Supplementary Data

$Fe_2(CO)_9$-mediated [5+1] cycloaddition of vinylcyclopropanes and CO for the synthesis of α, β-cyclohexenones

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Contents

1. General 2
2. Experimental Procedures and Characterization Data 3
    2.1 Synthesis of VCP substrates 3
    2.2 [5+1] cycloaddition 7
    2.3 References 12
3. ^{1}H and ^{13}C-NMR Spectra 13

1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC.

Tetrahydrofuran, diethyl ether, 1,2-dimethoxyethane and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane, 1,2-dichloroethane and acetonitrile were distilled from CaH_2 prior to use. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated. Analytical pure ^{t}BuOH was used directly. $Fe_2(CO)_9$ was stored in glove box at -20 ℃ and weighted in the glovebox.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) nuclear magnetic resonance spectrometers. ^{1}H NMR spectra are reported relative to Me_4Si (0.00 ppm) or residual solvent signals (C_6D_6: 7.16 ppm, CD_2Cl_2: 5.32 ppm). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, s = singlet, br. = broad, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplet, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm, CD_2Cl_2: 53.8 ppm). Infrared spectra were recorded on Bruker Tensor 27 fourier transform infrared spectrometer (FT-IR) and were reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS mass spectrometer (ESI) and Micromass U.K. GCT GC–MS mass spectrometer (EI).

Abbreviations:

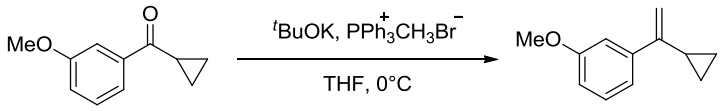
acac = acetylacetone
^{t}amylOH = *tert*-amyl alcohol
CPME = cyclopentyl methyl ether
DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene
DCE = 1,2-dichloroethane
DCM = dichloromethane
DME = 1,2-dimethoxyethane
DMF = *N*,*N*-dimethylformamide
EA = ethyl acetate
HFIP = hexafluoroisopropanol
MS = molecular sieve
NMO = *N*-methyl morpholine-*N*-oxide
NMP = *N*-methyl-2-pyrrolidone
PE = petroleum ether
Tf = trifluoromethanesulfonyl
THF = tetrahydrofuran
TLC = thin layer chromatography
TPAP = tetra-*n*-propylammonium perruthenate
Ts = *p*-toluenesulfonyl

2. Experimental Procedures and Characterization Data

2.1 Synthesis of VCP substrates

Substrates **1a**,[1] **1b**,[1] **1c**,[2] **1d**,[3] **1e**,[3] **1f**,[4] **1g**,[1] **1i**,[5] **1j**,[6] **1k**,[7] **1l**,[5] **1m**,[4] **1n**,[8] **1o**,[5] **1p**,[5] **1s**,[9] **1t**,[10] **1u**,[11] **1w**[12] were synthesized according to the reported literature.

VCP (1h)

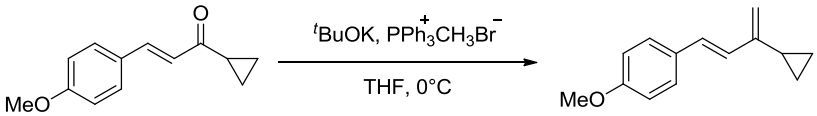


S1h **1h**

To a mixture of methyltriphenylphosphonium bromide (3.57 g, 10 mmol) and ^{t}BuOK (897 mg, 8 mmol) in round bottle was added THF (30 mL) under an argon atmosphere at 0 ℃, and the resulting solution was stirred for 30 min at 0 ℃. Then a solution of ketone **S1h**[13] (636 mg, 3.61 mmol) in THF (10 mL) was added dropwise at 0 ℃, and the resulting mixture was stirred for 30 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA, 100:1) to afford VCP **1h** (606 mg, 98%).

1h: Colorless oil, TLC R_f = 0.53 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.23 (m, 1H), 7.21–7.17 (m, 1H), 7.16–7.13 (m, 1H), 6.86–6.81 (m, 1H), 5.29–5.26 (m, 1H), 4.95–4.92 (m, 1H), 3.83 (s, 3H), 1.69–1.59 (m, 1H), 0.87– 0.79 (m, 2H), 0.62–0.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 149.2, 143.2, 129.1, 118.7, 112.6, 112.1, 109.3, 55.2, 15.6, 6.7. IR (KBr): υ 3083, 3002, 2955, 2834, 1927, 1603, 1579, 1488, 1461, 1429, 1285, 1223, 1049 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{15}O$ ($M+H^+$): 175.1117. Found: 175.1118.

VCP (1q)



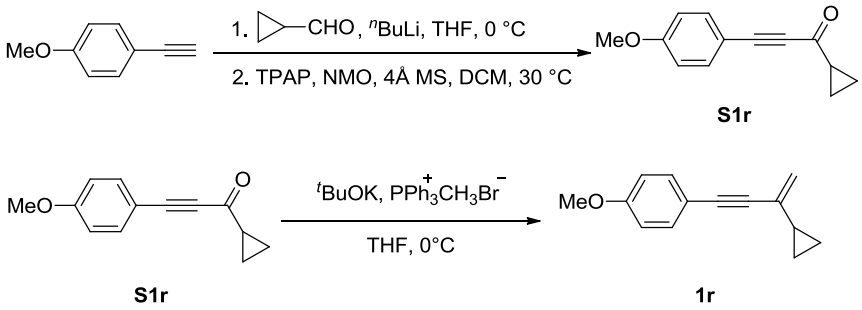
S1q **1q**

To a mixture of methyltriphenylphosphonium bromide (2.15 g, 6 mmol) and ^{t}BuOK (562 mg, 5 mmol) in round bottle was added THF (20 mL) under an argon atmosphere at 0 ℃, and the resulting solution was stirred for 30 min at 0 ℃. Then a solution of ketone **S1q**[14] (428 mg, 2.12 mmol) in THF (10 mL) was added dropwise at 0 ℃, and the resulting mixture was stirred for 30 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA, 100:1 then 50:1) to afford VCP **1q** (286 mg, 67%).

1q: White powder, TLC R_f= 0.79 (PE/EA 5:1), m.p. = 74–76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.39 (d, J = 8.7 Hz, 2H), 6.91–6.84 (m, 3H), 6.75 (d, J = 16.1 Hz, 1H), 5.01 (s, 1H), 4.91 (s, 1H), 3.82 (s, 3H), 1.62–1.54 (m, 1H), 0.81–0.74 (m, 2H), 0.54–0.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 147.5, 130.3, 129.4, 128.1, 127.7, 114.0, 112.8, 55.3, 12.6, 5.5. IR (KBr): υ 3084, 3005, 2955, 2838, 1599, 1510, 1269, 1247, 1178, 1020, 966 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{17}O$ ($M+H^+$): 201.1274. Found: 201.1276.

VCP (1r)



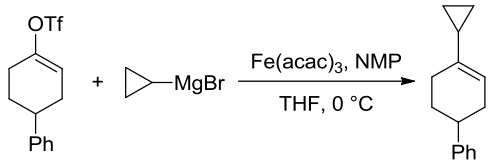
To a solution of 4-methoxyphenylacetylene (662 mg, 5 mmol) in THF (20 mL) at 0 ℃ was added ^{n}BuLi (1.6 M, 6 mL, 9.6 mmol), and the resulting yellow solution was stirred for 30 min at 0 ℃. Then cyclopropanecarboxaldehyde (700 mg, 10 mmol) was added slowly at 0 ℃, and the resulting mixture was stirred for 30 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA 5:1 then 3:1) to afford intermediate alcohol.

The intermediate alcohol was dissolved in DCM (25 mL). Then TPAP (70 mg, 0.2 mmol), NMO (1.17g, 10 mmol) and 4 Å MS (2.5 g) were added successively. The resulting mixture was stirred for 2 h at 30 ℃. After the accomplishment of the oxidation reaction, the mixture was filtered and the filtrate was concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA 10:1 then 5:1) to afford **S1r** (854 mg, 85% for 2 steps) as yellow oil. Compound **S1r** was used directly in the next reaction.

To a mixture of methyltriphenylphosphonium bromide (4.29 g, 12 mmol) and ^{t}BuOK (1.12 g, 10 mmol) in round bottle was added THF (30 mL) under an argon atmosphere at 0 ℃, and the resulting solution was stirred for 30 min at 0 ℃. Then a solution of ketone **S1r** (854 mg, 4.26 mmol) in THF (20 mL) was added dropwise at 0 ℃, and the resulting mixture was stirred for 30 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA, 50:1 then 30:1) to afford VCP **1r** (807 mg, 95%).

1r: Colorless oil, TLC R_f = 0.73 (PE/EA 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 5.37–5.32 (m, 2H), 3.79 (s, 3H), 1.66–1.57 (m, 1H), 0.81–0.75 (m, 2H), 0.74–0.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 134.0, 133.0, 118.2, 115.1, 113.9, 89.4, 85.2, 55.2, 16.5, 5.9. IR (KBr): υ 3087, 3006, 2958, 2838, 2200, 1770, 1599, 1509, 1462, 1288, 1249, 1175, 1032 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{15}O$ ($M+H^+$): 199.1117. Found: 199.1120.

VCP (1v)[15]

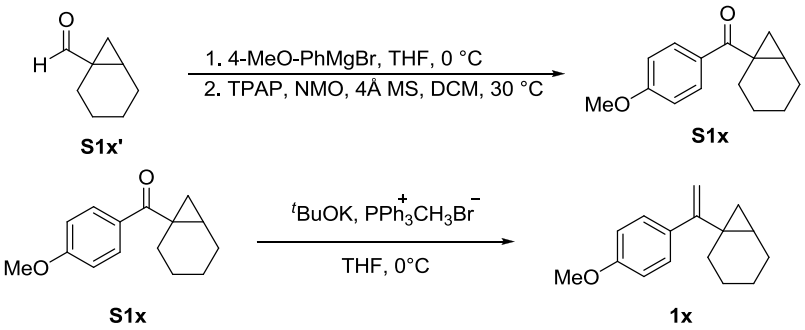


S1v **1v**

To a red solution of **S1v**[16] (612 mg, 2 mmol) and $Fe(acac)_3$ (36.3 mg, 0.10 mmol) in THF (15 mL) was added NMP (1.2 mL, 12.4 mmol) at 0 ℃ under an argon atmosphere. Then a solution of cyclopropylmagnesium bromide (0.5 M, 8 mL, 4 mmol) was added slowly at 0 ℃, and the reaction system was stirred overnight at room temperature. Saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE) to afford VCP **1v** (254 mg, 64%).

1v: Colorless oil, TLC R_f= 0.49 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.26 (m, 2H), 7.23–7.15 (m, 3H), 5.55–5.50 (m, 1H), 2.80–2.68 (m, 1H), 2.33–2.23 (m, 1H), 2.18–2.03 (m, 2H), 2.00–1.90 (m, 2H), 1.80–1.67 (m, 1H), 1.40–1.30 (m, 1H), 0.60–0.51 (m, 2H), 0.51–0.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.2, 138.2, 128.3, 126.9, 125.9, 119.2, 40.4, 33.5, 30.0, 27.1, 17.1, 4.6, 3.9. IR (KBr): υ 3081, 3026, 3005, 2915, 2835, 1603, 1493, 1453, 1435, 1018 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{18}$ (M^+): 198.1409. Found: 198.1406.

VCP (1x)



To a solution of **S1x'**[12] (620 mg, 5 mmol) in THF (25 mL) at 0 ℃ was added 4-methoxyphenylmagnesiumbromide (1M, 10 ml, 10 mmol), and the resulting mixture was stirred for 30 min at 0 ℃. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA 5:1) to afford intermediate alcohol.

The intermediate alcohol was dissolved in DCM (25 mL). Then TPAP (70 mg, 0.2 mmol), NMO (1.17g, 10 mmol) and 4 Å MS (2.5 g) were added successively. The resulting mixture was stirred overnight at 30 ℃. After the accomplishment of the oxidation reaction, the mixture was filtered and the filtrate was concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA 20:1) to afford **S1x** (773 mg, 67% for 2 steps). Compound **S1x** was used directly in the next reaction.

To a mixture of methyltriphenylphosphonium bromide (3.57 g, 10 mmol) and ^{t}BuOK (899 mg, 8 mmol) in round bottle was added THF (15 mL) under an argon atmosphere at 0 ℃, and the resulting solution was stirred for 30 min at 0 ℃. Then a solution of ketone **S1x** (770 mg, 3.34 mmol) in THF (5 mL) was added dropwise at 0 ℃, and the resulting mixture was stirred for 3 h at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA, 100:1) to afford VCP **1x** (446 mg, 58%).

1x: Colorless oil, TLC R_f = 0.80 (PE/EA 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 5.17 (d, J = 1.4 Hz, 1H), 4.96 (d, J = 1.4 Hz, 1H), 3.82 (s, 3H), 2.09–1.98 (m, 1H), 1.84–1.76 (m, 1H), 1.72–1.66 (m, 2H), 1.41–1.32 (m, 1H), 1.29–1.13 (m, 4H), 0.94–0.89 (m, 1H), 0.53–0.48 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 154.1, 133.0, 127.9, 113.4, 109.4, 55.2, 29.7, 24.4, 23.6, 22.0, 20.5, 18.8, 16.7. IR (KBr): υ 3063, 2999, 2929, 2855, 2059, 1609, 1510, 1453, 1290, 1246, 1176, 1114, 1036, 891, 835 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}O$ ($M+H^+$): 229.1587. Found: 229.1593.

