

Supporting Information for

Nickel-catalysed SET-reduction-based access to functionalized allenes *via* 1,4-carbohydrogenation of 1,3-enynes with alkyl bromides

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1 General Information

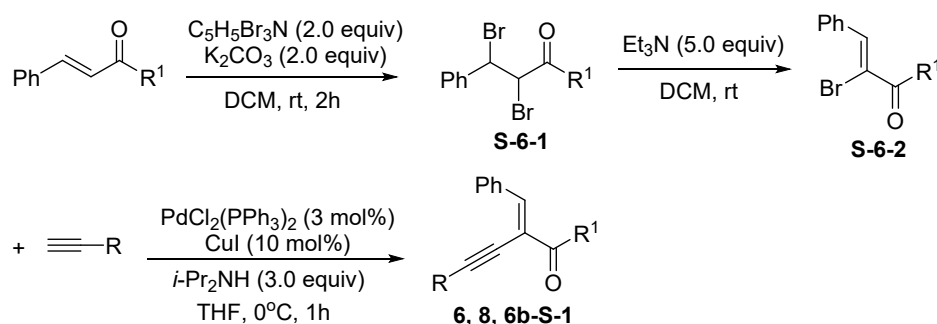
1.1 Solvents, Reagents, and Starting Materials

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. 2-(1-Alkynyl)-2-alken-1-ones **1**, **4**, and **12** were reported in our previous works.^{1, 2} Tertiary alkyl bromides **2** and **9** were prepared according to the published procedures.³ 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 and 126 MHz for ¹³C NMR). Chemical shifts were reported in ppm downfield from tetramethylsilane and calibrated using residue undeuterated solvent (CDCl₃ at 7.26 ppm ¹H NMR; 77.0 ppm ¹³C 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 are reported in Hertz where available. High resolution mass spectra (HRMS) were recorded on Waters Premier GC-TOF MS. Analytical thin layer chromatography was performed on Polygram SIL G/UV₂₅₄ plates. Visualization was accomplished with short wave UV light, or KMnO₄ staining solutions. Flash column chromatography was performed using silica gel (300-400 mesh) with solvents to use.

2 Synthesis of 1,3-enynes **6**, **8**, and **14**

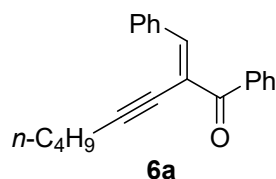


To a solution of (*E*)-chalcone (15.0 mmol, 1.0 equiv) in DCM (50 mL), pyridinium tribromide (9.6 g, 30.0 mmol, 1.0 equiv) and potassium carbonate (4.2 g, 30.0 mmol, 2.0 equiv) was added, and the mixture was stirred for 2 h at room temperature. Then, the saturated Na₂S₂O₃ solution was added, the mixture was filtered and extracted with ethyl acetate (3x25 mL), dried over MgSO₄, the solvent was evaporated in vacuum.

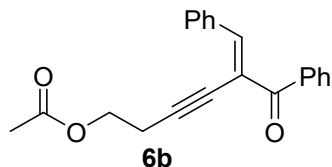
The product was recrystallized from DCM/hexane to afford the desired product **S-6-1** with good yield.

To a solution of 2,3-dibromopropan-1-one **S-6-1** (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 NH₄Cl 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 MgSO₄ and evaporated in vacuo. The mixture was purified by flash column chromatography to afford **S-6-2**.

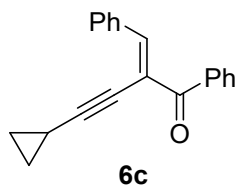
A solution of (*Z*)-2-bromoprop-2-en-1-one **S-6-2** (5.0 mmol, 1.0 equiv) in THF (25 mL) was treated with PdCl₂(PPh₃)₂ (105.3 mg, 0.15 mmol, 3 mol%) and CuI (95.2 mg, 0.5 mmol, 10 mol%) and cooled down to 0°C in the dark. After 10 min of stirring, 3,3-dimethylbut-1-yne (1.2 mL, 10.0 mmol, 2.0 equiv) 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 MgSO₄, 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 **6, 8 (6b-S-1)**. Additional reaction of **6b-S-1** with acetyl chloride (1.1 equiv) and trimethylamine (2.7 equiv) in DCM is required to obtain **6b**.



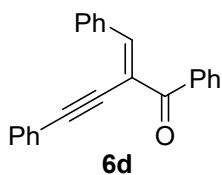
(E)-2-Benzylidene-1-phenyloct-3-yn-1-one (6a). Yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.06-8.03 (m, 2H), 7.93-7.91 (m, 2H), 7.57-7.54 (m, 1H), 7.47-7.40 (m, 6H), 2.46 (t, *J* = 7.0 Hz, 2H), 1.58-1.52 (m, 2H), 1.42-1.37 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 194.3, 144.0, 137.3, 134.9, 132.3, 130.2, 130.0, 129.7, 128.4, 128.0, 121.8, 103.2, 78.0, 30.2, 21.9, 19.7, 13.6. These data are consistent with the published literature.⁴



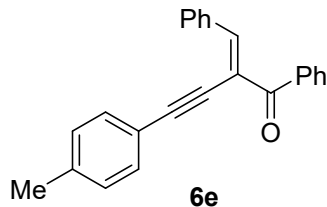
(E)-5-Benzoyl-6-phenylhex-5-en-3-yn-1-yl acetate (6b). Yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.03-8.01 (m, 2H), 7.92-7.90 (m, 2H), 7.58-7.55 (m, 1H), 7.49-7.40 (m, 6H), 4.21 (t, *J* = 6.6 Hz, 2H), 2.81 (t, *J* = 6.7 Hz, 2H), 2.04 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 193.9, 170.8, 145.2, 137.1, 134.6, 132.4, 130.5, 130.1, 129.7, 128.5, 128.0, 121.1, 97.9, 79.2, 61.9, 20.8, 20.5. HRMS (ESI) [M+Na]⁺: calculated for C₂₁H₁₈O₃Na: 341.1154, found 341.1152.



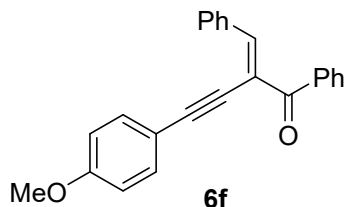
(E)-2-Benzylidene-4-cyclopropyl-1-phenylbut-3-yn-1-one (6c). Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.02-8.00 (m, 2H), 7.91-7.89 (m, 2H), 7.57-7.54 (m, 1H), 7.47-7.39 (m, 6H), 1.52-1.47 (m, 1H), 0.89-0.85 (m, 2H), 0.77-0.74 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 194.1, 144.0, 137.3, 134.9, 132.3, 130.2, 129.9, 129.7, 128.4, 127.9, 121.6, 106.1, 73.3, 8.7, 0.9. These data are consistent with the published literature.⁵



(E)-2-Benzylidene-1,4-diphenylbut-3-yn-1-one (6d). Yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 8.14-8.12 (m, 2H), 8.02-8.00 (m, 2H), 7.64 (s, 1H), 7.61-7.57 (m, 1H), 7.51-7.44 (m, 5H), 7.41-7.39 (m, 2H), 7.36-7.32 (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.⁶

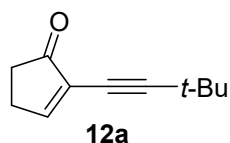


(E)-2-Benzylidene-1-phenyl-4-(p-tolyl)but-3-yn-1-one (6e). Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 8.14-8.12 (m, 2H), 8.02-8.00 (m, 2H), 7.61 (s, 1H), 7.60-7.57 (m, 1H), 7.50-7.43 (m, 4H), 7.31-7.29 (m, 2H), 7.15-7.11 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.5, 144.6, 139.1, 137.2, 134.9, 132.5, 131.2, 130.5, 130.3, 129.7, 129.2, 128.5, 128.0, 121.0, 119.8, 101.2, 86.6, 21.6. These data are consistent with the published literature.⁵

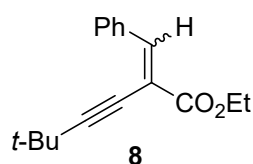


(E)-2-Benzylidene-4-(4-methoxyphenyl)-1-phenylbut-3-yn-1-one (6f). Yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 8.13-8.11 (m, 2H), 8.01-7.99 (m, 2H), 7.60-7.56 (m, 2H), 7.50-7.42 (m, 5H), 7.35-7.32 (m, 2H), 6.91-6.84 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.6, 160.1, 144.1, 137.2, 135.0, 132.9, 132.4, 130.4,

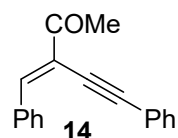
130.3, 129.7, 128.5, 128.0, 121.1, 115.0, 114.1, 101.1, 86.1, 55.3. These data are consistent with the published literature.⁶



2-(3,3-Dimethylbut-1-yn-1-yl)cyclopent-2-en-1-one (12a). Pale yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, *J* = 3.1 Hz, 1H), 2.67-2.65 (m, 2H), 2.44-2.42 (m, 2H), 1.28 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 206.0, 163.8, 130.5, 105.4, 69.7, 33.9, 30.8, 28.1, 27.0. HRMS (ESI) [M+H]⁺: calculated for C₁₁H₁₅O: 163.1123, found 163.1121.

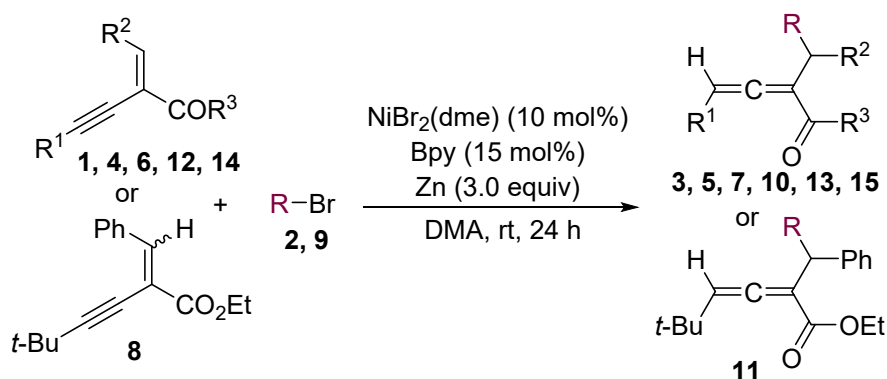


Ethyl 2-benzylidene-5,5-dimethylhex-3-ynoate (8): *E/Z* isomer (1:1 based on ¹H NMR). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.05-8.04 (m, 1H), 7.80 (s, 0.5H), 7.41-7.27 (m, 4H), 7.07 (s, 0.5H), [4.29 (q, *J* = 7.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 1H)], [1.36 (s, 4.5H), 1.29 (s, 4.5H)], [1.38-1.35 (t, *J* = 7.2 Hz, 1.5H), 1.20 (t, *J* = 7.1 Hz, 1.5H)]. ¹³C NMR (126 MHz, CDCl₃) δ 166.2, 166.1, 143.7, 141.5, 135.0, 134.7, 130.2, 130.1, 128.6, 128.4, 128.2(2), 128.1(8), 117.4, 113.8, 107.8, 101.1, 76.7, 75.1, 61.5, 61.4, 30.8, 30.6, 28.6, 28.1, 14.1, 13.7. HRMS (ESI) [M+H]⁺: calculated for C₁₇H₂₁O₂: 257.1542, found 257.1546.

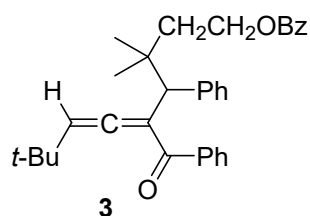


(*E*)-2-benzylidene-1,4-diphenylbut-3-yn-1-one (14). Pale yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.11-8.09 (m, 2H), 7.83 (s, 1H), 7.57-7.55 (m, 2H), 7.45-7.40 (m, 6H), 2.62 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.2, 142.9, 134.5, 131.4, 130.7, 128.9, 128.6, 122.8, 120.0, 99.1, 87.0, 28.2. These data are consistent with the published literature.⁷

3 General procedure for the preparation of 1,3-allenes **3**, **5**, **7**, **10**, **11**, **13**, and **15**

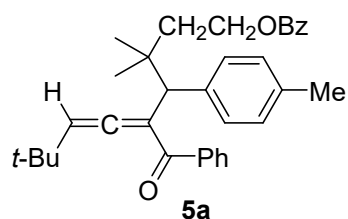


To an oven-dried Schlenk tube was charged with 2-(1-alkynyl)-2-alken-1-one (0.2 mmol, 1.0 equiv), NiBr₂(dme) (10 mol%), 2,2'-bipyridine (15 mol%), Zn (0.6 mmol, 3.0 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point DMA (2 mL) was added via a syringe prior to the addition of alkyl halide (0.4 mmol, 2.0 equiv). The reaction mixture was allowed to stir at room temperature for 24 h, 3 mL of H₂O was added to quench the reaction and the mixture was extracted by ethyl acetate. The combined organic layer was dried over MgSO₄. After filtration and concentration, the residue was purified by column chromatography on silica gel. The ratio of diastereoisomers was determined by ¹H NMR analysis.

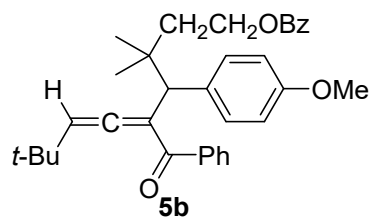


5-Benzoyl-3,3,8,8-tetramethyl-4-phenylnona-5,6-dien-1-yl benzoate (3). Flash column chromatography to afford product **3** as a white solid (85.5 mg, 89% yield, dr = 49:51). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.03-8.00 (m, 2H), 7.65-7.63 (m, 1H), 7.56-7.51 (m, 2H), 7.47-7.39 (m, 5H), 7.36-7.25 (m, 4H), 7.24-7.20 (m, 1H), [5.47 (d, *J* = 0.9 Hz, 0.45H), 5.46 (d, *J* = 1.0 Hz, 0.55H)], 4.49-4.39 (m, 2H), [4.26 (s, 0.45H), 4.23 (s, 0.55H)], 2.05-1.80 (m, 2H), 1.16-1.13 (m, 6H), [0.95 (s, 4.95H), 0.69 (s, 4.05H)]. ¹³C NMR (126 MHz, CDCl₃) δ 213.4, 212.5, 196.2, 195.5, 166.6(0), 166.5(8), 141.0, 140.9, 138.5(2), 138.4(7), 132.8, 131.2, 131.0, 130.5, 130.4(5), 130.4(1), 129.5, 128.7, 128.5, 128.3(1), 128.2(6), 127.6(3), 127.5(5), 127.4(6), 126.5(2), 126.5(0), 111.5, 111.3, 108.7, 108.5, 62.3, 52.4, 51.7, 38.7, 38.3, 38.0, 36.8, 33.6, 33.3, 29.5, 29.1, 25.8, 25.4, 25.1, 24.9. HRMS (ESI) [M+H]⁺: calculated for

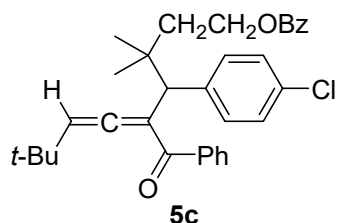
C₃₃H₃₇O₃: 481.2743, found 481.2733.



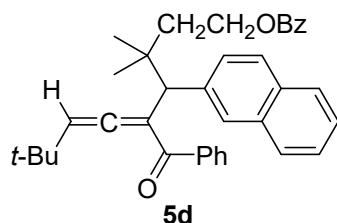
5-Benzoyl-3,3,8,8-tetramethyl-4-(*p*-tolyl)nona-5,6-dien-1-yl benzoate (5a). Flash column chromatography to afford product **5a** as a white solid (79.1 mg, 80% yield, dr = 30:70). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.04-8.01 (m, 2H), 7.65-7.52 (m, 3H), 7.44-7.39 (m, 3H), 7.37-7.30 (m, 4H), 7.12-7.08 (m, 2H), [5.48 (d, *J* = 0.9 Hz, 0.24H), 5.46 (d, *J* = 1.0 Hz, 0.76H)], 4.50-4.41 (m, 2H), [4.22 (s, 0.24H), 4.18 (s, 0.76H)], [2.33 (s, 2.28H), 2.32 (s, 0.72H)], 2.06-1.82 (m, 2H), 1.17-1.13 (m, 6H), [0.95 (s, 6.84H), 0.73 (s, 2.16H)]. ¹³C NMR (126 MHz, CDCl₃) δ 213.3, 212.5, 196.2, 195.6, 166.6, 166.5, 138.5, 137.7, 136.0, 135.9, 132.7, 131.1, 131.0, 130.4(2), 130.4(0), 130.3(4), 130.2(8), 129.5, 128.6, 128.5, 128.3(4), 128.2(7), 128.2(3), 127.5, 127.4, 111.7, 111.4, 108.5, 108.3, 62.3, 52.0, 51.2, 38.6, 38.3, 37.9, 36.8, 33.6, 33.3, 29.5, 29.1, 25.7, 25.3, 25.0, 24.9, 20.9(6), 20.9(5). HRMS (ESI) [M+H]⁺: calculated for C₃₄H₃₉O₃: 495.2899, found 495.2899.



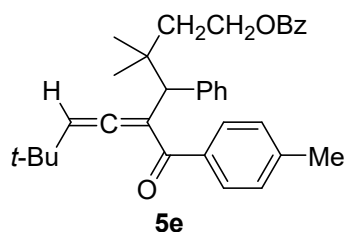
5-Benzoyl-4-(4-methoxyphenyl)-3,3,8,8-tetramethylnona-5,6-dien-1-yl benzoate (5b). Flash column chromatography to afford product **5b** as a white solid (86.7 mg, 85% yield, dr = 24:76). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.03-8.00 (m, 2H), 7.64-7.51 (m, 3H), 7.44-7.29 (m, 7H), 6.85-6.81 (m, 2H), [5.47 (d, *J* = 0.9 Hz, 0.22H), 5.45 (d, *J* = 1.0 Hz, 0.78H)], 4.49-4.39 (m, 2H), [4.20 (s, 0.22H), 4.10 (s, 0.78H)], [3.79 (s, 2.34H), 3.79 (s, 0.66)], 2.25-1.80 (m, 2H), 1.15-1.12 (m, 6H), [0.94 (s, 7.02H), 0.71 (s, 1.98H)]. ¹³C NMR (126 MHz, CDCl₃) δ 213.3, 212.3, 196.2, 195.6, 166.5(9), 166.5(7), 158.1(8), 158.1(5), 138.5(5), 138.5(1), 133.0, 132.9, 132.7, 131.4, 131.3, 131.2, 131.0, 130.4(3), 130.4(2), 129.5, 128.7, 128.5, 128.3, 127.5, 127.4, 113.0, 112.9, 111.8, 111.5, 108.6, 108.4, 62.3, 55.2, 55.1, 51.6, 50.8, 38.6, 38.3, 38.0, 36.8, 33.6, 33.3, 29.5, 29.1, 25.7, 25.3, 25.0, 24.9. HRMS (ESI) [M+H]⁺: calculated for C₃₄H₃₉O₄: 511.2848, found 511.2844.



5-Benzoyl-4-(4-chlorophenyl)-3,3,8,8-tetramethylnona-5,6-dien-1-yl benzoate (5c). Flash column chromatography to afford product **5c** as a pale yellow solid (69.9 mg, 68% yield, dr = 40:60). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.05-7.97 (m, 2H), 7.64-7.50 (m, 3H), 7.44-7.30 (m, 7H), 7.28-7.25 (m, 2H), [5.50 (d, J = 1.0 Hz, 0.26H), 5.47 (d, J = 1.0 Hz, 0.74H)], 4.49-4.41 (m, 2H), [4.25 (s, 0.26H), 4.19 (s, 0.74H)], 2.03-1.77 (m, 2H), 1.15-1.12 (m, 6H), [0.95 (s, 6.66H), 0.71 (s, 2.34H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 213.1, 212.3, 195.9, 195.3, 166.5(3), 166.5(1), 139.5, 139.4, 138.2(8), 138.2(5), 132.8, 132.4, 132.3, 131.7, 131.6, 131.3, 131.1, 130.3(2), 130.3(0), 129.5, 128.6, 128.5, 128.3, 128.3, 127.8, 127.7, 127.6, 127.5, 111.1, 111.0, 109.0, 108.7, 62.1, 51.7, 50.9, 38.6, 38.3, 37.9, 36.7, 33.7, 33.3, 29.5, 29.1, 25.6, 25.3, 24.9, 24.8. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{33}\text{H}_{36}\text{O}_3\text{Cl}$: 515.2353, found 515.2346.

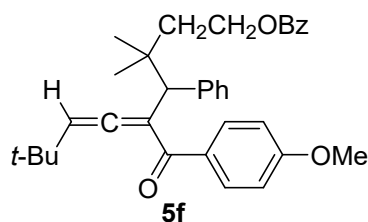


5-Benzoyl-3,3,8,8-tetramethyl-4-(naphthalen-2-yl)nona-5,6-dien-1-yl benzoate (5d). Flash column chromatography to afford product **5d** as a white solid (89.1 mg, 84% yield, dr = 44:56). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.04-8.01 (m, 2H), 7.95-7.86 (m, 1H), 7.85-7.77 (m, 3H), 7.68-7.62 (m, 2H), 7.56-7.52 (m, 2H), 7.49-7.39 (m, 5H), 7.37-7.29 (m, 2H), [5.56 (s, 0.32H), 5.52 (s, 0.68H)], 4.54-4.41 (m, 3H), 2.12-1.88 (m, 2H), 1.24-1.21 (m, 6H), [1.00 (s, 6.12H), 0.71 (s, 2.88H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 213.4, 212.5, 196.1, 195.6, 166.6, 138.5(4), 138.4(9), 138.5, 138.4, 133.0, 132.7, 132.3, 131.2, 131.1, 130.3(9), 130.3(6), 129.5, 129.3, 129.0, 128.7, 128.6, 128.5, 128.2, 127.9, 127.8, 127.5(5), 127.4(5), 127.4(1), 127.4(0), 127.0(1), 126.9(6), 125.8, 125.7, 125.5, 125.4, 111.5, 111.3, 108.8, 108.6, 62.2, 52.5, 51.7, 38.8, 38.5, 38.3, 37.1, 33.7, 33.3, 29.5, 29.1, 25.8, 25.5, 25.2, 25.1. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{37}\text{H}_{39}\text{O}_3$: 531.2899, found 531.2892.

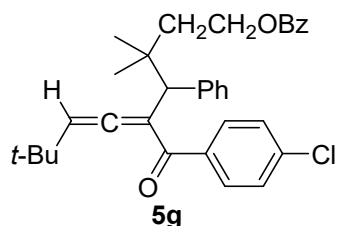


3,3,8,8-Tetramethyl-5-(4-methylbenzoyl)-4-phenylnona-5,6-dien-1-yl benzoate

(5e). Flash column chromatography to afford product **5e** as a white solid (67.2 mg, 68% yield, dr = 26:74). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.05-8.00 (m, 2H), 7.62-7.40 (m, 7H), 7.30-7.26 (m, 2H), 7.24-7.20 (m, 1H), 7.16-7.11 (m, 2H), [5.48 (d, *J* = 1.0 Hz, 0.25H), 5.46 (d, *J* = 1.1 Hz, 0.75H)], 4.49-4.39 (m, 2H), [4.26 (s, 0.25H), 4.19 (s, 0.75H)], [2.37 (s, 0.75H), 2.35 (s, 2.25H)], 2.05-1.80 (m, 2H), 1.17-1.10 (m, 6H), [0.99 (s, 6.75H), 0.72 (s, 2.25H)]. ¹³C NMR (126 MHz, CDCl₃) δ 212.6, 211.6, 195.6, 194.9, 166.6, 142.0, 141.7, 141.0, 140.9, 135.5, 135.4, 132.8, 132.7, 130.5, 130.4(4), 130.4(1), 130.3(9), 129.5, 129.1, 128.9, 128.3, 128.2(3), 128.2(2), 128.1, 127.6, 126.5, 126.4, 111.3, 111.0, 108.4, 108.2, 62.3, 62.2, 52.7, 52.0, 38.7, 38.3, 38.0, 36.8, 33.6, 33.3, 29.6, 29.1, 25.9, 25.4, 25.1, 24.9, 21.4(9), 21.4(6). HRMS (ESI) [M+H]⁺: calculated for C₃₄H₃₉O₃: 495.2899, found 495.2896.

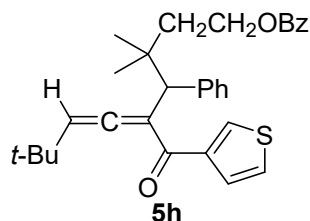


5-(4-Methoxybenzoyl)-3,3,8,8-tetramethyl-4-phenylnona-5,6-dien-1-yl benzoate (5f). Flash column chromatography to afford product **5f** as a white solid (66.3 mg, 65% yield, dr = 43:57). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.02-7.99 (m, 2H), 7.76-7.60 (m, 2H), 7.55-7.51 (m, 1H), 7.47-7.39 (m, 4H), 7.29-7.19 (m, 3H), 6.87-6.80 (m, 2H), [5.48 (d, *J* = 0.9 Hz, 0.43H), 5.47 (d, *J* = 1.0 Hz, 0.57H)], 4.49-4.38 (m, 2H), [4.23 (s, 0.43H), 4.14 (s, 0.57H)], [3.83 (s, 1.29H), 3.81 (s, 1.71H)], 2.06-1.79 (m, 2H), 1.16-1.11 (m, 6H), [1.01 (s, 5.13H), 0.72 (s, 3.87H)]. ¹³C NMR (126 MHz, CDCl₃) δ 211.7, 210.7, 194.4, 193.7, 166.6, 162.5, 162.3, 141.1, 140.9, 132.7, 131.4, 131.3, 130.6, 130.5(3), 130.4(9), 130.4(5), 130.4(1), 129.5, 128.2, 127.6(1), 127.5(9), 126.5, 126.4, 112.8, 112.7, 111.0, 110.7, 108.3, 108.1, 62.2(8), 62.2(5), 55.4, 55.3, 53.2, 52.4, 38.7, 38.4, 38.0, 36.8, 33.6, 33.3, 29.7, 29.2, 26.0, 25.5, 25.1, 25.0. HRMS (ESI) [M+H]⁺: calculated for C₃₄H₃₉O₄: 511.2848, found 511.2850.

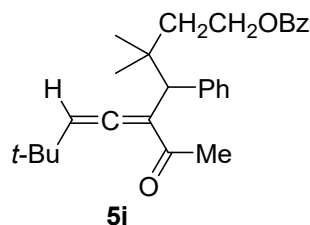


5-(4-chlorobenzoyl)-3,3,8,8-tetramethyl-4-phenylnona-5,6-dien-1-yl benzoate (5g). Flash column chromatography to afford product **5g** as a white solid (60.7 mg, 59% yield, dr = 53:47). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.02-7.99 (m, 2H), 7.62-7.59 (m, 1H), 7.56-7.52 (m, 1H), 7.49-7.38 (m, 5H), 7.34-7.20 (m, 5H), [5.51 (d, *J* = 1.0 Hz, 0.53H), 5.50 (d, *J* = 1.0 Hz, 0.47H)], 4.48-4.38 (m, 2H), [4.23 (s, 0.53H), 4.16(s, 0.47H)], 2.04-1.79 (m, 2H), 1.15-1.11 (m, 6H), [0.98 (s, 4.23H), 0.72 (s,

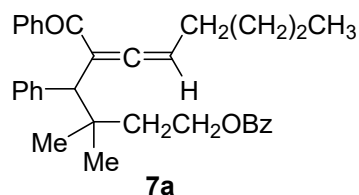
4.77H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 213.1, 212.2, 194.8, 194.1, 166.5(8), 166.5(6), 140.8, 140.7, 137.6, 137.3, 136.6(3), 136.5(9), 132.7(9), 132.7(8), 130.4(3), 130.4(0), 130.3(8), 130.2, 130.1, 129.5, 128.3, 127.9, 127.8, 127.7(0), 127.6(9), 126.6(2), 126.5(9), 111.4, 111.2, 108.9, 108.7, 62.2, 52.5, 51.8, 38.7, 38.3, 38.0, 36.8, 33.8, 33.4, 29.6, 29.1, 25.9, 25.4, 25.0(3), 24.9(8). HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{33}\text{H}_{36}\text{O}_3\text{Cl}$: 515.2353, found 515.2350.



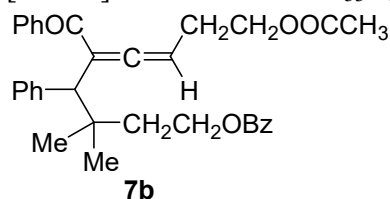
3,3,8,8-Tetramethyl-4-phenyl-5-(thiophene-3-carbonyl)nona-5,6-dien-1-yl benzoate (5h). Flash column chromatography to afford product **5h** as a white solid (65.2 mg, 67% yield, dr = 59:41). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.02-7.99 (m, 2H), 7.96-7.81 (m, 1H), 7.56-7.52 (m, 1H), 7.46-7.33 (m, 5H), 7.29-7.17 (m, 4H), [5.61 (d, J = 1.0 Hz, 0.58H), 5.60 (d, J = 0.9 Hz, 0.42H)], 4.48-4.38 (m, 2H), [4.23 (s, 0.42H), 4.16 (s, 0.58H)], 2.05-1.78 (m, 2H), 1.15-1.07 (m, 6H), [1.07 (s, 5.22H), 0.78 (s, 3.78H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 212.1, 211.2, 188.8, 188.0, 166.6, 141.0, 140.9, 140.8(2), 140.7(7), 132.7, 131.5, 131.3, 130.5, 130.4(3), 130.4(1), 129.5, 128.3(2), 128.2(8), 128.2(6), 127.6(5), 127.6(3), 126.5(2), 126.4(9), 124.8, 124.7, 112.0, 111.8, 108.9, 108.6, 62.3, 62.2, 52.7, 52.0, 38.7, 38.3, 38.0, 36.8, 33.8, 33.4, 29.6, 29.2, 26.0, 25.4, 25.0, 24.9. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{31}\text{H}_{35}\text{O}_3$: 487.2307, found 487.2306.



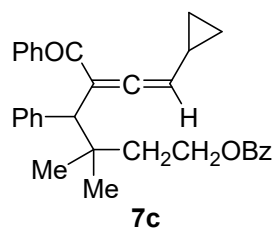
5-Acetyl-3,3,8,8-tetramethyl-4-phenylnona-5,6-dien-1-yl benzoate (5i). Flash column chromatography to afford product **5i** as a white solid (77.8 mg, 93% yield, dr = 62:38). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.02-8.00 (m, 2H), 7.56-7.52 (m, 1H), 7.44-7.41 (m, 2H), 7.39-7.33 (m, 2H), 7.27-7.23 (m, 2H), 7.22-7.19 (m, 1H), [5.75 (s, 0.79H), 5.74 (d, J = 1.0 Hz, 0.21H)], 4.43-4.05 (m, 2H), [4.09 (s, 0.79H), 4.06 (s, 0.21H)], [2.26 (s, 2.37H), 2.25 (s, 0.63H)], 1.94-1.73 (m, 2H), [1.27 (s, 7.11H), 1.09 (s, 1.89H)], 1.07-1.02 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 211.6, 211.5, 198.3(4), 198.3(2), 166.6, 166.5, 141.3, 140.9, 132.7, 130.4(3), 130.4(1), 130.3, 129.5, 128.2, 127.6, 127.5, 126.4, 112.5, 112.4, 108.1, 107.7, 62.3, 62.2, 50.3, 50.1, 38.6, 38.2, 37.4, 36.6, 34.0, 33.7, 29.9, 29.5, 26.5, 26.4, 25.2, 25.1, 24.8. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{28}\text{H}_{35}\text{O}_3$: 419.2586, found 419.2586.



5-Benzoyl-3,3-dimethyl-4-phenylundeca-5,6-dien-1-yl benzoate (7a). Flash column chromatography to afford product **7a** as a pale yellow solid (78.8 mg, 82% yield, dr = 36:64). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.03-7.99 (m, 2H), 7.64-7.60 (m, 2H), 7.56-7.53 (m, 1H), 7.46-7.41 (m, 5H), 7.35-7.28 (m, 4H), 7.24-7.21 (m, 1H), [5.50 (t, *J* = 7.4 Hz, 0.41H), 5.46 (t, *J* = 7.6 Hz, 0.59H)], 4.48-4.39 (m, 2H), [4.16 (s, 0.41H), 4.15 (s, 0.59H)], 2.28-2.03 (m, 2H), 2.02-1.82 (m, 2H), 1.37-1.16 (m, 4H), 1.14-1.12 (m, 6H), 0.83-0.77 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 214.6, 214.5, 195.6(5), 195.5(8), 166.6, 166.5, 140.9, 140.7, 138.5(2), 138.4(6), 132.8, 131.5, 130.4(2), 130.4(1), 130.3(3), 130.2(9), 129.5, 128.9, 128.3, 127.6(7), 127.6(5), 127.6(0), 126.5(0), 126.4(8), 108.8, 108.3, 97.2, 96.8, 62.3, 62.2, 52.1(0), 52.0(7), 38.5(1), 38.4(8), 37.4, 37.0, 30.9, 30.7, 28.6, 28.4, 25.4, 25.3, 25.2, 22.1, 13.7. HRMS (ESI) [M+Na]⁺: calculated for C₃₃H₃₆O₃Na: 503.2562, found 503.2561.

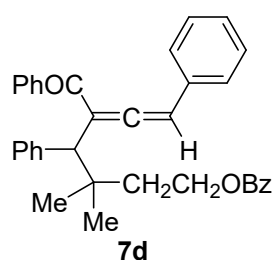


9-Acetoxy-5-benzoyl-3,3-dimethyl-4-phenylnona-5,6-dien-1-yl benzoate (7b). Flash column chromatography to afford product **7b** a pale yellow oil (74.5 mg, 73% yield, dr = 34:66). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.03-8.01 (m, 2H), 7.66-7.64 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.40 (m, 5H), 7.37-7.34 (m, 2H), 7.32-7.28 (m, 2H), 7.26-7.21 (m, 1H), [5.54 (t, *J* = 7.3 Hz, 0.41H), 5.49 (t, *J* = 7.5 Hz, 0.59H)], 4.49-4.40 (m, 2H), [4.16 (s, 0.41H), 4.15 (s, 0.59H)], 4.12-3.88 (m, 2H), 2.61-2.35 (m, 2H), 2.10-1.83 (m, 5H), 1.15-1.12 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 214.7, 214.6, 195.0, 194.9, 170.7, 166.4(7), 166.4(5), 140.5, 140.4, 138.1, 138.0, 132.7(3), 132.7(1), 131.8(2), 131.8(1), 130.3(2), 130.3(0), 130.2, 129.4, 128.8(8), 128.8(6), 128.2, 127.6(9), 127.6(7), 127.7, 126.6(0), 126.5(8), 109.1, 108.7, 93.2, 92.9, 62.7, 62.6, 62.1(2), 62.0(9), 52.3, 52.2, 38.6, 38.5, 37.4, 37.0, 28.4, 28.2, 25.3, 25.2(2), 25.2(0), 25.1, 20.6(9), 20.6(6). HRMS (ESI) [M+Na]⁺: calculated for C₃₃H₃₄O₅Na: 533.2304, found 533.2299.

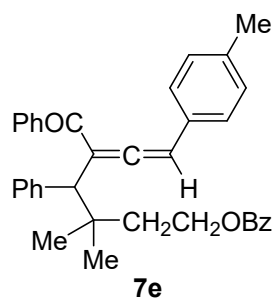


5-Benzoyl-7-cyclopropyl-3,3-dimethyl-4-phenylhepta-5,6-dien-1-yl benzoate (7c).

Flash column chromatography to afford product **7c** as a pale yellow oil (60.4 mg, 65% yield, dr = 33:67). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.04-8.02 (m, 2H), 7.69-7.66 (m, 2H), 7.56-7.53 (m, 1H), 7.48-7.41 (m, 5H), 7.37-7.28 (m, 4H), 7.24-7.21 (m, 1H), [5.27 (d, $J = 8.2$ Hz, 0.35H), 5.19 (d, $J = 8.3$ Hz, 0.65H)], 4.50-4.40 (m, 2H), [4.19 (s, 0.35H), 4.18 (s, 0.65H)], 2.04-1.83 (m, 2H), 1.53-1.37 (m, 1H), 1.17-1.12 (m, 6H), 0.81-0.67 (m, 2H), 0.35-0.22 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 215.1, 214.9, 195.1(4), 195.0(9), 166.5(4), 166.5(2), 140.9, 140.6, 138.2(3), 138.1(8), 132.7(3), 132.7(1), 131.5(9), 131.5(8), 130.4, 130.3, 129.4(7), 129.4(6), 129.0(1), 129.0(0), 128.2, 127.6(5), 127.6(3), 127.5(7), 126.5, 110.1, 109.7, 101.3, 101.0, 62.3, 52.2(9), 52.2(5), 38.5(3), 38.4(9), 37.4, 37.1, 25.4, 25.3, 25.2, 25.1, 9.8, 9.6, 6.4, 6.3, 5.9, 5.8. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{32}\text{H}_{32}\text{O}_3\text{Na}$: 487.2249, found 487.2245.

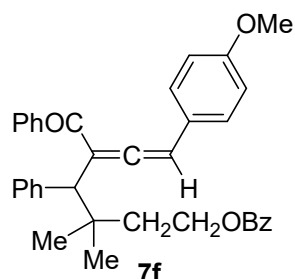


5-Benzoyl-3,3-dimethyl-4,7-diphenylhepta-5,6-dien-1-yl benzoate (7d). Flash column chromatography to afford product **7d** as a pale yellow solid (63.0 mg, 63% yield, dr = 43:57). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.02-7.96 (m, 2H), 7.72-7.68 (m, 2H), 7.56-7.46 (m, 3H), 7.44-7.36 (m, 3H), 7.33-7.22 (m, 9H), 7.15-7.13 (m, 1H), [6.63 (s, 0.54H), 6.59 (s, 0.46H)], 4.49-4.39 (m, 2H), 4.30 (s, 1H), 2.03-1.87 (m, 2H), 1.18-1.12 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 216.4, 215.1, 194.3, 194.2, 166.6, 166.5, 140.4, 140.3, 137.9, 137.8, 132.8, 132.7, 132.2, 132.1(2), 132.0(6), 132.0(4), 130.3(8), 130.3(7), 130.3(5), 129.5, 128.9(4), 128.8(8), 128.8(2), 128.7(6), 128.3, 128.2, 127.9(0), 127.8(7), 127.8(1), 127.8(0), 127.7(7), 127.5, 127.4, 126.7(4), 126.7(0), 112.4, 111.8, 100.6, 100.2, 62.2, 62.1, 53.9, 53.6, 38.7, 38.6, 37.7, 37.1, 25.5, 25.3, 25.2(5), 25.2(0). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{35}\text{H}_{32}\text{O}_3\text{Na}$: 523.2249, found 523.2247.

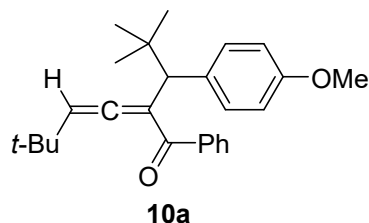


5-Benzoyl-3,3-dimethyl-4-phenyl-7-(p-tolyl)hepta-5,6-dien-1-yl benzoate (7e). Flash column chromatography to afford product **7e** as a pale yellow solid (60.1 mg, 59% yield, dr = 52:48). Two diastereoisomers are hard to be separated by column

chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.03-7.97 (m, 2H), 7.72-7.68 (m, 2H), 7.56-7.53 (m, 1H), 7.49-7.46 (m, 2H), 7.44-7.36 (m, 3H), 7.33-7.30 (m, 1H), 7.28-7.20 (m, 5H), 7.14-7.10 (m, 2H), 7.06-7.04 (m, 1H), [6.61(s, 0.49H), 6.57 (s, 0.51H)], 4.48-4.41 (m, 2H), 4.30 (s, 1H), [2.34 (s, 1.47H), 2.31(s, 1.53H)], 2.03-1.87 (m, 2H), 1.18-1.12 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 216.4, 215.1, 194.4, 194.3, 166.6, 166.5, 140.5, 140.4, 137.8(5), 137.8(3), 137.7(5), 132.7(5), 132.7(1), 132.0(2), 131.9(7), 130.4(2), 130.3(9), 130.3(7), 129.7, 129.5, 129.2, 129.0, 128.9, 128.8, 128.3, 128.2, 127.9, 127.7(7), 127.7(6), 127.7(3), 127.4, 127.3, 126.6(9), 126.6(5), 112.4, 111.8, 100.4, 100.1, 62.2, 62.1, 53.8, 53.5, 38.6, 37.7, 37.0, 25.6, 25.4, 25.2(0), 25.1(6), 21.2(3), 21.1(9). HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{36}\text{H}_{35}\text{O}_3$: 515.2586, found 515.2582.

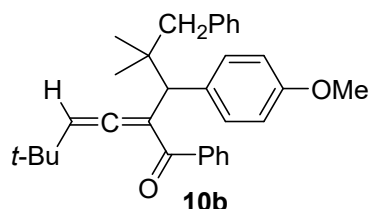


5-Benzoyl-7-(4-methoxyphenyl)-3,3-dimethyl-4-phenylhepta-5,6-dien-1-yl benzoate (7f). Flash column chromatography to afford product **7f** as a white solid (75.3 mg, 71% yield, dr = 45:55). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.03-7.98 (m, 2H), 7.72-7.68 (m, 2H), 7.56-7.53 (m, 1H), 7.49-7.47 (m, 2H), 7.44-7.37 (m, 3H), 7.34-7.30 (m, 1H), 7.28-7.23 (m, 5H), 7.09-7.08 (m, 1H), 6.88-6.83 (m, 2H), [6.60 (d, $J = 1.0$ Hz, 0.42H), 6.56 (d, $J = 1.0$ Hz, 0.58H)], 4.50-4.41 (m, 2H), 4.30 (s, 1H), [3.81 (s, 1.26H), 3.76 (s, 1.74H)], 2.03-1.88 (m, 2H), 1.18-1.13 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 216.3, 214.9, 194.5, 194.4, 166.6, 166.5, 159.4, 159.3, 140.6, 140.4, 138.0, 137.9, 132.7(4), 132.7(2), 132.0, 131.9, 130.3(9), 130.3(7), 130.3(6), 129.5, 128.8(5), 128.7(9), 128.7(4), 128.6, 128.3, 128.2, 127.9, 127.8, 127.7(5), 127.7(4), 126.7, 126.6, 124.4, 124.2, 114.5, 114.3, 112.4, 111.8, 100.0, 99.7, 62.2(3), 62.1(5), 55.3, 55.2, 53.7, 53.4, 38.6(3), 38.6(1), 37.7, 37.0, 25.6, 25.3, 25.2(2), 25.1(6). HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{36}\text{H}_{35}\text{O}_4$: 531.2535, found 531.2544

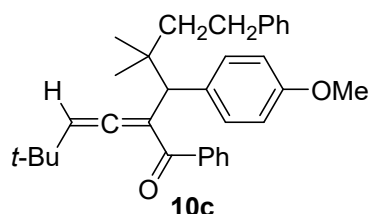


2-(1-(4-Methoxyphenyl)-2,2-dimethylpropyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (10a). Flash column chromatography to afford product **10a** as a white solid (60.2 mg, 80% yield, dr = 14:86). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.64-7.51 (m, 2H), 7.43-7.38 (m, 1H), 7.37-7.29 (m, 4H), 6.83-6.78 (m, 2H), [5.43 (d, $J = 0.9$ Hz, 0.38H), 5.40 (d, $J = 1.1$ Hz, 0.62H)], [4.08 (s, 0.38H), 4.03 (s, 0.62H)], [3.79 (s,

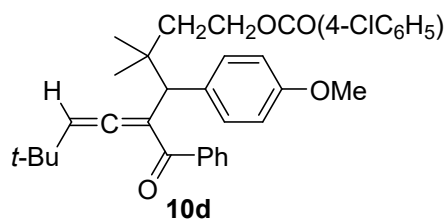
1.86H), 3.78 (s, 1.14H)], [1.03 (s, 5.58H), 1.00 (s, 3.42H), 0.95 (s, 5.58H), 0.70 (s, 3.42H)]. ¹³C NMR (126 MHz, CDCl₃) δ 213.2, 212.4, 196.5, 195.8, 157.98, 157.96, 138.8, 138.7, 134.0, 133.9, 131.2, 131.1(1), 131.0(9), 130.9, 128.7, 128.5, 127.5, 127.4, 112.8, 112.7, 112.3, 112.2, 108.4, 108.1, 55.1(3), 55.1(2), 51.8, 51.2, 36.1, 34.9, 33.6, 33.2, 29.5, 29.1, 28.4, 28.3. HRMS (ESI) [M+H]⁺: calculated for C₂₆H₃₃O₂: 377.2481, found 377.2486.



