

Supporting Information

Palladium Catalyzed Allylation and Carbonylation: Access to Allylhydrazones and Allyl Acylhydrazones

Qianqian Liang,^a Yan Cai,^b Mengdi Pang,^b Wenjun Jiang,^b Liming Fan,^b Guoying Zhang^{*a}

^a *State Key Laboratory of Coal Conversion, Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, P. R. China; University of Chinese Academy of Sciences, Beijing 100049, China*

^b *School of Chemistry and Chemical Engineering, North University of China, Taiyuan 030001, P. R. China.*

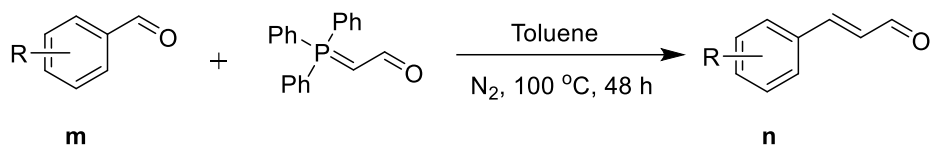
Contents

| | |
|--|------------|
| 1. General..... | 3 |
| 2. Synthesis of Starting Materials..... | 4 |
| 3. Screening of Reaction Parameters | 9 |
| 4. General Procedure for the products | 39 |
| 5. Characterization Data | 41 |
| 6. Mechanism Investigations..... | 92 |
| 7. Gram-Scale Synthesis | 109 |
| 8. Further Transformation..... | 114 |
| 9. References..... | 122 |
| 10. NMR Spectra..... | 122 |

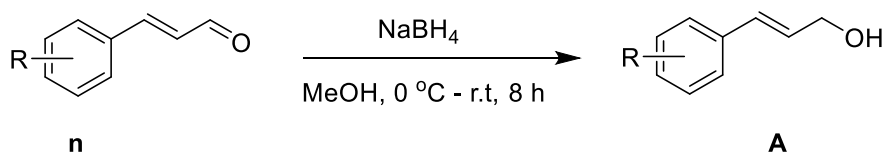
1. General

Experimental: All reactions and manipulations with air sensitive compounds being present were performed under dry argon (Ar 5.0) or nitrogen (N₂ 5.0), using Schlenk and glove box techniques. Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 300 and 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signal. Coupling constants (J) are given in Hz (coupling patterns: s: singlet, s_br: broad singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Machinery-Nagel (MN) Optima 5 HT column (30 m, 320 μ m, 0.25 μ m) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 μ m, 0.25 μ m). GC/MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 μ m, 0.25 μ m). High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass (ESI). MN silica gel 60 (0.040 – 0.063 mm particle size) was used for flash column chromatography.

2. Synthesis of Starting Materials¹

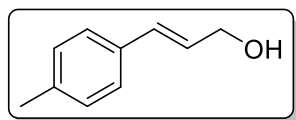


General procedure 1: (Triphenylphosphoranylidene) acetaldehyde **m** (18.26 g, 60 mmol) and aldehyde (20 mmol) were added to a 250 mL dry flask blocked with nitrogen. The reaction mixture was stirred at 100 °C for 48 h in toluene. After completion of the reaction, the reaction was confirmed by TLC and GC-MS. Thereafter, the reaction solvent was evaporated under reduced pressure in a rotary evaporator to obtain a residue. The residue was purified by flash column chromatography with a mixture of petroleum ether and ethyl acetate as eluent to obtain the desired compound **n**.



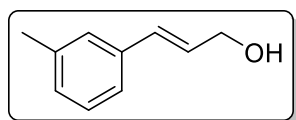
General procedure 2: Aldehyde **n** (5 mmol) was dissolved in 50 mL of methanol and cooled down to 0 °C. NaBH₄ (567.5 mg, 15 mmol) was added in batches, then the reaction mixture was slowly warmed to room temperature and stirred for 8 h. After completion of the reaction, the reaction was confirmed by TLC and GC-MS. The reaction was quenched with 0.1 N NaOH (50 mL) and extracted with ethyl acetate three times. The organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the resulting yellow oil was subjected to flash chromatography to give the product **A** in the reported yields.

Preparation of (E)-3-(p-tolyl)prop-2-en-1-ol (A2)



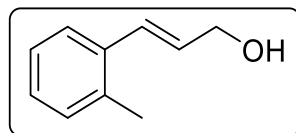
A2 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ethyl acetate =5:1) to give product as a white solid in 90% yield (666 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.20 – 7.06 (m, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.41 (m, 1H), 6.15 (m, 1H), 4.12 (m, 2H), 2.83 (s, 1H), 2.20 (s, 3H).

Preparation of (E)-3-(m-tolyl)prop-2-en-1-ol (A3)



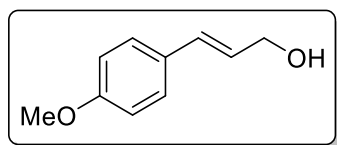
A3 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ethyl acetate =5:1) to give product as the light-yellow oil in 89% yield (659 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.14 – 6.99 (m, 3H), 6.92 (m, 1H), 6.41 (d, J = 16.0 Hz, 1H), 6.18 (m, 1H), 4.13 (m, 2H), 2.94 (s, 1H), 2.19 (s, 3H).

Preparation of (E)-3-(o-tolyl)prop-2-en-1-ol (A4)



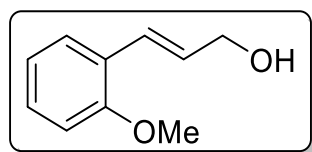
The **n4** was prepared according to the general procedure 1 and purified by column chromatography (petroleum ether/ ethyl acetate =20:1) to give product as the light-yellow oil in 37% yield (1096 mg). Then **A4** was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give product as the light-yellow oil in 89% yield (659 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.40 (m, 1H), 7.18 – 7.07 (m, 3H), 6.78 (m, 1H), 6.20 (m, 1H), 4.28 (m, 2H), 2.56 (s, 1H), 2.31 (s, 3H).

Preparation of (E)-3-(4-methoxyphenyl)prop-2-en-1-ol (A5)



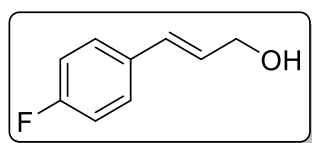
A5 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give product as a white solid in 85% yield (697mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.18 (m, 2H), 6.87 – 6.72 (m, 2H), 6.47 (m, 1H), 6.16 (m, 1H), 4.21 (m, 2H), 3.73 (s, 3H), 3.25 (s, 1H).

Preparation of (E)-3-(2-methoxyphenyl)prop-2-en-1-ol (A6)



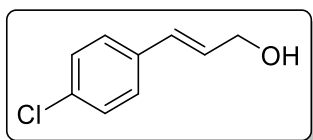
A6 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give product as the light-yellow oil in 87% yield (714 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.35 (m, 1H), 7.18 – 7.10 (m, 1H), 6.94 – 6.79 (m, 2H), 6.75 (m, 1H), 6.30 (m, 1H), 4.23 (m, 2H), 3.68 (s, 3H), 3.59 (s, 1H).

Preparation of (E)-3-(4-fluorophenyl)prop-2-en-1-ol (A7)



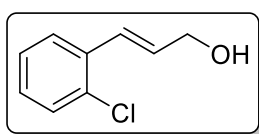
A7 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give product as the light-yellow oil in 86% yield (654 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.43 – 7.18 (m, 2H), 7.11 – 6.88 (m, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.24 (m, 1H), 4.41 – 4.13 (m, 2H), 2.62 (s, 1H).

Preparation of (E)-3-(4-chlorophenyl)prop-2-en-1-ol (A8)



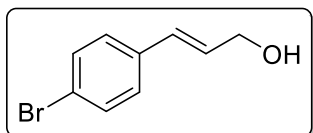
A8 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give product as a white solid in 87% yield (731 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.08 (m, 4H), 6.35 (d, $J = 16.0$ Hz, 1H), 6.12 (m, 1H), 4.12 (m, 2H), 3.48 (s, 1H).

Preparation of (E)-3-(2-chlorophenyl)prop-2-en-1-ol (A9)



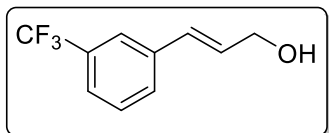
A9 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give product 1 as the light-yellow oil in 86% yield (723 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 (m, 1H), 7.22 – 7.13 (m, 1H), 7.08 – 6.93 (m, 2H), 6.85 (m, 1H), 6.17 (m, 1H), 4.18 (m, 2H), 3.38 (s, 1H).

Preparation of (E)-3-(4-bromophenyl)prop-2-en-1-ol (A10)



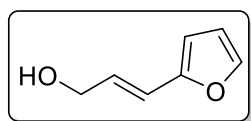
A10 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give t product a white solid oil in 87% yield (922 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.28 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.37 (d, $J = 16.0$ Hz, 1H), 6.17 (m, 1H), 4.15 (m, 2H), 3.06 (s, 1H).

Preparation of (E)-3-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol (A11)



A11 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give product as the light-yellow oil in 88% yield (889 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 (s, 1H), 7.31 (m, 2H), 7.20 (m, 1H), 6.46 (d, $J = 16.0$ Hz, 1H), 6.33 – 6.14 (m, 1H), 4.26 – 4.05 (m, 2H), 3.68 – 3.26 (m, 1H).

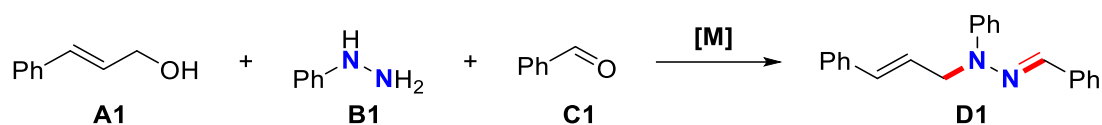
Preparation of (E)-3-(furan-2-yl)prop-2-en-1-ol(A12)



A12 was prepared according to the general procedure 2 and purified by column chromatography (petroleum ether/ ethyl acetate =5:1) to give t product as the light-yellow oil in 71% yield (440 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32 (m, 1H), 6.40 (m, 1H), 6.34 (m, 1H), 6.30 – 6.16 (m, 2H), 4.23 (m, 2H), 3.16 – 2.92 (m, 1H).

3. Screening of reaction parameters

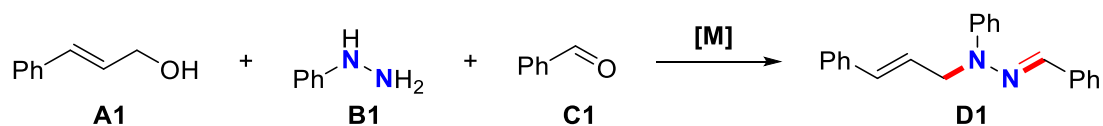
3.1 Screening of tandem allylation reaction parameters



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, solvent, benzaldehyde (**C1**), phenyl hydrazine (**B1**), catalyst and cinnamyl alcohol (**A1**). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated metal bath (design temperature) for design time. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in the reported yields.

| Entry | Parameter |
|-----------------|--------------------------------------|
| Table S1 | The difference of catalyst screening |
| Table S2 | The difference ligand screening |
| Table S3 | The difference of solvent screening |
| Table S4 | The ratio of substrates screening |
| Table S5 | The loading of solvent screening |
| Table S6 | The Pd-catalyst loading screening |
| Table S7 | Reaction temperature screening |
| Table S8 | Reaction time screening |
| Table S9 | The reaction system screening |

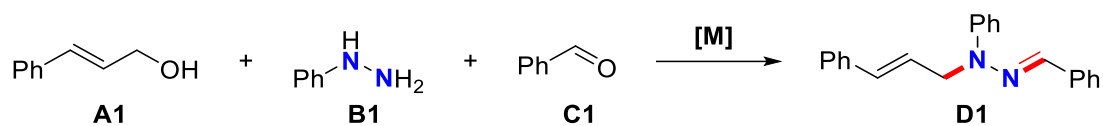
Table S1. The difference of catalyst screening ^a



| Entry | Catalyst | D1 (%) |
|-----------------|--|-----------|
| 1 | - | 0 |
| 2 | PdCl ₂ | 72 |
| 3 | PdBr ₂ | <5 |
| 4 | PdI ₂ | <5 |
| 5 | PdCl₂(CH₃CN)₂ | 95 |
| 6 | PdBr ₂ (CH ₃ CN) ₂ | 43 |
| 7 | Pd(OAc) ₂ | 70 |
| 8 | Pd(TFA) ₂ | 87 |
| 9 | PdCl ₂ (COD) | 63 |
| 10 | PdBr ₂ (COD) | 39 |
| 11 | Pd/C | 0 |
| 12 ^b | [Pd(Cl)(C ₃ H ₅) ₂] | 81 |
| 13 ^b | [Pd(Cl)(C ₉ H ₉) ₂] | 88 |
| 14 | NiCl ₂ | 0 |
| 15 | CoCl ₂ | 0 |
| 16 | MnCl ₂ | 0 |
| 17 | CuCl ₂ | 0 |
| 18 | FeCl ₂ | 0 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), catalyst (0.01 mmol, 2 mol%), Xantphos (0.011 mmol, 2.2 mol%), toluene (2.0 mL), 60 °C (extern temperature), 4 h, N₂. Isolated yield. ^b Catalyst (0.005 mmol, 1 mol%).

Table S2. The difference of ligand screening ^a



| Entry | Ligand | D1 (%) |
|-------|--------|--------|
| 1 | - | 0 |
| 2 | L1 | 3 |
| 3 | L2 | 4 |
| 4 | L3 | 5 |
| 5 | L4 | 4 |
| 6 | L5 | 5 |
| 7 | L6 | 3 |
| 8 | L7 | 4 |
| 9 | L8 | 4 |
| 10 | L9 | 5 |
| 11 | L10 | 3 |
| 12 | L11 | 4 |
| 13 | L12 | 2 |
| 14 | L13 | 1 |
| 15 | L14 | 2 |
| 16 | L15 | 2 |
| 17 | L16 | 4 |
| 18 | L17 | 95 |
| 19 | L18 | 52 |
| 20 | L19 | 73 |
| 21 | L20 | 90 |
| 22 | L21 | 26 |

| Entry | Ligand | D1 (%) |
|-----------------|--|-----------|
| 23 | L22 | 12 |
| 24 | L23 | 4 |
| 25 | L24 | 5 |
| 26 | L25 | 11 |
| 27 | L26 | 8 |
| 28 | L27 | 12 |
| 29 | L28 | 6 |
| 30 | L29 | 7 |
| 31 | L30 | 61 |
| 32 | L31 | 18 |
| 33 | L32 | 5 |
| 34 | L33 | 3 |
| 35 | L34 | 13 |
| 36 | L35 | 12 |
| 37 ^b | PdCl₂(Xantphos) | 95 |
| 38 ^b | Pd(Xantphos)(OTf)₂(CH₃CN)₂ | 93 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μL), **C1** (0.7 mmol, 72 μL), PdCl₂(CH₃CN)₂ (0.01 mmol, 2 mol%), Ligand (**L1-L7** 0.021 mmol, 4.2 mol%; **L8-L20** 0.012 mmol, 2.2 mol%), toluene (2.0 mL), 60 °C (extern temperature), 4 h, N₂. Isolated yield. ^b Catalyst (0.01 mmol, 2 mol%).

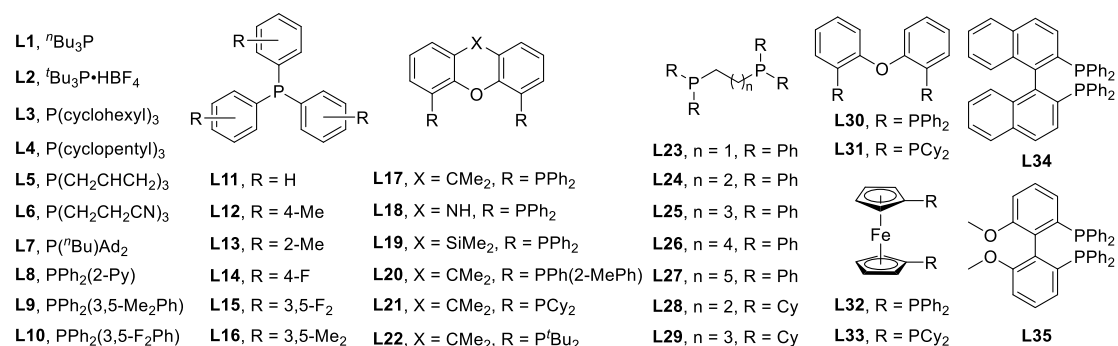
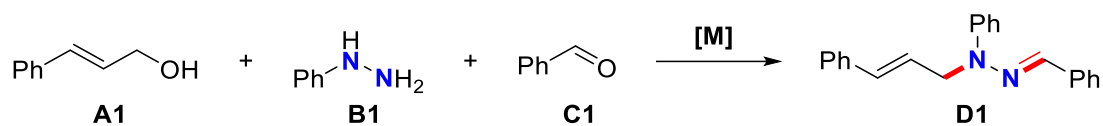


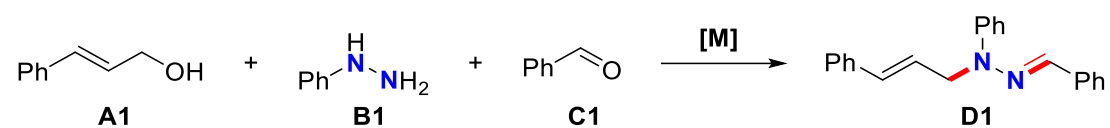
Table S3. The difference of solvent screening ^a



| Entry | Solvent (2 mL) | D1 (%) |
|----------|--------------------|-----------|
| 1 | anisole | 88 |
| 2 | THF | 44 |
| 3 | 1,4-dioxane | 10 |
| 4 | DME | 36 |
| 5 | toluene | 95 |
| 6 | xylene | 72 |
| 7 | mesitylene | 83 |
| 8 | DCM | 0 |
| 9 | CH ₃ CN | 0 |
| 10 | pyridine | 39 |
| 11 | methanol | 0 |
| 12 | ethanol | 6 |
| 13 | isopropanol | <5 |
| 14 | <i>t</i> -AmOH | 70 |
| 15 | DMF | <5 |
| 16 | DMAc | <5 |
| 17 | NMP | <5 |
| 18 | DMSO | 31 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), solvent (2.0 mL), 60 °C (extern temperature), 4 h, N₂. Isolated yield.

Table S4. The ratio of substrates screening ^a



| Entry | A1 | B1 | C1 | D1 (%) |
|-----------|-------------|------------|------------|-----------|
| 1 | 0.5 | 0.5 | 0 | 0 |
| 2 | 0.5 | 0.5 | 0.5 | 70 |
| 3 | 0.5 | 0.5 | 0.65 | 82 |
| 4 | 0.5 | 0.5 | 0.75 | 86 |
| 5 | 0.5 | 0.5 | 0.85 | 85 |
| 6 | 0 | 0.5 | 0.5 | 0 |
| 7 | 0.65 | 0.5 | 0.5 | 88 |
| 8 | 0.75 | 0.5 | 0.5 | 90 |
| 9 | 0.85 | 0.5 | 0.5 | 90 |
| 10 | 0.5 | 0 | 0.5 | 0 |
| 11 | 0.5 | 0.65 | 0.5 | 51 |
| 12 | 0.5 | 0.75 | 0.5 | 43 |
| 13 | 0.5 | 0.85 | 0.5 | 42 |
| 14 | 0.75 | 0.5 | 0.6 | 92 |
| 15 | 0.75 | 0.5 | 0.7 | 95 |
| 16 | 0.75 | 0.5 | 0.75 | 95 |
| 17 | 0.75 | 0.5 | 0.8 | 95 |

^a Reaction conditions: A1 (x mmol), B1 (x mmol), C1 (x mmol), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), 60 °C (extern temperature), 4 h, N₂. Isolated yield.

Table S5. The loading of solvent screening ^a

| Entry | toluene (mL) | D1 (%) |
|----------|--------------|-----------|
| 1 | 0 | <5 |
| 2 | 0.5 | 85 |
| 3 | 1.0 | 89 |
| 4 | 1.5 | 93 |
| 5 | 2.0 | 95 |
| 6 | 3.0 | 95 |
| 7 | 4.0 | 95 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (x mL), 60 °C (extern temperature), 4 h, N₂. Isolated yield.

Table S6. The Pd-catalyst loading screening ^a

| Entry | Pd-catalyst | D1 (%) |
|----------|-------------|-----------|
| 1 | 0 | 0 |
| 2 | 0.0005 | 9 |
| 3 | 0.001 | 43 |
| 4 | 0.002 | 78 |
| 5 | 0.005 | 92 |
| 6 | 0.01 | 95 |
| 7 | 0.02 | 95 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (x mmol), toluene (2.0 mL), 60 °C (extern temperature), 4 h, N₂. Isolated yield.

Table S7. Reaction temperature screening ^a

| Entry | T (° C) | D1 (%) |
|-------|-----------|-----------|
| 1 | RT | 51 |
| 2 | 40 | 70 |
| 3 | 50 | 90 |
| 4 | 60 | 95 |
| 5 | 70 | 95 |

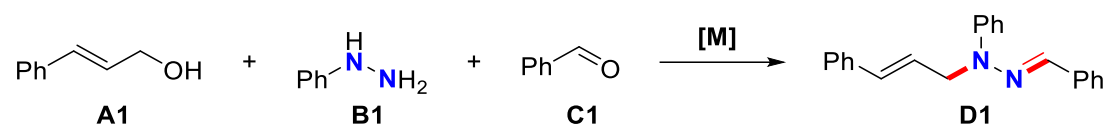
^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), T (extern temperature), 4 h, N₂. Isolated yield.

Table S8. Reaction time screening ^a

| Entry | t (h) | D1 (%) |
|-------|----------|-----------|
| 1 | 1 | 65 |
| 2 | 2 | 89 |
| 3 | 3 | 93 |
| 4 | 4 | 95 |
| 5 | 5 | 95 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), 60 °C (extern temperature), t h, N₂. Isolated yield.

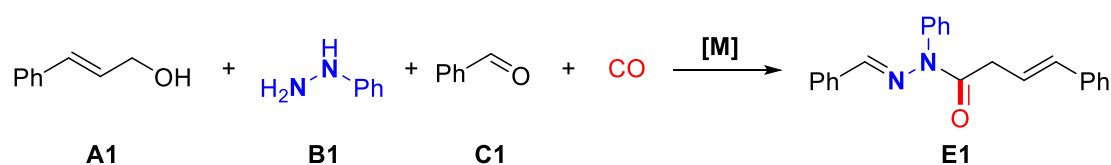
Table S9. The reaction system screening ^a



| Entry | System | atmosphere | D1 (%) |
|----------|-------------|----------------------|-----------|
| 1 | open | N ₂ | 93 |
| 2 | open | O ₂ | <5 |
| 3 | open | air | 28 |
| 4 | seal | N₂ | 95 |
| 5 | seal | O ₂ | <5 |
| 6 | seal | air | 26 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μL), **C1** (0.7 mmol, 72 μL), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), 60 °C (extern temperature), 4 h, Isolated yield.

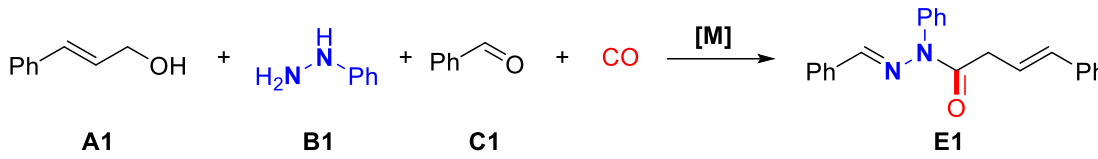
3.2 Screening of tandem allylation/carbonylation parameters



Using a nitrogen-filled glove box, an oven-dried glass bottle (10 mL volume) was charged with a magnetic stirring bar, catalyst (ligand), solvent, benzaldehyde (**C1**), phenyl hydrazine (**B1**) and cinnamyl alcohol (**A1**). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. Then a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) on silica gel to give the product **E1** in the reported yields.

| Entry | Parameter |
|------------------|--------------------------------------|
| Table S10 | The difference of catalyst screening |
| Table S11 | The difference ligand screening |
| Table S12 | The difference of solvent screening |
| Table S13 | The ratio of substrates screening |
| Table S14 | The loading of solvent screening |
| Table S15 | The Pd-catalyst loading screening |
| Table S16 | Reaction pressure screening |
| Table S17 | Reaction temperature screening |
| Table S18 | Reaction time screening |

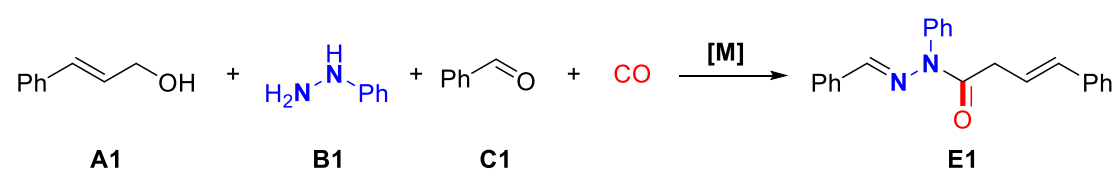
Table S10. The difference of catalyst screening^a



| Entry | Catalyst | D1 (%) |
|-----------------|--|-----------|
| 1 | - | 0 |
| 2 | PdCl ₂ | 33 |
| 3 | PdBr ₂ | 20 |
| 4 | PdI ₂ | trace |
| 5 | PdCl₂(CH₃CN)₂ | 46 |
| 6 | Pd(OAc) ₂ | 12 |
| 7 | Pd(TFA) ₂ | 27 |
| 8 | Pd/C | 0 |
| 9 ^b | [Pd(Cl)(C ₃ H ₅) ₂] | 38 |
| 10 ^b | [Pd(Cl)(C ₉ H ₉) ₂] | 42 |
| 11 | NiCl ₂ | 0 |
| 12 | CoCl ₂ | 0 |
| 13 | MnCl ₂ | 0 |
| 14 | CuCl ₂ | 0 |
| 15 | FeCl ₂ | 0 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), catalyst (0.01 mmol, 2 mol%), Xantphos (0.01 mmol, 2 mol%), toluene (2.0 mL), 120 $^{\circ}$ C (extern temperature), 12 h, CO (2 MPa), GC yield. ^b Catalyst (0.005 mmol, 2 mol%).

Table S11. The difference ligand screening ^a



| Entry | Ligand | D1 (%) |
|-----------|------------|-----------|
| 1 | - | 0 |
| 2 | L1 | 1 |
| 3 | L2 | 2 |
| 4 | L3 | 1 |
| 5 | L4 | 2 |
| 6 | L5 | 1 |
| 7 | L6 | 1 |
| 8 | L7 | 1 |
| 9 | L8 | 1 |
| 10 | L9 | 1 |
| 11 | L10 | 1 |
| 12 | L11 | 1 |
| 13 | L12 | 3 |
| 14 | L13 | 3 |
| 15 | L14 | 3 |
| 16 | L15 | 2 |
| 17 | L16 | 2 |
| 18 | L17 | 46 |
| 19 | L18 | 12 |
| 20 | L19 | 31 |
| 21 | L20 | 15 |

| Entry | Ligand | D1 (%) |
|-----------------------|--|-----------|
| 22 | L21 | 6 |
| 23 | L22 | 5 |
| 24 | L23 | 2 |
| 25 | L24 | 2 |
| 26 | L25 | 5 |
| 27 | L26 | 2 |
| 28 | L27 | 5 |
| 29 | L28 | 2 |
| 30 | L29 | 2 |
| 31 | L30 | 26 |
| 32 | L31 | 6 |
| 33 | L32 | 1 |
| 34 | L33 | 1 |
| 35 | L34 | 1 |
| 36 | L35 | 12 |
| 37^b | PdCl₂(Xantphos) | 46 |
| 38^b | Pd(Xantphos)(OTf)₂(CH₃CN)₂ | 43 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(CH₃CN)₂ (0.01 mmol, 2 mol%), Ligand (**L1-L16** 0.021 mmol, 4.2 mol%; **L17-L35** 0.011 mmol, 2.2 mol%), toluene (2.0 mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield. ^b ccatalyst (0.01 mmol, 2 mol%).

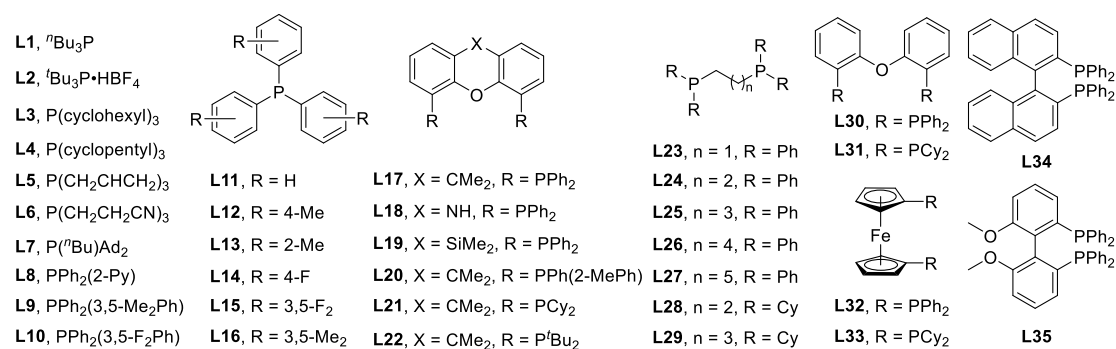
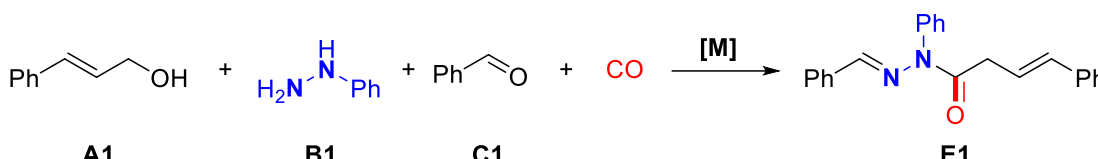


Table S12. The difference of solvent screening ^a

A1 **B1** **C1** **E1**

| Entry | Solvent (2 mL) | D1 (%) |
|----------|--------------------|---------------|
| 1 | anisole | 42 |
| 2 | THF | trace |
| 3 | 1,4-dioxane | 30 |
| 4 | DME | 23 |
| 5 | toluene | 46 |
| 6 | xylene | 38 |
| 7 | mesitylene | 41 |
| 8 | DCM | 10 |
| 9 | CH ₃ CN | 0 |
| 10 | pyridine | 8 |
| 11 | methanol | 0 |
| 12 | ethanol | 0 |
| 13 | isopropanol | 0 |
| 14 | <i>t</i> -AmOH | 6 |
| 15 | DMF | 0 |
| 16 | DMAc | 0 |
| 17 | DMSO | 0 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), solvent (2.0 mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield.

Table S13. The ratio of substrates screening^a

$\text{Ph-CH=CH-CH}_2\text{-OH} + \text{H}_2\text{N-N(Ph)} + \text{Ph-CHO} + \text{CO} \xrightarrow{[\text{M}]} \text{Ph-CH=N-N(Ph)-C(=O)-CH=CH-Ph}$

| | A1 | B1 | C1 | | E1 |
|-----------|-------------|------------|------------|--|---------------|
| Entry | A1 | B1 | C1 | | D1 (%) |
| 1 | 0.5 | 0.5 | 0 | | 0 |
| 2 | 0.5 | 0.5 | 0.5 | | 26 |
| 3 | 0.5 | 0.5 | 0.65 | | 35 |
| 4 | 0.5 | 0.5 | 0.75 | | 41 |
| 5 | 0.5 | 0.5 | 0.85 | | 39 |
| 6 | 0 | 0.5 | 0.5 | | 0 |
| 7 | 0.65 | 0.5 | 0.5 | | 37 |
| 8 | 0.75 | 0.5 | 0.5 | | 40 |
| 9 | 0.85 | 0.5 | 0.5 | | 41 |
| 10 | 0.5 | 0 | 0.5 | | 0 |
| 11 | 0.5 | 0.65 | 0.5 | | 25 |
| 12 | 0.5 | 0.75 | 0.5 | | 21 |
| 13 | 0.5 | 0.85 | 0.5 | | 18 |
| 14 | 0.75 | 0.5 | 0.6 | | 43 |
| 15 | 0.75 | 0.5 | 0.7 | | 46 |
| 16 | 0.75 | 0.5 | 0.75 | | 46 |
| 17 | 0.75 | 0.5 | 0.8 | | 44 |

^a Reaction conditions: **A1** (x mmol), **B1** (x mmol), **C1** (x mmol), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield.

Table S14. The loading of solvent screening^a

| Entry | toluene (mL) | D1 (%) |
|----------|--------------|-----------|
| 1 | 0.5 | 29 |
| 2 | 1.0 | 36 |
| 3 | 1.5 | 43 |
| 4 | 2.0 | 46 |
| 5 | 3.0 | 46 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (x mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield.

Table S15. The Pd-catalyst loading screening^a

| Entry | Pd-catalyst | D1 (%) |
|----------|-------------|-----------|
| 1 | 0 | 0 |
| 2 | 0.001 | 7 |
| 3 | 0.002 | 15 |
| 4 | 0.005 | 33 |
| 5 | 0.01 | 46 |
| 6 | 0.02 | 46 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (x mmol), toluene (2.0 mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield.

Table S16. Reaction pressure screening ^a

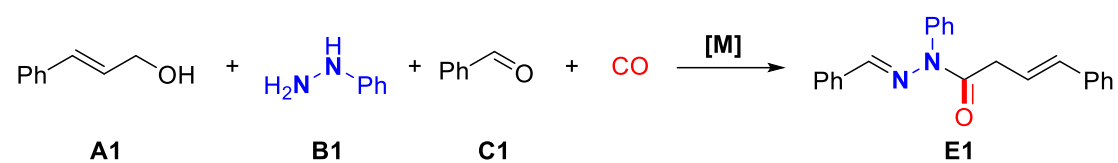
| Entry | CO (MPa) | D1 (%) |
|----------|----------|-----------|
| 1 | 1 | 21 |
| 2 | 2 | 46 |
| 3 | 3 | 72 |
| 4 | 4 | 85 |
| 5 | 5 | 85 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), 120 $^{\circ}$ C (extern temperature), 12 h, CO (x MPa), GC yield.

Table S17. Reaction temperature screening ^a

| Entry | T ($^{\circ}$ C) | D1 (%) |
|----------|-------------------|-----------|
| 1 | 40 | 0 |
| 2 | 60 | 32 |
| 3 | 80 | 48 |
| 4 | 100 | 73 |
| 5 | 120 | 85 |
| 6 | 140 | 85 |

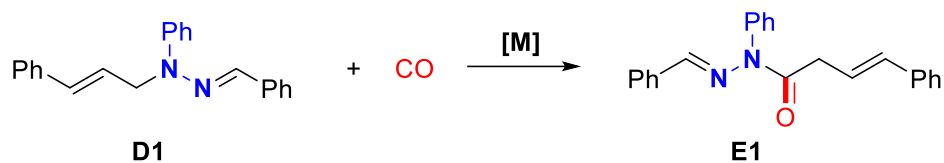
^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), T (extern temperature), 12 h, CO (4 MPa), GC yield.

Table S18. Reaction time screening^a

| Entry | t (h) | D1 (%) |
|----------|-----------|----------------------------|
| 1 | 2 | 6 |
| 2 | 4 | 41 |
| 3 | 6 | 58 |
| 4 | 8 | 72 |
| 5 | 10 | 80 |
| 6 | 12 | 85 (78^b) |
| 7 | 15 | 85 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μ L), **C1** (0.7 mmol, 72 μ L), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), T (extern temperature), x h, CO (4 MPa), GC yield. ^b Isolated yield.

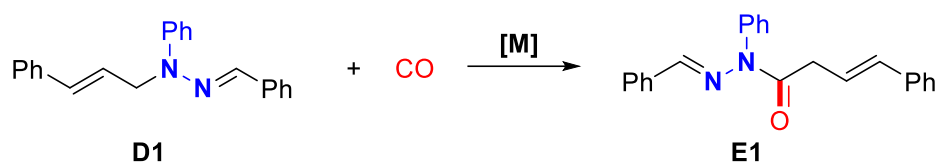
3.3 Screening of carbonylation from allylhydrazones parameters



Using a nitrogen-filled glove box, an oven-dried glass bottle (10 mL volume) was charged with a magnetic stirring bar, catalyst, solvent and allylhydrazone (**D1**). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO and immersed into a pre-heated metal bath for desired time. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. Then a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) on silica gel to give the product **E1** in the reported yields.

| Entry | Parameter |
|------------------|--------------------------------------|
| Table S19 | The difference of catalyst screening |
| Table S20 | The difference ligand screening |
| Table S21 | The difference of solvent screening |
| Table S22 | The loading of solvent screening |
| Table S23 | The Pd-catalyst loading screening |
| Table S24 | Reaction pressure screening |
| Table S25 | Reaction temperature screening |
| Table S26 | Reaction time screening |

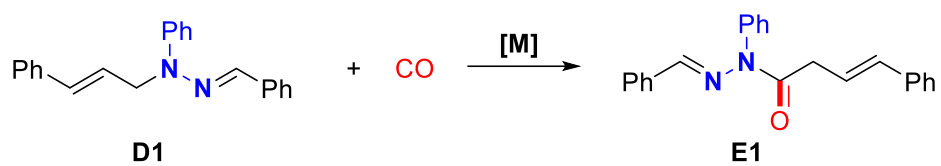
Table S19. The difference of catalyst screening ^a



| Entry | Catalyst | D1 (%) |
|-----------------|--|-----------|
| 1 | - | 0 |
| 2 | PdCl ₂ | 23 |
| 3 | PdBr ₂ | 16 |
| 4 | PdI ₂ | trace |
| 5 | PdCl₂(CH₃CN)₂ | 39 |
| 6 | Pd(OAc) ₂ | 7 |
| 7 | Pd(TFA) ₂ | 21 |
| 8 | Pd/C | 0 |
| 9 ^b | [Pd(Cl)(C ₃ H ₅) ₂] | 31 |
| 10 ^b | [Pd(Cl)(C ₉ H ₉) ₂] | 36 |
| 11 | NiCl ₂ | 0 |
| 12 | CoCl ₂ | 0 |
| 13 | MnCl ₂ | 0 |
| 14 | CuCl ₂ | 0 |
| 15 | FeCl ₂ | 0 |

^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), catalyst (0.01 mmol, 2 mol%), Xantphos (0.01 mmol, 2 mol%), toluene (2.0 mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield. ^b Catalyst (0.005 mmol, 1 mol%).

Table S20. The difference ligand screening ^a



| Entry | Ligand | D1 (%) |
|-----------|------------|-----------|
| 1 | - | 0 |
| 2 | L1 | 1 |
| 3 | L2 | 2 |
| 4 | L3 | 1 |
| 5 | L4 | 2 |
| 6 | L5 | 1 |
| 7 | L6 | 1 |
| 8 | L7 | 1 |
| 9 | L8 | 2 |
| 10 | L9 | 2 |
| 11 | L10 | 2 |
| 12 | L11 | 2 |
| 13 | L12 | 1 |
| 14 | L13 | 1 |
| 15 | L14 | 2 |
| 16 | L15 | 2 |
| 17 | L16 | 0 |
| 18 | L17 | 39 |
| 19 | L18 | 10 |
| 20 | L19 | 25 |
| 21 | L20 | 11 |
| 22 | L21 | 5 |

| Entry | Ligand | D1 (%) |
|-----------------------|--|-----------|
| 23 | L22 | 6 |
| 24 | L23 | 0 |
| 25 | L24 | 0 |
| 26 | L25 | 0 |
| 27 | L26 | 3 |
| 28 | L27 | 2 |
| 29 | L28 | 3 |
| 30 | L29 | 2 |
| 31 | L30 | 10 |
| 32 | L31 | 8 |
| 33 | L32 | 2 |
| 34 | L33 | 2 |
| 35 | L34 | 0 |
| 36 | L35 | 5 |
| 37^b | PdCl₂(Xantphos) | 39 |
| 38^b | Pd(Xantphos)(OTf)₂(CH₃CN)₂ | 36 |

^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), PdCl₂(CH₃CN)₂ (0.01 mmol, 2 mol%), Ligand (**L1-L16** 0.021 mmol, 4.2 mol%; **L17-L35** 0.011 mmol, 2.2 mol%), toluene (2.0 mL), 120 °C (extern temperature), 12 h, CO (2 MPa). GC yield. ^b catalyst (0.01 mmol, 2 mol%).

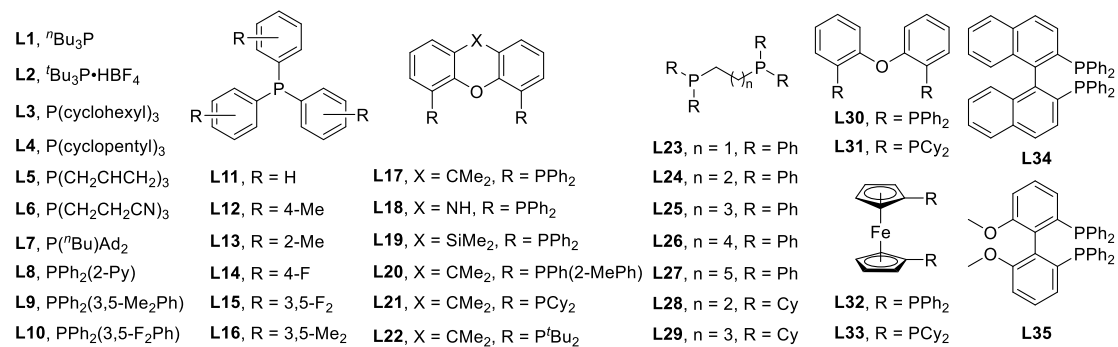
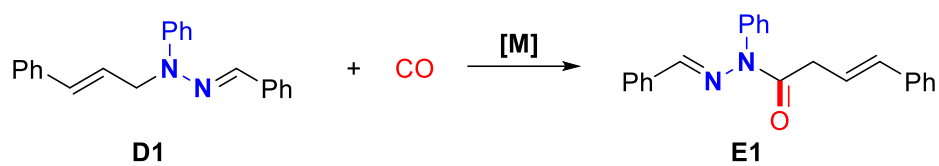
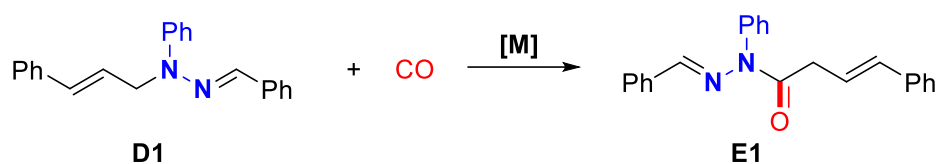


Table S21. The difference of solvent screening ^a



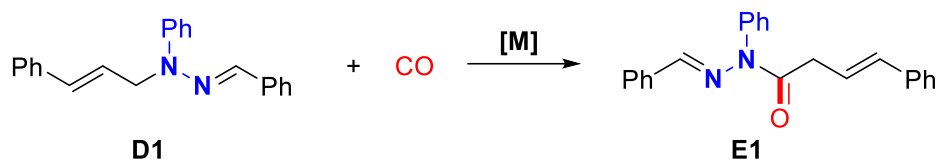
| Entry | Solvent (2 mL) | D1 (%) |
|----------|--------------------|---------------|
| 1 | anisole | 35 |
| 2 | THF | <5 |
| 3 | 1,4-dioxane | 23 |
| 4 | DME | 12 |
| 5 | toluene | 39 |
| 6 | xylene | 19 |
| 7 | mesitylene | 33 |
| 8 | DCM | 5 |
| 9 | CH ₃ CN | 0 |
| 10 | pyridine | <5 |
| 11 | methanol | 0 |
| 12 | ethanol | 0 |
| 13 | isopropanol | 0 |
| 14 | <i>t</i> -AmOH | <5 |
| 15 | DMF | 0 |
| 16 | DMAc | 0 |
| 17 | NMP | 0 |
| 18 | DMSO | 0 |

^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), solvent (2.0 mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield.

Table S22. The loading of solvent screening ^a

| Entry | toluene (mL) | D1 (%) |
|----------|--------------|---------------|
| 1 | 0.5 | 11 |
| 2 | 1.0 | 27 |
| 3 | 1.5 | 35 |
| 4 | 2.0 | 39 |
| 5 | 3.0 | 39 |

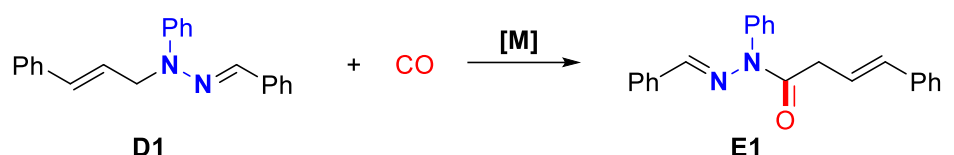
^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (x mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield.

Table S23. The Pd-catalyst loading screening ^a

| Entry | Pd-catalyst | D1 (%) |
|----------|-------------|---------------|
| 1 | 0 | 0 |
| 2 | 0.001 | 5 |
| 3 | 0.002 | 13 |
| 4 | 0.005 | 28 |
| 5 | 0.01 | 39 |
| 6 | 0.02 | 39 |

^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), PdCl₂(Xantphos) (x mol%), toluene (2.0 mL), 120 °C (extern temperature), 12 h, CO (2 MPa), GC yield.


Table S24. Reaction pressure screening ^a



| Entry | CO (MPa) | D1 (%) |
|-------|----------|-----------|
| 1 | 1 | 23 |
| 2 | 2 | 39 |
| 3 | 3 | 59 |
| 4 | 4 | 68 |
| 5 | 5 | 68 |

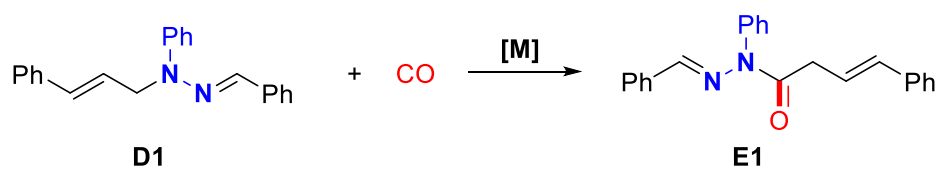
^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), 120 °C (extern temperature), 12 h, CO (x MPa), GC yield.

Table S25. Reaction temperature screening ^a



| Entry | T (°C) | D1 (%) |
|-------|------------|-----------|
| 1 | 40 | 0 |
| 2 | 60 | 29 |
| 3 | 80 | 45 |
| 4 | 100 | 62 |
| 5 | 120 | 68 |
| 6 | 140 | 68 |

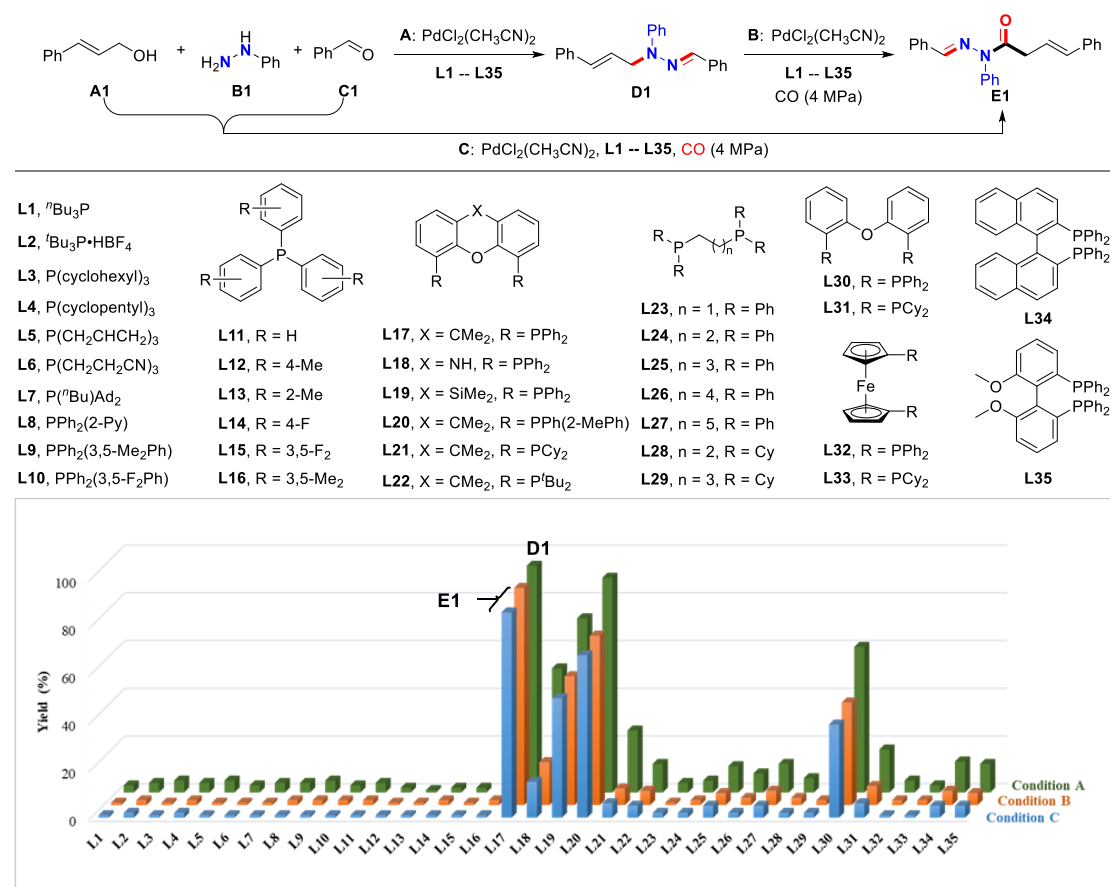
^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), T °C (extern temperature), 12 h, CO (4 MPa), GC yield.

Table S26. Reaction time screening^a

| Entry | t (h) | D1 (%) |
|----------|-----------|----------------------------|
| 1 | 3 | 15 |
| 2 | 6 | 33 |
| 3 | 9 | 54 |
| 4 | 12 | 68 |
| 5 | 14 | 77 |
| 6 | 16 | 81 |
| 7 | 18 | 83 (76^b) |
| 8 | 21 | 83 |

^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), PdCl₂(Xantphos) (0.01 mmol, 2 mol%), toluene (2.0 mL), 120 °C (extern temperature), x h, CO (4 MPa), GC yield. ^b Isolated yield.

Table S27. Optimization of Reaction Conditions ^a



^aConditions A: **A1** (0.75 mmol), **B1** (0.5 mmol), **C1** (0.7 mmol), PdCl₂(CH₃CN)₂ (2 mol.%), **L** (2.2 mol.% or 4.2 mol.%), toluene (2.0 mL), 60 °C, N₂, 4 h. Conditions B: **D1** (0.5 mmol), PdCl₂(CH₃CN)₂ (2 mol.%), **L** (2.2 mol.% or 4.2 mol.%), toluene (2.0 mL), 120 °C, CO (4 MPa), 18 h. Conditions C: **A1** (0.75 mmol), **B1** (0.5 mmol), **C1** (0.7 mmol), PdCl₂(CH₃CN)₂ (2 mol.%), **L** (2.2 mol.% or 4.2 mol.%), toluene (2.0 mL), 120 °C, CO (4 MPa), 12 h.

3.4 Screening of parameters with nickel salts

Table R1 Screening of allylation parameters with nickel salts ^a

c1ccc(cc1)/C=C/CO (A1) + c1ccc(cc1)N(N)H (B1) + c1ccc(cc1)C=O (C1) $\xrightarrow{[M]}$ c1ccc(cc1)/C=C/CN(c2ccccc2)C(=O)c3ccccc3 (D1)

| Entry | Catalyst | Ligand | Solvent (2 mL) | T (°C) | t (h) | D1 (%) |
|-------|---|------------------|--------------------|--------|-------|-------------------|
| 1 | NiCl ₂ | - | anisole | 60 | 4 | 0 |
| 2 | NiBr ₂ | - | anisole | 60 | 4 | 0 |
| 3 | NiI ₂ | - | anisole | 60 | 4 | 0 |
| 4 | Ni(OAc) ₂ ·4H ₂ O | - | anisole | 60 | 4 | 0 |
| 5 | NiCl ₂ ·DME | - | anisole | 60 | 4 | 0 |
| 6 | Ni(COD) ₂ | - | anisole | 60 | 4 | 0 |
| 7 | Ni(acac) ₂ | - | anisole | 60 | 4 | 0 |
| 8 | NiCl ₂ ·DME | DPPM | anisole | 60 | 4 | 0 |
| 9 | NiCl ₂ ·DME | DPPF | anisole | 60 | 4 | 0 |
| 10 | NiCl ₂ ·DME | PPh ₃ | anisole | 60 | 4 | 0 |
| 11 | NiCl ₂ ·DME | Xantphos | anisole | 60 | 4 | 0(0) ^b |
| 12 | NiCl ₂ ·DME | 1,10-phen | anisole | 60 | 4 | 0 |
| 13 | NiCl ₂ ·DME | bpy | anisole | 60 | 4 | 0 |
| 14 | NiCl ₂ ·DME | - | DMSO | 60 | 4 | 0 |
| 15 | NiCl ₂ ·DME | - | CH ₃ CN | 60 | 4 | 0 |
| 16 | NiCl ₂ ·DME | - | DCE | 60 | 4 | 0 |
| 17 | NiCl ₂ ·DME | - | anisole | 120 | 4 | 0 |
| 18 | NiCl ₂ ·DME | - | anisole | 120 | 12 | 0 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μL), **C1** (0.7 mmol, 72 μL), catalyst (0.01 mmol, 5 mol%), ligand (5 mol% / 10 mol%), solvent (2.0 mL), T (extern temperature),

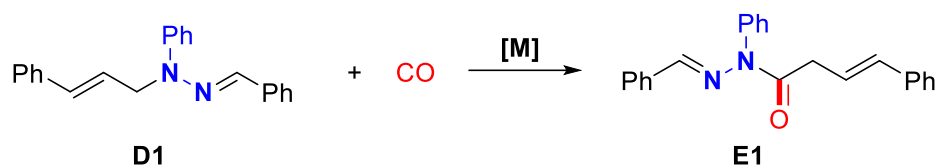
x h, N₂. Isolated yield. ^b AgOTf (0.02 mmol, 10 mol%).

Table R2 Screening of tandem carbonylation parameters with nickel salts ^a

| Entry | A1 Catalyst | B1 Ligand | C1 Solvent (2 mL) | T (°C) | t (h) | D1 (%) |
|-------|---|------------------|----------------------|-----------|----------|-------------------|
| 1 | NiCl ₂ | - | anisole | 120 | 12 | 0 |
| 2 | NiBr ₂ | - | anisole | 120 | 12 | 0 |
| 3 | NiI ₂ | - | anisole | 120 | 12 | 0 |
| 4 | Ni(OAc) ₂ ·4H ₂ O | - | anisole | 120 | 12 | 0 |
| 5 | NiCl ₂ ·DME | - | anisole | 120 | 12 | 0 |
| 6 | Ni(COD) ₂ | - | anisole | 120 | 12 | 0 |
| 7 | Ni(acac) ₂ | - | anisole | 120 | 12 | 0 |
| 8 | NiCl ₂ ·DME | DPPM | anisole | 120 | 12 | 0 |
| 9 | NiCl ₂ ·DME | DPPF | anisole | 120 | 12 | 0 |
| 10 | NiCl ₂ ·DME | PPh ₃ | anisole | 120 | 12 | 0 |
| 11 | NiCl ₂ ·DME | Xantphos | anisole | 120 | 12 | 0(0) ^b |
| 12 | NiCl ₂ ·DME | 1,10-phen | anisole | 120 | 12 | 0 |
| 13 | NiCl ₂ ·DME | bpy | anisole | 120 | 12 | 0 |
| 14 | NiCl ₂ ·DME | - | DMSO | 120 | 12 | 0 |
| 15 | NiCl ₂ ·DME | - | CH ₃ CN | 120 | 12 | 0 |
| 16 | NiCl ₂ ·DME | - | DCE | 120 | 12 | 0 |
| 17 | NiCl ₂ ·DME | - | anisole | 120 | 24 | 0 |

^a Reaction conditions: **A1** (0.75 mmol, 100.6 mg), **B1** (0.5 mmol, 49 μL), **C1** (0.7 mmol, 72 μL), catalyst (0.01 mmol, 5 mol%), ligand (5 mol% / 10 mol%), solvent (2.0 mL), 120 °C, x h, CO (2.0 MPa), GC yield. ^b AgOTf (0.02 mmol, 10 mol%).

Table R3 Screening of carbonylation from allylhydrazone parameters with nickel salts ^a

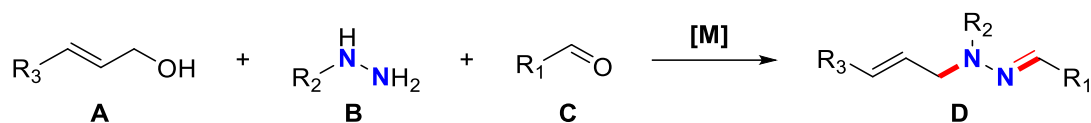


| Entry | Catalyst | Ligand | Solvent (2 mL) | T (°C) | t (h) | D1 (%) |
|-------|---|------------------|--------------------|--------|-------|-------------------|
| 1 | NiCl ₂ | - | anisole | 120 | 12 | 0 |
| 2 | NiBr ₂ | - | anisole | 120 | 12 | 0 |
| 3 | NiI ₂ | - | anisole | 120 | 12 | 0 |
| 4 | Ni(OAc) ₂ ·4H ₂ O | - | anisole | 120 | 12 | 0 |
| 5 | NiCl ₂ ·DME | - | anisole | 120 | 12 | 0 |
| 6 | Ni(COD) ₂ | - | anisole | 120 | 12 | 0 |
| 7 | Ni(acac) ₂ | - | anisole | 120 | 12 | 0 |
| 8 | NiCl ₂ ·DME | DPPM | anisole | 120 | 12 | 0 |
| 9 | NiCl ₂ ·DME | DPPF | anisole | 120 | 12 | 0 |
| 10 | NiCl ₂ ·DME | PPh ₃ | anisole | 120 | 12 | 0 |
| 11 | NiCl ₂ ·DME | Xantphos | anisole | 120 | 12 | 0(0) ^b |
| 12 | NiCl ₂ ·DME | 1,10-phen | anisole | 120 | 12 | 0 |
| 13 | NiCl ₂ ·DME | bpy | anisole | 120 | 12 | 0 |
| 14 | NiCl ₂ ·DME | - | DMSO | 120 | 12 | 0 |
| 15 | NiCl ₂ ·DME | - | CH ₃ CN | 120 | 12 | 0 |
| 16 | NiCl ₂ ·DME | - | DCE | 120 | 12 | 0 |
| 17 | NiCl ₂ ·DME | - | anisole | 120 | 24 | 0 |

^a Reaction conditions: **D1** (0.5 mmol, 156.1 mg), catalyst (0.01 mmol, 5 mol%), ligand (5 mol% / 10 mol%), solvent (2.0 mL), 120 °C, x h, CO (2.0 MPa), GC yield. ^b AgOTf (0.02 mmol, 10 mol%).

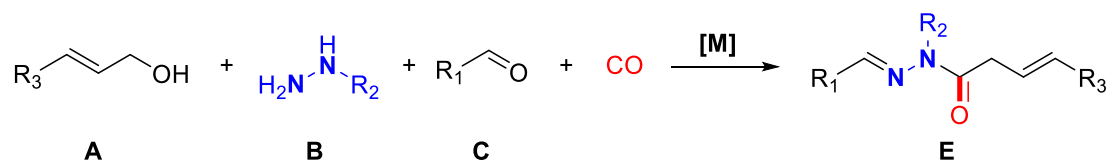
4. General Procedure for the products

4.1 Screening of tandem allylation reaction parameters



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), hydrazines (**B** 0.5 mmol), aldehydes (**C** 0.7 mmol), PdCl₂(Xantphos) (0.01 mmol, 2 mol%) and allyl alcohol (**A** 0.75 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the products **D1-D61** in the reported yields.

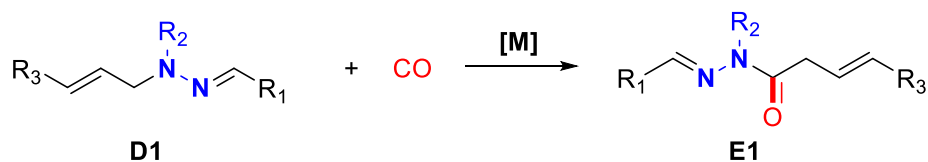
4.2 Screening of allylation/ carbonylation parameters



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, hydrazines (**B** 0.5 mmol), aldehydes (**C** 0.7 mmol), toluene (2.0 mL), PdCl₂(Xantphos) (0.01 mmol, 2 mol%) and allyl alcohol (**A** 0.75 mmol). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. Then a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum

ether/ ethyl acetate = 20:1 – 5:1) on silica gel to give the products **E1-E25** in the reported yields.

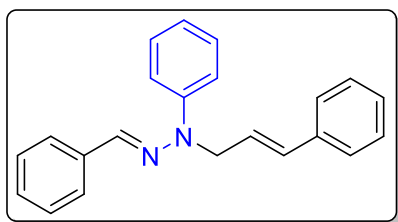
4.3 Screening of carbonylation of allylhydrazones parameters



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, allyl hydrazones (**D** 0.5 mmol), toluene (2.0 mL) and $PdCl_2(Xantphos)$ (0.01 mmol, 2 mol%). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4 MPa) and immersed into a pre-heated metal bath (120 °C) for 18 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. Then a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 – 5:1) on silica gel to give the products **E1-E25** in the reported yields.

5. Characterization data

2-((*E*)-benzylidene)-1-cinnamyl-1-phenylhydrazine (D1)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 95% yield (148.3 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.65 (m, 2H), 7.57 – 7.16 (m, 13H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.52 – 6.40 (m, 1H), 6.31 – 6.22 (m, 1H), 4.71 (dd, *J* = 4.0, 2.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 136.6, 136.3, 132.4, 131.3, 129.1, 128.6, 127.9, 127.7, 126.4, 126.2, 121.7, 120.7, 114.9, 48.5.

HRMS (ESI) calcd. for C₂₂H₂₁N₂ [M+H]: 313.1699, found: 313.1695.

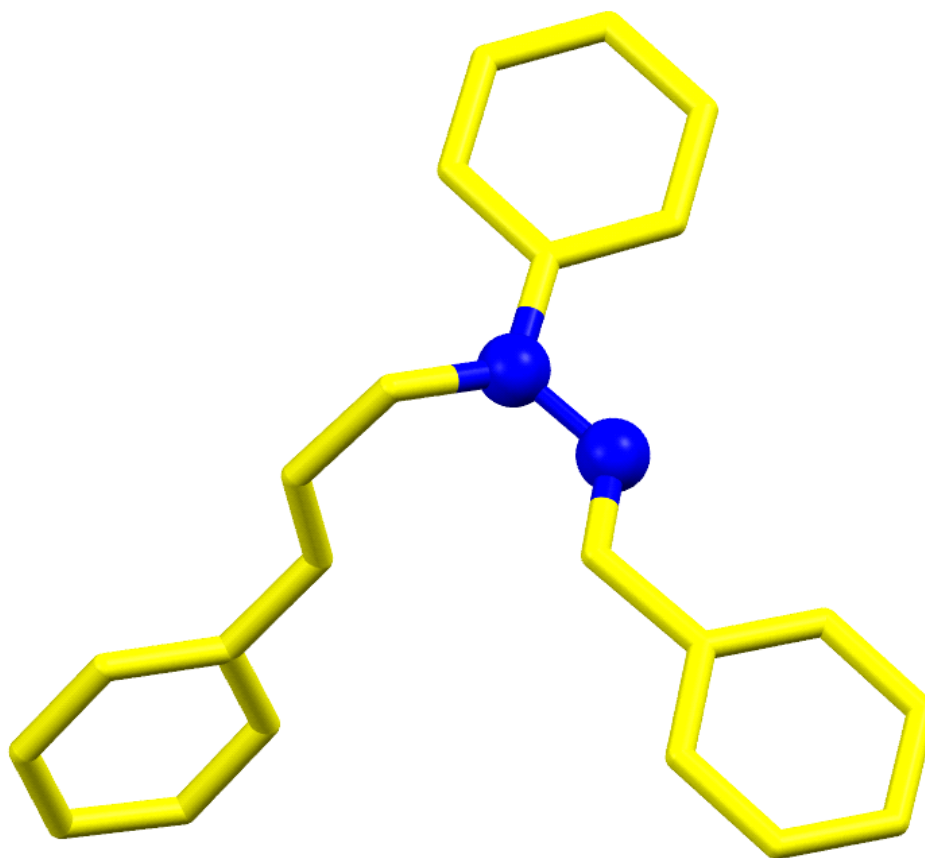
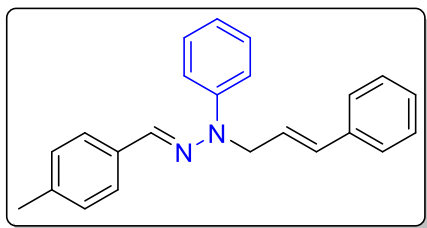


Figure S1 X-ray of D1 (CCDC 2249897)

1-cinnamyl-2-((*E*)-4-methylbenzylidene)-1-phenylhydrazine (D2)



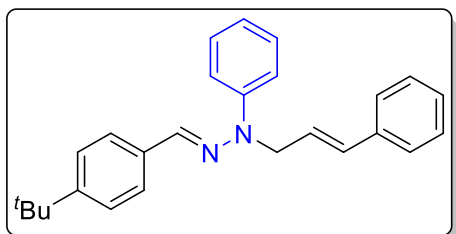
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 94 % yield (153.3 mg).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.0$ Hz, 2H), 7.45 (s, 1H), 7.43 – 7.36 (m, 2H), 7.35 – 7.27 (m, 4H), 7.23 (t, $J = 7.2$ Hz, 2H), 7.20 – 7.09 (m, 3H), 6.92 (t, $J = 7.2$ Hz, 1H), 6.46 – 6.37 (m, 1H), 6.26 – 6.16 (m, 1H), 4.69 – 4.53 (m, 2H), 2.32 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.8, 137.9, 136.5, 134.0, 132.7, 131.3, 129.4, 129.2, 128.7, 127.8, 126.5, 126.3, 122.0, 120.6, 114.9, 48.5, 21.5.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]$: 327.1855, found: 327.1853.

2-((*E*)-4-(*tert*-butyl)benzylidene)-1-cinnamyl-1-phenylhydrazine (D3)



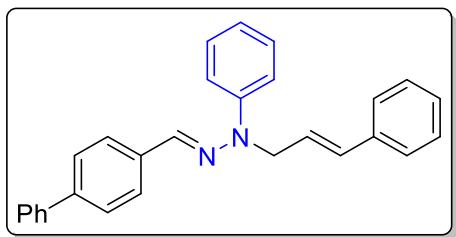
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 81% yield (149.1 mg).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 – 7.57 (m, 2H), 7.49 – 7.11 (m, 13H), 6.95 – 6.86 (m, 1H), 6.45 – 6.34 (m, 1H), 6.28 – 6.14 (m, 1H), 4.60 (s, 1H), 1.37 – 1.19 (m, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.2, 147.8, 136.5, 134.1, 132.6, 131.3, 129.3, 128.7, 127.8, 126.5, 126.1, 125.7, 121.9, 120.6, 114.9, 48.5, 34.8, 31.5.

HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_2$ $[\text{M}+\text{H}]$: 369.2325, found: 369.2330.

(E)-2-([1,1'-biphenyl]-4-ylmethylene)-1-cinnamyl-1-phenylhydrazine (D4)



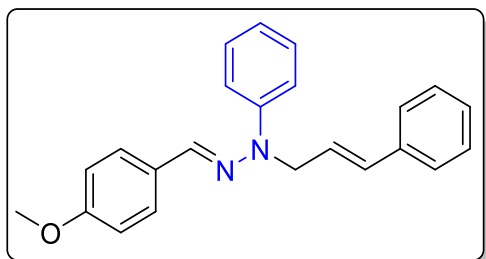
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 96 % yield (186.3 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.65 (m, 2H), 7.63 – 7.09 (m, 17H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.22 – 6.12 (m, 1H), 4.68 – 4.47 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 140.9, 140.6, 136.5, 135.9, 132.2, 131.5, 129.4, 129.0, 128.8, 127.9, 127.5, 127.1, 126.8, 126.6, 121.9, 121.0, 115.1, 48.57.

HRMS (ESI) calcd. for C₂₈H₂₅N₂ [M+H]: 389.2012, found: 389.2013.

1-cinnamyl-2-((E)-4-methoxybenzylidene)-1-phenylhydrazine (D5)



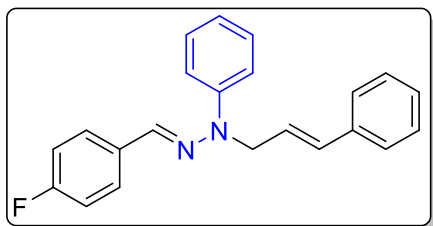
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 88 % yield (150.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.57 (m, 2H), 7.45 – 7.10 (m, 10H), 6.95 – 6.82 (m, 3H), 6.44 – 6.35 (m, 1H), 6.22 – 6.13 (m, 1H), 4.61 – 4.51 (m, 2H), 3.72 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.8, 147.8, 136.6, 132.5, 131.3, 129.7, 129.3, 128.7, 127.8, 127.7, 126.5, 122.2, 120.5, 114.8, 114.2, 55.4, 48.5.

HRMS (ESI) calcd. for C₂₃H₂₃N₂O [M+H]: 343.1805, found: 343.1804.

1-cinnamyl-2-((E)-4-fluorobenzylidene)-1-phenylhydrazine (D6)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 92% yield (151.9 mg).

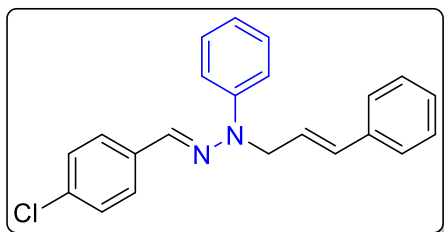
¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.48 – 7.16 (m, 10H), 7.08 – 6.88 (m, 3H), 6.49 – 6.37 (m, 1H), 6.31 – 6.18 (m, 1H), 4.71 – 4.62 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 162.6 (d, *J* = 248.46 Hz), 147.6, 136.4, 132.9, 131.4, 131.3, 129.2, 128.6, 127.8, 127.7, 126.4, 121.3 (d, *J* = 91.91 Hz), 115.6 (d, *J* = 22.22 Hz), 48.6.

¹⁹F NMR (376 MHz, CDCl₃) δ = -113.7.

HRMS (ESI) calcd. for C₂₂H₂₀FN₂ [M+H]: 331.1605, found: 331.1600.

1-((*E*)-4-chlorobenzylidene)-1-cinnamyl-1-phenylhydrazine (D7)



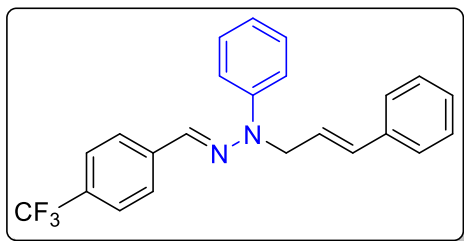
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 90% yield (155.8 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.11 (m, 12H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.43 – 6.33 (m, 1H), 6.22 – 6.10 (m, 1H), 4.65 – 4.49 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 136.4, 135.4, 133.4, 131.5, 131.1, 129.4, 128.9, 128.8, 128.0, 127.5, 126.6, 121.7, 121.2, 115.1, 48.6.

HRMS (ESI) calcd. for C₂₂H₂₀ClN₂ [M+H]: 347.1309, found: 347.1313.

1-cinnamyl-1-phenyl-2-((E)-4-(trifluoromethyl)benzylidene)hydrazine (D8)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 86% yield (163.5 mg).

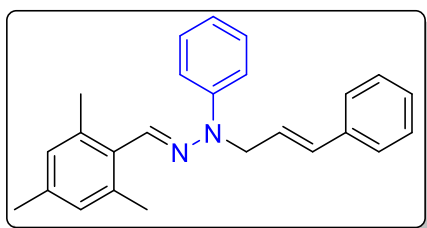
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.47 – 7.14 (m, 10H), 7.02 – 6.91 (m, 1H), 6.45 – 6.36 (m, 1H), 6.24 – 6.15 (m, 1H), 4.68 – 4.56 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.4, 140.2, 136.3, 131.6, 130.5, 129.4, 128.7, 128.0, 126.5, 126.2, 125.6 (q, $J = 8.08, 4.04$ Hz), 124.5 (q, $J = 490.86, 272.70$ Hz), 121.6, 121.3, 115.4, 48.7.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) $\delta = -62.1$.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{20}\text{F}_3\text{N}_2$ [$\text{M}+\text{H}$]: 381.1573, found: 381.1576.

1-cinnamyl-1-phenyl-2-((E)-2,4,6-trimethylbenzylidene)hydrazine (D9)



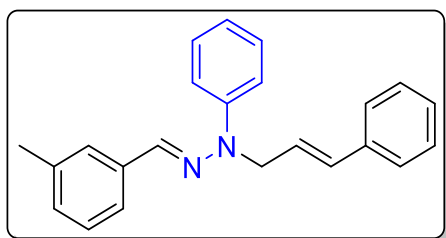
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 73 % yield (129.3 mg).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (s, 1H), 7.38 – 7.13 (m, 9H), 6.94 – 6.82 (m, 3H), 6.51 – 6.39 (m, 1H), 6.28 – 6.17 (m, 1H), 4.73 – 4.62 (m, 2H), 2.43 (s, 6H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.9, 137.1, 136.6, 136.5, 133.3, 131.7, 130.3, 129.6, 129.3, 128.7, 127.8, 126.4, 121.7, 120.4, 114.6, 48.2, 21.9, 21.2.

HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{27}\text{N}_2$ $[\text{M}+\text{H}]$: 355.2168, found: 355.2162.

1-cinnamyl-2-((*E*)-3-methylbenzylidene)-1-phenylhydrazine (D10)



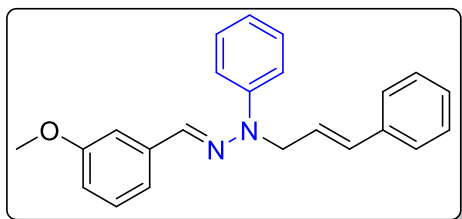
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 93 % yield (151.7 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.38 (m, 5H), 7.36 – 7.26 (m, 4H), 7.26 – 7.19 (m, 3H), 7.19 – 7.13 (m, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 6.96 – 6.89 (m, 1H), 6.44 – 6.35 (m, 1H), 6.24 – 6.15 (m, 1H), 4.67 – 4.56 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 175.6, 147.9, 147.2, 142.9, 142.1, 136.3, 130.2, 129.2, 129.2, 128.7, 127.6, 126.8, 126.6, 122.5, 114.6, 108.1, 56.0, 43.3, 19.7.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]$: 327.1855, found: 327.1858.

1-cinnamyl-2-((*E*)-3-methoxybenzylidene)-1-phenylhydrazine (D11)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 85% yield (145.4 mg).

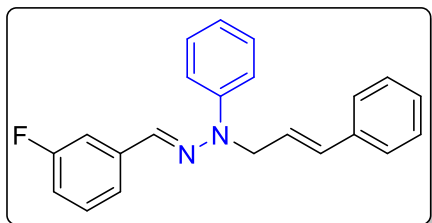
^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.38 (m, 3H), 7.37 – 7.12 (m, 10H), 6.97 – 6.90 (m, 1H), 6.84 – 6.76 (m, 1H), 6.46 – 6.38 (m, 1H), 6.26 – 6.16 (m, 1H), 4.67 – 4.60 (m,

2H), 3.81 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.0, 147.6, 138.2, 136.4, 132.3, 131.4, 129.7, 129.3, 128.7, 127.8, 126.5, 121.7, 120.9, 119.4, 115.0, 114.0, 110.8, 55.4, 48.6.

HRMS (ESI) calcd. for C₂₃H₂₃N₂O [M+H]: 343.1805, found: 343.1805.

2-cinnamyl-2-((*E*)-3-fluorobenzylidene)-1-phenylhydrazine (D12)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 90% yield (148.6 mg).

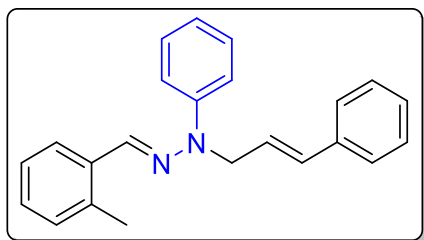
¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.09 (m, 13H), 7.00 – 6.83 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.26 – 6.13 (m, 1H), 4.67 – 4.56 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 163.3 (d, *J* = 246.44 Hz), 147.5, 139.2 (d, *J* = 7.07 Hz), 136.3, 131.5, 131.0, 130.1 (d, *J* = 95.95 Hz), 129.3, 128.7, 128.0, 126.5, 122.4, 121.5, 121.2, 115.2, 114.7 (d, *J* = 21.21 Hz), 112.2 (d, *J* = 22.22 Hz), 48.6.

¹⁹F NMR (376 MHz, CDCl₃) δ = -113.1.

HRMS (ESI) calcd. for C₂₂H₂₀FN₂ [M+H]: 331.1605, found: 331.1605.

1-cinnamyl-2-((*E*)-2-methylbenzylidene)-1-phenylhydrazine (D13)



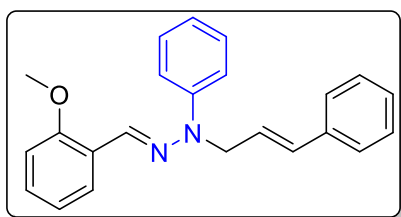
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 91 % yield (148.4 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.70 (s, 1H), 7.46 – 7.07 (m, 11H), 6.97 – 6.89 (m, 1H), 6.50 – 6.40 (m, 2H), 6.25 – 6.15 (m, 1H), 4.69 – 4.58 (m, 2H), 2.40 (d, *J* = 1.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 136.5, 135.4, 134.6, 131.8, 131.6, 130.8, 129.3, 128.7, 127.8, 126.5, 126.3, 126.0, 121.7, 120.8, 115.0, 48.6, 20.2.

HRMS (ESI) calcd. for C₂₃H₂₃N₂ [M+H]: 327.1855, found: 327.1857.

1-cinnamyl-2-((*E*)-2-methoxybenzylidene)-1-phenylhydrazine (D14)



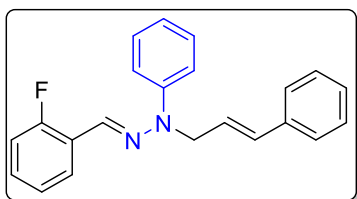
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 81% yield (138.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.90 (s, 1H), 7.46 – 7.36 (m, 2H), 7.35 – 7.09 (m, 8H), 7.01 – 6.84 (m, 2H), 7.01 – 6.86 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.24 – 6.13 (m, 1H), 4.68 – 4.57 (m, 2H), 3.72 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 147.9, 136.7, 131.5, 129.3, 129.1, 128.7, 128.5, 127.7, 126.6, 125.6, 125.4, 122.1, 120.6, 114.9, 111.2, 55.7, 48.4.

HRMS (ESI) calcd. for C₂₃H₂₃N₂O [M+H]: 343.1805, found: 343.1800.

1-cinnamyl-2-((*E*)-2-fluorobenzylidene)-1-phenylhydrazine (D15)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 87% yield (143.6 mg).

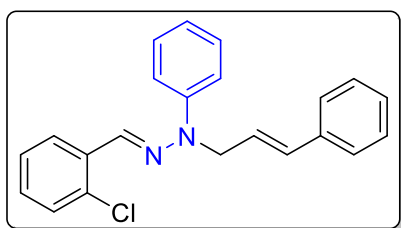
¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.01 (m, 1H), 7.70 (s, 1H), 7.48 – 7.07 (m, 11H), 7.06 – 6.90 (m, 2H), 6.51 – 6.41 (m, 1H), 6.28 – 6.19 (m, 1H), 4.75 – 4.63 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 160.6 (d, *J* = 249.47 Hz), 147.5, 136.4, 131.7, 129.2, 129.1 (d, *J* = 8.08 Hz), 128.9, 128.6, 127.8, 126.5, 125.9, 125.3, 124.4 (d, *J* = 10.10 Hz), 124.3, 124.2, 121.3, 121.1 (d, *J* = 26.26 Hz), 115.6 (d, *J* = 21.21 Hz), 115.1, 48.5.

¹⁹F NMR (376 MHz, CDCl₃) δ = -122.5.

HRMS (ESI) calcd. for C₂₂H₂₀FN₂ [M+H]: 331.1605, found: 331.1605.

3-((*E*)-2-chlorobenzylidene)-1-cinnamyl-1-phenylhydrazine (D16)



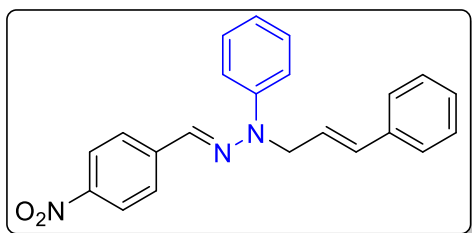
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 85% yield (147.1 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.04 (m, 1H), 7.87 (s, 1H), 7.48 – 7.03 (m, 12H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.21 – 6.10 (m, 1H), 4.69 – 4.56 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.5, 136.5, 134.0, 133.0, 132.3, 129.8, 129.4, 129.3, 128.7, 127.9, 127.0, 126.6, 126.5, 121.4, 121.3, 115.3, 48.8.

HRMS (ESI) calcd. for C₂₂H₂₀ClN₂ [M+H]: 347.1309, found: 347.1304.

1-cinnamyl-2-((*E*)-4-nitrobenzylidene)-1-phenylhydrazine (D17)



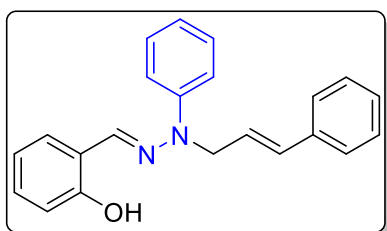
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give an orange-red solid in 86% yield (153.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.07 (m, 2H), 7.84 – 7.65 (m, 2H), 7.51 – 7.13 (m, 10H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.49 – 6.36 (m, 1H), 6.30 – 6.17 (m, 1H), 4.76 – 4.62 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.0, 146.6, 143.1, 136.1, 131.8, 129.4, 128.7, 128.1, 126.5, 126.3, 124.1, 122.1, 120.9, 115.7, 49.0.

HRMS (ESI) calcd. for C₂₂H₂₀N₃O₂ [M+H]: 358.1550, found: 358.1546.

1-((*E*)-2-cinnamyl-2-phenylhydrazineylidene)methylphenol (D18)



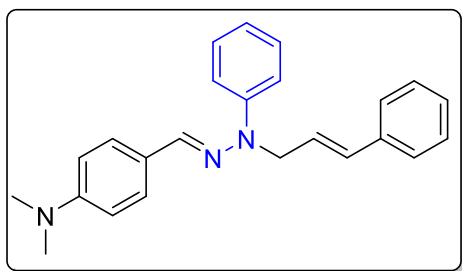
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 65% yield (106.7 mg).

¹H NMR (400 MHz, CDCl₃) δ 11.45 (s, 1H), 7.62 (s, 1H), 7.43 – 7.09 (m, 11H), 7.04 – 6.95 (m, 2H), 6.88 – 6.81 (m, 1H), 6.53 – 6.42 (m, 1H), 6.30 – 6.18 (m, 1H), 4.70 – 4.63 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.8, 146.7, 137.3, 136.1, 131.9, 129.7, 129.6, 129.5, 128.7, 128.0, 126.5, 121.9, 121.2, 119.5, 119.4, 116.6, 115.4, 49.3.

HRMS (ESI) calcd. for C₂₂H₂₁N₂O [M+H]: 329.1648, found: 329.1651.

4-((*E*)-(2-cinnamyl-2-phenylhydrazineylidene)methyl)-*N,N*-dimethylaniline (D19)



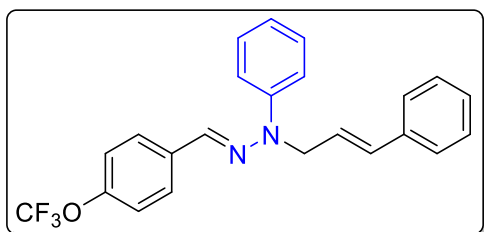
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 63% yield (111.9 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.54 (m, 2H), 7.48 (s, 1H), 7.44 – 7.15 (m, 9H), 6.93 – 6.86 (m, 1H), 6.77 – 6.64 (m, 2H), 6.51 – 6.40 (m, 1H), 6.34 – 6.22 (m, 1H), 4.72 – 4.62 (m, 2H), 2.97 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 147.9, 136.6, 133.6, 131.1, 129.1, 128.6, 127.6, 127.4, 126.4, 122.4, 119.8, 114.4, 112.3, 48.5, 40.5.

HRMS (ESI) calcd. for C₂₄H₂₆N₃ [M+H]: 356.2121, found: 356.2121.

1-cinnamyl-1-phenyl-2-((*E*)-4-(trifluoromethoxy)benzylidene)hydrazine (D20)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 85% yield (168.4 mg).

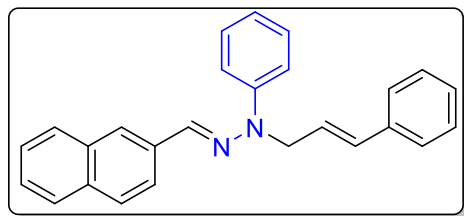
¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 8.8, 2.4 Hz, 2H), 7.54 – 7.11 (m, 12H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.39 (dd, *J* = 16.0, 2.4 Hz, 1H), 6.24 – 6.11 (m, 1H), 4.58 (t, *J* = 2.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.8, 148.7, 147.6, 136.0, 131.5, 130.8, 129.4, 128.8, 128.0, 127.4, 126.5, 121.5, 121.3, 121.2, 120.7 (q, *J* = 515.10, 257.55 Hz), 115.2, 48.6.

¹⁹F NMR (376 MHz, CDCl₃) δ = -57.5.

HRMS (ESI) calcd. for C₂₃H₂₀F₃N₂O [M+H]: 397.1522, found: 397.1522.

(E)-1-cinnamyl-2-(naphthalen-2-ylmethylene)-1-phenylhydrazine (D21)



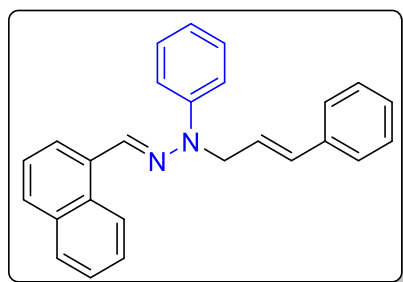
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 83% yield (150.3 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.64 – 8.51 (m, 1H), 8.19 (s, 1H), 8.01 – 7.93 (m, 1H), 7.89 – 7.71 (m, 2H), 7.58 – 7.15 (m, 12H), 7.02 – 6.93 (m, 1H), 6.61 – 6.49 (m, 1H), 6.36 – 6.25 (m, 1H), 4.85 – 4.70 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 136.4, 134.1, 132.1, 131.8, 131.6, 130.7, 129.3, 128.8, 128.7, 128.4, 127.8, 126.5, 125.8, 125.7, 125.2, 124.0, 121.8, 120.9, 115.1, 48.7.

HRMS (ESI) calcd. for C₂₆H₂₃N₂ [M+H]: 363.1855, found: 363.1855.

(E)-1-cinnamyl-2-(naphthalen-1-ylmethylene)-1-phenylhydrazine (D22)

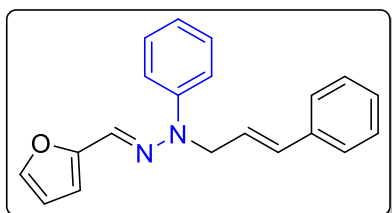


The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 44% yield (79.7 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.13 – 8.04 (m, 1H), 7.90 – 7.75 (m, 4H), 7.67 (s, 1H), 7.53 – 7.12 (m, 11H), 7.03 – 6.93 (m, 1H), 6.55 – 6.45 (m, 1H), 6.36 – 6.27 (m, 1H), 4.81 – 4.68 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 136.4, 134.4, 133.6, 133.3, 132.6, 131.4, 129.2, 128.6, 128.3, 127.9, 127.8, 126.6, 126.4, 126.3, 125.9, 123.1, 121.8, 120.8, 115.0, 48.7.
HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]$: 363.1855, found: 363.1852.

(E)-1-cinnamyl-2-(furan-2-ylmethylene)-1-phenylhydrazine (D23)



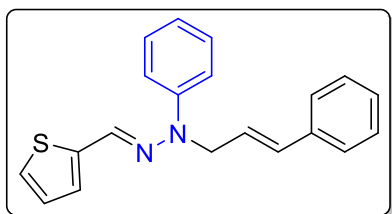
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 87% yield (131.4 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.12 (m, 11H), 6.93 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 3.2 Hz, 1H), 6.45 – 6.34 (m, 2H), 6.29 – 6.16 (m, 1H), 4.68 – 4.57 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 152.2, 147.4, 142.4, 136.4, 131.5, 129.2, 128.7, 127.8, 126.5, 123.4, 121.5, 121.1, 115.2, 111.6, 108.9, 48.7.

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}$ $[\text{M}+\text{H}]$: 303.1491, found: 303.1488.

(E)-1-cinnamyl-1-phenyl-2-(thiophen-2-ylmethylene)hydrazine (D24)



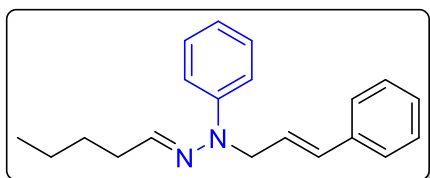
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 84% yield (133.6 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.65 (s, 1H), 7.50 – 7.13 (m, 10H), 7.07 – 6.87 (m, 3H), 6.51 – 6.39 (m, 1H), 6.29 – 6.15 (m, 1H), 4.69 – 4.58 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.3, 142.5, 136.4, 131.4, 129.2, 128.7, 127.8, 127.6, 127.3, 126.5, 125.9, 125.1, 121.6, 120.9, 114.9, 48.8.

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{S}$ $[\text{M}+\text{H}]$: 319.1263, found: 319.1258.

(E)-1-cinnamyl-2-hexylidene-1-phenylhydrazine (D25)



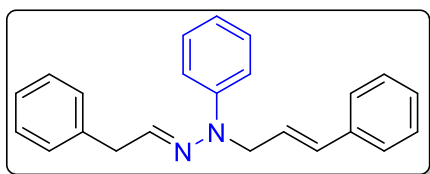
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 88% yield (128.6 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.22 (m, 8H), 7.22 – 7.15 (m, 1H), 6.90 – 6.77 (m, 2H), 6.40 – 6.31 (m, 1H), 6.20 – 6.10 (m, 1H), 4.52 – 4.41 (m, 2H), 2.41 – 2.28 (m, 2H), 1.59 – 1.46 (m, 2H), 1.36 (h, $J = 7.2$ Hz, 2H), 0.90 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.1, 136.9, 136.7, 131.1, 129.1, 128.6, 127.6, 126.5, 126.4, 122.6, 119.8, 114.3, 48.5, 32.8, 29.7, 22.4, 14.1.

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_2$ $[\text{M}+\text{H}]$: 293.2012, found: 293.2010.

(E)-1-phenyl-2-(2-phenylethylidene)-1-(3-phenylpropyl)hydrazine (D26)



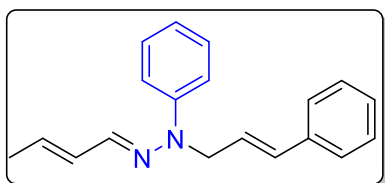
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 89% yield (145.1 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.05 (m, 14H), 6.93 – 6.79 (m, 2H), 6.40 – 6.25 (m, 1H), 6.12 – 5.97 (m, 1H), 4.50 – 4.34 (m, 2H), 3.72 – 3.60 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.0, 138.7, 136.7, 134.8, 131.4, 129.3, 129.1, 128.8, 128.7, 127.8, 126.6, 126.5, 122.5, 120.3, 114.7, 48.5, 39.7.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]$: 327.1855, found: 327.1853.

(E)-2-((E)-but-2-en-1-ylidene)-1-cinnamyl-1-phenylhydrazine (D27)



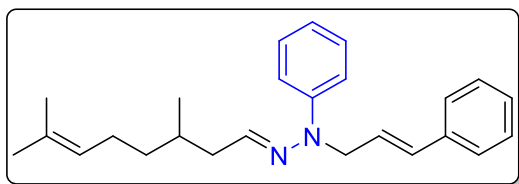
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 81% yield (121.5 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.07 (m, 12H), 6.97 – 6.84 (m, 1H), 6.48 – 6.24 (m, 2H), 6.23 – 6.13 (m, 1H), 5.93 – 5.76 (m, 1H), 4.59 – 4.49 (m, 2H), 1.87 – 1.76 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 136.5, 135.8, 131.7, 131.2, 130.4, 129.2, 128.7, 127.8, 127.7, 126.5, 122.2, 120.4, 115.0, 114.7, 48.5, 18.5.

HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]$: 277.1699, found: 277.1697.

(E)-1-cinnamyl-2-(3,7-dimethyloct-6-en-1-ylidene)-1-phenylhydrazine (D28)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 80% yield (144.1 mg).

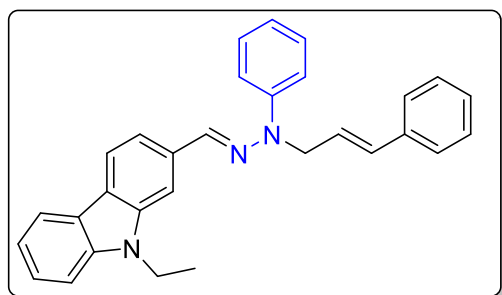
^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.10 (m, 9H), 6.92 – 6.75 (m, 2H), 6.41 – 6.31 (m, 1H), 6.19 – 6.08 (m, 1H), 5.13 – 4.97 (m, 1H), 4.58 – 4.42 (m, 2H), 2.41 – 2.28 (m, 1H), 2.25 – 2.13 (m, 1H), 2.08 – 1.89 (m, 2H), 1.79 – 1.62 (m, 4H), 1.57 (s, 2H),

1.46 – 1.12 (m, 3H), 0.92 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.1, 136.6, 135.9, 131.3, 131.1, 129.1, 128.6, 127.6, 126.4, 124.8, 122.4, 119.8, 114.4, 48.5, 40.2, 36.9, 31.8, 25.9, 25.6, 19.7, 17.8.

HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{33}\text{N}_2$ $[\text{M}+\text{H}]$: 361.2638, found: 361.2638.

2-((*E*)-(2-cinnamyl-2-phenylhydrazineylidene)methyl)-9-methyl-9H-carbazole (D29)



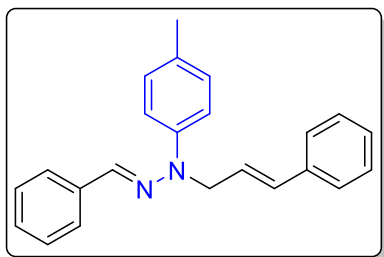
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 92 % yield (197.4 mg).

^1H NMR (400 MHz, CDCl_3) δ 8.35 – 8.29 (m, 1H), 8.15 – 8.08 (m, 1H), 7.96 – 7.88 (m, 1H), 7.73 (s, 1H), 7.51 – 7.41 (m, 3H), 7.41 – 7.32 (m, 6H), 7.31 – 7.15 (m, 4H), 6.89 – 7.00 (m, 1H), 6.56 – 6.46 (m, 1H), 6.40 – 6.26 (m, 1H), 4.79 – 4.65 (m, 2H), 4.32 (q, $J = 7.2$ Hz, 2H), 1.40 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.9, 140.4, 140.0, 136.5, 134.2, 131.3, 129.2, 128.6, 127.9, 127.7, 126.5, 125.8, 124.1, 123.2, 122.3, 120.6, 120.2, 119.1, 118.9, 114.7, 108.7, 48.7, 37.7, 13.9.

HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{28}\text{N}_3$ $[\text{M}+\text{H}]$: 430.2278, found: 430.2276.

2-((*E*)-benzylidene)-1-cinnamyl-1-(*p*-tolyl)hydrazine (D30)



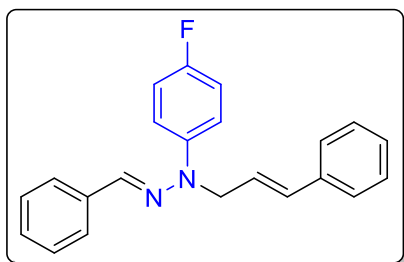
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 89% yield (145.1 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.61 (m, 2H), 7.40 (s, 1H), 7.35 – 7.07 (m, 12H), 6.45 – 6.32 (m, 1H), 6.22 – 6.11 (m, 1H), 4.62 – 4.48 (m, 2H), 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.7, 137.0, 136.6, 132.0, 131.4, 130.3, 129.9, 128.8, 127.9, 126.6, 126.3, 122.1, 115.3, 48.8, 20.8.

HRMS (ESI) calcd. for C₂₃H₂₃N₂ [M+H]: 327.1855, found: 327.1856.

2-((*E*)-benzylidene)-1-cinnamyl-1-(4-fluorophenyl)hydrazine (D31)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 76% yield (125.5 mg).

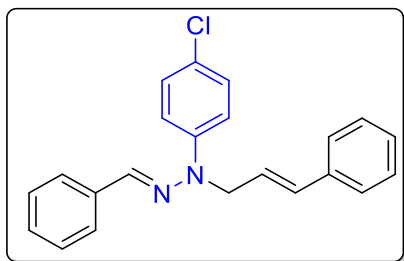
¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.58 (m, 2H), 7.43 (s, 1H), 7.37 – 7.11 (m, 10H), 7.05 – 6.94 (m, 2H), 6.45 – 6.35 (m, 1H), 6.27 – 6.13 (m, 1H), 4.63 – 4.50 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.9 (d, *J* = 239.37 Hz), 144.2, 136.6, 136.4, 132.6, 131.5, 128.7, 128.6, 128.0, 126.5, 126.3, 121.7, 116.3 (d, *J* = 7.07 Hz), 115.7 (d, *J* = 22.22 Hz), 49.1.

¹⁹F NMR (376 MHz, CDCl₃) δ = -123.9.

HRMS (ESI) calcd. for C₂₂H₂₀FN₂ [M+H]: 331.1605, found: 331.1603.

2-((*E*)-benzylidene)-1-(4-chlorophenyl)-1-cinnamylhydrazine (D32)



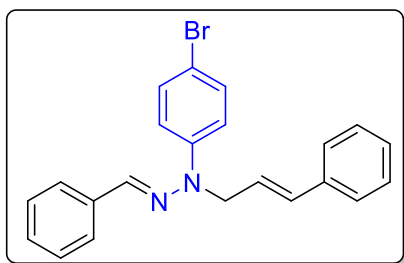
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 81% yield (140.2 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.61 (m, 2H), 7.47 (s, 1H), 7.38 – 7.13 (m, 12H), 6.38 (dt, *J* = 16.0, 2.0 Hz, 1H), 6.23 – 6.13 (m, 1H), 4.63 – 4.54 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 146.2, 136.4, 136.3, 133.2, 131.5, 129.1, 128.7, 128.3, 127.9, 126.5, 126.4, 125.6, 121.3, 116.0, 48.4.

HRMS (ESI) calcd. for C₂₂H₂₀ClN₂ [M+H]: 347.1309, found: 347.1306.

2-((*E*)-benzylidene)-1-(4-bromophenyl)-1-cinnamylhydrazine (D33)



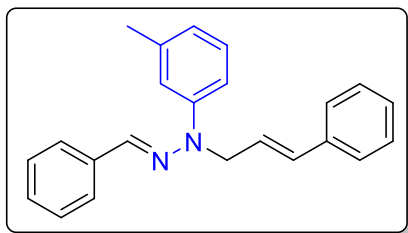
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a pink solid in 60% yield (117.0 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.60 (m, 2H), 7.54 – 7.11 (m, 13H), 6.42 – 6.30 (m, 1H), 6.20 – 6.12 (m, 1H), 4.62 – 4.50 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 146.7, 136.4, 136.3, 133.4, 132.0, 131.6, 128.8, 128.4, 128.0, 126.6, 126.5, 121.3, 116.4, 113.0, 48.2.

HRMS (ESI) calcd. for C₂₂H₂₀BrN₂ [M+H]: 391.0804, found: 391.0800.

2-((*E*)-benzylidene)-1-cinnamyl-1-(*m*-tolyl)hydrazine (D34)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 85% yield (138.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.60 (m, 2H), 7.45 (s, 1H), 7.40 – 7.08 (m, 11H), 6.81 – 6.73 (m, 1H), 6.48 – 6.38 (m, 1H), 6.28 – 6.16 (m, 1H), 4.67 – 4.58 (m, 2H), 2.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 139.0, 136.8, 136.5, 132.4, 131.4, 129.1, 128.7, 128.7, 127.9, 126.5, 126.3, 122.0, 121.8, 115.7, 112.3, 48.7, 22.0.

HRMS (ESI) calcd. for C₂₃H₂₃N₂ [M+H]: 327.1855, found: 327.1855.

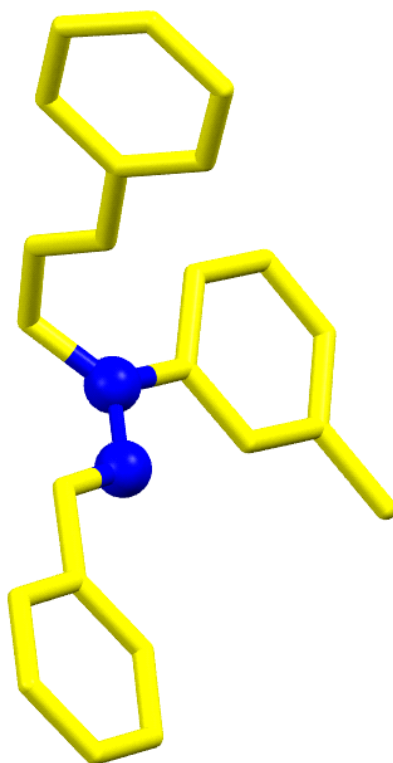
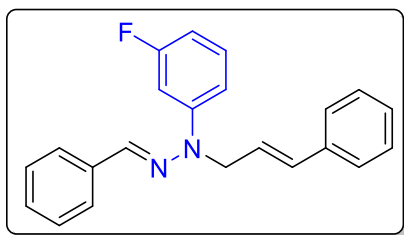


Figure S2 X-ray of D34 (CCDC 2249896)

2-((*E*)-benzylidene)-1-cinnamyl-1-(3-fluorophenyl)hydrazine (D35)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 71% yield (117.2 mg).

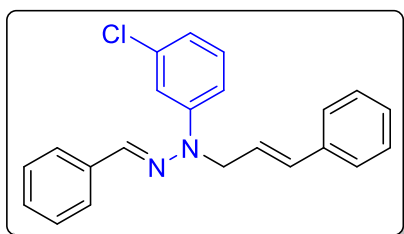
¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.61 (m, 2H), 7.49 (s, 1H), 7.41 – 7.11 (m, 10H), 7.09 – 6.99 (m, 1H), 6.67 – 6.55 (m, 1H), 6.45 – 6.32 (m, 1H), 6.25 – 6.12 (m, 1H), 4.70 – 4.51 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 164.0 (d, *J* = 243.41 Hz), 149.3 (d, *J* = 11.11 Hz), 136.3, 133.6, 131.6, 130.3 (d, *J* = 9.09 Hz), 128.7, 128.4, 127.9, 126.5, 121.3, 109.9, 107.1 (d, *J* = 22.22 Hz), 102.2 (d, *J* = 27.27 Hz), 48.3.

¹⁹F NMR (376 MHz, CDCl₃) δ = -112.0.

HRMS (ESI) calcd. for C₂₂H₂₀FN₂ [M+H]: 331.1605, found: 331.1601.

2-((*E*)-benzylidene)-1-(3-chlorophenyl)-1-cinnamylhydrazine (D36)



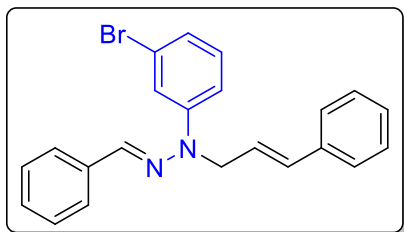
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 70% yield (121.1 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.60 (m, 2H), 7.53 – 7.42 (m, 2H), 7.40 – 7.13 (m, 10H), 6.94 – 6.83 (m, 1H), 6.45 – 6.32 (m, 1H), 6.22 – 6.12 (m, 1H), 4.68 – 4.52 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.7, 136.2, 135.1, 133.8, 131.6, 130.2, 128.7, 128.4, 128.0, 126.5, 121.2, 120.5, 114.9, 112.64, 48.2.

HRMS (ESI) calcd. for C₂₂H₂₀ClN₂ [M+H]: 347.1309, found: 347.1304.

2-((*E*)-benzylidene)-1-(3-bromophenyl)-1-cinnamylhydrazine (D37)



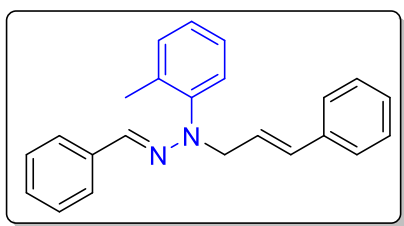
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a pink solid in 48% yield (93.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.64 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 (s, 1H), 7.40 – 7.11 (m, 10H), 7.08 – 6.99 (m, 1H), 6.46 – 6.33 (m, 1H), 6.28 – 6.14 (m, 1H), 4.70 – 4.58 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.7, 136.2, 136.1, 133.8, 131.5, 130.4, 128.7, 128.4, 127.9, 126.5, 123.4, 123.3, 121.1, 117.7, 113.1, 48.3.

HRMS (ESI) calcd. for C₂₂H₂₀BrN₂ [M+H]: 391.0804, found: 391.0801.

2-((*E*)-benzylidene)-1-cinnamyl-1-(*o*-tolyl)hydrazine (D38)



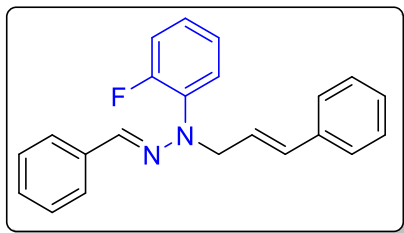
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 82% yield (133.7 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.46 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 5H), 7.22 – 7.11 (m, 5H), 7.08 (s, 1H), 6.59 – 6.47 (m, 1H), 6.43 – 6.29 (m, 1H), 4.51 – 4.39 (m, 2H), 2.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.1, 137.1, 136.9, 135.4, 133.4, 132.3, 131.3, 128.7, 128.6, 127.7, 127.6, 127.3, 126.7, 126.5, 126.3, 125.8, 125.6, 57.7, 18.8.

HRMS (ESI) calcd. for C₂₃H₂₃N₂ [M+H]: 327.1855, found: 327.1853.

2-((*E*)-benzylidene)-1-cinnamyl-1-(2-fluorophenyl)hydrazine (D39)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 61% yield (100.7 mg).

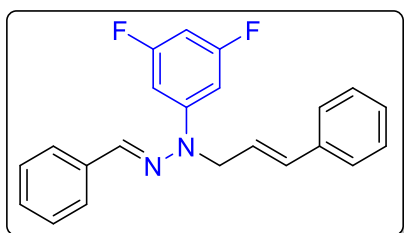
¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.45 (m, 5H), 7.42 – 6.91 (m, 10H), 6.64 – 6.47 (m, 1H), 6.34 – 6.19 (m, 1H), 4.61 – 4.45 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 154.9 (d, *J* = 248.46 Hz), 136.7 (d, *J* = 39.39 Hz), 134.8, 132.2, 128.0 (d, *J* = 40.4 Hz), 126.5 (d, *J* = 24.24 Hz), 125.1, 125.0, 124.8, 124.2, 116.8 (d, *J* = 21.21 Hz), 54.7.

¹⁹F NMR (376 MHz, CDCl₃) δ = -122.1.

HRMS (ESI) calcd. for C₂₂H₂₀FN₂ [M+H]: 331.1605, found: 331.1600.

2-((*E*)-benzylidene)-1-cinnamyl-1-(3,5-difluorophenyl)hydrazine (D40)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 75% yield (130.6 mg).

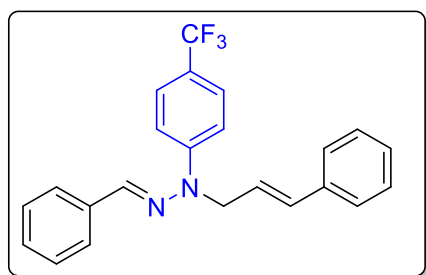
¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.61 (m, 2H), 7.50 (s, 1H), 7.39 – 7.13 (m, 8H), 6.96 – 6.83 (m, 2H), 6.41 – 6.30 (m, 2H), 6.18 – 6.09 (m, 1H), 4.59 – 4.48 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 165.2 (d, *J* = 15.15 Hz), 162.8 (d, *J* = 16.16 Hz), 149.7 (t, *J* = 13.13 Hz), 136.1, 135.9, 134.7, 131.8, 128.8, 128.7, 128.1, 126.7, 126.6, 120.8, 97.5 (d, *J* = 30.3 Hz), 97.5 (d, *J* = 12.12 Hz), 95.4 (t, *J* = 26.26 Hz), 48.0.

¹⁹F NMR (376 MHz, CDCl₃) δ = -109.3.

HRMS (ESI) calcd. for C₂₂H₁₉F₂N₂ [M+H]: 349.1510, found: 349.1509.

2-((*E*)-benzylidene)-1-cinnamyl-1-(4-(trifluoromethyl)phenyl)hydrazine (D41)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 81% yield (154.0 mg).

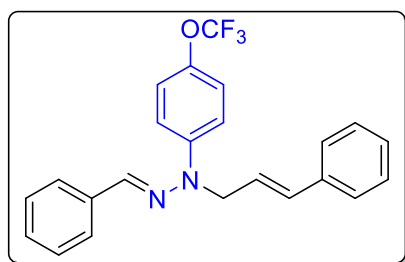
¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.67 (m, 2H), 7.62 – 7.52 (m, 3H), 7.51 – 7.42 (m, 2H), 7.43 – 7.13 (m, 8H), 6.51 – 6.35 (m, 1H), 6.31 – 6.19 (m, 1H), 4.72 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 149.7, 136.1, 136.0, 134.5, 131.7, 128.7, 128.6, 128.0, 126.5, 126.4, 124.9 (q, *J* = 543.38 Hz, 271.69 Hz), 122.0 (q, *J* = 65.65 Hz, 33.33 Hz), 120.8, 114.0, 47.9.

¹⁹F NMR (376 MHz, CDCl₃) δ = -61.3.

HRMS (ESI) calcd. for C₂₃H₂₀F₃N₂ [M+H]: 381.1573, found: 381.1569.

2-((*E*)-benzylidene)-1-cinnamyl-1-(4-(trifluoromethoxy)phenyl)hydrazine (D42)



The title compound was prepared according to the general procedure and purified by

column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 83% yield (164.4 mg).

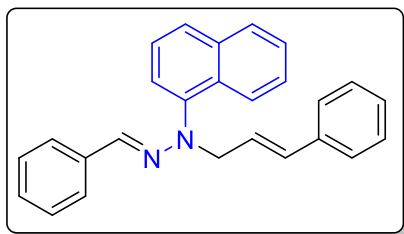
¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 1H), 7.41 – 7.12 (m, 12H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.25 – 6.13 (m, 1H), 4.67 – 4.54 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 146.3, 143.0, 136.3, 136.2, 133.4, 131.6, 128.7, 128.3, 128.0, 126.5, 126.4, 122.2, 122.1, 121.3, 120.8 (q, *J* = 513.08 Hz, 256.54 Hz), 115.4, 48.4.

¹⁹F NMR (376 MHz, CDCl₃) δ = -58.1.

HRMS (ESI) calcd. for C₂₃H₂₀F₃N₂O [M+H]: 397.1522, found: 397.1518.

2-((*E*)-benzylidene)-1-cinnamyl-1-(naphthalen-1-yl)hydrazine (D43)



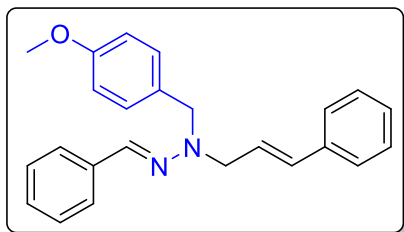
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 85% yield (153.9 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.01 (m, 1H), 7.88 – 7.76 (m, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.08 (m, 15H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.46 – 6.34 (m, 1H), 4.64 – 4.49 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 143.6, 137.1, 136.8, 135.1, 135.0, 132.5, 130.1, 128.8, 128.7, 127.8, 127.1, 126.7, 126.6, 126.5, 126.2, 126.1, 125.7, 124.1, 123.7, 58.4.

HRMS (ESI) calcd. for C₂₆H₂₃N₂ [M+H]: 363.1855, found: 363.1852.

2-((*E*)-benzylidene)-1-cinnamyl-1-(4-methoxybenzyl)hydrazine (D44)



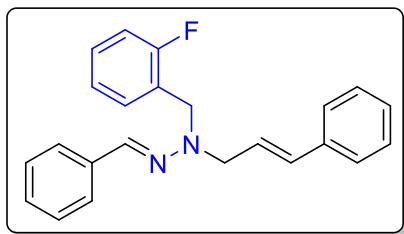
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 58% yield (103.3 mg).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.60 – 7.47 (m, 2H), 7.38 – 7.11 (m, 11H), 6.87 – 6.78 (m, 2H), 6.52 – 6.39 (m, 1H), 6.28 – 6.15 (m, 1H), 4.45 (s, 2H), 4.08 – 3.98 (m, 2H), 3.72 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.0, 137.2, 137.0, 132.6, 132.1, 129.8, 129.1, 128.7, 128.6, 127.7, 127.4, 126.5, 125.7, 125.1, 114.1, 57.3, 55.5, 55.4.

HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}$ [M+H]: 357.1961, found: 357.1961.

2-((*E*)-benzylidene)-1-cinnamyl-1-(2-fluorobenzyl)hydrazine (D45)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 62% yield (107.0 mg).

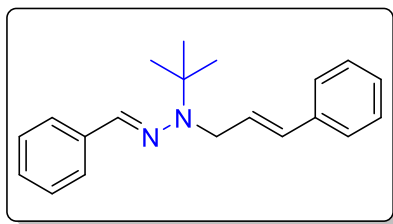
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (d, $J = 7.2$ Hz, 2H), 7.39 – 7.21 (m, 8H), 7.20 – 7.10 (m, 3H), 7.08 – 6.95 (m, 2H), 6.49 (d, $J = 16.0$ Hz, 1H), 6.31 – 6.15 (m, 1H), 4.56 (s, 2H), 4.16 – 4.03 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.8 (d, $J = 246.44$ Hz), 137.1, 137.0, 132.8, 132.3, 130.2 (d, $J = 4.04$ Hz), 129.0 (d, $J = 8.08$ Hz), 128.8, 128.7, 127.8, 127.5, 126.6, 125.8, 125.0, 124.8, 124.4 (d, $J = 4.04$ Hz), 115.5 (d, $J = 21.21$ Hz), 56.5, 51.0.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) $\delta = -117.8$.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{21}\text{FN}_2$ [M+H]: 345.1761, found: 345.1762.

2-((*E*)-benzylidene)-1-(tert-butyl)-1-cinnamylhydrazine (D46)



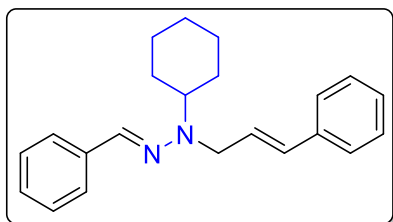
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 43% yield (62.8 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.47 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.19 (m, 5H), 7.18 – 7.09 (m, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.28 – 6.12 (m, 1H), 3.99 – 3.85 (m, 2H), 1.34 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 138.3, 137.3, 130.4, 129.4, 128.7, 128.6, 127.5, 126.8, 126.5, 126.2, 125.5, 60.0, 48.4, 28.5.

HRMS (ESI) calcd. for C₂₀H₂₅N₂ [M+H]: 293.2012, found: 293.2013.

2-((*E*)-benzylidene)-1-cinnamyl-1-cyclohexylhydrazine (D47)



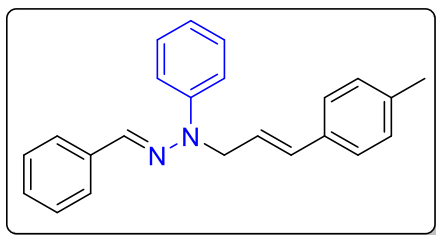
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a light yellow liquid in 33% yield (52.5 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.47 (m, 2H), 7.39 – 7.10 (m, 9H), 6.58 – 6.49 (m, 1H), 6.29 – 6.17 (m, 1H), 4.07 – 3.96 (m, 2H), 3.38 – 3.22 (m, 1H), 2.02 – 1.90 (m, 2H), 1.88 – 1.78 (m, 2H), 1.72 – 1.48 (m, 3H), 1.42 – 1.06 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 137.8, 137.0, 130.8, 129.4, 128.6, 128.4, 127.4, 126.6, 126.3, 125.3, 125.2, 65.7, 50.6, 31.3, 26.0.

HRMS (ESI) calcd. for C₂₂H₂₇N₂ [M+H]: 319.2169, found: 319.2170.

2-((*E*)-benzylidene)-1-phenyl-1-((*E*)-3-(*p*-tolyl)allyl)hydrazine (D48)



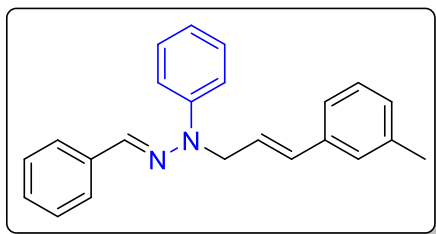
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 90% yield (146.8 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.61 (m, 2H), 7.47 (s, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.27 (m, 4H), 7.26 – 7.17 (m, 3H), 7.09 – 6.89 (m, 3H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.20 – 6.11 (m, 1H), 4.67 – 4.57 (m, 2H), 2.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 137.6, 136.8, 133.7, 132.5, 131.3, 129.4, 129.2, 128.7, 128.0, 126.4, 126.3, 120.7, 115.0, 48.6, 21.3.

HRMS (ESI) calcd. for C₂₃H₂₃N₂ [M+H]: 327.1855, found: 327.1855.

2-((*E*)-benzylidene)-1-phenyl-1-((*E*)-3-(*o*-tolyl)allyl)hydrazine (D49)



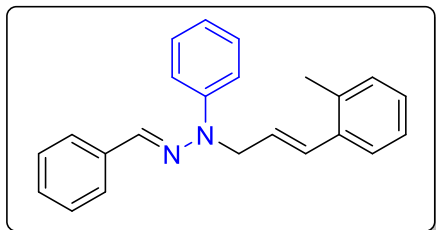
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 87% yield (141.9 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.61 (m, 2H), 7.48 – 7.35 (m, 3H), 7.35 – 7.24 (m, 4H), 7.24 – 7.15 (m, 1H), 7.15 – 7.03 (m, 3H), 7.00 – 6.86 (m, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.21 – 6.07 (m, 1H), 4.61 – 4.48 (m, 2H), 2.30 – 2.12 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.8, 138.3, 136.9, 136.5, 132.6, 131.6, 129.4, 128.8, 128.7, 128.1, 127.5, 126.4, 123.6, 121.7, 120.9, 115.1, 48.5, 21.6.

HRMS (ESI) calcd. for C₂₃H₂₃N₂ [M+H]: 327.1855, found: 327.1856.

2-((*E*)-benzylidene)-1-phenyl-1-((*E*)-3-(*m*-tolyl)allyl)hydrazine (D50)



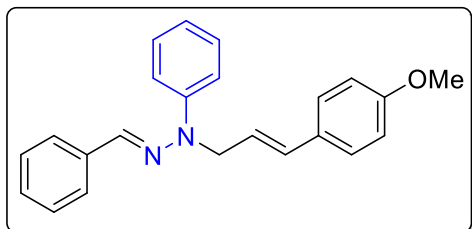
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 85% yield (138.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.65 (m, 2H), 7.54 (s, 1H), 7.46 – 7.39 (m, 3H), 7.38 – 7.30 (m, 4H), 7.28 – 7.21 (m, 1H), 7.18 – 7.04 (m, 3H), 6.97 – 6.88 (m, 1H), 6.72 – 6.60 (m, 1H), 6.11 – 5.98 (m, 1H), 4.74 – 4.53 (m, 2H), 2.18 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 136.6, 135.8, 135.5, 132.6, 130.3, 129.9, 129.1, 128.6, 127.9, 127.6, 126.2, 126.1, 125.7, 123.2, 120.8, 115.1, 48.9, 19.8.

HRMS (ESI) calcd. for C₂₃H₂₃N₂ [M+H]: 327.1855, found: 327.1855.

2-((*E*)-benzylidene)-1-((*E*)-3-(4-methoxyphenyl)allyl)-1-phenylhydrazine (D51)



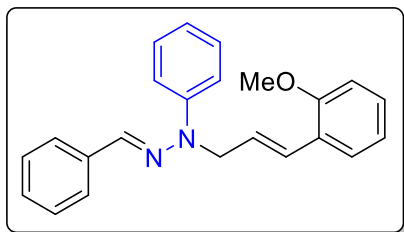
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 88% yield (150.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.64 (m, 2H), 7.44 (s, 1H), 7.42 – 7.37 (m, 2H), 7.35 – 7.27 (m, 4H), 7.23 – 7.16 (m, 3H), 6.95 – 6.87 (m, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.07 – 5.96 (m, 1H), 4.60 – 4.51 (m, 2H), 3.66 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.4, 147.8, 136.8, 132.5, 130.8, 129.3, 128.7, 128.0, 127.7, 126.4, 120.8, 119.5, 115.0, 114.1, 55.4, 48.5.

HRMS (ESI) calcd. for C₂₃H₂₃N₂O [M+H]: 343.1805, found: 343.1802.

2-((*E*)-benzylidene)-1-((*E*)-3-(2-methoxyphenyl)allyl)-1-phenylhydrazine (D52)



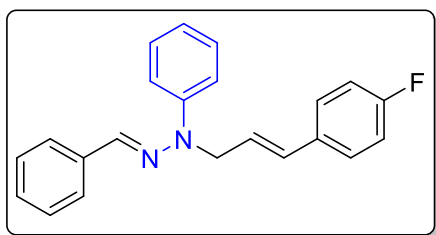
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 83% yield (142.0 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.65 (m, 2H), 7.55 (s, 1H), 7.45 – 7.40 (m, 2H), 7.38 – 7.28 (m, 5H), 7.26 – 7.12 (m, 2H), 6.98 – 6.75 (m, 4H), 6.35 – 6.23 (m, 1H), 4.73 – 4.63 (m, 2H), 3.73 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.8, 147.8, 136.8, 132.5, 129.2, 128.8, 128.6, 127.8, 127.4, 127.2, 126.3, 123.1, 120.7, 115.1, 111.0, 55.4, 49.2.

HRMS (ESI) calcd. for C₂₃H₂₃N₂O [M+H]: 343.1805, found: 343.1801.

2-((*E*)-benzylidene)-1-((*E*)-3-(4-fluorophenyl)allyl)-1-phenylhydrazine (D53)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 91% yield (150.2 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.61 (m, 2H), 7.46 – 7.13 (m, 10H), 6.97 – 6.80 (m, 3H), 6.38 – 6.27 (m, 1H), 6.12 – 6.02 (m, 1H), 4.63 – 4.47 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.5 (d, $J = 247.45$ Hz), 147.7, 136.7, 132.7 (d, $J = 3.03$ Hz), 132.5, 130.2, 129.3, 128.8, 128.1 (d, $J = 4.04$ Hz), 126.4, 121.6, 120.9, 115.6 (d, $J = 22.22$ Hz), 115.0, 48.3.

^{19}F NMR (376 MHz, CDCl_3) $\delta = -113.9$.

HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{20}\text{FN}_2$ [$\text{M}+\text{H}$]: 331.1605, found: 331.1601.

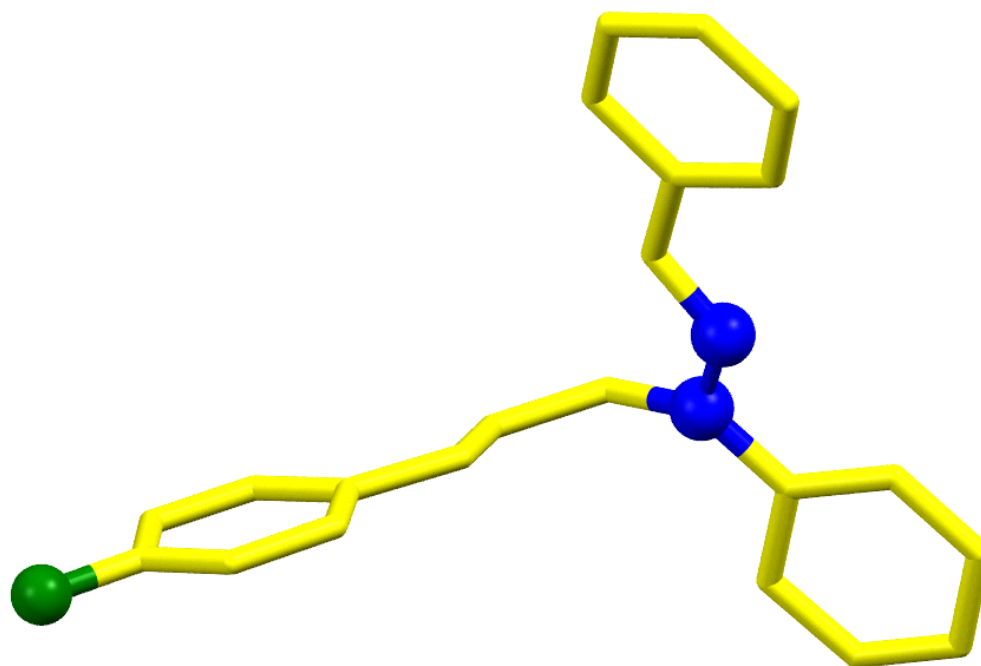
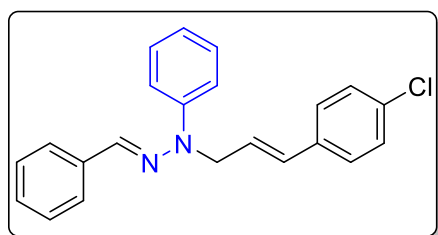


Figure S3 X-ray of D53 (CCDC 2249898)

2-((*E*)-benzylidene)-1-((*E*)-3-(4-chlorophenyl)allyl)-1-phenylhydrazine (D54)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 91% yield (157.5 mg).

