Supporting Information

Oxidative Alkylalkynylation of Terminal Alkenes Enabled by Alkyl Aldehyde Decarbonylation and 1,2-Alkynyl Migration

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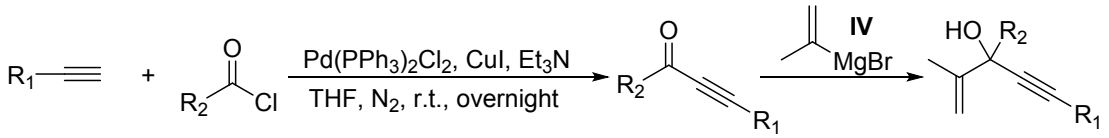
(A) General Information

For column chromatography, silica gel (300-400 mesh) was employed.high-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI) or Thermo Scientific LTQ-Orbitrap XL (MALDI). Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for 1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.00 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration.

(a) General procedure for synthesis of compounds 1:[1,2]



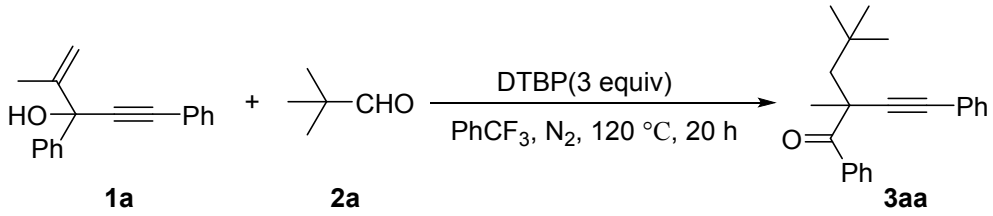
I II III 1

A mixture of $Pd(PPh_3)Cl_2$ (2 mol%, 0.2 mmol), CuI (4 mol%, 0.4 mmol), Et_3N (1.5 equiv, 15 mmol) and terminal alkyne (1.0 equiv, 10 mmol) , dissolving in 20 mL anhydrous tetrahydrofuran (THF), were stirred for 15 minutes at room temperature under nitrogen conditions. Then, acyl chloride II (1.2 equiv, 12 mmol) was added to the reaction vial by dropwise and stirred for overnight. The reaction process was determined by TLC until the starting material consumed completely.The resulting mixture was extracted with 50 mL H_2O and ethyl acetate (2×40 mL).. The organic phase was concentrated to a bottle and was dried over Na_2SO_4. Then, the mixture was filtrated and the colature was evaporated on a rotary evaporator. The crude product

was purified by chromatography on silica gel with petroleum ether/ethyl acetate (100:1) as the eluent to afford compound III.

Compound III was dissolved in 10 mL THF,After that, 20 mL (0.5 mol/L) isopropenylmagnesium bromide solution IV was added to the flask by dropwise at -10℃and stirred for 10mins under nitrogen conditions. Then, the mixture was moved to room temperature for another 6 hours. The resulting mixture was stirred until TLC indicated complete consumption of the starting material III. Subsequently, the mixture was quenched by saturated ammonium chloride solution at -10℃and extracted with 20 mL ethyl acetate for three times at room temperature. The organic phase was concentrated and evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1) as the eluent to afford compound 1.

(b) The synthesis of compounds 3:



1a **2a** **3aa**

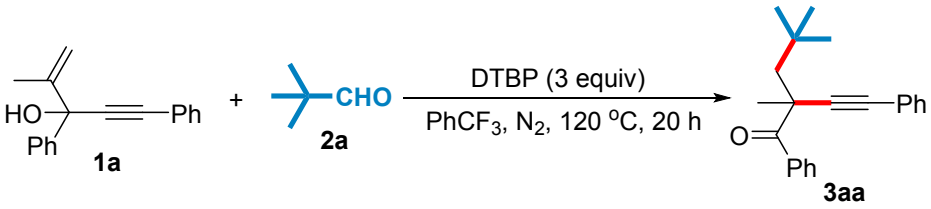
Example for the synthesis of 3aa:

Under nitrogen, pivalaldehyde (0.6 mmol, 3.0 equivalents, 51.7 mg) was added to the pressure tube. Then, 1,4-enyne 1a (0.2 mmol, 1.0 equivalent, 49.6 mg) was dissolved in 2.0 mL of benzotrifluoride, and the mixture was added to a test tube. Subsequently, di-*tert*-butyl peroxide (DTBP) (0.6 mmol, 3.0 equivalents, 87.7 mg) was added to the reaction system. The container was sealed and the mixture was stirred with heating at 120 ℃(oil bath temperature) for 20 hours until complete consumption was monitored by TLC analysis for 1a. Thereafter, the solvent was removed in vacuo, and the residue was purified by silica gel column chromatography

using a mixture of petroleum ether dissolving agents to obtain product 3aa as a colorless oil.

(c) Screening of optimal reaction conditions

Table 1. Screening of optimal reaction conditions[a]

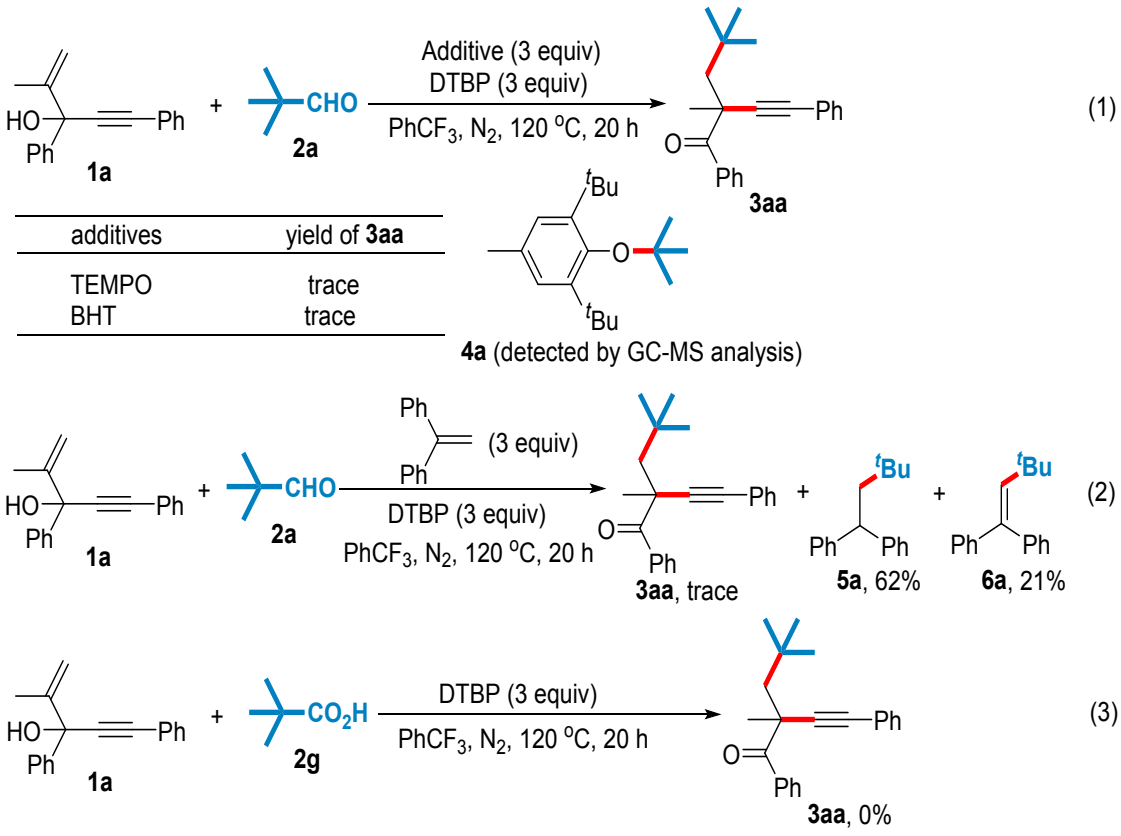


Entry	Variations in Reaction Conditions	Yield[c] (%)
1	none	76
2	without DTBP	0
3	DTBP (2 equiv)	75
4	DTBP (4 equiv)	73
5	TBHP instead of DTBP	trace
6	TBPB instead of DTBP	65
7	DCP instead of DTBP	66
8	H_2O_2 (30% in water) instead of DTBP	trace
9	$K_2S_2O_8$ instead of DTBP	0
10	PhCl instead of $PhCF_3$	72
11	benzene instead of $PhCF_3$	70
12	toluene instead of $PhCF_3$	45
13	EtOAc instead of $PhCF_3$	37
14	MeCN instead of $PhCF_3$	trace
15	1,4-dioxane instead of $PhCF_3$	0
16	at 80 °C	0
17	at 100 °C	37
18	at 140 °C	75
19	air atmosphere instead of N_2	20
20	12 h instead of 20 h	70

[a]Reaction conditions: **1a** (0.6 mmol, 1.0 equiv.), **2a** (1.8 mmol, 3.0 equiv.), oxidant (1.8 mmol, 3.0 equiv.) and solvent (6 mL) under a N_2 atmosphere for 20 h and all reactions were carried out at 120℃ in an oil bath unless otherwise noted. [b]TBHP: *tert*-butyl hydroperoxide 70% in water, DTBP: di-*tert*-butyl peroxide 98%. [c]Isolated yield.

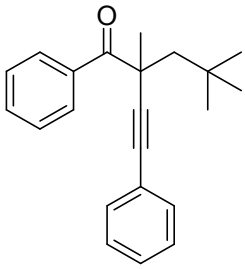
(d) Control experiments (Scheme 1)

Scheme 1. Control experiments.



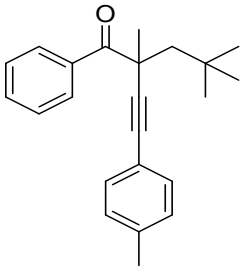
(B) Analytical data

2,4,4-trimethyl-1-phenyl-2-(phenylethynyl)pentan-1-one (3aa):



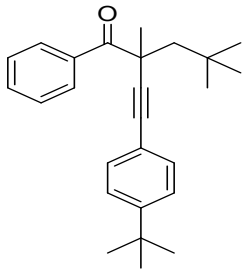
colorless oil (231.4 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.99 Hz, 2H), 7.52 (t, *J* = 6.84 Hz, 1H), 7.43 (t, *J* = 7.46 Hz, 2H), 7.33-7.28 (m, 5H), 2.50 (d, *J* = 14.28 Hz, 1H), 1.72 (s, 3H), 1.69 (d, *J* = 14.49 Hz, 1H), 1.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.57, 136.68, 131.95, 130.94, 129.52, 128.25, 127.96, 127.69, 123.47, 93.68, 87.19, 51.69, 45.91, 31.97, 31.25, 30.10. HRMS *m/z* (ESI) calcd for $C_{22}H_{24}O$ $[M+H]^+$ 304.3550 , found 304.3547.

2,4,4-trimethyl-1-phenyl-2-(p-tolylethynyl)pentan-1-one (3ba):



colorless oil (212.3 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.94 Hz, 2H), 7.51 (t, *J* = 6.86 Hz, 1H), 7.43 (t, *J* = 7.26 Hz, 2H), 7.22 (d, *J* = 7.56 Hz,2H), 7.09 (d, *J* = 7.71 Hz, 2H), 2.50 (d, *J* = 14.21 Hz, 1H), 2.34 (s, 3H), 1.71 (s, 3H), 1.69 (d, *J* = 14.93Hz, 1H), 1.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.68, 138.01, 136.71, 131.90, 130.82, 129.55, 129.00, 127.66, 120.44, 92.91, 87.25, 51.70, 45.90, 31.96, 31.25, 30.11, 21.40. HRMS *m/z* (ESI) calcd for $C_{23}H_{26}O$ $[M+H]^+$ 318.3640, found 318.3642.

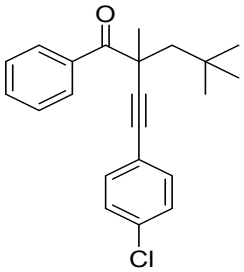
2-((4-(tert-butyl)phenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ca):



colorless oil (237.9 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.75 Hz, 2H), 7.49 (t, *J* = 6.88 Hz, 1H), 7.41 (t, *J* = 7.64 Hz, 2H), 7.30 (t, *J* = 6.05 Hz, 2H), 7.25 (d, *J* = 8.28 Hz, 2H), 2.48 (d, *J* = 14.01 Hz, 1H), 1.70 (s, 3H), 1.66 (d, *J* = 14.40Hz, 1H), 1.29 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.69, 151.18, 136.70, 131.90, 130.66, 129.55, 127.67, 125.24, 120.49, 92.93, 87.23, 51.67, 45.88,

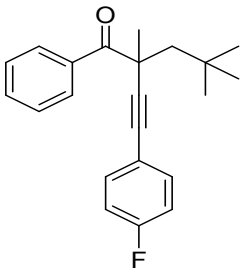
34.69, 31.96, 31.26, 31.14, 30.16. HRMS *m/z* (ESI) calcd for $C_{26}H_{32}O$ $[M+H]^+$ 360.3970, found 360.3992.

2-((4-chlorophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3da):



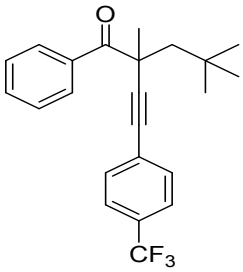
colorless oil (254.2 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.18 Hz, 2H), 7.50 (t, *J* = 6.32 Hz, 1H), 7.41 (t, *J* = 6.88 Hz, 2H), 7.25-7.20 (m, 4H), 2.49 (d, *J* = 14.23 Hz, 1H), 1.70 (s, 3H), 1.66 (s, 1H), 1.06 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.30, 136.60, 133.99, 132.15, 132.01, 129.43, 128.59, 127.71, 121.87, 94.74, 86.16, 51.65, 45.92, 31.96, 31.22, 30.01. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}ClO$ $[M+H]^+$ 339.0746, found 339.0742.

2-((4-fluorophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ea):



colorless oil (220.1 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.65 Hz, 2H), 7.51 (t, *J* = 6.92 Hz, 1H), 7.42 (t, *J* = 7.29 Hz, 2H), 7.26 (t, *J* = 6.42 Hz, 2H), 6.96 (t, *J* = 8.25 Hz, 2H), 2.49 (d, *J* =14.23 Hz, 1H), 1.70 (s, 3H), 1.65 (d, *J* = 5.33 Hz, 1H), 1.07 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.45, 162.31(d, J_{C-F} = 249.10 Hz), 136.67, 132.76(d, J_{C-F} = 8.30 Hz), 131.98, 129.46, 127.70, 119.50(d, J_{C-F} = 3.44 Hz), 115.52(d, J_{C-F} = 22.06 Hz), 93.36, 86.16, 51.67, 45.88, 31.96, 31.23, 30.05. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}FO$ $[M+H]^+$ 322.2619, found 322.2631.

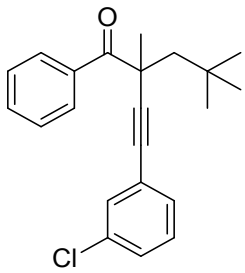
2,4,4-trimethyl-1-phenyl-2-((4-(trifluoromethyl)phenyl)ethynyl)pentan-1-one (3fa):



colorless oil (305.4 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.07 Hz, 2H), 7.53 (t, *J* = 7.75 Hz, 3H), 7.46- 7.39 (m, 4H), 2.53 (d, *J* =14.24 Hz, 1H), 1.74 (s, 3H) 1.69 (s, 1H), 1.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.10, 136.59,

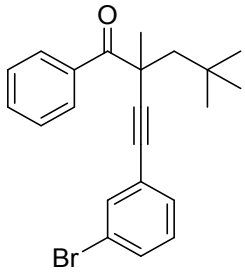
132.09, 131.20, 129.78(q, J_{C-F} = 32.73 Hz, J_{C-F} = 65.47 Hz), 129.39, 129.38(q, J_{C-F} = 213.33 Hz, J_{C-F} = 360.04 Hz), 127.77, 125.22(q, J_{C-F} = 3.65 Hz, J_{C-F} = 7.48 Hz), 122.54, 96.45, 86.10, 51.69, 45.99, 31.98, 31.22, 29.97. HRMS *m/z* (ESI) calcd for $C_{23}H_{23}F_3O$ $[M+H]^+$ 372.3590, found 372.3576.

2-((3-chlorophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ga):



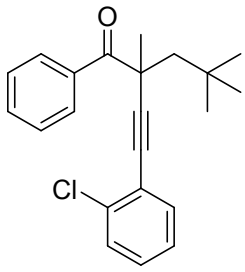
colorless oil (237.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.22 Hz, 2H), 7.51 (t, *J* = 7.22 Hz, 1H), 7.43 (t, *J* = 7.40 Hz, 2H), 7.27-7.23 (m, 2H), 7.21-7.15 (m, 2H), 2.49 (d, *J* = 14.21 Hz, 1H), 1.70 (s, 3H), 1.66 (s, 1H), 1.07 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.20, 136.56, 134.09, 132.06, 130.81, 129.48, 129.40, 129.09, 128.26, 127.74, 125.07, 95.05, 85.93, 51.66, 45.90, 31.95, 31.23, 30.01. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}ClO$ $[M+H]^+$ 339.0746, found 339.0745.

2-((3-bromophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ha):



colorless oil (305.7mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.59 Hz,2H), 7.52 (t, *J* = 6.98 Hz, 1H), 7.41 (q, 4H), 7.21 (d, *J* = 7.74 Hz, 1H), 7.12 (t, *J* = 7.89Hz, 1H), 2.49 (d, *J* = 14.20 Hz, 1H), 1.70 (s, 3H), 1.66 (s, 1H), 1.06 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.16, 136.56, 133.67, 132.05, 131.14, 129.69, 129.53, 129.39, 127.75, 125.36, 122.10, 95.20, 85.80, 51.66, 45.91, 31.95, 31.23, 30.01. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}BrO$ $[M+H]^+$ 383.4011, found 383.4012.

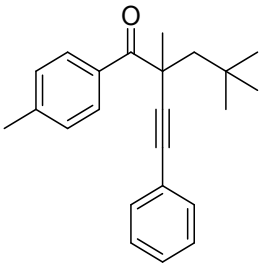
2-((2-chlorophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ia):



colorless oil (247.4 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.01 Hz, 2H), 7.51 (t, *J* = 7.21 Hz, 1H), 7.42 (t, *J* = 7.15 Hz, 2H), 7.37-7.32 (m, 2H), 7.22-7.14 (m, 2H), 2.52 (d, *J* = 14.25 Hz, 1H), 1.77 (s, 3H), 1.73 (d, *J* = 14.61Hz, 1H), 1.10(s,

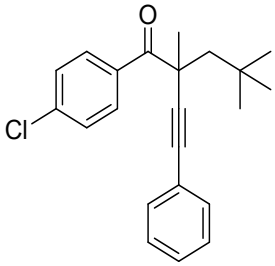
9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.90, 136.35, 135.73, 132.90, 132.06, 129.72, 129.20, 128.92, 127.75, 126.30, 123.22, 98.66, 84.32, 51.77, 46.17, 32.01, 31.31, 30.01. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}ClO$ $[M+H]^+$ 339.0746, found 339.0745.

2,4,4-trimethyl-2-(phenylethynyl)-1-(p-tolyl)pentan-1-one (3ka):



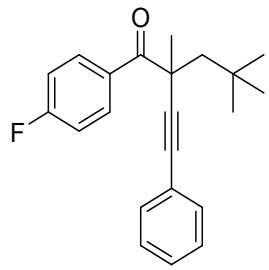
colorless oil (194.8 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* =7.91 Hz, 2H), 7.32 (d, *J* =5.05 Hz, 2H), 7.27 (s, 3H), 7.21 (d, *J* =7.81 Hz, 2H), 2.47 (d, *J* =14.22 Hz, 1H), 2.38 (s, 3H), 1.69 (s, 3H), 1.65 (s, 1H), 1.07 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.69, 142.67, 133.75, 130.95, 129.82, 128.40, 128.24, 127.90, 123.55, 93.89, 86.94, 51.71, 45.76, 32.00, 31.25, 29.97, 21.55. HRMS *m/z* (ESI) calcd for $C_{23}H_{26}O$ $[M+H]^+$ 318.3640, found 318.3641.

1-(4-chlorophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3la):



colorless oil (237.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* =8.33 Hz, 2H), 7.41 (d, *J* = 8.33 Hz, 2H), 7.31 (s, 5H), 2.46 (d, *J* =14.30 Hz, 1H), 1.71 (s, 3H), 1.67 (s, 1H), 1.08 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.10, 138.40, 134.76, 131.09, 130.94, 128.34, 128.14, 128.02, 123.22, 93.31, 87.43, 51.69, 45.87, 32.00, 31.23, 29.92. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}ClO$ $[M+H]^+$ 339.0746, found 339.0740.