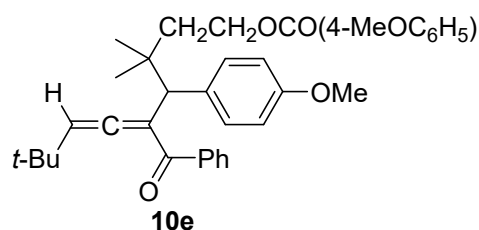
2-(1-(4-methoxyphenyl)-2,2-dimethyl-3-phenylpropyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (10b). Flash column chromatography to afford product **10b** as a pale yellow solid (73.3 mg, 81% yield, dr = 38:62). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 7.67-7.54 (m, 2H), 7.46-7.31 (m, 5H), 7.27-7.17 (m, 3H), 7.12-7.09 (m, 2H), 6.86-6.83 (m, 2H), [5.50 (s, 0.62H), 5.48 (d, *J* = 1.0 Hz, 0.38H)], [4.23 (s, 0.62H), 4.19 (s, 0.38H)], 3.81 (s, 3H), 2.81-2.65 (m, 2H), [1.01-0.91 (m, 9.42H), 0.76 (s, 5.58H)]. ¹³C NMR (126 MHz, CDCl₃) δ 213.3, 212.5, 196.4, 195.7, 158.1(0), 158.0(9), 139.1, 139.0, 138.7, 138.6, 133.4, 133.3, 131.6, 131.5, 131.2, 130.9(5), 130.9(0), 130.8(8), 128.7, 128.5, 127.6, 127.5, 127.4, 125.7, 112.9(5), 112.8(7), 112.1, 111.9, 108.5, 108.3, 55.1(5), 55.1(3), 52.3, 51.7, 46.4, 46.1, 39.7, 38.6, 33.6, 33.3, 29.6, 29.1, 24.7, 24.6, 24.3, 23.9. HRMS (ESI) [M+H]⁺: calculated for C₃₂H₃₇O₂: 453.2794, found 453.2788.



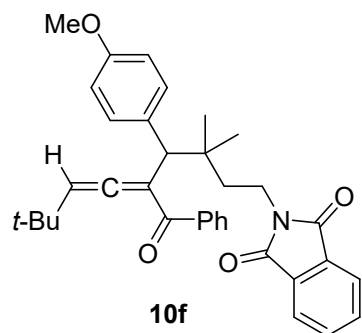
2-(1-(4-Methoxyphenyl)-2,2-dimethyl-4-phenylbutyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (10c). Flash column chromatography to afford product **10c** as a pale yellow solid (69.0 mg, 74% yield, dr = 25:75). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 7.66-7.51 (m, 2H), 7.46-7.39 (m, 2H), 7.37-7.30 (m, 3H), 7.27-7.22 (m, 2H), 7.17-7.09 (m, 3H), 6.84-6.81 (m, 2H), [5.43 (d, *J* = 0.9 Hz, 0.45H), 5.42 (d, *J* = 1.0 Hz, 0.55H)], [4.28 (s, 0.45H), 4.22 (s, 0.55H)], 3.80 (s, 3H), 2.73-2.58 (m, 2H), 1.83-1.55 (m, 2H), 1.14-1.09 (m, 6H), [0.93 (s, 4.95H), 0.72 (s, 4.05H)]. ¹³C NMR (126 MHz, CDCl₃) δ 213.3, 212.5, 196.4, 195.7, 158.0(4), 158.0(2), 143.3, 143.3, 138.7, 138.6, 133.5, 133.4, 131.3(4), 131.2(7), 131.2, 130.9, 128.7, 128.5, 128.4, 128.3, 128.2, 127.5, 127.4, 125.4, 112.9, 112.8, 112.1, 111.9, 108.4, 108.2, 55.1(4), 55.1(1), 50.6, 49.5, 43.4, 42.8, 38.7, 37.6, 33.6, 33.2, 30.6(3), 30.5(6), 29.5, 29.1, 25.6, 25.4, 25.1, 24.9. HRMS (ESI) [M+H]⁺: calculated for C₃₃H₃₉O₂: 467.2950, found 467.2947.



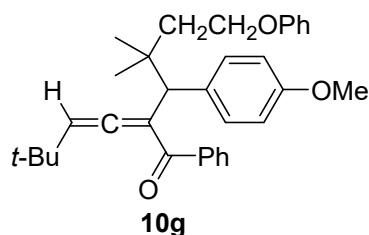
5-Benzoyl-4-(4-methoxyphenyl)-3,3,8,8-tetramethylnona-5,6-dien-1-yl 4-chlorobenzoate (10d). Flash column chromatography to afford product **10d** as a white solid (66.4 mg, 61% yield, dr = 33:67). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.95-7.92 (m, 2H), 7.63-7.50 (m, 2H), 7.44-7.29 (m, 7H), 6.85-6.80 (m, 2H), [5.46 (s, 0.37H), 5.45 (d, $J = 0.9$ Hz, 0.63H)], 4.47-4.38 (m, 2H), [4.20 (s, 0.37), 4.14 (s, 0.63H)], [3.79 (s, 1.89H), 3.78 (s, 1.11H)], 2.01-1.78 (m, 2H), 1.16-1.09 (m, 6H), [0.94 (s, 5.67H), 0.71 (s, 3.33H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 213.3, 212.3, 196.2, 195.6, 165.7(2), 165.7(0), 158.2(0), 158.1(7), 139.2, 138.4(9), 138.4(8), 133.0, 132.8, 131.4, 131.3, 131.2, 131.0, 130.9, 128.8(7), 128.8(5), 128.7, 128.6, 128.5, 127.5(4), 127.4(5), 113.0(4), 112.9(6), 111.7, 111.5, 108.6, 108.4, 62.6, 55.2, 55.1, 51.5, 50.6, 38.7, 38.3, 38.0, 36.8, 33.6, 33.3, 29.5, 29.1, 25.7, 25.3, 25.0, 24.9. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{34}\text{H}_{37}\text{ClO}_4\text{Na}$: 567.2278, found 567.2279.



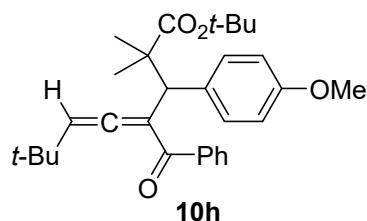
5-Benzoyl-4-(4-methoxyphenyl)-3,3,8,8-tetramethylnona-5,6-dien-1-yl 4-methoxybenzoate (10e). Flash column chromatography to afford product **10e** as a pale yellow solid (97.3 mg, 90% yield, dr = 38:62). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.98-7.95 (m, 2H), 7.64-7.51 (m, 2H), 7.43-7.29 (m, 5H), 6.91-6.80 (m, 2H), 6.85-6.79 (m, 2H), [5.46 (s, 0.40H), 5.44 (s, 0.60H)], 4.45-4.36 (m, 2H), [4.20 (s, 0.40H), 4.14 (s, 0.60H)], 3.84-3.76 (m, 6H), 1.99-1.80 (m, 2H), 1.14-1.11 (m, 6H), [0.94 (s, 5.40H), 0.71 (s, 3.60H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 213.2, 212.3, 196.2, 195.6, 166.3(1), 166.2(9), 163.2, 158.2, 158.1, 138.5(5), 138.5(1), 133.1, 132.9, 131.5, 131.4, 131.3, 131.2, 131.0, 128.7, 128.5, 127.5, 127.4, 122.8(8), 122.8(6), 113.5(3), 113.4(8), 113.0, 112.9, 111.8, 111.5, 108.6, 108.4, 61.9, 55.3, 55.1(2), 55.1(0), 51.6, 50.8, 38.7, 38.3, 38.0, 36.8, 33.6, 33.2, 29.5, 29.1, 25.7, 25.3, 25.0, 24.9. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{35}\text{H}_{40}\text{O}_5\text{Na}$: 563.2773, found 563.2772.



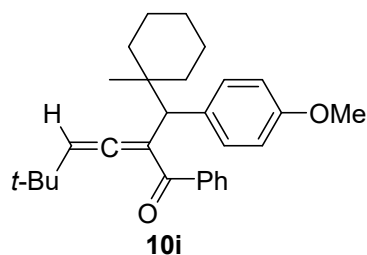
2-(5-Benzoyl-4-(4-methoxyphenyl)-3,3,8,8-tetramethylnona-5,6-dien-1-yl)isoindoline-1,3-dione (10f). Flash column chromatography to afford product **10f** as a white solid (92.1 mg, 86% yield, dr = 62:38). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.81-7.77 (m, 2H), 7.67-7.64 (m, 2H), 7.62-7.50 (m, 2H), 7.43-7.28 (m, 5H), 6.82-6.79 (m, 2H), [5.48 (d, J = 1.1 Hz, 0.62H), 5.43 (s, 0.38H)], [4.18 (s, 0.62H), 4.15 (s, 0.38H)], 3.82-3.66 (m, 5H), 1.83-1.60 (m, 2H), 1.15-1.11 (m, 6H), [0.93 (s, 3.42H), 0.73 (s, 5.58H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 213.2, 212.6, 196.2, 195.7, 168.1, 168.0, 158.1(0), 158.0(7), 138.6(4), 138.6(0), 133.7, 132.8(3), 132.7(5), 132.2(0), 132.1(8), 131.4, 131.2, 131.0, 130.8, 128.6, 128.5, 127.4, 127.3, 122.9(7), 122.9(6), 113.0, 112.9, 111.7, 111.5, 108.5, 108.4, 55.0(6), 55.0(5), 50.8, 50.1, 38.6, 38.5, 37.9, 36.9, 34.3, 34.2, 33.6, 33.2, 29.5, 29.1, 25.0, 24.9, 24.5. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{35}\text{H}_{38}\text{NO}_4$: 536.2801, found 536.2796.



2-(1-(4-Methoxyphenyl)-2,2-dimethyl-4-phenoxybutyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (10g). Flash column chromatography to afford product **10g** as a colorless oil (76.2 mg, 79% yield, dr = 39:61). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.66-7.53 (m, 2H), 7.45-7.26 (m, 7H), 6.95-6.83 (m, 5H), 5.47 (s, 1H), [4.24 (s, 0.67H), 4.18 (s, 0.33H)], 4.12-4.03 (m, 2H), 3.80 (s, 3H), 2.10-1.85 (m, 2H), 1.16-1.09 (m, 6H), [0.97 (s, 2.97H), 0.74 (s, 6.03H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 213.2, 212.3, 196.2, 195.6, 159.0, 158.9, 158.1(5), 158.1(3), 138.6, 138.5, 133.1, 133.0, 131.4, 131.3, 131.2, 131.0, 129.3, 128.7, 128.5, 127.5, 127.4, 120.4(0), 120.3(7), 114.5, 113.0, 112.9, 111.8, 111.6, 108.5, 108.3, 64.8, 64.7, 55.1(2), 55.1(0), 51.3, 50.6, 39.1, 38.9, 37.9, 36.8, 33.6, 33.2, 29.5, 29.1, 25.8, 25.6, 25.2(4), 25.1(8). HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{33}\text{H}_{39}\text{O}_3$: 483.2899, found 483.2896.



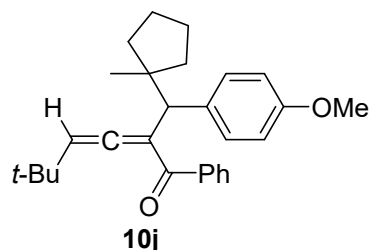
tert-Butyl 4-benzoyl-3-(4-methoxyphenyl)-2,2,7,7-tetramethylocta-4,5-dienoate (10h). Flash column chromatography to afford product **10h** as a pale yellow oil (84.1 mg, 91% yield, dr = 25:75). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.62-7.52 (m, 2H), 7.43-7.29 (m, 5H), 6.82-6.79 (m, 2H), [5.44 (s, 0.32H), 5.40 (d, $J = 1.6$ Hz, 0.68H)], [4.65 (s, 0.32H), 4.58 (s, 0.68H)], [3.77 (s, 0.96H), 3.76 (s, 2.04H)], [1.40 (s, 2.88H), 1.36 (s, 6.12H)], 1.21-1.18 (m, 6H), [0.96 (s, 2.88H), 0.80 (s, 6.12H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 212.5, 212.3, 195.3, 194.9, 176.1, 176.0, 158.2(8), 158.2(7), 138.7, 138.6, 132.3, 132.0, 131.3(7), 131.3(5), 131.1, 130.9, 128.6, 128.5, 127.4(4), 127.3(7), 112.9(4), 112.9(1), 111.7, 111.6, 108.8, 108.5, 80.1, 80.0, 55.1(3), 55.1(0), 47.9, 47.4, 47.3, 47.1, 33.4, 33.2, 29.4, 29.2, 28.0, 27.9, 25.5, 25.2, 22.2, 21.9. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{30}\text{H}_{38}\text{O}_4\text{Na}$: 485.2668, found 485.2663.



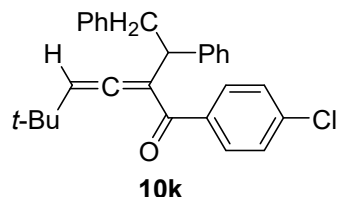
2-((4-Methoxyphenyl)(1-methylcyclohexyl)methyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (10i). Flash column chromatography to afford product **10i** (76.6 mg, 92% yield, dr = 42:58).

The first fraction: colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.65-7.63 (m, 2H), 7.45-7.41 (m, 1H), 7.38-7.33 (m, 4H), 6.80-6.77 (m, 2H), 5.41 (d, $J = 0.8$ Hz, 1H), 4.15 (s, 1H), 3.78 (s, 3H), 1.55-1.40 (m, 6H), 1.36-1.26 (m, 2H), 1.22-1.17 (m, 2H), 1.06 (s, 3H), 0.68 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 213.6, 195.7, 157.9, 138.6, 133.5, 131.5, 131.1, 128.8, 127.5, 112.7, 111.9, 108.3, 55.1, 51.2, 38.7, 37.0, 36.2, 33.2, 29.1, 26.2, 22.0, 20.4. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{29}\text{H}_{37}\text{O}_2$: 417.2794, found 417.2789.

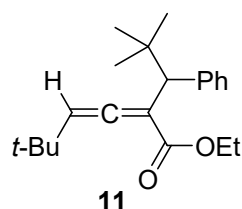
The second fraction: white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.53-7.51 (m, 2H), 7.42-7.38 (m, 1H), 7.32-7.29 (m, 4H), 6.83-6.80 (m, 2H), 5.37 (s, 1H), 4.11 (s, 1H), 3.79 (s, 3H), 1.60-1.49 (m, 6H), 1.43-1.34 (m, 2H), 1.29-1.20 (m, 2H), 1.05 (s, 3H), 0.95 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 212.6, 196.5, 158.0, 138.9, 133.4, 131.4, 130.9, 128.6, 127.4, 112.8, 111.7, 107.7, 55.1, 51.9, 37.4, 36.7, 35.7, 33.5, 29.6, 26.2, 21.9(2), 21.8(7), 20.4. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{29}\text{H}_{37}\text{O}_2$: 417.2794, found 417.2790.



2-((4-Methoxyphenyl)(1-methylcyclopentyl)methyl)-5,5-dimethyl-1-phenylhexa-2,3-dien-1-one (10j). Flash column chromatography to afford product **10j** as a pale yellow oil (59.5 mg, 74% yield, dr = 60:40). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.64-7.62 (m, 2H), 7.45-7.39 (m, 1H), 7.37-7.29 (m, 4H), 6.82-6.78 (m, 2H), 5.40 (s, 1H), [4.20 (s, 0.62H), 4.15 (s, 0.38H)], 3.78 (s, 3H), 1.79-1.21 (m, 8H), [1.07 (s, 1.14H), 1.04 (s, 1.86H)], [0.92 (s, 3.42H), 0.71 (s, 5.58H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 213.1, 212.1, 196.4, 195.8, 157.9, 157.9, 138.8, 138.7, 134.7, 134.4, 131.2, 131.0, 130.9(2), 130.8(7), 128.7, 128.6, 127.5, 127.4, 112.9(3), 112.8(8), 112.7, 112.5, 108.2(5), 108.1(7), 55.2, 55.1, 51.2, 50.6, 47.6, 46.7, 39.0, 38.9, 38.0, 37.3, 33.5, 33.2, 29.5, 29.2, 24.3, 24.2, 24.0, 23.9, 23.8. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{28}\text{H}_{35}\text{O}_2$: 403.2637, found 403.2637.

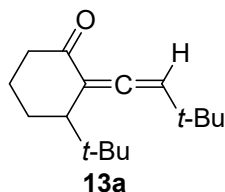


1-(4-Chlorophenyl)-2-(1,2-diphenylethyl)-5,5-dimethylhexa-2,3-dien-1-one (10k). Flash column chromatography to afford product **10k** as a white solid (44.7 mg, 54% yield, dr = 41:59). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.60-7.50 (m, 2H), 7.35-7.25 (m, 5H), 7.23-7.12 (m, 6H), 7.07-7.05 (m, 1H), [5.59 (d, J = 1.9 Hz, 0.40H), 5.48 (d, J = 1.8 Hz, 0.60H)], 4.51-4.42 (m, 1H), 3.24-3.01 (m, 2H), [0.95 (s, 3.6H), 0.83 (s, 5.4H)]. ^{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, 136.8, 130.2, 130.1, 129.0(3), 128.9(9), 128.2, 128.1(2), 128.0(9), 128.0(6), 128.0, 127.8(3), 127.7(7), 126.4(4), 126.4(1), 126.0, 125.9, 114.0, 113.9, 109.3, 109.2, 44.4(5), 44.4(0), 41.5, 40.8, 33.3, 33.2, 29.7, 29.5. These data are consistent with the published literature.¹

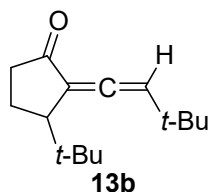


Ethyl 2-(2,2-dimethyl-1-phenylpropyl)-5,5-dimethylhexa-2,3-dienoate (11). Flash column chromatography to afford product **11** as a colorless oil (44.0 mg, 70% yield, dr = 51:49). Two diastereoisomers are hard to be separated by column

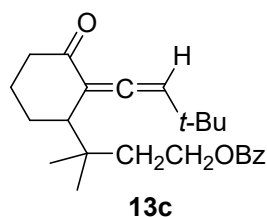
chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.31 (m, 2H), 7.26-7.22 (m, 2H), 7.21-7.17 (m, 1H), 5.63 (s, 1H), 4.20-3.98 (m, 2H), [3.80 (s, 0.52H), 3.78 (s, 0.48H)], 1.22 (s, 4.68H), 1.20 (m, 3H), 1.07 (s, 4.32H), [1.00 (s, 4.68H), 0.96 (s, 4.32H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 209.2, 209.1, 168.4, 168.3, 142.1, 141.6, 130.3, 130.1, 127.3(1), 127.2(8), 126.2, 126.1, 107.5, 107.2, 103.9, 60.8, 53.5, 53.4, 35.6, 34.9, 33.7, 33.4, 29.9, 29.6, 28.2(2), 28.1(9), 14.1. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{21}\text{H}_{31}\text{O}_2$: 315.2324, found 315.2323.



3-(tert-Butyl)-2-(3,3-dimethylbut-1-en-1-ylidene)cyclohexan-1-one (13a). Flash column chromatography to afford product **13a** as a pale yellow oil (29.0 mg, 62% yield, dr = 48:52). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ [5.45 (d, $J = 3.1$ Hz, 0.60H), 5.41 (d, $J = 2.6$ Hz, 0.40H)], 2.51-2.37 (m, 2H), 2.29-2.17 (m, 1H), 2.01-1.94 (m, 1H), 1.93-1.87 (m, 1H), 1.73-1.61 (m, 1H), 1.54-1.41 (m, 1H), [1.11 (s, 5.4H), 1.05 (s, 3.6H), 0.95 (s, 5.4H), 0.88 (s, 3.6H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 206.7, 205.1, 203.6, 203.4, 109.2, 108.9, 105.4, 105.0, 48.9, 48.5, 40.0, 35.8, 34.2, 33.0, 32.9, 30.1, 30.0, 27.7, 27.4, 25.6, 25.0, 21.4, 21.1. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{16}\text{H}_{27}\text{O}$: 235.2062, found 235.2056.

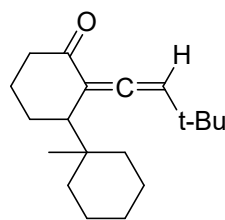


3-(tert-Butyl)-2-(3,3-dimethylbut-1-en-1-ylidene)cyclopentan-1-one (13b). Flash column chromatography to afford product **13b** as a pale yellow oil (23.8 mg, 54% yield, dr = 71:29). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ [5.64 (d, $J = 5.2$ Hz, 0.72H), 5.61 (d, $J = 5.0$ Hz, 0.28H)], 2.80-2.75 (m, 1H), 2.42-2.23 (m, 2H), 2.04-1.97 (m, 1H), 1.78-1.68 (m, 1H), [1.13 (s, 6.48H), 1.09 (s, 2.52H)], [0.99 (s, 6.48H), 0.95 (s, 2.52H)]. ^{13}C NMR (126 MHz, CDCl_3) δ 207.6(5), 207.6(3), 204.2, 203.7, 107.9, 107.8, 107.7, 107.5, 51.5, 51.2, 38.2(3), 38.2(0), 34.2, 33.6(0), 33.5(7), 33.3, 30.2, 30.1(5), 27.5, 27.3, 23.0, 22.7. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{15}\text{H}_{24}\text{O}$: 221.1905, found 221.1906.



3-(2-(3,3-Dimethylbut-1-en-1-ylidene)-3-oxocyclohexyl)-3-methylbutyl benzoate

(13c). Flash column chromatography to afford product **13c** as a pale yellow oil (35.4 mg, 48% yield, dr = 48:52). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 8.01 (m, 2H), 7.57-7.51 (m, 1H), 7.45-7.43 (m, 2H), [5.49 (d, $J = 3.1$ Hz, 0.55H), 5.46 (d, $J = 2.7$ Hz, 0.45H)], 4.45-4.31 (m, 2H), 2.71-2.54 (m, 1H), 2.55-2.45 (m, 1H), 2.31-2.17 (m, 1H), 2.07-1.82 (m, 4H), 1.76-1.65 (m, 1H), 1.58-1.45 (m, 1H), [1.12 (s, 4.95H), 1.05 (s, 4.05H)], 1.05-0.96 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 206.6, 205.2, 203.2, 203.0, 166.6, 132.8, 130.3, 129.5, 128.3(2), 128.3(0), 108.6, 108.3, 105.8, 105.4, 62.1(2), 62.0(7), 47.4, 46.6, 39.9, 38.0, 37.9, 37.6, 36.2, 33.1, 33.0, 30.1, 30.0, 25.1, 24.9, 24.8, 24.7, 24.6, 21.3, 21.0. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{24}\text{H}_{32}\text{O}_3\text{Na}$: 391.2252, found 391.2249.

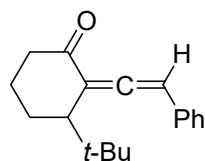


13d

2-(3,3-Dimethylbut-1-en-1-ylidene)-1'-methyl-[1,1'-bi(cyclohexan)]-3-one (13d). Flash column chromatography to afford product **13d** as a pale yellow oil (33.5 mg, 61% yield, dr = 52:48).

The first fraction: pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 5.43 (d, $J = 2.8$ Hz, 1H), 2.65-2.61 (m, 1H), 2.50-2.44 (m, 1H), 2.26-2.20 (m, 1H), 1.97-1.86 (m, 2H), 1.71-1.65 (m, 1H), 1.52-1.24 (m, 11H), 1.11 (s, 9H), 0.85 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 205.5, 203.7, 108.6, 104.9, 46.2, 40.0, 36.7, 35.8, 32.9, 30.1, 26.2, 24.3, 21.9, 21.6, 21.3, 21.0. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{19}\text{H}_{31}\text{O}$: 275.2375, found 275.2377.

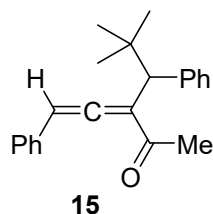
The second fraction: pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 5.40 (d, $J = 2.6$ Hz, 1H), 2.76-2.72 (m, 1H), 2.50-2.45 (m, 1H), 2.23-2.16 (m, 1H), 1.96-1.87 (m, 2H), 1.67-1.62 (m, 1H), 1.48-1.17 (m, 11H), 1.05 (s, 9H), 0.76 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 206.5, 203.9, 108.4, 104.8, 45.3, 40.0, 38.0, 35.9, 35.6, 33.0, 30.2, 26.2, 23.8, 21.8, 21.6, 21.1, 20.9. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{19}\text{H}_{31}\text{O}$: 274.2375, found 274.2375.



13e

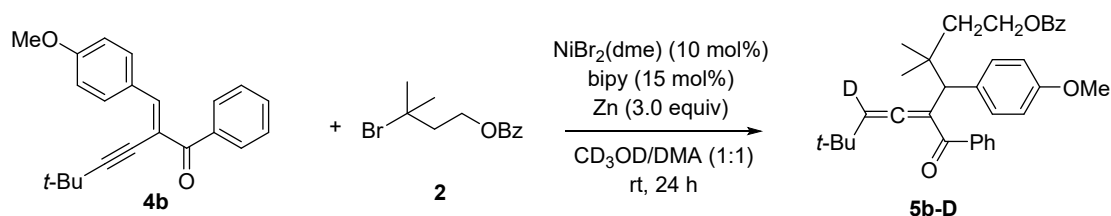
3-(tert-Butyl)-2-(2-phenylvinylidene)cyclohexan-1-one (13e). Flash column chromatography to afford product **13e** as a pale yellow oil (23.4 mg, 46% yield, dr = 50:50). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ 7.32-7.29 (m, 3H), 7.23-7.21 (m, 2H), [6.53 (d, $J = 3.0$ Hz, 0.47H), 6.45 (d, $J = 3.0$ Hz, 0.53H)], 2.67-2.53 (m, 2H), 2.37-2.29 (m,

1H), 2.11-1.97 (m, 2H), 1.87-1.73 (m, 1H), 1.58-1.52 (m, 1H), [0.95 (s, 4.77H), 0.94 (s, 4.23H)]. ¹³C NMR (126 MHz, CDCl₃) δ 210.2, 209.4, 202.6, 202.3, 132.8, 132.6, 128.7(3), 128.6(7), 127.5, 127.4, 127.3, 127.0, 110.9, 110.8, 97.6, 97.2, 49.7, 48.5, 40.3, 40.3, 35.5, 34.4, 27.5, 27.4, 25.5, 25.1, 21.5, 21.4. HRMS (ESI) [M+H]⁺: calculated for C₁₈H₂₂O: 255.1749, found 255.1751.

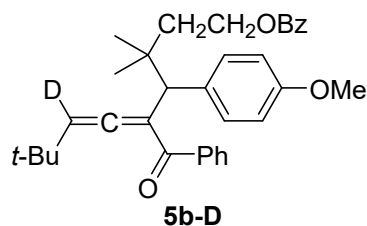


5,5-Dimethyl-4-phenyl-3-(2-phenylvinylidene)hexan-2-one (15). Flash column chromatography to afford product **15** as a white solid (44.9 mg, 74% yield, dr = 49:51). Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.28 (m, 3H), 7.29-7.18 (m, 4H), 7.20-7.08 (m, 3H), 6.73 (s, 1H), [3.98 (s, 0.49H), 3.97 (s, 0.51H)], [2.22 (s, 1.47H), 2.20 (s, 1.53H)], [0.90 (s, 4.59H), 0.87 (s, 4.41H)]. ¹³C NMR (126 MHz, CDCl₃) δ 217.0, 216.5, 197.4, 197.3, 141.6, 141.3, 132.1, 131.9, 130.1, 130.0, 129.1, 128.9, 127.9(8), 127.9(7), 127.6, 127.5, 127.4, 127.2, 126.3(4), 126.2(8), 114.8, 114.3, 100.3, 99.9, 51.7, 35.5, 35.0, 28.2(0), 28.1(6), 26.8, 26.7. These data are consistent with the published literature.⁷

4 Deuteration study

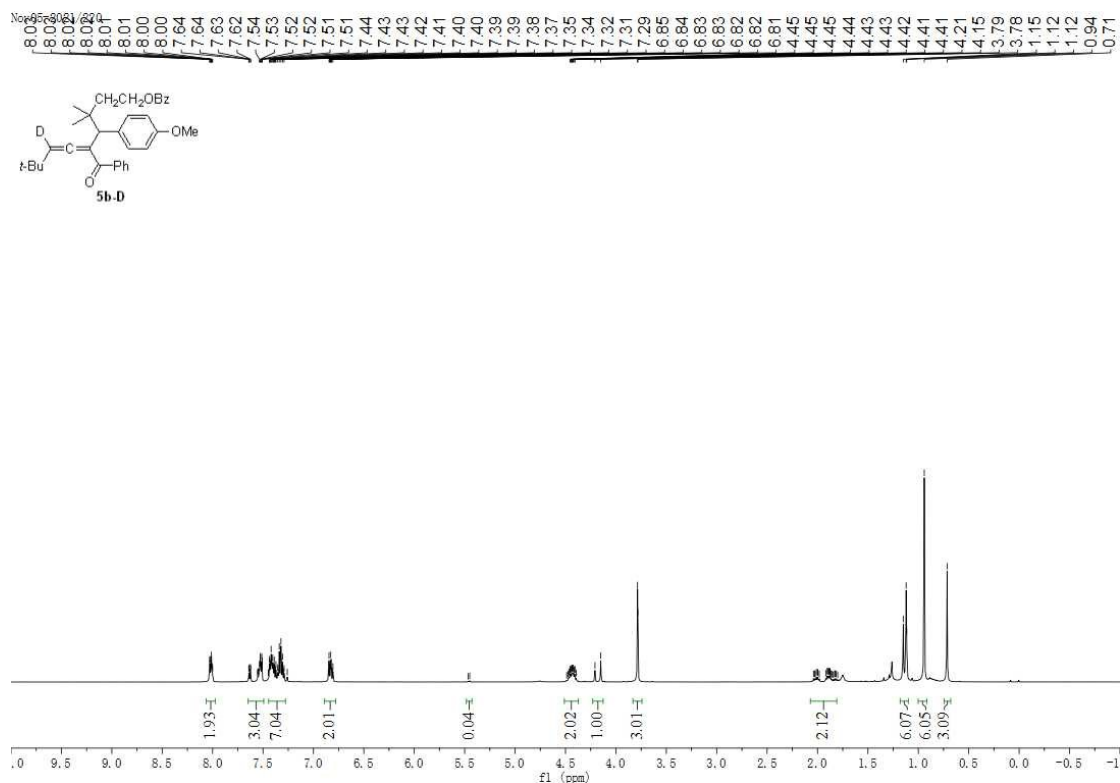


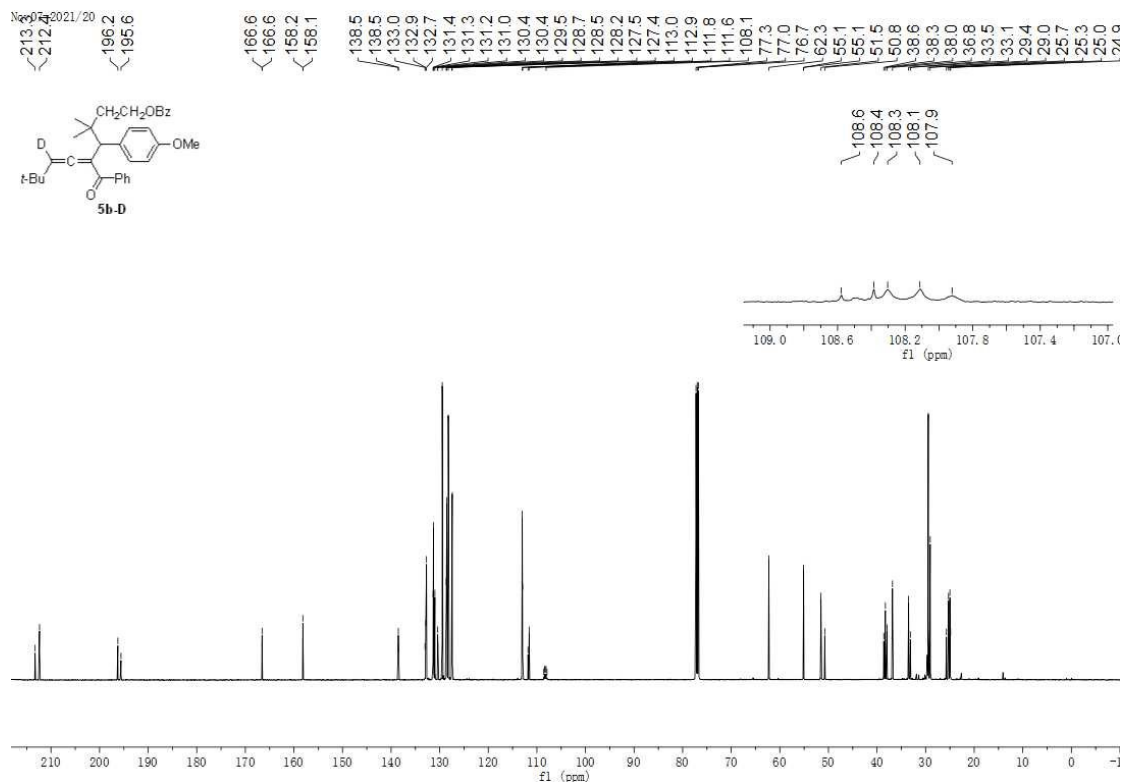
To an oven-dried Schlenk tube was charged with **4b** (63.8 mg, 0.2 mmol, 1.0 equiv), NiBr₂(dme) (6.2 mg, 10 mol%), 2,2'-bipyridine (4.7 mg, 15 mol%), Zn (39 mg, 0.6 mmol, 3.0 equiv). The tube was capped with a rubber septum, evacuated and back-filled with nitrogen three times, at which point DMA (1 mL) and CD₃OD (1 mL) was added via a syringe prior to the addition of tertiary alkyl bromide **2** (108.2 mg, 0.4 mmol, 2.0 equiv). The reaction mixture was allowed to stir at room temperature for 24 h, 3 mL of H₂O was added to quench the reaction and the mixture was extracted by ethyl acetate. The combined organic layer was dried over MgSO₄. After filtration and concentration, the residue was purified by column chromatography on silica gel. The product **5b-D** with 95% D-incorporation was determined by ¹H NMR.



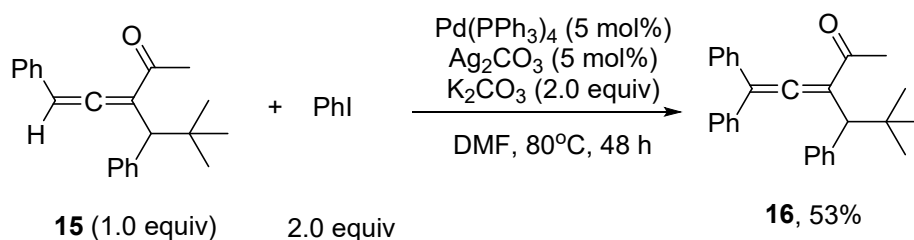
5-Benzoyl-4-(4-methoxyphenyl)-3,3,8,8-tetramethylnona-5,6-dien-1-yl-7-*d*

benzoate (5b-D). The product 5b-D was obtained in 74% yield (75.7 mg, D-incorporation > 95 %, dr = 36:64) as a white solid after column chromatography. The mixtures are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ 8.03-8.00 (m, 2H), 7.64-7.51 (m, 3H), 7.45-7.29 (m, 7H), 6.85-6.81 (m, 2H), 4.49-4.39 (m, 2H), [4.21 (s, 0.37H), 4.15 (s, 0.63H)], 3.78 (s, 3H), 2.04-1.80 (m, 2H), 1.15-1.12 (m, 6H), [0.94 (s, 5.67H), 0.71 (s, 3.33H)]. ¹³C NMR (126 MHz, CDCl₃) δ 213.3, 212.4, 196.2, 195.6, 166.5(7), 166.5(6), 158.2, 158.1, 138.5(2), 138.4(9), 133.0, 132.9, 132.7, 131.4, 131.3, 131.2, 131.0, 130.4(1), 130.3(9), 129.5, 128.7, 128.5, 128.2, 127.5, 127.4, 113.0, 112.9, 111.8, 111.6, 108.6, 108.4, 108.1(t, *J* = 23.9 Hz), 62.3, 55.1(2), 55.1(1), 51.5, 50.8, 38.6, 38.3, 38.0, 36.8, 33.5, 33.1, 29.4, 29.0, 25.7, 25.3, 25.0, 24.9. HRMS (ESI) [M+Na]⁺: calculated for C₃₄H₃₇DO₄Na: 534.2731, found 534.2731.

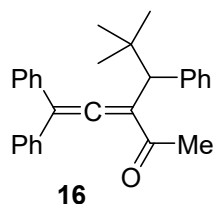




5 Transformation of 1,2-allenyl ketones



The reaction of **15** (55.2 mg, 0.2 mmol), iodobenzene (81.3 mg, 0.4 mmol), Pd(PPh₃)₄ (11.3 mg, 0.01 mmol), Ag₂CO₃ (2.8 mg, 0.01 mmol), and K₂CO₃ (55.3 mg, 0.4 mmol) in 2 mL dried DMF at 80 °C under N₂ for 48 h. Then, 3 mL of H₂O was added to quench the reaction and the mixture was extracted by ethyl ester (3x10 mL). The combined organic layer was dried over MgSO₄. After filtration and concentration, the residue was purified by column chromatography on silica gel to give **16** (40.3 mg) in 53% yield.



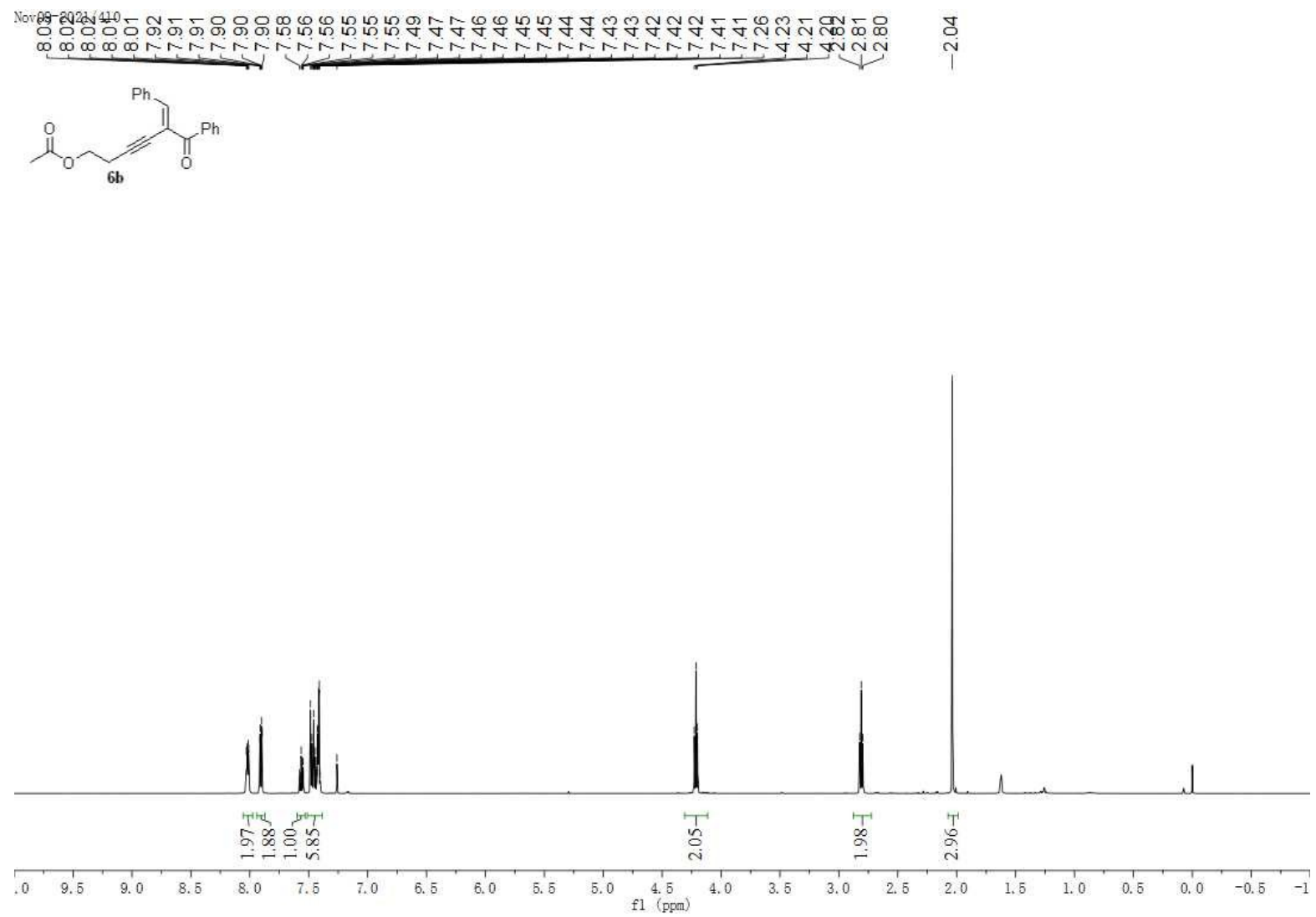
3-(2,2-Diphenylvinylidene)-5,5-dimethyl-4-phenylhexan-2-one (16). White solid.
¹H NMR (500 MHz, CDCl₃) δ 7.47-7.45 (m, 4H), 7.41-7.38 (m, 1H), 7.34-7.30 (m,

5H), 7.24-7.22 (m, 2H), 7.20-7.18 (m, 3H), 4.07 (s, 1H), 2.36 (s, 3H), 0.89 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 215.4, 197.6, 141.3, 134.9, 134.7, 130.3, 128.9, 128.7(2), 128.6(8), 128.4, 128.1, 128.0(1), 127.9(6), 127.5, 126.3, 113.7, 52.5, 35.1, 28.3, 27.1. HRMS (ESI) [M+ Na]⁺: calculated for C₂₈H₂₈ONa: 403.2038, found 403.2039.

