Supporting Information

A Combined Experimental and Computational Study of NHC-Catalyzed Allylation of Allenoate with MBH Esters: New Regiospecific and Seteroselective Access to 1,5-Enyne

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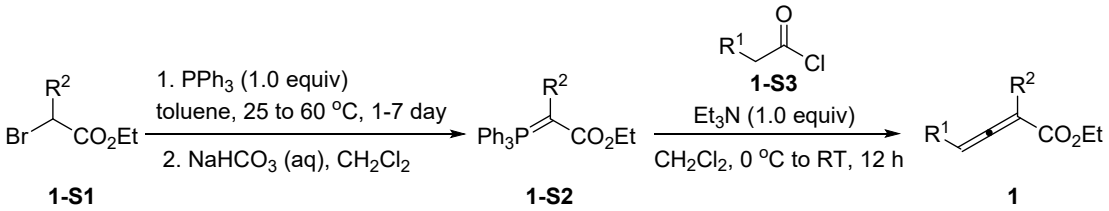
Table of Contents

1. General Information

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. ^{1}H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard. High resolution mass spectra (HRMS) were obtained on a micrOTOF-QII HRMS/MS instrument (Bruker) with the technique of electrospray ionization. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light.

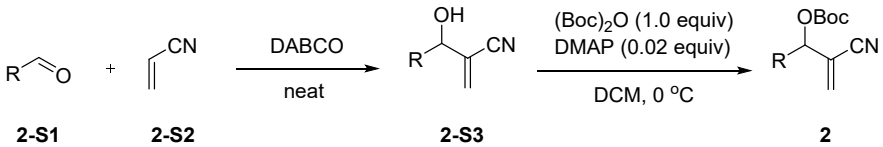
2. Synthesis of Allenoates (1a-1g)

Allenoates**1a-1g** were prepared according to the literature[1]



To a solution of PPh_3 (1.0 equiv.) in toluene (0.5 M) at corresponding temperature was added the relevant 2-bromoacetate **1-S1** (1.0 equiv.). The resulting suspension was stirred and filtered to leave the phosphonium salt. The salt was dissolved in CH_2Cl_2 and washed with saturated aqueous Na_2CO_3 solution (×3) and brine, dried (Na_2SO_4), filtered, and concentrated in vacuo to leave the ylide **1-S2**. To a solution of the ylide in CH_2Cl_2 (0.1 M) at 0 °C was added Et_3N (1.0 equiv.) and a solution of chloride **1-S3** (1.1 equiv.) in CH_2Cl_2 (10 mL) and the solution was stirred at room temperature overnight. The solution was concentrated in vacuo. The residue was suspended in 10% EtOAc/petroleum ether (250 mL) and silica gel was added. The mixture was stirred vigorously at room temperature for 40 min and then filtered. The filtrate was concentrated onto silica then purified by column chromatography to give the allenoates **1**.

3. Synthesis of MBH Carbonates (2a-2k)

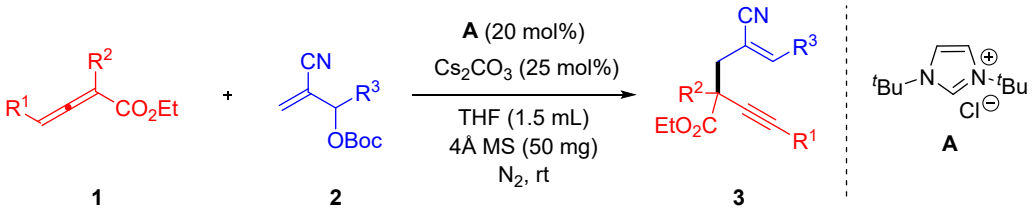


To a 100 mL round-bottom flask were added aldehyde (10 mmol) **2-S1** and activated vinyl cyanide **2-S2** (10 mmol), and the mixture was stirred for 12 h at room temperature. After completion of the reaction (by TLC), the reaction mixture was partitioned with diethyl ether (2×50 mL) and water (1×60 mL). The organic phase

was washed with brine (2×50 mL), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, mixtures of petroleum ether/ethyl acetate, 7:1, v/v) to afford product **2-S3**.

Then, alcohol **2-S2** were converted to the corresponding carbonate **2**: alcohol **2-S3** (1.0 equiv., 10 mmol) and $(Boc)_2O$ (1.0 equiv., 10 mmol) were dissolved in DCM (100 mL) and the solution was cooled to 0 °C. Afterward, DMAP (0.02 equiv., 0.2 mmol) was added and the reaction mixture stirred at the same temperature for 12 h After completion of the reaction (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2. The combined organic phase was washed with 4 N aq. HCl solution, saturated aq. $NaHCO_3$ and brine. The organic layer, dried over anhydrous Na_2SO_4, filtered and vacuum at rotary evaporator to obtain an oil or solid. The crude product was purified by chromatography (silica gel, mixtures of petroleum ether/ethyl acetate, 20:1, v/v) to afford **2.**

4. General Procedure for the Syntheses of Products



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with imidazolium salt **A** (4.3 mg, 0.02 mmol), MBH Carbonates **2** (0.10 mmol), Cs_2CO_3 (0.025 mmol) and 4Å MS (50 mg). Freshly distilled THF (1.5 mL), allenoates **1** (0.12 mmol) ware added into the mixture with a syringe. Then tube was closed with a septum, evacuated, and refilled with nitrogen. The mixture was stirred at 25 °C until completion (monitored by TLC). After removal of the solvent under reduced pressure, the resulted crude residue was purified by column chromatography (silica gel, mixtures of petroleum ether/ethyl acetate, 3:1-20:1, v/v) to afford the desired product **3**.

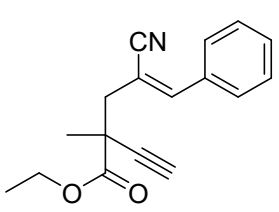
References

1. Chen, W.; Walker, J. C. L.; Oestreich, M., Metal-Free Transfer Hydroiodination of C–C Multiple Bonds. *J. Am. Chem. Soc.* **2019**, *141*, 1135-1140.

5. Characterization Data of Products

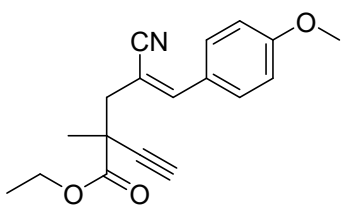
Ethyl (*Z*)-4-cyano-2-ethynyl-2-methyl-5-phenylpent-4-enoate (3aa)

Colourless oil (19.0 mg, 71% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m,



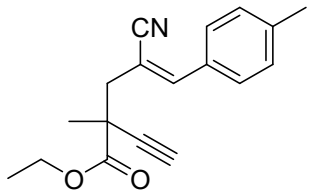
2H), 7.45 – 7.38 (m, 3H), 7.11 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.94 (d, J = 13.8 Hz, 1H), 2.76 (d, J = 13.7 Hz, 1H), 2.43 (s, 1H), 1.62 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.64, 148.46, 133.42, 130.47, 128.97, 128.87, 118.99, 105.65, 83.22, 73.65, 62.29, 44.67, 43.56, 25.41, 14.05. HRMS (ESI) calcd for $[C_{17}H_{17}NNaO_2$, M+Na$]^+$: 290.1151, found: 290.1160

Ethyl (*Z*)-4-cyano-2-ethynyl-5-(4-methoxyphenyl)-2-methylpent-4-enoate (3ab)



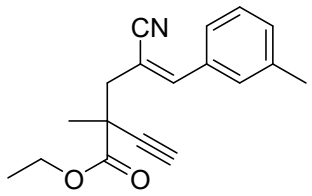
Colourless oil (10.7 mg, 36% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.01 (s, 1H), 6.95 – 6.91 (m, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 2.90 (d, J = 13.8 Hz, 1H), 2.74 (d, J = 13.8 Hz, 1H), 2.42 (s, 1H), 1.61 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.78, 161.36, 148.00, 130.88, 126.25, 119.60, 114.30, 102.41, 83.45, 73.52, 62.27, 55.48, 44.79, 43.68, 25.34, 14.10. HRMS (ESI) calcd for $[C_{18}H_{19}NNaO_3$, M+Na$]^+$: 320.1257, found: 320.1255

Ethyl (*Z*)-4-cyano-2,2-dimethyl-5-(p-tolyl)pent-4-enoate (3ac)



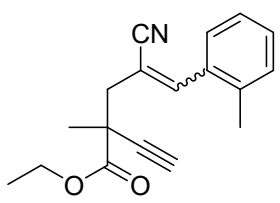
Colourless oil (20.8 mg, 74% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.06 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.92 (d, J = 13.7 Hz, 1H), 2.75 (d, J = 13.8 Hz, 1H), 2.42 (s, 1H), 2.38 (s, 3H), 1.61 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.68, 148.43, 140.98, 130.72, 129.57, 129.00, 119.24, 104.26, 83.31, 73.54, 62.25, 44.72, 43.59, 25.34, 21.53, 14.06. HRMS (ESI) calcd for [$C_{18}H_{19}NNaO_2$, M+Na$]^+$: 304.1308, found: 304.1305

Ethyl (*Z*)-4-cyano-2-ethynyl-2-methyl-5-(m-tolyl)pent-4-enoate (3ad)



Colourless oil (19.1 mg, 68% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.07 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.93 (d, J = 14.7 Hz, 1H), 2.75 (d, J = 13.8 Hz, 1H), 2.43 (s, 1H), 2.38 (s, 3H), 1.61 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.72, 148.68, 138.63, 133.45, 131.34, 129.67, 128.83, 126.13, 119.10, 105.34, 83.31, 73.66, 62.32, 44.75, 43.61, 25.41, 21.41, 14.09. HRMS (ESI) calcd for $[C_{18}H_{19}NNaO_2$, M+Na$]^+$: 304.1308, found: 304.1293

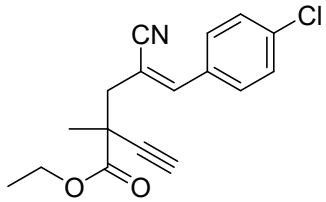
Ethyl 4-cyano-2-ethynyl-2-methyl-5-(o-tolyl)pent-4-enoate (3ae)



Colourless oil (20.0 mg, 71% yield), NMR data for (*Z*)-**3ae**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz, 1H), 7.36 – 7.19 (m, 4H), 4.26 (q, J = 7.1 Hz, 2H), 2.97 (d, J = 13.8 Hz, 1H), 2.77 (d, J = 13.8 Hz, 1H), 2.44 (s, 1H), 2.33 (s, 3H), 1.63

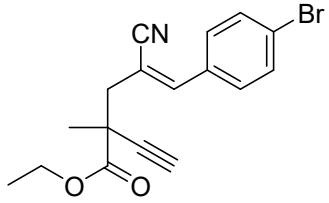
(s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.66 (d, J = 1.9 Hz), 147.64, 136.85, 132.99, 130.36, 130.08, 128.08, 126.33, 118.72, 107.98, 83.34, 73.60, 62.30, 44.25, 43.56, 25.50, 19.89, 14.03. Selected NMR data for (*E*)-**3ae**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, J = 7.1 Hz, 2H), 2.98 (d, J = 14.3 Hz, 1H), 2.81 (d, J = 14.6 Hz, 1H), 2.27 (s, 3H), 1.29 (t, J = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.67, 148.24, 132.85, 130.47, 129.40, 128.53, 125.94, 119.65, 111.76, 83.16, 73.23, 59.74, 42.23, 37.42, 25.86, 19.97, 13.91. HRMS (ESI) calcd for [$C_{18}H_{19}NNaO_2$, M+Na]$^+$: 304.1308, found: 304.1294

Ethyl-(*Z*)-5-(4-chlorophenyl)-4-cyano-2-ethynyl-2-methylpent-4-enoate (3af)



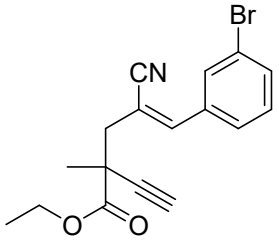
Colourless oil (24.7 mg, 82% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.44 – 7.41 (m, 2H), 7.10 (s, 1H), 4.29 (q, J = 7.1 Hz, 2H), 2.98 (d, J = 13.8 Hz, 1H), 2.78 (d, J = 13.8 Hz, 1H), 2.45 (s, 1H), 1.66 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.54, 147.64, 136.85, 132.99, 130.36, 130.08, 128.08, 126.33, 118.72, 107.98, 83.34, 73.60, 62.30, 44.25, 43.56, 25.50, 19.89, 14.03. HRMS (ESI) calcd for [$C_{17}H_{16}ClNNaO_2$, M+Na]$^+$: 324.0762, found: 324.0743

Ethyl-(*Z*)-5-(4-bromophenyl)-4-cyano-2-ethynyl-2-methylpent-4-enoate (3ag)



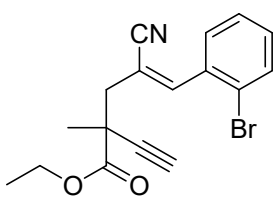
Colourless oil (26.3 mg, 76% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.56 – 7.53 (m, 2H), 7.04 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.94 (d, J = 13.6 Hz, 1H), 2.74 (d, J = 14.8 Hz, 1H), 2.44 (s, 1H), 1.62 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.56, 147.04, 132.25, 132.13, 130.38, 124.78, 118.68, 106.56, 83.08, 73.77, 62.33, 44.59, 43.50, 25.53, 14.05. HRMS (ESI) calcd for [$C_{17}H_{16}BrNNaO_2$, M+Na]$^+$: 368.0257, found: 368.0240

Ethyl-(*Z*)-5-(3-bromophenyl)-4-cyano-2-ethynyl-2-methylpent-4-enoate (3ah)



Colourless oil (27.0 mg, 78% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 2H), 7.53 (d, J = 8.8 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.04 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.95 (d, J = 13.7 Hz, 1H), 2.75 (d, J = 13.8 Hz, 1H), 2.45 (s, 1H), 1.62 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.51, 146.60, 135.36, 133.29, 131.98, 130.41, 127.09, 122.87, 118.41, 107.58, 83.02, 73.86, 62.35, 44.51, 43.51, 25.55, 14.05. HRMS (ESI) calcd for [$C_{17}H_{16}BrNNaO_2$, M+Na]$^+$: 368.0257, found:368.0242

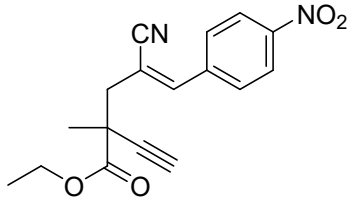
Ethyl-(*Z*)-5-(2-bromophenyl)-4-cyano-2-ethynyl-2-methylpent-4-enoate (3ai)



Colourless oil (20.4 mg, 59% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.7, 1.7 Hz, 1H), 7.62 (dd, J = 8.1, 1.2 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.26 (td, J = 7.5, 1.7 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.00 (d, J = 13.8 Hz, 1H), 2.80 (d, J

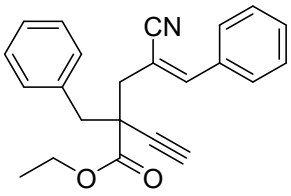
= 13.8 Hz, 1H), 2.46 (s, 1H), 1.64 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.54, 147.48, 133.78, 133.01, 131.42, 129.76, 127.80, 124.27, 118.18, 109.37, 83.01, 73.90, 62.38, 44.20, 43.35, 25.49, 14.04. HRMS (ESI) calcd for $[C_{17}H_{16}BrNNaO_2, M+Na]^+$: 368.0257, found: 368.0257

Ethyl-(*Z*)-4-cyano-2-ethynyl-2-methyl-5-(4-nitrophenyl)pent-4-enoate (3aj)



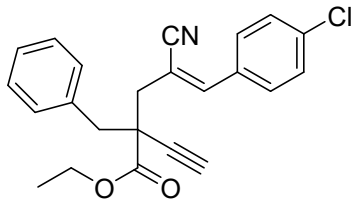
Colourless oil (22.5 mg, 72% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 2H), 7.91 – 7.86 (m, 2H), 7.20 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.02 (d, *J* = 13.8 Hz, 1H), 2.78 (d, *J* = 13.8 Hz, 1H), 2.47 (s, 1H), 1.64 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.39, 148.35, 145.57, 139.27, 129.70, 124.10, 118.00, 110.64, 82.80, 74.09, 62.46, 44.48, 43.48, 25.78, 14.04. HRMS (ESI) calcd for $[C_{17}H_{16}N_2NaO_4, M+Na]^+$: 335.1002, found: 335.0980

Ethyl-(*Z*)-2-benzyl-4-cyano-2-ethynyl-5-phenylpent-4-enoate (3ba)



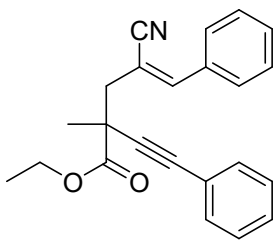
Colourless oil (22.7 mg, 66% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.40 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.29 (s, 5H), 7.09 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.25 (d, *J* = 13.1 Hz, 1H), 3.08 (d, *J* = 15.0 Hz, 2H), 2.71 (d, *J* = 13.7 Hz, 1H), 2.53 (s, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.82, 148.44, 135.30, 133.46, 130.44, 130.42, 128.99, 128.86, 128.16, 127.43, 118.88, 105.71, 81.44, 62.29, 50.25, 45.24, 44.06, 13.99. HRMS (ESI) calcd for $[C_{23}H_{21}NNaO_2, M+Na]^+$: 366.1465, found: 366.1445

Ethyl-(*Z*)-2-benzyl-5-(4-chlorophenyl)-4-cyano-2-ethynylpent-4-enoate (3bf)



Colourless oil (31.7 mg, 84% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 2H), 7.40 – 7.35 (m, 2H), 7.31 – 7.25 (m, 5H), 7.04 (s, 1H), 4.15 (qd, *J* = 7.1, 1.7 Hz, 2H), 3.24 (d, *J* = 13.1 Hz, 1H), 3.07 (dd, *J* = 13.3, 2.0 Hz, 2H), 2.69 (d, *J* = 12.9 Hz, 1H), 2.54 (s, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.75, 146.95, 136.36, 135.18, 131.86, 130.40, 130.22, 129.14, 128.18, 127.47, 118.60, 106.44, 81.36, 62.33, 50.17, 45.30, 43.91, 13.99. HRMS (ESI) calcd for $[C_{23}H_{20}ClNNaO_2, M+Na]^+$: 400.1075, found: 400.1084

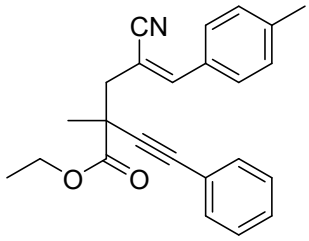
Ethyl-(*Z*)-4-cyano-2-methyl-5-phenyl-2-(phenylethynyl)pent-4-enoate (3ca)



Colourless oil (31.3 mg, 91% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.0, 2.8 Hz, 2H), 7.46 – 7.37 (m, 5H), 7.31 – 7.24 (m, 3H), 7.13 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.03 (d, *J* = 13.6 Hz, 1H), 2.82 (d, *J* = 13.7 Hz, 1H), 1.68 (s, 3H), 1.31 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.16, 148.36, 133.57, 131.83, 130.47, 129.02, 128.93,

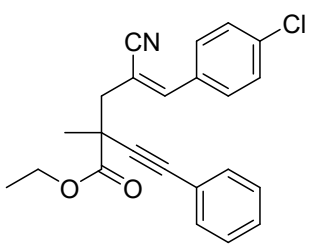
128.39, 128.31, 122.86, 119.22, 106.16, 88.62, 85.40, 62.20, 45.08, 44.24, 25.58, 14.17. HRMS (ESI) calcd for $[C_{23}H_{21}NNaO_2, M+Na]^+$: 366.1465, found: 366.1444

Ethyl-(*Z*)-4-cyano-2-methyl-2-(phenylethynyl)-5-(p-tolyl)pent-4-enoate (3cc)



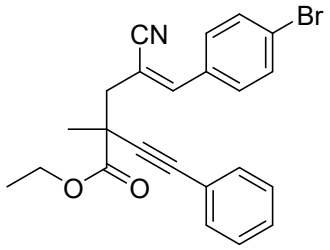
Colourless oil (31.5 mg, 88% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.31 – 7.25 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.08 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.01 (d, J = 13.7 Hz, 1H), 2.81 (d, J = 13.7 Hz, 1H), 2.37 (s, 3H), 1.67 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.21, 148.34, 140.96, 131.83, 130.86, 129.62, 129.05, 128.35, 128.29, 122.90, 119.46, 104.76, 88.71, 85.30, 62.17, 45.12, 44.27, 25.50, 21.58, 14.17. HRMS (ESI) calcd for $[C_{24}H_{23}NNaO_2, M+Na]^+$: 380.1621, found: 380.1603

Ethyl(*Z*)-5-(4-chlorophenyl)-4-cyano-2-methyl-2-(phenylethynyl)pent-4-enoate(3cf)



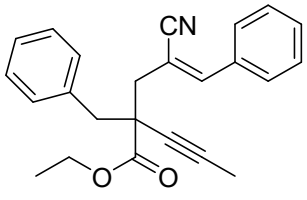
Colourless oil (34.8 mg, 92% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.45 – 7.41 (m, 2H), 7.40 – 7.35 (m, 2H), 7.31 – 7.26 (m, 3H), 7.08 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.03 (d, J = 13.7 Hz, 1H), 2.80 (d, J = 13.7 Hz, 1H), 1.68 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.09, 146.88, 136.39, 131.97, 131.79, 130.25, 129.21, 128.46, 128.34, 122.76, 118.94, 106.90, 88.46, 85.53, 62.24, 45.00, 44.22, 25.68, 14.16. HRMS (ESI) calcd for $[C_{23}H_{20}ClNNaO_2, M+Na]^+$: 400.1075, found: 400.1071

Ethyl(*Z*)-5-(4-bromophenyl)-4-cyano-2-methyl-2-(phenylethynyl)pent-4-enoate (3cg)



Colourless oil (38.0 mg, 90% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.56 – 7.51 (m, 2H), 7.45 – 7.40 (m, 2H), 7.32 – 7.27 (m, 3H), 7.07 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.03 (dd, J = 13.7, 1.0 Hz, 1H), 2.80 (dd, J = 13.7, 0.9 Hz, 1H), 1.68 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.02, 146.90, 132.34, 132.13, 131.73, 130.36, 128.41, 128.29, 124.72, 122.70, 118.87, 107.01, 88.39, 85.49, 62.20, 44.97, 44.14, 25.65, 14.12. HRMS (ESI) calcd for $[C_{23}H_{20}BrNNaO_2, M+Na]^+$: 444.0570, found: 445.0574

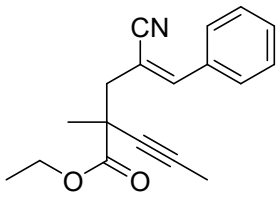
Ethyl-(*Z*)-2-benzyl-4-cyano-5-phenyl-2-(prop-1-yn-1-yl)pent-4-enoate (3da)



Colourless oil (29.7 mg, 83% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 7.6, 2.1 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.31 – 7.24 (m, 5H), 7.05 (s, 1H), 4.12 (q, J = 6.9 Hz, 2H), 3.18 (d, J = 13.1 Hz, 1H), 3.03 (dd, J = 13.3, 8.5 Hz, 2H), 2.67 (d, J = 13.5 Hz, 1H), 1.88 (s, 3H), 1.17 (t, J = 7.1 Hz,

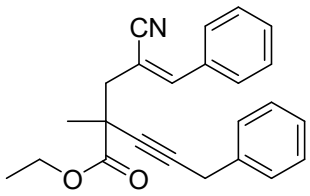
3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.72, 148.02, 135.88, 133.66, 130.39, 130.28, 128.92, 128.83, 128.05, 127.19, 119.04, 106.55, 84.66, 61.95, 50.26, 45.58, 44.48, 14.08, 3.86. HRMS (ESI) calcd for $[C_{24}H_{23}NNaO_2, M+Na]^+$: 380.1621, found: 380.1605

Ethyl (Z)-4-cyano-2-methyl-5-phenyl-2-(prop-1-yn-1-yl) pent-4-enoate (3ea)



