

Table of Contents

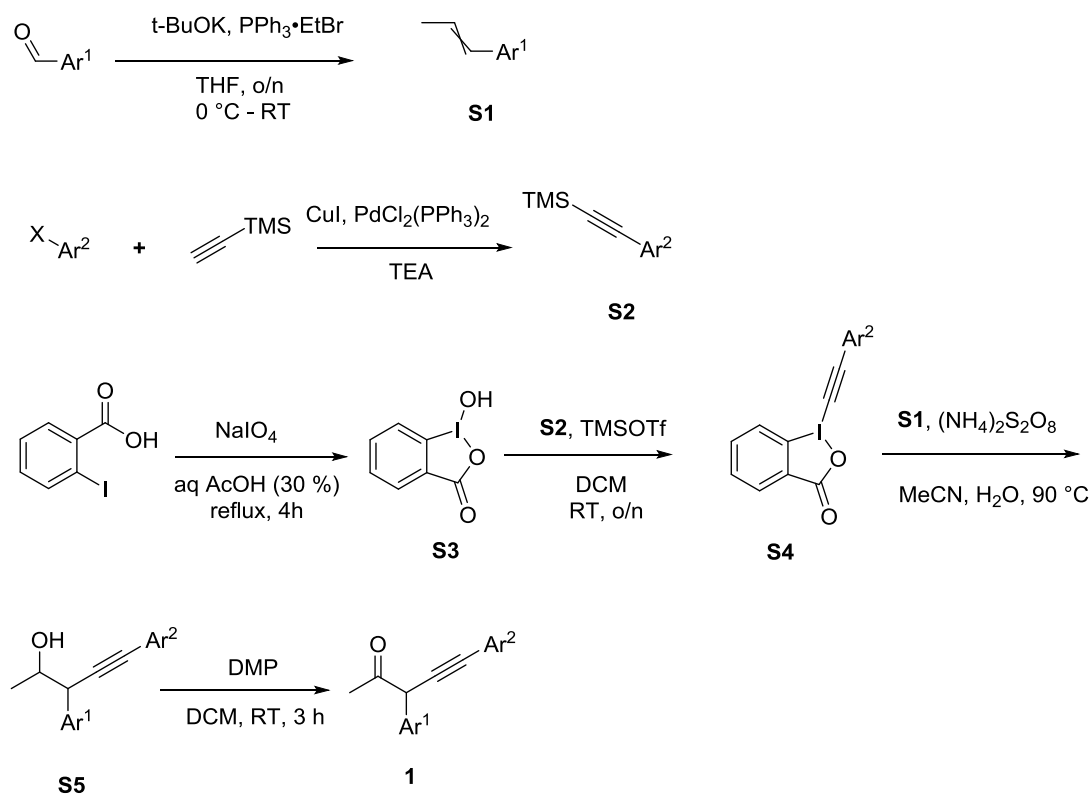
General Information	2
Synthesis of substrates 1	3
Asymmetric amination of α -alkynyl ketone 3	19
Control experiments:	33
Derivatizations of chiral products:	34
References:	38
X-Ray structures.....	39
HPLC traces:	41
NMR spectrums.....	72

General Information

Unless otherwise noted, all commercial reagents were used without further purification. Dichloromethane, toluene, ether, THF were purified by passage through an activated alumina column under argon. Thin-layer chromatography (TLC) analysis of reaction mixtures were performed using Huanghai silica gel HSGF254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or potassium permanganate. Flash column chromatography was carried out on Huanghai Silica Gel HHGJ-300, 300-400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance III HD spectrometer (FT, 500 MHz or 400 MHz for ^1H , 126 MHz or 101 MHz for ^{13}C , 471 MHz for ^{19}F , 202 MHz for ^{31}P). Data for ^1H NMR were reported as follows: chemical shift (δ ppm downfield from tetramethylsilane and referenced to residual solvent peaks), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance), integration, coupling constant (Hz). Data for ^{13}C NMR were reported in terms of chemical shift. Mass spectral data were obtained from the Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI⁺) mode. Optical rotations were measured with an Autopol V Plus/VI digital polarimeter. X-Ray structure analyses were performed using a Bruker D8 Venture X-ray single crystal diffractometer. Enantiomeric excesses were determined on an Agilent 1260 Chiral HPLC using IA, IB, IC, ID and IG columns. Acid-wash molecular sieves (AW-300 MS) were purchased from Shanghai TOP Molecular Sieve Co., Ltd.

Synthesis of substrates 1

Method A:



Substrates **1a-1j** and **1n-1w** were synthesized with method A. Compounds **S1** and **S2** were prepared with the known method if it is not commercial available.

General procedure of method A:

Synthesis of S1 (if **S1** is not commercial available): To the mixture of EtPPh_3Br (1.4 equiv.) and $t\text{-BuOK}$ (1.3 equiv.) was added THF at $0\text{ }^\circ\text{C}$. The mixture was stirred at $0\text{ }^\circ\text{C}$ for 1 h, which was followed by adding the corresponding aldehyde (1.0 equiv.) dropwisely. After stirring overnight at rt, the mixture was quenched with saturated aqueous NH_4Cl solution, and the organic phase was separated. The aqueous phase was extracted with ethyl acetate for three times. The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to give a residue, which was purified by column chromatography to afford the corresponding alkenes **S1**.

Synthesis of S2 (if **S2** is not commercial available): To a solution of the ArX (1.0

equiv.), PdCl₂(PPh₃)₂ (0.01 equiv.), and CuI (0.01 equiv.) in Et₃N was added the trimethylsilane acetylene (1.5 equiv.) under N₂ atmosphere. The resulting mixture was stirred at 80 °C for 6 hours. After the complete consumption of ArX as monitored by TLC analysis, the reaction mixture was quenched with water and extracted with ethyl acetate for three times. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel to afford the desired product **S2**.

Alcohol **S5** was synthesized following a known protocol¹:

Step 1: NaIO₄ (7.24 g, 33.8 mmol, 1.05 equiv.) and 2-iodobenzoic acid (8.00 g, 32.2 mmol, 1.0 equiv.) were suspended in 30% (v:v) aq. AcOH (48 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (180 mL) and allowed to cool to rt, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 20 mL) and acetone (3 x 20 mL), and air-dried in the dark to give the pure product **S3** as a colorless solid.

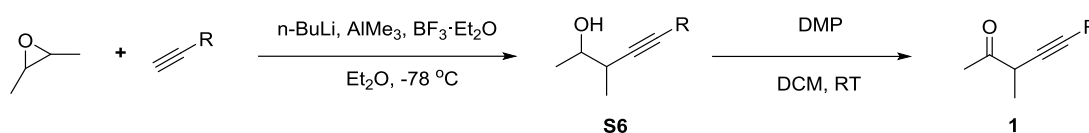
Step 2: Trimethylsilyl triflate (0.397 mL, 2.2 mmol, 1.1 equiv.) was added to a suspension of 2-iodosylbenzoic acid **S3** (528 mg, 2 mmol, 1.0 equiv.) in CH₂Cl₂ (5.3 mL) at room temperature. The resulting yellow mixture was stirred for 1 h, followed by the addition of **S2** (2.2 mmol, 1.1 equiv.). After stirring for 6 h at room temperature, saturated NaHCO₃ solution (5.3 mL) was added and the mixture was stirred vigorously for 30 min. After filtration, the filtrate was washed with saturated NaHCO₃ solution, dried over Na₂SO₄, filtered and concentrated in vacuo to give a residue, which was purified by column chromatography on silica gel (CH₂Cl₂/MeOH as eluent) to afford **S4**.

Step 3: A mixture of alkene **S1** (0.3 mmol, 3.0 eq), alkynyl benziodoxole **S4** (0.1 mmol, 1.0 eq), and (NH₄)₂S₂O₈ (0.2 mmol, 2.0 eq) in a solution of CH₃CN and H₂O (1.0 mL, v:v = 1:1) in a seal tube was stirred at 90 °C for 1-2 h. Then the reaction was cooled to room temperature, quenched by Et₃N, and extracted with ethyl acetate. Organic layers were combined and dried over Na₂SO₄. Solvent was evaporated under

reduced pressure to give a residue, which was purified by flash column chromatography (ethyl acetate/petroleum ether as eluent) to give the expected product **S5**.

Step 4: To a solution of **S5** (1.0 equiv.) in dichloromethane at room temperature was added Dess-Martin periodinane (2.0 equiv.) at rt. After stirring for 2 hours, the mixture was diluted with DCM and washed with water. The organic phase was dried over Na_2SO_4 , and concentrated in vacuo to give a residue. After adding petroleum ether into this residue, the mixture was filtered through Celite and the filtrate was concentrated in vacuo to give the desired compound **1** as yellow oil.

Method B:



Substrates **1k**, **1x** and **1y** were synthesized with method B.

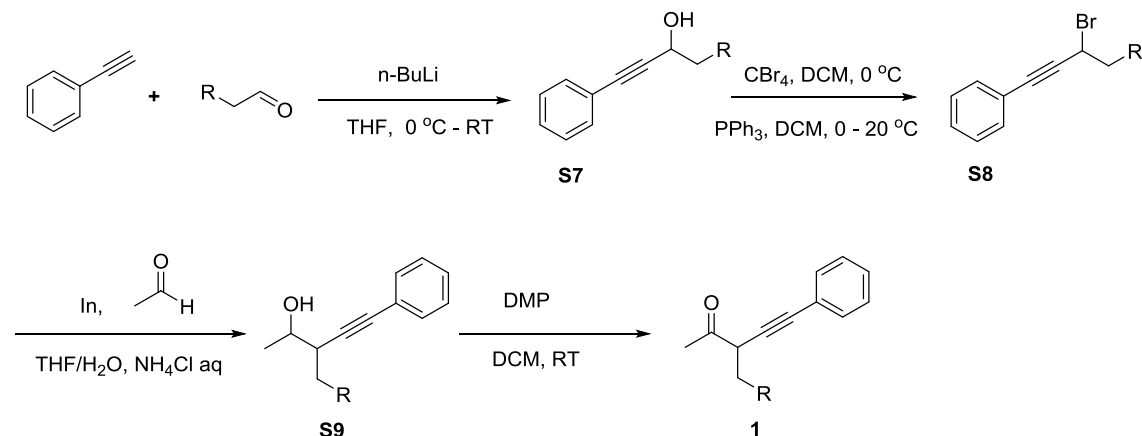
General procedure for method B:

Step 1: To a solution of the corresponding alkyne (1.9 mL, 13.4 mmol) in Et_2O (55 mL) at $-78\text{ }^\circ\text{C}$ was added $n\text{-BuLi}$ (2.5 M in hexane, 5.35 mL, 13.4 mmol) over 20 min. After stirring at $-78\text{ }^\circ\text{C}$ for additional 20 min, trimethylalumina (2.0 M in toluene, 6.7 mL, 13.4 mmol) was added via syringe pump over 40 min. The reaction was stirred at $-78\text{ }^\circ\text{C}$ for 30 min, $-45\text{ }^\circ\text{C}$ for 30 min, and then cooled to $-78\text{ }^\circ\text{C}$, whereupon 2,3-epoxybutane (1 mL, 1.2 mmol) in Et_2O (6 mL) was added over 15 min. After stirring for 15 min at the same temperature, boron trifluoride diethylether (1.56 mL, 12.3 mmol) in Et_2O (6 mL) was added slowly over 15 min. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h, whereupon methanol (20 mL) was added slowly to quench the reaction. The reaction was then allowed to warm to $0\text{ }^\circ\text{C}$ over 25 min before saturated aqueous NH_4Cl solution (20 mL) was added. After stirring at room temperature for additional 30 min, the mixture was diluted with water, extracted with ethyl acetate, dried over Na_2SO_4 , filtered, and concentrated under vacuum to give a residue, which

was purified by column chromatography on silica gel to give the desired product **S6** as colorless oil.

Step 2: Transformation of **S6** into substrate **1** was using the same procedure as described above in method A.

Method C:



Substrates **1l** and **1m** were synthesized with method C.

General procedure of **method C**:

Step 1: n-BuLi (1.58 M in hexane, 11.5 mL, 18.2 mmol) was added to a stirred solution of phenylacetylene (1.9 g, 18.2 mmol) in THF (20 mL) at 0 °C, and the mixture was stirred at 0 °C for 30 min. To the resulting solution was added the corresponding aldehyde (1.3 mL, 18.2 mmol) at 0 °C, and the mixture was gradually warmed to rt. The reaction was quenched by the addition of water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under vacuum to give a residue, which was purified by column chromatography (hexane:EtOAc = 8:1) to furnish the desired product **S7** as pale yellow oil.

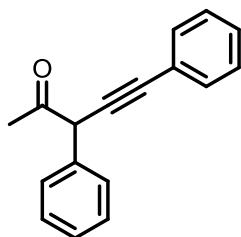
Step 2: To a solution of the corresponding alcohol **S7** (1 equiv.) in dry CH₂Cl₂ (0.6 M) at 0 °C was added CBr₄ (1.2 equiv.) slowly. After stirring for 10 min, a solution of Ph₃P (1.5 equiv.) in CH₂Cl₂ (1.5 M) was added dropwisely at 0 °C. Then the reaction mixture was allowed to warm to rt. After completion of this reaction as monitored by TLC analysis, the solvent was removed under vacuum to give a residue, which was

purified by column chromatography to afford the desired product **S8**.

Step 3: To a well stirred suspension of aldehyde (1.0 mmol) and indium powder (2.0 mmol) in THF/H₂O (1:1, 5 mL) was added **S8** (2.0 mmol) slowly at 0 °C. A saturated NH₄Cl aqueous solution (7 mL) was added after one hour and the reaction was stirred at room temperature until the disappearance of the starting material (as monitored by TLC analysis). The mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was then washed with brine, dried with MgSO₄ and concentrated under reduced pressure to give a residue, which was purified by column chromatography to afford the product **S9**.

Step 4: Transformation of **S9** into substrate **1** was using the same procedure as described above in method A.

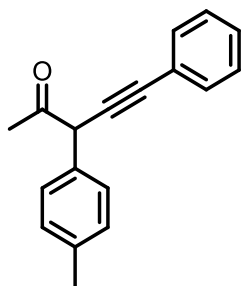
3,5-diphenylpent-4-yn-2-one (**1a**)



This reaction was performed on 0.4 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1a** (93 mg, 99%).

¹H NMR (400 MHz, Chloroform-d) δ 7.54 – 7.49 (m, 4H), 7.40 (dd, *J* = 8.4, 6.5 Hz, 2H), 7.37 – 7.33 (m, 4H), 4.78 (s, 1H), 2.28 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 202.8, 135.0, 131.9, 129.1, 128.6, 128.5, 128.1, 128.1, 122.9, 87.4, 85.0, 53.3, 26.3. *m/z* HRMS (ESI) found [M+H]⁺ 235.1114, C₁₇H₁₅O⁺ requires 235.1117.

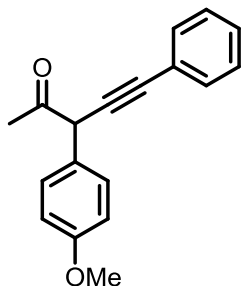
5-phenyl-3-(p-tolyl)pent-4-yn-2-one (**1b**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1b** (74 mg, 99%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.37 (m, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.23 (p, $J = 3.4, 2.9$ Hz, 3H), 7.09 (d, $J = 7.9$ Hz, 2H), 4.63 (s, 1H), 2.25 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.9, 137.8, 132.0, 131.8, 129.7, 128.5, 128.4, 127.9, 122.9, 87.1, 85.2, 52.9, 26.2, 21.2. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 249.1272, $\text{C}_{18}\text{H}_{17}\text{O}^+$ requires 249.1274.

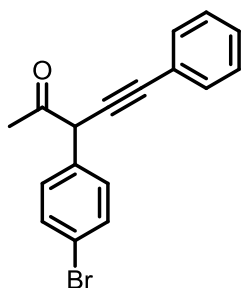
3-(4-methoxyphenyl)-5-phenylpent-4-yn-2-one (**1c**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1c** (79 mg, 99%).

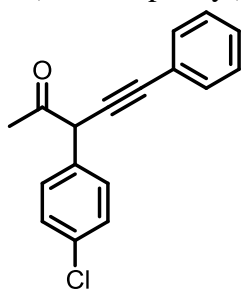
^1H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 2H), 7.45 – 7.39 (m, 2H), 7.37 – 7.31 (m, 3H), 6.94 – 6.90 (m, 2H), 4.71 (s, 1H), 3.82 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 203.1, 159.5, 131.9, 129.2, 128.6, 128.5, 127.0, 123.0, 114.5, 87.1, 85.3, 55.5, 52.5, 26.1. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 265.1219, $\text{C}_{18}\text{H}_{17}\text{O}_2^+$ requires 265.1223.

3-(4-bromophenyl)-5-phenylpent-4-yn-2-one (**1d**)



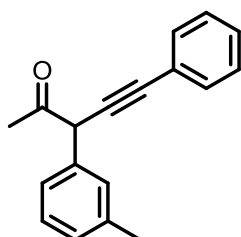
This reaction was performed on 0.84 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1d** (220 mg, 83%). ^1H NMR (400 MHz, Chloroform-d) δ 7.41 (td, $J = 7.7, 7.1, 3.0$ Hz, 4H), 7.29 – 7.25 (m, 5H), 4.63 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 202.1, 134.0, 132.1, 131.8, 129.8, 128.8, 128.5, 122.5, 122.2, 87.6, 84.4, 52.6, 26.4. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 313.0218, $\text{C}_{17}\text{H}_{14}\text{BrO}^+$ requires 313.0223.

3-(4-chlorophenyl)-5-phenylpent-4-yn-2-one (**1e**)



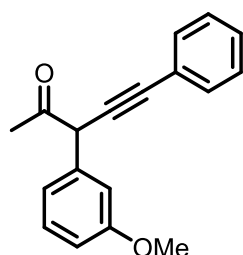
This reaction was performed on 0.45 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1e** (115 mg, 96%). ^1H NMR (500 MHz, Chloroform-d) δ 7.50 (dd, $J = 7.0, 2.8$ Hz, 2H), 7.46 – 7.42 (m, 2H), 7.37 (d, $J = 1.9$ Hz, 1H), 7.36 (d, $J = 2.1$ Hz, 2H), 7.34 (t, $J = 2.5$ Hz, 1H), 7.32 (s, 1H), 4.74 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 202.3, 134.1, 133.5, 131.9, 129.5, 129.2, 128.8, 128.6, 122.6, 87.7, 84.5, 52.6, 26.4. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 269.0726, $\text{C}_{17}\text{H}_{14}\text{ClO}^+$ requires 269.0728.

5-phenyl-3-(m-tolyl)pent-4-yn-2-one (**1f**)



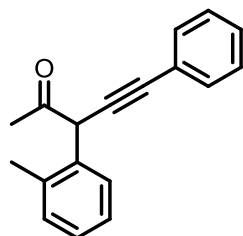
This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1f** (68.7 mg, 92%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.48 (m, 2H), 7.35 – 7.30 (m, 4H), 7.30 – 7.27 (m, 2H), 7.13 (d, $J = 7.4$ Hz, 1H), 4.73 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.9, 138.8, 134.9, 131.8, 128.9, 128.8, 128.7, 128.6, 128.5, 125.1, 122.9, 87.2, 85.2, 53.2, 53.2, 26.2, 21.5. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 249.1272, $\text{C}_{18}\text{H}_{17}\text{O}^+$ requires 249.1274.

3-(3-methoxyphenyl)-5-phenylpent-4-yn-2-one (**1g**)



This reaction was performed on 0.37 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1g** (87 mg, 88%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.50 (dd, $J = 6.6, 3.1$ Hz, 2H), 7.37 – 7.28 (m, 4H), 7.11 – 7.05 (m, 2H), 6.87 (dd, $J = 8.3, 2.6$ Hz, 1H), 4.74 (s, 1H), 3.83 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.7, 160.2, 136.5, 131.9, 130.1, 128.7, 128.5, 122.9, 120.4, 113.8, 113.5, 87.4, 84.9, 55.4, 53.4, 26.2. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 265.1219, $\text{C}_{18}\text{H}_{17}\text{O}_2^+$ requires 265.1223.

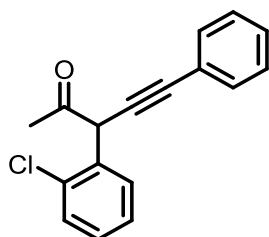
5-phenyl-3-(*o*-tolyl)pent-4-yn-2-one (**1h**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1h** (71 mg, 96%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, $J = 7.4$ Hz, 1H), 7.39 (dd, $J = 6.9, 3.1$ Hz, 2H), 7.22 (p, $J = 3.5$ Hz, 3H), 7.18 (td, $J = 7.4, 1.6$ Hz, 1H), 7.15 – 7.11 (m, 1H), 7.09 (d, $J = 8.2$ Hz, 1H), 4.82 (s, 1H), 2.23 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.2, 136.5, 133.8, 131.8, 130.9, 128.8, 128.5, 128.4, 128.1, 126.7, 122.9, 86.7, 85.5, 50.8, 26.6, 19.6. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 249.1269, $\text{C}_{18}\text{H}_{17}\text{O}^+$ requires 249.1274.

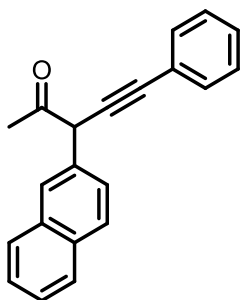
3-(2-chlorophenyl)-5-phenylpent-4-yn-2-one (**1i**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1i** (79.8 mg, 99%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.73 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.51 – 7.46 (m, 2H), 7.41 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.37 – 7.31 (m, 4H), 7.29 (dd, $J = 7.7, 1.8$ Hz, 1H), 5.26 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 200.8, 133.8, 133.8, 131.9, 130.6, 129.7, 129.4, 128.8, 128.5, 127.5, 122.7, 87.0, 84.2, 49.9, 28.1. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 269.0726, $\text{C}_{17}\text{H}_{14}\text{ClO}^+$ requires 269.0728.

3-(naphthalen-2-yl)-5-phenylpent-4-yn-2-one (**1j**)

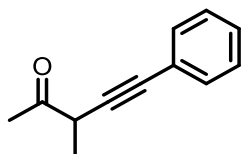


This reaction was performed on 0.35 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1j** (89.7 mg, 88%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.74 (t, $J = 9.4$ Hz, 3H), 7.49 – 7.42 (m, 3H), 7.42 – 7.35 (m, 2H), 7.27 – 7.21 (m, 3H), 4.83 (s, 1H), 2.19 (s, 3H). ^{13}C

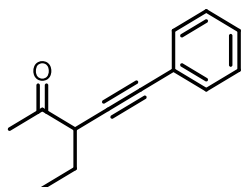
NMR (126 MHz, Chloroform-*d*) δ 202.7, 133.6, 133.0, 132.4, 131.9, 128.9, 128.7, 128.5, 128.1, 127.8, 127.2, 126.6, 126.4, 125.7, 122.9, 87.6, 85.0, 53.4, 26.4. *m/z* HRMS (ESI) found $[M+H]^+$ 285.1271, $C_{21}H_{17}O^+$ requires 285.1274.

3-methyl-5-phenylpent-4-yn-2-one (**1k**)



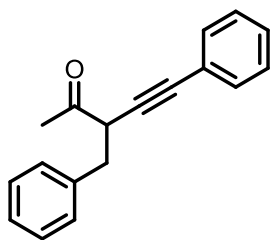
This reaction was performed on 0.71 mmol scale of **S6** according to **method B**. Purification by extraction with petroleum ether to give the product **1k** (115 mg, 94%). 1H NMR (500 MHz, Chloroform-*d*) δ 7.42 (dd, $J = 6.8, 3.1$ Hz, 2H), 7.34 – 7.28 (m, 3H), 3.51 (q, $J = 7.1$ Hz, 1H), 2.39 (s, 3H), 1.42 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 205.5, 131.7, 128.4, 128.4, 123.1, 87.8, 84.1, 40.5, 27.6, 16.7. *m/z* HRMS (ESI) found $[M+H]^+$ 173.0960, $C_{12}H_{13}O^+$ requires 173.0961.

3-ethyl-5-phenylpent-4-yn-2-one (**1l**)



This reaction was performed on 0.47 mmol scale of **S9** according to **method C**. Purification by extraction with petroleum ether to give the product **1l** (85.4 mg, 97%). 1H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.39 (m, 2H), 7.34 – 7.27 (m, 3H), 3.36 (dd, $J = 8.1, 5.9$ Hz, 1H), 2.37 (s, 3H), 1.96 – 1.73 (m, 2H), 1.07 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 205.6, 131.7, 128.4, 128.3, 123.2, 86.7, 85.2, 48.1, 27.9, 24.9. *m/z* HRMS (ESI) found $[M+H]^+$ 187.1116, $C_{13}H_{15}O^+$ requires 187.1117.

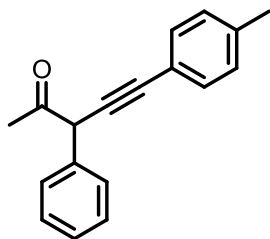
3-benzyl-5-phenylpent-4-yn-2-one (**1m**)



This reaction was performed on 0.97 mmol scale of **S9** according to **method C**. Purification by extraction with petroleum ether to give the product **1m** (196.9 mg, 82%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.28 (m, 7H), 7.26 – 7.22 (m, 1H), 3.70 (dd, $J = 8.5, 5.8$ Hz, 1H), 3.21 (dd, $J = 13.6, 5.8$ Hz, 1H), 3.03 (dd, $J = 13.6, 8.5$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 204.6, 138.4, 131.7, 129.4, 128.5, 128.4, 126.8, 123.0, 86.3, 86.0, 48.3, 37.4, 28.5. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 249.1273, $\text{C}_{18}\text{H}_{17}\text{O}^+$ requires 249.1274.

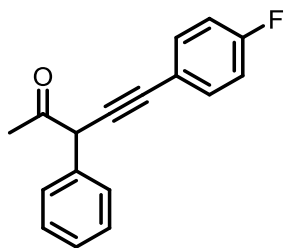
3-phenyl-5-(*p*-tolyl)pent-4-yn-2-one (**1n**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1n** (73.6 mg, 99%).

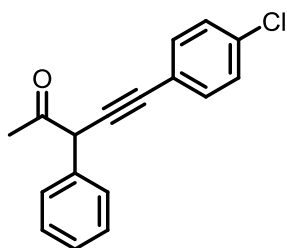
^1H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.39 (dd, $J = 8.0, 6.3$ Hz, 4H), 7.35 – 7.31 (m, 1H), 7.15 (d, $J = 7.9$ Hz, 2H), 4.76 (s, 1H), 2.36 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 203.0, 138.8, 135.1, 131.7, 129.3, 129.1, 128.1, 128.1, 119.8, 84.3, 53.4, 21.6. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 249.1269, $\text{C}_{18}\text{H}_{17}\text{O}^+$ requires 249.1274.

5-(4-fluorophenyl)-3-phenylpent-4-yn-2-one (**1o**)



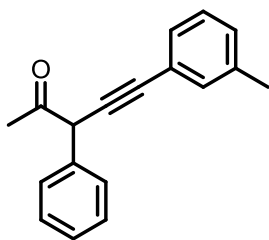
This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1o** (71.8 mg, 95%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 4H), 7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 1H), 7.06 – 7.01 (m, 2H), 4.76 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.6, 135.0, 133.8 (d, $J = 8.3$ Hz),, 129.1, 128.2, 128.1, 119.0, 115.8 (d, $J = 22.3$ Hz), 86.2, 84.8, 53.3, 26.4. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -110.6. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 253.1019, $\text{C}_{17}\text{H}_{14}\text{FO}^+$ requires 253.1023.

5-(4-chlorophenyl)-3-phenylpent-4-yn-2-one (**1p**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1p** (75.6 mg, 94%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 2H), 7.43 (d, $J = 1.9$ Hz, 1H), 7.42 – 7.39 (m, 3H), 7.33 (q, $J = 2.3$ Hz, 2H), 7.30 (d, $J = 1.9$ Hz, 1H), 4.76 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.5, 134.9, 134.7, 133.1, 129.2, 128.9, 128.2, 128.1, 53.3, 26.4. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 269.0722, $\text{C}_{17}\text{H}_{14}\text{ClO}^+$ requires 269.0728.

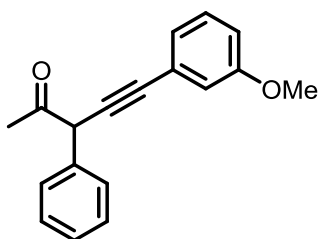
3-phenyl-5-(*m*-tolyl)pent-4-yn-2-one (**1q**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1q** (69.2 mg, 93%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.51 (dd, $J = 7.4, 1.8$ Hz, 2H), 7.41 – 7.37 (m, 2H), 7.32 (qd, $J = 7.2, 1.4$ Hz, 3H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.16 (d, $J = 7.5$ Hz, 1H), 4.76 (s, 1H), 2.35 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.9, 138.2, 135.1, 132.4, 129.5, 129.1, 128.9, 128.4, 128.1, 122.7, 87.6, 84.6, 53.4, 26.3, 21.4. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 249.1269, $\text{C}_{18}\text{H}_{17}\text{O}^+$ requires 249.1274.

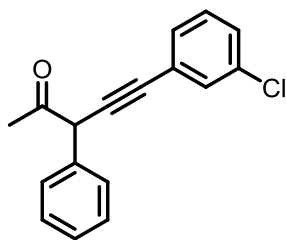
5-(3-methoxyphenyl)-3-phenylpent-4-yn-2-one (**1r**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1r** (71 mg, 90%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.33 (t, $J = 7.3$ Hz, 1H), 7.24 (d, $J = 7.9$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 2.4$ Hz, 1H), 6.91 (dd, $J = 8.3, 2.4$ Hz, 1H), 4.76 (s, 1H), 3.82 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 159.5, 135.0, 129.6, 129.1, 128.1, 128.1, 124.4, 123.9, 116.8, 115.2, 87.2, 84.9, 55.5, 53.3, 26.3. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 265.1217, $\text{C}_{18}\text{H}_{17}\text{O}_2^+$ requires 265.1223.

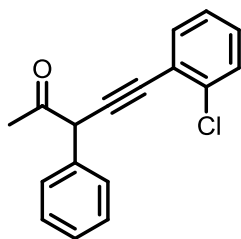
5-(3-chlorophenyl)-3-phenylpent-4-yn-2-one (**1s**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1s** (76 mg, 95%).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.44 (m, 3H), 7.41 – 7.36 (m, 2H), 7.35 (dt, $J = 5.2, 1.4$ Hz, 1H), 7.33 – 7.28 (m, 2H), 7.23 (d, $J = 7.9$ Hz, 1H), 4.76 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.3, 134.8, 134.4, 131.8, 130.0, 129.8, 129.2, 129.0, 128.2, 128.1, 124.6, 86.4, 85.9, 53.3, 26.4. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 269.0726, $\text{C}_{17}\text{H}_{14}\text{ClO}^+$ requires 269.0728.

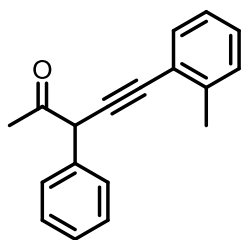
5-(2-chlorophenyl)-3-phenylpent-4-yn-2-one (**1t**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1t** (74 mg, 93%).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 (ddd, $J = 14.5, 7.3, 1.8$ Hz, 3H), 7.45 – 7.37 (m, 3H), 7.36 – 7.32 (m, 1H), 7.31 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 4.81 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.6, 136.4, 134.7, 133.5, 129.7, 129.5, 129.1, 128.2, 128.1, 126.7, 122.8, 90.3, 84.4, 53.6, 26.3. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 269.0724, $\text{C}_{17}\text{H}_{14}\text{ClO}^+$ requires 269.0728.

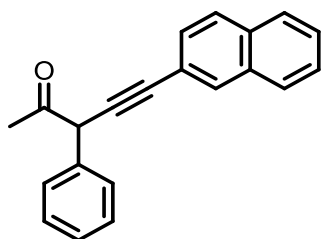
3-phenyl-5-(*o*-tolyl)pent-4-yn-2-one (**1u**)



This reaction was performed on 0.3 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1u** (68 mg, 92%).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 2H), 7.49 – 7.44 (m, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 7.24 (dd, $J = 6.4, 1.5$ Hz, 2H), 7.16 (td, $J = 7.0, 6.4, 2.4$ Hz, 1H), 4.82 (s, 1H), 2.49 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.9, 140.5, 135.2, 132.3, 129.7, 129.1, 128.7, 128.1, 125.8, 122.7, 88.8, 86.4, 53.6, 26.3, 21.0. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 249.1269, $\text{C}_{18}\text{H}_{17}\text{O}^+$ requires 249.1274.

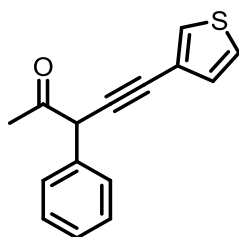
5-(naphthalen-2-yl)-3-phenylpent-4-yn-2-one (**1v**)



This reaction was performed on 0.95 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1v** (221 mg, 81%).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.03 (d, $J = 1.6$ Hz, 1H), 7.82 (td, $J = 8.6, 4.5$ Hz, 3H), 7.55 (dt, $J = 8.2, 3.5$ Hz, 3H), 7.52 – 7.48 (m, 2H), 7.44 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 4.82 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.8, 135.1, 133.1, 133.0, 131.8, 129.1, 128.5, 128.2, 128.1, 128.1, 127.9, 127.9, 126.9, 126.8, 120.1, 87.7, 85.3, 53.4, 26.4. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 285.1269, $\text{C}_{21}\text{H}_{17}\text{O}^+$ requires 285.1274.

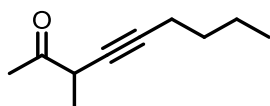
3-phenyl-5-(thiophen-3-yl)pent-4-yn-2-one (**1w**)



This reaction was performed on 0.83 mmol scale of **S5** according to **method A**. Purification by extraction with petroleum ether to give the product **1w** (161 mg, 81%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.48 (m, 3H), 7.42 – 7.38 (m, 2H), 7.35 – 7.33 (m, 1H), 7.29 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.17 (dd, $J = 5.0, 1.2$ Hz, 1H), 4.76 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.7, 135.0, 130.0, 129.1, 129.1, 128.1, 128.1, 125.5, 121.8, 84.6, 82.4, 53.3, 26.3. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 241.0680, $\text{C}_{15}\text{H}_{13}\text{SO}^+$ requires 241.0682.

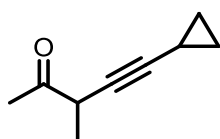
3-methylnon-4-yn-2-one (**1x**)



This reaction was performed on 2.1 mmol scale of **S6** according to **method B**. Purification by extraction with petroleum ether to give the product **1x** (302 mg, 94%).

^1H NMR (500 MHz, Chloroform-*d*) δ 3.24 (qt, $J = 7.0, 2.4$ Hz, 1H), 2.29 (s, 3H), 2.18 (td, $J = 7.0, 2.4$ Hz, 2H), 1.51 – 1.44 (m, 2H), 1.43 – 1.35 (m, 2H), 1.28 (d, $J = 7.0$ Hz, 3H), 0.90 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.5, 84.4, 78.4, 40.0, 31.0, 27.3, 22.1, 18.6, 17.0, 13.7. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 153.1274, $\text{C}_{10}\text{H}_{17}\text{O}^+$ requires 153.1274.

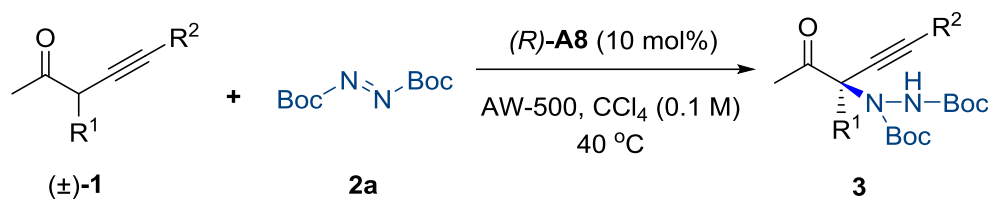
5-cyclopropyl-3-methylpent-4-yn-2-one (**1y**)



This reaction was performed on 2.17 mmol scale of **S6** according to **method B**. Purification by extraction with petroleum ether to give the product **1y** (255 mg, 86%).

^1H NMR (400 MHz, Chloroform-*d*) δ 3.21 (qd, $J = 7.1, 2.0$ Hz, 1H), 2.27 (s, 3H), 1.26 (d, $J = 7.1$ Hz, 3H), 1.24 – 1.18 (m, 1H), 0.79 – 0.69 (m, 2H), 0.66 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 87.3, 73.7, 40.0, 27.3, 17.0, 8.2. m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 137.0961, $\text{C}_9\text{H}_{13}\text{O}^+$ requires 137.0961.

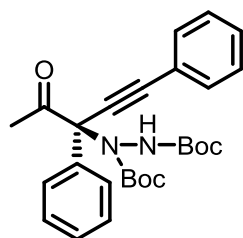
Asymmetric amination of α -alkynyl ketone **3**:



General procedure for the asymmetric synthesis of products **3**:

To a 8 mL vial was added **2a** (0.4 mmol, 2.0 equiv.) and (*R*)-**A8** (0.02 mmol, 0.1 equiv.) and AW-500 MS (200 mg) subsequently under N₂ atmosphere. Then a solution of **1** (0.2 mmol, 1.0 equiv.) in dry CCl₄ (2 mL) was added using a syringe. After stirring at 40 °C for 16 h, the reaction mixture was cooled to rt and filtered through Celite. The filtrate were concentrated under vacuum to afford a residue, which was purified by column chromatography (petroleum ether/EtOAc = 15:1 to 8:1) to give the product **3**.

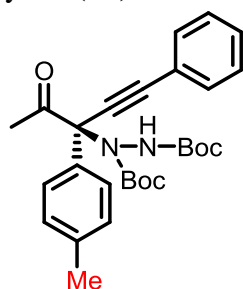
Di-tert-butyl-(*R*)-1-(4-oxo-1,3-diphenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3a**)



The reaction was performed on 1 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3a** as yellow oil (243 mg, 52% yield.)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.86 (m, 1H), 7.71 – 7.51 (m, 3H), 7.38 (m, 6H), 6.62 – 6.26 (m, 1H), 2.72 – 2.13 (m, 3H), 1.56 – 1.41 (m, 18H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 201.4, 156.0, 154.5, 134.5, 131.8, 128.8, 128.7, 128.3, 128.1, 127.7, 122.2, 87.6, 83.4, 80.7, 75.3, 28.0, 27.8, 25.6. $[\alpha]_D^{21} = 3.60$ (*c* = 1.0, CHCl₃). *m/z* HRMS (ESI) found $[M+H]^+$ 465.2390, C₂₇H₃₃N₂O₅⁺ requires 465.2384. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; *t_R* = 7.15 min (minor), 8.43 min (major); 96.5:3.5 er.

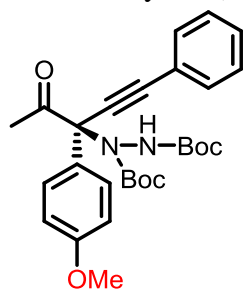
Di-tert-butyl-(*R*)-1-(4-oxo-1-phenyl-3-(*p*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3b**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3b** as yellow oil (52 mg, 77% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.56 (m, 1H), 7.50 (m, 3H), 7.33 (m, 3H), 7.18 (m, 2H), 6.58 – 5.89 (m, 1H), 2.62 – 2.13 (m, 6H), 1.53 – 1.35 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.1, 154.6, 138.6, 132.0, 131.9, 129.6, 129.1, 128.5, 125.6, 122.6, 83.8, 81.2, 80.9, 28.2, 28.0, 21.2, 14.2. $[\alpha]_D^{21} = 3.40$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 479.2551, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 479.2540. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_R = 7.45$ min (minor), 9.87 min (major); 96.5:3.5 er.

Di-tert-butyl-(*R*)-1-(3-(4-methoxyphenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3c**)

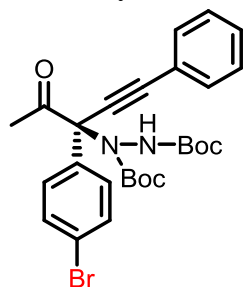


The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3c** as yellow oil (65 mg, 73% yield.)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (m, 1H), 7.51 (m, 3H), 7.41 – 7.28 (m, 3H), 6.89 (m, 2H), 6.36 – 5.89 (m, 1H), 3.79 (m, 3H), 2.61 – 2.14 (m, 3H), 1.50 – 1.35 (m,

18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.9, 155.0, 153.5, 130.9, 128.9, 128.6, 127.8, 127.4, 121.4, 112.6, 87.7, 80.4, 79.8, 54.3, 27.1, 27.1, 24.8. $[\alpha]_{\text{D}}^{21} = -2.20$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 495.2495, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_6^+$ requires 495.2490. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 9.39$ min (minor), 13.71 min (major); 96.5:3.5 er.

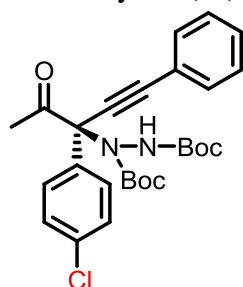
Di-tert-butyl-(*R*)-1-(3-(4-bromophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3d**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3d** as yellow oil (61 mg, 56% yield.)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.69 (m, 1H), 7.56 – 7.42 (m, 5H), 7.41 – 7.28 (m, 3H), 6.37 – 5.98 (m, 1H), 2.68 – 2.12 (m, 3H), 1.48 – 1.34 (m, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.9, 154.7, 132.0, 131.9, 131.4, 130.3, 129.0, 128.6, 123.3, 122.1, 81.5, 81.3, 28.2, 28.1, 25.7. $[\alpha]_{\text{D}}^{21} = 12.20$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 543.1495, $\text{C}_{27}\text{H}_{32}\text{BrN}_2\text{O}_5^+$ requires 543.1489. HPLC: Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 10.94$ min (minor), 18.01 min (major); 97.5:2.5 er.

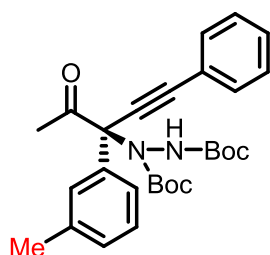
Di-tert-butyl-(*R*)-1-(3-(4-chlorophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3e**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3e** as yellow oil (38.2 mg, 48% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.80 (m, 1H), 7.57 – 7.47 (m, 3H), 7.40 – 7.30 (m, 5H), 6.34 – 5.93 (m, 1H), 2.66 – 2.31 (m, 3H), 1.50 – 1.38 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.9, 135.0, 133.4, 131.9, 130.0, 129.8, 129.2, 128.5, 122.1, 81.3, 61.3, 28.2, 28.1, 25.7. $[\alpha]_D^{21} = 14.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 499.2004, $\text{C}_{27}\text{H}_{32}\text{ClN}_2\text{O}_5^+$ requires 499.1994. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_R = 5.27$ min (minor), 7.80 min (major); 97:3 er .

Di-tert-butyl-(*R*)-1-(4-oxo-1-phenyl-3-(*m*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3f**)

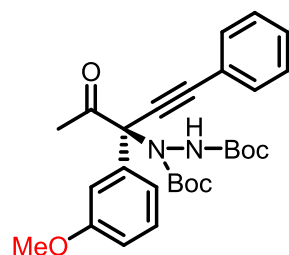


The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3f** as yellow oil (47.5 mg, 66% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.41 (m, 2H), 7.35 – 7.19 (m, 5H), 7.19 – 7.04 (m, 2H), 6.45 – 5.65 (m, 1H), 2.57 – 2.09 (m, 5H), 1.84 – 1.78 (m, 1H), 1.43 – 1.28 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.0, 154.6, 154.3, 137.7, 134.5, 132.0, 129.9, 128.9, 128.2, 126.9, 126.5, 125.6, 122.5, 86.3, 83.8, 81.0, 28.2, 28.0, 21.7, 14.7. $[\alpha]_D^{21} = 3.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 479.2549, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 479.2540. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_R = 6.73$ min (minor), 8.17 min (major); 95.5:4.5 er .

Di-tert-butyl-(*R*)-1-(3-(3-methoxyphenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,

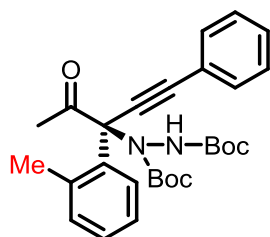
2-dicarboxylate (**3g**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3g** as yellow oil (54 mg, 58% yield.)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 (m, 3H), 7.42 – 7.25 (m, 4H), 7.20 (m, 1H), 6.90 (m, 1H), 6.40 – 5.96 (m, 1H), 3.83 (m, 3H), 2.66 – 2.17 (m, 3H), 1.53 – 1.37 (m, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 159.6, 154.6, 136.0, 132.0, 129.9, 129.0, 128.5, 122.4, 120.7, 115.8, 114.4, 83.2, 81.3, 81.0, 55.3, 28.2, 28.2, 25.9. $[\alpha]_D^{21} = 3.40$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 495.2499, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_6^+$ requires 495.2490. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_R = 8.27$ min (minor), 9.43 min (major); 96.5:3.5 er .

Di-tert-butyl-(*S*)-1-(4-oxo-1-phenyl-3-(*o*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3h**)

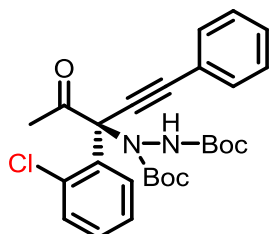


The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3h** as yellow oil (45 mg, 47% yield.)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 (m, 2H), 7.29 – 7.07 (m, 6H), 7.06 – 6.88 (m, 1H), 6.39 – 6.00 (m, 1H), 2.67 – 2.22 (m, 6H), 1.40 – 1.28 (m, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 154.8, 139.4, 138.6, 133.6, 133.1, 131.7, 128.8, 128.4, 126.2, 125.7, 122.5, 88.9, 85.3, 83.5, 81.0, 28.3, 28.1, 26.0, 22.3. $[\alpha]_D^{21} = 34.60$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 479.2549, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_5^+$

requires 479.2540. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 8.00 min (minor), 9.04 min (major); 98:2 er .

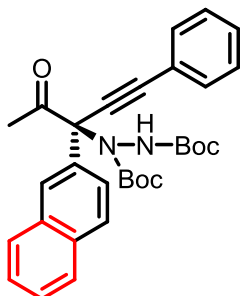
Di-tert-butyl-(*S*)-1-(3-(2-chlorophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3i**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3i** as yellow oil (50 mg, 69% yield.)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.42 (m, 3H), 7.40 (m, 1H), 7.31 (m, 5H), 6.44 (m, 1H), 2.55 (m, 3H), 1.49 – 1.34 (m, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.9, 154.3, 134.5, 133.6, 132.0, 131.8, 131.5, 129.7, 128.9, 128.3, 126.7, 122.4, 89.3, 83.8, 81.3, 28.3, 28.1, 25.5. $[\alpha]_D^{21}$ = 67.20 (c = 1.0, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 499.1999, $\text{C}_{27}\text{H}_{32}\text{ClN}_2\text{O}_5^+$ requires 499.1994. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 8.38 min (minor), 11.80 min (major); 99:1 er .

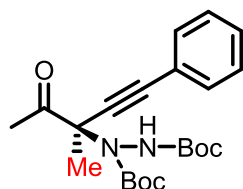
Di-tert-butyl-(*R*)-1-(3-(naphthalen-2-yl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3j**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3j** as yellow oil (50 mg, 58% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 8.43 – 7.97 (m, 1H), 7.86 (m, 3H), 7.76 – 7.66 (m, 1H), 7.62 – 7.46 (m, 4H), 7.42 – 7.31 (m, 3H), 6.52 – 5.90 (m, 1H), 2.69 – 2.15 (m, 3H), 1.53 – 1.33 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.2, 154.7, 133.6, 133.2, 132.1, 132.0, 129.1, 128.6, 128.4, 127.8, 127.6, 127.0, 126.7, 126.4, 125.4, 122.5, 83.8, 81.7, 81.1, 28.2, 28.1, 26.0. $[\alpha]_{\text{D}}^{21} = 6.40$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 515.2551, $\text{C}_{31}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 515.2540. HPLC: Chiralpak IC column, 97:03 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 23.16$ min (minor), 28.56 min (major); 95:5 er .

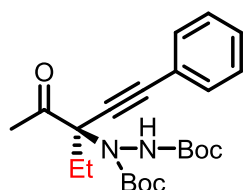
Di-tert-butyl-(*R*)-1-(3-methyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3k**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3k** as yellow oil (45 mg, 70% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.43 (m, 1H), 7.40 (m, 2H), 7.30 (m, 2H), 6.37 (m, 1H), 2.59 – 2.27 (m, 3H), 1.74 – 1.62 (m, 3H), 1.48 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 133.3, 131.9, 128.4, 122.4, 40.8, 30.3, 28.3, 25.5. $[\alpha]_{\text{D}}^{21} = 33.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 403.2233, $\text{C}_{22}\text{H}_{31}\text{N}_2\text{O}_5^+$ requires 403.2227. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 6.51$ min (minor), 7.35 min (major); 99:1 er .

Di-tert-butyl-(*R*)-1-(3-ethyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3l**)

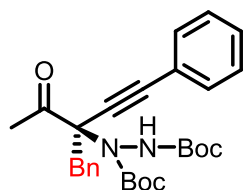


The reaction was performed on 0.2 mmol scale under the standard conditions.

Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3l** as yellow oil (60 mg, 72% yield.)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.34 (m, 2H), 7.22 (m, 3H), 6.47 – 6.15 (m, 1H), 2.40 (m, 3H), 2.21 – 1.87 (m, 2H), 1.43 – 1.36 (m, 18H), 0.98 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.5, 154.8, 153.9, 132.0, 128.8, 128.3, 122.4, 88.4, 84.4, 81.2, 31.6, 28.3, 28.2, 25.3, 9.2. $[\alpha]_D^{21} = 62.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 417.2389, $\text{C}_{23}\text{H}_{33}\text{N}_2\text{O}_5^+$ requires 417.2384 HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_R = 5.92$ min (minor), 7.03 min (major); 99:1 er.

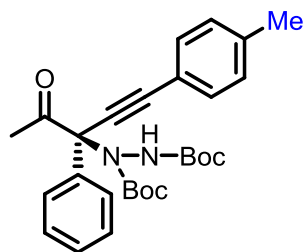
Di-tert-butyl-(*R*)-1-(3-benzyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3m**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3m** as yellow oil (65 mg, 72% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 2H), 7.25 (m, 6H), 7.22 – 7.17 (m, 2H), 4.86 (m, 1H), 3.57 – 3.35 (m, 1H), 3.25 (m, 1H), 2.46 (m, 3H), 1.44 – 1.25 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 131.8, 130.4, 129.0, 128.7, 128.4, 127.7, 127.3, 122.1, 90.2, 83.6, 81.8, 81.0, 31.6, 30.2, 28.1, 24.5. $[\alpha]_D^{21} = 185.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 479.2550, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 479.2540. HPLC: Chiralpak IC column, 95:05 hexanes/isopropanol, 1 ml/min; $t_R = 9.50$ min (minor), 15.37 min (major); 99.5:0.5 er .

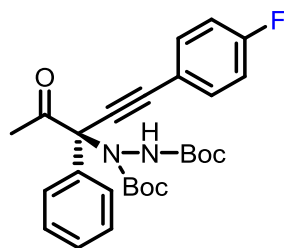
Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*p*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3n**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3n** as yellow oil (52 mg, 73% yield.)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 (m, 1H), 7.60 (m, 1H), 7.39 (m, 5H), 7.15 (m, 2H), 6.38 – 5.91 (m, 1H), 2.71 – 2.13 (m, 6H), 1.52 – 1.36 (m, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 139.2, 134.8, 131.9, 129.1, 128.9, 128.3, 127.9, 119.4, 83.8, 81.0, 31.5, 28.2, 28.0, 21.6. $[\alpha]_{\text{D}}^{21} = 7.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 479.2549, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 479.2540. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 8.61$ min (minor), 10.08 min (major); 96.5:3.5 er.

Di-tert-butyl-(*R*)-1-(1-(4-fluorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3o**)

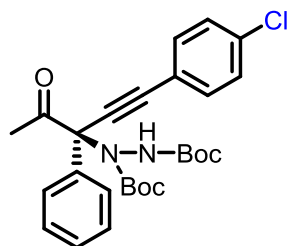


The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3o** as yellow oil (55 mg, 65% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.67 (m, 1H), 7.60 – 7.55 (m, 1H), 7.55 – 7.46 (m, 2H), 7.43 – 7.31 (m, 3H), 7.03 (m, 2H), 6.32 – 5.90 (m, 1H), 2.63 – 2.07 (m, 3H), 1.50 – 1.35 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.9, 162.0, 156.2, 154.7, 135.4, 134.6, 134.0, 133.8, 129.0, 128.4, 128.2, 118.6, 115.8, 115.6, 87.9, 83.8, 81.4, 81.1, 28.2, 28.1, 25.9. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -109.5 –

-110.2 (m). $[\alpha]_D^{21} = 3.20$ (c = 1.0, CHCl₃). m/z HRMS (ESI) found $[M+H]^+$ 483.2297, C₂₇H₃₂FN₂O₅⁺ requires 483.2290. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 6.17 min (minor), 7.17 min (major); 95.5:4.5 er.

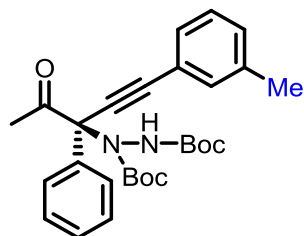
Di-tert-butyl-(*R*)-1-(1-(4-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3p**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3p** as yellow oil (62 mg, 81% yield.)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.77 (m, 1H), 7.57 (m, 1H), 7.44 (m, 2H), 7.33 (m, 5H), 6.56 – 5.95 (m, 1H), 2.65 – 2.10 (m, 3H), 1.49 (s, 3H), 1.47 – 1.34 (m, 18H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 154.5, 134.5, 133.1, 128.8, 128.5, 128.2, 127.8, 121.0, 119.2, 81.1, 31.5, 28.0, 25.9. $[\alpha]_D^{21} = 1.20$ (c = 1.0, CHCl₃). m/z HRMS (ESI) found $[M+H]^+$ 499.2004, C₂₇H₃₂ClN₂O₅⁺ requires 499.1994. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 6.68 min (minor), 7.81 min (major); 91% ee.

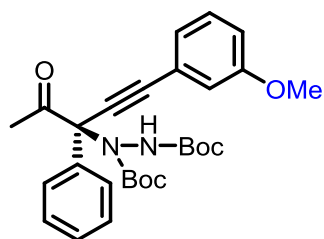
Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*m*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3q**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3q** as yellow oil (78 mg, 72% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.68 (m, 1H), 7.59 (m, 1H), 7.45 – 7.28 (m, 5H), 7.19 (m, 2H), 6.37 – 5.92 (m, 1H), 2.63 – 2.15 (m, 6H), 1.51 – 1.38 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.8, 156.1, 154.7, 138.0, 134.7, 132.6, 129.7, 129.0, 128.9, 128.6, 128.5, 128.3, 122.2, 83.2, 81.6, 81.0, 31.5, 28.2, 28.0, 21.3. $[\alpha]_{\text{D}}^{21} = 8.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 479.2548, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 479.2540. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 7.51$ min (minor), 8.87 min (major); 93.5:6.5 er .

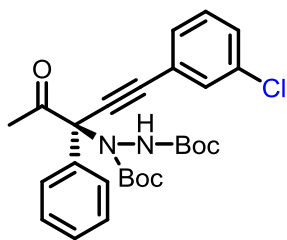
Di-tert-butyl-(*R*)-1-(1-(3-methoxyphenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3r**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3r** as yellow oil (81 mg, 79% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.72 (m, 1H), 7.56 – 7.47 (m, 1H), 7.28 (m, 3H), 7.21 – 7.11 (m, 1H), 7.04 (m, 1H), 7.00 – 6.92 (m, 1H), 6.88 – 6.78 (m, 1H), 6.35 – 5.92 (m, 1H), 3.72 (m, 3H), 2.55 – 2.04 (m, 3H), 1.38 – 1.18 (m, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.5, 134.6, 129.6, 128.6, 128.4, 124.6, 116.6, 115.6, 81.1, 55.4, 28.2, 28.1, 25.9. $[\alpha]_{\text{D}}^{21} = 2.60$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 495.2500, $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_6^+$ requires 495.2490. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 9.15$ min (minor), 10.51 min (major); 97:3 er .

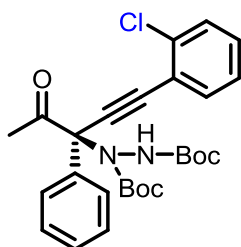
Di-tert-butyl-(*R*)-1-(1-(3-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3s**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3s** as yellow oil (56 mg, 56% yield.)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.57 (m, 1H), 7.53 – 7.39 (m, 2H), 7.38 – 7.13 (m, 6H), 6.28 – 5.84 (m, 1H), 2.56 – 2.04 (m, 3H), 1.41 – 1.28 (m, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.6, 154.5, 135.1, 134.3, 131.9, 129.9, 129.3, 129.0, 128.5, 128.2, 127.8, 124.1, 87.4, 83.3, 81.7, 81.1, 28.2, 28.0, 25.9. $[\alpha]_{\text{D}}^{21} = 2.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 499.2002, $\text{C}_{27}\text{H}_{32}\text{ClN}_2\text{O}_5^+$ requires 499.1994. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 9.23$ min (minor), 11.17 min (major); 96.5:3.5 er.

Di-tert-butyl-(*R*)-1-(1-(2-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3t**)

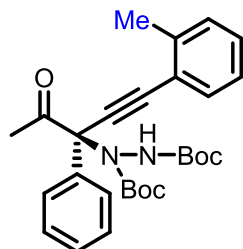


The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3t** as yellow oil (60 mg, 81% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.73 (m, 1H), 7.65 (m, 1H), 7.60 – 7.51 (m, 1H), 7.45 – 7.27 (m, 5H), 7.25 – 7.19 (m, 1H), 6.32 – 5.89 (m, 1H), 2.63 – 2.18 (m, 3H), 1.50 – 1.33 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.0, 153.1, 135.2, 132.6, 128.9, 127.8, 127.5, 127.2, 125.6, 123.3, 122.5, 121.4, 90.4, 84.7, 82.7, 79.9, 27.0, 26.9, 25.1. $[\alpha]_{\text{D}}^{21} = 1.40$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$

499.2001, $C_{27}H_{32}ClN_2O_5^+$ requires 499.1994. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 6.94 min (minor), 7.97 min (major); 97:3 er .

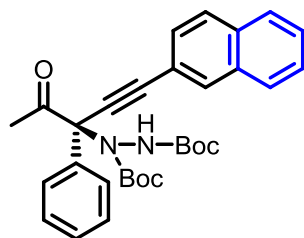
Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*o*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3u**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3u** as yellow oil (54 mg, 75% yield.)

1H NMR (500 MHz, Chloroform-*d*) δ 7.97 – 7.72 (m, 1H), 7.63 (m, 1H), 7.51 (m, 1H), 7.39 (m, 3H), 7.31 – 7.12 (m, 3H), 6.36 – 5.91 (m, 1H), 2.68 – 2.17 (m, 6H), 1.52 – 1.35 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.1, 154.6, 140.8, 135.7, 132.6, 129.7, 128.9, 128.3, 125.7, 124.5, 123.6, 122.3, 83.8, 81.3, 81.0, 31.6, 28.2, 25.7, 20.9. $[\alpha]_D^{21} = 7.20$ ($c = 1.0$, $CHCl_3$). m/z HRMS (ESI) found $[M+H]^+$ 479.2549, $C_{28}H_{35}N_2O_5^+$ requires 479.2540. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 6.05 min (minor), 6.96 min (major); 95.5:4.5 er .

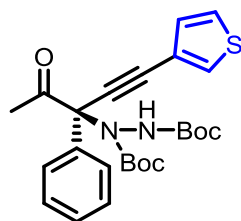
Di-tert-butyl-(*R*)-1-(1-(naphthalen-2-yl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3v**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3v** as yellow oil (62 mg, 75% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 8.10 – 8.02 (m, 1H), 7.91 (m, 1H), 7.86 – 7.74 (m, 3H), 7.64 (m, 1H), 7.60 – 7.46 (m, 3H), 7.45 – 7.33 (m, 3H), 6.39 – 5.93 (m, 1H), 2.70 – 2.18 (m, 3H), 1.52 – 1.36 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.7, 133.1, 133.0, 132.2, 132.0, 129.0, 128.6, 128.4, 127.9, 127.1, 127.0, 126.8, 126.7, 119.7, 83.4, 81.7, 81.1, 68.1, 28.2, 28.1, 25.9. $[\alpha]_{\text{D}}^{21} = 3.20$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 515.2550, $\text{C}_{31}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 515.2540. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 7.95$ min (minor), 9.29 min (major); 96.5:3.5 er .

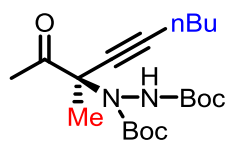
Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(thiophen-3-yl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3w**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3w** as yellow oil (39 mg, 65% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.78 (m, 1H), 7.61 – 7.48 (m, 2H), 7.44 – 7.27 (m, 4H), 7.22 – 7.12 (m, 1H), 6.53 – 5.86 (m, 1H), 2.62 – 2.12 (m, 3H), 1.48 – 1.27 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.3, 134.6, 130.0, 129.6, 128.9, 128.5, 128.4, 125.6, 125.5, 83.8, 81.0, 31.6, 28.1, 25.9. $[\alpha]_{\text{D}}^{21} = 1.20$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 471.1958, $\text{C}_{25}\text{H}_{31}\text{SN}_2\text{O}_5^+$ requires 471.1948. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 8.37$ min (minor), 9.80 min (major); 96:4 er .

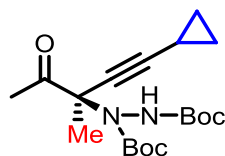
Di-tert-butyl (*R*)-1-(3-methyl-2-oxonon-4-yn-3-yl)hydrazine-1,2-dicarboxylate (**3x**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3x** as yellow oil (41 mg, 53% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 6.29 (m, 1H), 2.51 – 2.24 (m, 3H), 2.18 (m, 2H), 1.48 (m, 13H), 1.42 – 0.87 (m, 15H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 31.6, 30.5, 28.3, 24.3, 23.4, 22.0, 18.6, 13.6. $[\alpha]_{\text{D}}^{21} = 36.60$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 383.2543, $\text{C}_{20}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 383.2540. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 7.31$ min (major); > 99.5:0.5 er .

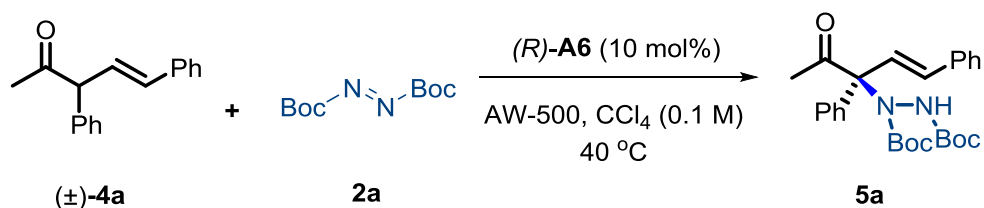
Di-tert-butyl-(*R*)-1-(1-cyclopropyl-3-methyl-4-oxopent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3y**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **3y** as yellow oil (22 mg, 32% yield.)

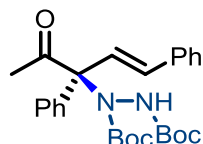
^1H NMR (500 MHz, Chloroform-*d*) δ 6.50 – 6.31 (m, 1H), 2.48 – 2.24 (m, 3H), 1.48 – 1.43 (m, 21H), 1.26 – 1.20 (m, 1H), 0.75 (m, 2H), 0.65 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 29.8, 28.1, 22.8, 14.3, 8.6, 1.2. $[\alpha]_{\text{D}}^{21} = 19.00$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 367.2233, $\text{C}_{19}\text{H}_{31}\text{N}_2\text{O}_5^+$ requires 367.2227. HPLC: Chiralpak IC column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 7.06$ min (minor), 8.69 min (major); 97:3 er .

Control experiments:



Transformation of **4a** into product **5a** was using the same procedure as described above in the general procedure for the asymmetric synthesis of products **3**.

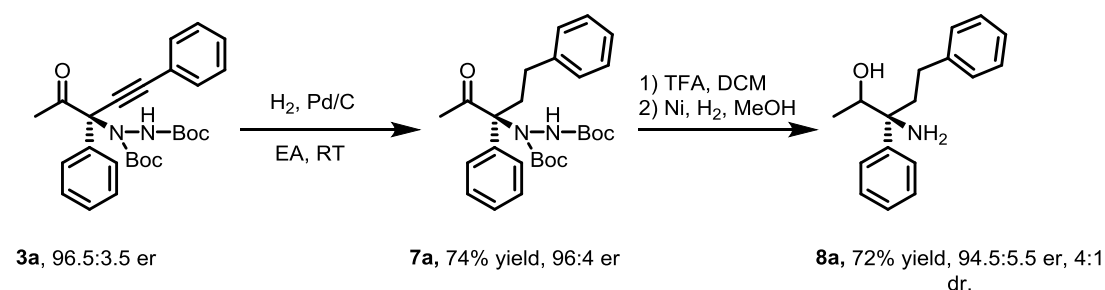
Di-tert-butyl (*S,E*)-1-(4-oxo-1,3-diphenylpent-1-en-3-yl)hydrazine-1,2-dicarboxylate (**5a**)



The reaction was performed on 0.2 mmol scale under the standard conditions. Purification by column chromatography (petroleum ether/EtOAc = 10:1) provided **5a** as yellow oil (35 mg, 56% yield.)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.28 (m, 7H), 6.73 – 6.33 (m, 2H), 6.33 – 5.82 (m, 1H), 2.63 – 2.21 (m, 3H), 1.43 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.4, 129.4, 128.8, 128.7, 128.3, 128.2, 128.2, 128.0, 126.8, 81.5, 28.3, 28.1. $[\alpha]_{\text{D}}^{23} = 4.40$ (*c* = 1.0, CHCl_3). *m/z* HRMS (ESI) found $[\text{M}+\text{H}]^+$ 467.2535, $\text{C}_{27}\text{H}_{35}\text{N}_2\text{O}_5^+$ requires 467.2540. HPLC: Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min; $t_{\text{R}} = 10.15$ min (minor), 14.10 min (major); 72:28 er.

