Supplementary Information

For

Visible-Light-Mediated Photocatalytic Cross- Coupling of Acetenyl Ketones with Benzyl Trifluoroborate

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Contents

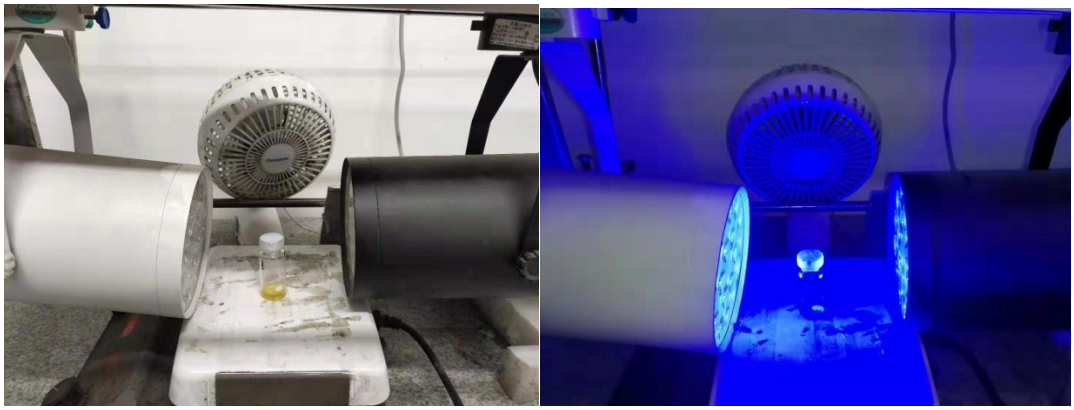
1. General information

General methods. All reagents were purchased from commercial suppliers such as Aldrich, Energy Chemical Chemicals and Aladdin. All were used as received. Unless other noted, all photochemical reactions were carried out in a 10 ml, flame-dried glass tube under nitrogen atmosphere. 1H NMR (400 MHz) and 13C NMR (101 MHz) were recorded on Bruker AV-400 instrument in CDCl3 with TMS as internal standard. The chemical shifts (δ) are given in parts per million relative to the chemical shift of TMS at 0.00 ppm in CDCl3 for 1H, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet) and for 13C NMR spectra were relative to the center line signal of the CDCl3 triplet at 77.00 ppm. Cyclic voltammogram was obtained with CHI 620E electrochemical analyzer. HRMS (ESI) spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS analysis was performed on a 7890A-5975C/Agilent. Fluorescence spectra were measured on a Shimadzu RF-5301PC Spectrofluorometer at room temperature. For irradiation with blue light NVC SLED 320B (blue, 18W) was used. The reaction process was monitored by thin-layer chromatography on silica gel GF 254. Flash column chromatography was performed using 200-300 mesh silica gel with petroleum and ethyl acetate as eluent. The removal of solvent was performed on a rotary evaporator.

Solvents. All the relevant solvents were purified according to the procedure from "Purification of Laboratory Chemicals book".

Photocatalytic reactions. The photocatalytic reactions were carried out in a dried glass tube, which was sealed with a rubber septum and a coiled seal film. The used light source is blue LEDs with a power output of 36 W. To maintain the temperature at room temperature, a clip fan was placed in front of the reaction system.

The picture of irradiation equipment is as below.



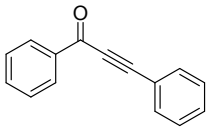
2. The preparation procedure for acetenyl ketones.

2.1 General procedure for the preparation of acetenyl ketones[1]

To a dry, 50 ml two-neck flask was added acid chloride (6 mmol), alkyne (4 mmol), $PdCl_2(PPh_3)_2$ (0.02 equiv) and CuI (0.02 equiv). The flask was filled with N_2 for three times by evacuating air. Then degassed THF (8 ml) was added to the flask by syringe. After stirring at room temperature for 2 min, Et_3N (5 mmol) was added. The reaction system was stirred for 5 hours then diluted by EtOAc (20 ml) and washed by H_2O for three times. The organic layer was combined and dried by anhydrous Na_2SO_4 overnight. The suspension was filtered and the filtrate was evacuated under

reduced pressure. The resulting residue was purified by column chromatography (PE/EtOAc as eluent) to afford corresponding acetenyl ketones.

2.2 Characterization of acetenyl ketones.

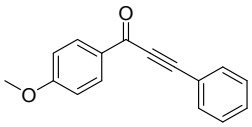


1,3-diphenylprop-2-yn-1-one (1a), colorless oil. Yield = 97%. Prepared according to the general method by employing benzoyl chloride and ethynylbenzene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.17 (m, 2H), 7.72 – 7.65 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.37 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.91, 136.77, 134.05, 132.98, 130.73, 129.47, 128.61, 128.55, 119.99, 93.03, 86.81.

HRMS (ESI): calc. for $C_{15}H_{10}NaO$ $[M+Na]^+$: 229.0624, found: 229.0623.

The ^{1}H and ^{13}C NMR data are consistent with previous literature.[2]

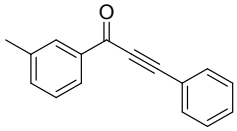


1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (1b), slightly brown oil. Yield = 80%. Prepared according to the general method by employing 4-methoxybenzoyl chloride and ethynylbenzene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.04 (m, 2H), 7.69 – 7.56 (m, 2H), 7.48 – 7.29 (m, 3H), 7.00 – 6.84 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.63, 164.44, 132.91, 131.94, 130.55, 130.25, 128.61, 120.30, 113.84, 92.27, 86.87, 55.55.

HRMS (ESI): calc. for $C_{16}H_{12}NaO_2$ $[M+Na]^+$: 259.0730, found: 259.0734.

The ^{1}H and ^{13}C NMR data are consistent with previous literature.[3]

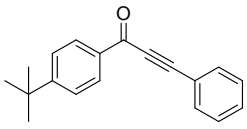


3-phenyl-1-(m-tolyl)prop-2-yn-1-one (1d), colorless oil. Yield = 87%. Prepared according to the general method by employing 3-methylbenzoyl chloride and ethynylbenzene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.99 (m, 2H), 7.75 – 7.65 (m, 2H), 7.55 – 7.37 (m, 5H), 2.46 (d, *J* = 3.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.99, 138.32, 136.73, 134.84, 132.87, 130.61, 129.59, 128.53, 128.37, 126.95, 119.99, 92.72, 86.87, 21.17.

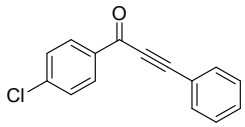
HRMS (ESI): calc. for $C_{16}H_{12}NaO$ $[M+Na]^+$: 243.0780, found: 243.0782.

The ^{1}H and ^{13}C NMR data are consistent with previous literature.[3]

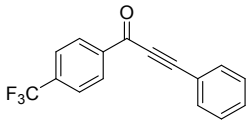


1-(4-(tert-butyl)phenyl)-3-phenylprop-2-yn-1-one (1e), colorless oil. Yield = 80%. Prepared according to the general method by employing 4-(tert-butyl)benzoyl chloride and ethynylbenzene.

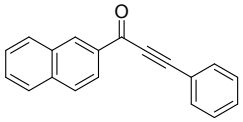
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.12 (m, 2H), 7.71 – 7.63 (m, 2H), 7.55 – 7.50 (m, 2H), 7.42 (ddd, *J* = 14.6, 7.9, 6.4 Hz, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.58, 158.00, 134.42, 132.92, 130.60, 129.46, 128.57, 125.53, 120.15, 92.52, 86.94, 35.17, 30.96.
HRMS (ESI): calc. for $C_{19}H_{18}NaO$ $[M+Na]^+$: 285.1250, found: 285.1251.



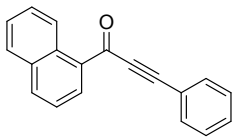
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (1f), slightly yellow oil. Yield = 85%. Prepared according to the general method by employing 4-chlorobenzoyl chloride and ethynylbenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.74 – 7.62 (m, 2H), 7.58 – 7.32 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.64, 140.68, 135.25, 133.08, 130.96, 130.84, 128.97, 128.71, 119.84, 93.61, 86.54.
HRMS (ESI): calc. for $C_{15}H_9ClNaO$ $[M+Na]^+$: 263.0234, found: 263.0236.



3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (1g), colorless oil. Yield = 73%. Prepared according to the general method by employing 4-(trifluoromethyl)benzoyl chloride and ethynylbenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.1 Hz, 2H), 7.89 – 7.65 (m, 4H), 7.59 – 7.36 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.70, 139.35, 135.15 (q, *J* = 32.7 Hz), 133.18, 131.19, 129.78, 128.78, 125.69 (q, *J* = 3.7 Hz), 123.51 (q, *J* = 272.9 Hz), 119.63, 94.46, 86.55.
HRMS (ESI): calc. for $C_{16}H_9F_3NaO$ $[M+Na]^+$: 297.0498, found: 297.0500.
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[4]

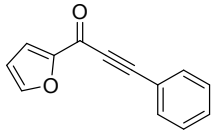


1-(naphthalen-2-yl)-3-phenylprop-2-yn-1-one (1h), colorless solid. Yield = 92%. Prepared according to the general method by employing 2-naphthoyl chloride and ethynylbenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.21 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.10 – 7.84 (m, 3H), 7.79 – 7.70 (m, 2H), 7.68 – 7.35 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.92, 136.13, 134.38, 133.04, 132.64, 132.38, 130.76, 129.86, 129.00, 128.69, 128.52, 127.89, 126.93, 123.94, 120.18, 93.03, 87.03.
HRMS (ESI): calc. for $C_{19}H_{12}NaO$ $[M+Na]^+$: 279.0780, found: 279.0781.
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[5]

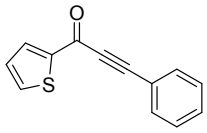


1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-one (1i), colorless solid. Yield = 70%. Prepared according to the general method by employing 1-naphthoyl chloride and ethynylbenzene.

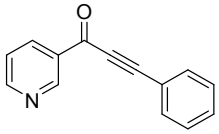
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 8.7 Hz, 1H), 8.64 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.64 (m, 3H), 7.57 (dt, *J* = 8.1, 4.6 Hz, 2H), 7.51 – 7.35 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.70, 135.08, 134.51, 133.83, 132.91, 130.69, 130.58, 128.93, 128.62, 128.54, 126.73, 125.95, 124.44, 120.30, 91.66, 88.45.
HRMS (ESI): calc. for $C_{19}H_{12}NaO$ $[M+Na]^+$: 279.0780, found: 279.0783.
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[5]



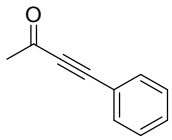
1-(furan-2-yl)-3-phenylprop-2-yn-1-one (1j), colorless oil. Yield = 79%. Prepared according to the general method by employing furan-2-carbonyl chloride and ethynylbenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.59 (m, 3H), 7.53 – 7.34 (m, 4H), 6.61 (dd, *J* = 3.6, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.59, 153.03, 147.97, 132.90, 130.77, 128.56, 120.92, 119.67, 112.59, 91.75, 86.09.
HRMS (ESI): calc. for $C_{13}H_8NaO_2$ $[M+Na]^+$: 219.0417, found: 219.0419.
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[6]



3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-one (1k), colorless oil. Yield = 95%. Prepared according to the general method by employing thiophene-2-carbonyl chloride and ethynylbenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.71 – 7.49 (m, 3H), 7.45 – 7.27 (m, 3H), 7.09 (dd, *J* = 4.9, 3.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.69, 144.81, 135.21, 135.05, 132.94, 130.78, 128.61, 128.29, 119.79, 91.66, 86.38.
HRMS (ESI): calc. for $C_{13}H_8NaOS$ $[M+Na]^+$: 235.0188, found: 235.0189.
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[7]



3-phenyl-1-(pyridin-3-yl)prop-2-yn-1-one (1l), brown oil. Yield = 86%. Prepared according to the general method by employing nicotinoyl chloride and ethynylbenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 – 9.26 (m, 1H), 8.77 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.36 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.75 – 7.56 (m, 2H), 7.53 – 7.30 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.37, 154.20, 151.41, 136.16, 133.22, 132.16, 131.23, 128.76, 123.52, 119.51, 94.70, 86.23.
HRMS (ESI): calc. for $C_{14}H_9NNaO$ $[M+Na]^+$: 230.0576, found: 230.0575.

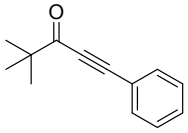


4-phenylbut-3-yn-2-one (1m), colorless oil. Yield = 36%. Prepared according to the general method by employing acetyl chloride and ethynylbenzene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.49 – 7.41 (m, 1H), 7.41 – 7.34 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.44, 132.89, 130.61, 128.50, 119.73, 90.17, 88.13, 32.59.

HRMS (ESI): calc. for $C_{10}H_8NaO$ $[M+Na]^+$: 167.0467, found: 167.0465.

The ^{1}H and ^{13}C NMR data are consistent with previous literature.[8]

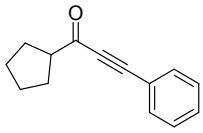


4,4-dimethyl-1-phenylpent-1-yn-3-one (1n), slightly yellow oil. Yield = 87%. Prepared according to the general method by employing pivaloyl chloride and ethynylbenzene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 2H), 7.50 – 7.35 (m, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.30, 132.94, 130.53, 128.58, 120.24, 92.21, 85.97, 44.87, 26.12.

HRMS (ESI): calc. for $C_{13}H_{14}NaO$ $[M+Na]^+$: 209.0937, found: 209.0938.

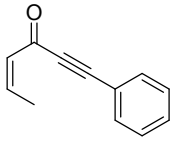
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[6]



1-cyclopentyl-3-phenylprop-2-yn-1-one (1o), colorless oil. Yield = 57%. Prepared according to the general method by employing cyclopentanecarbonyl chloride and ethynylbenzene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.48 – 7.41 (m, 1H), 7.41 – 7.33 (m, 2H), 3.17 – 2.92 (m, 1H), 2.07 – 1.89 (m, 4H), 1.78 – 1.59 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.01, 132.89, 130.49, 128.51, 120.07, 91.08, 87.19, 53.67, 29.04, 25.91.

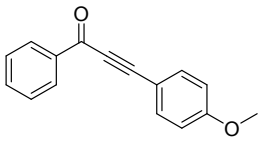
HRMS (ESI): calc. for $C_{14}H_{14}NaO$ $[M+Na]^+$: 221.0937, found: 221.0938.



1-phenylhex-4-en-1-yn-3-one (1p), slightly yellow oil. Yield = 57%. Prepared according to the general method by employing but-2-enoyl chloride and ethynylbenzene.

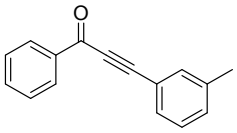
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 2H), 7.48 – 7.34 (m, 3H), 7.28 (dt, J = 13.7, 6.9 Hz, 1H), 6.35 – 6.19 (m, 1H), 2.02 (dd, J = 6.9, 0.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.27, 149.48, 133.78, 132.76, 132.72, 130.41, 128.49, 120.03, 90.98, 86.06, 18.37.

HRMS (ESI): calc. for $C_{12}H_{10}NaO$ $[M+Na]^+$: 193.0624, found: 193.0625.

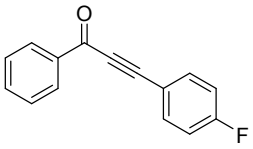


3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (1q), colorless oil. Yield = 93%. Prepared

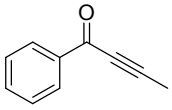
according to the general method by employing benzoyl chloride and 1-ethynyl-4-methoxybenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.16 (m, 2H), 7.63 (dd, *J* = 14.5, 8.1 Hz, 3H), 7.52 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.04, 161.72, 137.04, 135.14, 133.88, 129.48, 128.54, 114.41, 111.89, 94.29, 86.86, 55.43.
HRMS (ESI): calc. for $C_{16}H_{12}NaO_2$ $[M+Na]^+$: 259.0730, found: 259.0732.
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[3]



1-phenyl-3-(m-tolyl)prop-2-yn-1-one (1r), colorless oil. Yield = 80%. Prepared according to the general method by employing benzoyl chloride and 1-ethynyl-3-methylbenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.13 (m, 2H), 7.67 – 7.57 (m, 1H), 7.56 – 7.42 (m, 4H), 7.36 – 7.23 (m, 2H), 2.36 (d, *J* = 3.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.92, 138.44, 136.83, 134.01, 133.47, 131.71, 130.16, 129.47, 128.54, 128.52, 119.81, 93.44, 86.61, 21.11.
HRMS (ESI): calc. for $C_{16}H_{12}NaO$ $[M+Na]^+$: 243.0780, found: 243.0782.
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[9]

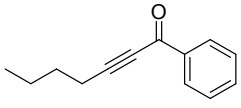


3-(4-fluorophenyl)-1-phenylprop-2-yn-1-one (1s), slightly brown oil. Yield = 40%. Prepared according to the general method by employing benzoyl chloride and 1-ethynyl-4-fluorobenzene.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.08 (m, 2H), 7.60 (ddd, *J* = 26.8, 14.2, 6.4 Hz, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 8.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.87, 164.00 (d, *J* = 253.9 Hz), 136.76, 135.34 (d, *J* = 8.9 Hz), 134.17, 129.52, 128.63, 116.23 (d, *J* = 22.4 Hz), 116.22 (d, *J* = 3.6 Hz), 91.97, 86.79.
HRMS (ESI): calc. for $C_{15}H_9FNaO$ $[M+Na]^+$: 247.0530, found: 247.0533.
The ^{1}H and ^{13}C NMR data are consistent with previous literature.[9]



1-phenylbut-2-yn-1-one (1t), slightly brown oil. Yield = 45%. Prepared according to the general method by employing benzoyl chloride and prop-1-yne.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.07 (m, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.42 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.08, 136.64, 133.81, 129.42, 128.36, 92.44, 78.84, 4.17.

HRMS (ESI): calc. for $C_{10}H_8NaO$ $[M+Na]^+$: 167.0467, found: 167.0466.

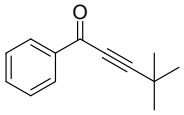


1-phenylhept-2-yn-1-one (1u), colorless oil. Yield = 67%. Prepared according to the general method by employing benzoyl chloride and hex-1-yne.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.07 (m, 2H), 7.59 (ddd, *J* = 6.9, 4.6, 1.2 Hz, 1H), 7.47 (dd, *J* = 10.6, 4.7 Hz, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.73 – 1.43 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.11, 136.80, 133.75, 129.40, 128.37, 96.73, 79.54, 29.71, 21.95, 18.77, 13.40.

HRMS (ESI): calc. for $C_{13}H_{14}NaO$ $[M+Na]^+$: 209.0937, found: 209.0935.

The ^{1}H and ^{13}C NMR data are consistent with previous literature.[6]

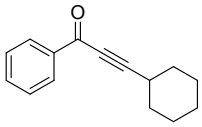


4,4-dimethyl-1-phenylpent-2-yn-1-one (1v), brown oil. Yield = 90%. Prepared according to the general method by employing benzoyl chloride and 3,3-dimethylbut-1-yne.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.00 (m, 2H), 7.59 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.29, 136.95, 133.75, 129.42, 128.40, 103.89, 78.04, 30.10, 27.97.

HRMS (ESI): calc. for $C_{13}H_{14}NaO$ $[M+Na]^+$: 209.0937, found: 209.0938.

The ^{1}H and ^{13}C NMR data are consistent with previous literature.[10]

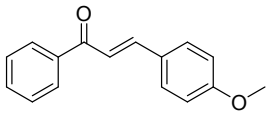


3-cyclohexyl-1-phenylprop-2-yn-1-one (1x), brown oil. Yield = 73%. Prepared according to the general method by employing benzoyl chloride and ethynylcyclohexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.05 (m, 2H), 7.64 – 7.53 (m, 1H), 7.46 (dd, *J* = 10.5, 4.7 Hz, 2H), 2.69 (ddd, *J* = 12.8, 8.8, 3.8 Hz, 1H), 1.92 (dd, *J* = 9.6, 3.5 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.67 – 1.52 (m, 3H), 1.47 – 1.31 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.23, 136.86, 133.71, 129.37, 128.34, 100.30, 79.41, 31.55, 29.23, 25.51, 24.56.

HRMS (ESI): calc. for $C_{15}H_{16}NaO$ $[M+Na]^+$: 235.1093, found: 235.1092.

The ^{1}H and ^{13}C NMR data are consistent with previous literature.[9]



3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1y).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.87 (m, 2H), 7.72 (d, *J* = 15.7 Hz, 1H), 7.60 – 7.26 (m, 6H), 6.97 – 6.80 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.58, 161.66, 144.69, 138.49, 132.53, 130.21, 128.54, 128.39, 127.60, 119.77, 114.40, 55.40.

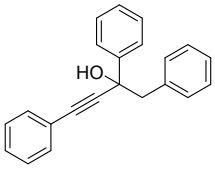
3. The photocatalytic cross-coupling reactions of acetenyl ketones.

3.1 General procedure for the photocatalytic cross-coupling reactions

Acetenyl ketone (0.1 mmol), potassium trifluoroborates (0.15 mmol) and $Ir[dF(CF_3)(ppy)]_2$(dtbbp-

y)PF_6 (2.0 mmol%) were added to a transparent glass tube equipped with a magnetic stir bar. Then the tube was covered with a rubber septum and sealed with a coiled seal film. By evacuating air with N_2 for three times at -78 °C, dried and degassed acetone (1mL) was added. Subsequently, the reaction system was treated under the irradiation of blue LEDs (36 W) at room temperature for 24 hours. Monitored the reaction process with TLC till completed, the reaction mixture was filtered and the residue was washed with acetone (2 mL). The resulting filter liquor was concentrated under reduced pressure and purified by column chromatography to afford propargyl alcohols.

3.2 Characterization of the cross-coupling products.



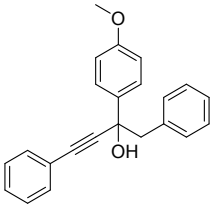
1,2,4-triphenylbut-3-yn-2-ol (2a), was prepared following the general procedure by the reaction of **1a** with benzyl trifluoroborate, and flash column chromatography afforded **2a** as colorless oil in 72% yield (21.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.45 – 7.20 (m, 13H), 3.24 (s, 2H), 2.52 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.13, 135.90, 131.64, 131.01, 128.53, 128.29, 128.13, 127.87, 127.76, 127.02, 125.63, 122.52, 91.05, 87.33, 73.63, 51.96.

GC-MS (EI): 298.1, 280.1, 265.1, 202.1, 178.1. 77.1

HRMS (ESI): calc. for $C_{22}H_{18}NaO$ $[M+Na]^+$: 321.1250, found: 321.1250.

The ^{1}H and ^{13}C NMR data are consistent with previous literature.[11]

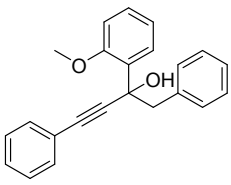


2-(4-methoxyphenyl)-1,4-diphenylbut-3-yn-2-ol (2b), was prepared following the general procedure by the reaction of **1b** with benzyl trifluoroborate, and flash column chromatography afforded **2b** as colorless oil in 70% yield (22.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.35 – 7.29 (m, 2H), 7.25 – 7.17 (m, 6H), 7.16 – 7.13 (m, 2H), 6.85 – 6.76 (m, 2H), 3.72 (s, 3H), 3.15 (q, *J* = 13.1 Hz, 2H), 2.49 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.11, 136.28, 136.00, 131.58, 130.98, 128.45, 128.25, 127.79, 126.91, 122.53, 113.37, 91.20, 87.19, 73.33, 55.26, 51.90.

GC-MS (EI): 328.1, 295.1, 279.2, 252.1, 131.1

HRMS (ESI): calc. for $C_{23}H_{20}NaO_2$ $[M+Na]^+$: 351.1356, found: 351.1356.



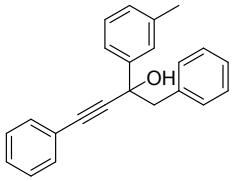
2-(2-methoxyphenyl)-1,4-diphenylbut-3-yn-2-ol (2c), was prepared following the general

procedure by the reaction of **1c** with benzyl trifluoroborate, and flash column chromatography afforded **2c** as colorless oil in 64% yield (21.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.23 – 7.16 (m, 4H), 7.14 – 7.09 (m, 3H), 7.04 (dd, *J* = 7.0, 2.6 Hz, 2H), 6.89 – 6.77 (m, 2H), 4.46 (s, 1H), 3.80 (s, 3H), 3.38 (dd, *J* = 40.9, 12.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.50, 136.53, 131.59, 130.81, 130.43, 129.09, 128.44, 128.22, 128.12, 127.48, 126.51, 122.80, 120.82, 111.45, 90.50, 86.96, 74.87, 55.60, 49.04.

GC-MS (EI): 328.2, 310.3, 295.1, 279.1, 189.1, 77.1

HRMS (ESI): calc. for $C_{23}H_{20}NaO_2$ $[M+Na]^+$: 351.1356, found: 351.1354.

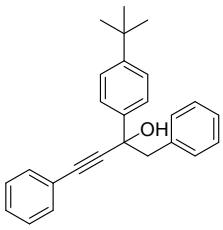


1,4-diphenyl-2-(m-tolyl)but-3-yn-2-ol (2d), was prepared following the general procedure by the reaction of **1d** with benzyl trifluoroborate, and flash column chromatography afforded **2d** as colorless oil in 56% yield (17.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 7.16 (ddd, *J* = 15.6, 8.5, 4.8 Hz, 9H), 7.01 (d, *J* = 7.5 Hz, 1H), 3.19 – 3.04 (m, 2H), 2.49 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.05, 137.69, 135.96, 131.58, 130.98, 128.42, 128.21, 127.97, 127.78, 126.93, 126.13, 122.72, 122.52, 91.14, 87.16, 73.50, 51.87, 21.53.

GC-MS (EI): 312.1, 220.1, 192.1, 143.1, 77.1

HRMS (ESI): calc. for $C_{23}H_{20}NaO$ $[M+Na]^+$: 335.1406, found: 335.1407.

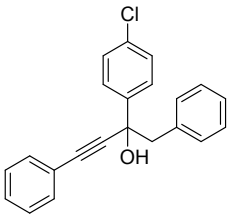


2-(4-(tert-butyl)phenyl)-1,4-diphenylbut-3-yn-2-ol (2e), was prepared following the general procedure by the reaction of **1e** with benzyl trifluoroborate, and flash column chromatography afforded **2e** as colorless oil in 71% yield (25.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.13 (m, 8H), 3.21 – 3.05 (m, 2H), 2.45 (s, 1H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.69, 141.28, 136.12, 131.60, 131.02, 128.42, 128.23, 127.82, 126.94, 125.27, 125.04, 122.59, 91.16, 87.21, 73.41, 51.81, 34.48, 31.34.

GC-MS (EI): 354.3, 336.3, 321.1, 215.1, 202.1.

HRMS (ESI): calc. for $C_{26}H_{26}NaO$[M+Na]$^+$: 377.1876, found: 377.1874.

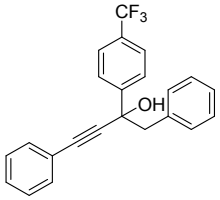


2-(4-chlorophenyl)-1,4-diphenylbut-3-yn-2-ol (2f), was prepared following the general procedure by the reaction of **1f** with benzyl trifluoroborate, and flash column chromatography afforded **2f** as colorless oil in 53% yield (17.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.16 (m, 8H), 7.16 – 7.10 (m, 2H), 3.12 (s, 2H), 2.52 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.61, 135.46, 133.54, 131.60, 130.95, 128.67, 128.32, 128.18, 127.93, 127.16, 127.12, 122.20, 90.55, 87.51, 73.20, 51.88.

GC-MS (EI): 332.1, 255.2, 241.1, 215.2, 202.1, 189.1.

HRMS (ESI): calc. for $C_{22}H_{17}ClNaO$ $[M+Na]^+$: 355.0860, found: 355.0861.

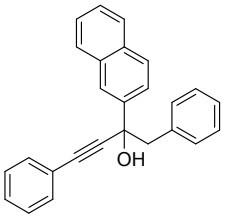


1,4-diphenyl-2-(4-(trifluoromethyl)phenyl)but-3-yn-2-ol (2g), was prepared following the general procedure by the reaction of **1g** with benzyl trifluoroborate, and flash column chromatography afforded **2g** as colorless oil in 41% yield (15.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.19 (m, 6H), 7.19 – 7.13 (m, 2H), 3.14 (s, 2H), 2.56 (s, 1H); 13C NMR (101 MHz, CDCl3) δ 148.03, 135.26, 131.64, 130.97, 129.93 (q, J = 32.3 Hz),128.80, 128.37, 128.03,127.28, 126.09,125.10 (q, J = 3.7 Hz), 123.95 (q, J = 234.7 Hz),122.08, 90.28, 87.72, 73.27, 51.90.

GC-MS (EI): 366.2, 348.2, 275.3, 295.1, 173.1, 129.1.

HRMS (ESI): calc. for $C_{23}H_{17}F_3NaO$ $[M+Na]^+$: 389.1124, found: 389.1127.

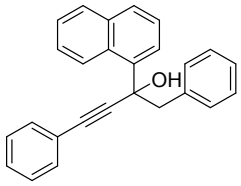


2-(naphthalen-2-yl)-1,4-diphenylbut-3-yn-2-ol, (2h), was prepared following the general procedure by the reaction of **1h** with benzyl trifluoroborate, and flash column chromatography afforded **2h** as colorless oil in 61% yield (21.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 1.8 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.70 (dd, J = 8.6, 1.8 Hz, 1H), 7.44 – 7.33 (m, 4H), 7.28 – 7.16 (m, 8H), 3.25 (s, 2H), 2.59 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.43, 135.81, 132.96, 132.89, 131.67, 131.02, 128.57, 128.37, 128.31, 127.92, 127.54, 127.05, 126.12, 126.08, 124.36, 123.91, 122.48, 91.05, 87.47, 73.69, 51.73.

GC-MS (EI): 348.2, 330.3, 313.2, 228.1, 202.1, 163.1.

HRMS (ESI): calc. for $C_{26}H_{20}NaO$ $[M+Na]^+$: 371.1406, found: 371.1407.

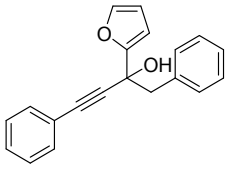


2-(naphthalen-1-yl)-1,4-diphenylbut-3-yn-2-ol, (2i), was prepared following the general procedure by the reaction of **1i** with benzyl trifluoroborate, and flash column chromatography afforded **2i** as colorless oil in 58% yield (20.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 8.7 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.50 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.37 – 7.16 (m, 11H), 3.53 (dd, *J* = 64.5, 13.4 Hz, 2H), 2.68 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.45, 136.09, 134.66, 131.57, 131.08, 130.07, 129.21, 129.13, 128.51, 128.25, 127.87, 127.02, 126.10, 125.62, 125.31, 124.88, 124.31, 122.50, 91.69, 88.12, 73.87, 49.16.

GC-MS (EI): 348.1, 330.1, 313.3, 252.1, 202.2, 163.1.

HRMS (ESI): calc. for $C_{26}H_{20}NaO$ $[M+Na]^+$: 371.1406, found: 371.1403.

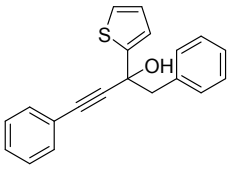


2-(furan-2-yl)-1,4-diphenylbut-3-yn-2-ol, (2j), was prepared following the general procedure by the reaction of **1j** with benzyl trifluoroborate, and flash column chromatography afforded **2j** as colorless oil in 48% yield (13.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.16 (m, 8H), 6.30 (ddd, *J* = 5.1, 3.2, 1.3 Hz, 2H), 3.36 (s, 2H), 2.58 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.81, 142.60, 135.51, 131.75, 130.83, 128.74, 128.33, 127.99, 127.14, 122.22, 110.41, 107.74, 88.79, 86.57, 69.40, 47.64.

GC-MS (EI): 288.1, 270.1, 212.2, 156.1, 128.1, 91.1.

HRMS (ESI): calc. for $C_{20}H_{16}NaO_2$ $[M+Na]^+$: 311.1043, found: 311.1042.

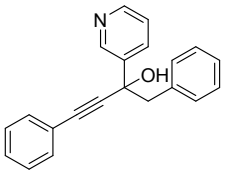


1,4-diphenyl-2-(thiophen-2-yl)but-3-yn-2-ol, (2k), was prepared following the general procedure by the reaction of **1k** with benzyl trifluoroborate, and flash column chromatography afforded **2k** as colorless oil in 43% yield (13.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.29 – 7.18 (m, 9H), 7.08 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.89 (dd, *J* = 5.1, 3.6 Hz, 1H), 3.30 (q, *J* = 13.1 Hz, 2H), 2.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.86, 135.62, 131.64, 130.92, 128.69, 128.30, 127.90, 127.15, 126.54, 125.16, 124.77, 122.18, 90.24, 86.85, 71.40, 51.90.

GC-MS (EI): 304.1, 286.3, 252.2, 239.1, 209.1, 77.1.

HRMS (ESI): calc. for $C_{20}H_{16}NaOS$ $[M+Na]^+$: 327.0814, found: 327.0817.

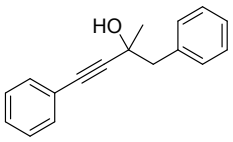


1,4-diphenyl-2-(pyridin-3-yl)but-3-yn-2-ol, (2l), was prepared following the general procedure by the reaction of **1l** with benzyl trifluoroborate, and flash column chromatography afforded **2l** as colorless oil in 66% yield (20.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 1.2 Hz, 1H), 8.37 (d, *J* = 4.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.04 (m, 11H), 4.04 (s, 1H), 3.15 (q, *J* = 13.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.49, 147.40, 140.09, 135.37, 133.80, 131.67, 131.06, 128.76, 128.39, 127.96, 127.18, 122.87, 122.21, 90.37, 87.73, 71.96, 52.01.

GC-MS (EI): 299.1, 281.1, 189.1, 141.1, 115.1, 93.1, 77.1

HRMS (ESI): calc. for $C_{21}H_{17}NNaO$ $[M+Na]^+$: 322.1202, found: 322.1204.

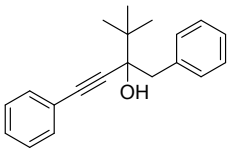


2-methyl-1,4-diphenylbut-3-yn-2-ol, (2m), was prepared following the general procedure by the reaction of **1m** with benzyl trifluoroborate, and flash column chromatography afforded **2m** as colorless oil in 36% yield (8.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.19 (m, 10H), 2.98 (dd, *J* = 29.7, 13.1 Hz, 2H), 2.05 (s, 1H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.34, 131.55, 130.77, 128.30, 128.24, 128.13, 127.02, 122.66, 92.37, 84.57, 68.43, 49.75, 29.56.

GC-MS (EI): 236.1, 208.1, 193.1, 159.1, 116.1.

HRMS (ESI): calc. for $C_{17}H_{16}NaO$ $[M+Na]^+$: 259.1093, found: 259.1093.

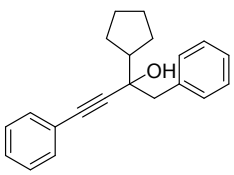


3-benzyl-4,4-dimethyl-1-phenylpent-1-yn-3-ol, (2n), was prepared following the general procedure by the reaction of **1n** with benzyl trifluoroborate, and flash column chromatography afforded **2n** as colorless oil in 49% yield (13.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.24 (dddd, *J* = 9.5, 7.0, 5.9, 1.7 Hz, 8H), 2.93 (s, 2H), 1.81 (s, 1H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.17, 131.49, 131.28, 128.20, 128.13, 127.94, 126.78, 122.99, 91.21, 86.66, 76.84, 42.17, 38.72, 25.53.

GC-MS (EI): 278.1, 260.1, 217.1, 188.1, 109.1, 91.1.

HRMS (ESI): calc. for $C_{20}H_{22}NaO$ $[M+Na]^+$: 301.1563, found: 301.1569.

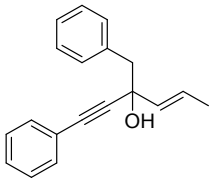


2-cyclopentyl-1,4-diphenylbut-3-yn-2-ol, (2o), was prepared following the general procedure by the reaction of **1o** with benzyl trifluoroborate, and flash column chromatography afforded **2o** as colorless oil in 54% yield (15.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 10H), 2.95 (dd, *J* = 67.7, 13.2 Hz, 2H), 2.15 (dd, *J* = 16.7, 8.4 Hz, 1H), 1.97 (s, 1H), 1.86 – 1.71 (m, 3H), 1.63 (tdd, *J* = 8.7, 6.4, 3.1 Hz, 3H), 1.55 – 1.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.38, 131.59, 130.93, 128.23, 128.06, 126.87, 122.86, 90.79, 85.95, 74.67, 49.59, 47.53, 28.86, 27.80, 26.17, 26.13.

GC-MS (EI): 290.1, 238.2, 146.1, 120.1, 105.1, 77.1.

HRMS (ESI): calc. for $C_{21}H_{22}NaO$ $[M+Na]^+$: 313.1563, found: 313.1560.

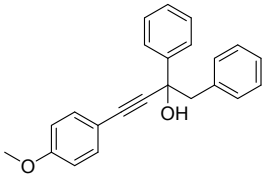


3-benzyl-1-phenylhex-4-en-1-yn-3-ol, (2p), was prepared following the general procedure by the reaction of **1p** with benzyl trifluoroborate, and flash column chromatography afforded **2p** as colorless oil in 24% yield (6.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dt, *J* = 13.4, 6.1 Hz, 5H), 7.26 – 7.19 (m, 5H), 5.99 (dq, *J* = 13.2, 6.5 Hz, 1H), 5.67 – 5.58 (m, 1H), 3.00 (s, 2H), 2.13 (s, 1H), 1.68 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.90, 133.61, 131.57, 131.00, 128.36, 128.22, 127.94, 126.94, 126.82, 122.60, 90.21, 86.88, 71.46, 49.18, 17.43.

GC-MS (EI): 262.1, 247.1, 219.1, 204.1, 176.1.

HRMS (ESI): calc. for $C_{19}H_{18}NaO$ $[M+Na]^+$: 285.1250, found: 285.1252.

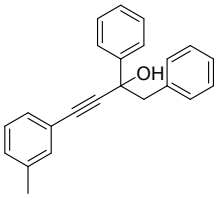


4-(4-methoxyphenyl)-1,2-diphenylbut-3-yn-2-ol, (2q), was prepared following the general procedure by the reaction of **1q** with benzyl trifluoroborate, and flash column chromatography afforded **2q** as colorless oil in 73% yield (24.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.49 (m, 2H), 7.31 – 7.13 (m, 10H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.69 (s, 3H), 3.14 (d, *J* = 3.3 Hz, 2H), 2.50 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.71, 144.28, 136.00, 133.04, 130.99, 128.05, 127.77, 127.64, 126.90, 125.63, 114.56, 113.89, 89.67, 87.25, 73.62, 55.22, 51.98.

GC-MS (EI): 328.1, 311.2, 295.1, 279.2, 265.1, 239.1.

HRMS (ESI): calc. for $C_{23}H_{20}NaO_2$ $[M+Na]^+$: 351.1356, found: 351.1361.



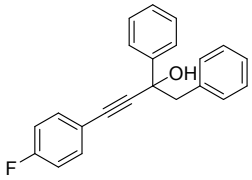
1,2-diphenyl-4-(m-tolyl)but-3-yn-2-ol, (2r), was prepared following the general procedure by the

reaction of **1r** with benzyl trifluoroborate, and flash column chromatography afforded **2r** as colorless oil in 44% yield (13.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.19 (dt, *J* = 5.4, 2.2 Hz, 1H), 7.17 – 7.03 (m, 8H), 7.01 (d, *J* = 7.4 Hz, 1H), 3.20 – 3.06 (m, 2H), 2.53 (s, 1H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.10, 137.89, 135.88, 132.15, 130.97, 129.34, 128.65, 128.13, 128.04, 127.76, 127.65, 126.90, 125.61, 122.27, 90.69, 87.43, 73.59, 51.90, 21.13.

GC-MS (EI): 312.1, 221.1, 192.2, 143.1, 77.2

HRMS (ESI): calc. for $C_{23}H_{20}NaO$ $[M+Na]^+$: 335.1406, found: 335.1409.

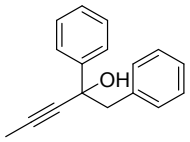


4-(4-fluorophenyl)-1,2-diphenylbut-3-yn-2-ol, (2s), was prepared following the general procedure by the reaction of **1s** with benzyl trifluoroborate, and flash column chromatography afforded **2s** as colorless oil in 68% yield (21.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.29 – 7.22 (m, 4H), 7.20 (dt, *J* = 5.4, 2.2 Hz, 1H), 7.18 – 7.13 (m, 3H), 7.13 – 7.09 (m, 2H), 6.91 – 6.82 (m, 2H), 3.22 – 2.99 (m, 2H), 2.54 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ162.56 (d, *J* = 249.8 Hz), 143.96, 135.82, 133.48 (d, *J* = 8.4 Hz), 130.93, 128.09, 127.80, 127.75, 126.97, 125.55, 118.51 (d, *J* = 3.5 Hz), 115.53 (d, *J* = 22.1 Hz), 90.75, 86.21, 73.57, 51.84.

GC-MS (EI): 316.1, 298.1, 226.1, 196.1, 147.1, 105.1.

HRMS (ESI): calc. for $C_{22}H_{17}FNaO$ $[M+Na]^+$: 339.1156, found: 339.1155.

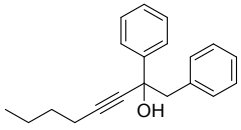


1,2-diphenylpent-3-yn-2-ol, (2t), was prepared following the general procedure by the reaction of **1t** with benzyl trifluoroborate, and flash column chromatography afforded **2t** as colorless oil in 39% yield (9.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 2H), 7.27 – 7.13 (m, 6H), 7.06 (dd, *J* = 6.8, 2.7 Hz, 2H), 3.04 (s, 2H), 2.33 (s, 1H), 1.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.52, 136.02, 130.89, 127.91, 127.69, 127.47, 126.74, 125.56, 83.42, 81.46, 73.14, 51.82, 3.56.

