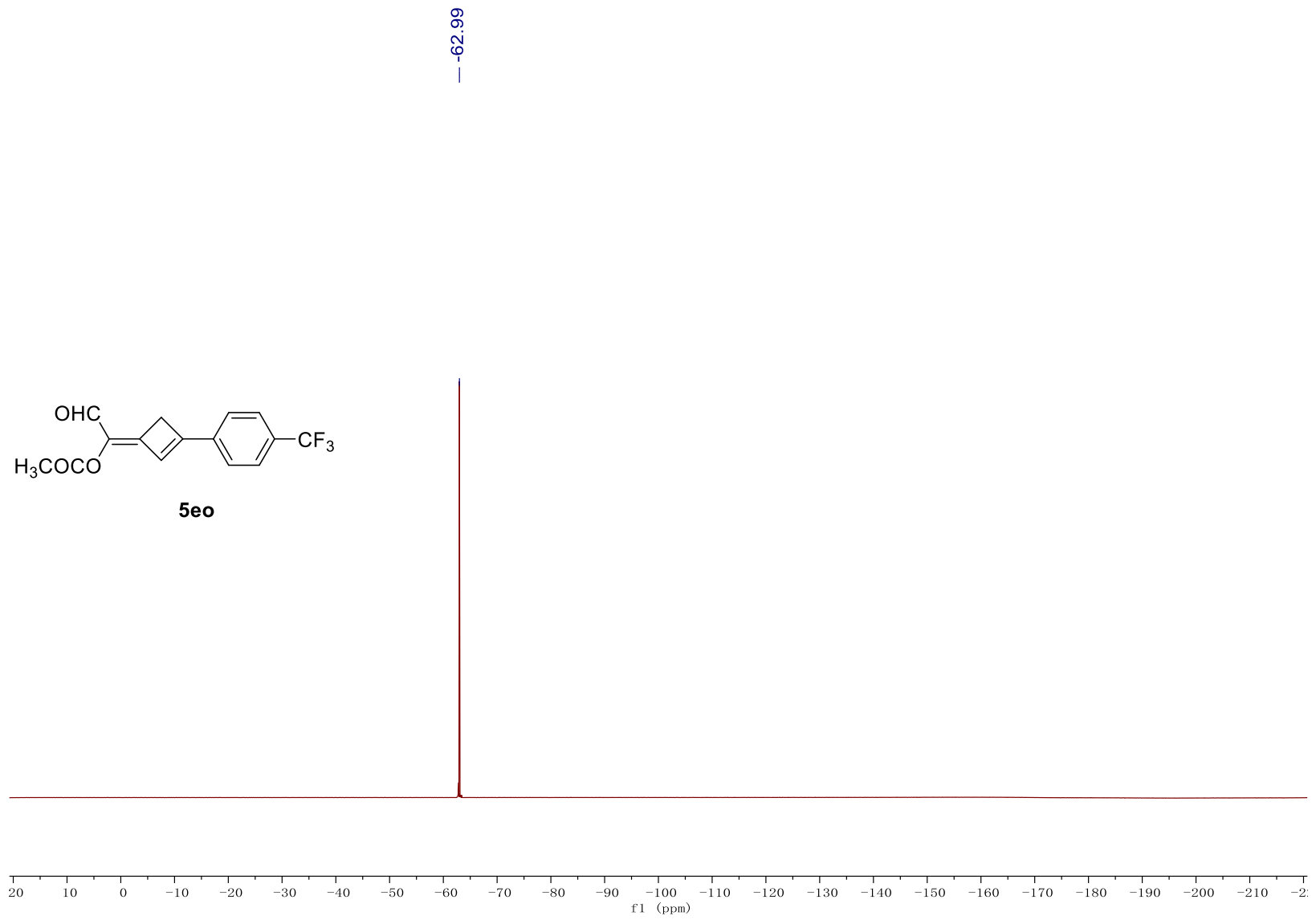
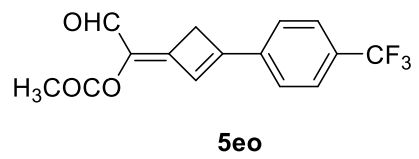
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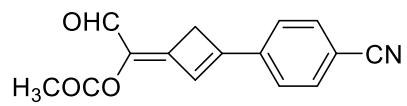




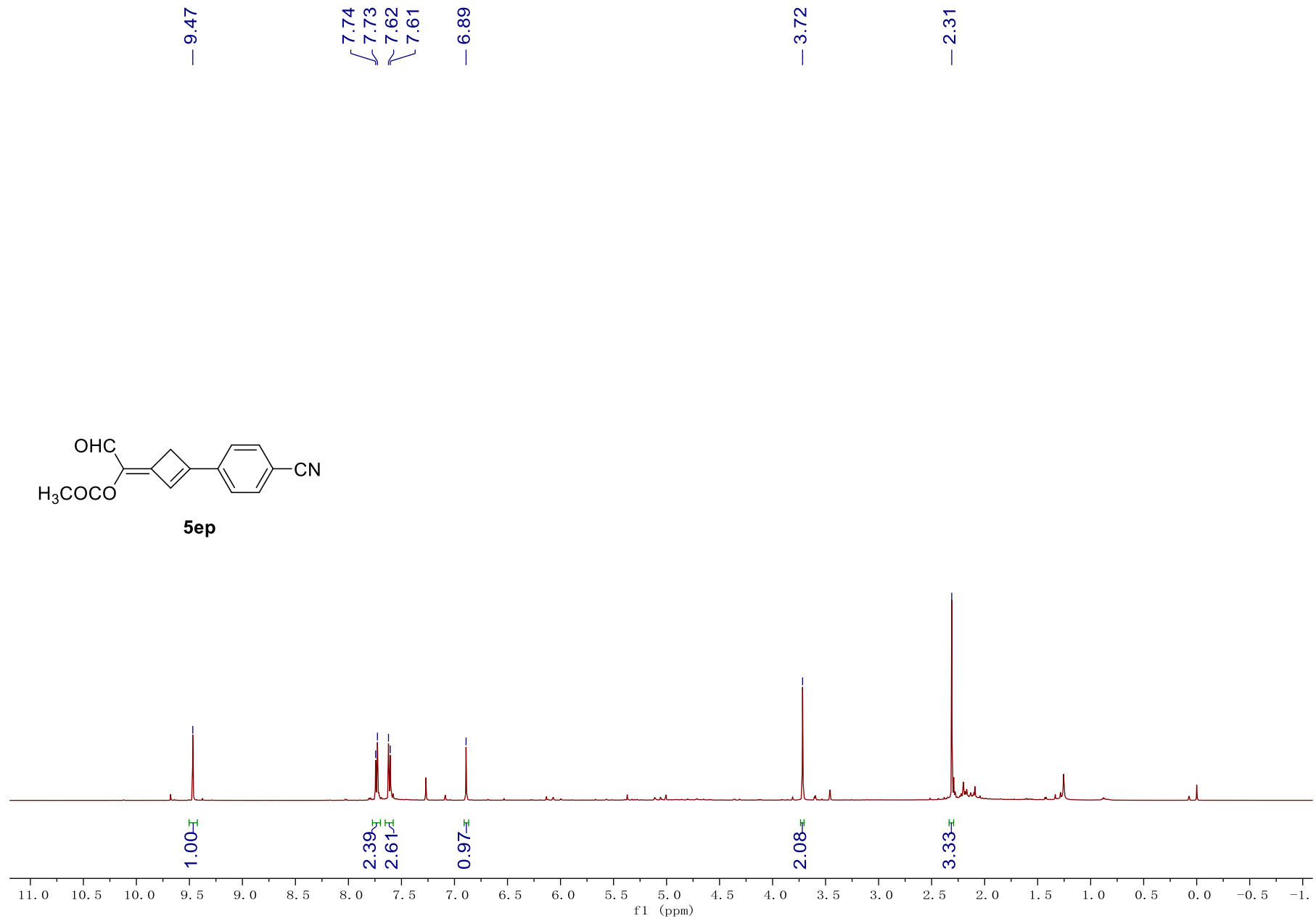
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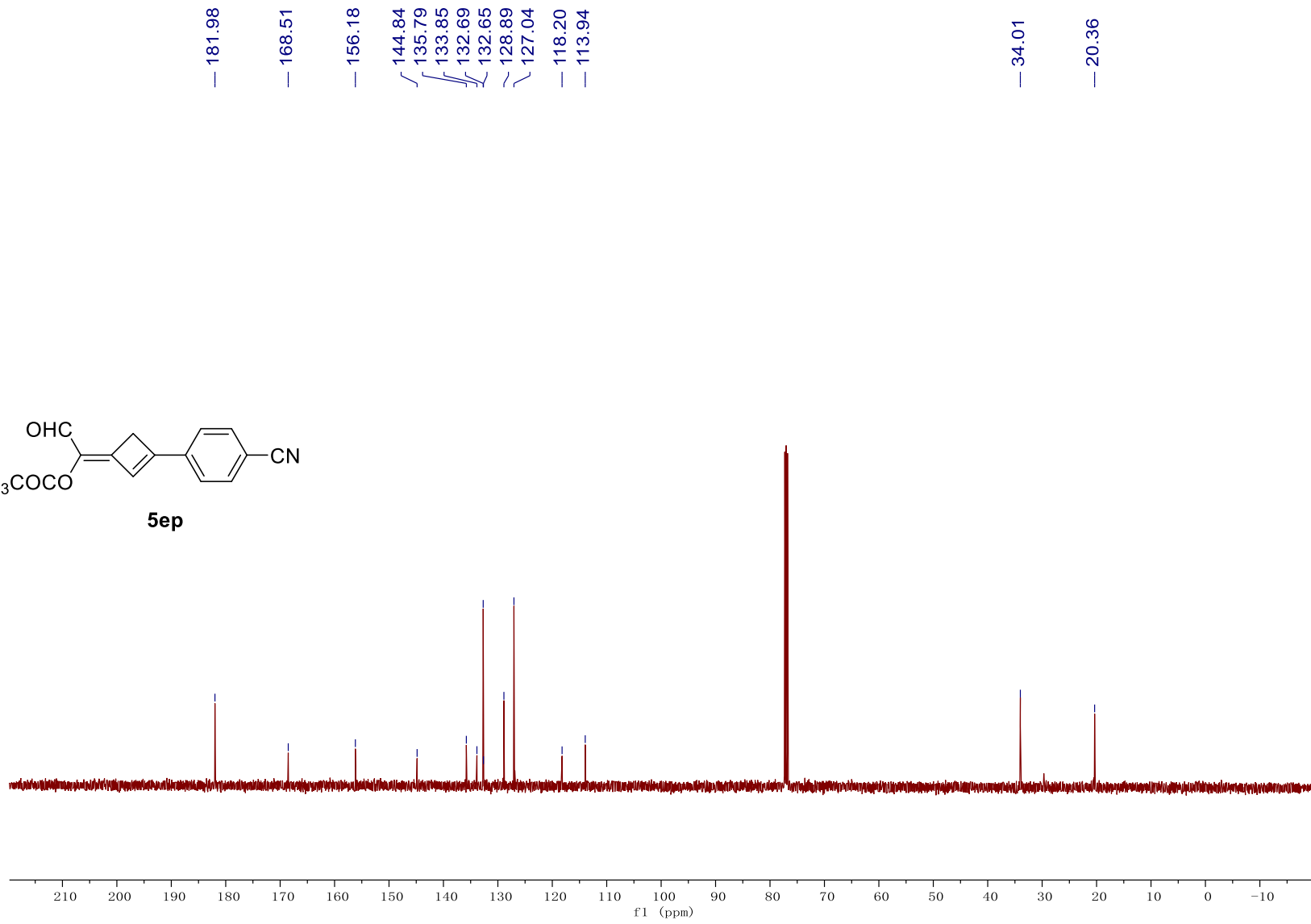
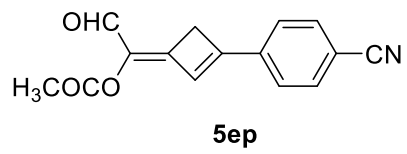




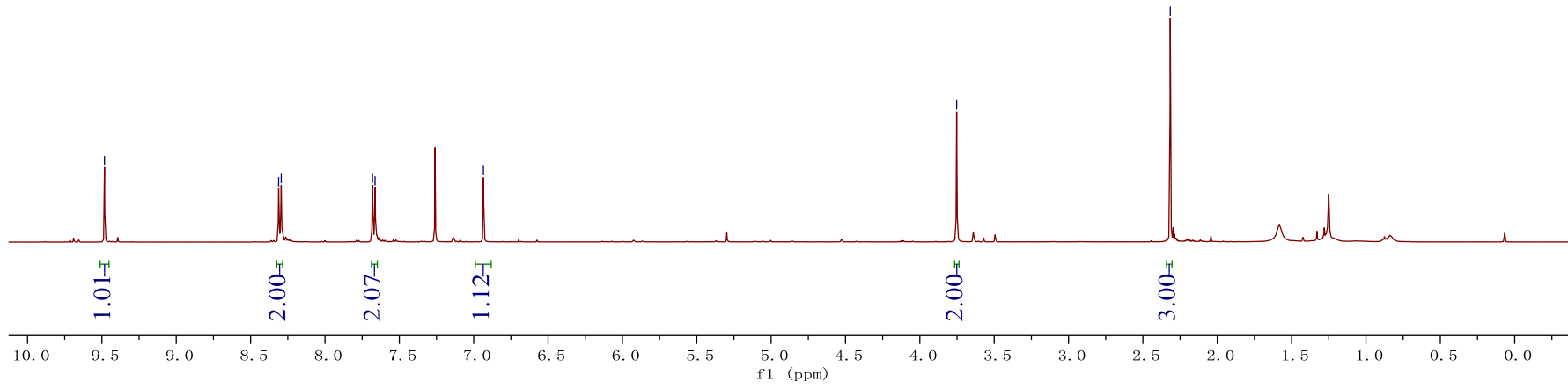
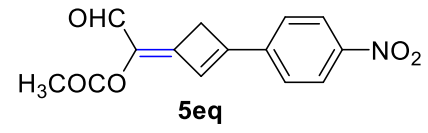
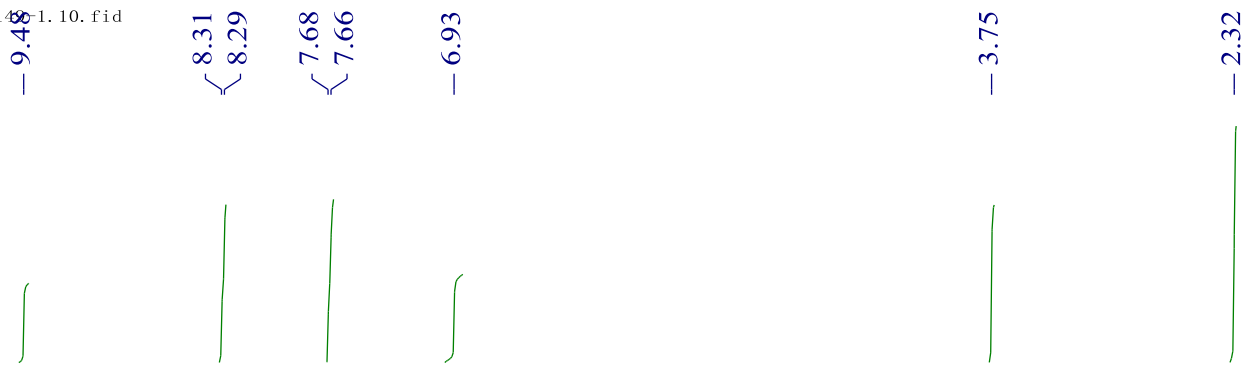


