Supporting Information for

Modular access to 1,2-allenyl ketones based on photoredox-catalysed radical-polar crossover process

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1 General information

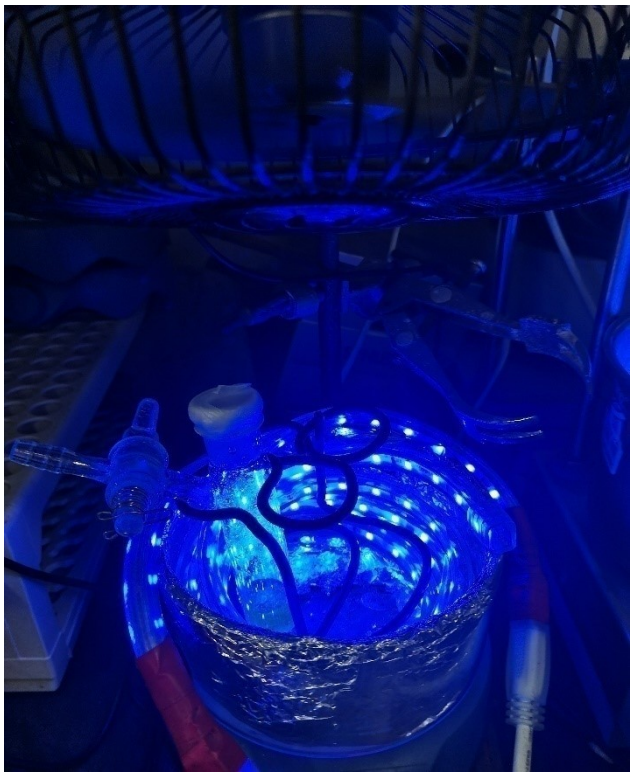
1.1 Solvents, reagents, and starting materials

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Photocatalysts $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$,[1a] 4CzIPN,[1b] and$Ru(bpz)_3(PF6)_2$[1c] were prepared according to published procedures. Alkylbis(catecholato)silicates **2** were reported in our previous literatures.[2] 4-Alkyldihydropyridines **3**,[3] were prepared using available protocols. Dried solvents were obtained from commercial sources and used without further purification unless otherwise noted.

1.2 Instruments

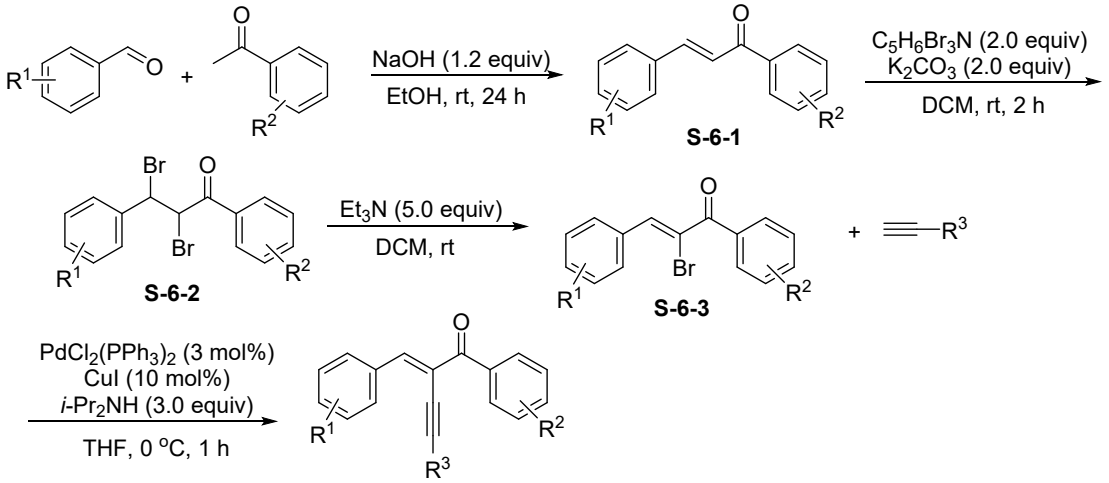
NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz) (500 MHz for ^1H NMR, 126 MHz for ^{13}C NMR, and 471 MHz for ^{19}F NMR). Chemical shifts were reported in ppm downfield from tetramethylsilane, and calibrated using residue undeuterated solvent ($CDCl_3$ at 7.26 ppm ^1H NMR; 77.0 ppm ^{13}C NMR, Aceton-*d*6 at 2.05 ppm ^1H NMR; 206.68, 29.92 ppm ^{13}C NMR, DMSO-*d*6 at 2.50 ppm ^1H NMR, 39.51ppm ^{13}C NMR). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m= multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on Agilent 6210 ESI/TOF MS, Thermo QExactive Plus, and Waters G2-Xs QTOF mass spectrometers. Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions. Flash column chromatography was performed using silica gel (300-400 mesh) with solvents to use.

1.3 Picture of a typical reaction setup



2 Synthesis of various 2-(1-alkynyl)-2-alken-1-ones

2.1 General procedure for the preparation of various 2-(1-alkynyl)-2-alken-1-ones 1, 6a-6e, 6g-6j, 6l-6n, 8a, and 10[4-7]



To a mixture of acetophenone (20.0 mmol, 1.0 equiv) and corresponding aldehyde (20.0 mmol, 1.0 equiv) in mixture ethanol/water (100 mL, 1:1), solution of sodium hydroxide (0.96 g, 24.0 mmol, 1.2 equiv) in 5 mL of water was added dropwise at room temperature and the resulted solution was stirred for 20 hours at room temperature. The precipitate formed was then filtered, washed with water and ethanol. The product was recrystallized from ethyl acetate/hexane to afford the desired product **S-6-1** with good yield.

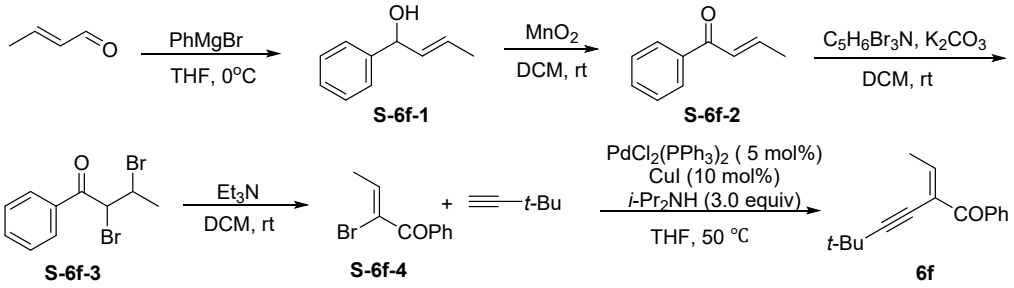
To a solution of (*E*)-prop-2-en-1-one **S-6-1** (15.0 mmol, 1.0 equiv) in DCM (50 mL), pyridinium tribromide (9.6 g, 30.0 mmol, 1.0 equiv) and potassium carbonate (4.2 g, 30.0 mmol, 2.0 equiv) was added, and the mixture was stirred for 2 h at room temperature. Then, the saturated $Na_2S_2O_3$ solution was added, the mixture was filtered and extracted with ethyl acetate (3x15 mL), dried over $MgSO_4$,the solvent was evaporated in vacuum. The product was recrystallized from DCM/hexane to afford the desired product **S-6-2** with good yield.

To a solution of 2,3-dibromopropan-1-one **S-6-2** (10.0 mmol, 1.0 equiv) in DCM (30 mL), triethylamine (7 mL, 50.0 mmol, 5.0 equiv) was added and the reaction mixture was stirred at room temperature for 12-36 h. Then, the saturated NH_4Cl solution (20 mL) was added, phases were separated, water phase was extracted by ethyl acetate (3x15 mL). Combined organic phase was washed with 1M HCl (4x15 mL), dried over $MgSO_4$ and evaporated in vacuo. The mixture was purified by flash

column chromatography to afford **S-6-3**.

A solution of (*Z*)-2-bromoprop-2-en-1-one **S-6-3** (5.0 mmol, 1.0 equiv) in THF (25 mL) was treated with $PdCl_2(PPh_3)_2$ (105.3 mg, 0.15 mmol, 3 mol%) and CuI (95.2 mg, 0.5 mmol, 10 mol%) and cooled down to 0°C in the dark. After 10 min of stirring, 3,3-dimethylbut-1-yne (1.2 mL, 10.0 mmol, 2.0 equiv) and diisopropylamine (2.1 mL, 15.0 mmol, 3.0 equiv) were added, and the resulting dark brown solution was stirred at 0 °C for 1 h. The reaction mixture was partitioned between ethyl acetate and 0.5 N aqueous HCl solution. The aqueous layer was extracted with ethyl acetate (3x10 mL) and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield the corresponding 2-(1-alkynyl)-2-alken-1-one.

2.2 Procedure for the preparation of 1,3-enyne 6f[5-9]



To a solution of crotonaldehyde (6.5 mL, 78.0 mmol, 1.0 equiv) in THF (100 mL), newly prepared phenyl Grignard reagent (80.0 mmol, 1.03 equiv) was added dropwise at 0°C. The mixture was stirred for 1 h. Then, the reaction solution was diluted with saturated NH_4Cl aqueous solution, and was extracted with ethyl acetate (4 x 15 mL). The organic layer was washed with saturated brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **S-6f-1** (eluent = petroleum ether / ethyl acetate 10:1 v/v).

To a solution of (*E*)-1-phenylbut-2-en-1-ol **S-6f-1** (35.0 mmol, 1.0 equiv) in DCM, MnO_2 (33.5 g, 385.0 mmol, 11.0 equiv) was added. The mixture was stirred at room temperature for 6 h. The reaction was completed monitored by TLC analysis, then filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **S-6f-2**.

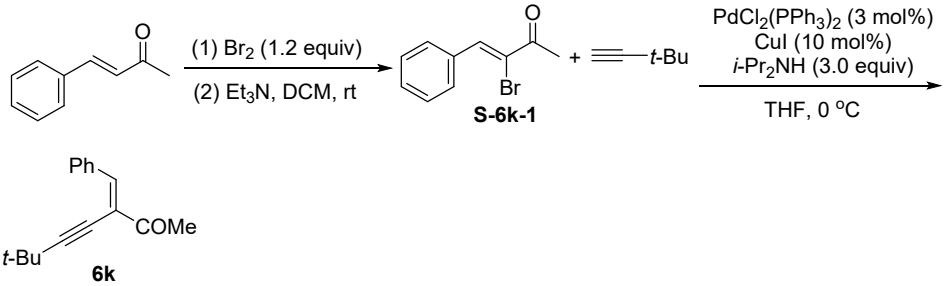
To a solution of (*E*)-1-phenylbut-2-en-1-one **S-6f-2** (15.0 mmol, 1.0 equiv) in DCM (50 mL), pyridinium tribromide (9.6 g, 30.0 mmol, 2.0 equiv) and potassium carbonate (4.2 g, 30.0 mmol, 2.0 equiv) was added, and the mixture was stirred for 2 h at room temperature. Then the saturated $Na_2S_2O_3$ solution was added, the mixture was filtered and extracted with ethyl acetate (3 x 15 mL), dried over $MgSO_4$, the solvent was evaporated in vacuum to give **S-6f-3**.

To a solution of 2,3-dibromo-1-phenylbutan-1-one **S-6f-3** (10.0 mmol, 1.0 equiv) in DCM (30 mL), triethylamine (7 mL, 50.0 mmol, 5.0 equiv)was added and the reaction mixture was stirred at room temperature for 24 h. Then, the saturated NH_4Cl solution (20 mL) was added, phases were separated, water phase was extracted by ethyl acetate (3 x 15 mL). Combined organic phase was washed with 1M HCl (3 x 10 ml),

dried over $MgSO_4$ and evaporated in vacuo. The mixture was purified by flash column chromatography to afford **S-6f-4**.

A solution of (*Z*)-2-bromo-1-phenylbut-2-en-1-one **S-6f-4** (5.0 mmol, 1.0 equiv) in THF (25 mL) was treated with $PdCl_2(PPh_3)_2$ (105.3 mg, 0.15 mmol, 3 mol%) and CuI (95.2 mg, 0.5 mmol, 10 mol%) and cooled down to 0°C in the dark. After 10 min of stirring, 3,3-dimethylbut-1-yne (1.2 mL, 10.0 mmol, 2.0 equiv) and diisopropylamine (2.1 mL, 15.0 mmol, 3.0 equiv) were added, and the resulting dark brown solution was stirred at 0 °C for 1 h. The reaction mixture was partitioned between ethyl acetate and 0.5 N aqueous HCl solution. The aqueous layer was extracted with ethyl acetate (3 x 10mL) and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield 1,3-enyne **6f** as a yellow liquid.

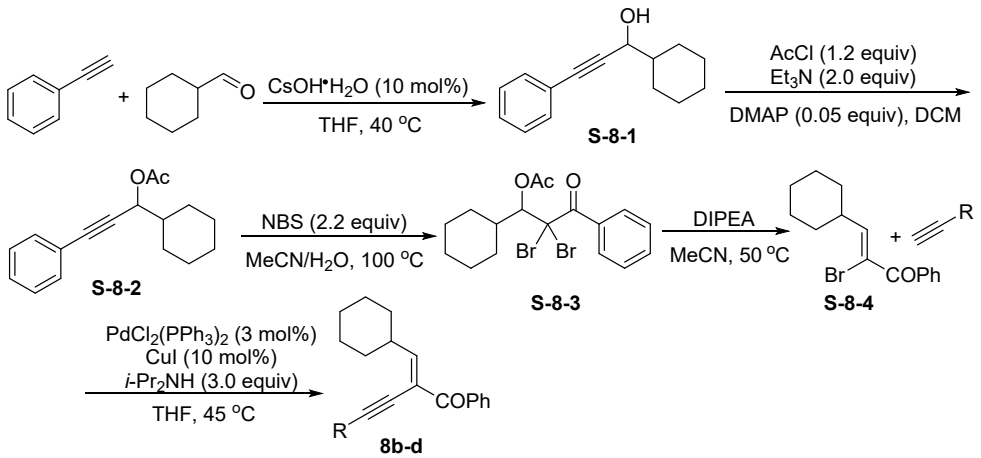
2.3 Procedure for the preparation of 1,3-enyne 6k[6,7]



To a solution of benzalacetone (2.9 g, 20 mmol) in chloroform (40 mL), bromine (1.3 mL, 24 mmol, 1.2 equiv) was added and the mixture was stirred for 16 h at room temperature and the solvent was evaporated in vacuum. Then a solution of triethylamine (6 mL, 43.1 mmol, 2.15 equiv) in DCM (40 mL) was added and the reaction mixture was stirred at room temperature for next 16 h. Then the concentrated NH_4Cl solution (25 mL) was added, phases were separated, water phase was extracted by ethyl acetate (3x15 mL). Combined organic phase was washed with1M HCl (4x15 mL), dried over Na_2SO_4 and evaporated in vacuo. The mixture was purified by flash column chromatography to afford **S-6k-1**.

A solution of (*Z*)-3-bromo-4-phenylbut-3-en-2-one **S-6k-1** (1.1 g, 5.0 mmol, 1.0 equiv) in THF (25 mL) was treated with $PdCl_2(PPh_3)_2$ (105.3 mg, 0.15 mmol, 3 mol%) and CuI (95.2 mg, 0.5 mmol, 10 mol%) and cooled down to 0°C in the dark. After 10 min of stirring, 3,3-dimethylbut-1-yne (1.2 mL, 10.0 mmol, 2.0 equiv) and diisopropylamine (2.1 mL, 15.0 mmol, 3.0 equiv) were added, and the resulting dark brown solution was stirred at 0 °C for 1 h. The reaction mixture was partitioned between ethyl acetate and 0.5 N aqueous HCl solution. The aqueous layer was extracted with ethyl acetate (3x10 mL) and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield 1,3-enyne **6k** as a yellow liquid.

2.4 General procedure for the preparation of various 2-(1-alkynyl)-2-alken-1-ones 8b-8d[7,10-12]



A 250 mL Schlenk flask was charged with CsOH•H_2O (840 mg, 5.0 mmol, 10 mol%). THF (100 mL) and phenylacetylene (7.6 g, 75.0 mmol, 1.5 equiv) were added successively by syringe. The reaction mixture was vigorously stirred and cyclohexanecarboxaldehyde (5.6 g, 50.0 mmol, 1.0 equiv) was added slowly and stirred at 40 °C for 6 h. Then, H_2O (30 mL) was added to quench the reaction and the mixture was extracted by ethyl acetate. The combined organic layer was dried over $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography on silica gel (eluent = petroleum ether /ethyl acetate 20:1 v/v) to afford the desired product **S-8-1** as a colorless oil.

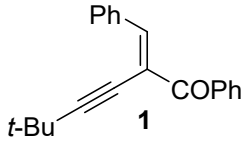
To a solution of 1-cyclohexyl-3-phenylprop-2-yn-1-ol **S-8-1** (8.5 g, 39.7 mmol, 1.0 equiv), Et_3N (11 mL, 79.4 mmol, 2.0 equiv), and DMAP (243 mg, 2.0 mmol, 5 mol%) in DCM (100 mL) was added acetylchloride (3.4 mL, 47.7 mmol, 1.2 equiv) and the mixture was stirred at room temperature overnight. Then the mixture was quenched with water (30 mL) and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (15 mL) and dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether /ethyl acetate 30:1 v/v) to give propargylic acetate **S-8-2**.

The solution of propargylic acetate **S-8-2** (2.0 g, 7.8 mmol, 1.0 equiv) and NBS (3.15 g, 17.7 mmol, 2.2 equiv) in CH_3CN/H_2O (40 mL, 1:1 mixture) was stirred for 2 h at 100 °C. Reaction mixture was quenched with saturated brine solution (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with saturated brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure and purification of the crude reaction mixture by flash column chromatography (petroleum ether /ethyl acetate 40:1 v/v) gave the 2,2-dibromopropargylic acetate **S-8-3** as a colorless oil.

The solution of 2,2-dibromopropargylic acetate **S-8-3** (2.58 g, 6.0 mmol, 1.0 equiv)

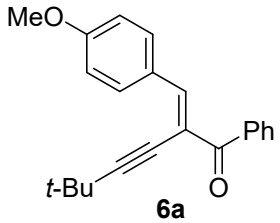
and DIPEA (3.0 mL, 18.0 mmol, 3.0 equiv) in MeCN (40 mL) was stirred overnight at 50 °C. The reaction solution was diluted with 1N HCl aqueous solution, and was extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **S-8-4** (eluent = petroleum ether / ethyl acetate 40:1 v/v).

A solution of (*Z*)-2-bromo-3-cyclohexyl-1-phenylprop-2-en-1-one **S-8-4** (1.39 g, 5.0 mmol, 1.0 equiv) in THF (25 mL) was treated with $PdCl_2(PPh_3)_2$ (105.3 mg, 0.15 mmol, 3 mol%) and CuI (95.2 mg, 0.5 mmol, 10 mol%) and cooled down to 0°C in the dark. After 10 min of stirring, alkyne (10.0 mmol, 2.0 equiv) and diisopropylamine (2.1 mL, 15.0 mmol, 3.0 equiv) were added, and the resulting dark brown solution was stirred at 45 °C for several hours. The reaction mixture was partitioned between ethyl acetate and 0.5 N HCl aqueous solution. The aqueous layer was extracted with ethyl acetate (3 x 10mL) and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography to yield the corresponding 2-(1-alkynyl)-2-alken-1-one **8**.



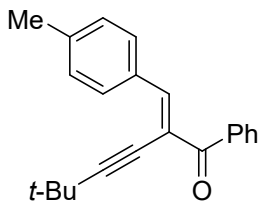
1

(*E*)-2-benzylidene-5,5-dimethyl-1-phenylhex-3-yn-1-one (1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 7.96-7.93 (m, 2H), 7.56-7.53 (m, 1H), 7.51 (s, 1H), 7.47-7.39 (m, 5H), 1.26 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 143.6, 137.2, 135.0, 132.2, 130.2, 130.1, 129.7, 128.3, 127.8, 121.5, 110.7, 77.2, 30.3, 28.7. These data are consistent with the published literature.[7]



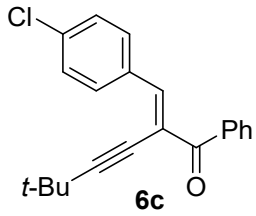
6a

(*E*)-2-(4-methoxybenzylidene)-5,5-dimethyl-1-phenylhex-3-yn-1-one (6a), bright yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 7.92-7.90 (m, 2H), 7.54-7.51 (m, 2H), 7.44-7.41 (m, 2H), 6.94-6.91 (m, 2H), 3.87 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 161.2, 143.9, 137.7, 132.1, 131.9, 129.6, 127.9, 127.7, 118.9, 113.7, 110.0, 77.5, 55.4, 30.4, 28.6. HRMS (ESI) $[M+H]^+$: calculated for $C_{22}H_{23}O_2$: 319.1698, found 319.1697.



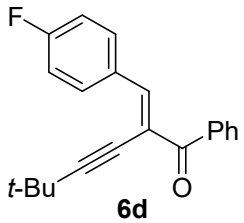
6b

(*E*)-5,5-dimethyl-2-(4-methylbenzylidene)-1-phenylhex-3-yn-1-one (6b), pale yellow oil. 1H NMR (500 MHz, CDCl3) δ 8.00-7.98 (m, 2H), 7.94-7.92 (m, 2H), 7.55-7.52 (m, 1H), 7.50 (s, 1H), 7.45-7.42 (m, 2H), 7.22 (d, *J* = 5.0 Hz, 2H), 2.40 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 144.0, 140.7, 137.5, 132.3, 132.1, 130.2, 129.7, 129.1, 127.7, 120.4, 110.4, 77.4, 30.4, 28.6, 21.6. HRMS (ESI) $[M+H]^+$: calculated for $C_{22}H_{23}O$: 303.1749, found 303.1752.



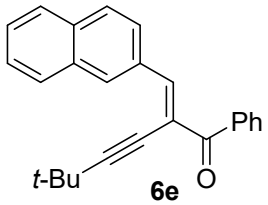
6c

(*E*)-2-(4-chlorobenzylidene)-5,5-dimethyl-1-phenylhex-3-yn-1-one (6c), pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.95-7.93 (m, 2H), 7.57-7.53 (m, 1H), 7.47-7.43 (m, 3H), 7.40-7.37 (m, 2H), 1.25 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 141.9, 137.0, 135.8, 133.5, 132.4, 131.2, 129.7, 128.6, 127.8, 121.9, 111.5, 77.1, 30.3, 28.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{20}OCl$: 323.1203, found 323.1202.



6d

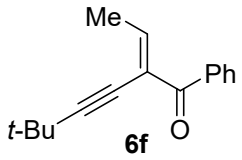
(*E*)-2-(4-fluorobenzylidene)-5,5-dimethyl-1-phenylhex-3-yn-1-one (6d), yellow brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.07 (m, 2H), 7.94-7.91 (m, 2H), 7.56-7.53 (m, 1H), 7.48 (s, 1H), 7.46-7.43 (m, 2H), 7.12-7.07 (m, 2H), 1.25 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 163.5 (d, *J*=253.2 Hz), 142.3, 137.1, 132.3, 132.1(d, *J* = 8.8 Hz), 131.3 (d, *J*=3.8 Hz), 129.7, 127.8, 121.0 (d, *J* = 2.6 Hz), 115.4 (d, *J*=21.4 Hz), 110.7, 77.1, 30.3, 28.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.75. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{20}OF$: 307.1498, found 307.1501.



6e

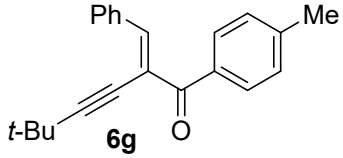
(*E*)-5,5-dimethyl-2-(naphthalen-2-ylmethylene)-1-phenylhex-3-yn-1-one (6e), yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65-8.60 (m, 1H), 8.18-8.13 (m, 1H), 7.99-7.97 (m, 2H), 7.87-7.84 (m, 3H), 7.68 (s, 1H), 7.58-7.49 (m, 3H), 7.48-7.44 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 143.7, 137.3, 134.1, 133.1, 132.6, 132.2, 130.4, 129.7, 128.7, 127.8, 127.7, 127.3, 127.0, 126.4, 121.6, 110.8,

77.5, 30.4, 28.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{25}H_{23}O$: 339.1749, found 339.1745.



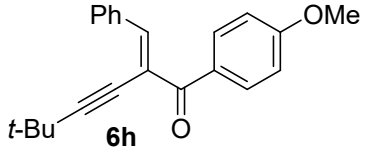
6f

(*E*)-2-ethylidene-5,5-dimethyl-1-phenylhex-3-yn-1-one (6f), pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.53-7.50 (m, 1H), 7.43-7.40 (m, 2H), 6.88 (q, *J* = 7.0 Hz, 1H), 2.07 (d, *J* = 6.9 Hz, 3H), 1.24 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 146.5, 137.3, 132.1, 129.5, 127.8, 126.3, 108.3, 74.3, 30.8, 28.3, 16.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{16}H_{19}O$:227.1436, found 227.1432.



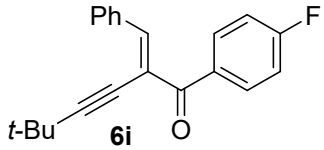
6g

(*E*)-2-benzylidene-5,5-dimethyl-1-(*p*-tolyl)hex-3-yn-1-one (6g), yellow brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.90-7.88 (m, 2H), 7.46 (s, 1H), 7.43-7.39 (m, 3H), 7.26-7.24 (m, 2H), 2.43 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 143.3, 143.1, 135.0, 134.3, 130.0 (2), 130.0 (1), 129.9 (9), 128.5, 128.2, 121.7, 110.4, 77.2, 30.3, 28.6, 21.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{22}H_{23}O$: 303.1749, found 303.1748.



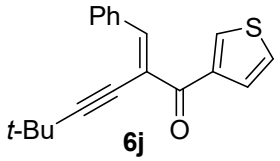
6h

(*E*)-2-benzylidene-1-(4-methoxyphenyl)-5,5-dimethylhex-3-yn-1-one (6h), yellow brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 8.04-8.01 (m, 2H), 7.43-7.37 (m, 4H), 6.95-6.92 (m, 2H), 3.88 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.3, 163.1, 142.7, 135.2, 132.3, 129.9(3), 129.8(9), 129.6, 128.2, 121.8, 113.1, 110.4, 77.4, 55.4, 30.4, 28.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{22}H_{23}O_2$: 319.1698, found 319.1693.



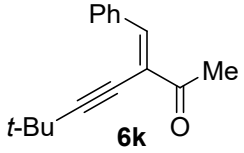
6i

(*E*)-2-benzylidene-1-(4-fluorophenyl)-5,5-dimethylhex-3-yn-1-one (6i), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 8.03-7.99 (m, 2H), 7.50 (s, 1H), 7.44-7.40 (m, 3H), 7.14-7.10 (m, 2H), 1.26 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 191.4, 164.6 (d, *J* = 251.7 Hz), 143.5, 134.3, 133.1(d, *J* = 2.9 Hz), 132.3 (d, *J* = 9.4 Hz), 130.7, 129.9, 128.5, 120.4, 115.3 (d, *J* = 22.1 Hz), 110.4, 76.9, 30.0, 28.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -106.18. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{20}OF$: 307.1498, found 307.1497.



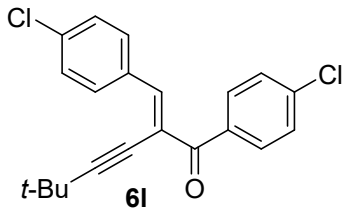
6j

(*E*)-2-benzylidene-5,5-dimethyl-1-(thiophen-3-yl)hex-3-yn-1-one (6j), bright yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.36 (m, 1H), 8.08-8.05 (m, 2H), 7.69-7.68 (m, 1H), 7.58 (s, 1H), 7.43-7.38 (m, 3H), 7.31-7.30 (m, 1H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.4, 143.3, 140.5, 135.0, 133.7, 130.1, 128.8, 128.3, 125.1, 121.5, 110.0, 77.4, 30.4, 28.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{19}H_{19}OS$: 295.1157, found 295.1159.



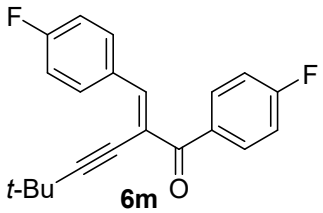
6k

(*E*)-3-benzylidene-6,6-dimethylhept-4-yn-2-one (6k), dark green solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.04 (m, 2H), 7.69 (s, 1H), 7.41-7.38 (m, 3H), 2.51 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 141.2, 134.7, 130.4, 130.3, 128.3, 120.5, 108.7, 77.0, 30.6, 28.7, 28.0. HRMS (ESI) $[M+H]^+$: calculated for $C_{16}H_{19}O$: 227.1436, found 227.1431.



6l

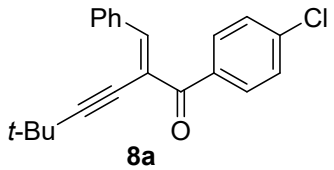
(*E*)-2-(4-chlorobenzylidene)-1-(4-chlorophenyl)-5,5-dimethylhex-3-yn-1-one (6l), pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-7.99 (m, 2H), 7.93-7.90 (m, 2H), 7.46 (s, 1H), 7.44-7.41 (m, 2H), 7.40-7.37 (m, 2H), 1.26 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 142.3, 138.8, 136.0, 135.3, 133.3, 131.2(5), 131.1(9), 128.6, 128.1, 121.4, 111.8, 77.0, 30.3, 28.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{19}OCl_2$: 357.0813, found 357.0813.



6m

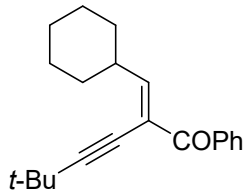
(*E*)-2-(4-fluorobenzylidene)-1-(4-fluorophenyl)-5,5-dimethylhex-3-yn-1-one (6m), yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10-8.07 (m, 2H), 8.03-7.99 (m, 2H), 7.48 (s, 1H), 7.14-7.08 (m, 4H), 1.26 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 165.4 (d, J = 221.8 Hz), 163.4 (d, J = 220.6 Hz), 142.2, 133.3 (d, J = 3.8 Hz), 132.4 (d, J = 10.0 Hz), 132.1 (d, J = 8.8 Hz), 131.2 (d, J = 3.8 Hz), 120.7 (d, J = 2.6 Hz), 115.5 (d, J = 25.2 Hz), 114.9 (d, J = 21.4 Hz), 111.0, 77.1, 30.3, 28.7. ^{19}F NMR (471 MHz,

$CDCl_3$) δ -106.06, -108.63. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{19}OF_2$: 325.1404, found 325.1400.



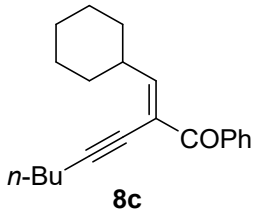
8a

(*E*)-2-benzylidene-1-(4-chlorophenyl)-5,5-dimethylhex-3-yn-1-one (8a), pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.94-7.91 (m, 2H), 7.51 (s, 1H), 7.44-7.40 (m, 5H), 1.27 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 143.9, 138.6, 135.5, 134.8, 131.2, 130.4, 130.2, 128.3, 128.1, 120.9, 111.0, 77.1, 30.3, 28.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{20}OCl$: 323.1203, found 323.1200.



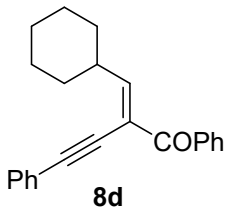
8b

(*E*)-2-(cyclohexylmethylene)-5,5-dimethyl-1-phenylhex-3-yn-1-one (8b), pale yellow oil. ^{1} H NMR (500 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2H), 7.53-7.50 (m, 1H), 7.42-7.39 (m, 2H), 6.65 (d, *J* = 9.2 Hz, 1H), 2.75-2.67 (m, 1H), 1.84-1.74 (m, 4H), 1.71-1.66 (m,1H), 1.41-1.16(m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 156.8, 137.4, 132.1, 129.6, 128.3, 127.8, 123.4, 107.4, 74.4, 40.1, 31.5, 30.7, 30.6, 28.3, 25.9, 25.6. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{27}O$: 295.2062, found 295.2060.



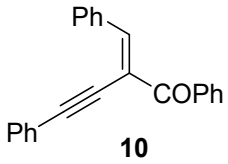
8c

(*E*)-2-(cyclohexylmethylene)-1-phenyloct-3-yn-1-one (8c), pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.79 (m, 2H), 7.55-7.50 (m, 1H), 7.44-7.40 (m, 2H), 6.58 (d, *J* = 9.5 Hz, 1H), 2.82-2.70 (m, 1H), 2.40 (t, *J* = 6.9 Hz, 2H), 1.84-1.73 (m, 4H), 1.72-1.66 (m, 1H), 1.59-1.48 (m, 2H), 1.46-1.37 (m, 2H), 1.37-1.29 (m, 2H), 1.28-1.14 (m, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.9, 157.0, 137.5, 132.1, 129.5, 127.9, 123.5, 99.1, 75.6, 40.1, 31.6, 30.6, 25.8, 25.5, 21.8, 19.3, 13.6. These data are consistent with the published literature.[13]



8d

(*E*)-2-(cyclohexylmethylene)-1,4-diphenylbut-3-yn-1-one (8d), pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.57-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.42-7.39 (m, 2H), 7.33-7.30 (m, 3H), 6.78 (d, *J* = 9.6 Hz, 1H), 2.91-2.83 (m, 1H), 1.89-1.85 (m, 2H),1.82-1.77 (m,2H),1.74-1.69 (m,1H), 1.44-1.35 (m,2H), 1.31-1.20 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 158.0, 137.3, 132.4, 131.4, 129.6, 128.5, 128.3, 128.0, 123.1, 122.9, 97.8, 84.6, 40.4, 31.6, 25.8, 25.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{23}O$: 315.1749, found 315.1745.

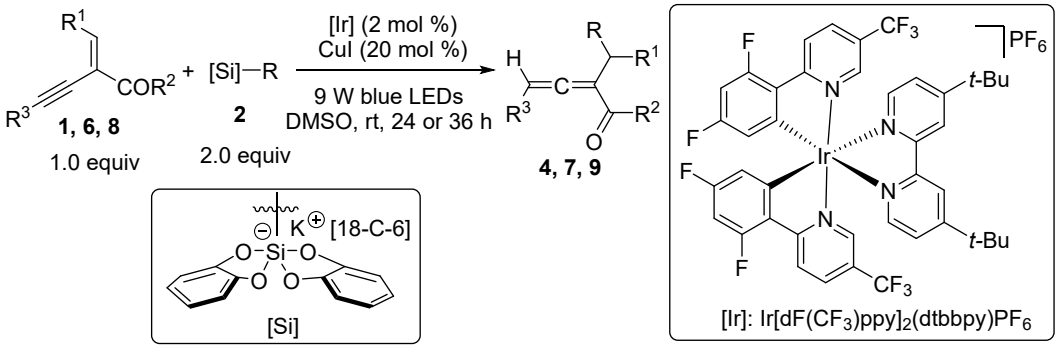


10

(*E*)-2-benzylidene-1,4-diphenylbut-3-yn-1-one (10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18-8.09 (m, 2H), 8.07-7.98 (m, 2H), 7.64 (s, 1H), 7.62-7.56 (m, 1H), 7.54-7.43 (m, 5H), 7.43-7.38 (m, 2H), 7.37-7.30 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 145.1, 137.1, 134.8, 132.5, 131.3, 130.6, 130.4, 129.7, 128.8, 128.6, 128.4, 128.1, 122.8, 120.9, 100.8, 87.1. These data are consistent with the published literature.[7]

3 General procedures of photocatalytic reactions between 1,3-enynes and alkylsilicates

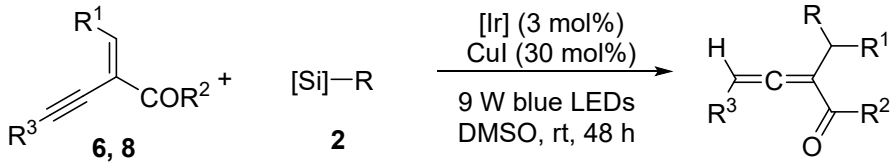
3.1 General procedure for the preparation of 1,2-allenyl ketones 4, 7a, 7e-7m, 9a-9c, and 9e-9g



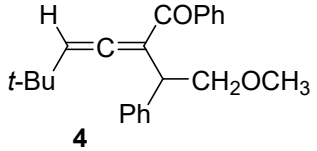
To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, CuI (7.6 mg, 0.04 mmol, 20 mol%), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5mg, 0.004 mmol, 2 mol%) and the 2-(1-alkynyl)-2-alken-1-one (0.2 mmol, 1.0 equiv) were added. In a glovebox, potassium [18-Crown-6] bis(catecholato) alkylsilicate **2** (0.4 mmol, 2.0

equiv) was added in the tube. The tube was sealed with a rubber septum and removed from the glovebox. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) *via* a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 or 36 h (cooling with a fan). After the reaction was completed, the reaction solution was diluted with saturated Na_2CO_3 aqueous solution, and was extracted with ethyl acetate (4 x 5 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product (eluent = petroleum ether / ethyl acetate 25:1 v/v).

3.2 General procedure for the preparation of 1,2-allenyl ketones 7b, 7c-7d, 9d, and 9h-j.



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 2 mol %) and the 2-(1-alkynyl)-2-alken-1-one (0.2 mmol, 1.0 equiv) were added. In a glovebox, potassium [18-Crown-6] bis(catecholato) alkylsilicate **2** (0.4 mmol, 2.0 equiv) and CuI (7.6 mg, 0.04 mmol, 20 mol%) were added in the tube. The tube was sealed with a rubber septum and removed from the glovebox. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 36 h (cooling with a fan). After 36 h, an additional portion of $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1 mol%), potassium [18-Crown-6] bis(catecholato) alkylsilicate **2** (0.2 mmol, 1.0 equiv), and CuI (3.8 mg, 0.02 mmol, 10 mol %) were added, and the reaction was stirred for an additional 12 h under irradiation. After the reaction was completed, the reaction solution was diluted with saturated Na_2CO_3 aqueous solution, and was extracted with ethyl acetate (4 x 5 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product (eluent = petroleum ether / ethyl acetate 25:1 v/v).



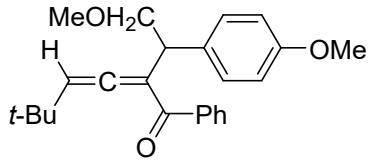
4

2-(2-Methoxy-1-phenylethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (4). Flash column chromatography to afford product **4** (52.8 mg, 79% yield, dr = 50:50).

The first fraction**:**colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.46-7.43 (m, 1H), 7.37-7.28 (m, 6H), 7.22-7.18 (m, 1H), 5.46 (d, *J* = 1.9 Hz, 1H), 4.48-4.45 (m, 1H), 3.77-3.71 (m, 2H), 3.35 (s, 3H), 0.80 (s, 9H). ^{13}C NMR (126 MHz,

$CDCl_3$) δ 211.4, 194.5, 140.8, 138.8, 131.4, 128.7, 128.3, 128.2, 127.5, 126.7, 111.6, 108.6, 74.8, 58.7, 43.1, 33.0, 29.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{27}O_2$: 335.2011, found 335.2013.

The second fraction: solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.45-7.41 (m, 1H), 7.36-7.28 (m, 6H), 7.22-7.19 (m, 1H), 5.51 (d, J = 1.8 Hz, 1H), 4.47-4.44 (m, 1H), 3.78-3.65 (m, 2H), 3.34 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.4, 141.1, 138.6, 131.4, 128.7, 128.3, 128.1, 127.5, 126.7, 111.2, 108.8, 75.4, 58.5, 42.9, 33.2, 29.6. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{27}O_2$: 335.2011, found 335.2015.

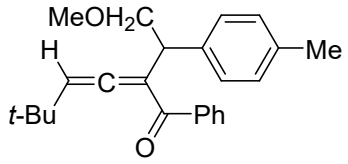


7a

2-(2-Methoxy-1-(4-methoxyphenyl)ethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (7a). Flash column chromatography to afford product **7a** (55.6 mg, 72% yield, dr = 43:57).

The first fraction**:** colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.44-7.41 (m, 1H), 7.34-7.31 (m, 2H), 7.28-7.25 (m, 2H), 6.85-6.82 (m, 2H), 5.50 (d, J = 1.8 Hz, 1H), 4.40-4.37 (m, 1H), 3.77 (s, 3H), 3.74-3.61 (m, 2H), 3.33 (s, 3H), 0.95 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 194.5, 158.3, 138.6, 133.2, 131.4, 129.0, 128.7, 127.5, 113.8, 111.4, 108.8, 75.6, 58.5, 55.2, 42.1, 33.2, 29.7.HRMS (ESI) $[M+Na]^+$: calculated for $C_{24}H_{28}O_3Na$: 387.1936, found 387.1932.

The second fraction: colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.46-7.43 (m, 1H), 7.34-7.32 (m, 2H), 7.28-7.26 (m, 2H), 6.85-6.82 (m, 2H), 5.46 (d, J = 2.1 Hz, 1H), 4.44-4.38 (m, 1H), 3.77 (s, 3H), 3.71-3.69 (m, 2H), 3.34 (s, 3H), 0.83 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.6, 158.3, 138.9, 133.0, 131.4, 129.3, 128.7, 127.5, 113.7, 111.8, 108.5, 75.1, 58.7, 55.2, 42.4, 33.0, 29.6. HRMS (ESI) $[M+Na]^+$: calculated for $C_{24}H_{28}O_3Na$: 387.1936, found 387.1934.

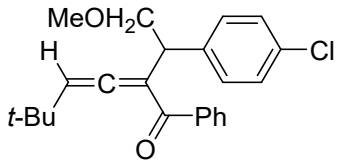


7b

2-(2-Methoxy-1-(*p*-tolyl)ethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (7b). Flash column chromatography to afford product **7b** (45.4 mg, 65% yield, dr = 37:63).

The first fraction**:** solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.65-7.62 (m, 2H), 7.44-7.41 (m, 1H), 7.34-7.31 (m, 2H), 7.24-7.23 (m, 2H), 7.11-9.09 (m, 2H), 5.51 (d, J = 1.8 Hz, 1H), 4.42-4.39 (m, 1H), 3.75-3.62 (m, 2H), 3.33 (s, 3H), 2.30 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.5, 138.6, 138.0, 136.2, 131.3, 129.0, 128.7, 128.0, 127.5, 111.3, 108.7, 75.6, 58.5, 42.5, 33.2, 29.7, 21.0.HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{29}O_2$: 349.2168, found 349.2165.

The second fraction: solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.46-7.42 (m, 1H), 7.35-7.32 (m, 2H), 7.26-7.23 (m, 2H), 7.11-7.00 (m, 2H), 5.47 (d, *J* = 2.0 Hz, 1H), 4.43-4.40 (m, 1H), 3.74-3.69 (m, 2H), 3.34 (s, 3H), 2.30 (s, 3H), 0.84 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.5, 138.9, 137.7, 136.1, 131.4, 128.9, 128.7, 128.2, 127.5, 111.7, 108.5, 75.0, 58.6, 42.8, 33.0, 29.6, 21.0. HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{29}O_2$: 349.2168, found 349.2163.

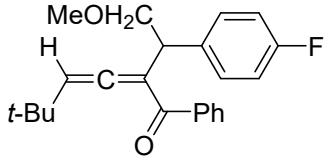


7c

2-(1-(4-Chlorophenyl)-2-methoxyethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (7c). Flash column chromatography to afford product **7c** (66.2 mg, 90% yield, dr = 48:52).

The first fraction**:** solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.46-7.42 (m, 1H), 7.35-7.32 (m, 2H), 7.29-7.25 (m, 4H), 5.51 (d, *J* = 1.8 Hz, 1H), 4.42-4.39 (m,1H), 3.75-0.61 (m, 2H), 3.33 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 194.2, 139.7, 138.4, 132.4, 131.5, 129.5, 128.7, 128.4, 127.6, 110.8, 109.0, 75.1, 58.6, 42.4, 33.2, 29.6. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}O_2Cl$: 369.1621, found 369.1614.

The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.47-7.44 (m, 1H), 7.36-7.33 (m, 2H), 7.31-7.26 (m, 4H), 5.48 (d, *J* = 2.0 Hz, 1H), 4.44-4.41 (m, 1H), 3.73-3.67 (m, 2H), 3.33 (s, 3H), 0.81 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 194.3, 139.5, 138.6, 132.4, 131.6, 129.7, 128.6, 128.4, 127.6, 111.2, 108.8, 74.6, 58.7, 42.6, 33.1, 29.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}O_2Cl$: 369.1621, found 369.1613.

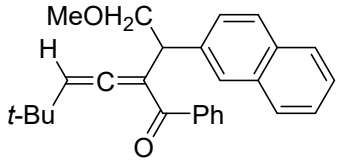


7d

2-(1-(4-Fluorophenyl)-2-methoxyethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (7d). Flash column chromatography to afford product **7d** (54.9 mg, 78% yield, dr = 45:55).

The first fraction**:** solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.46-7.42 (m, 1H), 7.36-7.29 (m, 4H), 7.00-6.95 (m, 2H), 5.50 (d, *J* = 1.8 Hz, 1H), 4.44-4.40 (m, 1H), 3.75-3.61 (m, 2H), 3.33 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 194.3, 161.7 (d, *J* = 122.9 Hz), 138.5, 136.9 (d, *J* = 1.9 Hz), 131.5, 129.6 (d, *J* = 3.8 Hz), 128.7, 127.5, 115.1 (d, *J* = 10.7 Hz), 111.1, 108.9, 75.3, 58.6, 42.2, 33.2, 29.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.45. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}O_2F$: 353.1917, found 353.1913.

The second fraction: solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.47-7.43 (m, 1H), 7.36-7.30 (m, 4H), 7.01-6.96 (m, 2H), 5.47 (d, *J* = 2.0 Hz, 1H), 4.46-4.42 (m, 1H), 3.73-3.68 (m, 2H), 3.34 (s, 3H), 0.79 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 194.4, 161.7 (d, *J* = 122.2 Hz), 138.7, 136.6 (d, *J* = 1.9 Hz), 131.5, 129.8 (d, *J* = 3.8 Hz), 128.7, 127.6, 115.0 (d, *J* = 4.4 Hz), 111.5, 108.8, 74.8, 58.7, 42.4, 33.1, 29.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.51. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}O_2F$: 353.1917, found 353.1913.

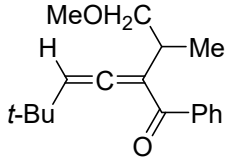


7e

2-(2-Methoxy-1-(naphthalen-2-yl)ethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (7e). Flash column chromatography to afford product **7e** (52.2 mg, 68% yield, dr = 54:46).

The first fraction**:** solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.78 (m, 4H), 7.65-7.63 (m, 2H), 7.50-7.48 (m, 1H), 7.43-7.40 (m, 3H), 7.323-7.30 (m, 2H), 5.54 (d, *J* = 1.7 Hz, 1H), 4.64-4.61 (m, 1H), 3.87-3.76 (m, 2H), 3.36 (s, 3H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.4, 138.6, 138.5, 133.4, 132.5, 131.4, 128.7, 127.9, 127.8, 127.5(3), 127.5(1), 126.8, 126.4, 125.8, 125.4, 111.2, 108.9, 75.3, 58.6, 43.0, 33.2, 29.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{27}H_{29}O_2$: 385.2168, found 385.2164.

The second fraction: solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.74 (m, 4H), 7.69-7.67 (m, 2H), 7.52-7.49 (m, 1H), 7.48-7.39 (m, 3H), 7.36-7.32 (m, 2H), 5.51 (s, 1H), 4.64-4.62 (m, 1H), 3.91-3.76 (m, 2H), 3.37 (s, 3H), 0.79 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 194.5, 138.8, 138.4, 133.4, 132.5, 131.4, 128.7, 127.8, 127.7, 127.5(4), 127.5(2), 126.9, 126.8, 125.8, 125.4, 111.6, 108.7, 74.9, 58.8, 43.2, 33.1, 29.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{27}H_{29}O_2$: 385.2168, found 385.2168.



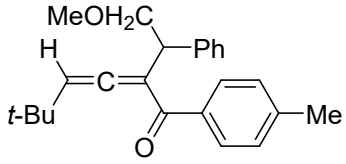
7f

2-(1-Methoxypropan-2-yl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (7f). Flash column chromatography to afford product **7f** (24.5 mg, 48% yield, dr = 52:48).

The first fraction**:** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.65 (m, 2H), 7.48-7.43 (m, 1H), 7.37-7.34 (m, 2H), 5.46 (d, *J* = 1.7 Hz, 1H), 3.48-3.45 (m, 1H), 3.34 (s, 3H), 3.29-3.26 (m, 1H), 3.23-3.18 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 195.2, 139.1, 131.3, 128.6, 127.5, 112.6, 108.2, 58.5, 32.8, 31.6, 29.8, 16.6. ^{13}C NMR (126 MHz, Acetone-d_6) δ 211.1, 195.2, 140.3, 132.3, 129.4, 128.6, 113.3, 109.0, 77.6, 58.7, 33.5, 32.6, 17.1. HRMS (ESI) $[M+H]^+$: calculated for $C_{18}H_{25}O_2$: 273.1855, found 273.1853.

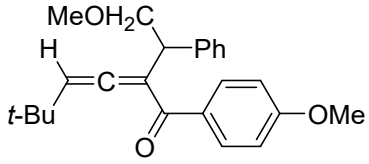
The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2H), 7.47-7.44 (m, 1H), 7.37-7.34 (m, 2H), 5.46 (d, *J* = 1.7 Hz, 1H), 3.48-3.45 (m, 1H),

3.34 (s, 3H), 3.29-3.26 (m, 1H), 3.23-3.18 (m, 1H), 1.11 (d, J = 6.8 Hz, 3H), 0.95 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 195.2, 139.1, 131.3, 128.6, 127.5, 112.6, 108.2, 58.5, 32.8, 31.6, 29.8, 16.6. ^{13}C NMR (126 MHz, Acetone-d_6) δ 211.3, 195.1, 140.1, 132.3, 129.5, 128.6, 113.4, 109.1, 77.5, 58.8, 33.5, 32.6, 17.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{18}H_{25}O_2$: 273.1855, found 273.1852.



7g

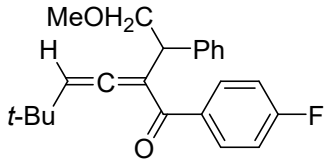
2-(2-Methoxy-1-phenylethyl)-5,5-dimethyl-1-(p-tolyl)hexa-2,3-dien-1-one (7g). Flash column chromatography to afford product **7g** (68.2 mg, 98% yield, dr = 36:64).
The first fraction**:** solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.35-7.33 (m, 2H), 7.30-7.27 (m, 2H), 7.21-7.18 (m, 1H), 7.14-7.12 (m, 2H), 5.50 (d, J = 1.8 Hz, 1H), 4.46-4.42 (m, 1H), 3.78-3.65 (m, 2H), 3.33 (s, 3H), 2.36 (s, 3H), 0.99 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.5, 193.8, 142.1, 141.2, 135.7, 129.0, 128.3, 128.2, 128.1, 126.7, 110.9, 108.6, 75.5, 58.5, 43.1, 33.2, 29.7, 21.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{29}O_2$: 349.2168, found 349.2159.
The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.37-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.21-7.18 (m, 1H), 7.16-7.14 (m, 2H), 5.47 (d, J = 2.0 Hz, 1H), 4.49-4.45 (m, 1H), 3.77-3.71 (m, 2H), 3.34 (s, 3H), 2.37 (s, 3H), 0.83 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 193.8, 142.1, 140.9, 135.9, 129.0, 128.4, 128.2(1), 128.1(9), 126.6, 111.3, 108.4, 74.8, 58.6, 43.3, 33.0, 29.5, 21.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{29}O_2$: 349.2168, found 349.2164.



7h

2-(2-Methoxy-1-phenylethyl)-1-(4-methoxyphenyl)-5,5-dimethylhexa-2,3-dien-1-one(7h). Flash column chromatography to afford product **7h** (59.7mg, 82% yield, dr = 35:65).
The first fraction**:** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.69 (m, 2H), 7.34-7.32 (m, 2H), 7.29-7.26 (m, 2H), 7.20-7.17 (m, 1H), 6.85-6.79 (m, 2H), 5.51 (d, J =1.9 Hz, 1H), 4.44-4.41 (m, 1H), 3.82 (s, 3H), 3.78-3.64 (m, 2H), 3.33 (s, 3H), 1.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 192.5, 162.5, 141.2, 131.3, 131.0, 128.3, 128.1, 126.7, 112.8, 110.7, 108.5, 75.5, 58.5, 55.3, 43.3, 33.2, 29.8. HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{29}O_3$: 365.2117, found 365.2116.
The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.36-7.34 (m, 2H), 7.30-7.27 (m, 2H), 7.21-7.17 (m, 1H), 6.86-6.83 (m, 2H), 5.46 (d, J = 2.0 Hz, 1H), 4.47-4.40 (m, 1H), 3.83 (s, 3H), 3.82-3.70 (m, 2H), 3.33 (s, 3H), 0.83 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.9, 192.6, 162.6, 140.9, 131.2, 131.2,

128.4, 128.2, 126.6, 112.8, 111.1, 108.3, 74.9, 58.7, 55.3, 43.5, 33.0, 29.6. HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{29}O_3$: 365.2117, found 365.2117.

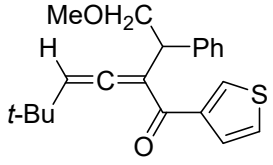


7i

1-(4-Fluorophenyl)-2-(2-methoxy-1-phenylethyl)-5,5-dimethylhexa-2,3-dien-1-one (7i). Flash column chromatography to afford product **7i** (50.0 mg, 71% yield, dr = 46:54).

The first fraction**:** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.67 (m, 2H), 7.34-7.27 (m, 4H), 7.22-7.19 (m, 1H), 7.03-6.99 (m, 2H), 5.54 (d, *J*= 1.8 Hz, 1H), 4.44-4.41 (m, 1H), 3.77-3.63 (m, 2H), 3.33 (s, 3H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.8, 192.7, 164.7(d, *J* = 252.0Hz), 141.0, 134.6(d, *J* = 3.8 Hz), 131.3(d, *J* = 8.8 Hz), 128.4, 128.1, 126.8, 114.6(d, J = 21.4 Hz), 111.1, 109.0, 75.4, 58.6, 43.1, 33.3, 29.7.^{19}F NMR (471 MHz, $CDCl_3$) δ -107.64. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}OF$: 353.1917, found 353.1911.

The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7.35-7.28 (m, 4H), 7.22-7.19 (m, 1H), 7.05-7.01 (m, 2H), 5.49 (d, *J* = 2.0 Hz, 1H), 4.47-4.43 (m, 1H), 3.77-3.71 (m, 2H), 3.34 (s, 3H), 0.81 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.9, 192.8, 164.8(d, *J* = 252.0 Hz), 140.7, 134.9(d, *J* = 3.8 Hz), 131.3(d, *J* = 8.8 Hz), 128.3, 128.3, 126.7, 114.6(d, *J* = 22.6 Hz), 111.6, 108.8, 74.8, 58.7, 43.3, 33.1, 29.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.58. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}O_2F$: 353.1917, found 353.1910.



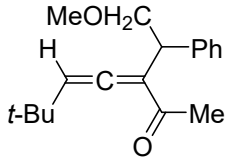
7j

2-(2-Methoxy-1-phenylethyl)-5,5-dimethyl-1-(thiophen-3-yl)hexa-2,3-dien-1-one (7j). Flash column chromatography to afford product **7j** (54.4 mg, 80 % yield, dr = 48:52).

The first fraction**:** solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.98 (m, 1H), 7.47-7.46 (m, 1H), 7.33-7.27 (m, 4H), 7.22-7.18 (m, 2H), 5.65 (d, *J* = 1.7 Hz, 1H), 4.44-4.42 (m, 1H), 3.77-3.62 (m, 2H), 3.33 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.0, 186.4, 141.3, 141.1, 131.6, 128.3, 128.1, 126.7, 124.7, 111.5, 109.1, 75.4, 58.5, 43.0, 33.4, 29.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{25}O_2S$: 341.1575, found 341.1565.

The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-8.02(m, 1H), 7.50-7.49 (m, 1H), 7.34-7.27 (m, 4H), 7.23-7.18 (m, 2H), 5.59 (d, *J* = 1.9 Hz, 1H), 4.47-4.44 (m, 1H), 3.75-3.68 (m, 2H), 3.33 (s, 3H), 0.87 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 186.5, 141.5, 140.8, 131.6, 128.4, 128.3, 128.2, 126.7, 124.8, 111.9,

109.0, 74.8, 58.7, 43.2, 33.2, 29.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{21}H_{25}O_2S$: 341.1575, found 341.1580.

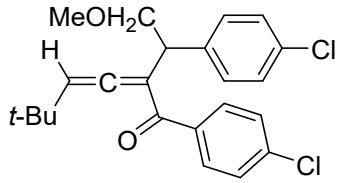


7k

3-(2-Methoxy-1-phenylethyl)-6,6-dimethylhepta-3,4-dien-2-one (7k). Flash column chromatography to afford product **7k** (43.5 mg, 74% yield, dr = 40:60).

The first fraction**:** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.24 (m, 4H), 7.20-7.17 (m, 1H), 5.70 (d, *J* = 1.7 Hz, 1H), 4.24-4.21 (m, 1H), 3.65-3.55 (m, 2H), 3.30 (s, 3H), 2.23 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.1, 197.7, 141.3, 128.2, 128.0, 126.6, 112.6, 108.8, 75.5, 58.5, 41.6, 33.4, 30.0, 26.9. HRMS (ESI) $[M+Na]^+$: calculated for $C_{18}H_{24}O_2Na$: 295.1674, found 295.1667.

The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.24 (m, 4H), 7.20-7.17 (m, 1H), 5.69 (d, *J* = 1.9 Hz, 1H), 4.47-4.44 (m, 1H), 3.65-3.58 (m, 2H), 3.31 (s, 3H), 2.24 (s, 3H), 0.99 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 197.8, 140.9, 128.2, 126.6, 112.8, 108.8, 74.8, 58.6, 41.8, 33.3, 29.8, 27.0. HRMS (ESI) $[M+Na]^+$: calculated for $C_{18}H_{24}O_2Na$: 295.1674, found 295.1670.

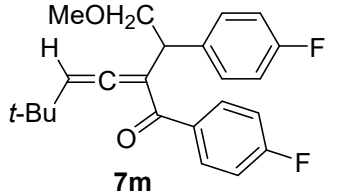


7l

1-(4-Chlorophenyl)-2-(1-(4-chlorophenyl)-2-methoxyethyl)-5,5-dimethylhexa-2,3-dien-1-one (7l). Flash column chromatography to afford product **7l** (68.3 mg, 85% yield, dr = 51:49).

The first fraction**:** solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.33-7.31 (m, 2H), 7.26 (br, 4H), 5.55 (d, *J* = 1.9 Hz, 1H), 4.40-4.37 (m, 1H), 3.74-3.60 (m, 2H), 3.32 (s, 3H), 0.98 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 210.9, 192.8, 139.5, 137.9, 136.6, 132.5, 130.2, 129.4, 128.5, 127.9, 110.8, 109.3, 75.0, 58.6, 42.5, 33.4, 29.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{25}O_2Cl_2$: 403.1232, found 403.1230.

The second fraction: solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.62 (m, 2H), 7.35-7.32 (m, 2H), 7.27 (br, 4H), 5.51 (d, *J* = 2.0 Hz, 1H), 4.41-4.38(m, 1H), 3.72-3.66 (m, 2H), 3.33 (s, 3H), 0.82 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.0, 192.8, 139.3, 137.9, 136.8, 132.5, 130.2, 129.7, 128.4, 127.9, 111.1, 109.2, 74.5, 58.8, 42.7, 33.2, 29.6. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{25}O_2Cl_2$: 403.1232, found 403.1230.

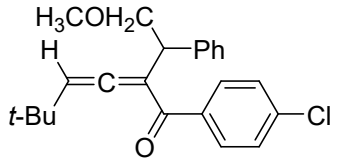


7m

1-(4-Fluorophenyl)-2-(1-(4-fluorophenyl)-2-methoxyethyl)-5,5-dimethylhexa-2,3-dien-1-one (7m). Flash column chromatography to afford product **7m** (62.2 mg, 84% yield, dr = 44:56).

The first fraction**:** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.30-7.27 (m, 2H), 7.04-6.96 (m, 4H), 5.53 (d, *J* = 1.8 Hz, 1H), 4.41-4.38 (m, 1H), 3.74-3.60 (m, 2H), 3.33 (s, 3H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.7, 192.6, 164.8(d, *J* = 253.2 Hz), 161.7(d, *J* = 245.8 Hz), 136.7(d, *J* = 3.8 Hz), 134.5(d, *J* = 2.6 Hz), 131.3(d, *J* = 8.8 Hz), 129.5(d, *J*=8.8 Hz), 115.1(d, *J*=20.2 Hz), 114.7(d, *J* = 22.6 Hz), 111.0, 109.1, 75.2, 58.6, 42.4, 33.3, 29.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.39, -116.28. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{25}O_2F_2$: 371.1823, found 371.1823.

The second fraction: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.32-7.26 (m, 2H), 7.06-6.96 (m, 4H), 5.49 (d, *J* = 2.0 Hz, 1H), 4.44-4.40 (m, 1H), 3.73-3.67 (m, 2H), 3.33 (s, 3H), 0.80 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.9, 192.7, 164.8(d, *J* = 253.2 Hz), 161.7(d,*J*=244.4 Hz), 136.5(d, *J* = 2.6 Hz), 134.7(d, *J* = 3.8 Hz), 131.3(d, *J* = 8.8 Hz), 129.8(d, *J* = 8.8 Hz), 115.1(d, *J* = 21.4 Hz), 114.7(d, *J* = 21.4 Hz), 111.4, 109.0, 74.8, 58.7, 42.6, 33.1, 29.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.36, -116.37. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{25}O_2F_2$: 371.1823, found 371.1818.

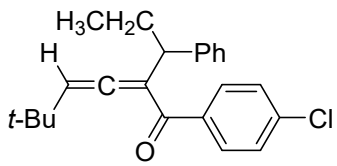


9a

1-(4-Chlorophenyl)-2-(2-methoxy-1-phenylethyl)-5,5-dimethylhexa-2,3-dien-1-one (9a). Flash column chromatography to afford product **9a** (67.0 mg, 91% yield, dr = 52:48).

The first fraction**:** solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.34-7.28 (m, 6H), 7.22-7.19 (m, 1H), 5.55 (d, *J* = 1.8 Hz, 1H), 4.44-4.41 (m, 1H), 3.77-3.63 (m, 2H), 3.33 (s, 3H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.9, 193.0, 140.9, 137.7, 136.8, 130.2, 128.4, 128.1, 127.8, 126.8, 111.1, 109.1, 75.3, 58.5, 43.0, 33.3, 29.7. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}O_2Cl$: 369.1621, found 369.1616.

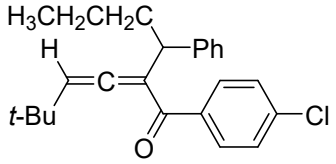
The second fraction: solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H), 7.34-7.28 (m, 6H), 7.22-7.19 (m, 1H), 5.50 (d, *J* = 2.0 Hz, 1H), 4.45-4.42 (m, 1H), 3.76-3.70 (m, 2H), 3.34 (s, 3H), 0.81 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 193.0, 140.7, 137.7, 137.0, 130.2, 128.3(2), 128.2(8), 127.9, 126.8, 111.6, 108.9, 74.8, 58.7, 43.2, 33.1, 29.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}O_2Cl$: 369.1621, found 369.1617.



9b

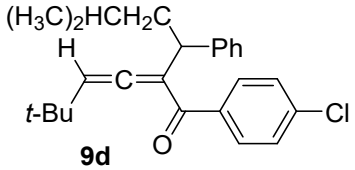
1-(4-Chlorophenyl)-5,5-dimethyl-2-(1-phenylpropyl)hexa-2,3-dien-1-one (9b). Flash column chromatography to afford product **9b** as a colorless oil (53.5 mg, 76% yield, dr = 44:56).

Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.60 (m, 1H), 7.59-7.55 (m, 1H), 7.35-7.24 (m, 7H), 7.22-7.14 (m, 1H), [5.52 (d, *J* = 1.8 Hz, 0.39H), 5.47 (d, *J* = 2.0 Hz, 0.61H)], 4.00-3.91 (m, 1H), 1.94-1.83 (m, 1H), 1.82-1.70 (m, 1H), 0.98 (s, 3.51H), 0.89 (t, *J* = 7.5 Hz, 3H), 0.82 (s, 5.49H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.7, 210.6, 193.5, 193.3, 143.4, 143.3, 137.6(4), 137.6 (2), 137.2, 136.9, 130.2, 130.1, 128.2 (2), 128.1 (8), 128.1, 128.0, 127.8 (3), 127.8 (0), 126.3 (1), 126.2 (7), 114.6 (3), 114.5 (9), 109.0, 108.7, 44.8, 44.6, 33.3, 33.1, 29.9, 29.6, 28.3, 27.7, 12.6, 12.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{23}H_{26}OCl$: 353.1672, found 353.1701.



9c

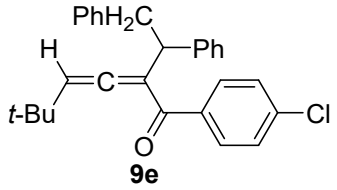
1-(4-Chlorophenyl)-5,5-dimethyl-2-(1-phenylbutyl)hexa-2,3-dien-1-one (9c). Flash column chromatography to afford product **9c** as a colorless oil (65.1 mg, 89% yield, dr = 46:54). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 1H), 7.59-7.57 (m, 1H), 7.33-7.26 (m, 6H), 7.19-7.16 (m, 1H), [5.53 (d, *J* = 1.8 Hz, 0.44H),5.47(d, *J* = 1.8 Hz, 0.56H)], 4.12-4.06 (m, 1H), 1.86-1.72 (m, 2H), 1.31-1.26 (m, 2H), 0.99 (s, 3.96H), 0.93-0.90 (m, 3H), 0.82 (s, 5.04H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.7, 210.6, 193.4, 193.3, 143.7, 143.4, 137.6 (2), 137.5 (9), 137.2, 136.9, 130.1 (5), 130.1 (3), 128.2, 128.1, 127.9, 127.8 (0), 127.7 (7), 126.3, 126.2, 114.7, 114.6, 109.0, 108.7, 42.7, 42.5, 37.6, 36.9, 33.2, 33.1, 29.8, 29.7, 29.5, 21.0, 20.8, 14.0. HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{28}OCl$: 367.1829, found 367.1826.



9d

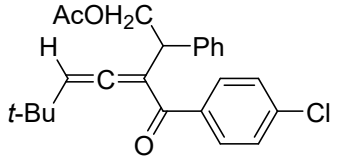
1-(4-Chlorophenyl)-5,5-dimethyl-2-(3-methyl-1-phenylbutyl)hexa-2,3-dien-1-one (9d). Flash column chromatography to afford product **9d** as a solid (63.8 mg, 84% yield, dr = 49:51). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 0H), 7.60-7.53 (m, 1H), 7.33-7.26 (m, 6H), 7.19-7.16 (m, 1H), [5.52 (d, *J* = 1.7 Hz, 0.47H), 5.46 (d, *J* = 2.0 Hz, 0.53H)], 4.23-4.18 (m, 1H), 1.77-1.59 (m, 2H), 1.49-1.40 (m, 1H), 0.98 (s, 4.23H), 0.95 (d, *J* = 5.0 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.81 (s, 4.77H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.8, 193.4, 193.3, 143.7, 143.4, 137.6 (4), 137.5 (9), 137.2, 137.0, 130.1, 128.2 (0), 128.1 (9), 128.1, 127.9, 127.8 (2), 127.7 (8), 126.3, 126.2, 114.9, 114.8, 109.1, 108.9, 44.6, 43.8, 40.8, 40.5, 33.2, 33.1, 29.8, 29.5, 25.7, 25.5,

23.4, 23.1, 22.1, 21.9. HRMS (ESI) $[M+H]^+$: calculated for $C_{25}H_{30}OCl$: 381.1980, found 381.1976



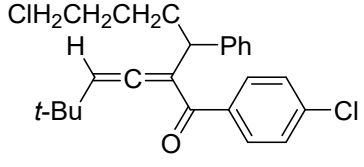
9e

1-(4-Chlorophenyl)-2-(1,2-diphenylethyl)-5,5-dimethylhexa-2,3-dien-1-one (9e). Flash column chromatography to afford product **9e** as a solid (72.0 mg, 87% yield, dr = 44:56). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.57 (m, 1H), 7.56-7.50 (m, 1H), 7.39-7.26 (m, 4H), 7.25-7.11 (m, 7H), 7.11-7.02 (m, 1H), [5.61 (d, *J* = 1.8 Hz, 0.39H),5.50 (d, *J* = 1.8 Hz, 0.61H)], 4.53-4.44 (m, 1H), 3.26-3.02 (m, 2H), 0.96 (s, 3.51H), 0.85(s, 5.49H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 210.6, 193.2, 193.0, 142.8, 142.4, 139.9, 139.7, 137.7, 137.6, 137.0, 136.7, 130.2, 130.0, 129.0 (1), 128.9 (7), 128.1 (5), 128.1 (0), 128.0 (7), 128.0 (4), 127.9 (9), 127.8 (1), 127.7 (9), 127.7, 126.4 (2), 126.4 (0), 126.0, 125.9, 113.9 (3), 113.8 (5), 109.3, 109.2, 44.4 (3), 44.3 (8), 41.5, 40.8, 33.3, 33.2, 29.7, 29.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{28}H_{28}OCl$: 415.1829, found 415.1826.