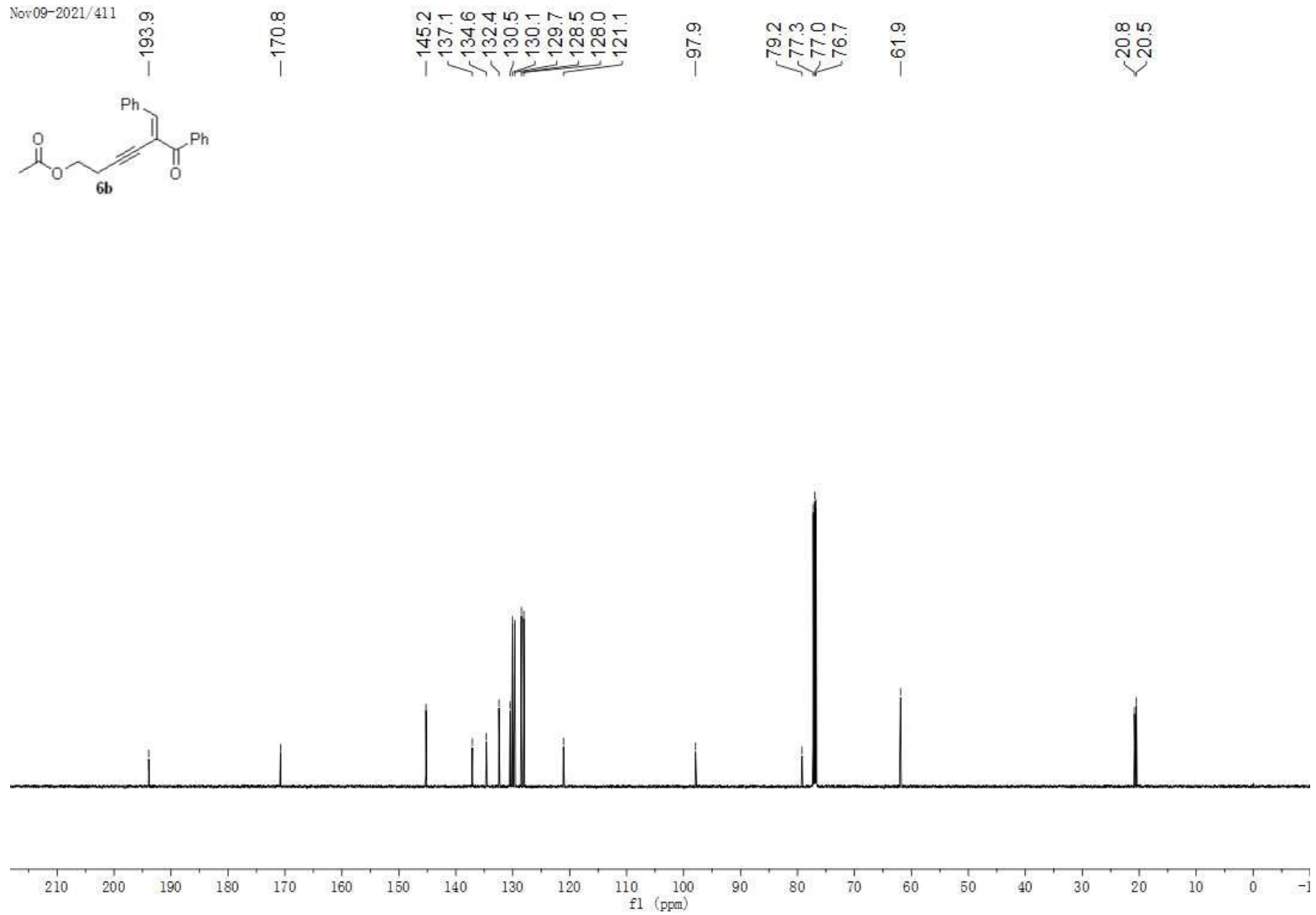
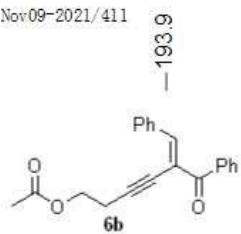
6 Reference

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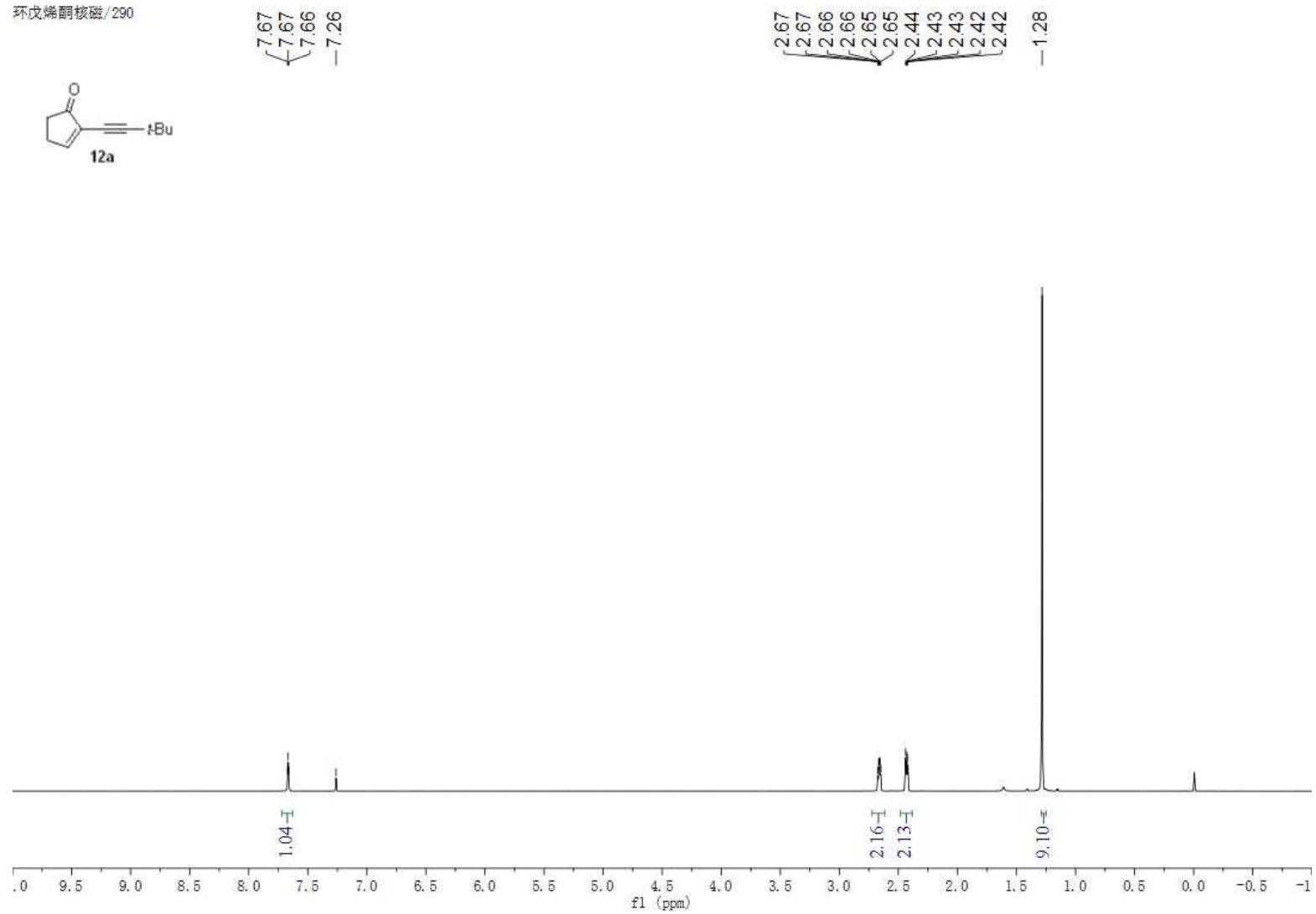
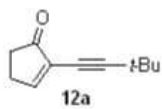
7 NMR spectra of new compound



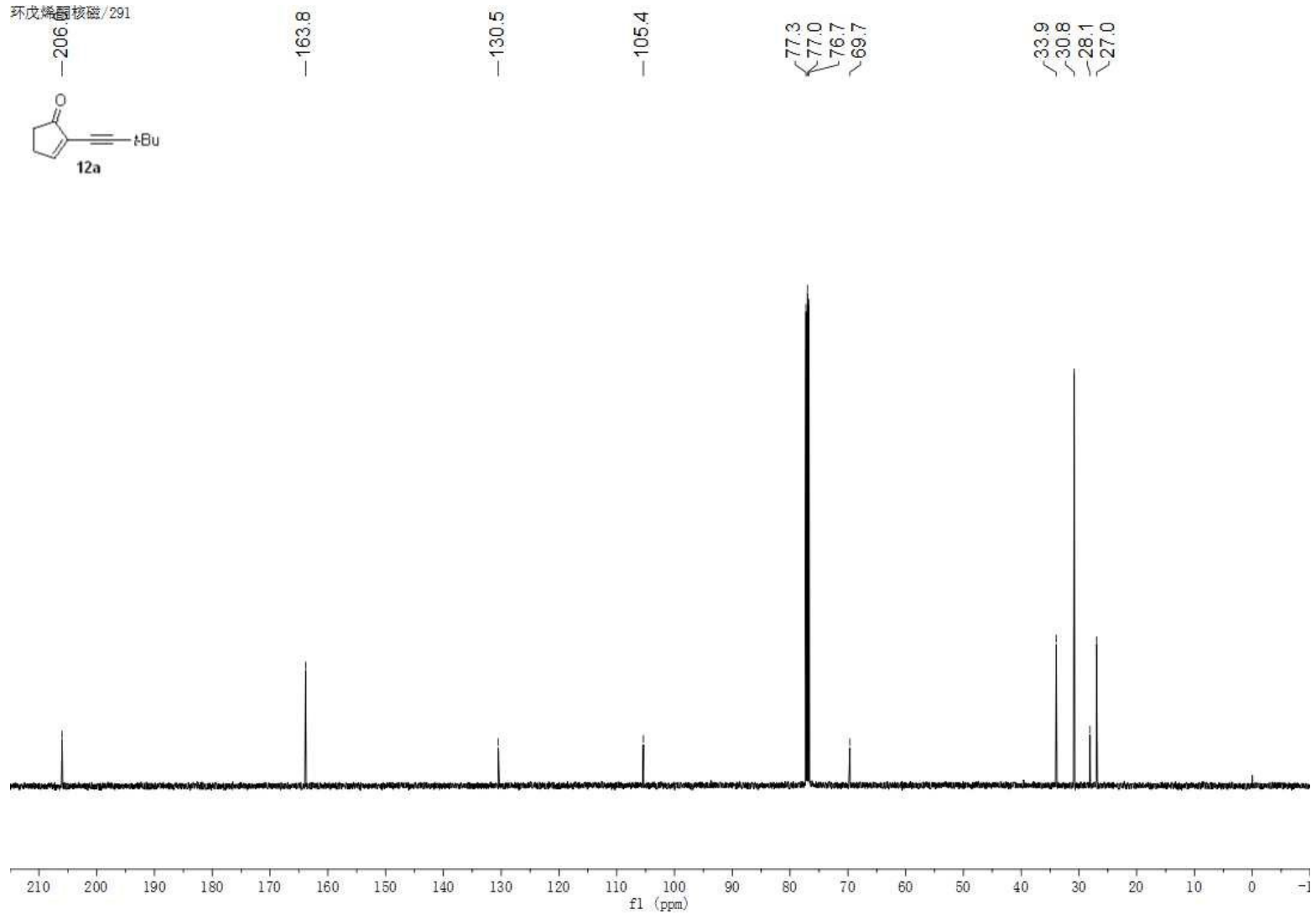
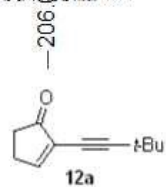
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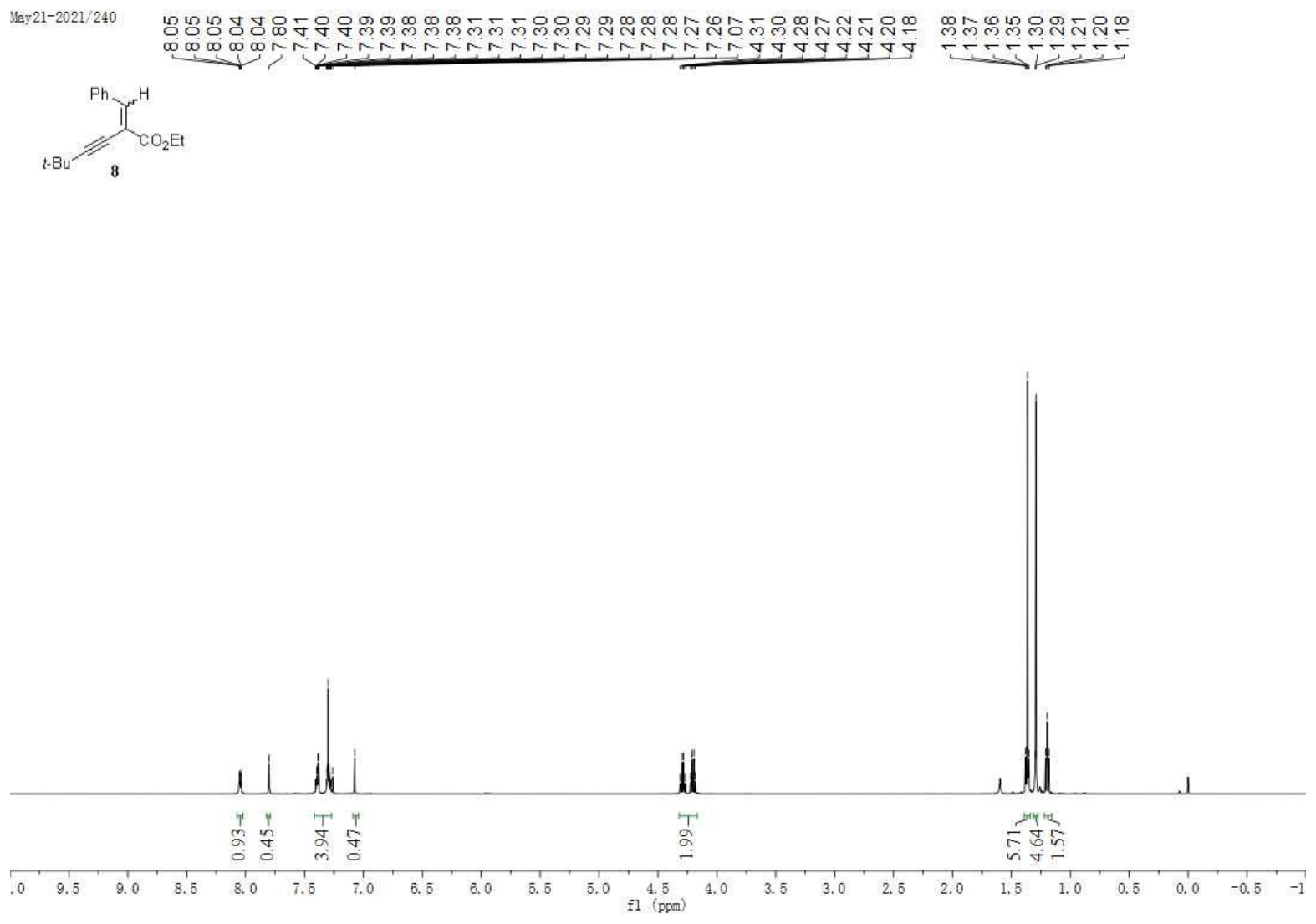
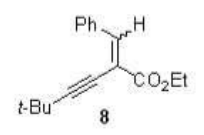
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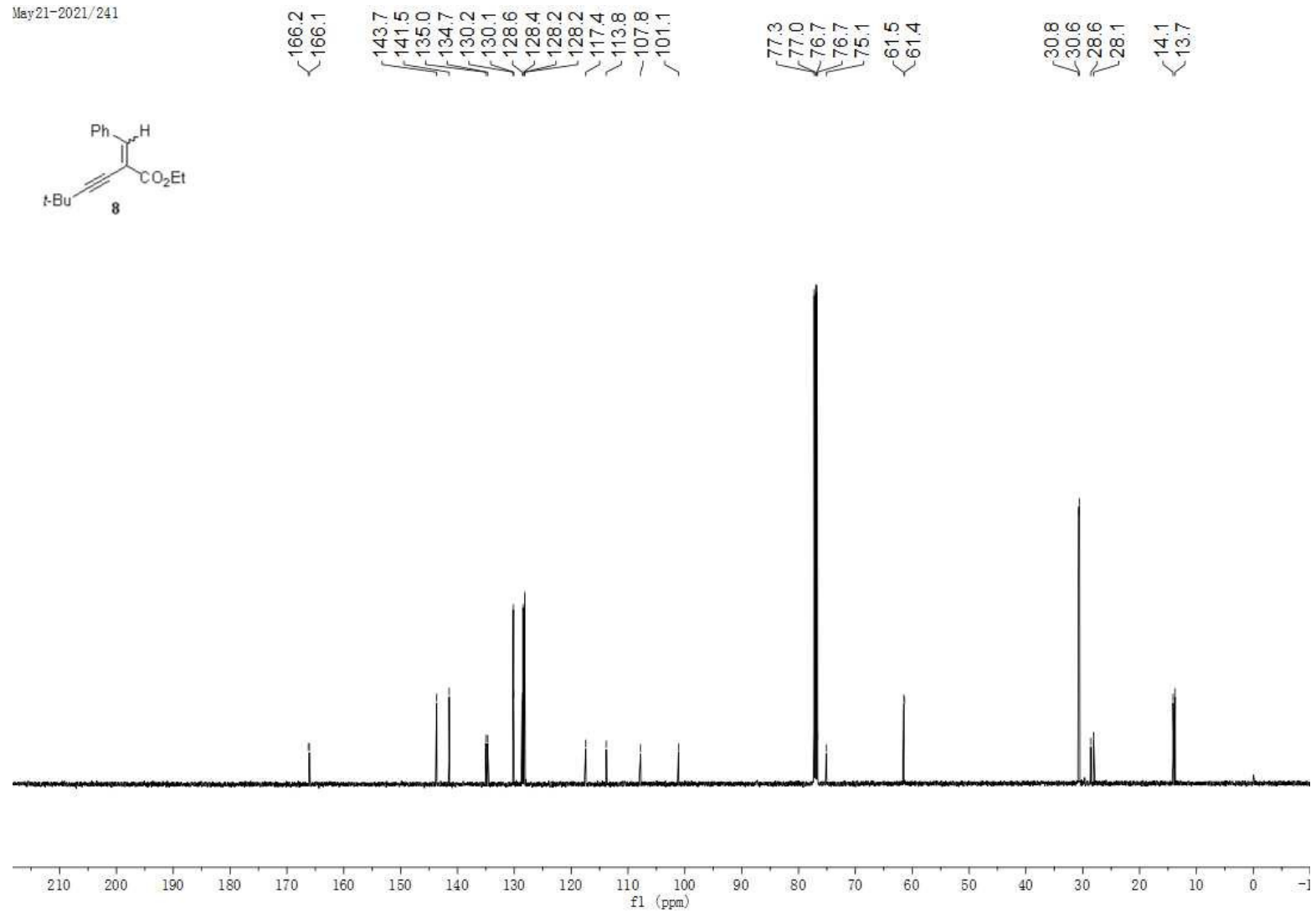
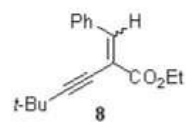
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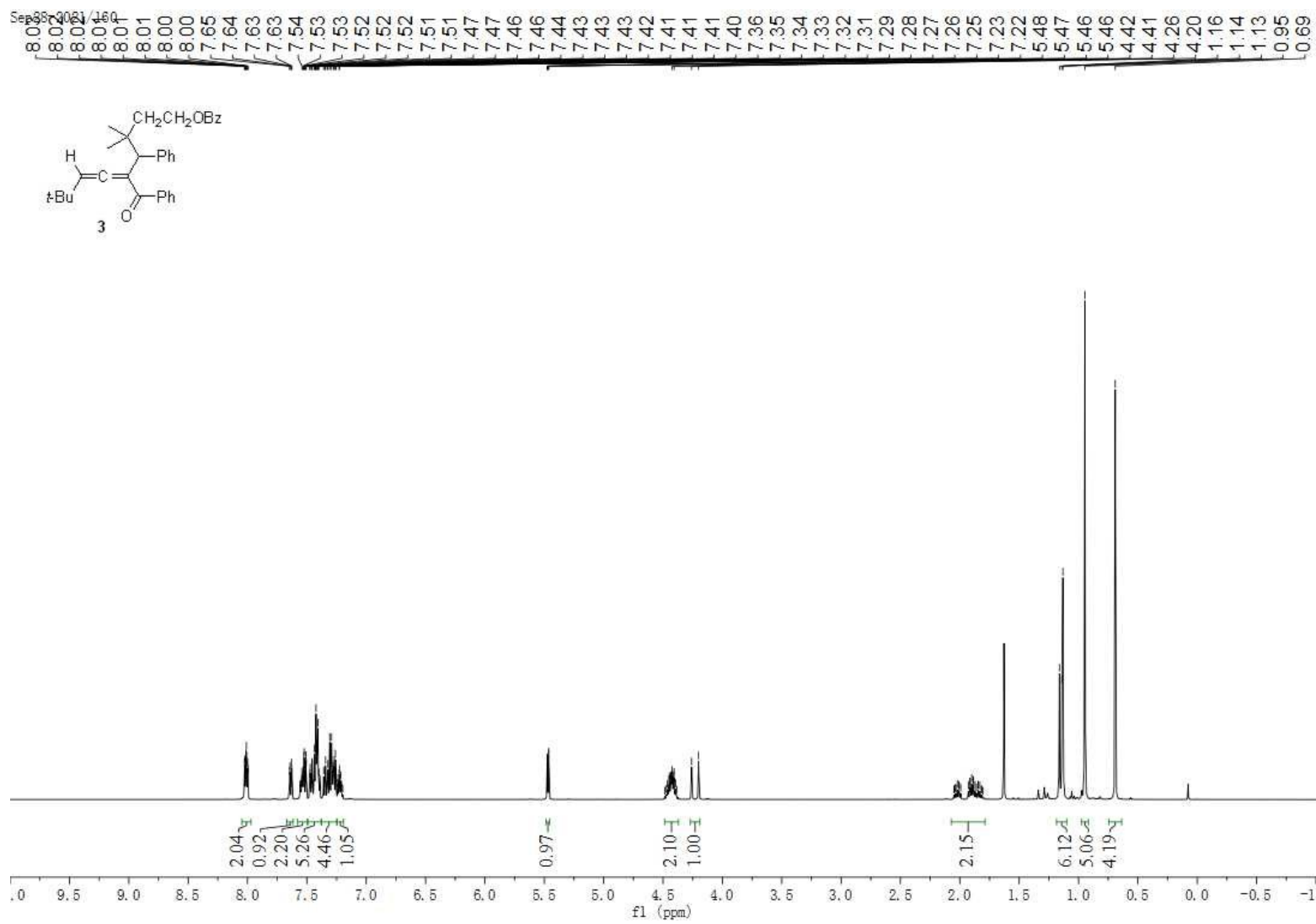


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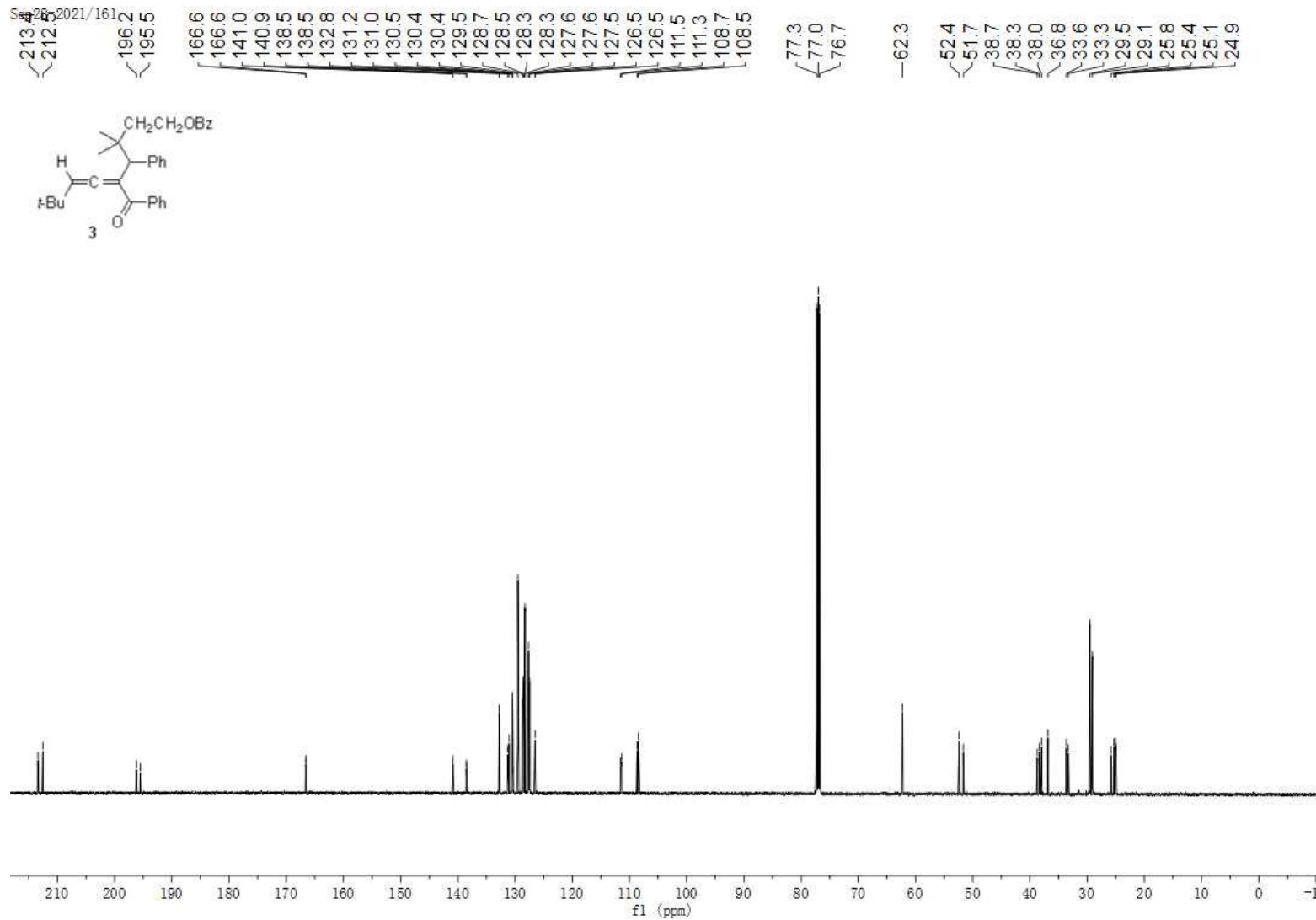
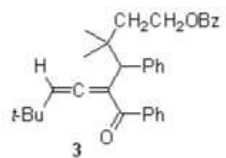


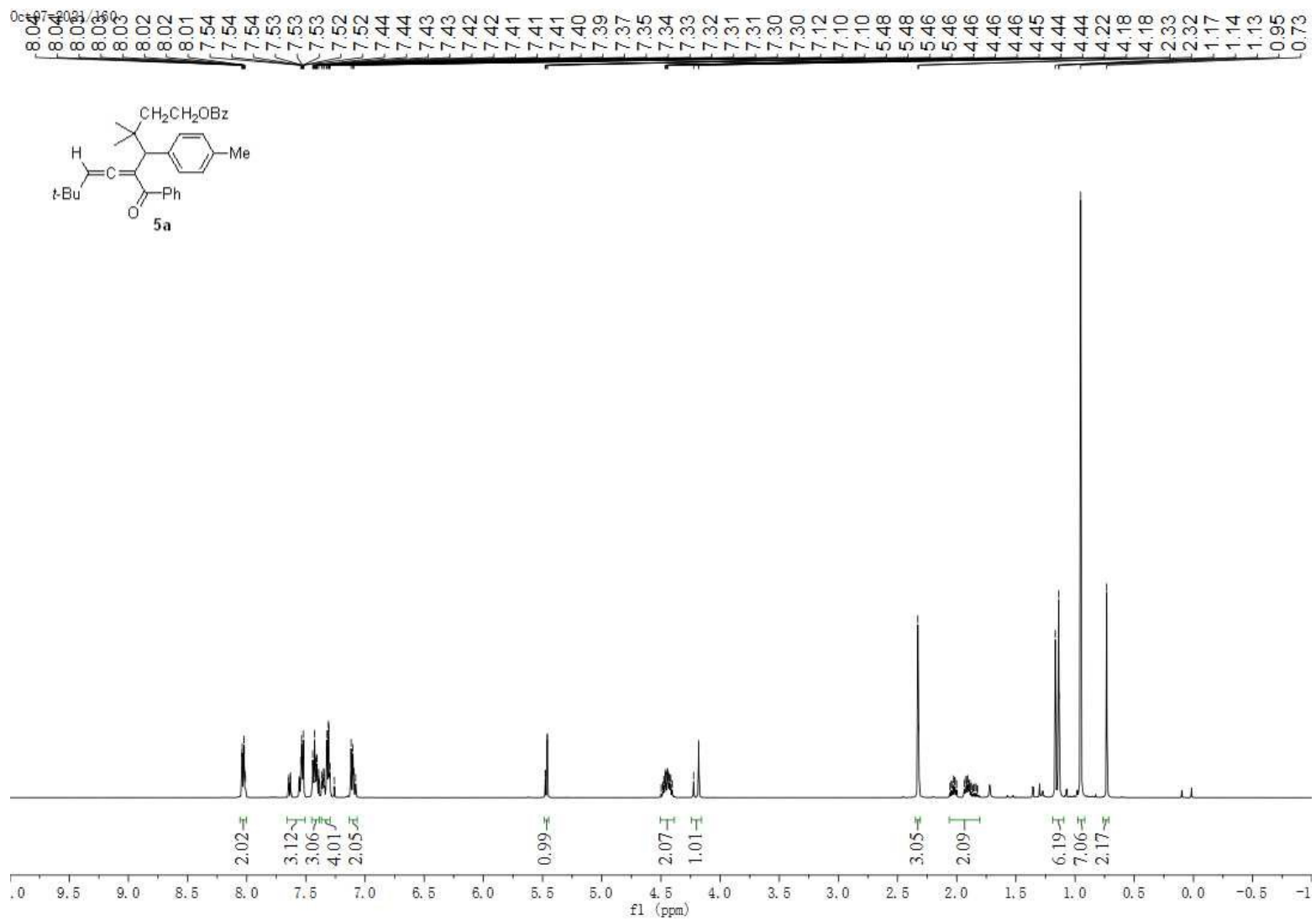
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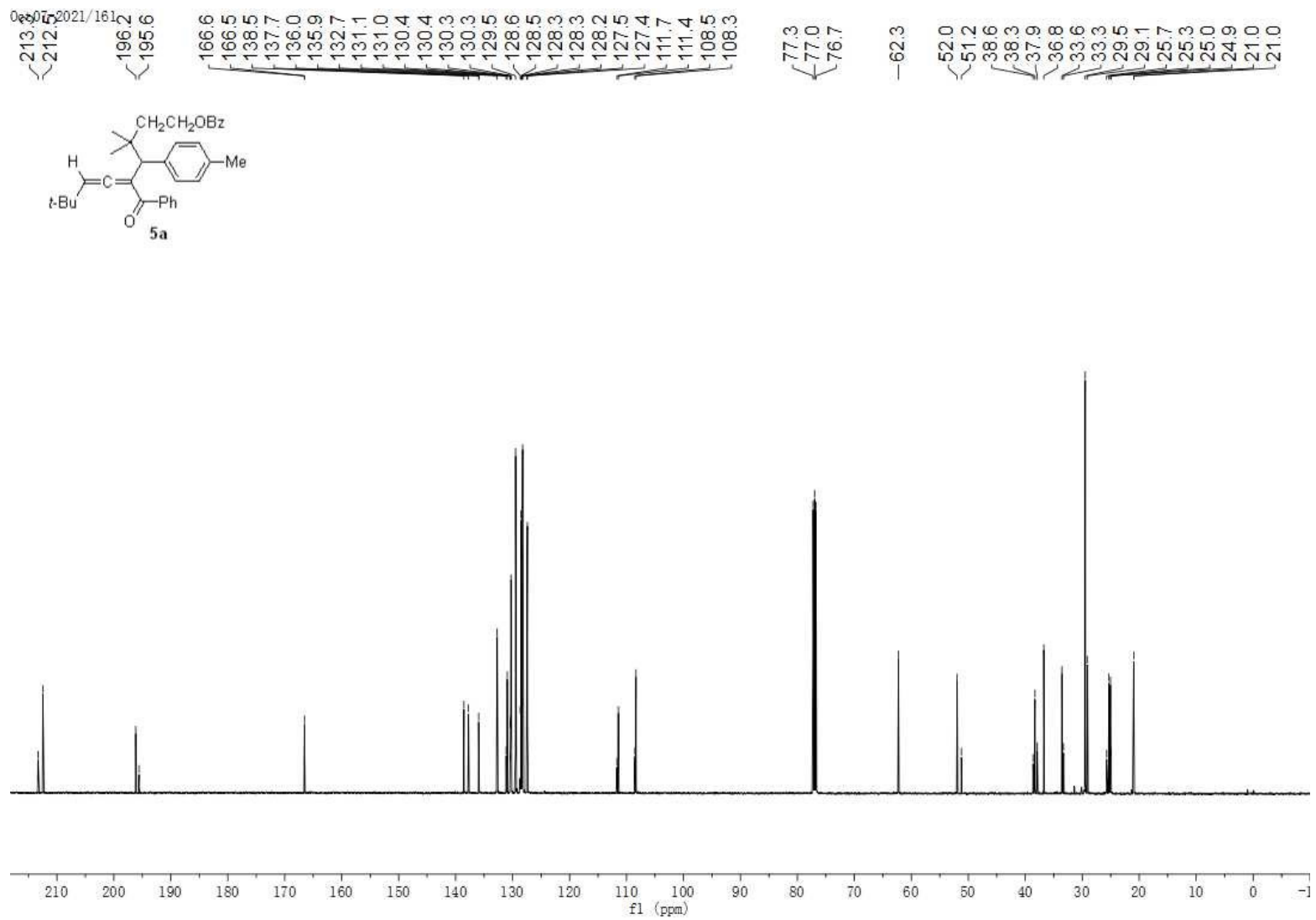


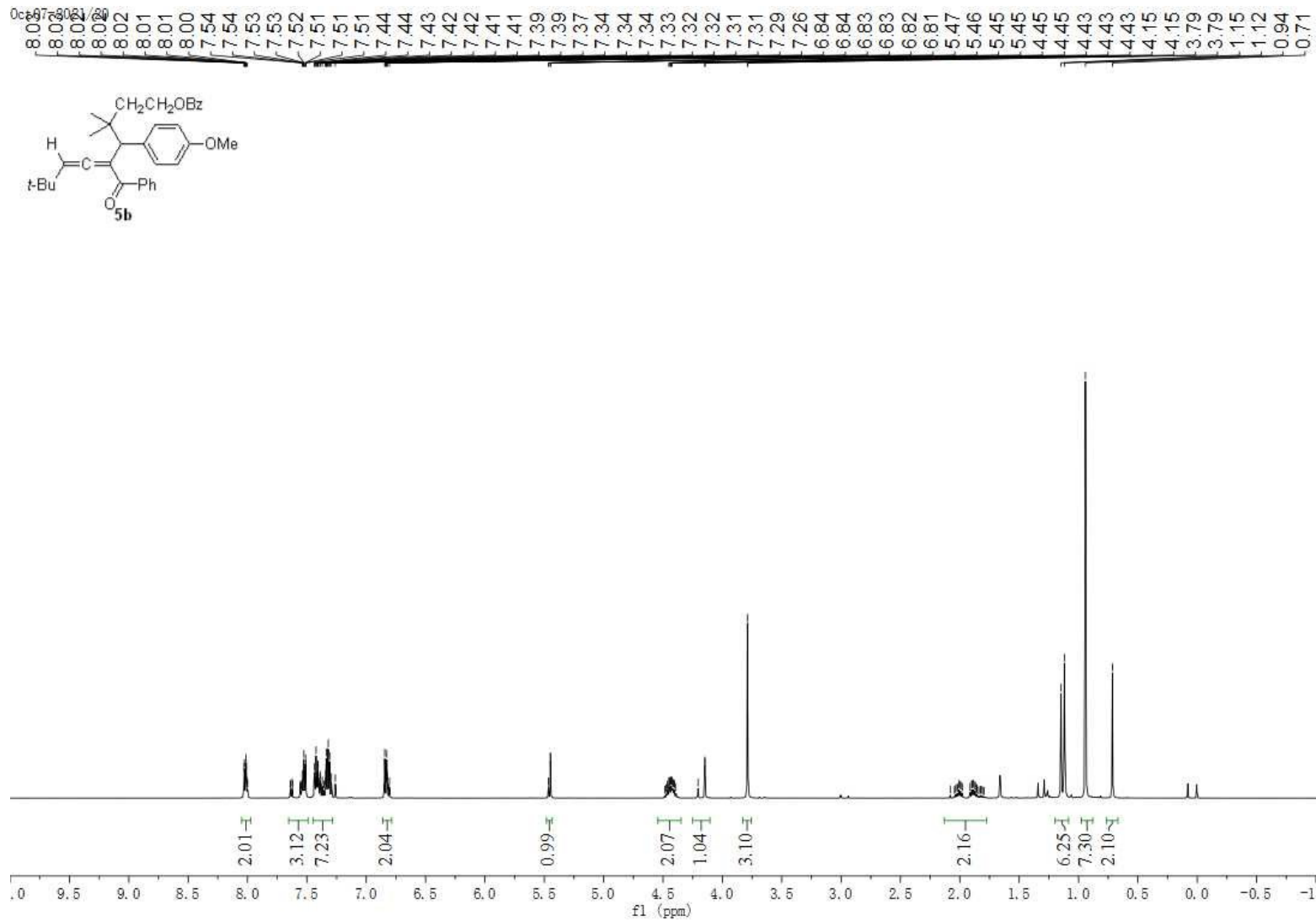


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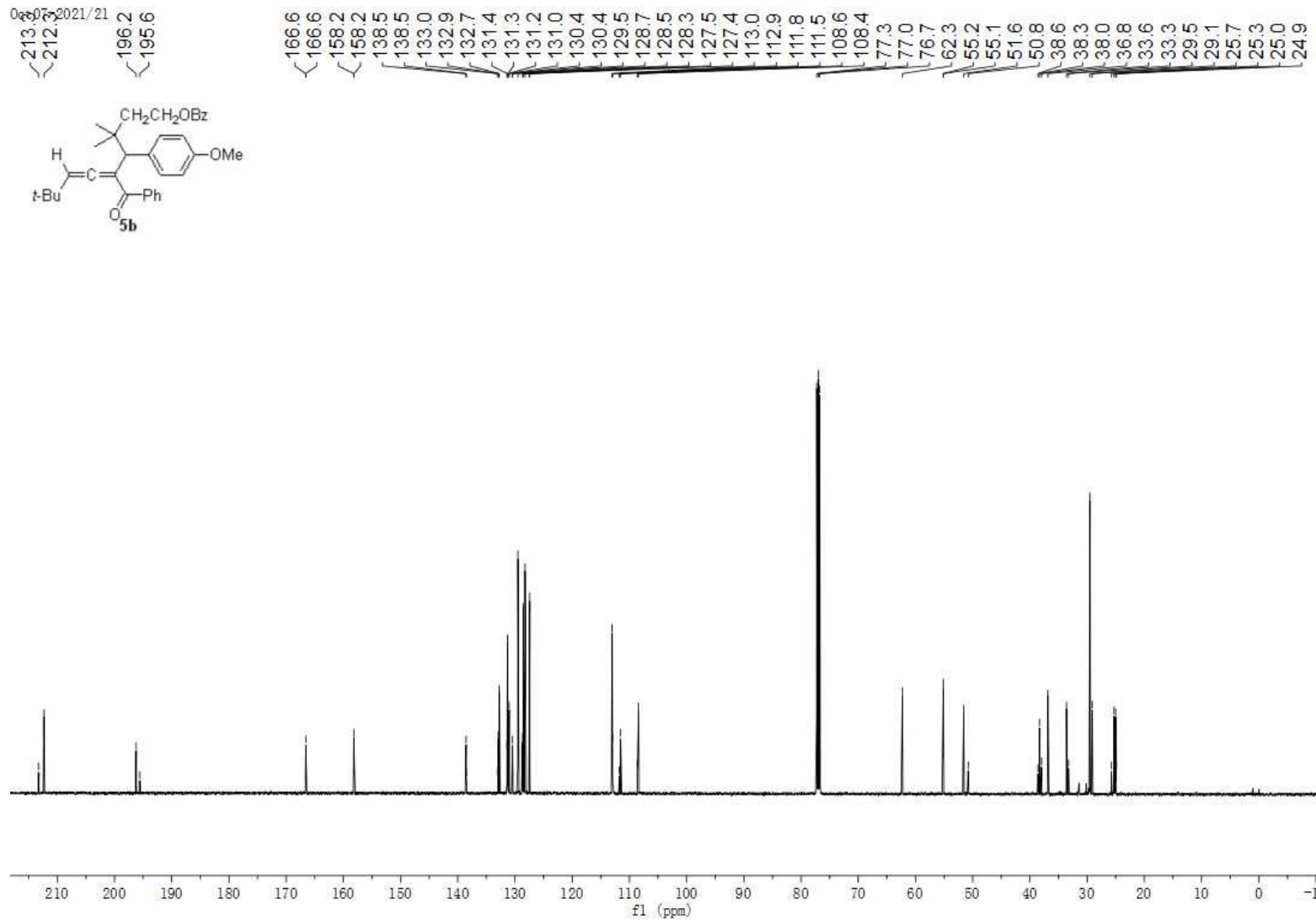
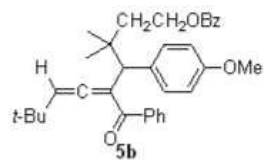