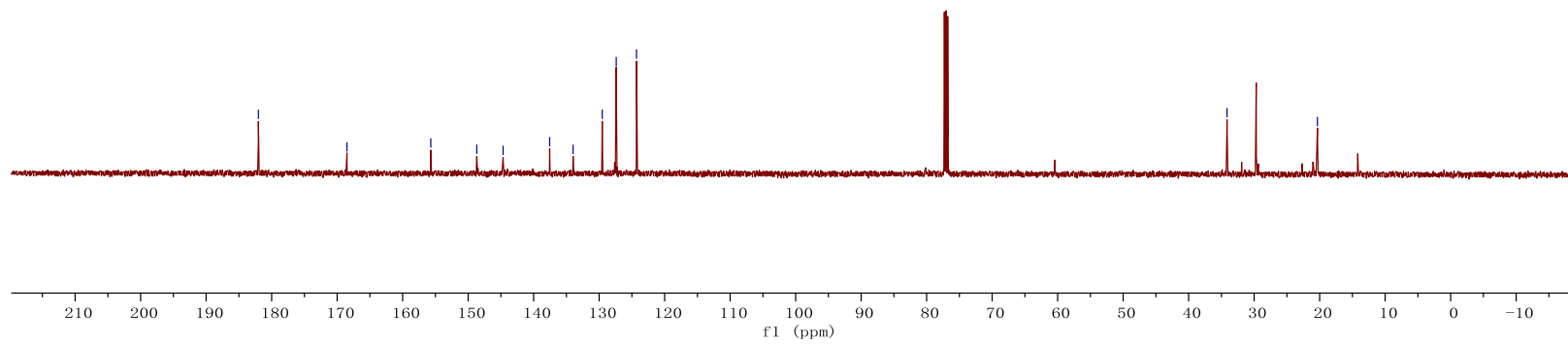
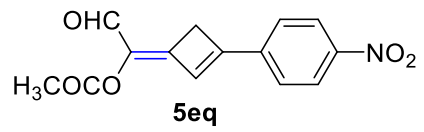
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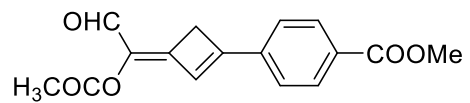




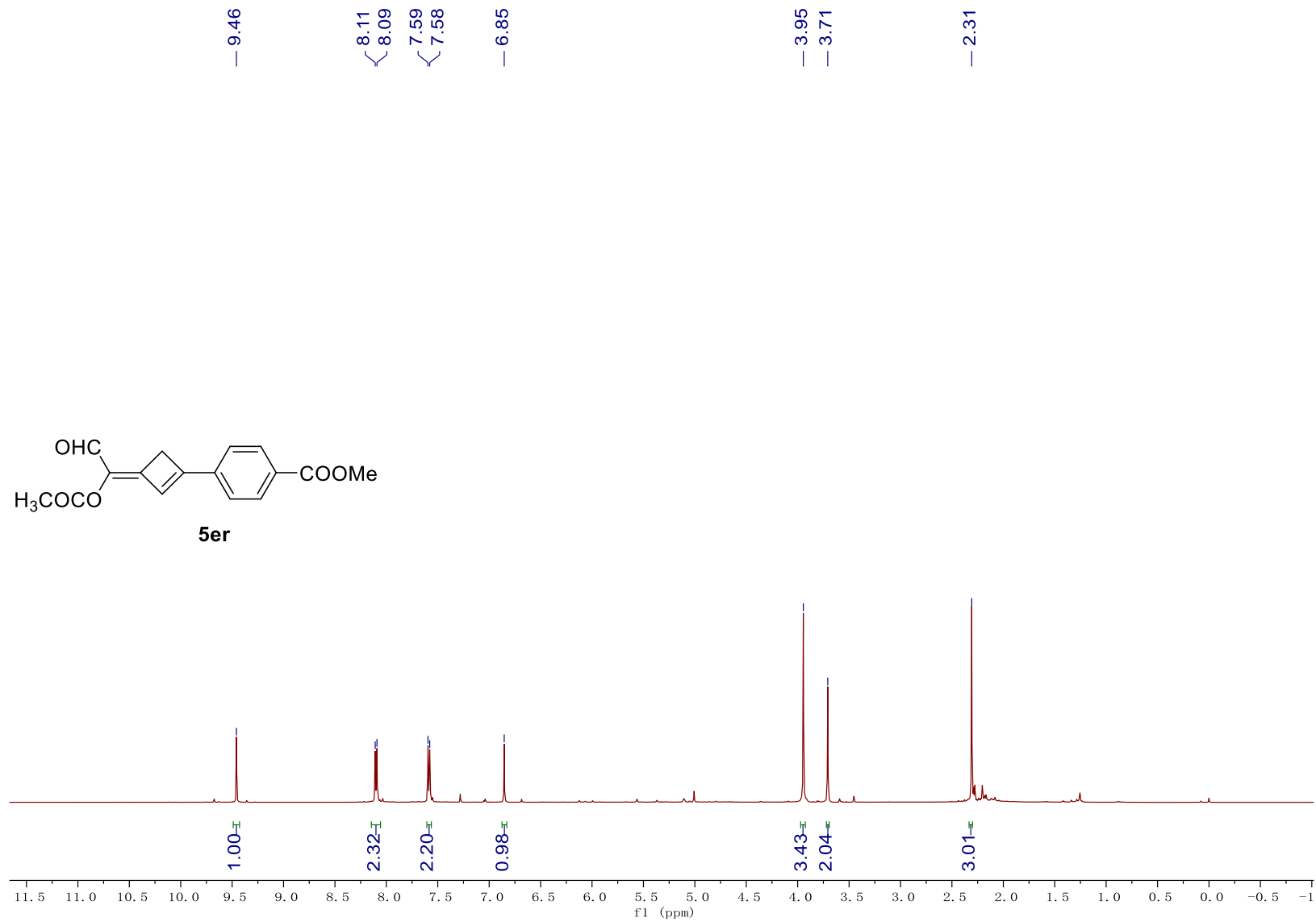
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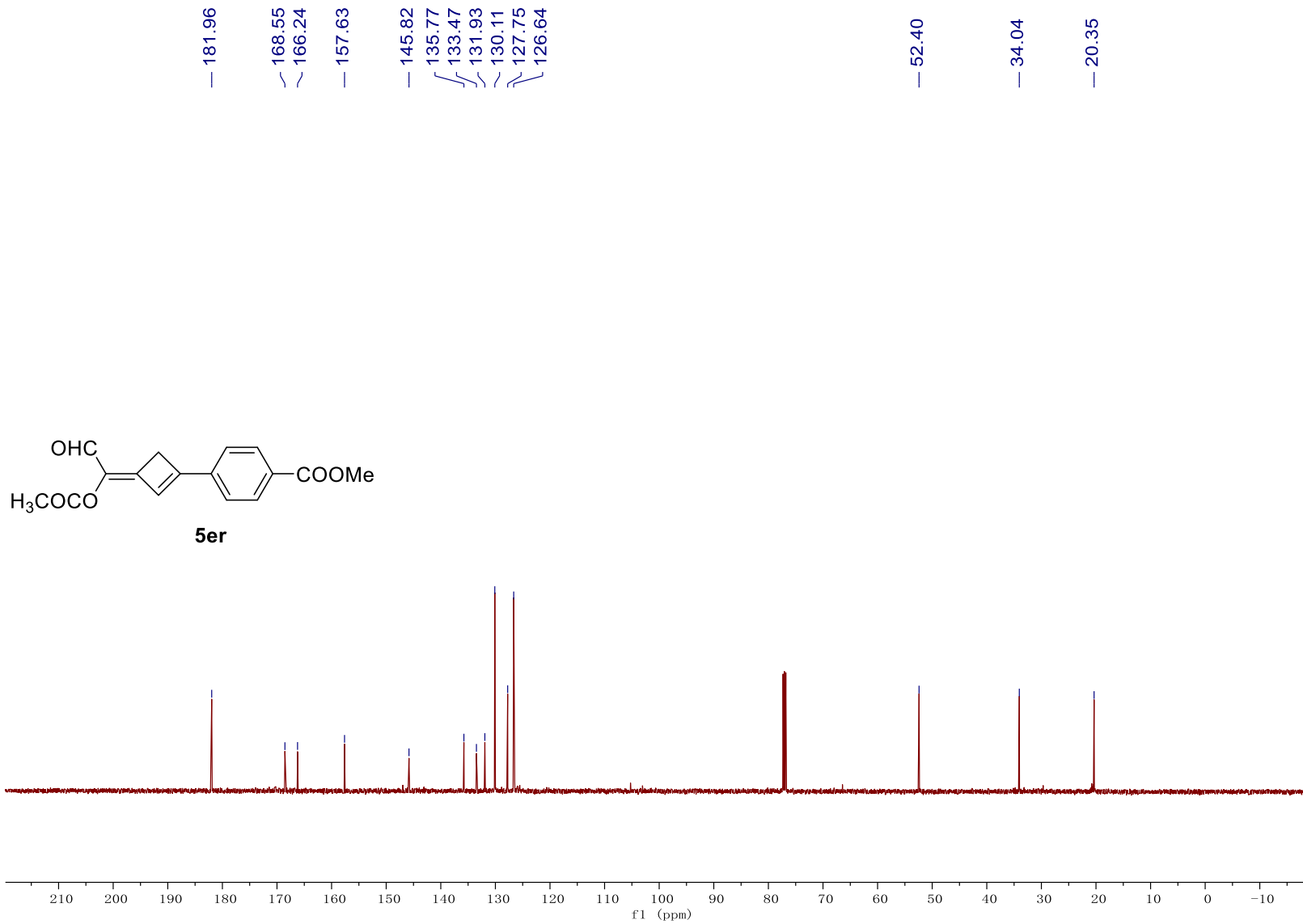