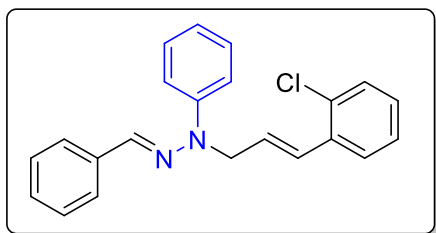
^1H NMR (400 MHz, CDCl_3) δ 7.71 – 7.65 (m, 2H), 7.47 (s, 1H), 7.44 – 7.30 (m, 6H), 7.28 – 7.20 (m, 5H), 6.99 – 6.92 (m, 1H), 6.42 – 6.35 (m, 1H), 6.27 – 6.17 (m, 1H),

4.74 – 4.61 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.5, 136.6, 134.9, 133.4, 132.5, 130.1, 129.2, 128.7, 128.6, 128.0, 127.6, 126.2, 122.5, 120.8, 114.9, 48.4.

HRMS (ESI) calcd. for C₂₂H₂₀ClN₂ [M+H]: 347.1309, found: 347.1308.

2-((*E*)-benzylidene)-1-((*E*)-3-(2-chlorophenyl)allyl)-1-phenylhydrazine (D55)



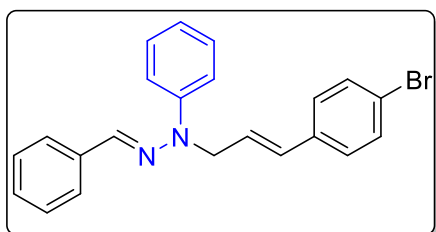
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 84% yield (145.3 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.65 (m, 2H), 7.46 (s, 1H), 7.43 – 7.21 (m, 9H), 7.21 – 7.13 (m, 2H), 6.99 – 6.91 (m, 1H), 6.41 – 6.32 (m, 1H), 6.29 – 6.19 (m, 1H), 4.72 – 4.58 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.5, 136.5, 135.3, 132.5, 131.7, 130.2, 129.2, 128.6, 128.0, 126.2, 122.6, 121.5, 120.8, 114.9, 48.4.

HRMS (ESI) calcd. for C₂₂H₂₀ClN₂ [M+H]: 347.1309, found: 347.1304.

2-((*E*)-benzylidene)-1-((*E*)-3-(4-bromophenyl)allyl)-1-phenylhydrazine (D56)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 86% yield (167.7 mg).

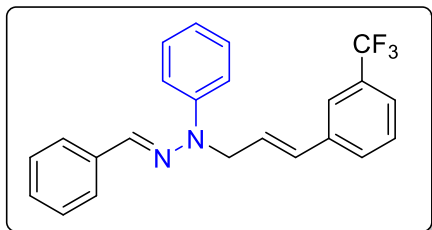
¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.64 (m, 2H), 7.54 (s, 1H), 7.46 – 7.18 (m, 9H),

7.17 – 7.04 (m, 2H), 6.98 – 6.86 (m, 2H), 6.20 – 6.10 (m, 1H), 4.72 – 4.63 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 136.7, 134.9, 133.1, 132.7, 129.4, 129.2, 128.9, 128.8, 128.7, 128.0, 127.3, 127.0, 126.3, 125.6, 120.9, 115.2, 48.7.

HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{20}\text{BrN}_2$ $[\text{M}+\text{H}]$: 391.0804, found: 391.0799.

2-((E)-benzylidene)-1-phenyl-1-((E)-3-(3-(trifluoromethyl)phenyl)allyl)hydrazine (D57)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 90% yield (171.1 mg).

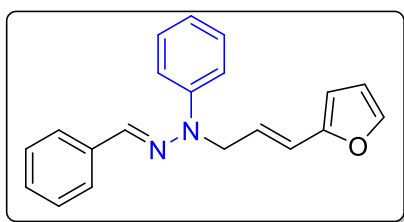
^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.65 (m, 2H), 7.55 (s, 1H), 7.47 – 7.19 (m, 11H), 7.01 – 6.92 (m, 1H), 6.41 (dd, J = 16.0, 2.0 Hz, 1H), 6.33 – 6.22 (m, 1H), 4.70 – 4.56 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 137.2, 136.6, 132.5, 131.0 (d, J = 64.64 Hz, 32.32 Hz), 130.0, 129.8, 129.3, 129.1, 128.7, 128.1, 126.4, 124.3 (q, J = 8.08, 4.04 Hz), 124.2 (q, J = 546.41, 272.70 Hz), 123.9, 123.1 (q, J = 8.08, 4.04 Hz), 121.0, 114.9, 48.2.

^{19}F NMR (376 MHz, CDCl_3) δ = -62.5.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{20}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]$: 381.1573, found: 381.1568.

2-((E)-benzylidene)-1-((E)-3-(furan-2-yl)allyl)-1-phenylhydrazine (D58)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the

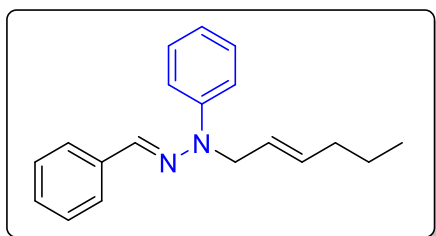
light-yellow oil in 48% yield (72.5 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.64 (m, 2H), 7.44 (s, 1H), 7.42 – 7.28 (m, 7H), 7.27 – 7.18 (m, 1H), 6.98 – 6.90 (m, 1H), 6.33 – 6.26 (m, 1H), 6.24 – 6.17 (m, 2H), 6.12 – 6.06 (m, 1H), 4.68 – 4.58 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 152.2, 147.6, 142.0, 136.6, 132.5, 129.2, 128.6, 128.0, 126.3, 120.8, 120.3, 119.6, 114.8, 111.4, 108.3, 48.1.

HRMS (ESI) calcd. for C₂₀H₁₉N₂O [M+H]: 303.1491, found: 303.1486.

2-((*E*)-benzylidene)-1-((*E*)-hex-2-en-1-yl)-1-phenylhydrazine (D59)



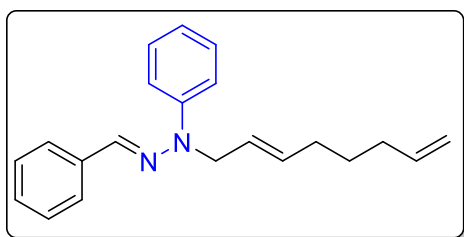
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 70% yield (97.4 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.52 (m, 2H), 7.37 (s, 1H), 7.32 – 7.18 (m, 6H), 7.18 – 7.12 (m, 1H), 6.90 – 6.75 (m, 1H), 5.52 – 5.27 (m, 2H), 4.53 – 4.31 (m, 2H), 1.97 – 1.85 (m, 2H), 1.31 – 1.11 (m, 2H), 0.84 – 0.66 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.7, 136.9, 133.2, 132.2, 129.1, 128.6, 127.8, 126.1, 121.7, 120.5, 114.8, 48.1, 34.3, 22.3, 13.6.

HRMS (ESI) calcd. for C₁₉H₂₃N₂ [M+H]: 279.1855, found: 279.1855.

2-((*E*)-benzylidene)-1-((*E*)-octa-2,7-dien-1-yl)-1-phenylhydrazine (D60)



The title compound was prepared according to the general procedure and purified by

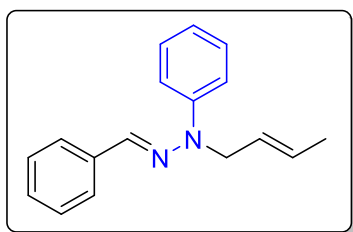
column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give the light-yellow oil in 52% yield (79.1 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.61 (m, 2H), 7.48 – 7.41 (m, 1H), 7.39 – 7.16 (m, 7H), 6.99 – 6.83 (m, 1H), 5.81 – 5.64 (m, 1H), 5.59 – 5.27 (m, 2H), 4.98 – 4.85 (m, 2H), 4.53 – 4.39 (m, 2H), 2.11 – 1.91 (m, 4H), 1.58 – 1.33 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 138.6, 136.9, 133.0, 132.2, 129.1, 128.6, 127.8, 126.2, 121.9, 114.8, 114.7, 48.1, 48.0, 33.2, 31.6, 28.4.

HRMS (ESI) calcd. for C₂₁H₂₅N₂ [M+H]: 305.2012, found: 305.2013.

(E)-2-benzylidene-1-(but-3-en-2-yl)-1-phenylhydrazine (D61)



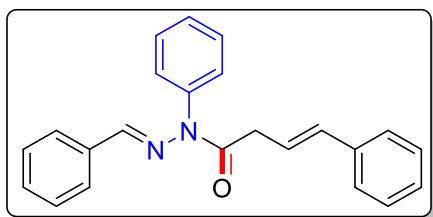
The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) to give a white solid in 76% yield (96.1 mg) from A15 and 71% yield (89 mg) from A16.

¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.58 (m, 2H), 7.55 – 7.15 (m, 8H), 6.93 – 6.87 (m, 1H), 5.73 – 5.27 (m, 2H), 4.61 – 4.29 (m, 2H), 1.84 – 1.58 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.6, 136.9, 132.0, 129.1, 128.6, 127.8, 127.7, 126.1, 126.1, 122.7, 120.4, 114.7, 47.8, 17.7.

HRMS (ESI) calcd. for C₁₇H₁₉N₂ [M+H]: 251.1542, found: 251.1539.

(E)-N'-((E)-benzylidene)-N,4-diphenylbut-3-enehydrazide (E1)



The title compound was prepared according to the general procedure and purified by

column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 78% yield (132.7 mg) based on reaction conditions C and 76% yield (129.3 mg) based on reaction conditions B.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 – 7.58 (m, 2H), δ 7.58 – 7.51 (m, 2H), δ 7.50 – 7.43 (m, 1H), δ 7.42 – 7.34 (m, 5H), 7.32 – 7.25 (m, 3H), 7.24 – 7.14 (m, 3H), 6.66 (d, J = 16.0 Hz, 1H), 6.60 – 6.49 (m, 1H), 4.05 – 3.89 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 173.0, 141.8, 137.3, 135.8, 134.3, 133.2, 130.3, 130.0, 129.4, 129.3, 128.8, 128.5, 127.3, 127.2, 126.3, 123.4, 38.7.

MS (70 eV): m/z (%) = 340 $[\text{M}]^+$ (100), 210, 194, 117.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}$ $[\text{M}+\text{H}]$: 341.1609, found: 341.1610.

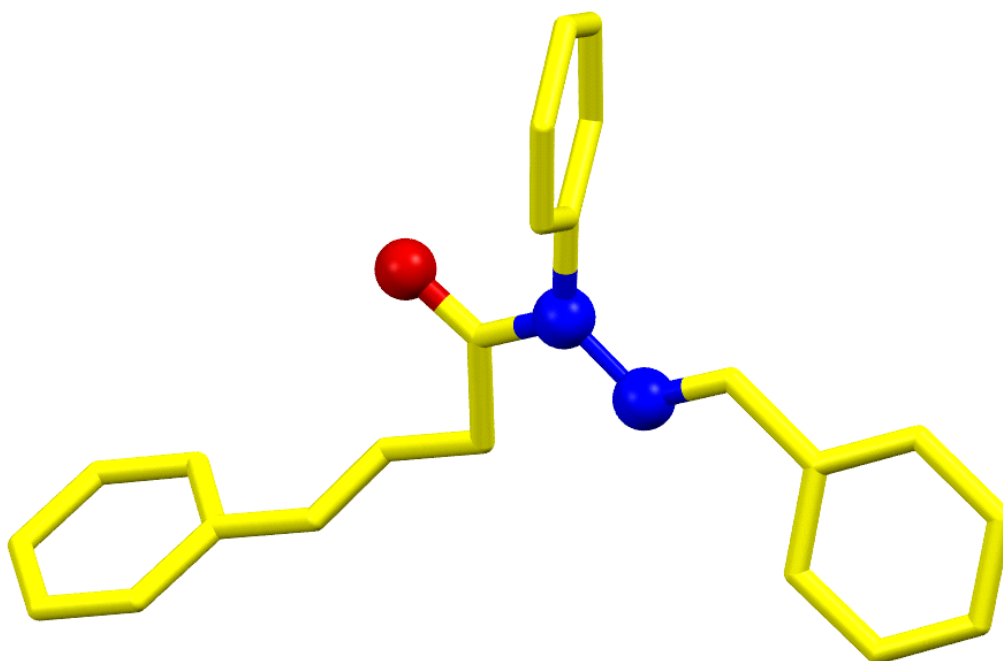
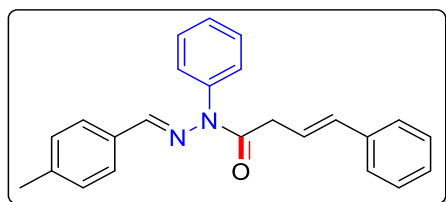


Figure S4 X-ray of E1 (CCDC 2249902)

(E)-*N'*-*(E)*-4-methylbenzylidene)-*N*,4-diphenylbut-3-enehydrazide (E2)



The title compound was prepared according to the general procedure and purified by

column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 78% yield (138.1 mg) based on reaction conditions C and 76% yield (134.6 mg) based on reaction conditions B.

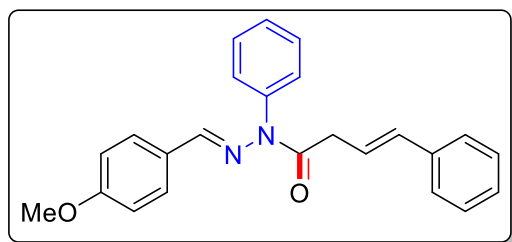
¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.43 (m, 5H), 7.42 – 7.37 (m, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.14 (m, 6H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.61 – 6.50 (m, 1H), 4.03 – 3.92 (m, 2H), 2.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.9, 141.9, 140.3, 137.4, 135.9, 133.1, 131.6, 130.2, 129.5, 129.3, 128.5, 127.3, 127.2, 126.3, 123.5, 38.7, 21.5.

MS (70 eV): *m/z* (%) = 354 [M]⁺ (100), 210, 194, 117.

HRMS (ESI) calcd. for C₂₄H₂₃N₂O [M+H]: 355.1805, found: 355.1804.

(*E*)-*N'*-((*E*)-4-methoxybenzylidene)-*N*,4-diphenylbut-3-enehydrazide (E3)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 73% yield (135.1 mg) based on reaction conditions C and 72% yield (131.4 mg) based on reaction conditions B.

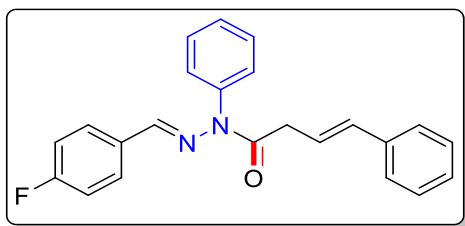
¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.50 (m, 4H), 7.49 – 7.43 (m, 1H), 7.42 – 7.36 (m, 2H), 7.33 – 7.26 (m, 2H), 7.25 – 7.13 (m, 4H), 6.94 – 6.85 (m, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.61 – 6.50 (m, 1H), 4.04 – 3.90 (m, 2H), 3.81 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.8, 161.1, 141.7, 137.4, 136.0, 133.1, 130.2, 129.3, 128.7, 128.5, 127.3, 127.1, 126.3, 123.5, 114.2, 55.4, 38.7.

MS (70 eV): *m/z* (%) = 370 [M]⁺ (100), 273, 194, 117.

HRMS (ESI) calcd. for C₂₄H₂₃N₂O₂ [M+H]: 371.1754, found: 371.1757.

(*E*)-*N'*-((*E*)-4-fluorobenzylidene)-*N*,4-diphenylbut-3-enehydrazide (E4)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 65% yield (116.4 mg) based on reaction conditions C and 61% yield (109.3 mg) based on reaction conditions B.

¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.51 (m, 4H), 7.50 – 7.44 (m, 1H), 7.43 – 7.35 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.13 (m, 4H), 7.11 – 7.00 (m, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.59 – 6.48 (m, 1H), 4.09 – 3.83 (m, 2H).

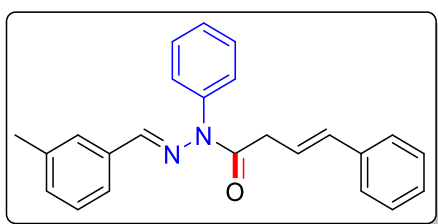
¹³C NMR (101 MHz, CDCl₃) δ = 172.9, 163.7 (d, *J* = 251.49 Hz), 140.5, 137.3, 135.8, 133.2, 130.6 (d, *J* = 4.04 Hz), 130.3, 129.4, 129.3, 129.0 (d, *J* = 8.08 Hz), 128.5, 127.4, 126.3, 123.3. 115.9 (d, *J* = 22.22 Hz), 38.7.

¹⁹F NMR (376 MHz, CDCl₃) δ = -110.1.

MS (70 eV): *m/z* (%) = 358 [M]⁺ (100), 214, 195, 117.

HRMS (ESI) calcd. for C₂₃H₂₀FN₂O [M+H]: 359.1554, found: 359.1556.

(*E*)-*N'*-((*E*)-3-methylbenzylidene)-*N*,4-diphenylbut-3-enehydrazide (E5)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 76% yield (134.6 mg) based on reaction conditions C and 75% yield (132.8 mg) based on reaction conditions B.

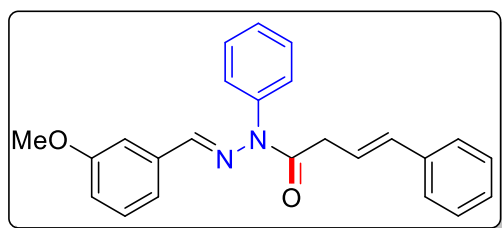
¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.50 (m, 2H), 7.48 – 7.35 (m, 5H), 7.33 – 7.23 (m, 4H), 7.22 – 7.13 (m, 4H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.60 – 6.50 (m, 1H), 4.06 – 3.88 (m, 2H), 2.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 173.0, 142.1, 138.5, 137.4, 135.9, 134.3, 133.2, 130.9, 130.3, 129.4, 129.3, 128.7, 128.5, 127.9, 127.3, 126.3, 124.4, 123.4, 38.7, 21.4.

MS (70 eV): *m/z* (%) = 354 [M]⁺ (100), 210, 194, 117.

HRMS (ESI) calcd. for C₂₄H₂₃N₂O [M+H]: 355.1805, found: 355.1802.

(*E*)-*N'*-((*E*)-3-methoxybenzylidene)-*N*,4-diphenylbut-3-enehydrazide (E6)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 73% yield (135.1 mg) based on reaction conditions C and 69% yield (127.7 mg) based on reaction conditions B.

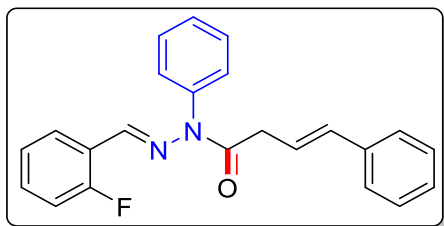
¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.51 (m, 2H), 7.50 – 7.42 (m, 1H), 7.42 – 7.36 (m, 2H), 7.31 – 7.25 (m, 3H), 7.23 (d, *J* = 1.2 Hz, 1H), 7.22 – 7.10 (m, 5H), 6.95 – 6.87 (m, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.61 – 6.49 (m, 1H), 4.03 – 3.92 (m, 2H), 3.80 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.9, 160.0, 141.7, 137.4, 135.9, 135.7, 133.2, 130.3, 129.8, 129.4, 129.3, 128.5, 127.4, 126.3, 123.4, 120.2, 116.0, 111.8, 55.4, 38.7.

MS (70 eV): *m/z* (%) = 370 [M]⁺ (100), 292, 194, 117.

HRMS (ESI) calcd. for C₂₄H₂₃N₂O₂ [M+H]: 371.1754, found: 371.1759.

(*E*)-*N'*-((*E*)-2-fluorobenzylidene)-*N*,4-diphenylbut-3-enehydrazide (E7)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 59% yield (105.7 mg) based on reaction conditions C and 57% yield (102.1 mg) based on reaction conditions B.

¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.95 (m, 1H), 7.61 – 7.45 (m, 4H), 7.43 – 7.27 (m, 5H), 7.26 – 7.15 (m, 4H), 7.07 – 6.98 (m, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.61 – 6.5 (m, 1H), 4.08 – 3.82 (m, 2H).

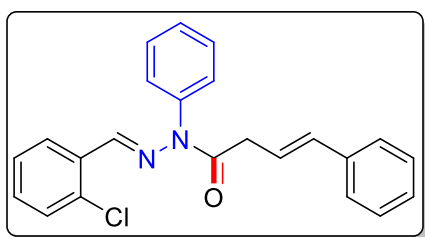
¹³C NMR (101 MHz, CDCl₃) δ = 173.0, 161.4 (d, *J* = 253.51 Hz), 137.3, 133.2, 131.4 (d, *J* = 8.08 Hz), 130.3, 129.5, 129.1, 128.5, 127.3, 126.6, 126.3, 124.5 (d, *J* = 4.04 Hz), 123.2, 115.9 (d, *J* = 21.21 Hz), 38.7.

¹⁹F NMR (376 MHz, CDCl₃) δ = -120.7.

MS (70 eV): *m/z* (%) = 358 [M]⁺ (100), 214, 195, 117.

HRMS (ESI) calcd. for C₂₃H₂₀FN₂O [M+H]: 359.1554, found: 359.1557.

(E)-N'-((E)-2-chlorobenzylidene)-N,4-diphenylbut-3-enehydrazide (E8)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 53% yield (99.1 mg) based on reaction conditions C and 52% yield (92.3 mg) based on reaction conditions B.

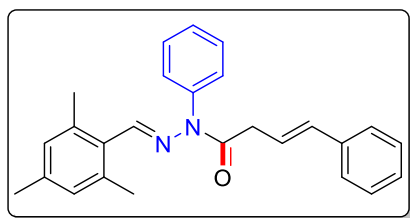
¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.01 (m, 1H), 7.71 (s, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.25 (m, 5H), 7.24 – 7.15 (m, 3H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.60 – 6.48 (m, 1H), 4.03 – 3.89 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.9, 138.7, 137.3, 135.7, 134.5, 133.3, 131.8, 130.8, 130.3, 129.9, 129.6, 129.0, 128.5, 127.4, 127.1, 127.0, 126.3, 123.2, 38.7.

MS (70 eV): *m/z* (%) = 374 [M]⁺ (100), 230, 195, 117.

HRMS (ESI) calcd. for C₂₃H₂₀ClN₂O [M+H]: 375.1259, found: 375.1261.

(*E*)-*N*,4-diphenyl-*N'*-((*E*)-2,4,6-trimethylbenzylidene)but-3-enehydrazide (E9)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 76% yield (145.2 mg) based on reaction conditions C and 73% yield (141.4 mg) based on reaction conditions B.

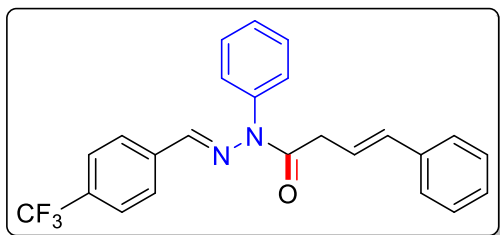
¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.41 – 7.35 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.16 (m, 3H), 6.86 (s, 2H), 6.63 – 6.48 (m, 2H), 3.97 – 3.82 (m, 2H), 2.29 (d, *J* = 13.6 Hz, 9H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.9, 142.8, 138.9, 137.5, 137.4, 136.1, 132.9, 130.3, 129.7, 129.3, 128.5, 128.1, 127.3, 126.3, 123.5, 38.4, 21.3, 21.1.

MS (70 eV): *m/z* (%) = 382 [M]⁺ (100), 224, 194, 117.

HRMS (ESI) calcd. for C₂₆H₂₇N₂O [M+H]: 383.2118, found: 383.2117.

(*E*)-*N*,4-diphenyl-*N'*-((*E*)-4-(trifluoromethyl)benzylidene)but-3-enehydrazide (E10)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 52% yield (106.1 mg) based on reaction conditions C and 51% yield (104.1 mg) based on reaction conditions B.

¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.54 (m, 2H), 7.53 – 7.45 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.25 – 7.15 (m, 3H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.59 – 6.46 (m, 1H), 4.11 – 3.80 (m, 2H).

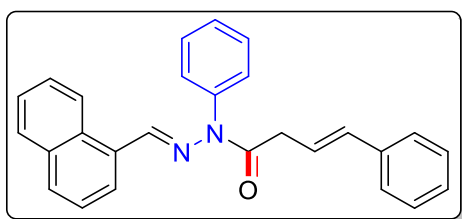
¹³C NMR (101 MHz, CDCl₃) δ = 173.0, 139.9, 137.7, 137.2, 135.6, 133.4, 131.4 (q, *J* = 65.29, 32.61 Hz), 130.4, 129.6, 129.1, 128.5, 127.4, 127.3, 126.3, 125.7 (q, *J* = 546.41, 272.70 Hz), 123.9 (q, *J* = 7.07, 3.03 Hz), 123.0, 38.6.

¹⁹F NMR (376 MHz, CDCl₃) δ = -62.7.

MS (70 eV): *m/z* (%) = 408 [M]⁺ (100), 264, 117, 91.

HRMS (ESI) calcd. for C₂₄H₂₀F₃N₂O [M+H]: 409.1522, found: 409.1523.

(*E*)-*N'*-((*E*)-naphthalen-1-ylmethylene)-*N,N*,4-diphenylbut-3-enhydrazide (E11)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 63% yield (123.1 mg) based on reaction conditions C and 60% yield (117.1 mg) based on reaction conditions B.

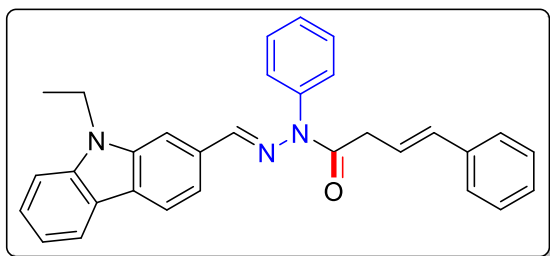
¹H NMR (400 MHz, CDCl₃) δ 8.40 – 8.31 (m, 1H), 7.96 (s, 1H), 7.89 – 7.79 (m, 3H), 7.63 – 7.55 (m, 2H), 7.54 – 7.43 (m, 4H), 7.43 – 7.36 (m, 2H), 7.32 – 7.24 (m, 4H), 7.22 – 7.14 (m, 1H), 6.76 – 6.54 (m, 2H), 4.15 – 3.92 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 173.0, 141.6, 137.4, 135.9, 134.0, 133.3, 130.8, 130.6, 130.4, 129.8, 129.5, 129.0, 128.6, 127.4, 127.1, 126.4, 126.2, 125.4, 123.7, 123.4, 38.8.

MS (70 eV): m/z (%) = 390 [M]⁺ (100), 245, 117, 91.

HRMS (ESI) calcd. for C₂₇H₂₃N₂O [M+H]: 391.1805, found: 391.1809.

(E)-N'-((E)-(9-ethyl-9H-carbazol-2-yl)methylene)-N,4-diphenylbut-3-enehydrazide (E12)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 47% yield (107.5 mg) based on reaction conditions C and 43% yield (98.3 mg) based on reaction conditions B.

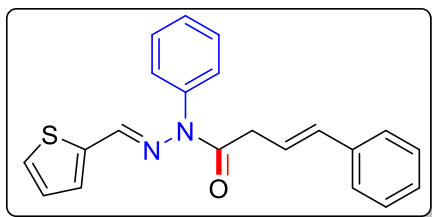
¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.15 (m, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.90 – 7.82 (m, 1H), 7.62 – 7.52 (m, 2H), 7.52 – 7.45 (m, 3H), 7.44 – 7.37 (m, 4H), 7.33 – 7.14 (m, 6H), 6.77 – 6.54 (m, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.12 – 3.95 (m, 2H), 1.48 – 1.36 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.8, 143.3, 141.0, 140.4, 137.5, 133.1, 130.2, 129.5, 129.2, 128.5, 127.3, 126.3, 125.4, 124.5, 123.8, 123.1, 122.9, 120.6, 119.5, 108.9, 38.9, 37.8, 13.9.

MS (70 eV): m/z (%) = 457 [M]⁺ (100), 312, 117, 91.

HRMS (ESI) calcd. for C₃₁H₂₈N₃O [M+H]: 458.2227, found: 458.2225.

(E)-N,4-diphenyl-N'-((E)-thiophen-2-ylmethylene)but-3-enehydrazide (E13)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 33% yield (57.1 mg) based on reaction conditions C and 30% yield (51.9 mg) based on reaction conditions B.

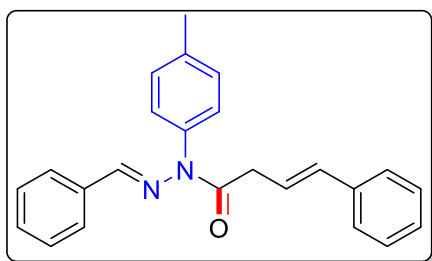
¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.51 (m, 2H), 7.51 – 7.45 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.36 (d, *J* = 5.2 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.24 – 7.15 (m, 3H), 7.07 – 7.03 (m, 1H), 7.03 – 6.97 (m, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.62 – 6.47 (m, 1H), 4.01 – 3.75 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.7, 139.7, 137.4, 136.2, 135.7, 133.3, 130.3, 129.7, 129.5, 129.2, 128.5, 127.8, 127.5, 127.3, 126.3, 123.3, 38.8.

MS (70 eV): *m/z* (%) = 346 [M]⁺ (100), 202, 186, 117.

HRMS (ESI) calcd. for C₂₁H₁₉N₂OS [M+H]: 347.1213, found: 347.1217.

(E)-N'-((E)-benzylidene)-4-phenyl-N-(p-tolyl)but-3-enehydrazide (E14)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 75% yield (132.8 mg) based on reaction conditions C and 73% yield (129.3 mg) based on reaction conditions B.

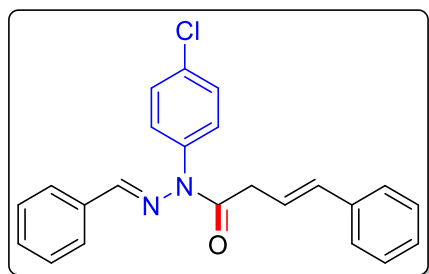
¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.54 (m, 2H), 7.43 – 7.25 (m, 10H), 7.24 – 7.16 (m, 1H), 7.09 – 7.00 (m, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.61 – 6.49 (m, 1H), 4.07 – 3.88 (m, 2H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 173.0, 141.7, 139.4, 137.4, 134.4, 133.1, 130.9, 129.9, 129.0, 128.8, 128.5, 127.3, 126.3, 123.5, 38.8, 21.4.

MS (70 eV): *m/z* (%) = 354 [M]⁺ (100), 250, 210, 106.

HRMS (ESI) calcd. for C₂₄H₂₃N₂O [M+H]: 355.1805, found: 355.1809.

(*E*)-*N'*-((*E*)-benzylidene)-*N*-(4-chlorophenyl)-4-phenylbut-3-enehydrazide (E15)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 61% yield (114.1 mg) based on reaction conditions C and 58% yield (108.5 mg) based on reaction conditions B.

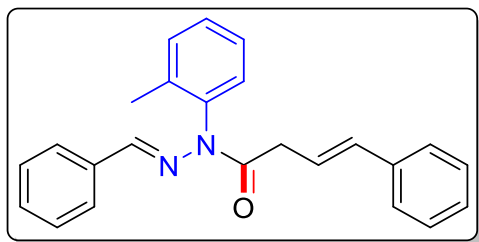
¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.57 (m, 2H), 7.56 – 7.50 (m, 2H), 7.44 – 7.36 (m, 5H), 7.34 – 7.25 (m, 3H), 7.24 – 7.18 (m, 1H), 7.17 – 7.10 (m, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.59 – 6.47 (m, 1H), 4.04 – 3.85 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.9, 142.0, 137.2, 135.4, 134.3, 134.0, 133.4, 130.7, 130.6, 130.2, 128.8, 128.5, 127.4, 127.2, 126.3, 123.0, 38.6.

MS (70 eV): *m/z* (%) = 374 [M]⁺ (100), 230, 194, 117.

HRMS (ESI) calcd. for C₂₃H₂₀ClN₂O [M+H]: 375.1259, found: 375.1258.

(*E*)-*N'*-((*E*)-benzylidene)-4-phenyl-*N*-(*o*-tolyl)but-3-enehydrazide (E16)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 70% yield (124.0 mg) based on reaction conditions C and 68% yield (120.4 mg) based on reaction conditions B.

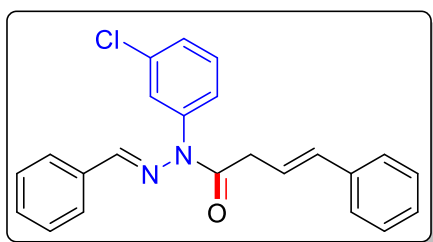
¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.49 (m, 2H), 7.33 – 7.23 (m, 8H), 7.23 – 7.18 (m, 2H), 7.17 – 7.07 (m, 1H), 7.05 – 6.99 (m, 2H), 6.61 (d, J = 16.0 Hz, 1H), 6.55 – 6.42 (m, 1H), 3.98 – 3.83 (m, 2H), 2.00 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 172.6, 141.1, 137.4, 136.9, 134.6, 134.4, 133.3, 131.5, 130.0, 129.8, 129.3, 128.8, 128.5, 127.8, 127.3, 126.3, 123.3, 38.7, 17.4.

MS (70 eV): m/z (%) = 354 [M]⁺ (100), 250, 210, 117.

HRMS (ESI) calcd. for C₂₄H₂₃N₂O [M+H]: 355.1805, found: 355.1805.

(E)-N'-((E)-benzylidene)-N-(3-chlorophenyl)-4-phenylbut-3-enehydrazide (E17)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 53% yield (99.1 mg) based on reaction conditions C and 52% yield (97.3 mg) based on reaction conditions B.

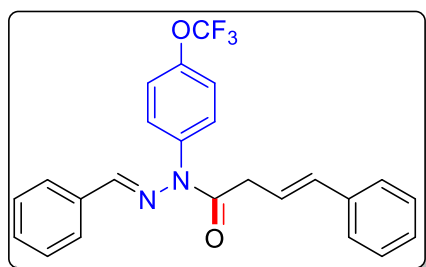
¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.49 (m, 2H), 7.44 – 7.34 (m, 2H), 7.33 – 7.26 (m, 5H), 7.24 – 7.17 (m, 3H), 7.15 – 7.08 (m, 2H), 7.03 – 6.98 (m, 1H), 6.57 (d, J = 16.0 Hz, 1H), 6.51 – 6.38 (m, 1H), 4.02 – 3.71 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 171.8, 141.1, 136.2, 136.0, 134.7, 132.9, 132.4, 130.1, 129.1, 128.7, 128.6, 127.8, 127.5, 126.6, 126.3, 126.2, 125.2, 121.9, 37.5.

MS (70 eV): m/z (%) = 374 $[\text{M}]^+$ (100), 230, 180, 117.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{20}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]$: 375.1259, found: 375.1259.

(E)-N'-((E)-benzylidene)-4-phenyl-N-(4-(trifluoromethoxy)phenyl)but-3-enehydrazide (E18)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 58% yield (123.0 mg) based on reaction conditions C and 56% yield (118.8 mg) based on reaction conditions B.

^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.58 (m, 2H), 7.47 – 7.36 (m, 7H), 7.35 – 7.17 (m, 6H), 6.67 (d, J = 16.0 Hz, 1H), 6.59 – 6.47 (m, 1H), 4.06 – 3.80 (m, 2H).

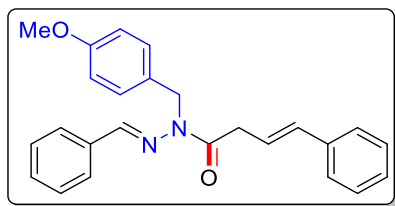
^{13}C NMR (101 MHz, CDCl_3) δ = 173.0, 149.5, 142.0, 137.2, 134.1, 134.0, 133.4, 131.0, 130.2, 128.8, 128.5, 127.4, 127.3, 126.3, 122.9, 122.5, 120.4 (q, J = 517.12, 258.56 Hz), 38.6.

^{19}F NMR (376 MHz, CDCl_3) δ = -57.8.

MS (70 eV): m/z (%) = 424 $[\text{M}]^+$ (100), 280, 176, 117.

HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{20}\text{F}_3\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]$: 425.1471, found: 425.1469.

(E)-N'-((E)-benzylidene)-N-(4-methoxybenzyl)-4-phenylbut-3-enehydrazide (E19)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give a white solid in 86% yield (165.2 mg) based on reaction conditions C and 85% yield (163.3 mg) based on reaction conditions B.

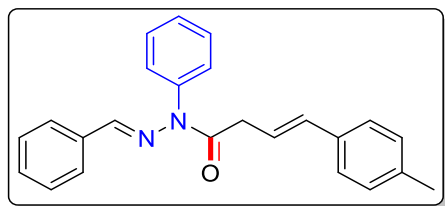
¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 7.63 – 7.56 (m, 2H), 7.42 – 7.31 (m, 5H), 7.31 – 7.23 (m, 2H), 7.22 – 7.14 (m, 1H), 7.14 – 7.09 (m, 2H), 6.84 – 6.79 (m, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.59 – 6.49 (m, 1H), 5.18 (s, 2H), 3.92 (d, *J* = 6.8 Hz, 2H), 3.71 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 173.4, 158.9, 140.1, 137.4, 134.7, 133.2, 129.8, 128.8, 128.6, 127.9, 127.4, 127.1, 127.0, 126.4, 123.6, 114.4, 55.3, 44.2, 38.5.

MS (70 eV): *m/z* (%) = 384 [M]⁺ (100), 280, 239, 117.

HRMS (ESI) calcd. for C₂₅H₂₅N₂O₂ [M+H]: 385.1911, found: 385.1911.

(*E*)-*N'*-((*E*)-benzylidene)-*N*-phenyl-4-(*p*-tolyl)but-3-enehydrazide (E20)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 77% yield (136.4 mg) based on reaction conditions C and 77% yield (136.4 mg) based on reaction conditions B.

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.58 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.32 – 7.23 (m, 3H), 7.22 – 7.13 (m, 2H), 7.10 (d,

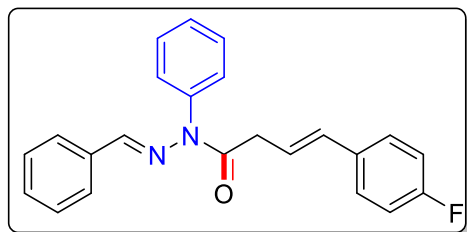
$J = 8.0$ Hz, 2H), 6.63 (d, $J = 16.0$ Hz, 1H), 6.56 – 6.44 (m, 1H), 4.03 – 3.82 (m, 2H), 2.31 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 173.1, 141.7, 137.1, 135.9, 134.6, 134.3, 133.1, 130.3, 130.0, 129.4, 129.3, 129.2, 128.8, 127.2, 126.2, 122.3, 38.7, 21.2$.

MS (70 eV): m/z (%) = 354 $[\text{M}]^+$ (100), 250, 196, 131.

HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}$ $[\text{M}+\text{H}]$: 355.1805, found: 355.1807.

(*E*)-*N'*-((*E*)-benzylidene)-4-(4-fluorophenyl)-*N*-phenylbut-3-enehydrazide (E21)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 63% yield (112.8 mg) based on reaction conditions C and 62% yield (111.0 mg) based on reaction conditions B.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.58 (m, 2H), 7.57 – 7.51 (m, 2H), 7.50 – 7.43 (m, 1H), 7.42 – 7.30 (m, 5H), 7.27 (s, 1H), 7.23 – 7.14 (m, 2H), 7.02 – 6.91 (m, 2H), 6.61 (d, $J = 16.0$ Hz, 1H), 6.52 – 6.38 (m, 1H), 4.08 – 3.82 (m, 2H).

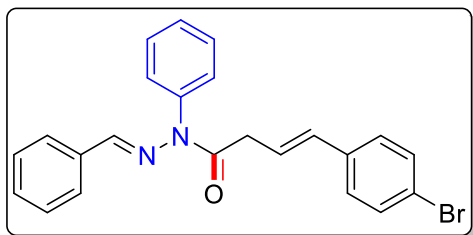
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 172.9, 162.2$ (d, $J = 247.45$ Hz), 141.9, 135.8, 134.3, 133.6, 132.0, 130.3, 130.0, 129.4, 129.3, 128.8, 127.8 (d, $J = 7.07$ Hz), 127.2, 123.1, 115.4 (d, $J = 22.22$ Hz), 38.6.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) $\delta = -114.9$.

MS (70 eV): m/z (%) = 358 $[\text{M}]^+$ (100), 254, 196, 135.

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{20}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]$: 359.1554, found: 359.1554.

(*E*)-*N'*-((*E*)-benzylidene)-4-(4-bromophenyl)-*N*-phenylbut-3-enehydrazide (E22)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 53% yield (110.8 mg) based on reaction conditions C and 51% yield (106.6 mg) based on reaction conditions B.

¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.57 (m, 2H), 7.57 – 7.51 (m, 2H), 7.50 – 7.44 (m, 1H), 7.44 – 7.33 (m, 5H), 7.29 – 7.21 (m, 3H), 7.20 – 7.15 (m, 2H), 6.63 – 6.49 (m, 2H), 4.08 – 3.82 (m, 2H).

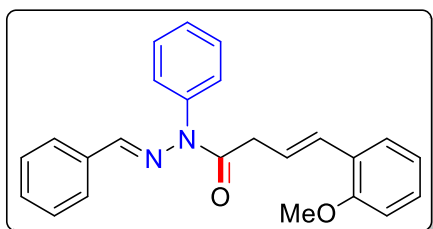
¹³C NMR (101 MHz, CDCl₃) δ = 172.7, 141.9, 136.3, 135.8, 134.2, 132.0, 131.6, 130.3, 130.0, 129.4, 129.2, 128.8, 127.9, 127.2, 124.3, 121.0, 38.6.

MS (70 eV): m/z (%) = 418 [M]⁺ (100), 293, 196, 104.

HRMS (ESI) calcd. for C₂₃H₂₀BrN₂O [M+H]: 419.0754, found: 419.0750.

(E)-N'-((E)-benzylidene)-4-(2-methoxyphenyl)-N-phenylbut-3-enehydrazide

(E23)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 66% yield (122.2 mg) based on reaction conditions C and 65% yield (120.3 mg) based on reaction conditions B.

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.58 (m, 2H), 7.57 – 7.51 (m, 2H), 7.51 – 7.41 (m, 2H), 7.40 – 7.30 (m, 3H), 7.25 (s, 1H), 7.23 – 7.14 (m, 3H), 7.00 (d, *J* = 16.0 Hz,

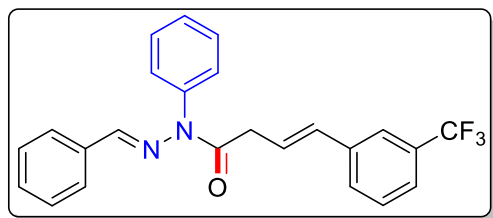
1H), 6.92 – 6.86 (m, 1H), 6.85 – 6.81 (m, 1H), 6.52 – 6.50 (m, 1H), 4.05 – 3.94 (m, 2H), 3.79 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 173.1, 156.6, 134.4, 130.2, 129.9, 129.3, 128.8, 128.4, 128.0, 127.3, 126.9, 126.5, 124.0, 120.7, 110.8, 55.5, 39.2.

MS (70 eV): m/z (%) = 370 [M]⁺ (100), 237, 196, 104.

HRMS (ESI) calcd. for C₂₄H₂₃N₂O₂ [M+H]: 371.1754, found: 371.1755.

(E)-N'-((E)-benzylidene)-N-phenyl-4-(3-(trifluoromethyl)phenyl)but-3-enehydrazide (E24)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 58% yield (118.4 mg) based on reaction conditions C and 56% yield (114.3 mg) based on reaction conditions B.

¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.53 (m, 6H), 7.52 – 7.44 (m, 2H), 7.43 – 7.35 (m, 4H), 7.29 (s, 1H), 7.23 – 7.16 (m, 2H), 6.75 – 6.57 (m, 2H), 4.16 – 3.84 (m, 2H).

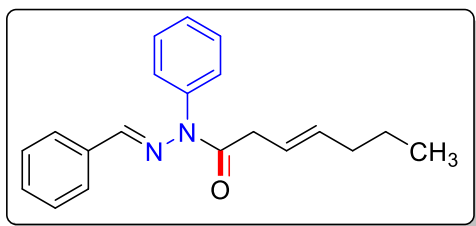
¹³C NMR (101 MHz, CDCl₃) δ = 172.6, 142.1, 138.1, 134.2, 131.8, 130.9 (q, *J* = 64.64, 32.32 Hz), 130.3, 130.1, 129.4, 129.2, 128.9, 128.8, 127.2, 125.6, 124.2 (q, *J* = 547.42, 273.71 Hz), 123.8 (q, *J* = 7.07, 3.03 Hz), 123.0 (q, *J* = 7.07, 4.04 Hz), 38.4.

¹⁹F NMR (376 MHz, CDCl₃) δ = -62.7.

MS (70 eV): m/z (%) = 408 [M]⁺ (100), 248, 196, 165.

HRMS (ESI) calcd. for C₂₄H₂₀F₃N₂O [M+H]: 409.1522, found: 409.1522.

(E)-N'-((E)-benzylidene)-N-phenylhept-3-enehydrazide (E25)



The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) to give the light-yellow oil in 36% yield (58.2 mg) based on reaction conditions C and 35% yield (53.6 mg) based on reaction conditions B.

¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.51 (m, 4H), 7.50 – 7.44 (m, 1H), 7.41 – 7.31 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.12 (m, 2H), 5.85 – 5.55 (m, 2H), 3.90 – 3.66 (m, 2H), 2.25 – 1.98 (m, 2H), 1.52 – 1.33 (m, 2H), 1.02 – 0.84 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 173.7, 141.4, 136.0, 134.4, 132.9, 130.2, 129.8, 129.3, 128.7, 127.2, 123.0, 122.3, 38.4, 34.8, 22.7, 22.5, 13.9, 13.7.

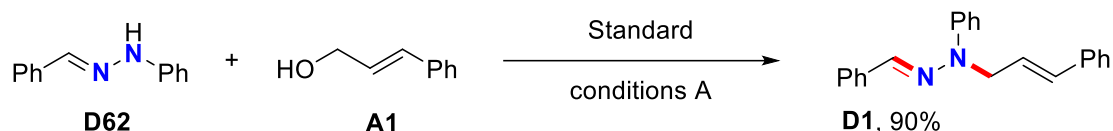
MS (70 eV): *m/z* (%) = 306 [M]⁺ (100), 277, 196, 104.

HRMS (ESI) calcd. for C₂₀H₂₃N₂O [M+H]: 307.1805, found: 307.1805.

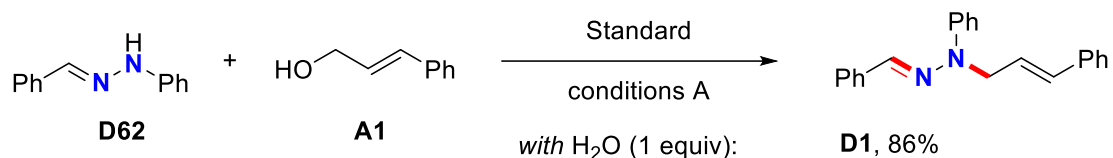
6. Mechanism investigations

6.1 Control experiments for tandem allylation reaction

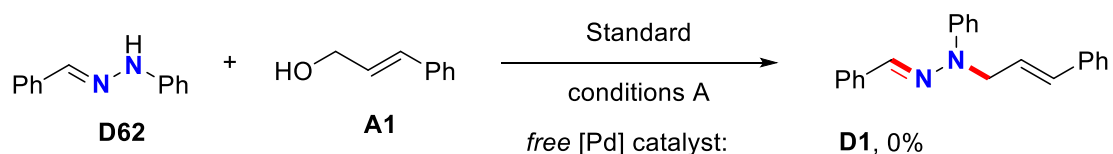
6.1.1 Control experiments with D62



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D62** (0.5 mmol), **A1** (0.75 mmol) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 90% yield.

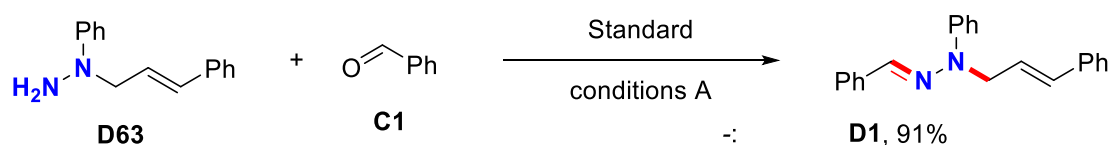


Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D62** (0.5 mmol), **A1** (0.75 mmol), H₂O (0.5 mmol) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 86% yield.

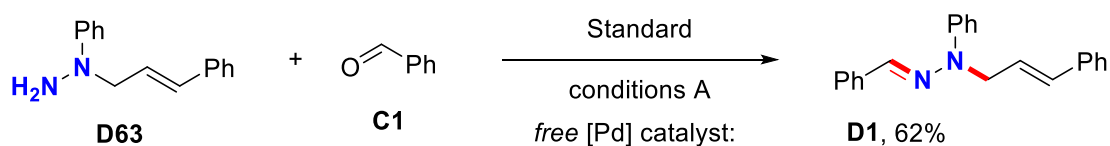


Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D62** (0.5 mmol), **A1** (0.75 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 0% yield and **D62** was recovered in 95% yield.

6.1.2 Control experiments with D63



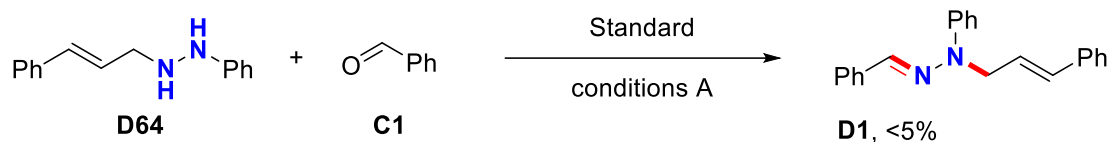
Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D63** (0.5 mmol), **C1** (0.7 mmol) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 91% yield.



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D63** (0.5 mmol) and **C1** (0.7 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography

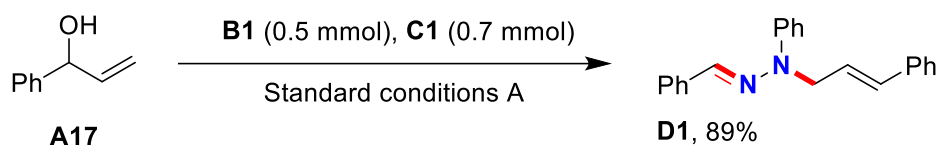
(petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 62% yield.

6.1.3 Control experiments with D64

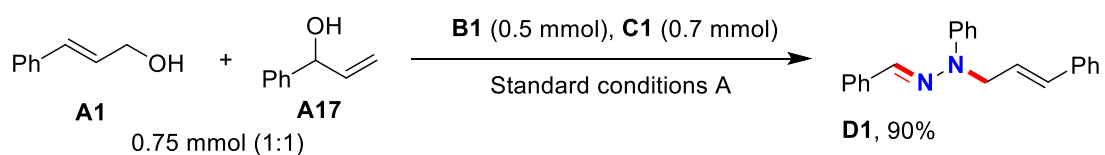


Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D64** (0.5 mmol), **C1** (0.7 mmol) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in <5% yield.

6.1.4 Control experiments with A17



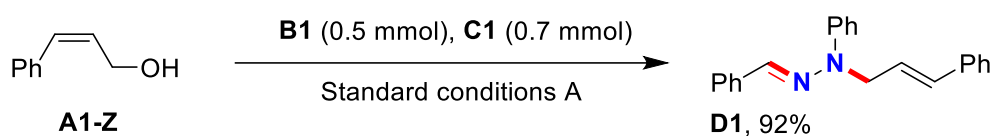
Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **A17** (0.75 mmol), **B1** (0.5 mmol), **C1** (0.7 mmol) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 89% yield.



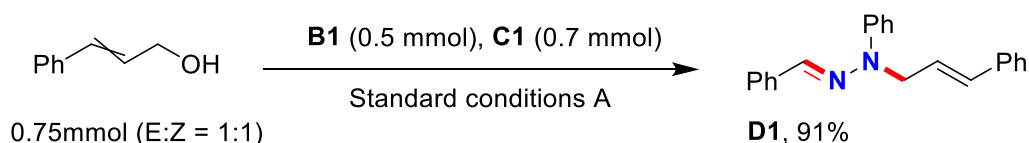
Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was

charged with a magnetic stirring bar, toluene (2.0 mL), **A1+A17** (0.75 mmol, **A1:A17** = 1:1), **B1** (0.5 mmol), **C1** (0.7 mmol) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 90% yield.

6.1.5 Control experiments with **A1-Z**



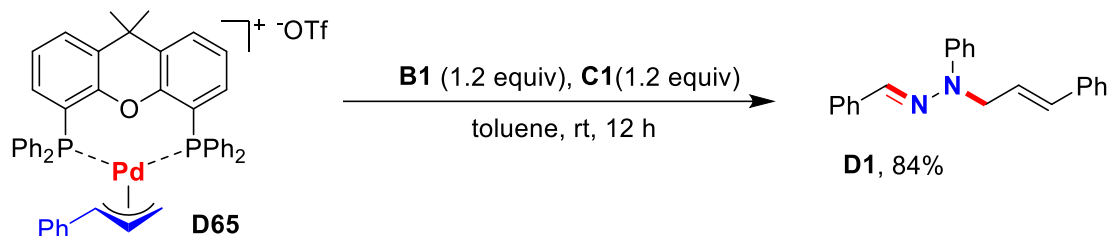
Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **A1-Z** (0.75 mmol), **B1** (0.5 mmol), **C1** (0.7 mmol) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 92% yield.



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **A1+A1-Z** (0.75 mmol, **A1:A1-Z** = 1:1), **B1** (0.5 mmol), **C1** (0.7 mmol) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under

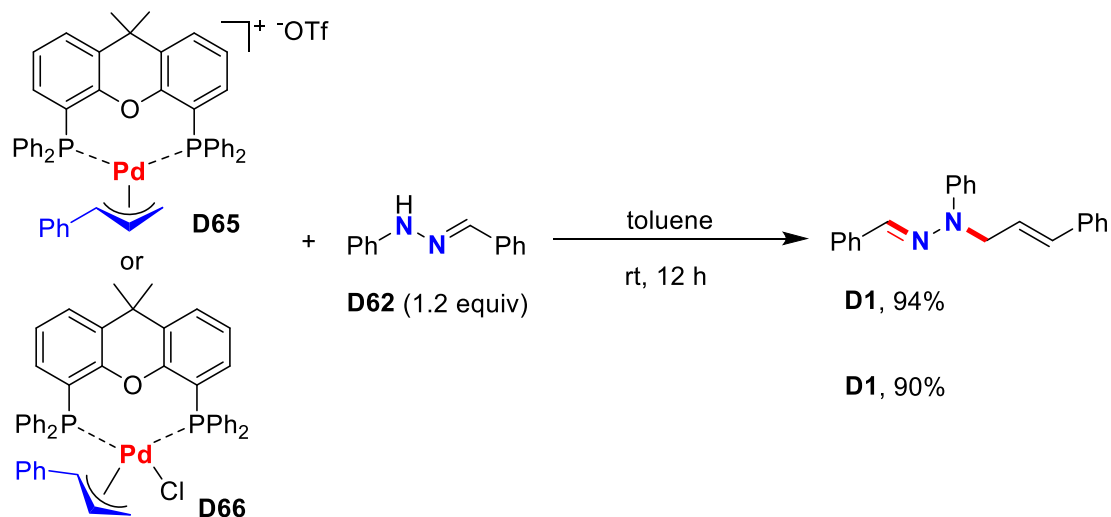
reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 91% yield.

6.1.6 Control experiments with D65



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D65** (0.5 mmol), **B1** (0.6 mmol) and **C1** (0.6 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at room temperature for 12 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 84% yield.

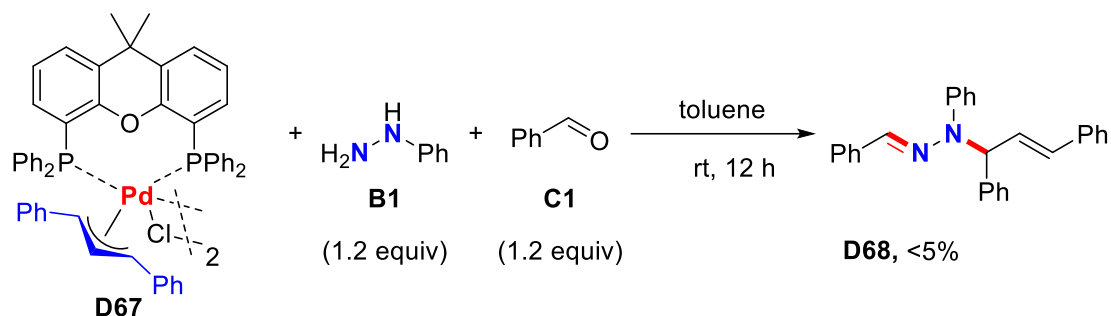
6.1.7 Control experiments with D65/D66 and D62



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D65/D66** (0.5 mmol) and **D62** (0.6 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at room temperature for 12 hours. After the reaction was finished,

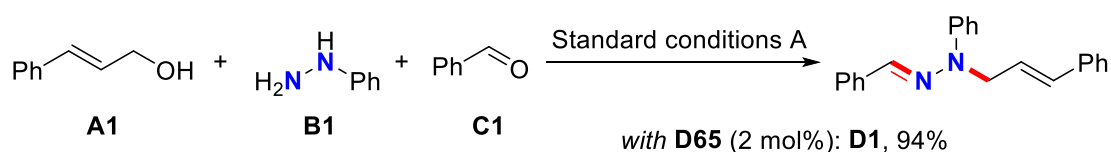
the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 94%/90% yield.

6.1.8 Control experiments with **D67**



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **D67** (0.5 mmol), **B1** (0.6 mmol), **C1** (0.6 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at room temperature for 12 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D68** in <5% yield.

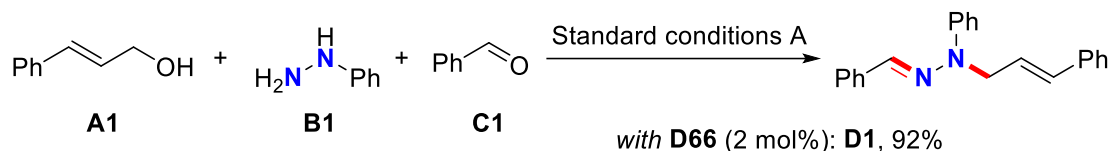
6.1.9 Control experiments with **D65**, **A1**, **B1** and **C1**



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **A1** (0.75 mmol), **B1** (0.5 mmol), **C1** (0.7 mmol) and **D65** (0.01 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash

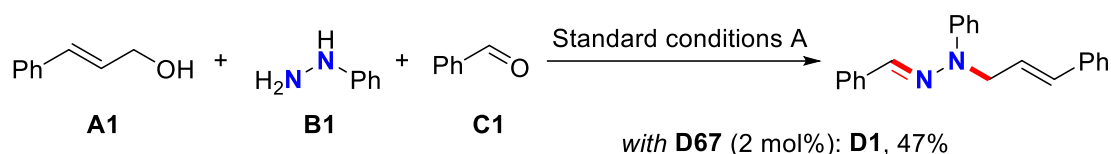
column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 94% yield.

6.1.10 Control experiments with **D66**, **A1**, **B1** and **C1**



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **A1** (0.75 mmol), **B1** (0.5 mmol), **C1** (0.7 mmol) and **D66** (0.01 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 92% yield.

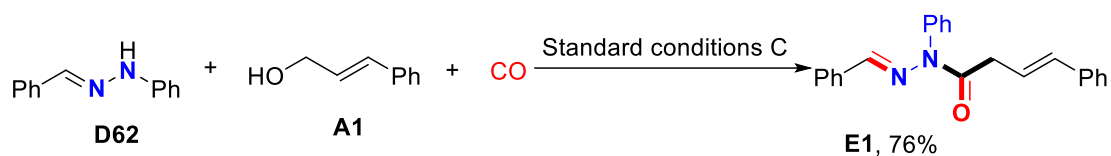
6.1.11 Control experiments with **D67**, **A1**, **B1** and **C1**



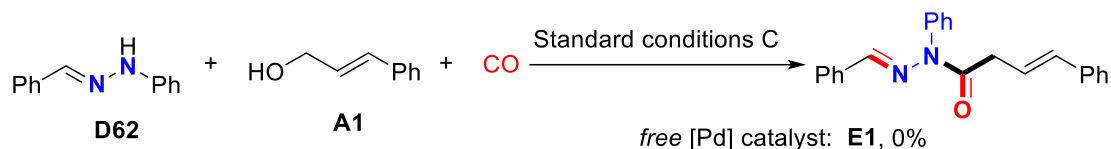
Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, toluene (2.0 mL), **A1** (0.75 mmol), **B1** (0.5 mmol), **C1** (0.7 mmol) and **D67** (0.01 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 60 °C for 4 hours. After the reaction was finished, the reaction was analyzed by TLC to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D1** in 47% yield.

6.2 Control experiments for carbonylation reaction

6.2.1 Control experiments with D62



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **D62** (0.5 mmol), toluene (2.0 mL), PdCl₂(Xantphos) (0.01 mmol, 2 mol%) and **A1** (0.75 mmol). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC to monitor product formation. The result showed that desired product **E1** was generated in 76% yield.

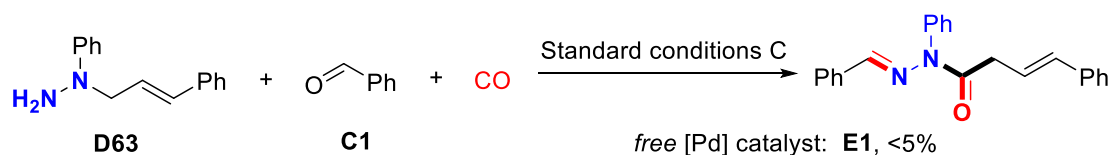


Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **D62** (0.5 mmol), toluene (2.0 mL) and **A1** (0.75 mmol). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC to monitor product formation. The result showed that desired product **E1** was generated in 0% yield.

6.2.2 Control experiments with D63

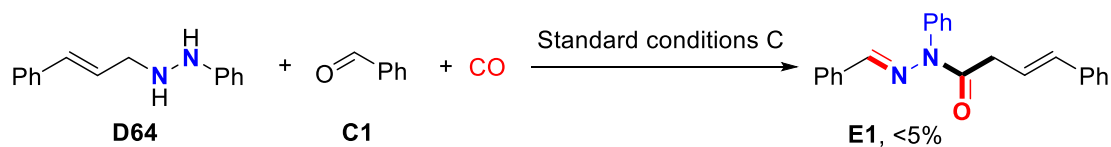


Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **D63** (0.5 mmol), **C1** (0.75 mmol), toluene (2.0 mL) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC to monitor product formation. The result showed that desired product **E1** was generated in 71% yield.



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **D63** (0.5 mmol), **C1** (0.75 mmol) and toluene (2.0 mL). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC to monitor product formation. The result showed that desired product **E1** was generated in <5% yield.

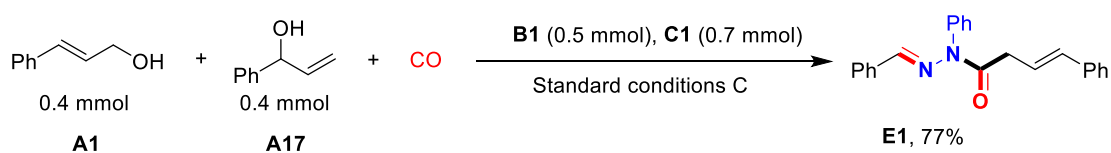
6.2.3 Control experiments with D64



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **D64** (0.5 mmol), **C1** (0.75 mmol), toluene (2.0 mL) and

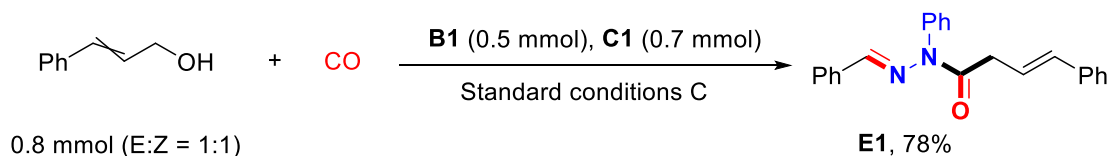
PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC to monitor product formation. The result showed that desired product **E1** was generated in <5% yield.

6.2.4 Control experiments with A1 and A17



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **B1** (0.5 mmol), **C1** (0.7 mmol), **A1** (0.4 mmol), **A17** (0.4 mmol), toluene (2.0 mL) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC to monitor product formation. The result showed that desired product **E1** was generated in 77% yield.

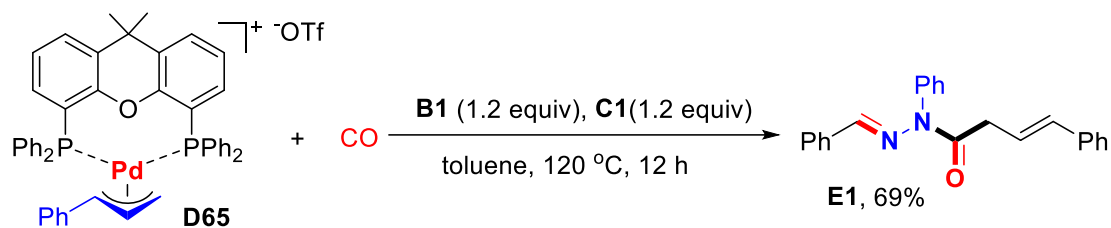
6.2.5 Control experiments with A1 and A17



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **B1** (0.5 mmol), **C1** (0.7 mmol), **A1** (0.4 mmol), **A1-Z** (0.4 mmol), toluene (2.0 mL) and PdCl₂(Xantphos) (0.01 mmol, 2 mol%). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave

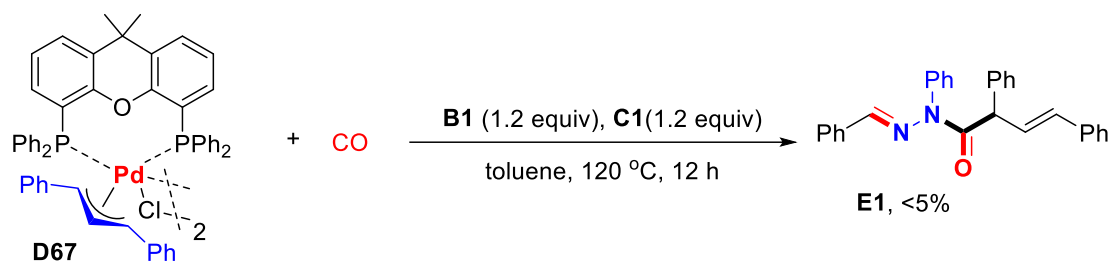
was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. The result showed that desired product **E1** was generated in 78% yield.

6.2.6 Control experiments with D65



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **D65** (0.5 mmol), **B1** (0.6 mmol), **C1** (0.6 mmol) and toluene (2.0 mL). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC to monitor product formation. The result showed that desired product **E1** was generated in 69% yield.

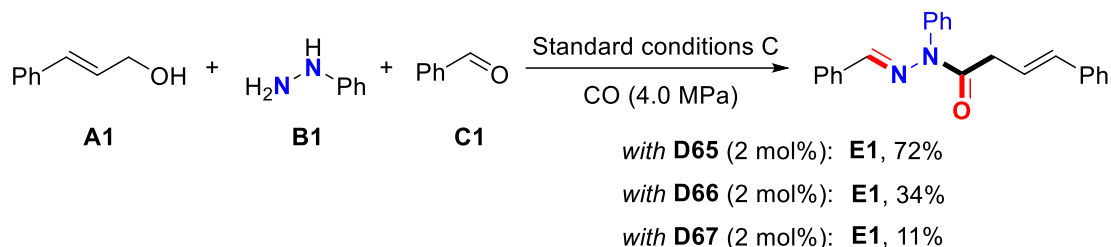
6.2.7 Control experiments with D67



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **D67** (0.5 mmol), **B1** (0.6 mmol), **C1** (0.6 mmol) and toluene (2.0 mL). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC

to monitor product formation. The result showed that desired product **E1** was generated in <5% yield.

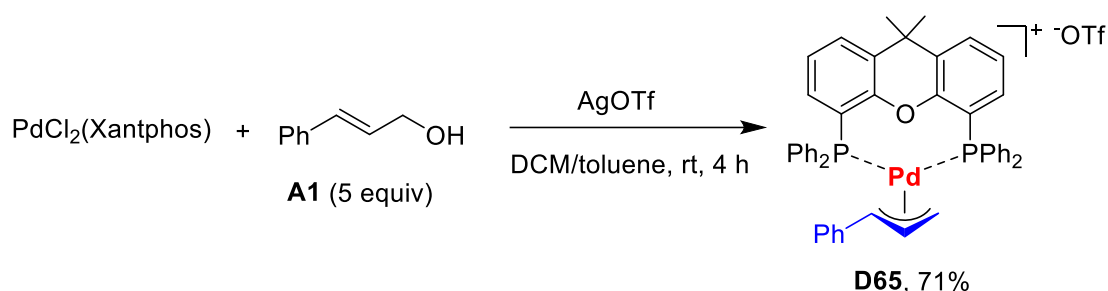
6.2.8 Control experiments with D65, D66 and D67



Using a nitrogen-filled glove box, an oven-dried glass bottle was charged with a magnetic stirring bar, **B1** (0.5 mmol), **C1** (0.7 mmol), **A1** (0.75 mmol), toluene (2.0 mL) and **D65/D66/D67**(0.01 mmol, 2 mol%). Then the glass bottle was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with CO (4.0 MPa) and immersed into a pre-heated metal bath (120 °C) for 12 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released. Then a small aliquot of the organic phase was analyzed by GC to monitor product formation. The result showed that desired product **E1** was generated in 72%, 34% or 11% yield.

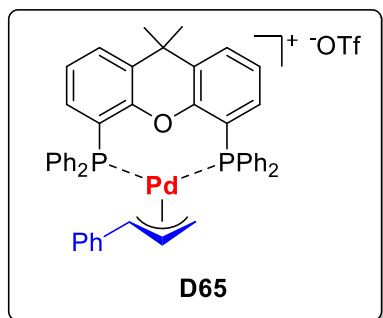
6.3 Synthesis of allyl metalated palladium complexes

6.3.1 Synthesis of D65



Using a nitrogen-filled glove box, an oven-dried pressure tube was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), AgOTf (0.42 mmol), **A1** (1 mmol) and DCM/Toluene. Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at room temperature for 4 hours. After the reaction was

finished, recrystallized in the DCM/Toluene under argon gave the ruby red clear crystal crystals **D65** in 71% yield.



Elemental Analysis calcd for $C_{49}H_{44}F_3O_4P_2PdS$: C, 61.67; H, 4.65; F, 5.97; O, 6.71; P, 6.49; Pd, 11.15; S, 3.36, found: C, 61.61; H, 4.60; S, 3.39.

HRMS (ESI): calcd. for $C_{48}H_{43}OP_2Pd [D65-OTf]^+$: 803.1824, found: 803.1822.

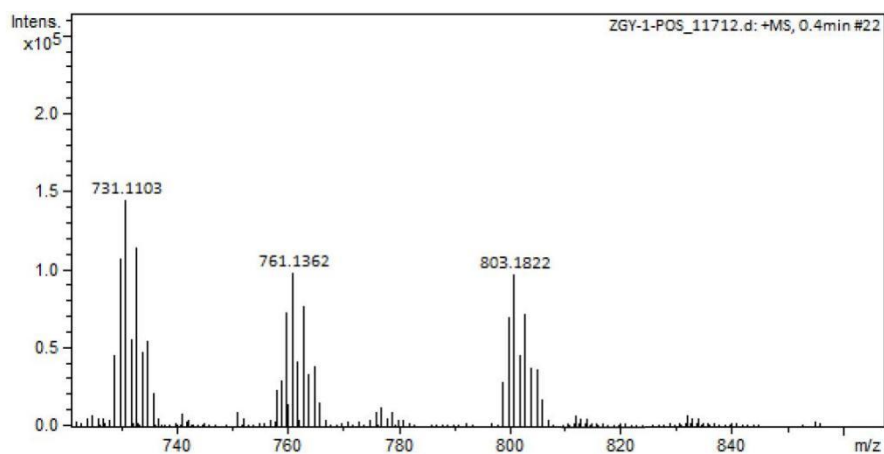


Figure S5 HRMS of D65-OTf

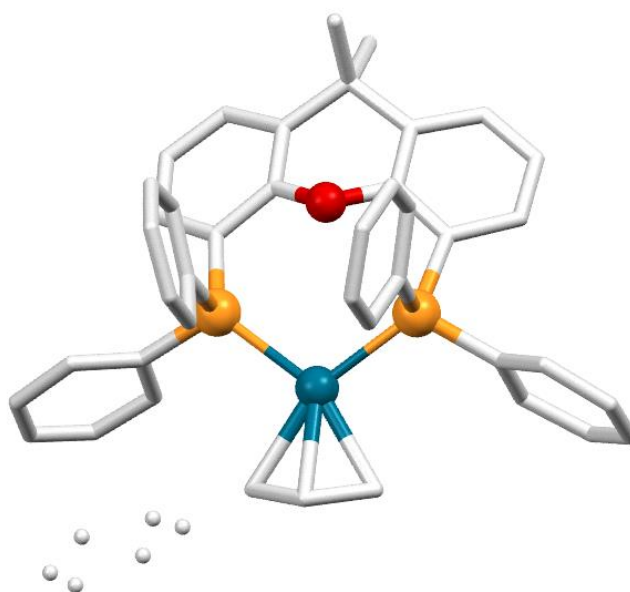
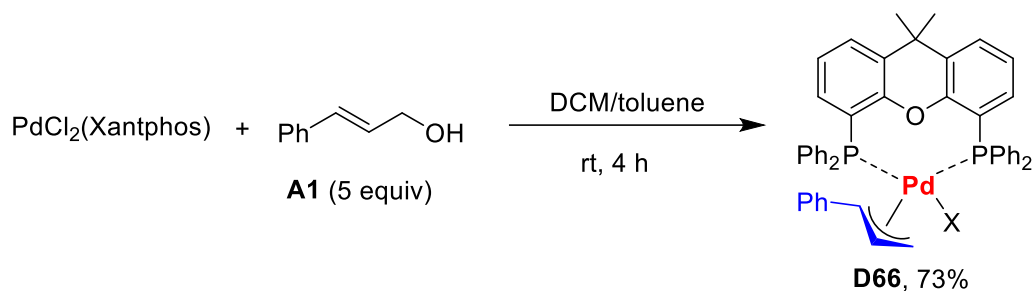
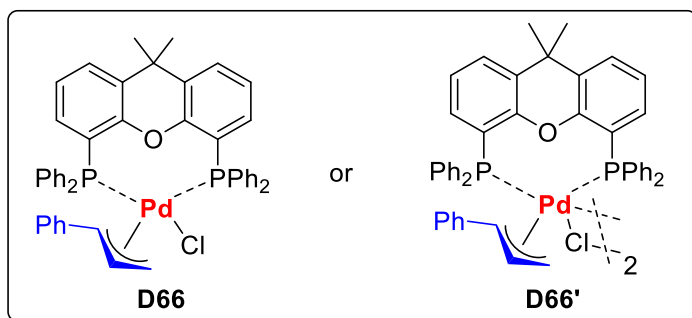


Figure S6 X-ray of D65 (CCDC 2249900)

6.3.2 Synthesis of D66



Using a nitrogen-filled glove box, an oven-dried pressure tube was charged with a magnetic stirring bar, $\text{PdCl}_2(\text{Xantphos})$ (0.2 mmol), **A1** (1 mmol) and DCM/Toluene. Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at room temperature for 4 hours. After the reaction was finished, recrystallized in the DCM/Toluene under argon gave the ruby red clear crystal crystals **D66** in 73% yield.



Elemental Analysis calcd for $\text{C}_{48}\text{H}_{43}\text{ClOP}_2\text{Pd}$: C, 68.66; H, 5.16; Cl, 4.22; O, 1.91; P, 7.38; Pd, 12.67, found: C, 68.69; H, 5.12.

HRMS (ESI): calcd. for $\text{C}_{48}\text{H}_{43}\text{OP}_2\text{Pd} [\text{D66-Cl}]^+$: 803.1824, found: 803.1817.

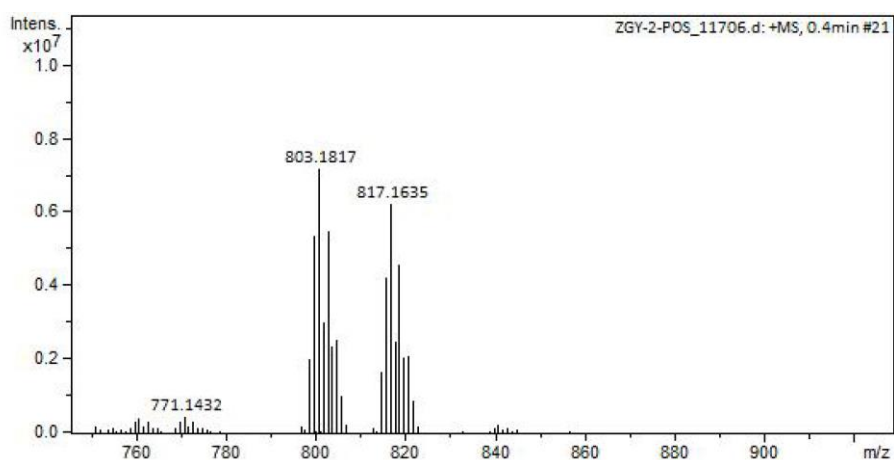
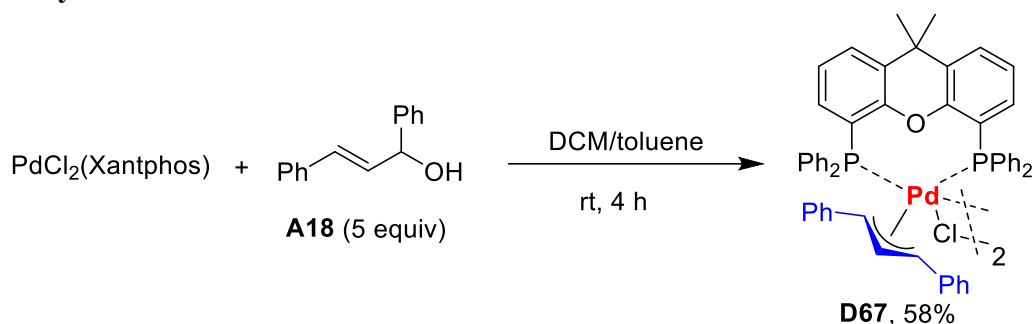
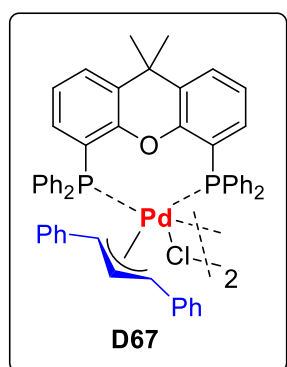


Figure S7 HRMS of D67

6.3.3 Synthesis of D67



Using a nitrogen-filled glove box, an oven-dried pressure tube was charged with a magnetic stirring bar, $\text{PdCl}_2(\text{Xantphos})$ (0.2 mmol), **A18** (1 mmol) and DCM/Toluene. Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at room temperature for 4 hours. After the reaction was finished, recrystallized in the DCM/Toluene under argon gave the ruby red clear crystal crystals **D67** in 58% yield.



Elemental Analysis calcd for $\text{C}_{54}\text{H}_{47}\text{ClOP}_2\text{Pd}$: C, 70.82; H, 5.17; Cl, 3.87; O, 1.75; P, 6.76; Pd, 11.62; found: C, 70.87; H, 5.14.

HRMS (ESI): calcd. for $\text{C}_{54}\text{H}_{47}\text{OP}_2\text{Pd} [\text{D67-Cl}]^+$: 879.2137, found: 879.2139.

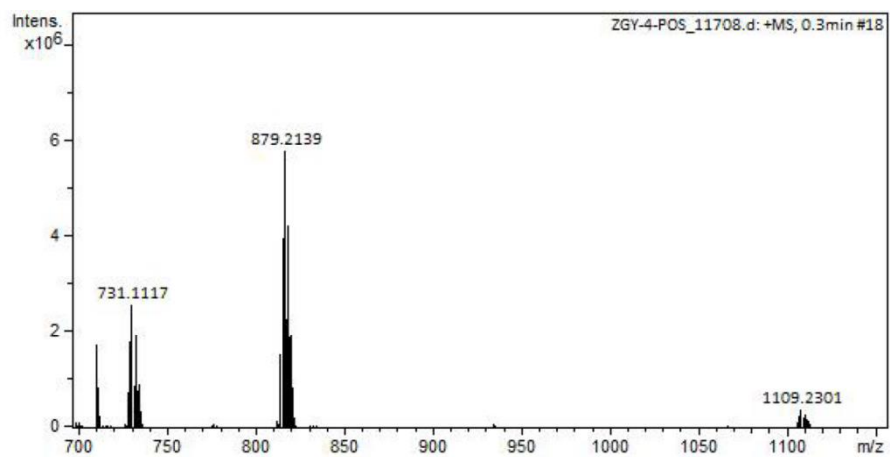


Figure S8 HRMS of D67

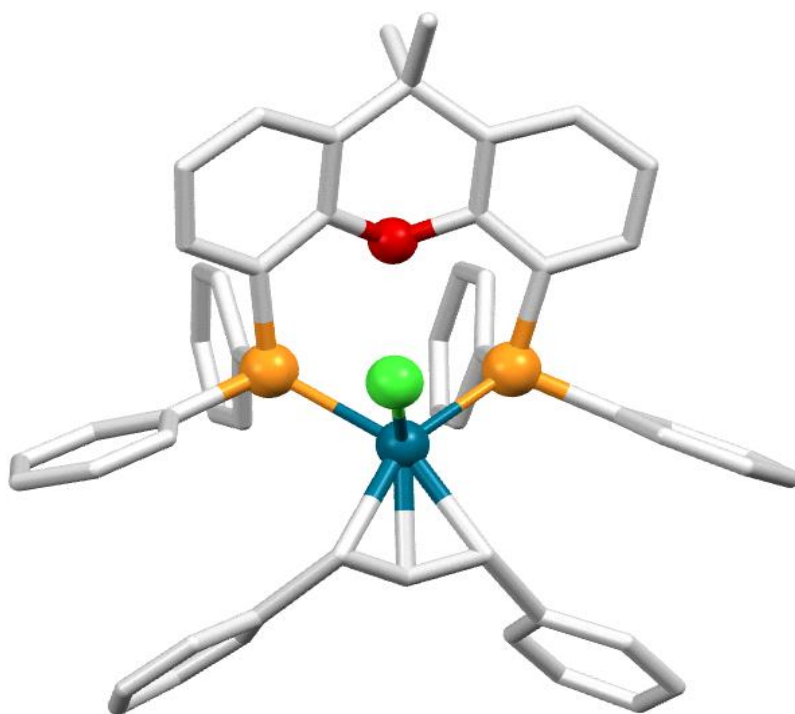


Figure S9 X-ray of D67 (CCDC 2249901)

6.4 Time conversion plot experiments on standard condition C

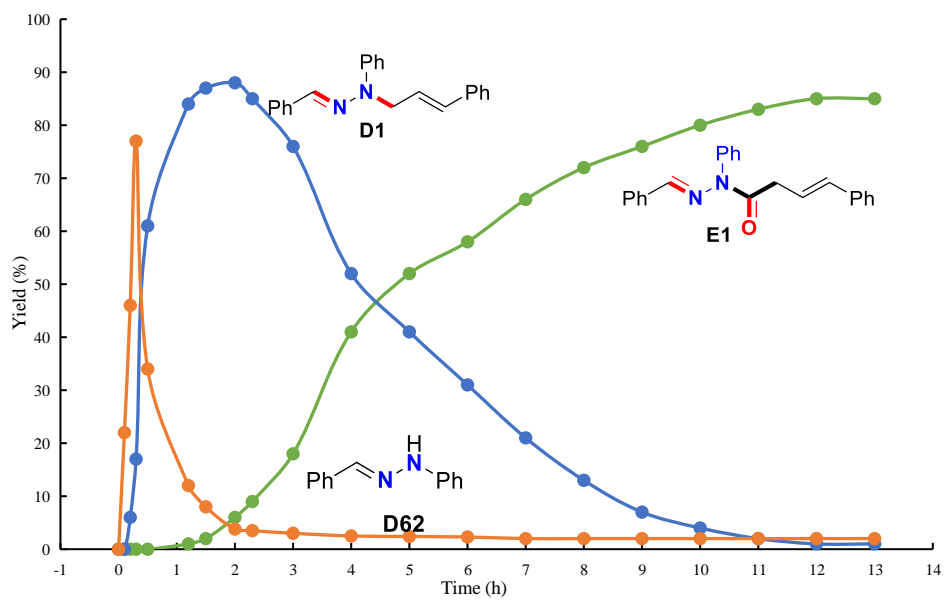
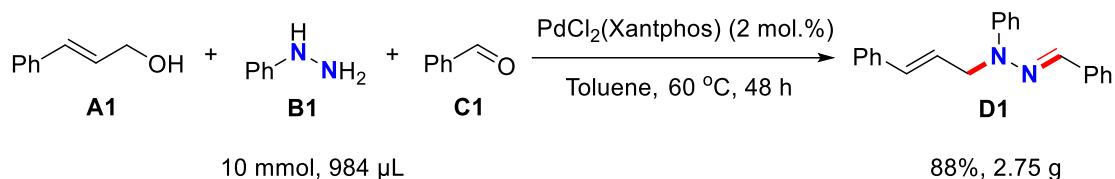


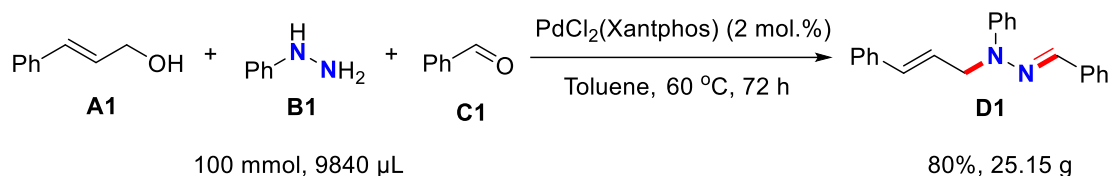
Figure S10 Time conversion plot

7. Gram-Scale Synthesis

7.1 Gram-Scale Synthesis of D1

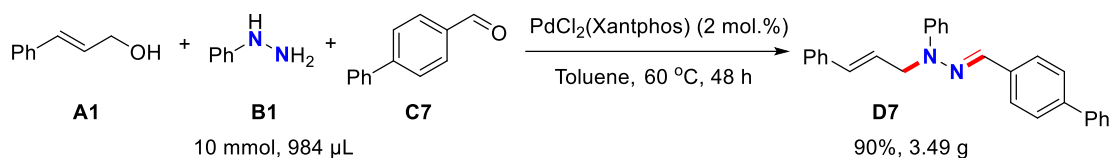


Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, toluene (30 mL), **C1** (14 mmol), **B1** (10 mmol), PdCl₂(Xantphos) (0.2 mmol) and **A1** (15 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D1** 2.75 g, the yield is 88%.



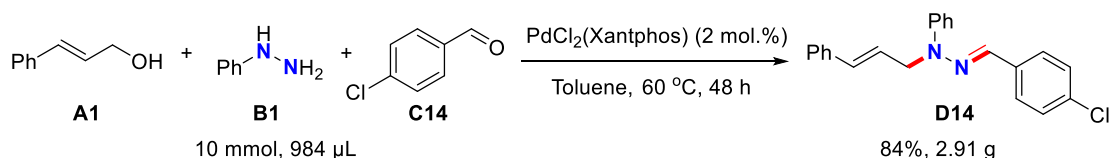
Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, toluene (50 mL), **C1** (140 mmol), **B1** (100 mmol), PdCl₂(Xantphos) (2 mmol) and **A1** (150 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 72 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D1** 25.15 g, the yield is 80%.

7.2 Gram-Scale Synthesis of D4



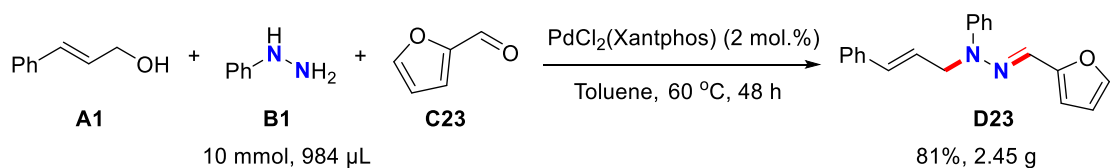
Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), toluene (30 mL), **C4** (14 mmol), **B1** (10 mmol) and **A1** (15 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D4** 3.49 g, the yield is 90%.

7.3 Gram-Scale Synthesis of D7



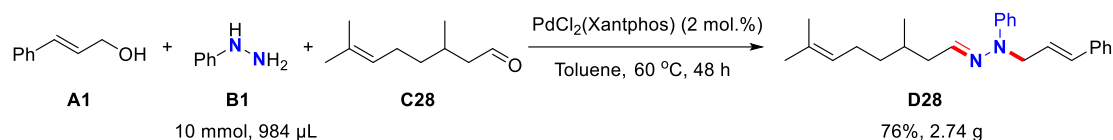
Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), toluene (30 mL), **C7** (14 mmol), **B1** (10 mmol) and **A1** (15 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D7** 2.91 g, the yield is 84%.

7.4 Gram-Scale Synthesis of D23



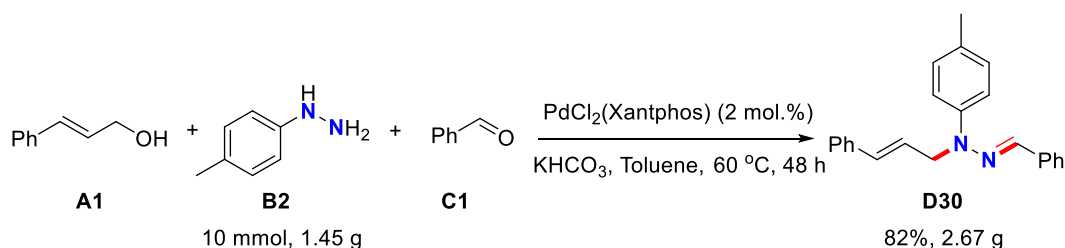
Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), toluene (30 mL), **C23** (14 mmol), **B1** (10 mmol) and **A1** (15 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D23** 2.45 g, the yield is 81%.

7.5 Gram-Scale Synthesis of D28



Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), toluene (30 mL), **C28** (14 mmol), **B1** (10 mmol) and **A1** (15 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D28** 2.74 g, the yield is 76%.

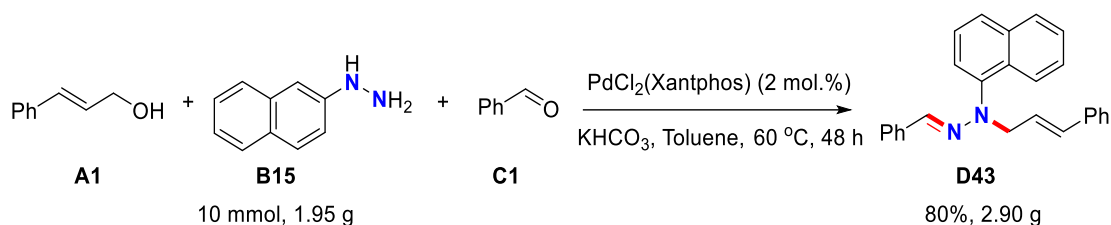
7.6 Gram-Scale Synthesis of D30



Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, **B2** (10 mmol), KHCO₃ (10 mmol) and toluene

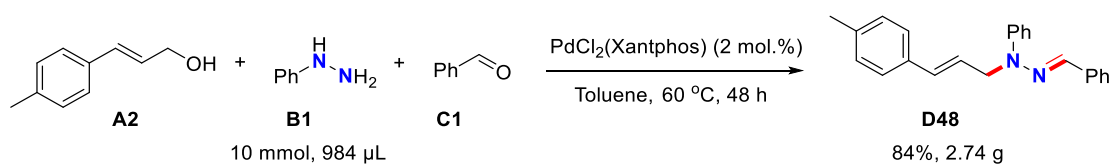
(30 mL). After the reaction mixture was stirred 15 min at room temperature, PdCl₂(Xantphos) (0.2 mmol), **C1** (14 mmol) and **A1** (15 mmol) were added in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D30** 2.67 g, the yield is 82%.

7.7 Gram-Scale Synthesis of D43



Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, **B15** (10 mmol), KHCO₃ (10 mmol) and toluene (30 mL). After the reaction mixture was stirred 15 min at room temperature, PdCl₂(Xantphos) (0.2 mmol), **C1** (14 mmol) and **A1** (15 mmol) were added in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D43** 2.90 g, the yield is 80%.

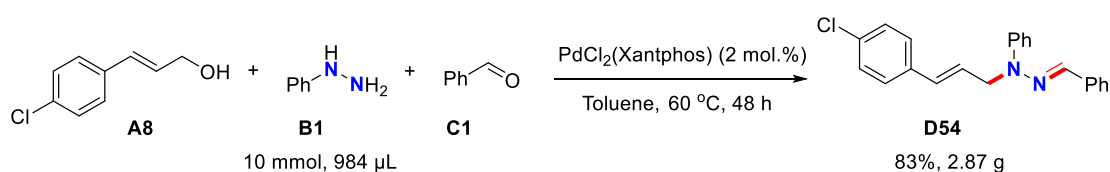
7.8 Gram-Scale Synthesis of D48



Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), toluene (30 mL),

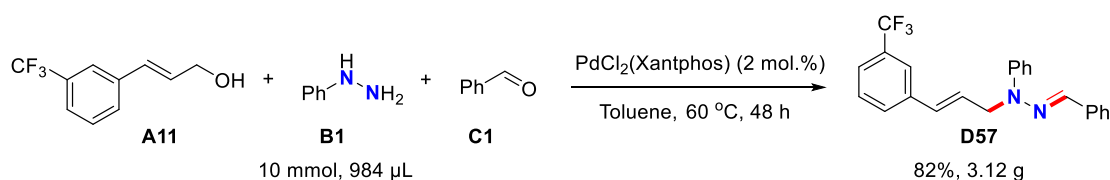
C1 (14 mmol), **B1** (10 mmol) and **A2** (15 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D48** 2.74 g, the yield is 84%.

7.9 Gram-Scale Synthesis of D54



Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), toluene (30 mL), **C1** (14 mmol), **B1** (10 mmol) and **A8** (15 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction mixture was stirred 24 hours at 48 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D54** 2.87 g, the yield is 83%.

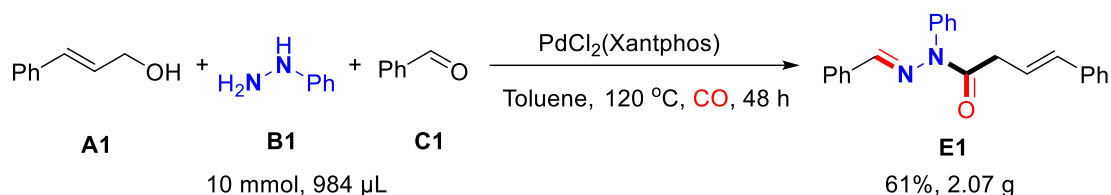
7.10 Gram-Scale Synthesis of D57



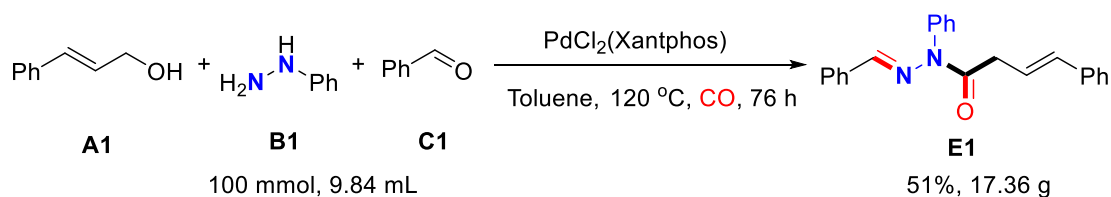
Using a nitrogen-filled glove box, an oven-dried Schlenk Flask (250 mL volume) was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), toluene (30 mL), **C1** (14 mmol), **B1** (10 mmol) and **A11** (15 mmol) in sequence. Then the Schlenk Flask was closed tightly with a rubber stopper, removed from the glove box. Then the reaction

mixture was stirred 48 hours at 60 °C under N₂ atmosphere in a metal bath. After the reaction was finished and the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the desired product **D57** 3.12 g, the yield is 82%.

7.11 Gram-Scale Synthesis of **E1**



An oven-dried autoclave liner pipe was charged with a magnetic stirring bar, PdCl₂(Xantphos) (0.2 mmol), toluene (20 mL), **C1** (14 mmol), **B1** (10 mmol) and **A1** (15 mmol). Then the liner pipe was placed in an autoclave which was closed tightly. After that, the autoclave was purged and charged with CO (4 MPa) and immersed into a pre-heated metal bath (120 °C) for 48 hours. After the reaction was finished, the autoclave was cooled to room temperature and the pressure was carefully released, and a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) on silica gel to give desired product **E1** 2.07 g, the yield is 61%.

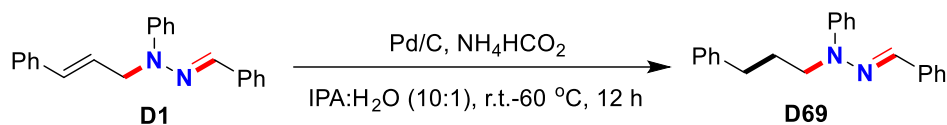


An oven-dried autoclave liner pipe was charged with a magnetic stirring bar, PdCl₂(Xantphos) (2 mmol), toluene (100 mL), **C1** (140 mmol), **B1** (100 mmol) and **A1** (150 mmol). Then the liner pipe was placed in an autoclave which was closed tightly. After that, the autoclave was purged and charged with CO (4 MPa) and immersed into a pre-heated metal bath (120 °C) for 76 hours. After the reaction was finished, the

autoclave was cooled to room temperature and the pressure was carefully released, and a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/ ethyl acetate = 20:1 – 5:1) on silica gel to give desired product **E1** 17.36 g, the yield is 51%.

8. Further Transformation

8.1 Synthesis of (*E*)-2-benzylidene-1-phenyl-1-(3-phenylpropyl)hydrazine²



Isopropyl alcohol (3 mL) was added to a 20 mL dry glass bottle with a magnetic stirring bar and Pd/C (5.3 mg, 0.05 mmol). Ammonium formate (315.3 mg, 5 mmol) dissolved in water (0.3 mL) was transferred to the same bottle. The reaction mixture was stirred for 5 min at room temperature to activate Pd/C. Next, the primary 2-((*E*)-benzylidene)-1-cinnamyl-1-phenylhydrazine (**D1**) (156.2 mg, 0.5 mmol) was added, and the reaction mixture was heated to 60 °C and reacted 12 h. After completion of the reaction based on TLC monitoring, the Pd/C catalyst was filtered off on Celite and the solvent and the solvent was removed by rotary evaporation. The reaction mixture was washed with brine solution and extracted with ethyl acetate (3×5 mL), then the organic solvents were dried by Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D69** as a colorless oil in 73% yield (115.5 mg).

(*E*)-2-benzylidene-1-phenyl-1-(3-phenylpropyl)hydrazine (**D69**)

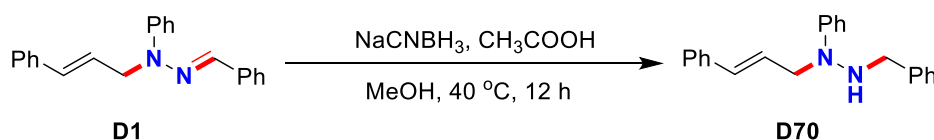
¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.55 (m, 2H), 7.38 – 7.17 (m, 13H), 6.90 (m, 1H), 3.93 – 3.79 (m, 2H), 2.73 (m, 2H), 2.00 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.1, 141.1, 136.8, 131.2, 129.2, 128.7, 128.6, 127.7, 126.4, 126.1, 120.4, 114.8, 44.3, 33.1, 25.9.

MS (70 eV): *m/z* (%) = 314 [M]⁺ (100), 209, 195, 106.

HRMS (ESI) calcd. for C₂₂H₂₃N₂ [M+H]: 315.1856, found: 315.1860.

8.2 Synthesis of 2-benzyl-1-cinnamyl-1-phenylhydrazine³



Methanol (3 mL) was added to a 20 mL dry glass bottle with a magnetic stirring bar,

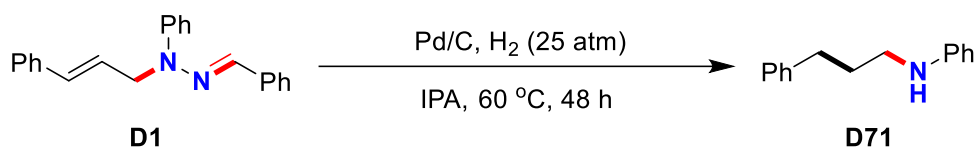
acetic acid (0.4 mL, 7 mmol), NaCNBH₃ (94.26 mg, 1.5 mmol) and 2-((*E*)-benzylidene)-1-cinnamyl-1-phenylhydrazine (**D1**) (156.2 mg, 0.5 mmol). The reaction mixture was stirred for 12 h at 40 °C. After completion of the reaction based on TLC monitoring, the reaction mixture was washed with brine solution and extracted with ethyl acetate (3×5 mL), then the organic solvents were dried by Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1, with 1% (v/v) triethylamine) on silica gel to give the product **D70** as a colorless oil in 96% yield (150.8 mg).

2-benzyl-1-cinnamyl-1-phenylhydrazine (**D70**)

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.22 (m, 9H), 7.21 – 7.16 (m, 1H), 7.11 – 7.05 (m, 2H), 6.78 (m, 1H), 6.55 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.19 (m, 1H), 4.21 (m, 2H), 4.01 (s, 2H), 3.75 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.3, 138.5, 136.8, 133.5, 129.4, 129.2, 128.8, 128.7, 127.9, 127.6, 126.7, 124.7, 118.6, 114.0, 53.5, 52.8.

8.3 Synthesis of *N*-(3-phenylpropyl)aniline (**D71**)



Isopropyl alcohol (2 mL) was added to a 10 mL dry glass bottle with a magnetic stirring bar, 2-((*E*)-benzylidene)-1-cinnamyl-1-phenylhydrazine (**D1**) (156.2 mg, 0.5 mmol) and Pd/C (5.3 mg, 0.05 mmol). Then the glass bottle was transferred into an autoclave under N₂ atmosphere. After flushing the autoclave three times with H₂ and adjusting the pressure to 25 atm, the reaction was performed for 48 h at 60 °C. After completion of the reaction, the autoclave was cooled to room temperature, the reaction mixture was washed with brine solution and extracted with ethyl acetate (3×5 mL), then the organic solvents were dried by Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product **D71** as a colorless oil in 99% yield (104.0 mg).

N-(3-phenylpropyl)aniline (**D71**)

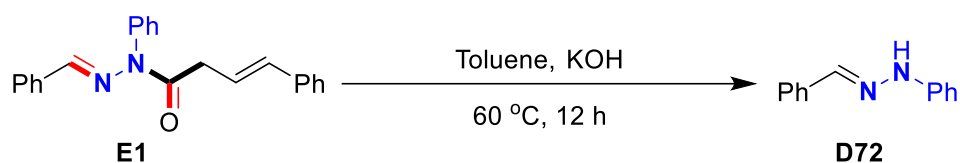
¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.11 (m, 5H), 6.68 (m, 1H), 6.60 – 6.52 (m, 2H), 3.56 (s, 1H), 3.13 (m, 2H), 2.78 – 2.66 (m, 2H), 2.00 – 1.84 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.4, 141.7, 129.3, 128.5, 126.0, 117.3, 112.8, 43.4, 33.5, 31.1.

MS (70 eV): m/z (%) = 211 [M]⁺ (100), 194, 106, 77.

HRMS (ESI) calcd. for C₁₅H₁₈N [M+H]: 212.1434, found: 212.1436.

8.4 Synthesis of 1-benzylidene-2-phenylhydrazine



Toluene (3 mL) was added to a 20 mL dry glass bottle with a magnetic stirring bar, 2-((*E*)-benzylidene)-1-cinnamyl-1-phenylhydrazine (**E1**) (156.2 mg, 0.5 mmol) and KOH (56.1 mg, 1 mmol). The reaction mixture was heated to 60 °C and reacted 12 h. After completion of the reaction based on TLC monitoring, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1 – 10:1) on silica gel to give the product as a colorless oil in 88% yield (86.2 mg).

1-benzylidene-2-phenylhydrazine (**D72**)

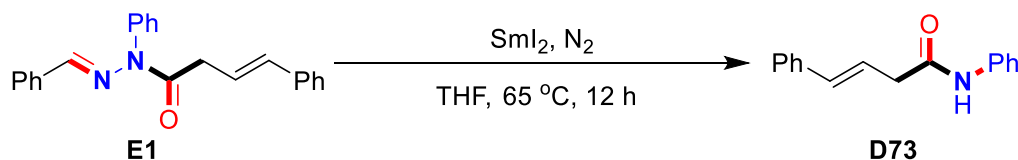
¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.62 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H)

¹³C NMR (101 MHz, CDCl₃) δ 144.7, 137.3, 135.3, 129.3, 128.6, 128.5, 126.2, 120.1, 112.8

MS (70 eV): m/z (%) = 196 [M]⁺ (100), 92, 65, 39.

HRMS (ESI) calcd. for C₁₃H₁₃N₂ [M+H]: 197.1073, found: 197.1070.

8.5 Synthesis of (*E*)-*N*,4-diphenylbut-3-enamide



Using a nitrogen-filled glove box, Samarium(II) Iodide solution (10 mL) was added to an oven-dried pressure tube (38 mL volume) with a magnetic stirring bar and (*E*)-*N'*-((*E*)-benzylidene)-*N*,4-diphenylbut-3-enehydrazide (**E1**) (170.1 mg, 0.5 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred at 65 °C for 12 hours. After completion of the reaction based on TLC monitoring, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1 – 5:1) on silica gel to give the product as a colorless oil in 97% yield (115.0 mg).

(*E*)-*N*,4-diphenylbut-3-enamide (**D73**)

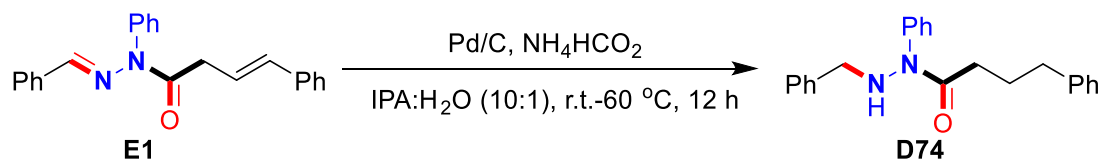
¹H NMR (400 MHz, DMSO-*d*₆) δ 10.04 (s, 1H), 7.66 – 7.57 (m, 2H), 7.48 – 7.40 (m, 2H), 7.38 – 7.26 (m, 4H), 7.28 – 7.19 (m, 1H), 7.09 – 7.00 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.49 – 6.36 (m, 1H), 3.32 – 3.23 (m, 2H).

¹³C NMR (101 MHz, DMSO) δ = 169.5, 139.6, 137.2, 132.7, 129.2, 129.1, 127.8, 126.5, 124.6, 123.6, 119.6, 41.1.

MS (70 eV): *m/z* (%) = 237 [*M*]⁺ (100), 144, 118, 77.

HRMS (ESI) calcd. for C₁₆H₁₆NO [*M*+H]: 238.1227, found: 238.1228.

8.6 Synthesis of *N'*-benzyl-*N*,4-diphenylbutanehydrazide



Isopropyl alcohol (3 mL) was added to a 20 mL dry glass bottle with a magnetic stirring bar and Pd/C (3.18 mg, 0.03 mmol). Ammonium formate (189.2 mg, 3 mmol) dissolved in water (0.3 mL) was transferred to the same bottle. The reaction mixture was stirred for 5 min at room temperature to activate Pd/C. Next, the primary (*E*)-*N'*-((*E*)-benzylidene)-*N*,4-diphenylbut-3-enehydrazidene (**E1**) (102 mg, 0.3 mmol) was added, and the reaction mixture was heated to 60 °C and reacted 12 h. After completion

of the reaction based on TLC monitoring, the Pd/C catalyst was filtered off on Celite and the solvent and the solvent was removed by rotary evaporation. The reaction mixture was washed with brine solution and extracted with ethyl acetate (3×5 mL), then the organic solvents were dried by Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/dichloromethane = 20:1 – 5:1) on silica gel to give the product as a colorless oil in 95% yield (98.1 mg).

***N*'-benzyl-*N*,4-diphenylbutanehydrazide (D74)**

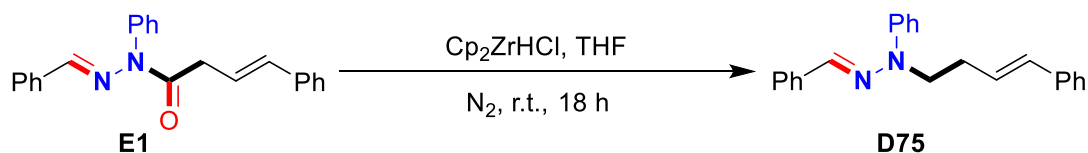
¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.11 (m, 13H), 7.10 – 7.01 (m, 2H), 6.14 (s, 1H), 3.95 (s, 2H), 2.60 – 2.45 (m, 2H), 2.24 – 2.09 (m, 2H), 1.97 – 1.83 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 171.2, 141.5, 141.1, 137.1, 129.2, 129.1, 128.4, 128.3, 127.8, 127.5, 125.8, 54.1, 35.1, 32.9, 26.9.

MS (70 eV): m/z (%) = 344 [M]⁺ (100), 239, 198, 107.

HRMS (ESI) calcd. for C₂₃H₂₅N₂O [M+H]: 345.1962, found: 345.1965.

8.7 Synthesis of 2-((*E*)-benzylidene)-1-phenyl-1-((*E*)-4-phenylbut-3-en-1-yl)hydrazine



Using a nitrogen-filled glove box, THF (3 mL) was added to an oven-dried pressure tube (38 mL volume) with a magnetic stirring bar, Cp₂ZrHCl (154.7 mg, 0.6 mmol) and (*E*)-*N*'-((*E*)-benzylidene)-*N*,4-diphenylbut-3-enehydrazide (**E1**) (102 mg, 0.3 mmol). Then the seal tube was closed tightly with a teflon cap, removed from the glove box, and stirred for 18 hours at room temperature. After completion of the reaction based on TLC monitoring, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1 – 10:1) on silica gel to give the product as a colorless oil in 41% yield (40.1 mg).

2-((*E*)-benzylidene)-1-phenyl-1-((*E*)-4-phenylbut-3-en-1-yl)hydrazine (D75)

¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.68 (m, 2H), 7.59 (s, 1H), 7.45 – 7.19 (m, 12H), 6.99 – 6.89 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.33 – 6.20 (m, 1H), 4.16 – 3.99 (m, 2H), 2.67 – 2.48 (m, 2H).

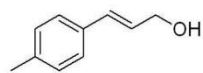
¹³C NMR (101 MHz, CDCl₃) δ = 147.0, 137.1, 136.7, 132.4, 131.5, 129.2, 128.6, 127.8, 127.4, 126.2, 126.1, 120.6, 115.0, 45.1, 28.7.

HRMS (ESI) calcd. for C₂₃H₂₃N₂ [M+H]: 327.1856, found: 327.1858.

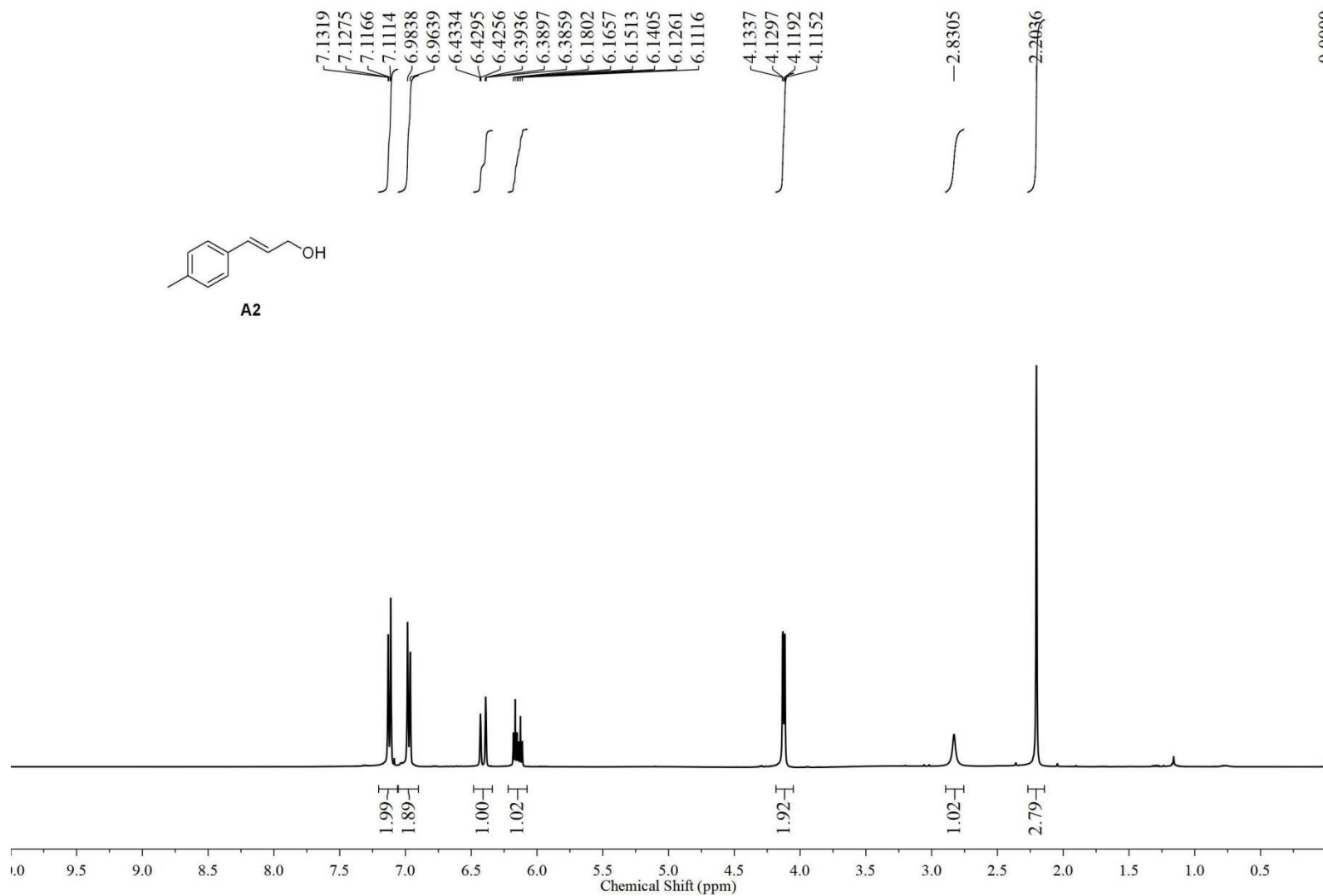
9. References

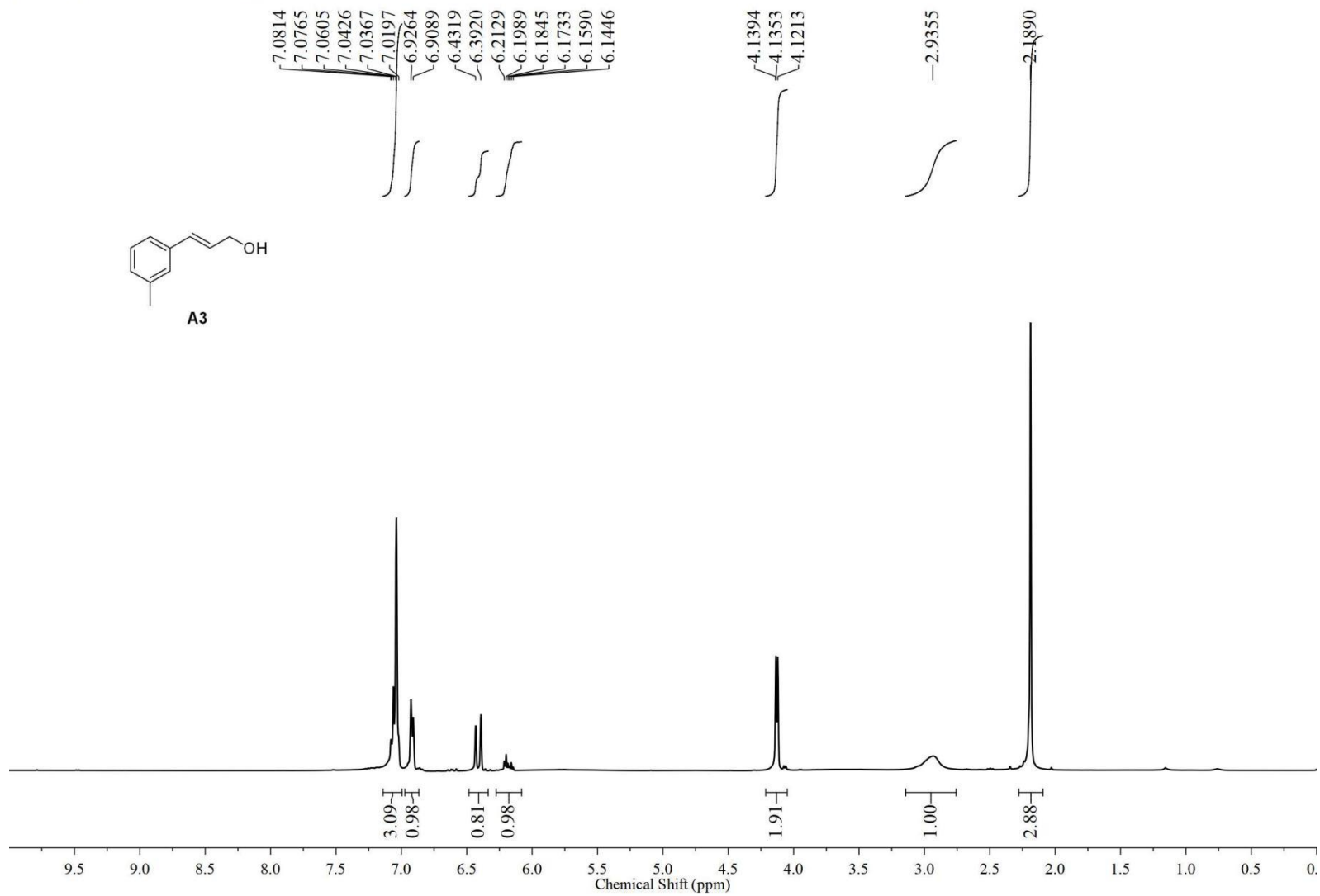
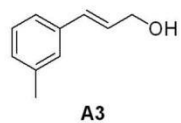
- 1 (a) G. S. Coelho, J. S. Andrade, V. F. Xavier, P. A. Sales Junior, B. C. Rodrigues de Araujo, K. S. Fonseca, M. S. Caetano, S. M. F. Murta, P. M. Vieira, C. M. Carneiro and J. G. Taylor, *Chem. Biol. Drug. Des.*, 2019, **93**, 337–350; (b) H. Wei, F. Mao, S. Ni, F. Chen, B. Li, X. Qiu, L. Hu, M. Wang, X. Zheng, J. Zhu, L. Lan and J. Li, *Eur. J. Med. Chem.*, 2018, **145**, 235-251.
- 2 E. Byun, B. Hong, K. A. De Castro, M. Lim and H. J. Rhee, *J. Org. Chem.*, 2007, **72**, 9815-9817.
- 3 G. Gros, L. Martinez, A. S. Gimenez, P. Adler, P. Maurin, R. Wolkowicz, P. Falso and J. Hasserodt, *Bioorg. Med. Chem.* 2013, **21**, 5407-5413.