GC-MS (EI): 236.1, 193.1, 176.1, 144.1, 88.1

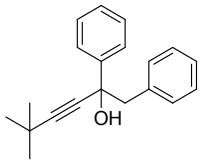
HRMS (ESI): calc. for $C_{17}H_{16}NaO$ $[M+Na]^+$: 259.1093, found: 259.1090.



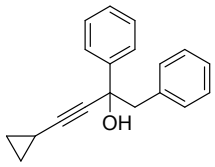
1,2-diphenyloct-3-yn-2-ol, (2u), was prepared following the general procedure by the reaction of **1u** with benzyl trifluoroborate, and flash column chromatography afforded **2u** as colorless oil in 45% yield (12.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.43 (m, 2H), 7.29 – 7.12 (m, 6H), 7.06 (dd, *J* = 6.7, 2.9 Hz,

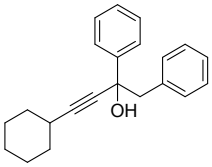
2H), 3.03 (q, *J* = 13.1 Hz, 2H), 2.33 (s, 1H), 2.15 (t, *J* = 7.0 Hz, 2H), 1.46 – 1.36 (m, 2H), 1.35 – 1.24 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.66, 136.10, 130.91, 127.88, 127.62, 127.43, 126.70, 125.59, 88.04, 82.16, 73.23, 51.92, 30.55, 21.91, 18.36, 13.54.
GC-MS (EI): 278.1, 260.2, 217.1, 202.1, 188.2, 105.1
HRMS (ESI): calc. for $C_{20}H_{22}NaO$ $[M+Na]^+$: 301.1563, found: 301.1569.



5,5-dimethyl-1,2-diphenylhex-3-yn-2-ol, (2v), was prepared following the general procedure by the reaction of **1v** with benzyl trifluoroborate, and flash column chromatography afforded **2v** as colorless oil in 53% yield (15.0 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.29 – 7.23 (m, 2H), 7.21 (dd, *J* = 4.9, 3.6 Hz, 1H), 7.19 – 7.15 (m, 3H), 7.09 (dd, *J* = 6.7, 3.0 Hz, 2H), 3.02 (dd, *J* = 31.9, 13.0 Hz, 2H), 2.27 (s, 1H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.79, 136.22, 131.04, 127.93, 127.59, 127.48, 126.75, 125.66, 96.36, 80.56, 73.19, 52.13, 30.82, 27.43.
GC-MS (EI): 278.1, 260.3, 217.1, 188.1, 109.3, 91.2.
HRMS (ESI): calc. for $C_{20}H_{22}NaO$ $[M+Na]^+$: 301.1563, found: 301.1562.

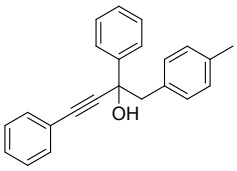


4-cyclopropyl-1,2-diphenylbut-3-yn-2-ol, (2w), was prepared following the general procedure by the reaction of **1w** with benzyl trifluoroborate, and flash column chromatography afforded **2w** as colorless oil in 48% yield (12.6 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.43 (m, 2H), 7.33 – 7.12 (m, 6H), 7.05 (dd, *J* = 6.6, 2.9 Hz, 2H), 3.01 (q, *J* = 13.1 Hz, 2H), 2.30 (s, 1H), 1.18 (tt, *J* = 8.3, 5.0 Hz, 1H), 0.80 – 0.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.55, 136.11, 130.89, 127.91, 127.64, 127.47, 126.75, 125.56, 91.15, 77.25, 73.15, 51.95, 8.17, 8.12, -0.57.
GC-MS (EI): 262.3, 170.1, 141.1, 115.1, 93.1, 77.1
HRMS (ESI): calc. for $C_{19}H_{18}NaO$ $[M+Na]^+$: 285.1250, found: 285.1252.

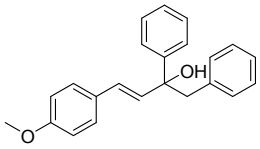


4-cyclohexyl-1,2-diphenylbut-3-yn-2-ol, (2x), was prepared following the general procedure by the reaction of **1x** with benzyl trifluoroborate, and flash column chromatography afforded **2x** as colorless oil in 65% yield (20.0 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.27 – 7.17 (m, 3H), 7.16 – 7.11 (m, 3H), 7.07 (dd, *J* = 6.7, 3.0 Hz, 2H), 3.03 (q, *J* = 13.0 Hz, 2H), 2.35 (dd, *J* = 9.7, 5.8 Hz, 2H), 1.77 – 1.53 (m, 4H), 1.47 – 1.29 (m, 3H), 1.21 (dt, *J* = 5.4, 4.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.88, 136.28, 131.10, 128.01, 127.72, 127.56, 126.83, 125.77, 92.27, 82.14, 73.38, 52.16, 32.56, 29.11, 25.94, 24.91.

GC-MS (EI): 304.4, 286.1, 286.1, 213.4, 204.1, 105.1
HRMS (ESI): calc. for $C_{22}H_{24}NaO$ $[M+Na]^+$: 327.1719, found: 327.1719.



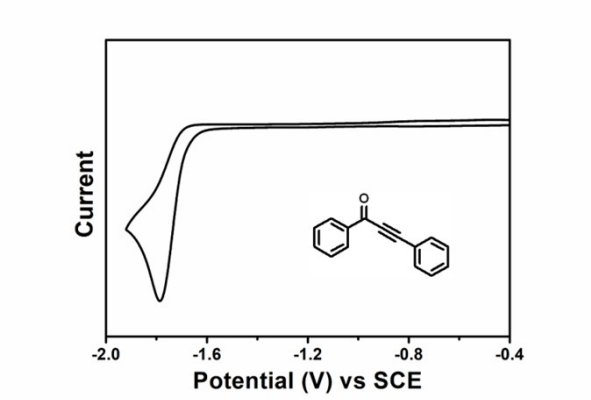
2,4-diphenyl-1-(p-tolyl)but-3-yn-2-ol, (2y), was prepared following the general procedure by the reaction of **1a** with 4-methylbenzyl trifluoroborate, and flash column chromatography afforded **2y** as colorless oil in 63% yield (20.0 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.18 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 3.12 (s, 2H), 2.49 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.28, 136.67, 132.79, 131.72, 130.95, 128.71, 128.56, 128.35, 128.19, 127.78, 125.71, 122.66, 91.28, 87.21, 73.67, 51.65, 21.19.
GC-MS (EI): 312.1, 220.1, 192.2, 143.1, 77.1, 51.1
HRMS (ESI): calc. for $C_{23}H_{20}NaO$ $[M+Na]^+$: 335.1406, found: 335.1402.



4-(4-methoxyphenyl)-1,2-diphenylbut-3-en-2-ol, (2z), was prepared following the general procedure by the reaction of **1y** with benzyl trifluoroborate, and flash column chromatography afforded **2z** as colorless oil in 19% yield (6.3 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 1.4 Hz, 1H), 7.40 (s, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.20 (d, *J* = 1.5 Hz, 1H), 7.18 (s, 1H), 7.14 (dd, *J* = 5.0, 1.9 Hz, 1H), 6.97 (dd, *J* = 6.8, 2.7 Hz, 1H), 6.80 – 6.73 (m, 1H), 6.43 (d, *J* = 3.6 Hz, 1H), 3.72 (s, 2H), 3.22 (s, 1H), 1.98 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.18, 145.51, 135.93, 133.20, 130.83, 129.57, 128.12, 128.05, 127.68, 126.90, 126.77, 125.66, 113.94, 76.64, 55.27, 49.47.
HRMS (ESI): calc. for $C_{23}H_{22}NaO_2$ $[M+Na]^+$: 353.1512, found: 353.1517.

4. Mechanistic studies

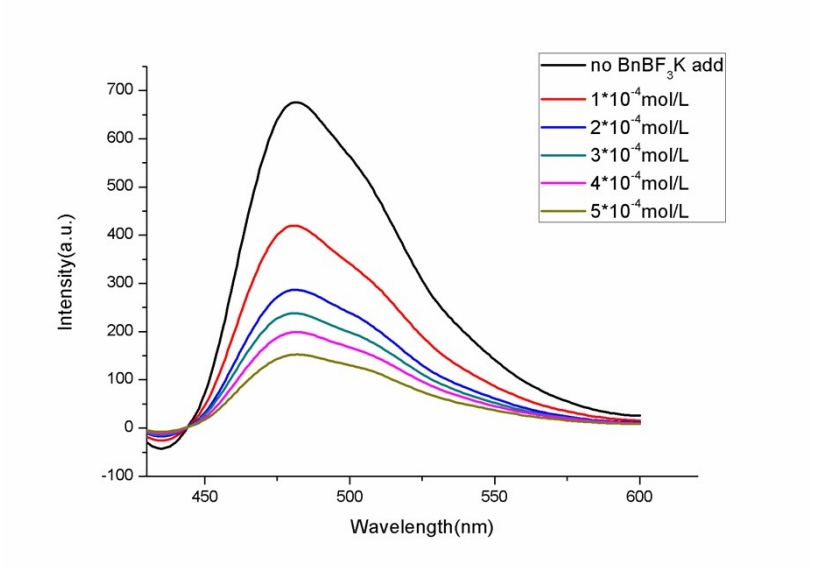
4.1 Cyclic voltammetry measurement



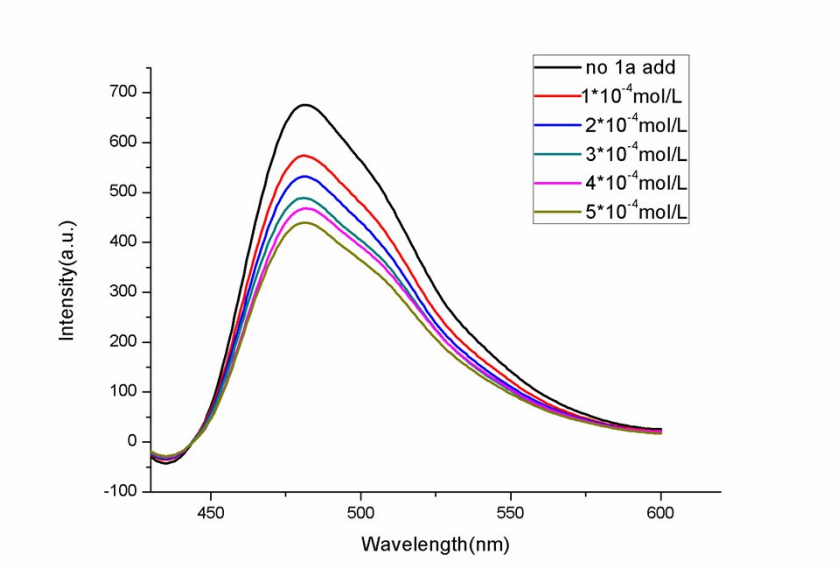
The cyclic voltammogram was obtained with CHI 620E electrochemical analyzer. The peak at -1.70 V shows the reduction of 1,3-diphenylprop-2-yn-1-one (**1a**) against SCE. The measurement employed a glassy carbon working electrode, platinum wire counter electrode, 3.5 M NaCl silver-silver chloride reference electrode, n-Bu4NPF6 was used as supporting electrolyte, and a scan rate of 100 mV/s. The sample was prepared with 1.0 mM solution in dry, degassed MeCN.

4.2 Stern-Volmer fluorescence quenching experiments

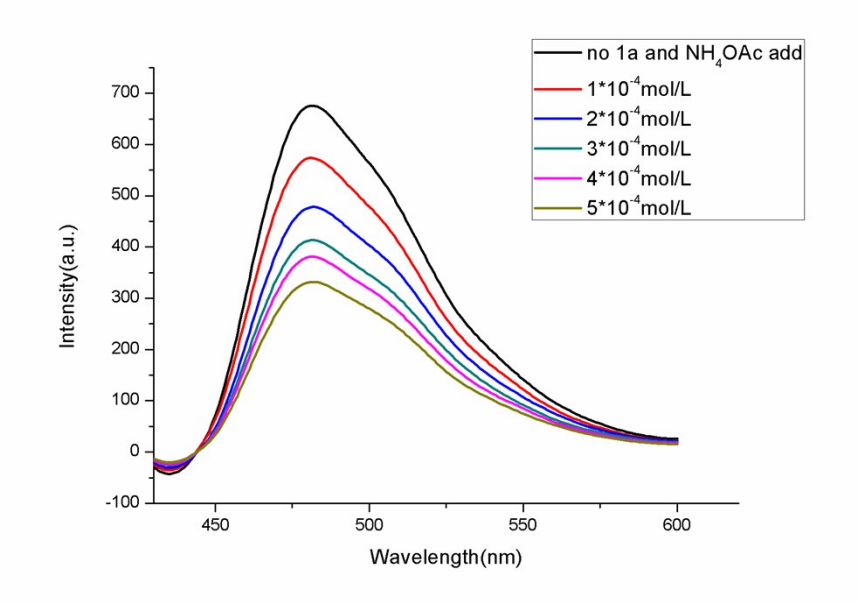
The quenching experiments were carried out in acetone solution of $Ir[dF(CF_3)(ppy)]_2(dtbbpy)PF_6$ (10^{-4} M), and variable concentrations of benzyl trifluoroborate, **1a**, **1a**(in the presence of NH_4OAc) were added, respectively. λ_{ex} = 410 nm, λ_{em}= 473 nm.



(A)

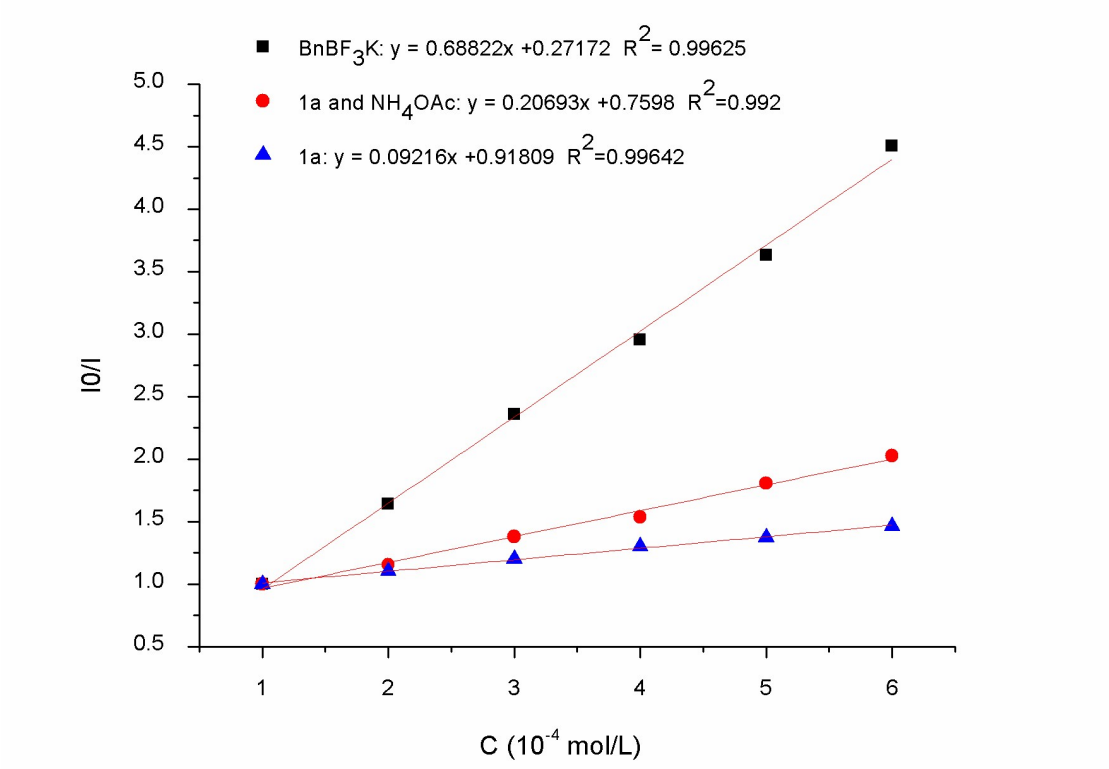


(B)



(C)

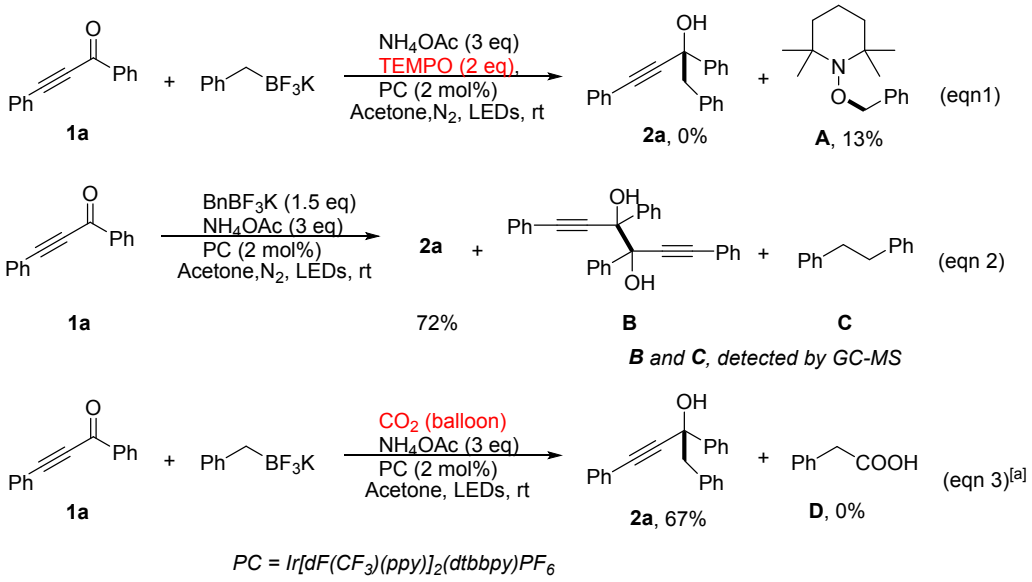
Fluorescence quenching experiments of photocatalyst upon addition of benzyl trifluoroborate (A), 1a (B), 1a and NH_4OAc (C)



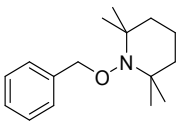
Stern-Volmer fluorescence quenching experiments.

4.3 Control experiments.

In the presence of radical trapping agent TEMPO, the cross-coupling reaction was totally repressed and meanwhile afforded alkyl-TEMPO adduct **A** in 13% yield (eqn 1). Additionally, we also detected the formation of **B** and **C** by GC-MS in the standard reaction system (eqn 2). This result provided a useful evidence for the generation of ketyl and benzyl radicals in the Barbier-type reaction process. To exclude the possibility of a benzyl anion-involved pathway, an experiment was carried out by bubbling CO_2 to the standard reaction system, in which no carboxylation product was detected (eqn 3).



[a]The reaction of eqn 3 was performed referred to previous method[12] according to the following procedure: **1a** (0.1 mmol, 20.7 mg), potassium benzyl trifluoroborates (0.15 mmol, 30.0 mg) and $Ir[dF(CF_3)(ppy)]_2(dtbbpy)PF_6$ (2.0 mmol%, 2.3 mg) were added to a transparent glass tube equipped with a magnetic stir bar. Then the tube was covered with a rubber septum and sealed with a coiled seal film. By evacuating air with CO_2 for three times at -78 °C, dried and degassed acetone (1mL) was added. After that, CO_2 (filled in a balloon) was injected into the reaction system via a syringe needle (under the surface of reaction liquid). Subsequently, the reaction system was treated under the irradiation of blue LEDs (36 W) at room temperature for 24 hours. The reaction mixture was filtered and the residue was washed with acetone (2 mL). The resulting filter liquor was concentrated under reduced pressure and purified by column chromatography to afforded **2a** in 67% yield but with no product D obtained (as well not detected by GC-MS).



1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (A), was obtained as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 4H), 7.23 – 7.17 (m, 1H), 4.75 (s, 2H), 1.59 – 1.39 (m, 5H), 1.31 – 1.24 (m, 1H), 1.18 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.31, 128.20, 127.44, 127.27, 78.72,

60.00, 39.71, 33.08, 20.29, 17.11.

GC-MS (EI): 232.2, 157.2, 123.2, 91.2, 69.2, 55.1.

HRMS (ESI): calc. for $C_{16}H_{25}NNaO$ $[M+Na]^+$: 270.1828, found: 270.1832.

5. Reference.

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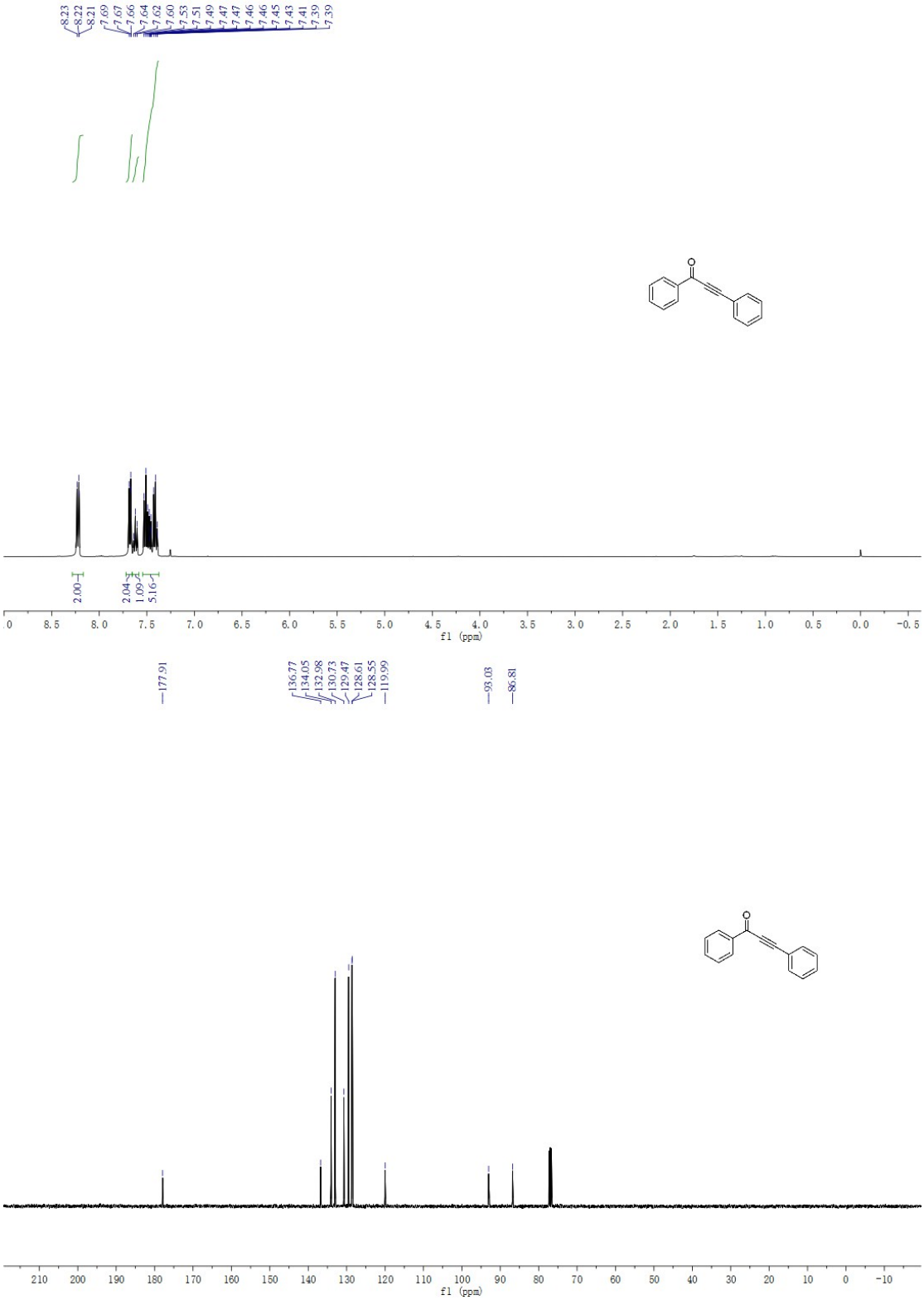
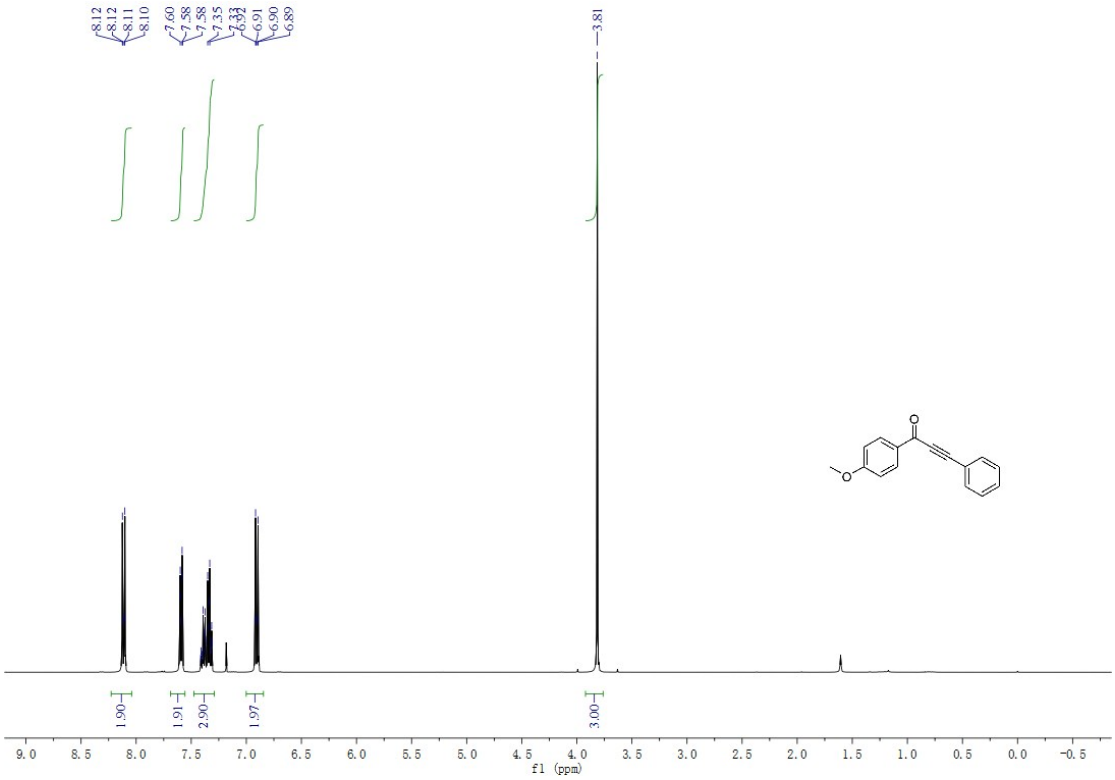
6. ^{1}H and ^{13}C spectra