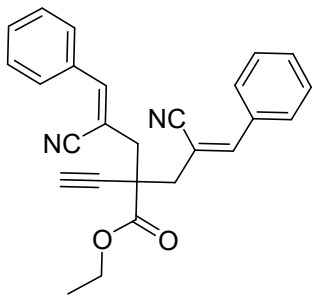
Colourless oil (13.7 mg, 49% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 6.6 Hz, 3H), 7.06 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.92 (d, J = 13.6 Hz, 1H), 2.70 (d, J = 13.6 Hz, 1H), 1.85 (s, 3H), 1.55 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.52, 148.01, 133.55, 130.26, 128.79, 119.07, 106.35, 81.56, 78.42, 61.91, 45.11, 43.53, 25.57, 14.05, 3.68. HRMS (ESI) calcd for $[C_{18}H_{20}NO_2, M+H]^+$: 282.1489, found: 282.1490

Ethyl (Z)-4-cyano-2-methyl-5-phenyl-2-(3-phenylprop-1-yn-1-yl) pent-4-enoate (3fa)



Colourless oil (16.8 mg, 47% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 2H), 7.44 – 7.36 (m, 4H), 7.32 (d, J = 7.4 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.04 (s, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.65 (s, 2H), 2.95 (d, J = 13.7 Hz, 1H), 2.74 (d, J = 13.7 Hz, 1H), 1.61 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.40, 148.15, 136.60, 133.44, 130.24, 128.87, 128.74, 128.37, 127.85, 126.47, 119.06, 106.08, 83.36, 81.60, 61.99, 45.08, 43.71, 25.63, 25.08, 14.04. HRMS (ESI) calcd for $[C_{24}H_{24}NO_2, M+H]^+$: 358.1802, found: 358.1800

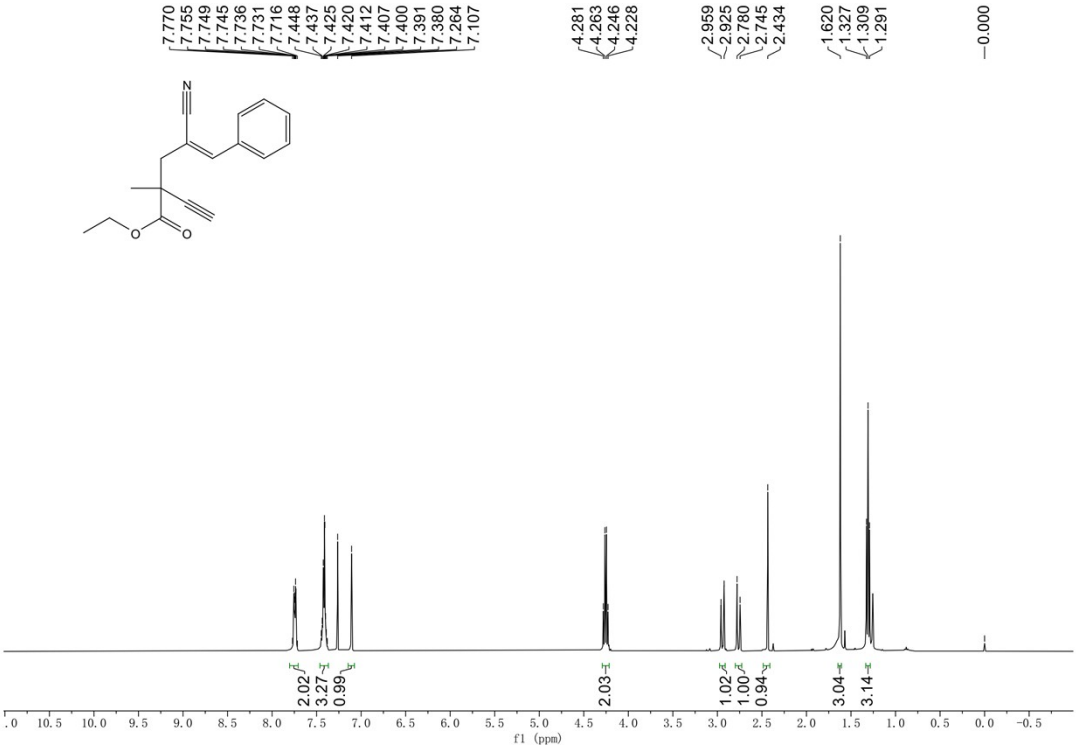
Ethyl (Z)-4-cyano-2-((Z)-2-cyano-3-phenylallyl)-2-ethynyl-5-phenylpent-4-enoate (3ga)

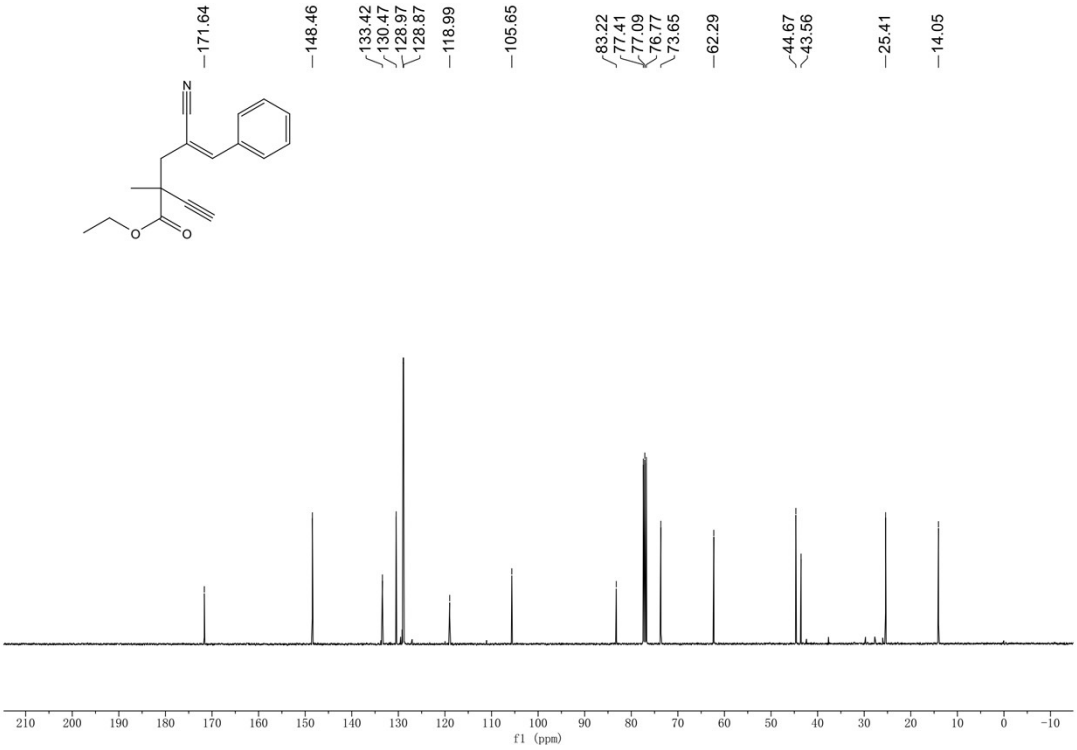


White solid (20.9 mg, 53% yield), mp: 179.6-181.4 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 3H), 7.47 – 7.37 (m, 7H), 7.15 (s, 2H), 4.29 (q, J = 7.1 Hz, 2H), 3.09 (d, J = 13.7 Hz, 2H), 2.85 (d, J = 13.7 Hz, 2H), 2.62 (s, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.79, 148.99, 133.16, 130.64, 129.00, 128.87, 118.65, 104.68, 79.86, 77.76, 62.88, 49.23, 43.98, 13.95. HRMS (ESI) calcd for $[C_{26}H_{22}N_2NaO_2, M+Na]^+$: 471.1573, found: 471.1576

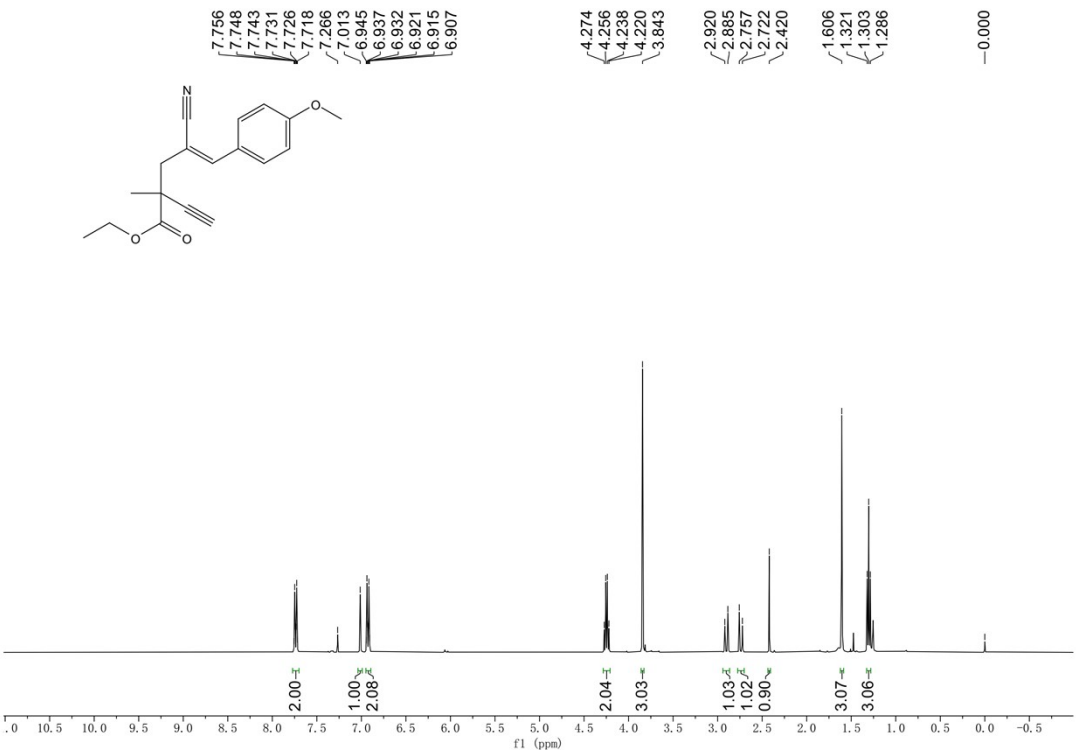
6. Copies of ^{1}H NMR and ^{13}C NMR Spectra of Products

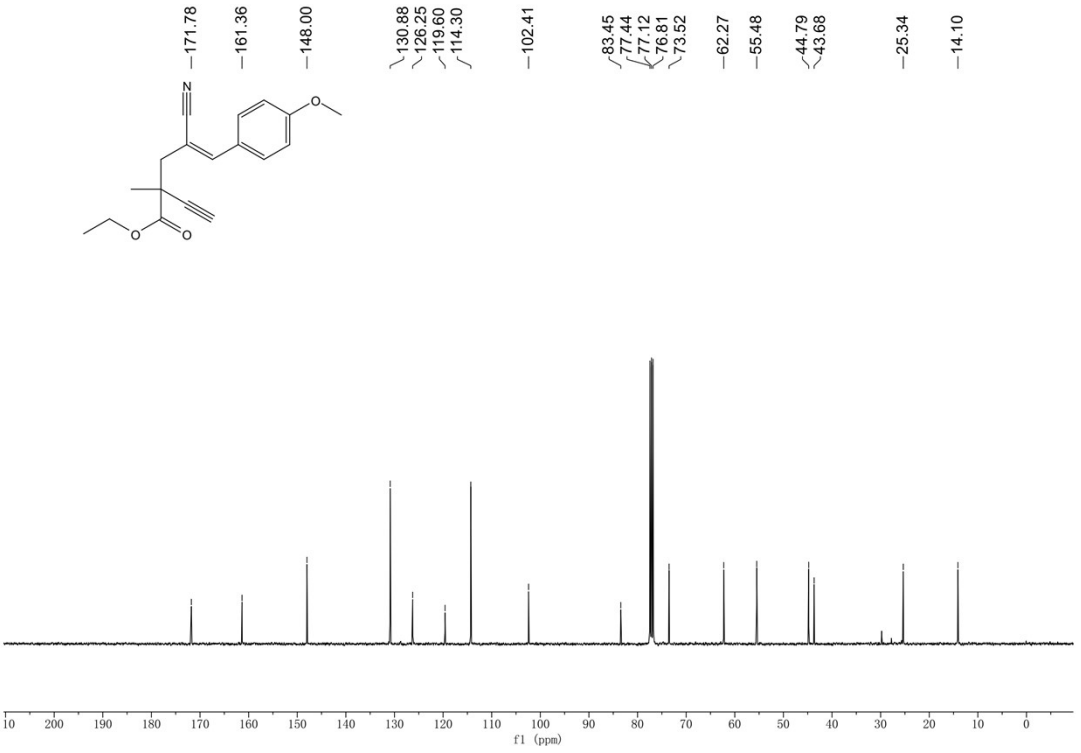
3aa



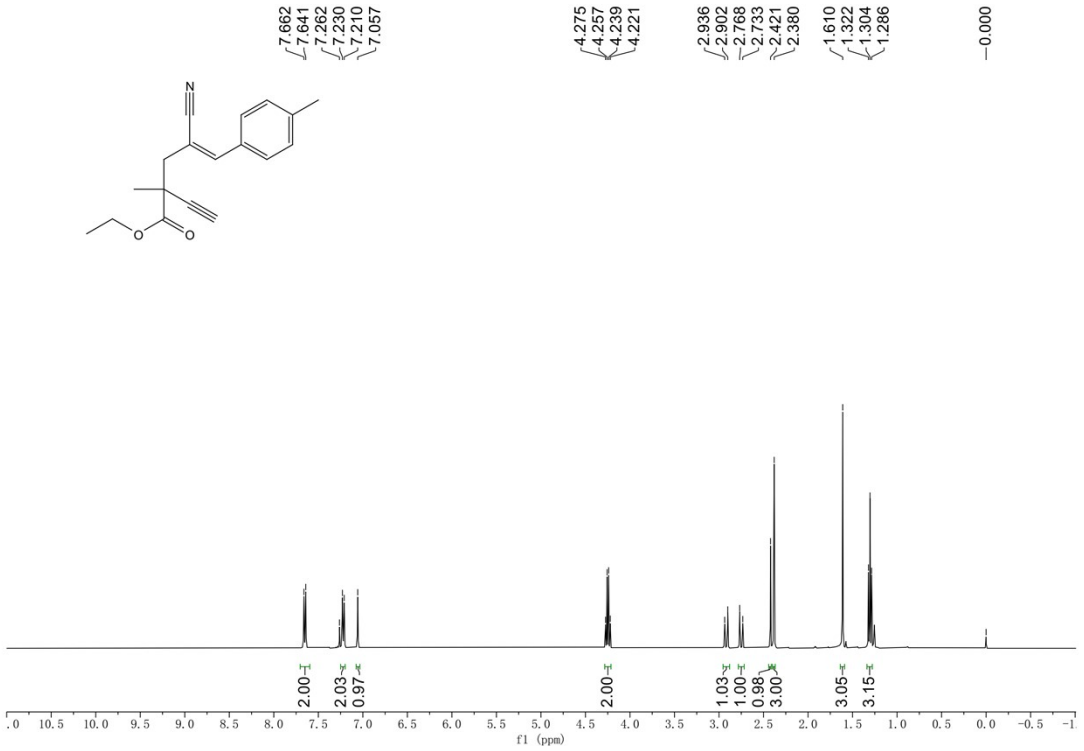


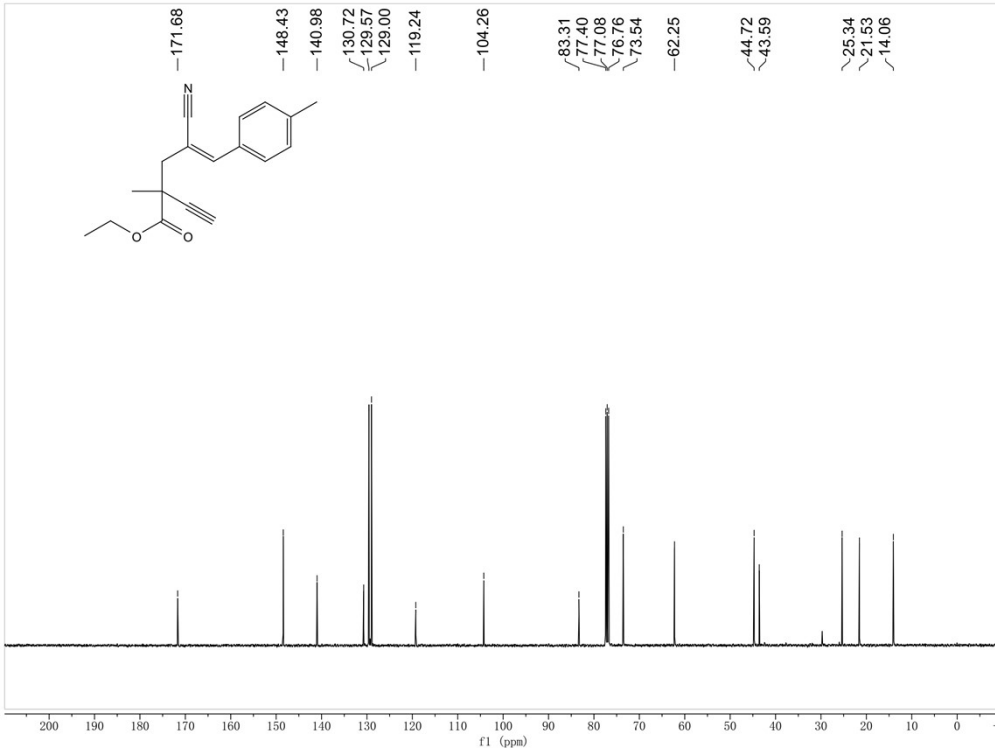
3ab


7.756
7.748
7.743
7.731
7.726
7.718
7.266
7.013
6.945
6.937
6.932
6.921
6.915
6.907
4.274
4.256
4.238
4.220
3.843
2.920
2.885
2.757
2.722
2.420
1.606
1.321
1.303
1.286
0.000
2.00
1.00
2.08
2.04
3.03
1.03
1.02
0.90
3.07
3.06
f1 (ppm)

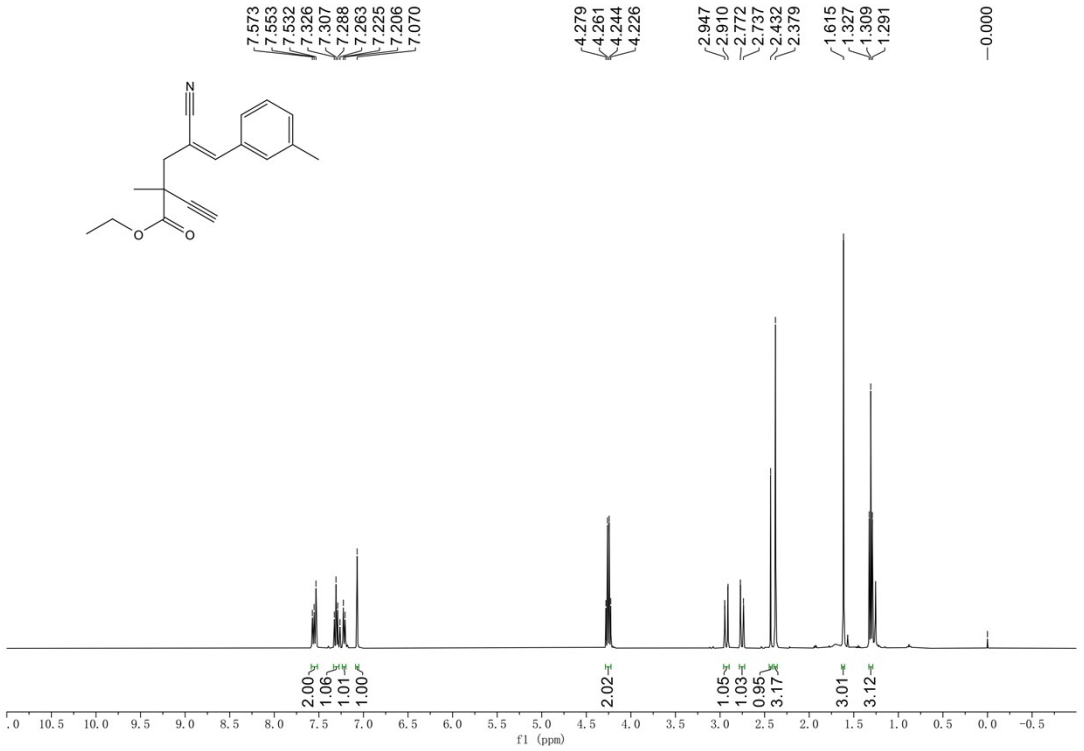

171.78
161.36
148.00
130.88
126.25
119.60
114.30
102.41
83.45
77.44
77.12
76.81
73.52
62.27
55.48
44.79
43.68
25.34
14.10
f1 (ppm)

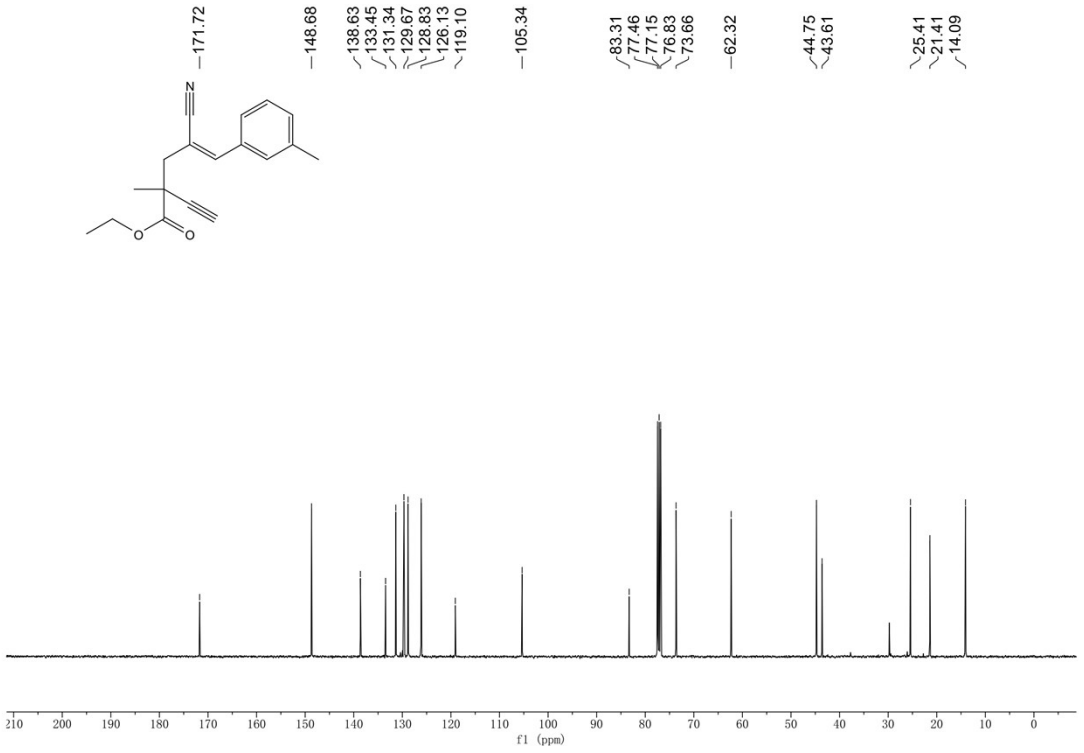
3ac


7.662
7.641
7.262
7.230
7.210
7.057
4.275
4.257
4.239
4.221
2.936
2.902
2.768
2.733
2.421
2.380
1.610
1.322
1.304
1.286
0.000
2.00
2.03
0.97
2.00
1.03
1.00
0.98
3.00
3.05
3.15
f1 (ppm)

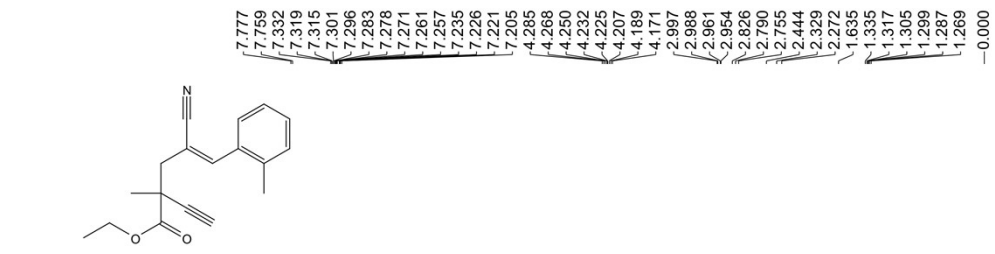

171.68
148.43
140.98
130.72
129.57
129.00
119.24
104.26
83.31
77.40
77.08
76.76
73.54
62.25
44.72
43.59
25.34
21.53
14.06
f1 (ppm)