2.2 [5+1] cycloaddition

Typical procedure for the [5+1] cycloaddition of (1-cyclopropylvinyl)benzene (1a) to 3-phenyl-cyclohex-2-enone (2a)

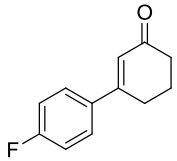
A solution of **1a** (44.5 mg, 0.30 mmol) and $Fe_2(CO)_9$ (109 mg, 0.30 mmol) in ^{t}BuOH (2 mL) was stirred under an argon atmosphere at 90 ℃ for 12 h. After the accomplishment of the [5+1] cycloaddition reaction, the reaction mixture was cooled to room temperature and then filtered through a short silica gel eluting with DCM. The filtrate was concentrated and a DCM solution of DBU (45 mg, 0.3 mmol in 2 mL DCM) was added. The mixture was stirred at room temperature for 30 min and then concentrated. The crude mixture was submitted to flash column chromatography on silica gel (eluted with PE/EA 20:1 then 10:1) to afford the corresponding product **2a** as a white solid (42.6 mg, 80% reaction yield).

The second run of this reaction using 44.0 mg **1a** gave 40.7 mg **2a**, with a reaction yield of 78%. Therefore, the average yield of two runs for this substrate was 79%, which has been reported in Table 2.

2a: White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.50 (m, 2H), 7.43–7.38 (m, 3H), 6.42 (t, J = 1.3 Hz, 1H), 2.79–2.74 (m, 2H), 2.51–2.45 (m, 2H), 2.19–2.11 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature.

The similar procedure was used for the [5+1] cycloaddition reactions of **1b**–**1p** and **1x**. For substrates **1j** and **1x**, the reaction system was stirred at 90 ℃ for 24 h. For substrate **1j**, after filtration, *para*-toluenesulfonic acid monohydrate was added instead of DBU and the mixture was stirred at room temperature for 2 h.

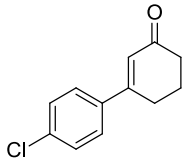
3-(4-fluorophenyl)-cyclohex-2-enone (2b)



Run 1: 49.4 mg **1b** was converted to 42.3 mg **2b**, yield 73%. Run 2: 49.3 mg **1b** was converted to 45.2 mg **2b**, yield 78%. So the average yield of two runs was 76%.

2b: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.50 (m, 2H), 7.14–7.06 (m, 2H), 6.38 (s, 1H), 2.78–2.72 (m, 2H), 2.52–2.45 (m, 2H), 2.20–2.12 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[5].

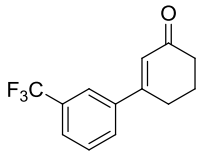
3-(4-chlorophenyl)-cyclohex-2-enone (2c)



Run 1: 53.9 mg **1c** was converted to 49.8 mg **2c**, yield 80%. Run 2: 53.2 mg **1c** was converted to 47.0 mg **2c**, yield 76%. So the average yield of two runs was 78%.

2c: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 6.39 (s, 1H), 2.74 (t, J = 5.9 Hz, 2H), 2.51–2.46 (m, 2H), 2.20–2.12 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[17a].

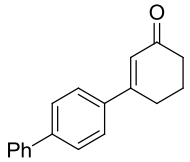
3-(3-trifluoromethylphenyl)-cyclohex-2-enone (2d)



Run 1: 64.1 mg **1d** was converted to 50.6 mg **2d**, yield 70%. Run 2: 63.6 mg **1d** was converted to 46.9 mg **2d**, yield 65%. So the average yield of two runs was 68%.

2d: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.74–7.64 (m, 2H), 7.55 (t, J = 7.8 Hz, 1H), 6.45–6.42 (m, 1H), 2.82–2.77 (m, 2H), 2.54–2.49 (m, 2H), 2.24–2.15 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[17a].

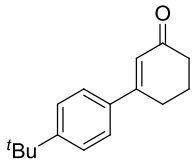
3-(4-phenylphenyl)-cyclohex-2-enone (2e)



Run 1: 64.7 mg **1e** was converted to 55.5 mg **2e**, yield 76%. Run 2: 66.3 mg **1e** was converted to 60.0 mg **2e**, yield 80%. So the average yield of two runs was 78%.

2e: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.60 (m, 6H), 7.49–7.43 (m, 2H), 7.41–7.35 (m, 1H), 6.69 (s, 1H), 2.84–2.79 (m, 2H), 2.54–2.48 (m, 2H), 2.22–2.14 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[17a].

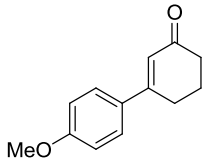
3-(4-tert-butylphenyl)-cyclohex-2-enone (2f)



Run 1: 62.0 mg **1f** was converted to 49.9 mg **2f**, yield 70%. Run 2: 62.1 mg **1f** was converted to 50.6 mg **2f**, yield 71%. So the average yield of two runs was 70%.

2f: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 6.44 (s, 1H), 2.80–2.75 (m, 2H), 2.51–2.46 (m, 2H), 2.19-2.11 (m, 2H), 1.34 (s, 9H). The ^{1}H NMR spectrum is consistent with the literature[17a].

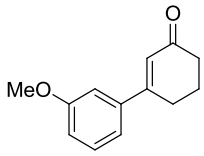
3-(4-methoxylphenyl)-cyclohex-2-enone (2g)



Run 1: 49.4 mg **1g** was converted to 45.2 mg **2g**, yield 79%. Run 2: 53.1 mg **1g** was converted to 48.5 mg **2g**, yield 79%. So the average yield of two runs was 79%.

2g: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.40 (s, 1H), 3.85 (s, 3H), 2.78–2.73 (m, 2H), 2.50–2.45 (m, 2H), 2.18-2.11 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[5].

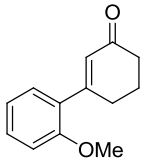
3-(3-methoxylphenyl)-cyclohex-2-enone (2h)



Run 1: 52.6 mg **1h** was converted to 49.1 mg **2h**, yield 80%. Run 2: 52.3 mg **1h** was converted to 45.5 mg **2h**, yield 75%. So the average yield of two runs was 78%.

2h: Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.06–7.04 (m, 1H), 6.95 (dd, J = 8.2 Hz, 2.5 Hz, 1H), 6.41 (s, 1H), 3.84 (s, 3H), 2.76 (t, J = 6.0 Hz, 2H), 2.52–2.46 (m, 2H), 2.20–2.12 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[17a].

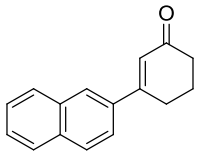
3-(2-methoxylphenyl)-cyclohex-2-enone (2i)



Run 1: 53.2 mg **1i** was converted to 44.7 mg **2i**, yield 72%. Run 2: 53.0 mg **1i** was converted to 47.2 mg **2i**, yield 77%. So the average yield of two runs was 74%.

2i: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 1H), 7.20 (dd, J = 7.6 and 1.7 Hz, 1H), 7.00-6.91 (m, 2H), 6.20 (s, 1H), 3.84 (s, 3H), 2.77–2.72 (m, 2H), 2.51–2.46 (m, 2H), 2.15-2.07 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[5].

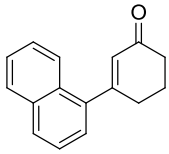
3-(2-naphthyl)-cyclohex-2-enone (2j)



Run 1: 57.8 mg **1j** was converted to 41.1 mg **2j**, yield 62%. Run 2: 58.6 mg **1j** was converted to 42.1 mg **2j**, yield 63%. So the average yield of two runs was 62%.

2j: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.91–7.82 (m, 3H), 7.68–7.63 (m, 1H), 7.57–7.49 (m, 2H), 6.58 (s, 1H), 2.96–2.88 (m, 2H), 2.58–2.49 (m, 2H), 2.27–2.17 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[5].

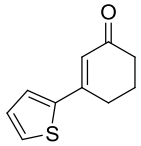
3-(1-naphthyl)-cyclohex-2-enone (2k)



Run 1: 58.8 mg **1k** was converted to 42.3 mg **2k**, yield 63%. Run 2: 57.7 mg **1k** was converted to 45.0 mg **2k**, yield 68%. So the average yield of two runs was 66%.

2k: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.81 (m, 3H), 7.52–7.43 (m, 3H), 7.33–7.29 (m, 1H), 6.20 (s, 1H), 2.78–2.73 (m, 2H), 2.62–2.56 (m, 2H), 2.29–2.21(m, 2H). The ^{1}H NMR spectrum is consistent with the literature[17b].

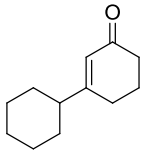
3-(2-thienyl)-cyclohex-2-enone (2l)



Run 1: 44.9 mg **1l** was converted to 38.8 mg **2l**, yield 73%. Run 2: 45.0 mg **1l** was converted to 36.1 mg **2l**, yield 68%. So the average yield of two runs was 70%.

2l: Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 5.1, 0.9 Hz, 1H), 7.39 (dd, J = 3.8, 0.9 Hz, 1H), 7.10 (dd, J = 5.1, 3.8 Hz, 1H), 6.43 (s, 1H), 2.82–2.77 (m, 2H), 2.50–2.44 (m, 2H), 2.19–2.10 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[5].

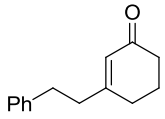
3-cyclohexyl-cyclohex-2-enone (2m)



Run 1: 44.1 mg **1m** was converted to 29.1 mg **2m**, yield 56%. Run 2: 43.8 mg **1m** was converted to 31.7 mg **2m**, yield 61%. So the average yield of two runs was 58%.

2m: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (s, 1H), 2.43–2.26 (m, 4H), 2.10–1.94 (m, 3H), 1.85–1.67 (m, 5H), 1.37–1.12 (m, 5H). The ^{1}H NMR spectrum is consistent with the literature[17c].

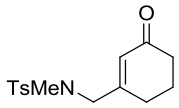
3-(2-phenylethyl)-cyclohex-2-enone (2n)



Run 1: 51.1 mg **1n** was converted to 32.7 mg **2n**, yield 55%. Run 2: 51.7 mg **1n** was converted to 35.1 mg **2n**, yield 58%. So the average yield of two runs was 56%.

2n: Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 2H), 7.23–7.15 (m, 3H), 5.90 (s, 1H), 2.86–2.79 (m, 2H), 2.56–2.50 (m, 2H), 2.38–2.33 (m, 2H), 2.32–2.27 (t, J = 5.9 Hz, 2H), 2.03–1.94 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[5].

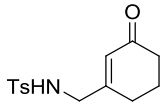
3- [(*N*,4-dimethylbenzenesulfonamino)methyl]-cyclohex-2-enone (2o)



Run 1: 79.2 mg **1o** was converted to 42.6 mg **2o**, yield 49%. Run 2: 78.3 mg **1o** was converted to 46.6 mg **2o**, yield 54%. So the average yield of two runs was 52%.

2o: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 5.94 (s, 1H), 3.70 (s, 2H), 2.65 (s, 3H), 2.45 (s, 3H), 2.43–2.36 (m, 4H), 2.07–1.99 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[5].

3- [(4-methylbenzenesulfonamino)methyl]-cyclohex-2-enone (2p)



Run 1: 72.6 mg **1p** was converted to 32.6 mg **2p**, yield 40%. Run 2: 76.1 mg **1p** was converted to 38.1 mg **2p**, yield 45%. So the average yield of two runs was 42%.

2p: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.95 (s, 1H), 4.81 (t, J = 6.3 Hz, 1H), 3.68 (d, J = 6.3 Hz, 2H), 2.43 (s, 3H), 2.35–2.29 (m, 2H), 2.27–2.21 (m, 2H), 1.97–1.89 (m, 2H). The ^{1}H NMR spectrum is consistent with the literature[5].

