Supplementary Information

Dihydroquinazolinones as Photocatalyst-Free Carbamoyl Radical Precursors for Ynamide Formation

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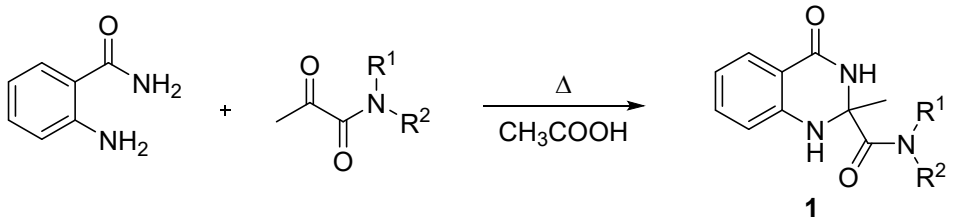
General Information

Commercially available chemicals were obtained from commercial suppliers and were used as received. All reactions were performed in a nitrogen-filled dry box, unless otherwise stated. Reaction temperature was reported corresponding to the oil bath temperature. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed using 40-63 μm silica gel (Si 60, Merck). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 MHz or 500 MHz NMR spectrometer in the solvents indicated. Chemical shifts (δ) are given in ppm relative to TMS. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo G2-S QTof mass spectrometer. The light employed in this work was bought from GeAo Chemical: model H106062, 40 W blue LEDs, λ = 450 ~ 465 nm. All The photo-reactions were carried out in a high-borosilicate glass tube (10 mL, 16×100 mm, purchased from Taobao: https://shop186071261.taobao.com/?spm=pc_detail.30350276.shop_block.dshopinfo.1c5d7dd6jFTvYw), with a light-to-vessel distance of approximately 1.5 cm.

Synthesis of Starting Materials
All starting materials were prepared according to the literature: **1a-1w** and **4a-4o**[1,2], **2a-2m**[3].



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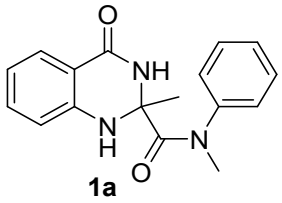
General Procedure: To a stirred solution of the appropriate anthranilamide (1 eq) in glacial AcOH was added α-keto carboxamide (1.2 eq) and the mixture was heated at reflux for 2 h. The crude mixture was then concentrated in vacuo. Et_2O was then added to the resultant residue and the mixture was stirred for 30 min. The formed precipitate was then collected by decantation and the residue was then washed with additional Et_2O and dried under vacuum to afford corresponding dihydroquinazolinone **1**.

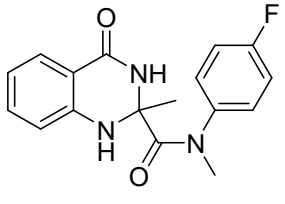
N,2-dimethyl-4-oxo-N-phenyl-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1a)



1a

White solid, 3.52 g, 90% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.04 (s, 1H), 7.80 – 7.77 (m, 2H), 7.49 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.24 – 7.20 (m, 1H), 7.02 (s, 1H), 6.67 – 6.63 (m, 1H), 6.52 (dd, *J* = 8.5, 1.0 Hz, 1H), 3.19 (s, 3H), 1.57 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 171.8, 162.1, 148.3, 145.9, 133.4, 133.3, 128.2, 127.18, 118.7, 117.3, 114.6, 113.7, 109.4, 71.7, 40.1, 26.8. **HRMS (ESI)** m/z calcd. for $C_{18}H_{17}N_3O_4Na$ $[M+Na^+]^+$ 362.1117, found 362.1121.

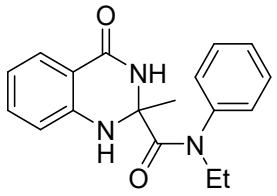
N-(4-fluorophenyl)-N,2-dimethyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1b)



1b

White solid, 1.43 g, 91% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.88 (s, 1H), 7.51 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.15 (d, *J* = 7.0 Hz, 4H), 6.91 (s, 1H), 6.65 (td, *J* = 7.5, 1.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 3.13 (s, 3H), 1.55 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 171.9, 162.2, 160.7 (d, *J* = 242.0 Hz), 146.2, 140.4, 133.2, 129.3 (d, *J* = 8.8 Hz), 127.2, 117.2, 116.0 (d, *J* = 22.6 Hz), 114.6, 113.9, 71.6, 40.8, 26.7. **HRMS (ESI)** m/z calcd. for $C_{17}H_{16}FN_3O_2Na$ $[M+Na^+]^+$ 336.1124, found 336.1126.

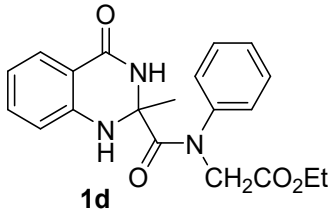
N-ethyl-2-methyl-4-oxo-N-phenyl-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1c)



1c

White solid, 1.36 g, 88% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.85 – 7.65 (m, 1H), 7.52 – 7.47 (m, 1H), 7.37 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 7.22 – 7.18 (m, 1H), 7.11 – 7.02 (m, 2H), 6.74 (s, 1H), 6.66 – 6.61 (m, 1H), 6.53 – 6.49 (d, J = 8.2 Hz, 1H), 3.61 – 3.51 (m, 2H), 1.55 (s, 3H), 0.92 (t, J = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 171.3, 162.2, 146.0, 141.9, 133.0, 129.0, 128.2, 127.2, 127.1, 117.1, 114.6, 113.9, 71.6, 46.8, 27.0, 12.6. **HRMS (ESI)** m/z calcd. for $C_{18}H_{19}N_3O_2Na$ $[M+Na^+]^+$ 332.1375, found 332.1379.

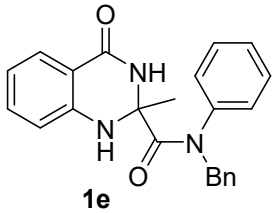
ethyl N-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-N-phenylglycinate (1d)



1d

White solid, 1.34 g, 73% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.70 – 7.50 (m, 2H), 7.41 – 7.36 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.20 (m, 3H), 6.70 – 6.59 (m, 2H), 6.50 (d, *J* = 8.0 Hz, 1H), 4.25 – 4.15 (m, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 1.56 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 172.5, 168.6, 162.4, 145.9, 142.8, 132.9, 129.2, 127.9, 127.7, 127.2, 117.3, 114.8, 114.2, 71.4, 60.5, 54.3, 26.5, 13.9. **HRMS (ESI)** m/z calcd. for $C_{20}H_{21}N_3O_4Na$ $[M+Na^+]^+$ 390.1430, found 390.1434.

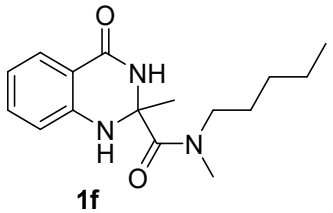
N-benzyl-2-methyl-4-oxo-N-phenyl-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1e)



1e

White solid, 1.58 g, 85% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.70 (s, 1H), 7.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.27 – 7.20 (m, 4H), 7.17 – 7.14 (m, 3H), 6.95 – 6.91 (m, 4H), 6.72 – 6.67 (m, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.79 – 4.69 (m, 2H), 1.59 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 172.4, 162.4, 146.0, 142.1, 137.1, 133.0, 129.0, 128.1, 127.9, 127.7, 127.4, 127.1, 127.0, 117.4, 114.8, 114.3, 71.9, 55.6, 26.9. **HRMS (ESI)** m/z calcd. for $C_{23}H_{21}N_3O_2Na$ $[M+Na^+]^+$ 394.1531, found 394.1531.

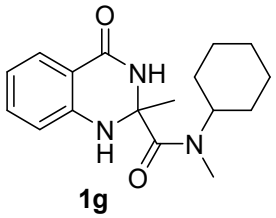
N,2-dimethyl-4-oxo-N-pentyl-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1f)



1f

White solid, 1.07 g, 74% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.42 (s, 1H), 7.55 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.20 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.68 – 6.64 (m, 1H), 3.30 – 2.65 (m, 5H), 1.54 (s, 3H), 1.47 – 1.29 (m, 2H), 1.25 – 1.13 (m, 2H), 1.10 – 0.95 (m, 2H), 0.78 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 171.4, 163.3, 147.5, 133.7, 127.7, 117.7, 115.1, 71.8, 49.9, 36.4, 28.6, 26.5, 25.1, 22.3, 14.3. **HRMS (ESI)** m/z calcd. for $C_{16}H_{24}N_3O_2$ $[M+H^+]^+$ 290.1869, found 290.1874.

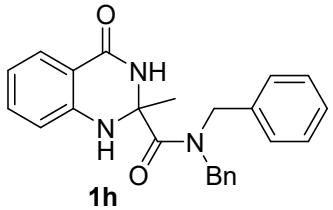
N-cyclohexyl-N,2-dimethyl-4- oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1g)



1g

White solid, 1.08 g, 72% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.43 (s, 1H), 7.56 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.21 (m, 2H), 6.74 – 6.62 (m, 2H), 4.29 – 4.06 (m, 1H), 2.97 (s, 1H), 2.64 (s, 1H), 1.72 – 1.35 (m, 10H), 1.26 – 1.17 (m, 1H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 170.8, 162.5, 147.1, 133.9, 127.7, 118.1, 114.9, 72.0, 56.5, 30.4, 29.4, 27.1, 25.6, 25.3, 19.0. **HRMS (ESI)** m/z calcd. for $C_{17}H_{23}N_3O_2Na$ $[M+Na^+]^+$ 324.1688, found 324.1691.

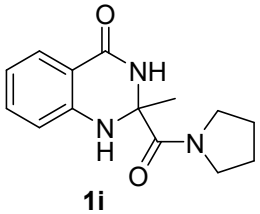
N,N-dibenzyl-2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1h)



1h

White solid, 1.50 g, 78% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.64 (s, 1H), 7.65 – 7.59 (m, 1H), 7.43 (s, 1H), 7.37 – 7.10 (m, 9H), 6.92 (s, 2H), 6.76 – 6.68 (m, 2H), 4.97 (d, *J* = 16.5 Hz, 1H), 4.71 (d, *J* = 16.5 Hz, 1H), 4.46 – 4.36 (m, 1H), 4.24 – 4.14 (m, 1H), 1.69 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 172.1, 163.2, 146.8, 136.8, 133.3, 128.5, 128.4, 127.3, 127.1, 117.7, 115.1, 114.6, 71.8, 50.3, 48.5, 25.3. **HRMS (ESI)** m/z calcd. for $C_{24}H_{23}N_3O_2Na$ $[M+Na^+]^+$ 408.1688, found 408.1689.

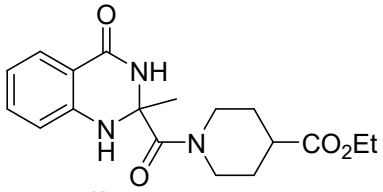
2-methyl-2-(pyrrolidine-1-carbonyl)-2,3-dihydroquinazolin-4(1H)-one (1i)



1i

White solid, 0.82 g, 63% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.45 (s, 1H), 7.56 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.27 – 7.22 (m, 2H), 6.77 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.67 (td, *J* = 7.5, 1.0 Hz, 1H), 3.60 (t, *J* = 7.0 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.68 – 1.61 (m, 2H), 1.51 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 170.6, 163.0, 147.3, 133.4, 127.4, 117.4, 114.7, 114.3, 71.0, 48.0, 47.1, 26.7, 24.5, 22.8. **HRMS (ESI)** m/z calcd. for $C_{14}H_{17}N_3O_2Na$ $[M+Na^+]^+$ 282.1218, found 282.1218.

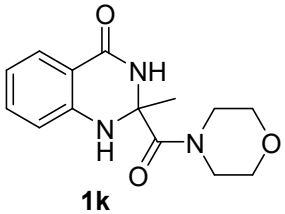
ethyl 1-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)piperidine-4-carboxylate (1j)



1j

White solid, 1.31 g, 76% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.49 (d, *J* = 1.5 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.27 – 7.22 (m, 2H), 6.72 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.67 (td, *J* = 7.5, 1.0 Hz, 1H), 4.32 – 4.24 (m, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 3.02 – 2.85 (m, 2H), 2.62 – 2.55 (m, 1H), 1.82 – 1.75 (m, 2H), 1.53 (s, 3H), 1.50 – 1.39 (m, 2H), 1.16 (t, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 173.9, 169.0, 162.7, 146.8, 133.4, 127.3, 117.2, 114.7, 113.9, 71.4, 60.0, 40.1, 28.0, 27.9, 25.6, 14.1. **HRMS (ESI)** m/z calcd. for $C_{18}H_{23}N_3O_4Na$ $[M+Na^+]^+$ 368.1586, found 368.1590.

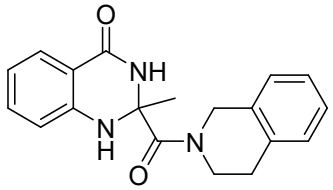
2-methyl-2-(morpholine-4-carbonyl)-2,3-dihydroquinazolin-4(1H)-one (1k)



1k

White solid, 1.07 g, 78% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.49 (s, 1H), 7.58 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.73 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.70 – 6.66 (m, 1H), 3.66 – 3.50 (m, 8H), 1.55 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 169.4, 162.8, 146.8, 133.5, 127.3, 117.5, 114.8, 114.1, 71.4, 66.1, 45.5, 25.3. **HRMS (ESI)** m/z calcd. for $C_{14}H_{17}N_3O_3Na$ $[M+Na^+]^+$ 298.1168, found 298.1172.

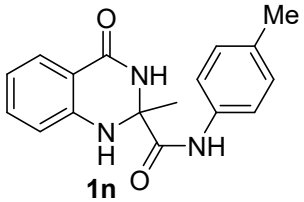
2-methyl-2-(1,2,3,4-tetrahydroisoquinoline-2-carbonyl)-2,3-dihydroquinazolin-4(1H)-one (1l)



1l

White solid, 1.25 g, 78% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.60 (d, *J* = 1.0 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.35 (s, 1H), 7.27 – 7.22 (m, 1H), 7.16 – 7.09 (m, 4H), 6.77 – 6.73 (m, 1H), 6.69 – 6.64 (m, 1H), 4.85 – 4.50 (m, 2H), 4.04 – 3.68 (m, 2H), 2.87 – 2.75 (m, 2H), 1.59 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 170.1, 162.9, 147.0, 134.4, 133.5, 128.6, 127.3, 126.4, 126.3, 126.1, 117.4, 114.8, 114.0, 71.5, 46.4, 43.0, 28.3, 25.4. **HRMS (ESI)** m/z calcd. for $C_{19}H_{20}N_3O_2$ $[M+H^+]^+$ 322.1556, found 322.1560.

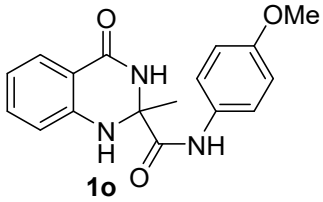
2-methyl-4-oxo-N-(p-tolyl)-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1n)



1n

White solid, 1.11 g, 75% yield.**^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.55 (s, 1H), 8.27 (d, *J* = 2.0 Hz, 1H), 7.60 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.31 – 7.26 (m, 2H), 7.11 – 7.07 (m, 2H), 6.83 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.73 – 6.69 (m, 1H), 2.22 (s, 3H), 1.62 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 172.07, 163.45, 146.86, 135.93, 133.51, 132.83, 129.18, 127.41, 119.48, 117.91, 114.77, 114.72, 71.04, 25.15, 20.42. **HRMS (ESI)** m/z calcd. for $C_{17}H_{17}N_3O_2Na$ $[M+Na^+]^+$ 318.1218, found 318.1222.

N-(4-methoxyphenyl)-2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1o)

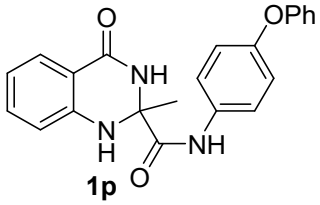


1o

White solid, 1.27g, 82% yield.**^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.50 (s, 1H), 8.23 (d, *J* = 1.5 Hz, 1H), 7.58 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.30 – 7.26 (m, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 6.87 – 6.84 (m, 2H), 6.82 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.71 (td, *J* = 8.0, 1.0 Hz, 1H), 3.68 (s, 3H), 1.61 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 171.91, 163.57, 155.71, 146.91, 133.61, 131.54, 127.47, 121.18, 118.02, 114.86, 114.77, 114.01, 71.02, 55.28, 25.24. **HRMS (ESI)** m/z calcd. for $C_{17}H_{17}N_3O_3Na$ $[M+Na^+]^+$ 334.1168, found 334.1172.

2-methyl-4-oxo-N-(4-phenoxyphenyl)-1,2,3,4-tetrahydroquinazoline-2-

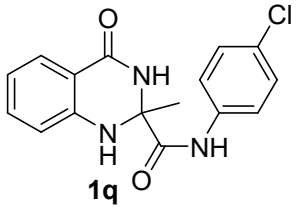
carboxamide (1p)



1p

White solid, 1.31 g, 70% yield.**^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.70 (s, 1H), 8.29 (d, *J* = 1.5 Hz, 1H), 7.61 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.35 – 7.26 (m, 4H), 7.10 – 7.06 (dd, *J* = 7.9, 6.7 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.96 – 6.92 (m, 2H), 6.84 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.72 (td, *J* = 7.0, 1.0 Hz, 1H), 1.64 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 172.15, 163.46, 157.26, 152.21, 146.83, 134.33, 133.50, 129.96, 127.42, 123.05, 121.15, 119.50, 117.94, 114.79, 71.06, 25.09. **HRMS (ESI)** m/z calcd. for $C_{22}H_{19}N_3O_3Na$ $[M+Na^+]^+$ 396.1324, found 396.1327.

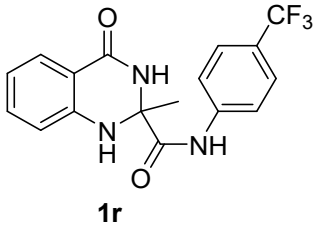
4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamido)phenyl hypochlorite (1q)



1q

White solid, 1.23 g, 78% yield.**^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.81 (s, 1H), 8.28 (d, *J* = 1.5 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.37 – 7.33 (m, 2H), 7.30 – 7.26 (m, 2H), 6.82 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.71 (td, *J* = 7.5, 1.0 Hz, 1H), 1.62 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 172.41, 163.37, 146.71, 137.41, 133.52, 128.72, 127.43, 127.41, 121.09, 117.99, 114.80, 114.73, 71.12, 24.99. **HRMS (ESI)** m/z calcd. for $C_{16}H_{15}N_3O_2Cl$ $[M+H^+]^+$ 316.0853, found 316.0855.

2-methyl-4-oxo-N-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1r)

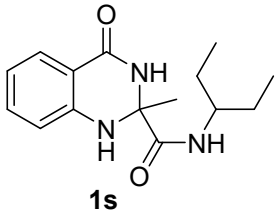


1r

White solid, 1.48 g, 85% yield.**^{1}H NMR (500 MHz, DMSO-d_6)** δ 10.03 (s, 1H), 8.31 (d, *J* = 2.0 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.61 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.31 – 7.26 (d, *J* = 1.5 Hz, 1H), 7.29 (m, 1H), 6.83 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.72 (td, *J* = 7.5, 1.0 Hz, 1H), 1.65 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 172.88, 163.40, 146.67, 142.07, 133.55, 127.44, 126.12 (q, *J* = 3.9 Hz), 124.28 (q, *J* = 269.6 Hz), 120.35, 119.48, 118.07, 114.83, 114.77, 71.23, 24.86. **HRMS (ESI)** m/z

calcd. for $C_{17}H_{15}N_3O_2F_3$ $[M+H^+]^+$ 350.1116, found 350.1114.

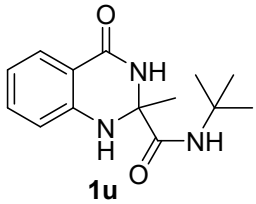
2-methyl-4-oxo-N-(pentan-3-yl)-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1s)



1s

White solid, 0.85 g, 62% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.19 (d, *J* = 1.5 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.17 (d, *J* = 9.0 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.68 (td, *J* = 7.5, 1.0 Hz, 1H), 3.45 – 3.40 (m, 1H), 1.50 (s, 3H), 1.44 – 1.32 (m, 2H), 1.26 – 1.12 (m, 2H), 0.67 (t, *J* = 7.5 Hz, 3H), 0.53 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 173.2, 163.7, 147.2, 133.2, 127.3, 117.7, 115.0, 114.7, 70.6, 52.0, 27.2, 27.1, 25.3, 10.2, 9.9. **HRMS (ESI)** m/z calcd. for $C_{15}H_{21}N_3O_2Na$ $[M+Na^+]^+$ 298.1531, found 298.1536.

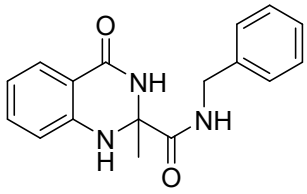
N-(tert-butyl)-2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1u)



1u

White solid, 0.89 g, 68% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.16 (d, *J* = 2.0 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.15 (d, *J* = 1.5 Hz, 1H), 7.03 (s, 1H), 6.75 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.70 – 6.65 (m, 1H), 1.45 (s, 3H), 1.15 (s, 9H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 172.8, 163.5, 159.5, 147.2, 133.3, 127.3, 117.5, 114.6, 114.5, 70.6, 50.6, 28.2. **HRMS (ESI)** m/z calcd. for $C_{14}H_{20}N_3O_2$ $[M+H^+]^+$ 262.1556, found 262.1560.

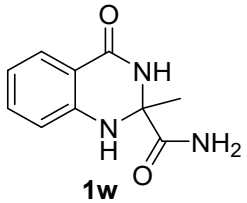
N-benzyl-2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1v)



1v

White solid, 1.07 g, 73% yield.**^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.30 – 8.25 (m, 2H), 7.62 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.21 – 7.16 (m, 4H), 6.99 – 6.96 (m, 2H), 6.80 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.75 (td, *J* = 7.5, 1.0 Hz, 1H), 4.31 – 4.22 (m, 2H), 1.55 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 173.70, 163.57, 147.08, 138.99, 133.37, 128.23, 127.42, 126.72, 126.67, 117.86, 115.06, 114.94, 70.55, 42.47, 25.22. **HRMS (ESI)** m/z calcd. for $C_{17}H_{17}N_3O_2Na$ $[M+Na^+]^+$ 318.1218, found 318.1216.

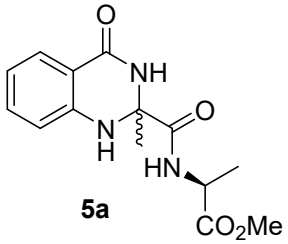
2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (1w)



1w

White solid, 0.65 g, 63% yield. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.15 (s, 1H), 7.57 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.17 (s, 1H), 7.08 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.71 – 6.67 (m, 1H), 1.49 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 175.6, 163.5, 147.2, 133.3, 127.3, 117.6, 114.72, 114.68, 70.2, 25.3. **HRMS (ESI)** m/z calcd. for $C_{10}H_{12}N_4O_2Na$ $[M+Na^+]^+$ 243.0858, found 243.0859.