3ad

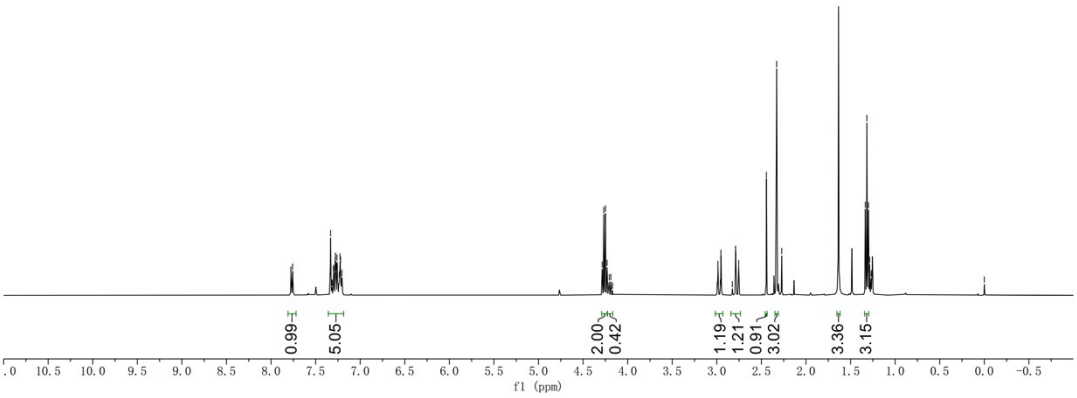

7.573
7.553
7.532
7.326
7.307
7.288
7.263
7.225
7.206
7.070
4.279
4.261
4.244
4.226
2.947
2.910
2.772
2.737
2.432
2.379
1.615
1.327
1.309
1.291
0.000
2.00
1.06
1.01
1.00
2.02
1.05
1.03
0.95
3.17
3.01
3.12
f1 (ppm)

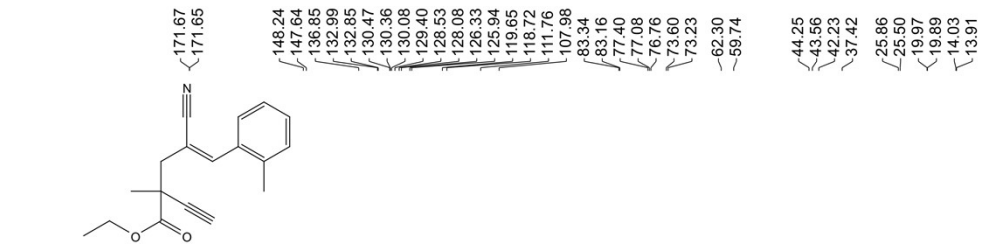

171.72
148.68
138.63
133.45
131.34
129.67
128.83
126.13
119.10
105.34
83.31
77.46
77.15
76.83
73.66
62.32
44.75
43.61
25.41
21.41
14.09
f1 (ppm)

3ae

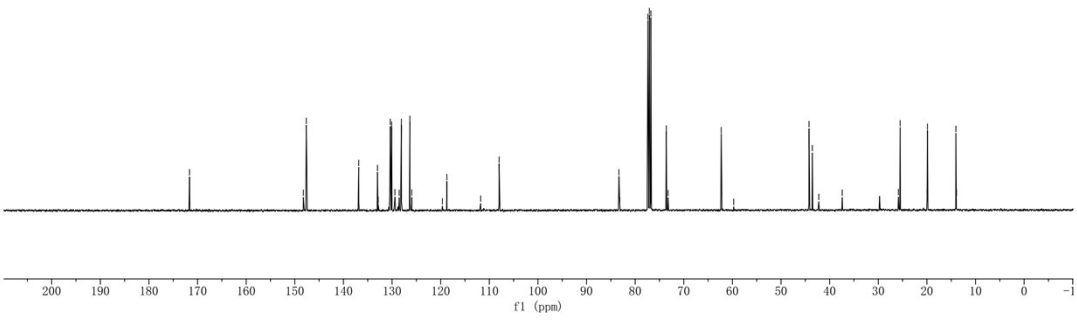


Z/E = 5:1

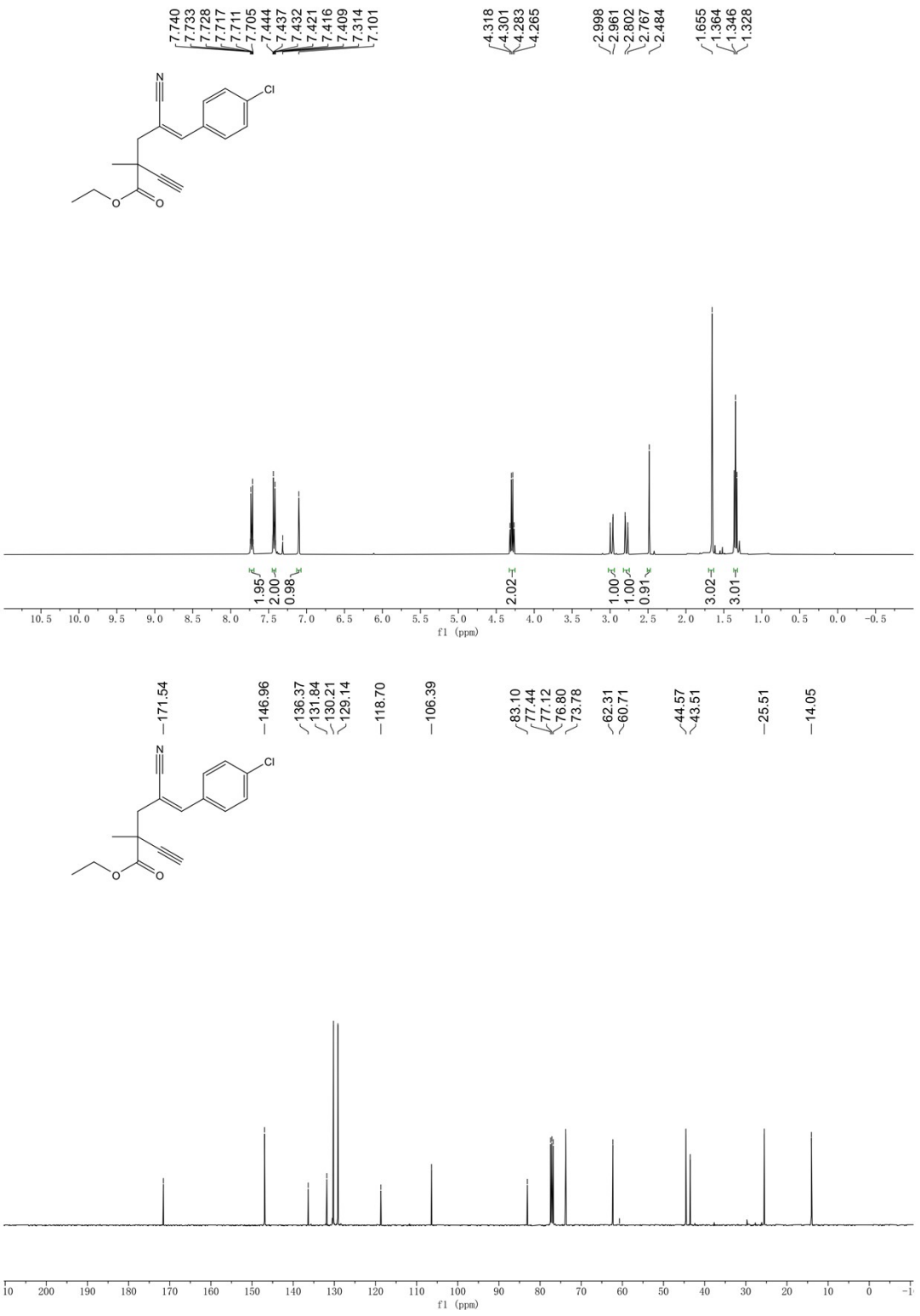




Z/E = 5:1



3af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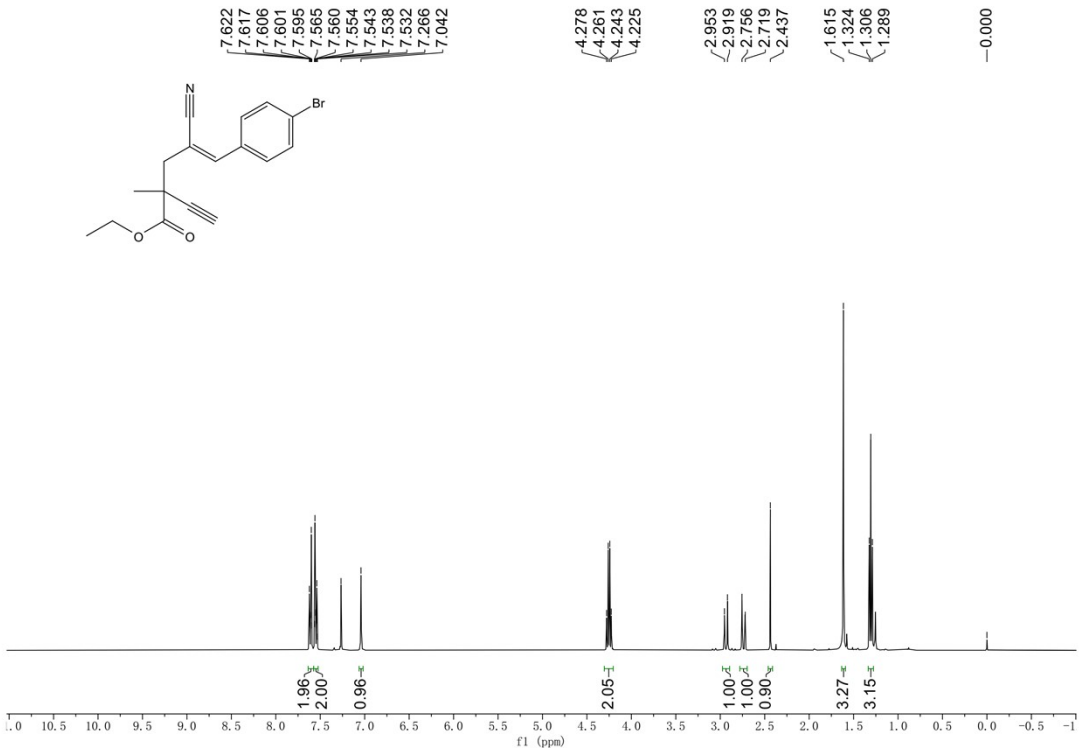
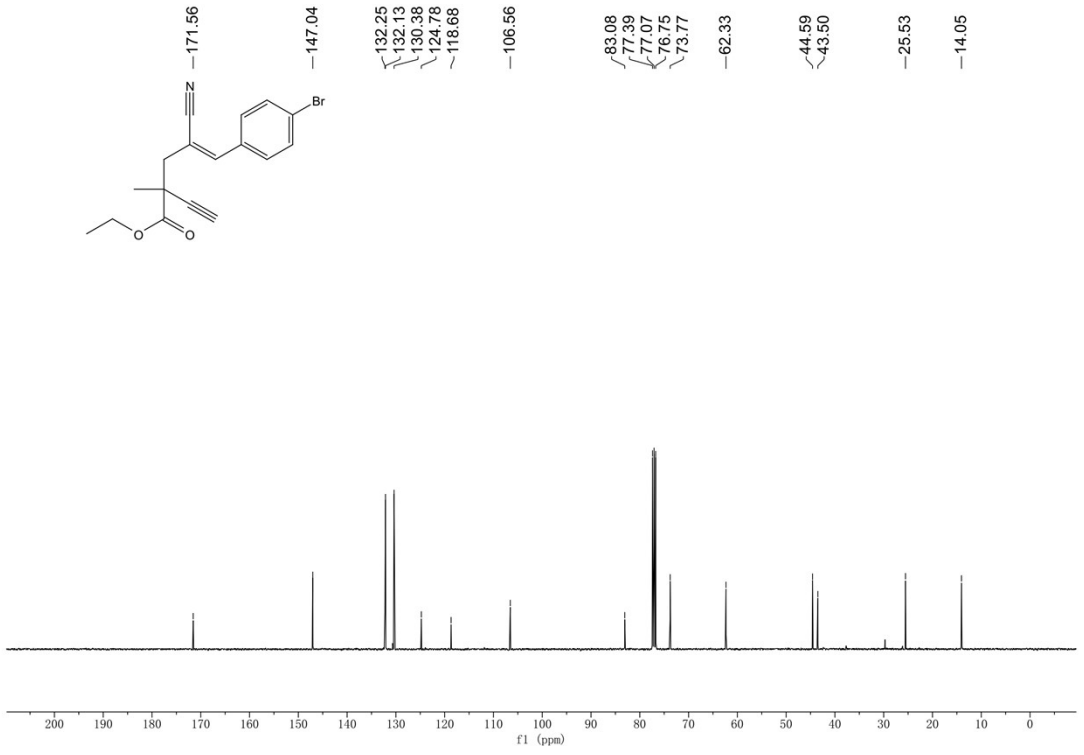
7.728
7.717
7.711
7.705
7.444
7.437
7.432
7.421
7.416
7.409
7.314
7.101
4.318
4.301
4.283
4.265
2.998
2.961
2.802
2.767
2.484
1.655
1.364
1.346
1.328
Cl
N
O
O
1.95
2.00
0.98
2.02
1.00
1.00
0.91
3.02
3.01
f1 (ppm)
171.54
146.96
136.37
131.84
130.21
129.14
118.70
106.39
83.10
77.44
77.12
76.80
73.78
62.31
60.71
44.57
43.51
25.51
14.05
f1 (ppm)

3ag


7.622
7.617
7.606
7.601
7.595
7.565
7.560
7.554
7.543
7.538
7.532
7.266
7.042
4.278
4.261
4.243
4.225
2.953
2.919
2.756
2.719
2.437
1.615
1.324
1.306
1.289
0.000
N
Br
O
O
1.96
2.00
0.96
2.05
1.00
1.00
0.90
3.27
3.15
f1 (ppm)


171.56
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132.25
132.13
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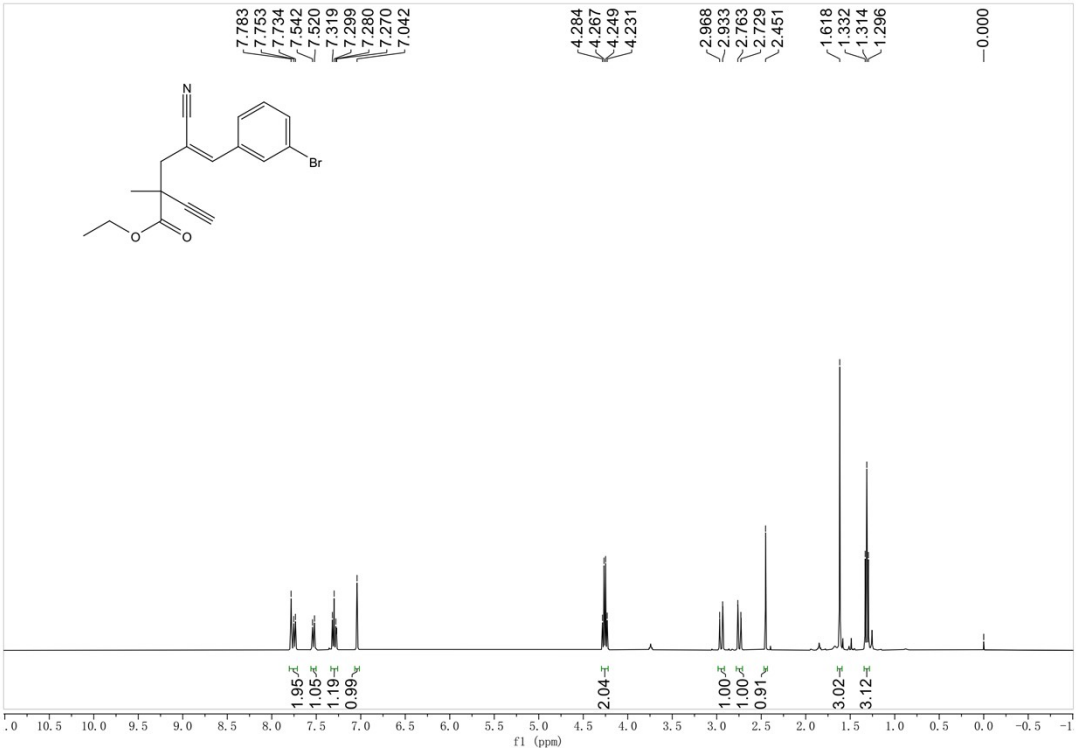
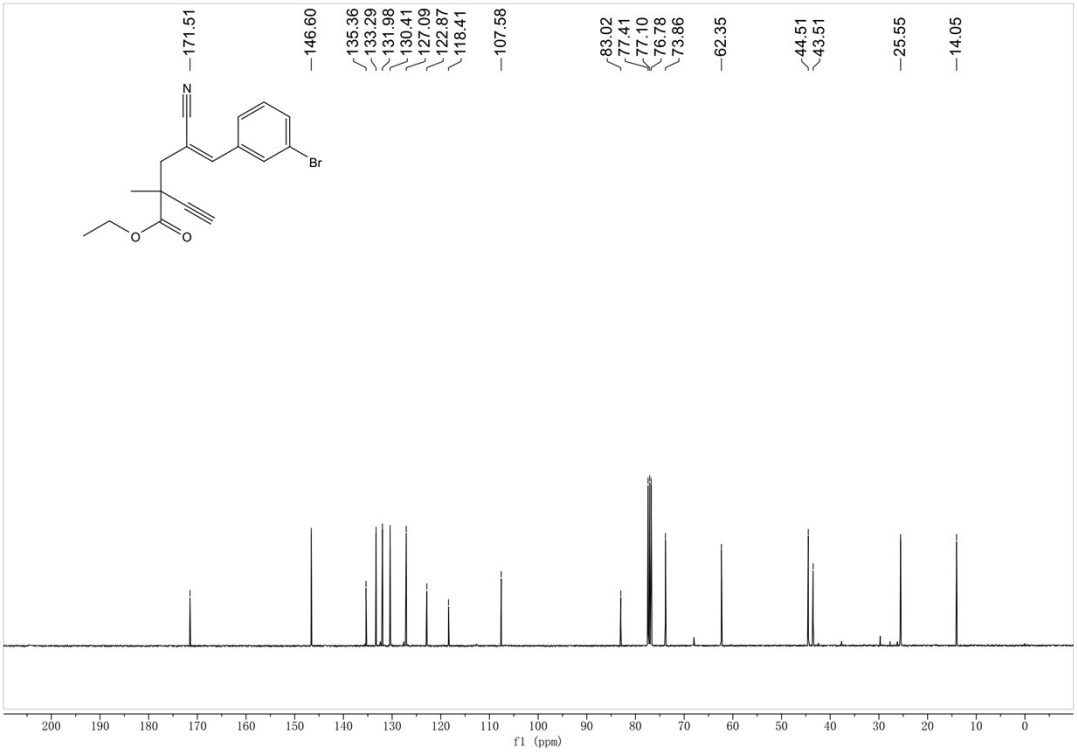
124.78
118.68
106.56
83.08
77.39
77.07
76.75
73.77
62.33
44.59
43.50
25.53
14.05
N
Br
O
O
f1 (ppm)

3ah


7.783
7.753
7.734
7.542
7.520
7.319
7.299
7.280
7.270
7.042
4.284
4.267
4.249
4.231
2.968
2.933
2.763
2.729
2.451
1.618
1.332
1.314
1.296
0.000
1.95
1.05
1.19
0.99
2.04
1.00
1.00
0.91
3.02
3.12
f1 (ppm)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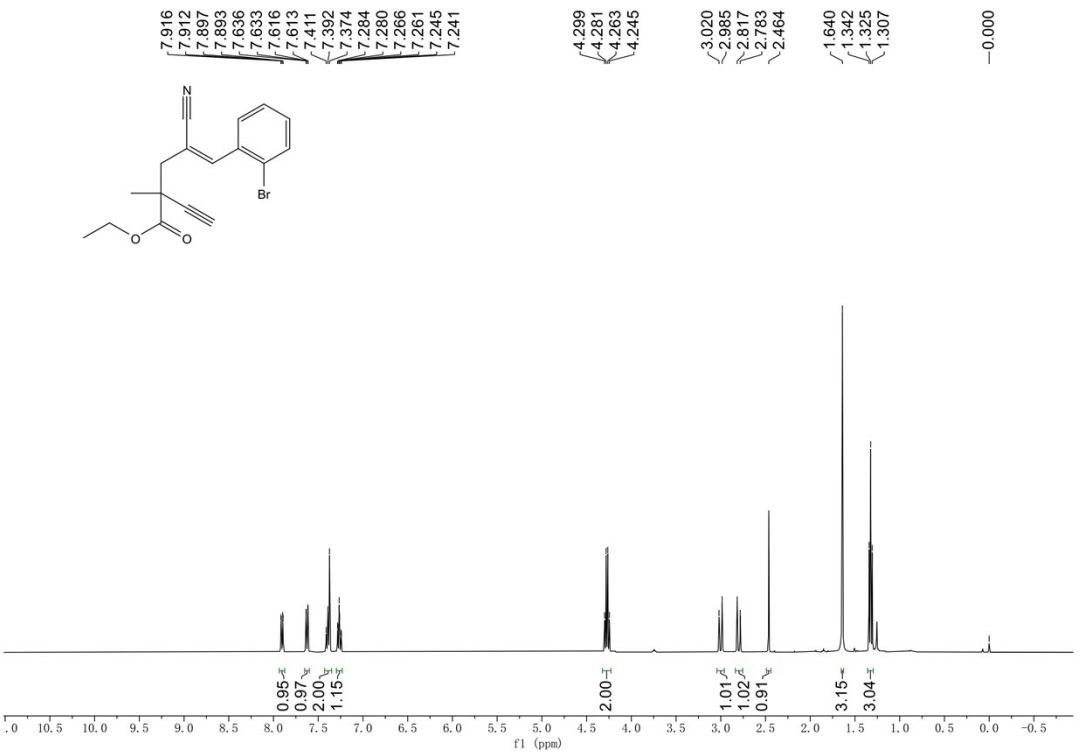
135.36
133.29
131.98
130.41
127.09
122.87
118.41
107.58
83.02
77.41
77.10
76.78
73.86
62.35
44.51
43.51
25.55
14.05
f1 (ppm)