9f

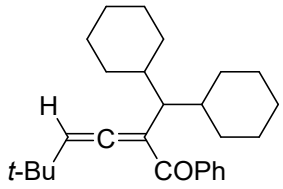
3-(4-Chlorobenzoyl)-6,6-dimethyl-2-phenylhepta-3,4-dien-1-yl acetate (9f). Flash column chromatography to afford product **9f** as a colorless oil. (68.6 mg, 82% yield, dr = 47:53). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.58 (m, 2H), 7.38-7.27 (m, 6H), 7.25-7.20 (m, 1H), [5.62 (d, *J* = 1.7 Hz, 0.34H),5.51 (d, *J* = 1.8 Hz, 0.66H)], 4.53-4.29 (m, 3H), 1.97 (d, *J* = 11.2 Hz, 3H), 0.98 (s, 3.06H), 0.80 (s, 5.94H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.0, 210.4, 192.6, 192.5, 170.9, 170.8, 139.8, 139.7, 138.0, 137.9, 136.7, 136.4, 130.1 (8), 130.1 (6), 128.5, 128.4, 128.2, 128.0 (2), 128.9 (5), 127.9, 127.1 (3), 127.0 (5), 111.0, 110.6, 109.8, 109.4, 66.5, 66.0, 42.2 (4), 42.1 (6), 33.4, 33.2, 29.7, 29.4, 20.9 (2), 20.8 (6). HRMS (ESI) $[M+Na]^+$: calculated for $C_{24}H_{25}O_3ClNa$: 419.1384, found 419.1382.



9g

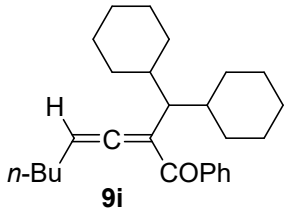
2-(4-Chloro-1-phenylbutyl)-1-(4-chlorophenyl)-5,5-dimethylhexa-2,3-dien-1-one (9g). Flash column chromatography to afford product **9g** as a colorless oil (71.4 mg, 89% yield, dr = 40:60). Two diastereoisomers are hard to be separated by column

chromatography on silica gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.61 (m, 1H), 7.59-7.56 (m, 1H), 7.34-7.27 (m, 6H), 7.21-7.17 (m, 1H), [5.56 (d, *J* = 1.8 Hz, 0.44H),5.51 (d, *J* = 2.0Hz, 0.56H)], 4.13-4.06 (m, 1H), 3.57-3.49 (m, 2H), 2.04-1.89 (m, 2H), 1.81-1.68 (m, 2H), 0.99 (s, 3.96H), 0.82(s, 5.04H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 210.5, 193.2, 193.0, 142.8, 142.6, 137.7, 137.0, 136.7, 130.1 (4), 130.1 (1), 128.4, 128.3, 128.1, 127.9, 127.8 (4), 127.8 (2), 126.6, 126.5, 114.3, 114.2, 109.4, 109.1, 44.9 (8), 44.9 (6), 42.4, 42.2, 33.3, 33.2, 32.6, 31.8, 30.9, 30.6, 29.8, 29.5. HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{27}OCl_2$: 401.1439, found 401.1438.



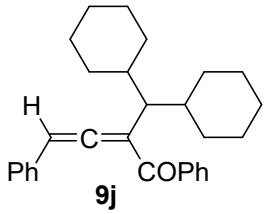
9h

2-(Dicyclohexylmethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (9h). Flash column chromatography to afford product **9h** as a solid (65.0 mg, 86% yield). The product 9**h** was obtained in 86% yield as a solid after column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.46-7.42 (m, 1H), 7.37-7.34 (m, 2H), 5.35 (s, 1H), 2.69 (m, 1H), 1.82-1.73 (m, 10H), 1.30-0.96 (m, 12H), 0.89 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 212.6, 196.3, 139.0, 131.0, 128.7, 127.5, 111.9, 107.9, 46.5, 39.3, 39.1, 33.4, 32.3, 31.2, 29.9, 28.0, 26.9 (3), 26.9 (0), 26.8, 26.7, 26.6, 26.4.HRMS (ESI) $[M+H]^+$: calculated for $C_{27}H_{39}O$: 379.3001, found 379.2991.



9i

2-(Dicyclohexylmethyl)-1-phenylocta-2,3-dien-1-one (9i). Flash column chromatography to afford product **9i** as a solid (28.7 mg, 38% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.51-7.45 (m, 1H), 7.39-7.36 (m, 2H), 5.28 (t, *J* = 7.5 Hz, 1H), 2.66 (t, *J* = 7.3 Hz, 1H), 2.15-1.99 (m, 2H), 1.76-1.51 (m, 10H), 1.35-1.09 (m, 12H), 1.09-0.91 (m, 4H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.8, 196.0, 138.8, 131.5, 129.1, 127.6, 108.4, 95.3, 46.7, 38.6, 38.5, 31.7, 31.3, 29.7, 29.3, 29.2, 28.2, 26.9 (0), 26.8 (6), 26.8, 26.7, 26.6, 22.0, 13.8. HRMS (ESI) $[M+H]^+$: calculated for $C_{27}H_{39}O$: 379.3001, found 379.3004.



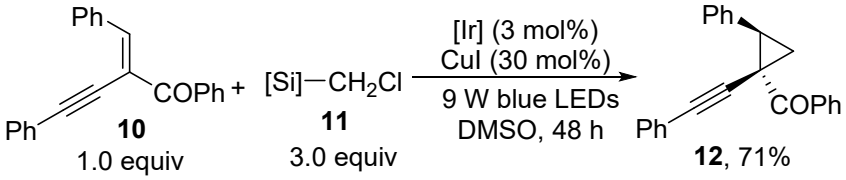
9j

2-(Dicyclohexylmethyl)-1,4-diphenylbuta-2,3-dien-1-one (9j). Flash column chromatography to afford product **9j** as a solid (46.2 mg, 58% yield). ^{1}H NMR (500

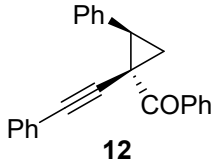
MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.44-7.41 (m, 1H), 7.36-7.23 (m, 7H), 6.45 (s, 1H), 2.84 (t, J = 7.4 Hz, 1H), 1.84-1.63 (m, 10H), 1.33-1.00 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.3, 194.6, 138.2, 132.9, 131.9, 128.9, 128.7, 127.8, 127.5, 127.3, 112.5, 99.1, 48.3, 39.0, 31.8, 31.6, 30.0, 29.3, 26.8 (3), 26.7 (6), 26.7 (1), 26.6, 26.5, 26.2. HRMS (ESI) $[M+H]^+$: calculated for $C_{29}H_{35}O$: 399.2688, found 399.2679.

4 Mechanistic experiments

4.1 Reaction of 1,3-enyne 10 with chloromethyl silicate



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 2 mol%) and the 2-(1-alkynyl)-2-alken-1-one **10** (64.5 mg, 0.2 mmol, 1.0 equiv) were added. In a glovebox, potassium [18-Crown-6] bis(catecholato) chloromethylsilicate **11** (238.4 mg, 0.4 mmol, 2.0 equiv) and CuI (7.6 mg, 0.04 mmol, 20 mol%) were added in the tube. The tube was sealed with a rubber septum and removed from the glovebox. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 36 h (cooling with a fan). After 36 h, an additional portion of $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1 mol%), potassium [18-Crown-6] bis(catecholato) chloromethylsilicate **11** (119.2 mg, 0.2 mmol, 1.0 equiv), and CuI (3.8 mg, 0.02 mmol, 10 mol%) were added, and the reaction was stirred for an additional 12 h under irradiation. After the reaction was completed, the reaction solution was diluted with saturated Na_2CO_3 aqueous solution, and was extracted with ethyl acetate (4 x 5 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **12** (eluent = petroleum ether / ethyl acetate 100:1 v/v).



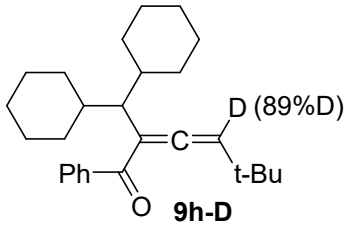
12

Phenyl((1*S, 2*R**)-2-phenyl-1-(phenylethynyl)cyclopropyl)methanone (12).** Flash column chromatography to afford product **12** as a solid. (45.7 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 7.55-7.52 (m, 1H), 7.45-7.37 (m, 6H), 7.36-7.33 (m, 1H), 7.21-7.14 (m, 3H), 7.00-6.98 (m, 2H), 3.06-3.04 (m, 1H), 2.54-2.51 (m, 1H), 1.98-1.96 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 136.8, 135.8,

132.6, 131.1, 129.2, 128.7, 128.1, 128.0, 127.9, 127.8, 127.3, 123.0, 88.2, 84.9, 38.0, 32.1, 23.6. These data are consistent with the published literature.[14]

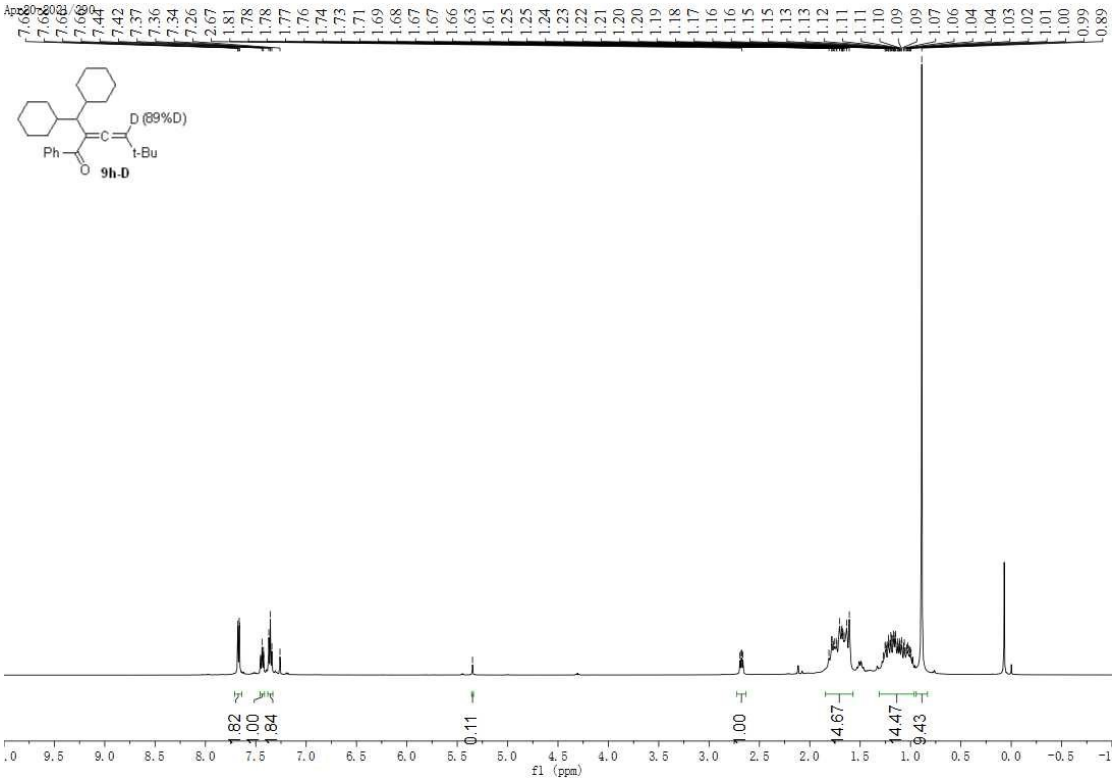
4.2 Deuteration study

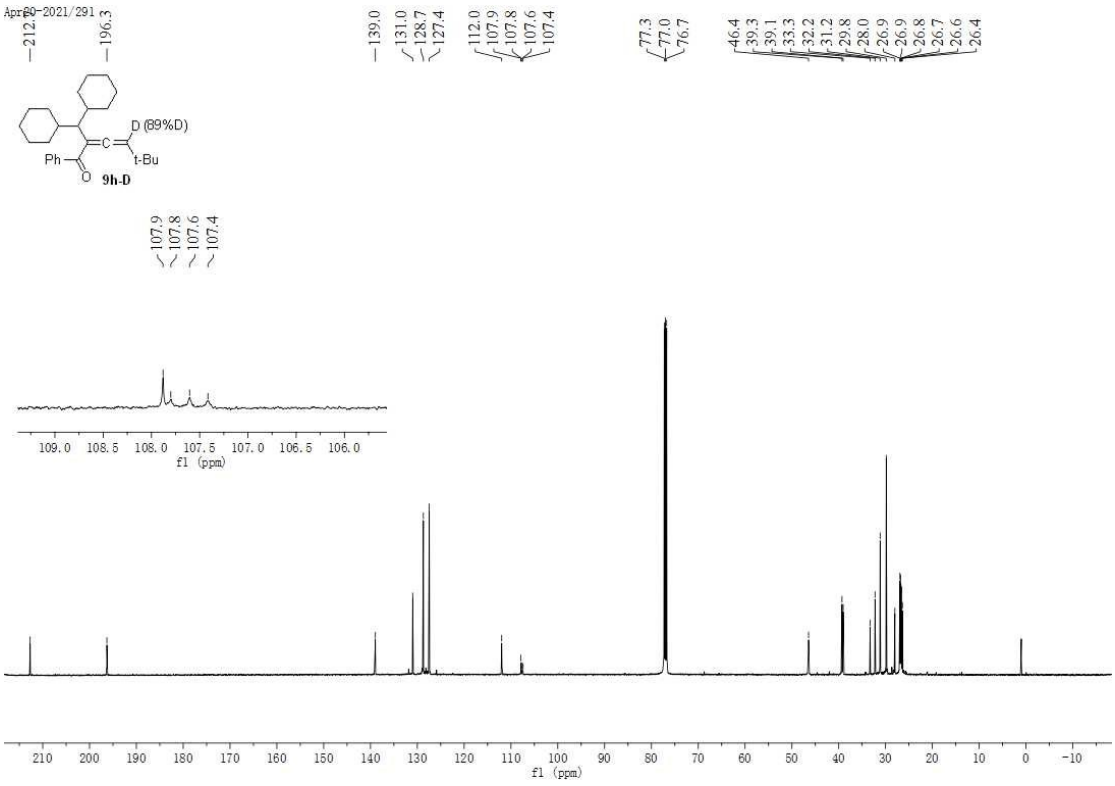
To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 2 mol %) and the (E)-2-(cyclohexylmethylene)-5,5-dimethyl-1-phenylhex-3-yn-1-one **8b** (58.9 mg, 0.2 mmol, 1.0 equiv) were added. In a glovebox, potassium [18-Crown-6] bis(catecholato) cyclohexylsilicate **2h** (252.1 mg, 0.4 mmol, 2.0 equiv) and CuI (7.6 mg, 0.04 mmol, 20 mol %) were added in the tube. The tube was sealed with a rubber septum and removed from the glovebox. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. Then CD_3OD (244.0 μL, 6 mmol, 30.0 equiv) was added via a micro syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 36 h (cooling with a fan). After 36 h, an additional portion of $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 1 mol%), potassium [18-Crown-6] bis(catecholato) cyclohexylsilicate **2h** (126.0 mg, 0.2 mmol, 1.0 equiv), and CuI (3.8 mg, 0.02 mmol, 10 mol%) were added, and the reaction was stirred for an additional 12 h under irradiation. After the reaction was completed, the reaction solution was diluted with saturated Na_2CO_3 aqueous solution, and was extracted with ethyl acetate (4 x 5 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **9h-D** in 82% yield (33.1 mg) (eluent = petroleum ether /ethyl acetate 100:1 v/v). The product **9h-D** with 89% D-incorporation was determined by ^1H NMR.



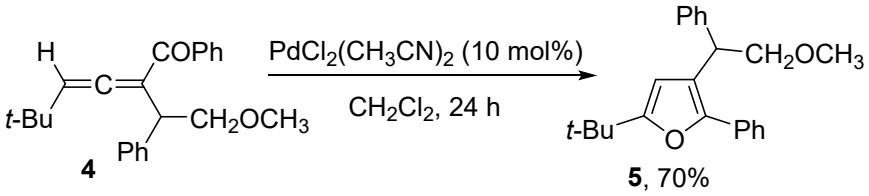
2-(Dicyclohexylmethyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one-4-d (9h-D). The product **9h-D** was obtained in 82% yield (62.1 mg, with 89% D-incorporation) as a solid after column chromatography.^1H NMR (500 MHz, $CDCl_3$) δ 7.70-7.64 (m, 2H), 7.48-7.40 (m, 1H), 7.38-7.32 (m, 1H), 5.35 (s, 0.11H), 2.69-2.66 (m, 1H), 1.81-1.61 (m, 10H), 1.27-0.99 (m, 12H), 0.89 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.7, 196.3, 139.0, 131.0, 128.7, 127.4, 112.0, 107.6 (t, *J*= 24.2 Hz, C-D), 46.4, 39.3,

39.1, 33.3, 32.2, 31.2, 29.8, 28.0, 26.9(3), 26.9(0), 26.8, 26.7, 26.6, 26.4. HRMS (ESI) $[M+H]^+$: calculated for $C_{27}H_{38}DO$: 380.3058, found 380.3056.

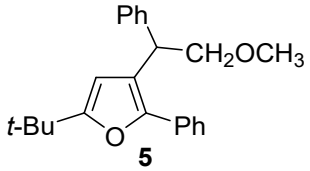




5 Transformation of 1,2-allenyl ketone



To a solution of **4** (0.25 mmol, 85.0 mg, 1.0 equiv) in dry DCM (3 mL) was added $PdCl_2(CH_3CN)_2$ (6.5 mg, 0.025 mmol, 10 mol%). After 24 hours, the reaction was quenched with H_2O (3 mL) and the mixture was extracted by ethyl acetate. The combined organic layer was dried over $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography on silica gel (eluent = petroleum ether /ethyl acetate 100:1 v/v) to give **5** in 70% yield.



5-(*tert*-Butyl)-3-(2-methoxy-1-phenylethyl)-2-phenylfuran (5). The product **5** was obtained in 70% yield (59.5 mg) as a colorless oil after column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.36-7.31 (m, 6H), 7.25-7.19 (m, 2H), 6.10 (s, 1H), 4.45 (t, J = 7.1 Hz, 1H), 3.88-3.75 (m, 2H), 3.34 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 147.3, 142.1, 131.7, 128.5, 128.4, 128.1, 126.7, 126.5, 125.9, 121.4, 104.1, 76.9, 58.8, 42.2, 32.7, 29.1. These data are consistent with the published literature.[7]

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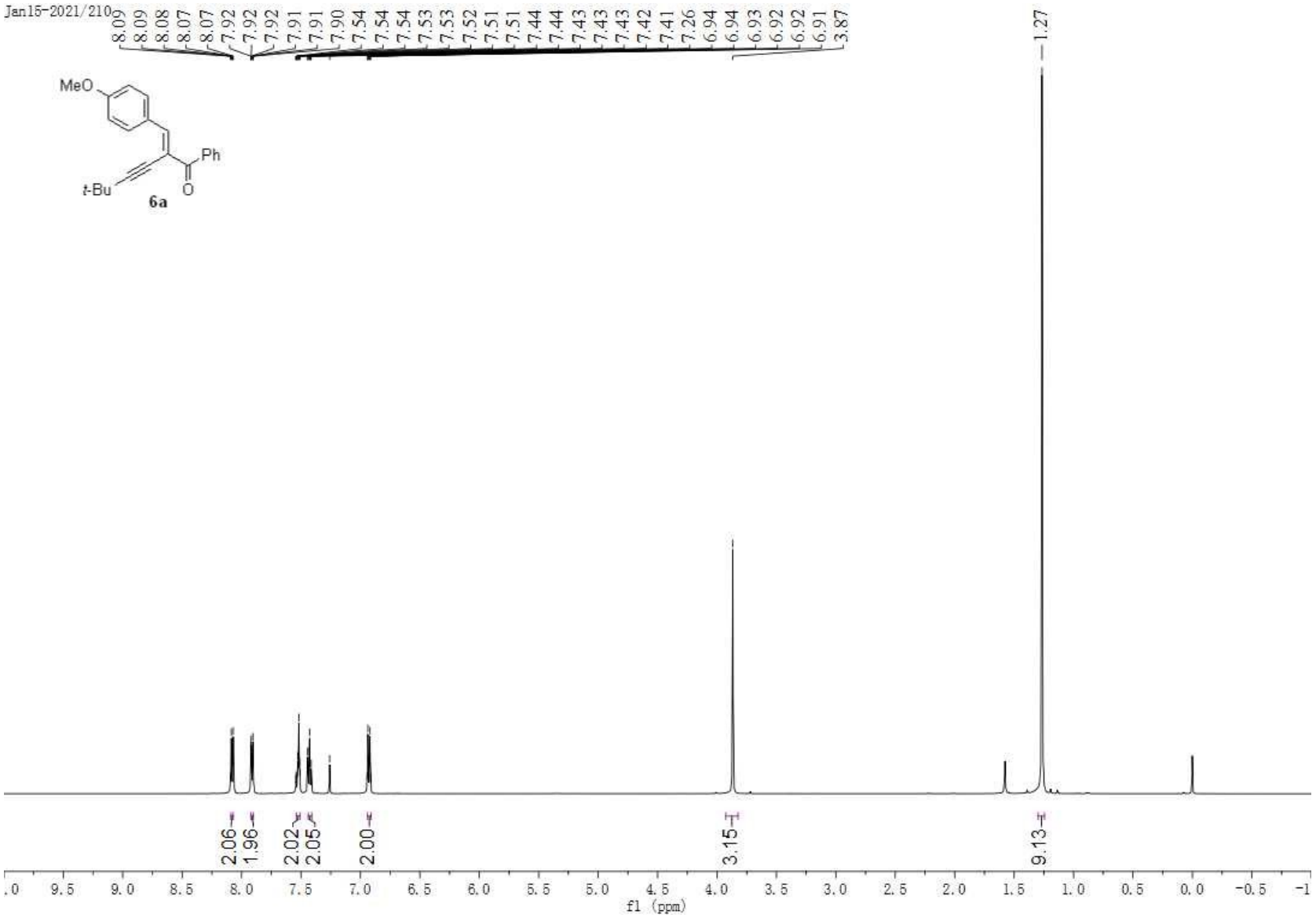
7 NMR spectra of new compound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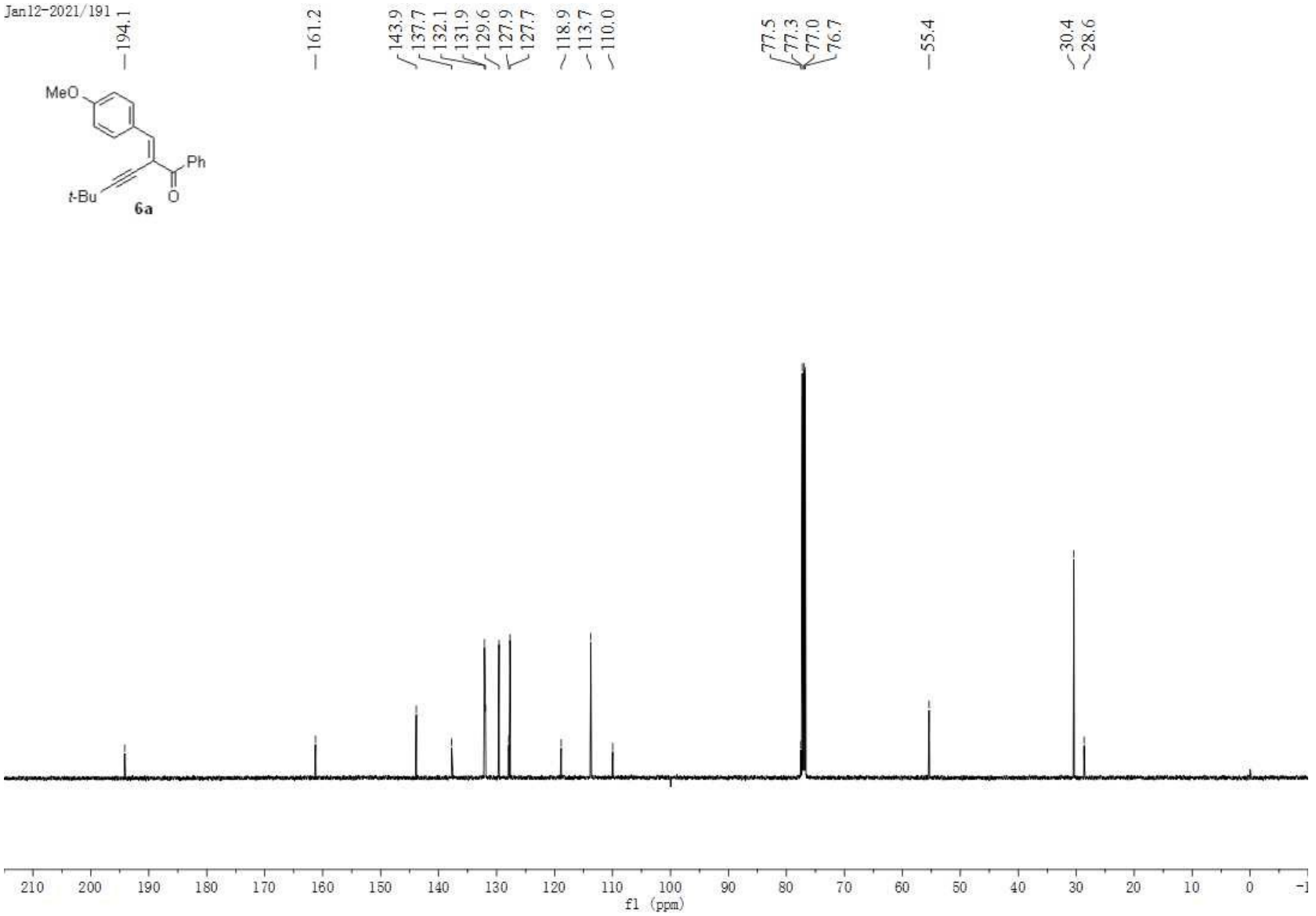
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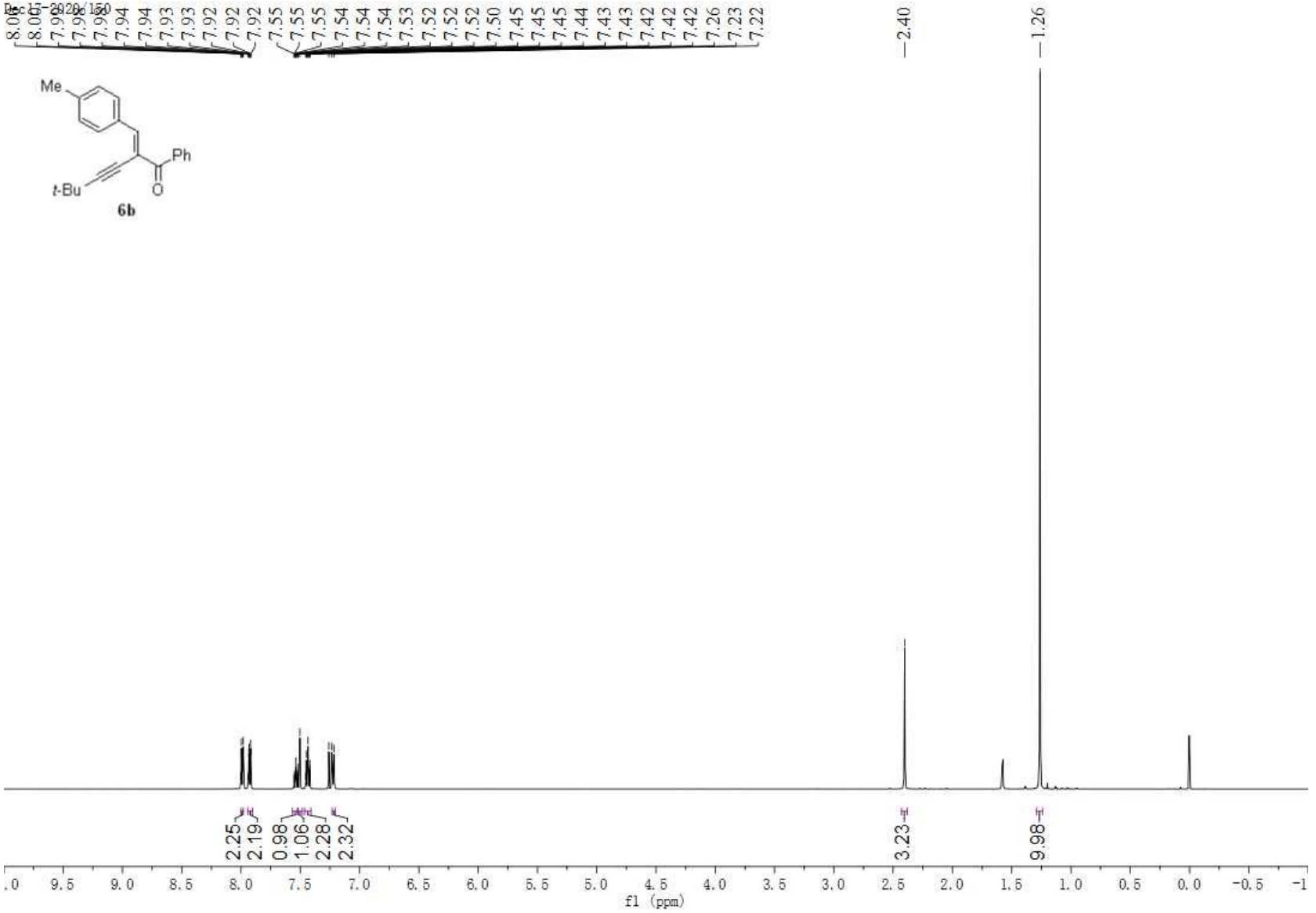
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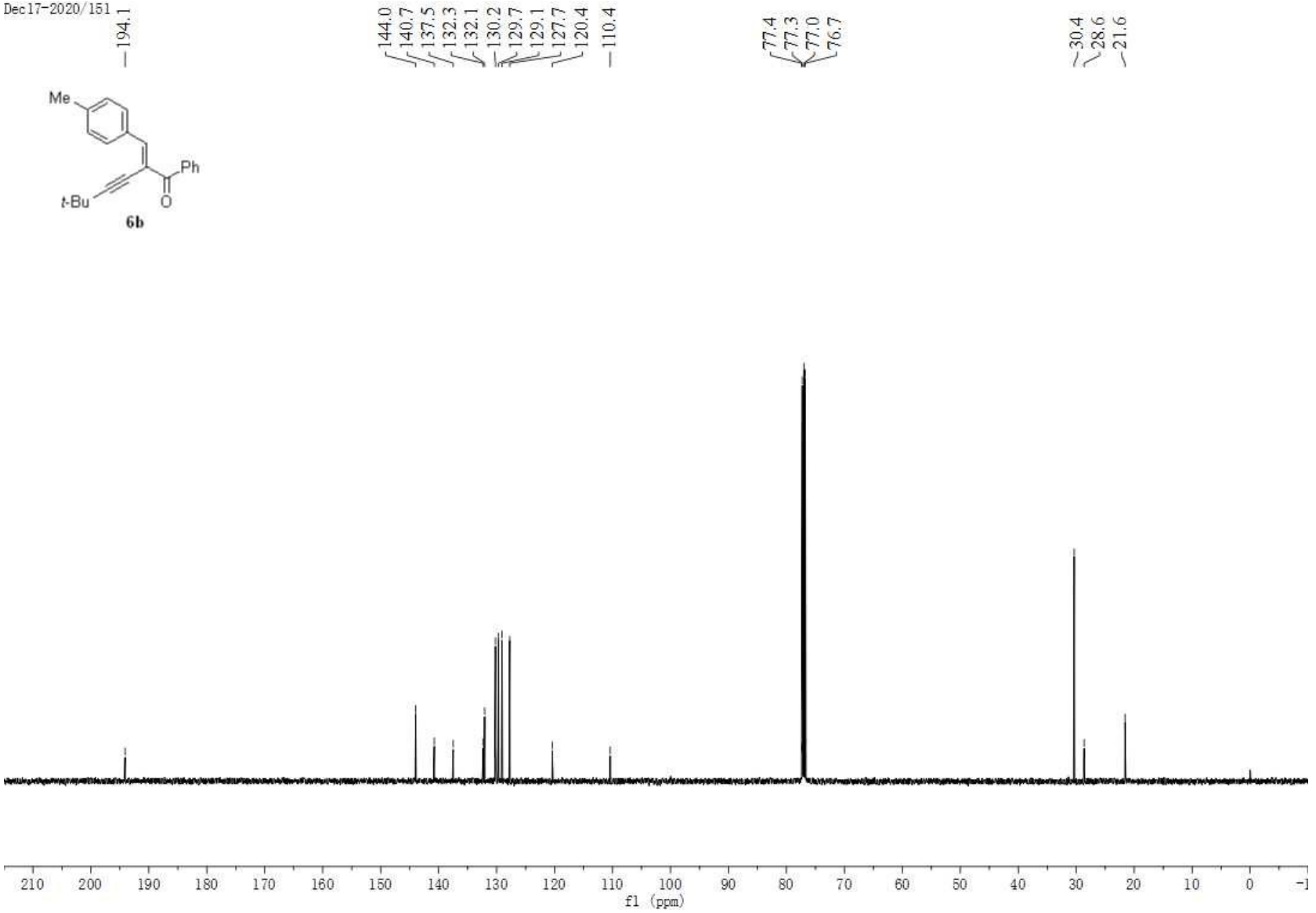
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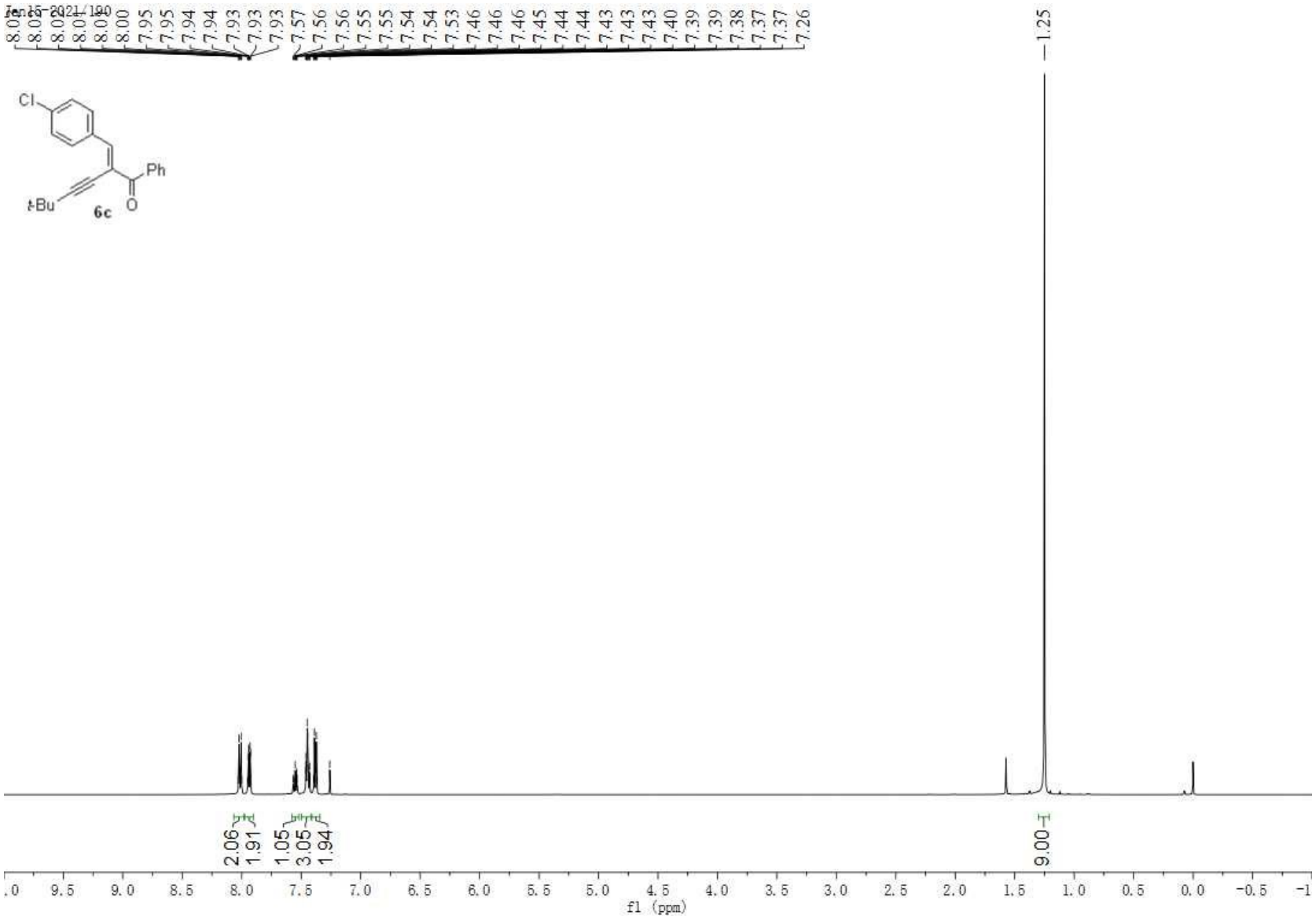
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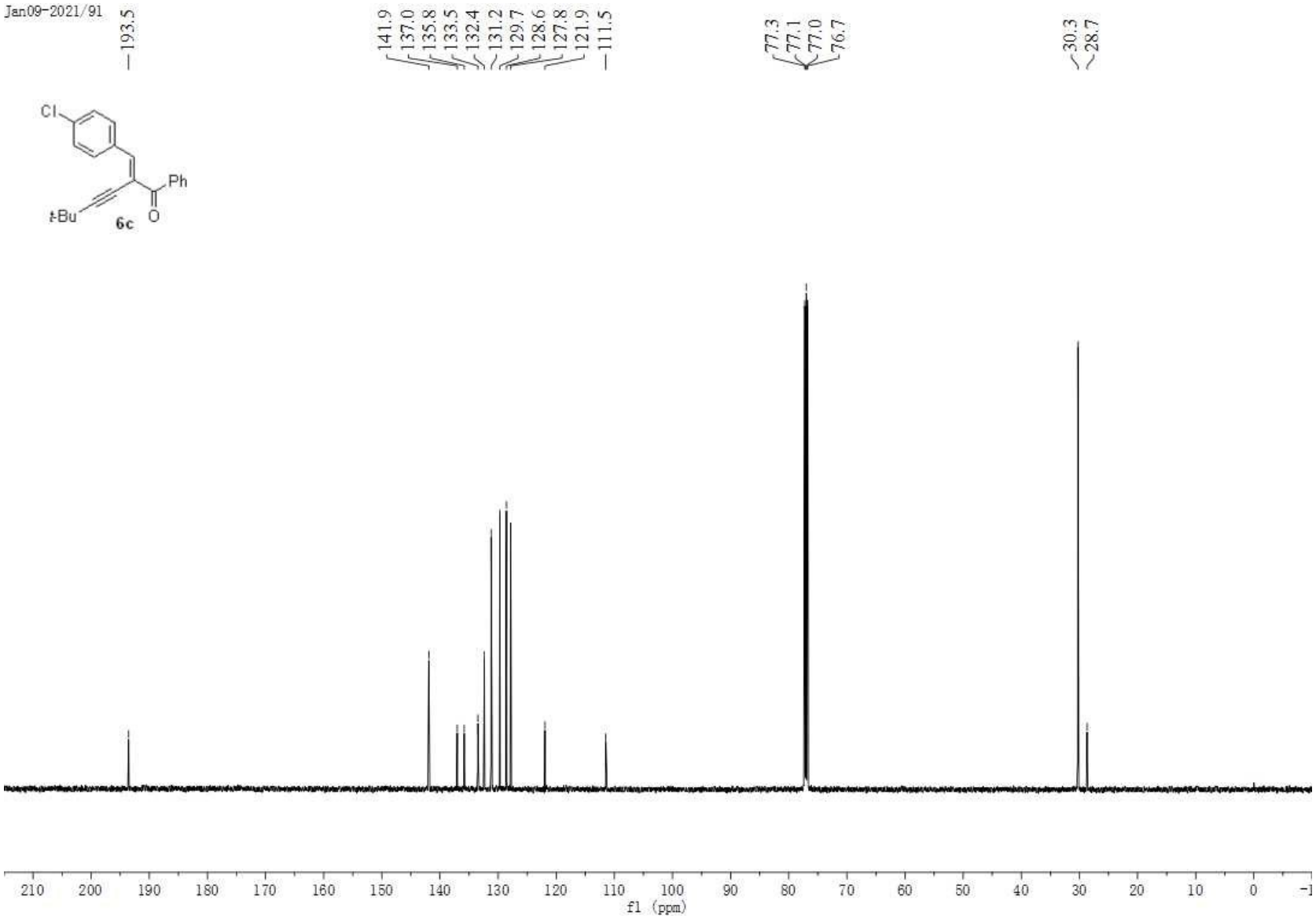
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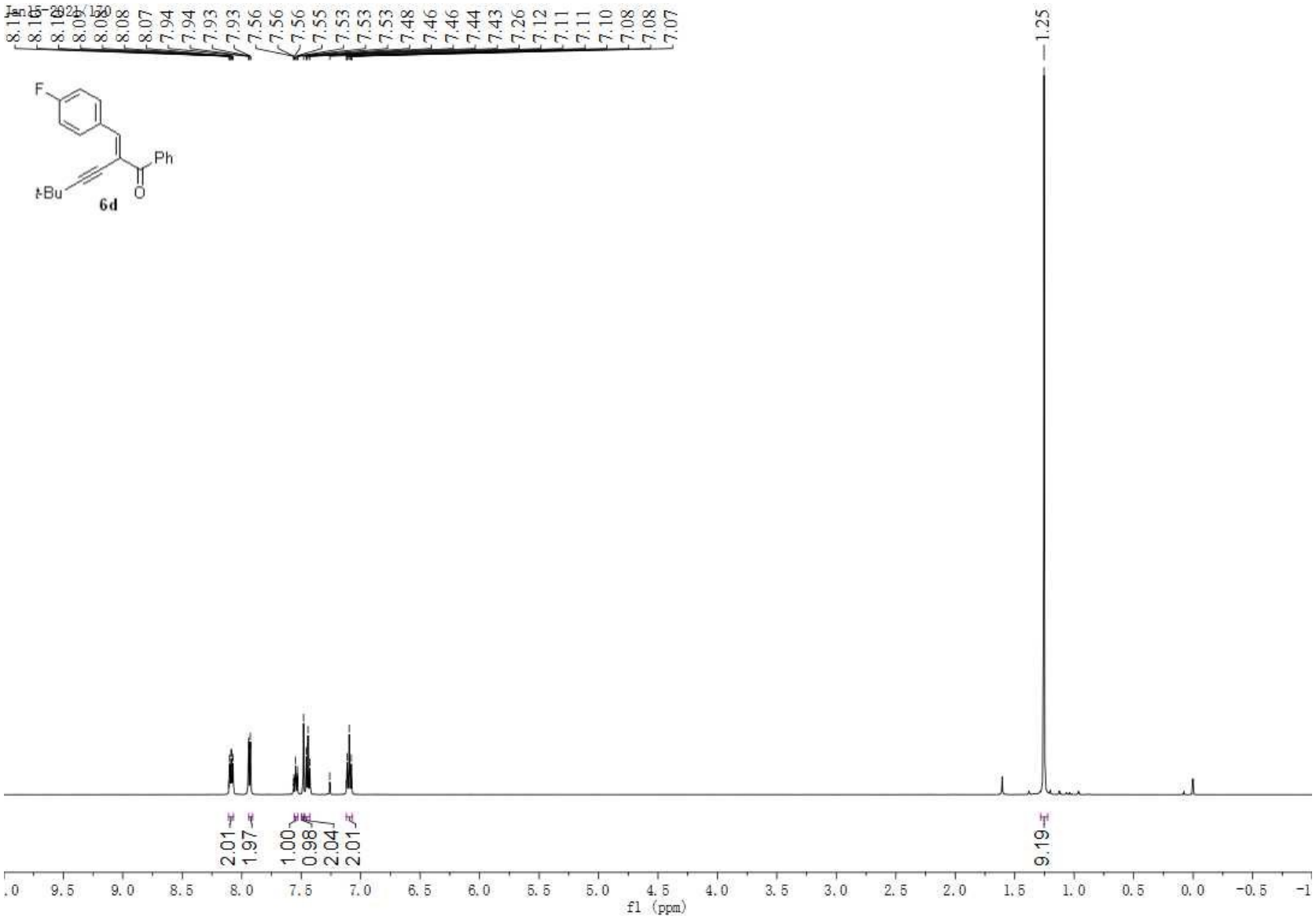
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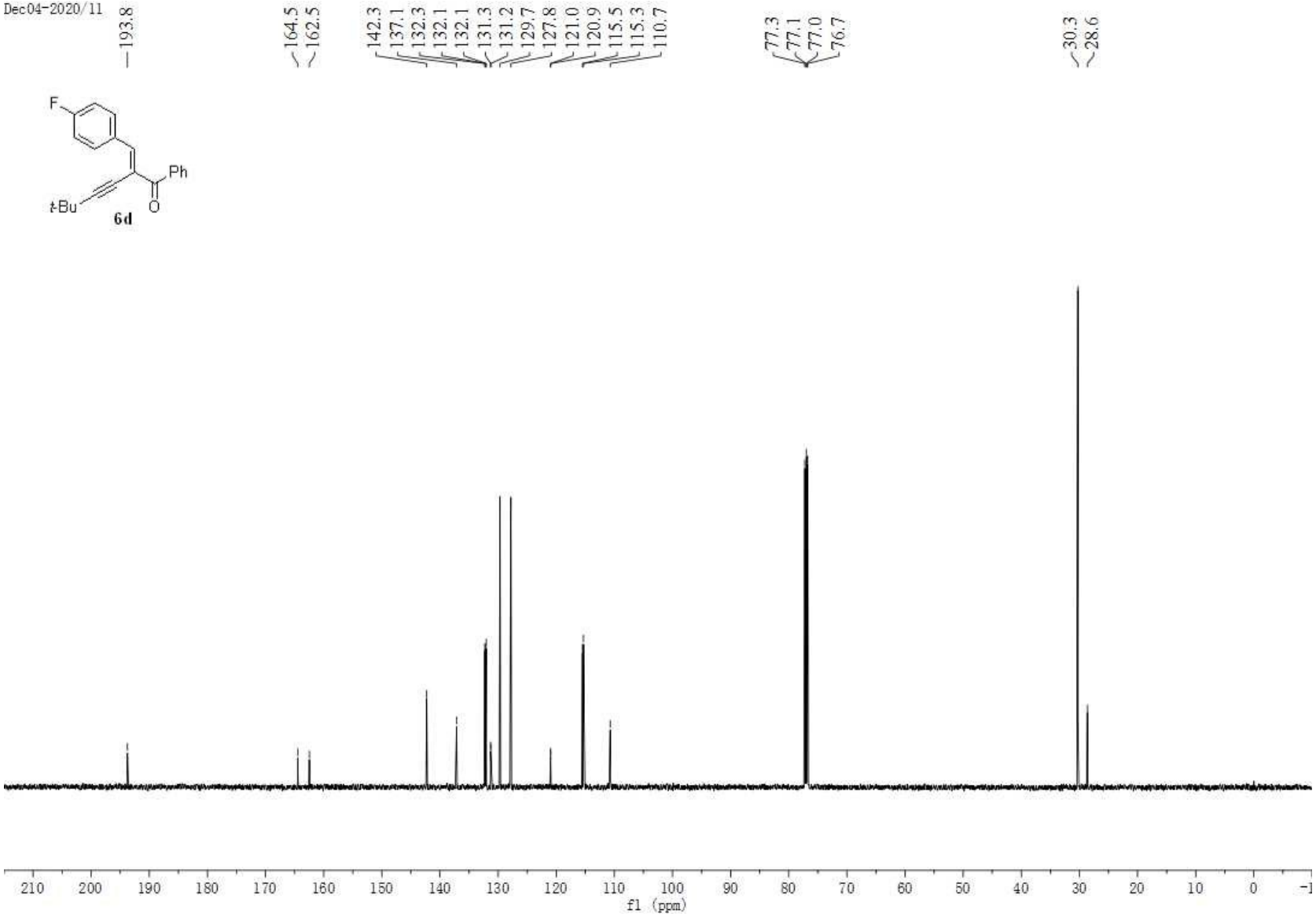
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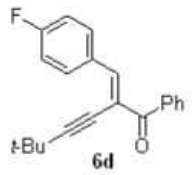