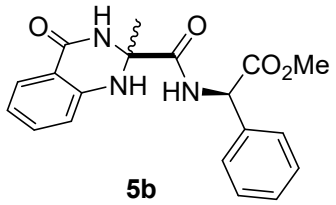
methyl (2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-alaninate (5a)



5a

White solid, 0.95 g, 65% yield. *dr* = 4:1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.20 – 8.10 (m, 1H), 8.03 – 7.98 (m, 1H), 7.58 – 7.54 (m, 1H), 7.28 – 7.23 (m, 1H), 7.18 – 7.10 (m, 1H), 6.78 – 6.74 (m, 1H), 6.71 – 6.66 (m, 1H), 4.23 – 4.15 (m, 1H), 3.54 (s, 1H), 3.48 (s, 2H), 1.51 (s, 3H), 1.26 – 1.19 (m, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 173.76, 173.55, 172.65, 172.56, 163.35, 147.19, 146.84, 133.28, 127.25, 117.69, 117.56, 114.80, 114.72, 114.59, 114.51, 70.29, 51.88, 51.79, 48.19, 47.98, 25.24, 25.17, 17.04, 16.87. **HRMS (ESI)** m/z calcd. for $C_{14}H_{17}N_3O_4Na$ $[M+Na^+]^+$ 314.1117, found 314.1121.

methyl (2R)-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamido)-2-phenylacetate (5b)

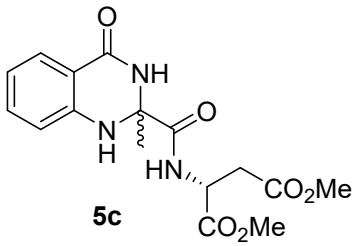


5b

White solid, 1.32 g, 75% yield. *dr* = 1:1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.37 (d, *J* = 7.0 Hz, 1H), 8.35 (d, *J* = 1.5 Hz, 1H), 8.32 (d, *J* = 1.5 Hz, 1H), 8.25 (d, *J* = 6.5 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.39 – 7.35 (m, 3H), 7.34 – 7.32 (m, 3H), 7.31 – 7.25 (m, 6H), 7.22 – 7.18 (m, 2H), 6.80 – 6.75 (m, 2H), 6.73 – 6.67 (m, 2H), 5.35 (d, *J* = 7.0 Hz, 1H), 5.29 (d, *J* = 7.0 Hz, 1H), 3.59 (s, 3H), 3.53 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 173.9, 173.6, 170.59, 170.55, 163.47, 147.3, 146.9,

136.1, 135.6, 133.4, 133.3, 128. 8, 128.6, 128.5, 128.2, 127.6, 127.4, 127.3, 127.2, 117.8, 117.6, 114.9, 114. 7, 114.6, 114.4, 70. 5, 56.9, 56.4, 52.4, 52.3, 25.2, 25.0.

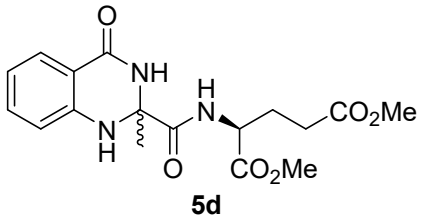
dimethyl (2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-D-aspartate (5c)



5c

White solid, 1.33 g, 76% yield. *dr* = 1:1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.26 (dd, *J* = 10.6, 1.6 Hz, 1H), 8.13 (dd, *J* = 16.2, 8.0 Hz, 1H), 7.56 (ddd, *J* = 7.8, 3.0, 1.6 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.18 (t, *J* = 2.3 Hz, 1H), 6.78 – 6.72 (m, 1H), 6.72 – 6.67 (m, 1H), 4.62 – 4.53 (m, 1H), 3.52 (d, *J* = 2.1 Hz, 3H), 3.49 (d, *J* = 7.9 Hz, 3H), 2.79 – 2.62 (m, 2H), 1.49 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 173.74, 173.64, 170.70, 170.61, 170.32, 170.25, 163.33, 163.31, 146.85, 133.18, 127.25, 117.69, 114.90, 114.85, 114.73, 114.69, 70.26, 70.22, 52.21, 52.16, 51.63, 49.00, 48.87, 35.46, 35.37, 24.91. **HRMS (ESI)** m/z calcd. for $C_{16}H_{22}N_3O_4$ $[M+H^+]^+$ 320.1610, found 320.1609.

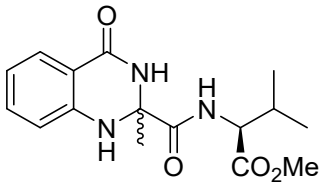
dimethyl (2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-glutamate (5d)



5d

White solid, 1.36 g, 75% yield. *dr* = 1:1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.32 – 8.15 (m, 1H), 8.10 – 8.00 (m, 1H), 7.62 – 7.54 (m, 1H), 7.28 – 7.22 (m, 1H), 7.19 – 7.12 (m, 1H), 6.80 – 6.74 (m, 1H), 6.72 – 6.67 (m, 1H), 4.28 – 4.17 (m, 1H), 3.58 – 3.46 (m, 6H), 2.25 – 2.19 (mii, 1H), 2.14 – 2.06 (m, 1H), 2.02 – 1.92 (m, 1H), 1.86 – 1.69 (m, 1H), 1.60 – 1.49 (m, 3H).**^{13}C NMR (125 MHz, DMSO-d_6)** δ 174.00, 173.87, 172.45, 172.39, 171.74, 171.54, 163.48, 147.08, 146.80, 133.25, 133.19, 127.31, 127.25, 117.85, 117.67, 115.06, 114.74, 114.71, 114.60, 70.45, 70.41, 52.00, 52.00, 51.88, 51.54, 51.36, 51.26, 29.26, 29.03, 26.06, 25.82, 24.99, 24.88. **HRMS (ESI)** m/z calcd. for $C_{17}H_{21}N_3O_6Na$ $[M+Na^+]^+$ 386.1328, found 386.1332.

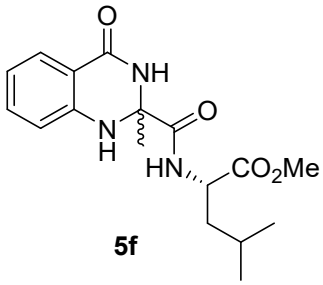
methyl (2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-valinate (5e)



5e

White solid, 1.02 g, 64% yield. *dr* = 1:1 **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.38 – 8.31 (m, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.35 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.72 – 6.66 (m, 1H), 4.20 – 4.09 (m, 1H), 3.61 (s, 2H), 3.53 (s, 2H), 2.04 – 1.92 (m, 1H), 1.54 – 1.50 (m, 3H), 0.78 (d, *J* = 7.0 Hz, 2H), 0.73 (d, *J* = 7.0 Hz, 2H), 0.67 (d, *J* = 7.0 Hz, 2H), 0.56 (d, *J* = 7.0 Hz, 2H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 173.94, 173.89, 171.8, 171.5, 163.6, 147.2, 146.9, 133.4, 133.2, 127.4, 127.3, 117.9, 117.7, 115.2, 114.7, 114.6, 114.5, 70.6, 57.6, 57.2, 51.9, 51.8, 30.2, 30.1, 24.9, 24.8, 18.8, 18.6, 17.8, 17.4. **HRMS (ESI)** m/z calcd. for $C_{16}H_{22}N_3O_4$ $[M+H^+]^+$ 320.1610, found 320.1609.

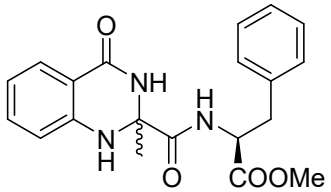
methyl (2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-leucinate (5f)



5f

White solid, 1.03 g, 62% yield. *dr* = 2.5:1 **^{1}H NMR (500 MHz, DMSO-d_6)** 8.25 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.28 – 7.23 (m, 1H), 7.11 (s, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.72 – 6.67 (m, 1H), 4.22 – 4.15 (m, 1H), 3.57 (s, 3H), 1.50 (s, 3H), 1.47 – 1.38 (m, 2H), 1.26 – 1.17 (m, 1H), 0.73 (d, *J* = 6.5 Hz, 3H), 0.56 (d, *J* = 6.5 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6)** δ 173.8, 172.7, 163.6, 146.9, 133.1, 127.3, 117.9, 115.2, 114.7, 70.5, 51.9, 50.4, 30.8, 24.8, 23.9, 22.8, 20.6. **HRMS (ESI)** m/z calcd. for $C_{17}H_{24}N_3O_4$ $[M+H^+]^+$ 334.1767, found 334.1771.

methyl (2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-phenylalaninate (5g)

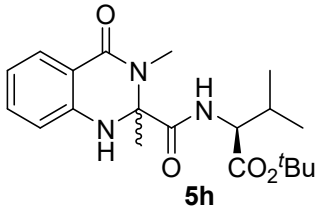


5g

White solid, 1.32 g, 72% yield. *dr* = 1:1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.22 – 8.18 (m, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.21 – 7.24 (m, 1H), 7.22 – 7.13 (m, 4H), 7.05 – 7.02 (m, 1H), 7.00 – 6.97 (m, 1H), 6.78 – 6.68 (m, 2H), 4.45 – 4.39 (m, 1H), 3.57 (s, 2H), 3.50 (s, 2H), 3.03 – 2.97 (m, 1H), 2.93 – 2.82 (m, 1H), 1.45 – 1.39 (m, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 173.79, 173.71,

171.49, 171.27, 163.31, 163.25, 146.90, 146.82, 136.76, 136.67, 133.26, 133.21, 129.08, 129.06, 128.21, 128.14, 127.30, 126.48, 126.41, 117.67, 117.62, 114.74, 114.69, 70.26, 70.20, 53.79, 51.96, 51.87, 36.57, 36.50, 25.16, 25.08. **HRMS (ESI)** m/z calcd. for $C_{20}H_{21}N_3O_4Na$ $[M+Na^+]^+$ 390.1430, found 390.1433.

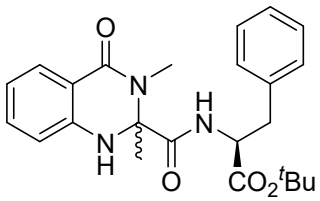
tert-butyl (2,3-dimethyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-D-valinate (5h)



5h

White solid, 0.18 g, 48% yield. *dr* = 10:1. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.89 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 (td, *J* = 7.5, 1.5 Hz, 1H), 6.89 – 6.84 (m, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 9.0 Hz, 1H), 5.33 (s, 1H), 4.31 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.27 (s, 3H), 2.07 – 2.0 (m, 1H), 1.80 (s, 3H), 1.43 (s, 9H), 0.65 (d, *J* = 7.0 Hz, 3H), 0.54 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 171.7, 170.1, 163.5, 144. 9, 133.6, 128.6, 120.2, 116.2, 115.1, 82.2, 75.4, 57.9, 31.2, 28.9, 28.0, 23.9, 18.5, 16.8. **HRMS (ESI)** m/z calcd. for $C_{19}H_{28}N_3O_4$ $[M+H^+]^+$ 362.2080, found 362.2076.

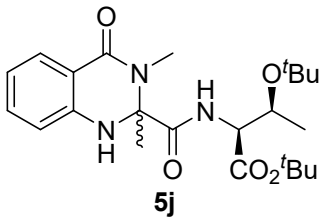
tert-butyl (2,3-dimethyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-phenylalaninate



5i

White solid, 0.43 g, 52% yield. *dr* = 4:1. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.91 – 7.87 (m, 1H), 7.30 – 7.25 (m, 1H), 7.22 – 7.15 (m, 3H), 6.95 – 6.91 (m, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.08 (s, 1H), 4.65 – 4.58 (m, 1H), 3.13 (s, 3H), 2.99 – 2.92 (m, 2H), 1.68 (s, 3H), 1.37 (s, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 171.5, 169.7, 163.0, 144.5, 135.6, 133.6, 129.2, 129.2, 128.7, 128.5, 127.0, 120.0, 115.8, 114.9, 82.6, 75.0, 53. 9, 37.7, 29.1, 27.9, 23.9. **HRMS (ESI)** m/z calcd. for $C_{23}H_{28}N_3O_4$ $[M+H^+]^+$ 410.2080, found 410.2079.

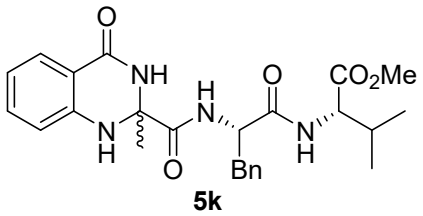
tert-butyl O-(tert-butyl)-N-(2,3-dimethyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-allothreoninate (5j)



5j

White solid, 0.39 g, 45% yield. *dr* = 1.6:1. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.30 (s, 1H), 7.29 – 7.18 (m, 1H), 6.91 – 6.82 (m, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 4.115 – 4.08 (m, 2H), 3.27 (s, 3H), 1.81 (s, 3H), 1.43 (s, 9H), 1.11 (s, 9H), 0.74 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 172.1, 171.9, 169.3, 169.1, 163.2, 163.1, 145.0, 144.0, 133.4, 133.3, 128.8, 128.6, 120.4, 119.8, 117.2, 116.1, 115.8, 114.8, 82.0, 81.9, 75.2, 74.5, 73.8, 73.7, 67.0, 66.9, 58.9, 58.7, 29.5, 28.8, 28.7, 28.6, 28.03, 27.99, 24.1, 23.7, 20.5. **HRMS (ESI)** m/z calcd. for $C_{22}H_{34}N_3O_5[M+H^+]^+$ 420.2498, found 420.2499.

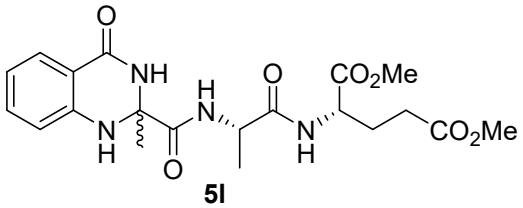
methyl (2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-phenylalanyl-L-valinate (5k)



5k

White solid, 47.3 mg, 53% yield. *dr* = 1.2:1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.30 (d, *J* = 8.0 Hz, 1H), 8.21 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.36 (s, 1H), 7.28 – 7.20 (m, 1H), 7.18 – 7.12 (m, 1H), 7.11 – 7.01 (m, 4H), 6.77i (dd, *J* = 8.0, 1.0 Hz, 1H), 6.70 – 6.67 (m, 1H), 4.57 – 4.52 (m, 1H), 4.16 – 4.10 (m, 1H), 3.62 (s, 3H), 2.97 – 2.89 (m, 1H), 2.82 – 2.71 (m, 1H), 2.05 – 1.93 (m, 1H), 1.36 (s, 3H), 0.89 – 0.78 (m, 6H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 173.4, 173.3, 171.65, 171.59, 171.2 170.7, 163.15, 163.12, 146.9, 146.8, 137.1, 136.9, 133.22, 133.18, 129.25, 129.16, 127.9, 127.80, 127.3, 126.1, 126.0, 117.5, 114.61, 114.56, 114.5, 70.3, 70.2, 57.5, 57.4, 54.0, 53.8, 51.7, 51.6, 37.8, 37.7, 29.9, 29.8, 25.4, 25.3, 18.83, 18.79, 18.2, 18.1. **HRMS (ESI)** m/z calcd. for $C_{25}H_{30}N_4O_5Na$ $[M+H^+]^+$ 489.2114, found 489.2116.

dimethyl (2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carbonyl)-L-alanyl-L-glutamate (5l)

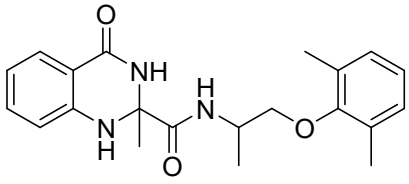


5l

White solid, 358 mg, 85% yield. *dr* = 1:1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.35 (d, *J* = 7.5 Hz, 1H), 8.31 (s, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 8.25 (s, 1H), 7.76 – 7.69 (m, 1H), 7.56 (s, 1H), 7.54 (s, 1H), 7.27 – 7.19 (m, 2H), 6.77 (s, 1H), 6.75 (s, 1H), 6.70 – 6.65 (m, 1H), 4.28 – 4.20 (m, 2H), 3.60 (s, 3H), 3.57 (s, 3H), 2.37 – 2.30 (m, 2H), 2.00 – 1.92 (m, 1H), 1.84 – 1.73 (m, 1H), 1.49 (s, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.09 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, DMSO-d_6)** δ 173.1, 172.9, 172.5, 172.0, 171.9, 171.8, 171.8, 163.25, 163.22, 147.1, 146.8, 133.3, 133.2, 127.3, 127.2, 117.6, 117.5, 114.7, 114.6, 114.5, 114.3, 70.3, 51.9, 51.3, 51.1, 51.1, 48.3, 48.0, 29.5, 26.0, 25.9,

25.3, 25.2, 18.5, 18.4. **HRMS (ESI)** m/z calcd. for $C_{20}H_{26}N_4O_7Na$ $[M+H^+]^+$ 457.1699, found 457.1702.

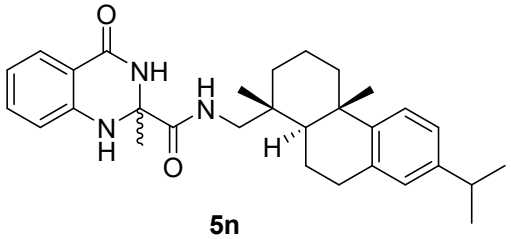
N-(1-(2,6-dimethylphenoxy)propan-2-yl)-2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (5m)



5m

White solid, 1.54 g, 84% yield.**^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.25 – 8.22 (m, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H), 6.99 – 6.95 (m, 2H), 6.90 – 6.86 (m, 1H), 6.80 – 6.75 (m, 1H), 6.71 – 6.66 (m, 1H), 4.07 – 4.01 (m, 1H), 3.60 – 3.53 (m, 2H), 2.11 (s, 3H), 2.08 (s, 3H), 1.52 (s, 3H), 1.20 (dd, *J* = 18.0, 7.0 Hz, 3H).**^{13}C NMR (100 MHz, DMSO-d_6)** δ 173.59, 173.45, 163.86, 163.82, 162.87, 155.18, 155.09, 147.47, 147.42, 133.85, 133.81, 130.87, 130.81, 129.22, 129.20, 127.80, 127.77, 124.34, 124.30, 118.11, 118.06, 115.13, 115.09, 114.86, 74.02, 73.93, 70.86, 70.81, 45.96, 45.89, 31.25, 26.03, 17.73, 17.62, 16.24, 16.22. **HRMS (ESI)** m/z calcd. for $C_{21}H_{26}N_3O_3$ $[M+H^+]^+$ 368.1974, found 368.1976.

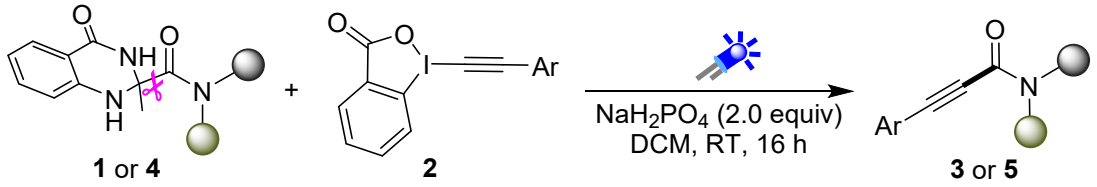
N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2-methyl-4-oxo-1,2,3,4-tetrahydroquinazoline-2-carboxamide (5n)



5n

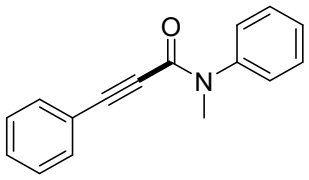
White solid, 1.94 g, 82% yield. *dr* = 1:1. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.29 – 8.24 (m, 2H), 7.39 – 7.29 (m, 3H), 7.18 – 7.11 (m, 3H), 7.06 – 6.90 (m, 5H), 6.78 – 6.75 (m, 2H), 6.67 – 6.60 (m, 2H), 6.56 – 6.53 (m, 1H), 6.34 – 6.29 (m, 1H), 6.08 (t, *J* = 7.5 Hz, 1H), 3.34 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.03 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.85 – 2.76 (m, 3H), 2.66 – 2.54 (m, 3H), 2.41 – 2.33 (m, 1H), 2.09 – 2.03 (m, 2H), 1.73 – 1.67 (m, 2H), 1.60 – 1.48 (m, 3H), 1.48 – 1.45 (m, 6H), 1.45 – 1.33 (m, 4H), 1.21 – 1.17 (m, 12H), 1.14 – 1.05 (m, 3H), 1.01 (s, 3H), 1.00 (s, 3H), 0.97 – 0.81 (m, 5H), 0.72 (s, 3H), 0.70 (s, 3H). **^{3}C NMR (100 MHz, DMSO-d_6)** δ 174.05, 173.95, 164.06, 147.23, 147.19, 147.05, 145.00, 144.89, 134.94, 133.35, 133.27, 127.58, 127.43, 126.98, 126.90, 124.47, 123.73, 123.64, 118.03, 117.92, 115.49, 114.83, 114.52, 71.00, 49.58, 49.34, 43.82, 43.72, 37.96, 37.82, 37.78, 37.61, 37.24, 37.18, 35.89, 35.76, 33.44, 33.41, 30.05, 25.84, 25.81, 25.46, 25.36, 24.53, 24.48, 24.41, 19.13, 19.05, 18.75, 18.69, 18.55. **HRMS (ESI)** m/z calcd. for $C_{30}H_{40}N_3O_2$ $[M+H^+]^+$ 474.3221, found 474.3220.

Typical Procedure for the alkynylation of carbamoyl radicals



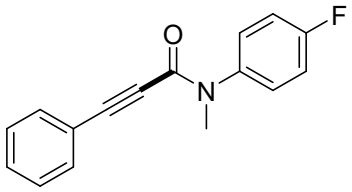
General procedure: A 10 ml oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with **1** or **4** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), NaH_2PO_4 (0.4 mmol, 2.0 equiv.) and exchanged with N_2 three times, then dichloromethane (DCM, 2 ml) was added. The reaction vessel was exposed to blue LED (450 nm) at room temperature for 16 hours. After that, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (Petroleum ether/EtOAc) to give the desired product **3** or **5**.

N-methyl-N,3-diphenylpropiolamide (3aa)



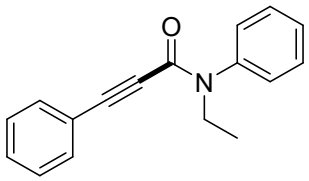
Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 83 % yield (39.1 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.46 – 7.42 (m, 2H), 7.40 – 7.37 (m, 1H), 7.37 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.11 (m, 2H), 3.38 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 154.2, 143.2, 132.3, 129.8, 129.1, 128.2, 127.9, 127.3, 120.4, 90.8, 82.5, 36.3. **HRMS (ESI)** m/z calcd. for $C_{16}H_{14}NO$ $[M+H^+]^+$ 236.1075, found 236.1078.

N-(4-fluorophenyl)-N-methyl-3-phenylpropiolamid (3ba)



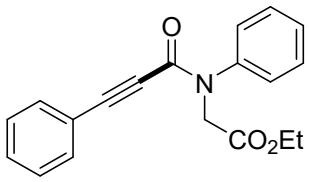
Prepared according to the general procedure using **1b** (62.6 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 88 % yield (44.6 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.36 – 7.31 (m, 3H), 7.28 – 7.23 (m, 2H), 7.19 – 7.11 (m, 4H), 3.36 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 161.8 (d, J = 246.4 Hz), 154.2, 139.2 (d, J = 3.3 Hz), 132.3, 130.0, 129.2 (d, J = 8.6 Hz), 128.3, 120.2, 116.0 (d, J = 22.5 Hz), 91.1, 82.3, 36.4. **^{19}F NMR (471 MHz, Chloroform-d)** δ -113.2. **HRMS (ESI)** m/z calcd. for $C_{16}H_{13}NOF$ $[M+H^+]^+$ 254.0981, found 254.0984.