3ai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7.897
7.893
7.636
7.633
7.616
7.613
7.411
7.392
7.374
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7.280
7.266
7.261
7.245
7.241
4.299
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4.263
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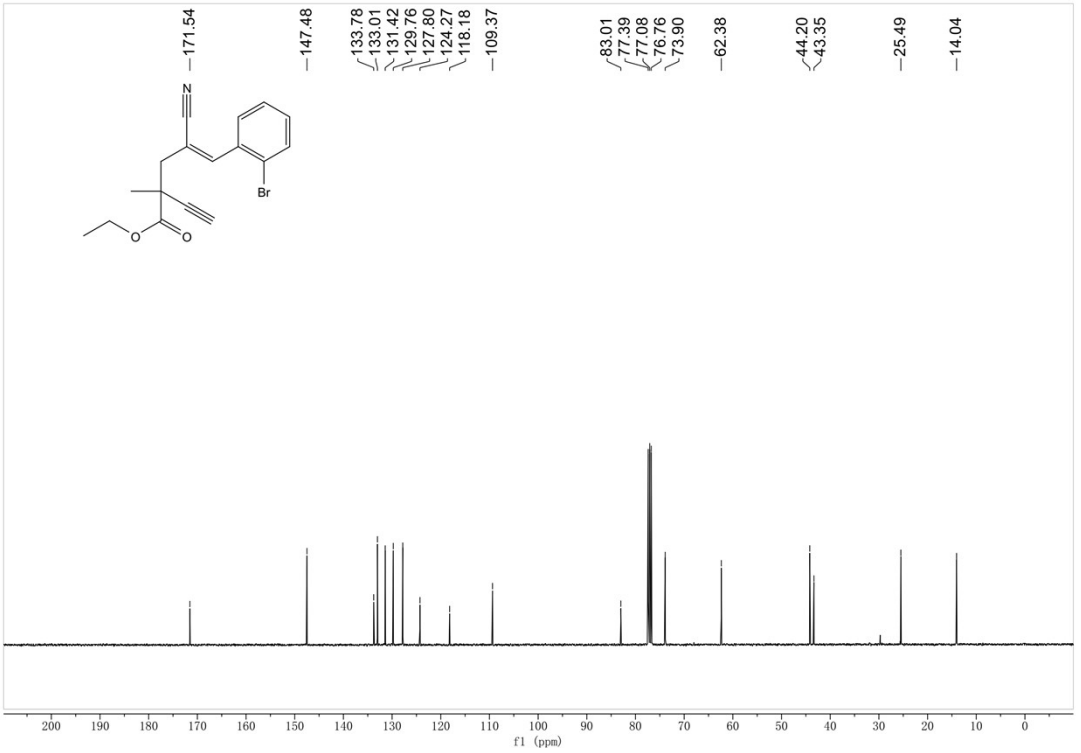
2.985
2.817
2.783
2.464
1.640
1.342
1.325
1.307
0.000
N
Br
O
O
0.95
0.97
2.00
1.15
2.00
1.01
1.02
0.91
3.15
3.04
f1 (ppm)


171.54
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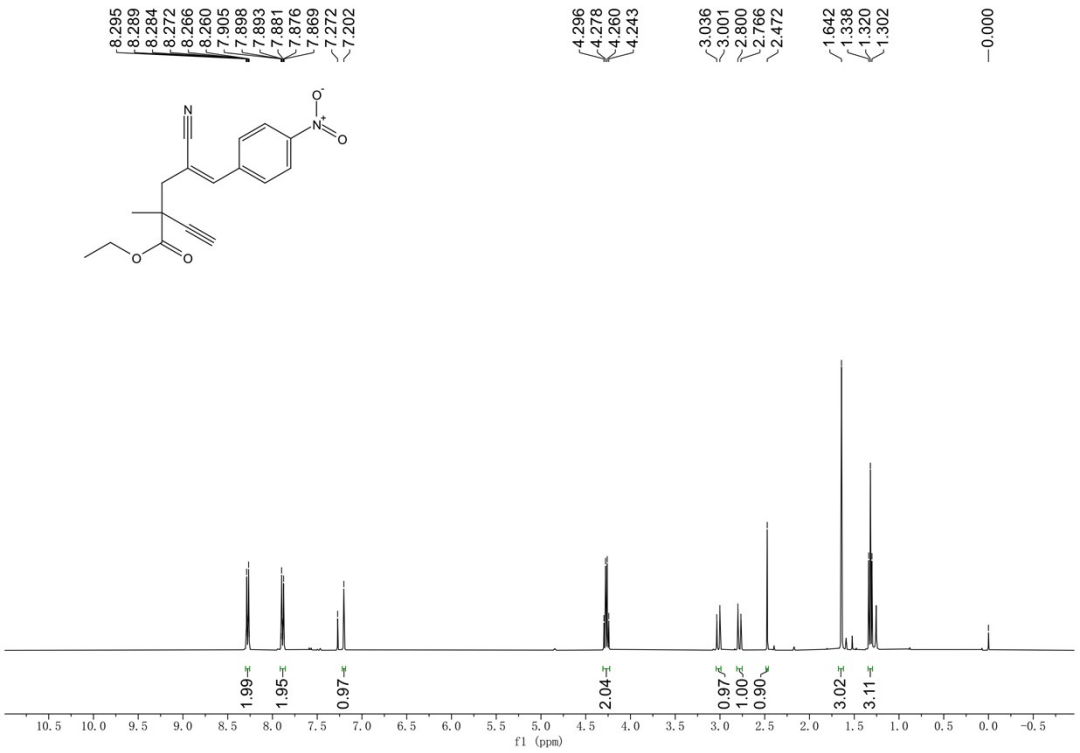
133.01
131.42
129.76
127.80
124.27
118.18
109.37
83.01
77.39
77.08
76.76
73.90
62.38
44.20
43.35
25.49
14.04
N
Br
O
O
f1 (ppm)

3aj


8.295
8.289
8.284
8.272
8.266
8.260
7.905
7.898
7.893
7.881
7.876
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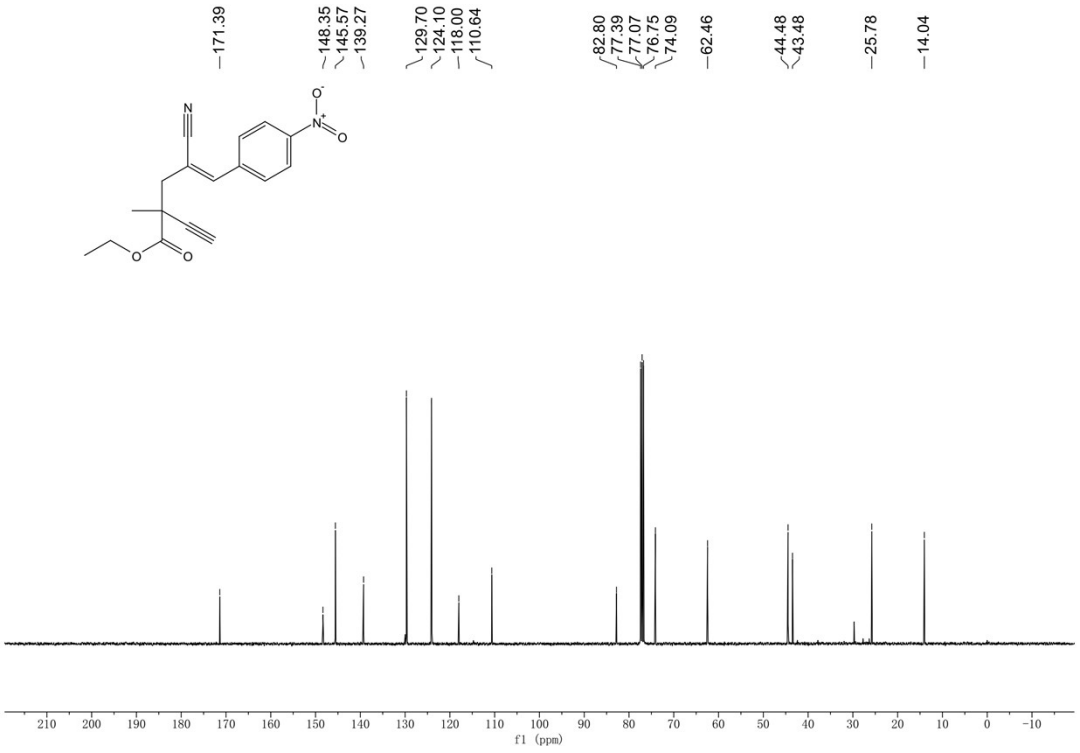
7.272
7.202
4.296
4.278
4.260
4.243
3.036
3.001
2.800
2.766
2.472
1.642
1.338
1.320
1.302
0.000
1.99
1.95
0.97
2.04
0.97
1.00
0.90
3.02
3.11
f1 (ppm)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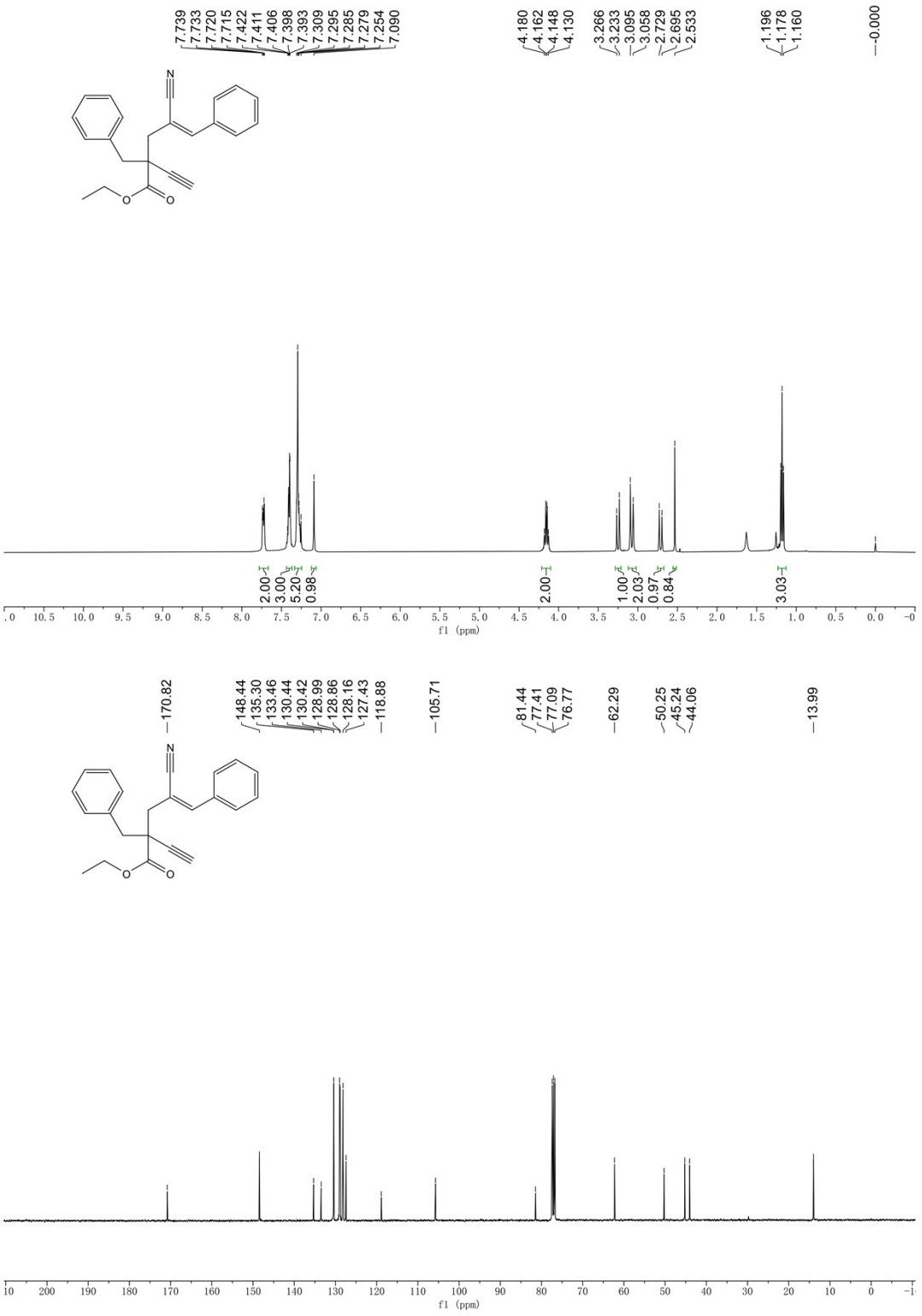
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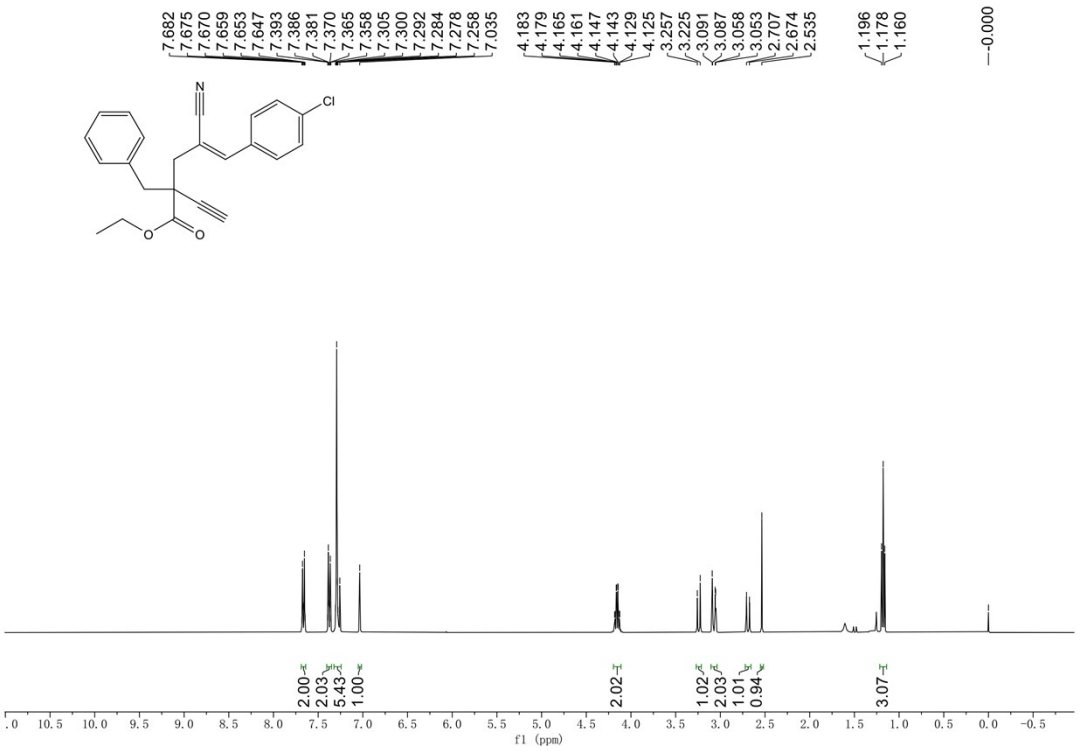
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4.129
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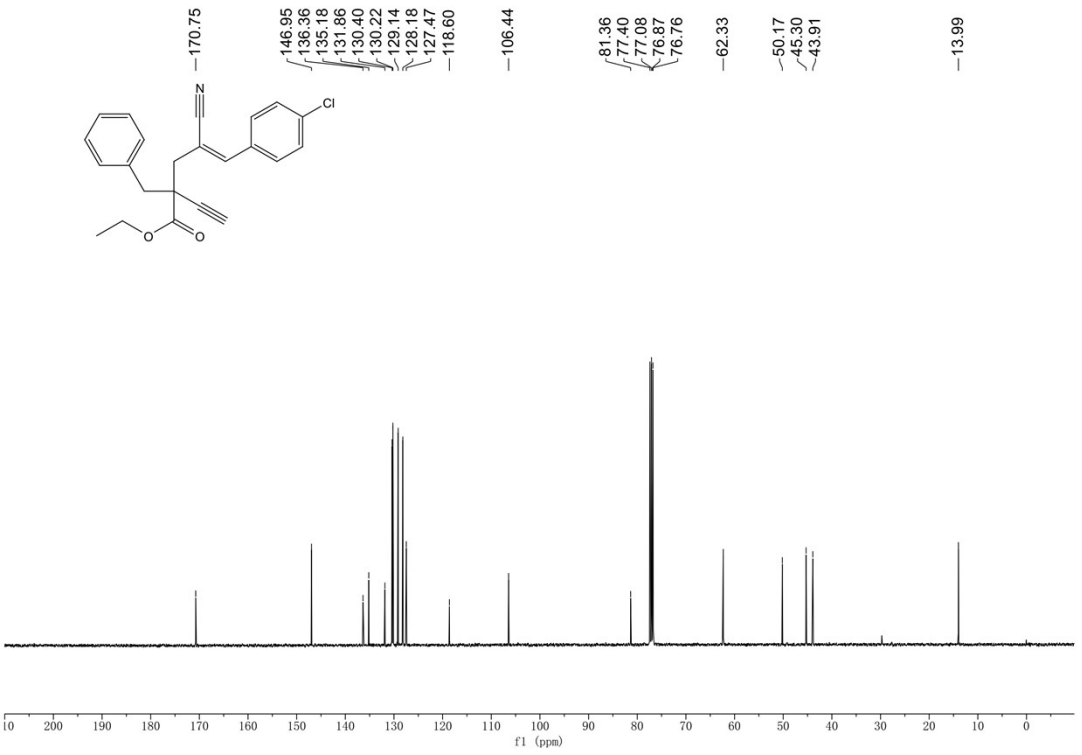
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f1 (ppm)

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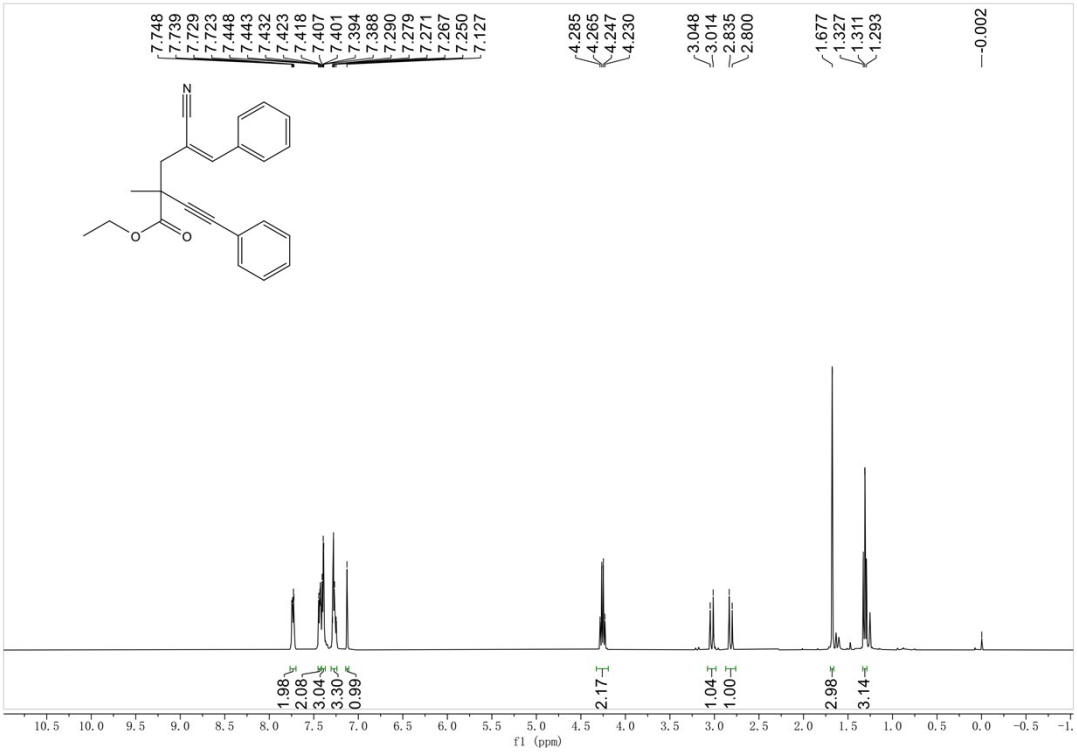
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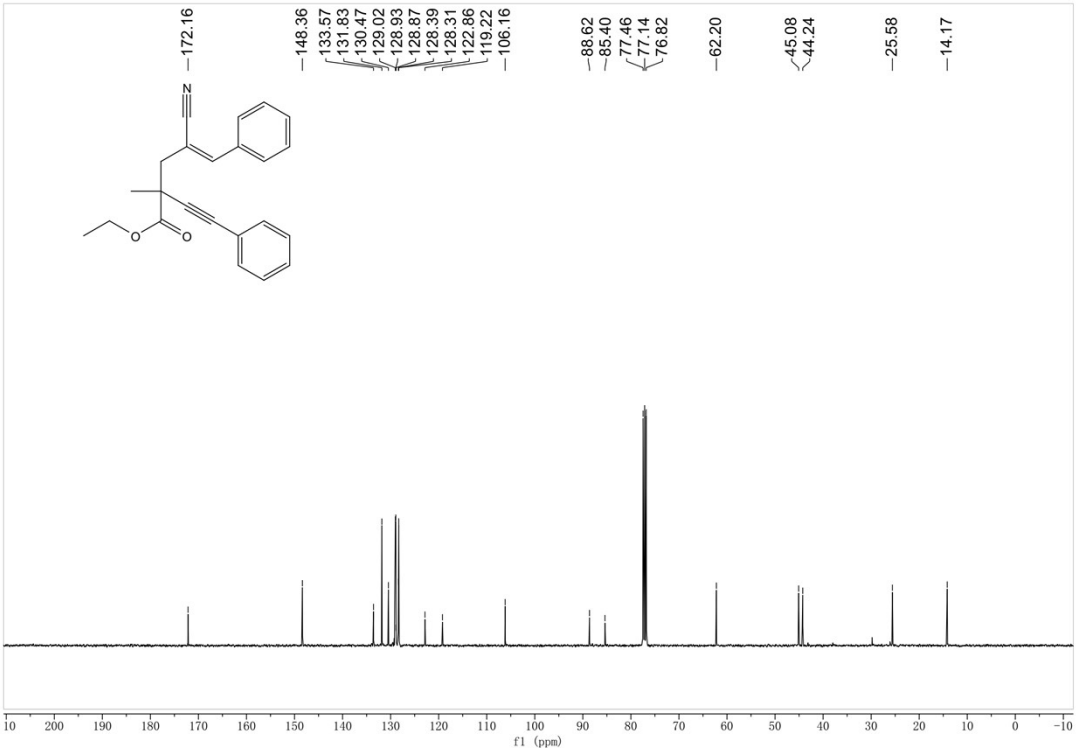
f1 (ppm)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f1 (ppm)

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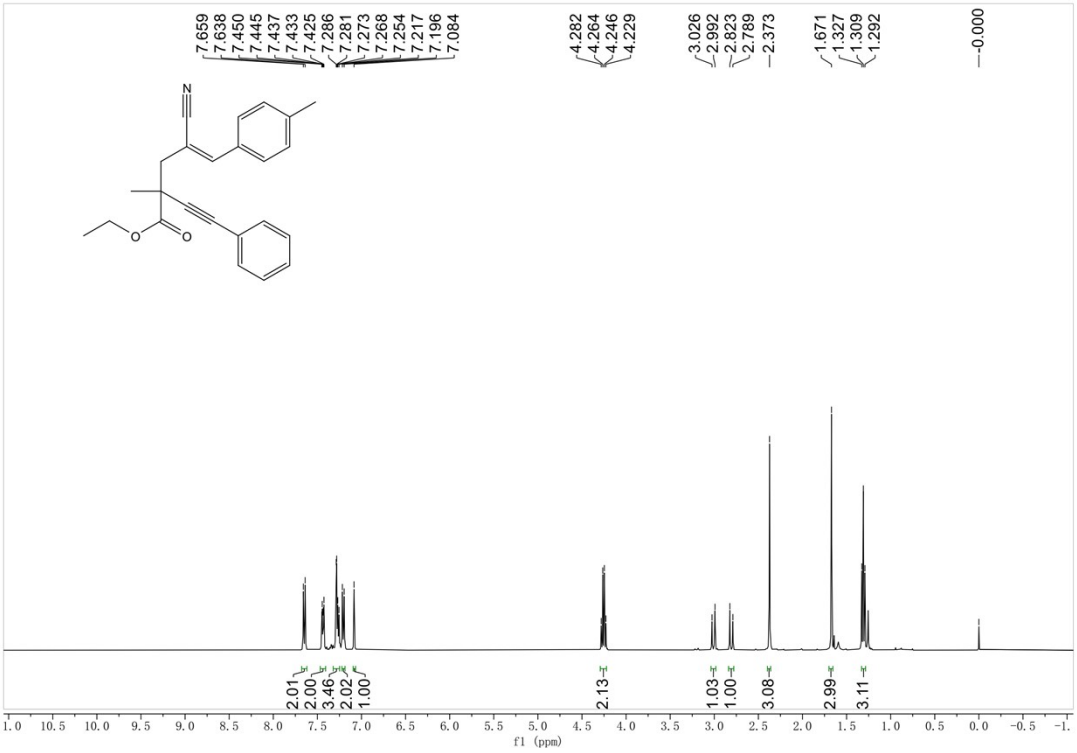
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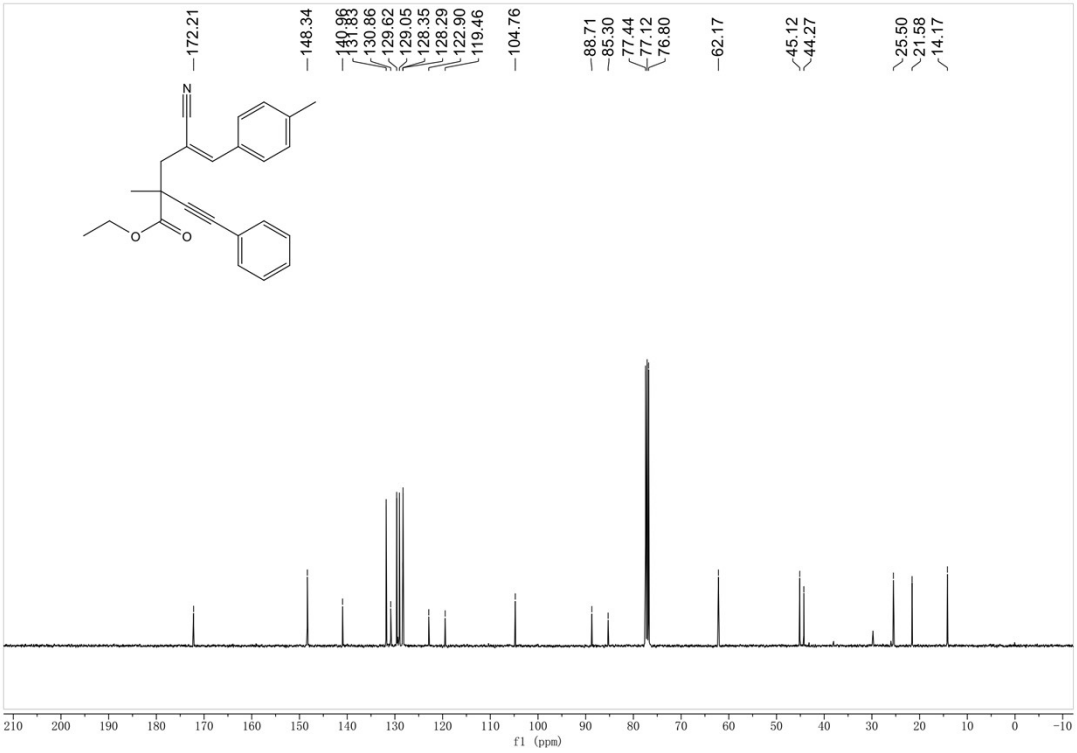
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f1 (ppm)