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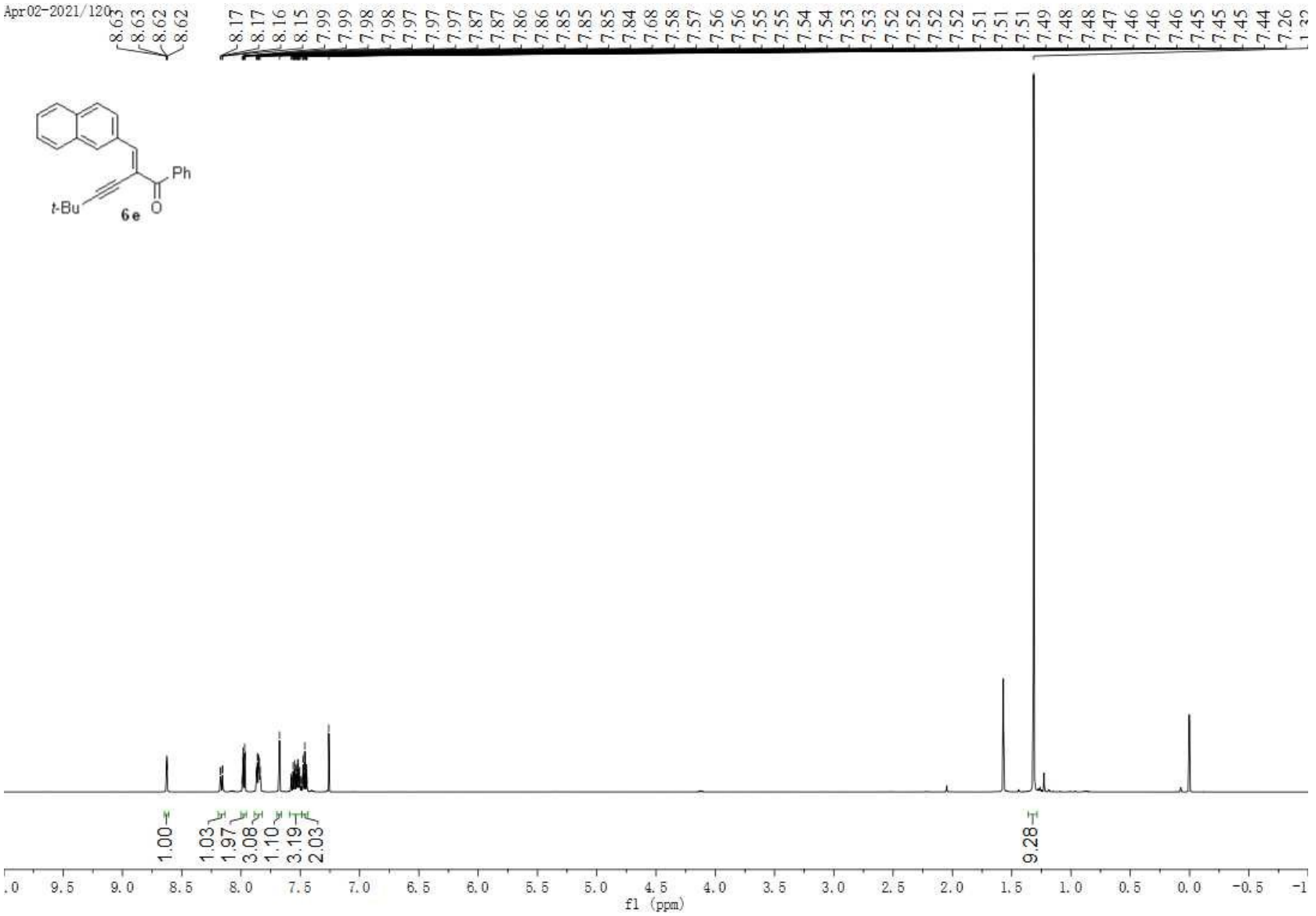
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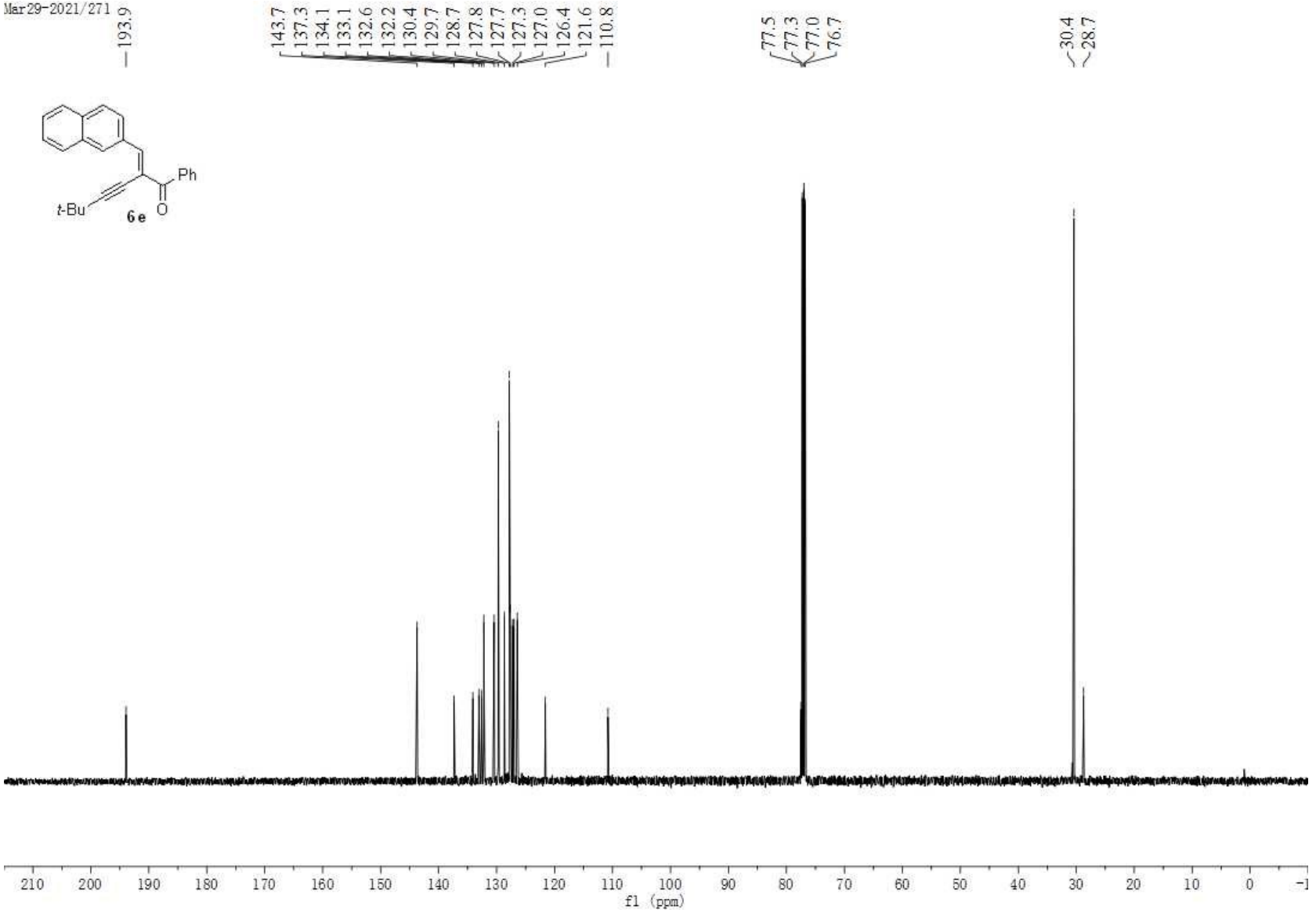
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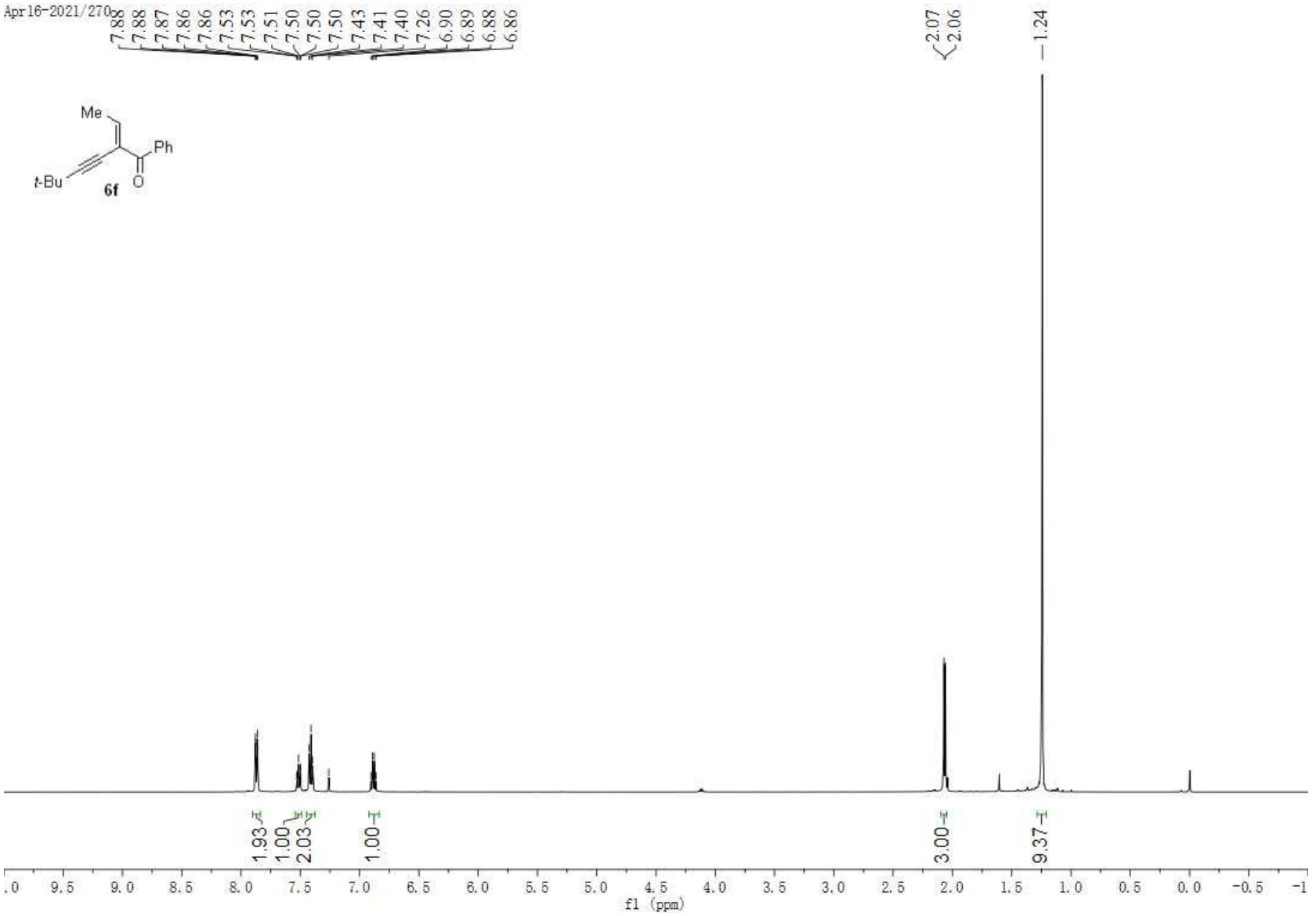
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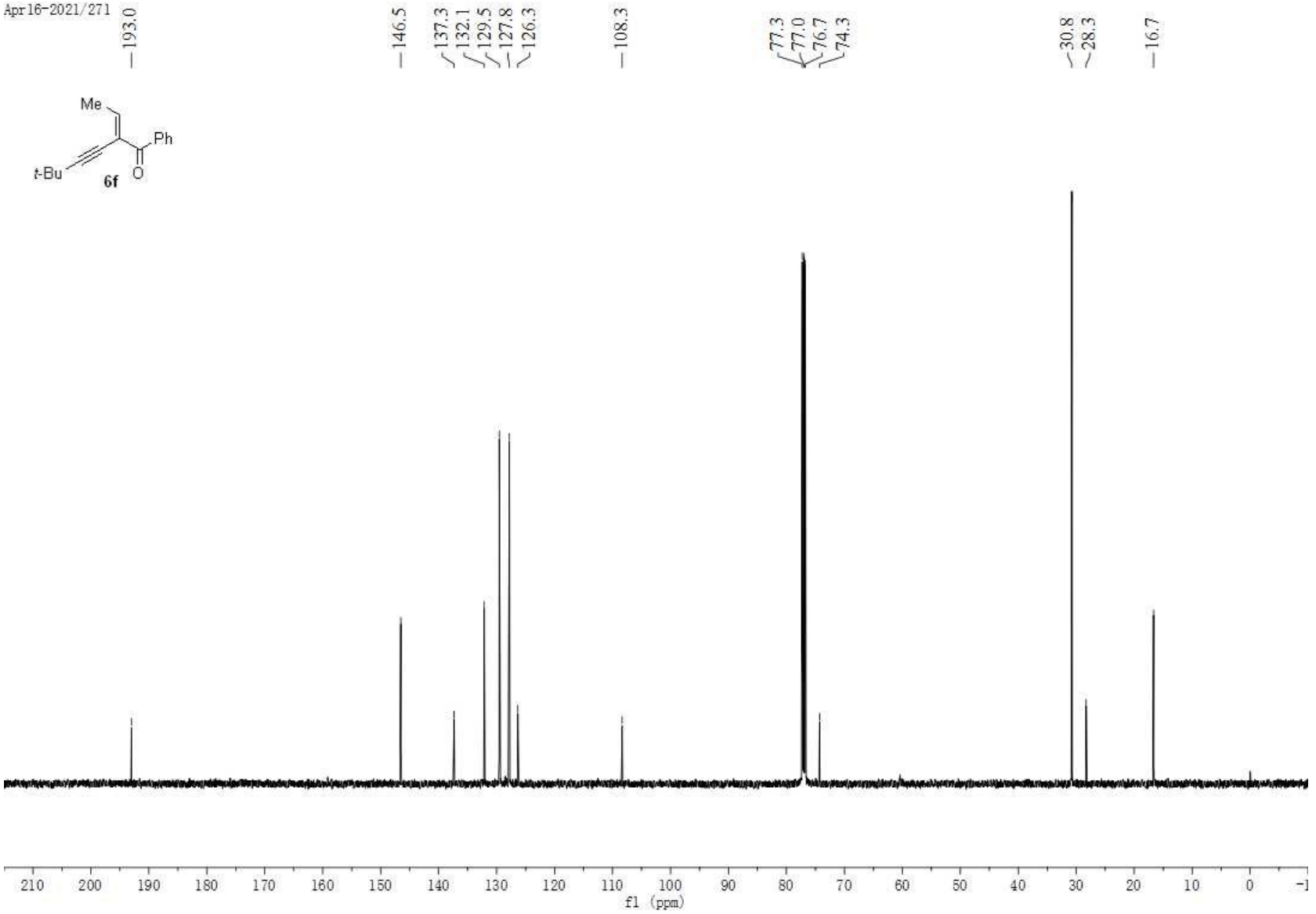
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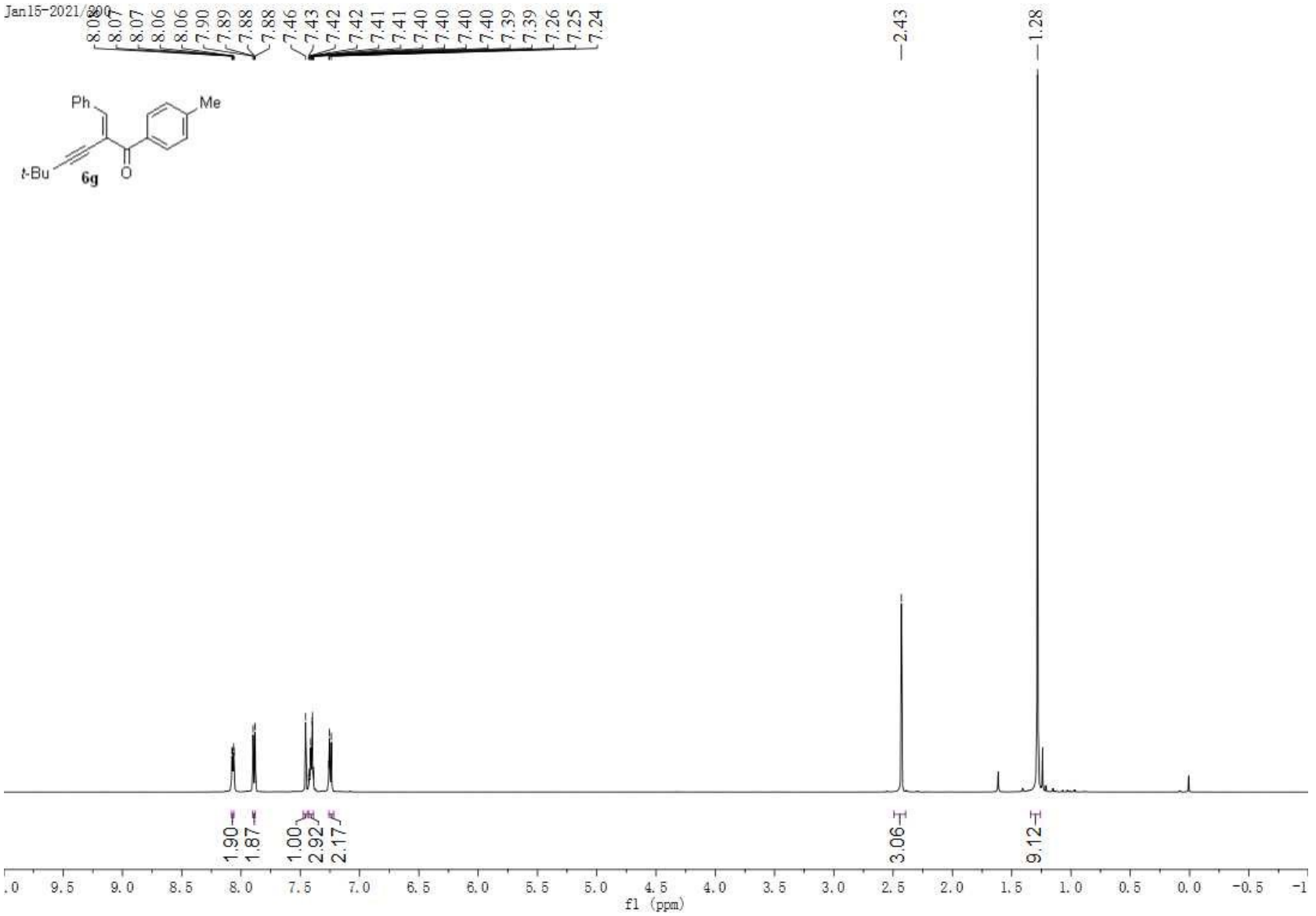
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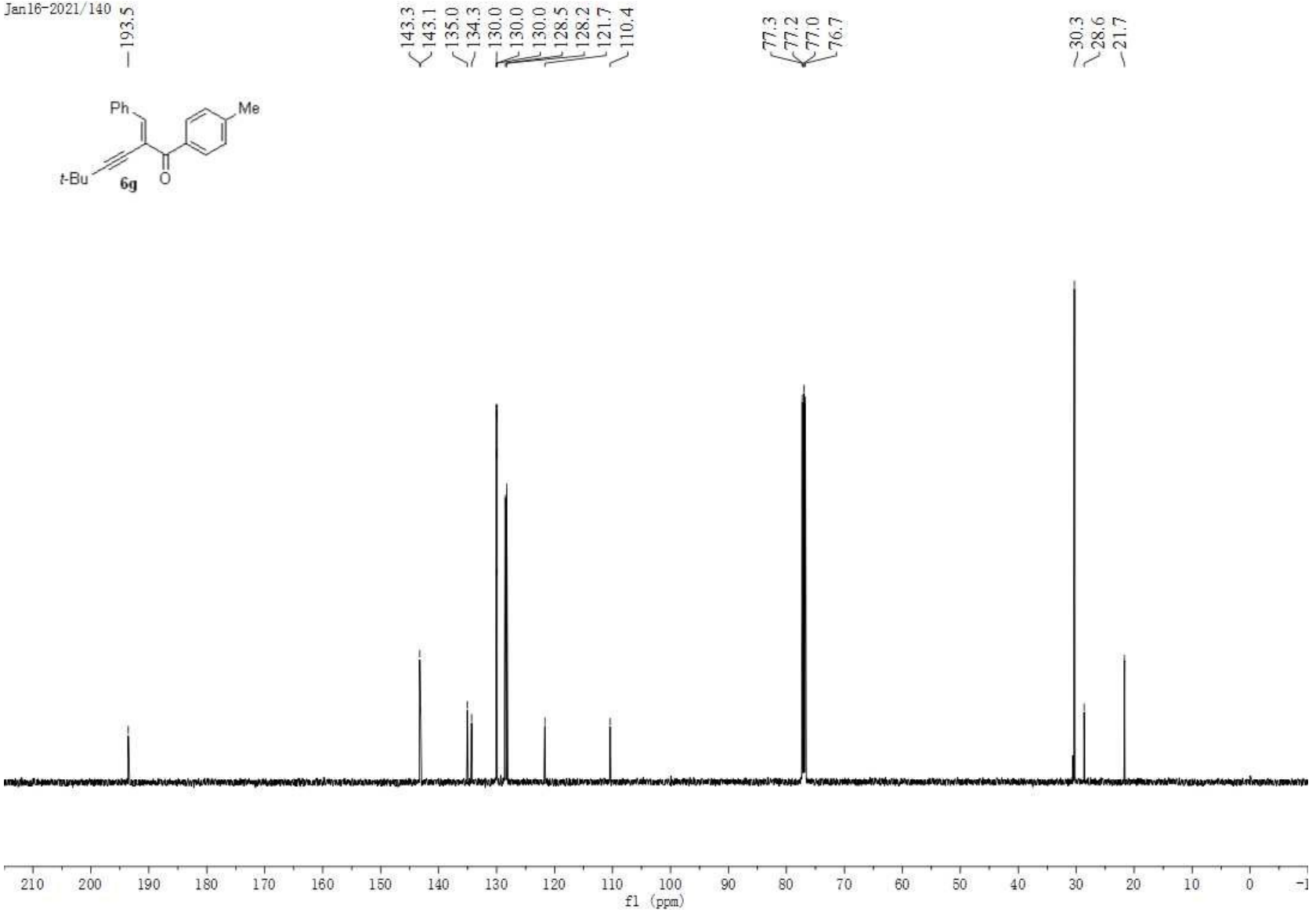
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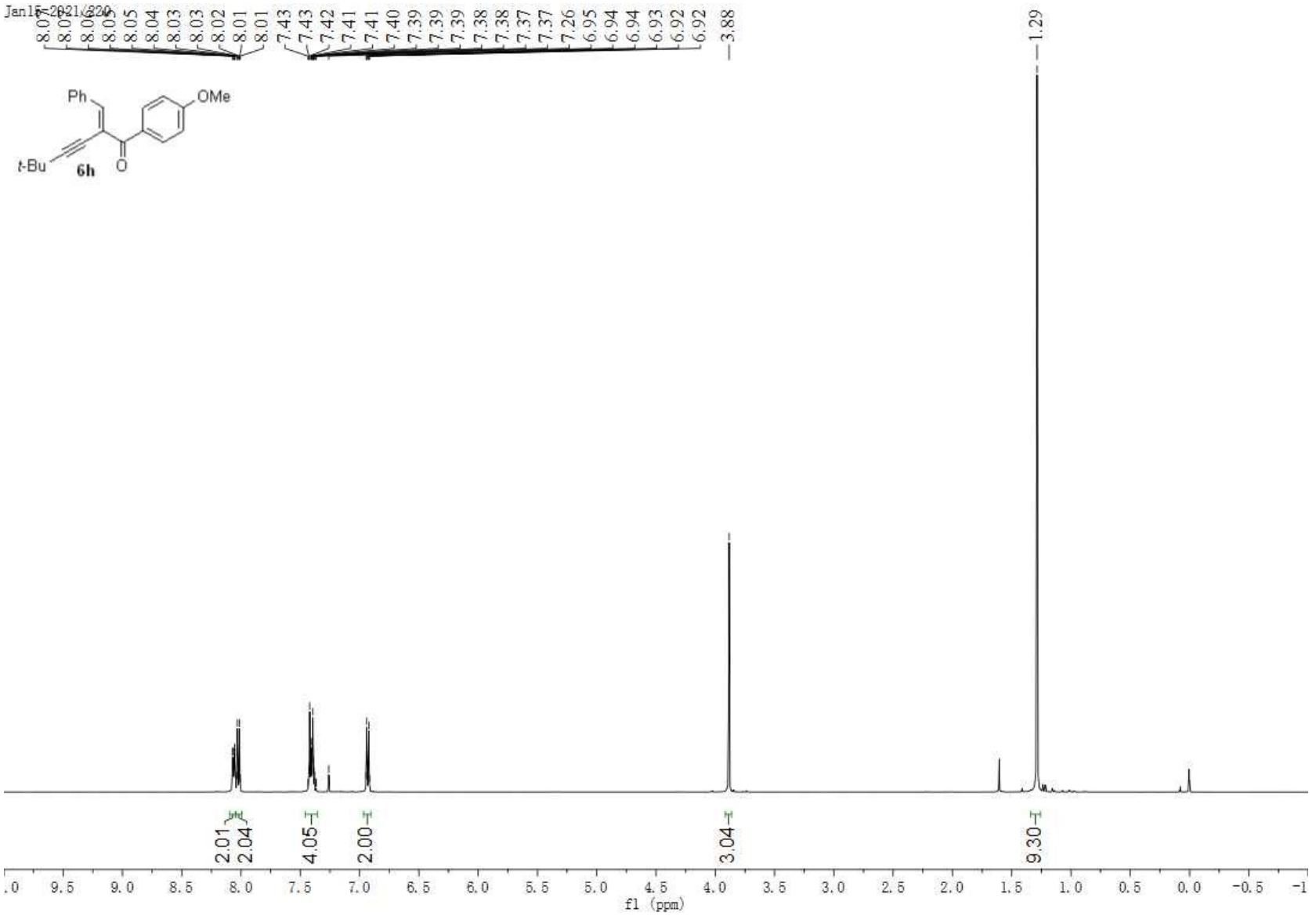
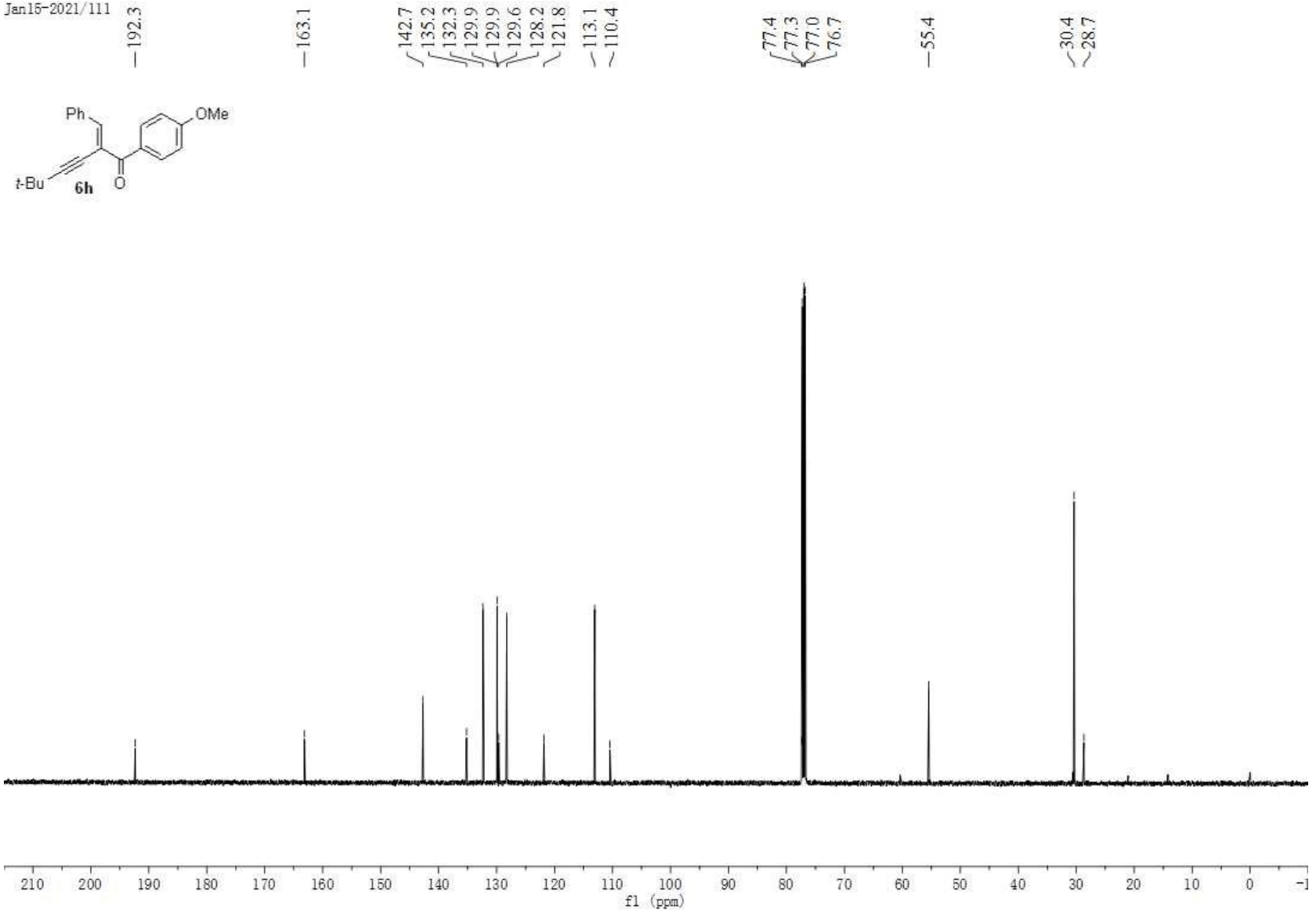
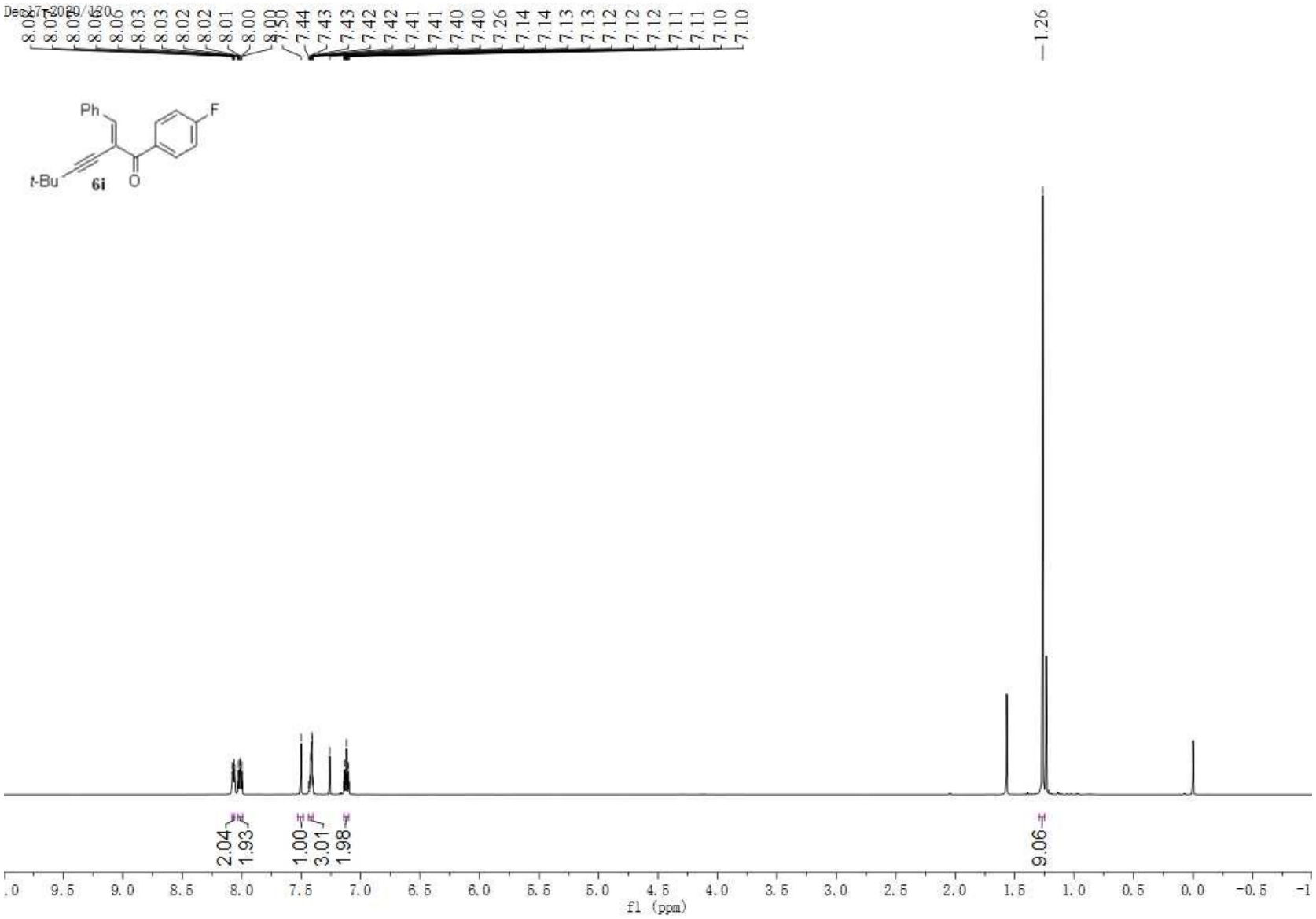
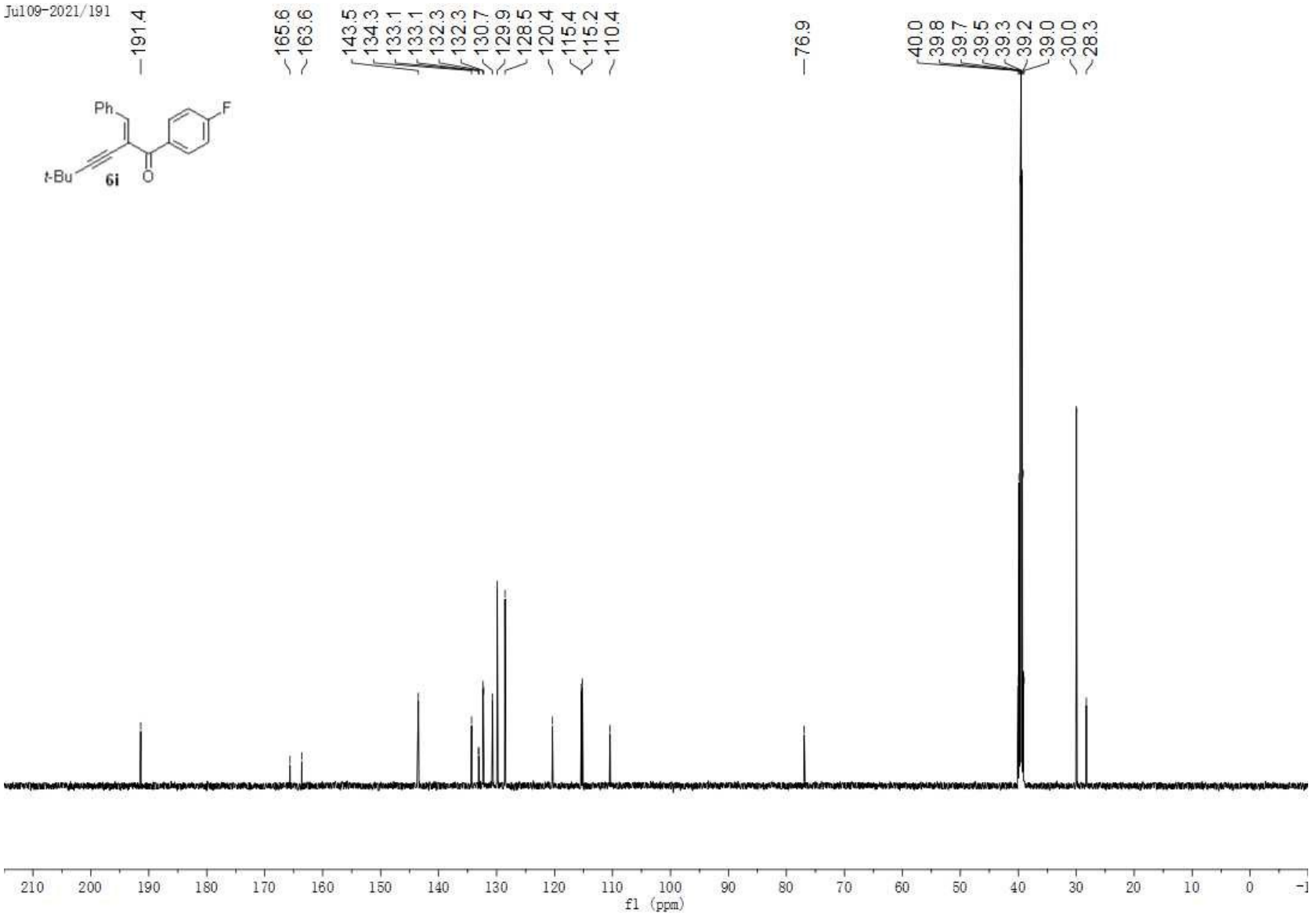
77.0
76.7
30.3
28.6
21.7
Ph
Me
t-Bu
O
6g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

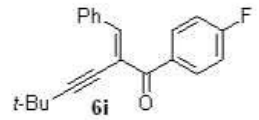

Jan15-2021-220
8.07
8.07
8.06
8.05
8.04
8.03
8.03
8.02
8.01
8.01
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.26
6.95
6.94
6.94
6.93
6.92
6.92
3.88
1.29
Ph
OMe
t-Bu
O
6h
2.01
2.04
4.05
2.00
3.04
9.30
f1 (ppm)

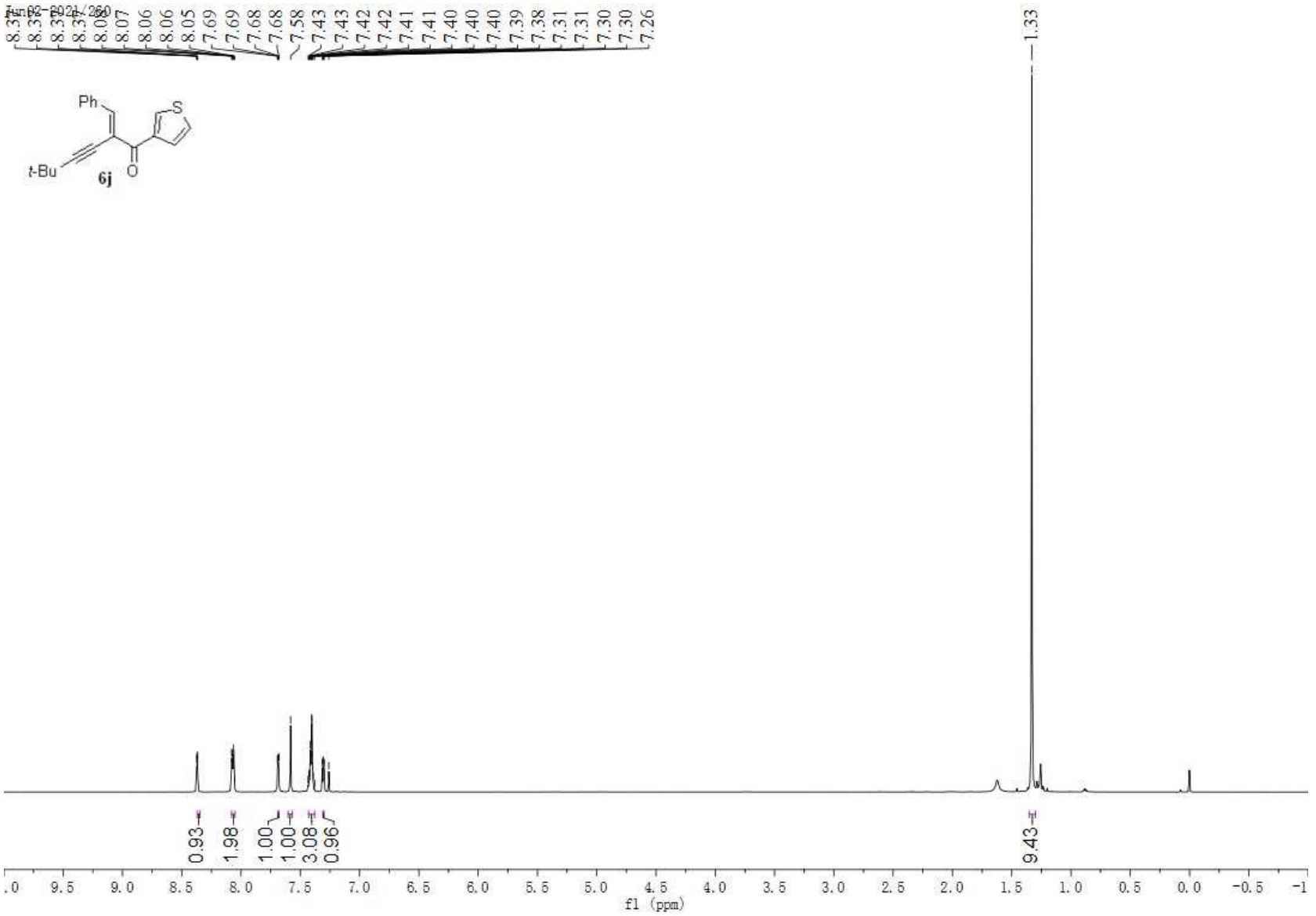

Jan15-2021/111
192.3
163.1
142.7
135.2
132.3
129.9
129.9
129.6
128.2
121.8
113.1
110.4
77.4
77.3
77.0
76.7
55.4
30.4
28.7
Ph
OMe
t-Bu
6h
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

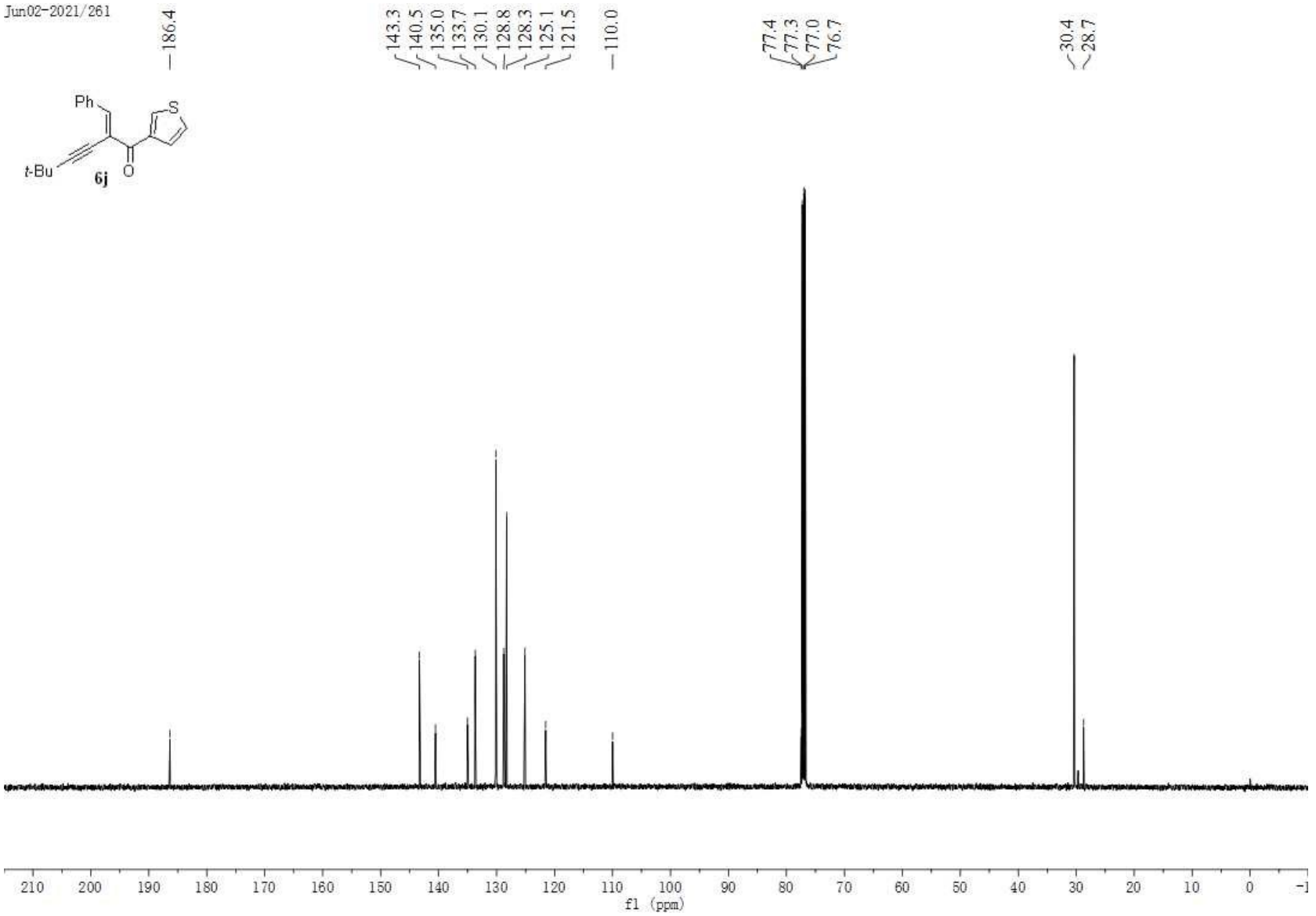

Dec 17 2020 120
8.07
8.07
8.06
8.06
8.03
8.03
8.02
8.02
8.01
8.00
8.00
7.50
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.26
7.14
7.14
7.13
7.13
7.12
7.12
7.12
7.11
7.11
7.10
7.10
1.26
Ph
F
t-Bu
6i
O
2.04
1.93
1.00
3.01
1.98
9.06
f1 (ppm)

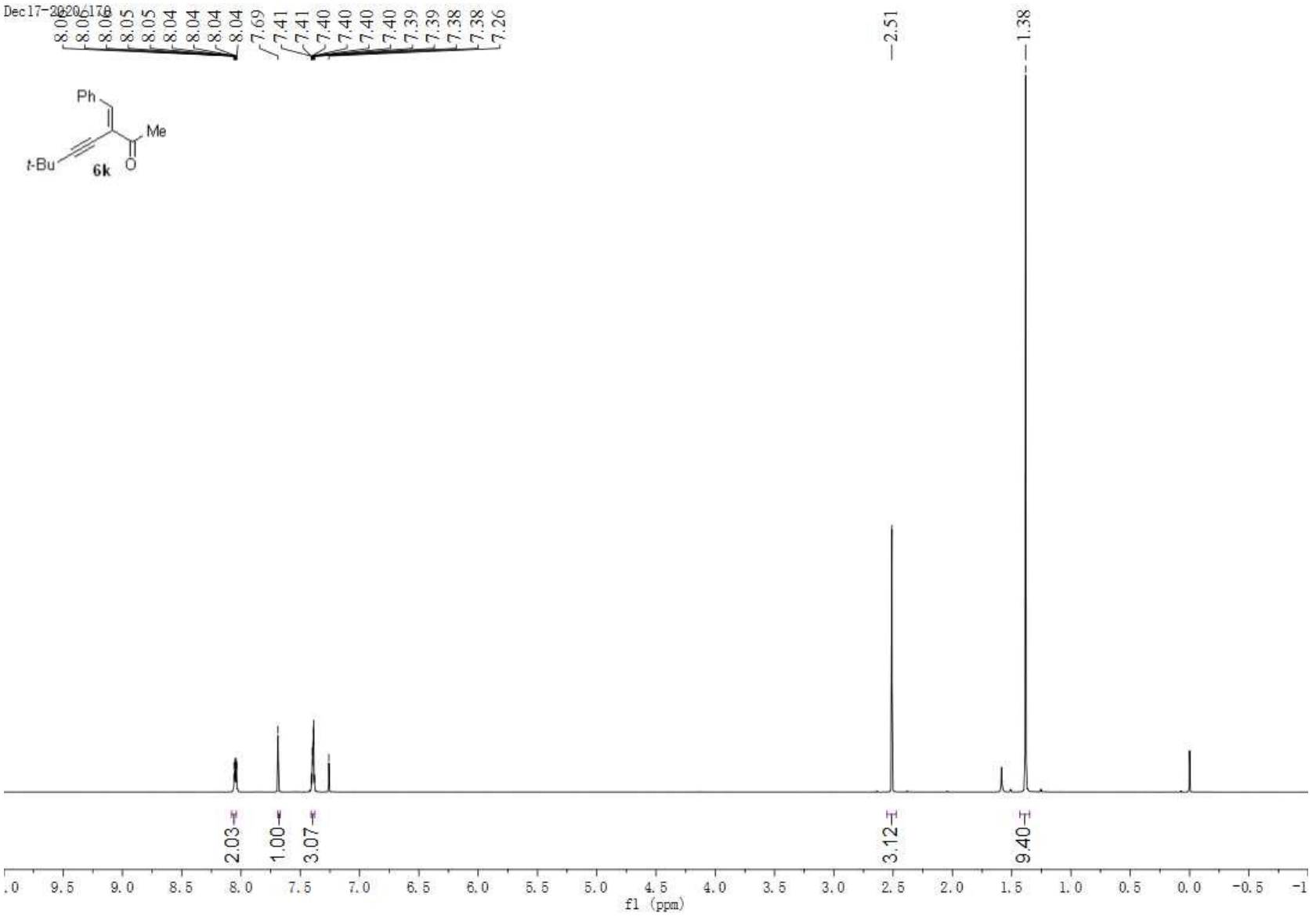

Jul09-2021/191
191.4
165.6
163.6
143.5
134.3
133.1
133.1
132.3
132.3
130.7
129.9
128.5
120.4
115.4
115.2
110.4
76.9
40.0
39.8
39.7
39.5
39.3
39.2
39.0
30.0
28.3
Ph
F
t-Bu
O
6i
f1 (ppm)

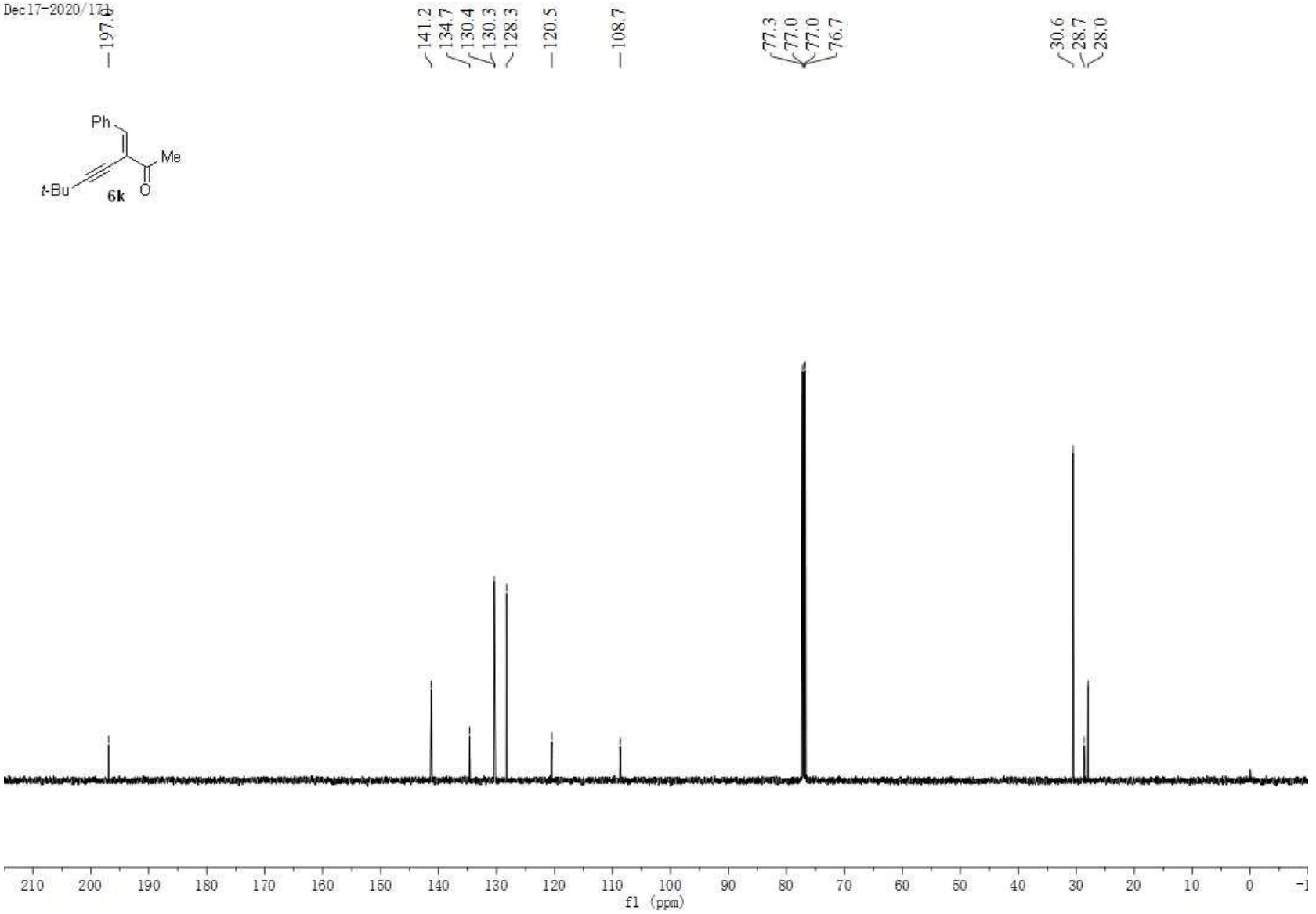
Dec17-2020/122
4-F-ONE

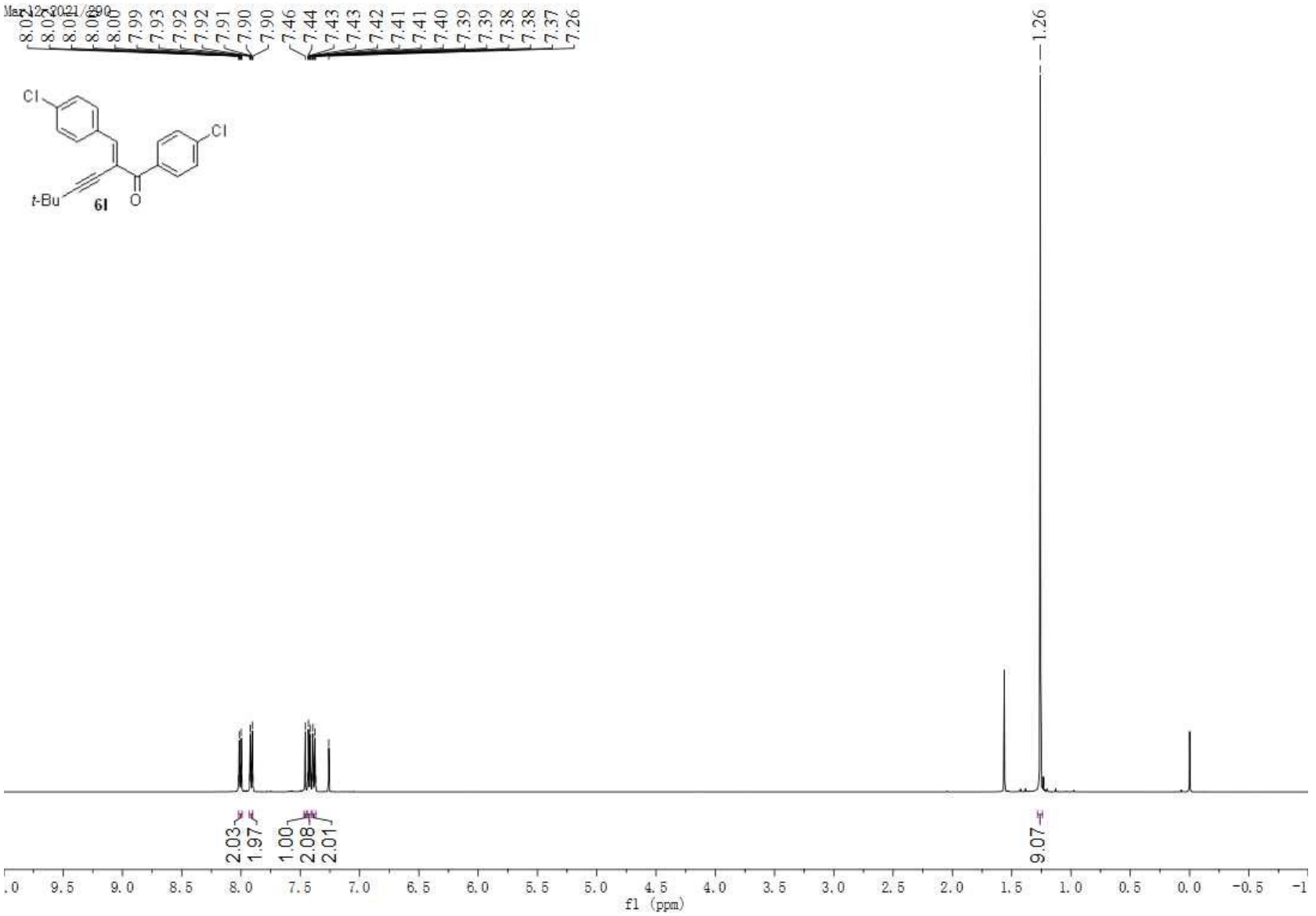


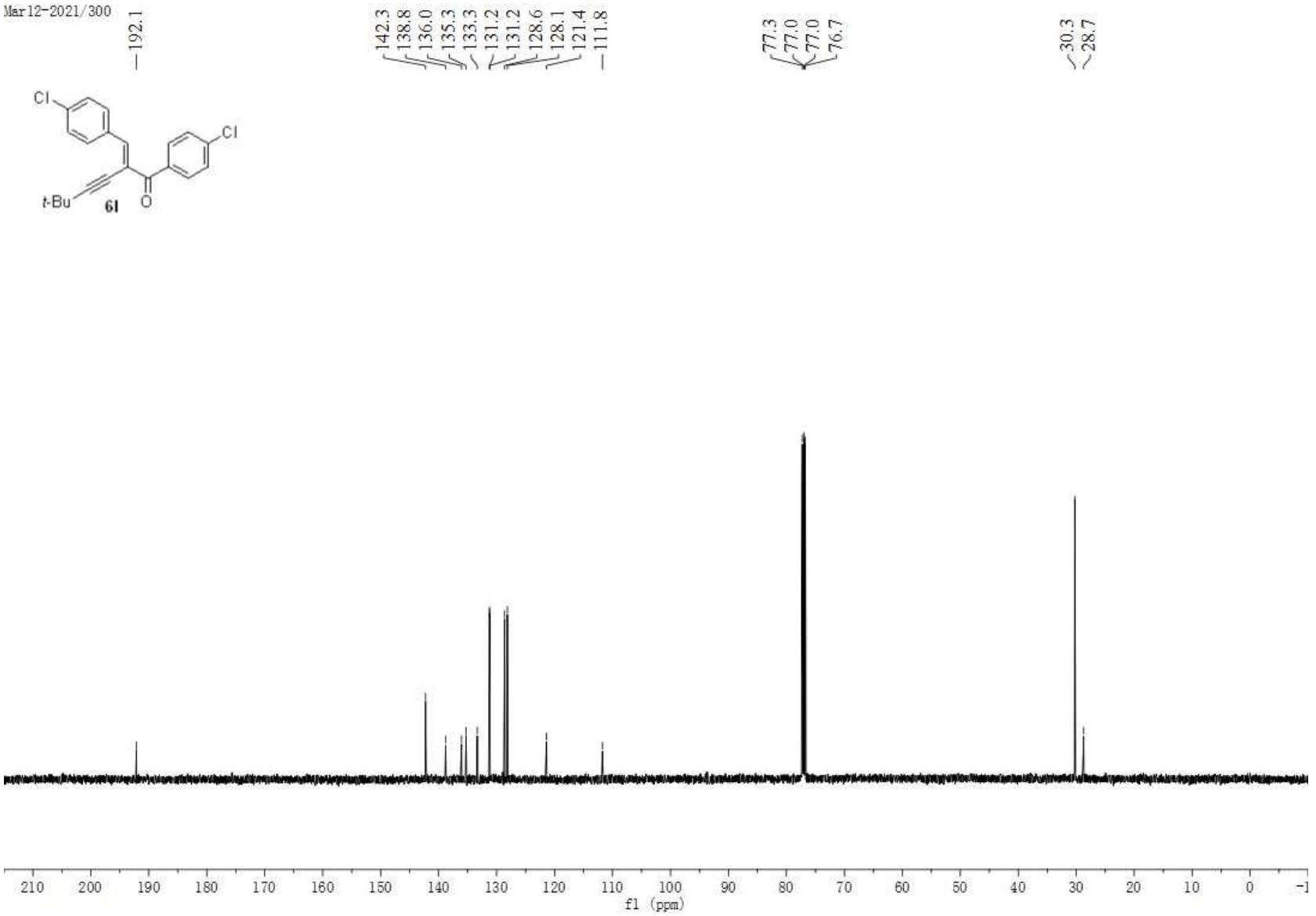

8.37
8.35
8.35
8.34
8.08
8.07
8.06
8.06
8.05
7.69
7.69
7.68
7.68
7.58
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.38
7.31
7.31
7.30
7.30
7.26
1.33
Ph
S
t-Bu
O
6j
0.93
1.98
1.00
1.00
3.08
0.96
9.43
f1 (ppm)

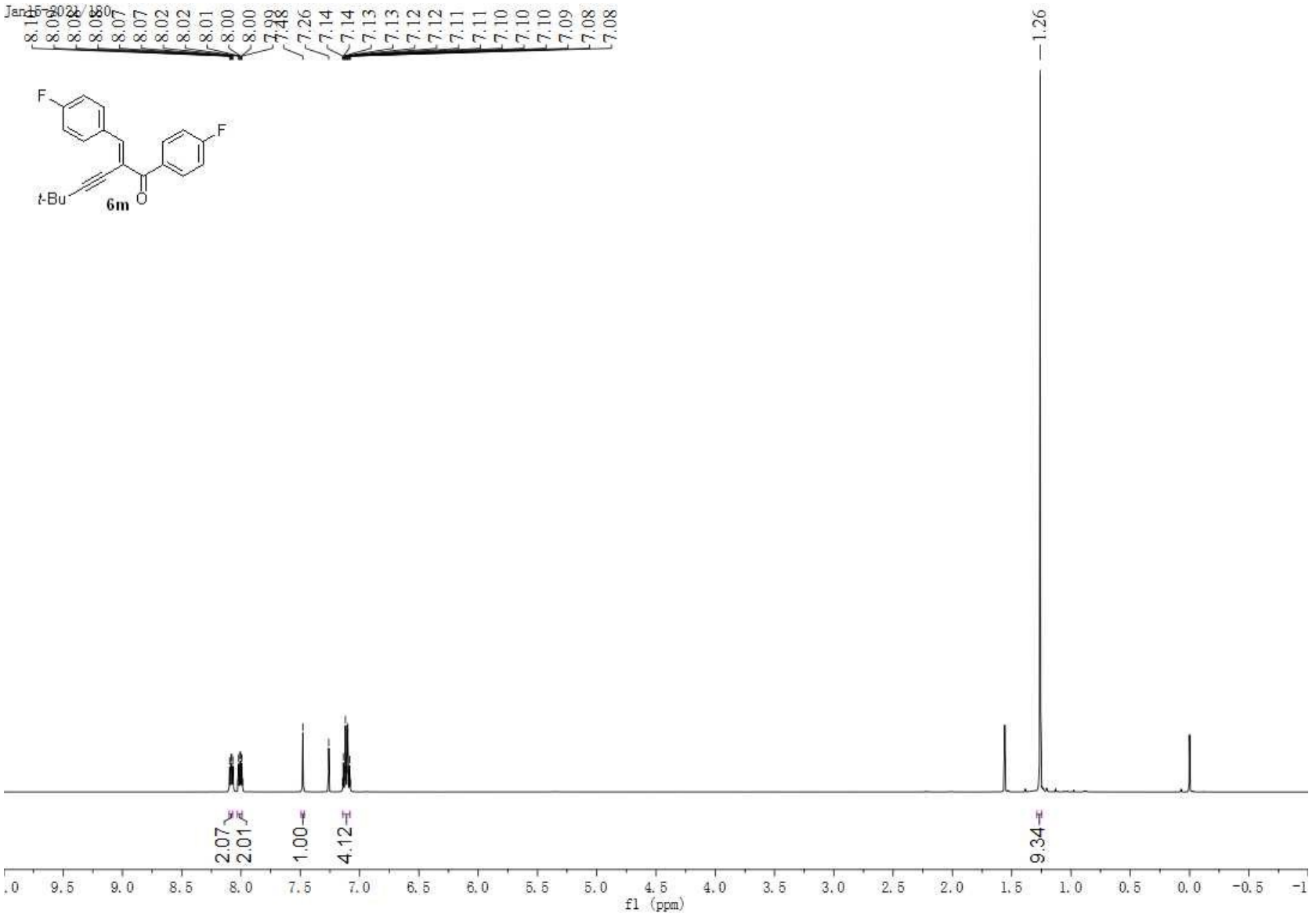

Jun02-2021/261
186.4
143.3
140.5
135.0
133.7
130.1
128.8
128.3
125.1
121.5
110.0
77.4
77.3
77.0
76.7
30.4
28.7
Ph
S
t-Bu
O
6j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

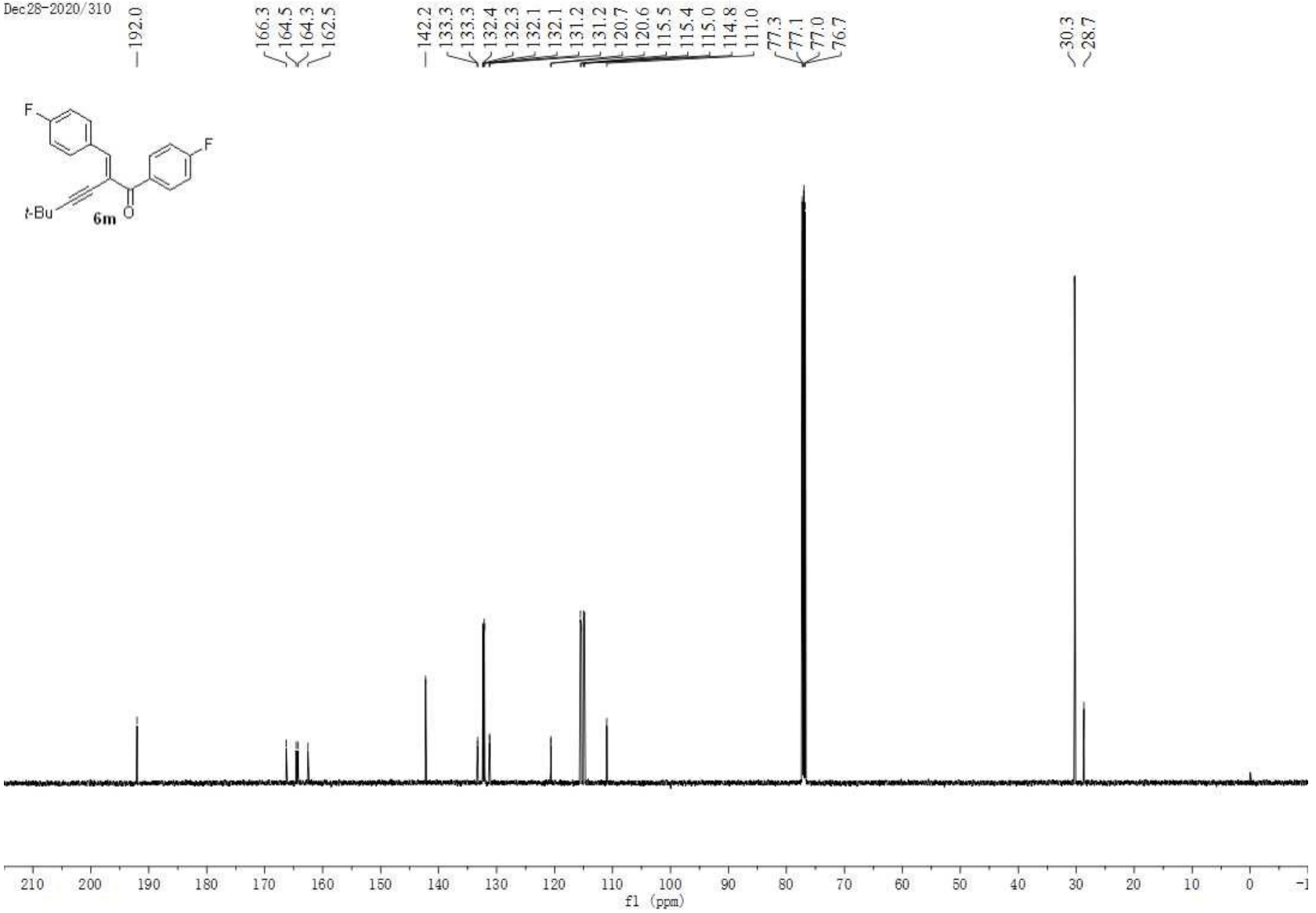

Dec17-2020-170
8.07
8.06
8.05
8.05
8.04
8.04
8.04
8.04
7.69
7.41
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.26
2.51
1.38
Ph
Me
t-Bu
O
6k
2.03
1.00
3.07
3.12
9.40
f1 (ppm)


Dec17-2020/17
197.6
141.2
134.7
130.4
130.3
128.3
120.5
108.7
77.3
77.0
77.0
76.7
30.6
28.7
28.0
Ph
Me
t-Bu
O
6k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

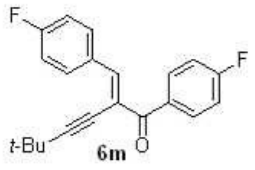

Mar 12 2021 /390
8.02
8.02
8.01
8.00
8.00
7.99
7.93
7.92
7.92
7.91
7.90
7.90
7.46
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.26
1.26
Cl
Cl
t-Bu
O
6l
2.03
1.97
1.00
2.08
2.01
9.07
f1 (ppm)


Mar12-2021/300
192.1
142.3
138.8
136.0
135.3
133.3
131.2
131.2
128.6
128.1
121.4
111.8
77.3
77.0
77.0
76.7
30.3
28.7
Cl
Cl
t-Bu
O
6l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Jan 15 2021 i80
8.12
8.03
8.02
8.02
8.01
8.00
8.00
7.99
7.48
7.26
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.10
7.10
7.09
7.08
7.08
1.26
F
F
t-Bu
O
6m
2.07
2.01
1.00
4.12
9.34
f1 (ppm)

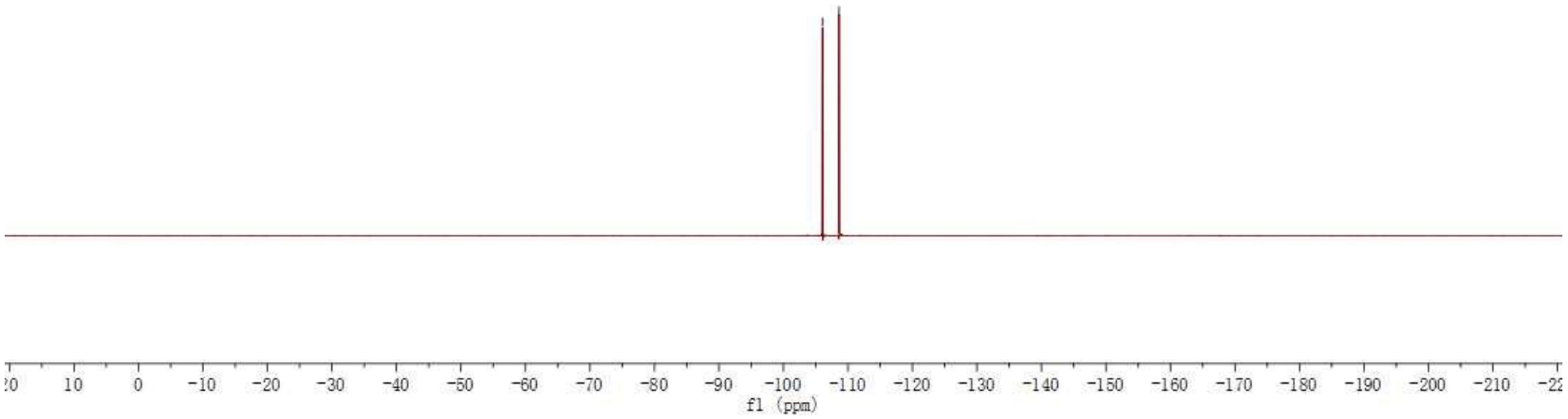

Dec28-2020/310
192.0
166.3
164.5
164.3
162.5
142.2
133.3
133.3
132.4
132.3
132.1
132.1
131.2
131.2
120.7
120.6
115.5
115.4
115.0
114.8
111.0
77.3
77.1
77.0
76.7
30.3
28.7
F
F
t-Bu
O
6m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

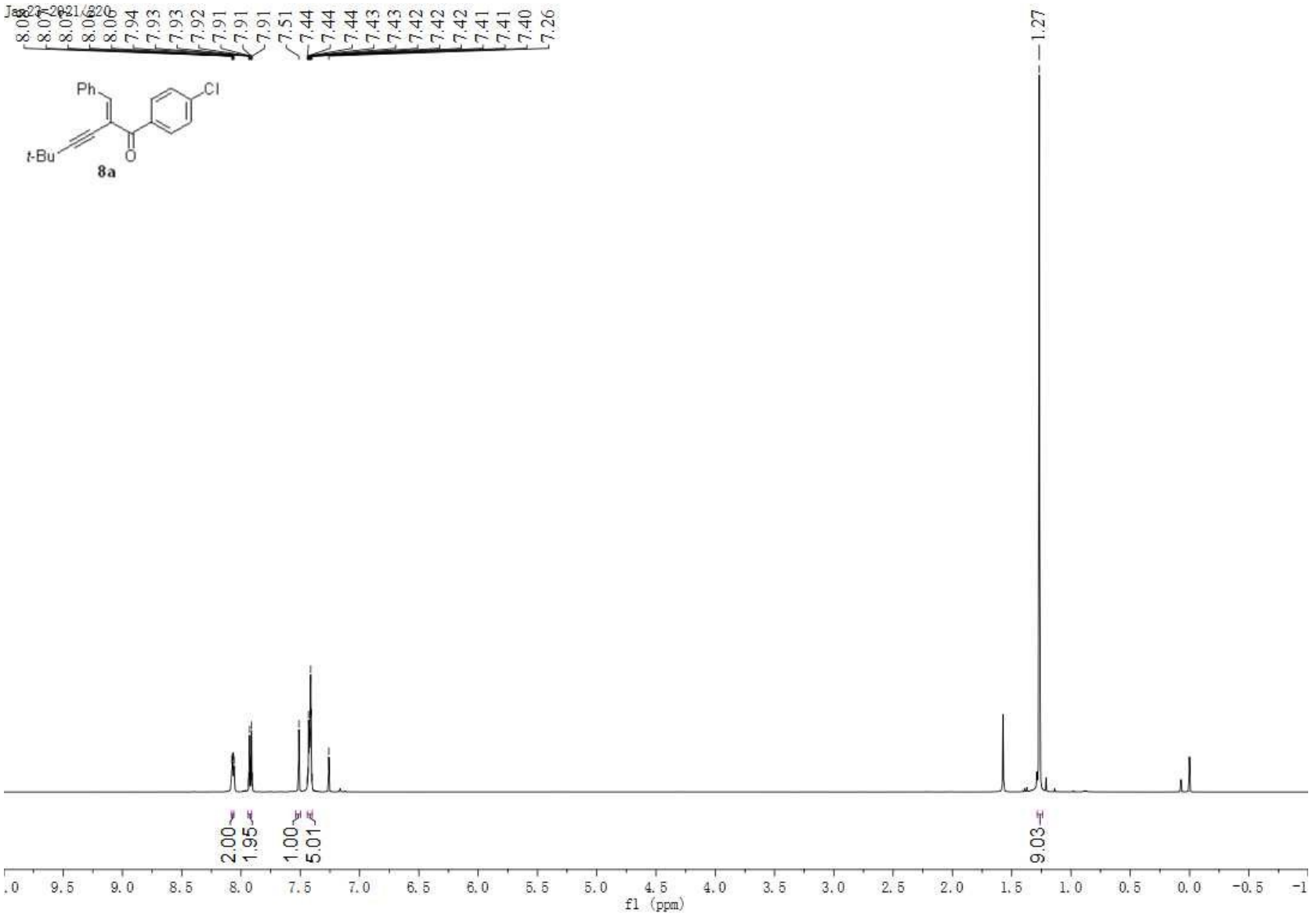
Dec28-2020/232

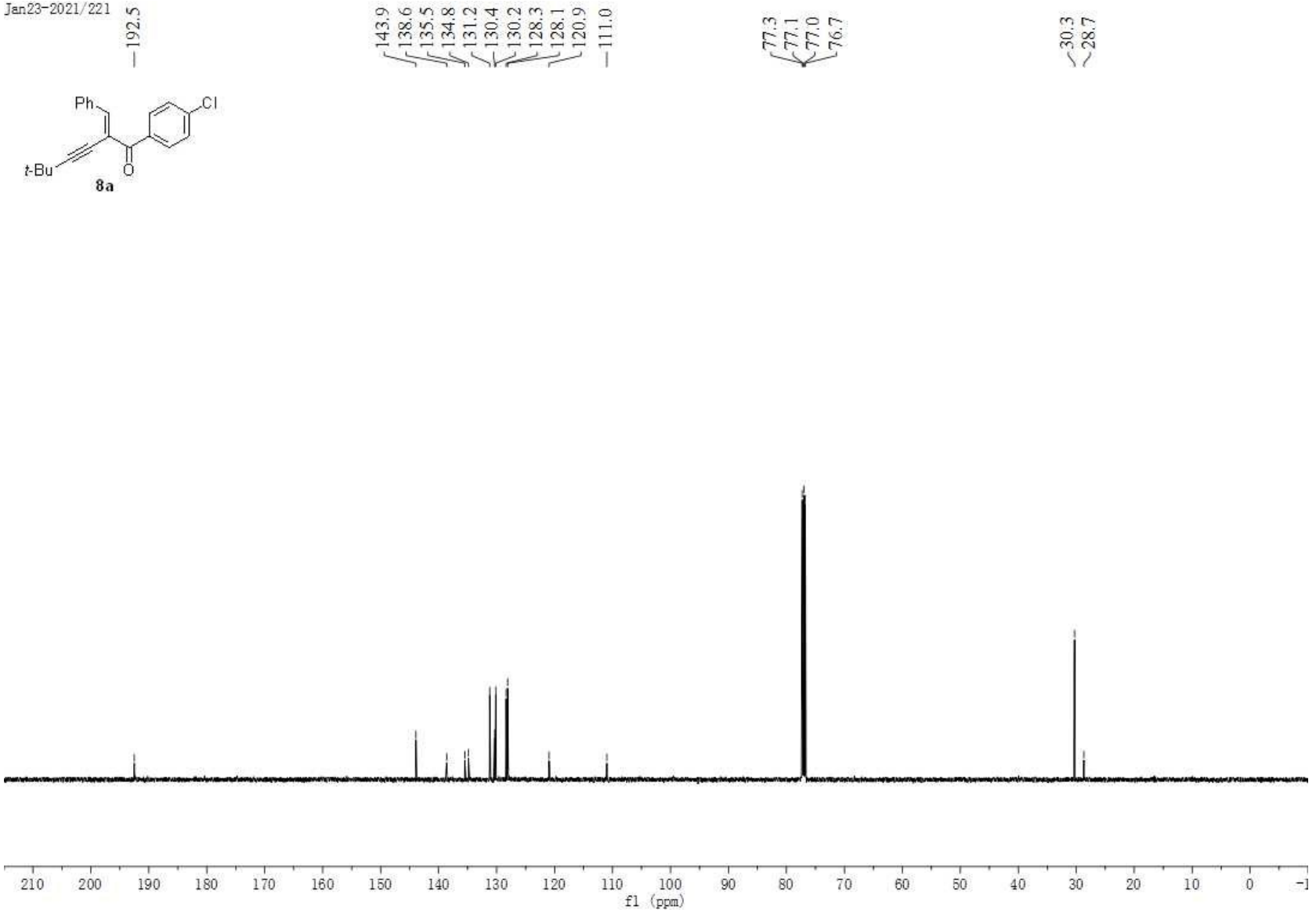


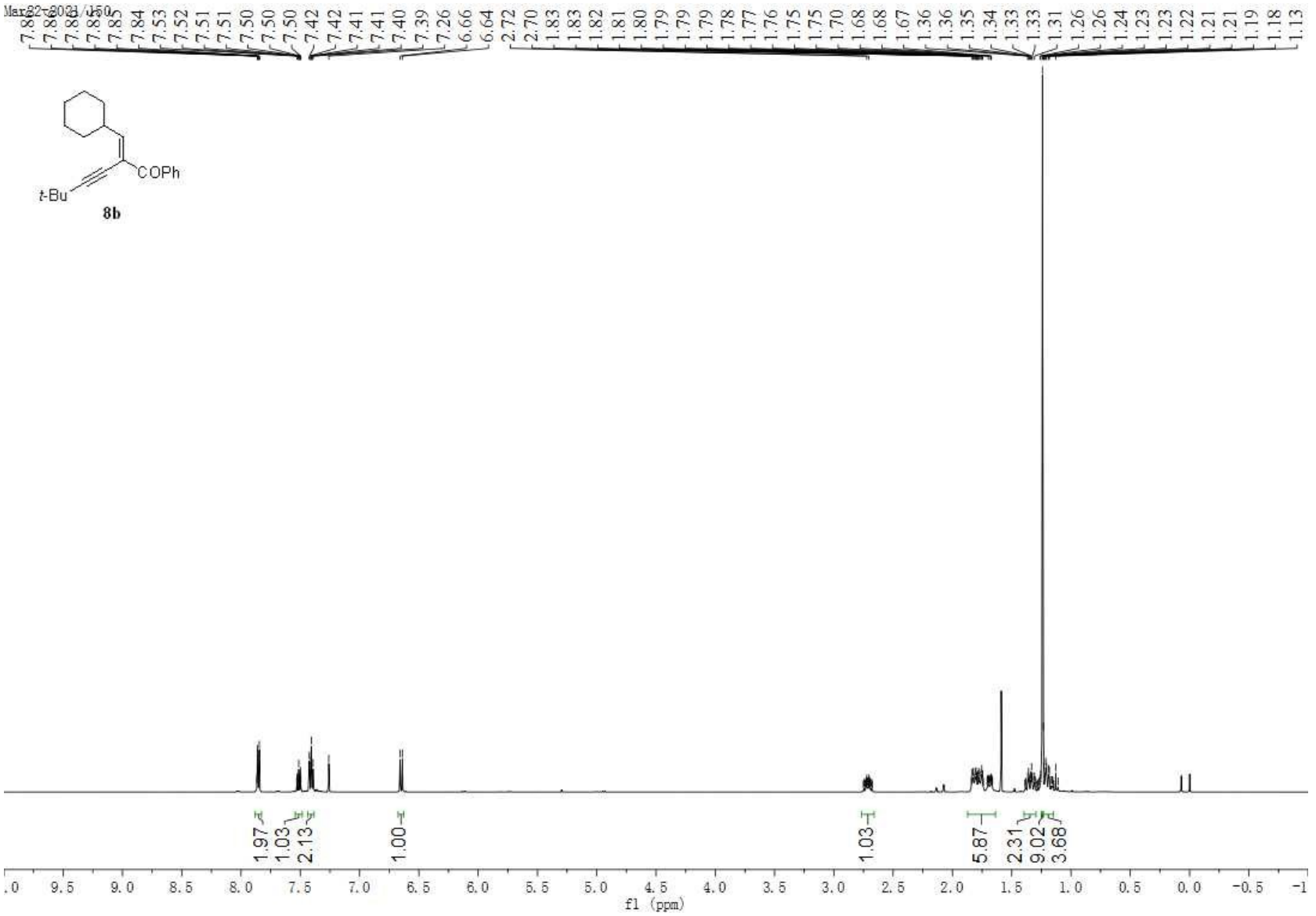
6m

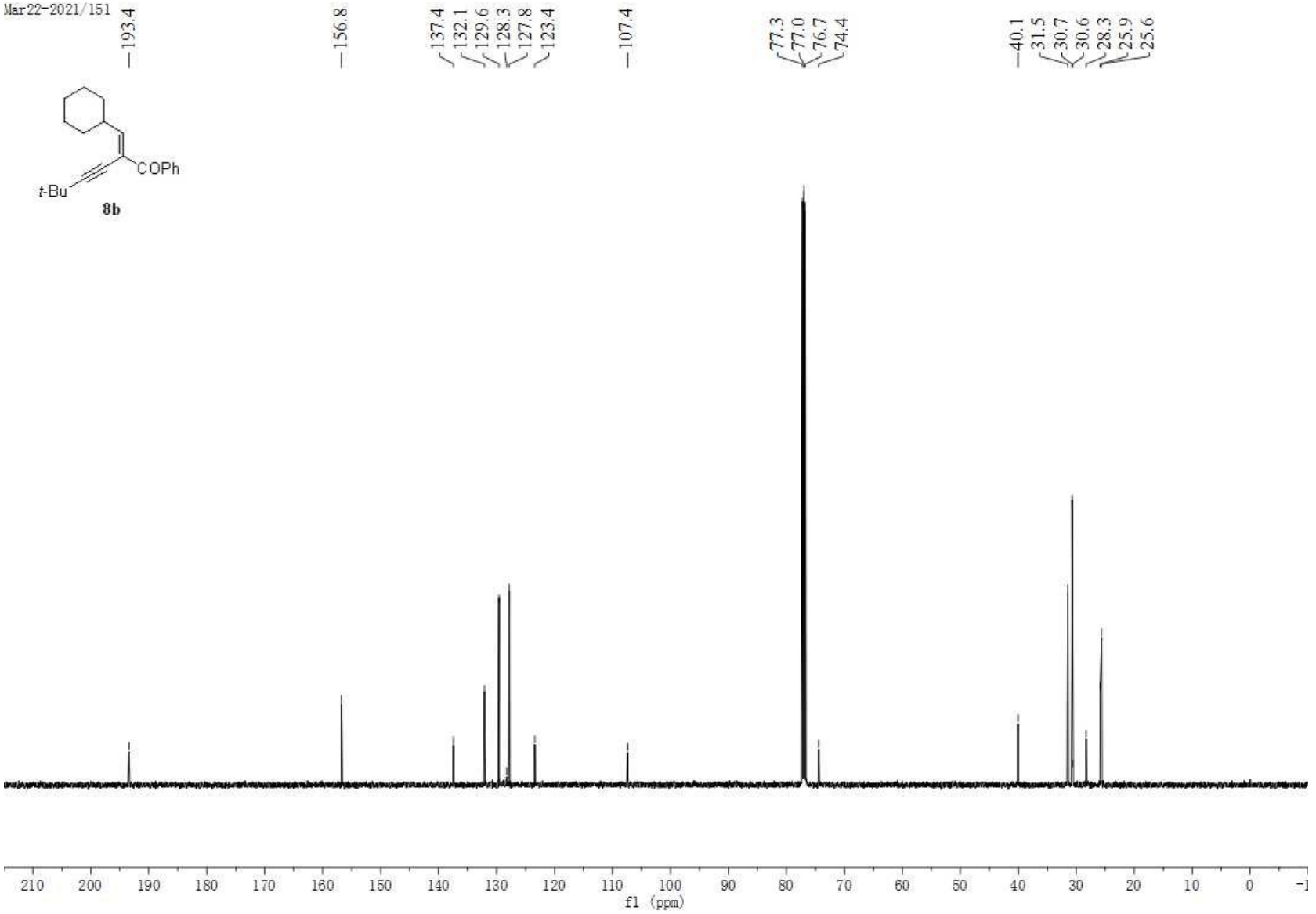
-106.06
-108.63

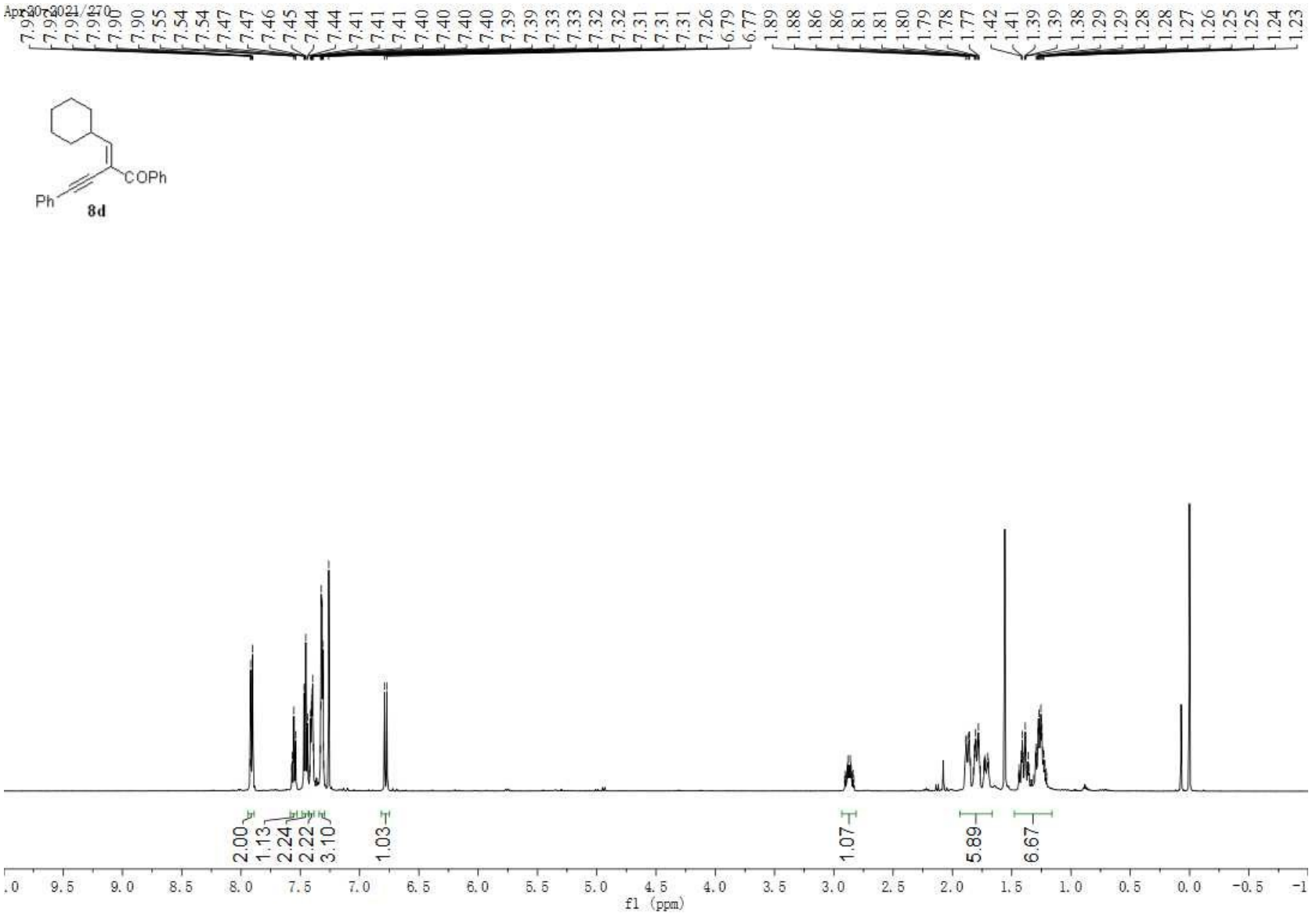


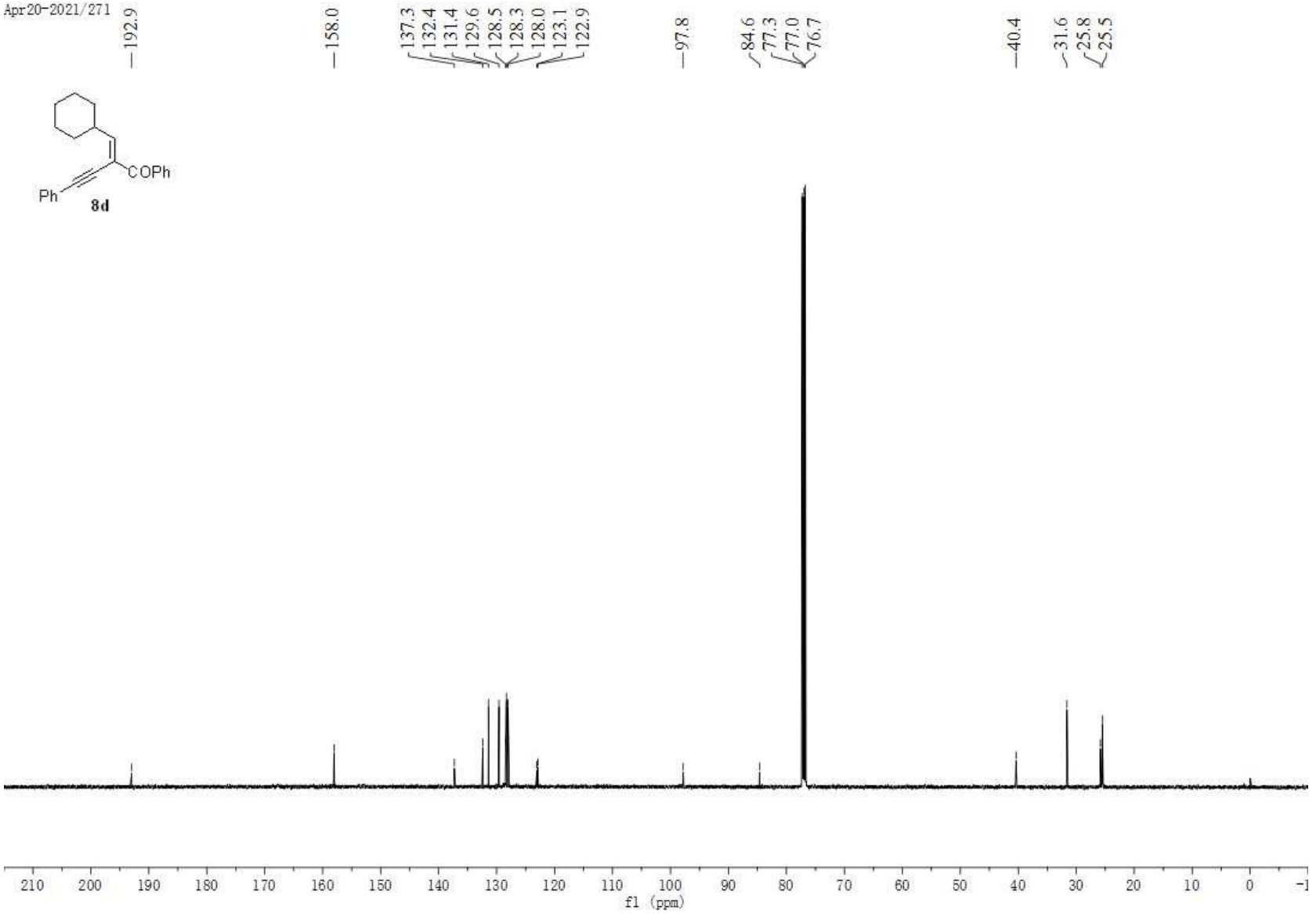

8.07
8.06
7.94
7.93
7.93
7.92
7.91
7.91
7.91
7.51
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.26
1.27
Ph
Cl
t-Bu
O
8a
2.00
1.95
1.00
5.01
9.03
f1 (ppm)