N-ethyl-N,3-diphenylpropiolamide (3ca)



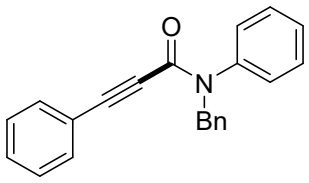
Prepared according to the general procedure using **1c** (61.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 90 % yield (44.9 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.47 – 7.40 (m, 3H), 7.34 – 7.28 (m, 3H), 7.23 – 7.19 (m, 2H), 7.13 – 7.05 (m, 2H), 3.87 (q, *J* = 7.5 Hz, 2H), 1.18 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.9, 141.7, 132.4, 129.8, 129.1, 128.6, 128.2, 128.1, 120.5, 90.7, 82.8, 43.4, 12.9.**HRMS (ESI)** m/z calcd. for $C_{17}H_{16}NO$ $[M+H^+]^+$ 250.1232, found 250.1235.

ethyl N-phenyl-N-(3-phenylpropioloyl)glycinate (3da)



Prepared according to the general procedure using **1d** (73. mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 92 % yield (56.5 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.51 – 7.46 (m, 2H), 7.46 – 7.38 (m, 3H), 7.34 – 7.30 (m, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.09 (m, 2H), 4.50 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 168.4, 154.6, 142.2, 132.5, 130.1, 129.2, 128.5, 128.3, 120.2, 91.8, 82.1, 61.5, 50.5, 14.2. **HRMS (ESI)** m/z calcd. for $C_{19}H_{17}NO_3Na$ $[M+Na^+]^+$ 330.1106, found 330.1109.

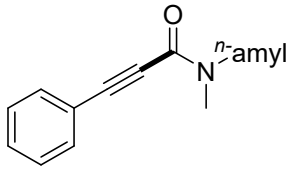
N-benzyl-N,3-diphenylpropiolamide (3ea)



Prepared according to the general procedure using **1e** (74.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 86 % yield (53.6 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.36 – 7.33 (m, 3H), 7.31- 7.29 (m, 1H), 7.28 – 7.24 (m, 5H), 7.23 – 7.19 (m, 2H), 7.18 – 7.14 (m, 2H), 7.11 – 7.07 (m, 2H), 5.00 (s, 2H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 154.4, 141.7, 136.6, 132.4, 129.9, 129.0, 128.7, 128.6, 128.4, 128.2, 128.1, 127.5, 120.3, 91.4, 82.5, 52.2. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}NONa$

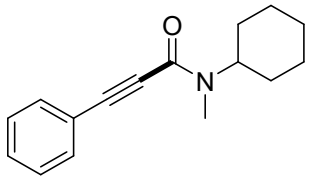
$[M+Na^+]^+$ 334.1208, found 334.1211.

N-methyl-N-pentyl-3-phenylpropiolamide (3fa)



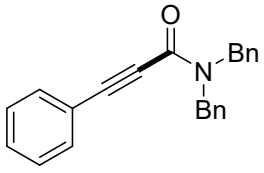
Prepared according to the general procedure using **1f** (57.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 90 % yield (52.1 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.56 – 7.51 (m, 2H), 7.43 – 7.34 (m, 3H), 3.64 (t, *J* = 7.5 Hz, 1H), 3.44 (t, *J* = 7.5 Hz, 1H), 3.26 (d, *J* = 1.5 Hz, 1H), 3.00 (d, *J* = 1.5 Hz, 2H), 1.69 – 1.63 (m, 1H), 1.62 – 1.54 (m, 1H), 1.41 – 1.28 (m, 4H), 0.93 – 0.89 (m, 3H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 154.5, 154.4, 132.2, 132.2, 129.8, 129.8, 128.4, 128.4, 120.7, 90.0, 89.5, 81.9, 81.7, 51.1, 46.6, 36.3, 32.2, 28.8, 28.6, 27.8, 26.5, 22.4, 22.3, 13.9, 13.9. **HRMS (ESI)** m/z calcd. for $C_{15}H_{20}NO$ $[M+H^+]^+$ 230.1545, found 230.1548

N-cyclohexyl-N-methyl-3-phenylpropiolamide (3ga)



Prepared according to the general procedure using **1g** (60.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 50 % yield (24.1 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.56 – 7.49 (m, 2H), 7.43 – 7.31 (m, 3H), 4.47 – 4.22 (m, 1H), 3.14 (s, 1H), 2.89 (s, 2H), 1.91 – 1.66 (m, 5H), 1.57 – 1.48 (m, 1H), 1.47 – 1.31 (m, 3H), 1.17 – 1.07 (m, 1H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 154.3, 154.3, 132.3, 132.2, 129.8, 129.8, 128.5, 128.4, 120.8, 120.8, 90.0, 89.8, 82.3, 81.7, 58.6, 52.3, 31.1, 30.9, 29.6, 26.9, 25.8, 25.5, 25.5, 25.2. **HRMS (ESI)** m/z calcd. for $C_{16}H_{20}NO$ $[M+H^+]^+$ 242.1545, found 242.1548.

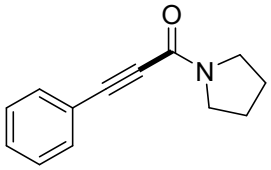
N,N-dibenzyl-3-phenylpropiolamide (3ha)



Prepared according to the general procedure using **1h** (77.1 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 93 % yield (60.5 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.52 – 7.48 (m, 2H), 7.41 – 7.36 (m, 3H), 7.36 – 7.27 (m, 8H), 7.27

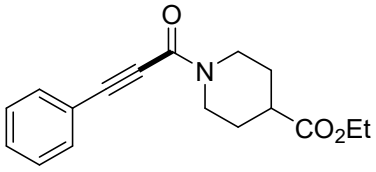
– 7.23 (m, 2H), 4.76 (s, 2H), 4.57 (s, 2H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 155.0, 136.2, 136.0, 132.4, 130.1, 128.8, 128.7, 128.5, 128.4, 127.9, 127.7, 127.6, 120.3, 90.8, 81.6, 51.4, 46.3. **HRMS (ESI)** m/z calcd. for $C_{23}H_{19}NONa$ $[M+Na^+]^+$ 348.1364, found 348.1368.

3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-one (3ia)



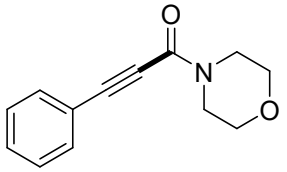
Prepared according to the general procedure using **1i** (51.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 98 % yield (39.1 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.55 – 7.49 (m, 2H), 7.44 – 7.37 (m, 1H), 7.37 – 7.30 (m, 2H), 3.72 (t, *J* = 6.5 Hz, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 2.01 – 1.86 (m, 4H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 152.7, 132.3, 129.9, 128.4, 120.6, 88.6, 82.6, 48.1, 45.3, 25.3, 24.7. **HRMS (ESI)** m/z calcd. for $C_{13}H_{14}NO$ $[M+H^+]^+$ 200.1075, found 200.1078.

ethyl 1-(3-phenylpropioloyl)piperidine-4-carboxylate (3ja)



Prepared according to the general procedure using **1j** (69.1 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 79 % yield (45.1 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.55 – 7.50 (m, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.32 (m, 2H), 4.41 – 4.29 (M, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.36 – 3.29 (m, 1H), 3.00 – 2.93 (m, 1H), 2.60 – 2.53 (m, 1H), 2.02 – 1.93 (m, 2H), 1.81 – 1.63 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 173.8, 152.9, 132.3, 129.9, 128.4, 120.4, 90.5, 81.1, 60.6, 46.1, 40.9, 40.6, 28.4, 27.5, 14.1. **HRMS (ESI)** m/z calcd. for $C_{17}H_{19}NO_3Na$ $[M+Na^+]^+$ 308.1263, found 308.1267.

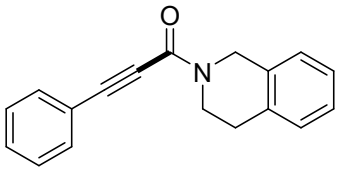
1-morpholino-3-phenylprop-2-yn-1-one (3ka)



Prepared according to the general procedure using **1k** (55.1 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 86 % yield (37.0 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.55 – 7.51 (m, 2H), 7.44 – 7.39 (m, 1H), 7.38 – 7.33 (m, 2H), 3.85

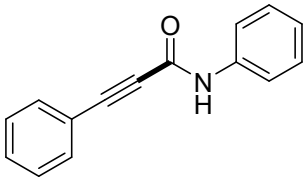
– 3.81 (m, 2H), 3.75 – 3.72 (m, 2H), 3.69 (s, 4H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.1, 132.3, 130.1, 128.5, 120.2, 91.1, 80.7, 66.8, 66.4, 47.3, 41.9. **HRMS (ESI)** m/z calcd. for C13H14NO2 $[M+H^+]^+$ 216.1025, found 216.1028.

1-(3,4-dihydroisoquinolin-2(1H)-yl)-3-phenylprop-2-yn-1-one (3la)



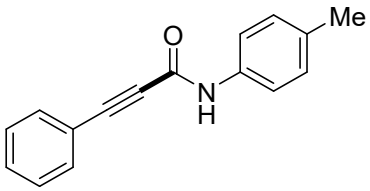
Prepared according to the general procedure using **1l** (64.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 75 % yield (39.2 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.61 – 7.55 (m, 2H), 7.46 – 7.35 (m, 3H), 7.24 – 7.14 (m, 4H), 4.98 (s, 1H), 4.82 (s, 1H), 4.08 (t, *J* = 6.0 Hz, 1H), 3.91 (t, *J* = 6.0 Hz, 1H), 2.98 (t, *J* = 6.0 Hz, 1H), 2.92 (t, *J* = 6.0 Hz, 1H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.7, 134.6, 133.8, 132.4, 132.3, 132.3, 130.0, 128.9, 128.6, 128.5, 127.0, 126.7, 126.7, 126.6, 126.5, 126.1, 120.5, 90.3, 81.3, 48.6, 44.7, 44.0, 39.6, 29.5, 28.3. **HRMS (ESI)** m/z calcd. for $C_{18}H_{16}NO$ $[M+H^+]^+$ 262.1232, found 262.1234.

N,3-diphenylpropiolamide (3ma)



Prepared according to the general procedure using **1m** (56.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 70 % yield (31.0 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.77 (s, 1H), 7.57 (t, *J* = 8.5 Hz, 4H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 151.0, 137.3, 132.6, 130.3, 129.1, 128.6, 124.9, 119.9, 119.9, 85.7, 83.4. **HRMS (ESI)** m/z calcd. for $C_{15}H_{12}NO$ $[M+H^+]^+$ 222.0919, found 222.0918.

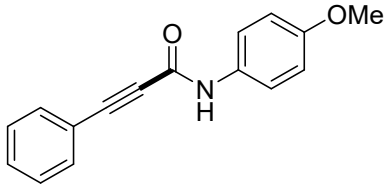
3-phenyl-N-(p-tolyl)propiolamide (3na)



Prepared according to the general procedure using **1n** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 81 % yield (38.1 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.70 (s, 1H), 7.58 – 7.54 (m, 2H), 7.48 – 7.41 (m, 3H), 7.39 – 7.34

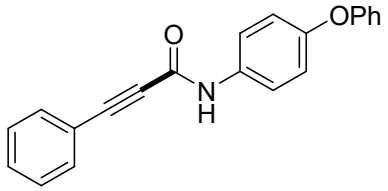
(m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 150.9, 134.8, 134.6, 132.6, 130.2, 129.6, 128.5, 120.0, 120.0, 85.5, 83.5, 20.9. **HRMS (ESI)** m/z calcd. for $C_{16}H_{14}NO$ $[M+H^+]^+$ 236.1075, found 236.1077.

N-(4-methoxyphenyl)-3-phenylpropiolamide (3oa)



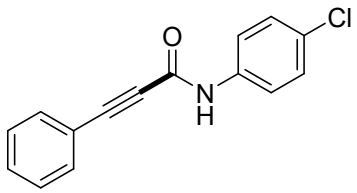
Prepared according to the general procedure using **1o** (62.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 74 % yield (37.2 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.82 (s, 1H), 7.55 – 7.52 (m, 2H), 7.51 – 7.48 (m, 2H), 7.44 – 7.40 (m, 1H), 7.37 – 7.33 (m, 2H), 6.88 – 6.84 (m, 2H), 3.79 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 156.3, 150.4, 132.7, 132.1, 130.9, 129.5, 121.6, 120.2, 114.5, 84.8, 84.5, 55.7. **HRMS (ESI)** m/z calcd. for $C_{16}H_{14}NO_2$ $[M+H^+]^+$ 252.1025, found 252.1019.

N-(4-phenoxyphenyl)-3-phenylpropiolamide (3pa)



Prepared according to the general procedure using **1p** (74.5 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 93 % yield (58.3 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.83 (s, 1H), 7.58 – 7.52 (m, 4H), 7.45 – 7.41 (m, 1H), 7.38 – 7.31 (m, 4H), 7.12 – 7.08 (m, 1H), 7.02 – 6.97 (m, 4H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 157.3, 154.1, 151.0, 132.7, 132.6, 130.3, 129.8, 128.6, 123.3, 121.7, 119.9, 119.5, 118.6, 85.8, 83.4. **HRMS (ESI)** m/z calcd. for $C_{21}H_{16}NO_2$ $[M+H^+]^+$ 314.1181, found 314.1186.

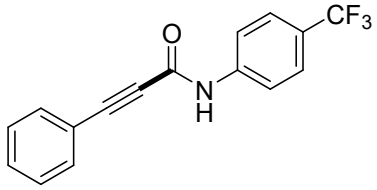
N-(4-chlorophenyl)-3-phenylpropiolamide (3qa)



Prepared according to the general procedure using **1q** (63.2 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 67 % yield (34.3 mg). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 11.02 (s, 1H), 7.70 – 7.63 (m, 4H), 7.57 – 7.52 (m, 1H), 7.52 - .47 (m, 2H), 7.43 – 7.39 (m, 2H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 150.3, 137.4, 132.3,

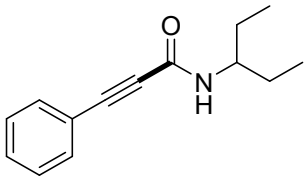
130.6, 129.1, 128.8, 127.8, 121.2, 119.4, 84.7, 84.0. **HRMS (ESI)** m/z calcd. for $C_{15}H_{11}NOCl$ $[M+H^+]^+$ 256.0529, found 256.0532.

3-phenyl-N-(4-(trifluoromethyl)phenyl)propiolamid (3ra)



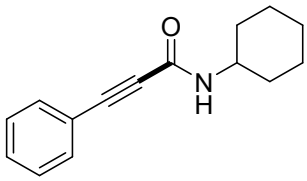
Prepared according to the general procedure using **1r** (69.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 76 % yield (44.0 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 8.01 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.47 – 7.42 (m, 1H), 7.39 – 7.34 (m, 2H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 151.2, 140.3, 132.6, 130.6, 128.6, 126.4 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 270.0 Hz), 119.6, 86.7, 83.0.**^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.2 (s, 3F). **HRMS (ESI)** m/z calcd. for $C_{16}H_{11}NOF_3$ $[M+H^+]^+$ 290.0793, found 290.0796.

N-(pentan-3-yl)-3-phenylpropiolamide (3sa)



Prepared according to the general procedure using **1s** (55.1 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 98 % yield (42.2 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.54 – 7.50 (m, 2H), 7.41 – 7.37 (m, 1H), 7.36 – 7.31 (m, 2H), 5.81 – 5.72 (m, 1H), 3.92 – 3.85 (m, 1H), 1.63 – 1.55 (m, 2H), 1.47 – 1.40 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.3, 132.5, 129.9, 128.5, 120.4, 84.3, 83.4, 52.8, 27.3, 10.2. **HRMS (ESI)** m/z calcd. for $C_{14}H_{18}NO$ $[M+H^+]^+$ 216.1388, found 216.1391.

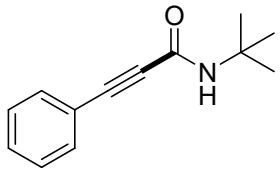
N-cyclohexyl-3-phenylpropiolamide (3ta)



Prepared according to the general procedure using **1t** (57.5 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 86 % yield (39.1 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.55 – 7.50 (m, 2H), 7.41 – 7.36 (m, 1H), 7.36 – 7.31 (m, 2H), 5.97 – 5.83 (m, 1H), 3.91 – 3.83 (m, 1H), 2.02 – 1.94 (m, 2H), 1.76 – 1.69 (m, 2H), 1.65 –

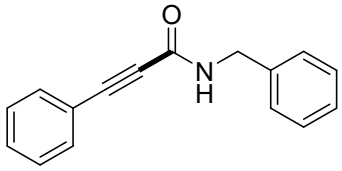
1.59 (m, 1H), 1.42 – 1.32 (m, 2H), 1.25 – 1.16 (m, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 152.5, 132.4, 129.9, 128.4, 120.3, 84.1, 83.3, 48.8, 32.8, 25.4, 24.7. **HRMS (ESI)** m/z calcd. for $C_{15}H_{18}NO$ $[M+H^+]^+$ 228.1388, found 228.1391.

N-(tert-butyl)-3-phenylpropiolamide (3ua)



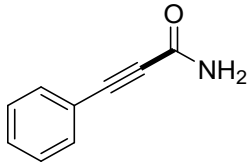
Prepared according to the general procedure using **1u** (52.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 76 % yield (30.6 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.52 – 7.48 (m, 2H), 7.41 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H), 5.83 (s, 1H), 1.40 (s, 9H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 152.5, 132.3, 129.7, 128.4, 120.4, 84.1, 82.5, 52.4, 28.6. **HRMS (ESI)** m/z calcd. for $C_{13}H_{15}NONa$ $[M+Na^+]^+$ 224.1051, found 224.1054.

N-benzyl-3-phenylpropiolamide (3va)



Prepared according to the general procedure using **1v** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 67 % yield (31.5 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.53 – 7.50 (m, 2H), 7.43 – 7.38 (m, 1H), 7.37 – 7.30 (m, 7H), 6.31 (s, 1H), 4.54 (d, *J* = 5.5 Hz, 2H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.3, 137.3, 132.5, 130.1, 128.8, 128.5, 128.0, 127.8, 120.2, 85.1, 82.9, 44.0. **HRMS (ESI)** m/z calcd. for $C_{16}H_{14}NO$ $[M+H^+]^+$ 236.1075, found 236.1078.

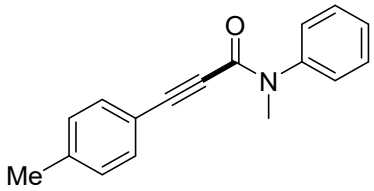
3-phenylpropiolamide (3wa)



Prepared according to the general procedure using **1w** (41.1 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 92 % yield (26.7 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.55 – 7.52 (m, 2H), 7.44 – 7.40 (m, 1H), 7.37 – 7.33 (m, 2H), 6.63 (s, 1H), 6.07 (s, 1H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 155.6, 132.6, 130.3, 128.5, 119.8, 86.2, 82.2. **HRMS (ESI)** m/z calcd. for C_9H_8NO $[M+H^+]^+$ 146.0606,

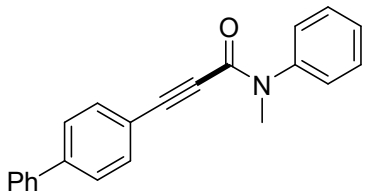
found 146.0609.

N-methyl-N-phenyl-3-(p-tolyl)propiolamide (3ab)



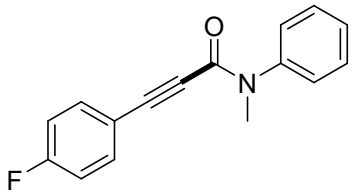
Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2b** (108.7 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 63 % yield (31.4 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.46 – 7.41 (m, 2H), 7.39 – 7.34 (m, 3H), 7.05 – 7.01 (m, 4H), 3.38 (s, 3H), 2.29 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 154.4, 143.3, 140.4, 132.3, 129.1, 129.0, 127.8, 127.4, 117.3, 91.2, 82.2, 36.3, 21.5. **HRMS (ESI)** m/z calcd. for $C_{17}H_{16}NO$ $[M+H^+]^+$ 250.1232, found 250.1235.

3-([1,1'-biphenyl]-4-yl)-N-methyl-N-phenylpropiolamide (3ac)



Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2c** (127.3 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 68 % yield (42.4 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.54 – 7.50 (m, 2H), 7.49 – 7.45 (m, 4H), 7.44 – 7.35 (m, 6H), 7.23 – 7.20 (m, 2H), 3.41 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 154.3, 143.2, 142.7, 139.8, 132.8, 129.1, 128.8, 127.9, 127.9, 127.4, 127.0, 126.9, 119.1, 90.8, 83.2, 36.3. **HRMS (ESI)** m/z calcd. for $C_{22}H_{18}NO$ $[M+H^+]^+$ 312.1388, found 312.1391.

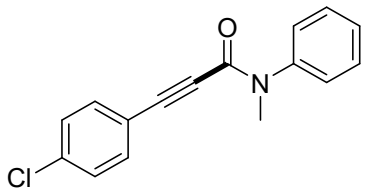
3-(4-fluorophenyl)-N-methyl-N-phenylpropiolamide (3ad)



Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2d** (109.8 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 95 % yield (48.1 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.46 – 7.41 (m, 2H), 7.40 – 7.37 (m, 1H), 7.36 – 7.32 (m, 2H), 7.12 – 7.08 (m, 2H), 6.91 (t, *J* = 8.5 Hz, 2H), 3.37 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 163.4 k, 154.1, 143.1, 134.5 (d, *J* = 8.6 Hz), 129.1, 127.9, 127.3, 116.5 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 22.3 Hz), 89.7, 82.4, 36.2. **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -107.6. **HRMS (ESI)** m/z calcd. for $C_{16}H_{13}NOF$ $[M+H^+]^+$ 254.0981,

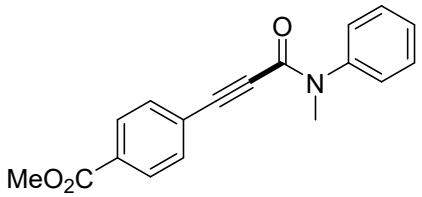
found 254.0985.

3-(4-chlorophenyl)-N-methyl-N-phenylpropiolamide (3ae)



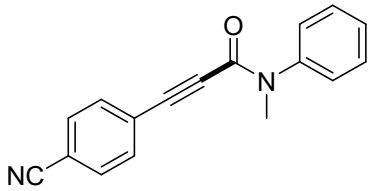
Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2e** (114.8 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 97 % yield (52.3 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.45 – 7.41 (m, 2H), 7.39 – 7.36 (m, 1H), 7.35 – 7.32 (m, 2H), 7.21 – 7.17 (m, 2H), 7.05 – 7.01 (m, 2H), 3.37 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 154.0, 143.0, 136.1, 133.5, 129.1, 128.7, 127.9, 127.3, 118.8, 89.5, 83.3, 36.3. **HRMS (ESI)** m/z calcd. for $C_{16}H_{13}NOCl$ $[M+H^+]^+$ 270.0686, found 270.0688.

methyl 4-(3-(methyl(phenyl)amino)-3-oxoprop-1-yn-1-yl)benzoate (3af)



Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2f** (121.9 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 67 % yield (39.3 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.91 – 7.87 (m, 2H), 7.47 – 7.42 (M, 2H), 7.41 – 7.34 (m, 3H), 7.20 – 7.17 (m, 2H), 3.88 (s, 3H), 3.39 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 166.1, 153.8, 143.0, 132.2, 131.0, 129.3, 129.2, 128.1, 127.3, 124.9, 89.4, 84.6, 52.3, 36.4. **HRMS (ESI)** m/z calcd. for $C_{18}H_{16}NO_3$ $[M+H^+]^+$ 294.1130, found 294.1134.