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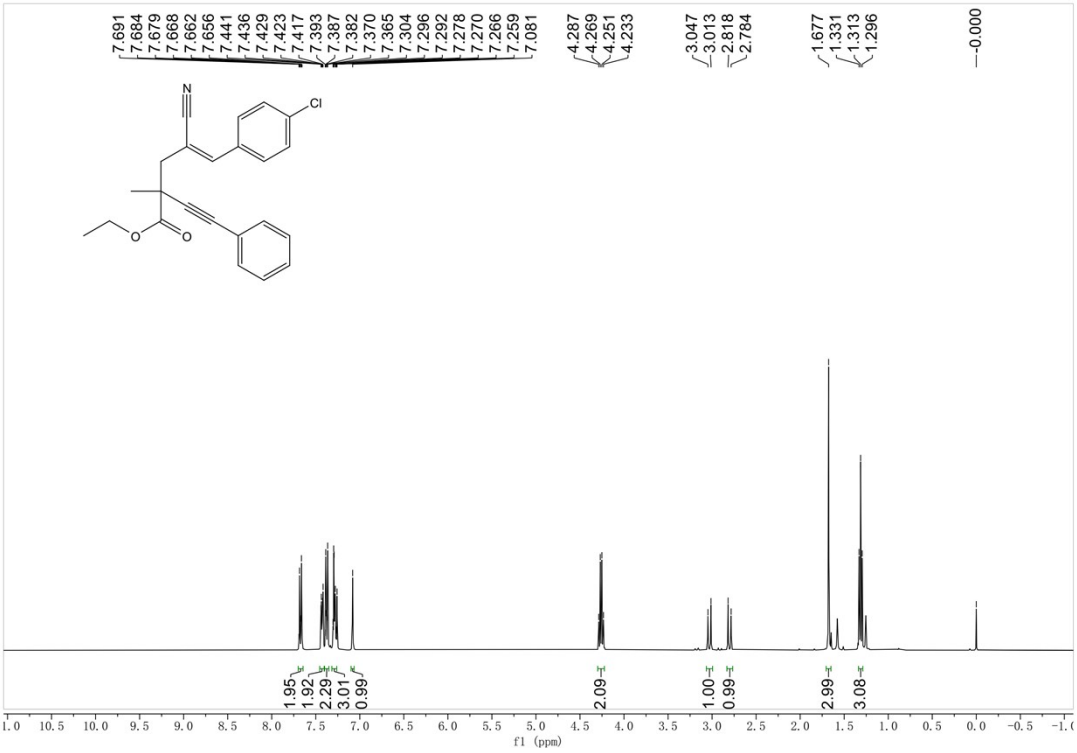
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7.370
7.365
7.304
7.296
7.292
7.278
7.270
7.266
7.259
7.081
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4.269
4.251
4.233
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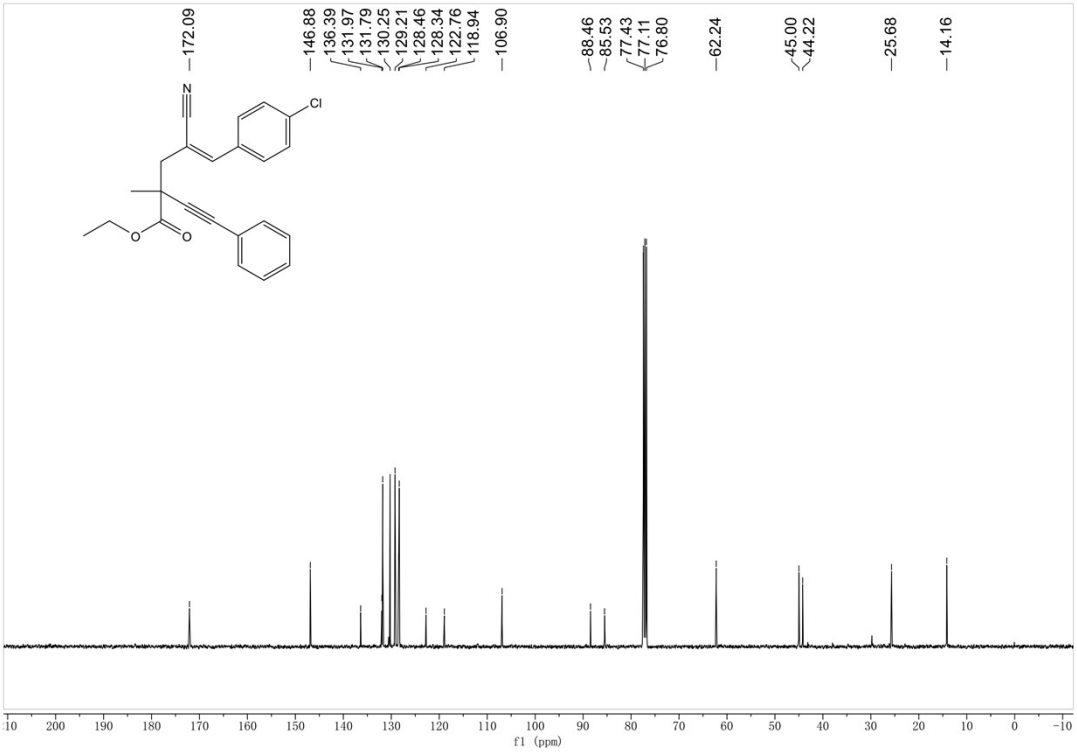
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85.53
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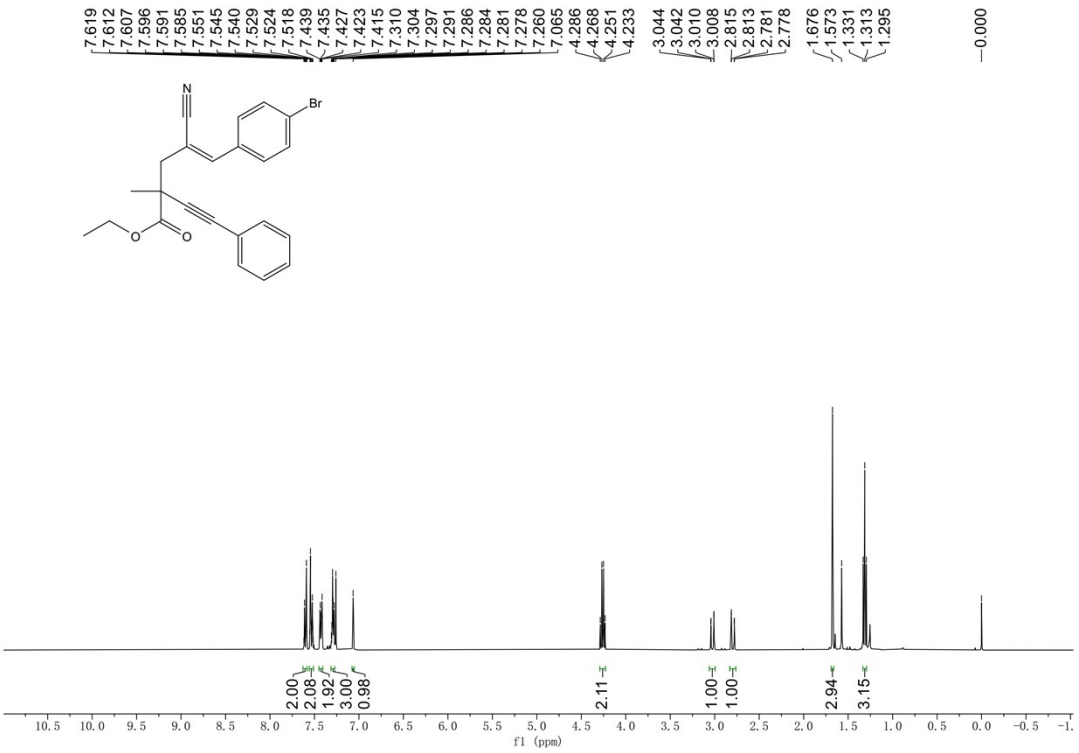
f1 (ppm)

3cg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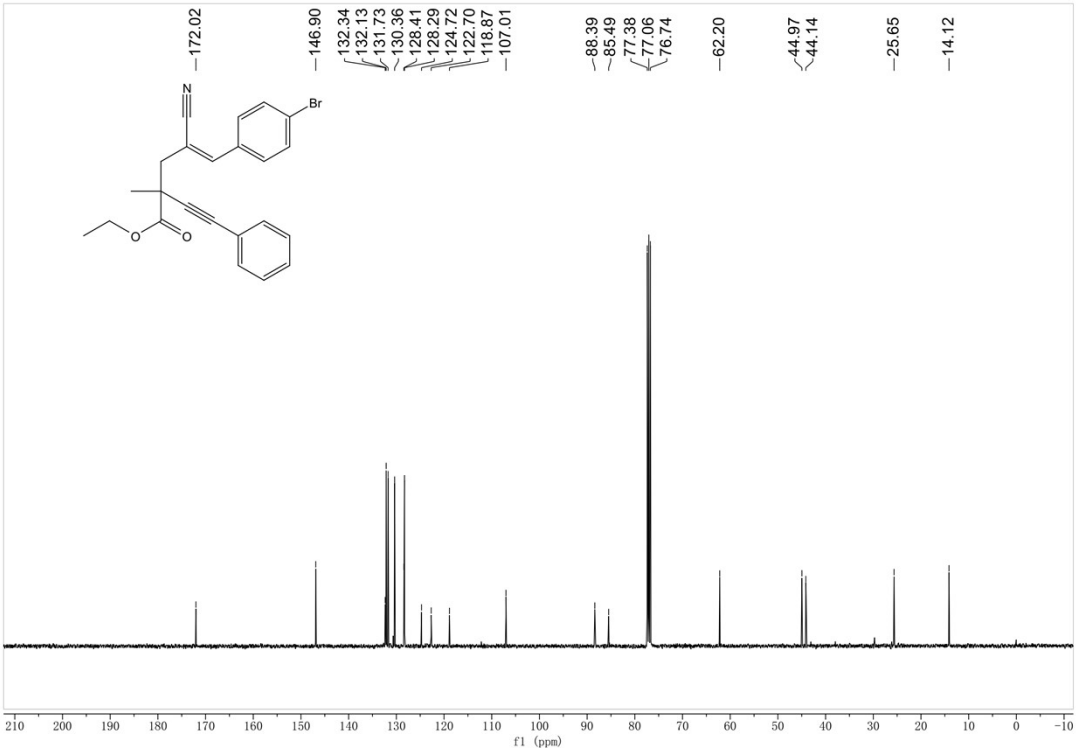
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Br
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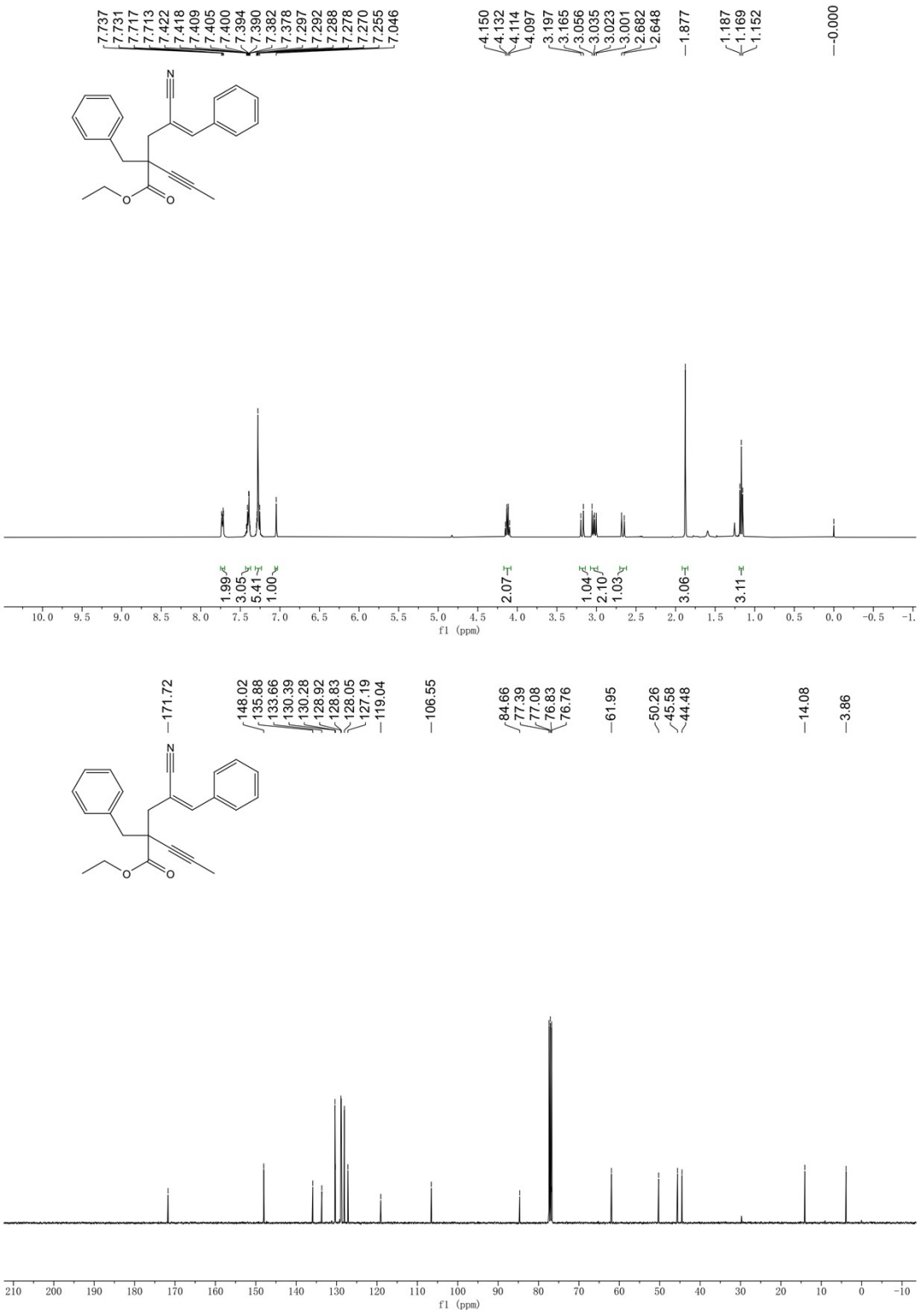
O
f1 (ppm)

3da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7.292
7.288
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f1 (ppm)
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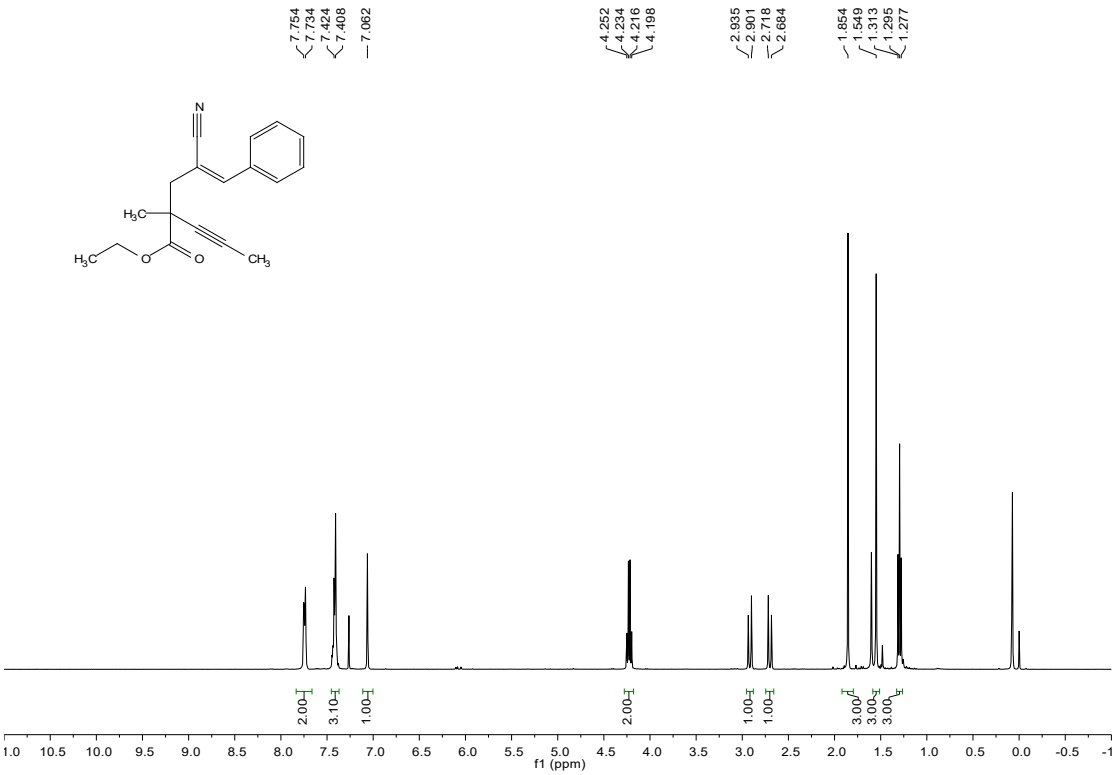
f1 (ppm)