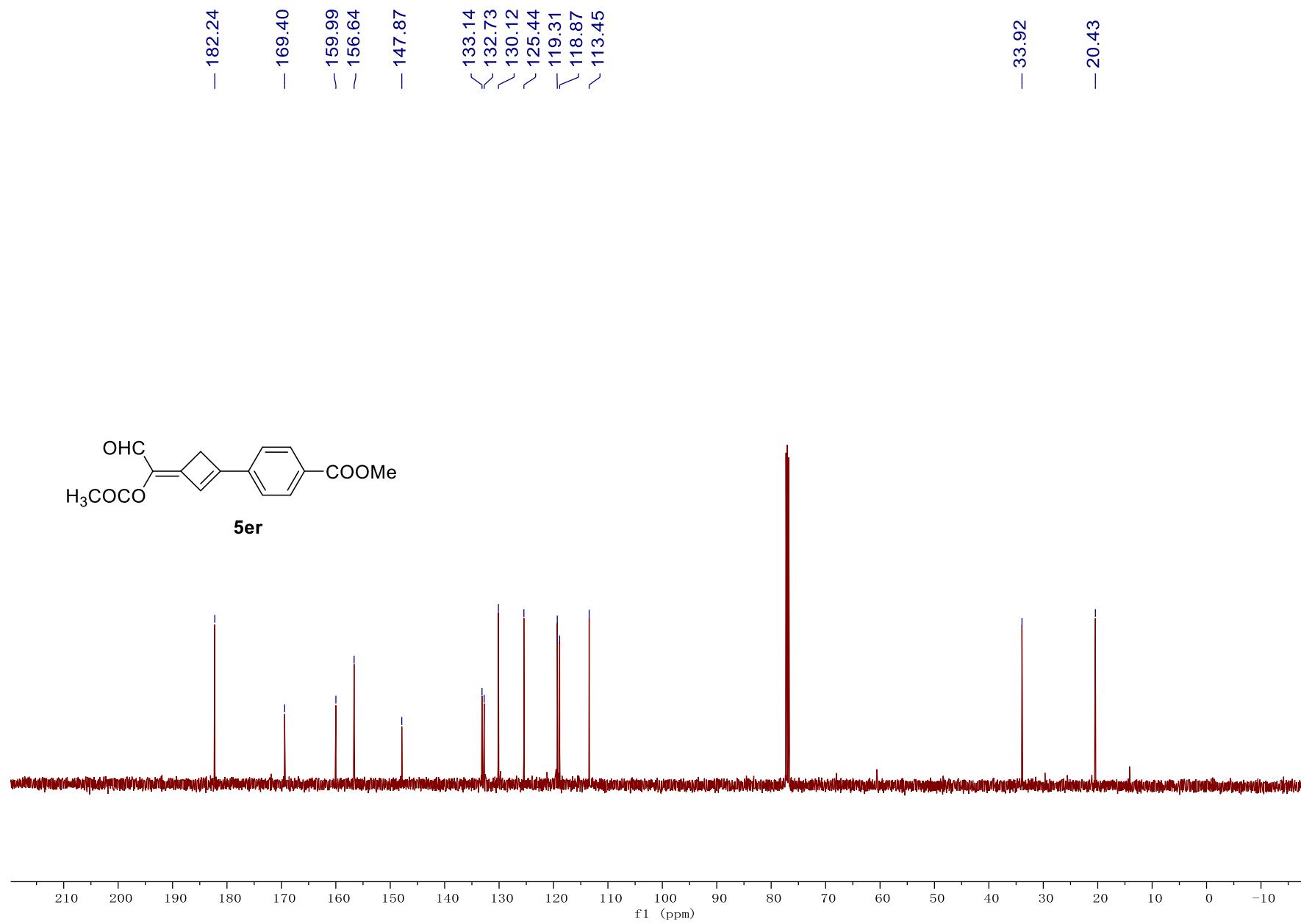


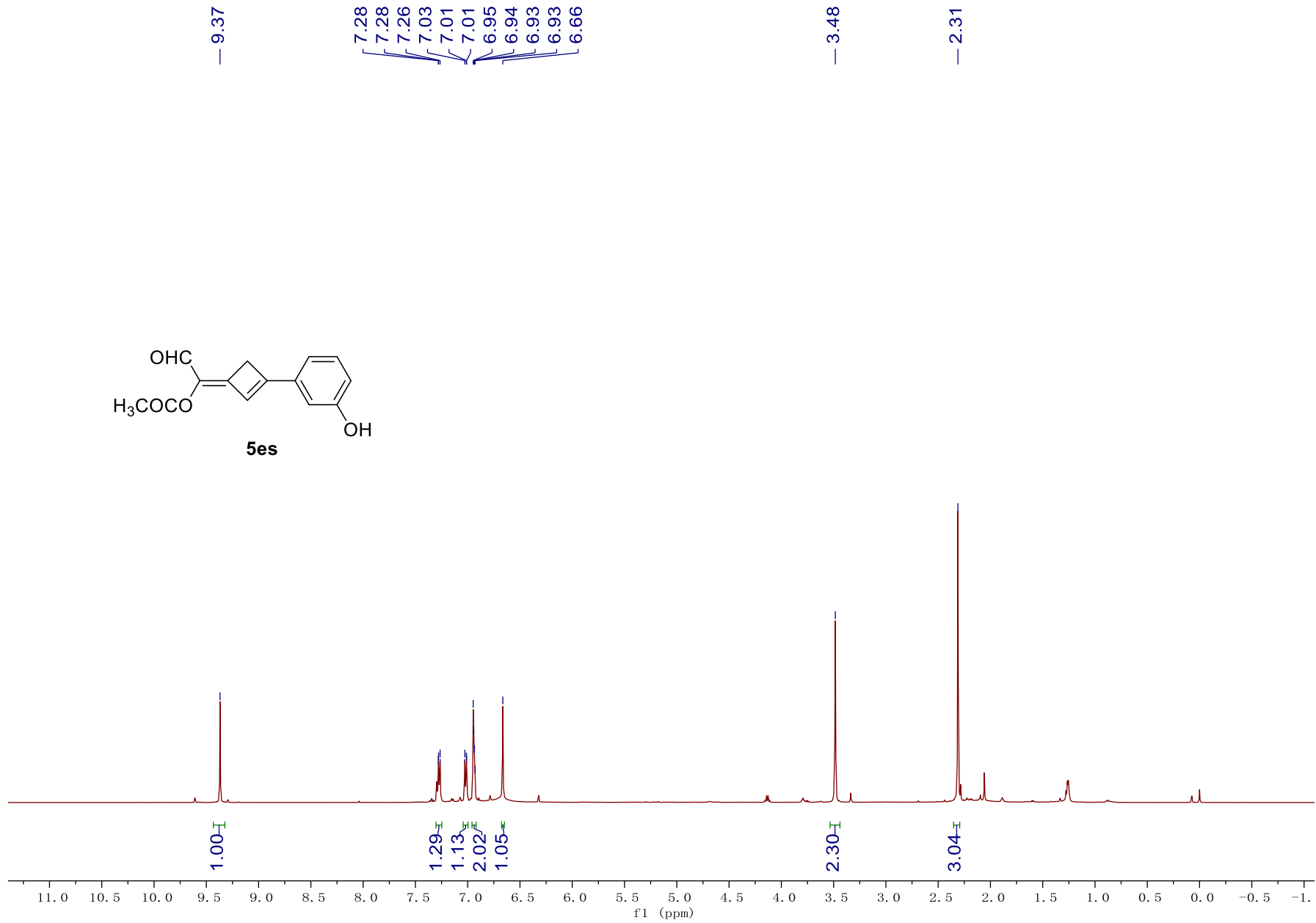
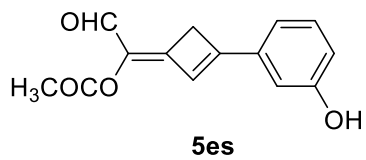


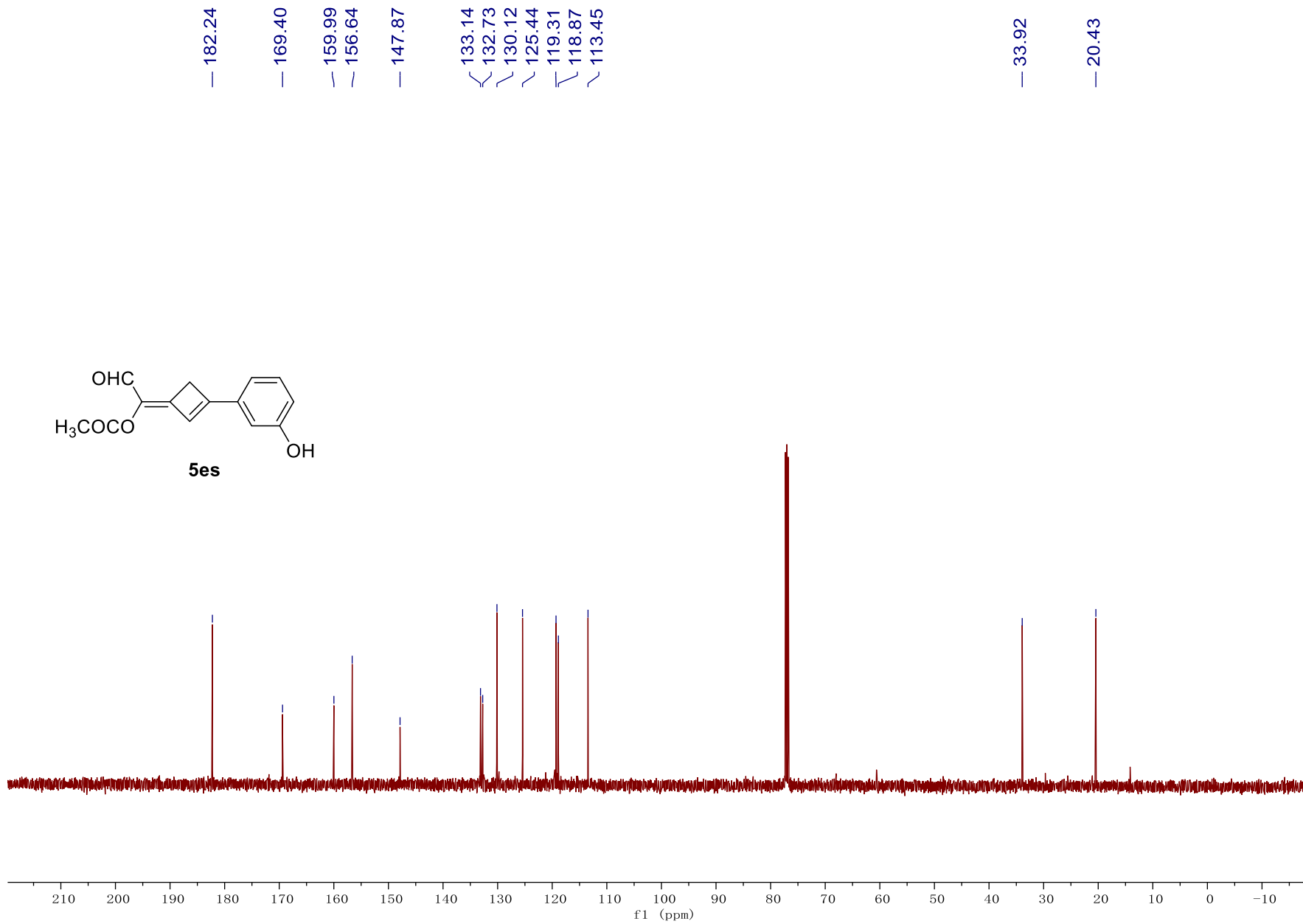
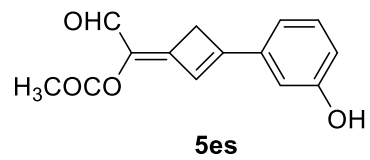
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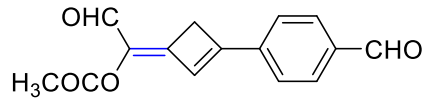
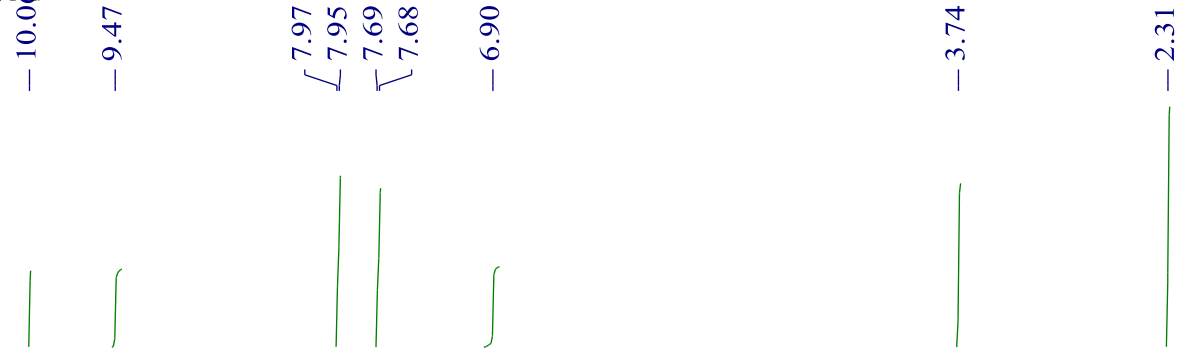




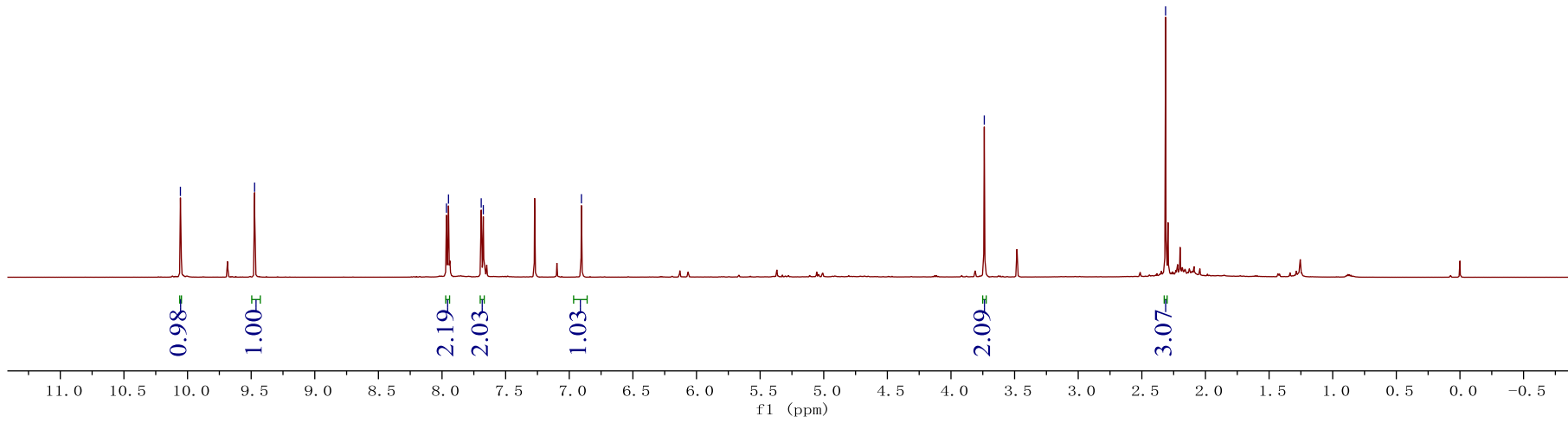




xzr-ii-174-6. 20. f1



5et



xzr-ii-174-6.21.fi

— 191.25

— 181.98

— 168.53

— 157.11

145.40

137.45

137.10

133.68

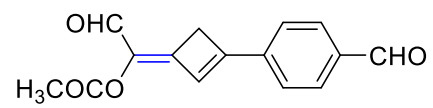
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128.57

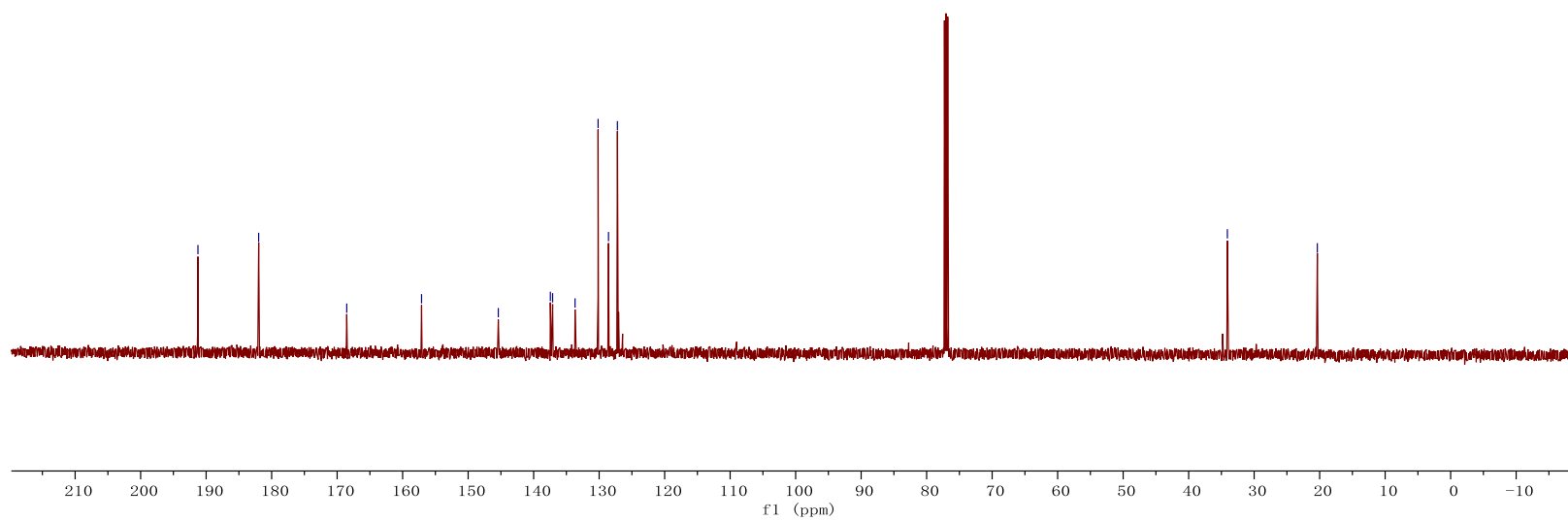
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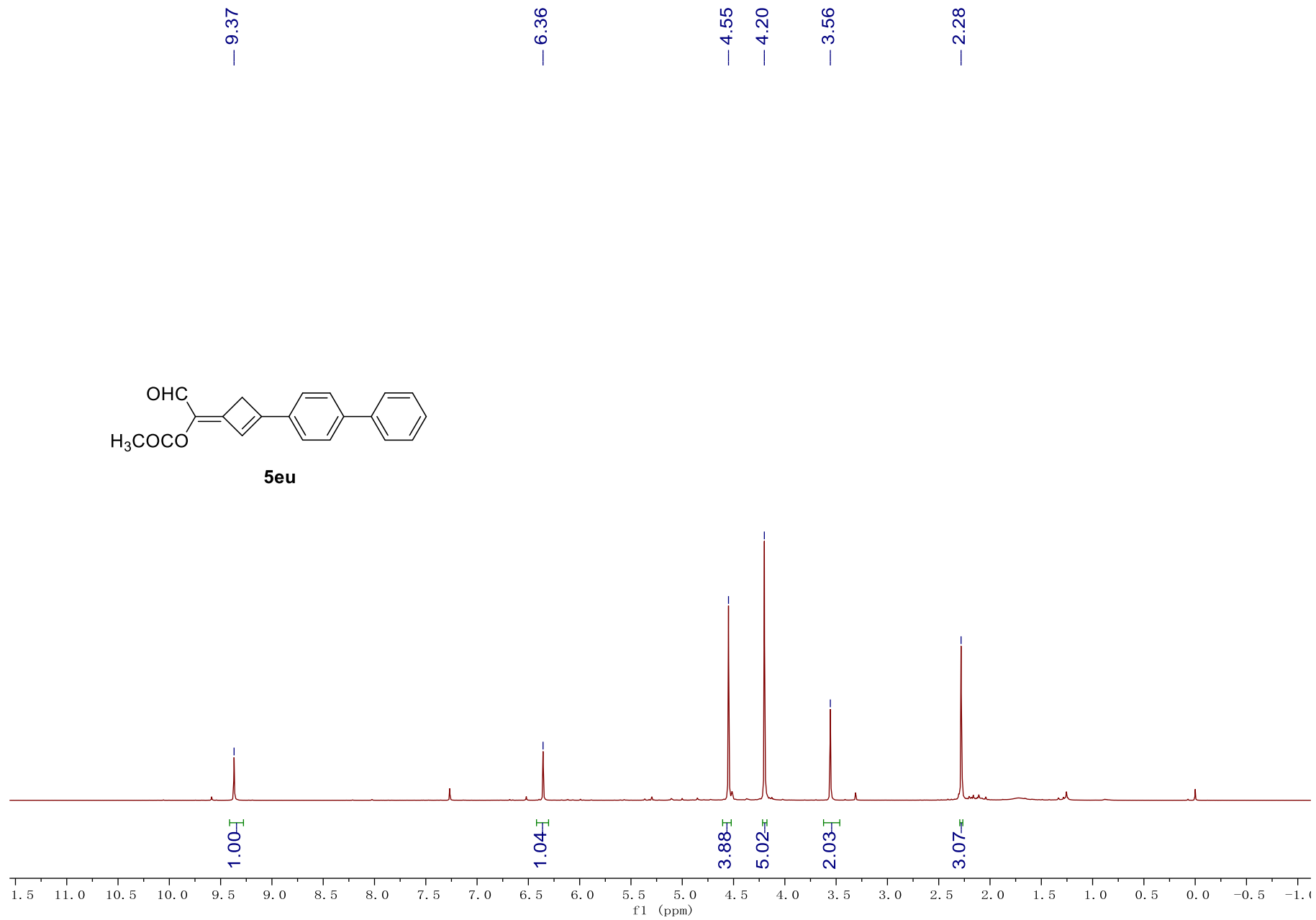
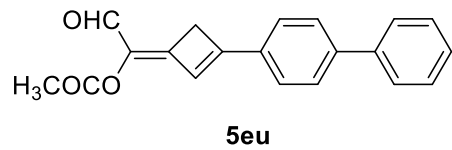
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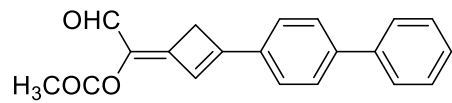
— 20.36