2.3 References

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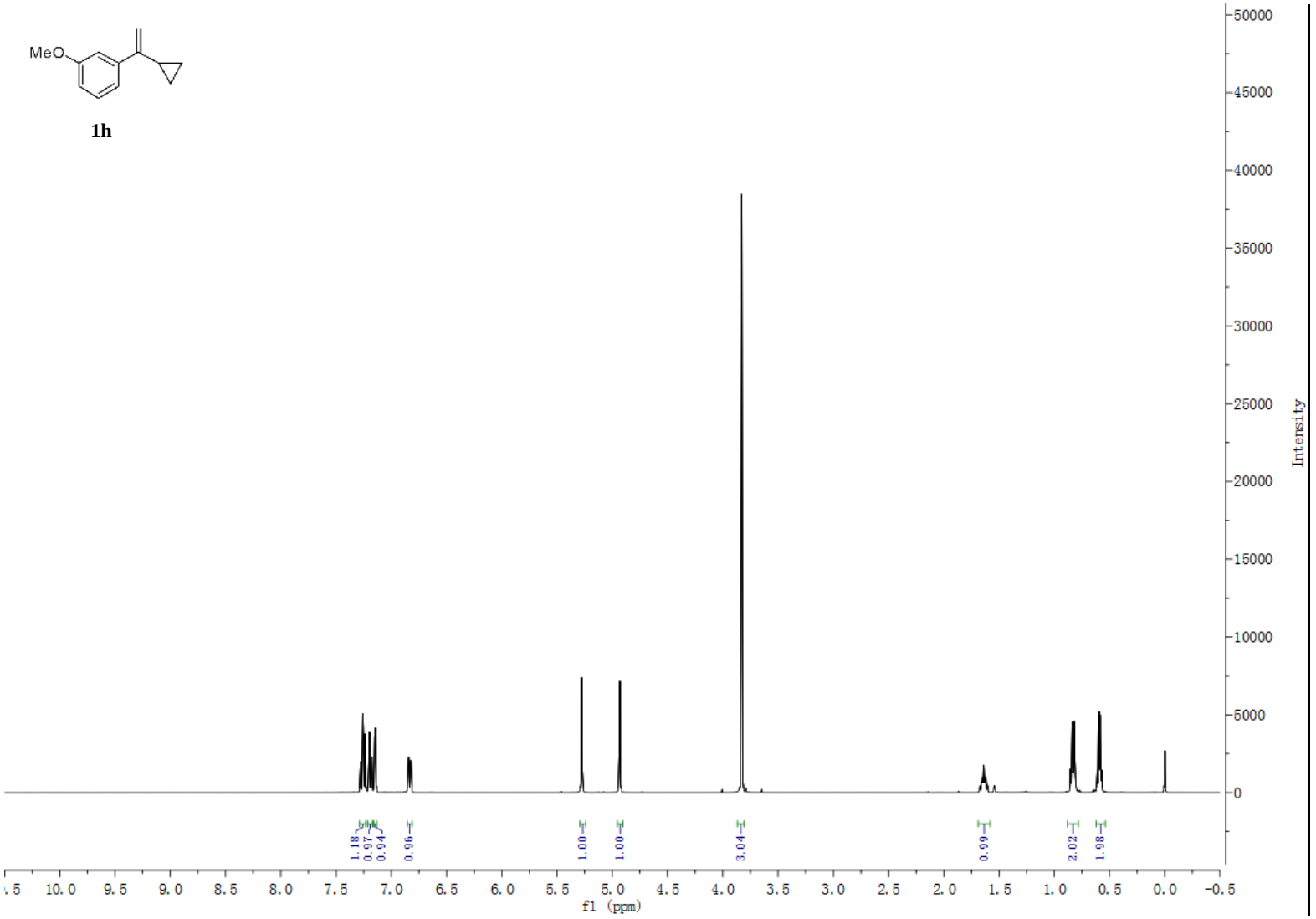
3. ^{1}H and ^{13}C-NMR Spectra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45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
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0.97
0.94
0.96
1.00
1.00
3.04
0.99
2.02
1.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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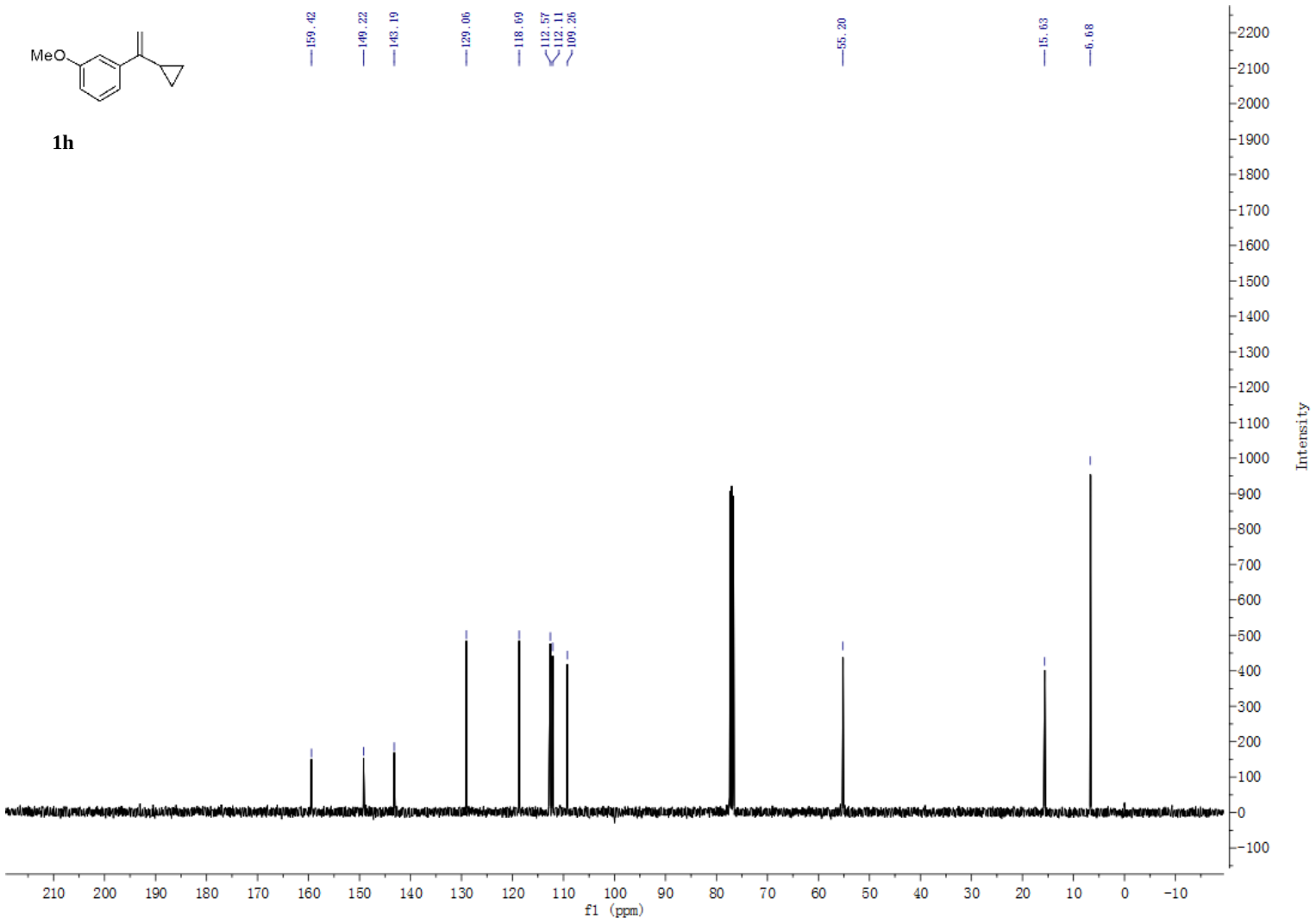
0.5
0.0
-0.5
f1 (ppm)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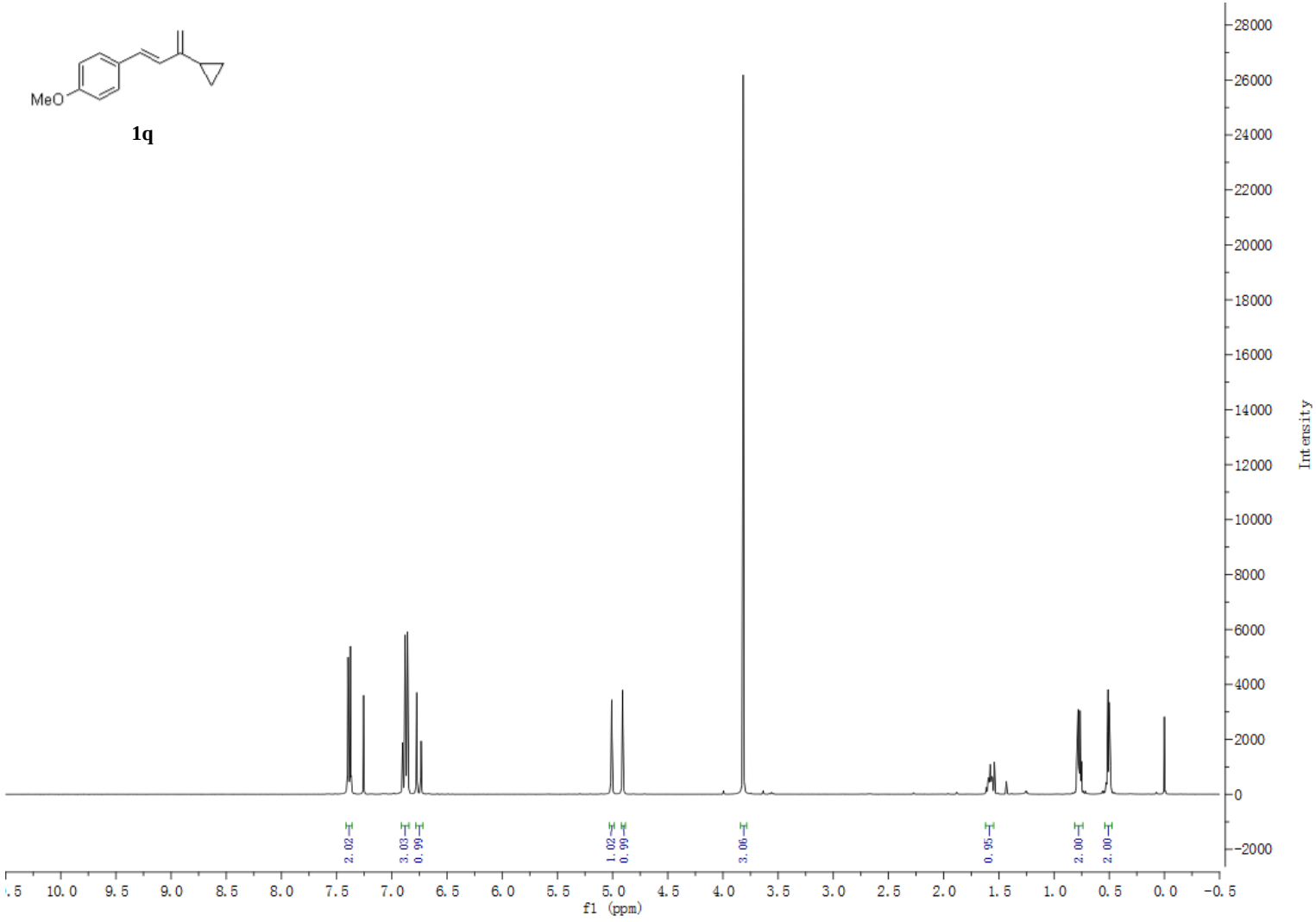
129.06
118.69
112.57
112.11
109.26
55.20
15.63
6.68
Intensity
f1 (ppm)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24000
22000
20000
18000
16000
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12000
10000
8000
6000
4000
2000
0
-2000
Intensity
2.02
3.03
0.99
1.02
0.99
3.06
0.95
2.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
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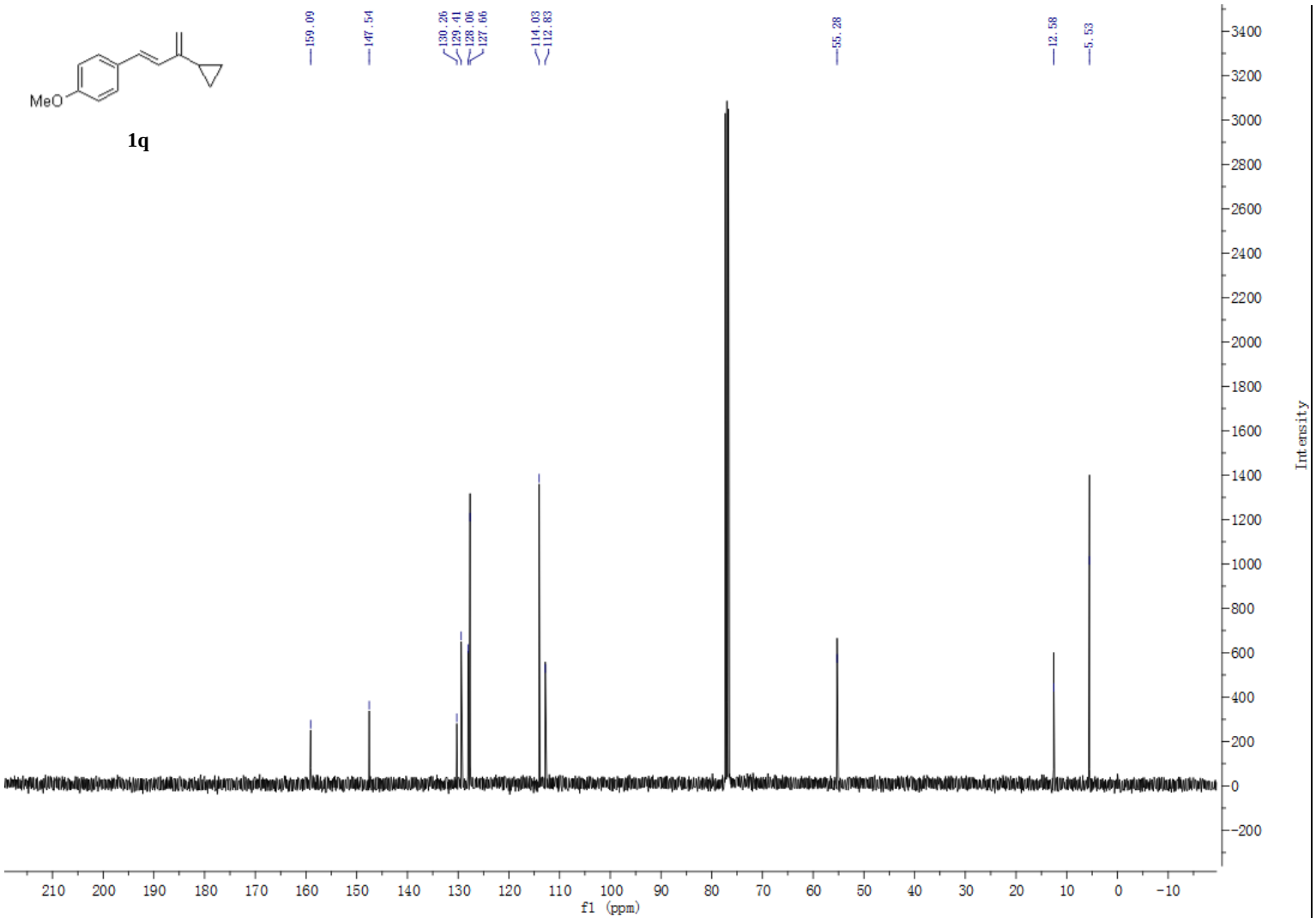
0.5
0.0
-0.5
f1 (ppm)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127.66
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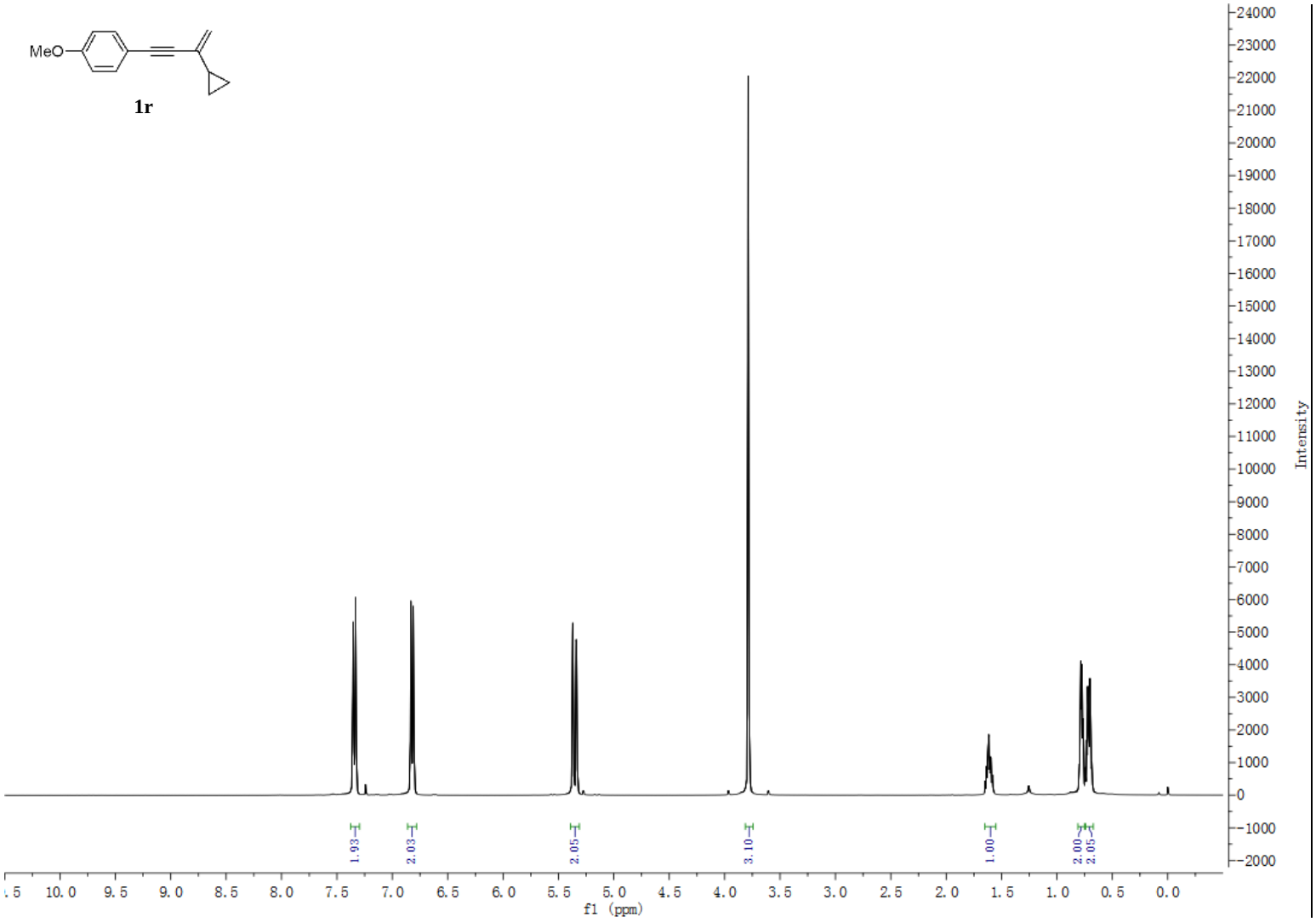
55.28
12.58
5.53
Intensity
f1 (ppm)