3ea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1.295
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H3C
H3C
O
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CH3
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1.00
1.00
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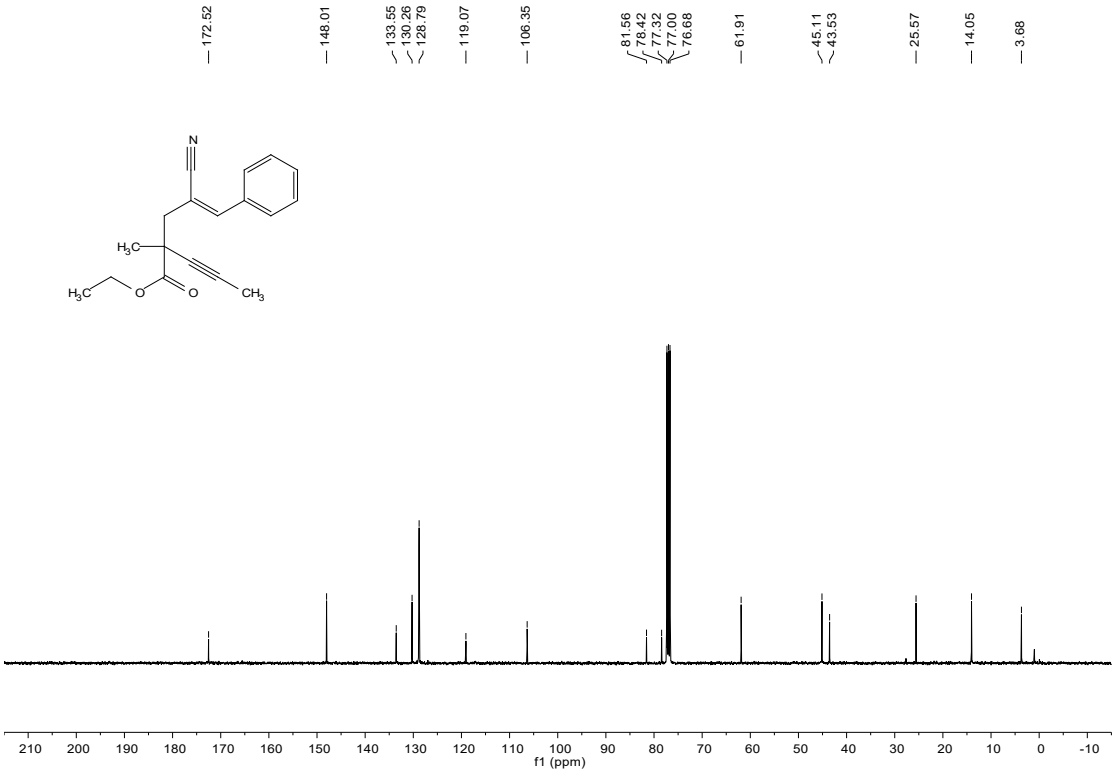
3.00
3.00
f1 (ppm)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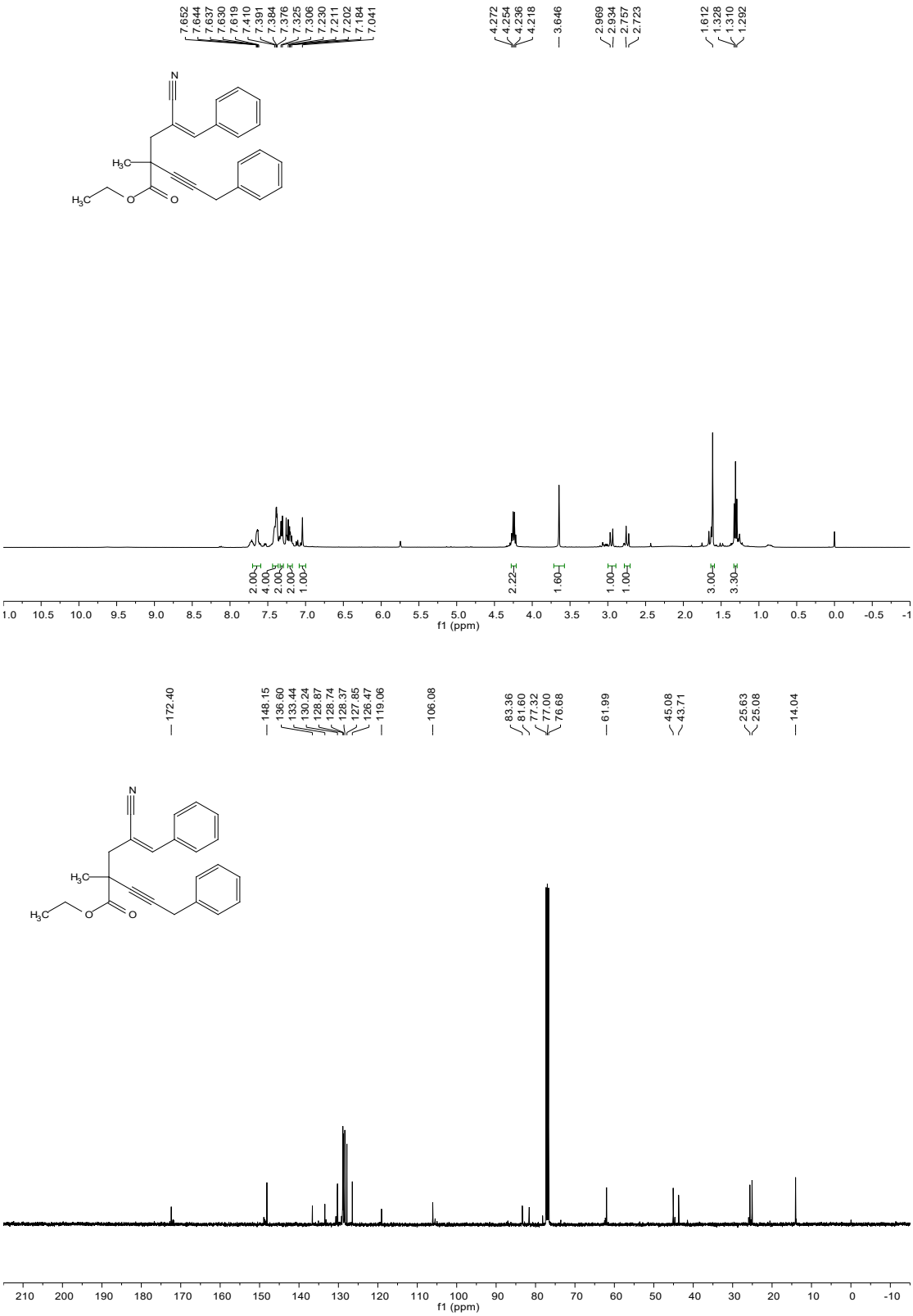
3fa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7.041
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4.218
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f1 (ppm)
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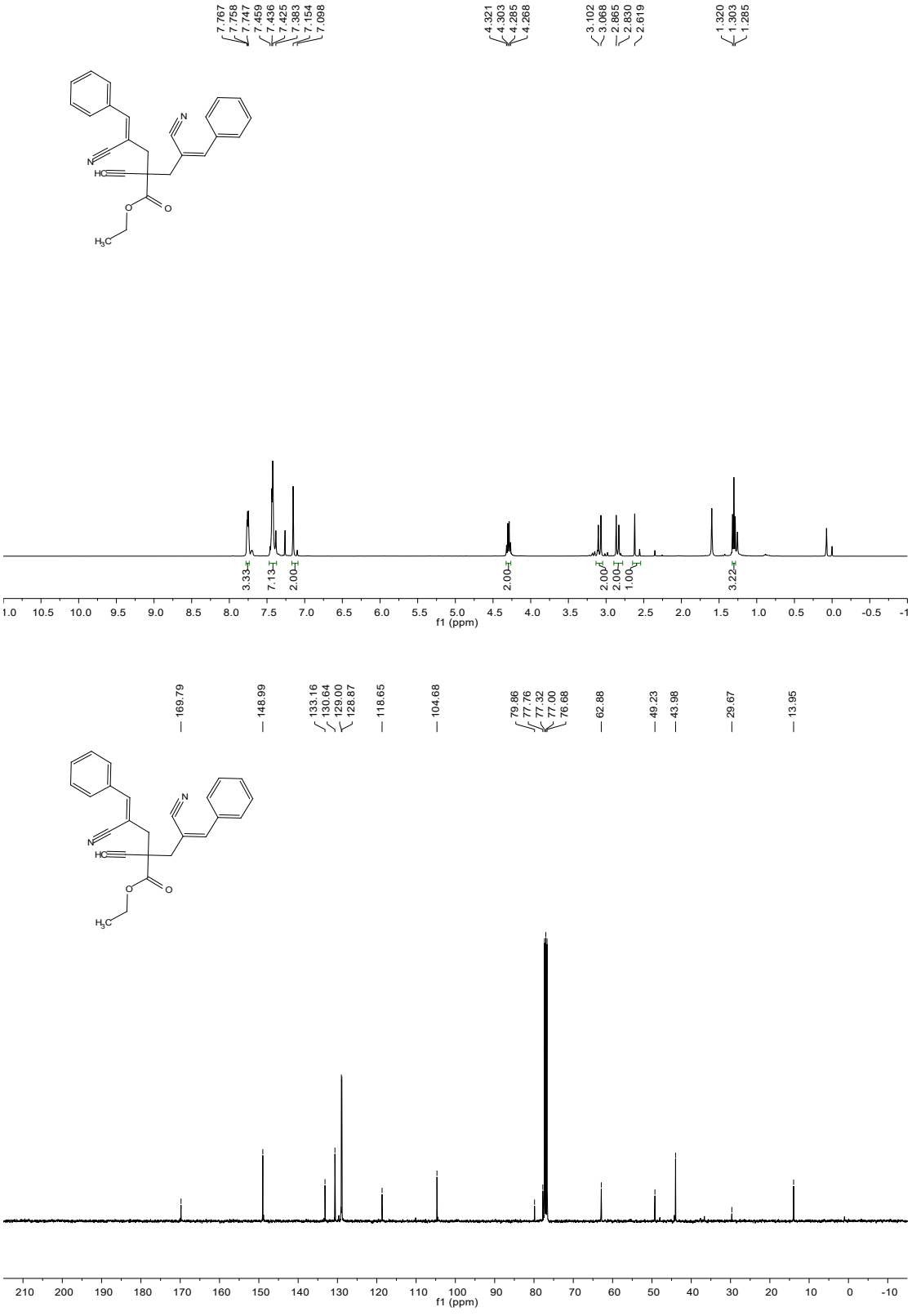
3ga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N
HC
O
O
H3C
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7.13
2.00
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2.00
2.00
1.00
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f1 (ppm)
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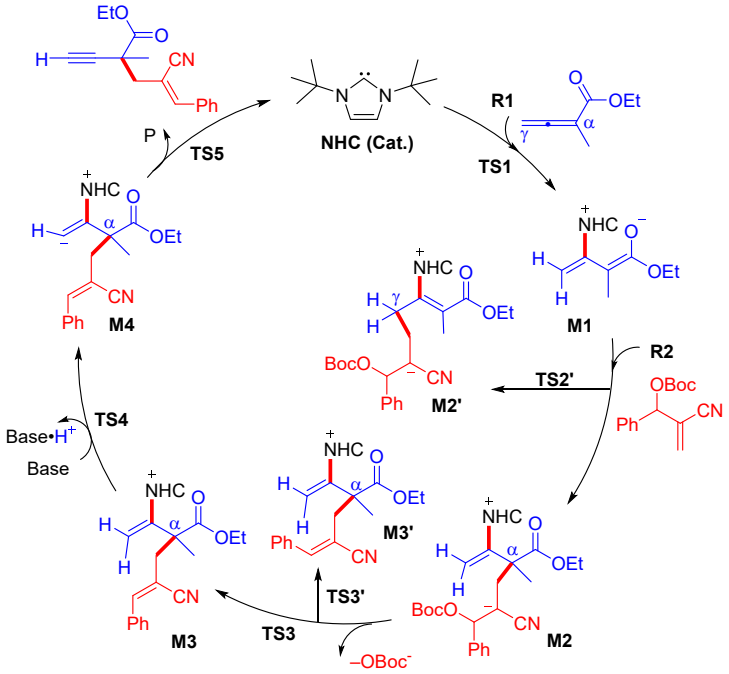
f1 (ppm)

7. DFT Study on Mechanism



Scheme 1. The possible NHC-catalyzed alkynylation cycle

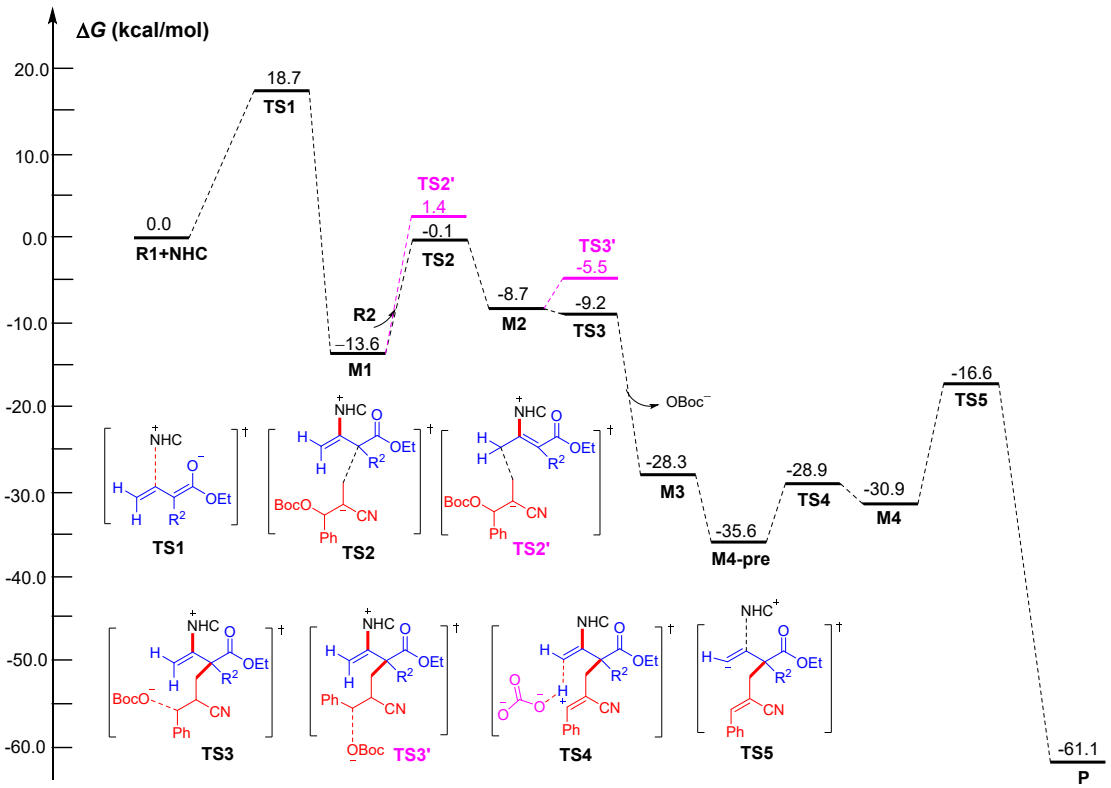


Figure 1. Relative Gibbs free-energy profile for NHC-catalyzed alkynylation by performing DFT calculations.

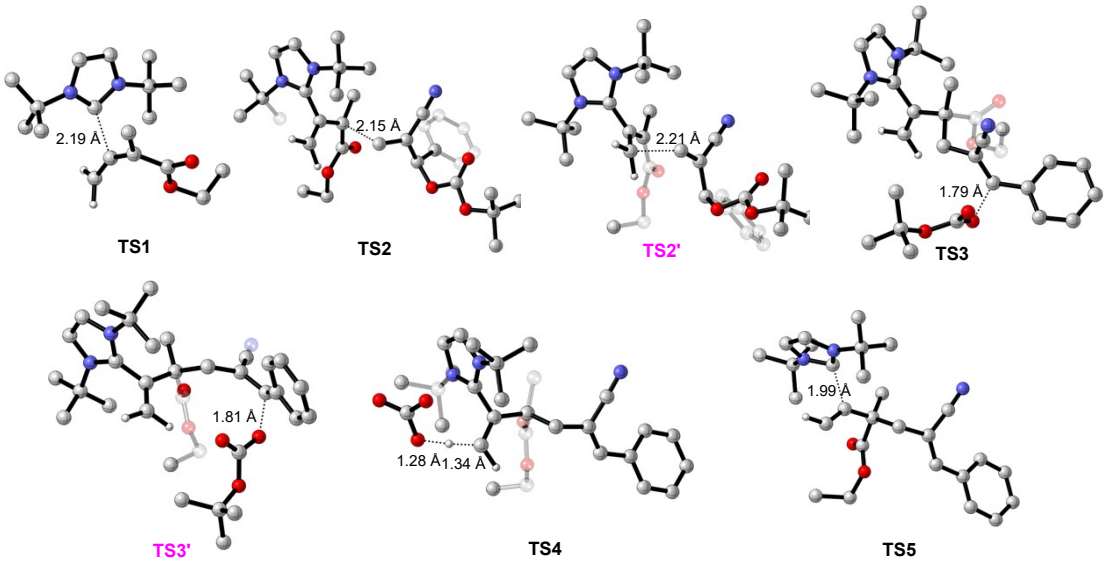


Figure 2. The optimized structures involved in the full NHC-catalyzed alkynylation cycle. The blue, red, white, and gray balls represent N, O, H, and C atoms, respectively.

As shown in Scheme 1 and Figure 1, DFT calculations confirmed that the possible catalytic cycle contains five steps. In the first step, the carbine carbon of NHC can nucleophilically attack on the allene via transition state **TS1** with an energy barrier of 18.7 kcal/mol. In the second step, the C-C bond formation occurs via transition state **TS2** with an energy barrier of 13.5 kcal/mol. We have also considered and excluded the C-C bond formation pathway associated with the γ-carbon position via transition state **TS2'** with an energy barrier of 15.0 kcal/mol. Subsequently, the $OBoc^-$ group can be dissociated via transition state **TS3**. It should be noted that the energy barrier via transition state **TS3** is 2.4 kcal/mol, but the energy difference between **M2** and **TS3** becomes negative (-0.5 kcal/mol), indicating the reaction step is a barrier-less process. In addition, we have also considered and excluded the dissociation pathway associated with the *Z*-isomer via transition state **TS3'** with an energy barrier of 3.2 kcal/mol. In the fourth step, it is a deprotonation process via transition state **TS4** with an energy barrier of 6.7 kcal/mol. The last step is the dissociation of the product **P** and NHC catalyst via transition state **TS5** with an energy barrier of 14.3 kcal/mol.

Computational Methods:

Gaussian 09 program[1] and density functional theory (DFT) were used for all the calculations. All structures were optimized and at the M06-2X/6-31G**[2-3] level in THF solvent using the in SMD model[4]. Then, frequency calculations at the same level of theory were carried out to identify all of the stationary points as minima (zero imaginary frequencies), and to confirm each transition state has only one imaginary frequency, which connected to the expected intermediates. The discussed energies of all the optimized geometries were gained by adding the single-point energies and the Gibbs free energy corrections at the M06-2X-GD3/6-31G(2df,2pd)/SMD_{THF} //M06-2X/6-31G(d,p)/SMD_{THF} computational level.

References

[1] G. W. Trucks, M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P.

Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Revision C.01, (2010).

[2] Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.* 2008, *4*, 1849.

[3] Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.* 2008, *41*, 157

[4] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, *113*, 6378.

Table S1. The Gibbs free energy corrections (GFEC) of all the stationary points involved in the reaction calculated at M06-2X/6-31G(d,p)/SMD_{THF} and the single-point energies (E) of all the stationary points involved in the reaction calculated at M06-2X-GD3/6-31G(2df, 2pd)/ SMD_{THF} (Unit: a.u.)

Species	GFEC	E
R1+NHC	0.402144	-963.791959
R2	0.248848	-862.203180
OBoc$^-$	0.105167	-421.760884
CO_3^{2-}	-0.010921	-263.997978
HCO_3^-	0.001311	-264.545281
TS1	0.406153	-963.766155
M1	0.409463	-963.820848
TS2	0.685022	-1826.029258
TS2'	0.684343	-1826.026164
M2	0.688710	-1826.046712
TS3	0.685079	-1826.043809
TS3'	0.689382	-1826.042264
M3	0.683833	-1826.069720
M4-pre	0.567353	-1668.321341
TS4	0.562863	-1668.306217
M4	0.564575	-1668.311080
TS5	0.536447	-1403.716243
P	0.251123	-863.119079
NHC	0.257320	-540.640065

Cartesian Coordinates of the Listed Complexes

NHC

0 1

C	-1.53087300	-0.00000800	0.67620400
C	0.65631000	-0.00005000	0.00000000
N	-0.19810700	-0.00001100	1.06323500
N	-0.19810700	-0.00001100	-1.06323500
C	-1.53087300	-0.00000800	-0.67620400
C	0.21353100	0.00000500	-2.48695900
C	-0.34782800	-1.25779400	-3.15608700
H	-1.44112500	-1.27706900	-3.12053200
H	-0.04474000	-1.28765000	-4.20677000
H	0.03126600	-2.15557800	-2.65873200
C	-0.34769200	1.25789800	-3.15602300
H	0.03151500	2.15561700	-2.65863500
H	-0.04462000	1.28776600	-4.20671100
H	-1.44098600	1.27729700	-3.12044600
C	1.73563100	-0.00007700	-2.59134600

H	2.16805200	0.88409300	-2.11844000
H	2.16795000	-0.88433100	-2.11850200
H	2.00871700	-0.00005700	-3.65089200
C	0.21353100	0.00000500	2.48695900
C	-0.34769200	1.25789800	3.15602300
H	-1.44098600	1.27729700	3.12044600
H	-0.04462000	1.28776600	4.20671100
H	0.03151500	2.15561700	2.65863500
C	1.73563100	-0.00007700	2.59134600
H	2.00871700	-0.00005700	3.65089200
H	2.16795000	-0.88433100	2.11850200
H	2.16805200	0.88409300	2.11844000
C	-0.34782800	-1.25779400	3.15608700
H	0.03126600	-2.15557800	2.65873200
H	-0.04474000	-1.28765000	4.20677000
H	-1.44112500	-1.27706900	3.12053200
H	-2.35481600	-0.00000100	1.37394600
H	-2.35481600	-0.00000100	-1.37394600

R1+NHC

0 1

C	0.17313700	-2.34144000	-1.81975700
H	-0.22682200	-1.56694800	-2.47067300
H	0.17526400	-3.37076900	-2.16940700
C	0.64491700	-2.01746200	-0.65022700
C	1.11080600	-1.66801900	0.52941800
C	0.25003200	-1.57886600	1.76770200
H	-0.26910000	-2.52076700	1.96040700
H	0.87914900	-1.34408600	2.62781000
H	-0.50001600	-0.78920200	1.65694500
C	2.55106900	-1.30275900	0.66417700
O	3.07115300	-1.02052300	1.72337500
O	3.20687600	-1.31914900	-0.50257700
C	4.59783300	-0.95237500	-0.45615800
H	5.07031700	-1.45299600	0.39225700
H	5.01454600	-1.35086600	-1.38260300
C	4.77029200	0.55050700	-0.37635100
H	4.37268500	0.93581700	0.56517300
H	5.83417600	0.79965800	-0.42852700
H	4.26096900	1.04081200	-1.21056100
C	-2.49365300	0.99086800	1.33725300
C	-1.45807400	0.62278100	-0.67172400
N	-2.51952800	0.30985800	0.12799900
N	-0.76652600	1.51776200	0.09360500

C	-1.38545300	1.76561700	1.31098100
C	0.45883600	2.23528600	-0.33595000
C	1.06151200	1.56049500	-1.56516300
H	0.35632800	1.54112800	-2.39711900
H	1.94493800	2.13022800	-1.86929700
H	1.36760800	0.53329900	-1.34250100
C	0.07932000	3.68155500	-0.66618100
H	-0.36631200	4.17799200	0.20169400
H	0.96804700	4.24667100	-0.96321200
H	-0.64153600	3.70872700	-1.48876100
C	1.47912300	2.20448900	0.80490700
H	1.14198400	2.77561700	1.67466700
H	1.67879800	1.17597300	1.12314000
H	2.41758300	2.65068100	0.46275400
C	-3.55346600	-0.70234100	-0.19659800
C	-4.93434600	-0.13370400	0.14269600
H	-5.09739500	0.81632500	-0.37526400
H	-5.70607300	-0.83896700	-0.17838000
H	-5.06333300	0.02790100	1.21654500
C	-3.26975400	-1.96036000	0.62807100
H	-4.04330000	-2.71373000	0.44941000
H	-2.29978900	-2.38100000	0.34378300
H	-3.25289000	-1.73287300	1.69917500
C	-3.49992900	-1.03932700	-1.68322500
H	-2.54235300	-1.48714100	-1.95389900
H	-4.29634200	-1.75595100	-1.90555700
H	-3.65096800	-0.14680500	-2.29608100
H	-3.23743900	0.87036300	2.10946300
H	-1.00377300	2.45528100	2.04779800

R2

0 1

C	2.13760500	-0.02406000	-0.35460200
C	2.25127500	-0.40217800	0.98676500
C	3.19514100	-1.35253900	1.36469000
C	4.02934200	-1.93465100	0.41157000
C	3.92039000	-1.56165400	-0.92541900
C	2.97941500	-0.60789400	-1.30384100
H	1.59522900	0.04259200	1.72634200
H	3.27775900	-1.64106400	2.40796000
H	4.76401800	-2.67527700	0.71253900
H	4.56993800	-2.00672700	-1.67252800
H	2.89427200	-0.31241300	-2.34665400
C	1.10503900	0.97080100	-0.84540900

H	1.44325900	1.35580100	-1.81199600
C	0.86913300	2.17848200	0.05230900
C	1.79729600	2.75309000	0.81877500
H	2.79126600	2.32639200	0.90366700
H	1.58138600	3.65974400	1.37326600
C	-0.43876200	2.78017700	-0.04158100
N	-1.50218200	3.22925500	-0.12762900
O	-0.13377500	0.32917100	-1.20905000
C	-0.93958800	-0.08821700	-0.21787200
O	-0.70611100	0.04689500	0.96069200
O	-2.00096200	-0.64044600	-0.77788700
C	-3.14909700	-1.02144900	0.05507300
C	-2.74739500	-2.11810300	1.03340000
C	-3.69822200	0.21868600	0.75059600
C	-4.14198600	-1.55146200	-0.96943500
H	-2.27881800	-2.94906200	0.49764600
H	-2.05635300	-1.74654400	1.79019400
H	-3.64504300	-2.49576900	1.53146500
H	-3.90379000	1.00338700	0.01611900
H	-4.63493500	-0.03710200	1.25394900
H	-2.99902200	0.60481600	1.49381900
H	-5.06120200	-1.85958500	-0.46469200
H	-4.38717700	-0.77793100	-1.70214400
H	-3.72624800	-2.41517400	-1.49569600

OBoc-

-1 1

O	-2.50787600	-0.86804900	0.00002600
C	-1.55210200	-0.08221400	0.00001000
O	-1.52917900	1.16382700	-0.00001400
O	-0.30120200	-0.76648300	0.00001600
C	0.93067900	-0.04769100	0.00002200
C	1.08220900	0.80536100	-1.26171400
C	1.08253600	0.80485800	1.26204000
C	1.99296400	-1.14674300	-0.00036000
H	0.94770200	0.17857700	-2.15050100
H	0.32901900	1.59312700	-1.26972600
H	2.08248800	1.25080700	-1.30801400
H	0.94867400	0.17763500	2.15058600
H	2.08268500	1.25066000	1.30806300
H	0.32905200	1.59233300	1.27074900
H	3.00131800	-0.71951100	-0.00011400
H	1.88363100	-1.78006800	0.88554900
H	1.88376000	-1.77935100	-0.88681500

CO_3^{2-}
-2 1

C	0.00000000	-0.00014600	0.00000100
O	0.00047500	1.29682400	0.00017000
O	1.12386900	-0.64876800	-0.00009200
O	-1.12434400	-0.64794600	-0.00007800

HCO_3^-
-1 1

C	-0.14338400	0.06607800	0.00000900
O	0.11880900	1.28684800	-0.00000600
O	0.99551600	-0.77710600	0.00011700
O	-1.22314100	-0.54025300	-0.00013800
H	1.73084200	-0.15237500	0.00016400

TS1
0 1

C	0.06383800	-1.88241500	-1.77886400
H	-0.32589300	-1.32592900	-2.62230700
H	0.39862300	-2.90434500	-1.93911300
C	0.18159000	-1.36066200	-0.57209900
C	0.79978700	-1.38416400	0.63517600
C	0.06959000	-1.29680400	1.95067300
H	-0.44027000	-2.23074600	2.21230000
H	0.78474800	-1.07331300	2.74435900
H	-0.68686800	-0.50327600	1.93611200
C	2.25938600	-1.33130400	0.69295600
O	2.90305300	-1.20897600	1.72597200
O	2.87134200	-1.45528000	-0.51136900
C	4.29759000	-1.32667400	-0.50212300
H	4.70521700	-1.87824400	0.34804300
H	4.62736800	-1.80480100	-1.42711900
C	4.71974600	0.12914800	-0.45905000
H	4.35752400	0.60128800	0.45764900
H	5.81100600	0.20327400	-0.47838500
H	4.32256400	0.67120800	-1.32153000
C	-2.60496000	1.28083400	1.00367300
C	-1.13346100	0.39031700	-0.48021800
N	-2.36564500	0.26382000	0.09295700
N	-0.62942000	1.52463900	0.07637400
C	-1.50964800	2.07259700	0.99422800
C	0.65219600	2.20227200	-0.26559200
C	1.31704400	1.53332000	-1.46461600