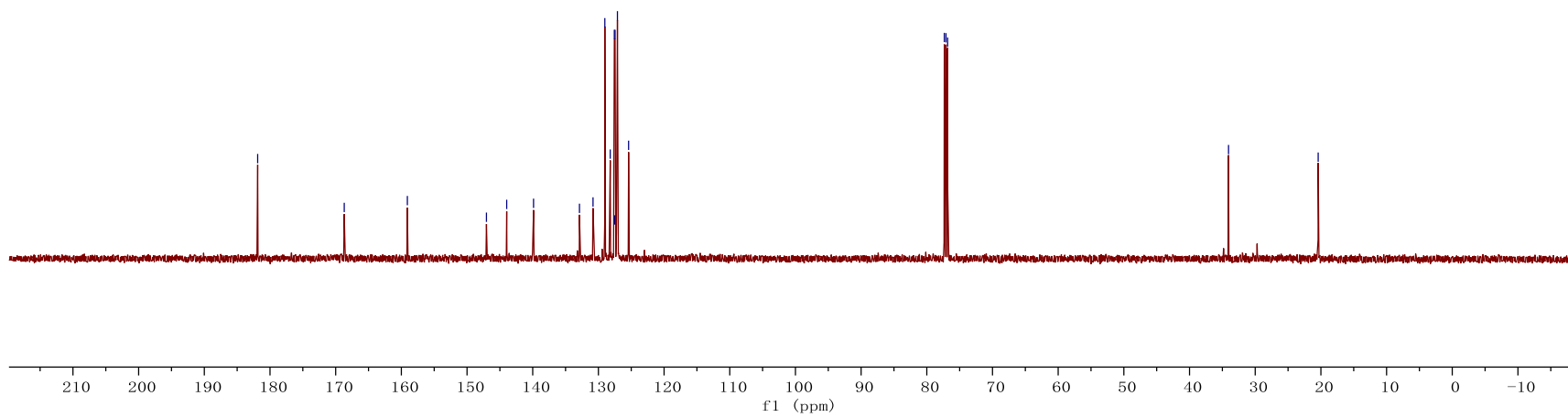
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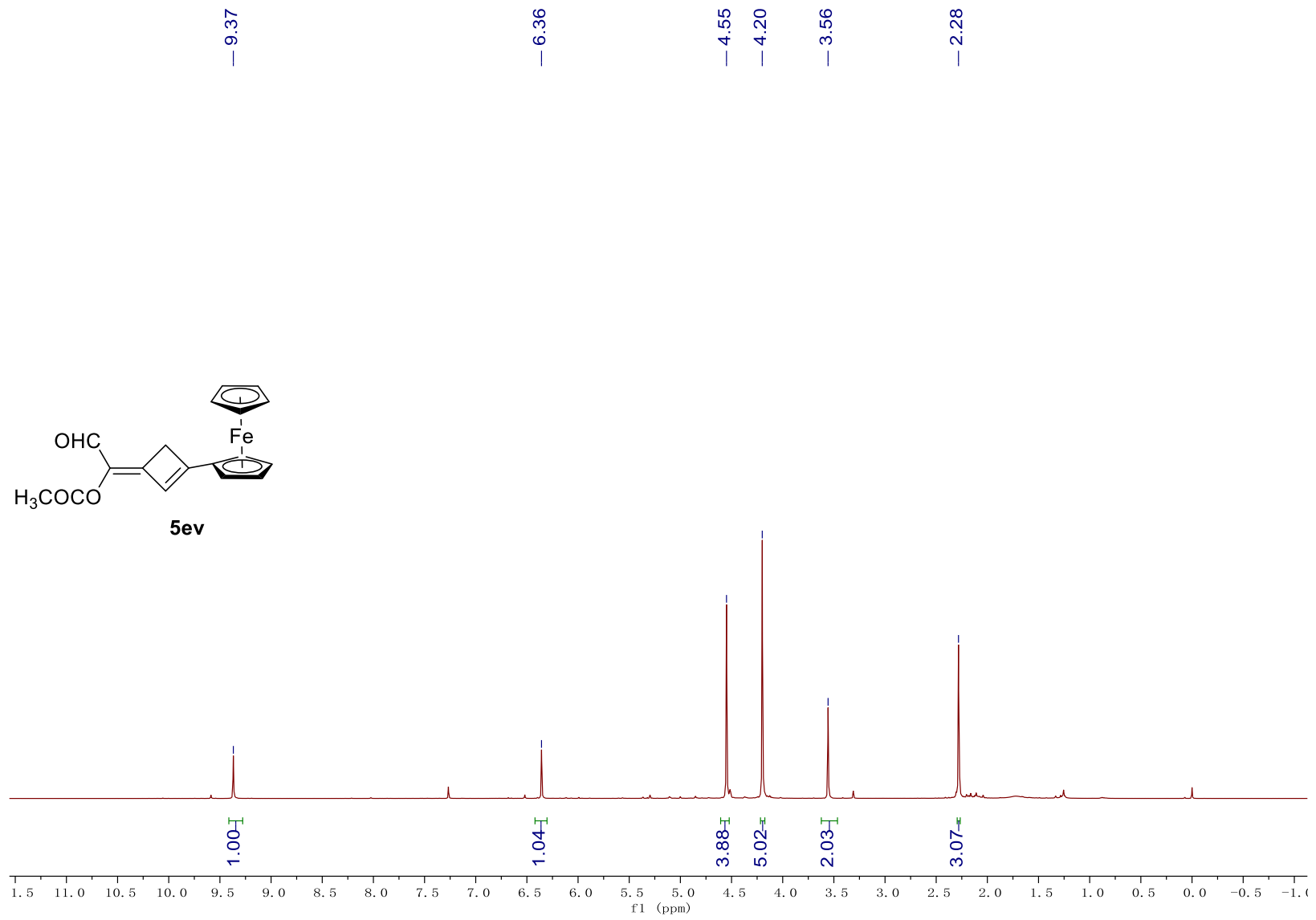
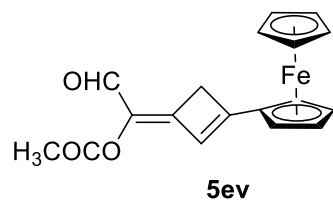


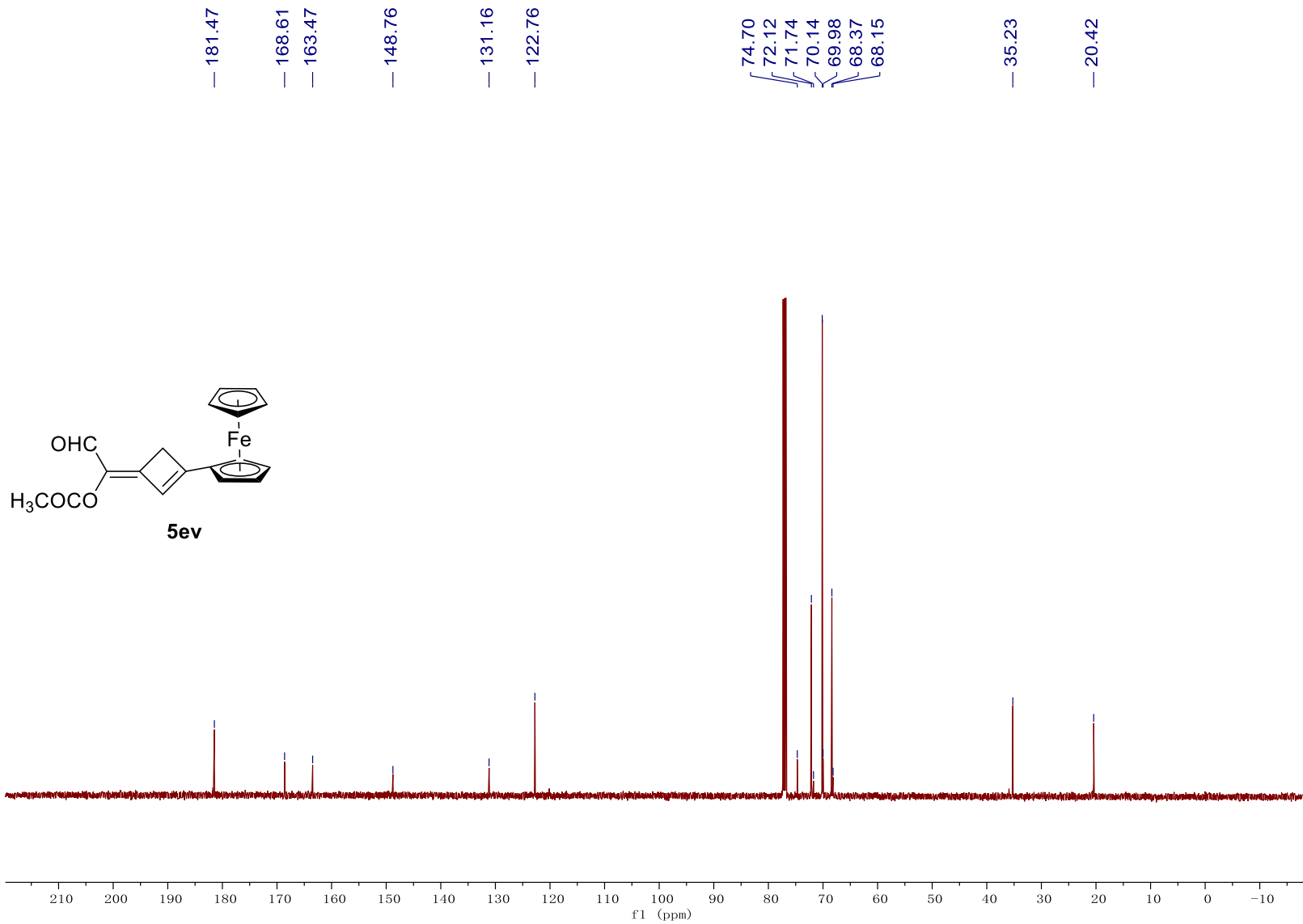


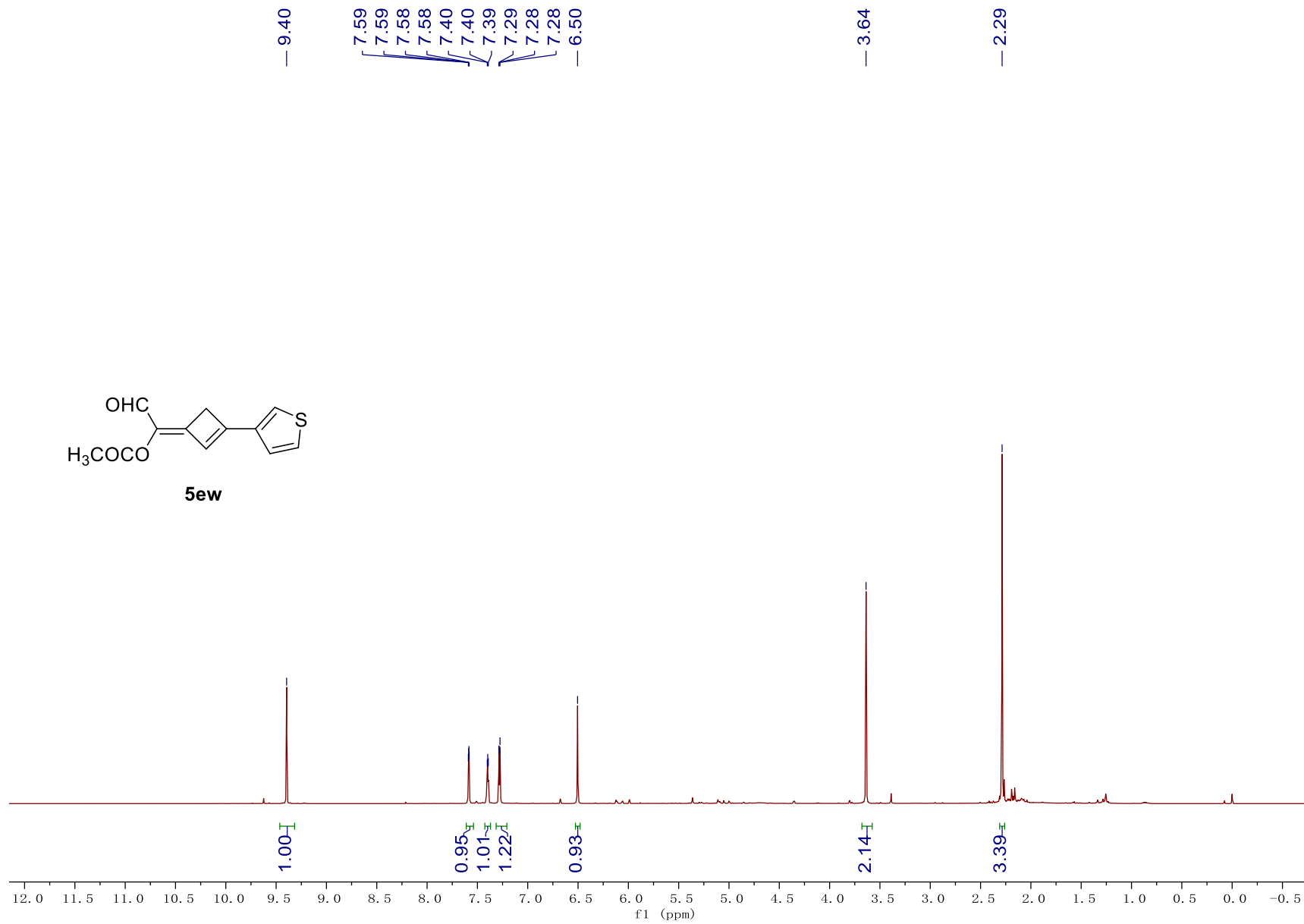
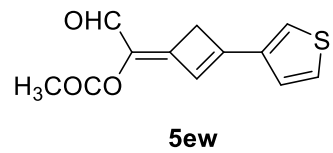