1q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3.10
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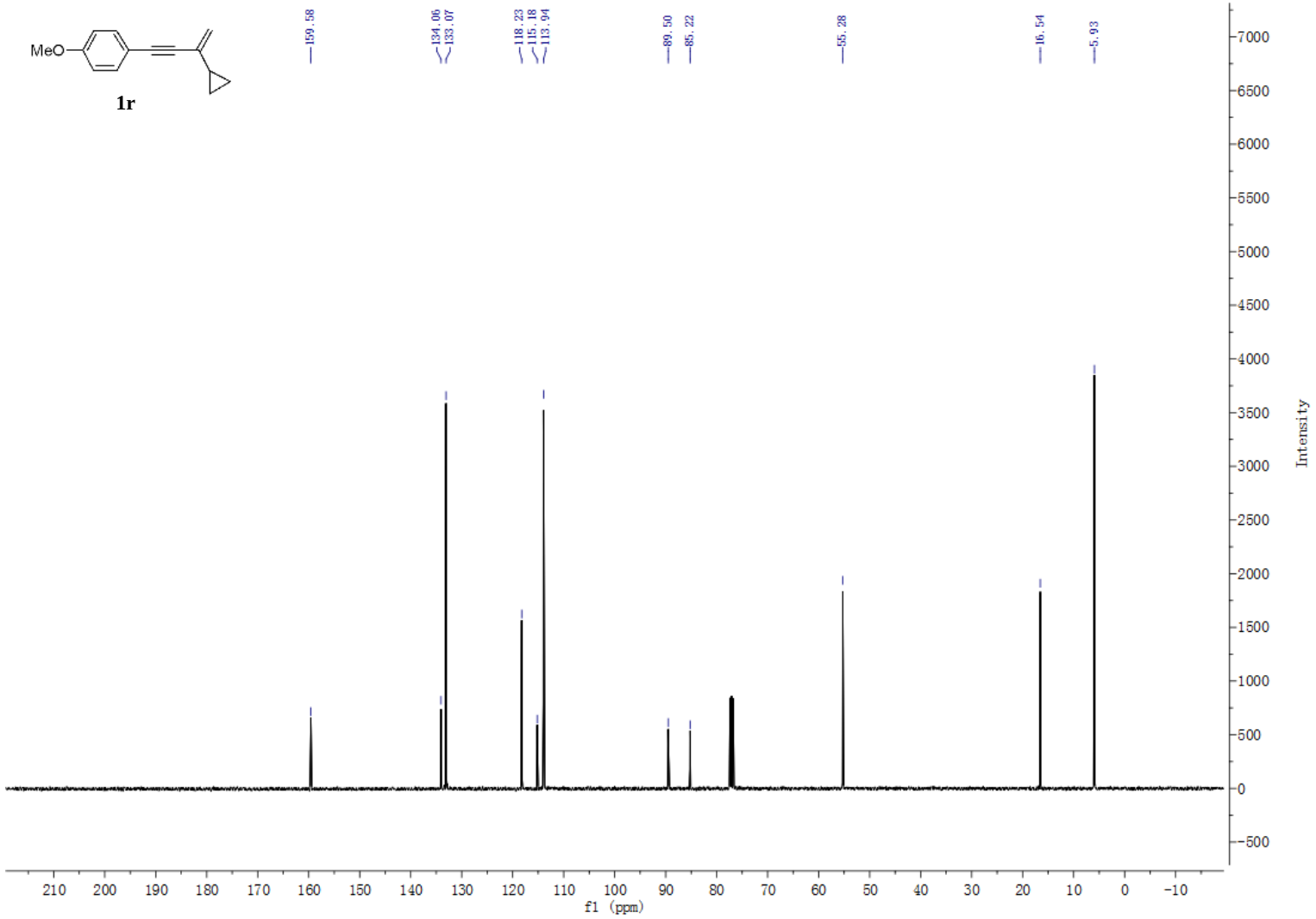
2.05
f1 (ppm)
Intensity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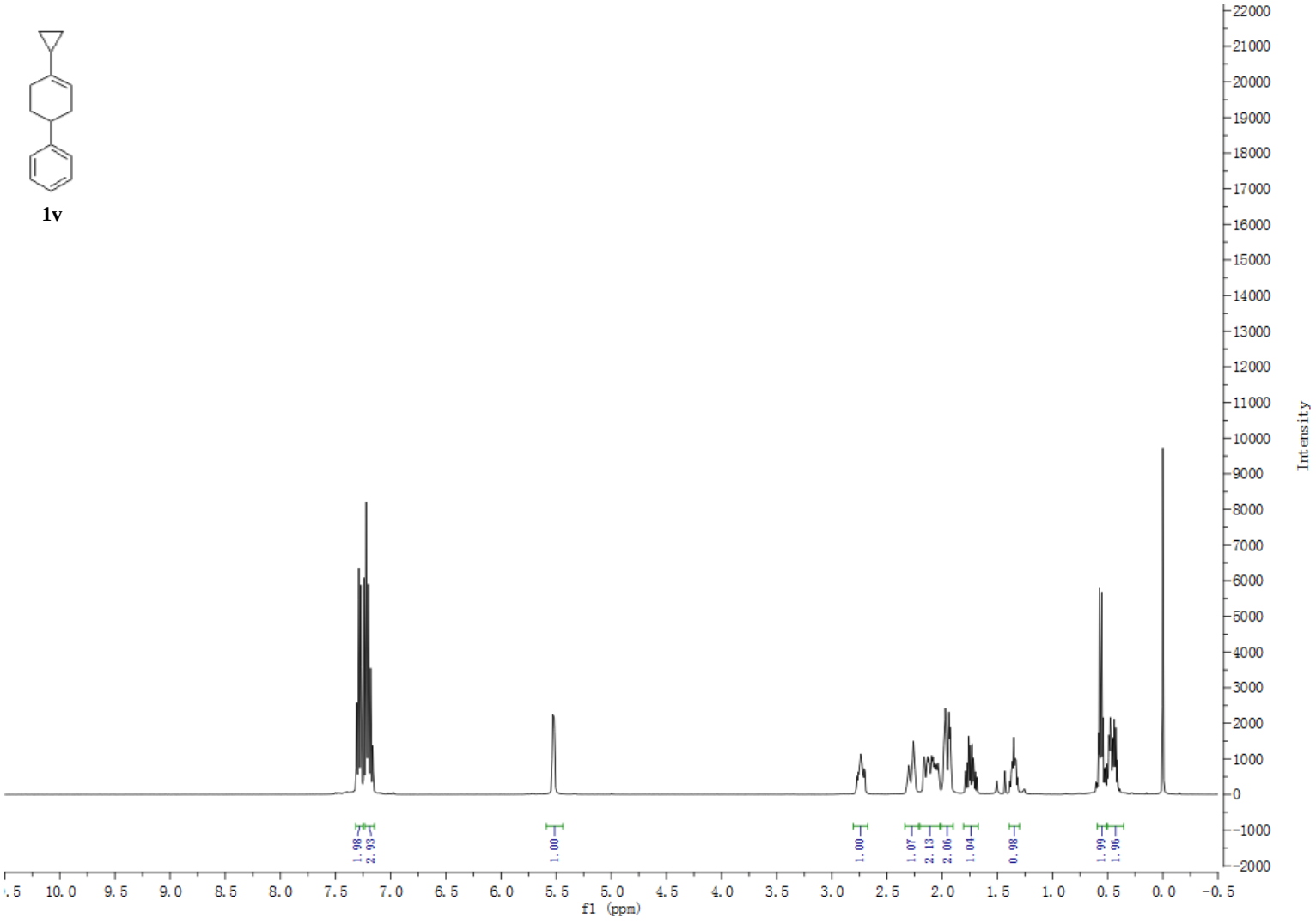
Intensity
f1 (ppm)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Intensity
f1 (ppm)
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1.00
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2.13
2.06
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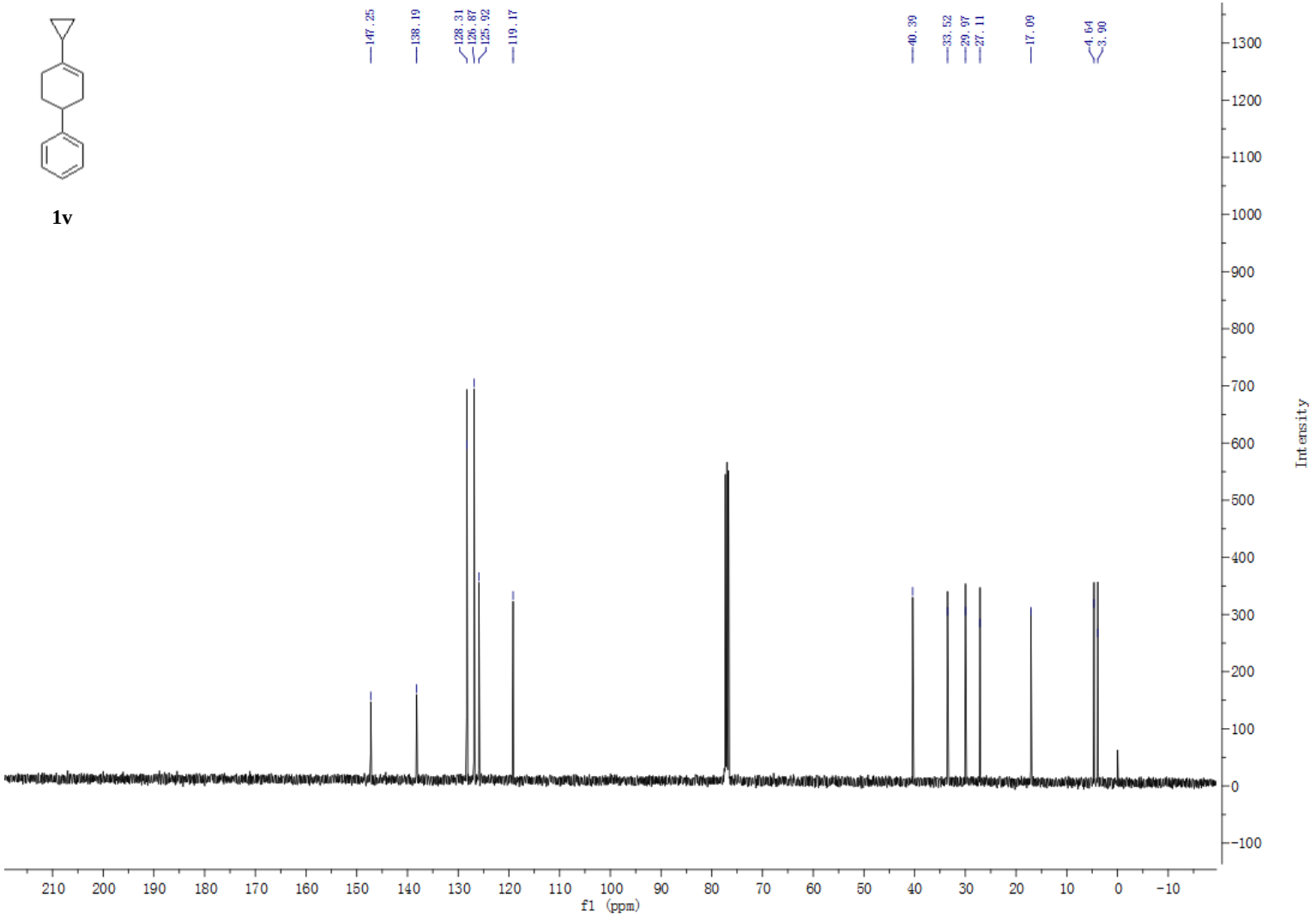
0.98
1.99
1.96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138.19
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126.87
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40.39
33.52
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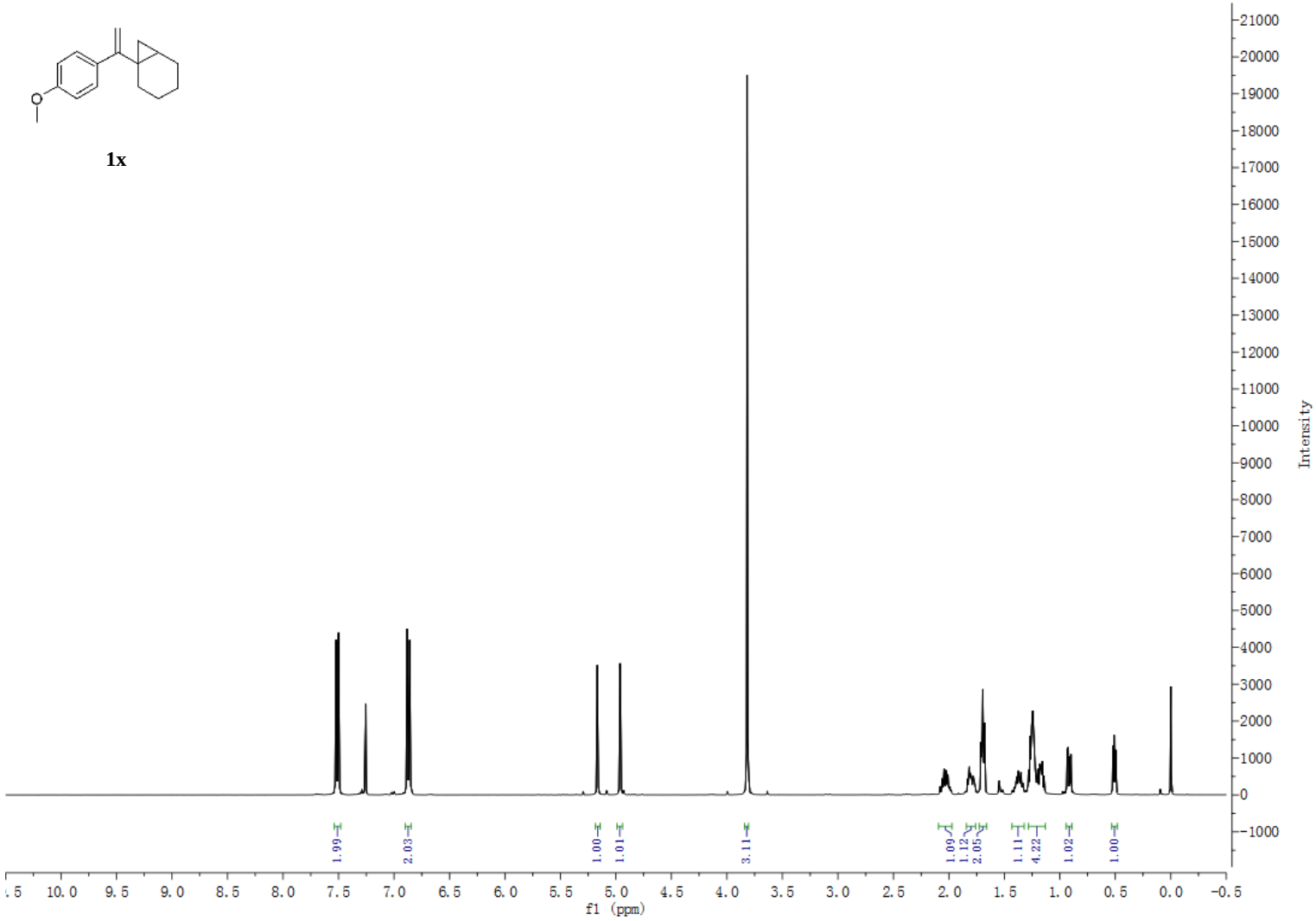
27.11
17.09
4.64
3.90
Intensity
f1 (ppm)