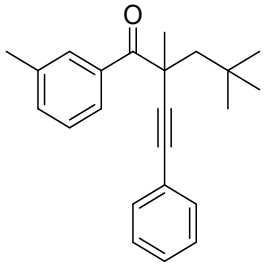
1-(4-fluorophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3ma):



colorless oil (232.1 mg, 72% yield). ^{1}H NMR (400 MHz, CDCl3) δ 8.29 (t, *J* = 7.23 Hz, 2H), 7.35-7.31 (m, 5H), 7.11 (t, *J* = 8.40 Hz, 2H), 2.48 (d, *J* = 14.32 Hz, 1H), 1.72 (s, 3H), 1.67 (d, *J* = 5.98 Hz, 1H), 1.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.69, 164.93(d, J_{C-F} = 253.73 Hz), 132.64(d, J_{C-F} = 3.21 Hz), 132.28(d,

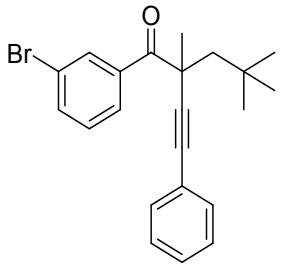
$J_{C\text{-}F}$ = 8.91 Hz), 130.93, 128.32, 128.10, 123.26, 114.78(d, $J_{C\text{-}F}$ = 21.64 Hz), 93.48, 87.36, 51.68, 45.78, 31.99, 31.22, 29.92. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}FO$ $[M+H]^+$ 322.2619, found 322.2630.

2,4,4-trimethyl-2-(phenylethynyl)-1-(m-tolyl)pentan-1-one (3na):



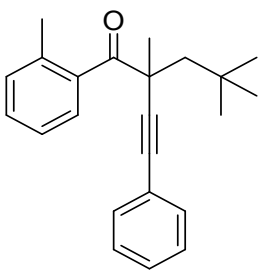
colorless oil (237.8 mg, 75% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 4.97 Hz, 1H), 7.97 (s, 1H), 7.31-7.28 (m, 7H), 2.49 (d, *J* = 9.49 Hz, 1H), 2.39 (s, 3H), 1.70 (s, 3H), 1.66 (d, *J* = 14.41 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.77, 137.38, 136.69, 132.69, 130.91, 130.12, 128.24, 127.92, 127.49, 126.70, 123.54, 93.83, 87.14, 51.70, 45.91, 31.95, 31.26, 30.26, 21.43. HRMS *m/z* (ESI) calcd for $C_{23}H_{26}O$ $[M+H]^+$ 318.3640, found 318.3639.

1-(3-bromophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3oa):



colorless oil (275.8 mg, 72% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.13 (d, *J* = 7.79 Hz, 1H), 7.65 (d, *J* = 7.83 Hz, 1H), 7.38 (d, *J* = 4.55 Hz, 2H), 7.32 (d, *J* = 7.79 Hz, 4H), 2.50 (d, *J* = 14.29 Hz, 1H), 1.73 (s, 3H), 1.68 (s, 1H), 1.11 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.11, 138.31, 134.79, 132.49, 130.95, 129.32, 128.27, 128.12, 128.01, 123.09, 121.78, 93.03, 87.67, 51.59, 45.90, 31.89, 31.21, 30.18. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}BrO$ $[M+H]^+$ 383.4011, found 383.4020.

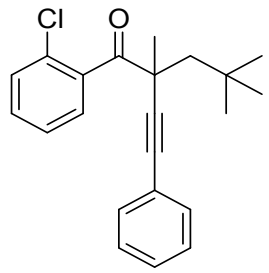
2,4,4-trimethyl-2-(phenylethynyl)-1-(o-tolyl)pentan-1-one (3pa):



colorless oil (240.7 mg, 76% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.72 Hz, 1H), 7.32 (t, *J* = 7.36 Hz, 1H), 7.25-7.18 (m, 7H), 2.43 (d, *J* = 14.24 Hz, 1H), 2.37 (s, 3H),

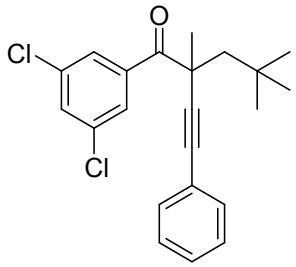
1.67 (d, J = 14.36 Hz, 1H), 1.63 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.46, 138.14, 136.58, 131.09, 130.91, 129.93, 128.21, 127.96, 127.87, 124.10, 123.50, 93.08, 87.24, 50.70, 47.50, 31.88, 31.27, 29.87, 20.39. HRMS *m/z* (ESI) calcd for $C_{23}H_{26}O$ $[M+H]^+$ 318.3640, found 318.3639.

1-(2-chlorophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3qa):



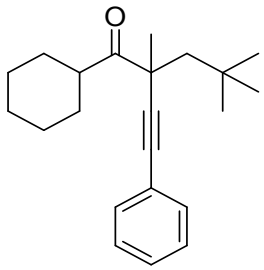
colorless oil (230.4 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.48 Hz, 1H), 7.42 (d, J = 7.82 Hz, 1H), 7.33 (t, J = 7.50 Hz, 1H), 7.28-7.24 (m, 4H), 7.22-7.19 (m, 2H), 2.38 (d, J = 14.24 Hz, 1H), 1.70 (d, J = 14.42 Hz, 1H), 1.67 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.49, 138.85, 130.98, 130.84, 130.55, 130.07, 128.58, 128.27, 128.03, 125.49, 123.31, 92.19, 87.19, 50.08, 48.05, 31.98, 31.30, 28.98. HRMS *m/z* (ESI) calcd for $C_{22}H_{23}ClO$ $[M+H]^+$ 339.0746, found 339.0738.

1-(3,5-dichlorophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3ra):



colorless oil (112.5 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 2.91 Hz, 2H), 7.49 (d, J = 0.86 Hz, 1H), 7.38-7.36 (m, 2H), 7.30 (t, J = 2.63 Hz, 3H), 2.47 (t, J =13.27 Hz, 1H), 1.69 (s, 3H), 1.65 (s, 1H), 1.07 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.10, 138.96, 134.58, 131.68, 130.95, 128.35, 128.30, 127.95, 122.89, 92.57, 88.11, 51.59, 46.04, 31.90, 31.21, 30.26. HRMS *m/z* (ESI) calcd for $C_{22}H_{22}Cl_2O$ $[M+H]^+$ 373.2560, found 373.2546.

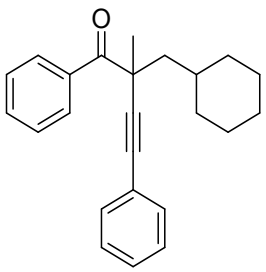
1-cyclohexyl-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3sa):



colorless oil (199.9 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 4.60 Hz, 2H), 7.32 (d, J = 4.72 Hz, 3H), 3.38 (t, J = 10.19 Hz, 1H), 2.22 (d, J = 14.14 Hz, 1H), 2.11 (d,

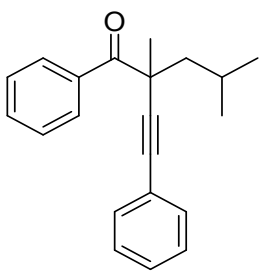
J = 6.91 Hz, 1H), 1.84 (t, *J* = 15.89 Hz, 3H), 1.69 (t, *J* = 11.79 Hz, 1H), 1.53-1.45 (m, 2H), 1.41 (s, 3H), 1.36-1.27 (m, 4H), 1.02 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.78, 131.08, 128.35, 127.93, 123.61, 92.79, 85.68, 51.16, 48.30, 46.81, 31.45, 31.00, 30.34, 30.04, 29.27, 26.00, 25.84, 25.57. HRMS *m/z* (ESI) calcd for $C_{22}H_{30}O$ $[M+H]^+$ 310.4815, found 318.4808.

2-(cyclohexylmethyl)-2-methyl-1,4-diphenylbut-3-yn-1-one (3ab)[1]:



colorless oil (201.2 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.75 Hz, 2H), 7.52 (t, *J* = 7.31 Hz, 1H), 7.44 (t, *J* = 7.44 Hz, 2H), 7.31 (d, *J* = 17.08 Hz, 5H), 2.21-2.16 (m, 1H), 1.89 (d, *J* = 12.71 Hz, 1H), 1.74-1.60 (m, 9H), 1.30-1.13 (m, 3H), 1.08-0.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.26, 136.12, 132.21, 131.20, 129.61, 128.23, 127.97, 127.85, 123.39, 92.94, 86.08, 46.99, 46.28, 35.31, 34.64, 34.52, 26.94, 26.42, 26.37, 26.24. The analytical data are in accordance with those reported in the literature.[1]

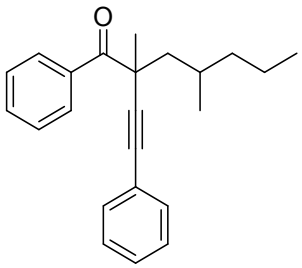
2,4-dimethyl-1-phenyl-2-(phenylethynyl)pentan-1-one (3ac):



colorless oil (180.1 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.56 Hz, 2H), 7.55 (t, *J* = 7.13 Hz, 1H), 7.46 (t, *J* = 7.49 Hz, 2H), 7.36 (d, *J* = 2.88 Hz, 2H), 7.32 (s, 3H), 2.25-2.19 (m, 1H), 2.06-1.96 (m, 1H), 1.77- 1.73 (m, 1H), 1.70 (s, 3H), 1.05 (d, *J* = 6.62 Hz, 3H),0.98 (d, *J* = 6.62 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.41, 136.16, 132.22, 131.19, 129.60, 128.23, 127.99, 127.86,

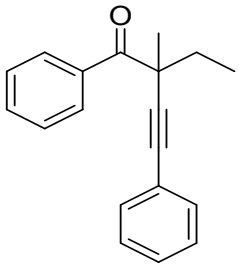
123.34, 92.88, 86.23, 48.29, 46.42, 26.95, 25.90, 24.17, 23.88. HRMS *m/z* (ESI) calcd for $C_{21}H_{22}O$ $[M+H]^+$ 290.2860, found 290.2846.

2,4-dimethyl-1-phenyl-2-(phenylethynyl)heptan-1-one (3ad):



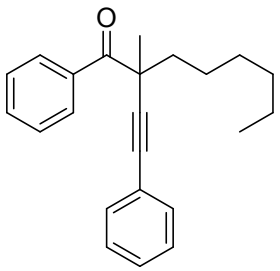
colorless oil (197.4 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.51 Hz, 2H), 7.52 (t, *J* = 7.25 Hz, 1H), 7.44 (t, *J* = 7.48 Hz, 2H), 7.34 (s, 2H), 7.29 (s, 3H), 2.29-2.24 (m, 1H), 2.17-2.11 (m, 1H), 1.87-1.75 (m, 2H), 1.67 (s, 3H), 1.65, 1.47-1.19 (m, 5H), 1.03 (d, *J* = 6.49 Hz, 1H), 0.95-0.85 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.42, 199.28, 135.18, 135.15, 131.21, 131.20, 130.18, 130.17, 128.61, 128.60, 127.23, 127.23, 126.97, 126.86, 126.83, 122.37, 122.35, 91.99, 91.89, 85.32, 85.14, 46.00, 45.60, 45.54, 45.42, 39.65, 39.46, 29.34, 29.11, 25.99, 25.74, 20.18, 20.11, 18.99, 13.28, 13.21. HRMS *m/z* (ESI) calcd for $C_{23}H_{26}O$ $[M+H]^+$ 318.3040, found 318.3046.

2-ethyl-2-methyl-1,4-diphenylbut-3-yn-1-one (3ae):



colorless oil (201.2 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.75 Hz, 2H), 7.53 (t, *J* = 7.31 Hz, 1H), 7.44 (t, *J* = 7.53 Hz, 2H), 7.37 (s, 2H), 7.30 (s, 3H), 2.24-2.15 (m, 1H), 1.92-1.83 (m, 1H), 1.62 (s, 3H), 1.07 (t, *J* = 7.45 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.83, 135.96, 132.36, 131.32, 129.58, 128.23, 128.04, 127.94, 123.27, 92.38, 86.07, 47.11, 33.22, 25.23, 9.37. HRMS *m/z* (ESI) calcd for $C_{19}H_{18}O$ $[M+H]^+$ 262.3162, found 290.3170.

2-methyl-1-phenyl-2-(phenylethynyl)octan-1-one (3af):

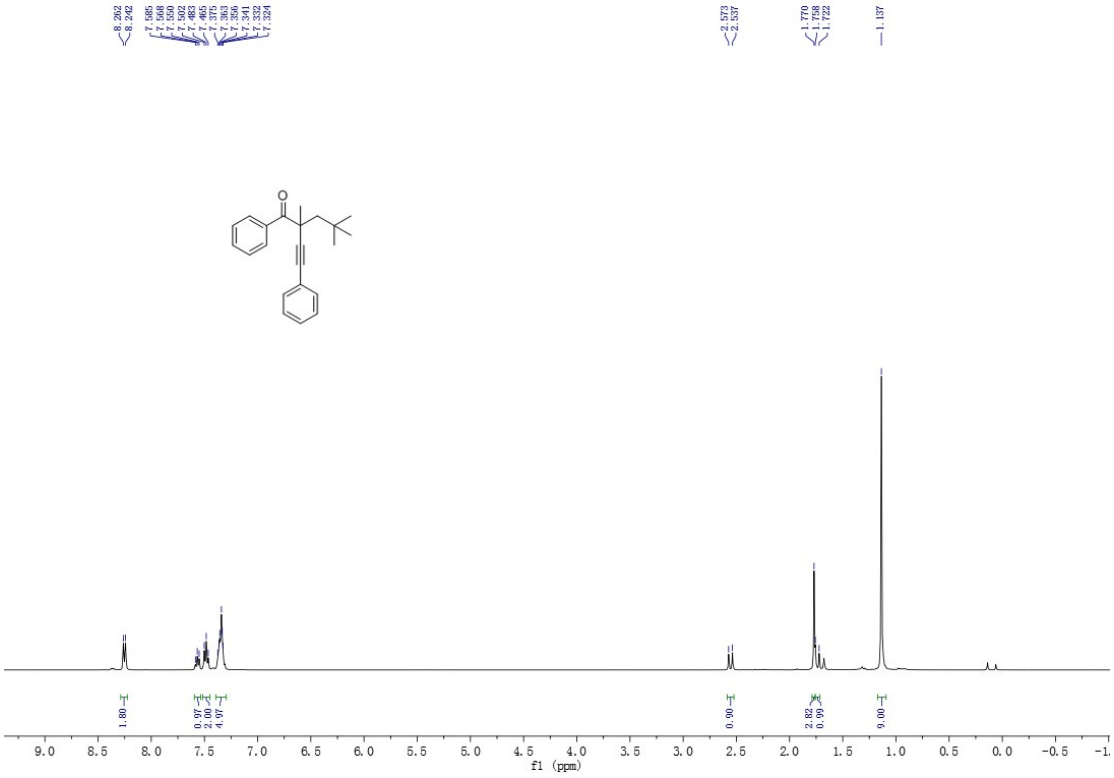


colorless oil (78.7 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.59Hz, 2H), 7.53 (t, *J* = 7.32 Hz, 1H),

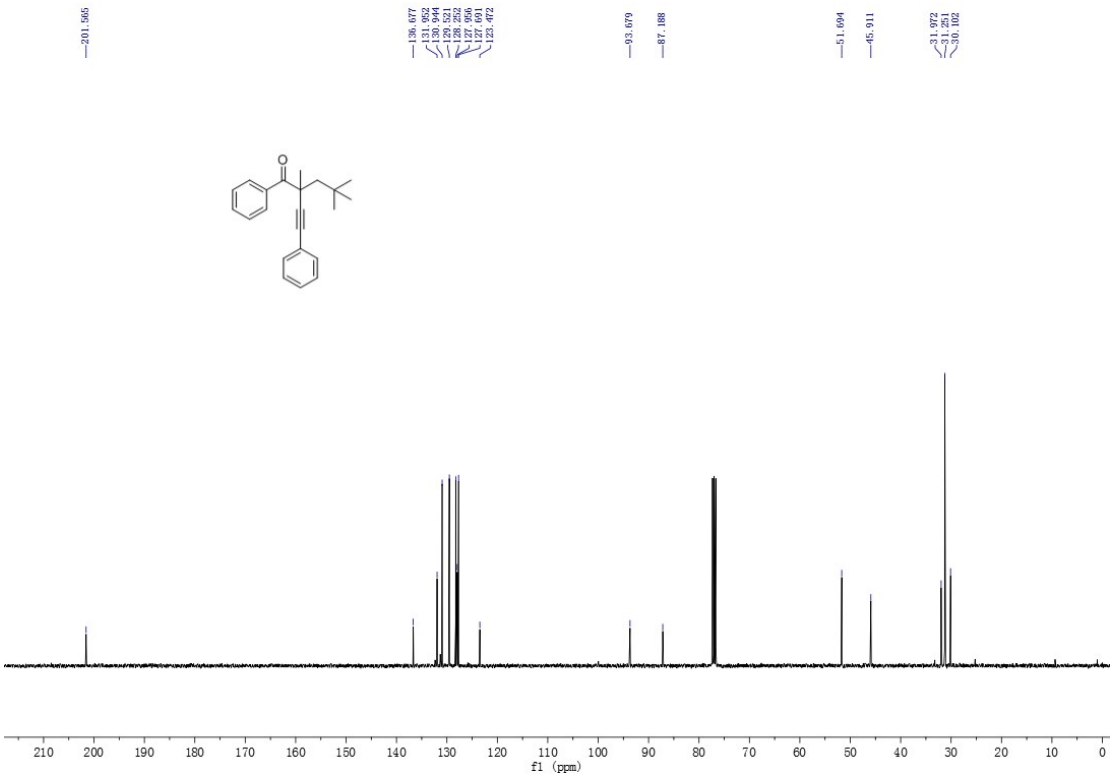
7.44 (t, *J* = 7.54 Hz, 2H), 7.36 (s, 2H), 7.30 (s, 3H), 2.17- 2.10 (m, 1H), 1.85-1.79 (m, 1H), 1.64 (s, 3H), 1.59-1.53 (m, 1H), 1.46- 1.29 (m, 7H), 0.87 (t, *J* = 5.69 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.90, 135.97, 132.32, 131.30, 129.57, 128.22, 128.01, 127.92, 123.29, 92.69, 85.93, 46.68, 40.30, 31.60, 29.51, 25.78, 24.90, 22.56, 14.03. HRMS *m/z* (ESI) calcd for $C_{23}H_{26}O$ $[M+H]^+$ 318.3040, found 318.3043.