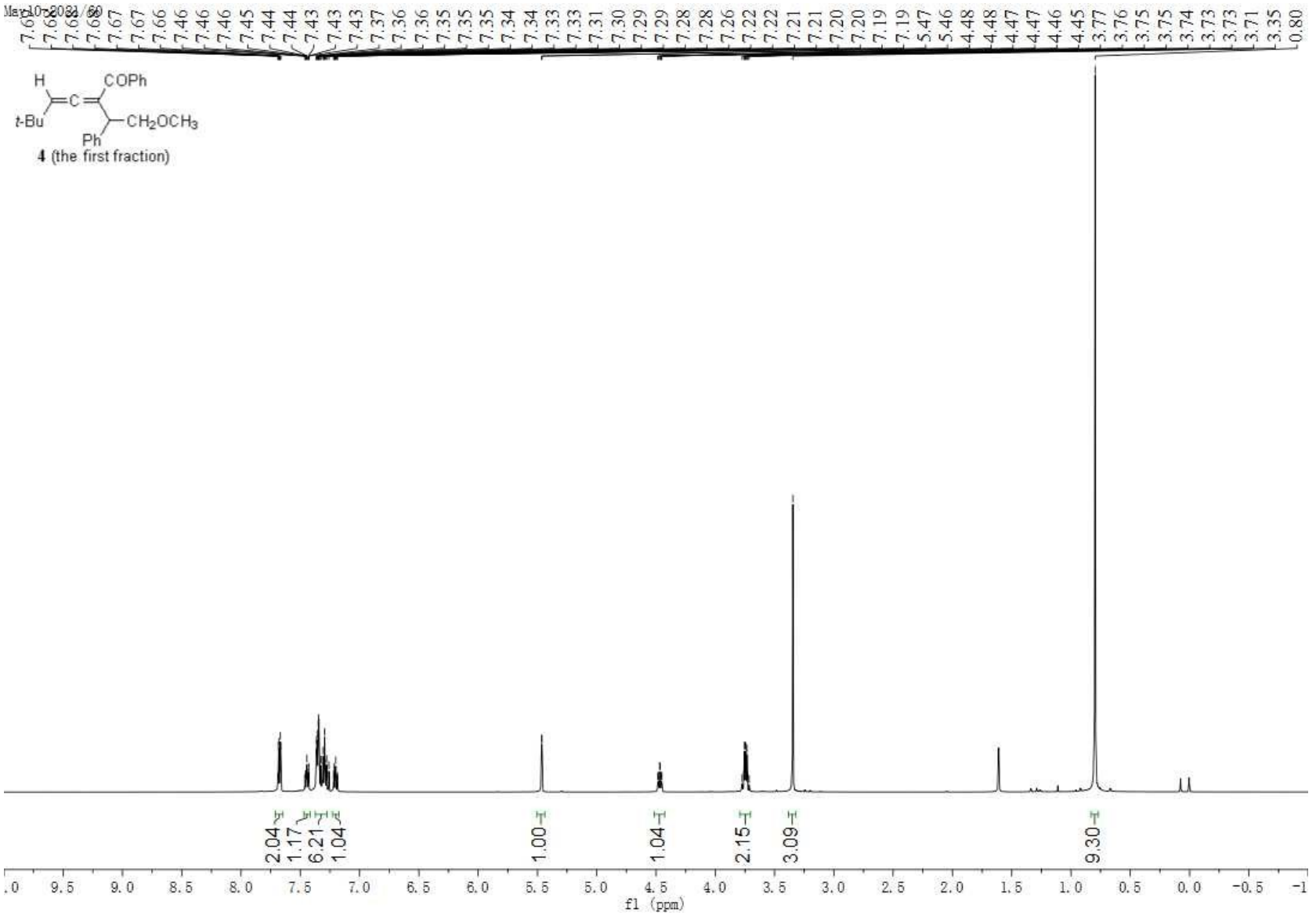

Jan23-2021/221
192.5
143.9
138.6
135.5
134.8
131.2
130.4
130.2
128.3
128.1
120.9
111.0
77.3
77.1
77.0
76.7
30.3
28.7
Ph
Cl
t-Bu
O
8a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

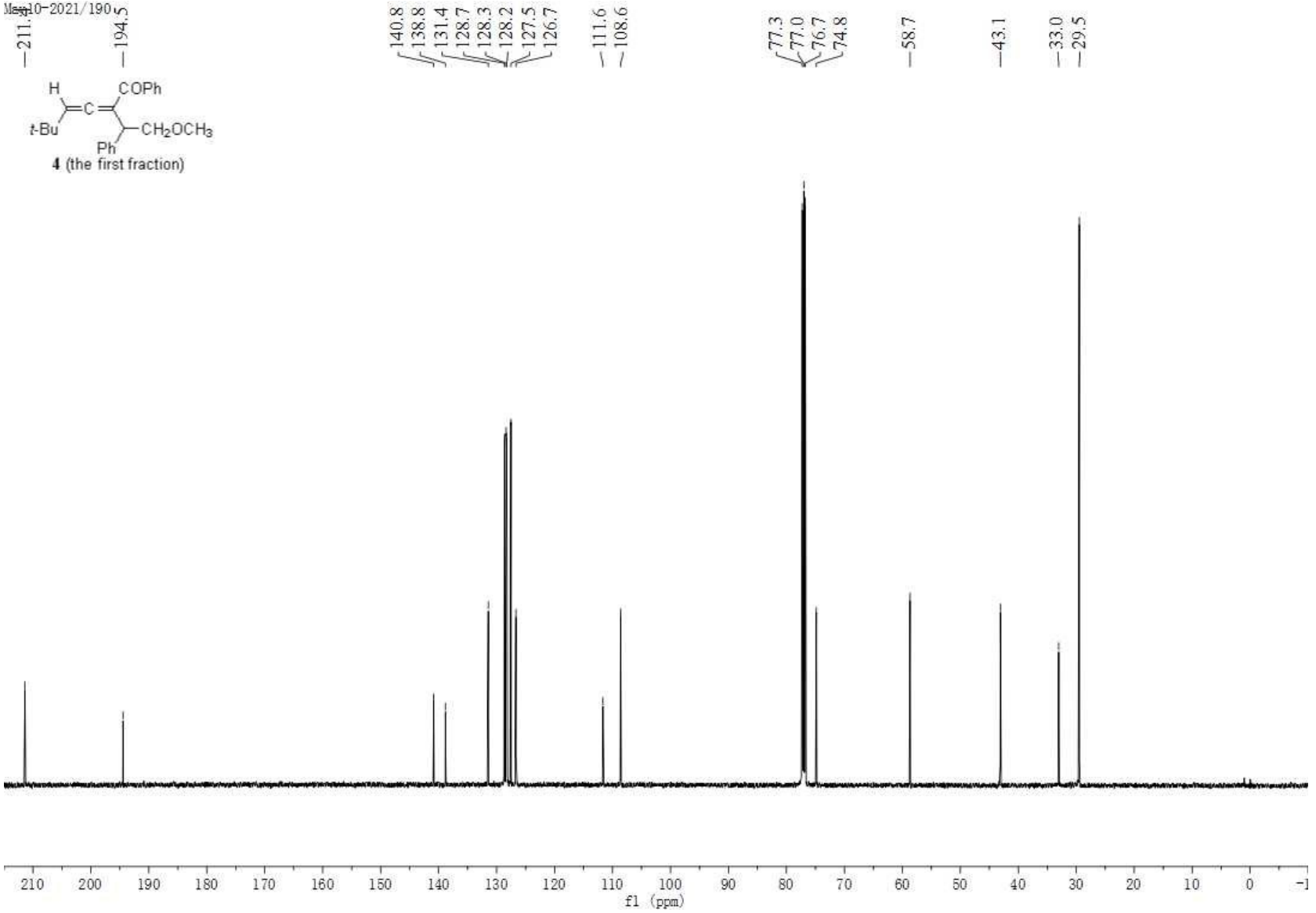

COPh
t-Bu
8b
f1 (ppm)

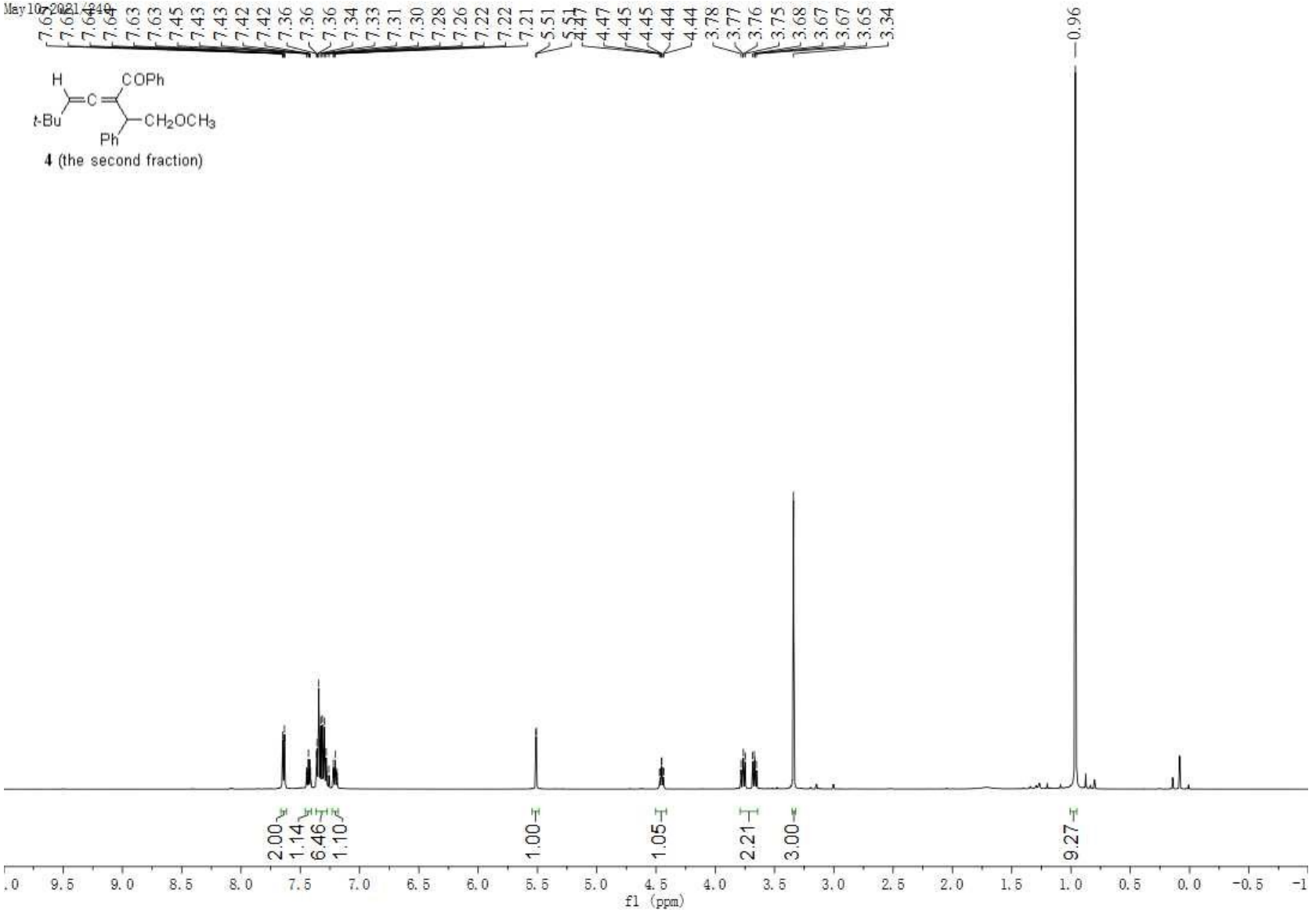

Mar22-2021/151
193.4
156.8
137.4
132.1
129.6
128.3
127.8
123.4
107.4
77.3
77.0
76.7
74.4
40.1
31.5
30.7
30.6
28.3
25.9
25.6
COPh
t-Bu
8b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

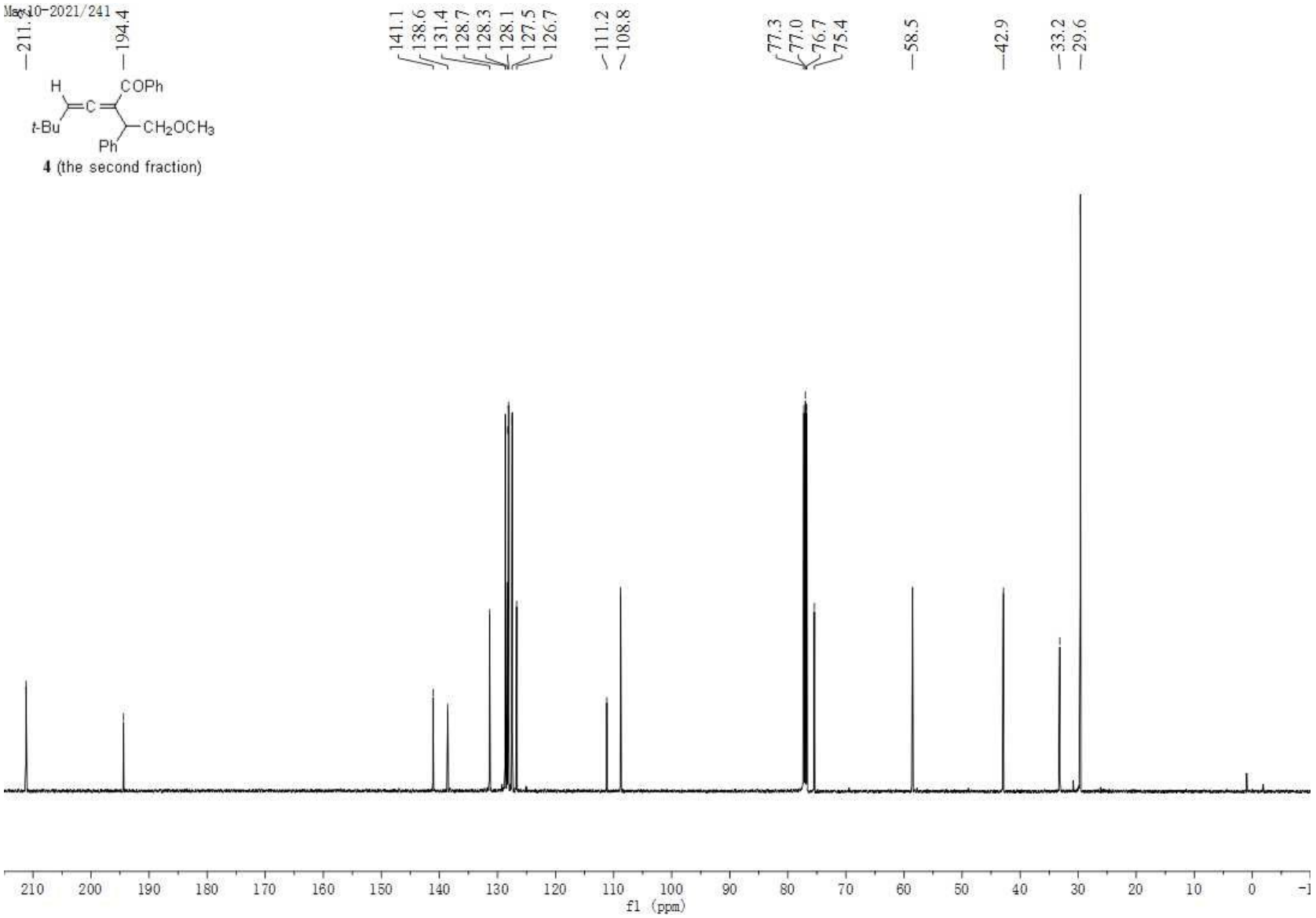

Apr 30 2021/270
7.93 7.93 7.91 7.91 7.90 7.90 7.55 7.54 7.54 7.47 7.47 7.46 7.45 7.44 7.44 7.41 7.41 7.41 7.40 7.40 7.40 7.40 7.39 7.39 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.26 6.79 6.77
1.89 1.88 1.86 1.86 1.81 1.81 1.80 1.79 1.78 1.77 1.42 1.41 1.39 1.39 1.38 1.29 1.29 1.28 1.28 1.27 1.26 1.25 1.25 1.24 1.23
COPh
Ph
8d
2.00
1.13
2.24
2.22
3.10
1.03
1.07
5.89
6.67
f1 (ppm)

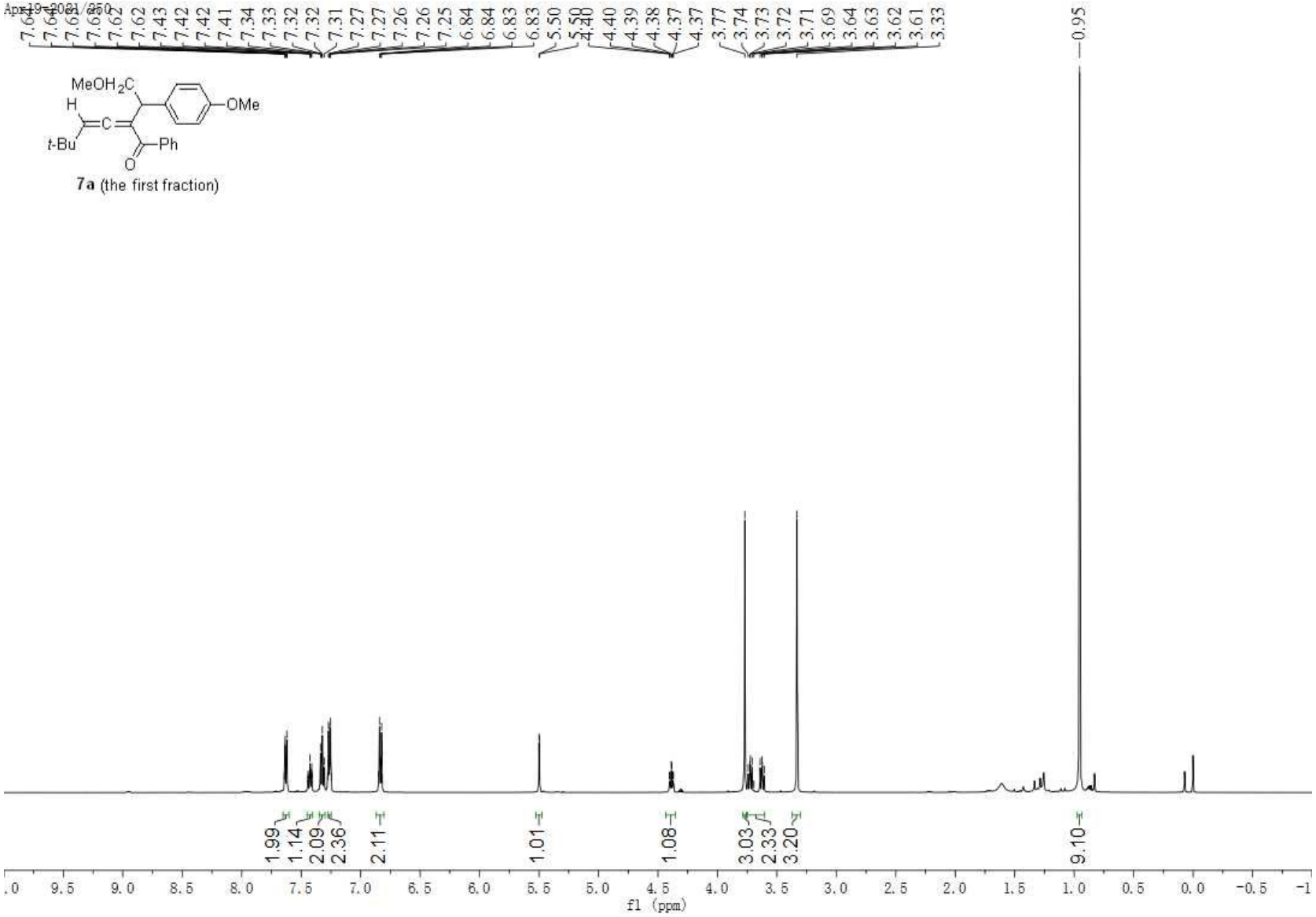

Apr20-2021/271
192.9
158.0
137.3
132.4
131.4
129.6
128.5
128.3
128.0
123.1
122.9
97.8
84.6
77.3
77.0
76.7
40.4
31.6
25.8
25.5
COPh
Ph
8d
f1 (ppm)

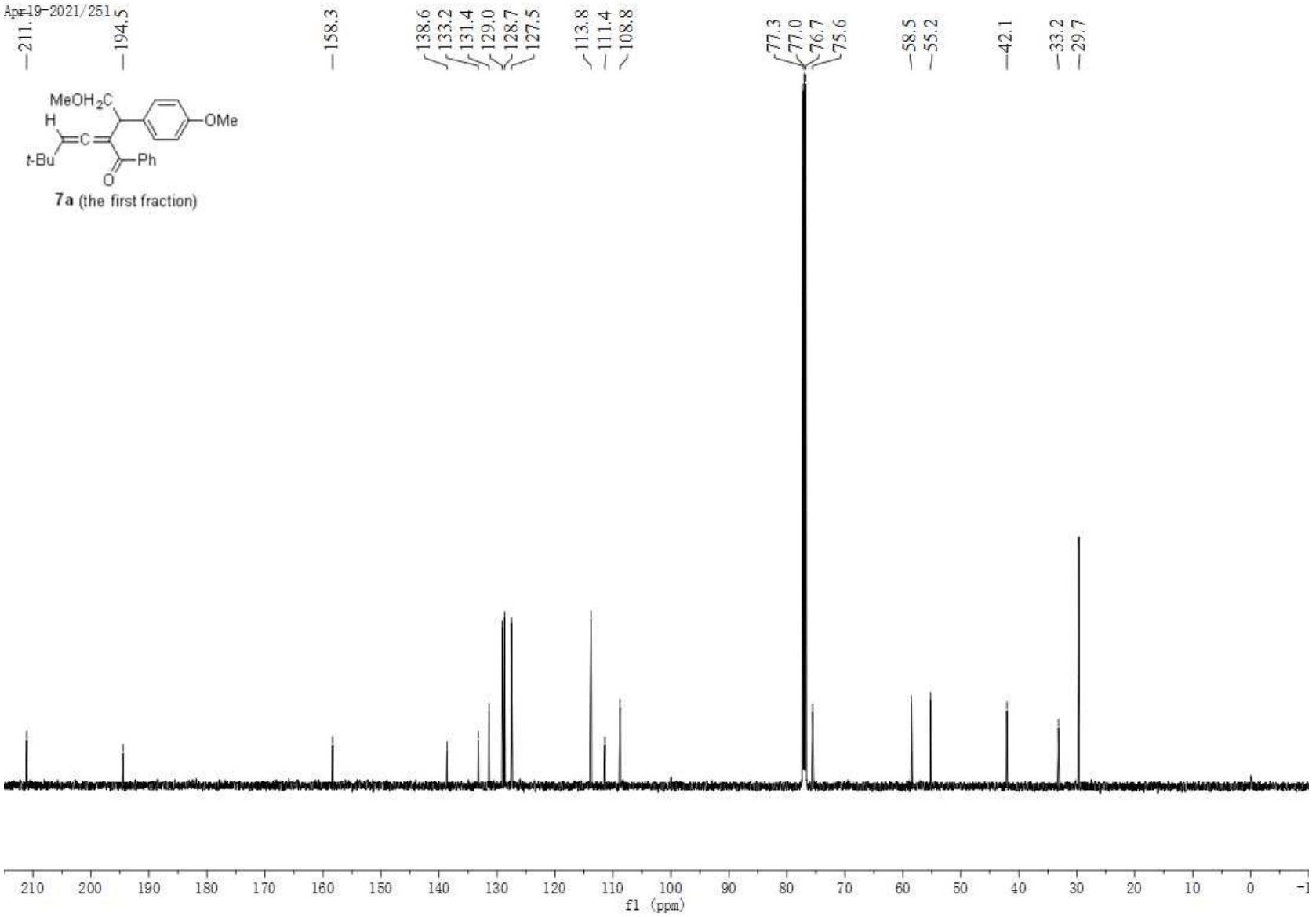

H
COPh
t-Bu
CH2OCH3
Ph
4 (the first fraction)
2.04
1.17
6.21
1.04
1.00
1.04
2.15
3.09
9.30
f1 (ppm)

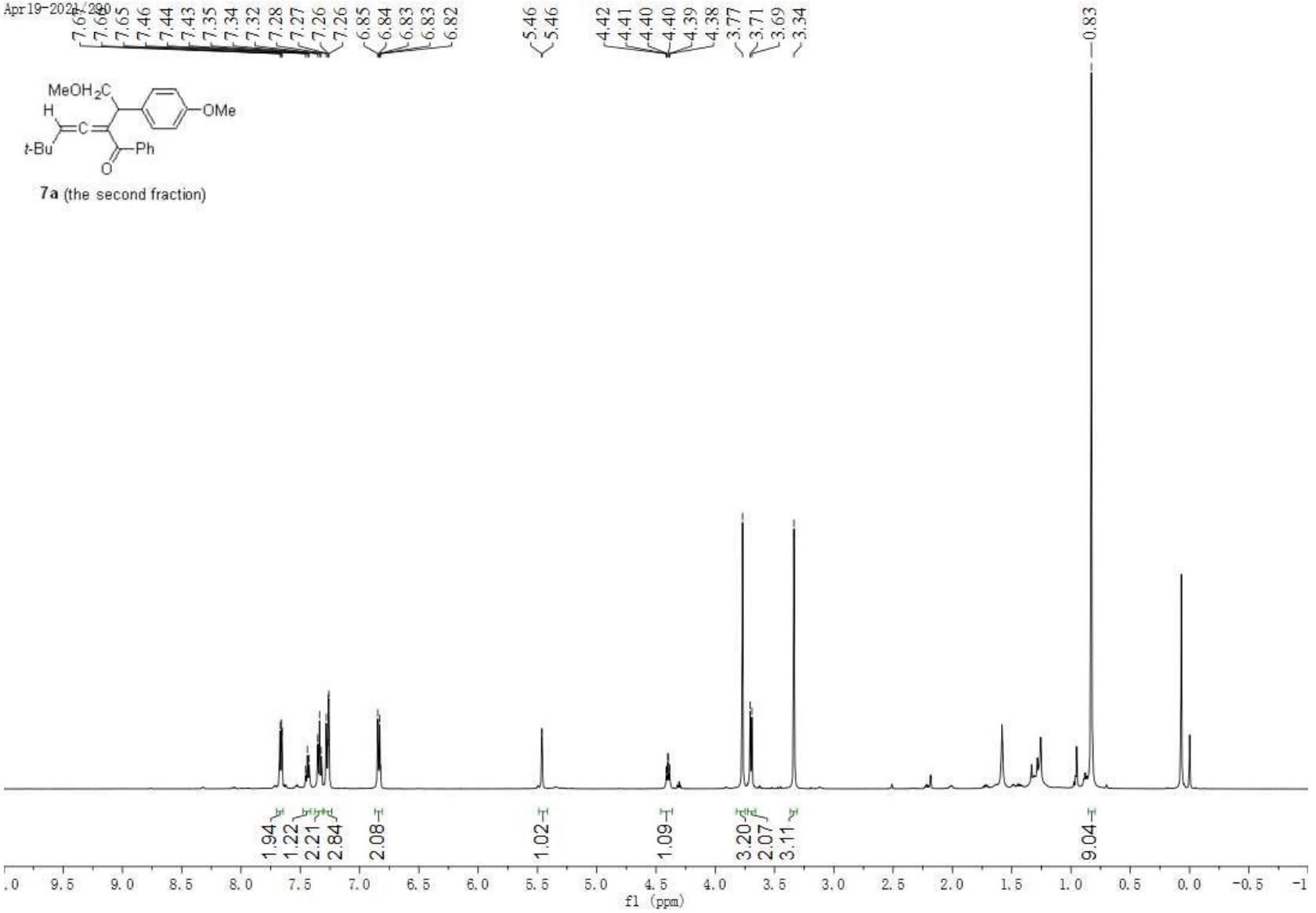

Mar10-2021/190
211.4
194.5
140.8
138.8
131.4
128.7
128.3
128.2
127.5
126.7
111.6
108.6
77.3
77.0
76.7
74.8
58.7
43.1
33.0
29.5
H
COPh
t-Bu
CH2OCH3
Ph
4 (the first fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


May10-2021-249
7.67
7.64
7.63
7.45
7.43
7.42
7.36
7.34
7.33
7.31
7.30
7.28
7.26
7.22
7.21
5.51
4.47
4.45
4.44
3.78
3.77
3.76
3.75
3.68
3.67
3.65
3.34
0.96
H
COPh
t-Bu
CH2OCH3
Ph
4 (the second fraction)
2.00
1.14
6.46
1.10
1.00
1.05
2.21
3.00
9.27
f1 (ppm)

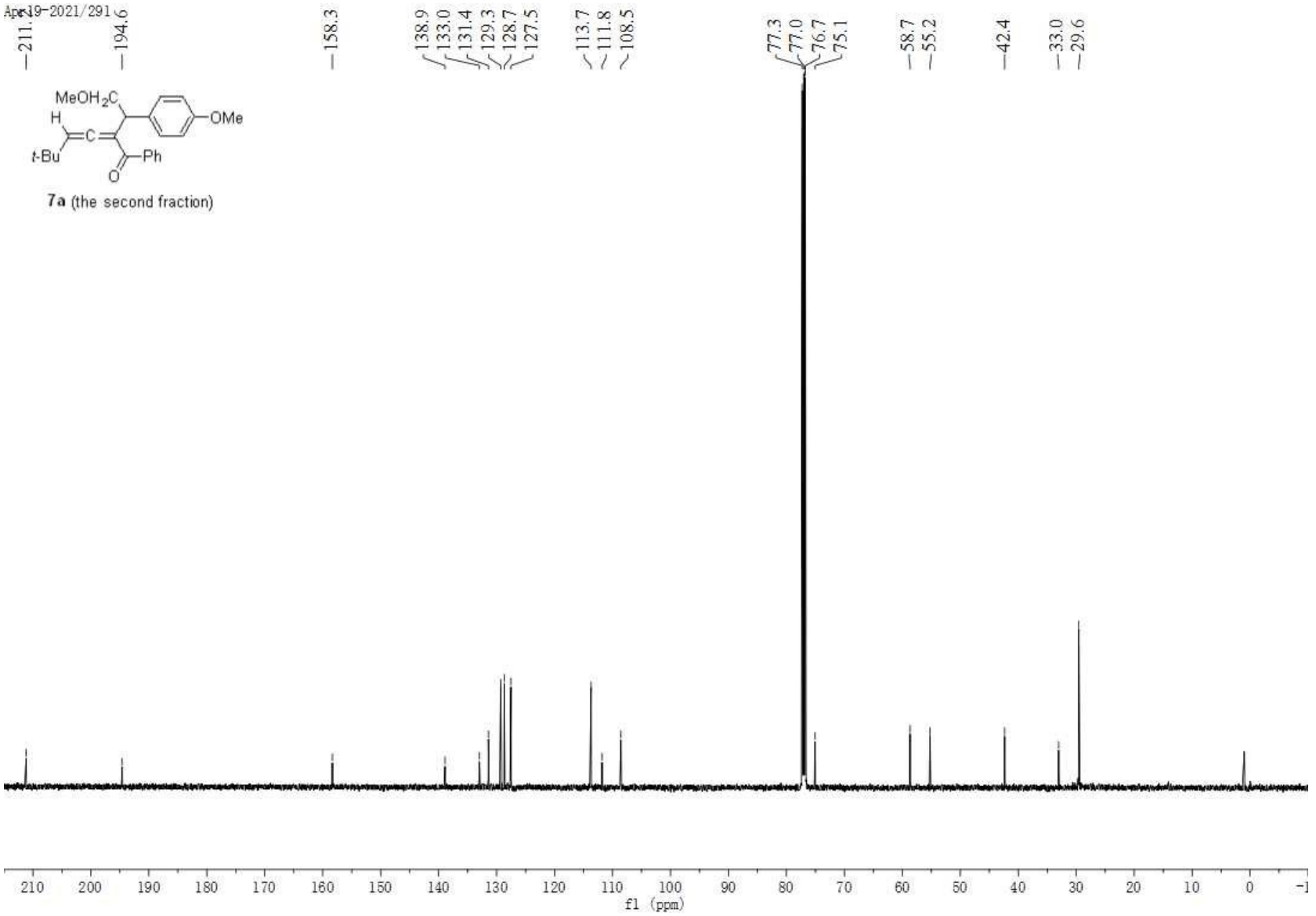

May10-2021/241
211.4
194.4
141.1
138.6
131.4
128.7
128.3
128.1
127.5
126.7
111.2
108.8
77.3
77.0
76.7
75.4
58.5
42.9
33.2
29.6
H
COPh
t-Bu
CH2OCH3
Ph
4 (the second fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

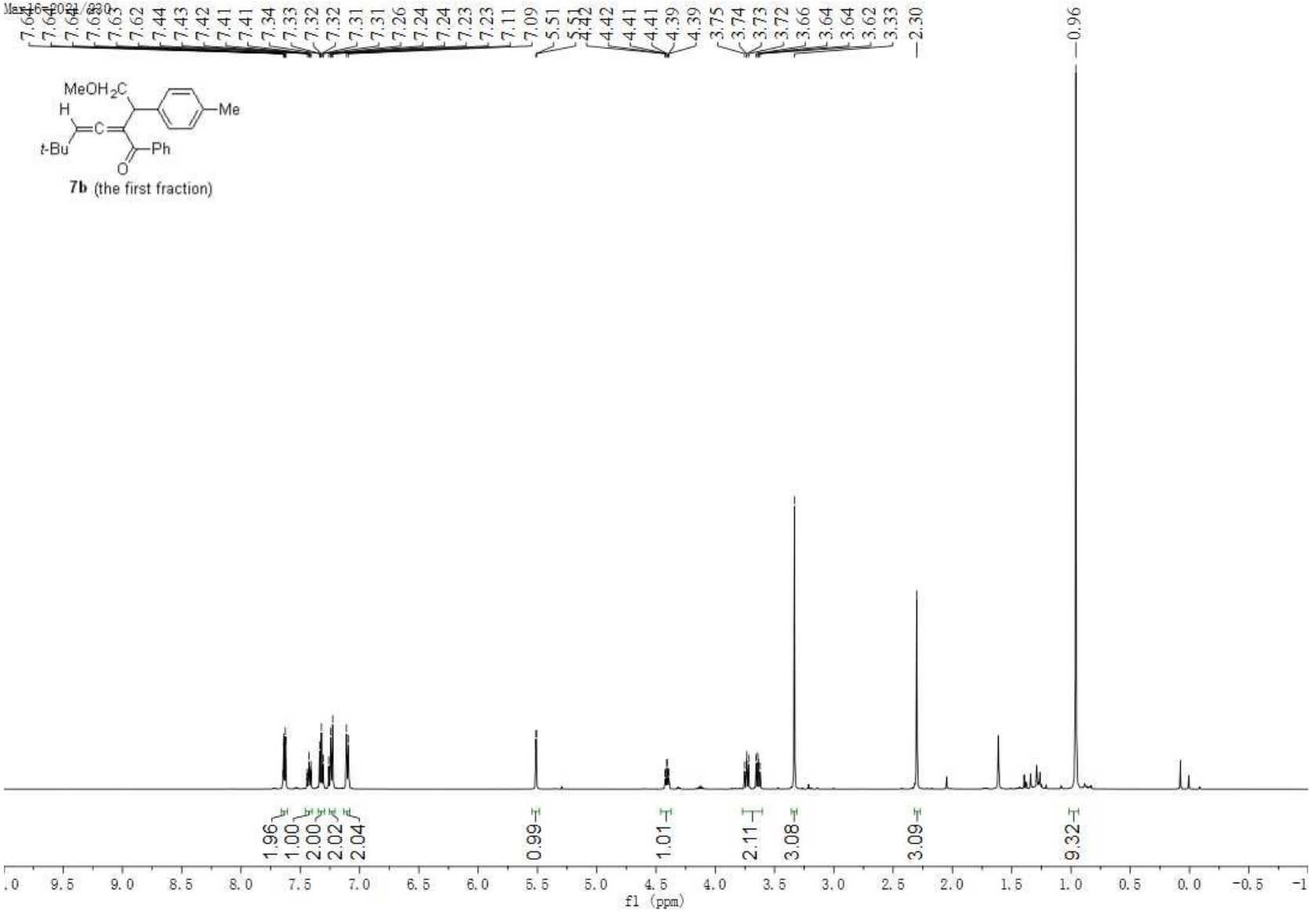

Apr-19-2021/250
7.64
7.64
7.63
7.63
7.62
7.62
7.43
7.42
7.42
7.41
7.34
7.33
7.32
7.32
7.31
7.27
7.27
7.26
7.26
7.25
6.84
6.84
6.83
6.83
5.50
5.50
4.40
4.40
4.39
4.38
4.37
4.37
3.77
3.74
3.73
3.72
3.71
3.69
3.64
3.63
3.62
3.61
3.33
0.95
MeOH2C
H
OMe
t-Bu
Ph
O
7a (the first fraction)
1.99
1.14
2.09
2.36
2.11
1.01
1.08
3.03
2.33
3.20
9.10
f1 (ppm)

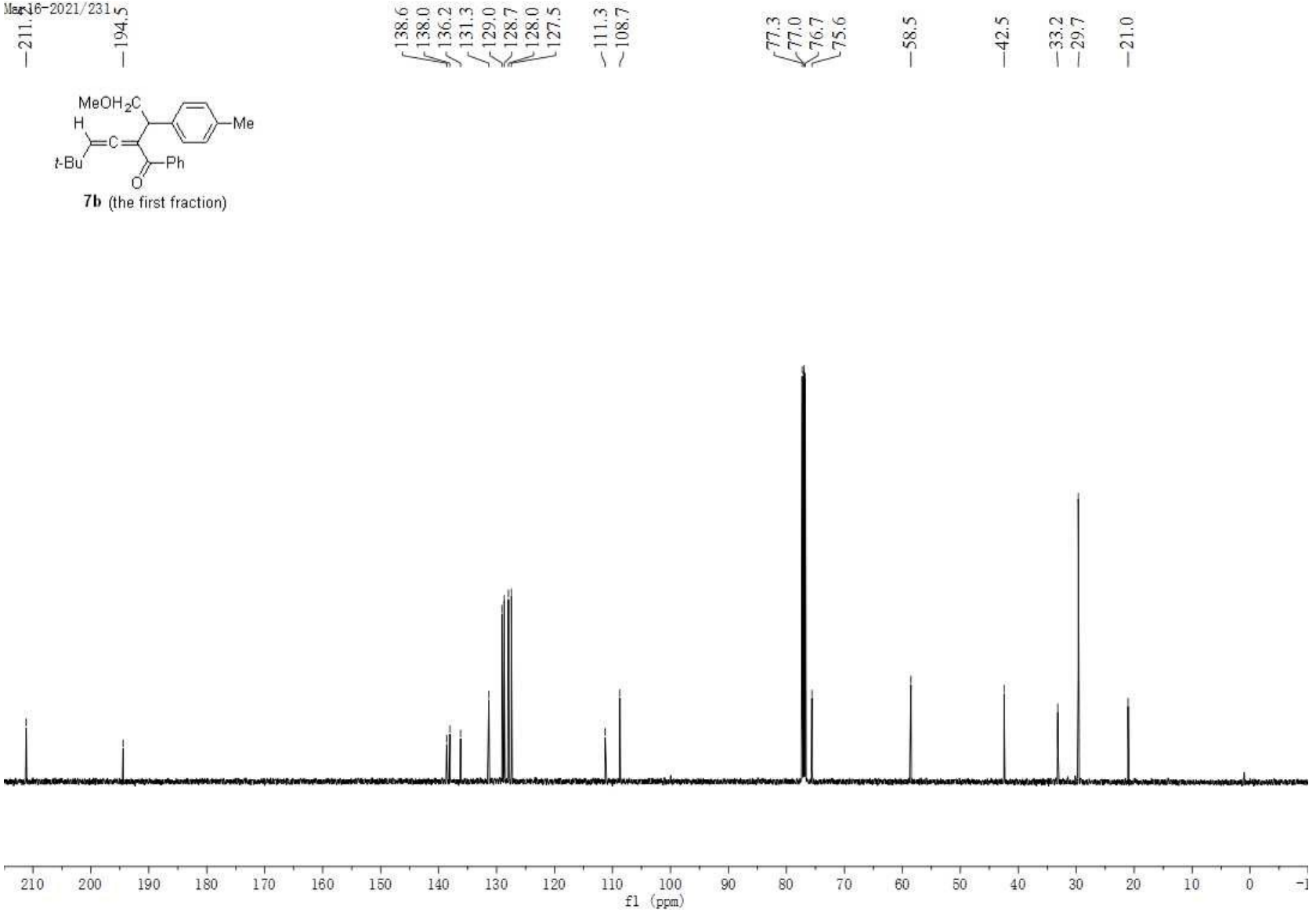

Apr-19-2021/251
211.1
194.5
158.3
138.6
133.2
131.4
129.0
128.7
127.5
113.8
111.4
108.8
77.3
77.0
76.7
75.6
58.5
55.2
42.1
33.2
29.7
MeOH2C
H
OMe
t-Bu
Ph
O
7a (the first fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

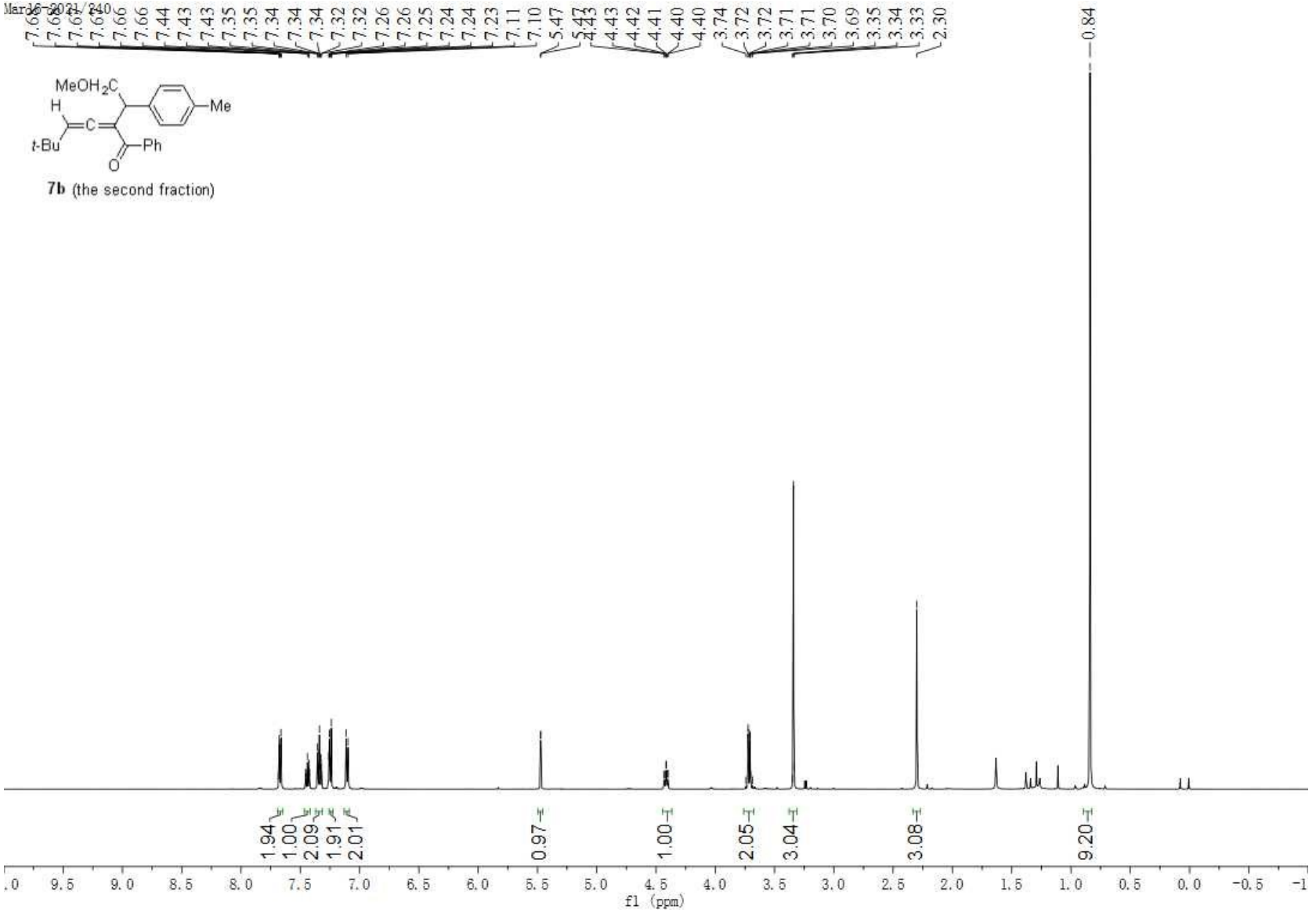


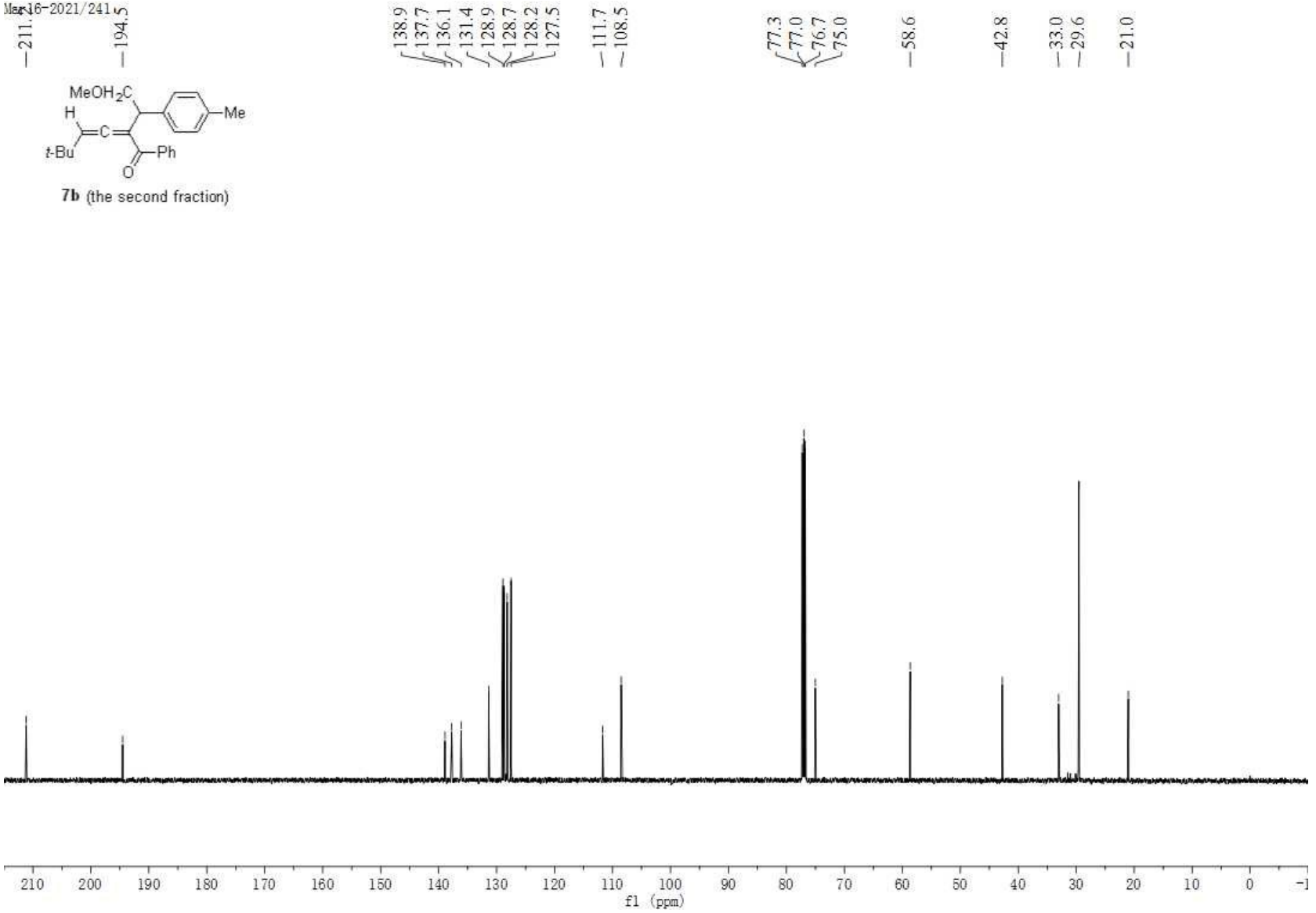
7a (the second fraction)

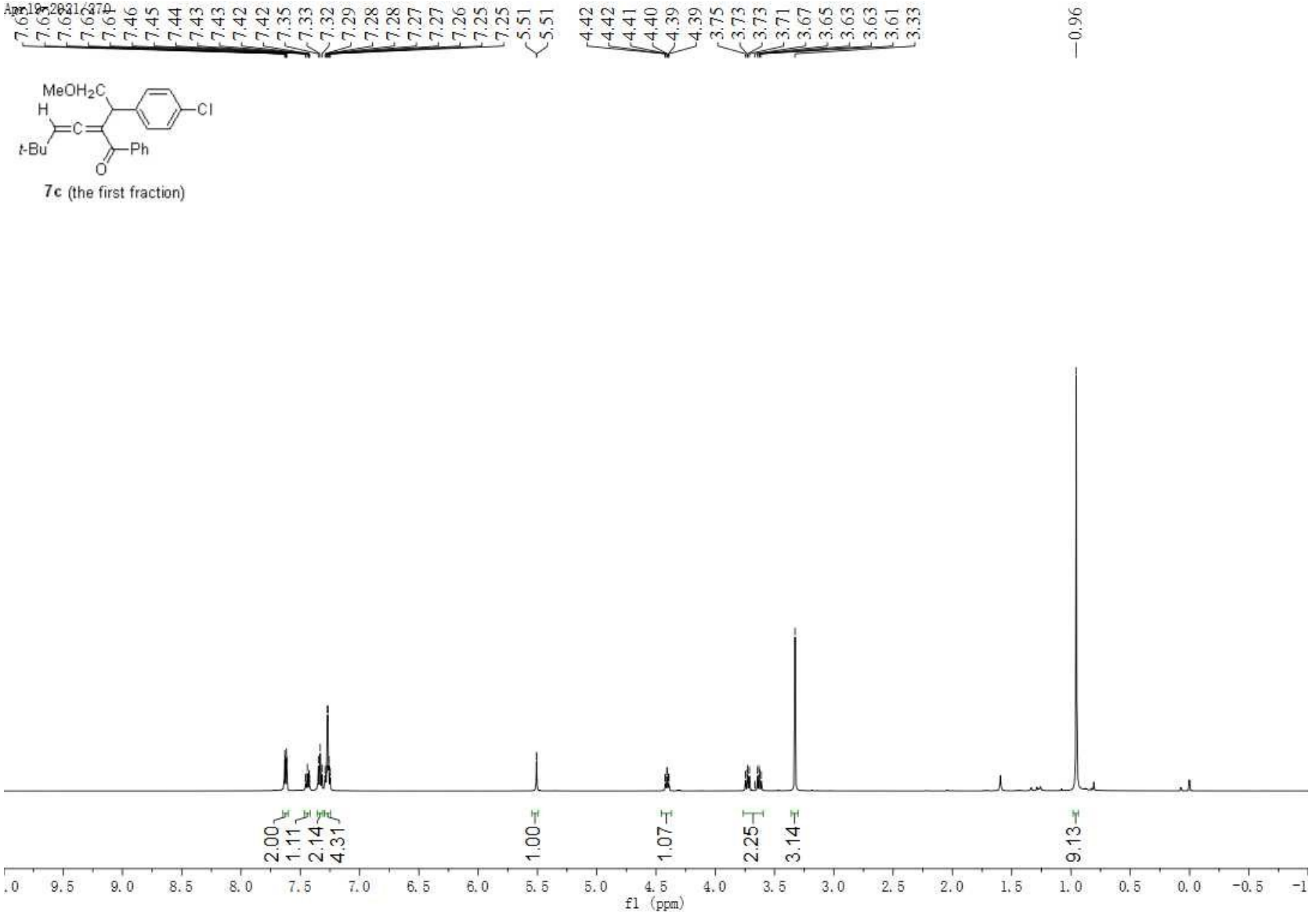

Apr-19-2021/291
211.2
194.6
158.3
138.9
133.0
131.4
129.3
128.7
127.5
113.7
111.8
108.5
77.3
77.0
76.7
75.1
58.7
55.2
42.4
33.0
29.6
MeOH2C
H
C
t-Bu
Ph
O
OMe
7a (the second fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.64
7.64
7.64
7.63
7.63
7.62
7.44
7.43
7.42
7.41
7.41
7.34
7.33
7.32
7.32
7.31
7.31
7.26
7.24
7.24
7.23
7.23
7.11
7.09
5.51
5.51
4.42
4.42
4.41
4.41
4.39
4.39
3.75
3.74
3.73
3.72
3.66
3.64
3.64
3.62
3.33
2.30
0.96
MeOH2C
H
t-Bu
Me
Ph
O
7b (the first fraction)
1.96
1.00
2.00
2.02
2.04
0.99
1.01
2.11
3.08
3.09
9.32
f1 (ppm)

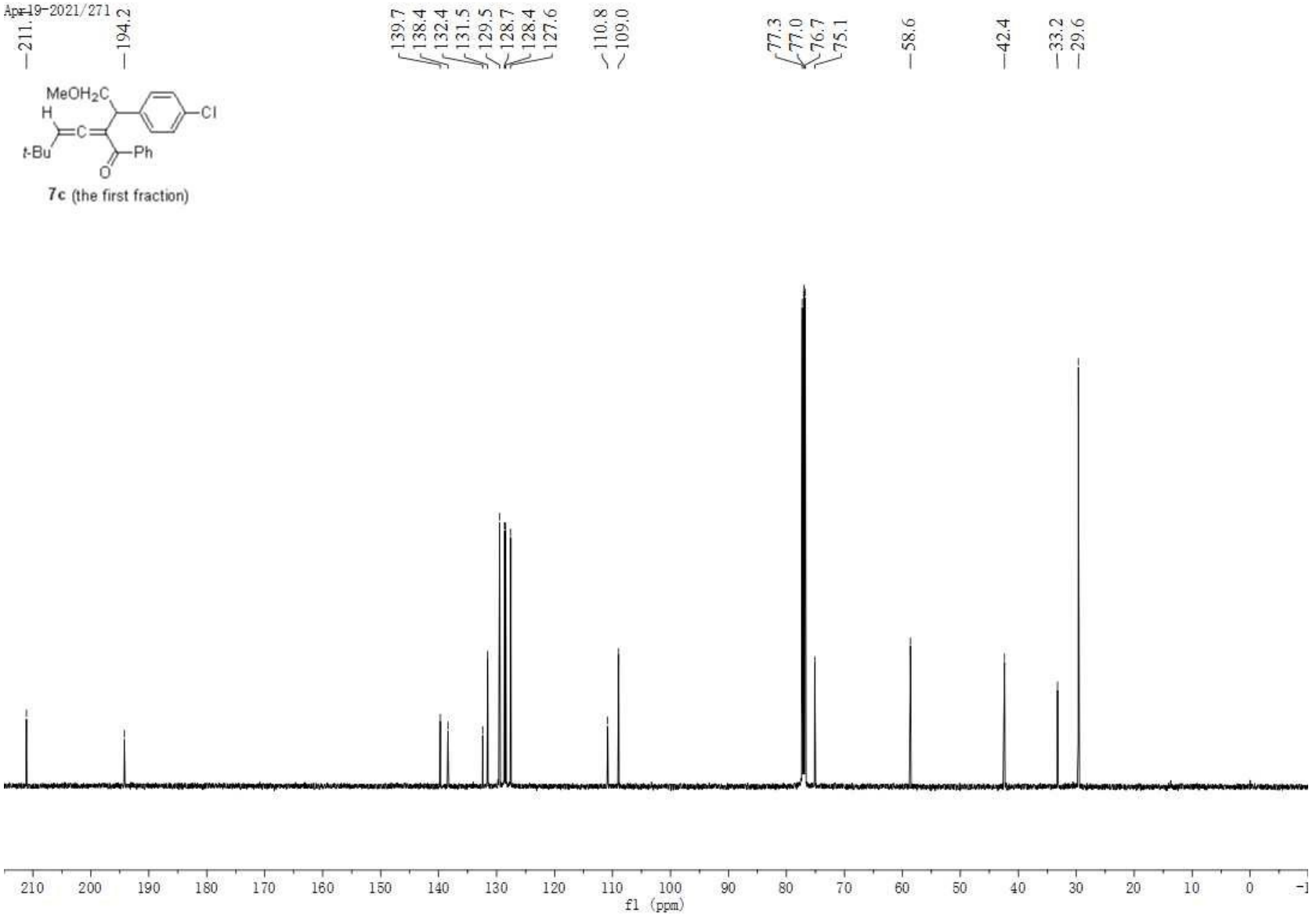

Mar-16-2021/231
211.2
194.5
138.6
138.0
136.2
131.3
129.0
128.7
128.0
127.5
111.3
108.7
77.3
77.0
76.7
75.6
58.5
42.5
33.2
29.7
21.0
MeOH2C
H
C
t-Bu
Ph
O
Me
7b (the first fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