10. NMR Spectra

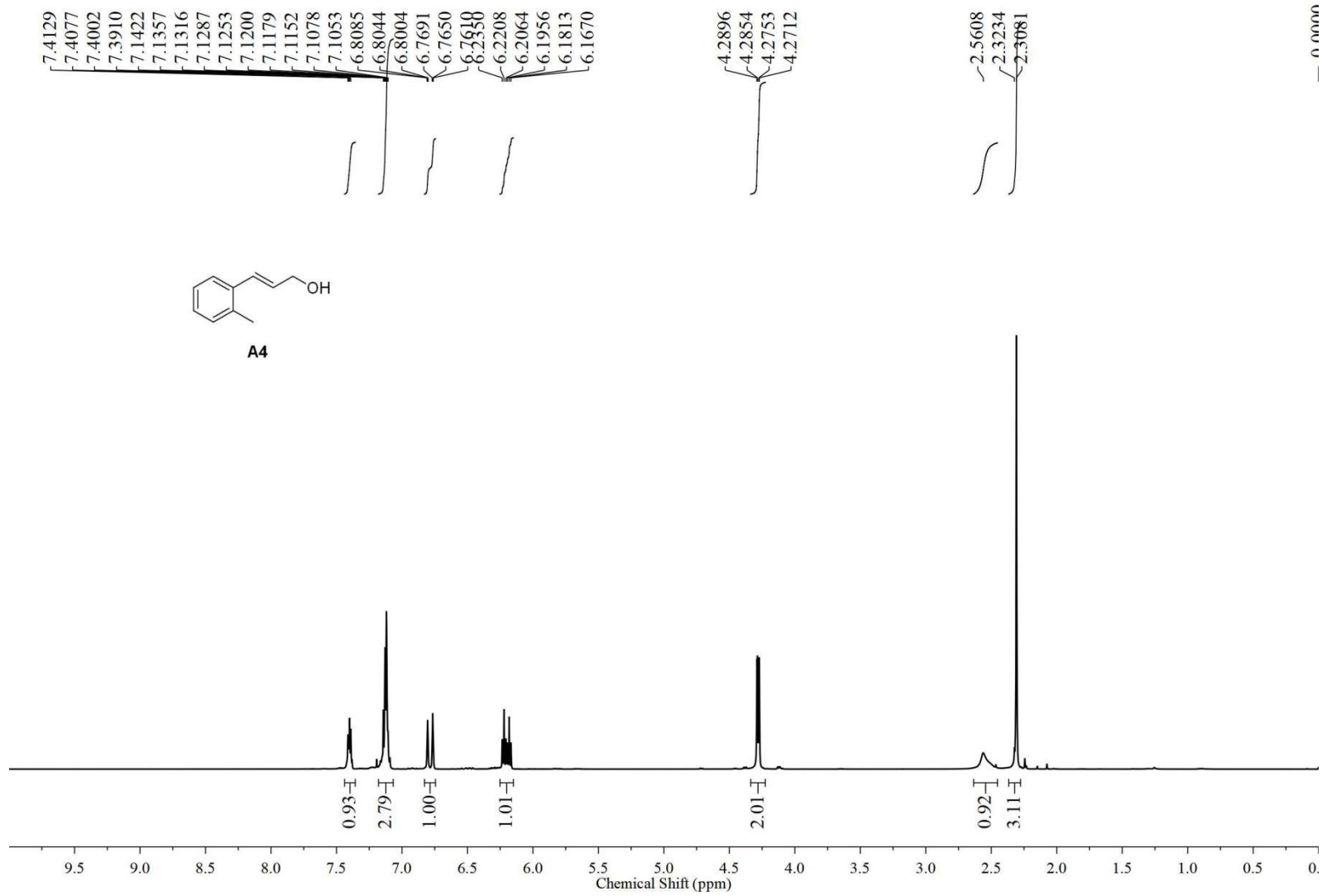


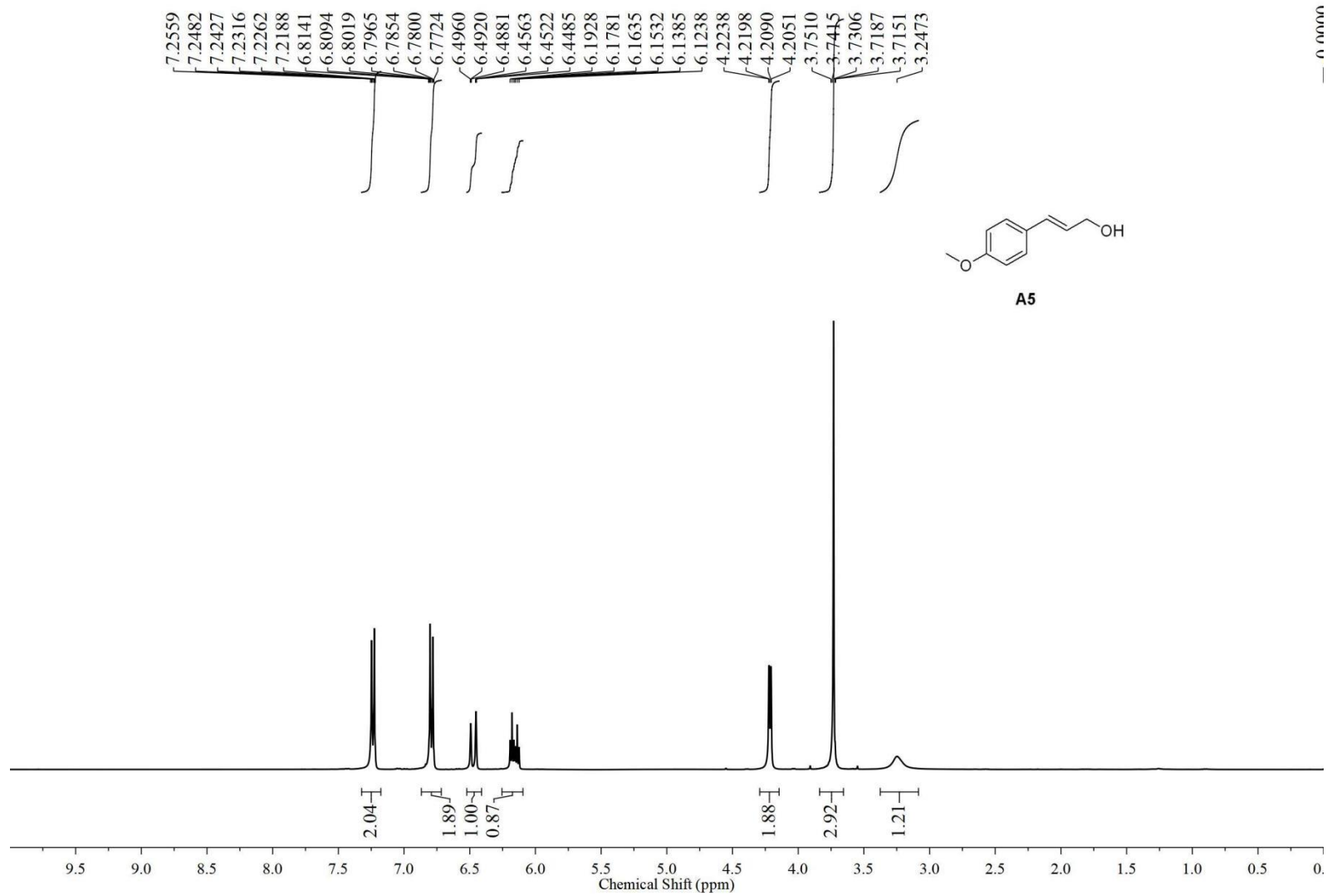
A2



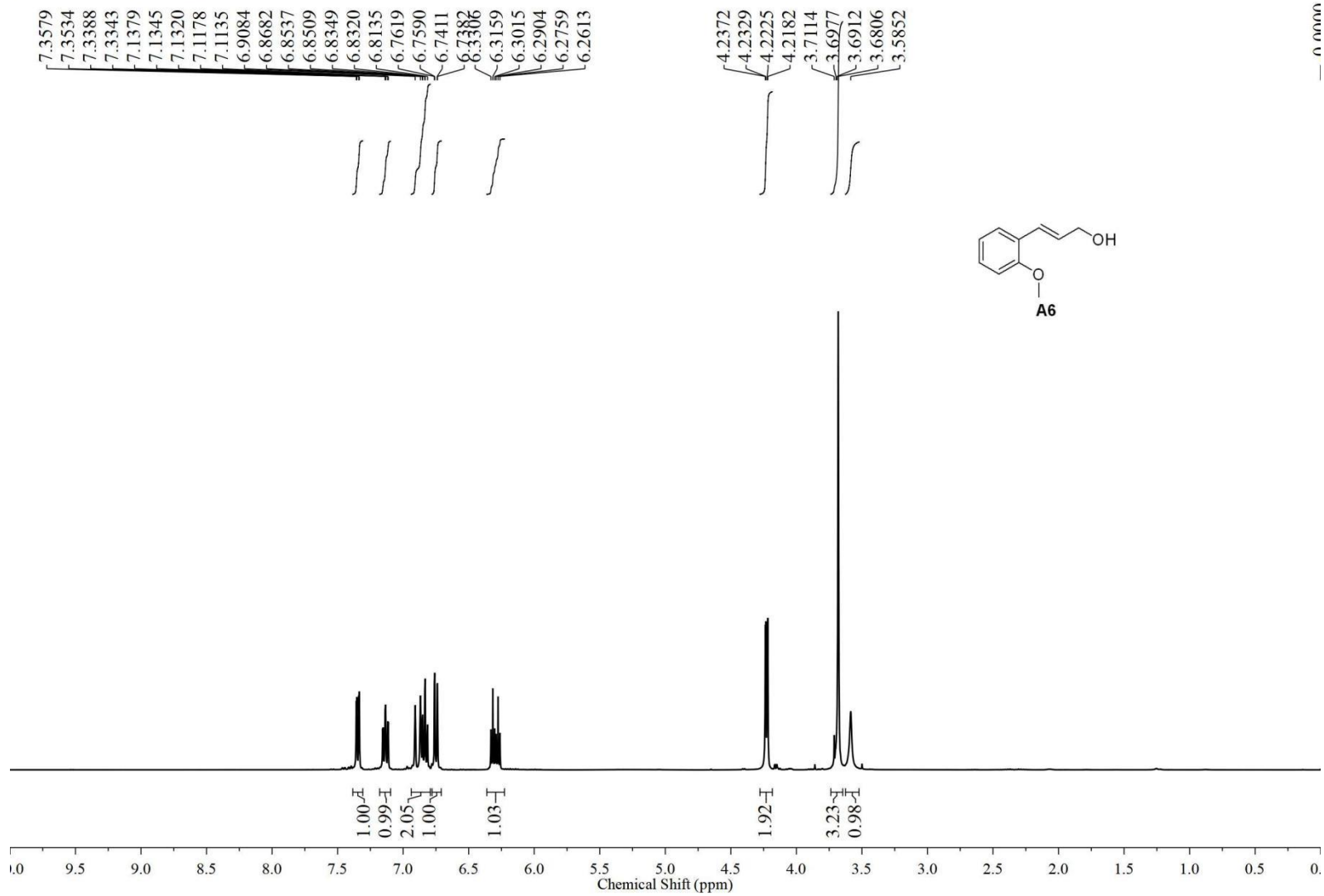


2022-09-08-YY0009-616-CH-15.10.fid

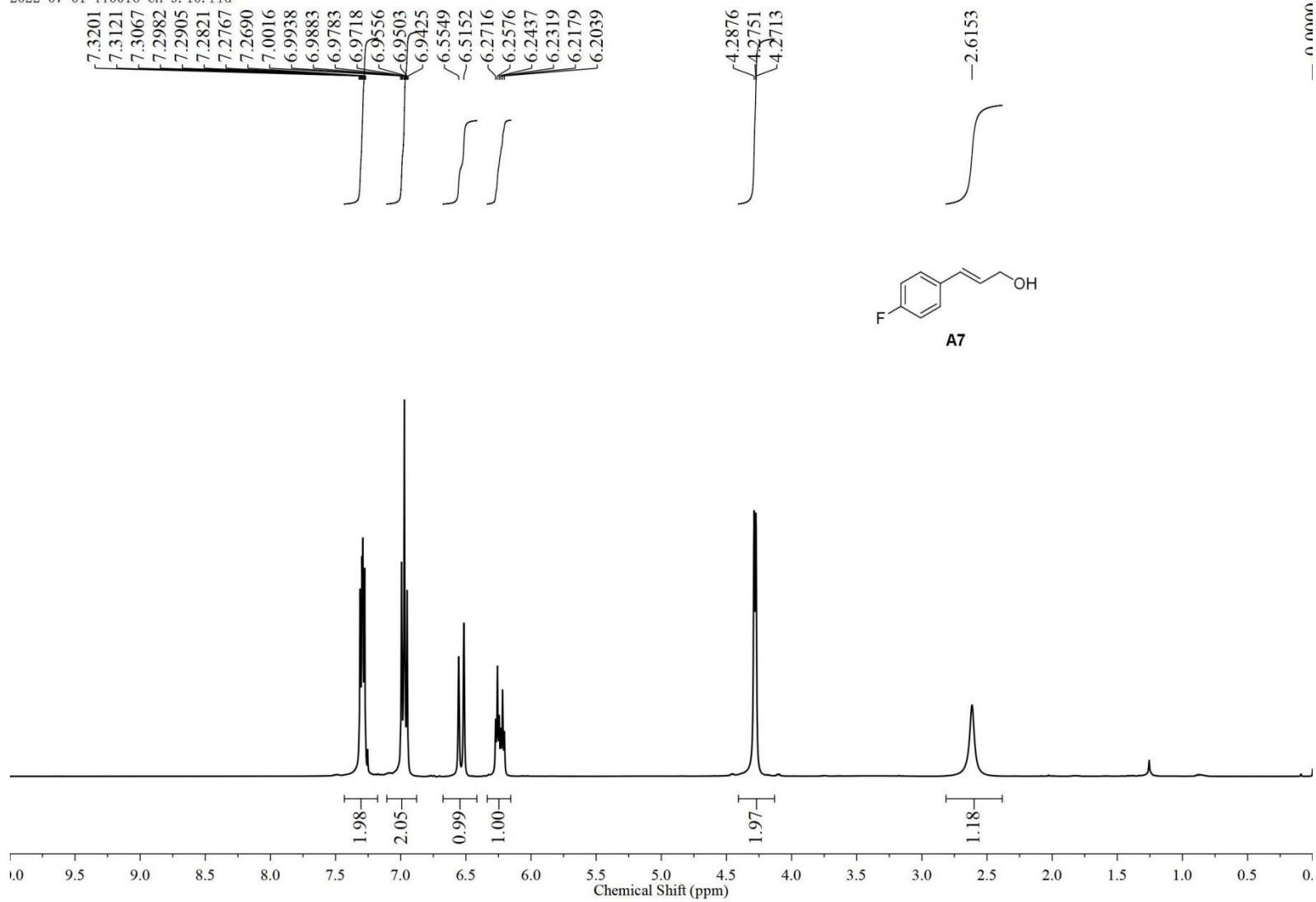


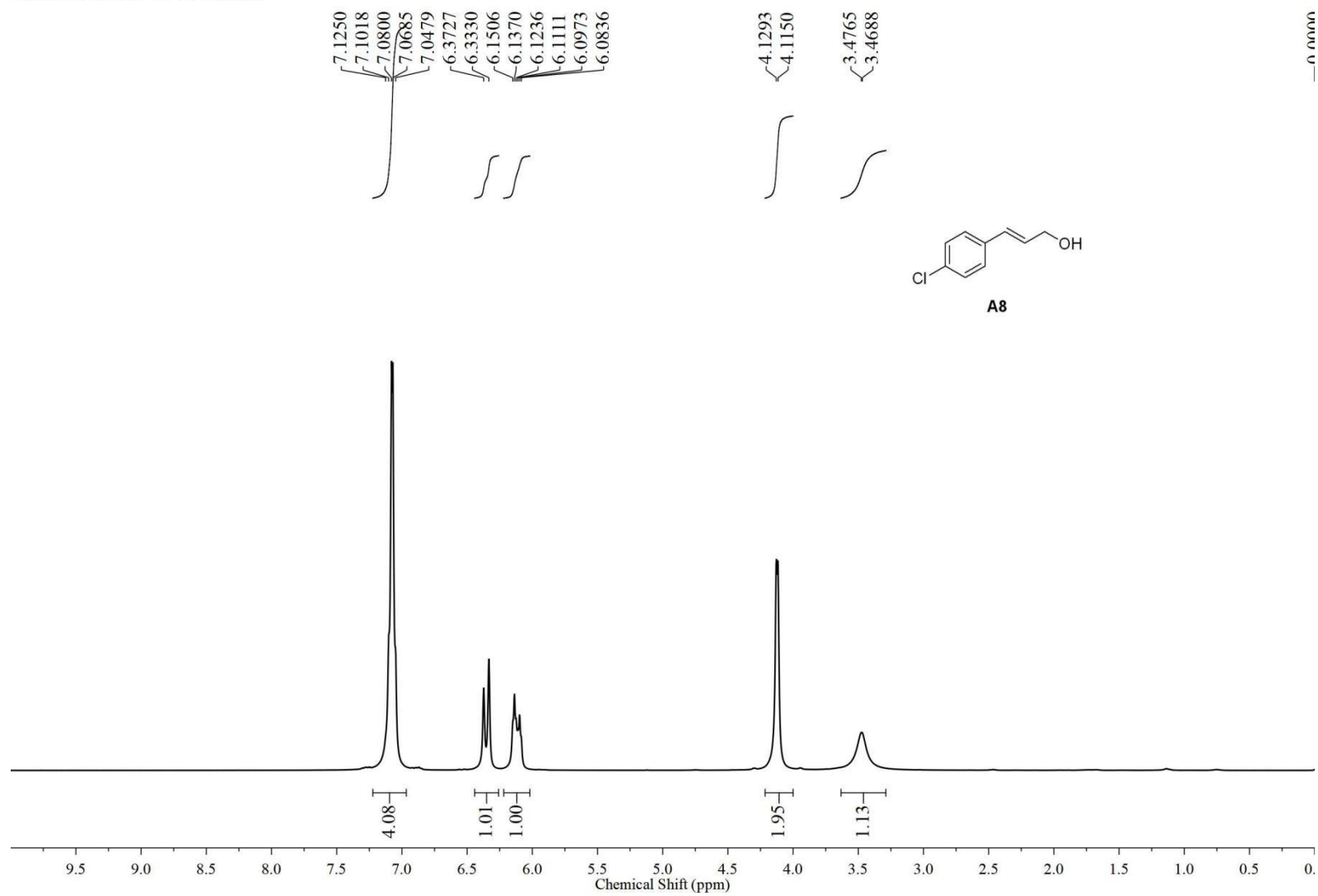


2022-06-30-yy0011-616-ch-7.20.fid

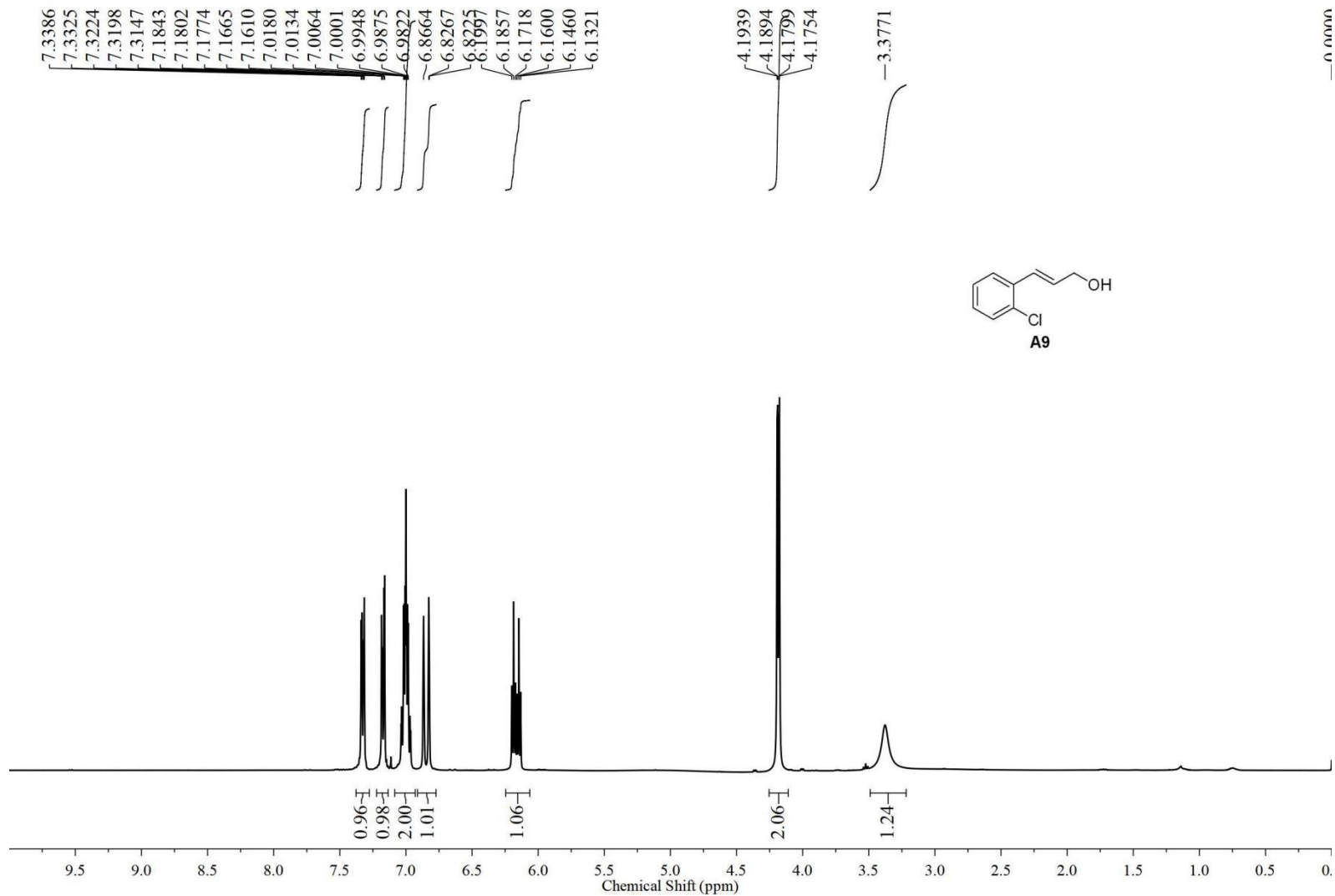


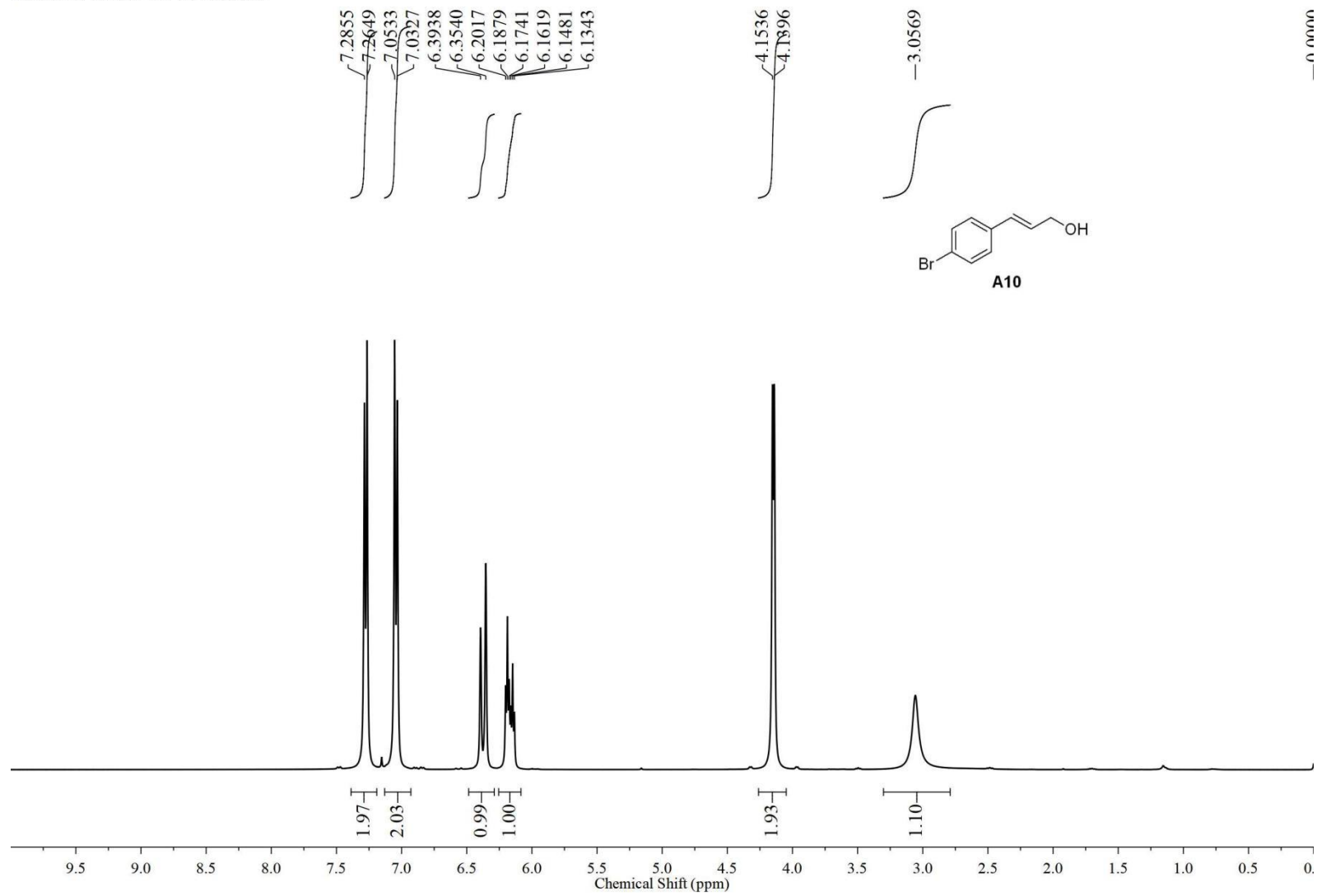
2022-07-01-YY0016-CH-9.10.fid



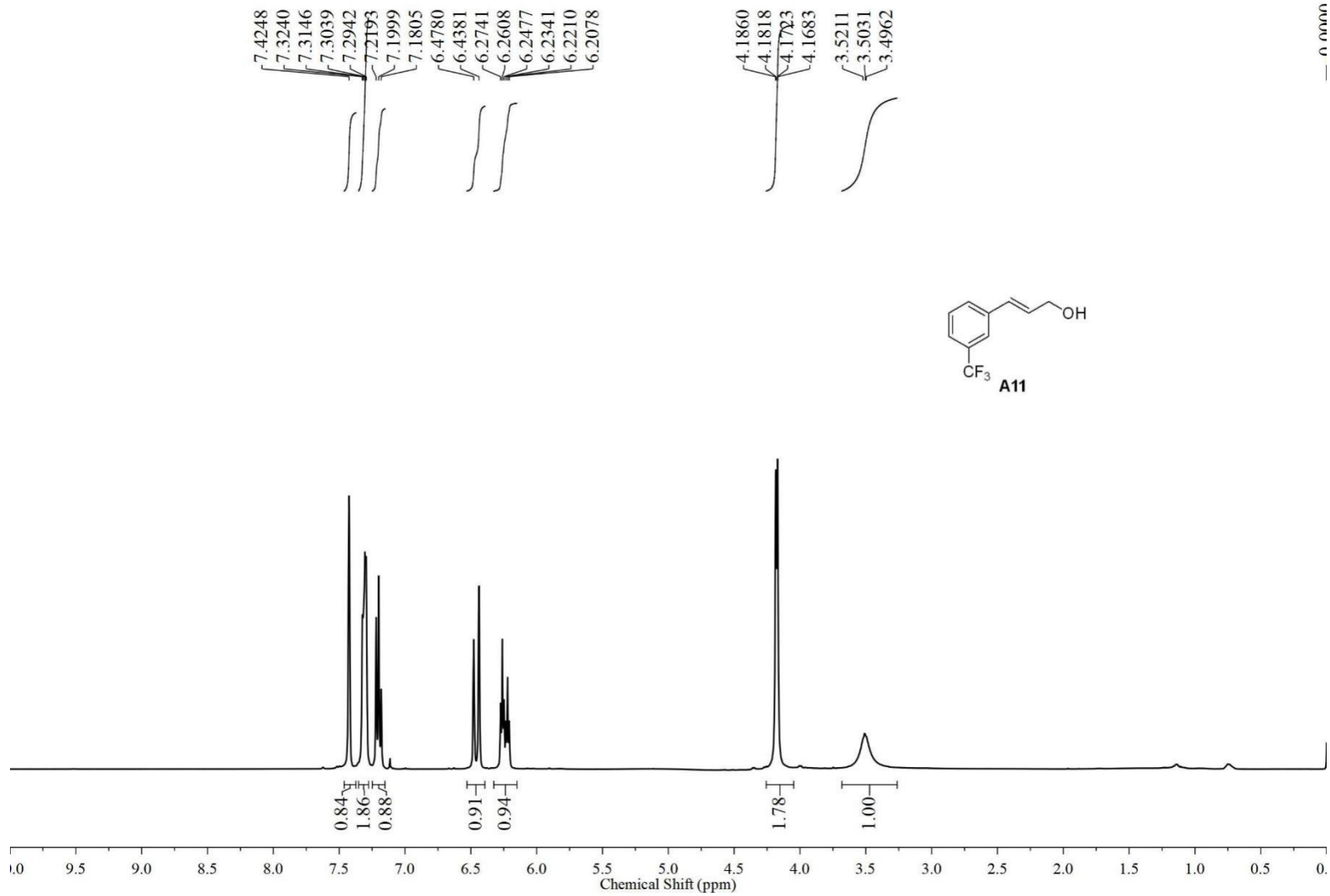


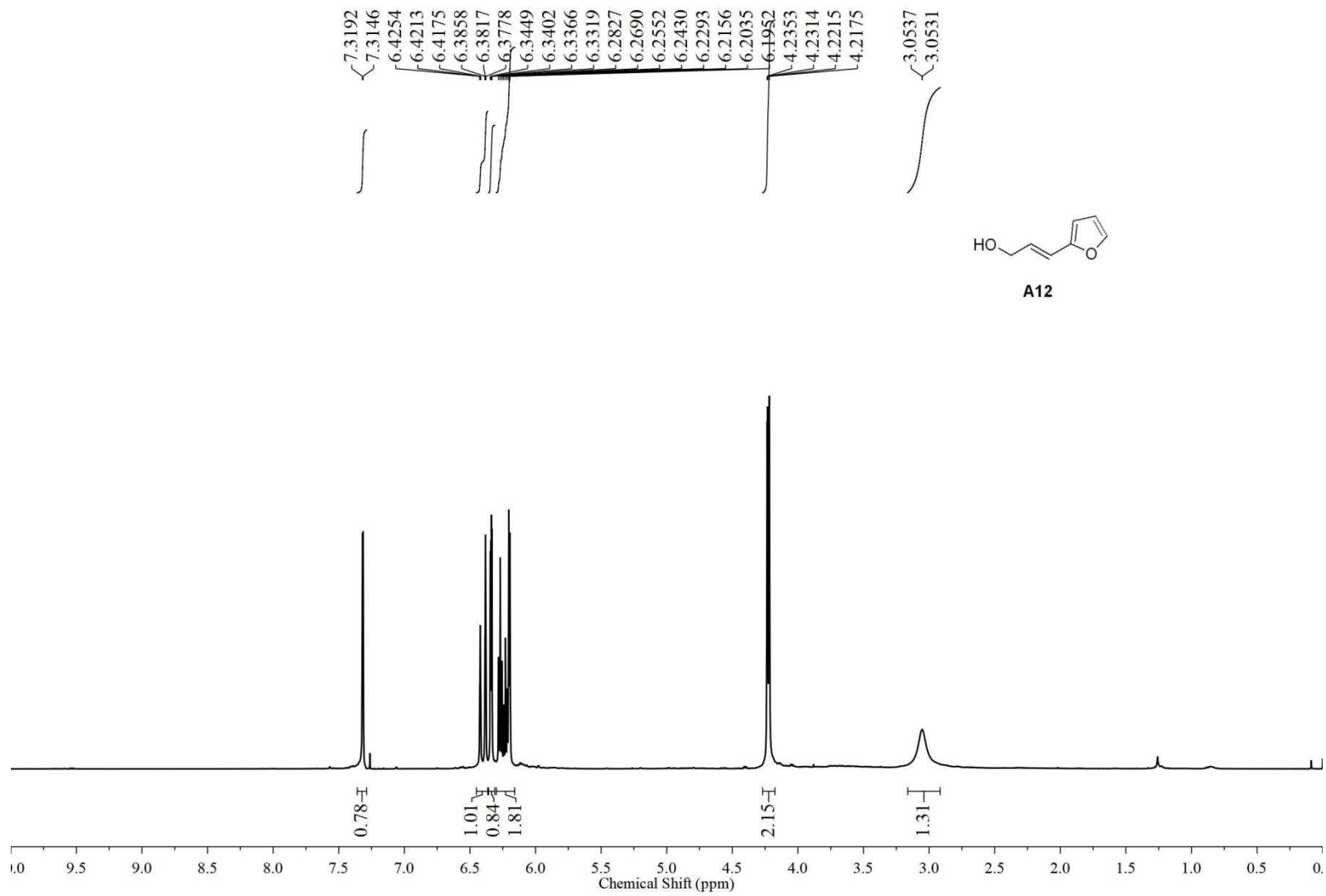
2022-06-29-yy0006-616-ch-2.10.fid



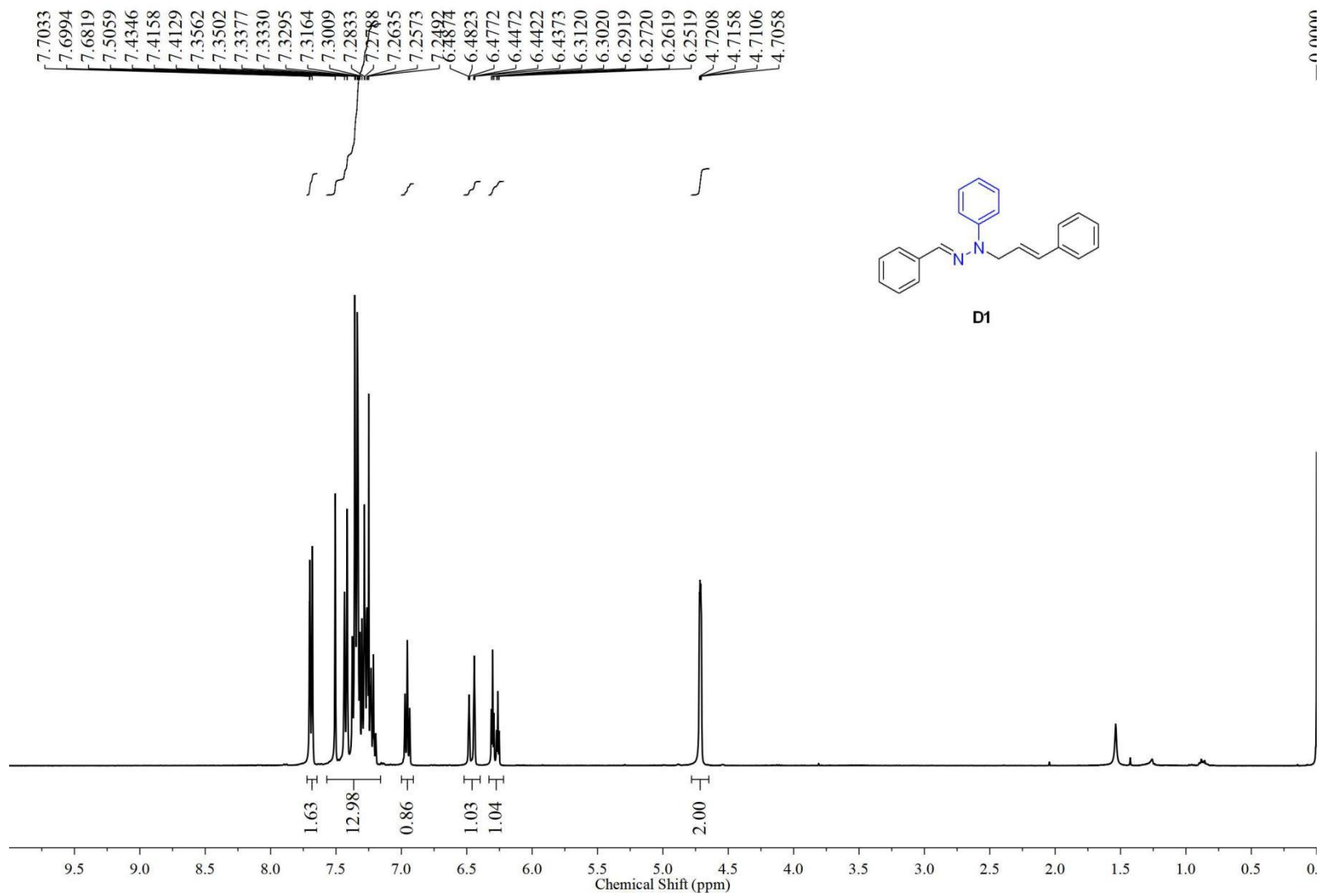


2022-06-30-yy0011-616-ch-5.10.fid

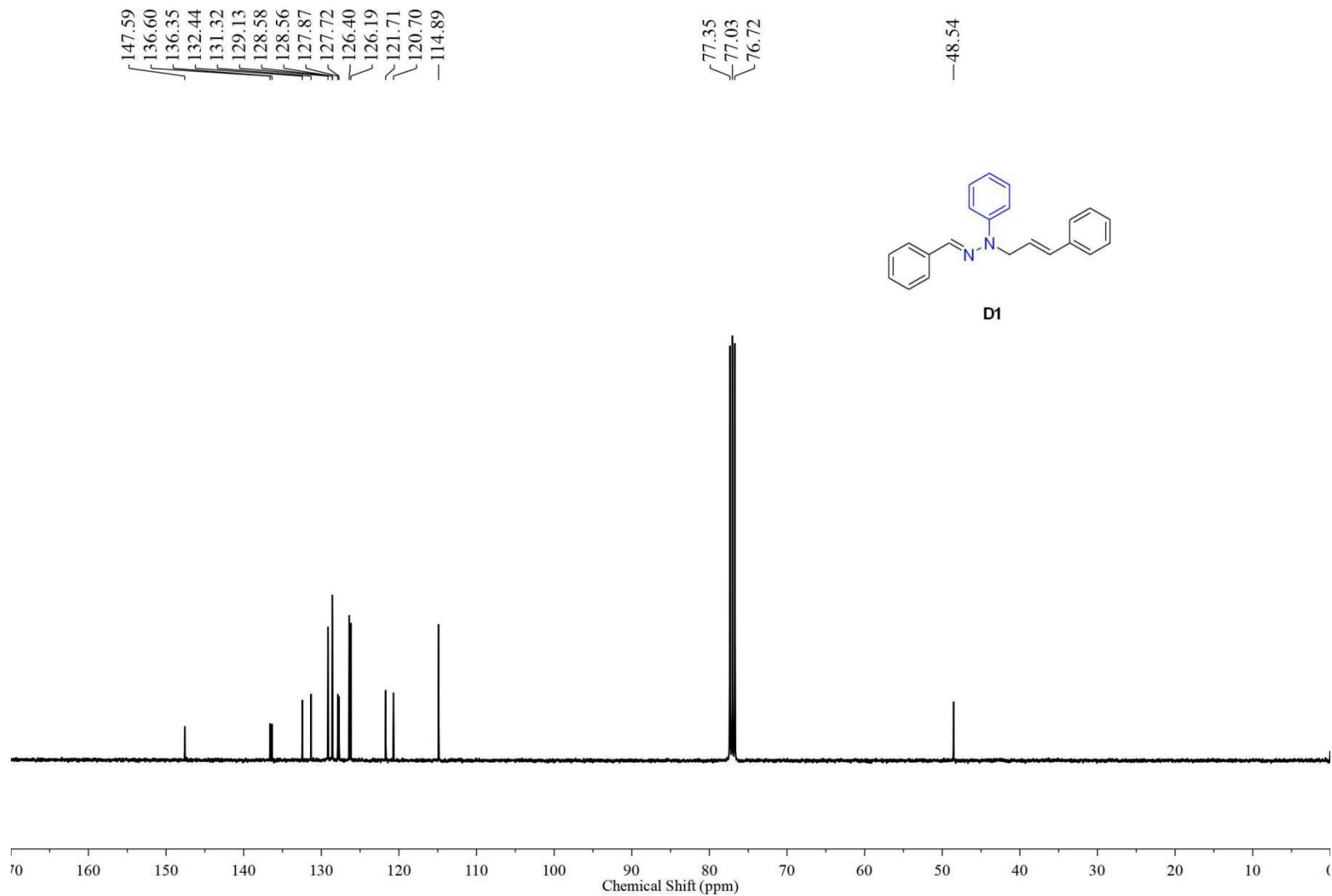




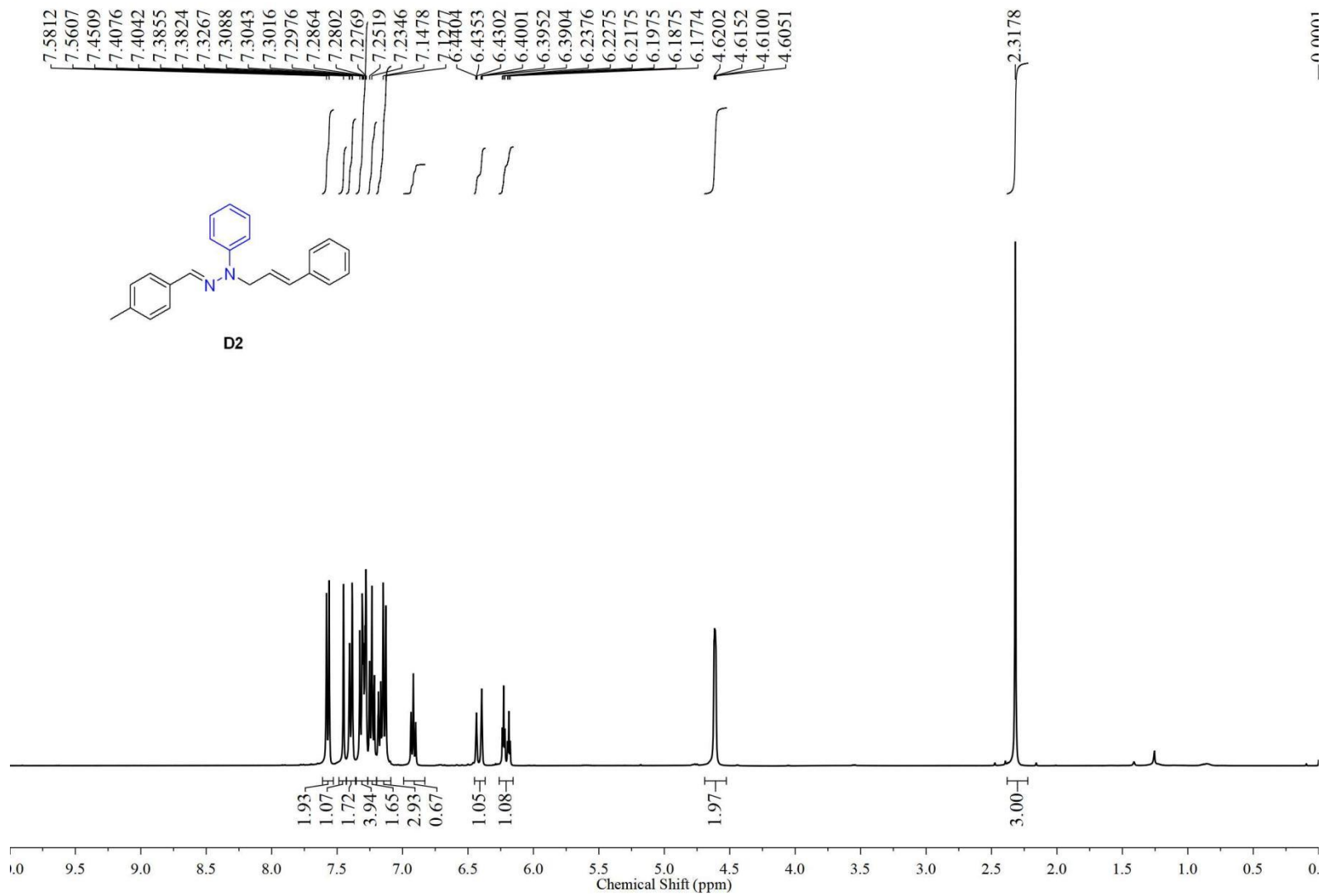
2022-04-18 yy0001 LQQ-1.10.fid



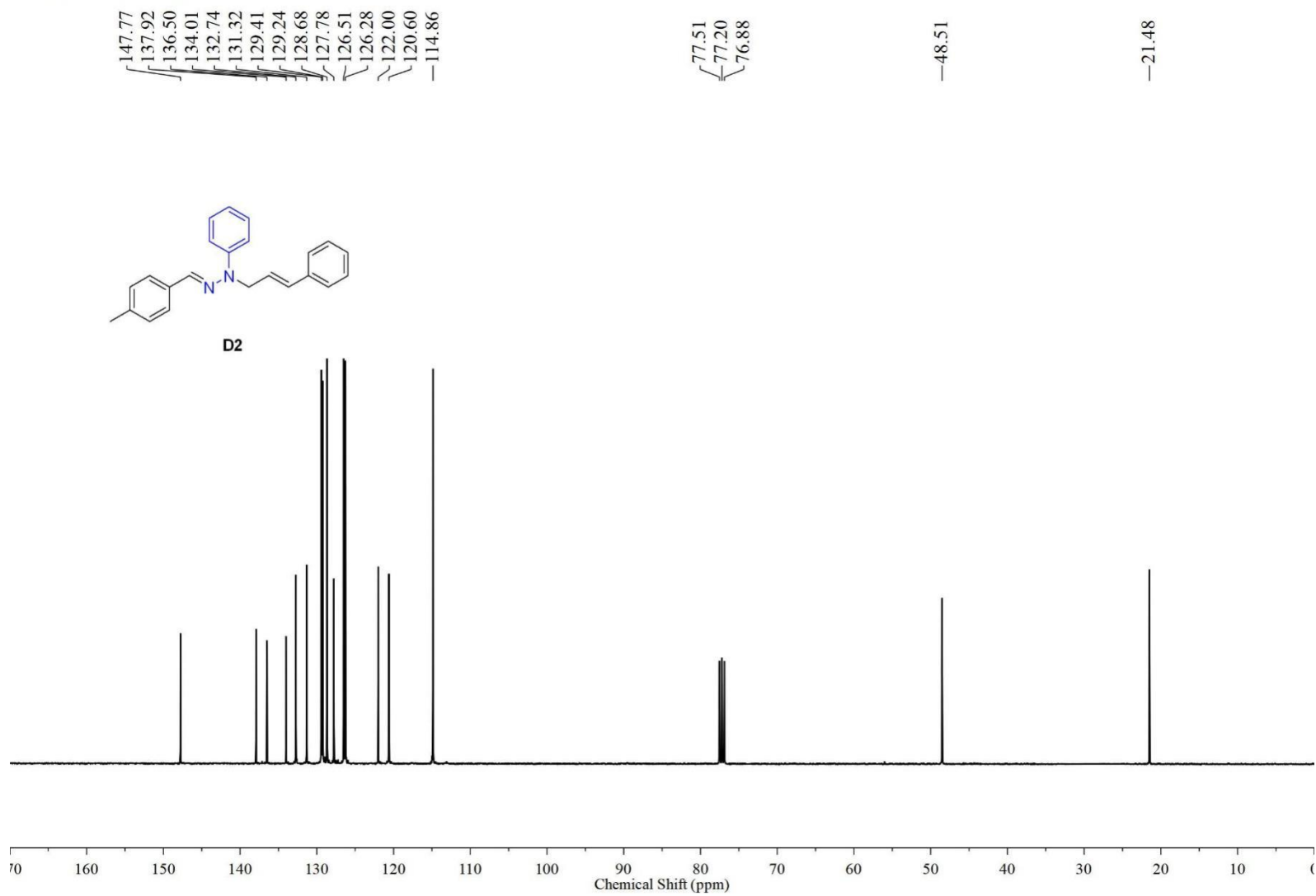
2022-04-20 YY0004 616-ZGH-5.10.fid



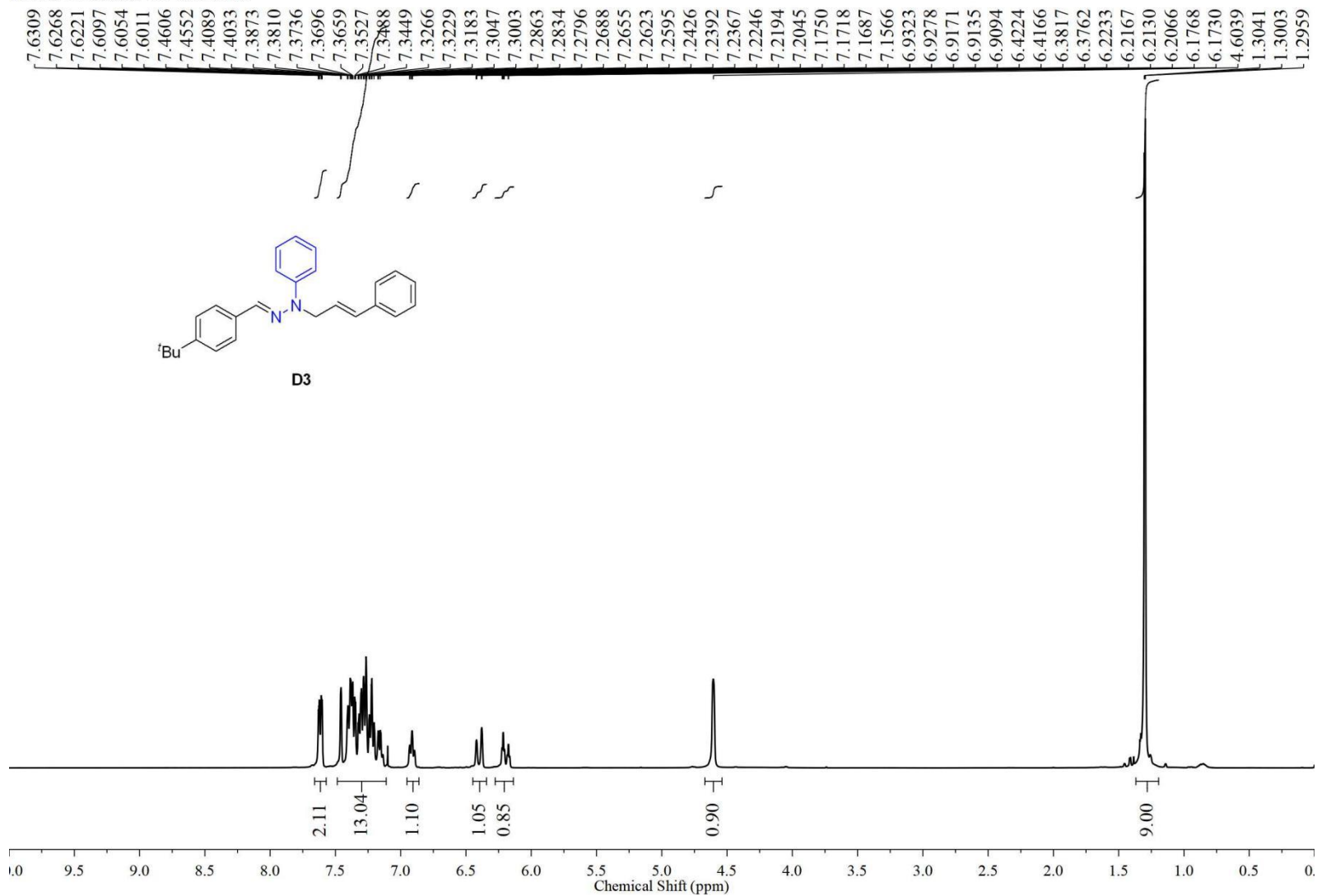
2022-05-18-yy0033-616-d2.10.fid



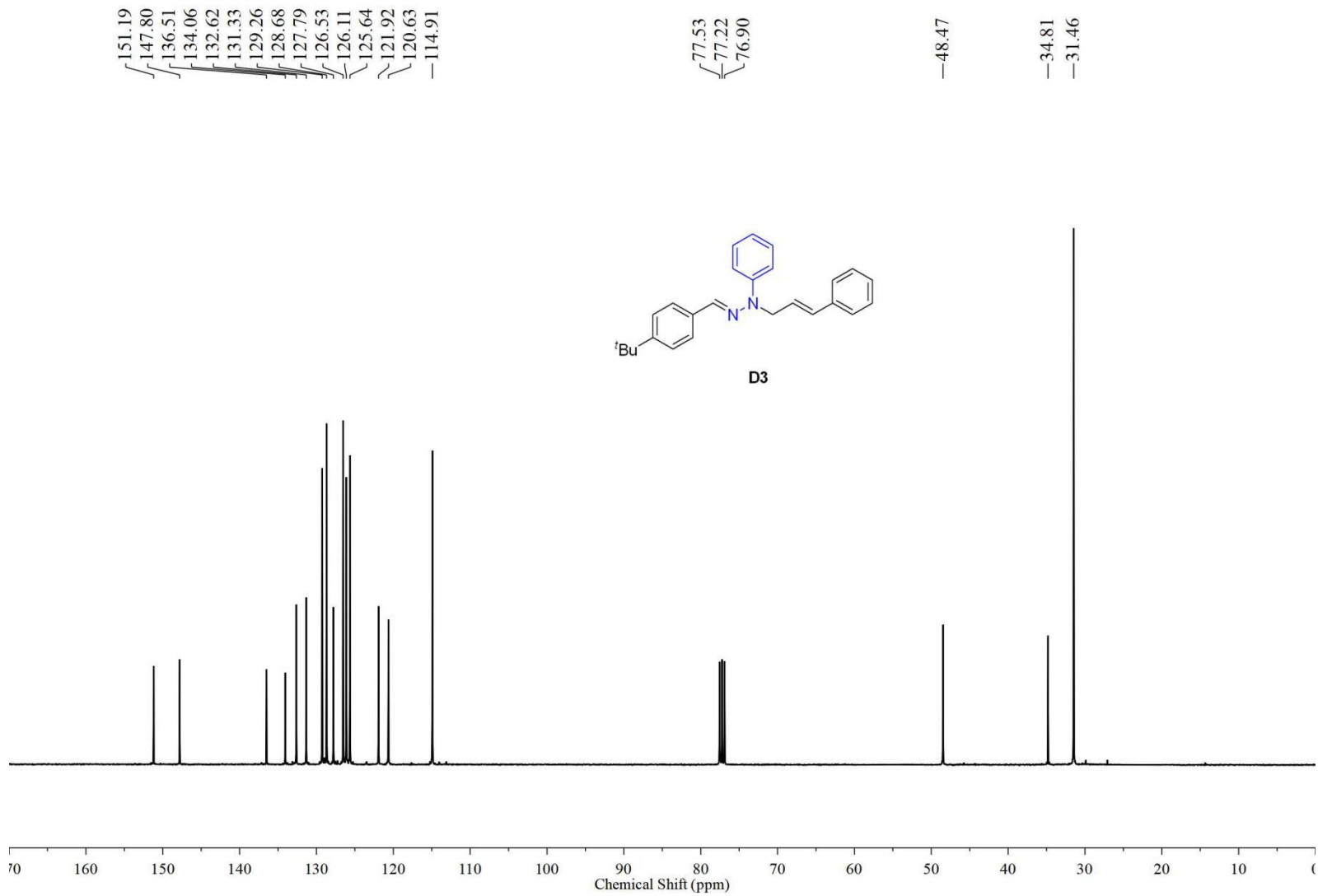
2022-05-20-yy0021-616-d2.10.fid



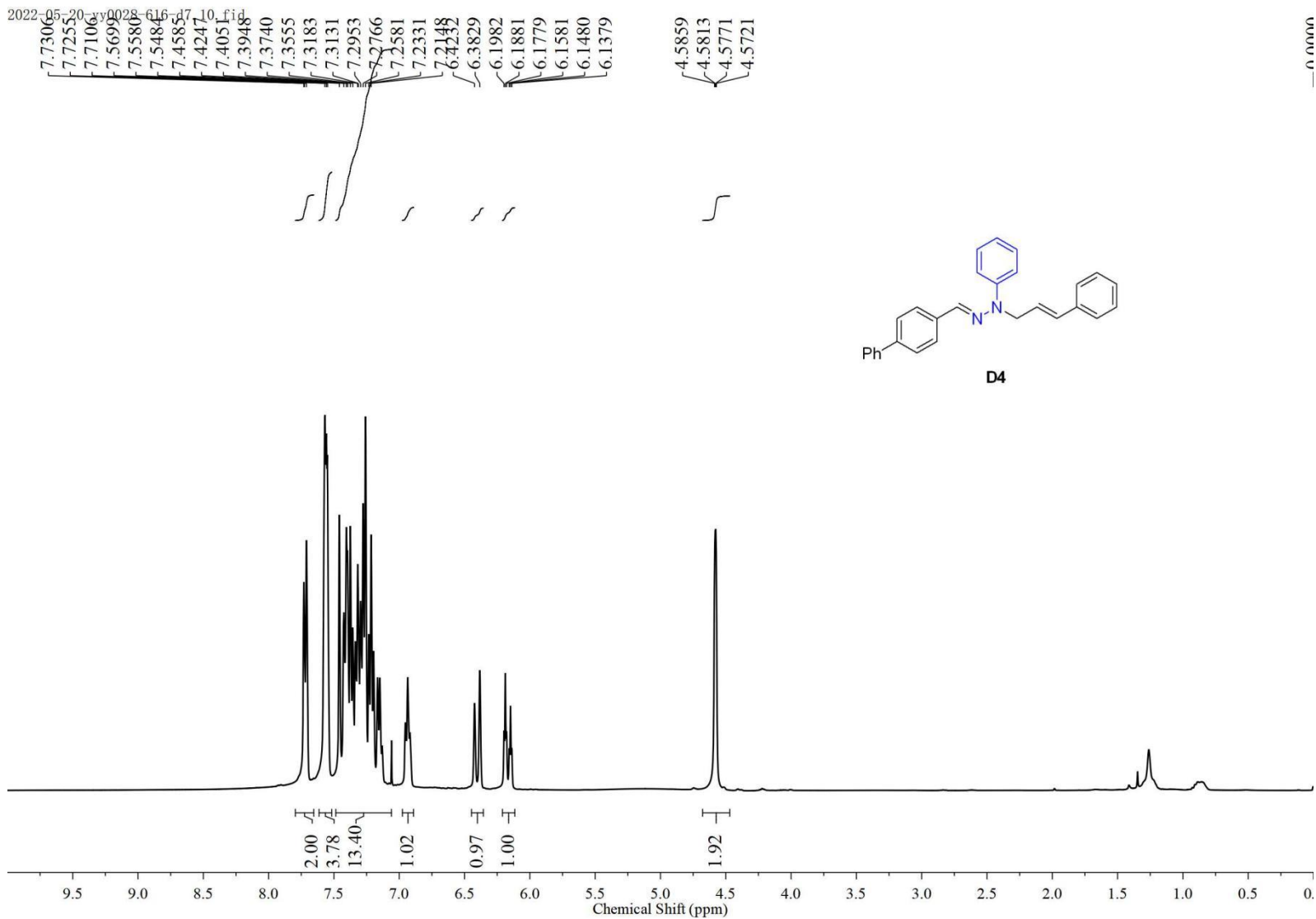
2022-05-20-yy0028-616-d6.10.fid



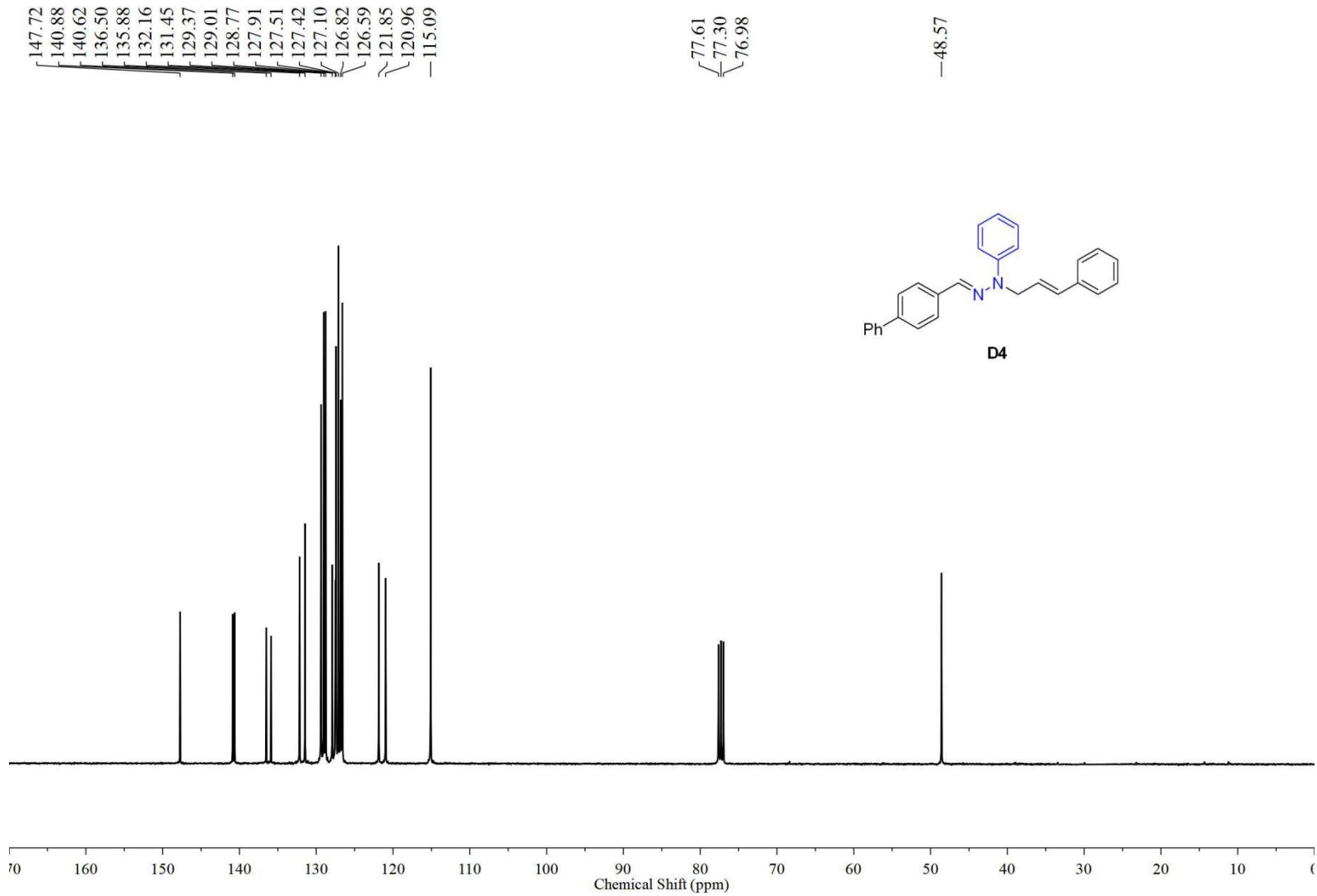
2022-05-20-yy0028-616-d6.11.fid



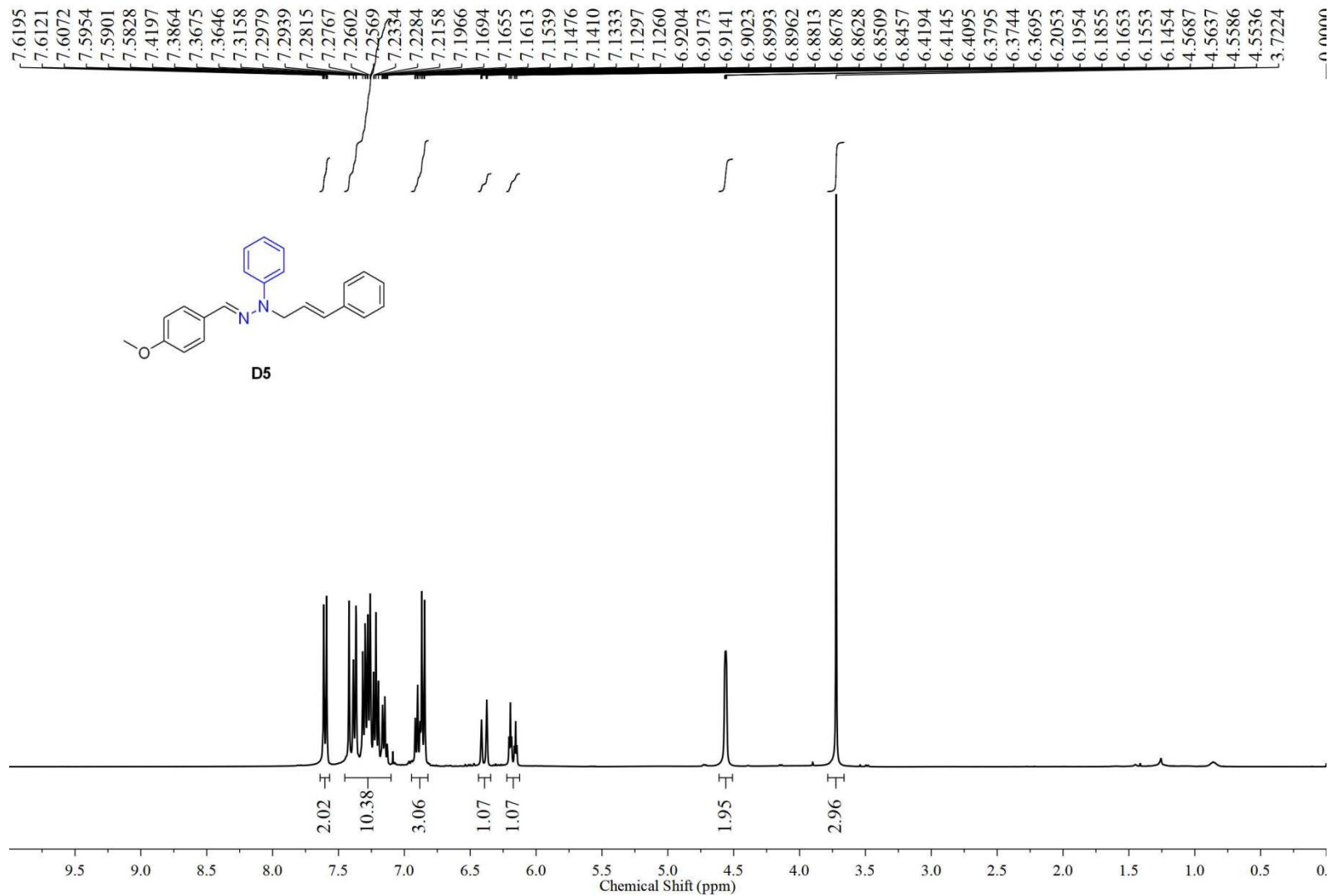
2022-05-20_yy0028-616-d7_10_fid



2022-05-20-yy0028-616-d7.11.fid

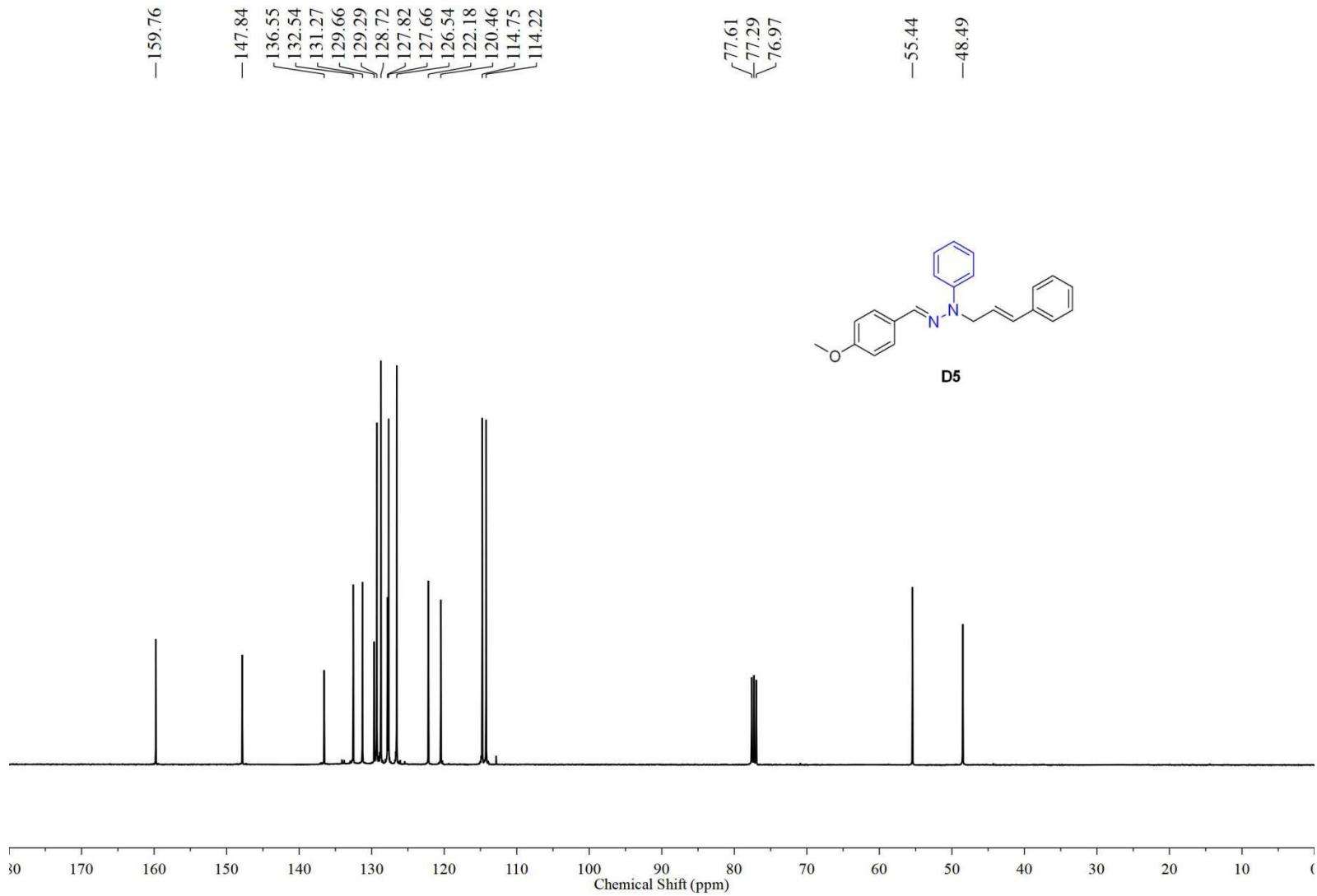


2022-05-29-YY0021-L-D8. 10. fid

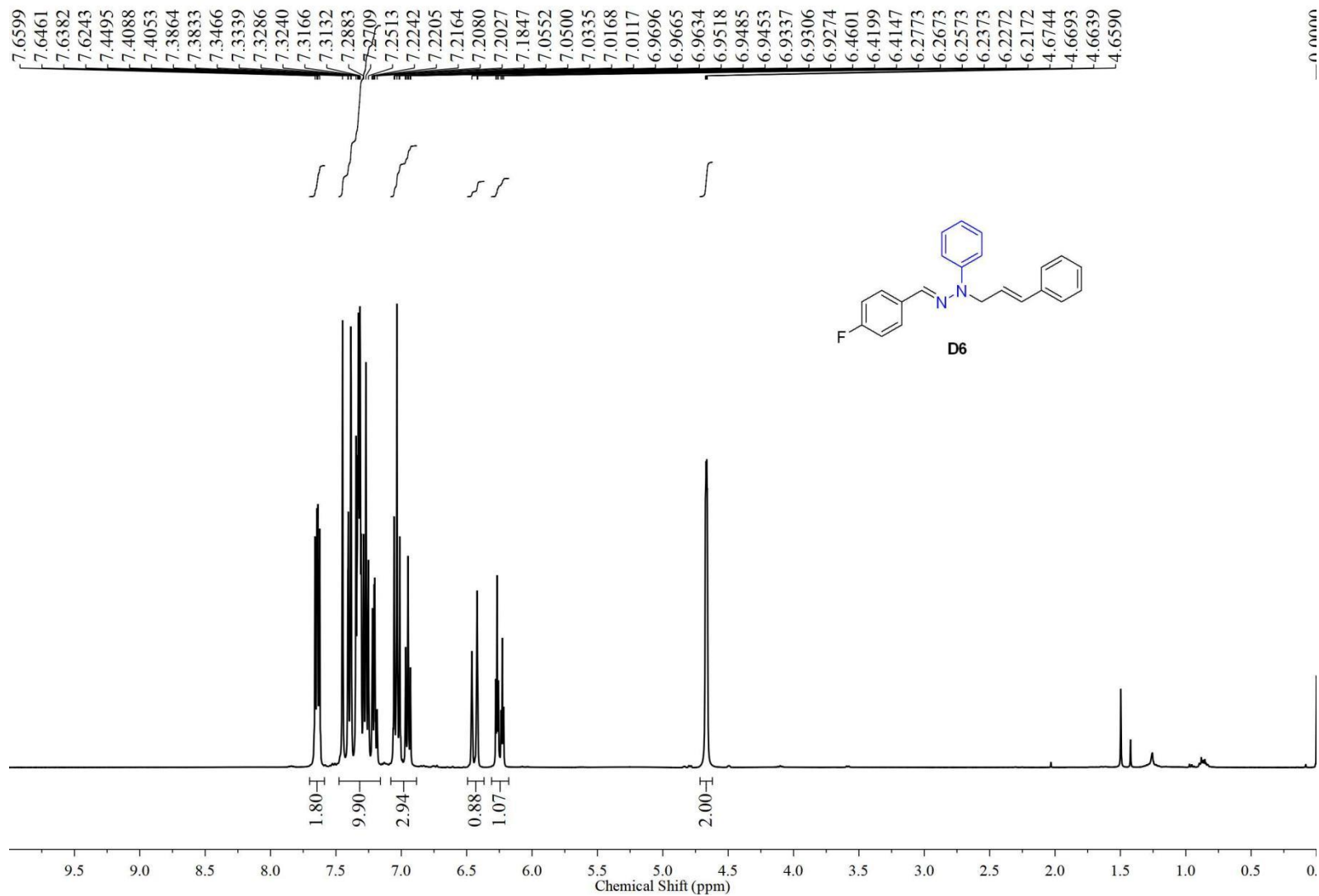


S142

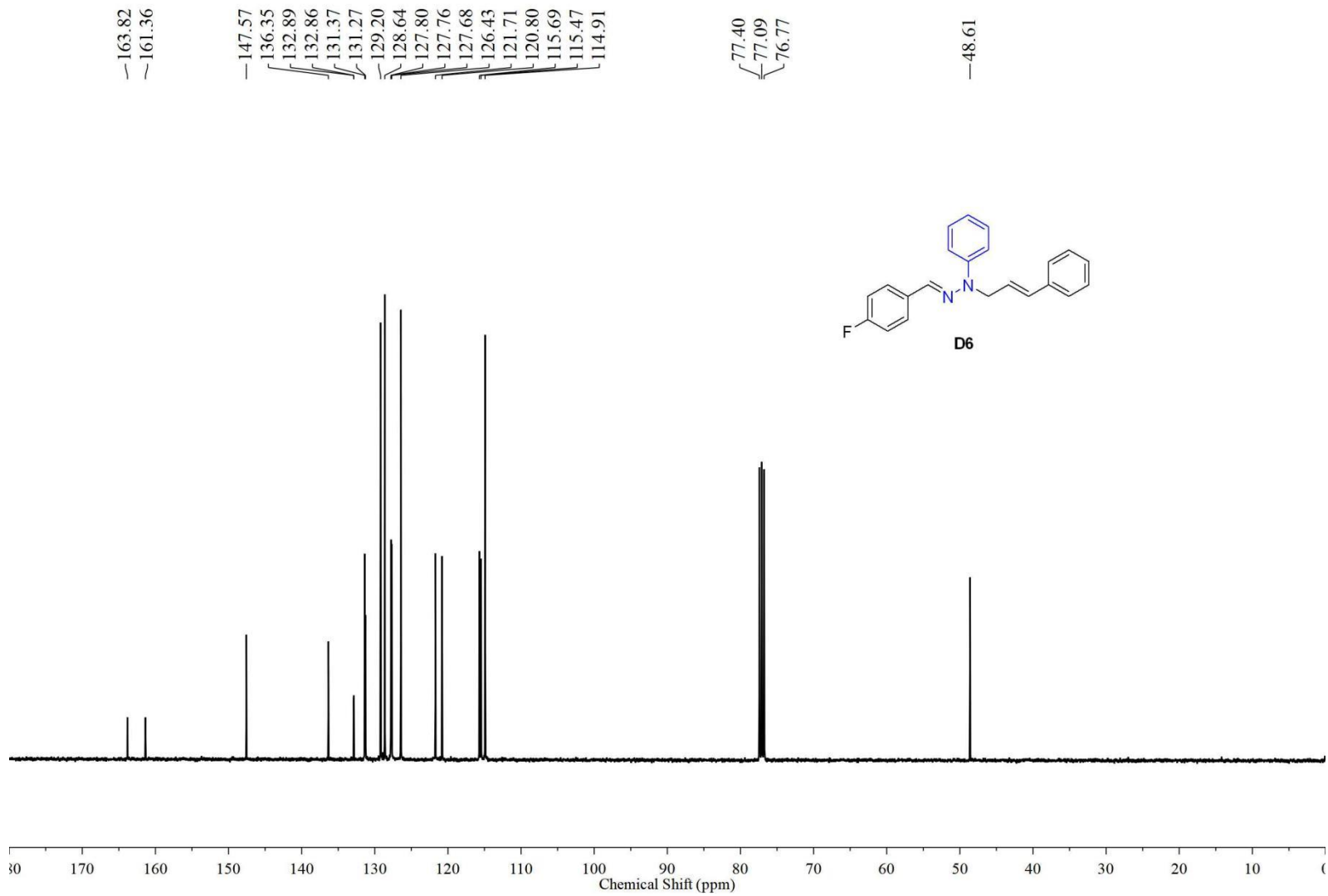
2022-05-29-YY0021-L-D8. 11. fid



2022-05-23-yy0006-616-1-d11.10.fid

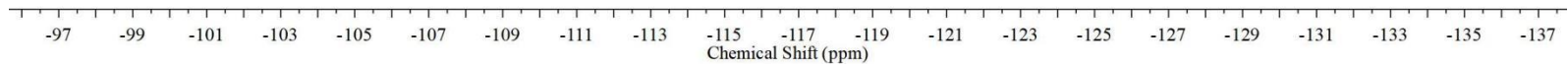
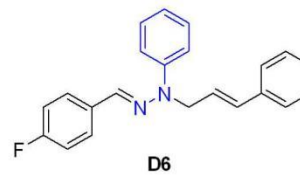


2022-05-23-yy0006-616-1-d11.11.fid



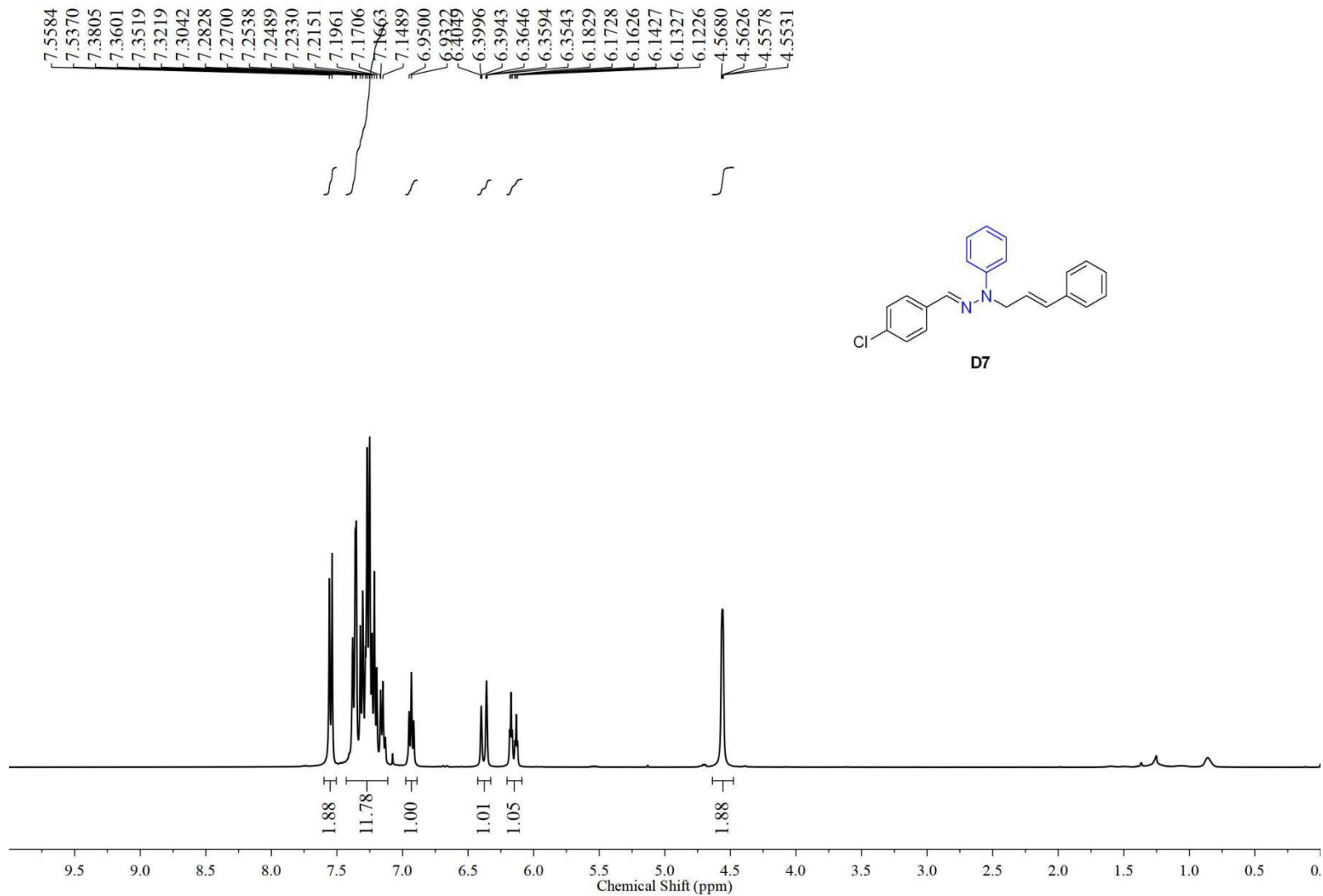
2022-05-23-yy0006-616-1-d11.12.fid

--113.68



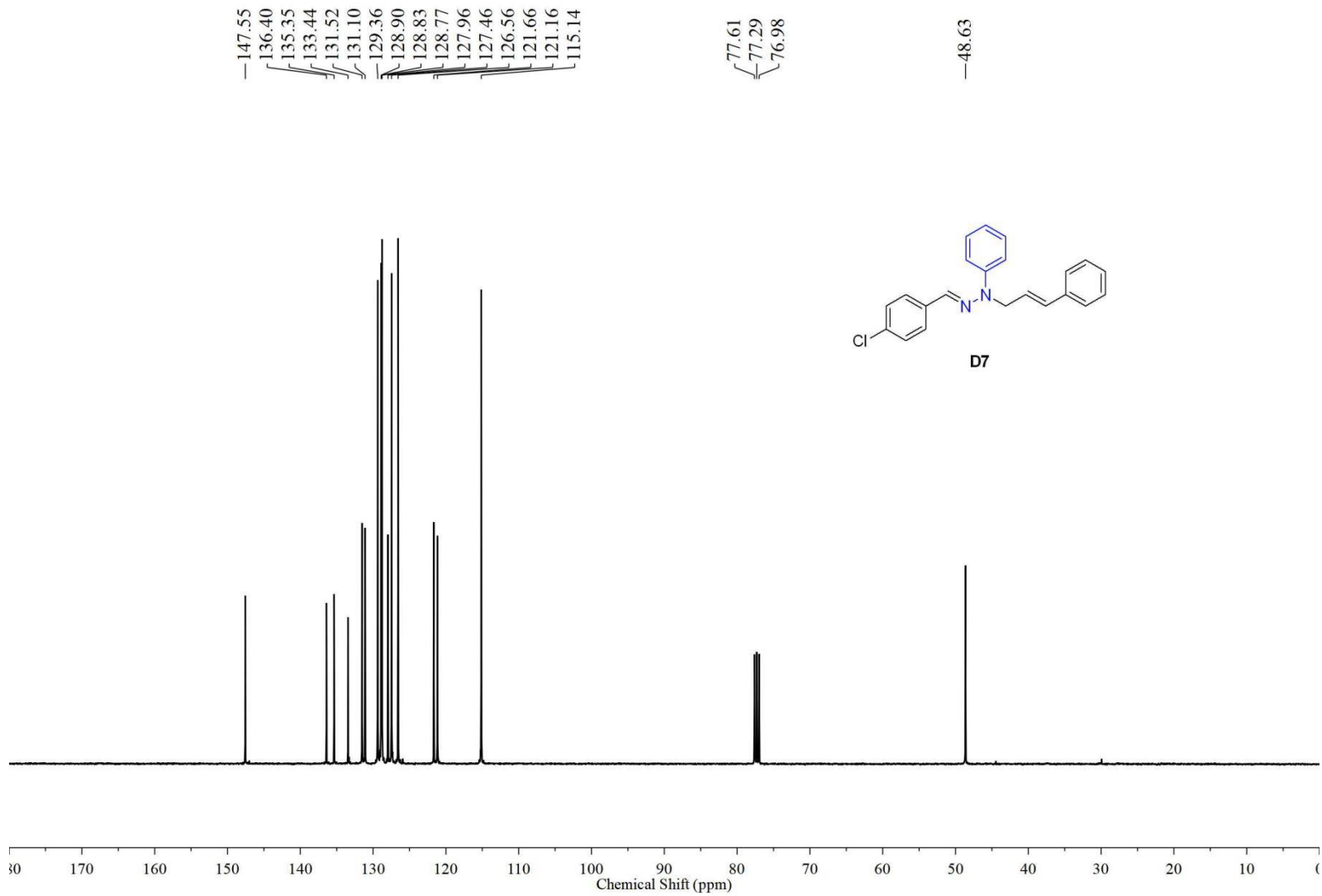
S146

2022-05-26-YY0032-616-LD15.10.fid

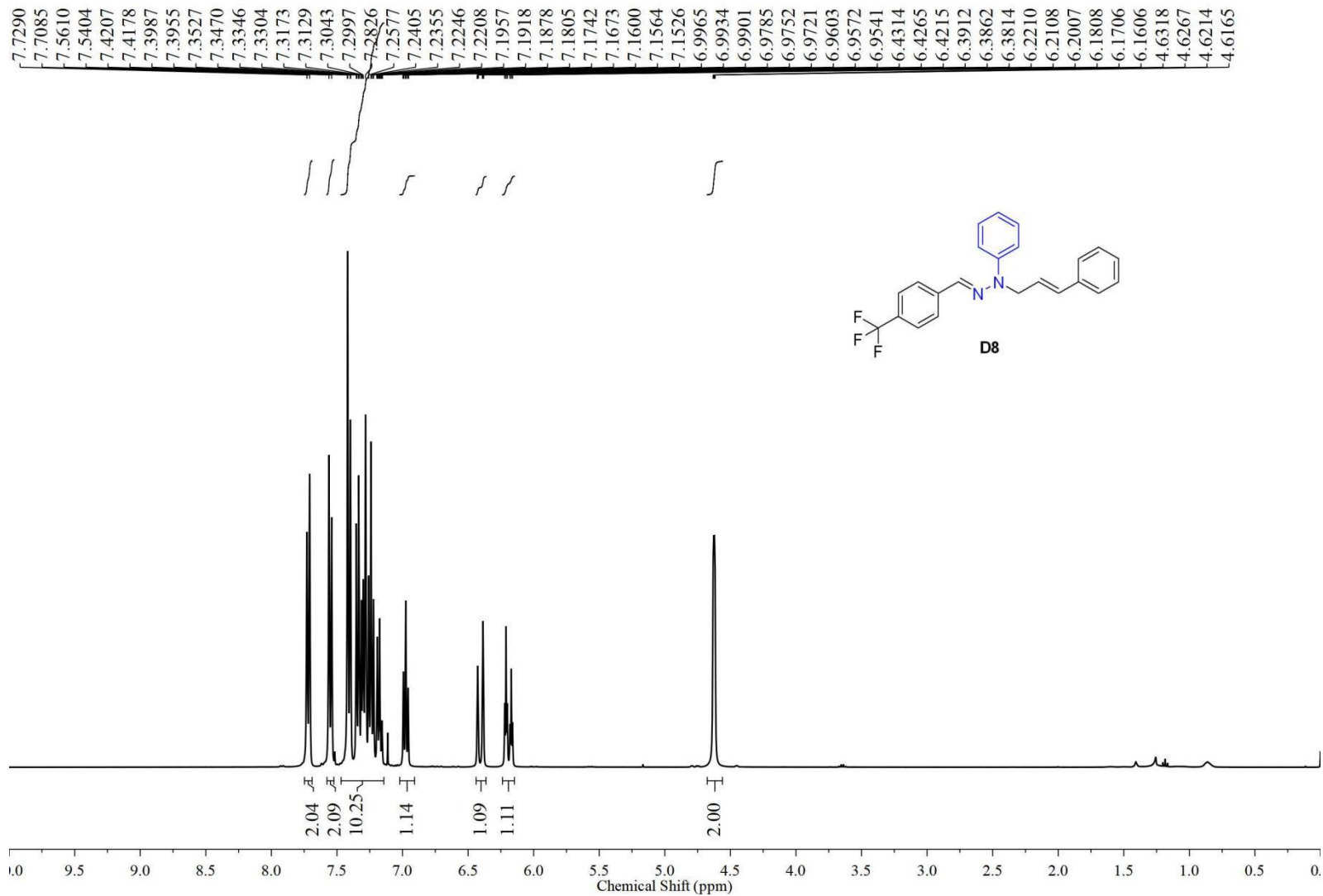


S147

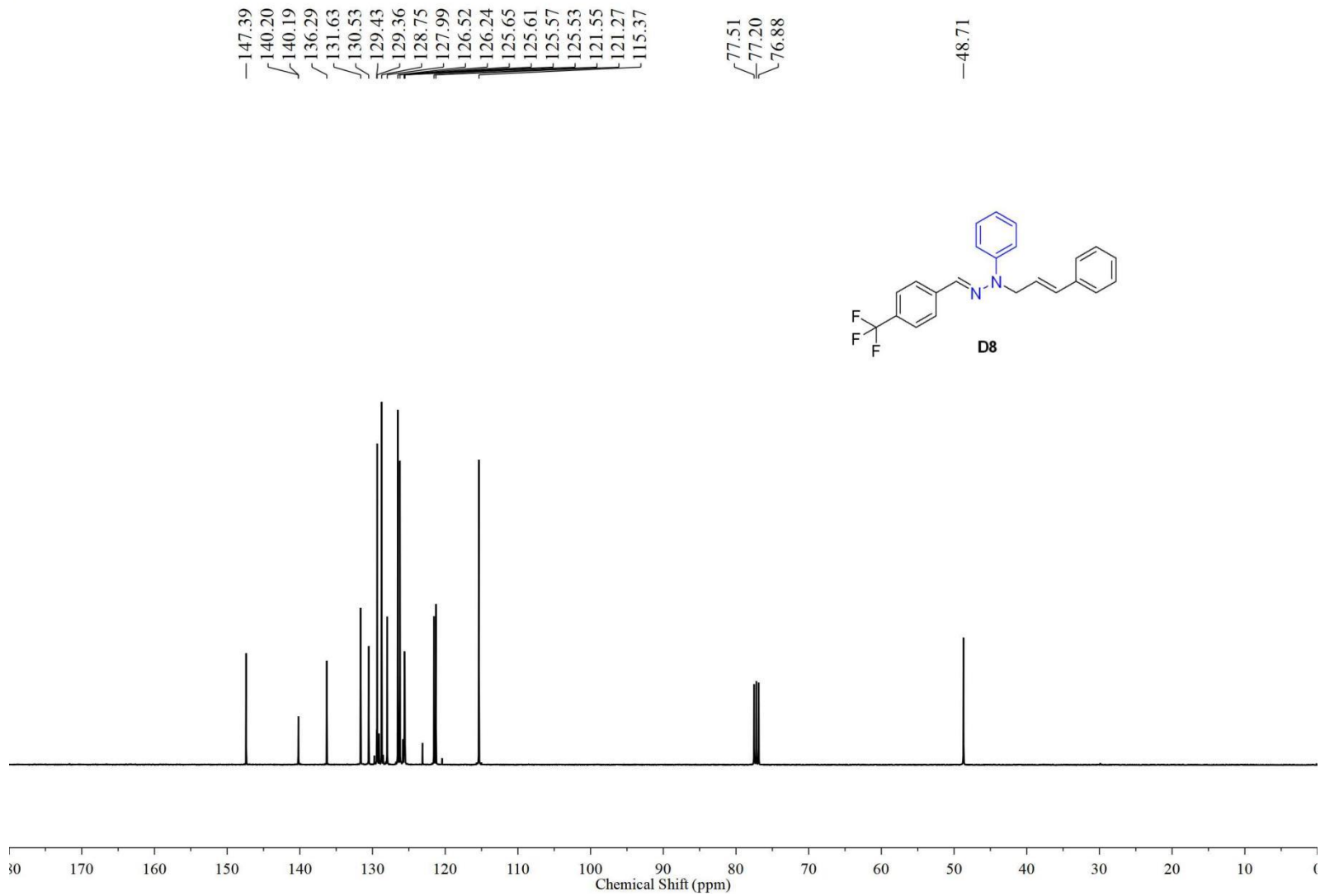
2022-05-26-YY0032-616-LD15.11.fid



2022-05-23-yy0028-616-1d14.10.fid



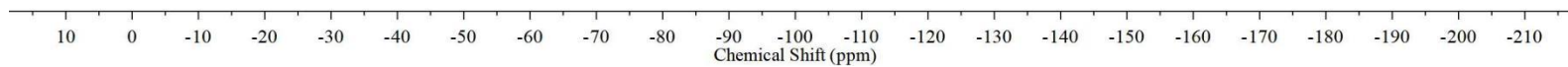
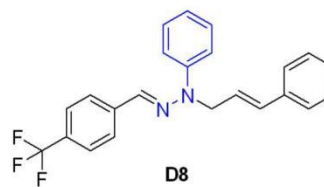
2022-05-23-yy0028-616-1d14.11.fid



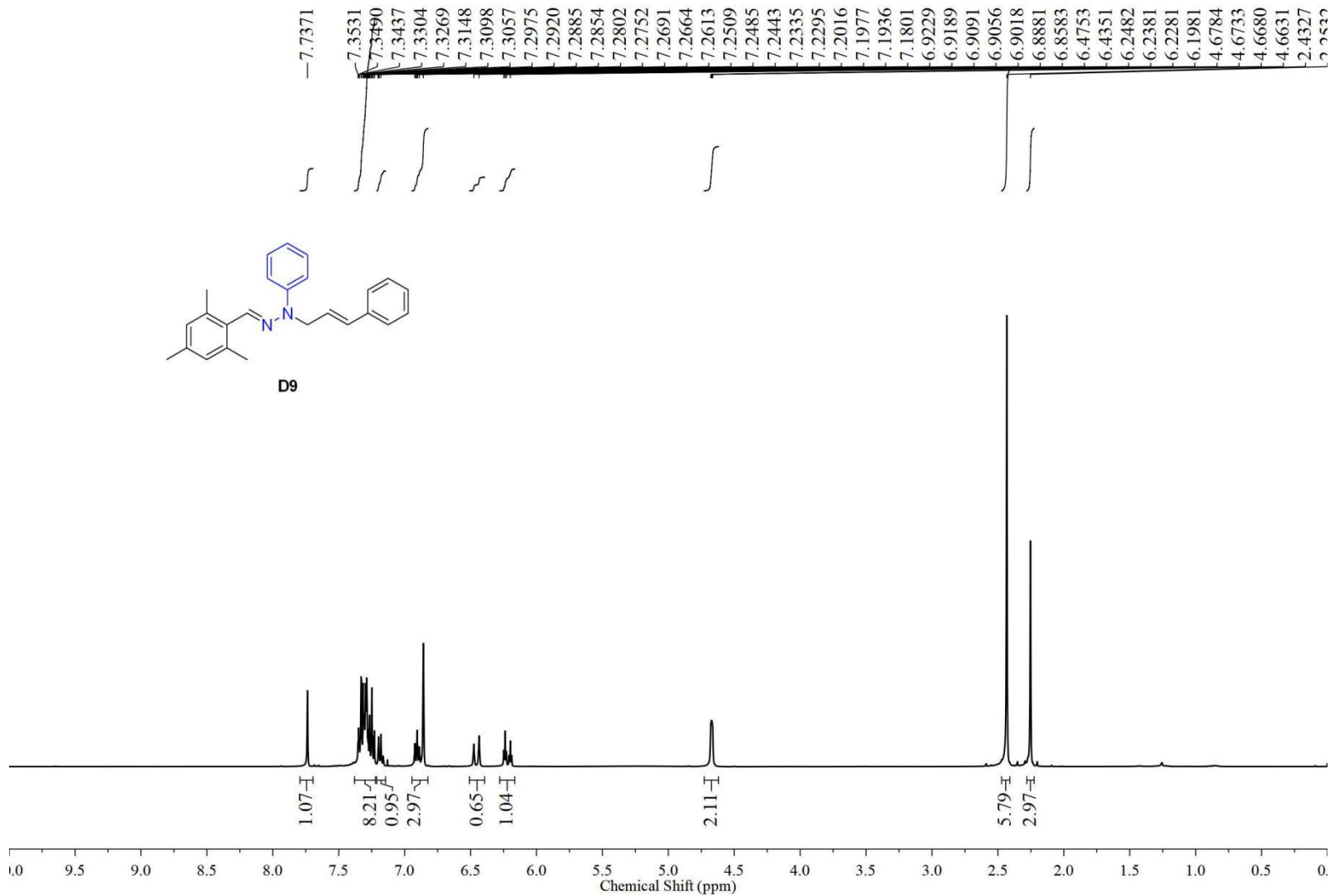
S150

2022-05-23-yy0028-616-1d14.12.fid

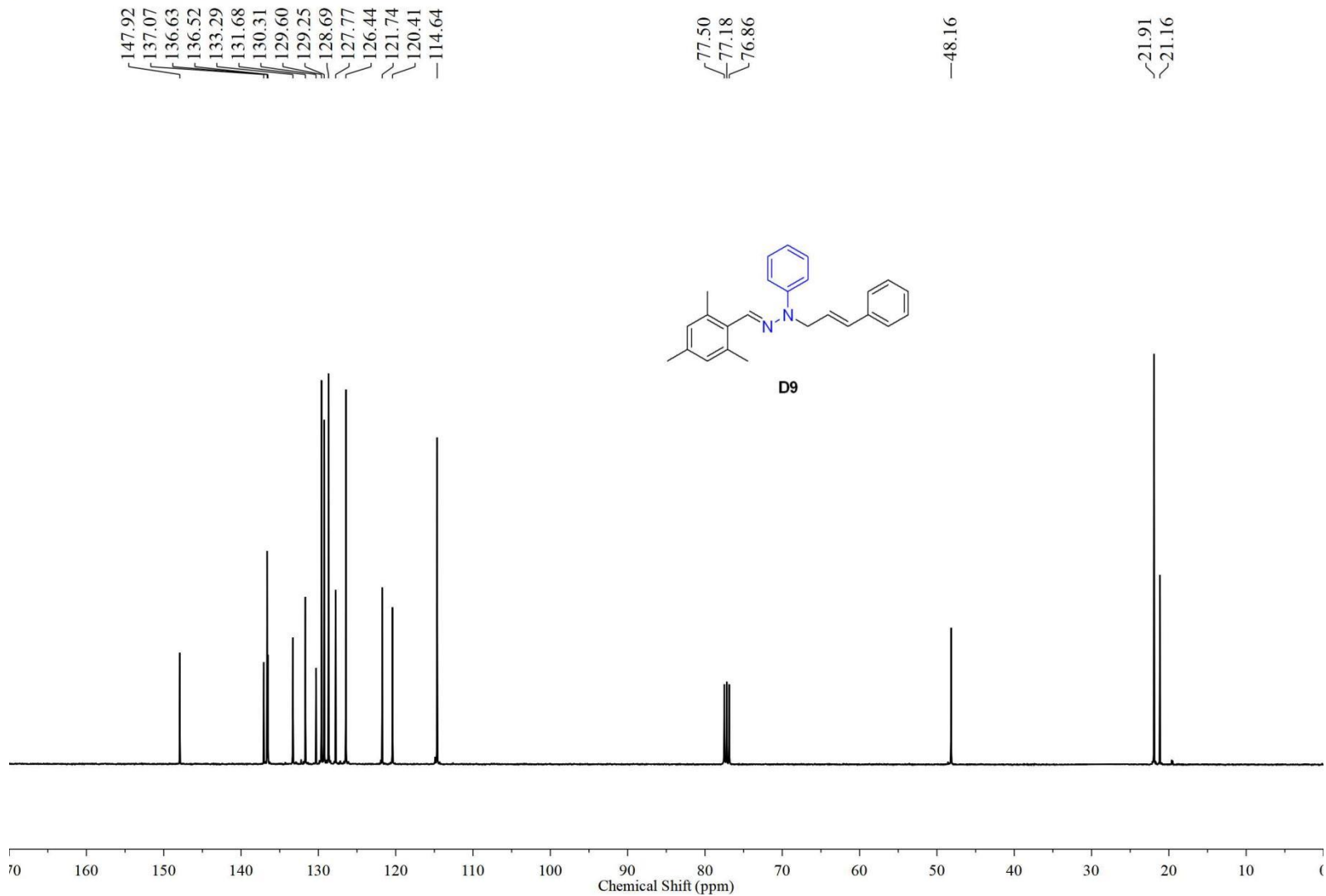
-62.10



S151

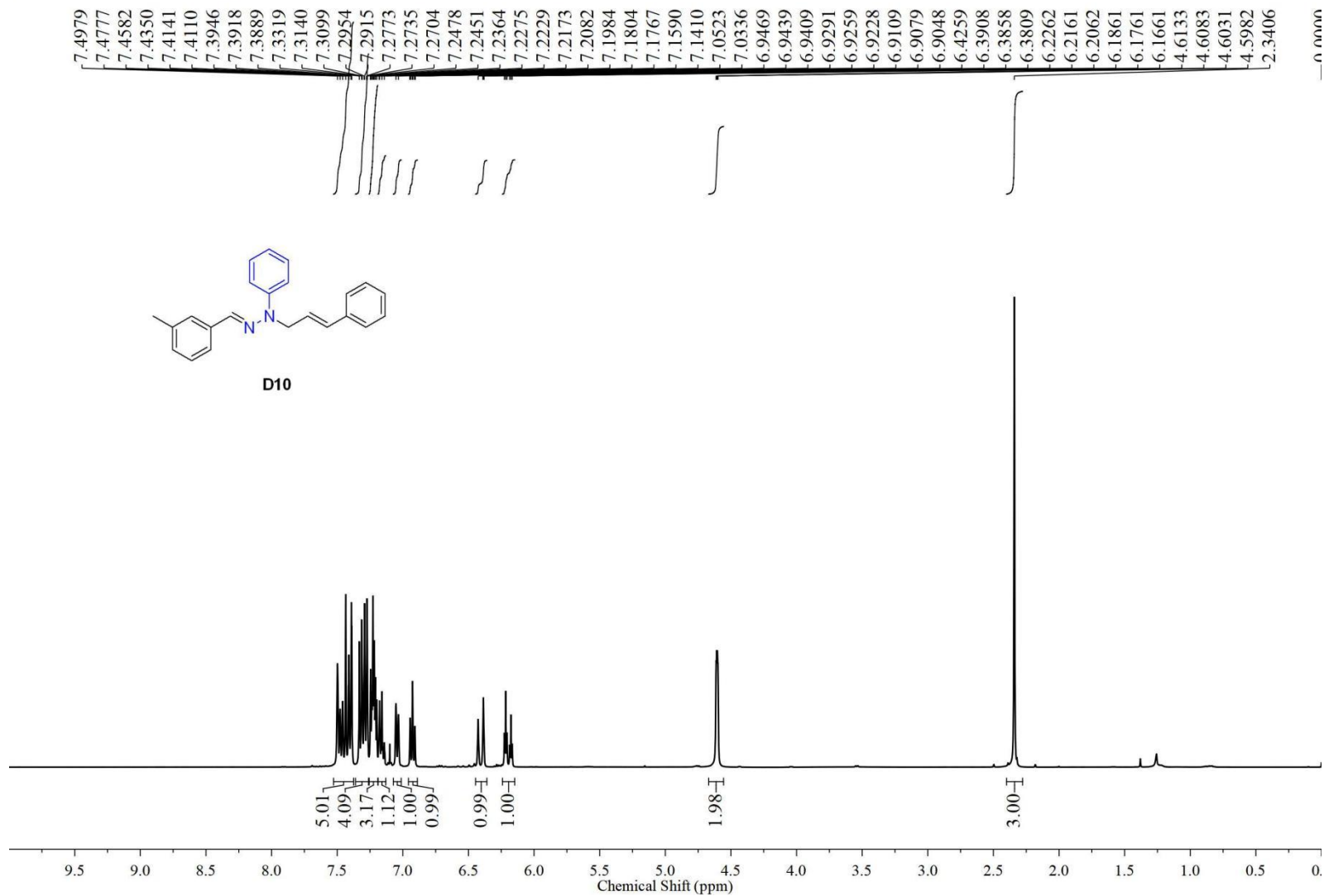


2022-05-20-yy0021-616-d5.11.fid



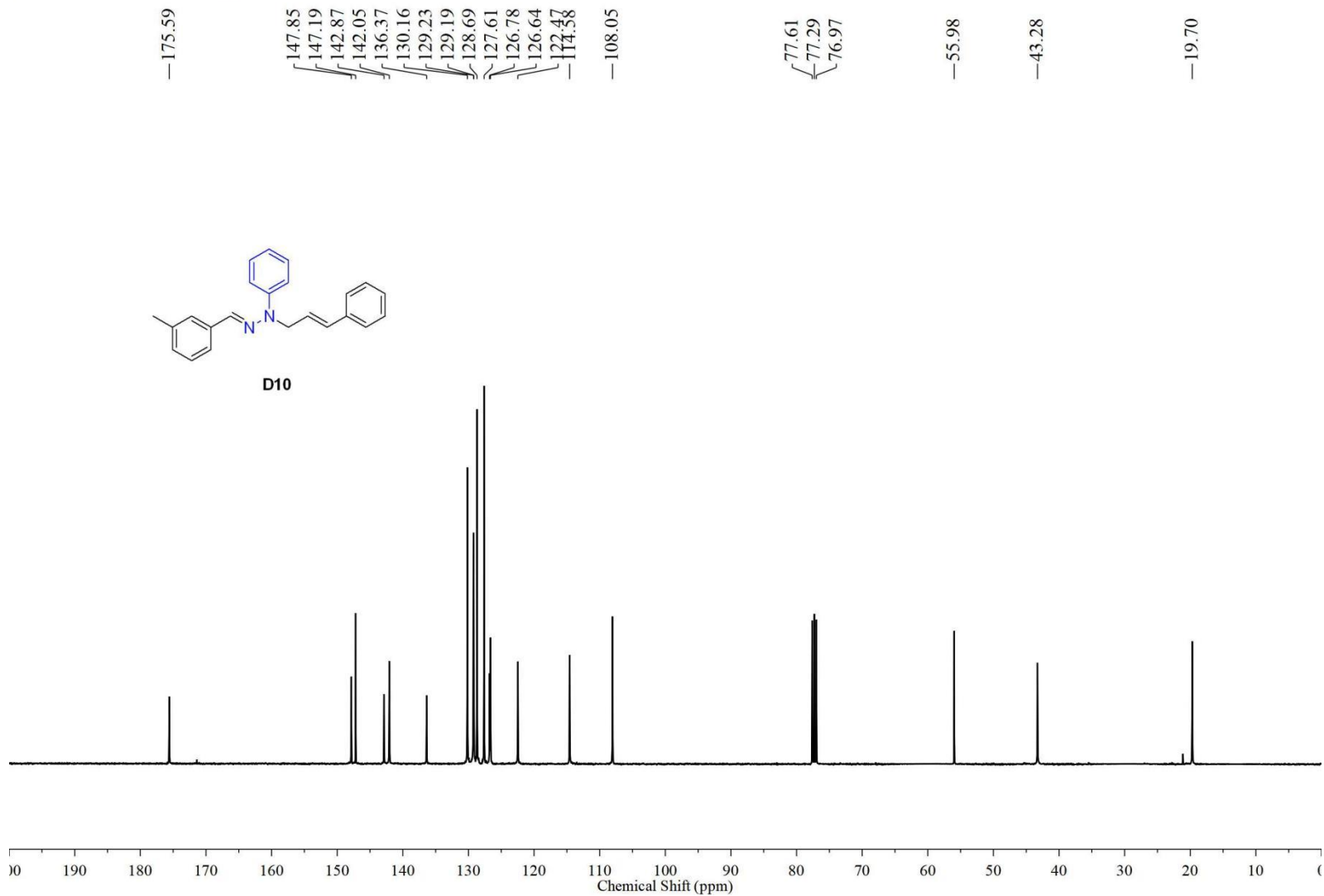
S153

2022-05-18-yy0033-616-d3.10.fid

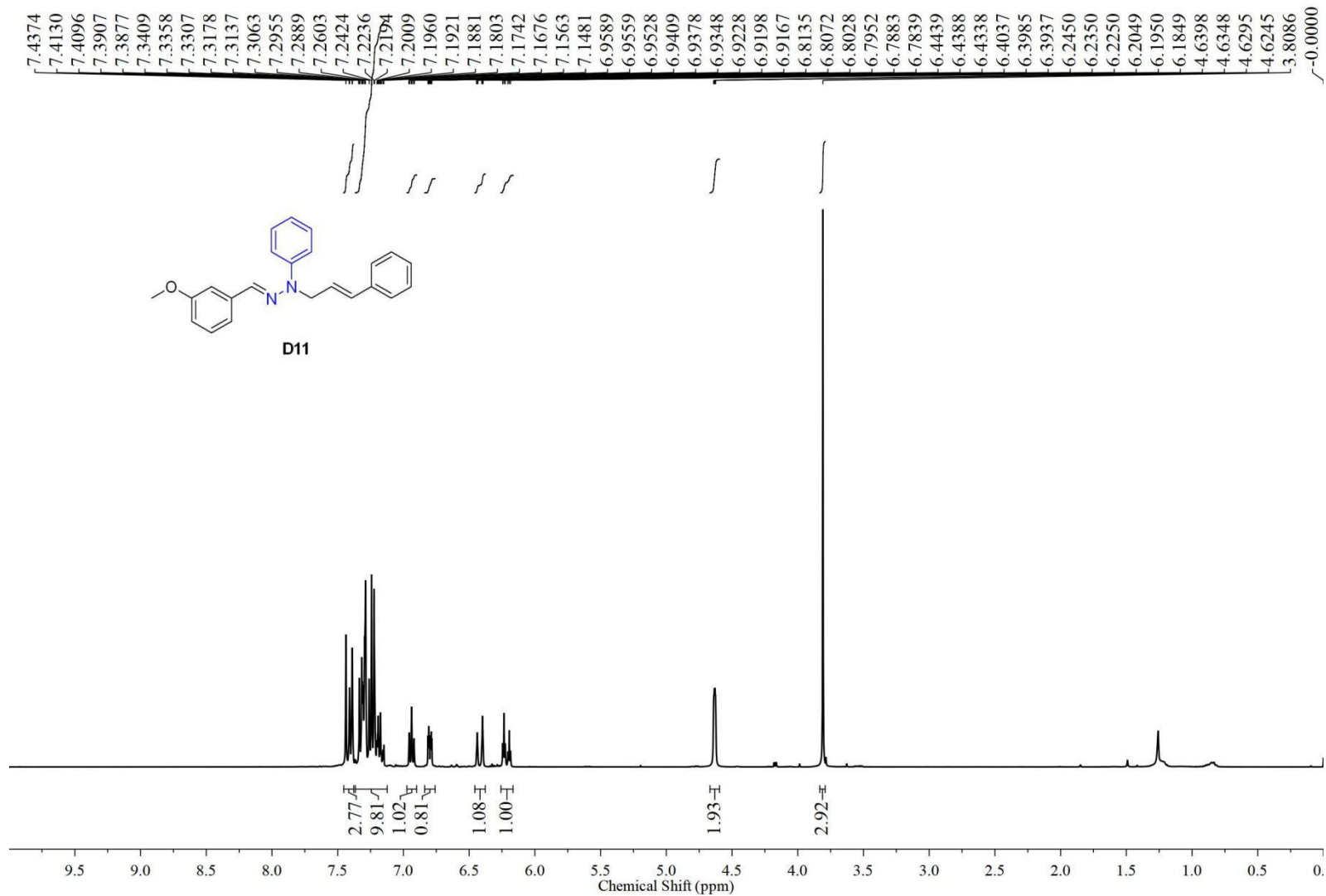


S154

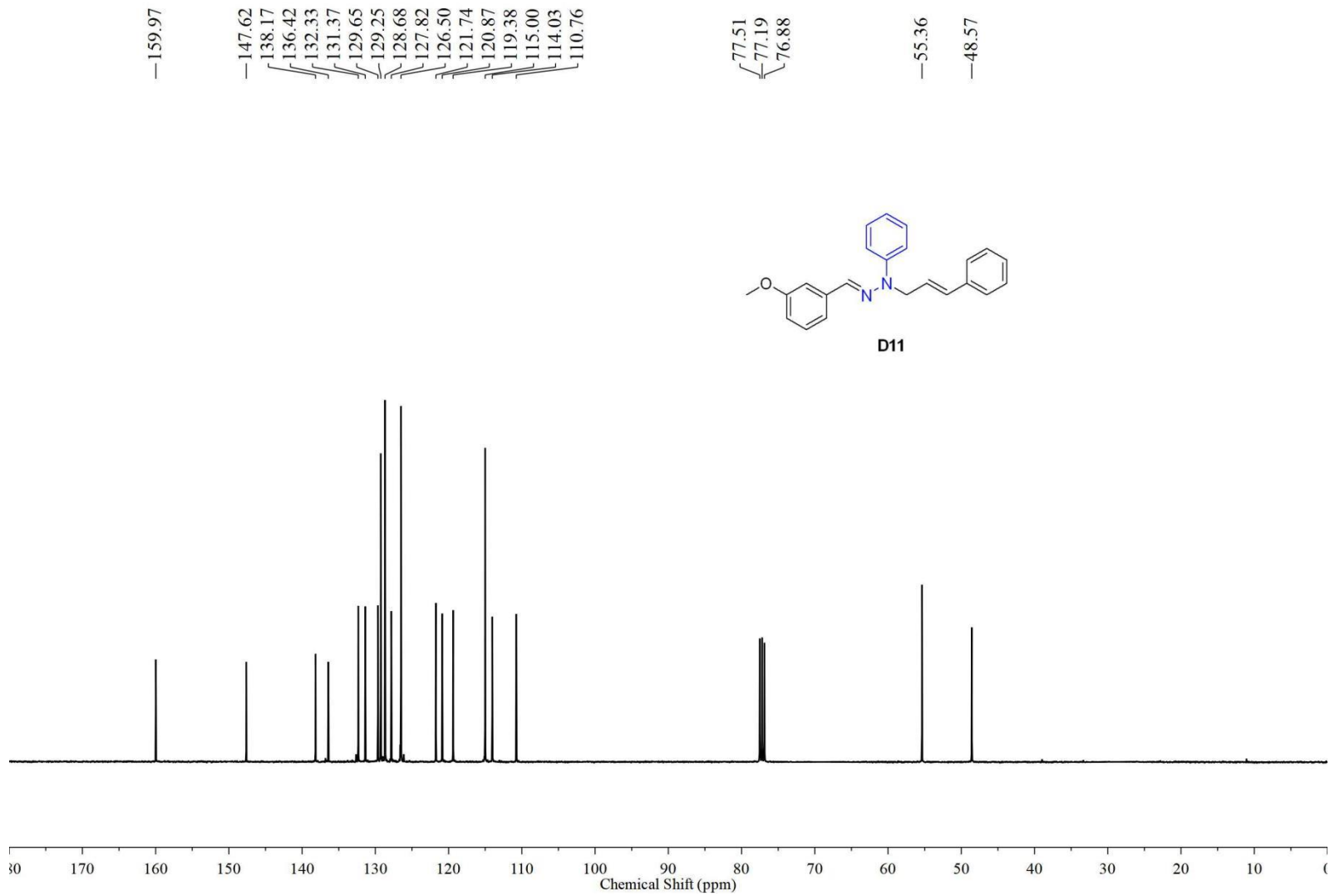
2022-05-20-yy0021-616-d3.10.fid



S155

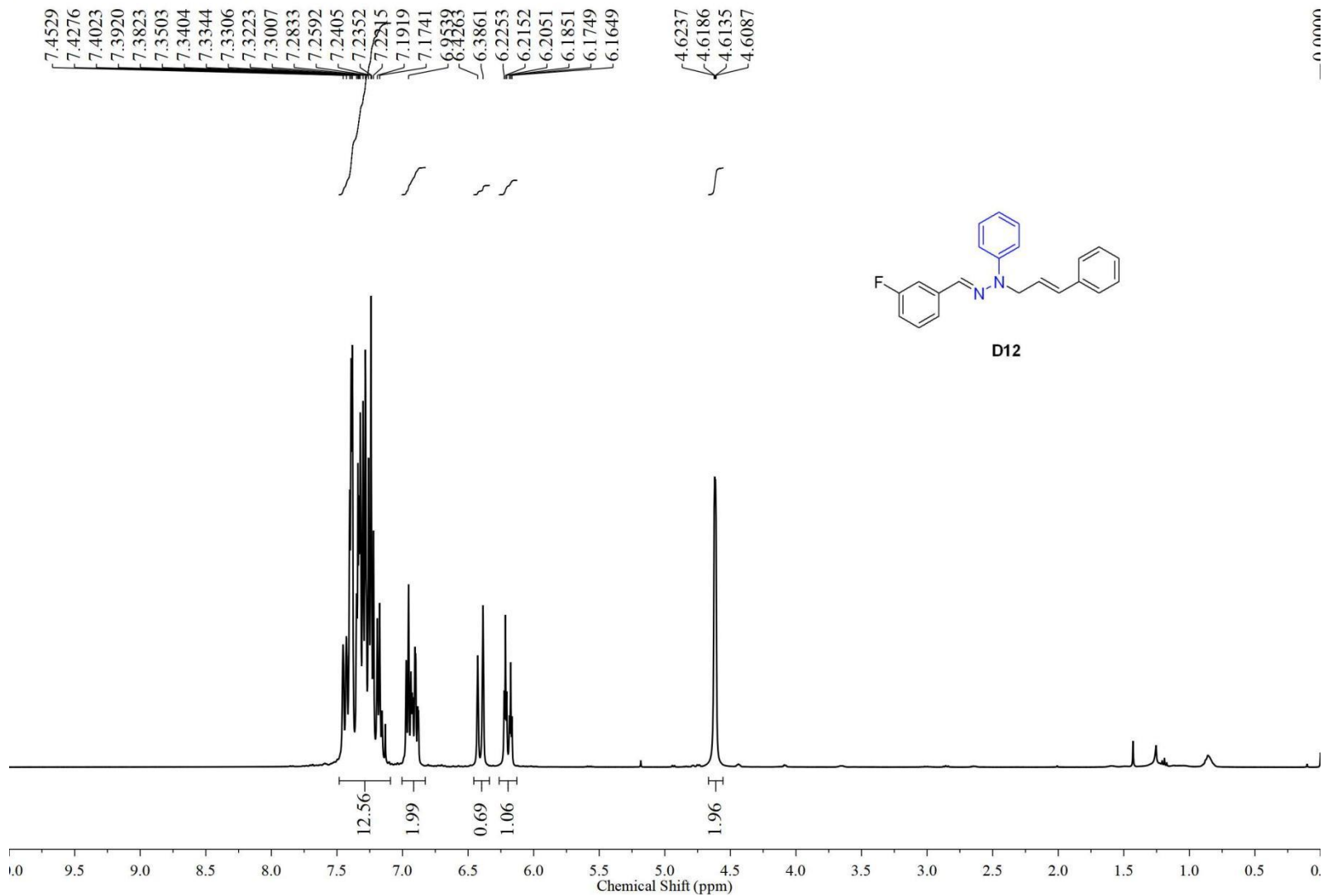


2022-05-23-yy0028-616-1d9. 11. fid

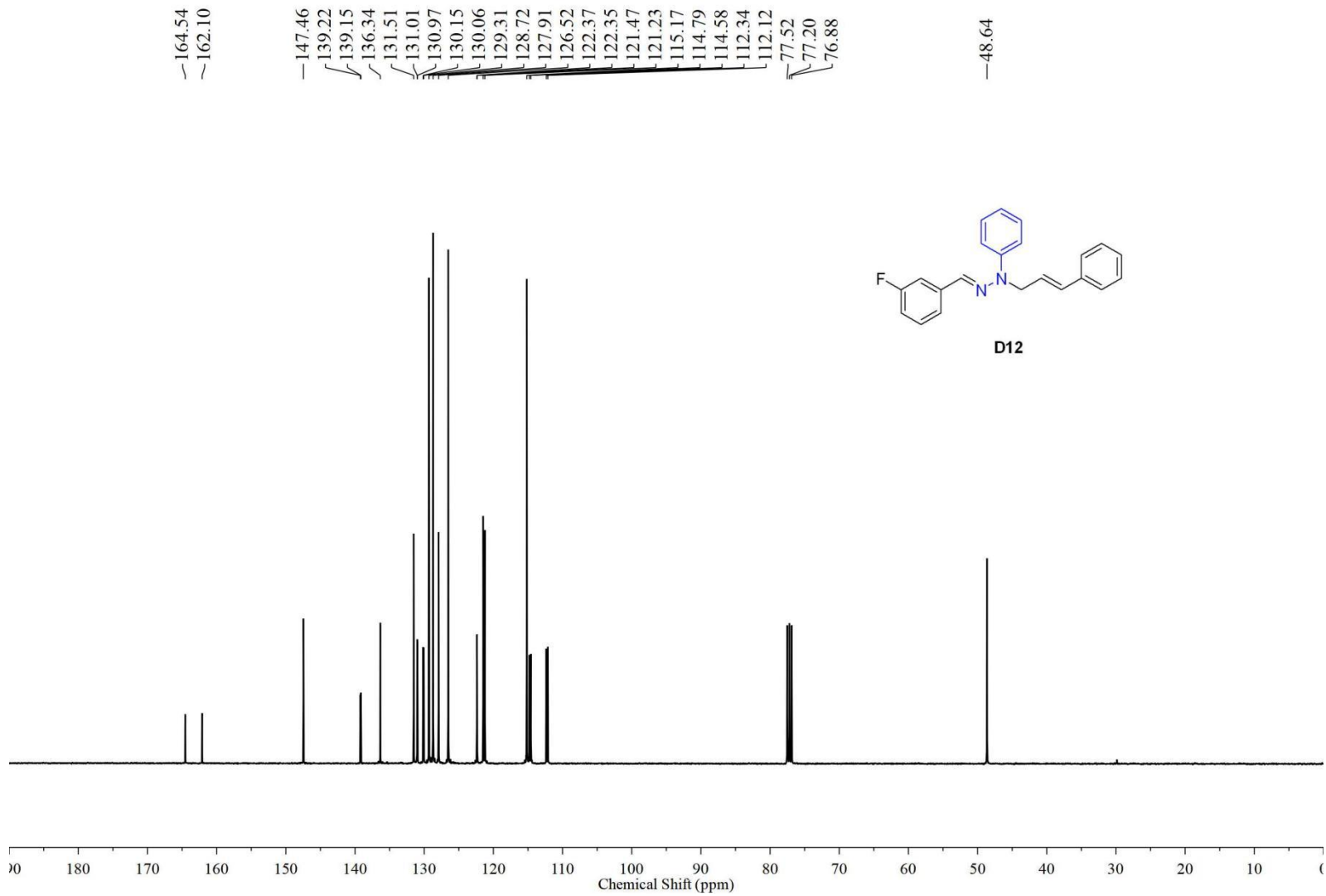


S157

2022-05-23-yy0028-616-1d12.50.fid

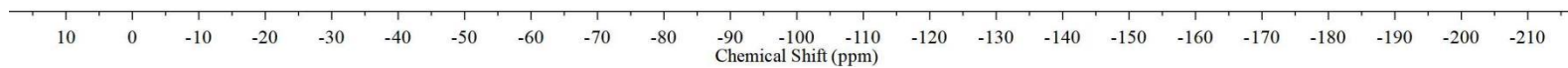
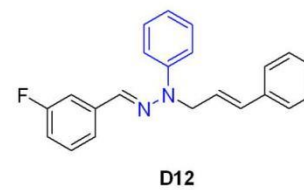


2022-05-23-yy0028-616-1d12.51.fid

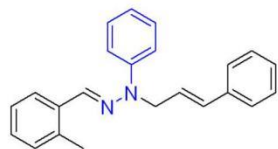
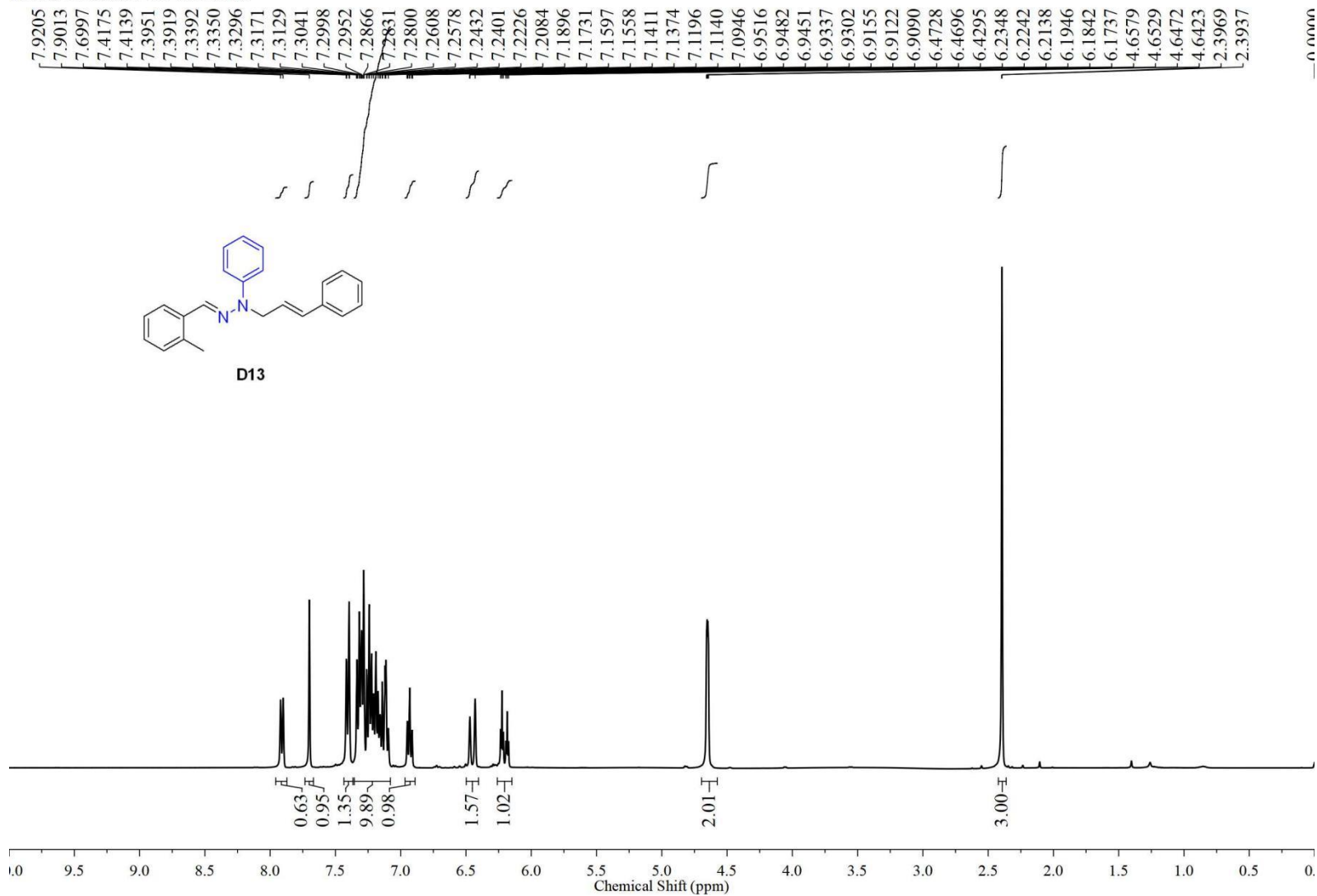