(D) Spectra

2,4,4-trimethyl-1-phenyl-2-(phenylethynyl)pentan-1-one (3aa):

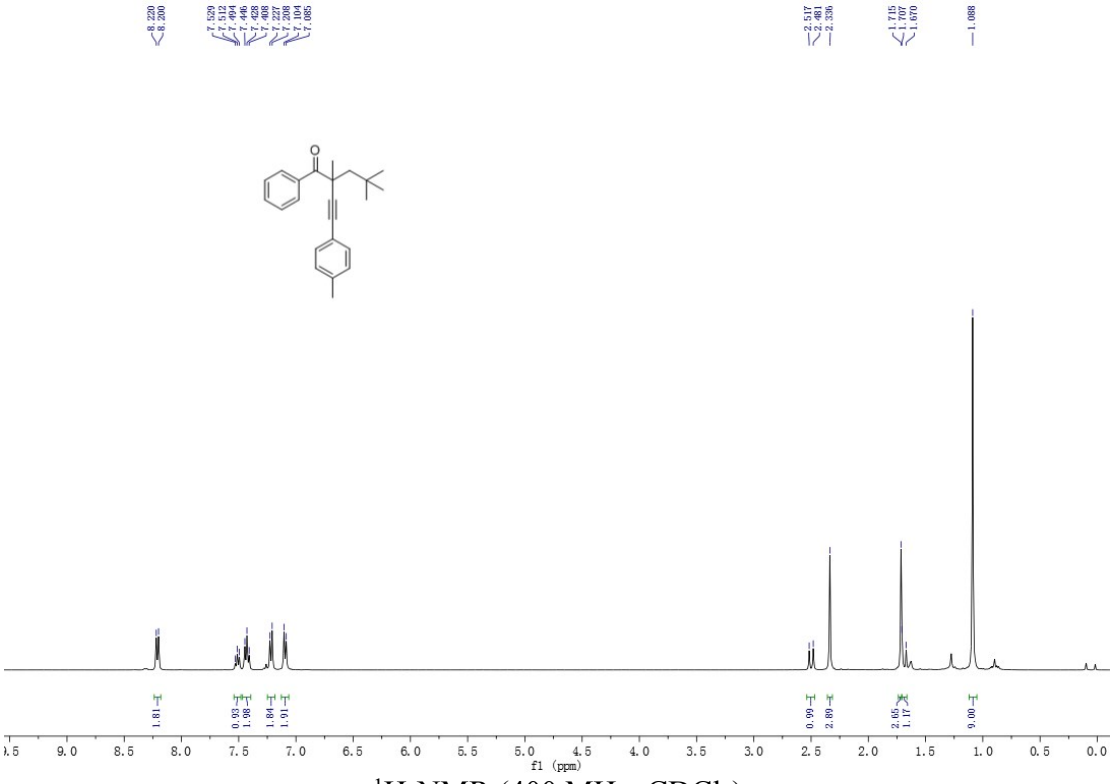


^{1}H-NMR (400 MHz, $CDCl_3$)

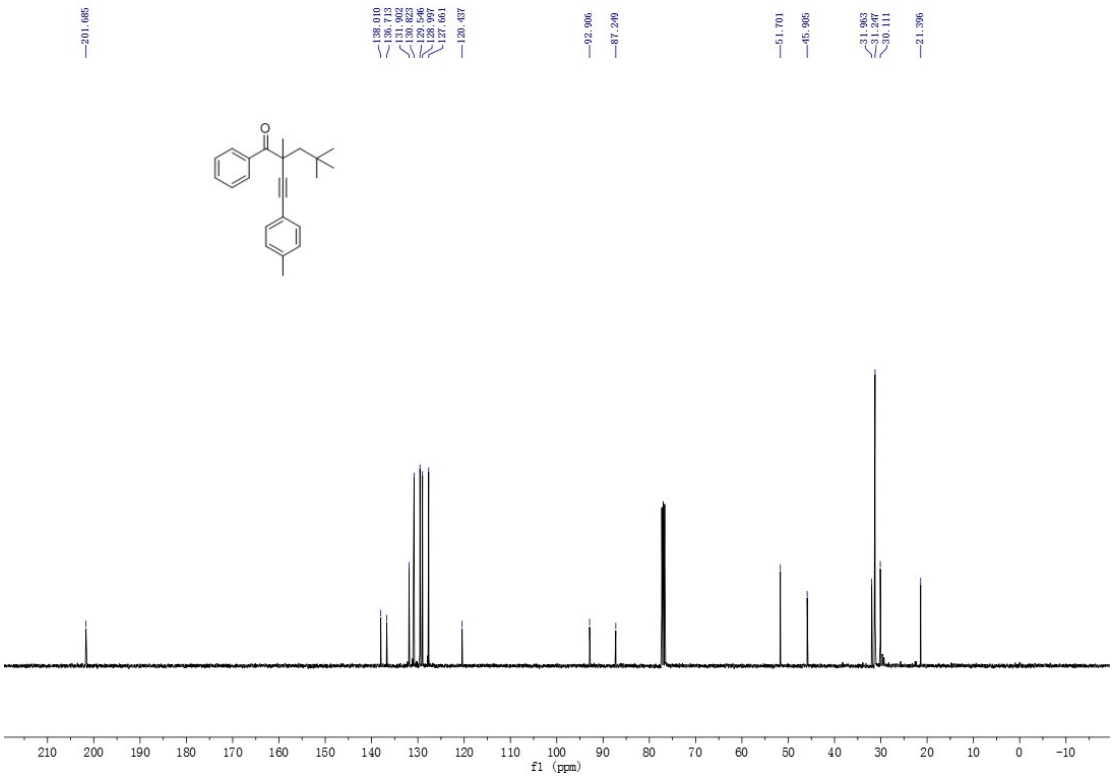


^{13}C-NMR (101 MHz, $CDCl_3$)

2,4,4-trimethyl-1-phenyl-2-(p-tolylethynyl)pentan-1-one (3ba):

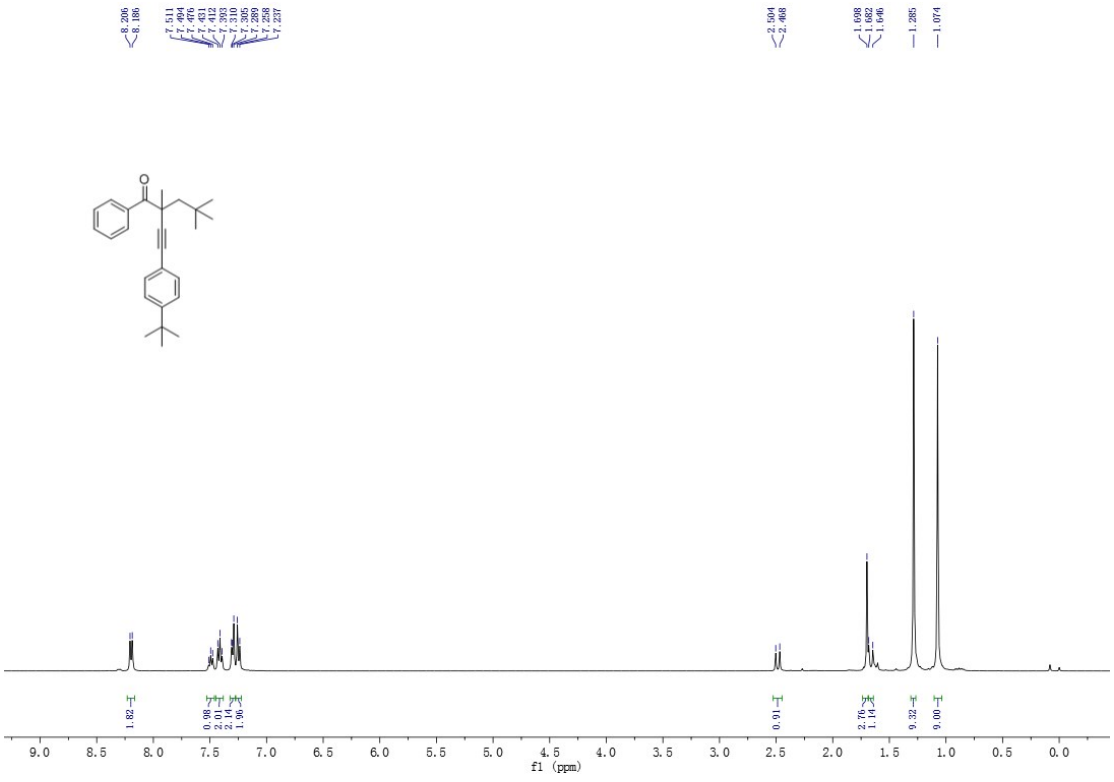


^{1}H-NMR (400 MHz, $CDCl_3$)

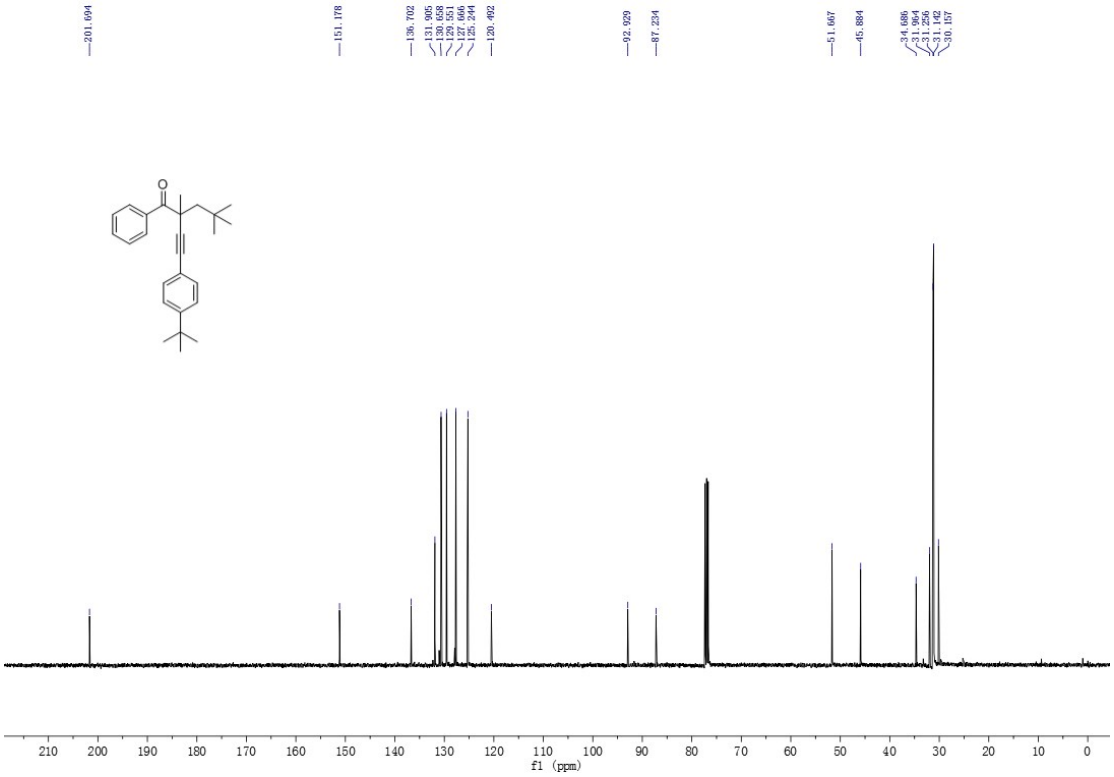


^{13}C-NMR (101 MHz, $CDCl_3$)

2-((4-(tert-butyl)phenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ca):

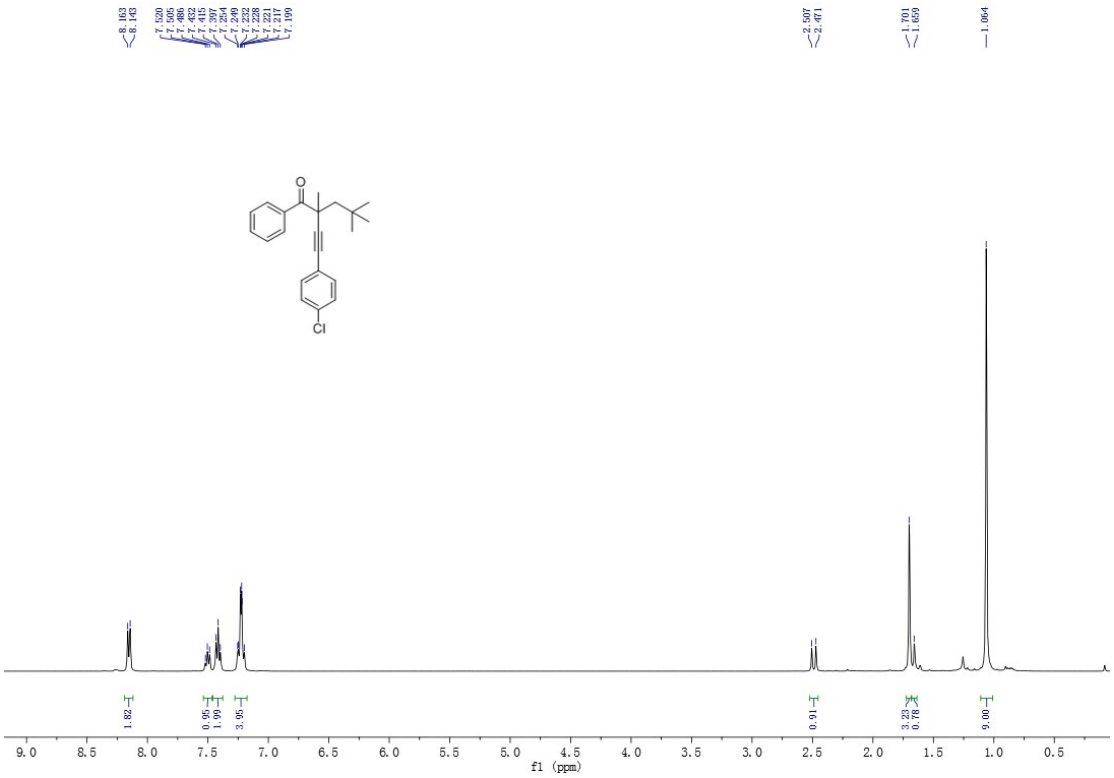


^{1}H-NMR (400 MHz, $CDCl_3$)

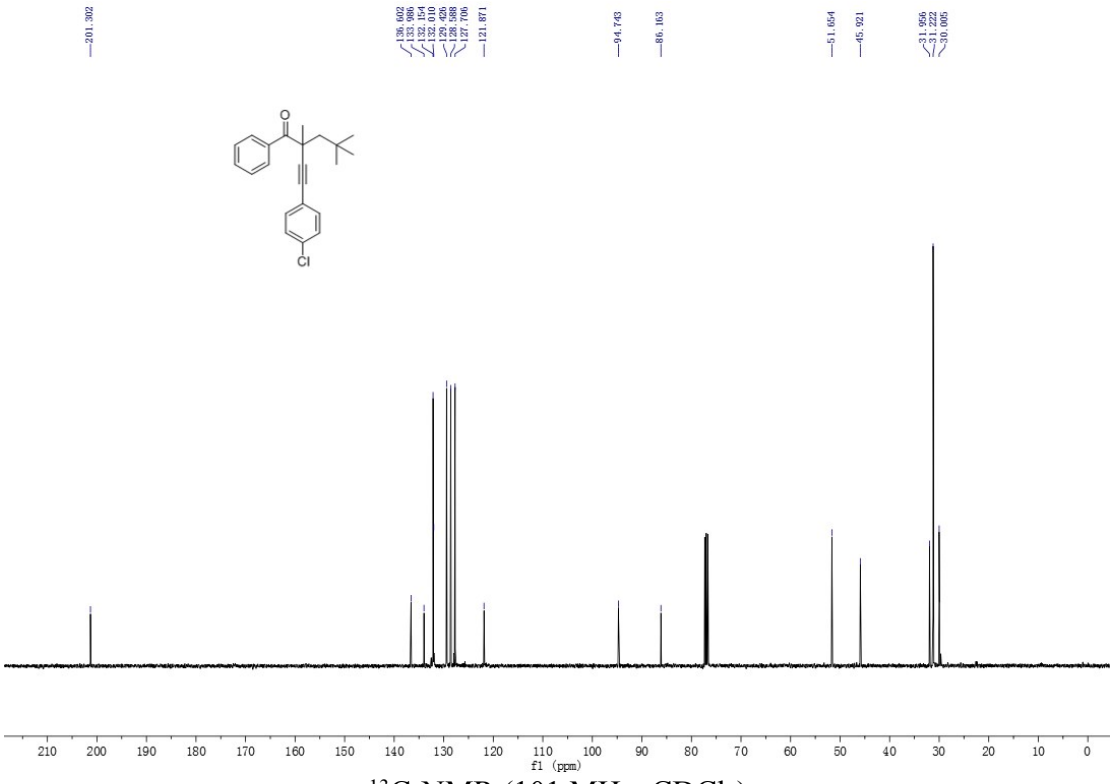


^{13}C-NMR (101 MHz, $CDCl_3$)

2-((4-chlorophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3da):

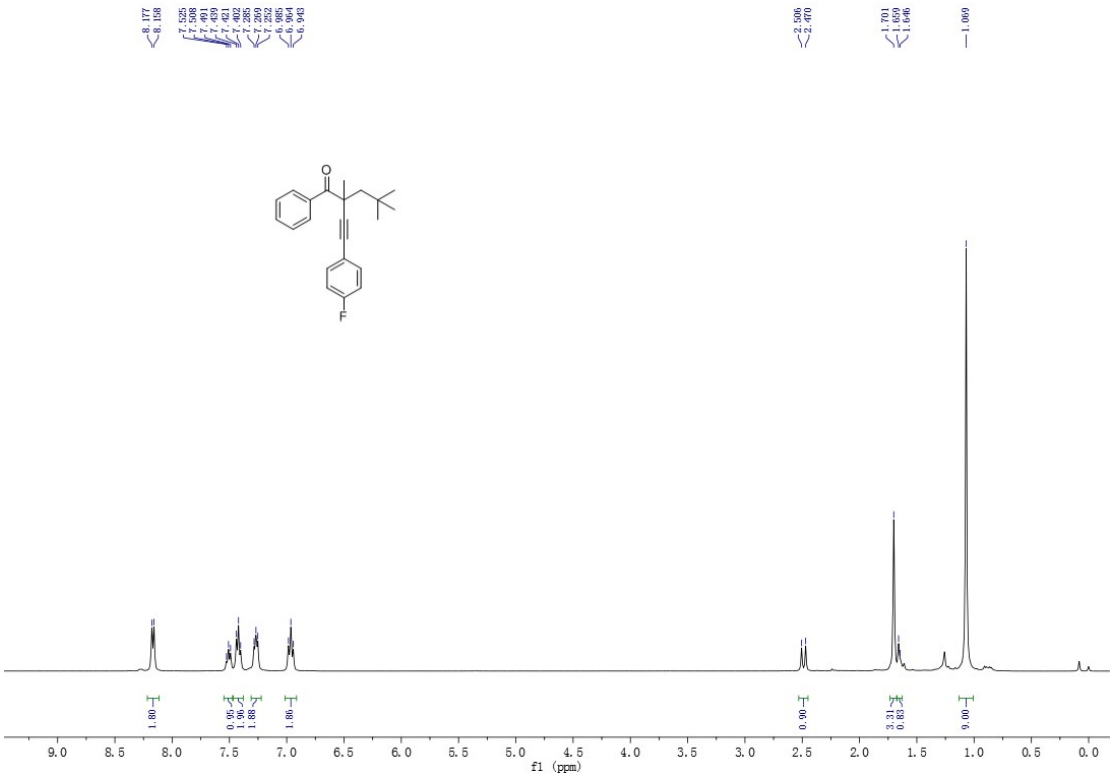


^{1}H-NMR (400 MHz, $CDCl_3$)

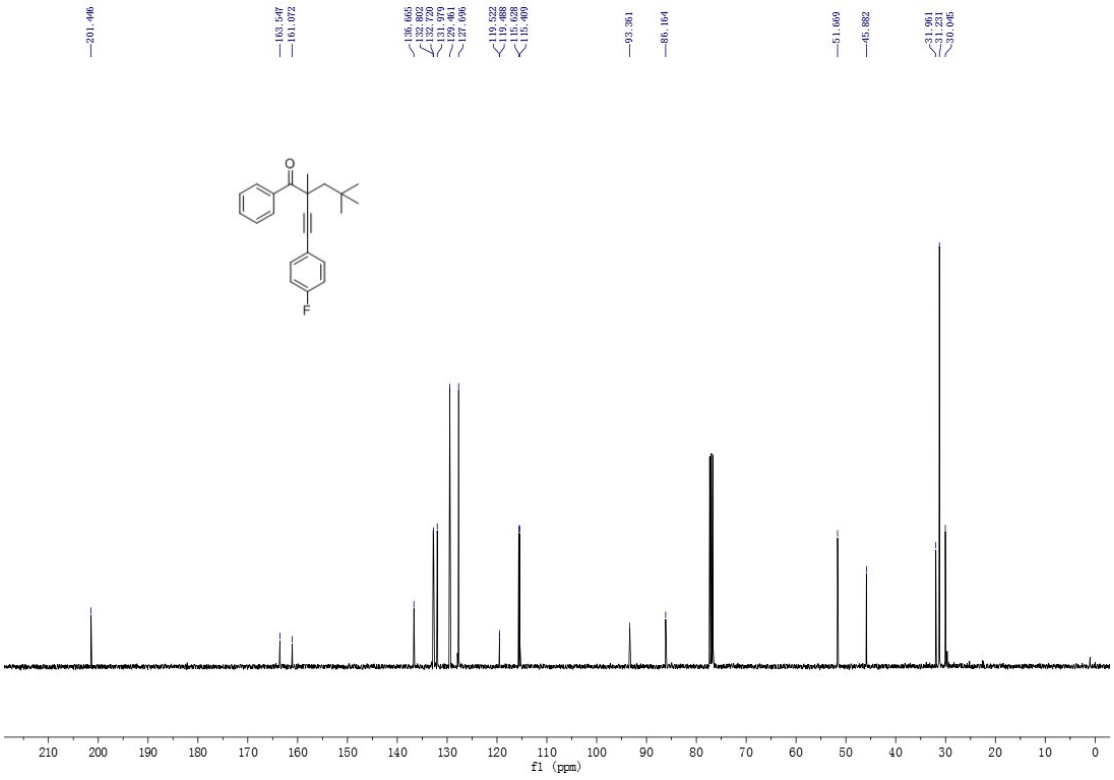


^{13}C-NMR (101 MHz, $CDCl_3$)