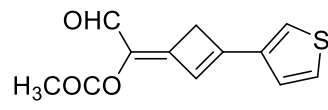
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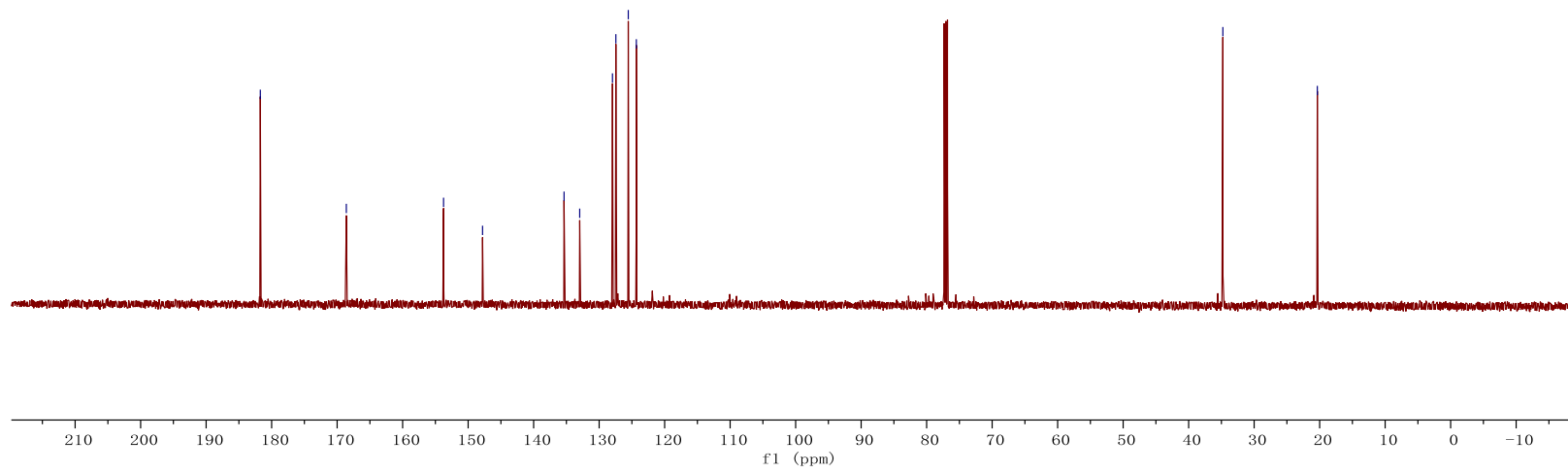


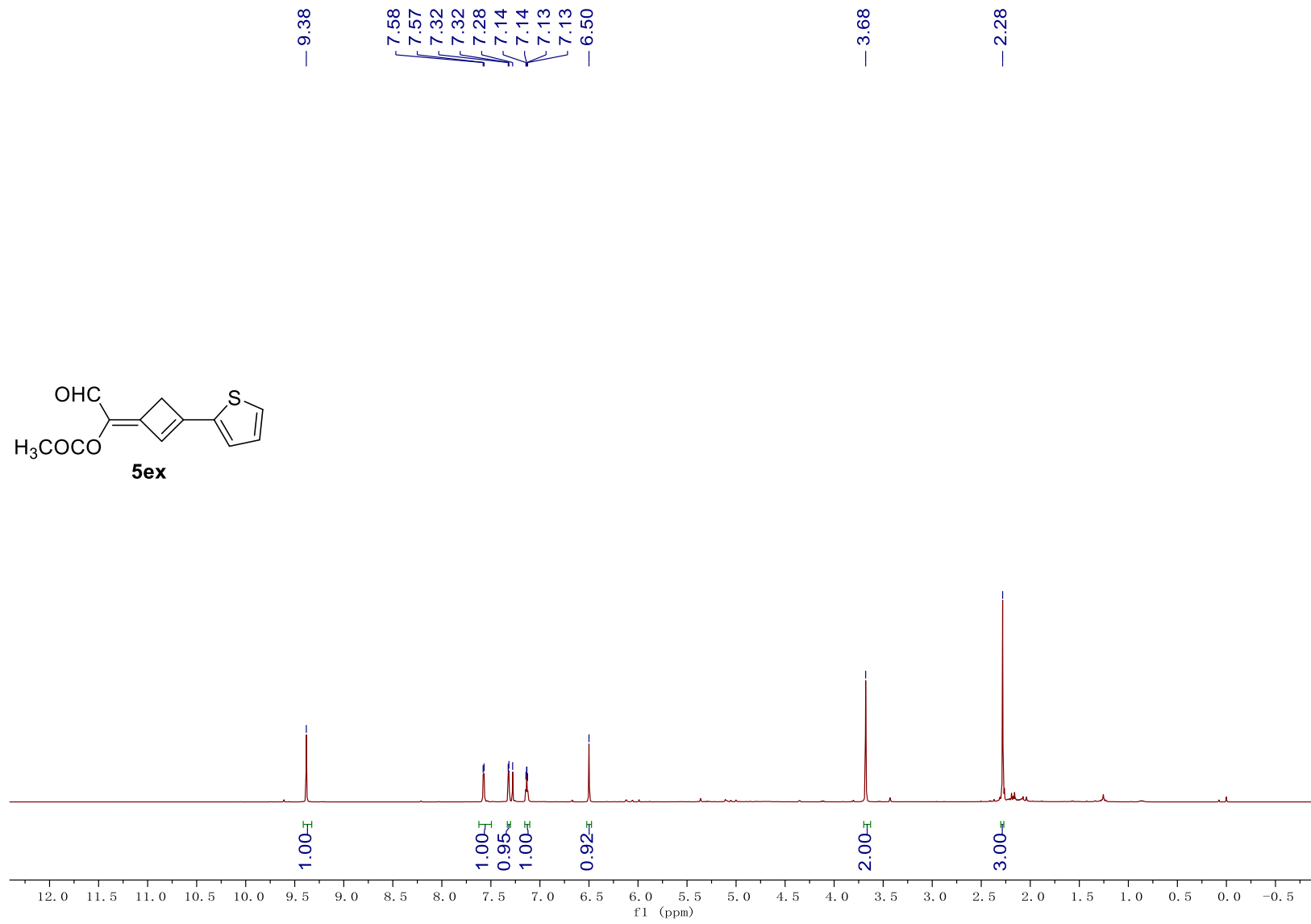
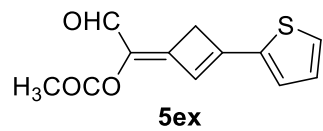


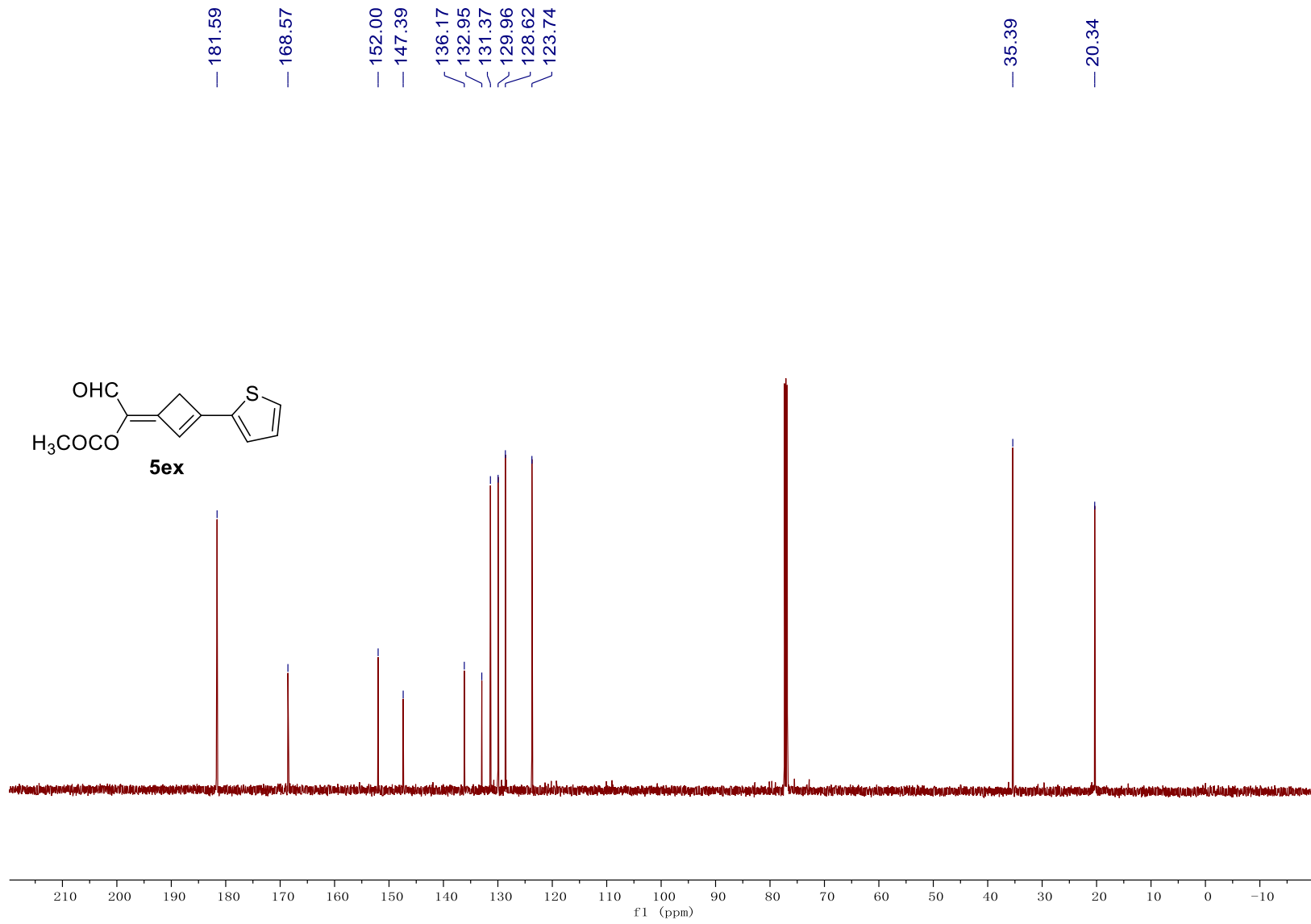


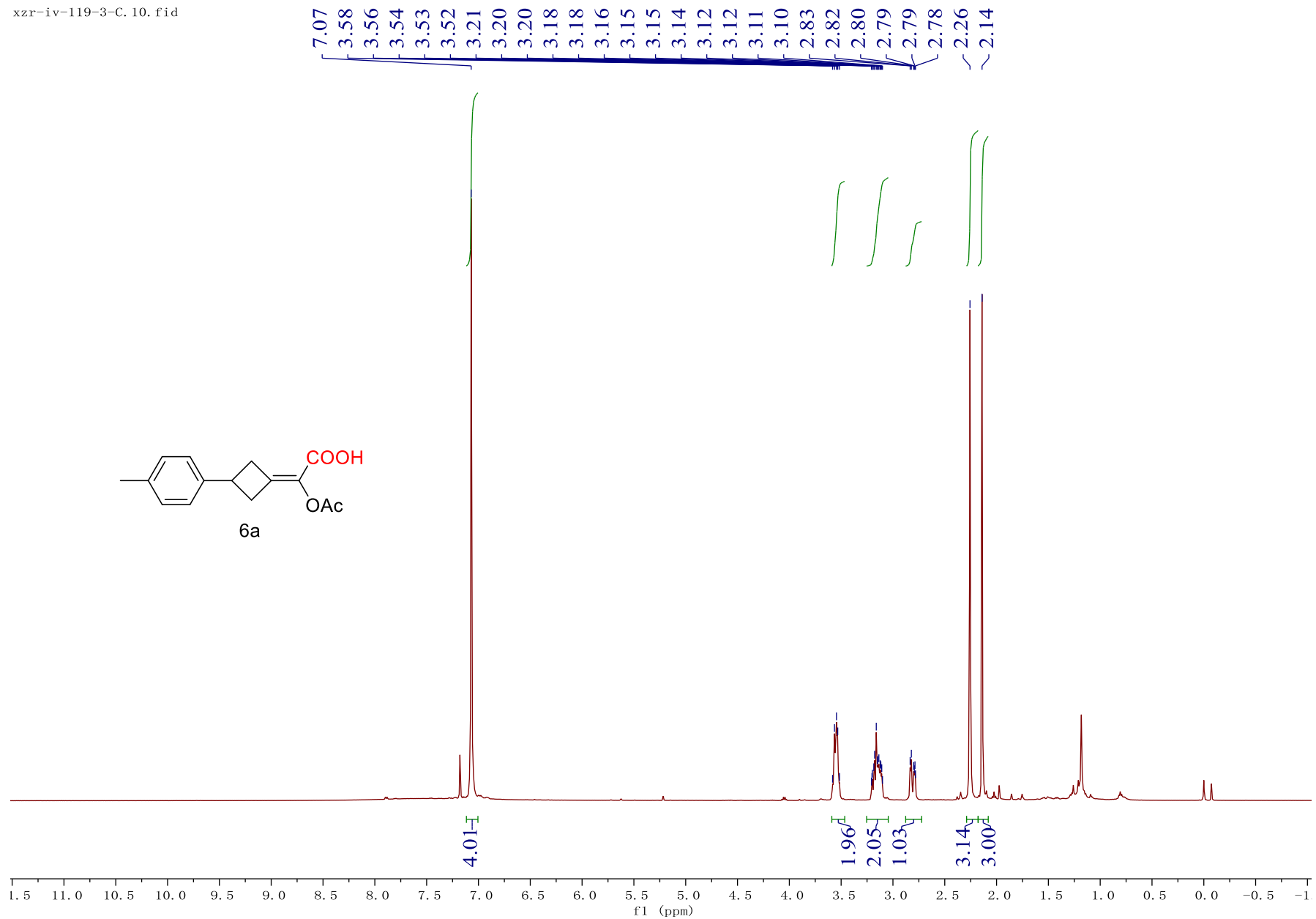
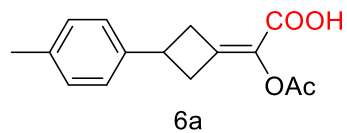