Derivatizations of chiral products:



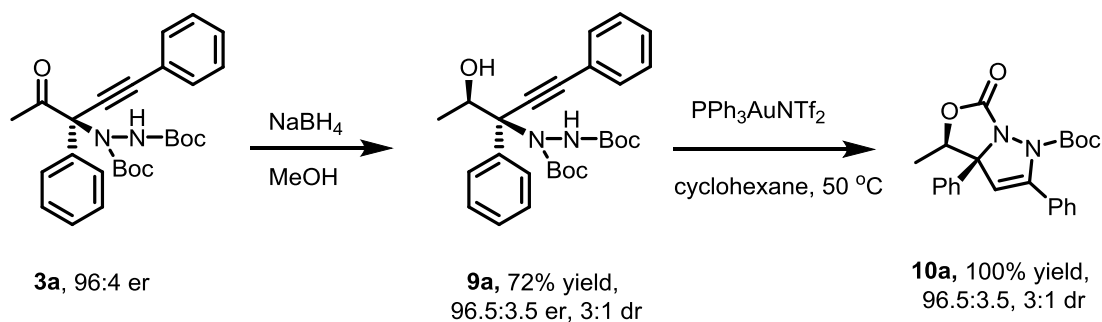
Di-tert-butyl(*S*)-1-(4-oxo-1,3-diphenylpentan-3-yl)hydrazine-1,2-dicarboxylate (**7a**)

To a solution of **3a** (87 mg, 0.19 mmol, 96.5:3.5 er) in EtOAc (5.0 mL) was added 10% Pd/C (200 mg) at room temperature. The mixture was stirred under H_2 atmosphere (1 atm) for 3 h, then filtered through celite and the filtrate were concentrated under

vacuum to afford a residue, which was purified by column chromatography (petroleum ether/EtOAc = 30:1 to 10:1) to give the product **7a** (65 mg, 74%, 96:4 er). ¹H NMR (400 MHz, Methanol-*d*₄) δ 7.96 – 7.40 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.27 – 7.05 (m, 5H), 2.80 – 2.48 (m, 2H), 2.48 – 2.32 (m, 3H), 2.22 (qt, *J* = 13.3, 6.6 Hz, 2H), 1.62 – 1.19 (m, 18H). ¹³C NMR (126 MHz, Methanol-*d*₄) δ 129.6, 129.5, 129.3, 129.3, 128.8, 128.3, 127.0, 81.9, 32.6, 28.7, 28.4, 28.0. [α]_D²³ = -66.40 (c = 1.0, CHCl₃). *m/z* HRMS (ESI) found [M+H]⁺ 469.2703, C₂₇H₃₇N₂O₅⁺ requires 469.2697. HPLC: Chiralpak IC column, 95:05 hexanes/isopropanol, 1 ml/min; t_R = 8.52 min (minor), 9.57 min (major); 96:4 er .

(3*S*)-3-amino-3,5-diphenylpentan-2-ol (**8a**)

To a solution of **7a** (96 mg, 0.2 mmol, 95:5 er) in DCM (5.0 mL) was added TFA (0.5 mL) at 0 °C. After stirring for 3 h at room temperature, the reaction mixture was concentrated under vacuum to afford a residue. To a solution of the above residue in MeOH (5 mL) was added a spoon of Raney Ni (~2 g) at rt. After stirring overnight under H₂ atmosphere (1 atm), the mixture was filtered through Celite and the filtrate were concentrated under vacuum to afford a residue, which was purified by preparative thin layer chromatography (petroleum ether/EtOAc = 5:1) to give the product **8a** (38 mg, 72%, 94.5:5.5 er, 4:1 dr). ¹H NMR (500 MHz, Methanol-*d*₄) δ 7.52 (dd, *J* = 8.8, 6.7 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.11 (m, 3H), 4.62 (s, 1H), 4.13 (q, *J* = 6.5 Hz, 1H), 2.57 (td, *J* = 12.2, 4.7 Hz, 1H), 2.50 – 2.36 (m, 2H), 2.32 (td, *J* = 12.1, 4.2 Hz, 1H), 1.10 – 0.93 (m, 3H). ¹³C NMR (126 MHz, Methanol-*d*₄) δ 142.2, 137.6, 130.1, 129.6, 129.3, 129.2, 127.2, 127.0, 72.2, 67.4, 39.8, 30.5, 18.0. [α]_D²³ = 38.40 (c = 1.0, CHCl₃). *m/z* HRMS (ESI) found [M+H]⁺ 256.1689, C₁₇H₂₂NO⁺ requires 256.1696. HPLC: Chiralpak IA column, 95:05 hexanes/ethanol, 1 ml/min; t_R = 10.02 min (major), 28.94 min (minor); 94.5:5.5 er .



Di-tert-butyl-1-((3*R*,4*R*)-4-hydroxy-1,3-diphenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**9a**)

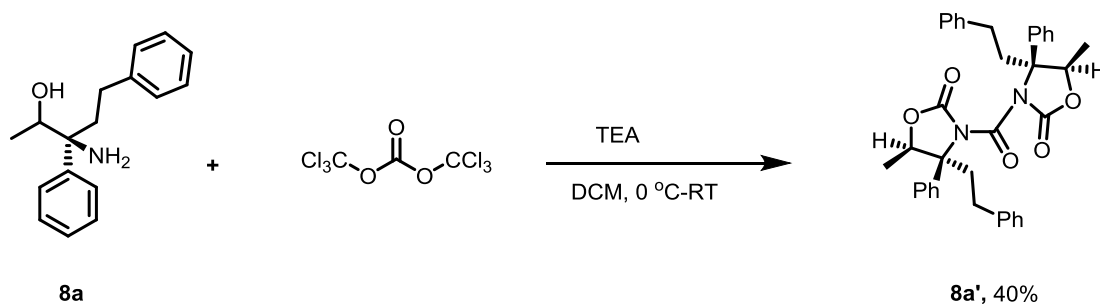
To a solution of **3a** (75 mg, 0.16 mmol, 96:4 er, 1 equiv.) in MeOH (7.0 mL) was added NaBH₄ (37 mg, 0.19 mmol, 1.2 equiv.) at 0 °C. After stirring for 1 h under N₂ atmosphere (1 atm) at room temperature, the solvent was evaporated under vacuum to afford a residue, which was dissolved in EtOAc. The organic phase was washed with water, dried over Na₂SO₄ and concentrated under reduced pressure to afford a residue, which was purified by column chromatography (petroleum ether/EtOAc = 10:1 to 8:1) to give the product **9a** (54 mg, 72%, 96.5:3.5 er, 3:1 dr). ¹H NMR (500 MHz, Acetone-*d*₆) δ 8.42 (m, 1H), 8.19 – 7.83 (m, 1H), 7.76 – 7.62 (m, 2H), 7.59 (d, *J* = 6.8 Hz, 2H), 7.46 (m, 6H), 5.11 (q, *J* = 6.6 Hz, 1H), 1.70 – 1.17 (m, 18H), 0.95 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (101 MHz, Acetone-*d*₆) δ 155.6, 136.1, 132.9, 132.7, 129.8, 129.4, 129.3, 128.4, 122.8, 81.5, 68.5, 28.3, 16.7. [α]_D²³ = 56.00 (c = 1.0, CHCl₃). *m/z* HRMS (ESI) found [M+H]⁺ 467.2551, C₂₇H₃₅N₂O₅⁺ requires 467.2540. HPLC: Chiralpak IA column, 90:10 hexanes/isopropanol, 1 ml/min; t_R = 8.73 min (minor), 12.85 min (major); 96.5:3.5 er.

Tert-butyl-(3*aS*,4*R*)-4-methyl-6-oxo-2,3*a*-diphenyl-3*a*,4-dihydro-1*H*,6*H*-pyrazolo[1,5-*c*]oxazole-1-carboxylate (**10a**)

To a solution of **9a** (32 mg, 0.07 mmol, 3:1 dr, 96.5:3.5 er, 1 equiv.) in cyclohexane (0.5 mL) was added PPh₃AuNTf₂ (3 mg, 0.0035 mmol, 0.05 equiv.) at room temperature. After stirring at 50 °C overnight, the reaction mixture was purified by preparative thin layer chromatography (petroleum ether/EtOAc = 6:1) to give the product **10a** (27 mg, 100%, 96.5:3.5 er, 3:1 dr). ¹H NMR (500 MHz, Acetone-*d*₆) δ

7.70 – 7.59 (m, 2H), 7.56 – 7.42 (m, 4H), 7.36 (m, 4H), 6.55 (d, $J = 9.6$ Hz, 1H), 5.26 (q, $J = 6.6$ Hz, 1H), 1.60 (d, $J = 6.4$ Hz, 1H), 1.20 (d, $J = 12.6$ Hz, 9H), 1.03 (d, $J = 6.6$ Hz, 2H). ^{13}C NMR (126 MHz, Acetone- d_6) δ 162.6, 162.3, 154.3, 154.2, 147.6, 146.0, 140.7, 138.4, 135.1, 135.0, 132.4, 132.3, 129.9, 129.9, 129.7, 129.6, 129.2, 128.9, 128.3, 128.2, 126.7, 126.2, 117.2, 111.9, 82.9, 82.9, 81.8, 80.4, 80.0, 78.7, 28.5, 27.9, 19.9, 17.1. $[\alpha]_D^{23} = 99.20$ ($c = 1.0$, CHCl_3). m/z HRMS (ESI) found $[\text{M}+\text{H}]^+$ 393.1812, $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_4^+$ requires 393.1809. HPLC: Chiralpak IA column, 90:10 hexanes/ethanol, 1 ml/min; $t_R = 8.42$ min (minor), 11.01 min (major); 96.5:3.5 er.

Determination of the relative configuration of **8a**.



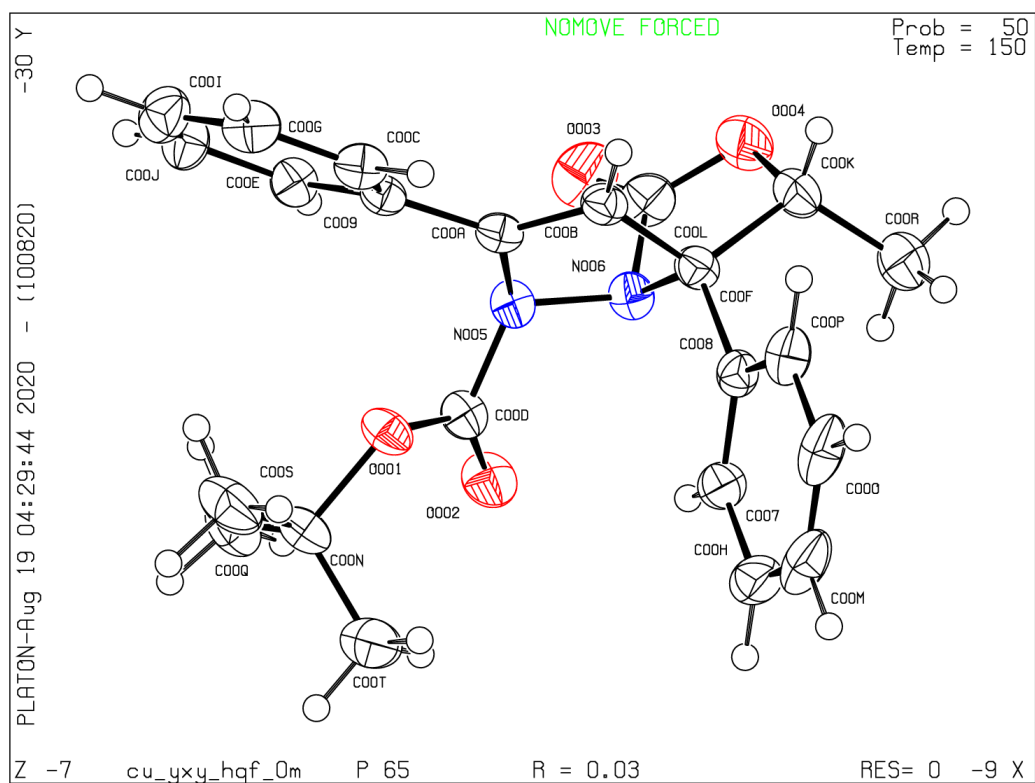
(4*S*,4'*S*,5*R*,5'*R*)-3,3'-carbonylbis(5-methyl-4-phenethyl-4-phenyloxazolidin-2-one)
(**8a'**)

To a solution of **8a** (18 mg, 0.07 mmol, 94.5:5.5 er, 1 equiv.) in DCM (1 mL) was added TEA (17.8 mg, 0.175 mmol, 2.5 equiv.) and triphosgene (11 mg in 0.5 mL DCM, 0.035 mmol, 0.5 equiv.) at 0 °C. After stirring overnight at room temperature, the solvent was evaporated under vacuum to afford a residue, which was purified by thin layer chromatography (petroleum ether/EtOAc = 5:1) to give the product **8a'** (9 mg, 40%). ^1H NMR (500 MHz, Chloroform- d) δ 7.41 (t, $J = 7.6$ Hz, 4H), 7.32 (m, $J = 16.9, 7.9$ Hz, 10H), 7.19 (m, 6H), 4.17 (q, $J = 6.4$ Hz, 2H), 2.94 – 2.80 (m, 2H), 2.63 (m, 2H), 2.53 (m, 4H), 1.01 (d, $J = 6.4$ Hz, 6H). ^{13}C NMR (126 MHz, Chloroform- d) δ 156.8, 156.5, 141.1, 138.3, 128.8, 128.7, 128.4, 128.1, 126.3, 126.3, 71.0, 67.0, 35.2, 30.2, 17.9.

References:

1. Li, Y.; Lu, R.; Sun, S.; Liu, L., Metal-Free Three-Component Oxyalkynylation of Alkenes. *Org. Lett.* **2018**, *20*, 6836-6839.
2. Brimble, M. A.; Duckworth, M. S.; Lee, C. K. Y., Synthesis of Chiral Diazanedicarboxylates. *Aust. J. Chem.* **1998**, *51*, 907-914.

X-Ray structures



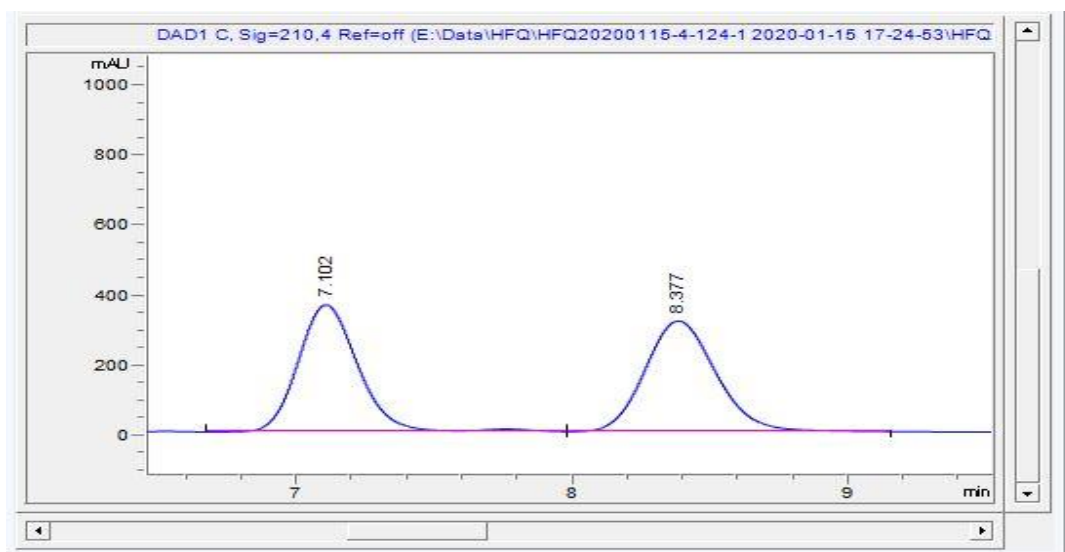
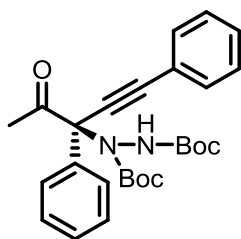
X-ray structure of **10a** (CCDC 2074968)

Single crystal data of **10a**

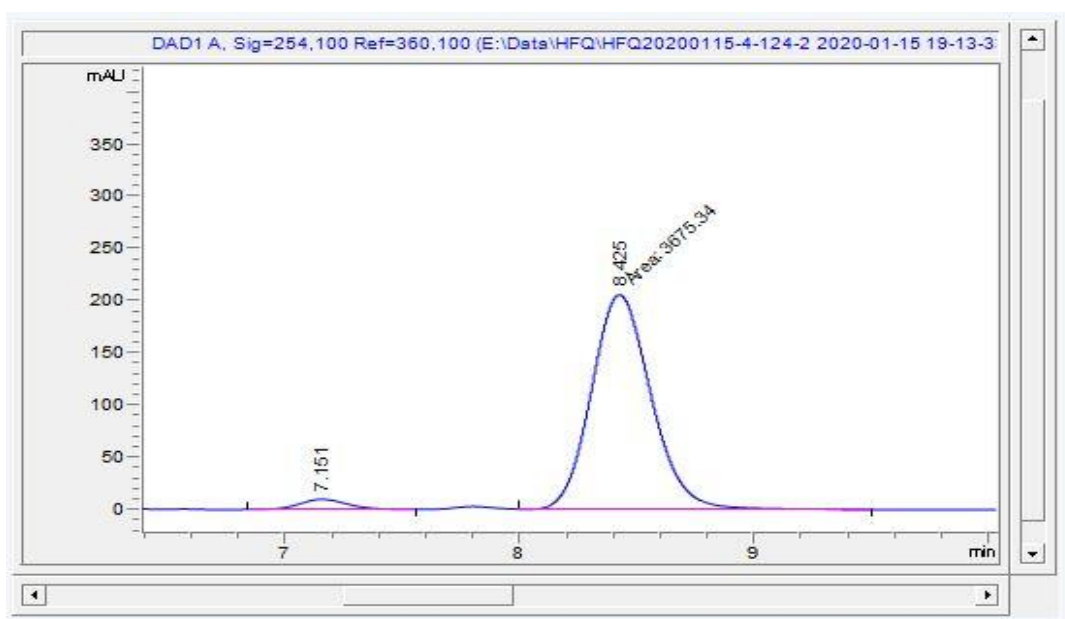
Identification code	
Empirical formula	C ₂₃ H ₂₄ IN ₂ O ₄
Formula weight	392.44
Temperature / K	150.0
Crystal system	hexagonal
Space group	P6 ₅
a/Å, b/Å, c/Å	10.8014(2), 10.8014(2), 31.6209(8)
α/°, β/°, γ/°	90, 90, 120
Volume/Å ³	3194.96(14)
Z	6
ρ _{calc} /cm ⁻³	1.224
μ/mm ⁻¹	0.685
F(000)	1248.0
Crystal size/mm ³	0.2 x 0.15 x 0.1
Theta range for data collection	9.454 to 158.562 °
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -40 ≤ l ≤ 37
Reflections collected	80320
Independent reflections	4587 [R _{int} = 0.0559, R _{sigma} = 0.0170]
Data/restraints/parameters	4587/1/266
Goodness-of-fit on F ²	1.075
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0271, wR ₂ = 0.0644
Final R indexes [all data]	R ₁ = 0.0293, wR ₂ = 0.0657
Largest diff. peak/hole / e Å ⁻³	0.14 and -0.13

HPLC traces:

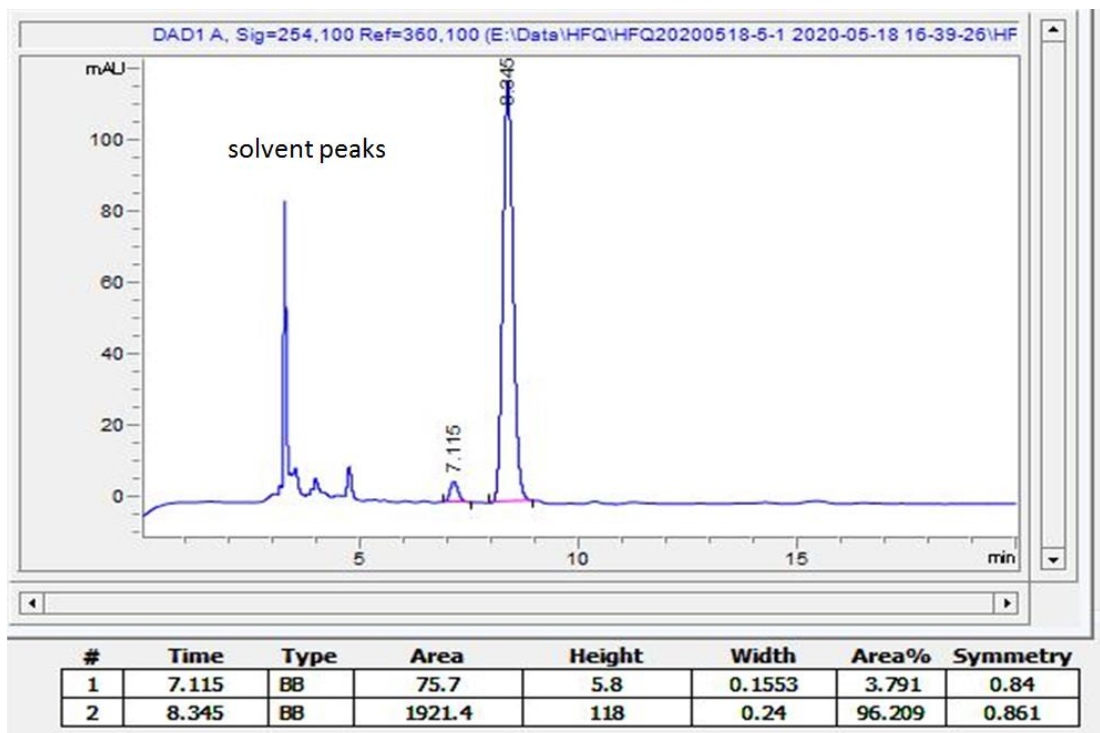
Di-tert-butyl-(*R*)-1-(4-oxo-1,3-diphenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate
(3a)



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.102	BV R	5515.3	363.5	0.2184	49.399	0.842
2	8.377	VV R	5649.6	317.1	0.2539	50.601	0.862

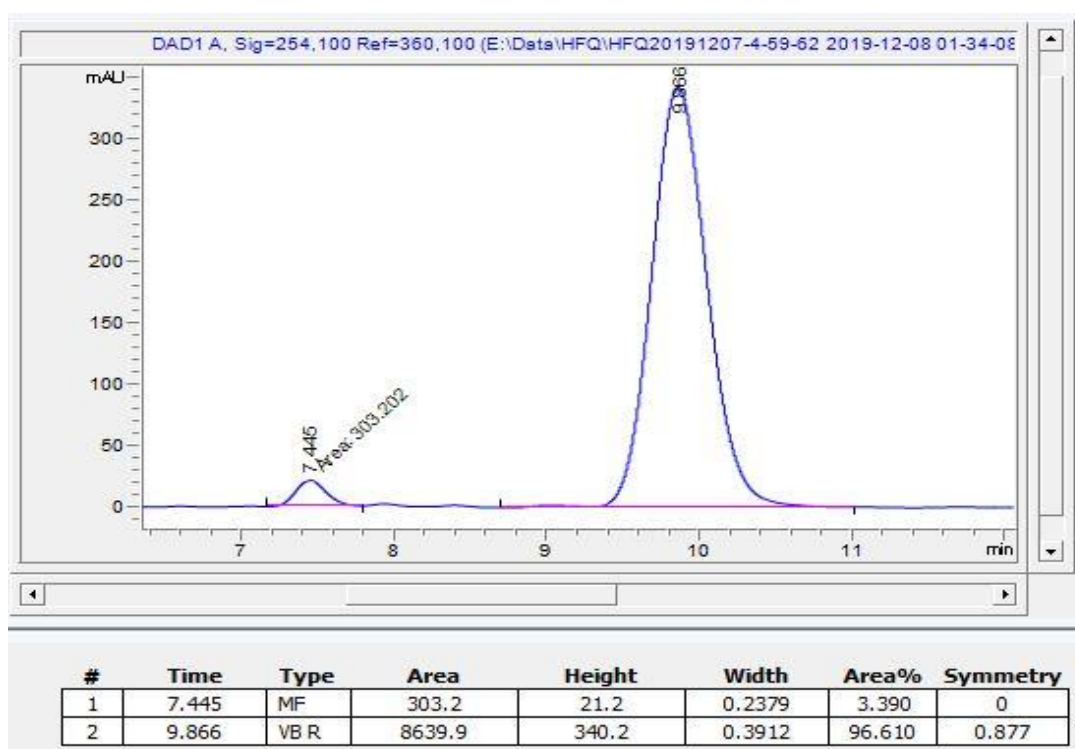
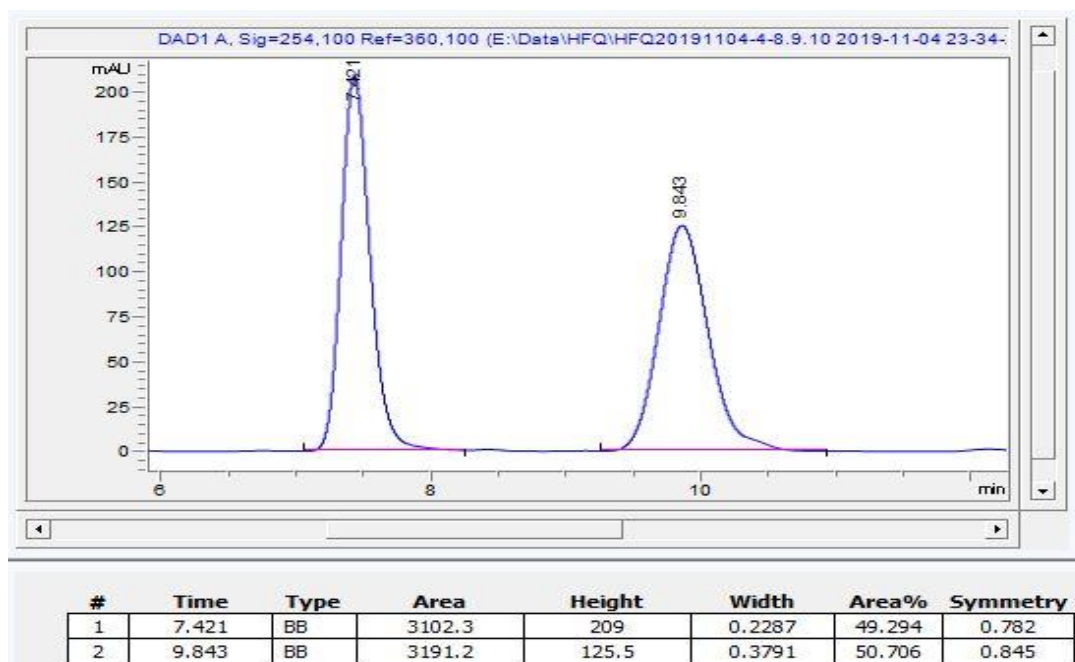
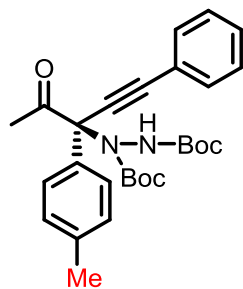


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.151	BB	139.3	9.7	0.1753	3.652	0.879
2	8.425	FM	3675.3	206.6	0.2965	96.348	0.851

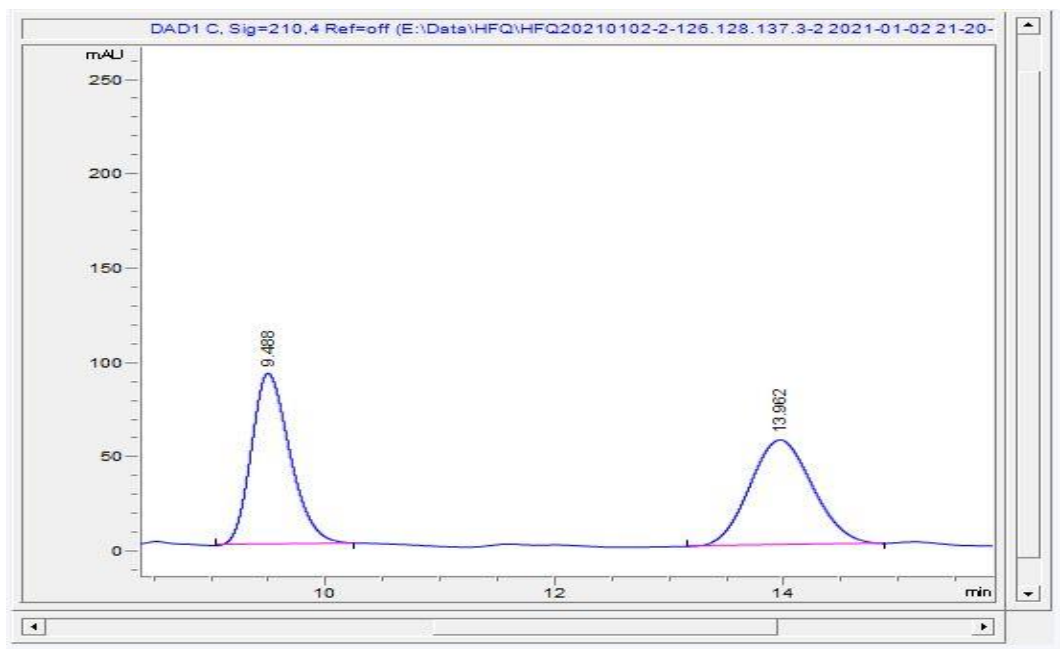
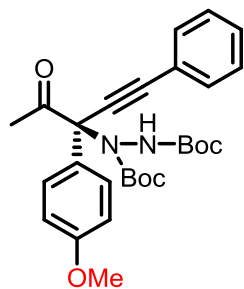


Full HPLC spectrum of 3a

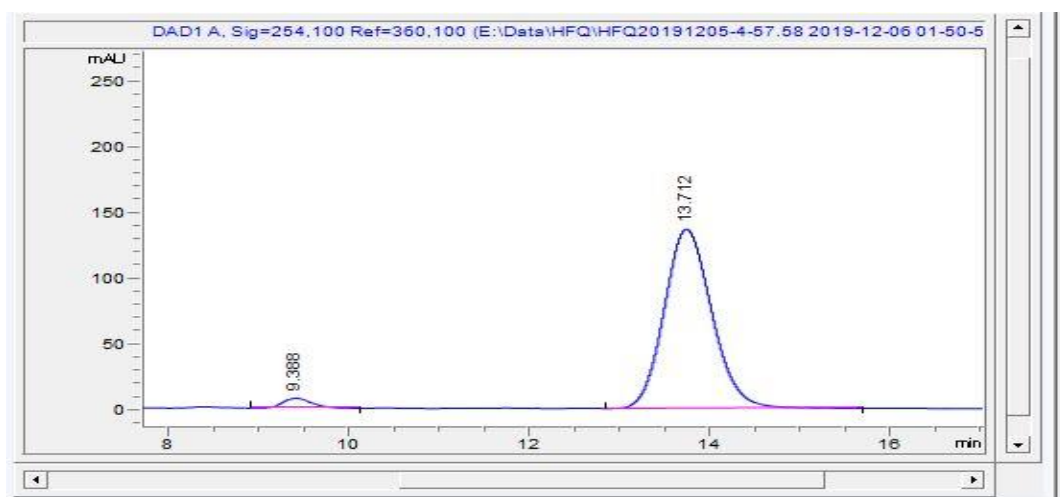
Di-tert-butyl-(*R*)-1-(4-oxo-1-phenyl-3-(*p*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3b**)



Di-tert-butyl-(*R*)-1-(3-(4-methoxyphenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3c**)

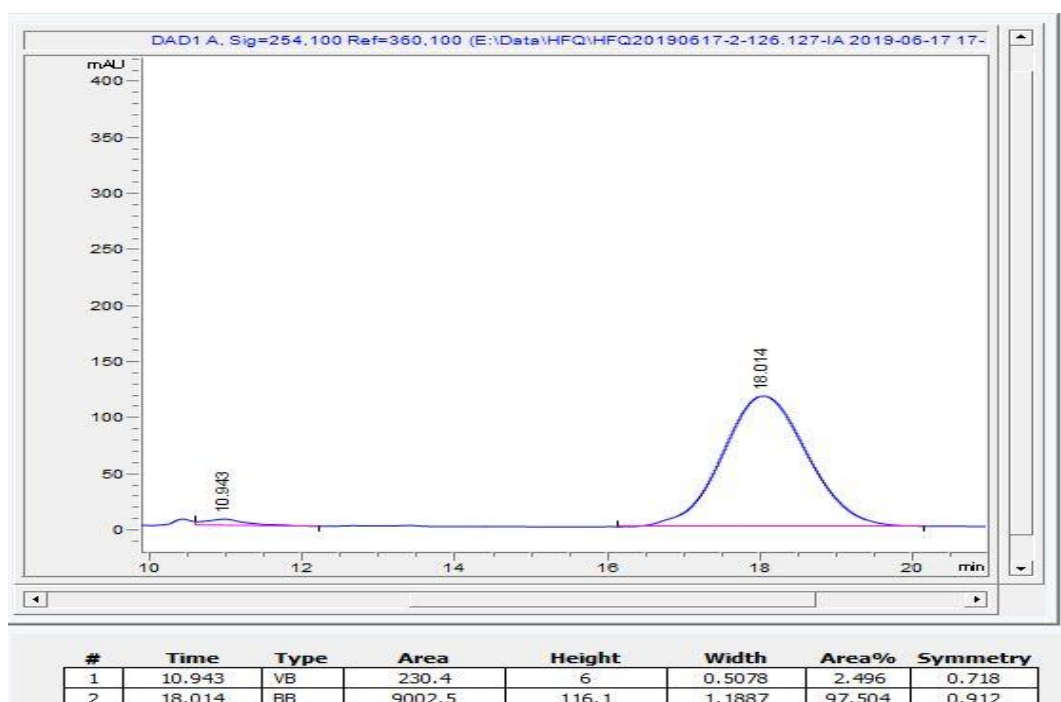
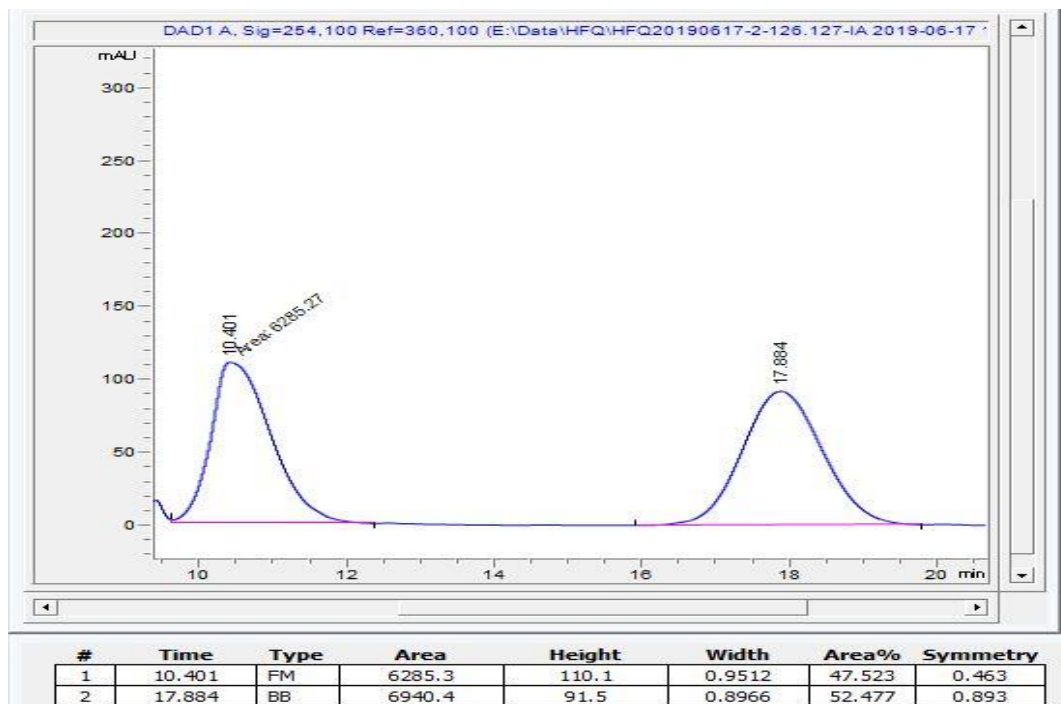
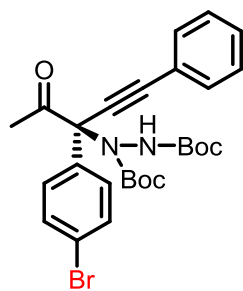


#	Time	Type	Area	Height	Width	Area%	Symmetry
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2	13.962	BB	2128.1	55.8	0.4489	49.910	0.943

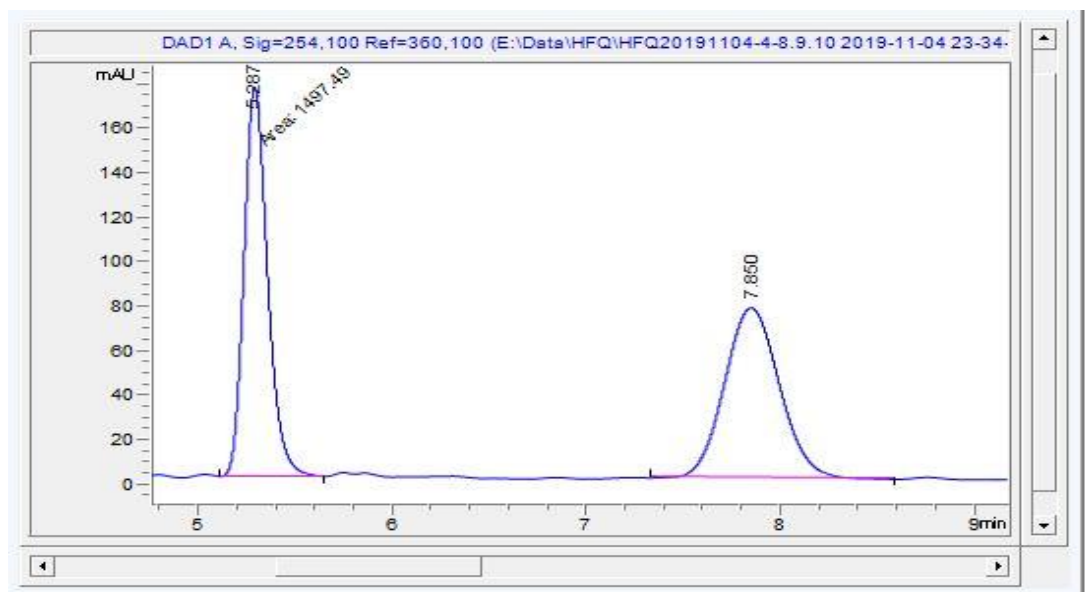
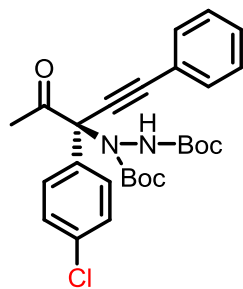


#	Time	Type	Area	Height	Width	Area%	Symmetry
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2	13.712	BB	4988.2	136.5	0.5413	96.735	0.834

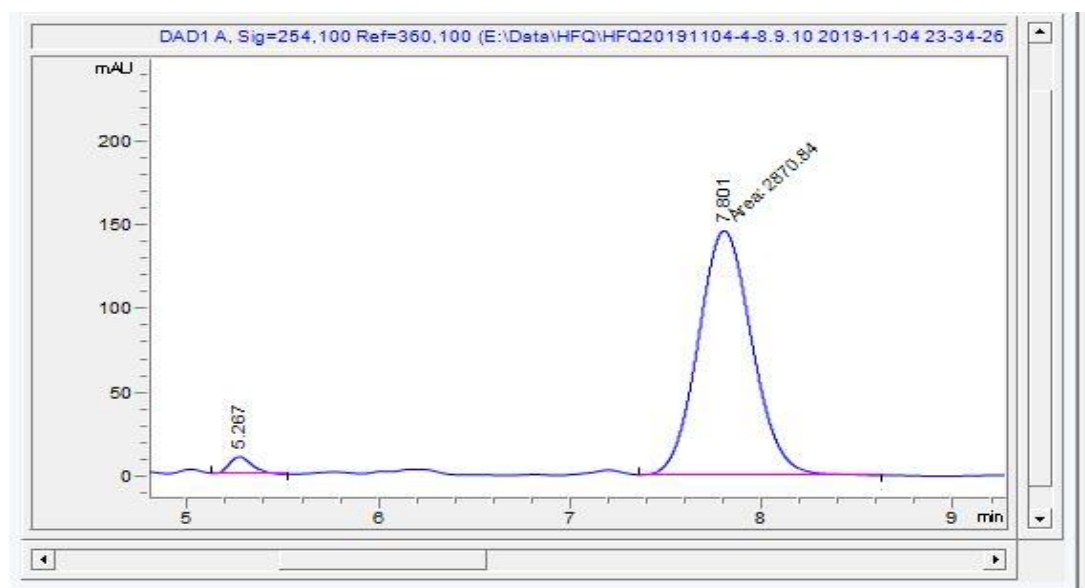
Di-tert-butyl-(*R*)-1-(3-(4-bromophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3d**)



Di-tert-butyl-(*R*)-1-(3-(4-chlorophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3e**)

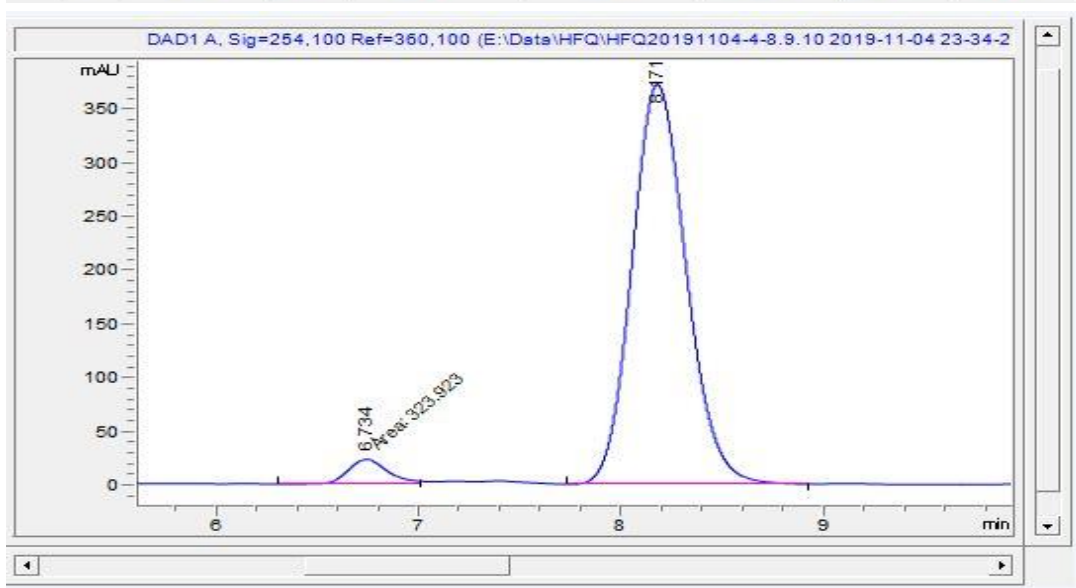
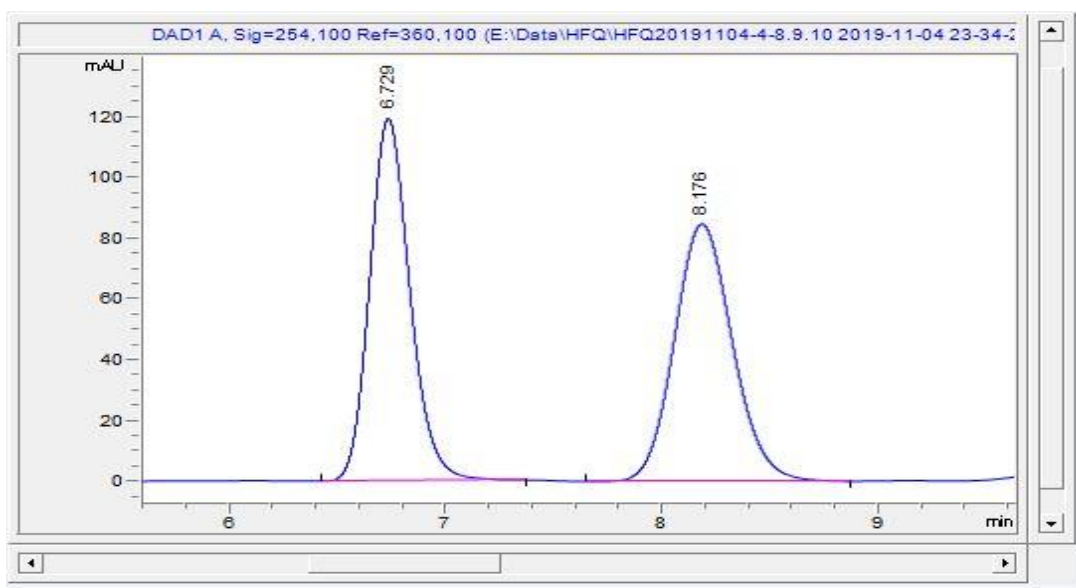
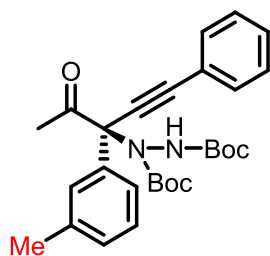


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.287	FM	1497.5	176.3	0.1416	49.529	0.783
2	7.85	BB	1526	77	0.3056	50.471	0.903

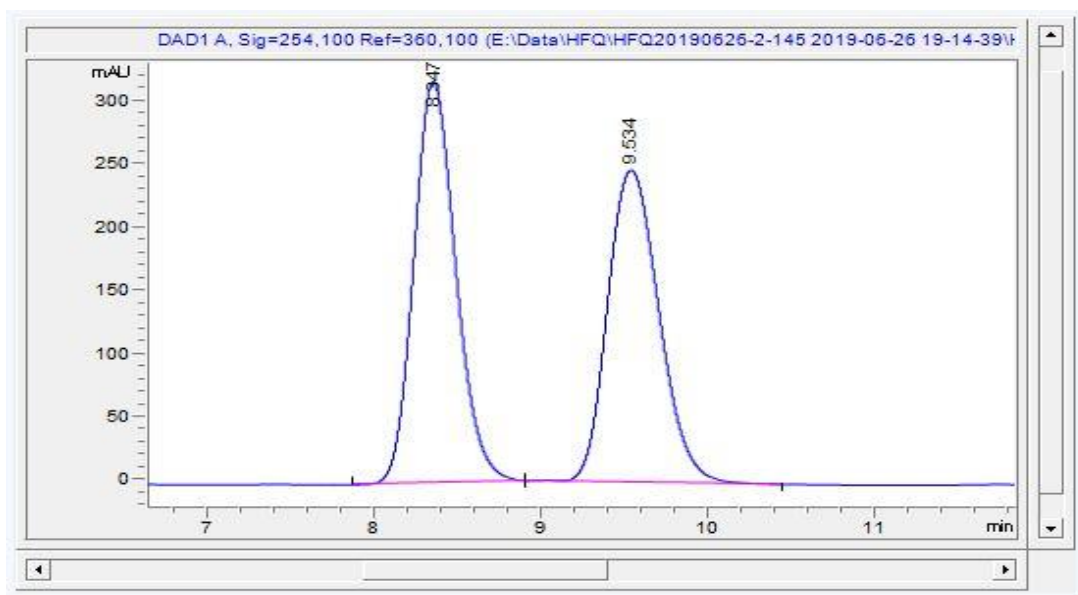
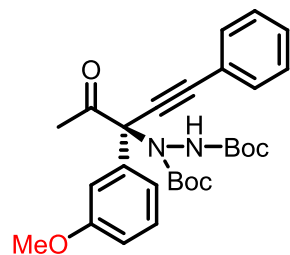


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.267	VB	87	10.3	0.1287	2.942	0.754
2	7.801	FM	2870.8	146.8	0.326	97.058	0.907

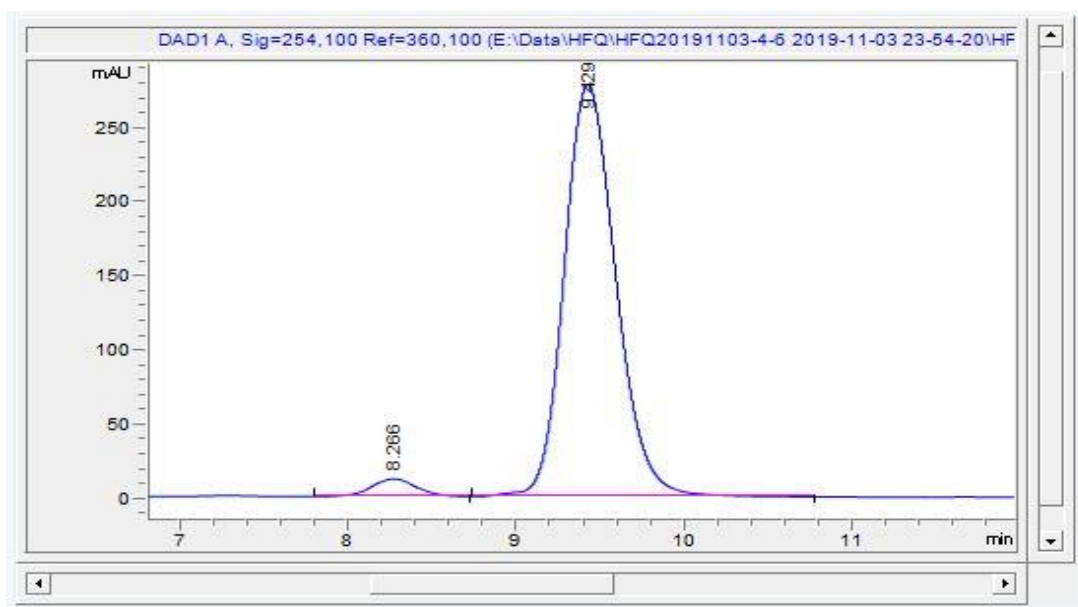
Di-tert-butyl-(*R*)-1-(4-oxo-1-phenyl-3-(*m*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3f**)



Di-tert-butyl-(*R*)-1-(3-(3-methoxyphenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3g**)

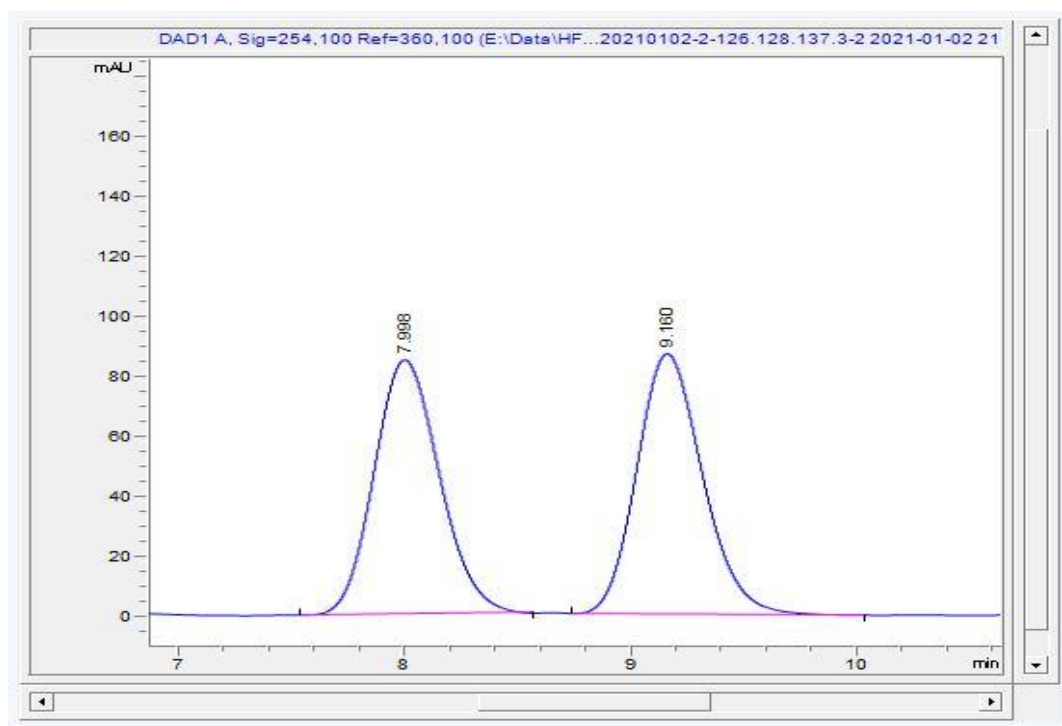
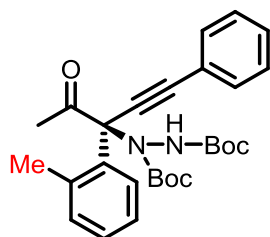


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.347	BB	5524	316.1	0.2694	51.239	0.824
2	9.534	VB R	5257	245.9	0.3329	48.761	0.802

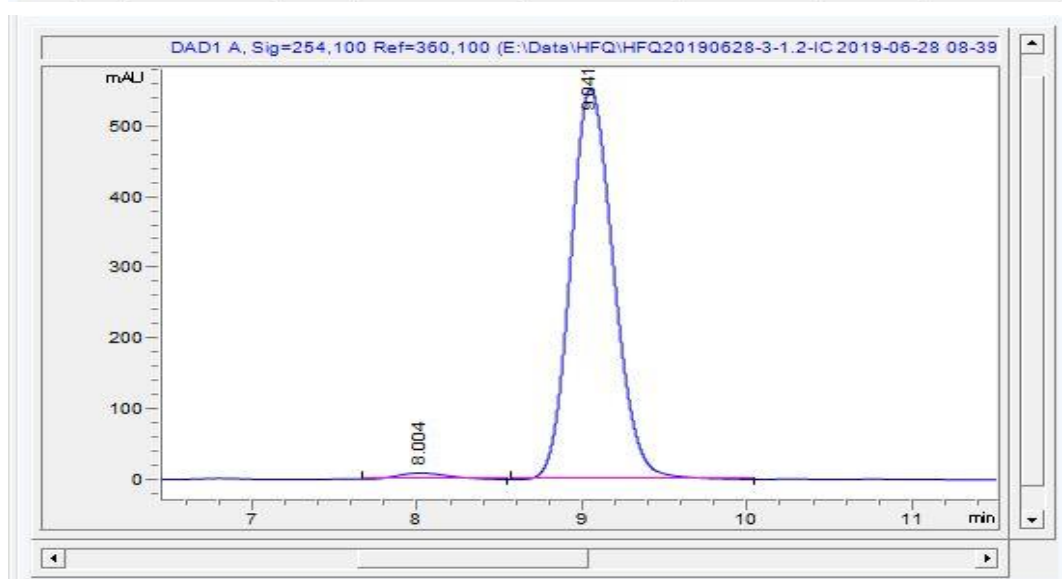


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.266	BB	225.1	11.9	0.2297	3.645	0.956
2	9.429	BB	5952.4	277.8	0.331	96.355	0.8

Di-tert-butyl-(S)-1-(4-oxo-1-phenyl-3-(o-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3h**)

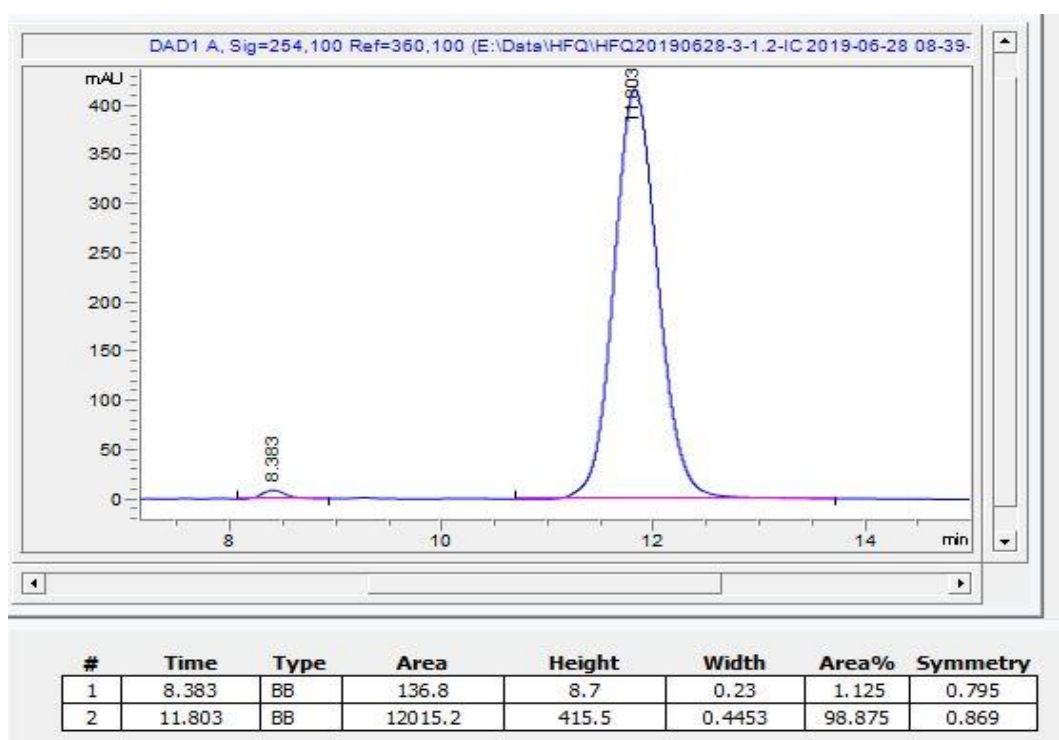
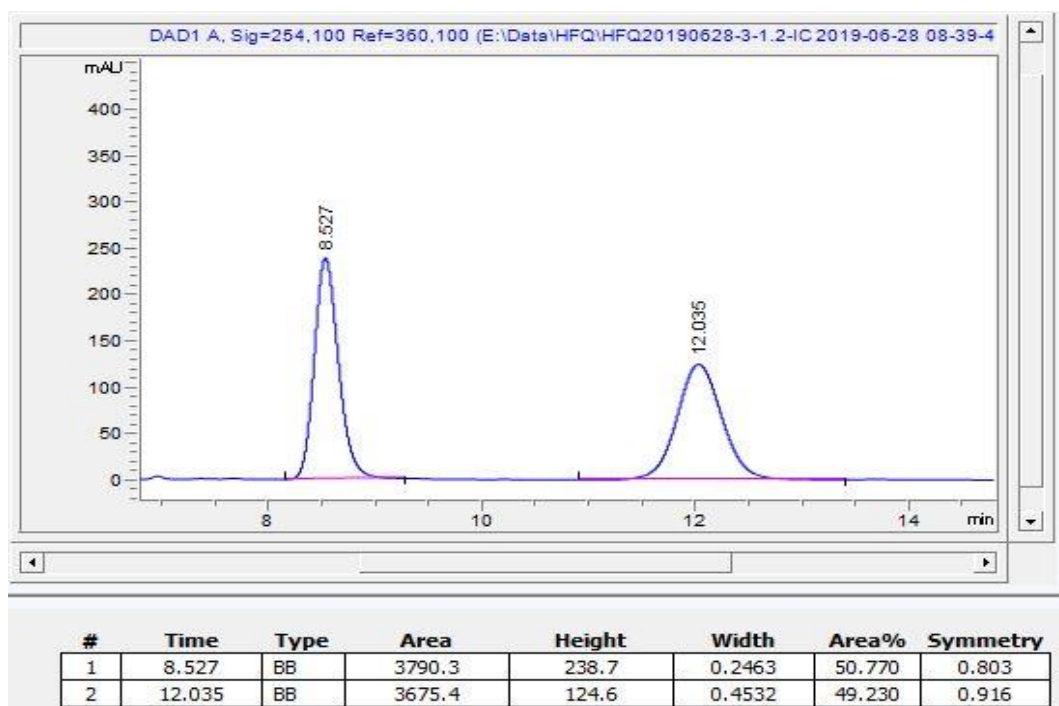
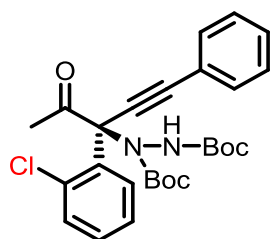


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.998	BB	1704.6	84.8	0.3106	49.235	0.847
2	9.16	BB	1757.6	86.8	0.3163	50.765	0.815

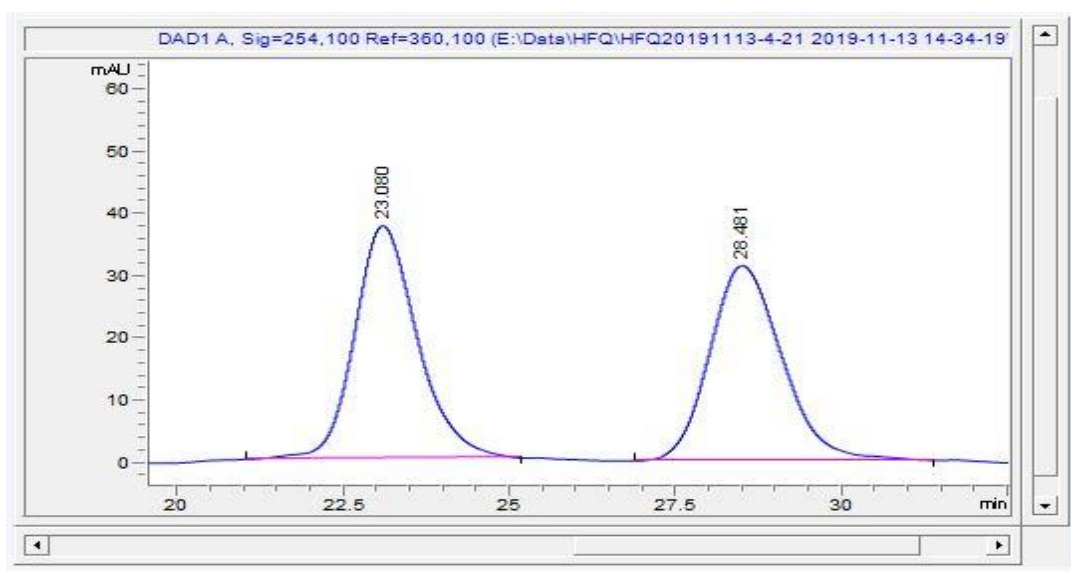
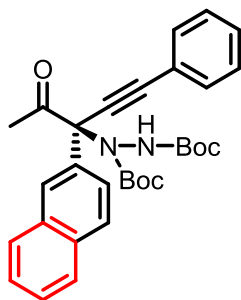


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.004	BB	191.1	8.8	0.2903	1.876	0.712
2	9.041	BB	9993.8	552.6	0.283	98.124	0.817

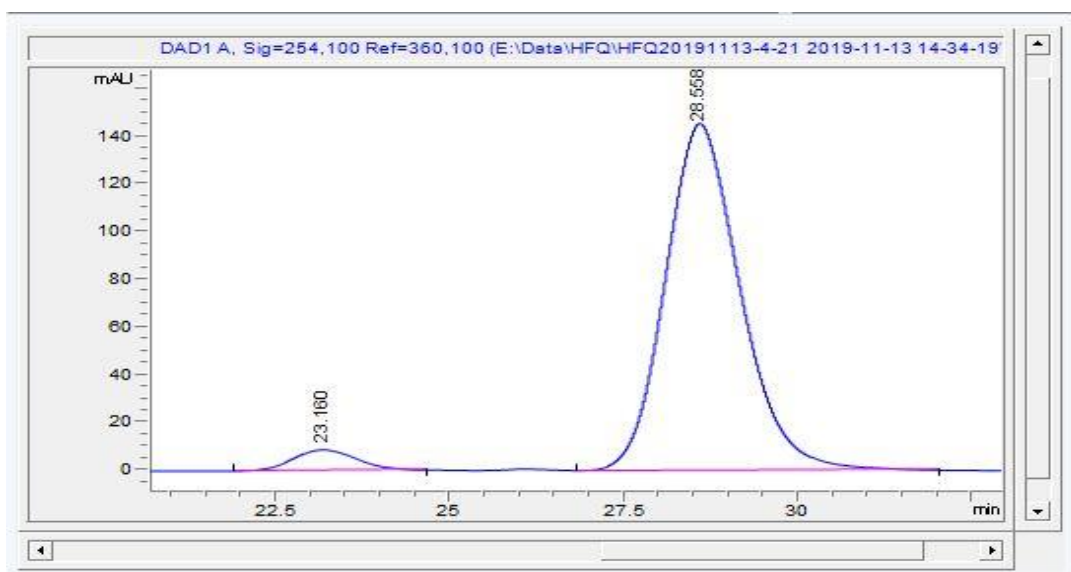
Di-tert-butyl-(S)-1-(3-(2-chlorophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3i**)



Di-tert-butyl-(*R*)-1-(3-(naphthalen-2-yl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3j**)

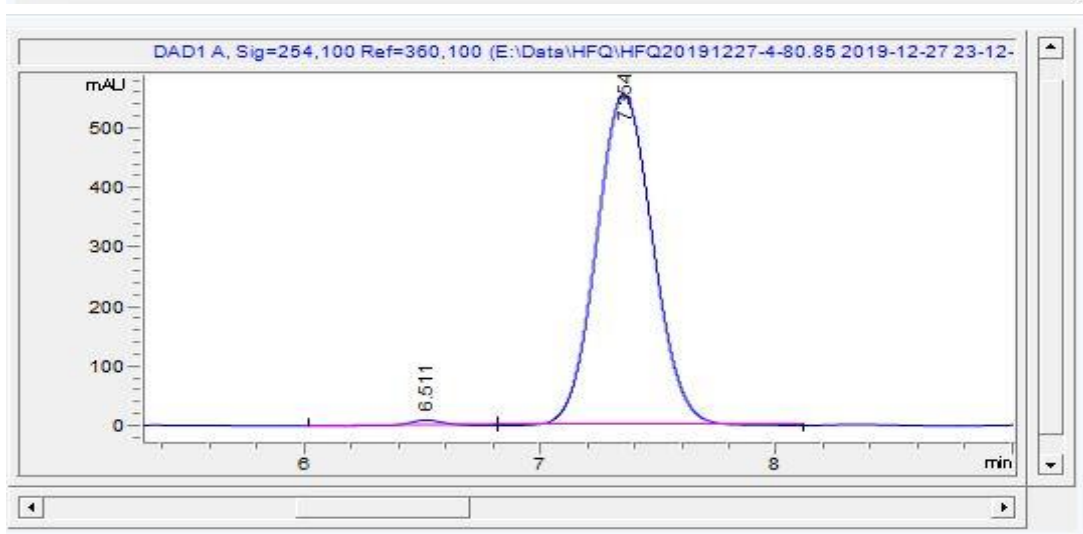
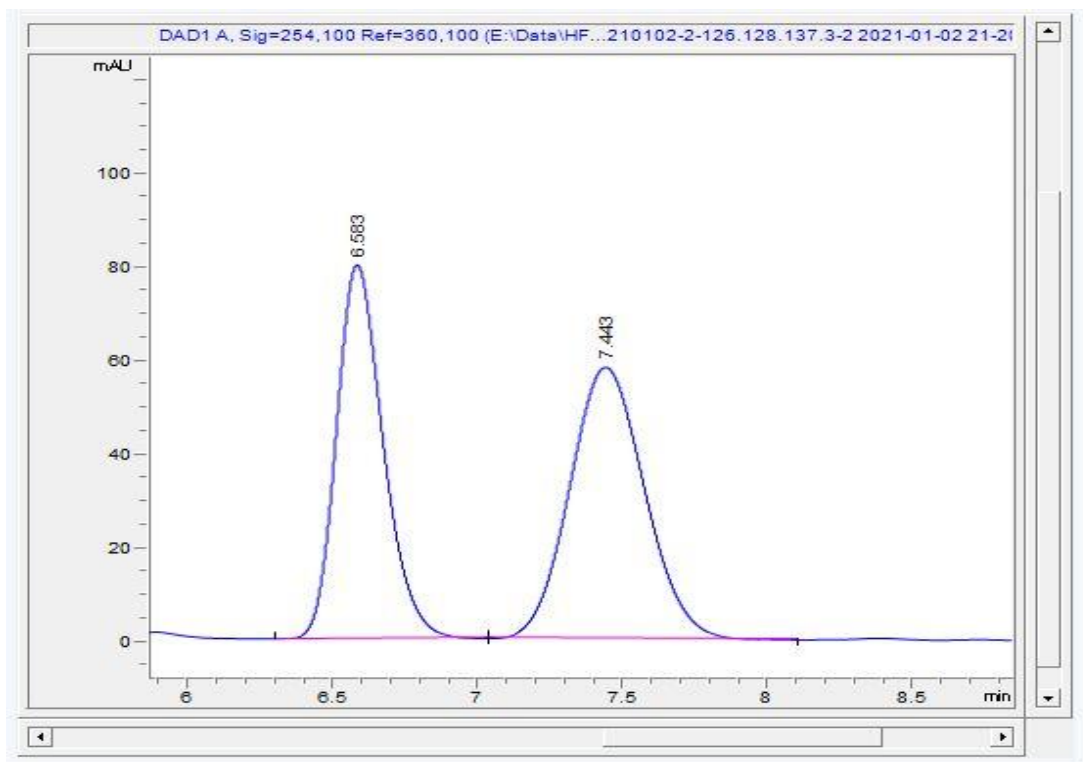
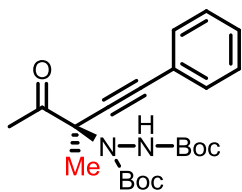