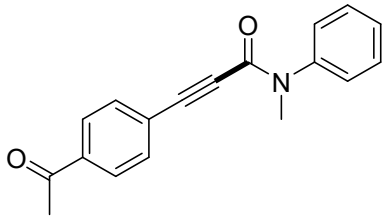
3-(4-cyanophenyl)-N-methyl-N-phenylpropiolamide (3ag)



Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2g** (111.9 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a black solid in 63 % yield (32.8 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.53 – 7.50 (m, 2H), 7.47 – 7.42 (m, 2H), 7.41 – 7.37 (m, 1H), 7.35 – 7.32 (m, 2H), 7.22 – 7.18 (m, 2H), 3.38 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.4, 142.8, 132.7, 131.9, 129.2, 128.2, 127.3, 125.2, 117.9, 113.2,

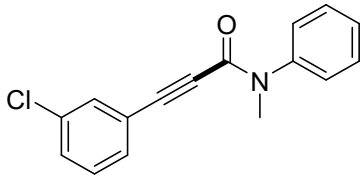
88.1, 85.6, 36.4. **HRMS (ESI)** m/z calcd. for $C_{17}H_{13}N_2O$ $[M+H^+]^+$ 261.1028, found 261.1031.

3-(4-acetylphenyl)-N-methyl-N-phenylpropiolamide (3ah)



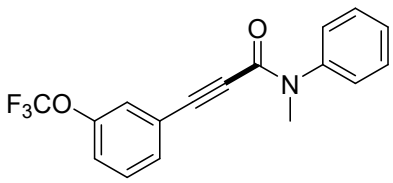
Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2h** (117.1 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 73 % yield (40.5 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.83 – 7.80 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 – 7.38 (m, 1H), 7.38 – 7.34 (m, 2H), 7.23 – 7.20 (m, 2H), 3.40 (s, 3H), 2.56 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 197.7, 152.9, 143.1, 137.9, 132.5, 129.7, 128.9, 128.5, 127.9, 124.3, 88.9, 85.4, 36.4, 27.3. **HRMS (ESI)** m/z calcd. for $C_{18}H_{16}NO_2$ $[M+H^+]^+$ 278.1181, found 278.1184.

3-(3-chlorophenyl)-N-methyl-N-phenylpropiolamide (3ai)



Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2i** (114.8 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 72 % yield (39.4 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.47 – 7.43 (m, 2H), 7.42 – 7.38 (m, 1H), 7.36 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 1.5 Hz, 1H), 7.02 (dt, *J* = 8.0, 1.5 Hz, 1H), 3.38 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.9, 143.0, 134.1, 132.0, 130.4, 130.1, 129.5, 129.2, 128.1, 127.3, 122.1, 89.0, 83.3, 36.3. **HRMS (ESI)** m/z calcd. for $C_{16}H_{13}NOCl$ $[M+H^+]^+$ 270.0686, found 270.0689.

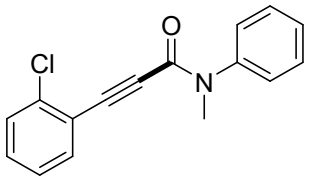
N-methyl-N-phenyl-3-(3-(trifluoromethoxy)phenyl)propiolamide (3aj)



Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2j** (126.9 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 73 % yield (46.6 mg). **^{1}H NMR (500 MHz,**

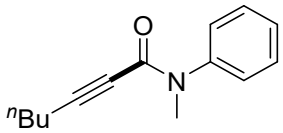
Chloroform-d) δ 7.47 – 7.43 (m, 2H), 7.42 – 7.38 (m, 1H), 7.36 – 7.33 (m, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.09 – 7.06 (m, 1H), 6.93 – 6.91 (m, 1H), 3.39 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.8, 148.8(q, *J* = 1.9 Hz), 143.0, 130.6, 129.9, 129.2, 128.1, 127.4, 124.5, 122.5, 122.2, 120.2 (q, *J* = 256.5 Hz), 88.8, 83.4, 36.3.**^{19}F NMR** (471 MHz, Chloroform-*d*) δ -58.0. **HRMS (ESI)** m/z calcd. for $C_{17}H_{13}NO_2F_3$ $[M+H^+]^+$ 320.0898, found 320.0901.

3-(2-chlorophenyl)-N-methyl-N-phenylpropiolamide (3ak)



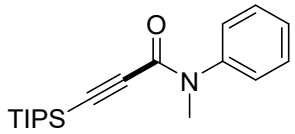
Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2k** (114.8 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 83 % yield (44.8 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.44 – 7.39 (m, 2H), 7.36 – 7.33 (m, 3H), 7.29 – 7.21 (m, 3H), 7.13 (td, *J* = 7.5, 1.5 Hz, 1H), 3.38 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.9, 142.9, 136.6, 134.3, 130.8, 129.3, 129.2, 127.9, 127.4, 126.3, 120.7, 87.0, 86.8, 36.5. **HRMS (ESI)** m/z calcd. for $C_{16}H_{13}NOCl$ $[M+H^+]^+$ 270.0686, found 270.0688.

N-methyl-N-phenylhept-2-ynamide (3al)



Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2l** (98.4 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 68 % yield (29.3 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.42 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 7.29 – 7.26 (m, 2H), 3.32 (s, 3H), 2.09 (t, J = 7.0 Hz, 2H), 1.24 – 1.19 (m, 2H), 1.10 – 1.03 (m, 2H), 0.75 (t, J = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d6)** δ 153.5, 143.5, 129.5, 128.1, 127.8, 93.6, 75.7, 36.3, 29.4, 21.3, 17.9, 13.8. **HRMS (ESI)** m/z calcd. for $C_{14}H_{18}NO$ $[M+H^+]^+$ 216.1388, found216.1390

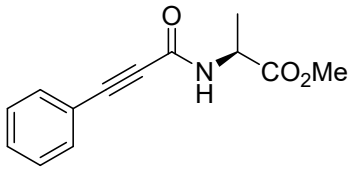
N-methyl-N-phenyl-3-(triisopropylsilyl)propiolamide (3am)



Prepared according to the general procedure using **1a** (59.1 mg, 0.2 mmol, 1.0 equiv.), **2m** (128.5 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow liquid in 61 % yield (38.5 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 3H), 3.31 (s, 3H),

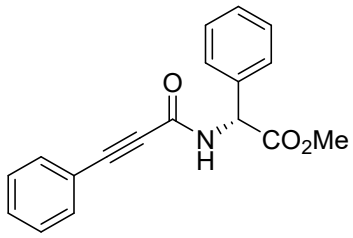
0.92 – 0.85 (m, 21H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 153.6, 143.3, 129.3, 127.9, 127.5, 98.6, 95.1, 36.5, 18.3, 10.8. **HRMS (ESI)** m/z calcd. for $C_{19}H_{30}NOSi$ $[M+H^+]^+$ 316.2097, found 316.2099.

methyl (3-phenylpropioloyl)-L-alaninate (5aa)



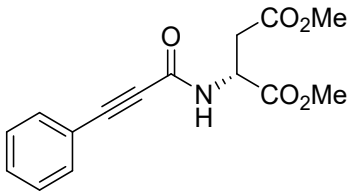
Prepared according to the general procedure using **1a** (58.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 85 % yield (39.3 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.55 – 7.52 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.33 (m, 2H), 6.59 (d, *J* = 7.5 Hz, 1H), 4.69 (p, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 1.47 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 172.8, 152.7, 132.5, 130.2, 128.5, 120.0, 85.3, 82.6, 52.6, 48.4, 18.3. **HRMS (ESI)** m/z calcd. for $C_{13}H_{13}NO_3Na$ $[M+Na^+]^+$ 254.0793, found 254.0797.

methyl (R)-2-phenyl-2-(3-phenylpropiolamido)acetate (5ba)



Prepared according to the general procedure using **1a** (70.7 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 69 % yield (40.5 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.54 – 7.52 (m, 2H), 7.42 – 7.39 (m, 3H), 7.38 – 7.32 (m, 5H), 7.04 – 6.99 (m, 1H), 5.68 (d, *J* = 7.0 Hz, 1H), 3.75 (s, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 170.7, 152.4, 135.8, 132.5, 130.2, 129.0, 128.7, 128.5, 127.3, 119.9, 85.7, 82.5, 56.5, 52.9. **HRMS (ESI)** m/z calcd. for $C_{18}H_{15}NO_3Na$ $[M+Na^+]^+$ 316.0950, found 316.0954.

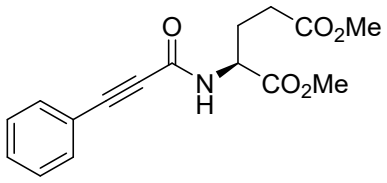
dimethyl (3-phenylpropioloyl)-D-aspartate (5ca)



Prepared according to the general procedure using **1a** (69.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 98 % yield (56.7 mg). **^{1}H NMR (500 MHz,**

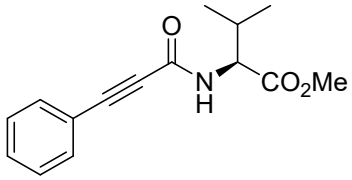
Chloroform-d) δ 7.55 – 7.52 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.33 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.95 – 4.90 (m, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.08 (dd, *J* = 17.5, 4.5 Hz, 1H), 2.92 (dd, *J* = 17.5, 4.5 Hz, 1H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 171.4, 170.4, 152.9, 132.6, 130.2, 128.5, 119.9, 85.9, 82.4, 52.9, 52.1, 48.6, 35.8. **HRMS (ESI)** m/z calcd. for $C_{15}H_{15}NO_5Na$ $[M+Na^+]^+$ 312.0848, found 312.0851.

dimethyl (3-phenylpropioloyl)-L-glutamate (5da)



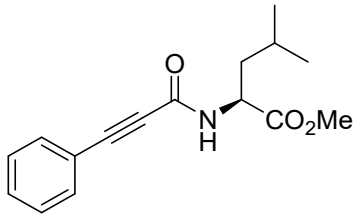
Prepared according to the general procedure using **1a** (72.7 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 73 % yield (44.3 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.54 – 7.50 (m, 2H), 7.42 – 7.38 (m, 1H), 7.36 – 7.31 (m, 2H), 6.80 – 6.72 (m, 1H), 4.75 – 4.69 (m, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 2.49 – 2.37 (m, 2H), 2.31 – 2.23 (m, 1H), 2.09 – 2.02 (m, 1H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 173.0, 171.6, 153.0, 132.5, 130.2, 128.5, 119.9, 85.7, 82.4, 52.7, 51.8, 51.8, 29.9, 27.3, 27.2. **HRMS (ESI)** m/z calcd. for $C_{16}H_{17}NO_5Na$ $[M+Na^+]^+$ 326.1004, found 326.1007.

methyl (3-phenylpropioloyl)-L-valinate (5ea)



Prepared according to the general procedure using **1a** (63.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 75 % yield (38.9 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.55 – 7.52 (m, 2H), 7.42 – 7.38 (m, 1H), 7.36 – 7.32 (m, 2H), 6.52 (d, *J* = 9.0 Hz, 1H), 4.65 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.75 (s, 3H), 2.25 – 2.17 (m, 1H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 171.8, 153.1, 132.5, 130.1, 128.5, 120.0, 85.5, 82.6, 57.3, 52.3, 31.4, 18.8, 17.8. **HRMS (ESI)** m/z calcd. for $C_{15}H_{17}NO_3Na$ $[M+Na^+]^+$ 282.1106, found 282.1110.

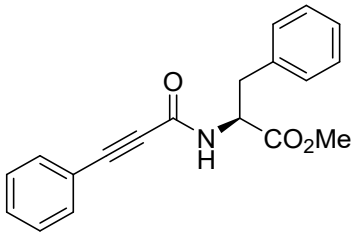
methyl (3-phenylpropioloyl)-L-leucinate (5fa)



Prepared according to the general procedure using **1a** (66.7 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL)

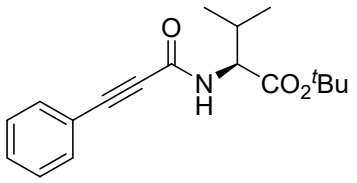
for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 71 % yield (38.8 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.54 – 7.51 (m, 2H), 7.43 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 6.43 (d, *J* = 9.0 Hz, 1H), 4.76 – 4.71 (m, 1H), 3.75 (s, 3H), 1.74 – 1.67 (m, 2H), 1.64 – 1.56 (m, 1H), 0.96 (t, *J* = 6.5 Hz, 6H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 172.9, 152.9, 132.5, 130.1, 128.5, 120.0, 85.5, 82.6, 52.4, 51.0, 41.6, 24.8, 22.7, 21.9. **HRMS (ESI)** m/z calcd. for $C_{16}H_{19}NO_3Na$ $[M+Na^+]^+$ 296.1263, found 296.1266.

methyl (3-phenylpropioloyl)-L-phenylalaninate (5ga)



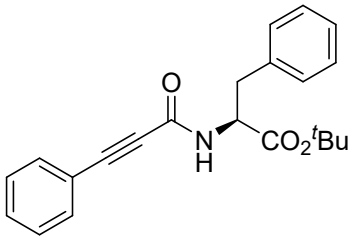
Prepared according to the general procedure using **1a** (73.5mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 94 % yield (57.8 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.55 – 7.52 (m, 2H), 7.44 – 7.40 (m, 1H), 7.38 – 7.30 (m, 4H), 7.28 – 7.25 (m, 1H), 7.16 – 7.13 (m, 2H), 6.43 (d, *J* = 8.0 Hz, 1H), 5.01 – 4.96 (m, 1H), 3.75 (s, 3H), 3.25 – 3.14 (m, 2H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 171.3, 152.7, 135.4, 132.6, 130.2, 129.3, 128.6, 128.5, 127.2, 120.0, 85.5, 82.5, 53.5, 52.5, 37.7. **HRMS (ESI)** m/z calcd. for $C_{19}H_{15}NOF_3$ $[M+H^+]^+$ 330.1106, found 330.1109.

tert-butyl (3-phenylpropioloyl)-L-valinate (5ha)



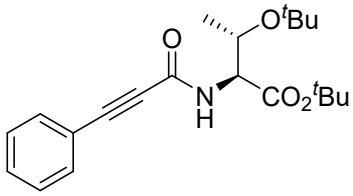
Prepared according to the general procedure using **1a** (72.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 98 % yield (59.1 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.56 – 7.3 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.33 (m, 2H), 6.48 (d, *J* = 8.5 Hz, 1H), 4.55 (dd, *J* = 8.5, 4.5 Hz, 1H), 2.24 – 2.18 (m, 1H), 1.48 (s, 9H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 170.5, 153.1, 132.5, 130.1, 128.5, 120.1, 85.2, 82.8, 82.4, 57.6, 31.6, 28.0, 28.0, 18.8, 17.7. **HRMS (ESI)** m/z calcd. for $C_{19}H_{15}NOF_3$ $[M+Na^+]^+$ 324.1576, found 324.1589.

tert-butyl (3-phenylpropioloyl)-L-phenylalaninate (5ia)



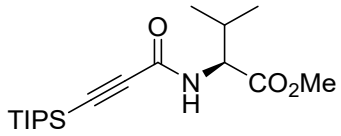
Prepared according to the general procedure using **1a** (81.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 76 % yield (53.1 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.54 – 7.51 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.33 (m, 2H), 7.31 – 7.28 (m, 2H), 7.26 – 7.24 (m, 1H), 7.21 – 7.18 (m, 2H), 6.48 (d, *J* = 7.5 Hz, 1H), 4.87 - .82 (m, 1H), 3.16 (d, *J* = 6.0 Hz, 2H), 1.41 (s, 9H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 170.0, 152.6, 135.8, 132.6, 130.1, 129.5, 128.5, 128.4, 127.0, 120.0, 85.2, 82.8, 82.7, 53.9, 37.8, 27.9. **HRMS (ESI)** m/z calcd. for $C_{22}H_{23}NO_3Na$ $[M+Na^+]^+$ 372.1576, found 372.1579.

tert-butyl O-(tert-butyl)-N-(3-phenylpropioloyl)-L-allothreoninate (5ja)



Prepared according to the general procedure using **1a** (83.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 45 % yield (32.4 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.57 – 7.53 (m, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 6.59 (d, *J* = 9.5 Hz, 1H), 4.46 (dd, *J* = 9.5, 2.0 Hz, 1H), 4.25 – 4.21 (m, 1H), 1.47 (d, *J* = 1.0 Hz, 9H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.17 (s, 9H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 169.2, 153.6, 132.5, 130.0, 128.4, 120.2, 85.3, 82.8, 82.2, 73.9, 67.1, 58.6, 28.6, 28.0, 21.0. **HRMS (ESI)** m/z calcd. for $C_{23}H_{32}N_2O_4Na$ $[M+Na^+]^+$ 382.4558, found 382.2025.

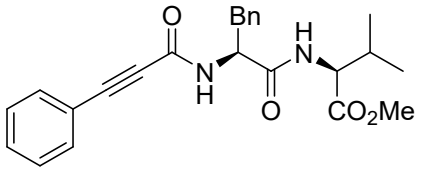
methyl (3-(triisopropylsilyl)propioloyl)-L-valinate (5bm)



Prepared according to the general procedure using **1a** (63.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (128.5 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil in 54 % yield (36.7 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 6.27 (d, *J* = 9.0 Hz, 1H), 4.59 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.75 (s, 3H), 2.21 – 2,13 (m, 1H), 1.11 – 1.08 (m, 21H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 171.9, 152.4, 99.3, 89.5, 57.3, 52.3, 31.5, 18.8, 18.5, 18.4, 17.9, 11.0. **HRMS (ESI)** m/z calcd. for $C_{18}H_{33}NO_3SiNa$

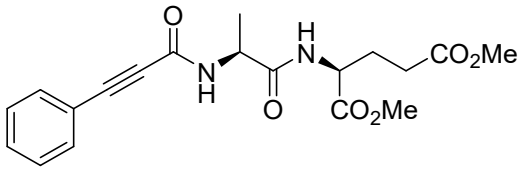
[M+Na$^+$]$^+$ 362.2127, found 362.2130.

methyl (3-phenylpropioloyl)-L-phenylalanyl-L-valinate (5ka)



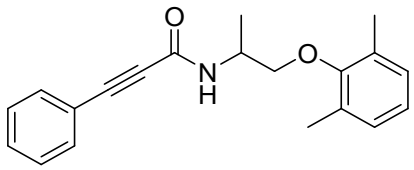
Prepared according to the general procedure using **1a** (93.3 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a green solid in 71 % yield (57.7 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.52 – 7.48 (m, 2H), 7.41 – 7.37 (m, 1H), 7.35 – 7.29 (m, 2H), 7.29 – 7.20 (m, 5H), 7.03 – 6.94 (m, 1H), 6.64 – 6.54 (m, 1H), 4.94 – 4.88 (m, 1H), 4.44 (dd, *J* = 8.5, 5.0 Hz, 1H), 3.69 (s, 3H), 3.13 (d, *J* = 7.0 Hz, 2H), 2.14 – 2.06 (m, 1H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 171.5, 170.3, 153.0, 136.0, 132.5, 130.1, 129.3, 128.6, 128.4, 127.0, 119.9, 85.7, 82.5, 57.5, 54.8, 52.0, 38.3, 31.0, 18.8, 17.7. **HRMS (ESI)** m/z calcd. for $C_{24}H_{26}N_2O_4Na$ [M+Na$^+$]$^+$ 429.1790, found 429.1793.

dimethyl (3-phenylpropioloyl)-L-alanyl-L-glutamate (5la)



Prepared according to the general procedure using **1a** (86.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a yellow solid in 66 % yield (49.2 mg). **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.54 – 7.47 (m, 2H), 7.41 – 7.35 (m, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.18 (m, 1H), 7.08 – 6.96 (m, 1H), 4.70 – 4.64 (m, 1H), 4.61 – 4.5 (m, 1H), 3.73 (d, *J* = 3.0 Hz, 3H), 3.62 (d, *J* = 3.3 Hz, 3H), 2.47 – 2.34 (m, 2H), 2.25 – 2.17 (m, 1H), 2.07 – 1.96 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, Chloroform-d)** δ 173.2, 171.8, 152.9, 132.5, 130.1, 128.4, 119.9, 85.6, 82.5, 52.5, 51.8, 51.8, 49.1, 29.91, 26.8, 18.5. **HRMS (ESI)** m/z calcd. for $C_{19}H_{22}N_2O_6Na$ [M+Na$^+$]$^+$ 397.1376, found 397.1377.

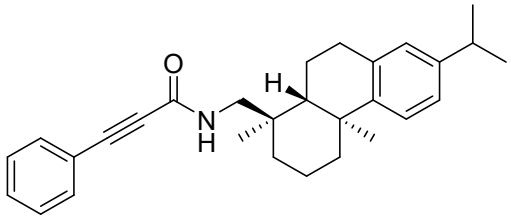
N-(1-(2,6-dimethylphenoxy)propan-2-yl)-3-phenylpropiolamide (5ma)



Prepared according to the general procedure using **1a** (72.9 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum

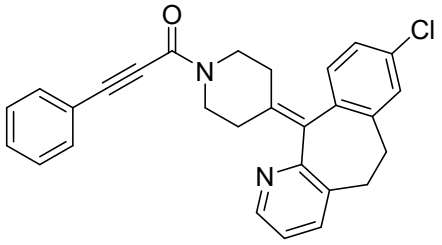
ether/EtOAc = 2:1) as a white solid in 80 % yield (49.2 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.56 – 7.53 (m, 2H), 7.44 – 7.40 (m, 1H), 7.38 – 7.34 (m, 2H), 7.03 – 6.99 (m, 2H), 6.96 – 6.92 (m, 1H), 6.46 (d, *J* = 8.5 Hz, 1H), 4.48 – 4.42 (m, 1H), 3.87 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.76 (dd, *J* = 9.0, 3.5 Hz, 1H), 2.30 (s, 6H), 1.48 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 155.5, 152.4, 132.6, 130.8, 130.7, 129.4, 129.3, 124.2, 120.4, 84.6, 83.5, 74.0, 45.9, 17.3, 16.4. **HRMS (ESI)** m/z calcd. for $C_{20}H_{22}NO_2$ $[M+H^+]^+$ 308.1651, found 308.1653.