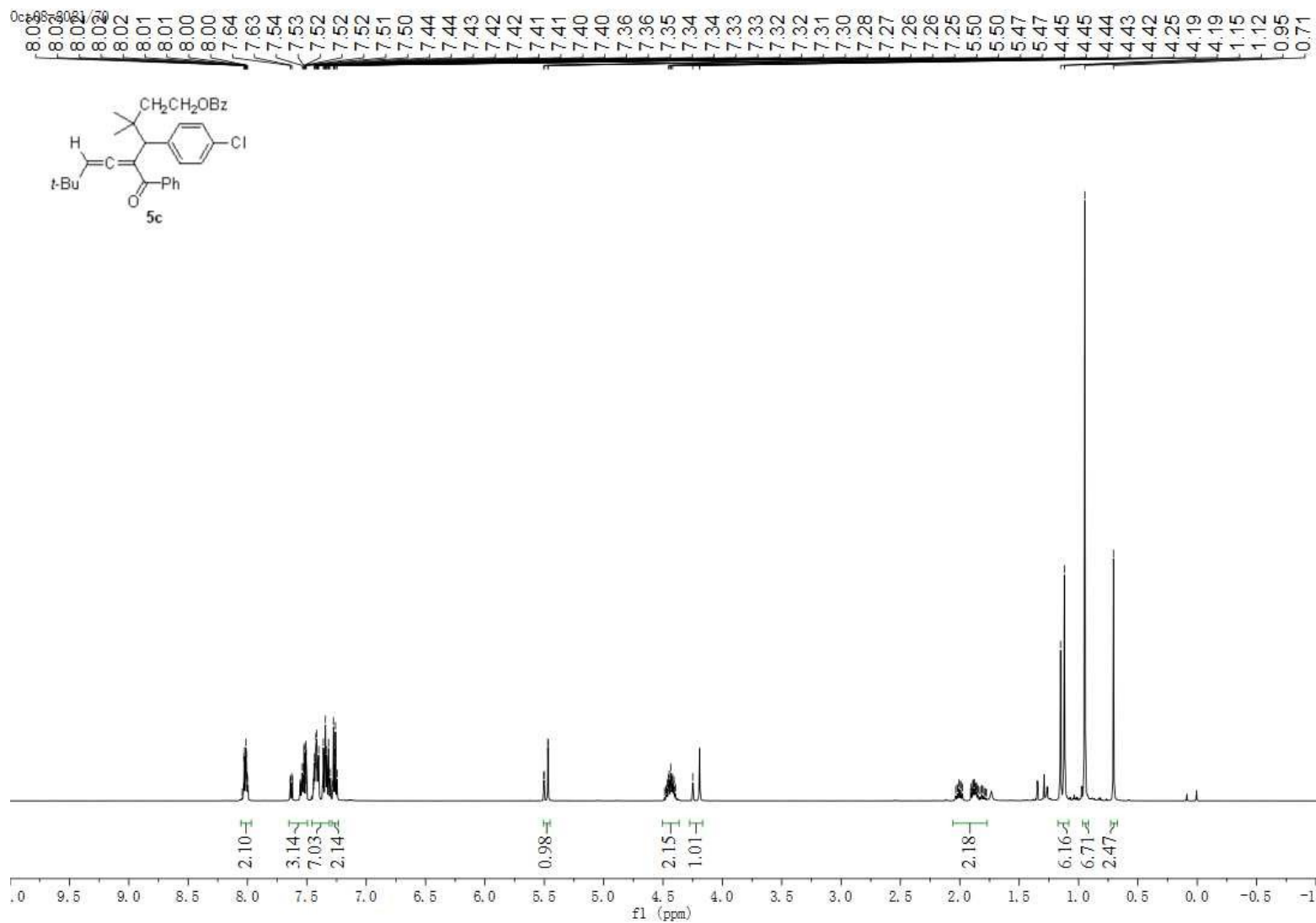




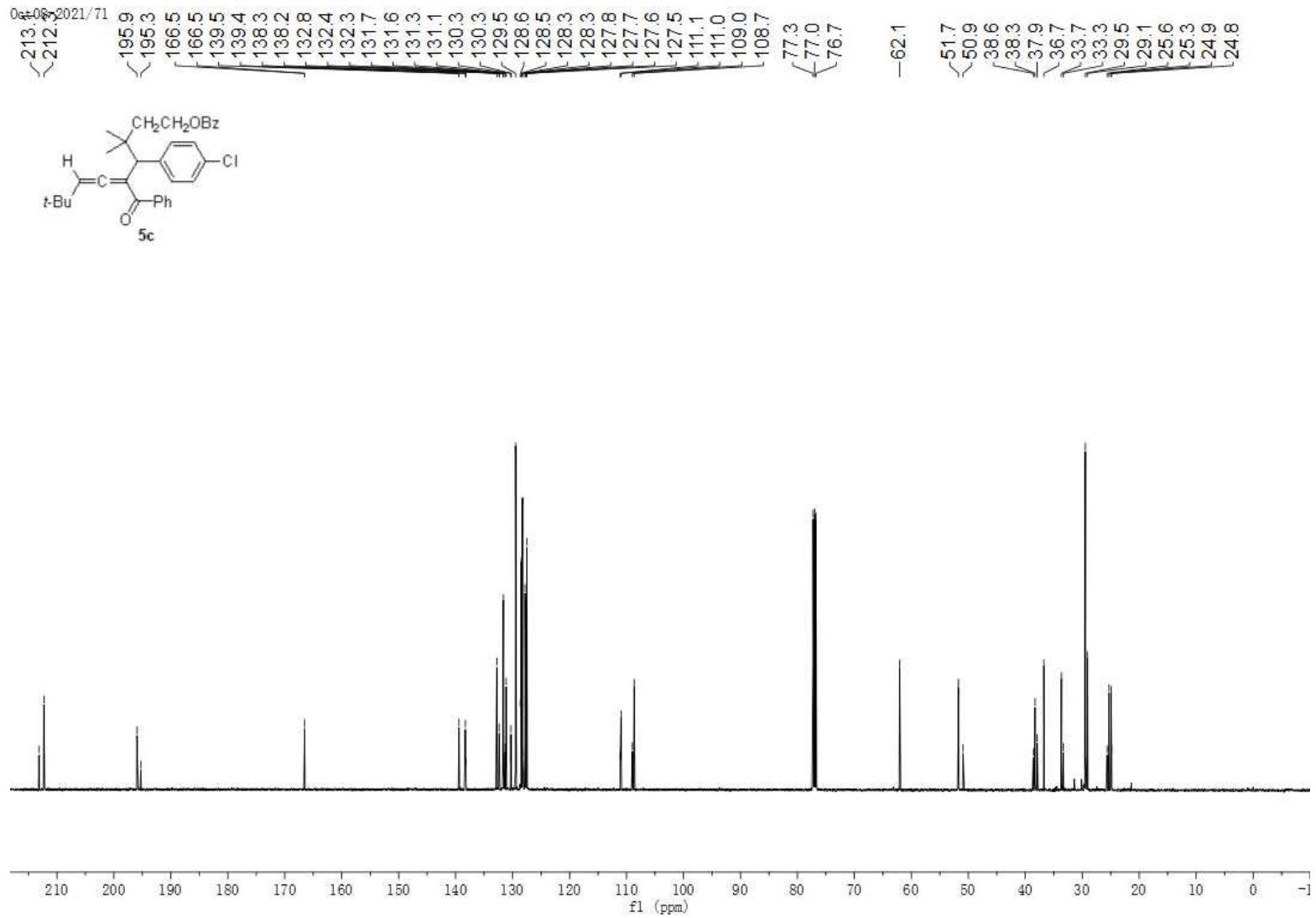


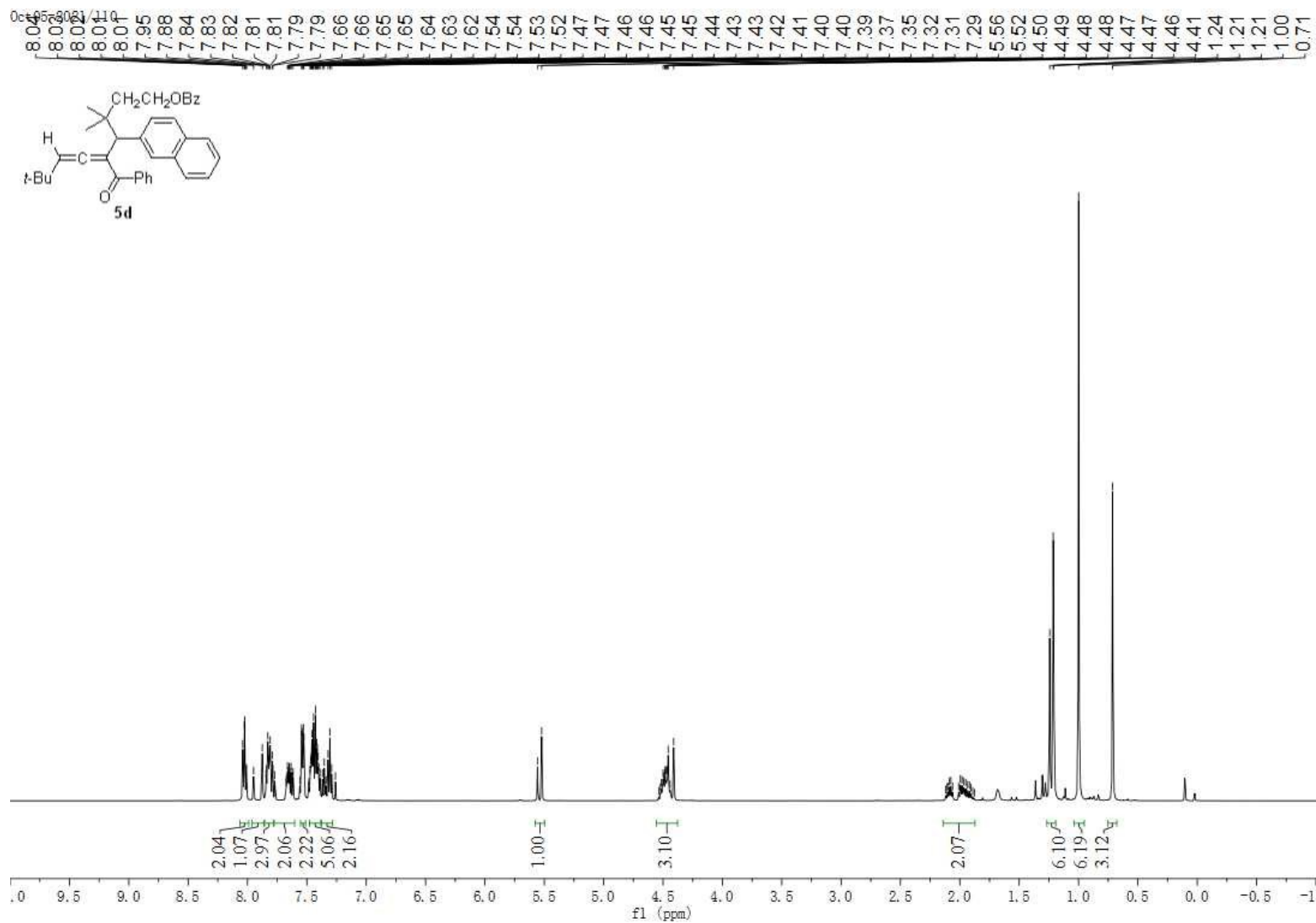
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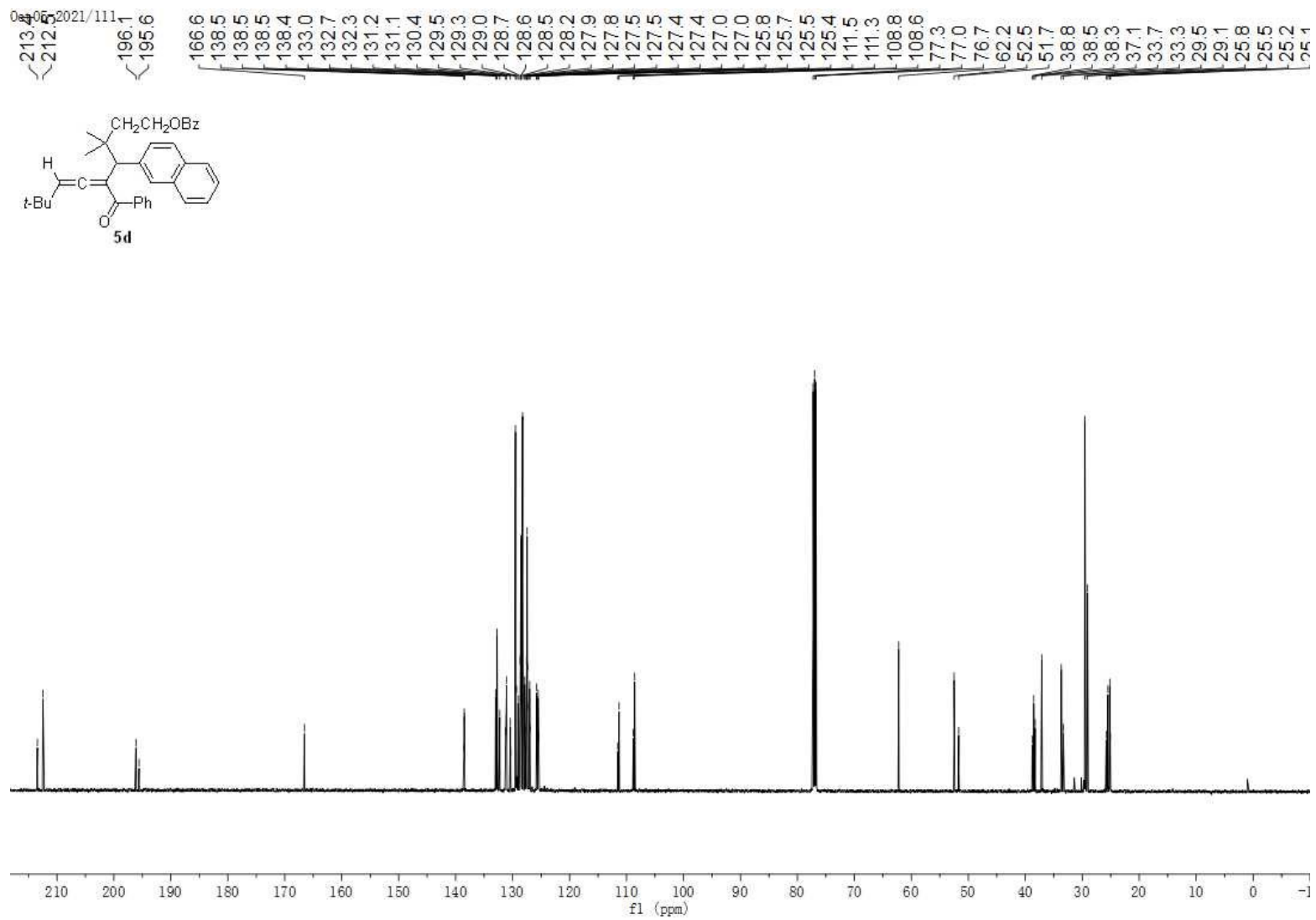


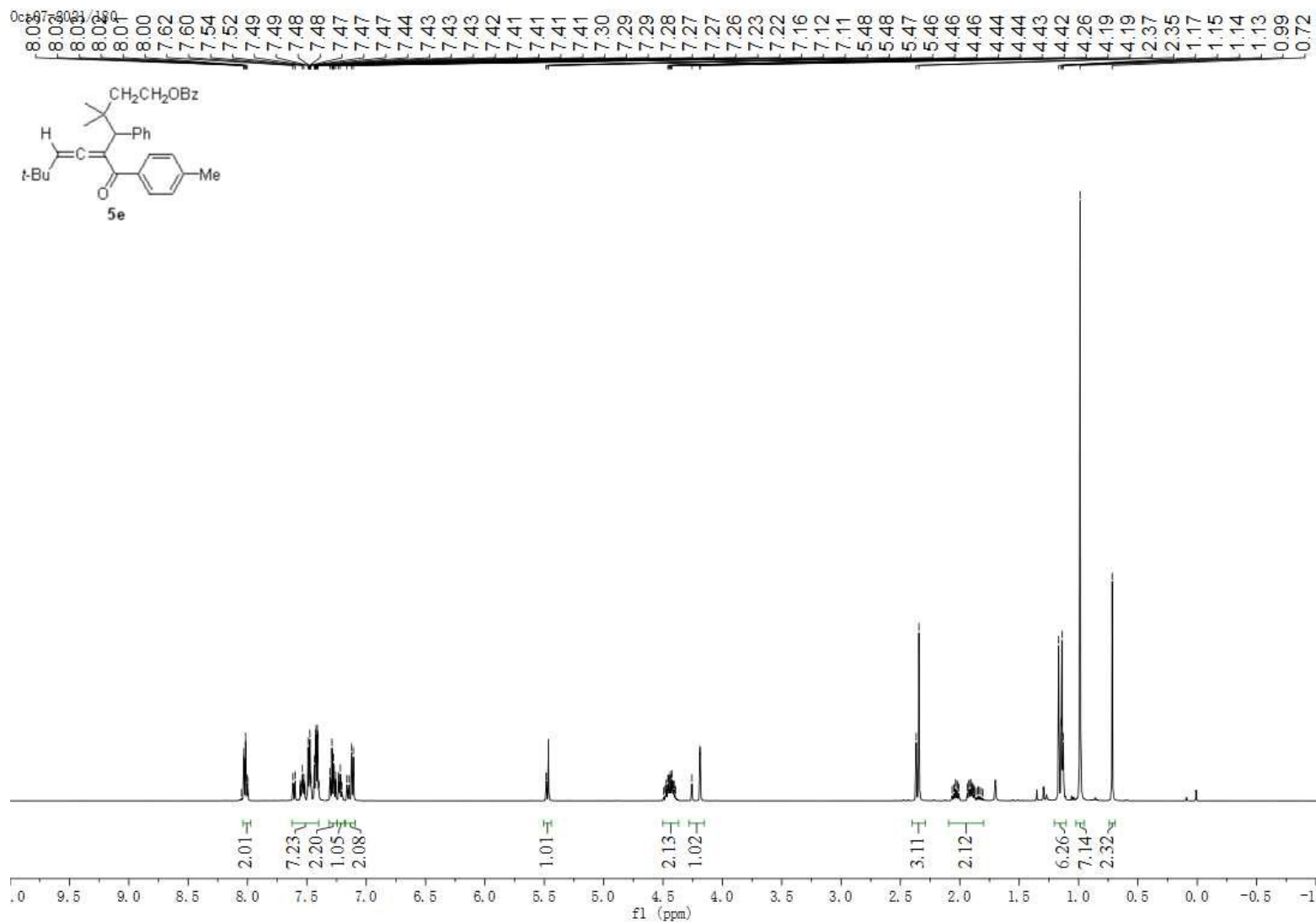


04-08-2021/71

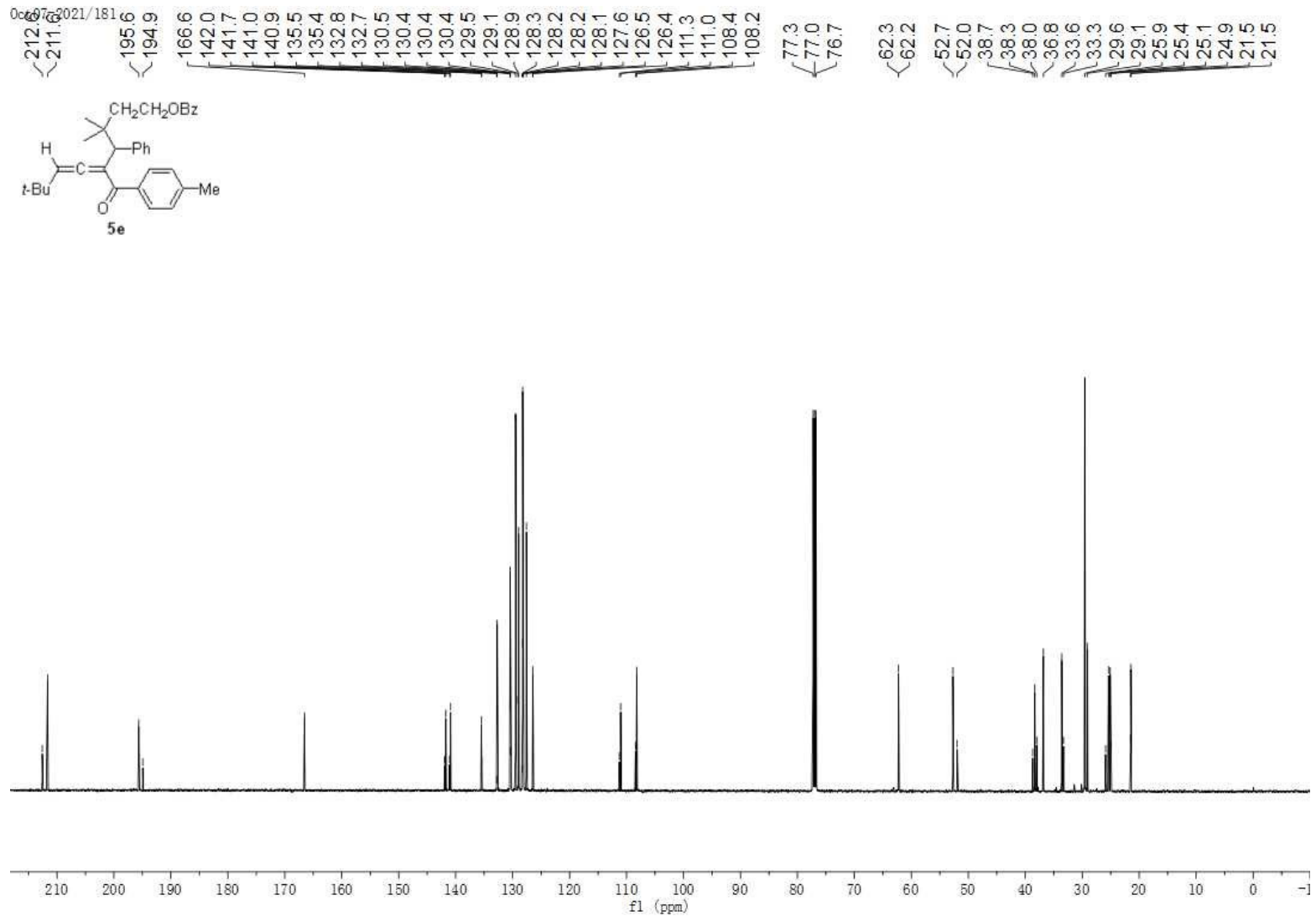
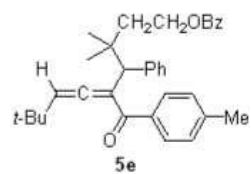


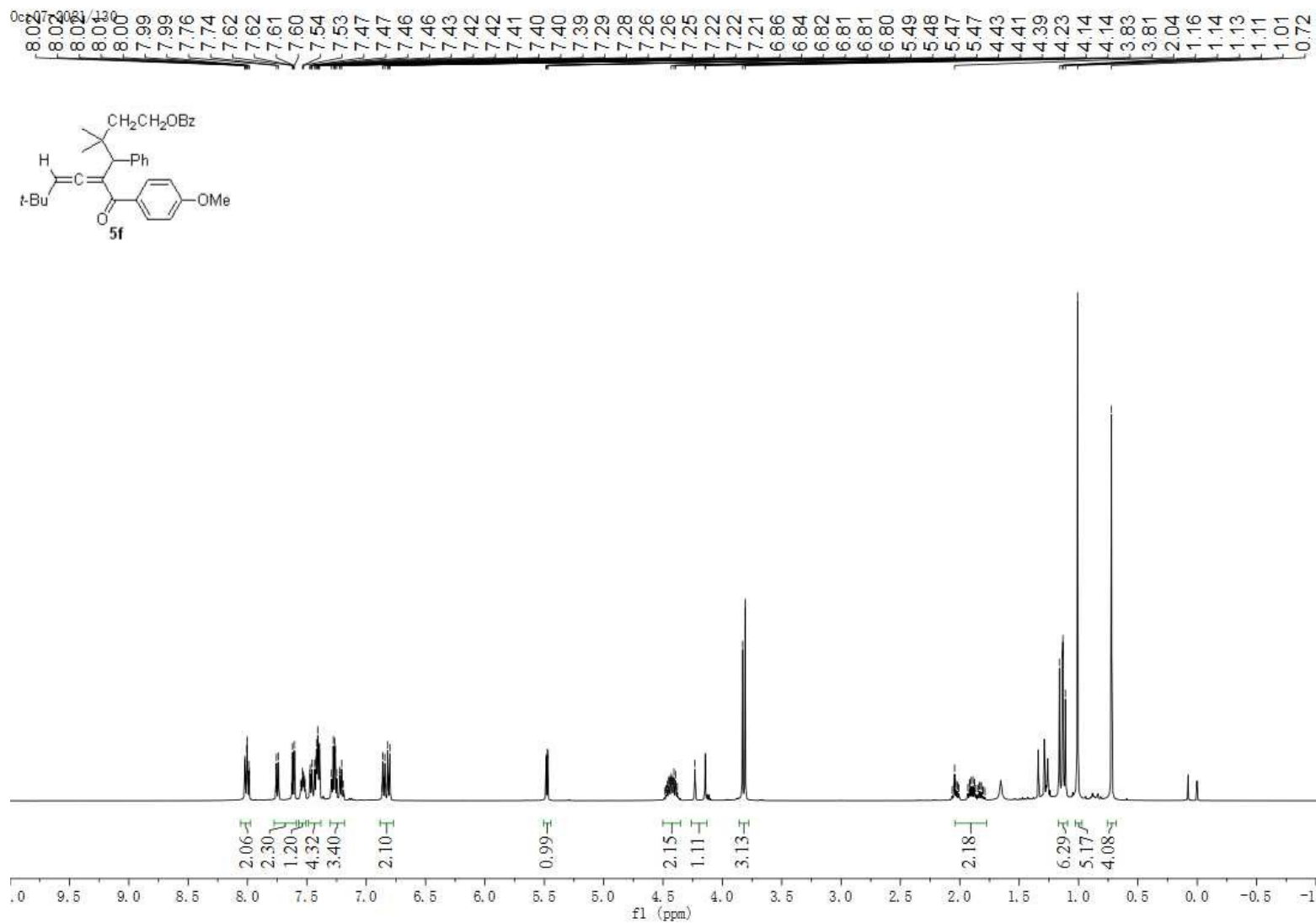




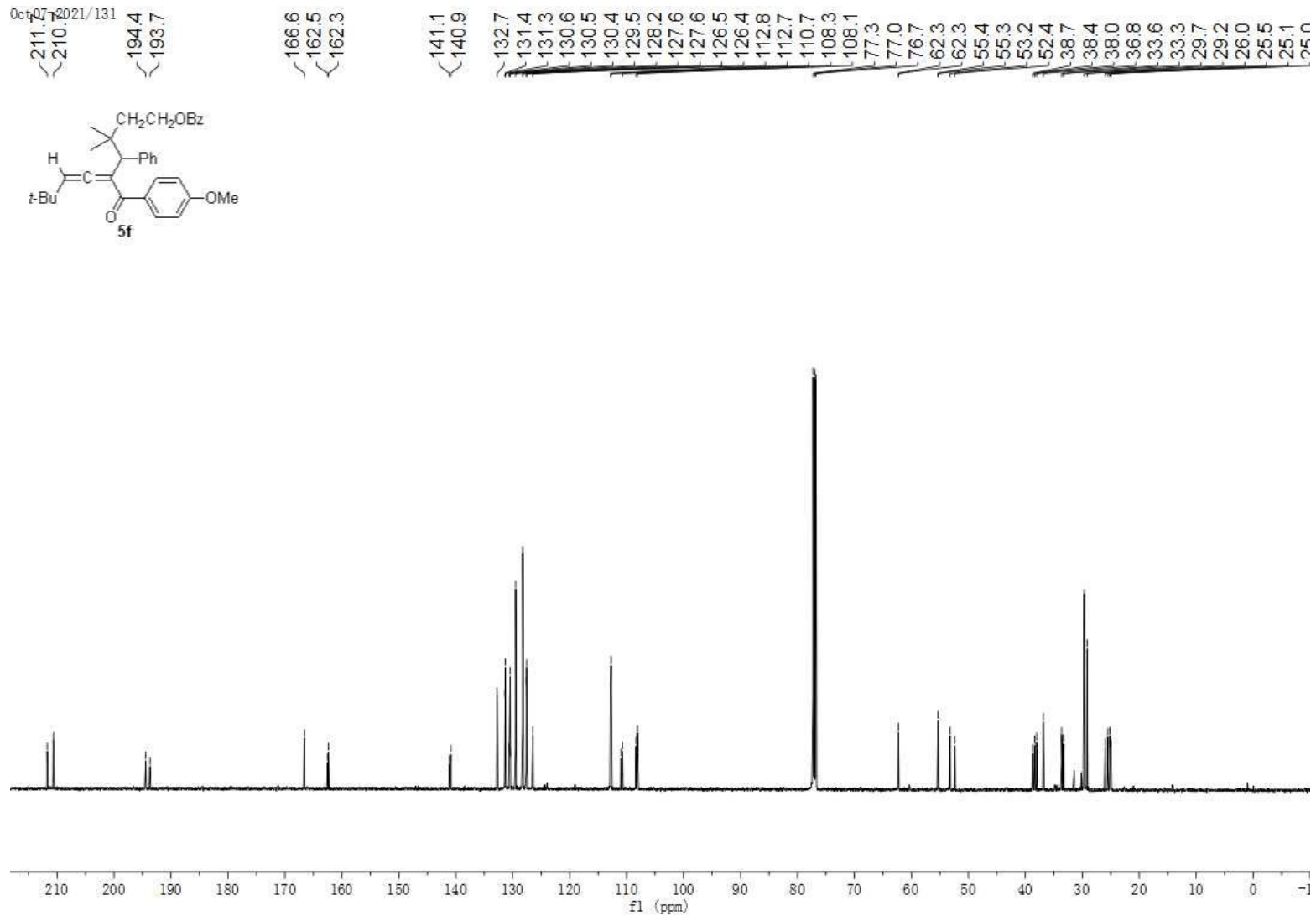
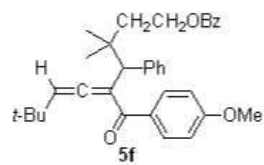


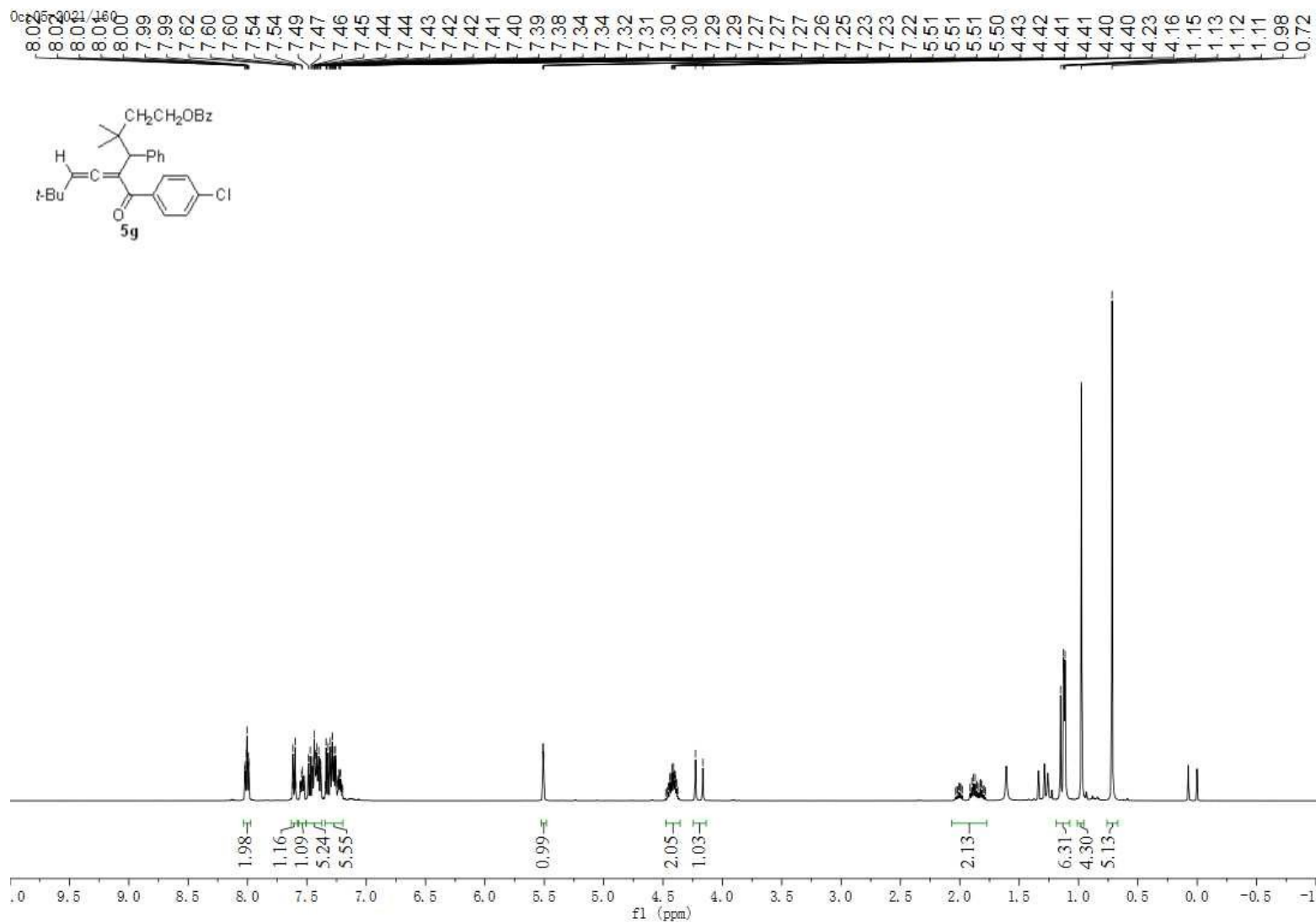
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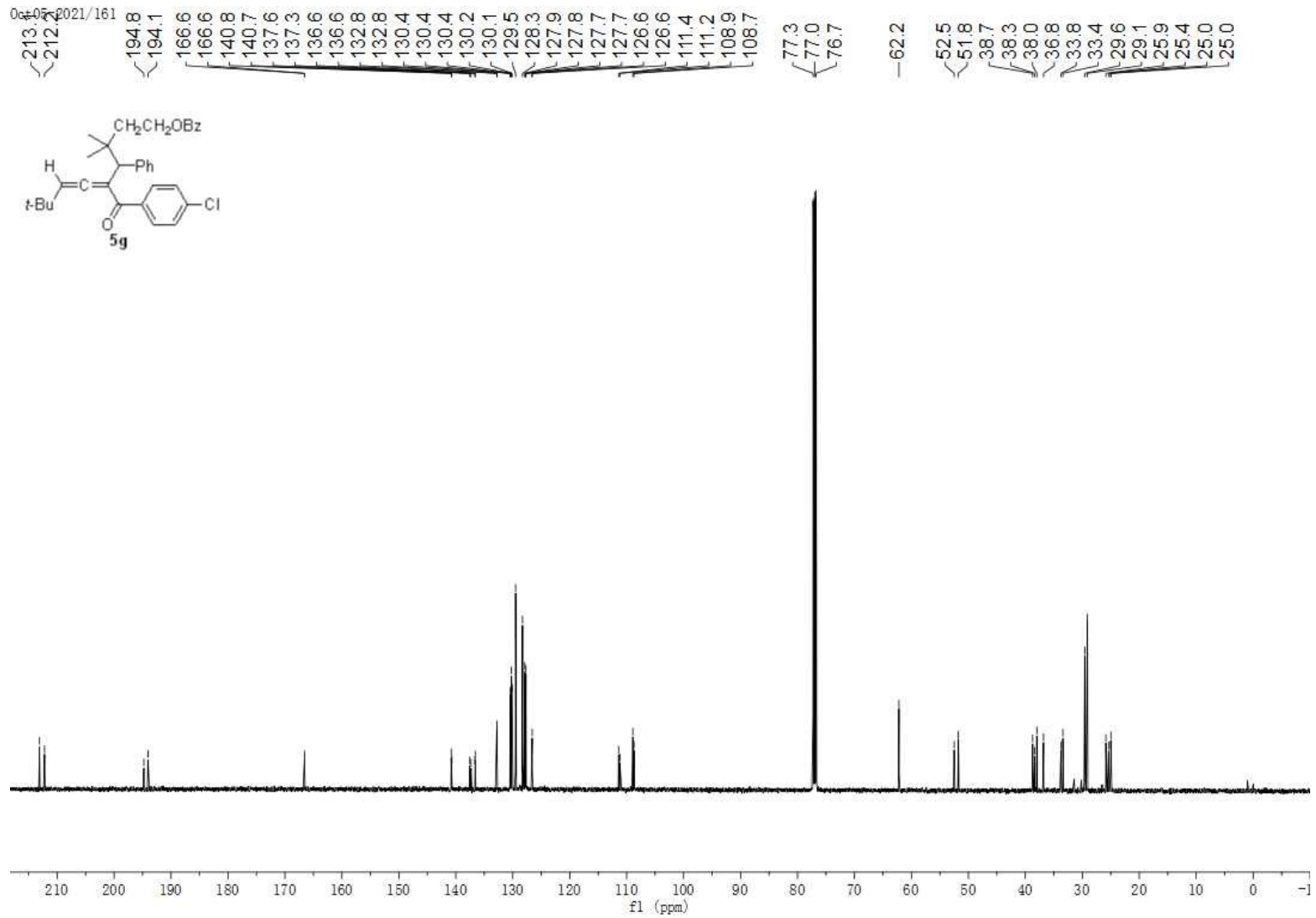


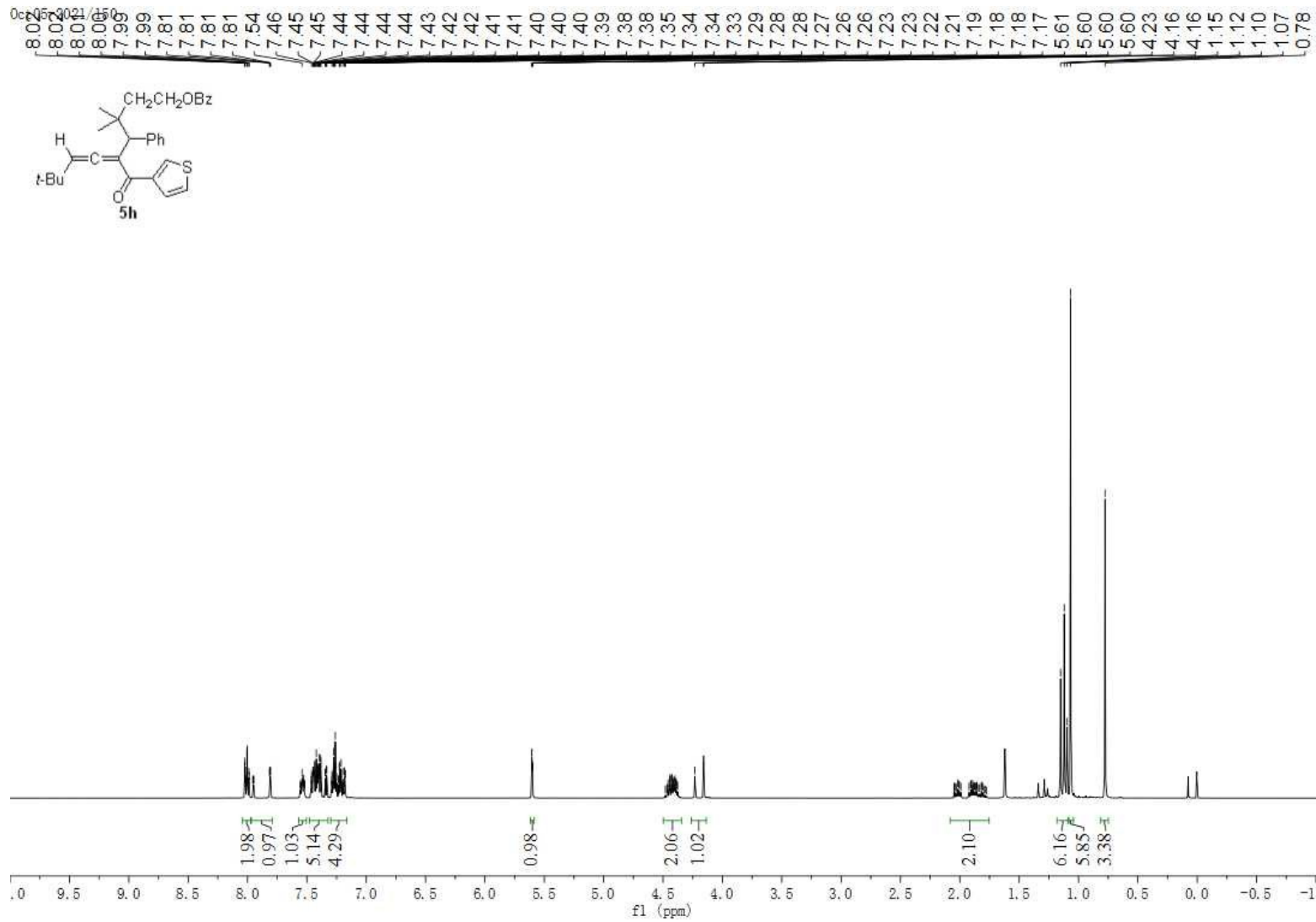
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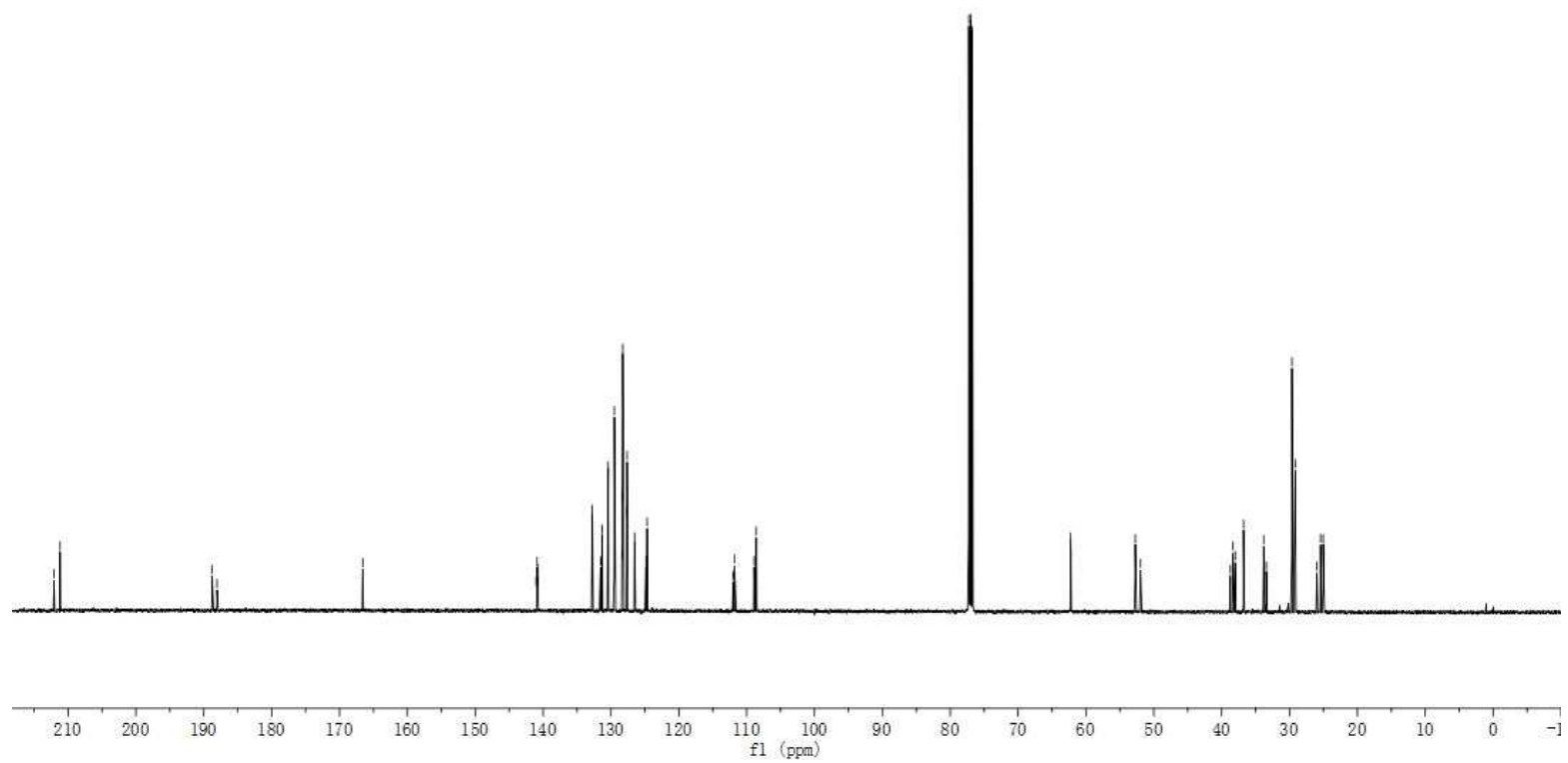
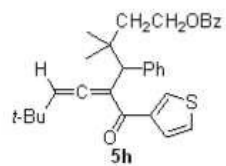
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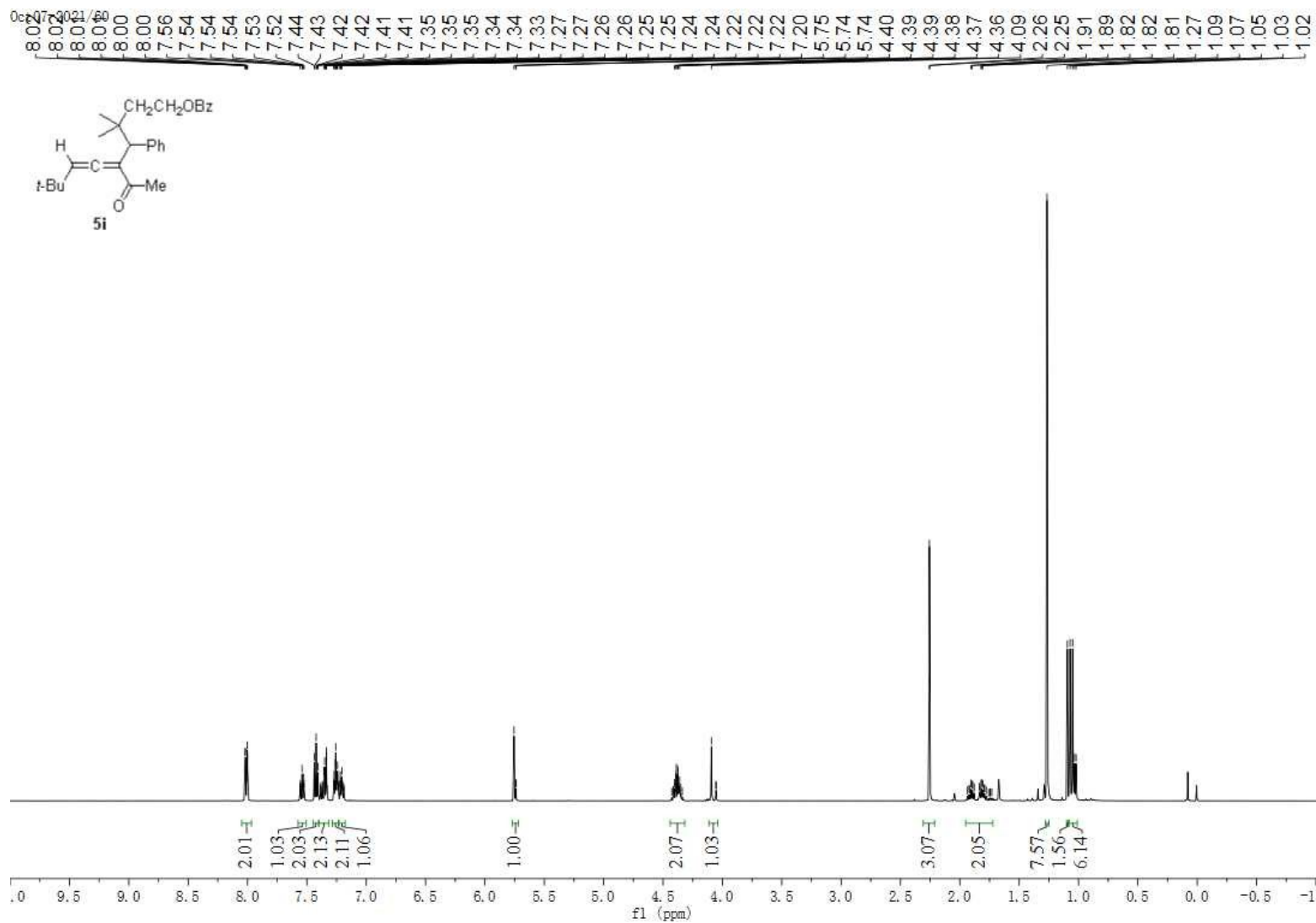
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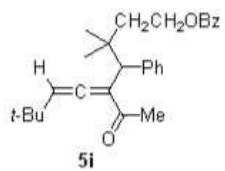
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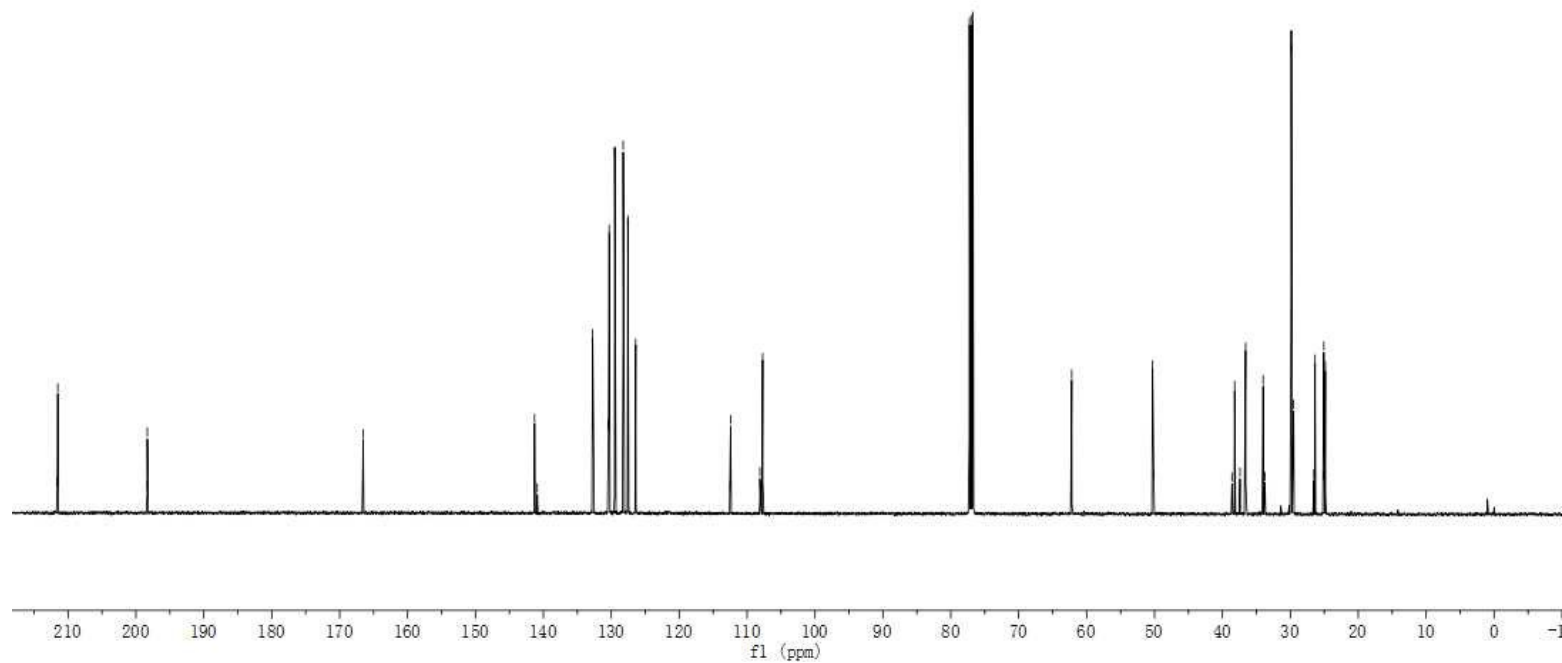
Oct 07 2021/61