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.08	BB	2458.8	37.3	0.7723	50.960	0.813
2	28.481	BB	2366.1	31.3	0.8858	49.040	0.809

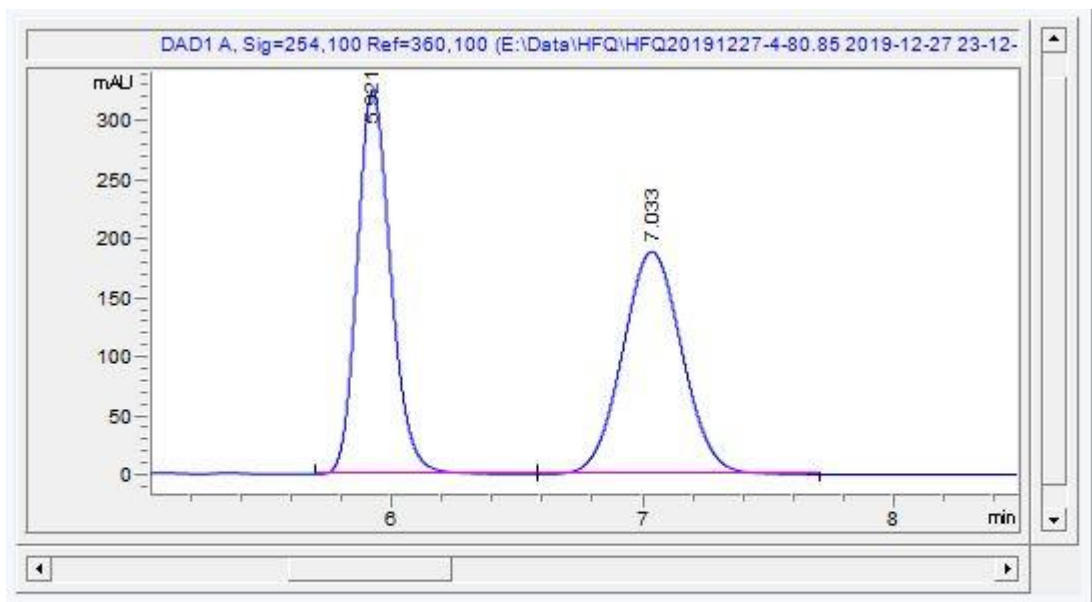
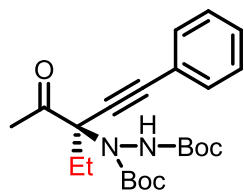


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.16	BB	551.6	8.7	0.7402	4.836	0.898
2	28.558	BB	10855.1	145.7	0.9784	95.164	0.815

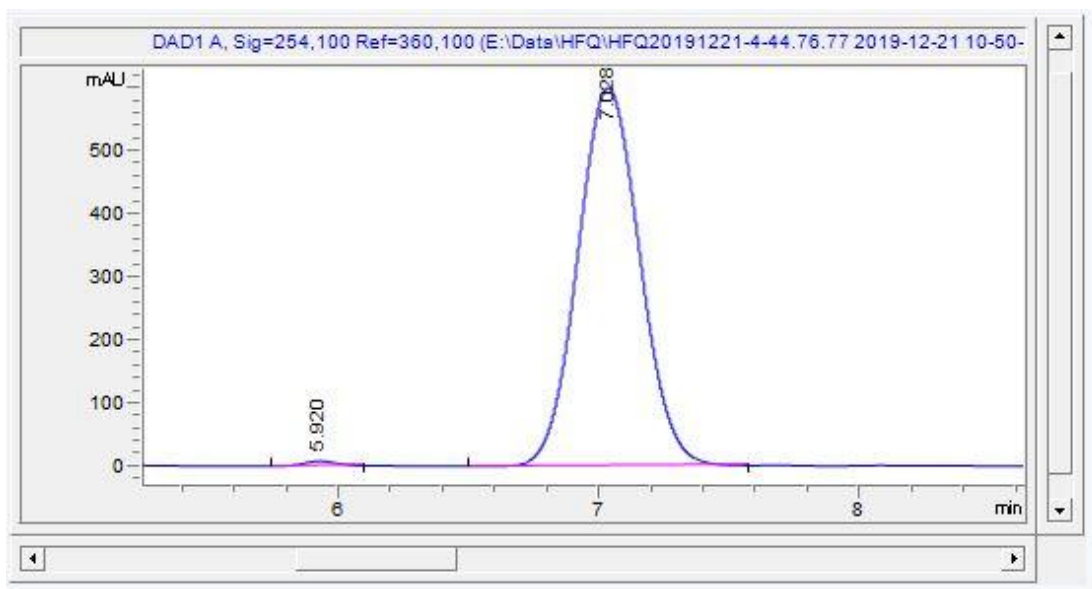
Di-tert-butyl-(*R*)-1-(3-methyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3k**)



Di-tert-butyl-(*R*)-1-(3-ethyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (3I)

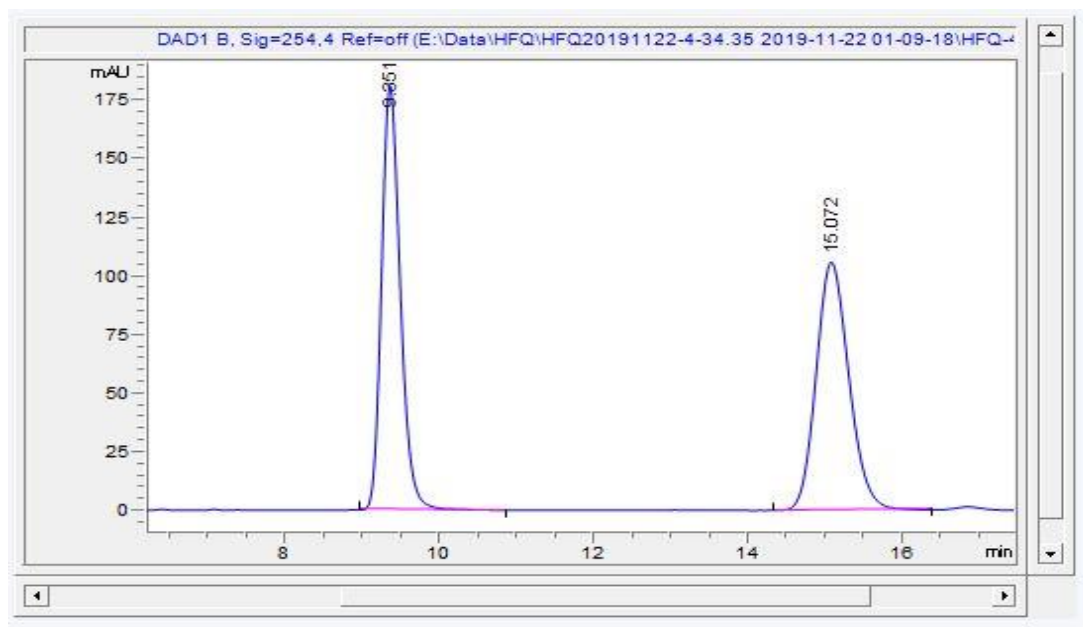
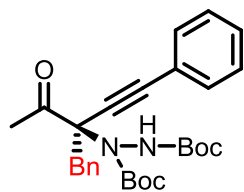


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.921	BB	3008.7	323.8	0.1434	49.296	0.804
2	7.033	BB	3094.6	187.8	0.2573	50.704	0.942

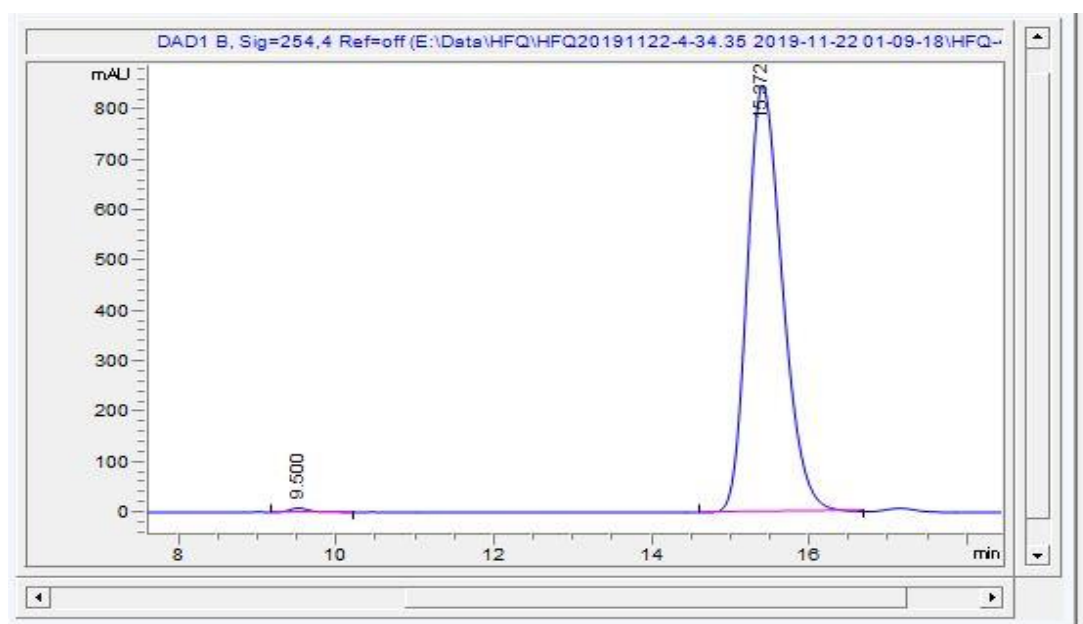


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.92	BB	68.1	8	0.1312	0.683	0.91
2	7.028	BB	9905.4	599	0.2599	99.317	0.929

Di-tert-butyl-(*R*)-1-(3-benzyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3m**)

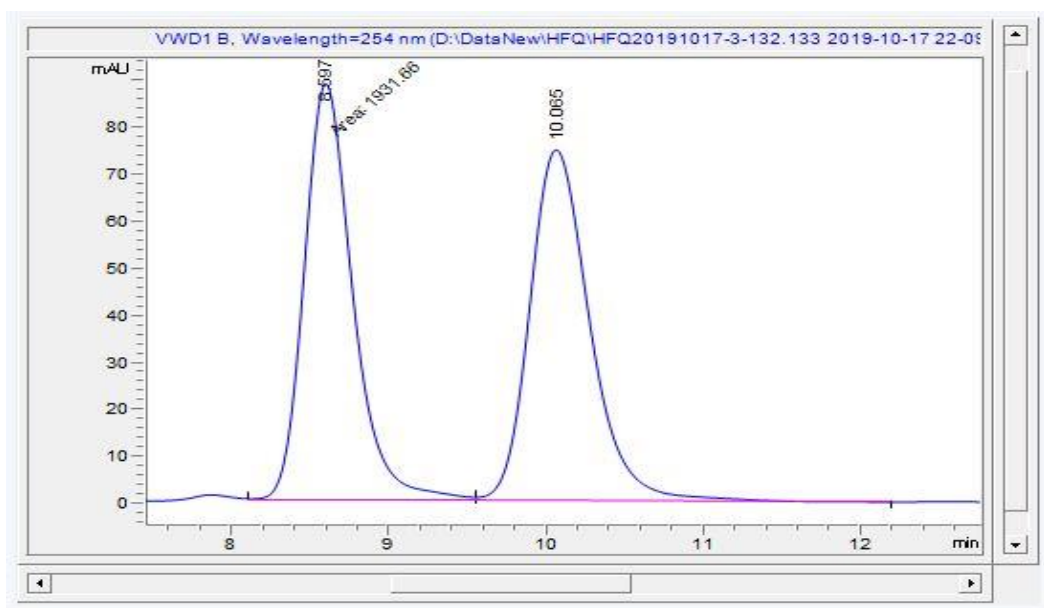
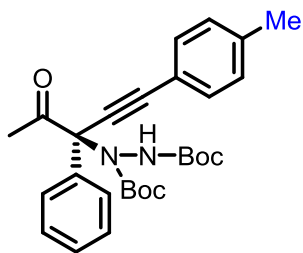


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.351	BB	3070.2	181.5	0.2593	49.476	0.759
2	15.072	BB	3135.2	106.1	0.4568	50.524	0.821

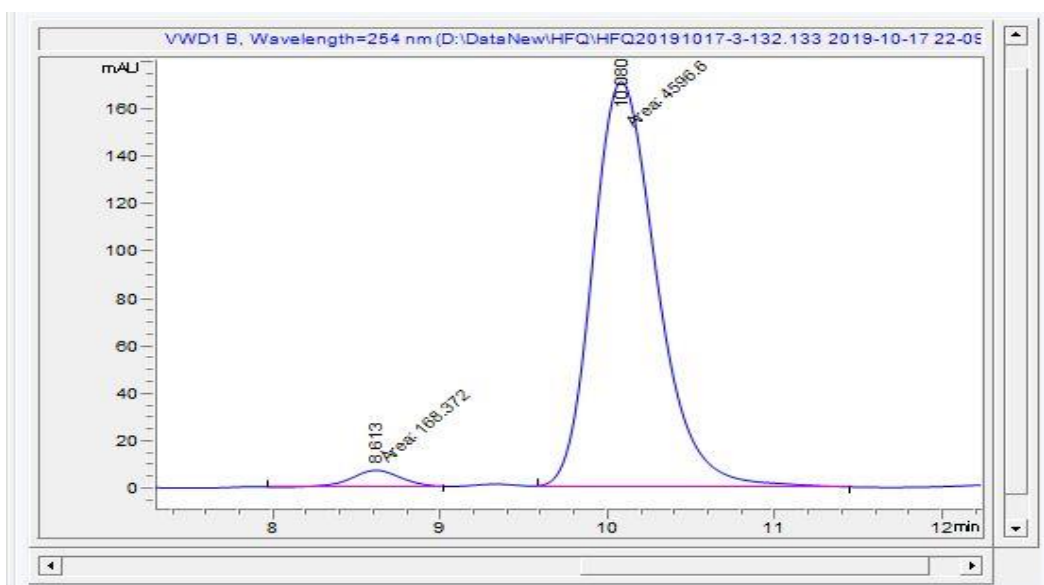


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.5	BB	157.8	8.6	0.28	0.600	0.701
2	15.372	BB	26145.4	845.1	0.4789	99.400	0.728

Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*p*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3n**)

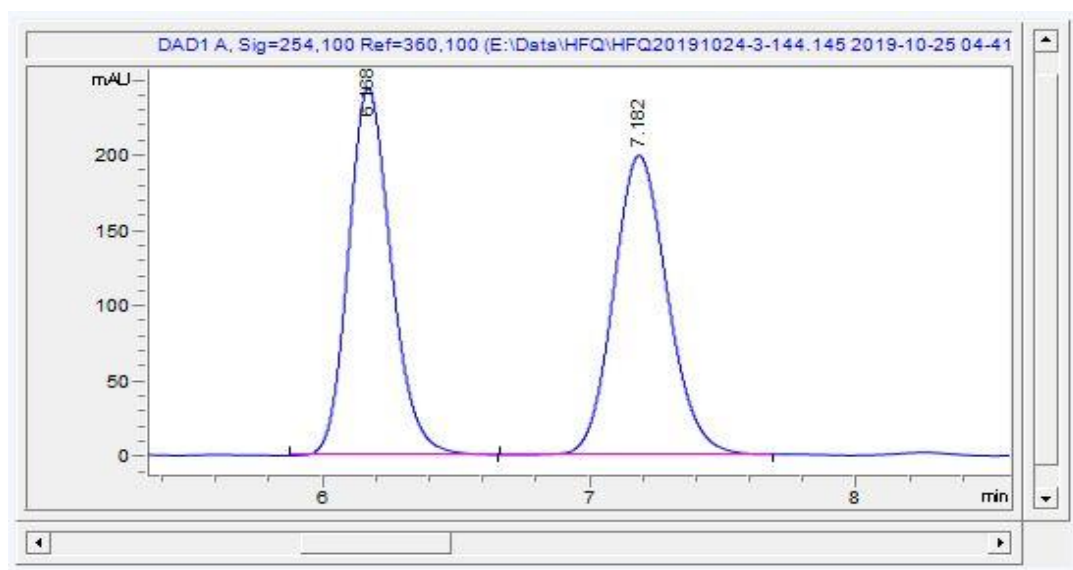
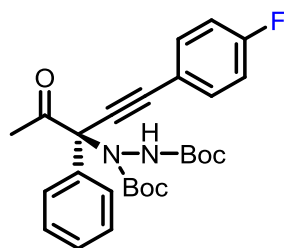


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.597	FM	1931.7	89.1	0.3613	49.040	0.764
2	10.065	VB	2007.3	75.1	0.412	50.960	0.738

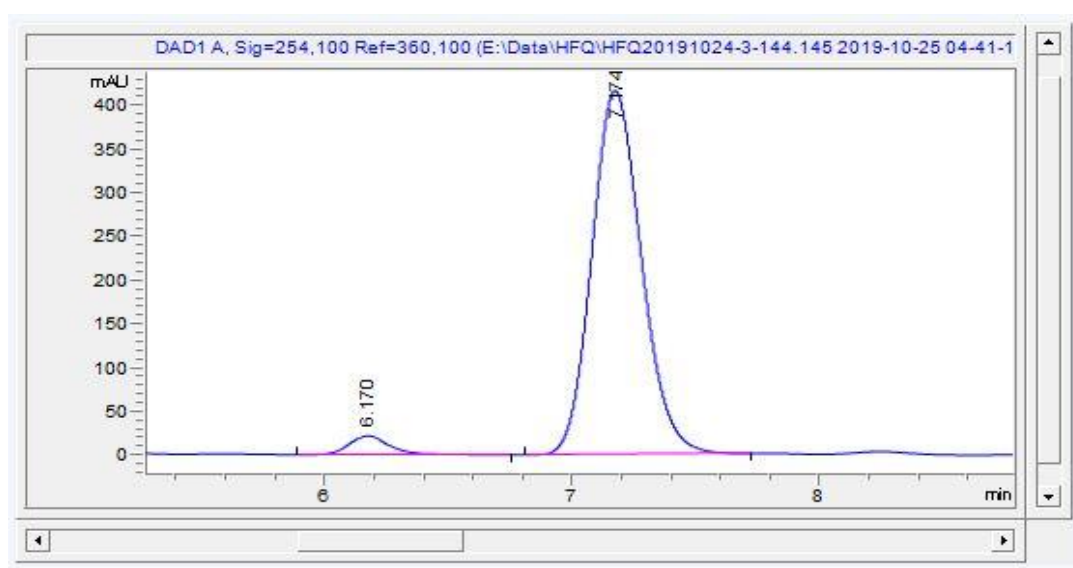


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.613	MF	168.4	7.4	0.3816	3.534	1.008
2	10.08	FM	4596.6	171.8	0.446	96.466	0.762

Di-tert-butyl-(*R*)-1-(1-(4-fluorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**30**)

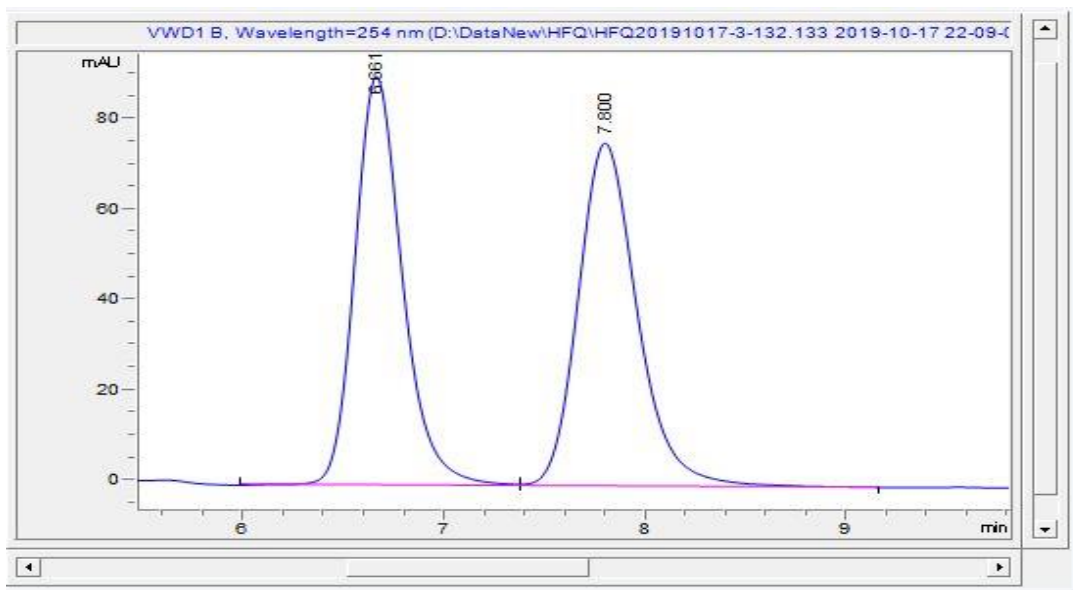
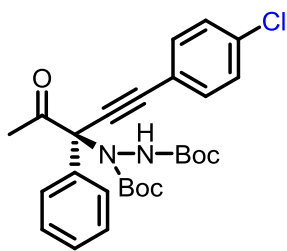


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.168	BB	2712.9	243.7	0.1719	49.359	0.815
2	7.182	BB	2783.4	198.5	0.2171	50.641	0.86

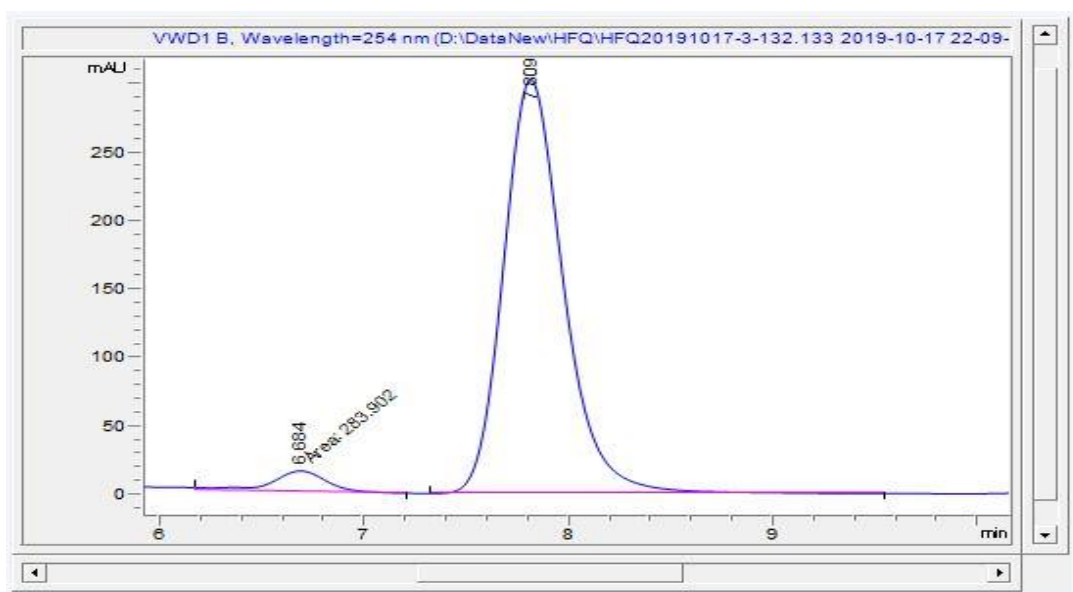


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.17	BB	252.7	21.8	0.175	4.174	0.796
2	7.174	BB	5801	415.9	0.2162	95.826	0.843

Di-tert-butyl-(*R*)-1-(1-(4-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3p**)

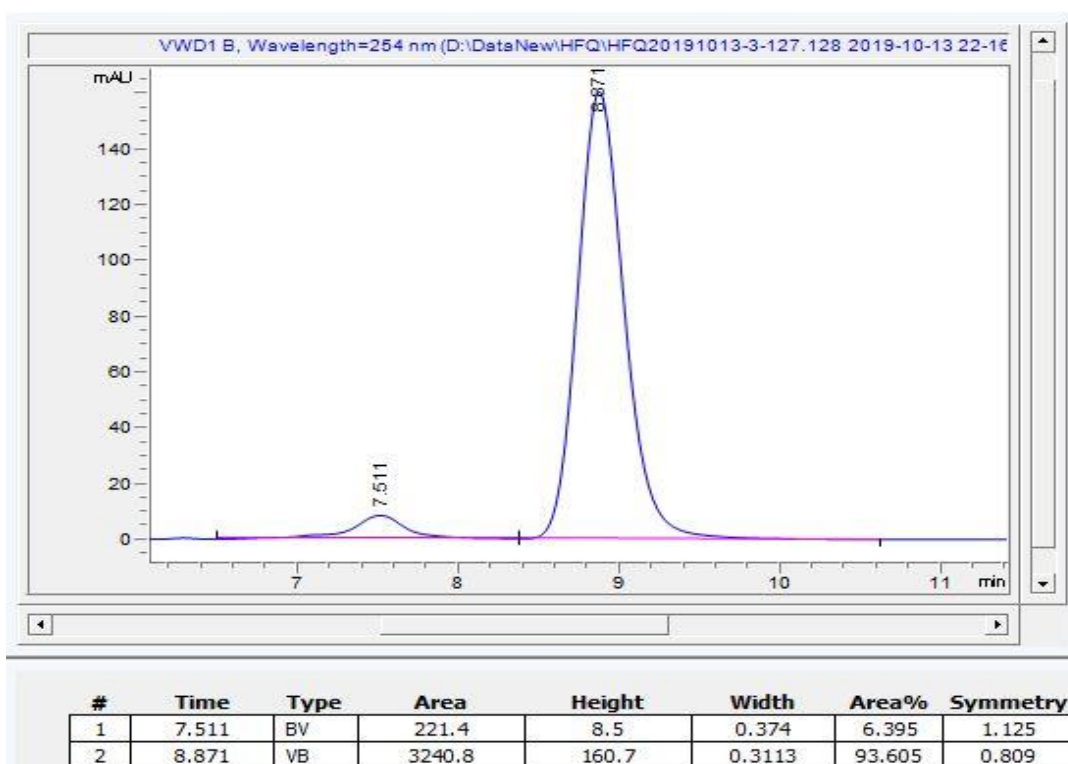
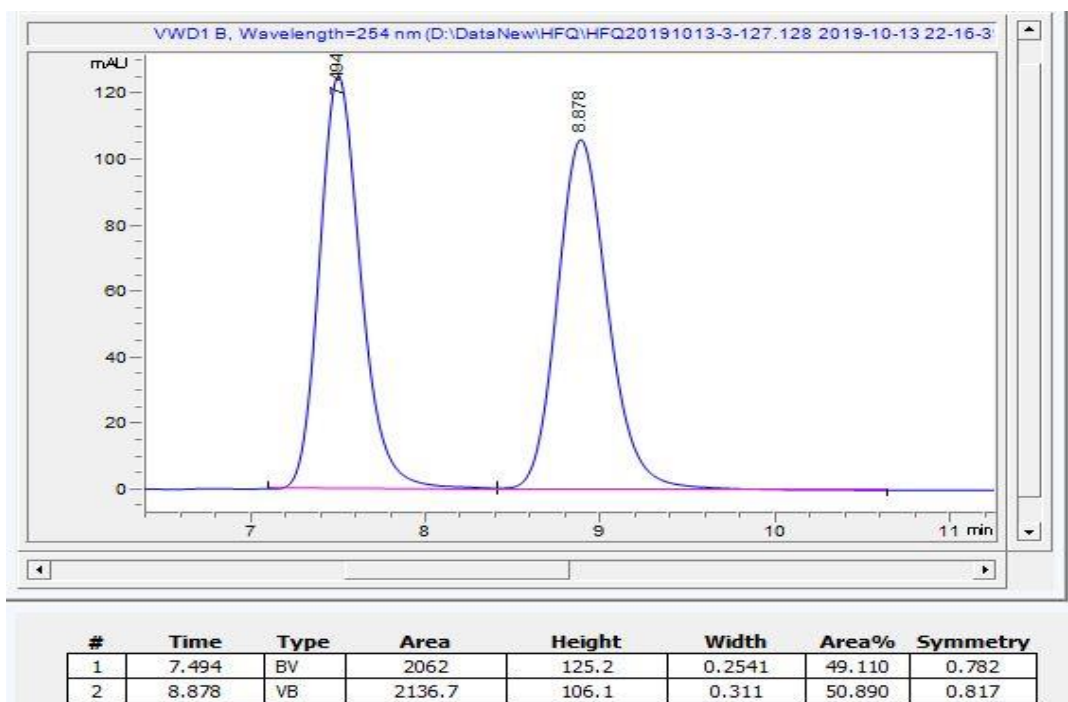
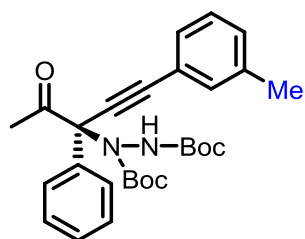


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.661	BV	1504.7	90.9	0.2531	49.026	0.782
2	7.8	VB	1564.5	76.3	0.3153	50.974	0.778

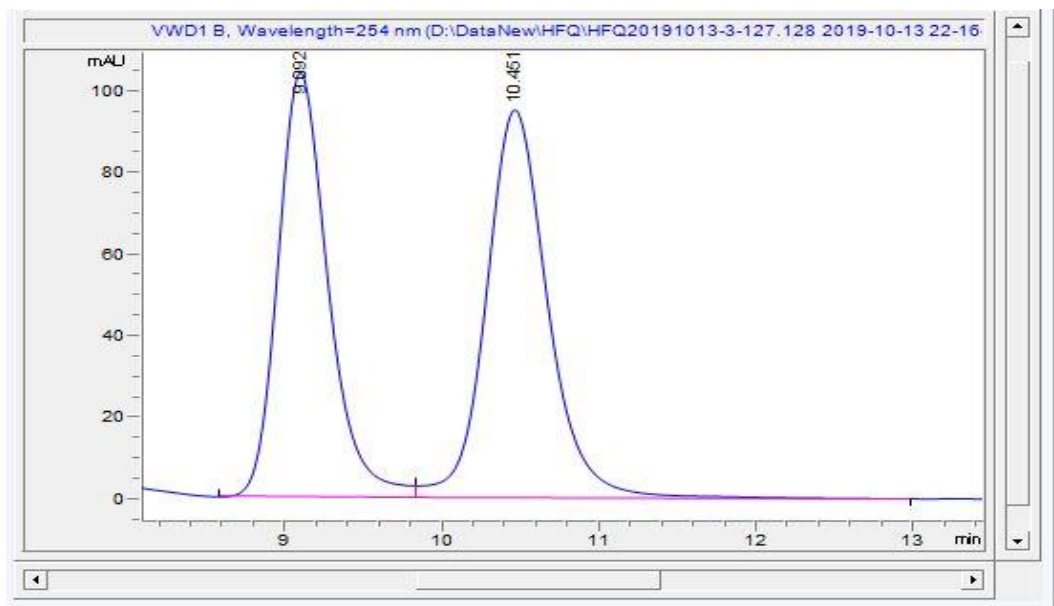
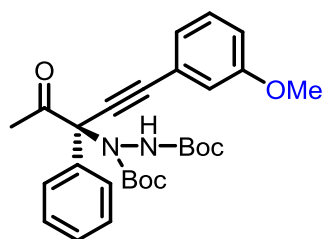


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.684	FM	283.9	15	0.3158	4.410	1.132
2	7.809	BB	6154.5	301.6	0.3141	95.590	0.776

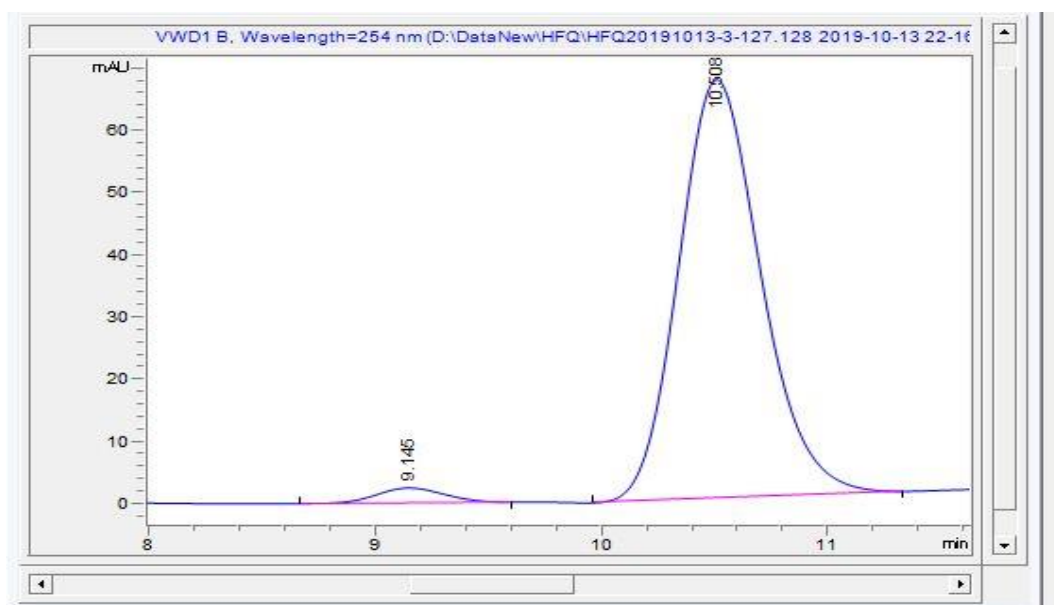
Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*m*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3q**)



Di-tert-butyl-(*R*)-1-(1-(3-methoxyphenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3r**)

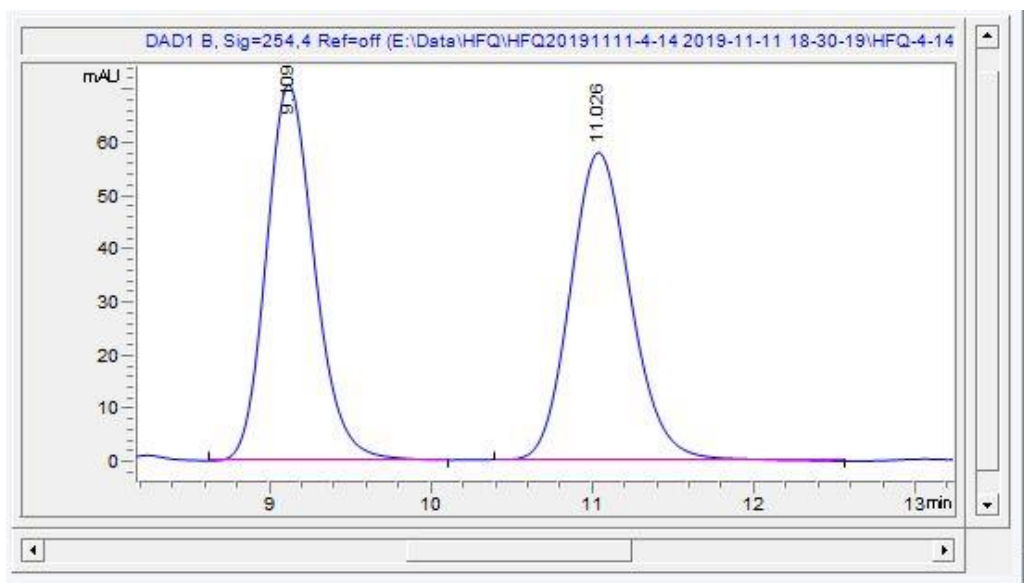
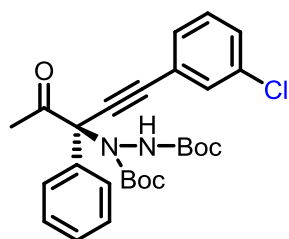


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.092	BV	2292	103.7	0.3378	47.122	0.753
2	10.451	VB	2572	94.8	0.4124	52.878	0.829

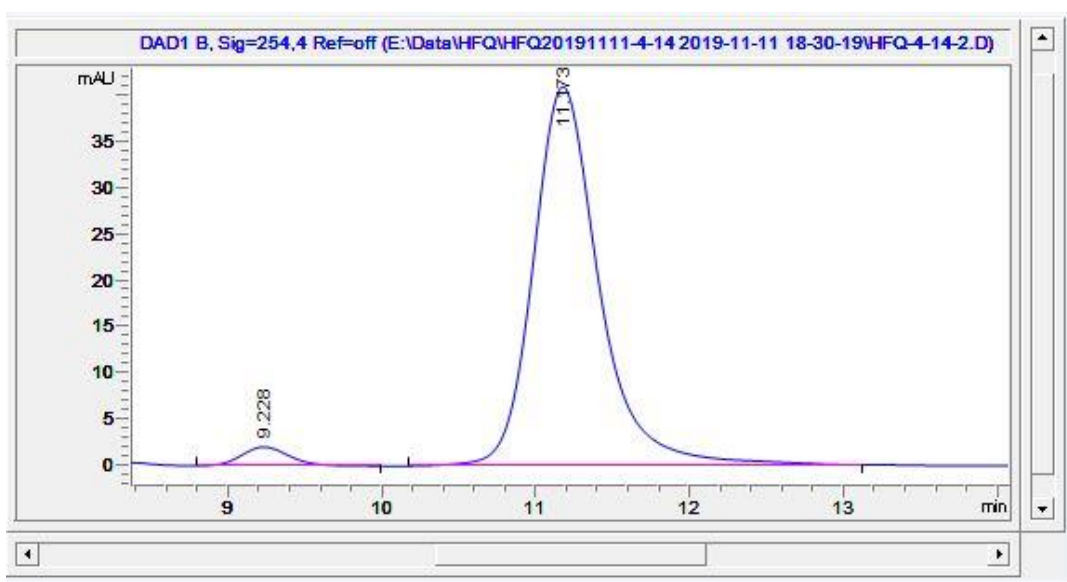


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.145	BB	50.6	2.4	0.3273	2.889	0.89
2	10.508	BB	1700.5	67.2	0.3912	97.111	0.823

Di-tert-butyl-(*R*)-1-(1-(3-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3s**)

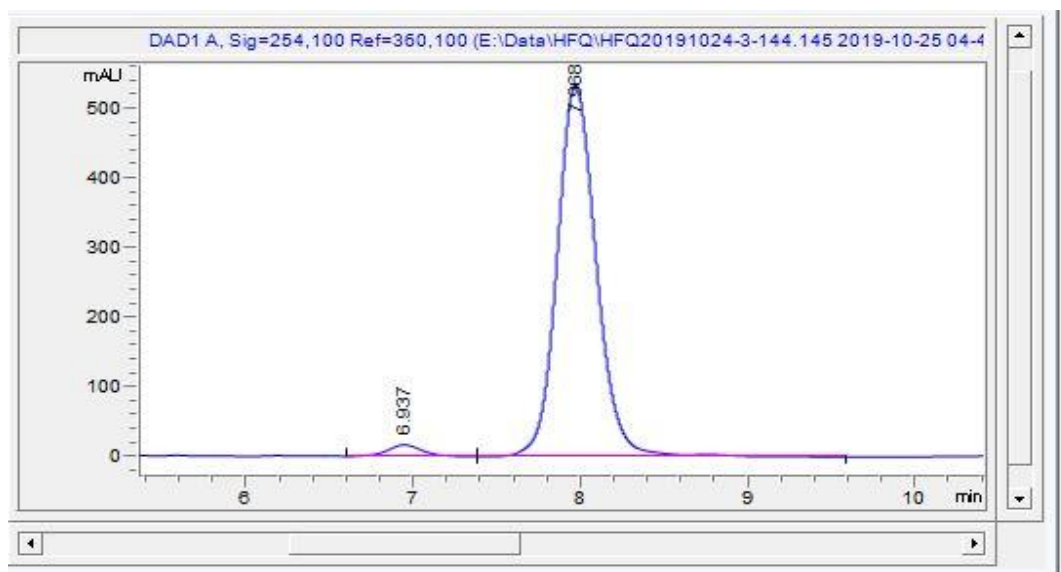
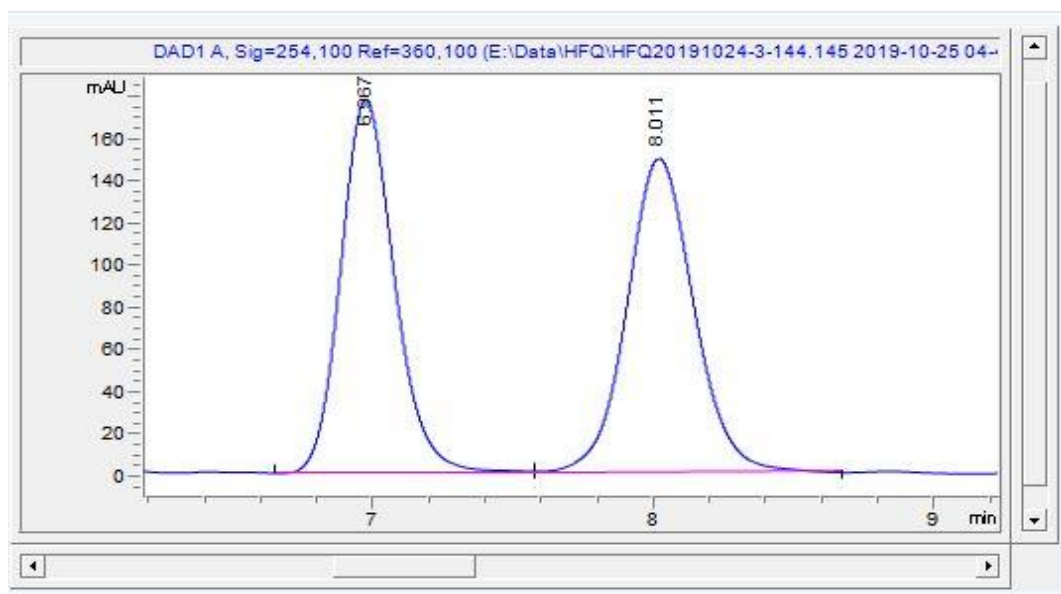
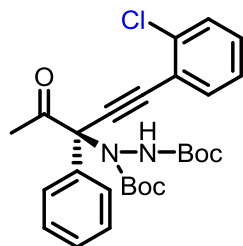


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.109	BB	1457.5	70.5	0.3194	49.441	0.811
2	11.026	BB	1490.4	57.6	0.3999	50.559	0.839

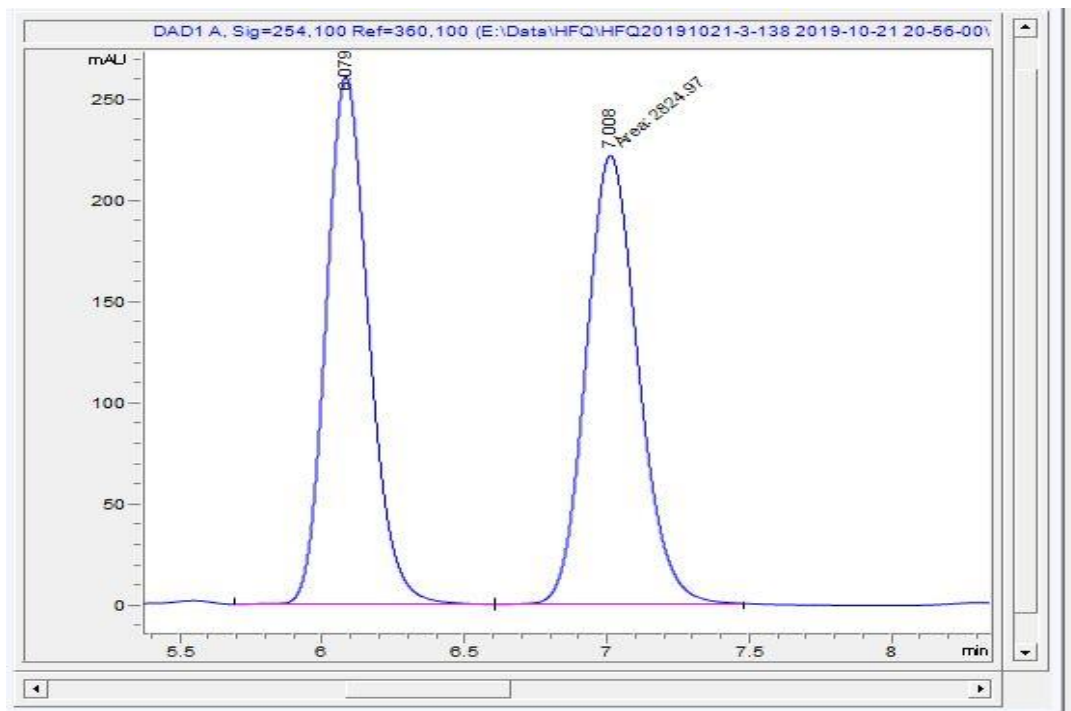
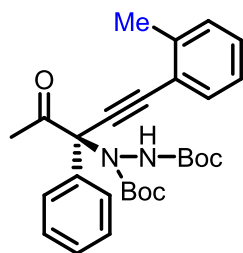


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.228	BB	44.1	2	0.3317	3.483	0.858
2	11.173	BB	1221.6	40.8	0.4531	96.517	0.764

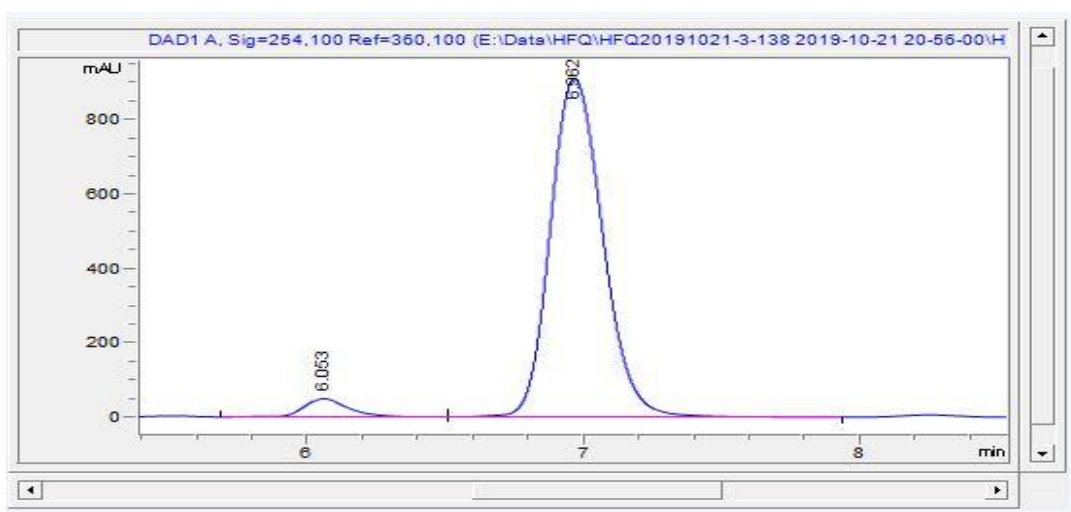
Di-tert-butyl-(*R*)-1-(1-(2-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3t**)



Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*o*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3u**)

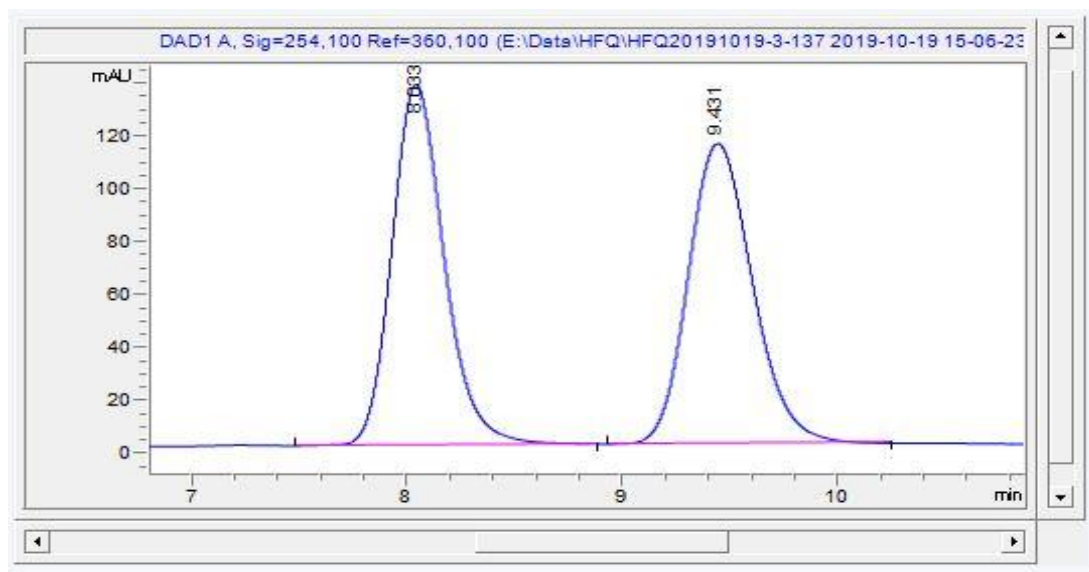
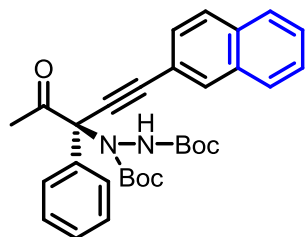


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.079	BB	2715.1	260.6	0.1605	49.008	0.814
2	7.008	MF	2825	222	0.2121	50.992	0.848

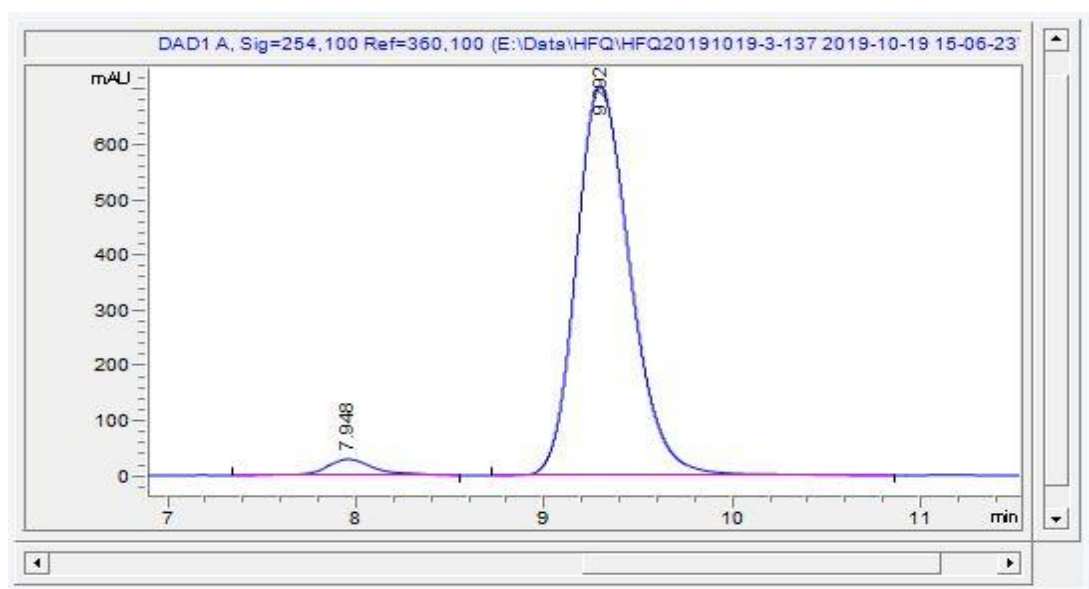


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.053	VV R	559.9	49.4	0.1683	4.446	0.778
2	6.962	VB	12031.9	912.4	0.2078	95.554	0.806

Di-tert-butyl-(*R*)-1-(1-(naphthalen-2-yl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3v**)

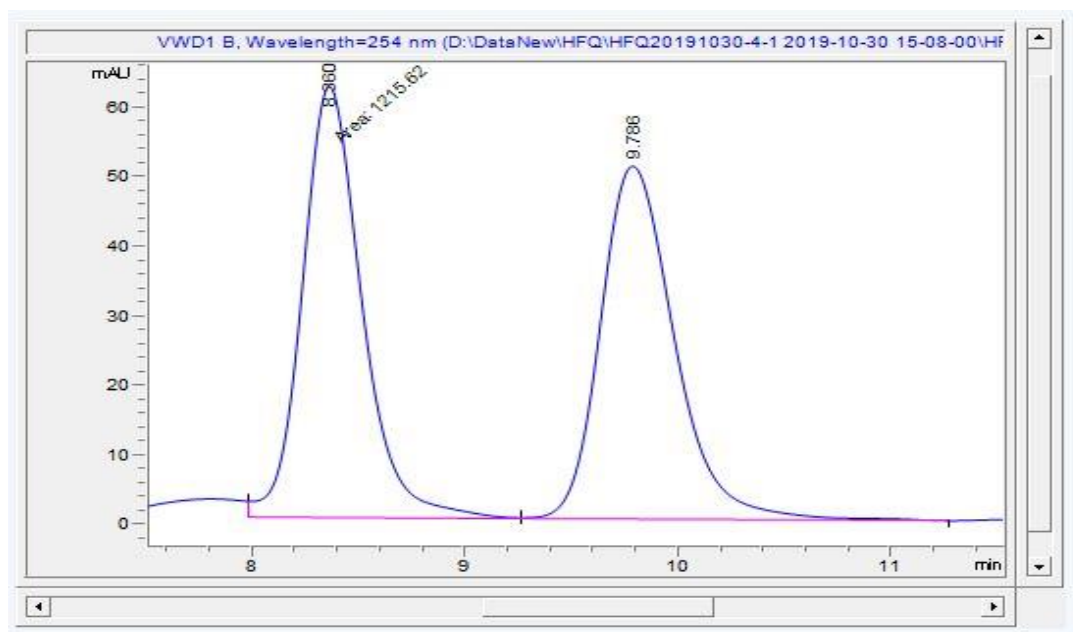
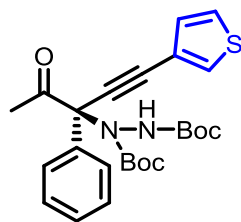


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.033	BB	2291	136	0.2545	49.494	0.803
2	9.431	BB	2337.8	113.3	0.3173	50.506	0.817

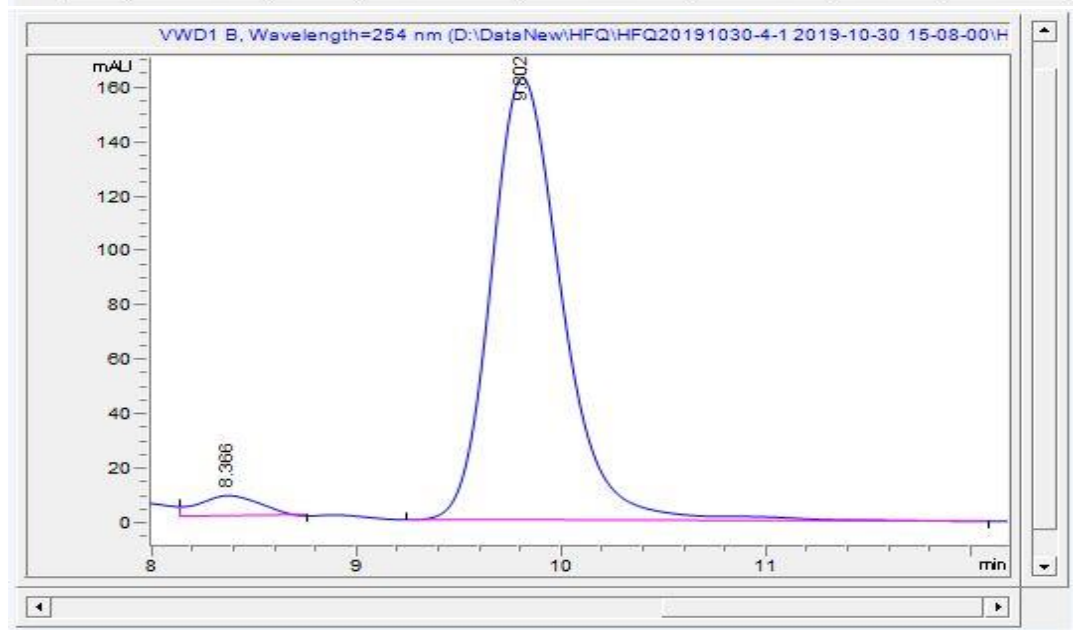


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.948	BB	532.6	29.2	0.2718	3.665	0.816
2	9.292	BB	13997.6	700.3	0.3082	96.335	0.749

Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(thiophen-3-yl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3w**)

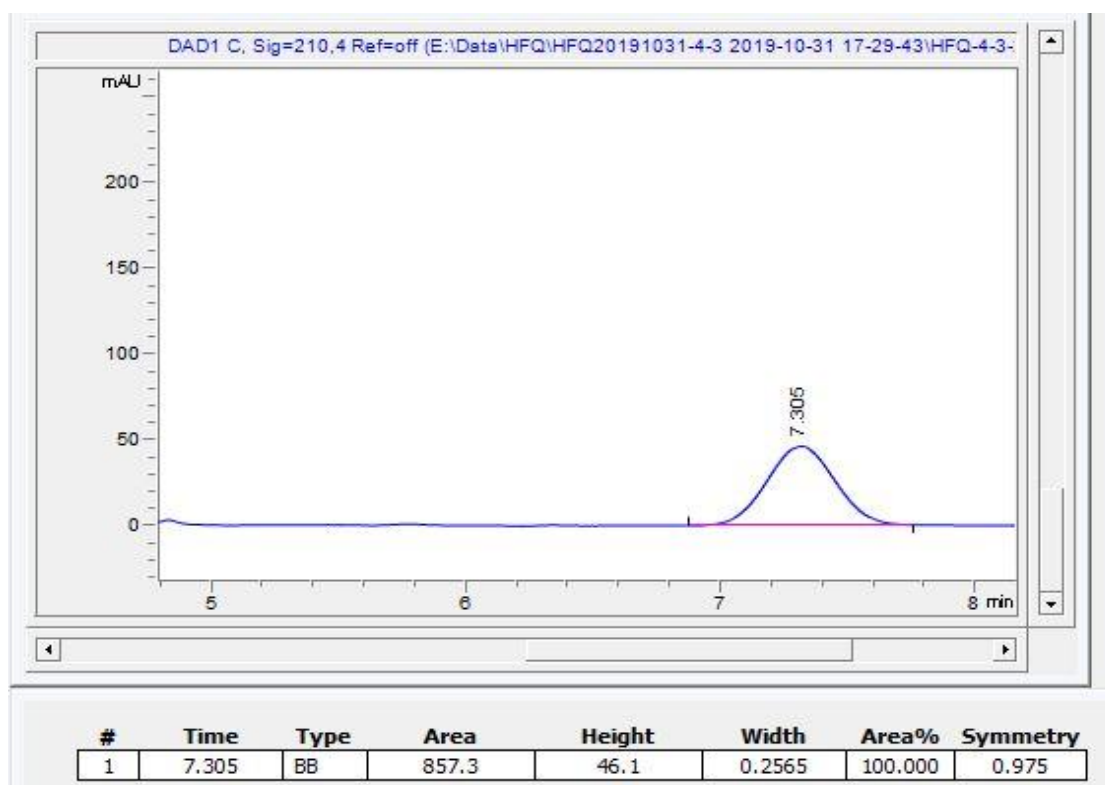
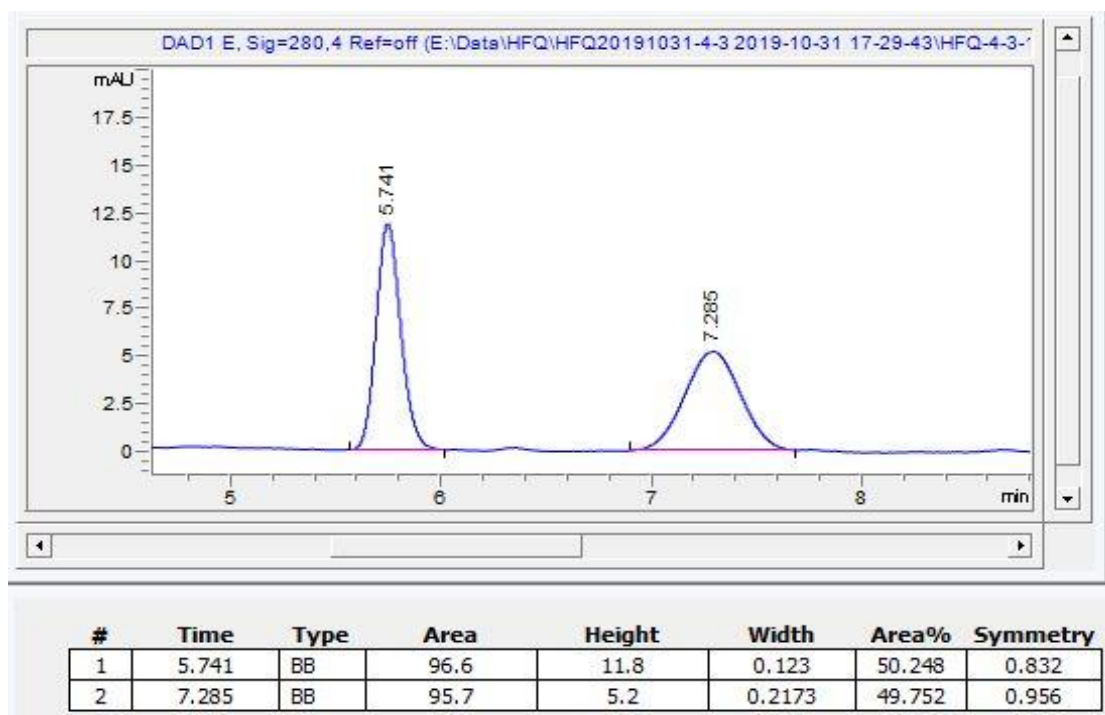
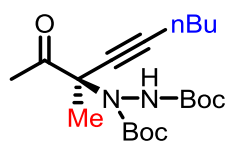


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.36	FM	1215.6	62.2	0.3257	49.614	0.8
2	9.786	VB	1234.5	50.9	0.3751	50.386	0.723

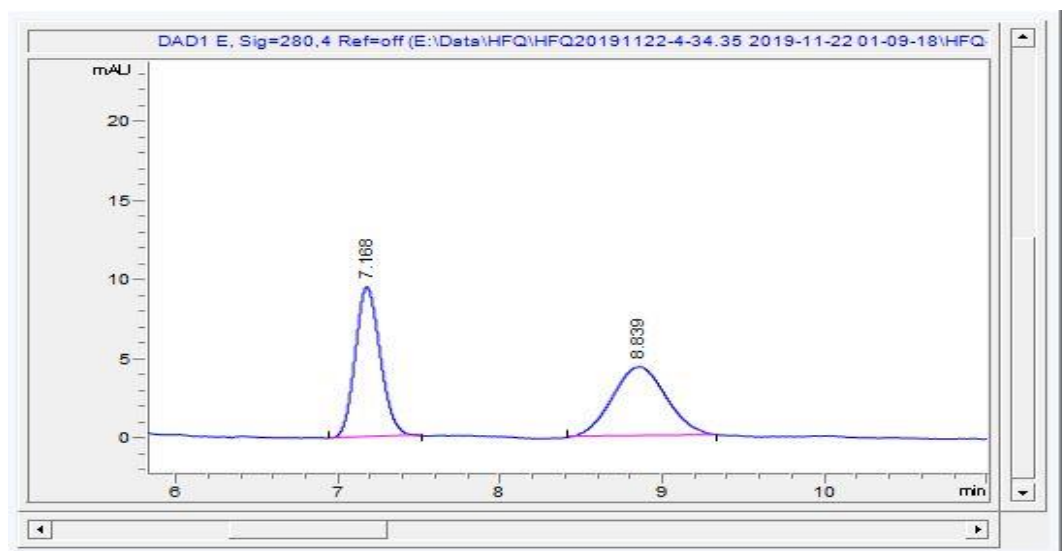
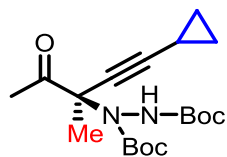


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.366	VB	161.7	7.7	0.3362	3.973	0.893
2	9.802	BB	3907.6	162.3	0.371	96.027	0.735

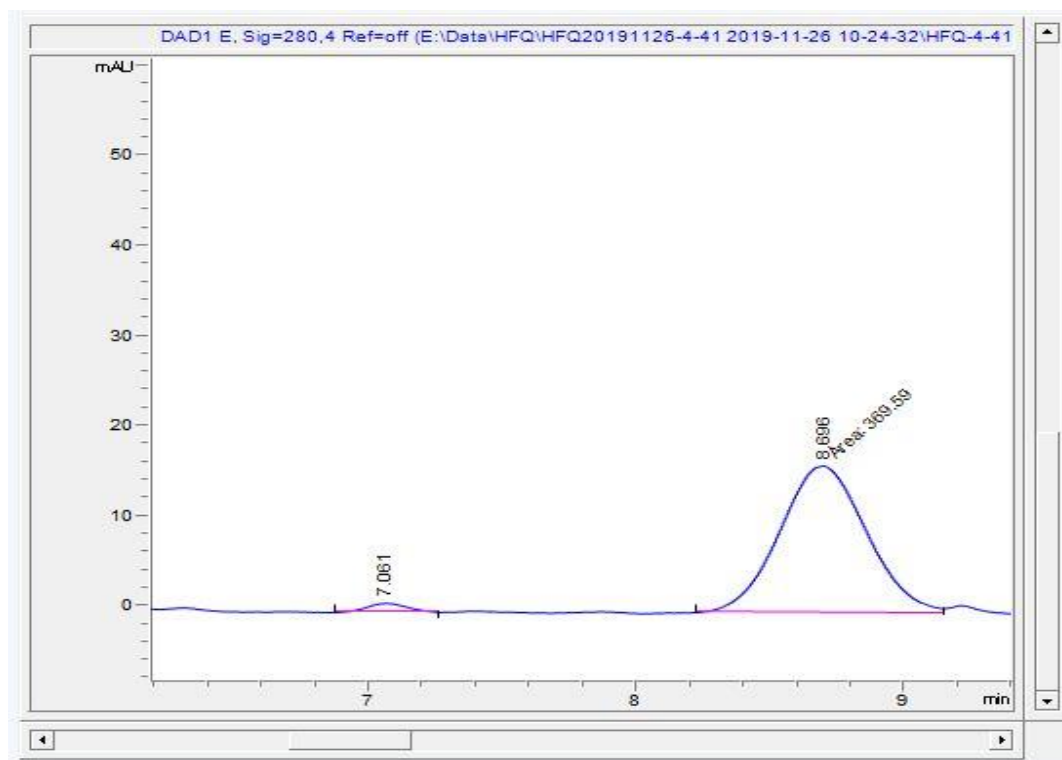
Di-tert-butyl (*R*)-1-(3-methyl-2-oxonon-4-yn-3-yl)hydrazine-1,2-dicarboxylate (**3x**)



Di-tert-butyl-(*R*)-1-(1-cyclopropyl-3-methyl-4-oxopent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3y**)