N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-3-phenylpropiolamide (5na)



Prepared according to the general procedure using **1a** (94.7 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 94 % yield (77.8 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.59 – 7.52 (m, 2H), 7.42 – 7.38 (m, 1H), 7.36 – 7.32 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.94 – 6.92 (m, 1H), 6.08 – 6.01 (m, 1H), 3.47 – 3.32 (m, 1H), 3.23 – 3.17 (m, 1H), 2.98 – 2.81 (m, 3H), 2.34 – 2.29 (m, 1H), 1.96 – 1.90 (m, 1H), 1.82 – 1.68 (m, 3H), 1.52 – 1.47 (m, 2H), 1.44 – 1.34 (m, 2H), 1.26 – 1.22 (m, 9H), 0.99 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 153.6, 147.0, 145.6, 134.7, 132.4, 129.9, 128.4, 126.9, 124.1, 123.8, 120.2, 84.8, 83.2, 50.0, 45.0, 38.2, 37.6, 37.4, 36.1, 33.4, 30.1, 29.6, 25.2, 23.9, 18.9, 18.7, 18.5. **HRMS (ESI)** m/z calcd. for $C_{29}H_{36}NO$ $[M+H^+]^+$ 414.2797, found 414.2799

1-(4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidin-1-yl)-3-phenylprop-2-yn-1-one (5oa)

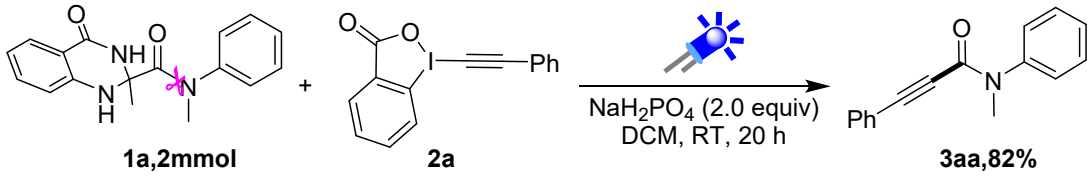


Prepared according to the general procedure using **1a** (99.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (97.2 mg, 0.3 mmol) and NaH_2PO_4 (48.0 mg, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) for 16 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 73 % yield (64.1 mg). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.43 – 8.39 (m, 1H), 7.53 – 7.50 (m, 2H), 7.45 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.36 – 7.32 (m, 2H), 7.19 – 7.09 (m, 4H), 4.18 – 4.03 (m, 2H), 3.60 – 3.52 (m, 1H), 3.43 – 3.24 (m, 3H), 2.90 – 2.78 (m, 2H), 2.65 – 2.50 (m, 1H), 2.49 – 2.36 (m, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 156.8, 156.5, 153.0,

153.0, 146.8, 146.7, 139.6, 139.4, 137.7, 137.6, 137.3, 136.6, 136.5, 135.0, 133.4, 133.3, 133.1, 133.0, 132.3, 130.4, 130.3, 130.0, 130.0, 129.0, 129.0, 128.5, 128.4, 126.3, 126.2, 122.4, 122.4, 120.5, 90.6, 81.2, 48.0, 42.4, 31.6, 31.6, 31.5, 31.4, 30.2, 30.0. **HRMS (ESI)** m/z calcd. for $C_{28}H_{24}N_2OCl$ $[M+H^+]^+$ 439.1577, found 439.1580

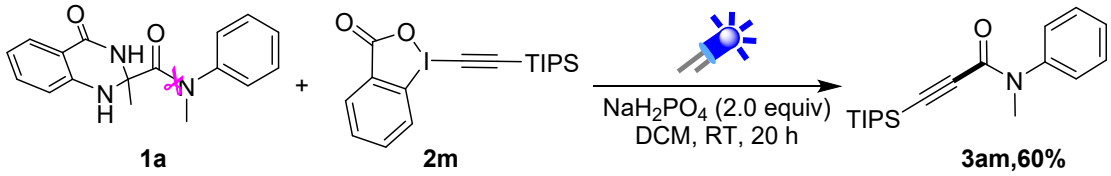
Follow-up chemistry

(a) Scale up reaction



N-methyl-N,3-diphenylpropiolamide(3aa)

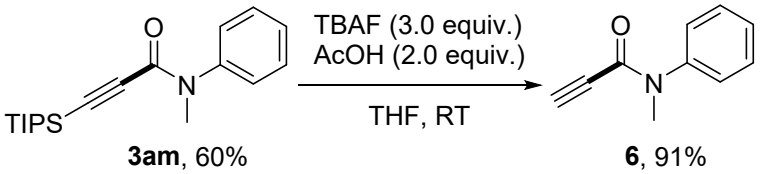
A 40 ml oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with **1a** (590.6 mg, 2.0 mmol, 1.0 equiv.), **2a** (972.3 mg, 3 mmol, 1.5 equiv.), NaH_2PO_4 (480 mg, 4 mmol, 2.0 equiv.) and exchanged with N_2 three times, then dichloromethane (DCM, 20 ml) was added. The reaction vessel was exposed to blue LED (450 nm) at room temperature for 20 hours. The title compound was obtained by flash chromatography (Petroleum ether/EtOAc = 2:1) as a white solid in 82 % yield



N-methyl-N-phenyl-3-(trimethylsilyl)propiolamide(3am)

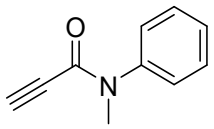
A 40 ml oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with **1a** (590.6 mg, 2.0 mmol, 1.0 equiv.), **2m** (1.03 g, 3 mmol, 1.5 equiv.), NaH_2PO_4 (480 mg, 4 mmol, 2.0 equiv.) and exchanged with N_2 three times, then dichloromethane (DCM, 20 ml) was added. The reaction vessel was exposed to blue LED (450 nm) at room temperature for 20 hours. The title compound **3am** was obtained by flash chromatography (Petroleum ether/EtOAc = 5:1) as a white solid in 60 % yield (375.0 mg).

(b) Synthetic transformation of 3am

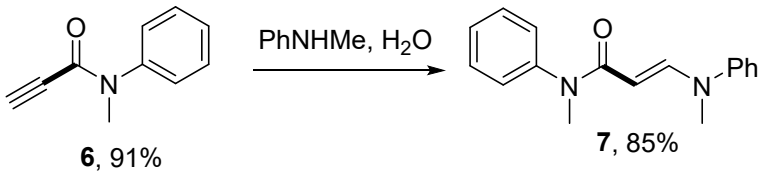


To a solution of ynamide (320.0mg, 1.0 mmol, 1.0equiv) in THF (30 mL) was added AcOH (120.0 mg, 2 mmol, 2.0equiv) and tetra-n-butylammonium fluoride (1.0 M in THF, 3 mL, 3 mmol, 3.0equiv). The reaction mixture was stirred atroom temperature until TLC indicated the complete consumption of material (30 min). The reaction mixture was concentrated and purified directly by column chromatography to afford the desilylation **6** product as a white solid (144.7 mg, 91% yield).

N-methyl-N-phenylpropiolamide (6)[4]

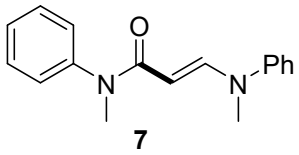


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 2H), 7.38 – 7.35 (m, 1H), 7.30 – 7.28 (m, 2H), 3.33 (s, 3H), 2.81 (s, 1H).



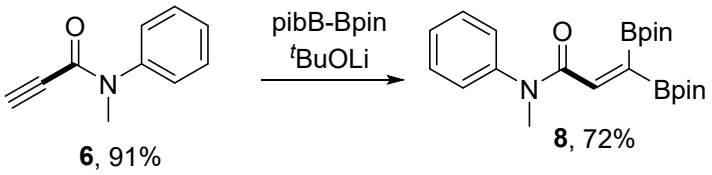
The mixture of N-methylaniline (64.3 mg, 0.6 mmol, 1.2 equiv) with distilled water (5 mmol, 11 equiv) in a 10 mL vial, then slowly add N-methyl-N-phenylpropiolamide (**6**, 79.6 mg, 0.5 mmol, 1.0 equiv) and react at 80°C for 8 hours. Quench the reaction with saturated sodium chloride solution (1.2 mL) and extract the resulting mixture in the same small vial using ethyl acetate (2 mL × 3) with a pipette. Purified by column chromatography and eluted with petroleum ether/ethyl acetate (3/1), the desired yellow solid product (E)-N-methyl-3-(methyl(phenyl)amino)-N-phenylpropenamide (**7**) was obtained (120.6 mg, yield 85%).

(E)-N-methyl-3-(methyl(phenyl)amino)-N-phenylacrylamide (7)[5]



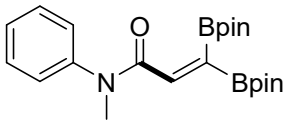
7

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 13.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 4.83 (d, *J* = 13.0 Hz, 1H), 3.36 (s, 3H), 2.98 (s, 3H).



The mixture of Bis(pinacolato)diboron (127.0 mg, 0.5 mmol, 1.0 equiv) was placed in a Schlenk flask equipped with a magnetic stir bar. The flask was evacuated and filled with argon. Acetonitrile (1 mL), N-methyl-N-phenylpropiolamide (**6**, 79.6 mg, 0.5 mmol, 1.0 equiv), and lithium tert-butoxide (4 mg, 0.05 mmol) were added to the flask sequentially. After stirring at 40 °C for 5 hours, the mixture was filtered through a short silica gel column with diethyl ether. The solvent was removed under reduced pressure to afford pure product (148.7 mg, 0.36 mmol, 72% yield).

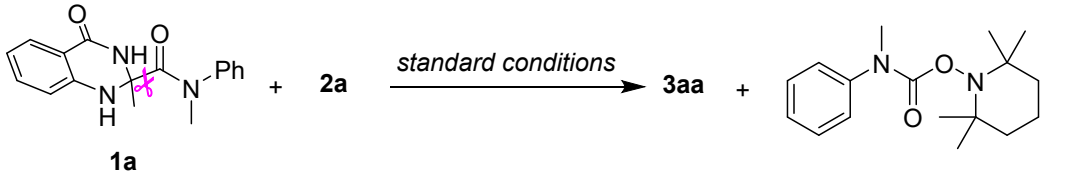
N-methyl-N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylamide (8)[6]



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 3H), 7.18 – 7.14 (m, 2H), 6.45 (s, 1H), 3.44 (s, 3H), 1.33 (s, 12H), 1.19 (s, 12H).

Mechanistic Study

(a) Control experiments



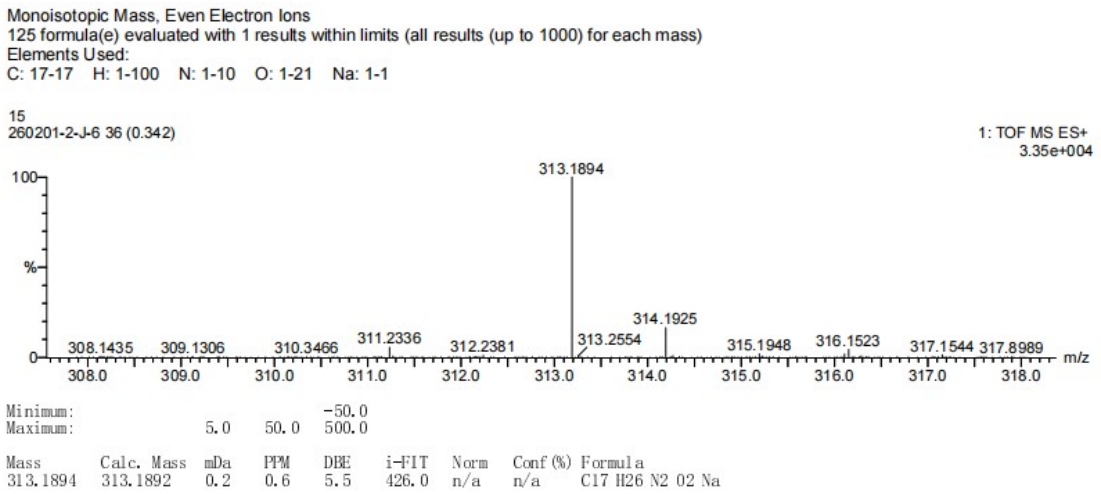
1a

additive: TEMPO **3aa**, 0% yield
1,4-dinitrobenzene **3aa**, 0% yield

9, Detected by HRMS
m/z [M+Na]$^+$: 313.1892
found: 313.1894

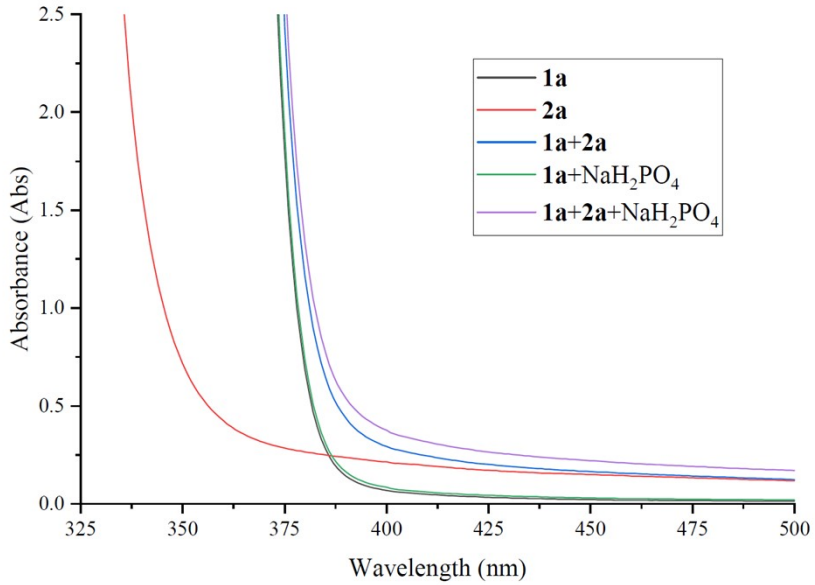
procedure: A 10 ml oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol), NaH_2PO_4 (0.4 mmol, 2.0 equiv.), TEMPO (46.9 mg, 0.3 mmol, 1.5 equiv.) or 1,4-dinitrobenzene (50.4 mg, 0.3 mmol, 1.5 equiv.) and exchanged with N_2 three times, then dichloromethane (DCM, 2 ml) was added. The reaction vessel was exposed to blue LED (450 nm) at room temperature for 16 hours. After that, the mixture was concentrated, crude NMR give the no desired product **3aa**.

This result showed no formation of product **3aa**, and indicated that this reaction involved a free radical intermediate. The TEMPO-adduct of carbamoyl radical **9** was found through high-resolution data of the resulting mixture, verifying the generation of carbamoyl radical in this reaction. HRMS m/z [M+Na]+: 313.1892, found: 313.1894.



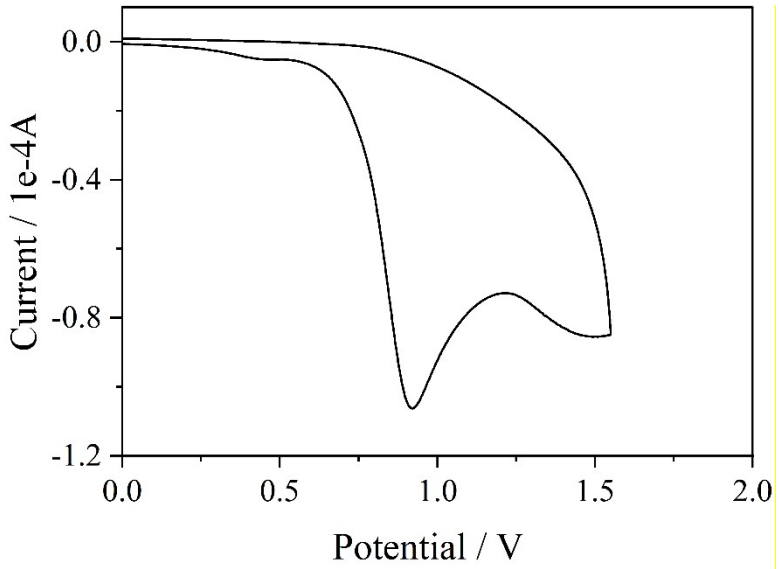
(b) UV-vis Absorption Experiments

Ultraviolet−visible spectroscopy (UV/vis) measurements were conducted. No obvious change of the absorption was observed when **1a** (0.1 mol/L) and **2a** (0.15 mol/L) were mixed under standard reaction conditions.

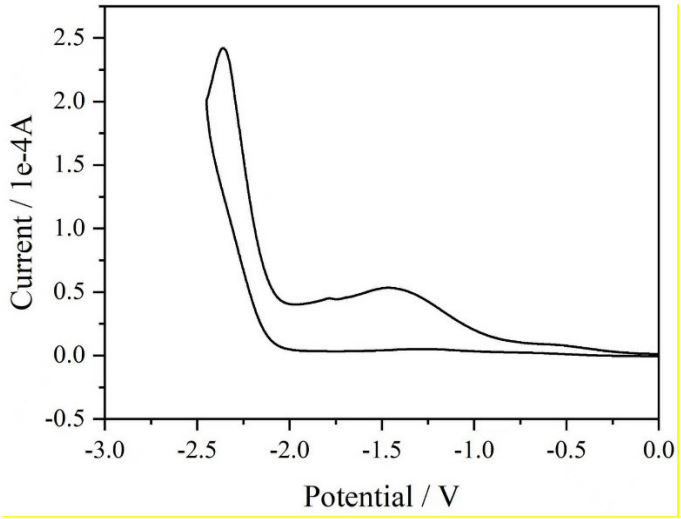


(c) Cyclic voltammetry experiment

Cyclic voltammograms were taken on a CH Instruments 660E potentiostat using a glassy carbon working electrode, an Ag/Ag^+ reference electrode, and a Pt mesh counter electrode. The voltammograms were taken at 20 °C in a 0.1 M CH_3CN solution of tetra-nbutylammonium hexafluorophosphate containing appropriate analytes and ferrocene as an internal standard (for voltammograms with the Ag/Ag+ reference electrode). The scan rate was 0.1 V/s.



Cyclic voltammogram of **1a** in CH_3CN. *E*p = 0.92 V vs. Fc/Fc^+.



Cyclic voltammogram of **2a** in CH_3CN. *E*p = -1.44 vs. Fc/Fc^+.

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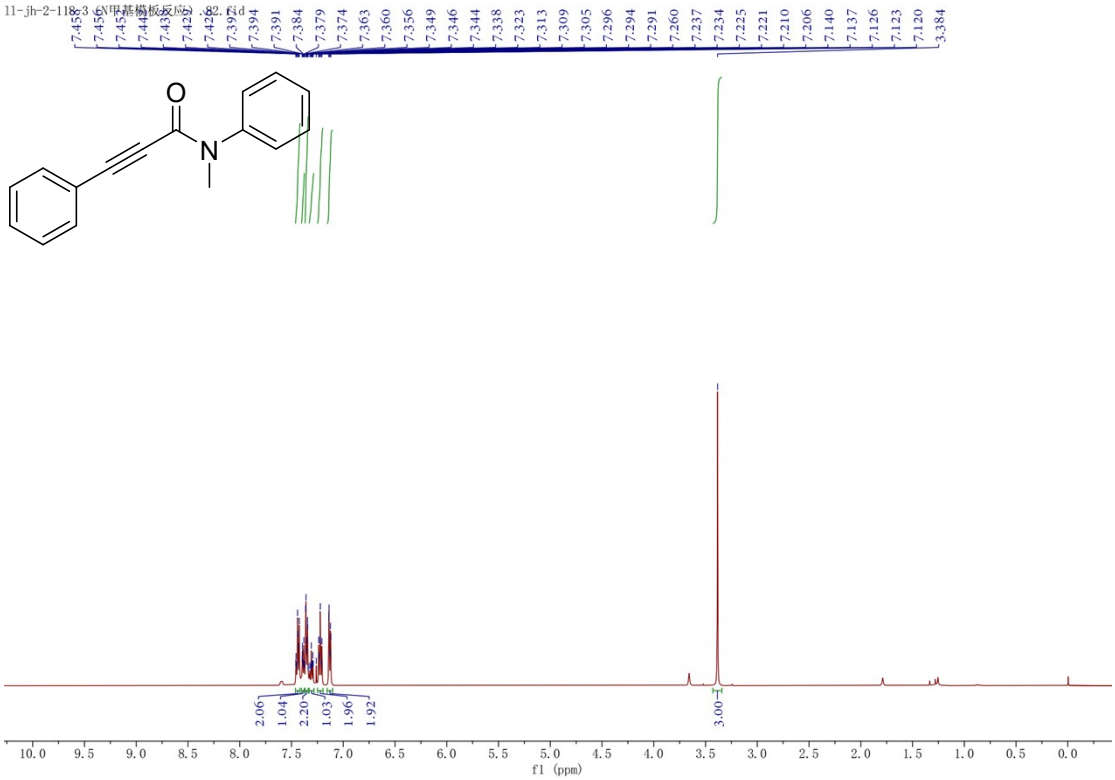
(5) X. Chen, L. Zhang, Y. Tang, S. Yuan, B. Zhu, G. Chen, Xi. Cheng, *Synlett*, **2020**, *31*, 878.

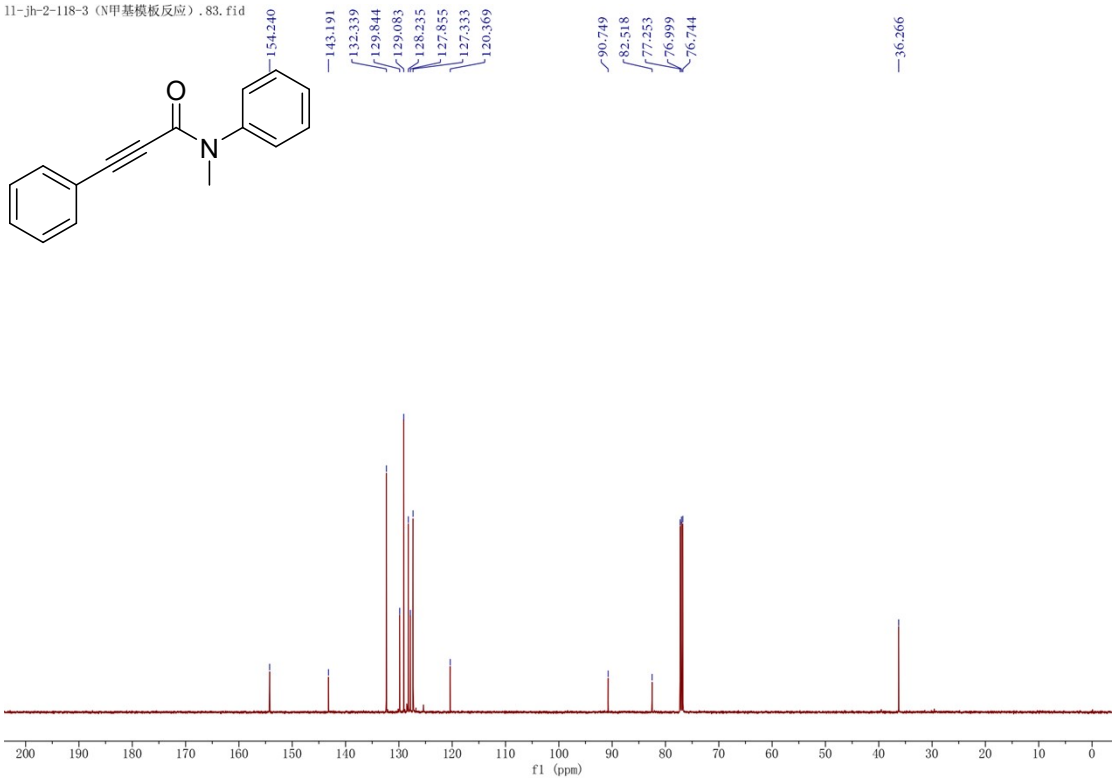
(6) A. Morinaga, K. Nagao, H. Ohmiya, M. Sawamura, *Angew. Chem. Int. Ed.*, **2015**, 54, 15859.