2-((4-fluorophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ea):

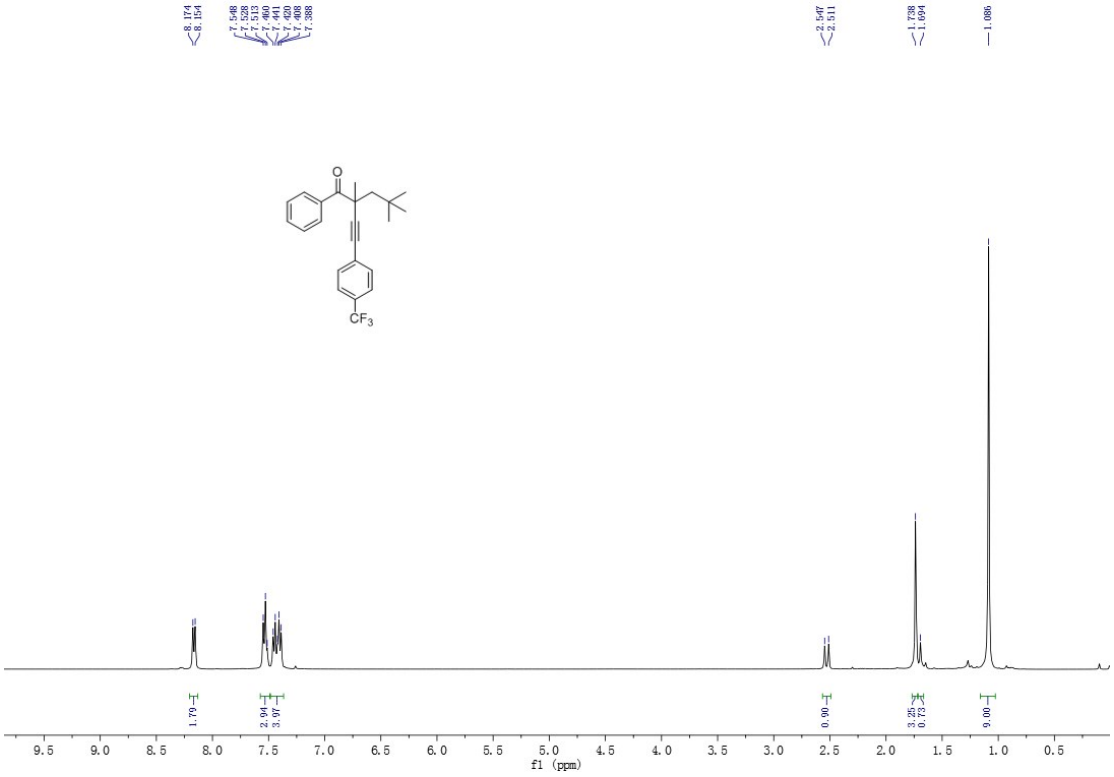


^{1}H-NMR (400 MHz, $CDCl_3$)

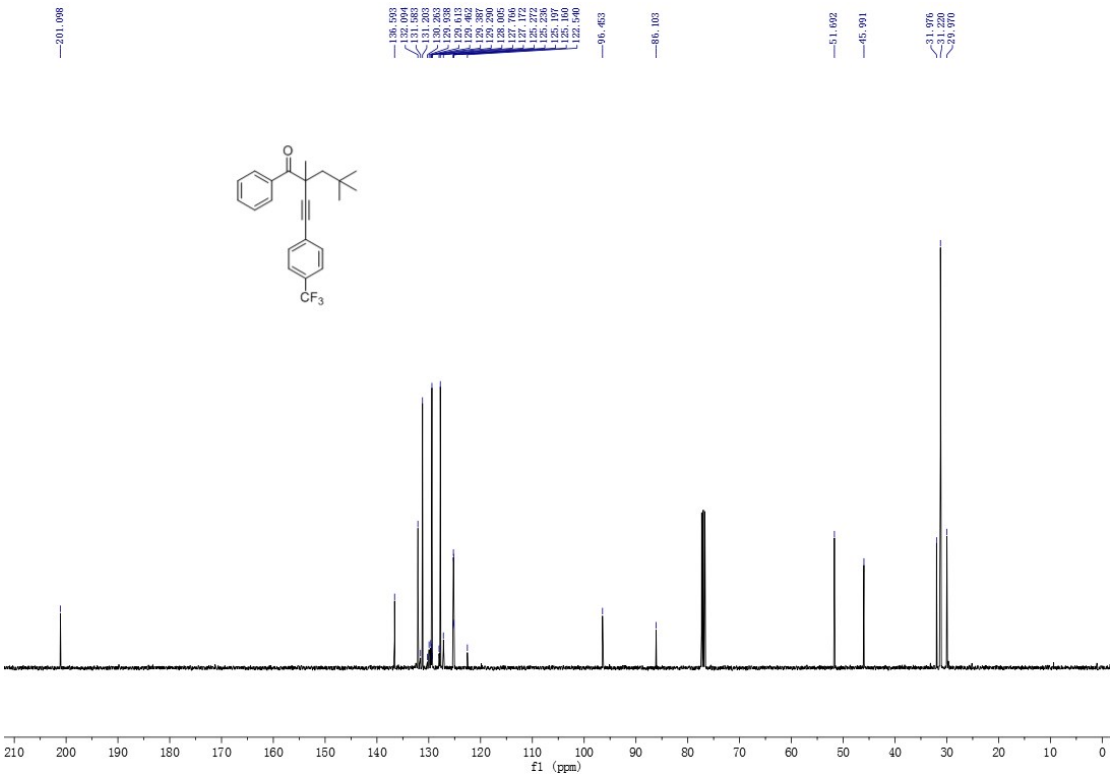


^{13}C-NMR (101 MHz, $CDCl_3$)

2,4,4-trimethyl-1-phenyl-2-((4-(trifluoromethyl)phenyl)ethynyl)pentan-1-one (3fa):

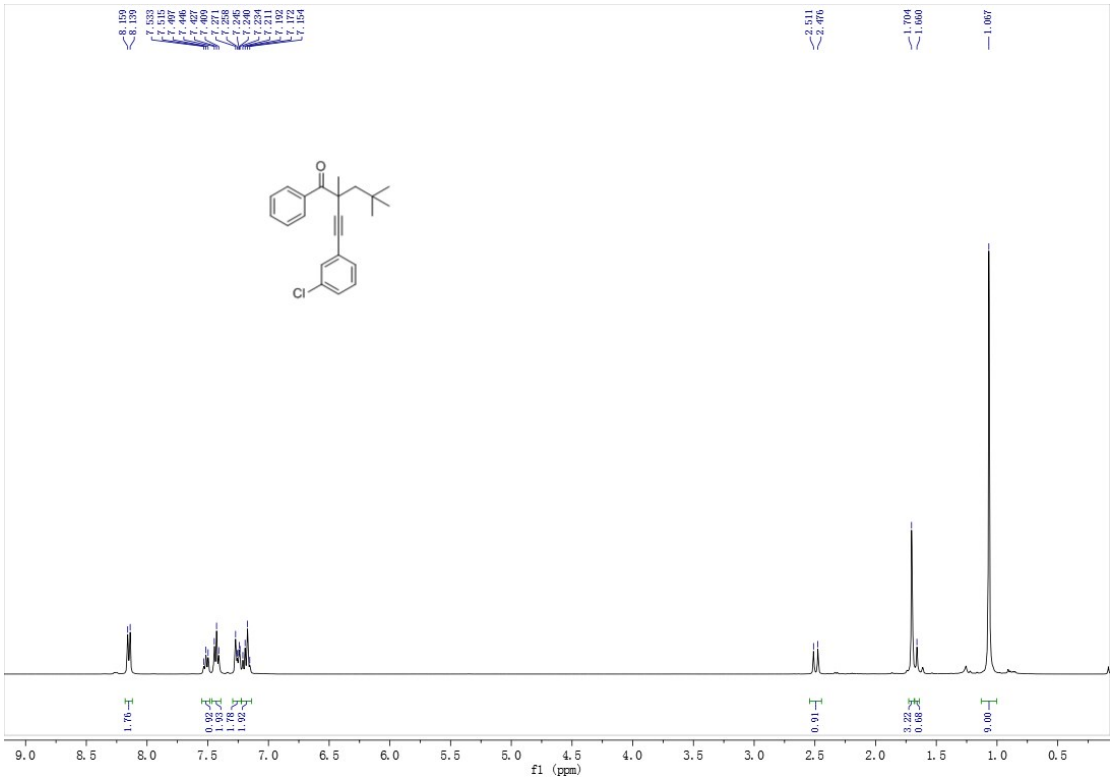


^{1}H-NMR (400 MHz, $CDCl_3$)

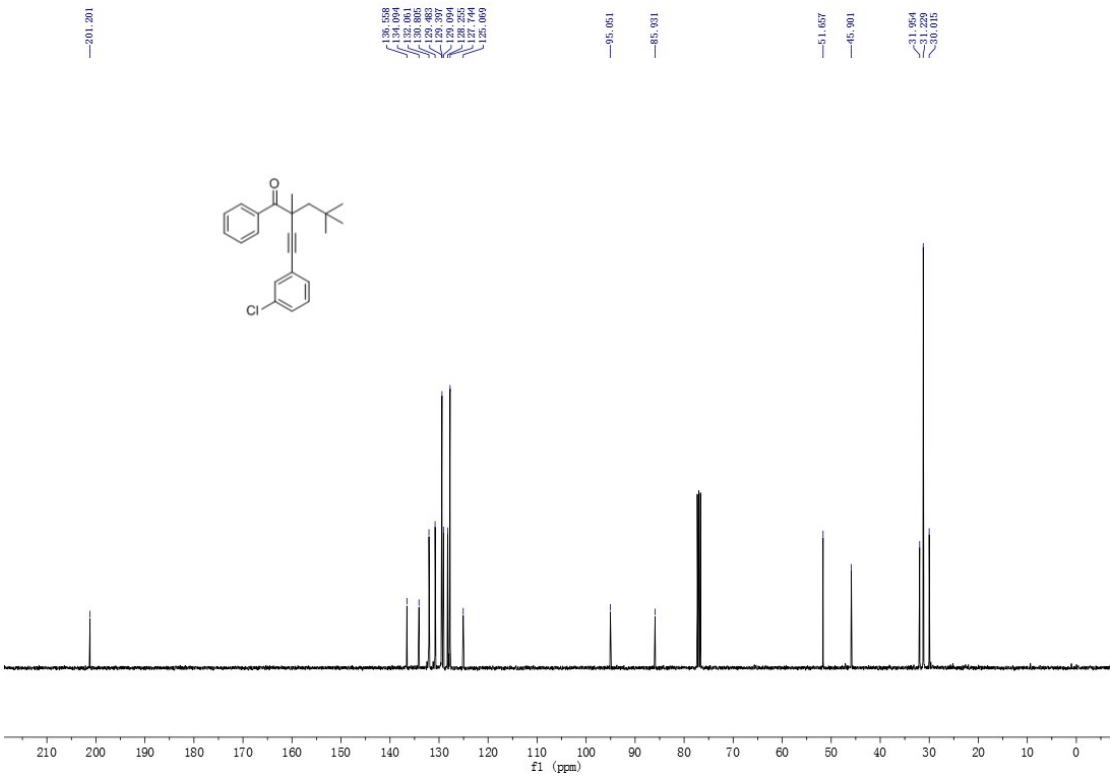


^{13}C-NMR (101 MHz, $CDCl_3$)

2-((3-chlorophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ga):

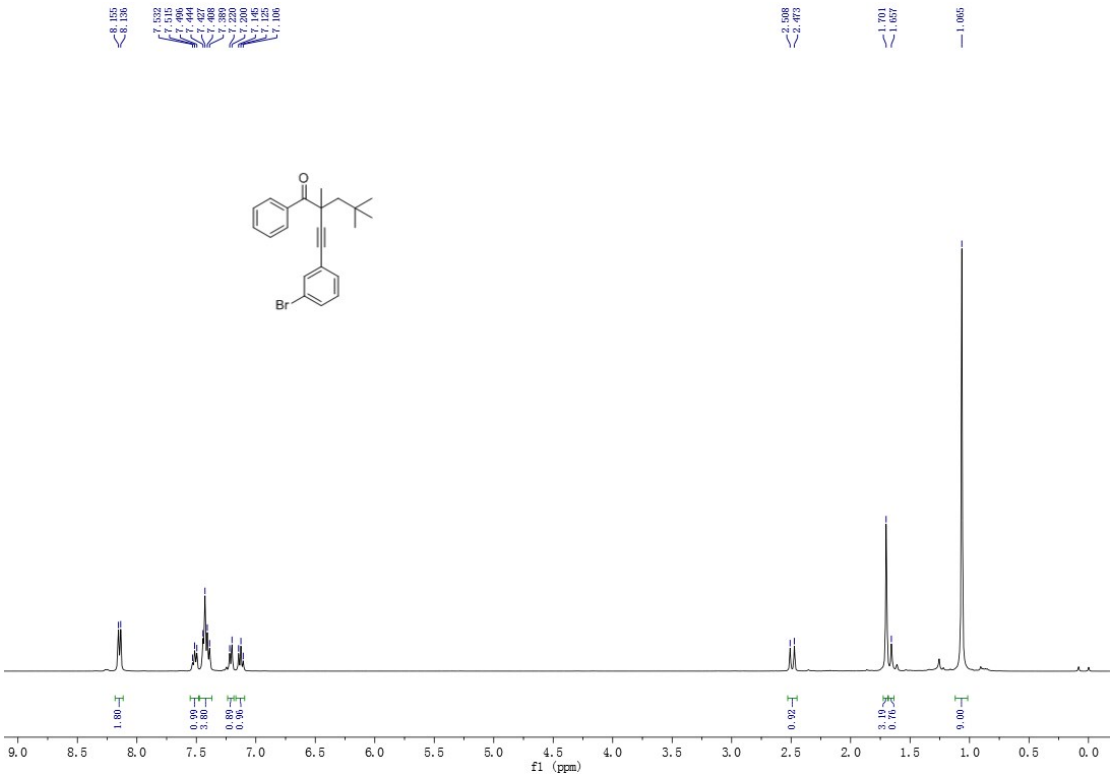


^{1}H-NMR (400 MHz, $CDCl_3$)

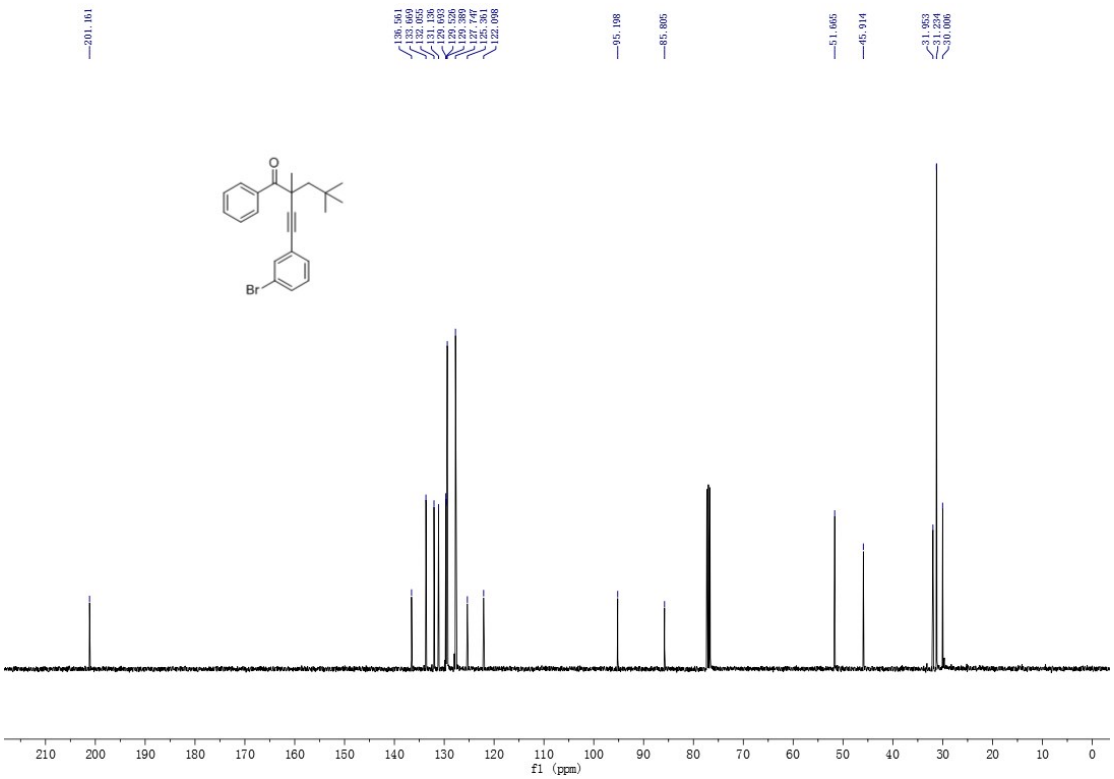


^{13}C-NMR (101 MHz, $CDCl_3$)

2-((3-bromophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ha):

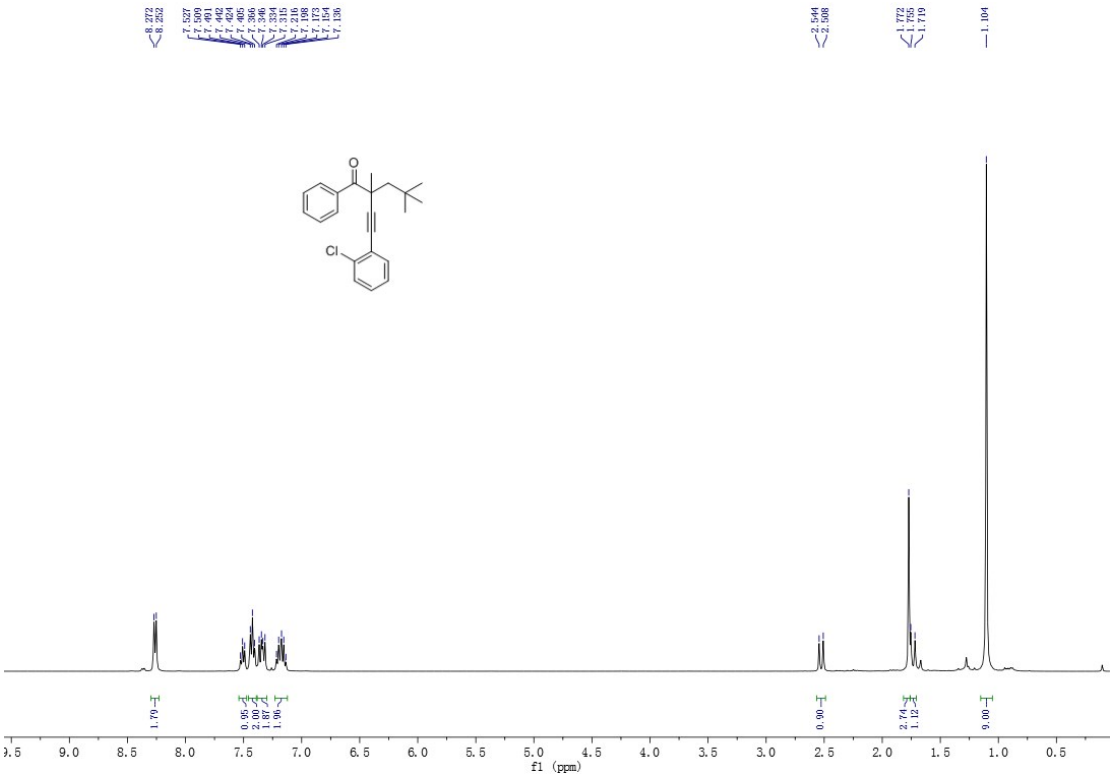


^{1}H-NMR (400 MHz, $CDCl_3$)