H	0.63812200	1.49558200	-2.32068100
H	2.18648900	2.13557200	-1.74471600
H	1.65895400	0.52271700	-1.24026000
C	0.33316200	3.65582200	-0.63724000
H	-0.08940800	4.21513300	0.20130400
H	1.25471000	4.15976000	-0.94122800
H	-0.37258300	3.69188400	-1.47267300
C	1.57079700	2.16095700	0.95831400
H	1.11461500	2.67800400	1.80861800
H	1.79059400	1.13227900	1.25729600
H	2.51363800	2.66527600	0.72559400
C	-3.35390700	-0.80776500	-0.22510000
C	-4.75493700	-0.33977000	0.17524500
H	-5.00274300	0.62047400	-0.28706400
H	-5.47752100	-1.08222200	-0.17262000
H	-4.87011600	-0.25464000	1.25935700
C	-3.00069900	-2.07782400	0.55065700
H	-3.75470000	-2.84665200	0.35571300
H	-2.02620900	-2.46503600	0.24464500
H	-2.98262000	-1.87858100	1.62672500
C	-3.33118100	-1.06576000	-1.73060800
H	-2.36080800	-1.44816100	-2.04724200
H	-4.09308000	-1.81069300	-1.97761800
H	-3.55027900	-0.14769200	-2.28388700
H	-3.51467800	1.37169000	1.57267300
H	-1.30171100	2.97228300	1.55144500

M1

0 1

C	-0.47434000	0.47162900	-1.82930800
H	0.26168400	0.06700800	-2.51608000
H	-1.37491900	0.90237500	-2.24099000
C	-0.23649600	0.44024700	-0.48334700
C	-1.01058200	0.85218100	0.64966600
C	-0.48025400	0.77371200	2.06295200
H	-0.45345600	1.75550100	2.55617400
H	-1.11742800	0.14092300	2.69569300
H	0.53567800	0.36821200	2.11680600
C	-2.38898100	1.17856100	0.59210400
O	-3.10263300	1.43847300	1.56833600
O	-2.93957000	1.16083700	-0.67542000
C	-4.35747000	1.27266400	-0.73101100
H	-4.69545600	2.05022700	-0.04124700
H	-4.58390200	1.58381500	-1.75513600

C	-5.02499400	-0.05270000	-0.41037000
H	-4.77265700	-0.35623700	0.60853100
H	-6.11317100	0.03412200	-0.48950900
H	-4.68904500	-0.82814800	-1.10535300
C	3.16265800	-0.66686100	0.37662500
C	1.04623900	-0.24608700	-0.13511800
N	2.26490300	0.31867700	0.01852900
N	1.16510300	-1.56625400	0.13014000
C	2.48290700	-1.83289300	0.44181100
C	0.14652000	-2.67199300	-0.04897900
C	0.16369600	-3.07215500	-1.52452100
H	1.17183200	-3.36278300	-1.83599100
H	-0.50477300	-3.92535200	-1.67253800
H	-0.18172700	-2.24567300	-2.15036100
C	0.57851700	-3.85575600	0.82199600
H	0.71334000	-3.55439000	1.86504600
H	-0.21354200	-4.60649200	0.78315300
H	1.49239700	-4.33340500	0.46164400
C	-1.25835800	-2.25041000	0.38436400
H	-1.25701900	-1.85565900	1.40380100
H	-1.69851500	-1.51388000	-0.28612400
H	-1.88071900	-3.14950000	0.36563200
C	2.66373200	1.75907300	-0.21365300
C	4.11843300	1.93621600	0.22341200
H	4.80820200	1.35145900	-0.39113700
H	4.37272100	2.99058600	0.09371800
H	4.26265000	1.68277100	1.27768200
C	1.78967600	2.69144600	0.62226000
H	2.14126400	3.71504800	0.46531800
H	0.73793300	2.63898500	0.33914700
H	1.88425900	2.45663200	1.68640400
C	2.55137300	2.06763800	-1.70670200
H	1.51196900	2.05504300	-2.03631500
H	2.96763600	3.06215000	-1.89095300
H	3.12197100	1.34022400	-2.29279800
H	4.20424100	-0.47583600	0.56175100
H	2.84248200	-2.81625100	0.68692800

TS2

0 1

C	2.52844800	0.66398400	-2.12826900
H	3.31712900	1.27719700	-2.55284000
H	1.75109200	0.31272800	-2.79463500
C	2.53213800	0.34674100	-0.81722900

C	1.53897800	-0.46127500	-0.09096200
C	1.61747800	-0.55148400	1.41790900
H	0.66222400	-0.25727700	1.87543700
H	1.81388400	-1.57789600	1.74423700
H	2.38979300	0.09327500	1.84546900
C	1.02315900	-1.69381800	-0.66011000
O	0.45228800	-2.55822600	-0.00367100
O	1.14095300	-1.80187100	-2.01369700
C	0.65800200	-3.02067000	-2.59235000
H	-0.28294800	-3.30179600	-2.11395700
H	0.46630700	-2.77827000	-3.64004500
C	1.68463300	-4.12925700	-2.46680300
H	1.88633800	-4.34166700	-1.41361700
H	1.30993300	-5.04231600	-2.93841900
H	2.61917000	-3.84638900	-2.95977900
C	5.68466600	0.91380400	0.95989900
C	3.70377300	0.85916600	-0.03637900
N	4.83834000	0.15325200	0.18306400
N	3.83282400	2.05147700	0.59429200
C	5.06172400	2.08441500	1.21772300
C	2.84705900	3.20033400	0.67889500
C	1.63124100	2.75467500	1.48432800
H	1.91295100	2.49231500	2.50846900
H	0.91019700	3.57562900	1.52310500
H	1.14014300	1.89702900	1.03164000
C	3.51860300	4.36973900	1.40074100
H	4.40585500	4.72612200	0.86954700
H	2.79470900	5.18669100	1.43364100
H	3.78184900	4.12343200	2.43244300
C	2.46167500	3.66215400	-0.72741100
H	3.35524100	3.86384200	-1.32600900
H	1.84282700	2.93316600	-1.24841000
H	1.89391000	4.59176300	-0.63640000
C	5.29939700	-1.14358400	-0.44877900
C	5.84526900	-0.80300700	-1.83567400
H	6.64628000	-0.06079100	-1.76701400
H	6.24947000	-1.70967000	-2.29472800
H	5.05199100	-0.41412500	-2.47919700
C	4.17330200	-2.17181600	-0.54798700
H	4.62995600	-3.12871200	-0.81489100
H	3.65634000	-2.29674700	0.40786200
H	3.45495100	-1.91829200	-1.32562900
C	6.41089500	-1.73008300	0.42578600
H	6.07806200	-1.85907000	1.45983900

H	6.66590000	-2.71295200	0.02452300
H	7.32305100	-1.12968200	0.40859500
H	6.65797400	0.57837500	1.27042200
H	5.40582900	2.92413400	1.79349300
C	-2.88532100	-1.57295000	1.24534500
C	-2.00752300	-1.96321900	2.26158700
C	-2.47262400	-2.66552500	3.36920300
C	-3.82362200	-2.98973300	3.47864800
C	-4.69962600	-2.61876300	2.46262900
C	-4.23316200	-1.92035900	1.35050400
H	-0.95116900	-1.73397800	2.15943800
H	-1.77660300	-2.96041800	4.14874200
H	-4.18872900	-3.53238100	4.34517300
H	-5.75281200	-2.87414200	2.53086500
H	-4.92939900	-1.65960400	0.56001800
C	-2.31676100	-0.86677500	0.02549900
H	-1.76829700	-1.61547000	-0.55324400
C	-1.36269200	0.26579500	0.28752900
C	-0.31021500	0.51259000	-0.58950200
H	-0.35710700	0.06022900	-1.57845800
H	0.16164900	1.48977600	-0.59148700
C	-1.49401600	1.08636600	1.43546100
N	-1.53661500	1.77881200	2.37382800
O	-3.37829700	-0.51687300	-0.91710400
C	-4.20513300	0.47549200	-0.58609700
O	-4.18847800	1.09606600	0.45033900
O	-5.05249500	0.63733800	-1.60387000
C	-6.12135600	1.62893700	-1.51417500
C	-7.05643100	1.28569400	-0.35962900
C	-5.53177200	3.02910900	-1.38783100
C	-6.83818000	1.47031900	-2.84890300
H	-7.40589800	0.25257200	-0.45265200
H	-6.56156700	1.40907600	0.60409600
H	-7.92856900	1.94503300	-0.39298700
H	-4.82070400	3.21320700	-2.19878200
H	-6.33681900	3.76583200	-1.46485300
H	-5.02548700	3.16287000	-0.43170800
H	-7.67308200	2.17330600	-2.90827800
H	-6.15352100	1.67140700	-3.67758300
H	-7.22793200	0.45440300	-2.95729400

TS2'

0 1

C	-1.33564200	-0.58356300	-1.42362400

H	-1.71153200	-1.34408100	-2.10464200
H	-0.71575600	0.17525000	-1.87857100
C	-2.12309800	-0.23827700	-0.32137000
C	-1.91645200	0.79289900	0.60966800
C	-2.53150800	0.75669100	1.98670100
H	-1.76287000	0.50669200	2.73552100
H	-2.94606300	1.72728900	2.27188100
H	-3.32176000	0.00424300	2.07468100
C	-1.21663900	2.02727100	0.33556700
O	-1.17593100	2.97116900	1.12159000
O	-0.66392400	2.14205400	-0.91239700
C	-0.21035300	3.45226900	-1.27550900
H	0.30369900	3.90782000	-0.42666700
H	0.51002400	3.28893600	-2.08150100
C	-1.36866800	4.31182800	-1.74391500
H	-2.09827000	4.43160800	-0.93845500
H	-1.01013800	5.30328200	-2.03570800
H	-1.86361100	3.85697400	-2.60686300
C	-5.59574700	-1.34868700	-0.12667600
C	-3.40263300	-0.99414700	-0.13668200
N	-4.60118700	-0.47106300	-0.50228700
N	-3.64586100	-2.19146200	0.44531400
C	-5.00471800	-2.41641100	0.45241600
C	-2.64801700	-3.19593700	0.95895600
C	-1.66521500	-2.49492100	1.89215500
H	-2.17259000	-2.17063100	2.80544100
H	-0.87578600	-3.19871100	2.17028000
H	-1.20159400	-1.62505300	1.43369800
C	-3.38266300	-4.27238200	1.75766800
H	-4.03157600	-4.88965000	1.13077600
H	-2.62440500	-4.92766000	2.19290100
H	-3.96502000	-3.84157200	2.57684000
C	-1.97938600	-3.84740100	-0.25220100
H	-2.72859500	-4.36358200	-0.86035000
H	-1.47484100	-3.11123700	-0.87746800
H	-1.24601900	-4.58252200	0.09075000
C	-4.92417100	0.86183500	-1.15295300
C	-3.91016900	1.22804100	-2.23880000
H	-3.77300900	0.40455100	-2.94547700
H	-4.31793500	2.08236200	-2.78644400
H	-2.94233200	1.51743700	-1.83269100
C	-4.98671000	1.94112300	-0.07145800
H	-5.39949900	2.85283500	-0.51331000
H	-5.63986300	1.63154700	0.75022700

H	-3.99572300	2.16961300	0.32306700
C	-6.29984600	0.73421500	-1.81913700
H	-7.11248300	0.64861500	-1.09411200
H	-6.47670400	1.64687400	-2.39143600
H	-6.33663600	-0.11381300	-2.50921500
H	-6.64044800	-1.16316000	-0.29874600
H	-5.44884000	-3.30590200	0.86224500
C	2.70340100	1.76177400	0.42733600
C	1.95869900	2.44467100	1.39186000
C	2.52330900	3.49900800	2.10774900
C	3.83964500	3.88536000	1.87485100
C	4.58592000	3.21361600	0.90934600
C	4.02086100	2.16618000	0.18772800
H	0.92858700	2.17509500	1.59172500
H	1.92400400	4.01541800	2.85139500
H	4.27973300	4.70348500	2.43657700
H	5.61284800	3.50591600	0.71199600
H	4.61316700	1.66961800	-0.57429100
C	2.06214700	0.67814800	-0.42547300
H	1.48048500	1.17723100	-1.21144900
C	1.14056700	-0.32223500	0.24118100
C	0.56032600	-1.29574400	-0.54898700
H	0.94202800	-1.43205600	-1.55676600
H	0.16688900	-2.18938500	-0.08269900
C	0.99013300	-0.37458500	1.64930000
N	0.85075600	-0.44382600	2.80555000
O	3.06662900	-0.01226100	-1.21309200
C	3.91717300	-0.80291100	-0.54292100
O	3.93234500	-0.96478200	0.65287900
O	4.73078400	-1.35050800	-1.44299300
C	5.82828100	-2.21191500	-1.00336100
C	6.78323900	-1.42356800	-0.11419300
C	5.27545700	-3.45195800	-0.31035700
C	6.50624100	-2.58695200	-2.31441200
H	7.11162300	-0.51413700	-0.62701800
H	6.31512700	-1.15061800	0.83191600
H	7.66568800	-2.03504700	0.09475900
H	4.53980800	-3.94516900	-0.95285500
H	6.09331000	-4.15401200	-0.12432900
H	4.80637600	-3.20061200	0.64107400
H	7.36438800	-3.23396400	-2.11509000
H	5.81086300	-3.12000900	-2.96861400
H	6.85747800	-1.69102000	-2.83363700

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C	2.28358900	0.28448700	-2.04797700
H	3.05686000	0.70781600	-2.68220900
H	1.40086800	-0.11515600	-2.53490800
C	2.41424900	0.26442200	-0.72031600
C	1.34388800	-0.26837400	0.25930000
C	1.77874100	-0.15216300	1.72109800
H	0.98053900	-0.52256700	2.36566300
H	2.68026200	-0.73385200	1.93441700
H	1.97092000	0.89068100	1.98338700
C	1.00299800	-1.74052400	0.00085300
O	1.04589800	-2.61176800	0.83769600
O	0.60458200	-1.95859400	-1.26132800
C	0.15160000	-3.29342900	-1.56587700
H	-0.49740600	-3.63439900	-0.75467000
H	-0.44243900	-3.17903500	-2.47466900
C	1.31640200	-4.23740000	-1.78337100
H	1.89250500	-4.35695200	-0.86301600
H	0.93999800	-5.21831800	-2.08714100
H	1.97458600	-3.86405000	-2.57352400
C	5.64280900	0.91213800	0.86325500
C	3.66361000	0.82739700	-0.13189300
N	4.76096000	0.09831600	0.18660800
N	3.86450300	2.09270600	0.30590300
C	5.08534300	2.13907600	0.94540600
C	3.03773500	3.36157900	0.17301300
C	2.27527200	3.58822500	1.47695200
H	2.94737500	3.53970400	2.33895300
H	1.82382100	4.58387800	1.44943100
H	1.47354600	2.85886900	1.60882500
C	4.01953500	4.51729300	-0.06439800
H	4.70176800	4.29427200	-0.88963300
H	3.43679100	5.40143900	-0.33126100
H	4.59845600	4.77257900	0.82535500
C	2.08445600	3.31365500	-1.01720200
H	2.61764900	3.11410200	-1.95075300
H	1.28640300	2.58581000	-0.89680700
H	1.62248500	4.30142200	-1.09364800
C	5.17302100	-1.27367000	-0.31164100
C	5.66879000	-1.10175100	-1.74745400
H	6.47387200	-0.36243500	-1.79510500
H	6.05436500	-2.05912400	-2.10901500
H	4.85499400	-0.78852000	-2.40670100

C	4.03006700	-2.28188800	-0.25315000
H	4.45223000	-3.26617200	-0.47408300
H	3.57484800	-2.32815900	0.73823200
H	3.26613800	-2.08584400	-1.00436900
C	6.30916800	-1.78357500	0.57843000
H	6.02488600	-1.77605700	1.63486000
H	6.51907000	-2.81577200	0.29092700
H	7.23379900	-1.21769000	0.44412500
H	6.59525300	0.57177800	1.22840600
H	5.47039200	3.03429000	1.40125700
C	-3.07576400	-1.88219900	0.20892800
C	-2.55642600	-2.78889800	1.13880000
C	-3.29677000	-3.90080500	1.53926300
C	-4.56869700	-4.12480200	1.02007900
C	-5.09217000	-3.22915700	0.08945900
C	-4.35099600	-2.12249800	-0.31423300
H	-1.56122600	-2.61999400	1.53928900
H	-2.87575700	-4.59093300	2.26465400
H	-5.14694300	-4.98832400	1.33484300
H	-6.08234000	-3.39171400	-0.32655400
H	-4.76931600	-1.43965800	-1.04737200
C	-2.21022700	-0.73685900	-0.29498900
H	-1.66686300	-1.10381900	-1.17409700
C	-1.24154800	-0.13756100	0.63023600
C	-0.01402300	0.51502100	0.05228600
H	-0.15467100	0.65240100	-1.02627700
H	0.15304200	1.51448000	0.47445300
C	-1.51357100	0.03081000	1.98360200
N	-1.66155200	0.16521600	3.14381300
O	-3.09450200	0.25652400	-1.02603200
C	-3.96667800	0.94551900	-0.30941100
O	-4.21067000	0.80335600	0.86709100
O	-4.55521900	1.83149100	-1.13181100
C	-5.63528900	2.67200500	-0.63674100
C	-6.80684700	1.80765500	-0.18096500
C	-5.13242800	3.59413000	0.46935300
C	-6.02459500	3.48442400	-1.86605600
H	-7.09736900	1.11955800	-0.98139100
H	-6.55163600	1.23049500	0.70820300
H	-7.66432800	2.44767000	0.04759700
H	-4.25180500	4.14624600	0.12641500
H	-5.91404900	4.31815100	0.71869000
H	-4.87108500	3.03286200	1.36625700
H	-6.84328800	4.16578800	-1.61909300

H	-5.17432800	4.07408100	-2.22054500
H	-6.35242400	2.82473400	-2.67442000

TS3

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C	-2.08071400	0.08536700	2.01198100
H	-2.89488400	0.56171700	2.54985000
H	-1.24694400	-0.28895600	2.59558000
C	-2.10532900	-0.02736000	0.68330600
C	-0.96845800	-0.63891900	-0.16758000
C	-1.29729400	-0.65171300	-1.66264700
H	-0.47083100	-1.09713600	-2.21614000
H	-2.19434500	-1.23833100	-1.87876900
H	-1.45243800	0.36268100	-2.03595600
C	-0.63819200	-2.08164100	0.23798500
O	-0.61077000	-3.01663800	-0.52751400
O	-0.31410300	-2.18379900	1.53386600
C	0.12924400	-3.48120100	1.98275100
H	0.82833500	-3.88483200	1.24574000
H	0.66631600	-3.27939400	2.91094200
C	-1.04038900	-4.41575100	2.21280600
H	-1.56599300	-4.61570600	1.27661400
H	-0.67466700	-5.36556800	2.61276100
H	-1.74081100	-3.98744900	2.93533300
C	-5.15478100	0.50663800	-1.24853000
C	-3.28835300	0.49921300	-0.05519600
N	-4.35800500	-0.24859500	-0.41689400
N	-3.42419400	1.72310700	-0.61848400
C	-4.57402200	1.71925200	-1.38007400
C	-2.58608800	2.98852700	-0.50715500
C	-1.62991000	3.06259600	-1.69725800
H	-2.17290600	2.95191300	-2.64068200
H	-1.14568800	4.04350000	-1.69368400
H	-0.84706800	2.30348800	-1.64967300
C	-3.55422300	4.17928600	-0.55473800
H	-4.35890300	4.06963000	0.17777800
H	-2.98713600	5.07889400	-0.30729700
H	-3.98404000	4.33631900	-1.54585400
C	-1.83644800	3.06205500	0.82111500
H	-2.52279500	2.96029100	1.66672500
H	-1.04607600	2.32174100	0.91426200
H	-1.37516900	4.05180300	0.87475700
C	-4.83251600	-1.57106300	0.15625700
C	-5.45186300	-1.27044200	1.52123900

H	-6.24504700	-0.52212000	1.43234800
H	-5.88448200	-2.18889300	1.92765300
H	-4.69650800	-0.90709500	2.22250500
C	-3.70343600	-2.59078100	0.28724200
H	-4.15870900	-3.54542600	0.56360900
H	-3.16981300	-2.73504100	-0.65450100
H	-3.00009800	-2.33023800	1.07713100
C	-5.89334700	-2.14553900	-0.78504600
H	-5.51234800	-2.24548400	-1.80545500
H	-6.15652900	-3.14091400	-0.42165300
H	-6.81022900	-1.55203300	-0.79318000
H	-6.07058500	0.14005100	-1.67665500
H	-4.89992100	2.57091400	-1.95061800
C	3.65505000	-1.85134100	-0.22828300
C	3.26737800	-2.95599400	-0.99813800
C	4.21934100	-3.81389700	-1.54223200
C	5.57583800	-3.57515200	-1.33231500
C	5.96781400	-2.47444100	-0.57426300
C	5.01603100	-1.61891800	-0.02273200
H	2.20847000	-3.13391800	-1.16788300
H	3.89974000	-4.66461200	-2.13671000
H	6.32098100	-4.23854600	-1.76093100
H	7.02321700	-2.27488400	-0.41307500
H	5.31564500	-0.75627400	0.55847300
C	2.56400100	-1.00443100	0.36577900
H	2.15616000	-1.41986300	1.28782800
C	1.59942100	-0.44492400	-0.48765800
C	0.34984000	0.16837700	0.09183800
H	0.47979700	0.27559900	1.17360400
H	0.19135100	1.17636000	-0.30582800
C	1.89269500	-0.17367100	-1.84050000
N	2.03507300	0.04298300	-2.98070100
O	3.39761200	0.23368900	1.35529700
C	3.57481700	1.32987400	0.69205800
O	4.03137100	1.43542800	-0.43555000
O	3.15075500	2.40294000	1.42327400
C	3.07954200	3.71322700	0.81647600
C	4.45960600	4.20838000	0.38961200
C	2.08867500	3.69220800	-0.34699500
C	2.53991700	4.58849200	1.94384300
H	5.16046600	4.12416400	1.22647100
H	4.84162000	3.63072200	-0.45093700
H	4.39769100	5.26292600	0.10243500
H	1.11499900	3.33618800	0.00862600

H	1.95755800	4.70330400	-0.74635800
H	2.43578000	3.03632300	-1.14717900
H	2.41443400	5.61870400	1.59831400
H	1.57039200	4.21419500	2.28682100
H	3.22991200	4.58796600	2.79274100

TS3'

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C	0.84745400	-0.38795500	-1.39770600
H	1.28609300	-0.46746500	-2.38861300
H	-0.21247200	-0.60246100	-1.28280100
C	1.57742800	0.00197400	-0.35277500
C	1.00398200	0.16151600	1.08028700
C	2.07193200	0.64726500	2.06737400
H	1.62729900	0.78312300	3.05442300
H	2.89301200	-0.06787000	2.16870900
H	2.48605400	1.60381800	1.74049700
C	0.47030200	-1.17614600	1.62325400
O	0.80701000	-1.63803400	2.68919800
O	-0.42167100	-1.76275000	0.82164200
C	-1.06500500	-2.93657900	1.36317400
H	-1.29647100	-2.74762700	2.41346300
H	-1.99670700	-3.02140700	0.80501500
C	-0.19827100	-4.16810100	1.19766600
H	0.72205300	-4.07982900	1.77944000
H	-0.74666600	-5.04691700	1.54970900
H	0.05796900	-4.32701100	0.14538900
C	5.22491800	0.22317900	-0.44254100
C	3.01317800	0.34537600	-0.55646600
N	4.05518600	-0.50044700	-0.36573300
N	3.52050800	1.57952600	-0.78913900
C	4.89405800	1.50791600	-0.69362000
C	2.87203000	2.90233900	-1.16370300
C	2.87438400	3.80740500	0.06734800
H	3.87065300	3.87191900	0.51433300
H	2.57038800	4.81286500	-0.23641500
H	2.16739300	3.45494900	0.82170700
C	3.72831000	3.51945100	-2.27931000
H	3.86692900	2.81325500	-3.10273000
H	3.20079200	4.39552600	-2.66279200
H	4.70478900	3.85938000	-1.92928300
C	1.45711900	2.73992700	-1.70829300
H	1.43291700	2.08011300	-2.57911200
H	0.74966400	2.37992300	-0.96623500