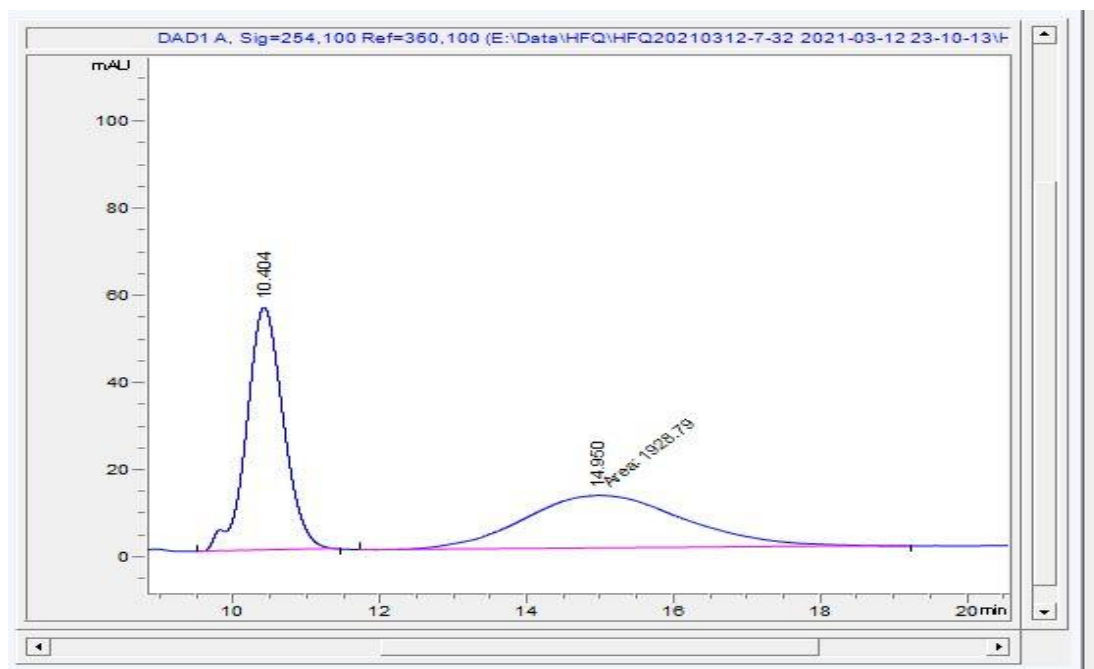
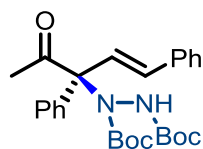


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.168	BB	102.8	9.5	0.1286	50.107	0.837
2	8.839	BB	102.4	4.4	0.2759	49.893	0.921

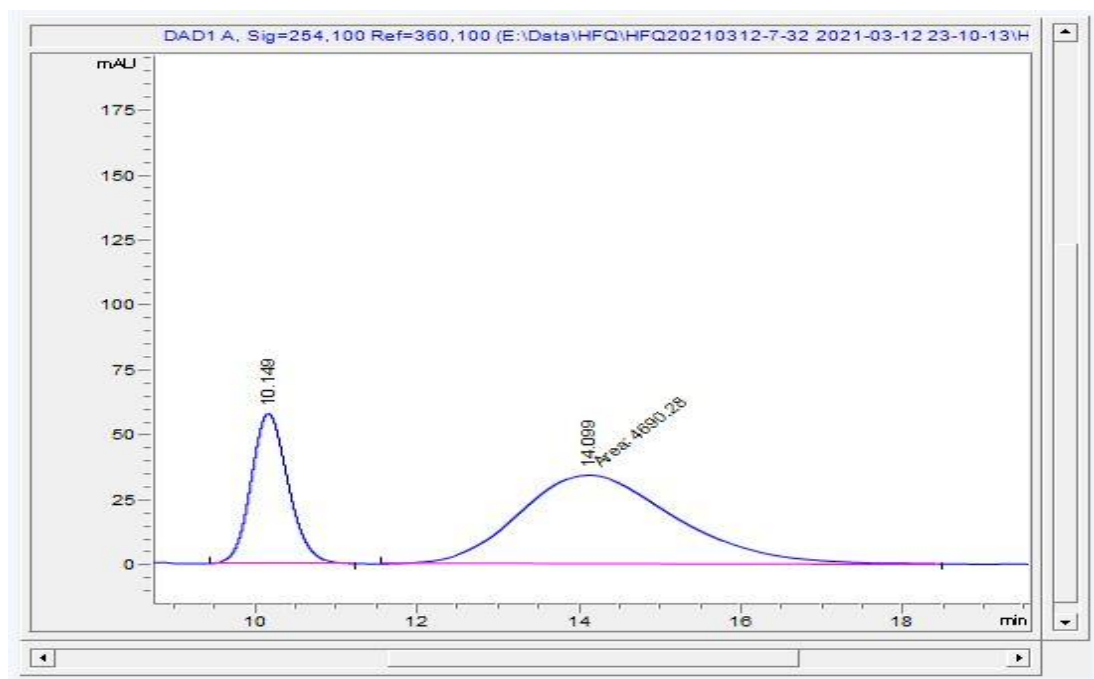


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.061	BB	10.8	1	0.1279	2.828	0.891
2	8.696	MF	369.6	16.3	0.3775	97.172	0

Di-tert-butyl (S,E)-1-(4-oxo-1,3-diphenylpent-1-en-3-yl)hydrazine-1,2-dicarboxylate
(5a)

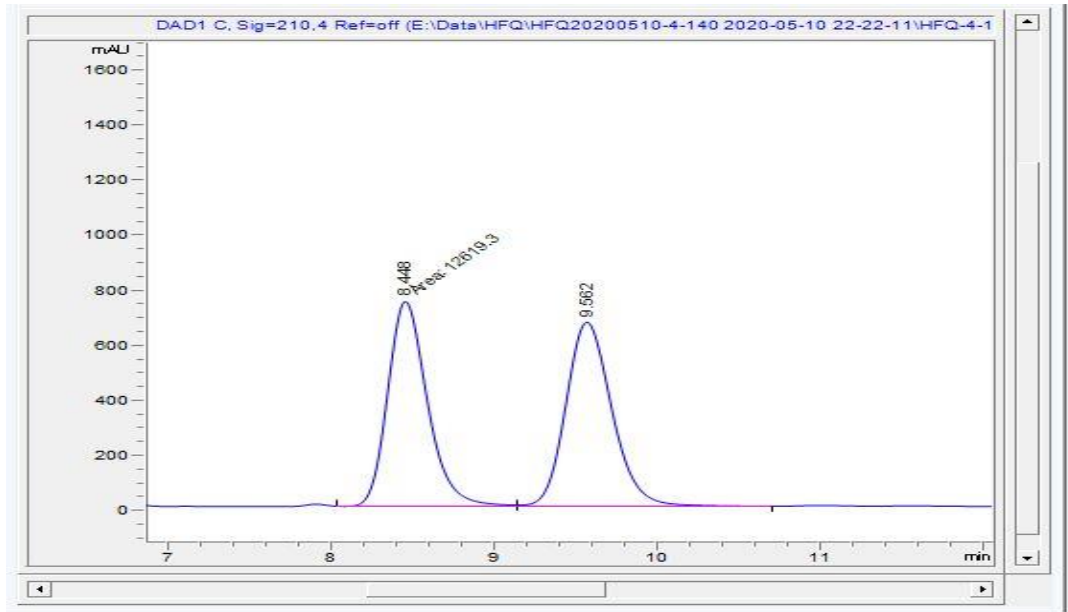
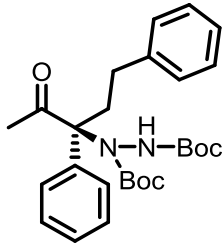


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.404	VB R	1947.4	56	0.4069	50.240	0.934
2	14.95	MM	1928.8	12.3	2.6113	49.760	0.843

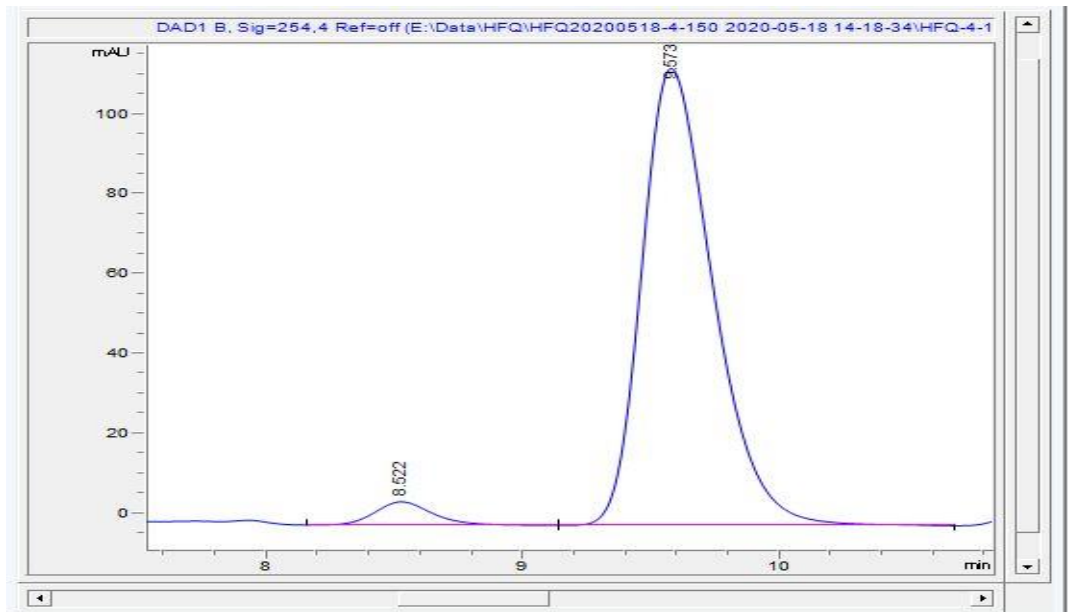


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.149	BB	1834.4	57.9	0.3808	28.115	0.875
2	14.099	MM	4690.3	34.4	2.2724	71.885	0.774

Di-tert-butyl (*S*)-1-(4-oxo-1,3-diphenylpentan-3-yl)hydrazine-1,2-dicarboxylate (**7a**)

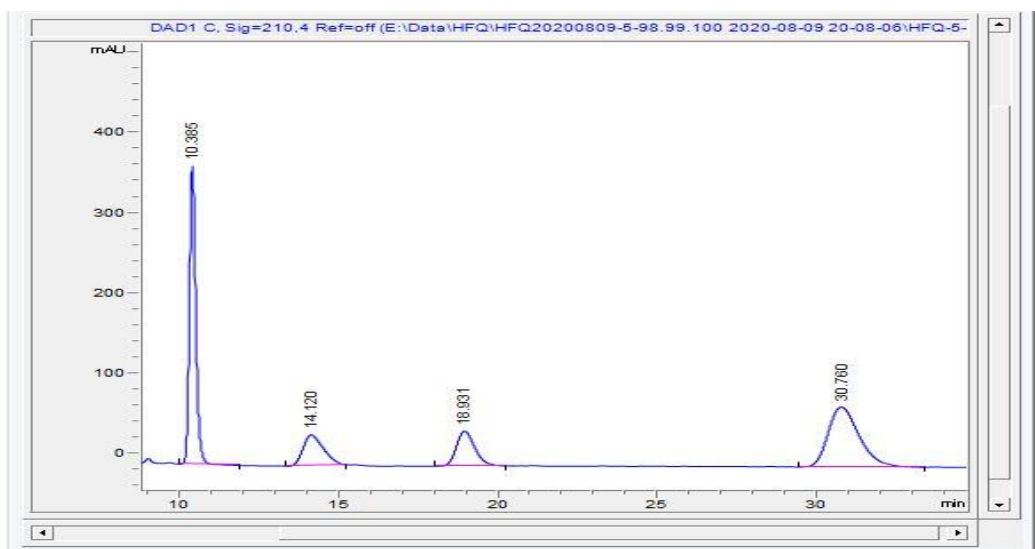
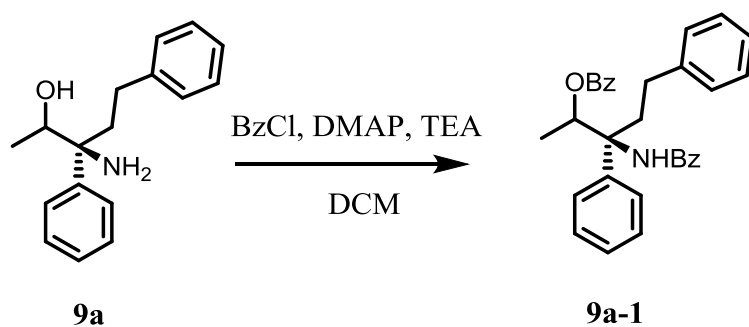


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.448	FM	12619.3	743.8	0.2828	49.001	0.777
2	9.562	VB	13133.8	668.1	0.3033	50.999	0.801

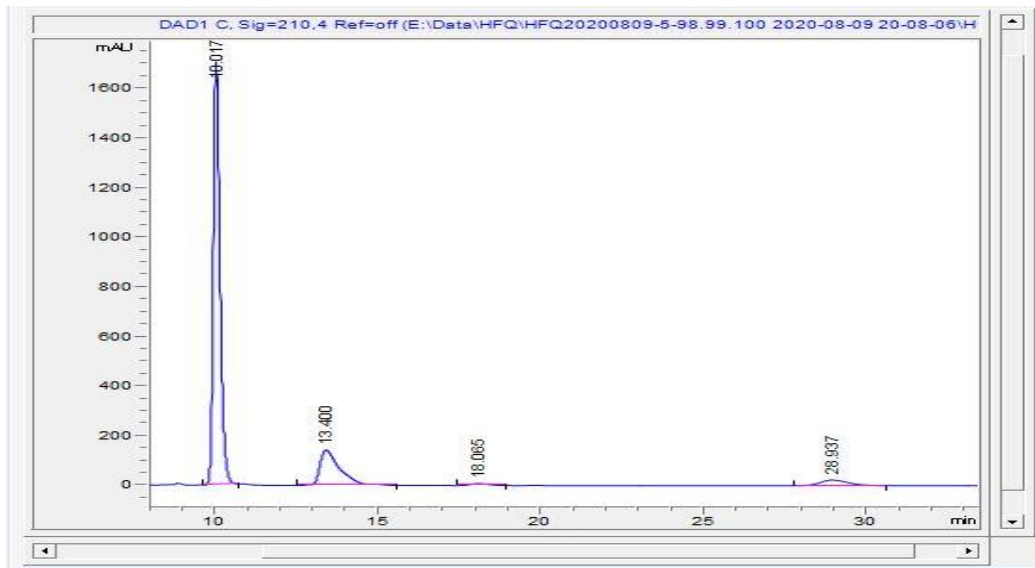


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.522	BB	91.6	5.9	0.2365	3.981	0.814
2	9.573	BB	2208.6	114.6	0.2969	96.019	0.663

(3S)-3-benzamido-3,5-diphenylpentan-2-yl benzoate (**8a-1**)

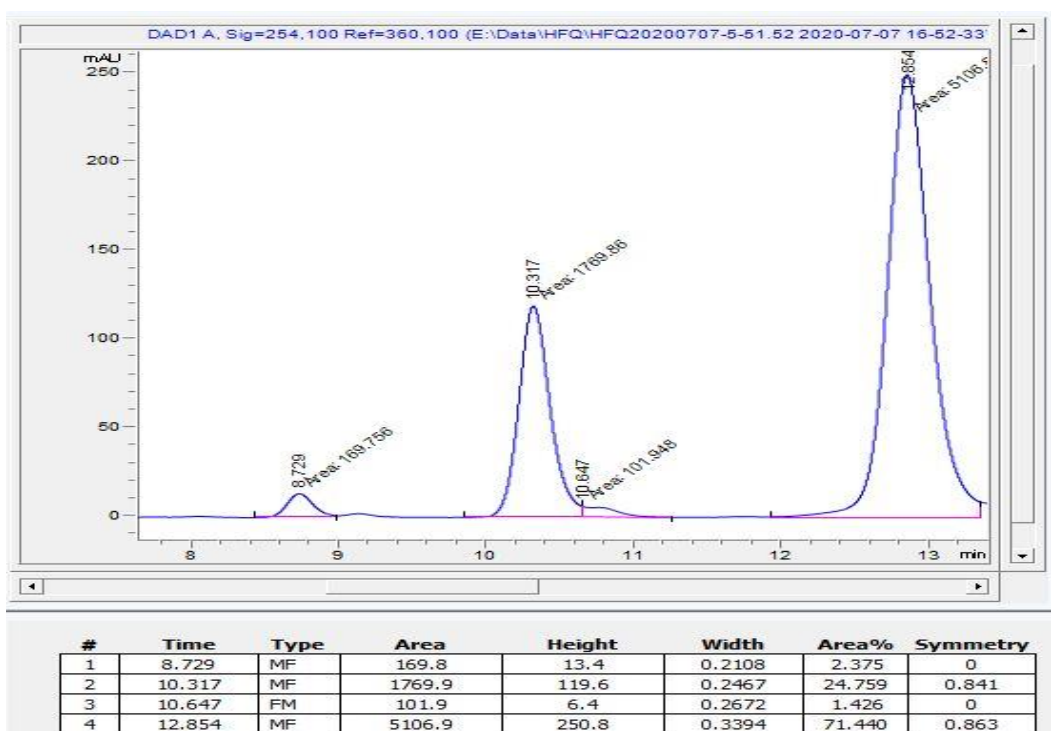
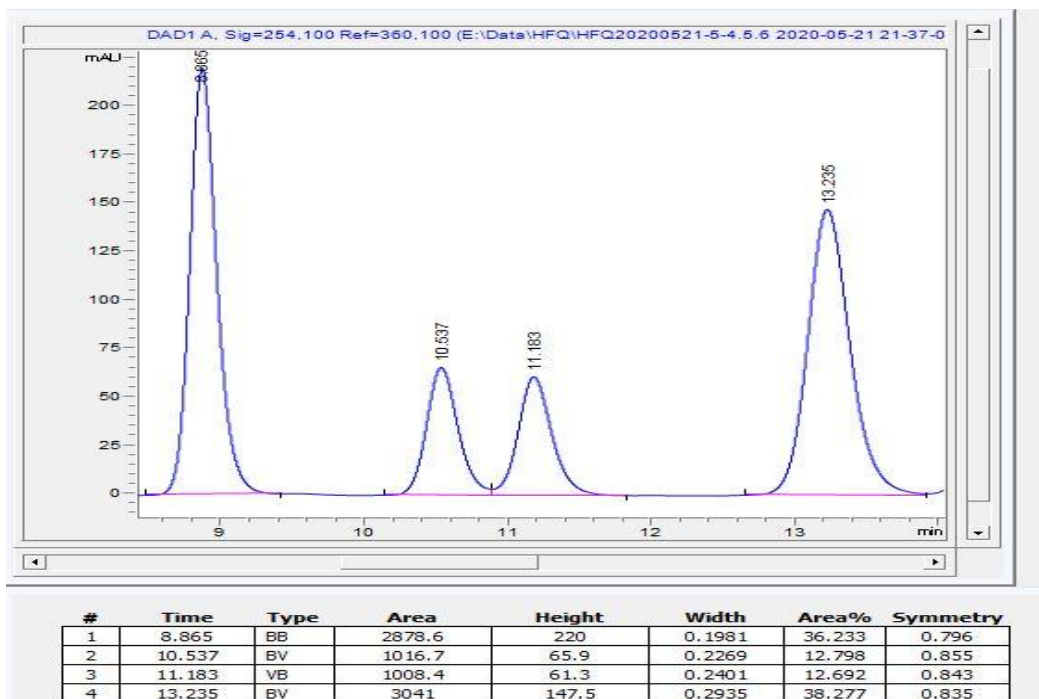
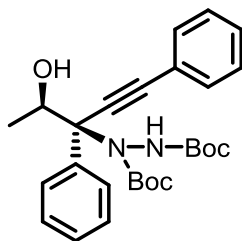


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.385	BB	5155.5	372.7	0.2114	37.525	0.772
2	14.12	BB	1726.7	38.7	0.6447	12.568	0.644
3	18.931	BB	1751.7	43.7	0.5896	12.750	0.747
4	30.76	BB	5104.8	75	0.99	37.156	0.702

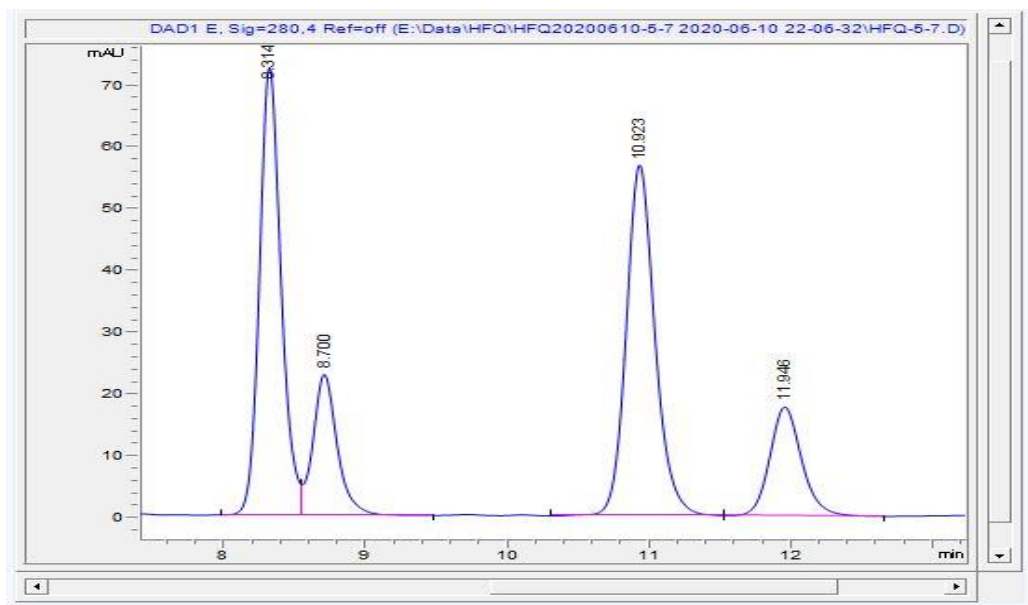
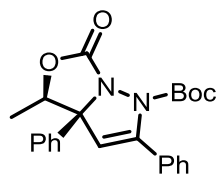


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.017	BB	24121	1707.1	0.2168	75.604	0.687
2	13.4	VV R	6120.7	142.7	0.6148	19.185	0.437
3	18.065	BB	299.2	8	0.5181	0.938	0.793
4	28.937	BB	1363.3	22.5	0.8003	4.273	0.763

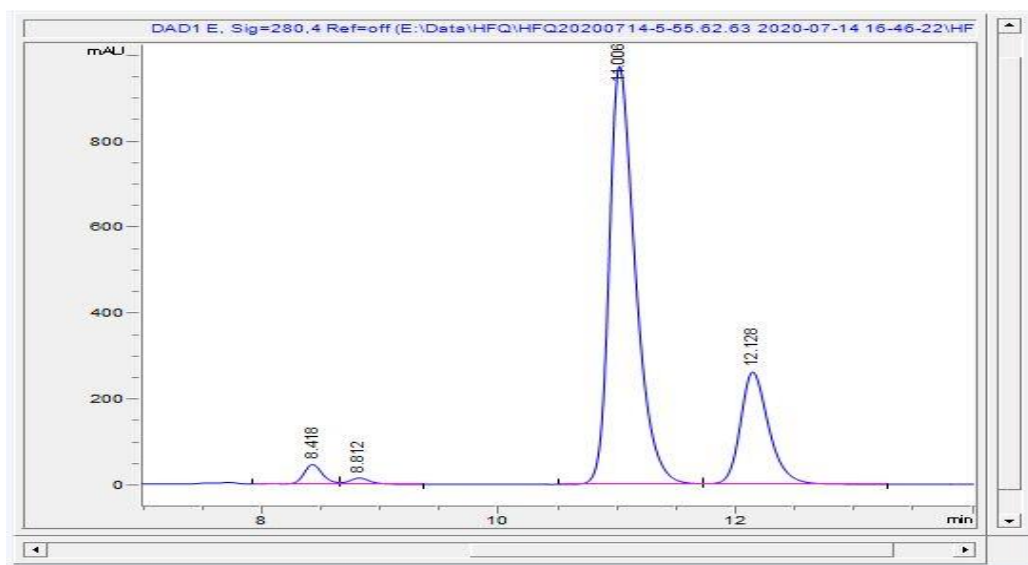
Di-tert-butyl-1-((3*R*,4*R*)-4-hydroxy-1,3-diphenylpent-1-yn-3-yl)hydrazine-1,2-dicarbonylate (**9a**)



Tert-butyl-(3*a*S,4*R*)-4-methyl-6-oxo-2,3*a*-diphenyl-3*a*,4-dihydro-1*H*,6*H*-pyrazolo[1,5-*c*]oxazole-1-carboxylate (**10a**)



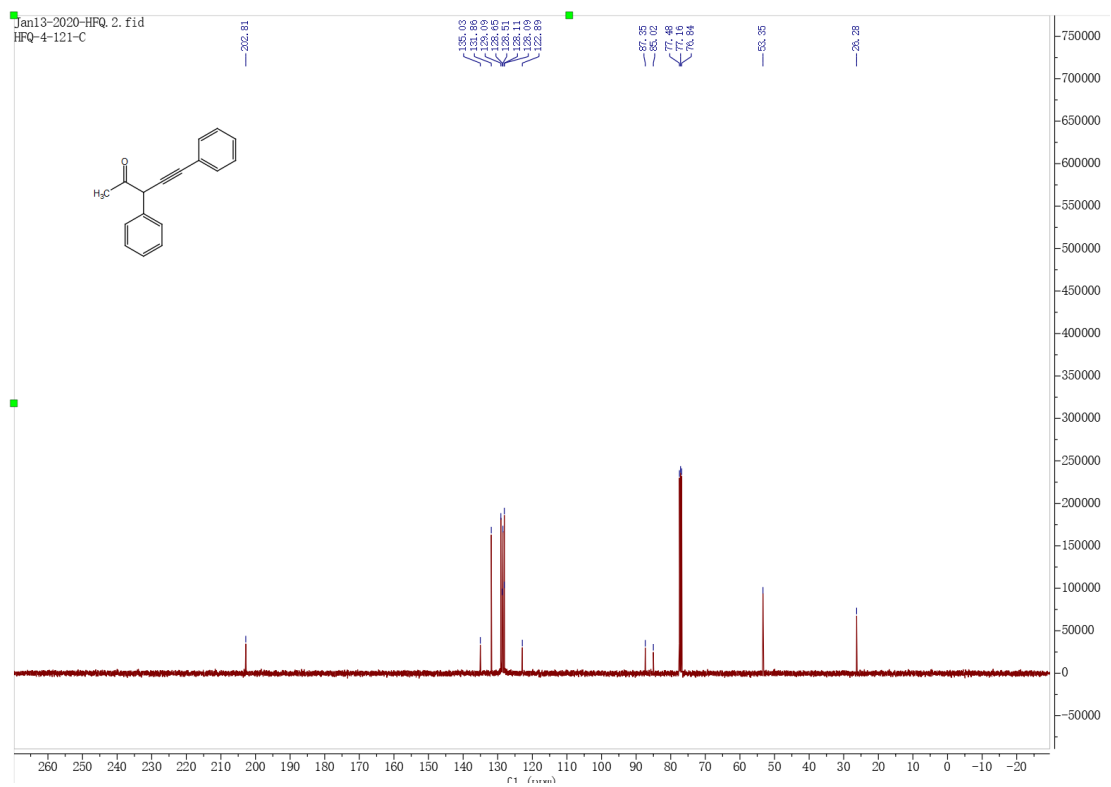
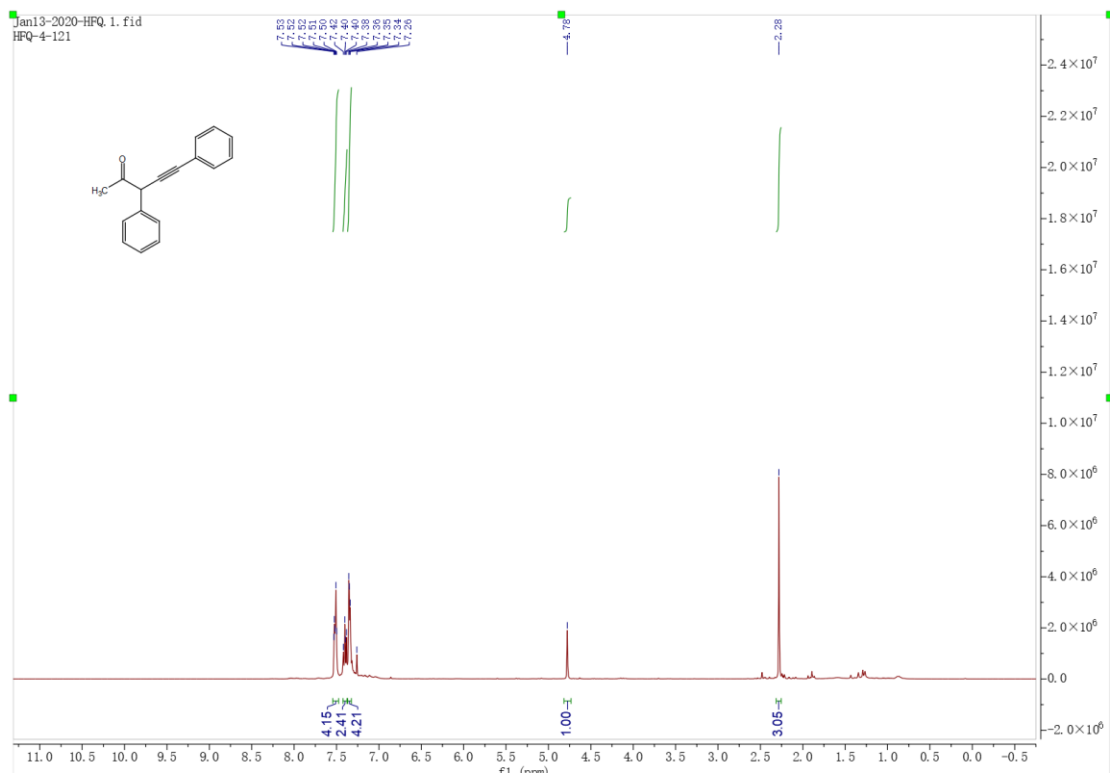
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.314	BV	768.9	72.4	0.1619	36.363	0.817
2	8.7	VB	269.5	22.7	0.1783	12.746	0.809
3	10.923	BB	800.3	56.7	0.2146	37.847	0.839
4	11.946	BB	275.8	17.6	0.2389	13.044	0.842



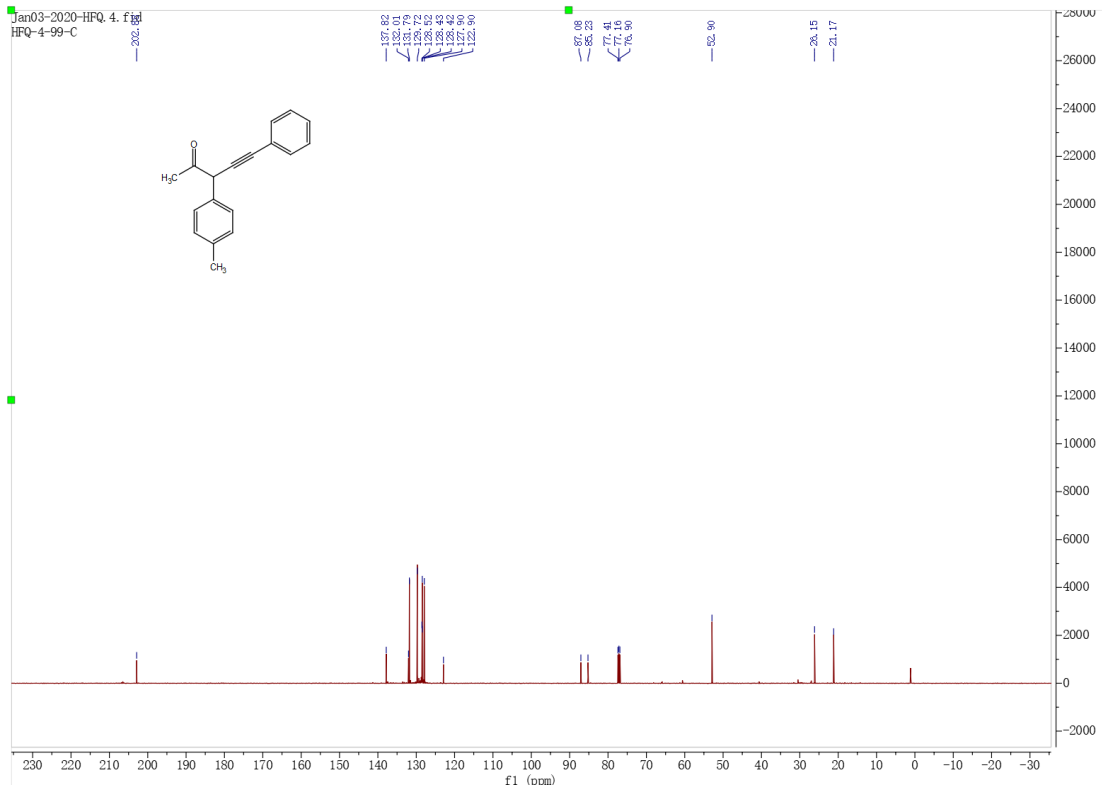
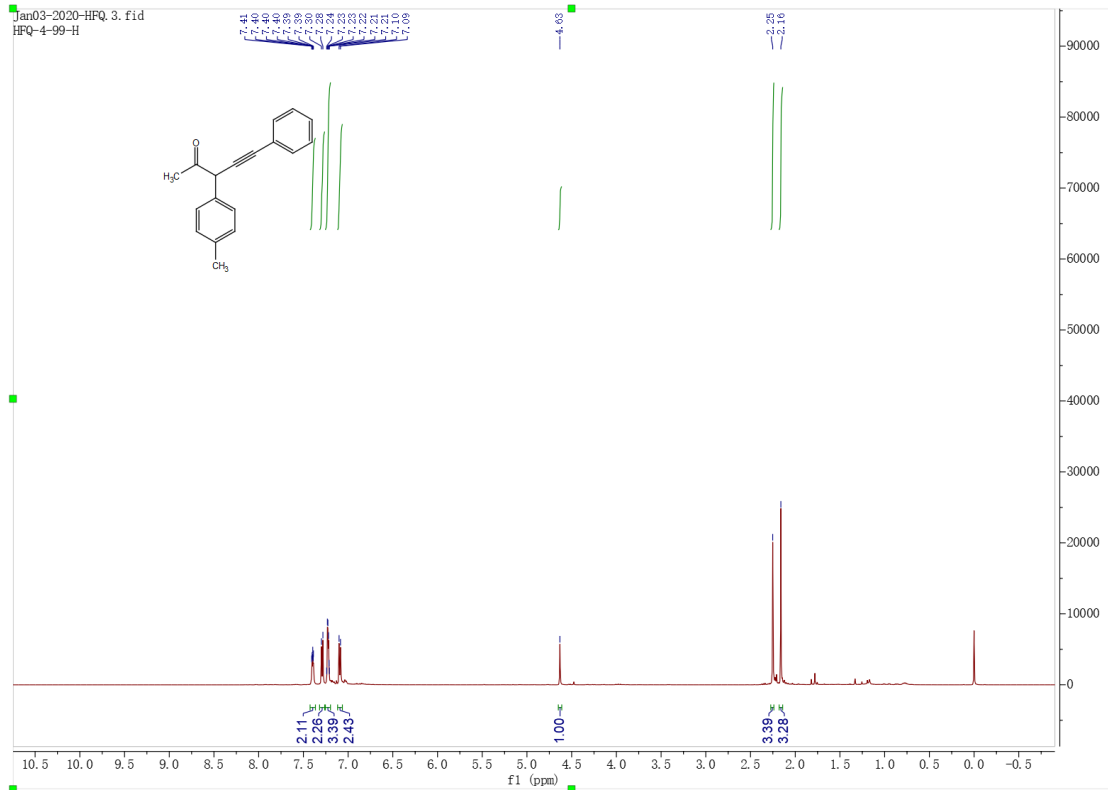
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	8.418	VV R	508.6	45.8	0.1677	2.552	0.831
2	8.812	VB	172.8	14.4	0.1805	0.867	0.866
3	11.006	BV	14884.6	973.8	0.2323	74.684	0.617
4	12.128	VB	4364	261.3	0.2529	21.897	0.732

NMR spectra

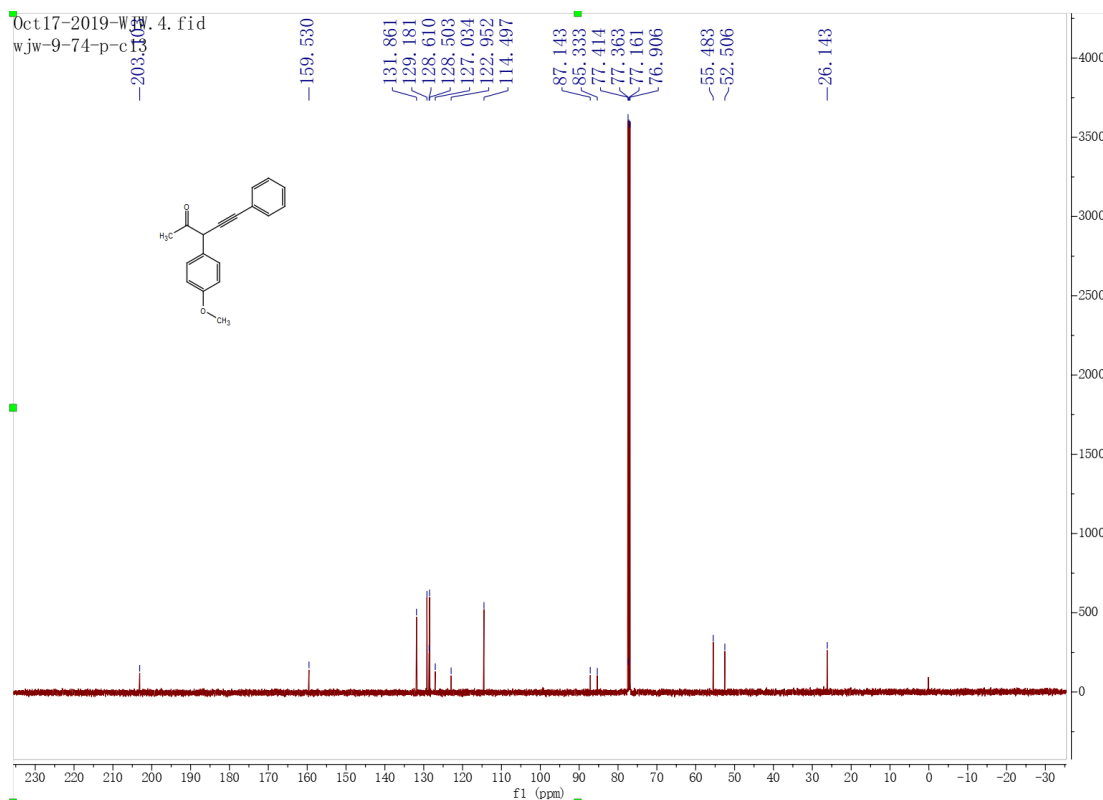
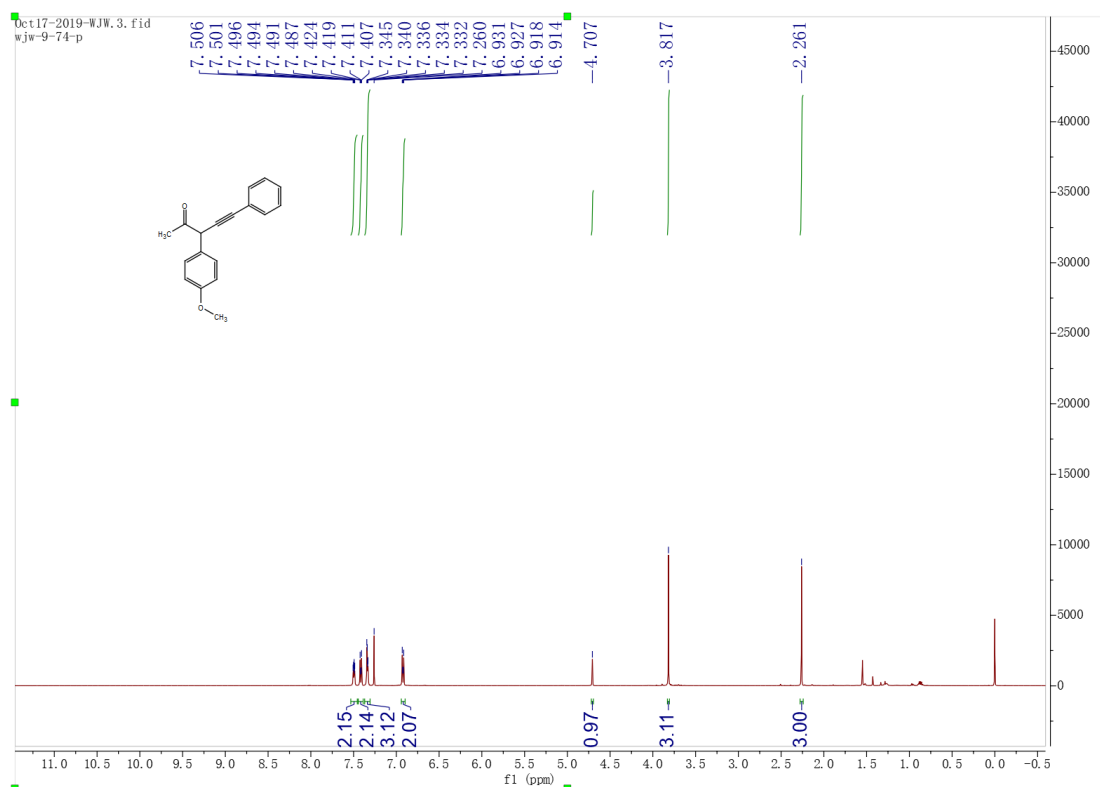
3,5-diphenylpent-4-yn-2-one (**1a**)



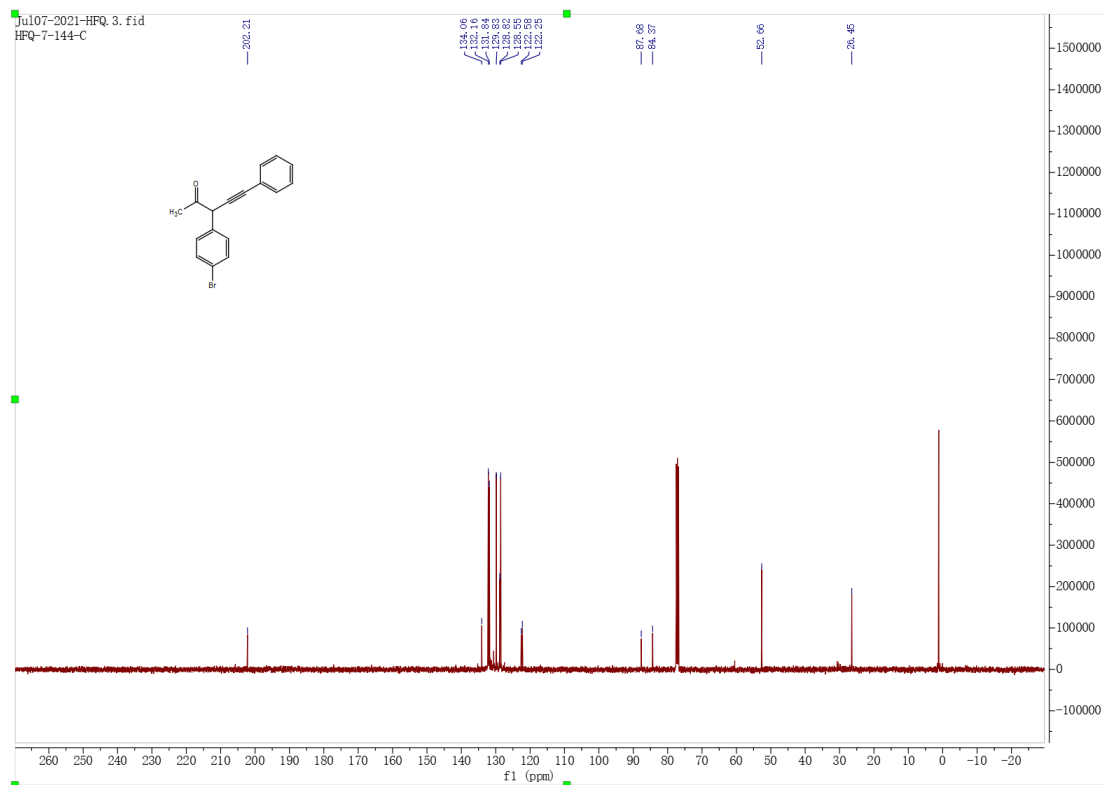
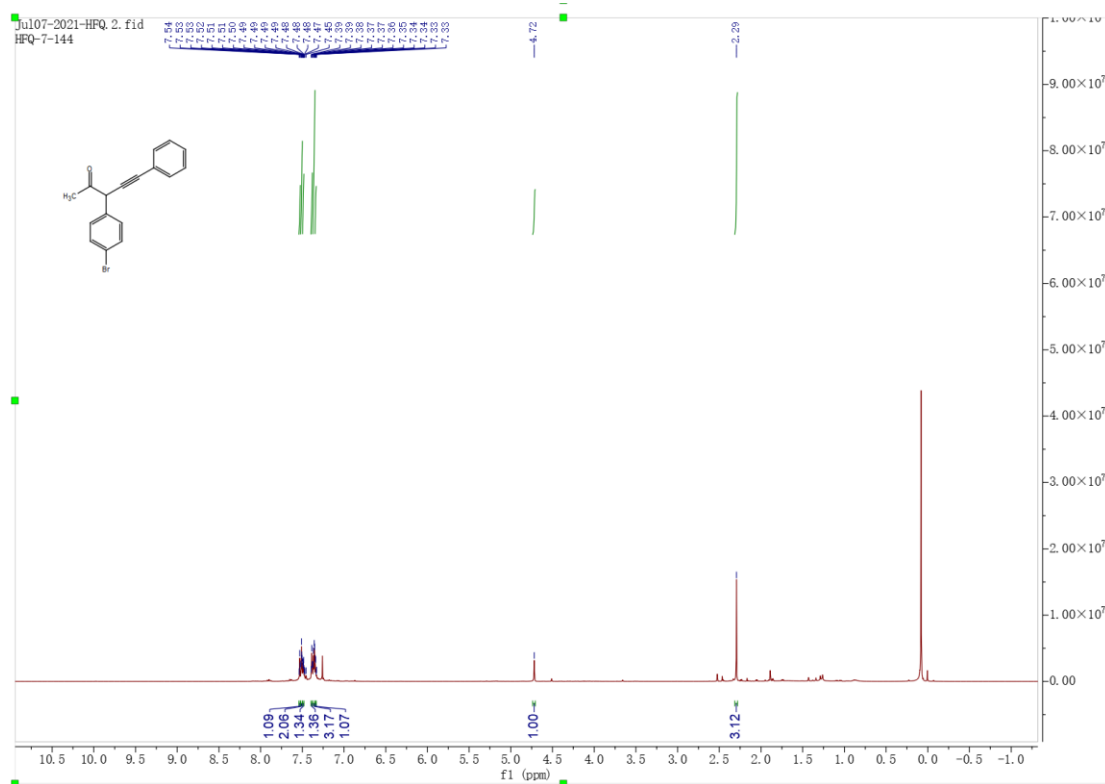
5-phenyl-3-(p-tolyl)pent-4-yn-2-one (**1b**)



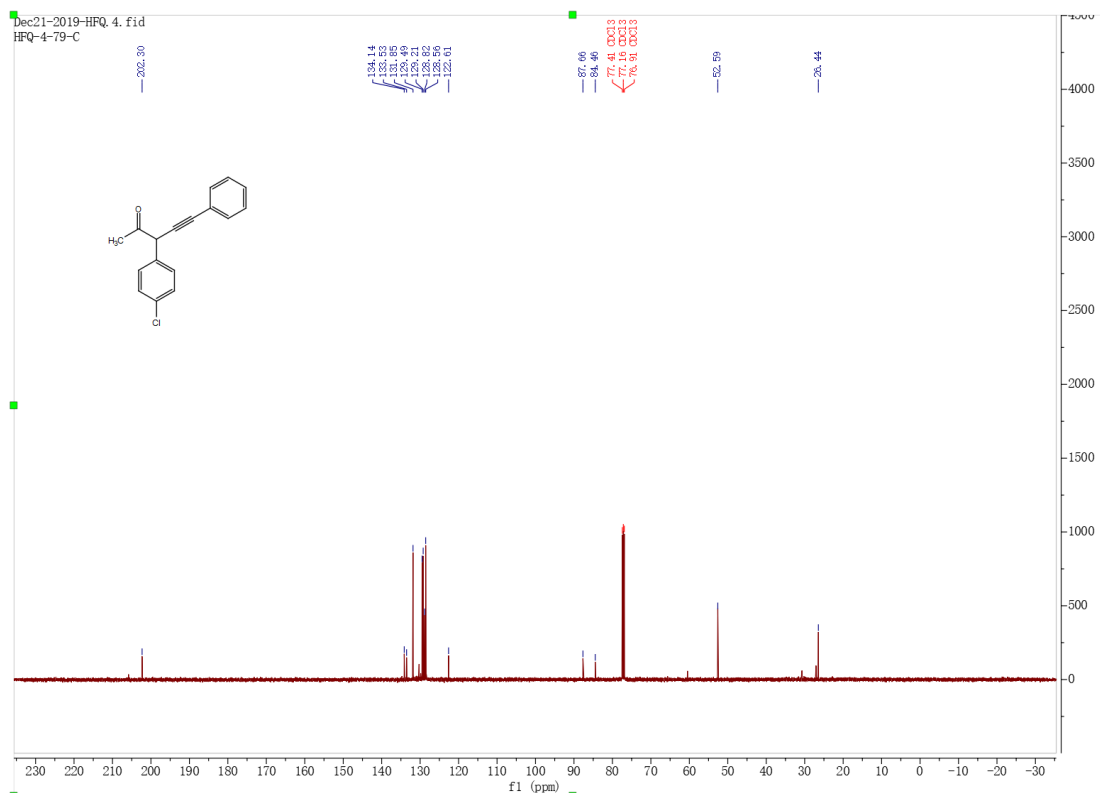
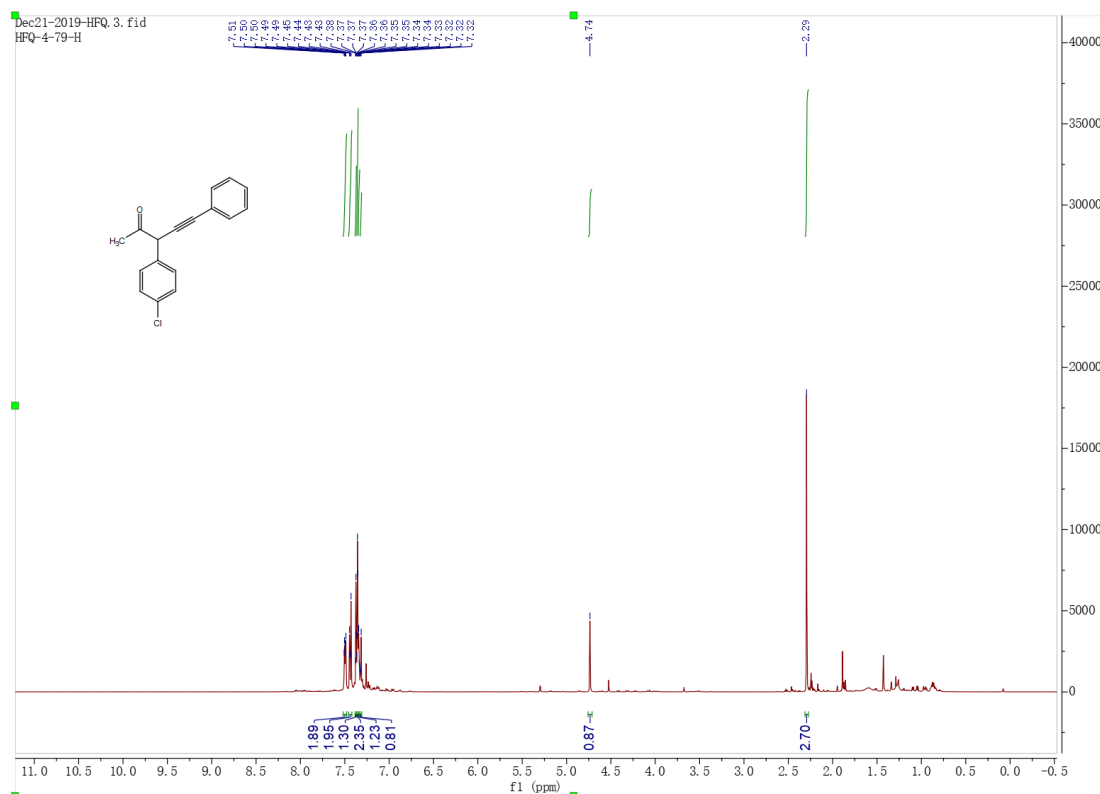
3-(4-methoxyphenyl)-5-phenylpent-4-yn-2-one (**1c**)



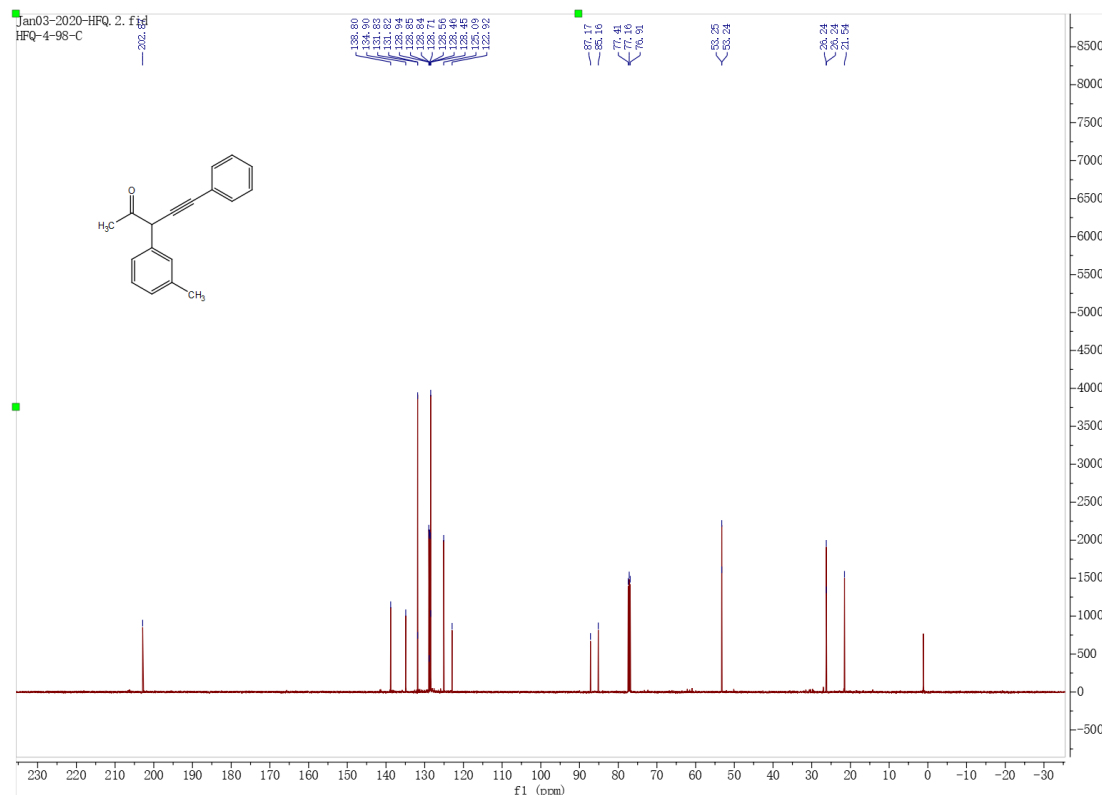
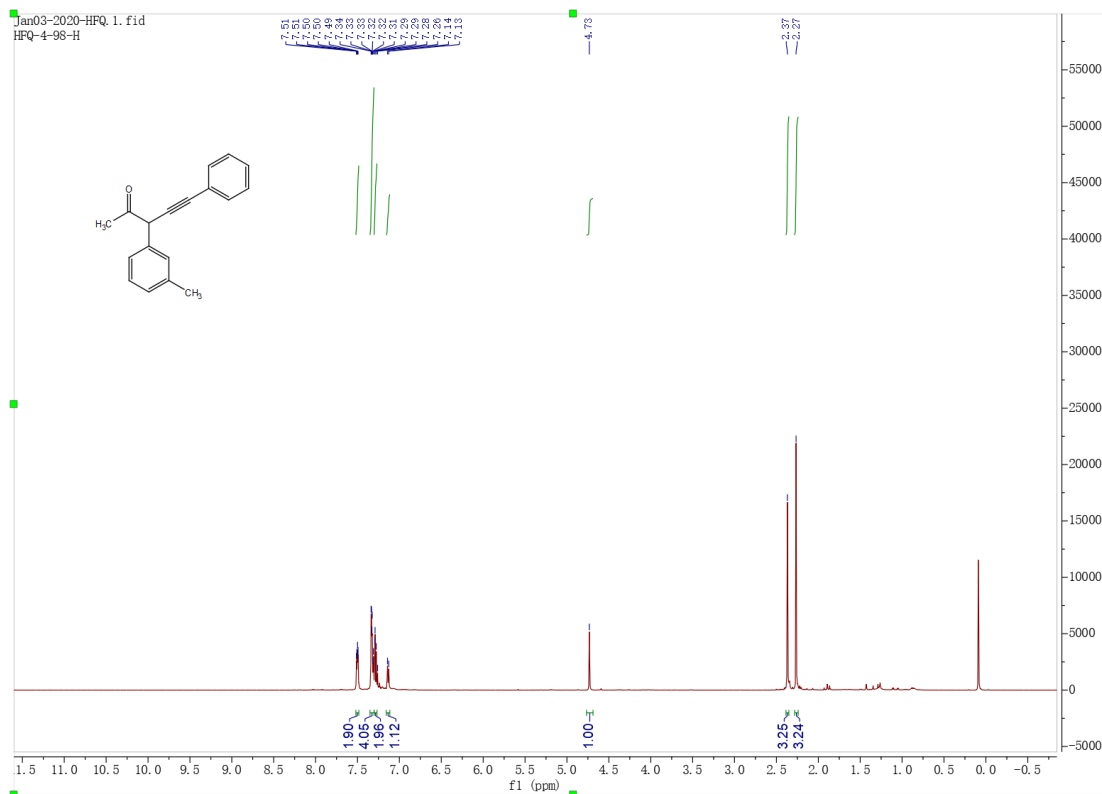
3-(4-bromophenyl)-5-phenylpent-4-yn-2-one (**1d**)



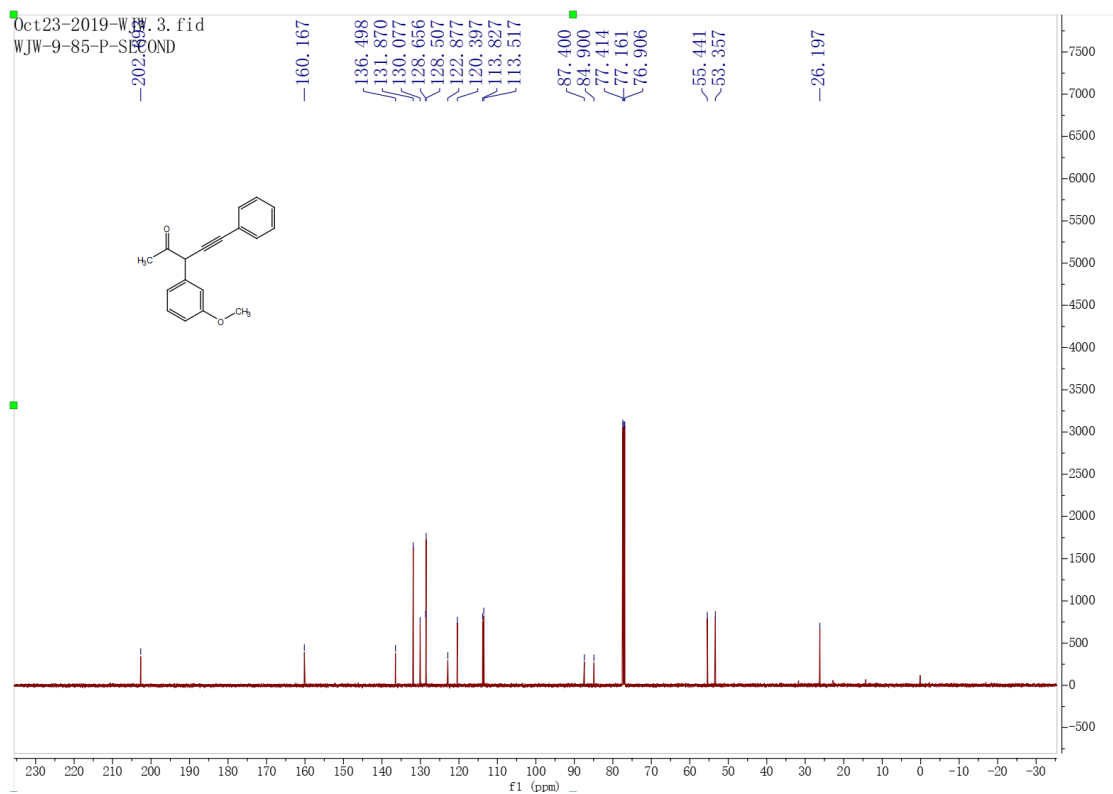
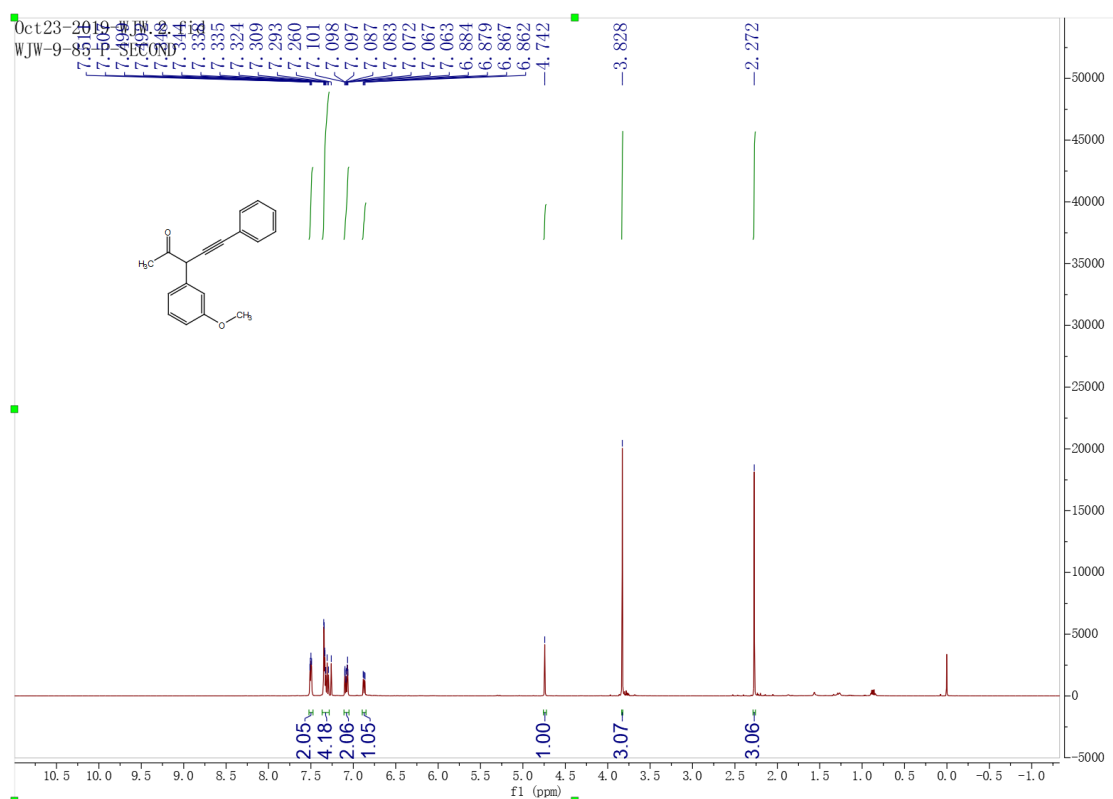
3-(4-chlorophenyl)-5-phenylpent-4-yn-2-one (**1e**)



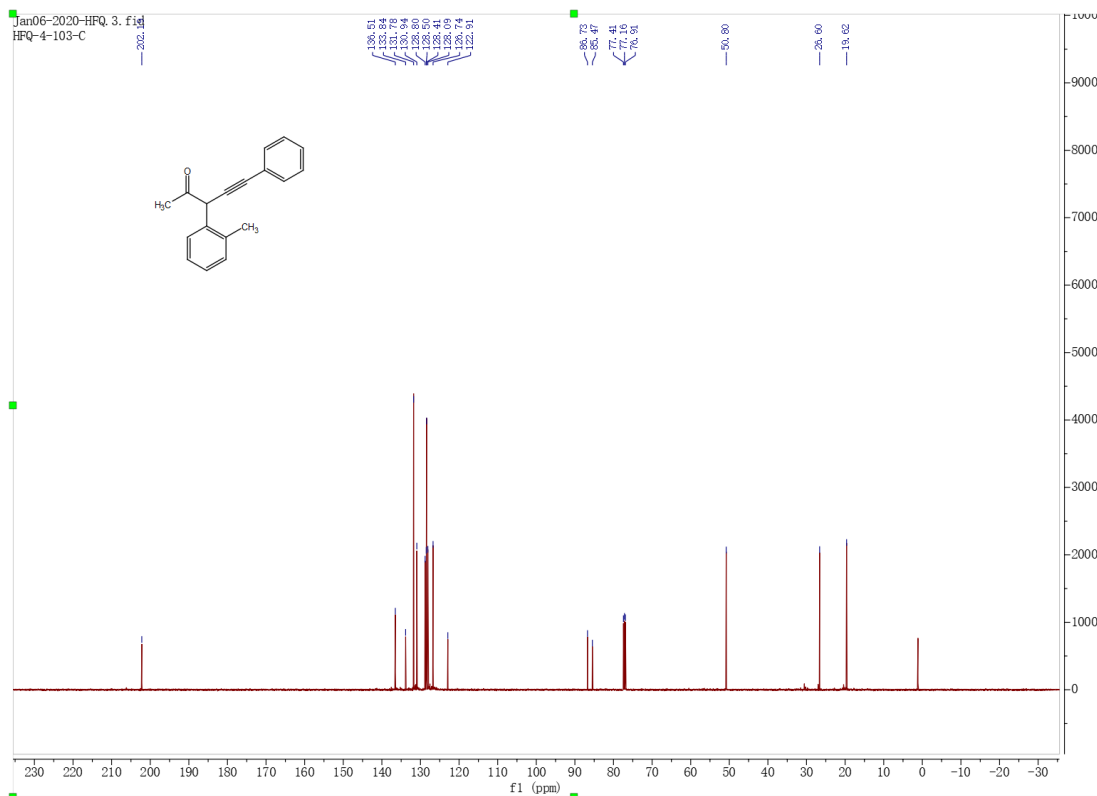
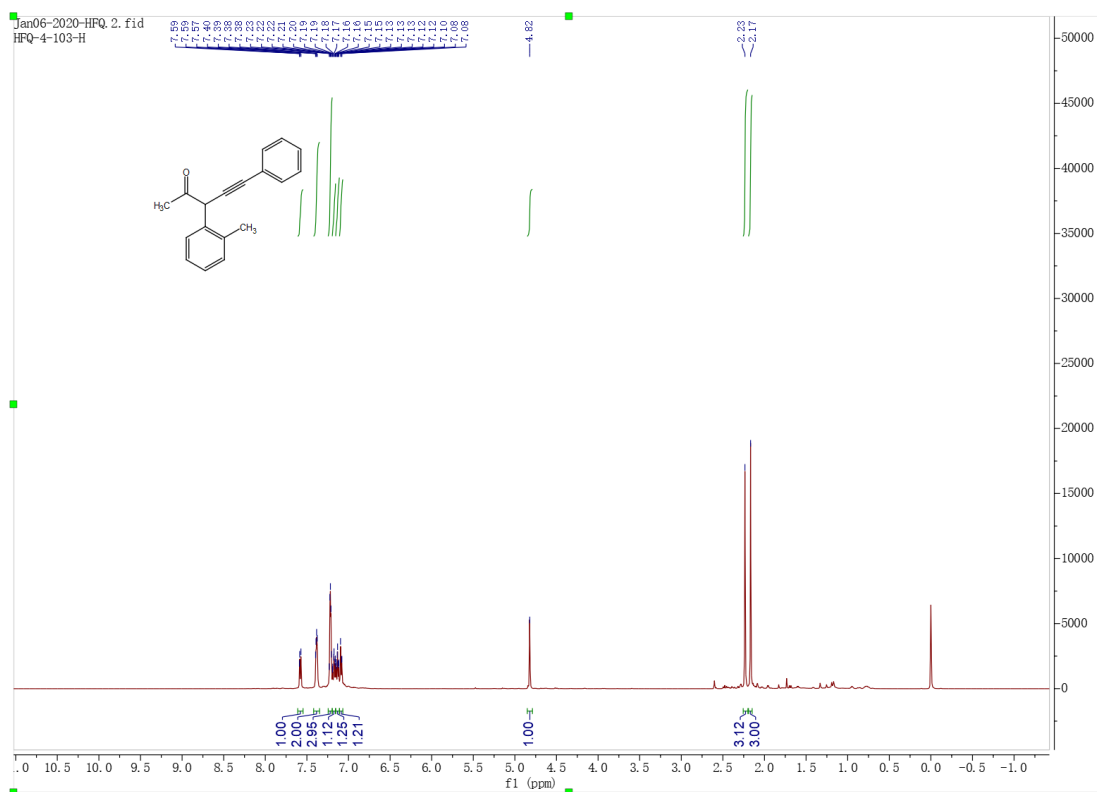
5-phenyl-3-(m-tolyl)pent-4-yn-2-one (**1f**)