1v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f1 (ppm)
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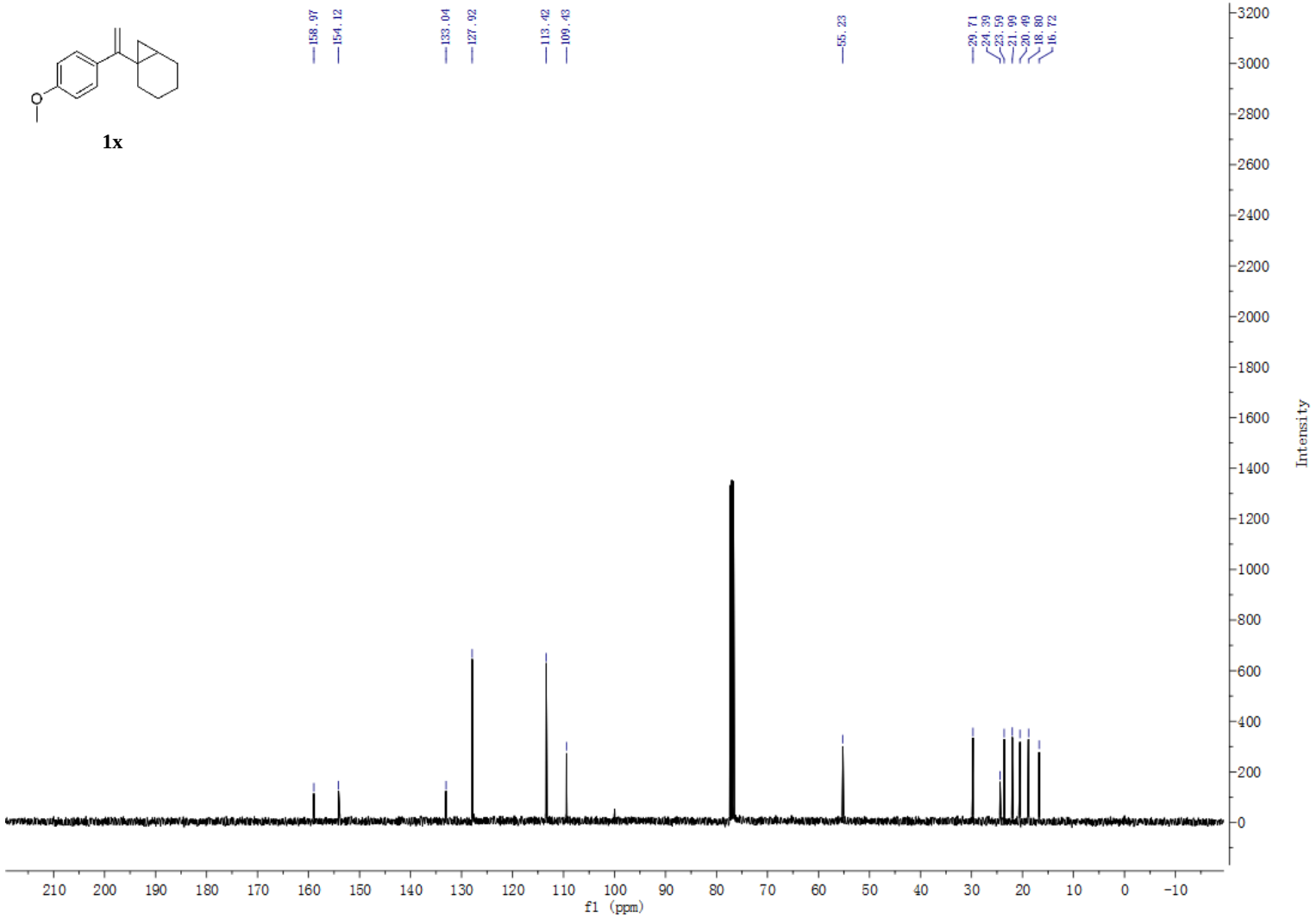
1.02
1.00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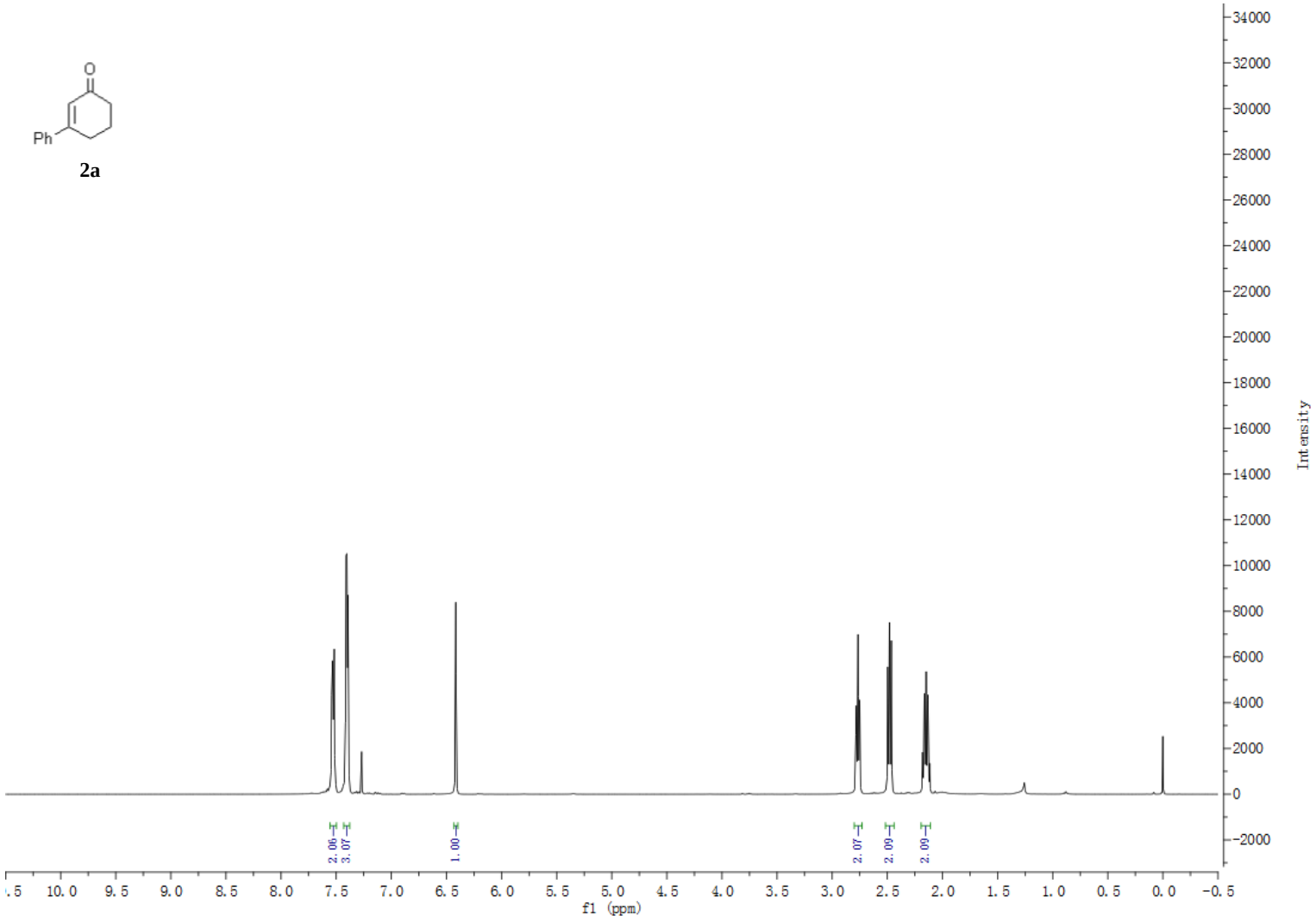
Intensity
f1 (ppm)