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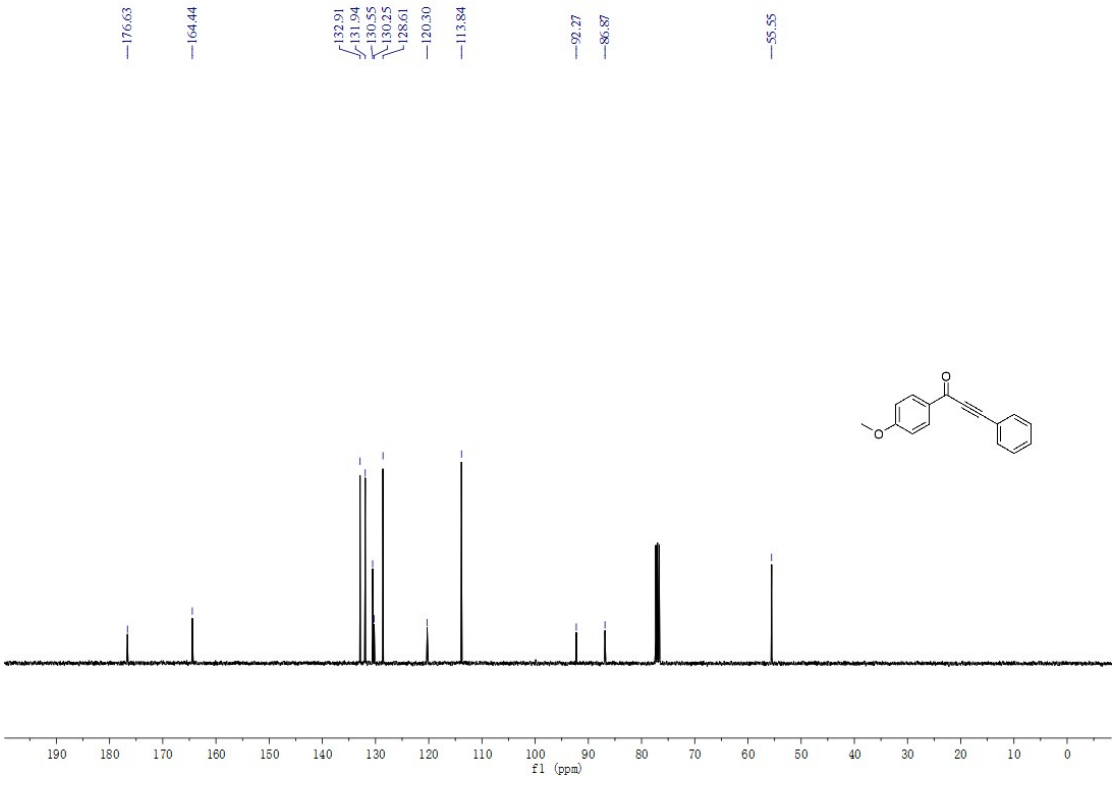
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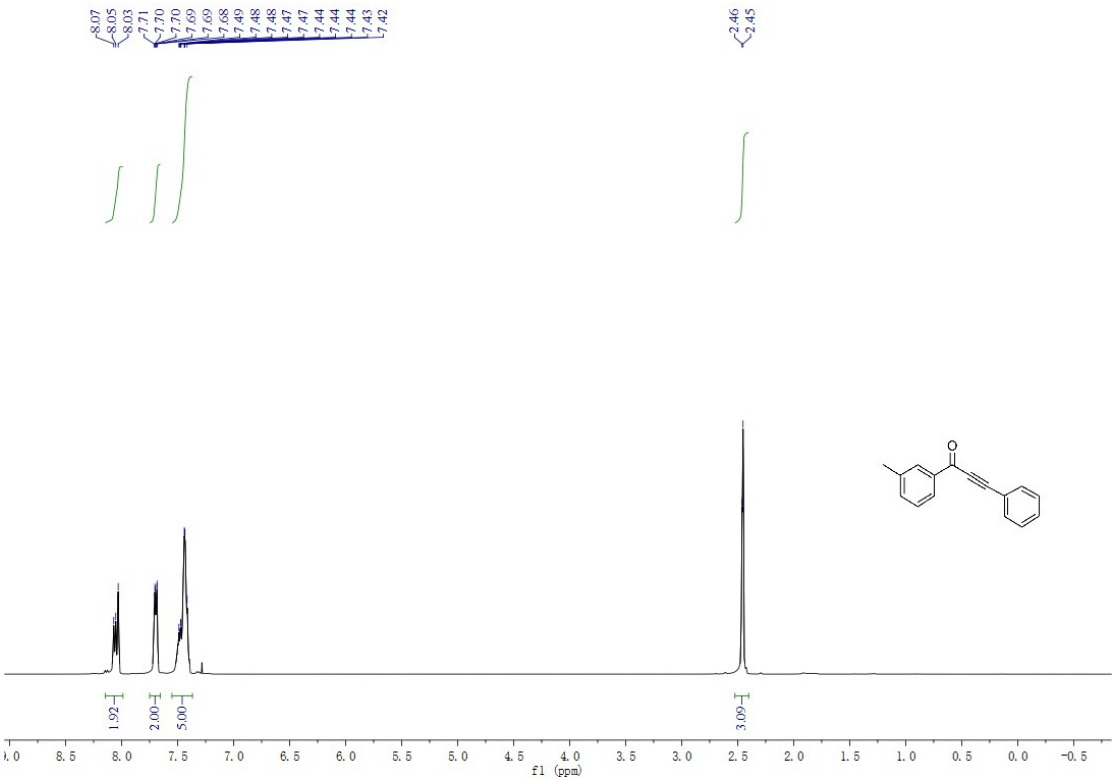
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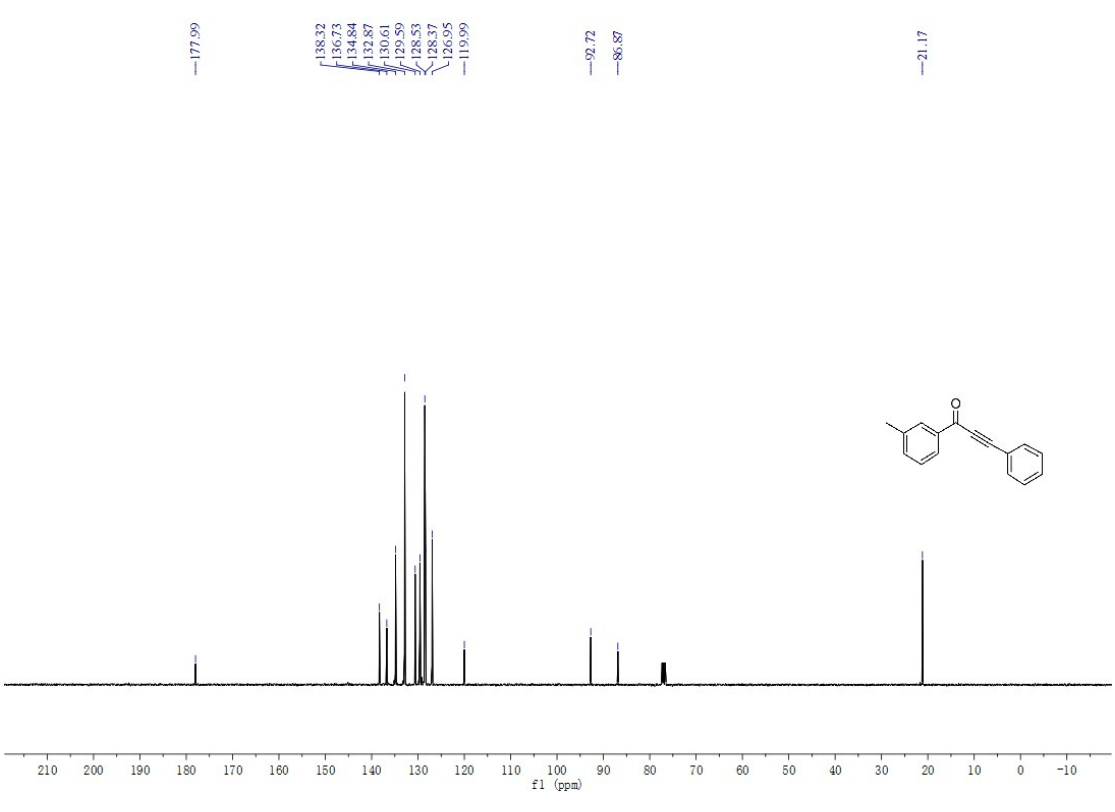
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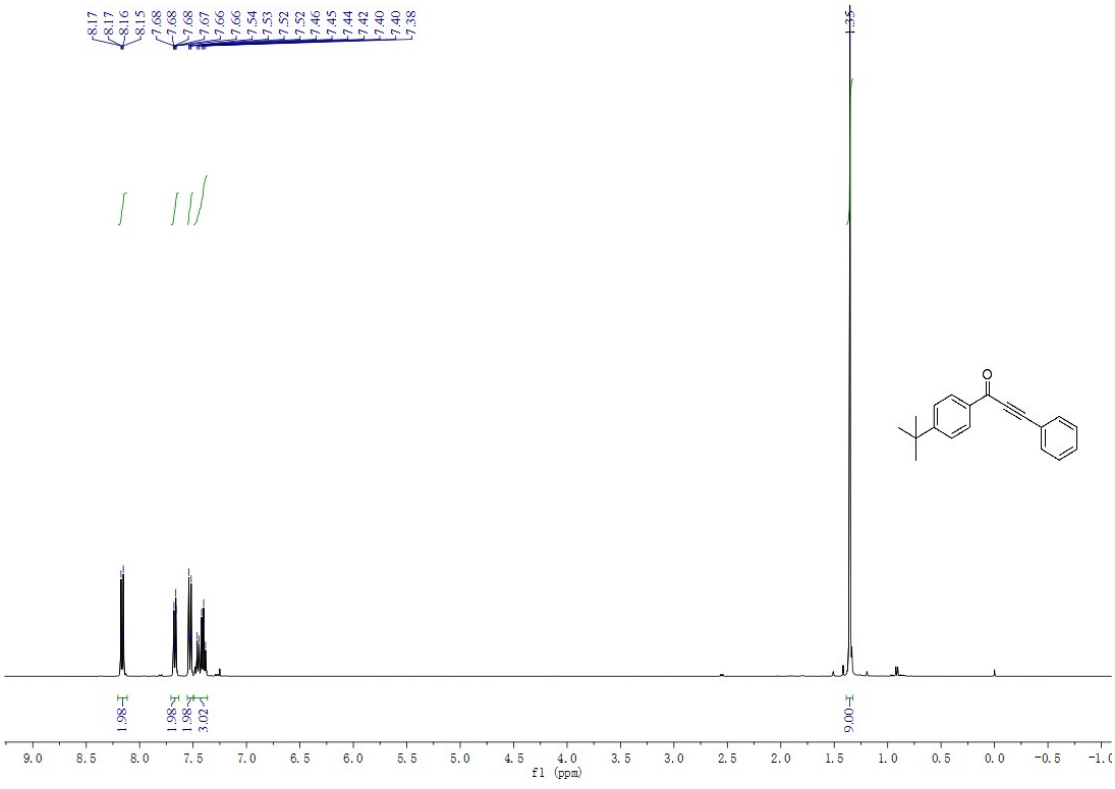
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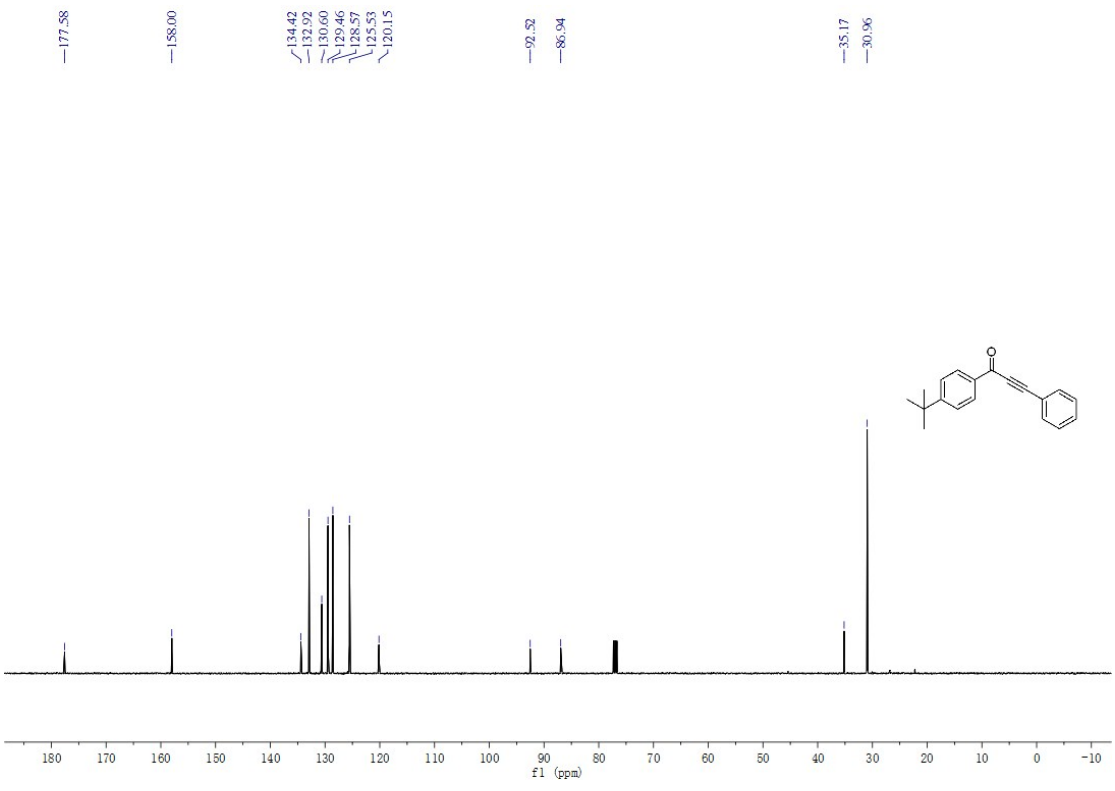
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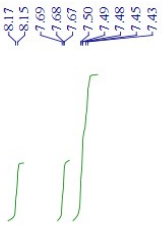
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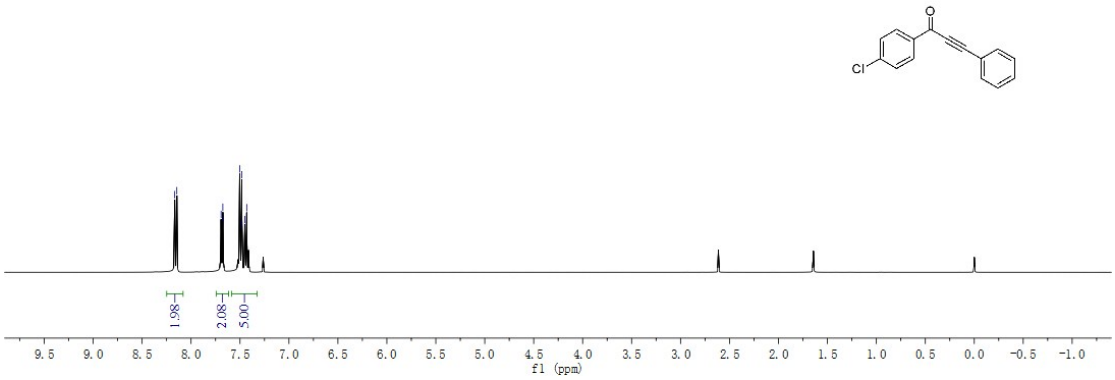
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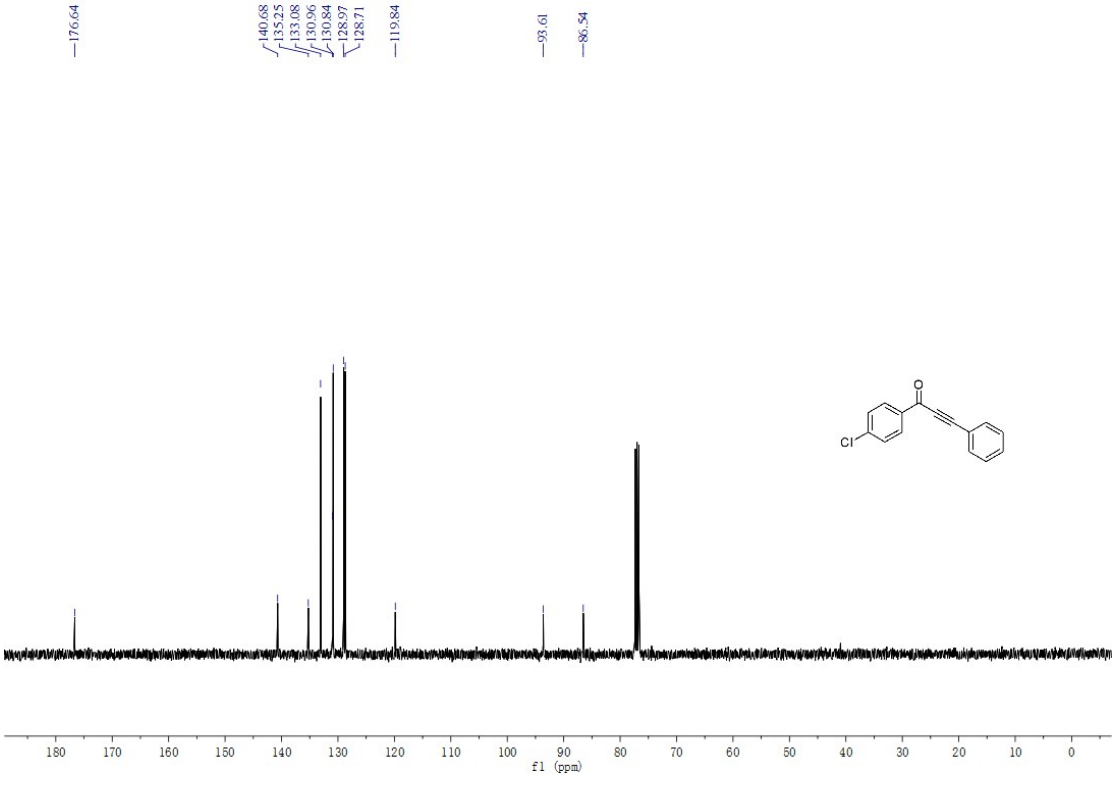
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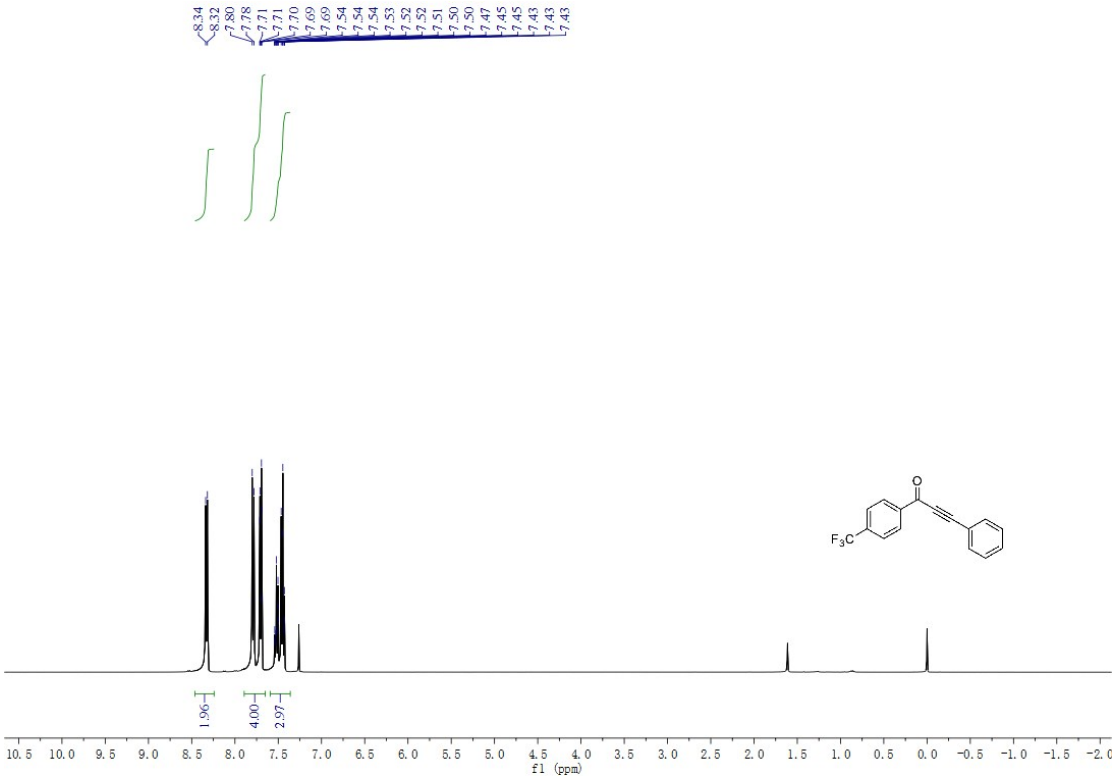
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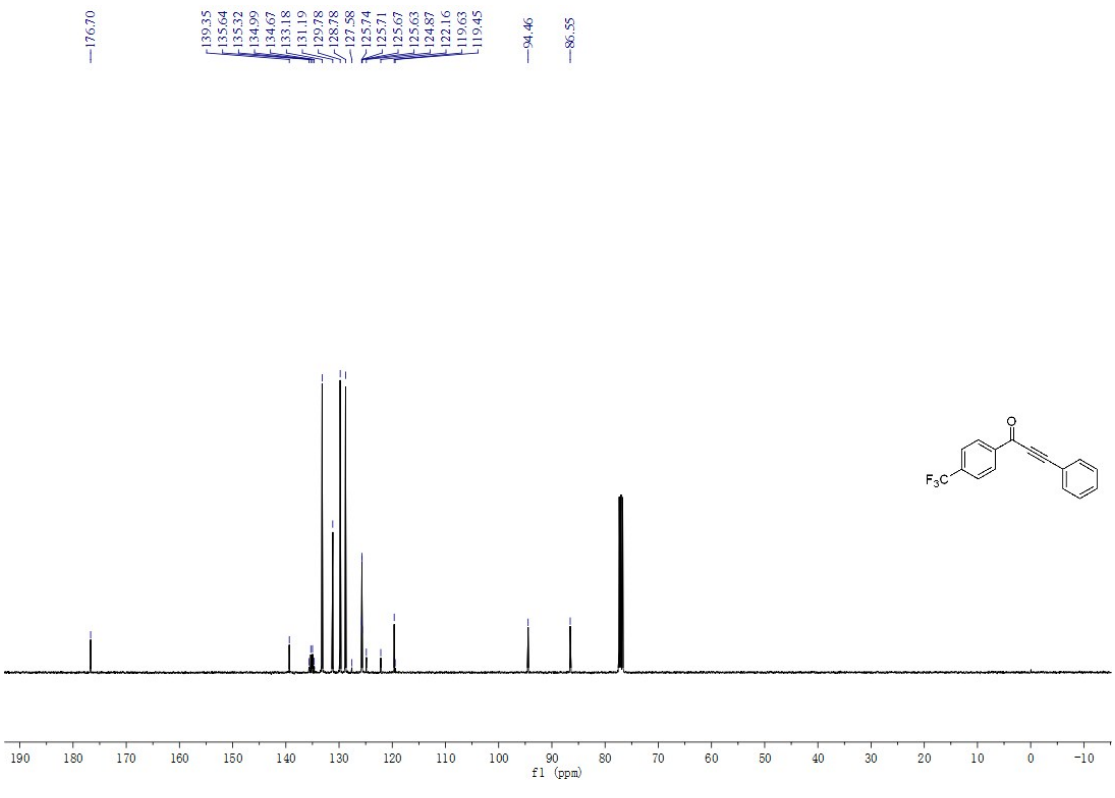
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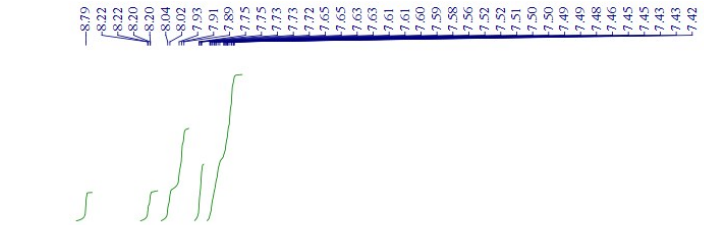
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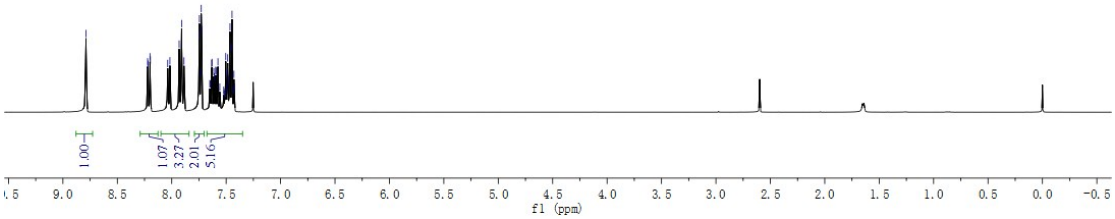
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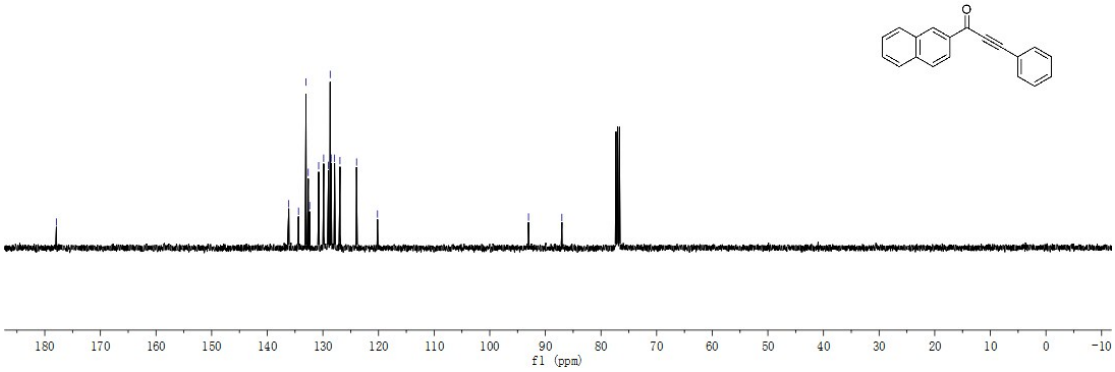
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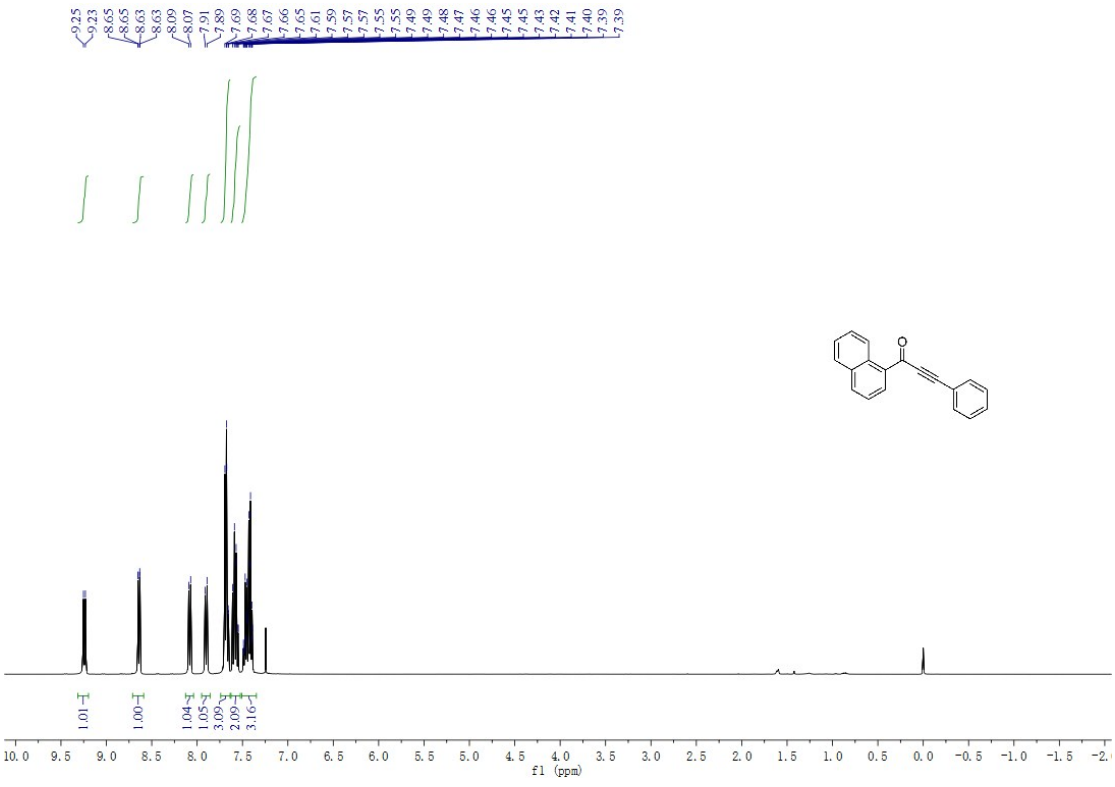
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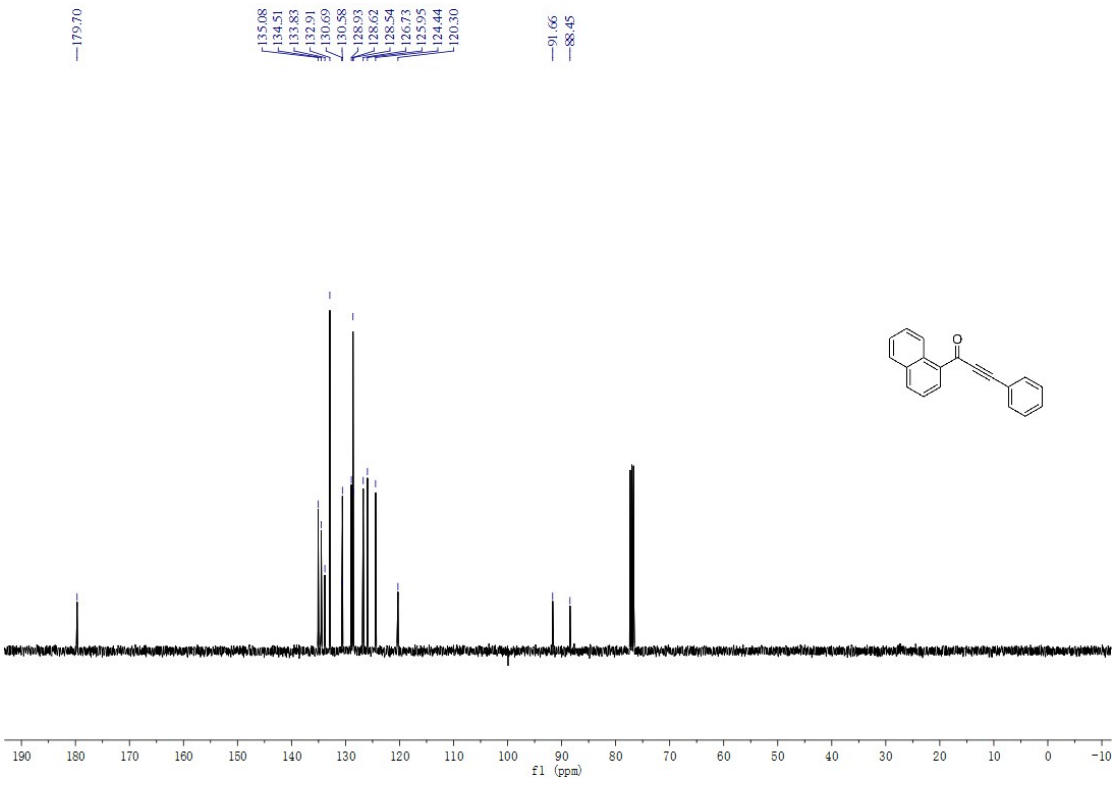
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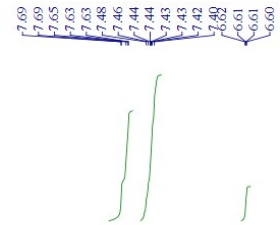
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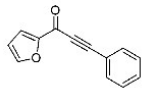