S159

113.14

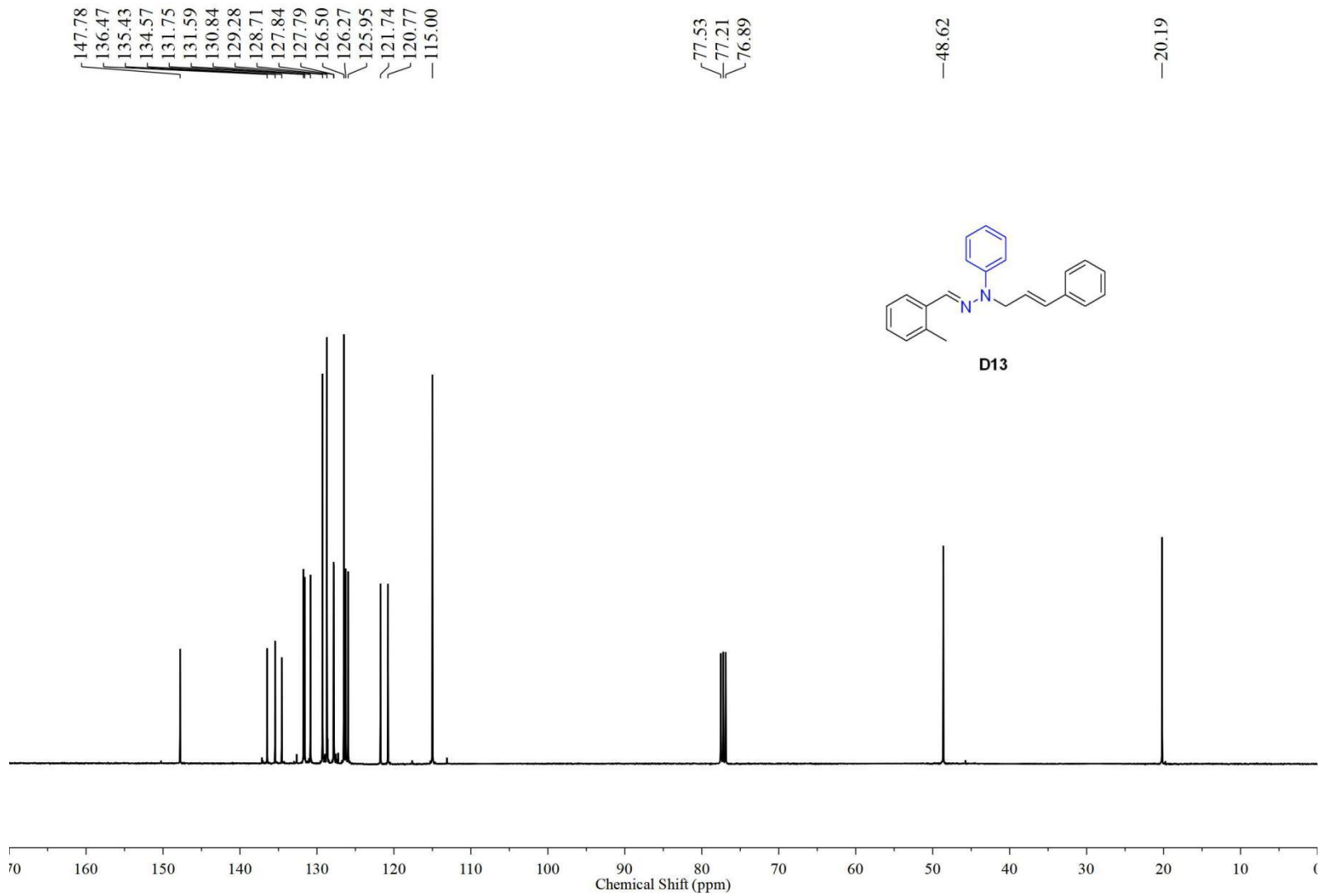


2022-05-20-yy0021-616-d4.10.fid

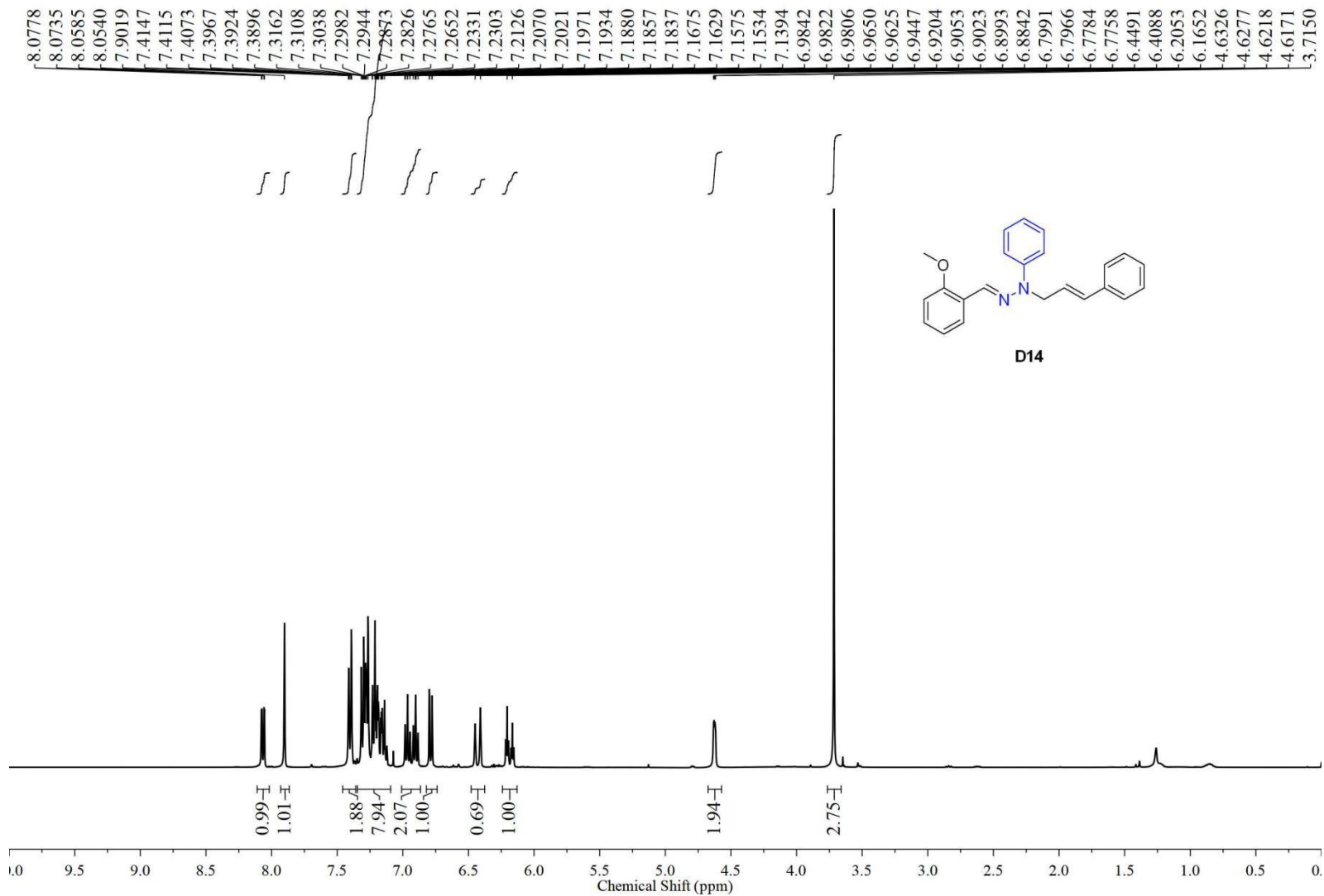


D13

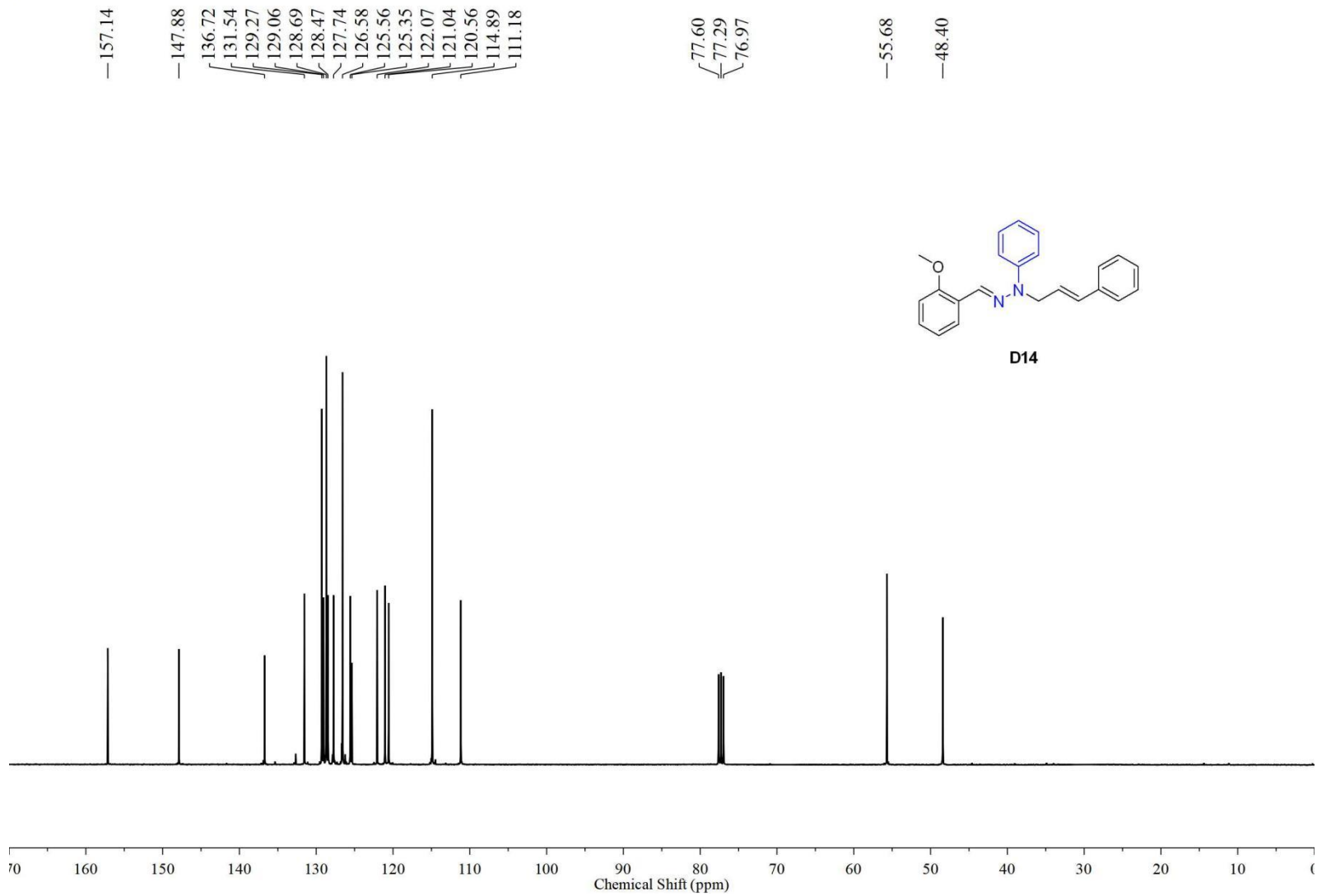
2022-05-20-yy0021-616-d4.11.fid



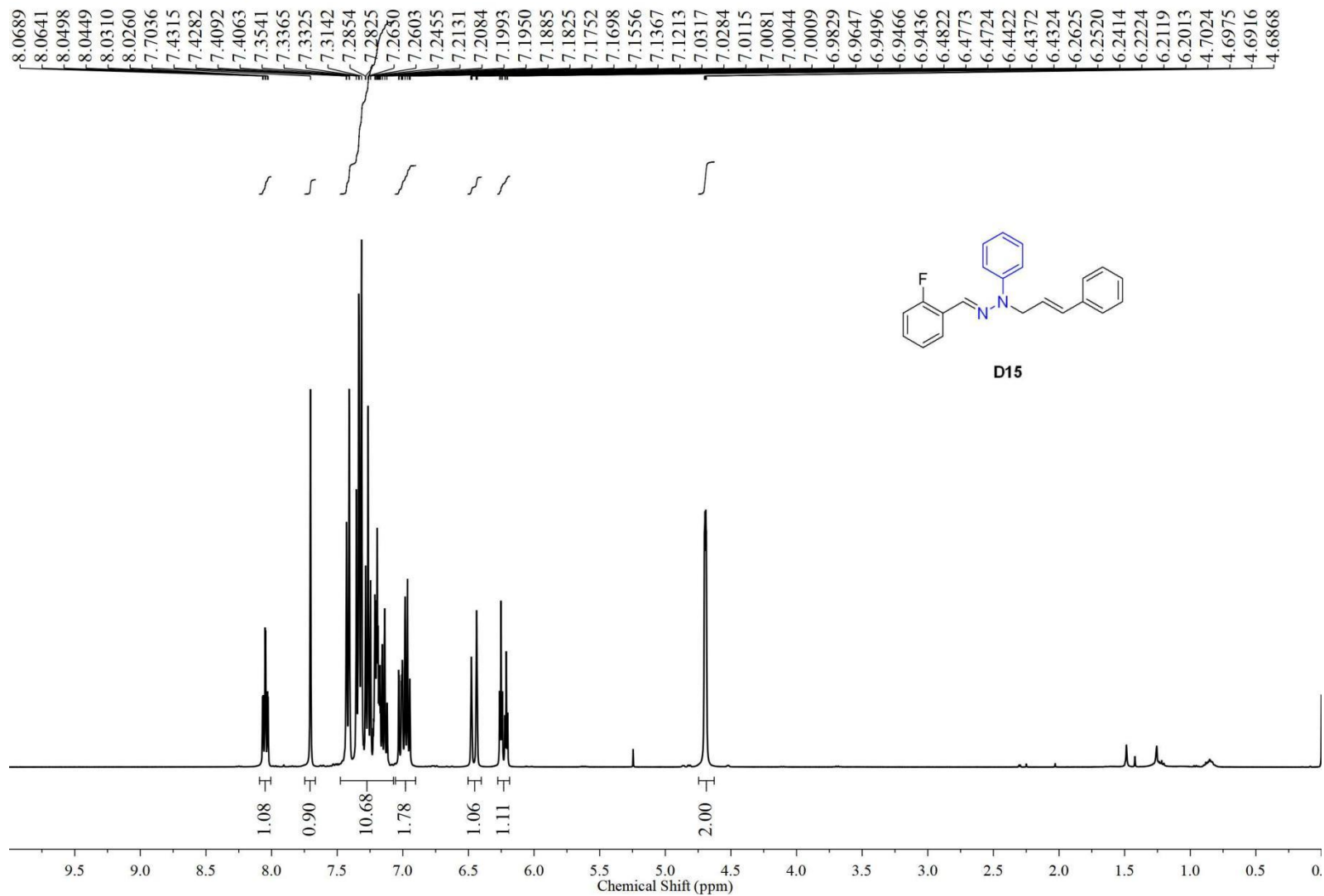
2022-05-20-yy0028-616-d10. 10. fid



2022-05-20-yy0028-616-d10. 11. fid

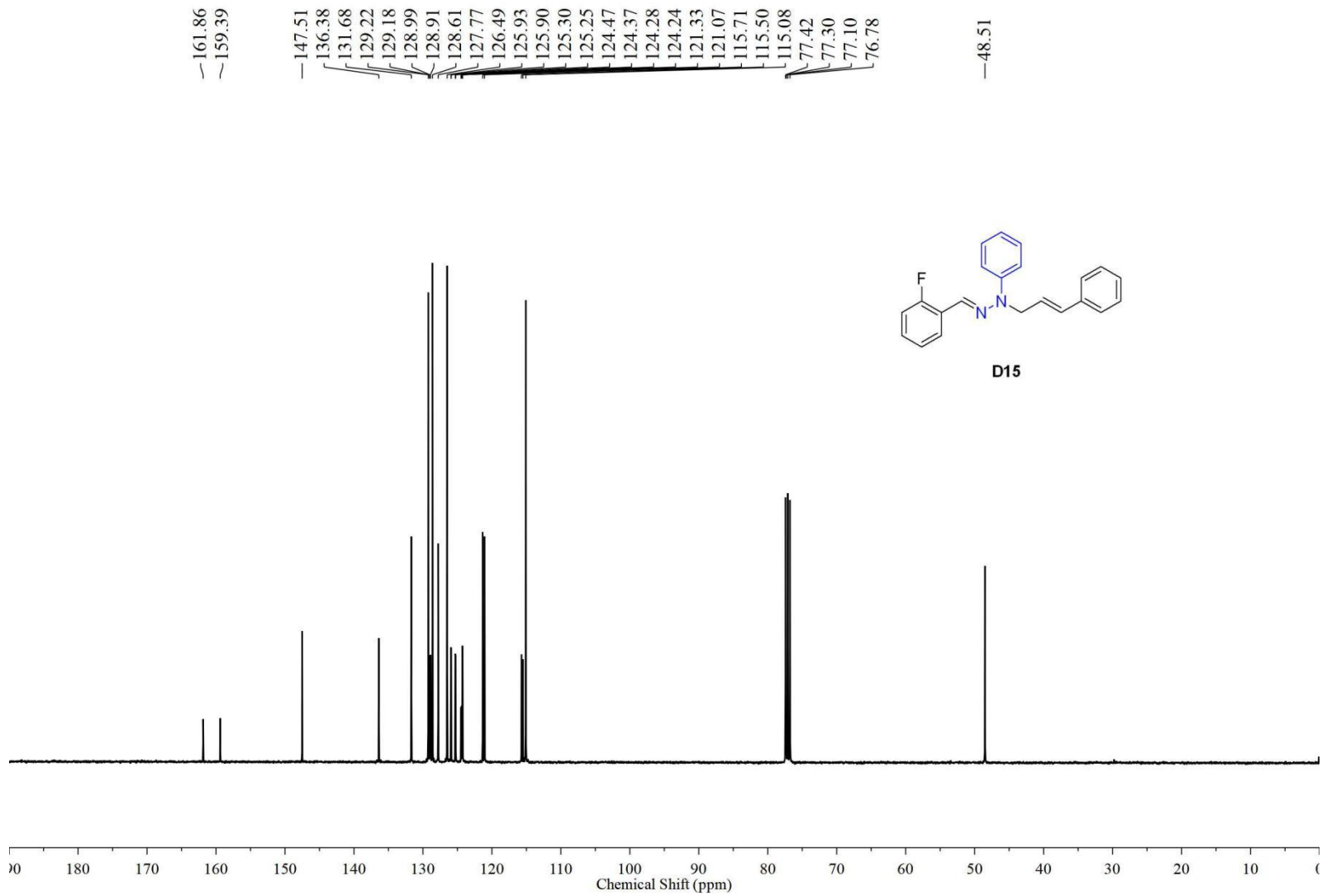


2022-05-23-yy0028-616-1d13.10.fid



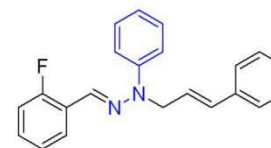
S165

2022-05-23-yy0028-616-1d13.11.fid

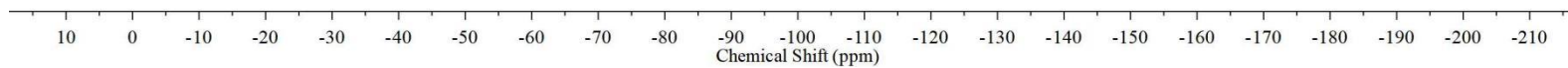


S166

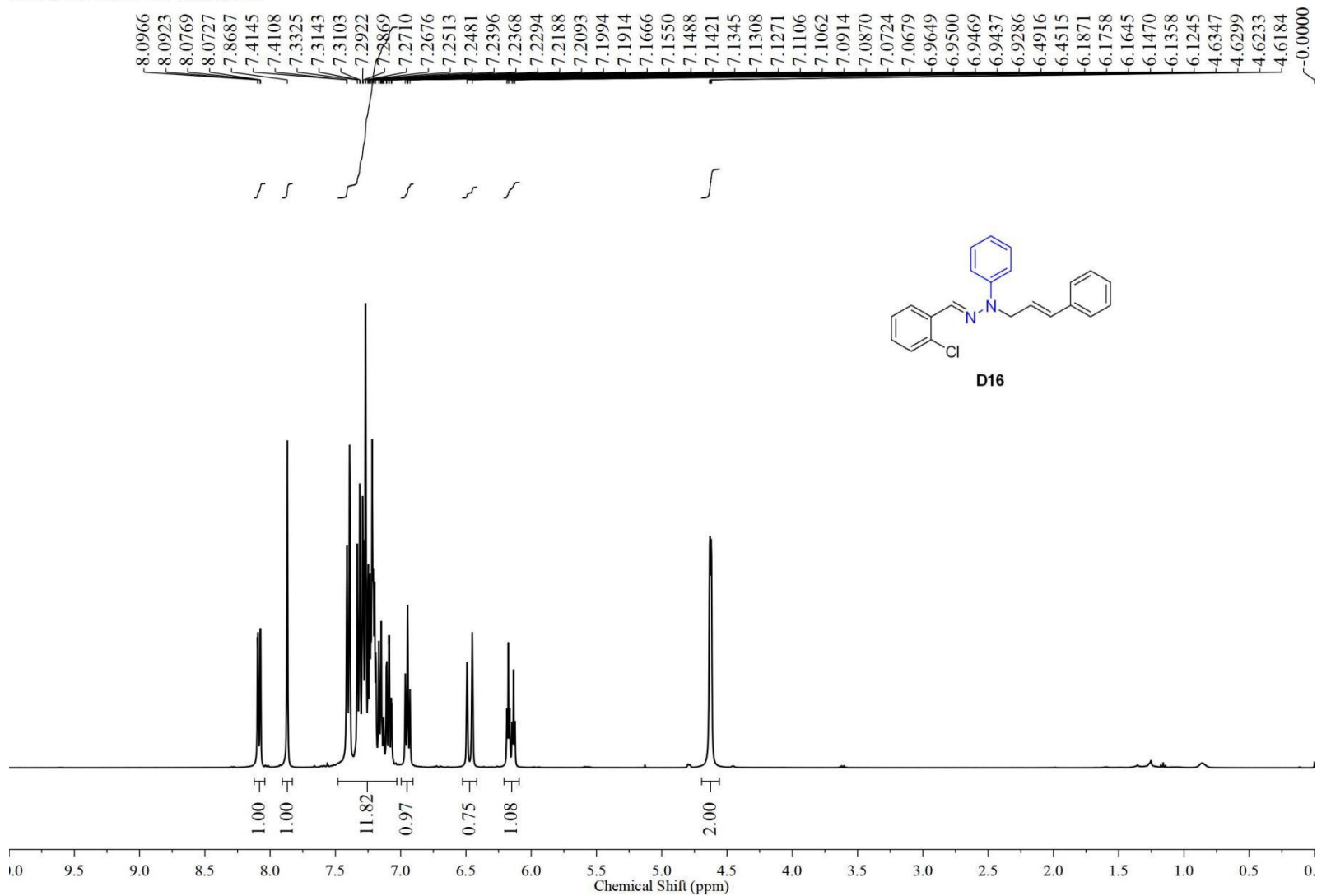
--122.49



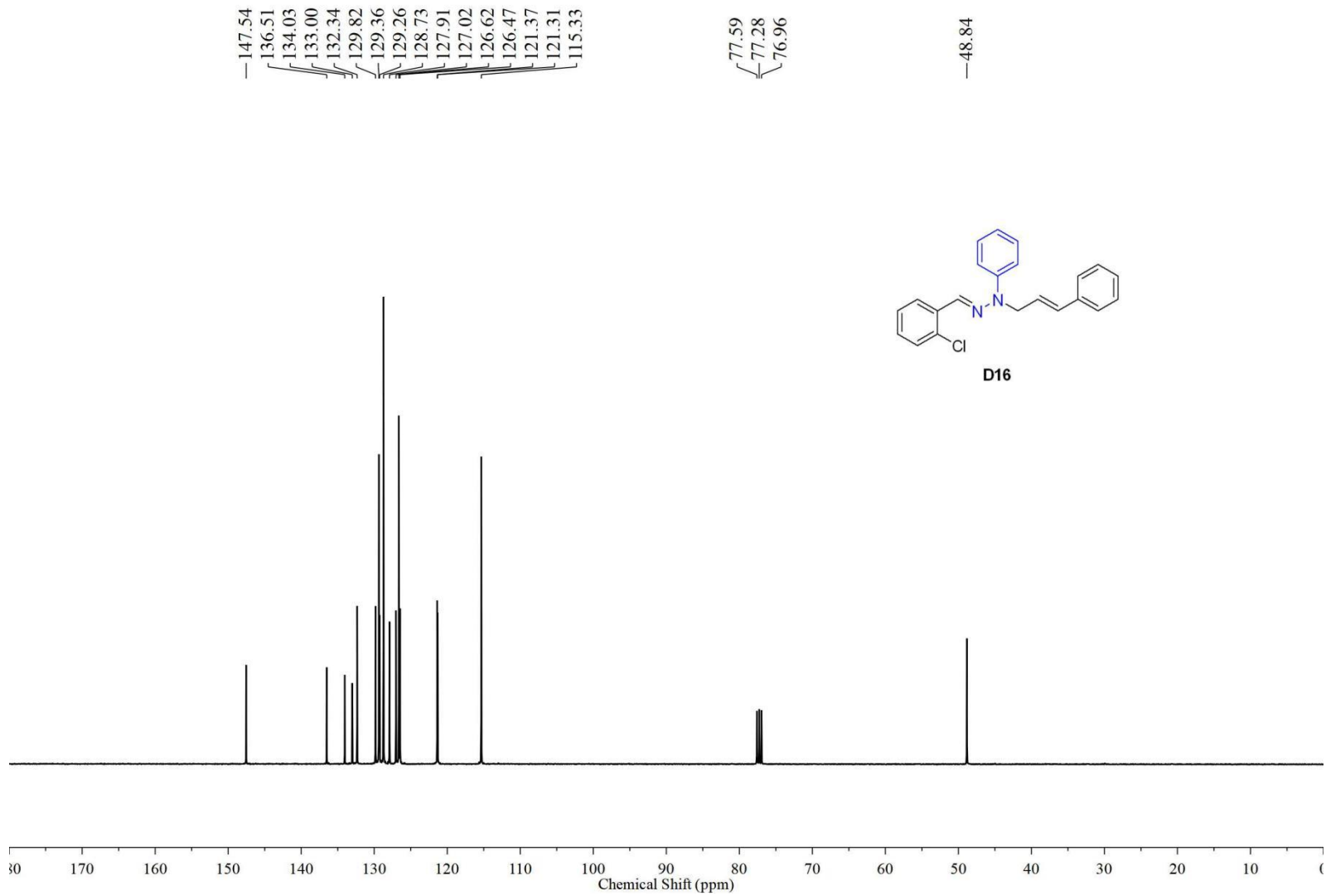
D15



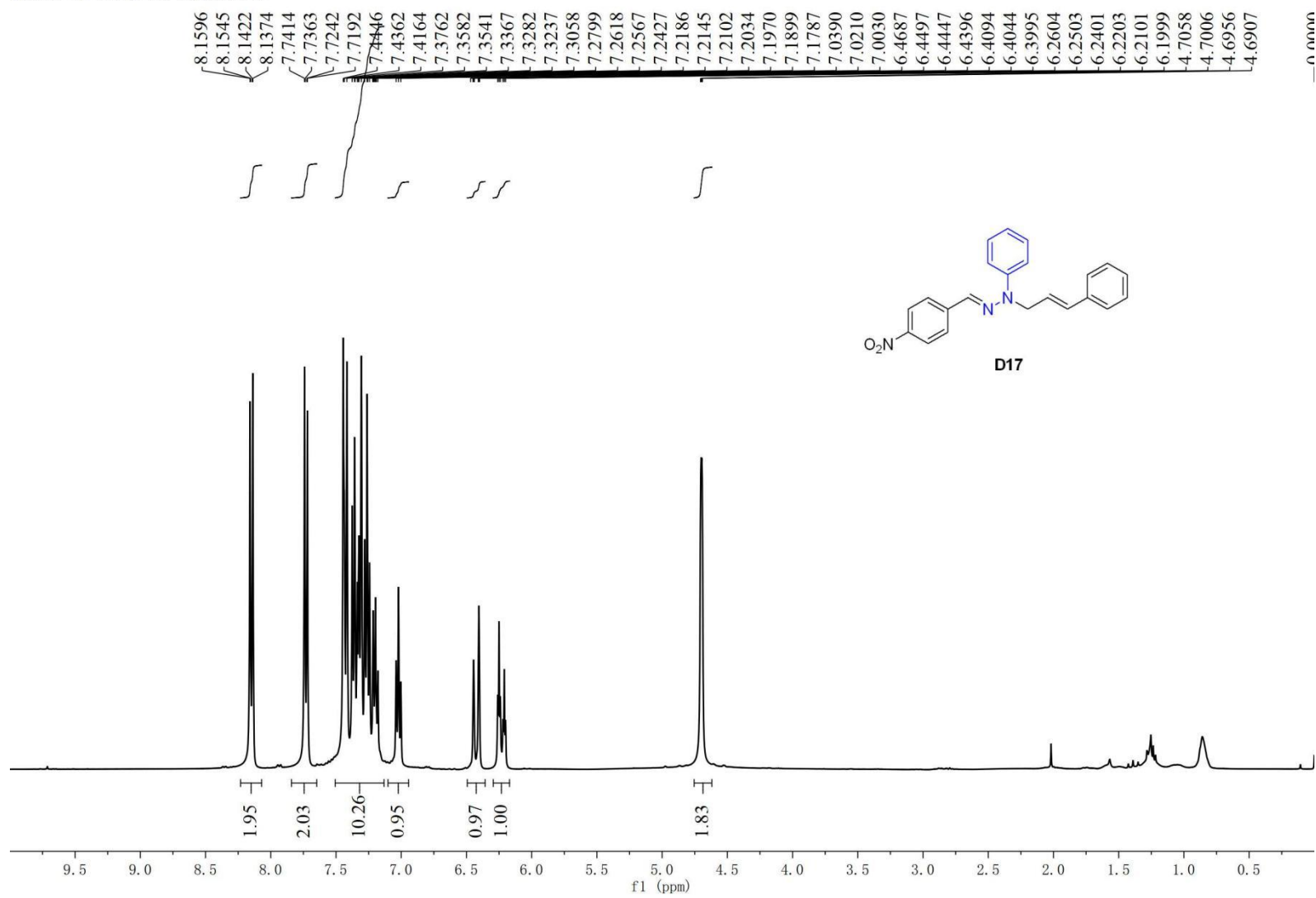
2022-05-26-YY0032-616-LD16.10.fid



2022-05-26-YY0032-616-LD16.11.fid

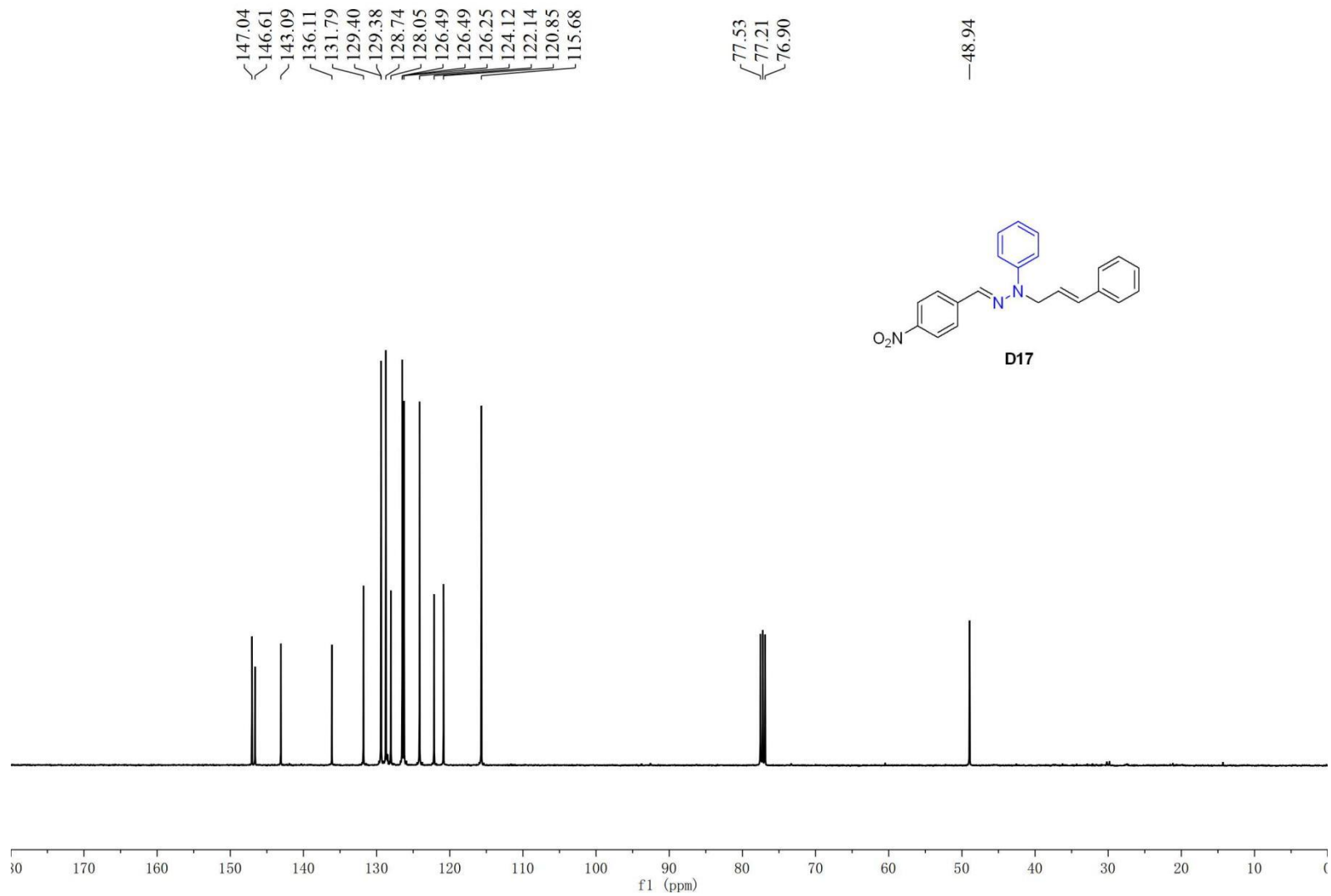


2022-05-31-YY0016-616-LD23.10.fid



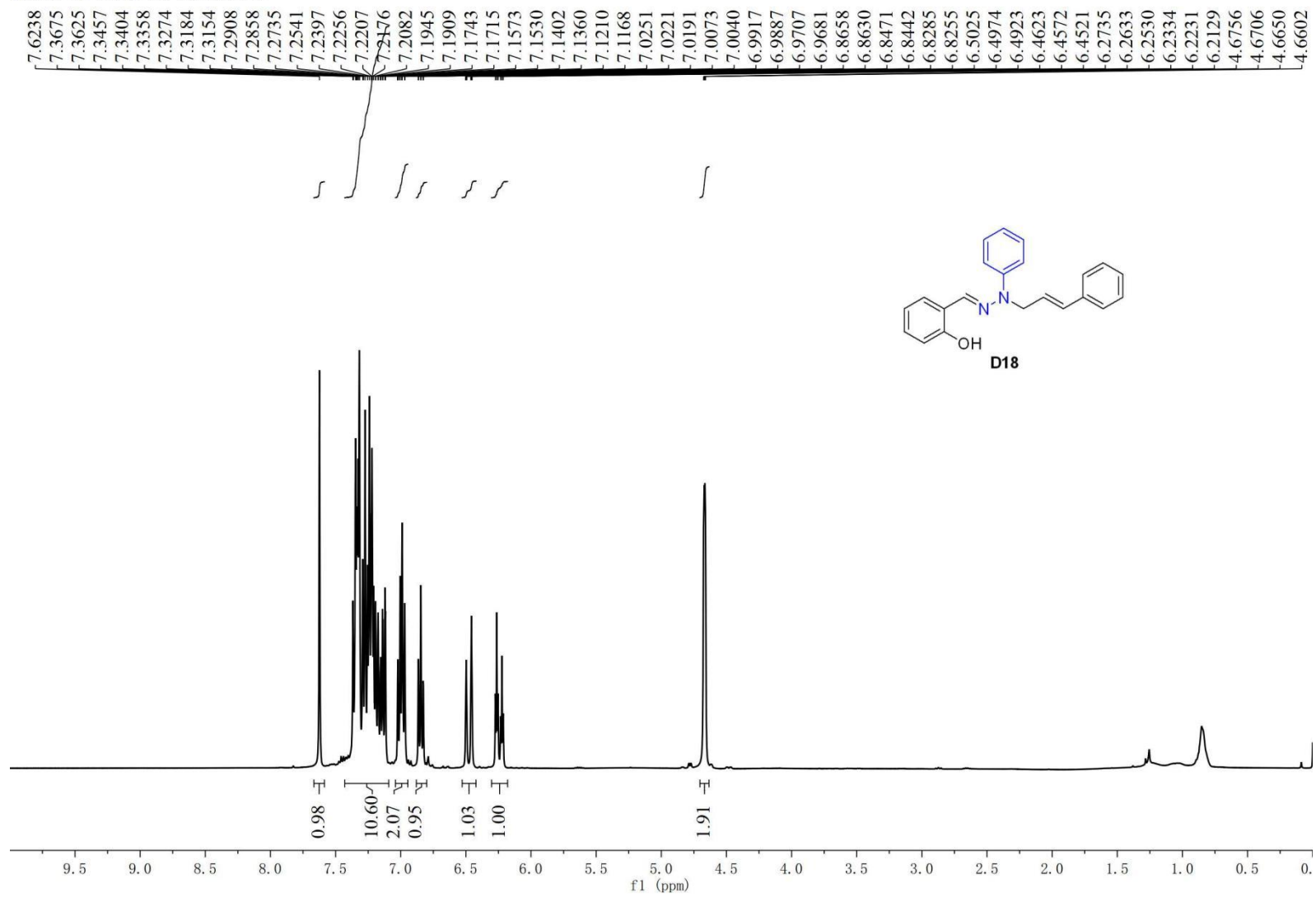
S170

2022-06-01 YY0003 616-1-D23.10.fid

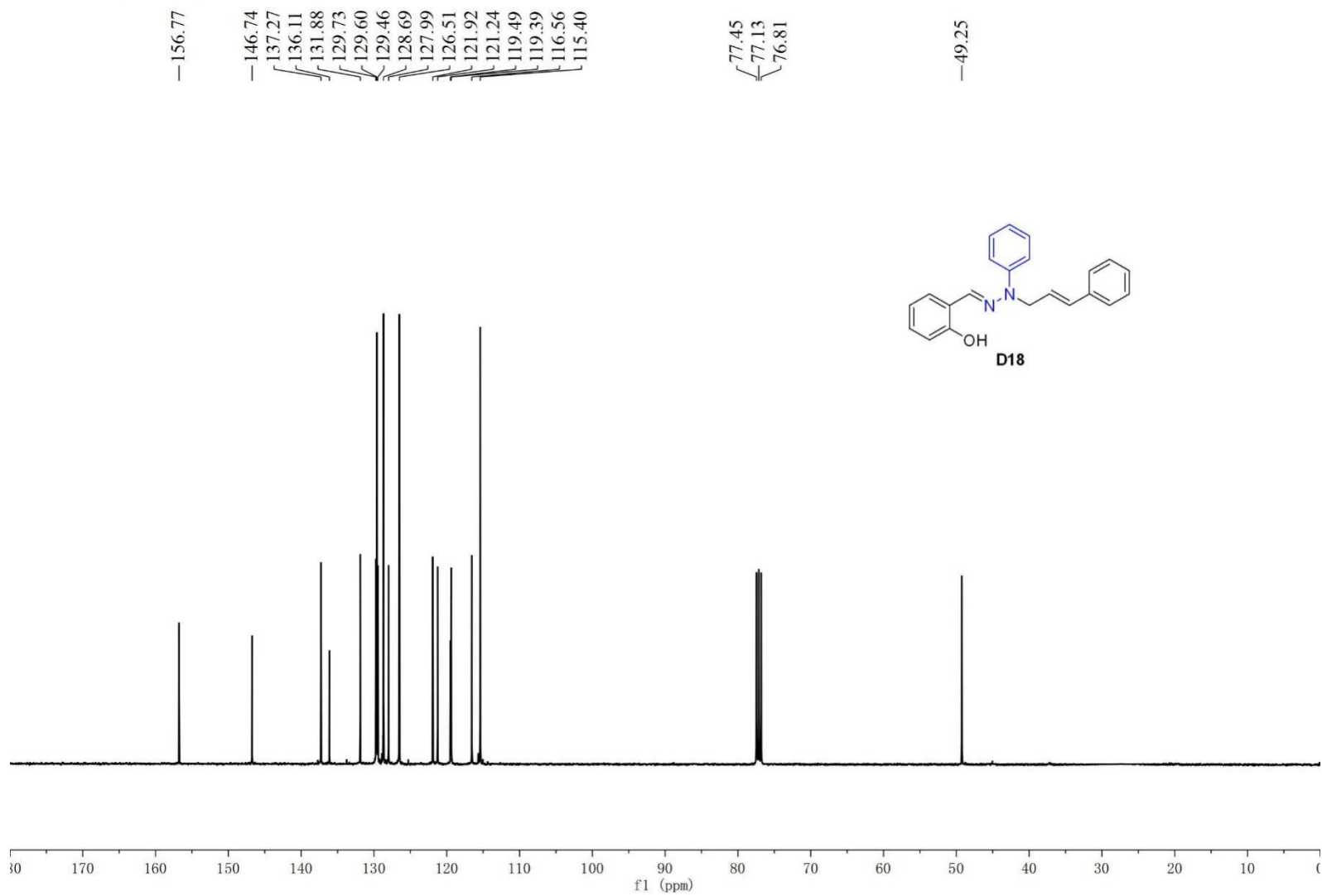


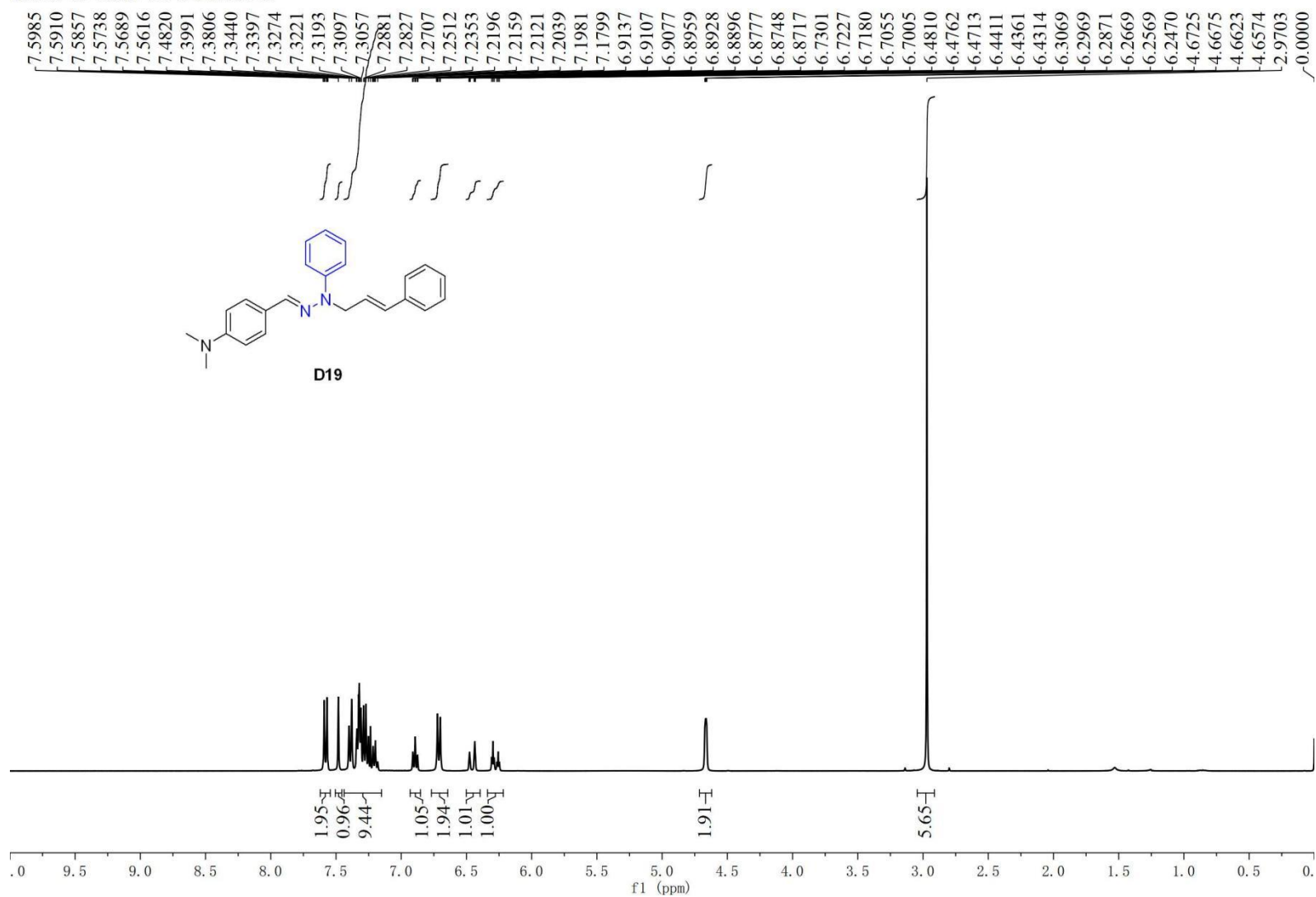
S171

2022-05-31-YY0016-616-LD22.10.fid

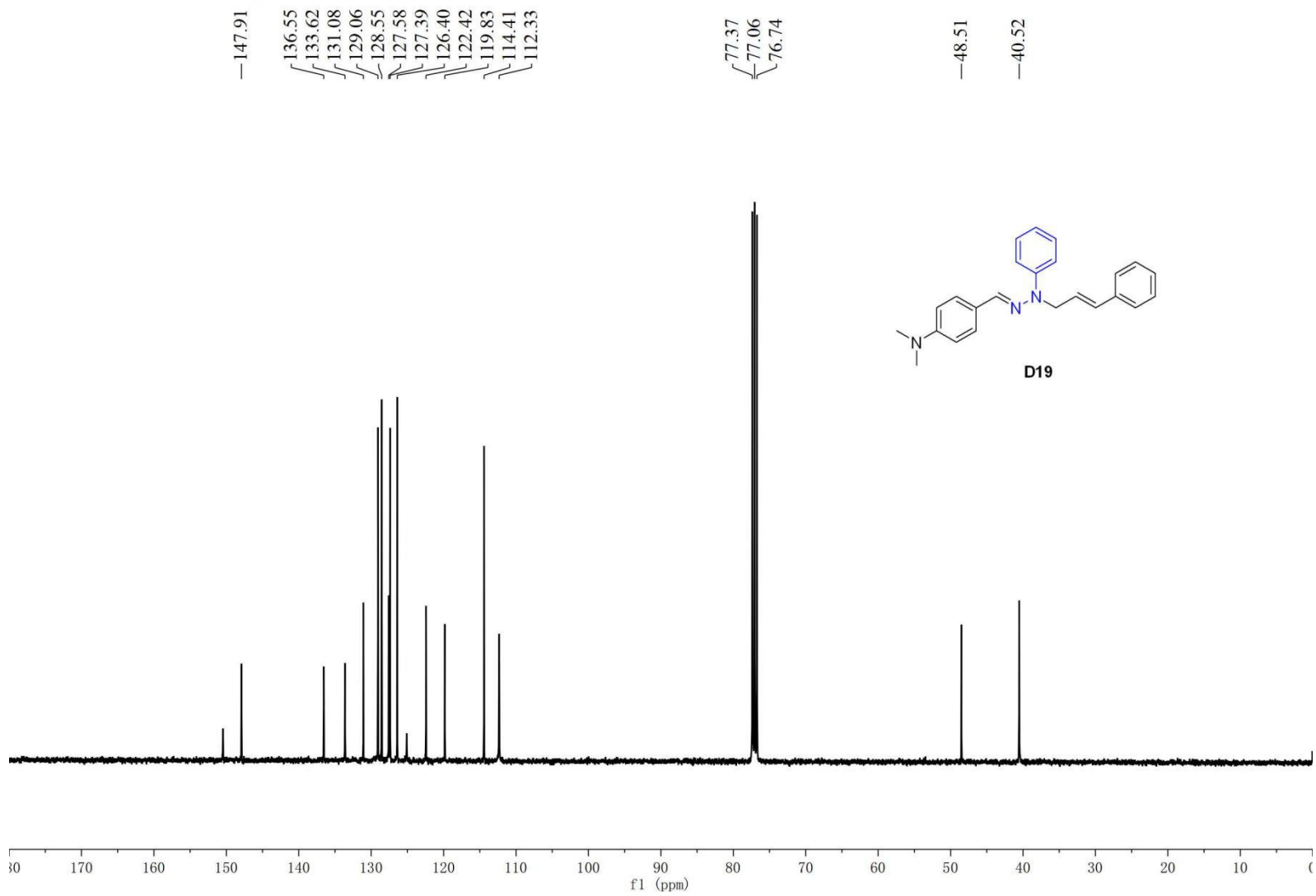


2022-06-01 YY0003 616-1-D22.10.fid

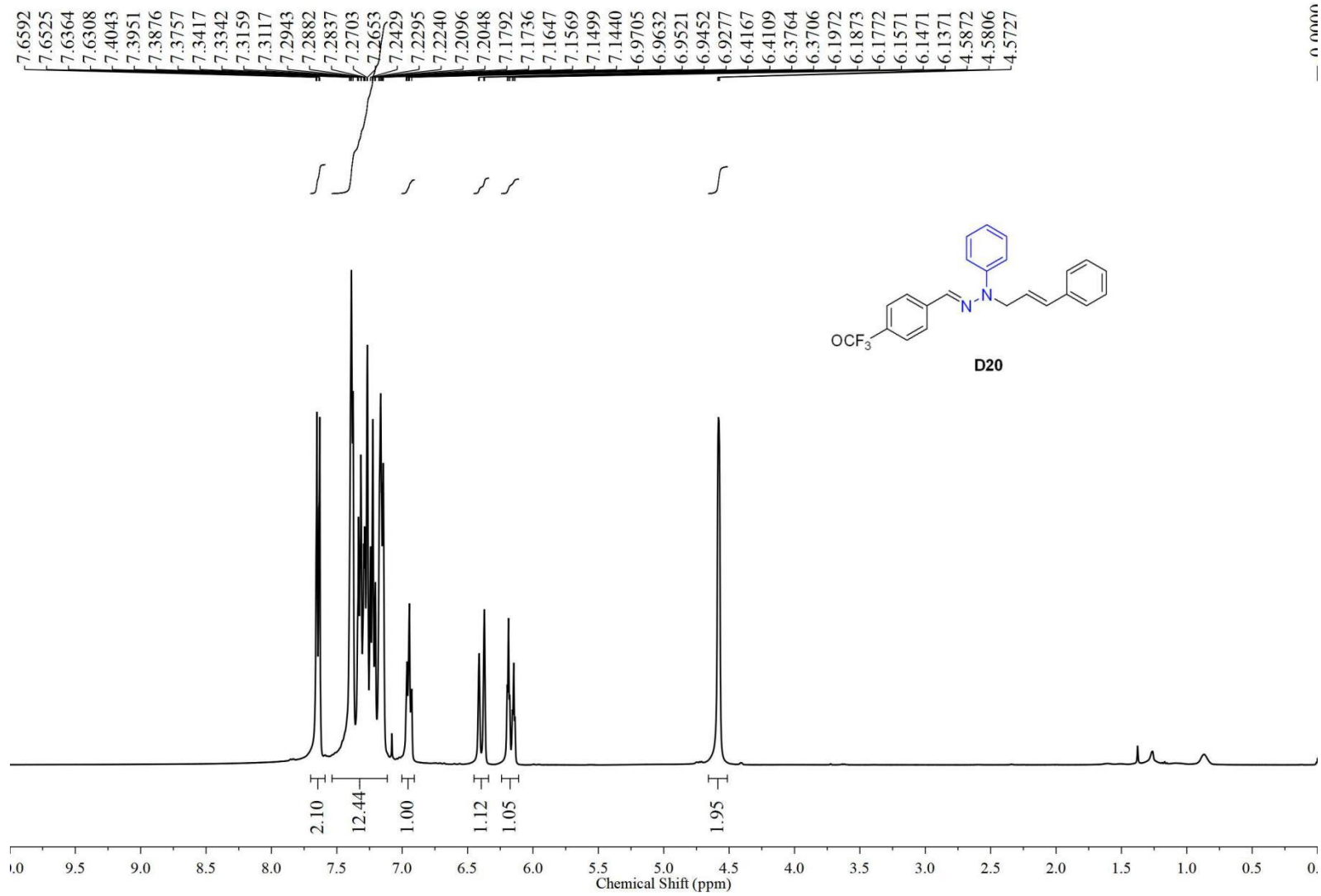




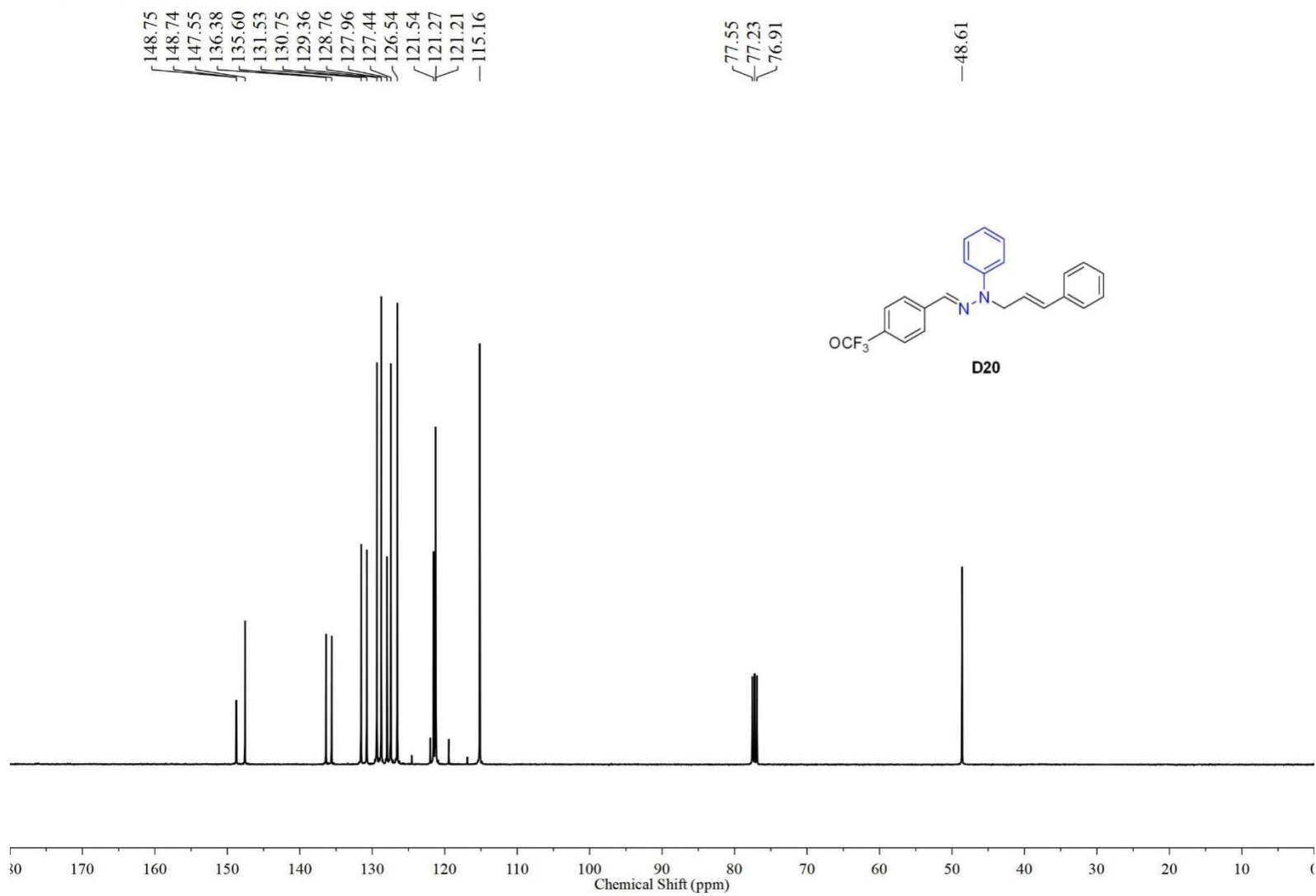
2022-06-01 YY0003 616-1-D24.10.fid



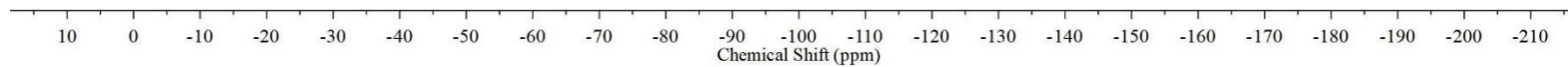
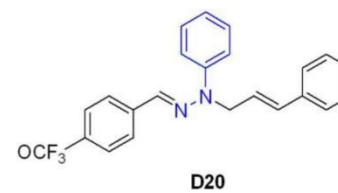
2022-05-29-YY0021-L-D25. 10. fid



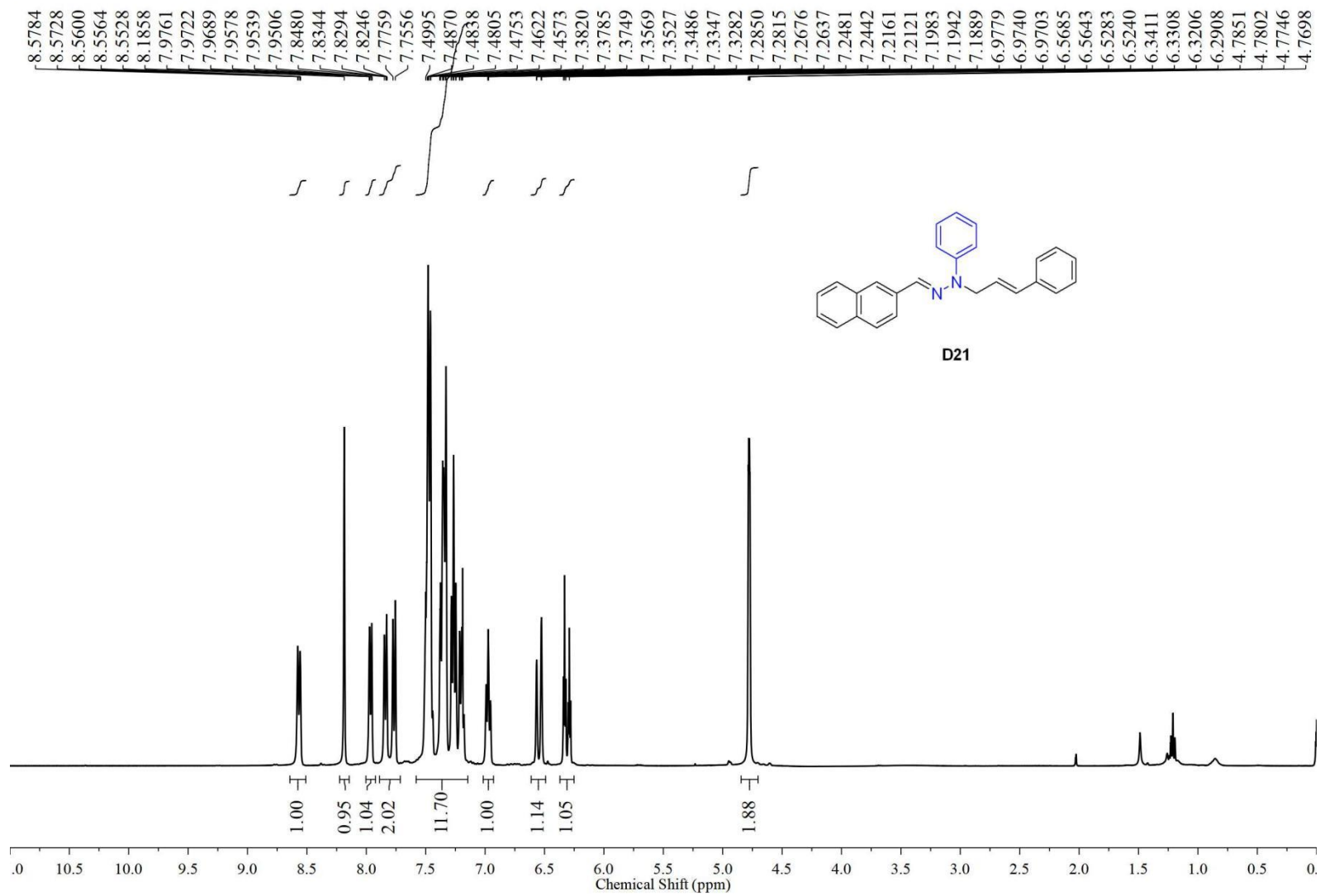
2022-05-29-YY0021-L-D25. 11. fid



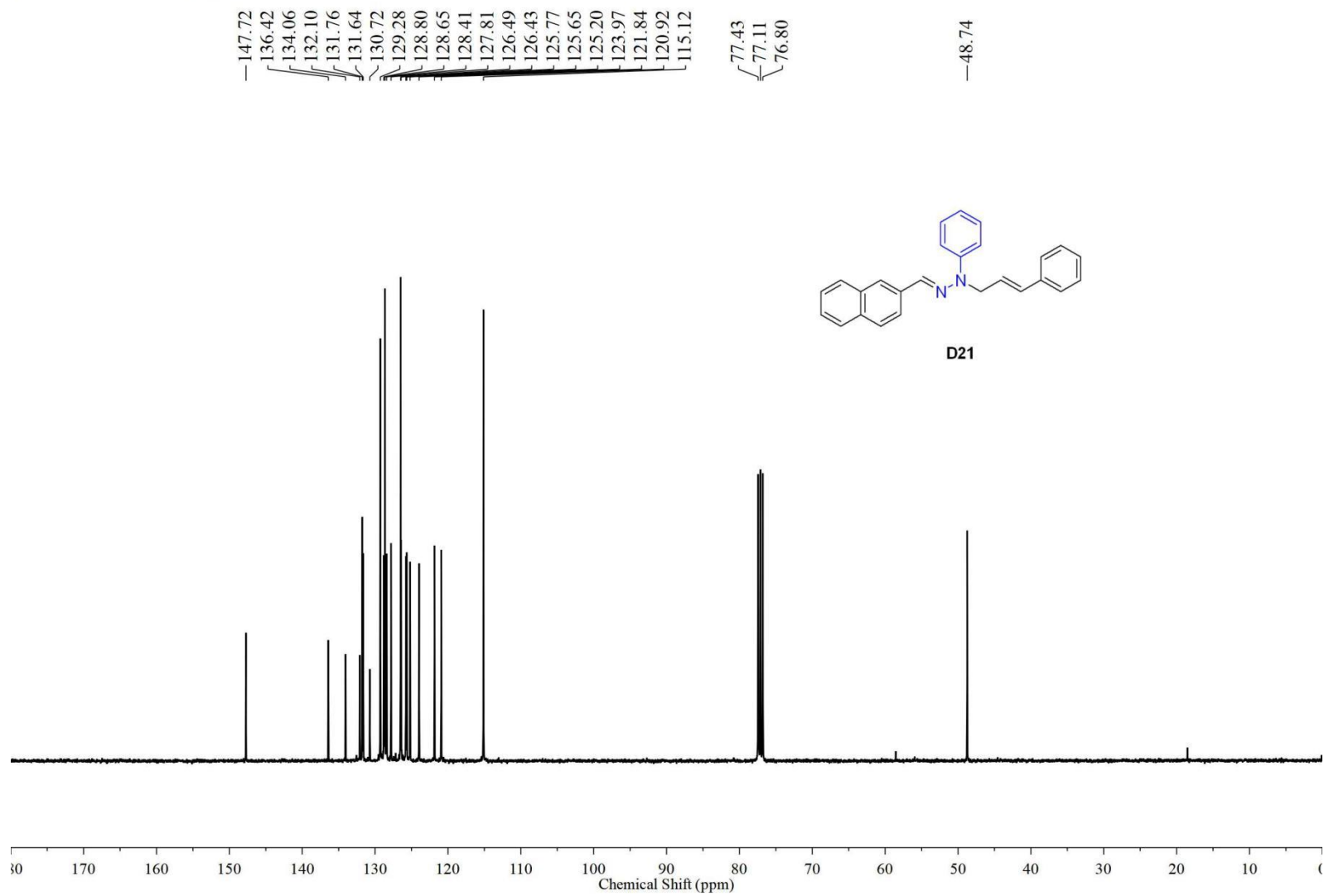
--57.52



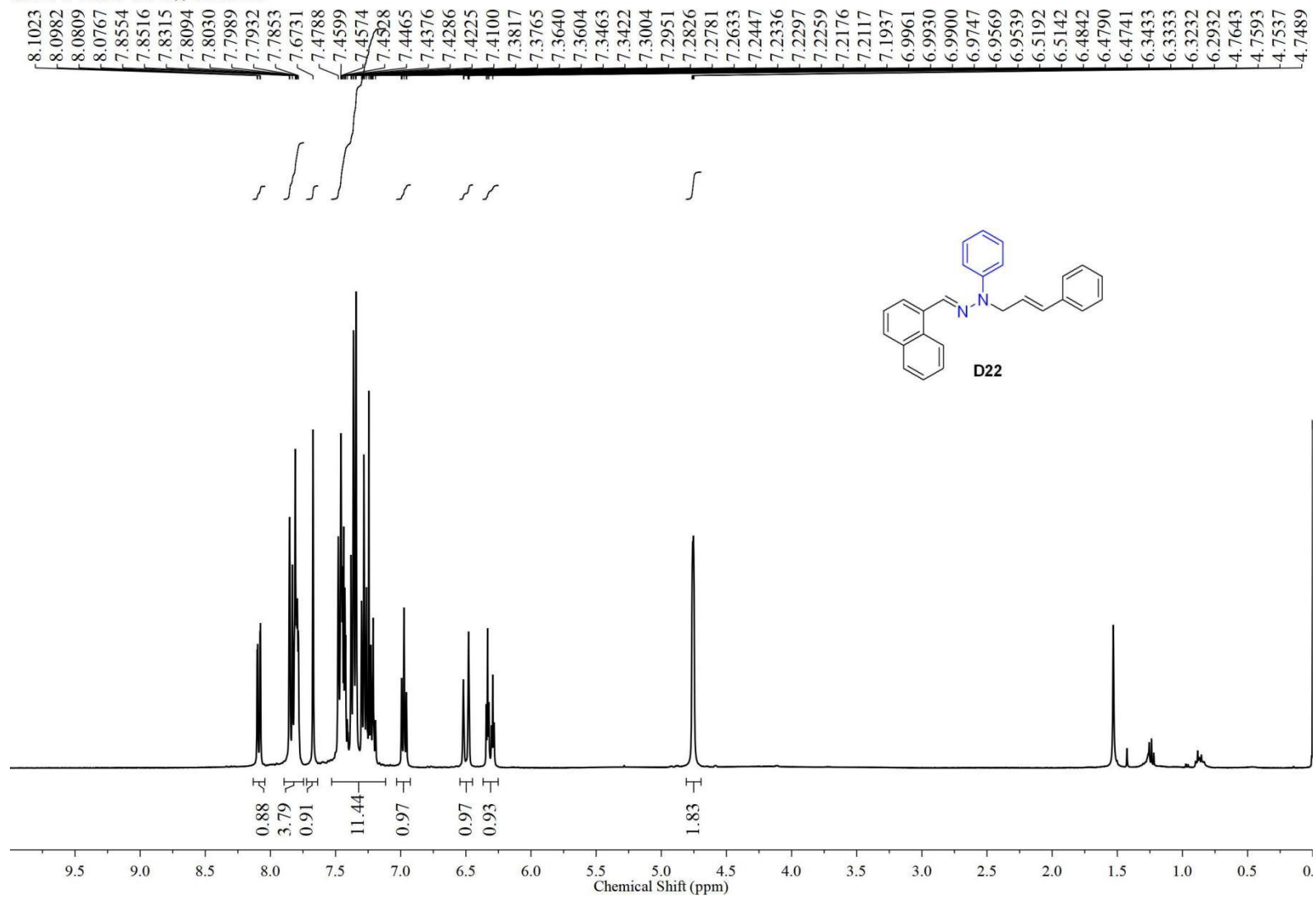
2022-6-6 YY0012-616-LQQ-33.10.fid



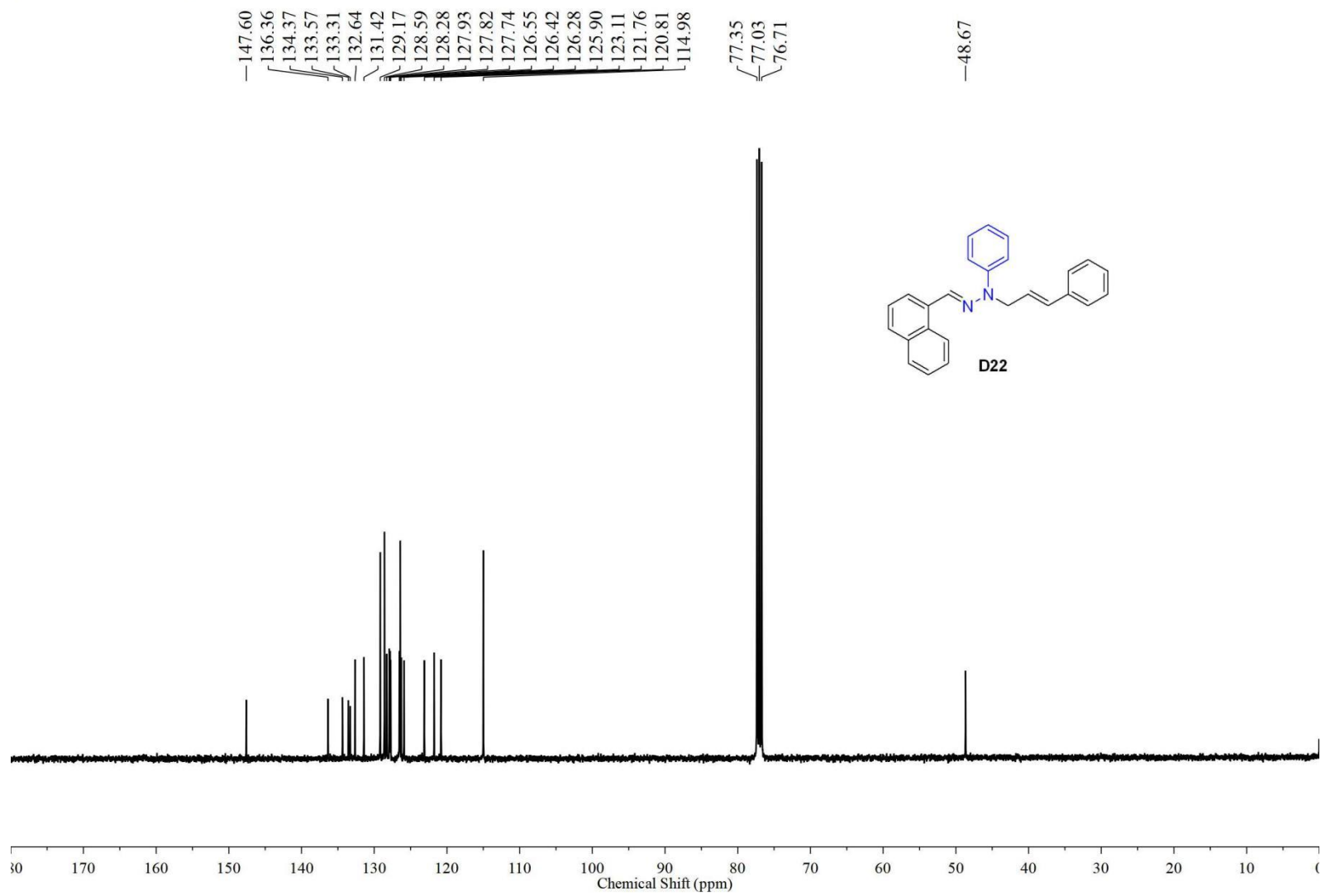
2022-6-6 YY0012-616-LQQ-33.12.fid



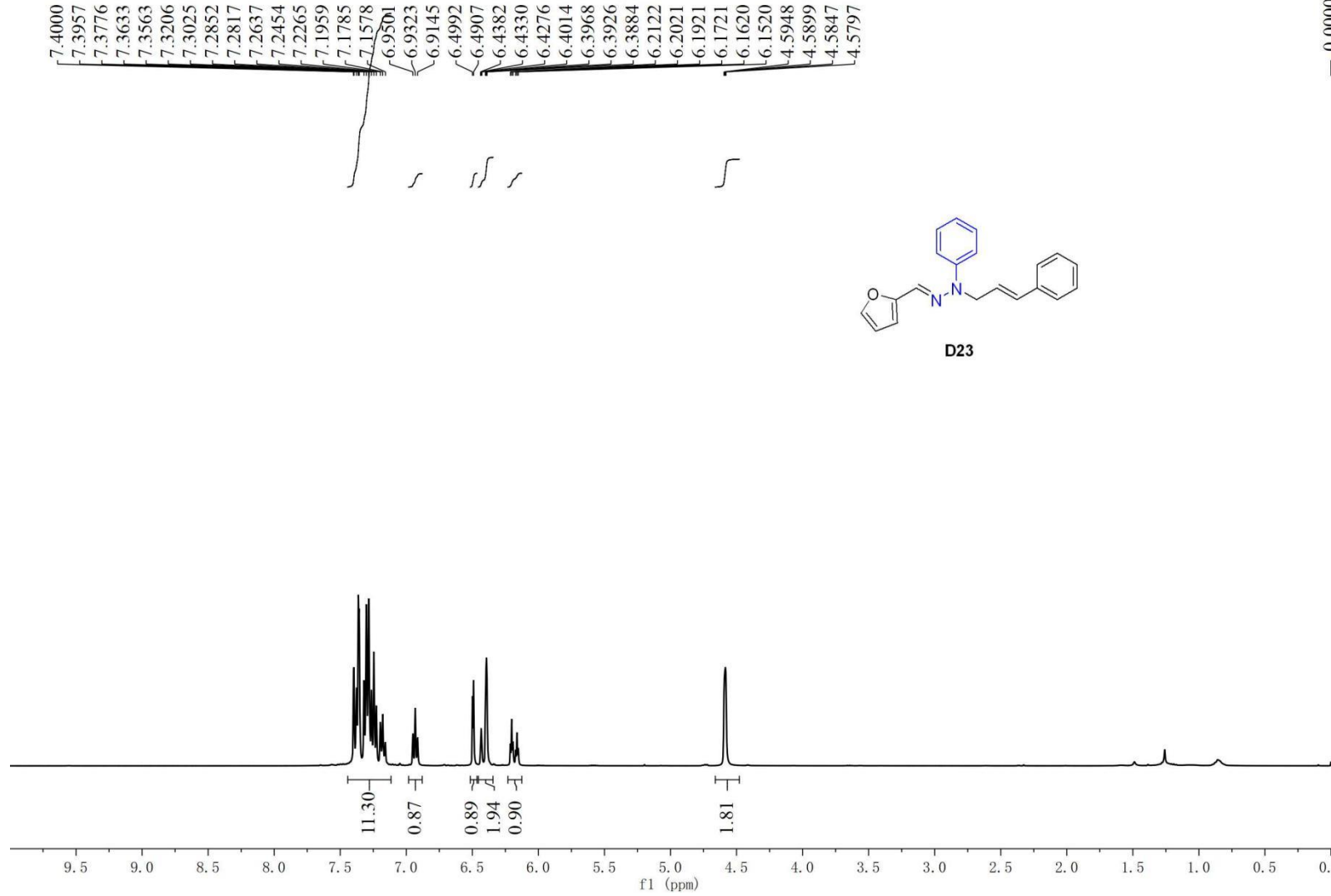
2022-6-6 YY0012-616-LQQ-34.10.fid



2022-6-6 YY0012-616-LQQ-34.12.fid



2022-6-9 yy0012-616-1-37.10.fid



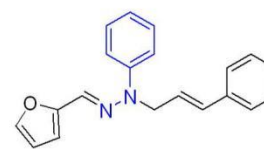
S183

2022-6-11 yy0042-616-lqq-d37.10.fid

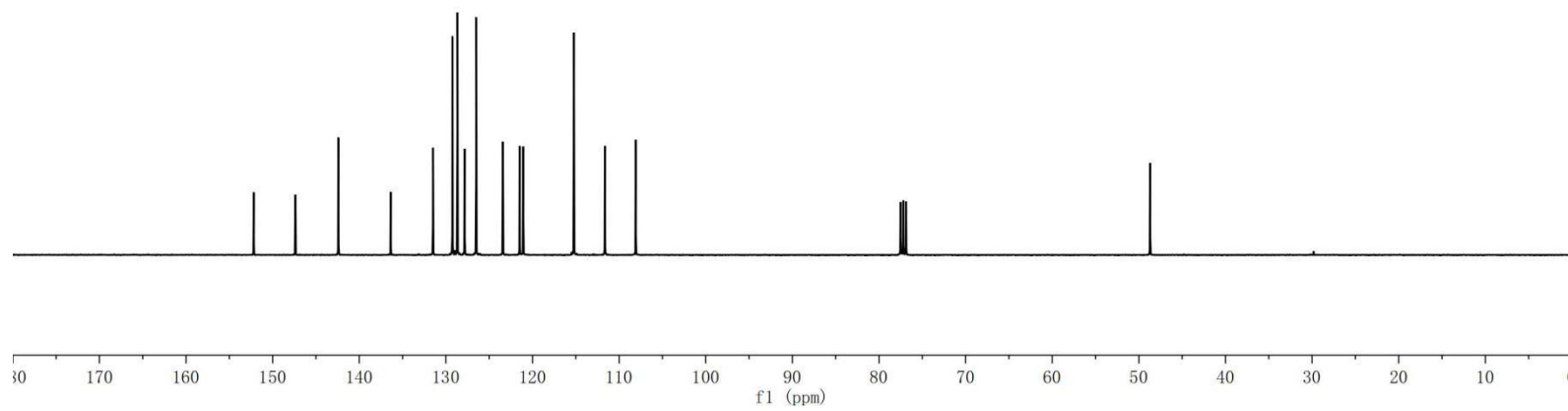
152.18
147.38
142.41
136.37
131.48
129.24
128.67
127.84
126.50
123.42
121.48
121.07
115.22
111.64
108.08

77.51
77.19
76.87

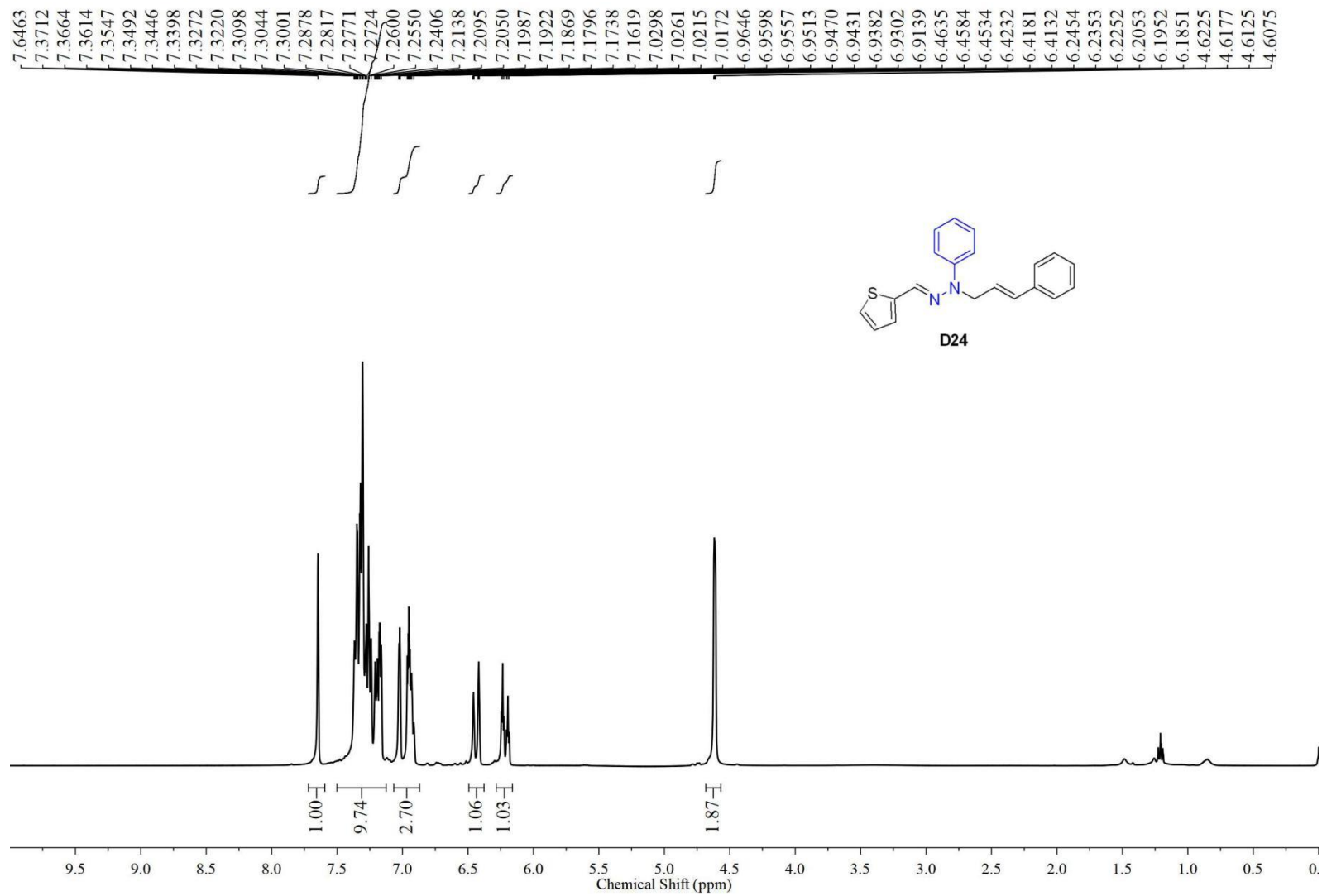
48.70



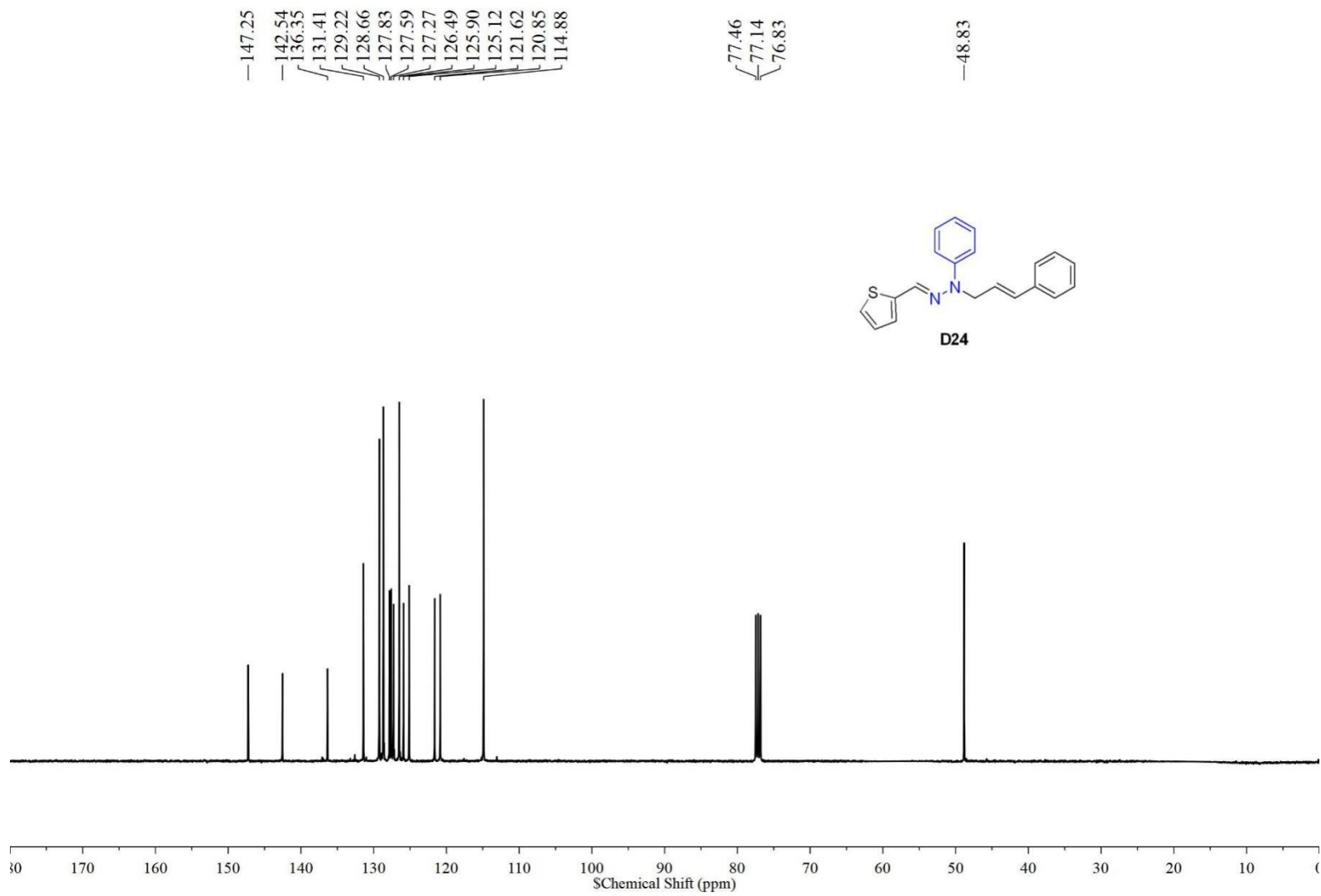
D23



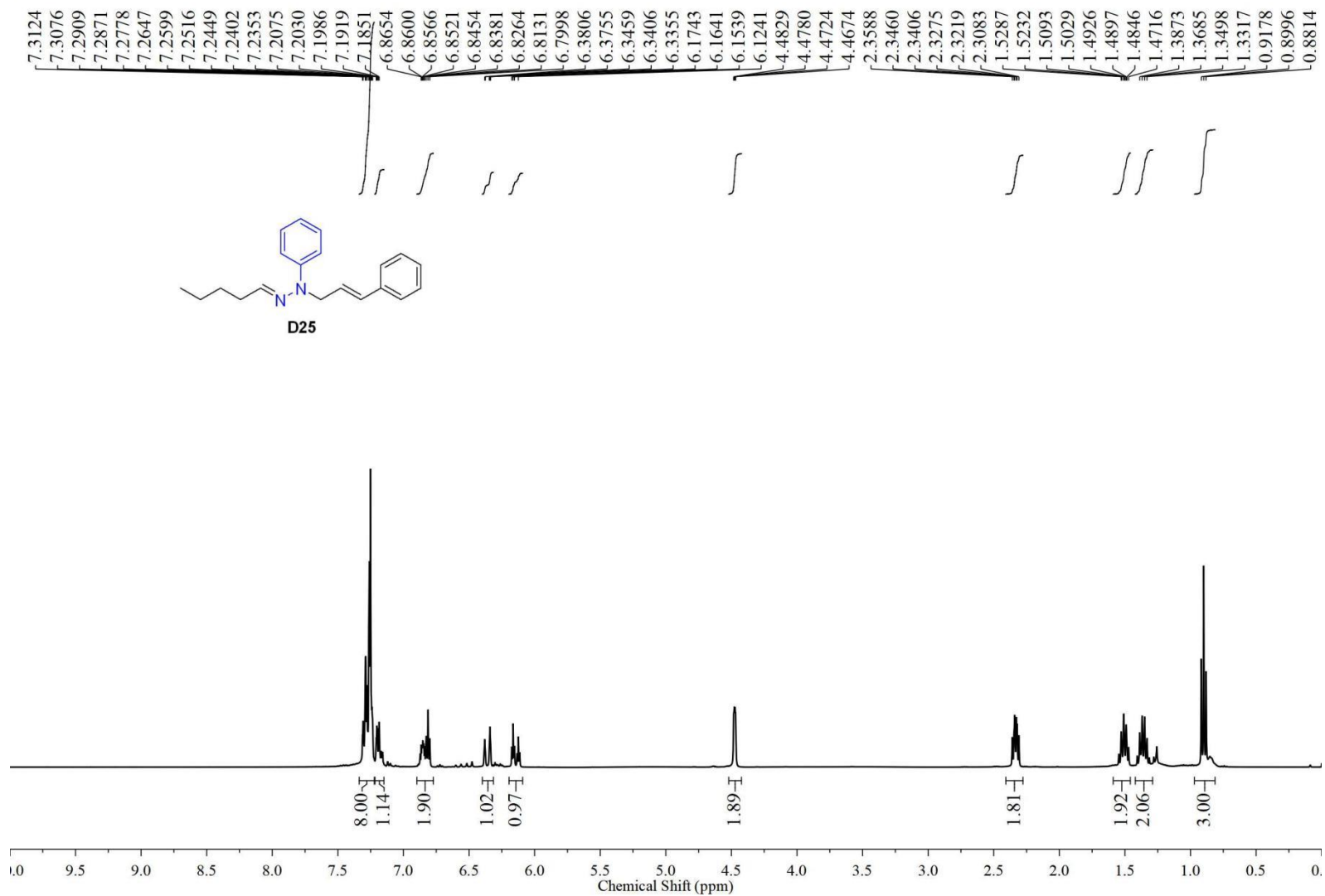
2022-6-6 YY0012-616-LQQ-38.10.fid



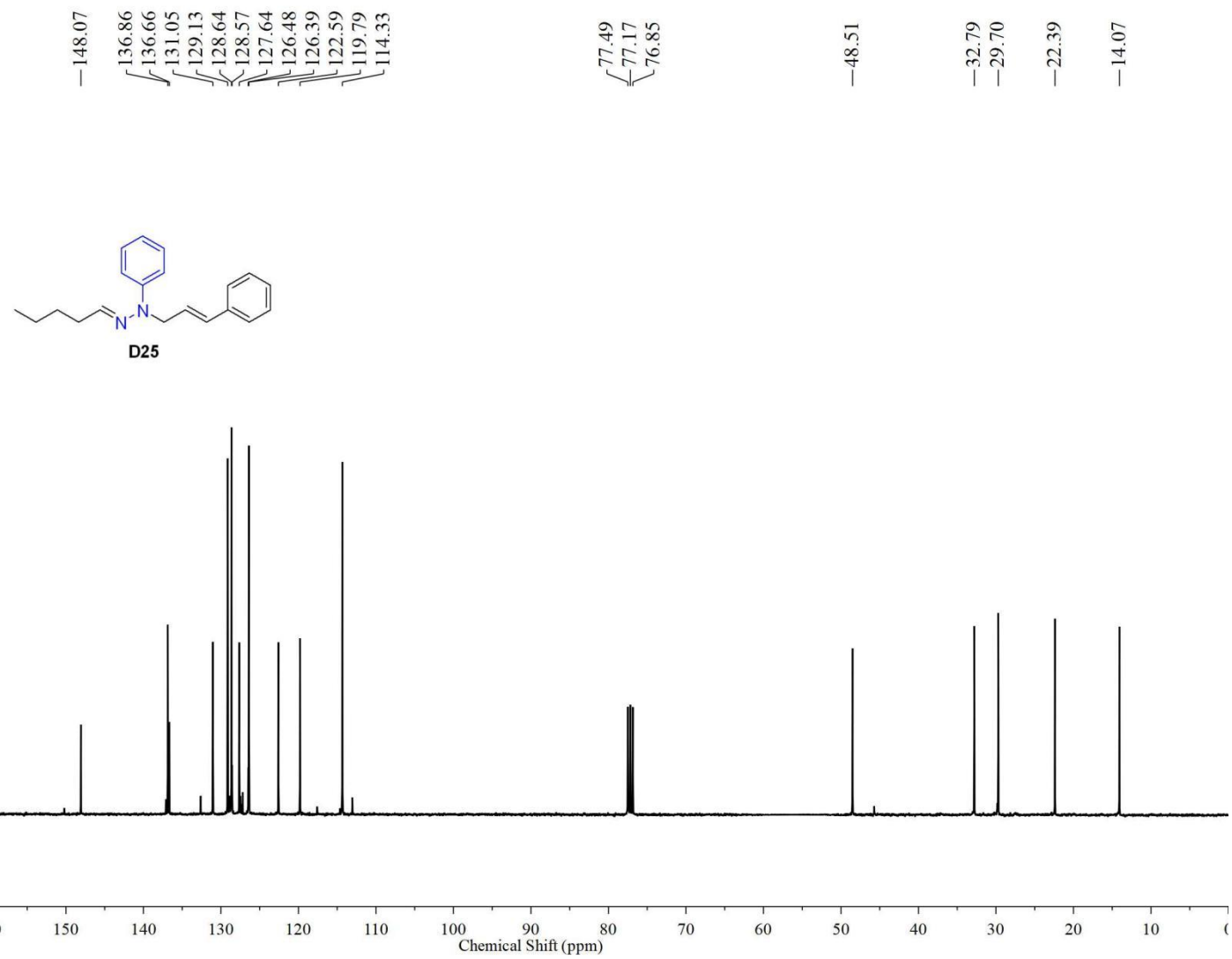
2022-6-6 YY0012-616-LQQ-38.12.fid



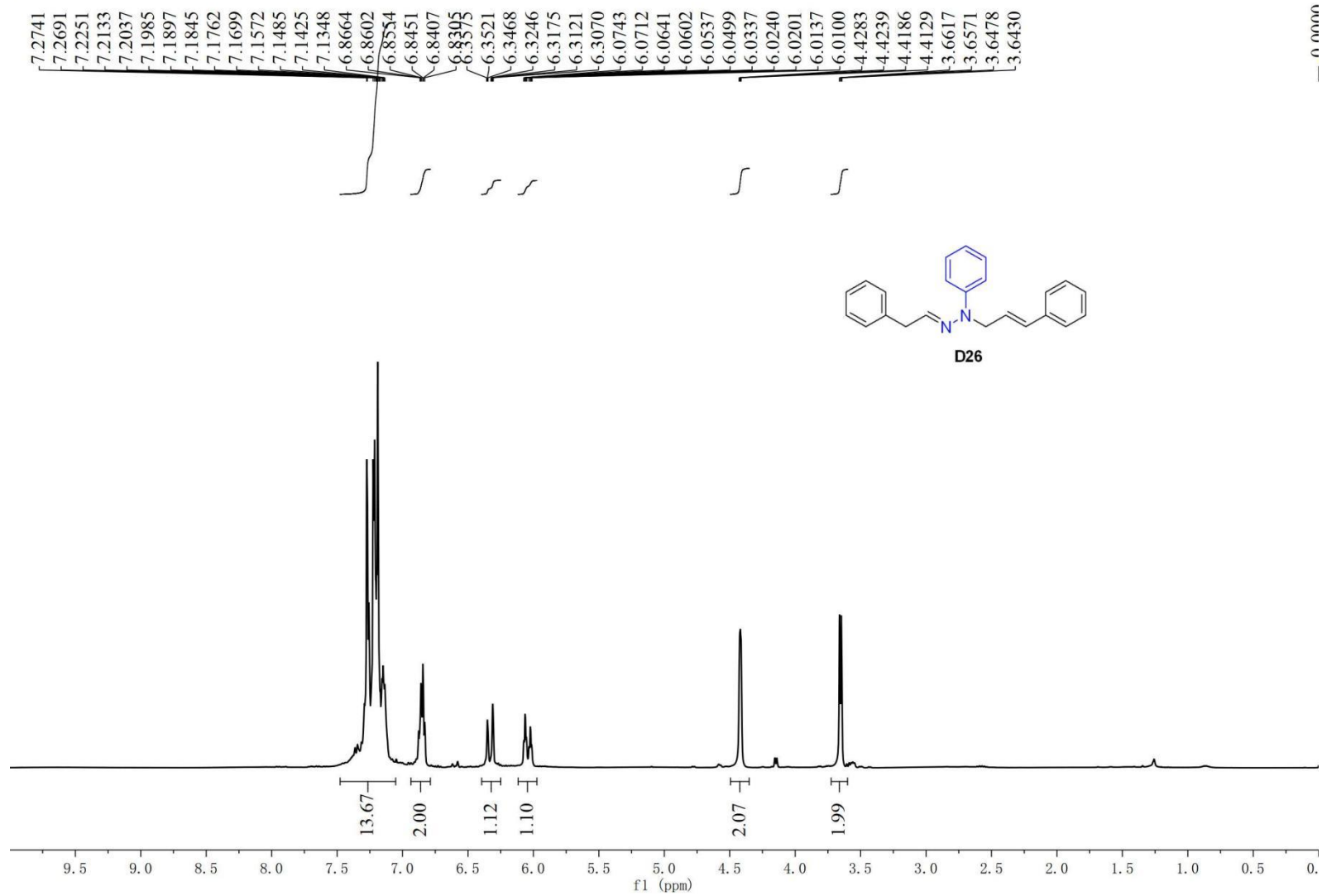
2022-6-8 YY0027-616-ZGH-42.10.fid



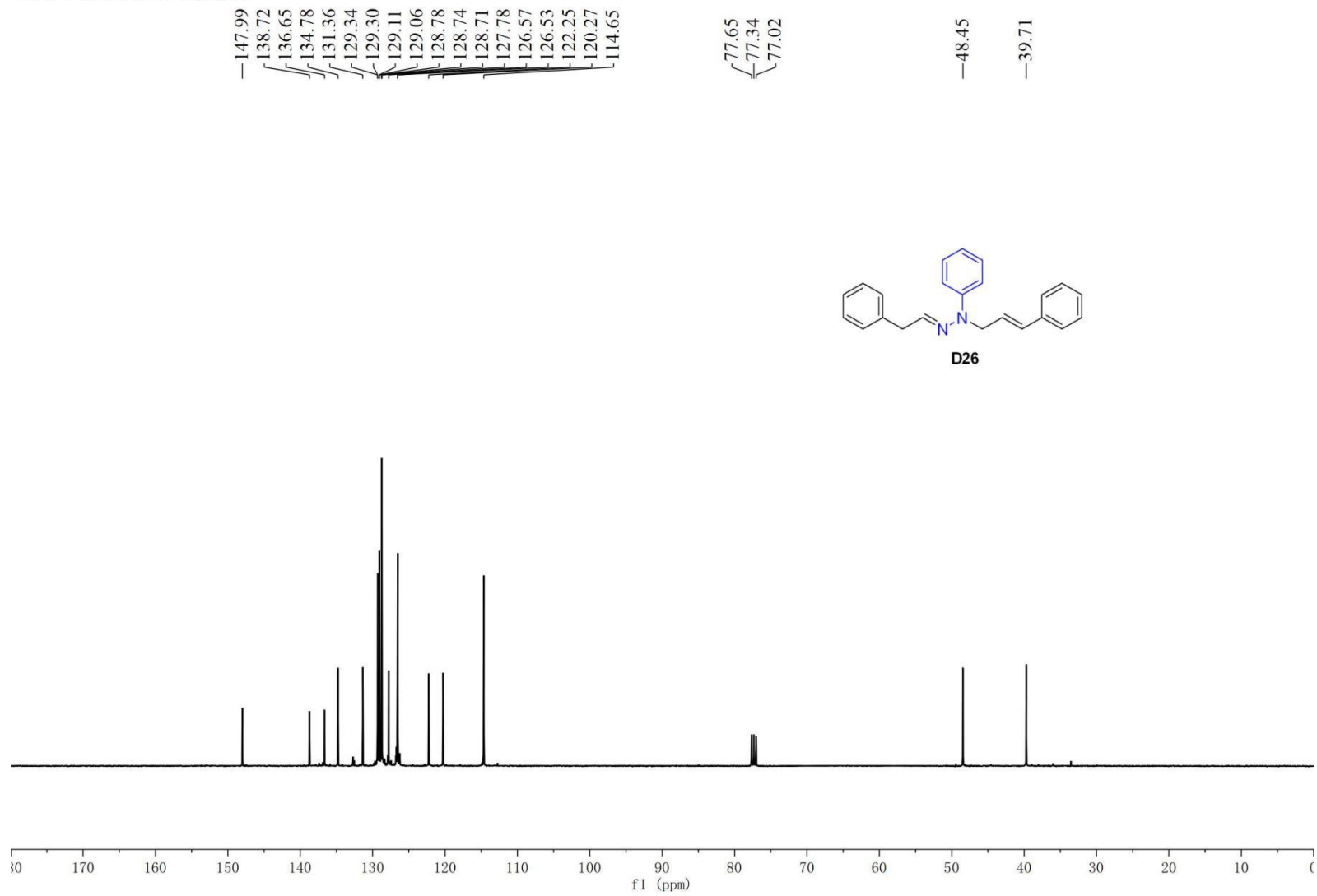
2022-6-9 yy0011-616-1-42.10.fid



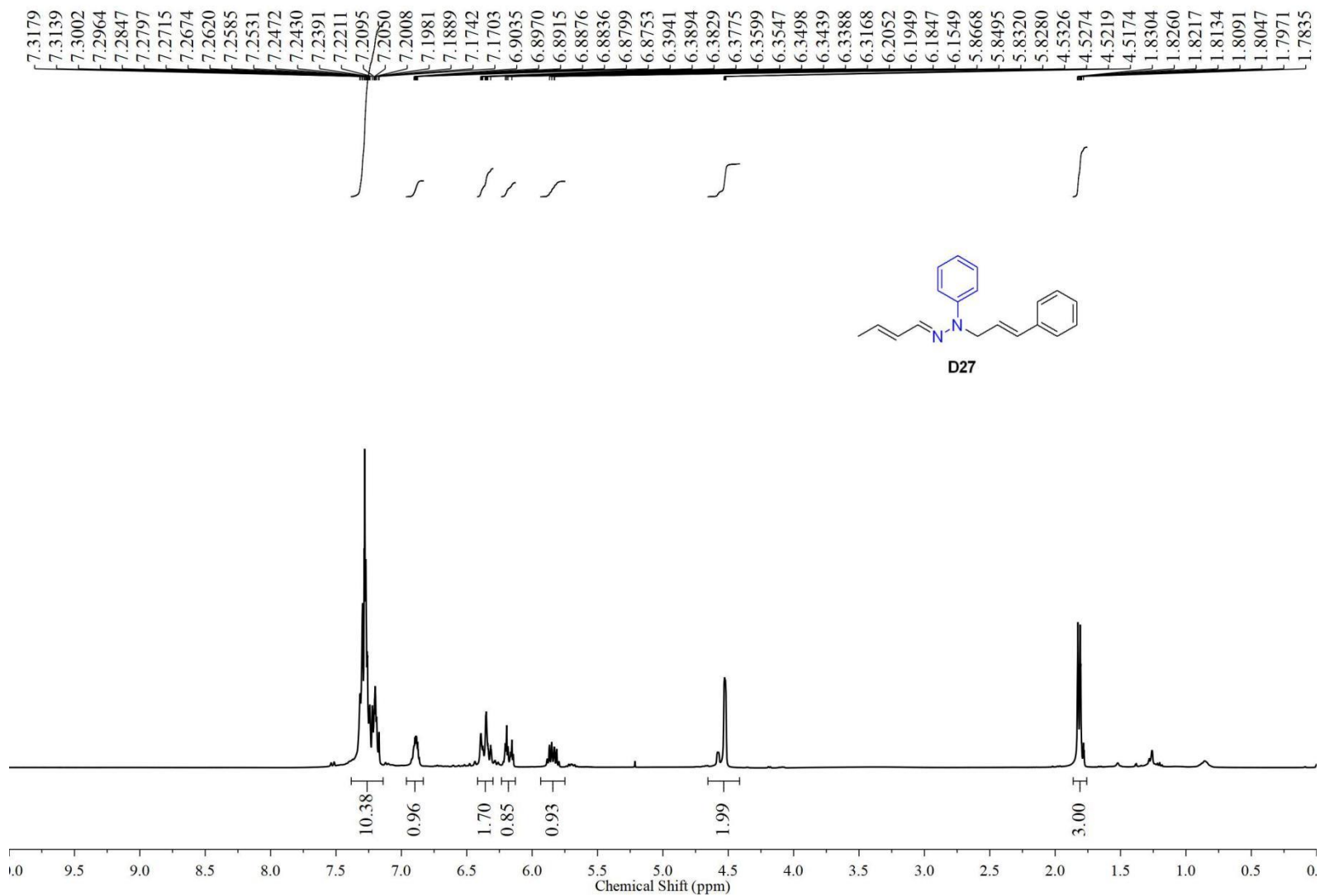
2022-6-8 YY0027-616-ZGH-40.10.fid



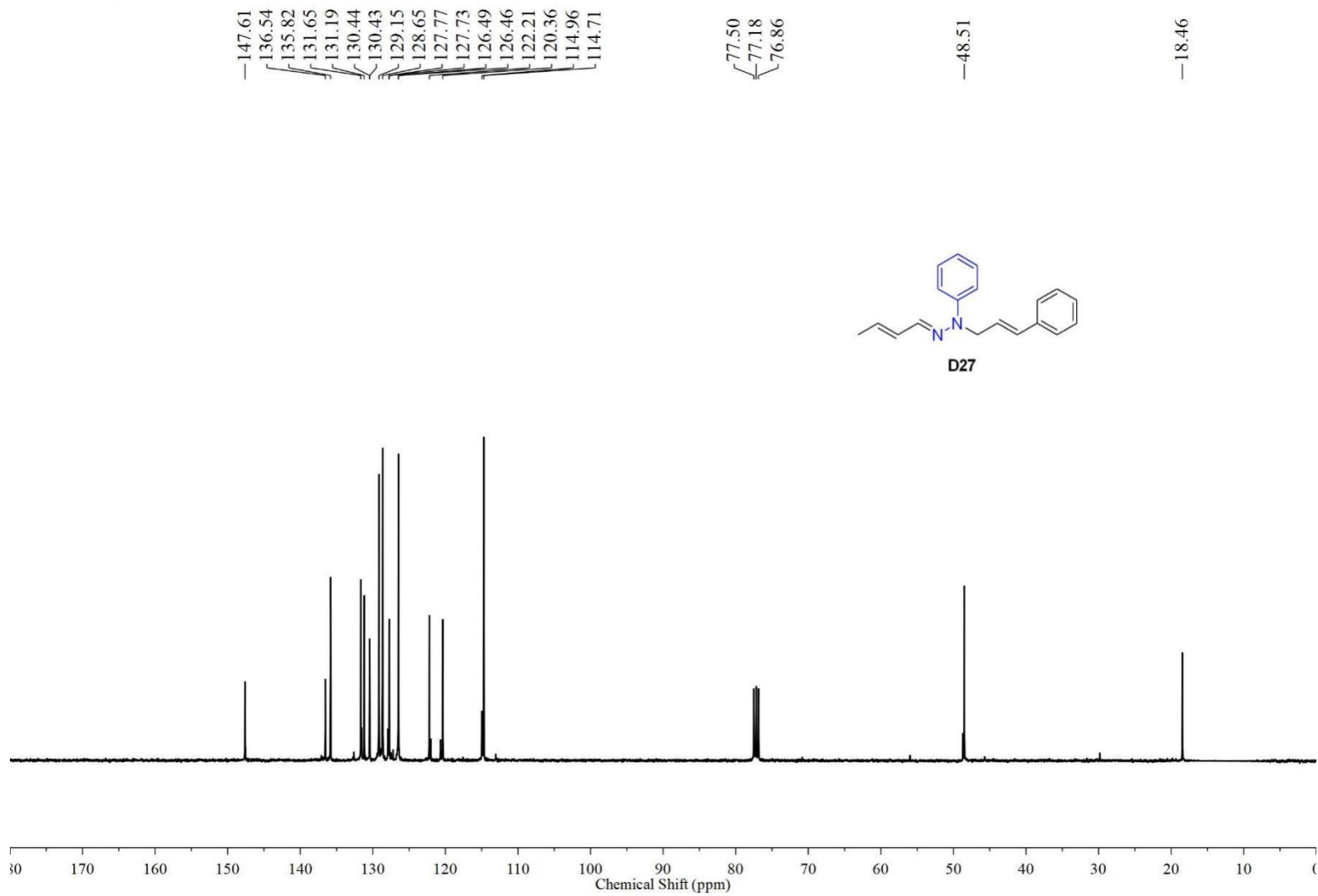
2022-6-9 yy0011-616-1-40.10.fid



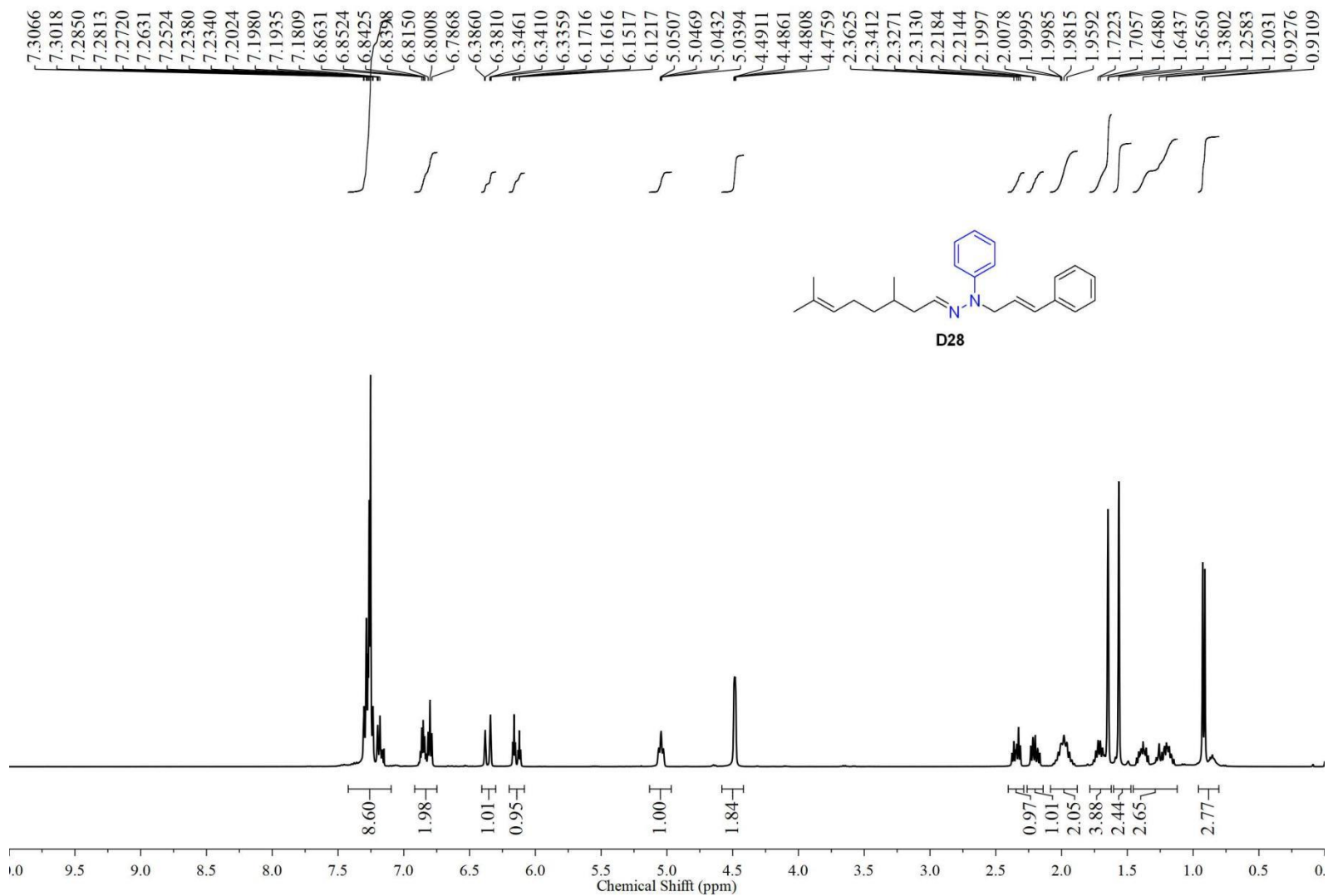
2022-6-8 YY0027-616-ZGH-41.10.fid



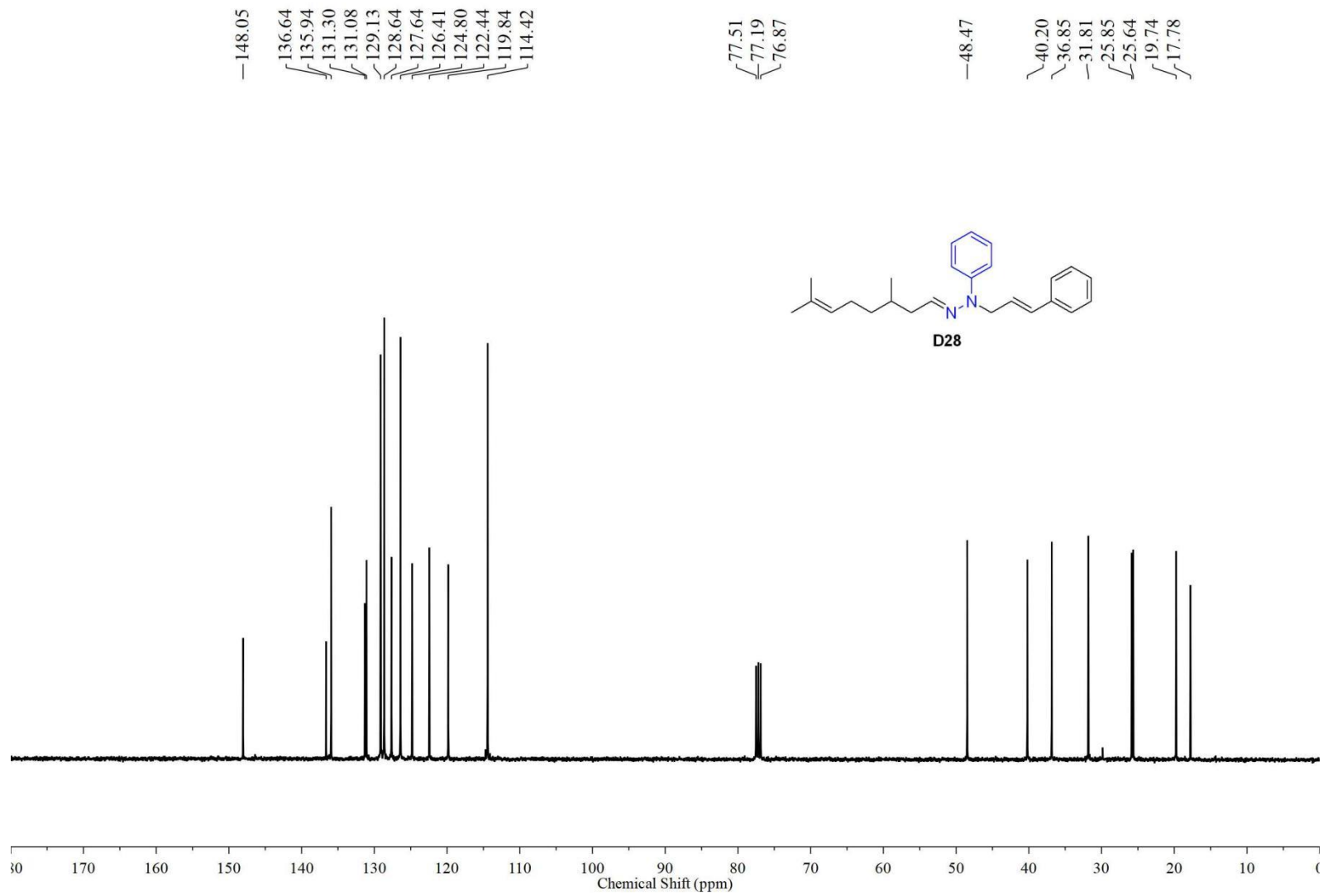
2022-6-9 yy0011-616-1-41.10.fid



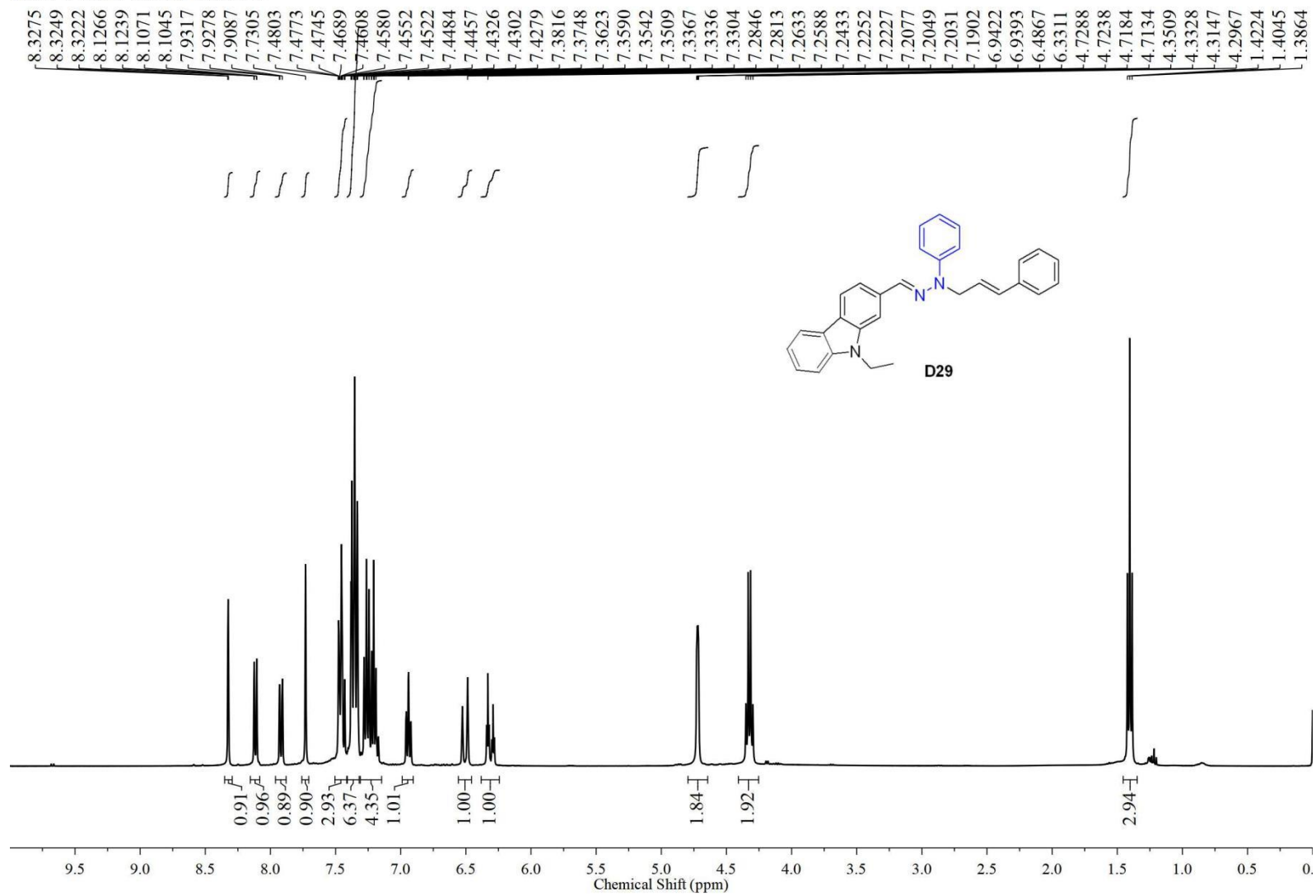
2022-6-8 YY0027-616-ZGH-45.10.fid



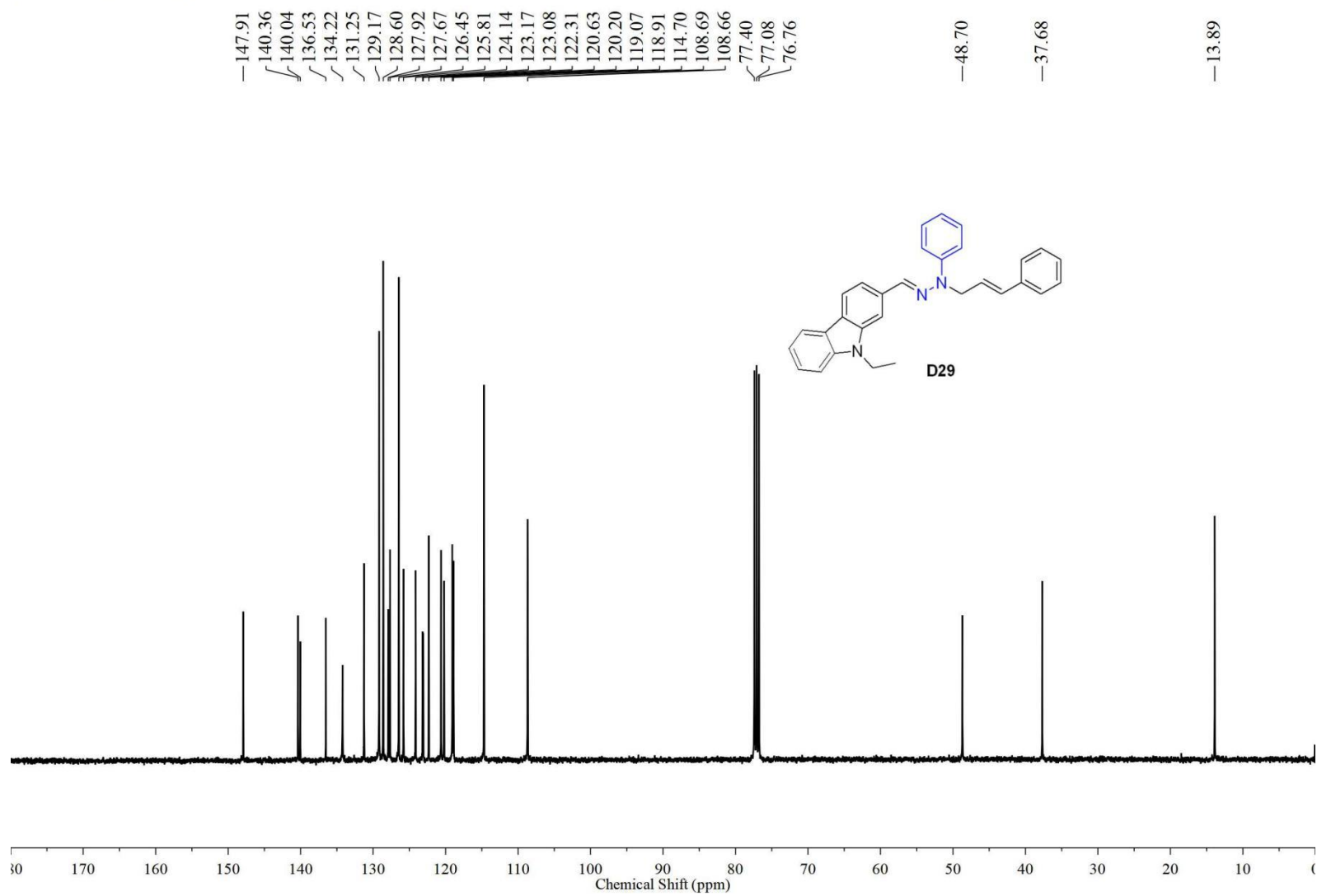
2022-6-9 yy0011-616-1-45.10.fid



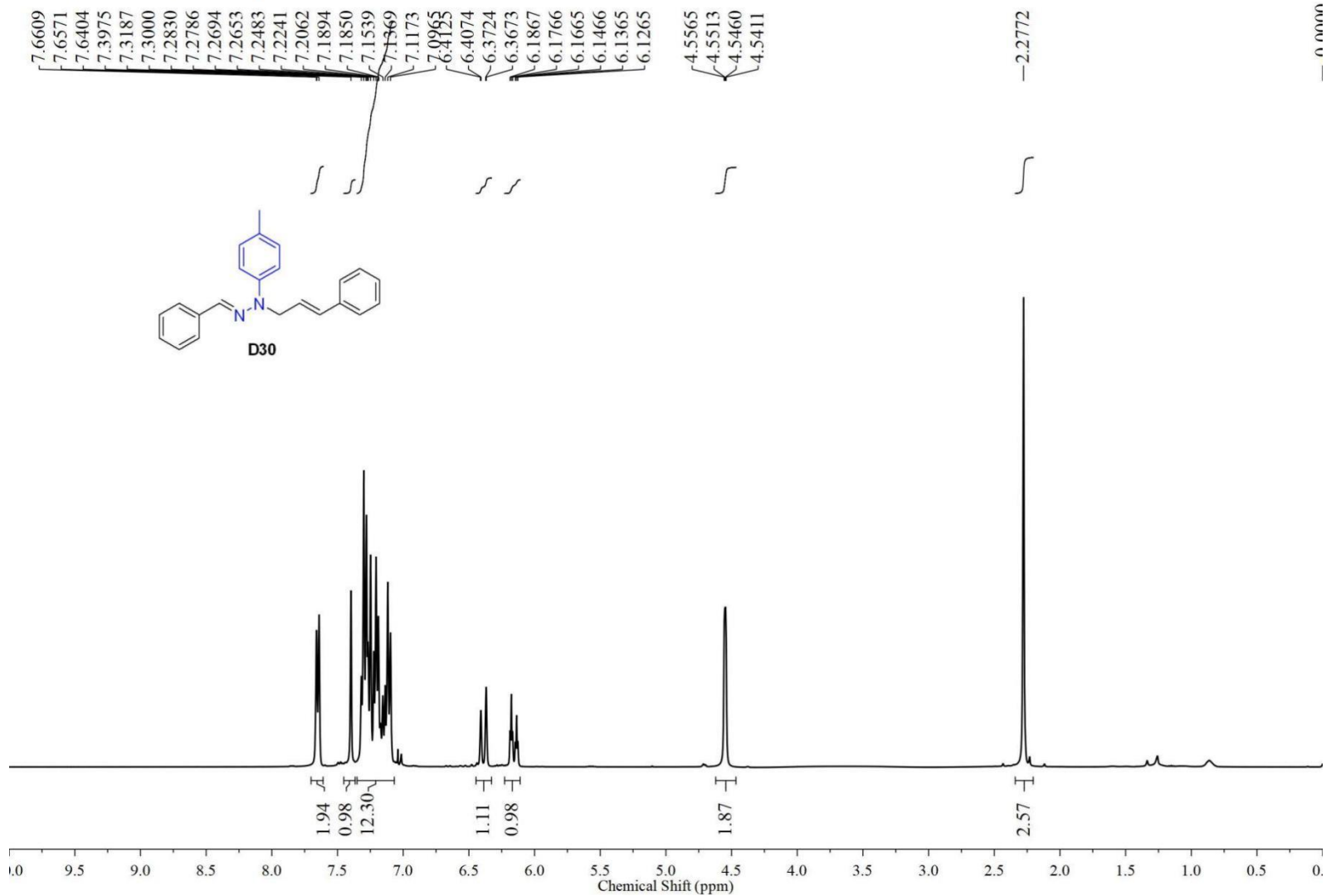
2022-6-6 YY0012-616-LQQ-36.10.fid



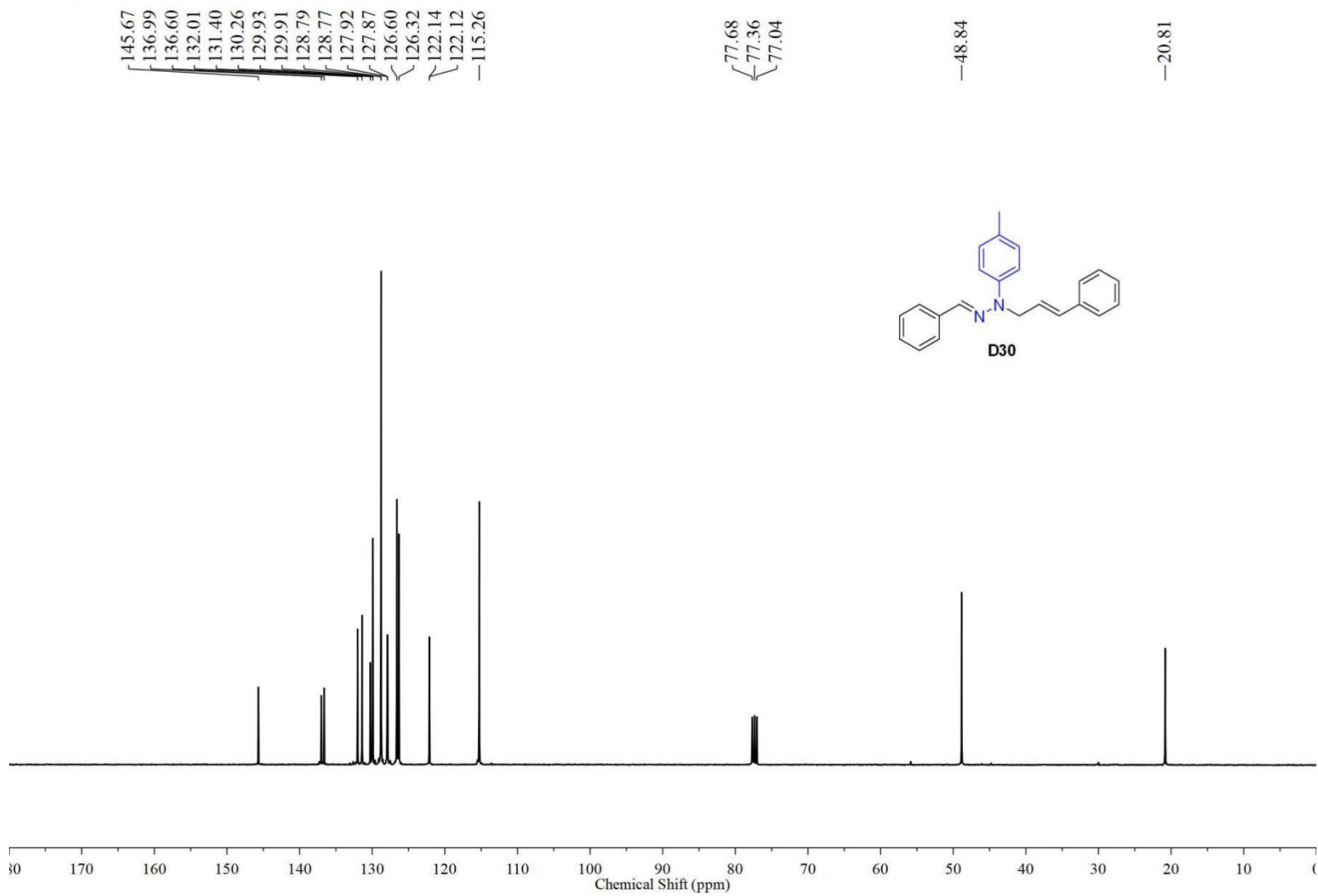
2022-6-6 YY0012-616-LQQ-36.12.fid



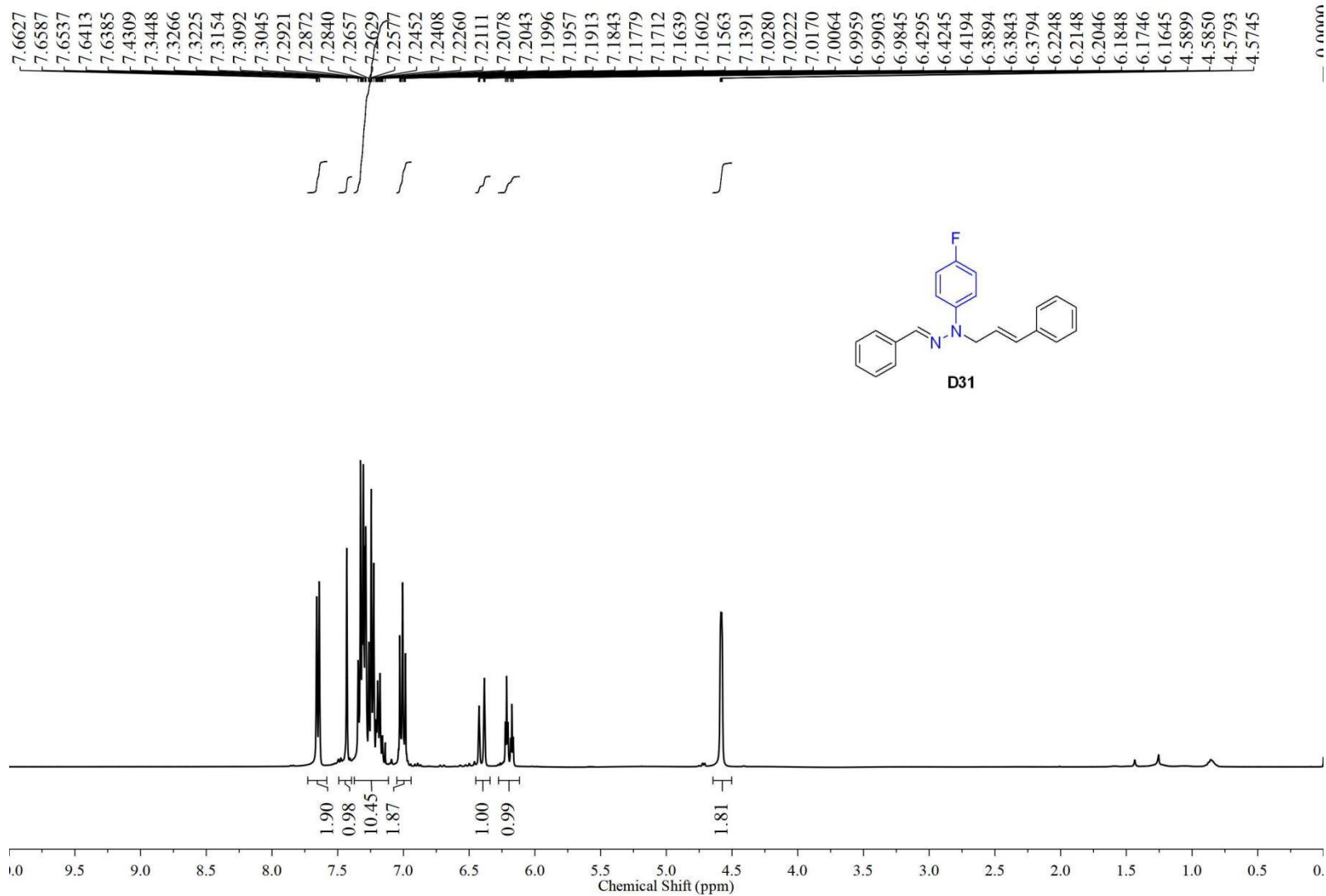
2022-6-11 YY0043-616-LQQ-B2.10.fid



2022-6-13 YY0012-616-L-B2. 10. fid

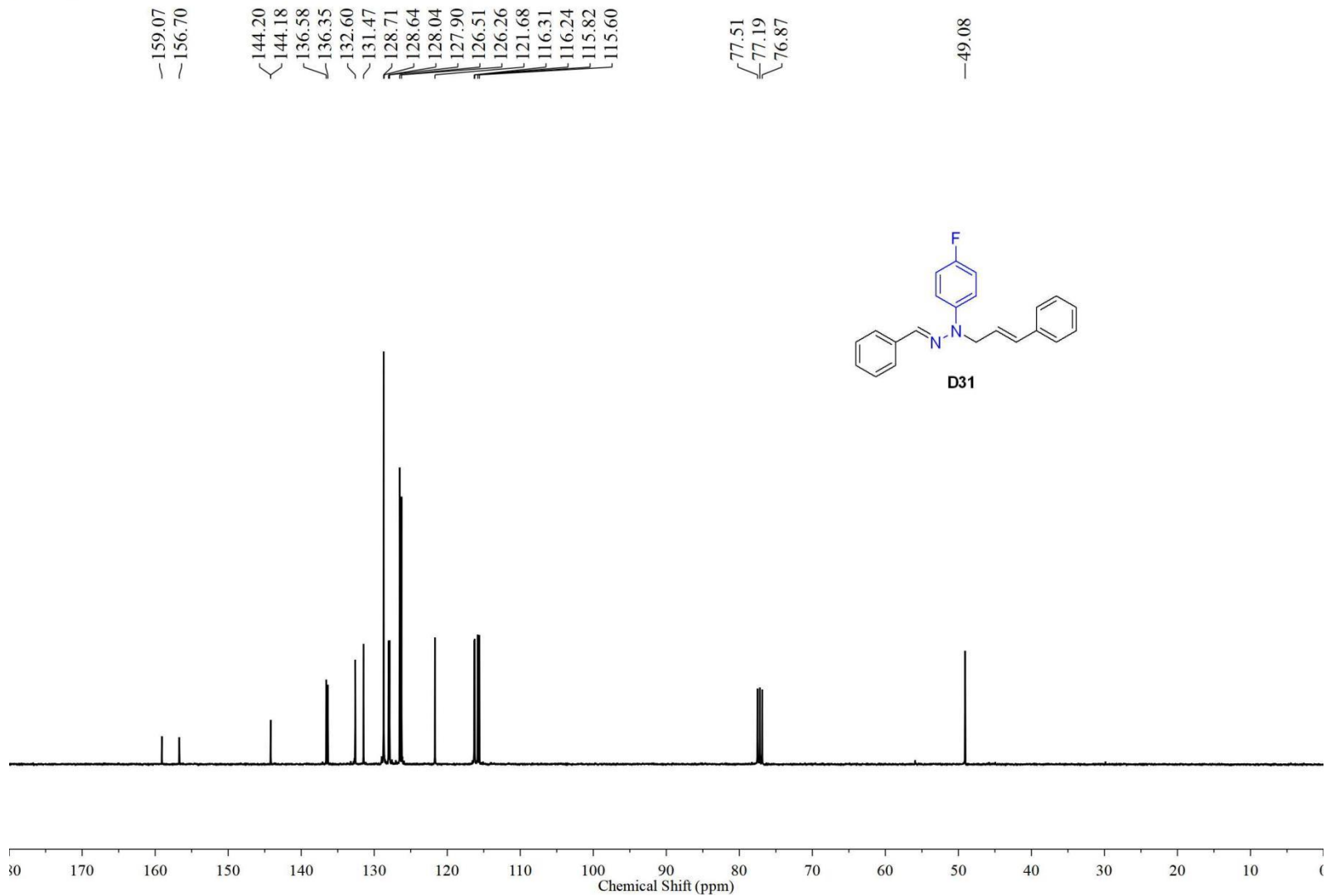


2022-6-14 YY0007-616-L-B7. 10. fid



S199

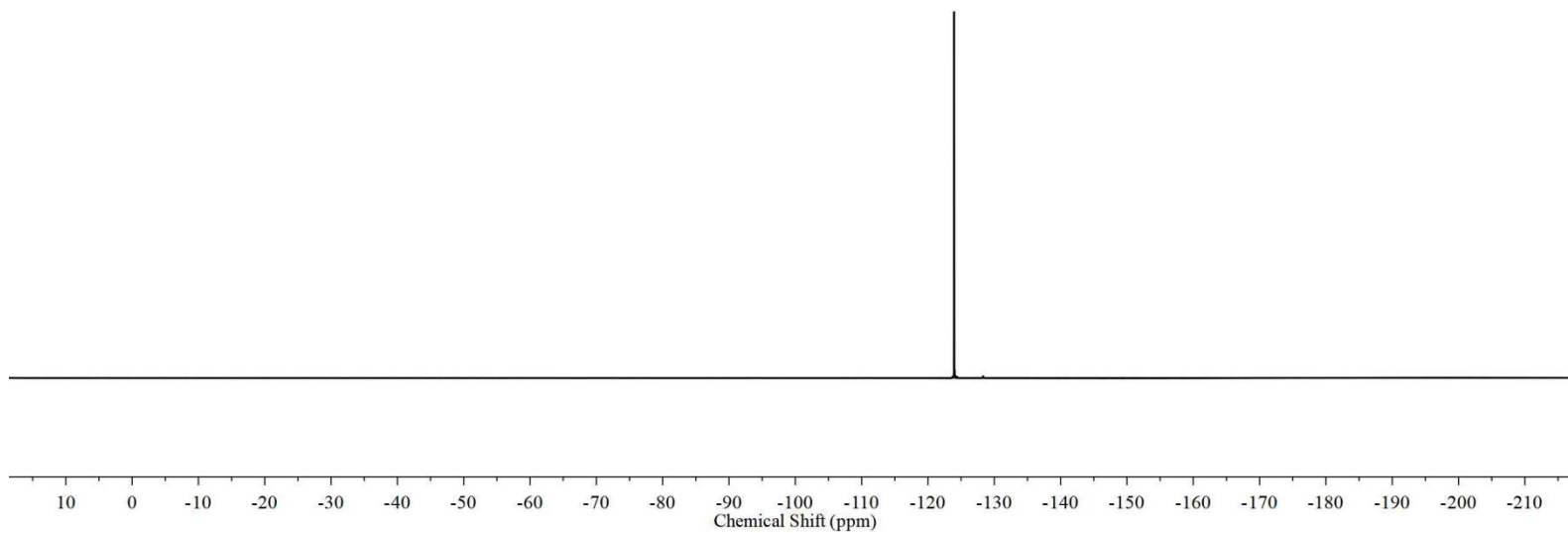
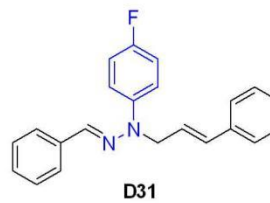
2022-6-15 yy0008-616-lqq-b7.10. fid