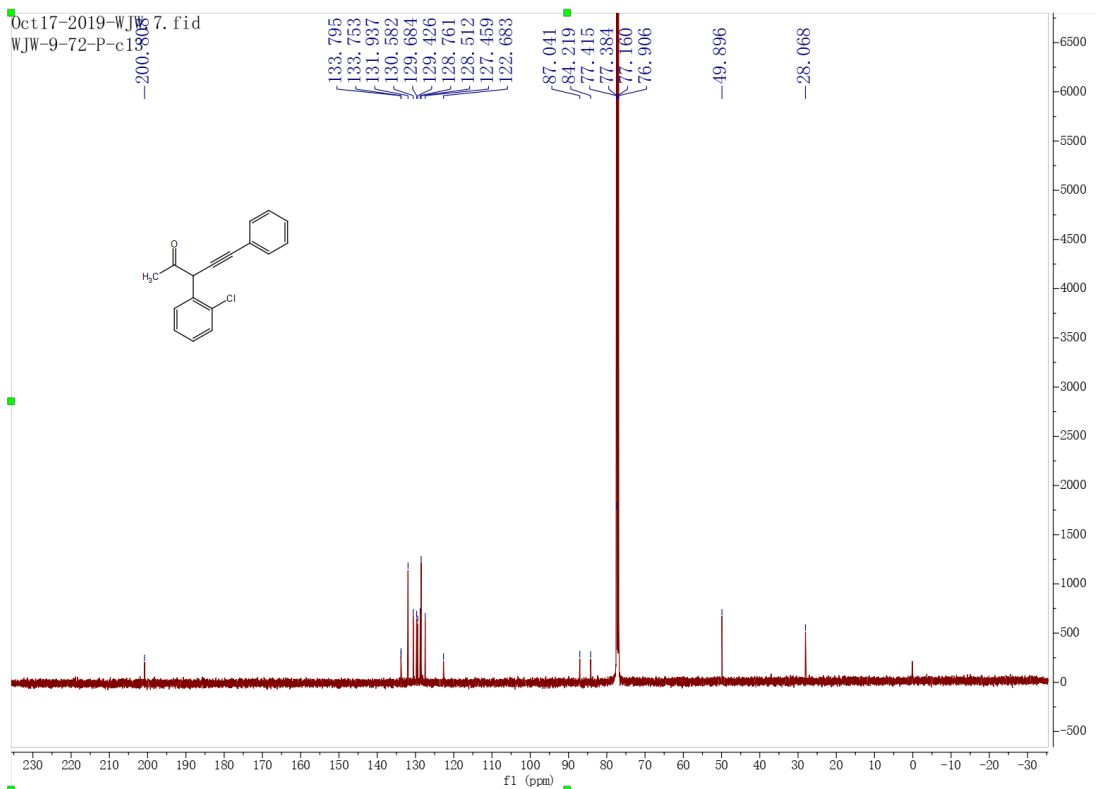
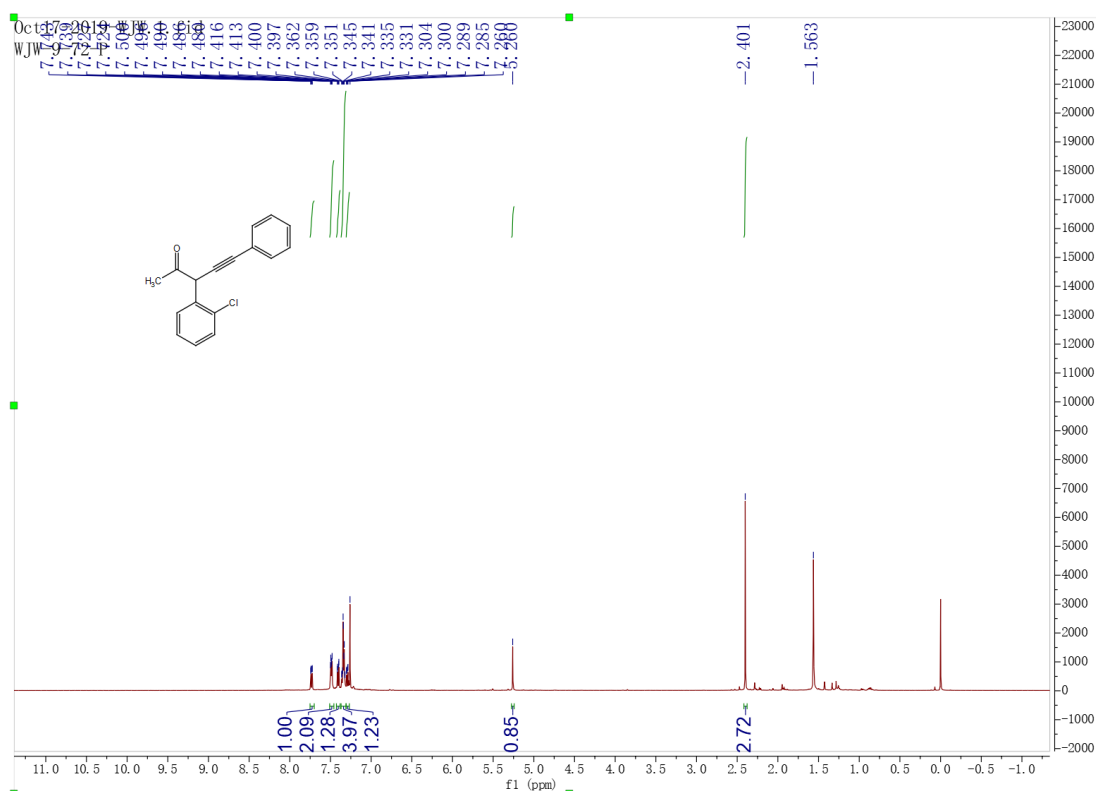
3-(3-methoxyphenyl)-5-phenylpent-4-yn-2-one (**1g**)



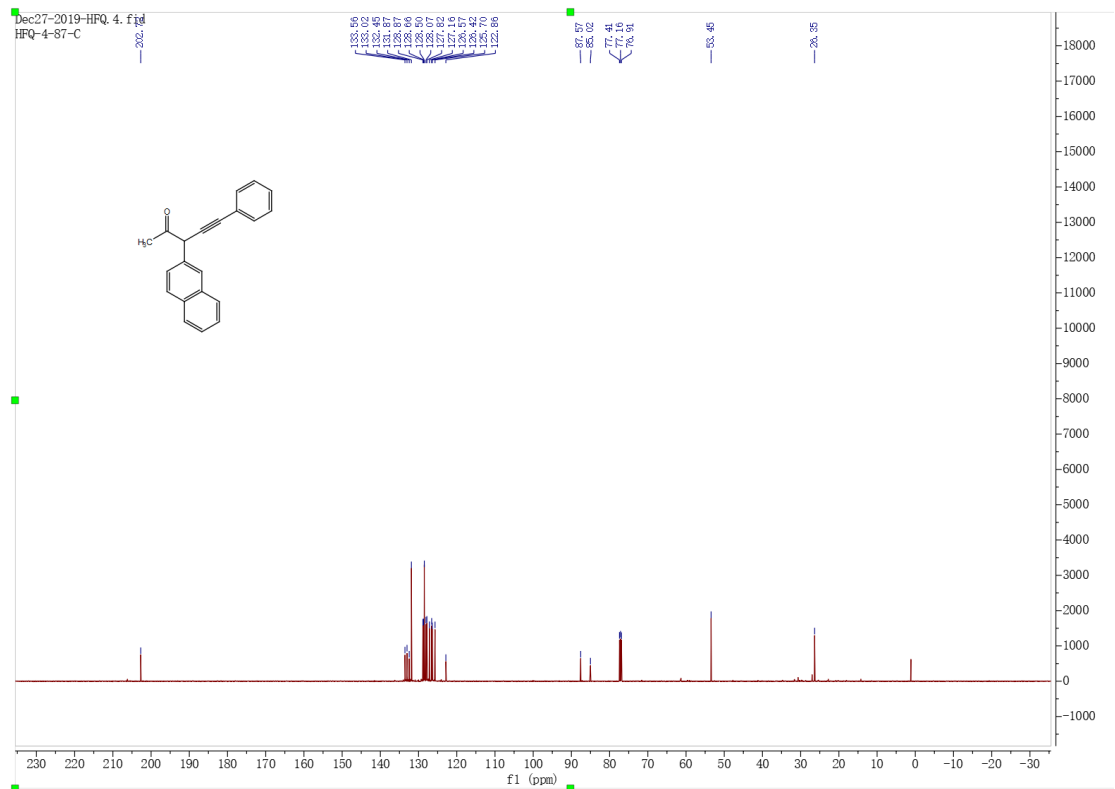
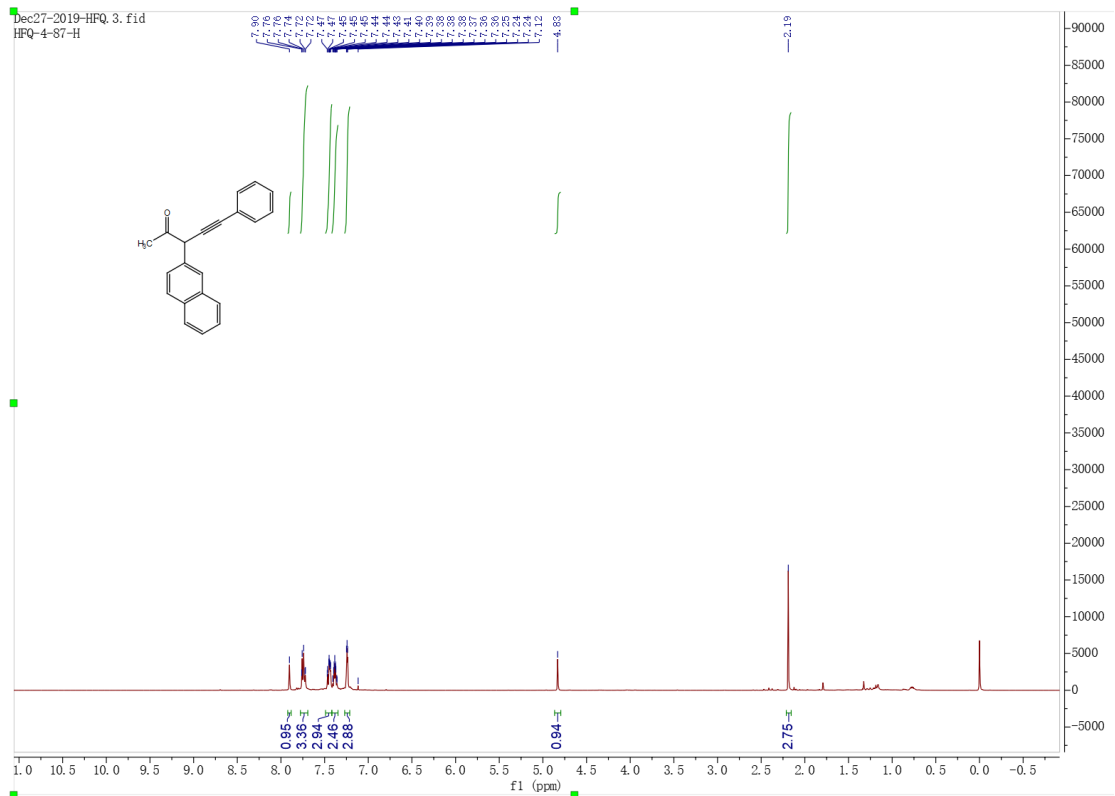
5-phenyl-3-(o-tolyl)pent-4-yn-2-one (**1h**)



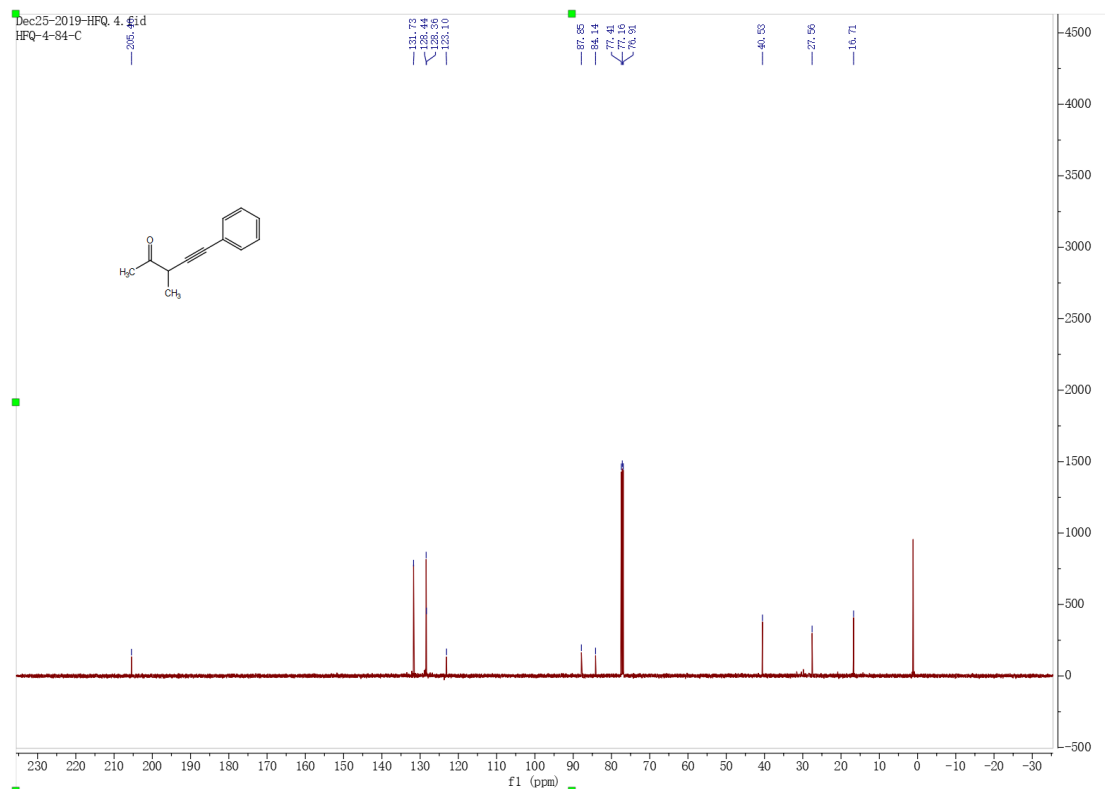
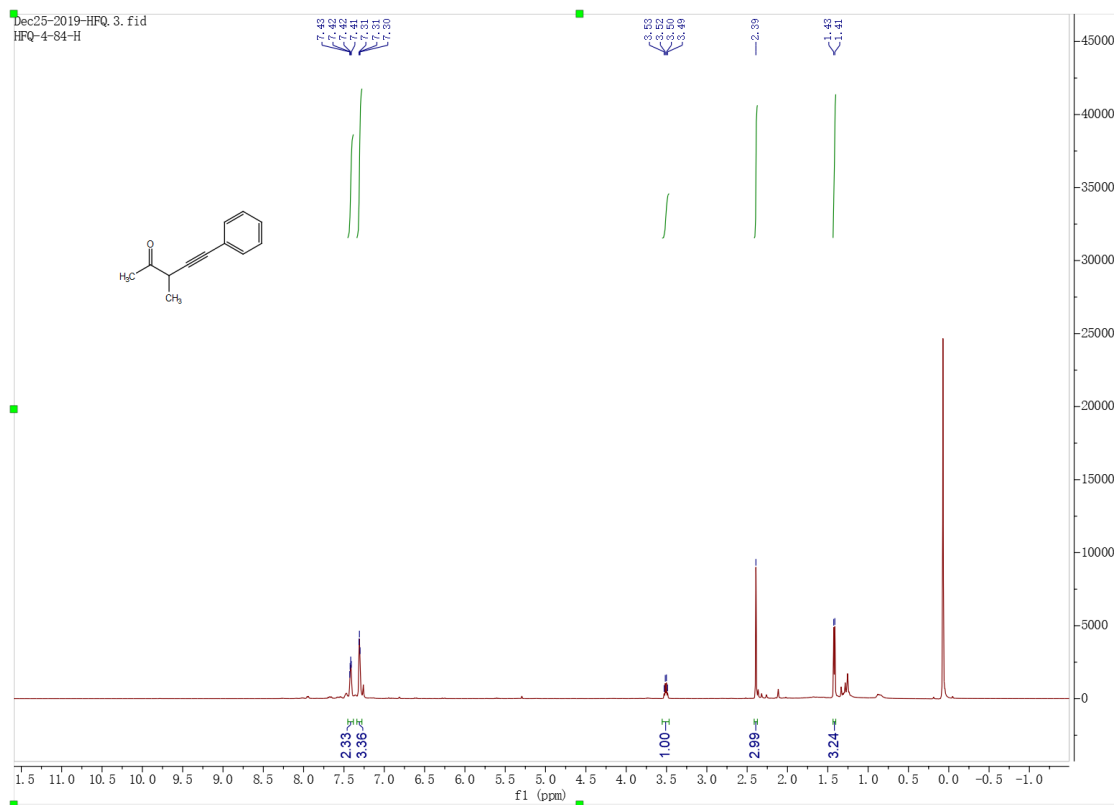
3-(2-chlorophenyl)-5-phenylpent-4-yn-2-one (**1i**)



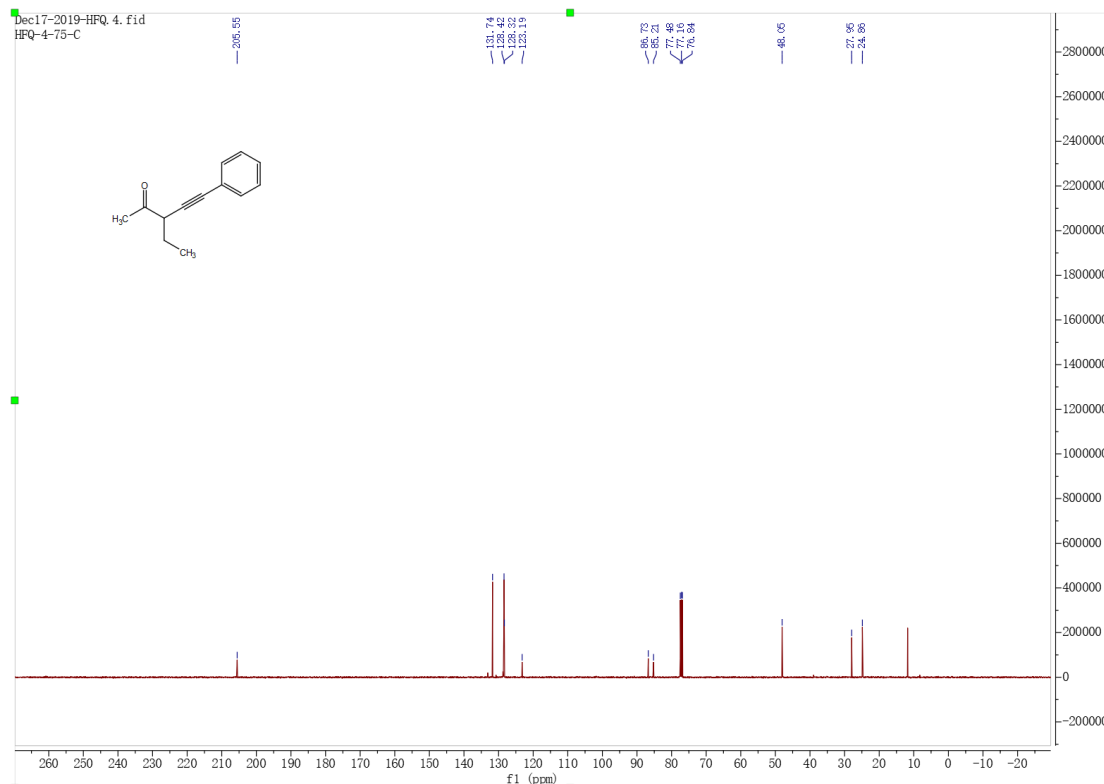
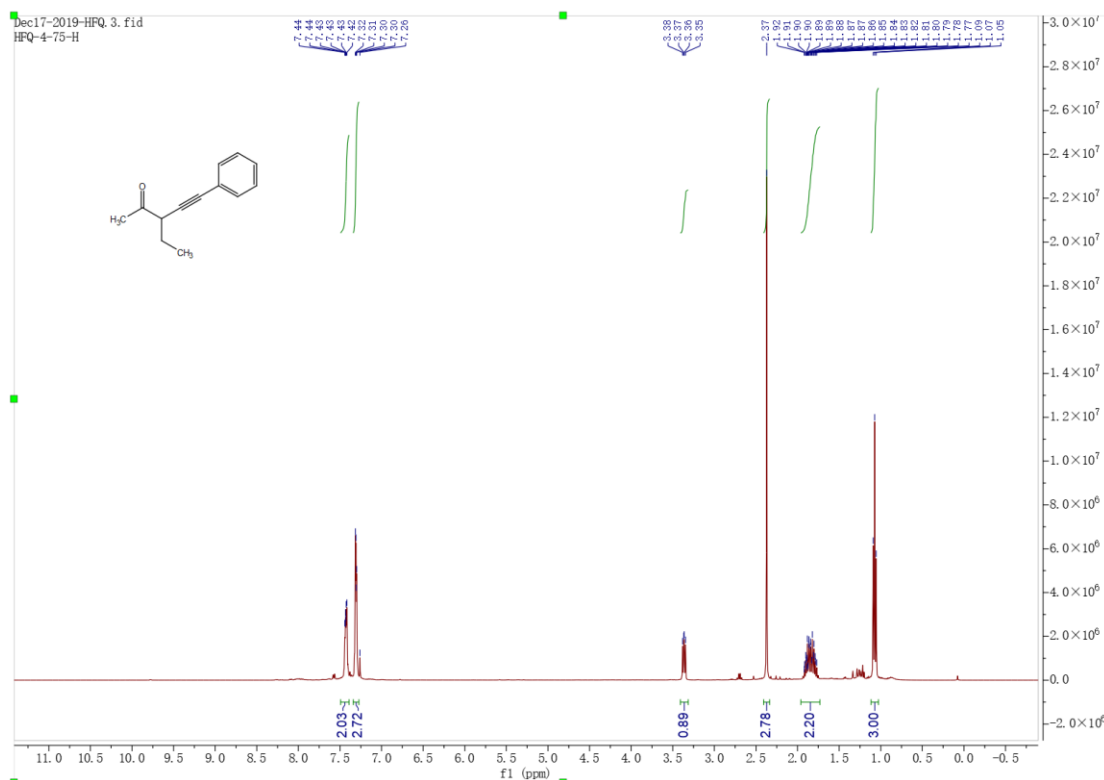
3-(naphthalen-2-yl)-5-phenylpent-4-yn-2-one (**1j**)



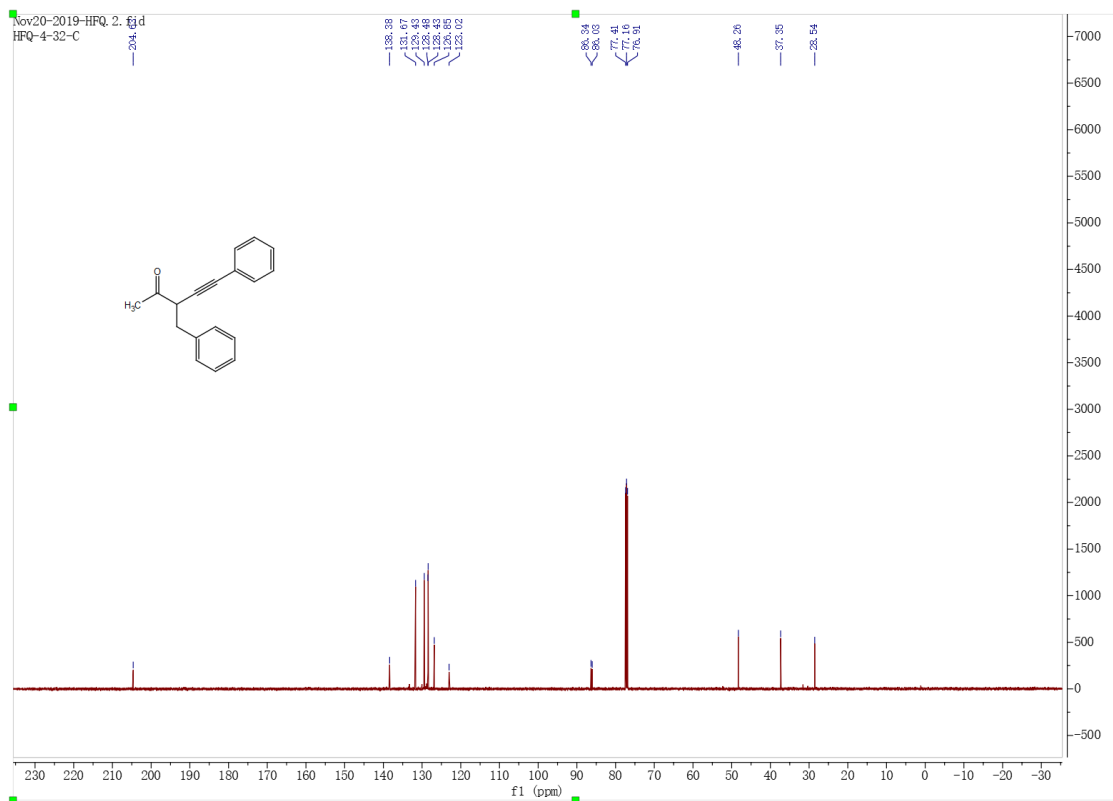
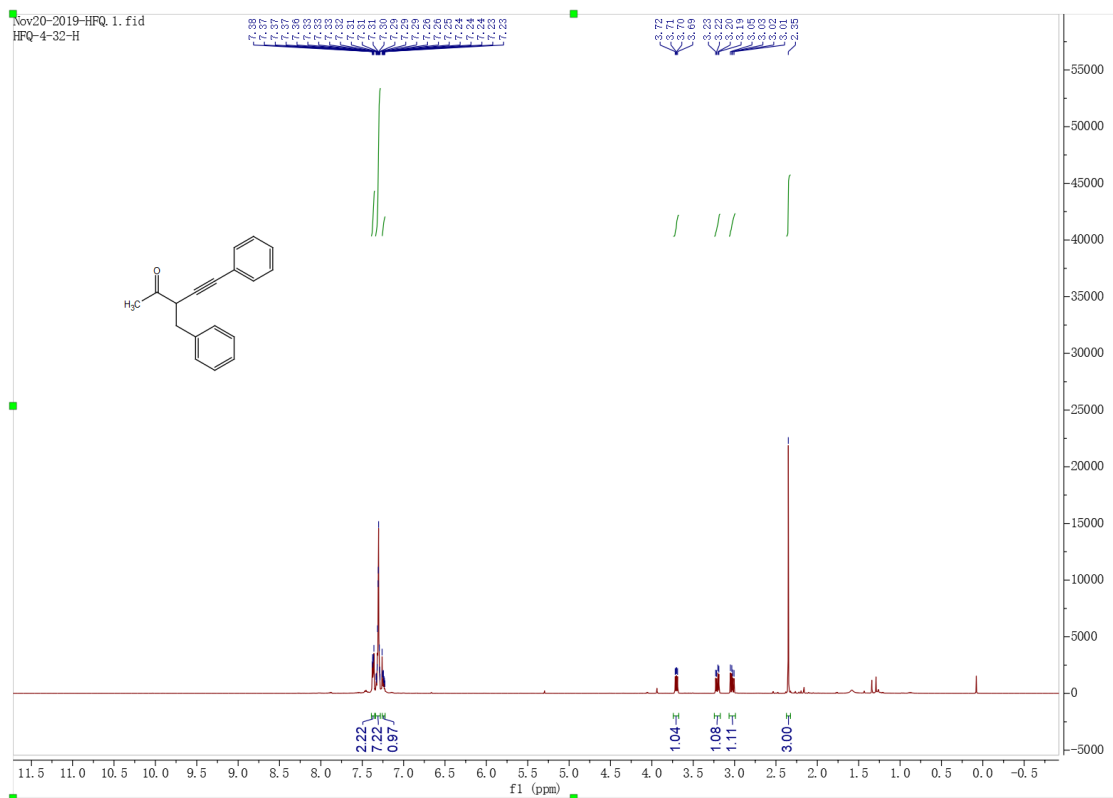
3-methyl-5-phenylpent-4-yn-2-one (**1k**)



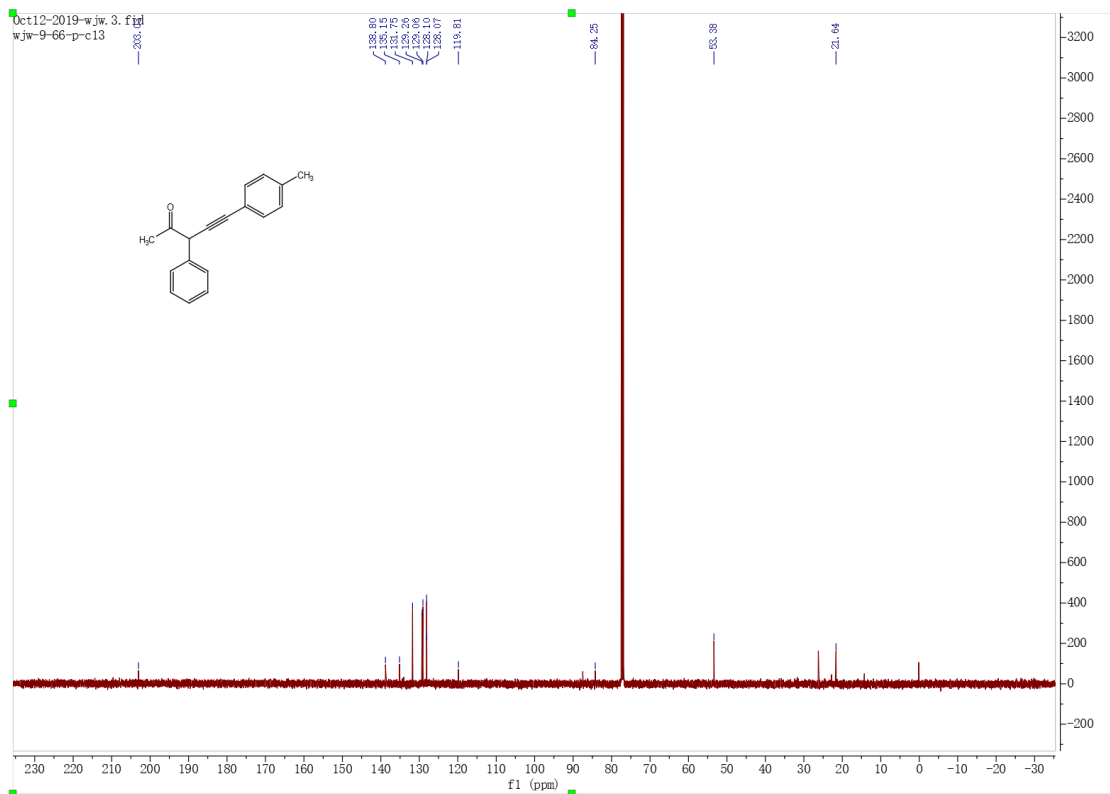
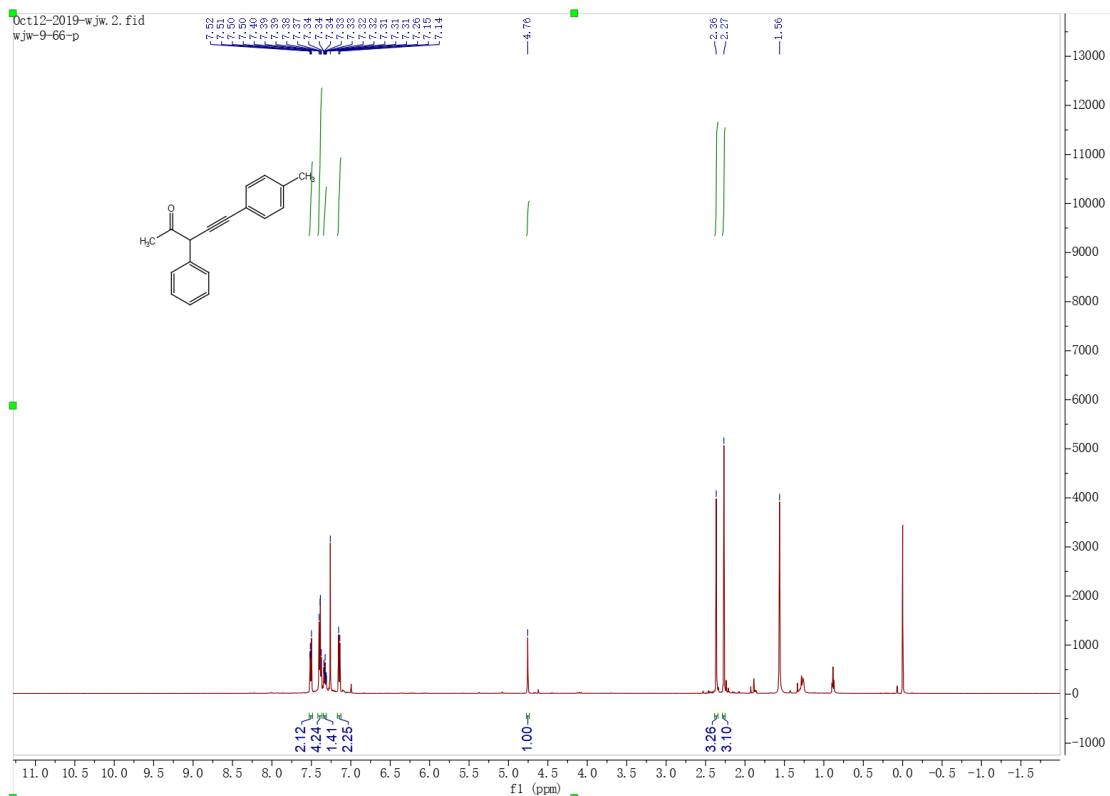
3-ethyl-5-phenylpent-4-yn-2-one (11)



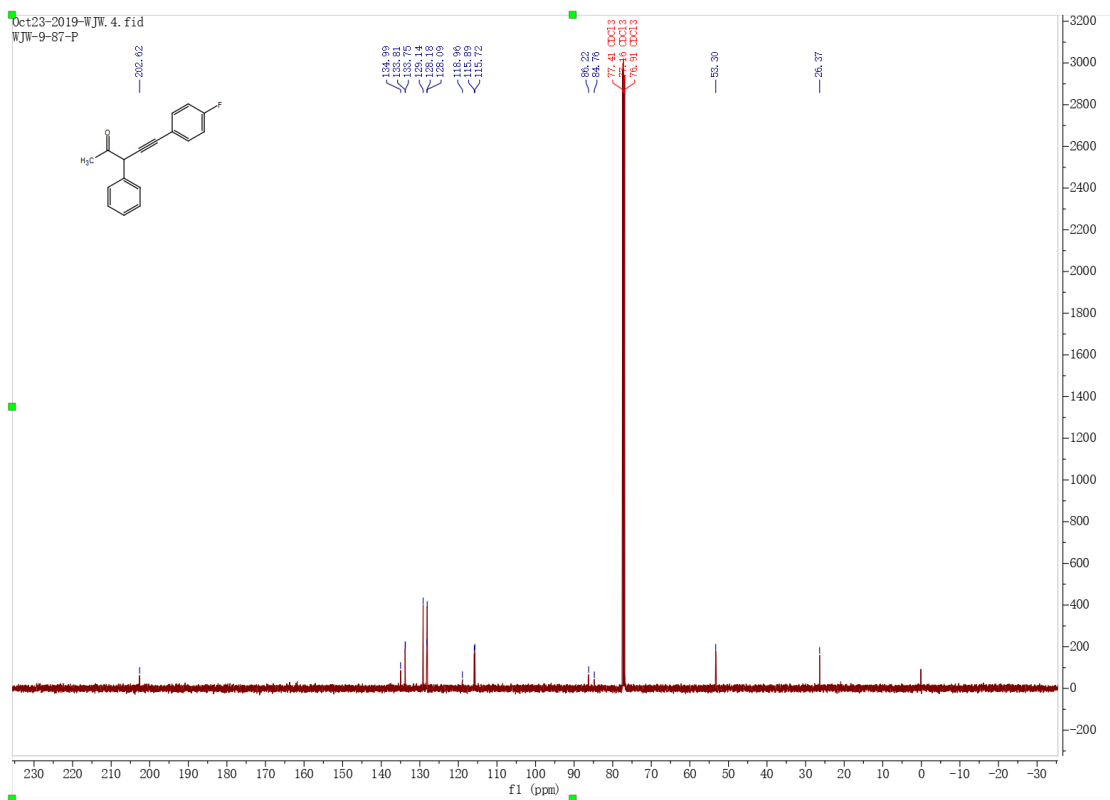
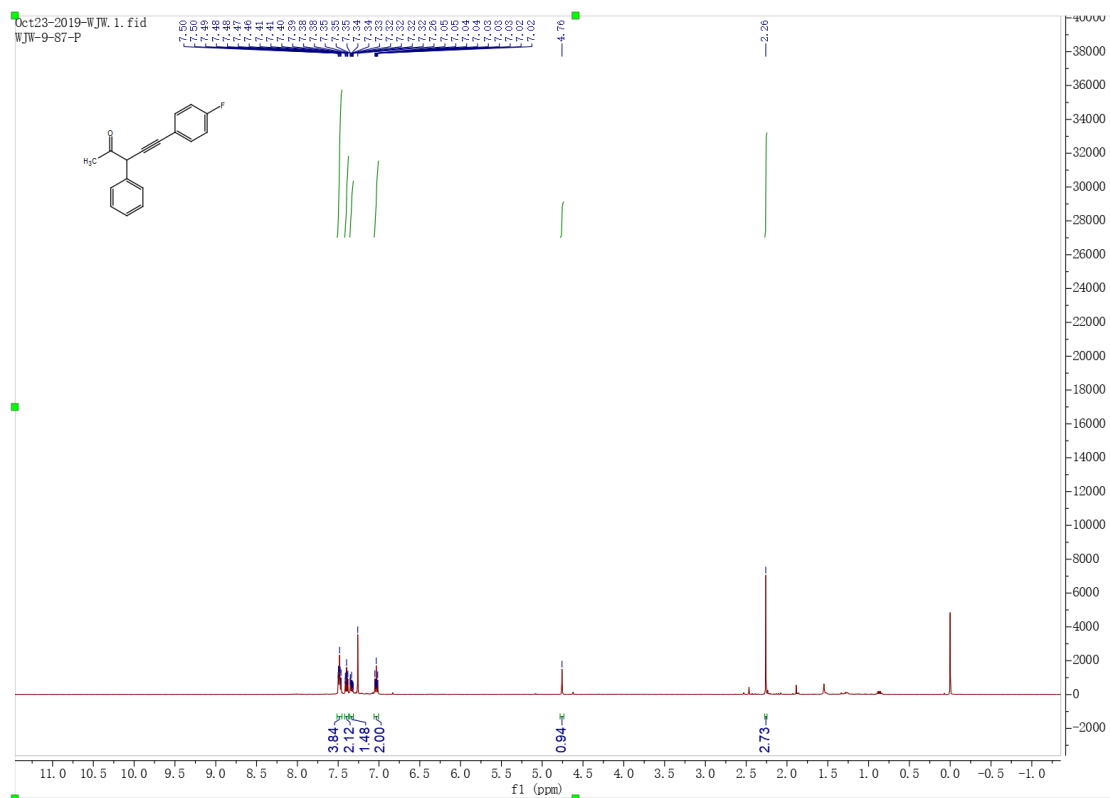
3-benzyl-5-phenylpent-4-yn-2-one (**1m**)

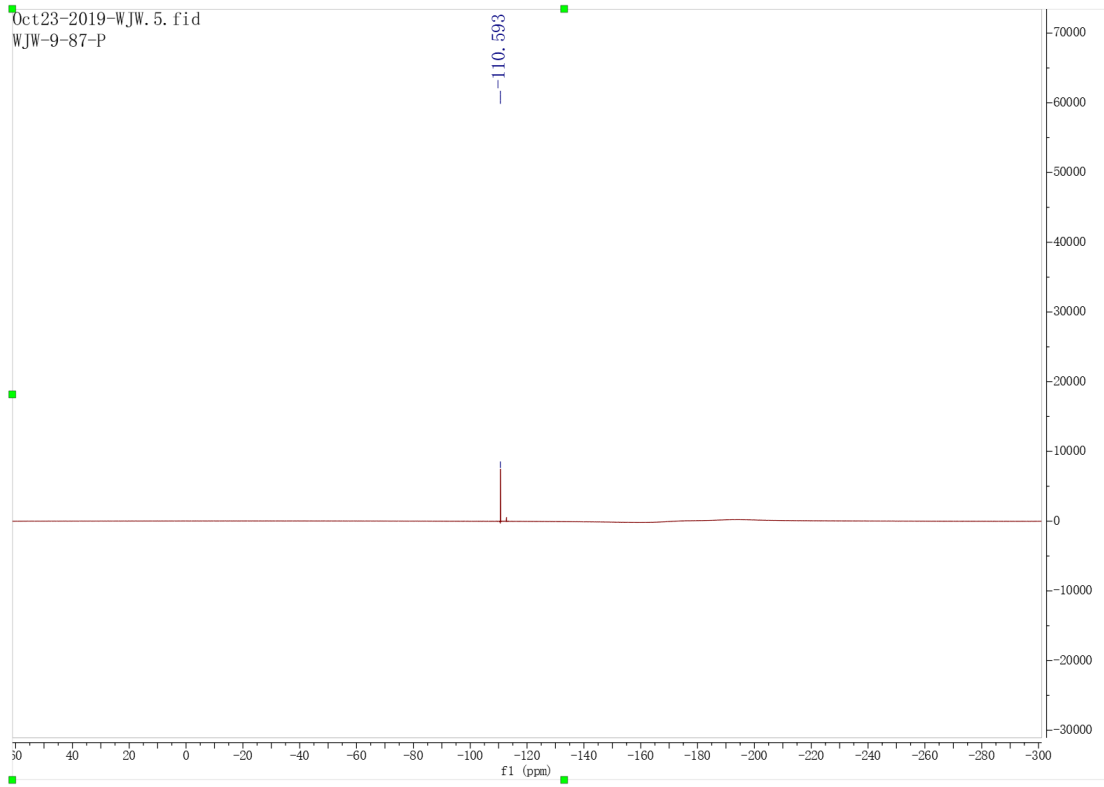


3-phenyl-5-(p-tolyl)pent-4-yn-2-one (**1n**)

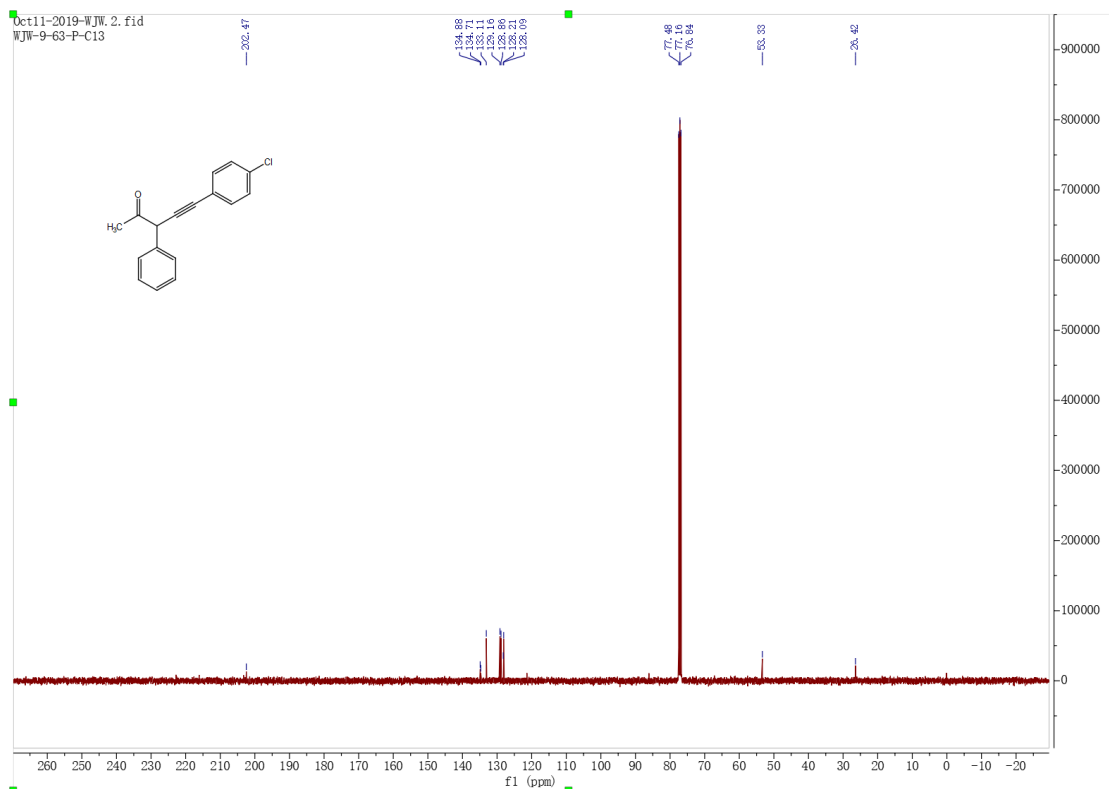
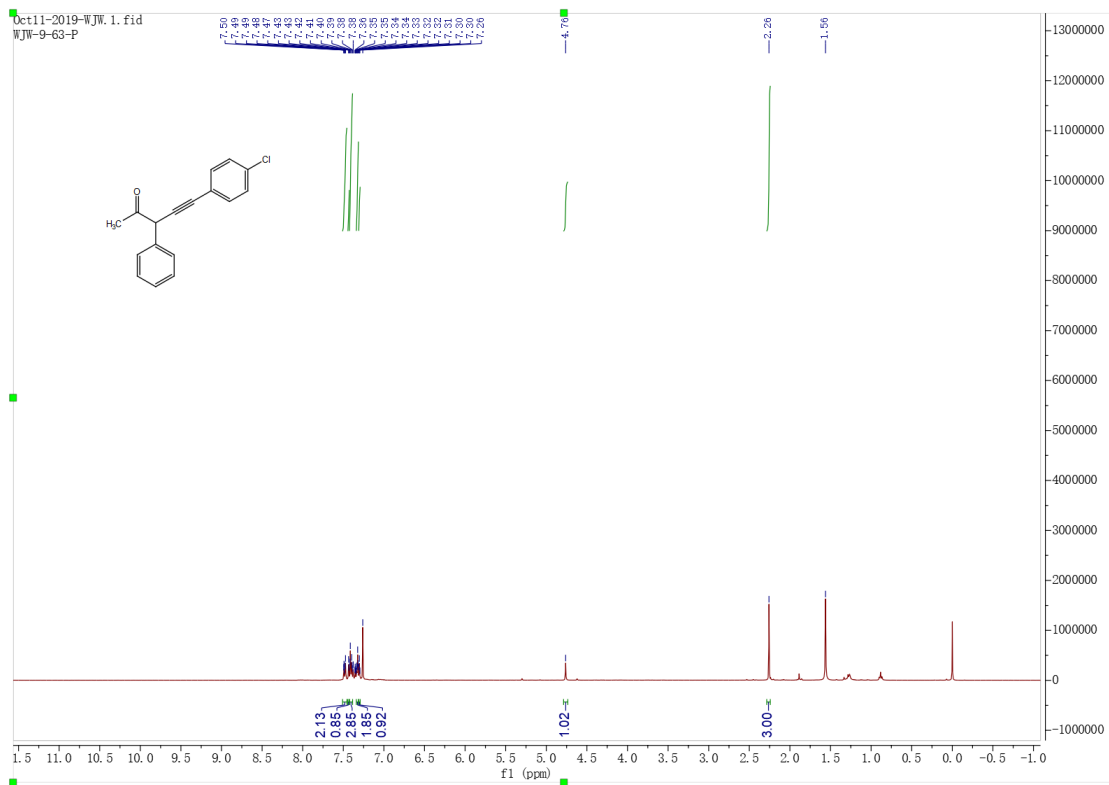


5-(4-fluorophenyl)-3-phenylpent-4-yn-2-one (**10**)

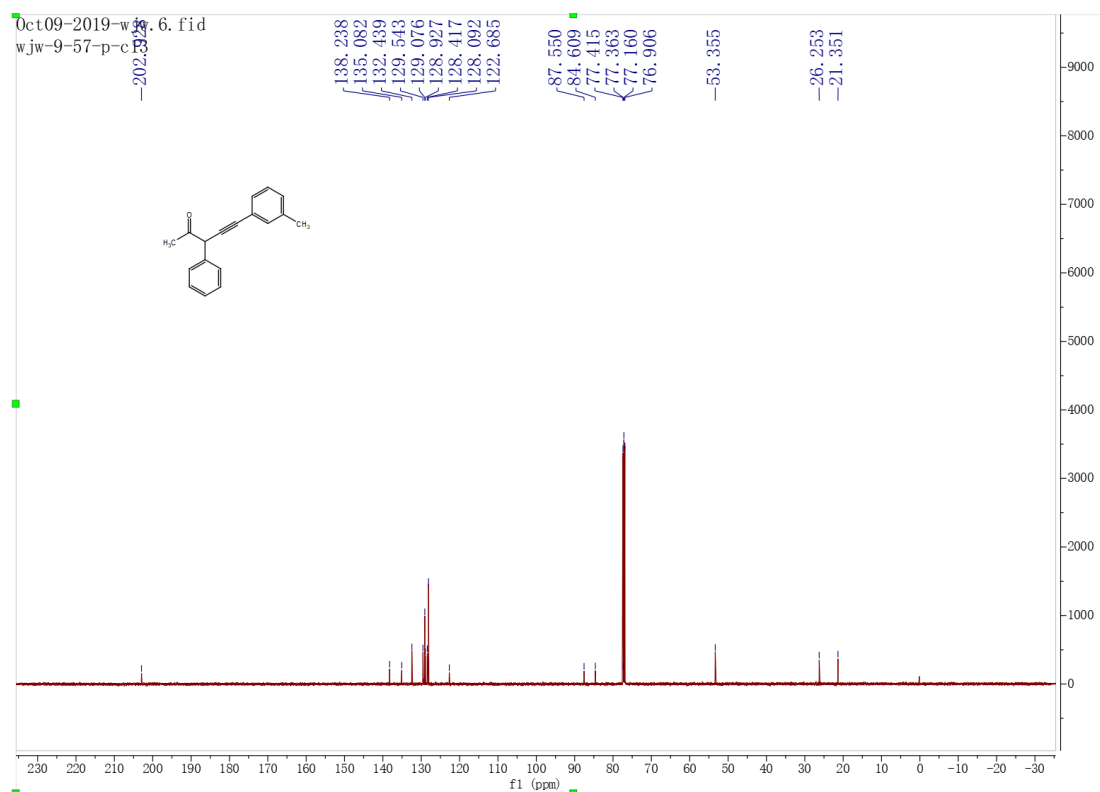
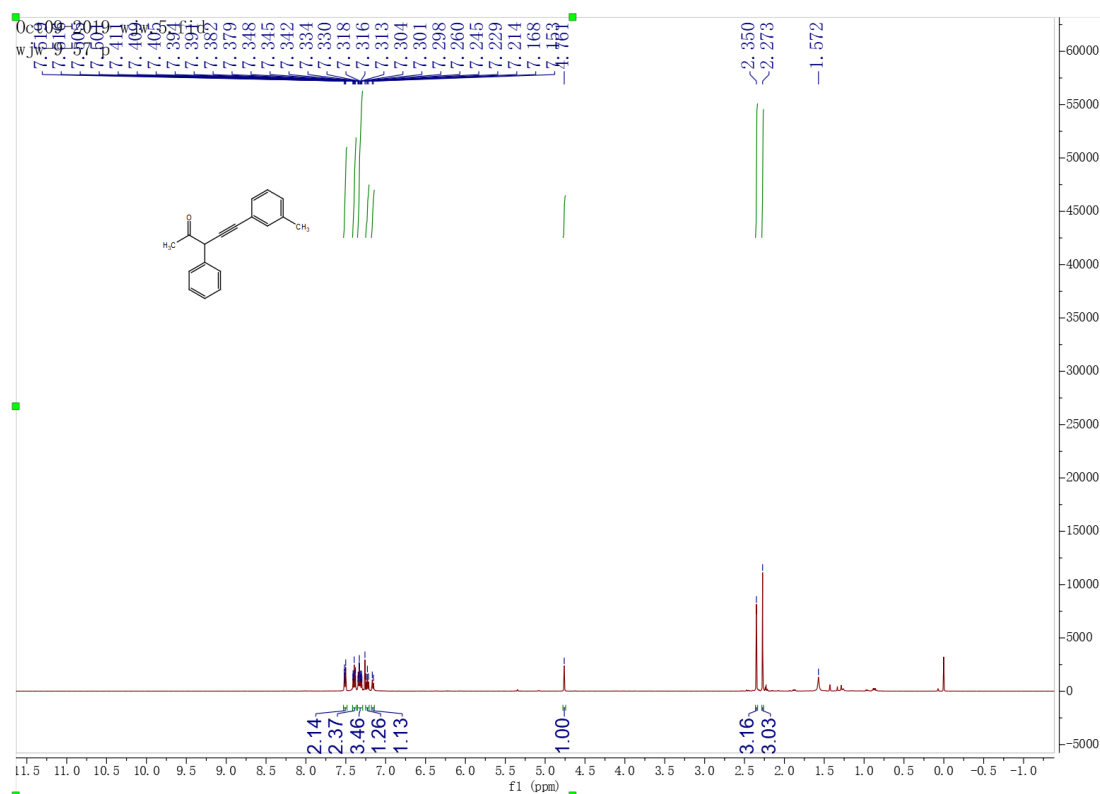




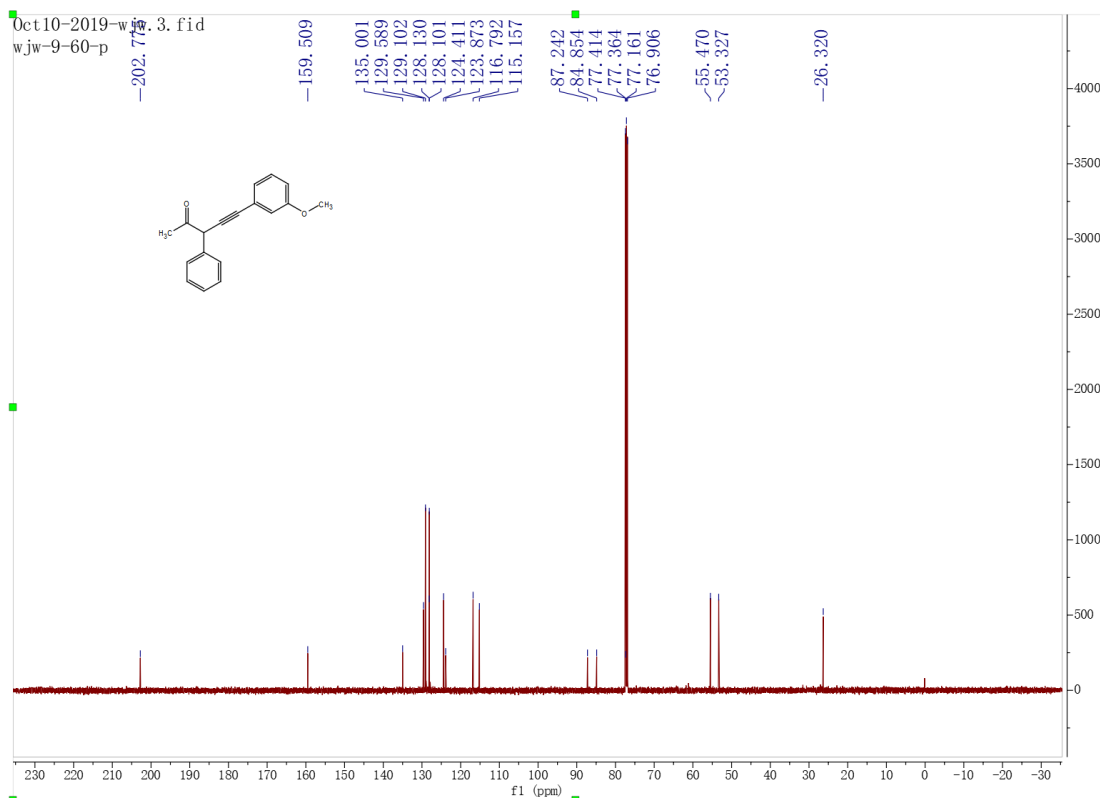
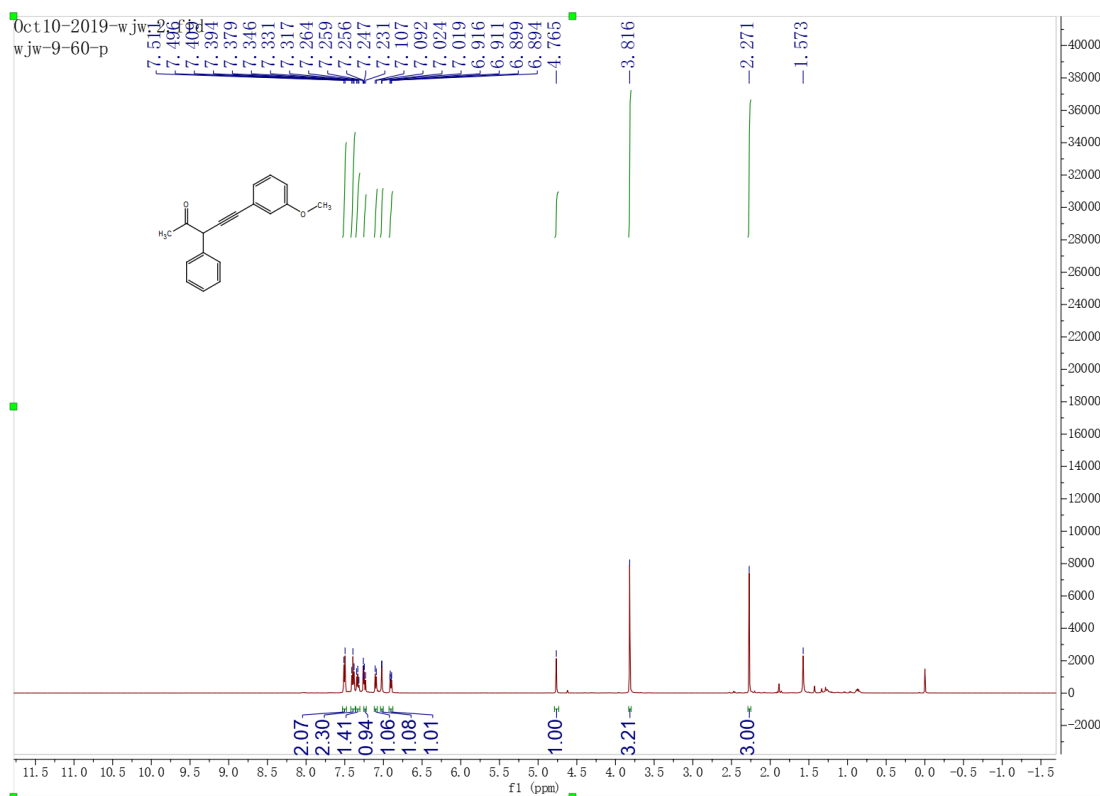
5-(4-chlorophenyl)-3-phenylpent-4-yn-2-one (**1p**)



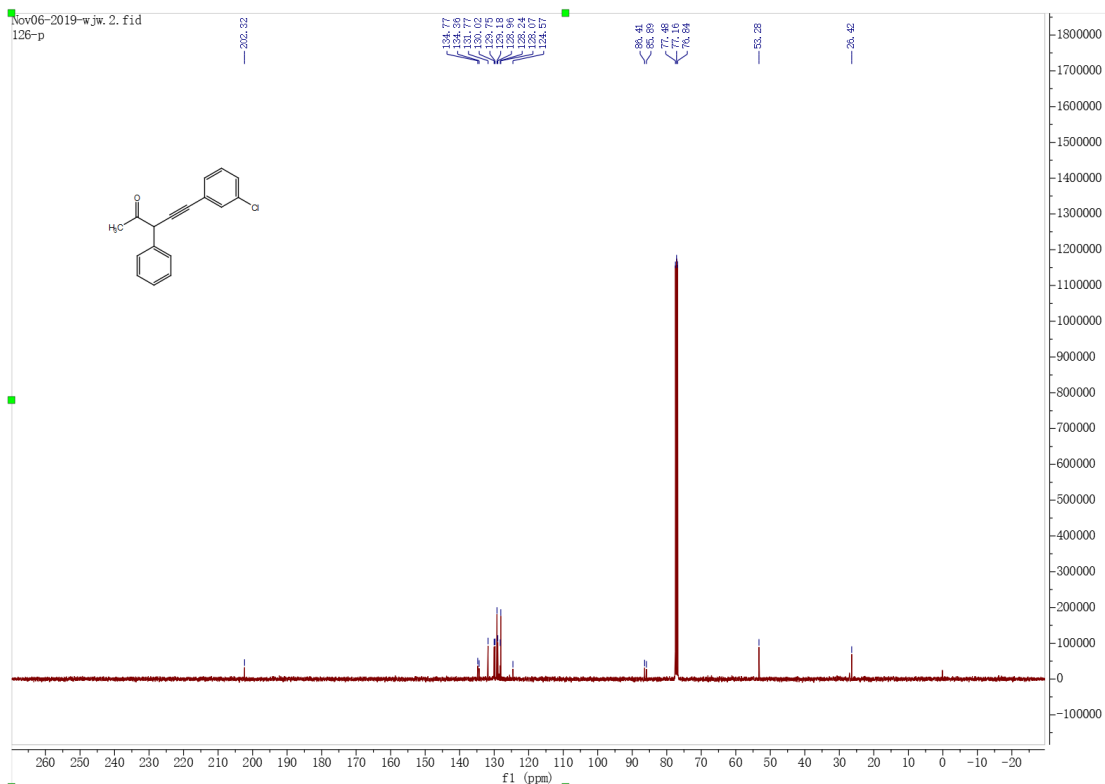
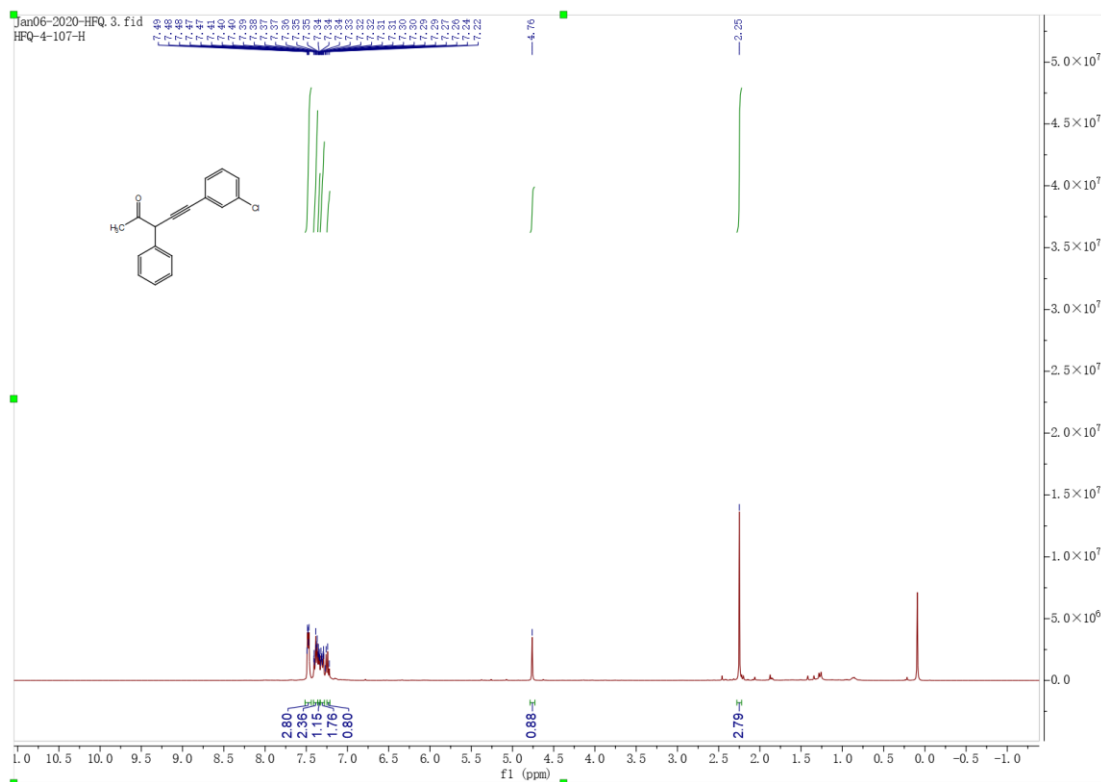
3-phenyl-5-(m-tolyl)pent-4-yn-2-one (**1q**)