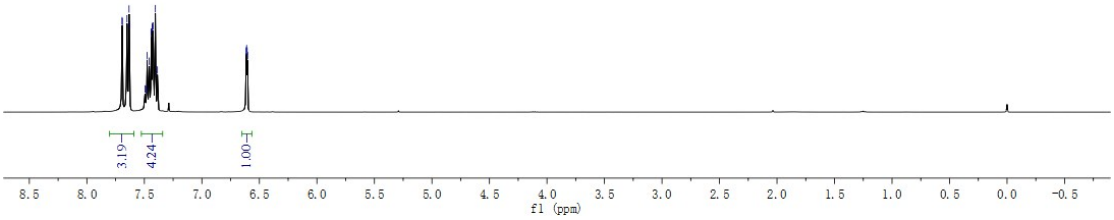
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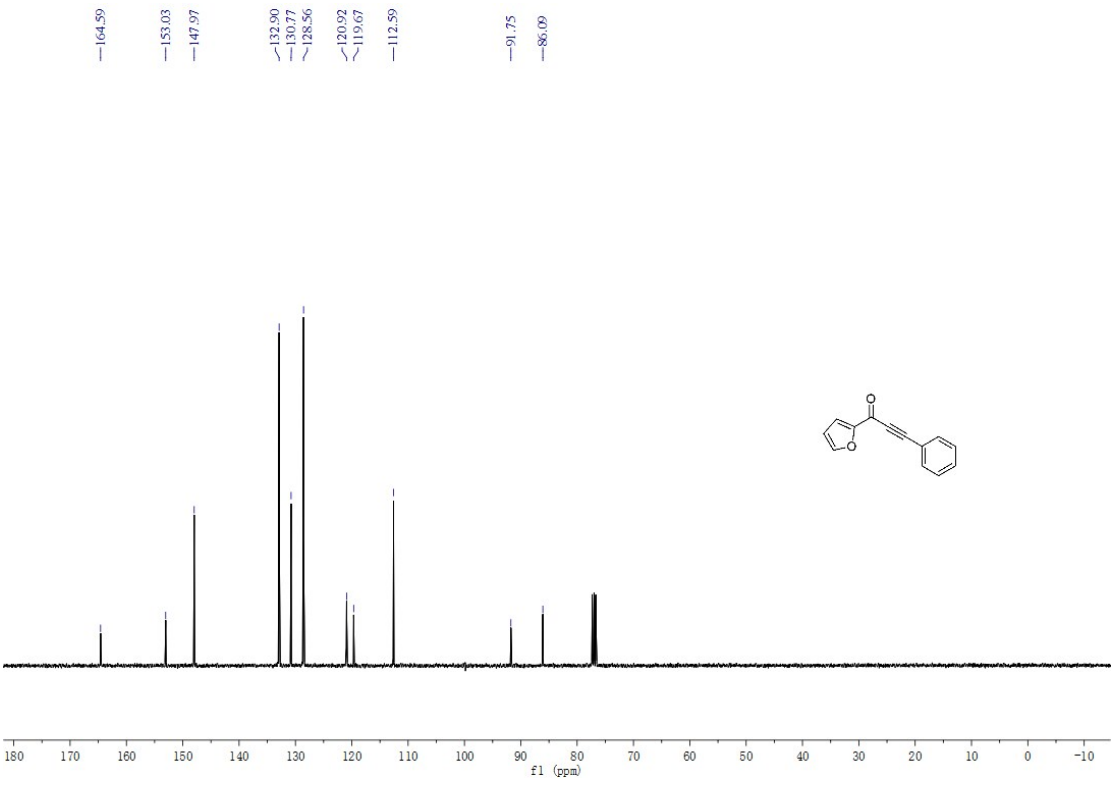
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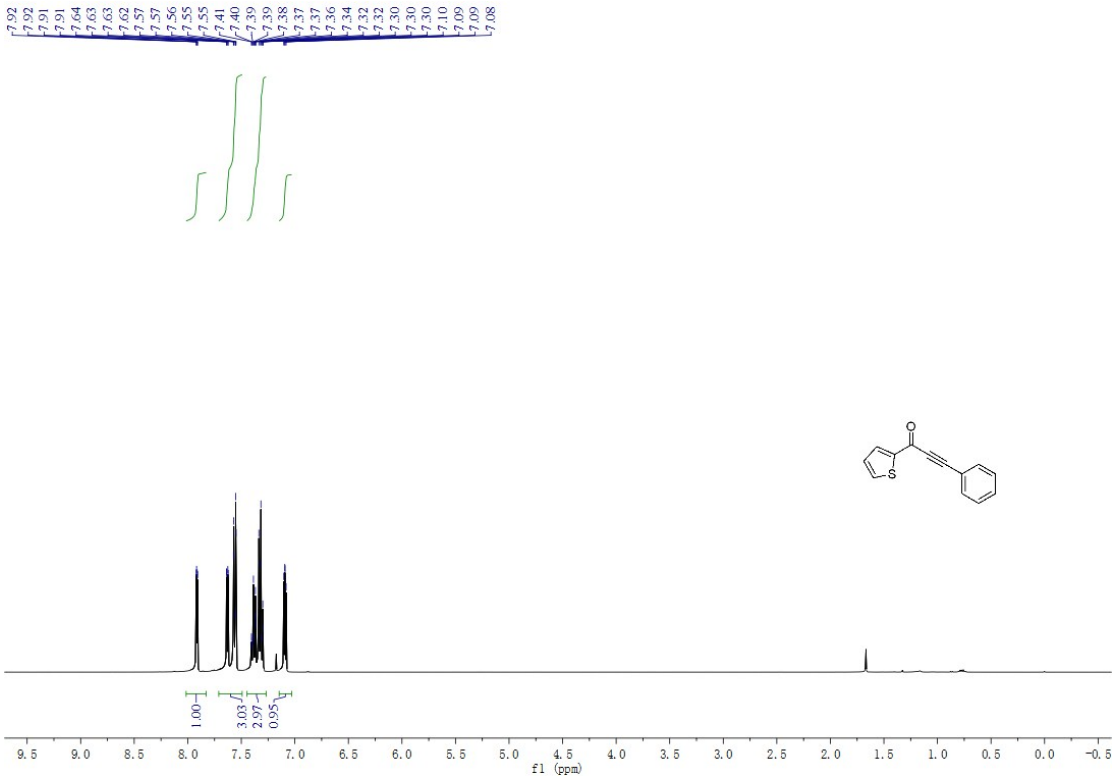
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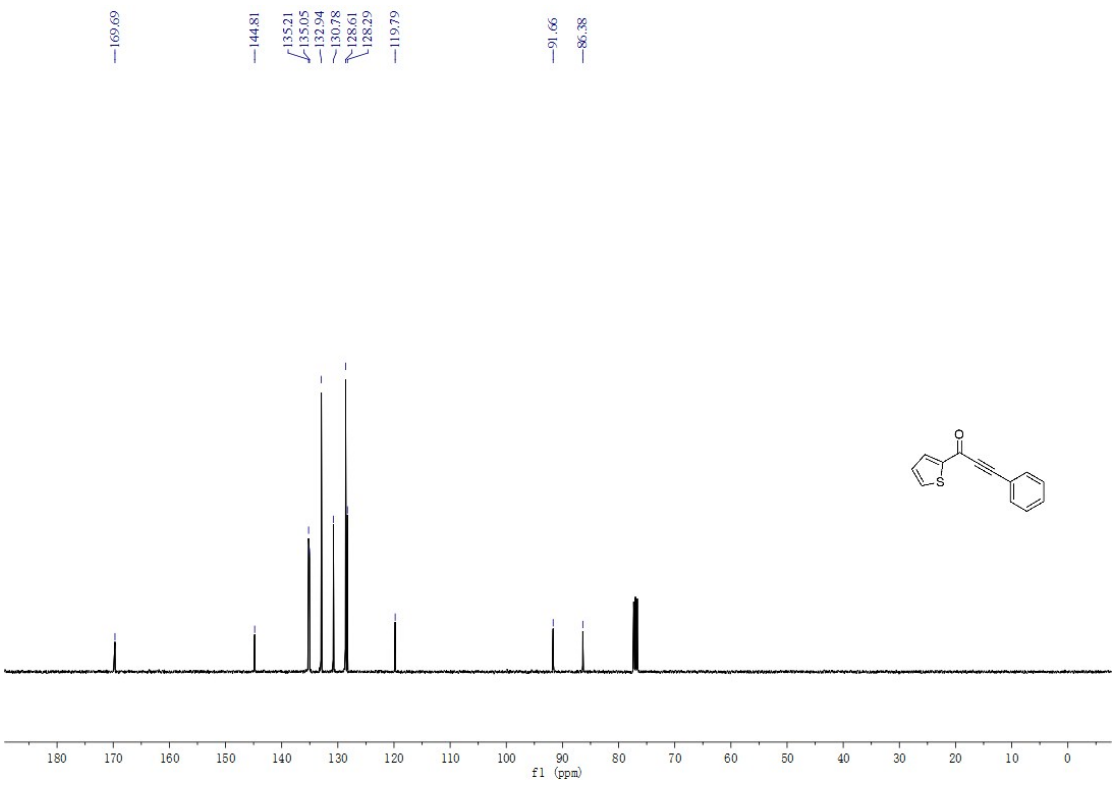
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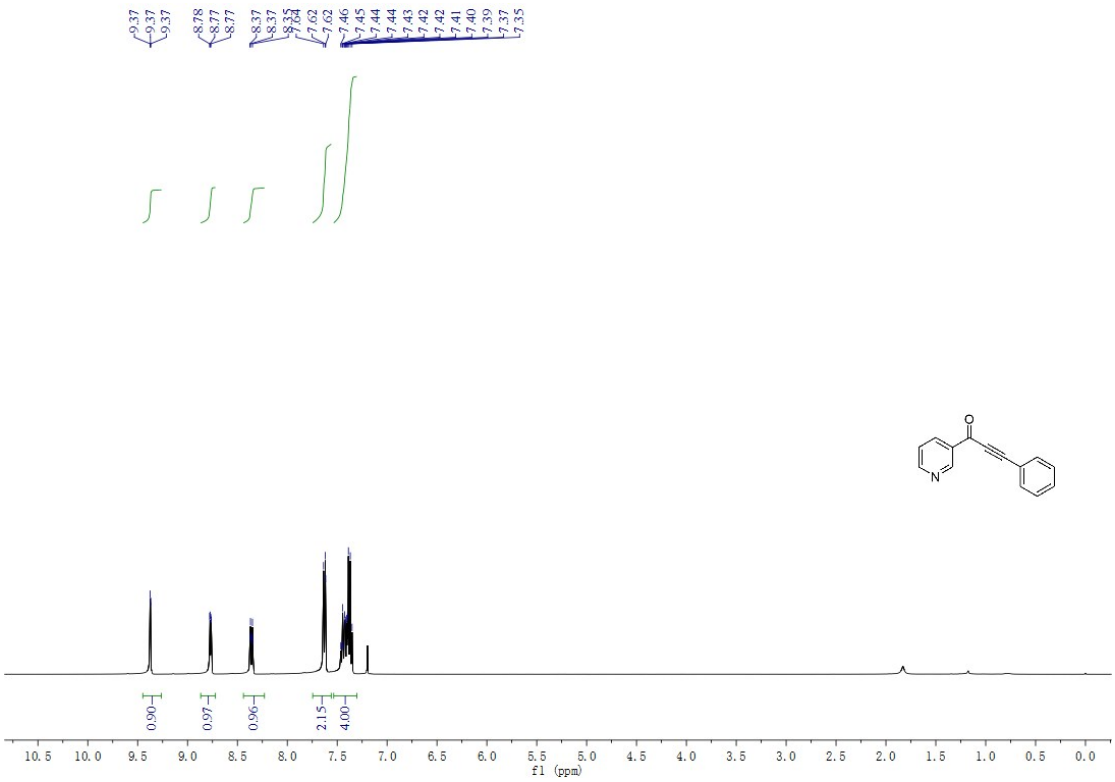
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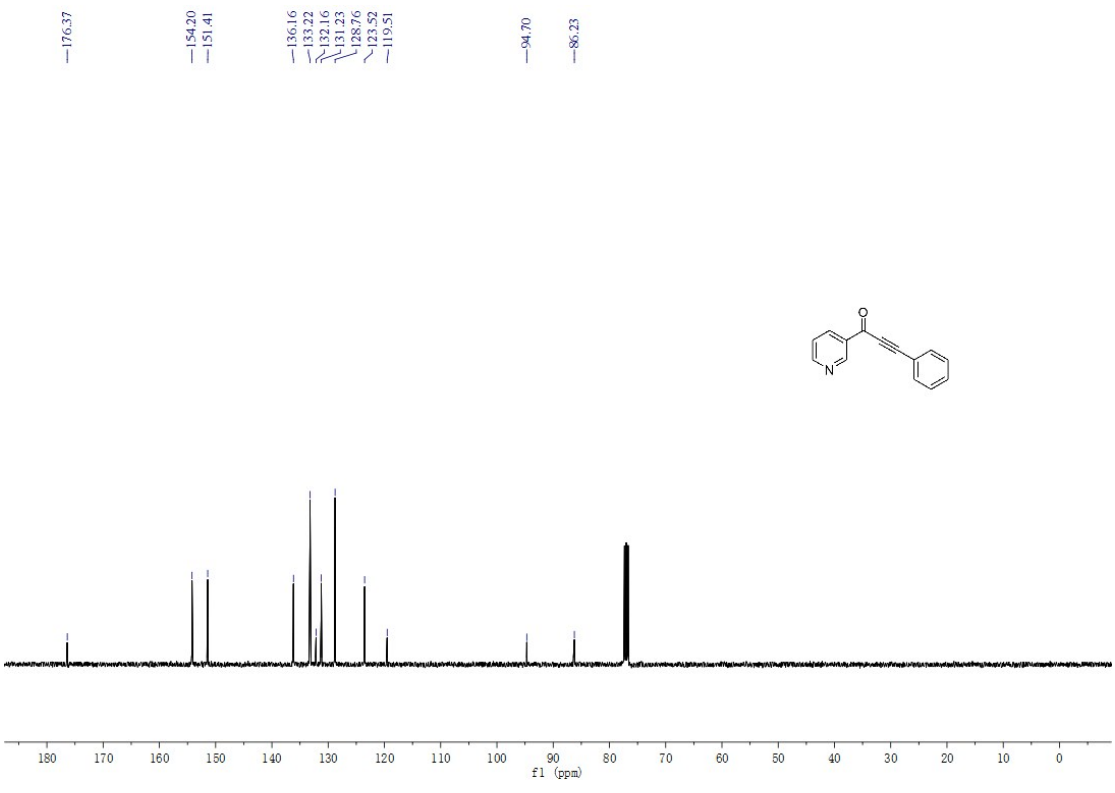
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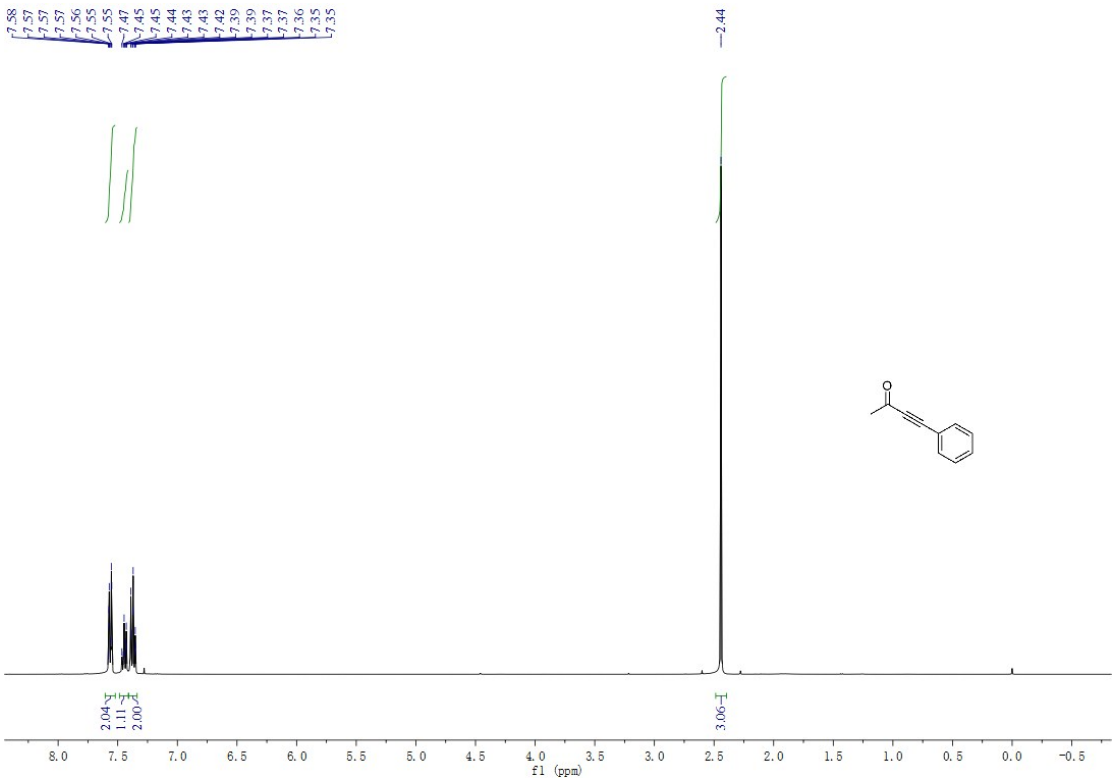
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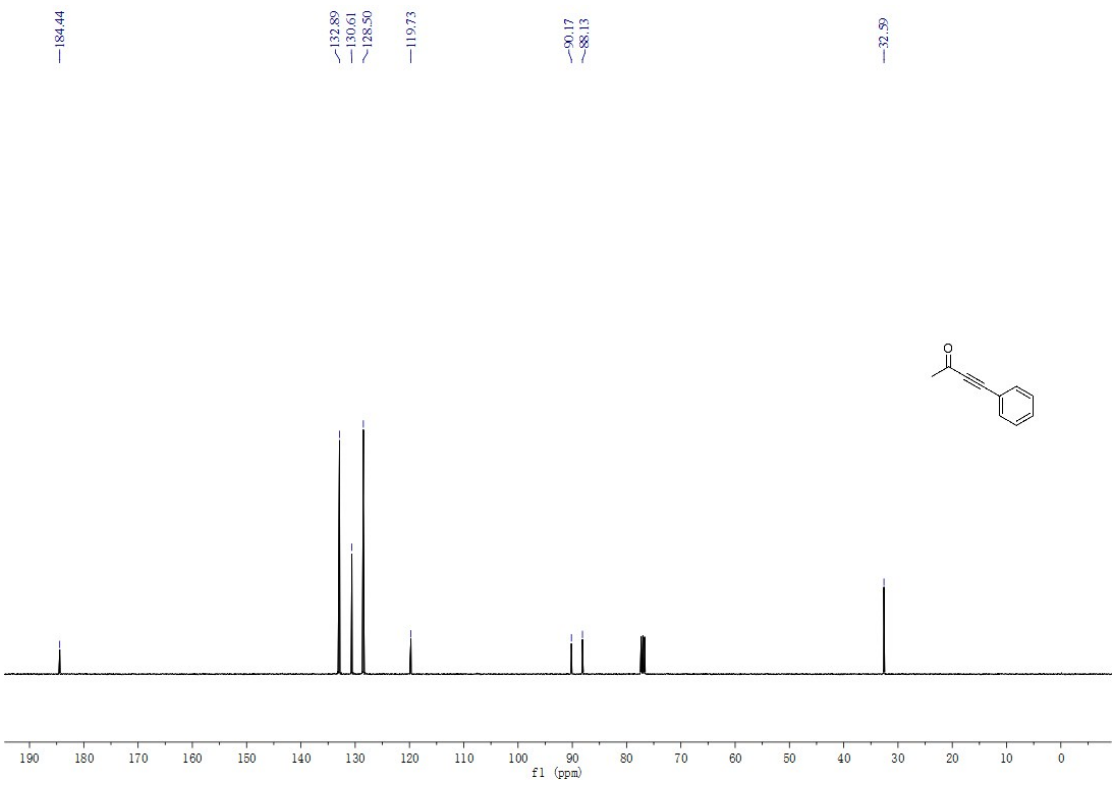
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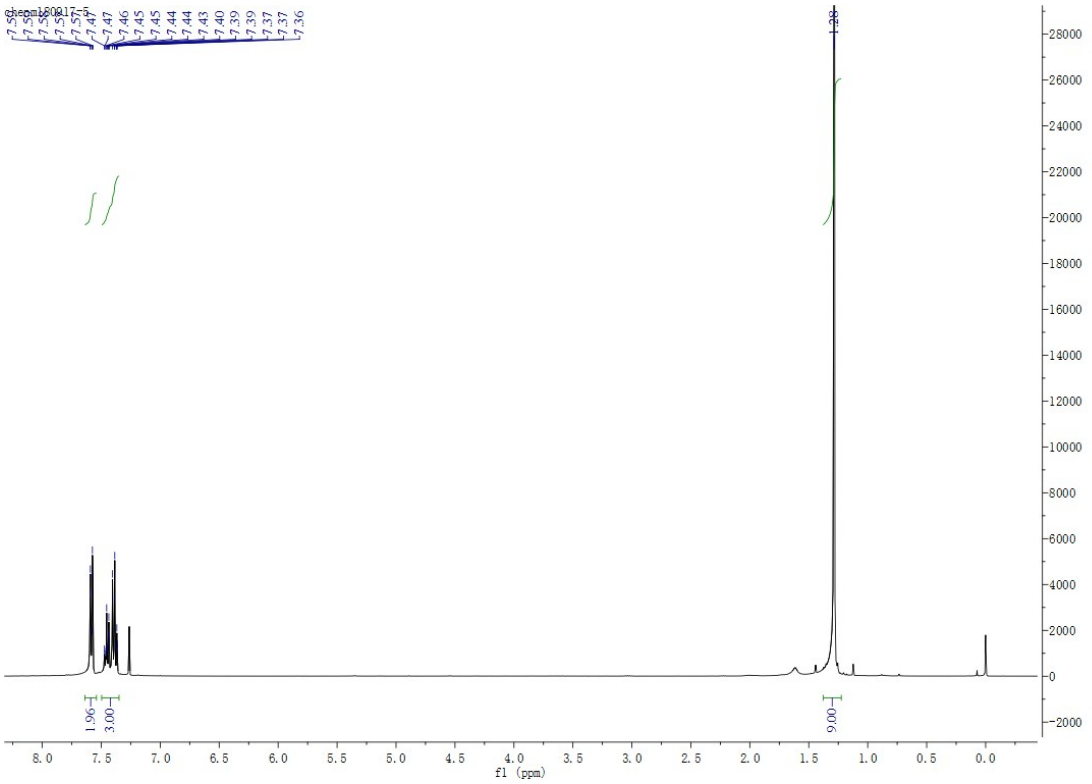
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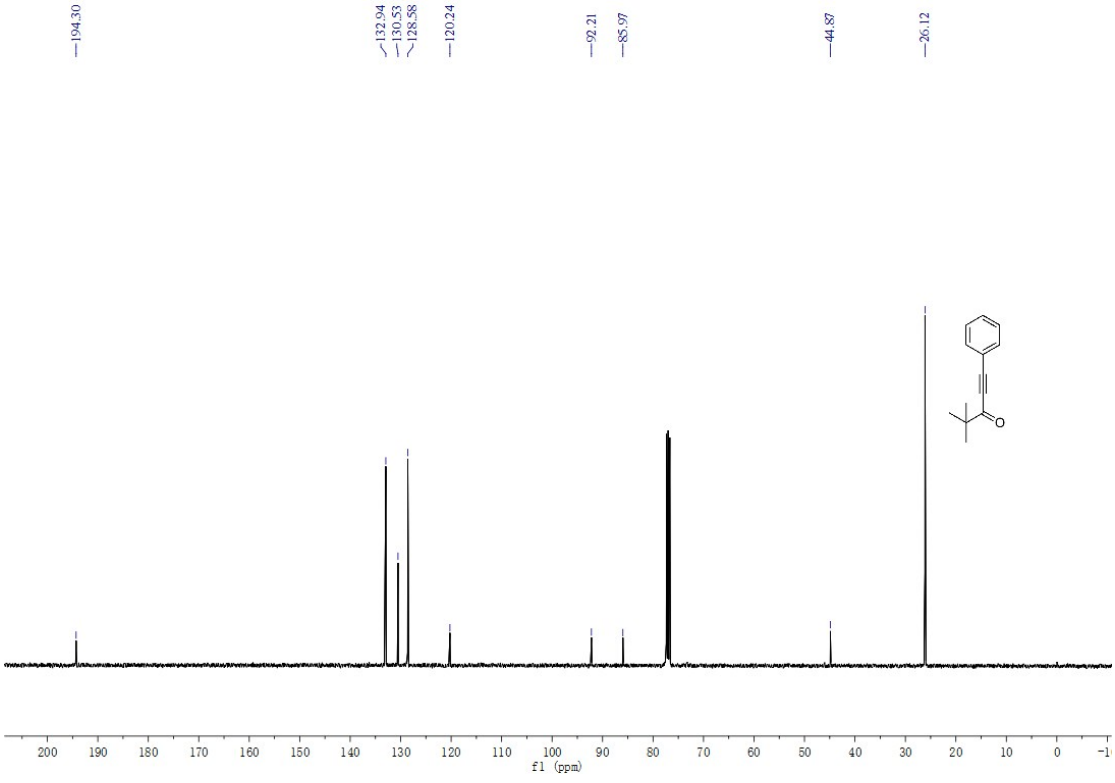
9.00
f1 (ppm)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26.12
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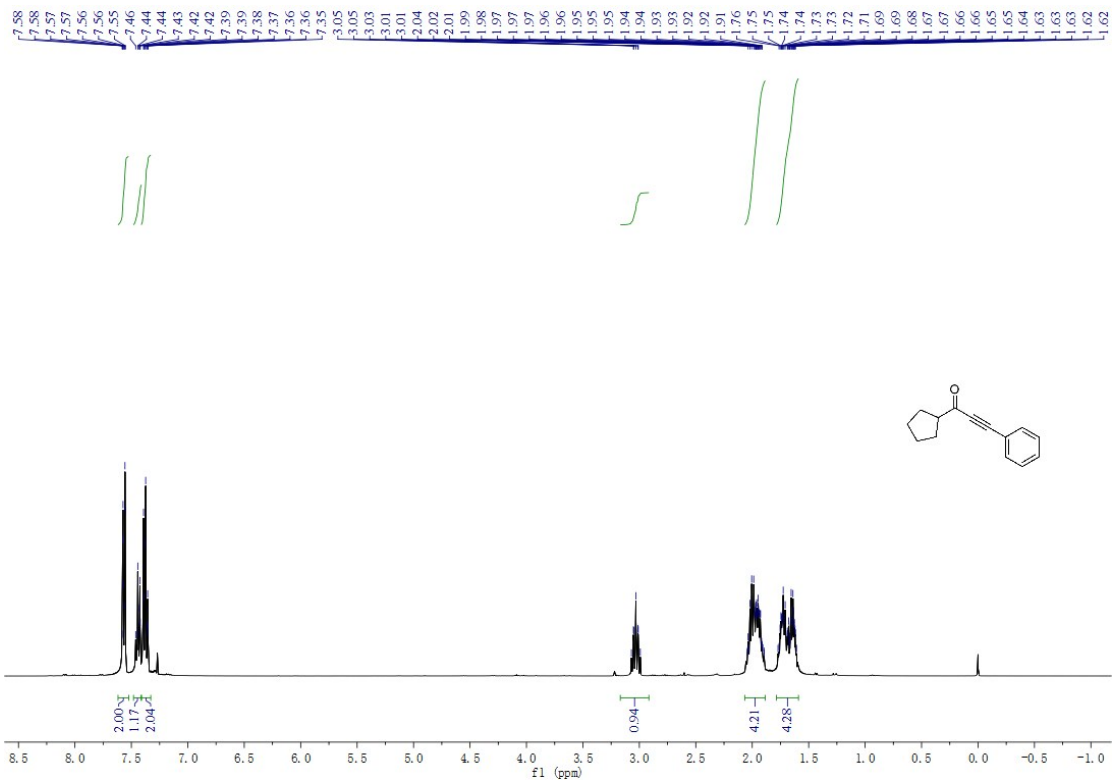
f1 (ppm)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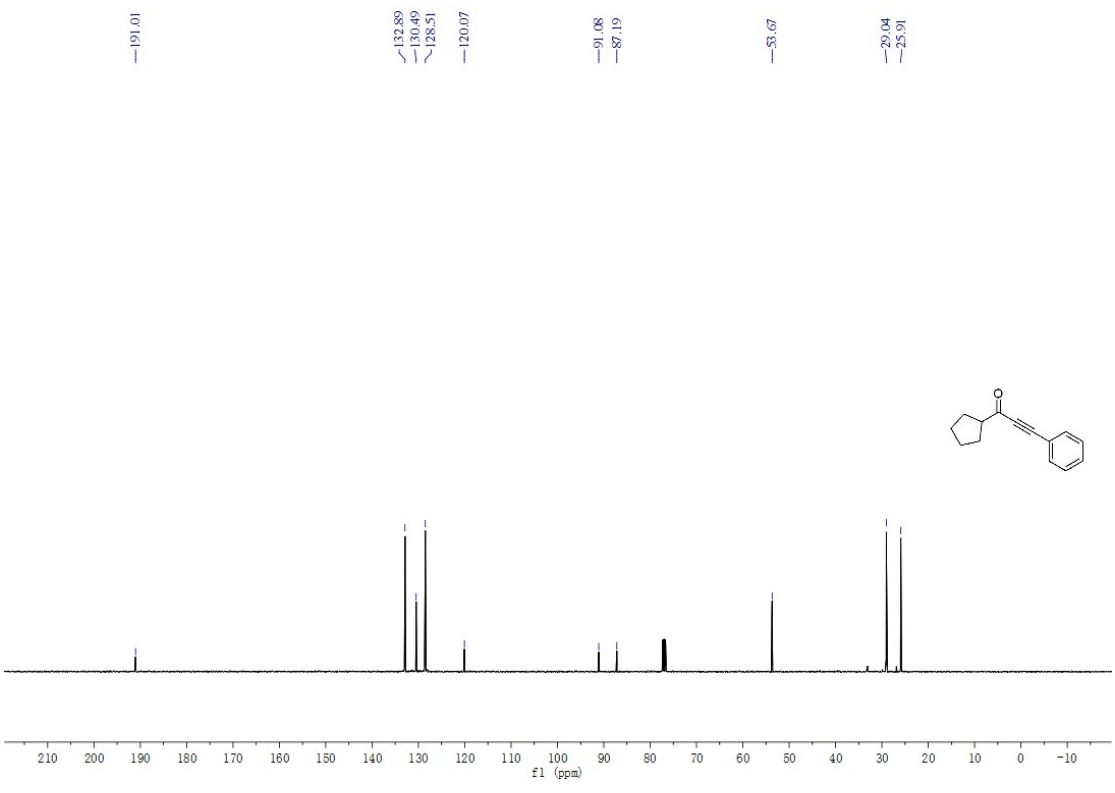
3.05 3.03 3.01 3.01 2.04 2.02 2.01 1.99 1.98 1.97 1.97 1.96 1.96 1.95 1.95 1.95 1.94 1.94 1.93 1.93 1.92 1.92 1.91 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.72 1.71 1.69 1.69 1.68 1.67 1.67 1.66 1.66 1.65 1.65 1.64 1.63 1.63 1.62 1.62
2.00
1.17
2.04
0.94
4.21
4.28
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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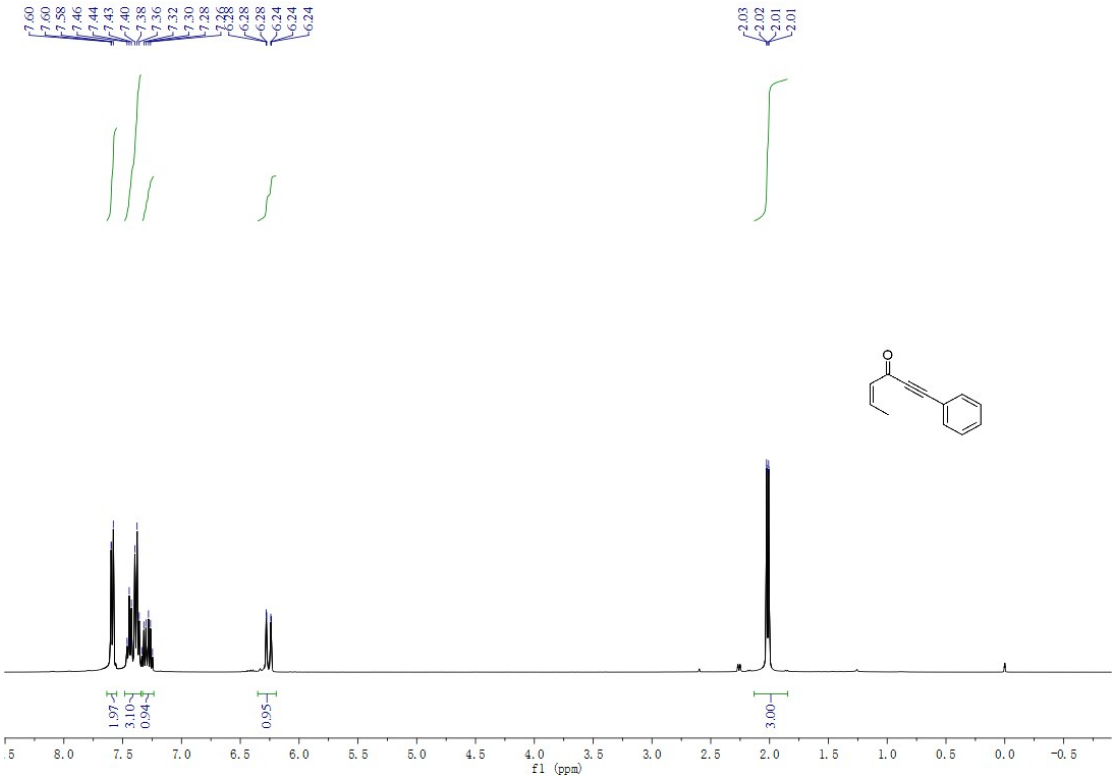
25.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.28
6.28
6.24
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2.01
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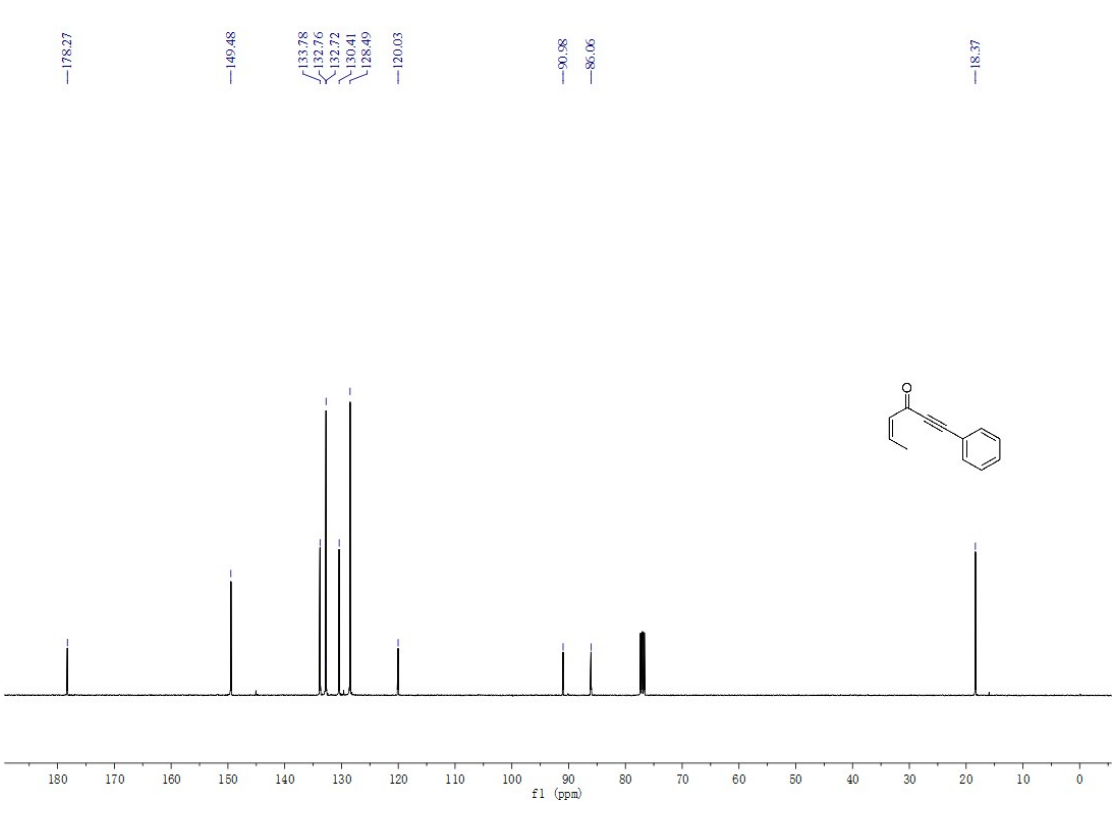
f1 (ppm)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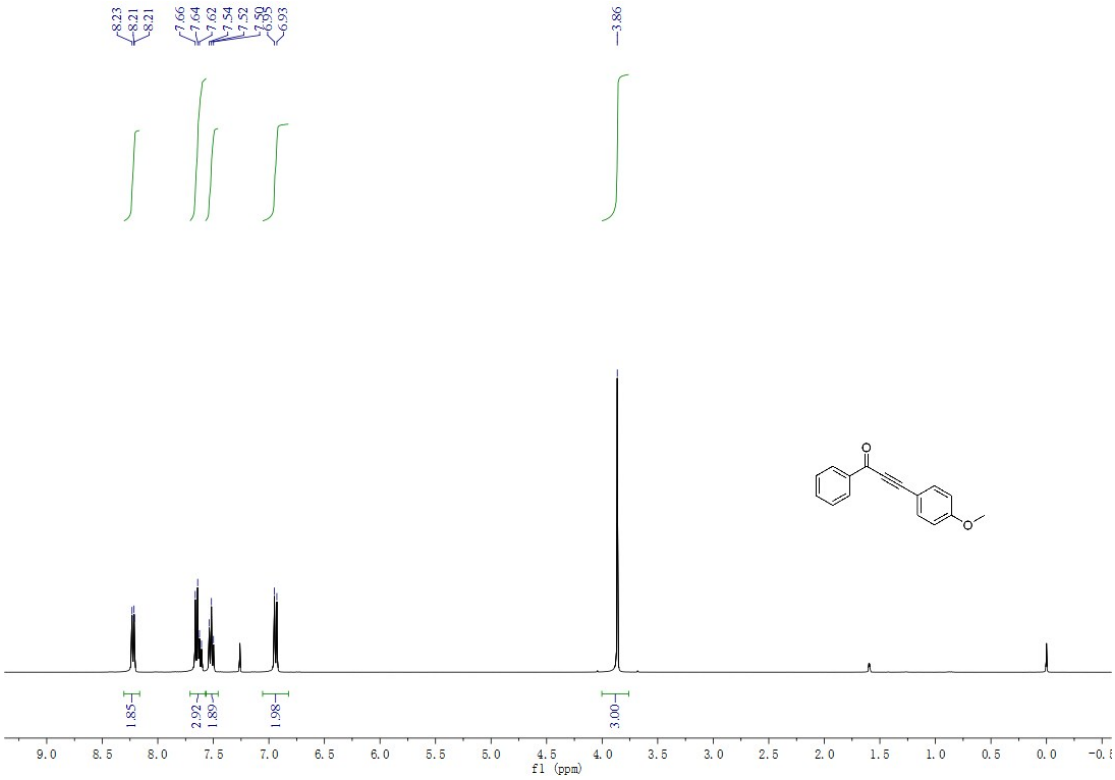
18.37
f1 (ppm)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7.62
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7.52
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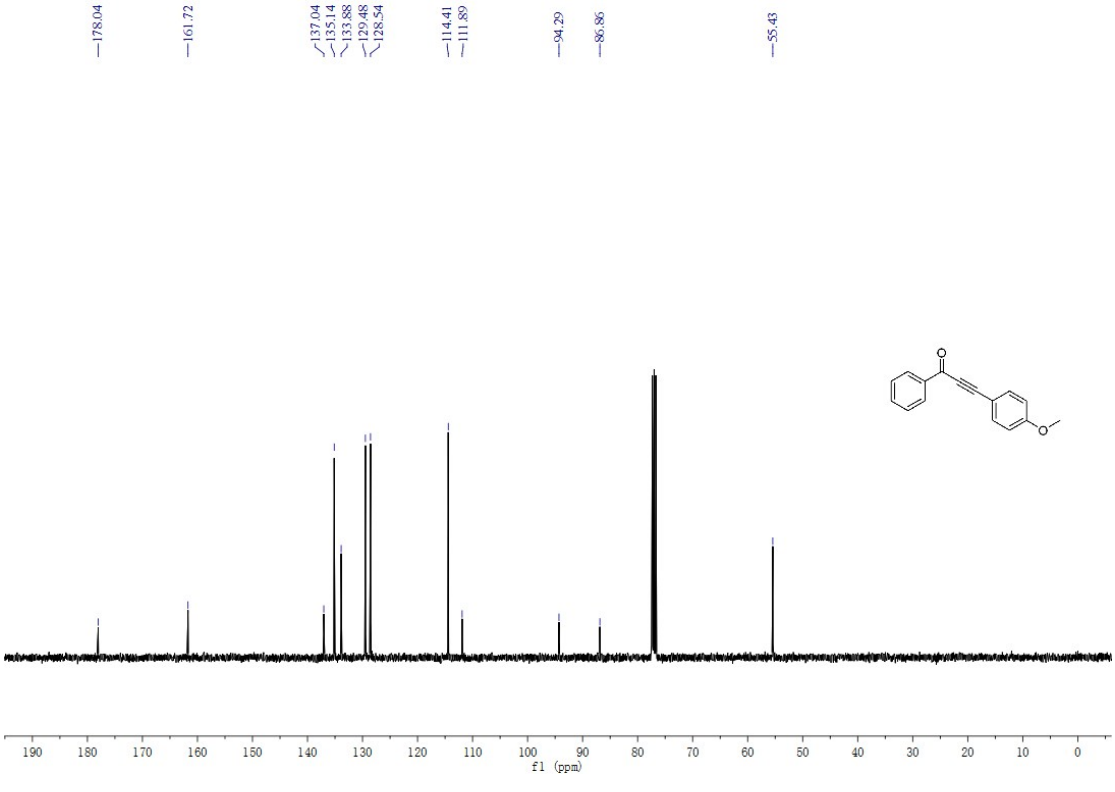
2.92
1.89
1.98
3.00
f1 (ppm)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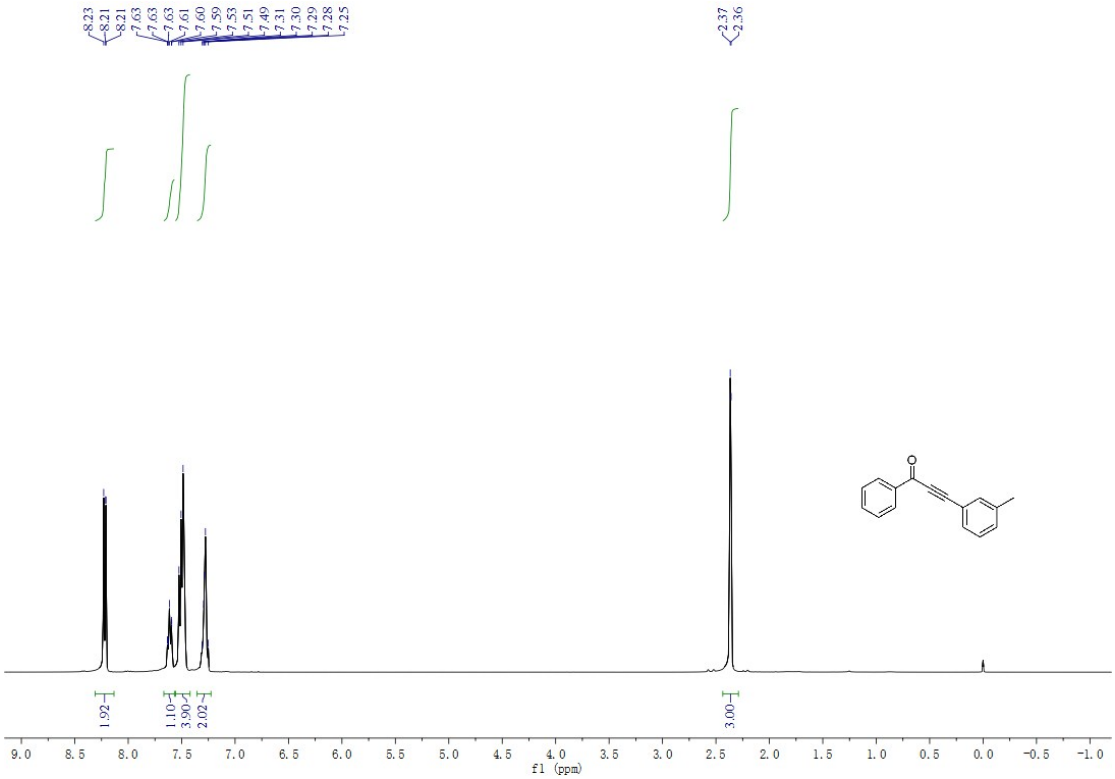
55.43
f1 (ppm)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1.10
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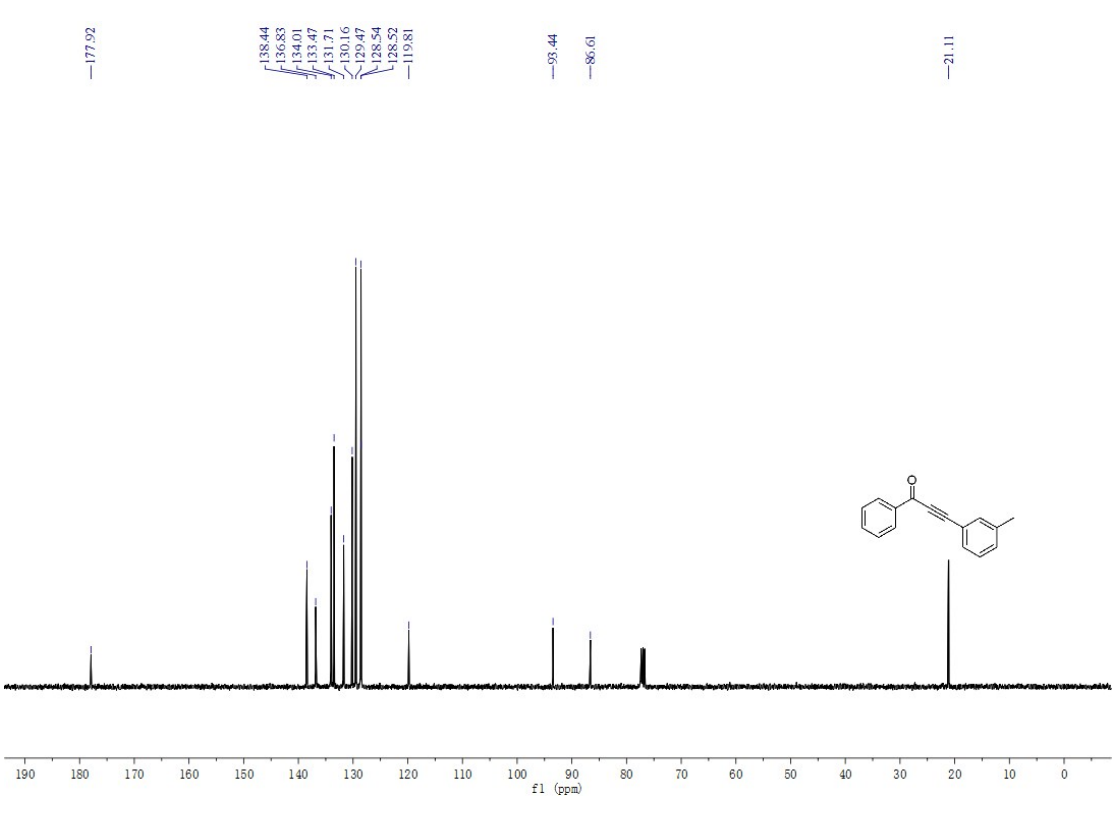
3.00
f1 (ppm)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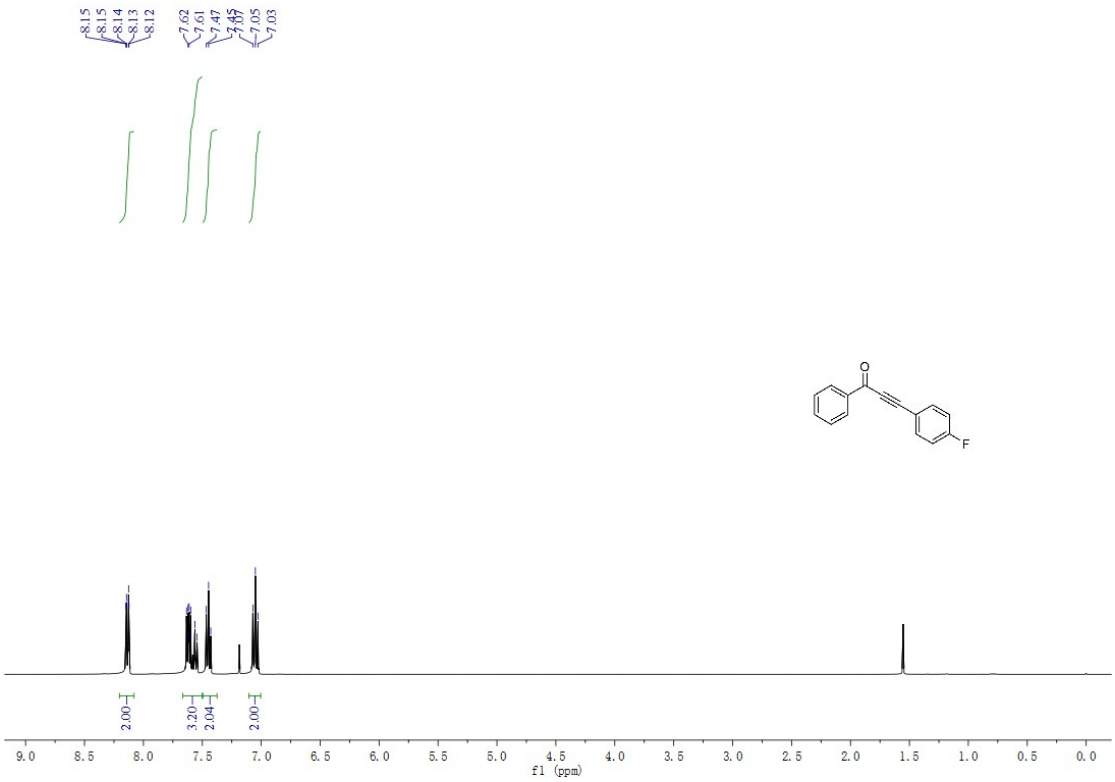
93.44
86.61
21.11
f1 (ppm)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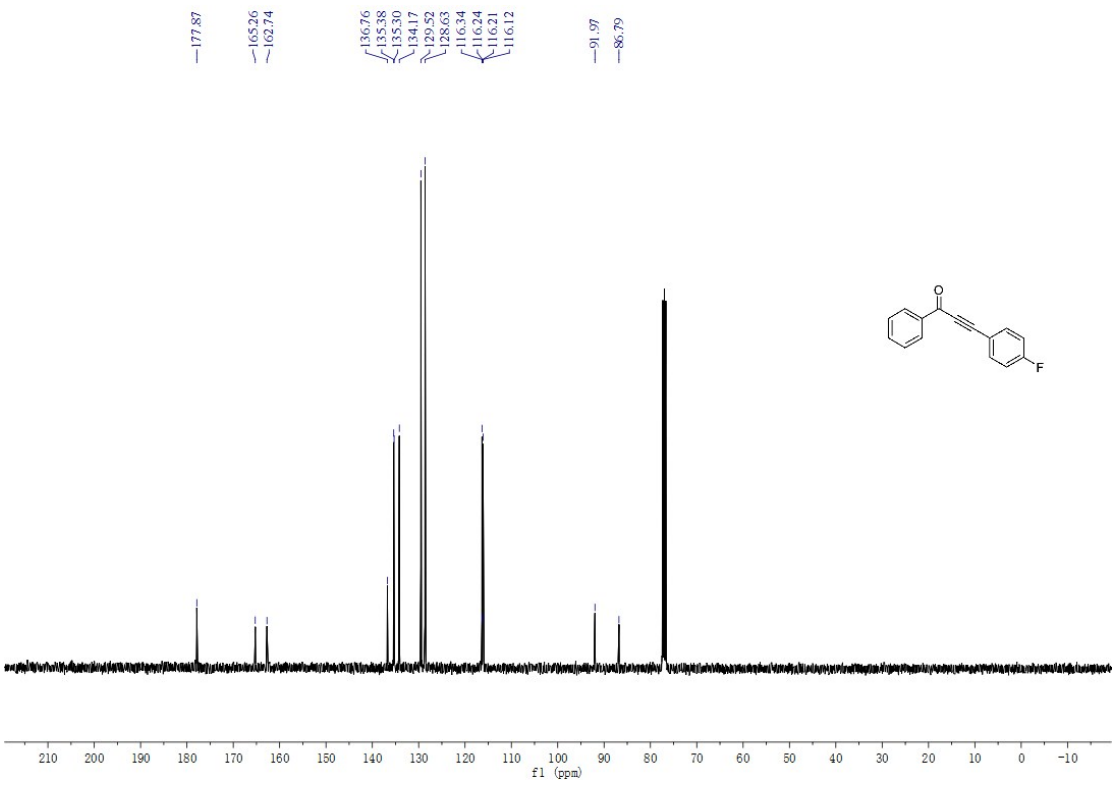
8.12
7.62
7.61
7.47
7.45
7.07
7.05
7.03
O
F
2.00
3.20
2.04
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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116.34
116.24
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91.97
86.79
O
F
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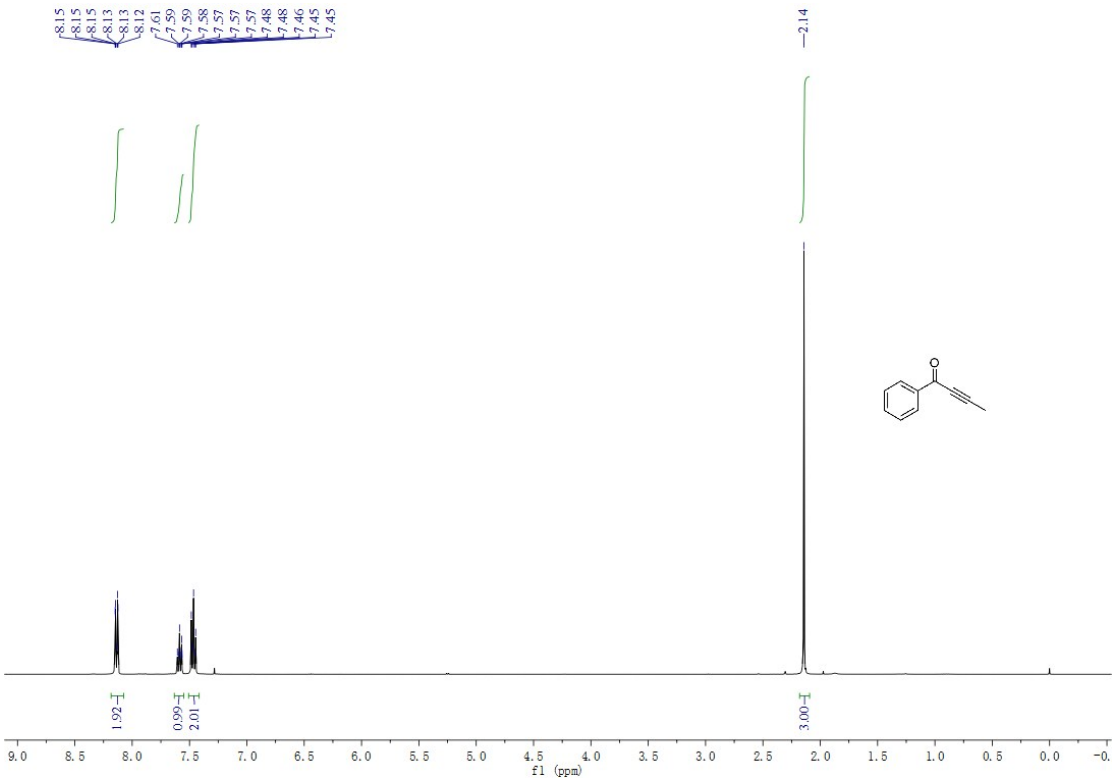
f1 (ppm)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7.48
7.46
7.45
7.45
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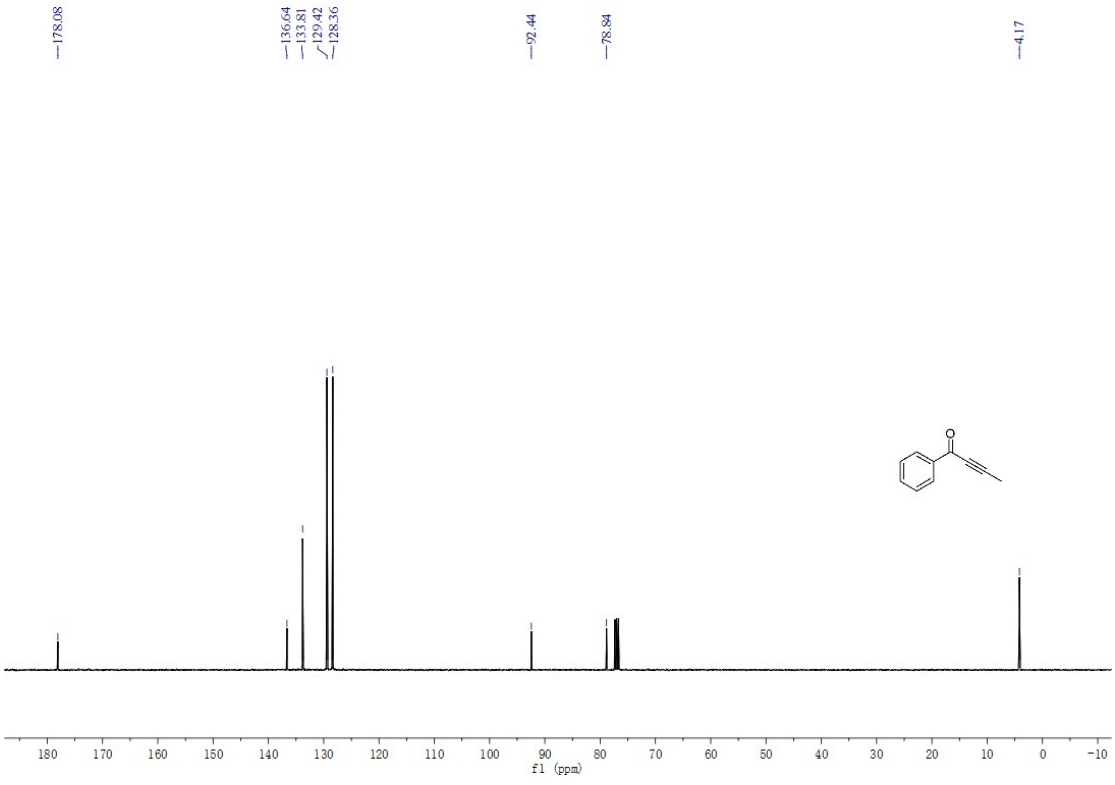