S200

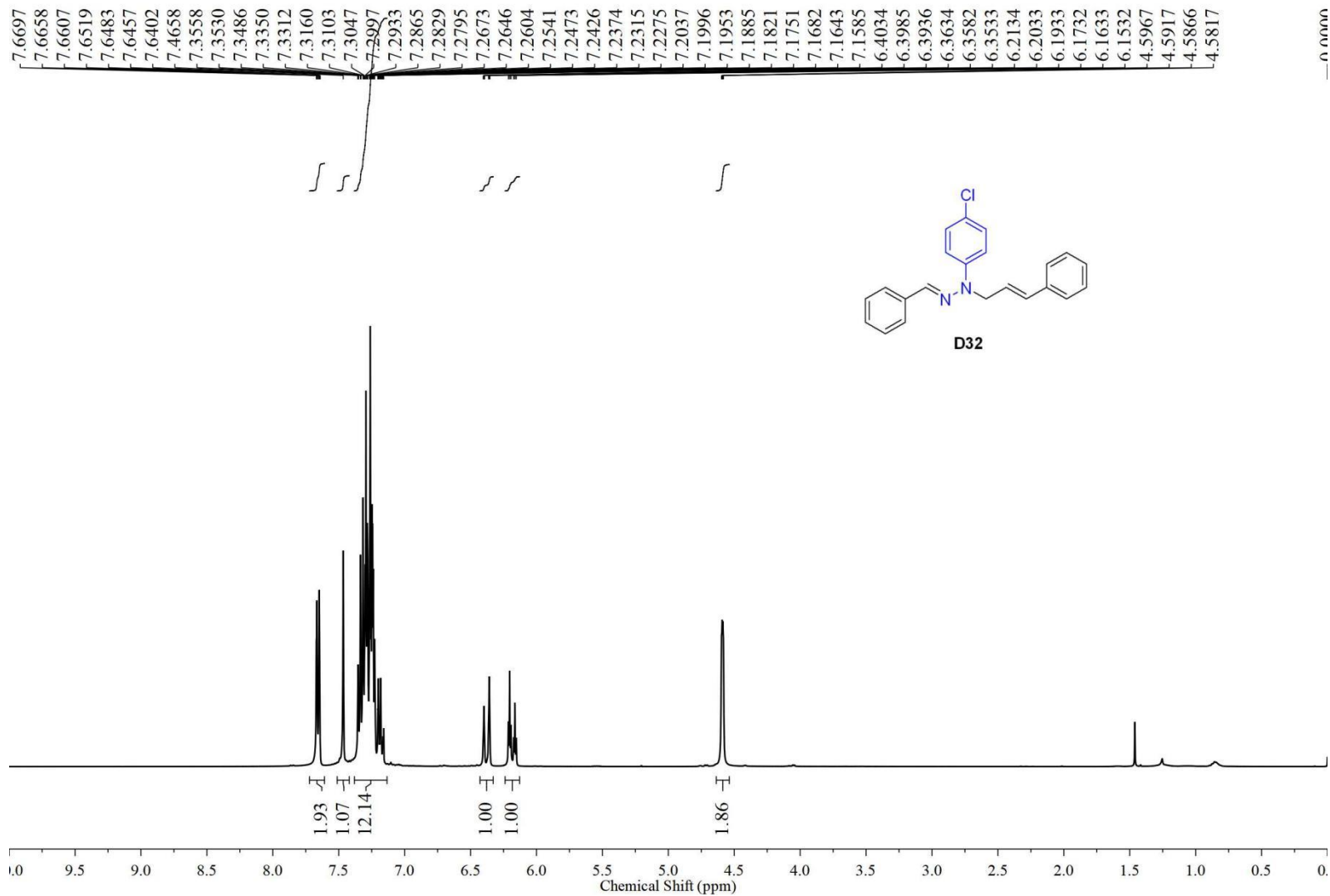
2022-6-15 yy0008-616-1qq-b7. 11. fid

--123.94



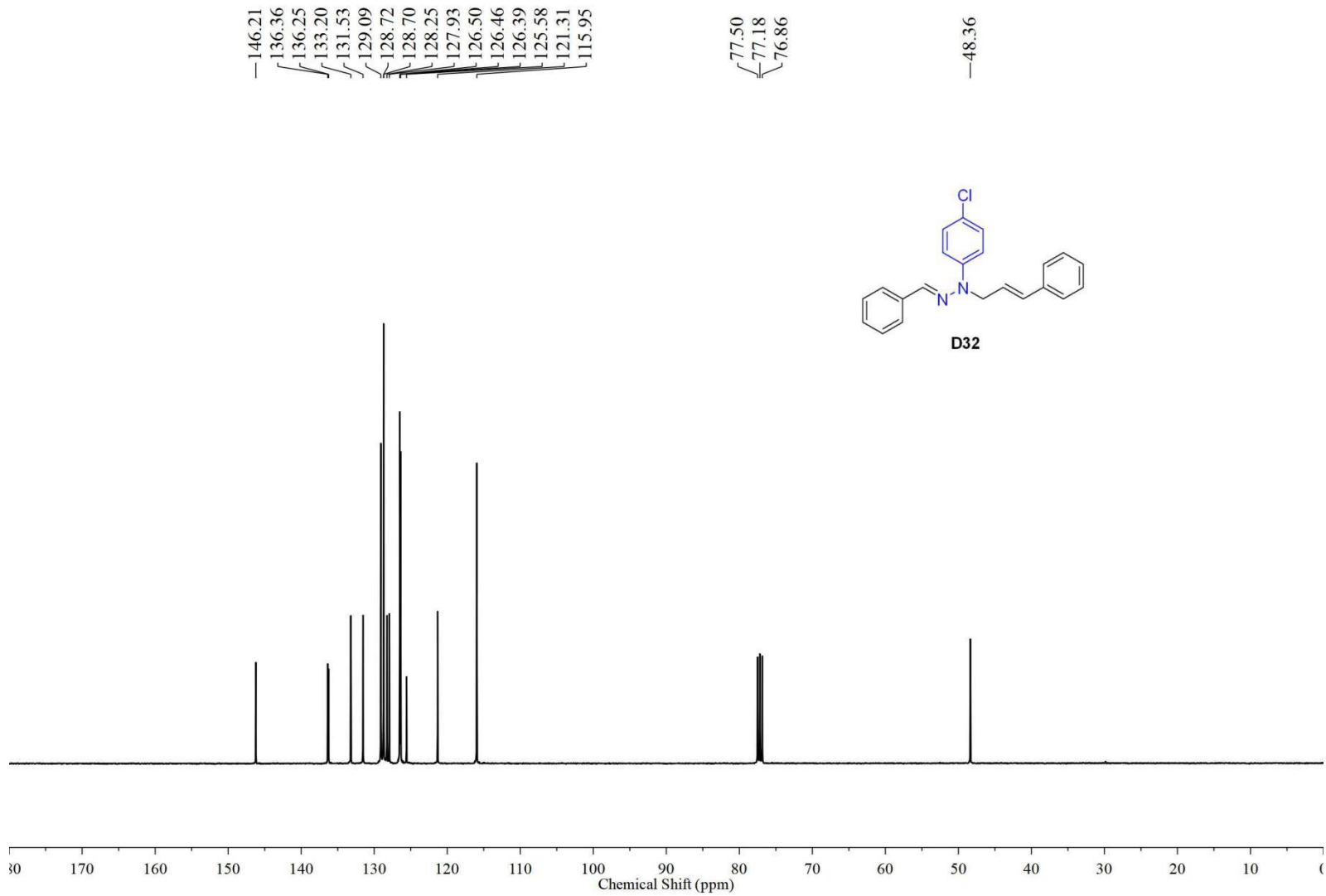
S201

2022-6-17 yy0011-616-1-b13.10.fid



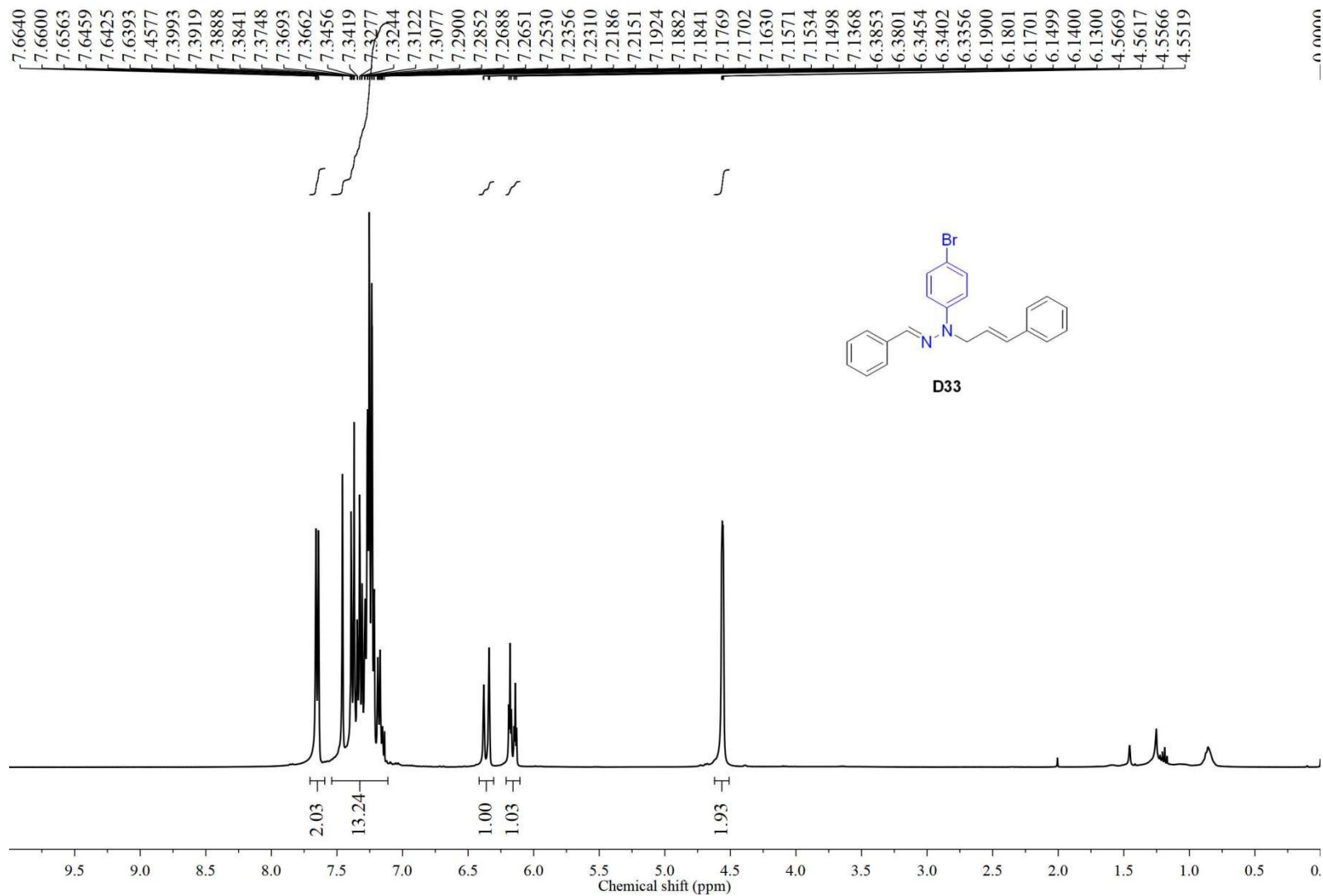
S202

2022-06-20 yy0016-616-Lqq-B13.10.fid



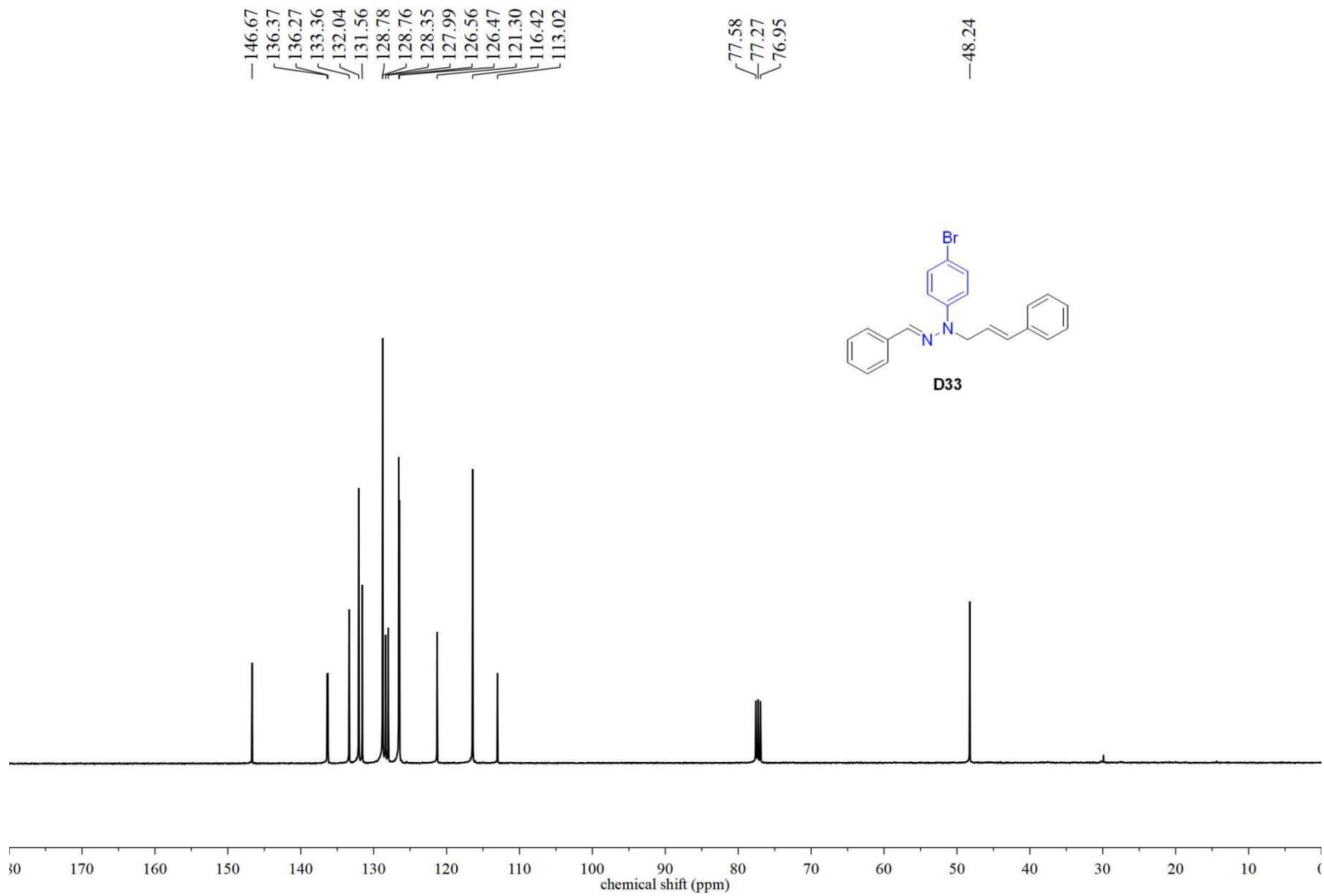
S203

2022-06-23 yy0042 616-lqq-b16.10.fid



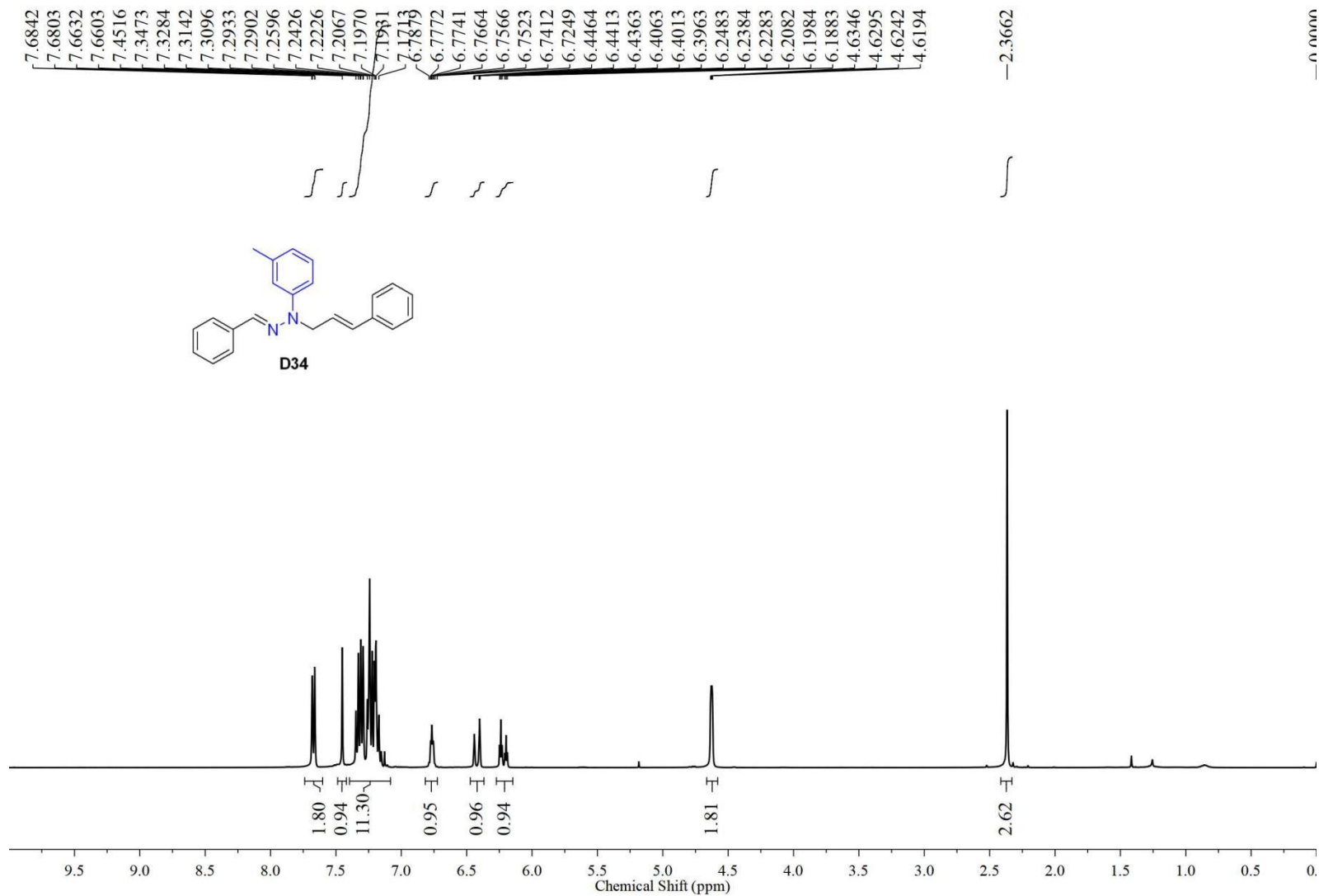
S204

2022-06-27-yy0001-616-1-b-16

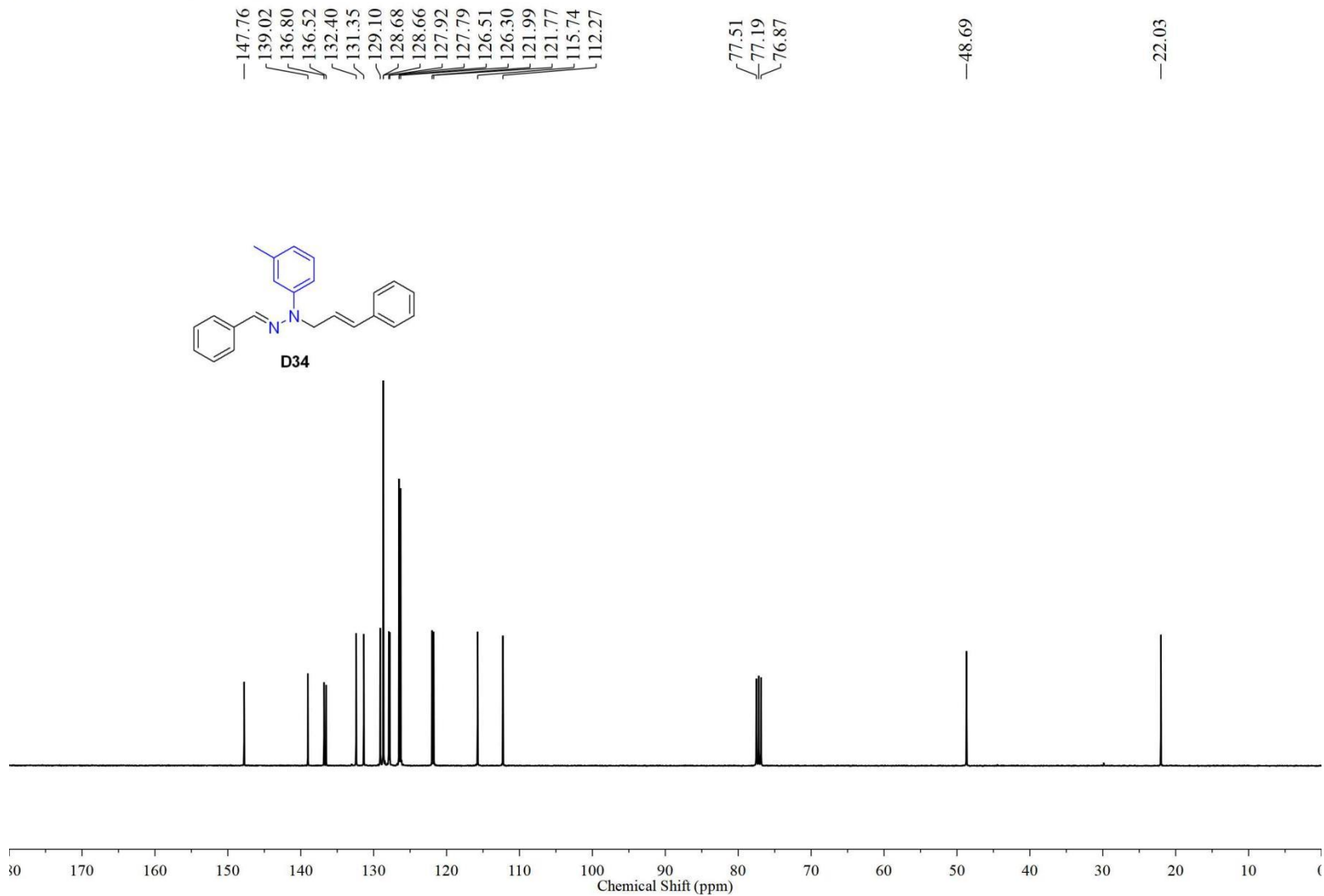


S205

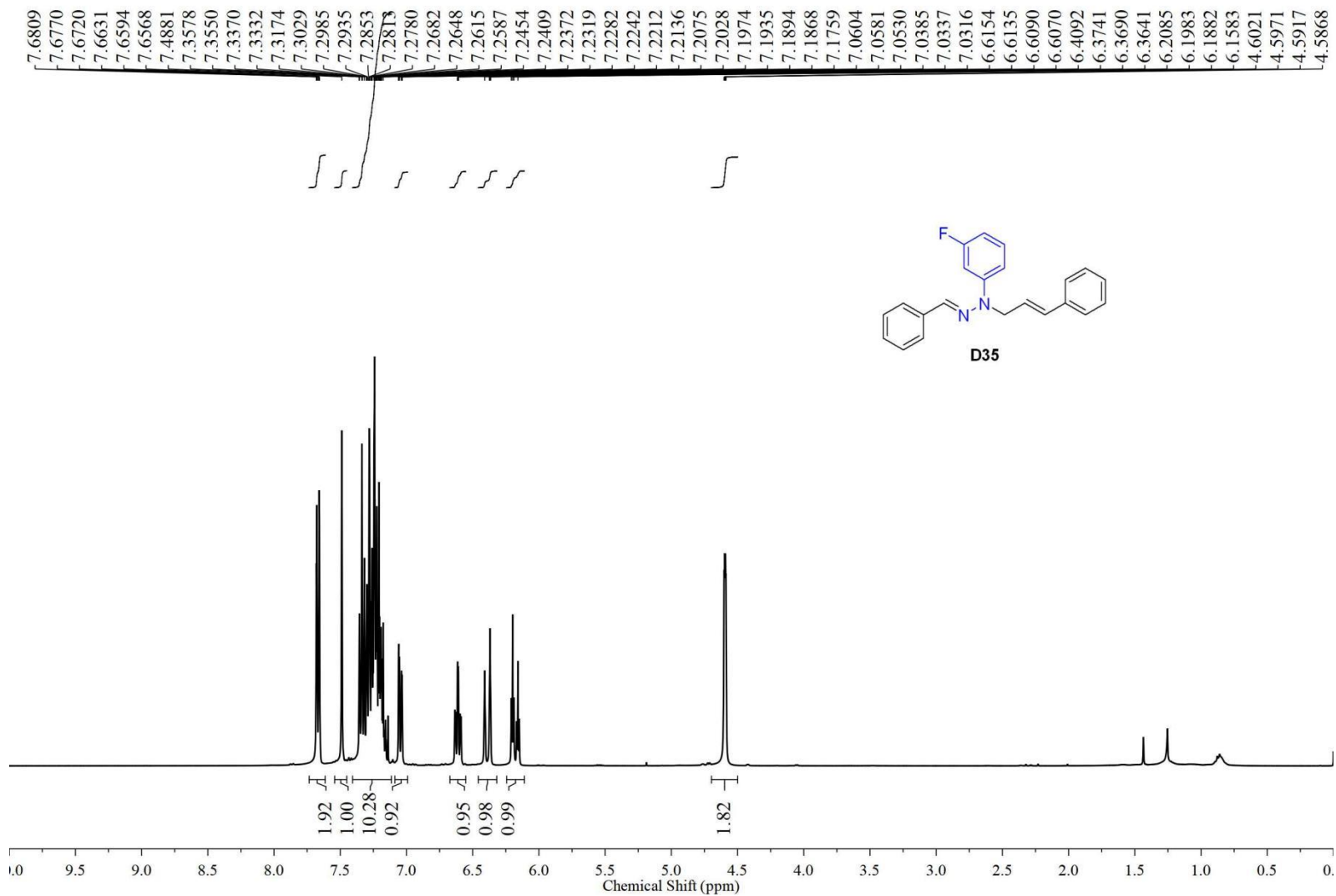
2022-6-9 yy0012-616-1-b3.10.fid



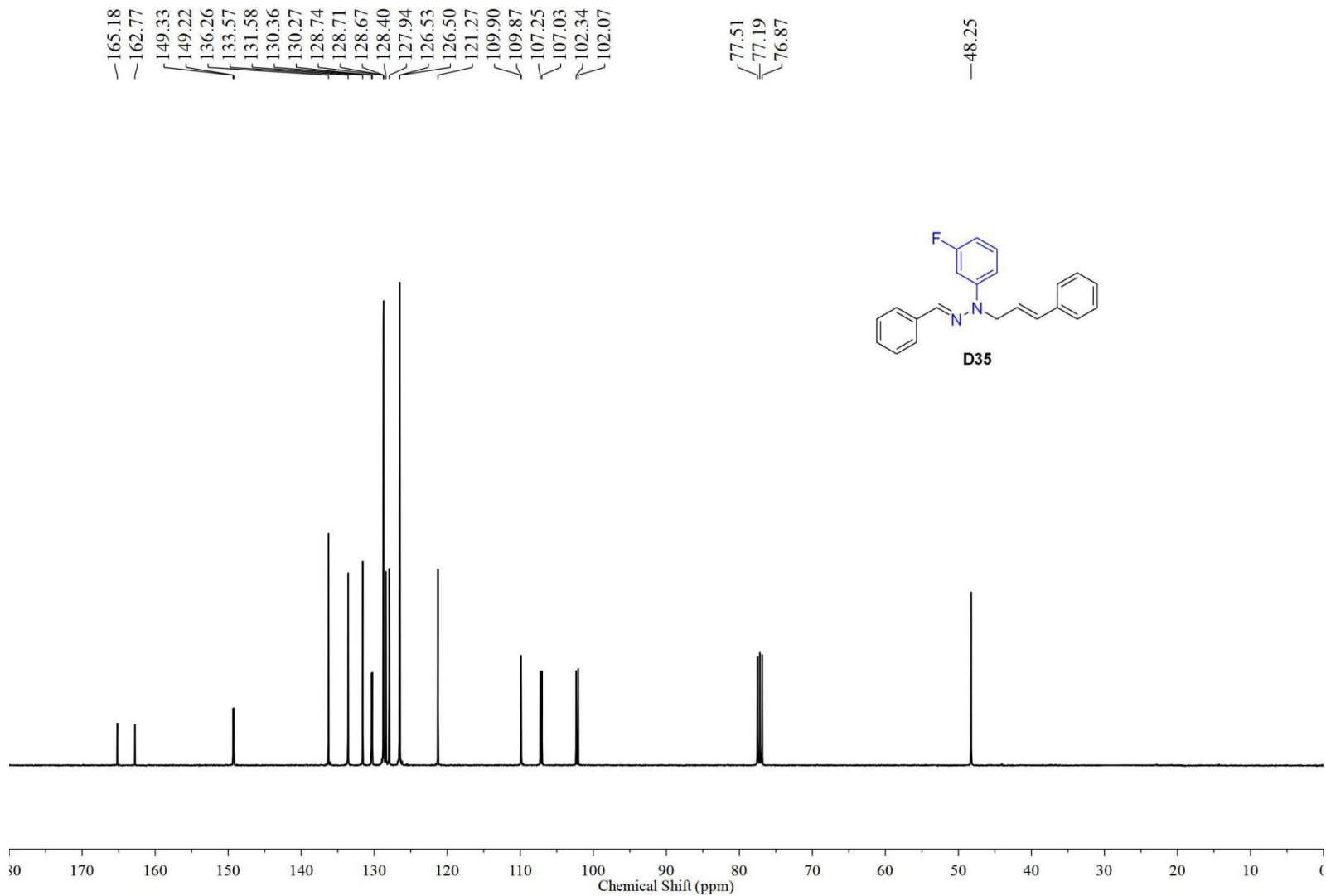
2022-6-11 yy0042-616-1qq-b3. 10. fid



S207



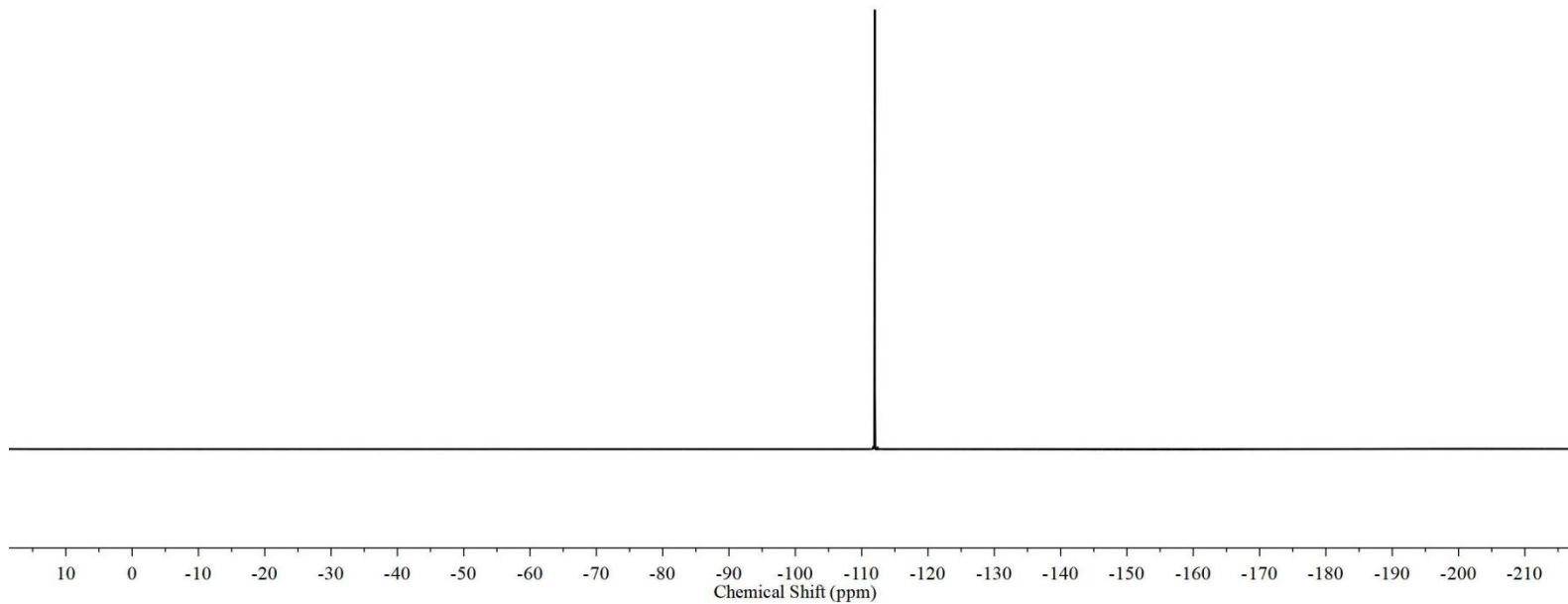
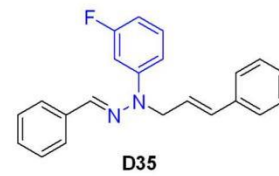
2022-6-17 yy0021-616-1-b8. 10. fid



S209

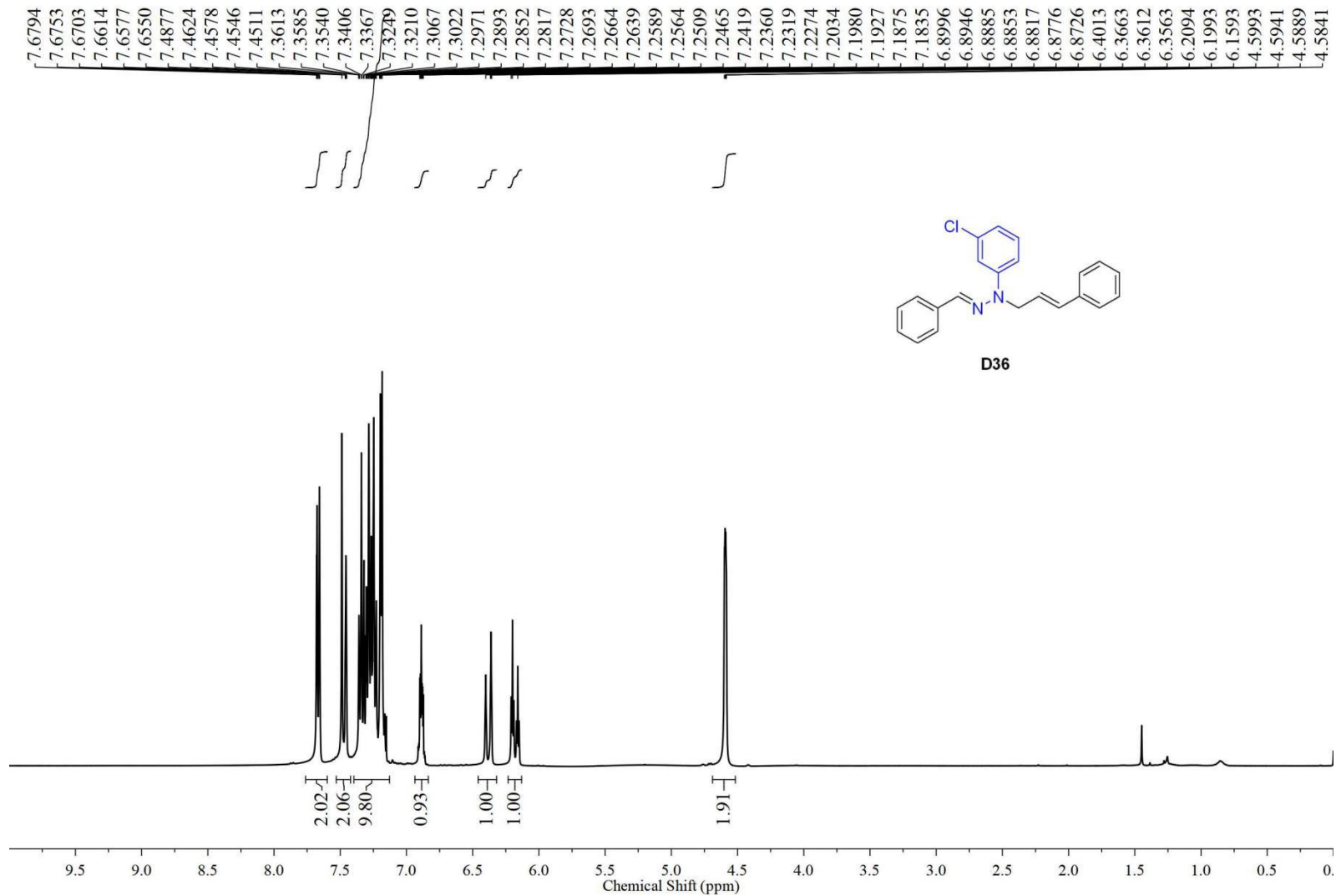
2022-6-17 yy0021-616-1-b8. 11. fid

86.111.98



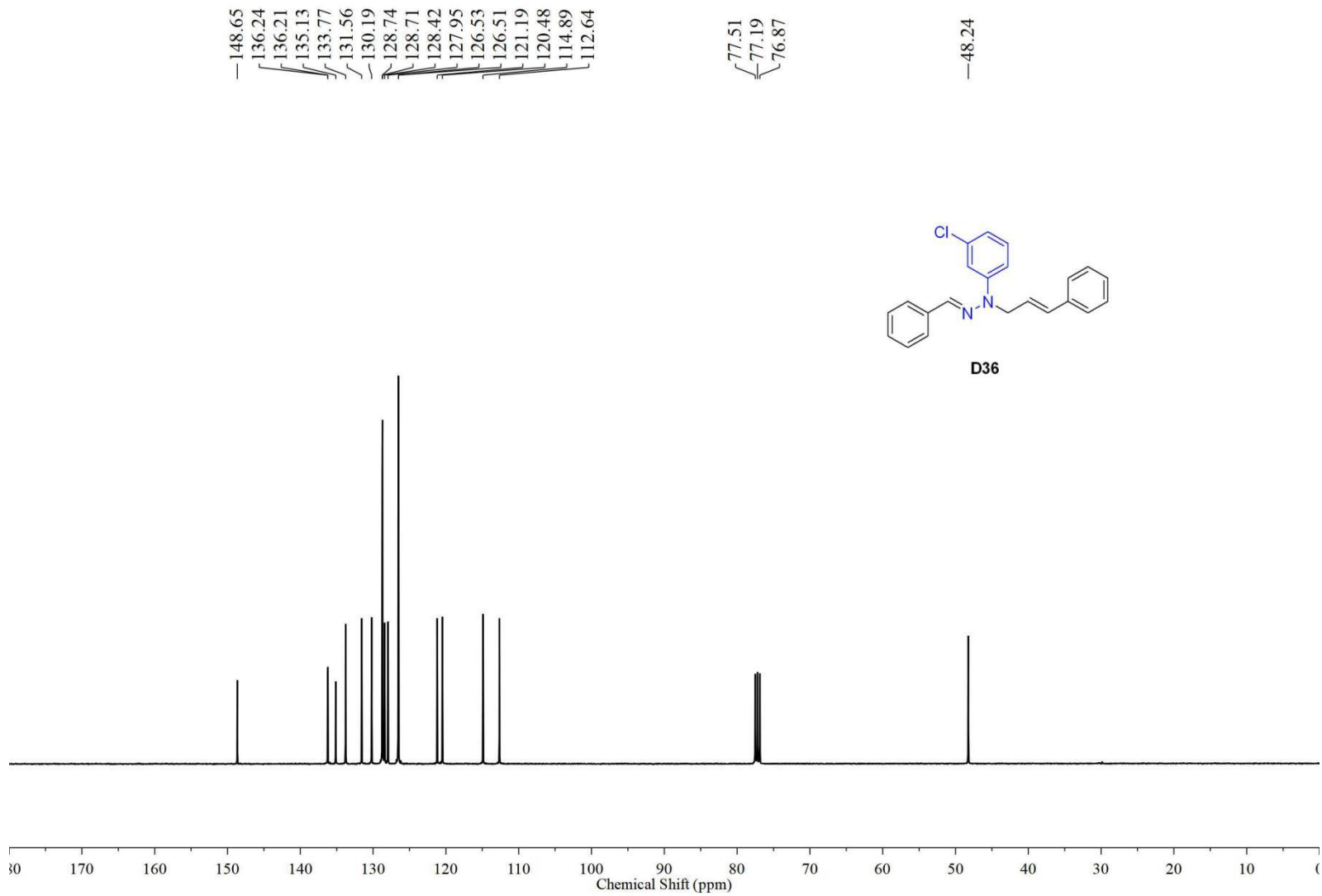
S210

2022-6-20 yy0027 616-lqq-14.10. fid



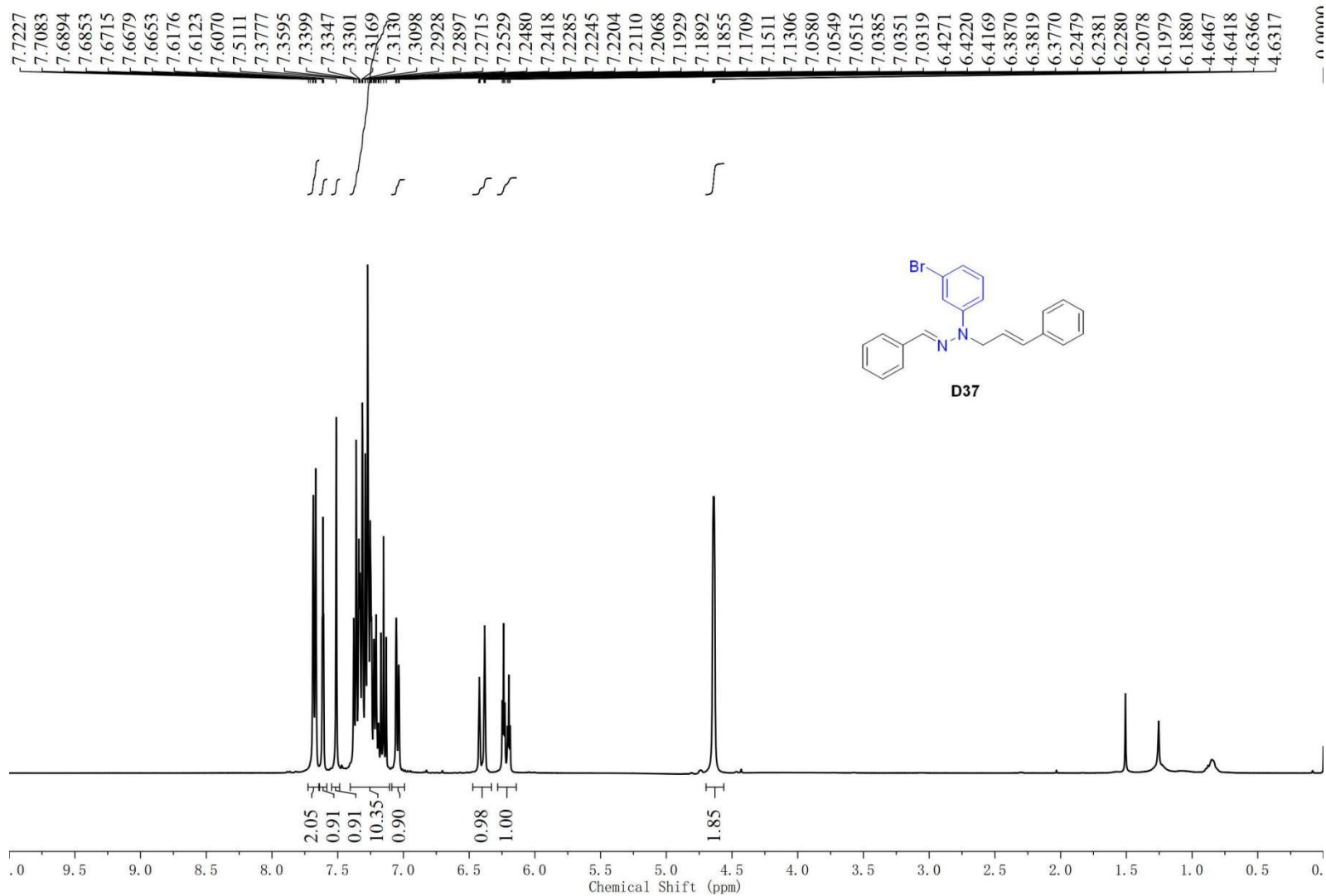
S211

2022-06-21 yy0025 616-lqq-14.10.fid



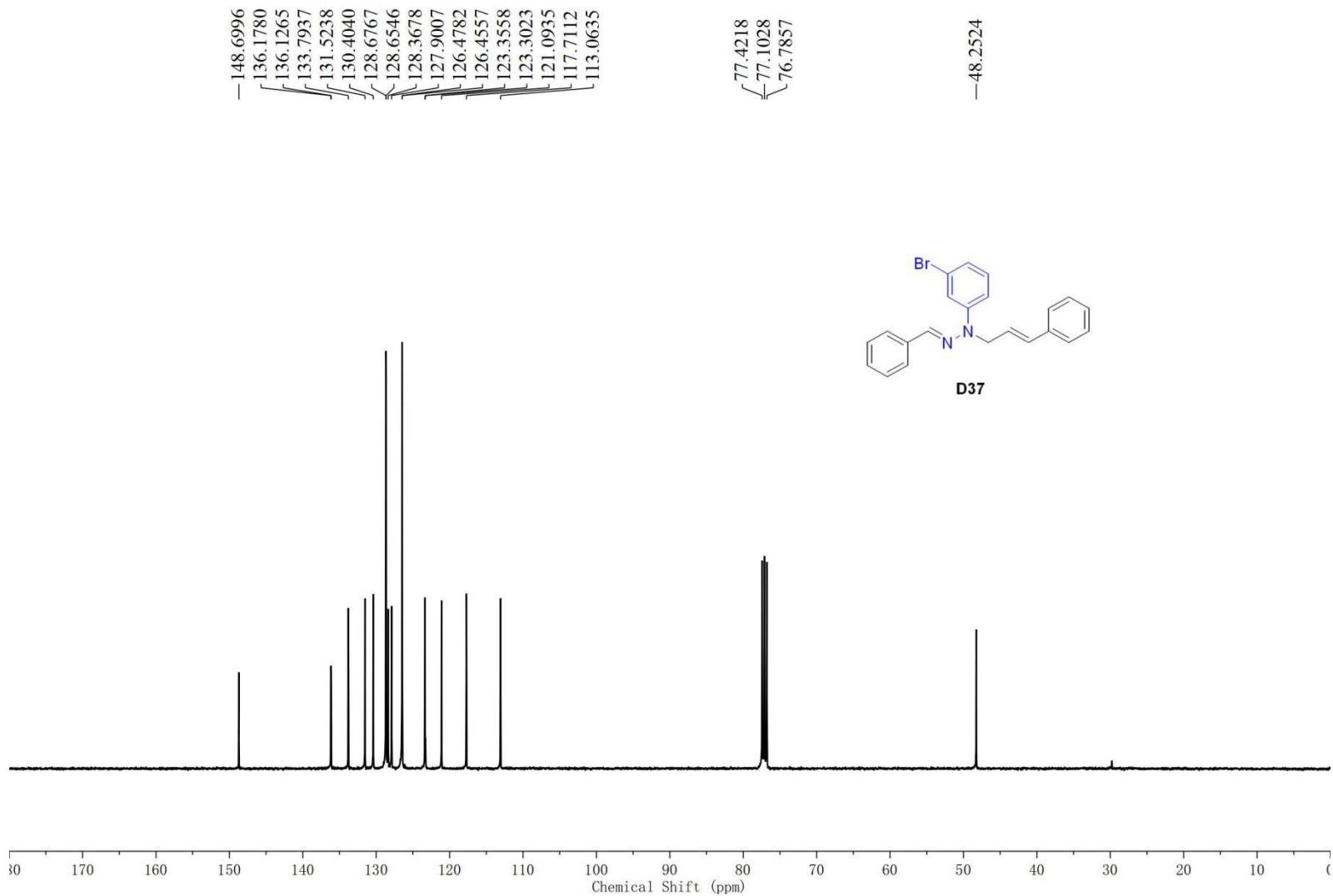
S212

2022-06-29-yy0006-616-1-b17.10.fid



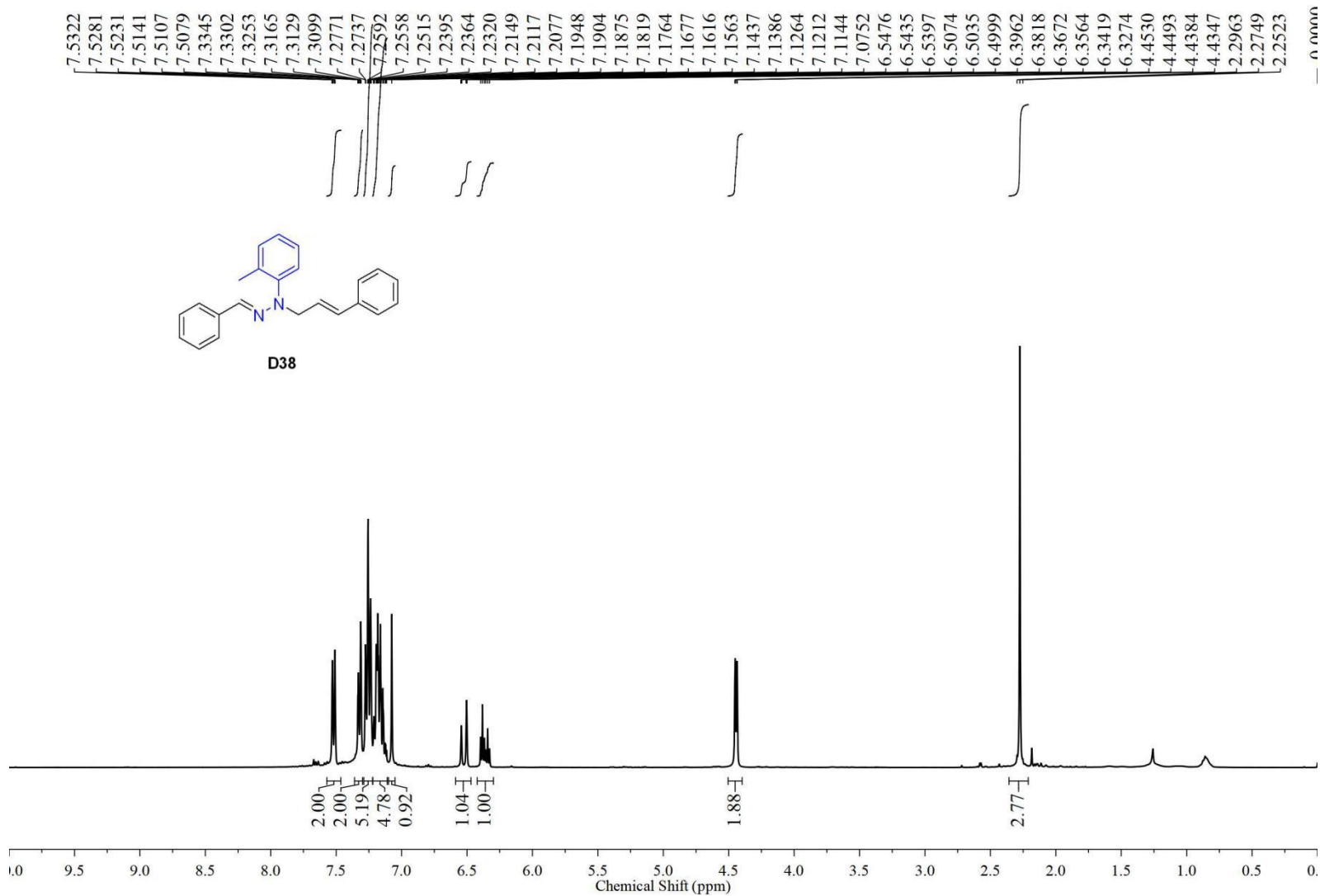
S213

2022-06-30-yy0021-616-1-b17.10.fid



S214

2022-6-14 YY0007-616-L-B4. 10. fid



S215

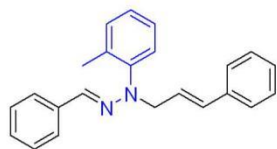
2022-6-15 yy0007-616-1qq-b4. 10. fid

145.08
137.05
136.85
135.38
133.36
132.31
131.34
128.68
128.58
127.66
127.55
127.27
126.73
126.52
126.31
125.84
125.55

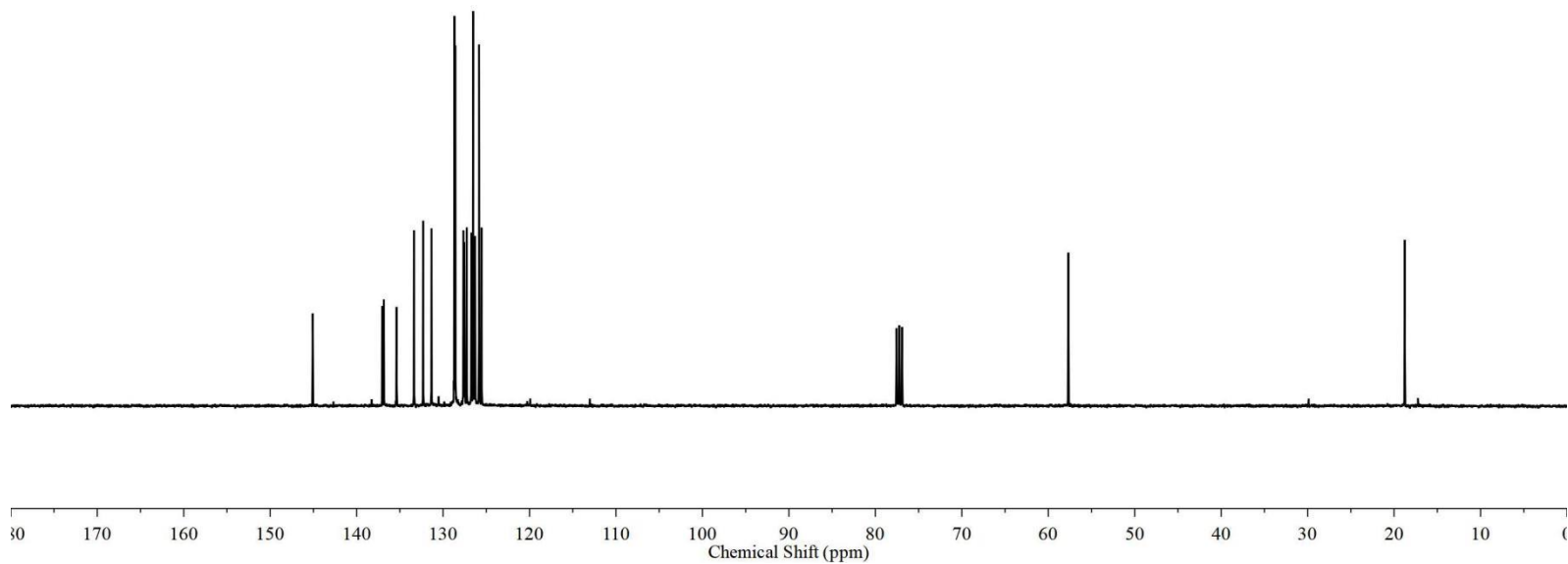
77.55
77.23
76.91

57.68

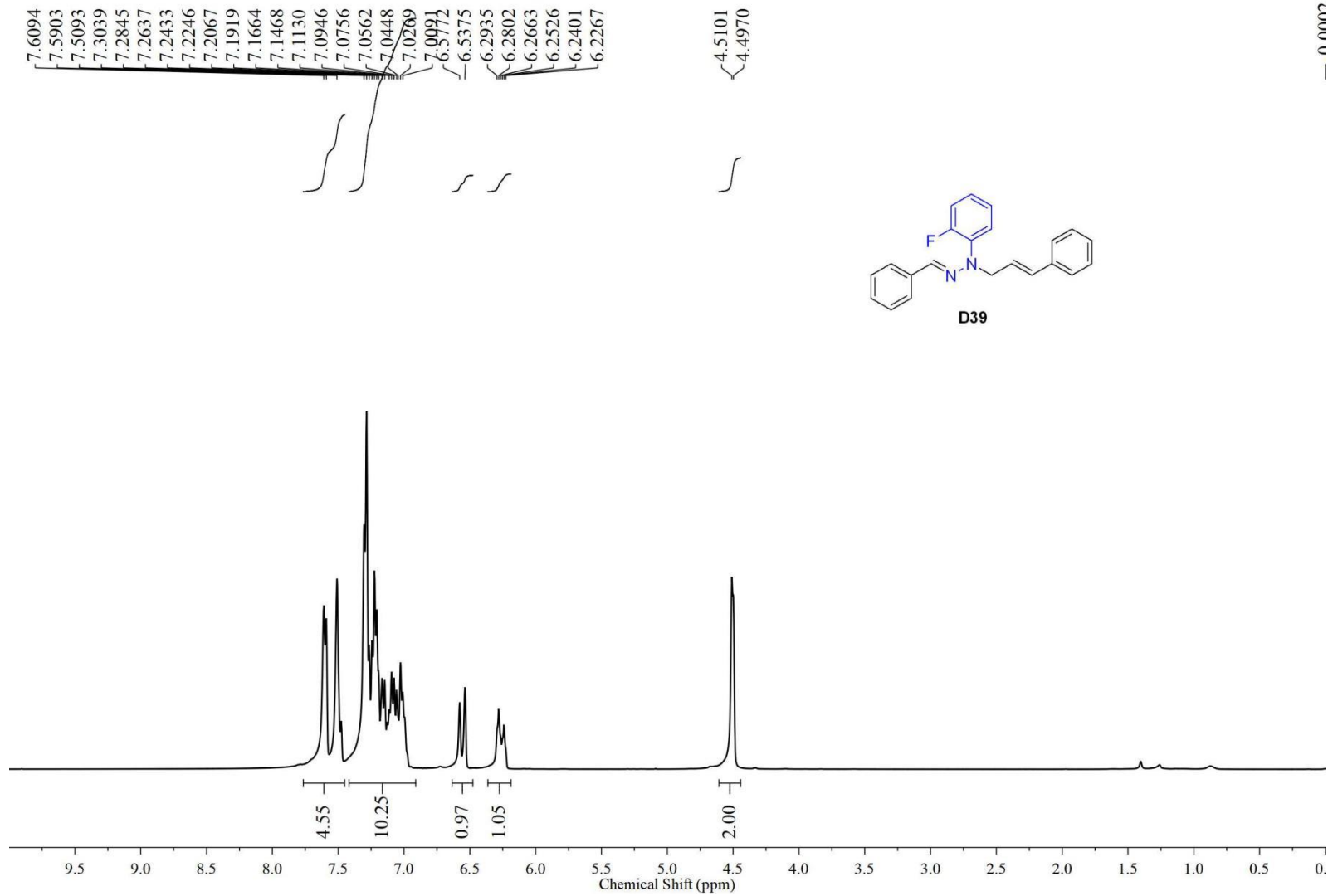
18.77



D38

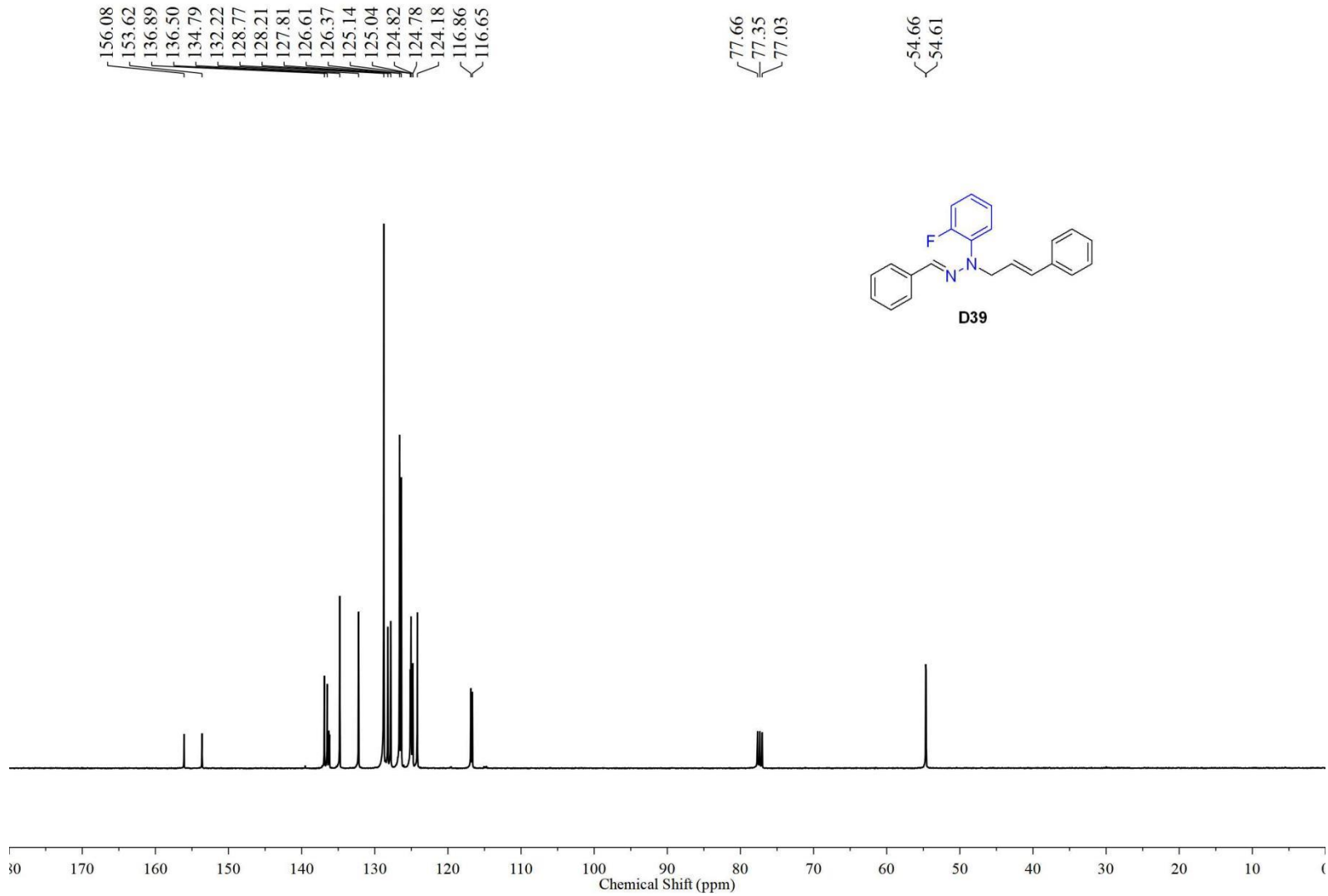


2022-07-11 YY0001 616-1-B9.10.fid



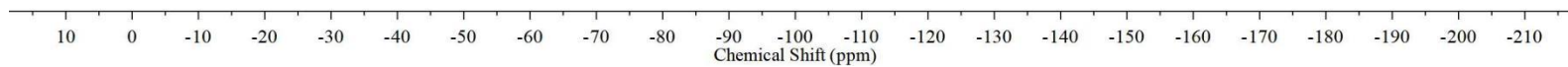
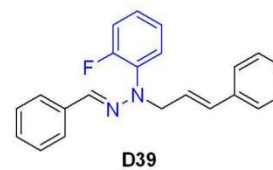
S217

2022-07-13 YY0019 616-lqq-1-B9. 11. fid

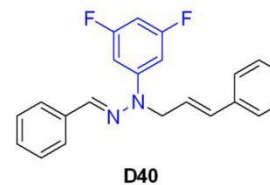
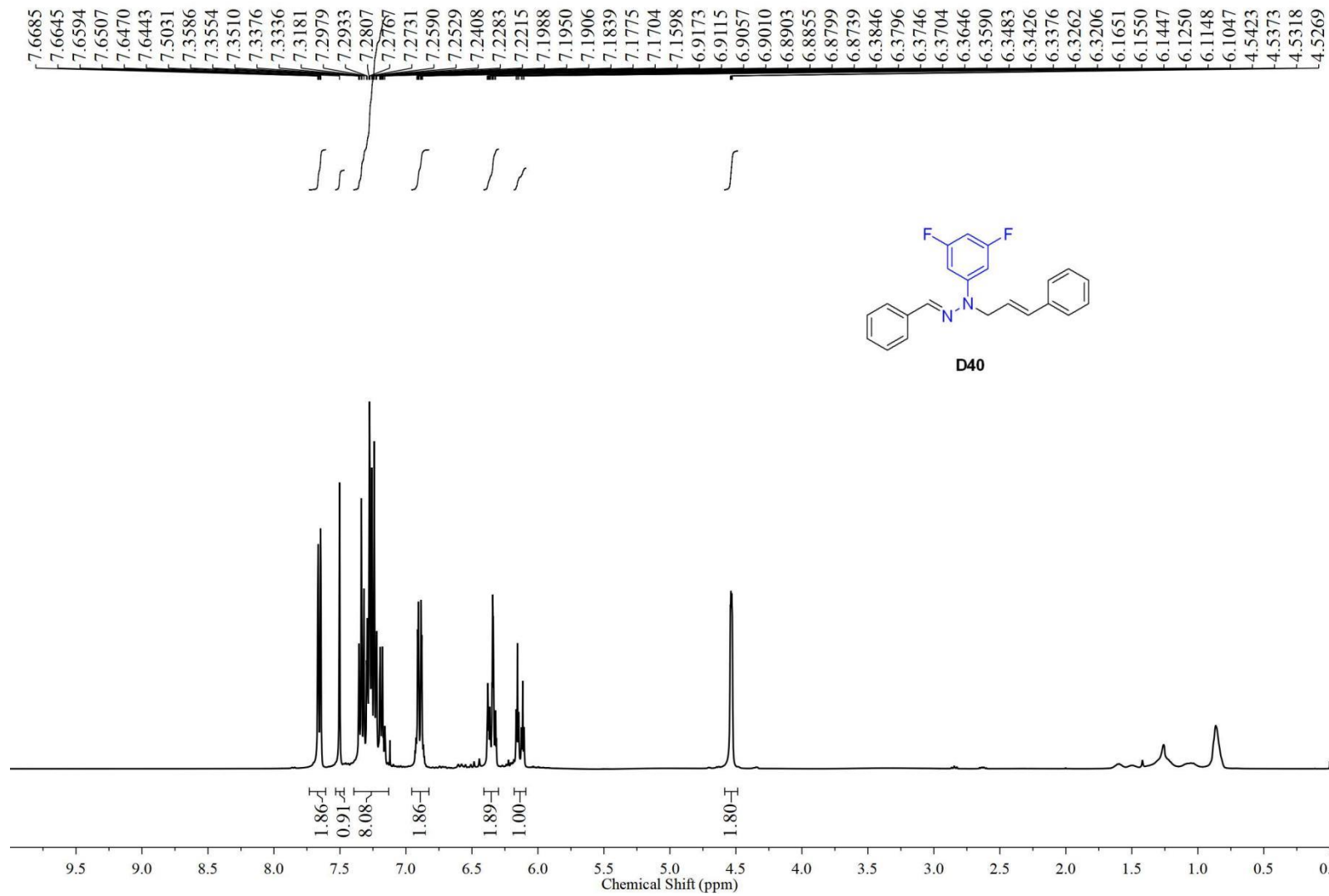


S218

--122.05

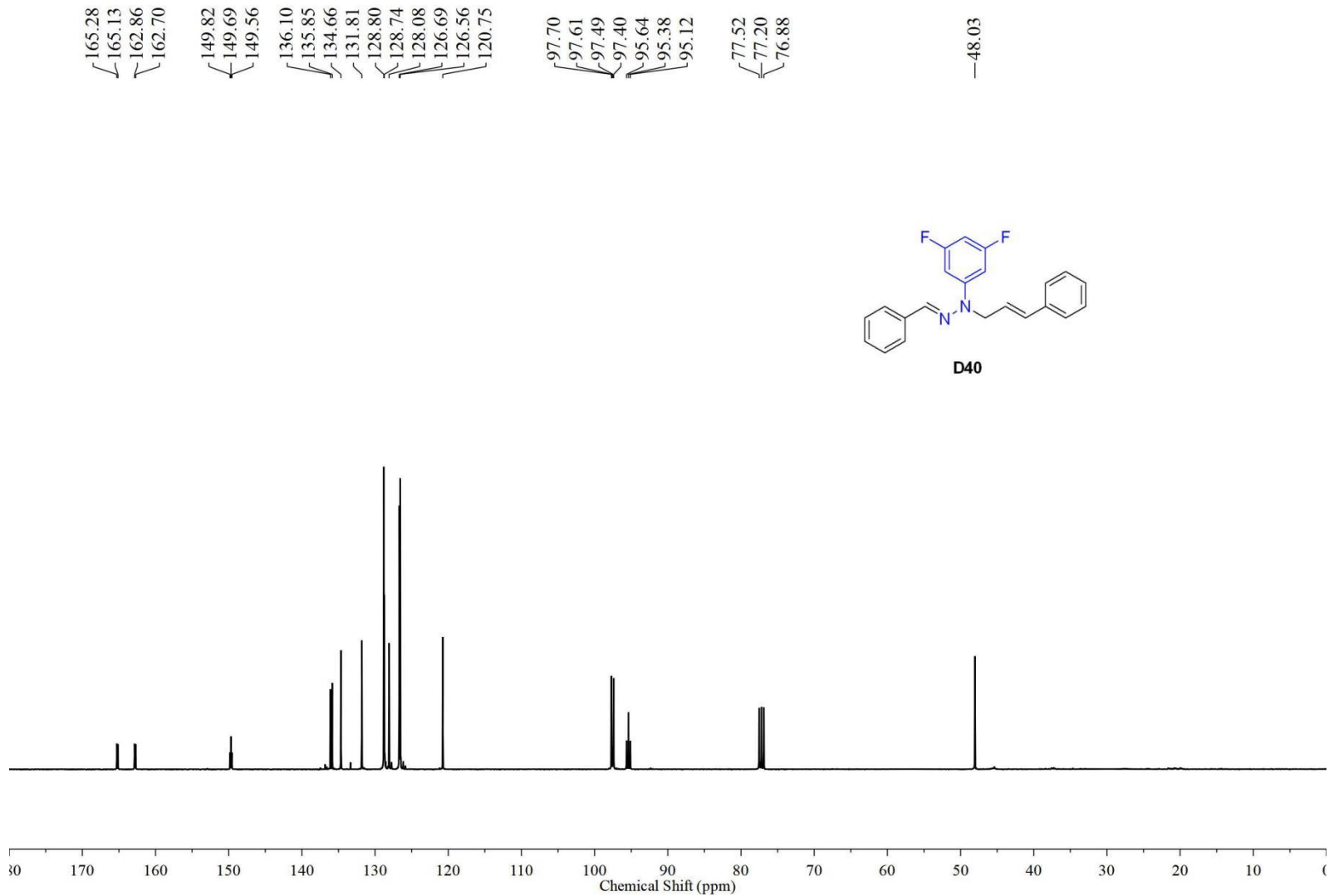


2022-7-6 yy0028-616-lqq-32.10.fid



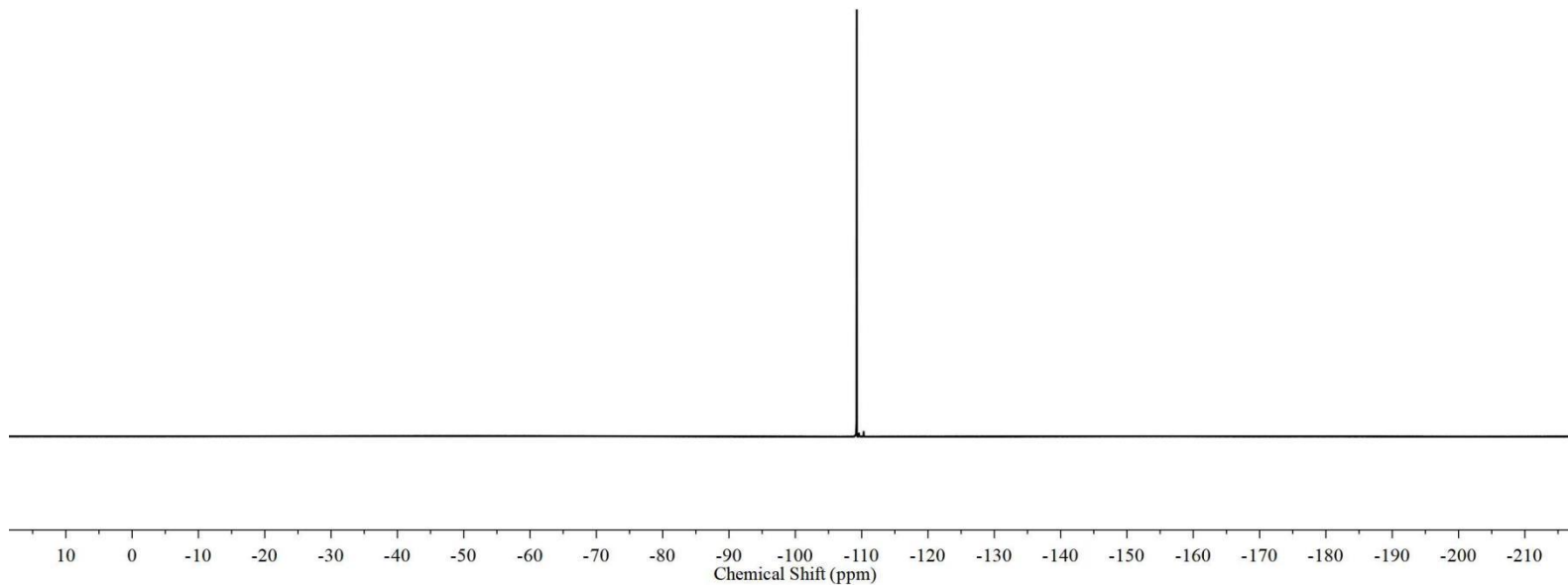
S220

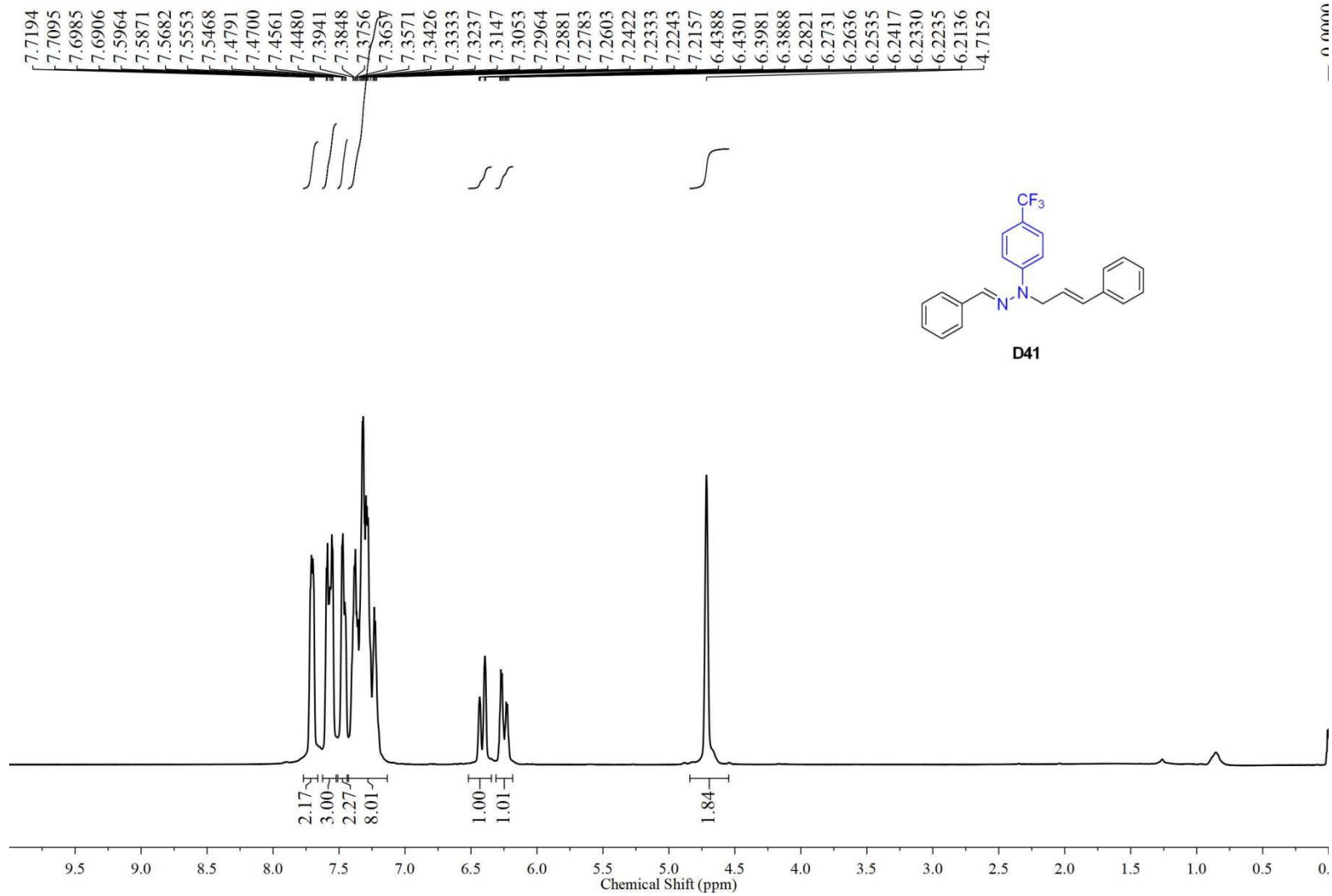
2022-7-6 yy0028-616-lqq-32.11.fid



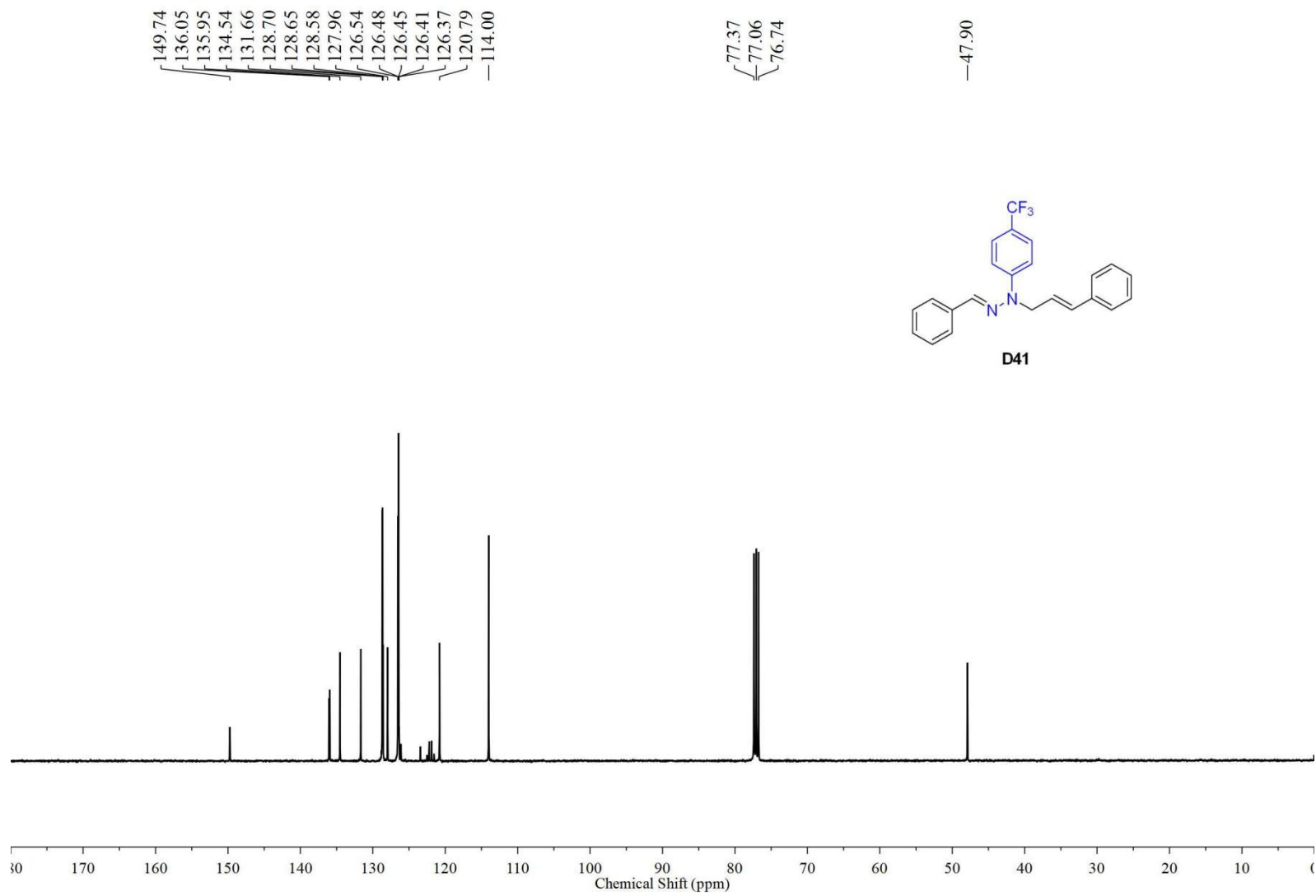
S221

-109.26



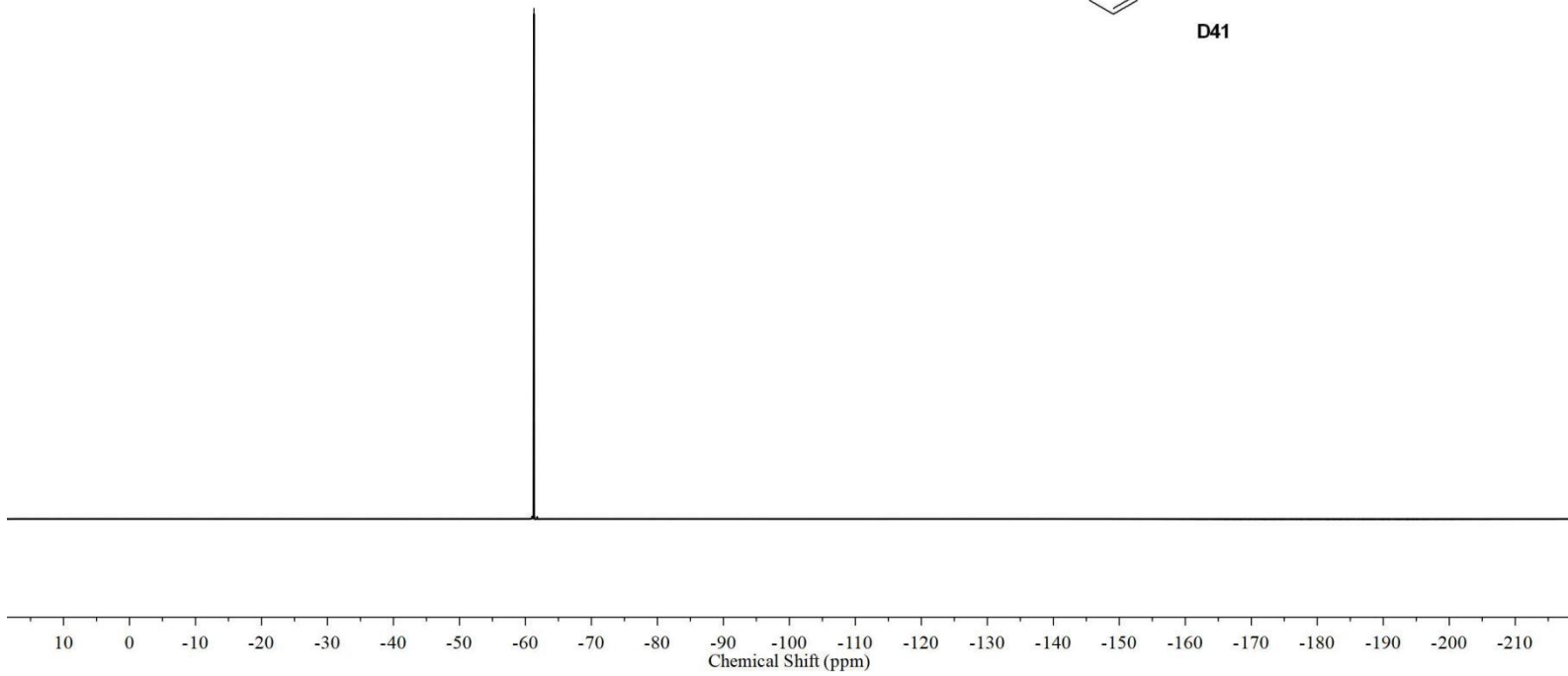
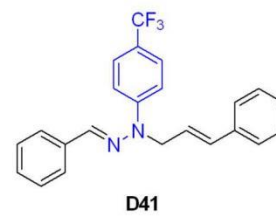


2022-06-20 yy0016-616-Lqq-B10.10.fid

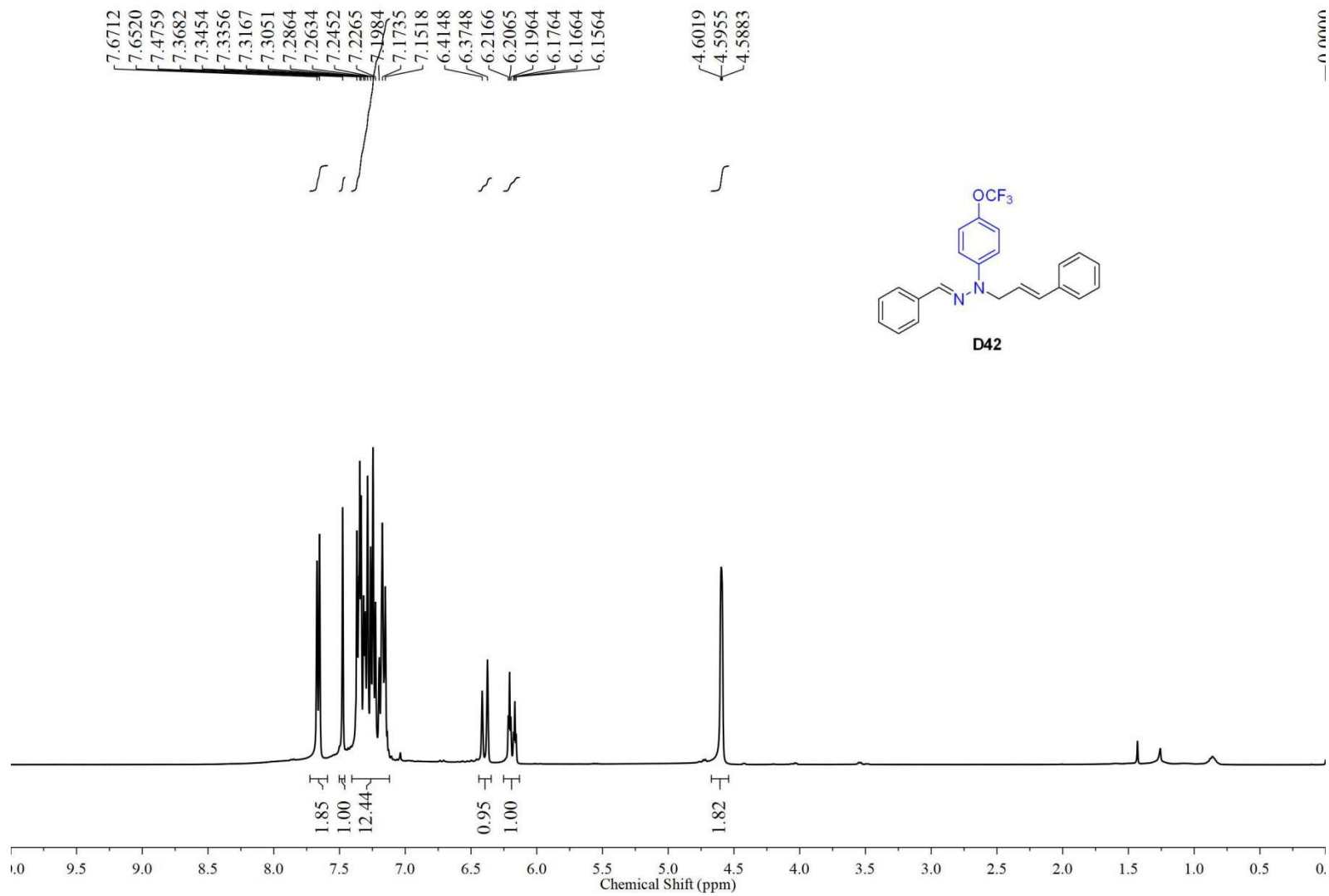


2022-06-20 yy0016-616-Lqq-B10.11.fid

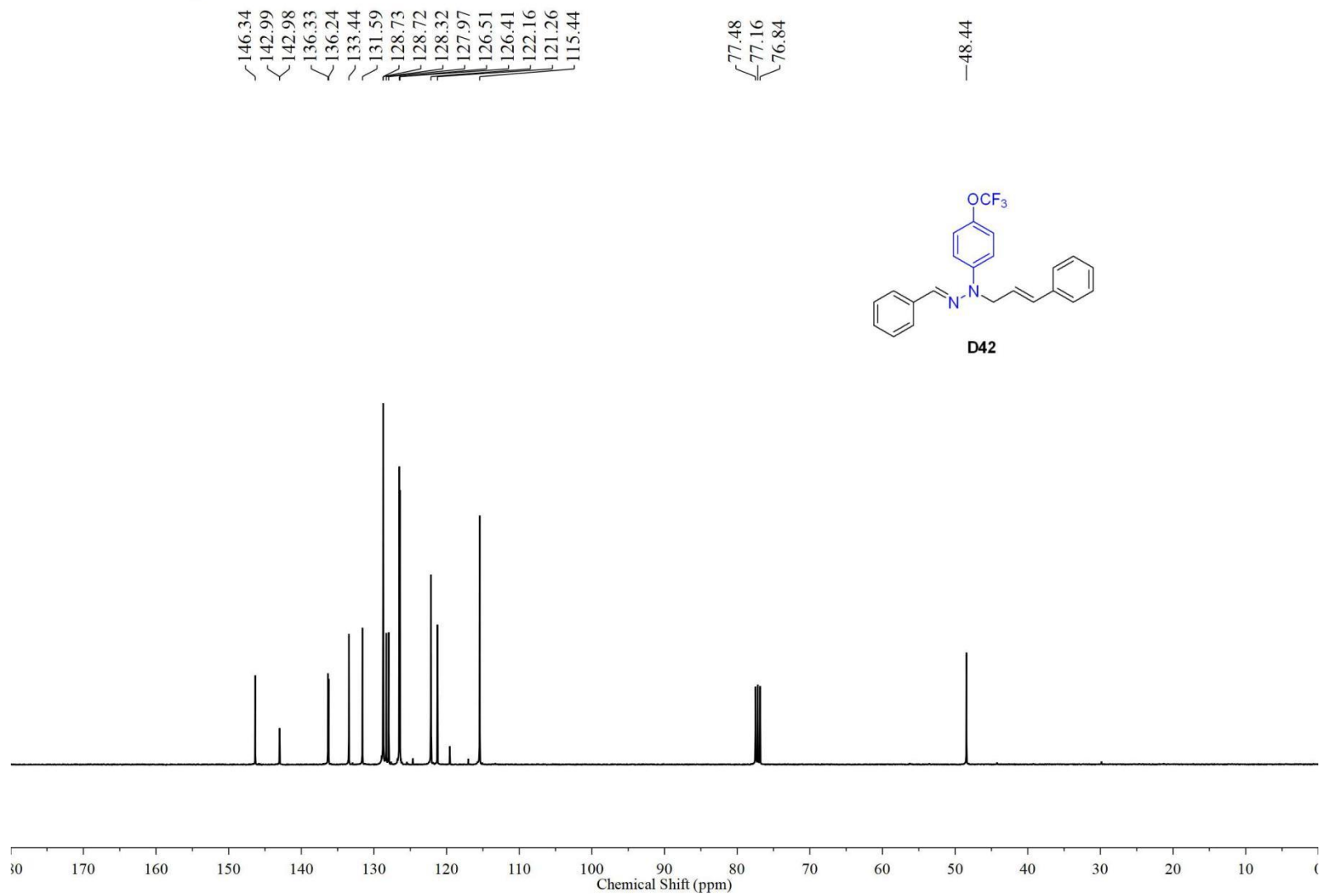
--61.29



2022-6-20 yy0027 616-lqq-12.10.fid

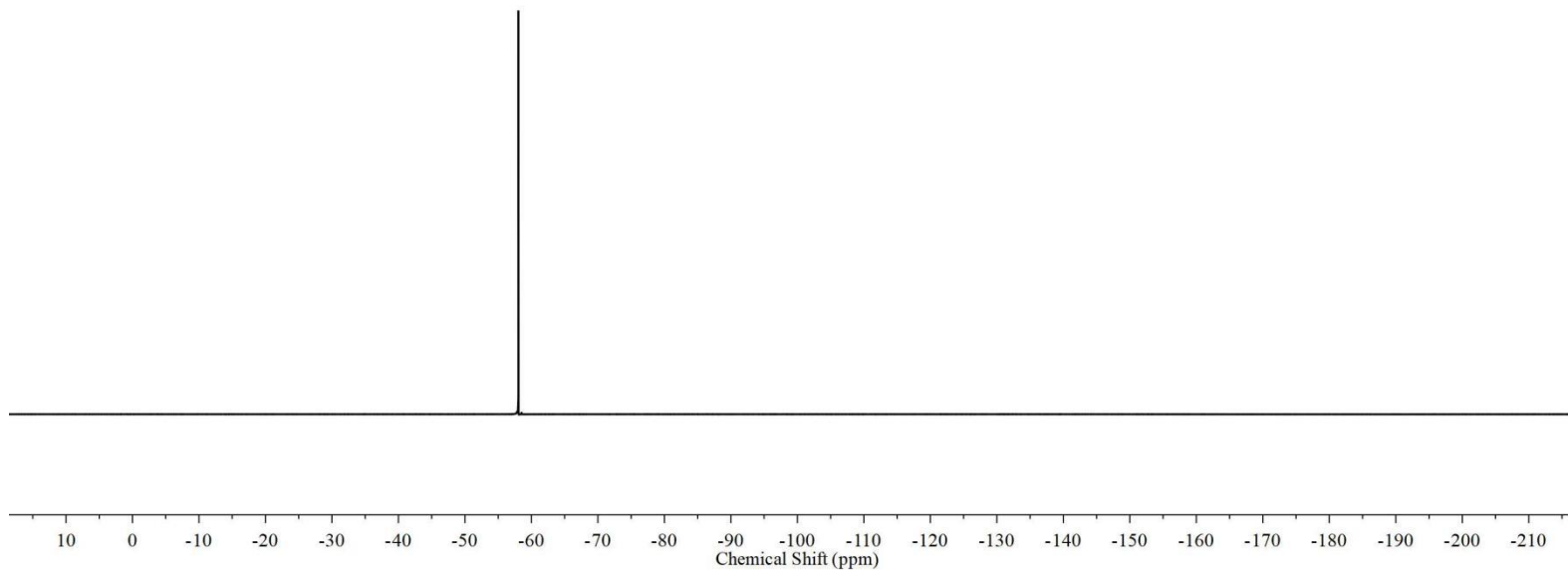
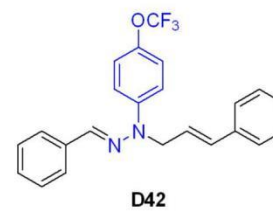


2022-06-21 yy0025 616-lqq-12.10.fid



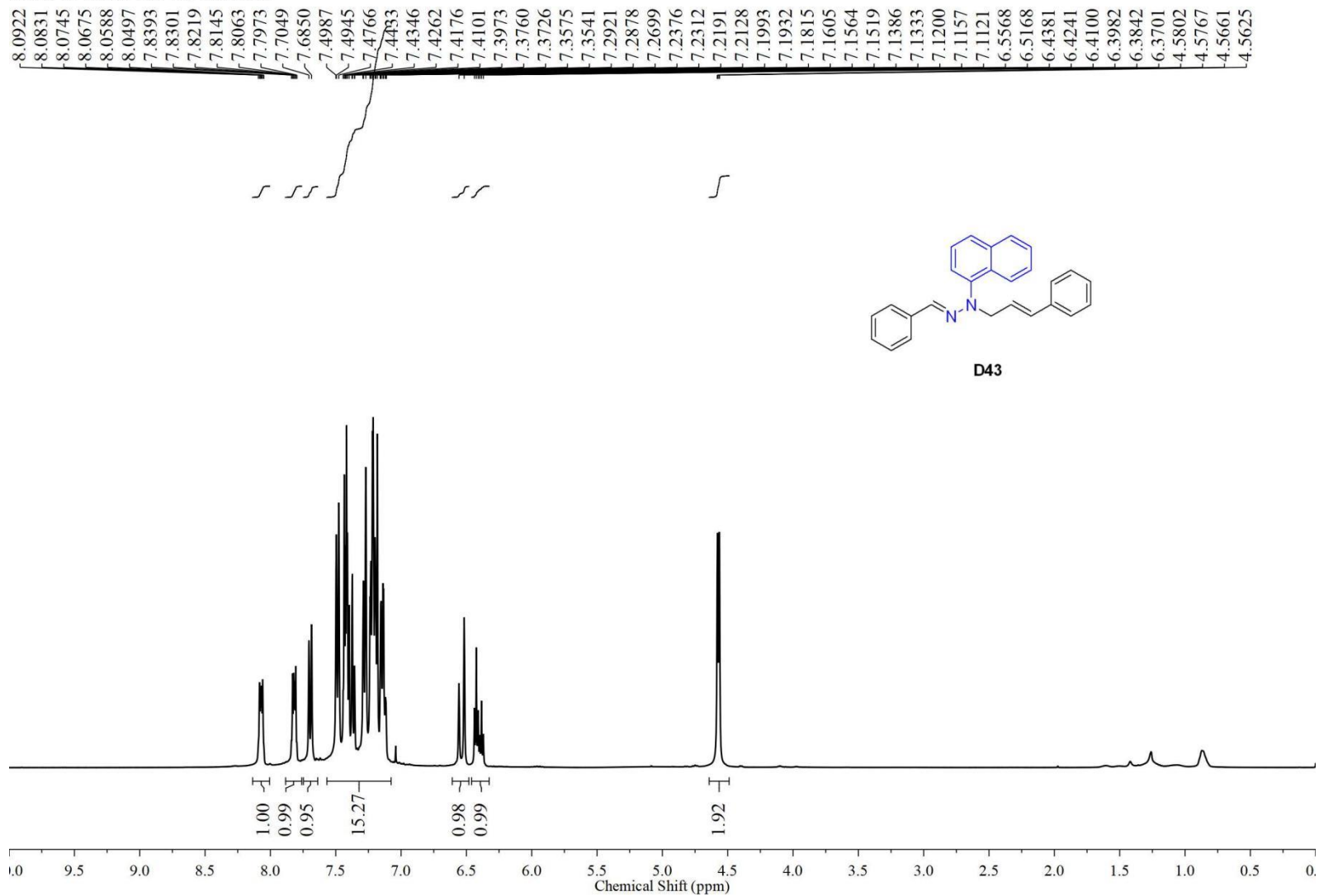
2022-06-21 yy0025 616-lqq-12.11.fid

--58.05

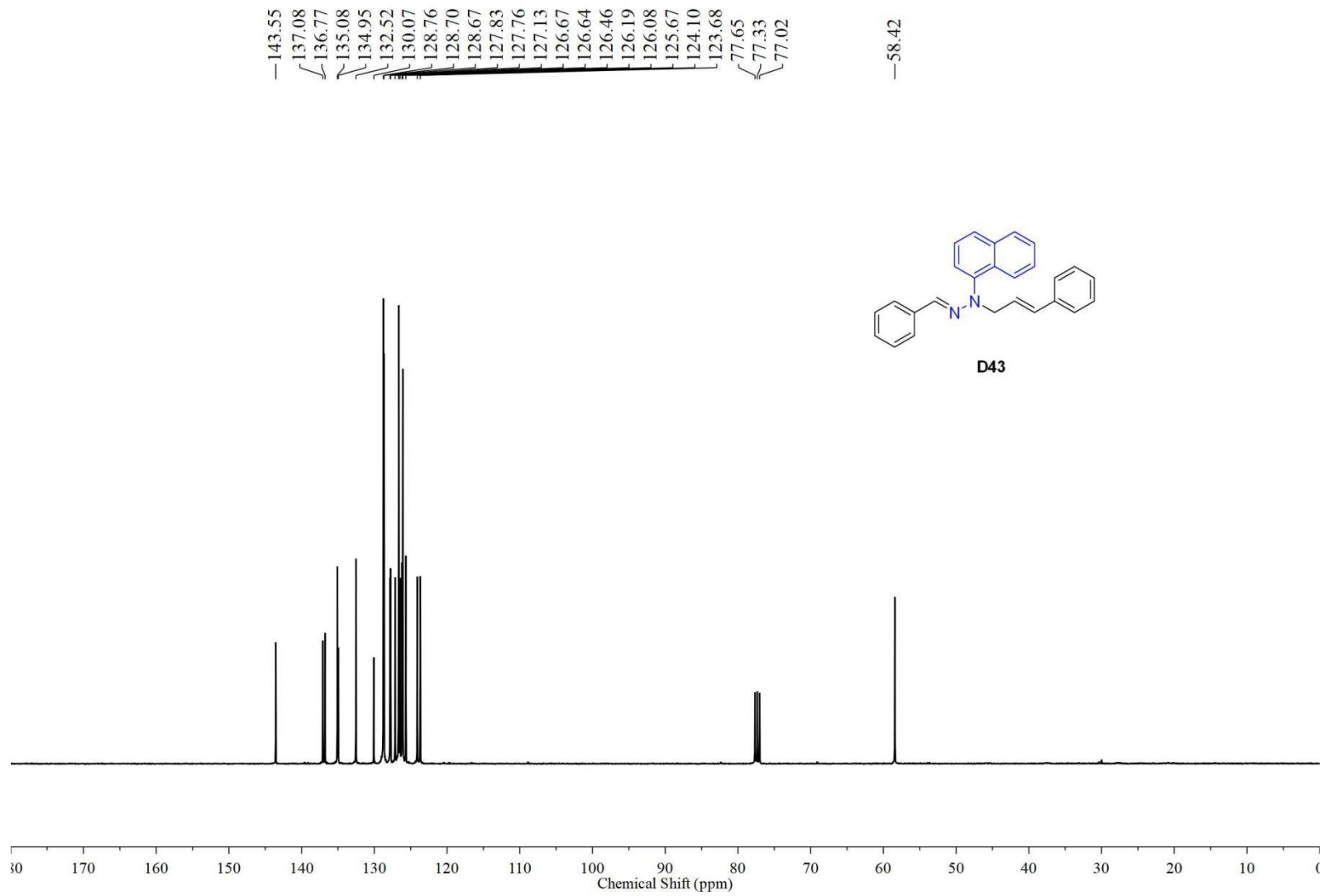


S228

2022-6-20 yy0027 616-lqq-20.10.fid

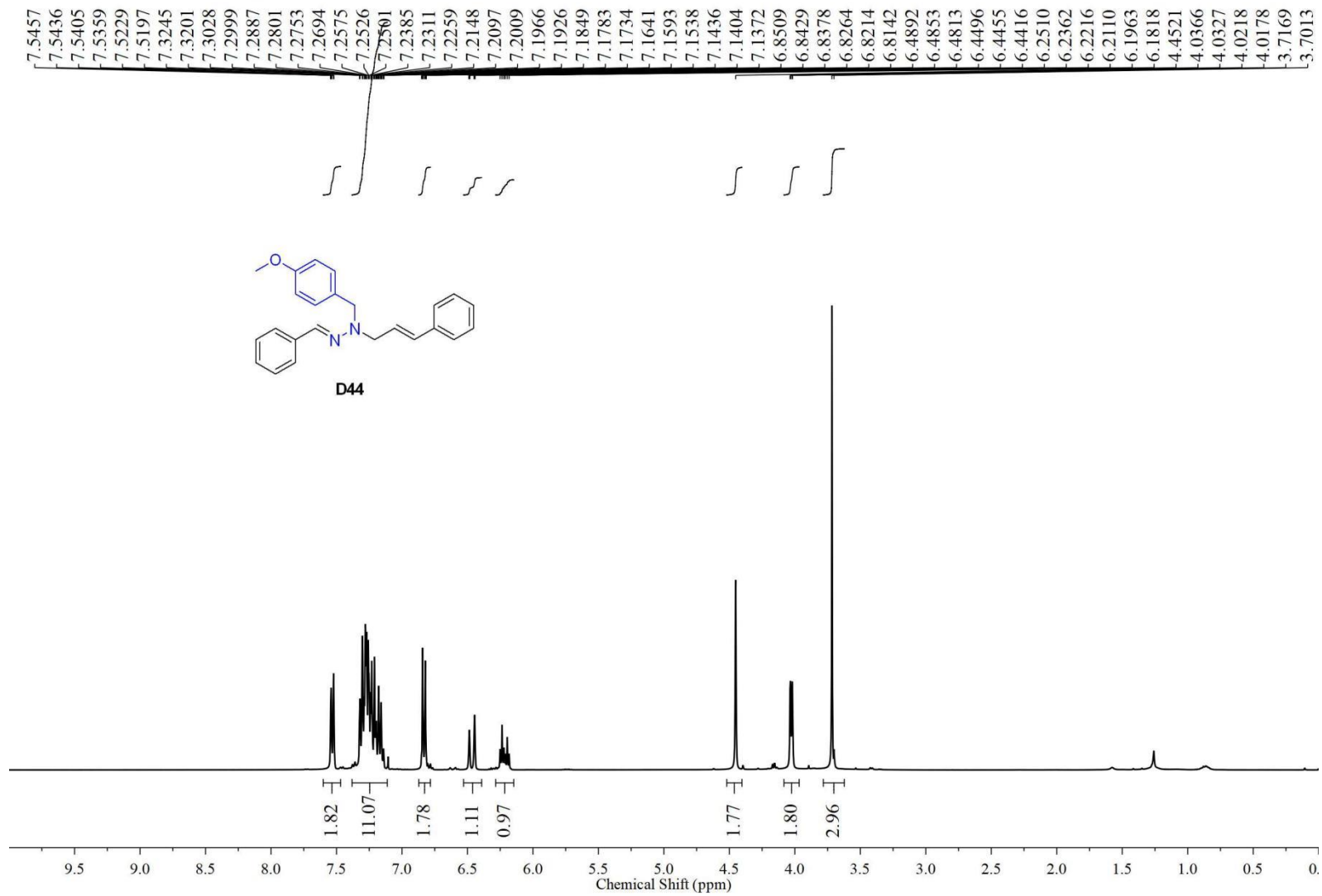


2022-06-21 yy0025 616-lqq-20.10.fid



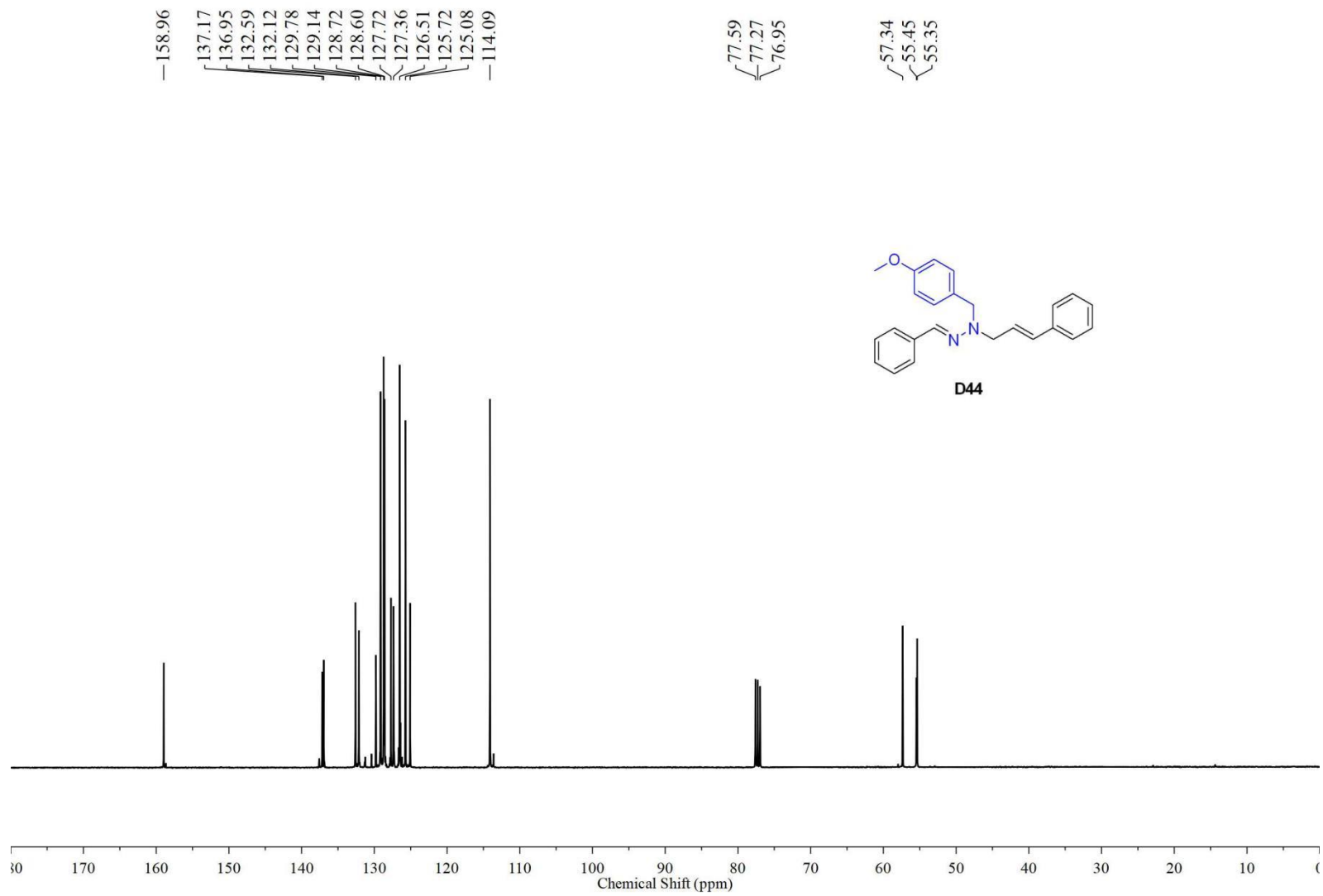
S230

2022-07-18-yy0004-616-1-b5.10.fid

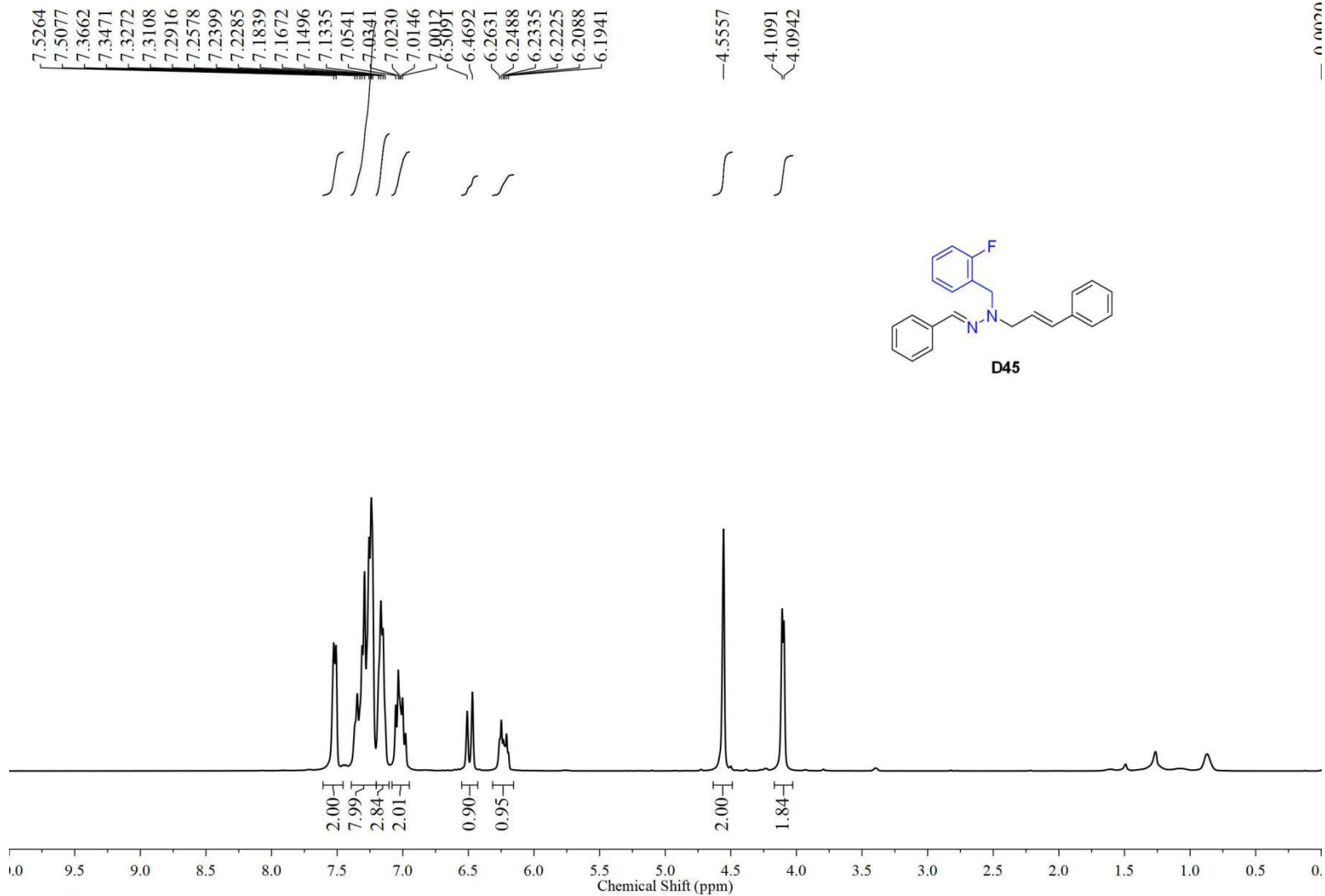


S231

2022-07-19-YY0059-616-L-B5.10.fid



2022-07-11 YY0001 616-1-B34.10. fid

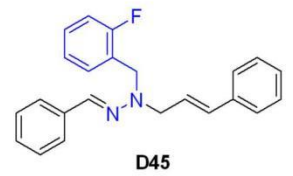
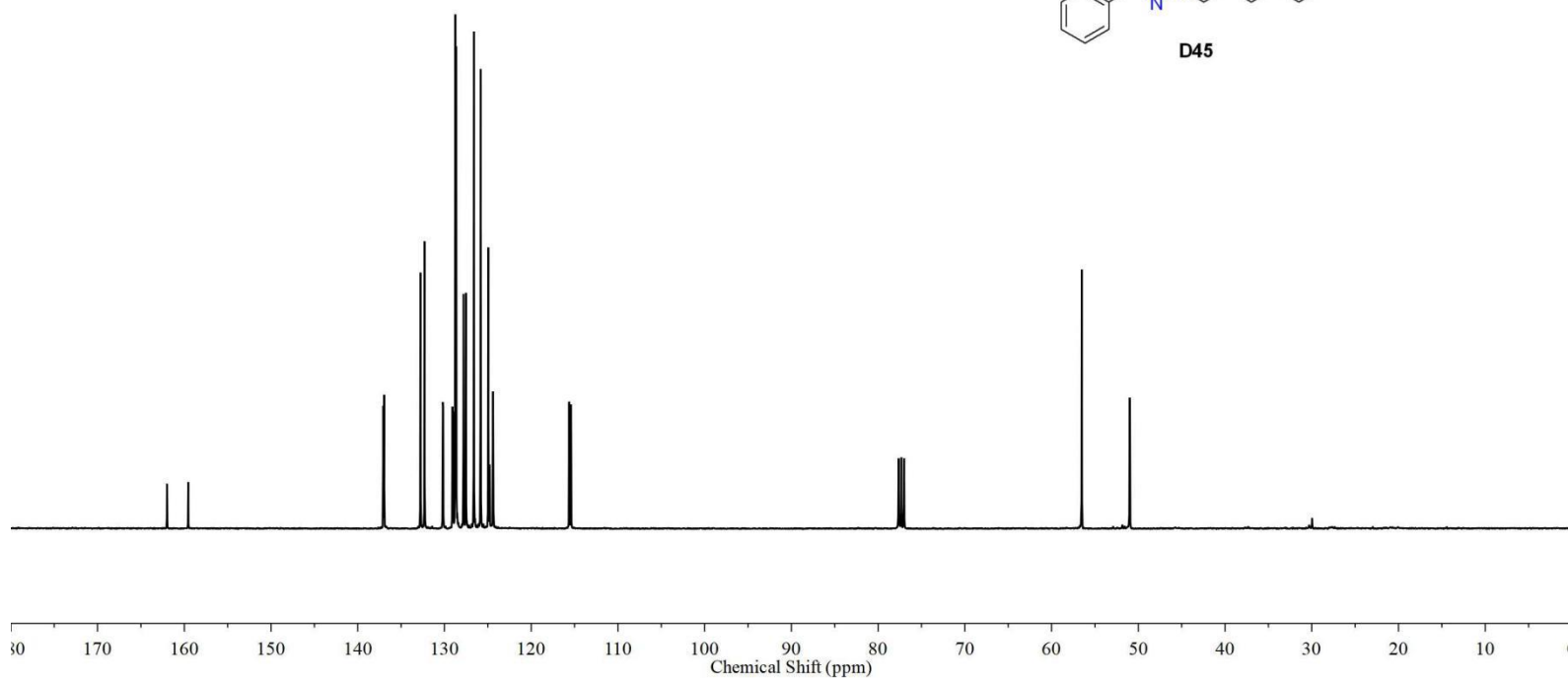