5ew









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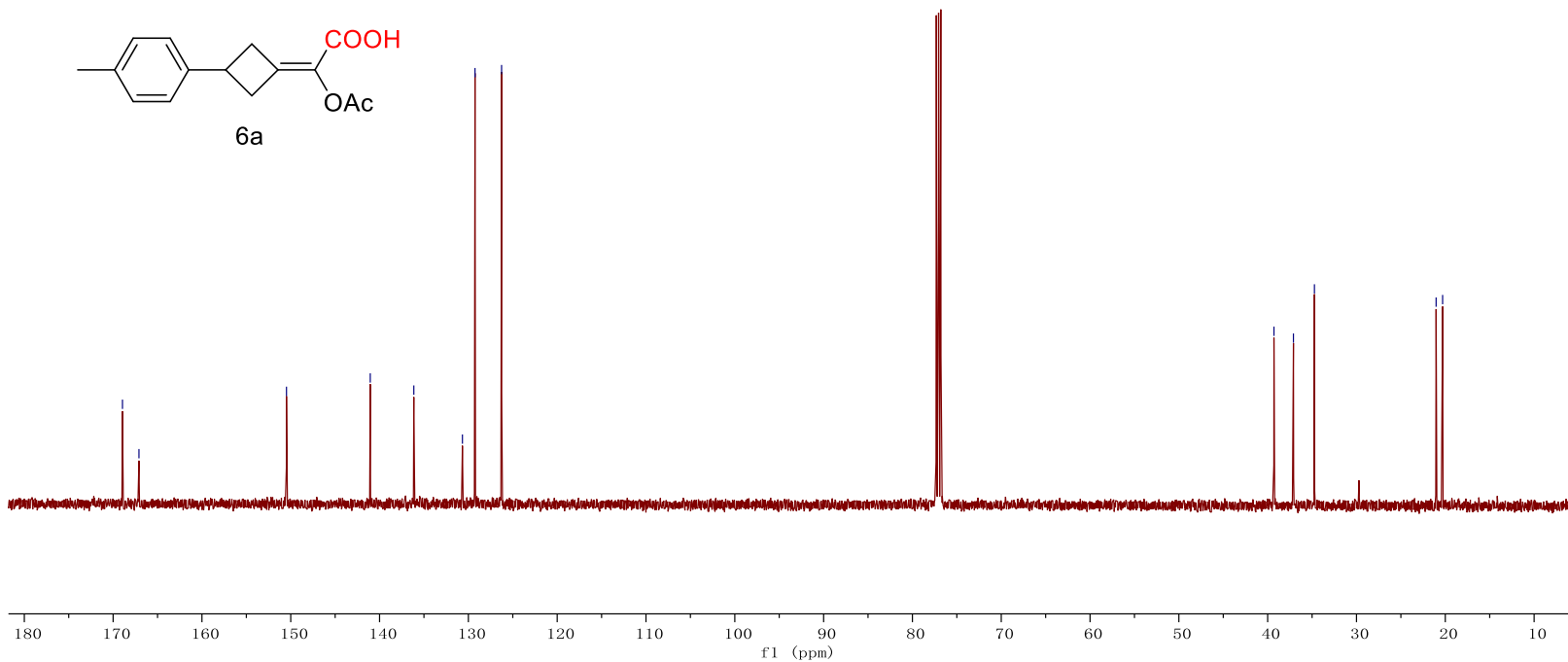
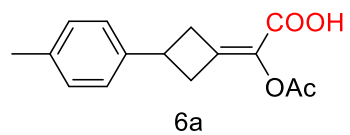
~ 168.93
~ 167.09

— 150.48

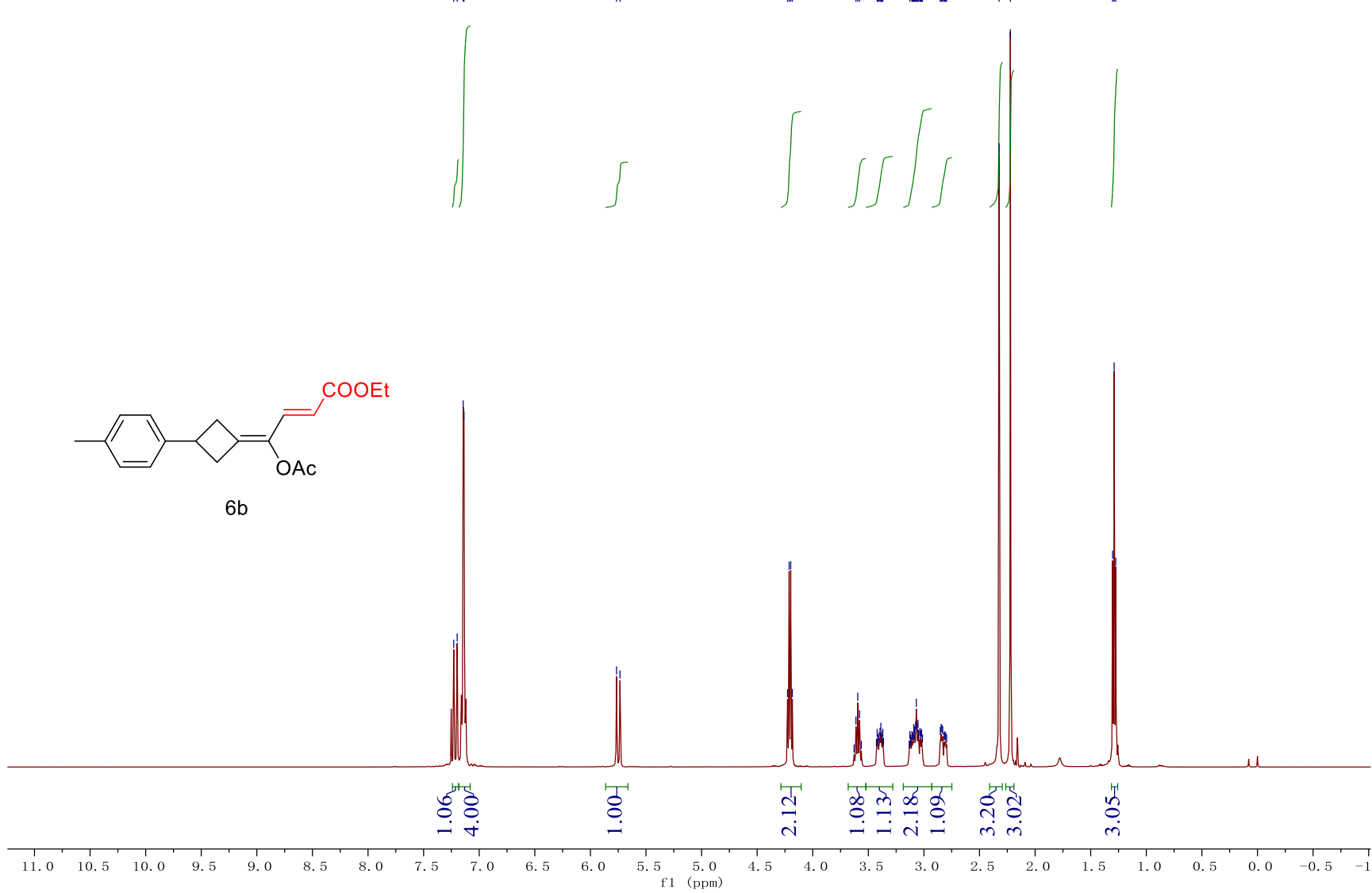
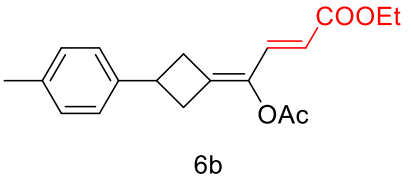
~ 141.05
~ 136.14
/ 130.67
/ 129.25
~ 126.26

~ 39.29
~ 37.10
~ 34.74

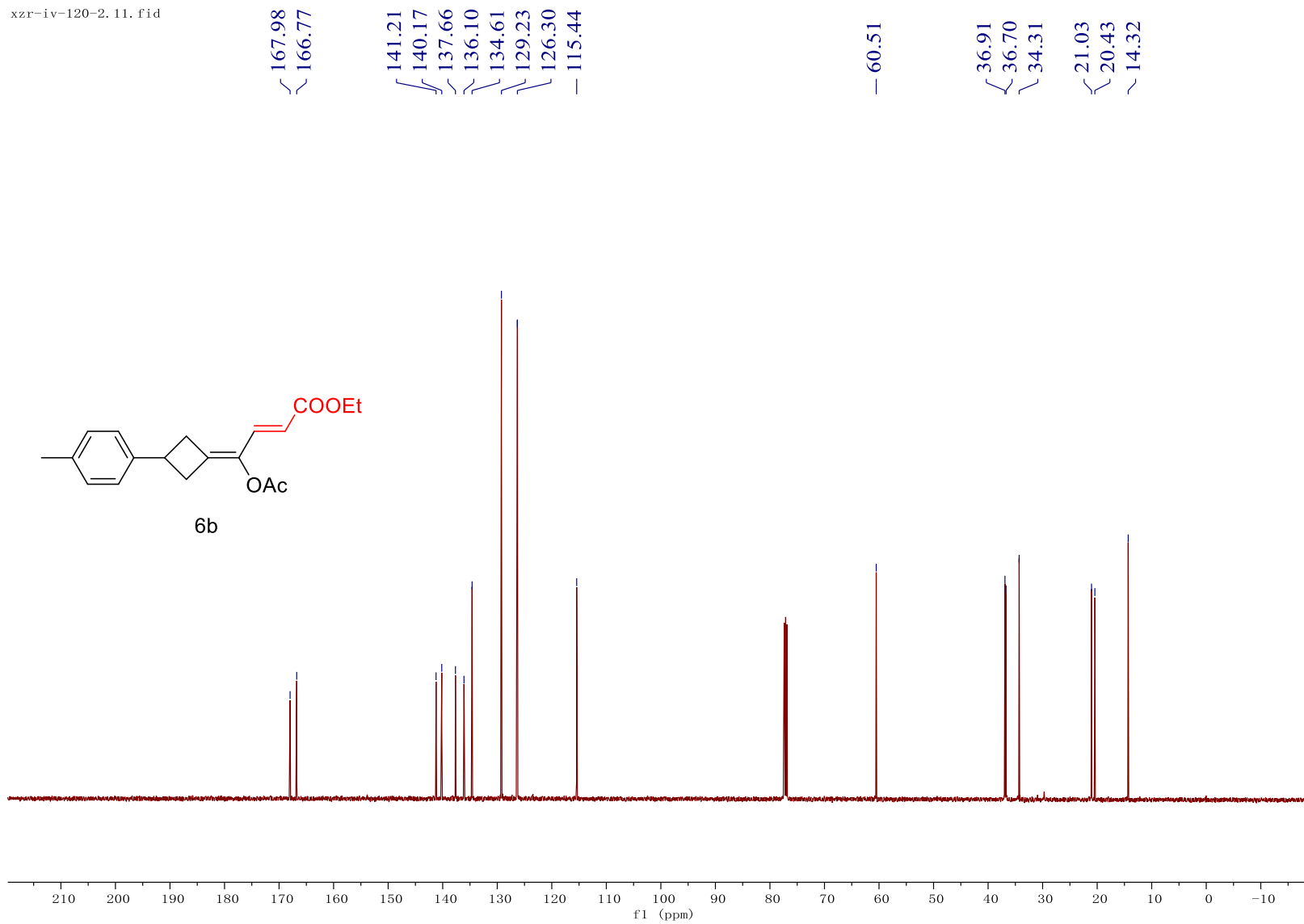
~ 21.03
~ 20.30

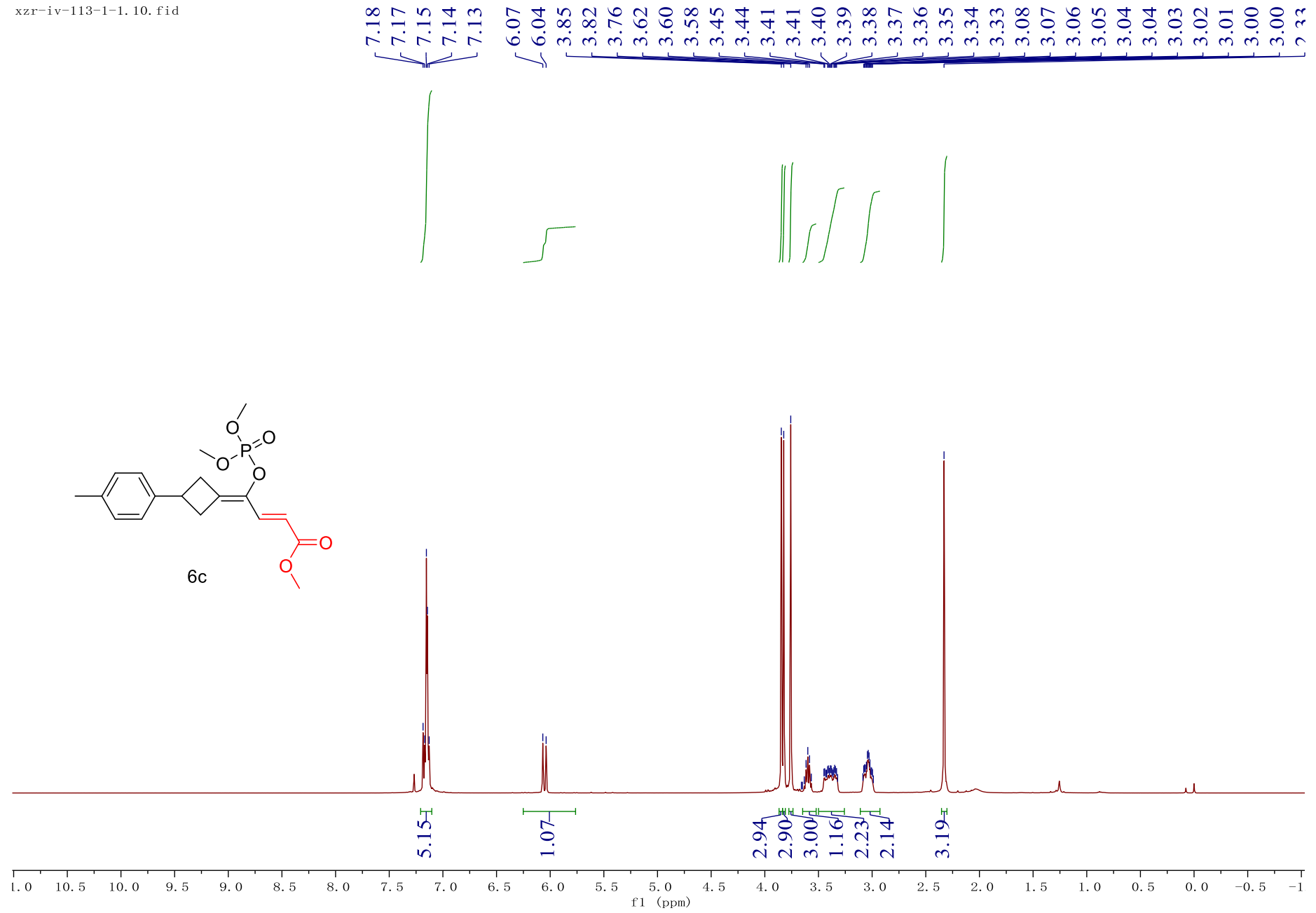


7.22
7.20
7.14
7.14
5.76
5.73
4.23
4.21
4.20
4.18
3.61
3.60
3.58
3.42
3.41
3.40
3.39
3.39
3.38
3.38
3.37
3.13
3.11
3.10
3.10
3.09
3.09
3.08
3.07
3.07
3.06
3.05
3.05
3.04
3.03
3.02
3.01
2.85
2.85
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2.83
2.82
2.81
2.80
2.80
2.32
2.22
1.30
1.29
1.27