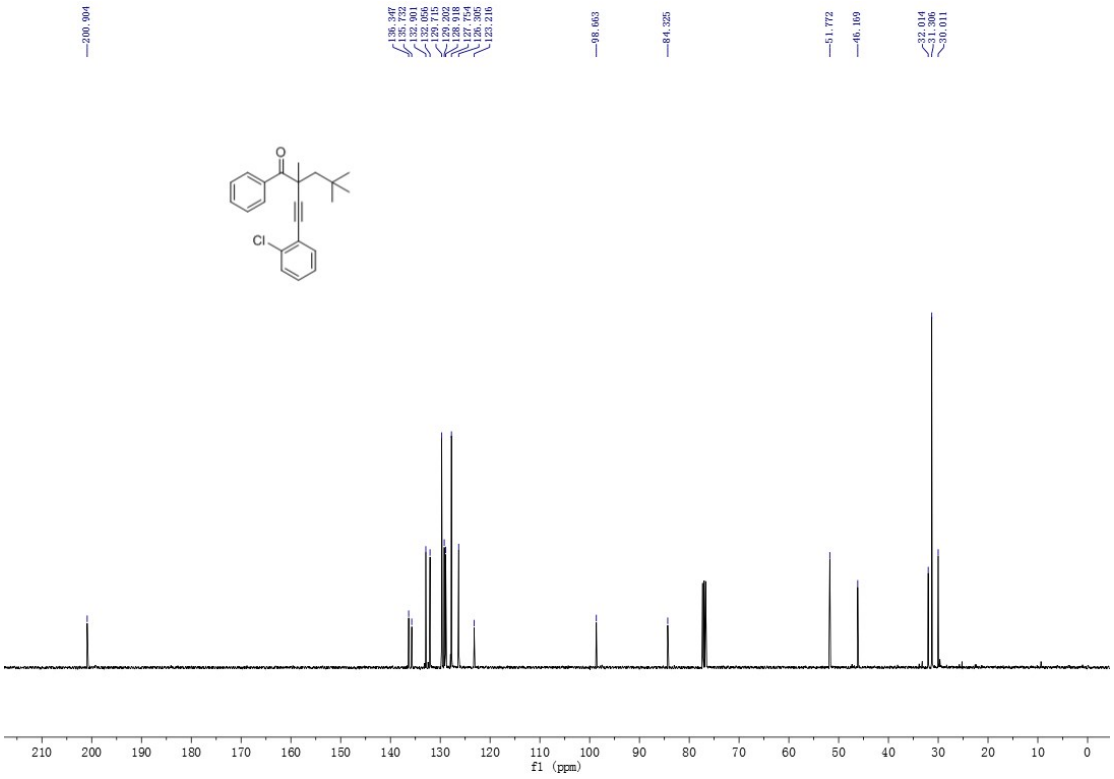


^{13}C-NMR (101 MHz, $CDCl_3$)

2-((2-chlorophenyl)ethynyl)-2,4,4-trimethyl-1-phenylpentan-1-one (3ia):

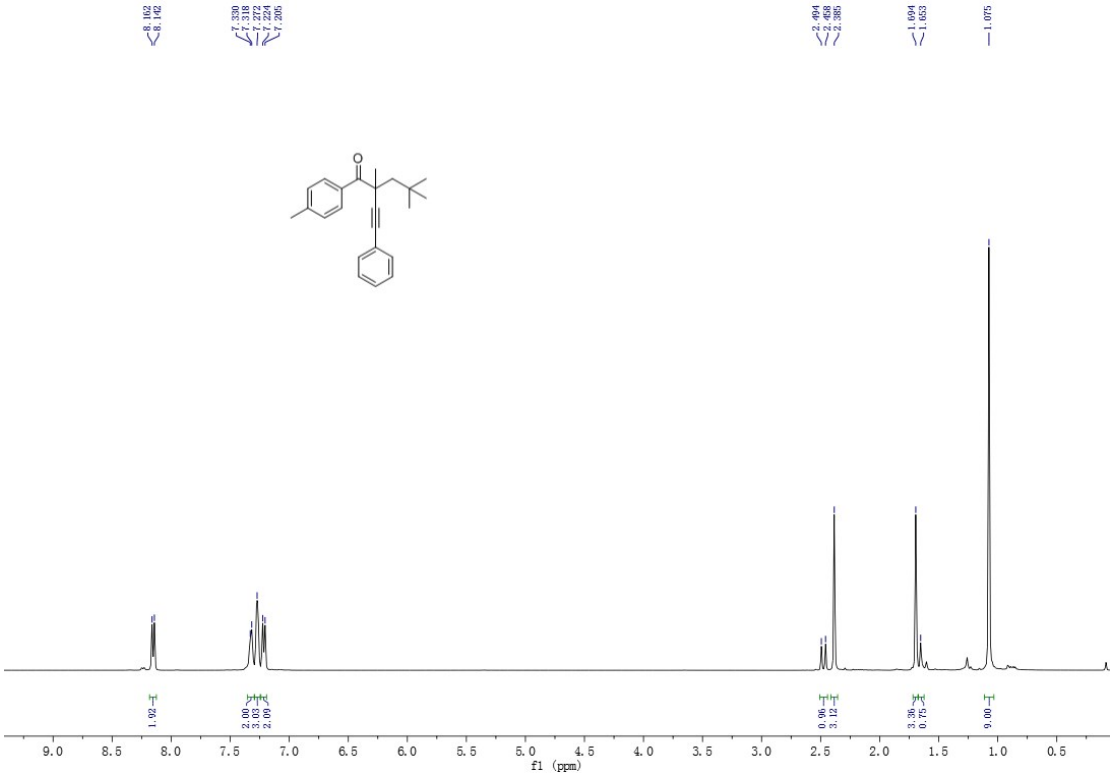


^{1}H-NMR (400 MHz, $CDCl_3$)

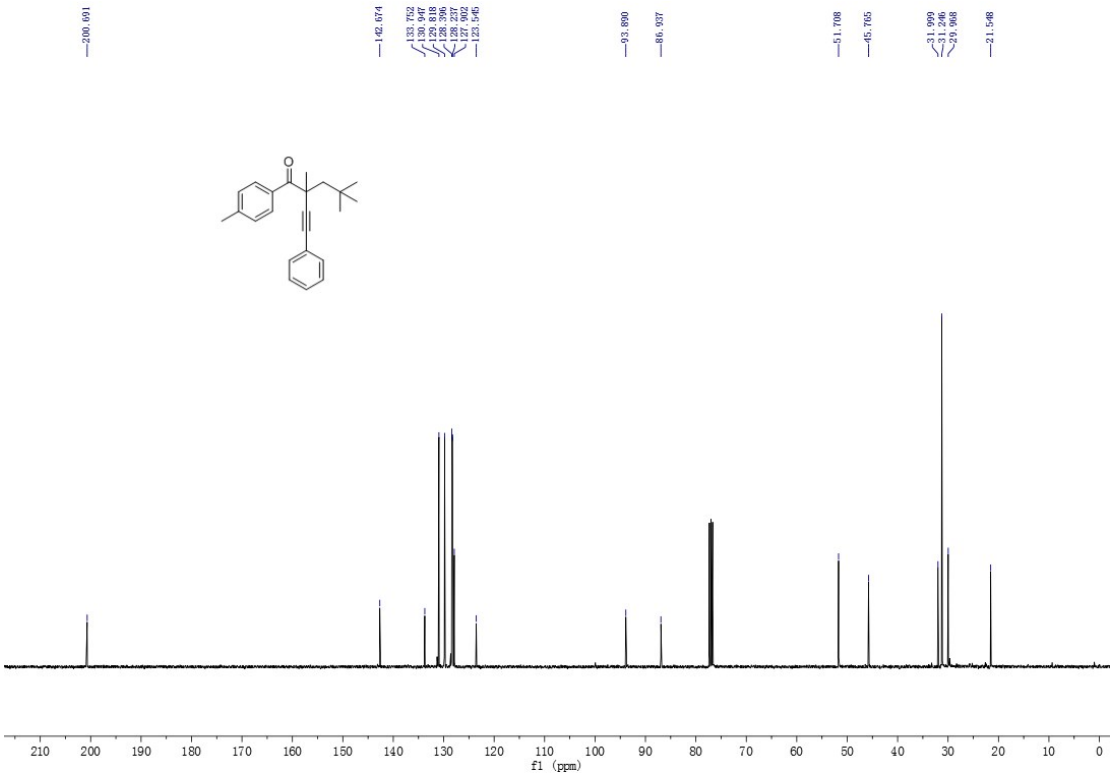


^{13}C-NMR (101 MHz, $CDCl_3$)

2,4,4-trimethyl-2-(phenylethynyl)-1-(p-tolyl)pentan-1-one (3ka):

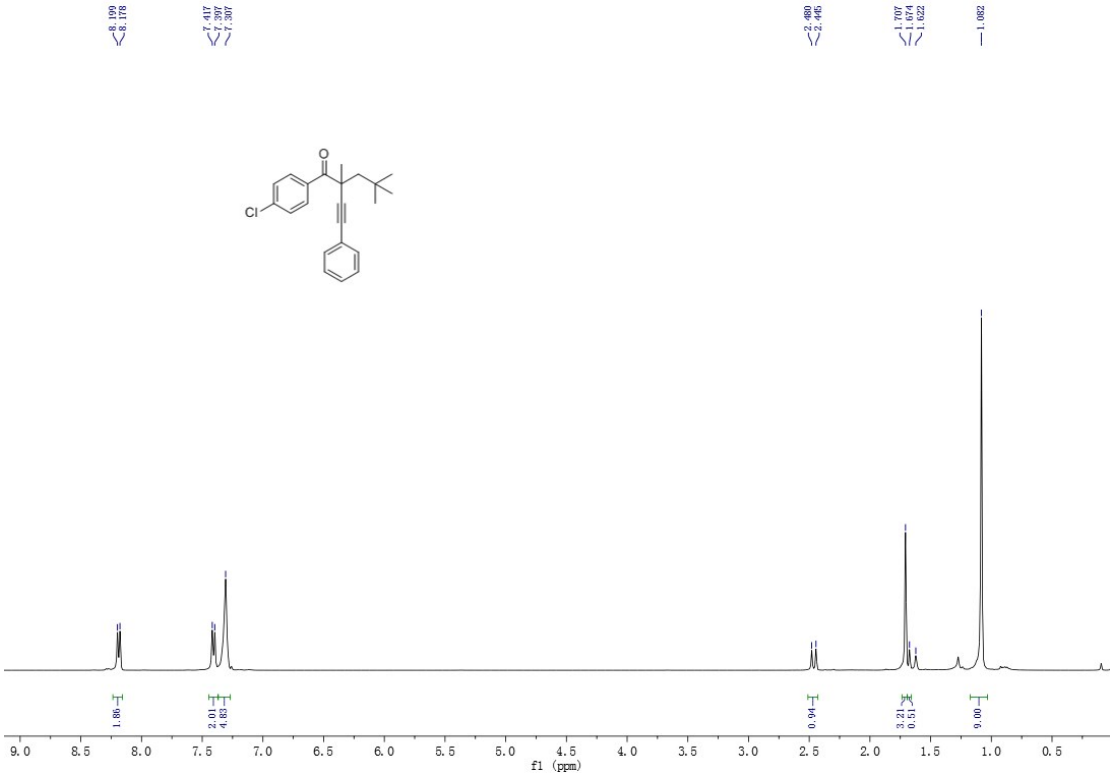


^{1}H-NMR (400 MHz, $CDCl_3$)

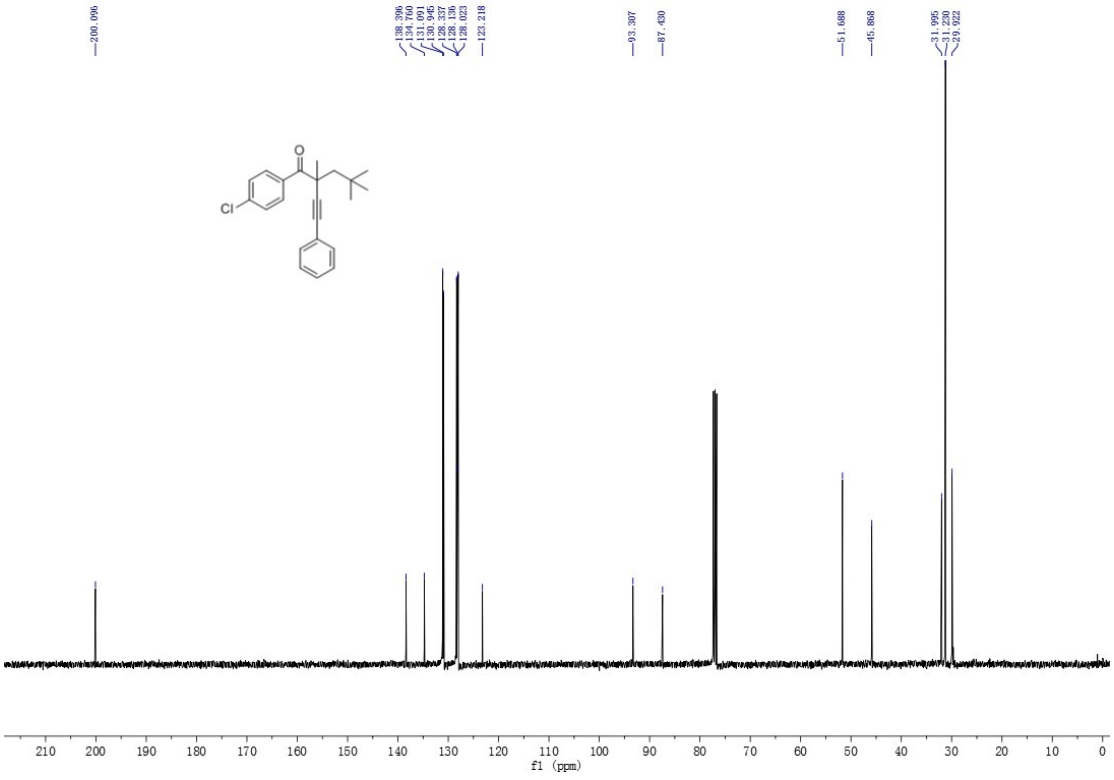


^{13}C-NMR (101 MHz, $CDCl_3$)

1-(4-chlorophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3la):

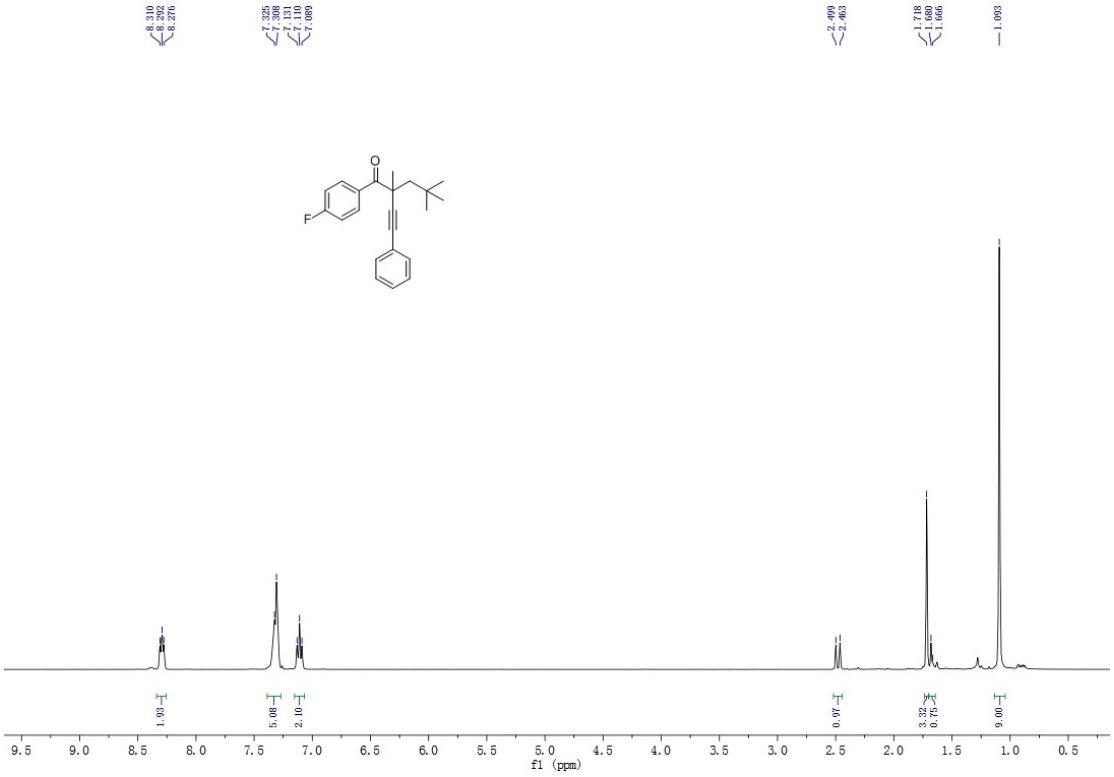


^{1}H-NMR (400 MHz, $CDCl_3$)

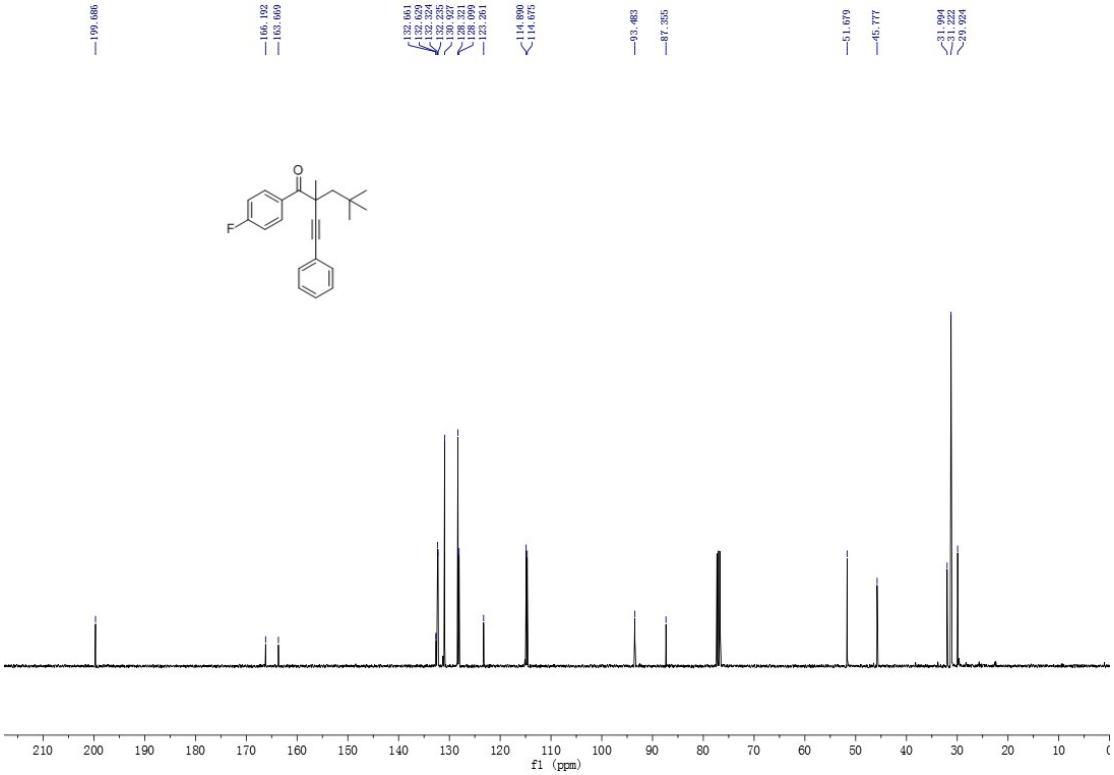


^{13}C-NMR (101 MHz, $CDCl_3$)

1-(4-fluorophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3ma):

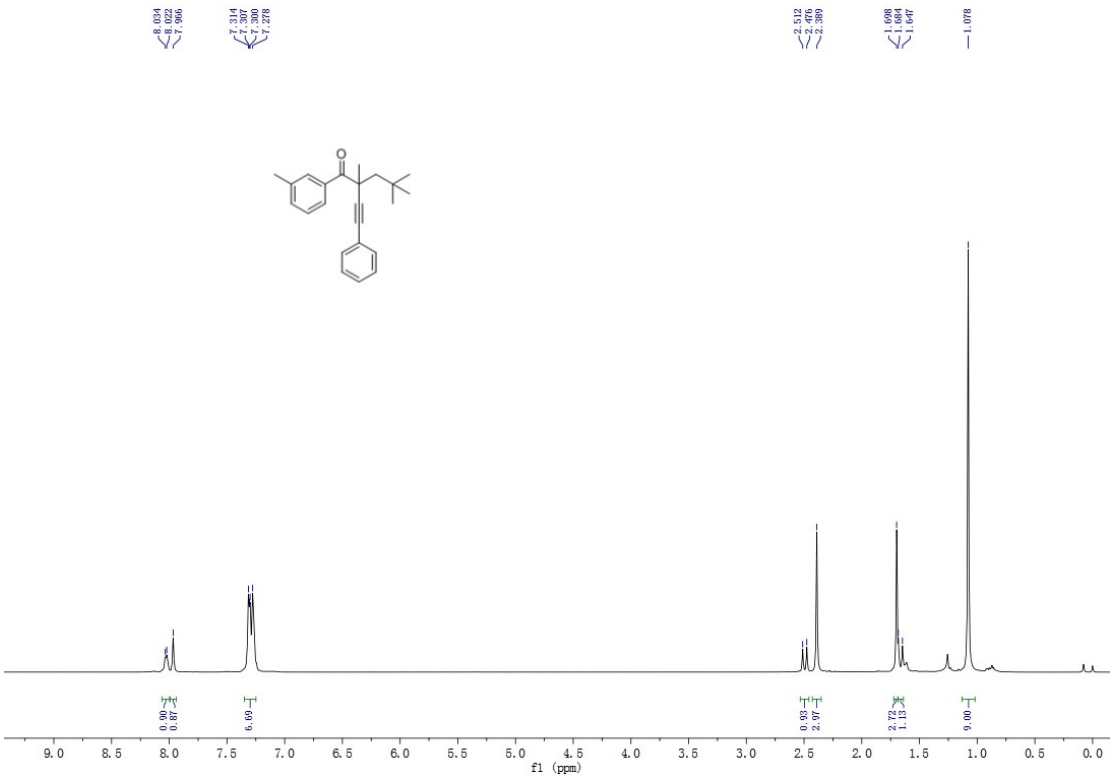


^{1}H-NMR (400 MHz, $CDCl_3$)