2022-07-13 YY0019 616-lqq-1-B34. 11. fid

161.99
159.55
137.05
136.96
132.77
132.31
130.19
130.15
129.07
128.99
128.76
128.66
127.80
127.52
126.61
125.83
124.95
124.79
124.41
124.37
115.62
115.41

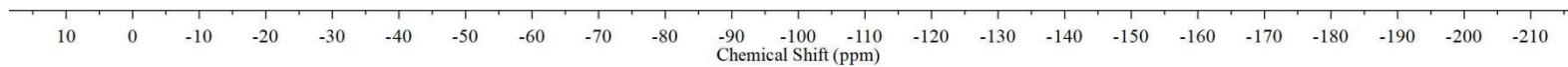
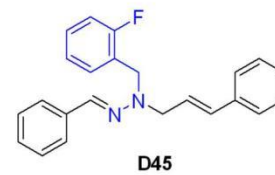
77.64
77.32
77.00

56.52
51.00
50.96



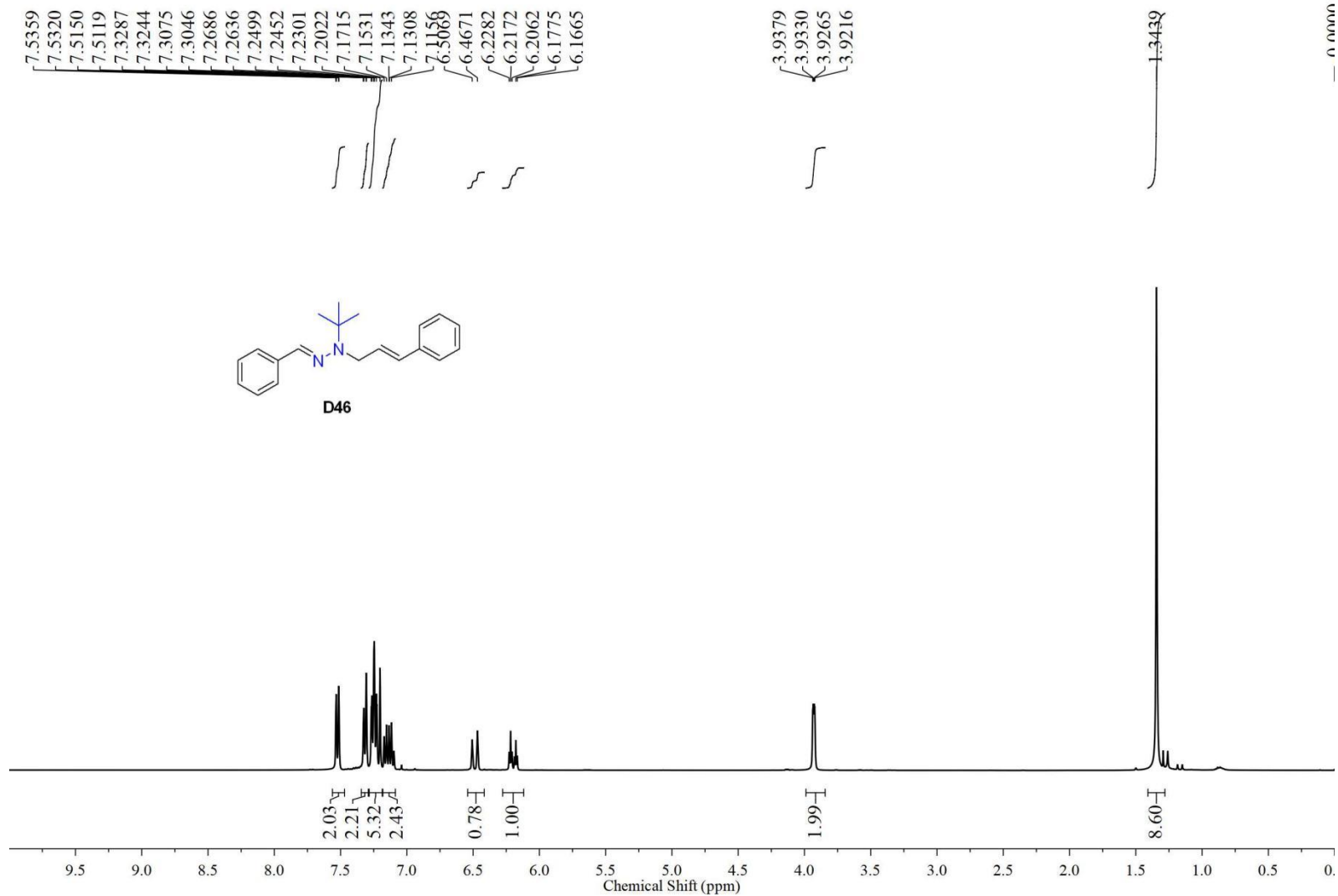
2022-07-13 YY0019 616-lqq-1-B34.10.fid

--117.81

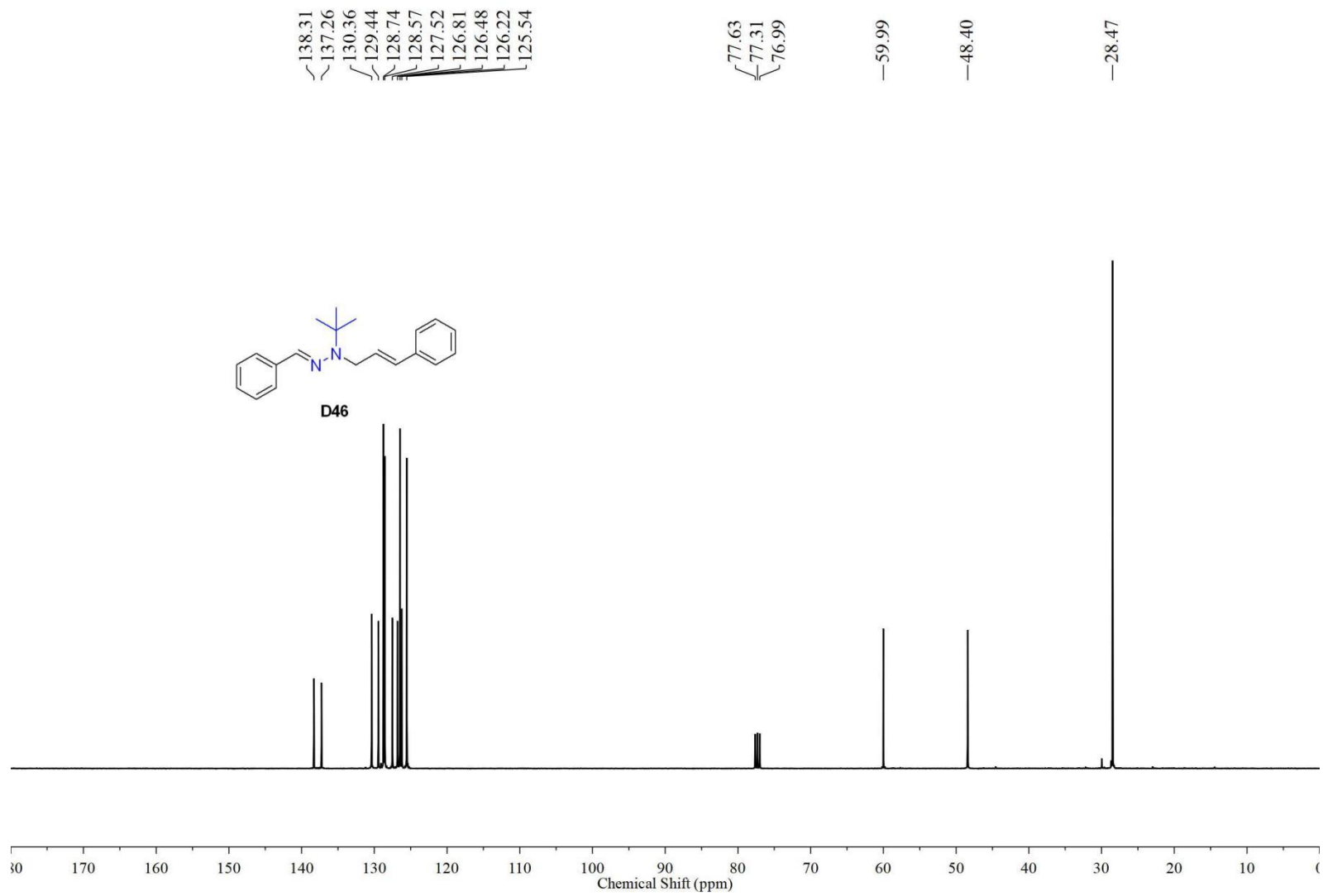


S235

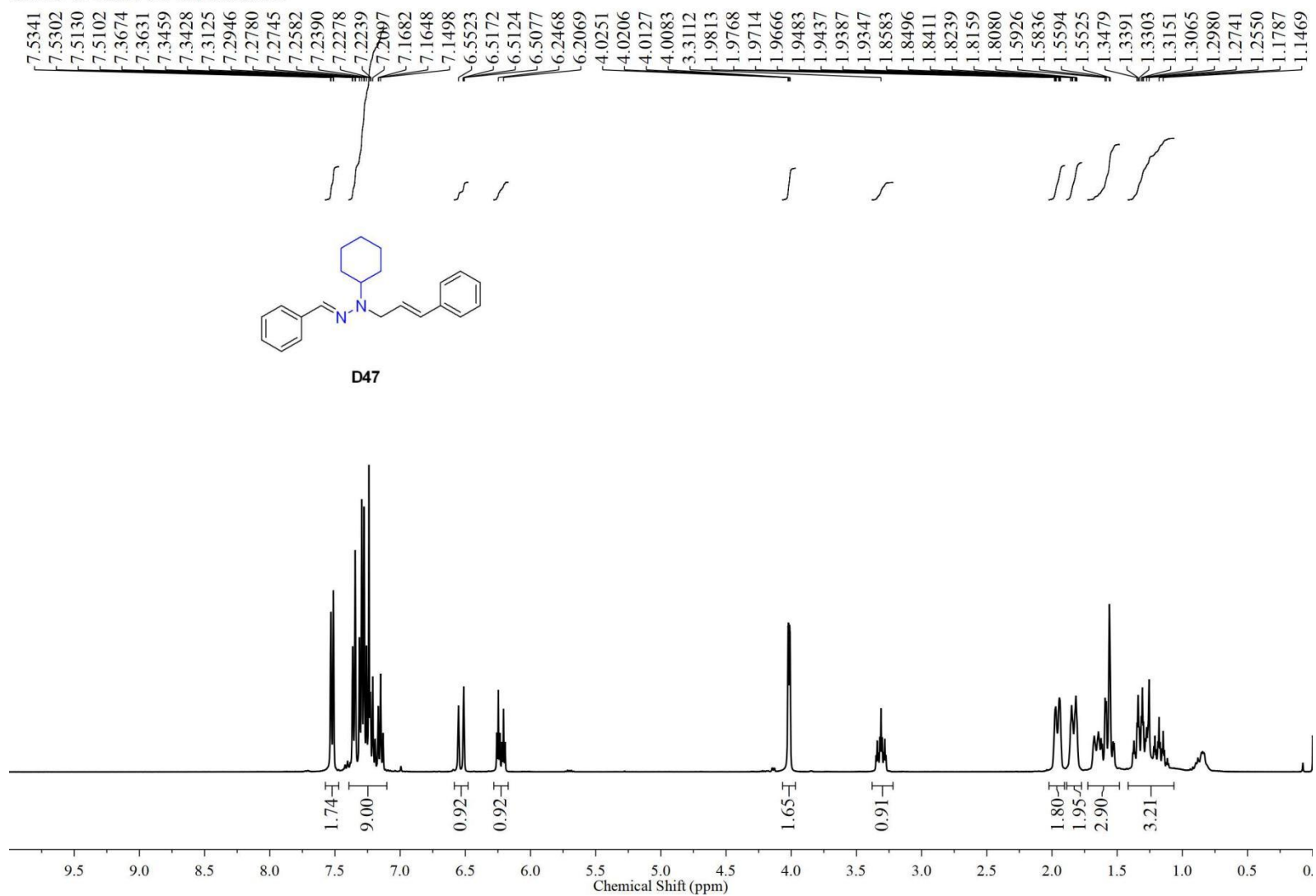
2022-7-25 YY0009-616-B27.10.fid



2022-07-26 yy0047 616-zxy-BZ7.10.fid



2022-08-15 YY0014 616-LQQ-B28.10.fid



2022-08-15 YY0014 616-LQQ-B28.11.fid

137.75
136.98
130.80
129.36
128.56
128.37
127.41
126.60
126.31
125.31
125.24

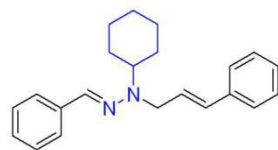
77.37
77.05
76.73

65.67

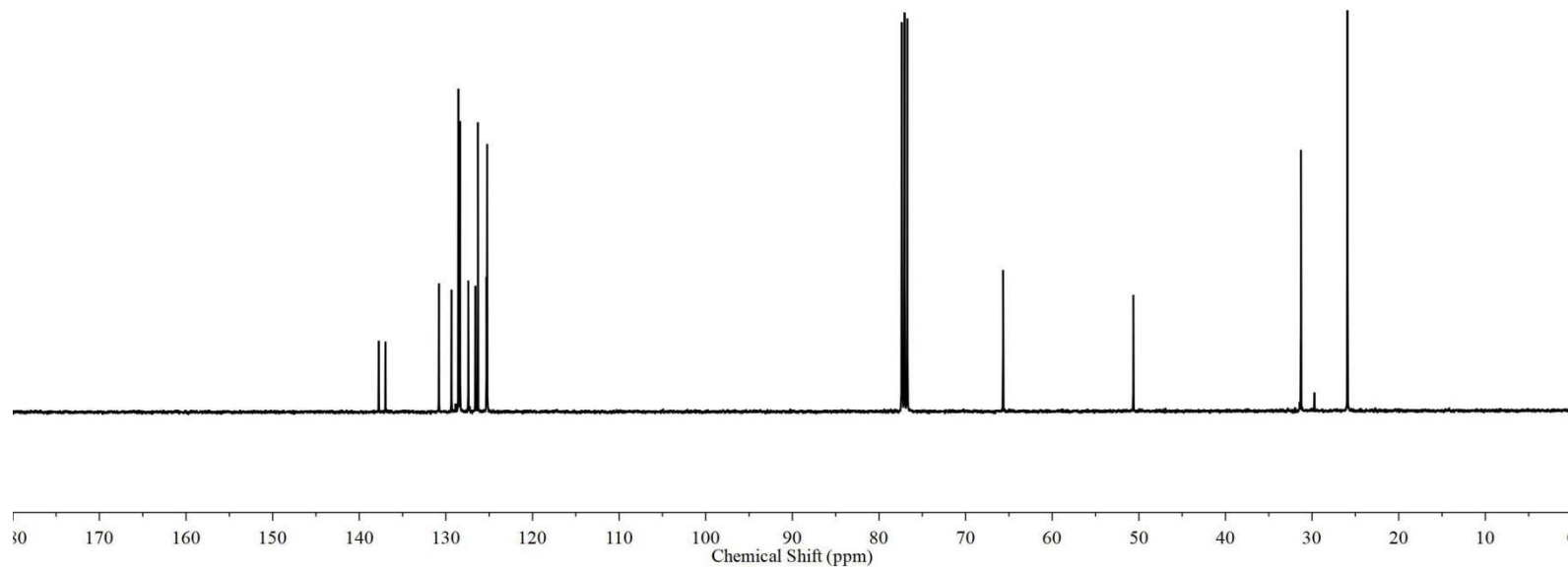
50.63

31.28

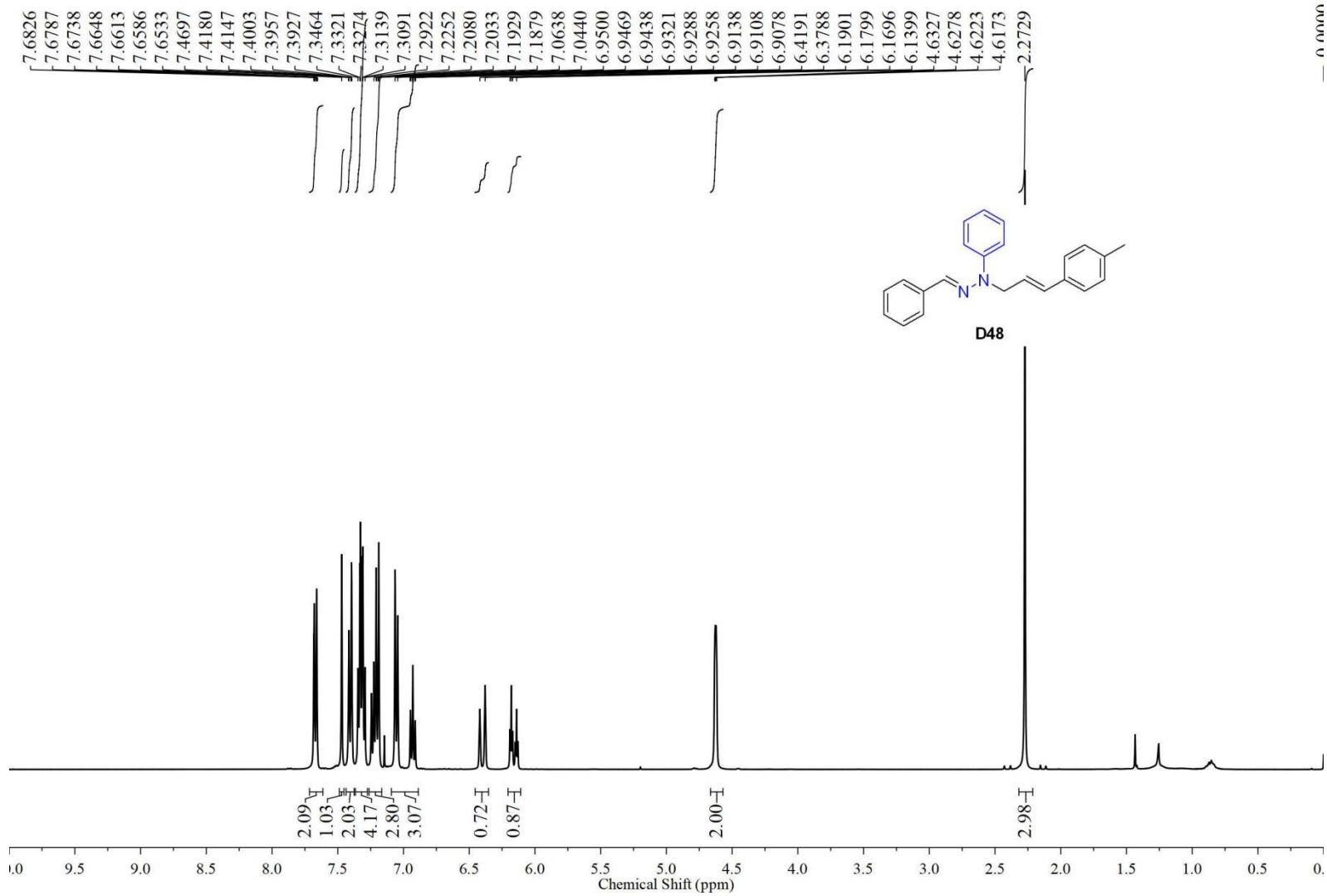
25.92



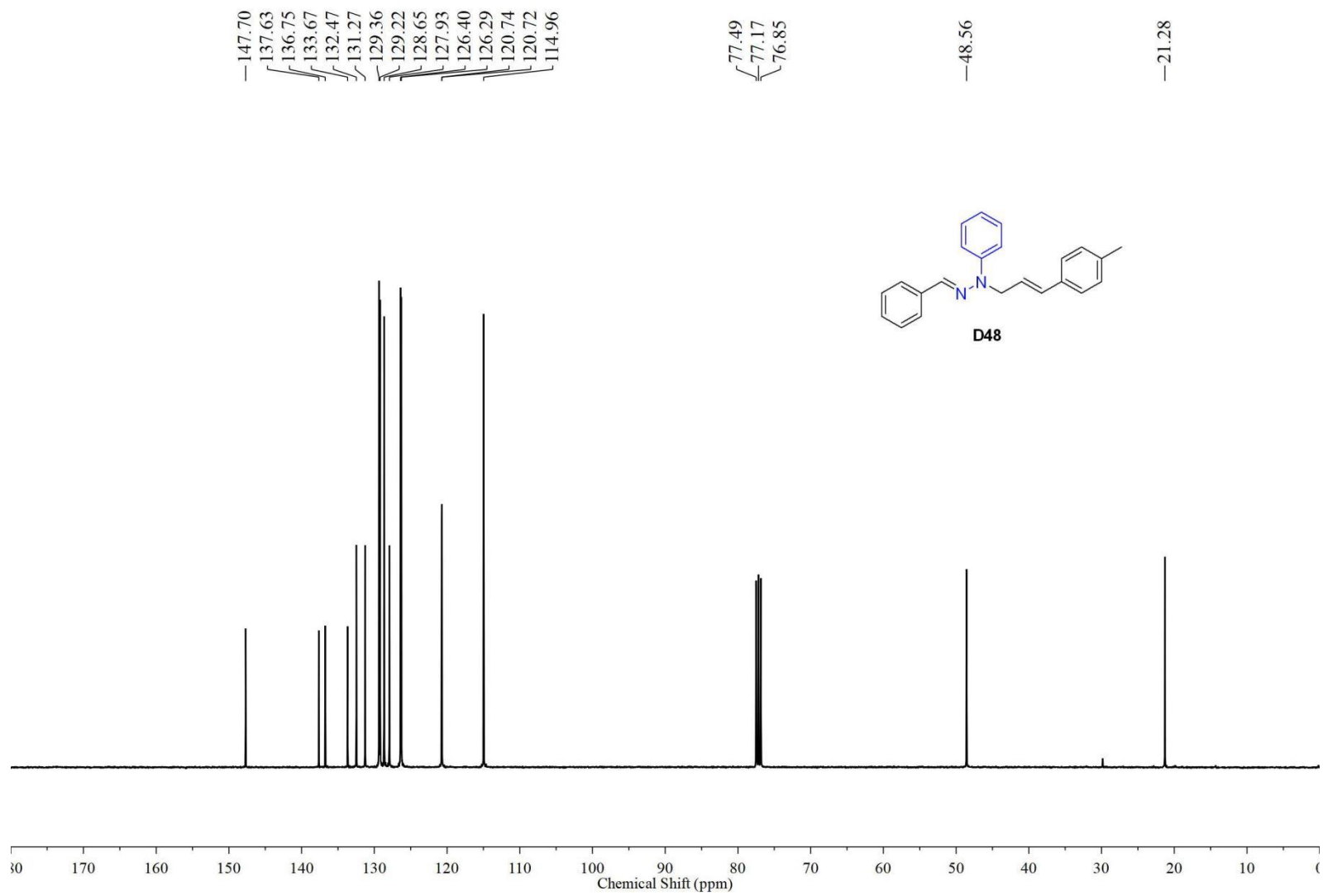
D47



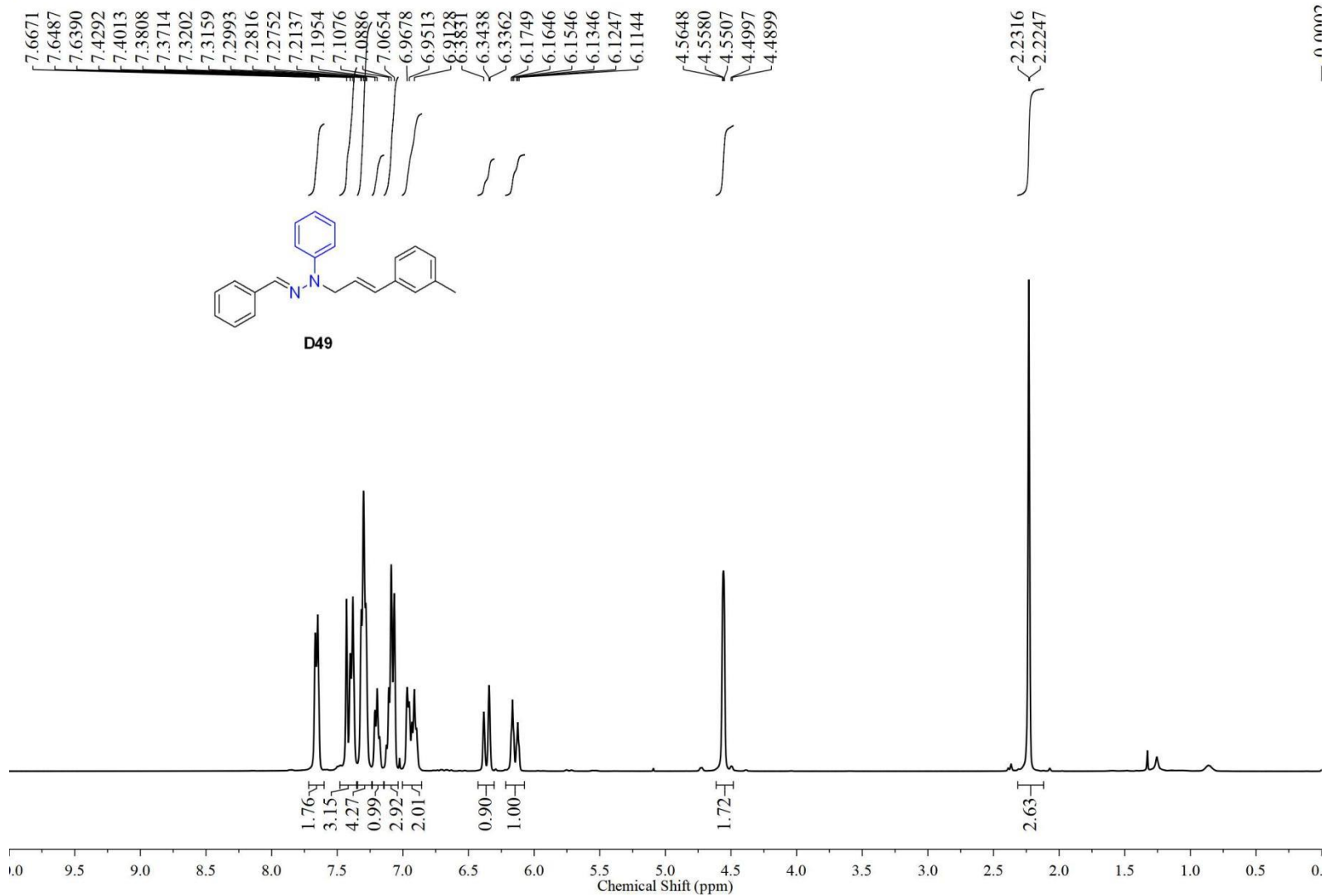
2022-07-01-yy0020-616-1-a2.10.fid



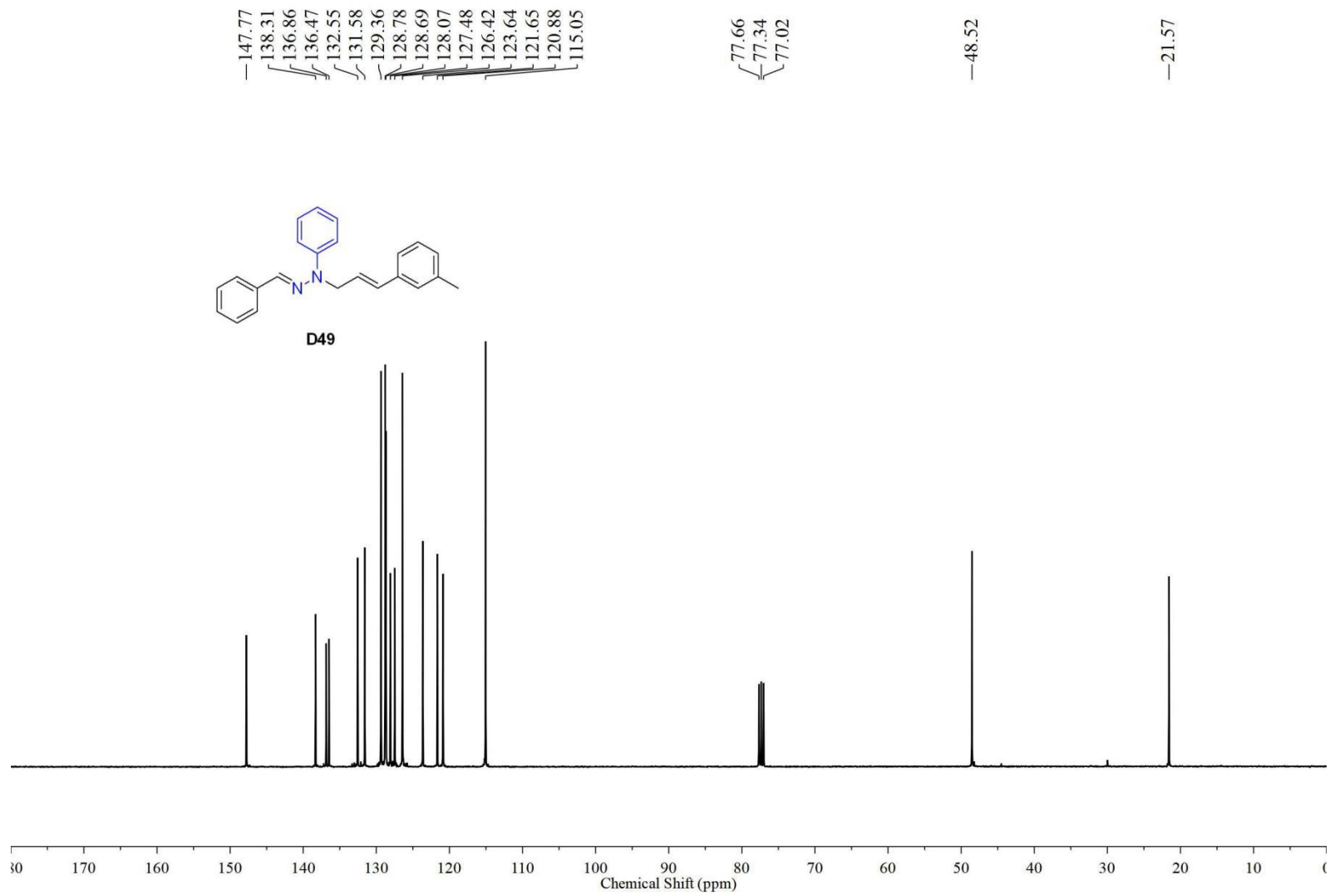
2022-06-30-yy0020-616-1-A2.10.fid



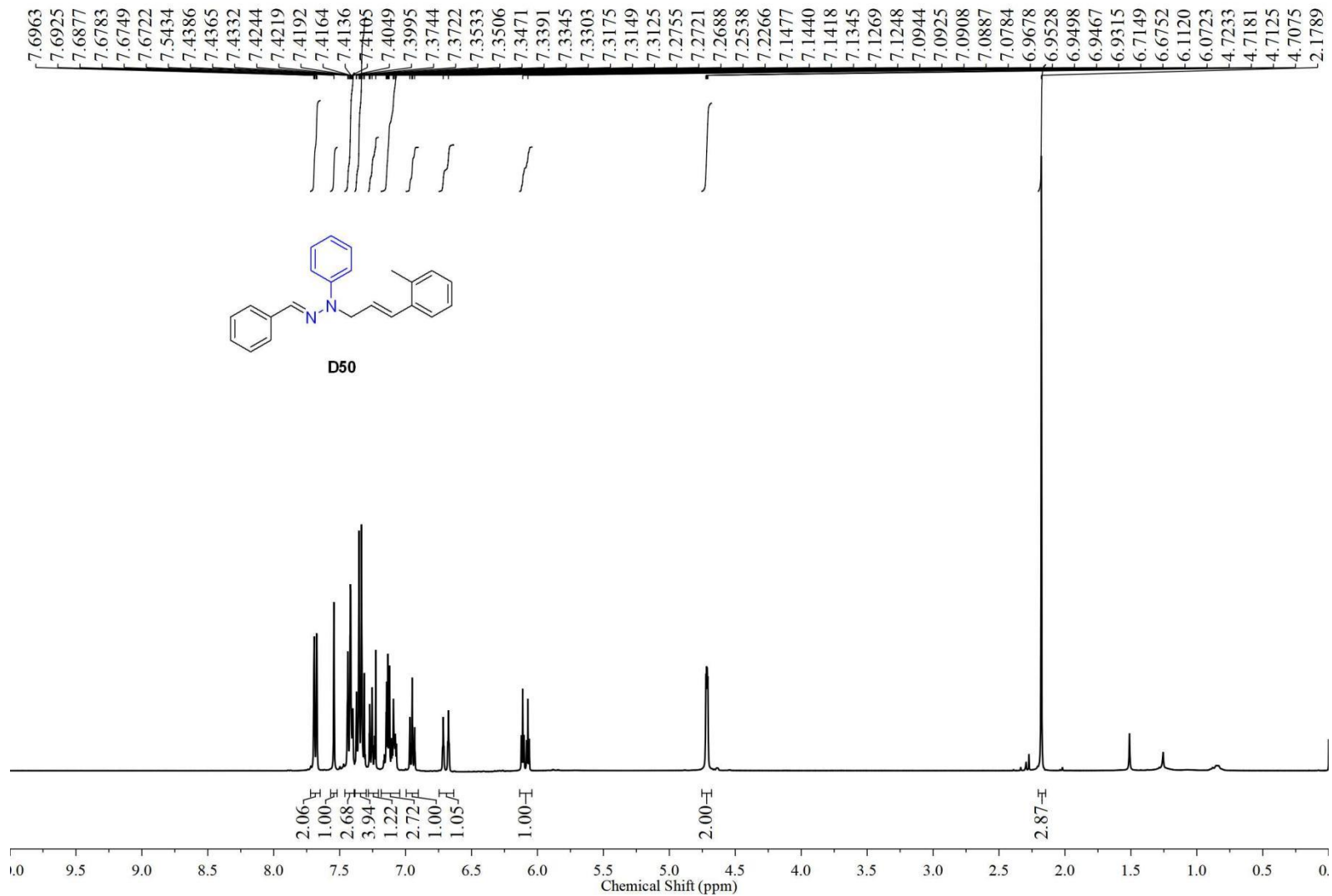
S241



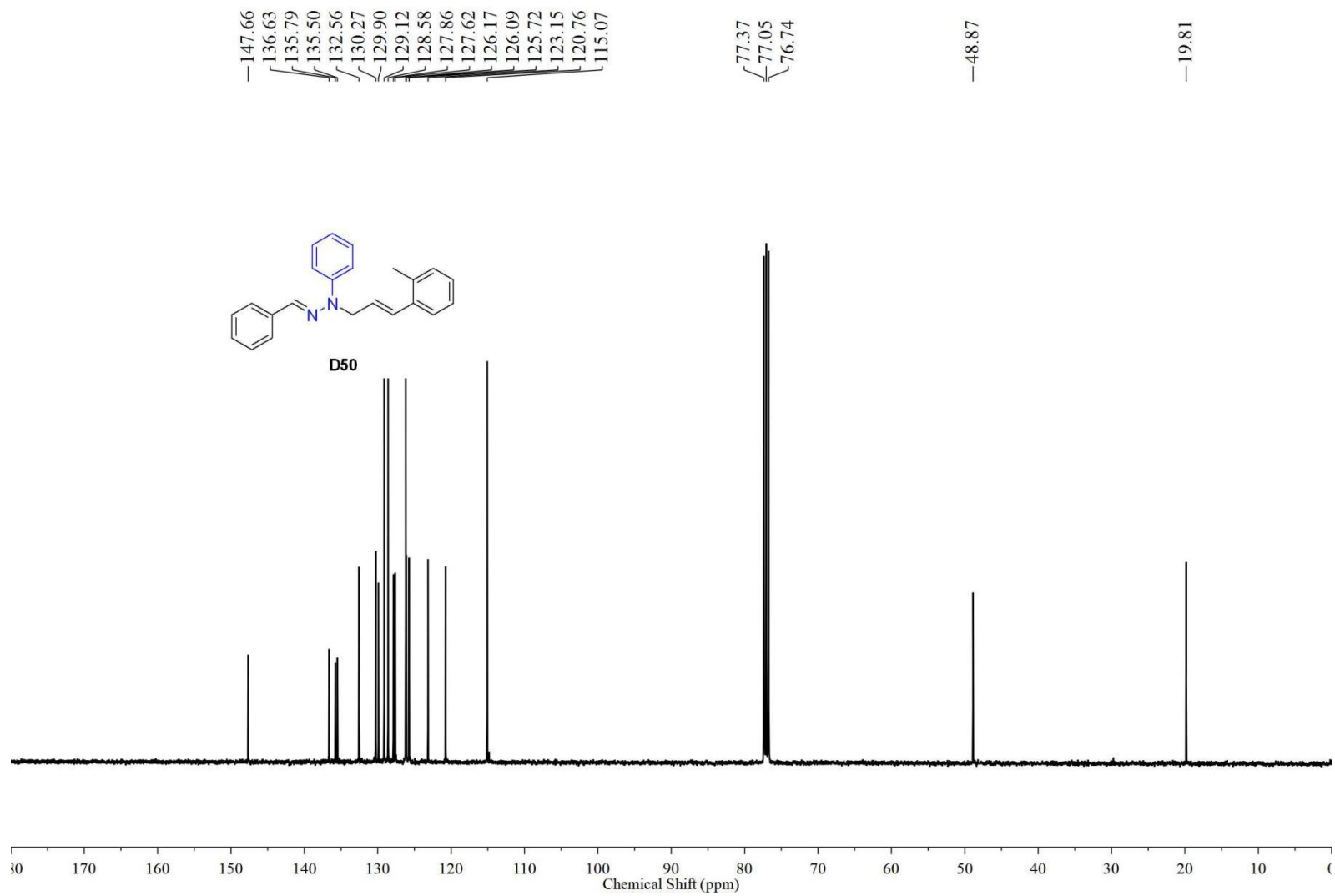
2022-07-12 YY0030 616-lqq-1-A21.11.fid



2022-09-28-YY0003-616-LQQ-1-A23-H. 10. fid

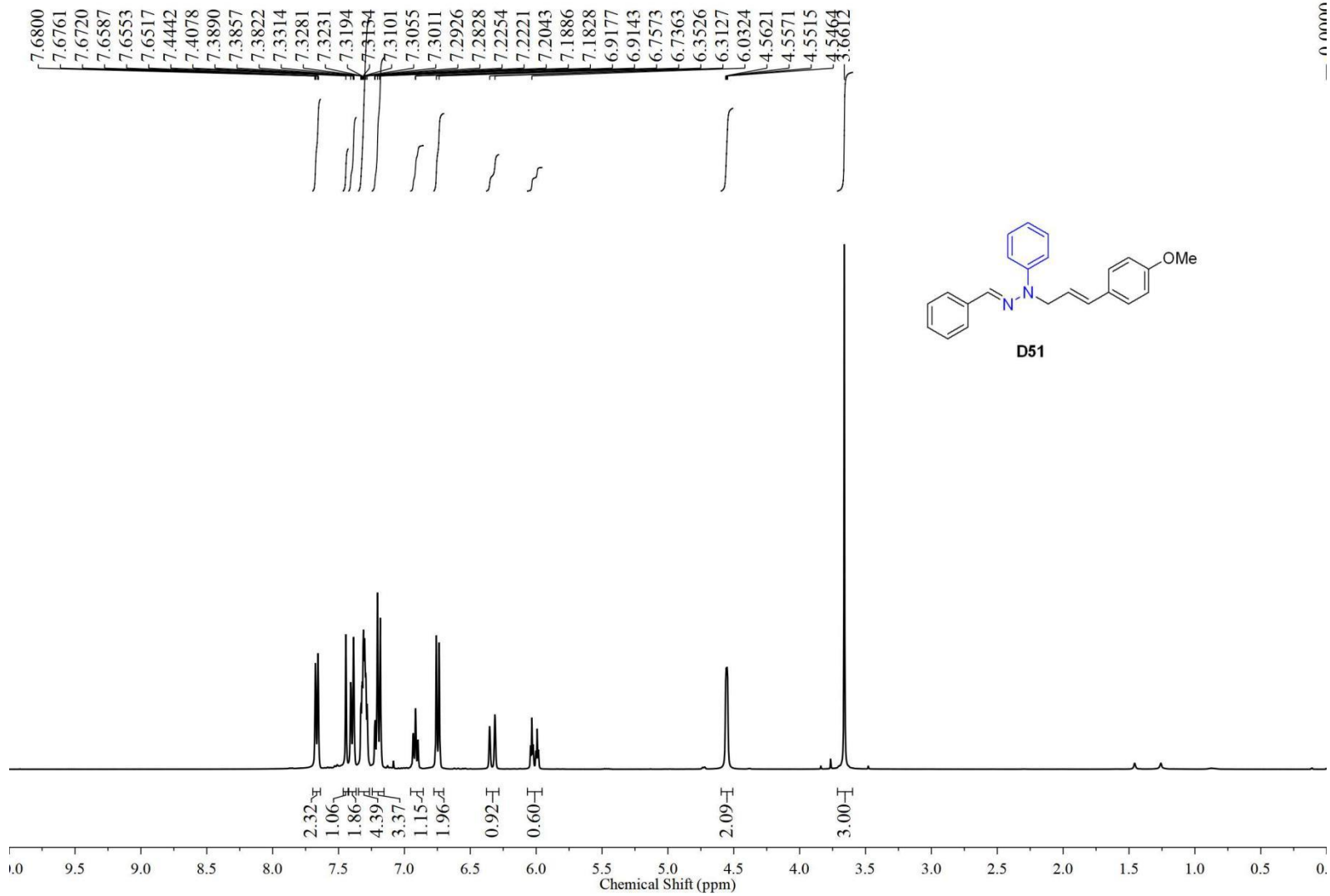


2022-09-27-YY0034-616-LQQ-1-A23.10.fid



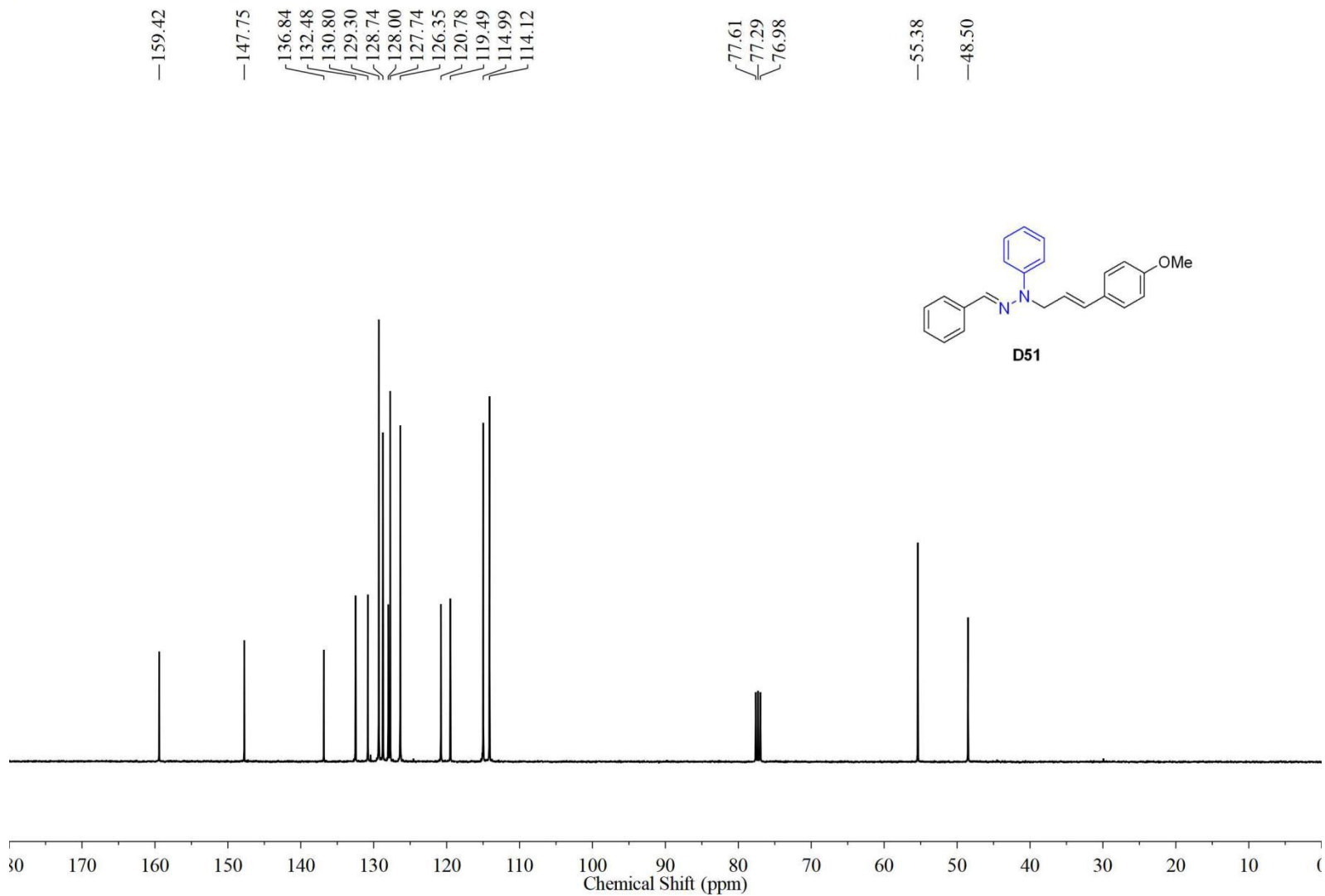
S245

2022-7-4 yy0006-616-1-a8.10.fid

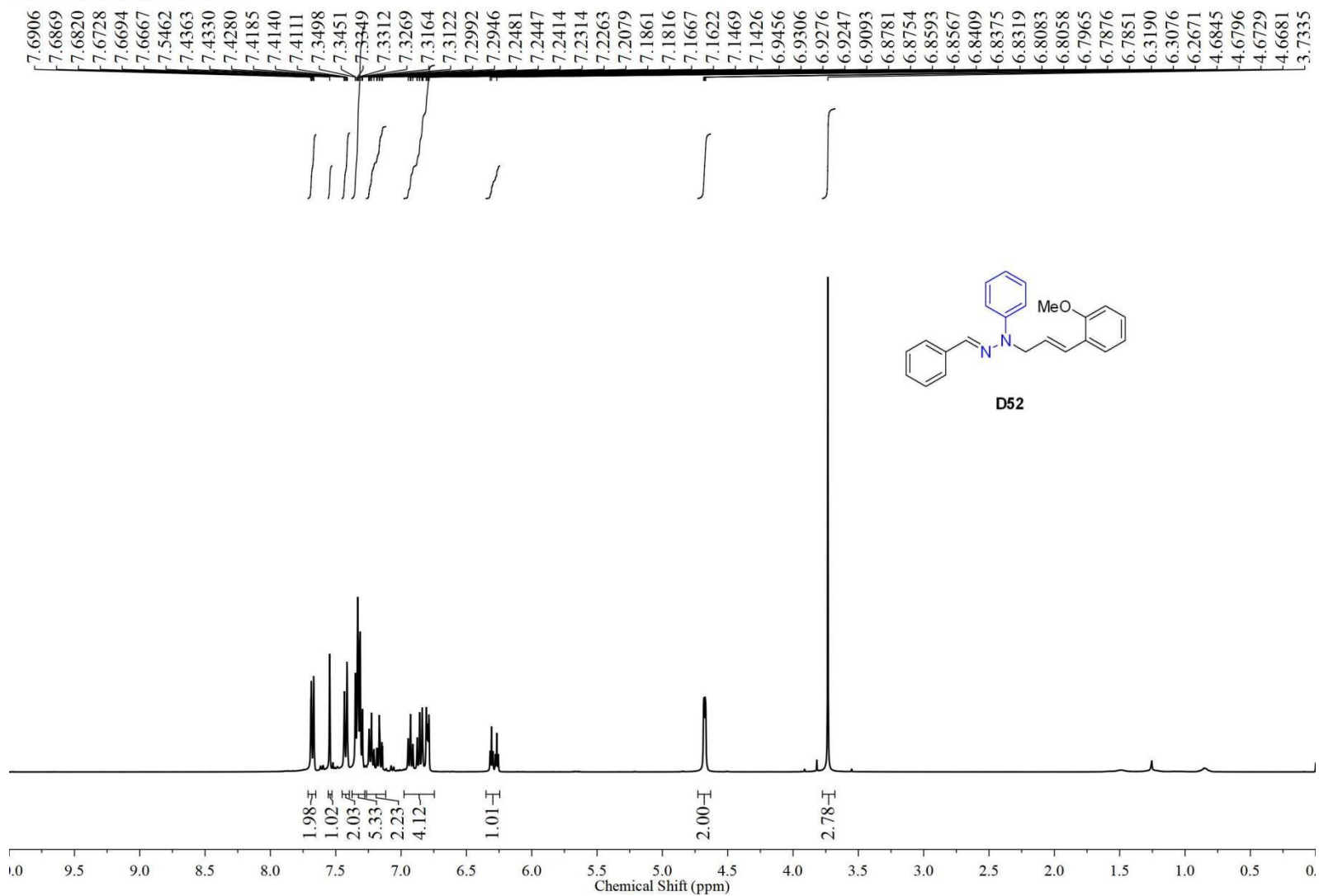


S246

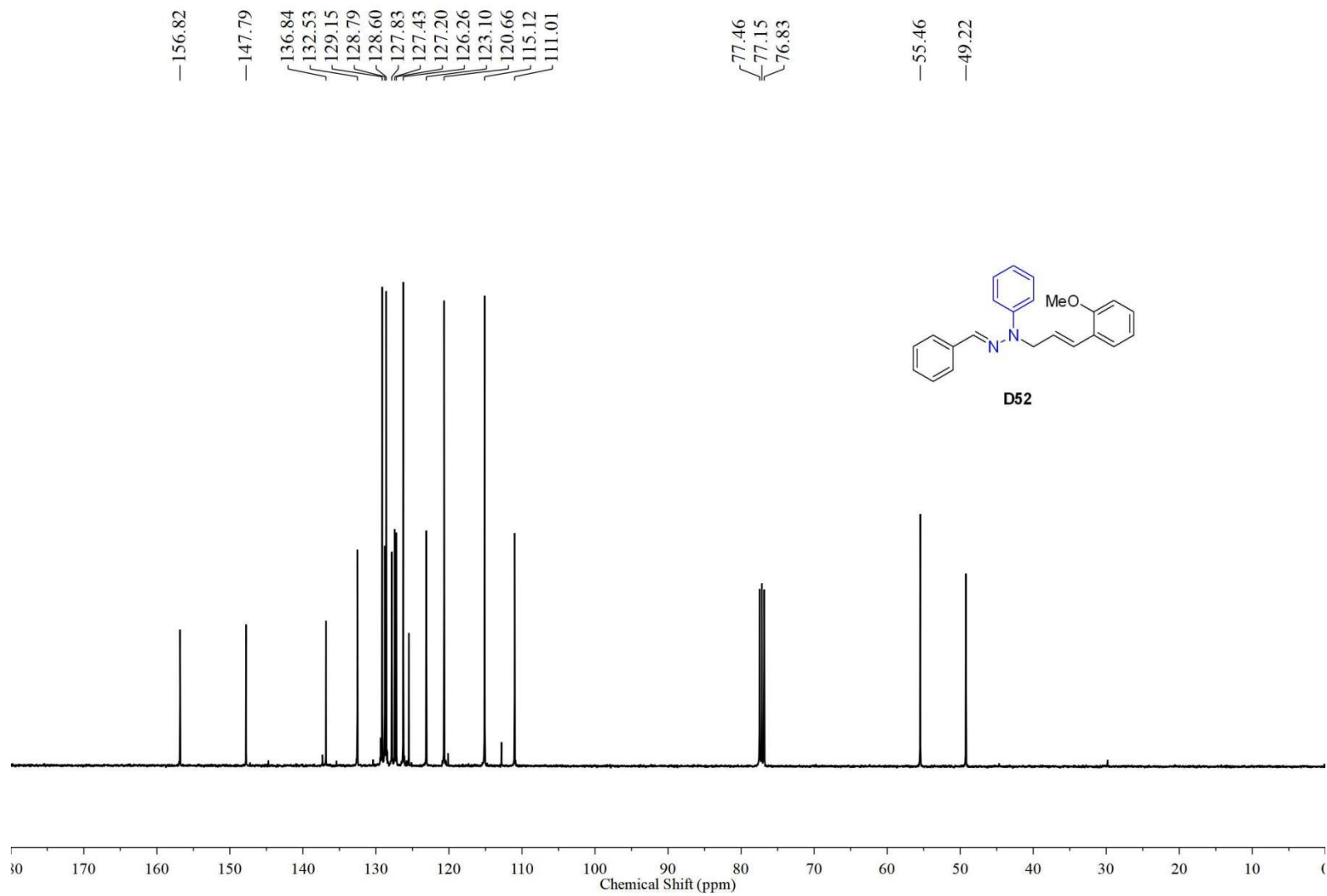
2022-7-4 yy0006-616-1-a8.11.fid



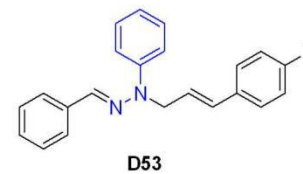
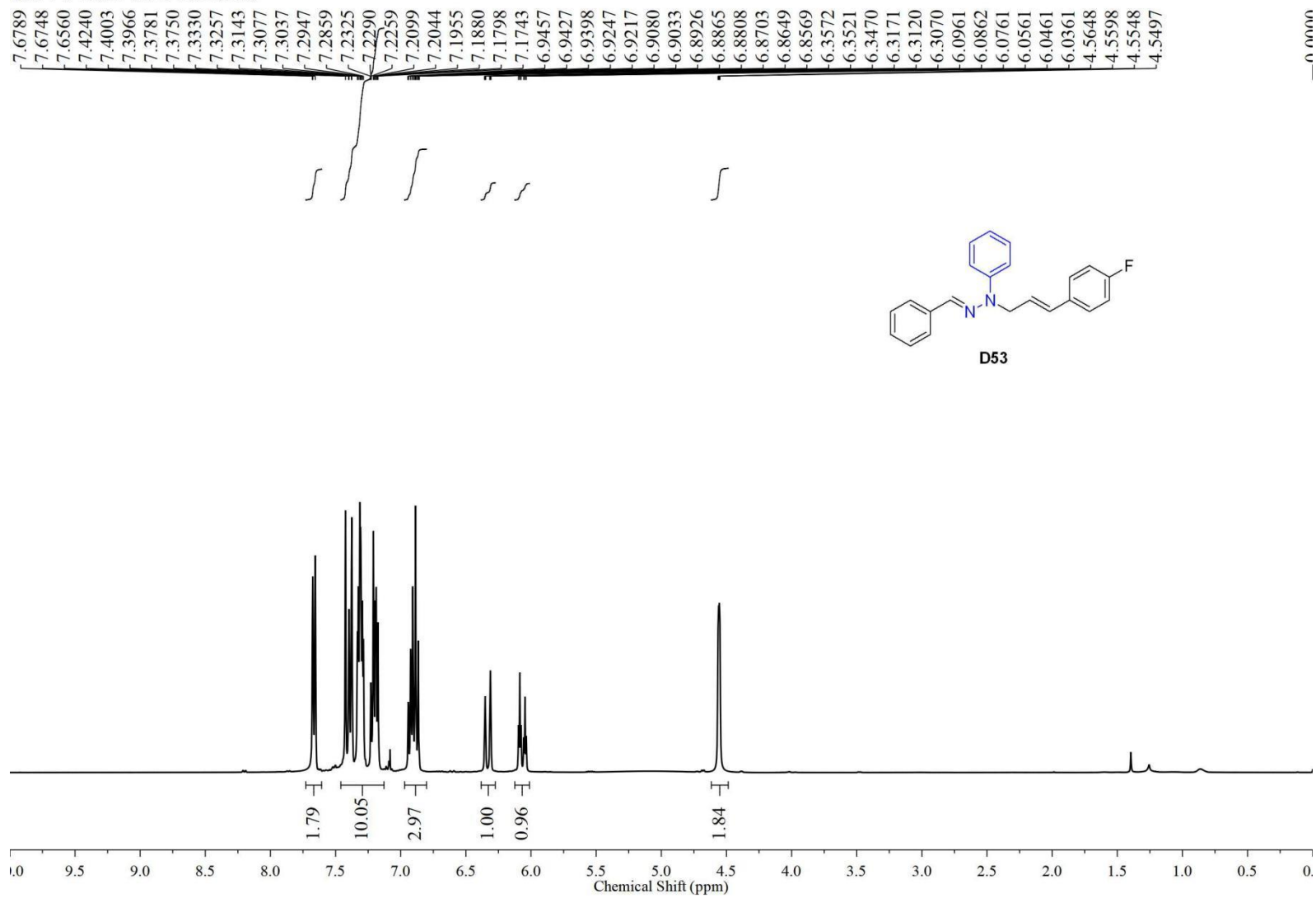
2022-7-4 yy0006-616-1-a7.10.fid



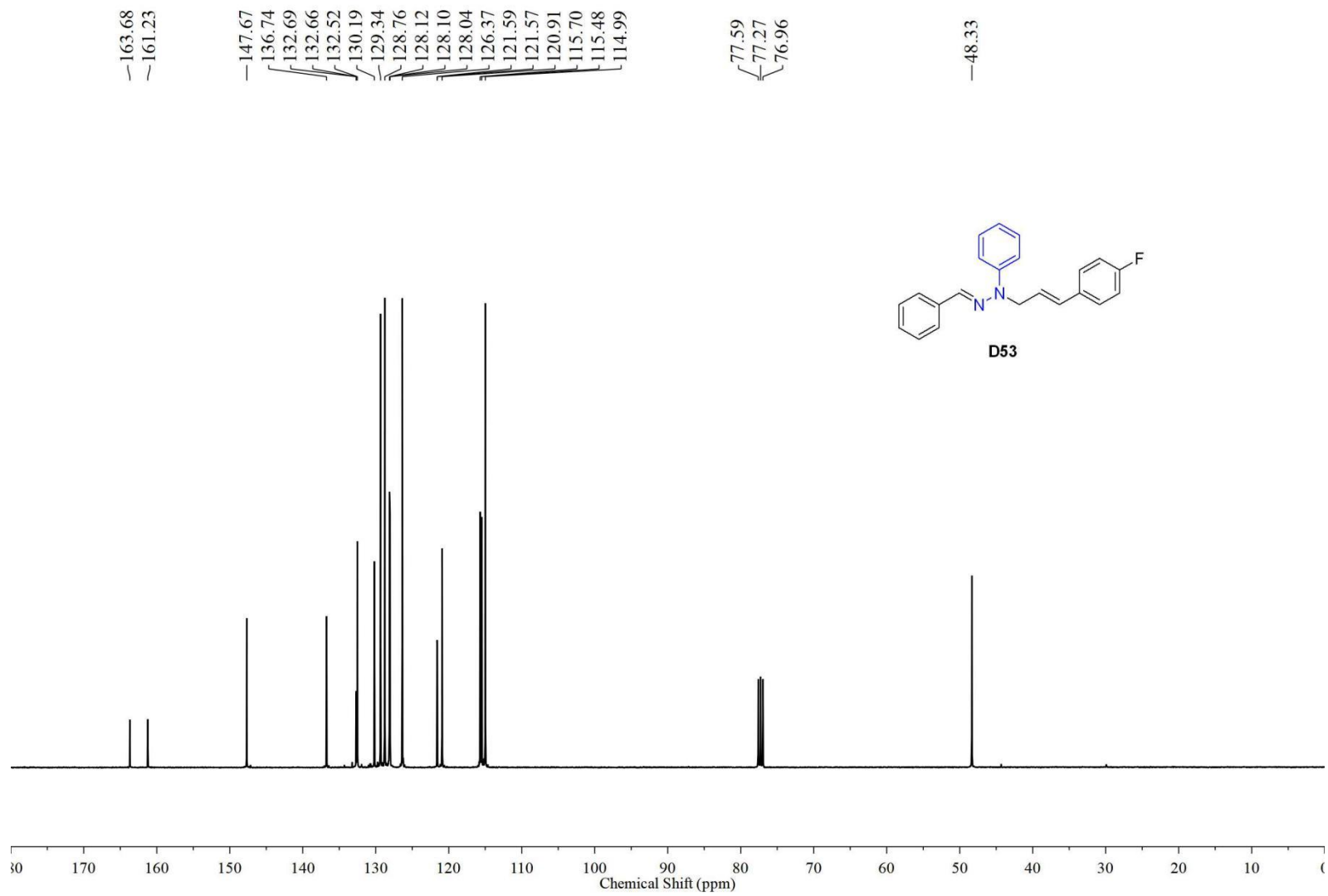
2022-7-4 yy0006-616-1-a7.11.fid



2022-7-5 YY0027-616-L-A10.10.fid



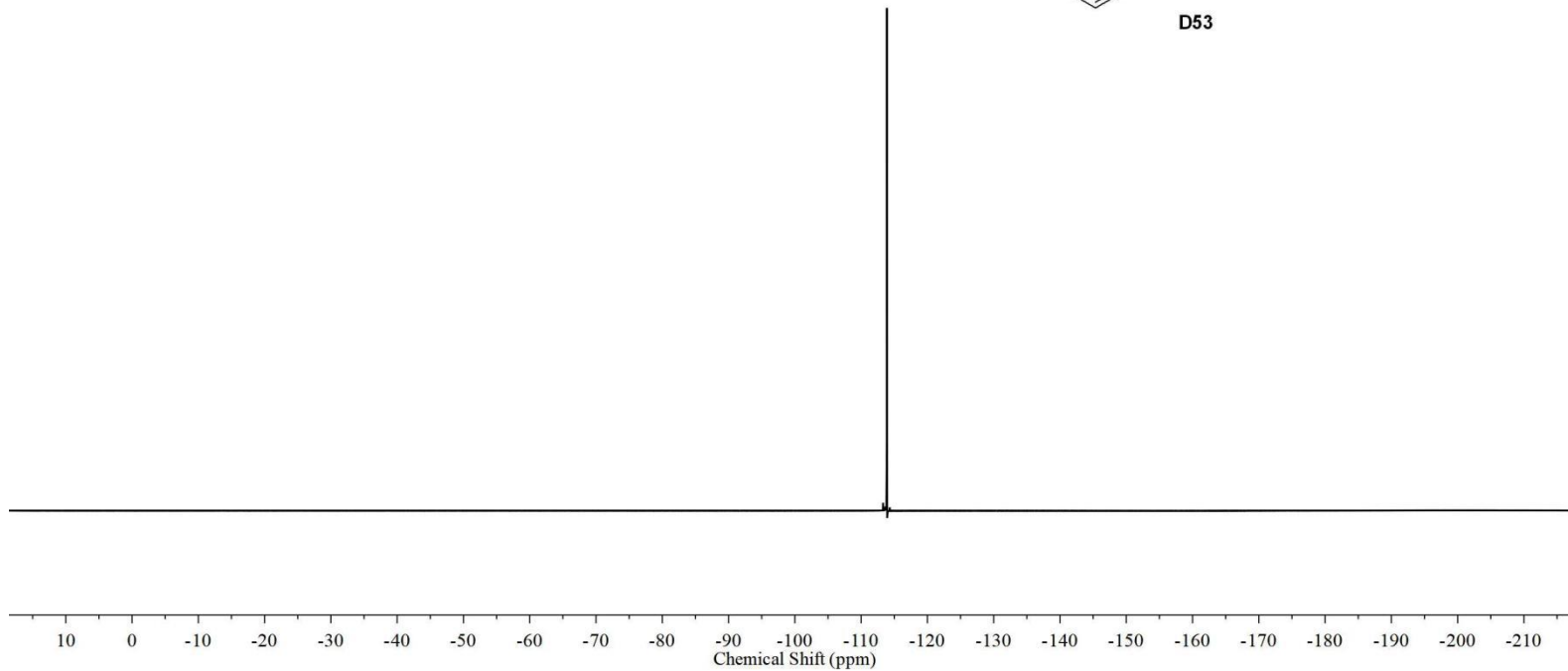
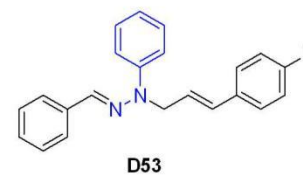
2022-7-5 YY0027-616-L-A10. 11. fid



S251

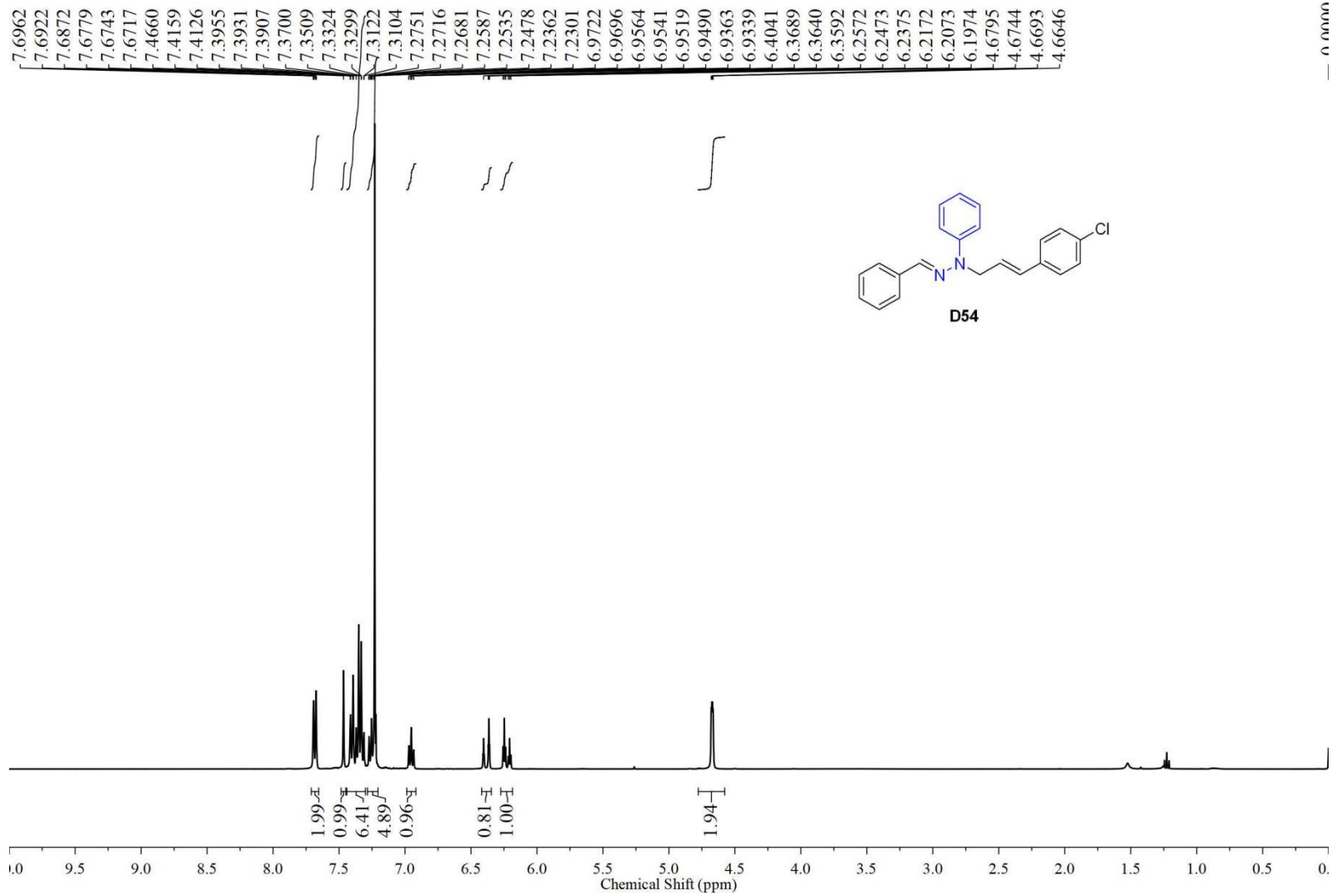
2022-7-5 YY0027-616-L-A10.12.fid

--113.90



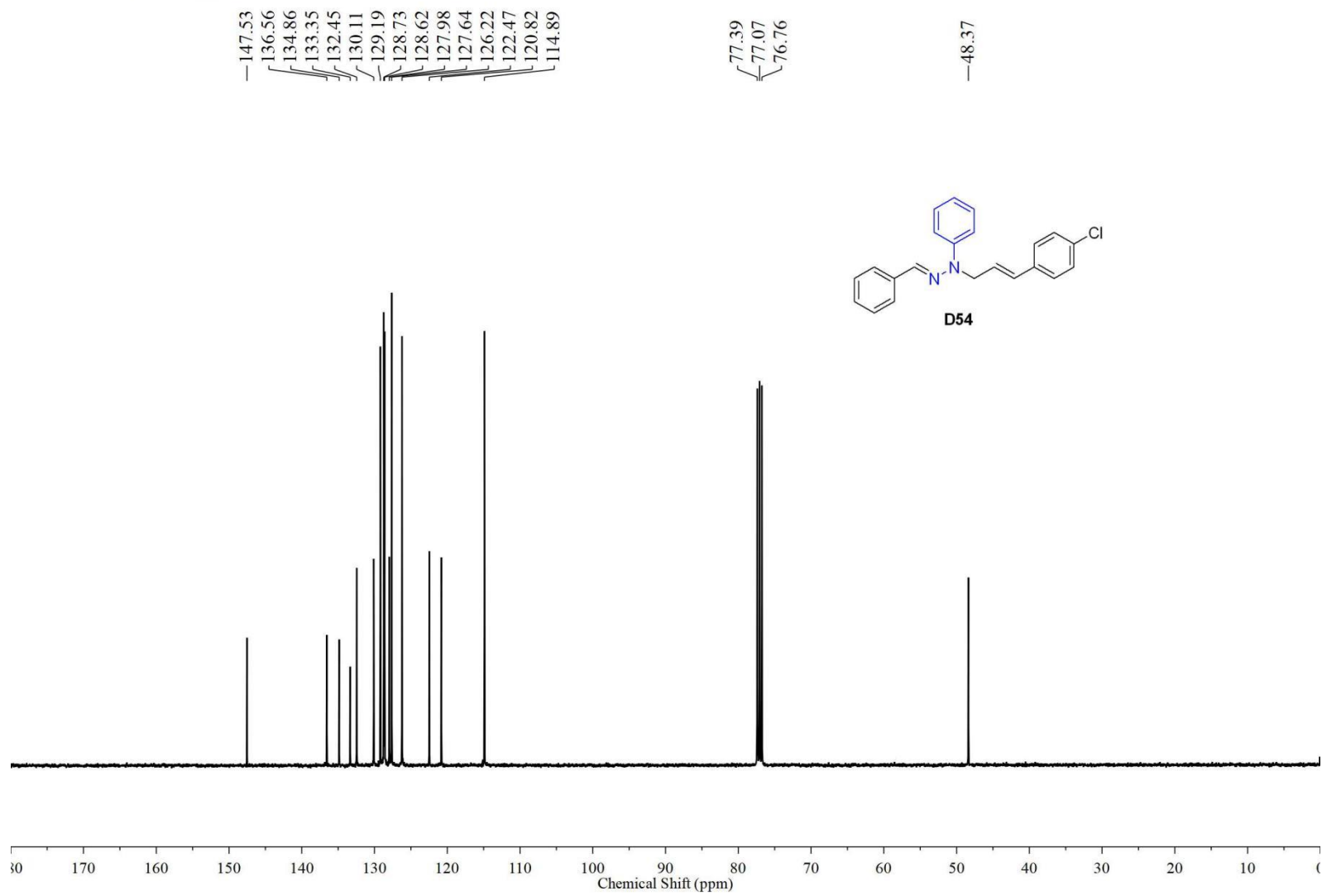
S252

2022-07-01-YY0017-616-L-A3.11.fid



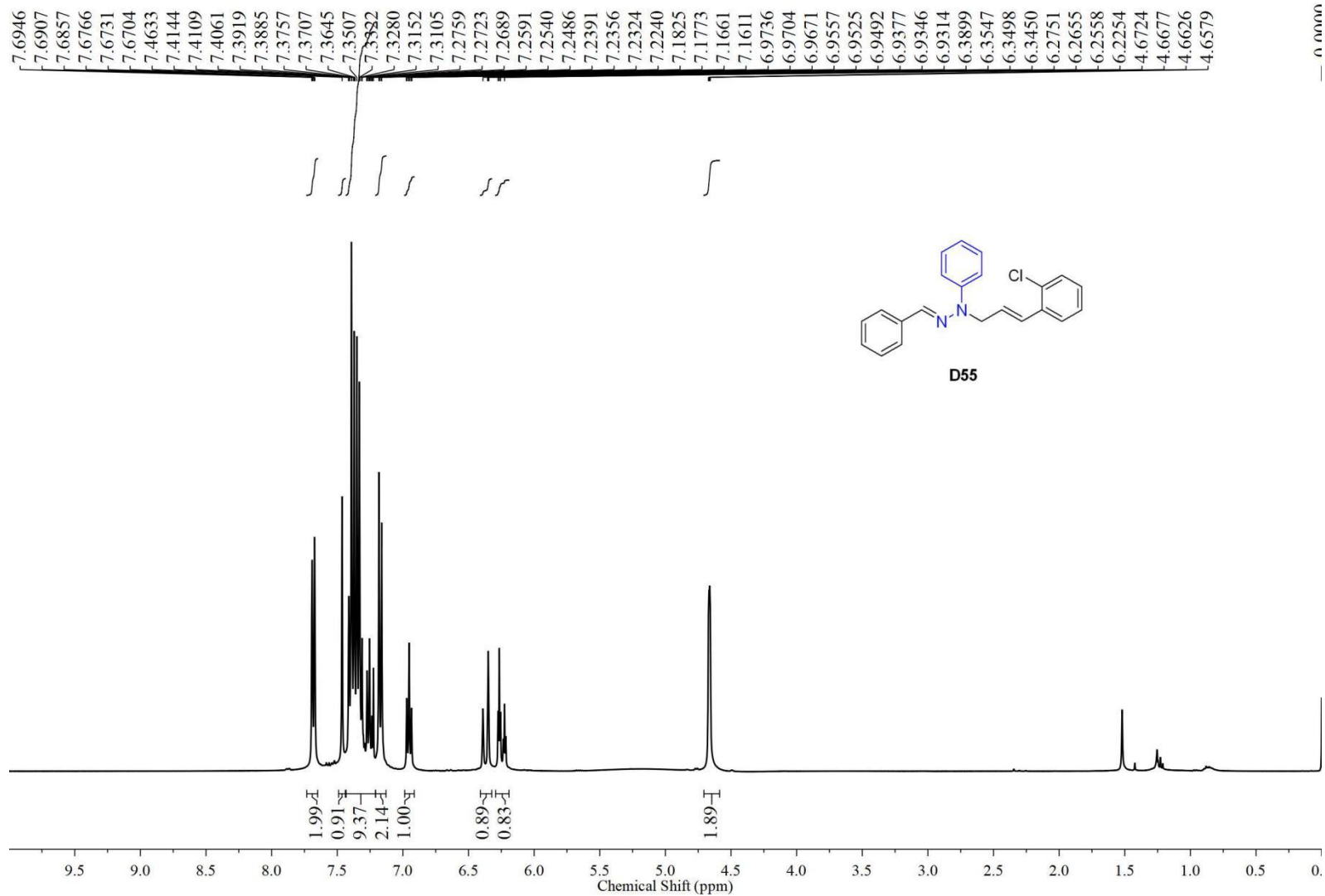
S253

2022-07-01-YY0017-616-L-A3.10.fid



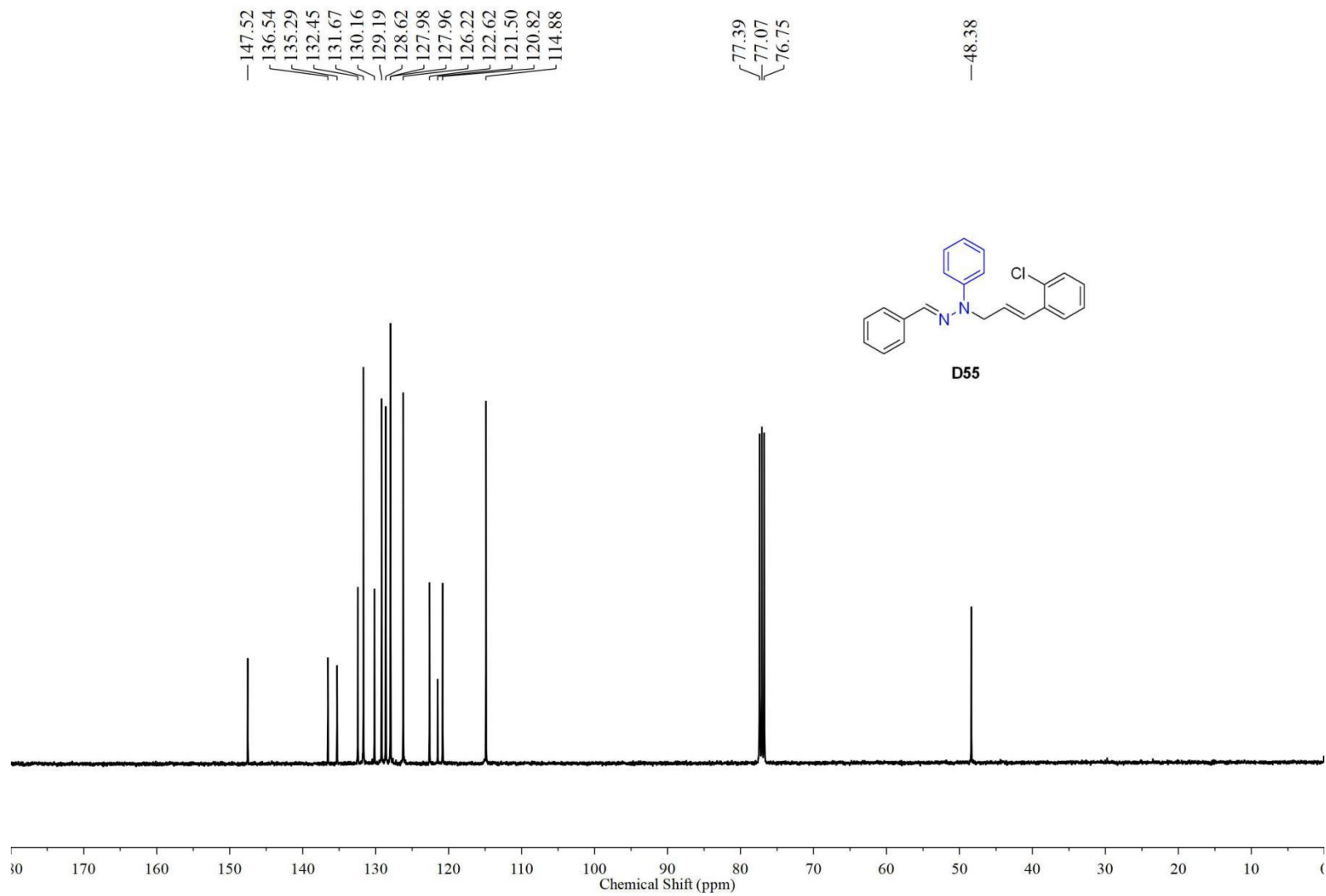
S254

2022-7-4 yy0006-616-1-a4.10.fid



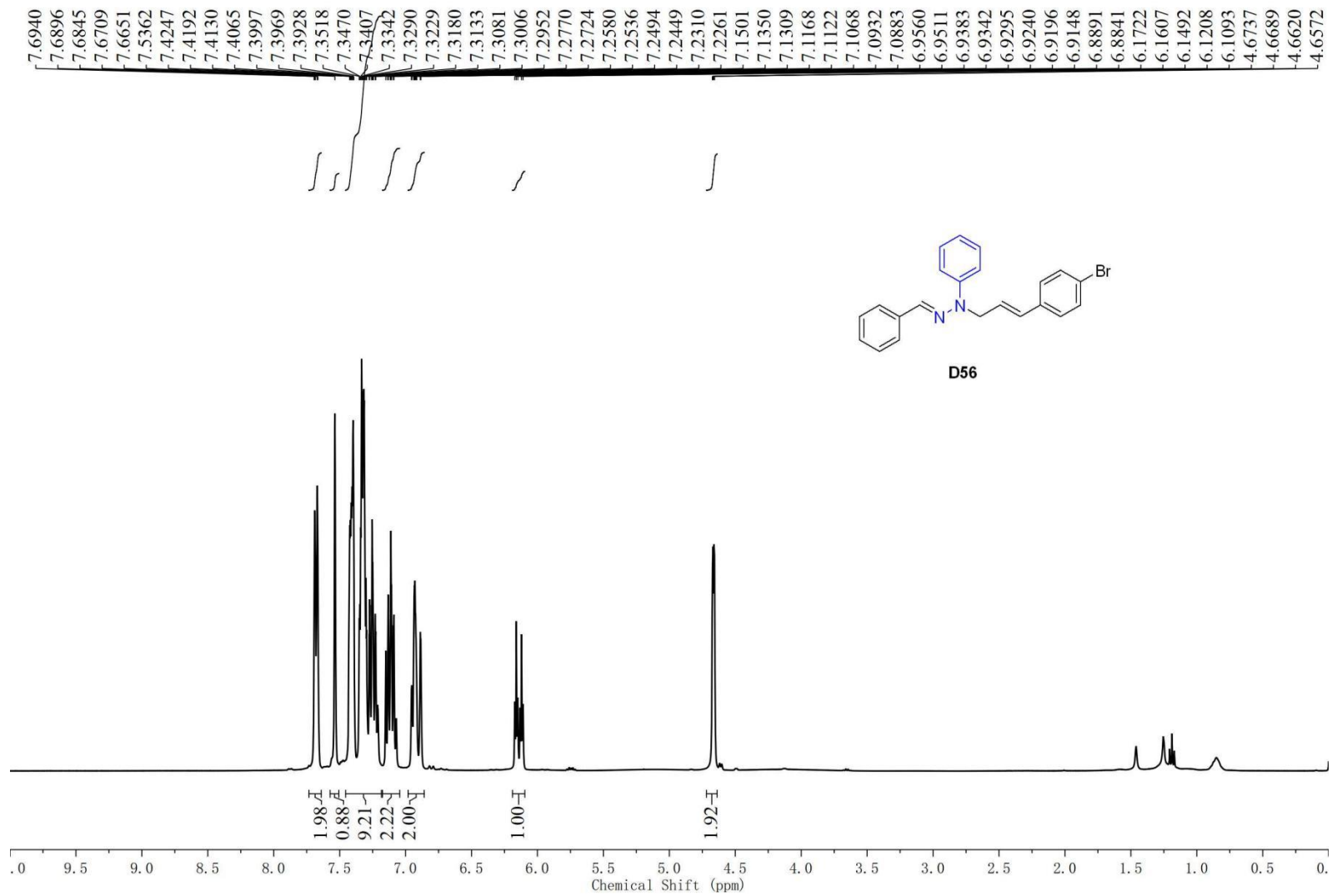
0.0000

2022-7-4 yy0006-616-1-a4.11.fid

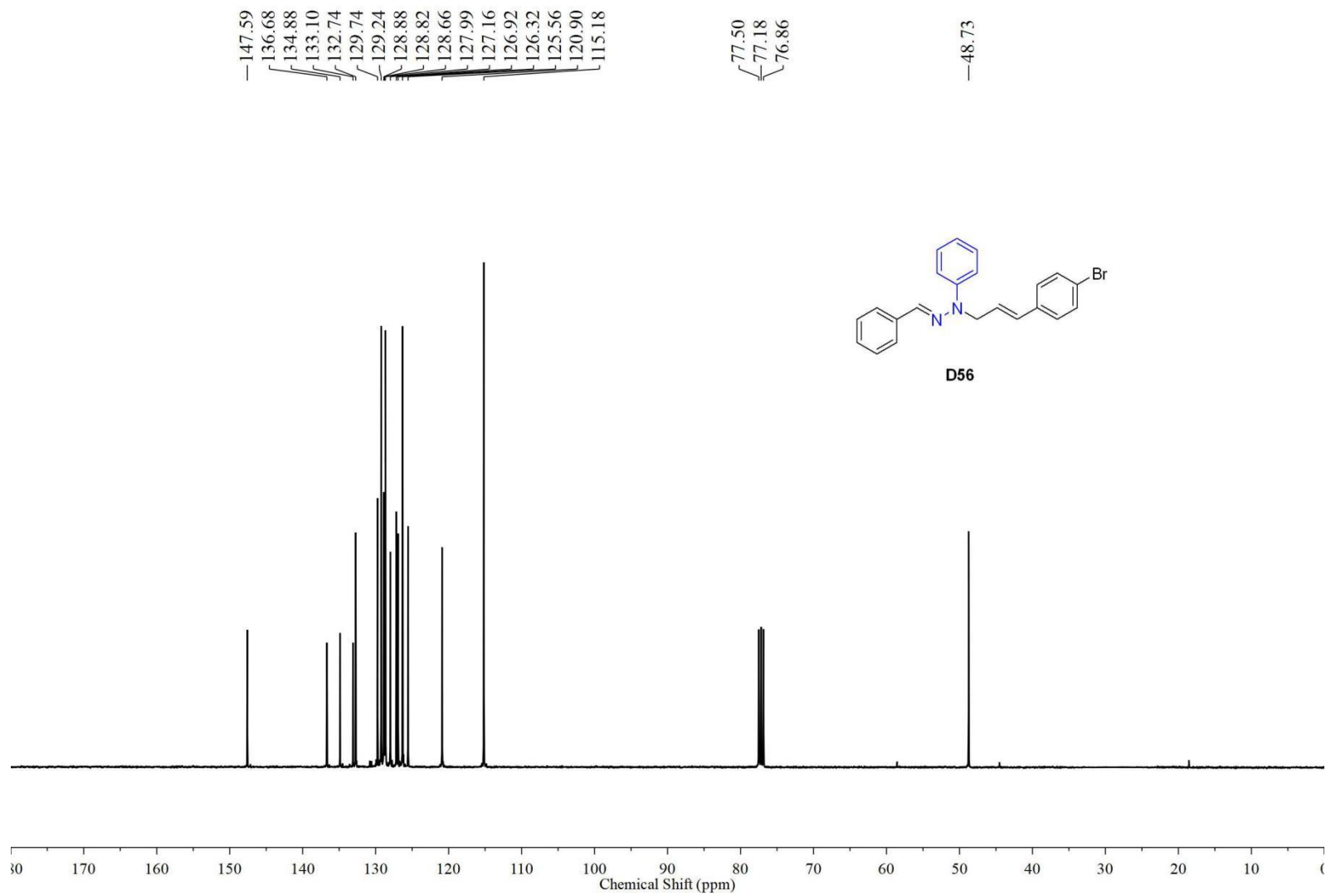


S256

2022-7-4 yy0006-616-1-a5.10.fid

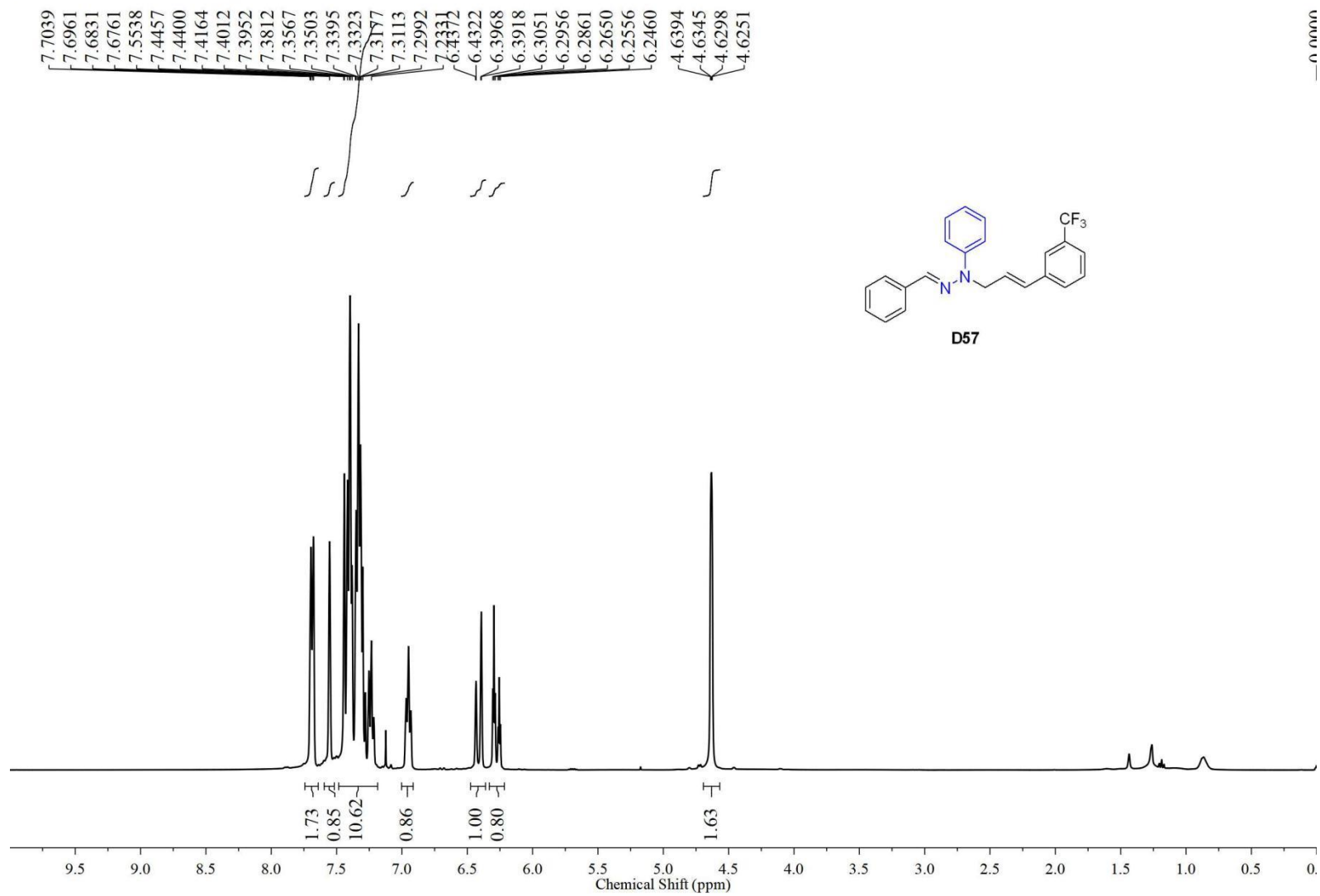


2022-7-4 yy0006-616-1-a5.11.fid



S258

2022-7-4 yy0008-616-1-a6.10.fid



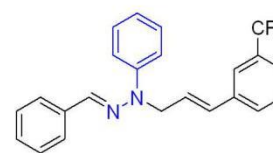
S259

2022-7-4 yy0008-616-1-a6.11.fid

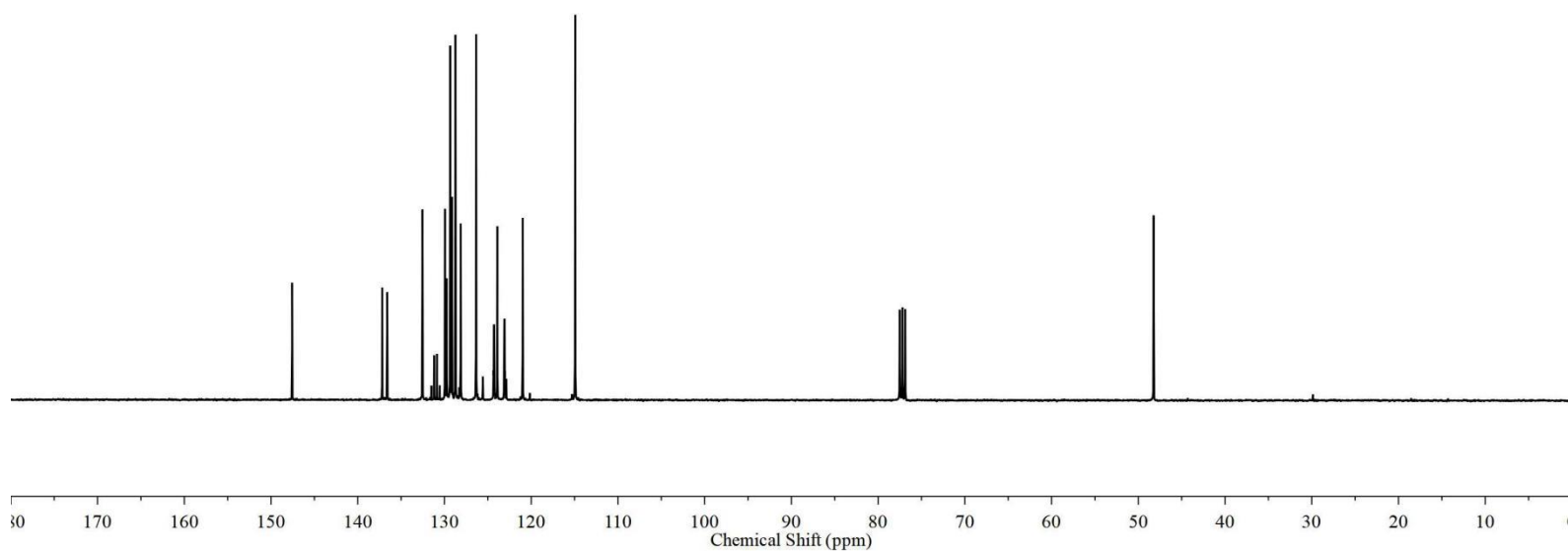
147.57
137.18
136.61
132.54
129.95
129.76
129.34
129.14
128.74
128.13
126.35
124.35
124.31
124.27
124.23
123.91
123.14
123.10
123.06
123.03
120.98
114.93

77.51
77.19
76.87

48.23

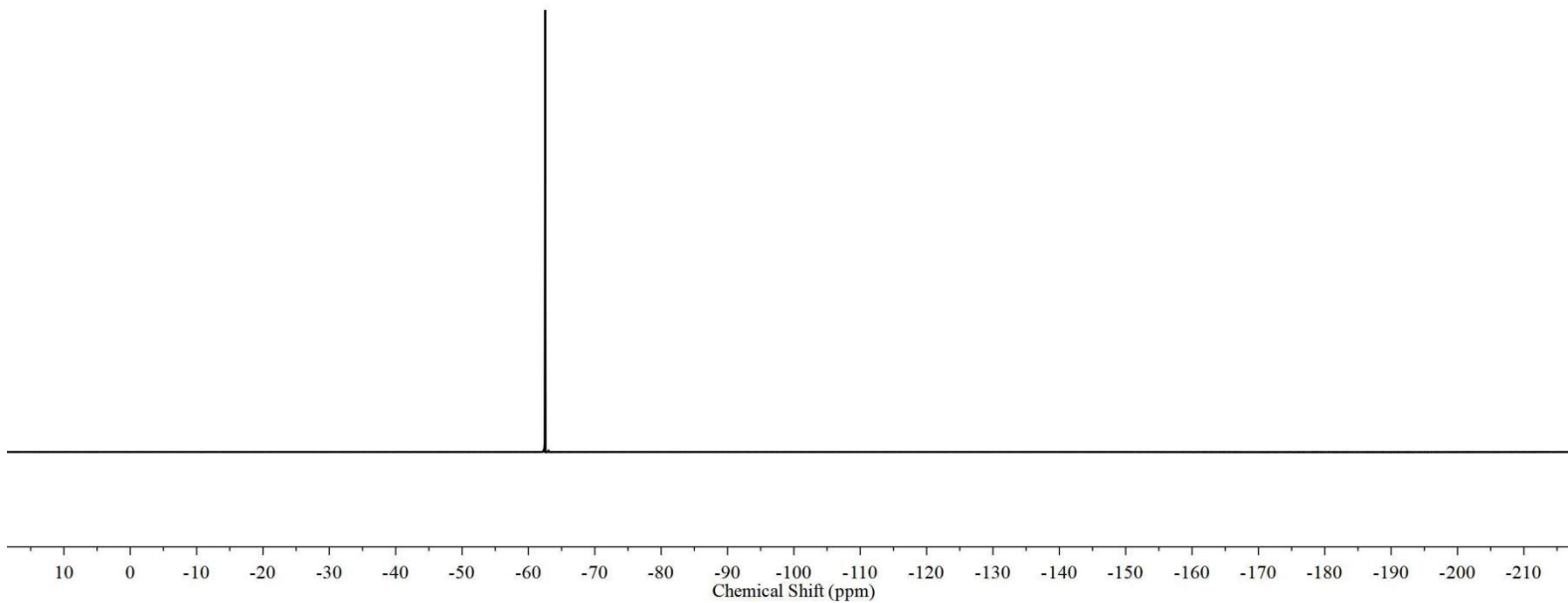
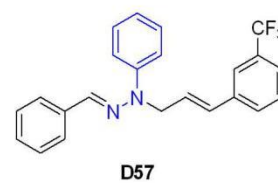


D57



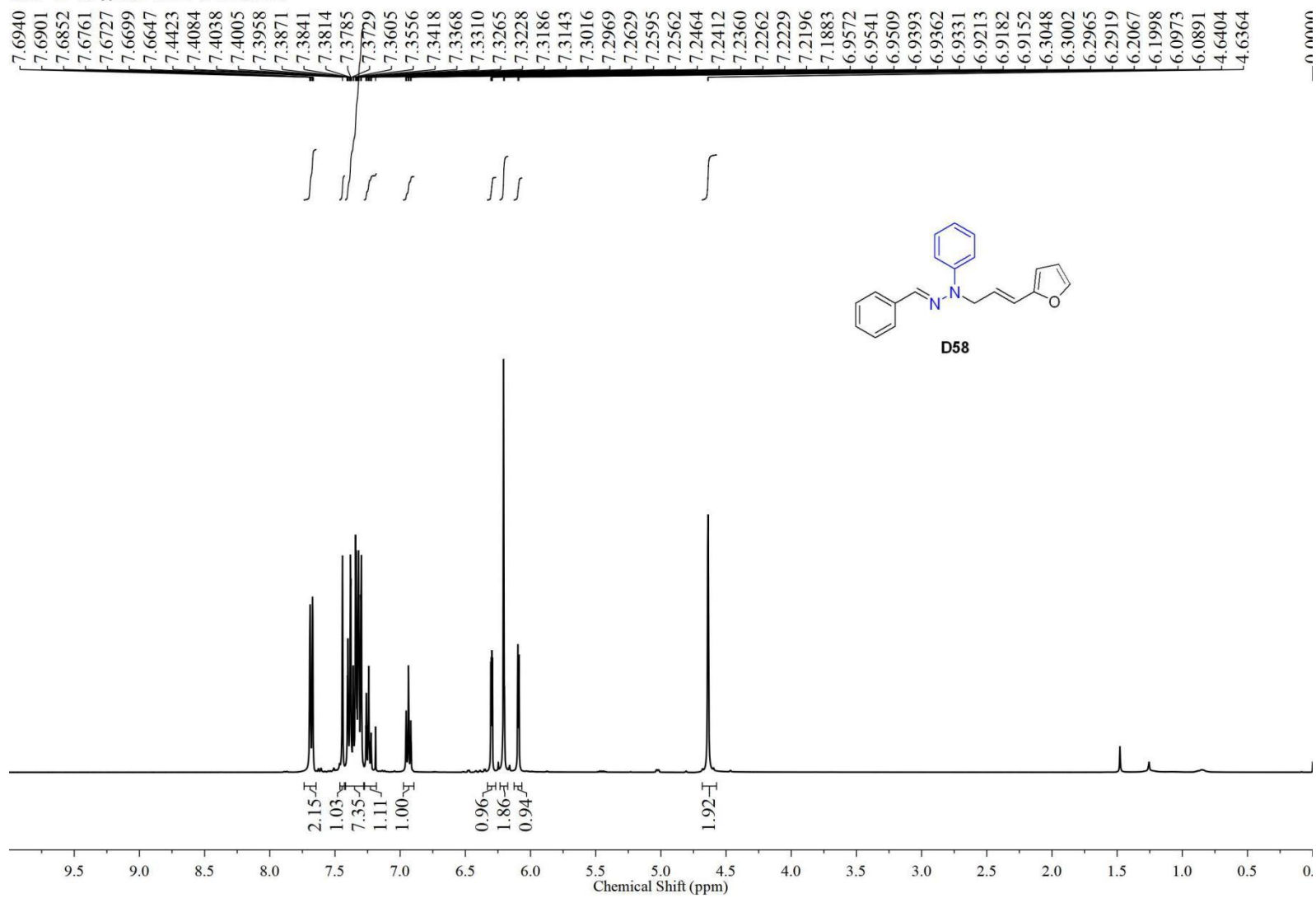
2022-7-4 yy0008-616-1-a6.12.fid

---62.53

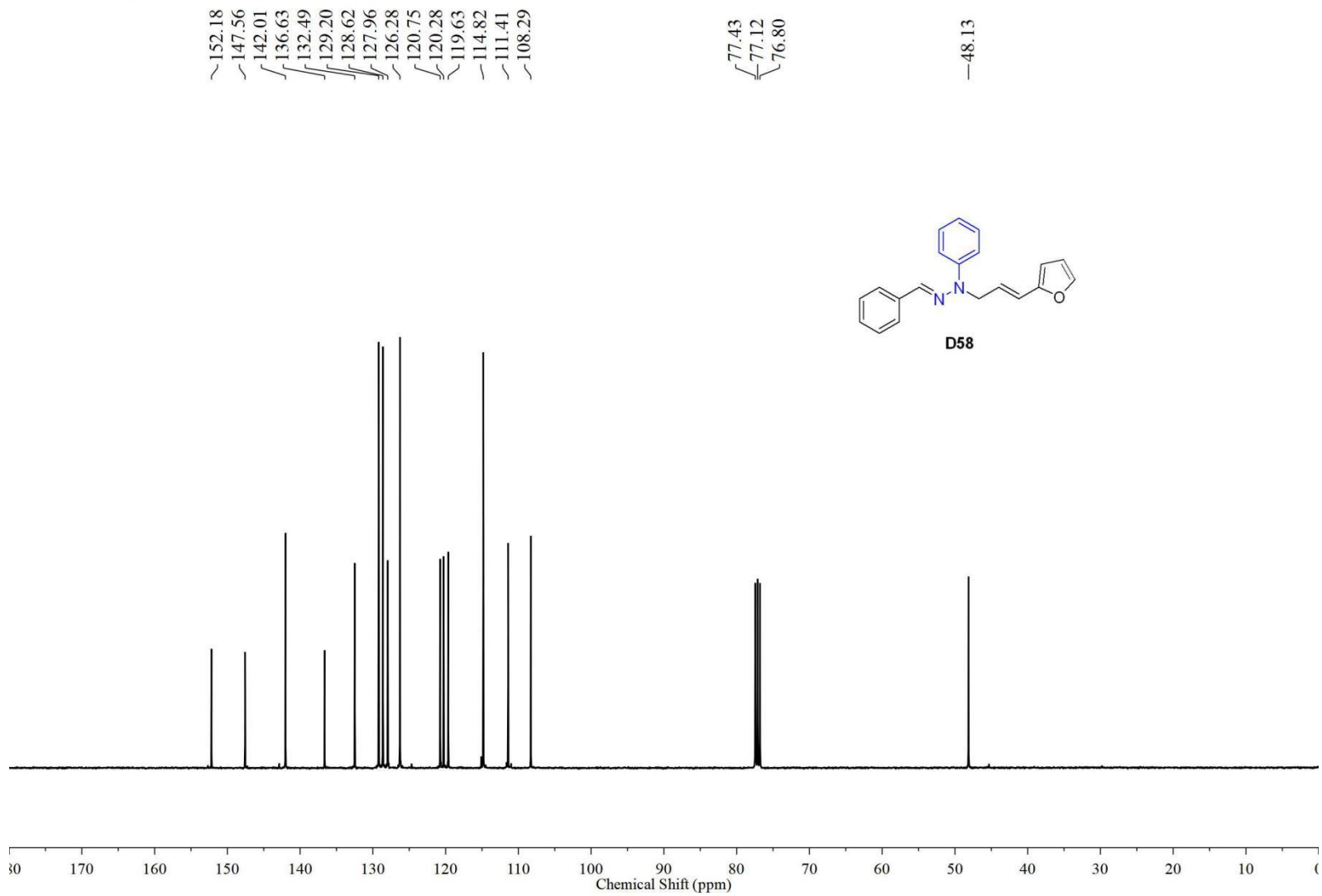


S261

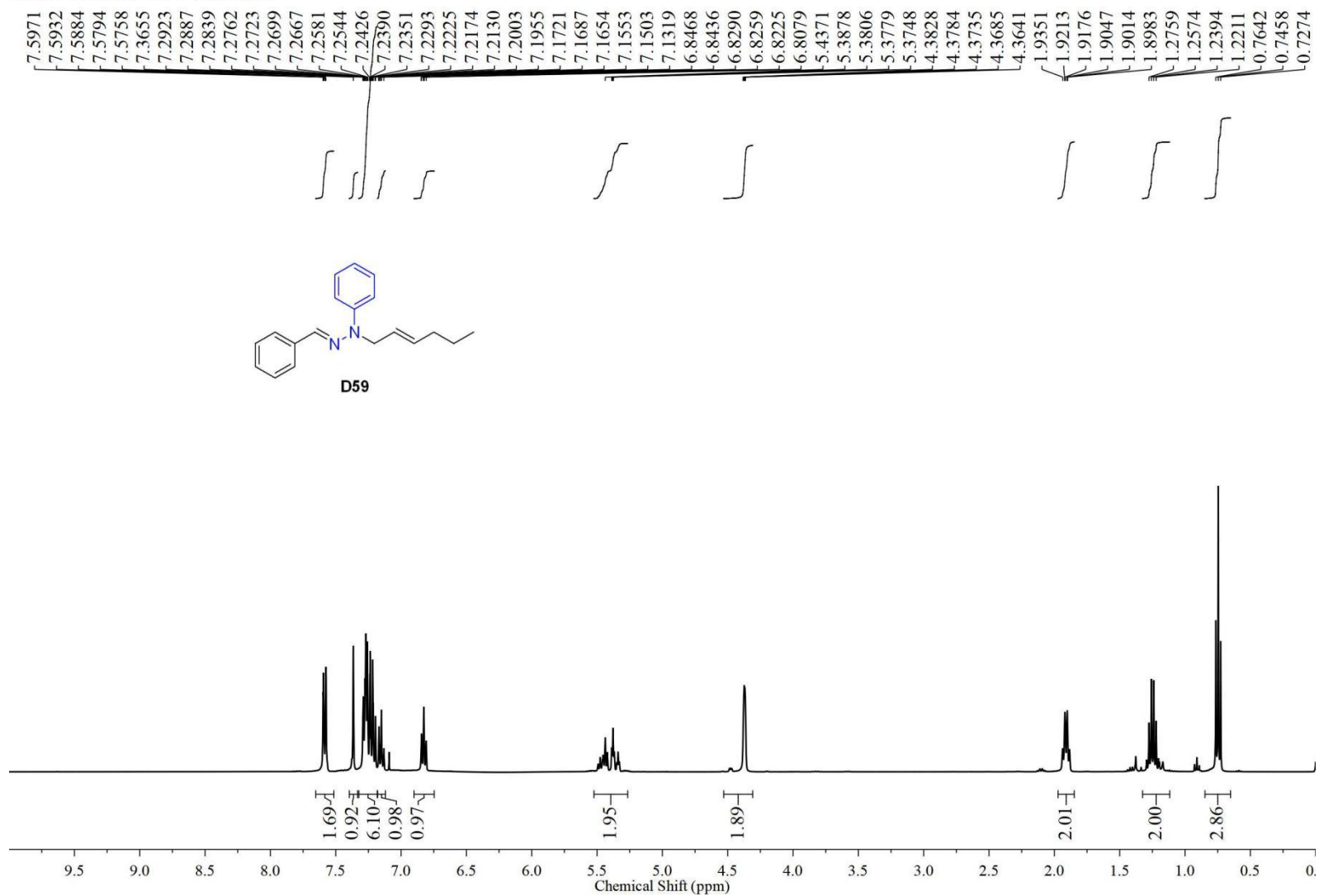
2022-07-18-yy0004-616-1-a-12.10.fid



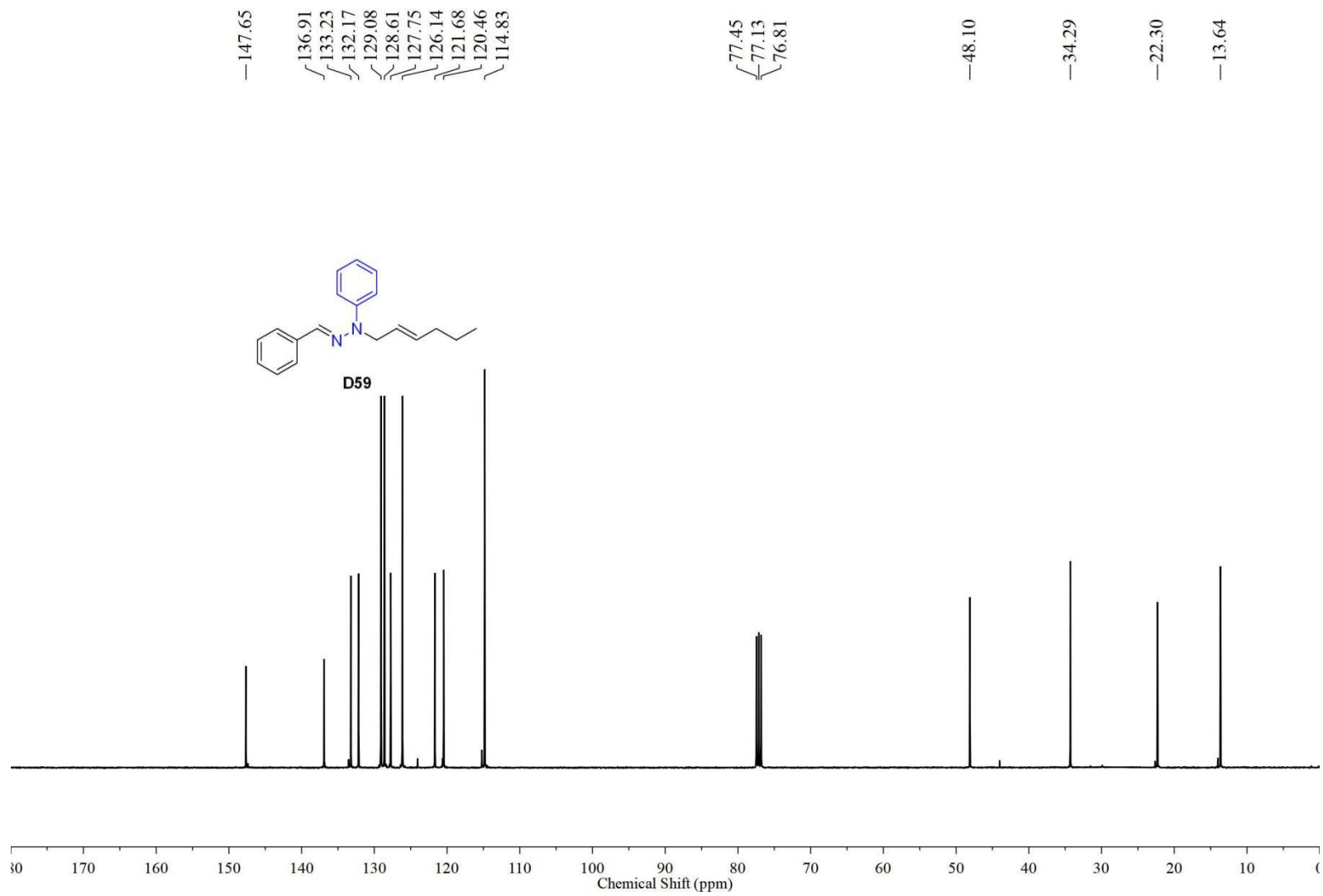
2022-07-19-YY0059-616-L-A12.10.fid



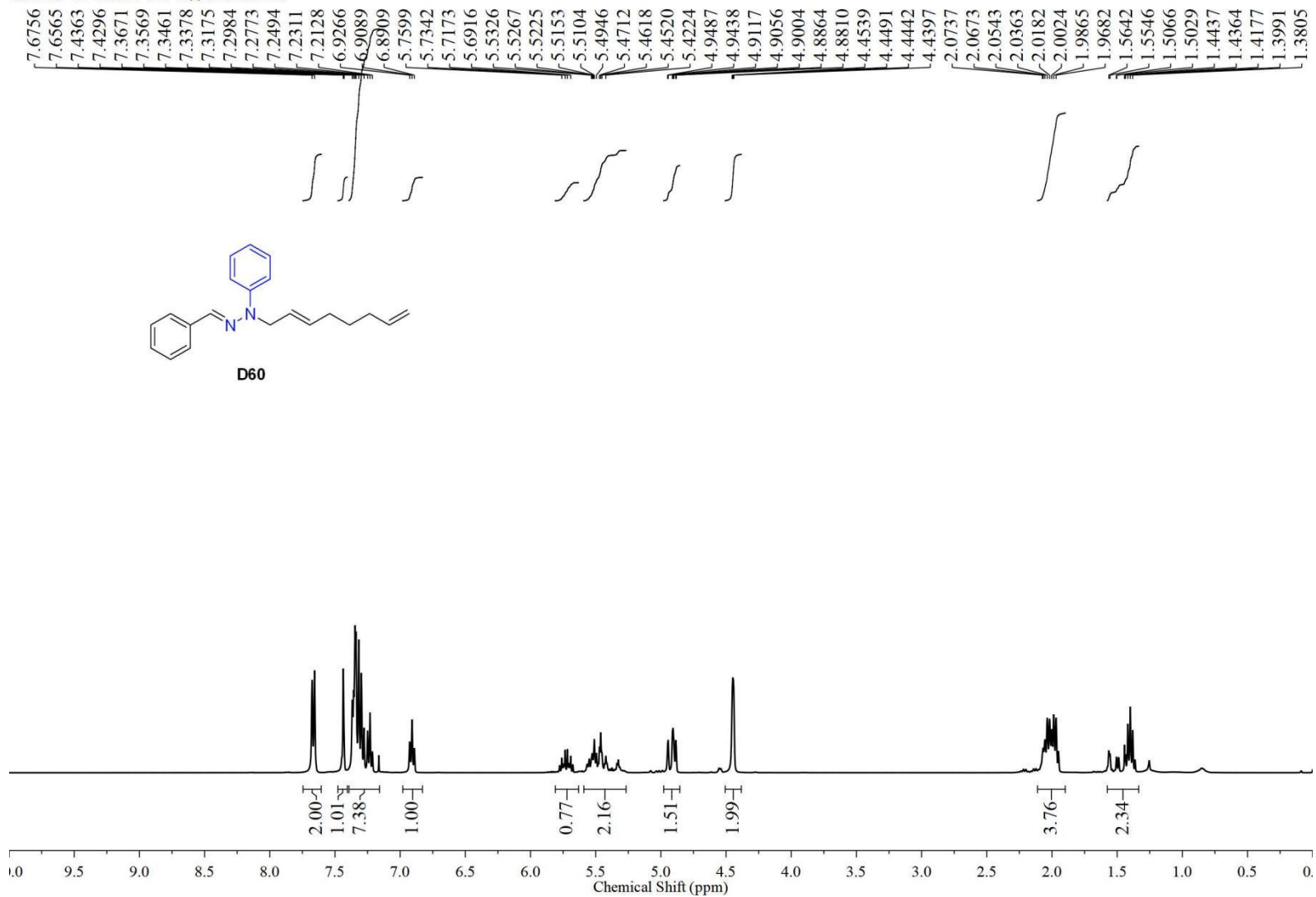
2022-07-20-yy0021-616-1-a13. 10. fid



2022-07-21-yy0026-616-1-a12.10.fid



2022-08-15 YY0014 616-LQQ-A25.10.fid



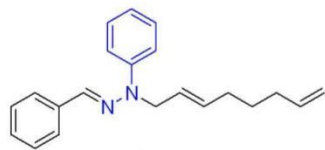
2022-10-17-YY0002-616-L-1.10.fid

147.58
138.57
136.82
132.96
132.13
129.05
128.58
127.74
126.10
121.79
120.45
114.78
114.65