1.92
0.99
2.01
3.00
f1 (ppm)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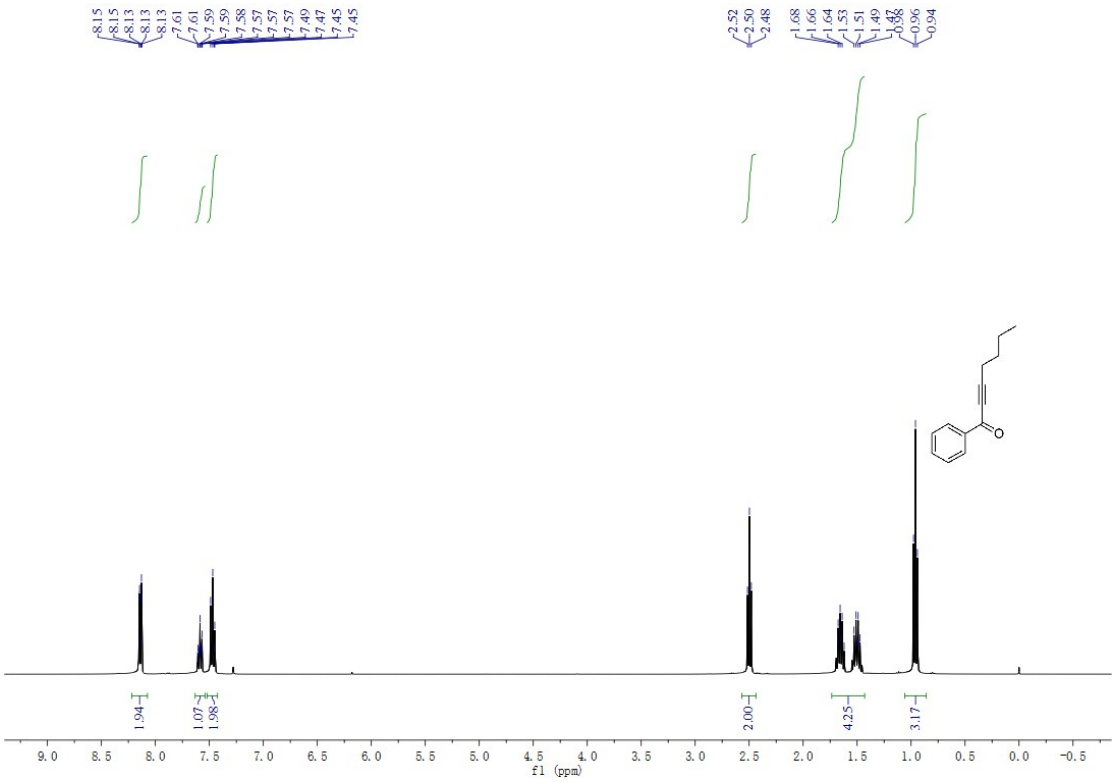
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2.48
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1.66
1.64
1.53
1.51
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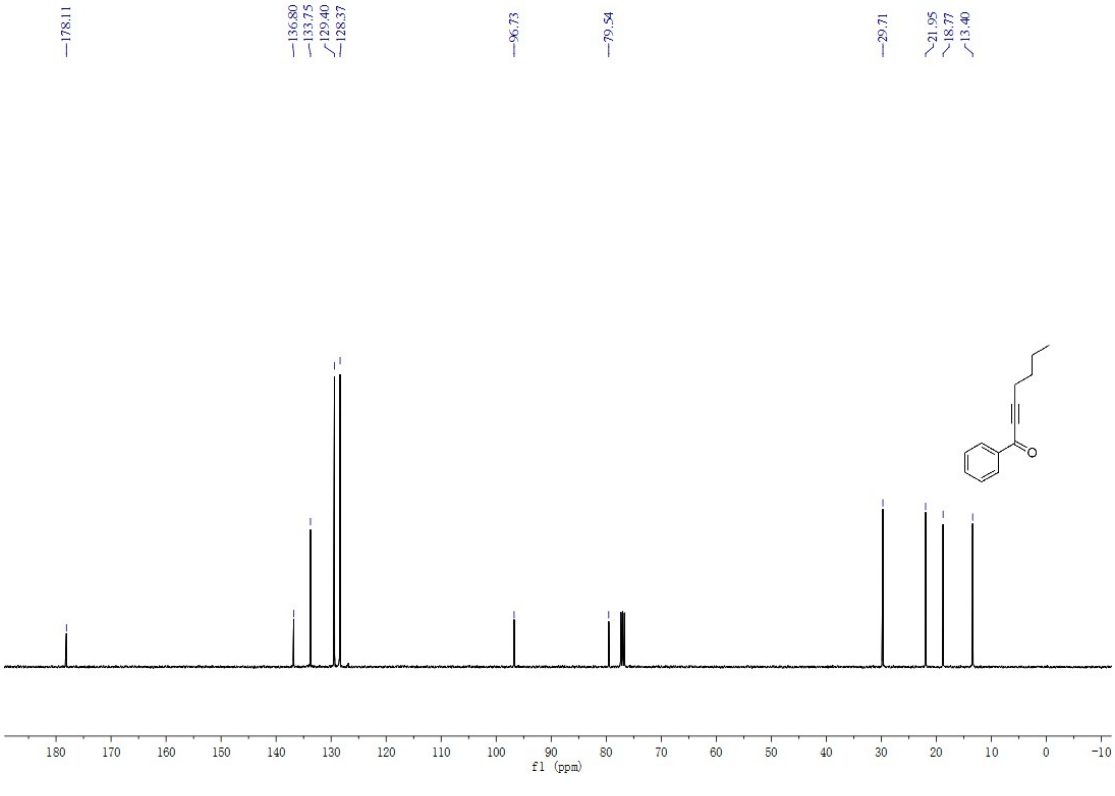
1.94
1.07
1.98
2.00
4.25
3.17
f1 (ppm)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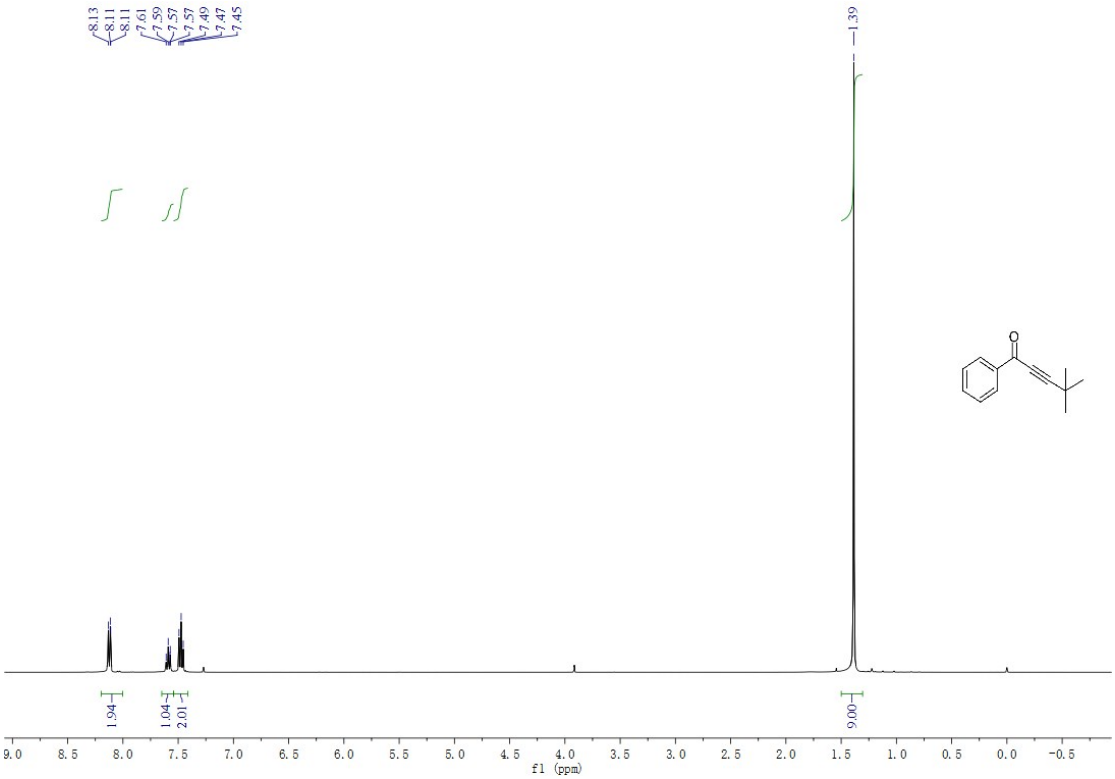
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7.45
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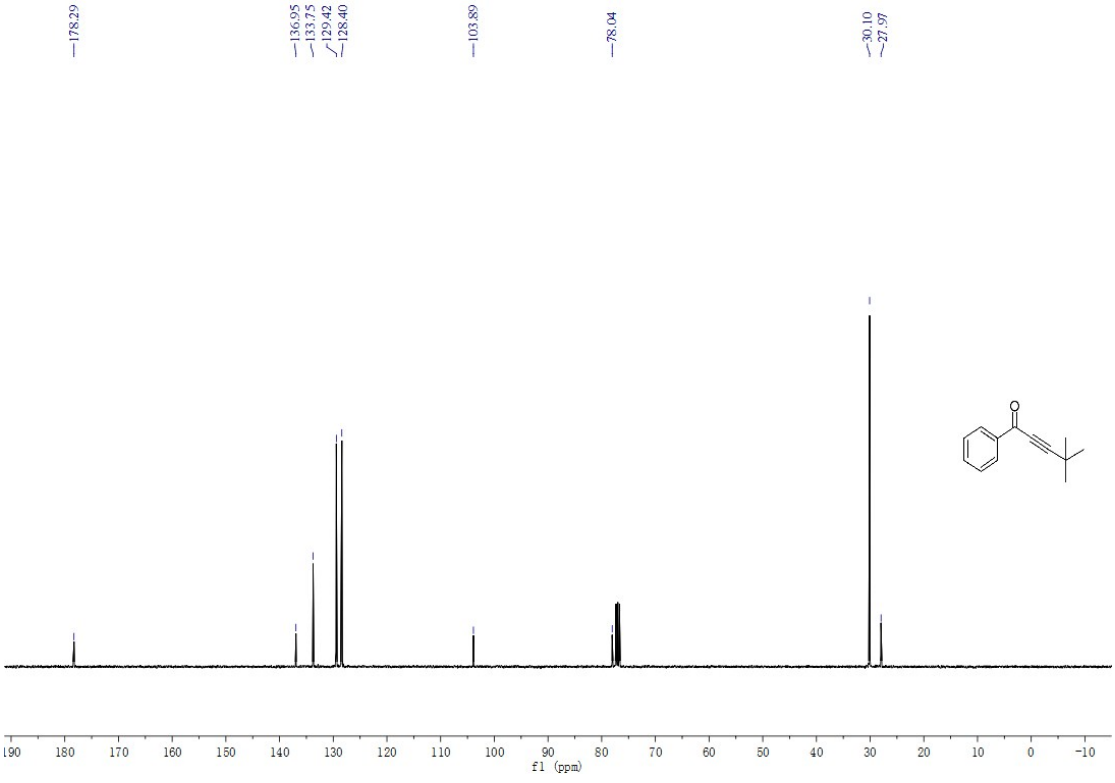
1.94
1.04
2.01
9.00
f1 (ppm)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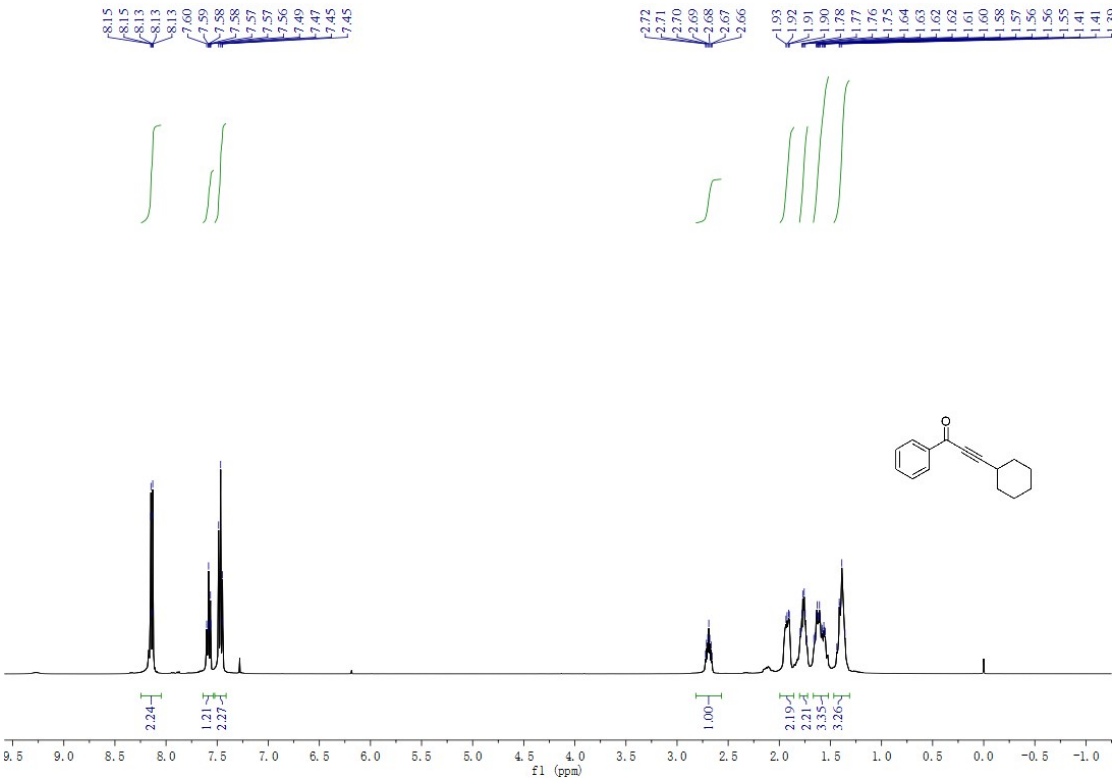
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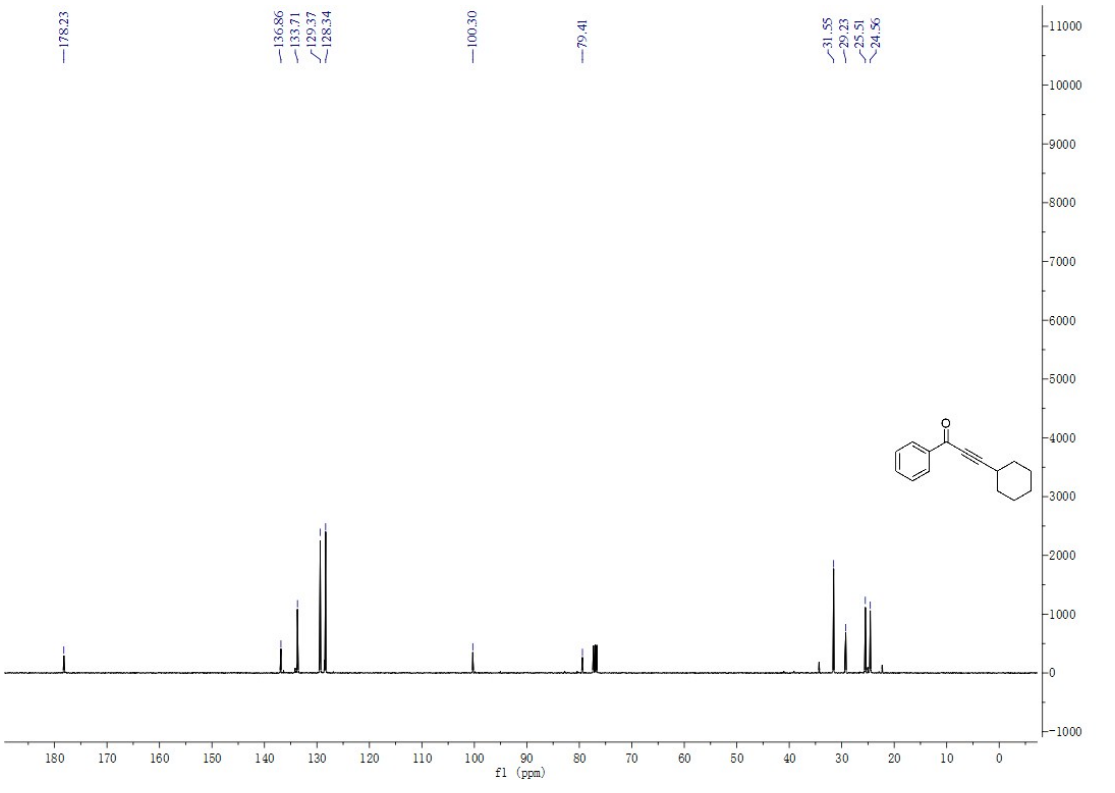
f1 (ppm)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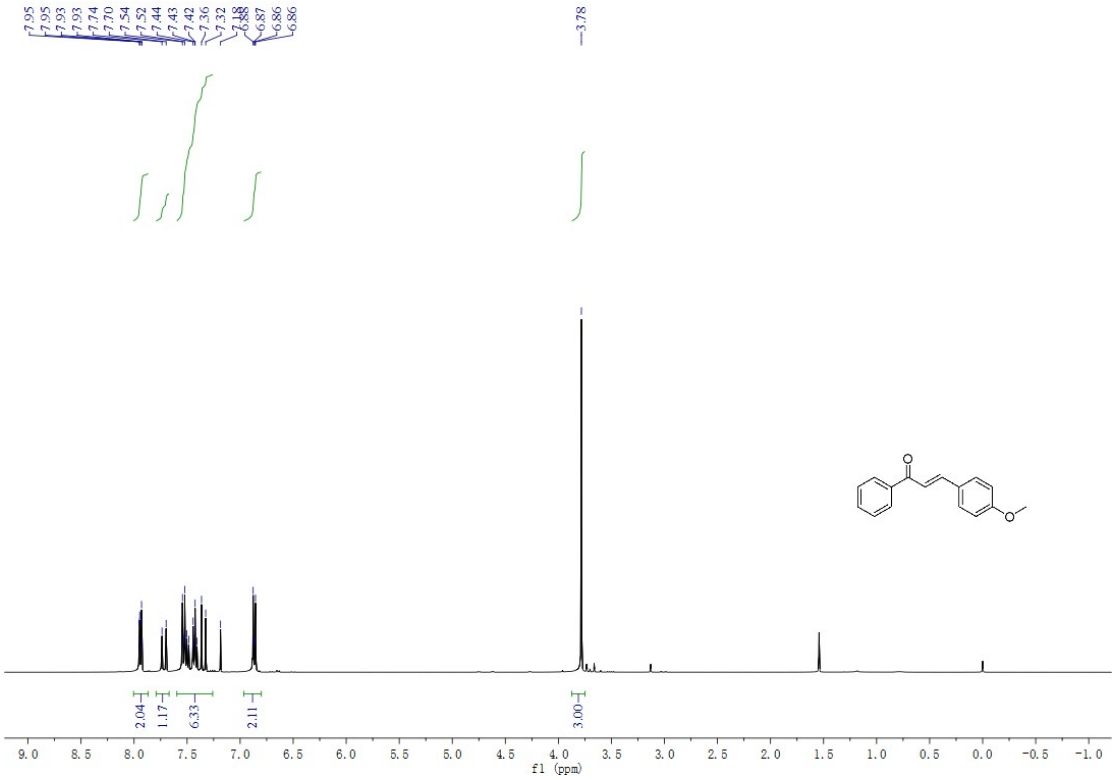
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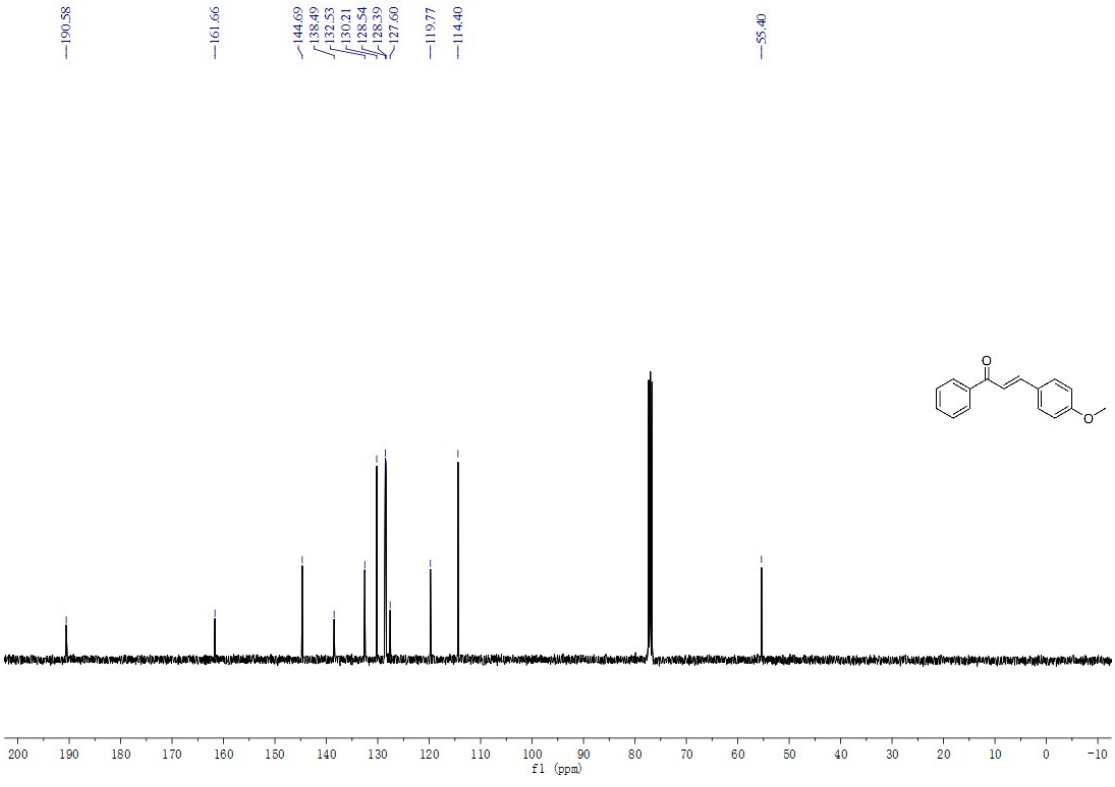
f1 (ppm)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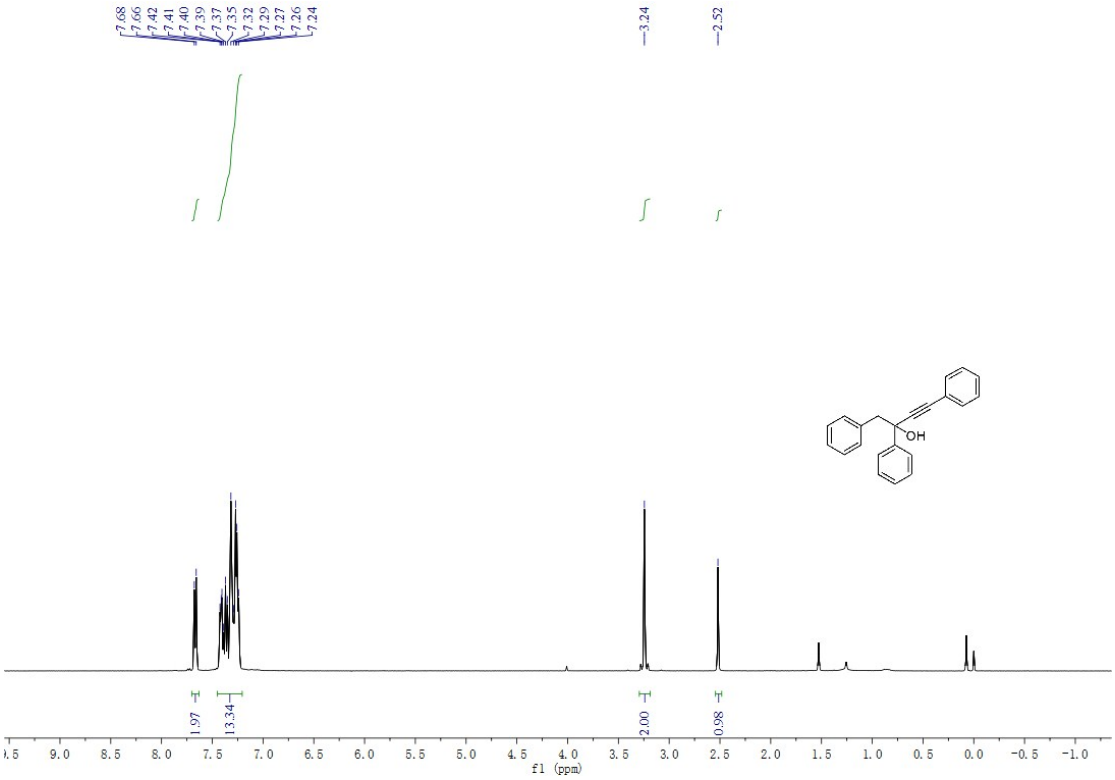
f1 (ppm)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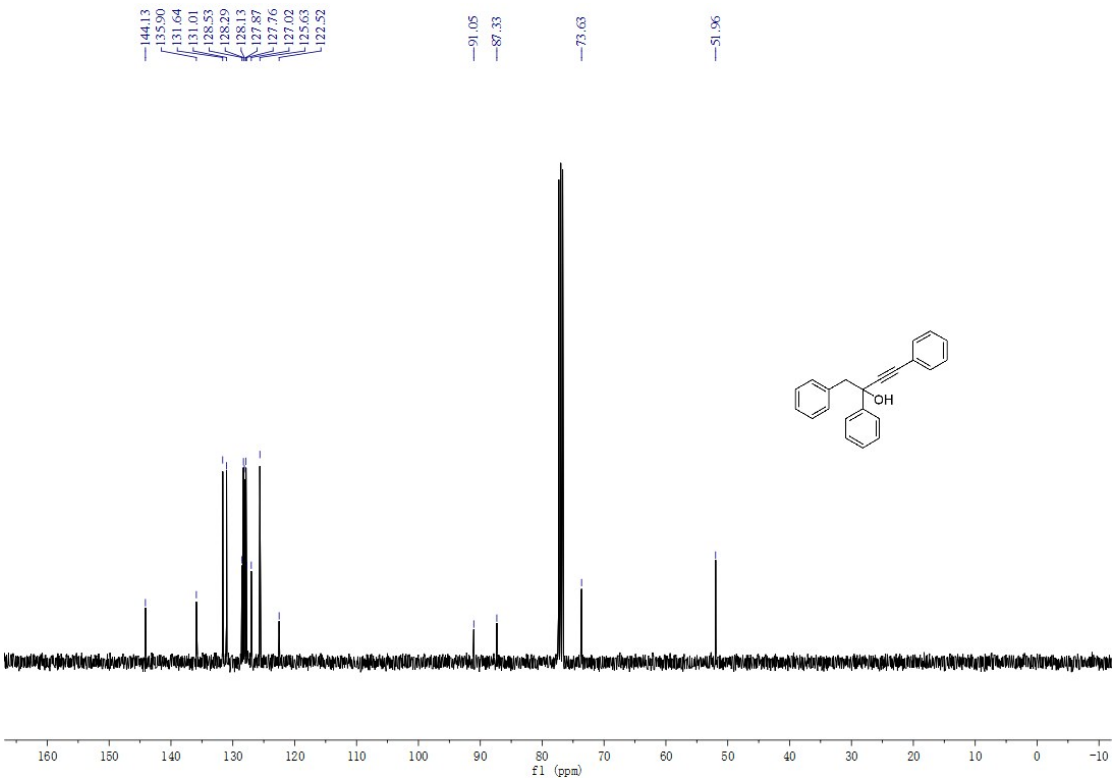
f1 (ppm)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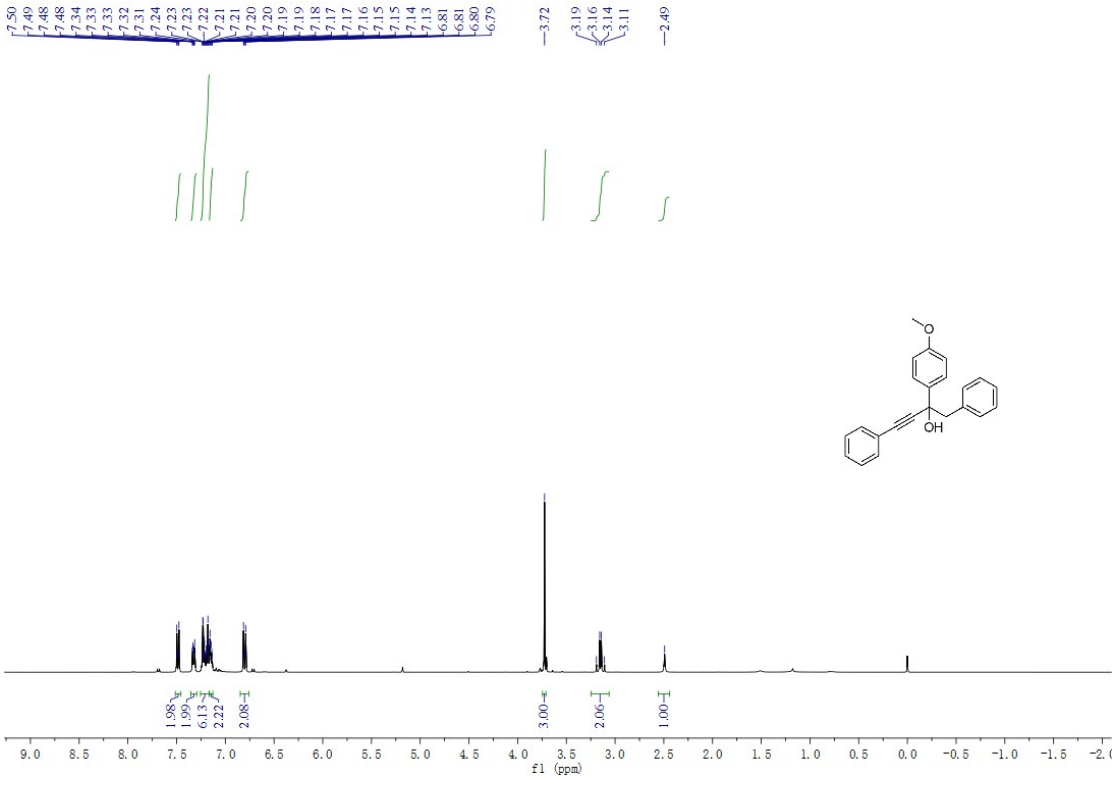
OH
f1 (ppm)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6.81
6.80
6.79
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3.16
3.14
3.11
2.49
O
OH
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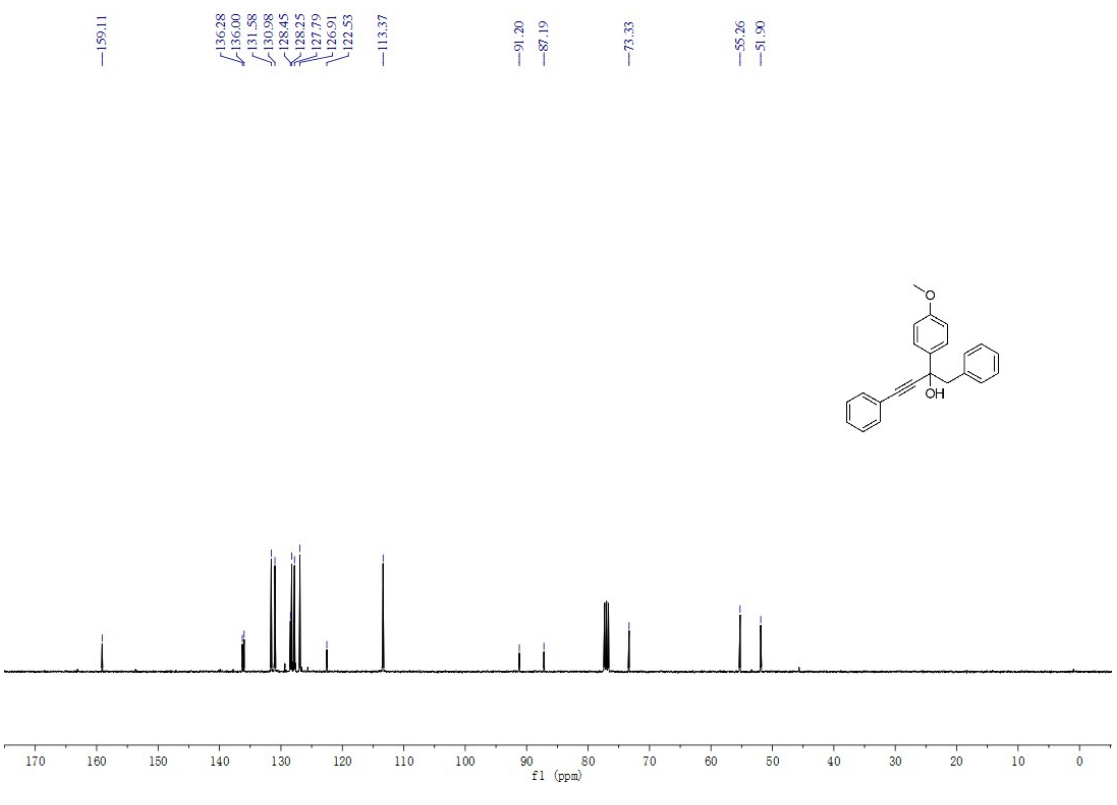
1.99
6.13
2.22
2.08
3.00
2.06
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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122.53
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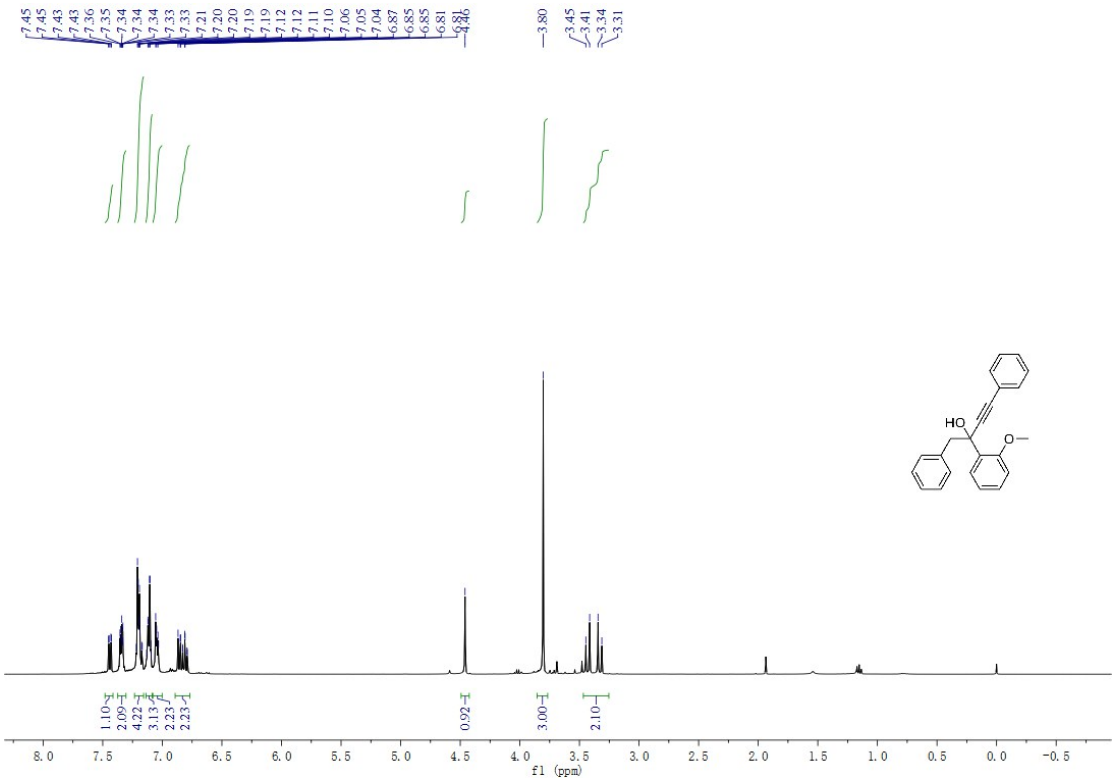
73.33
55.26
51.90
O
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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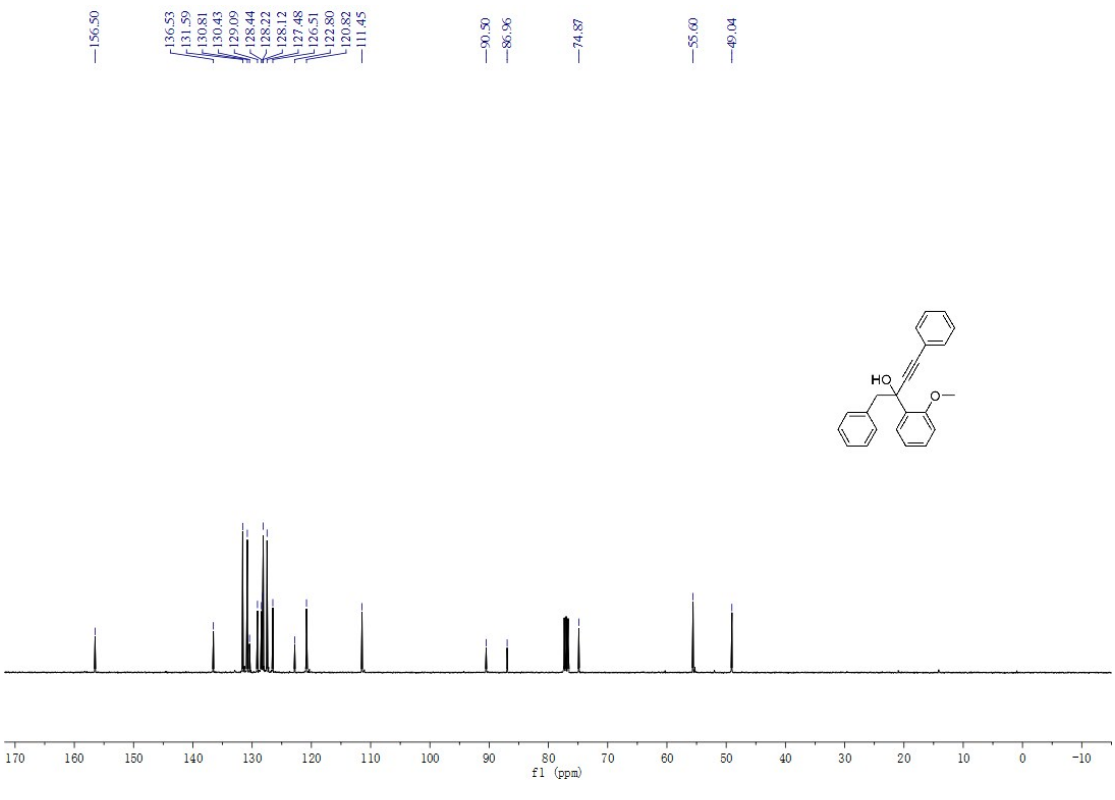
f1 (ppm)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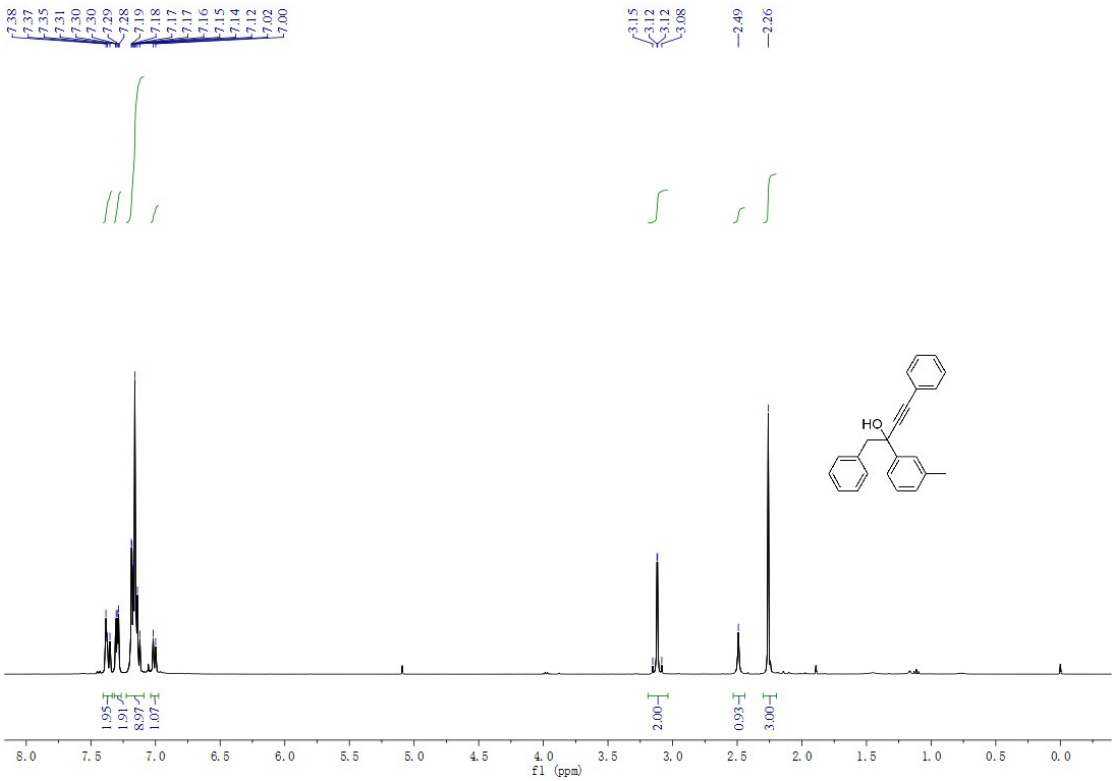
O
f1 (ppm)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3.12
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3.00
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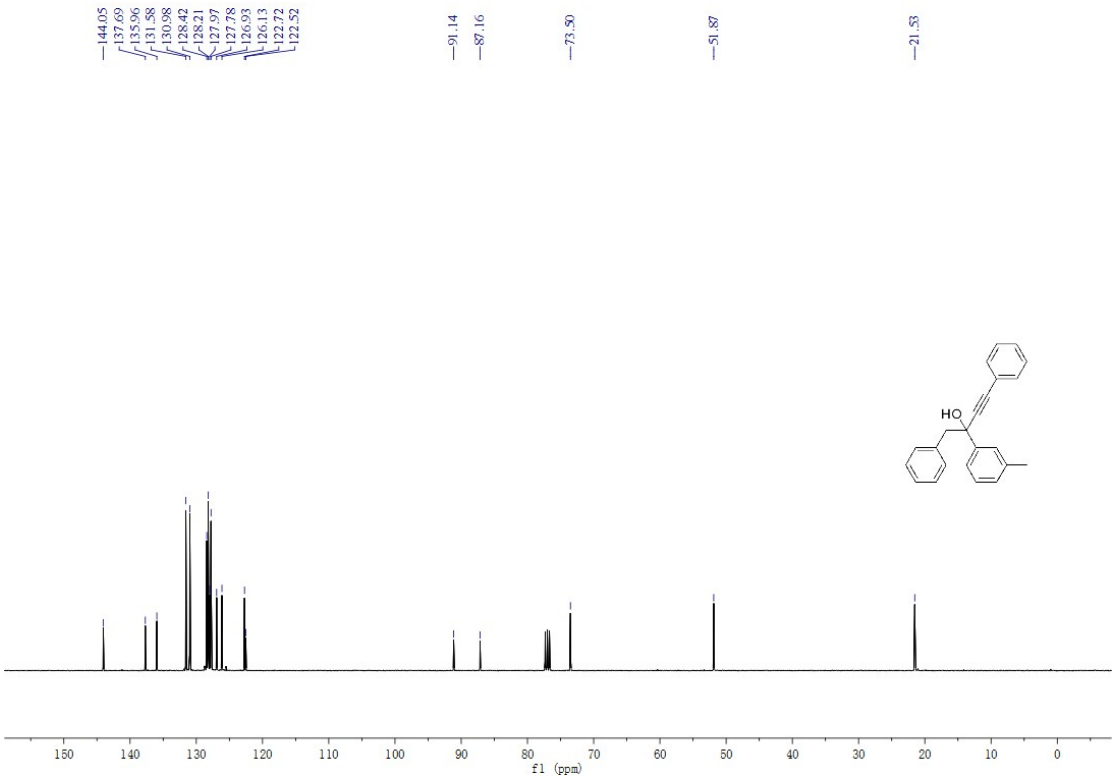
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21.53
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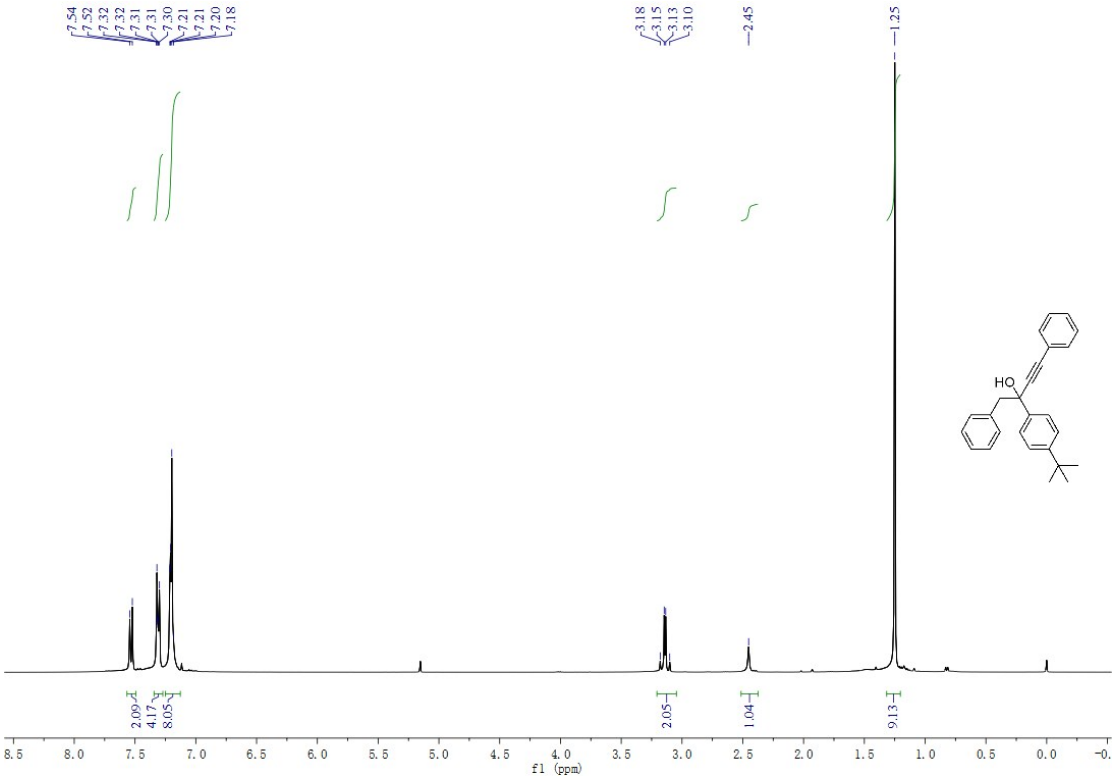
f1 (ppm)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HO
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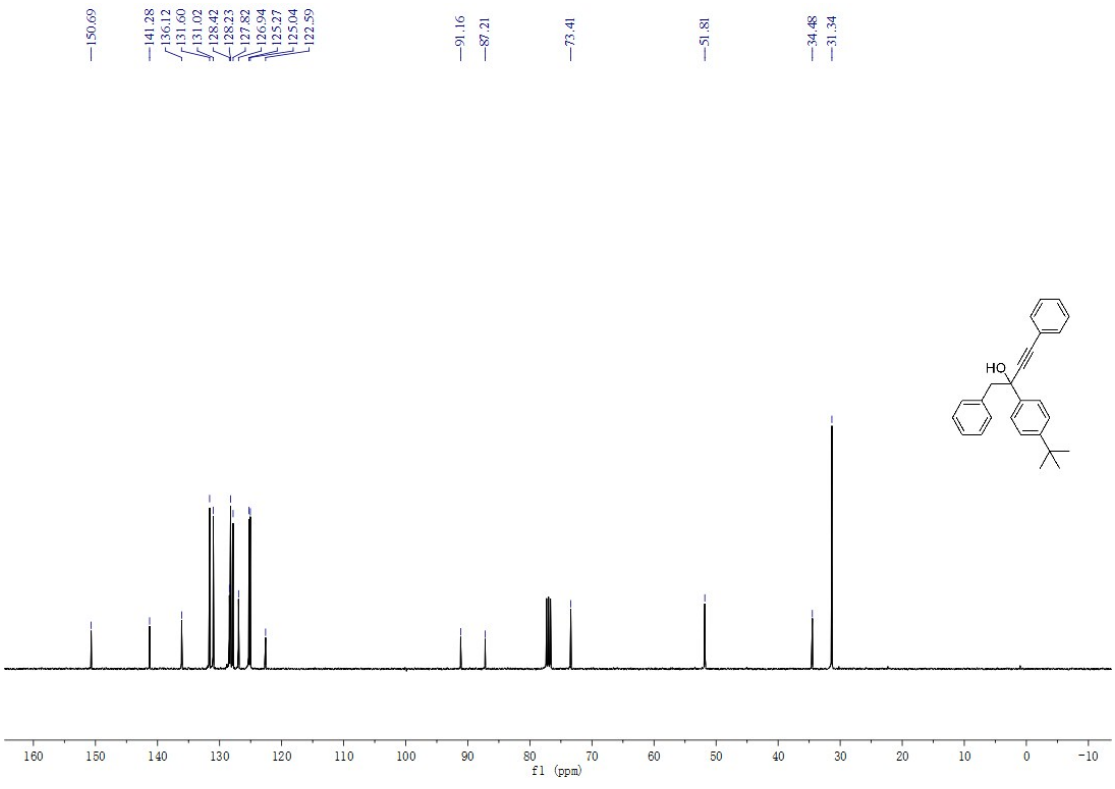
8.05
2.05
1.04
9.13
f1 (ppm)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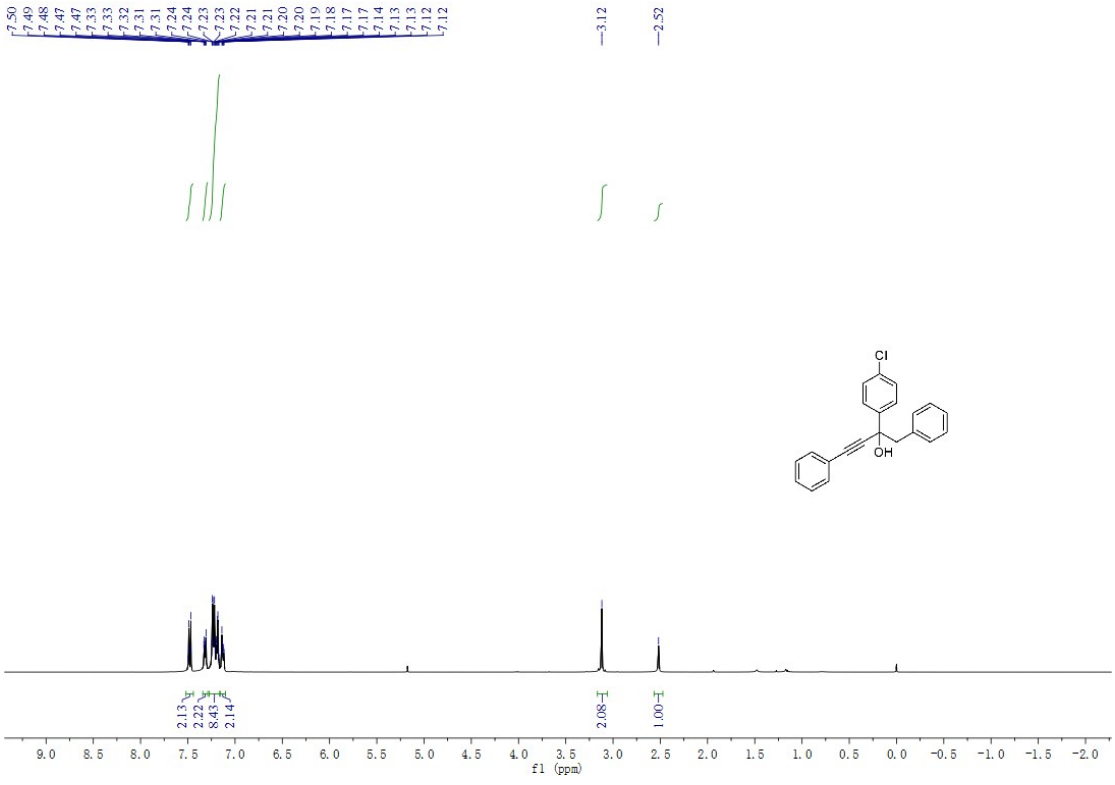
HO
f1 (ppm)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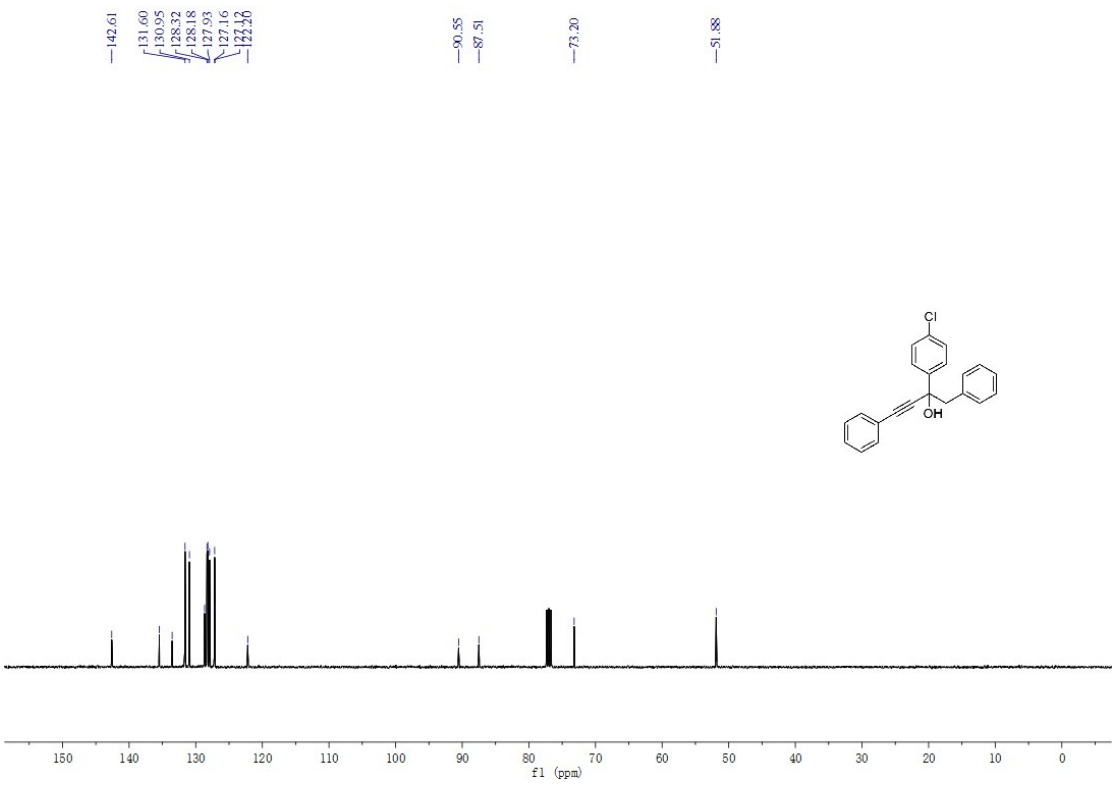
f1 (ppm)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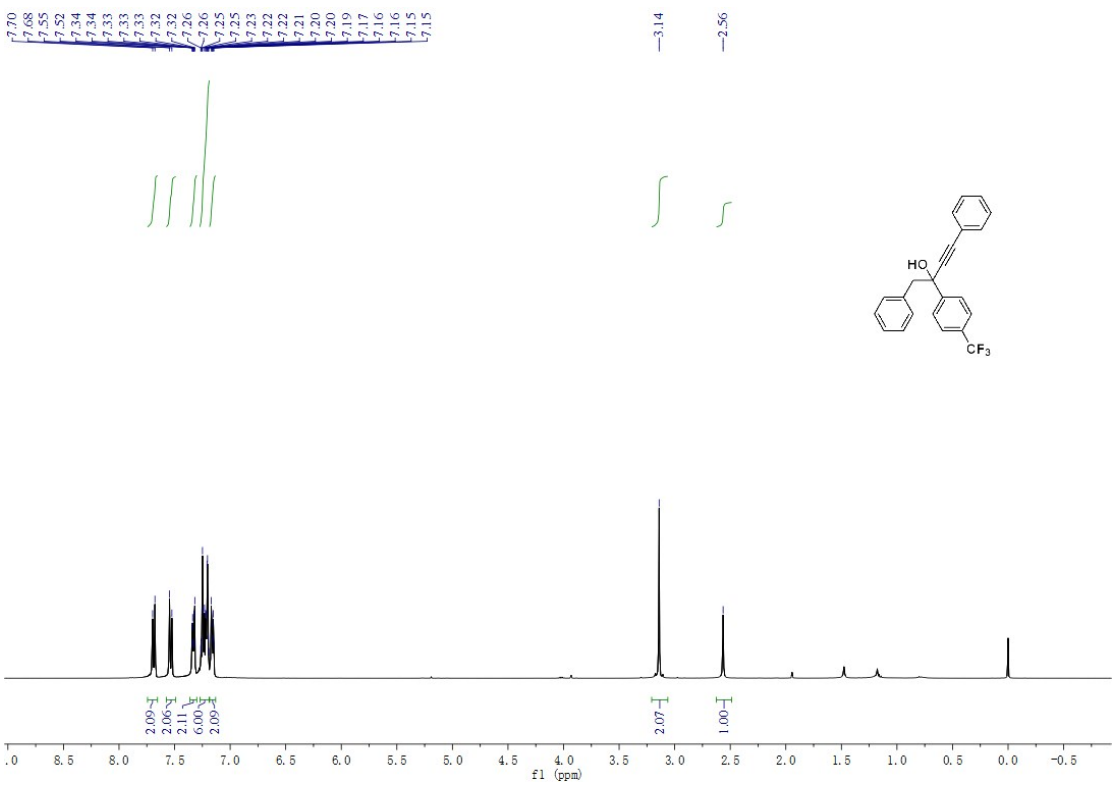
Cl
OH
f1 (ppm)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7.15
7.15
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2.09