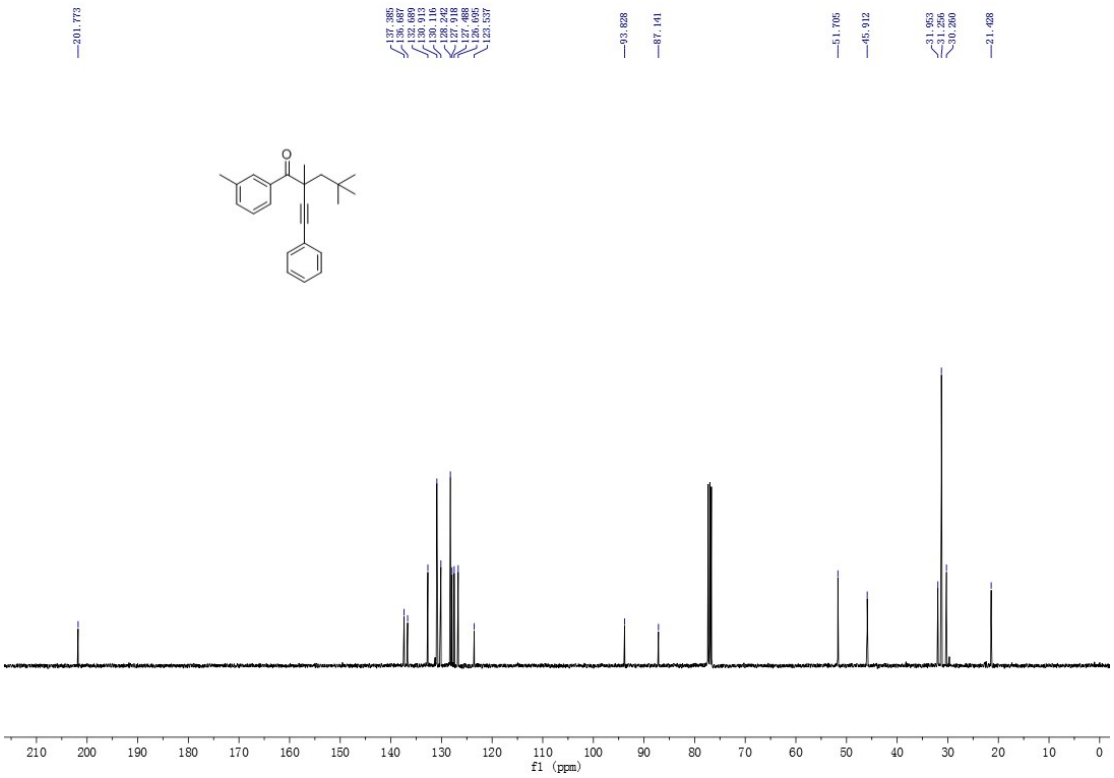


^{13}C-NMR (101 MHz, $CDCl_3$)

2,4,4-trimethyl-2-(phenylethynyl)-1-(m-tolyl)pentan-1-one (3na):

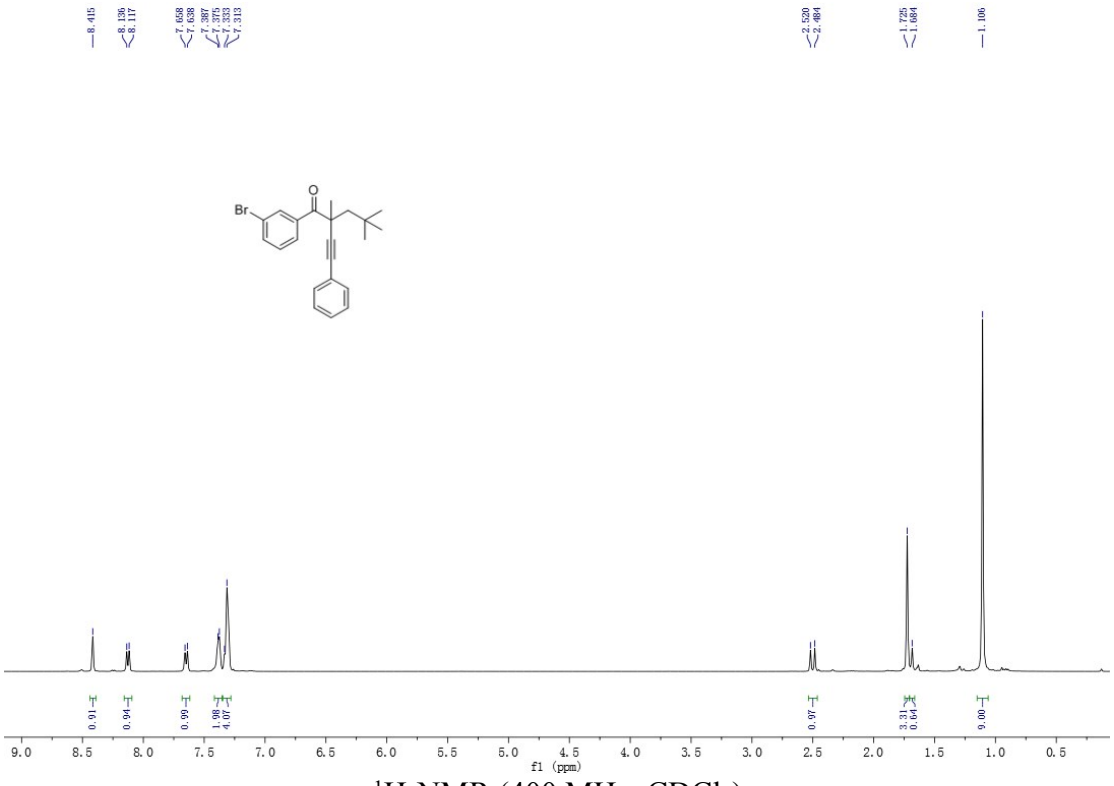


^{1}H-NMR (400 MHz, $CDCl_3$)

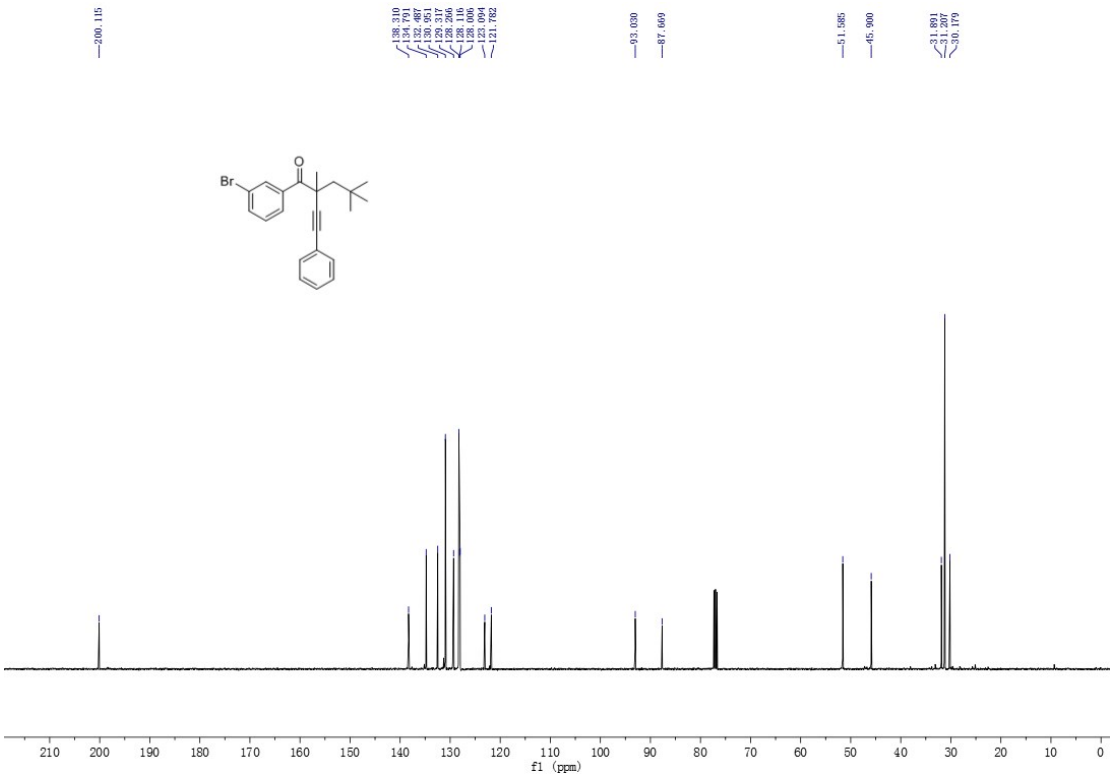


^{13}C-NMR (101 MHz, $CDCl_3$)

1-(3-bromophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3oa):

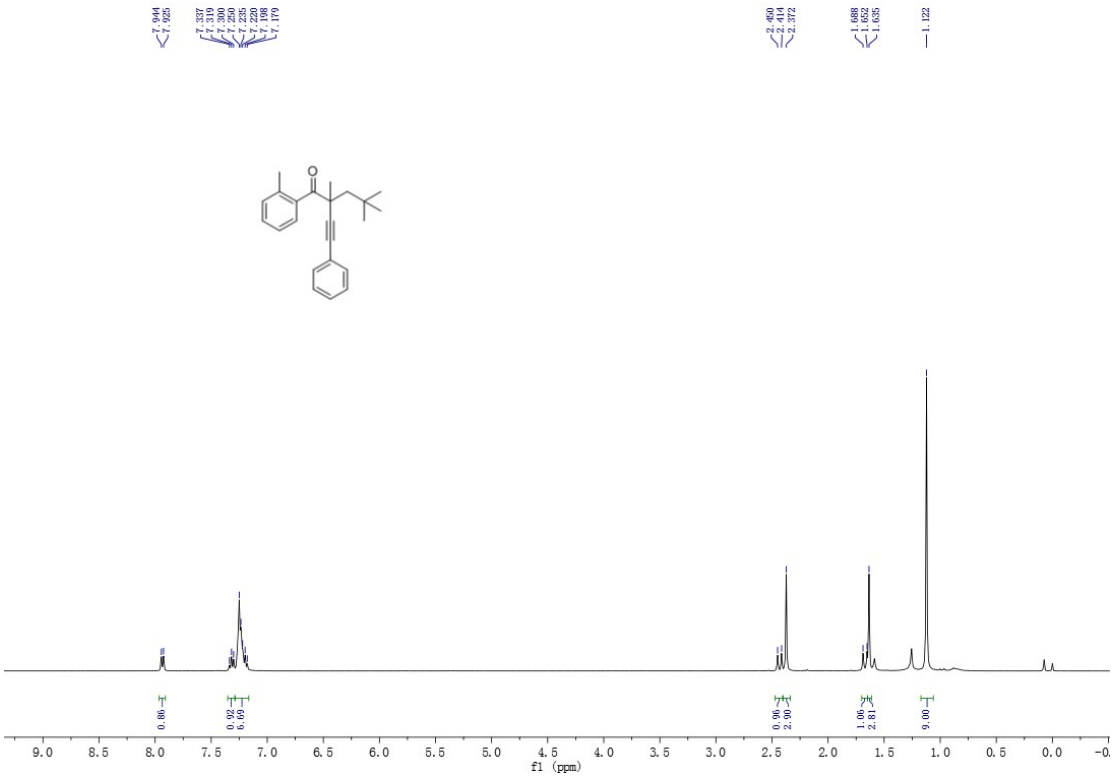


^{1}H-NMR (400 MHz, $CDCl_3$)

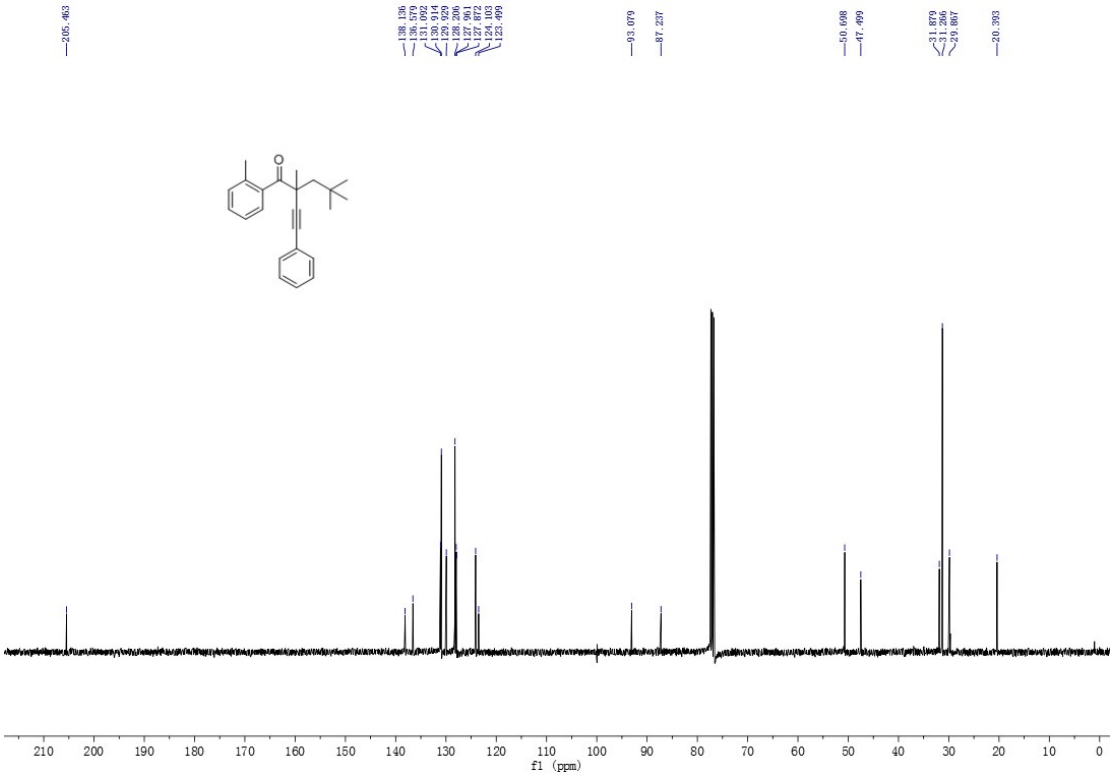


^{13}C-NMR (101 MHz, $CDCl_3$)

2,4,4-trimethyl-2-(phenylethynyl)-1-(o-tolyl)pentan-1-one (3pa):

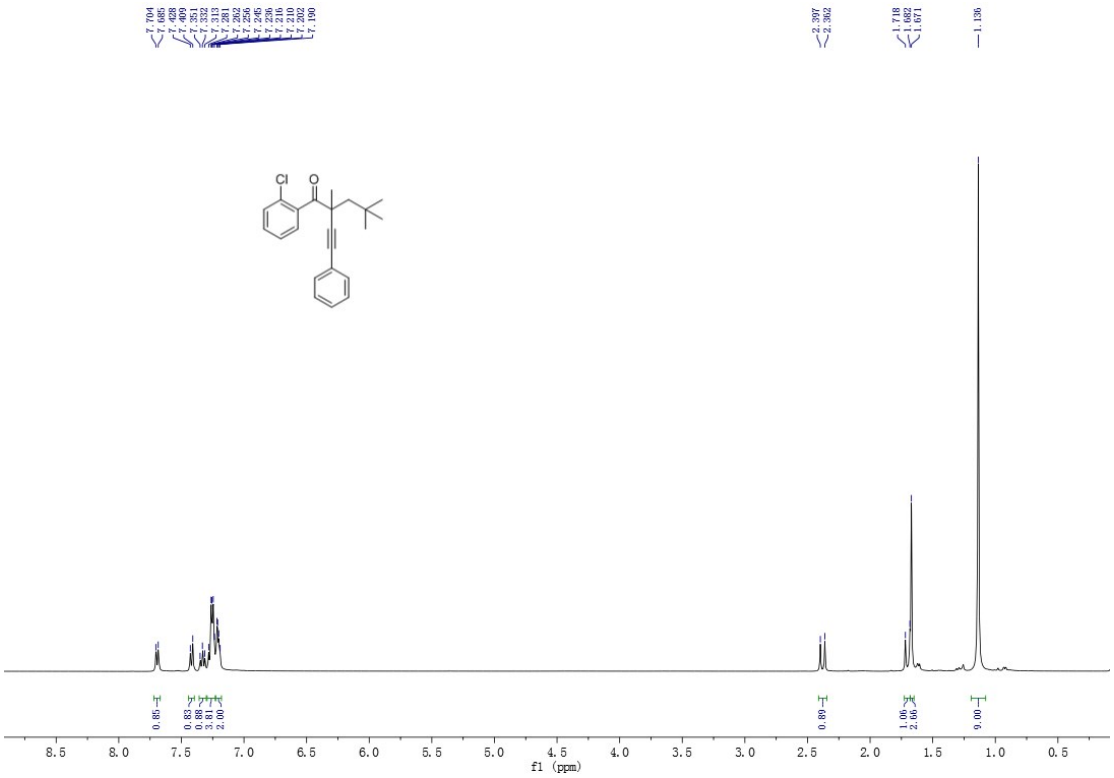


^{1}H-NMR (400 MHz, $CDCl_3$)

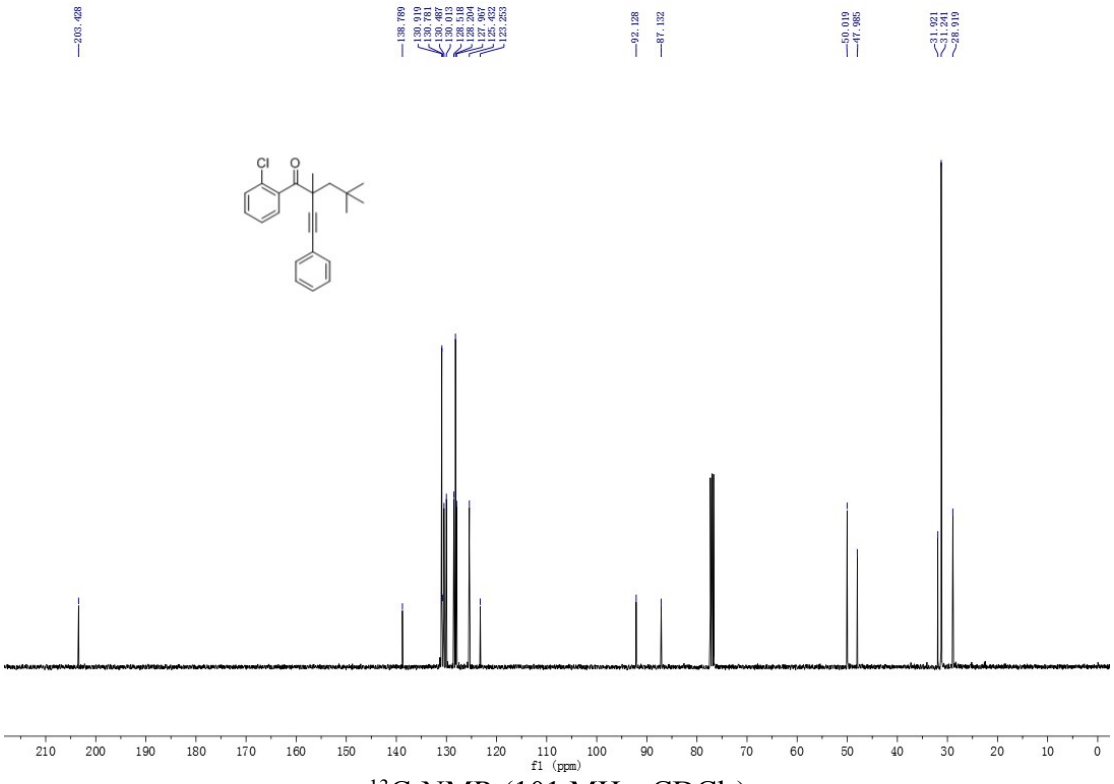


^{13}C-NMR (101 MHz, $CDCl_3$)