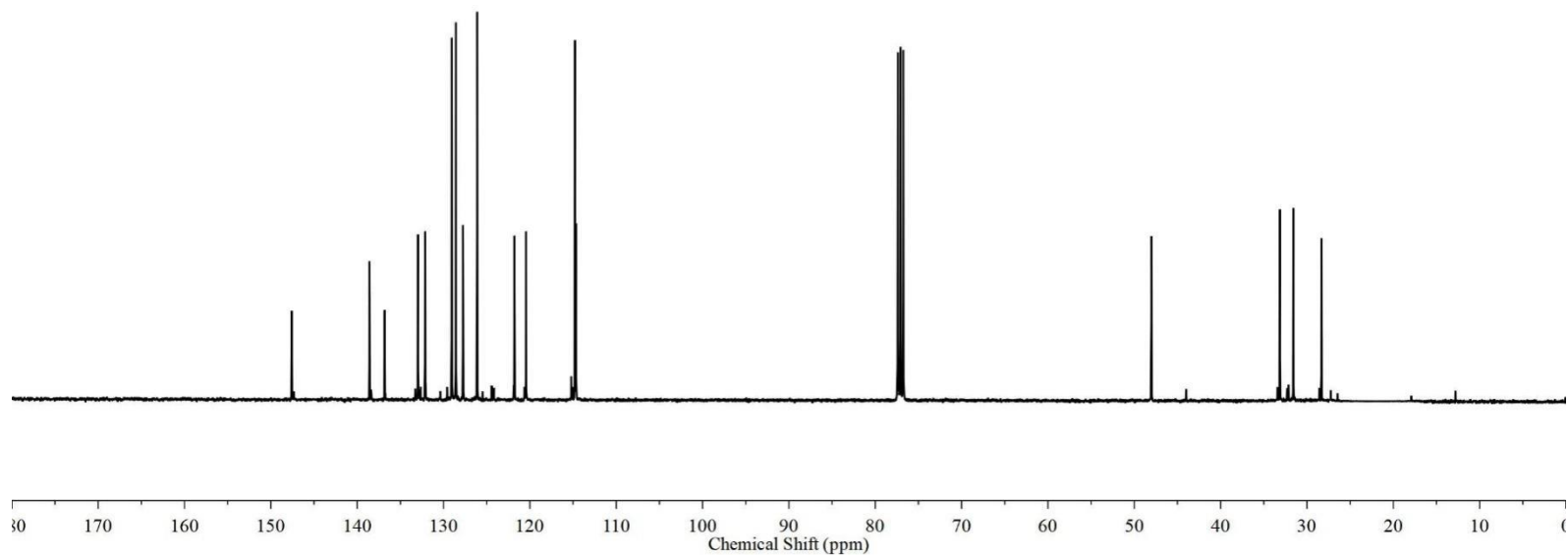
77.39
77.07
76.75

48.01

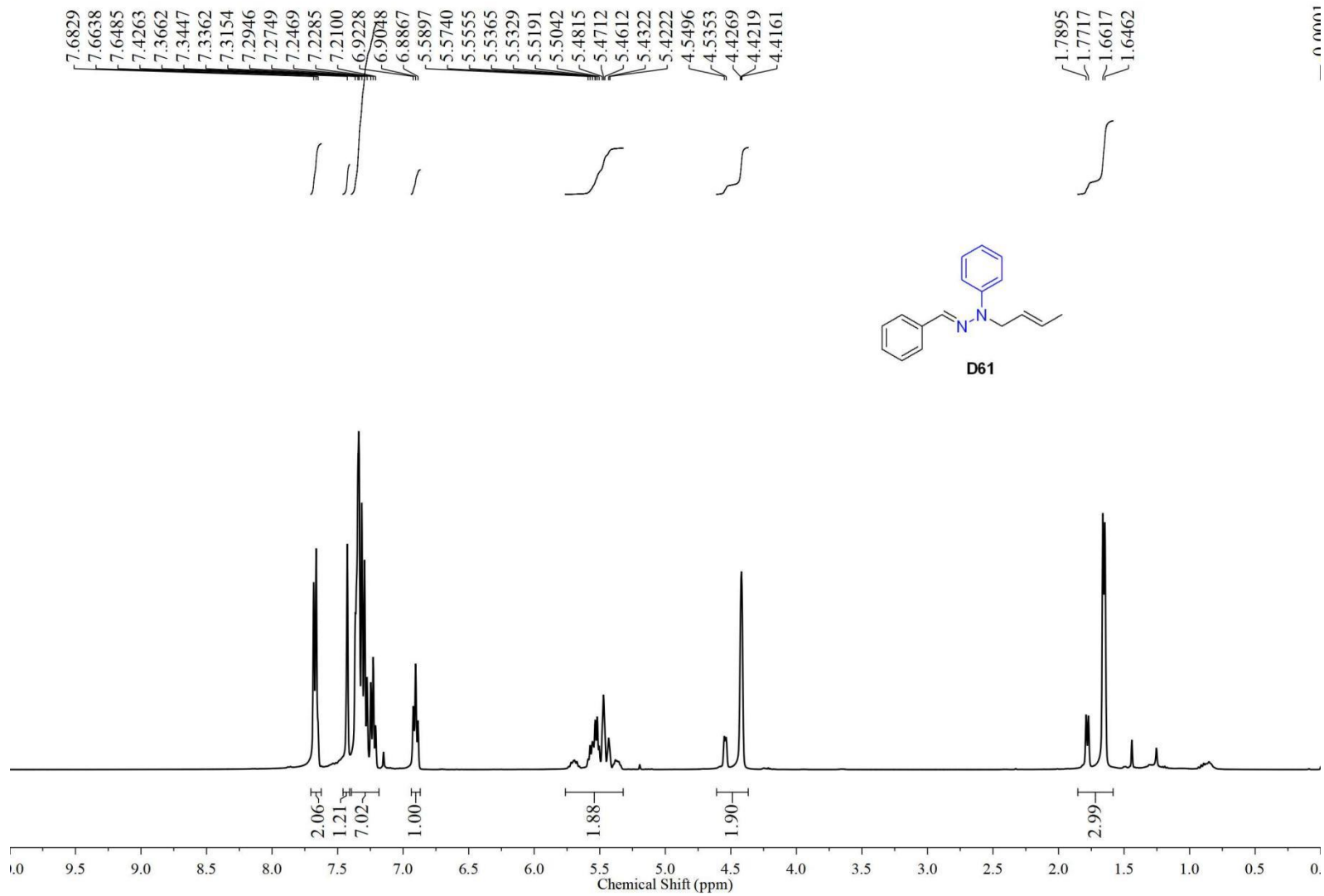
33.14
31.58
28.32



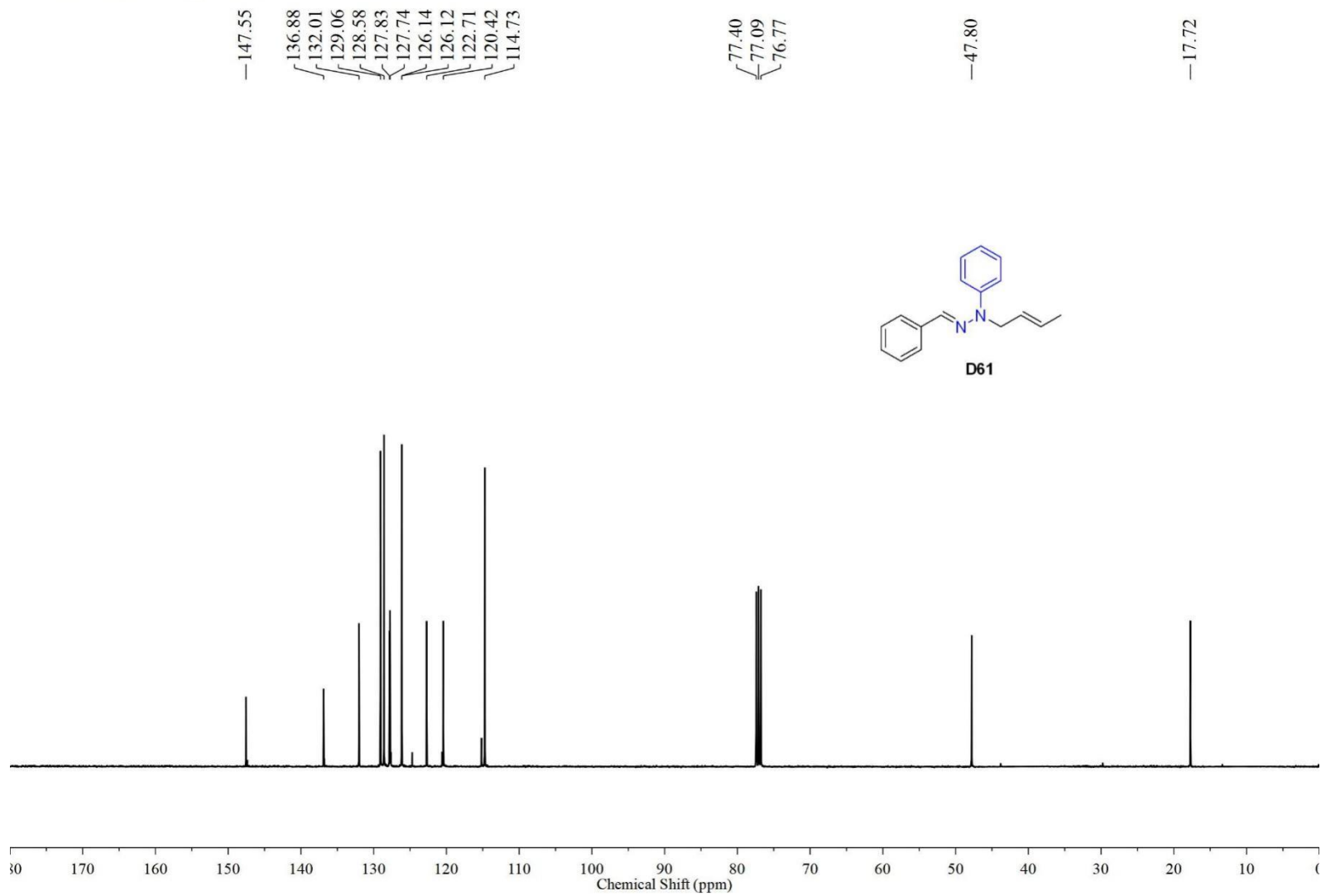
D60



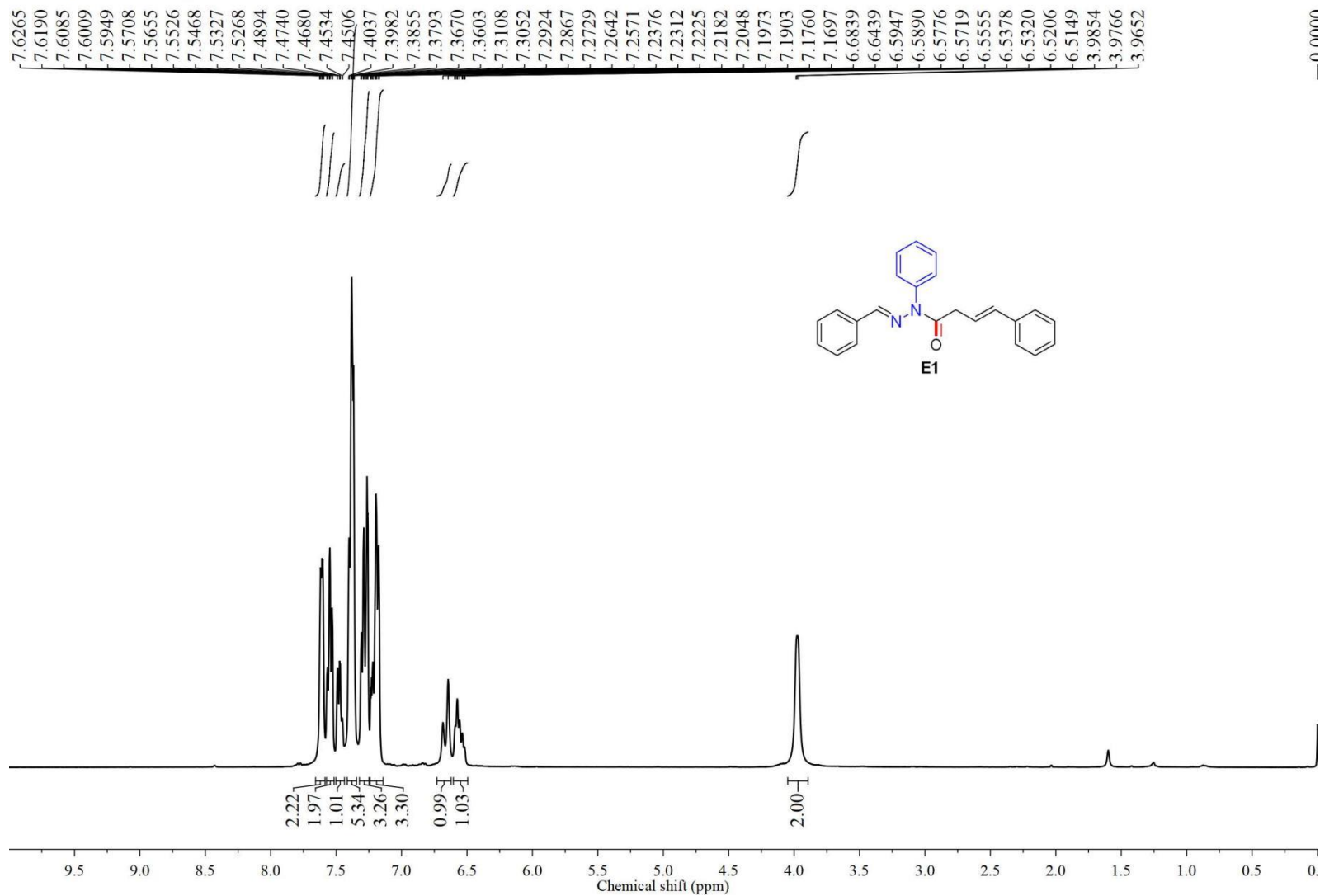
2022-07-12 YY0029 616-lqq-1-A9. 10. fid



2022-07-14 YY0037 616-lqq-1-A12.11.fid

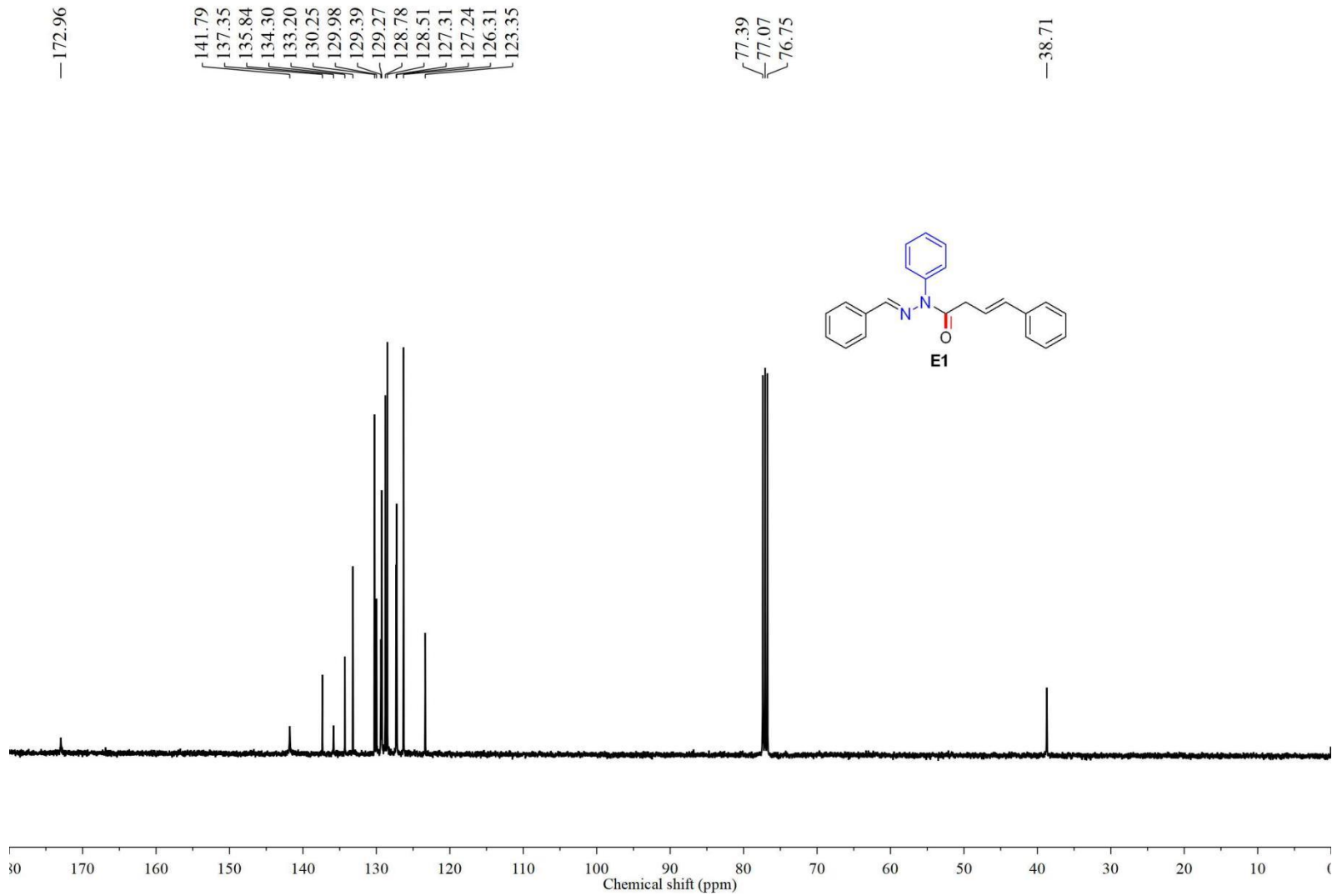


2022-4-14 yy0002-616-lqq-c.10.fid



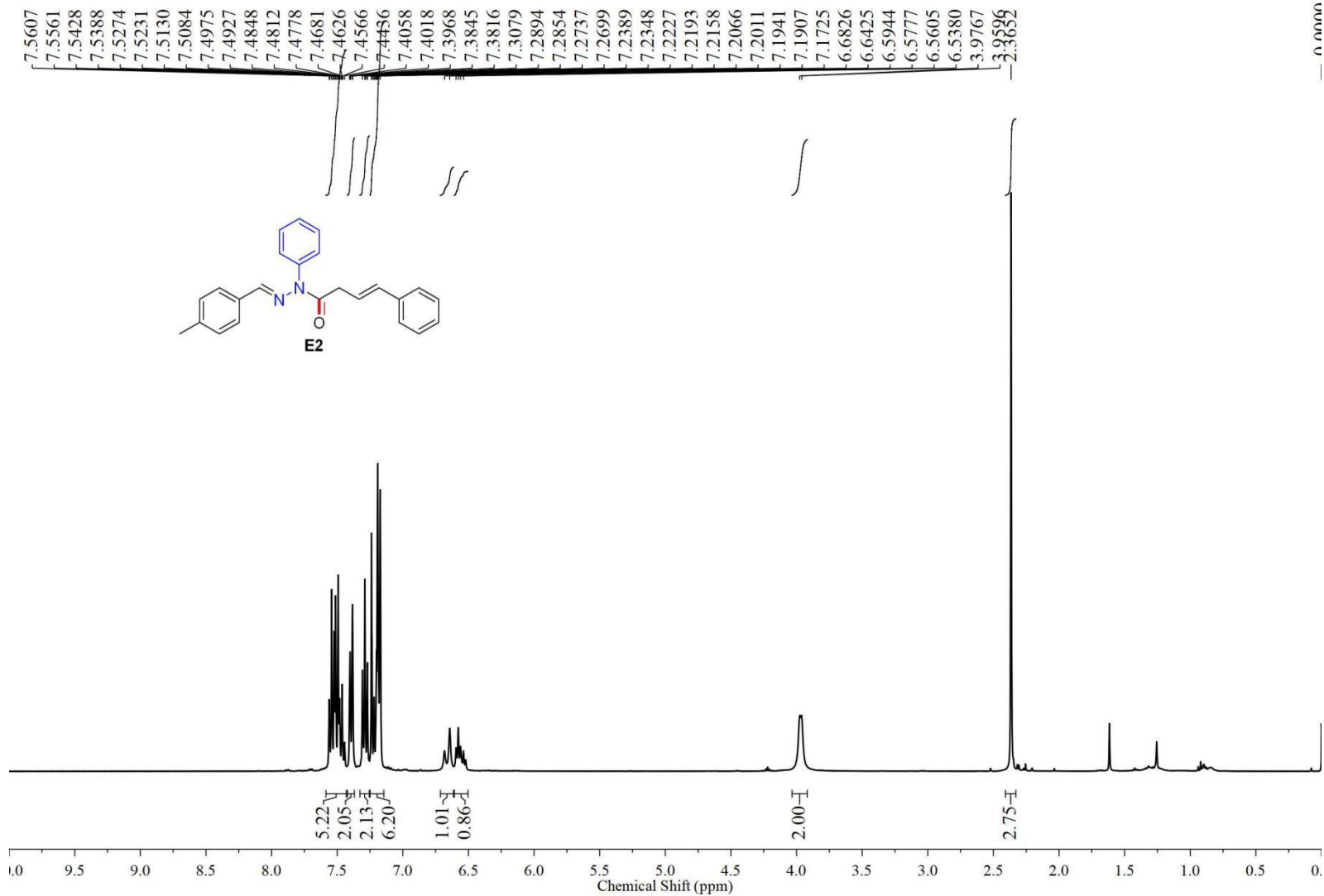
S270

2022-04-28-yy0014-616-lqq-d1.10.fid



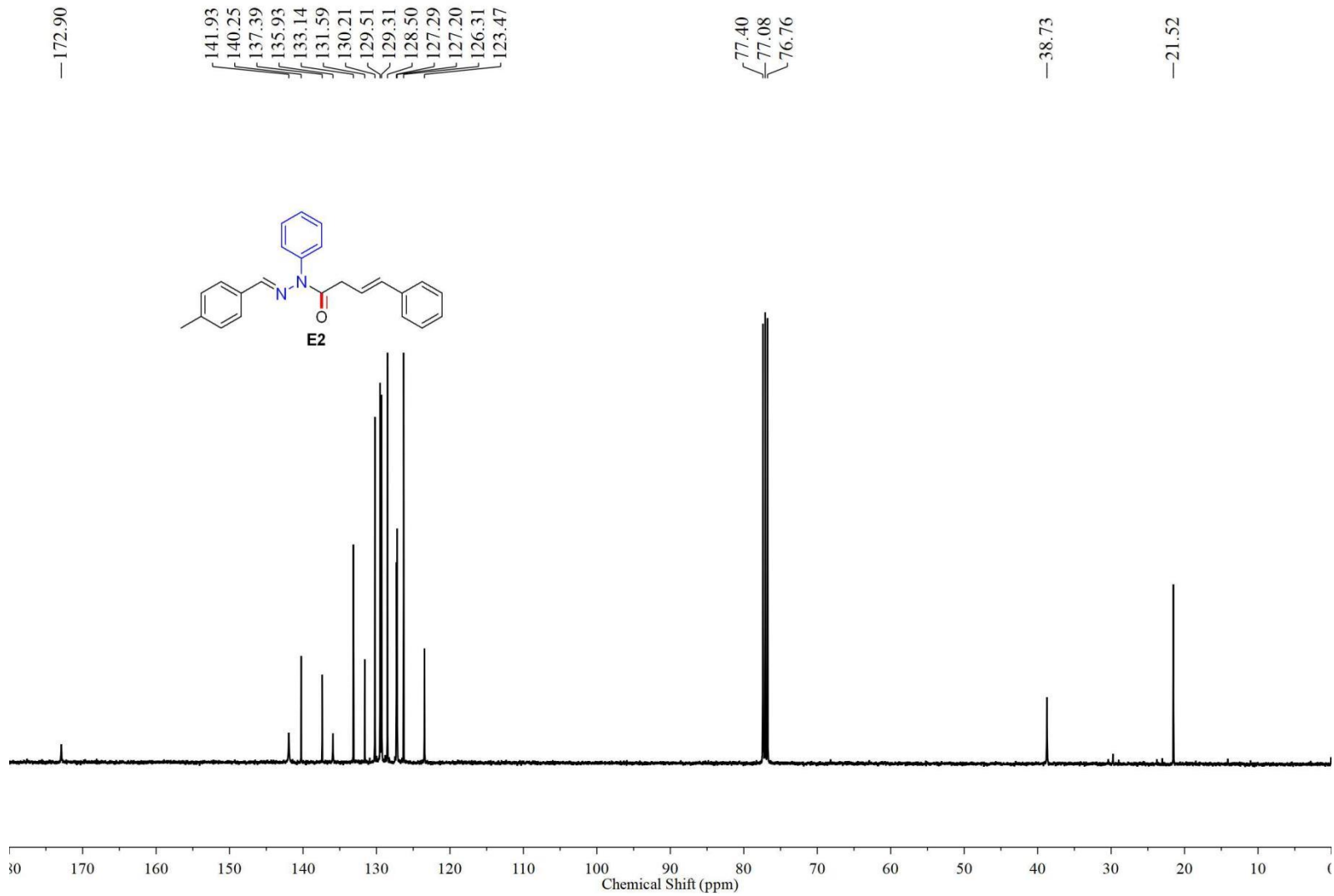
S271

2022-10-27 yy0015 616-lq2.10.fid

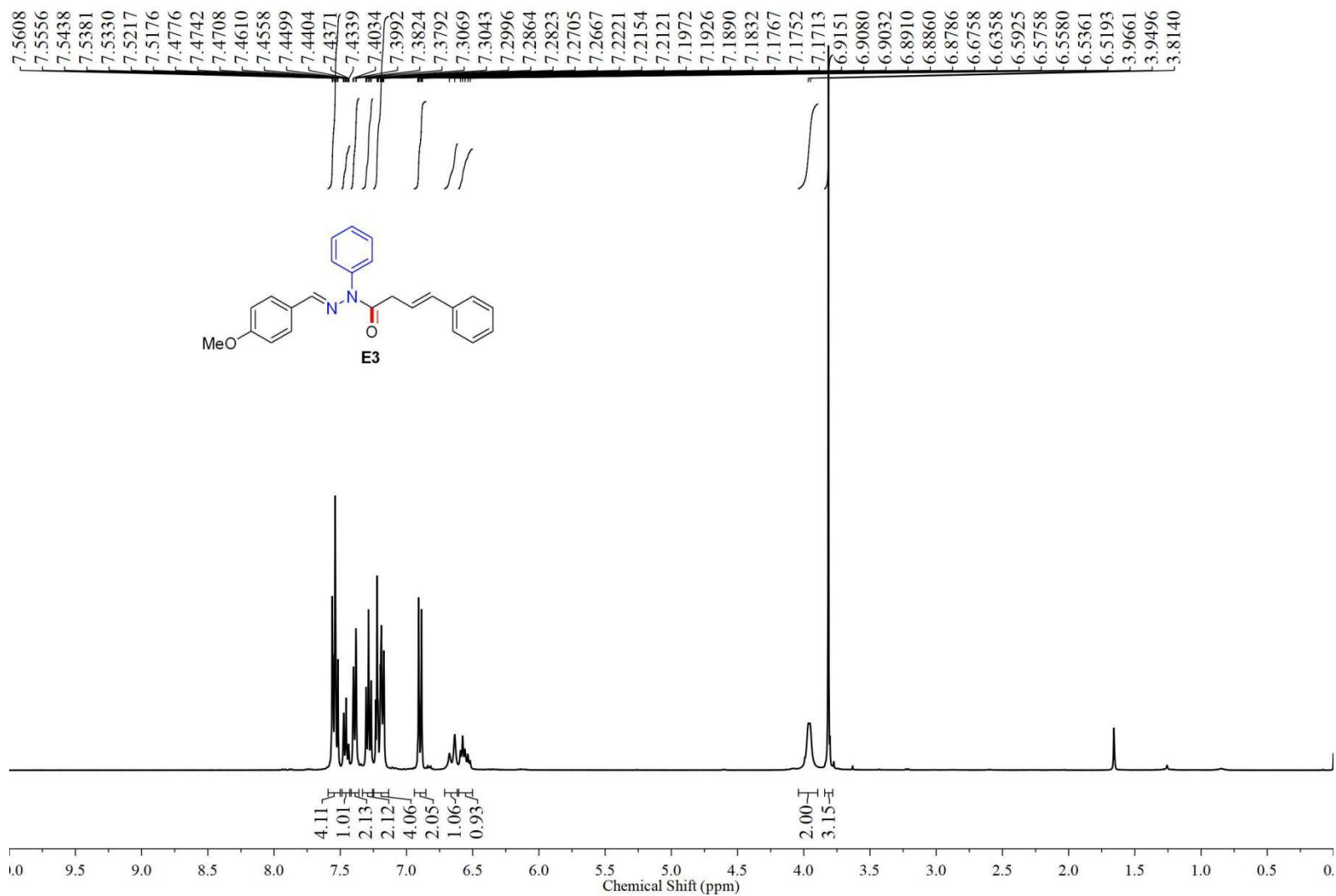


S272

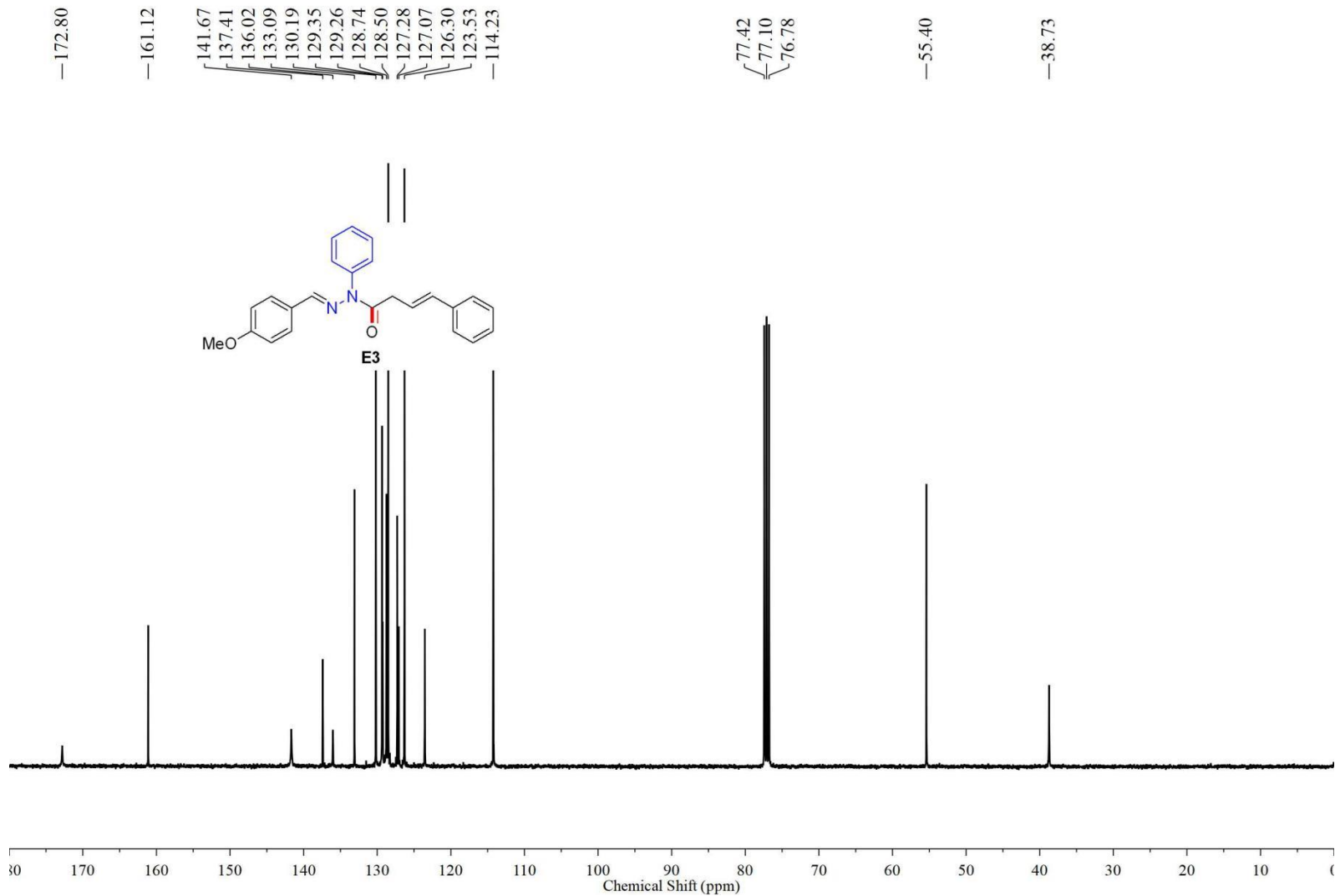
2022-10-28 yy0003 616-lqq-6.10. fid



2022-11-11-yy0017-616-1-h29. 10. fid

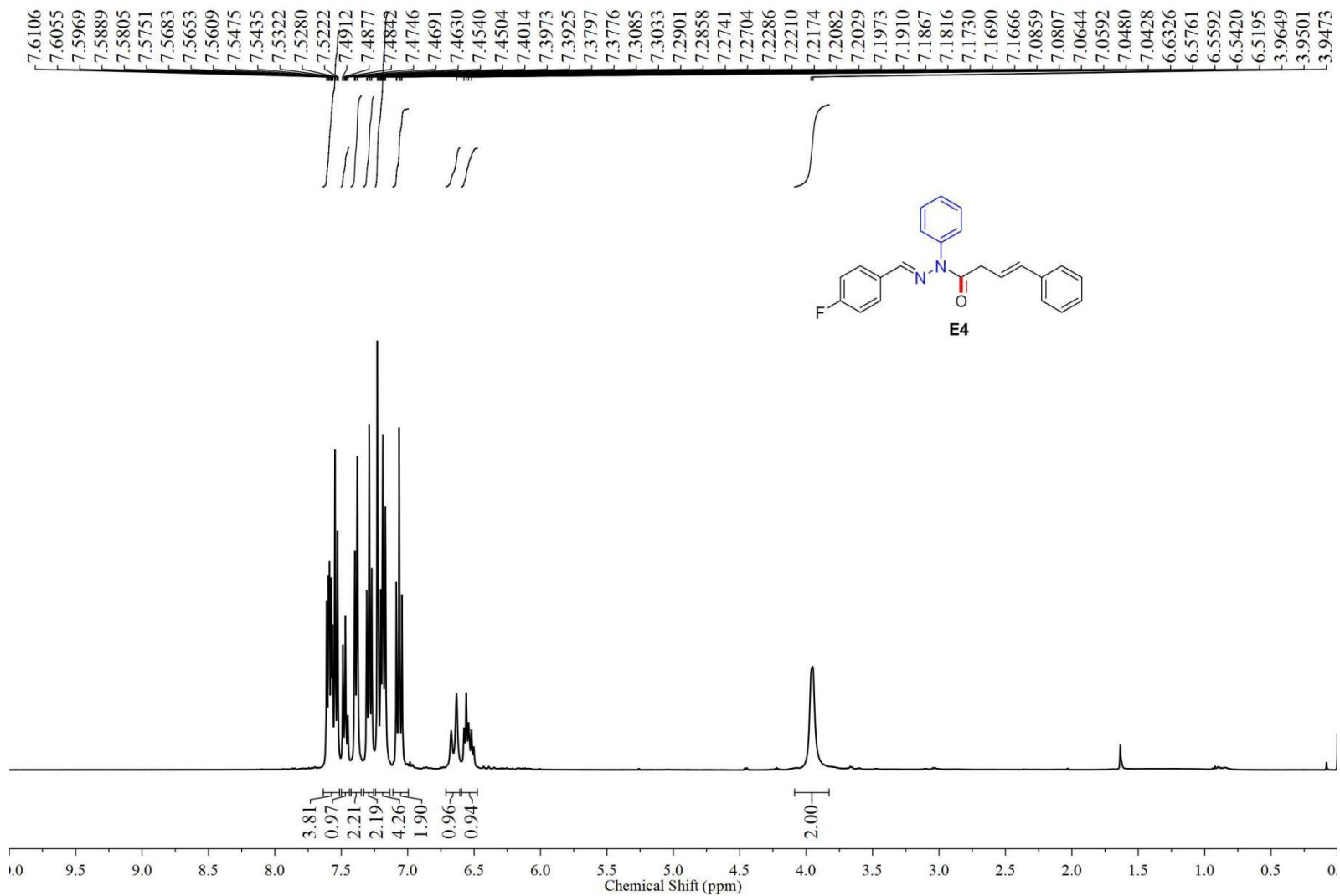


2022-11-11-yy0017-616-1-h29. 11. fid



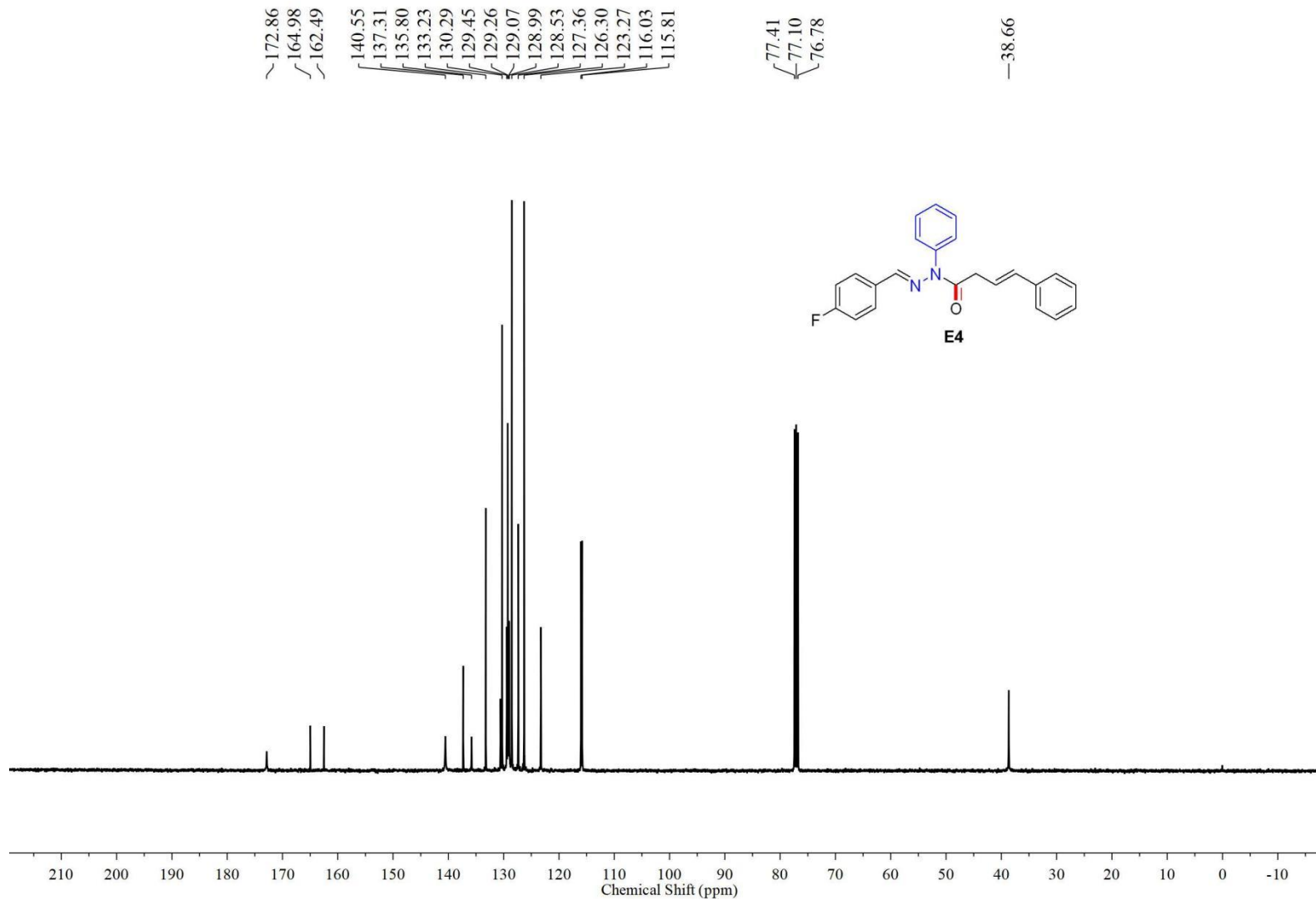
S275

2022-11-09-yy0020-616-h30. 10. fid



S276

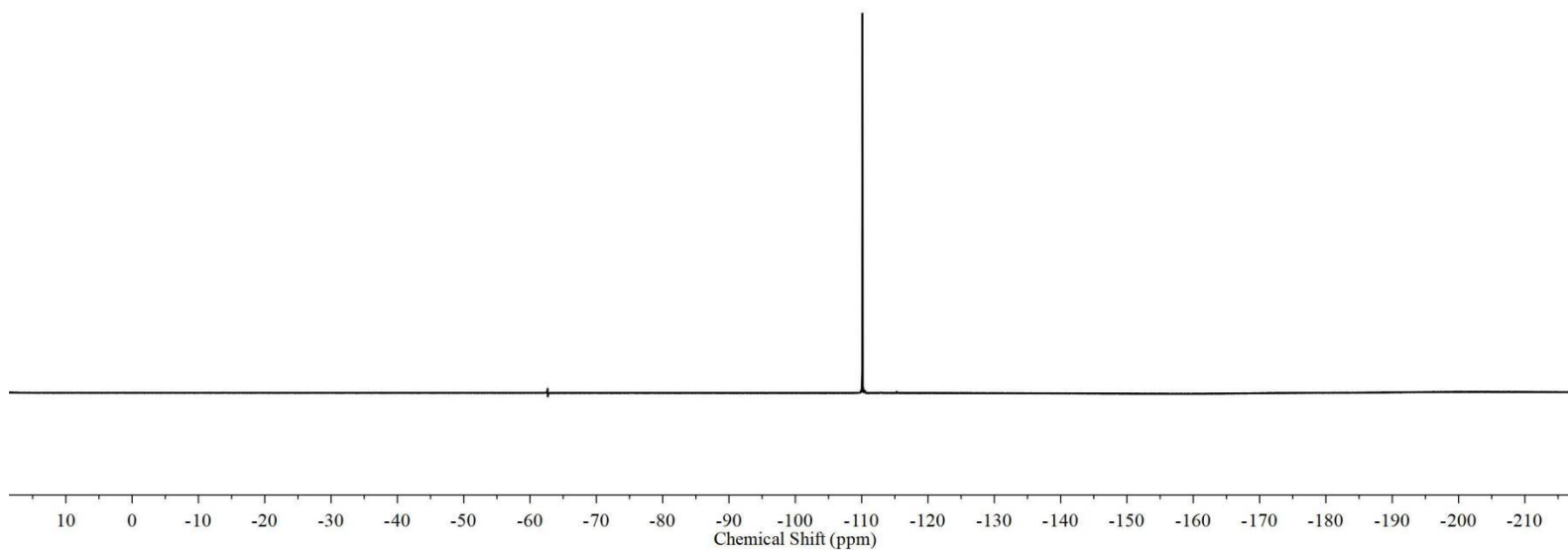
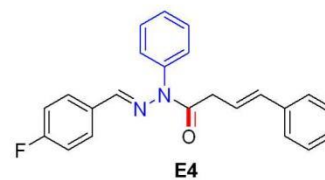
2022-11-10-yy0019-616-h30. 10. fid



S277

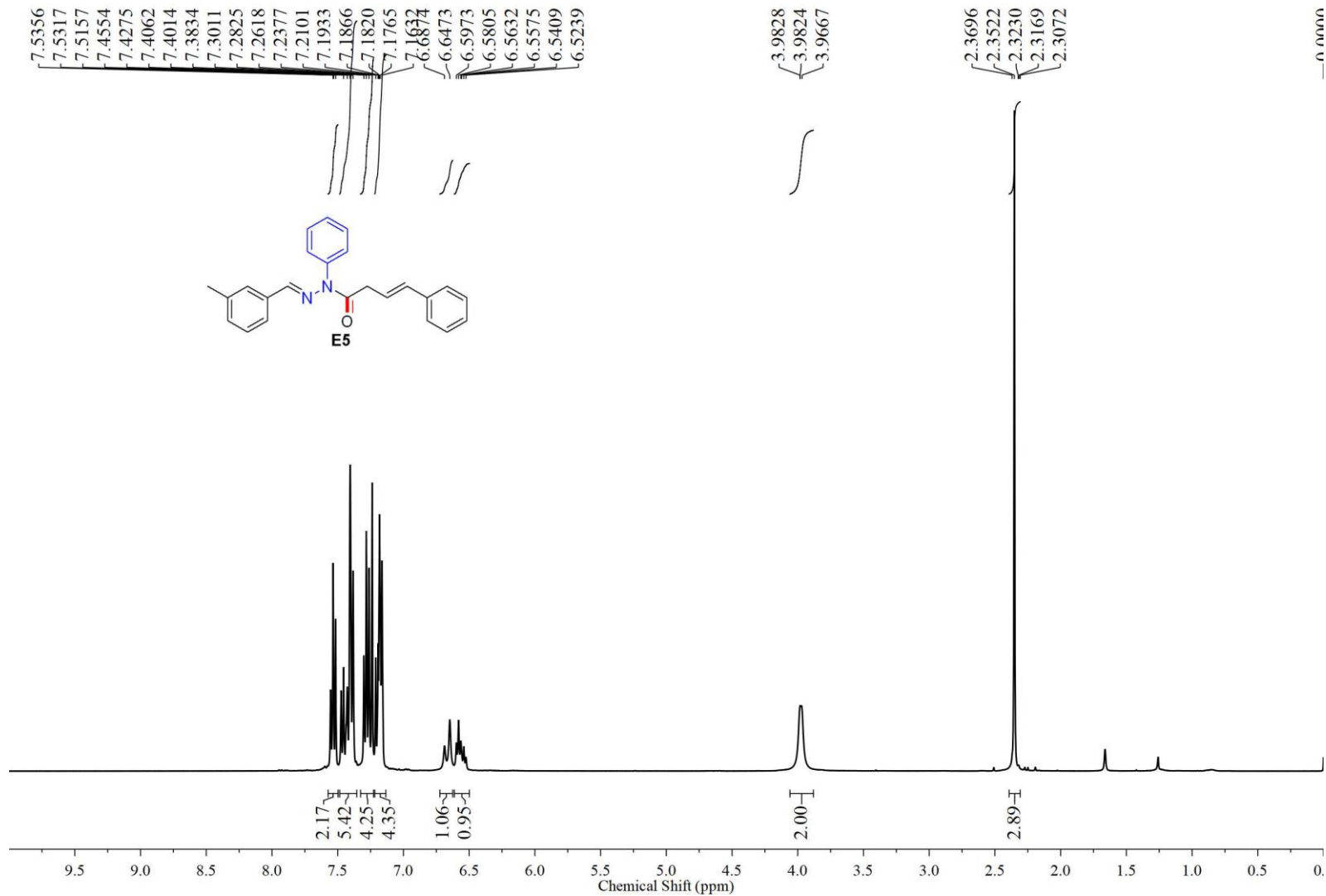
2022-11-10-yy0019-616-h30. 11. fid

-110.11

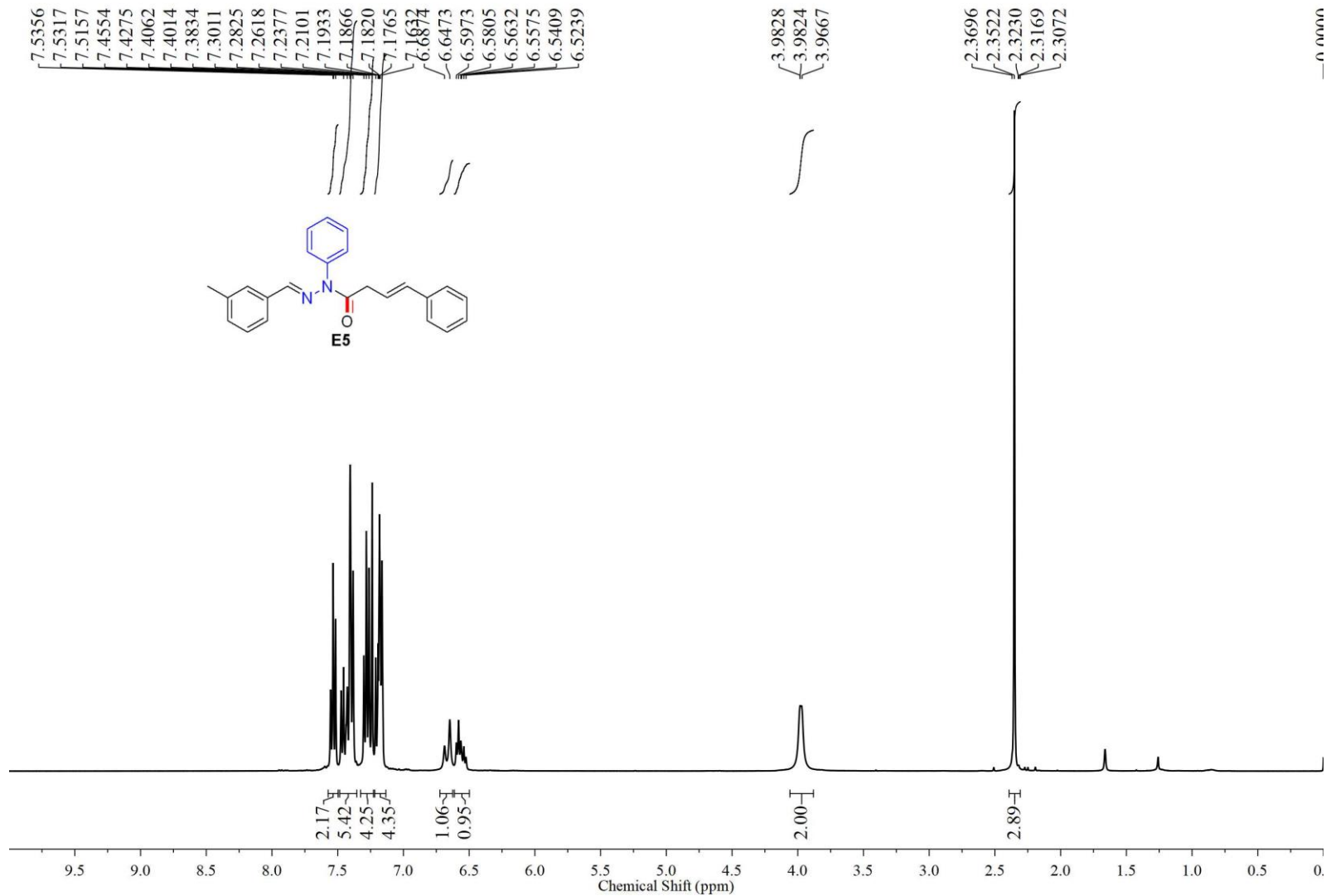


S278

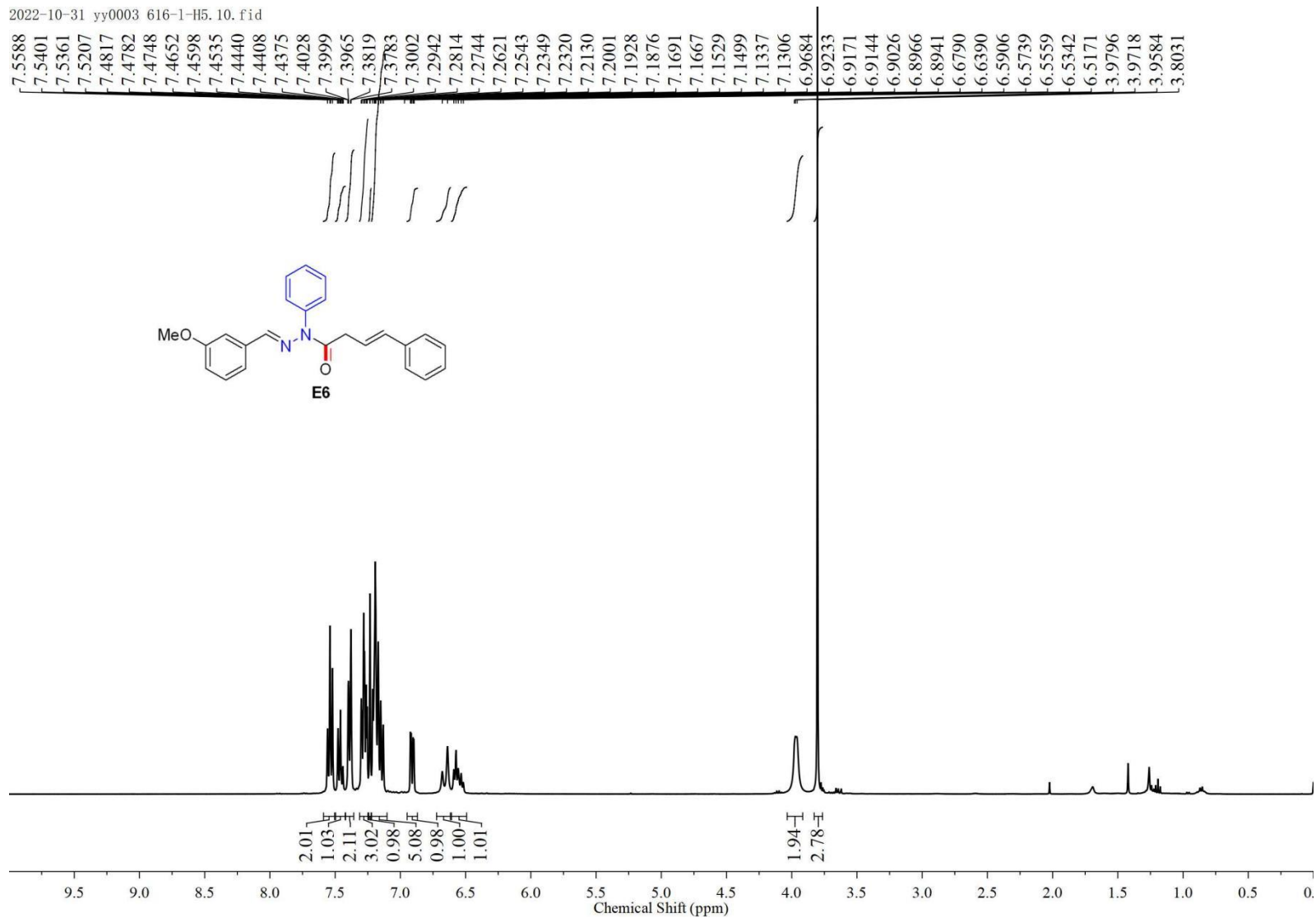
2022-11-11-yy0017-616-1-h31. 10. fid



2022-11-11-yy0017-616-1-h31. 10. fid

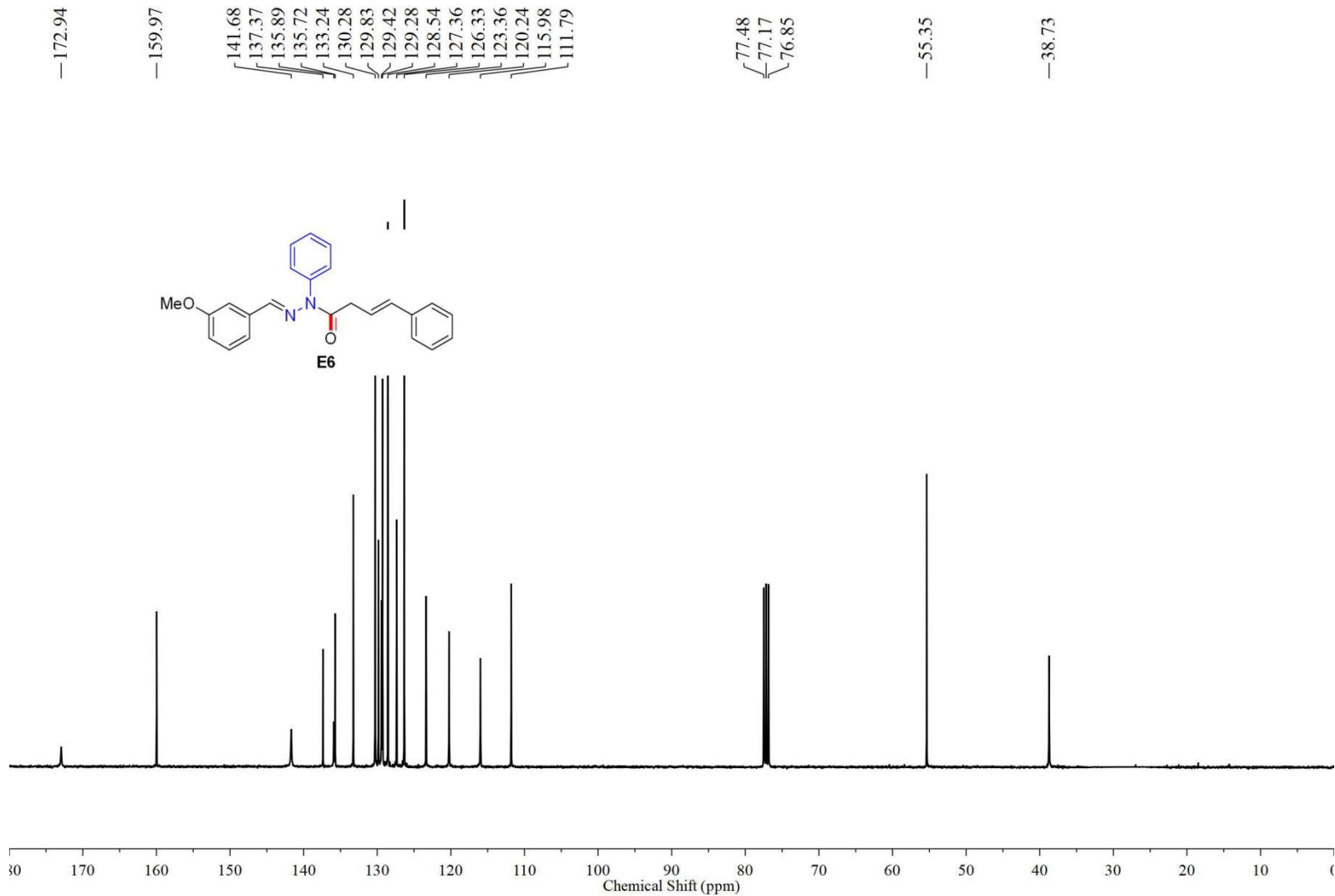


2022-10-31 yy0003 616-1-H5.10.fid

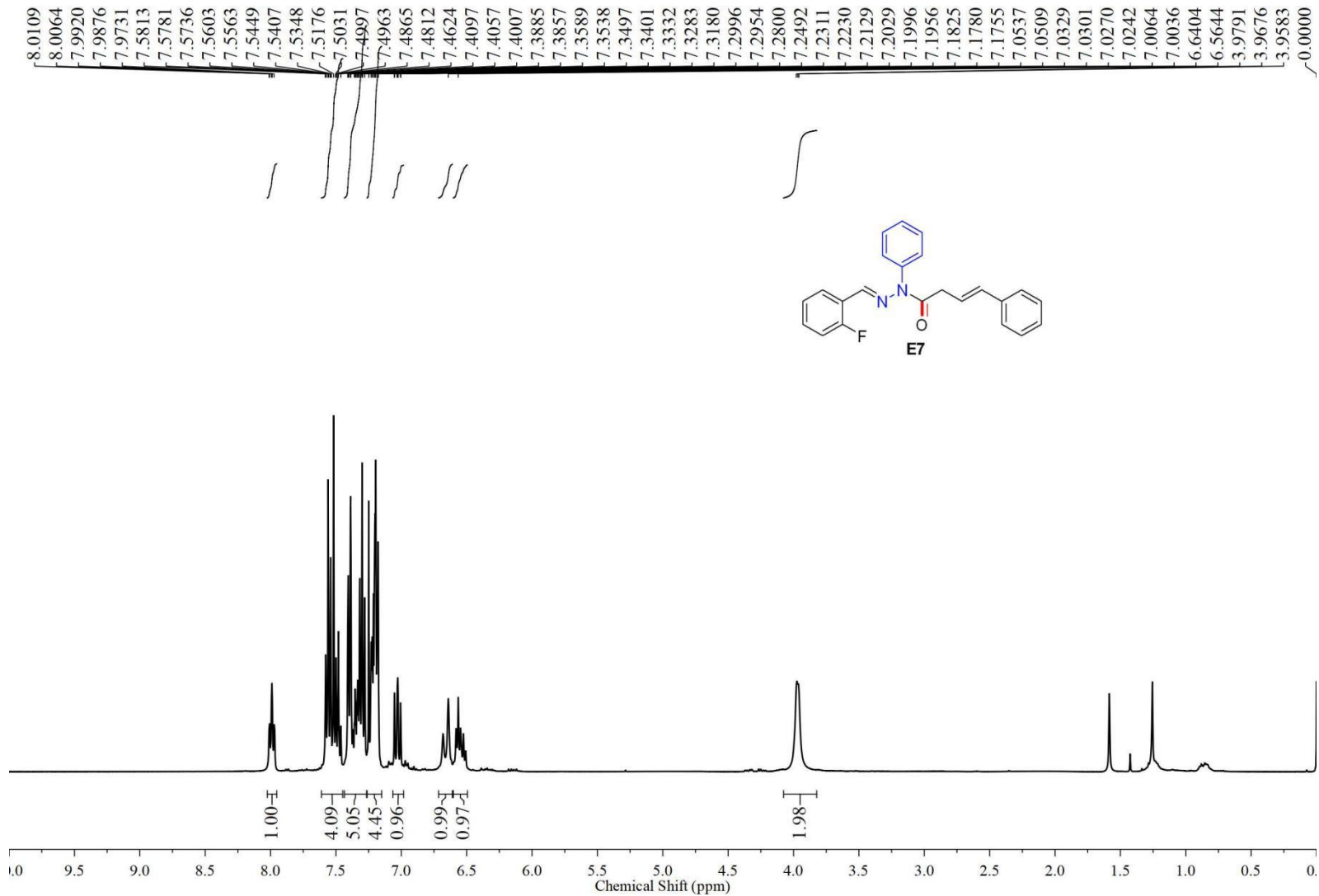


S281

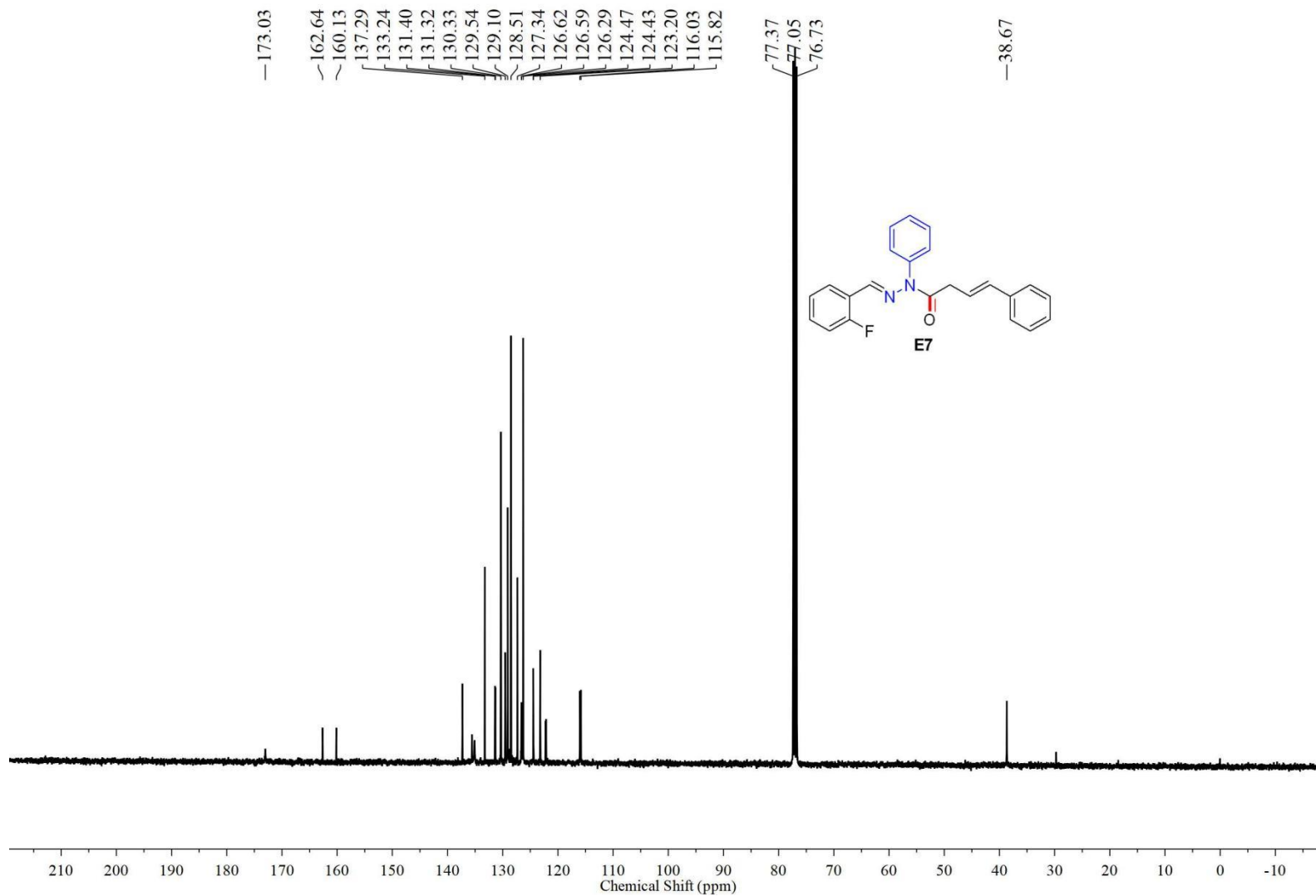
2022-11-1 yy0019-616-1qq-5.10.fid



2022-10-27 yy0015 616-lq6. 10. fid



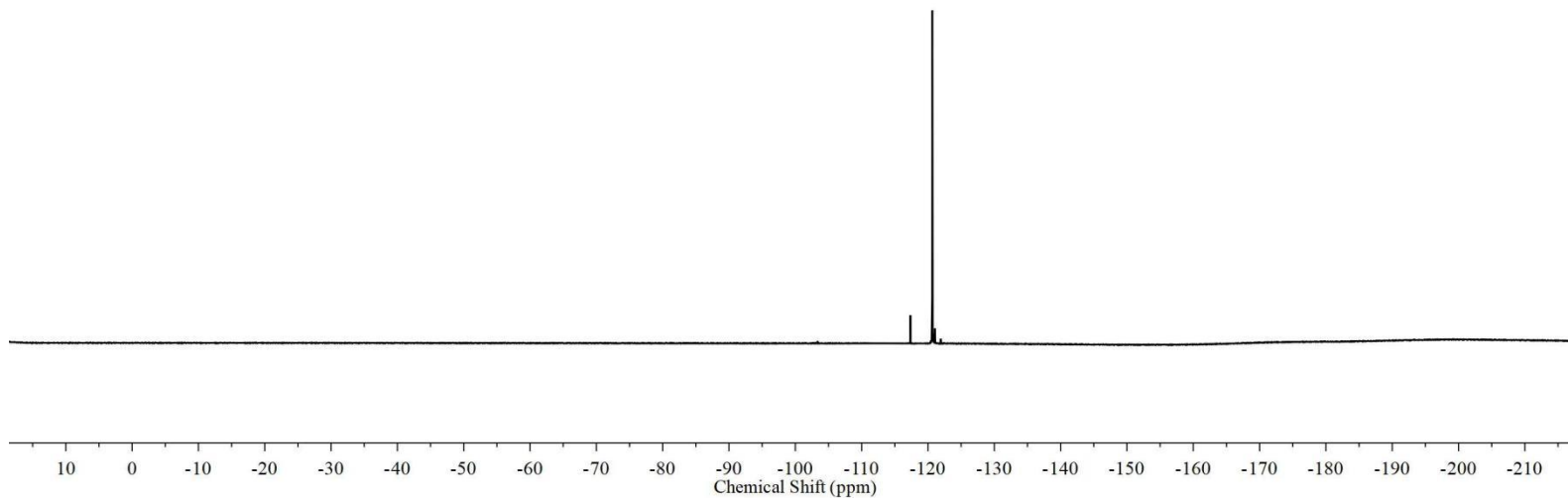
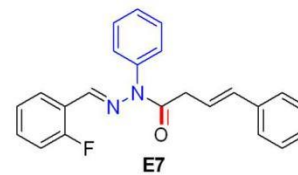
2022-10-28 yy0021 616-lqq-2.10. fid



S284

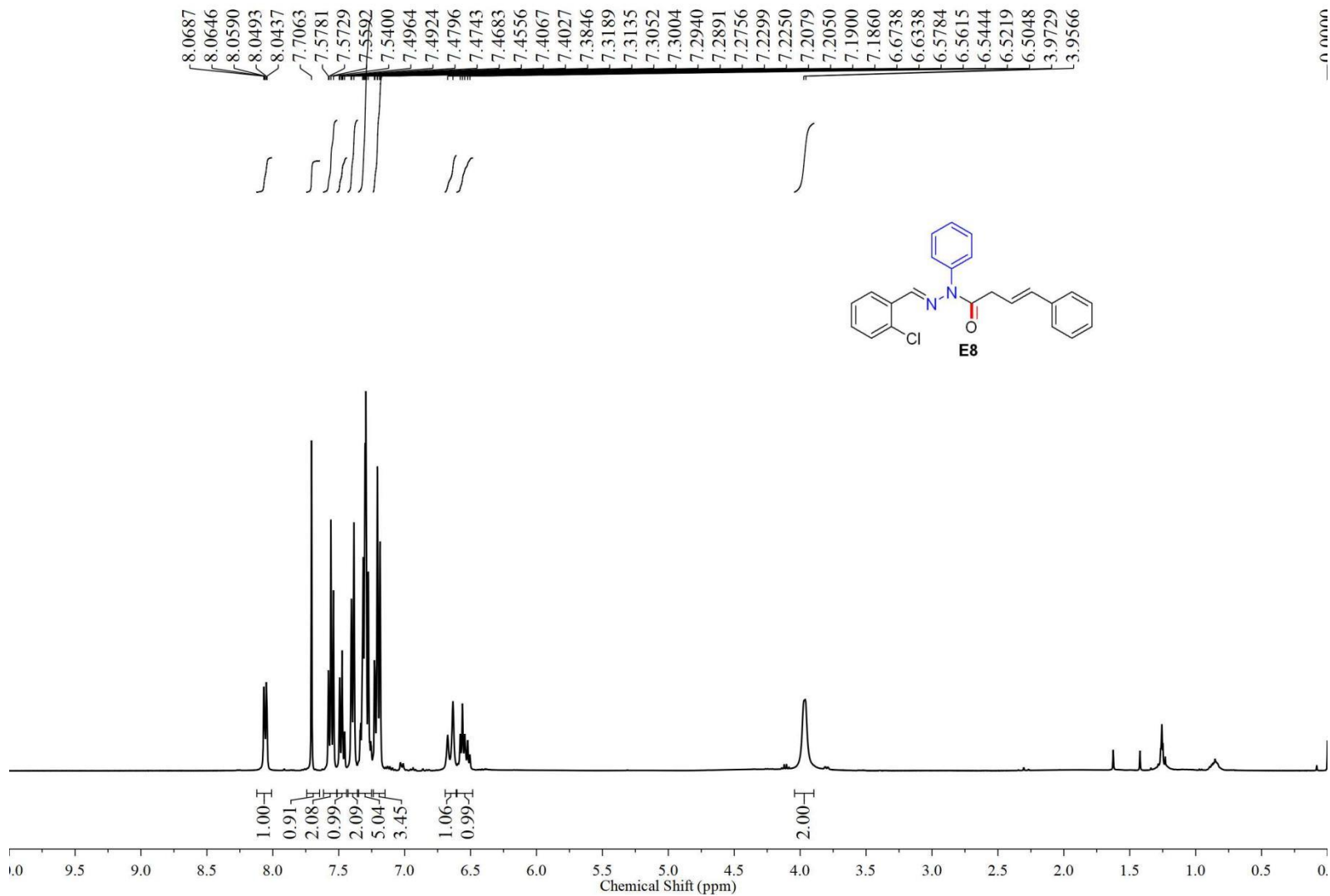
2022-10-31 yy0020 616-1-H6.10.fid

-120.66



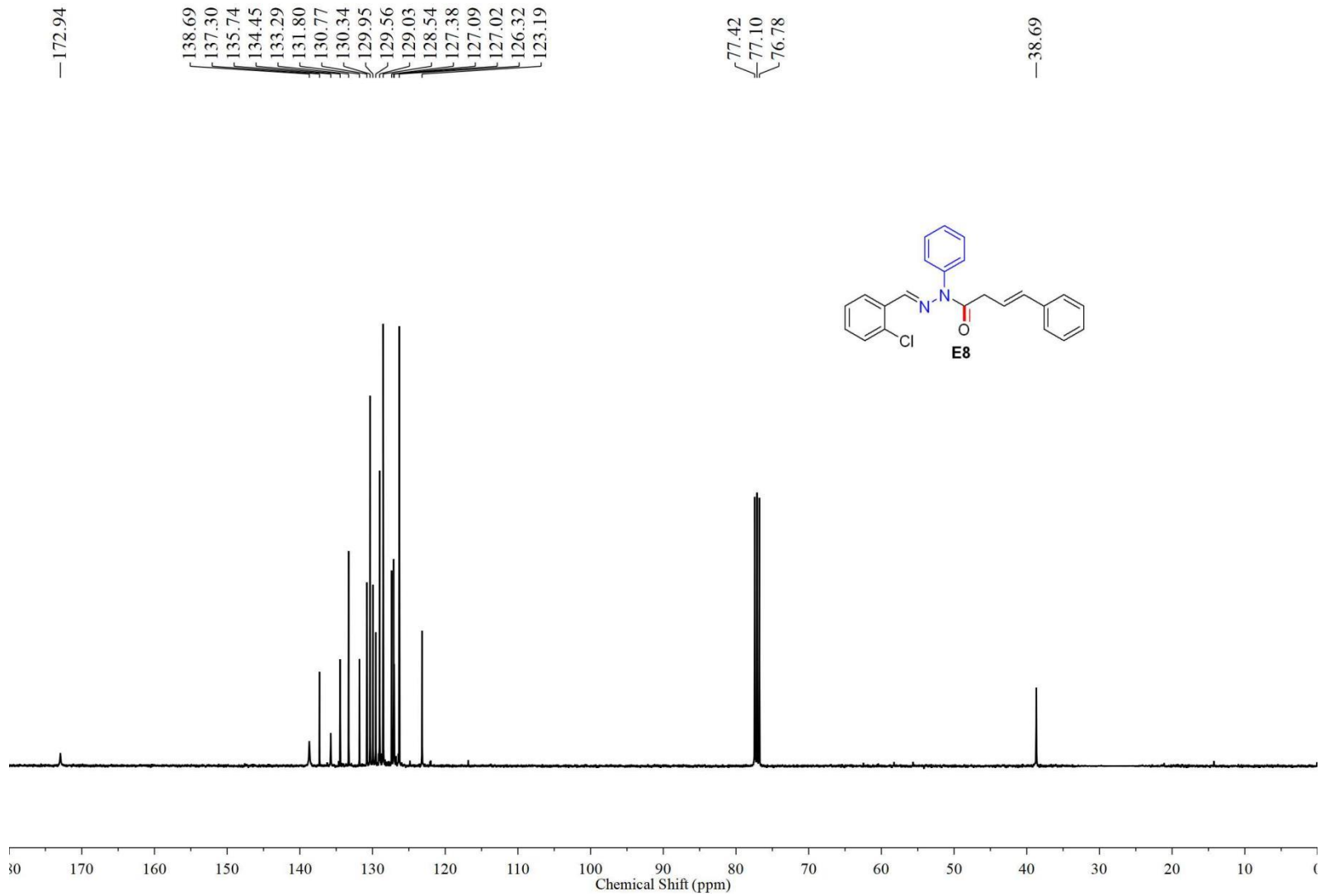
S285

2022-10-24 YY0003 616-LQQ-7.10. fid

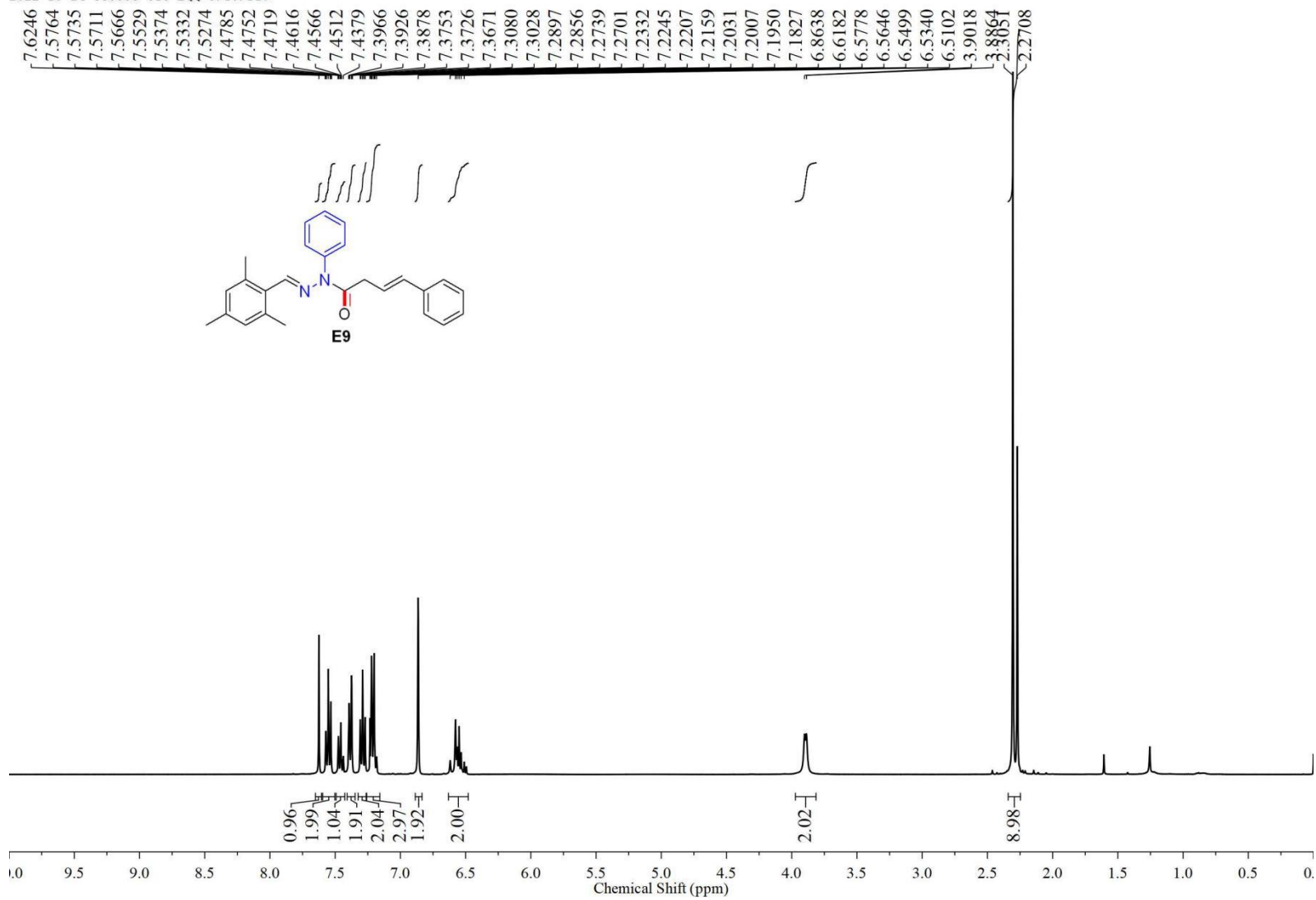


S286

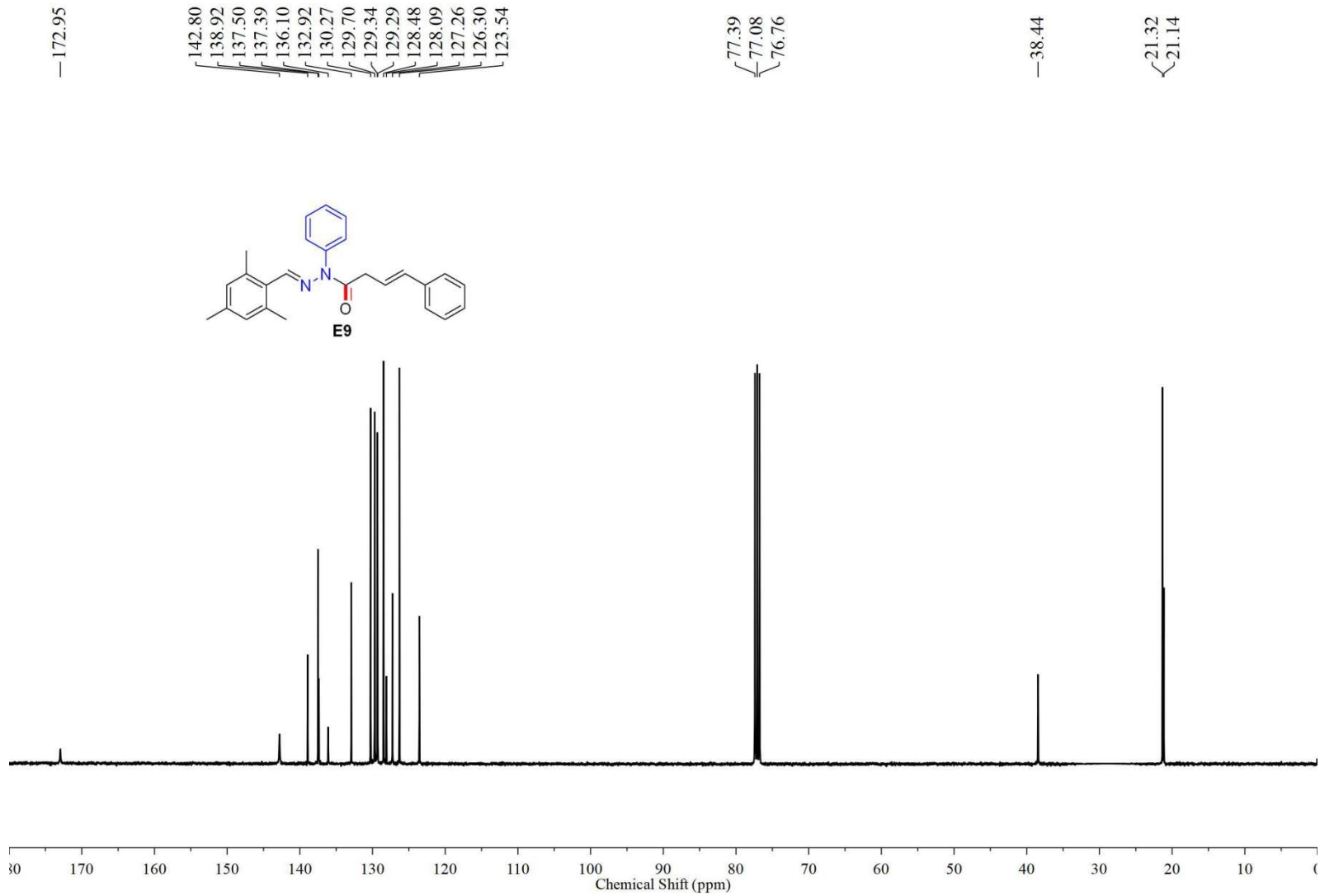
2022-10-26 YY0002 616 LQQ-7.10. fid



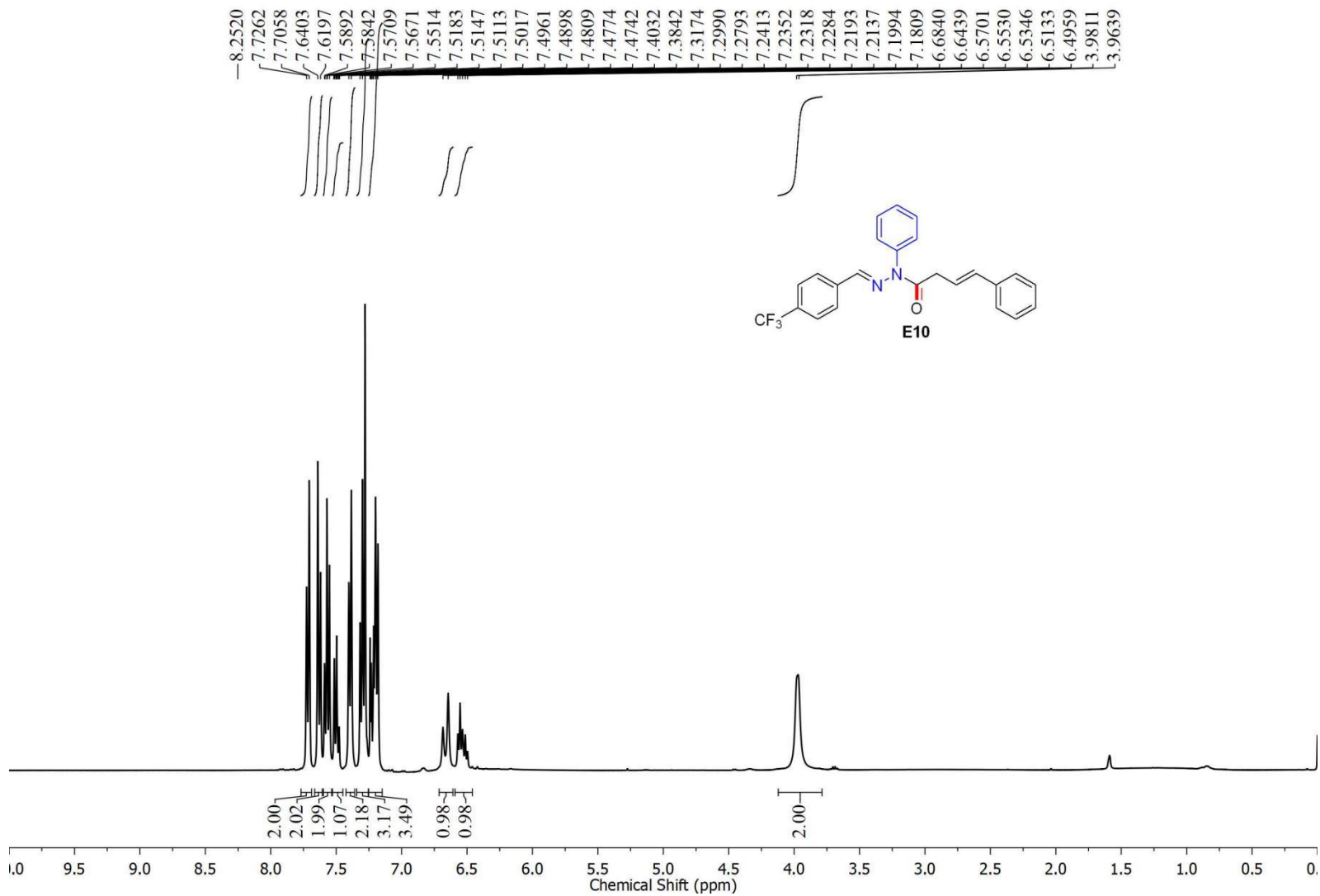
2022-10-24 YY0003 616-LQQ-3.10. fid



2022-10-26 YY0002 616 LQQ-3.10. fid

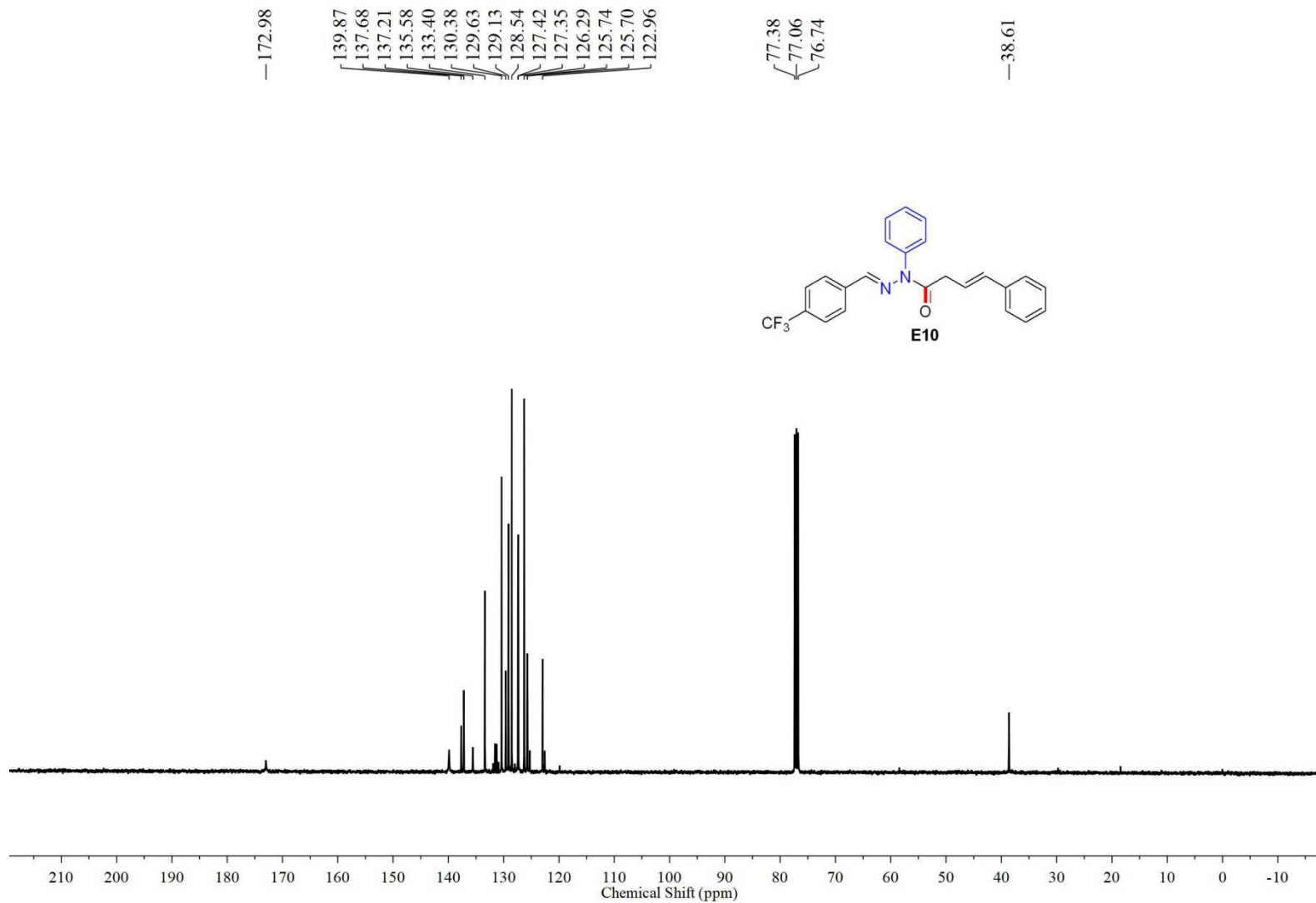


2022-11-09-yy0020-616-h31. 10. fid



S290

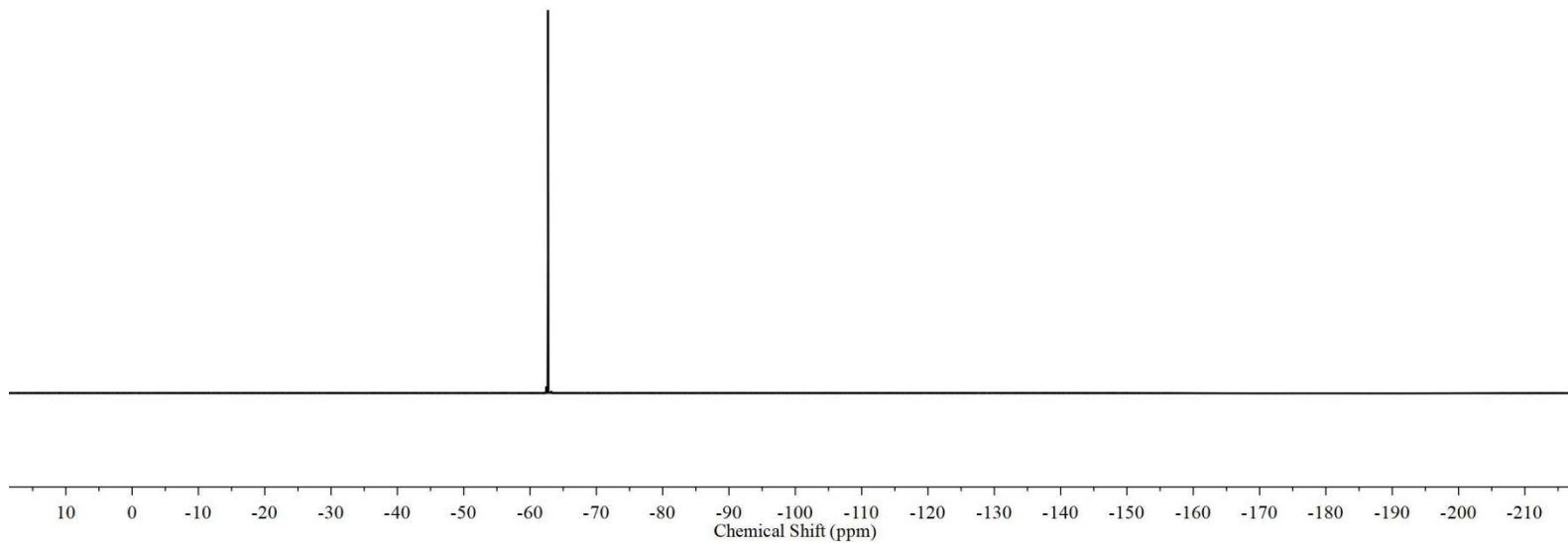
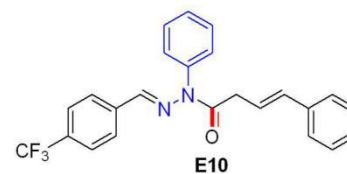
2022-11-10-yy0019-616-h31. 10. fid



S291

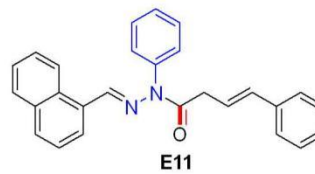
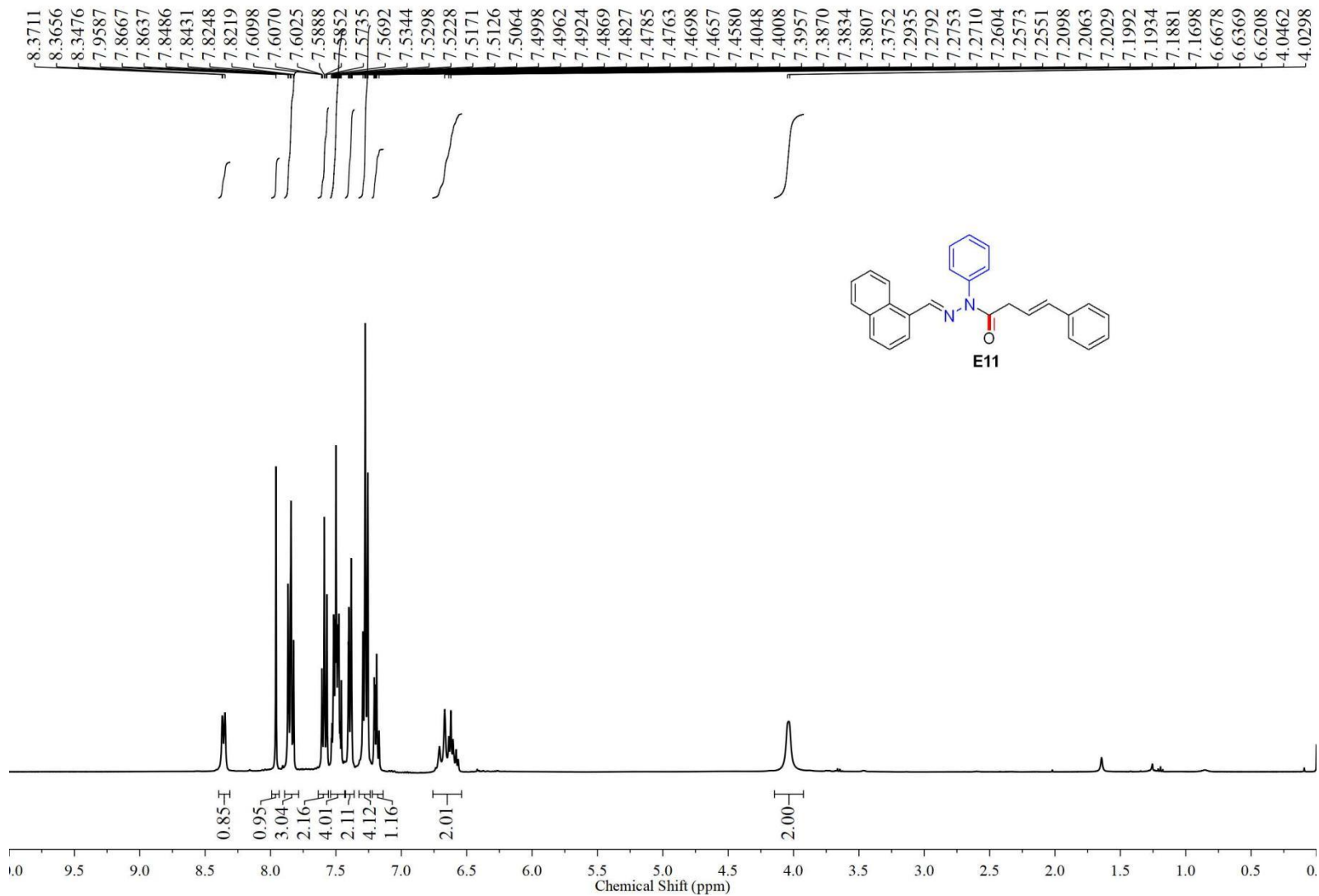
2022-11-10-yy0019-616-h31. 11. fid

—62.71

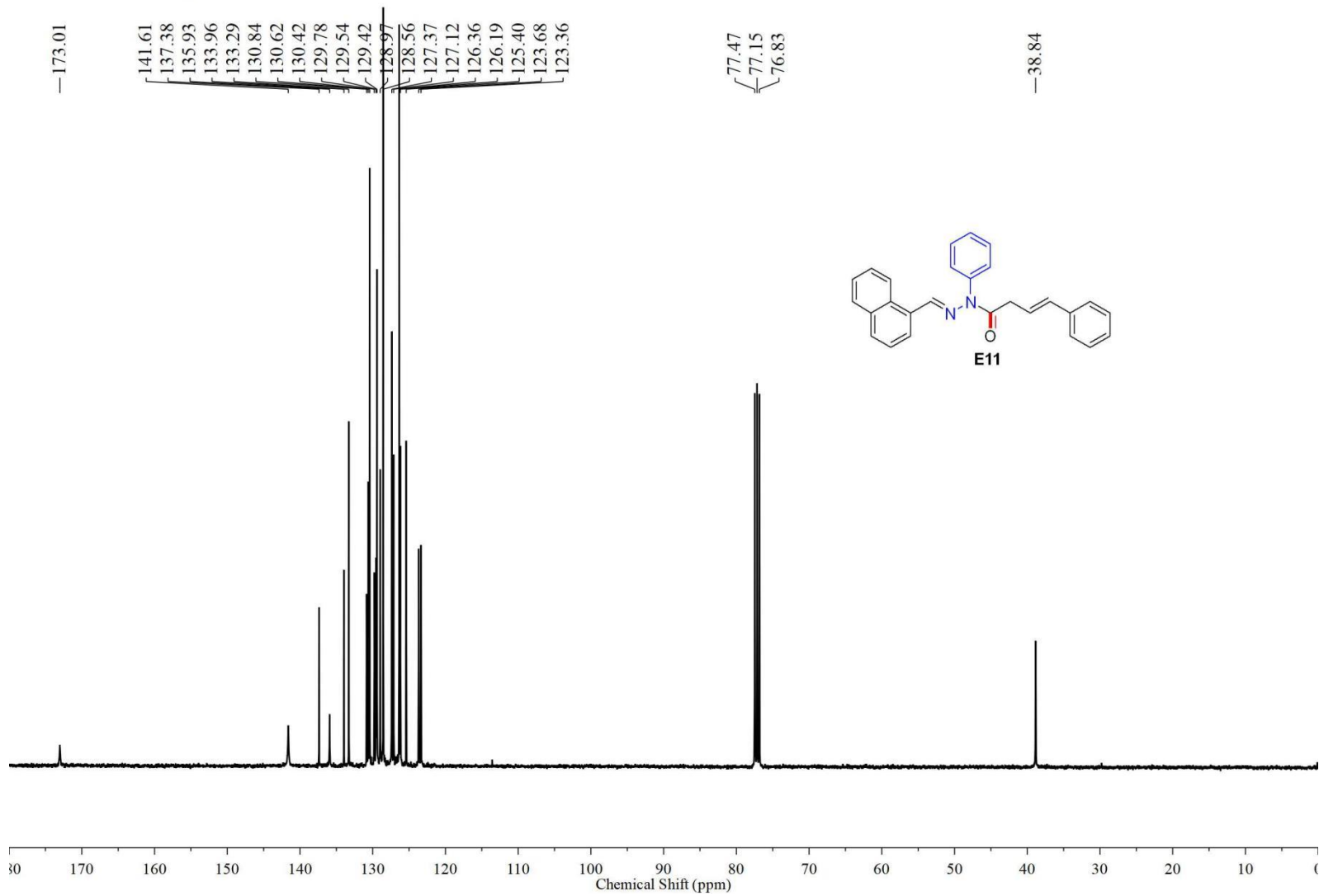


S292

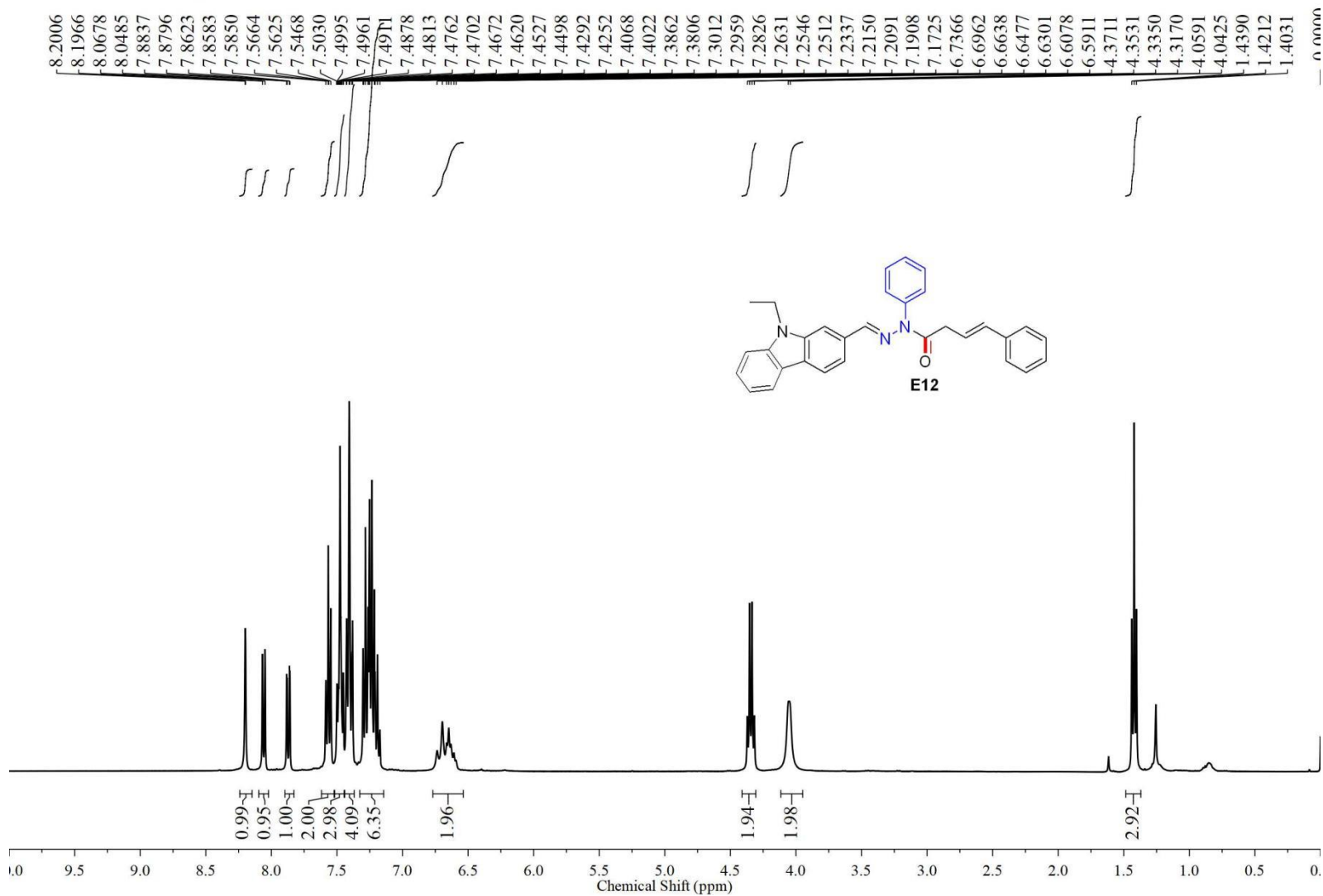
2022-10-31 yy0003 616-1-H9.10.fid



2022-11-1 yy0019-616-lqq-9.10.fid

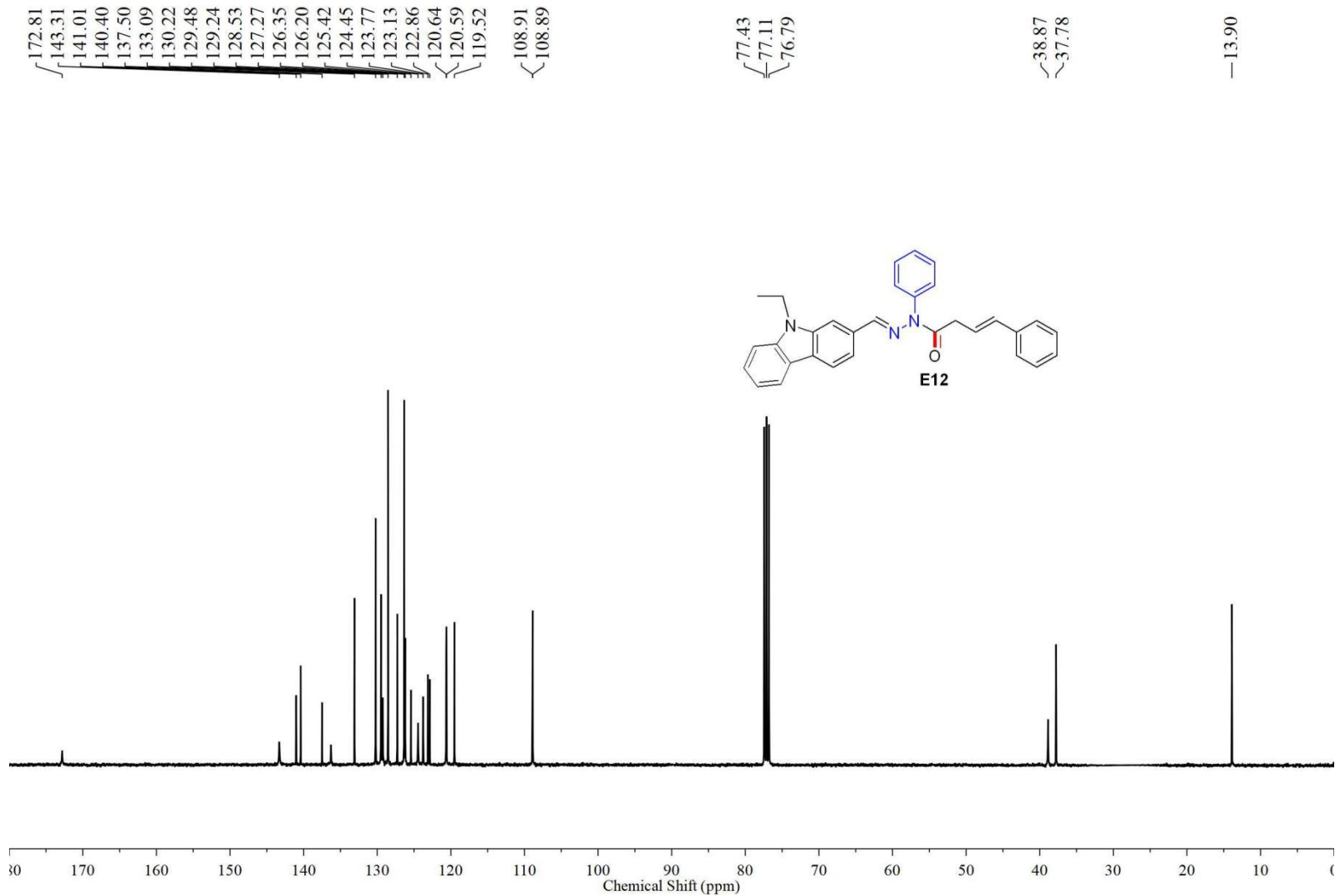


2022-10-26 YY0001 616 LQQ-10.10.fid

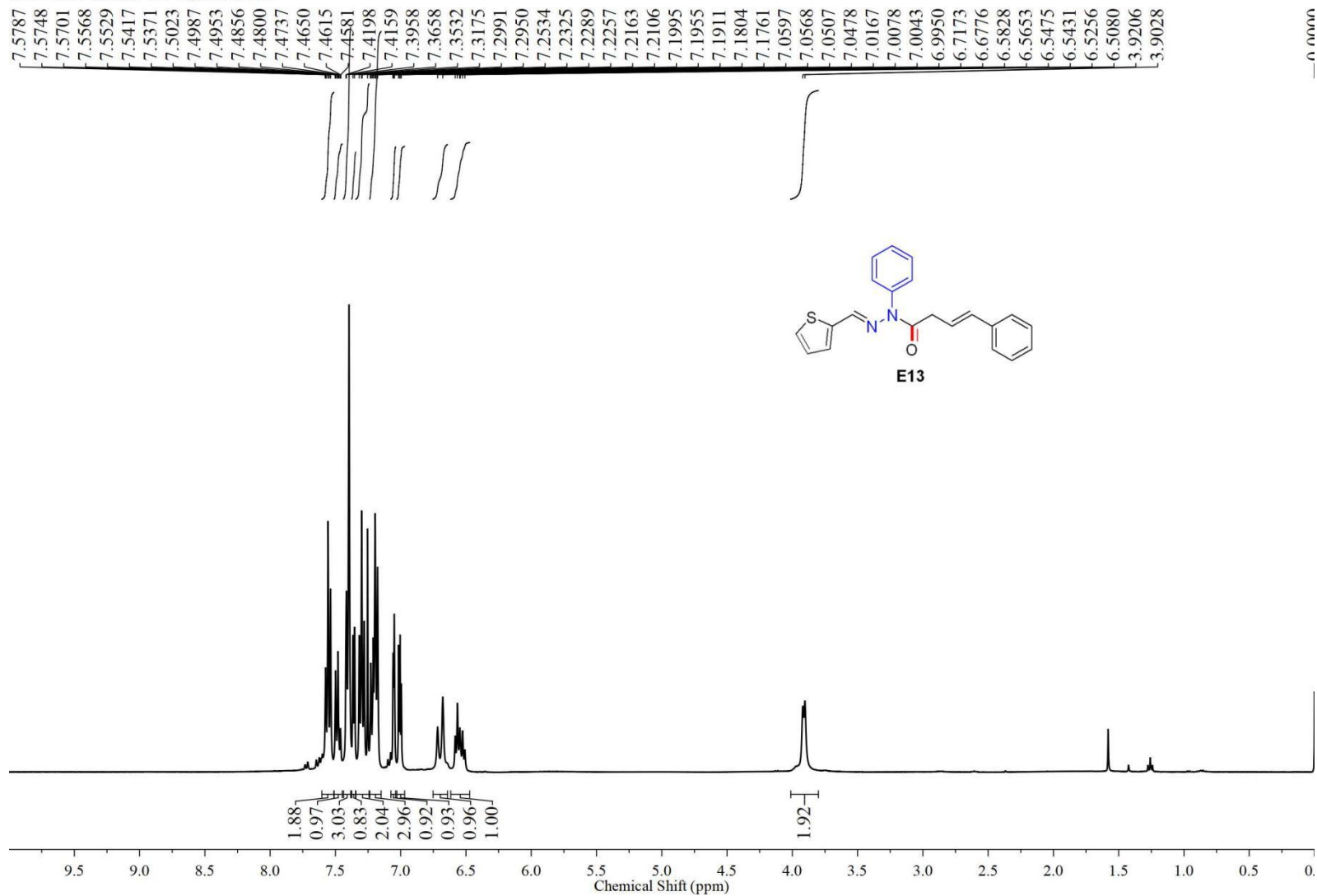


S295

2022-10-27 yy0005 616-lq10.10.fid

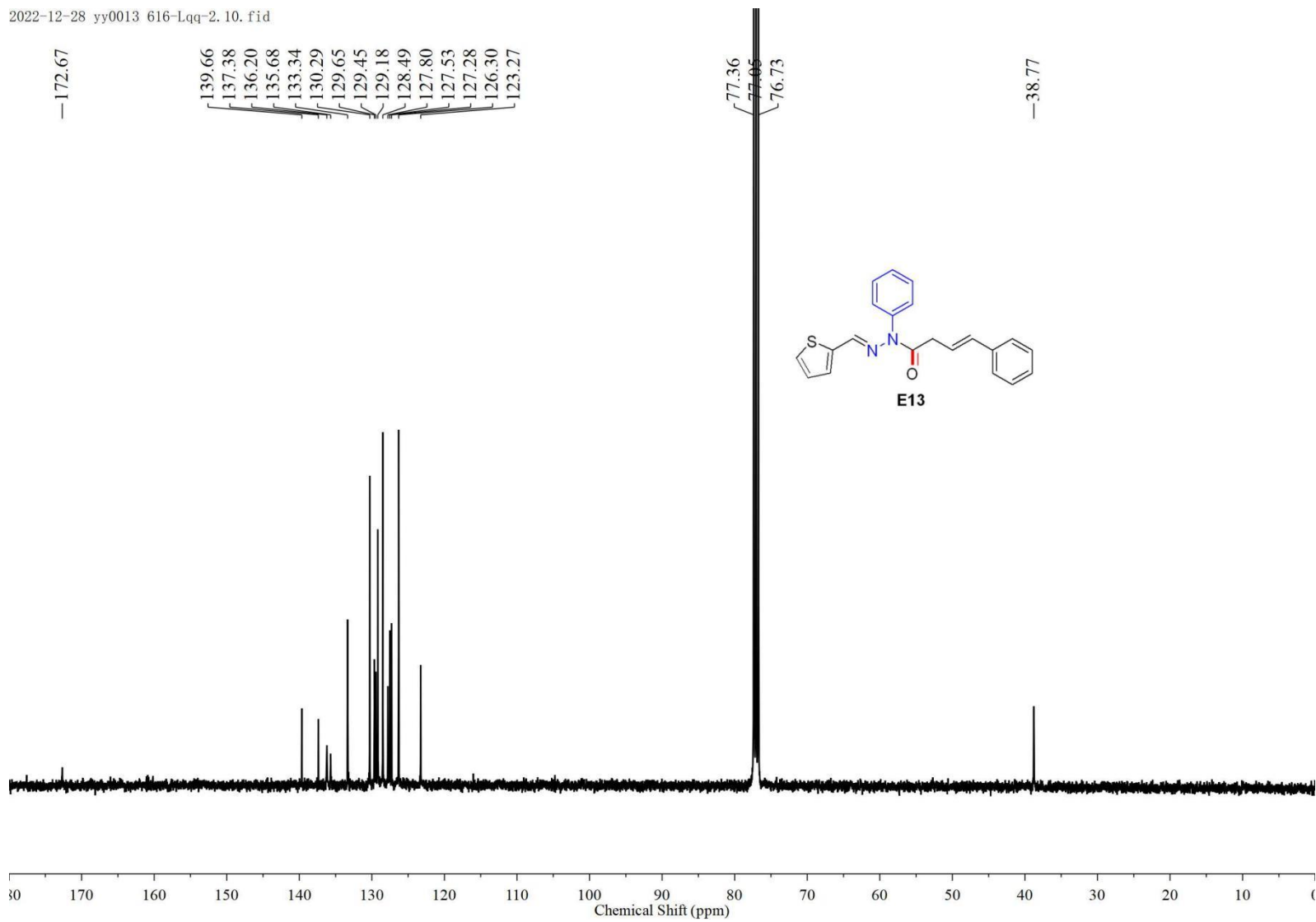


2022-12-29 yy0008 616-lqq-2.10. fid



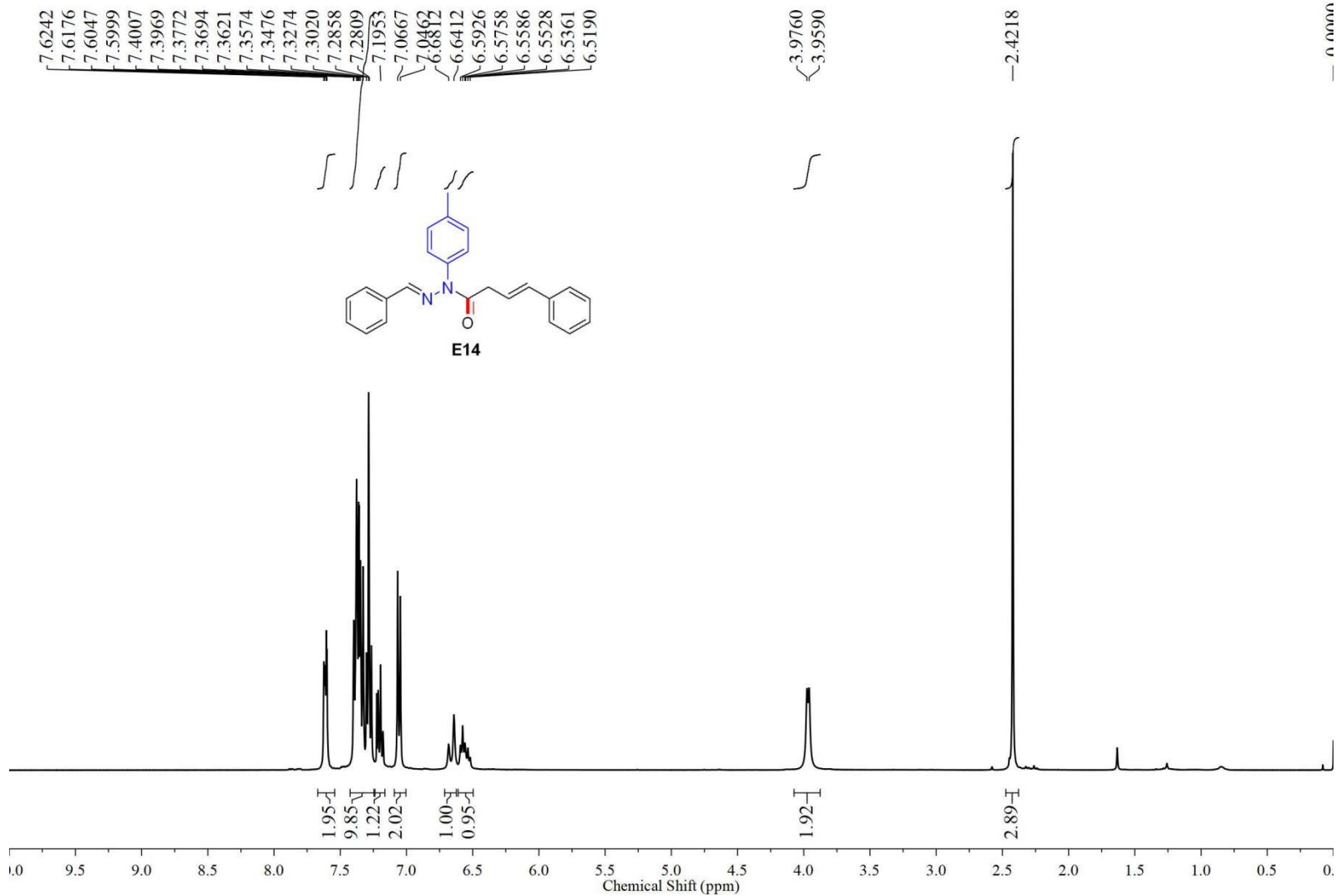
S297

2022-12-28 yy0013 616-Lqq-2.10. fid

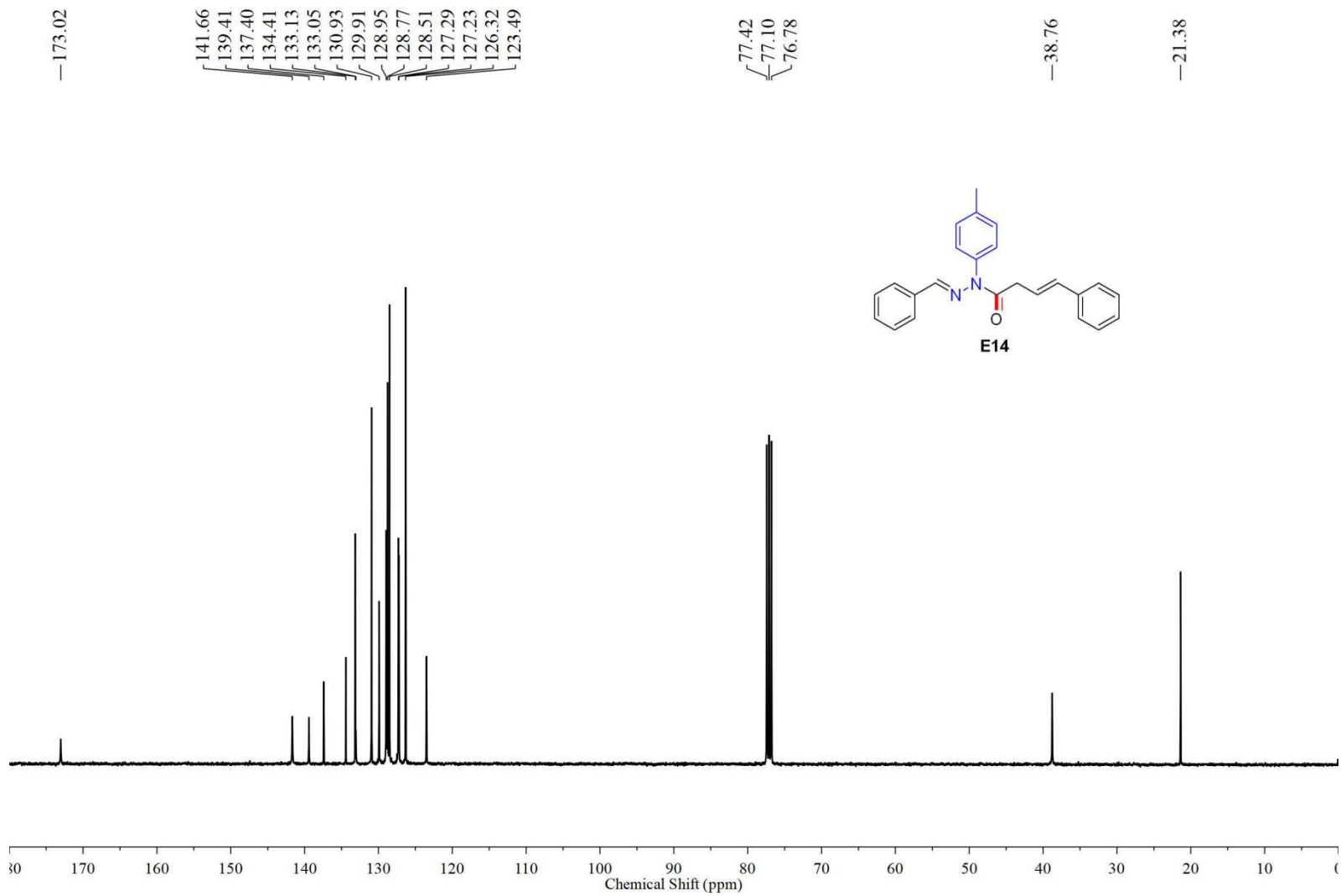


S298

2022-10-31 yy0003 616-1-H14. 10. fid

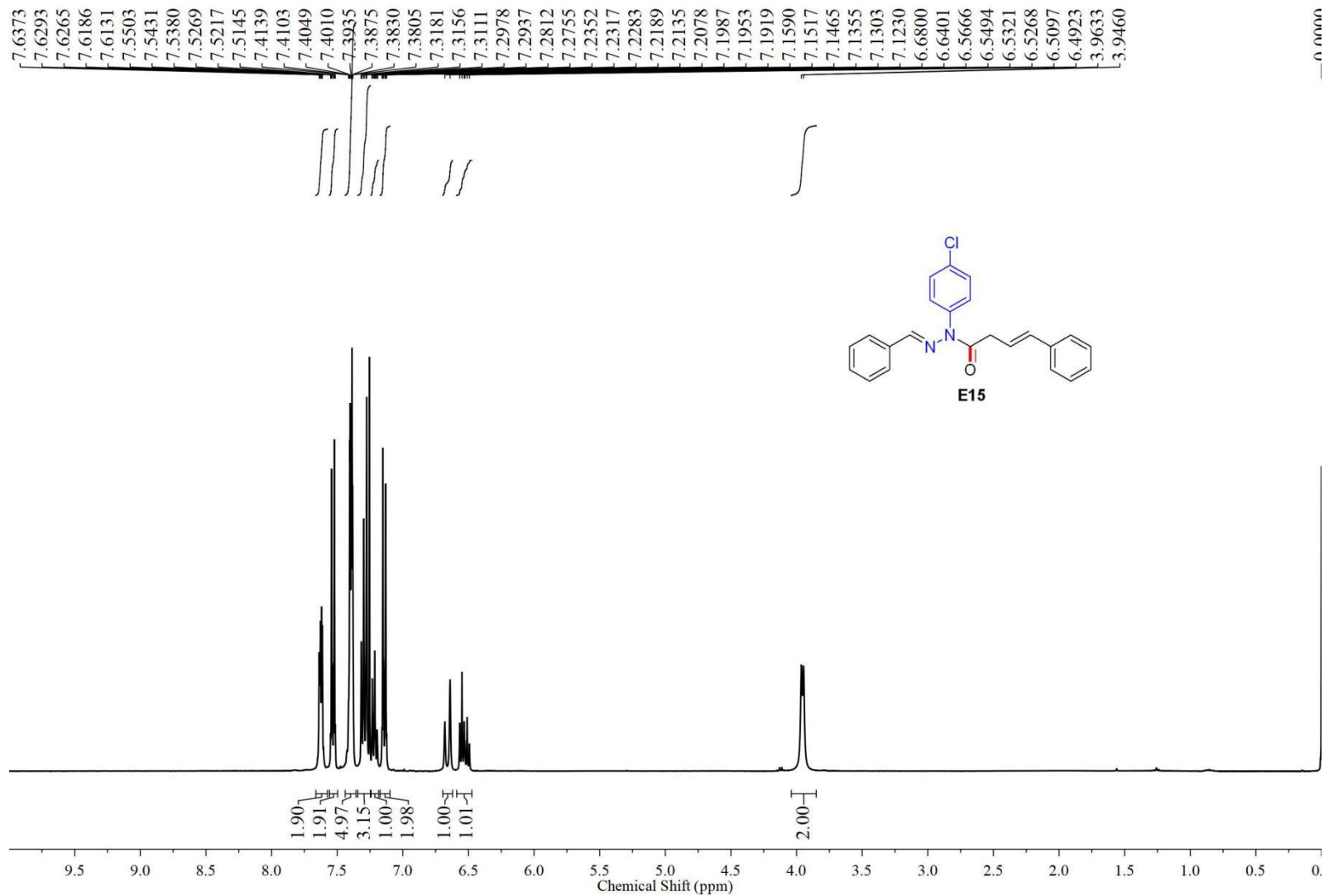


2022-11-1 yy0019-616-lqq-14. 10. fid



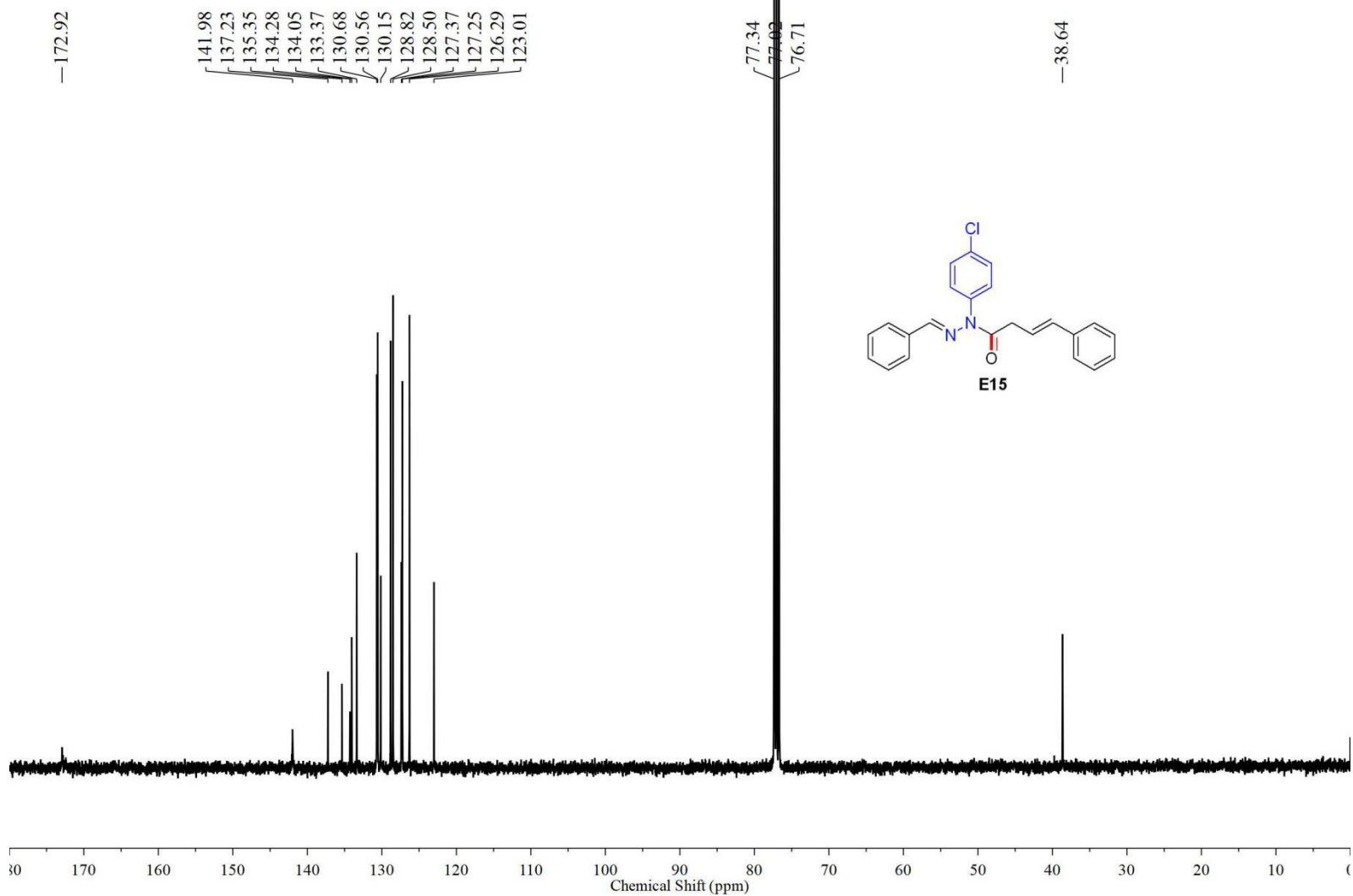
S300

2022-11-15 yy0013-616-lqq-16.10.fid



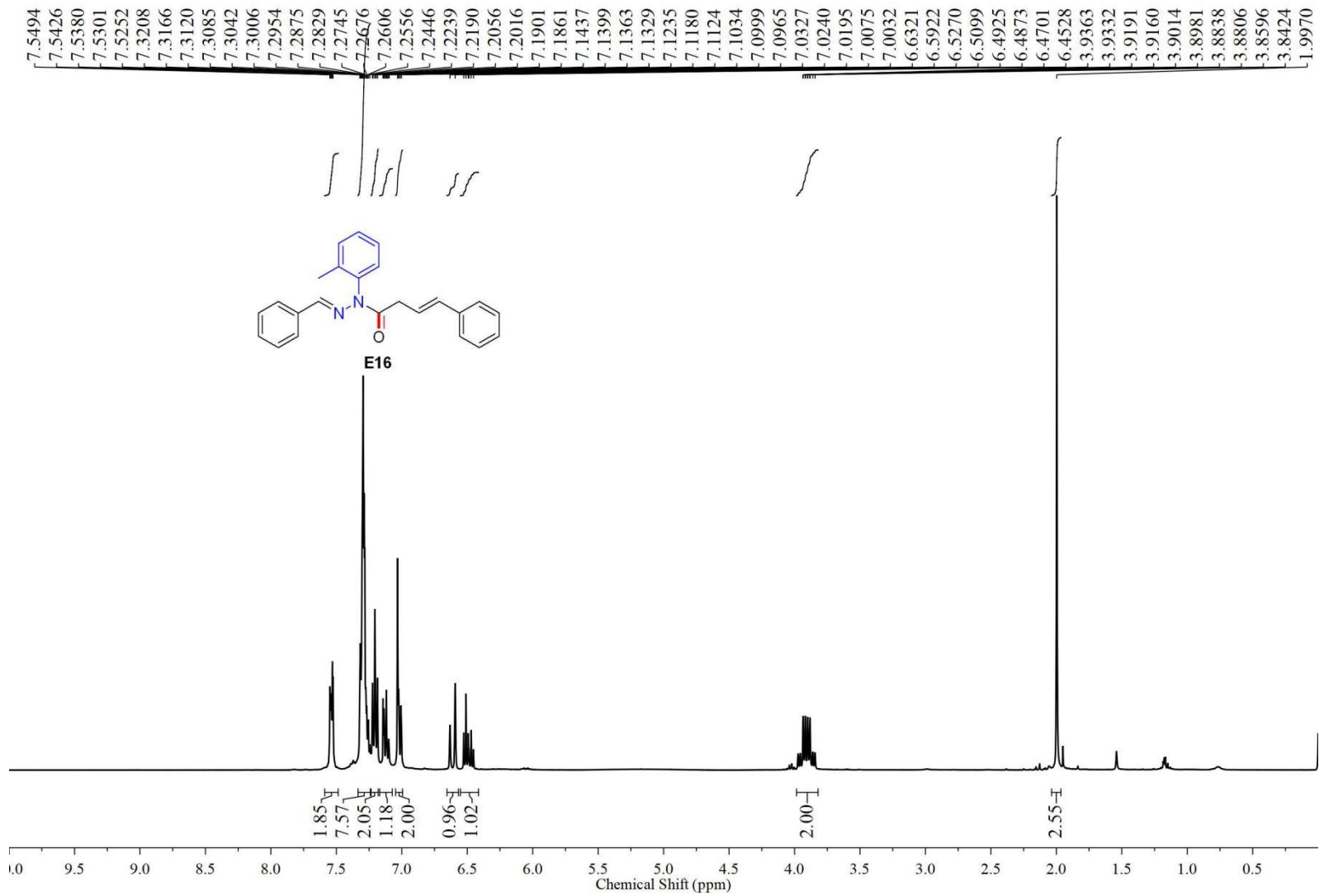
S301

2022-11-17 yy0013 616 lqq-16.10.fid



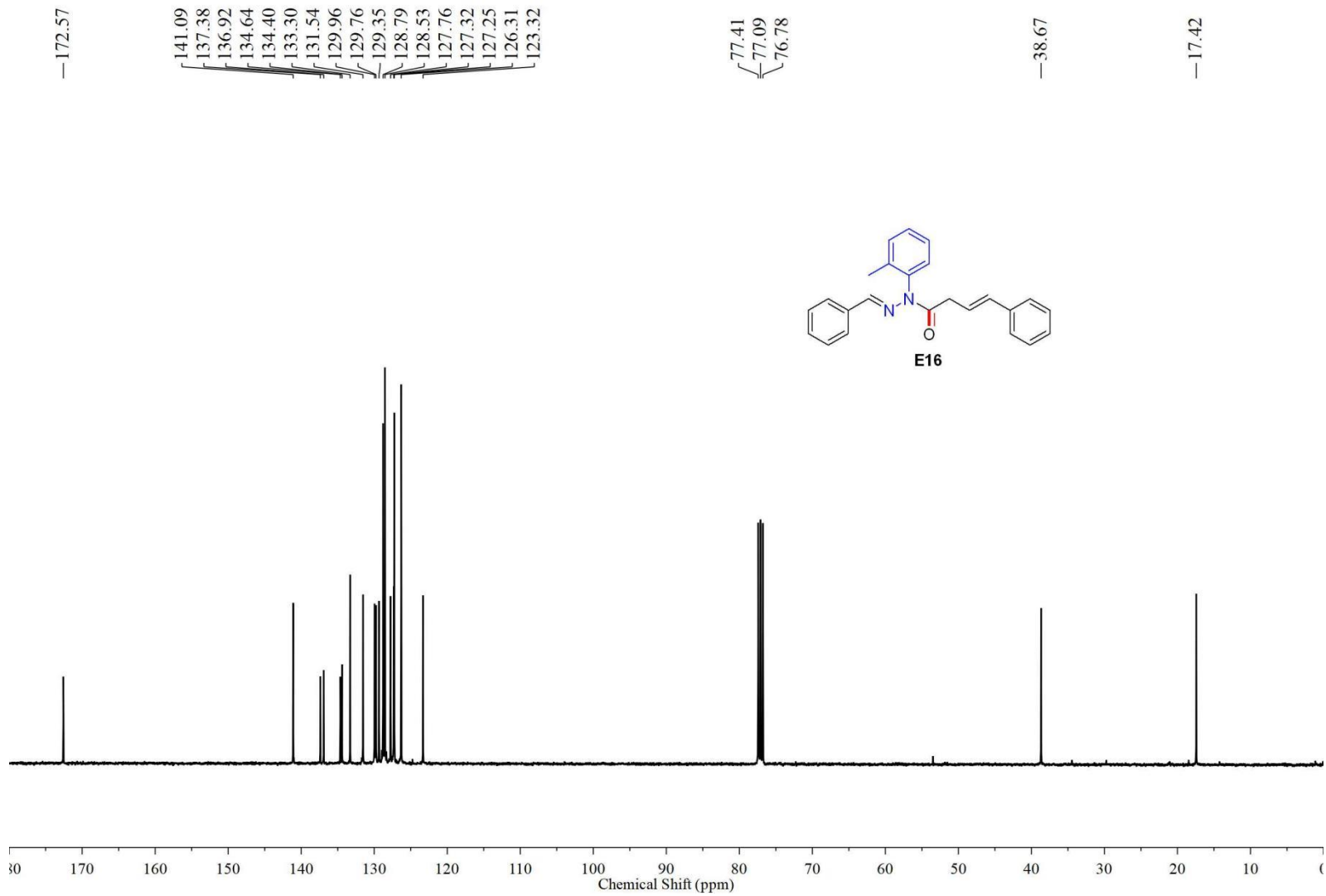
S302

2022-10-31 yy0003 616-1-H15.10. fid



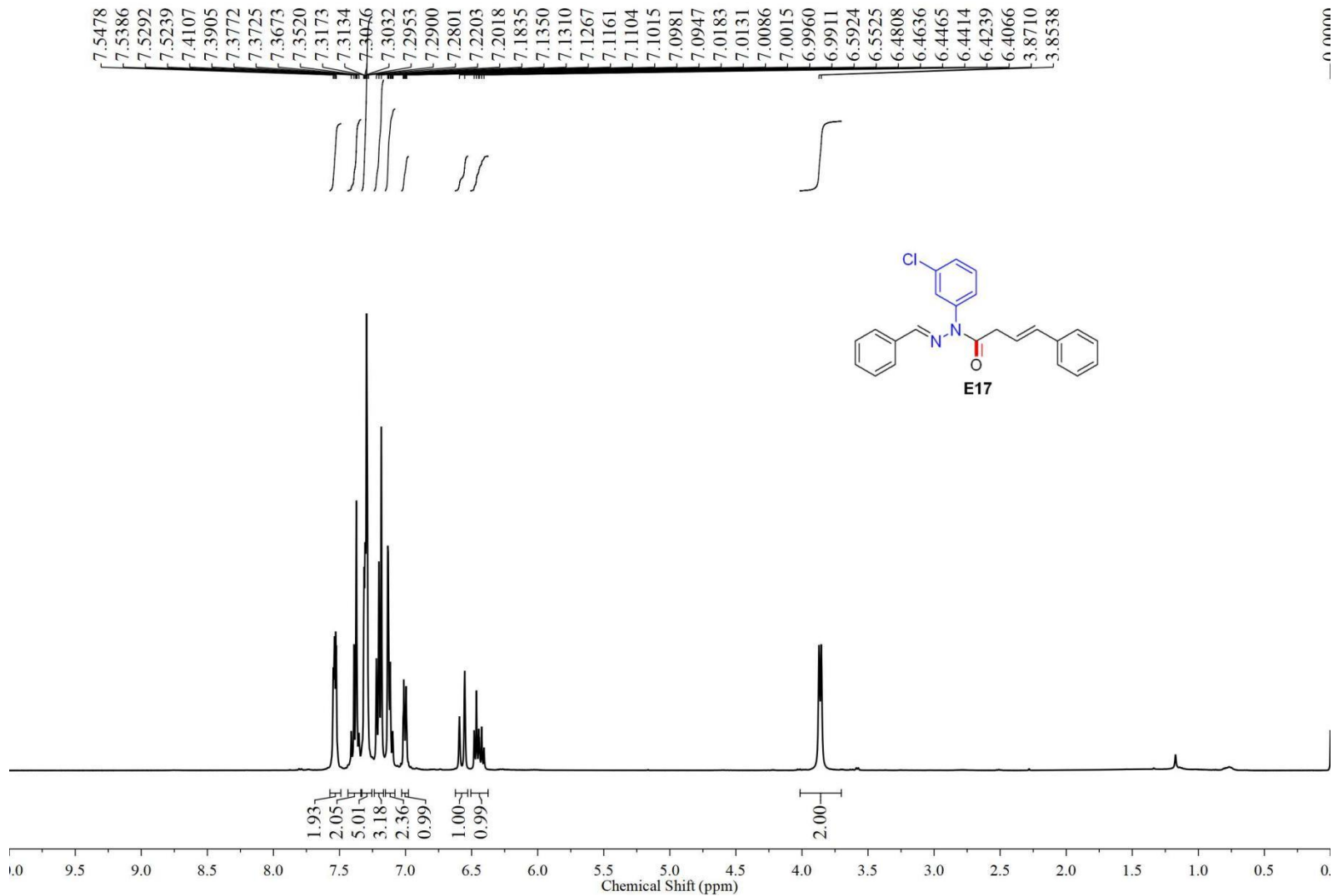
S303

2022-11-1 yy0019-616-lqq-15. 10. fid



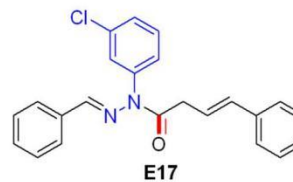
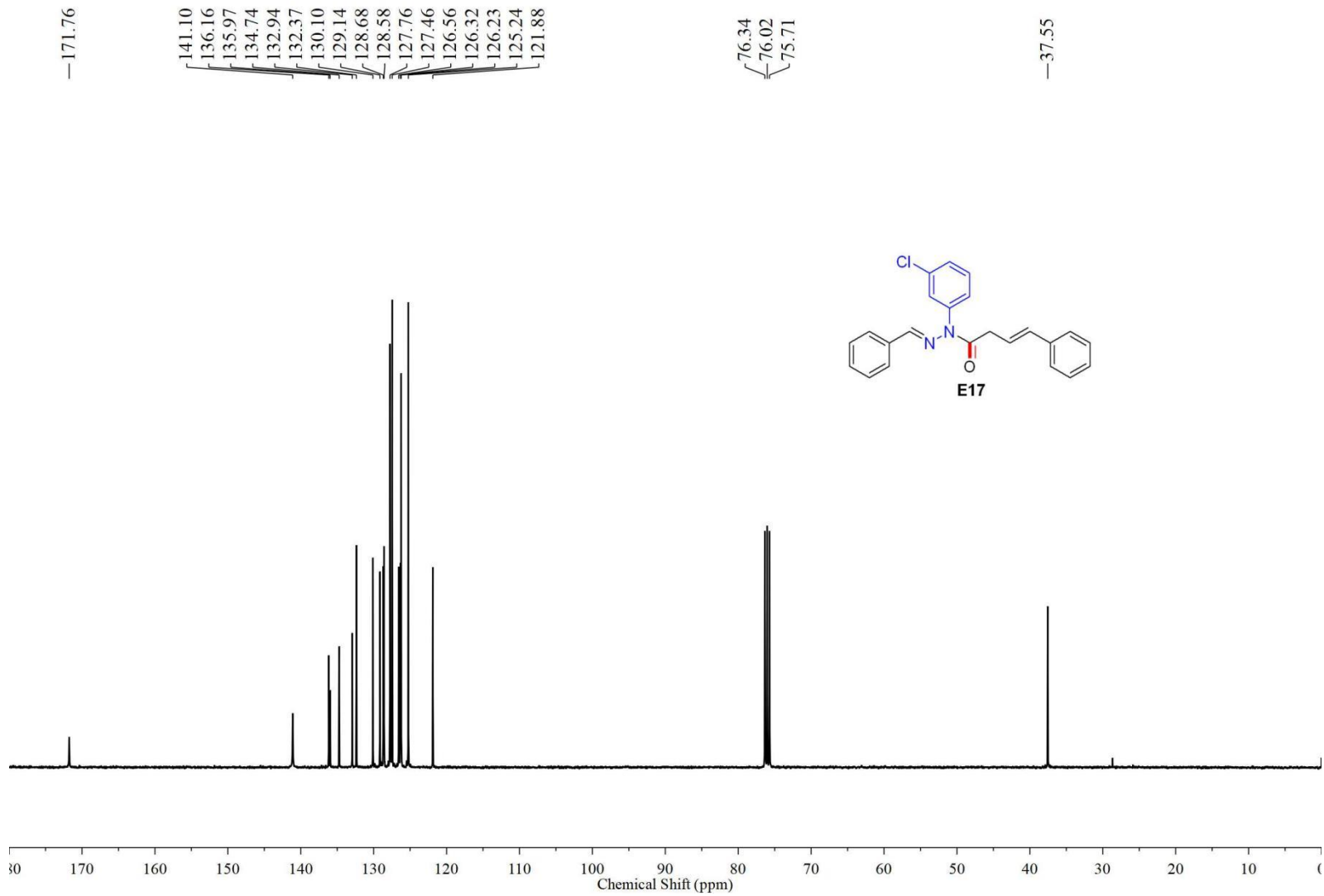
S304