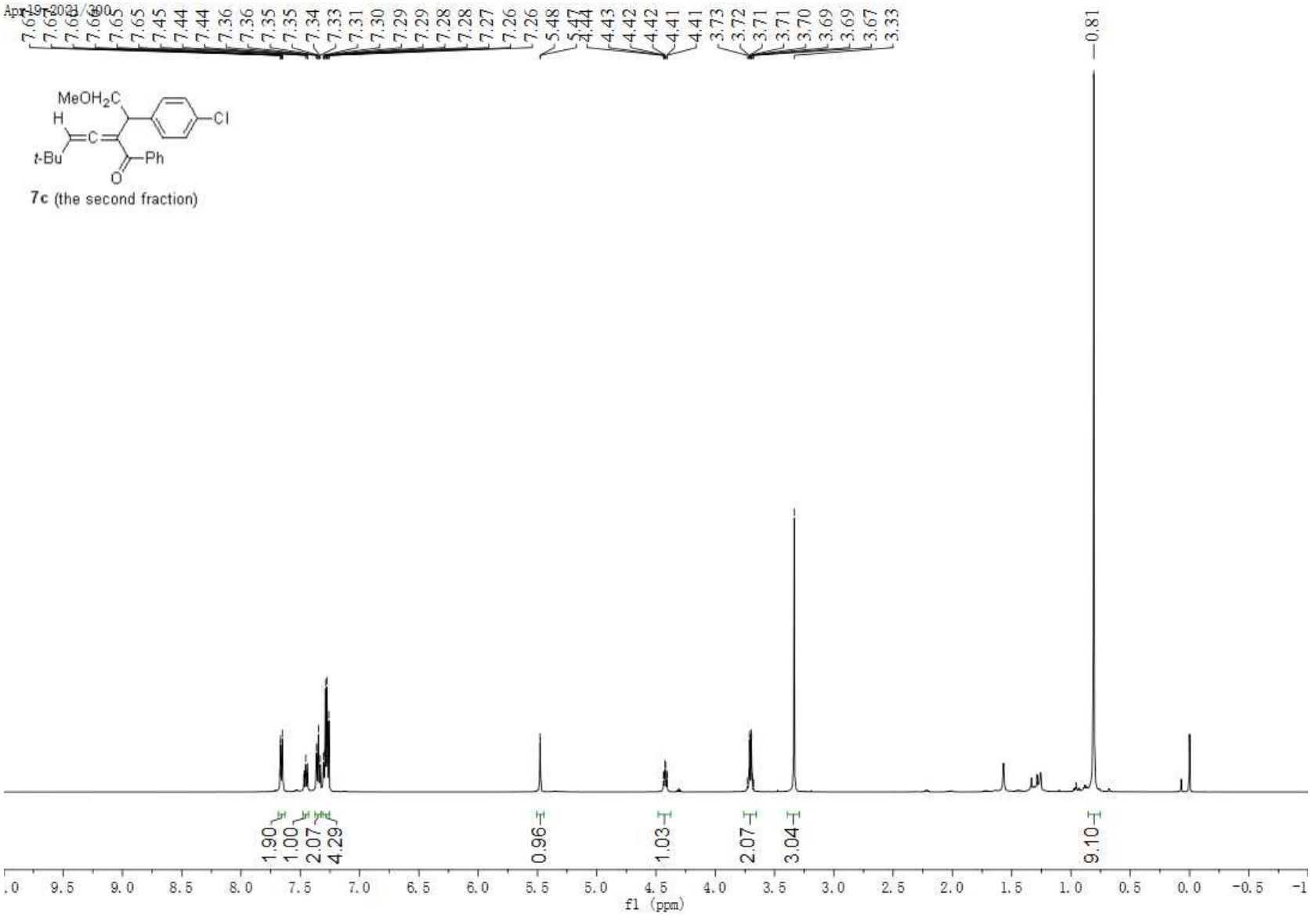

MeOH2C
H
t-Bu
Me
Ph
O
7b (the second fraction)
fl (ppm)

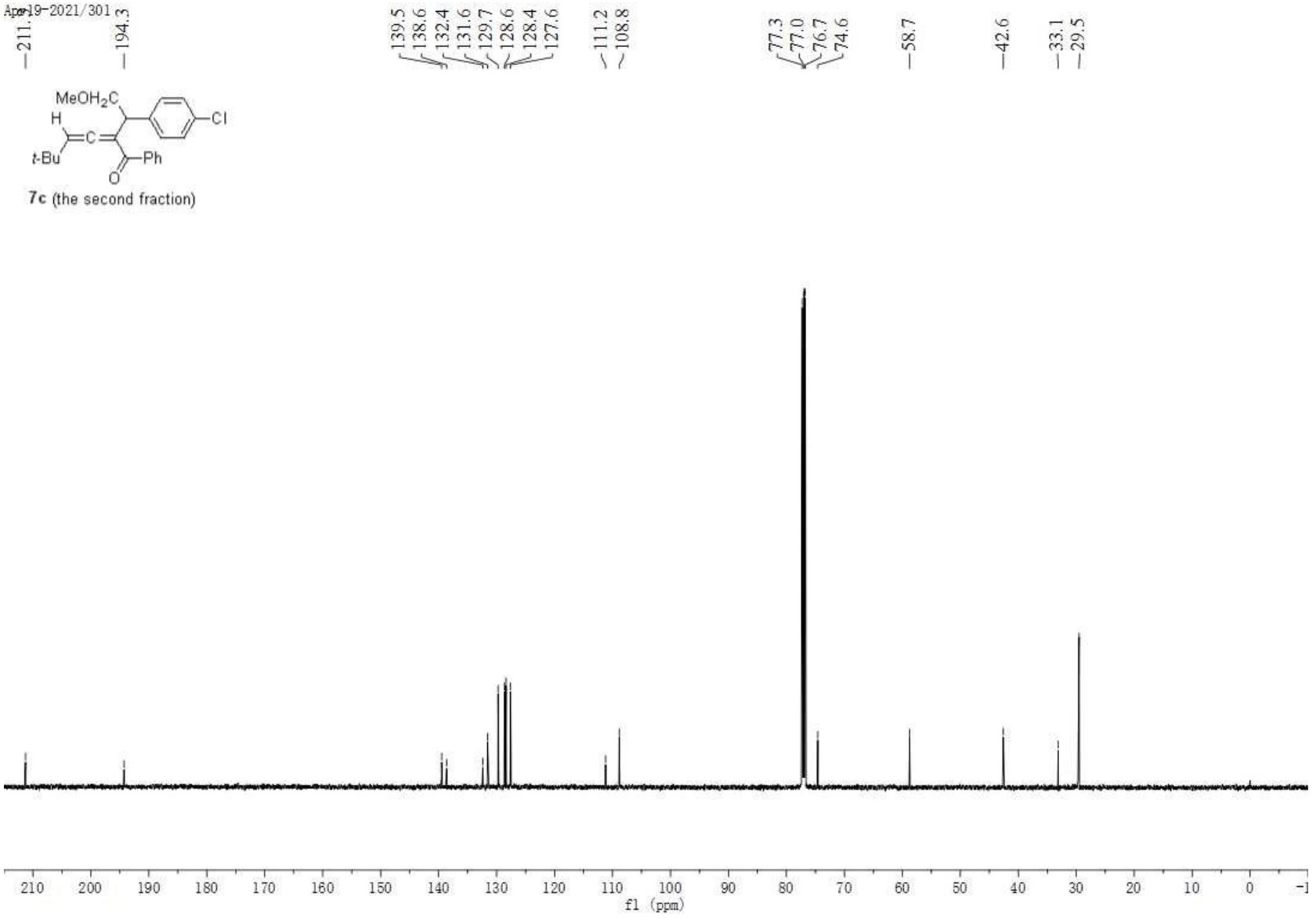

Mar-16-2021/241
211.2
194.5
138.9
137.7
136.1
131.4
128.9
128.7
128.2
127.5
111.7
108.5
77.3
77.0
76.7
75.0
58.6
42.8
33.0
29.6
21.0
MeOH2C
H
Me
t-Bu
Ph
O
7b (the second fraction)
f1 (ppm)

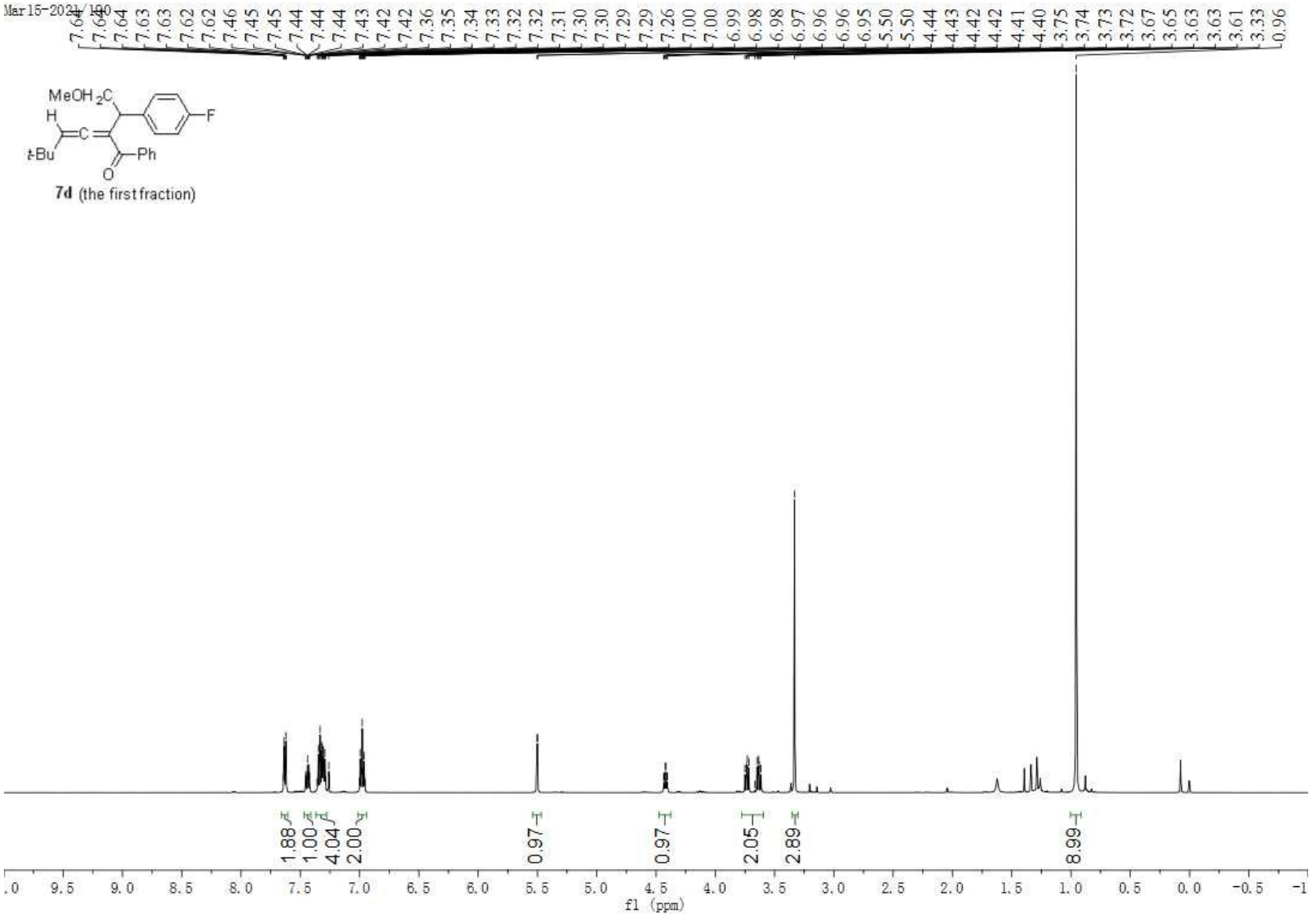


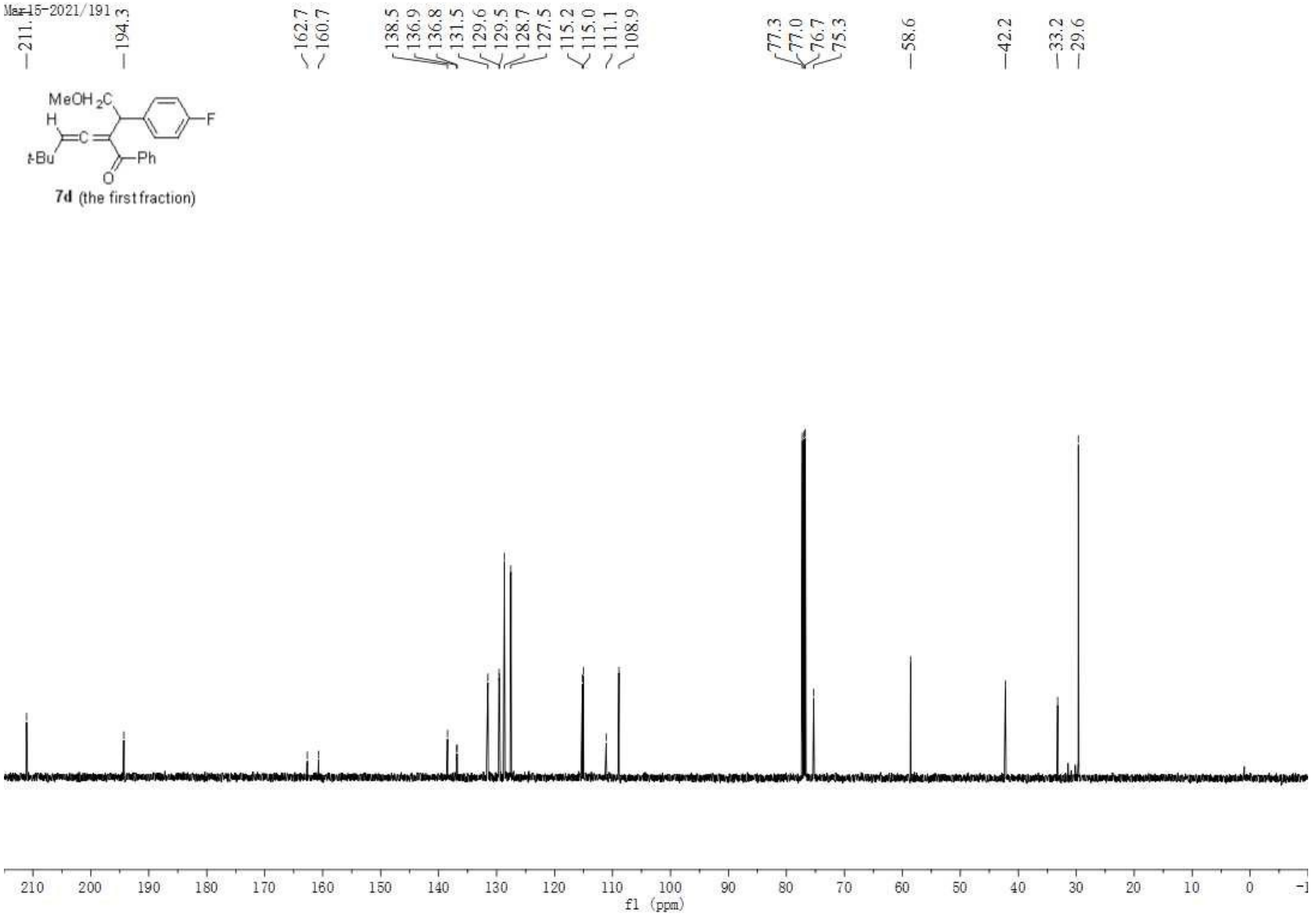
7c (the first fraction)


Apr-19-2021/271
211.1
194.2
139.7
138.4
132.4
131.5
129.5
128.7
128.4
127.6
110.8
109.0
77.3
77.0
76.7
75.1
58.6
42.4
33.2
29.6
MeOH2C
H
C
t-Bu
Ph
O
Cl
7c (the first fraction)
f1 (ppm)

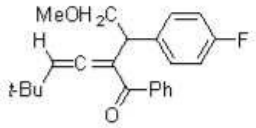

Apr-19-2021/300
7.67 7.67 7.66 7.66 7.65 7.65 7.45 7.44 7.44 7.36 7.36 7.35 7.35 7.34 7.33 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.26 5.48 5.47 4.44 4.43 4.42 4.42 4.41 4.41 3.73 3.72 3.71 3.71 3.70 3.69 3.69 3.67 3.33
0.81
MeOH2C
H
Cl
t-Bu
Ph
O
7c (the second fraction)
1.90
1.00
2.07
4.29
0.96
1.03
2.07
3.04
9.10
f1 (ppm)


Apr-19-2021/301
211.9
194.3
139.5
138.6
132.4
131.6
129.7
128.6
128.4
127.6
111.2
108.8
77.3
77.0
76.7
74.6
58.7
42.6
33.1
29.5
MeOH2C
H
C
t-Bu
Ph
O
Cl
7c (the second fraction)
f1 (ppm)

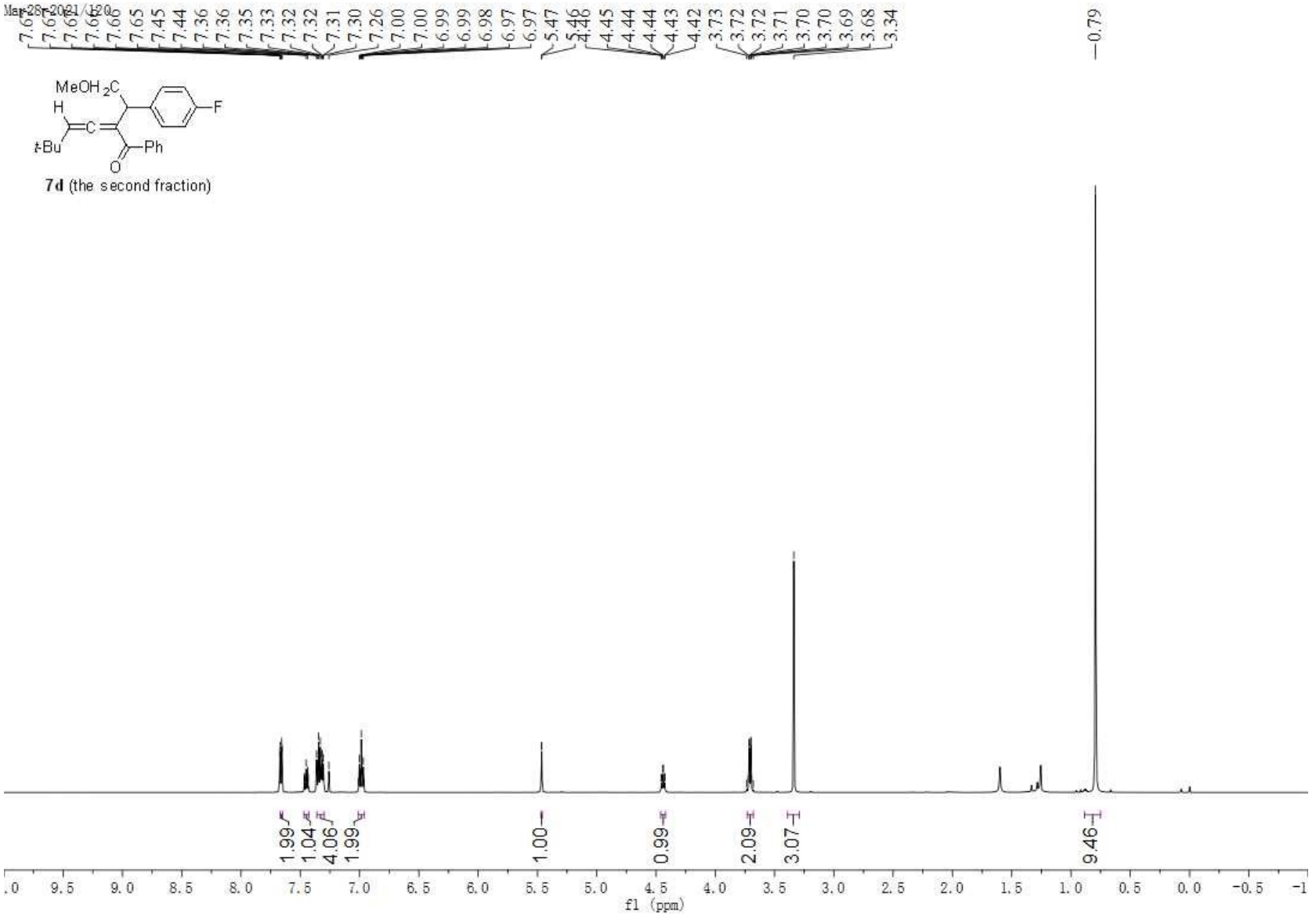

Mar15-2021-190
MeOH2C
H
C
t-Bu
Ph
O
F
7d (the first fraction)
1.88
1.00
4.04
2.00
0.97
0.97
2.05
2.89
8.99
f1 (ppm)

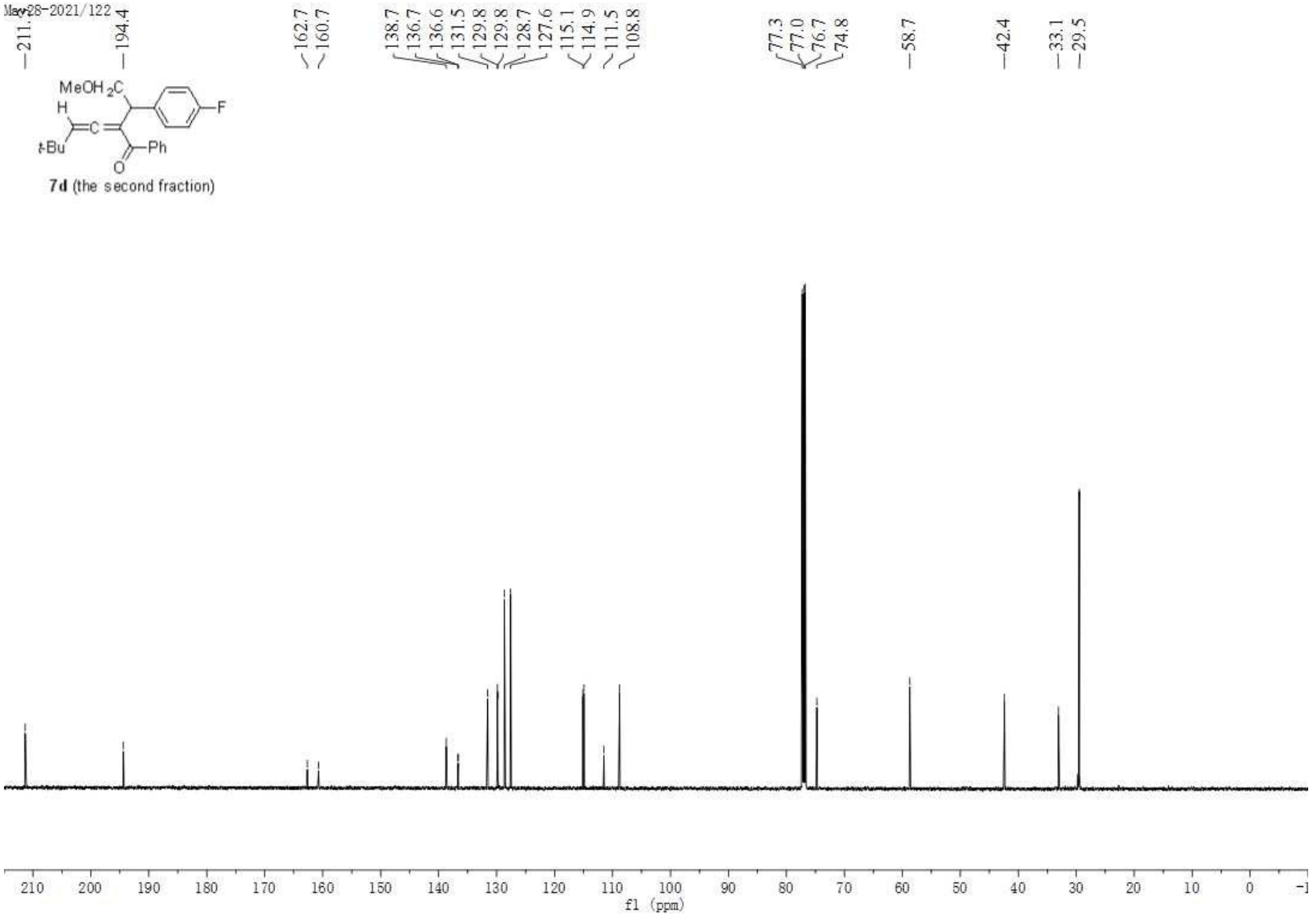

Mar-15-2021/191
211.1
194.3
162.7
160.7
138.5
136.9
136.8
131.5
129.6
129.5
128.7
127.5
115.2
115.0
111.1
108.9
77.3
77.0
76.7
75.3
58.6
42.2
33.2
29.6
MeOH2C
H
C
t-Bu
Ph
O
F
7d (the first fraction)
f1 (ppm)

Mar15-2021/170

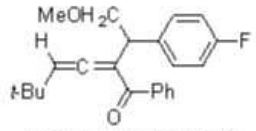


7d (the first fraction)

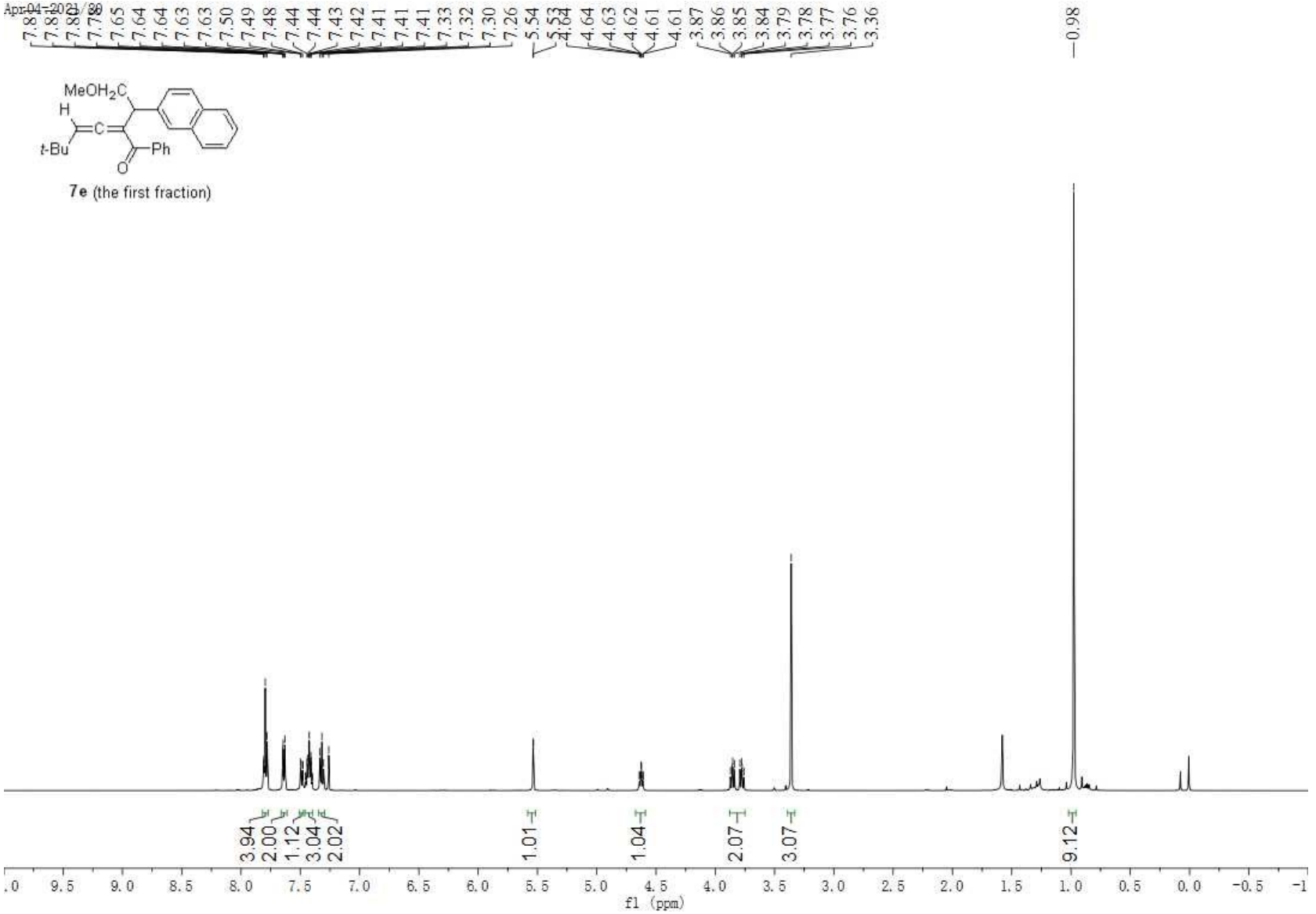

7.67
7.67
7.67
7.66
7.66
7.65
7.45
7.44
7.36
7.36
7.35
7.33
7.32
7.32
7.31
7.30
7.26
7.00
7.00
6.99
6.99
6.98
6.97
6.97
5.47
5.46
4.46
4.45
4.44
4.44
4.44
4.43
4.42
3.73
3.72
3.72
3.71
3.70
3.70
3.69
3.68
3.34
0.79
MeOH2C
H
F
t-Bu
Ph
O
7d (the second fraction)
1.99
1.04
4.06
1.99
1.00
0.99
2.09
3.07
9.46
f1 (ppm)

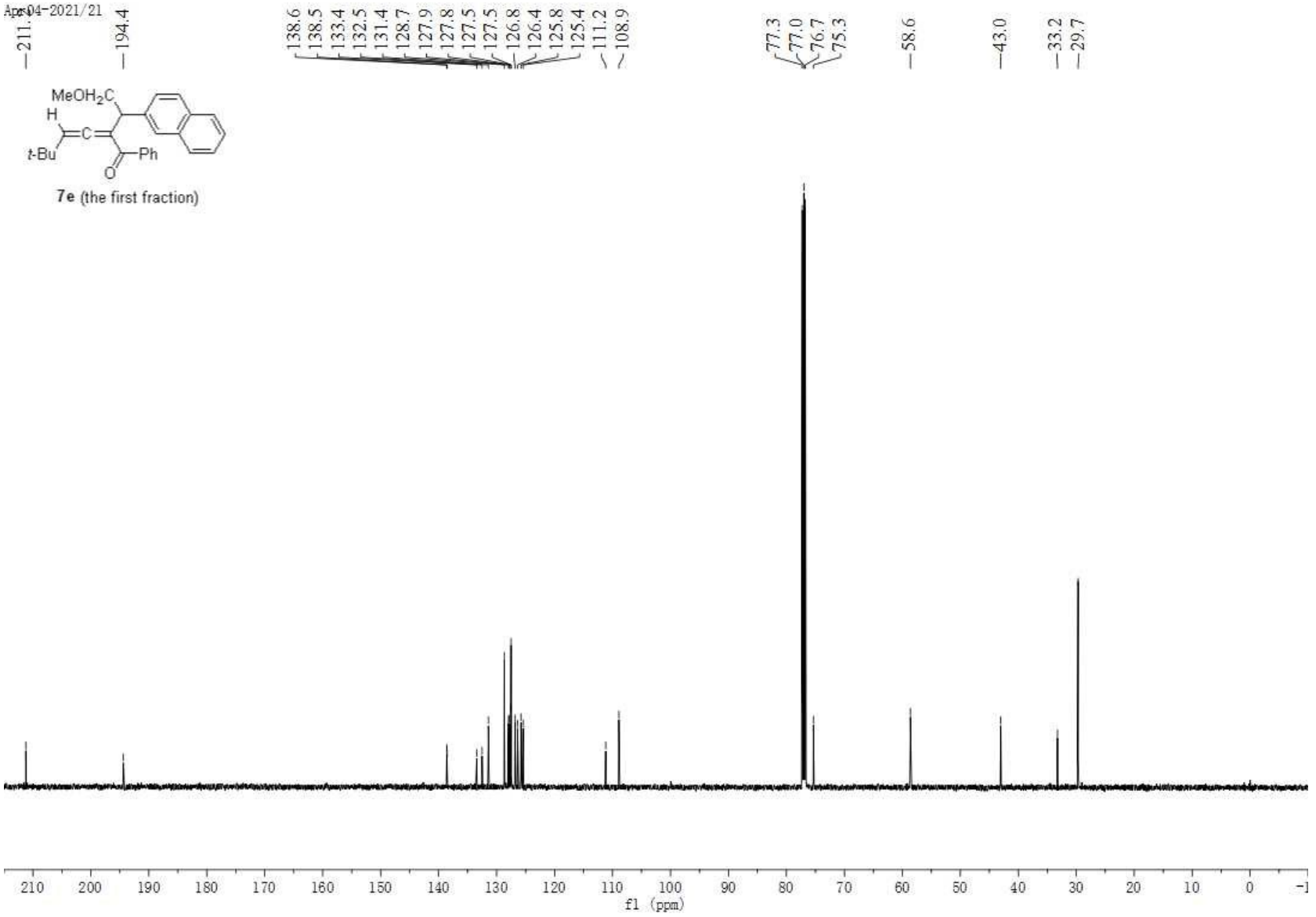

May-28-2021/122
211.3
194.4
162.7
160.7
138.7
136.7
136.6
131.5
129.8
129.8
128.7
127.6
115.1
114.9
111.5
108.8
77.3
77.0
76.7
74.8
58.7
42.4
33.1
29.5
MeOH2C
H
C
t-Bu
Ph
O
F
7d (the second fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

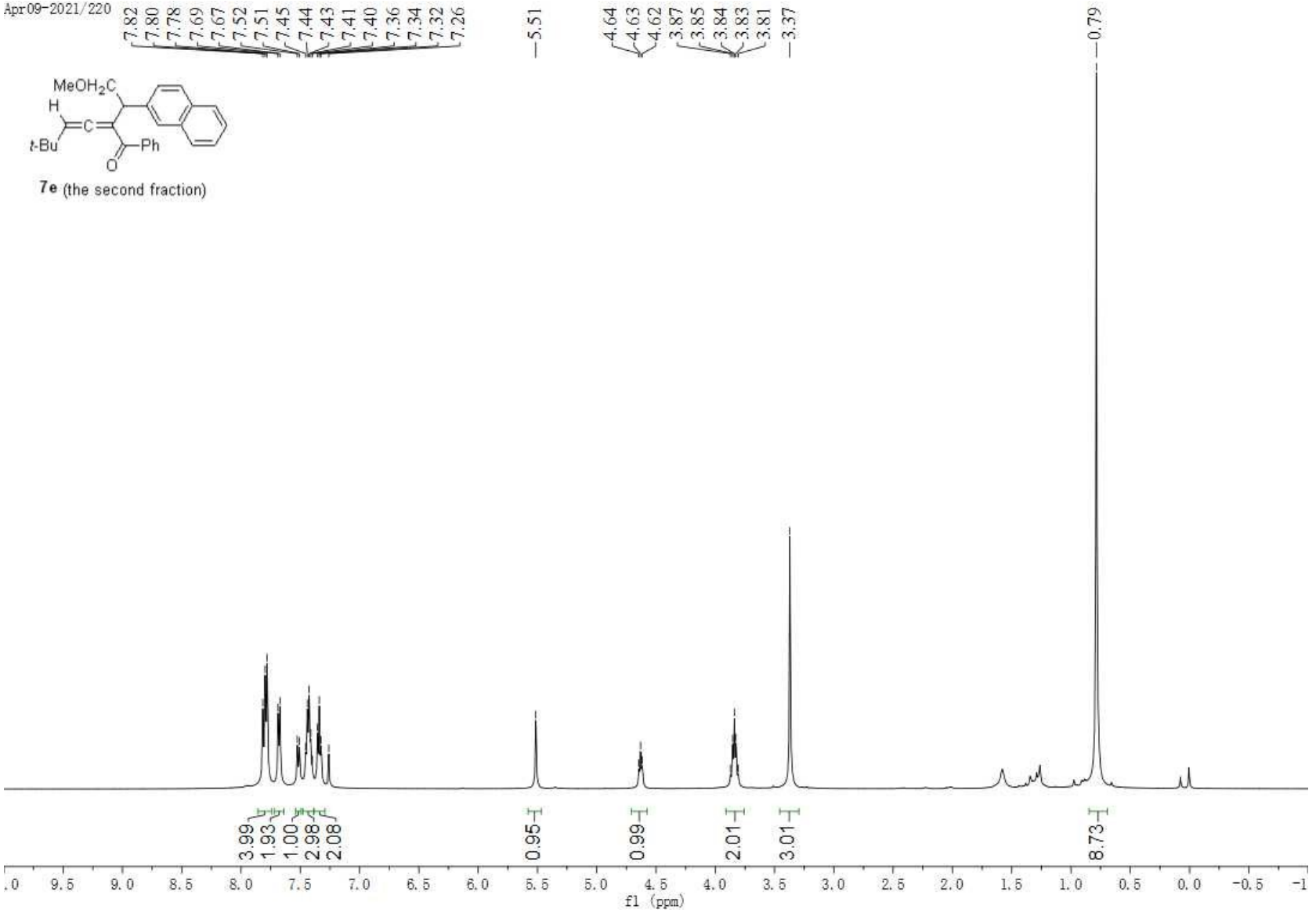
May28-2021/121

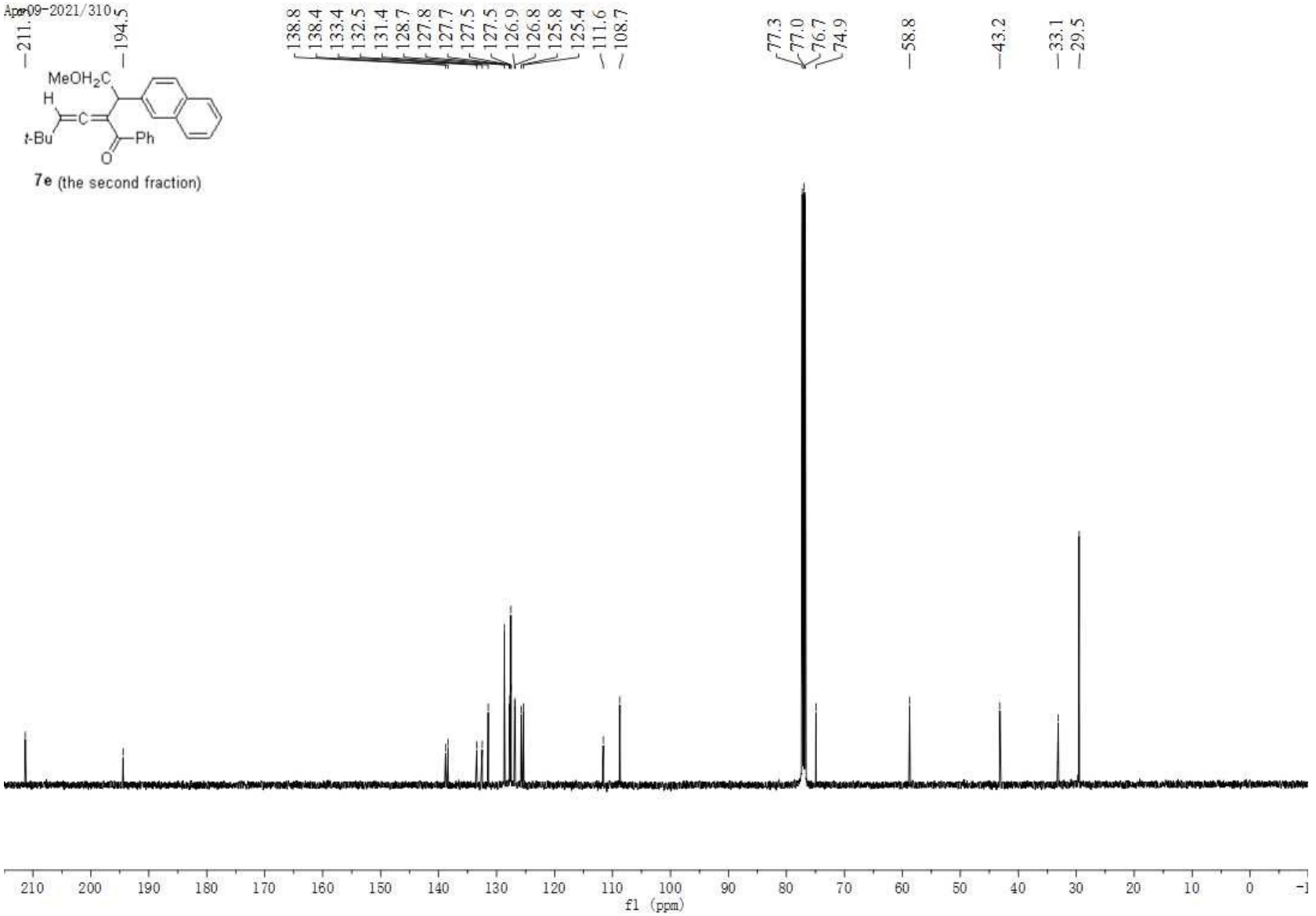


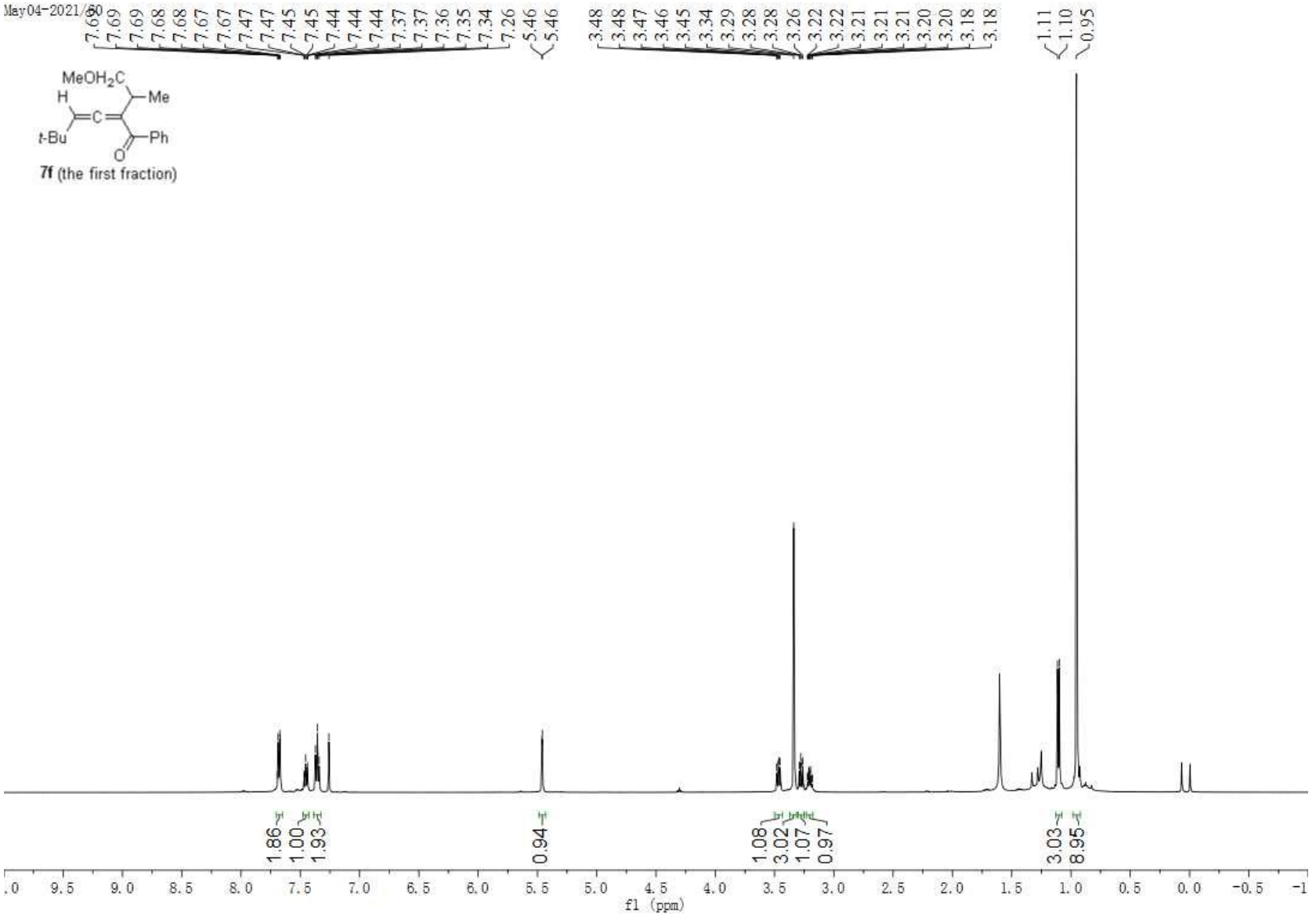
7d (the second fraction)

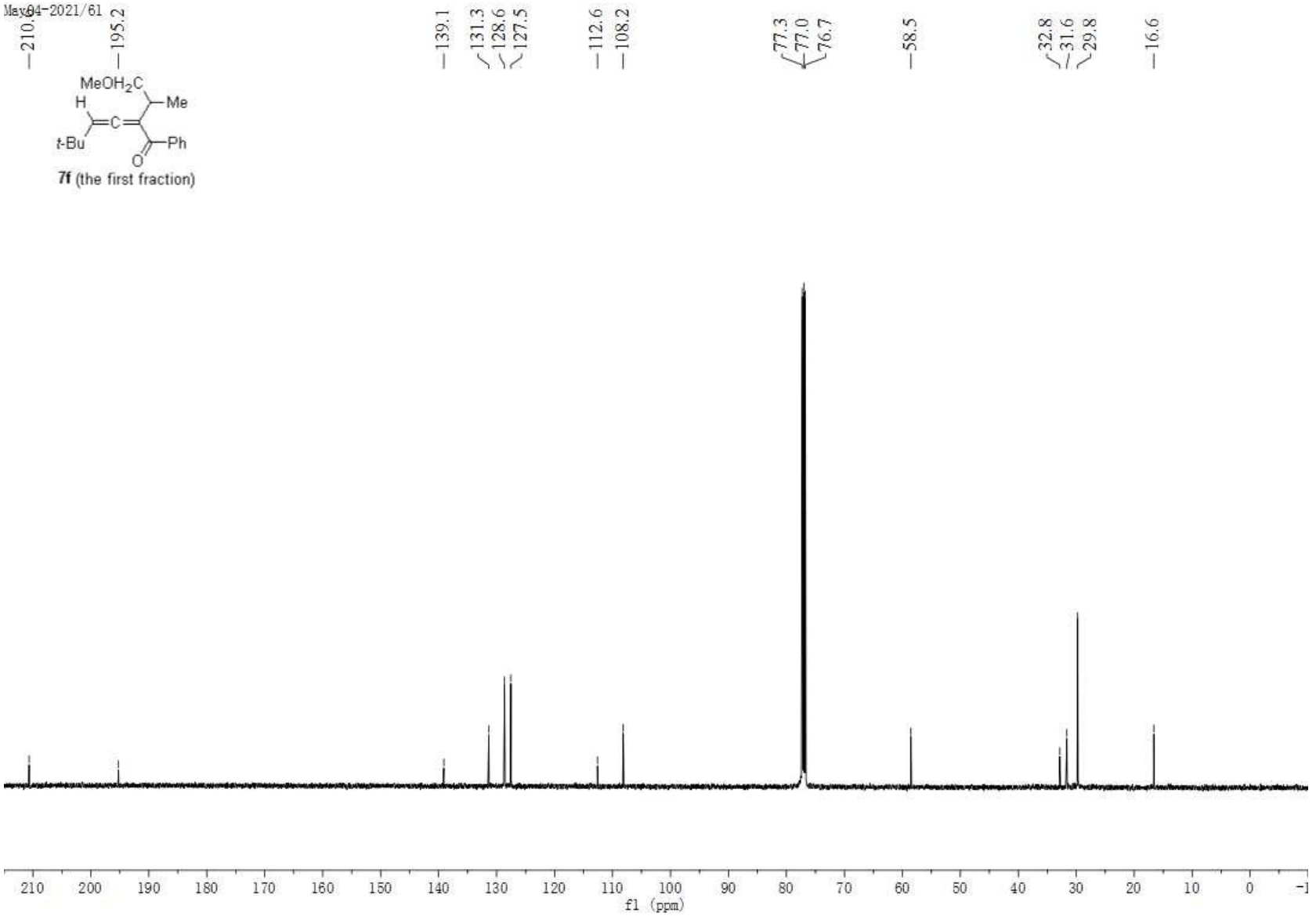

Apr-04-2021/80
7.81
7.81
7.80
7.79
7.65
7.64
7.64
7.63
7.63
7.50
7.49
7.48
7.44
7.44
7.43
7.42
7.41
7.41
7.41
7.33
7.32
7.30
7.26
5.54
5.53
4.64
4.64
4.63
4.62
4.61
4.61
3.87
3.86
3.85
3.84
3.79
3.78
3.77
3.76
3.36
0.98
MeOH2C
H
t-Bu
Ph
O
7e (the first fraction)
3.94
2.00
1.12
3.04
2.02
1.01
1.04
2.07
3.07
9.12
f1 (ppm)

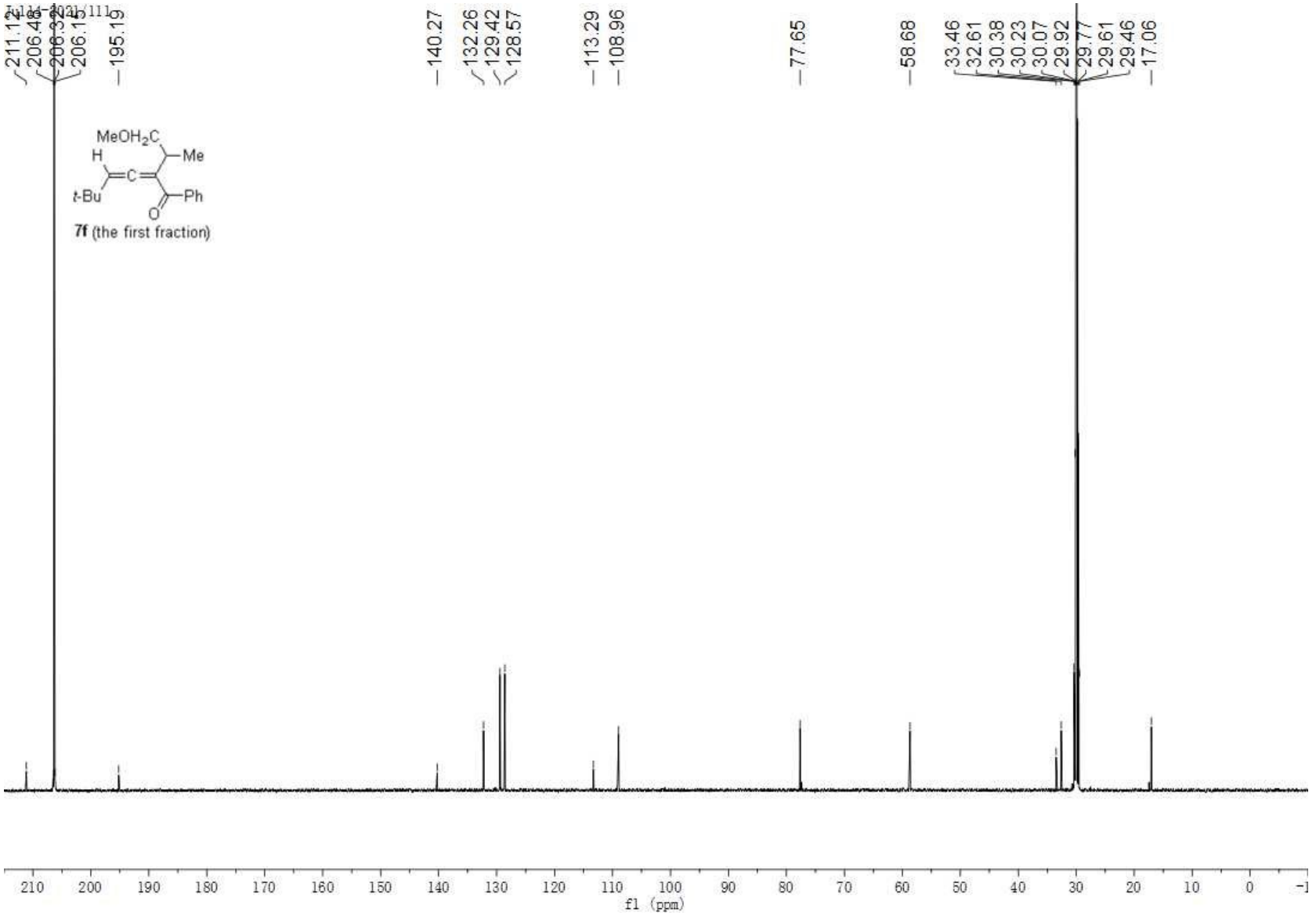

Apr-04-2021/21
211.4
194.4
138.6
138.5
133.4
132.5
131.4
128.7
127.9
127.8
127.5
127.5
126.8
126.4
125.8
125.4
111.2
108.9
77.3
77.0
76.7
75.3
58.6
43.0
33.2
29.7
MeOH2C
H
t-Bu
Ph
O
7e (the first fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Apr09-2021/220
7.82
7.80
7.78
7.69
7.67
7.52
7.51
7.45
7.44
7.43
7.41
7.40
7.36
7.34
7.32
7.26
5.51
4.64
4.63
4.62
3.87
3.85
3.84
3.83
3.81
3.37
0.79
MeOH2C
H
t-Bu
Ph
O
7e (the second fraction)
3.99
1.93
1.00
2.98
2.08
0.95
0.99
2.01
3.01
8.73
f1 (ppm)

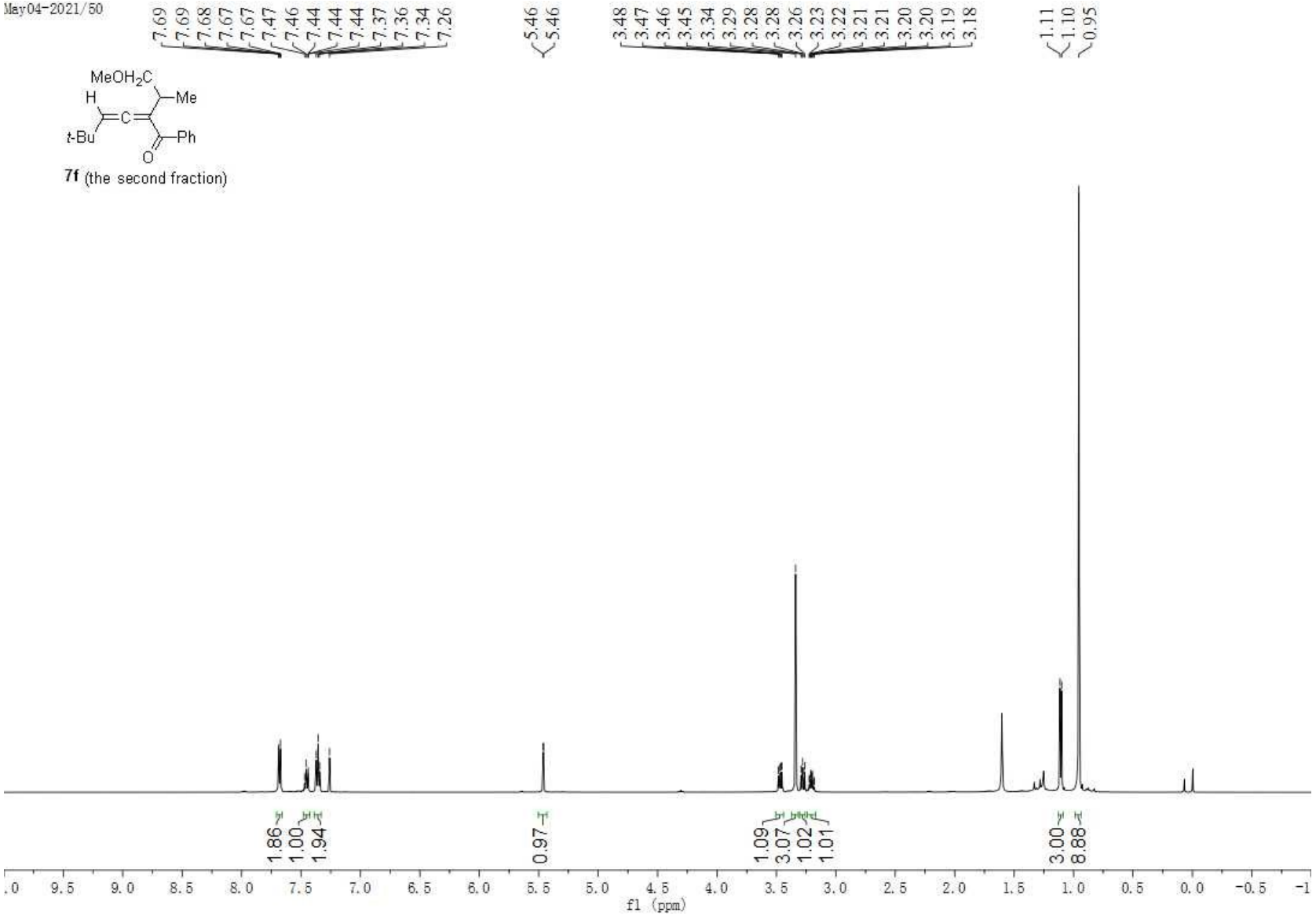

Apr-09-2021/310
211.5
194.5
MeOH2C
H
C
t-Bu
Ph
O
7e (the second fraction)
138.8
138.4
133.4
132.5
131.4
128.7
127.8
127.7
127.5
127.5
126.9
126.8
125.8
125.4
111.6
108.7
77.3
77.0
76.7
74.9
58.8
43.2
33.1
29.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


May04-2021/30
7.69 7.69 7.68 7.68 7.67 7.67 7.47 7.47 7.45 7.45 7.44 7.44 7.44 7.37 7.37 7.36 7.35 7.34 7.26 5.46 5.46
3.48 3.48 3.47 3.46 3.45 3.34 3.29 3.28 3.28 3.26 3.22 3.22 3.21 3.21 3.21 3.20 3.20 3.18 3.18
1.11 1.10 0.95
MeOH2C
H
Me
t-Bu
Ph
O
7f (the first fraction)
1.86 1.00 1.93 0.94 1.08 3.02 1.07 0.97 3.03 8.95
f1 (ppm)

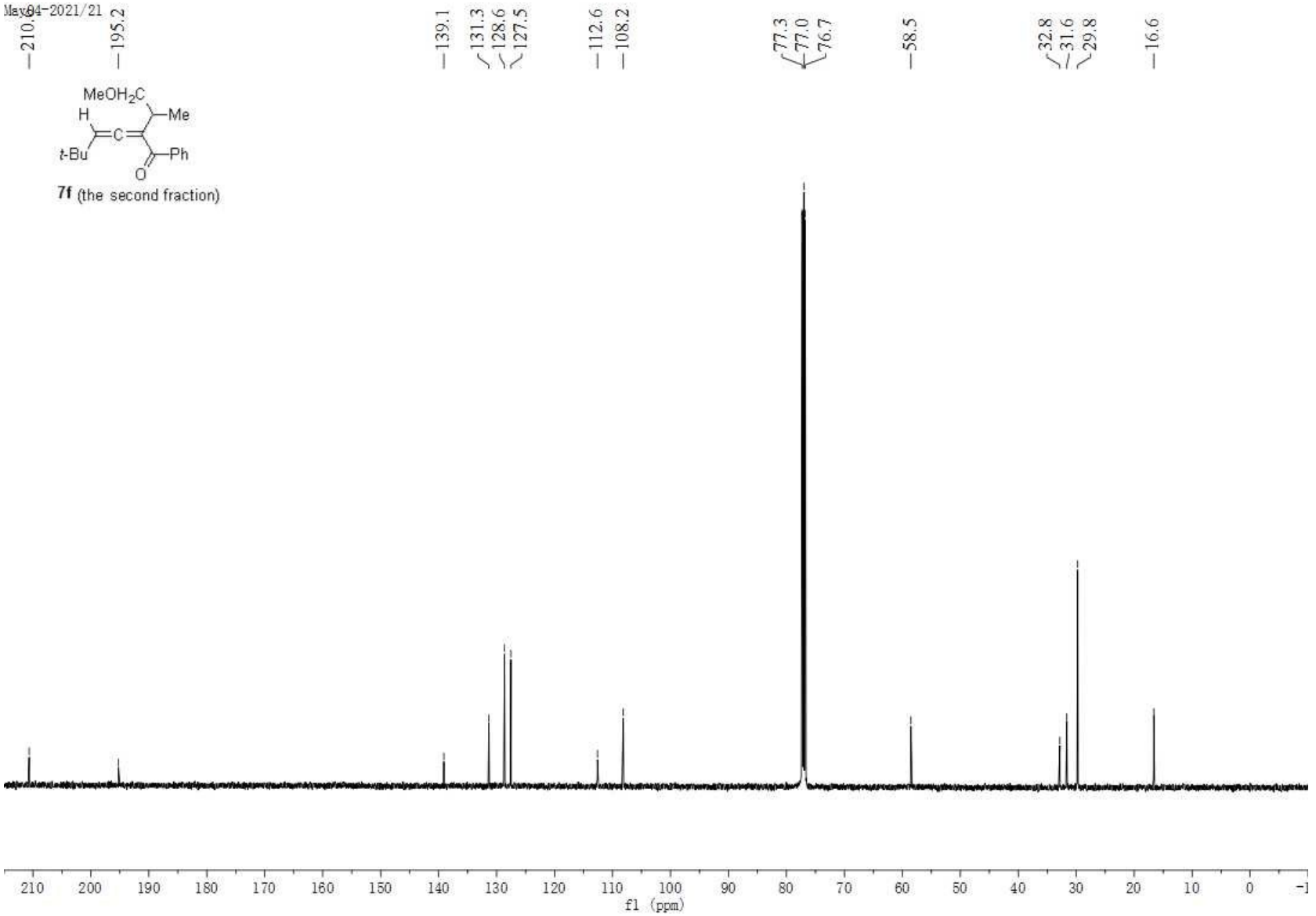

May04-2021/61
210.0
195.2
139.1
131.3
128.6
127.5
112.6
108.2
77.3
77.0
76.7
58.5
32.8
31.6
29.8
16.6
MeOH2C
Me
H
C
t-Bu
Ph
O
7f (the first fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

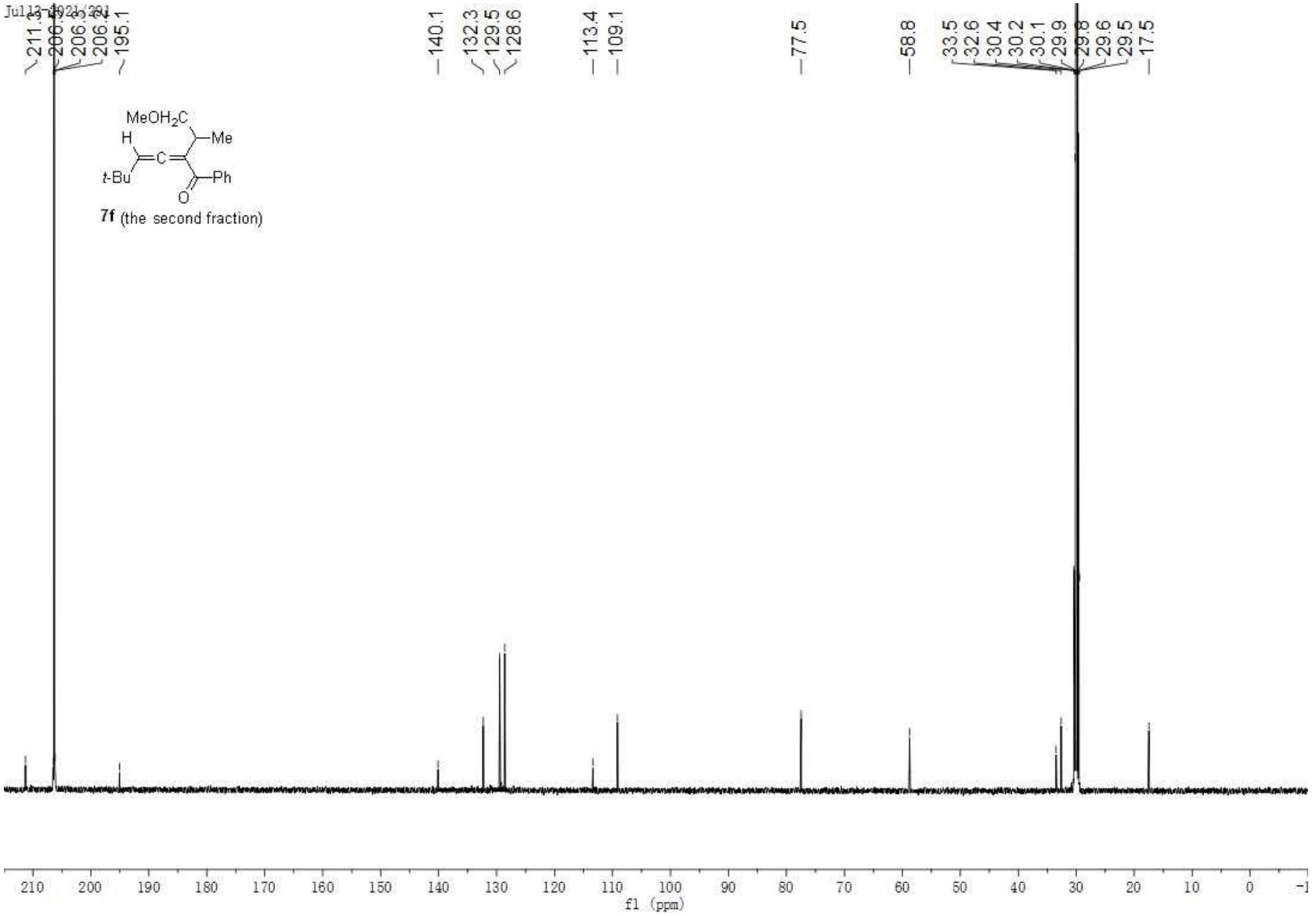

211.12
206.48
206.32
206.15
195.19
140.27
132.26
129.42
128.57
113.29
108.96
77.65
58.68
33.46
32.61
30.38
30.23
30.07
29.92
29.77
29.61
29.46
17.06
MeOH2C
H
Me
t-Bu
Ph
O
7f (the first fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