1-(2-chlorophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3qa):

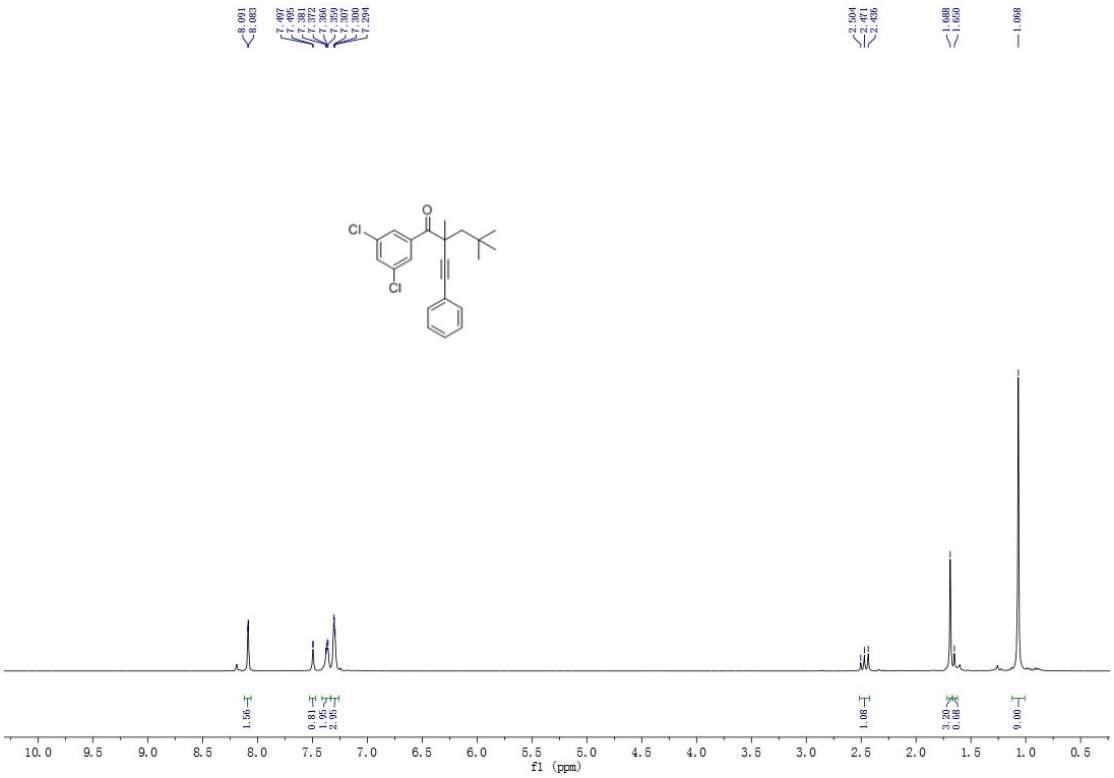


^{1}H-NMR (400 MHz, $CDCl_3$)

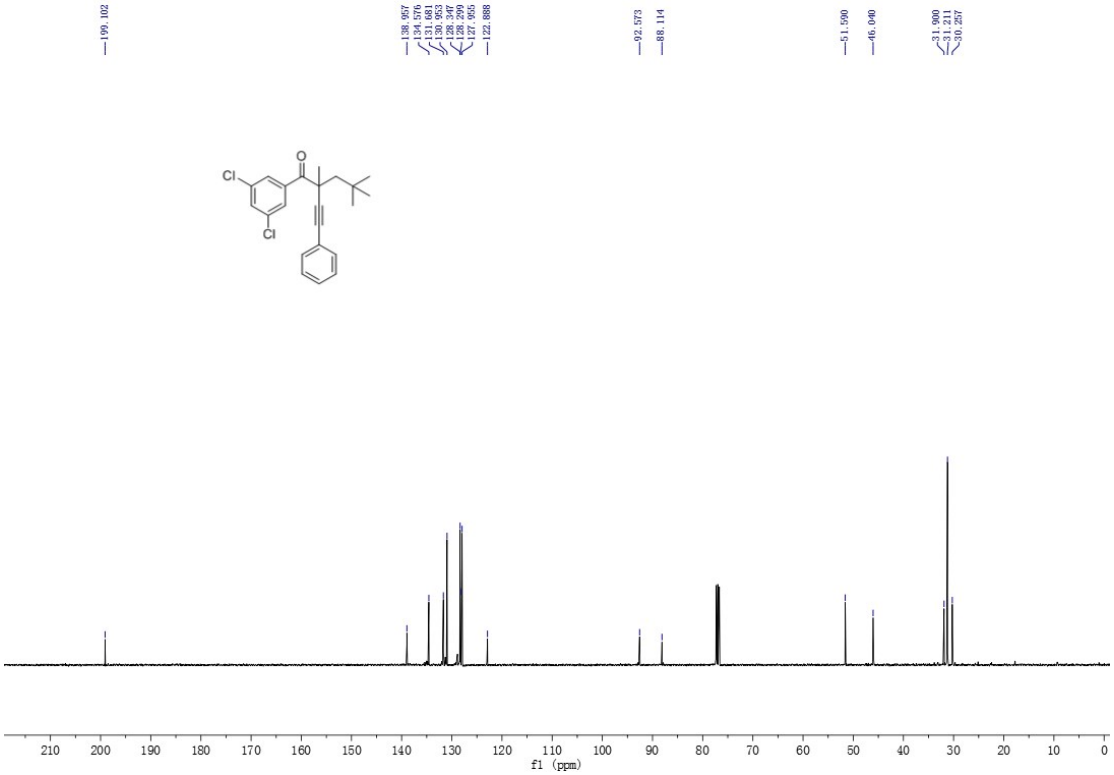


^{13}C-NMR (101 MHz, $CDCl_3$)

1-(3,5-dichlorophenyl)-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3ra):

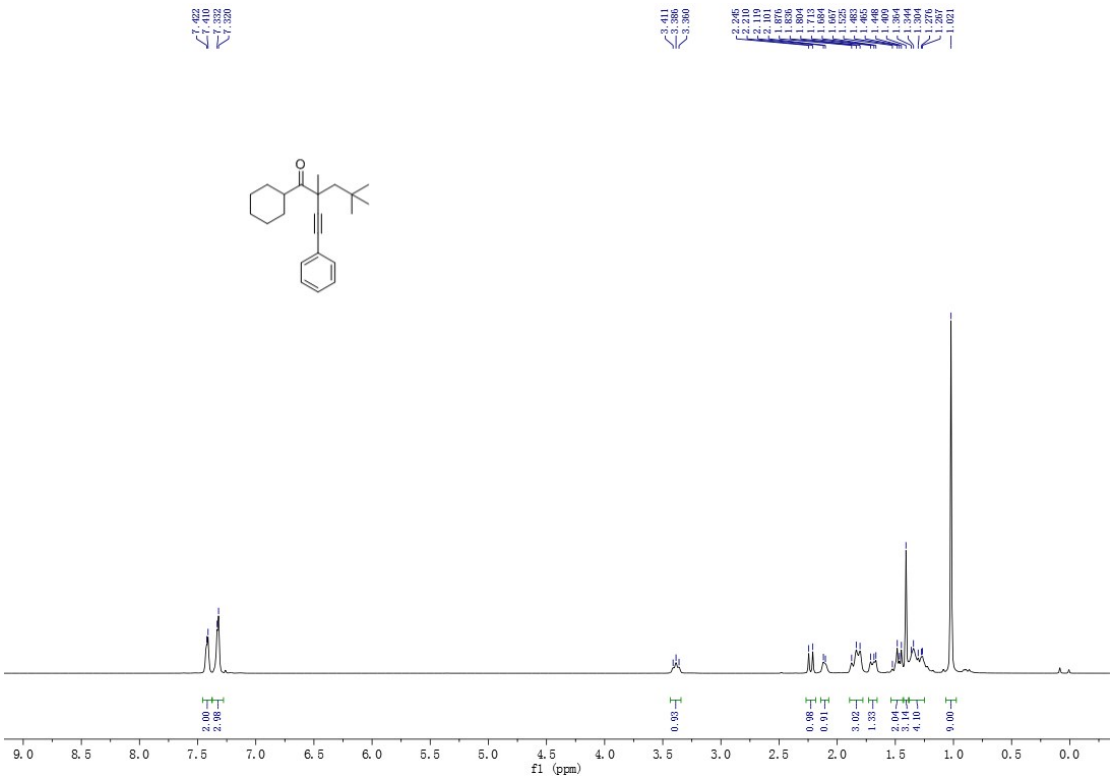


^{1}H-NMR (400 MHz, $CDCl_3$)

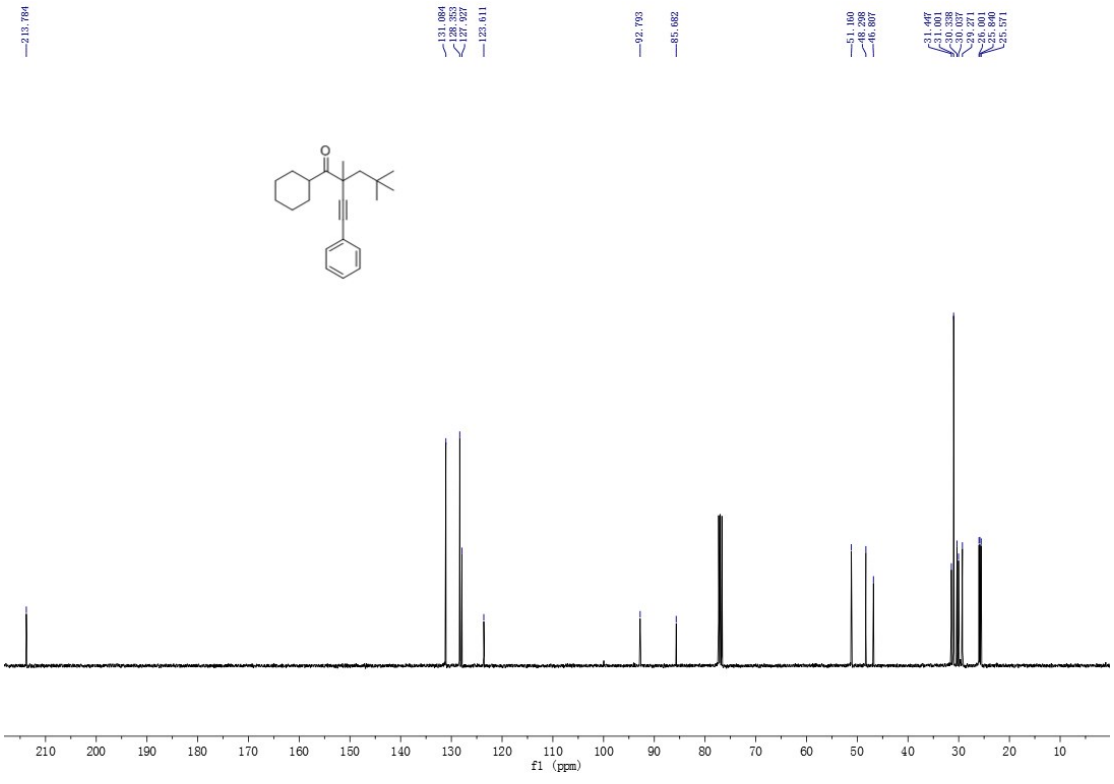


^{13}C-NMR (101 MHz, $CDCl_3$)

1-cyclohexyl-2,4,4-trimethyl-2-(phenylethynyl)pentan-1-one (3sa):

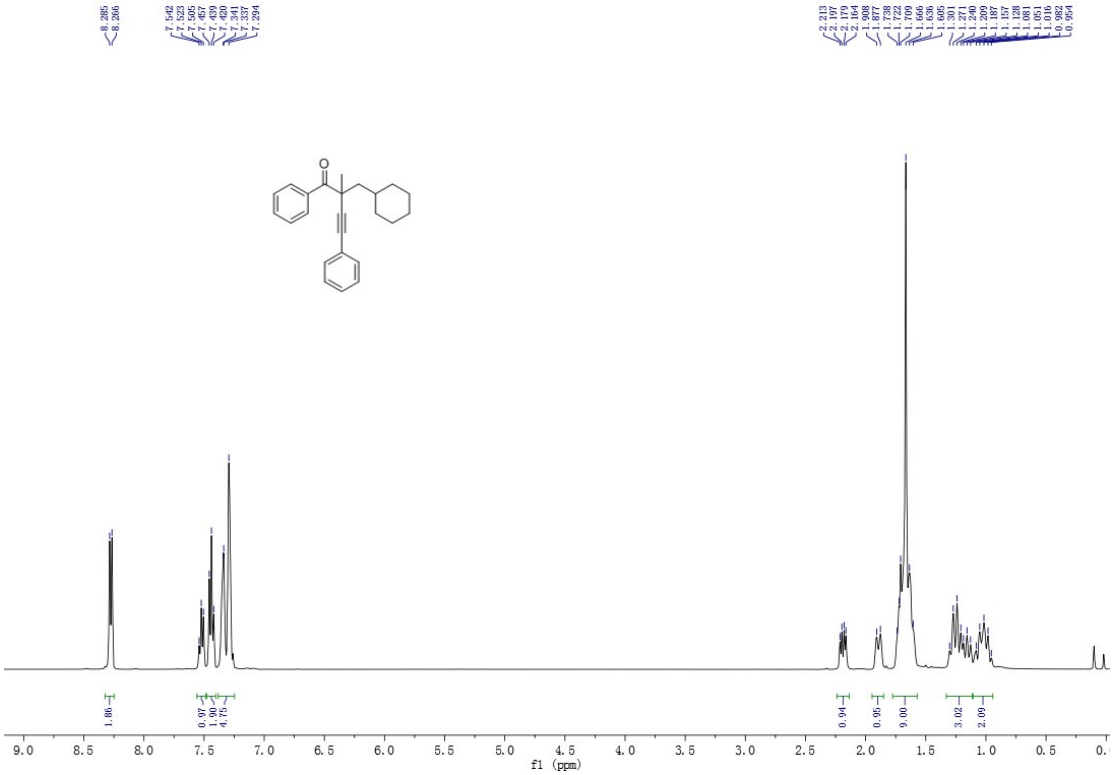


^{1}H-NMR (400 MHz, $CDCl_3$)

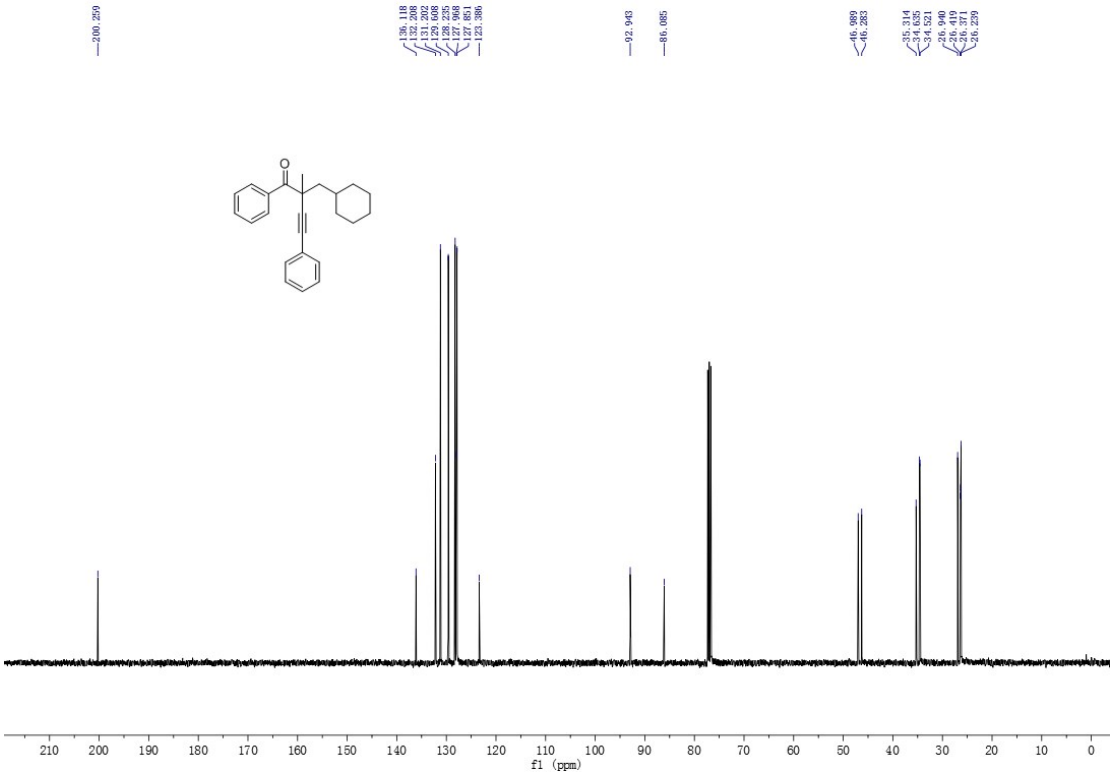


^{13}C-NMR (101 MHz, $CDCl_3$)

2-(cyclohexylmethyl)-2-methyl-1,4-diphenylbut-3-yn-1-one (3ab):

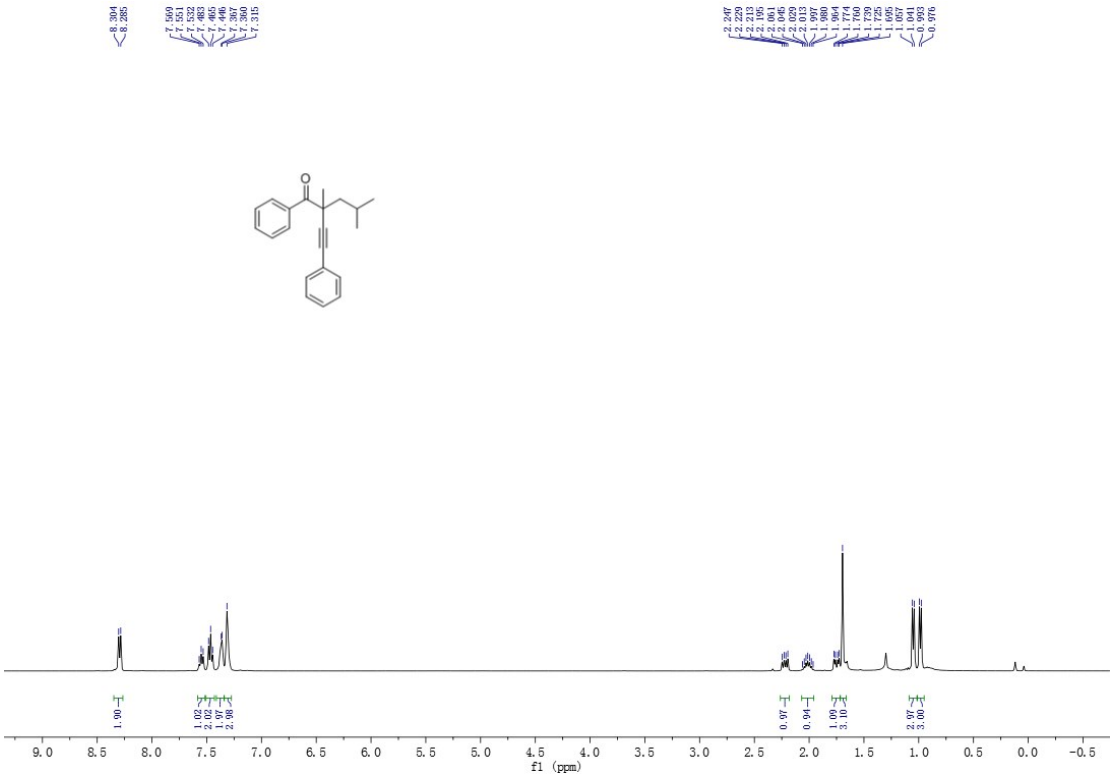


H-NMR (400 MHz, $CDCl_3$)