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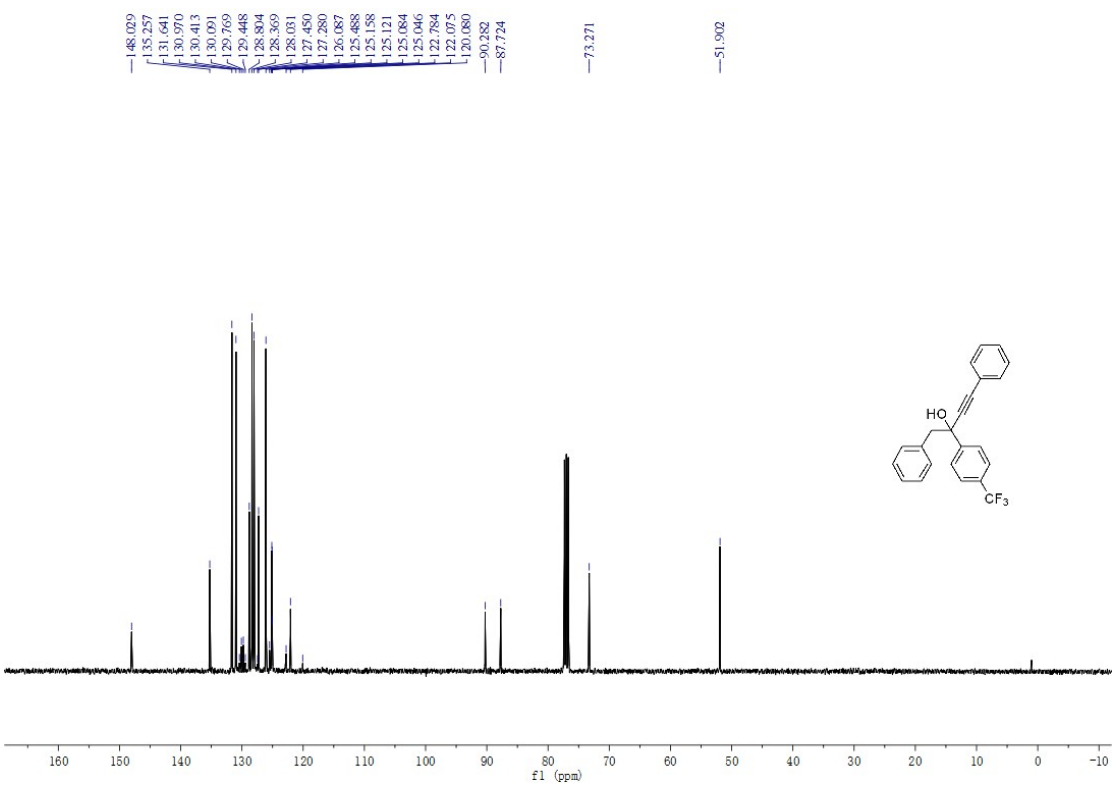
1.00
f1 (ppm)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CF3
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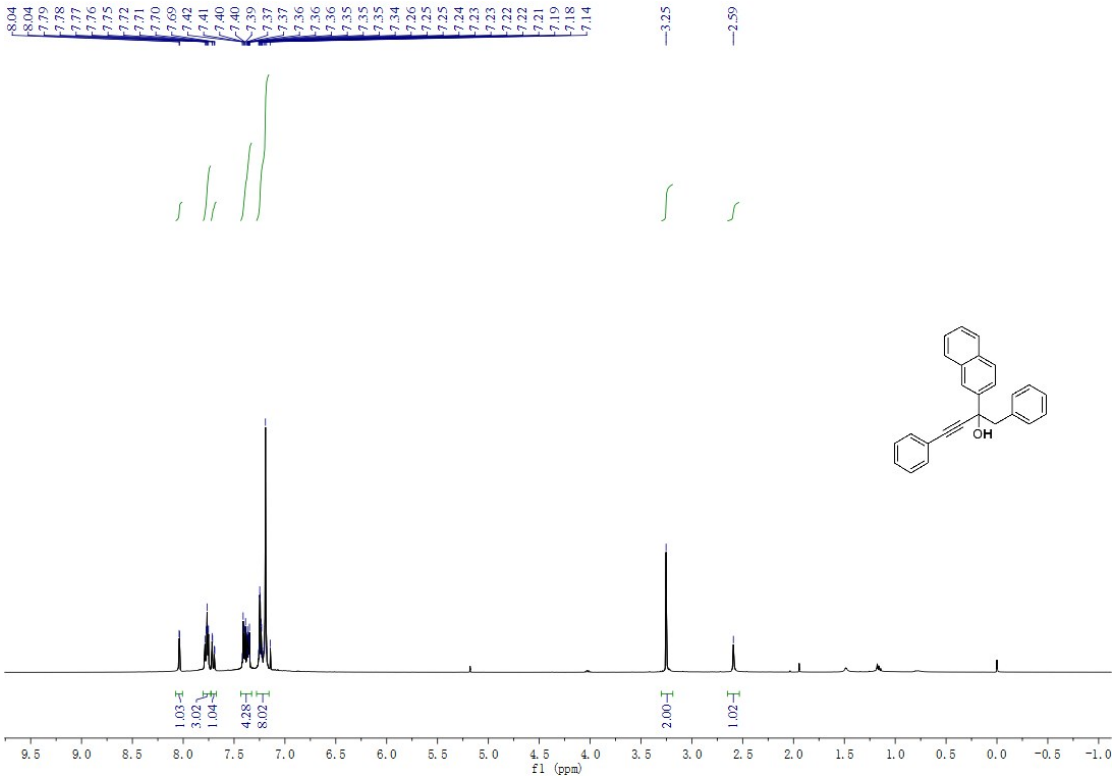
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7.18
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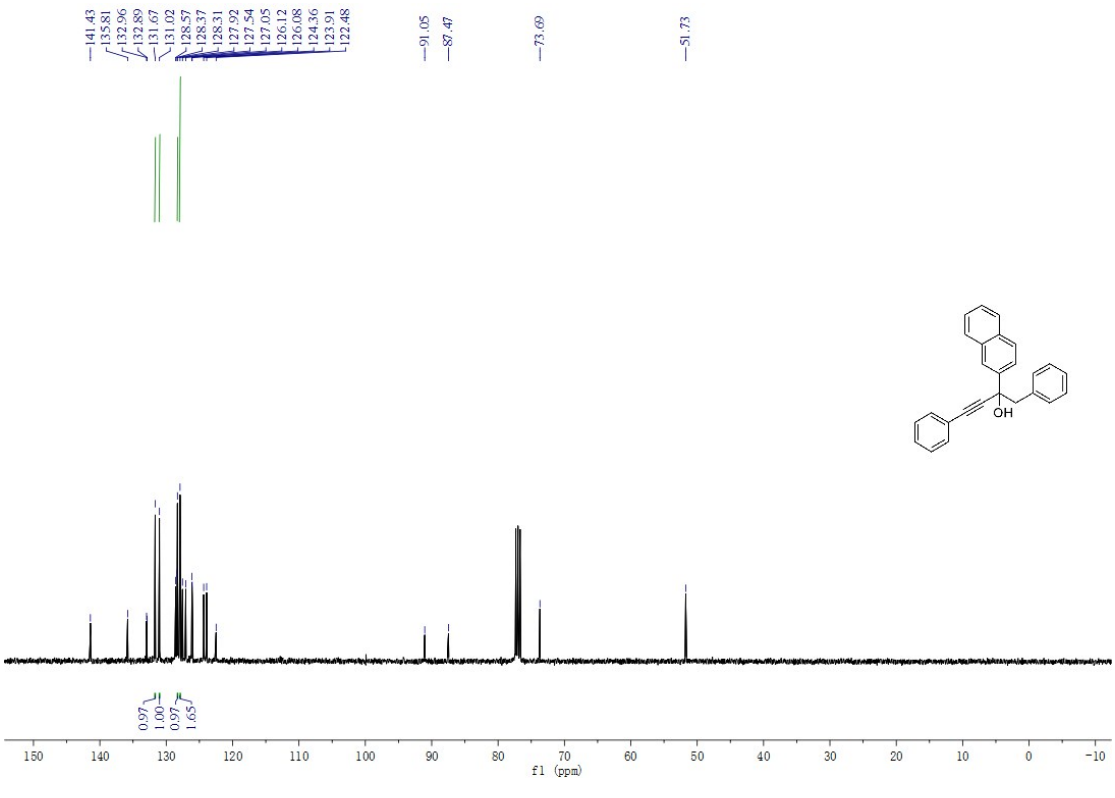
1.02
f1 (ppm)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124.36
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87.47
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OH
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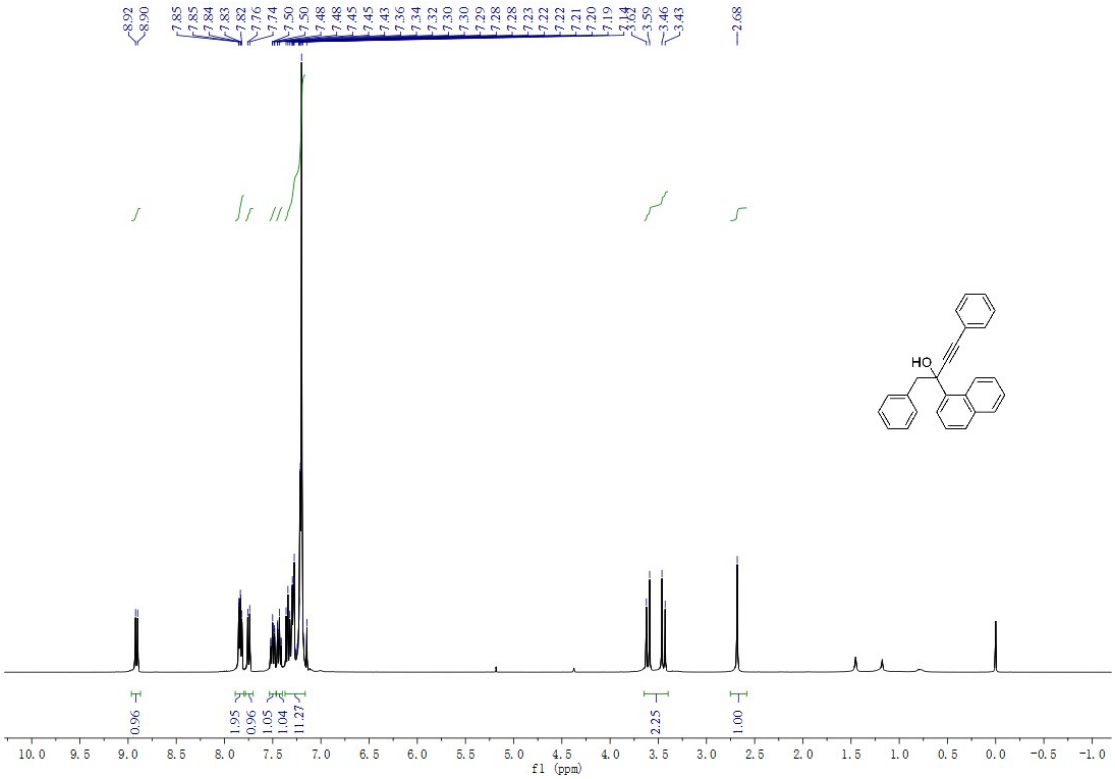
1.65
f1 (ppm)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7.45
7.43
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7.23
7.22
7.22
7.21
7.20
7.19
3.62
3.59
3.46
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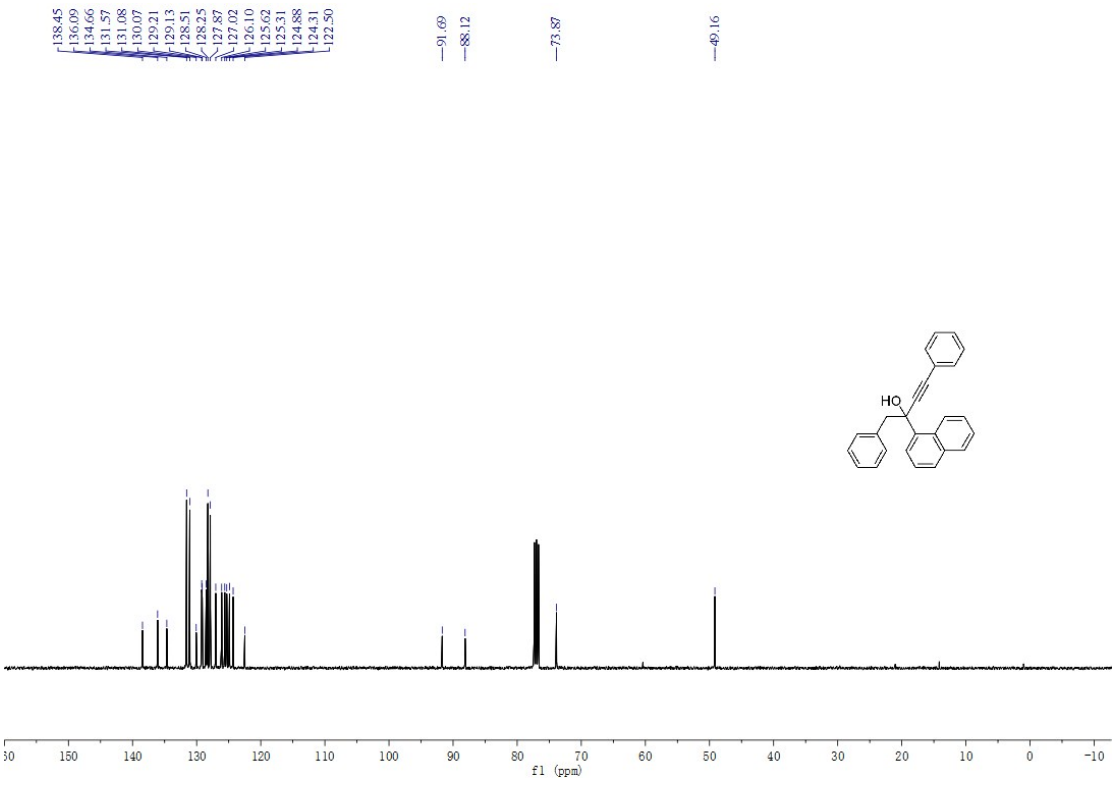
f1 (ppm)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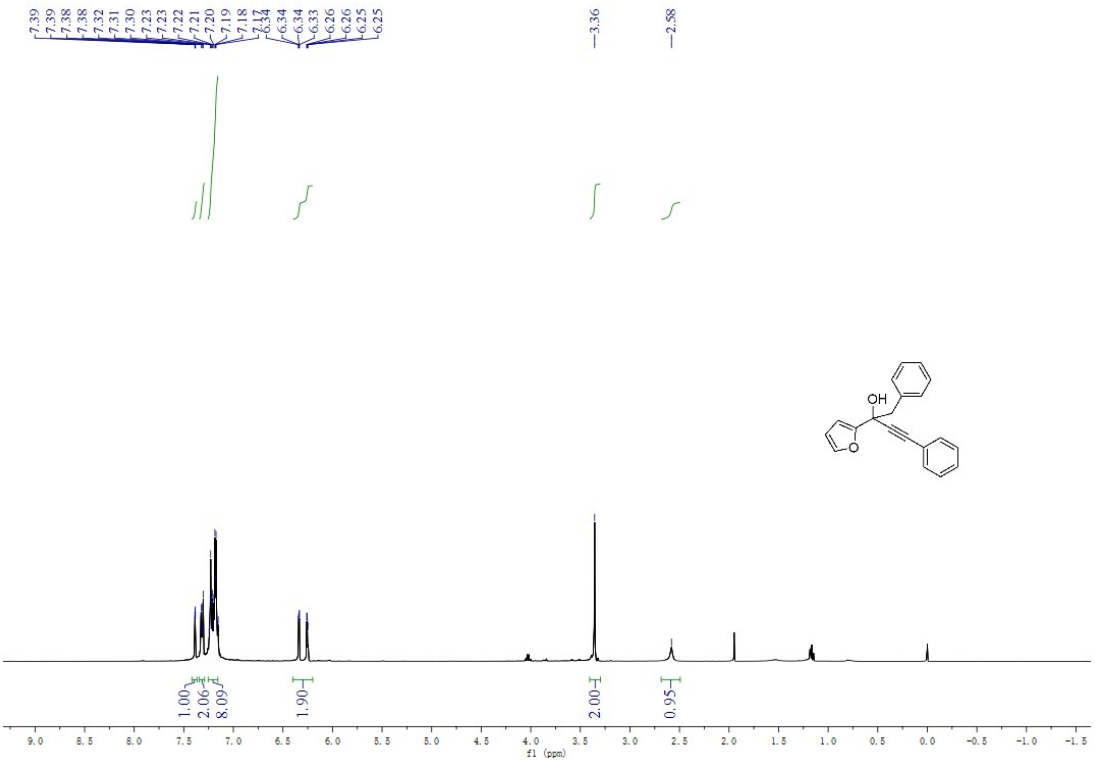
HO
f1 (ppm)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7.19
7.18
7.17
6.34
6.34
6.33
6.26
6.26
6.25
6.25
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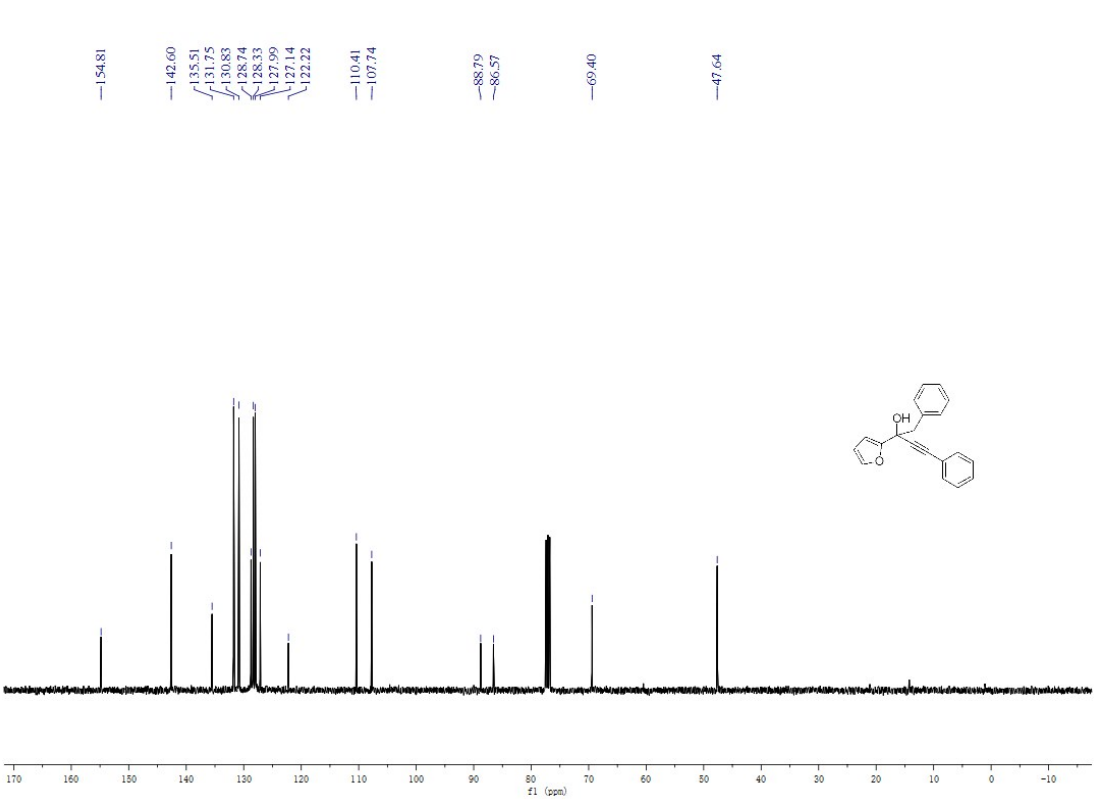
1.90
2.00
0.95
f1 (ppm)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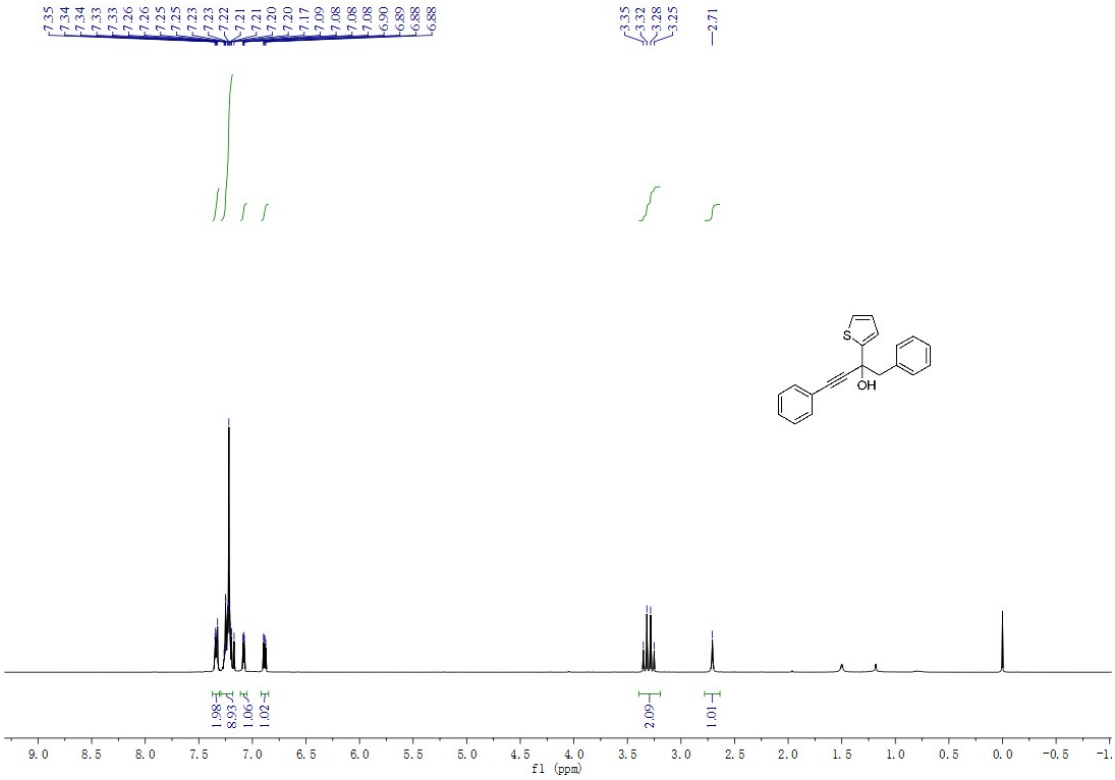
OH
O
f1 (ppm)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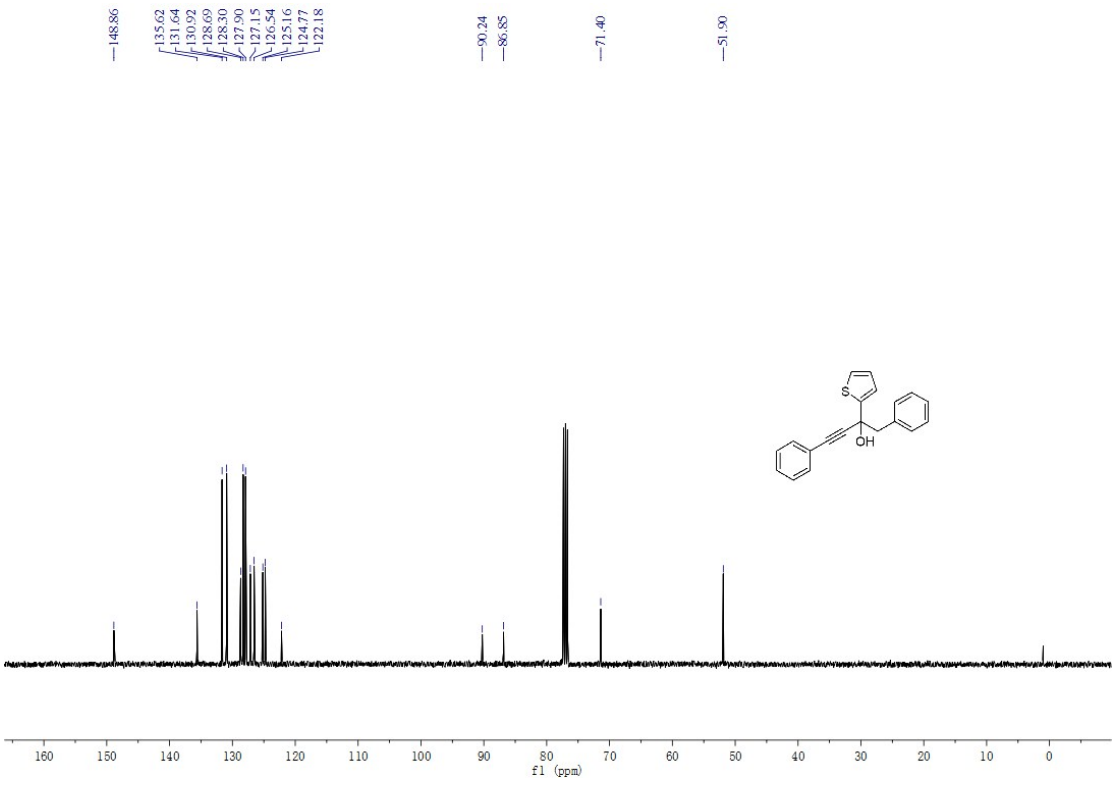
7.20
7.17
7.09
7.08
7.08
7.08
6.90
6.89
6.88
6.88
3.35
3.32
3.28
3.25
2.71
S
OH
1.98
8.93
1.06
1.02
2.09
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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S
OH
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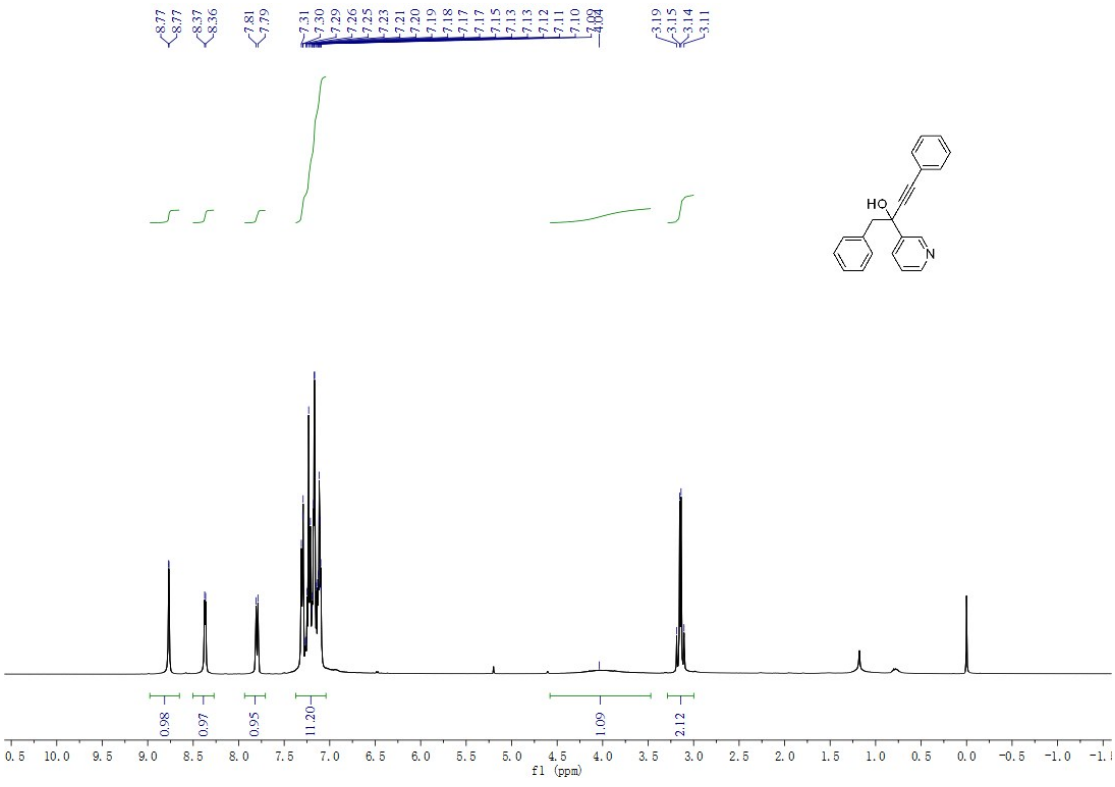
f1 (ppm)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7.18
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7.17
7.15
7.13
7.13
7.12
7.11
7.10
4.04
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3.11
HO
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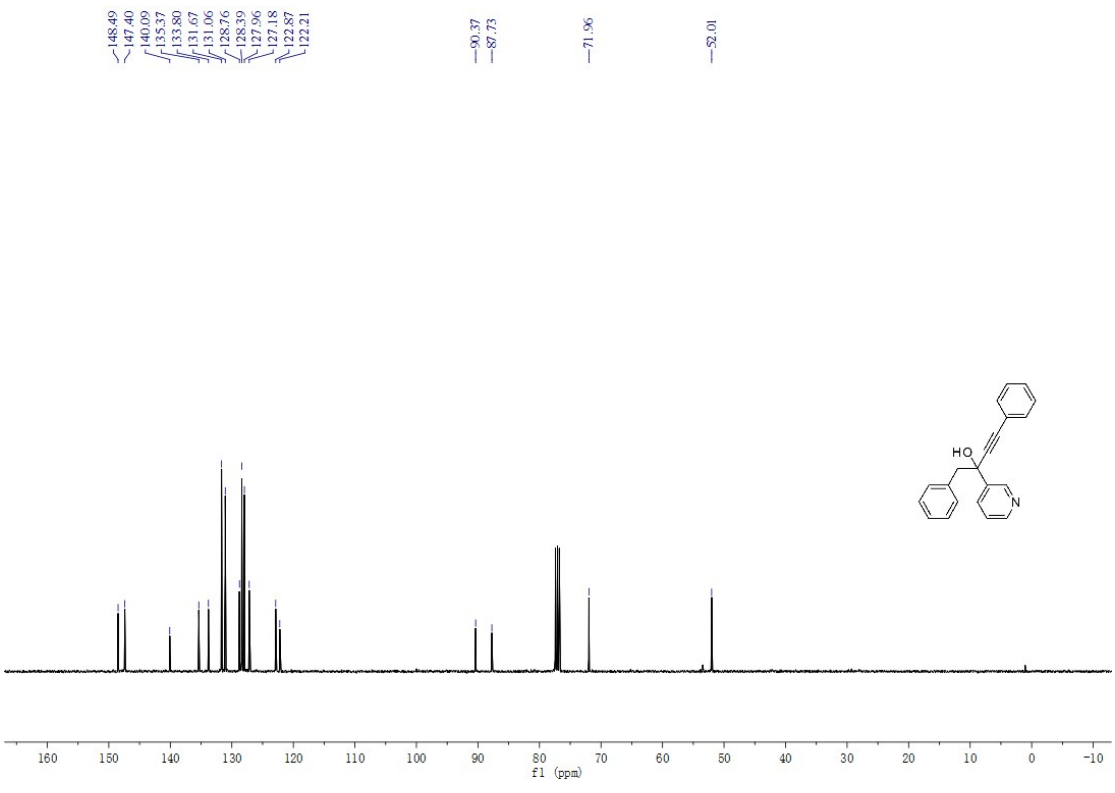
0.97
0.95
11.20
1.09
2.12
f1 (ppm)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71.96
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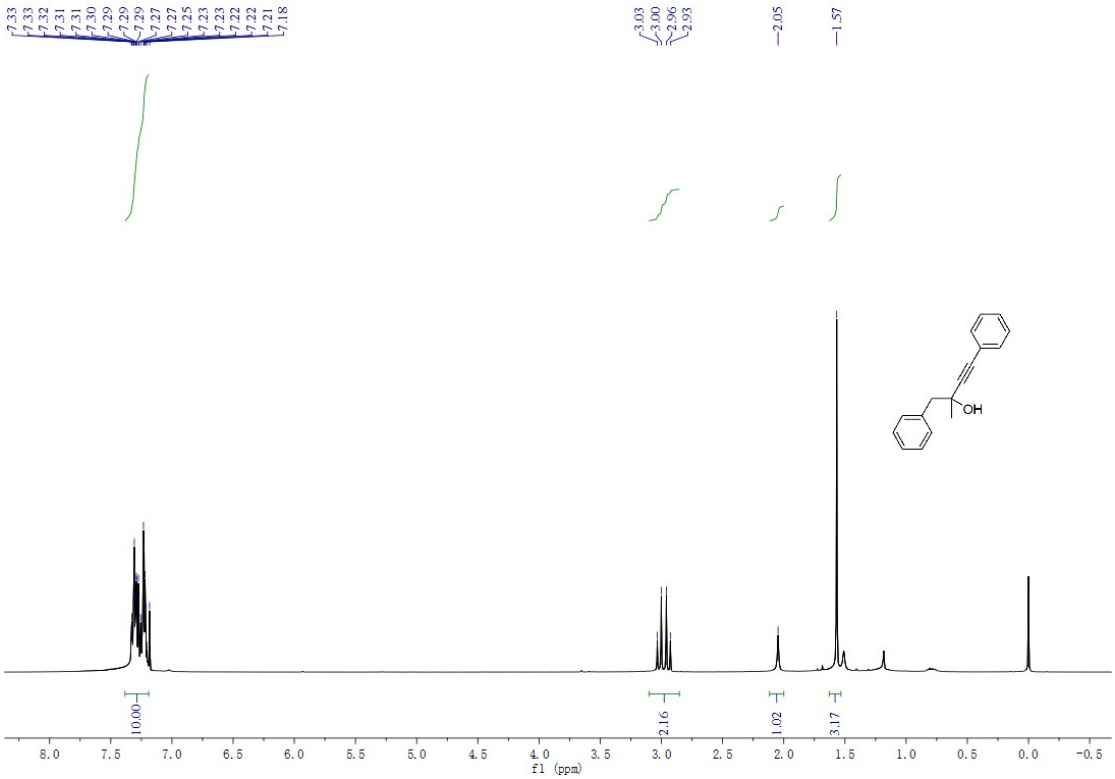
HO
N
f1 (ppm)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7.22
7.22
7.21
7.18
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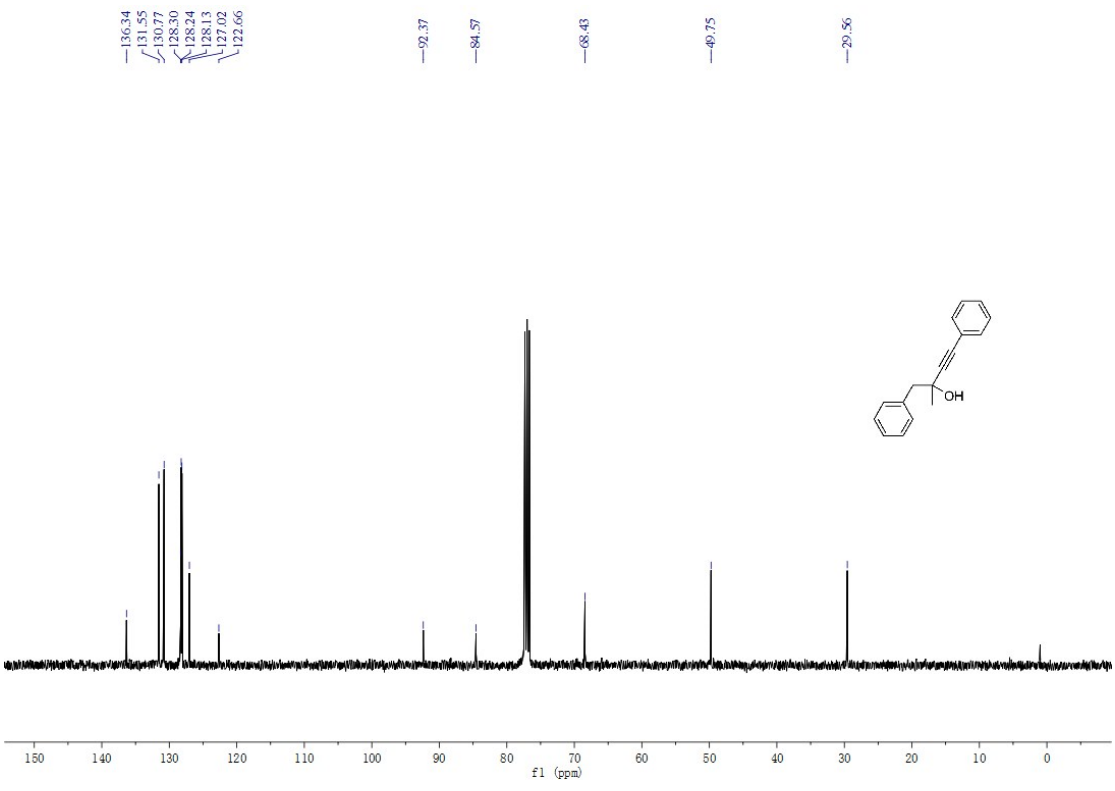
3.17
f1 (ppm)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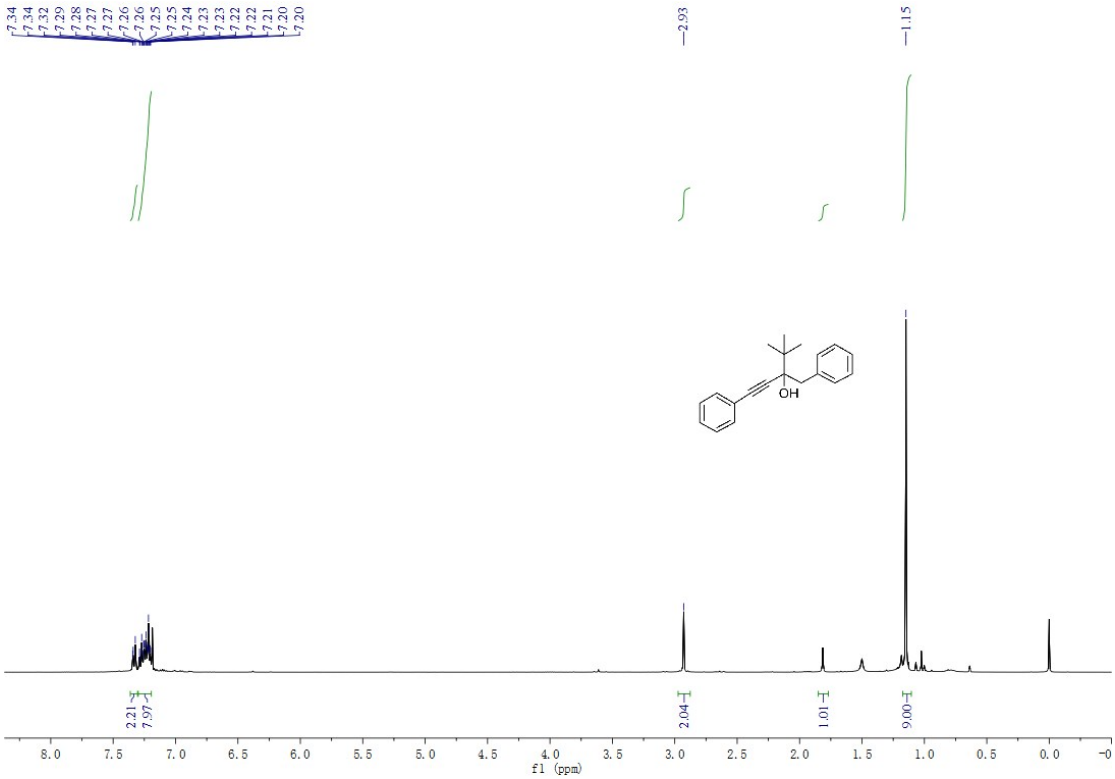
OH
f1 (ppm)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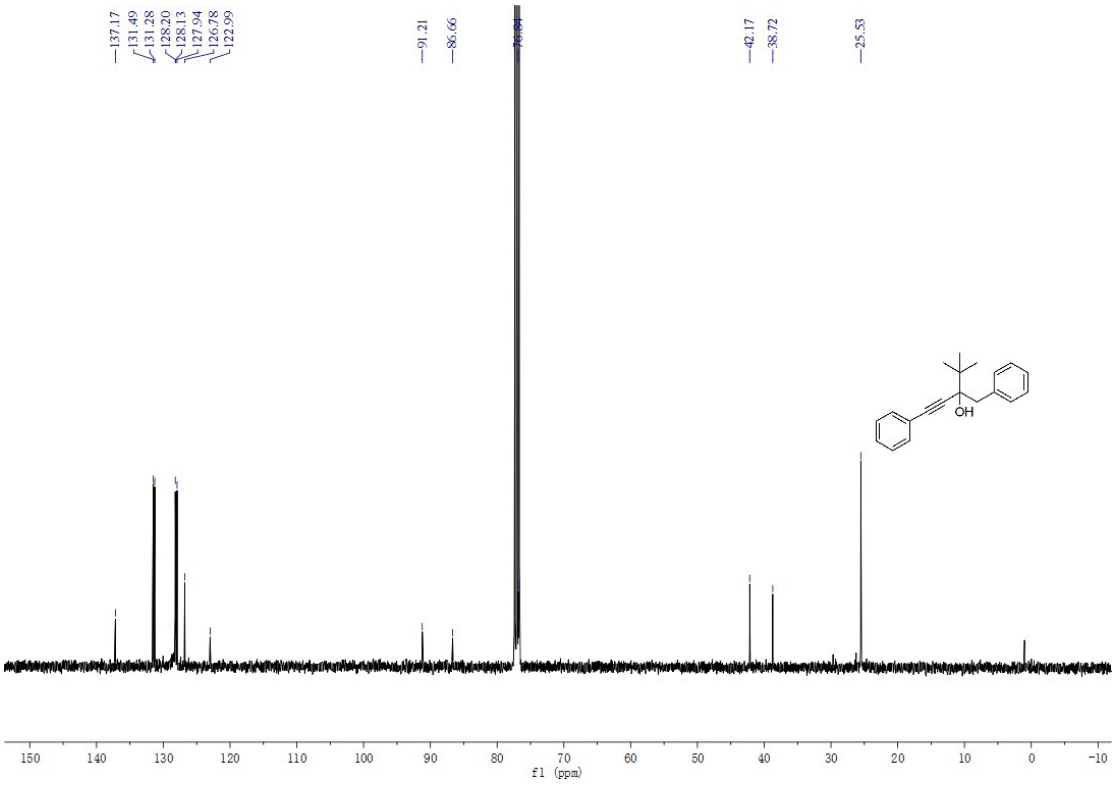
f1 (ppm)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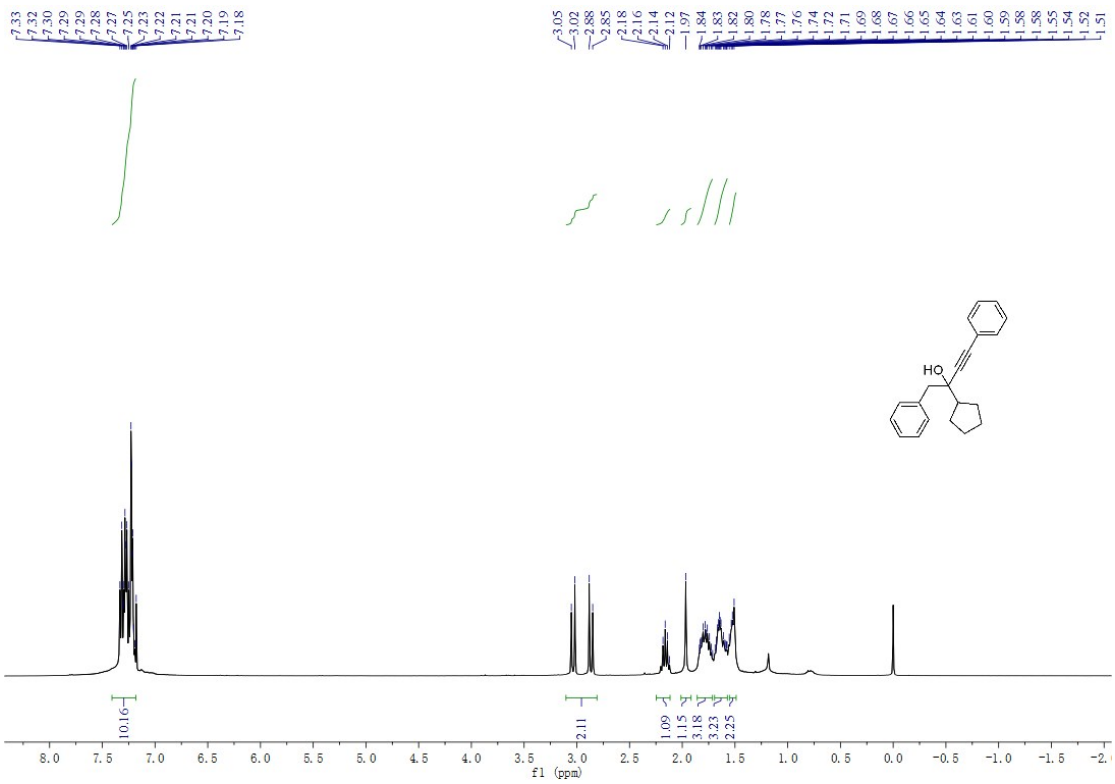
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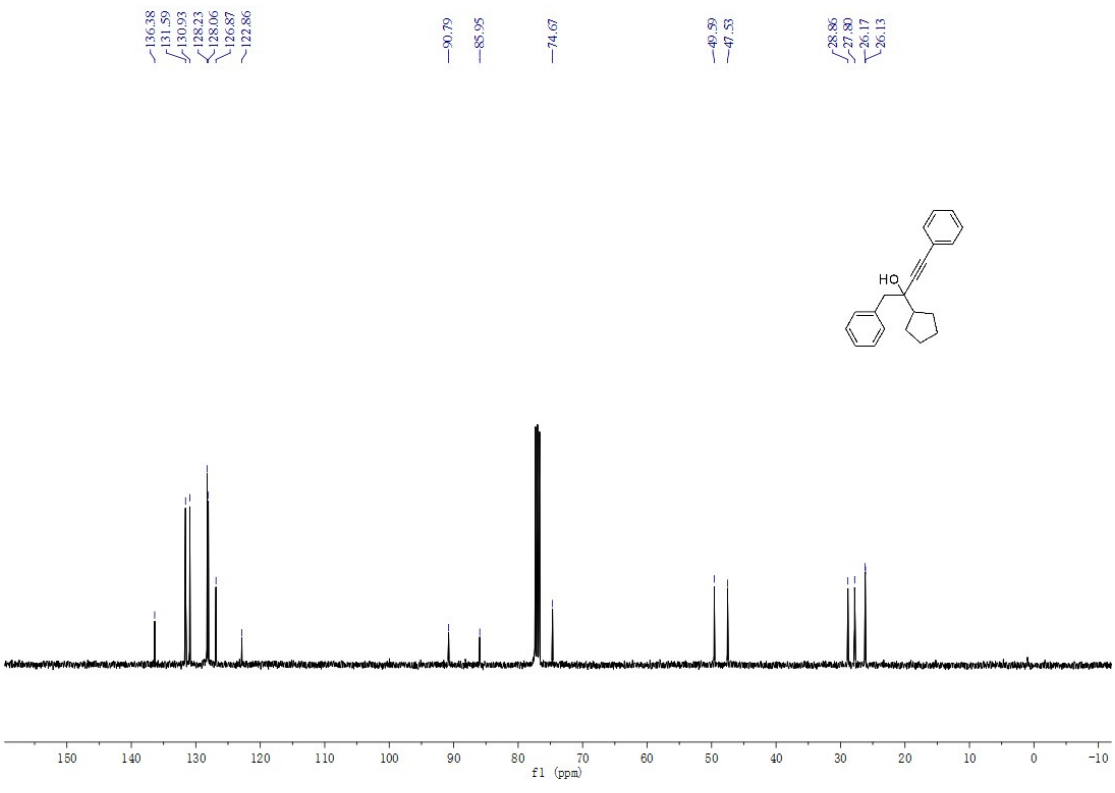
2.25
f1 (ppm)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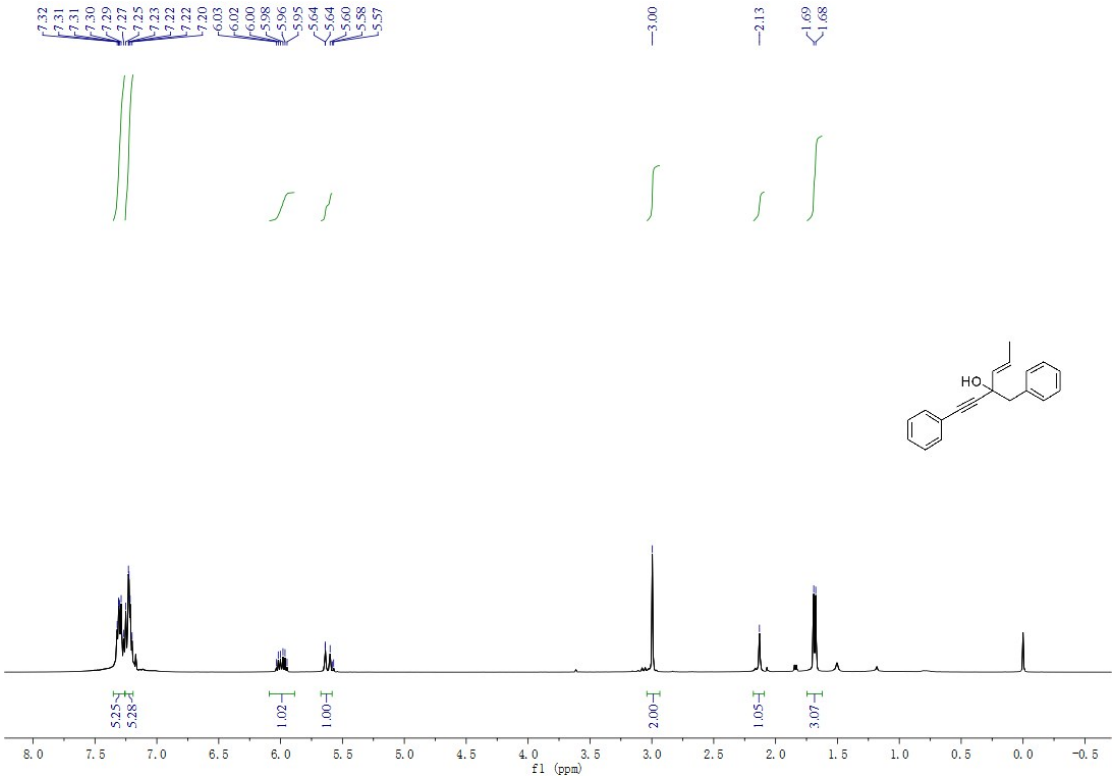
f1 (ppm)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5.95
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5.60
5.58
5.57
3.00
2.13
1.69
1.68
HO