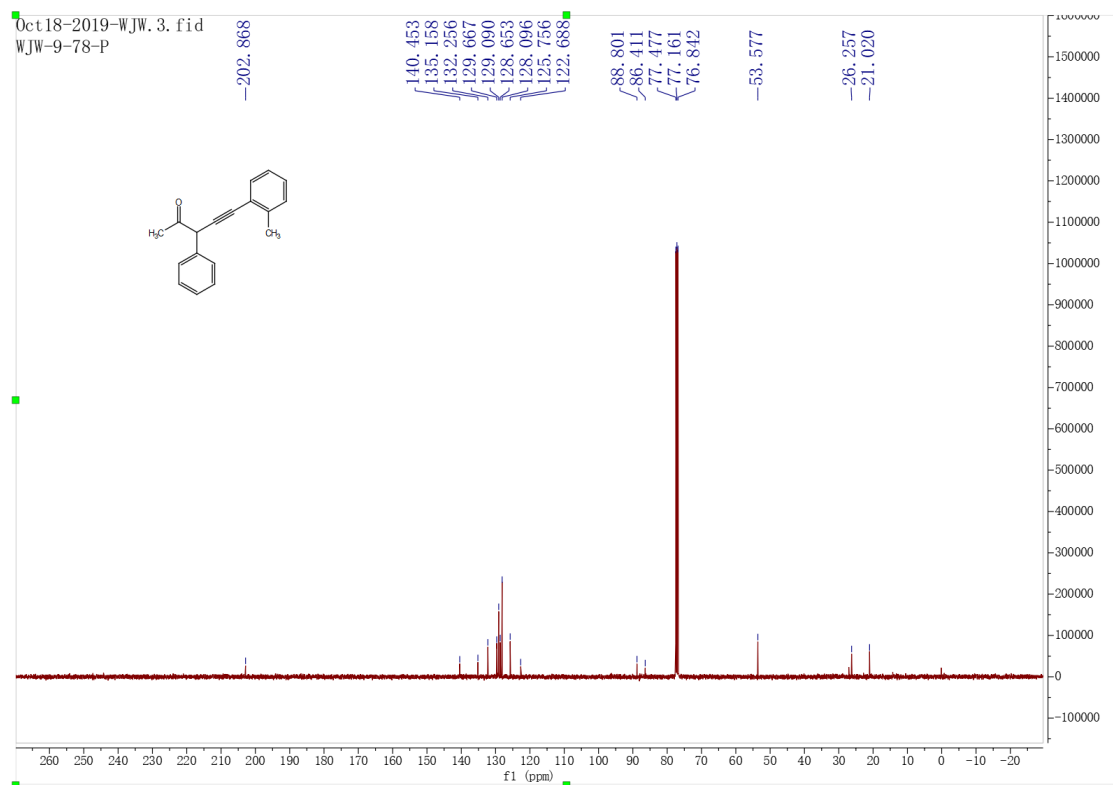
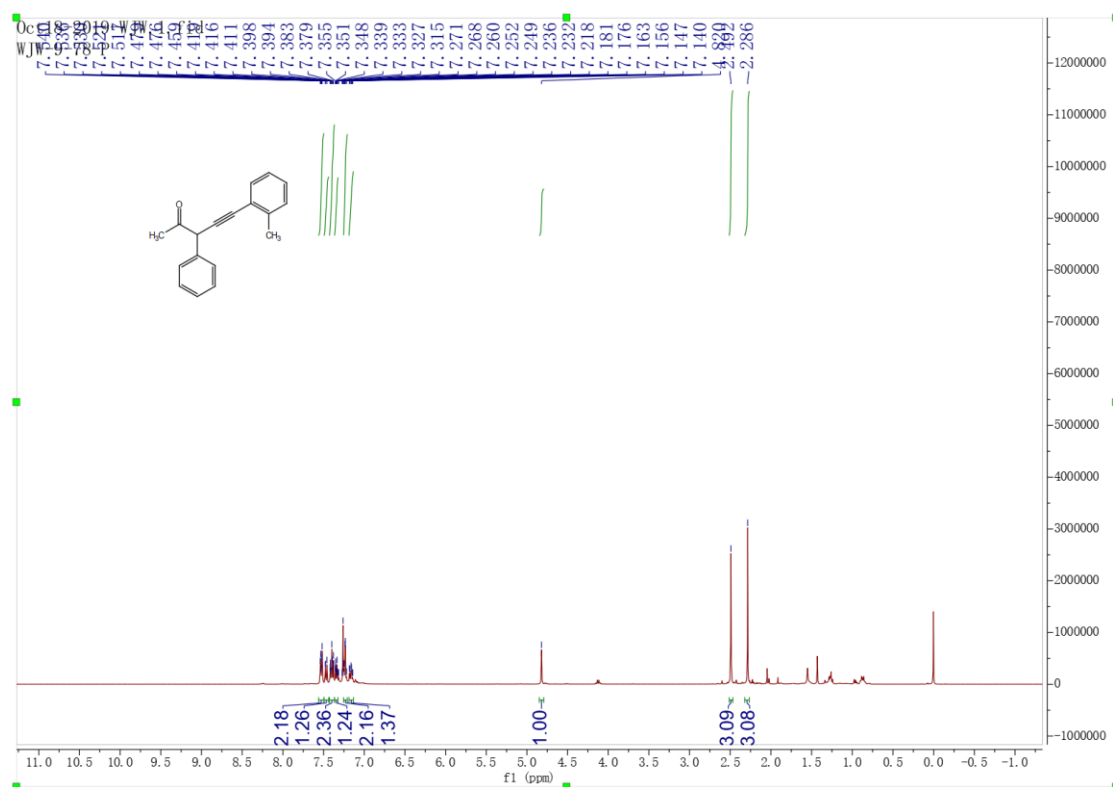
5-(3-methoxyphenyl)-3-phenylpent-4-yn-2-one (**1r**)



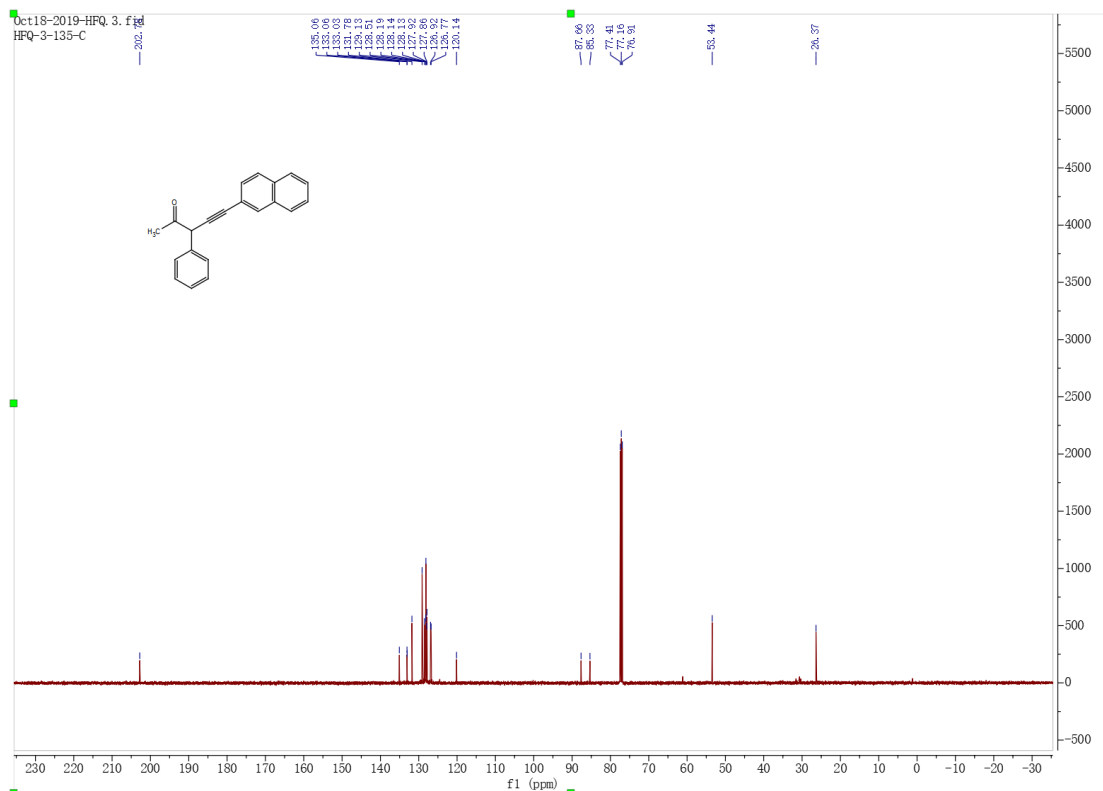
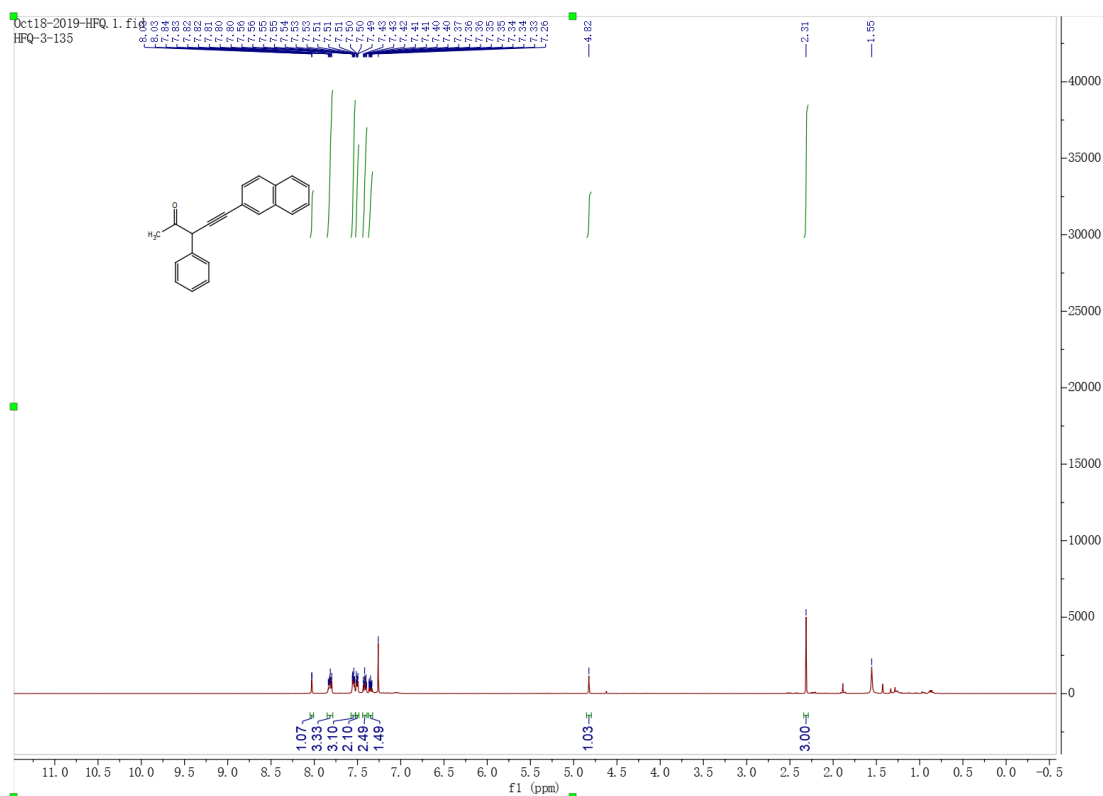
5-(3-chlorophenyl)-3-phenylpent-4-yn-2-one (**1s**)



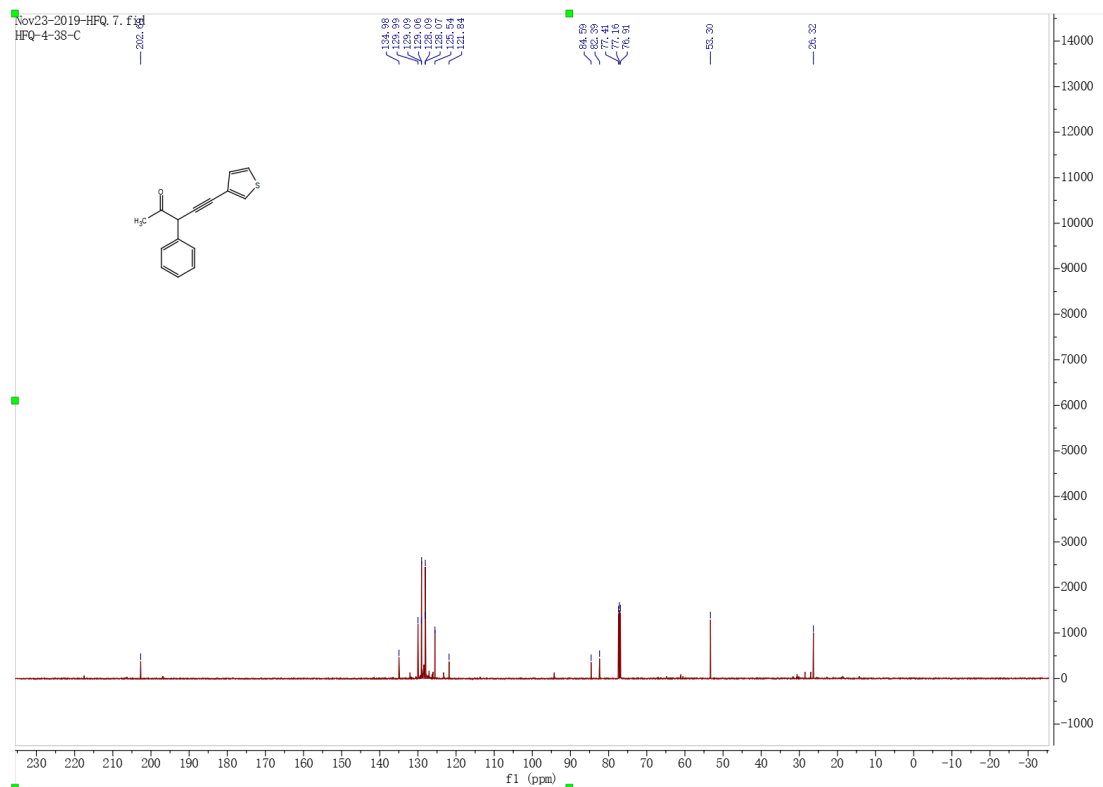
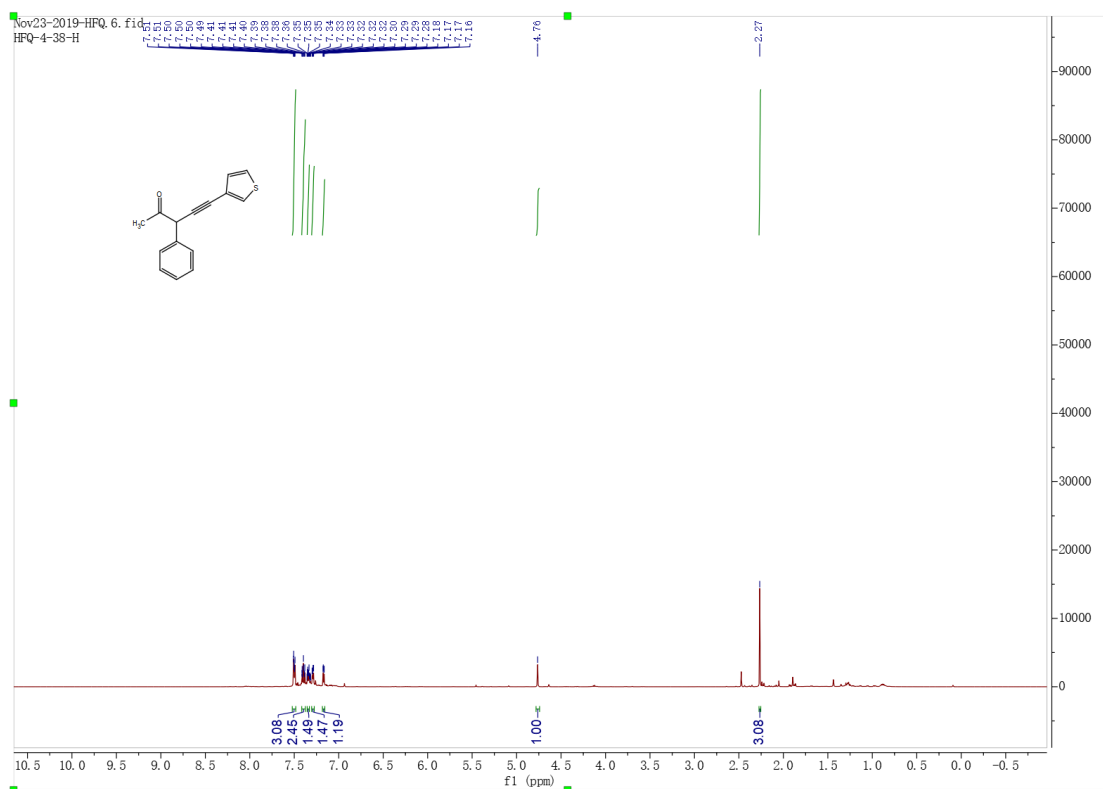
3-phenyl-5-(o-tolyl)pent-4-yn-2-one (**1u**)



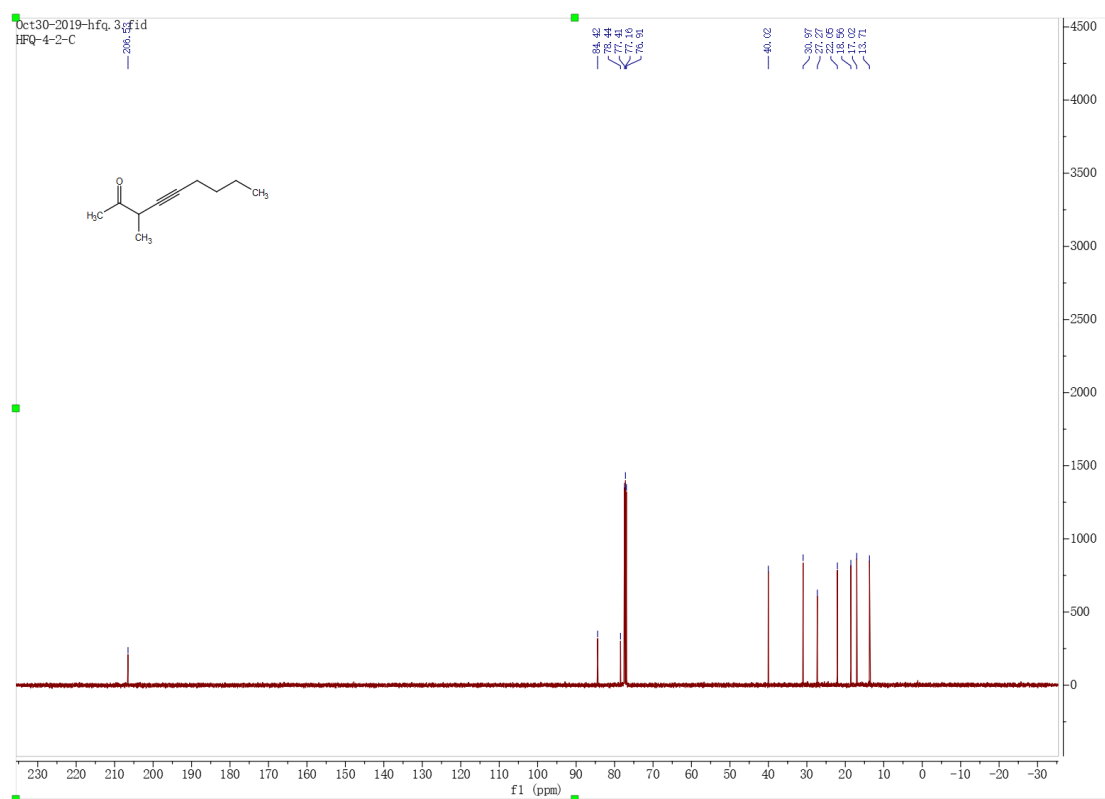
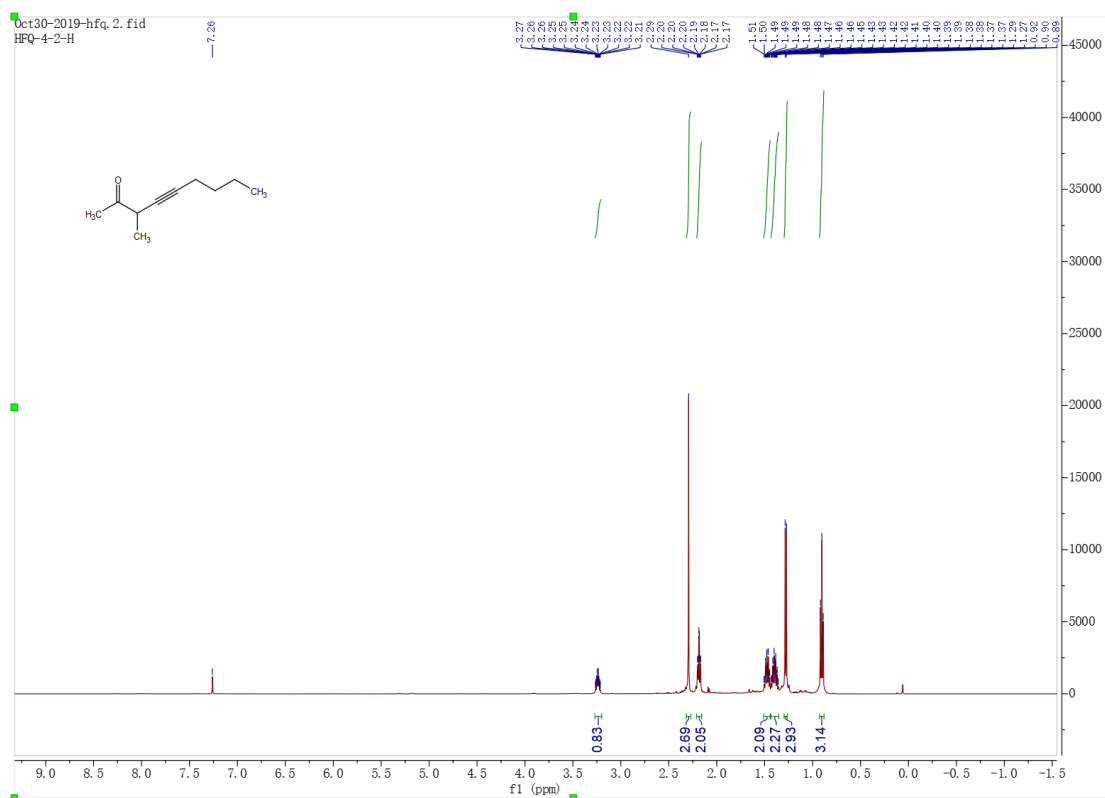
5-(naphthalen-2-yl)-3-phenylpent-4-yn-2-one (**1v**)



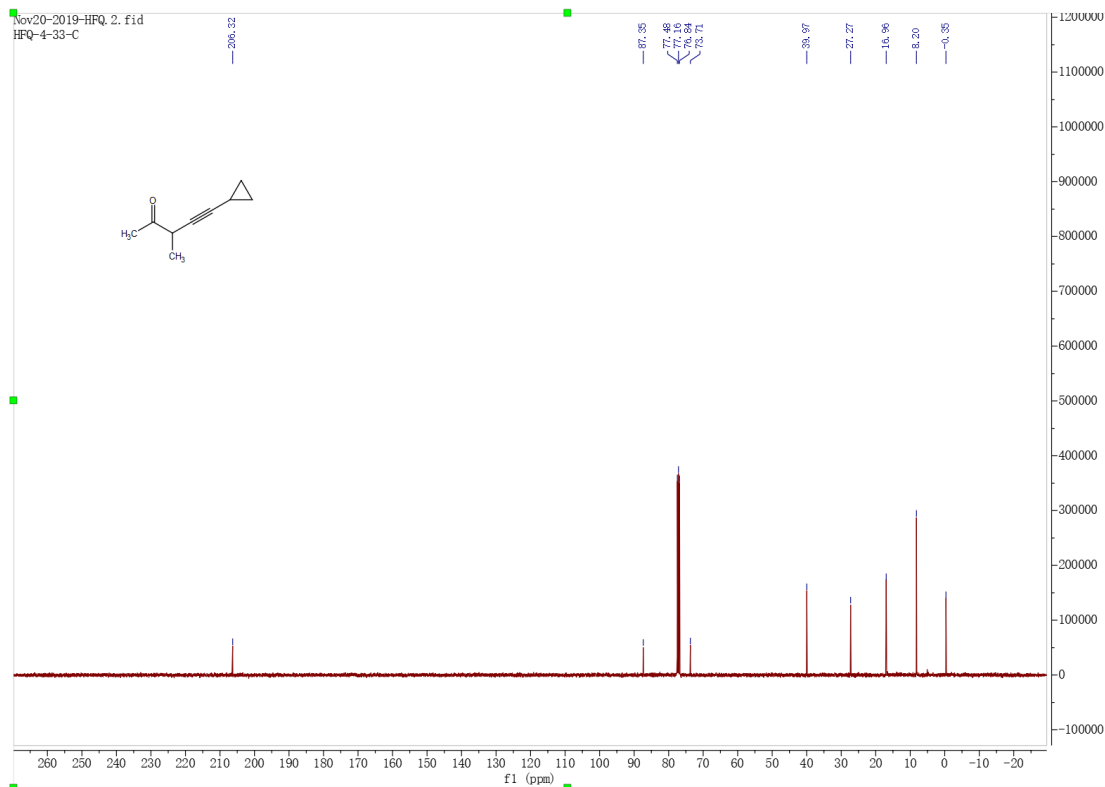
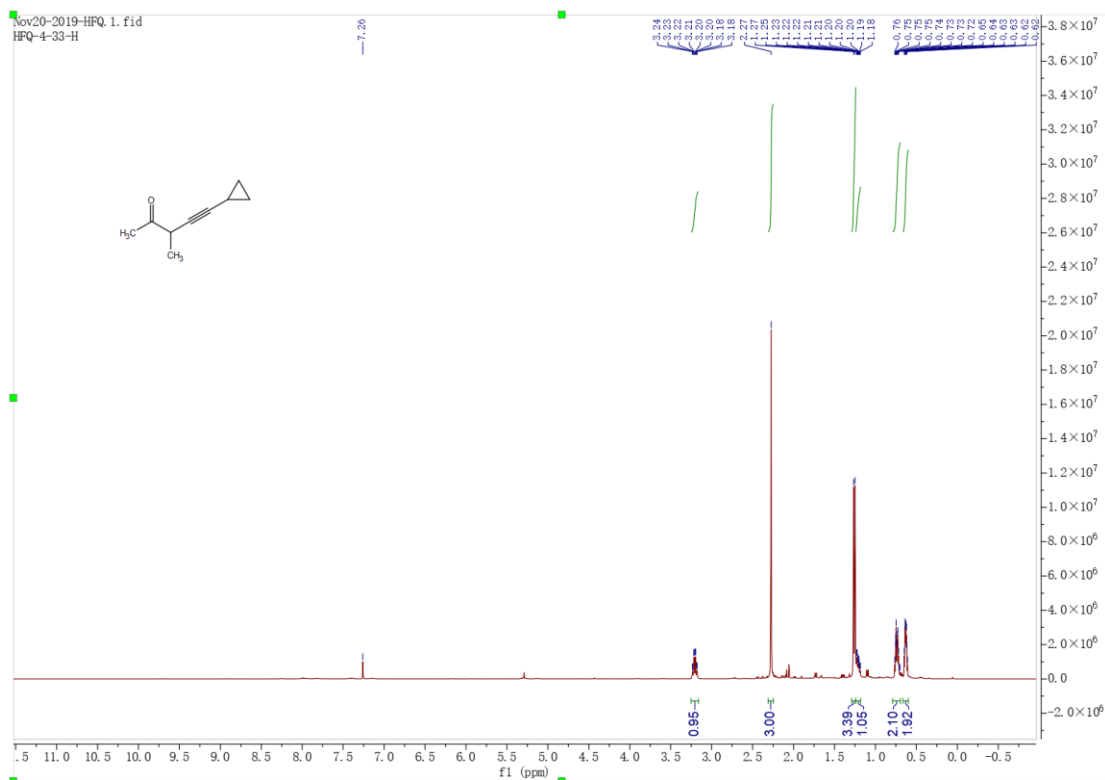
3-phenyl-5-(thiophen-3-yl)pent-4-yn-2-one (**1w**)



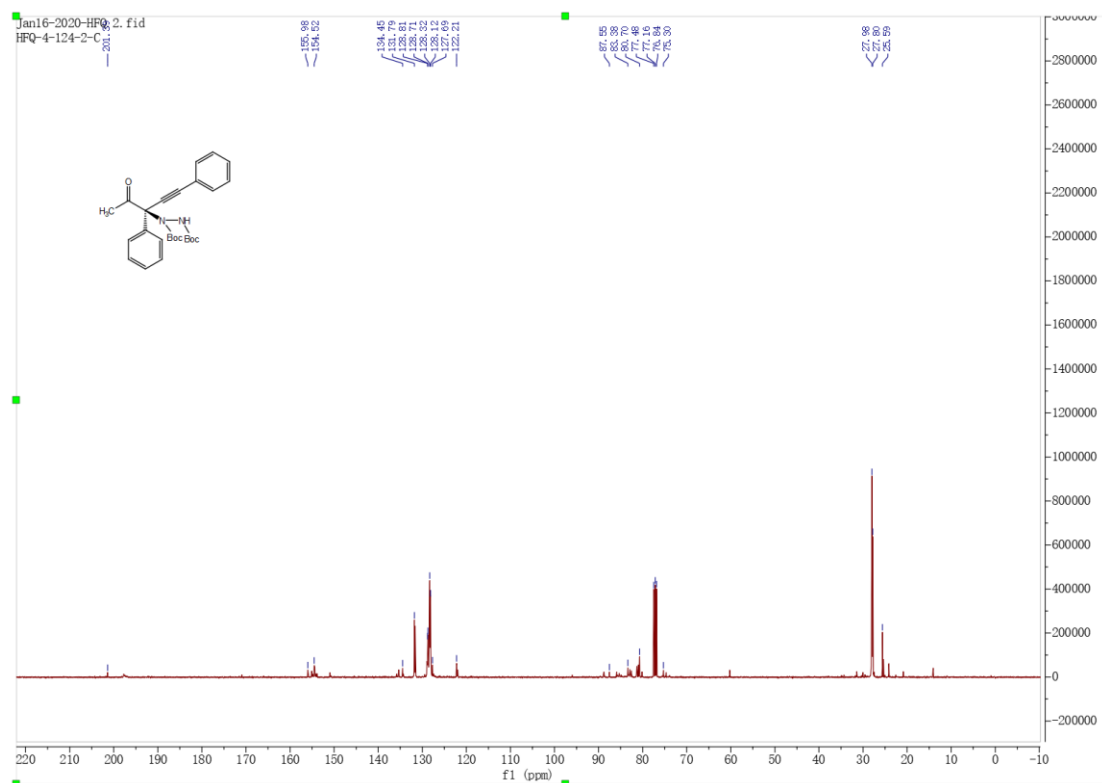
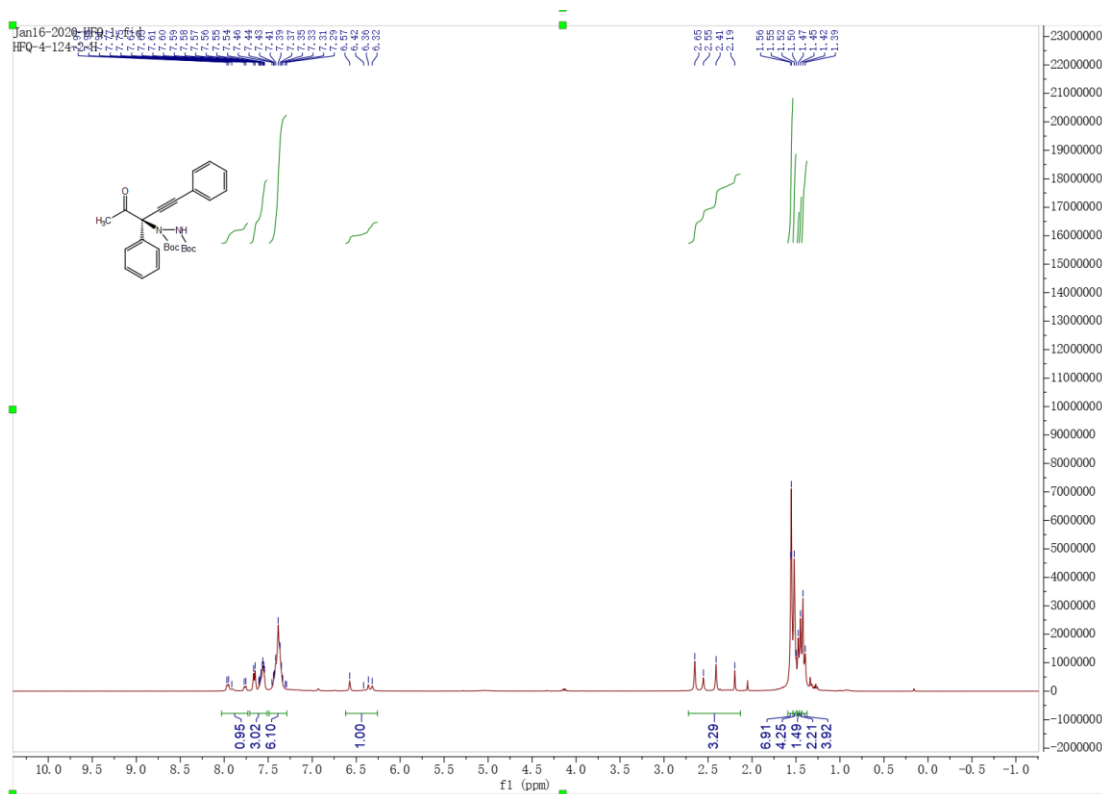
3-methylnon-4-yn-2-one (1x)



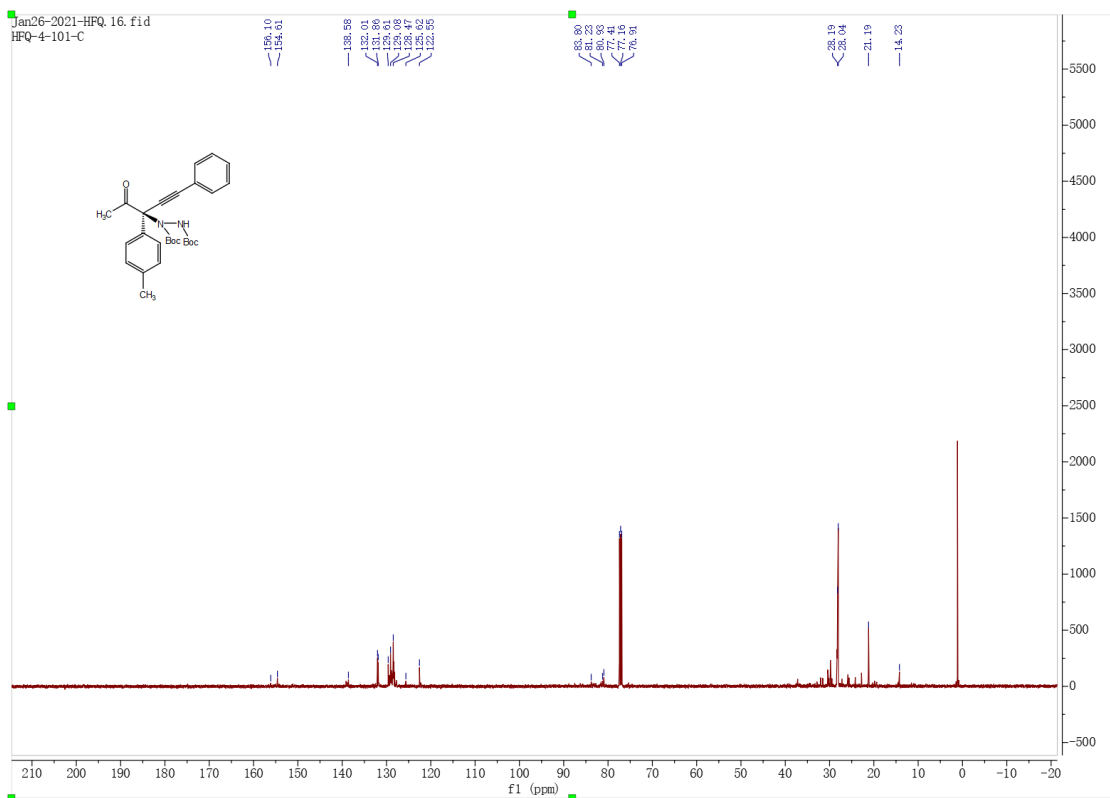
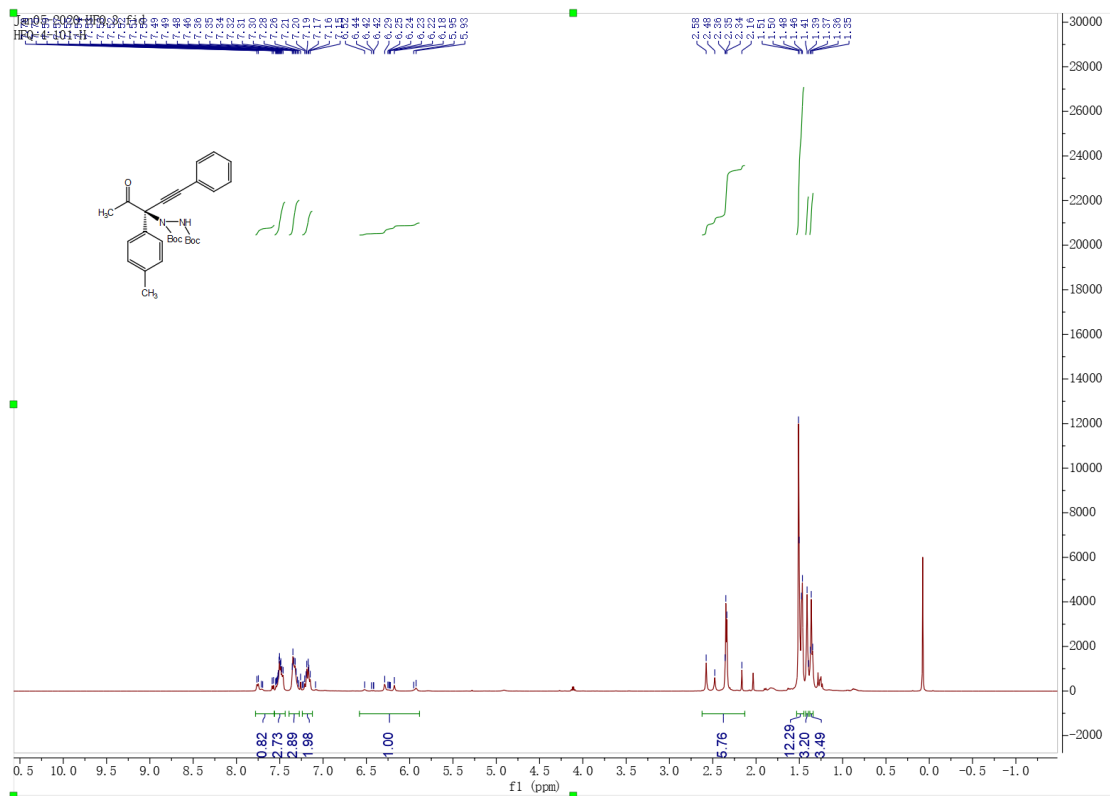
5-cyclopropyl-3-methylpent-4-yn-2-one (**1y**)



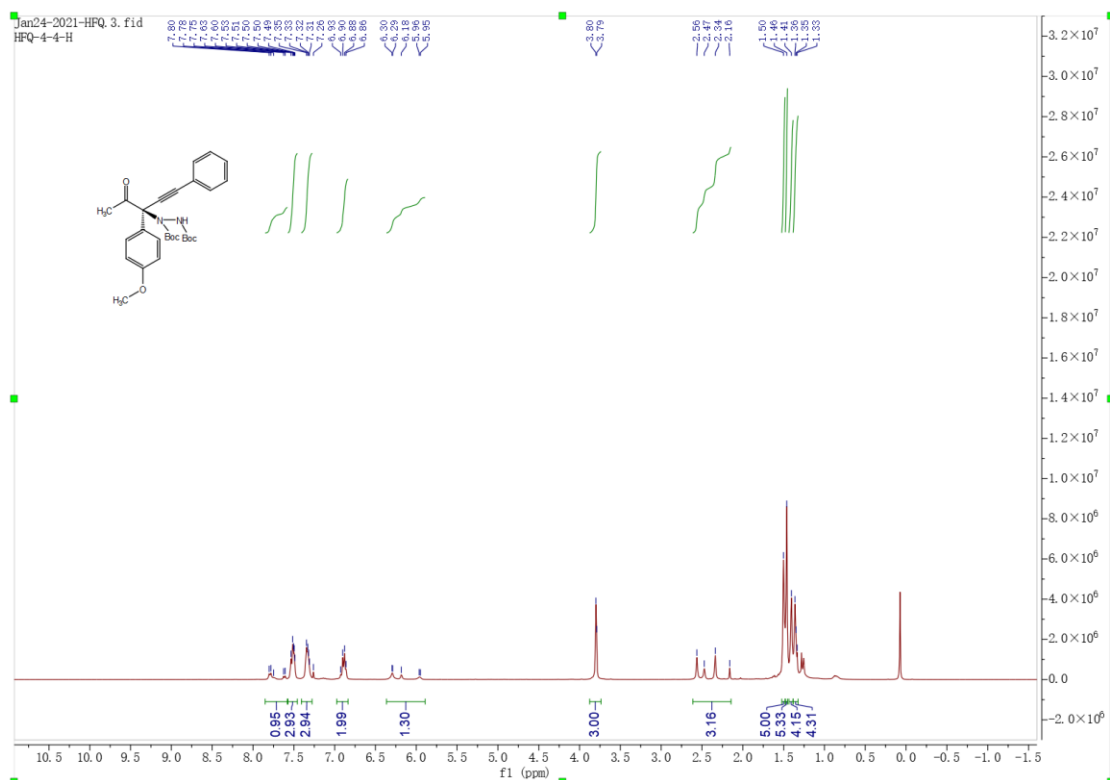
Di-tert-butyl (R)-1-(4-oxo-1,3-diphenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate
(3a)



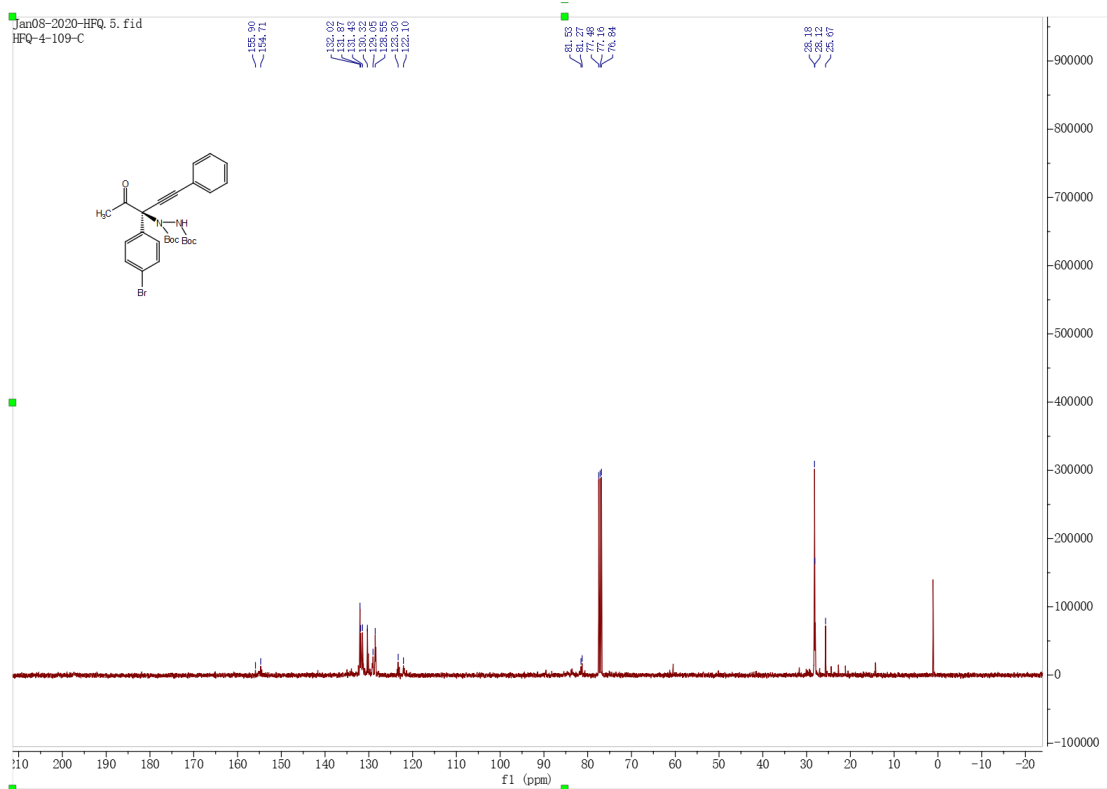
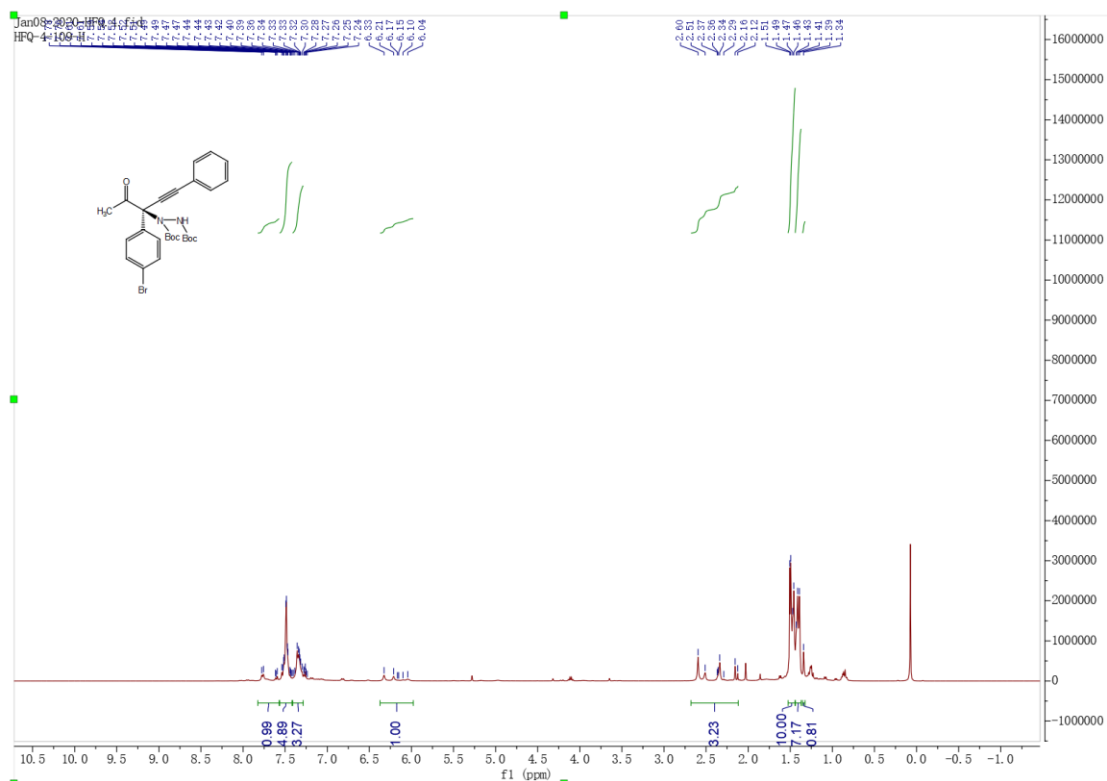
Di-tert-butyl-(*R*)-1-(4-oxo-1-phenyl-3-(*p*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3b**)



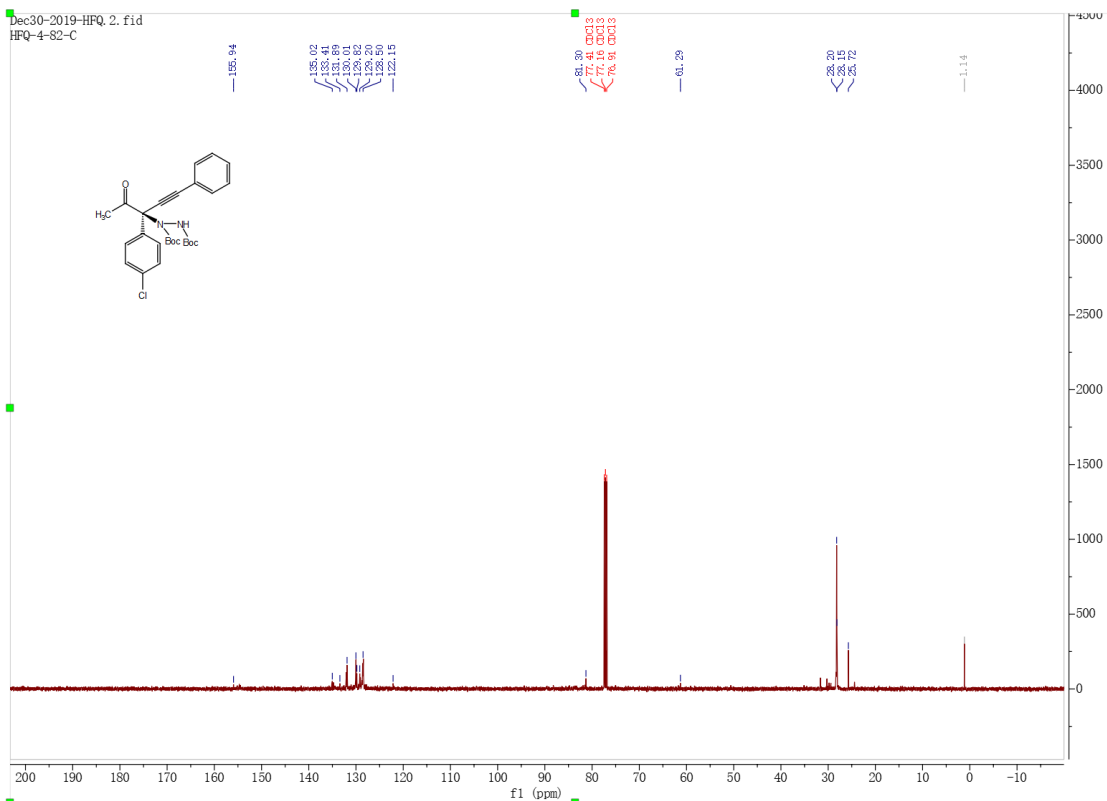
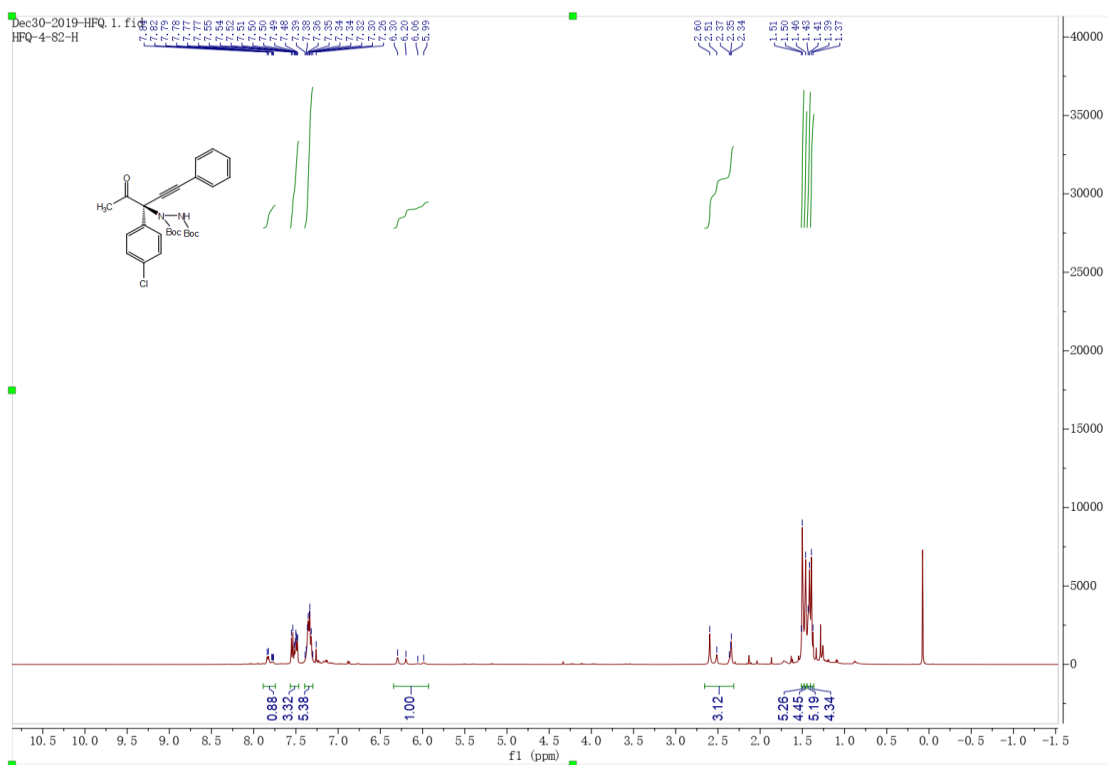
Di-tert-butyl-(*R*)-1-(3-(4-methoxyphenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3c**)



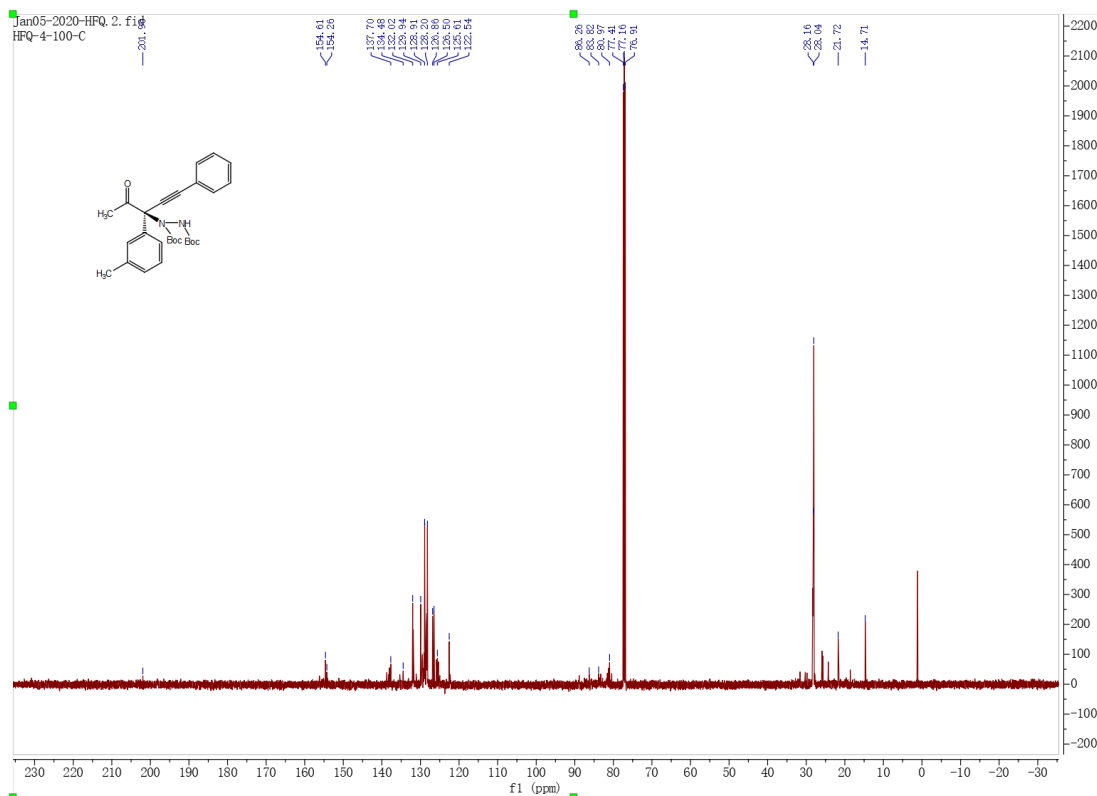
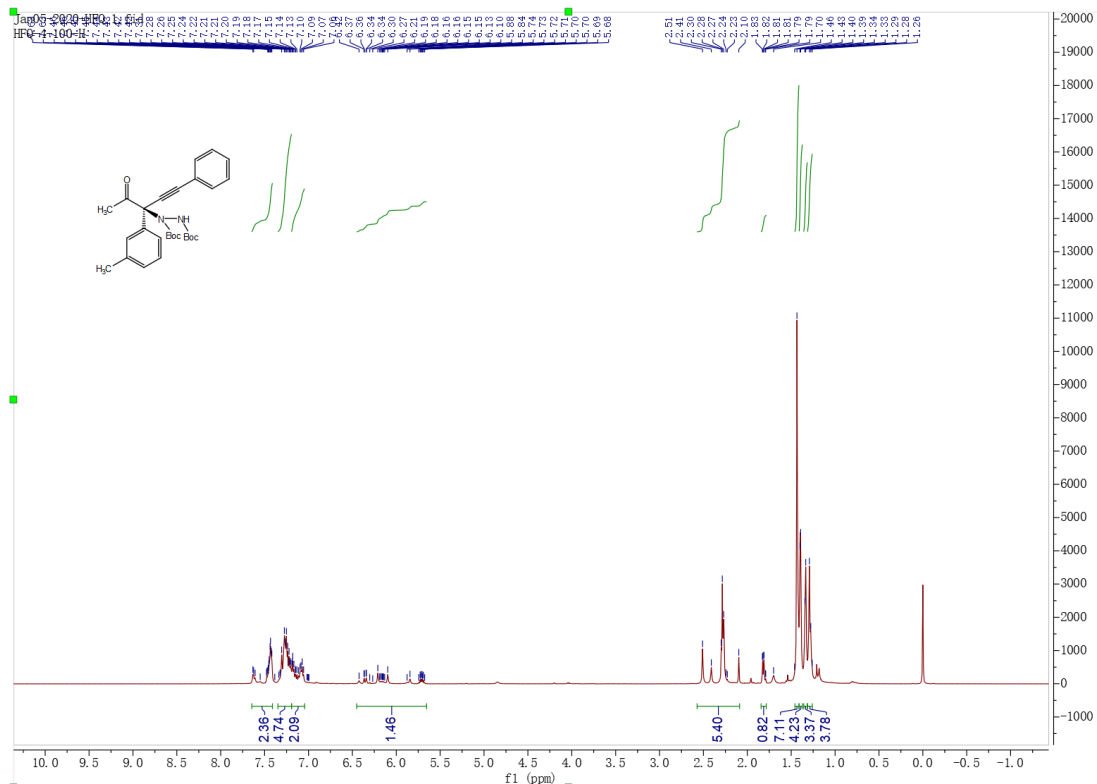
Di-tert-butyl-(*R*)-1-(3-(4-bromophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3d**)



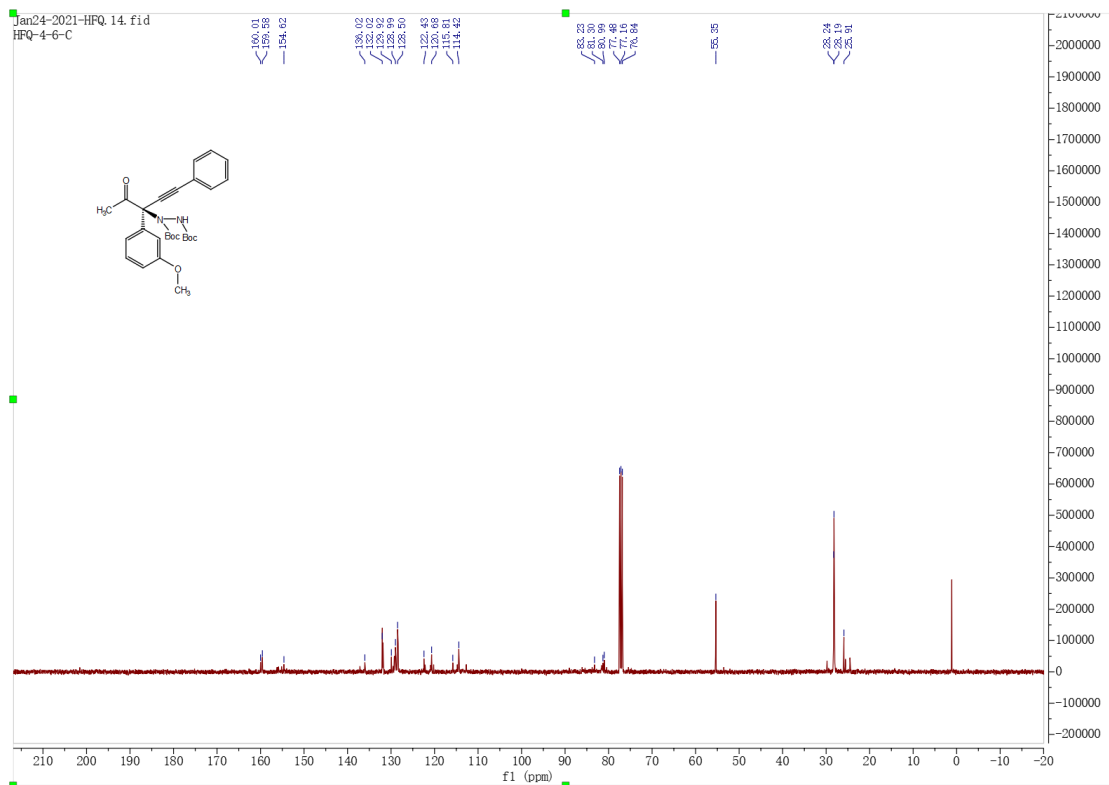
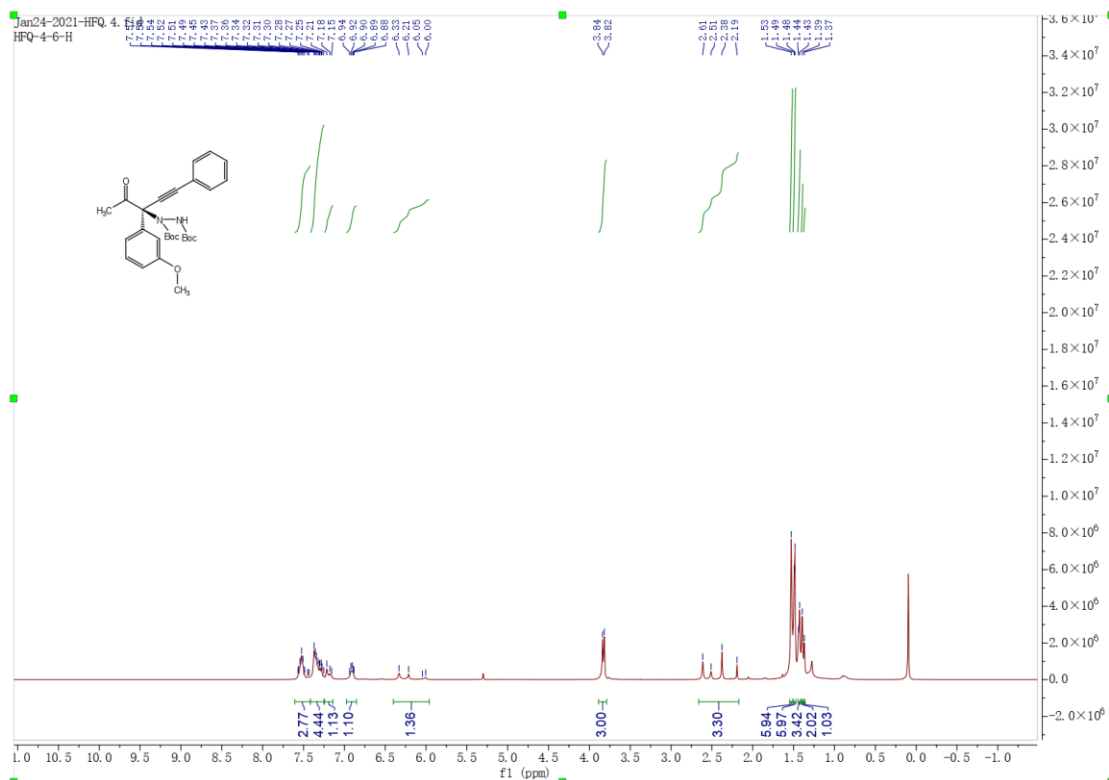
Di-tert-butyl-(*R*)-1-(3-(4-chlorophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3e**)



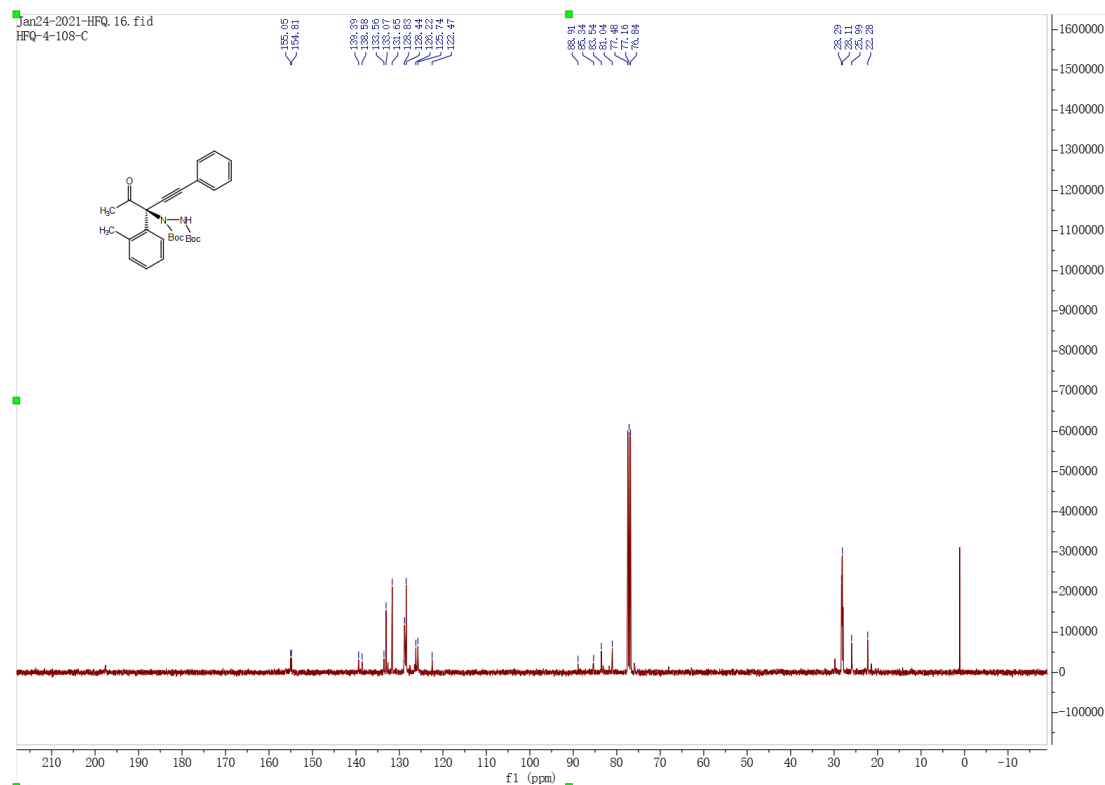
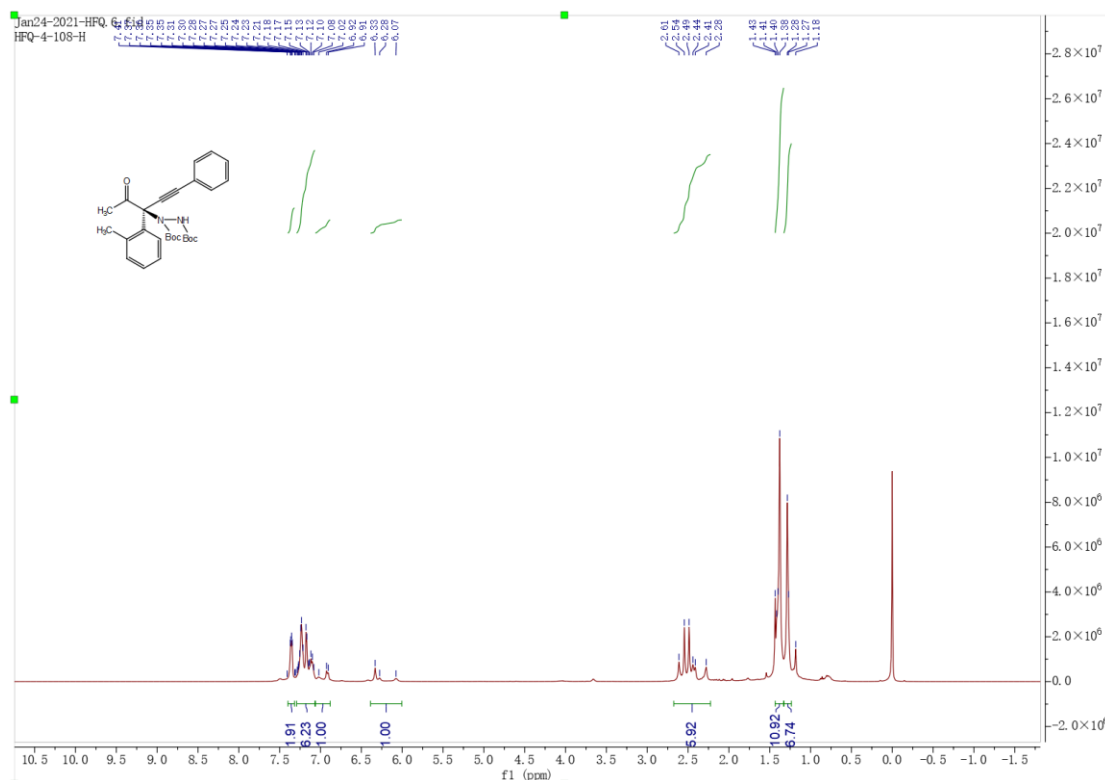
Di-tert-butyl-(*R*)-1-(4-oxo-1-phenyl-3-(*m*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3f**)