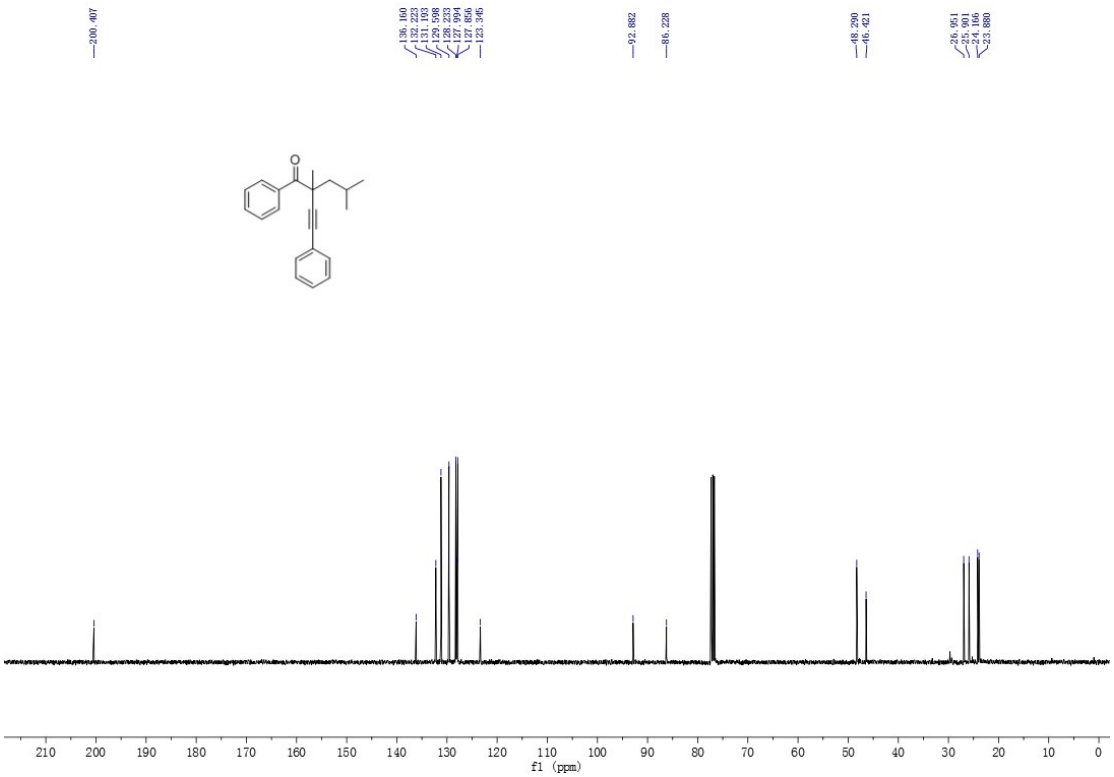


^{13}C-NMR (101 MHz, $CDCl_3$)

2,4-dimethyl-1-phenyl-2-(phenylethynyl)pentan-1-one (3ac):

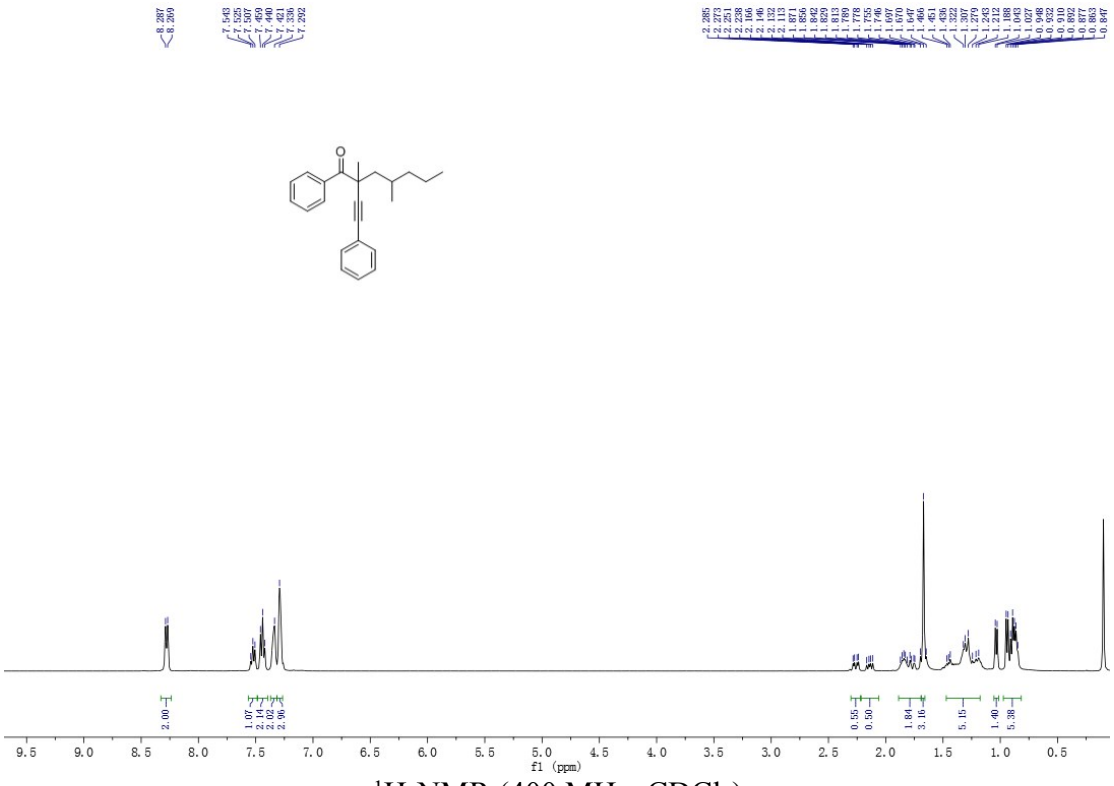


^{1}H-NMR (400 MHz, $CDCl_3$)

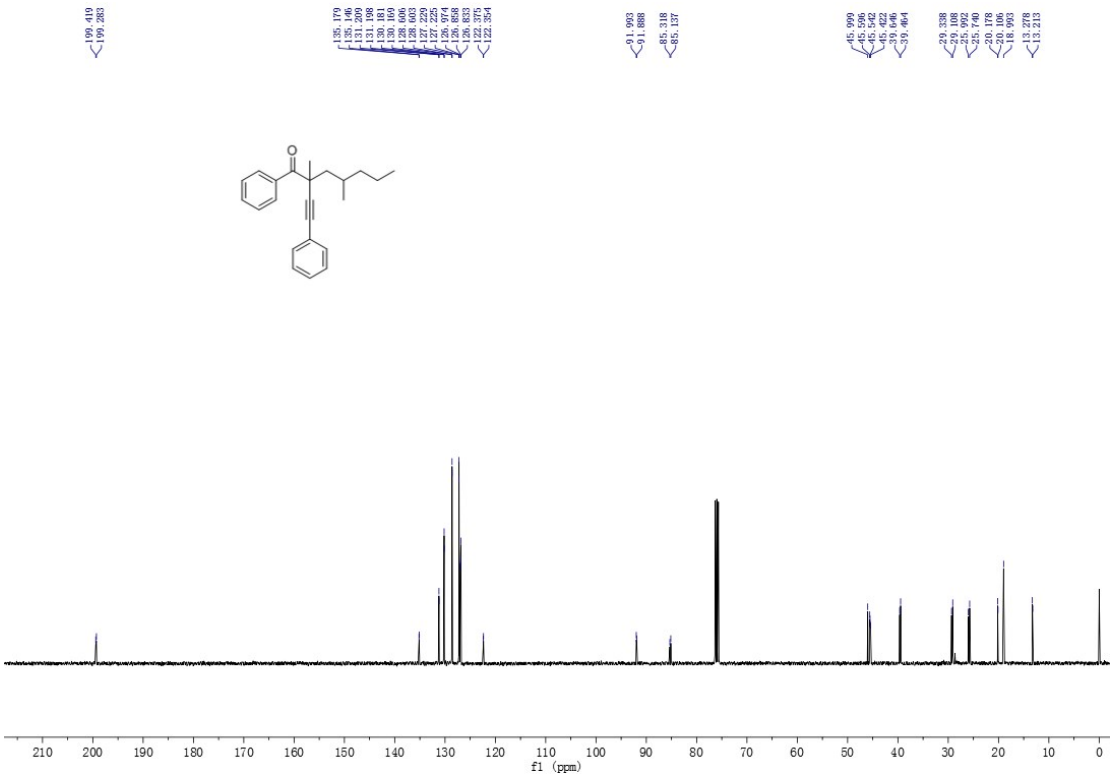


^{13}C-NMR (101 MHz, $CDCl_3$)

2,4-dimethyl-1-phenyl-2-(phenylethynyl)heptan-1-one (3ad):

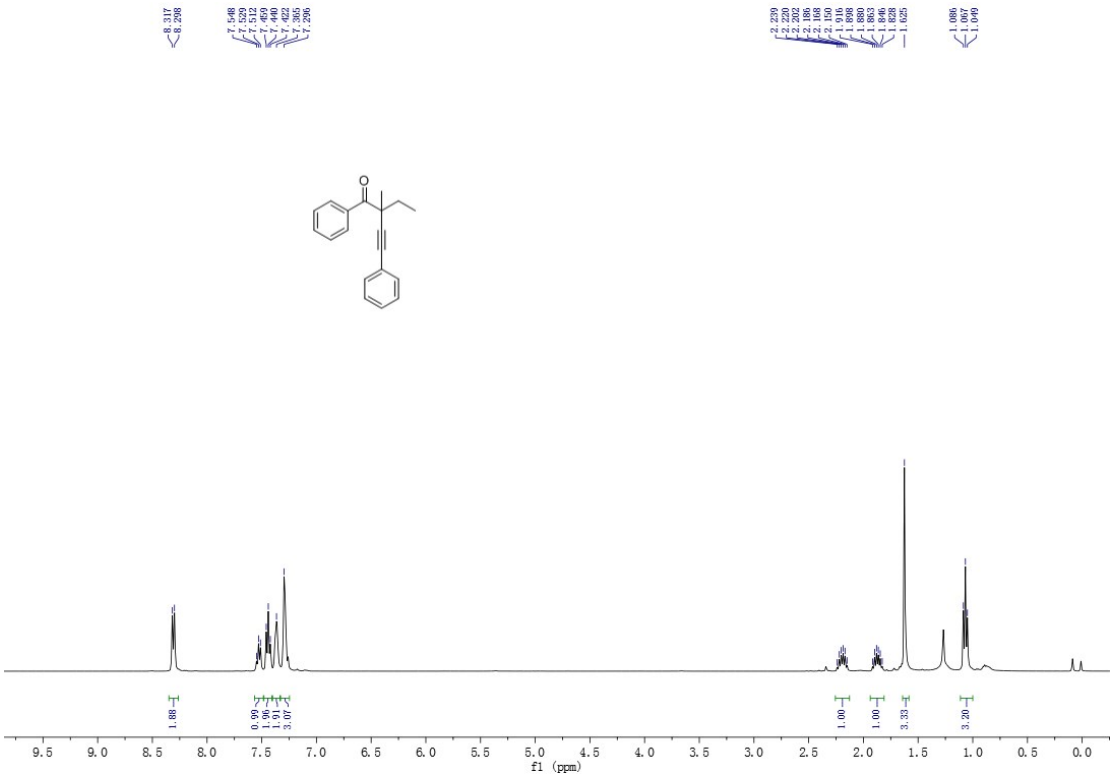


^{1}H-NMR (400 MHz, $CDCl_3$)

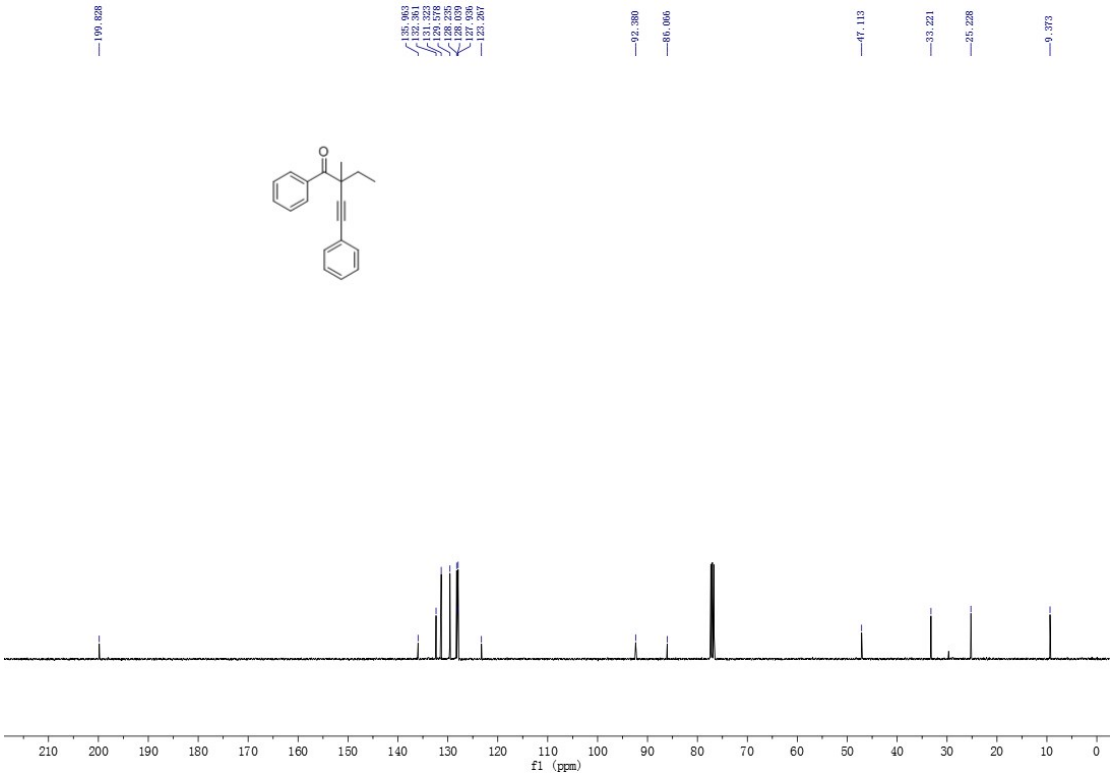


^{13}C-NMR (101 MHz, $CDCl_3$)

2-ethyl-2-methyl-1,4-diphenylbut-3-yn-1-one (3ae):

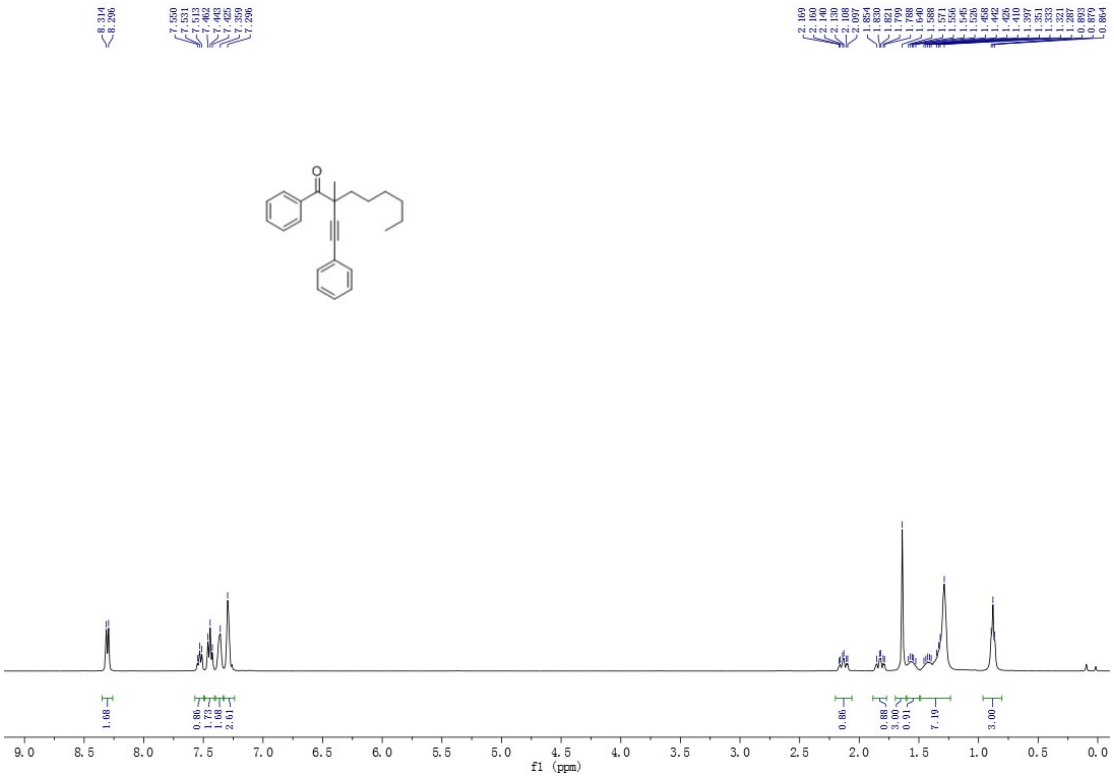


^{1}H-NMR (400 MHz, $CDCl_3$)

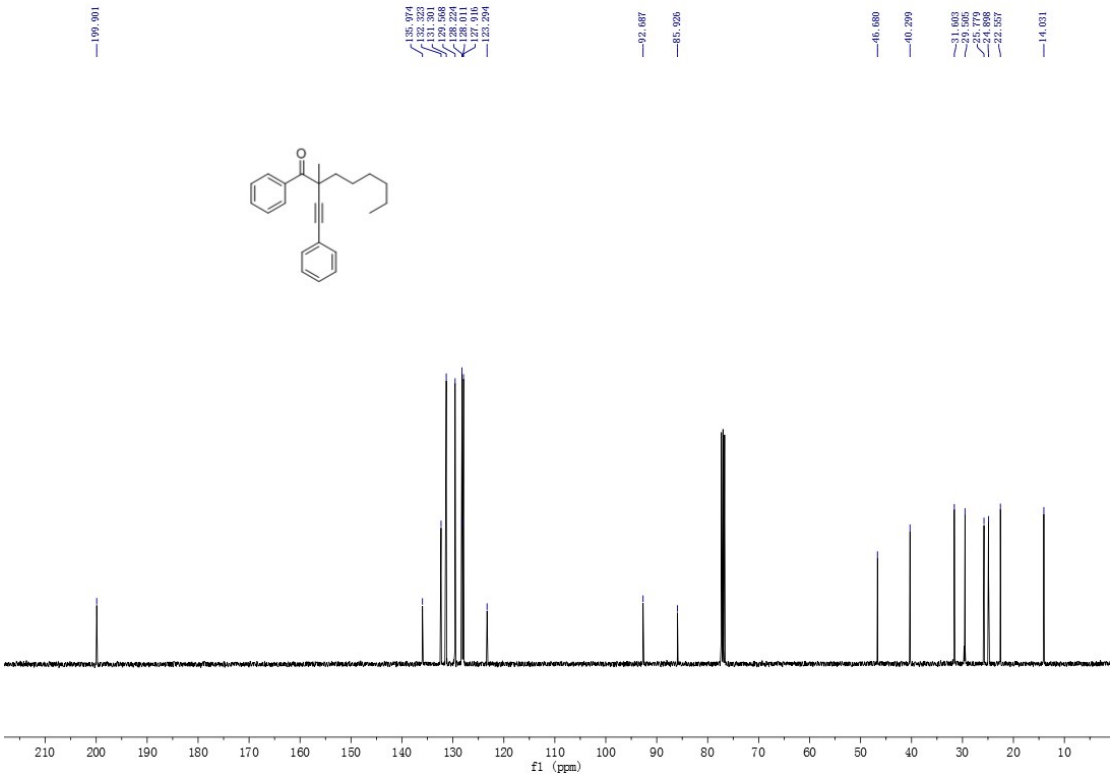


^{13}C-NMR (101 MHz, $CDCl_3$)

2-methyl-1-phenyl-2-(phenylethynyl)octan-1-one (3af):



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)

(D) References

[1] Q. Zhao, X. S. Ji, Y. Y. Gao, W. J. Hao, K. Y. Zhang, S. J. Tu and B. Jiang, Merging " Anti-Baldwin" 3- Exo-Dig Cyclization with 1,2-Alkynyl Migration for Radical Alkylalkynylation of Unactivated Olefins, *Org. Lett.*, 2018, **20**, 3596-3600.

[2] M. Li, X. Y. Zhu, Y. F. Qiu, Y. P. Han, Y. Xia, C. T. Wang, X. S. Li, W. X. Wei and Y. M. Liang, Metal - Free Promoted CF_2/CF_3 -Difunctionalization of Unactivated Alkenes, *Adv. Synth. Catal.,* 2019, **361**, 2945-2950.