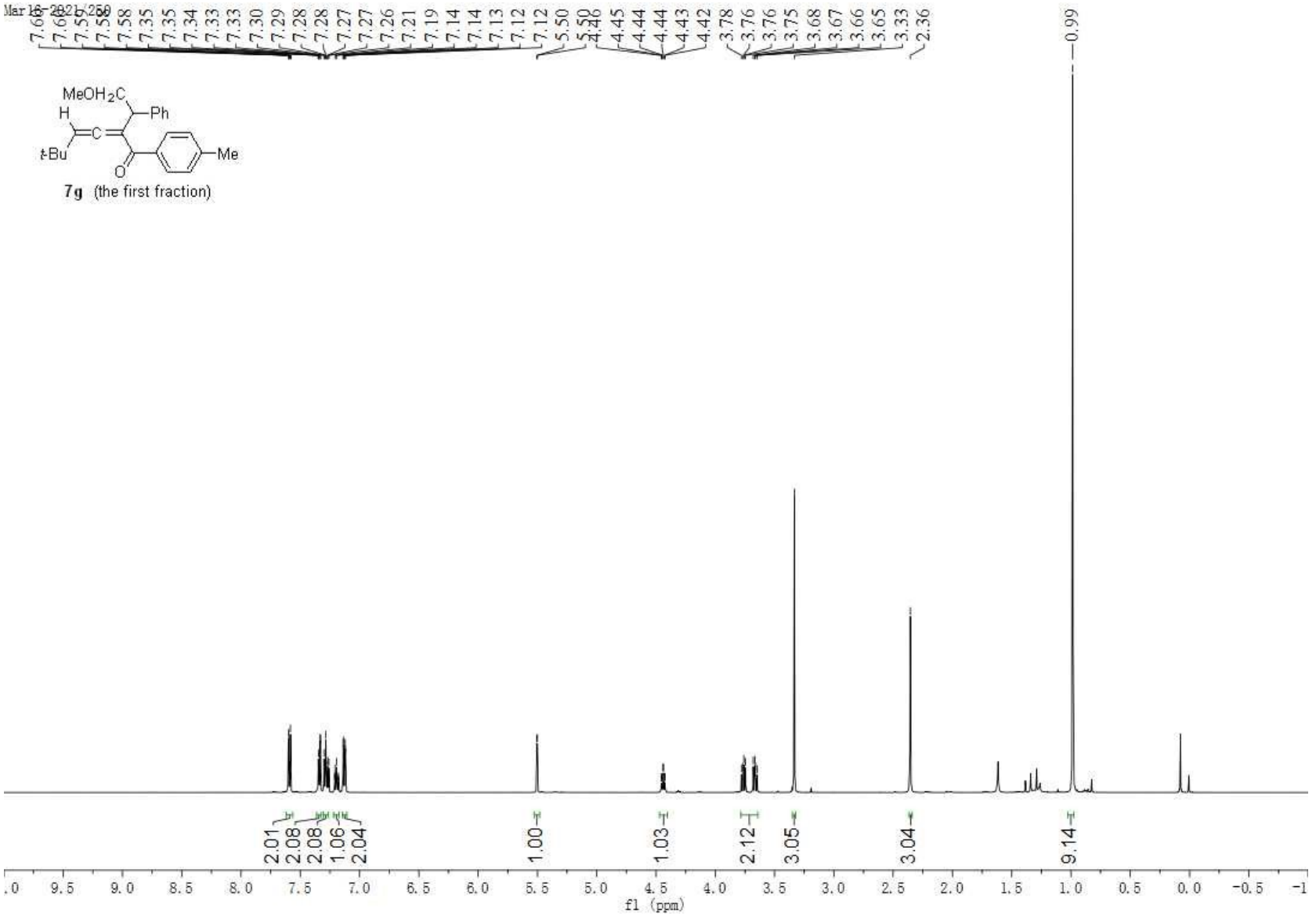
May04-2021/50

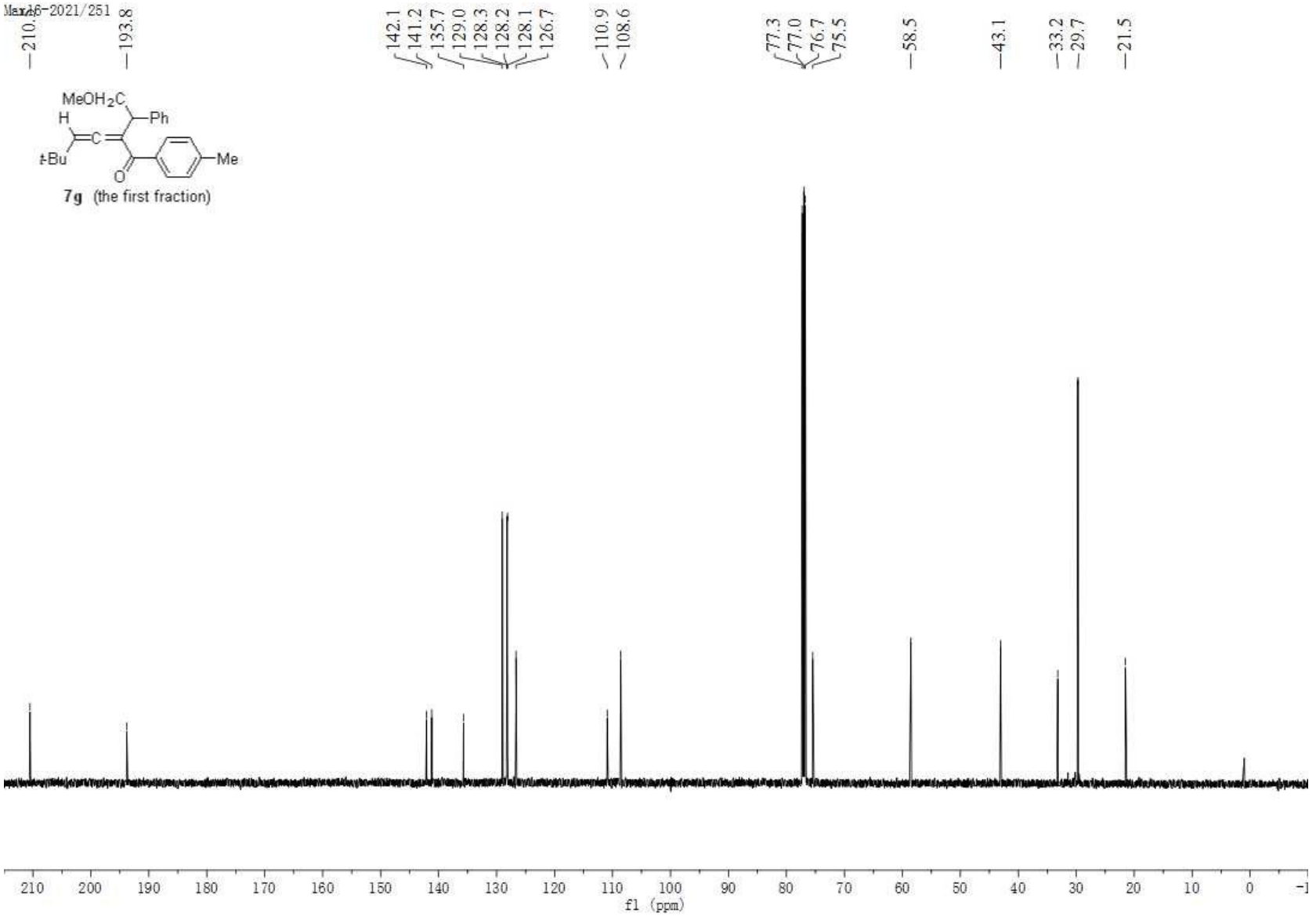


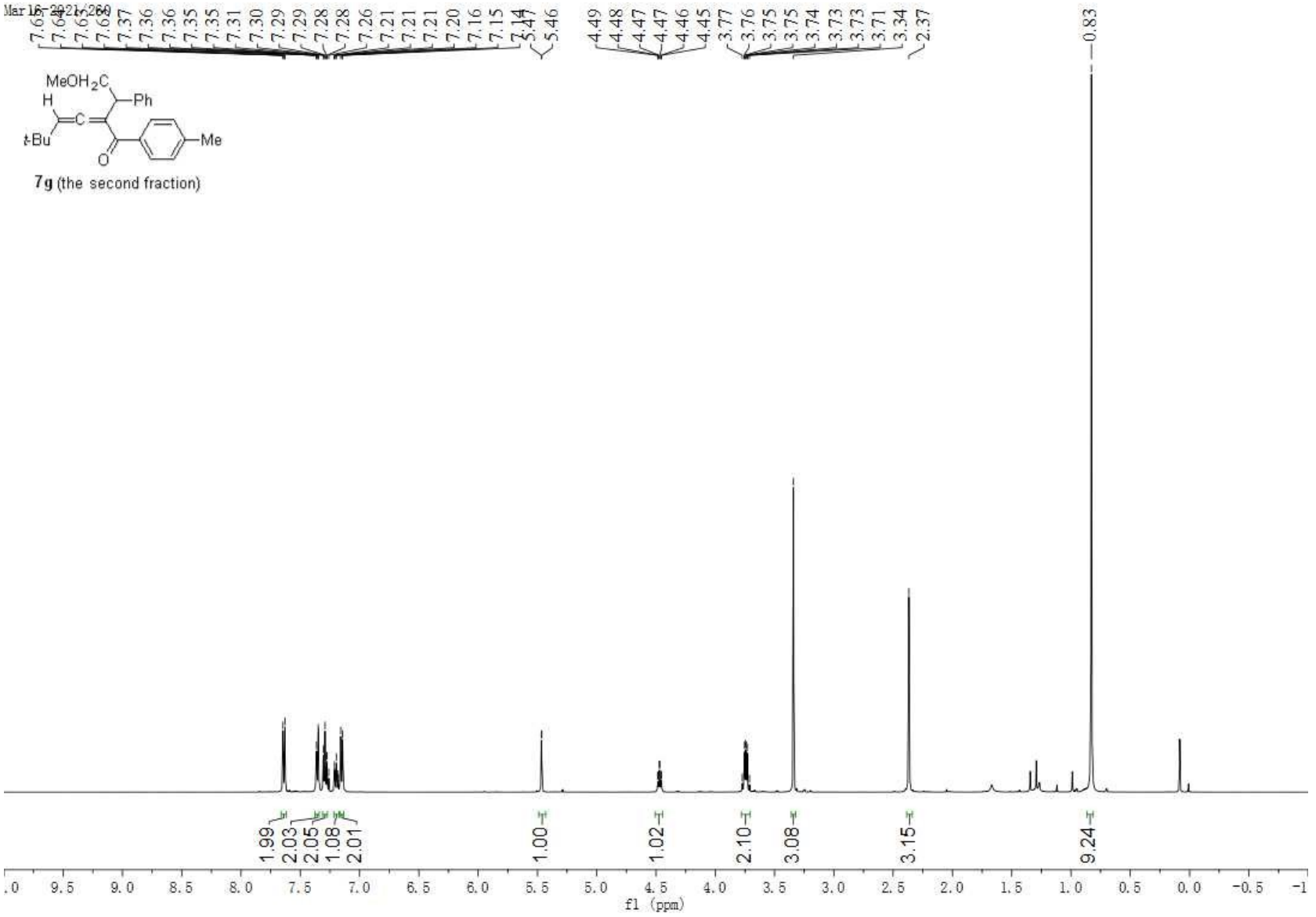
7f (the second fraction)

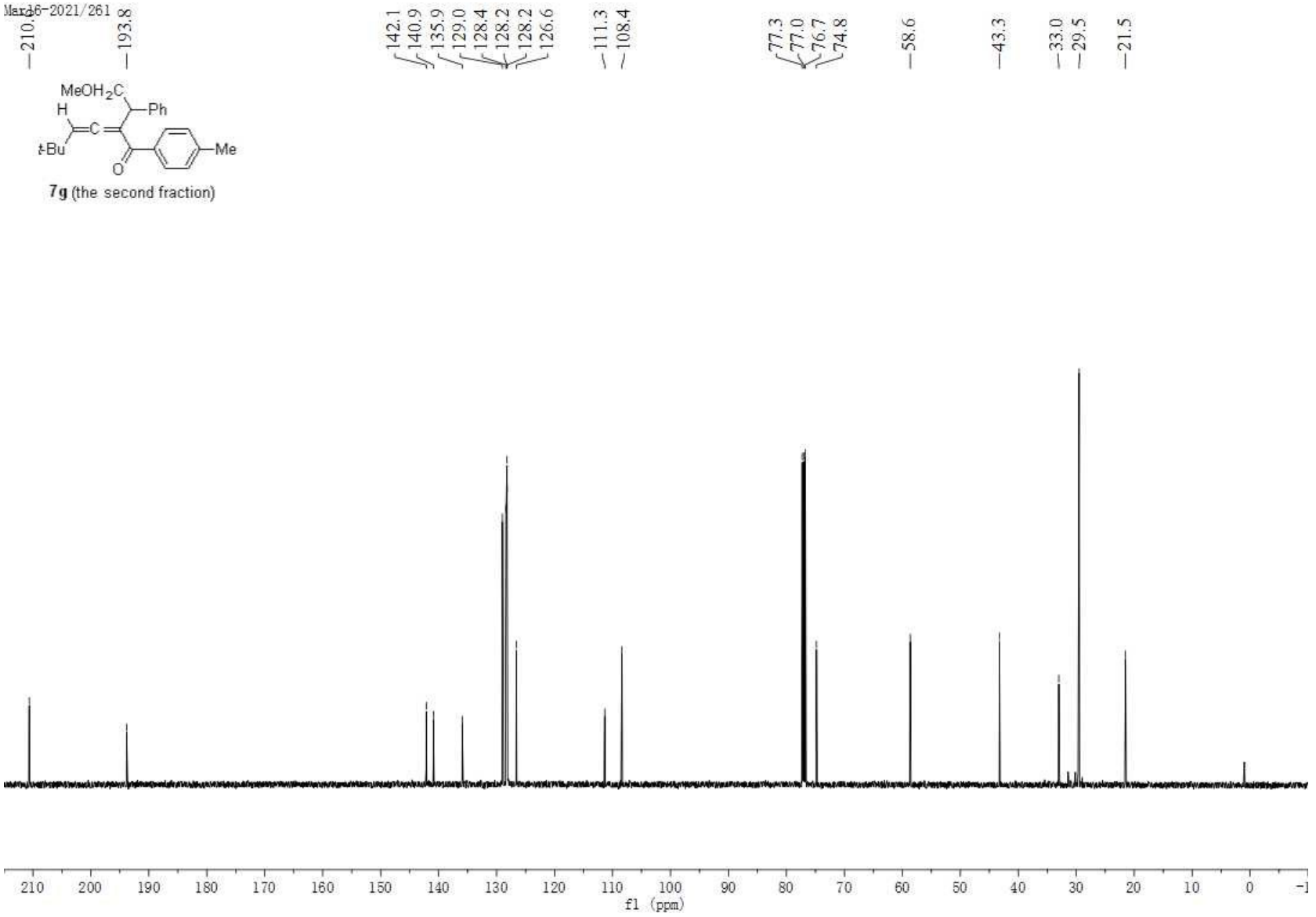

May-04-2021/21
210.0
195.2
139.1
131.3
128.6
127.5
112.6
108.2
77.3
77.0
76.7
58.5
32.8
31.6
29.8
16.6
MeOH2C
H
Me
t-Bu
Ph
O
7f (the second fraction)
f1 (ppm)


211.5
206.1
206.0
206.4
195.1
140.1
132.3
129.5
128.6
113.4
109.1
77.5
58.8
33.5
32.6
30.4
30.2
30.1
29.9
29.8
29.6
29.5
17.5
MeOH2C
H
Me
t-Bu
Ph
O
7f (the second fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

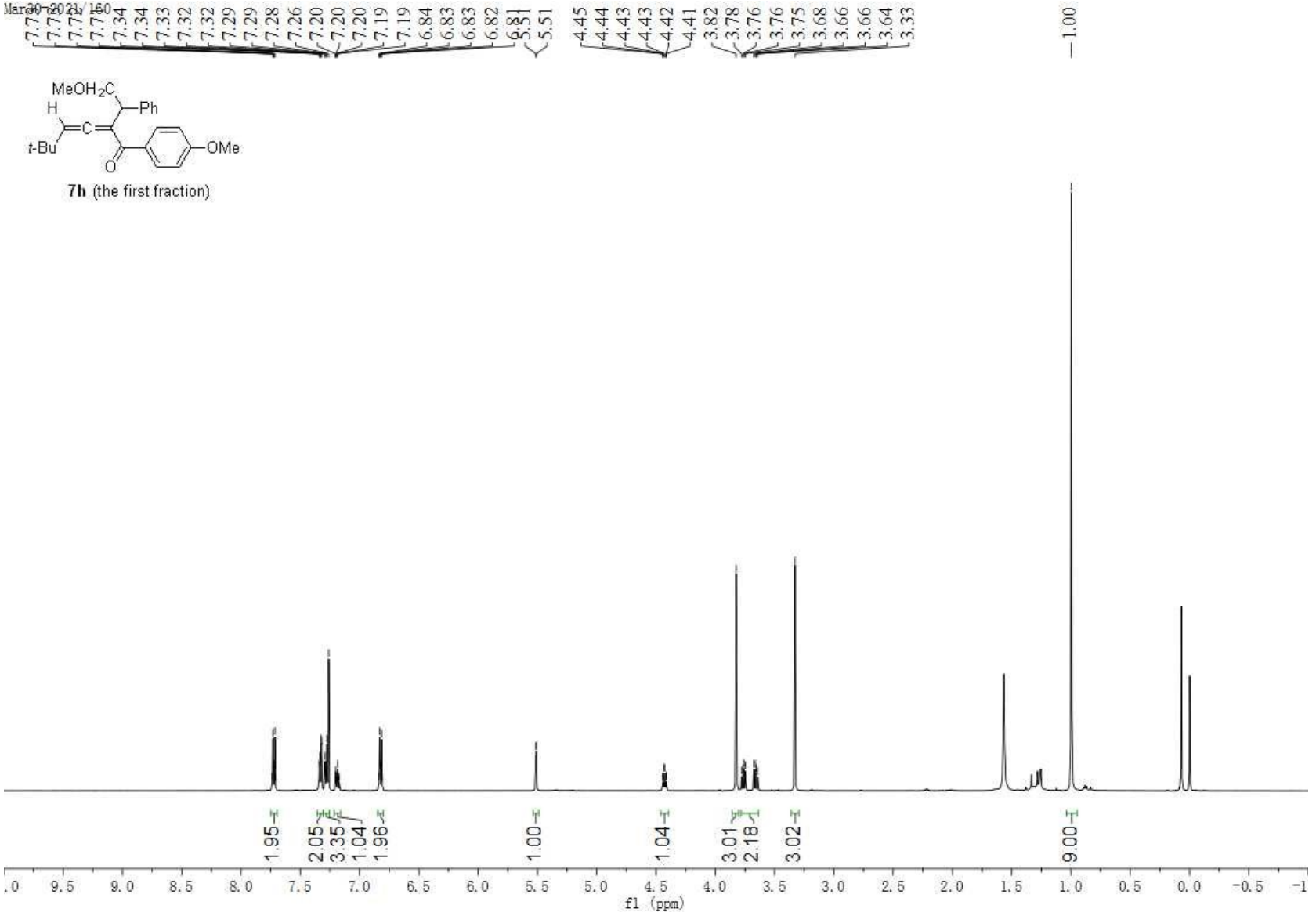

MeOH2C
H
Ph
t-Bu
Me
O
7g (the first fraction)
f1 (ppm)

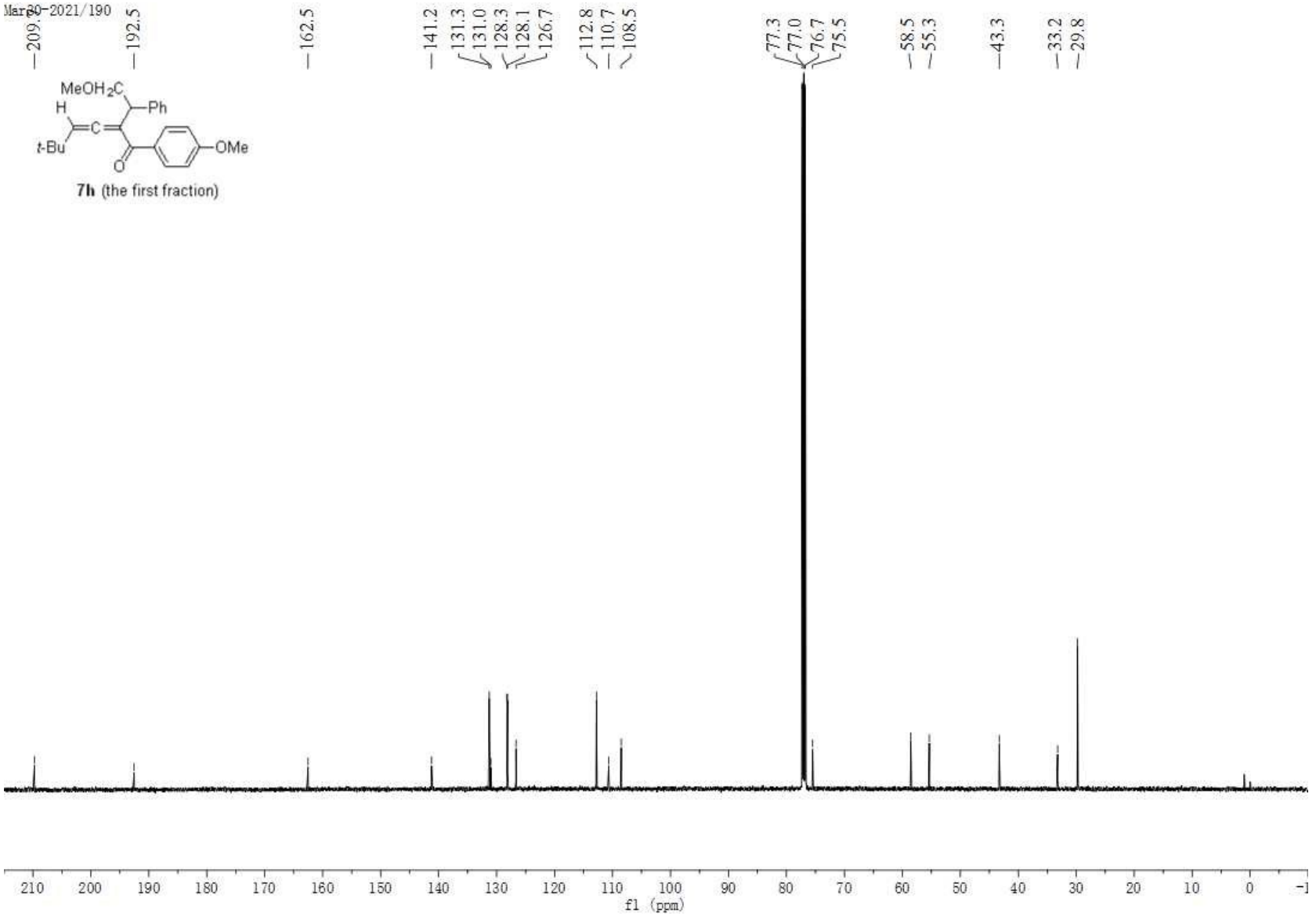

MaxAS-2021/251
210.5
193.8
142.1
141.2
135.7
129.0
128.3
128.2
128.1
126.7
110.9
108.6
77.3
77.0
76.7
75.5
58.5
43.1
33.2
29.7
21.5
MeOH2C
H
Ph
C
t-Bu
O
Me
7g (the first fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

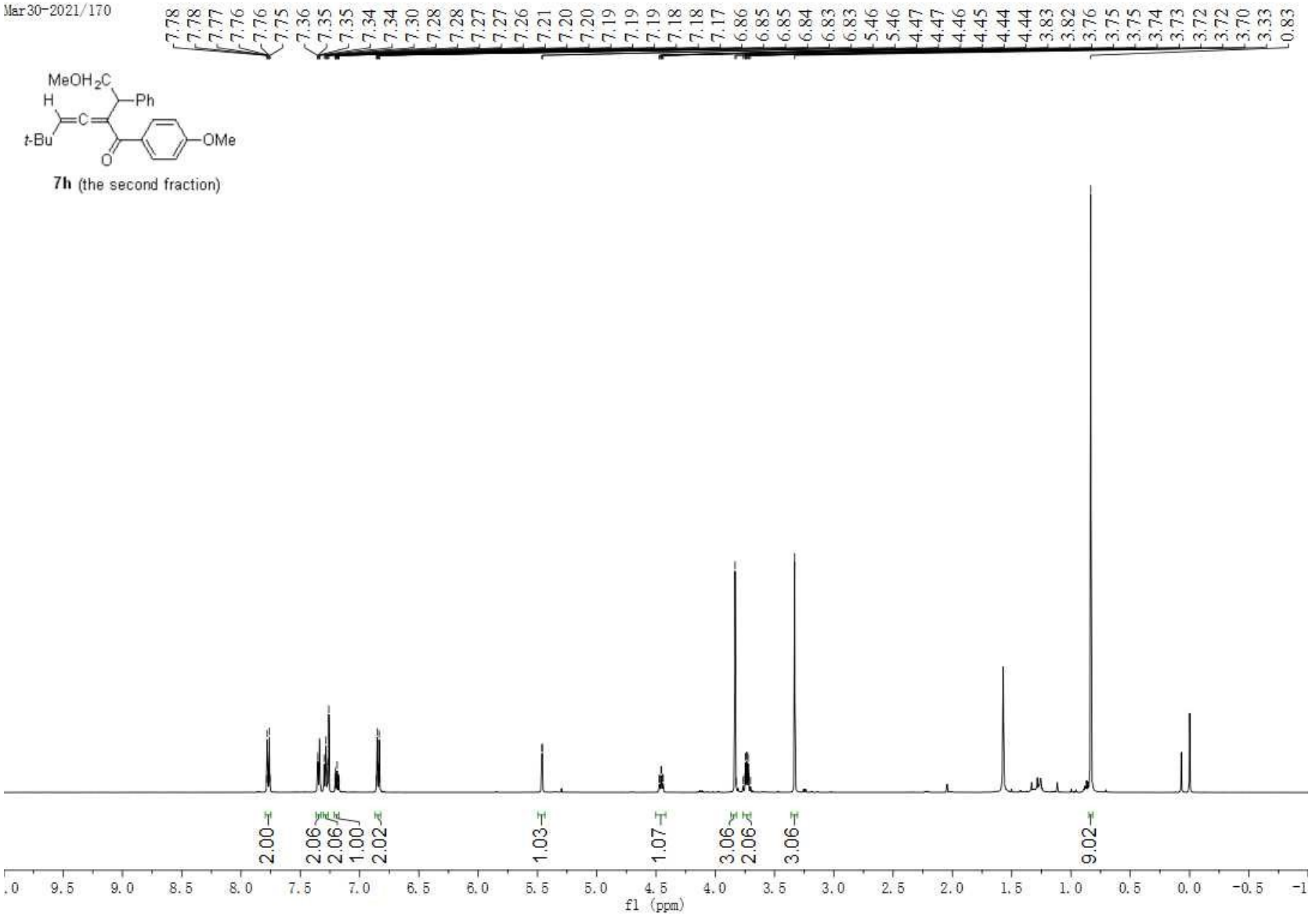

MeOH2C
H
Ph
t-Bu
Me
O
7g (the second fraction)
f1 (ppm)

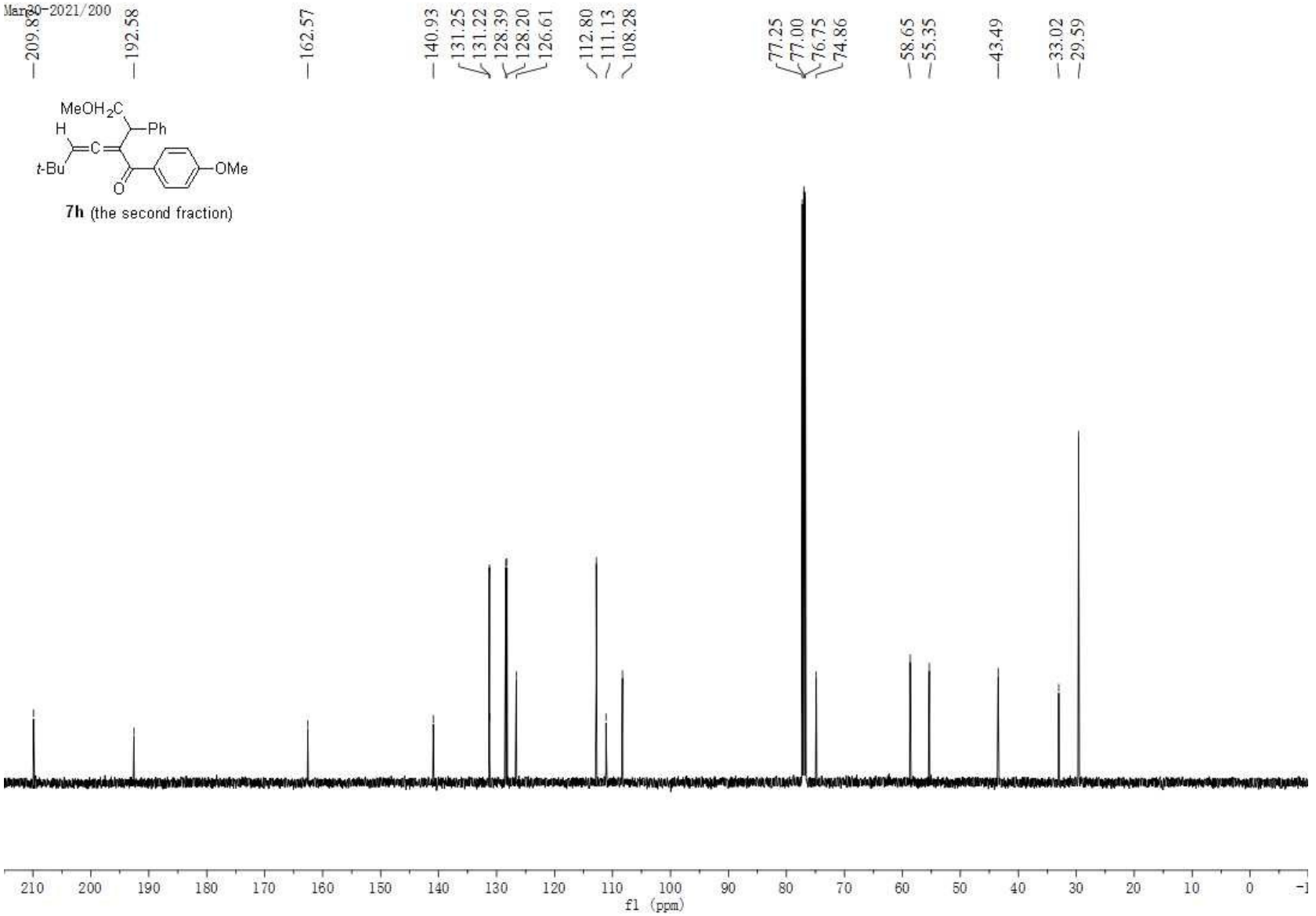


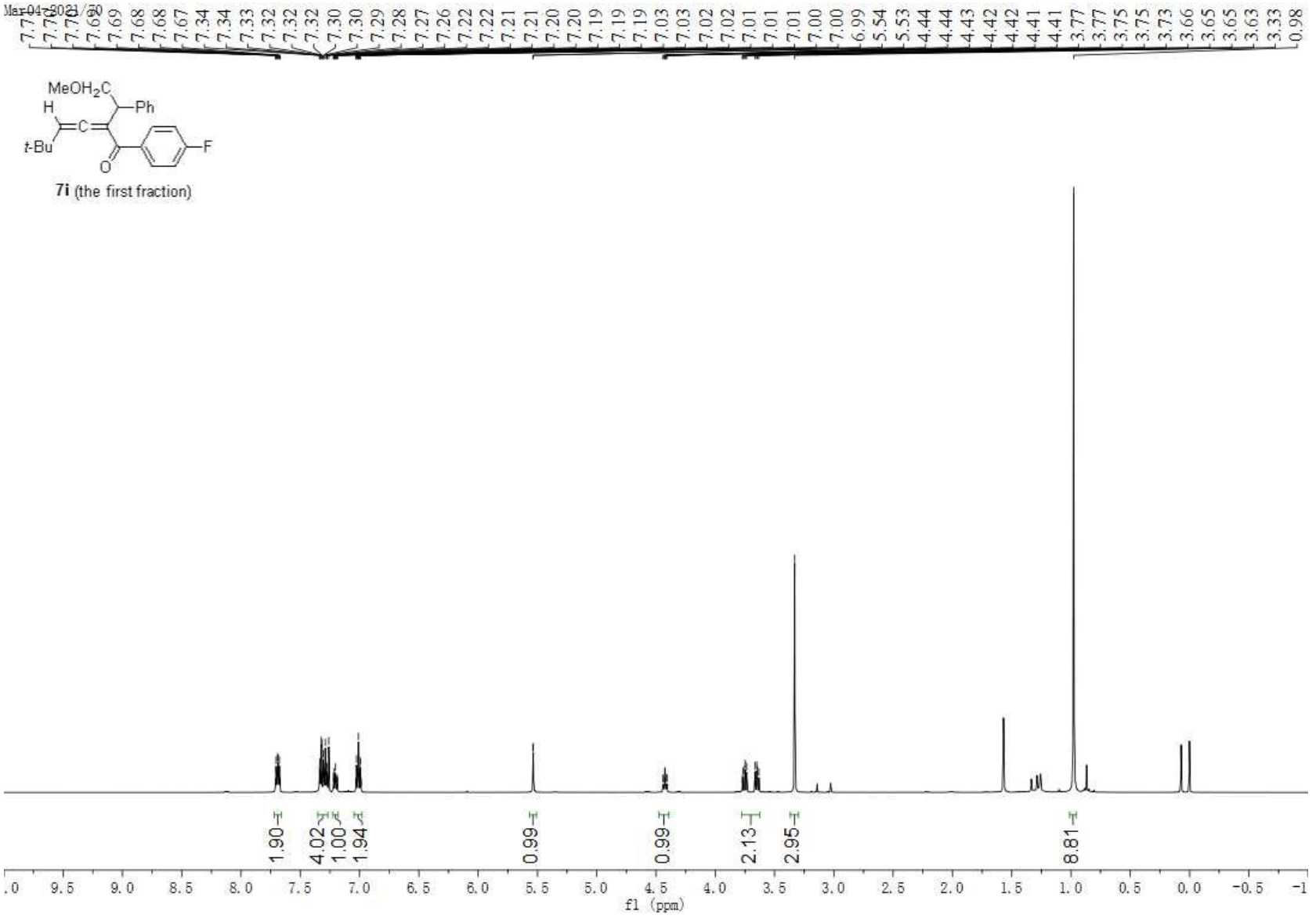
7g (the second fraction)

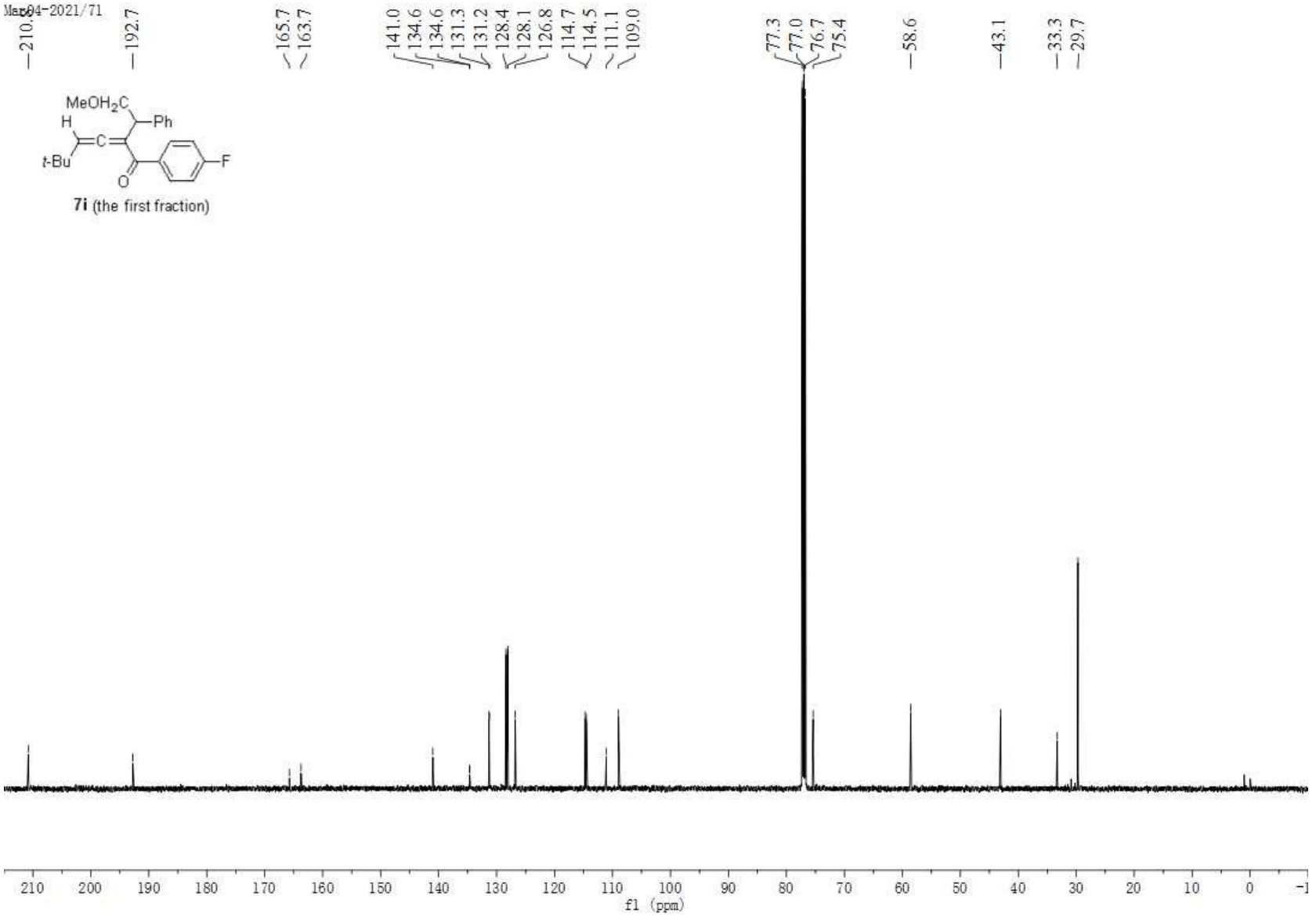

7.77
7.77
7.77
7.77
7.34
7.34
7.33
7.32
7.32
7.29
7.29
7.28
7.26
7.20
7.20
7.20
7.19
7.19
6.84
6.83
6.83
6.82
6.81
5.51
5.51
4.45
4.44
4.43
4.43
4.42
4.41
3.82
3.78
3.76
3.76
3.75
3.68
3.66
3.66
3.64
3.33
1.00
MeOH2C
H
Ph
t-Bu
OMe
O
7h (the first fraction)
1.95
2.05
3.35
1.04
1.96
1.00
1.04
3.01
2.18
3.02
9.00
f1 (ppm)


Mar30-2021/190
209.8
192.5
162.5
141.2
131.3
131.0
128.3
128.1
126.7
112.8
110.7
108.5
77.3
77.0
76.7
75.5
58.5
55.3
43.3
33.2
29.8
MeOH2C
H
Ph
t-Bu
OMe
O
7h (the first fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

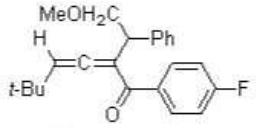

Mar30-2021/170
7.78 7.78 7.77 7.76 7.76 7.75 7.36 7.35 7.35 7.34 7.34 7.30 7.28 7.28 7.27 7.27 7.26 7.21 7.20 7.20 7.19 7.19 7.19 7.18 7.18 7.17 6.86 6.85 6.85 6.84 6.83 6.83 5.46 5.46 4.47 4.47 4.46 4.45 4.44 4.44 3.83 3.82 3.76 3.75 3.75 3.74 3.73 3.72 3.72 3.70 3.33 0.83
MeOH2C
H
Ph
t-Bu
OMe
O
7h (the second fraction)
2.00 2.06 2.06 1.00 2.02 1.03 1.07 3.06 2.06 3.06 9.02
f1 (ppm)


Mar30-2021/200
209.85
192.58
162.57
140.93
131.25
131.22
128.39
128.20
126.61
112.80
111.13
108.28
77.25
77.00
76.75
74.86
58.65
55.35
43.49
33.02
29.59
MeOH2C
H
Ph
t-Bu
OMe
O
7h (the second fraction)
f1 (ppm)

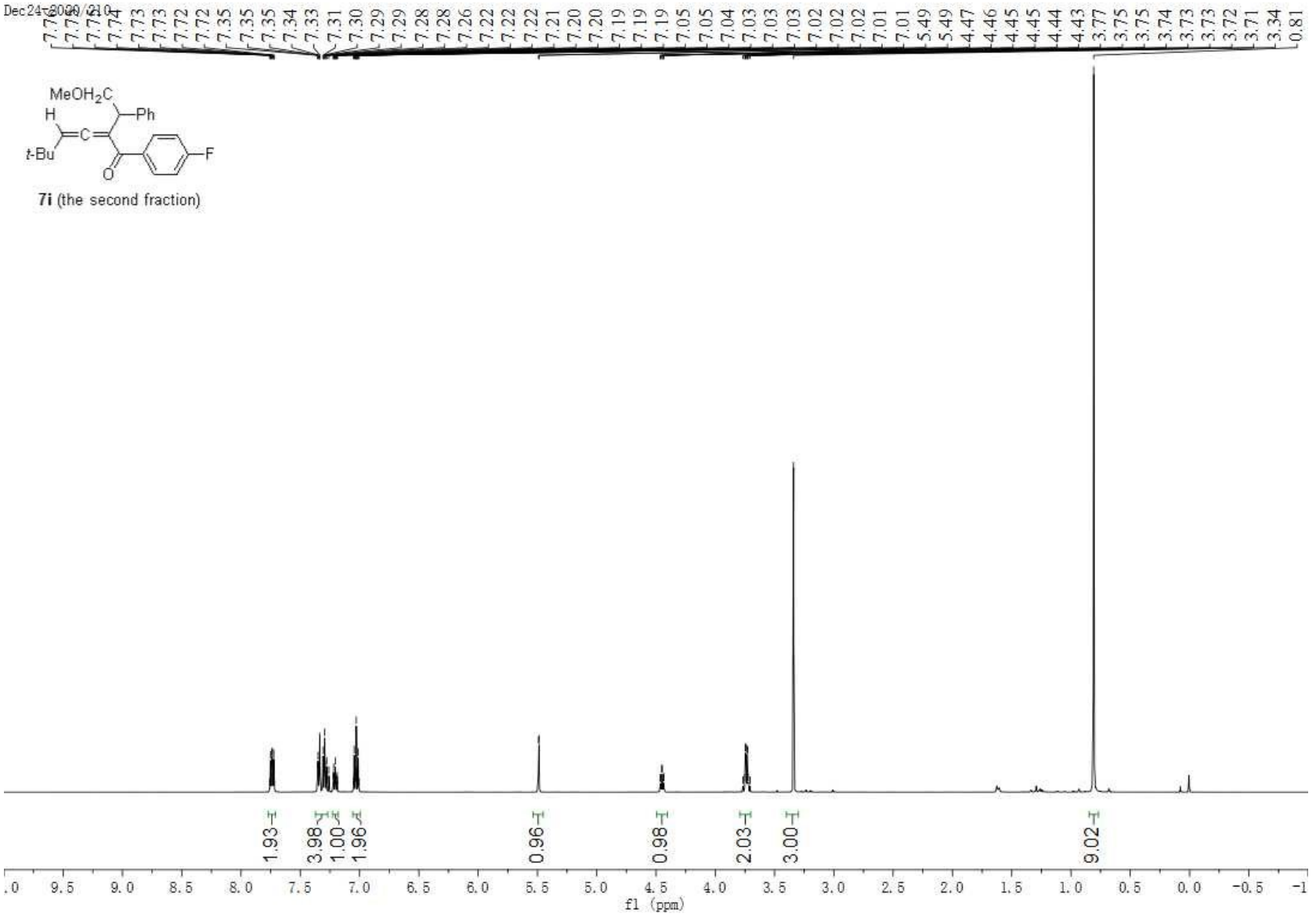

MeO2C
H
Ph
t-Bu
F
O
7i (the first fraction)
1.90
4.02
1.00
1.94
0.99
0.99
2.13
2.95
8.81
f1 (ppm)

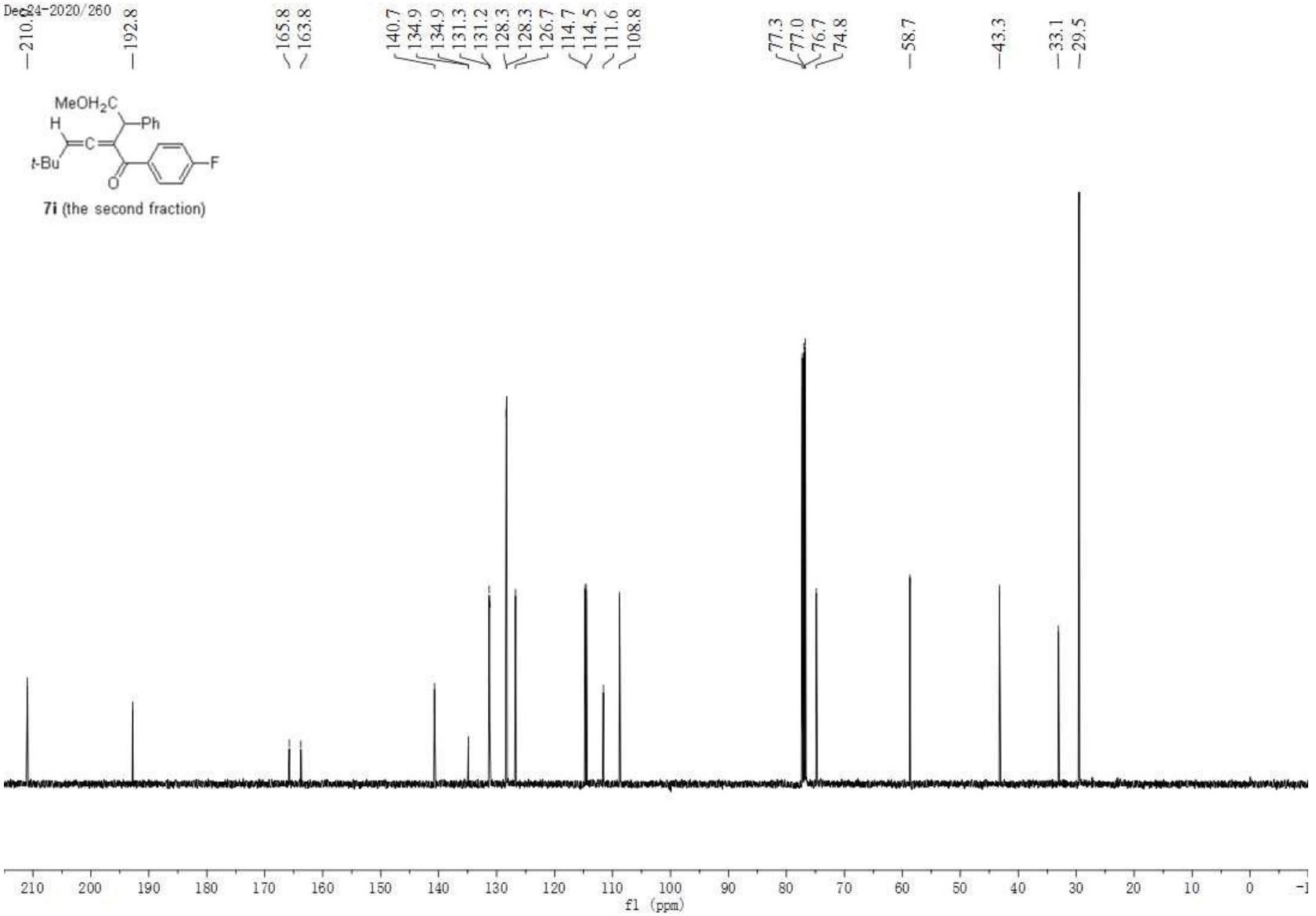

Mar04-2021/71
210.8
192.7
165.7
163.7
141.0
134.6
134.6
131.3
131.2
128.4
128.1
126.8
114.7
114.5
111.1
109.0
77.3
77.0
76.7
75.4
58.6
43.1
33.3
29.7
MeOH2C
H
Ph
t-Bu
F
O
7i (the first fraction)
f1 (ppm)

Mar04-2021/72

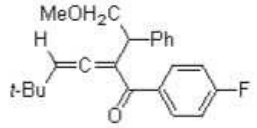


7i (the first fraction)

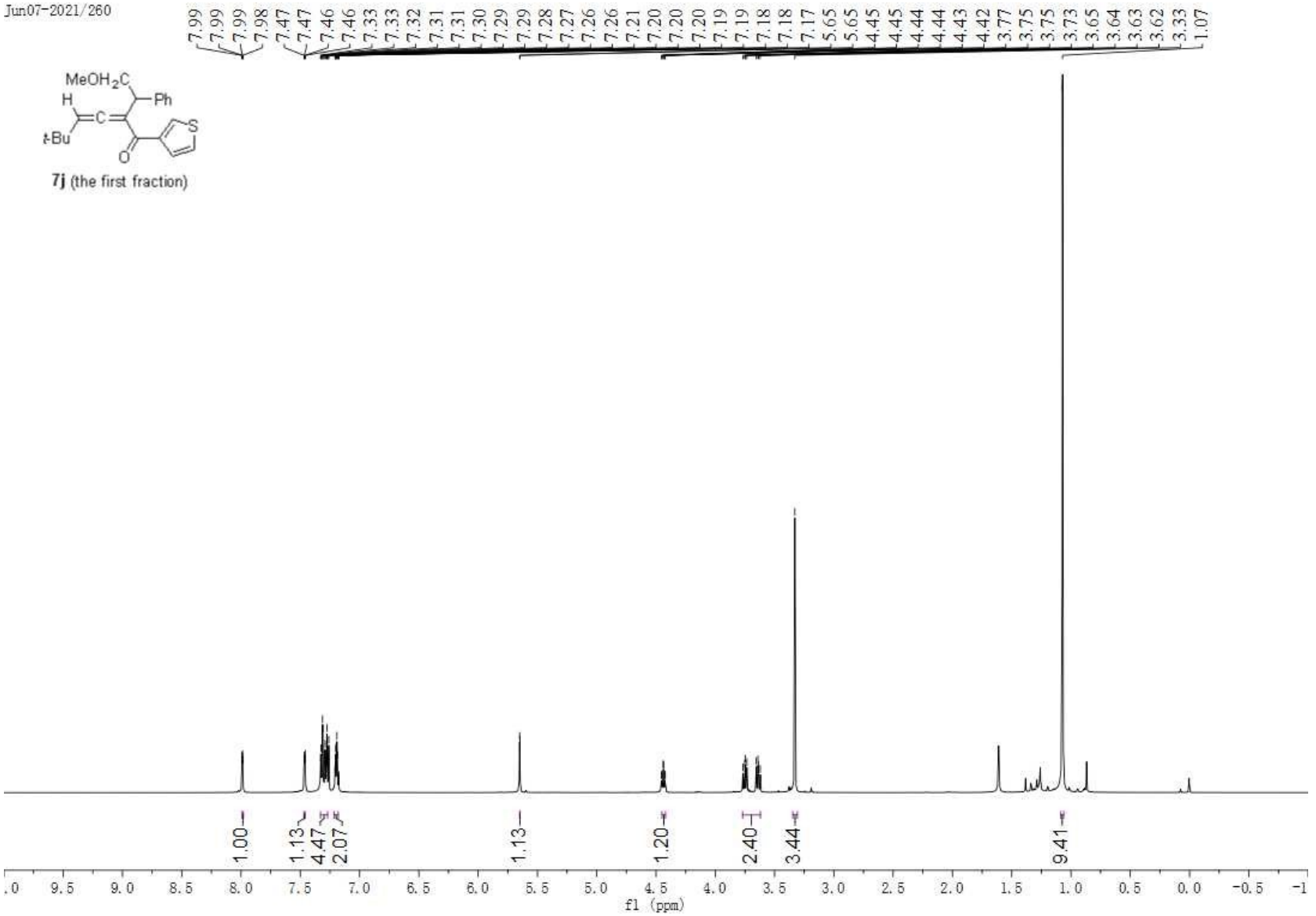

Dec24-2020/210
MeOH2C
H
Ph
t-Bu
C
O
F
7i (the second fraction)
1.93
3.98
1.00
1.96
0.96
0.98
2.03
3.00
9.02
f1 (ppm)

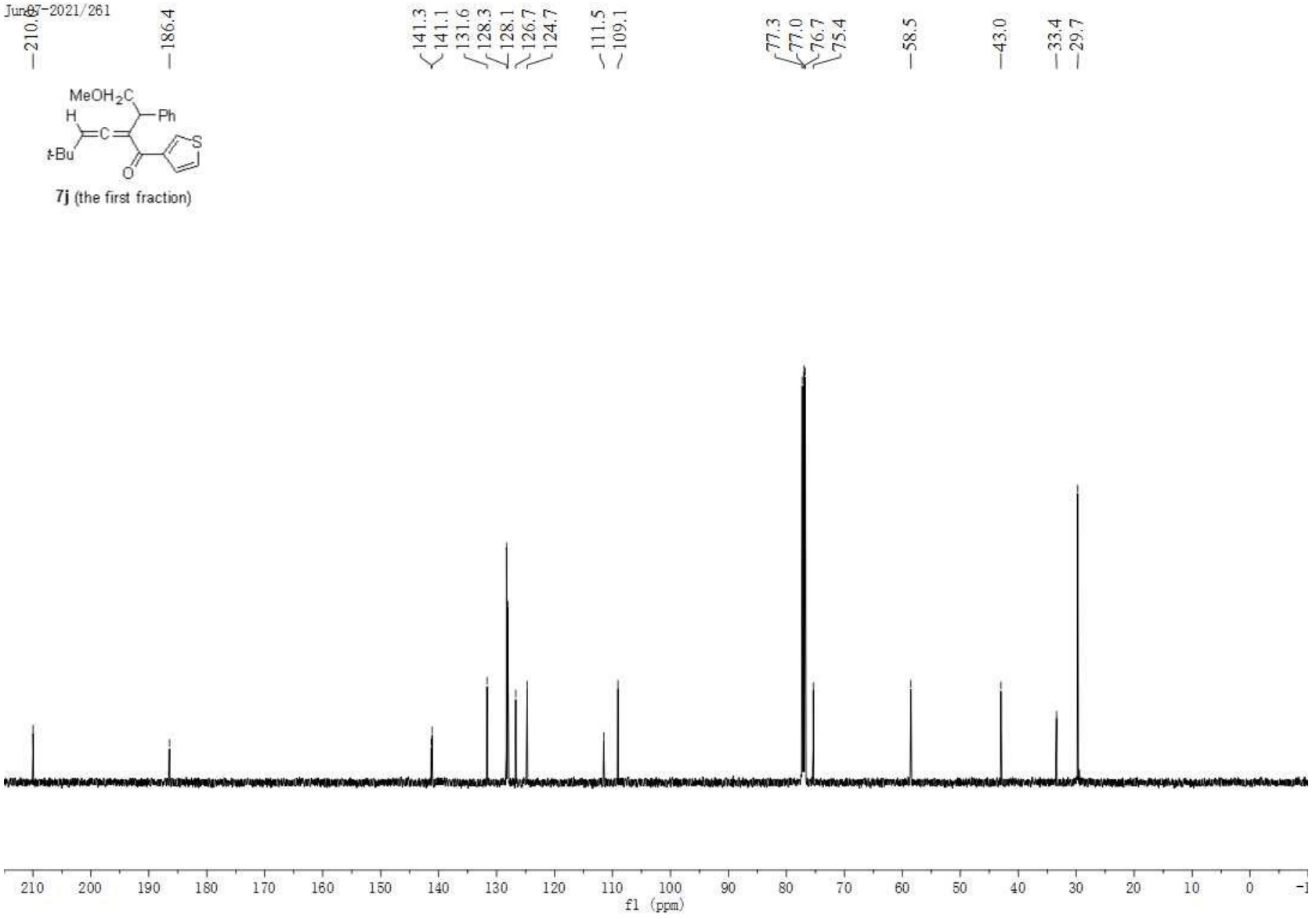

Dec24-2020/260
210.6
192.8
165.8
163.8
140.7
134.9
134.9
131.3
131.2
128.3
128.3
126.7
114.7
114.5
111.6
108.8
77.3
77.0
76.7
74.8
58.7
43.3
33.1
29.5
MeOH2C
H
Ph
t-Bu
F
O
7i (the second fraction)
f1 (ppm)

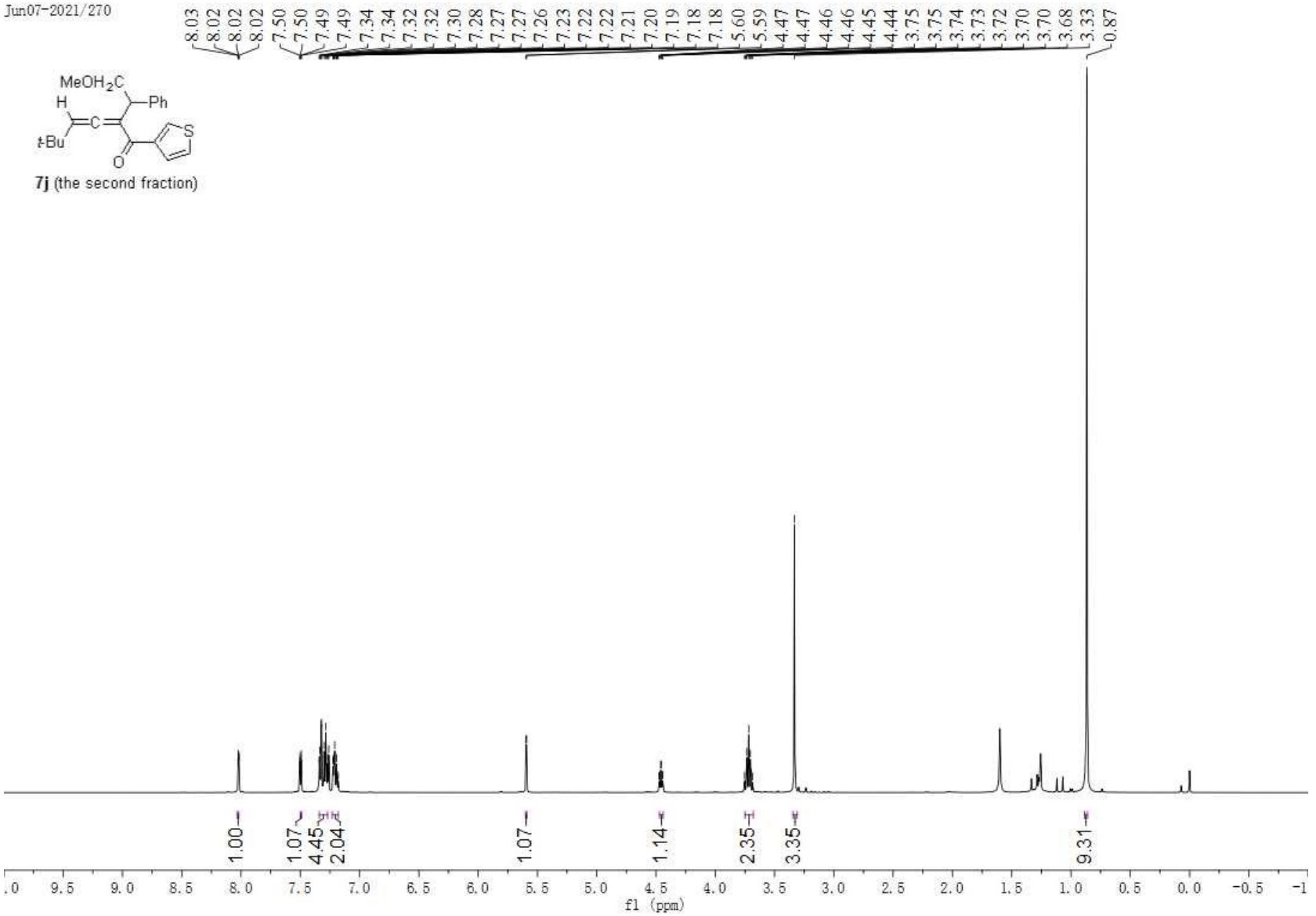
Dec24-2020/261

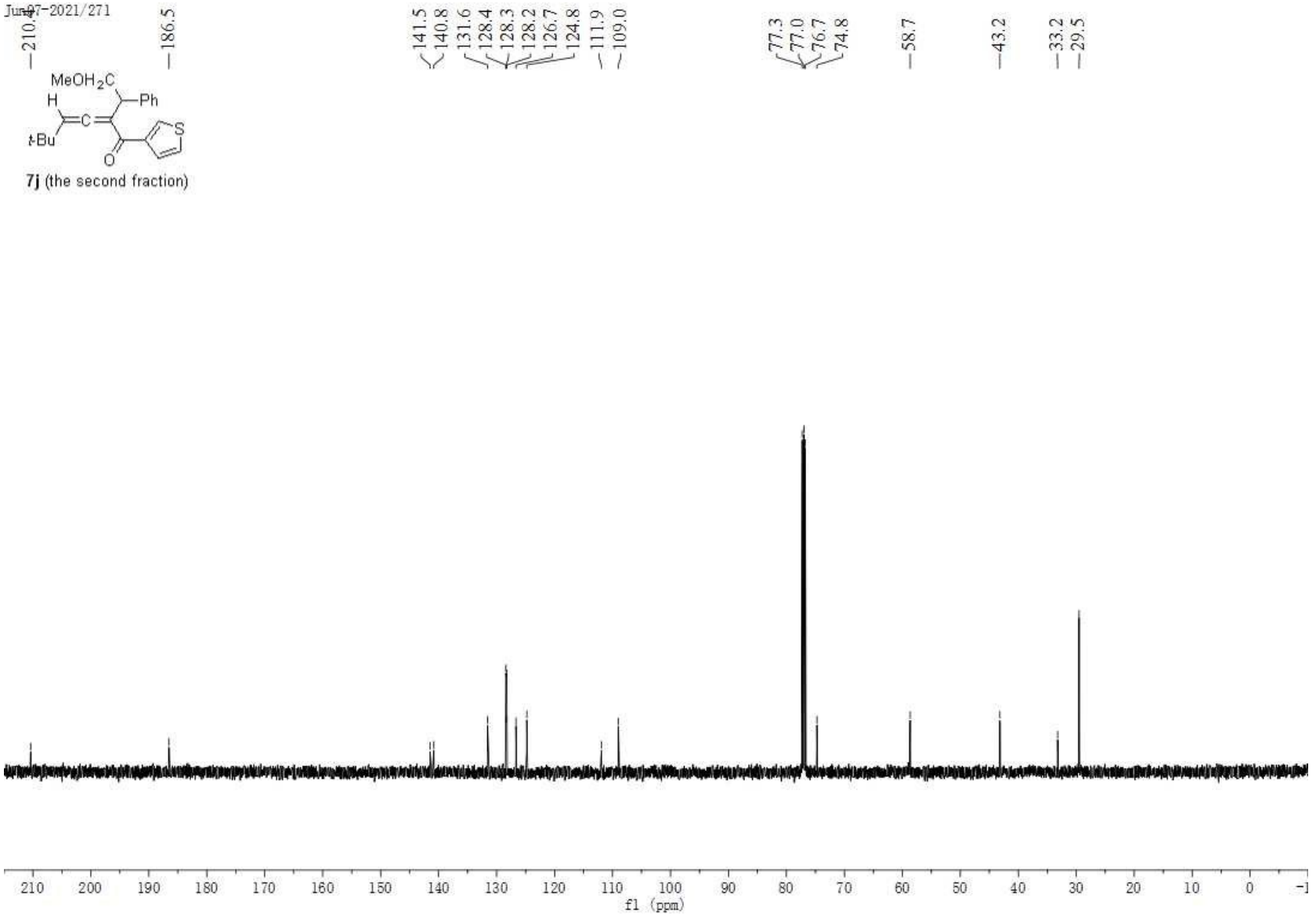


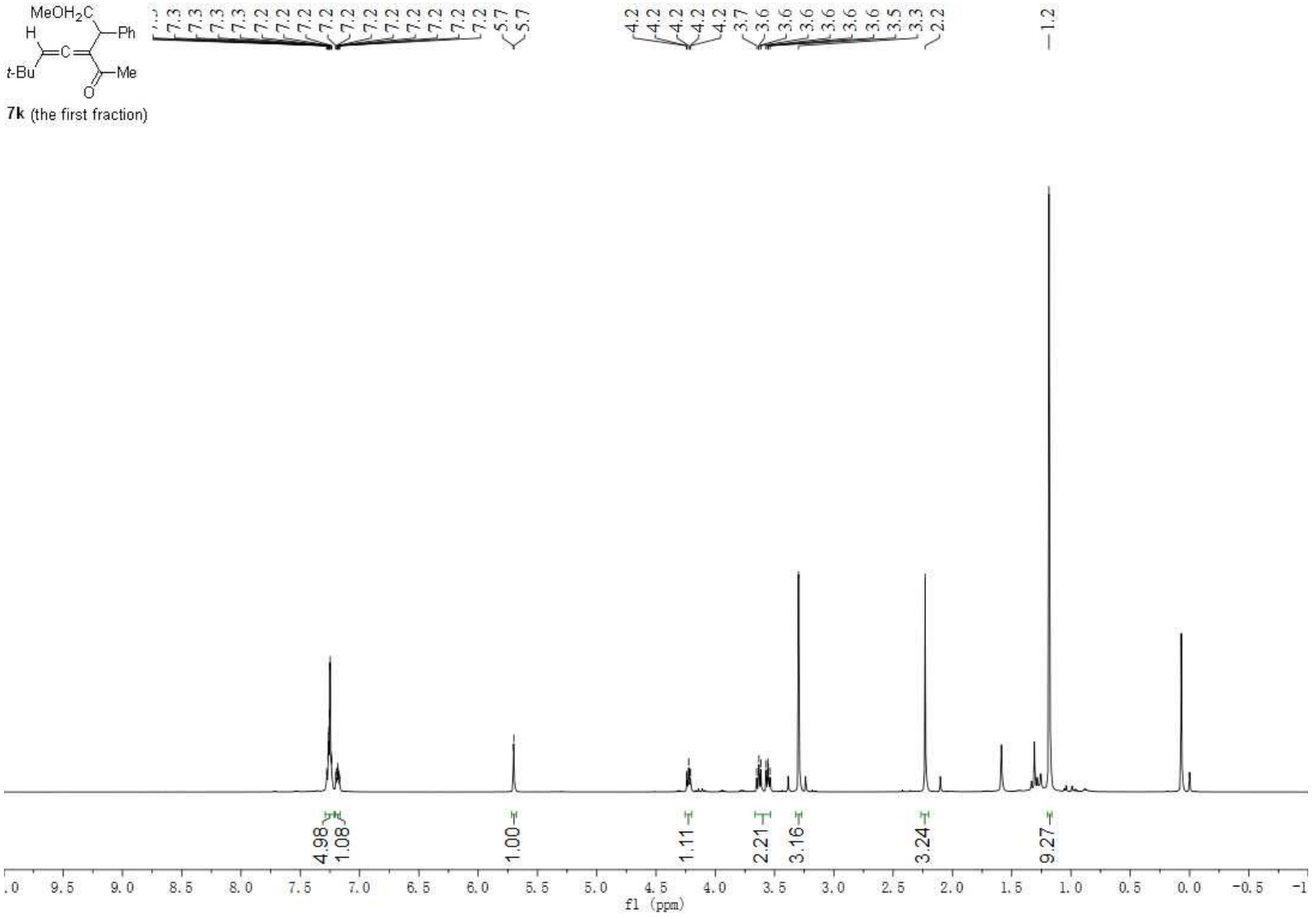
7i (the second fraction)

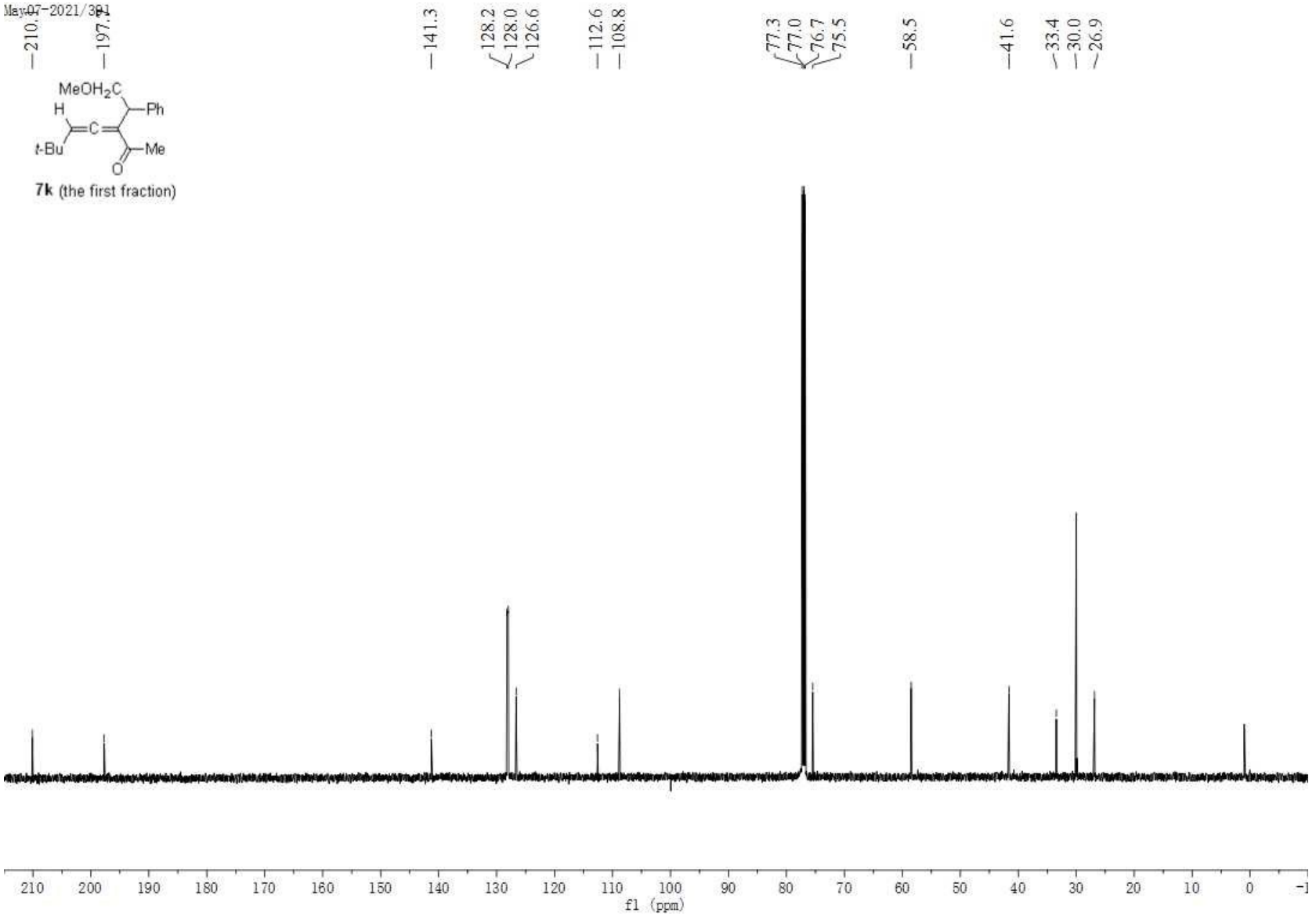

Jun07-2021/260
7.99 7.99 7.99 7.98 7.47 7.47 7.46 7.46 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.26 7.26 7.21 7.20 7.20 7.20 7.19 7.19 7.18 7.18 7.17 5.65 5.65 4.45 4.45 4.44 4.44 4.43 4.42 3.77 3.75 3.75 3.73 3.65 3.64 3.63 3.62 3.33 1.07
MeOH2C
H
Ph
t-Bu
S
O
7j (the first fraction)
1.00 1.13 4.47 2.07 1.13 1.20 2.40 3.44 9.41
f1 (ppm)