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5.28
1.02
1.00
2.00
1.05
3.07
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7.5
7.0
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5.0
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2.0
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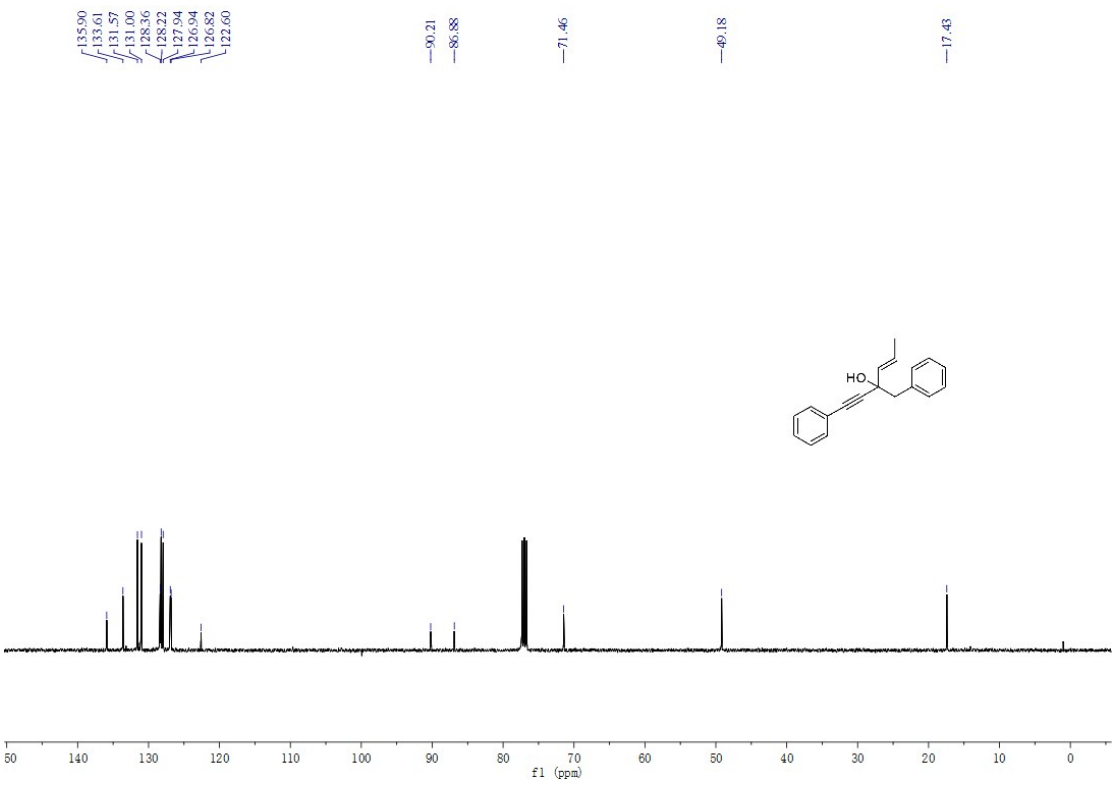
-0.5
f1 (ppm)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50
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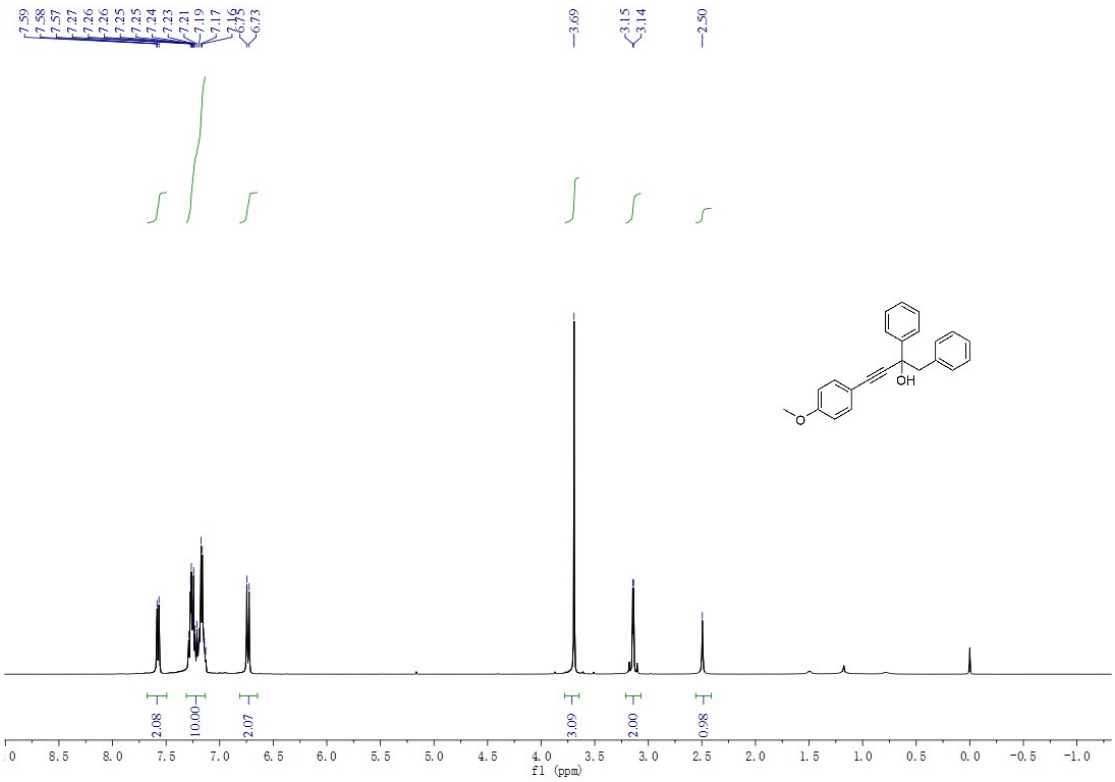
f1 (ppm)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7.17
7.16
6.75
6.73
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OH
O
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10.00
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3.09
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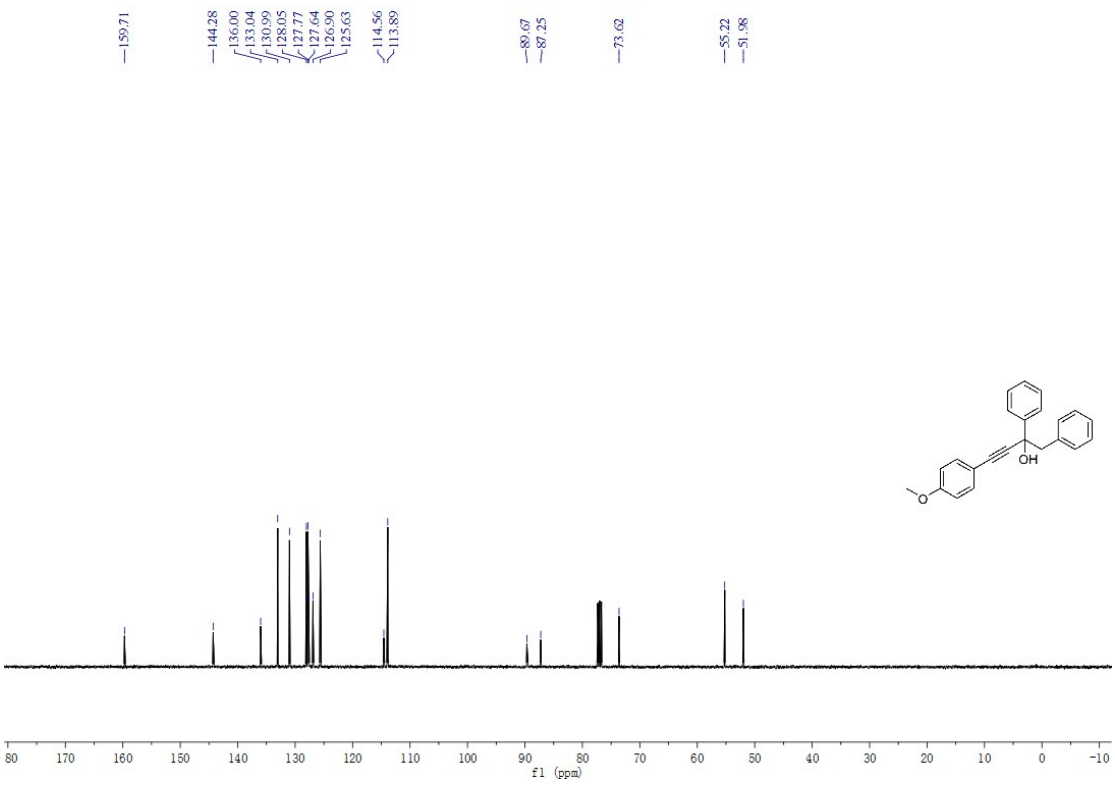
0.98
f1 (ppm)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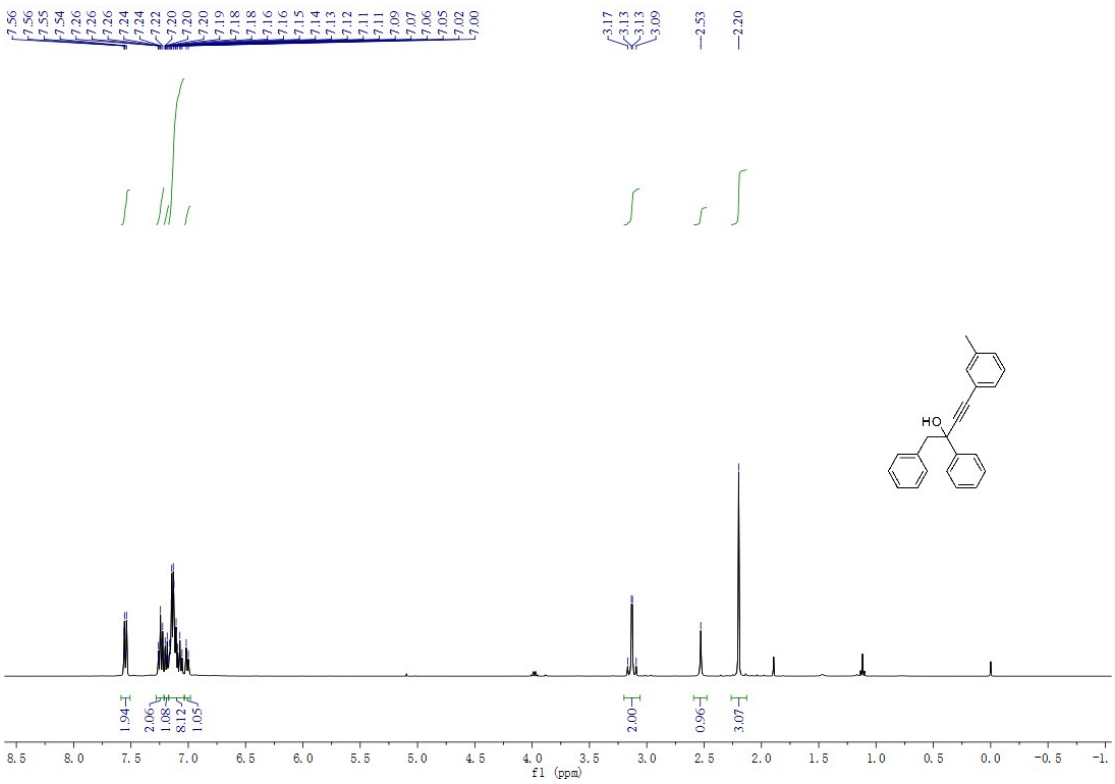
f1 (ppm)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7.12
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7.09
7.07
7.06
7.05
7.02
7.00
3.17
3.13
3.13
3.09
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HO
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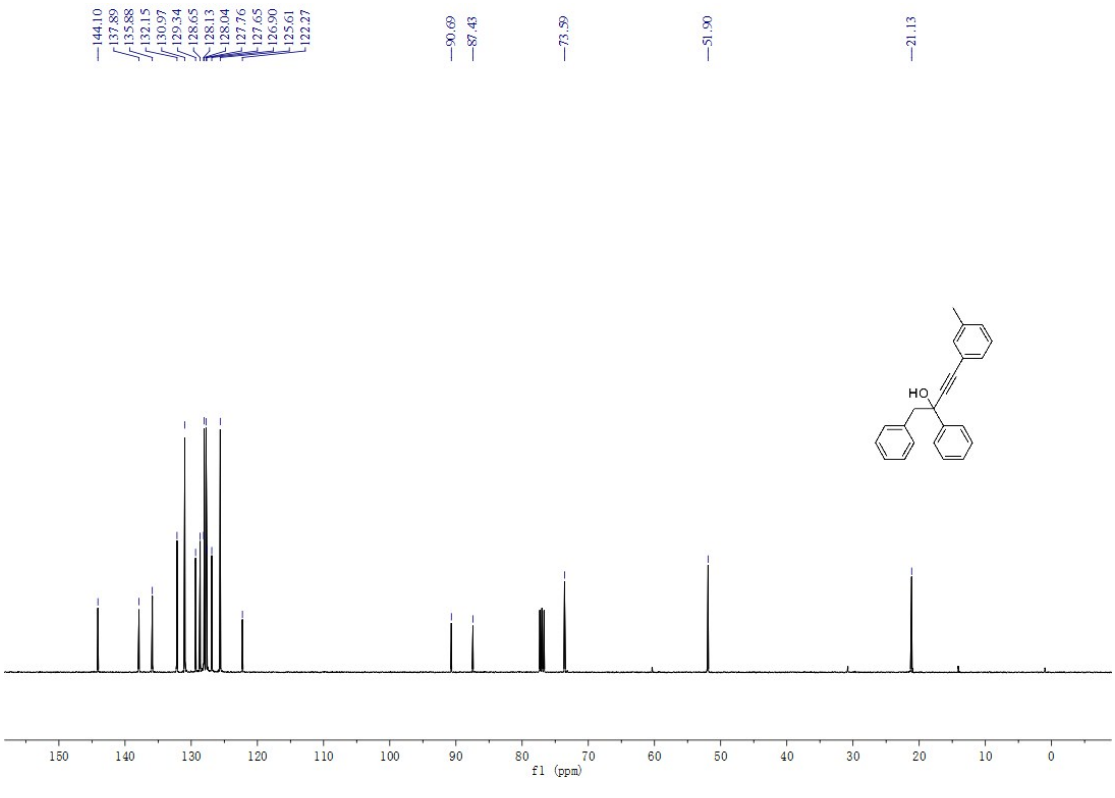
2.06
1.08
8.12
1.05
2.00
0.96
3.07
f1 (ppm)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73.59
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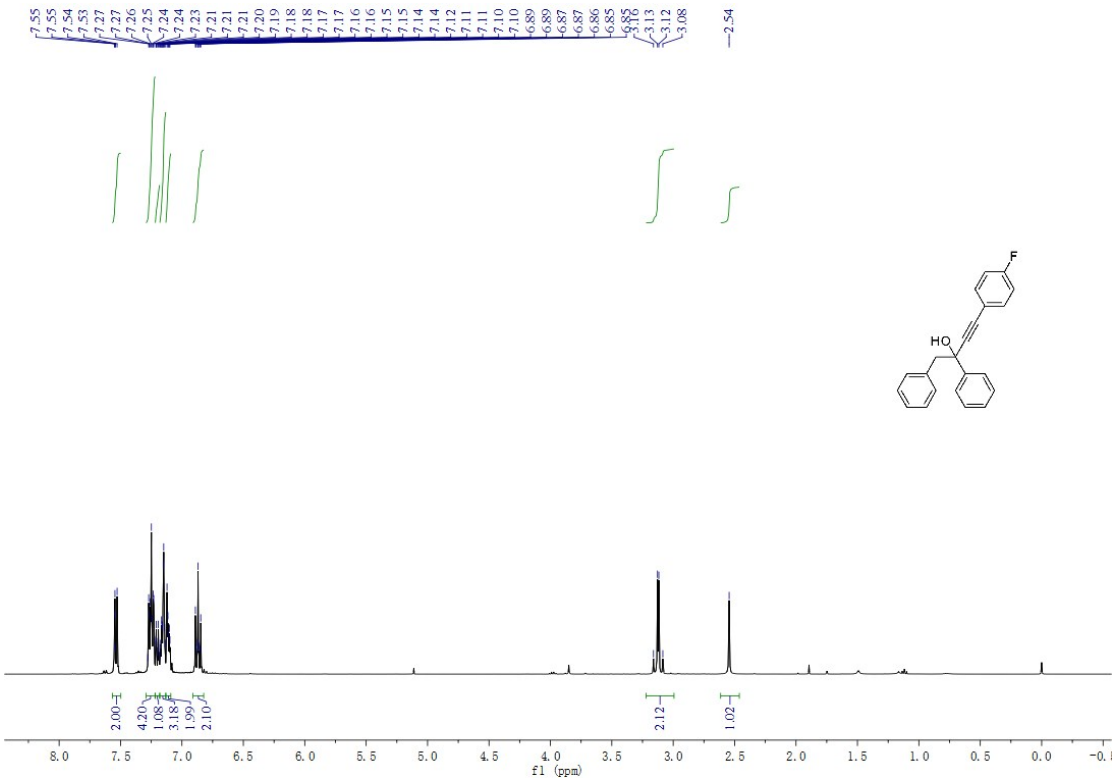
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6.85
3.16
3.13
3.12
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HO
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3.18
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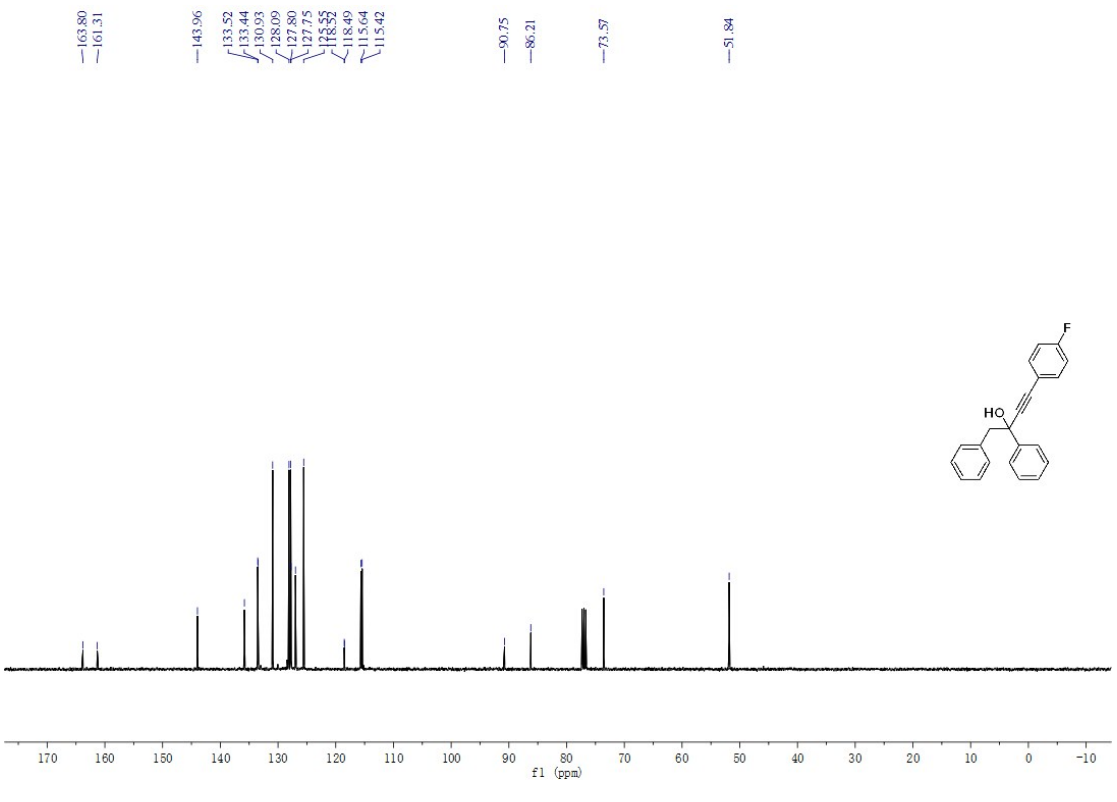
1.02
f1 (ppm)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73.57
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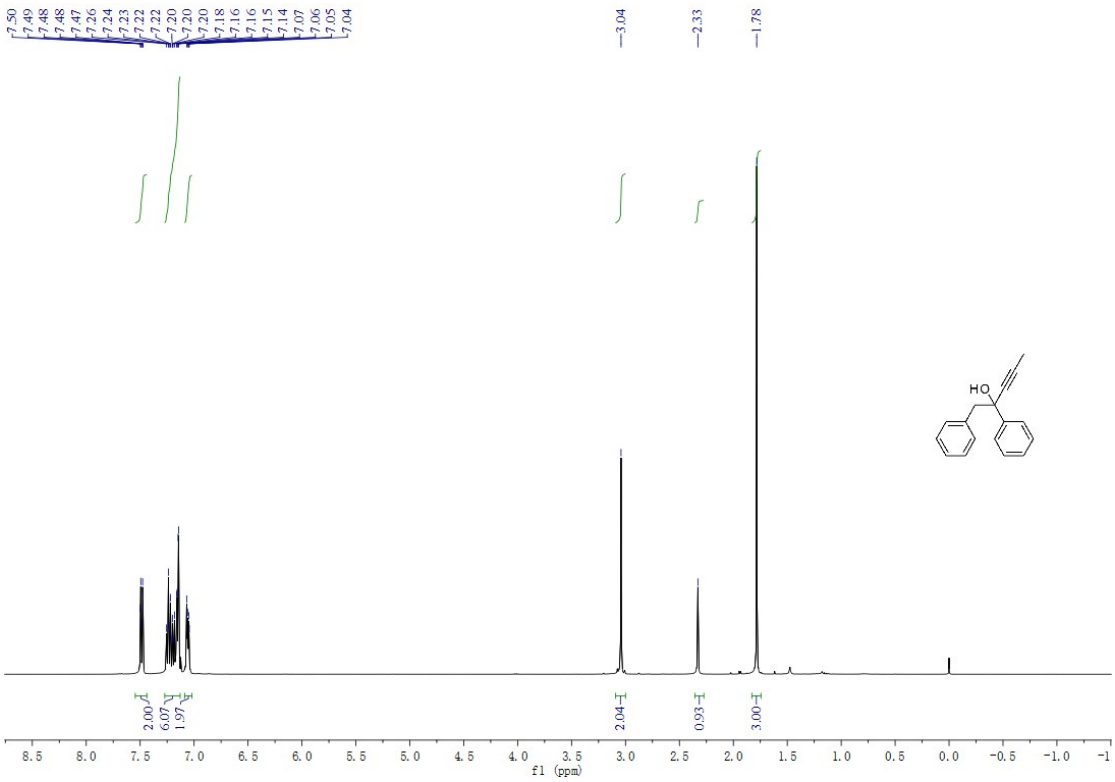
F
HO
f1 (ppm)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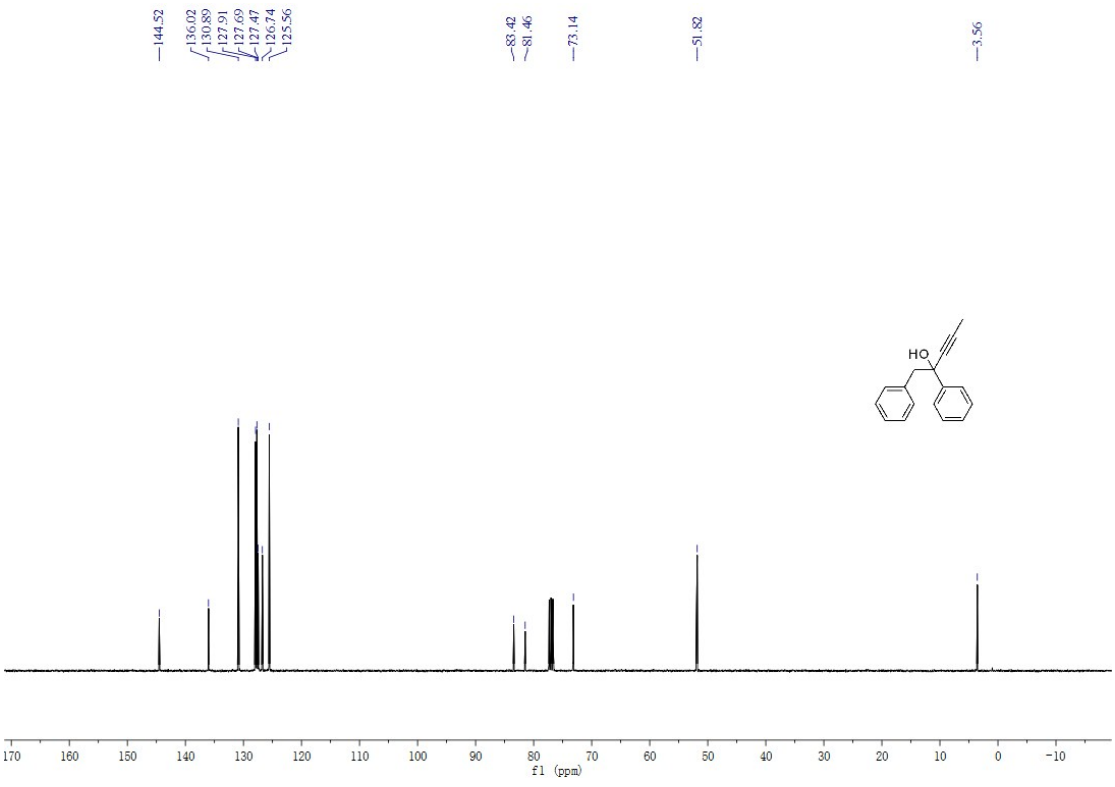
7.16
7.15
7.14
7.07
7.06
7.05
7.04
3.04
2.33
1.78
HO
2.00
6.07
1.97
2.04
0.93
3.00
f1 (ppm)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73.14
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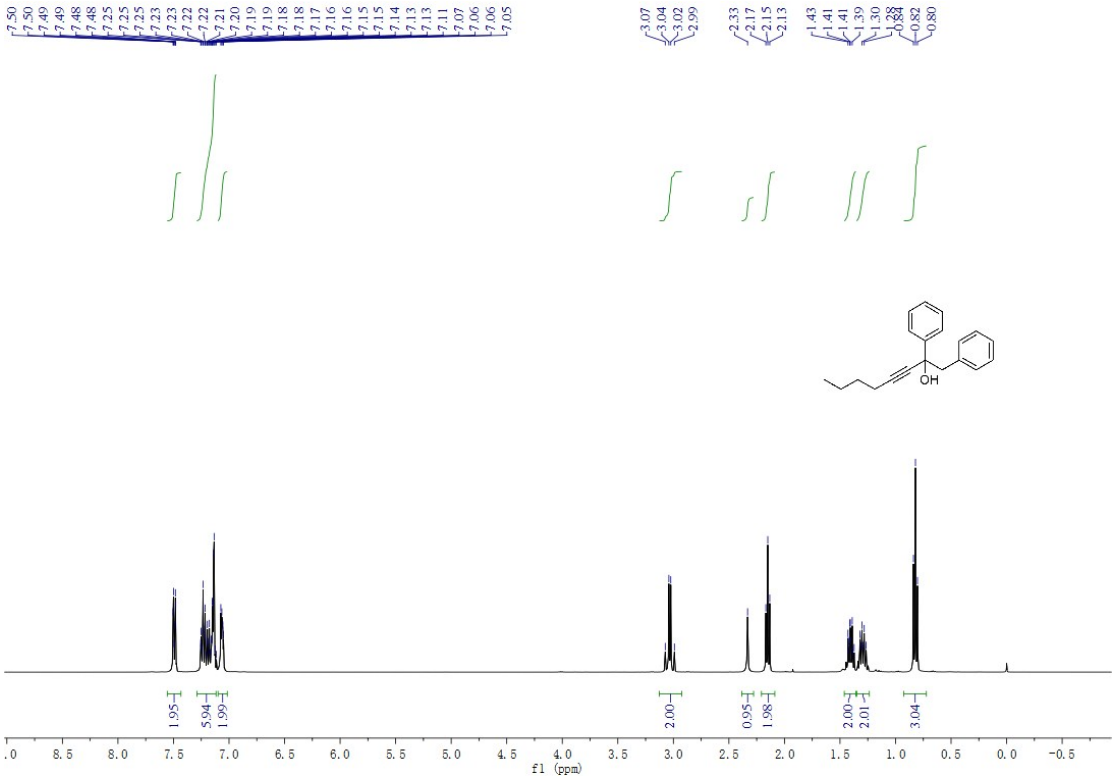
HO
f1 (ppm)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7.14
7.13
7.13
7.11
7.07
7.06
7.06
7.05
3.07
3.04
3.02
2.99
2.33
2.17
2.15
2.13
1.43
1.41
1.41
1.39
1.30
0.84
0.82
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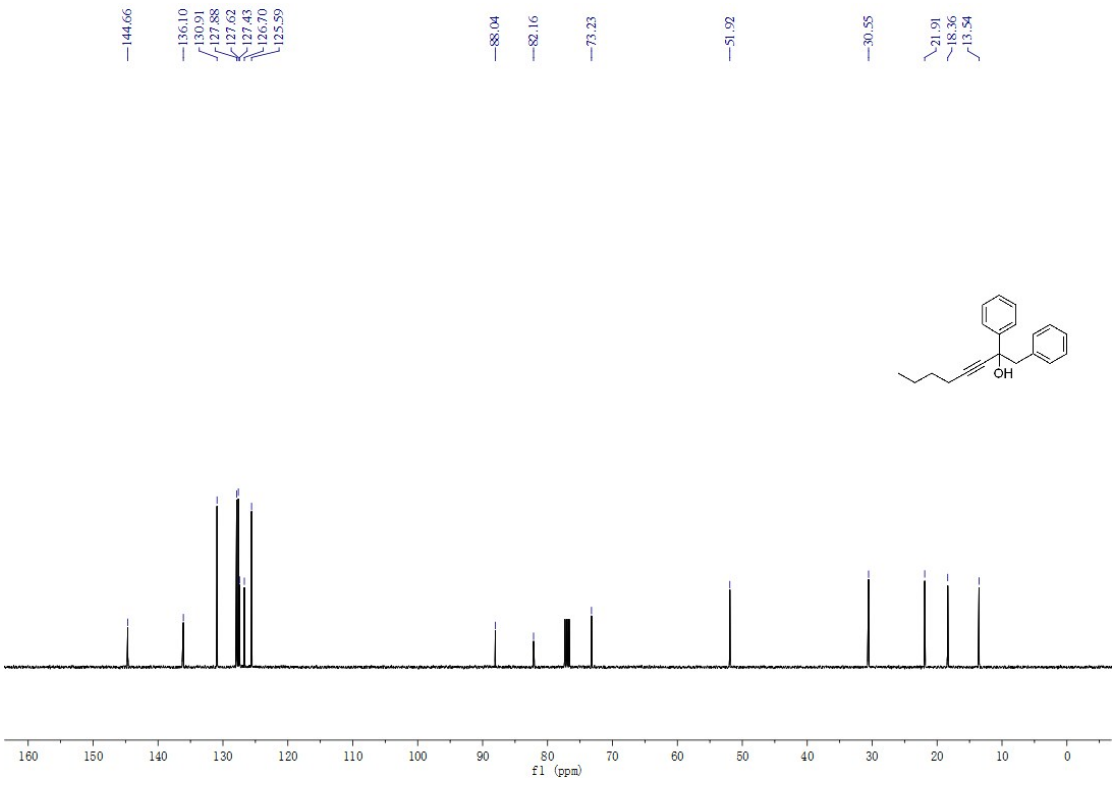
f1 (ppm)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21.91
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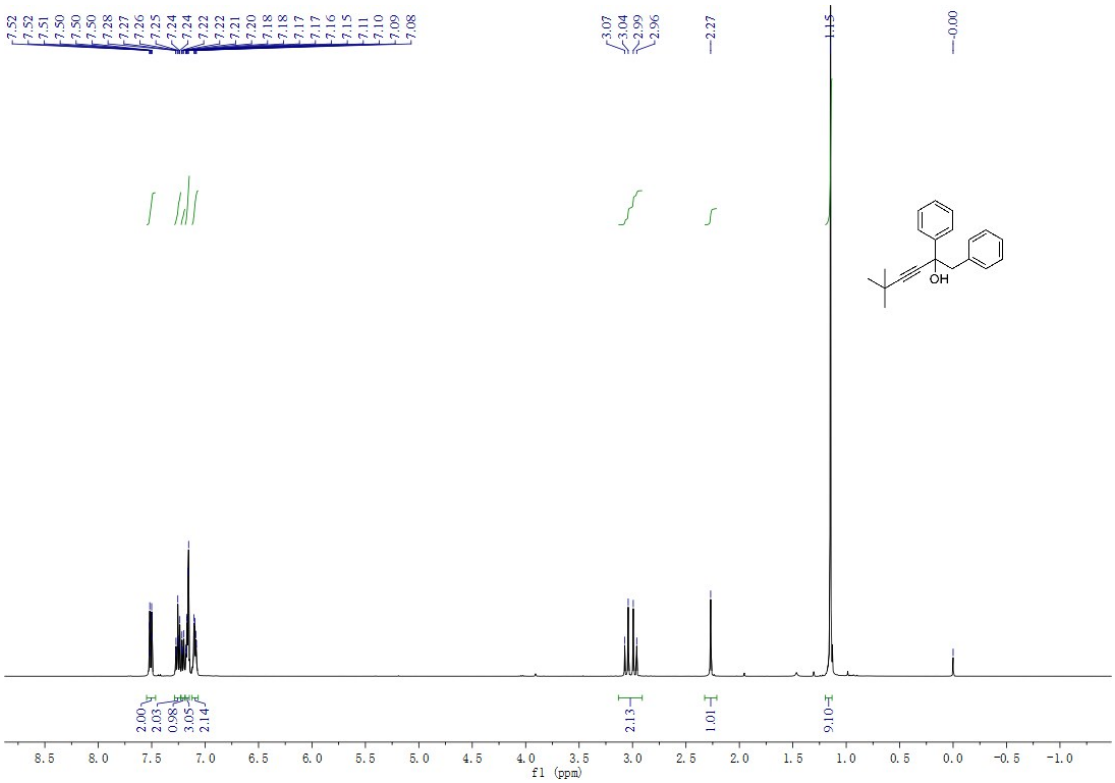
OH
f1 (ppm)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7.18
7.17
7.17
7.16
7.15
7.11
7.10
7.09
7.08
3.07
3.04
2.99
2.96
2.27
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OH
2.00
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0.98
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2.14
2.13
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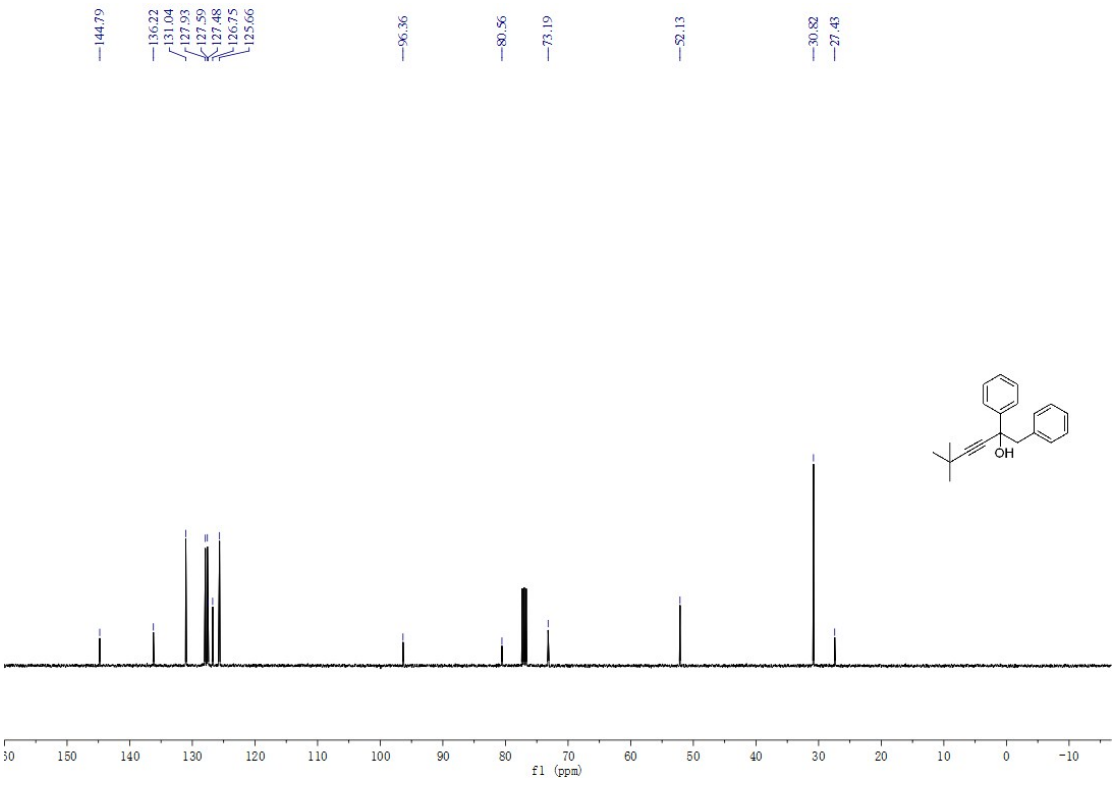