NMR Spectra of substrates and Products

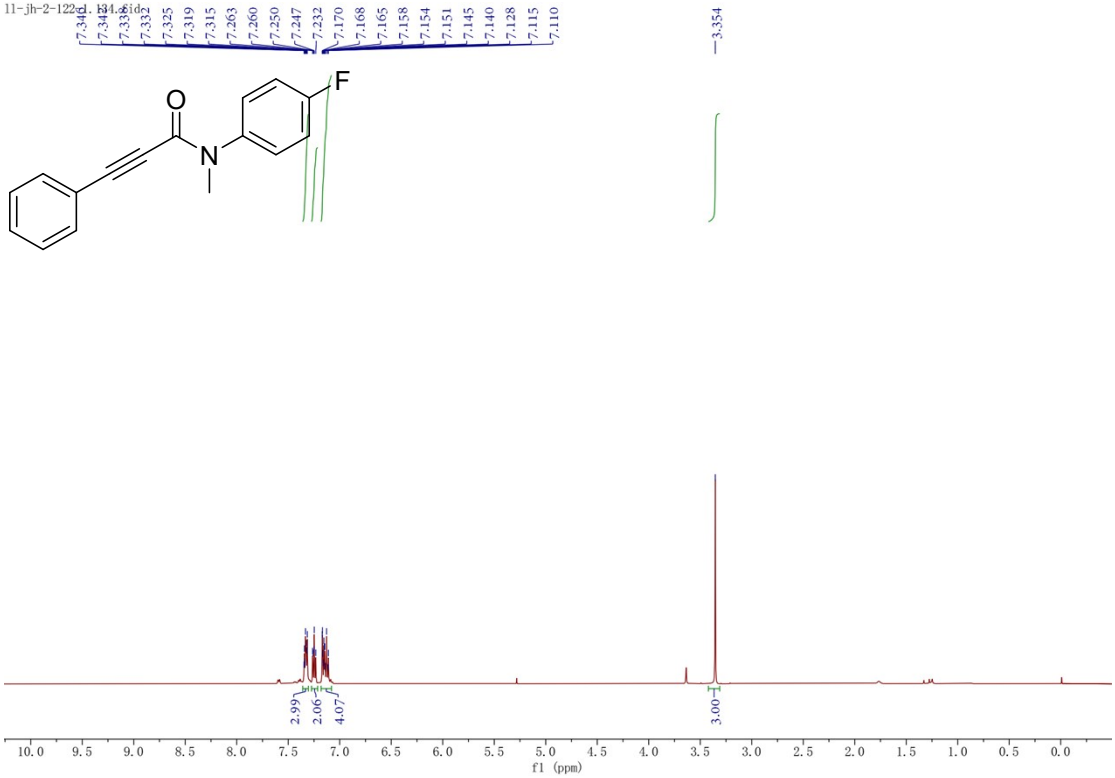
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3aa**



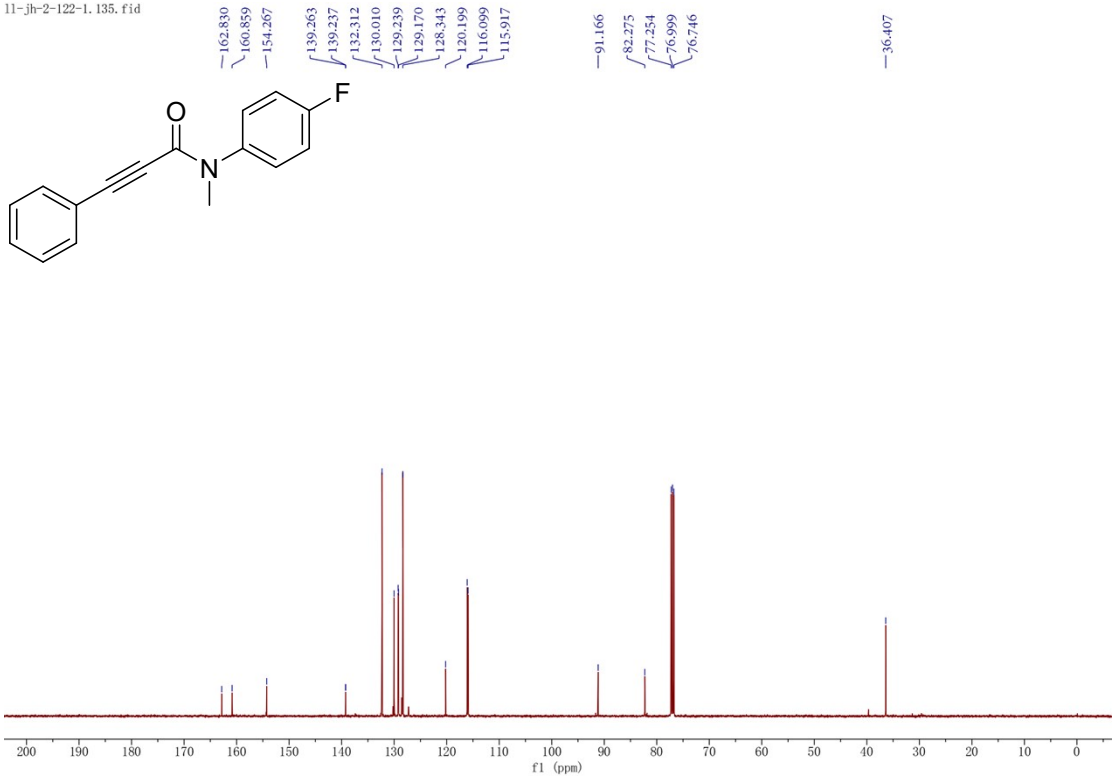
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3aa**



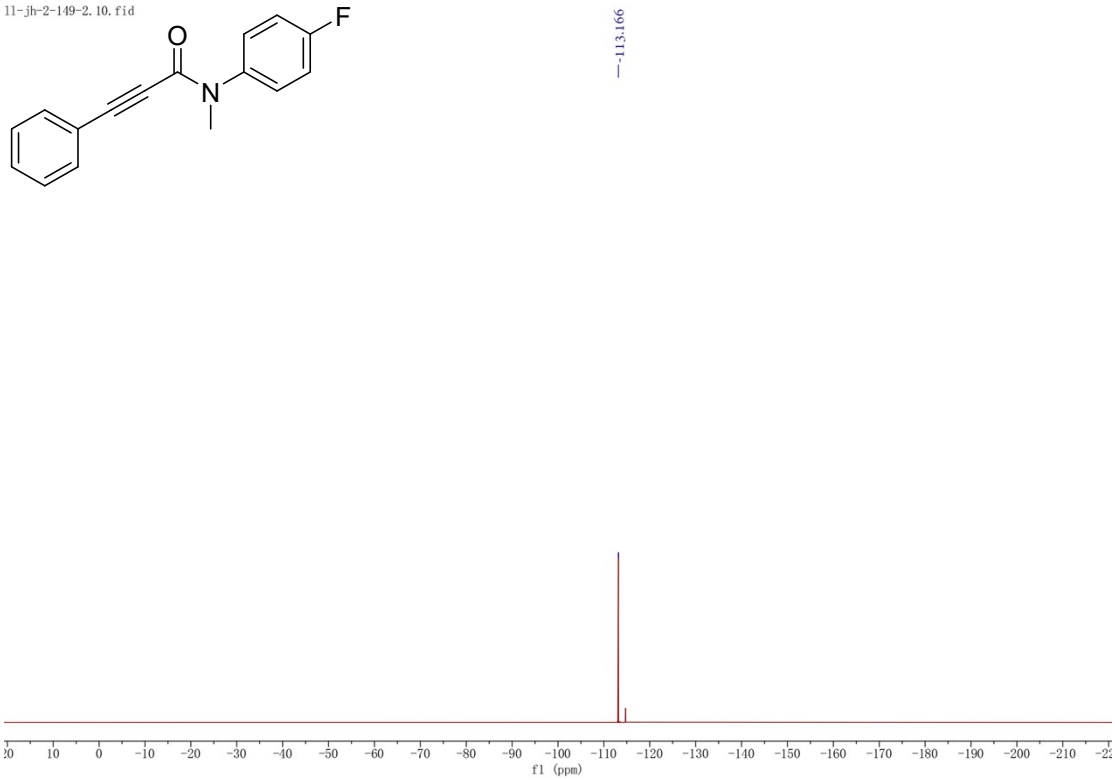
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ba**



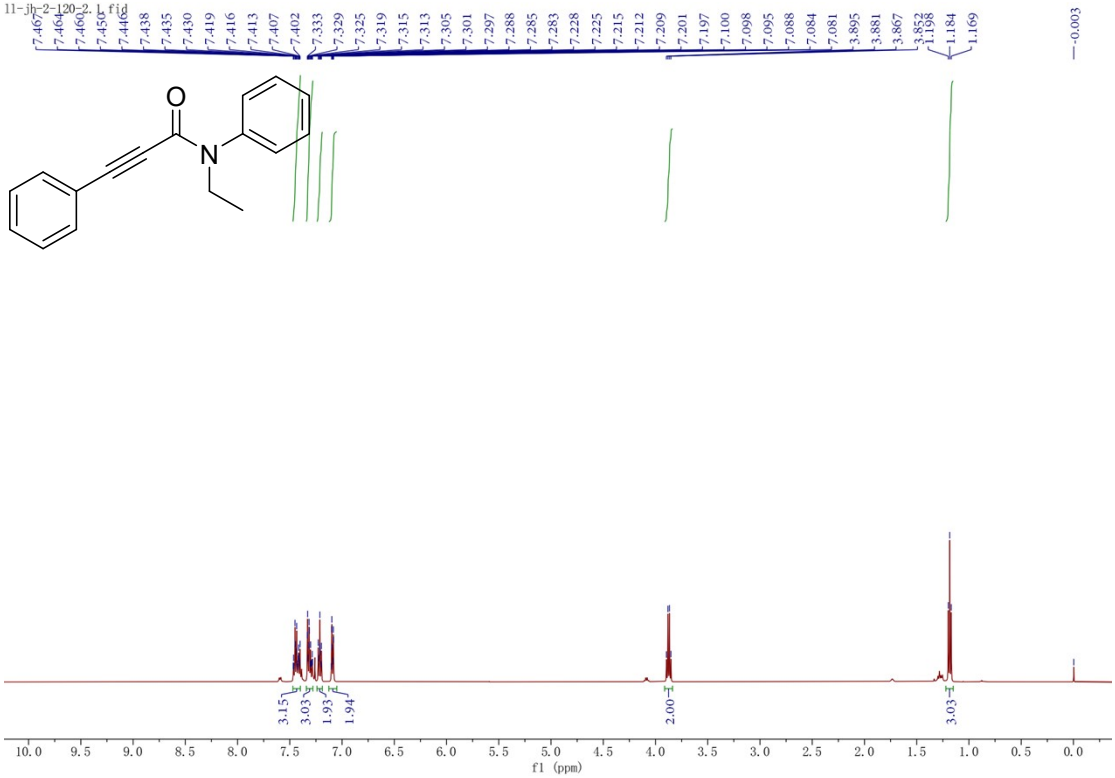
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ba**



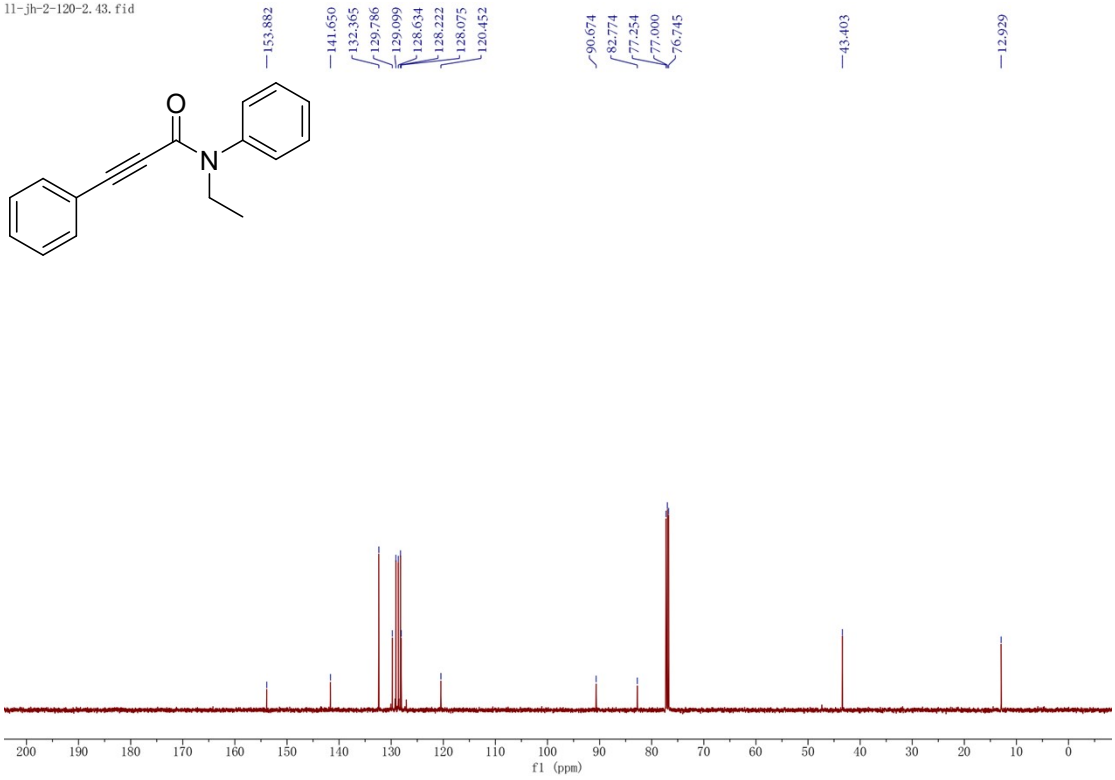
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3ba**



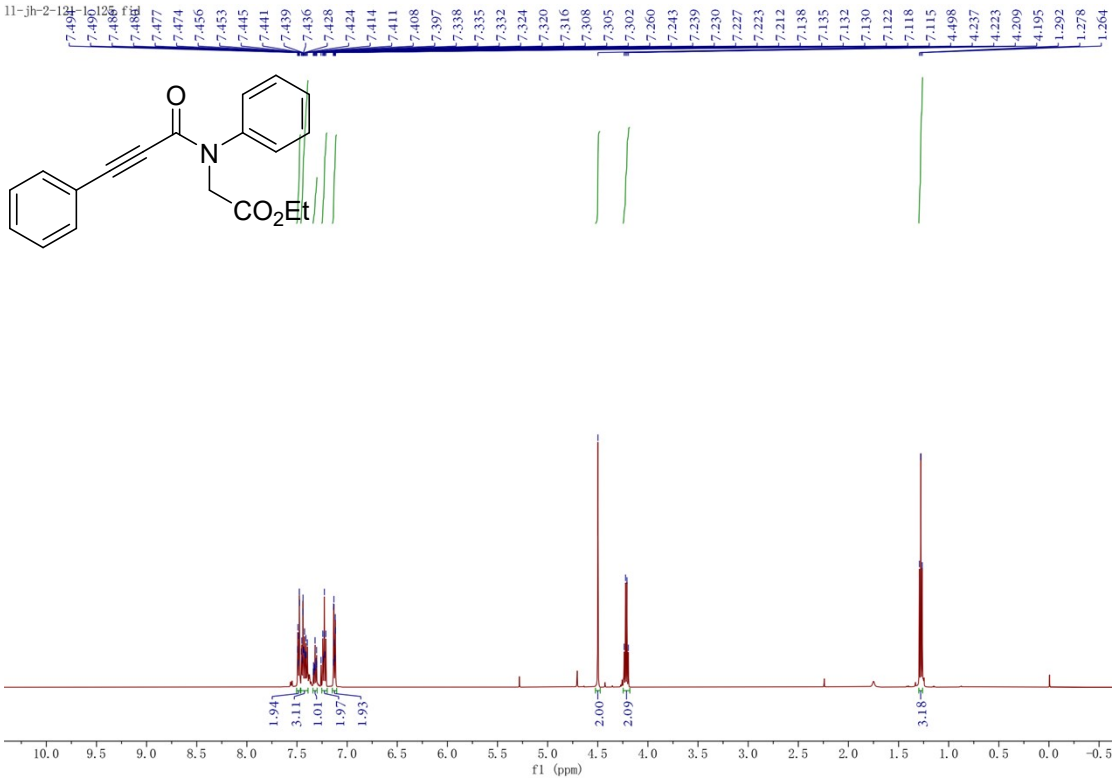
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ca**



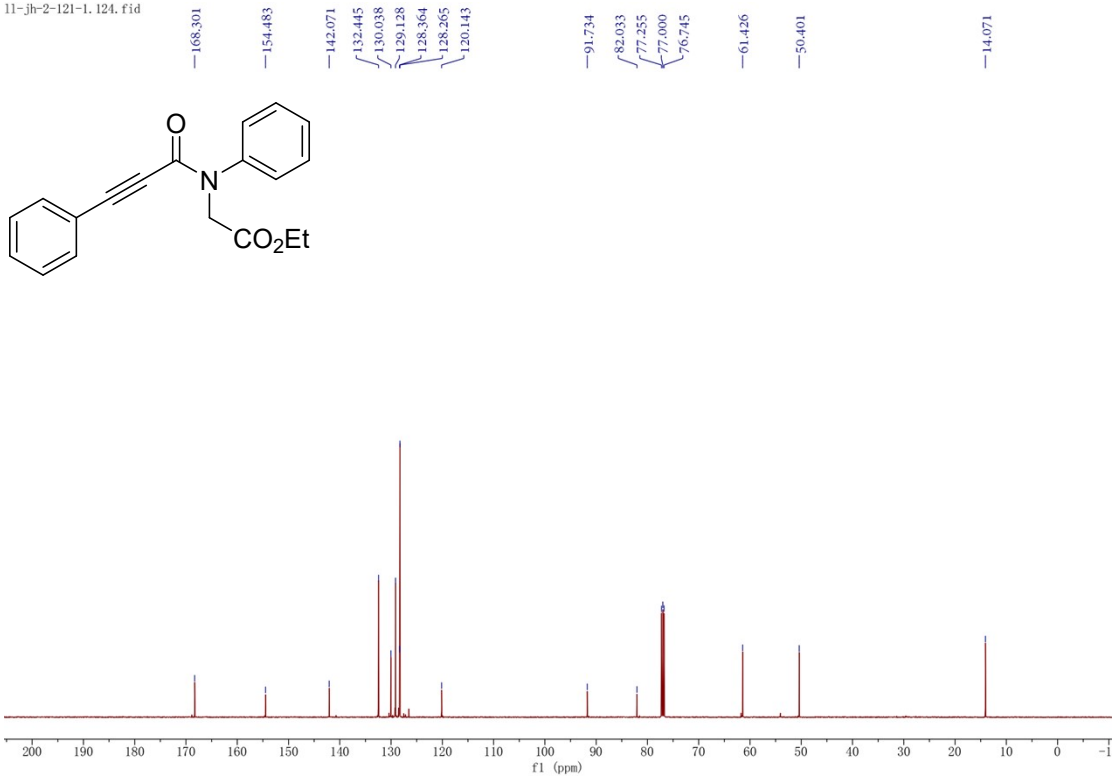
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ca**



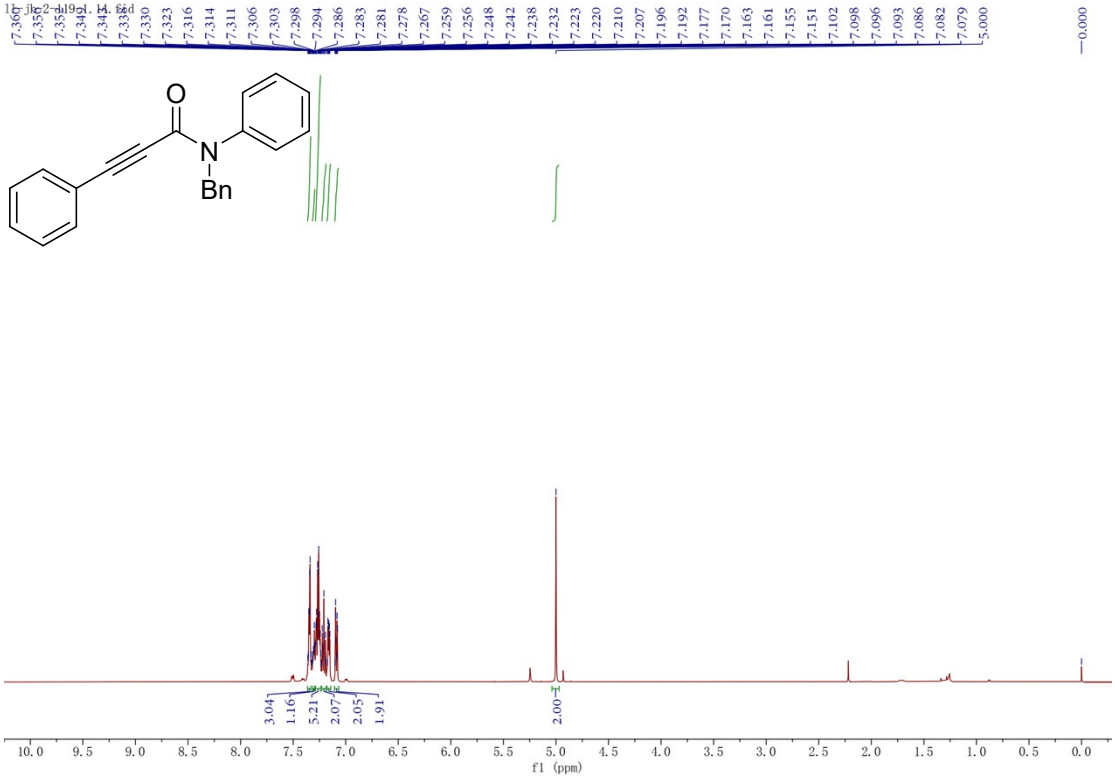
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3da**



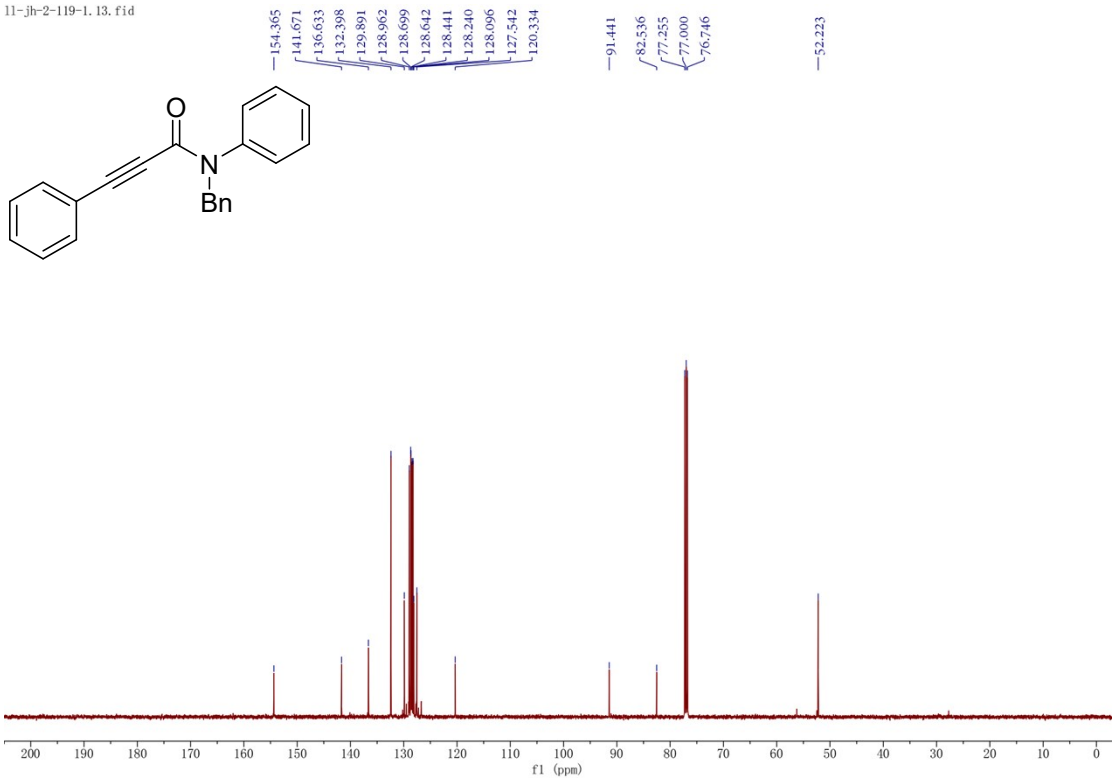
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3da**