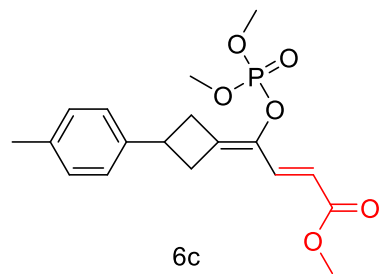


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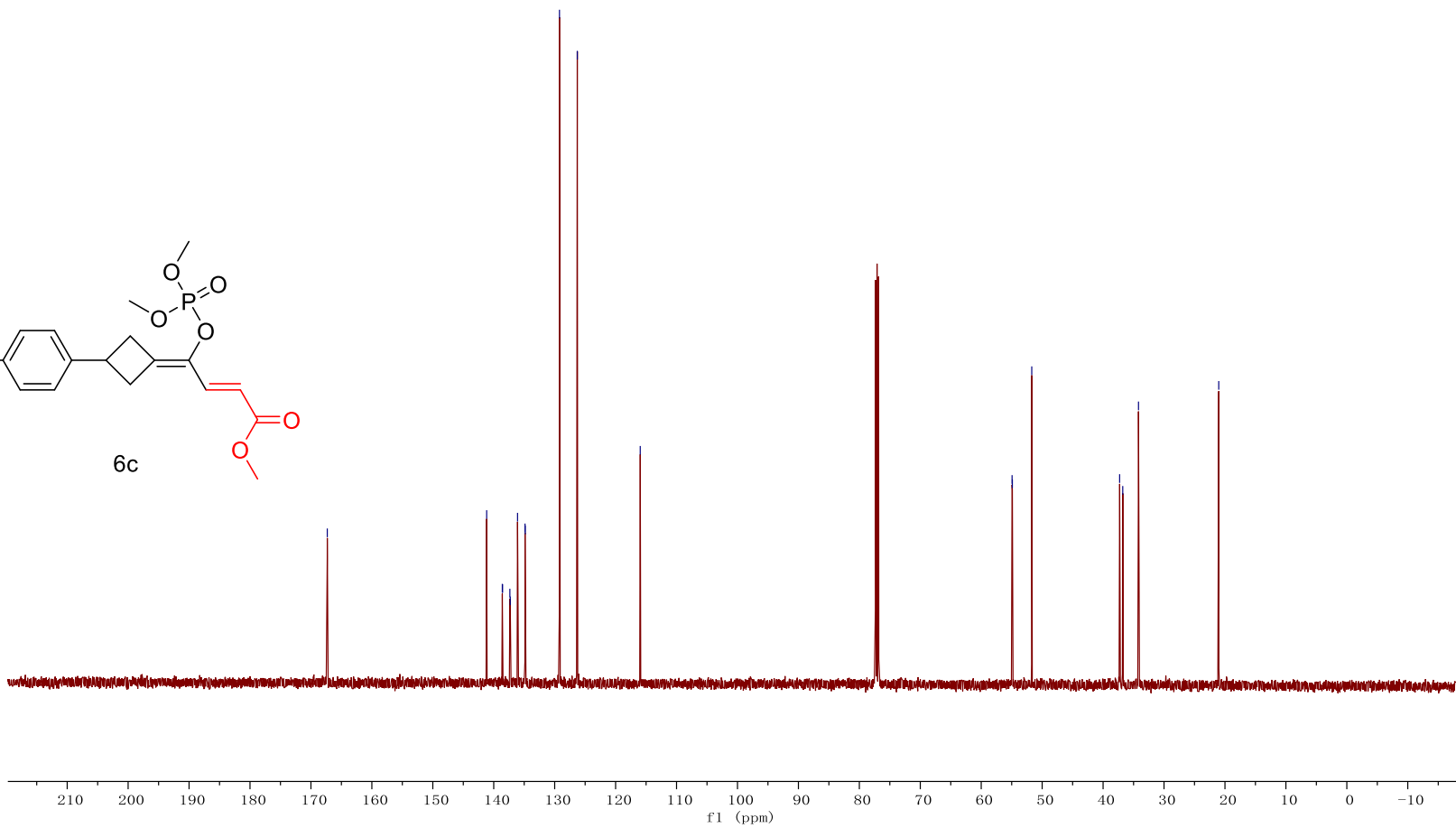


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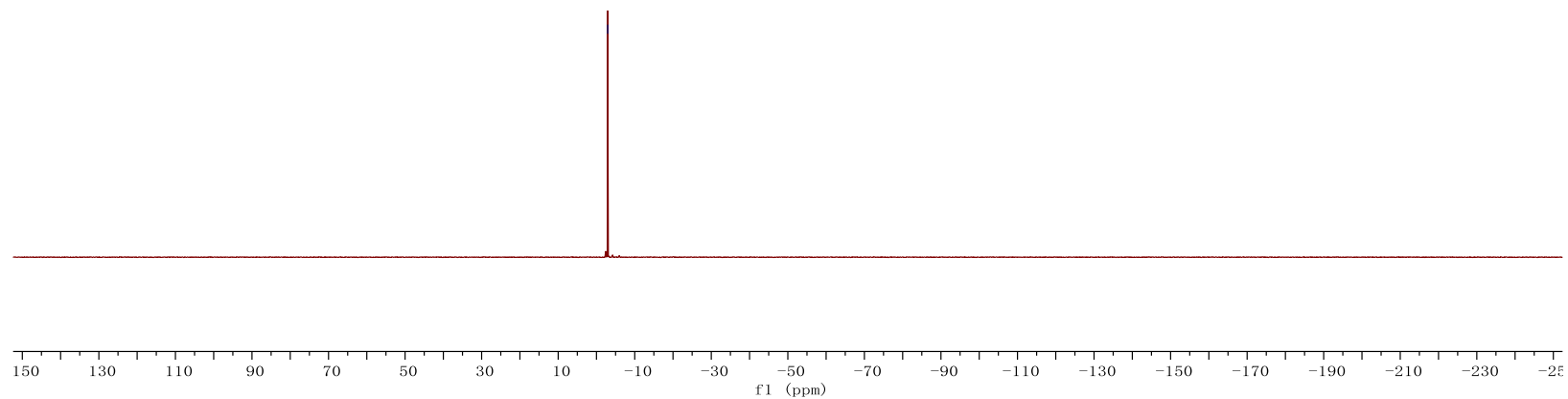
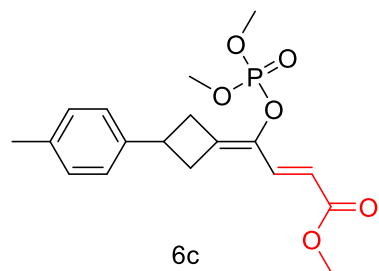


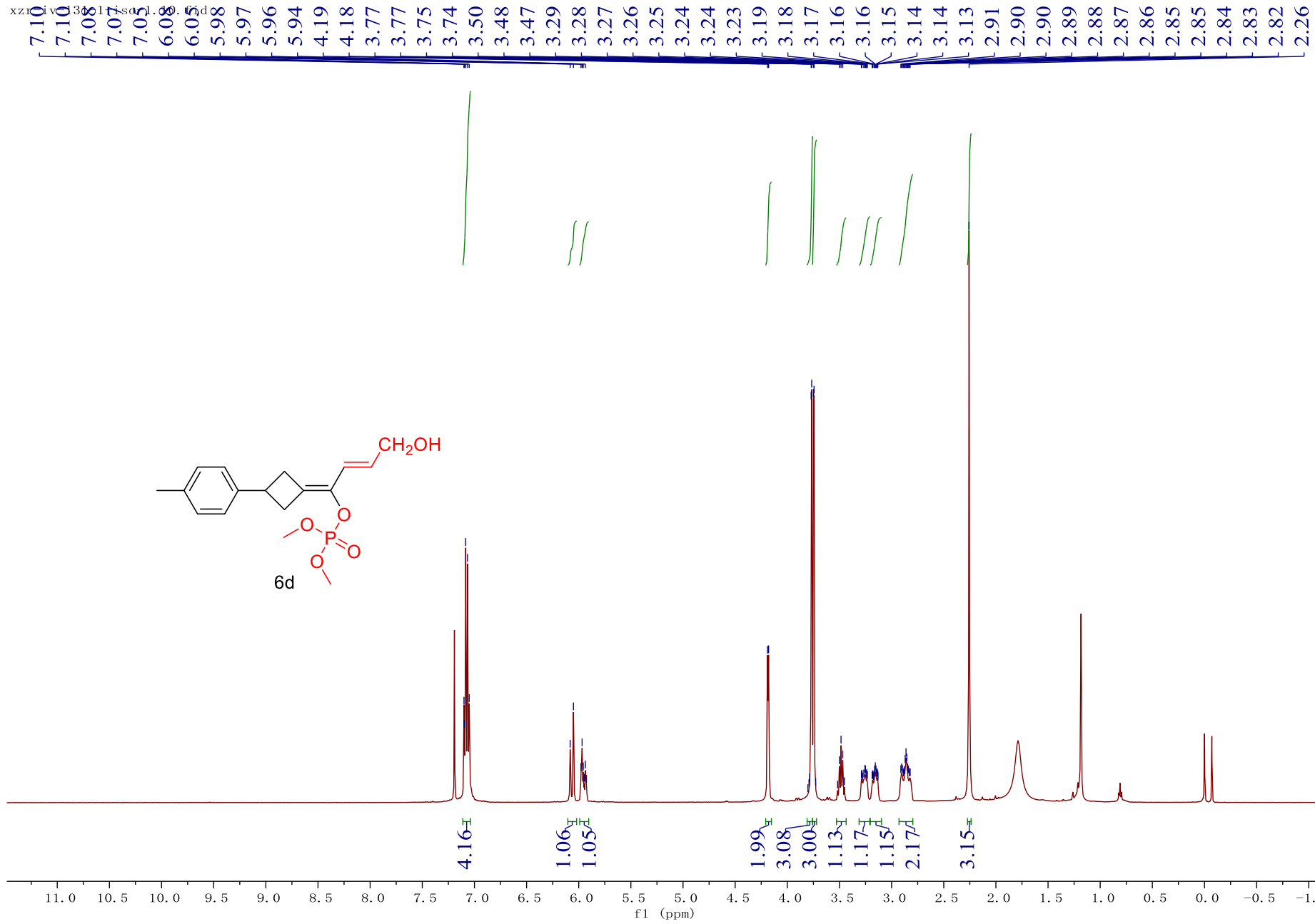
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138.60
138.56
137.35
137.29
136.09
134.86
134.84
129.21
126.29
— 115.96

54.94
54.89
51.71
37.29
36.77
34.19
— 21.02



P-NMR





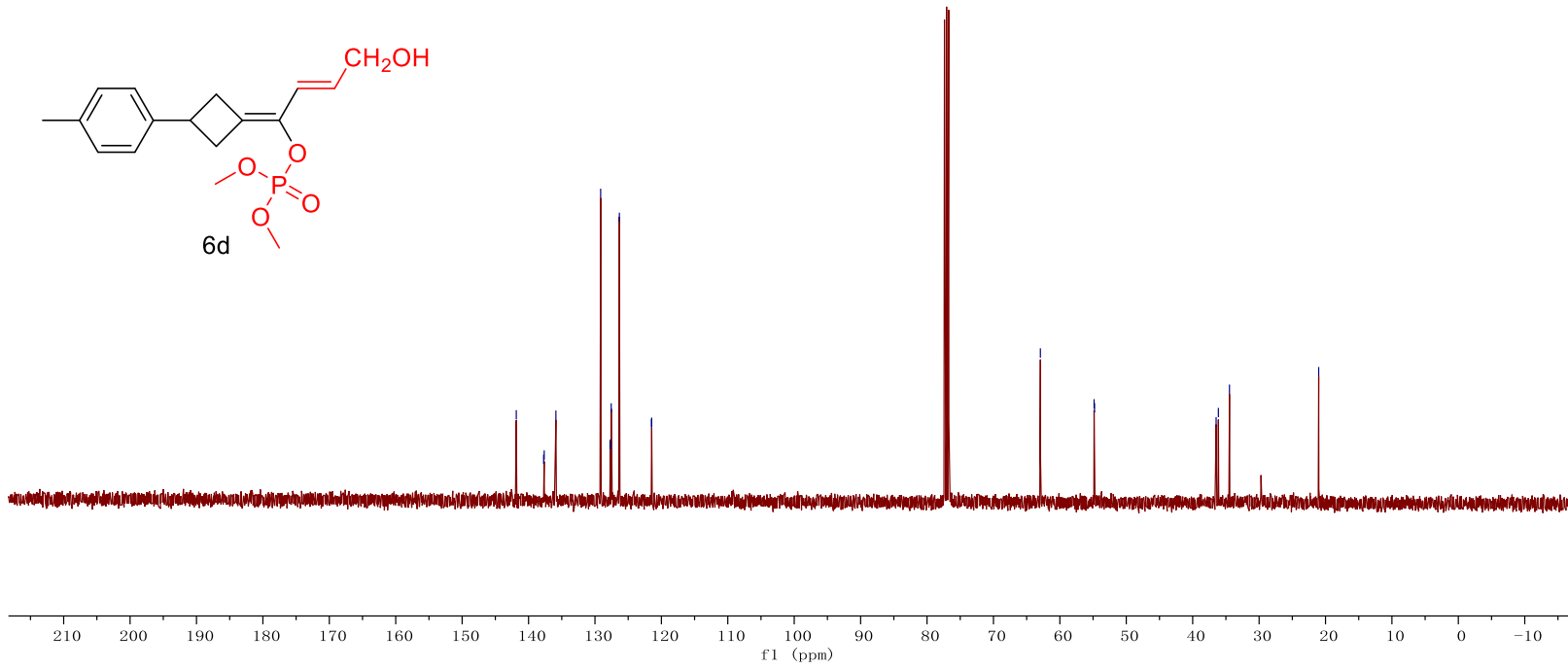
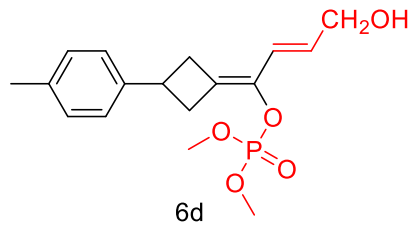
tjl-20240418-1.11.fid