f1 (ppm)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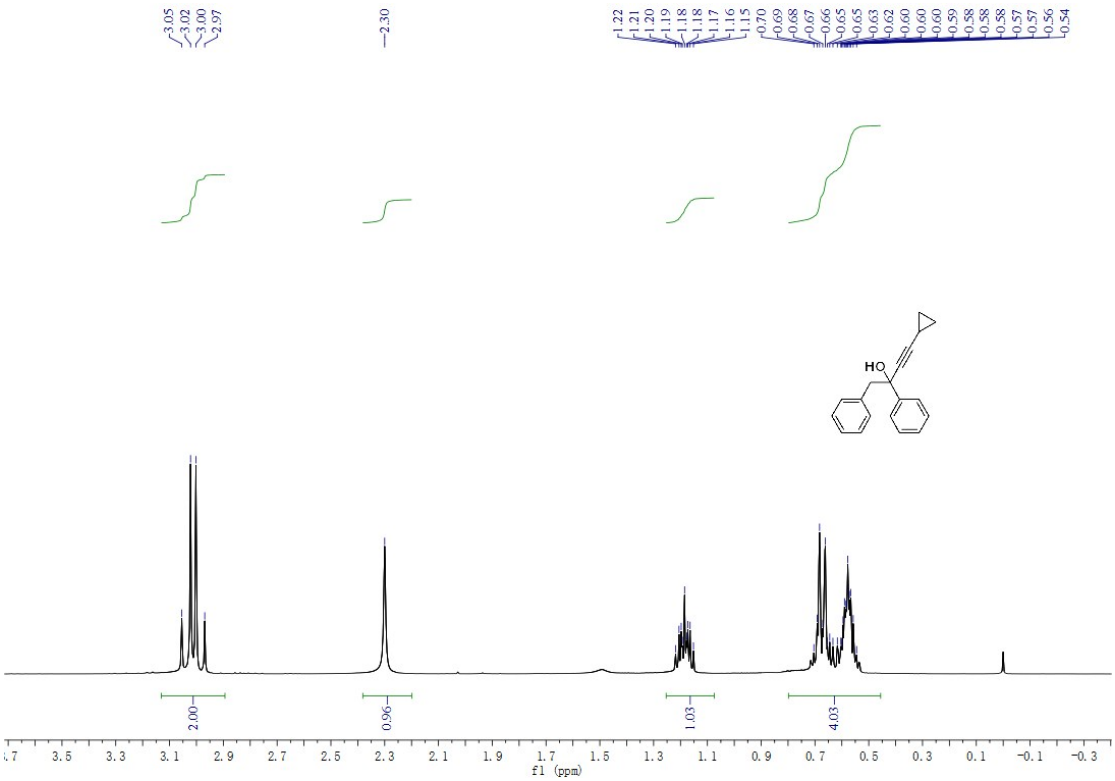
OH
f1 (ppm)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1.15
0.70
0.69
0.68
0.67
0.66
0.65
0.65
0.63
0.62
0.60
0.60
0.60
0.59
0.58
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0.57
0.57
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HO
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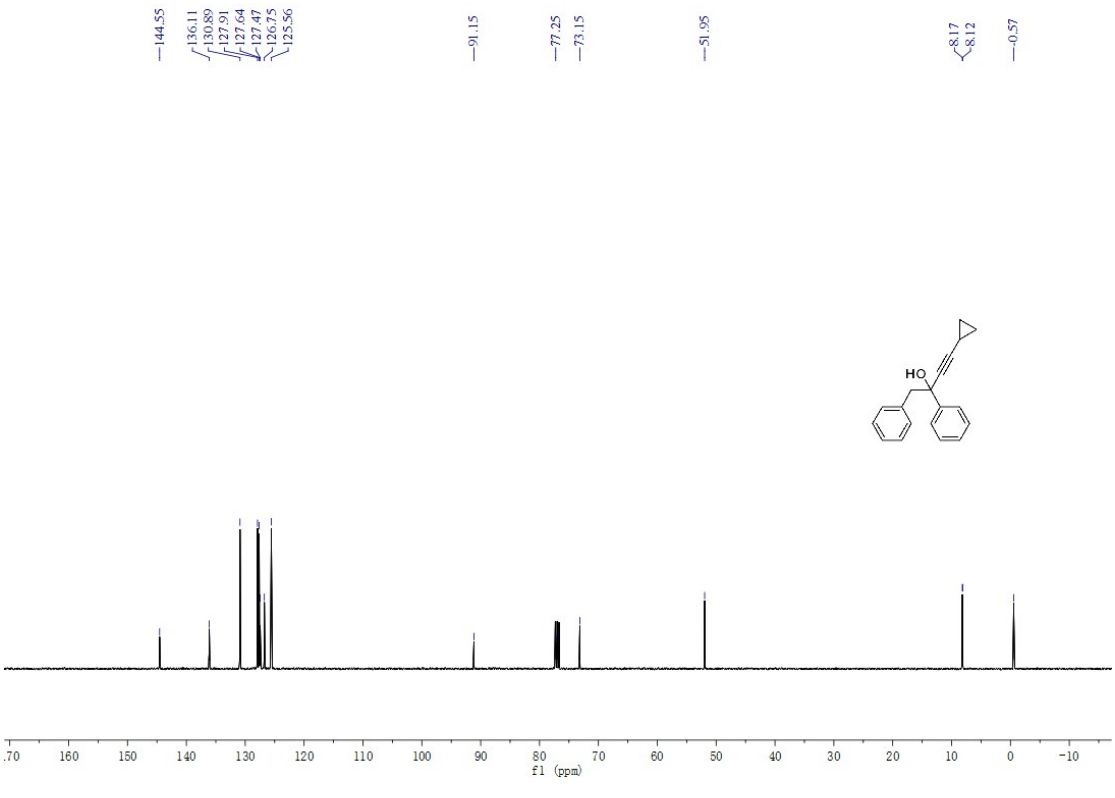
0.96
1.03
4.03
f1 (ppm)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8.12
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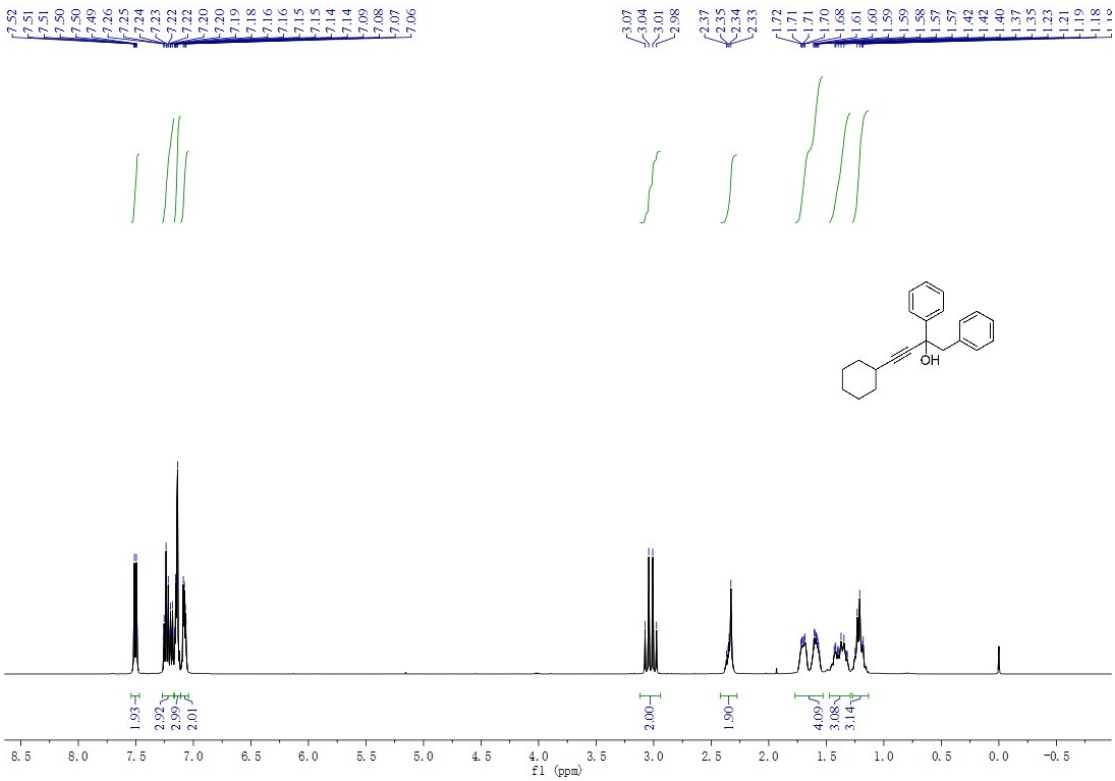
HO
f1 (ppm)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7.15
7.15
7.14
7.14
7.09
7.08
7.07
7.06
3.07
3.04
3.01
2.98
2.37
2.35
2.34
2.33
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1.71
1.70
1.68
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1.60
1.59
1.59
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1.57
1.57
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1.42
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1.37
1.35
1.23
1.21
1.19
1.18
OH
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2.92
2.99
2.01
2.00
1.90
4.09
3.08
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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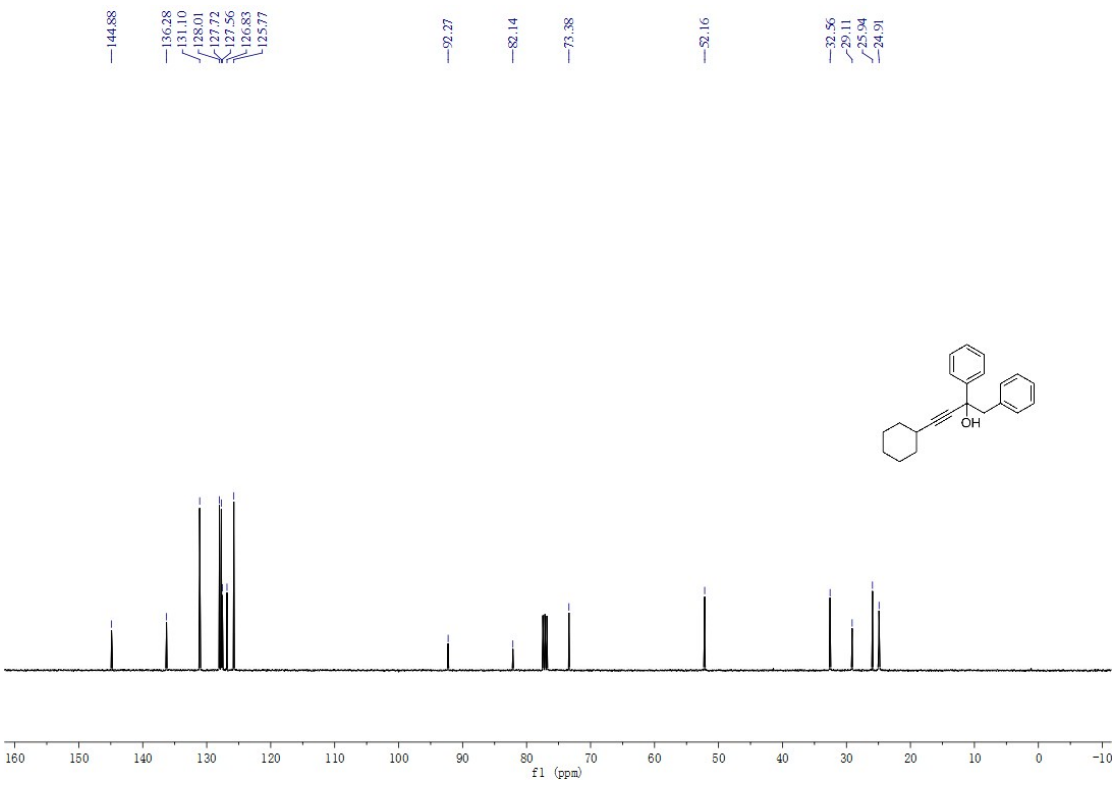
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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32.56
29.11
25.94
24.91
OH
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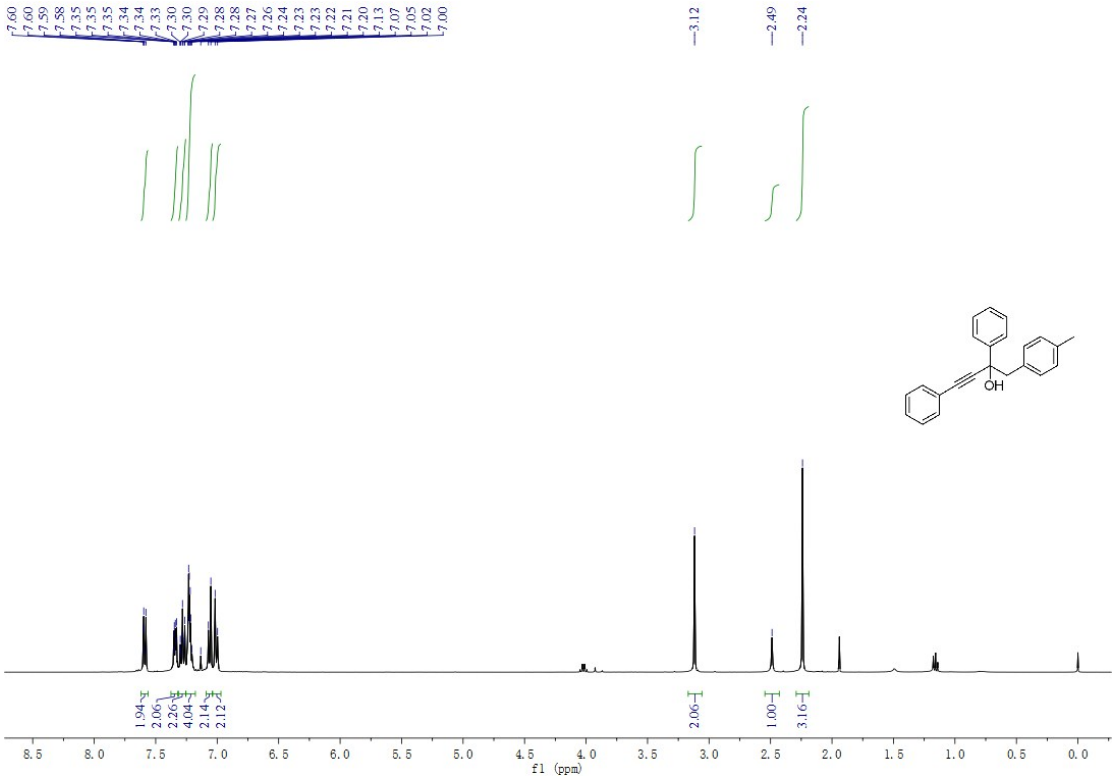
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.24
7.23
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7.22
7.21
7.20
7.13
7.07
7.05
7.02
7.00
3.12
2.49
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OH
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2.06
2.26
4.04
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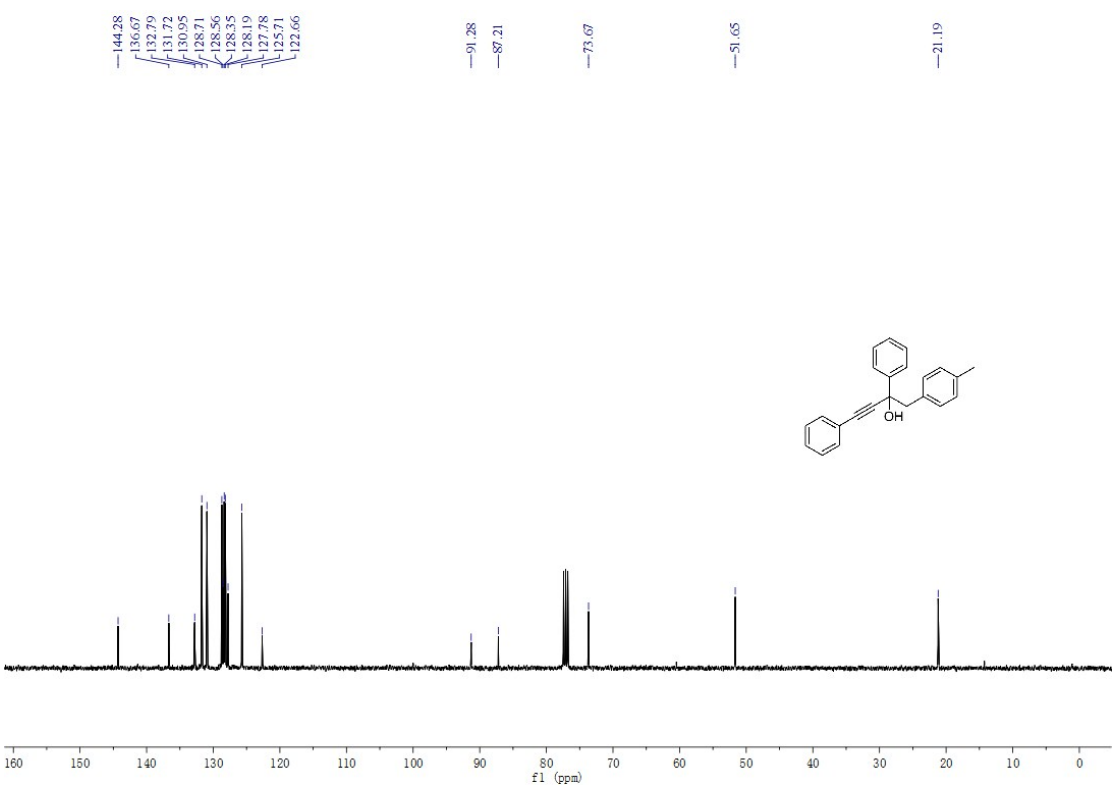
2.12
2.06
1.00
3.16
f1 (ppm)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73.67
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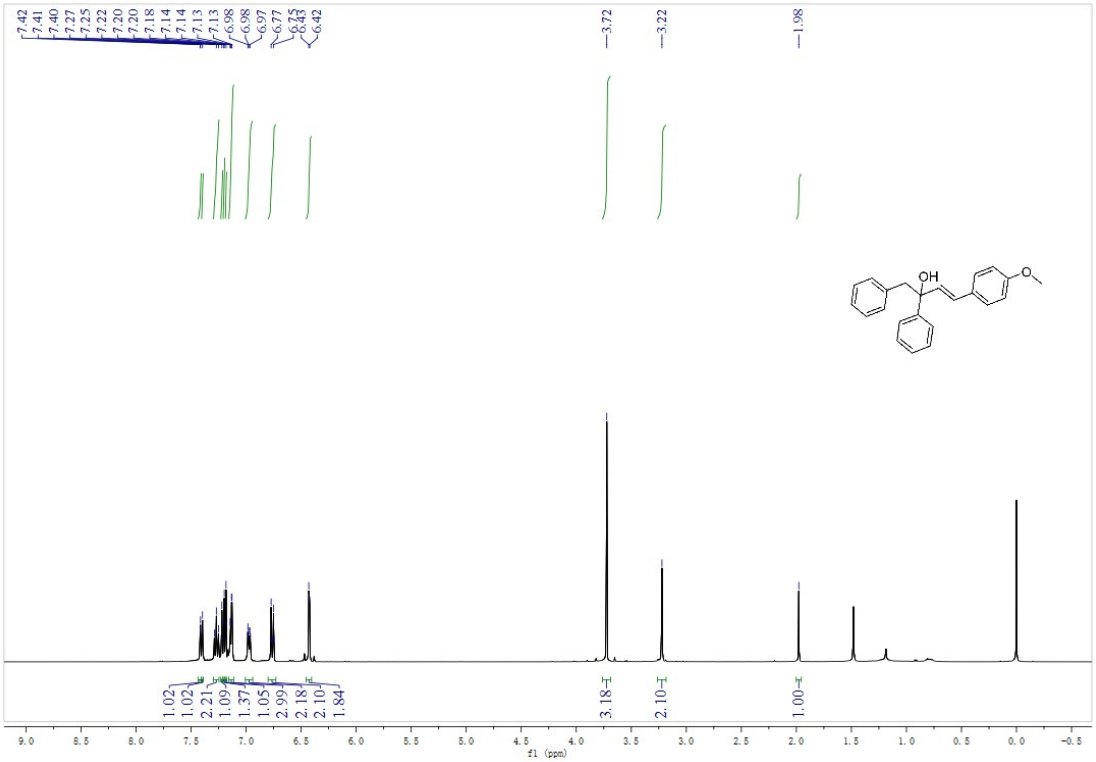
OH
f1 (ppm)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6.97
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6.43
6.42
3.72
3.22
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OH
O
1.02
1.02
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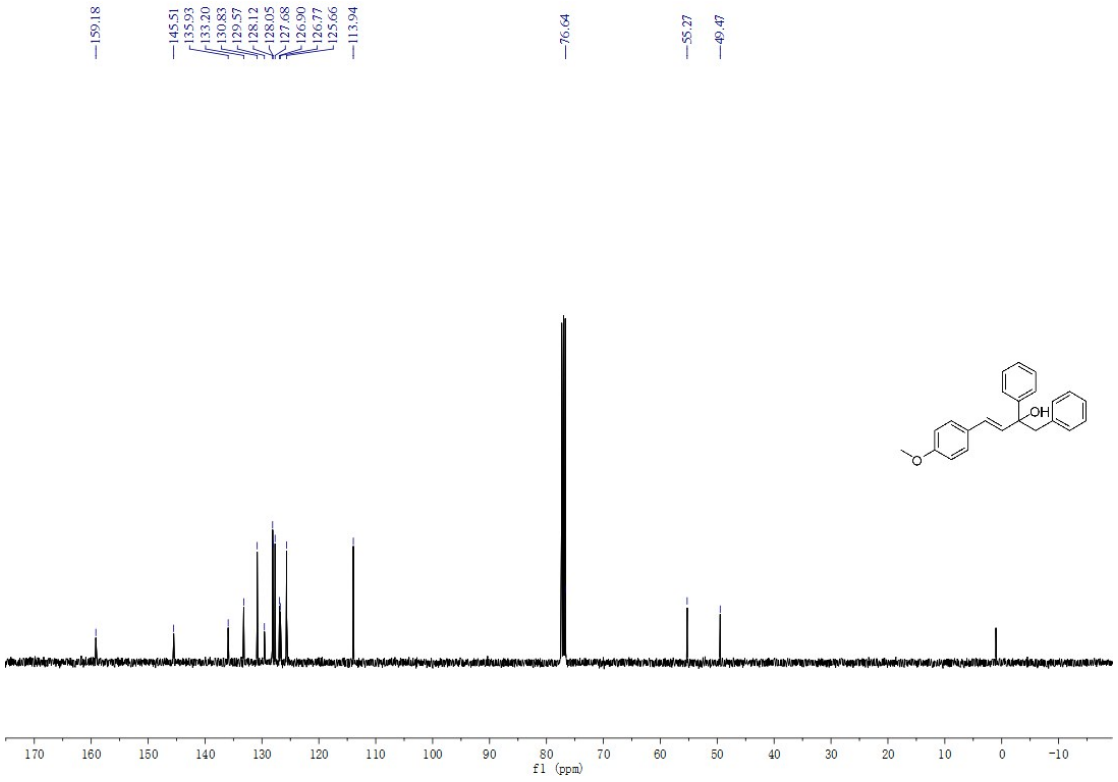
1.05
2.99
2.18
2.10
1.84
3.18
2.10
1.00
f1 (ppm)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113.94
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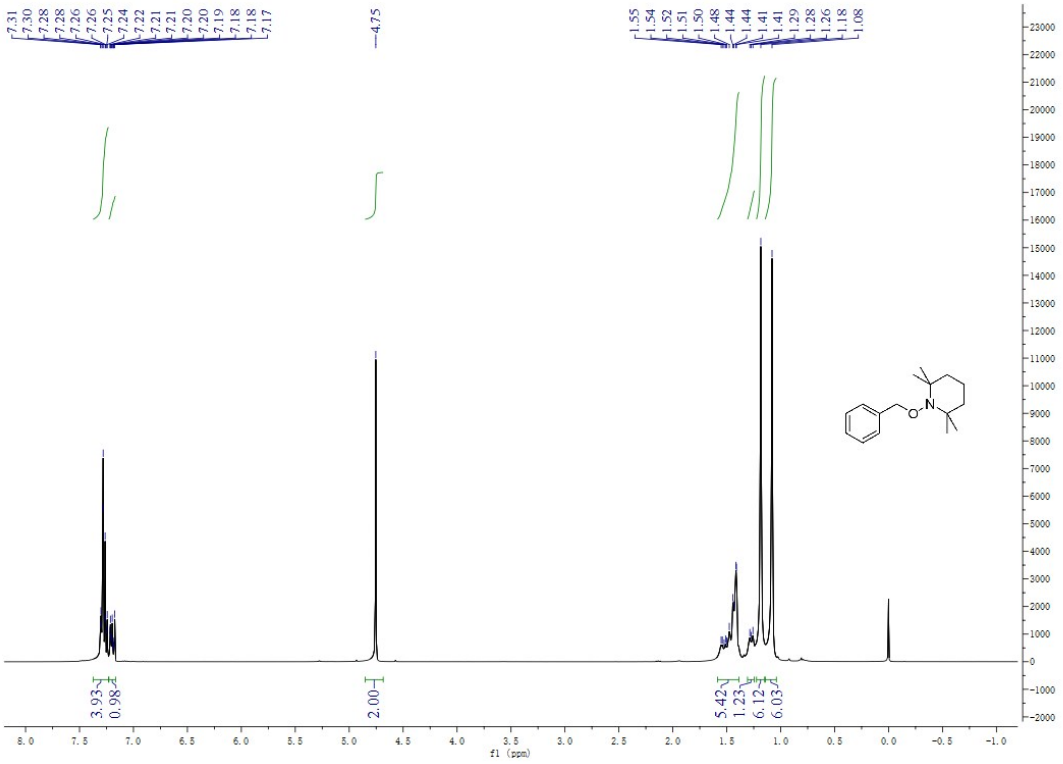
55.27
49.47
OH
O
f1 (ppm)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7.20
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7.18
7.18
7.17
4.75
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1.54
1.52
1.51
1.50
1.48
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1.44
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1.41
1.29
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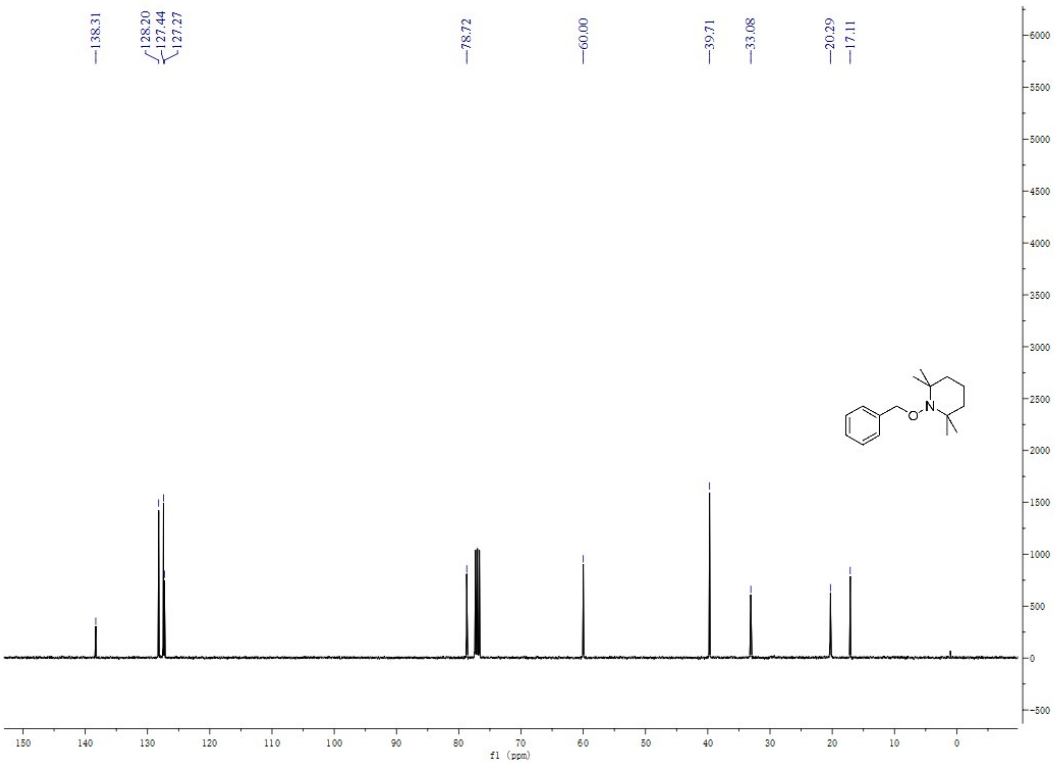
1.23
6.12
6.03
f1 (ppm)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f1 (ppm)