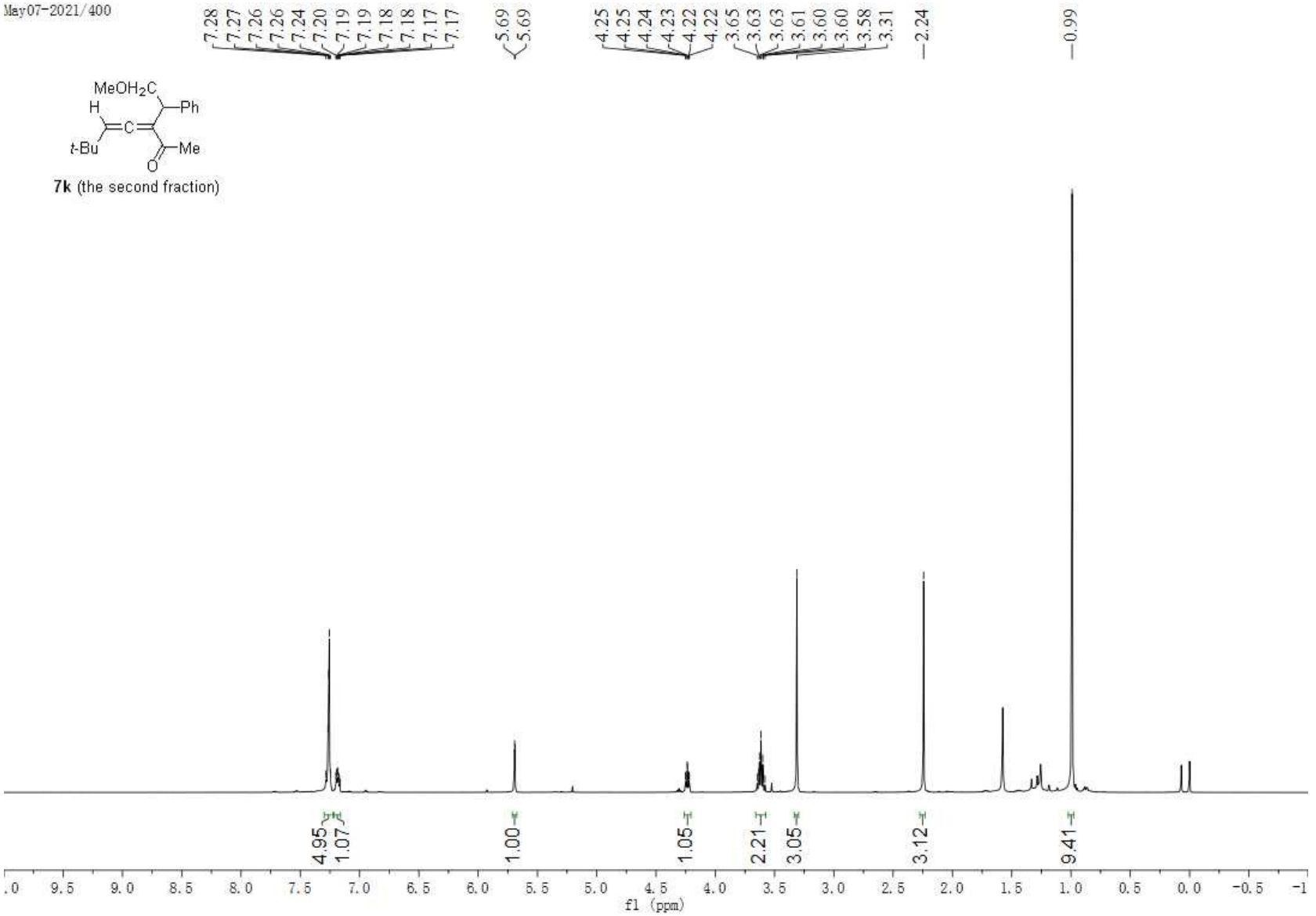

Jun-07-2021/261
210.8
186.4
141.3
141.1
131.6
128.3
128.1
126.7
124.7
111.5
109.1
77.3
77.0
76.7
75.4
58.5
43.0
33.4
29.7
MeOH2C
H
Ph
t-Bu
S
O
7j (the first fraction)
f1 (ppm)

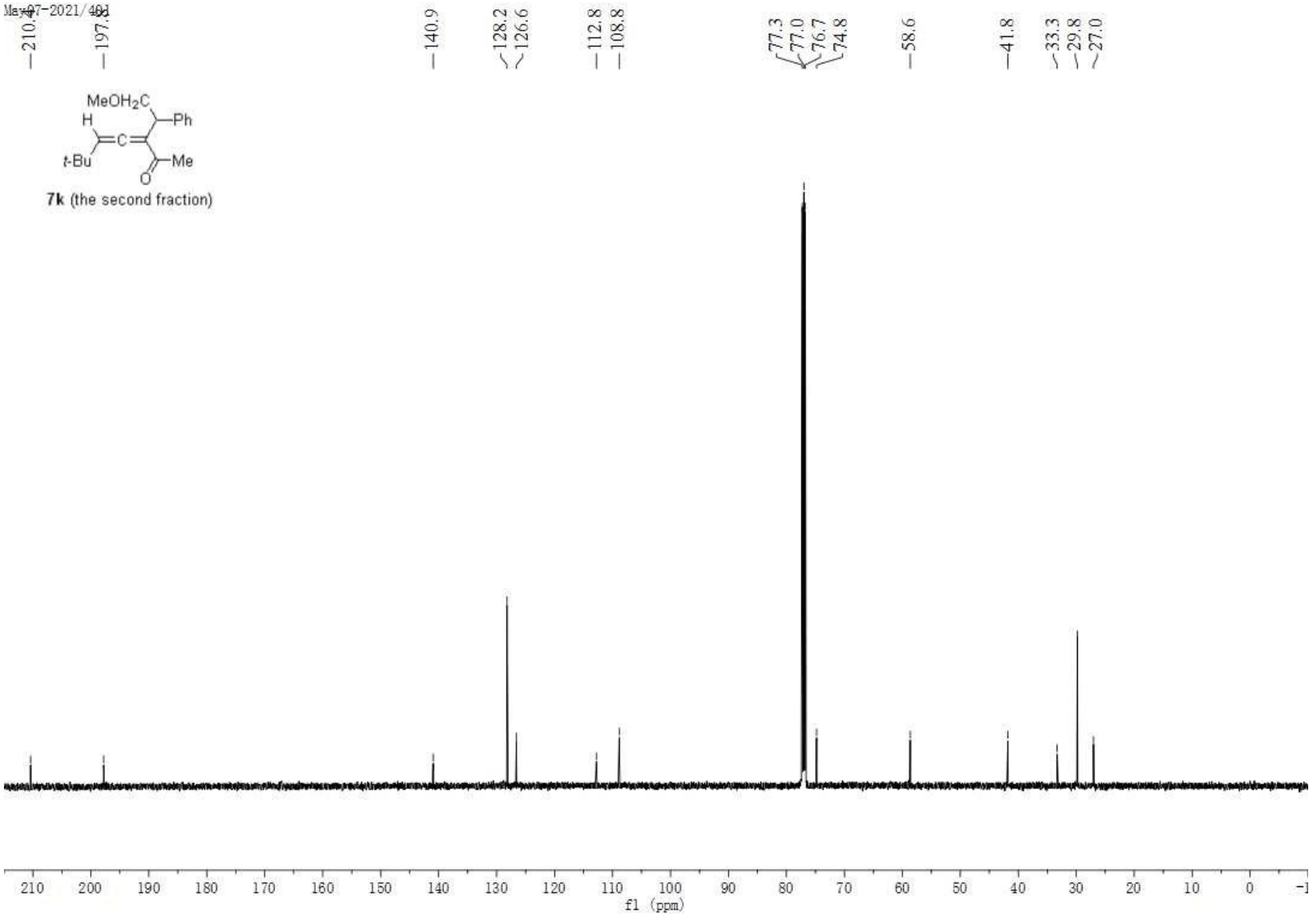

Jun07-2021/270
8.03 8.02 8.02 8.02 7.50 7.50 7.49 7.49 7.34 7.34 7.32 7.32 7.30 7.28 7.27 7.27 7.26 7.23 7.22 7.22 7.21 7.20 7.19 7.18 7.18 5.60 5.59 4.47 4.47 4.46 4.46 4.45 4.44 3.75 3.75 3.74 3.73 3.72 3.70 3.70 3.68 3.33 0.87
MeOH2C
H
Ph
t-Bu
S
O
7j (the second fraction)
1.00 1.07 4.45 2.04 1.07 1.14 2.35 3.35 9.31
f1 (ppm)

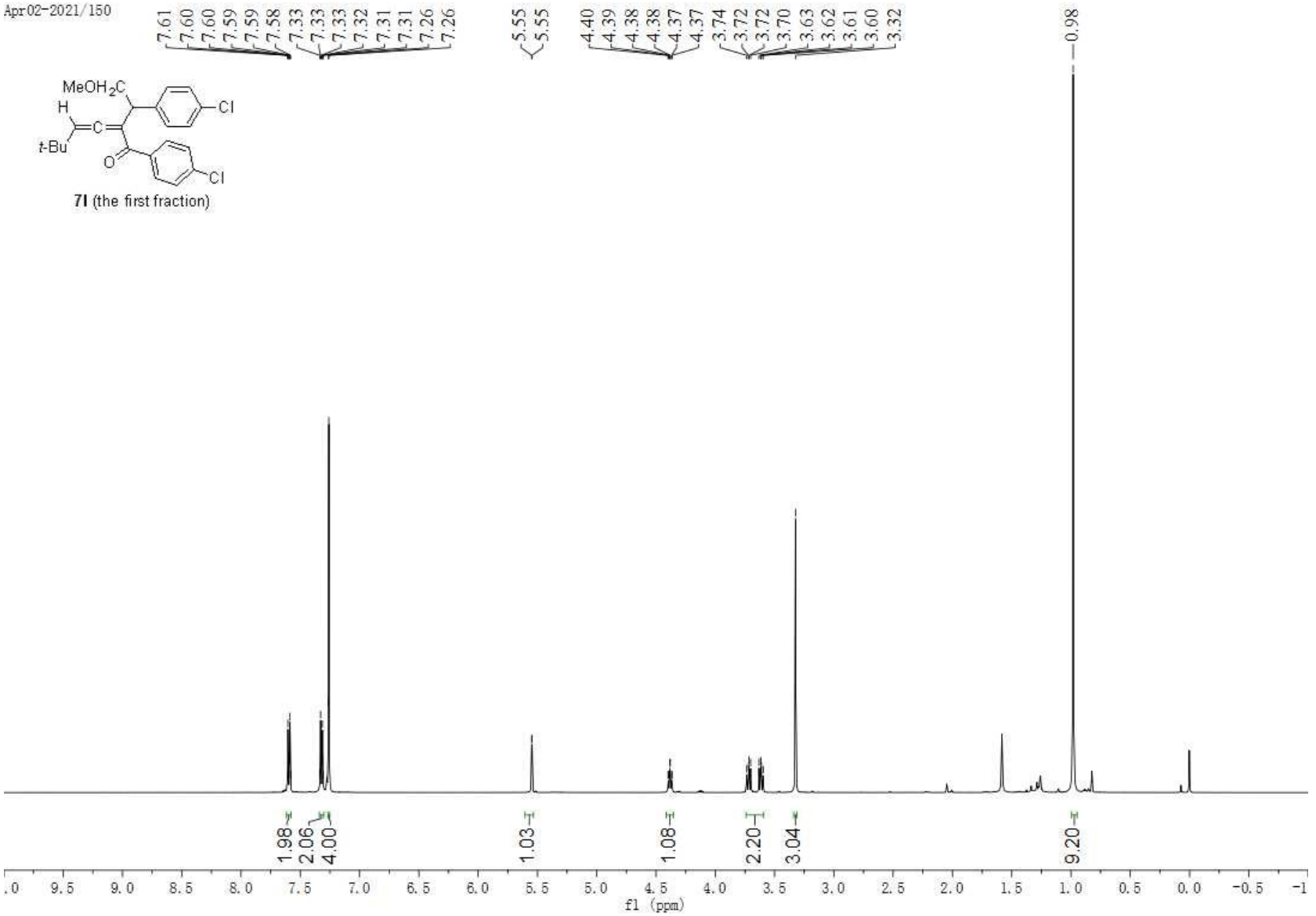

Jun-07-2021/271
210.4
186.5
141.5
140.8
131.6
128.4
128.3
128.2
126.7
124.8
111.9
109.0
77.3
77.0
76.7
74.8
58.7
43.2
33.2
29.5
MeOH2C
H
Ph
t-Bu
S
O
7j (the second fraction)
f1 (ppm)

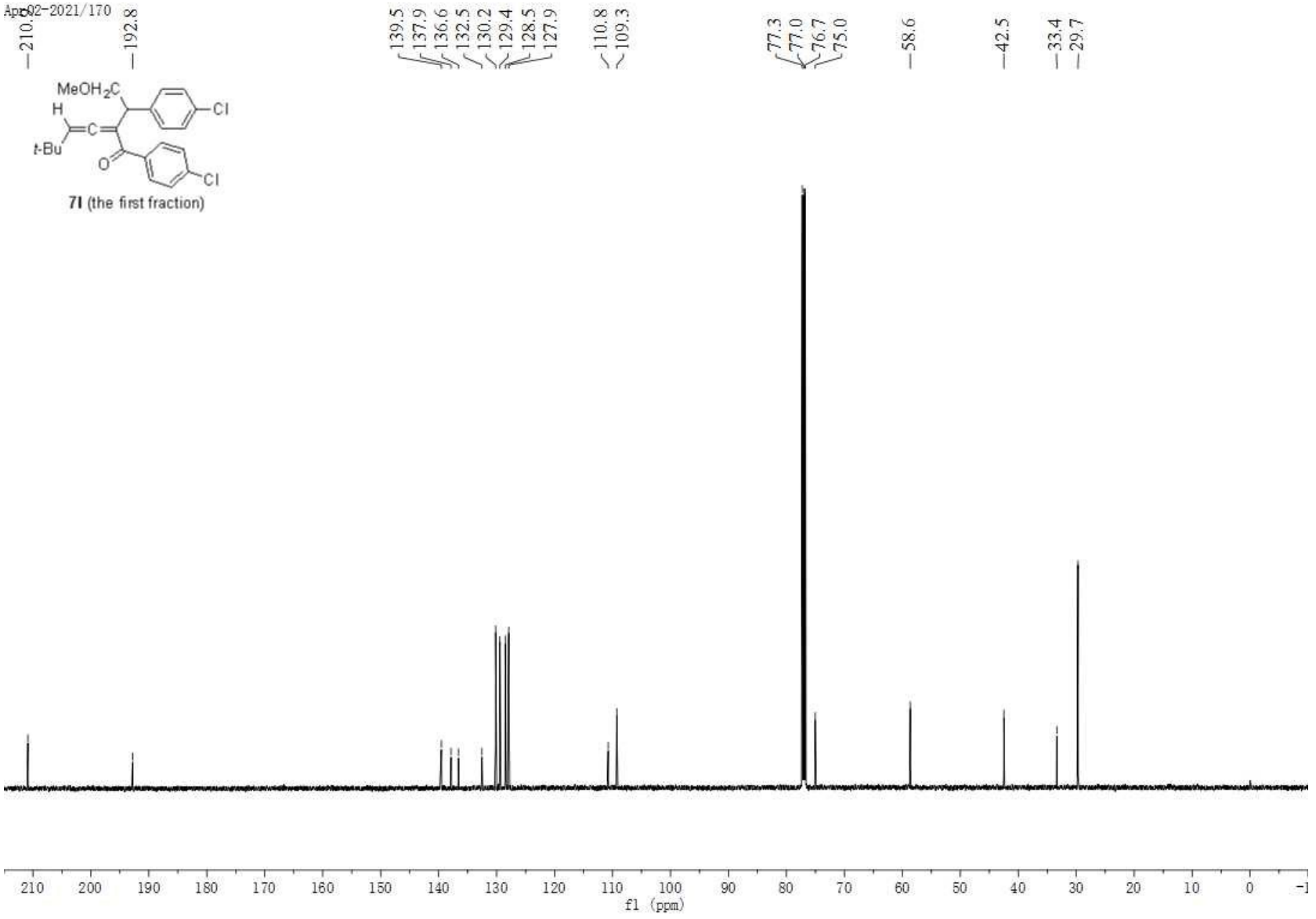

MeOH2C
H
Ph
t-Bu
Me
O
7k (the first fraction)
7.3
7.2
5.7
4.2
3.7
3.6
3.5
3.3
2.2
1.2
4.98
1.08
1.00
1.11
2.21
3.16
3.24
9.27
f1 (ppm)

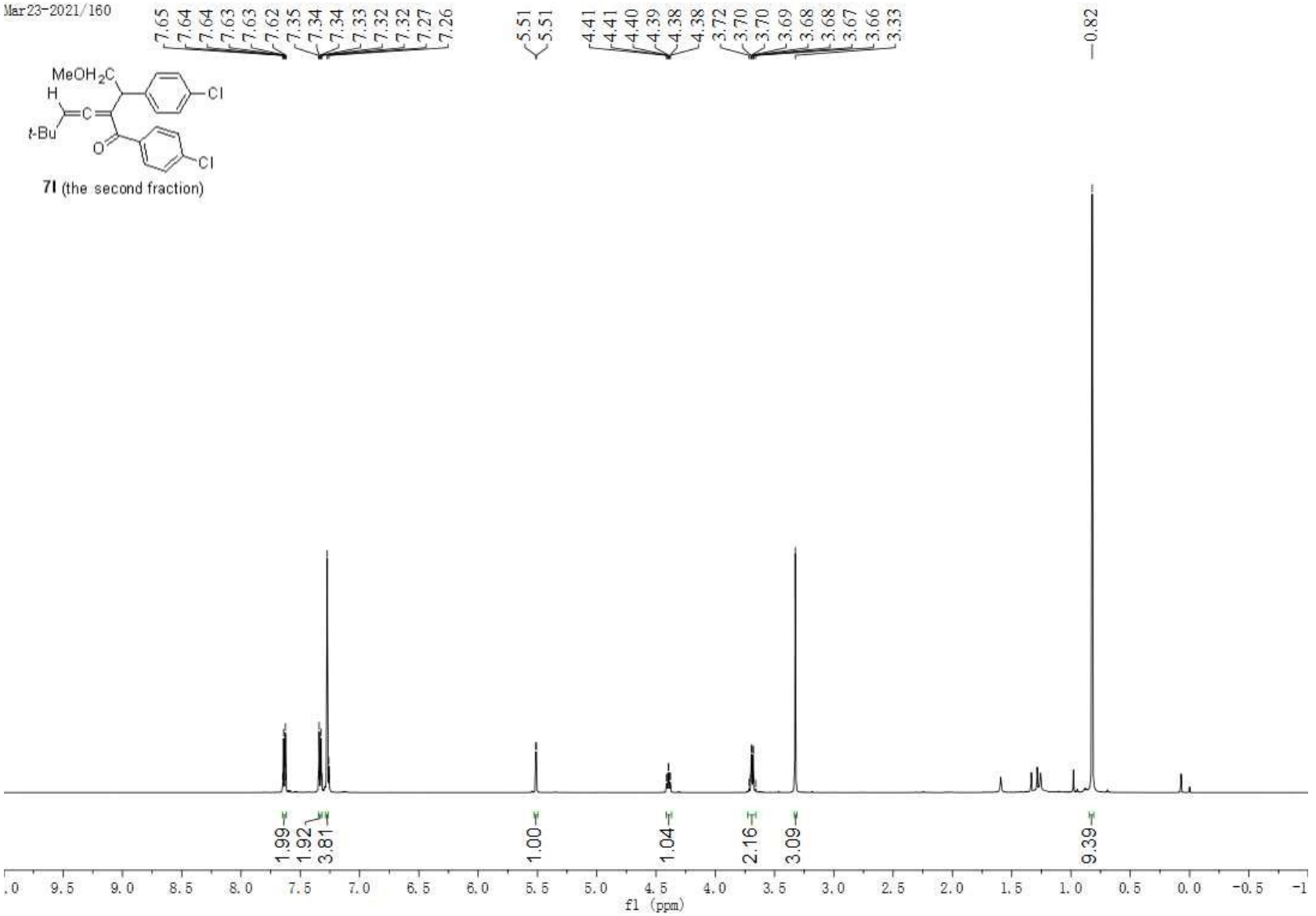

May-07-2021/3
210.1
197.1
141.3
128.2
128.0
126.6
112.6
108.8
77.3
77.0
76.7
75.5
58.5
41.6
33.4
30.0
26.9
MeOH2C
H
Ph
t-Bu
Me
O
7k (the first fraction)
f1 (ppm)

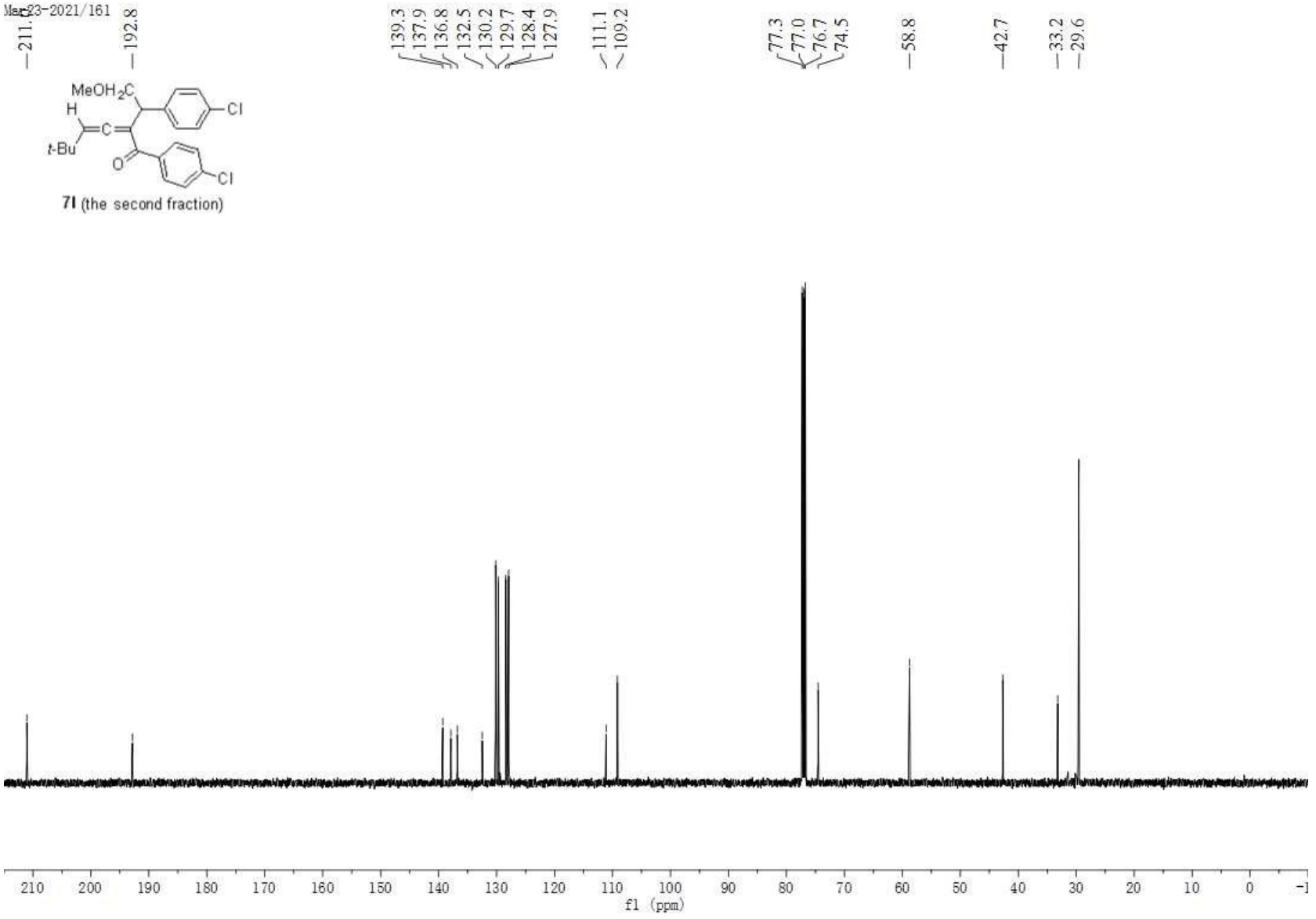

May07-2021/400
7.28
7.27
7.26
7.26
7.24
7.20
7.19
7.19
7.18
7.18
7.17
7.17
5.69
5.69
4.25
4.25
4.24
4.23
4.22
4.22
3.65
3.63
3.63
3.61
3.60
3.60
3.58
3.31
2.24
0.99
MeOH2C
H
Ph
t-Bu
Me
O
7k (the second fraction)
4.95
1.07
1.00
1.05
2.21
3.05
3.12
9.41
f1 (ppm)

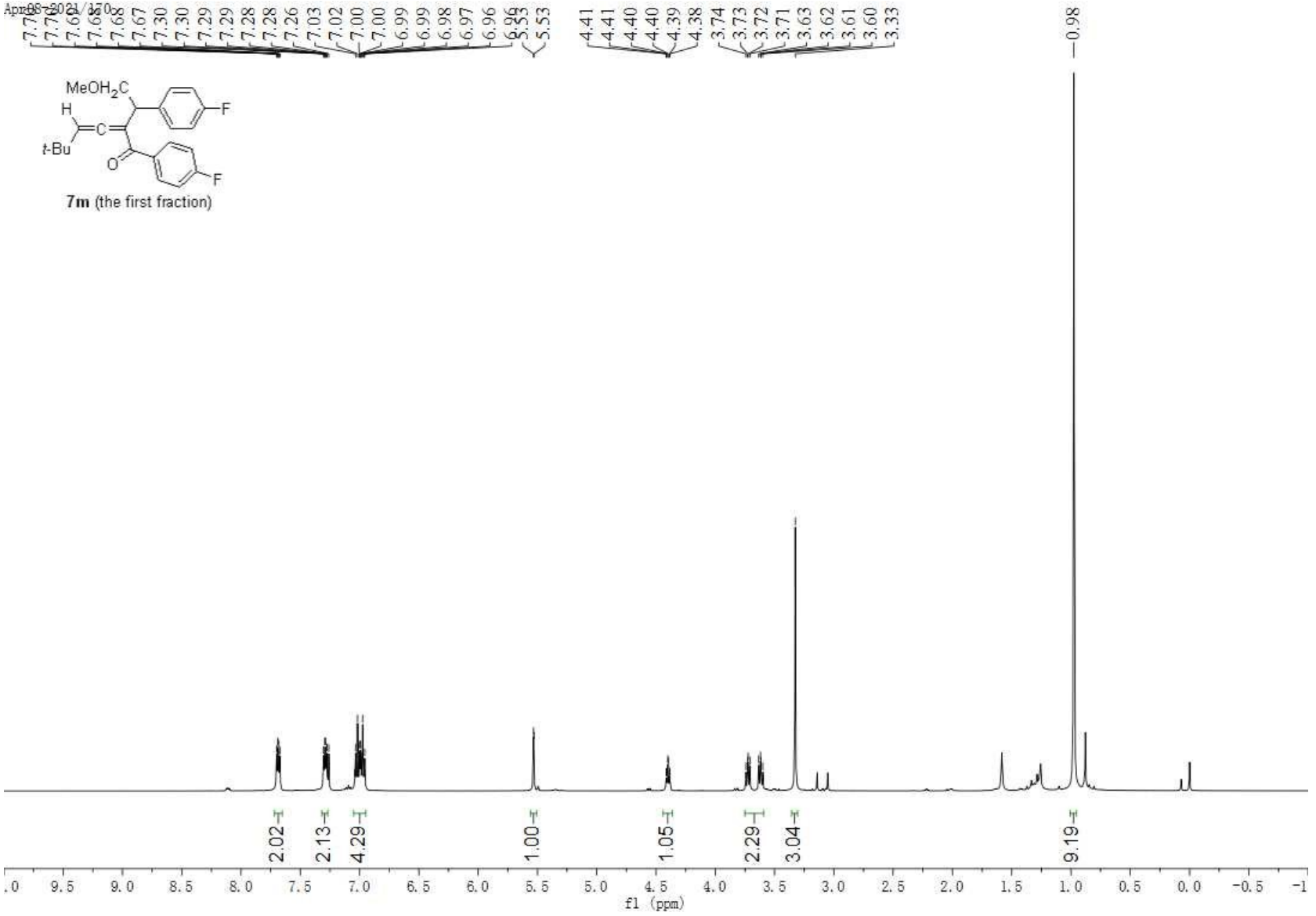

May-07-2021/491
210.4
197.1
140.9
128.2
126.6
112.8
108.8
77.3
77.0
76.7
74.8
58.6
41.8
33.3
29.8
27.0
MeOH2C
H
Ph
t-Bu
Me
O
7k (the second fraction)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

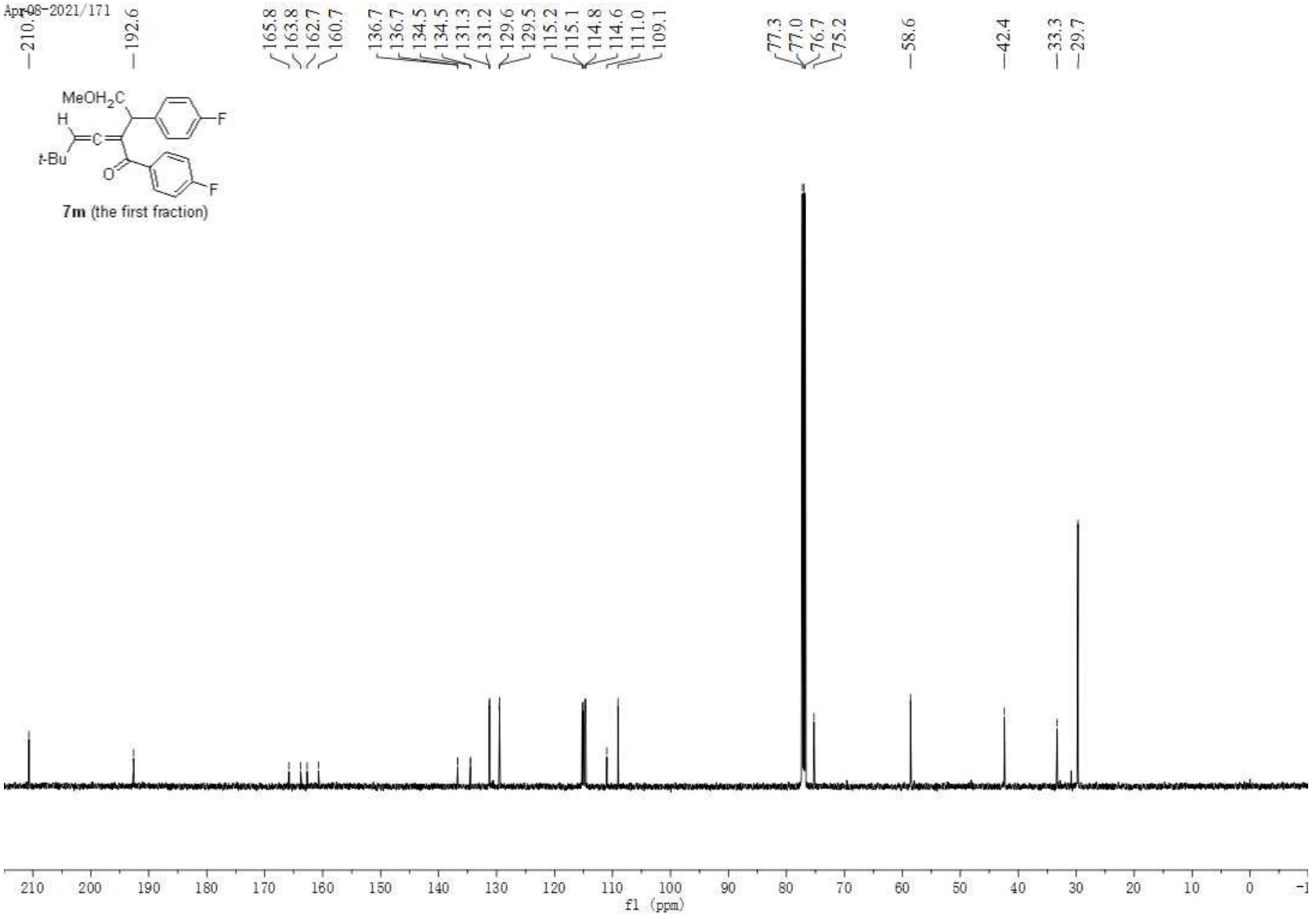

Apr02-2021/150
7.61
7.60
7.60
7.59
7.59
7.58
7.33
7.33
7.33
7.32
7.31
7.31
7.26
7.26
5.55
5.55
4.40
4.39
4.38
4.38
4.37
4.37
3.74
3.72
3.72
3.70
3.63
3.62
3.61
3.60
3.32
0.98
MeOH2C
H
t-Bu
Cl
Cl
O
7l (the first fraction)
1.98
2.06
4.00
1.03
1.08
2.20
3.04
9.20
f1 (ppm)


Apr-02-2021/170
210.0
192.8
139.5
137.9
136.6
132.5
130.2
129.4
128.5
127.9
110.8
109.3
77.3
77.0
76.7
75.0
58.6
42.5
33.4
29.7
MeOH2C
H
t-Bu
O
Cl
Cl
7l (the first fraction)
f1 (ppm)

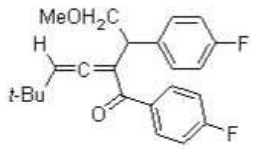

Mar23-2021/160
7.65
7.64
7.64
7.63
7.63
7.62
7.35
7.34
7.34
7.33
7.32
7.32
7.27
7.26
5.51
5.51
4.41
4.41
4.40
4.39
4.38
4.38
3.72
3.70
3.70
3.69
3.68
3.68
3.67
3.66
3.33
0.82
MeOH2C
H
t-Bu
O
Cl
Cl
7l (the second fraction)
1.99
1.92
3.81
1.00
1.04
2.16
3.09
9.39
f1 (ppm)


Mar-23-2021/161
211.6
192.8
139.3
137.9
136.8
132.5
130.2
129.7
128.4
127.9
111.1
109.2
77.3
77.0
76.7
74.5
58.8
42.7
33.2
29.6
MeOH2C
H
t-Bu
O
Cl
Cl
7l (the second fraction)
f1 (ppm)

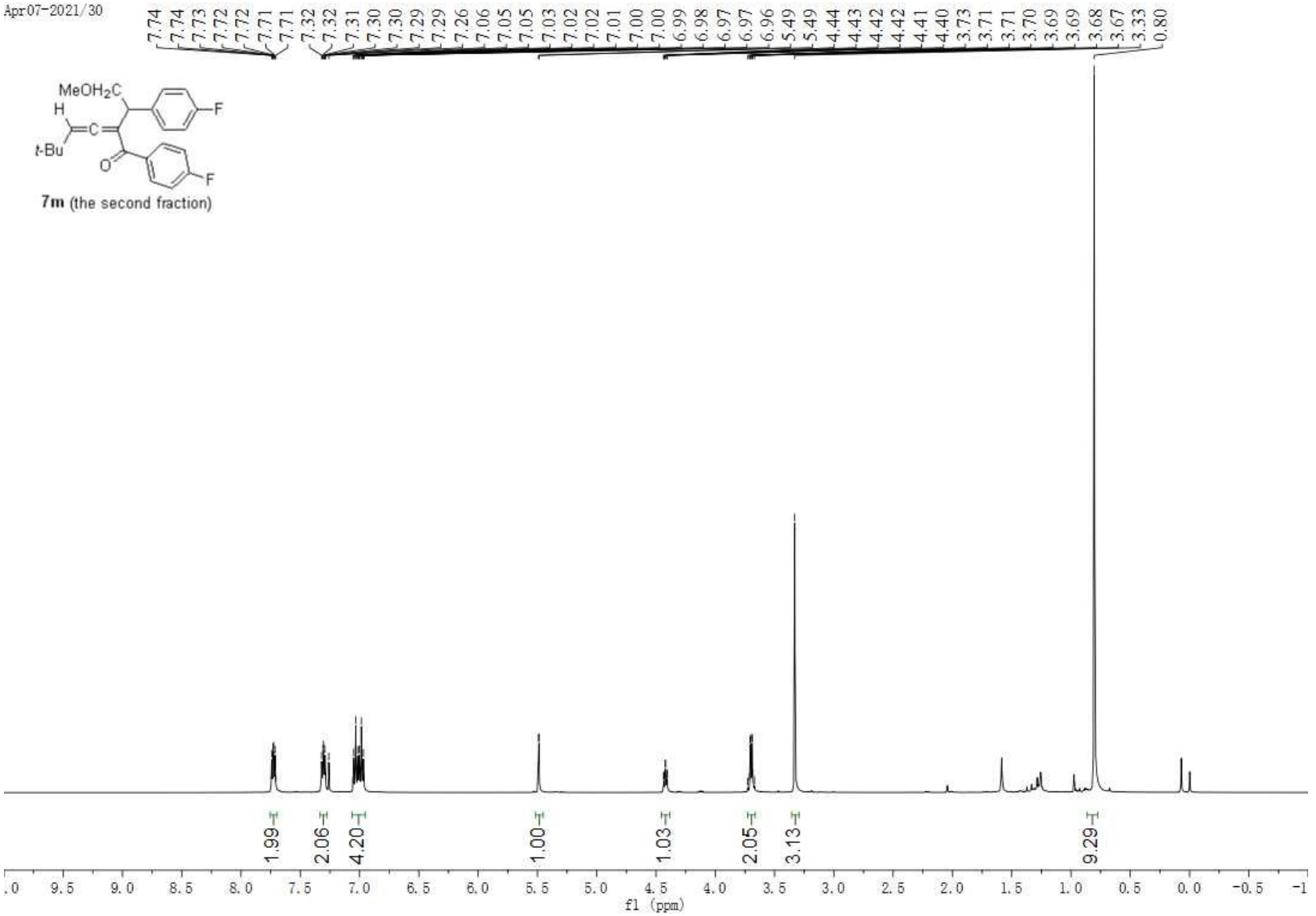

MeOH2C
H
t-Bu
O
F
F
7m (the first fraction)
7.77 7.76 7.68 7.68 7.67 7.30 7.30 7.29 7.29 7.28 7.28 7.26 7.03 7.02 7.00 7.00 6.99 6.99 6.98 6.97 6.96 6.96 5.53 5.53
4.41 4.41 4.40 4.40 4.39 4.38
3.74 3.73 3.72 3.71 3.63 3.62 3.61 3.60 3.33
0.98
2.02 2.13 4.29 1.00 1.05 2.29 3.04 9.19
f1 (ppm)

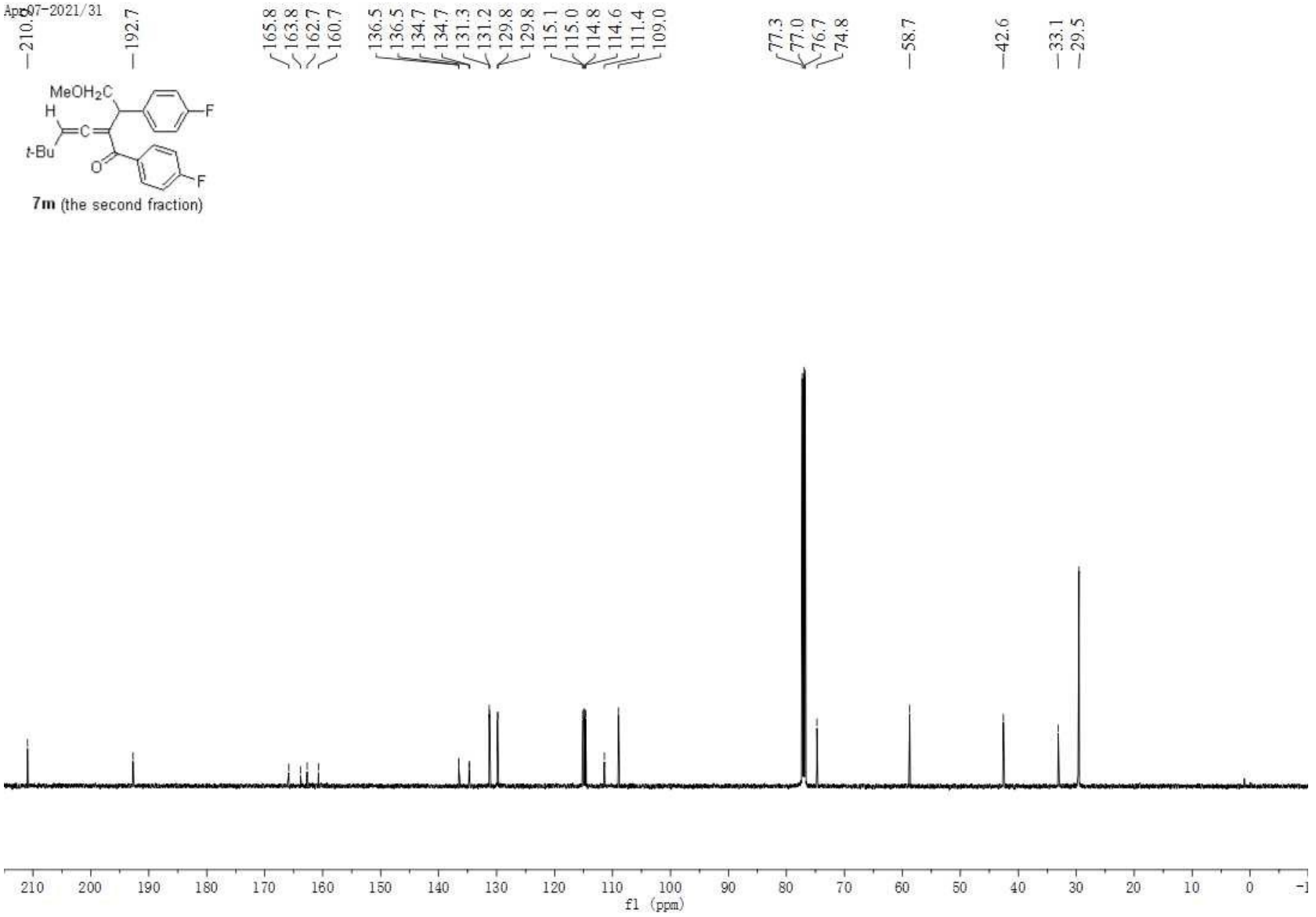

Apr-08-2021/171
210.4
192.6
165.8
163.8
162.7
160.7
136.7
136.7
134.5
134.5
131.3
131.2
129.6
129.5
115.2
115.1
114.8
114.6
111.0
109.1
77.3
77.0
76.7
75.2
58.6
42.4
33.3
29.7
MeOH2C
H
t-Bu
O
F
F
7m (the first fraction)
f1 (ppm)

Apr08-2021/172

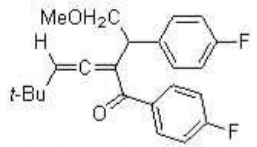


7m (the first fraction)

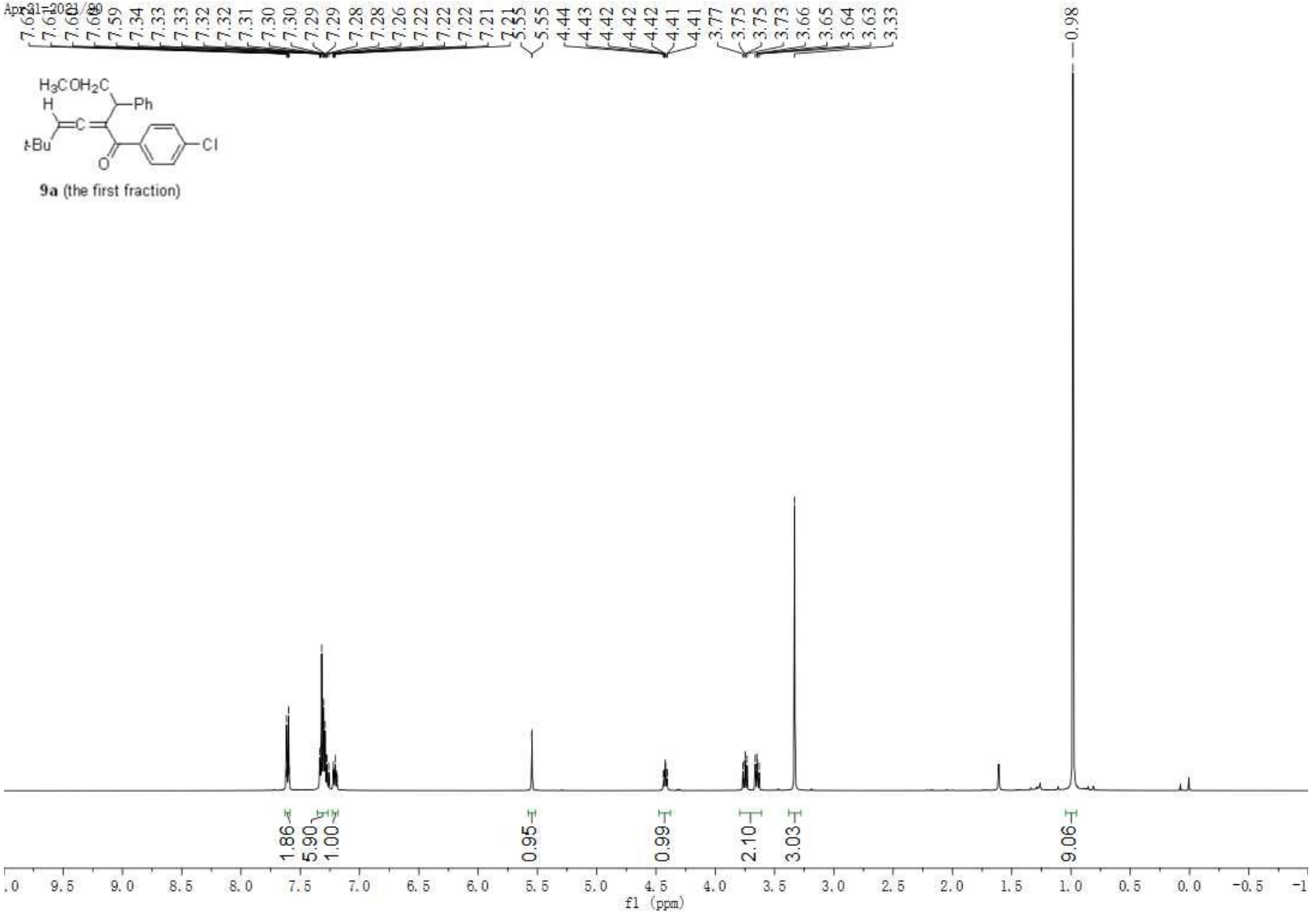

Apr07-2021/30
7.74 7.74 7.73 7.72 7.72 7.71 7.71 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.26 7.06 7.05 7.05 7.03 7.02 7.02 7.01 7.00 7.00 6.99 6.98 6.97 6.97 6.96 5.49 5.49 4.44 4.43 4.42 4.42 4.41 4.40 3.73 3.71 3.71 3.70 3.69 3.69 3.68 3.67 3.33 0.80
MeOH2C
H
C
t-Bu
O
F
F
7m (the second fraction)
1.99
2.06
4.20
1.00
1.03
2.05
3.13
9.29
f1 (ppm)

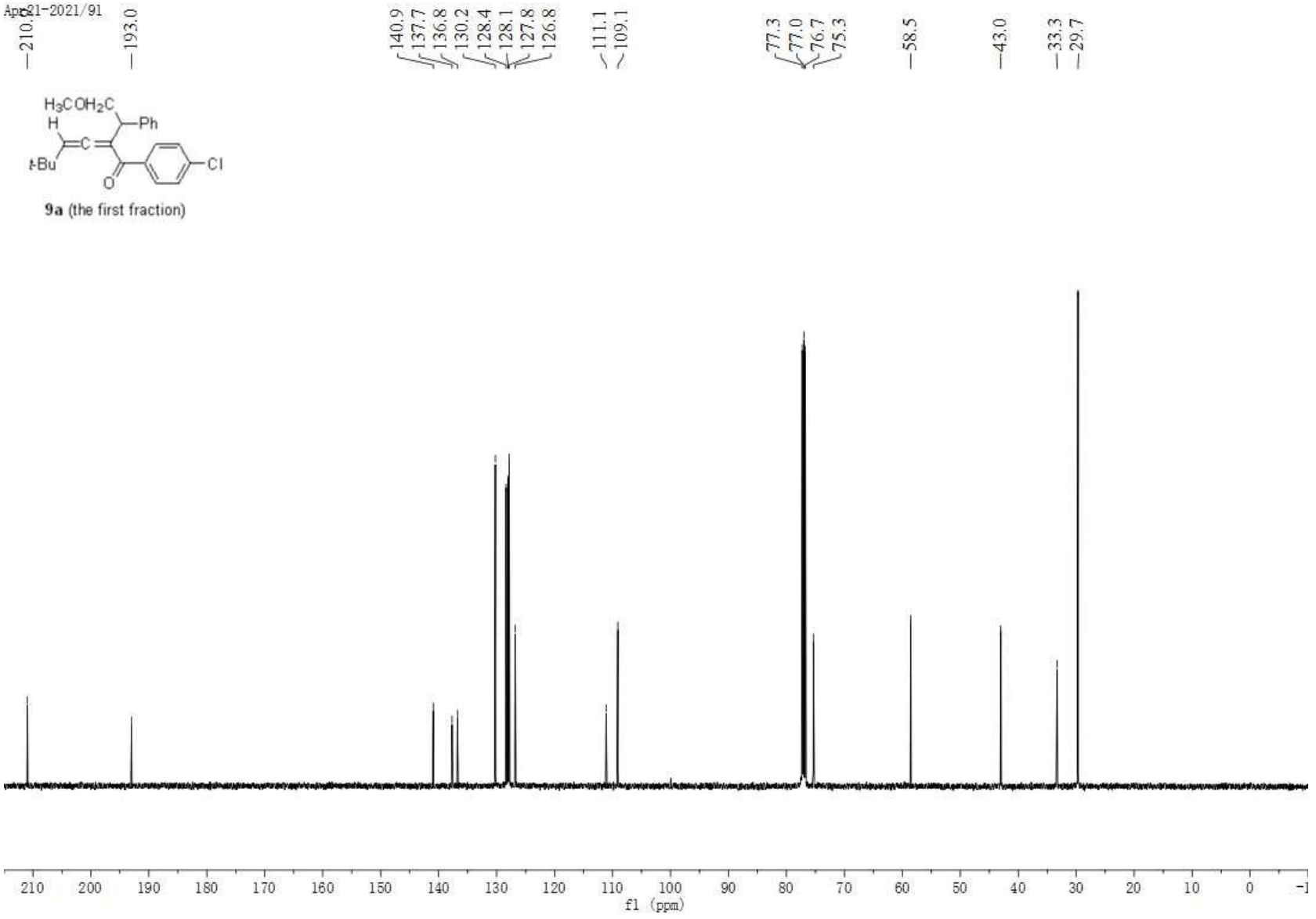

Apr-07-2021/31
210.5
192.7
165.8
163.8
162.7
160.7
136.5
136.5
134.7
134.7
131.3
131.2
129.8
129.8
115.1
115.0
114.8
114.6
111.4
109.0
77.3
77.0
76.7
74.8
58.7
42.6
33.1
29.5
MeOH2C
H
t-Bu
O
F
F
7m (the second fraction)
f1 (ppm)

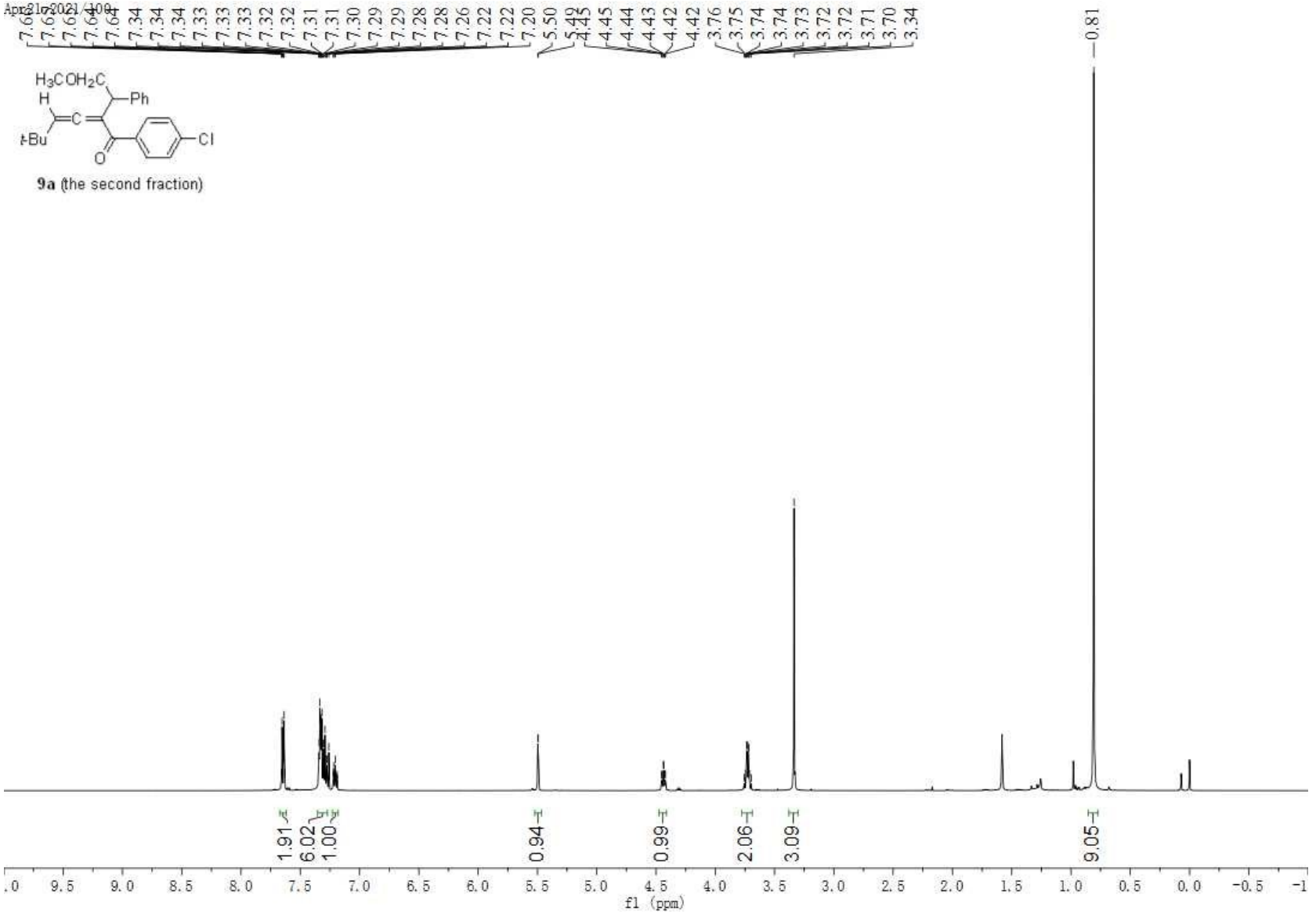
Apr07-2021/32

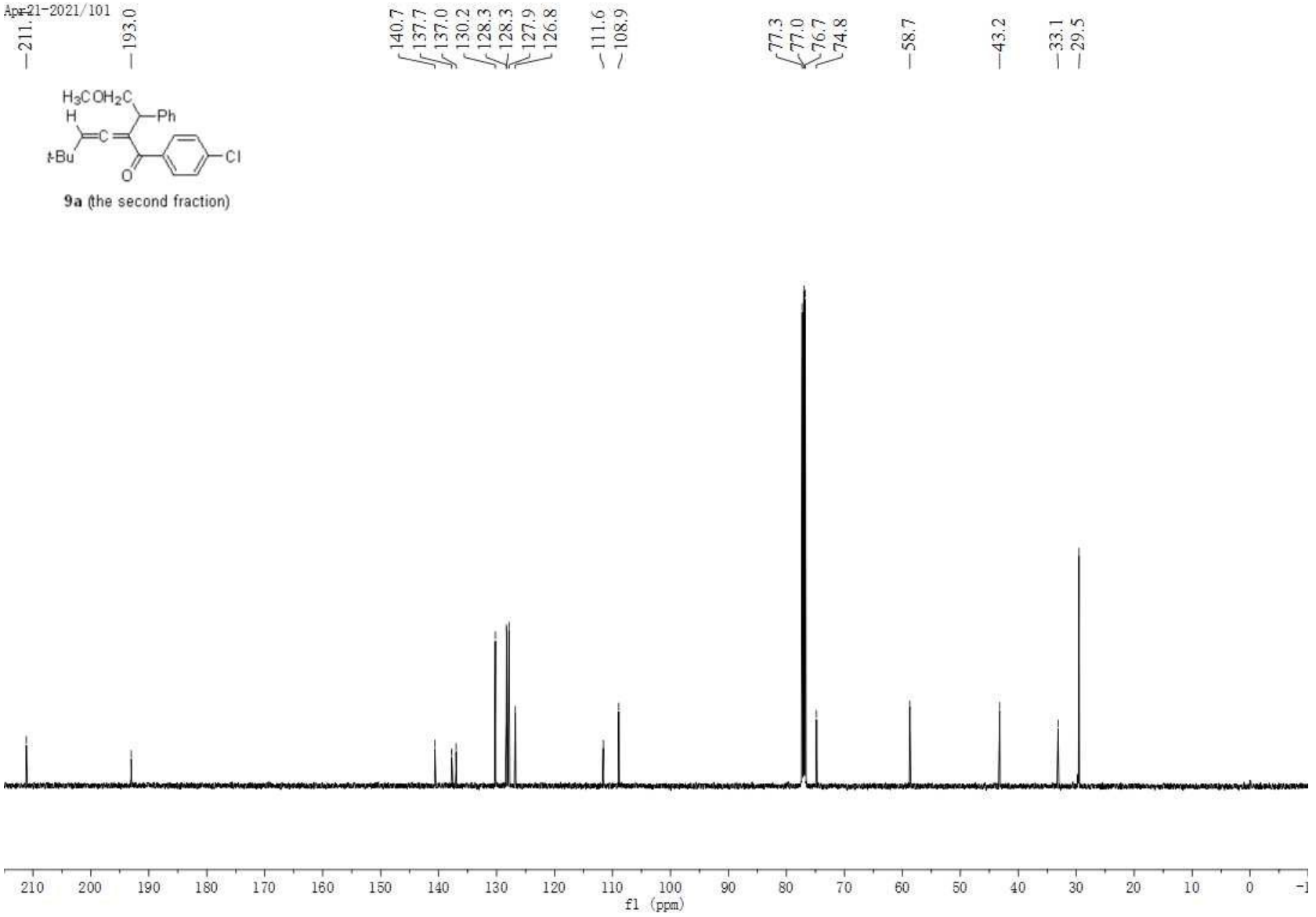


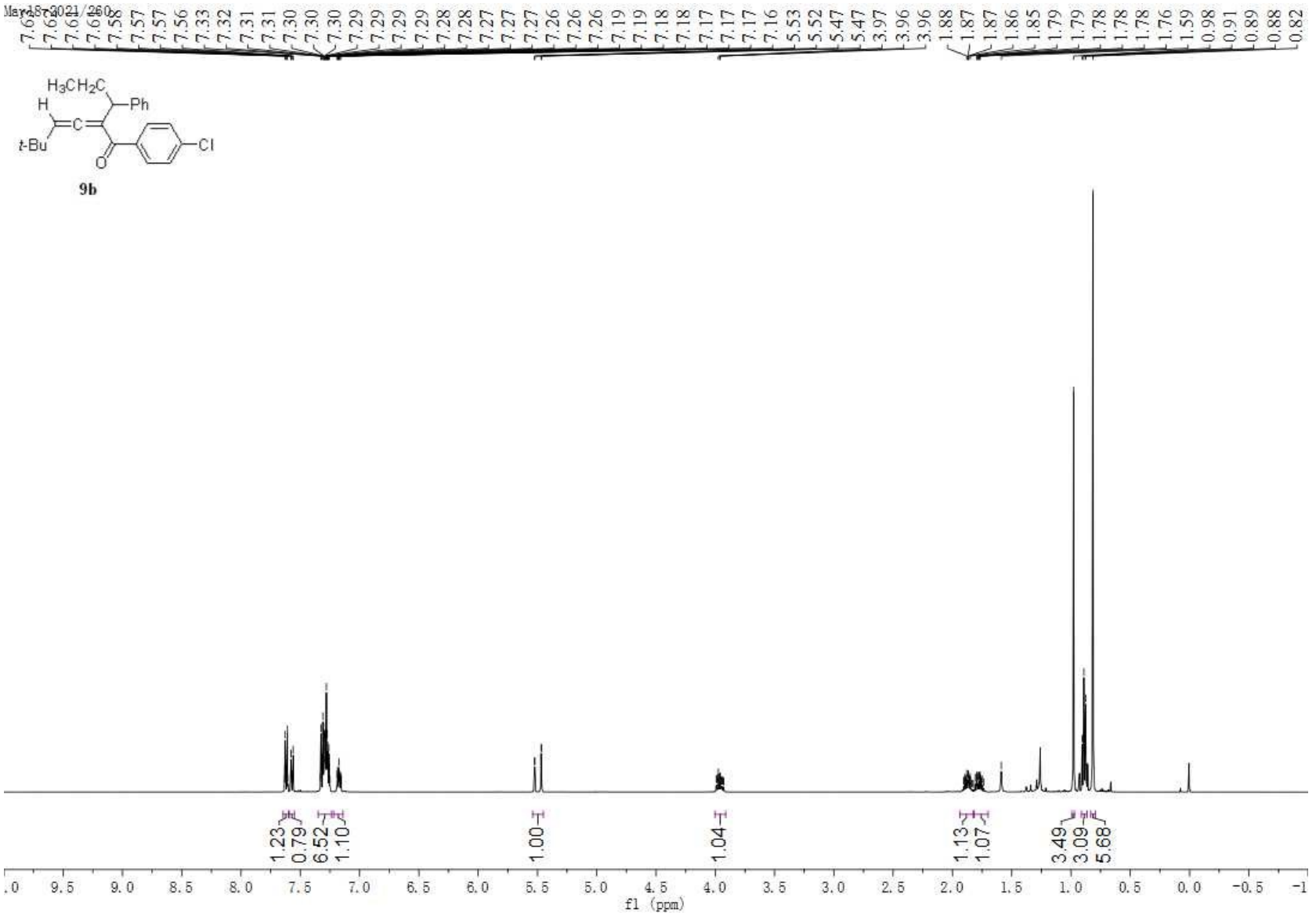
7m (the second fraction)

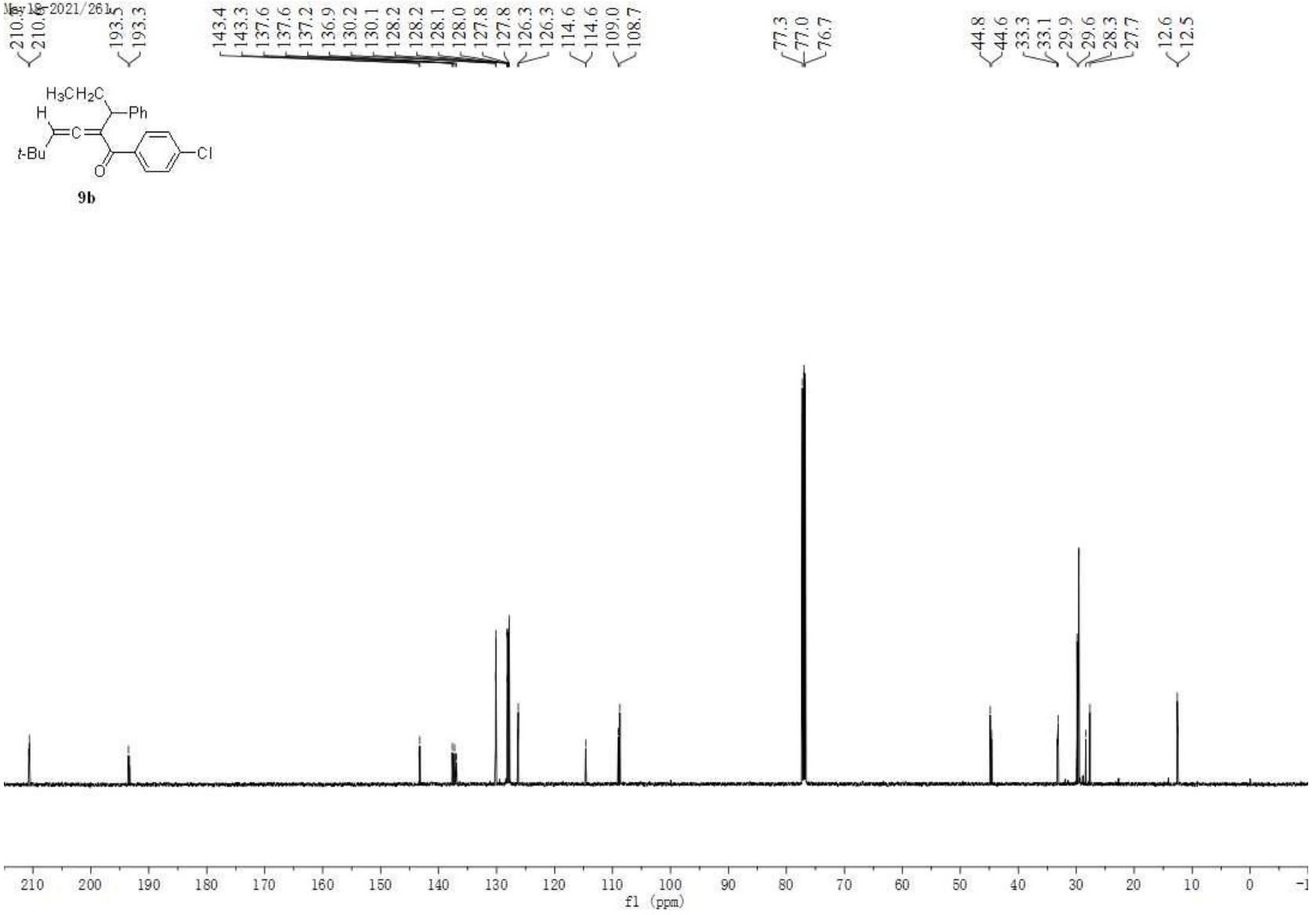

7.62 7.61 7.60 7.59 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.26 7.22 7.22 7.22 7.21 7.21 5.55 5.55 4.44 4.43 4.42 4.42 4.42 4.41 4.41 3.77 3.75 3.75 3.73 3.66 3.65 3.64 3.63 3.33 0.98
H3COH2C
H
Ph
t-Bu
Cl
O
9a (the first fraction)
1.86 5.90 1.00 0.95 0.99 2.10 3.03 9.06
f1 (ppm)