1x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10000
8000
6000
4000
2000
0
-2000
Intensity
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3.07
1.00
2.07
2.09
2.09
10.0
9.5
9.0
8.5
8.0
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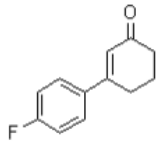
f1 (ppm)


O
F

2b

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5000
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3000
2000
1000
0
-1000
Intensity
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1.99
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2.00
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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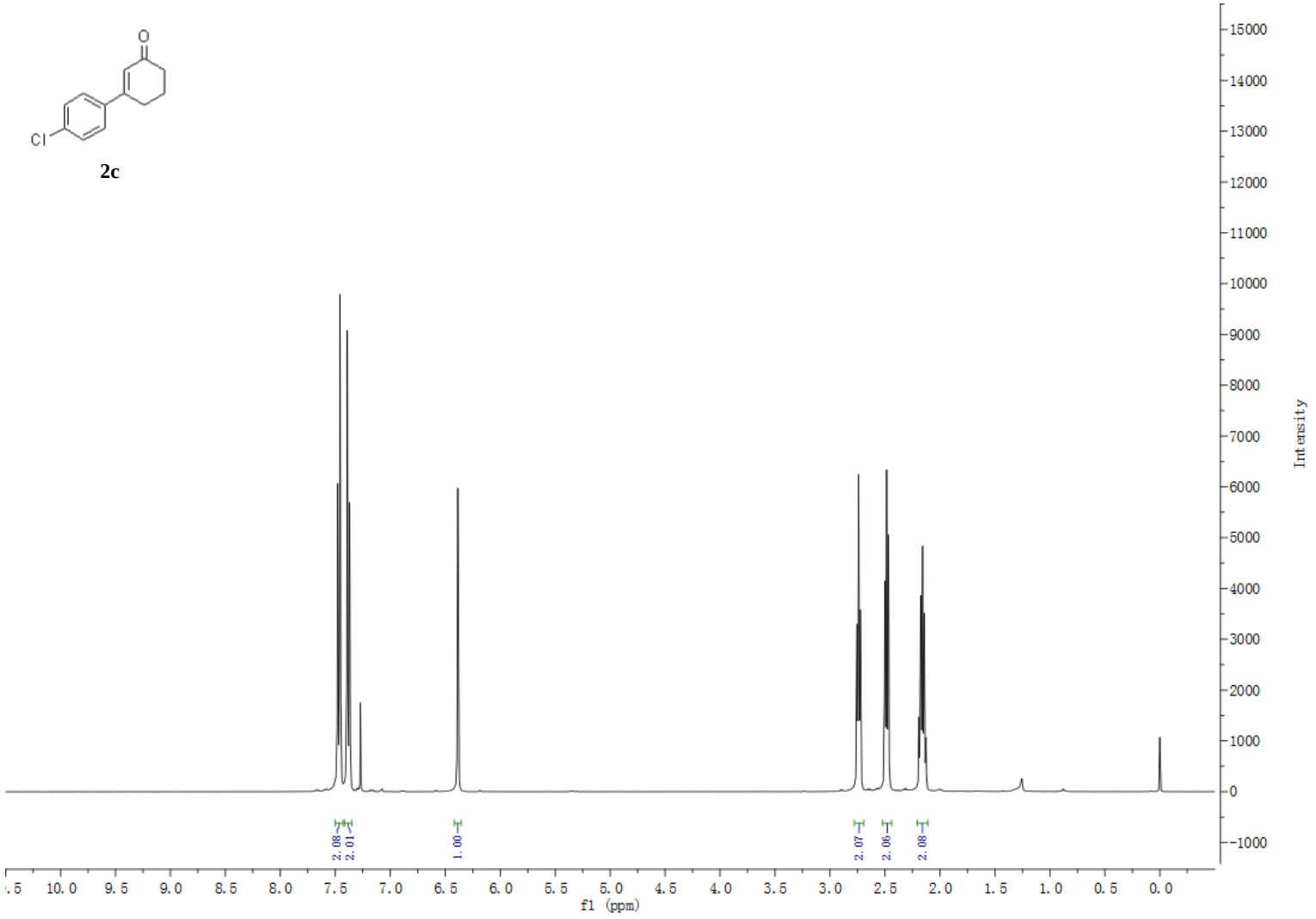
f1 (ppm)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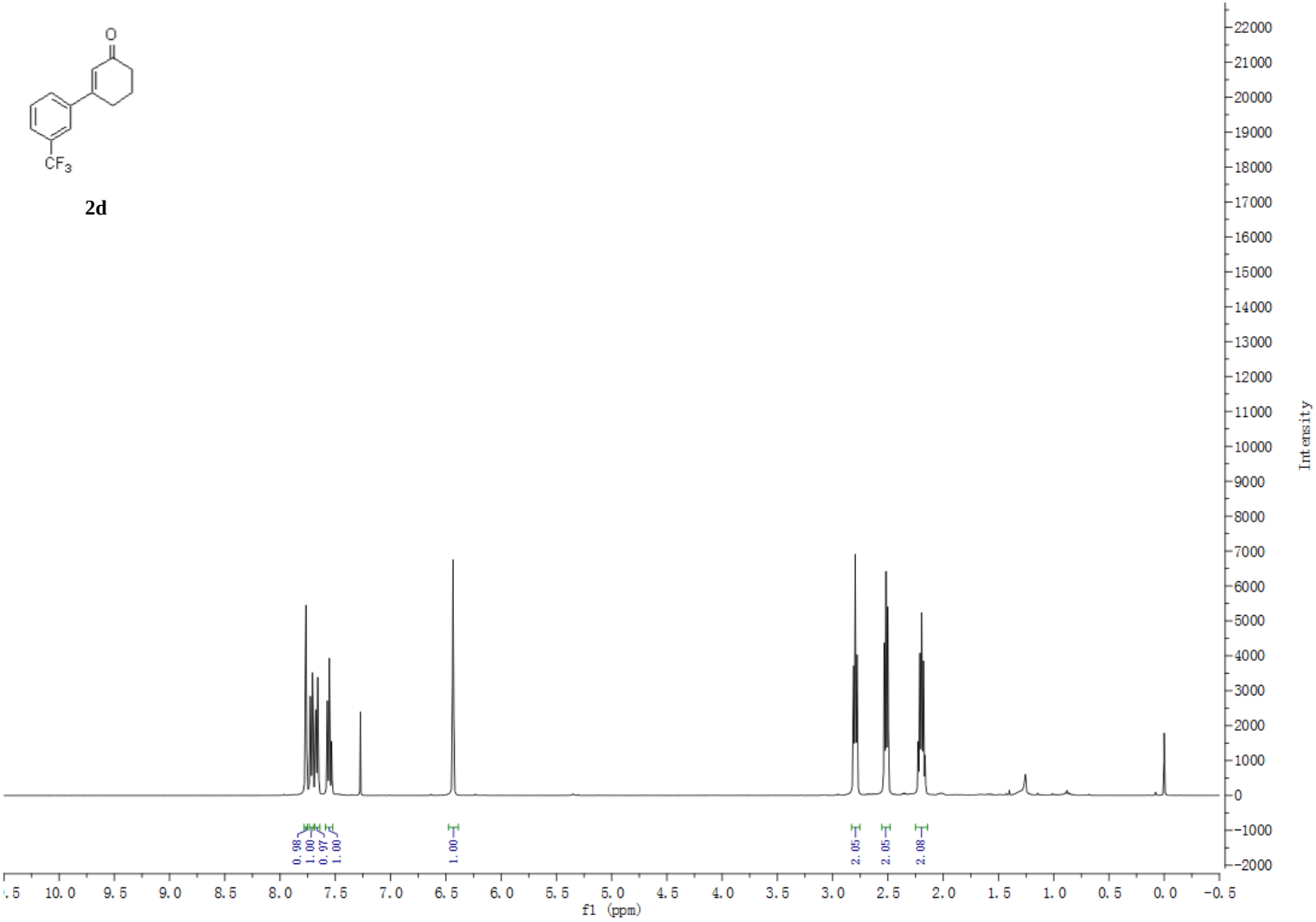
f1 (ppm)

2c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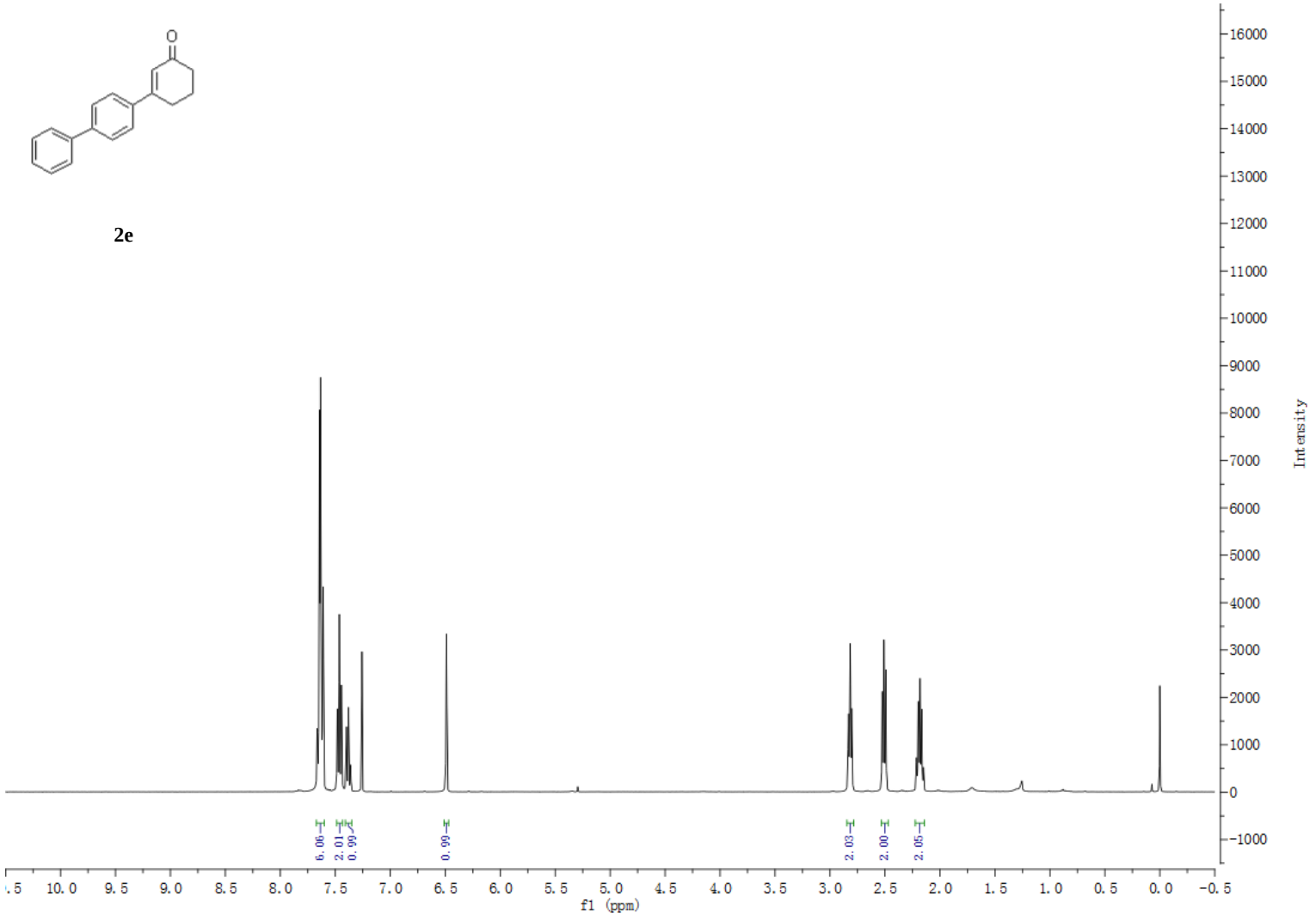
2.08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1000
0
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Intensity
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2.05
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7.5
7.0
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6.0
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5.0
4.5
4.0
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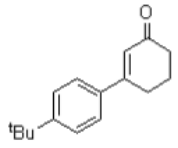
f1 (ppm)