H	1.12739800	3.73318300	-2.02404100
C	4.05831700	-2.01640100	-0.36175100
C	3.88231600	-2.46734900	-1.81196700
H	4.66338100	-2.04304500	-2.44965100
H	3.94917000	-3.55783100	-1.85842200
H	2.90461800	-2.16572300	-2.19706600
C	2.95568600	-2.59392600	0.51865300
H	3.11240900	-3.67477700	0.57110600
H	2.99533300	-2.19843300	1.53584700
H	1.96510400	-2.43251400	0.09581400
C	5.40761700	-2.49405200	0.17982000
H	5.61734700	-2.06604600	1.16446400
H	5.35706000	-3.57940000	0.28615800
H	6.23561100	-2.27434500	-0.49807800
H	6.19868900	-0.21680000	-0.32256700
H	5.53124800	2.36682800	-0.81355700
C	-3.23921200	1.96676600	0.78178200
C	-2.58937600	3.17405900	0.51691800
C	-3.16755000	4.13334400	-0.31506600
C	-4.41724000	3.90726200	-0.88142700
C	-5.08838200	2.71583500	-0.60201300
C	-4.50755500	1.75948900	0.22151100
H	-1.62844300	3.37301300	0.98011500
H	-2.63926200	5.06187900	-0.51097900
H	-4.87055500	4.65295900	-1.52737500
H	-6.06963100	2.53183500	-1.02967700
H	-5.03049500	0.83063000	0.42681700
C	-2.64189300	0.99005500	1.76379700
H	-3.28728400	0.86268100	2.63231600
C	-1.27295700	1.00464900	2.09605000
C	-0.19009900	1.18376800	1.05298500
H	-0.69249000	1.10457700	0.08649800
H	0.28193500	2.17657900	1.10830500
C	-0.94601600	0.79619900	3.44874700
N	-0.66892400	0.68048000	4.58013300
O	-3.20613700	-0.59293700	1.08381800
C	-2.97308800	-0.81514700	-0.16068900
O	-2.34527100	-0.12400200	-0.95696400
O	-3.56360900	-1.99087500	-0.53508200
C	-3.50256100	-2.44133300	-1.90862200
C	-4.31738700	-1.50198400	-2.79294600
C	-2.06211100	-2.57814900	-2.40514500
C	-4.15651400	-3.81820300	-1.84372100
H	-5.35428700	-1.46027600	-2.44499900

H	-3.89491700	-0.49602800	-2.76983300
H	-4.31486400	-1.86399100	-3.82596700
H	-1.43359700	-3.02045500	-1.62385900
H	-2.04049400	-3.24123300	-3.27612400
H	-1.64241600	-1.61322900	-2.68602700
H	-4.24379200	-4.24485300	-2.84692000
H	-3.55725400	-4.49672600	-1.22791300
H	-5.15608100	-3.74553700	-1.40643100

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C	1.42149200	0.13096200	2.13522600
H	2.34304700	0.29779800	2.68466800
H	0.49584600	0.16752100	2.69982600
C	1.43816600	-0.07398100	0.81850200
C	0.16955000	-0.28059800	-0.04723100
C	0.51441700	-0.72736600	-1.47083900
H	-0.38280100	-0.77370700	-2.08823400
H	1.20360200	-0.03345700	-1.95757800
H	0.97910900	-1.71605400	-1.45463300
C	-0.65446200	1.01674200	-0.13127800
O	-1.01533500	1.52545700	-1.16554000
O	-1.00658200	1.46501400	1.07788300
C	-1.94442800	2.56688200	1.10610100
H	-2.71192600	2.38662300	0.34884500
H	-2.39590100	2.50992200	2.09824000
C	-1.25421000	3.89671200	0.89184000
H	-0.78064200	3.93654000	-0.09232300
H	-1.99752900	4.69683500	0.94860400
H	-0.50030100	4.07297800	1.66349400
C	4.44891600	0.47904500	-1.19080600
C	2.75819900	-0.08710200	0.12124400
N	3.32583900	0.94603700	-0.54516700
N	3.53723900	-1.18173800	-0.06623200
C	4.58438200	-0.82999000	-0.88797400
C	3.54740900	-2.50991600	0.67354000
C	2.15153500	-3.09897300	0.84064900
H	1.64766200	-3.21643700	-0.12254600
H	2.26664700	-4.09287800	1.28036000
H	1.53584500	-2.51259200	1.51862300
C	4.39128100	-3.50178200	-0.13218000
H	5.45577800	-3.25798200	-0.11674100
H	4.28019700	-4.48370400	0.33184800
H	4.04601200	-3.57484500	-1.16744600

C	4.19456300	-2.25864100	2.03576900
H	5.18140600	-1.80128900	1.91939000
H	3.56979000	-1.60974800	2.65459200
H	4.31507200	-3.21457700	2.55329500
C	2.94271700	2.41286000	-0.65074200
C	4.24245700	3.22273100	-0.74493200
H	4.74693100	3.10121000	-1.70563100
H	3.98263600	4.27927100	-0.65215500
H	4.93212400	2.96625200	0.06408200
C	2.19040500	2.89313200	0.58633200
H	2.05656000	3.97295100	0.48095000
H	1.20335600	2.45127300	0.69409400
H	2.76264200	2.70588700	1.49967800
C	2.11832200	2.60892800	-1.92035700
H	1.13877200	2.13258600	-1.84692500
H	1.96071500	3.68066600	-2.07365100
H	2.64815500	2.21342000	-2.79227400
H	5.07281900	1.10245900	-1.80624400
H	5.35130800	-1.51974300	-1.18997200
C	-4.62516500	-0.60164900	0.25557700
C	-5.37590500	0.33983100	0.97873900
C	-6.71892900	0.55659000	0.69683500
C	-7.34110400	-0.17708000	-0.30999800
C	-6.61242100	-1.12611000	-1.02636500
C	-5.26704600	-1.34059400	-0.75145400
H	-4.89081300	0.90623400	1.76950100
H	-7.27882900	1.29349300	1.26361200
H	-8.39069400	-0.01455700	-0.53399000
H	-7.09637700	-1.70572200	-1.80594500
H	-4.73075700	-2.09206700	-1.31800400
C	-3.21279900	-0.72712600	0.62971600
H	-2.95267500	-0.18175800	1.53641700
C	-2.17964500	-1.37125600	0.04753300
C	-0.78094400	-1.32242200	0.63456300
H	-0.87468700	-1.09156800	1.69713200
H	-0.32078000	-2.30775500	0.54107800
C	-2.32572200	-2.14931200	-1.15078200
N	-2.38052900	-2.79863600	-2.10948000

M4-pre

-1 1

C	1.10823600	-0.32353100	-1.88543100
H	2.11018900	-0.40236900	-2.32800500
H	0.22330300	-0.51964900	-2.48686600

C	0.98175500	0.03623900	-0.60989100
C	-0.38019900	0.22897100	0.11594900
C	-0.21901100	0.82545300	1.51723200
H	-1.18333000	0.88486600	2.02433800
H	0.43432900	0.21186100	2.14215400
H	0.20462900	1.83107200	1.45397600
C	-1.11351400	-1.11189100	0.26240600
O	-1.42599500	-1.61311100	1.31824100
O	-1.43120600	-1.64265300	-0.92497700
C	-2.25069200	-2.82967200	-0.90525100
H	-3.04341100	-2.69253800	-0.16468300
H	-2.69434200	-2.86738300	-1.90216900
C	-1.43623800	-4.07452500	-0.62204900
H	-1.01459500	-4.04212500	0.38499900
H	-2.08249600	-4.95359300	-0.70031900
H	-0.62423700	-4.17792300	-1.34679000
C	3.52418800	0.01371000	1.98549700
C	2.19364700	0.25844600	0.23356300
N	2.68046200	-0.63920300	1.11852800
N	2.74771400	1.45785700	0.52161500
C	3.56673600	1.30892900	1.61555900
C	2.80344100	2.76271100	-0.24010900
C	4.28797800	2.99628500	-0.55720800
H	4.69134800	2.06905900	-0.98923600
H	4.36538100	3.82469400	-1.26865100
H	4.85260100	3.27877800	0.33759500
C	2.05000400	2.71380200	-1.56108600
H	0.98016800	2.55276100	-1.42863300
H	2.18120300	3.69335200	-2.03240600
H	2.49594700	1.93254800	-2.18555800
C	2.23148400	3.85669800	0.66177600
H	1.15659600	3.72153000	0.82203800
H	2.72765100	3.88990400	1.63644500
H	2.38117500	4.82623900	0.17758300
C	2.56895700	-2.14402300	1.21306600
C	4.00931200	-2.67463200	1.21271100
H	4.53897800	-2.43758200	2.14050800
H	3.97215200	-3.76544400	1.13033700
H	4.52551300	-2.24407500	0.34292800
C	1.85593800	-2.76848900	0.01988000
H	1.89451500	-3.85308900	0.16928200
H	0.80596900	-2.48903600	-0.03684800
H	2.39443500	-2.49681400	-0.89686300
C	1.82825000	-2.46760800	2.51064700

H	0.78934000	-2.12455100	2.46121100
H	1.82303100	-3.55237100	2.65611700
H	2.31115600	-2.01375200	3.38210100
H	4.05027900	-0.49661800	2.77358300
H	4.14604100	2.12330200	2.01572800
C	-5.13204300	0.38314000	-0.41207900
C	-5.61577200	0.67139700	0.87246200
C	-6.97467100	0.56992300	1.14879200
C	-7.86906500	0.17591600	0.15504700
C	-7.39662400	-0.13455900	-1.11866000
C	-6.03791100	-0.04187100	-1.39564400
H	-4.93138800	0.94801900	1.66671700
H	-7.33478100	0.79053200	2.14870900
H	-8.92898300	0.09878900	0.37661400
H	-8.08513900	-0.45590500	-1.89376800
H	-5.66595200	-0.29194100	-2.38575800
C	-3.71385200	0.46508500	-0.78300700
H	-3.42049300	-0.16781300	-1.61974300
C	-2.73186300	1.22832500	-0.26158500
C	-1.29829000	1.14730600	-0.74921900
H	-1.30966300	0.78178800	-1.77713000
H	-0.86251400	2.15022900	-0.75112900
C	-2.99879400	2.20795500	0.75787900
N	-3.16239200	3.03064700	1.55793200
C	4.37949500	-0.47421500	-1.61867500
O	5.14608200	-0.13996400	-0.64027800
O	4.04288300	-1.71050400	-1.80648000
O	3.91068700	0.43854400	-2.42280000

TS4

-1 1

C	1.23732000	0.52585700	1.80053600
H	2.52704200	0.78956000	2.06644100
H	0.35921600	0.82738800	2.38629700
C	0.96849900	0.05501900	0.57702400
C	-0.43252000	-0.08510000	-0.10267400
C	-0.35652000	-0.65993700	-1.52229600
H	-1.33164000	-0.61325700	-2.01252600
H	0.33935000	-0.09064500	-2.14258800
H	-0.02577300	-1.70031400	-1.50392400
C	-1.05518600	1.30903500	-0.22035600
O	-1.19233000	1.91677100	-1.25995800
O	-1.45258200	1.79426600	0.96295200
C	-2.08379700	3.08881700	0.95679200

H	-2.80113000	3.12674200	0.13267500
H	-2.62524600	3.12849600	1.90391300
C	-1.06551400	4.20650400	0.86126800
H	-0.58342000	4.21003200	-0.11816500
H	-1.56513600	5.16877700	1.00481300
H	-0.30050300	4.09483700	1.63480400
C	3.62750900	-0.36009200	-1.89859200
C	2.12241800	-0.35783800	-0.26978000
N	2.79675600	0.43310700	-1.13554800
N	2.55064400	-1.62909500	-0.45797900
C	3.47214000	-1.63203600	-1.48105100
C	2.33986200	-2.89029600	0.35481500
C	3.71275900	-3.57276500	0.47648100
H	4.43184700	-2.83010800	0.83747300
H	3.62543100	-4.38392500	1.20417100
H	4.04687400	-4.02232300	-0.46256000
C	1.86695100	-2.60099900	1.77772400
H	0.84622900	-2.22824300	1.82281900
H	1.90005900	-3.55074700	2.32108200
H	2.55470700	-1.87842100	2.22759500
C	1.35938200	-3.79753100	-0.38845800
H	0.33952100	-3.40271500	-0.36809500
H	1.65938500	-3.94131500	-1.43180500
H	1.34567400	-4.77710900	0.09899400
C	2.80284700	1.92751600	-1.37667600
C	4.27561100	2.35996400	-1.41418800
H	4.78948700	2.00566500	-2.31290600
H	4.30706900	3.45320100	-1.43996800
H	4.80055200	1.99459100	-0.51824900
C	2.12031500	2.73433600	-0.27769600
H	2.24450300	3.78810100	-0.54878200
H	1.05313200	2.53563700	-0.22016900
H	2.60376700	2.53849200	0.68305400
C	2.10476200	2.17711800	-2.71510100
H	1.03472900	1.95771600	-2.64119400
H	2.21656600	3.23246800	-2.98198900
H	2.54077700	1.57621100	-3.51934200
H	4.26758500	0.03933400	-2.66576000
H	3.96334900	-2.52564200	-1.82205100
C	-5.19007900	-0.24866000	0.36527600
C	-5.64951900	-0.61349500	-0.90876300
C	-7.00730700	-0.56536200	-1.20558300
C	-7.92534100	-0.14932800	-0.24275800
C	-7.47780100	0.23657000	1.01948700

C	-6.12052000	0.19736400	1.31612700
H	-4.94681300	-0.90943400	-1.67973800
H	-7.34795500	-0.84563700	-2.19723200
H	-8.98399900	-0.11406900	-0.47995900
H	-8.18511800	0.57393800	1.77034300
H	-5.76884900	0.50493900	2.29721700
C	-3.77500200	-0.27875500	0.75750500
H	-3.49874500	0.41491100	1.55017000
C	-2.78099200	-1.06752500	0.30340300
C	-1.35092800	-0.95831000	0.79487700
H	-1.35597200	-0.54336800	1.80492600
H	-0.91643400	-1.96021600	0.84396300
C	-3.02438100	-2.11345900	-0.65541900
N	-3.15584500	-2.98833300	-1.40473600
C	4.62710500	0.40386000	1.57638400
O	5.69676600	0.85932300	1.07483200
O	3.71177600	1.27482400	2.01490700
O	4.36718900	-0.84219900	1.69654900

M4

-1 1

C	1.11653000	0.17214900	1.85931400
H	2.93440000	0.02760000	2.27759400
H	0.14558400	0.24925700	2.38698300
C	0.92434900	-0.08115800	0.55192000
C	-0.42601400	-0.28218300	-0.22616000
C	-0.20917600	-0.82049700	-1.64332500
H	-1.14899600	-0.89887000	-2.19303800
H	0.44943700	-0.16958200	-2.22433400
H	0.25029700	-1.81129400	-1.59532500
C	-1.21340800	1.02362000	-0.33749000
O	-1.57636500	1.52874300	-1.37852300
O	-1.53501100	1.53265600	0.86132500
C	-2.40622700	2.67830300	0.85516500
H	-3.19564000	2.51538600	0.11582700
H	-2.84538800	2.69275800	1.85536500
C	-1.65141300	3.96248400	0.57716500
H	-1.19635600	3.93480100	-0.41587500
H	-2.34554200	4.80699900	0.61813400
H	-0.87013500	4.12173800	1.32477100
C	3.75891300	0.30597900	-1.75917400
C	2.15707700	-0.17678700	-0.29043500
N	2.69389800	0.81267300	-1.04889500
N	2.91101400	-1.28774700	-0.50258900

C	3.89478300	-0.99029500	-1.42150500
C	2.89950000	-2.68172300	0.08272000
C	4.34181000	-3.00577900	0.50609400
H	4.77578800	-2.17793300	1.07840600
H	4.32233000	-3.90852300	1.12380700
H	4.98036800	-3.22469000	-0.35524000
C	2.00281300	-2.83281700	1.30398800
H	0.95698800	-2.63567700	1.07889900
H	2.09089900	-3.87407300	1.63018400
H	2.32815000	-2.16880200	2.10447900
C	2.44199800	-3.64698300	-1.01478600
H	1.38252800	-3.51436700	-1.25164100
H	3.02354600	-3.52068600	-1.93282100
H	2.58309000	-4.67343000	-0.66320100
C	2.38023500	2.28860200	-1.12911500
C	3.70988000	3.03678000	-1.31170100
H	4.13276800	2.90835600	-2.31206100
H	3.51361800	4.10501700	-1.18671800
H	4.41536200	2.70250800	-0.54468200
C	1.74956300	2.81186000	0.15938600
H	1.69513400	3.90209900	0.07161400
H	0.74368300	2.43622300	0.32802600
H	2.38459300	2.53115400	1.00390800
C	1.47787400	2.52200800	-2.33952300
H	0.49635700	2.06112000	-2.20989900
H	1.33082700	3.59903600	-2.47283000
H	1.93938700	2.12821000	-3.25176500
H	4.35258800	0.90142300	-2.42885900
H	4.62321000	-1.71302700	-1.74561900
C	-5.19158700	-0.51250700	0.54679500
C	-5.94543400	-1.45692200	-0.16605000
C	-7.30745100	-1.26074700	-0.36681300
C	-7.94125400	-0.12661300	0.13796200
C	-7.20721700	0.80940400	0.86314400
C	-5.84803200	0.61076600	1.07363500
H	-5.48028100	-2.35811500	-0.54794800
H	-7.87778800	-2.00339200	-0.91586100
H	-9.00436600	0.02106300	-0.02472300
H	-7.69348100	1.68979000	1.27129100
H	-5.27662600	1.33523700	1.64837900
C	-3.74994600	-0.62359400	0.80823500
H	-3.39987300	-0.03296200	1.65415200
C	-2.78831600	-1.30318900	0.15072300
C	-1.33389800	-1.25986200	0.58179400

H	-1.30481700	-0.97192300	1.63389500
H	-0.90971800	-2.26437400	0.49239300
C	-3.08658500	-2.10163600	-1.00813200
N	-3.27596900	-2.76704200	-1.93861000
C	4.78244300	0.34321600	1.65488400
O	5.88901100	-0.21455000	1.50065000
O	3.85331800	-0.38424700	2.36843100
O	4.41962300	1.47933400	1.24970400

TS5

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C	-1.64272700	0.76388300	-1.83456100
H	-2.59628900	0.78021000	-2.34567100
C	-1.25619900	0.33603300	-0.70813900
C	0.07587800	0.27300400	0.02729600
C	-0.02055800	-0.02862700	1.52155400
H	0.96769700	0.04766900	1.98329100
H	-0.66299900	0.70224700	2.01165800
H	-0.42164200	-1.02483600	1.70886000
C	0.65672900	1.69381700	-0.10777700
O	0.55102700	2.54555700	0.74586700
O	1.27329600	1.90248100	-1.27454700
C	1.60363200	3.27025300	-1.58118600
H	2.06850200	3.73143900	-0.70708900
H	2.33881100	3.20399900	-2.38507400
C	0.36282200	4.01956400	-2.02180500
H	-0.36284200	4.07189000	-1.20605400
H	0.62902000	5.03873100	-2.31533000
H	-0.10373000	3.51685700	-2.87258600
C	-5.02108100	-0.04602000	-0.13426100
C	-2.81903600	-0.44506700	0.24193100
N	-3.86068200	0.42140000	0.45472100
N	-3.39809700	-1.49908400	-0.41213100
C	-4.72907200	-1.24538500	-0.68480300
C	-2.73465000	-2.77018400	-0.81834100
C	-1.69317800	-3.14209500	0.23174000
H	-2.16892800	-3.31773400	1.20158700
H	-1.17825300	-4.05668100	-0.07544300
H	-0.95251000	-2.35679200	0.35572000
C	-3.78132900	-3.88906600	-0.86702500
H	-4.47223400	-3.77642400	-1.70667900
H	-3.26095000	-4.84121000	-0.99913100
H	-4.35478600	-3.93845600	0.06339800
C	-2.10902500	-2.61481200	-2.20751800

H	-2.87032600	-2.30512900	-2.93135900
H	-1.31330600	-1.86930000	-2.21133900
H	-1.69970200	-3.57641200	-2.53223400
C	-3.82448000	1.61718300	1.34921400
C	-5.18416300	2.31775500	1.32429900
H	-5.98562100	1.67666600	1.70171800
H	-5.12573600	3.19250900	1.97620900
H	-5.44352700	2.66413200	0.31924500
C	-2.76107700	2.61315700	0.89146300
H	-2.83661500	3.51369800	1.50861100
H	-1.75180600	2.21983400	0.99752200
H	-2.91412900	2.89236900	-0.15513900
C	-3.54406100	1.12981600	2.77249100
H	-2.59391000	0.59449800	2.82133500
H	-3.50227500	1.98116400	3.45840000
H	-4.33724900	0.45300900	3.10563400
H	-5.96152400	0.47605500	-0.10088600
H	-5.37048500	-1.93413200	-1.20824800
C	4.83652100	-0.33485500	-0.04999400
C	5.84508400	0.07465200	-0.93601700
C	7.18332600	0.03174300	-0.56374400
C	7.53552100	-0.40438600	0.71195400
C	6.54170300	-0.78909600	1.61063300
C	5.20247900	-0.75435400	1.23823200
H	5.56779000	0.42118900	-1.92791500
H	7.94981500	0.34433200	-1.26564500
H	8.57900900	-0.43381400	1.00925100
H	6.80957400	-1.10989200	2.61225500
H	4.44520000	-1.03166300	1.96259100
C	3.45134300	-0.26946700	-0.53240200
H	3.29177500	0.39856100	-1.37684200
C	2.35589600	-0.93293000	-0.11321900
C	0.98715200	-0.73545300	-0.73140200
H	1.09897300	-0.38005300	-1.75661700
H	0.47805500	-1.70016700	-0.77523500
C	2.41028600	-1.92334500	0.92948500
N	2.38108800	-2.74331200	1.74856400

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C	-4.64795700	-1.08942900	-0.97244300
H	-5.63188900	-1.14838800	-1.38823000
C	-3.54130900	-1.01874400	-0.49903400
C	-2.19044600	-0.97435500	0.08407800

C	-2.11404200	-1.90793800	1.29719000
H	-1.14896500	-1.80967100	1.79785100
H	-2.89490500	-1.65517000	2.01676400
H	-2.25031500	-2.94322900	0.97526400
C	-1.89132800	0.46573500	0.53092500
O	-1.61738600	0.78279700	1.66166300
O	-1.94101000	1.31522800	-0.49966700
C	-1.66610000	2.70064200	-0.20222700
H	-0.81814200	2.75144600	0.48533400
H	-1.37907800	3.13393500	-1.16188900
C	-2.88961100	3.38296500	0.37238700
H	-3.16247300	2.94125800	1.33342400
H	-2.67819600	4.44429700	0.52785100
H	-3.73539600	3.29435900	-0.31396600
C	2.39866100	0.14580300	-0.44651700
C	3.38371100	-0.83314300	-0.24692100
C	4.67678000	-0.46323100	0.10565500
C	5.00923900	0.88118200	0.26277300
C	4.04380800	1.86284100	0.04783700
C	2.75351700	1.49680100	-0.31580800
H	3.15310800	-1.88282200	-0.38855800
H	5.43084300	-1.23013800	0.25108900
H	6.02020200	1.16253000	0.54047300
H	4.29743000	2.91255400	0.15641800
H	2.00141600	2.26128100	-0.49251800
C	1.00755800	-0.15078600	-0.81051200
H	0.48630900	0.66362100	-1.31377000
C	0.27238800	-1.25918100	-0.58936000
C	-1.17288400	-1.36497000	-1.02940900
H	-1.32915300	-0.70890200	-1.88793500
H	-1.39980200	-2.38871600	-1.34043000
C	0.79773800	-2.39965800	0.11190900
N	1.16112100	-3.34709300	0.67195900