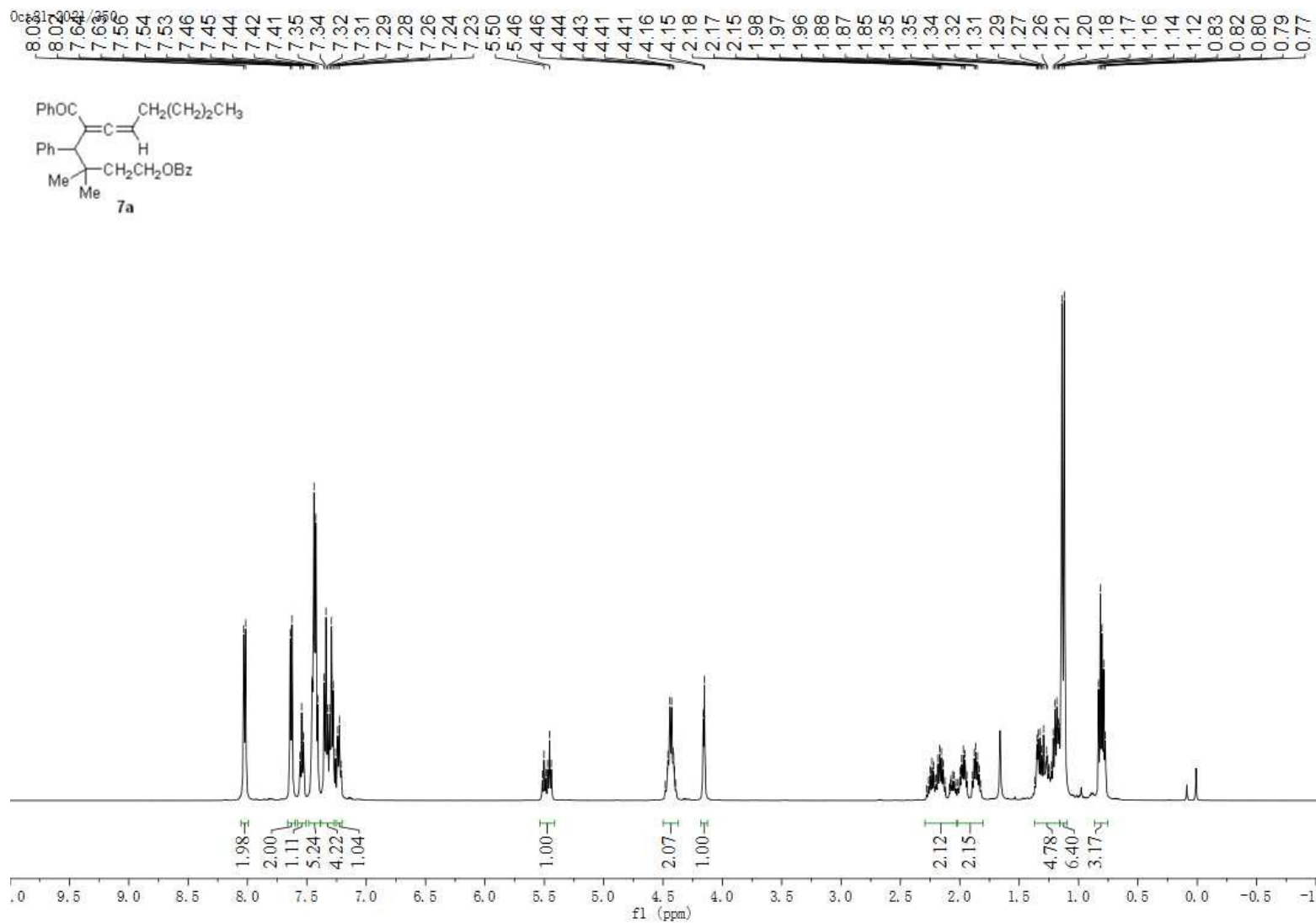
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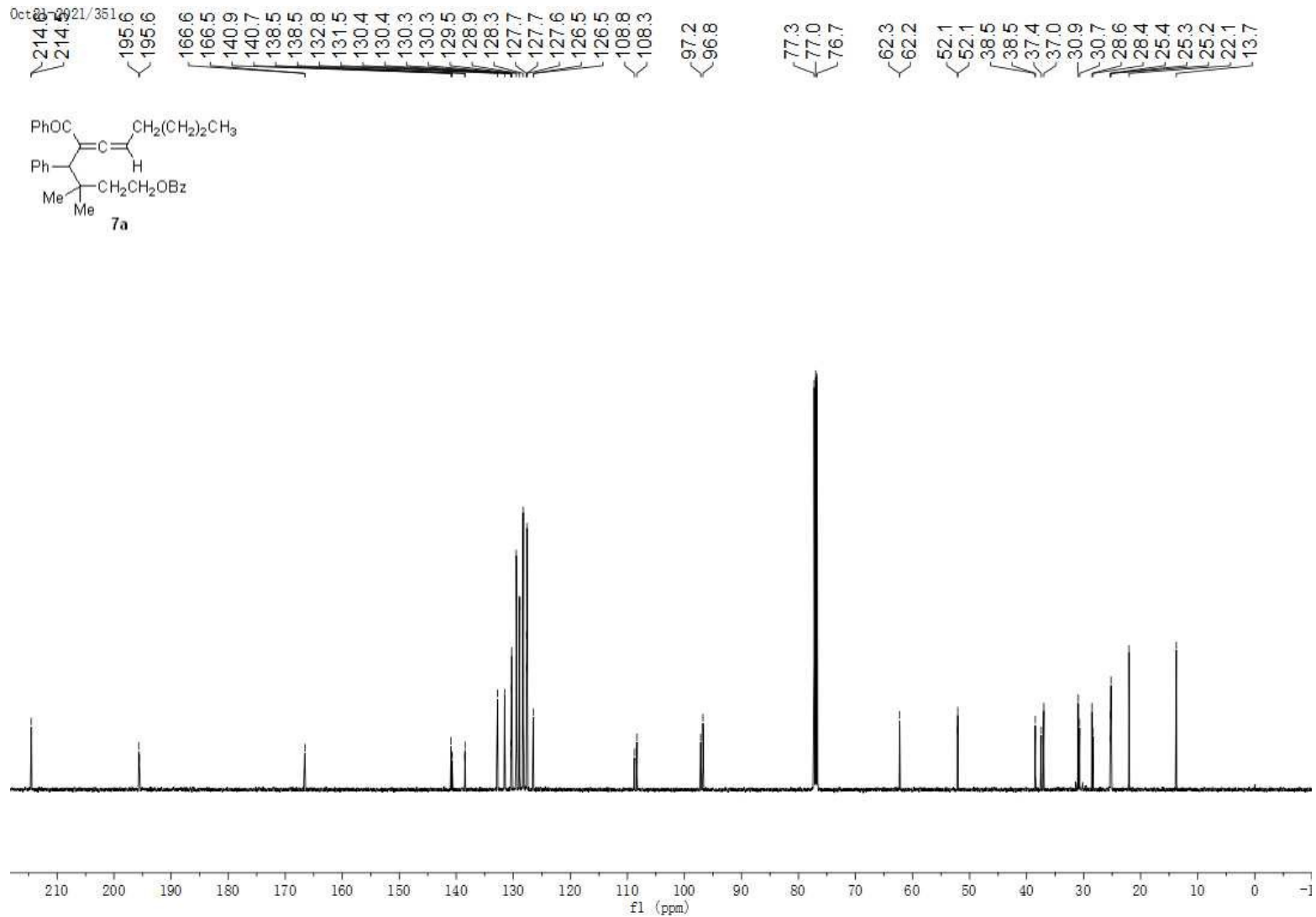
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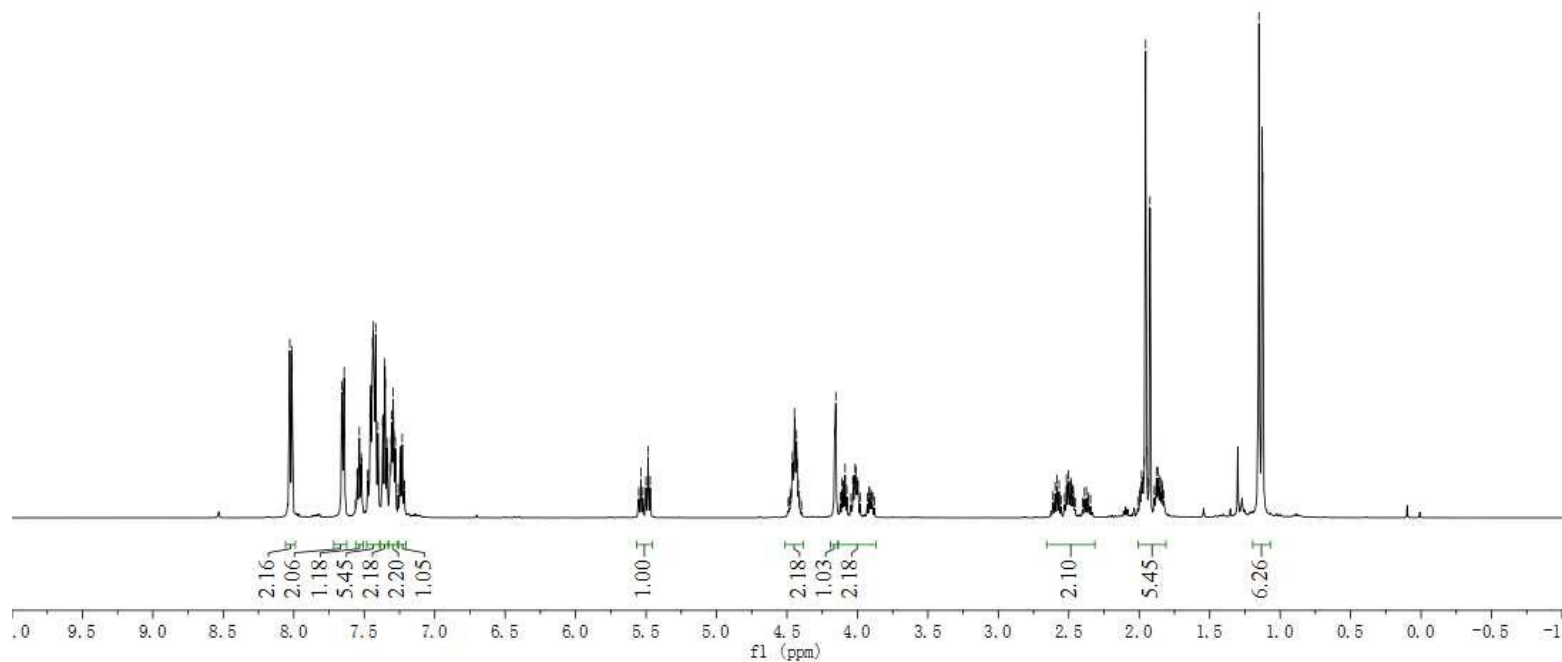
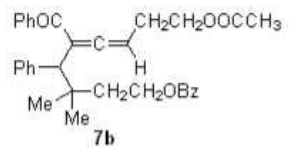




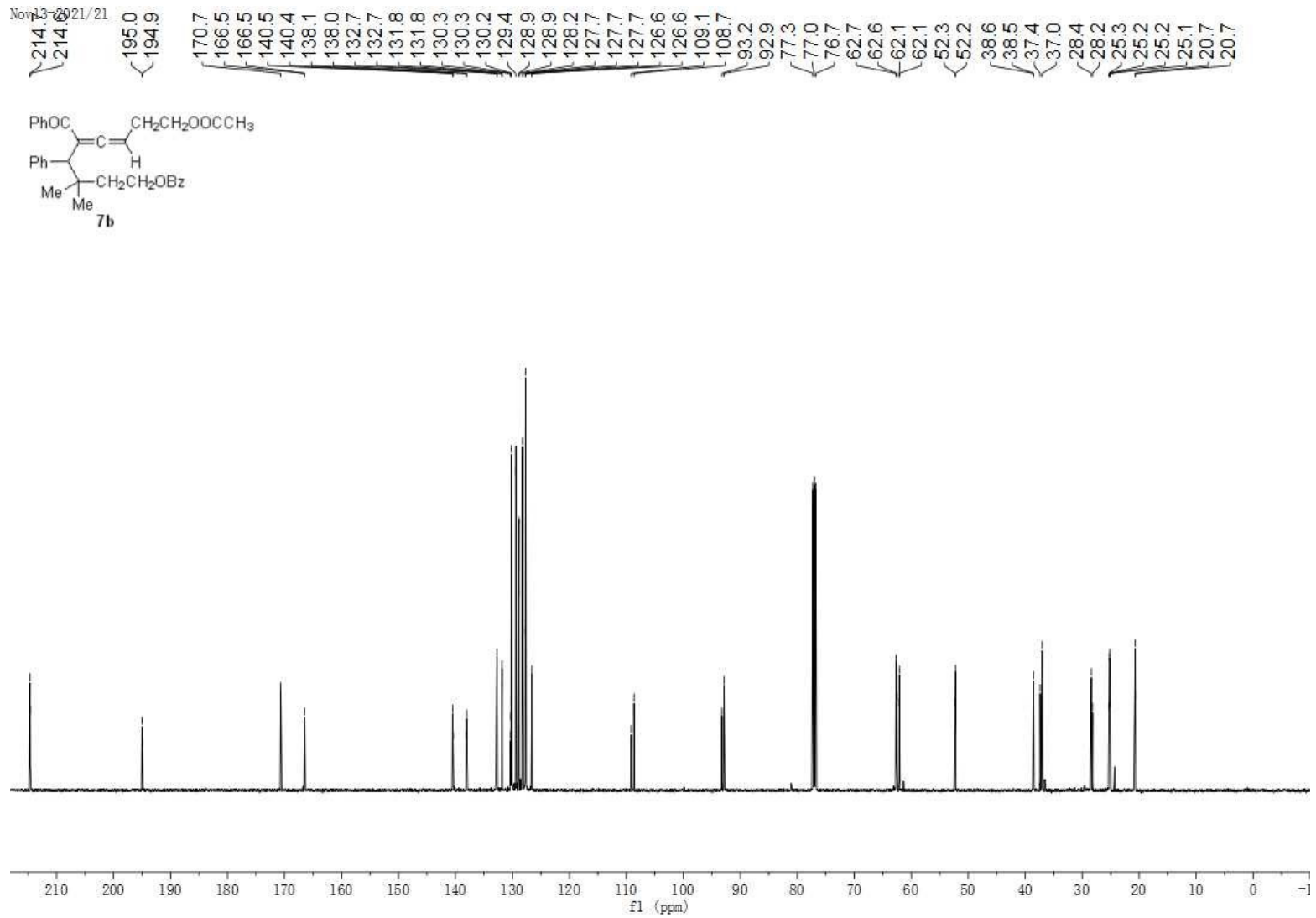
Oct 23, 2021/351

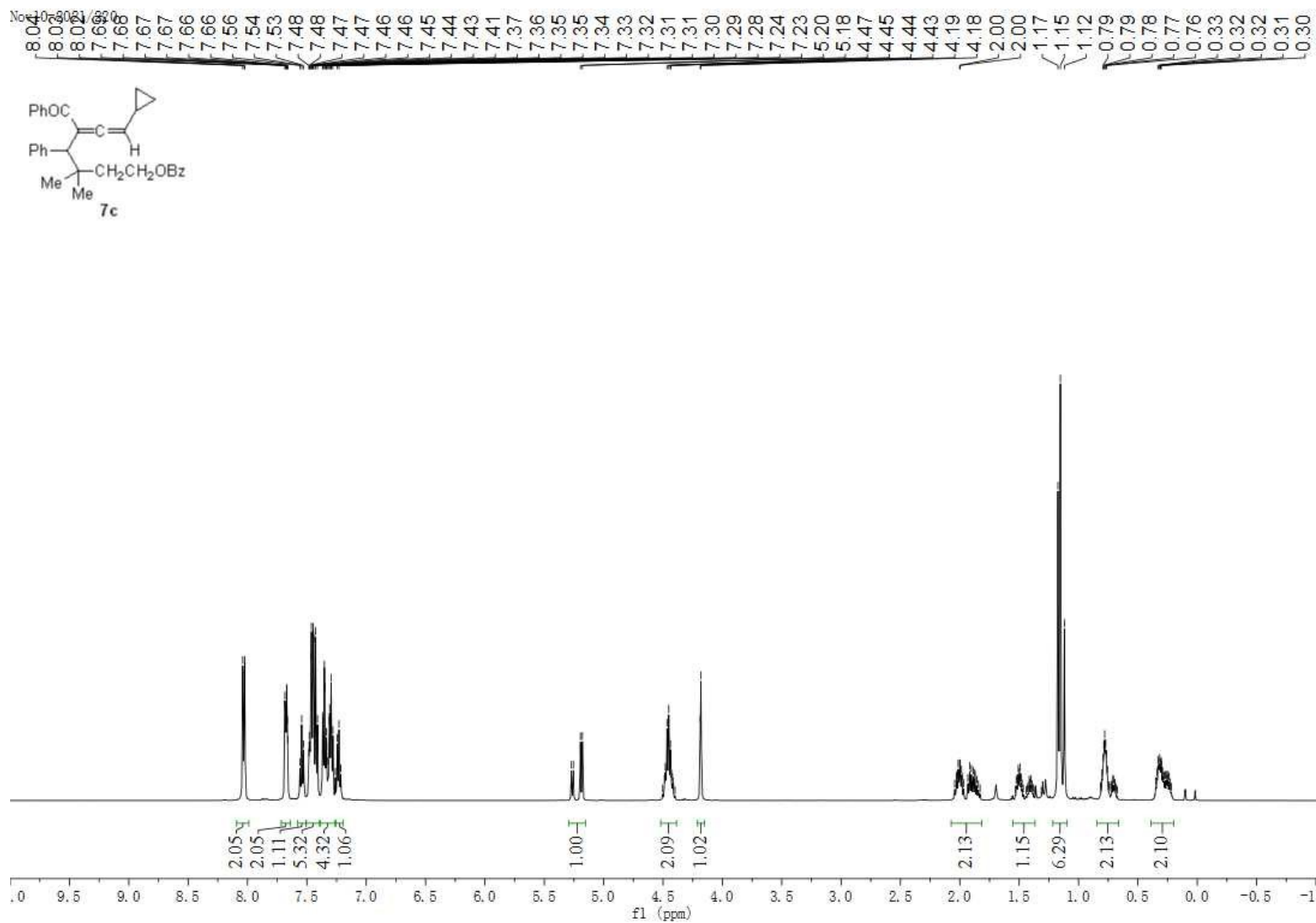


Nov 13-2021 / 20
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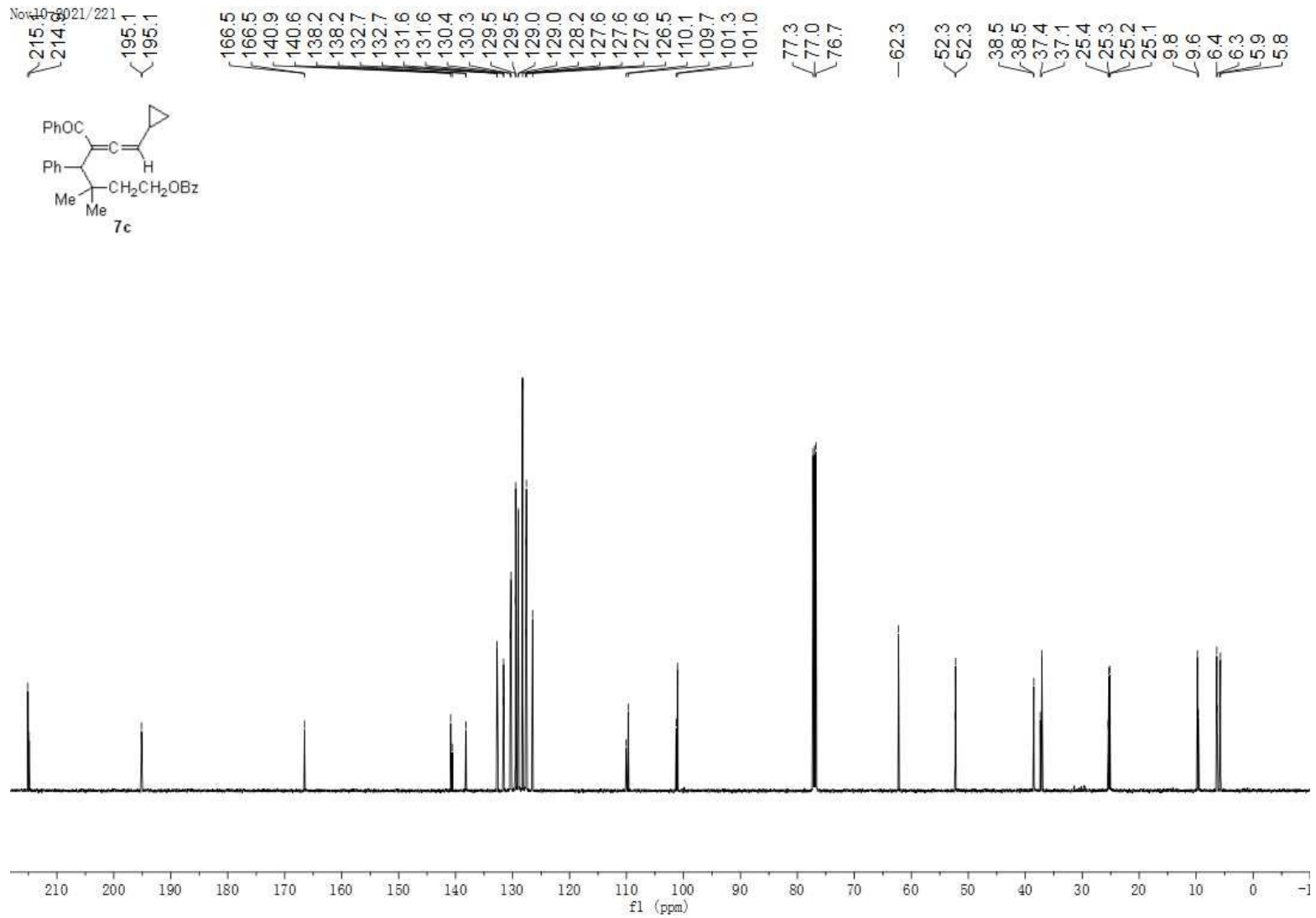
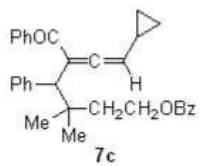


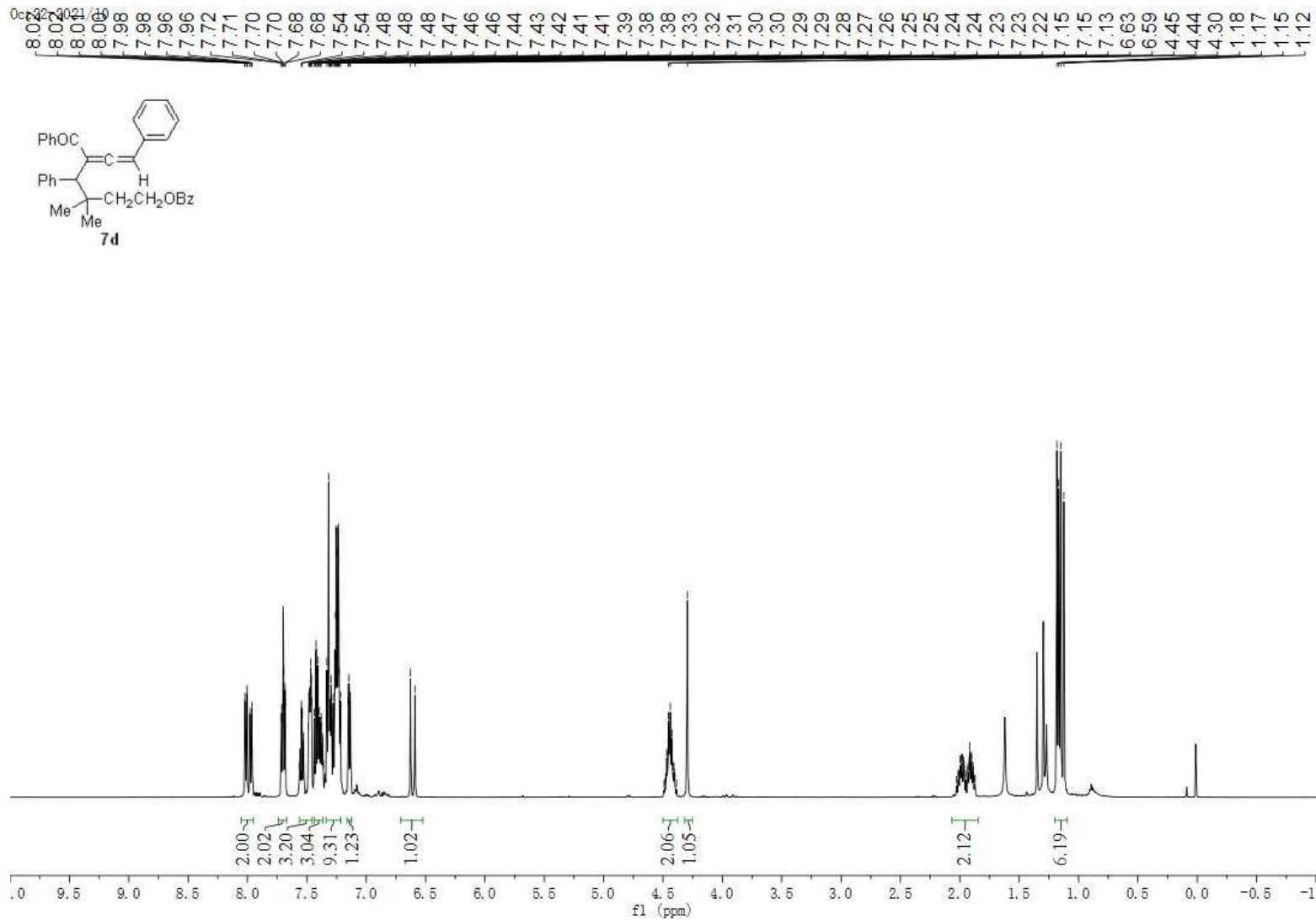
Nov 13 2021/21

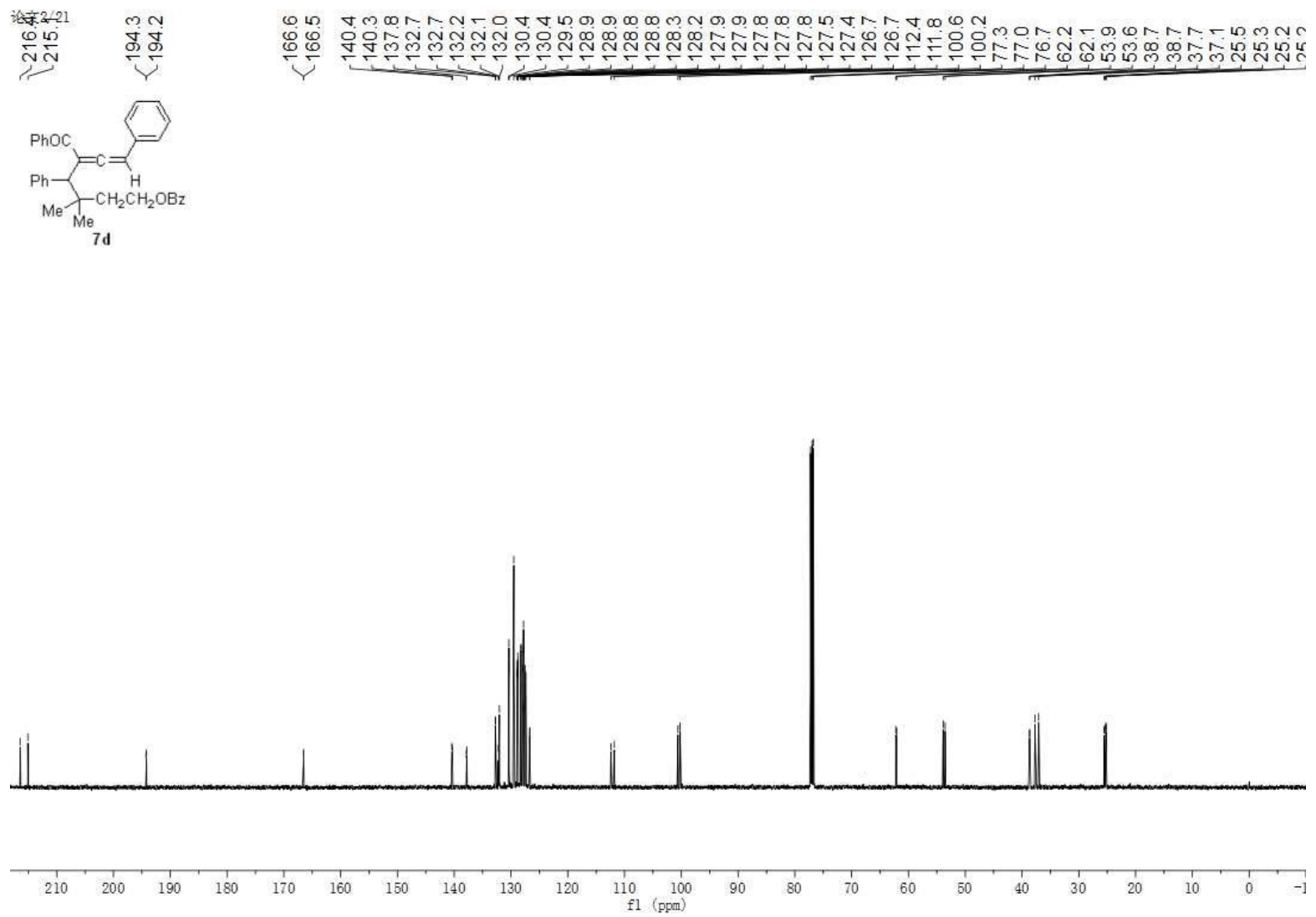


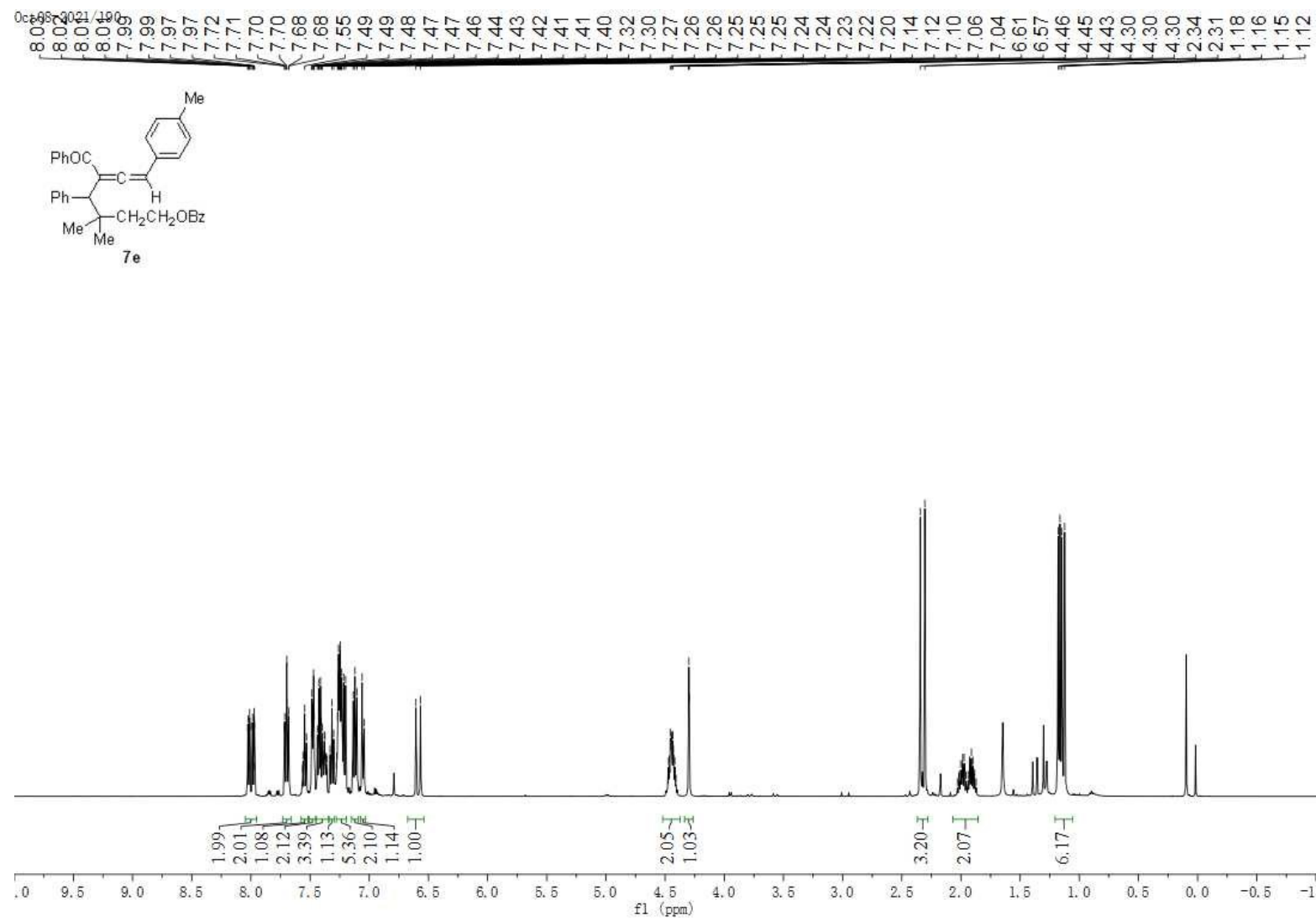


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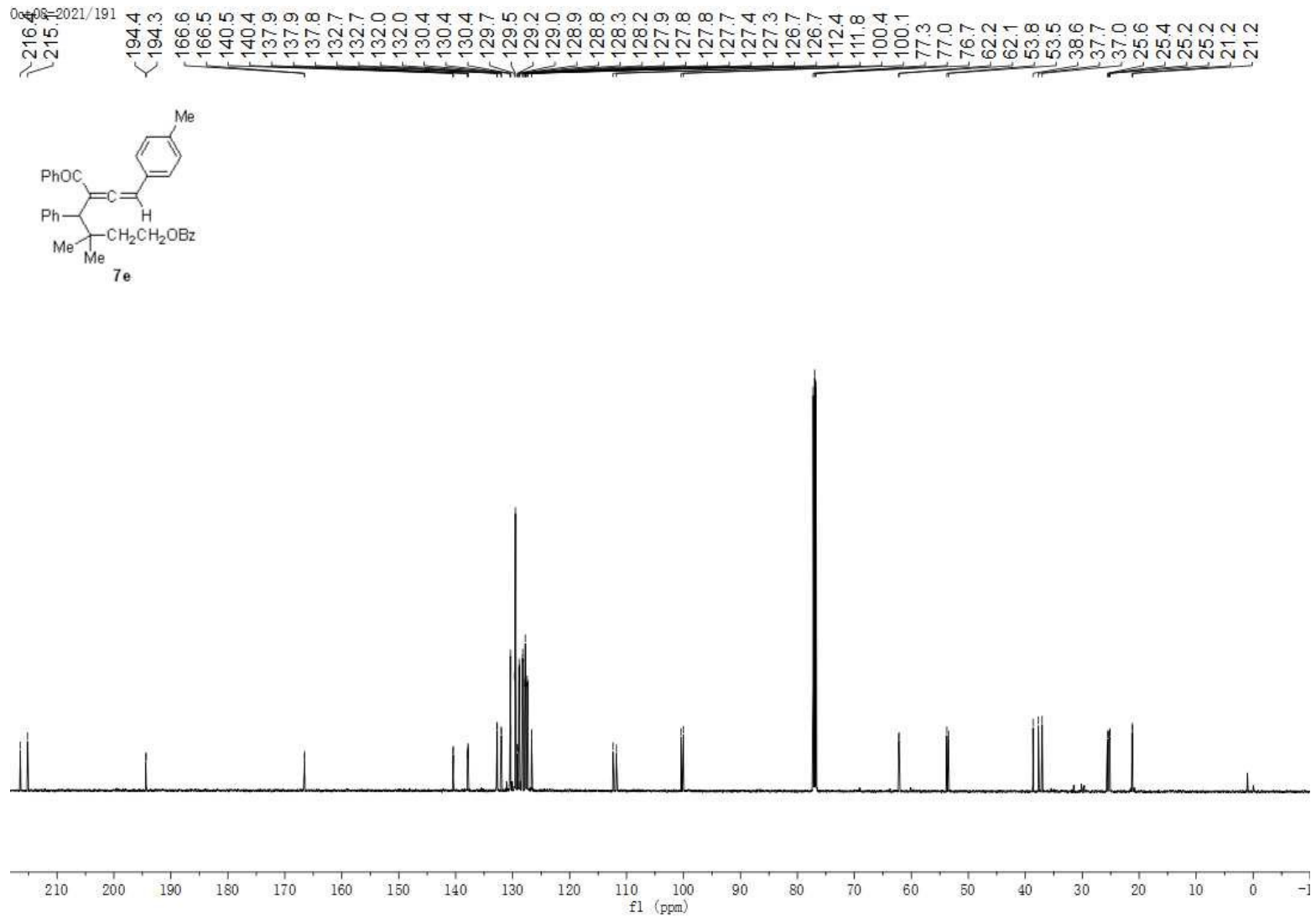


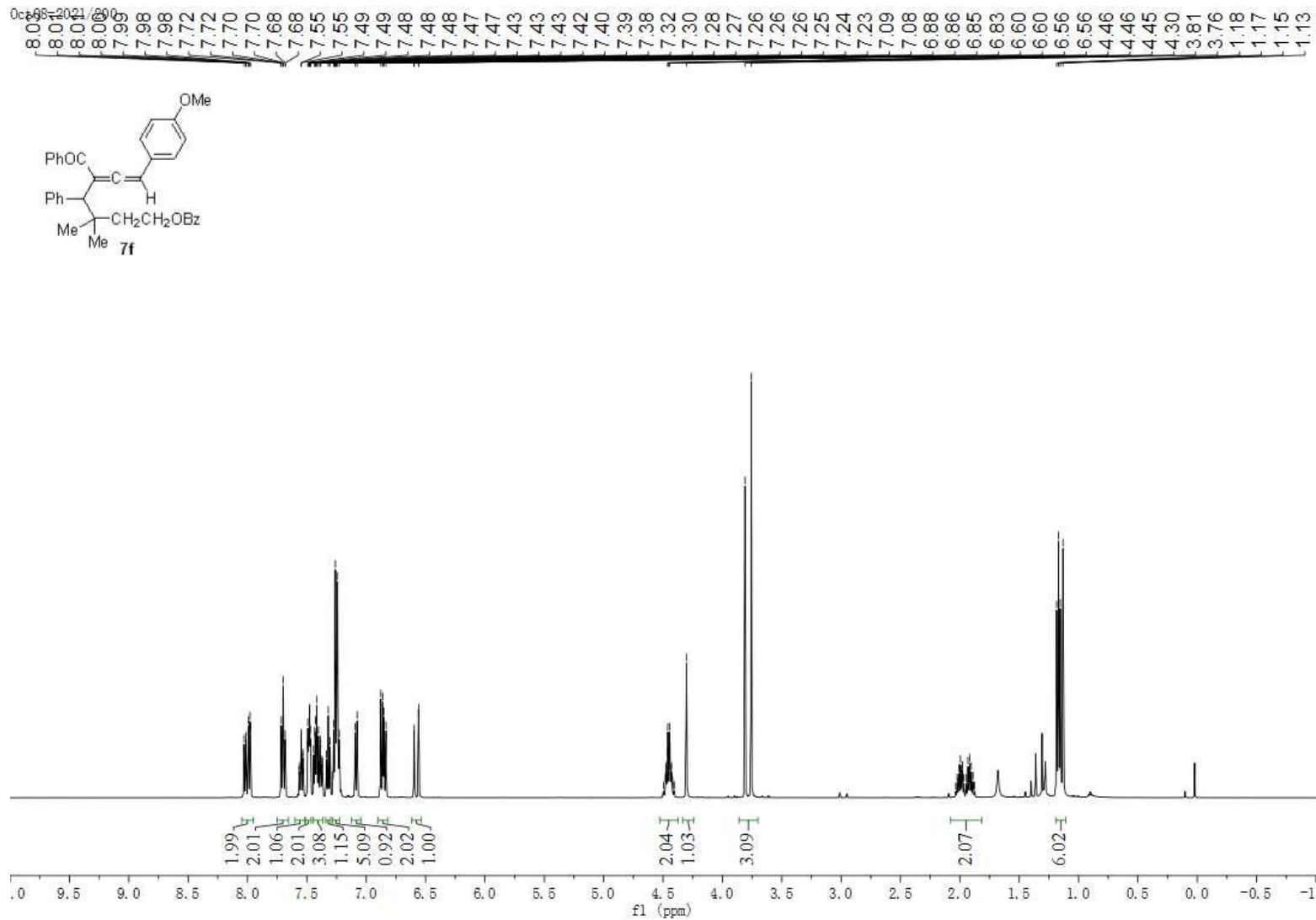




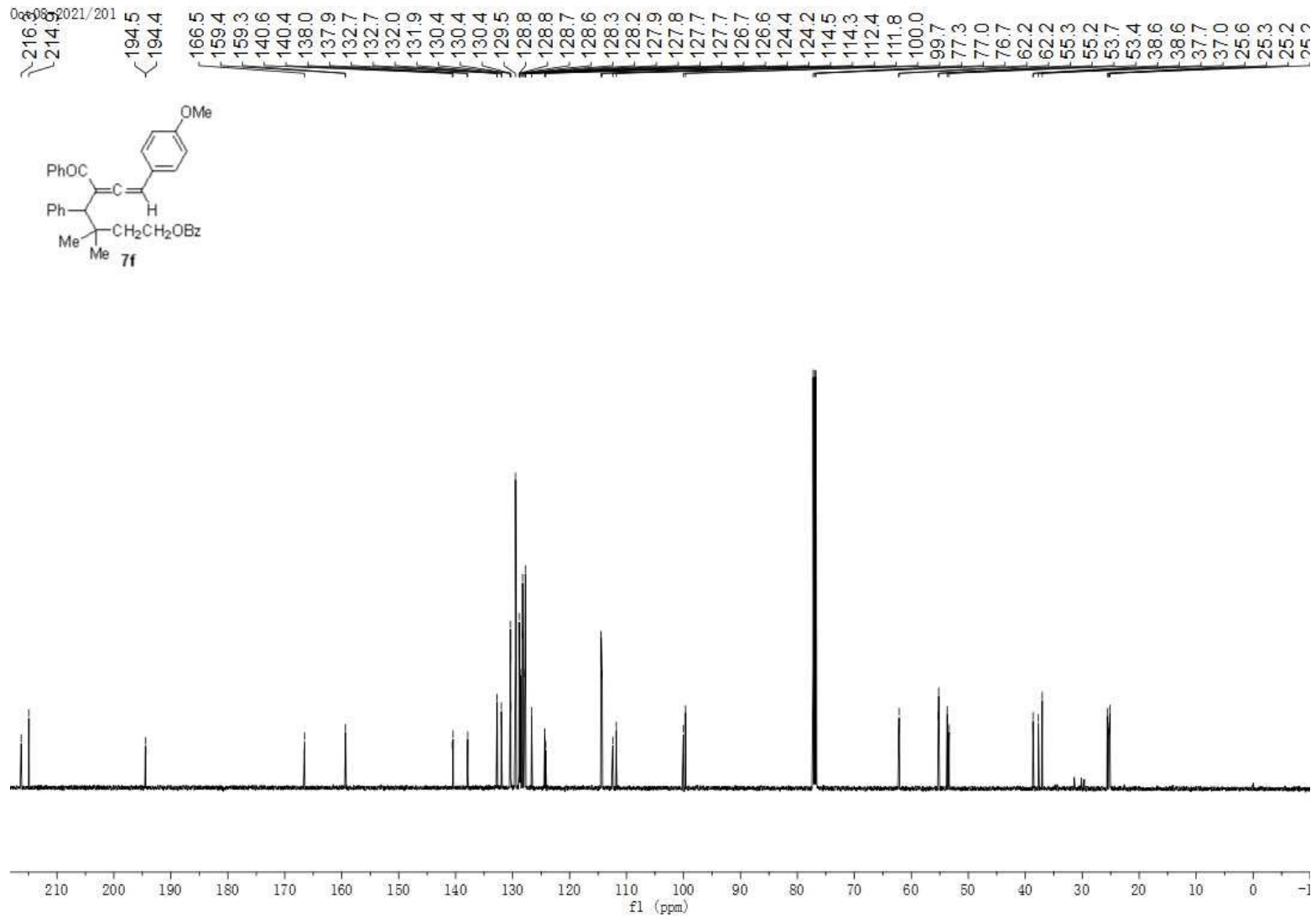


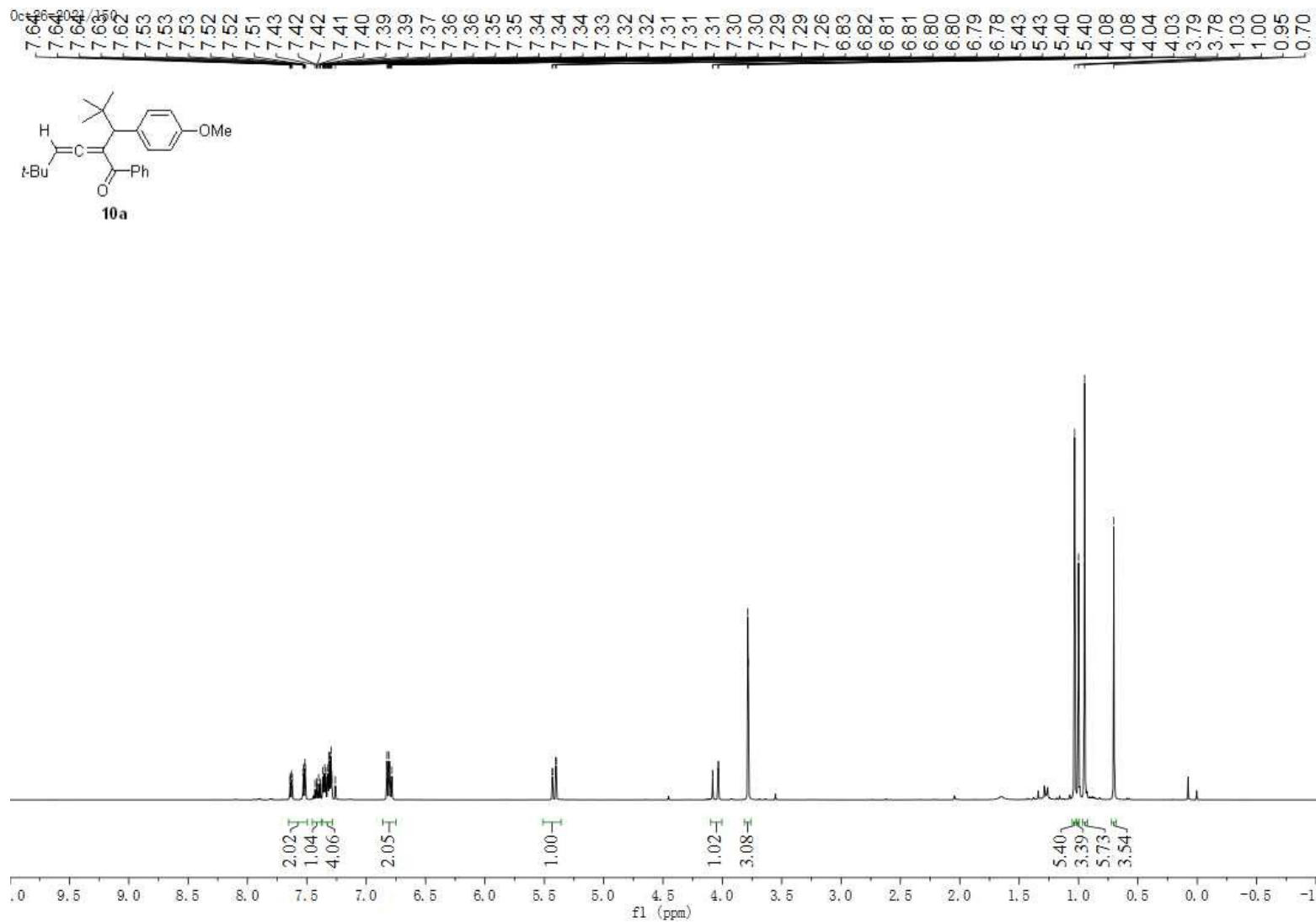
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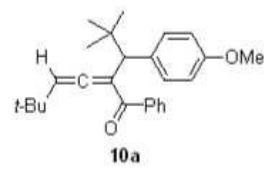
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06-26-2021/170