O
tBu

2f

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1E+05
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1E+05
1E+05
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70000
60000
50000
40000
30000
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10000
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9.13
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9.0
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8.0
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3.0
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1.0
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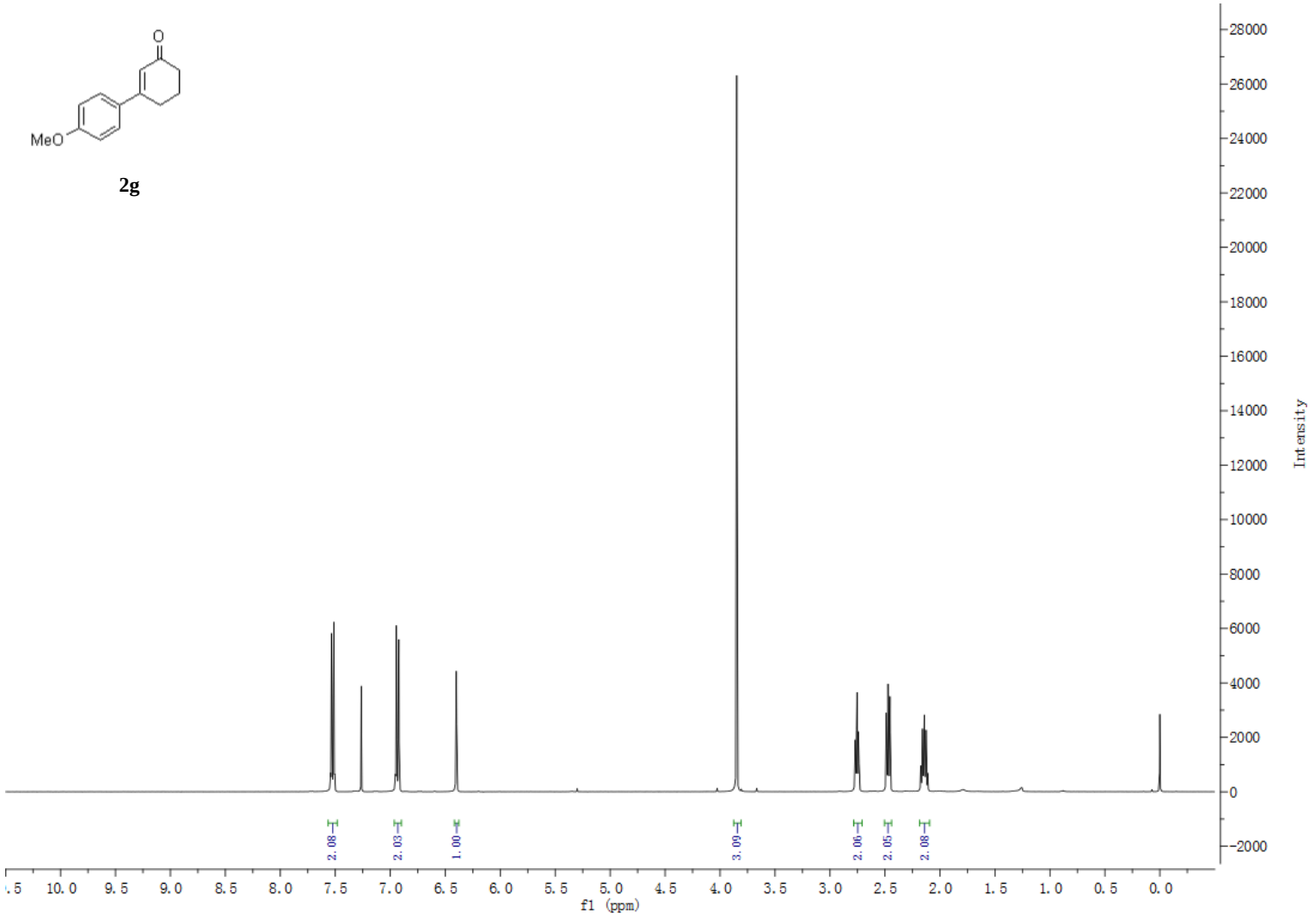
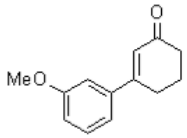
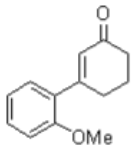
0.0
f1 (ppm)


O
MeO
2g
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
2.08
2.03
1.00
3.09
2.06
2.05
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


MeO
O

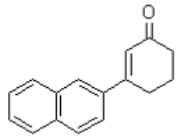
2h

38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
1.00
1.01
0.98
0.97
0.95
2.99
2.07
2.02
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

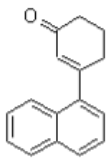

O
OMe

2i

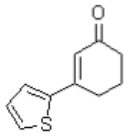
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
1.05
1.05
1.05
1.03
1.00
3.15
2.04
2.10
2.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



2j

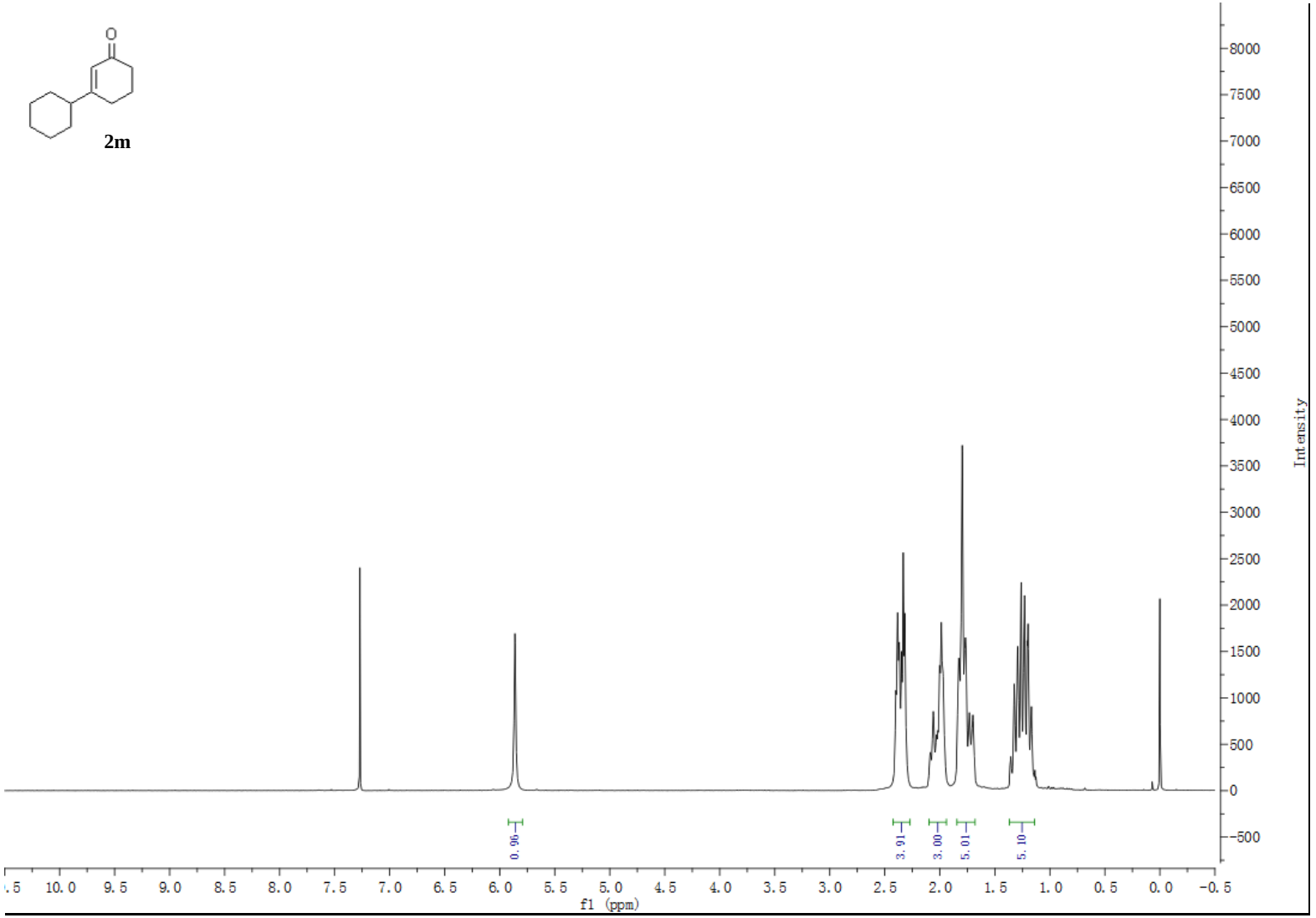


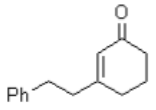
2k


O
S

21

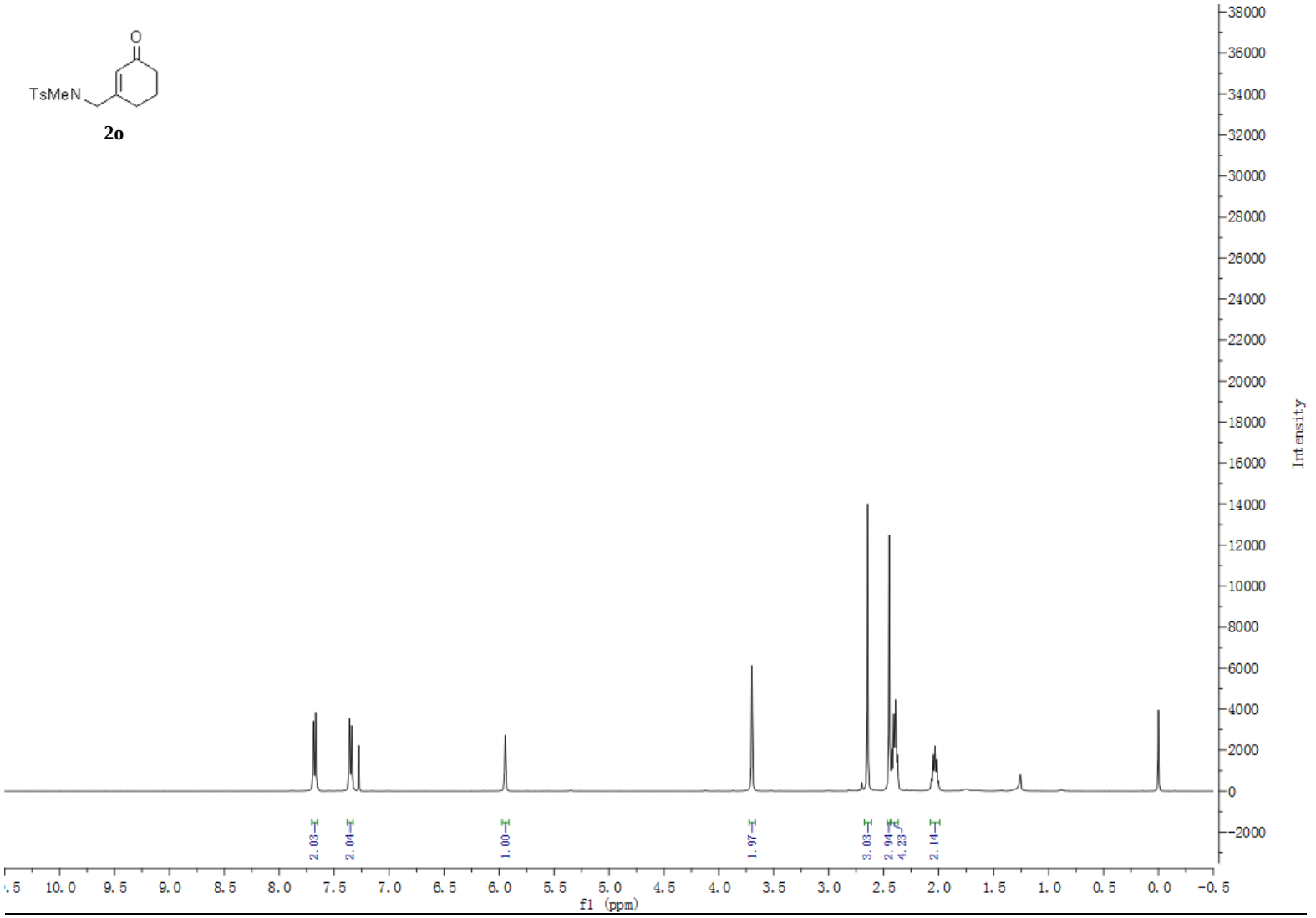
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
1.01
0.98
0.98
1.00
2.02
2.02
2.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

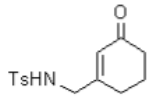

O
2m
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
Intensity
0.96
3.91
3.00
5.01
5.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
Ph