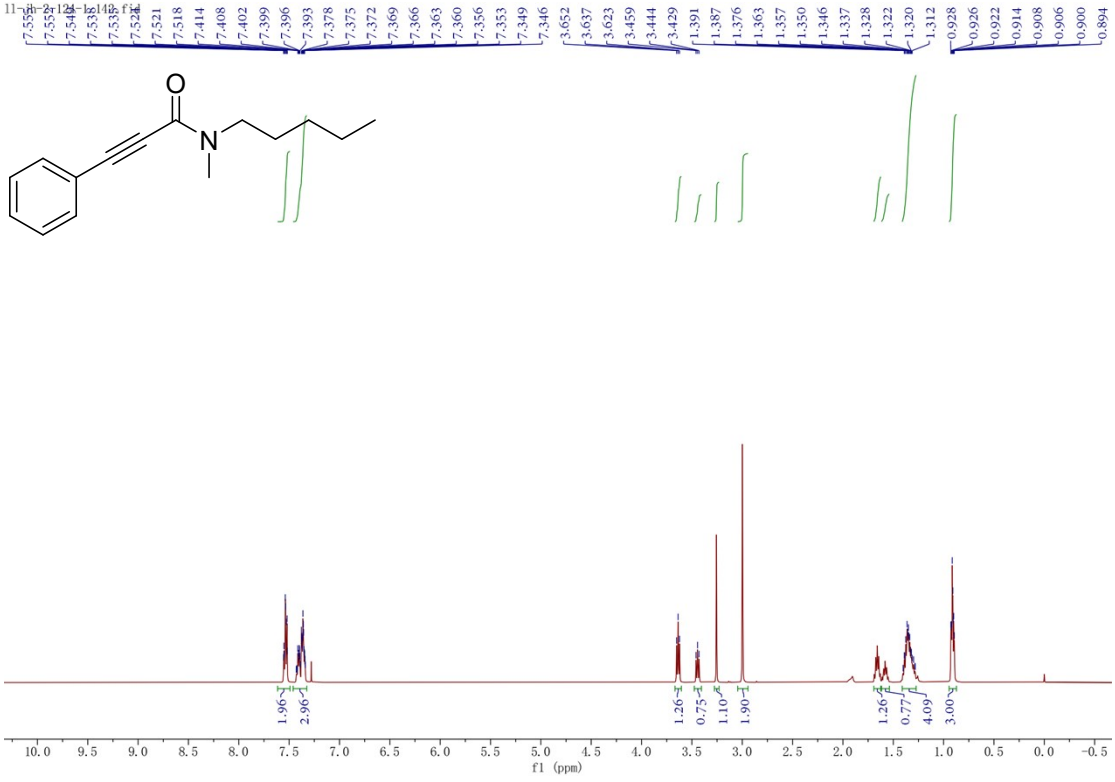
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ea**



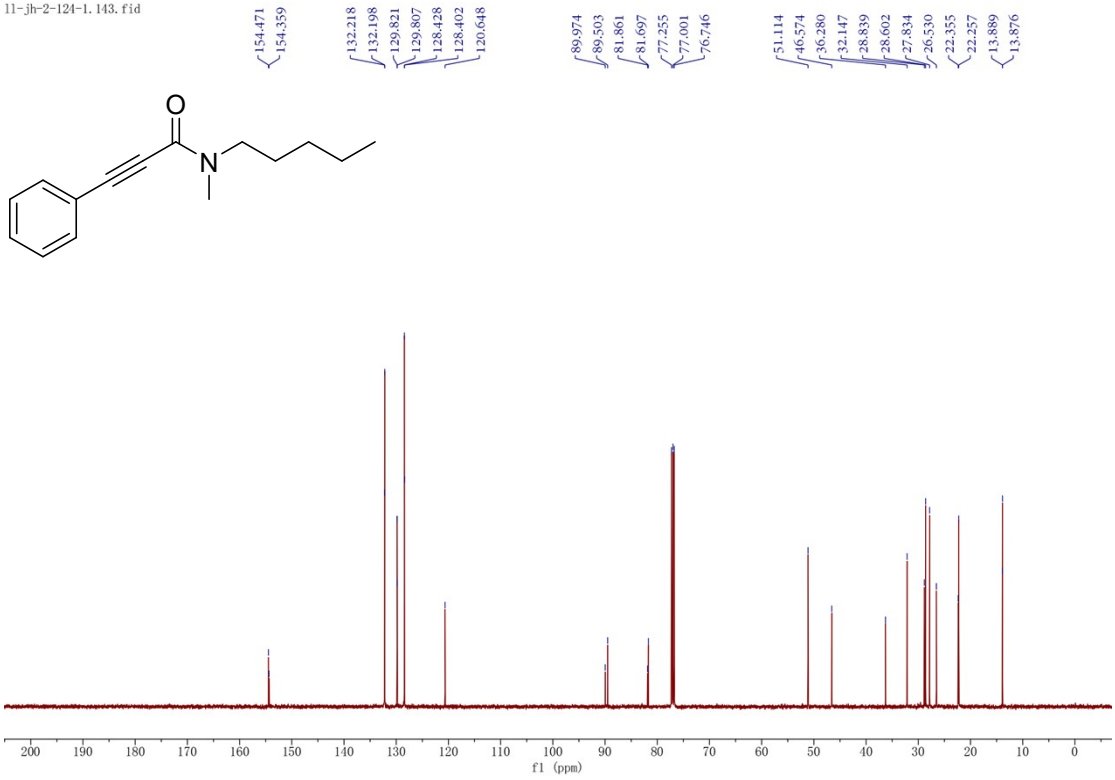
^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **3ea**



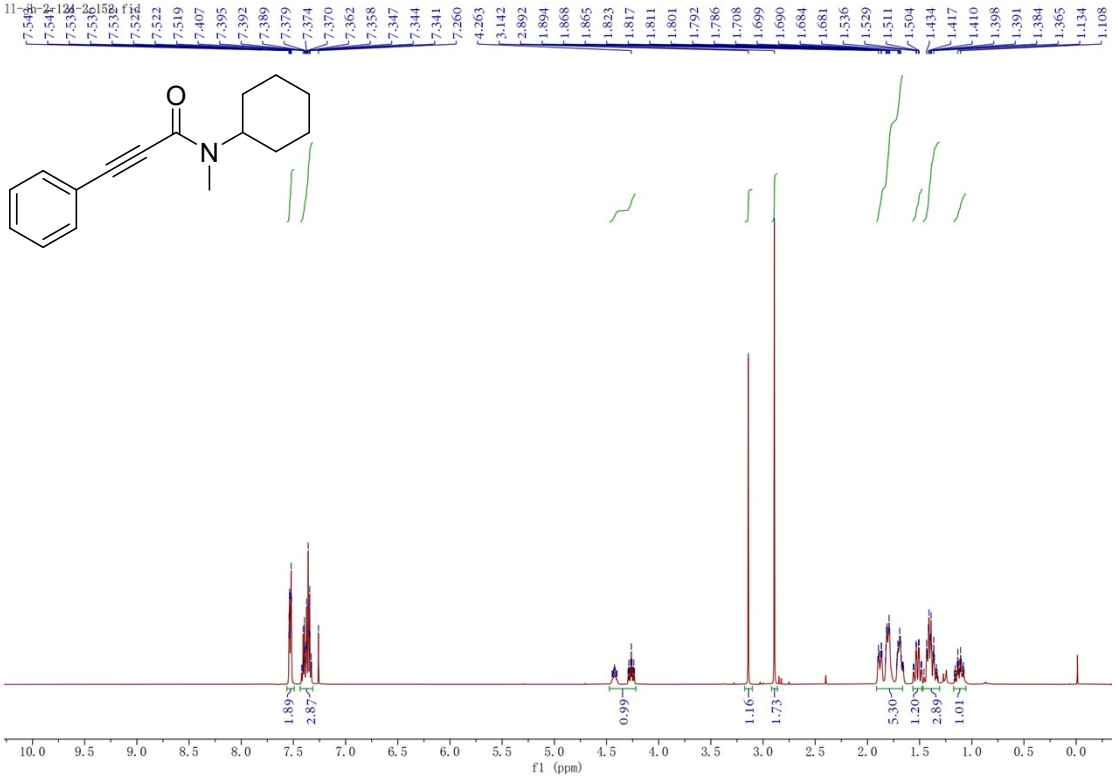
^{1}H **NMR**-spectrum (500 MHz, $CDCl_3$) of **3fa**



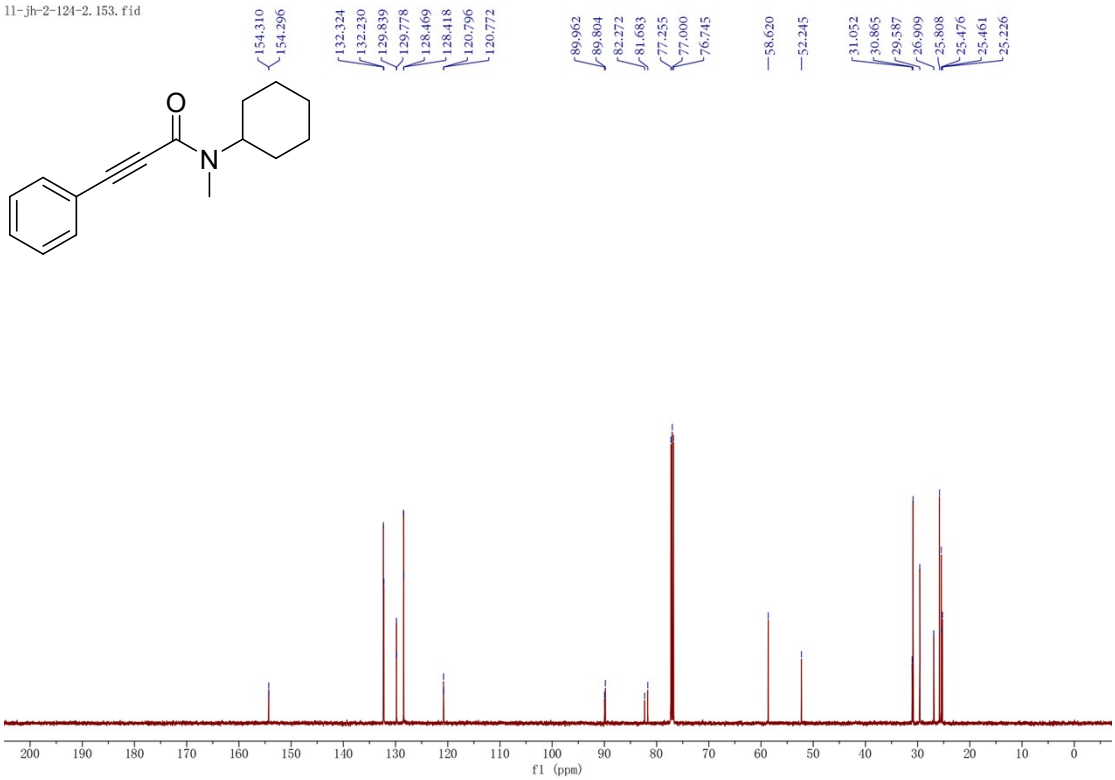
^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **3fa**



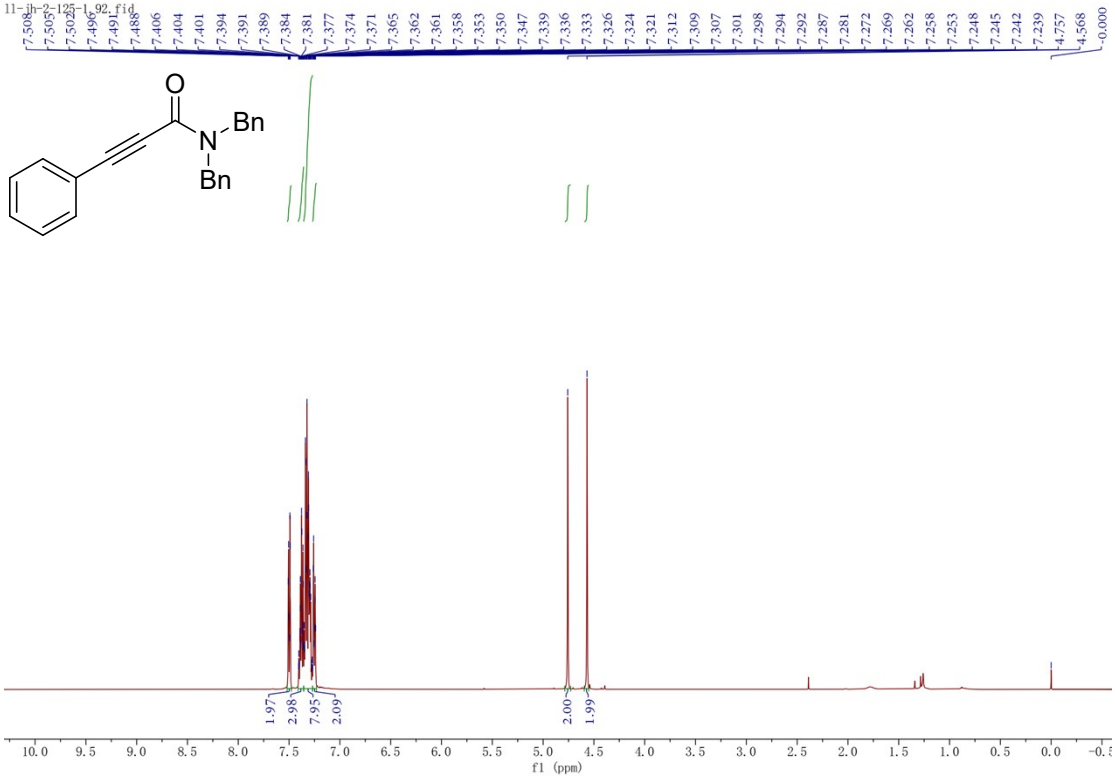
^{1}H **NMR**-spectrum (500 MHz, $CDCl_3$) of **3ga**



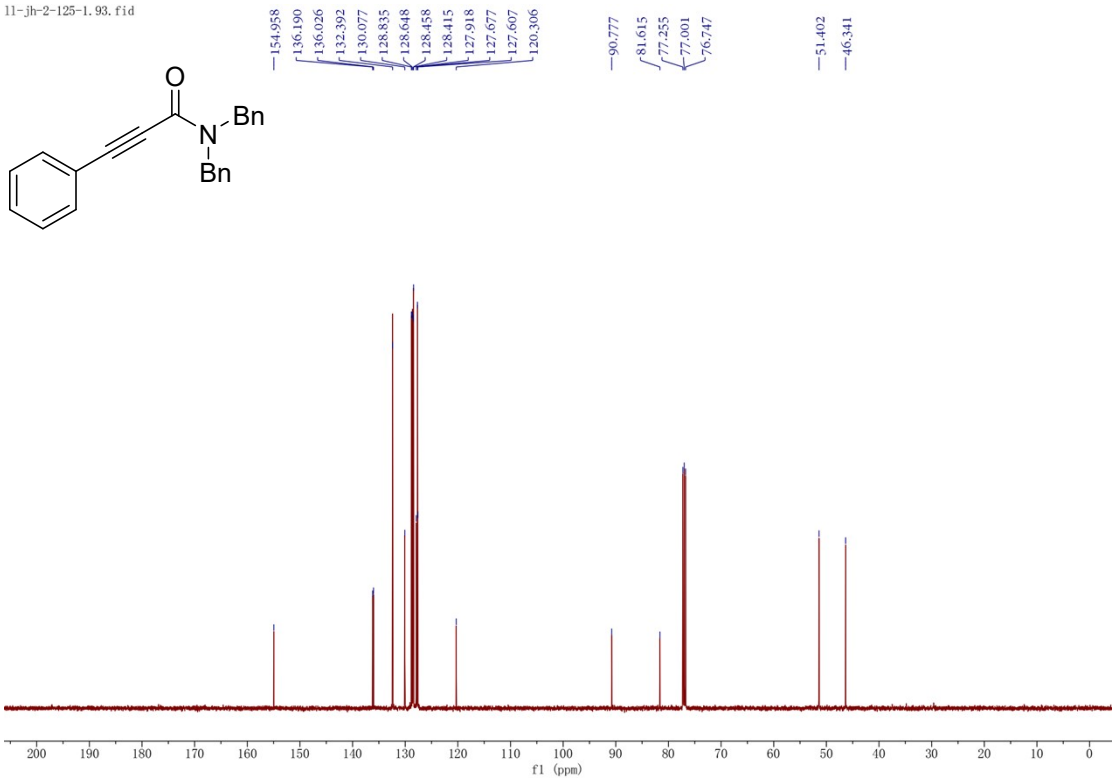
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ga**



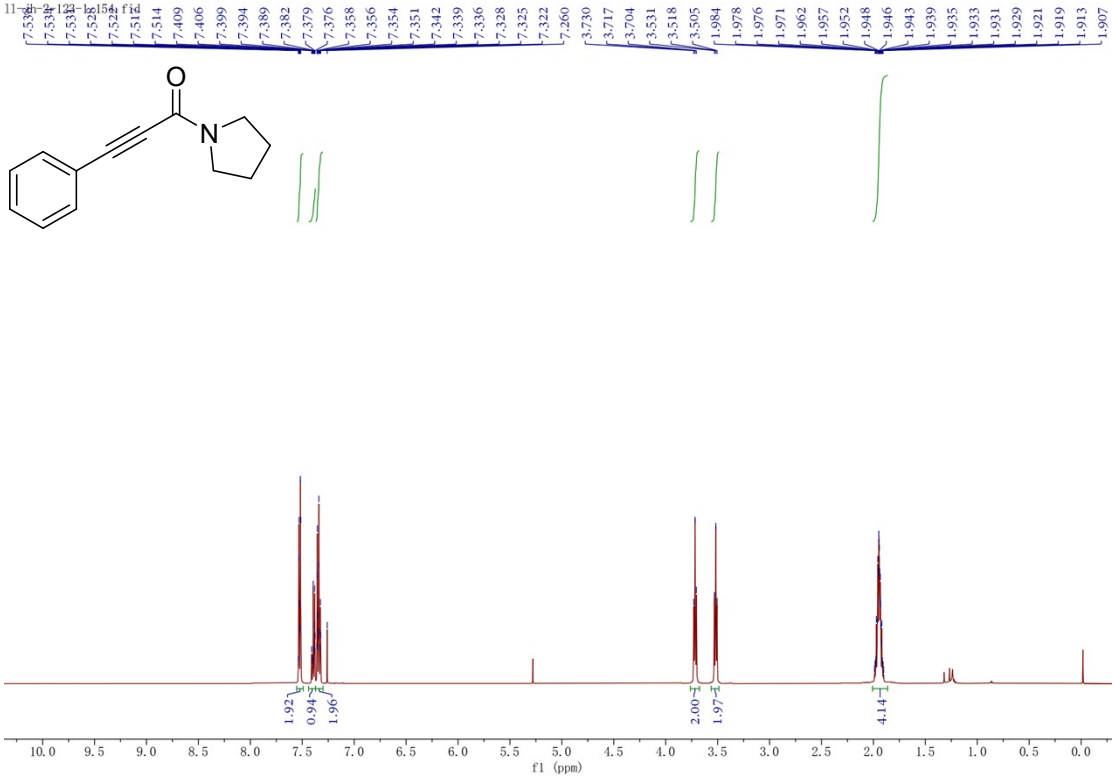
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ha**



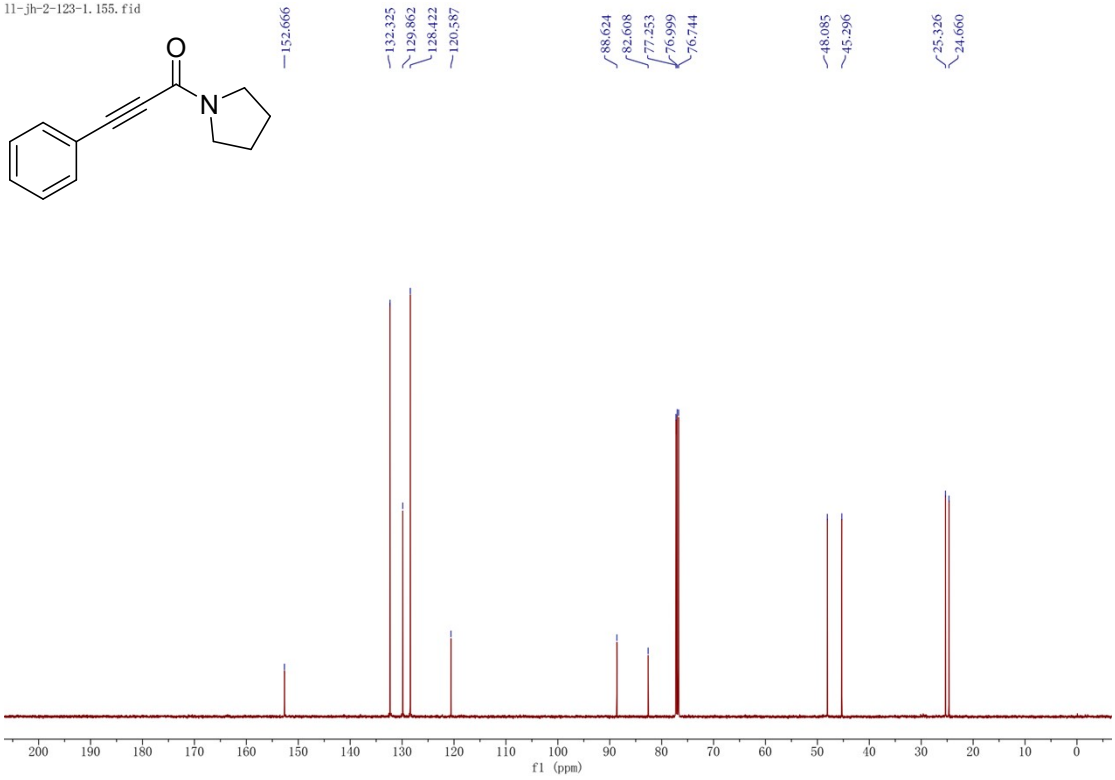
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ha**