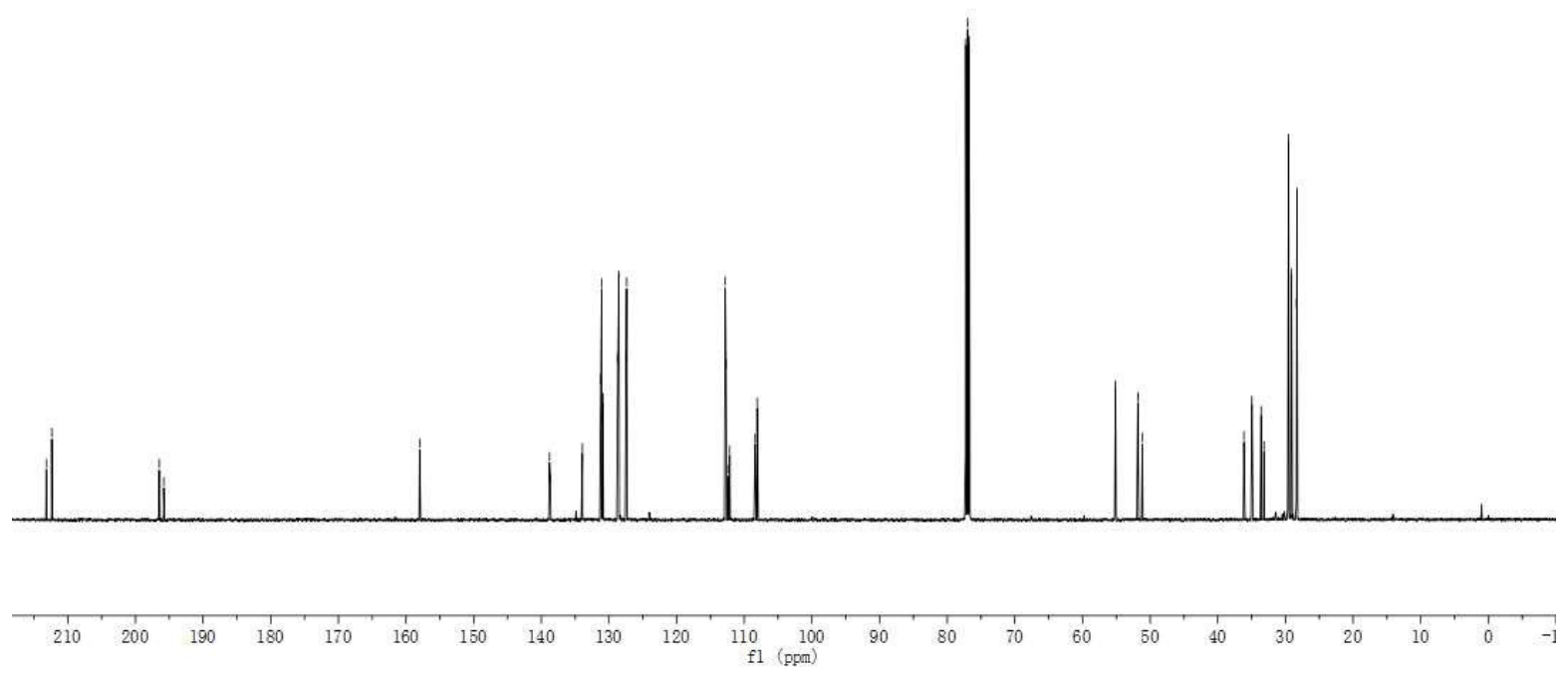
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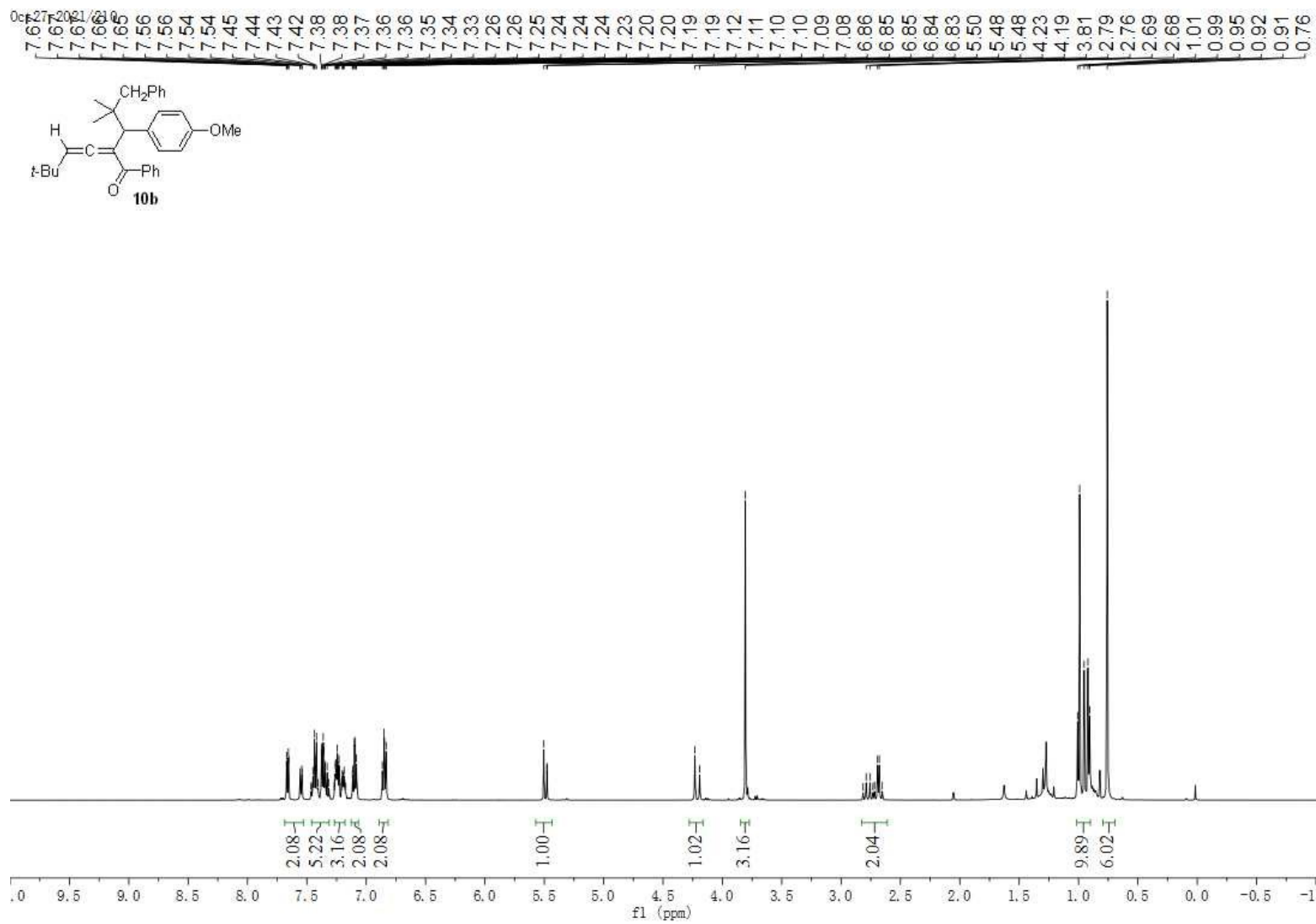


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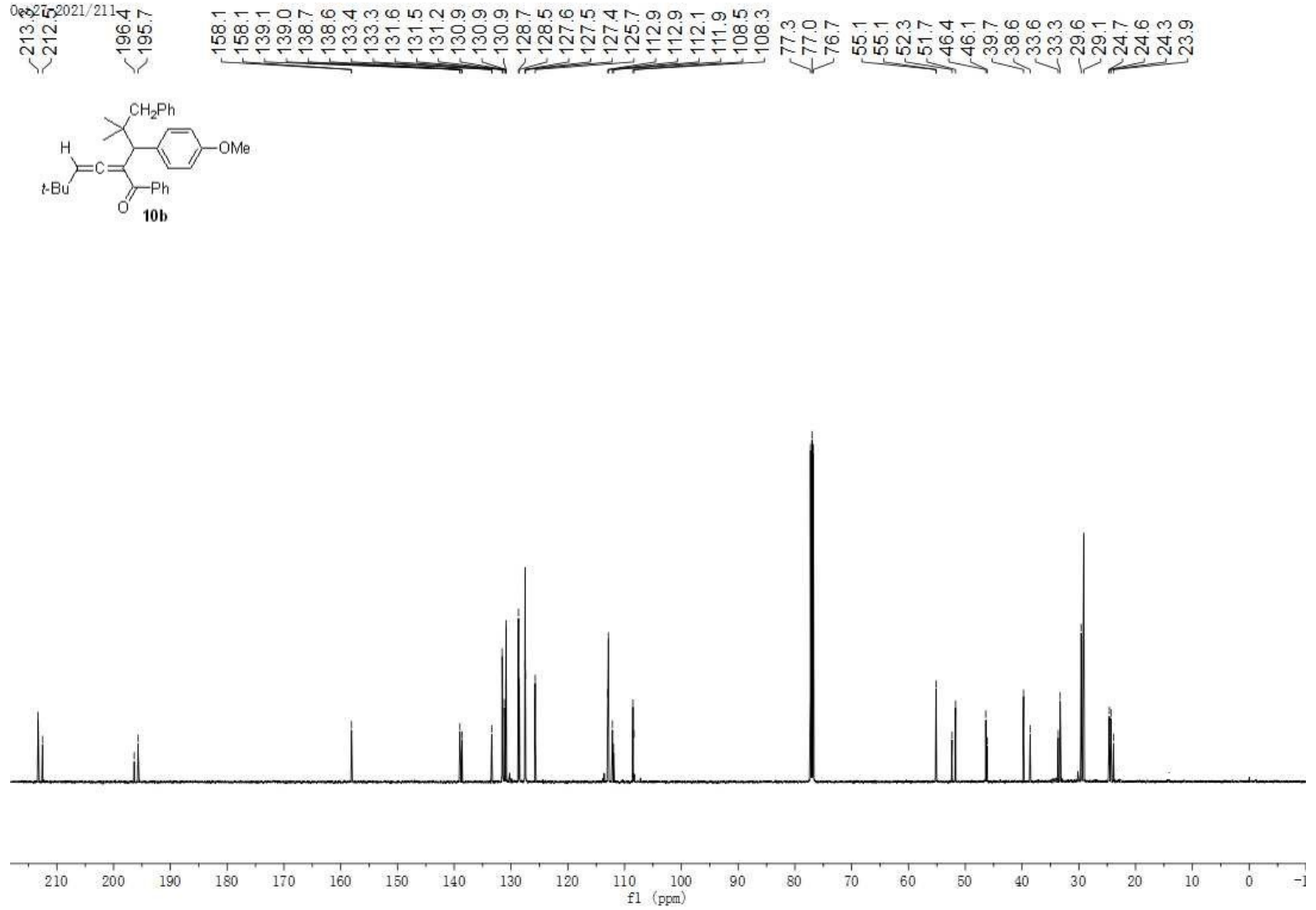
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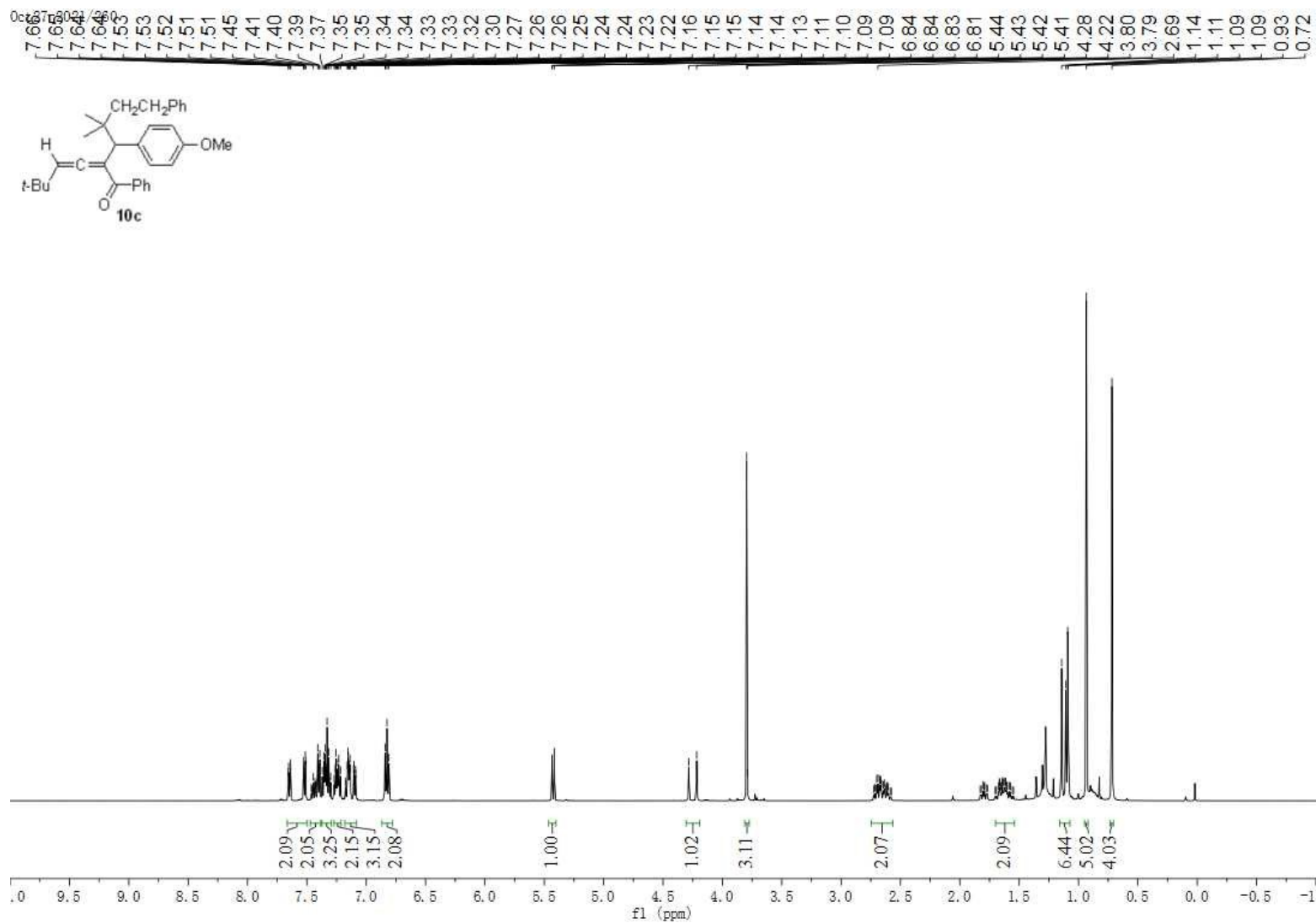
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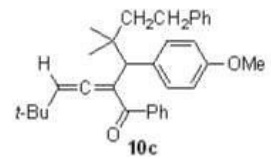


0852021/211

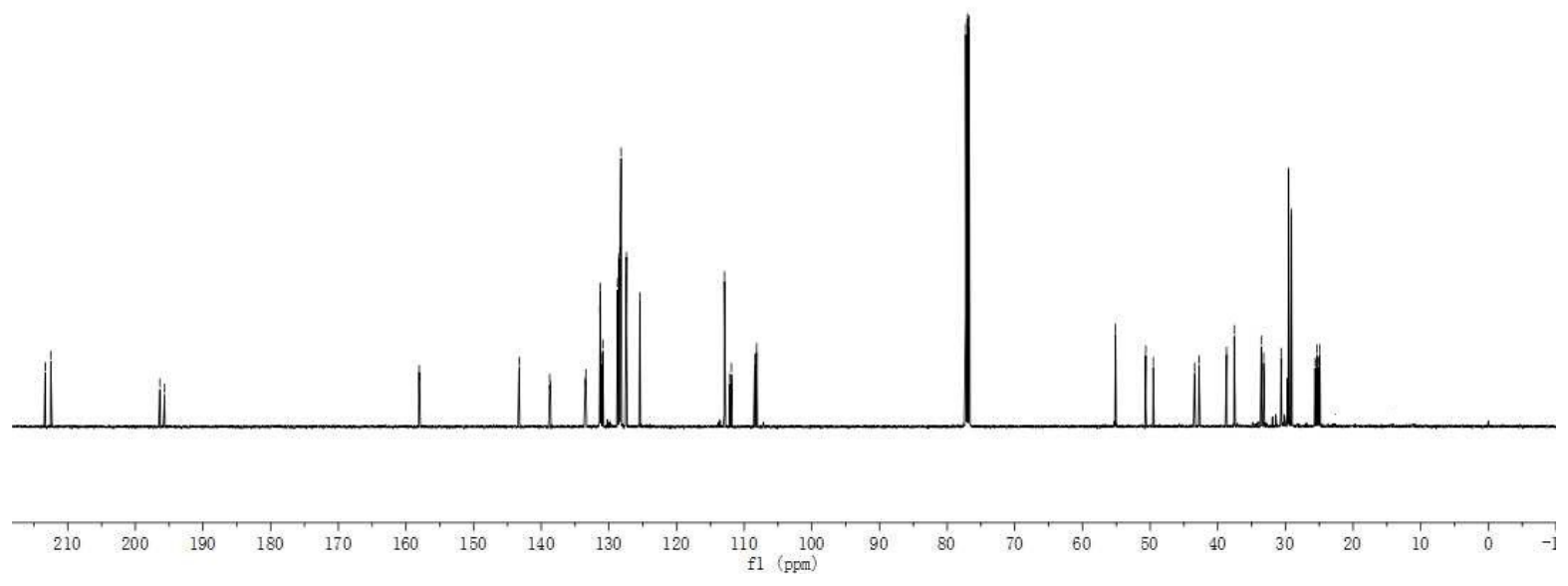


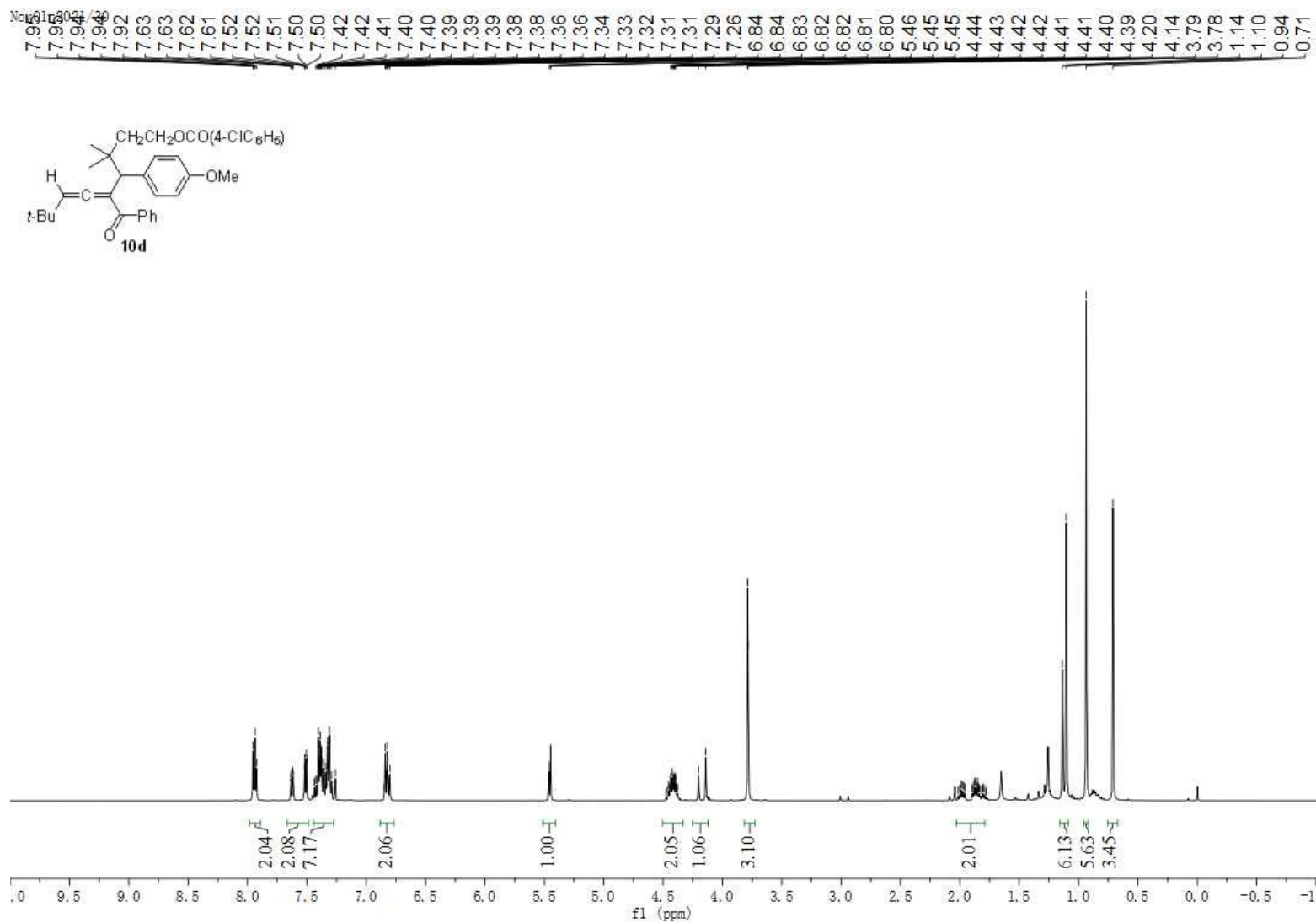


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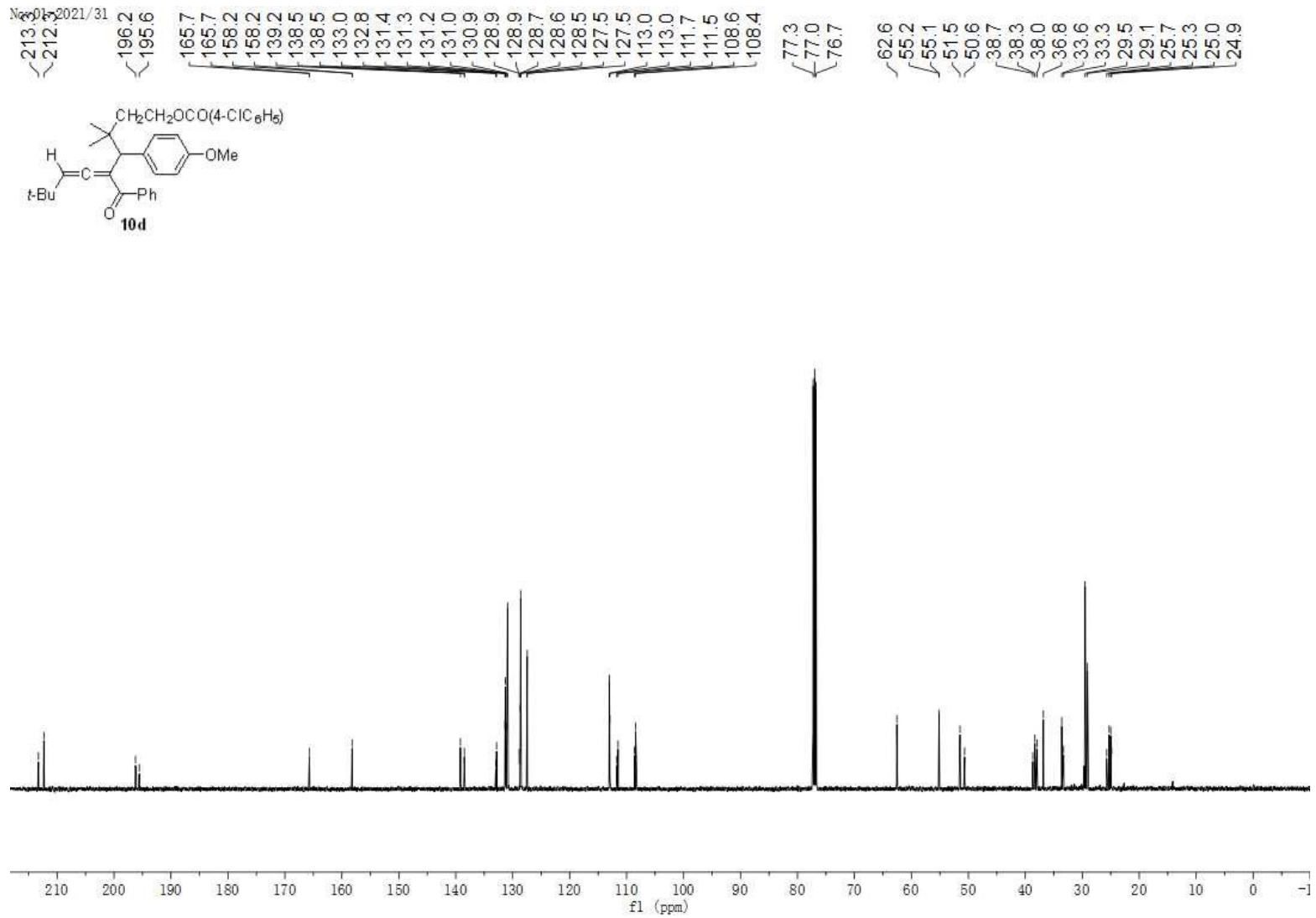


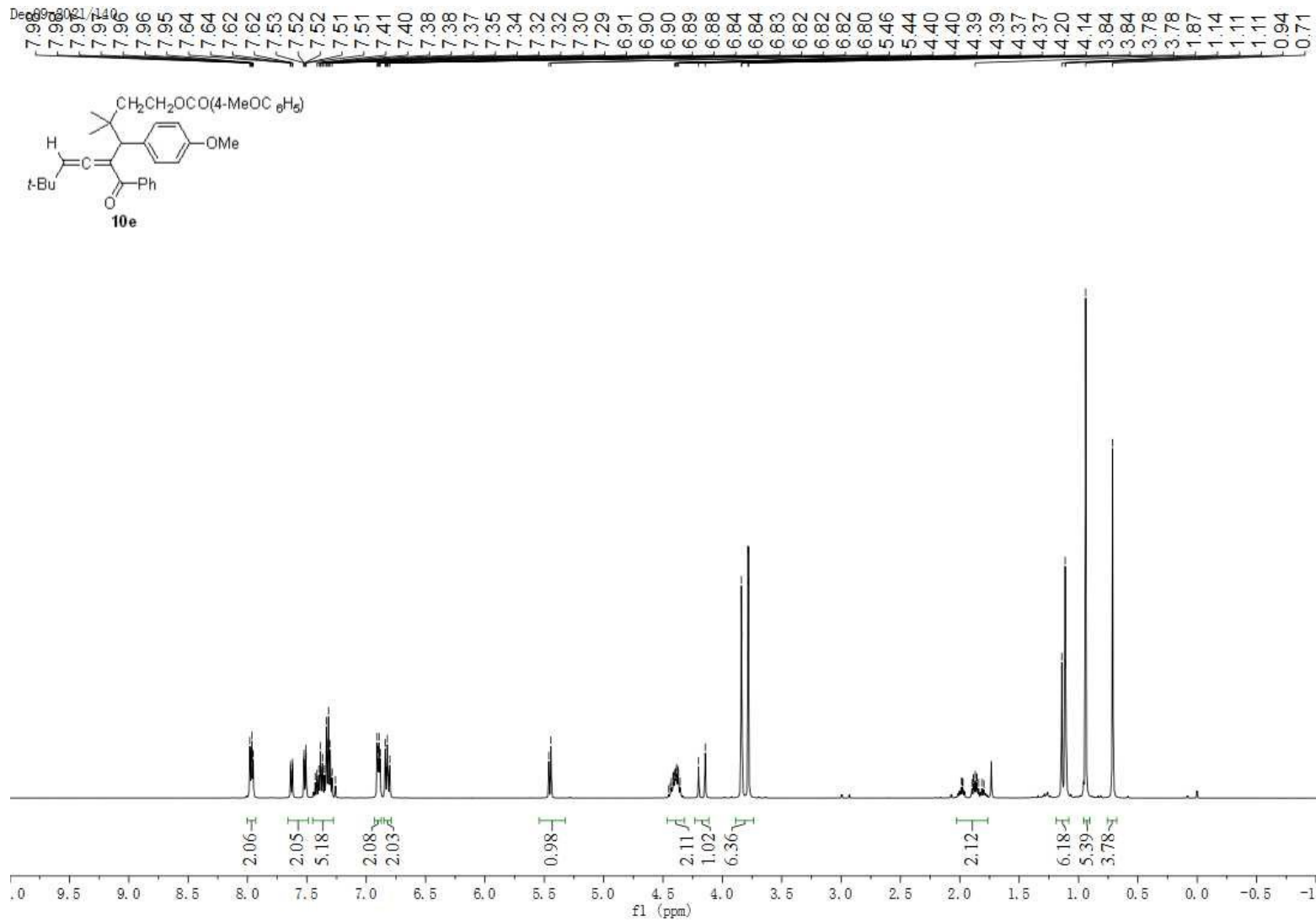
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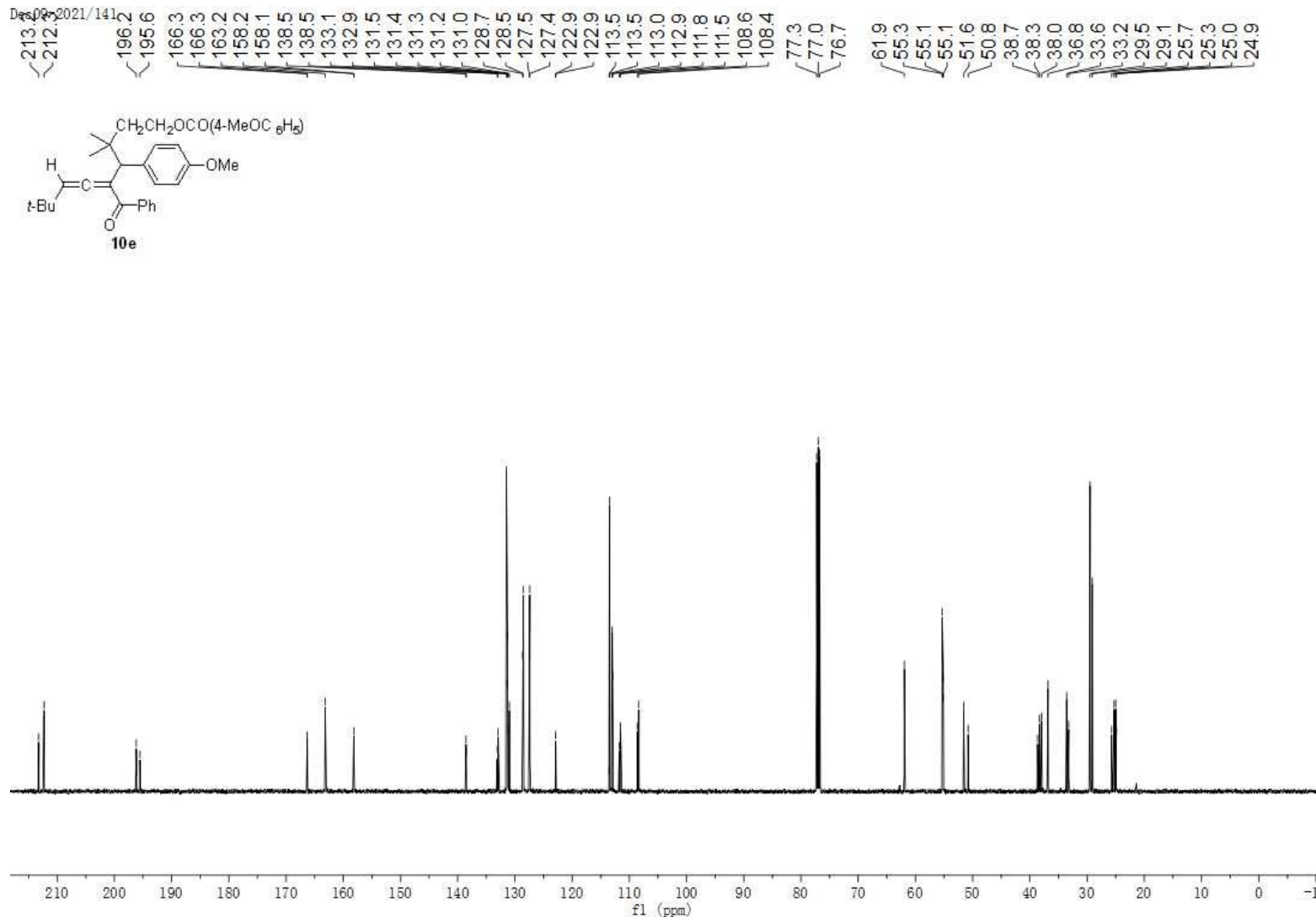


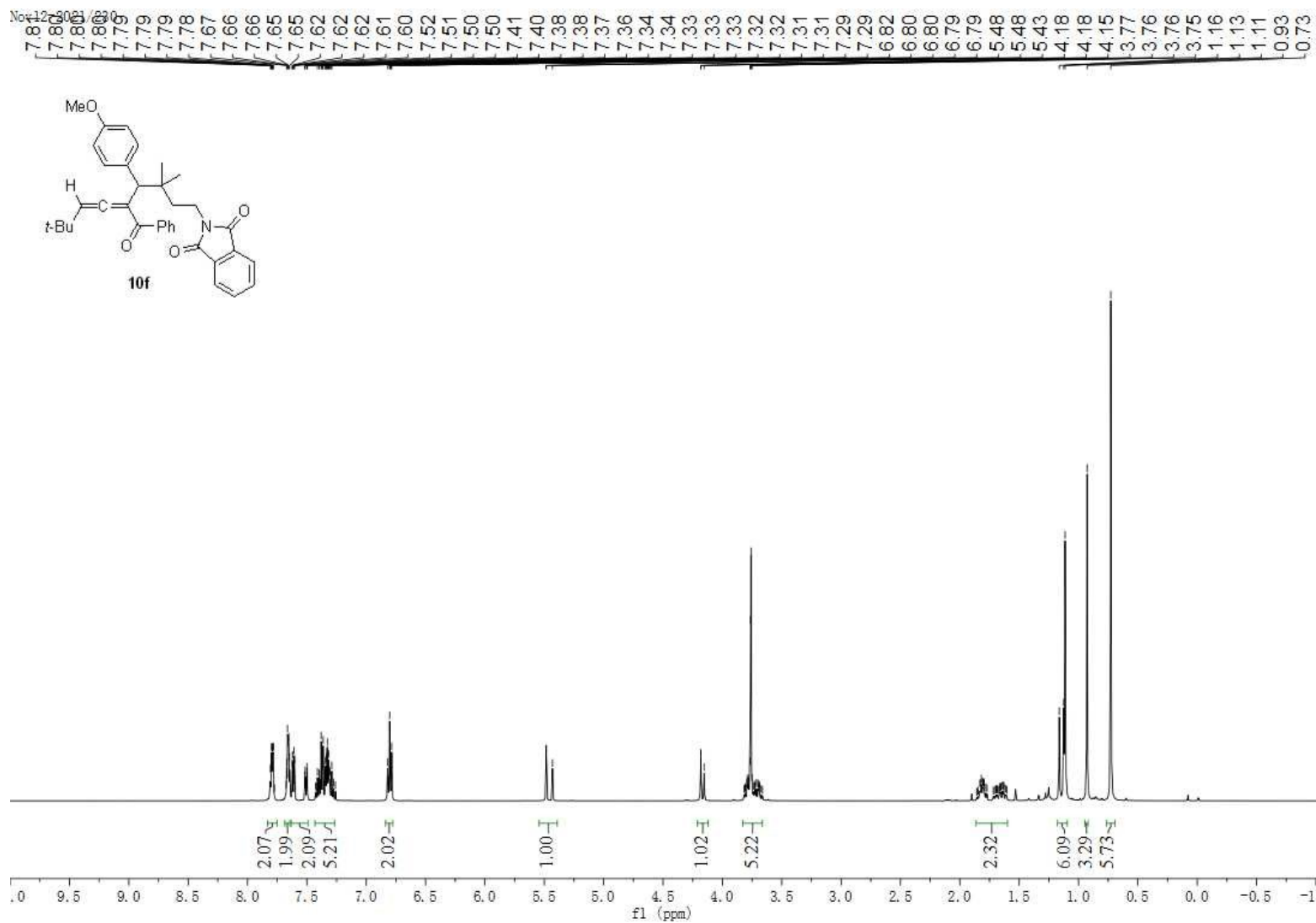
№ 2021/31



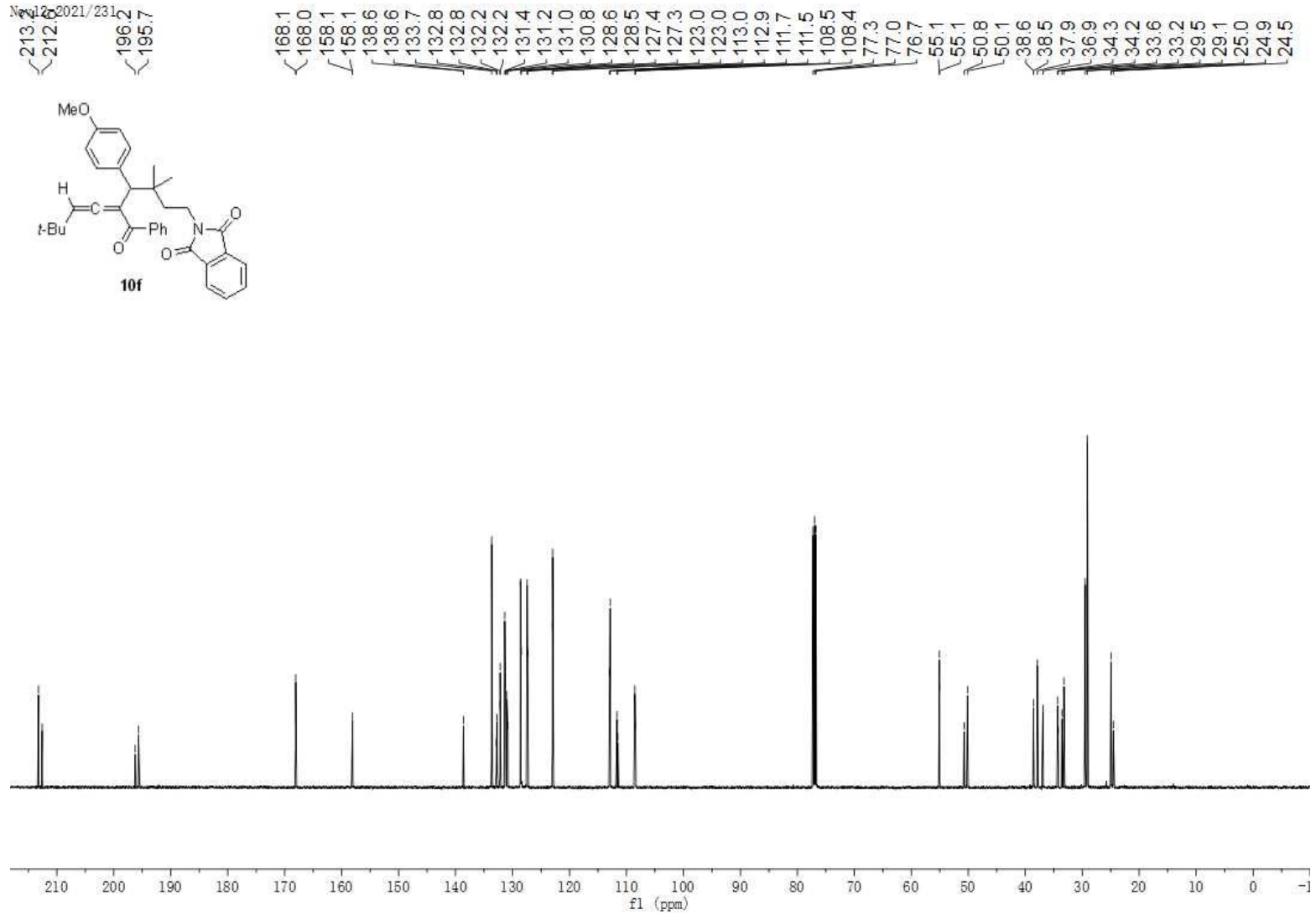
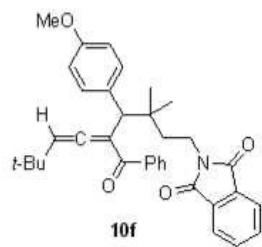


Dec 09 2021/141

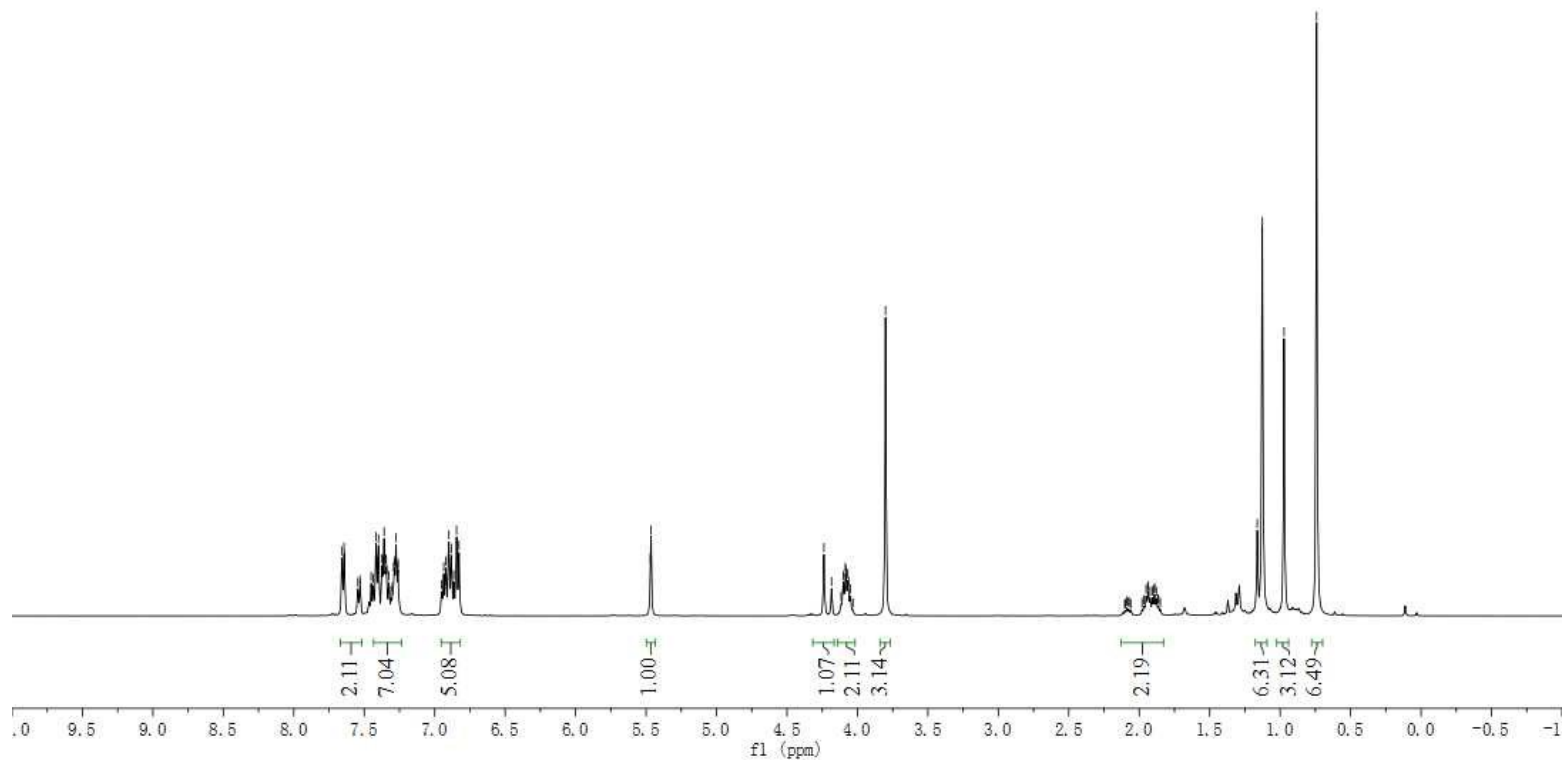
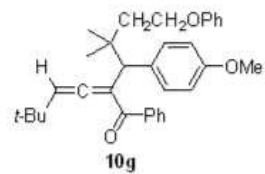