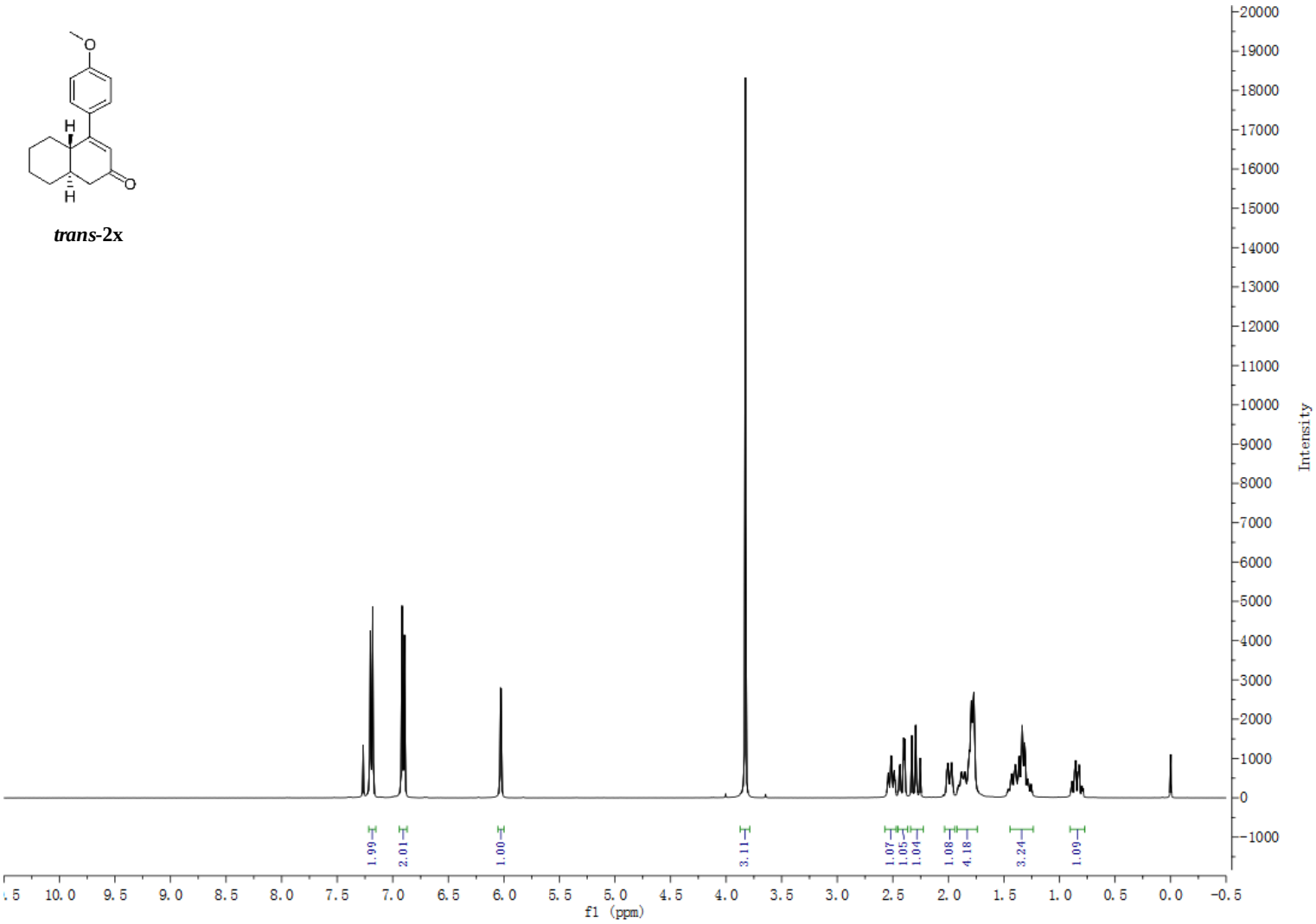
2n

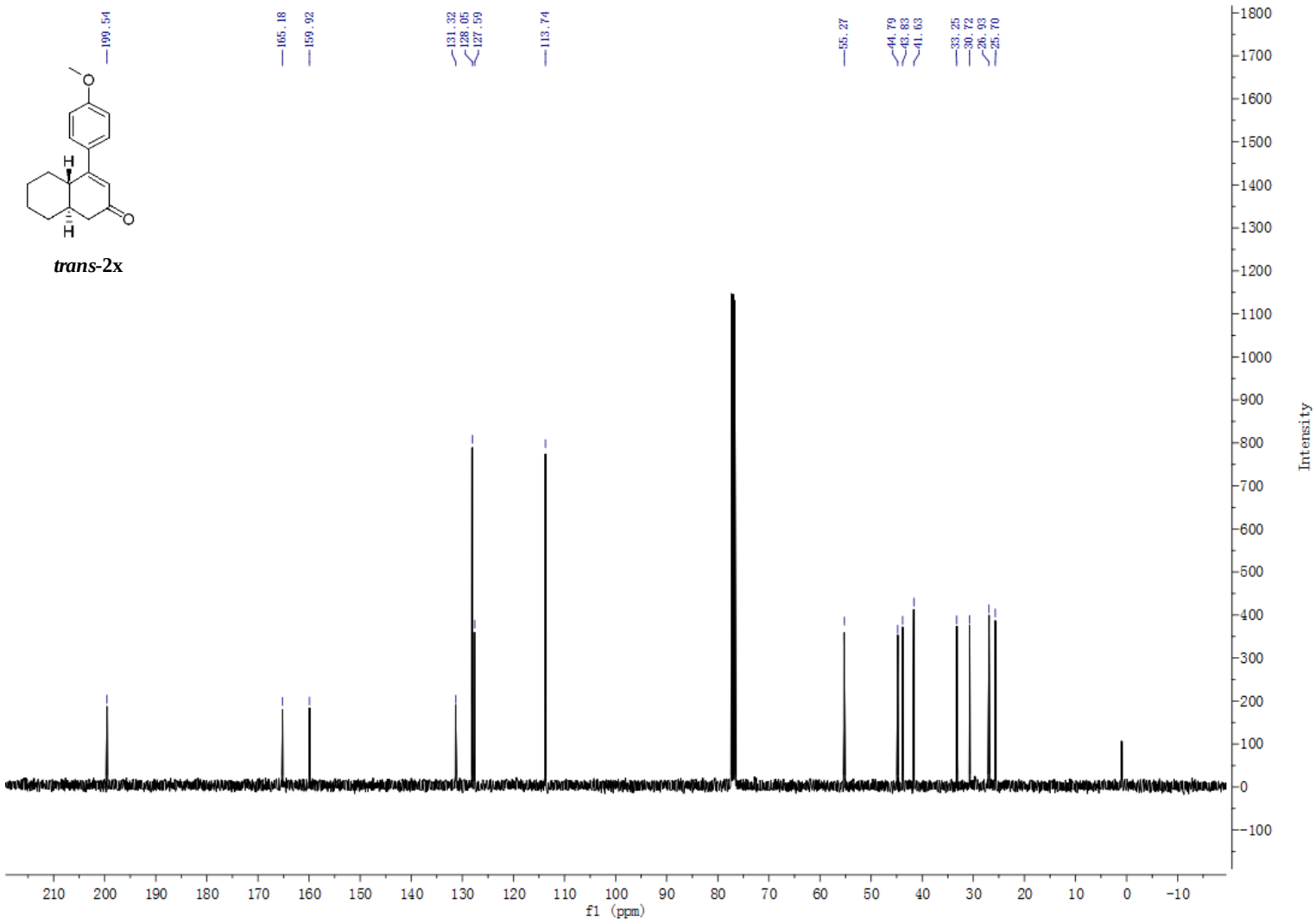
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
2.06
3.09
1.00
2.05
2.08
2.05
2.06
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
TsMeN
2o
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
2.03
2.04
1.00
1.97
3.03
2.94
4.23
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

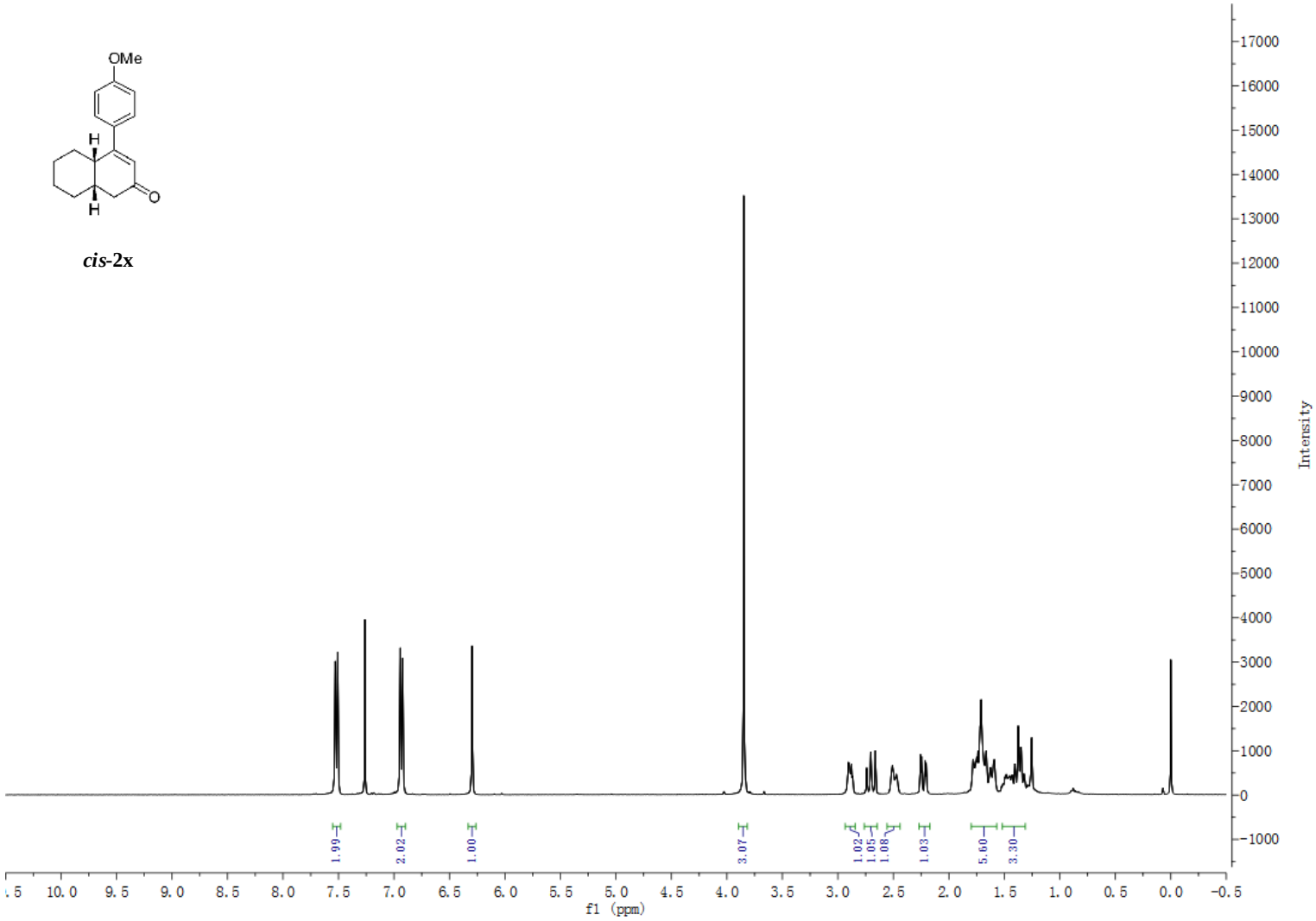


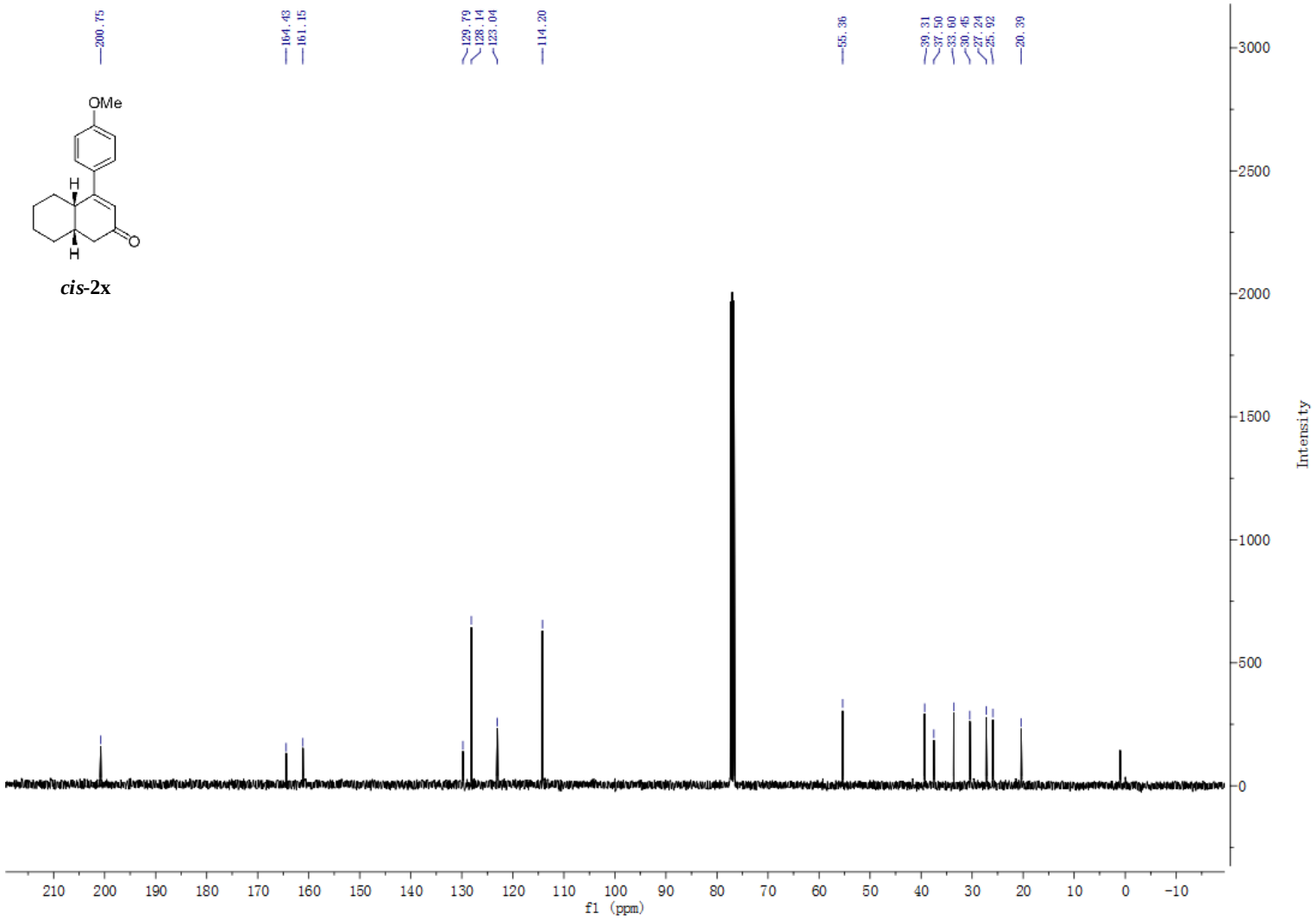
2p


O
H
H
O
trans-2x
1.99
2.01
1.00
3.11
1.07
1.05
1.04
1.08
4.18
3.24
1.09
f1 (ppm)
Intensity


199.54
165.18
159.92
131.32
128.05
127.59
113.74
55.27
44.79
43.83
41.63
33.25
30.72
26.93
25.70
Intensity
f1 (ppm)

***trans*-2x**


OMe
H
H
O
cis-2x
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
1.99
2.02
1.00
3.07
1.02
1.05
1.08
1.03
5.60
3.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


200.75
164.43
161.15
129.79
128.14
123.04
114.20
55.36
39.31
37.50
33.60
30.45
27.24
25.92
20.39
OMe
H
H
O
3000
2500
2000
1500
1000
500
0
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

***cis*-2x**