141.85
137.73
137.64
135.88
129.15
127.73
127.68
127.55
126.32
121.49
121.46

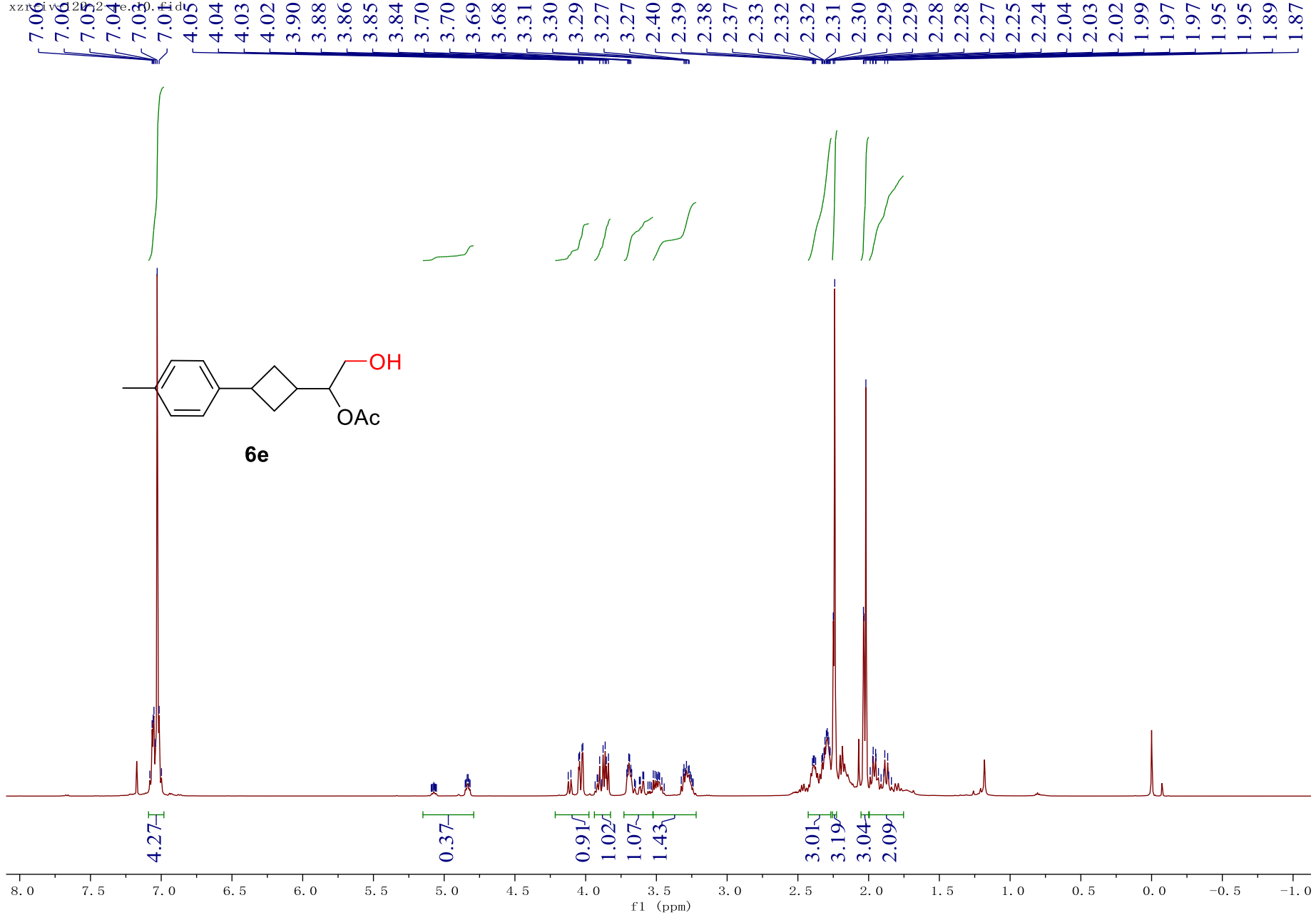
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54.84
54.78

36.47
36.13
34.46

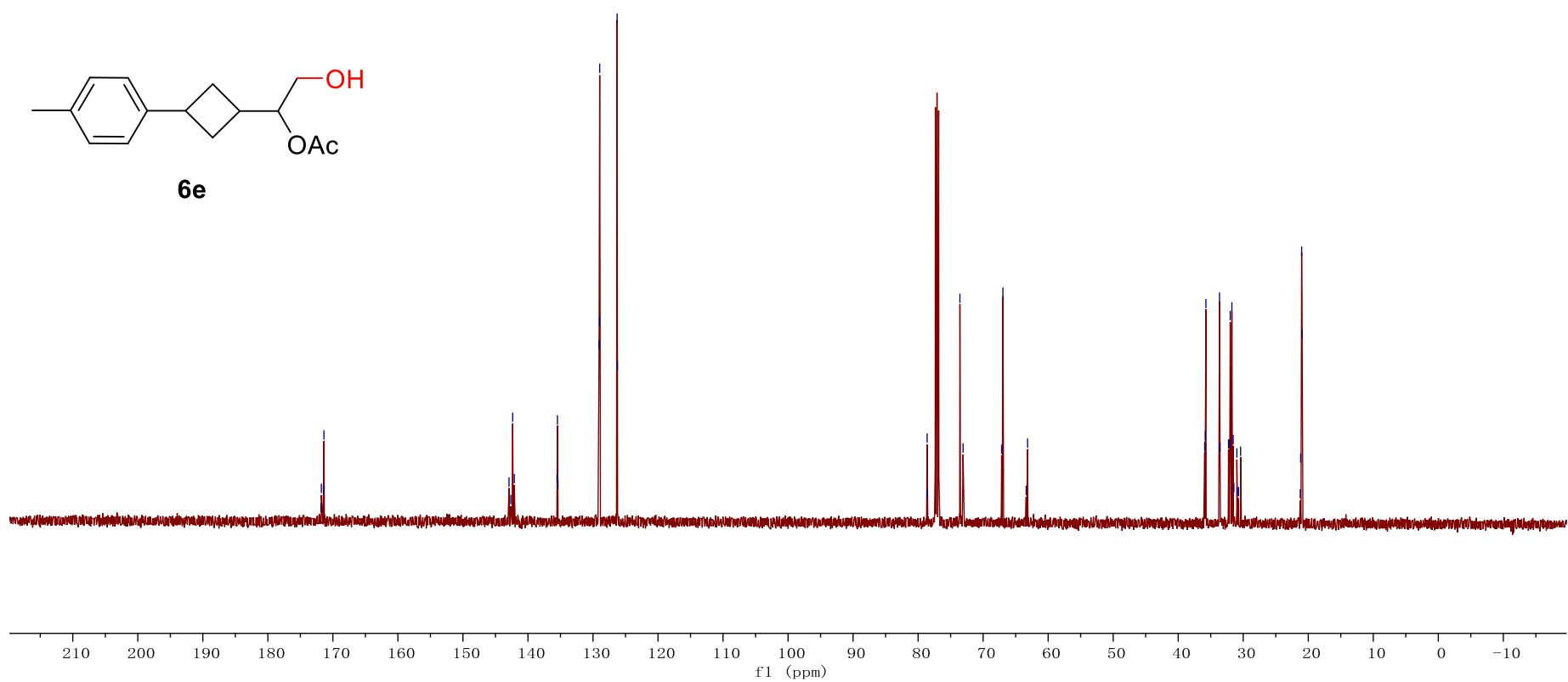
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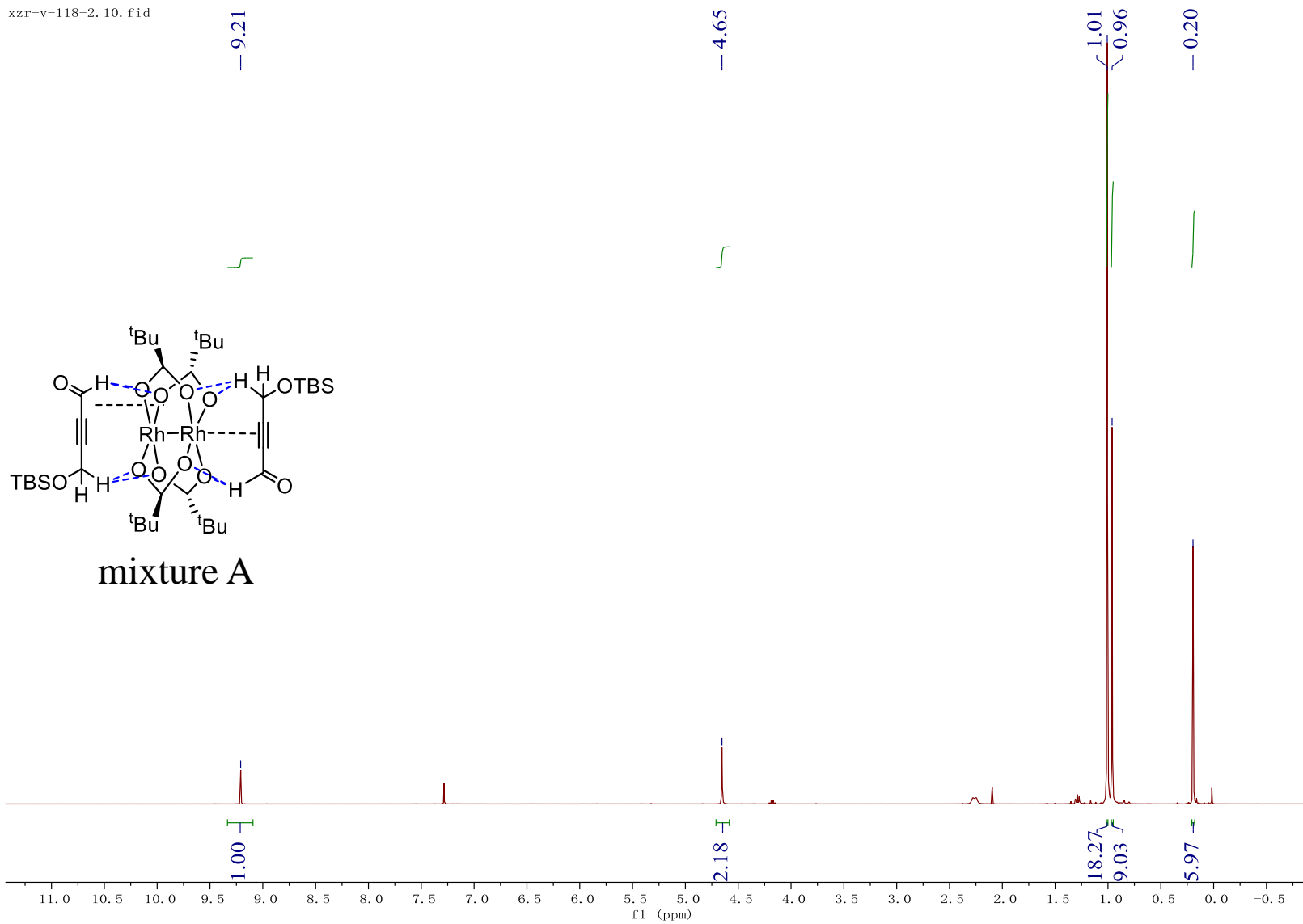
xzrviv12072re.0.fid



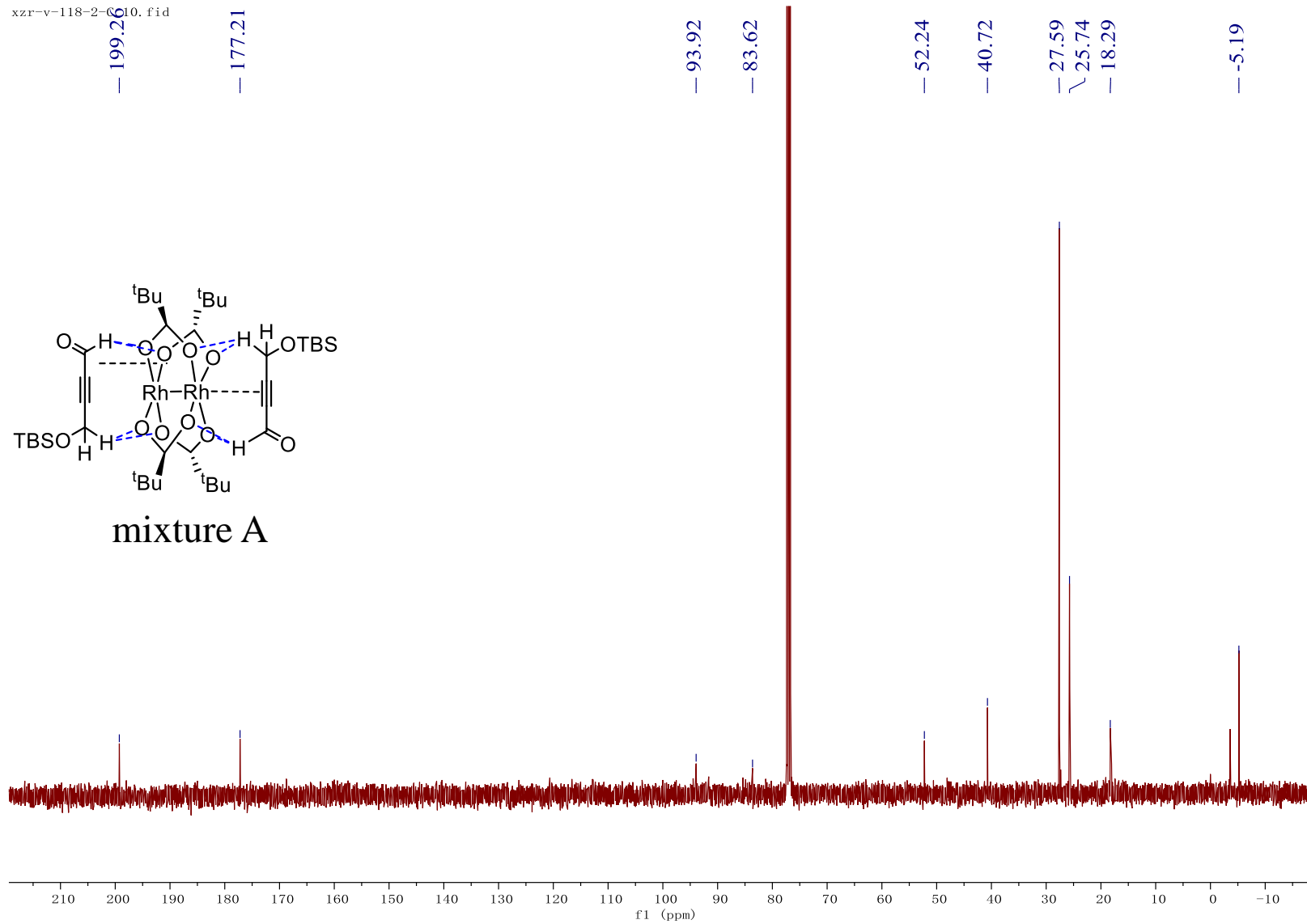
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xzr-v-118-2.10.fid



xzr-v-118-2-610.fid



mixture A