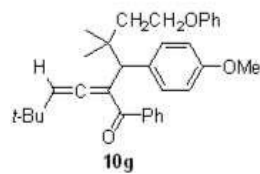
Nov 12, 2021/231



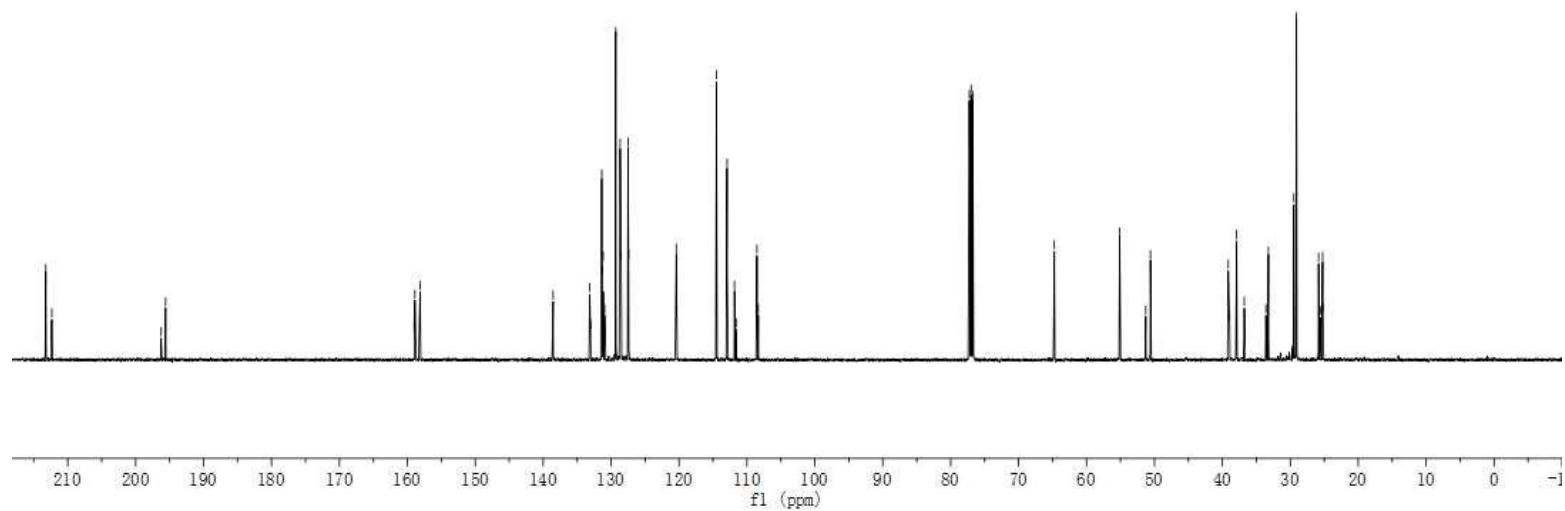
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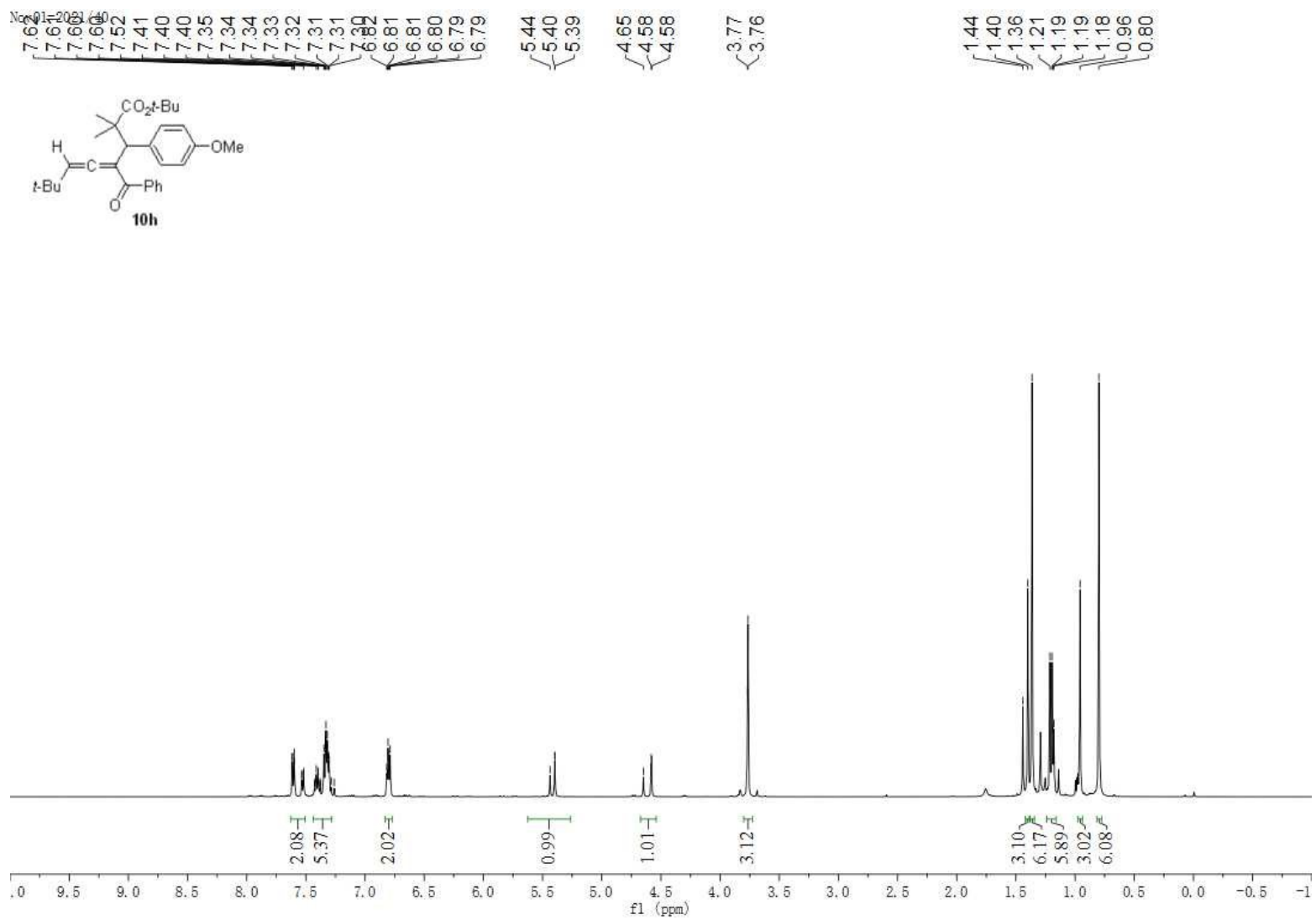


No. 2021/191
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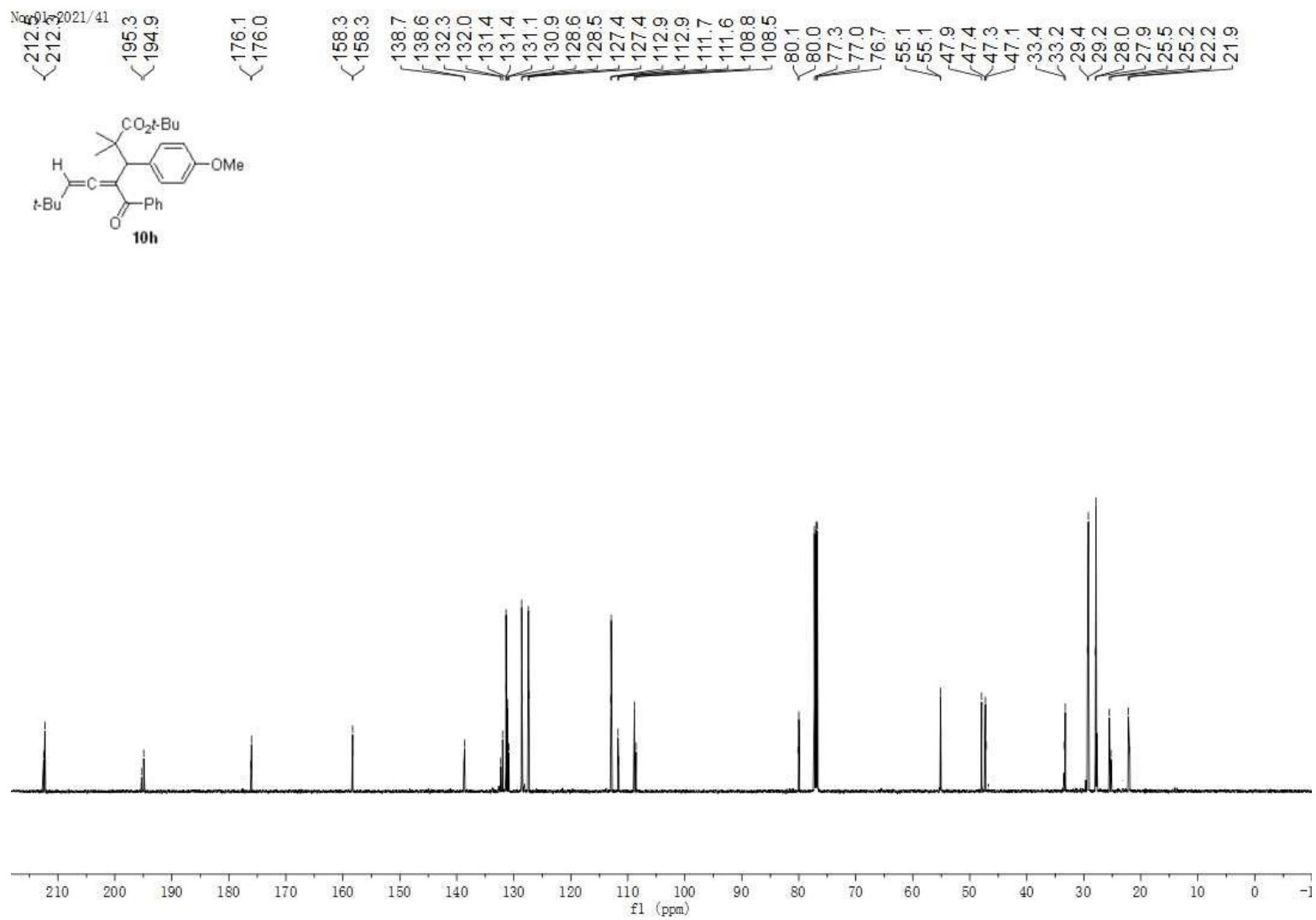
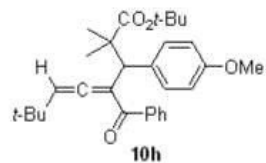


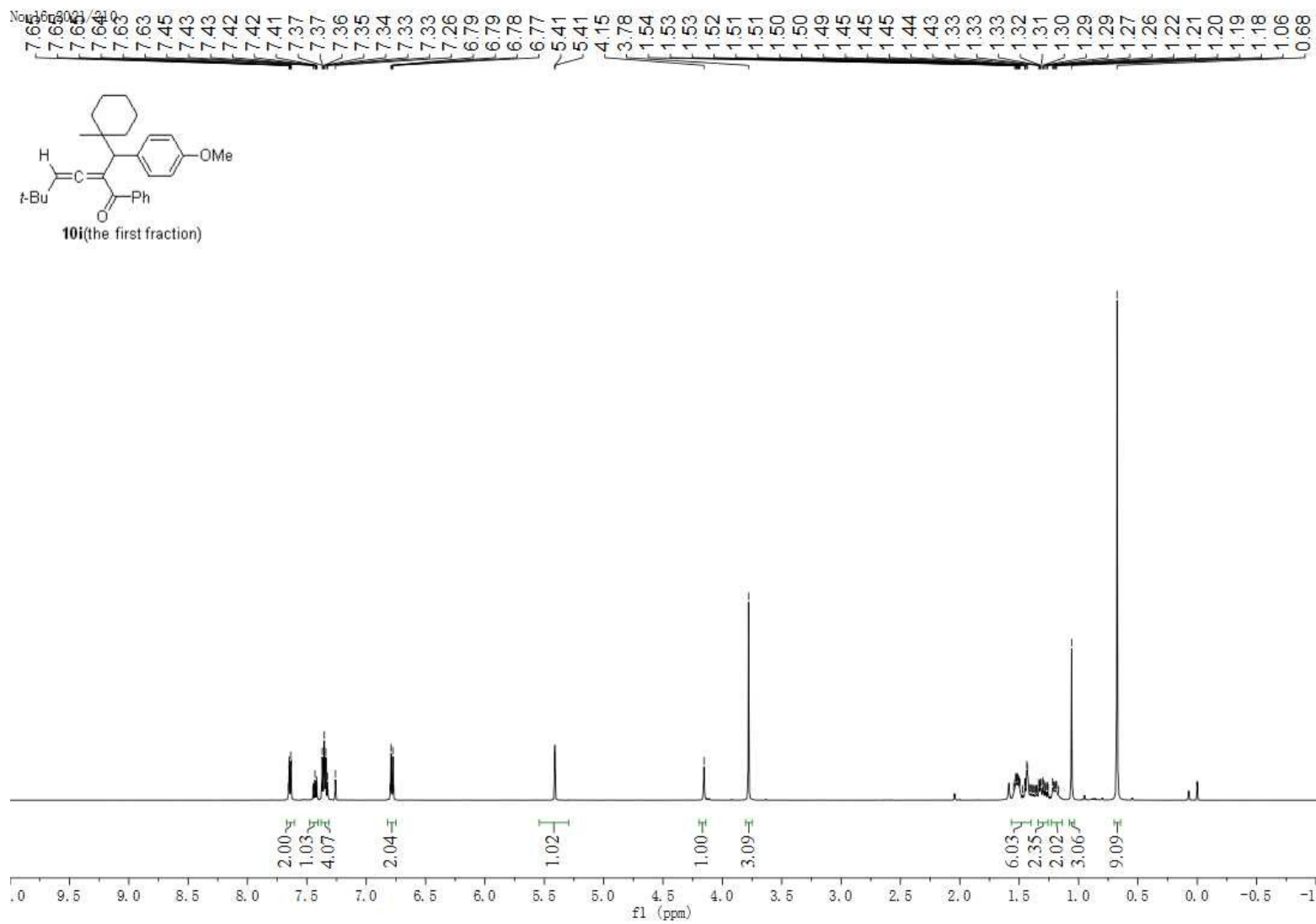
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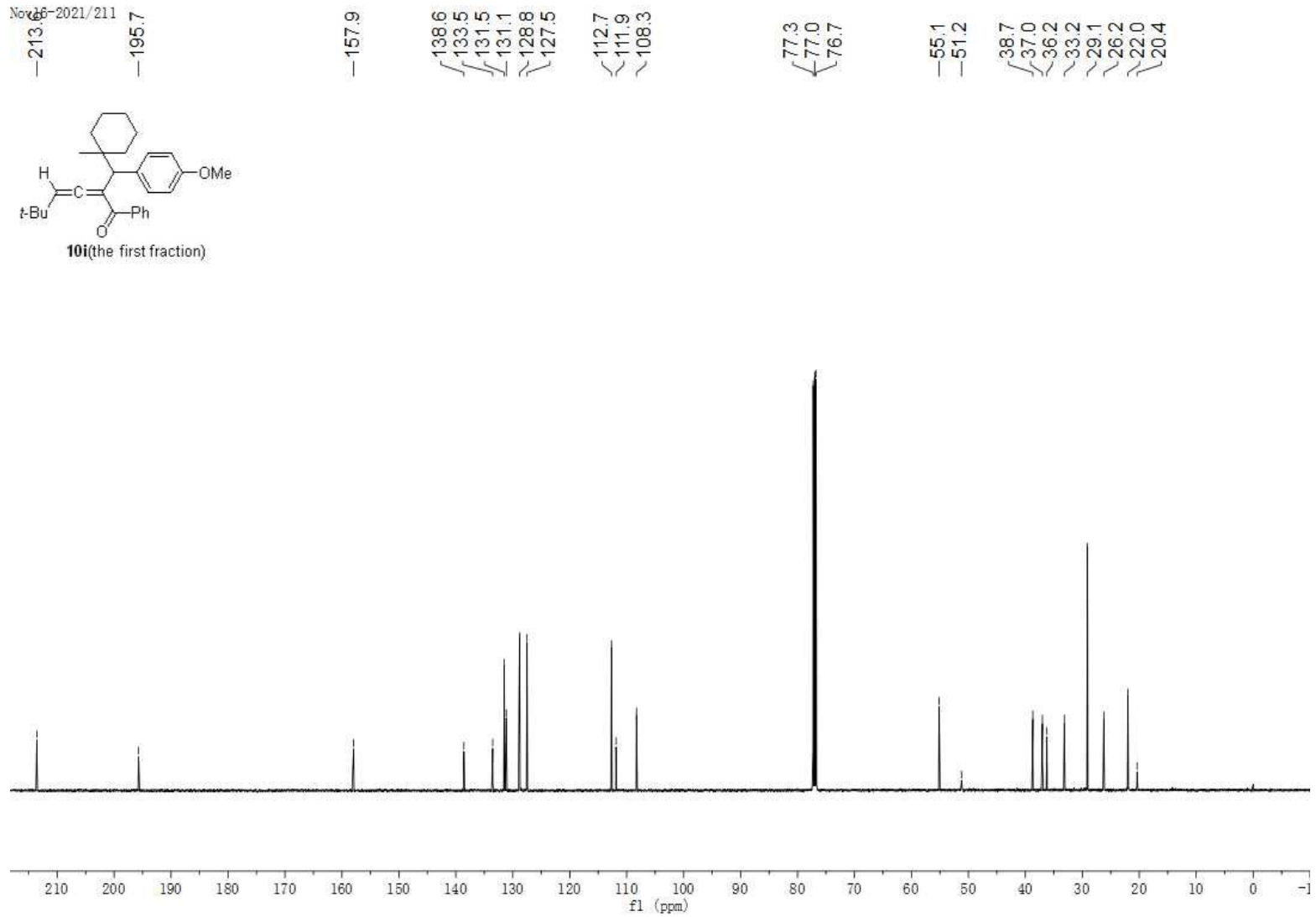
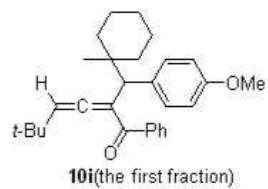


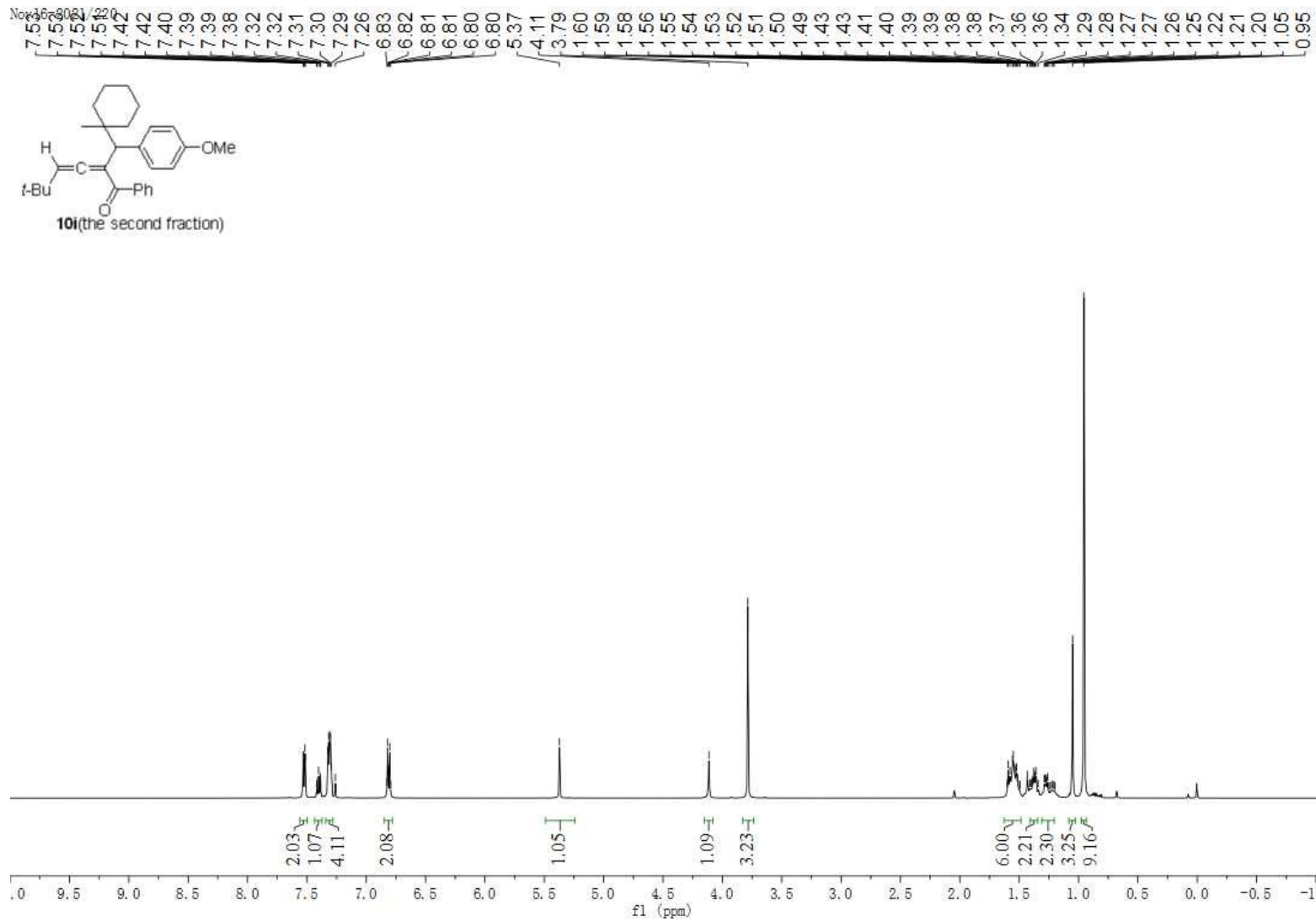
No. 2021/41



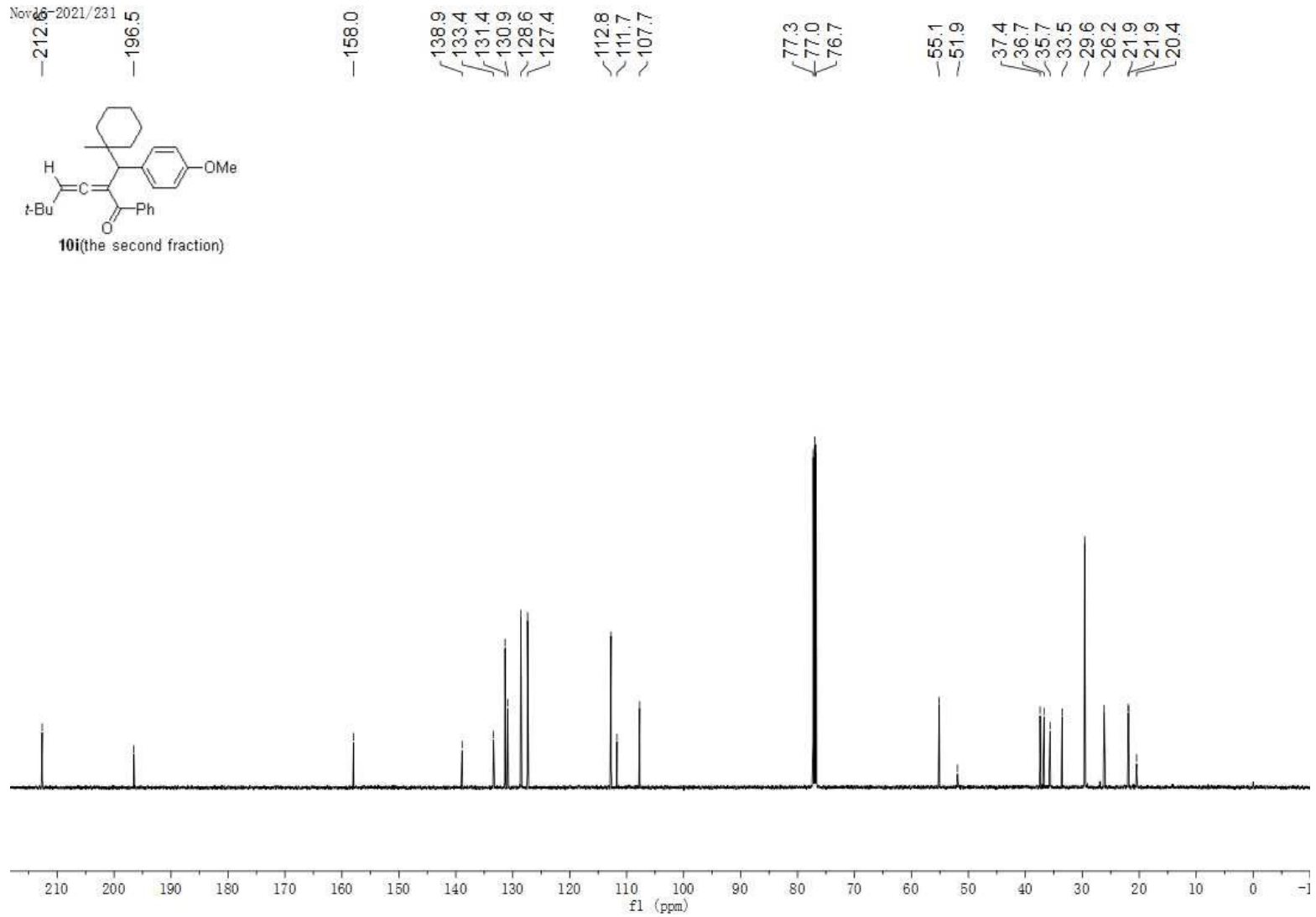
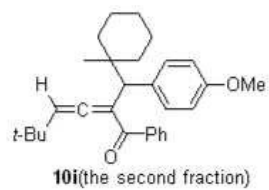


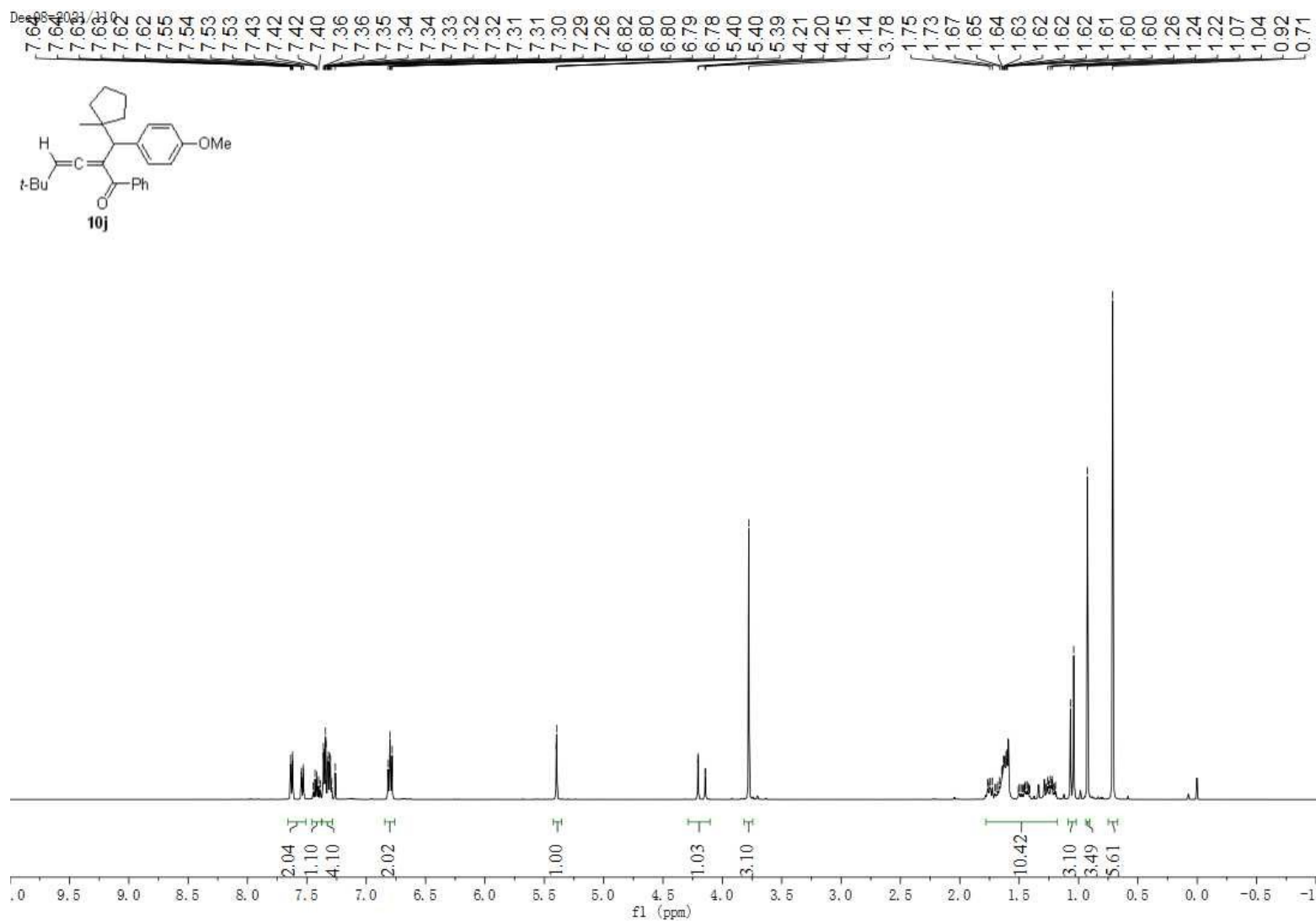
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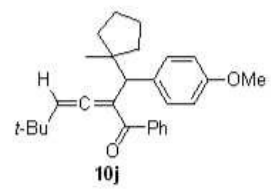
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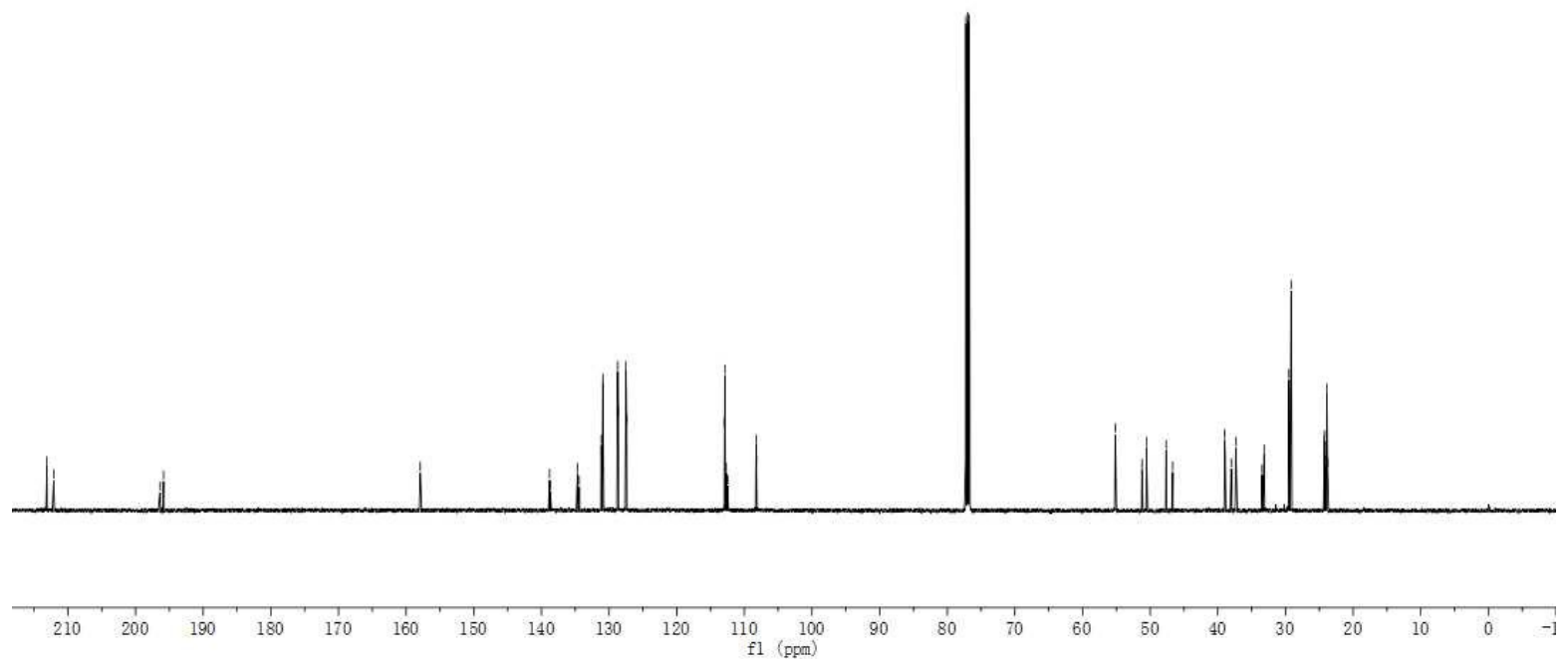
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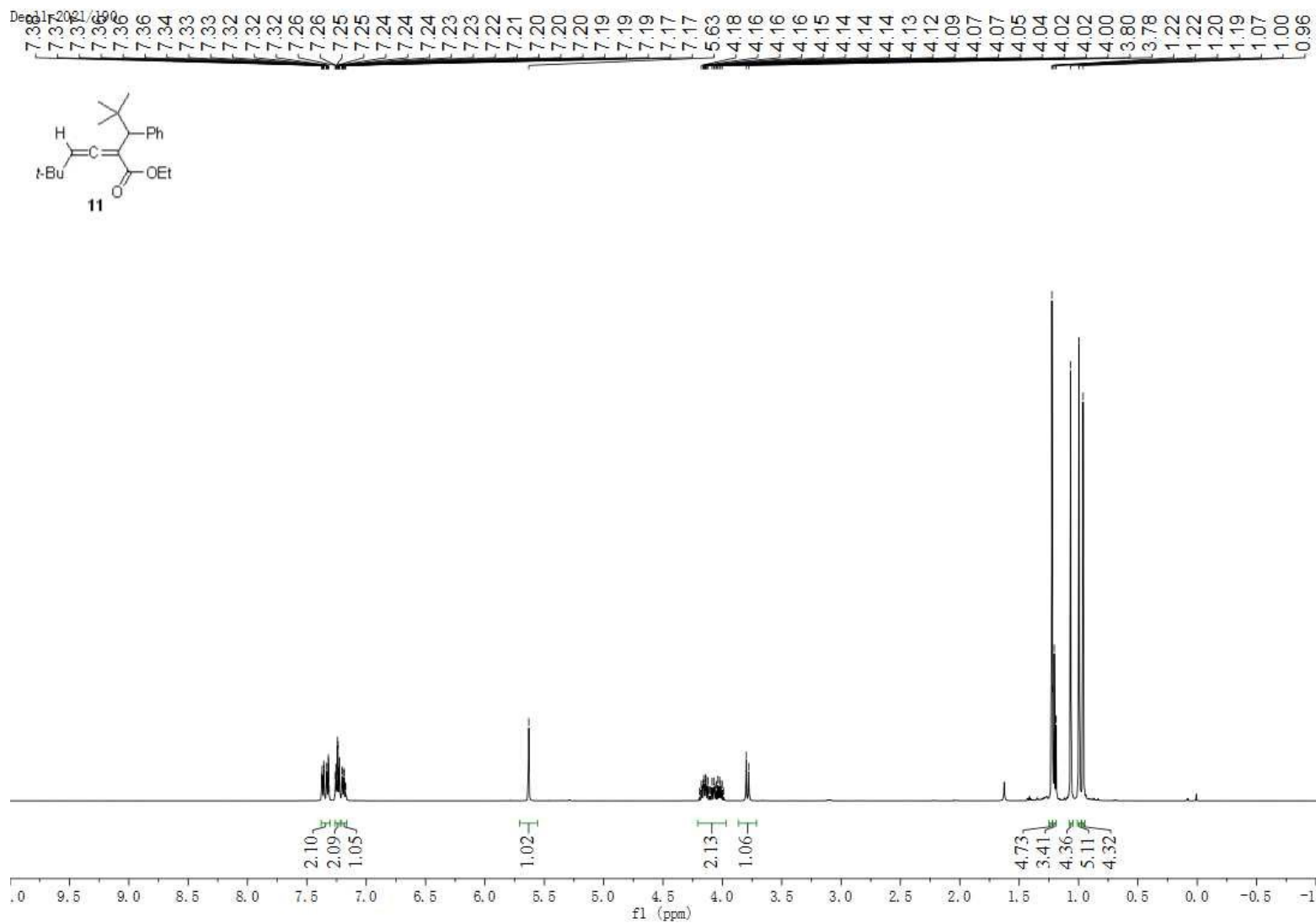


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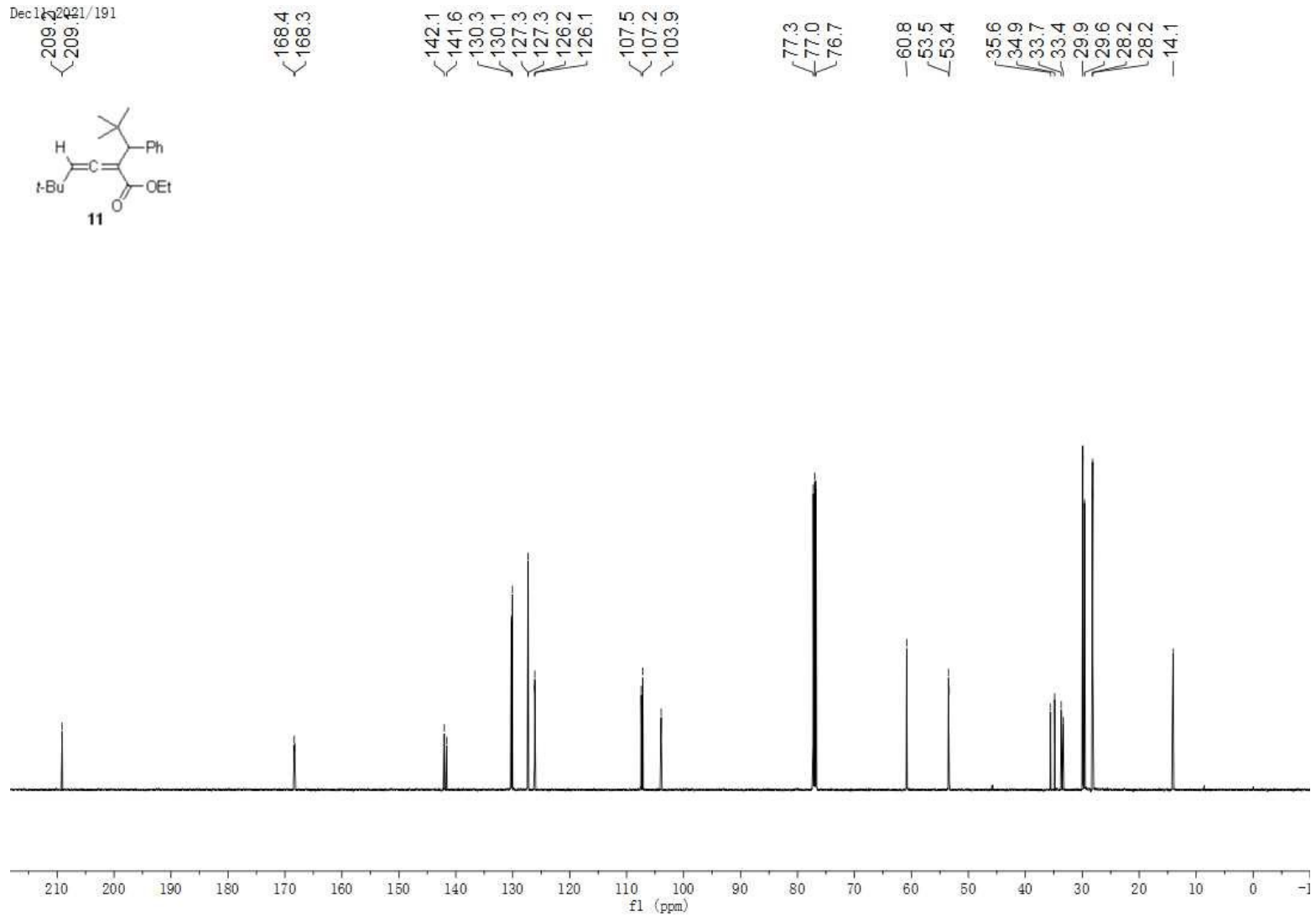
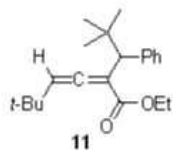
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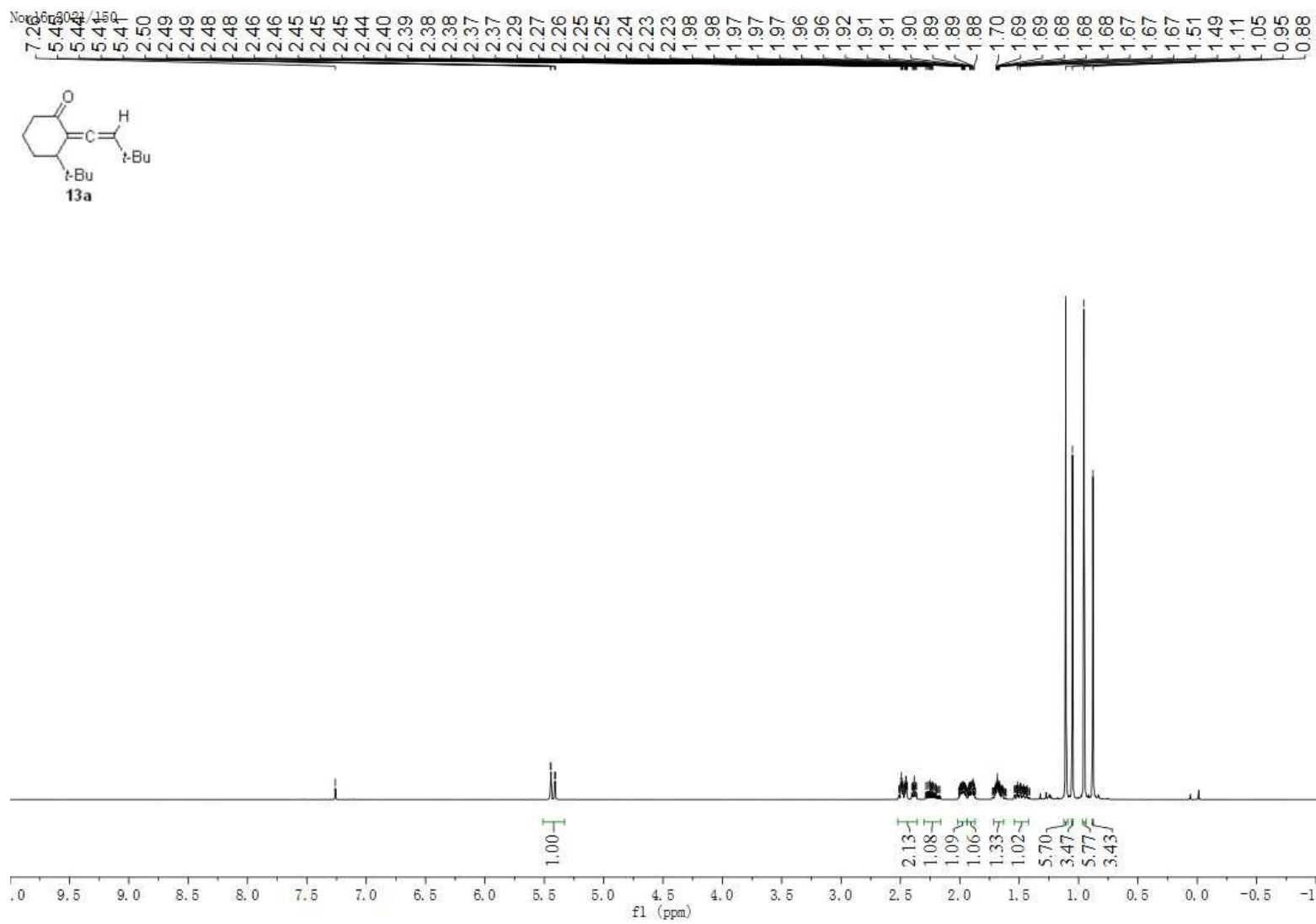
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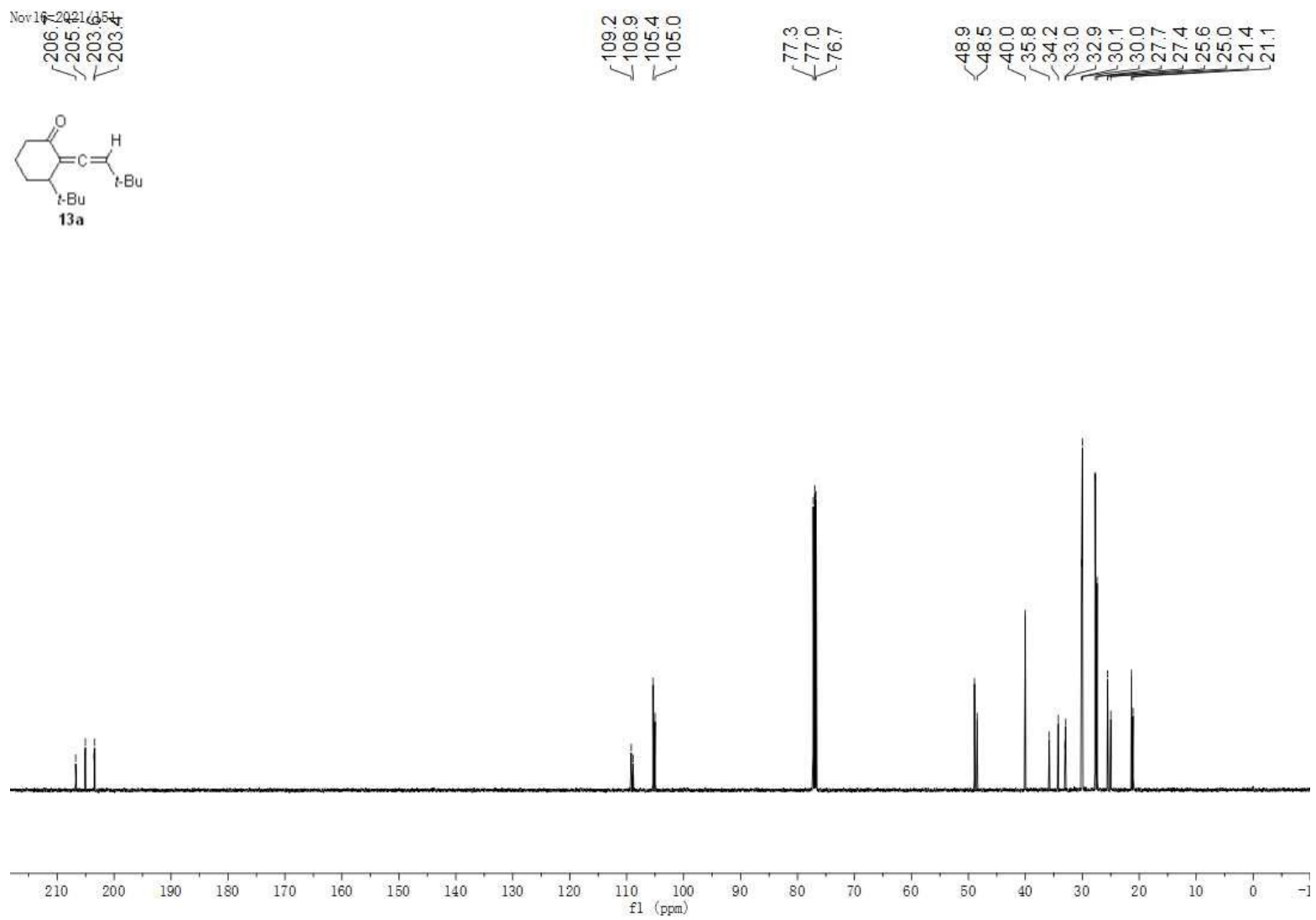
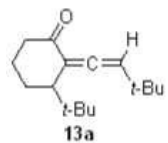