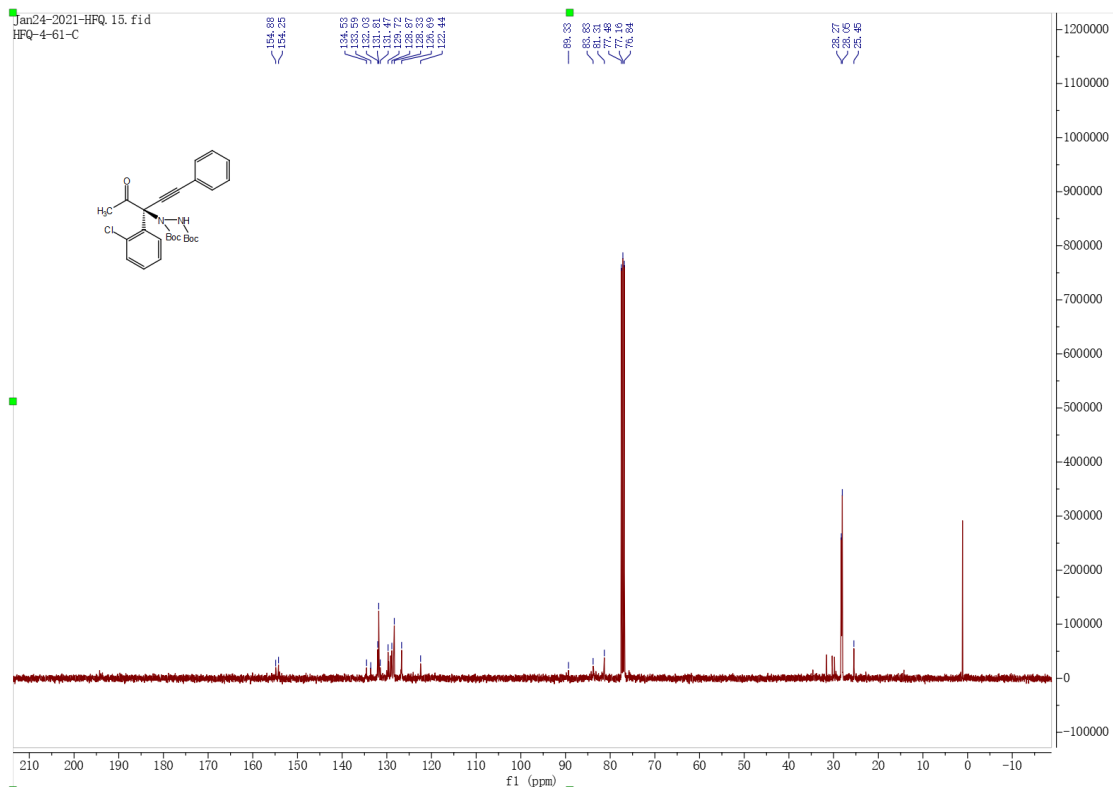
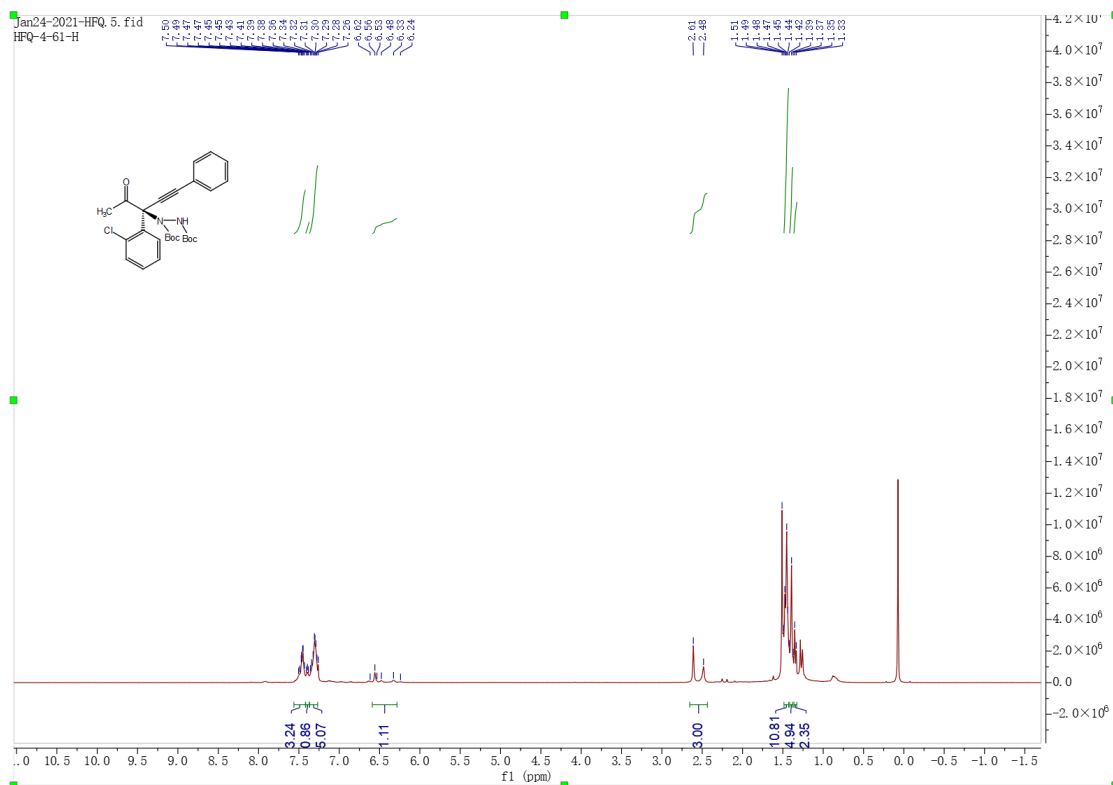
Di-tert-butyl-(*R*)-1-(3-(3-methoxyphenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3g**)



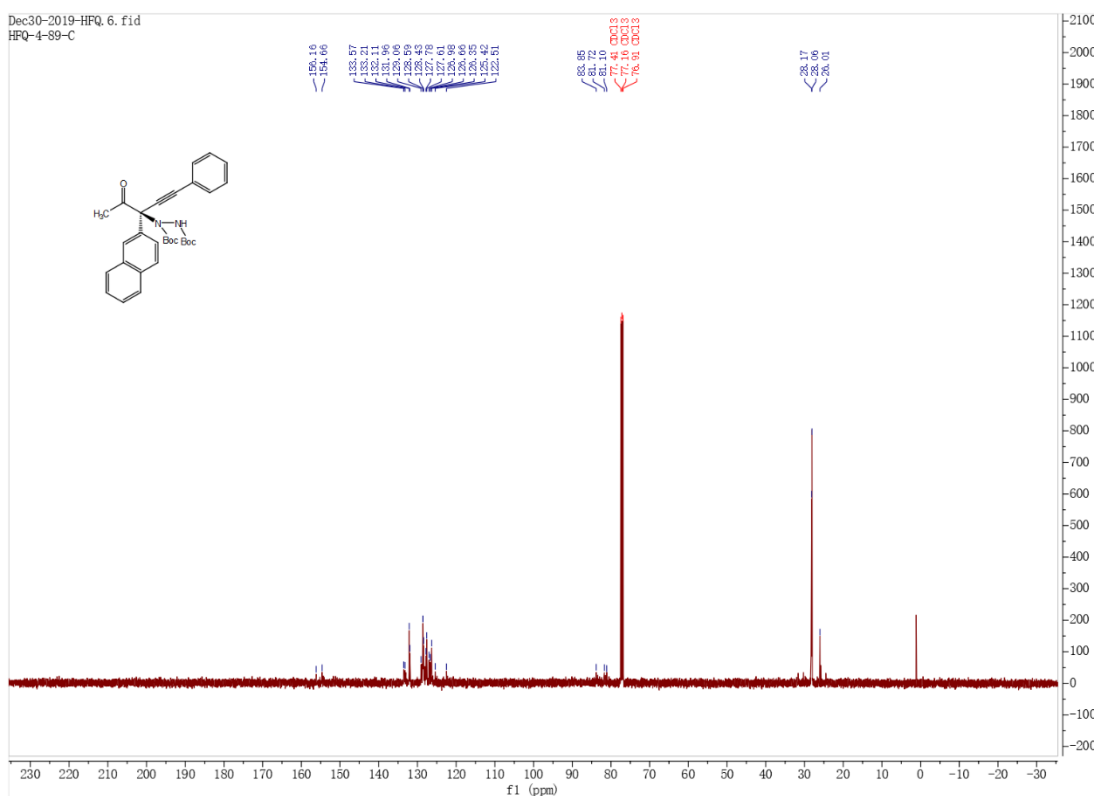
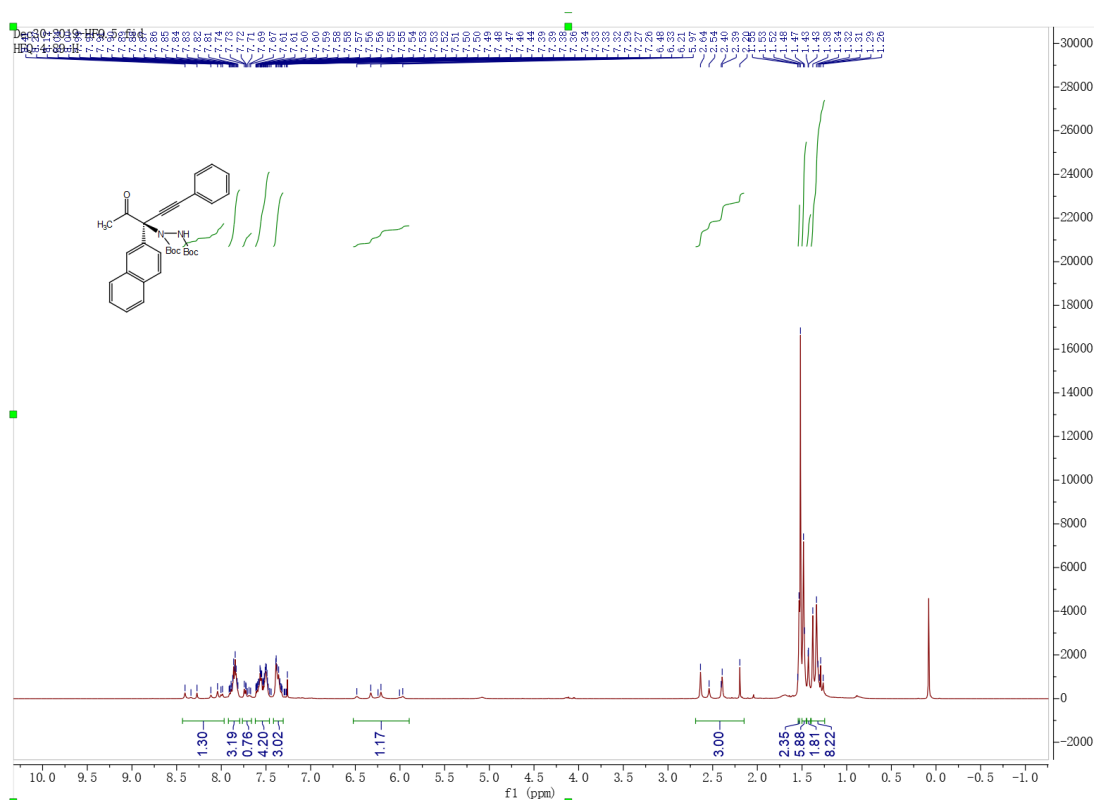
Di-tert-butyl-(S)-1-(4-oxo-1-phenyl-3-(o-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3h**)



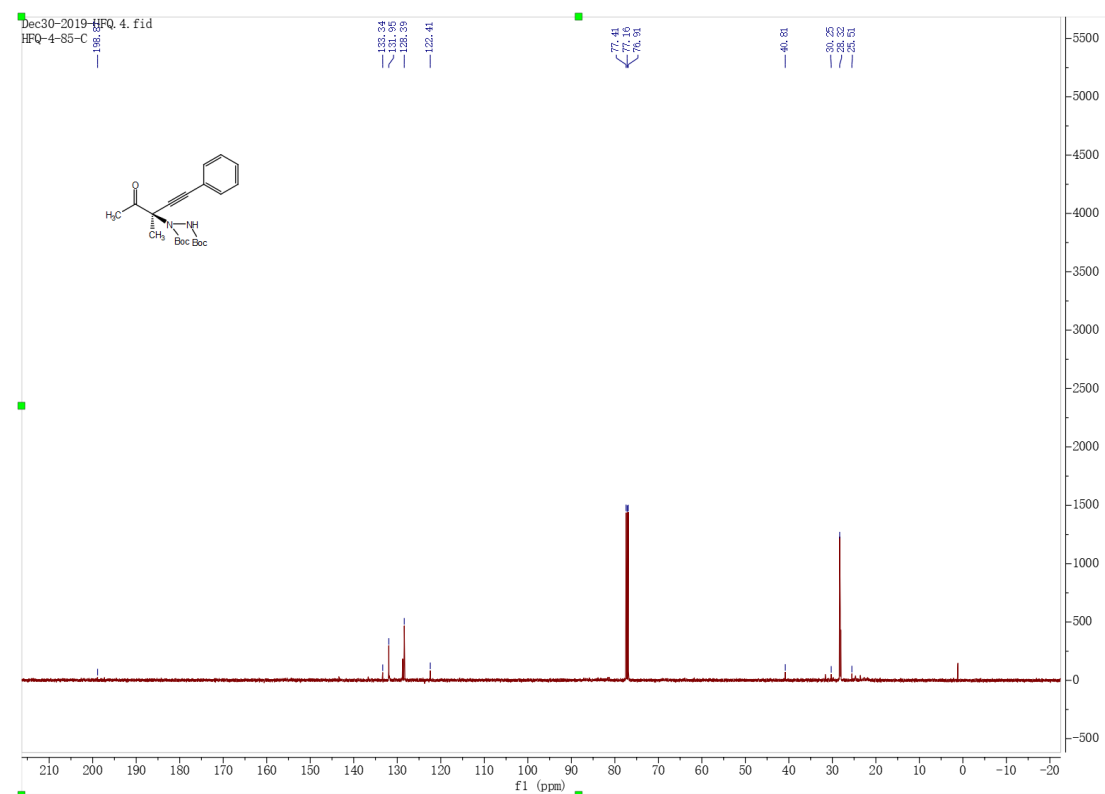
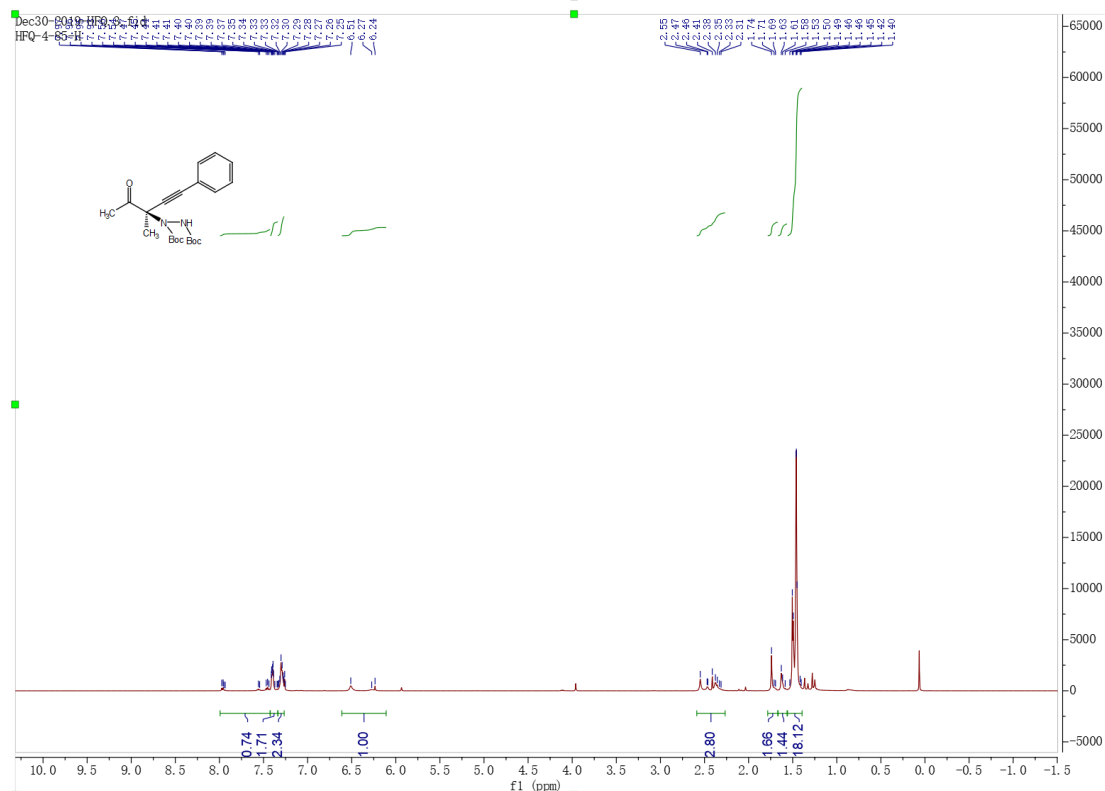
Di-tert-butyl-(*S*)-1-(3-(2-chlorophenyl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3i**)



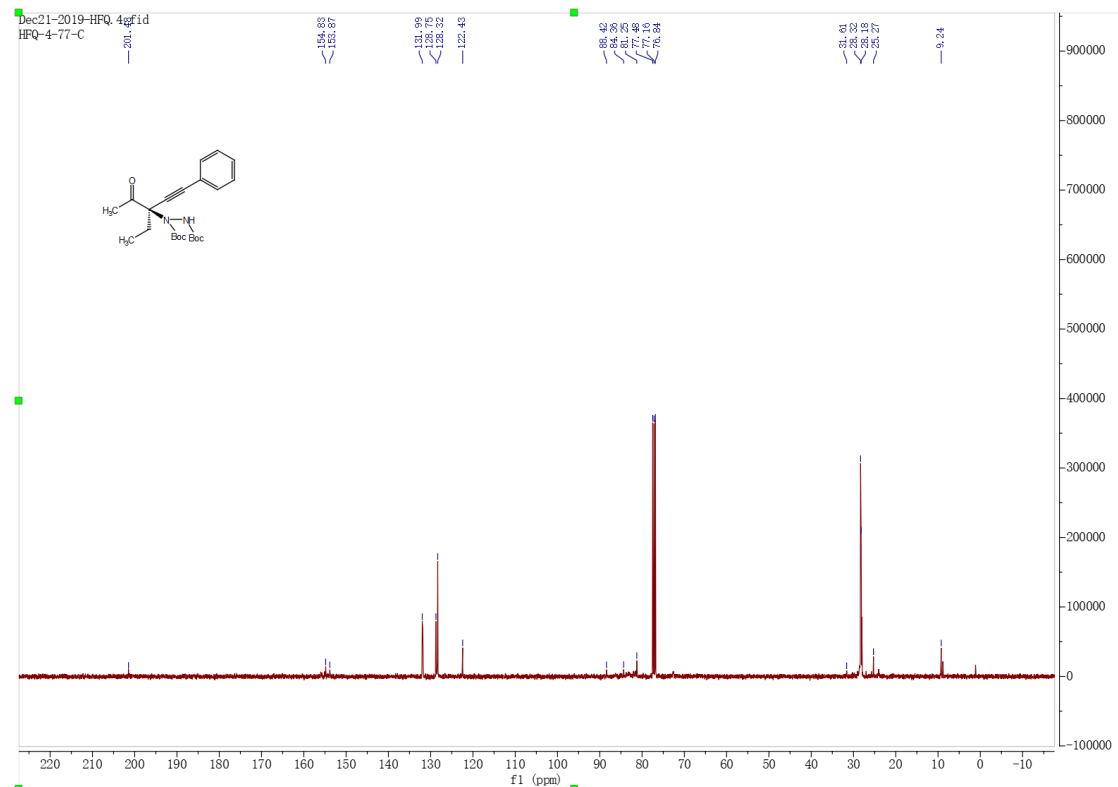
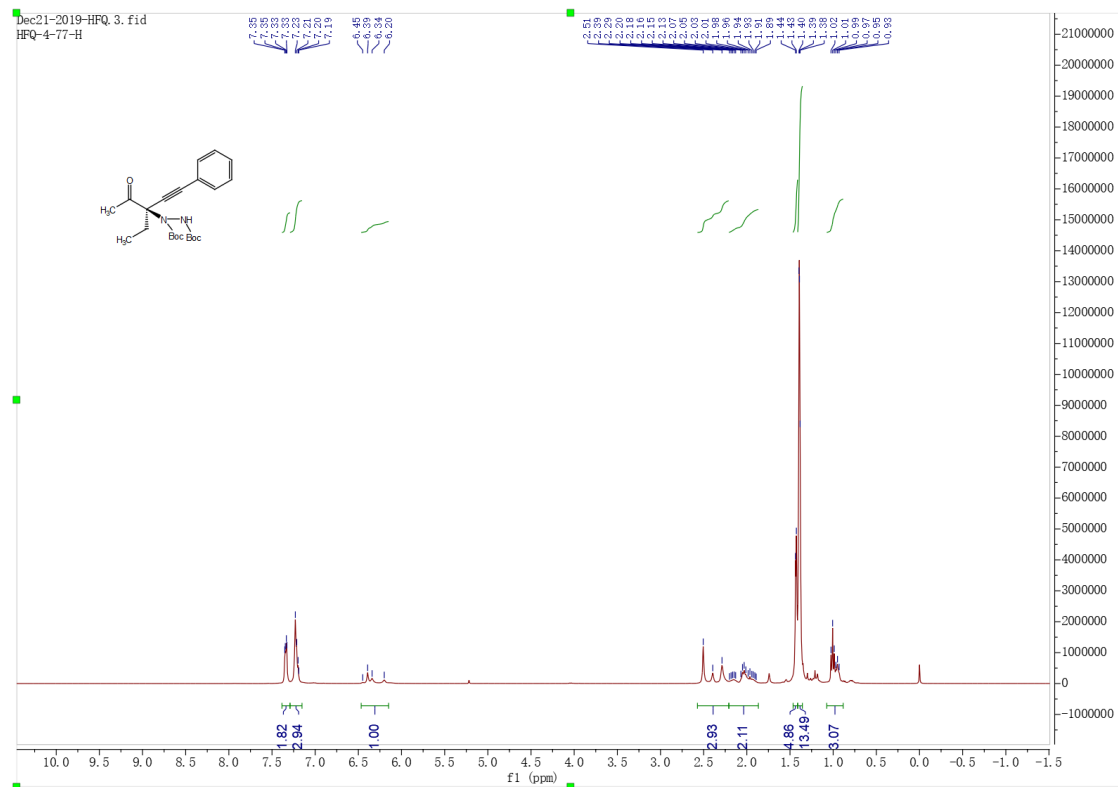
Di-tert-butyl-(*R*)-1-(3-(naphthalen-2-yl)-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3j**)



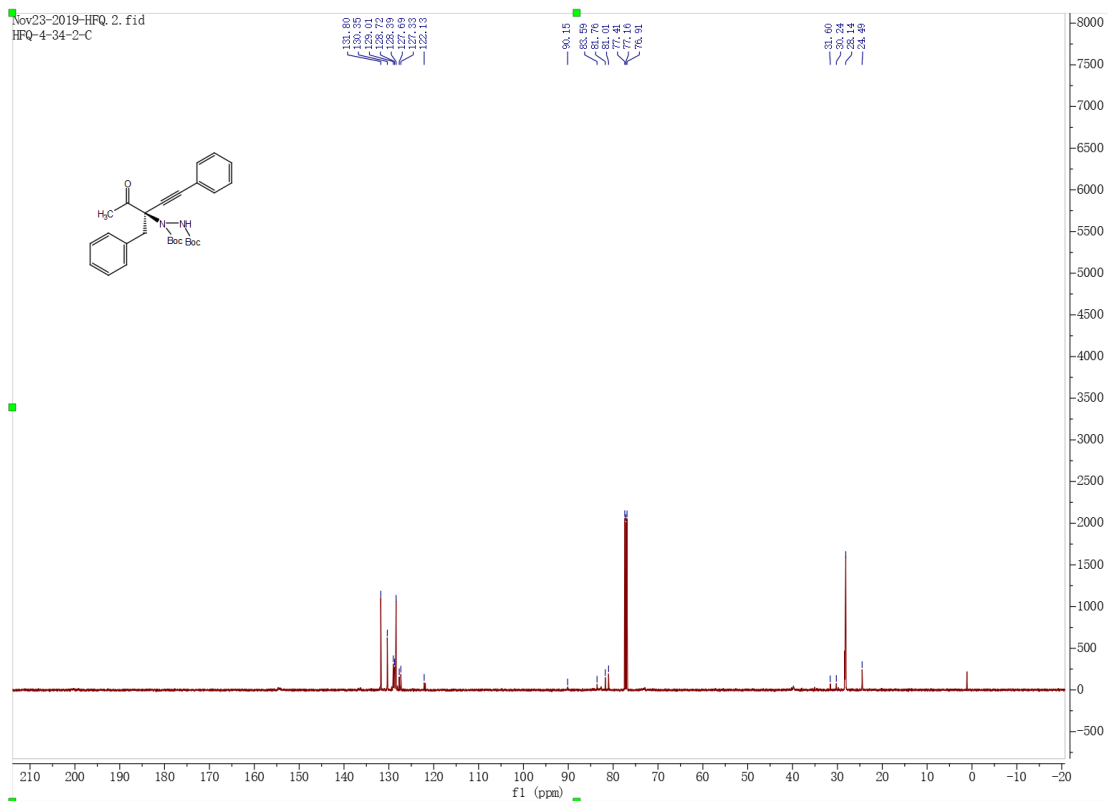
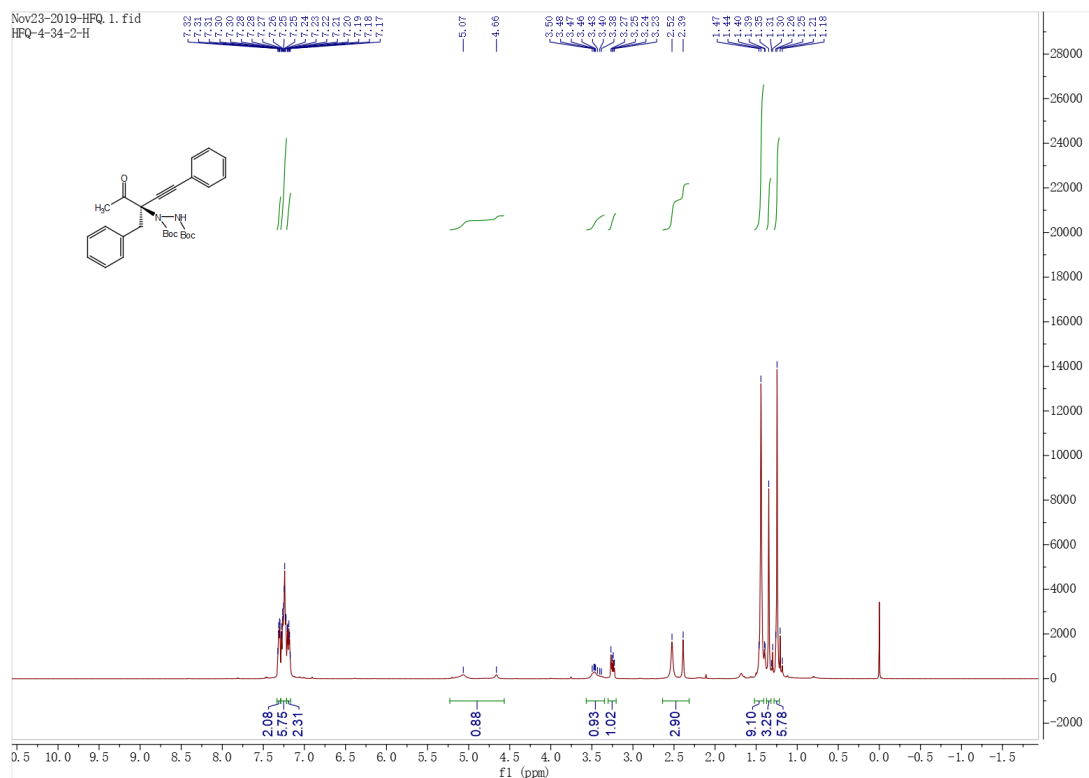
Di-tert-butyl-(*R*)-1-(3-methyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3k**)



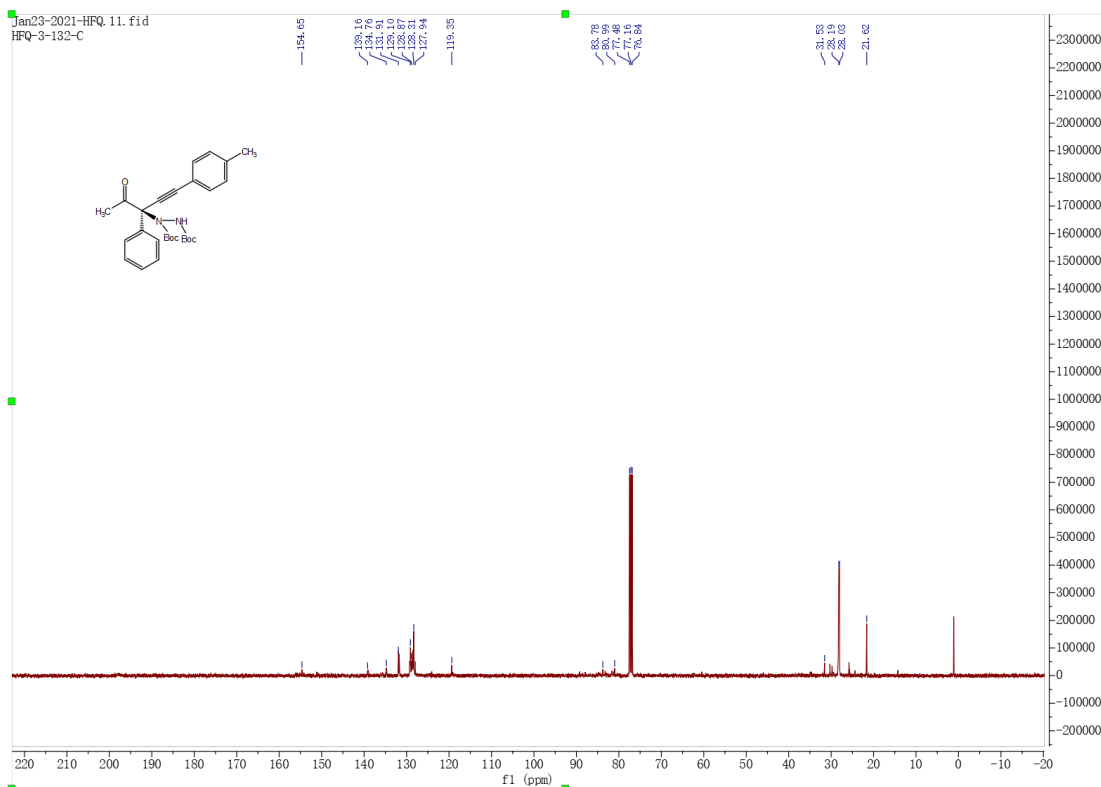
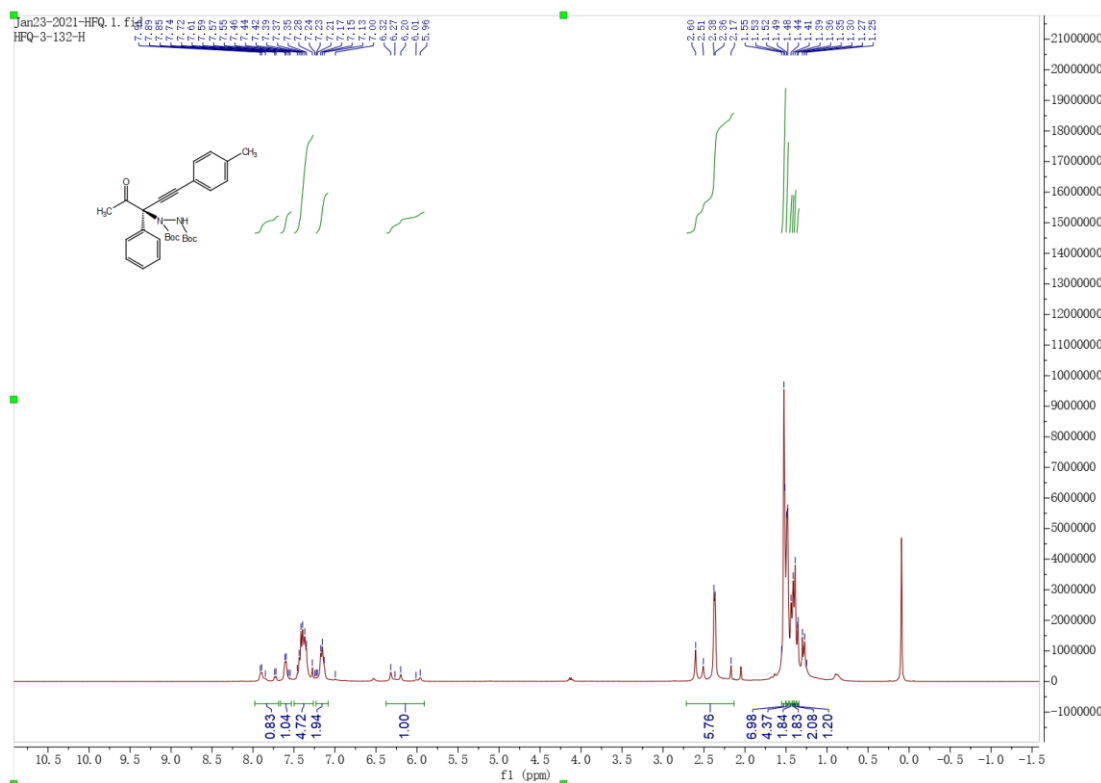
Di-tert-butyl-(*R*)-1-(3-ethyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**31**)



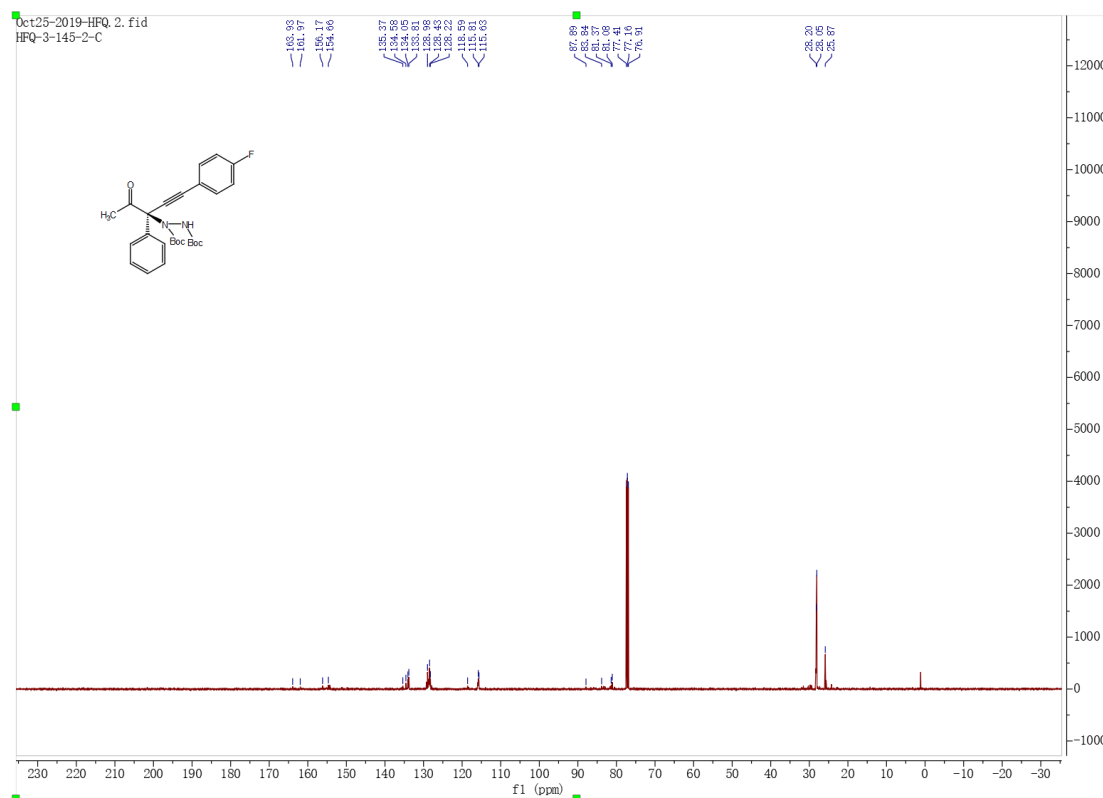
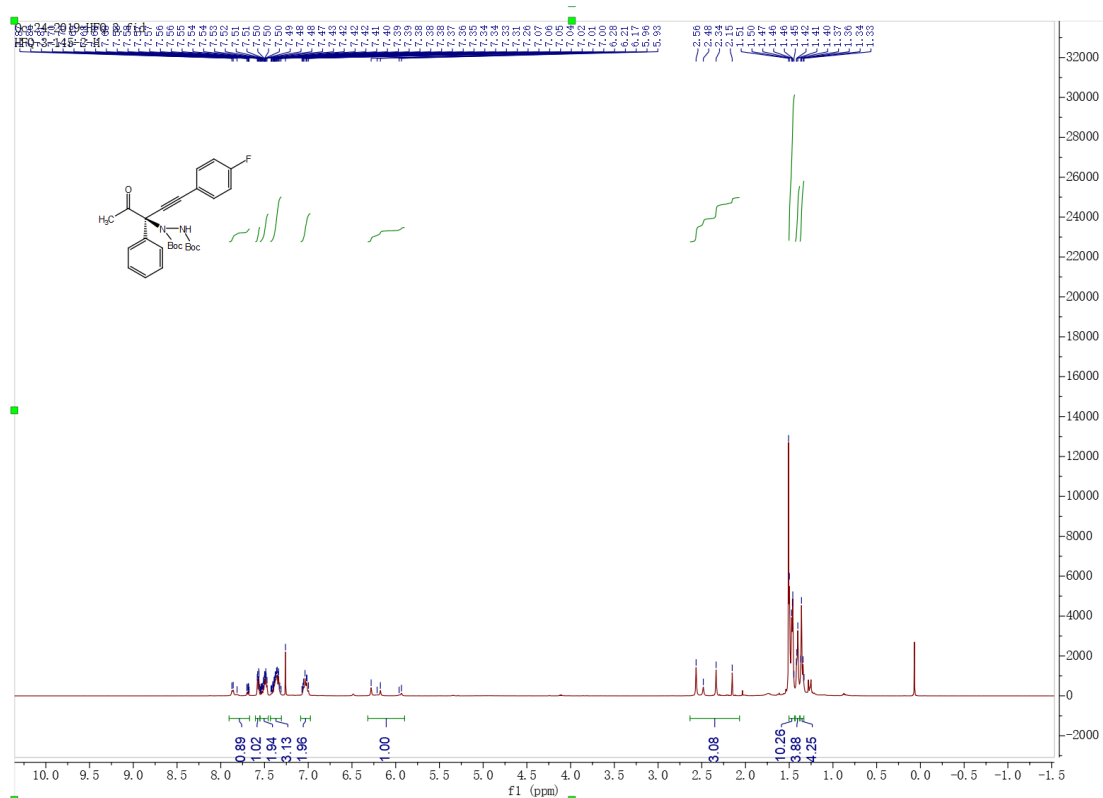
Di-tert-butyl-(*R*)-1-(3-benzyl-4-oxo-1-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3m**)

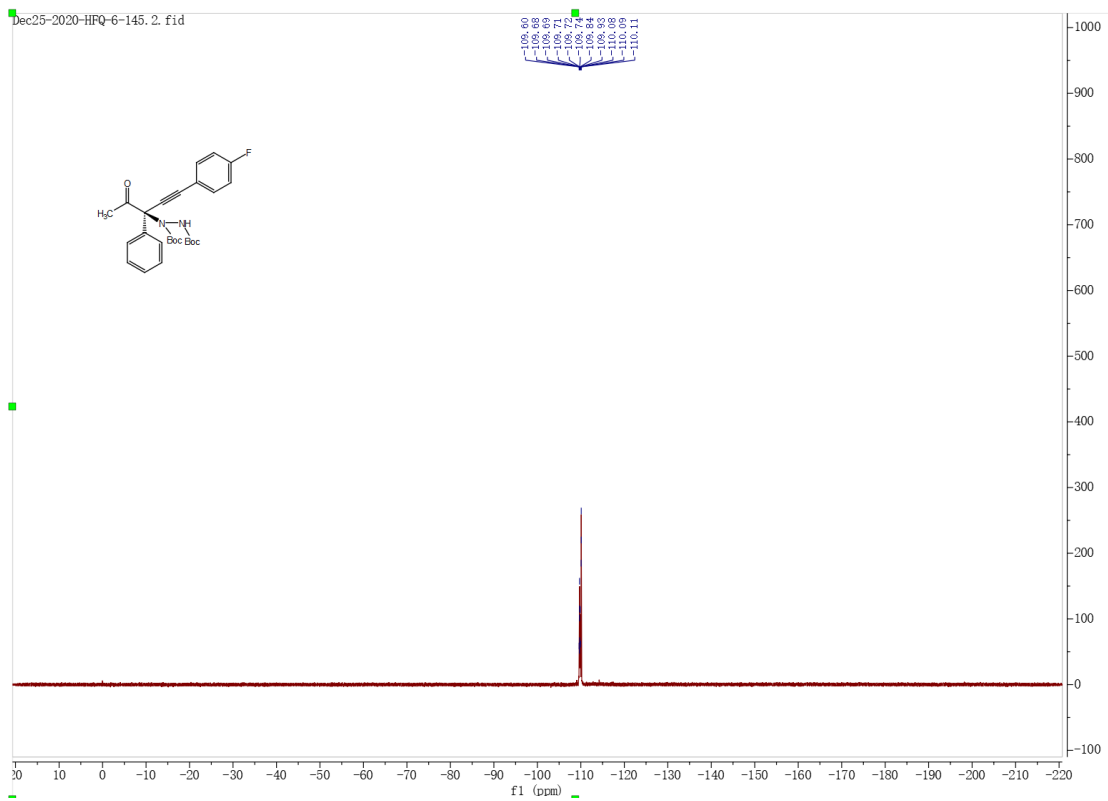


Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*p*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3n**)

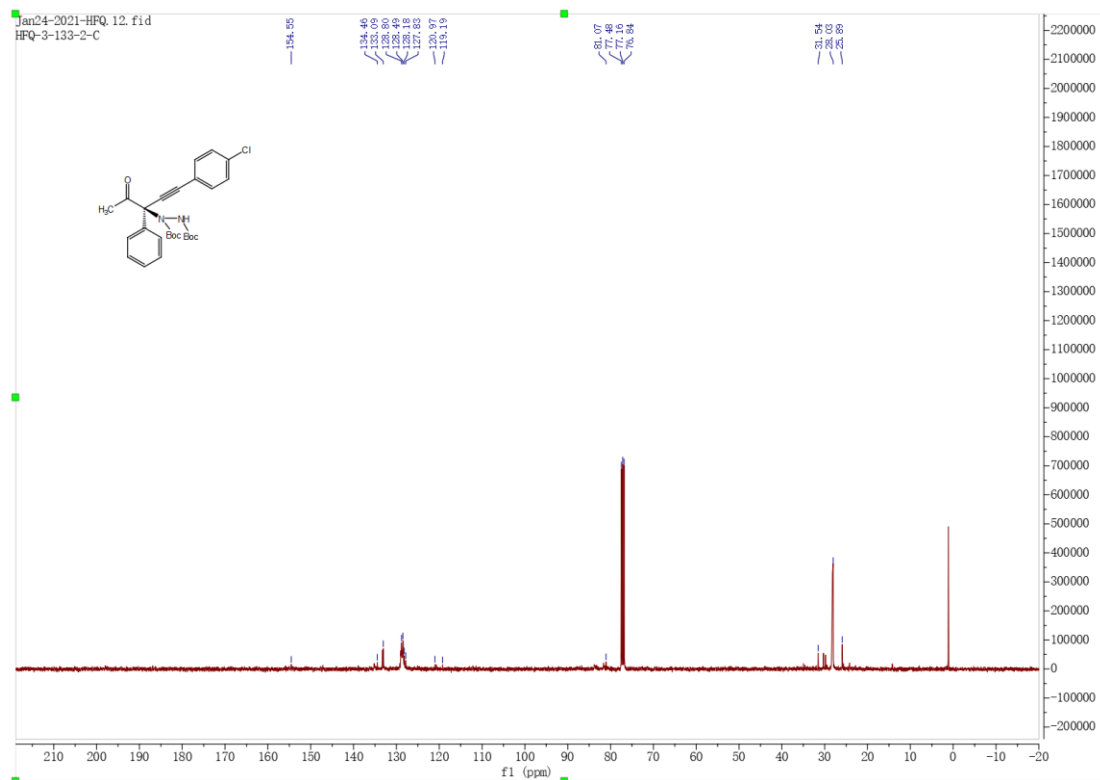
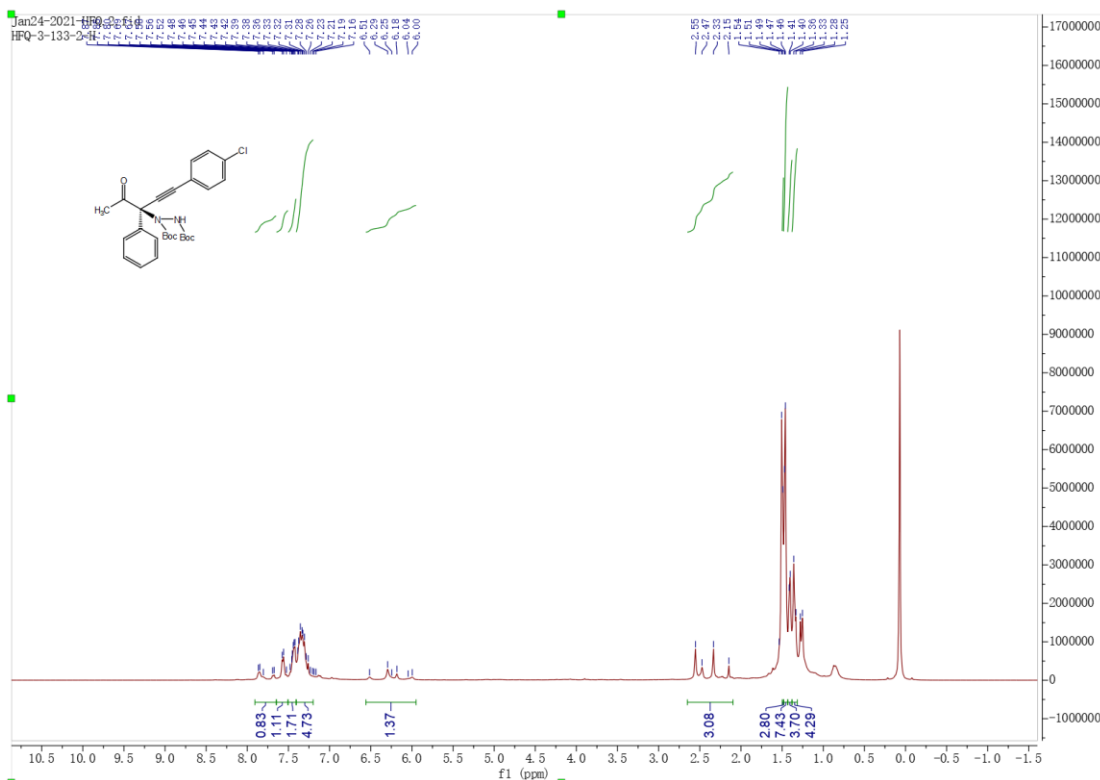


Di-tert-butyl-(*R*)-1-(1-(4-fluorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**30**)

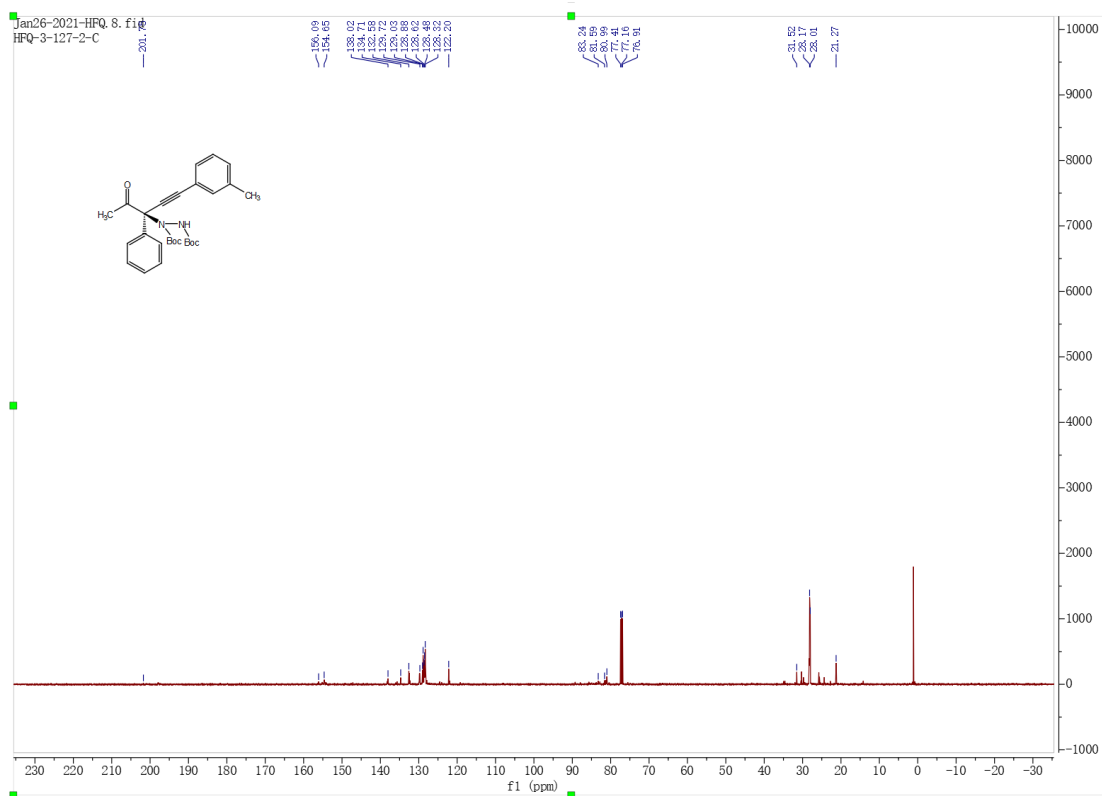
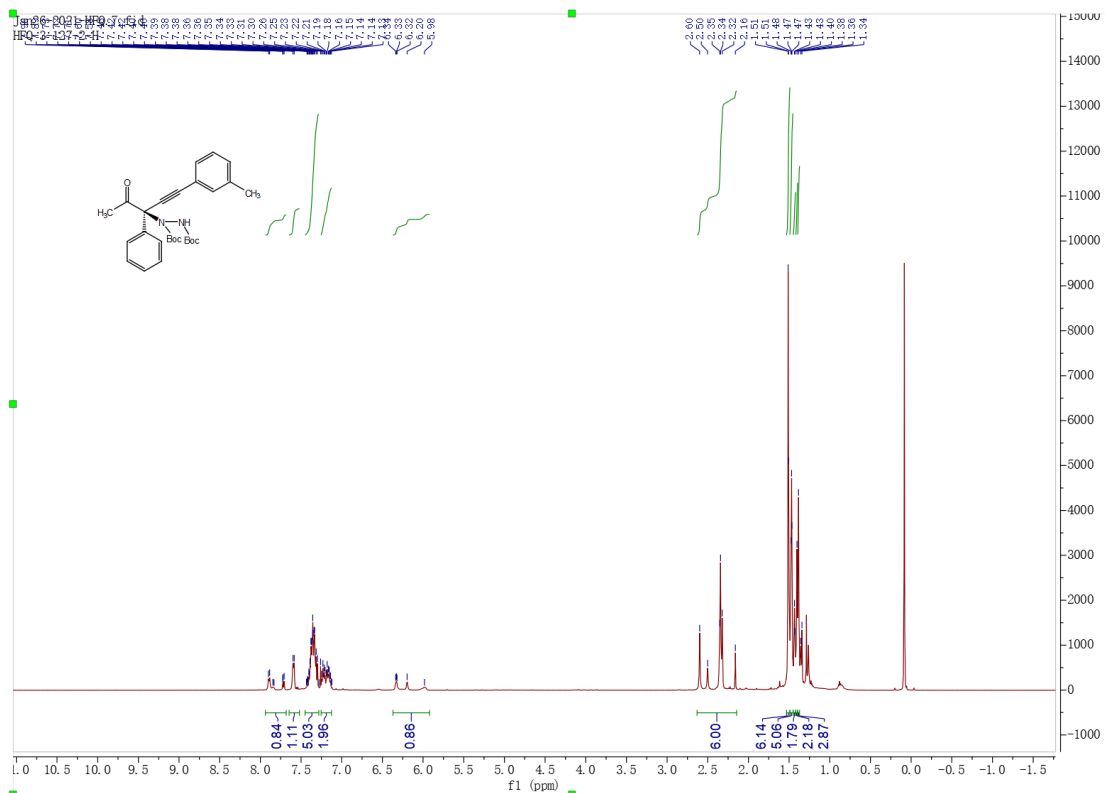




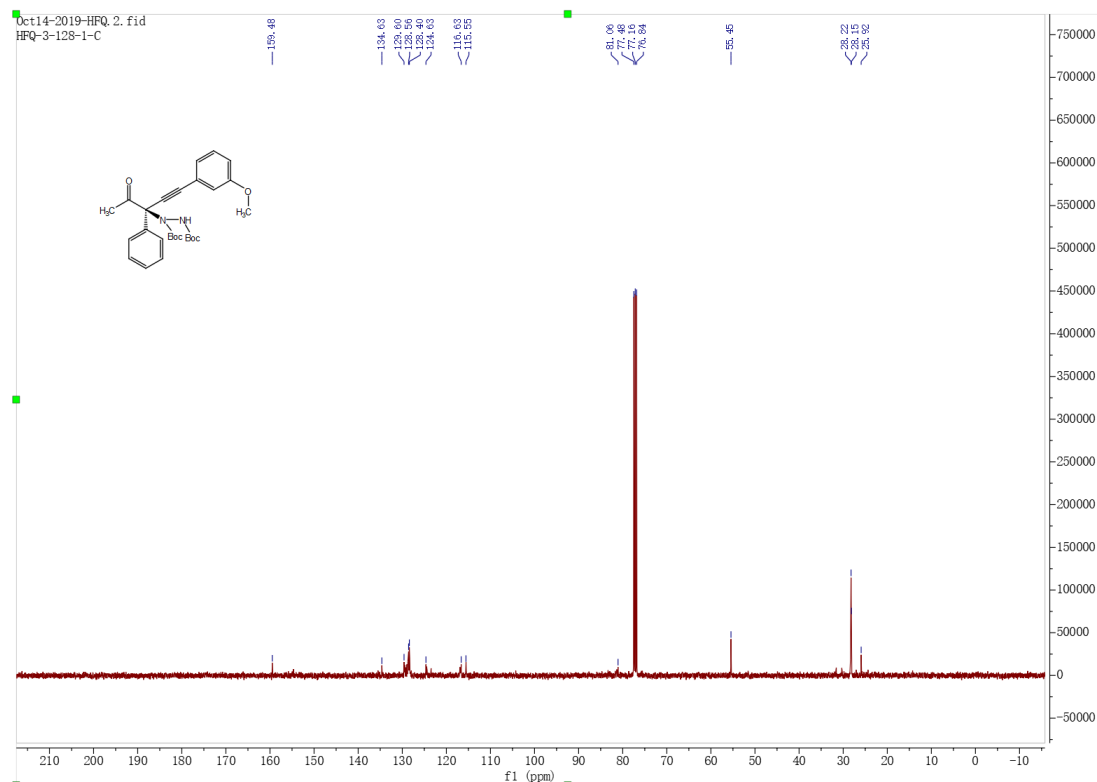
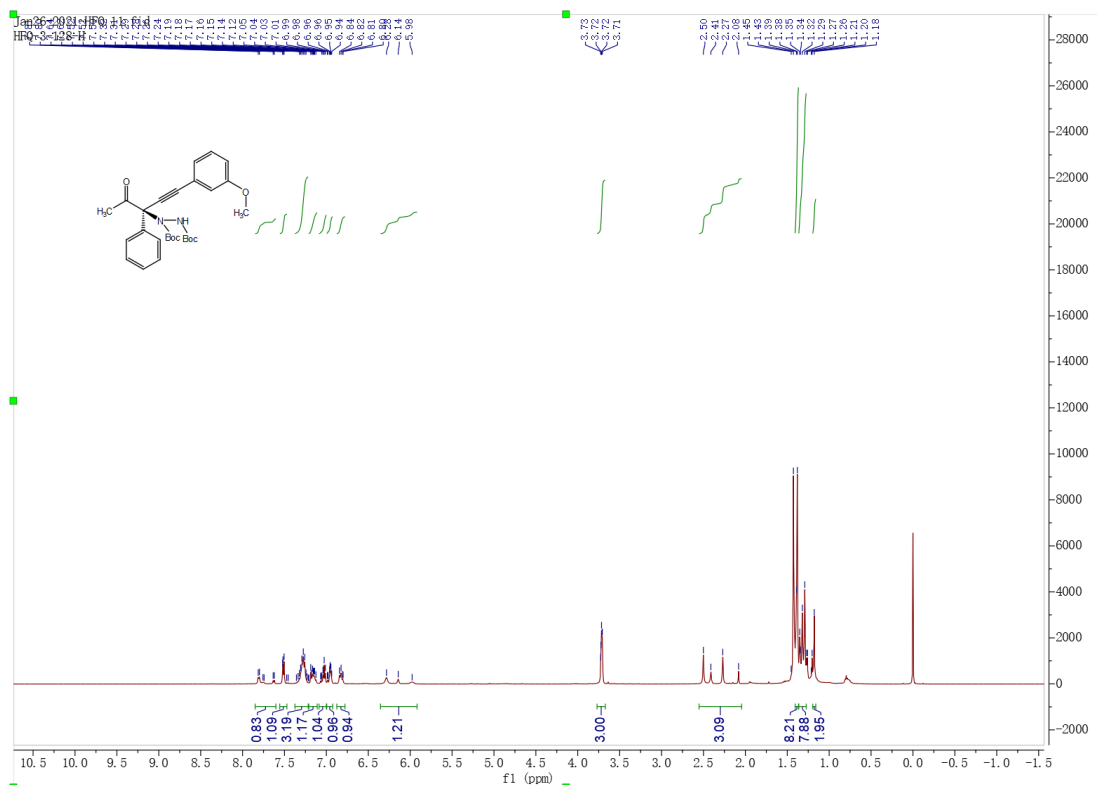
Di-tert-butyl-(*R*)-1-(1-(4-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3p**)



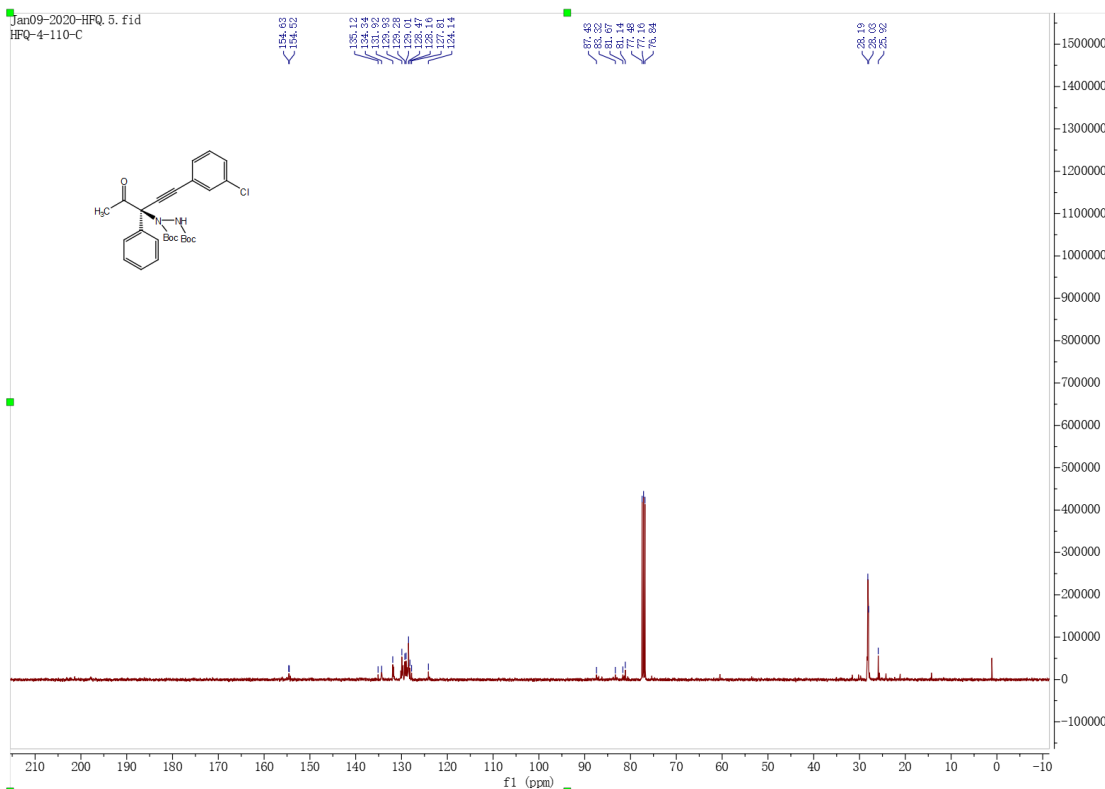
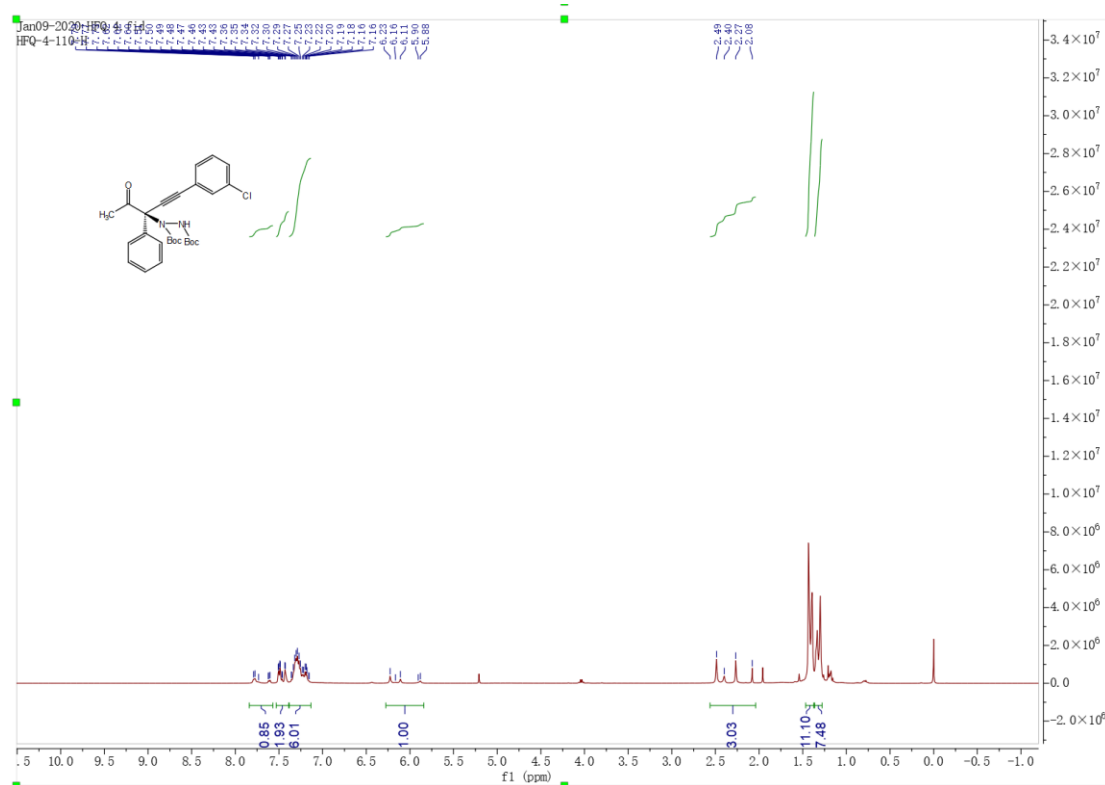
Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*m*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3q**)