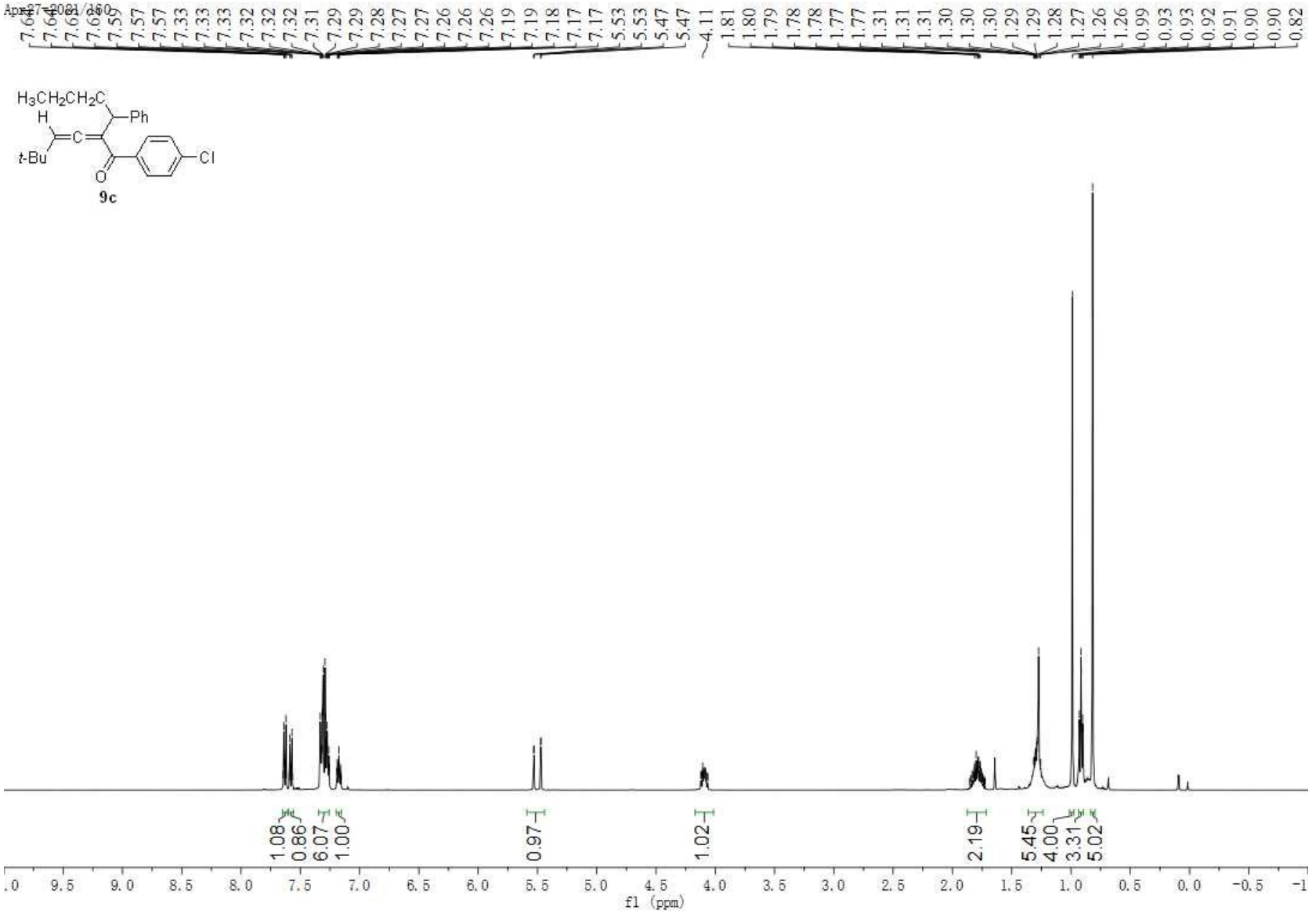

Apr-21-2021/91
210.0
193.0
140.9
137.7
136.8
130.2
128.4
128.1
127.8
126.8
111.1
109.1
77.3
77.0
76.7
75.3
58.5
43.0
33.3
29.7
H3COH2C
H
Ph
t-Bu
Cl
O
9a (the first fraction)
f1 (ppm)

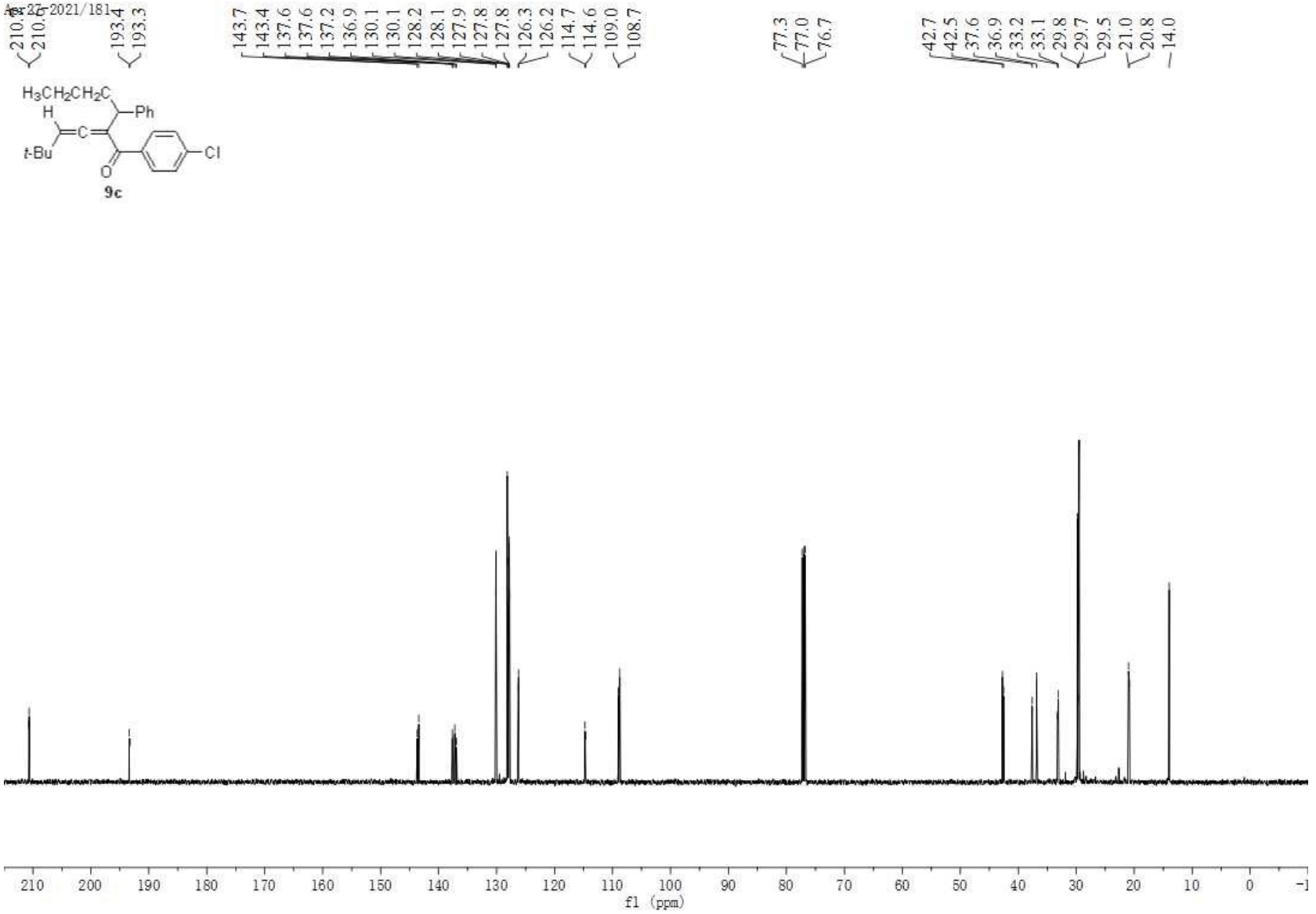

Apr 21 2021 109
7.65 7.64 7.64 7.64 7.64 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.28 7.26 7.22 7.22 7.20 5.50 5.49 4.45 4.45 4.44 4.43 4.42 4.42 3.76 3.75 3.74 3.74 3.73 3.72 3.72 3.71 3.70 3.34 0.81
H3COH2C
H
Ph
C
t-Bu
O
Cl
9a (the second fraction)
1.91 6.02 1.00 0.94 0.99 2.06 3.09 9.05
f1 (ppm)

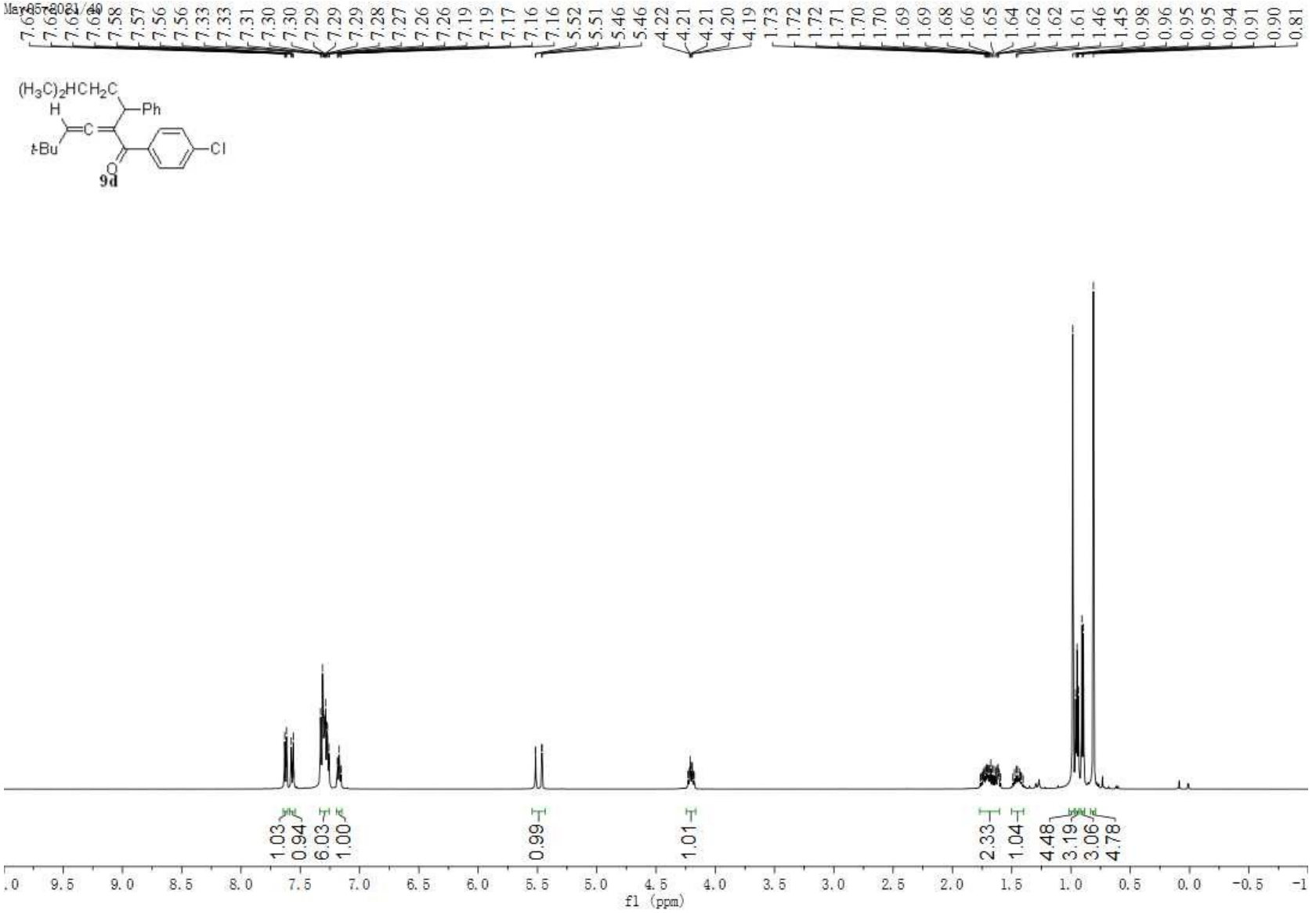

Apr-21-2021/101
211.1
193.0
140.7
137.7
137.0
130.2
128.3
128.3
127.9
126.8
111.6
108.9
77.3
77.0
76.7
74.8
58.7
43.2
33.1
29.5
H3COH2C
H
Ph
t-Bu
C
Cl
O
9a (the second fraction)
f1 (ppm)

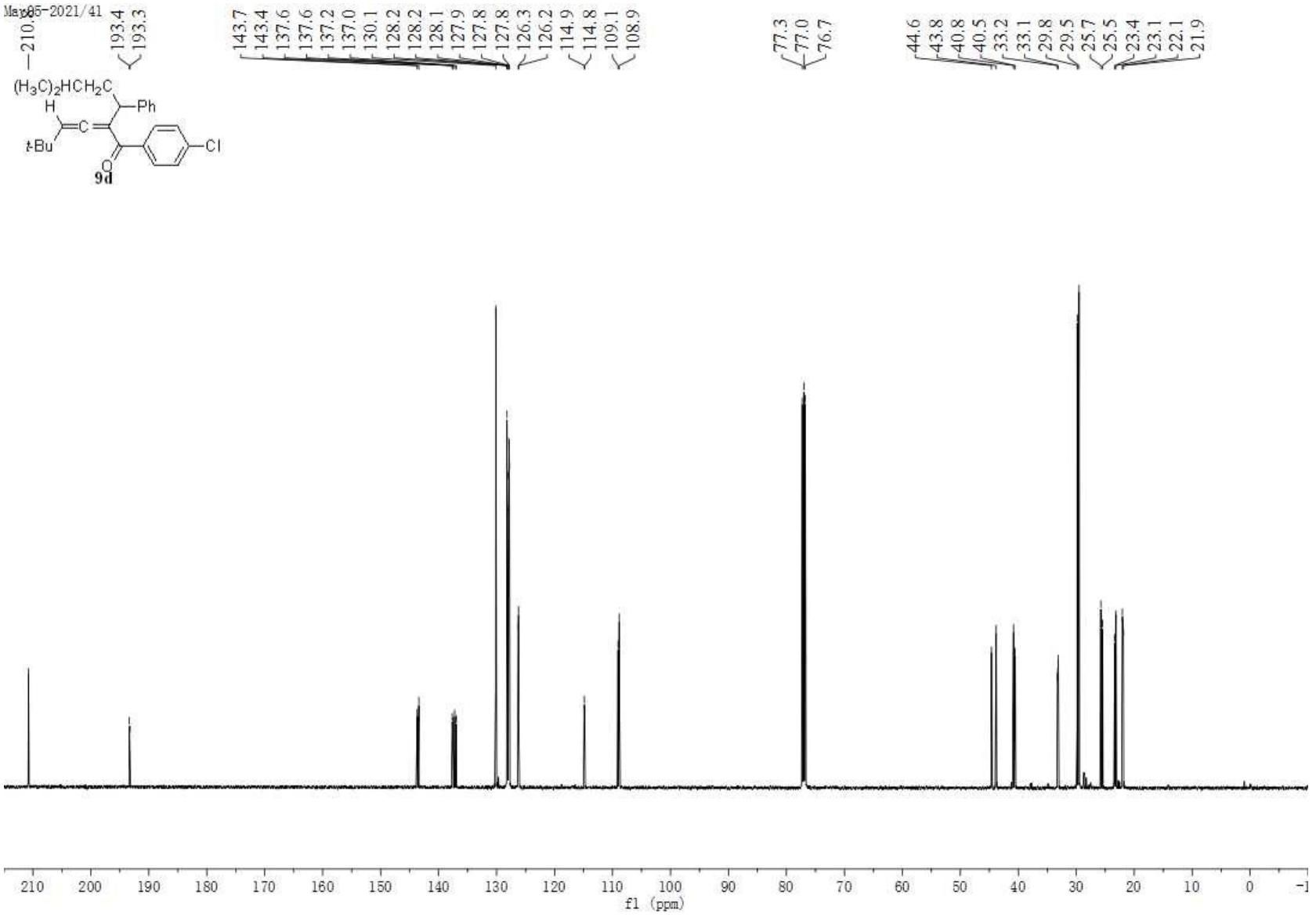

Mar 18 2021 /260
7.62 7.62 7.61 7.61 7.58 7.57 7.57 7.56 7.33 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.16 5.53 5.52 5.47 5.47 3.97 3.96 3.96 1.88 1.87 1.87 1.86 1.85 1.79 1.79 1.78 1.78 1.78 1.76 1.59 0.98 0.91 0.89 0.88 0.82
H3CH2C
Ph
H
C
t-Bu
Cl
O
9b
1.23
0.79
6.52
1.10
1.00
1.04
1.13
1.07
3.49
3.09
5.68
f1 (ppm)

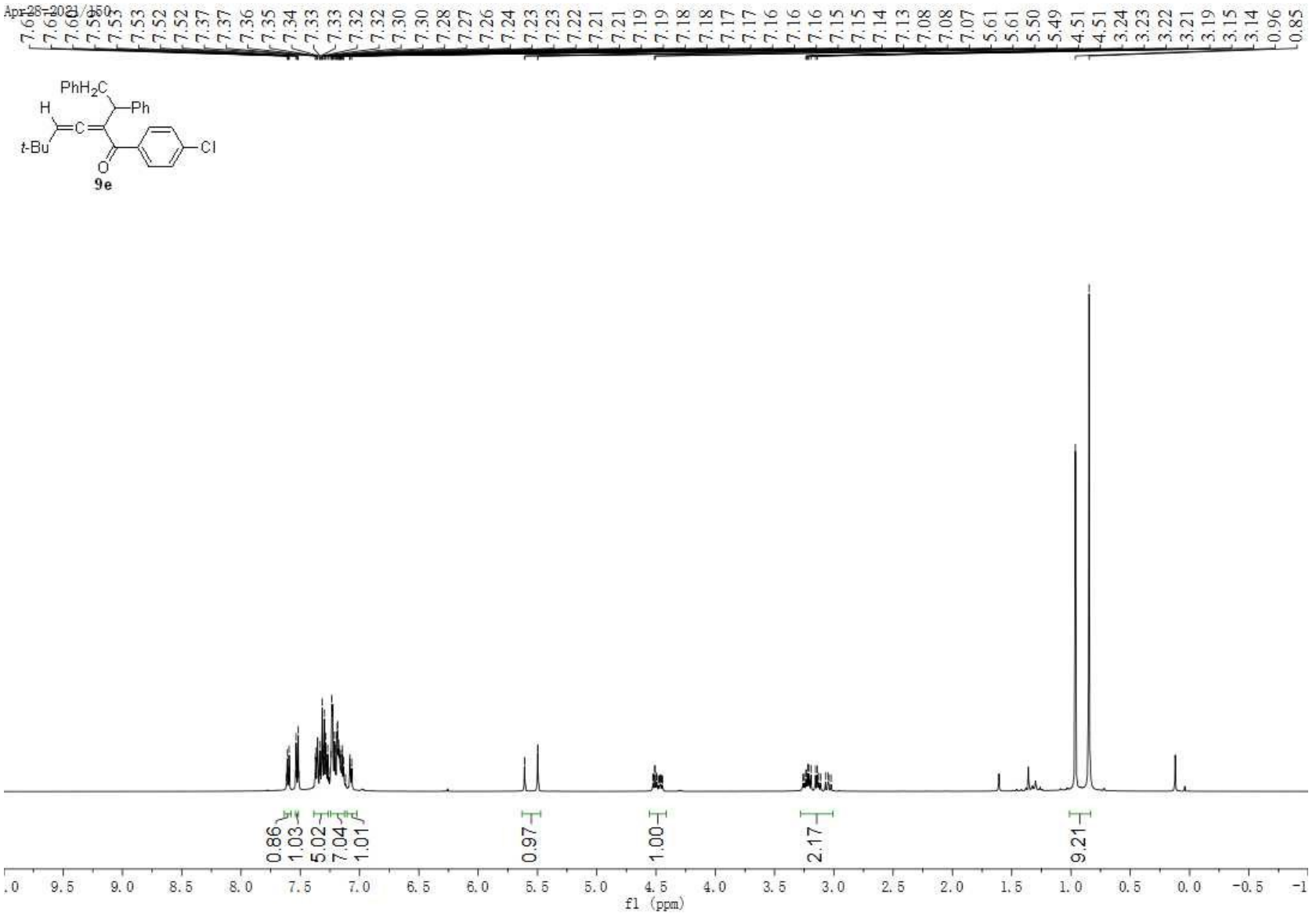

May 18 2021/26 1
210.5
210.4
193.5
193.3
143.4
143.3
137.6
137.6
137.2
136.9
130.2
130.1
128.2
128.2
128.1
128.0
127.8
127.8
126.3
126.3
114.6
114.6
109.0
108.7
77.3
77.0
76.7
44.8
44.6
33.3
33.1
29.9
29.6
28.3
27.7
12.6
12.5
H3CH2C
H
Ph
t-Bu
Cl
O
9b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

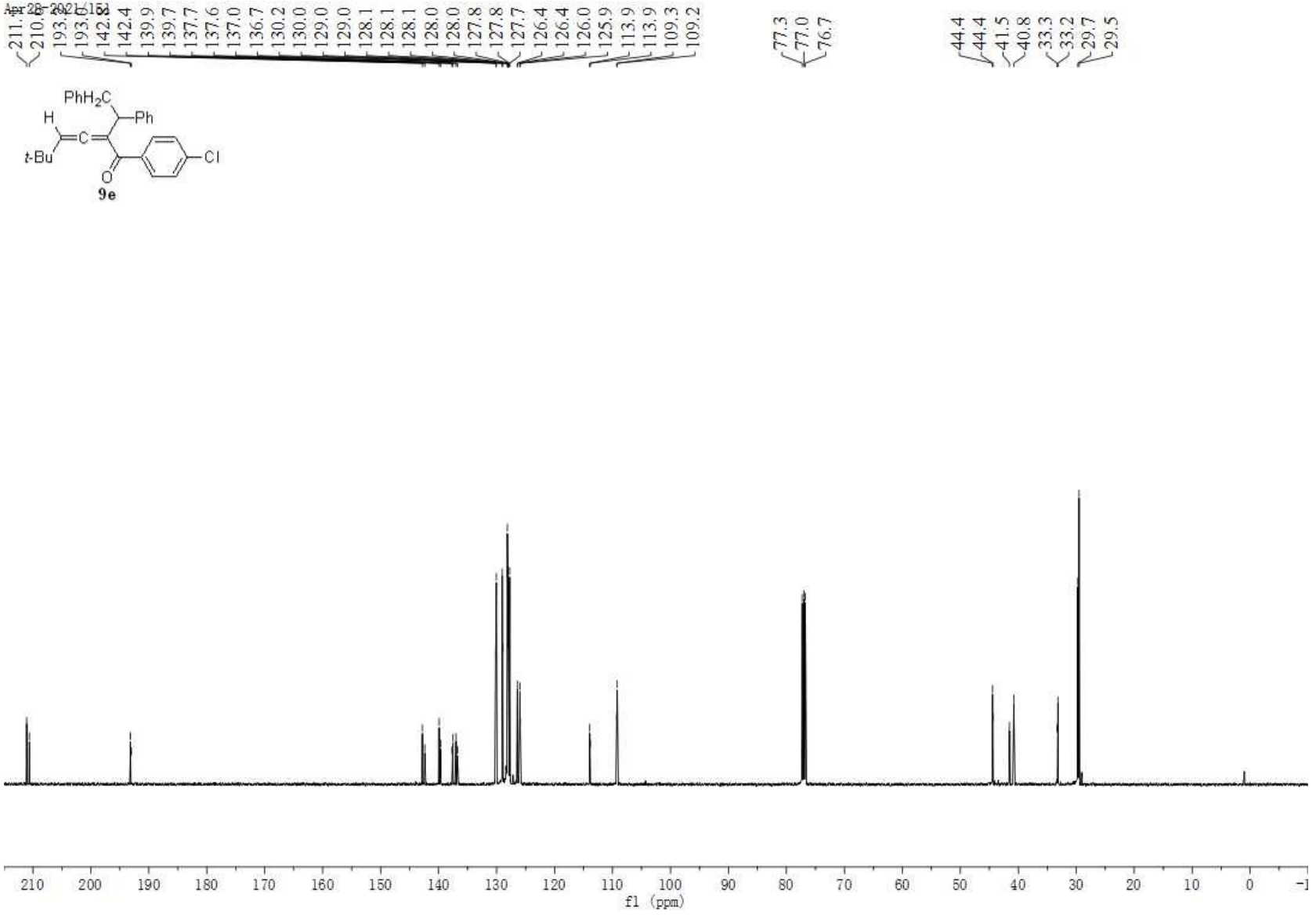

Apr-27-2021/160
7.64 7.64 7.62 7.62 7.59 7.57 7.57 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.26 7.19 7.19 7.18 7.17 7.17 5.53 5.53 5.47 5.47 4.11 1.81 1.80 1.79 1.78 1.78 1.77 1.77 1.31 1.31 1.31 1.30 1.30 1.30 1.29 1.29 1.28 1.27 1.26 1.26 0.99 0.93 0.93 0.92 0.91 0.90 0.90 0.82
H3CH2CH2C
H
Ph
t-Bu
Cl
O
9c
1.08
0.86
6.07
1.00
0.97
1.02
2.19
5.45
4.00
3.31
5.02
f1 (ppm)

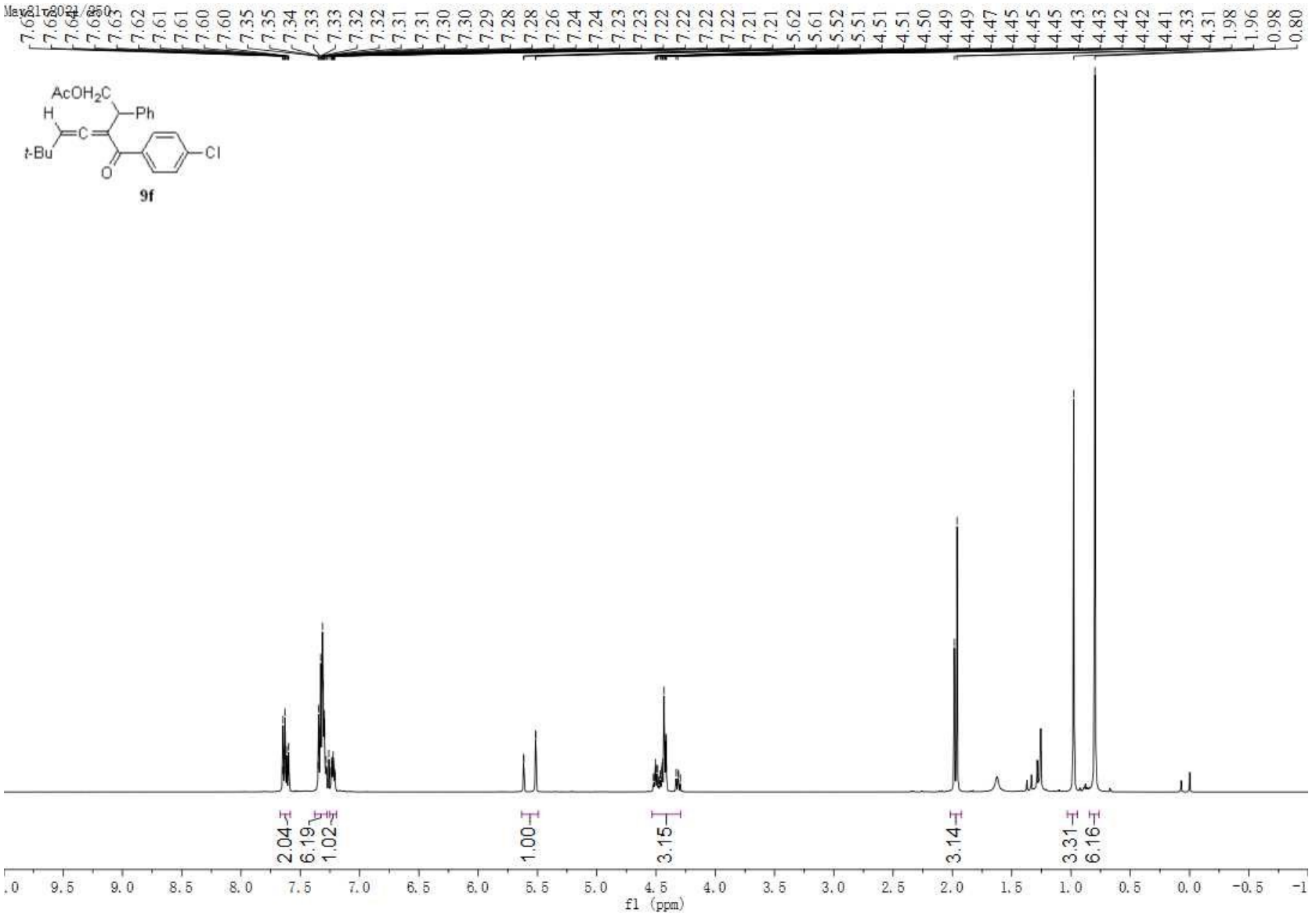

Apr 22 2021/181
210.8
210.6
193.4
193.3
143.7
143.4
137.6
137.6
137.2
136.9
130.1
130.1
128.2
128.1
127.9
127.8
127.8
126.3
126.2
114.7
114.6
109.0
108.7
77.3
77.0
76.7
42.7
42.5
37.6
36.9
33.2
33.1
29.8
29.7
29.5
21.0
20.8
14.0
H3CH2CH2C
H
Ph
t-Bu
Cl
O
9c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

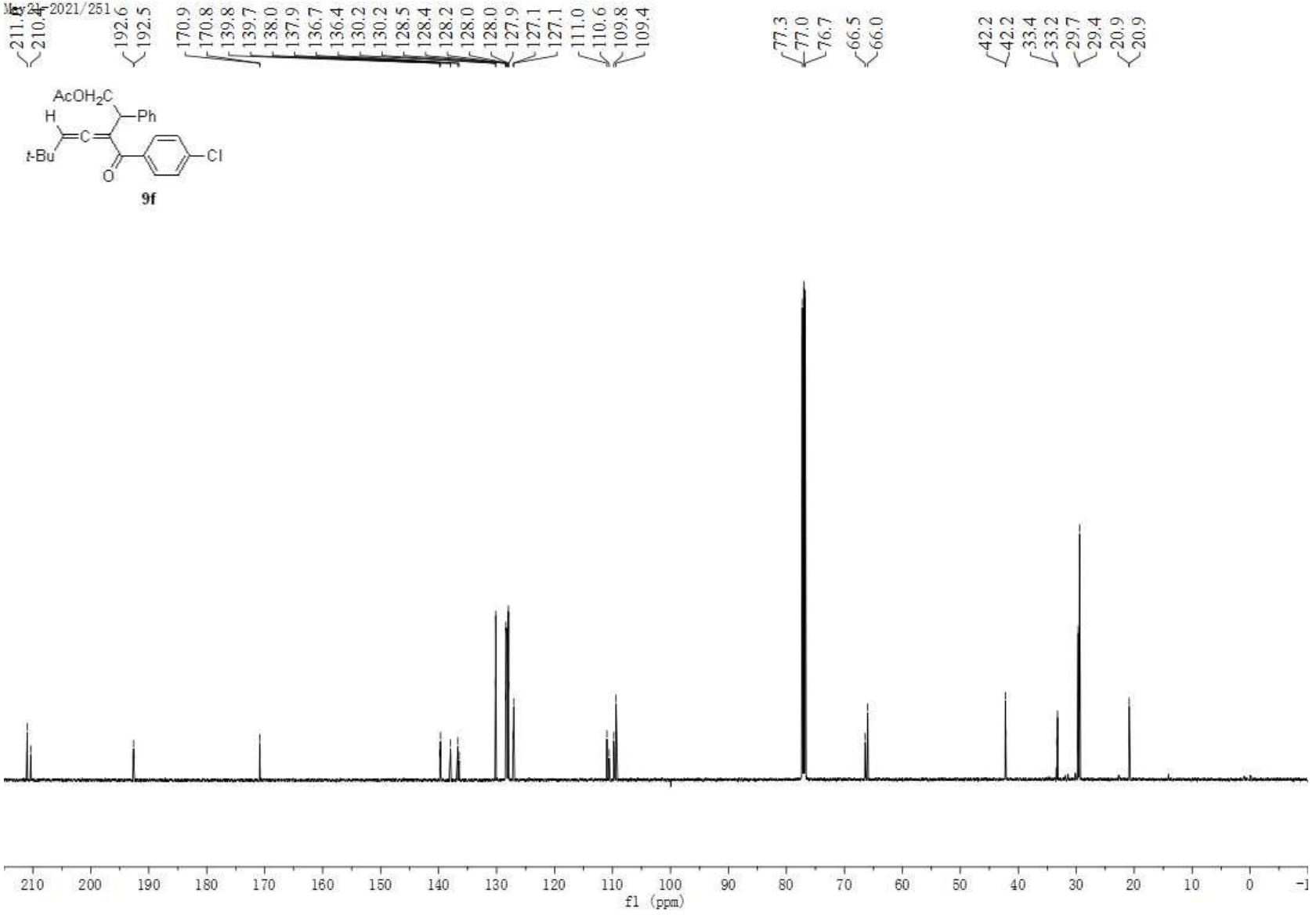

7.62 7.62 7.61 7.61 7.58 7.57 7.56 7.56 7.33 7.33 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.27 7.26 7.26 7.19 7.19 7.17 7.16 7.16 5.52 5.51 5.46 5.46 4.22 4.21 4.21 4.20 4.19 1.73 1.72 1.72 1.71 1.70 1.70 1.69 1.69 1.68 1.66 1.65 1.64 1.62 1.62 1.61 1.46 1.45 0.98 0.96 0.95 0.95 0.94 0.91 0.90 0.81
(H3C)2HCH2C
H
Ph
t-Bu
Cl
O
9d
1.03 0.94 6.03 1.00 0.99 1.01 2.33 1.04 4.48 3.19 3.06 4.78
f1 (ppm)

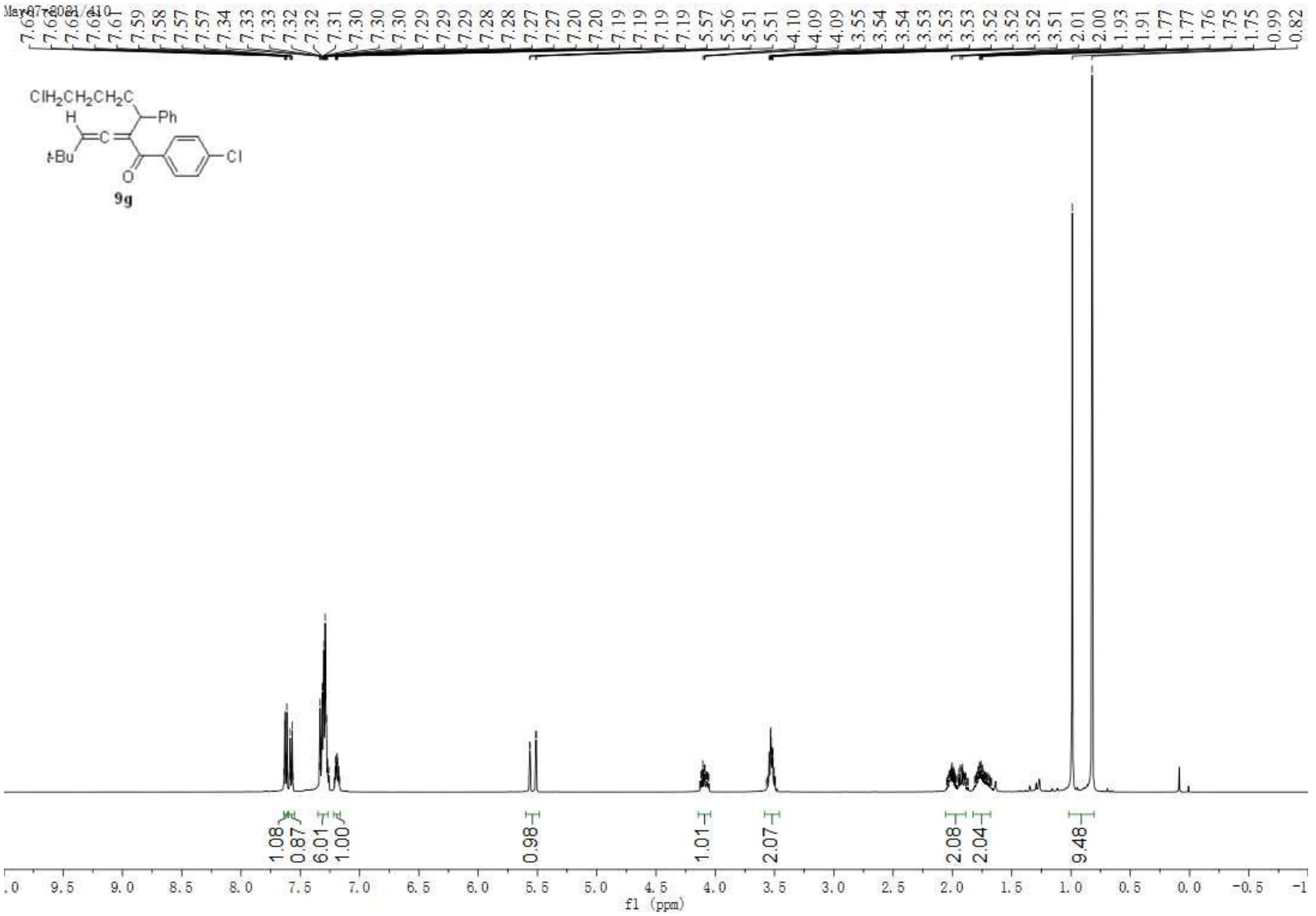

May05-2021/41
210.0
193.4
193.3
143.7
143.4
137.6
137.6
137.2
137.0
130.1
128.2
128.2
128.1
127.9
127.8
127.8
126.3
126.2
114.9
114.8
109.1
108.9
77.3
77.0
76.7
44.6
43.8
40.8
40.5
33.2
33.1
29.8
29.5
25.7
25.5
23.4
23.1
22.1
21.9
(H3C)2HCH2C
H
Ph
C
t-Bu
Cl
O
9d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

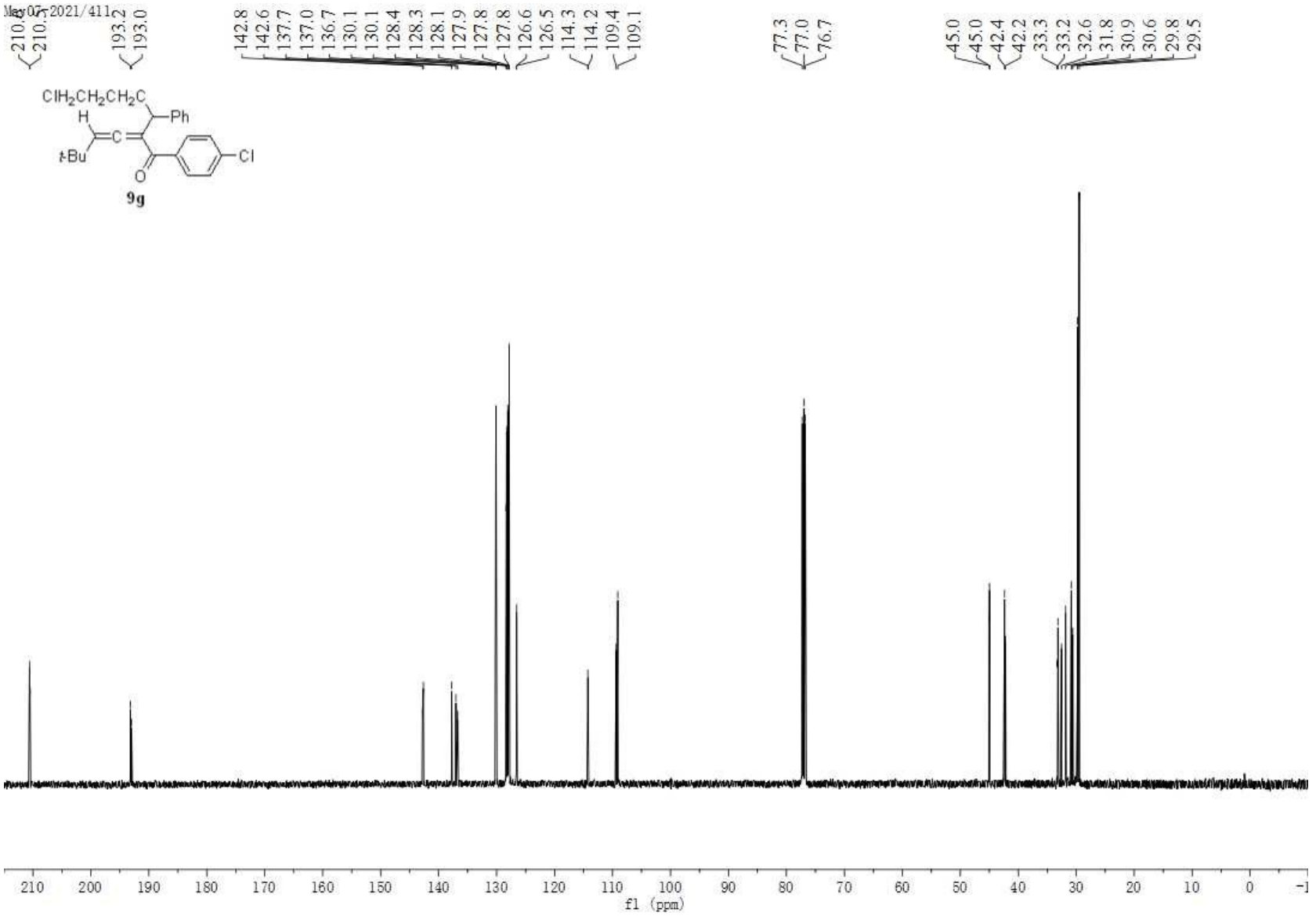

Apr-28-2021/150
7.61 7.61 7.60 7.59 7.53 7.53 7.52 7.52 7.37 7.37 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.30 7.30 7.28 7.27 7.26 7.24 7.23 7.23 7.22 7.21 7.21 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.16 7.15 7.15 7.14 7.13 7.08 7.08 7.07 5.61 5.61 5.50 5.49 4.51 4.51 3.24 3.23 3.22 3.21 3.19 3.15 3.14 0.96 0.85
PhH2C
H
Ph
t-Bu
Cl
O
9e
0.86
1.03
5.02
7.04
1.01
0.97
1.00
2.17
9.21
f1 (ppm)

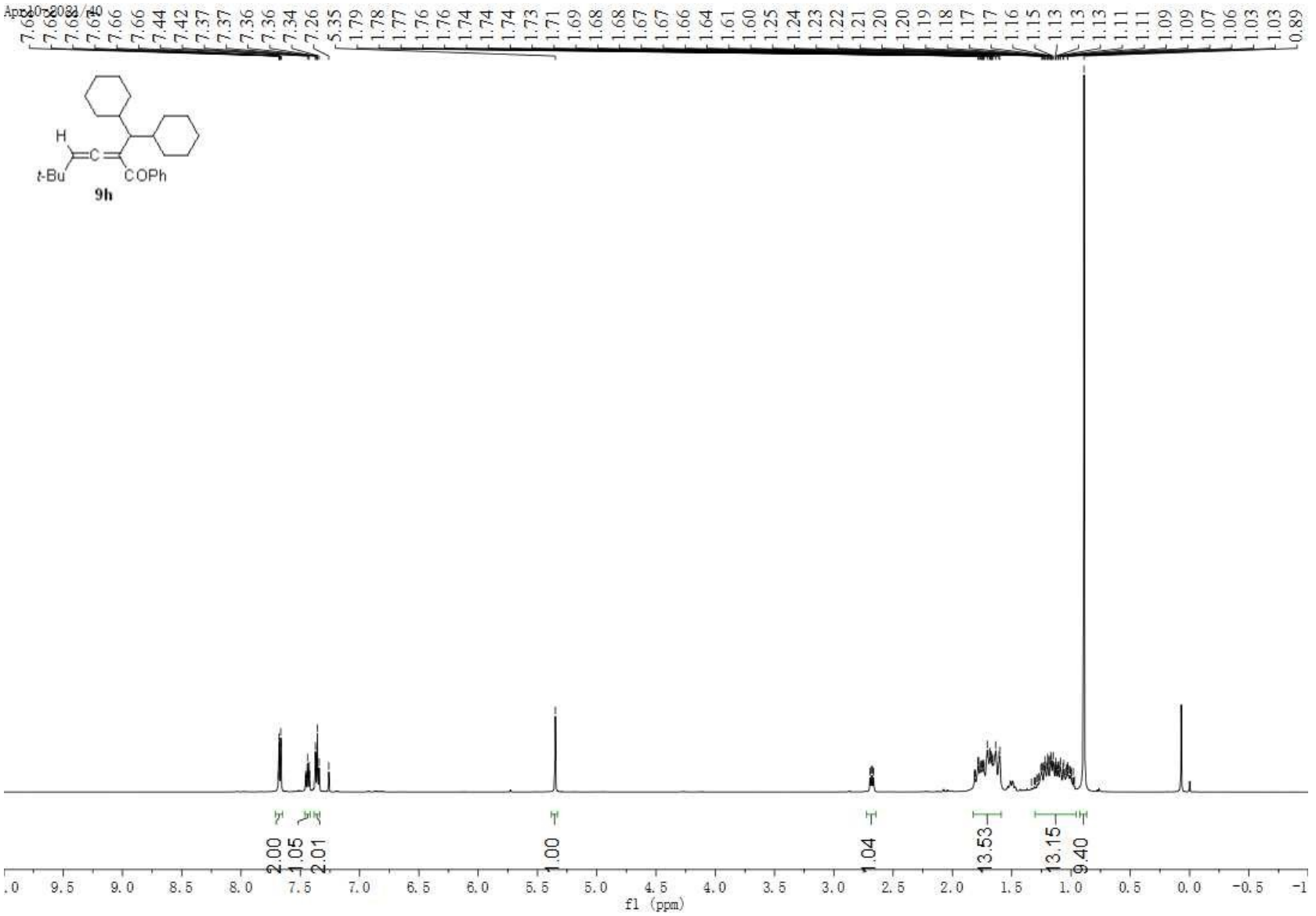

211.1
210.6
193.4
193.0
142.8
142.4
139.9
139.7
137.7
137.6
137.0
136.7
130.2
130.0
129.0
129.0
128.1
128.1
128.1
128.0
128.0
127.8
127.8
127.7
126.4
126.4
126.0
125.9
113.9
113.9
109.3
109.2
77.3
77.0
76.7
44.4
44.4
41.5
40.8
33.3
33.2
29.7
29.5
PhH2C
Ph
H
C
t-Bu
O
Cl
9e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

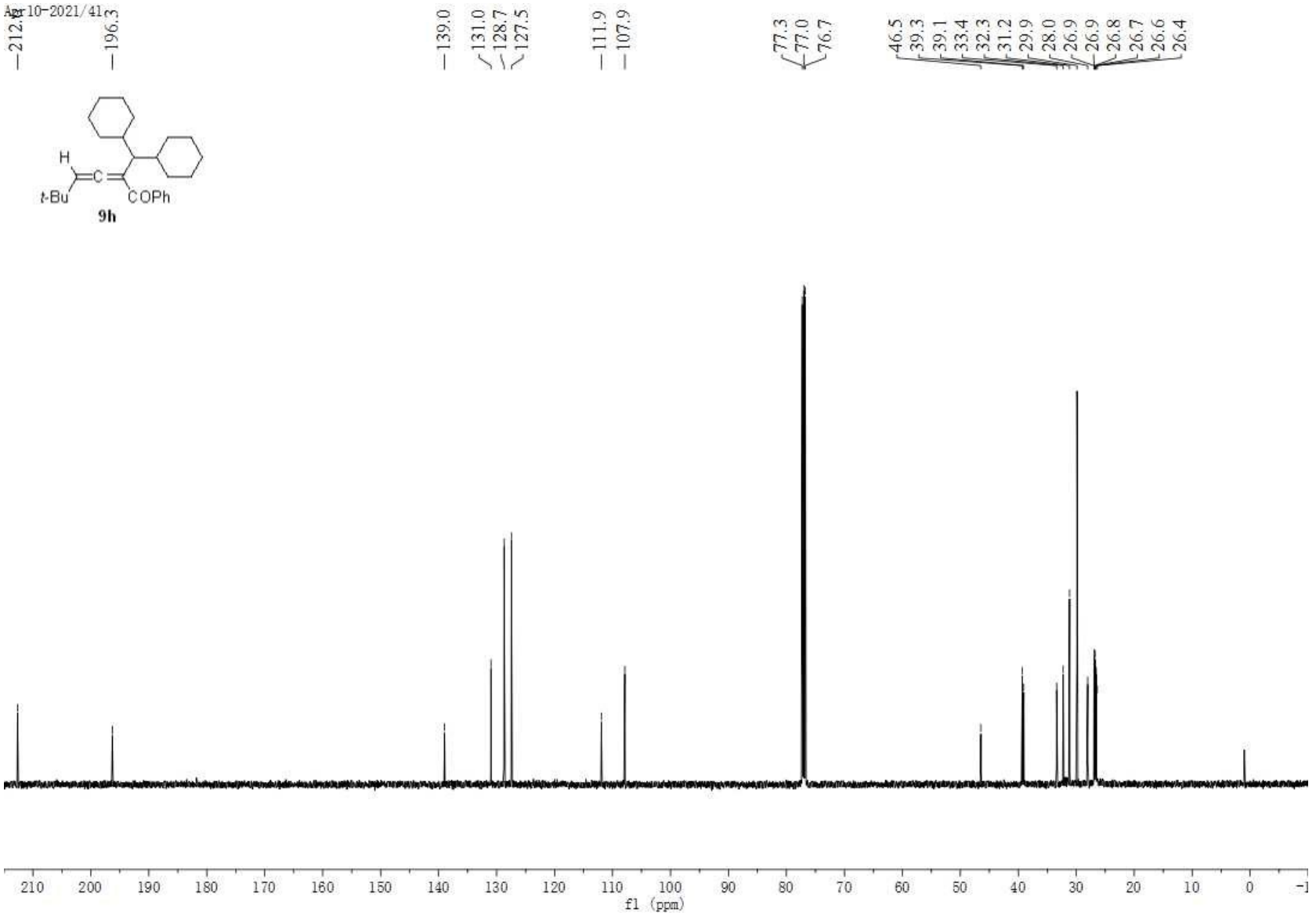

AcOH2C
H
Ph
t-Bu
C
O
Cl
9f
2.04
6.19
1.02
1.00
3.15
3.14
3.31
6.16
f1 (ppm)

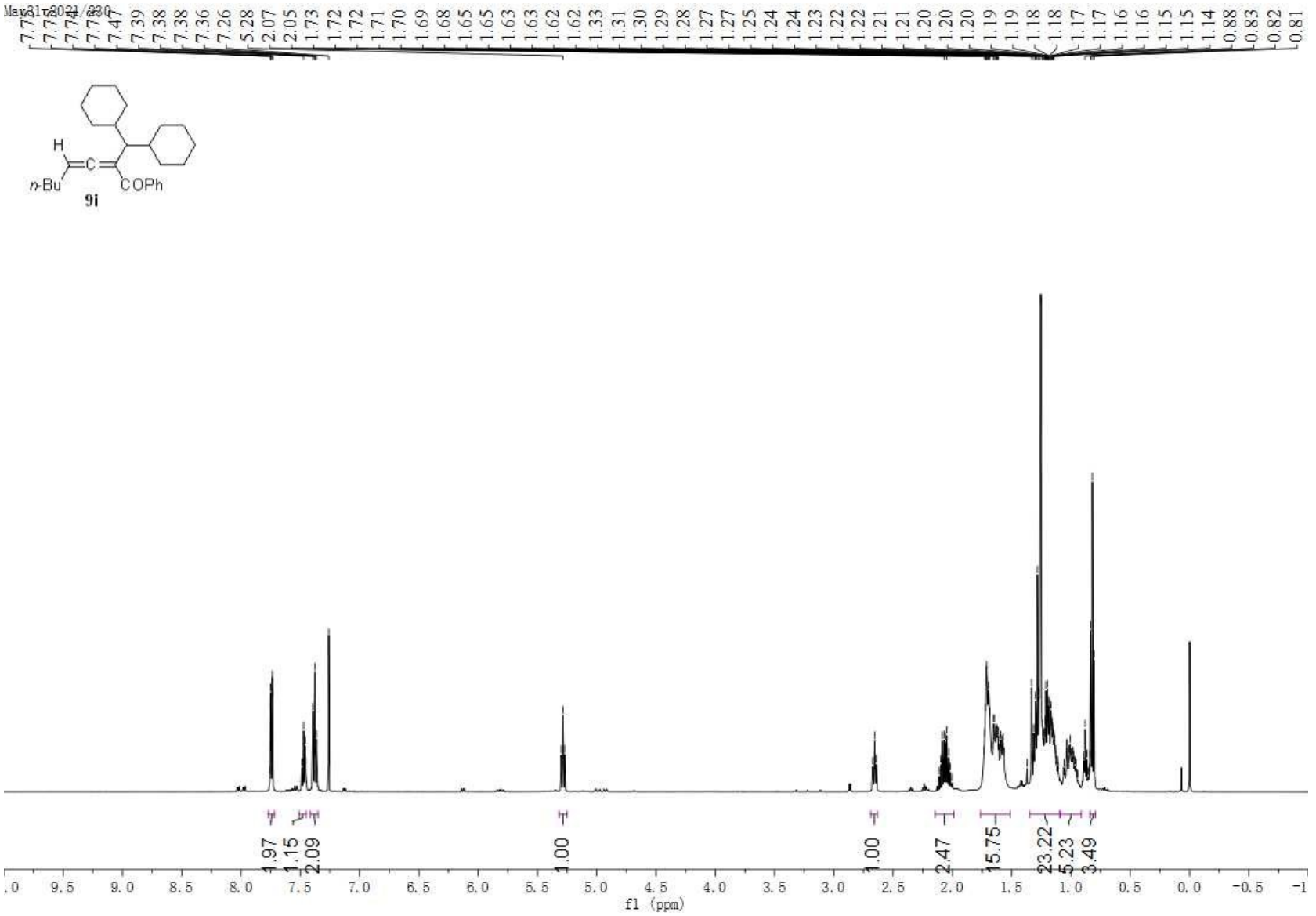

May 21 2021/251
211.8
210.4
192.6
192.5
170.9
170.8
139.8
139.7
138.0
137.9
136.7
136.4
130.2
130.2
128.5
128.4
128.2
128.0
128.0
127.9
127.1
127.1
111.0
110.6
109.8
109.4
77.3
77.0
76.7
66.5
66.0
42.2
42.2
33.4
33.2
29.7
29.4
20.9
20.9
AcOH2C
H
Ph
t-Bu
Cl
O
9f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

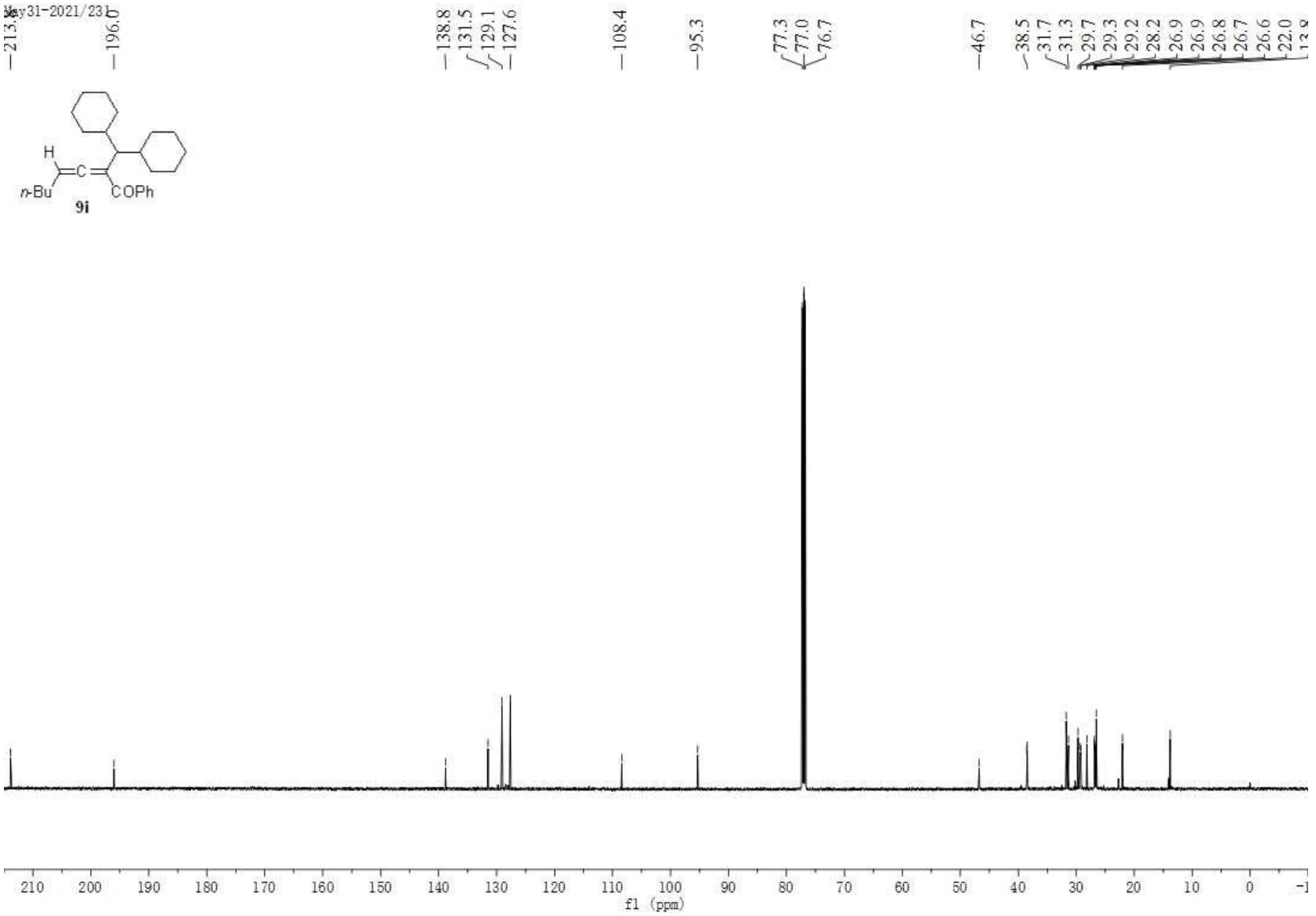

ClH2CH2CH2C
H
Ph
t-Bu
Cl
O
9g
fl (ppm)

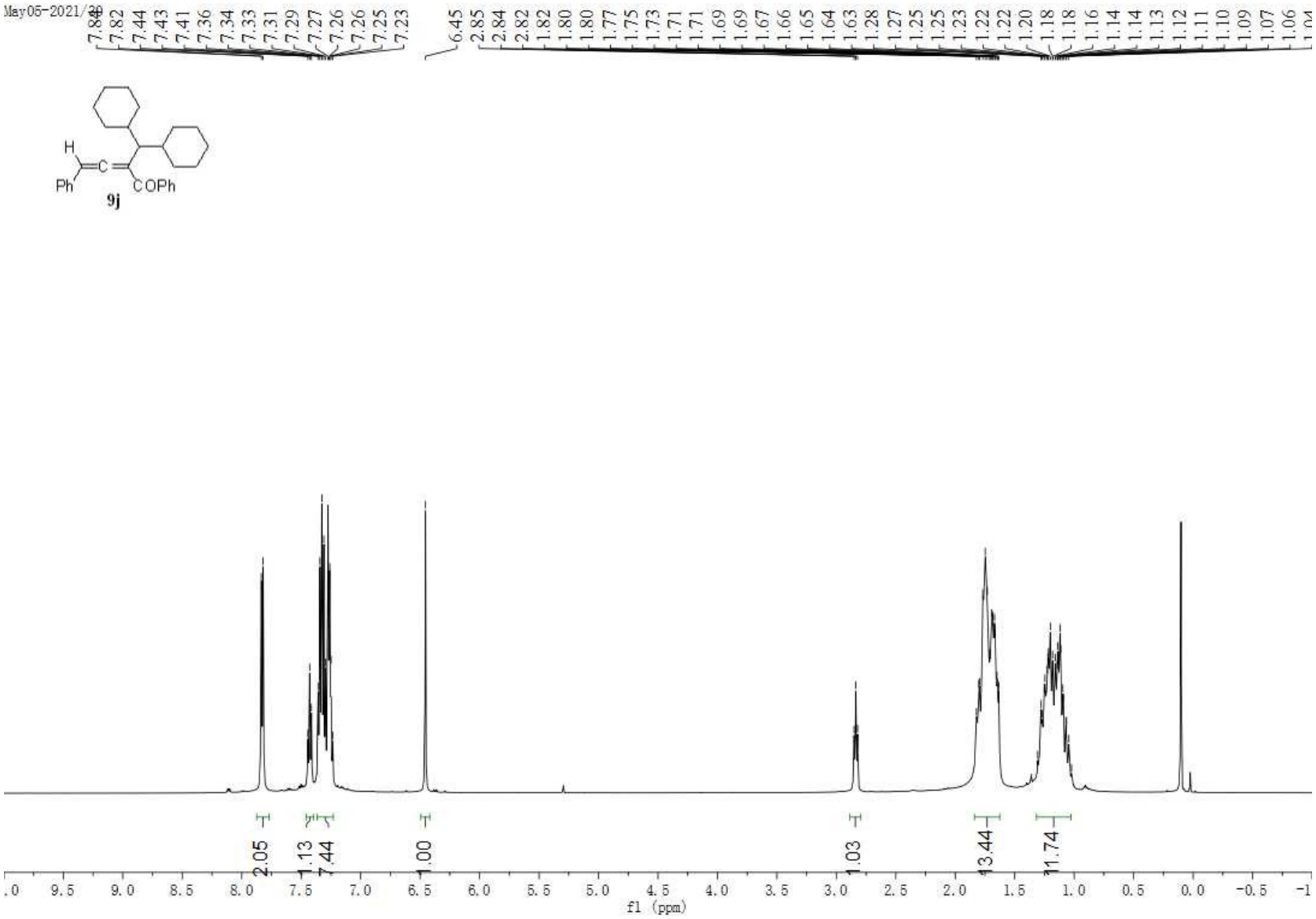

May 07 2021/411c
210.8
210.1
193.2
193.0
142.8
142.6
137.7
137.0
136.7
130.1
130.1
128.4
128.3
128.1
127.9
127.8
127.8
126.6
126.5
114.3
114.2
109.4
109.1
77.3
77.0
76.7
45.0
45.0
42.4
42.2
33.3
33.2
32.6
31.8
30.9
30.6
29.8
29.5
ClH2CH2CH2C
H
Ph
C
t-Bu
O
Cl
9g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

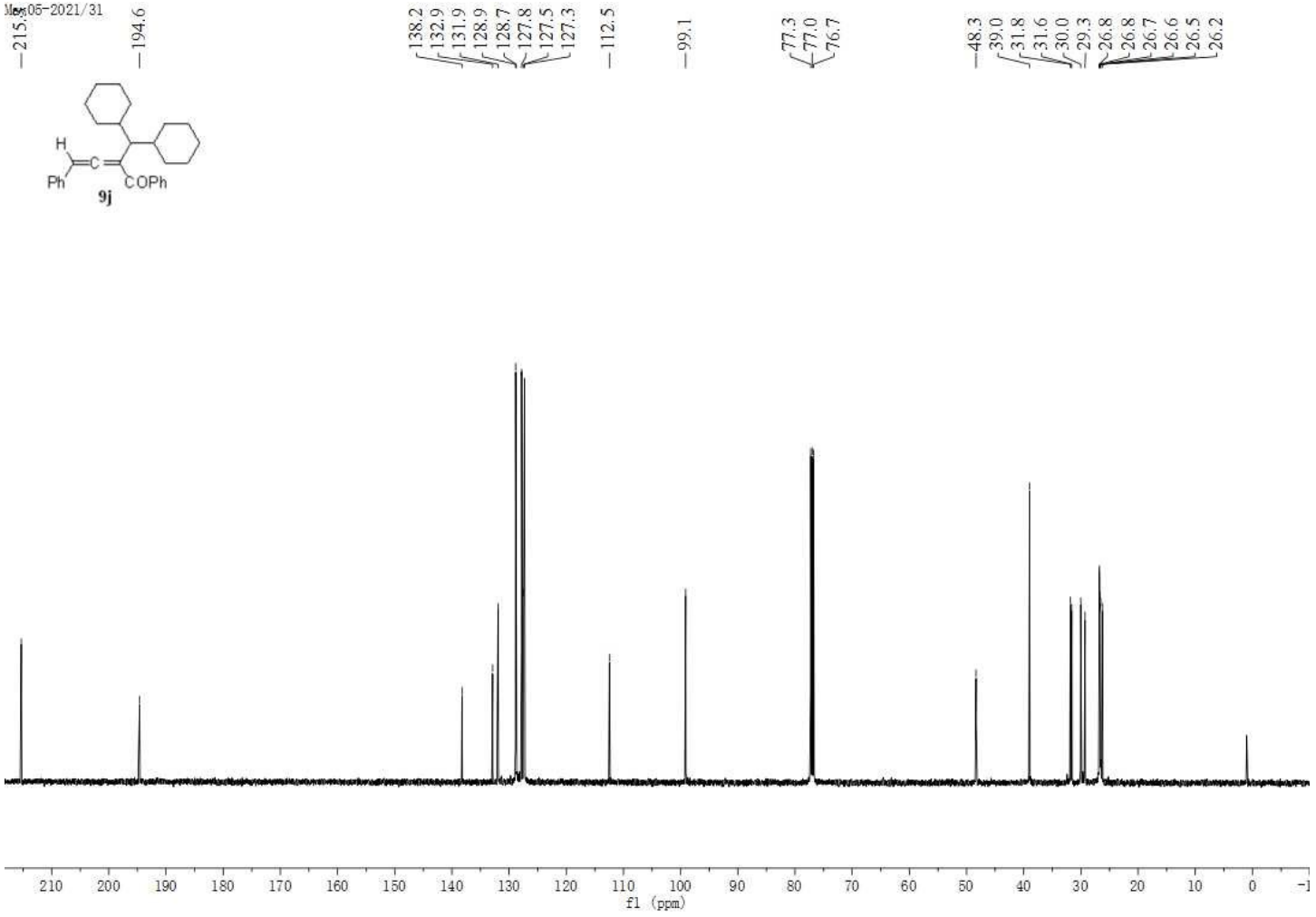

H
t-Bu
COPh
9h
2.00
1.05
2.01
1.00
1.04
13.53
13.15
9.40
f1 (ppm)


Apr10-2021/41
212.8
196.3
139.0
131.0
128.7
127.5
111.9
107.9
77.3
77.0
76.7
46.5
39.3
39.1
33.4
32.3
31.2
29.9
28.0
26.9
26.9
26.8
26.7
26.6
26.4
H
t-Bu
COPh
9h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.75 7.74 7.74 7.73 7.47 7.39 7.38 7.38 7.36 7.26 5.28 2.07 2.05 1.73 1.72 1.72 1.71 1.70 1.69 1.68 1.65 1.65 1.63 1.63 1.62 1.62 1.33 1.31 1.30 1.29 1.28 1.27 1.27 1.25 1.24 1.24 1.23 1.22 1.22 1.21 1.21 1.20 1.20 1.20 1.19 1.19 1.18 1.18 1.17 1.17 1.16 1.16 1.15 1.15 1.14 0.88 0.83 0.82 0.81
H
C
n-Bu
COPh
9i
1.97
1.15
2.09
1.00
1.00
2.47
15.75
23.22
5.23
3.49
f1 (ppm)


May31-2021/231
213.8
196.0
138.8
131.5
129.1
127.6
108.4
95.3
77.3
77.0
76.7
46.7
38.5
31.7
31.3
29.7
29.3
29.2
28.2
26.9
26.9
26.8
26.7
26.6
22.0
H
n-Bu
COPh
9i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


May05-2021/
7.84
7.82
7.44
7.43
7.41
7.36
7.34
7.33
7.31
7.29
7.27
7.26
7.26
7.25
7.23
6.45
2.85
2.84
2.82
1.82
1.80
1.80
1.77
1.75
1.73
1.71
1.71
1.69
1.69
1.67
1.66
1.65
1.64
1.63
1.28
1.27
1.25
1.25
1.23
1.22
1.22
1.20
1.18
1.18
1.16
1.14
1.14
1.13
1.12
1.11
1.10
1.09
1.07
1.06
H
Ph
C
COPh
9j
2.05
1.13
7.44
1.00
1.03
13.44
11.74
f1 (ppm)


May 06-2021/31
215.8
194.6
138.2
132.9
131.9
128.9
128.7
127.8
127.5
127.3
112.5
99.1
77.3
77.0
76.7
48.3
39.0
31.8
31.6
30.0
29.3
26.8
26.8
26.7
26.6
26.5
26.2
H
Ph
COPh
9j
f1 (ppm)