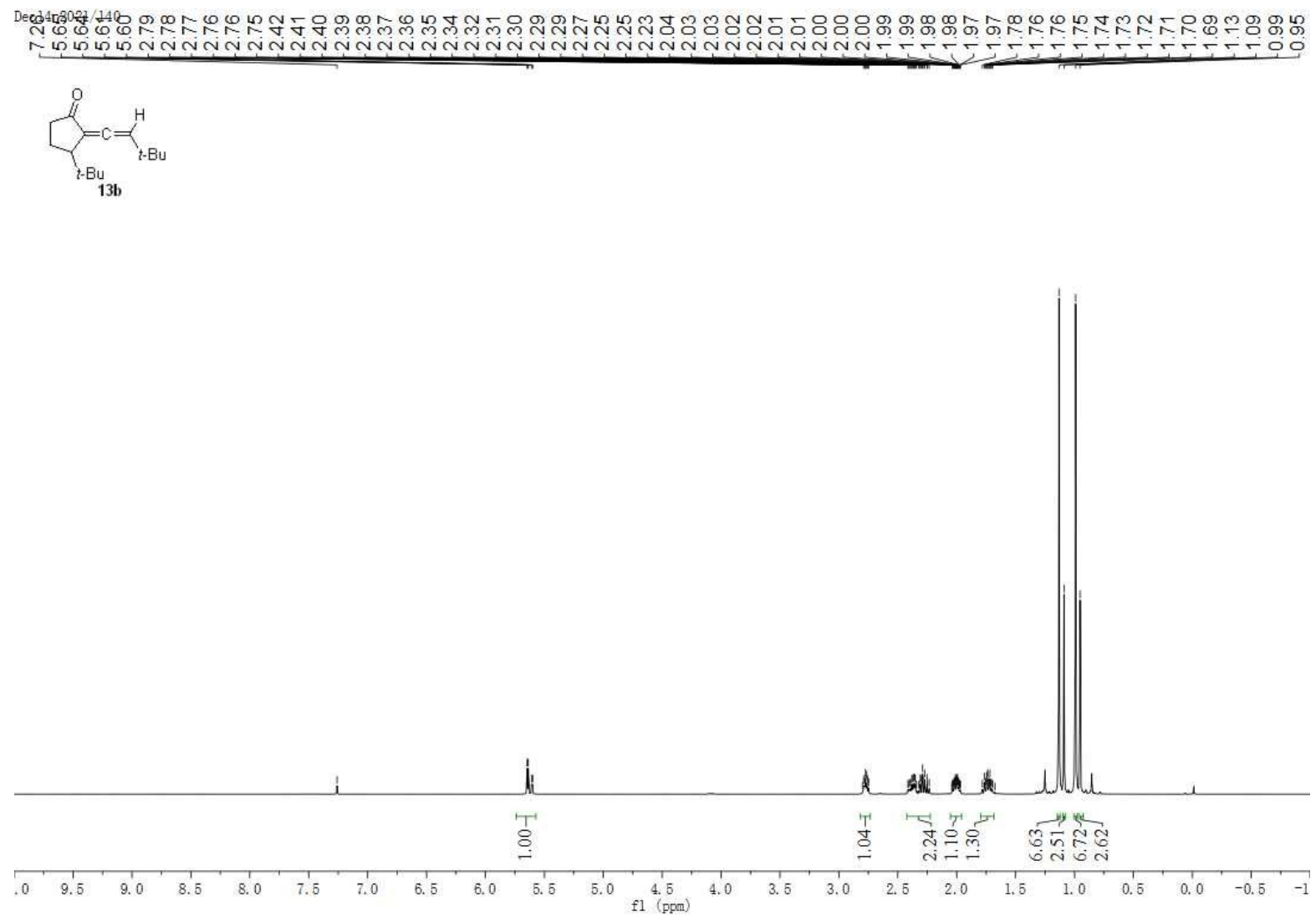
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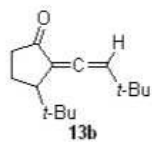
Nov 17, 2021 16:54





Dec 14 2021 14:11

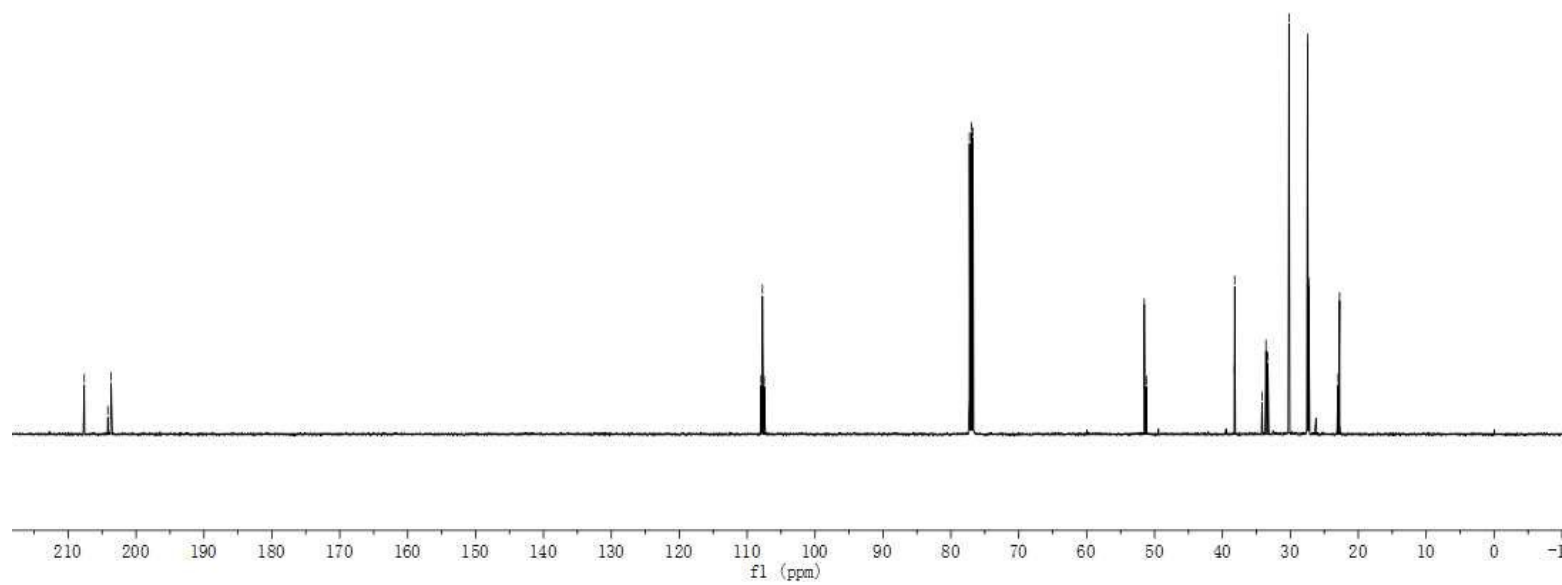
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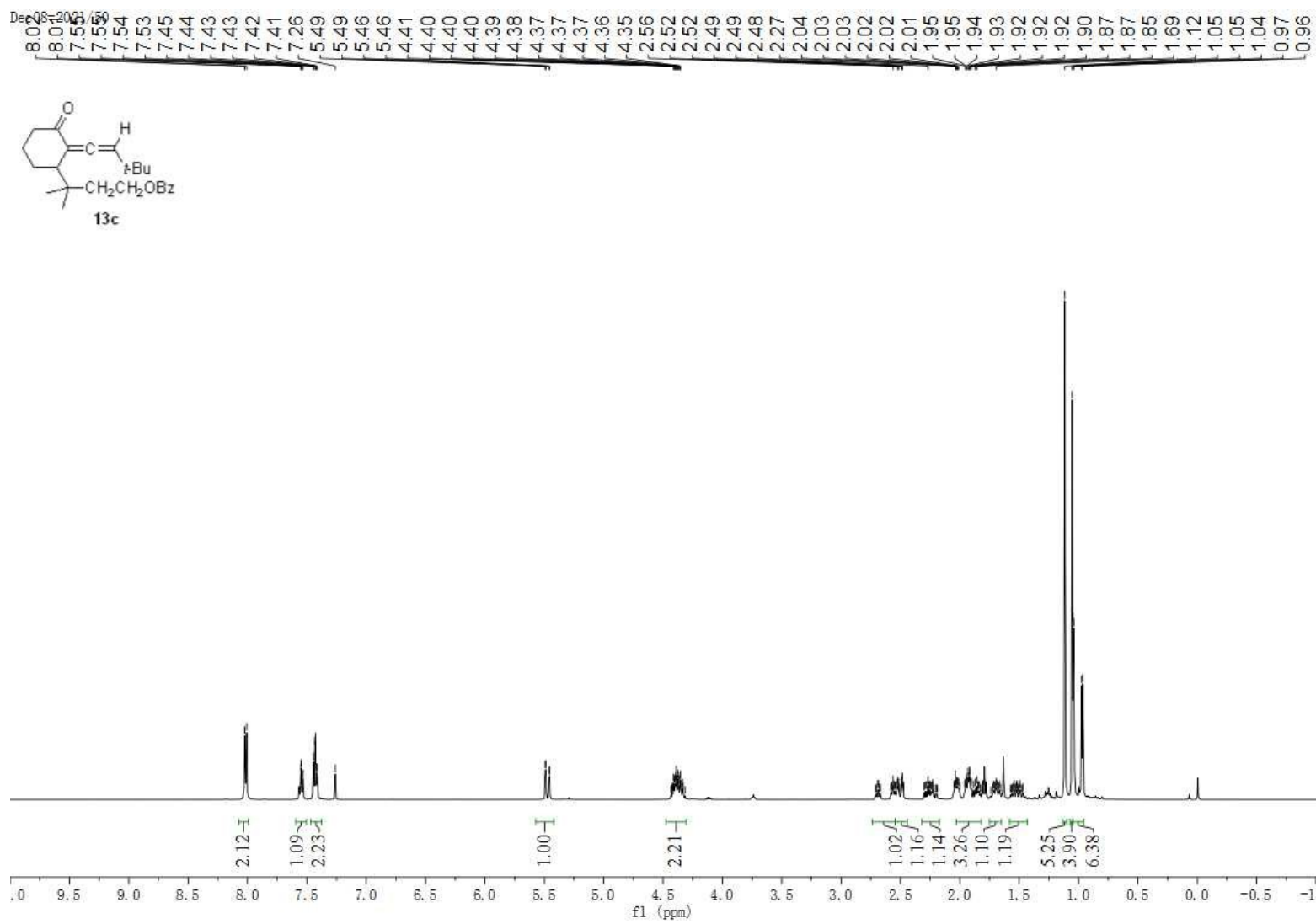


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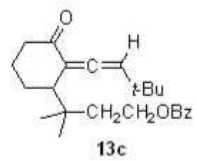
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27.3
23.0
22.7





Dec 08 2021
206.2
205.3
203.0



166.6

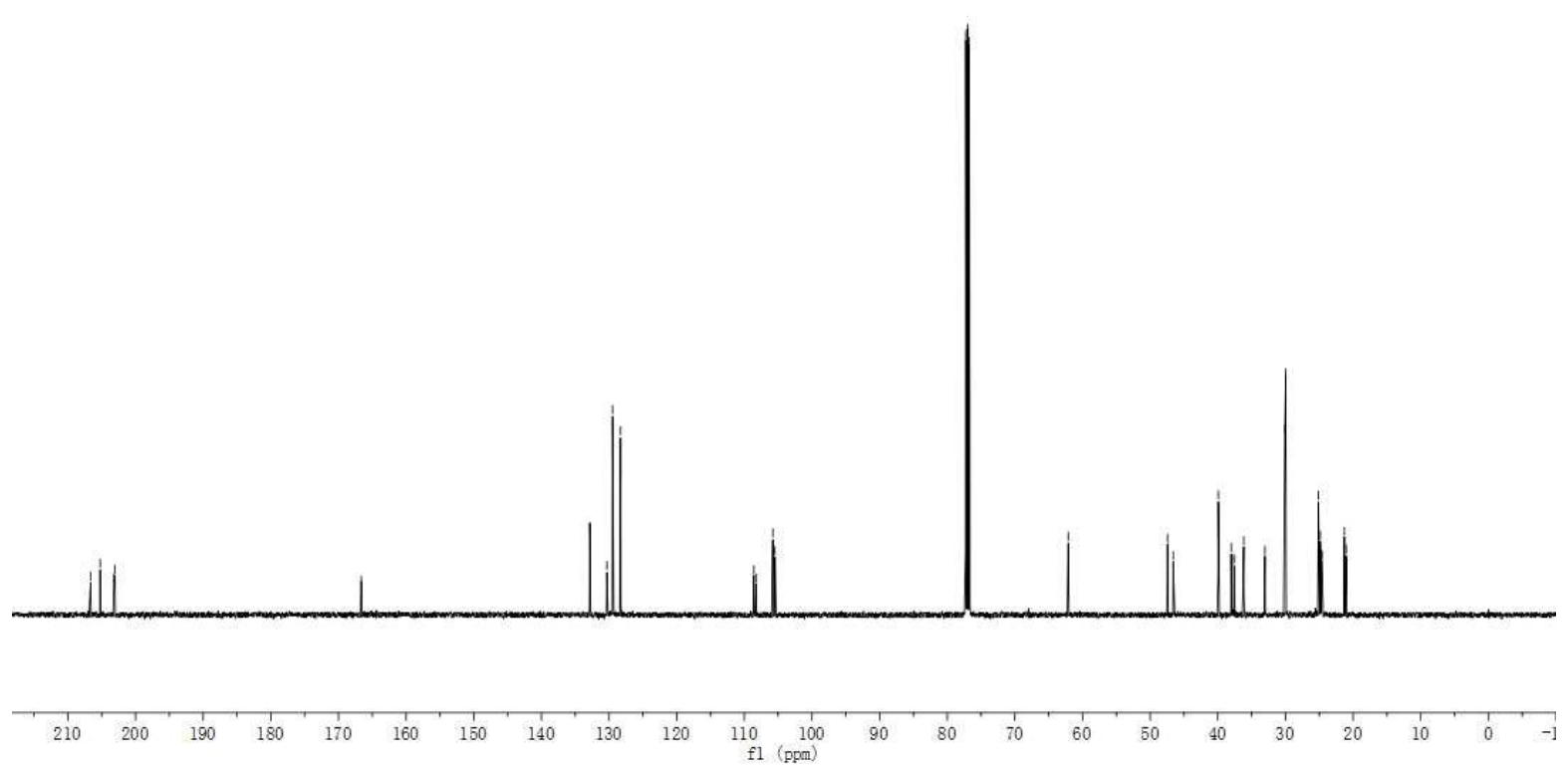
132.8
130.3
129.5
128.3
128.3

108.6
108.3
105.8
105.4

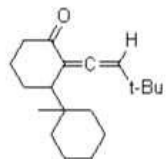
77.3
77.0
76.7

62.1
62.1

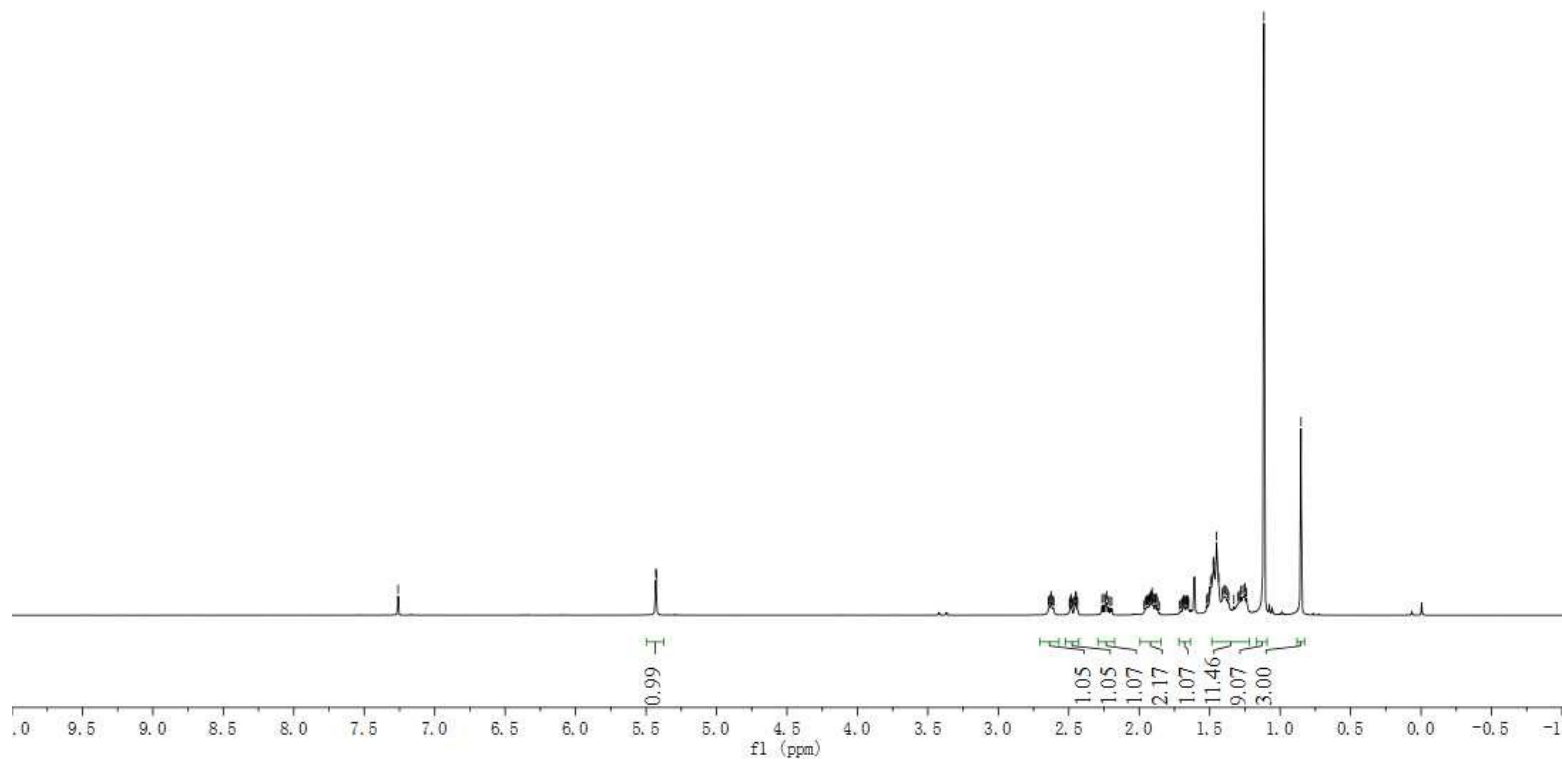
47.4
46.6
39.9
38.0
37.9
37.6
36.2
33.0
30.1
30.0
25.1
24.9
24.8
24.7
24.6
21.3
21.0



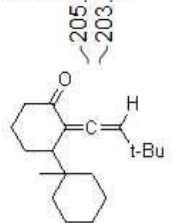
Dec 09 2013
 7.26
 5.43
 5.43
 2.63
 2.63
 2.49
 2.48
 2.46
 2.45
 2.45
 2.26
 2.25
 2.24
 2.23
 1.94
 1.94
 1.93
 1.93
 1.92
 1.92
 1.92
 1.91
 1.91
 1.90
 1.90
 1.89
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 1.88
 1.88
 1.69
 1.68
 1.66
 1.52
 1.51
 1.50
 1.49
 1.48
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 1.45
 1.44
 1.41
 1.40
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 1.38
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 1.25
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 1.24
 1.11
 0.85



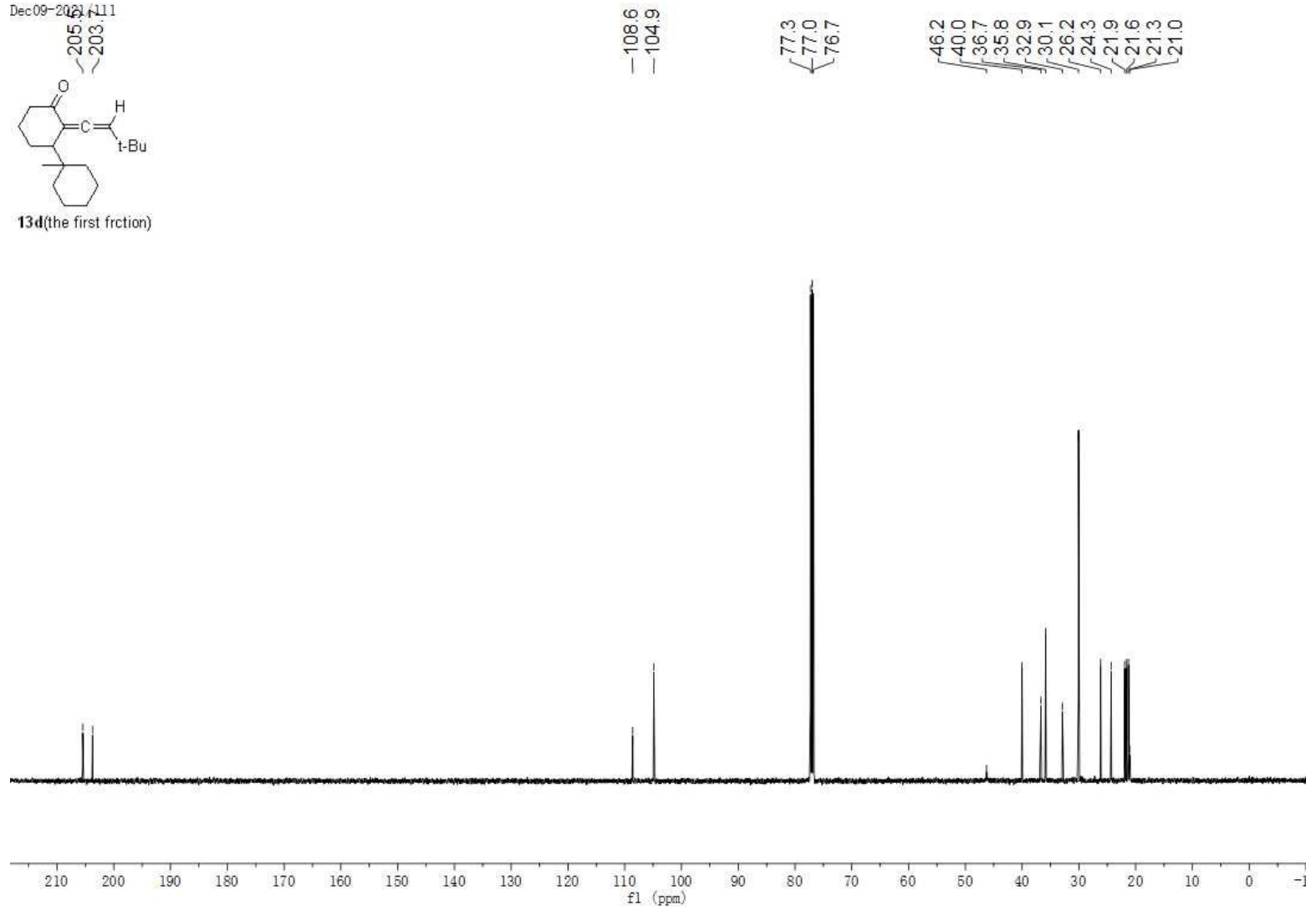
13d(the first fraction)

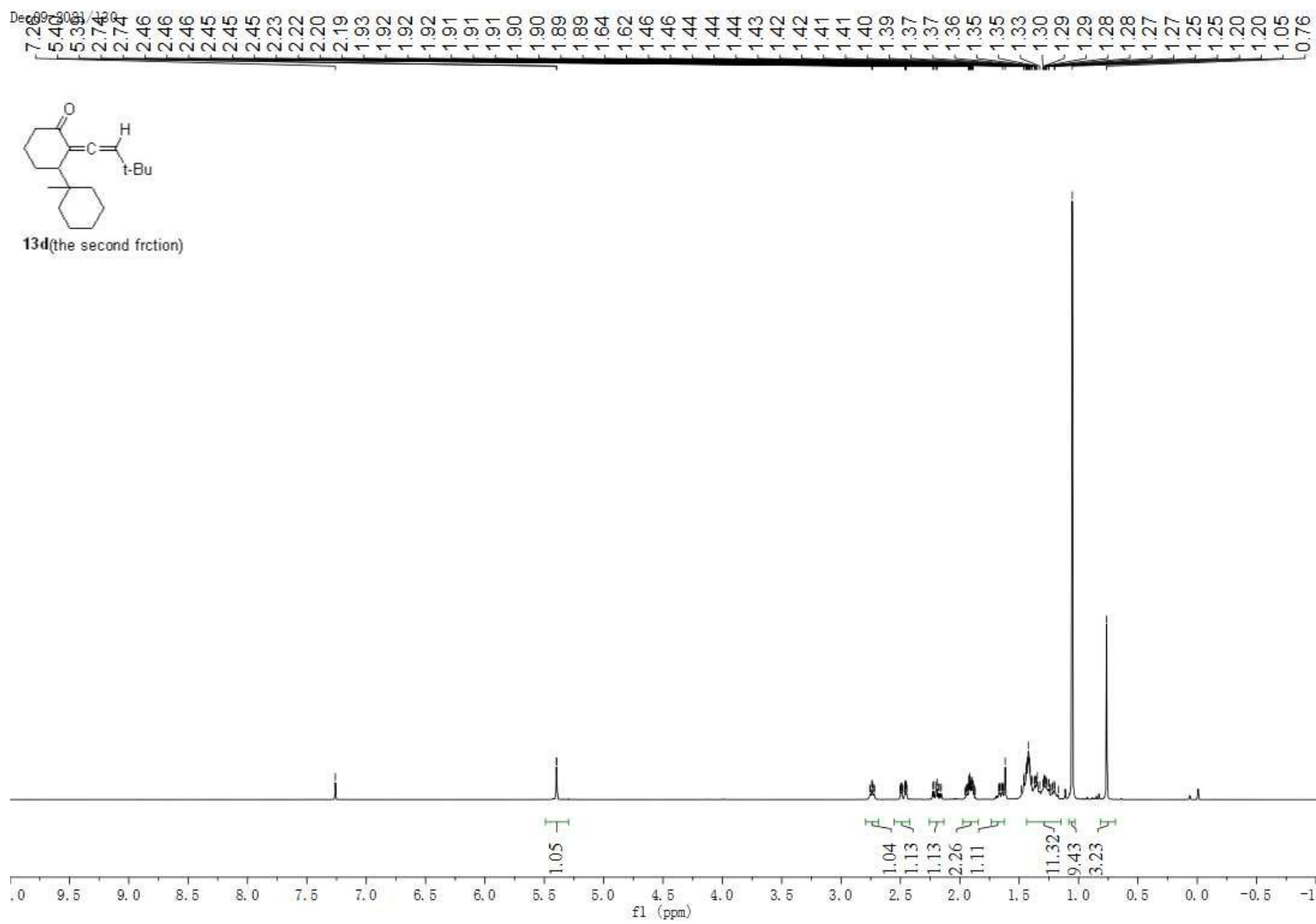


Dec09-2021 111



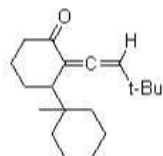
13d(the first fraction)





Dec09-2031.331

206.3
203.3

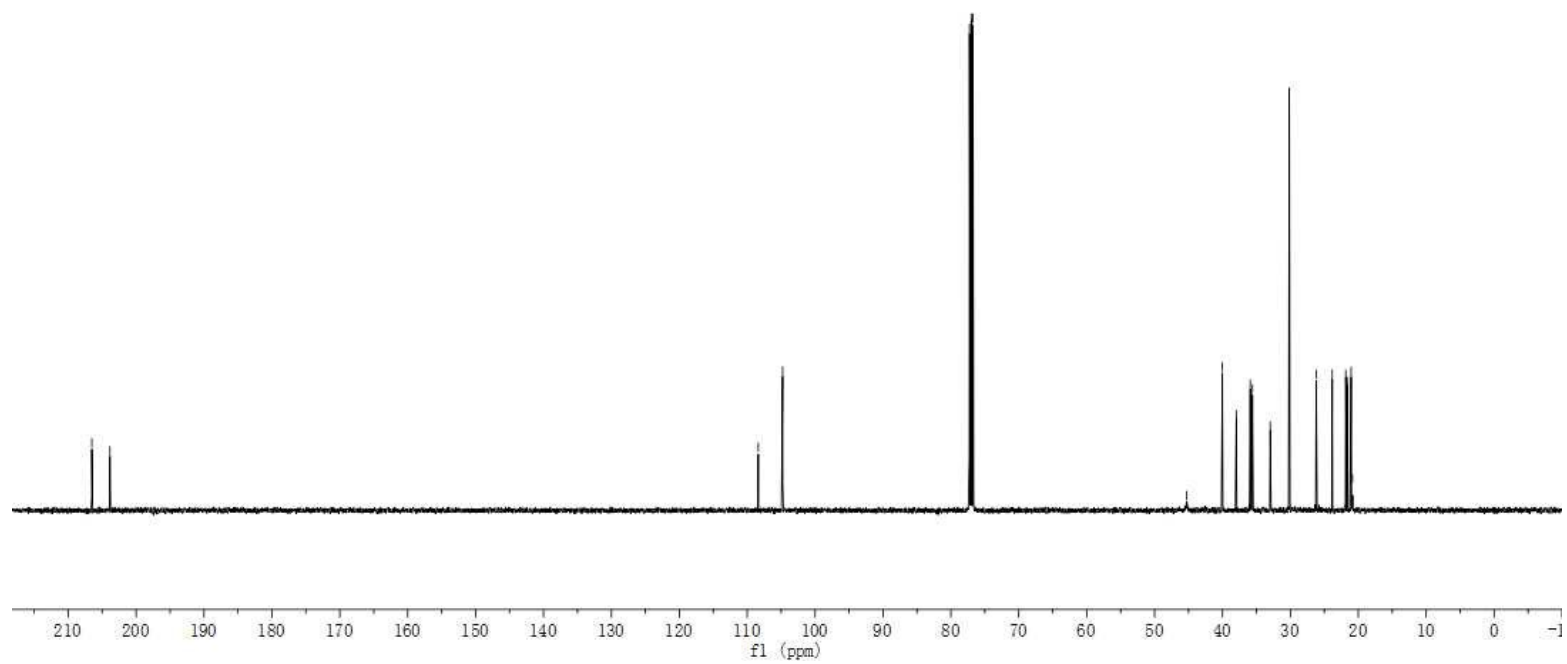


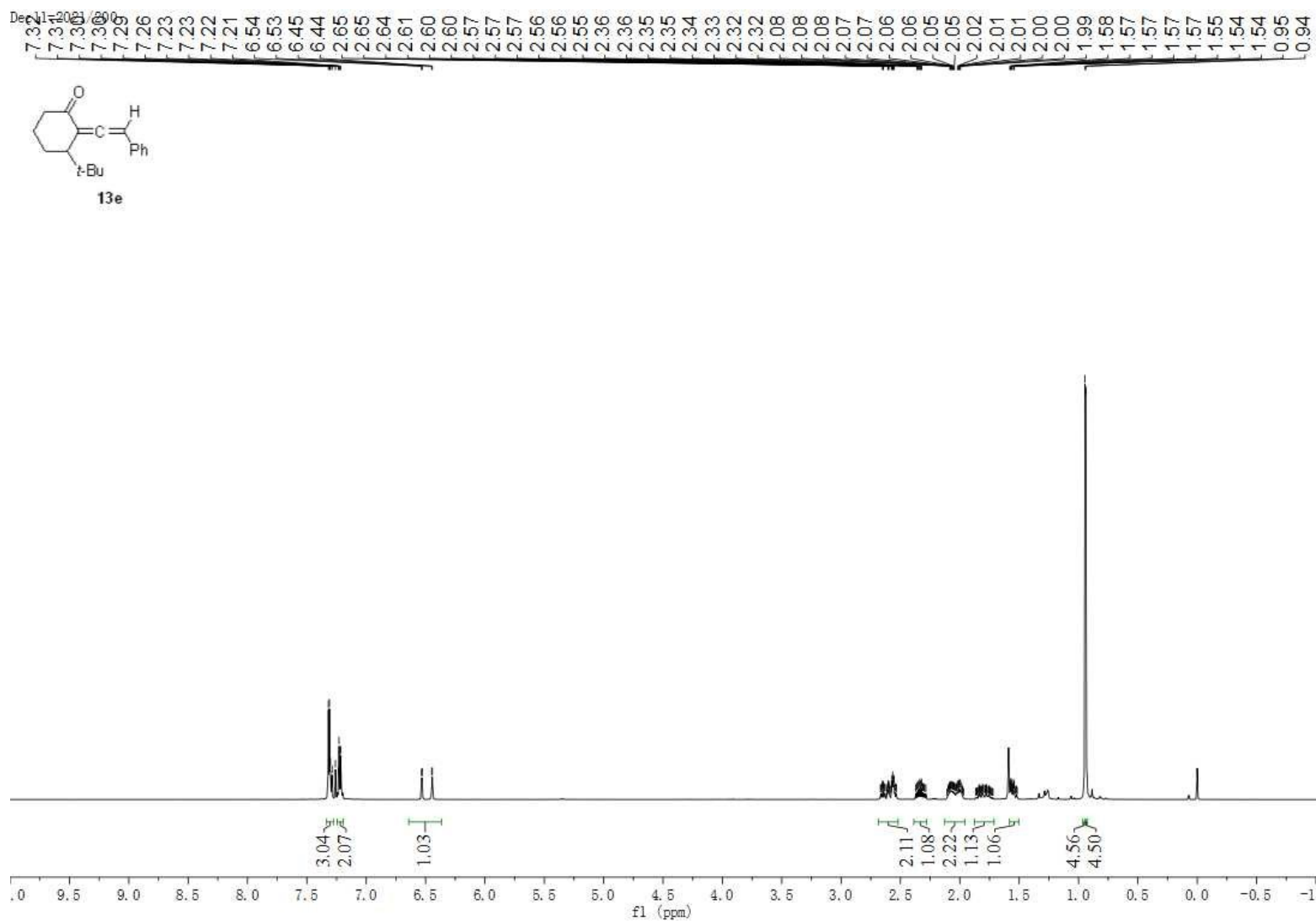
13d(the second frction)

108.4
104.8

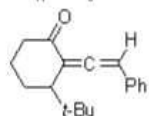
77.3
77.0
76.7

45.3
40.0
38.0
35.9
35.6
33.0
30.2
26.2
23.8
21.8
21.6
21.1
20.9

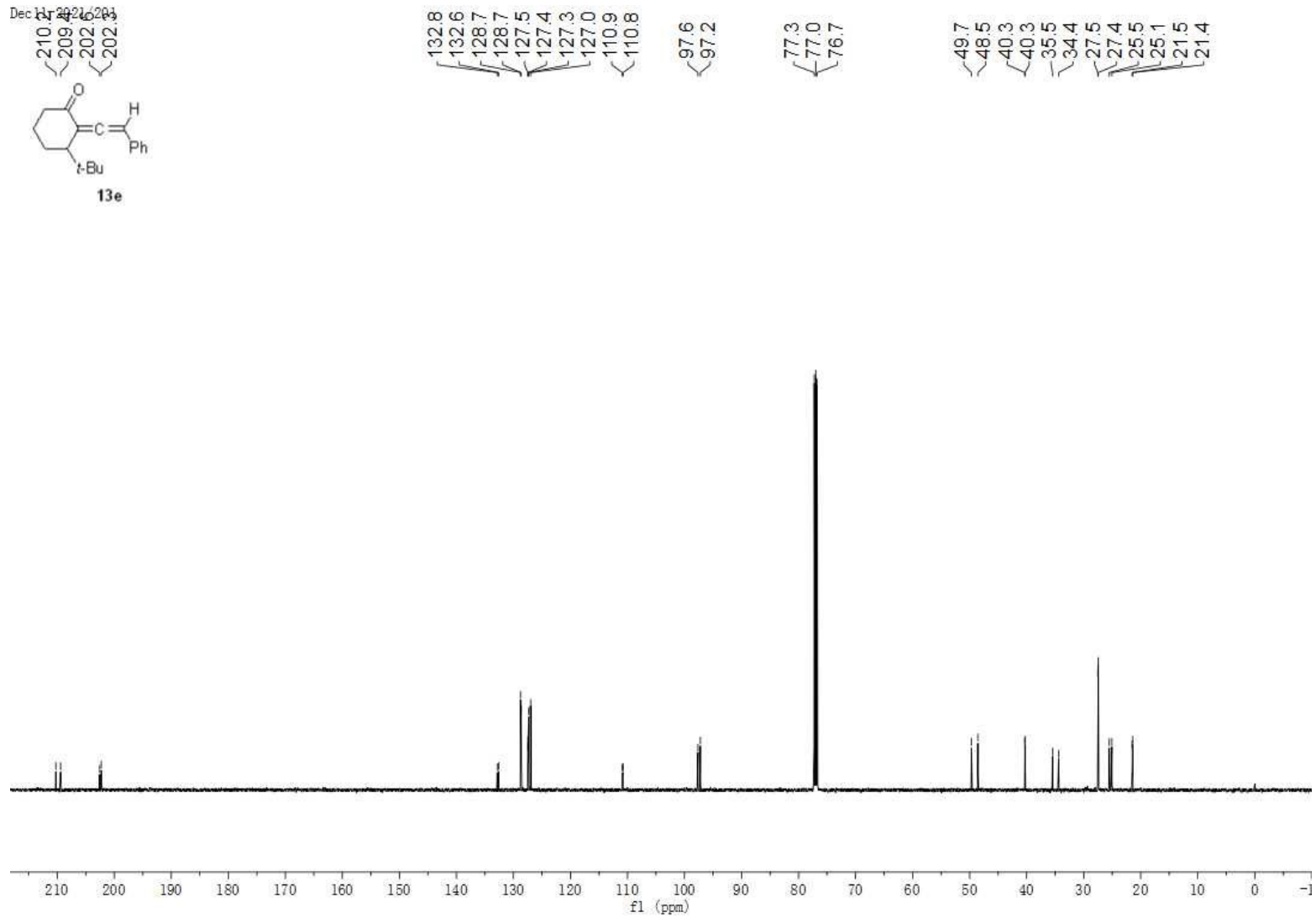


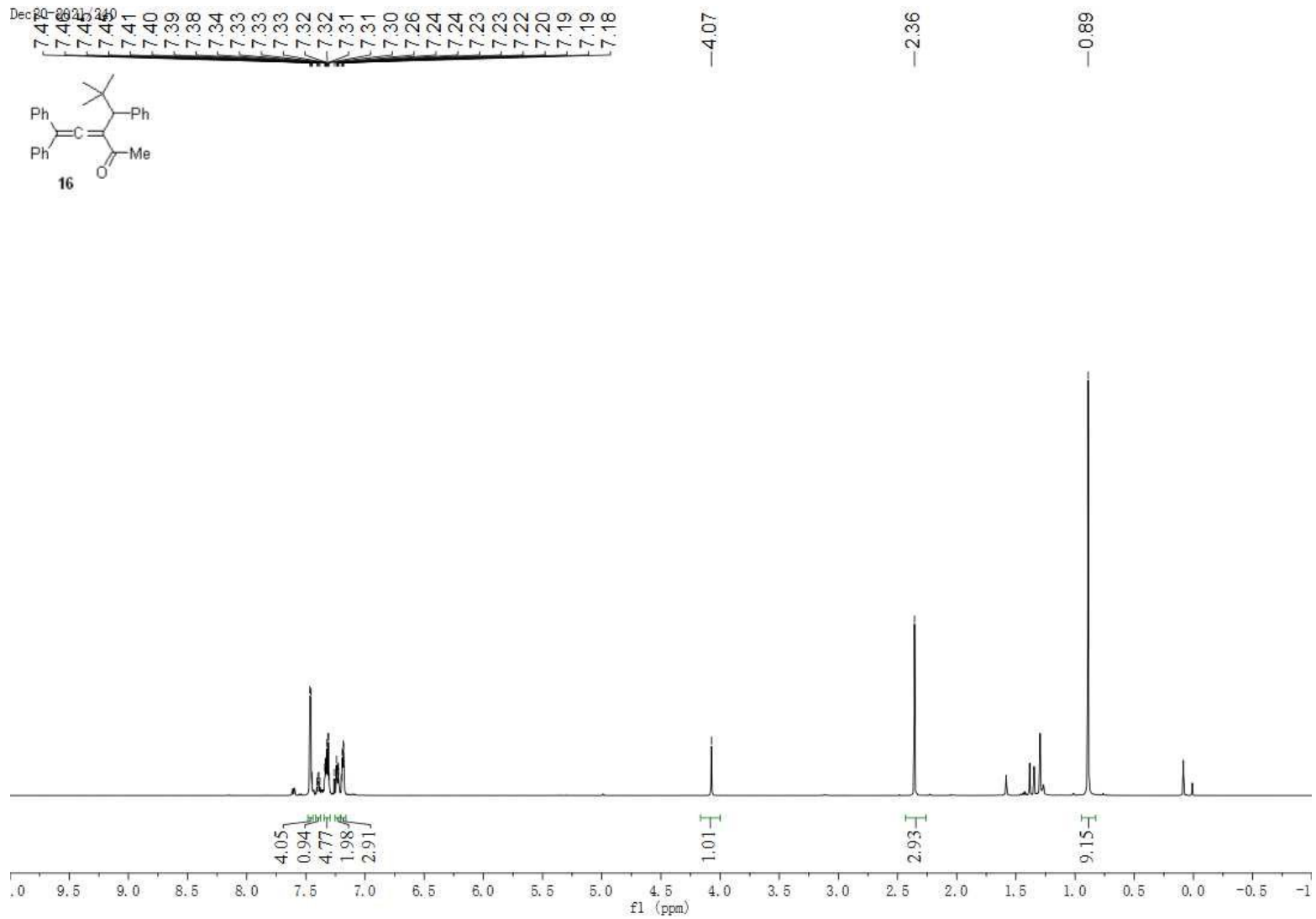


Dec 14, 2021, 2021



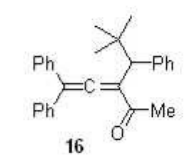
13e





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— 215.4
— 197.6



141.3
134.9
134.7
130.3
128.9
128.7
128.7
128.4
128.1
128.0
128.0
127.5
126.3
113.7

77.3
77.0
76.7

52.5

35.1
28.3
27.1