2022-11-09-yy0020-616-h17. 10. fid

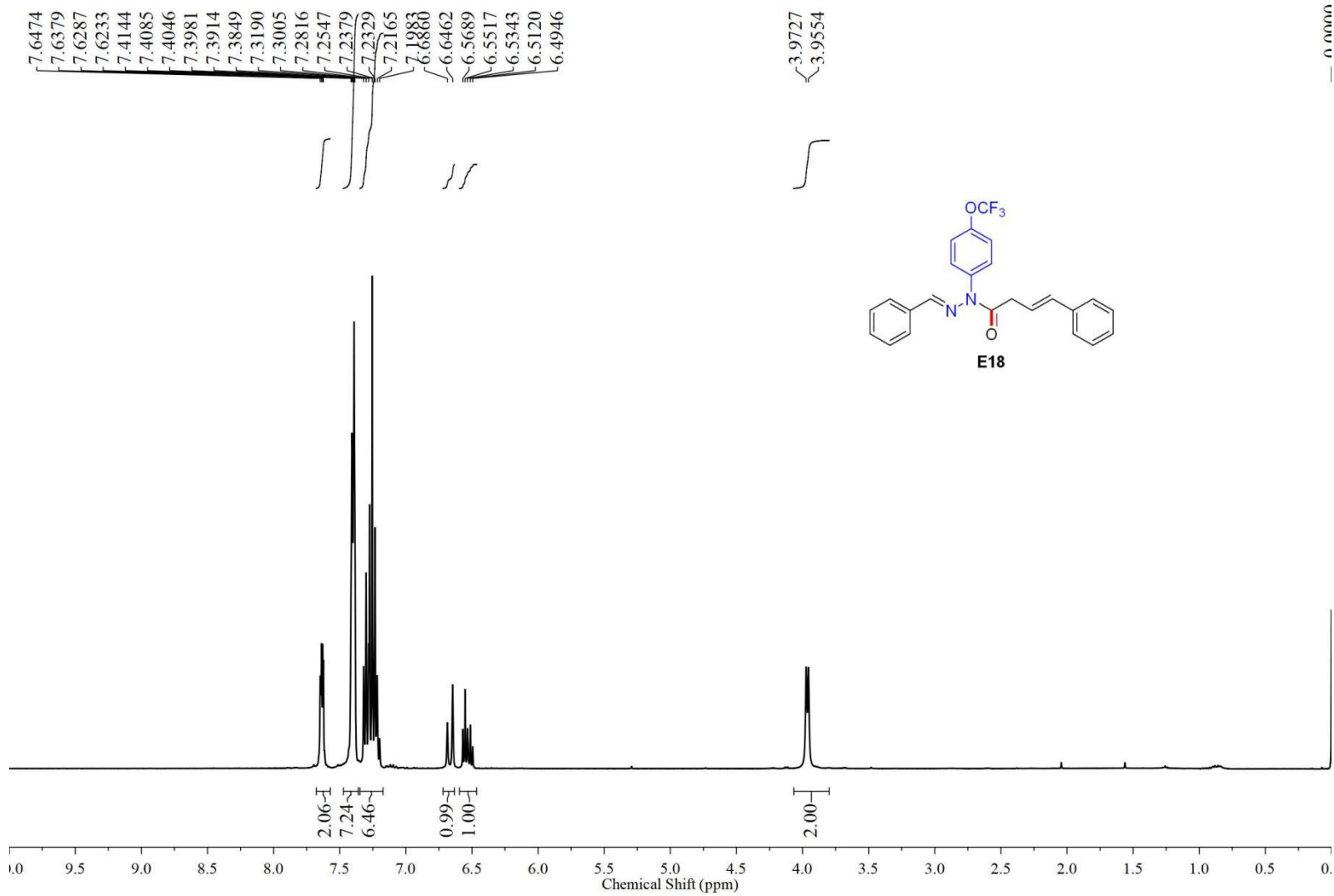


S305

2022-11-10-yy0019-616-h17. 10. fid

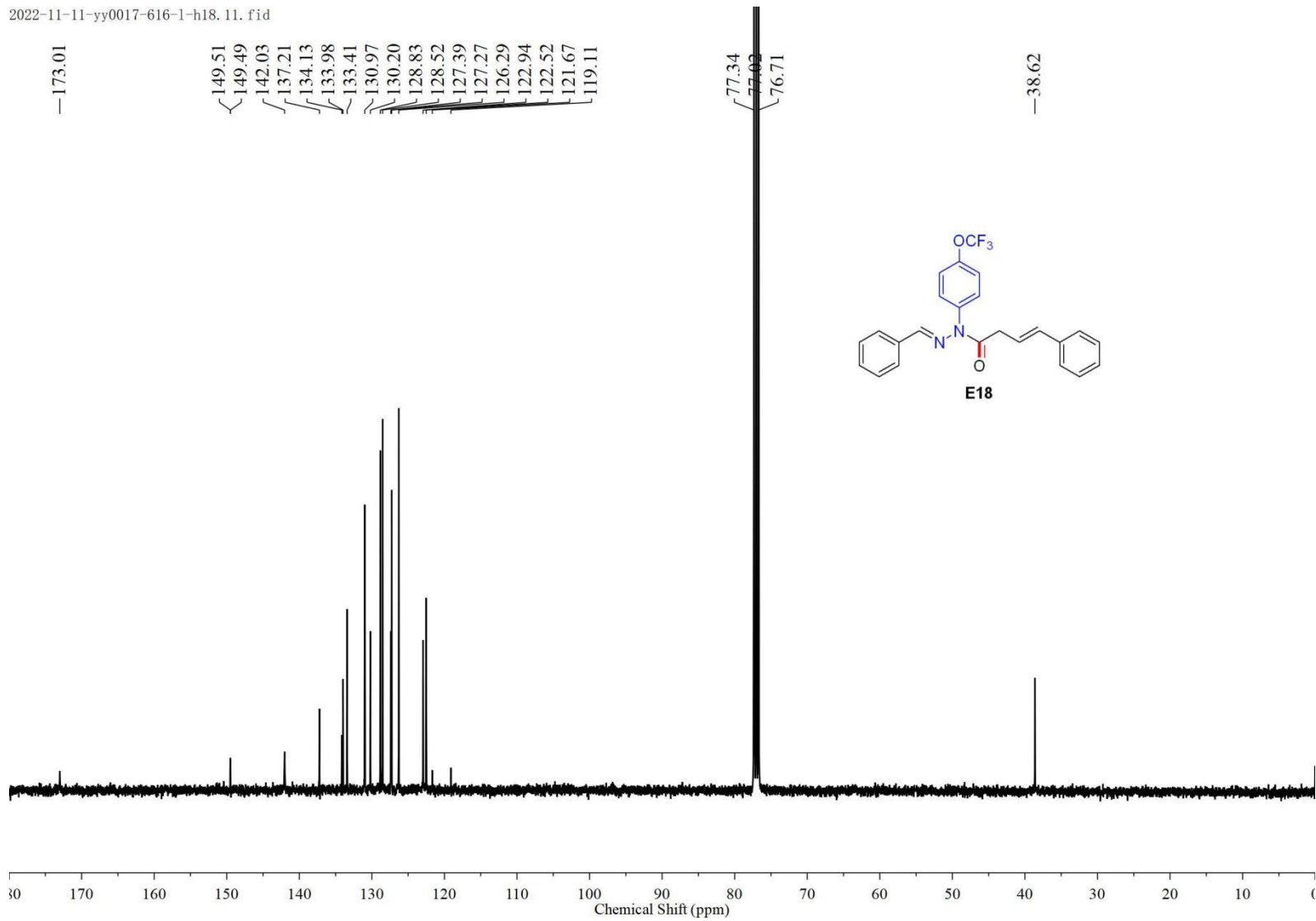


2022-11-11-yy0017-616-1-h18. 10. fid



S307

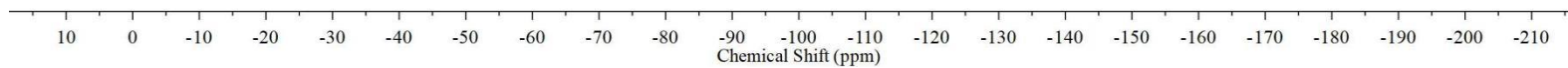
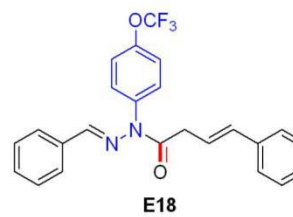
2022-11-11-yy0017-616-1-h18. 11. fid



S308

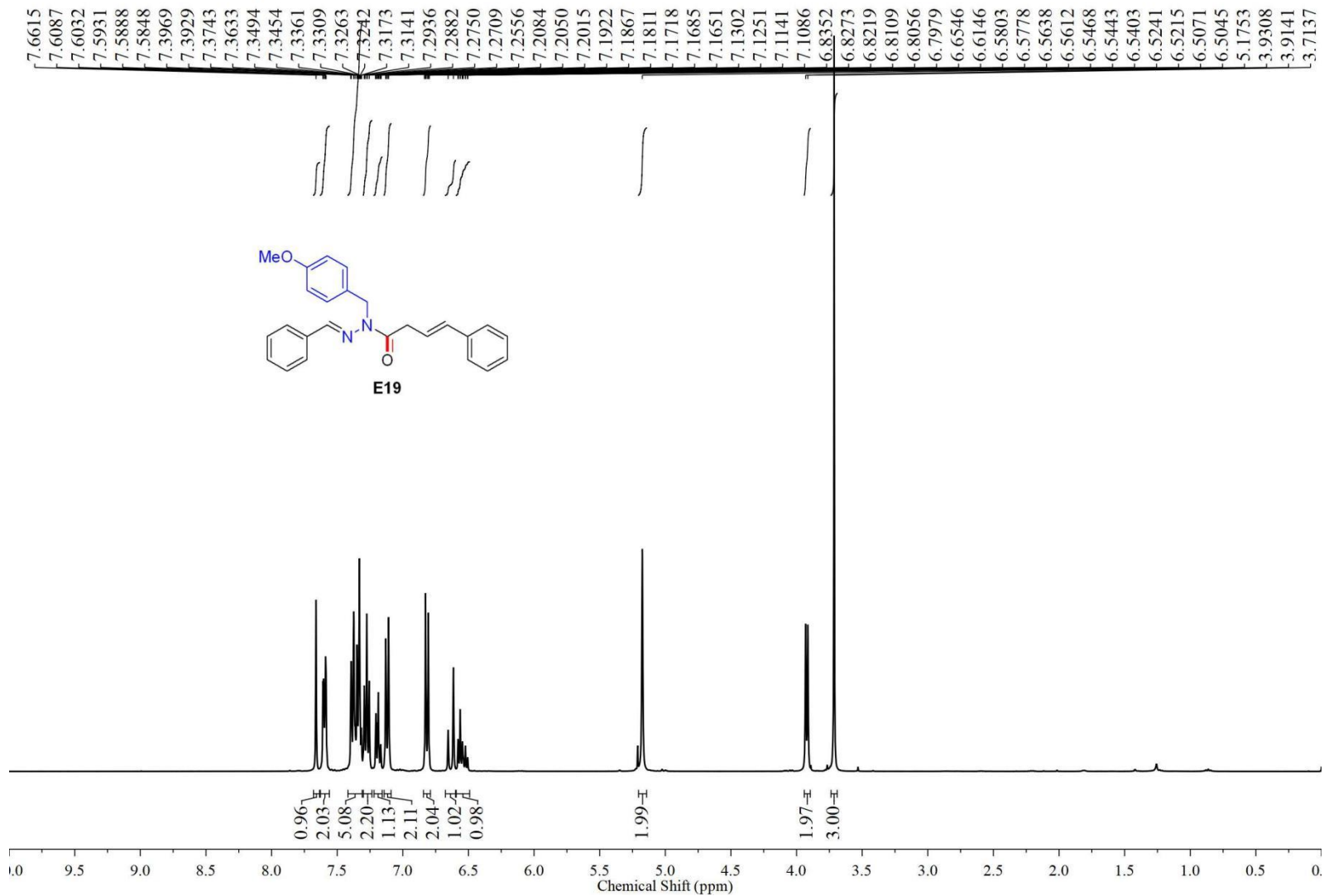
2022-11-17 yy616 lqq-f(bu).10.fid

—57.76

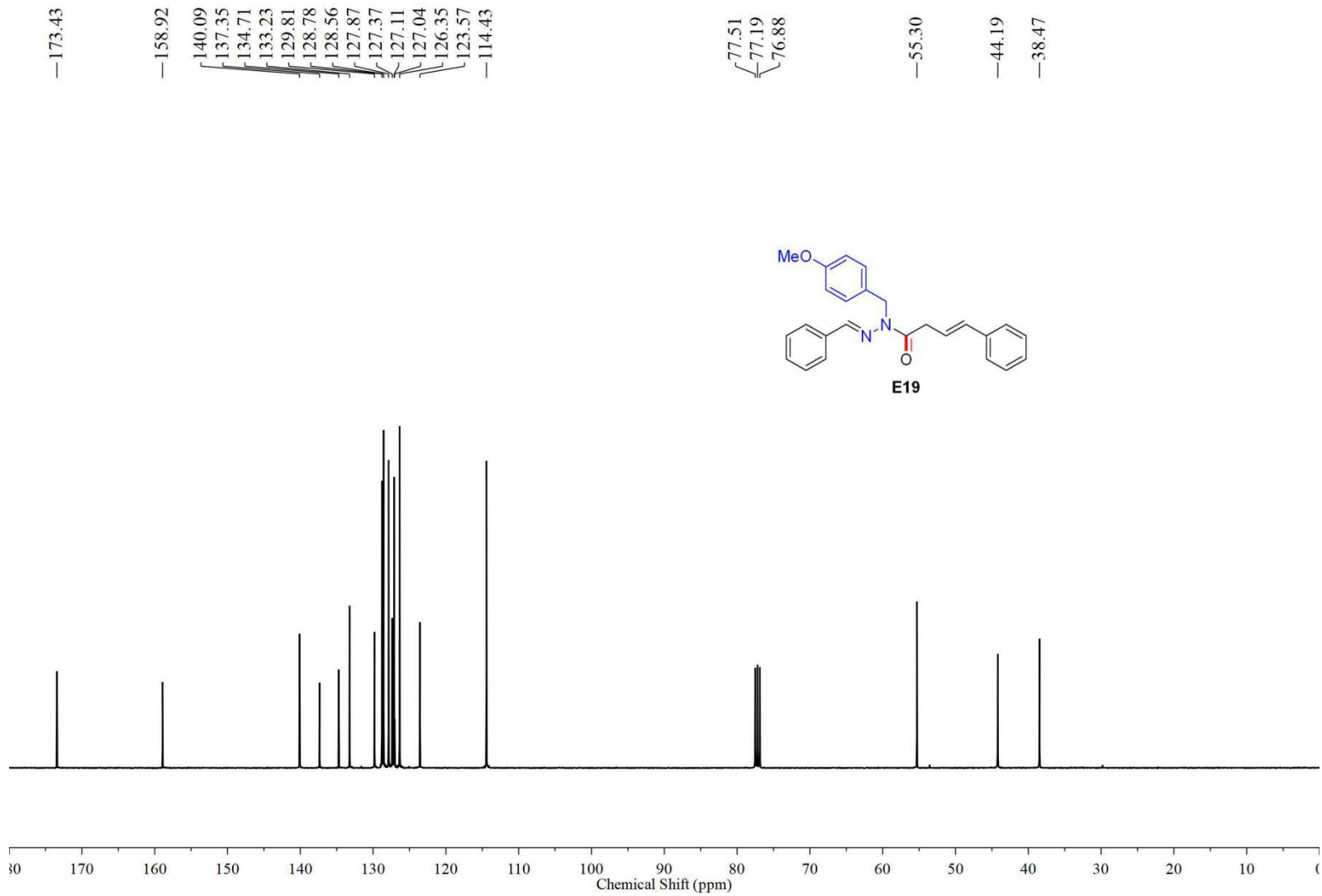


S309

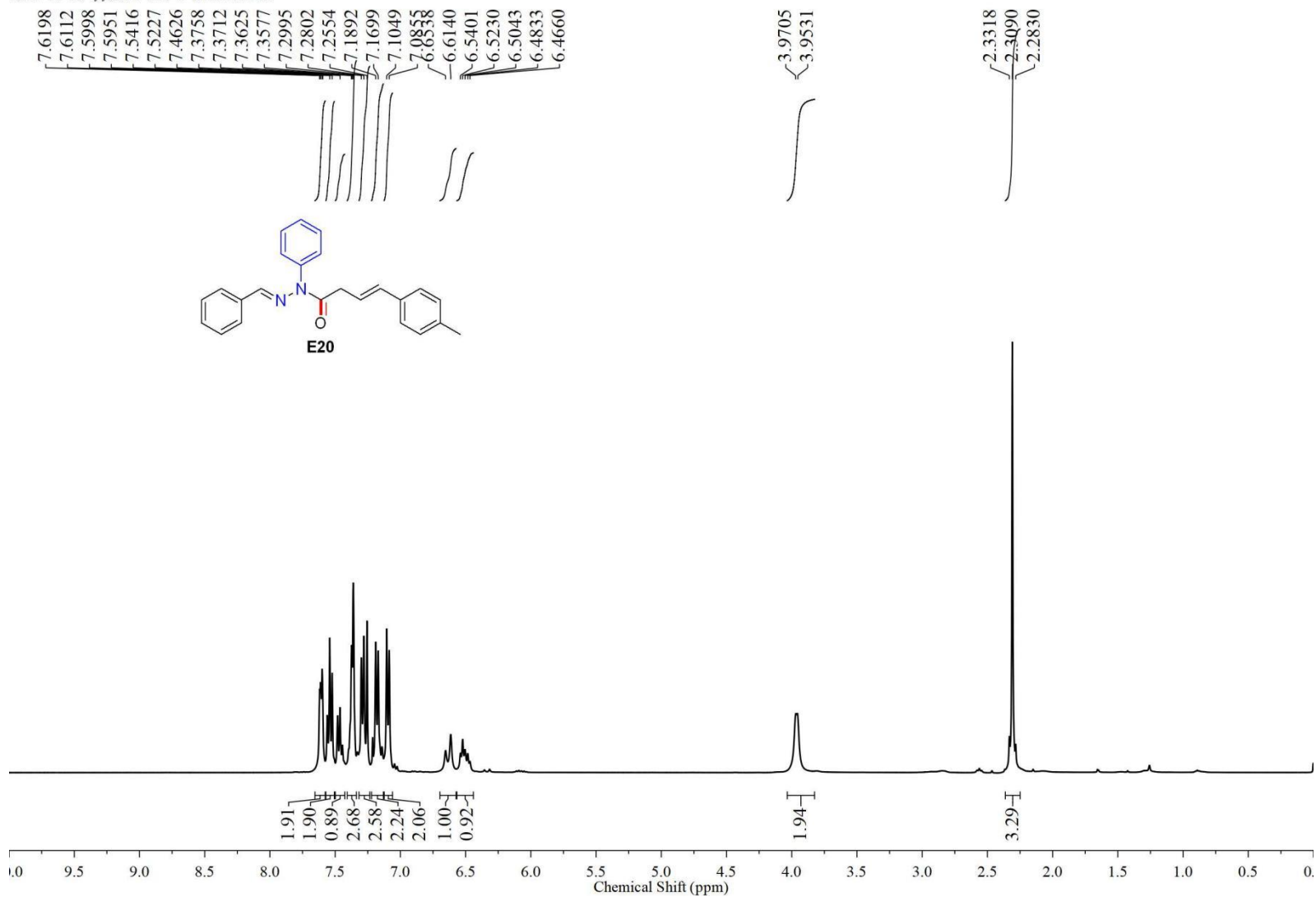
2022-12-03-yy0002-616-1-b27. 10. fid



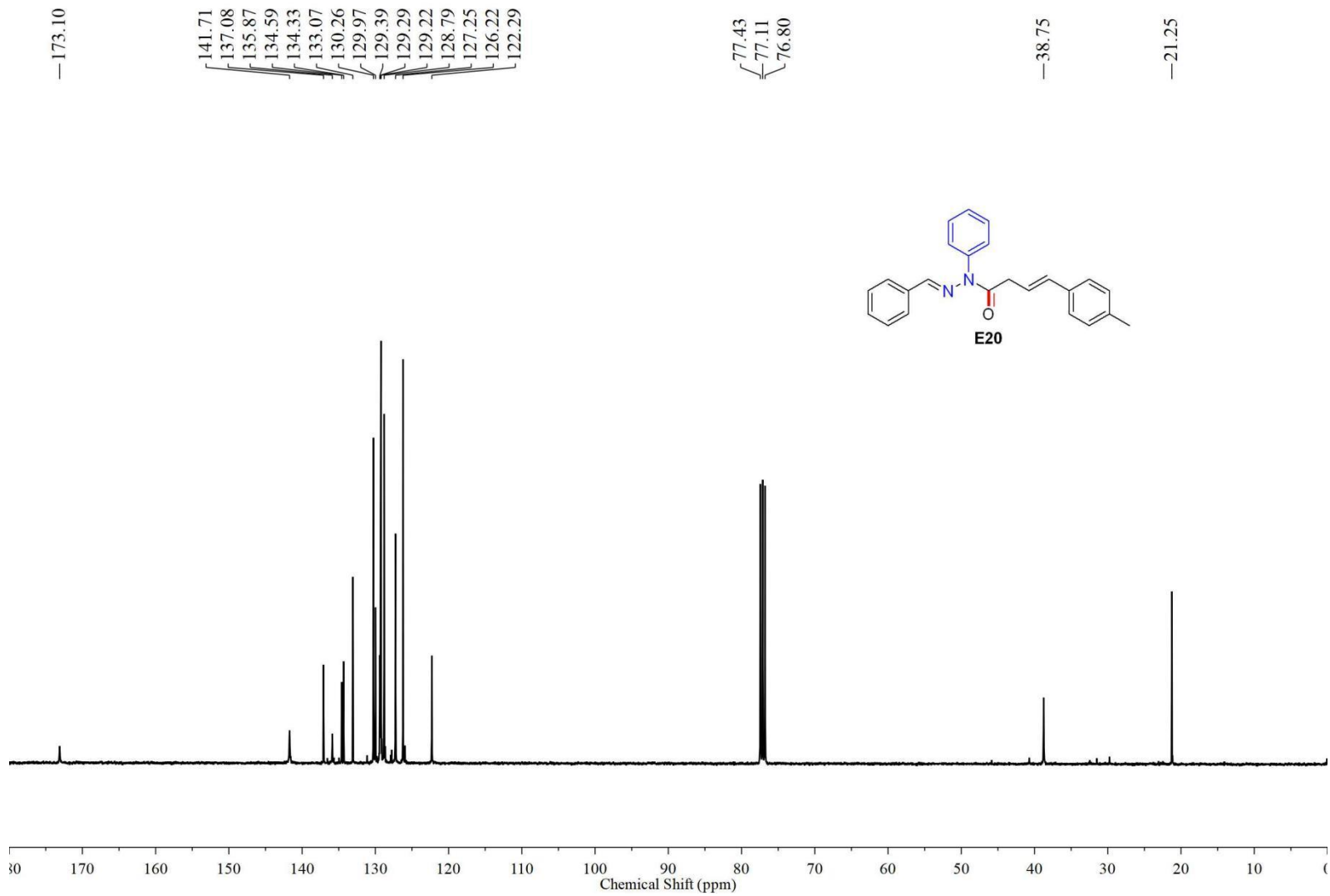
2022-12-05 yy0017 616-lqq-b27.10.fid



2022-11-29-yy0014-616-1-a18. 10. fid

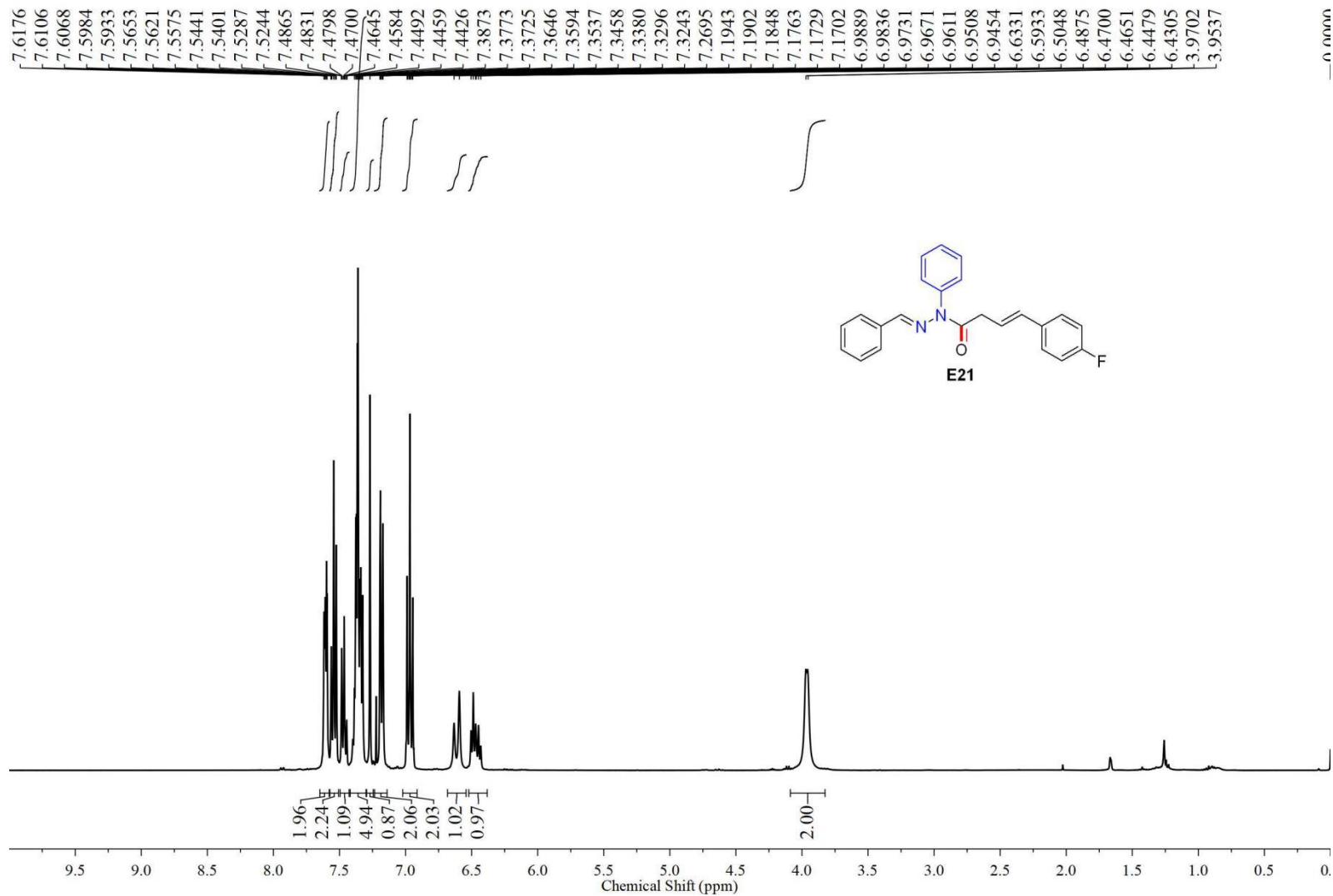


2022-12-01-yy0021-616-lqq-1-a15.10.fid



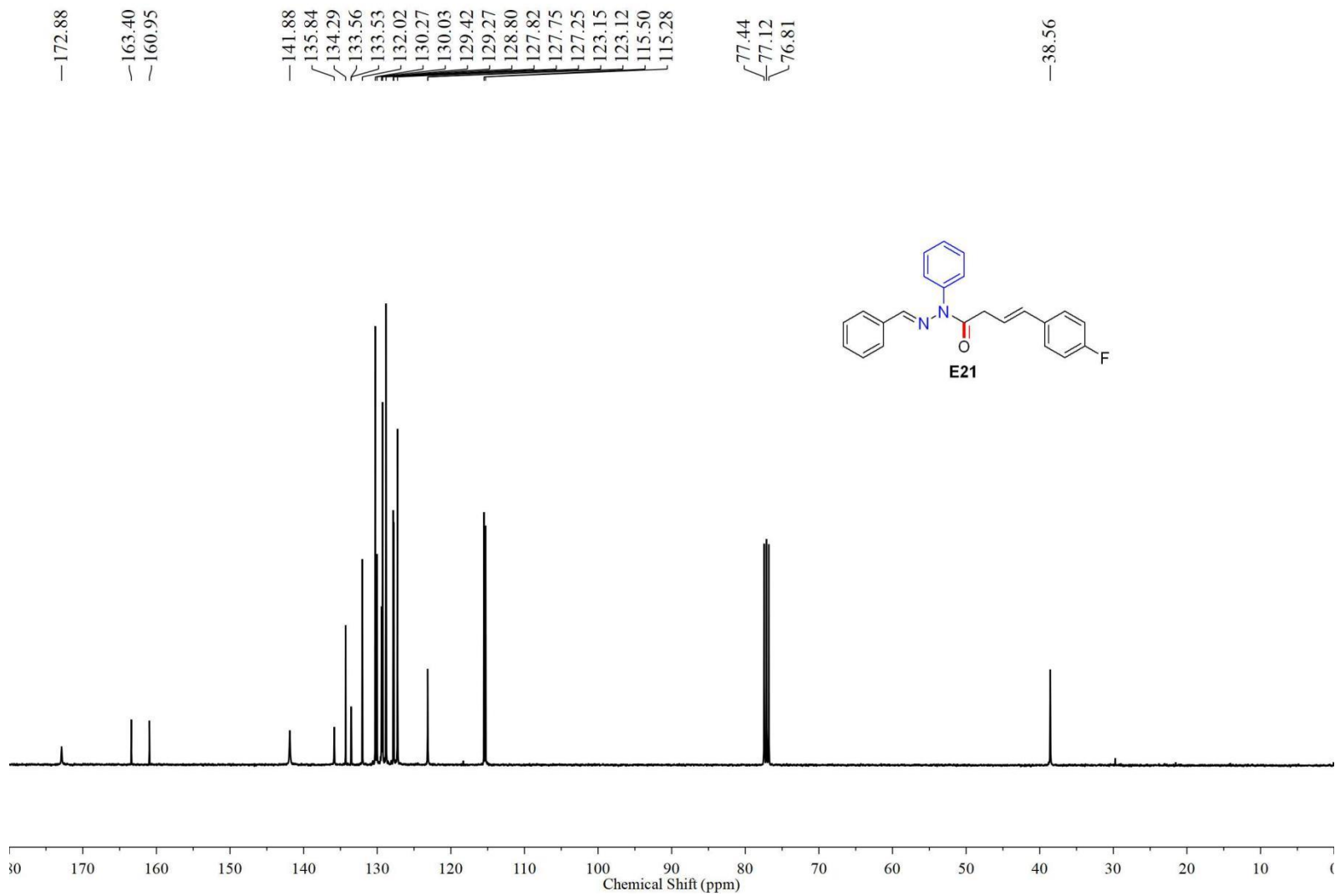
S313

2022-11-7-yy0031-616-1-h24.10.fid



S314

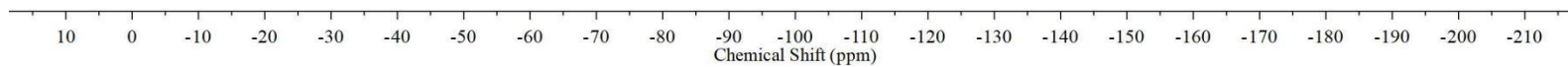
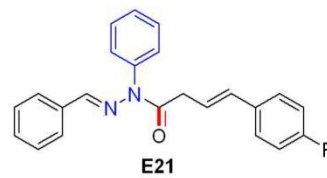
2022-11-7-yy0031-616-1-h24.11.fid



S315

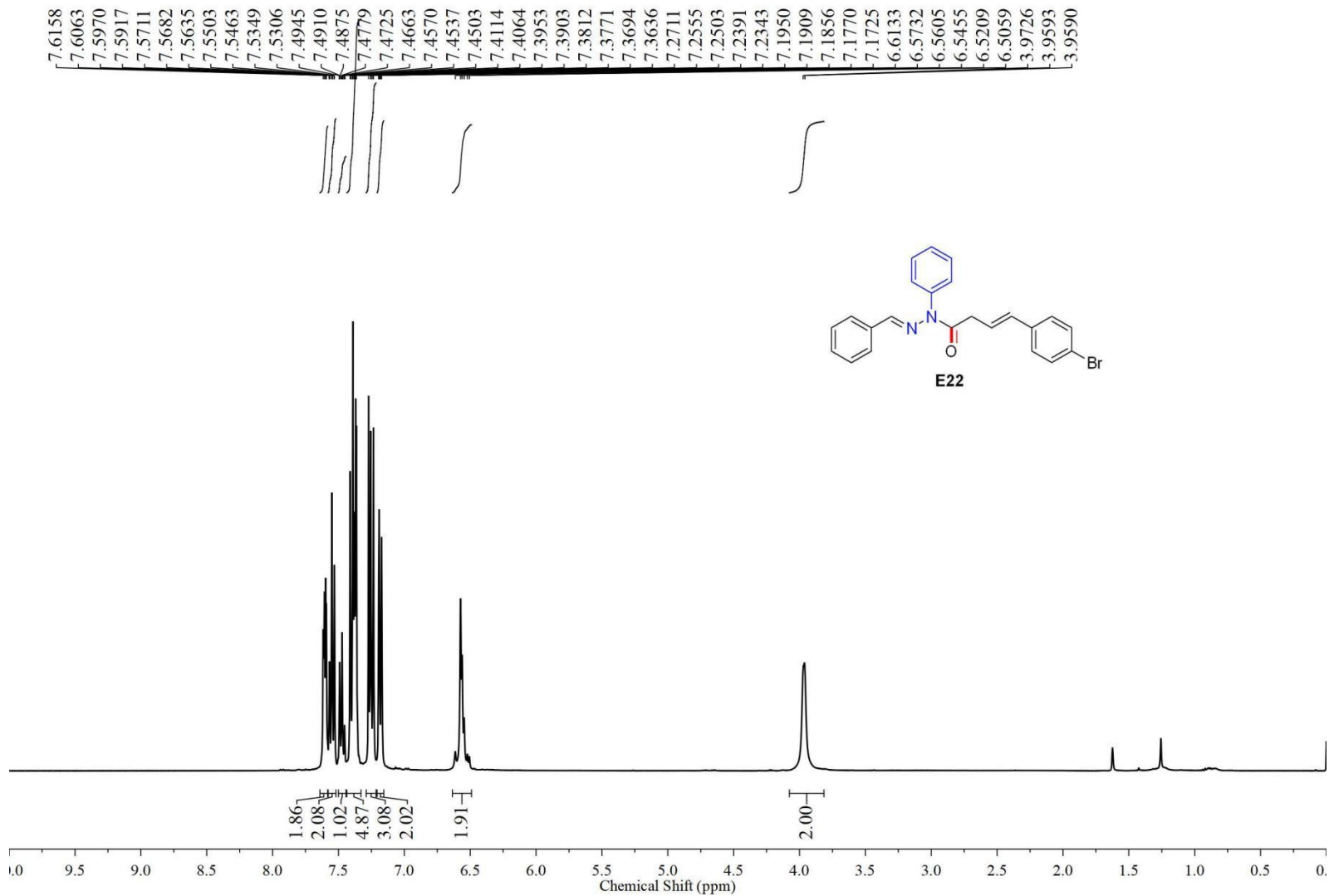
2022-11-7-yy0031-616-1-h24.12.fid

-114.94



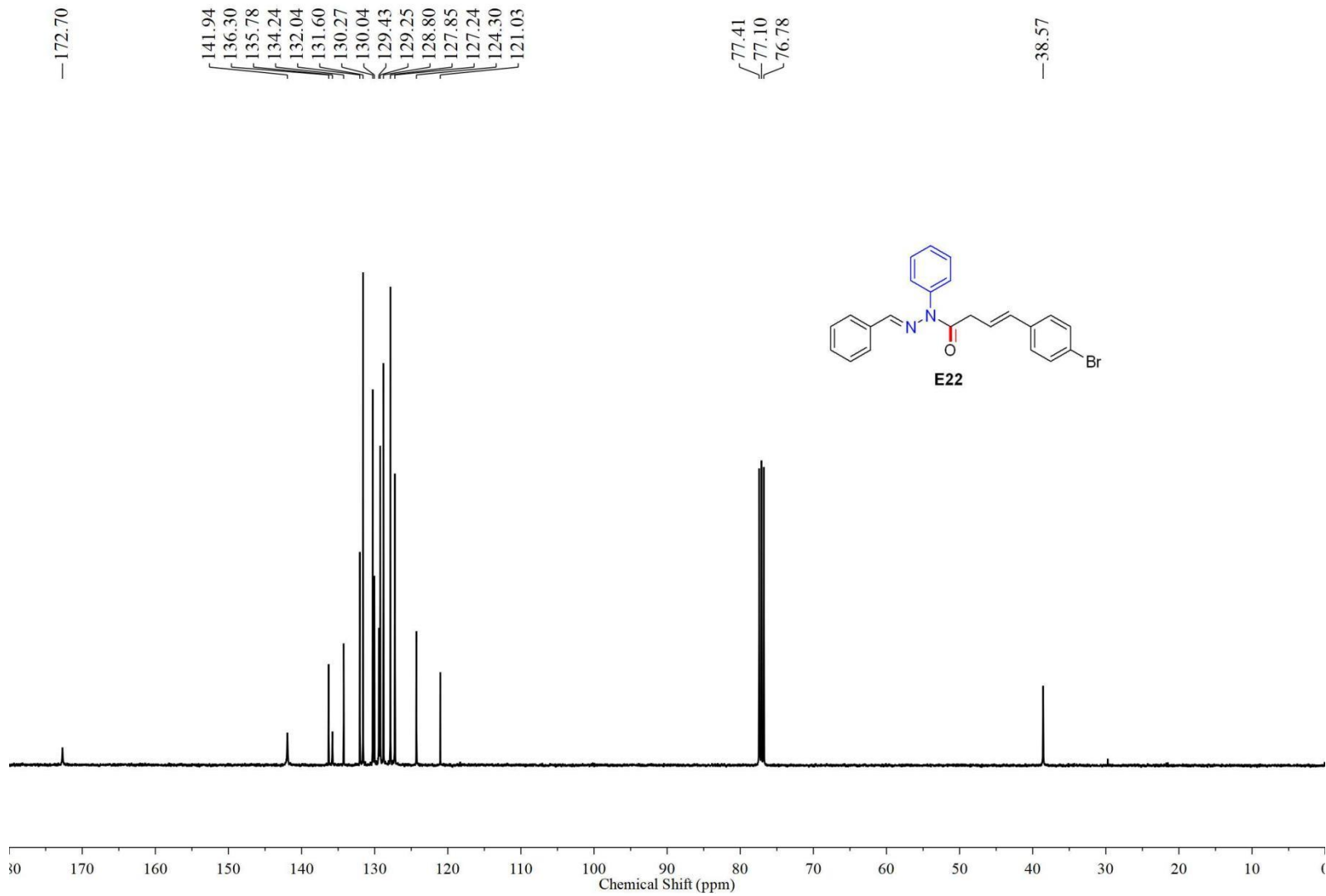
S316

2022-11-7-yy0001-616-1-h25.10.fid



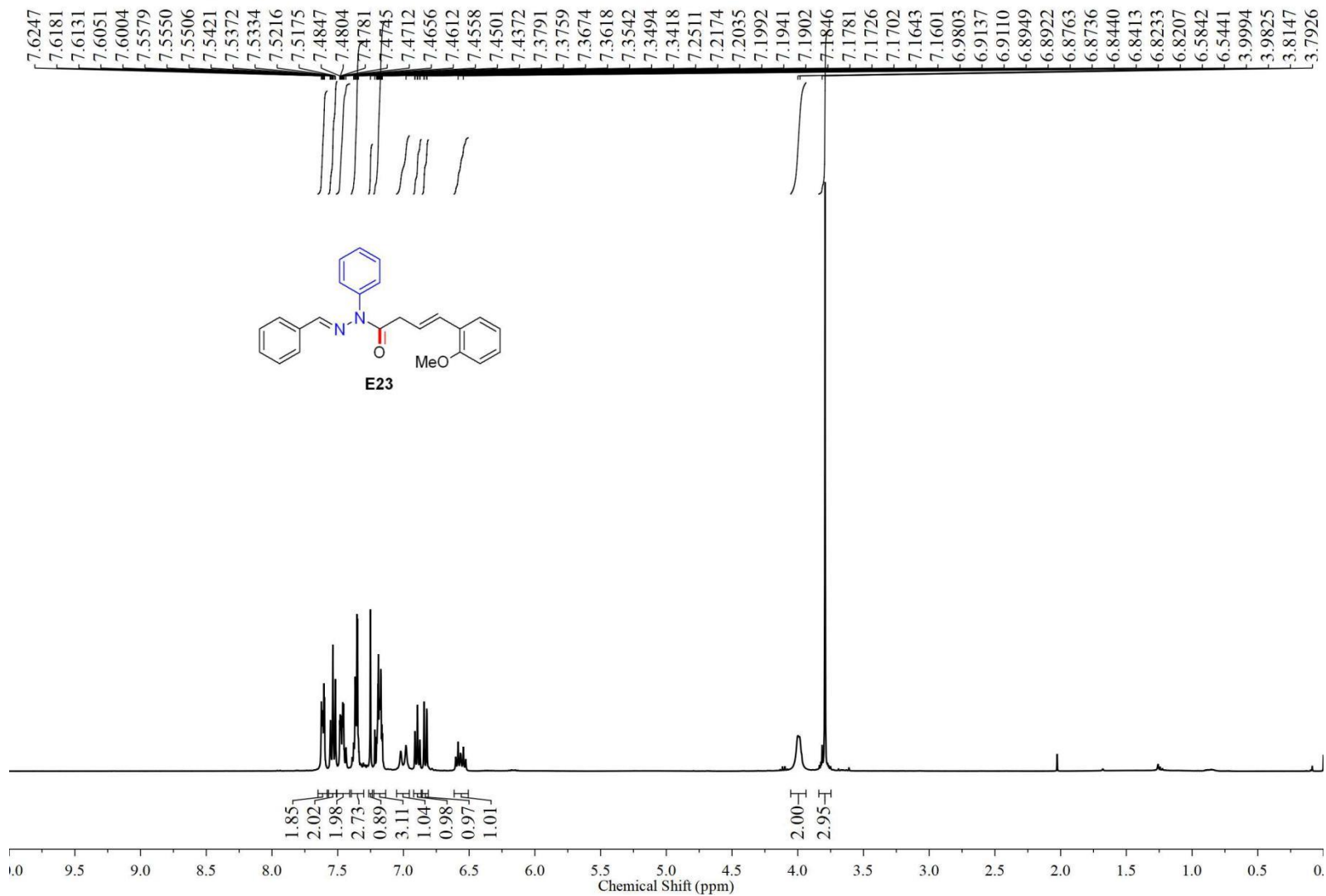
S317

2022-11-7-yy0001-616-1-h25.12.fid



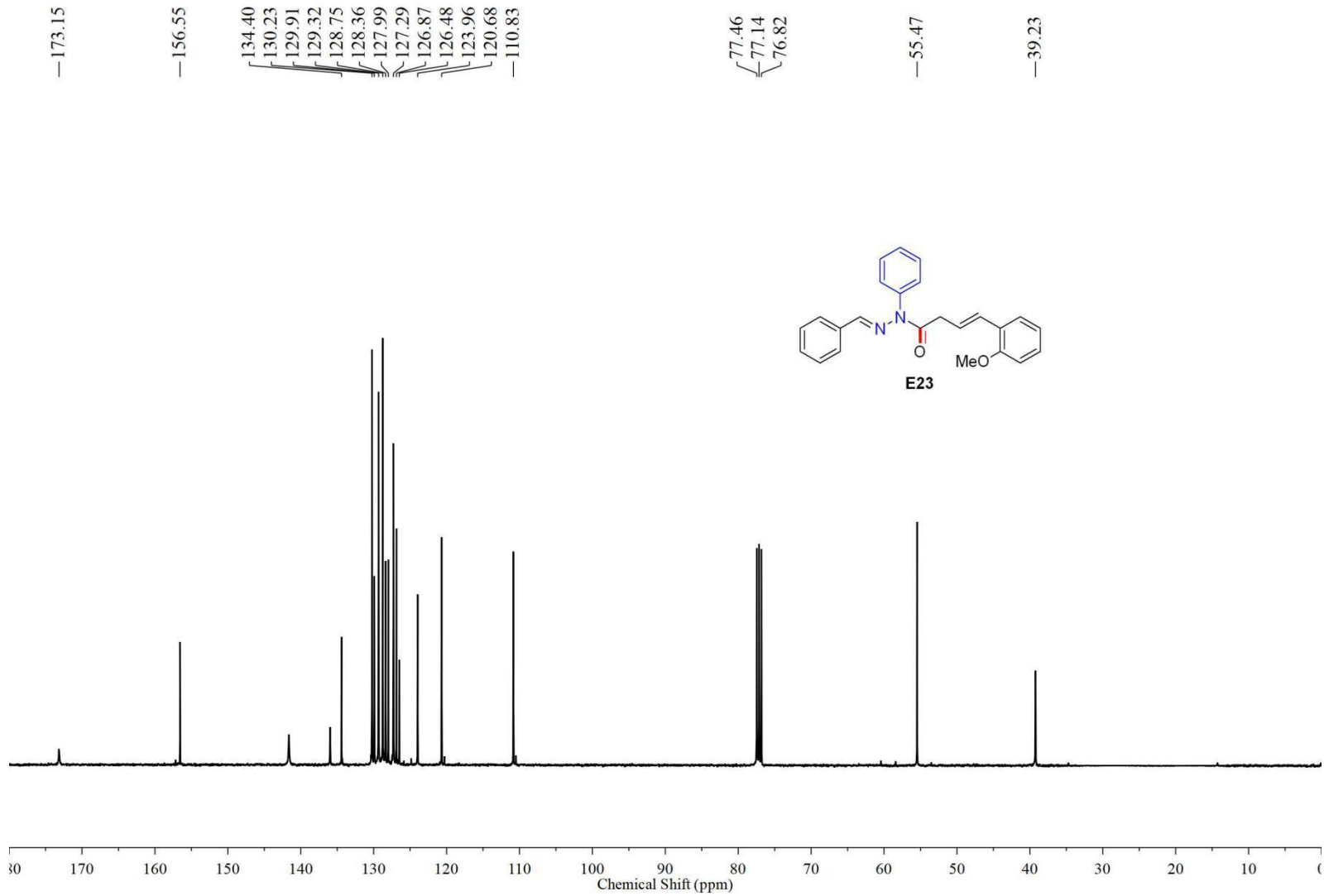
S318

2022-10-31 yy0003 616-1-H23. 10. fid



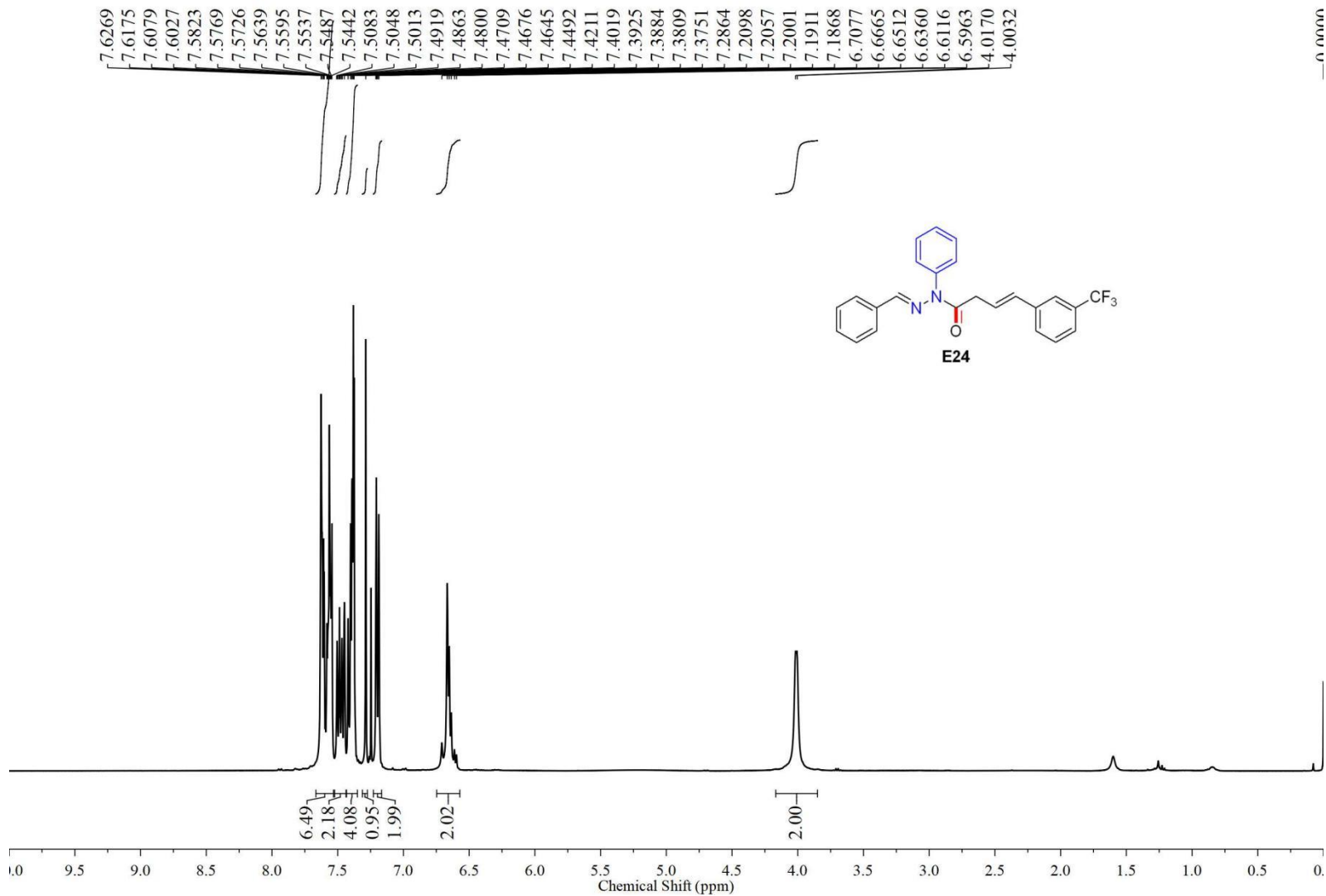
S319

2022-11-1 yy0019-616-1qq-23. 10. fid



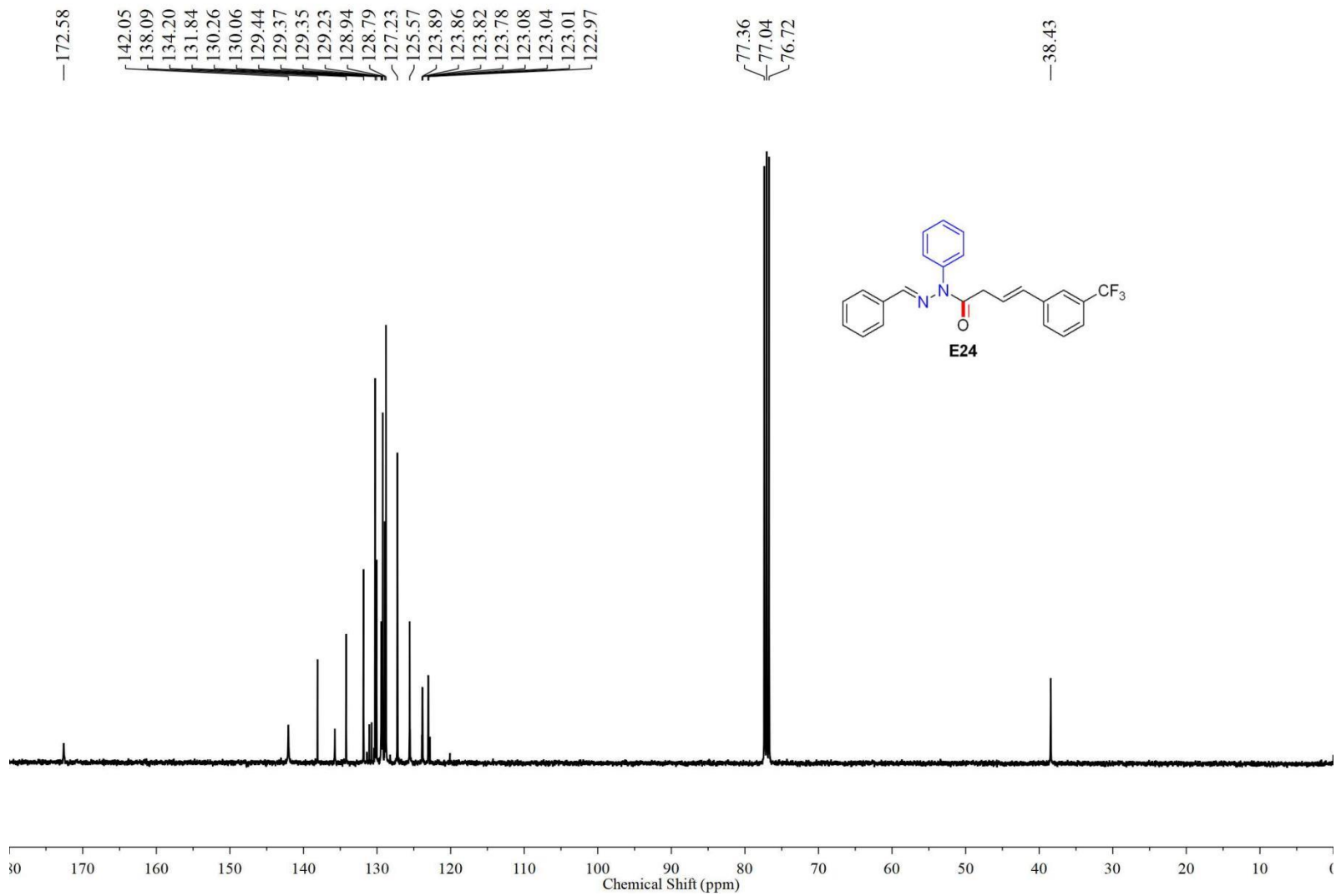
S320

2022-11-08-YY0019-616-L-H26. 10. fid



S321

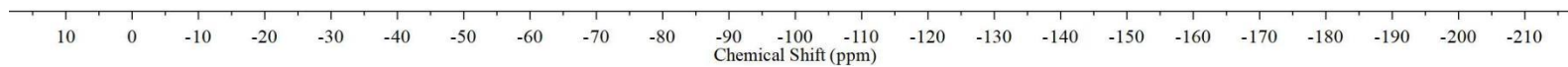
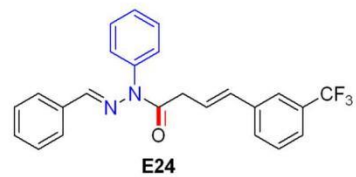
2022-11-08-YY0019-616-L-H26. 11. fid



S322

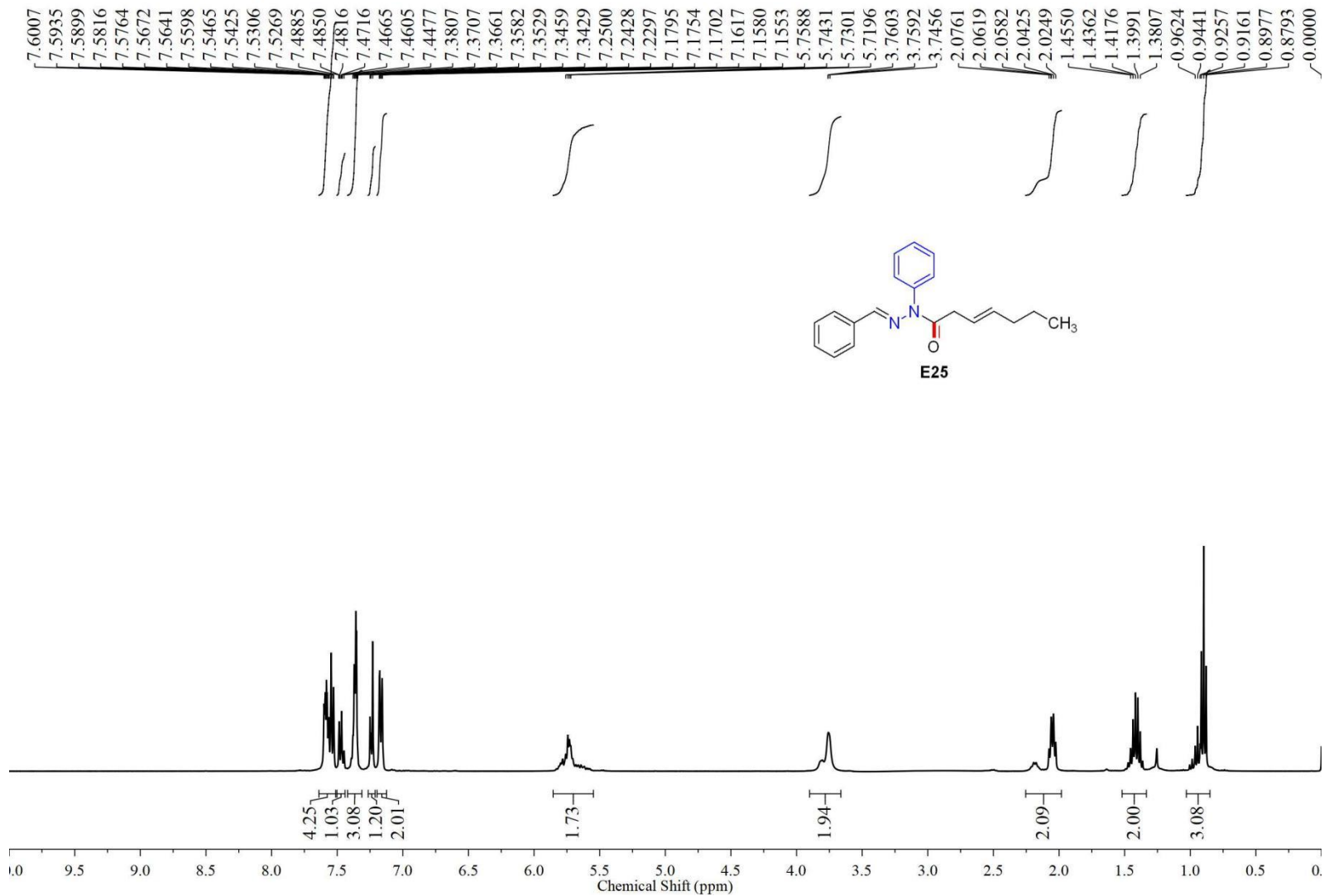
2022-11-08-YY0019-616-L-H26. 12. fid

—62.75



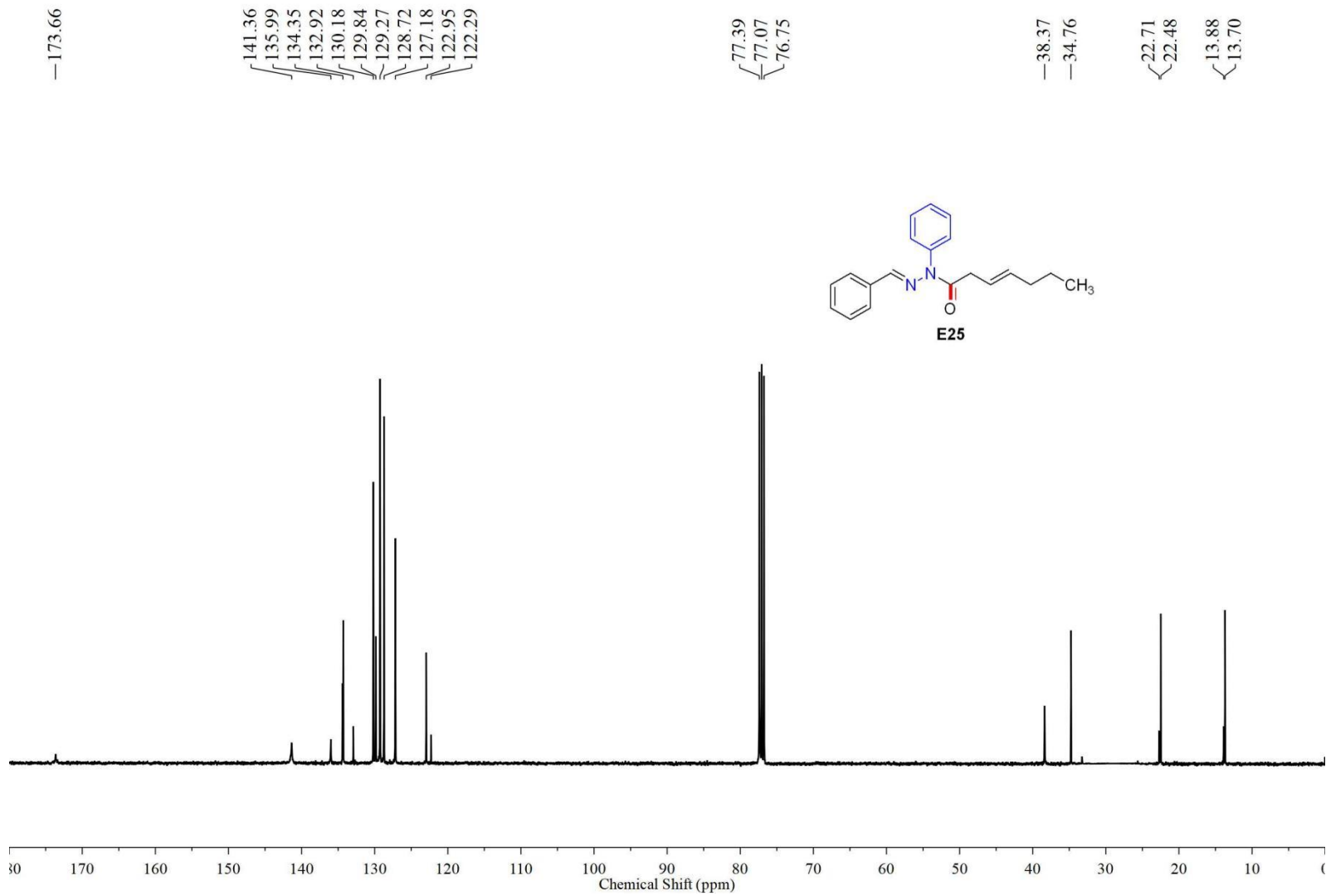
S323

2022-11-29-yy0013-616-1-a23. 10. fid



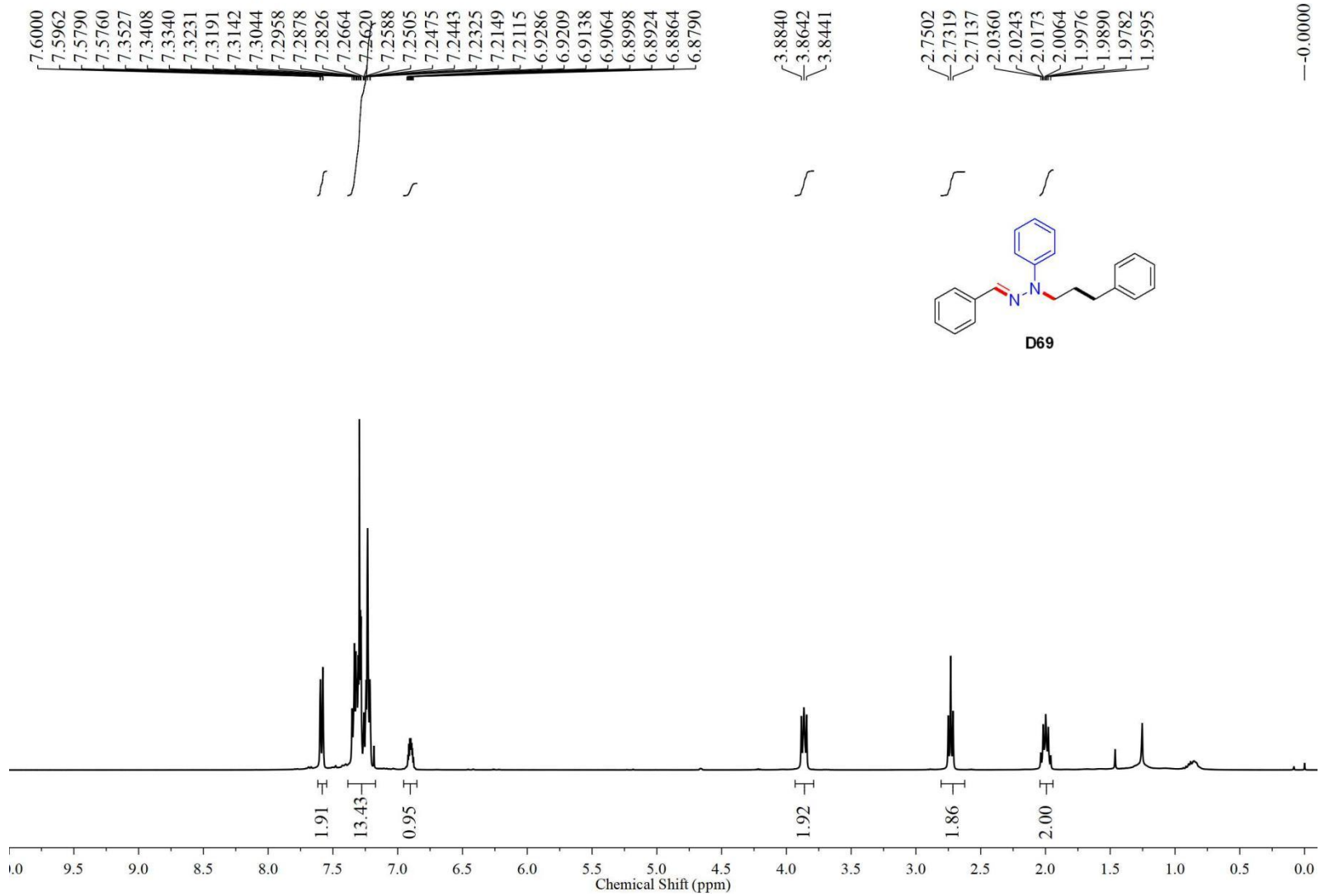
S324

2022-11-29-yy0013-616-1-a23. 11. fid



S325

2022-8-25 yy0027-616-LQQ-01.10.fid



S326

2022-08-26 YY0018 616-LQQ-01.10.fid

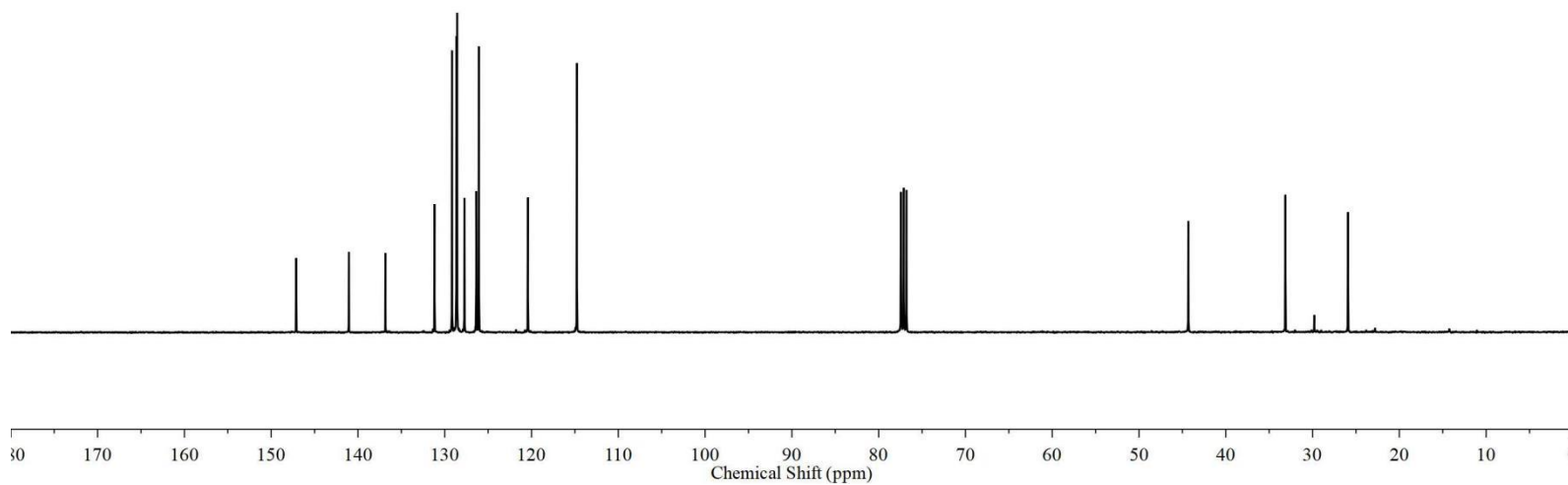
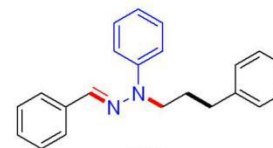
147.12
141.05
136.84
131.18
129.17
128.66
128.60
128.57
127.73
126.37
126.07
120.42
114.78

77.44
77.12
76.80

44.32

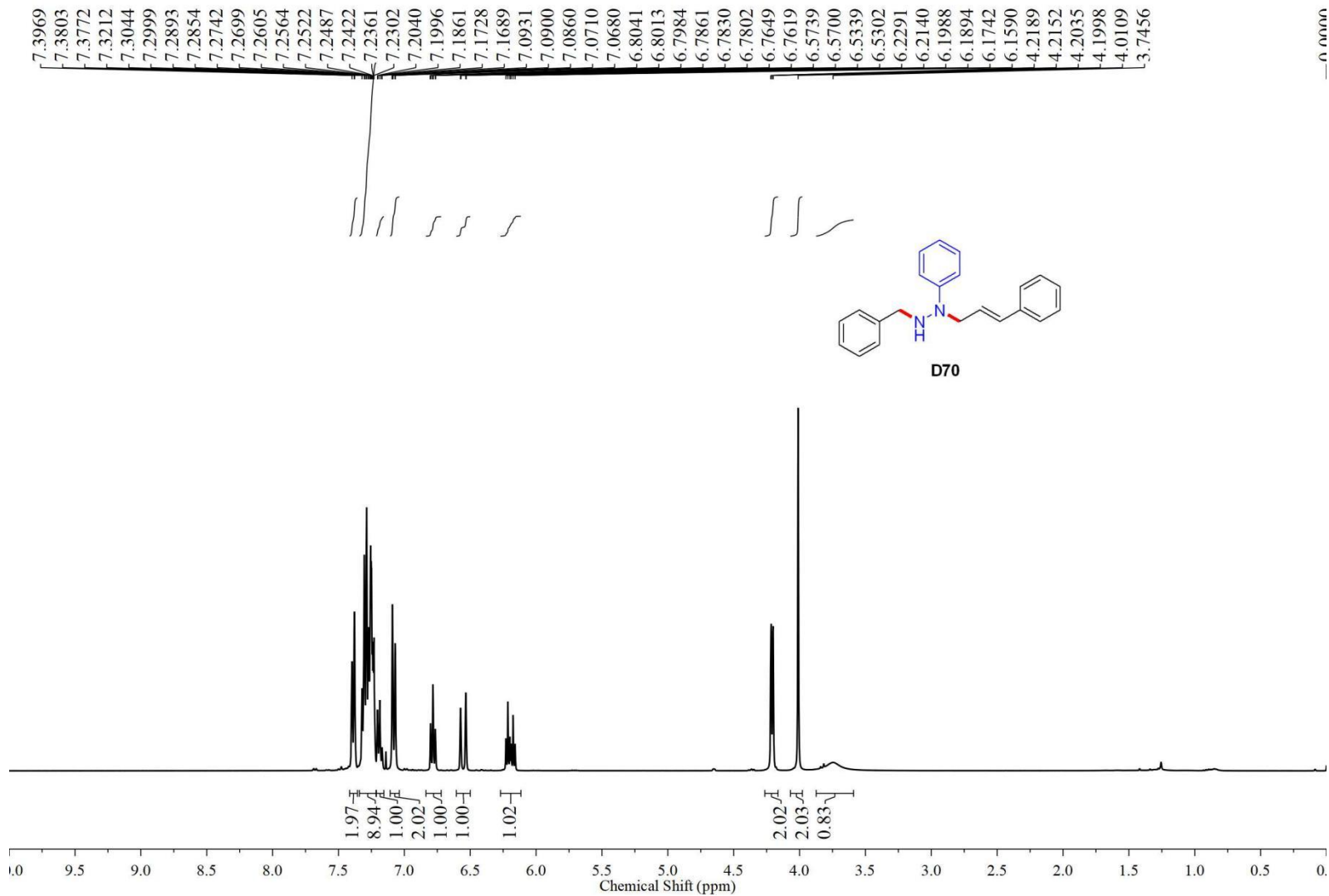
33.13

25.92



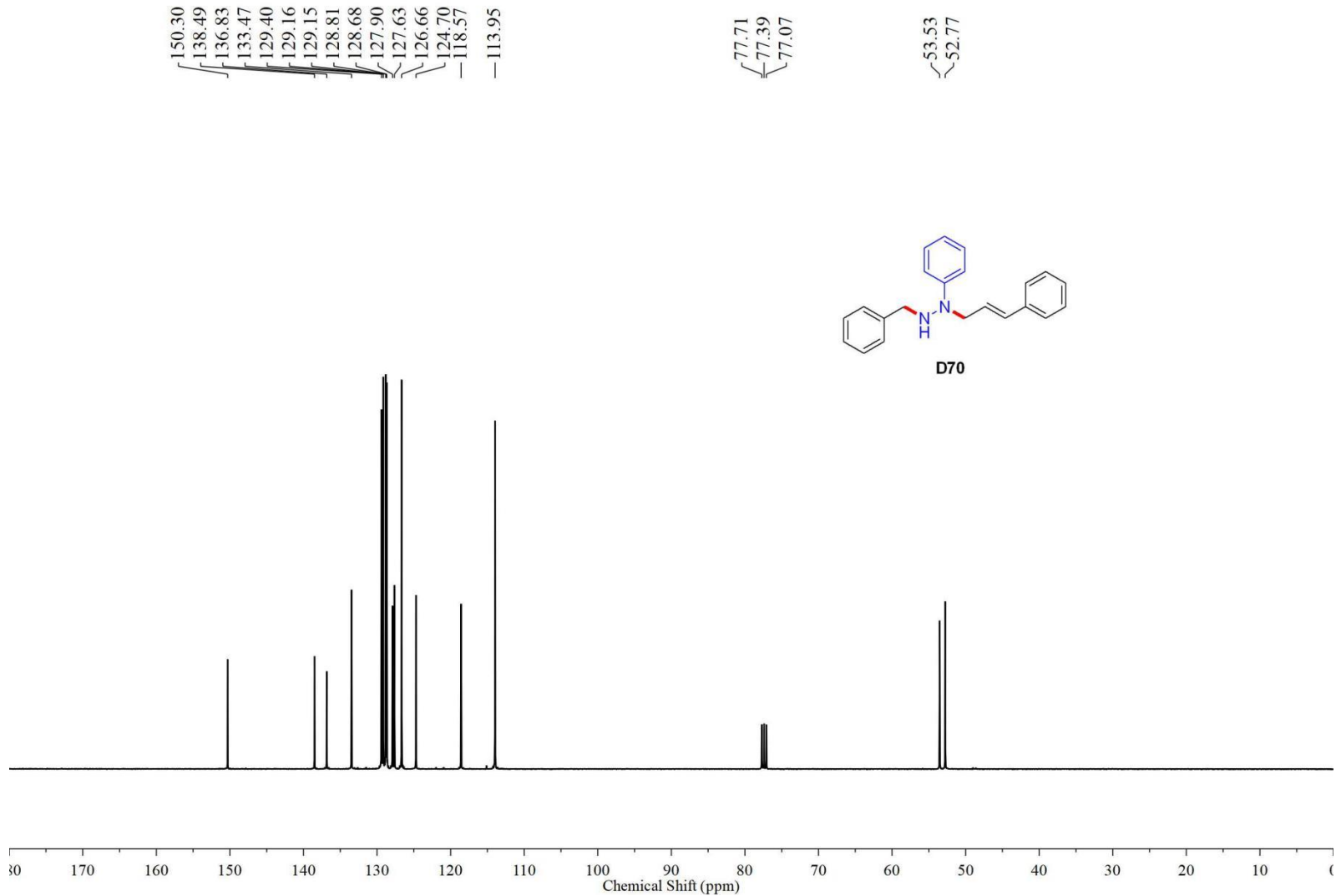
S327

2022-09-15 YY0023 616-LQQ-L-2.10.fid

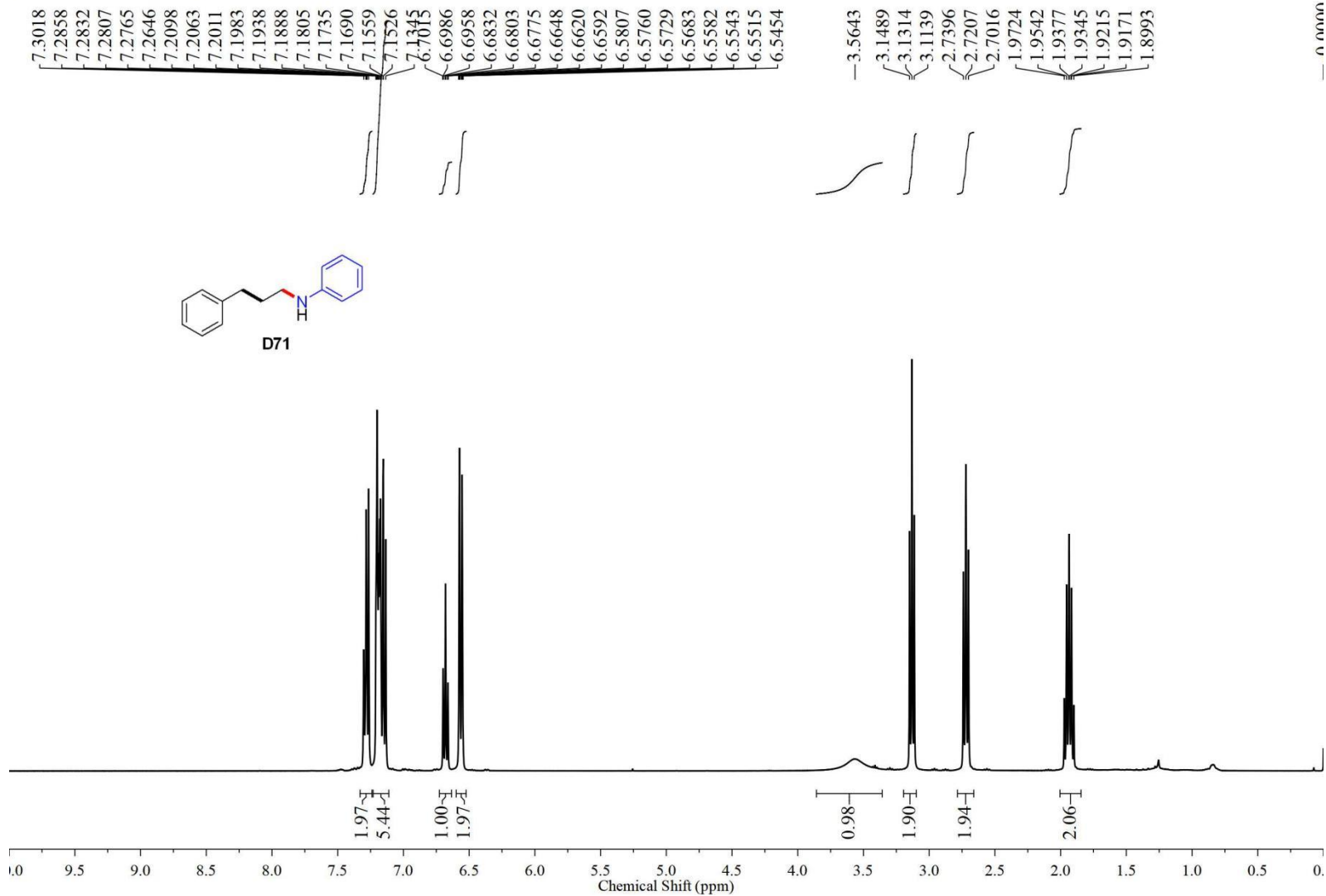


S328

2022-9-19 yy0015-616-lqq-2.11.fid



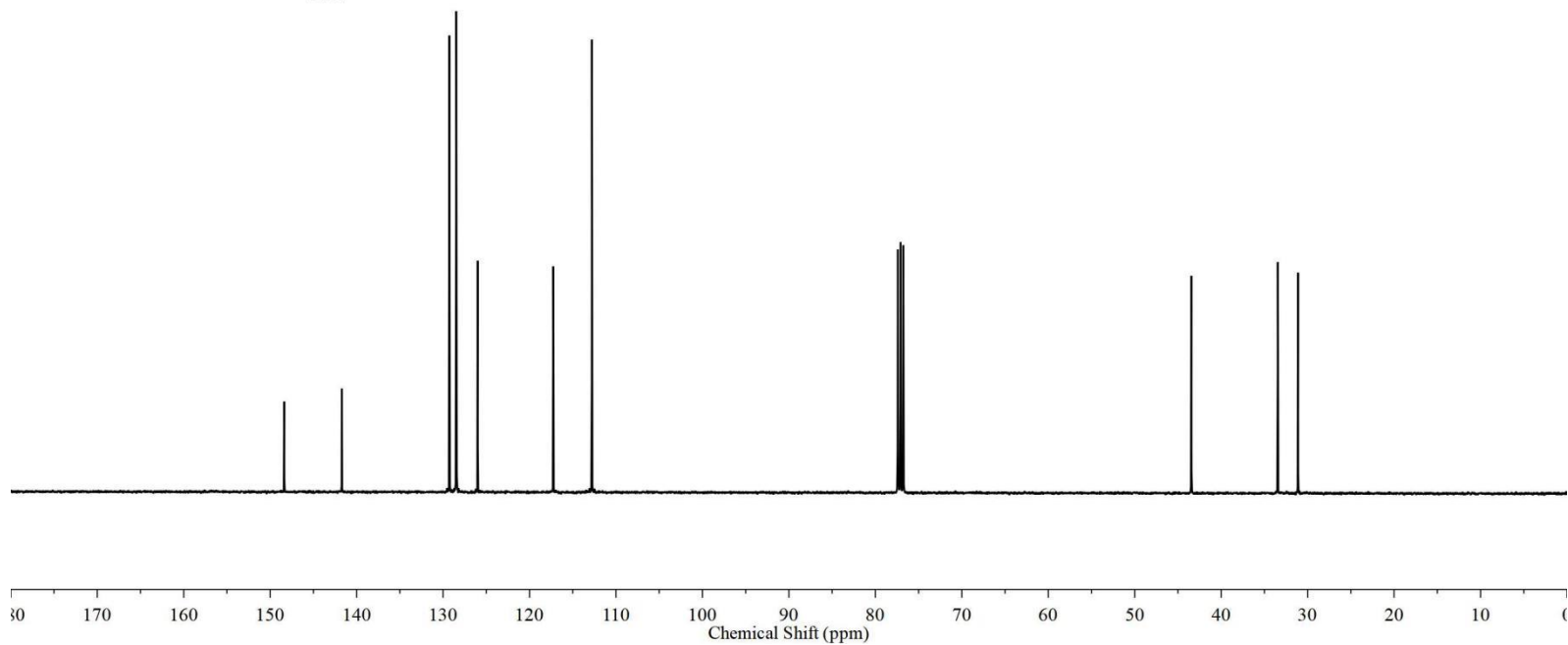
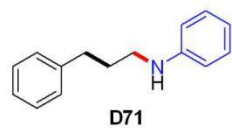
2022-09-28-YY0023-616-LQQ-L-C.30. fid



S330

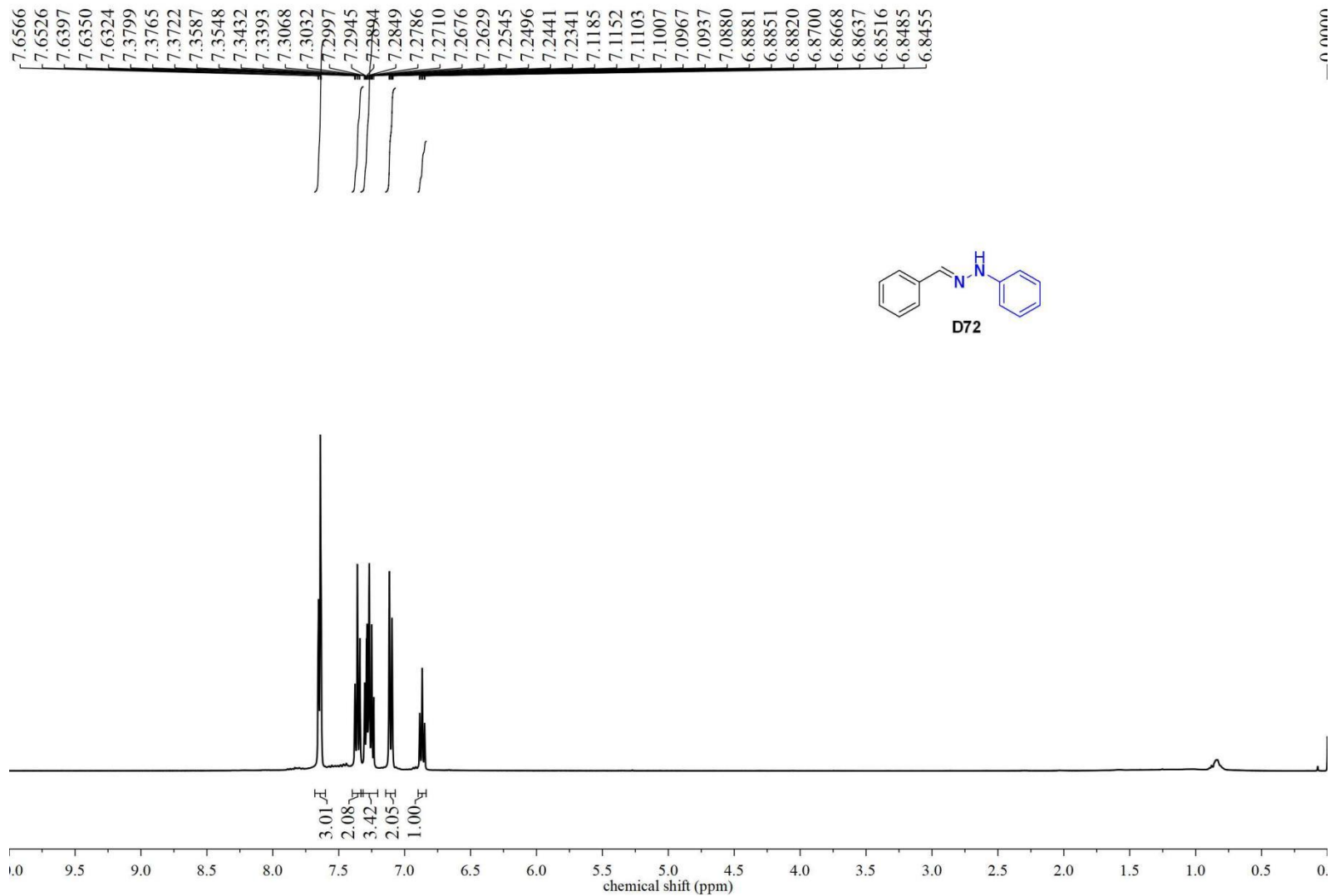
2022-09-28-YY0023-616-LQQ-L-C. 31. fid

—148.38
—141.71
—129.27
—128.48
—128.45
—126.00
—117.26
—112.79
—77.40
—77.08
—76.77
—43.45
—33.45
—31.11



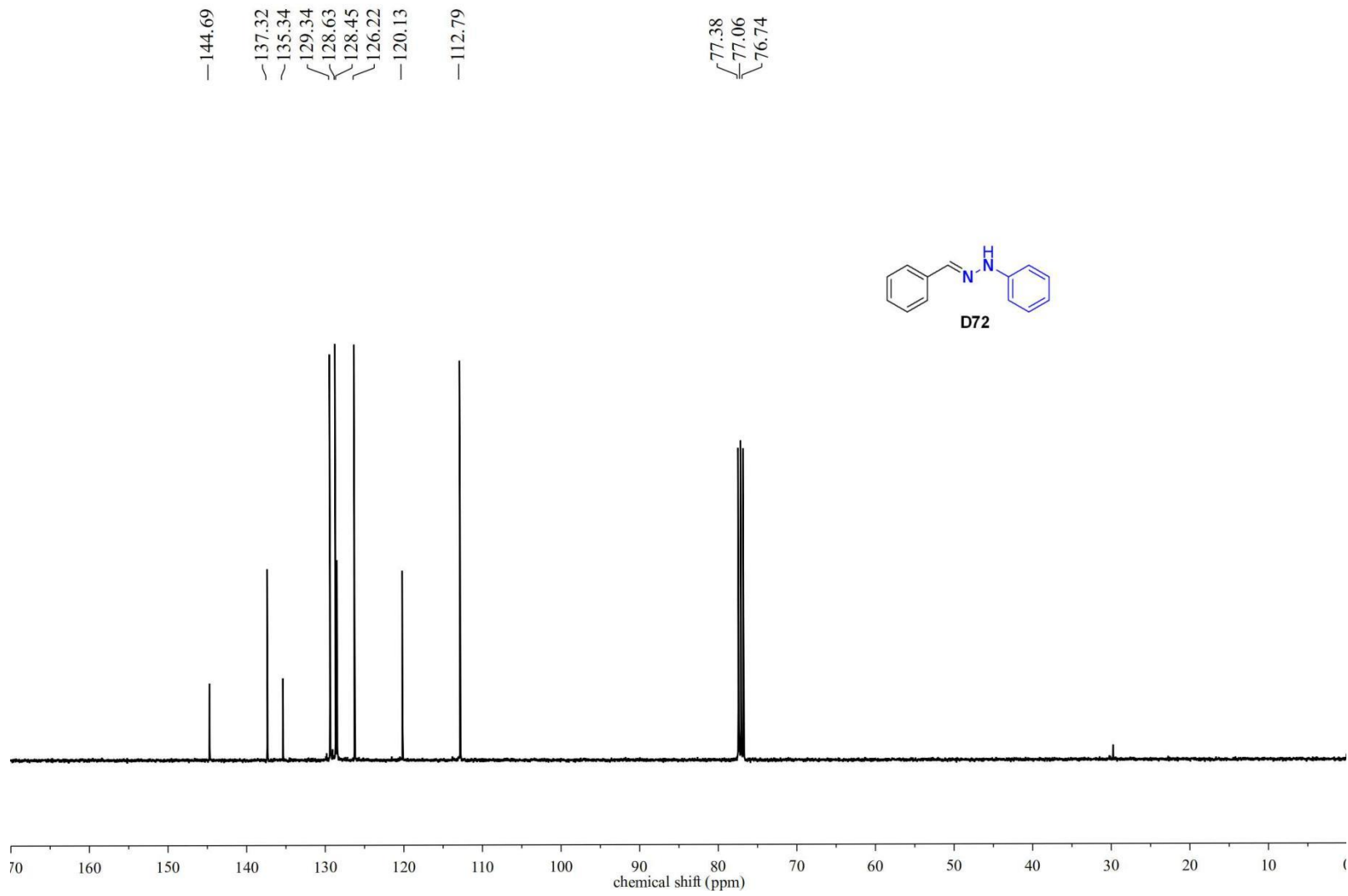
S331

2022-08-31-YY0023-616-zgh-1



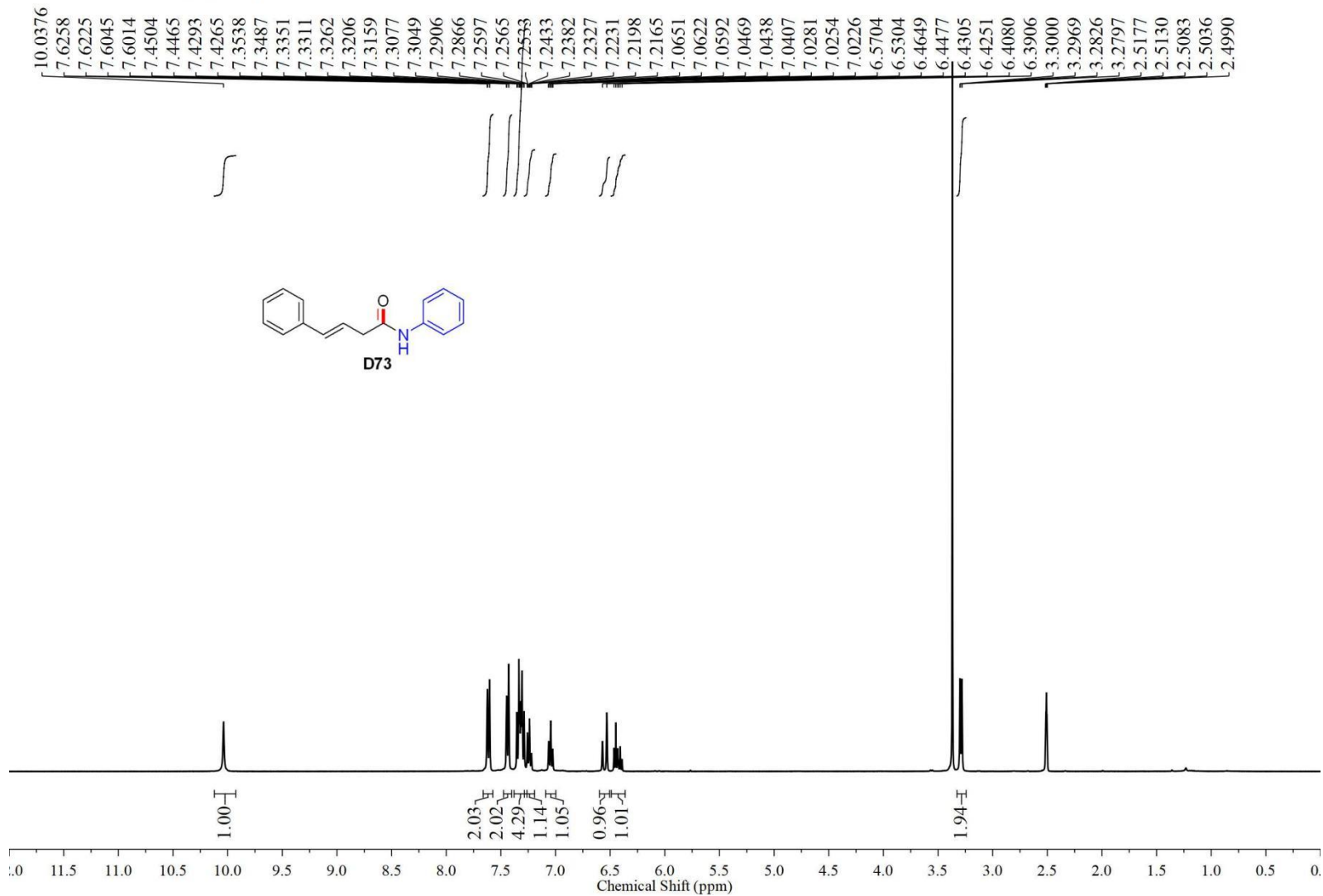
S332

2022-08-31-YY0023-616-zgh-1



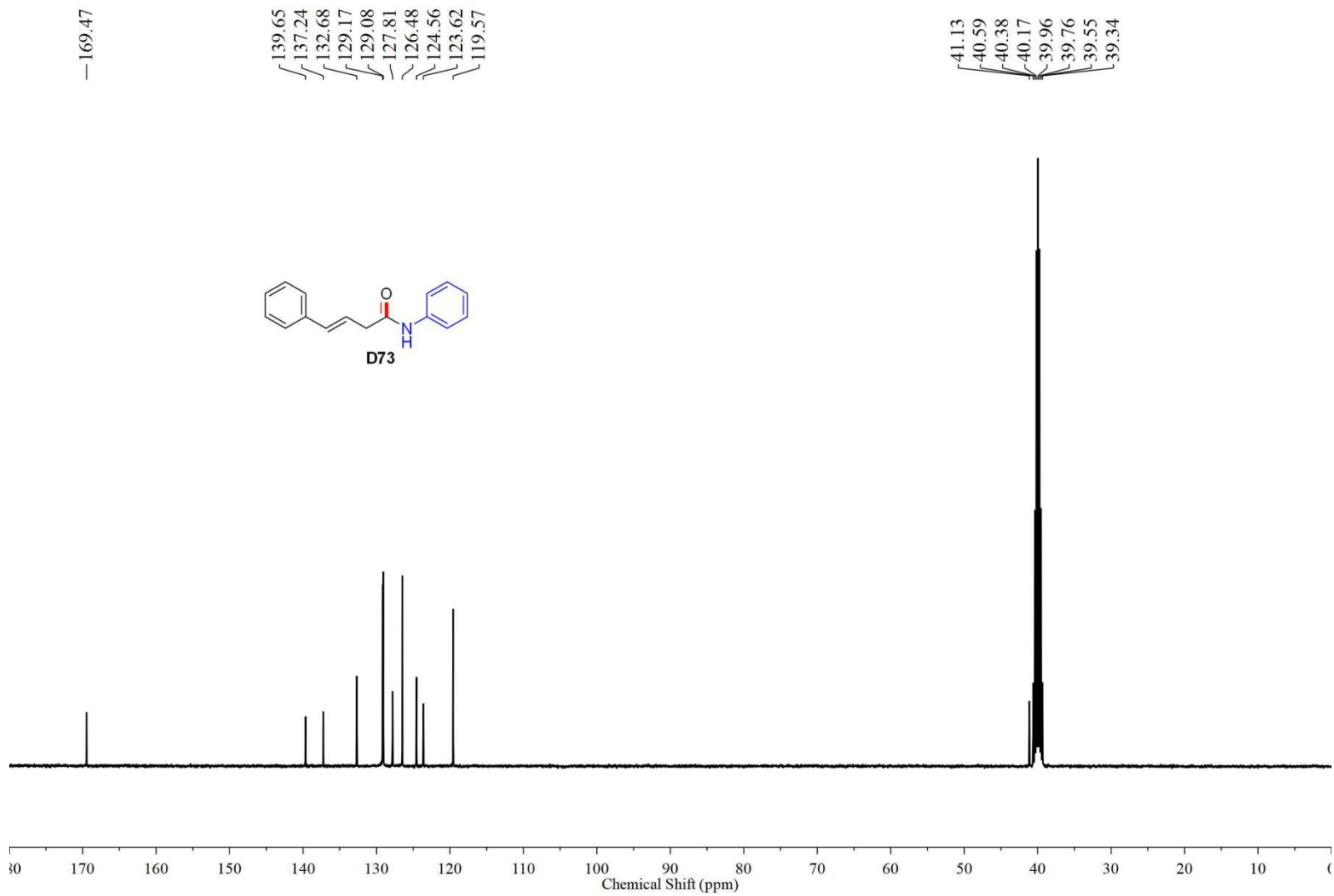
S333

2022-12-7 yy0020 616-1qq-23. 10. fid



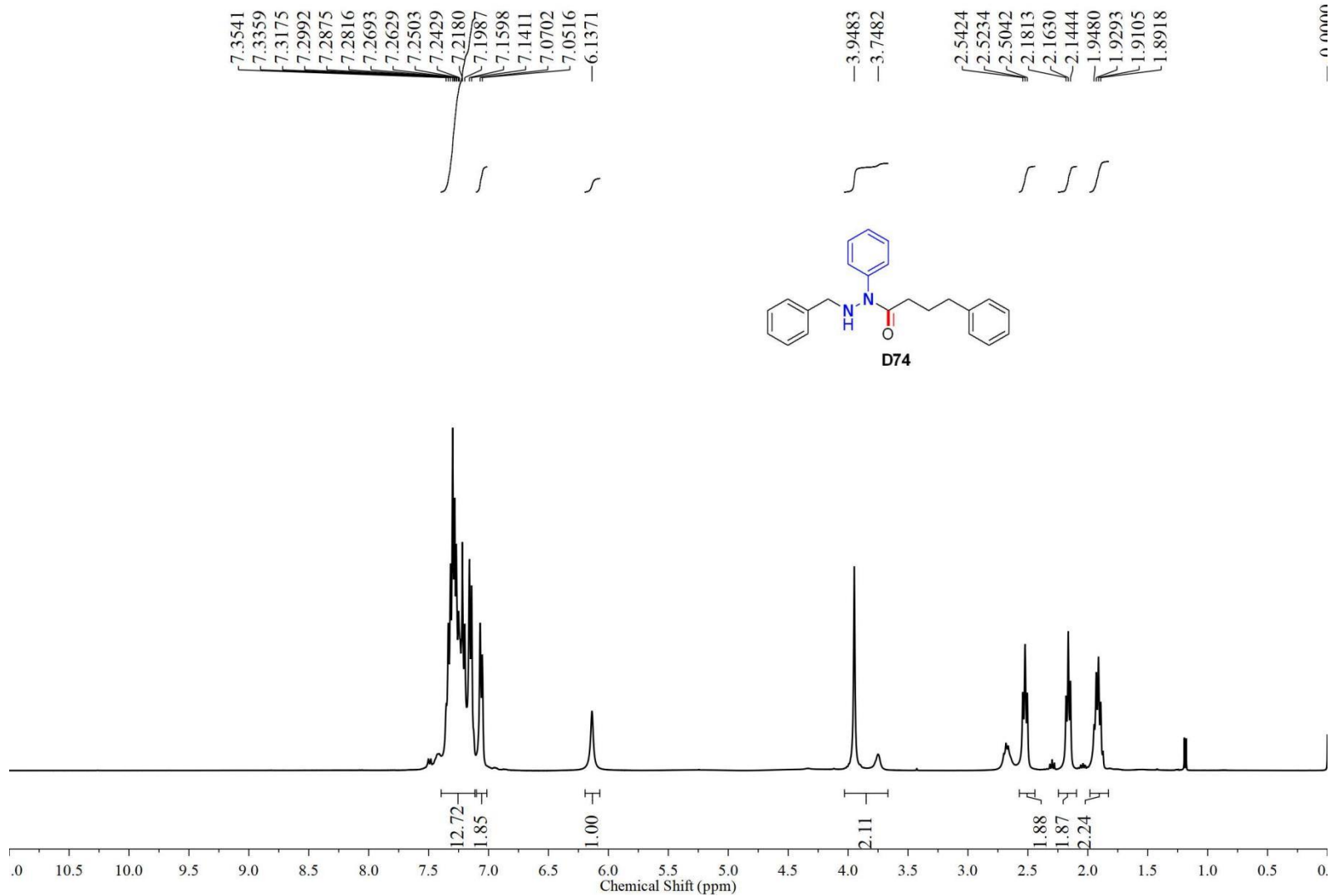
S334

2022-12-9 yy0018 616 1qq-23.10. fid



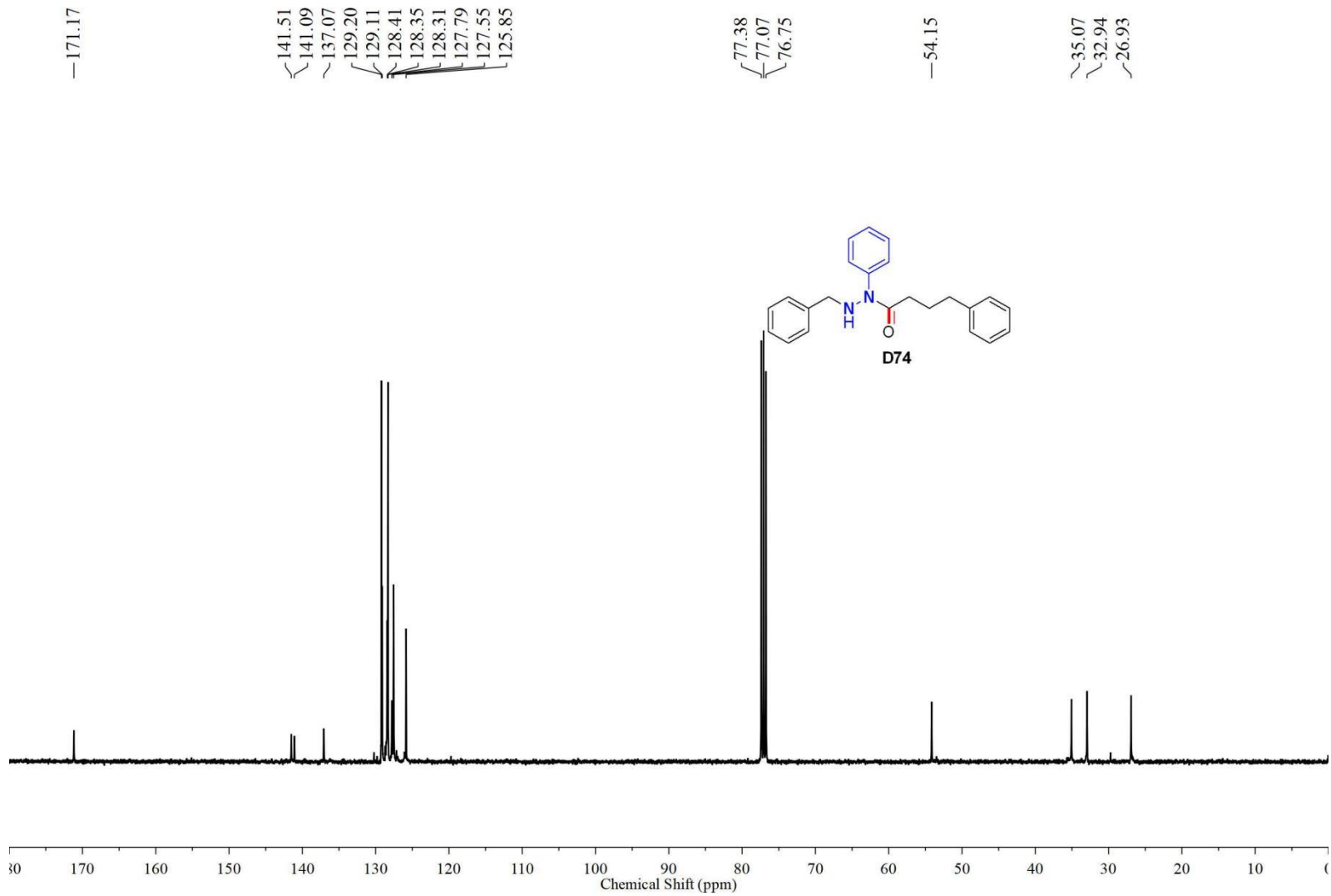
S335

2022-12-03-yy0002-616-1-z2.10.fid



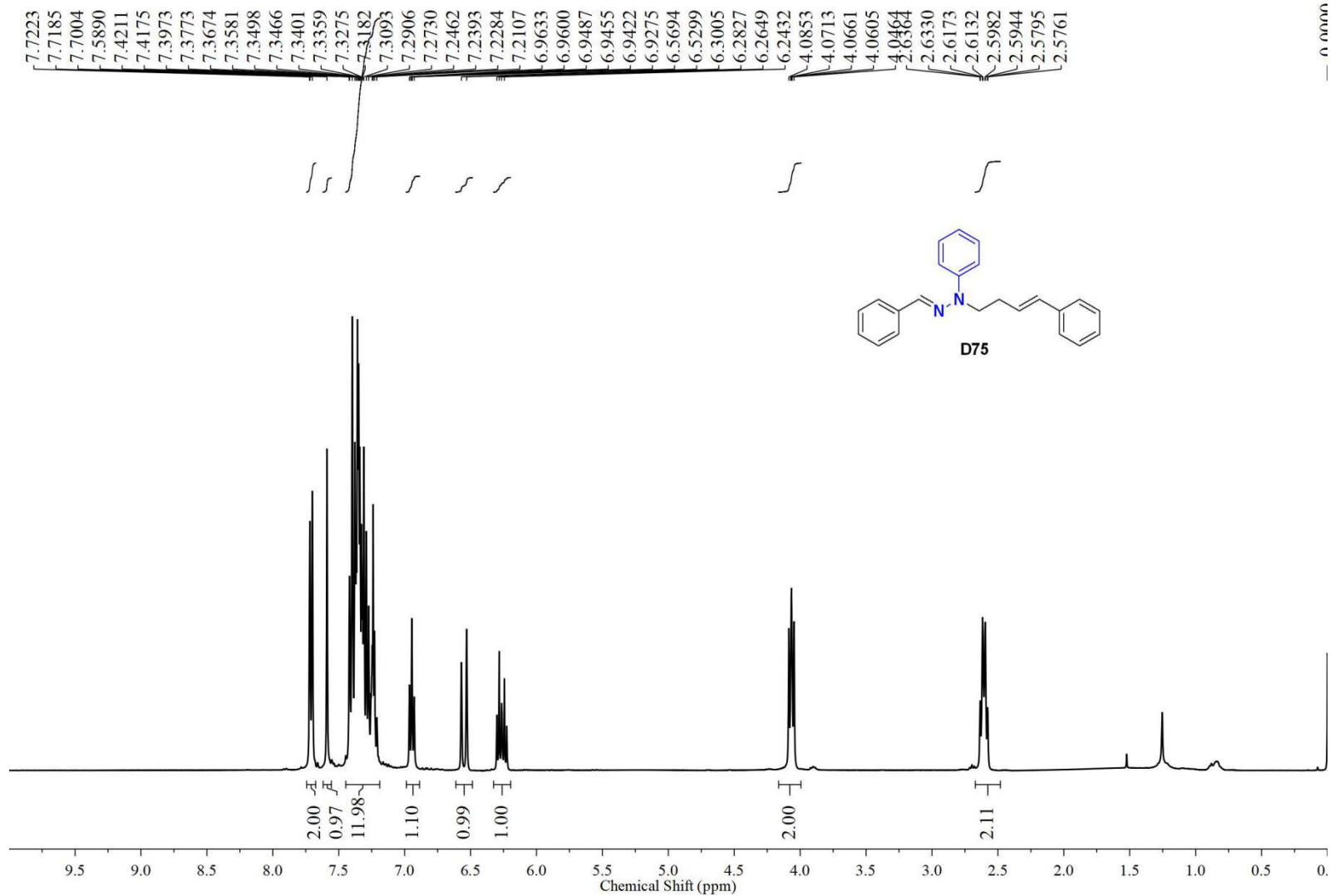
S336

2023-01-10-yy0014-616-lq-1.10.fid



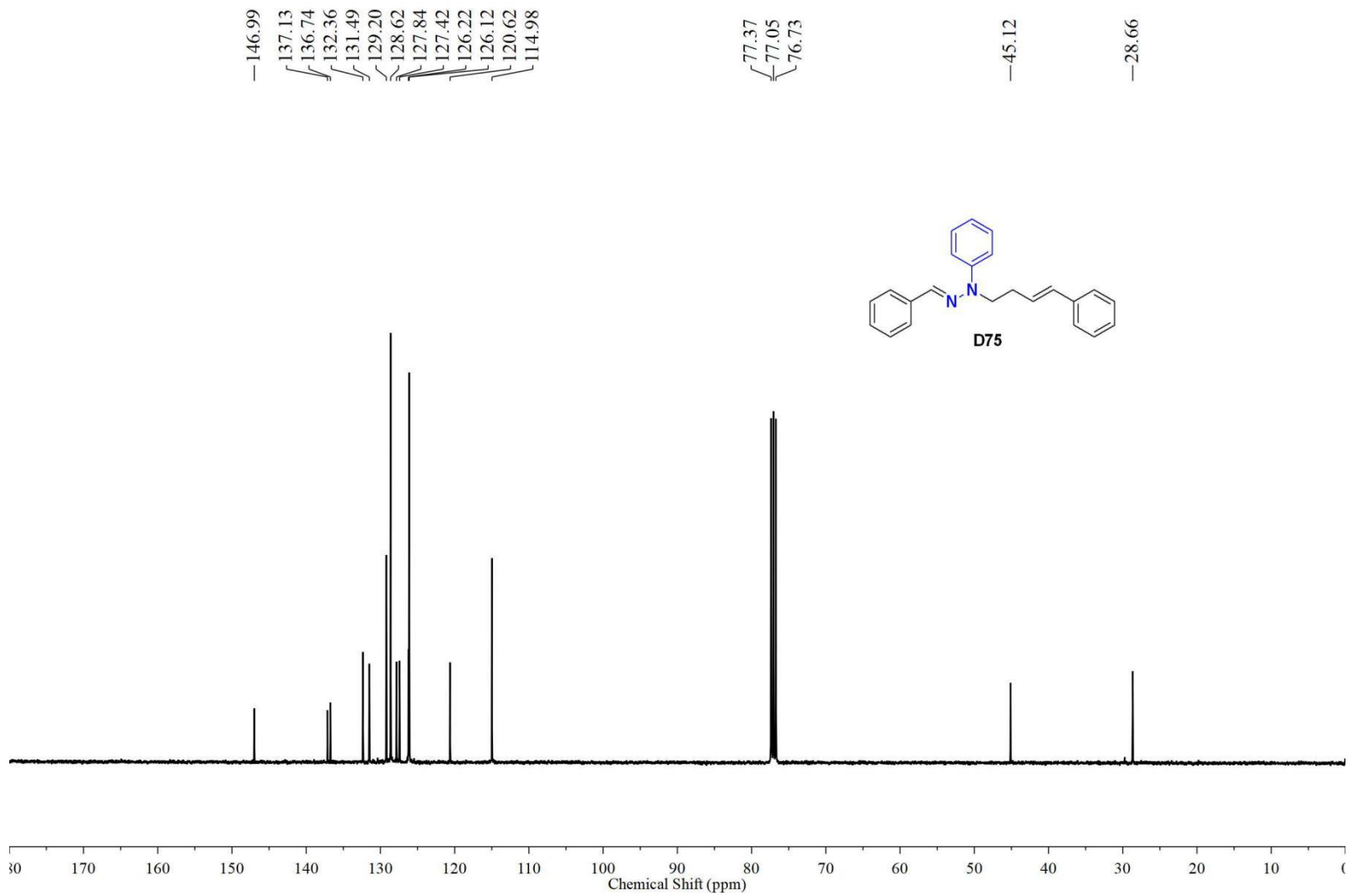
S337

2023-02-24-yy0013-tyut-616-1-3. 10. fid



S338

2023-02-25 YY0007 616-LQQ-L-3-01.10.fid



S339