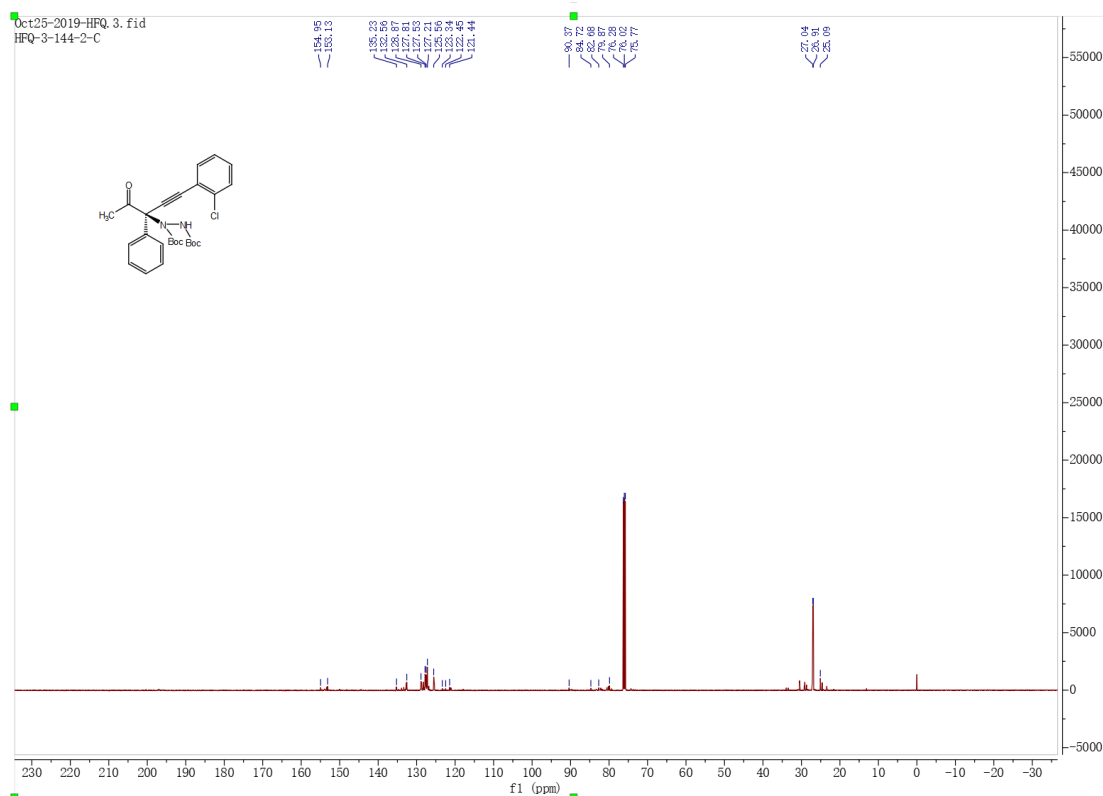
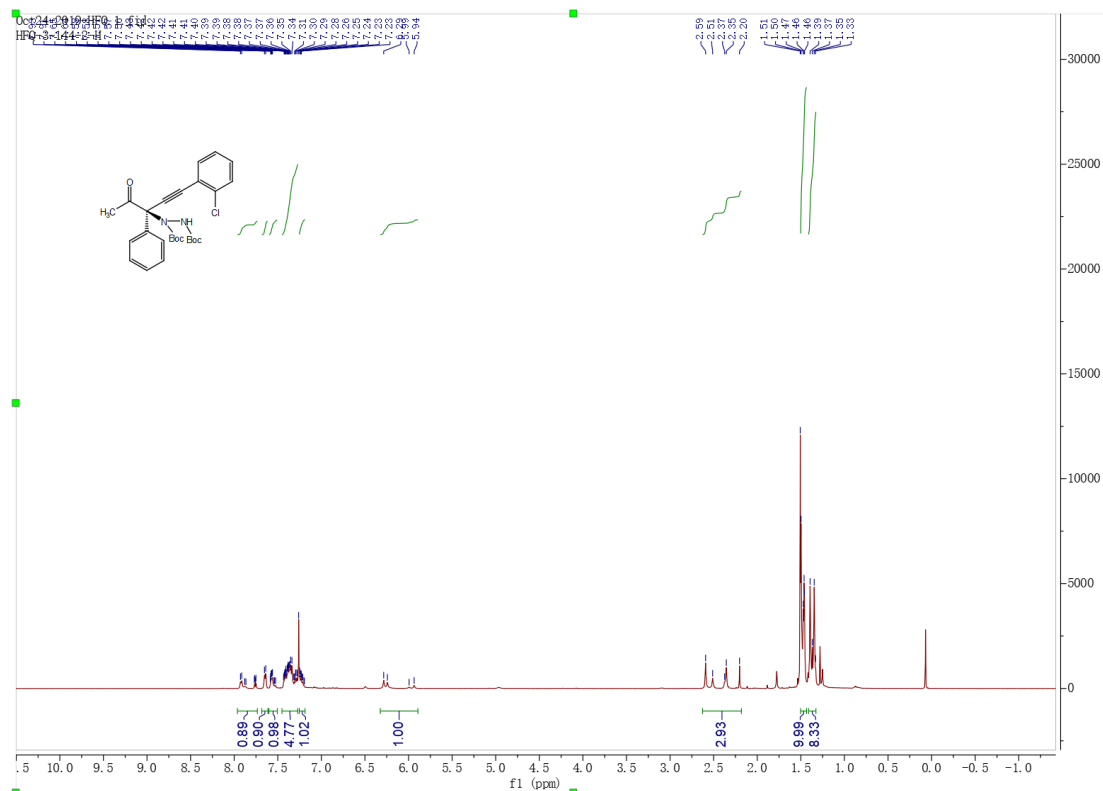
Di-tert-butyl-(*R*)-1-(1-(3-methoxyphenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3r**)



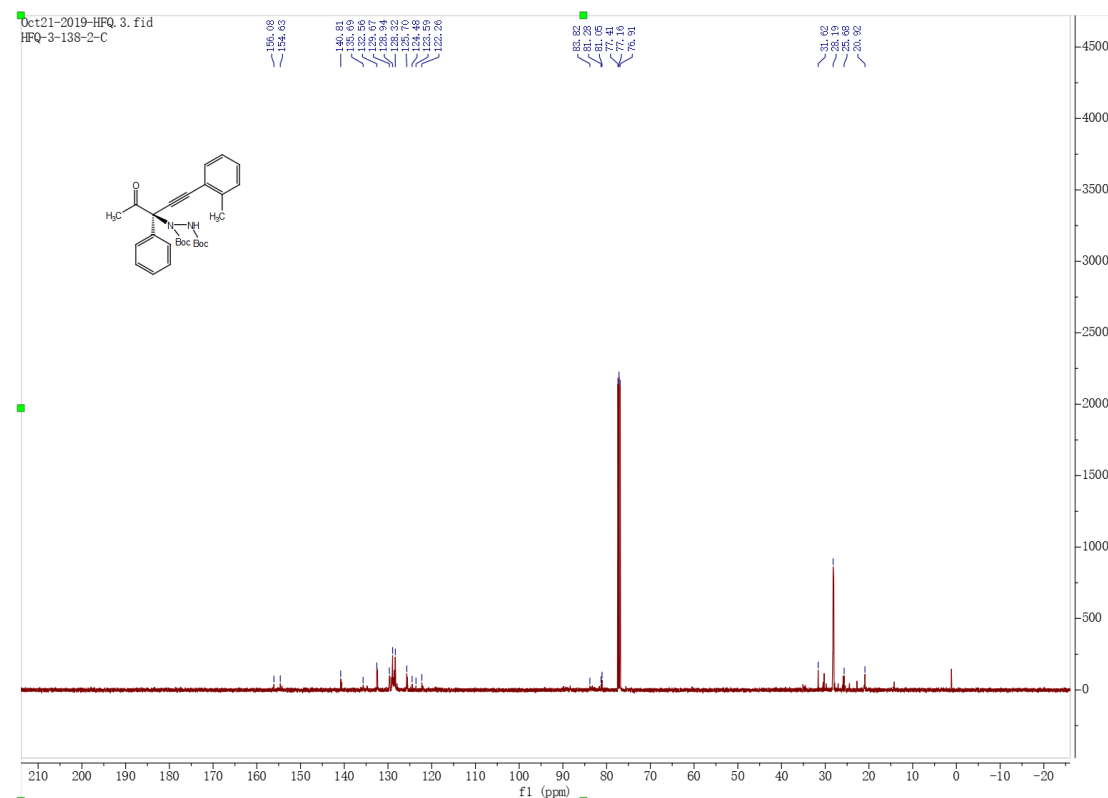
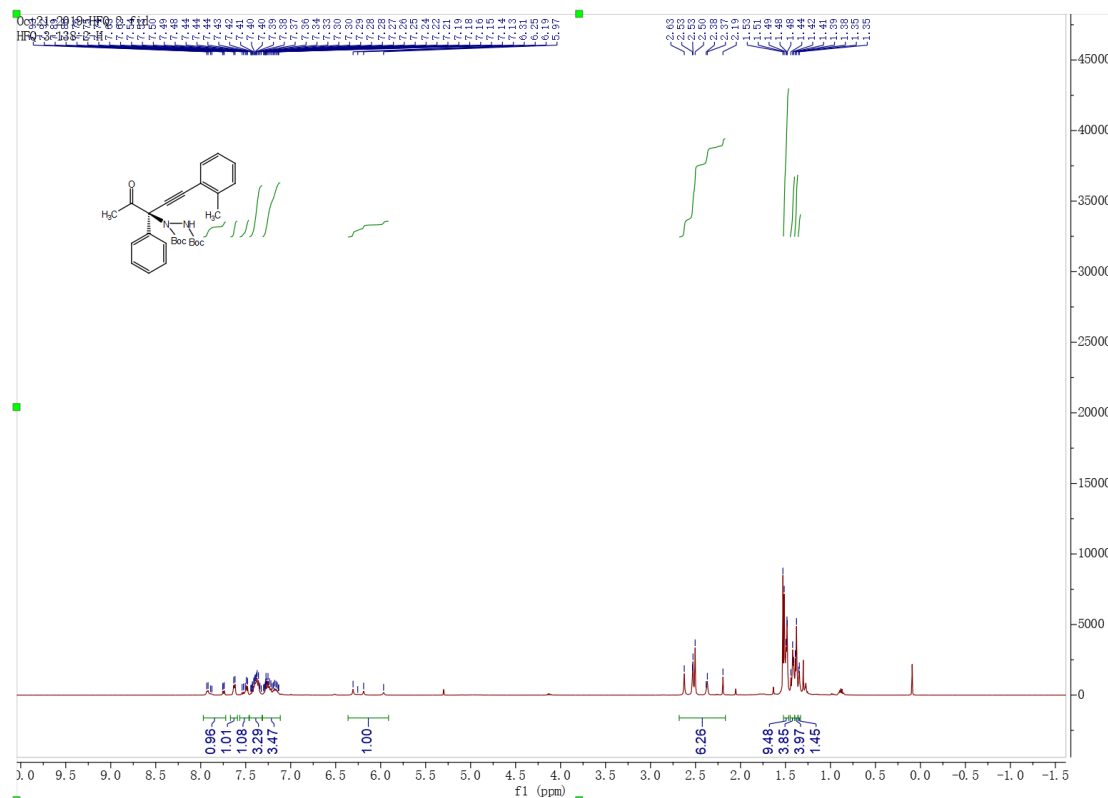
Di-tert-butyl-(*R*)-1-(1-(3-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3s**)



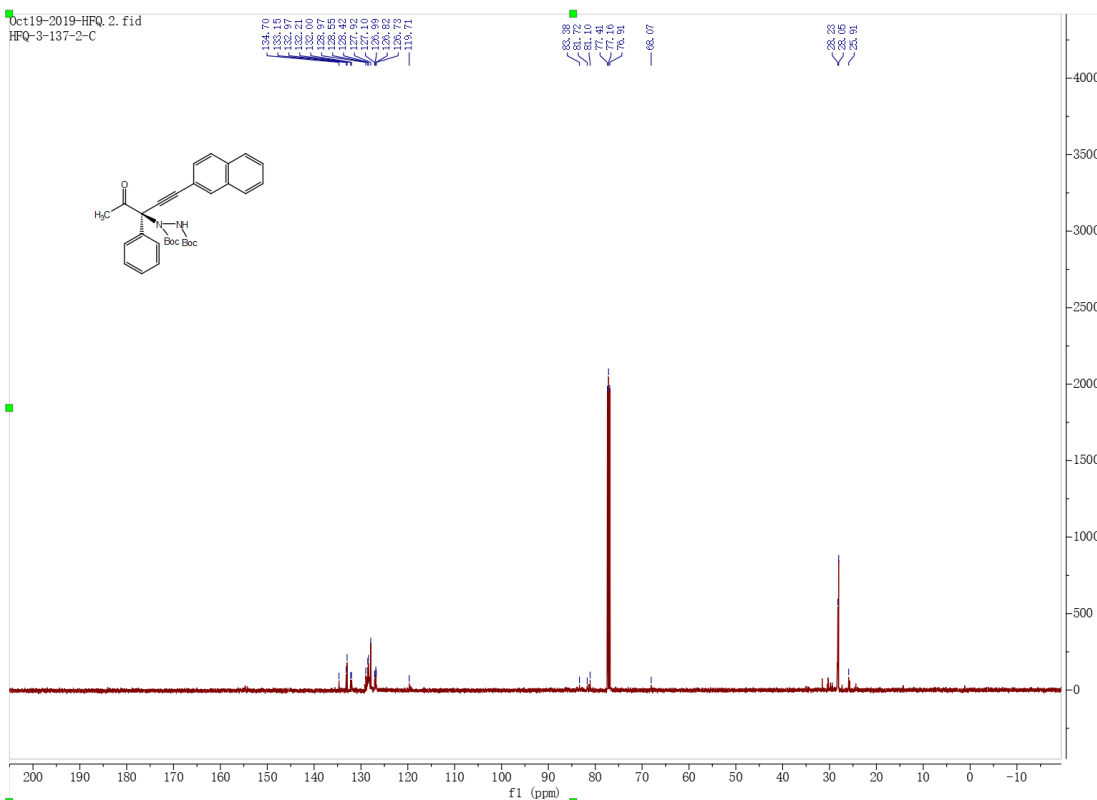
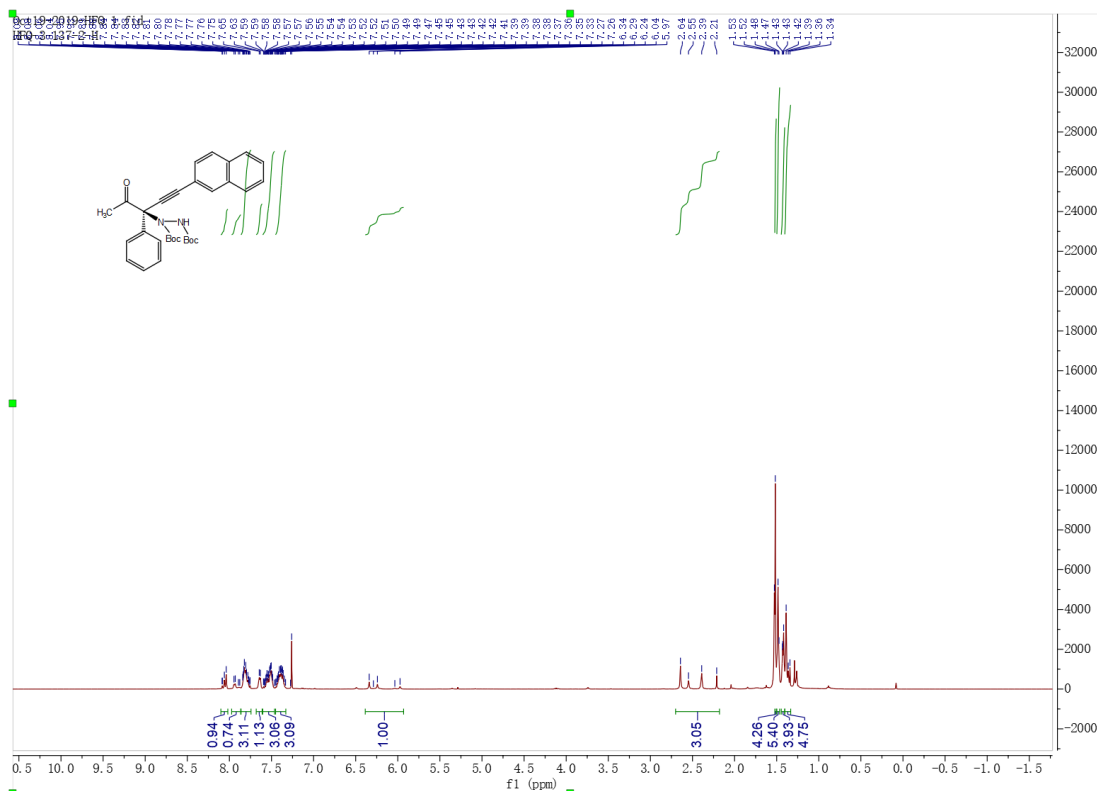
Di-tert-butyl-(*R*)-1-(1-(2-chlorophenyl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3t**)



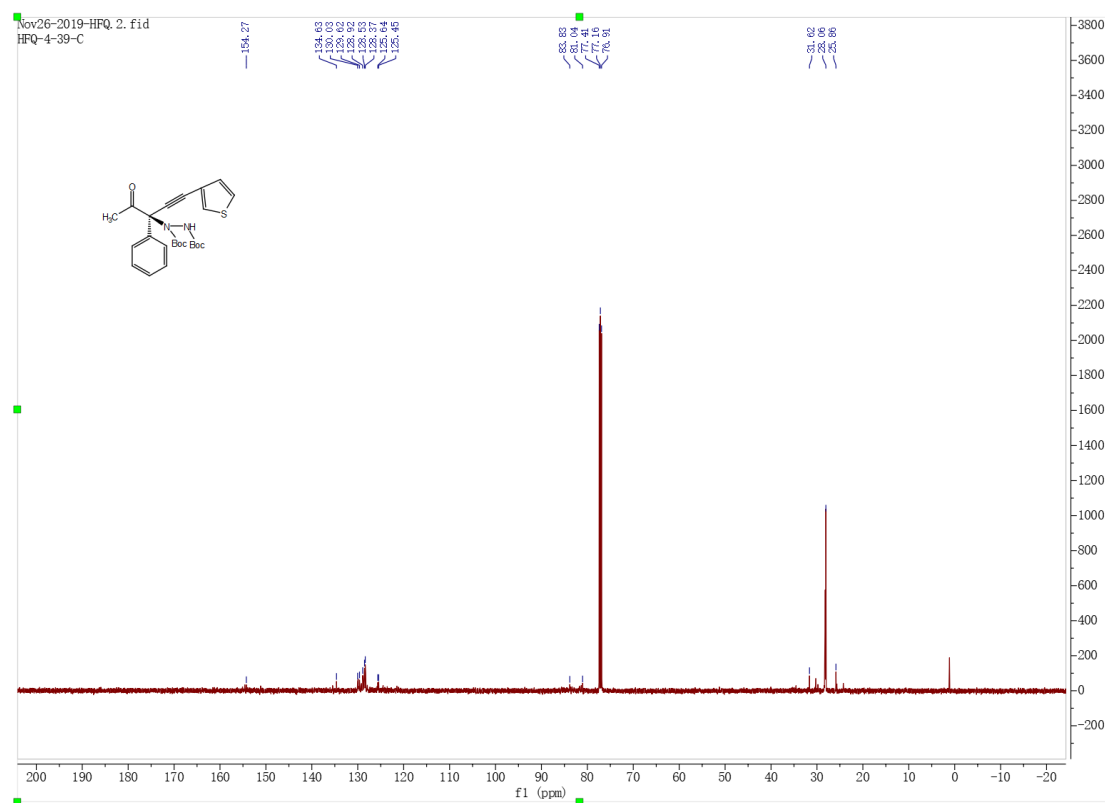
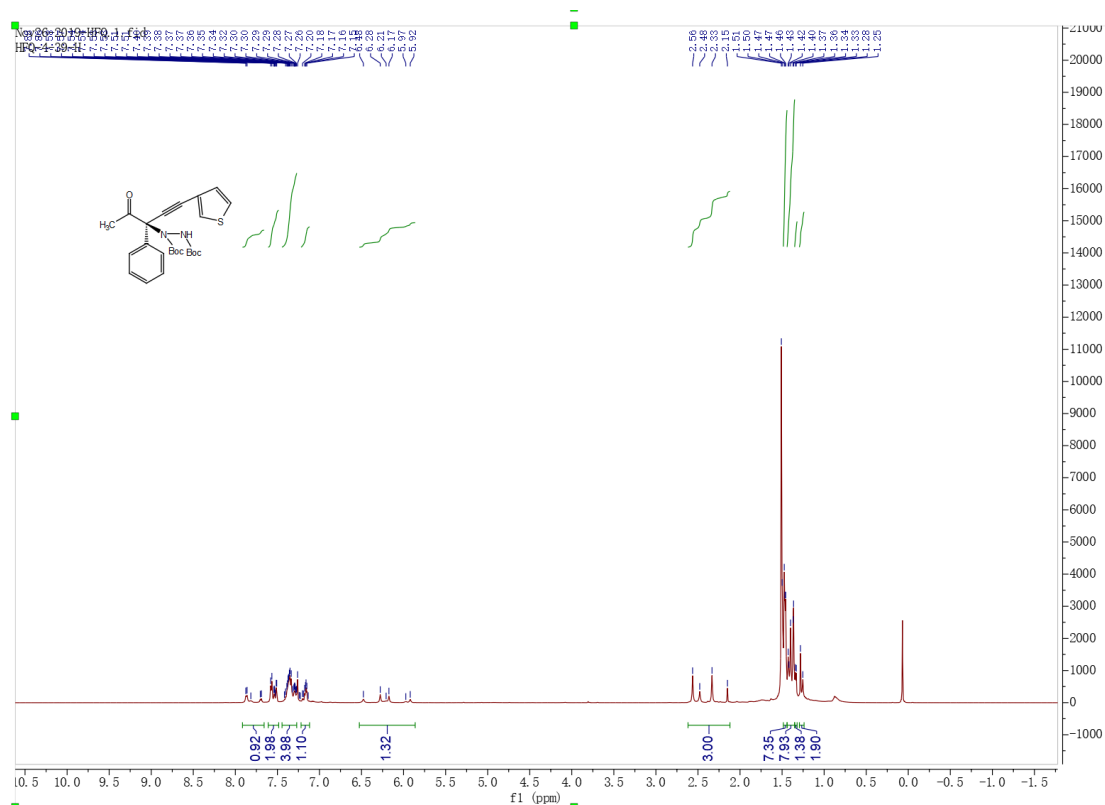
Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(*o*-tolyl)pent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3u**)



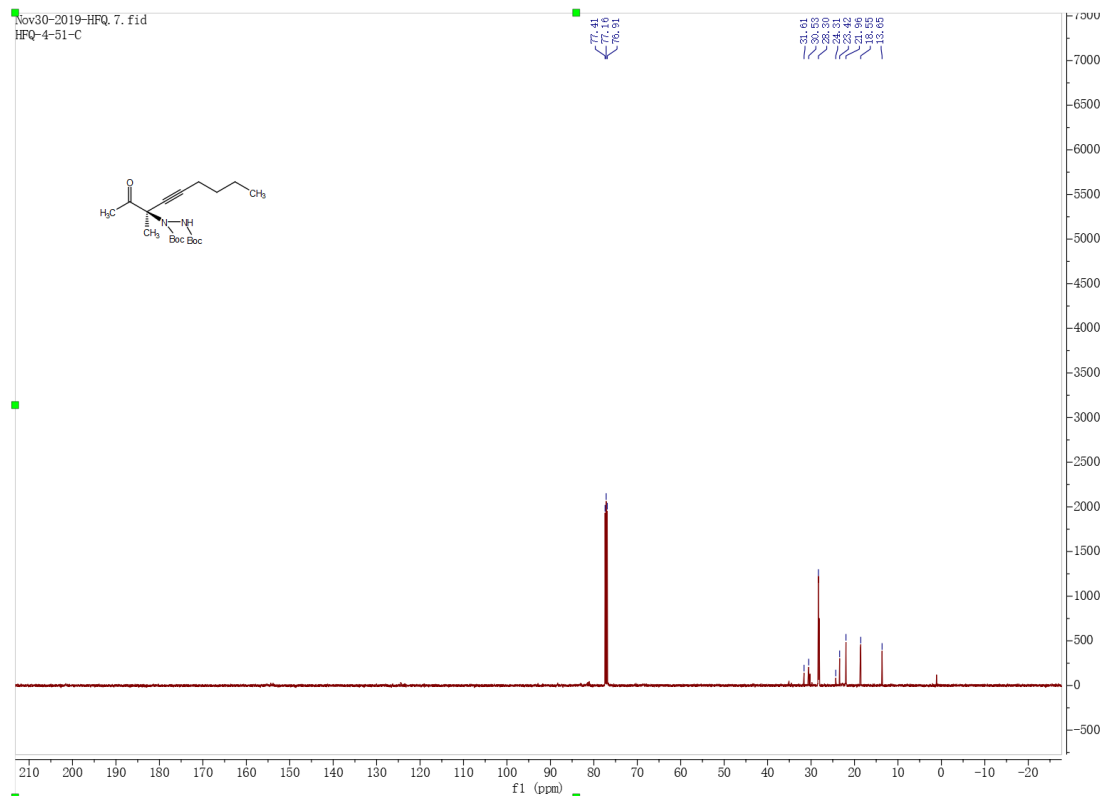
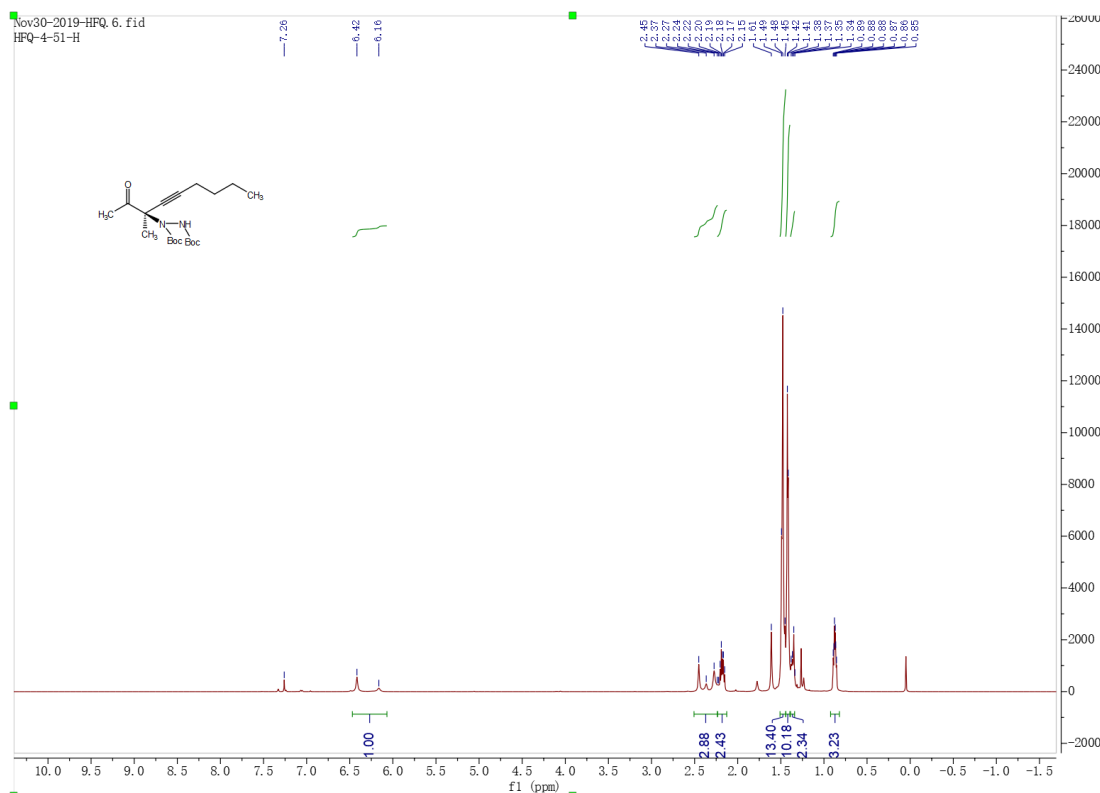
Di-tert-butyl-(*R*)-1-(1-(naphthalen-2-yl)-4-oxo-3-phenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3v**)



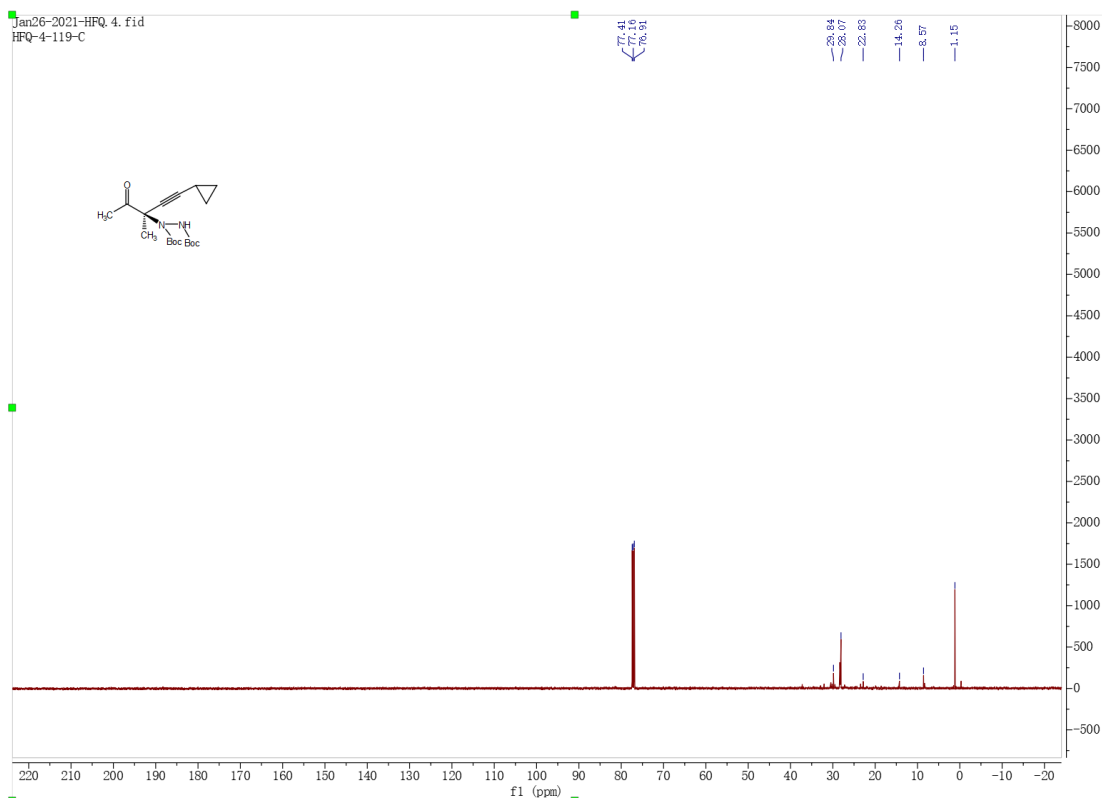
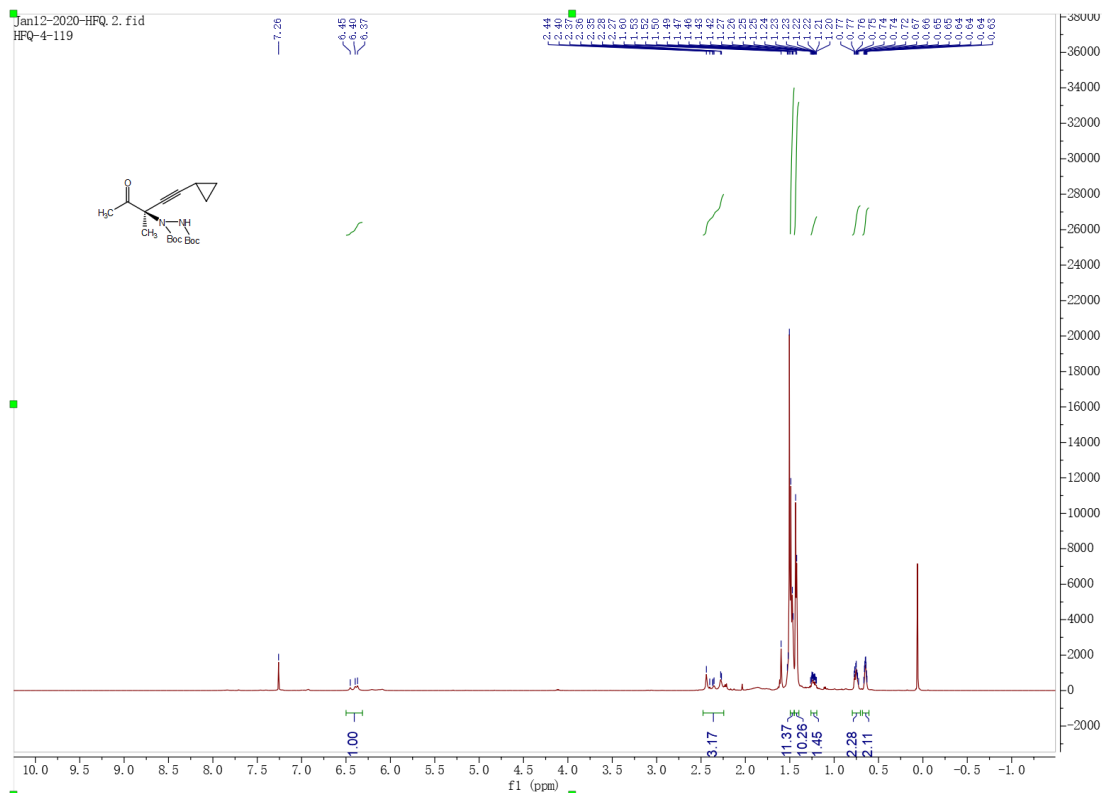
Di-tert-butyl-(*R*)-1-(4-oxo-3-phenyl-1-(thiophen-3-yl)pent-1-yn-3-yl)hydrazine-1,2-di
carboxylate (**3w**)



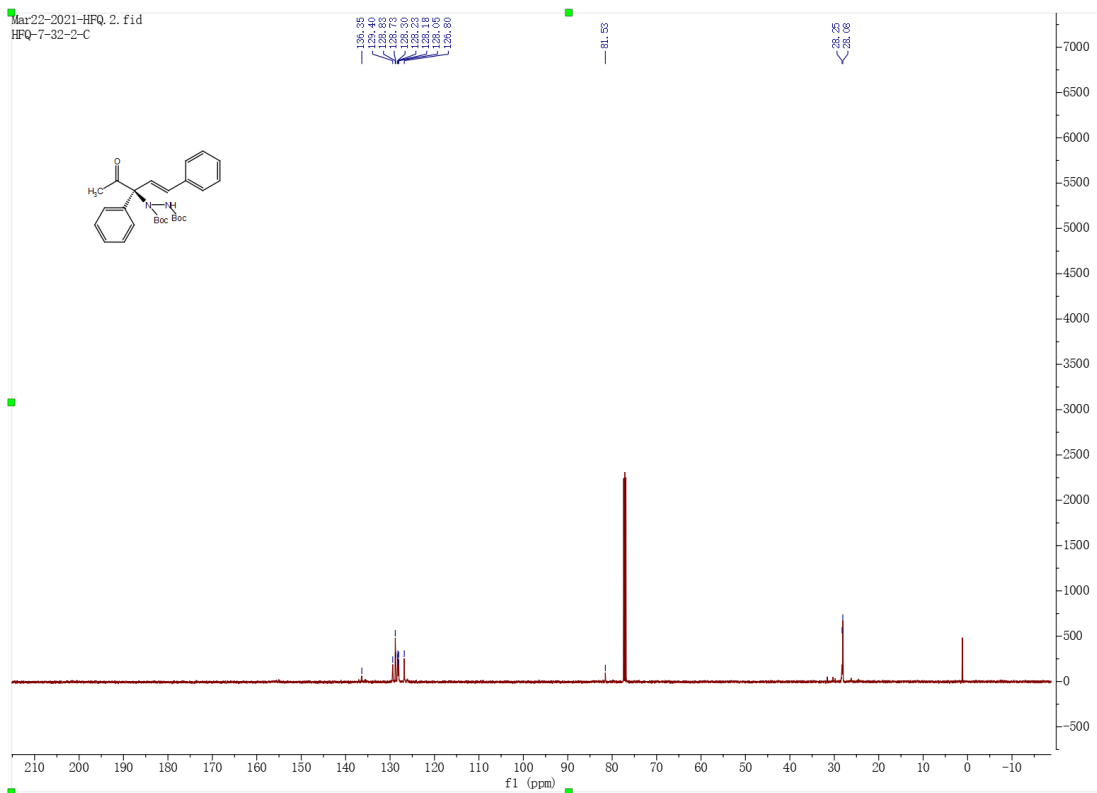
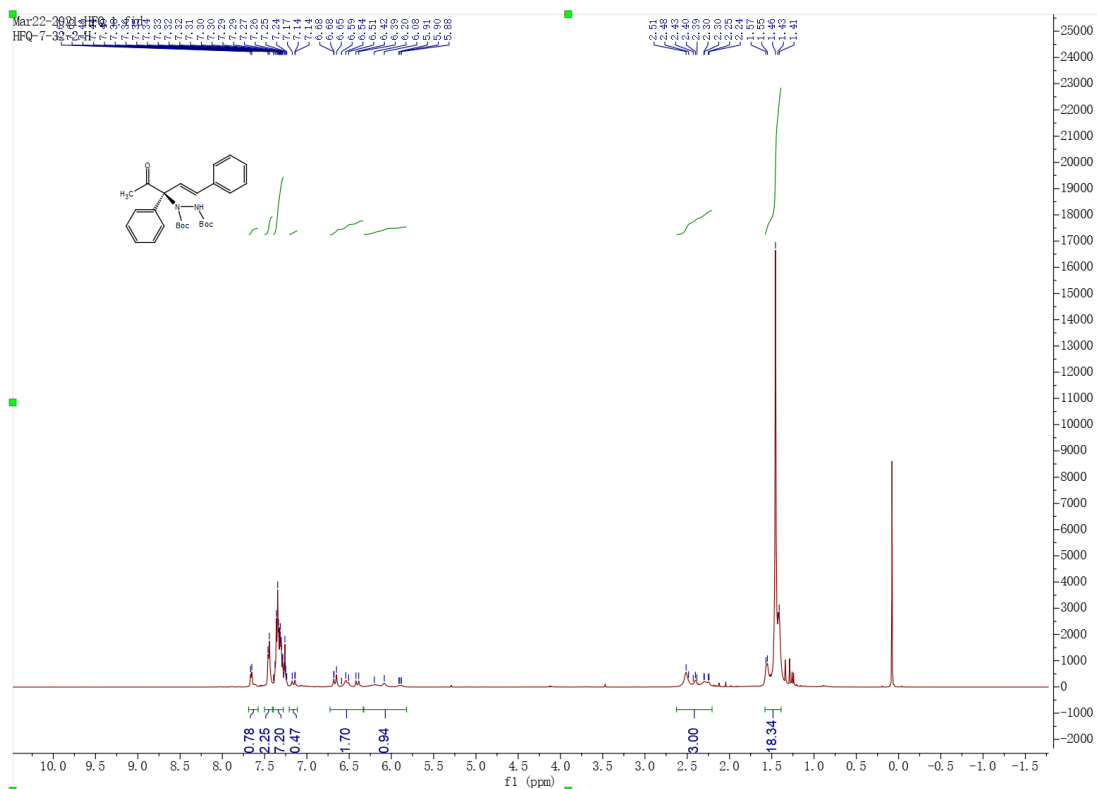
Di-tert-butyl-(*R*)-1-(3-methyl-2-oxonon-4-yn-3-yl)hydrazine-1,2-dicarboxylate (**3x**)



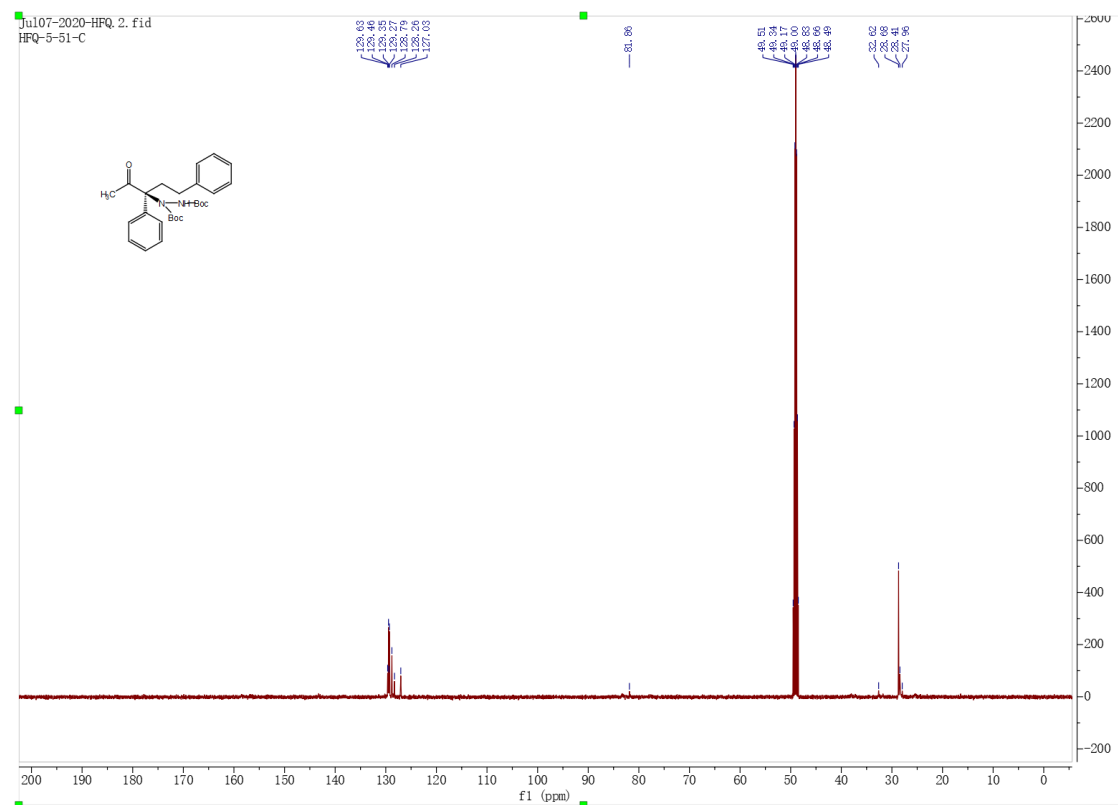
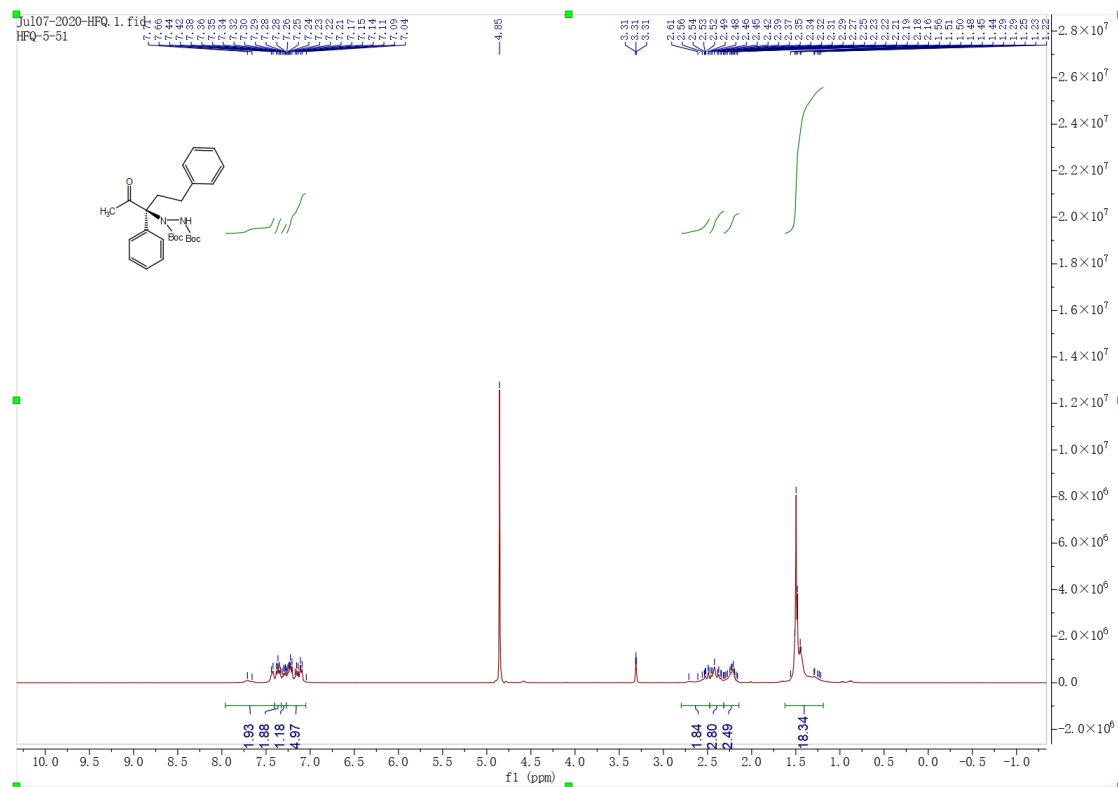
Di-tert-butyl-(*R*)-1-(1-cyclopropyl-3-methyl-4-oxopent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**3y**)



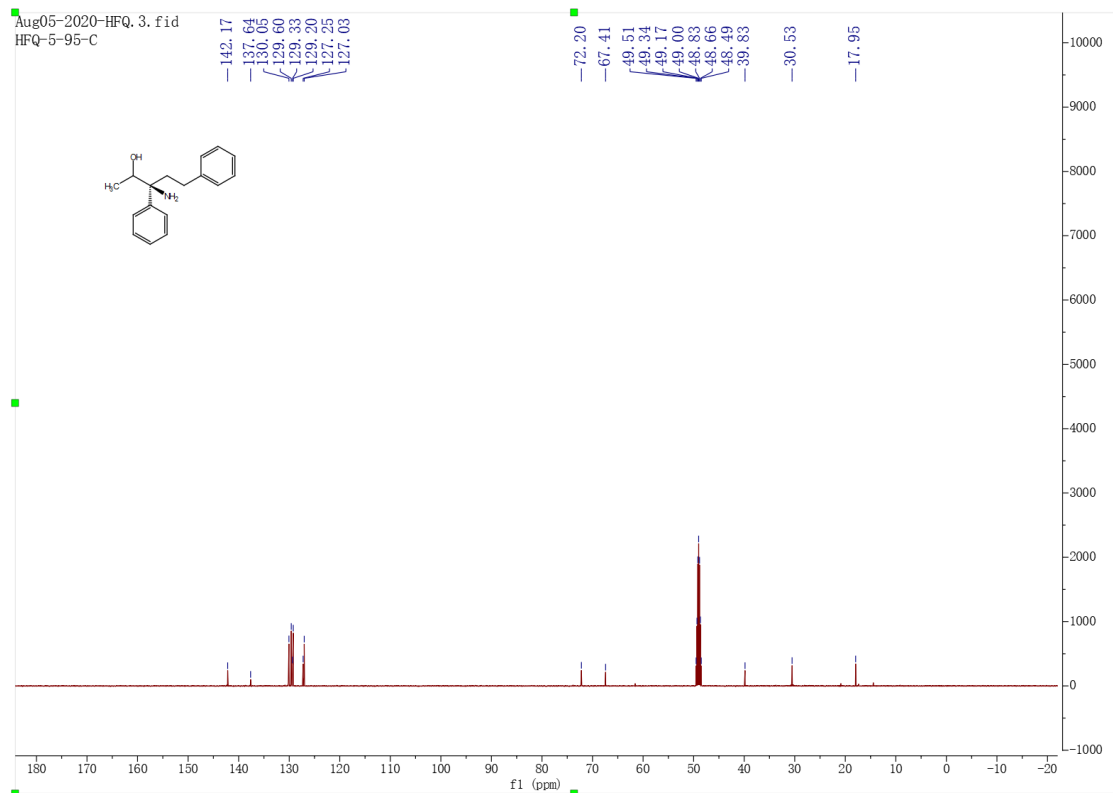
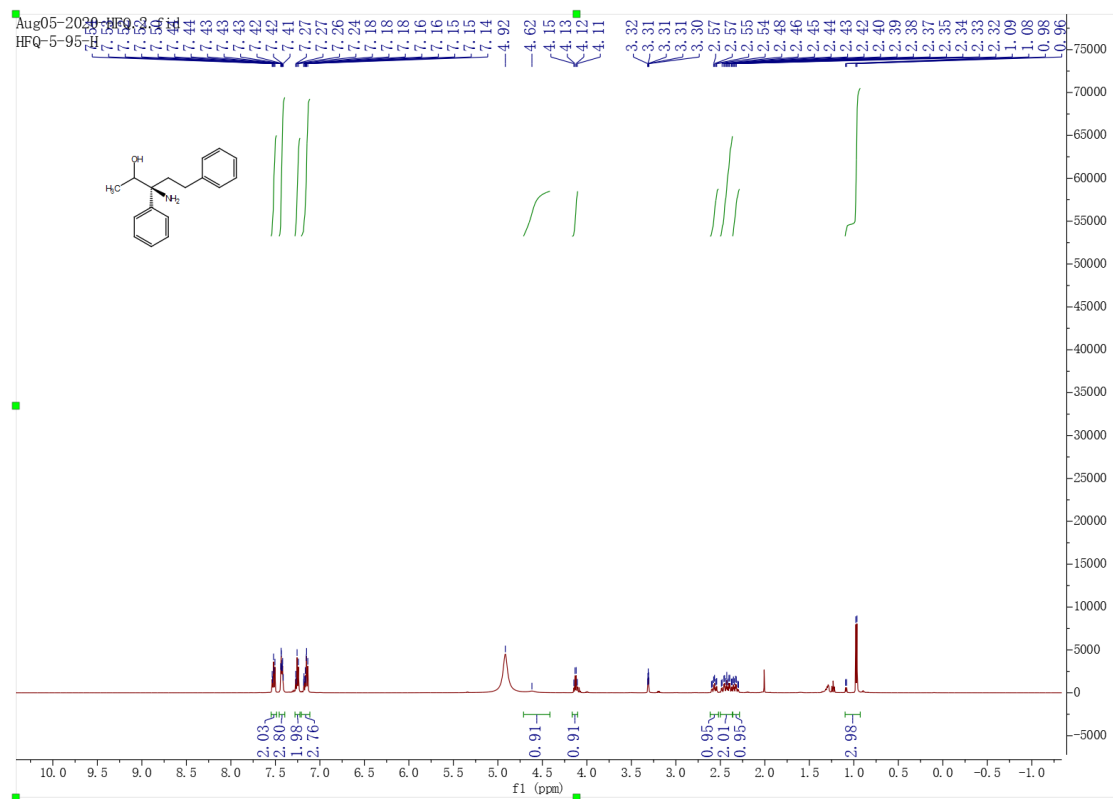
Di-tert-butyl (S,E)-1-(4-oxo-1,3-diphenylpent-1-en-3-yl)hydrazine-1,2-dicarboxylate (5a)



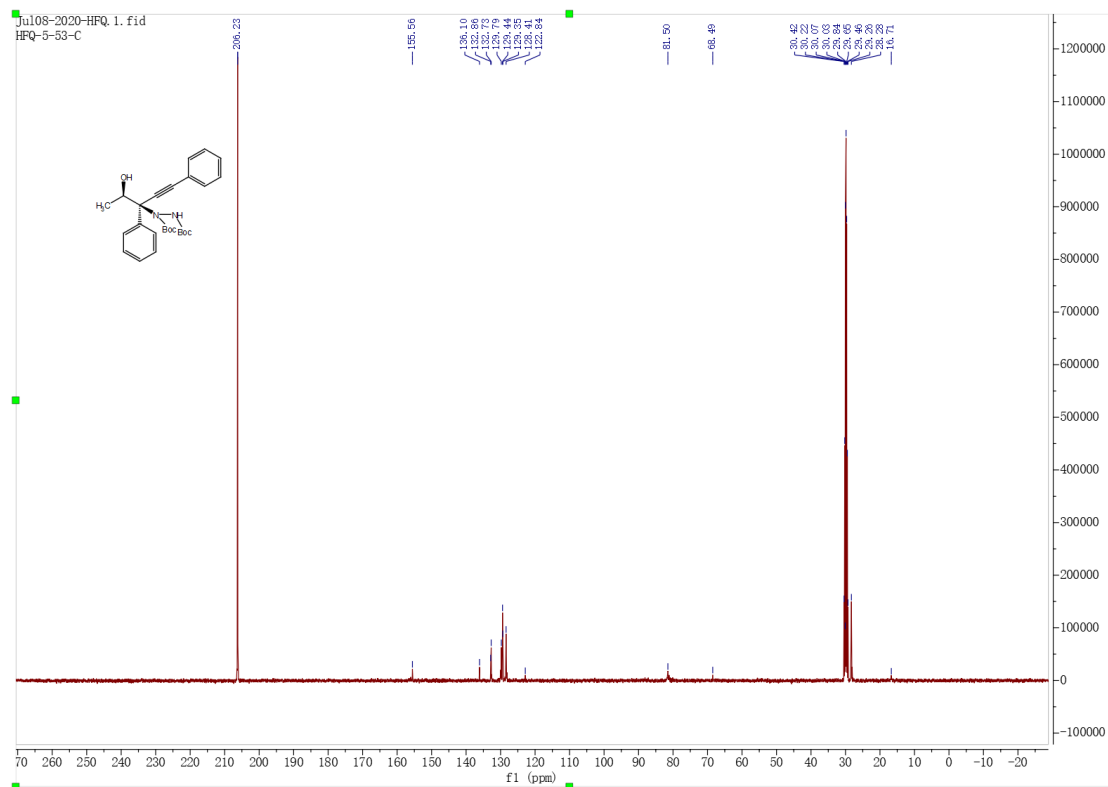
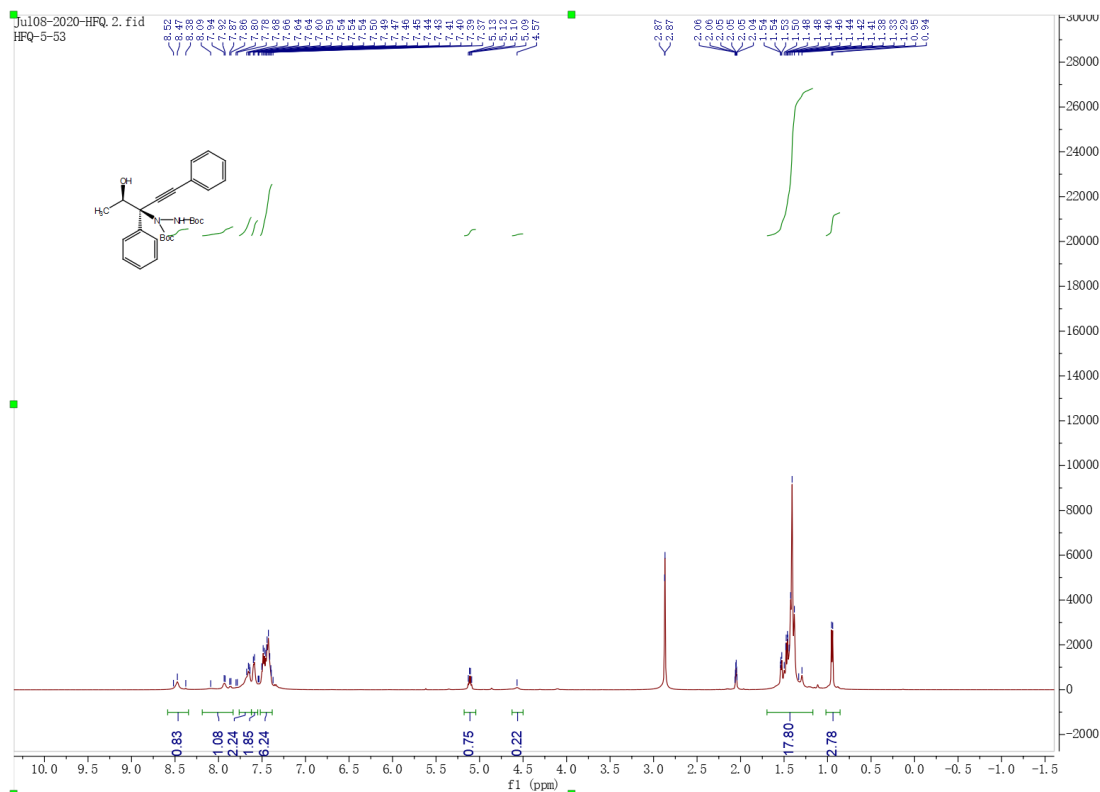
Di-tert-butyl-(S)-1-(4-oxo-1,3-diphenylpentan-3-yl)hydrazine-1,2-dicarboxylate (**7a**)



(3S)-3-amino-3,5-diphenylpentan-2-ol (**8a**)

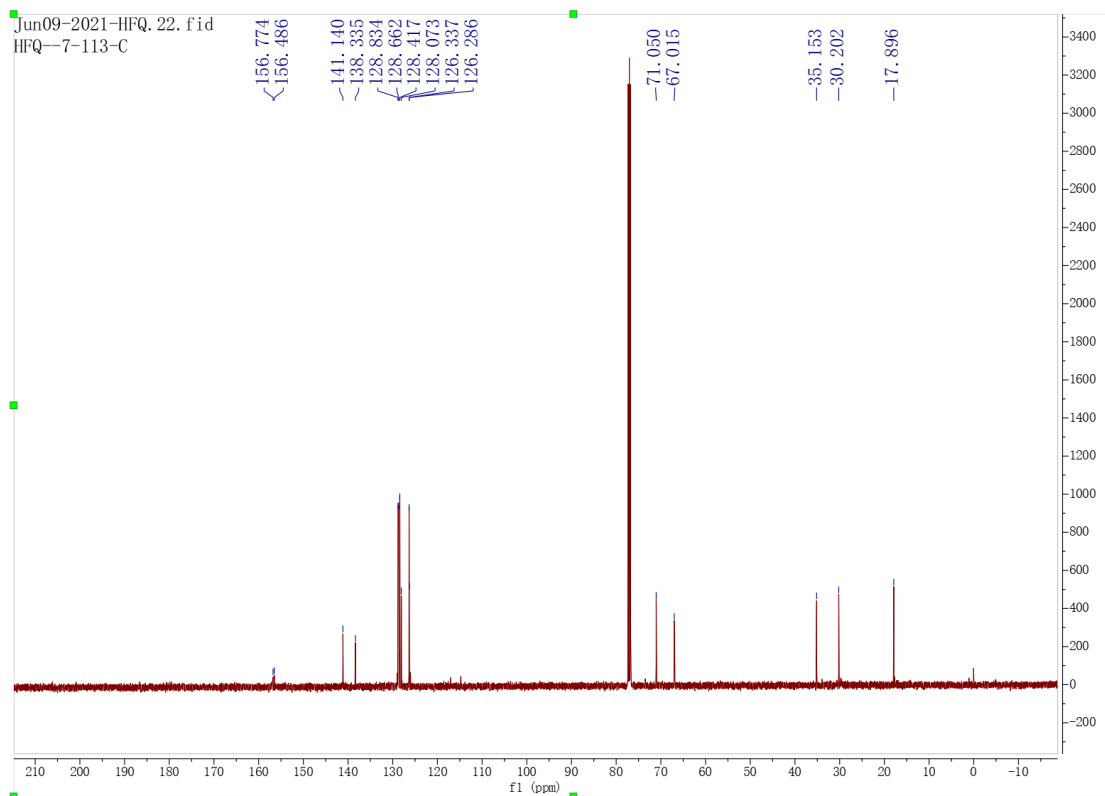
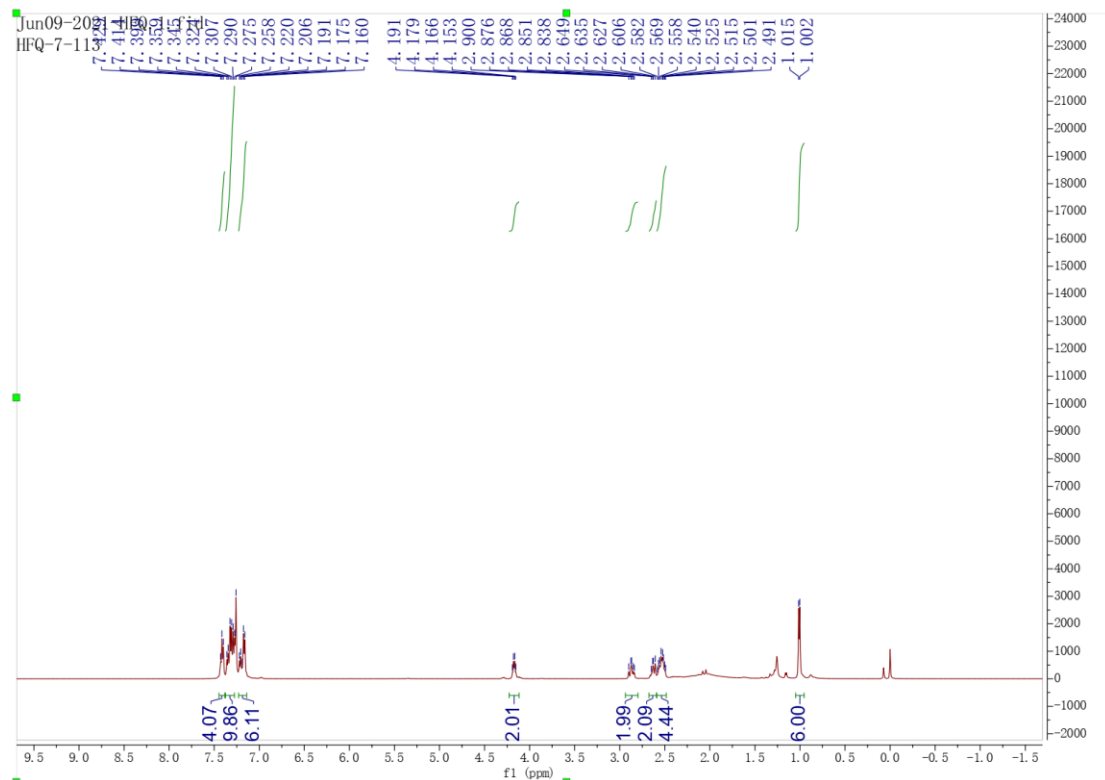


Di-tert-butyl-1-((3*R*,4*R*)-4-hydroxy-1,3-diphenylpent-1-yn-3-yl)hydrazine-1,2-dicarboxylate (**9a**)

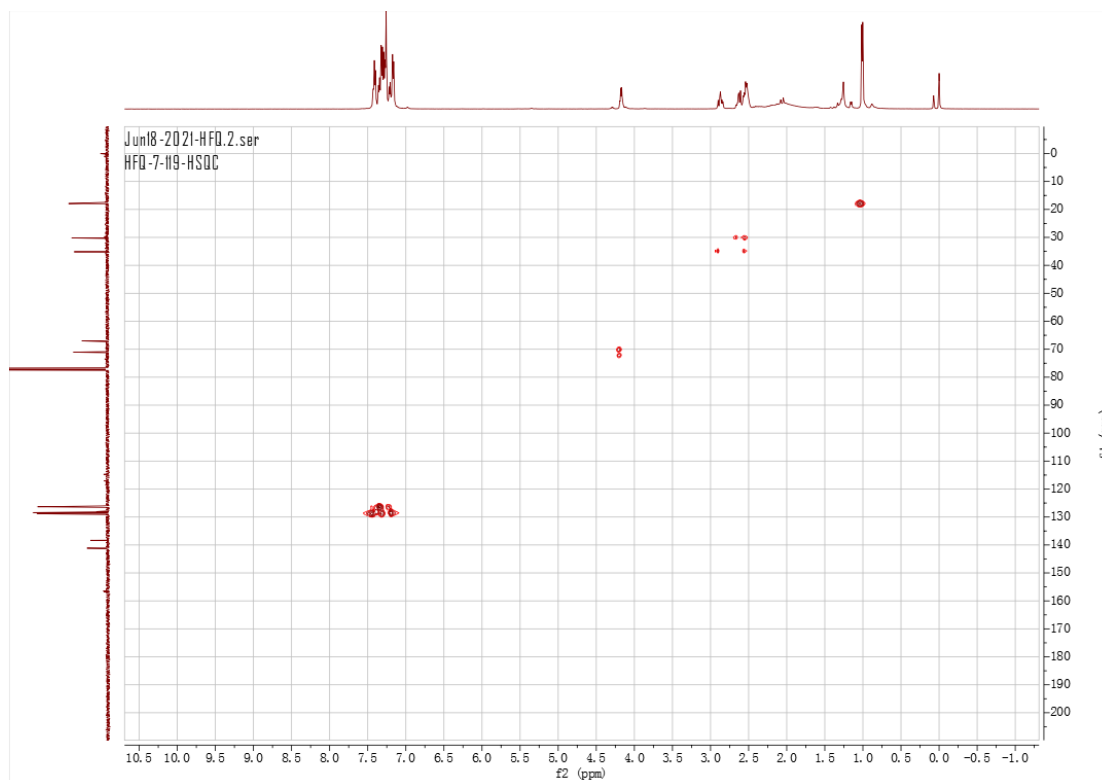


(4*S*,4'*S*,5*R*,5'*R*)-3,3'-carbonylbis(5-methyl-4-phenethyl-4-phenyloxazolidin-2-one)

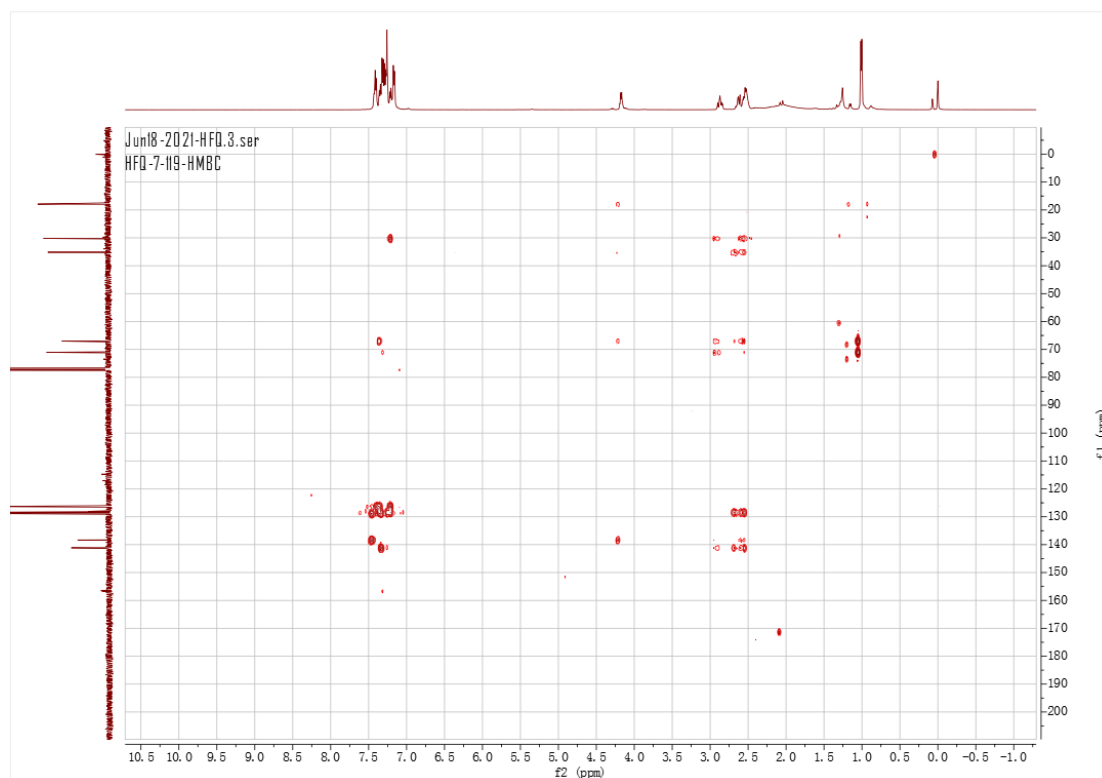
(8a')



HSQC



HMBC



NOE