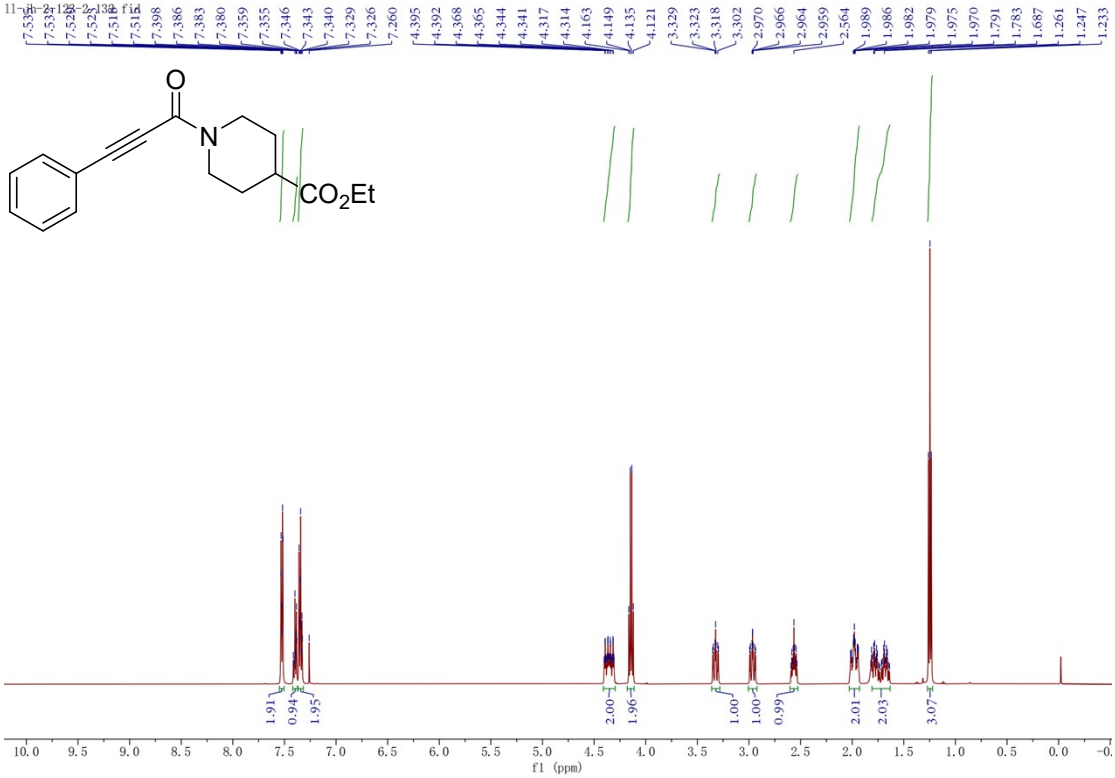
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ia**



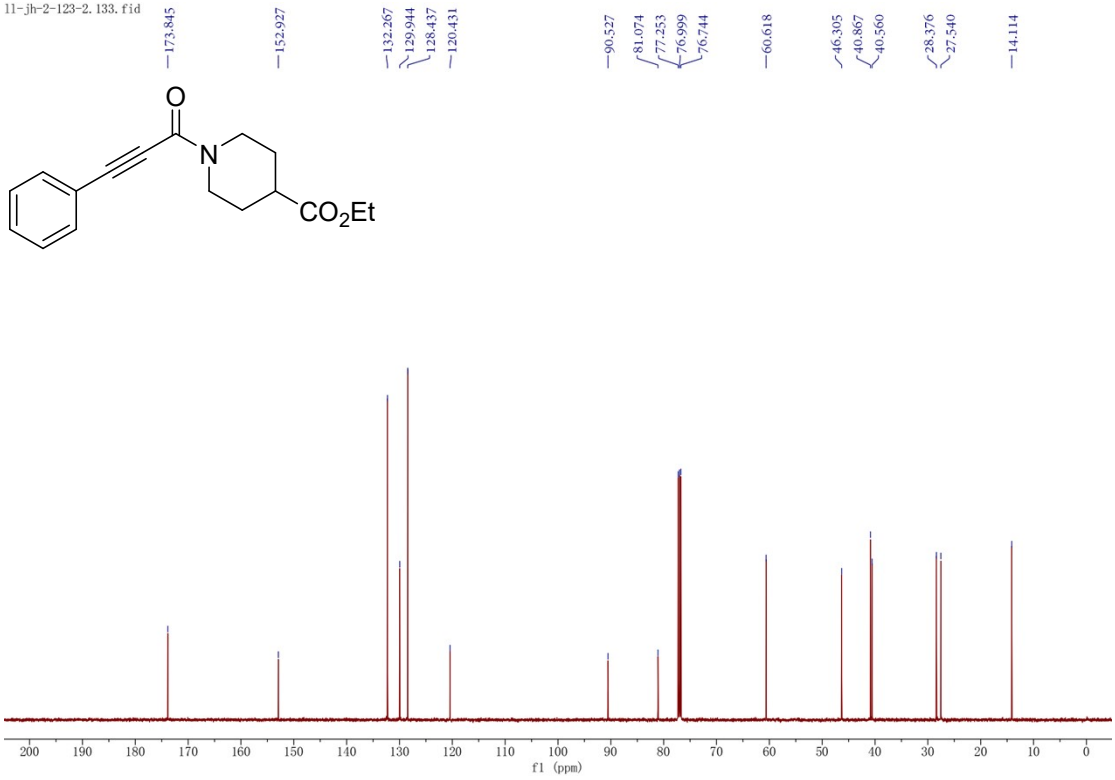
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ia**



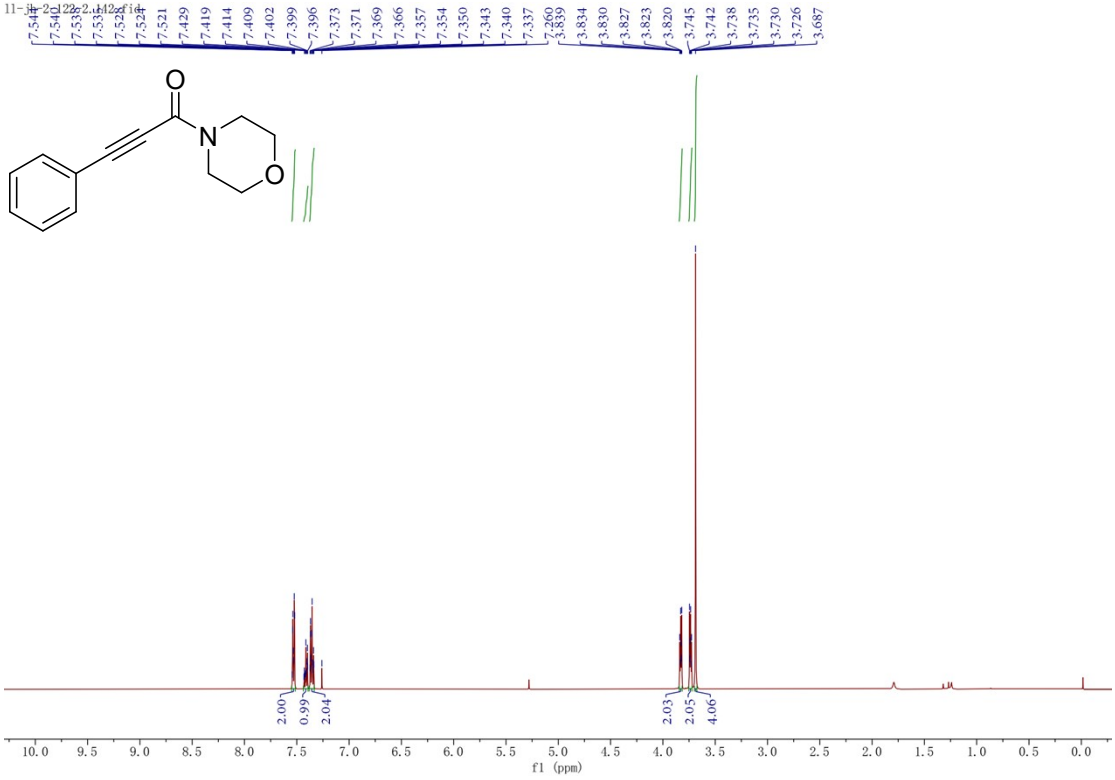
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ja**



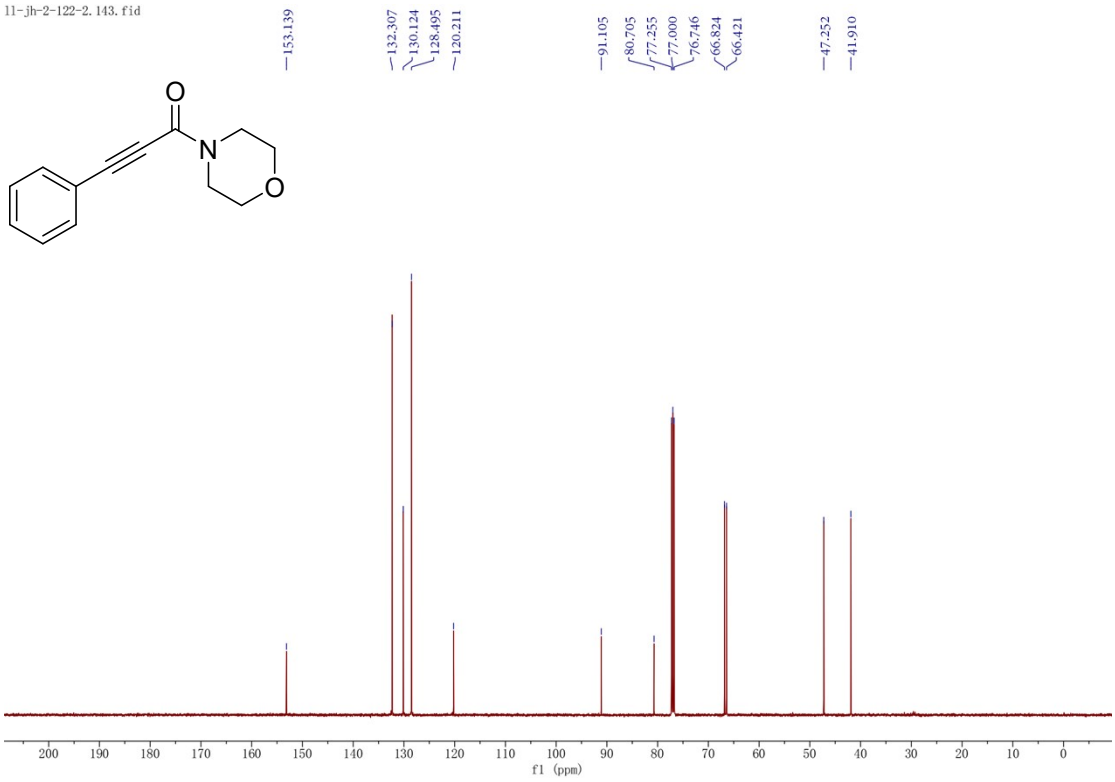
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ja**



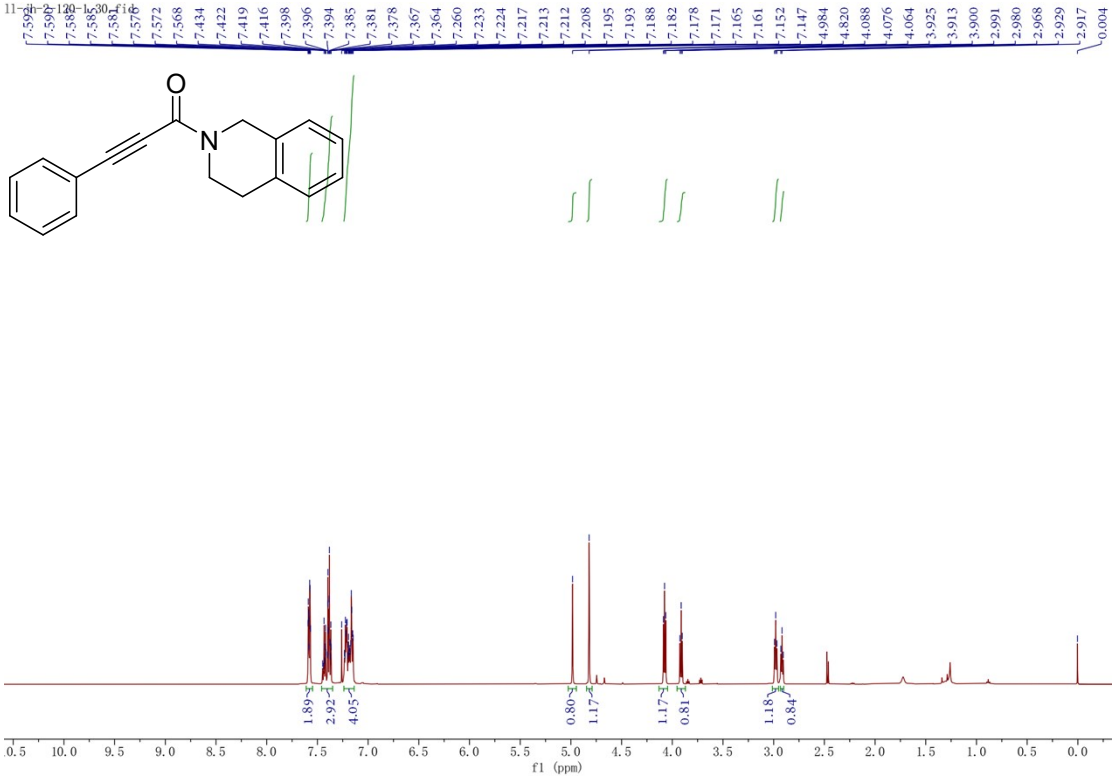
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ka**



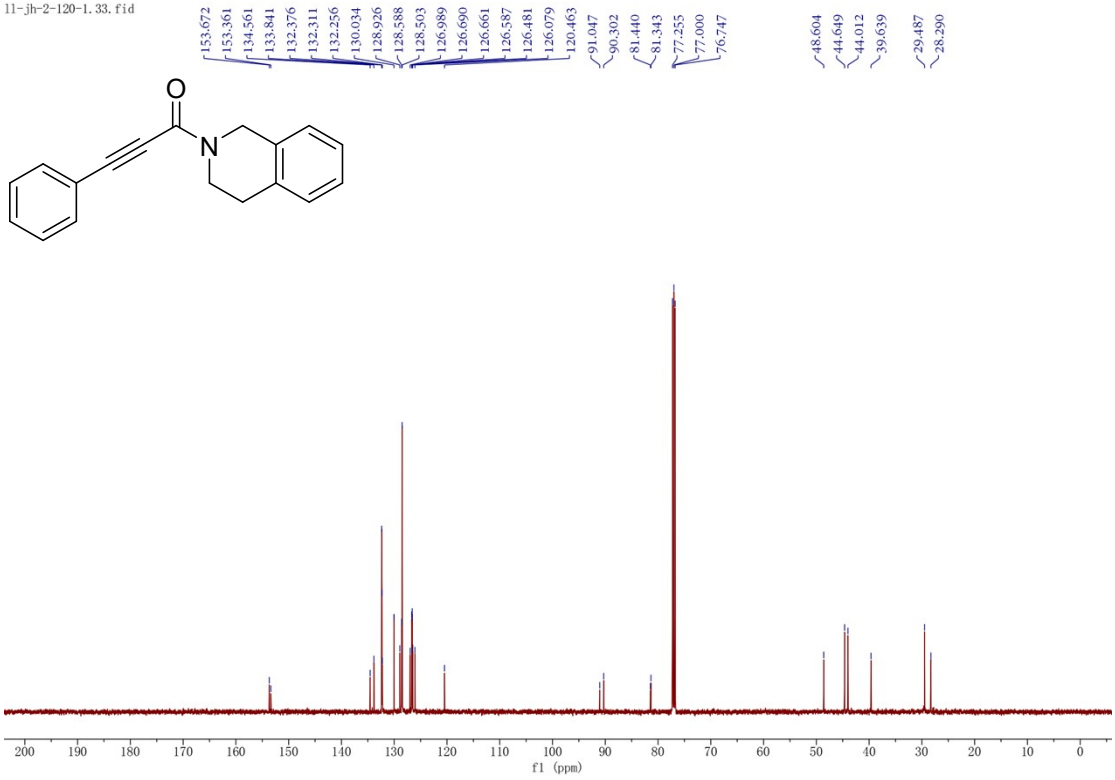
^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **3ka**



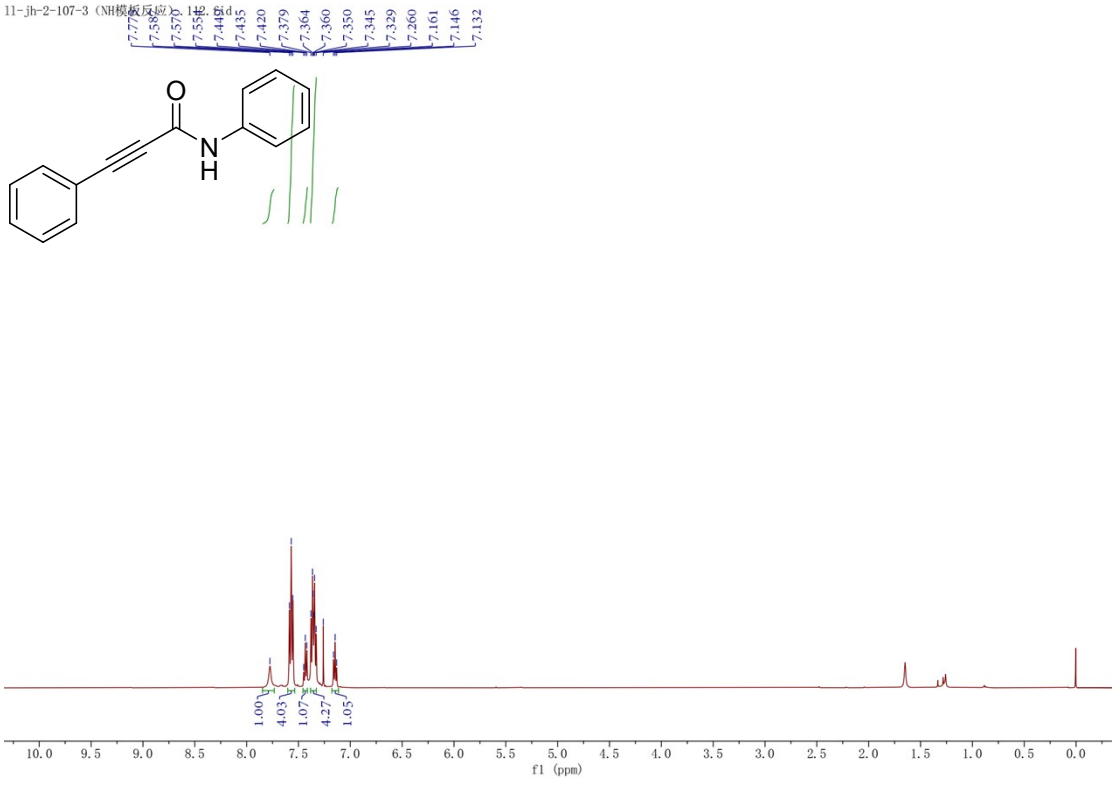
^{1}H **NMR**-spectrum (500 MHz, $CDCl_3$) of **3la**



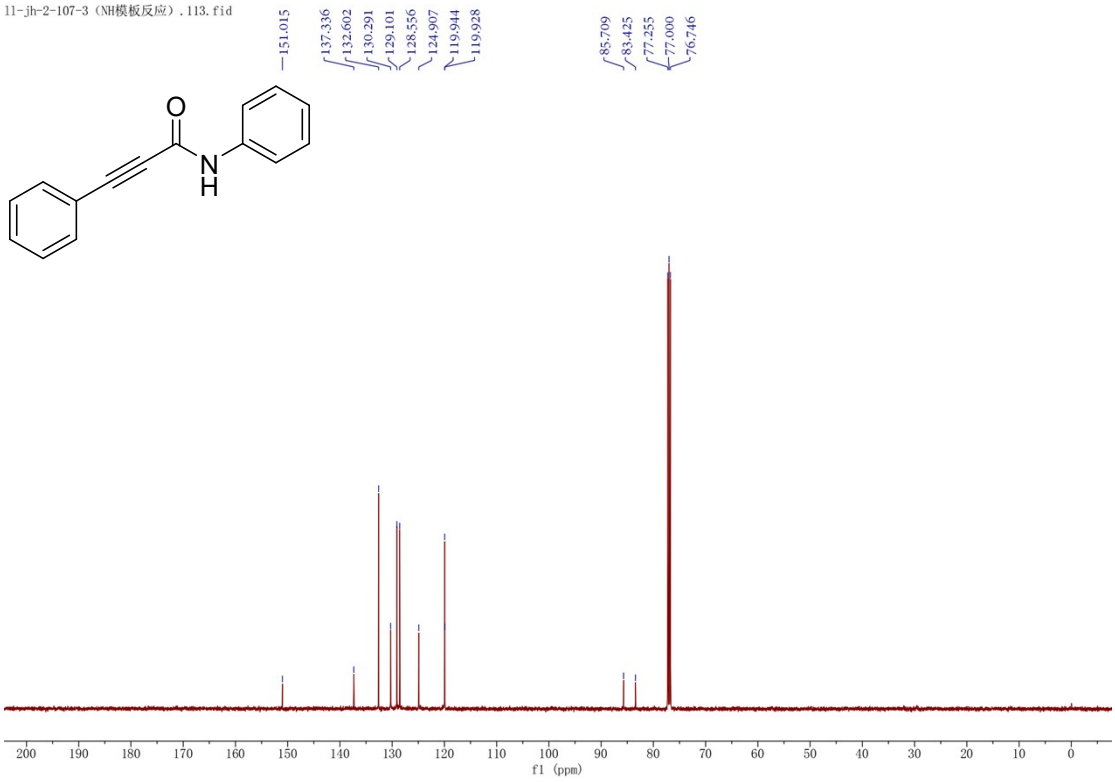
^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **3la**



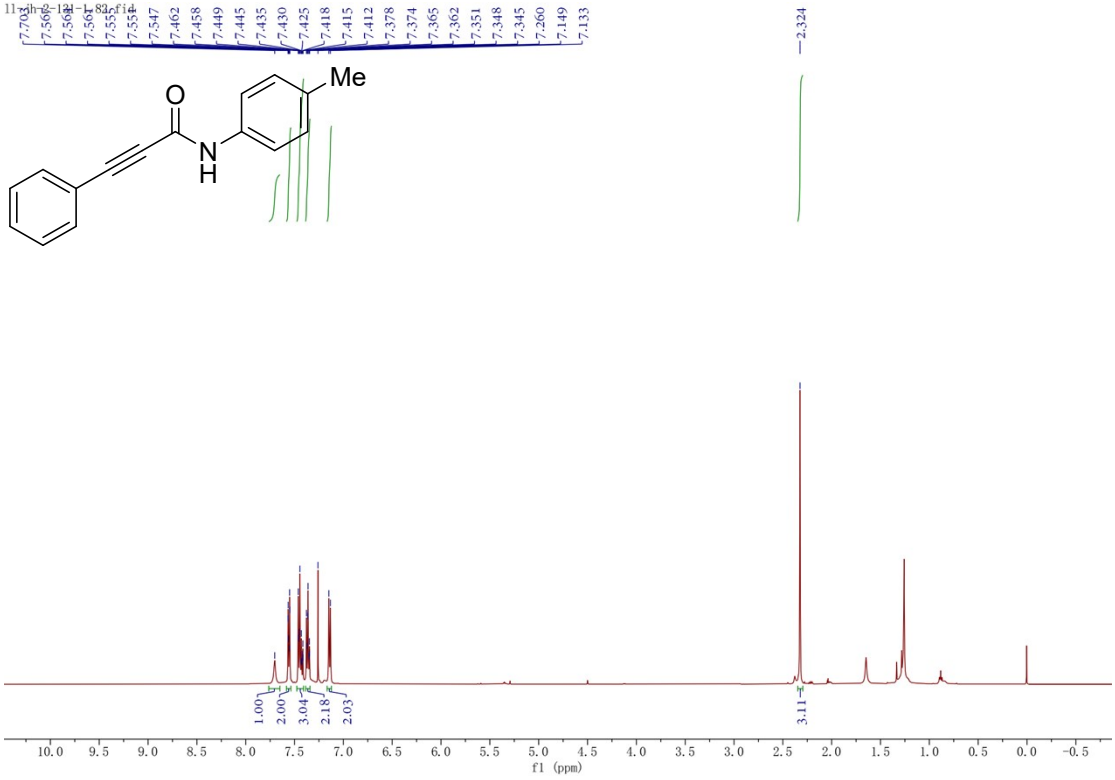
^{1}H **NMR**-spectrum (500 MHz, $CDCl_3$) of **3ma**



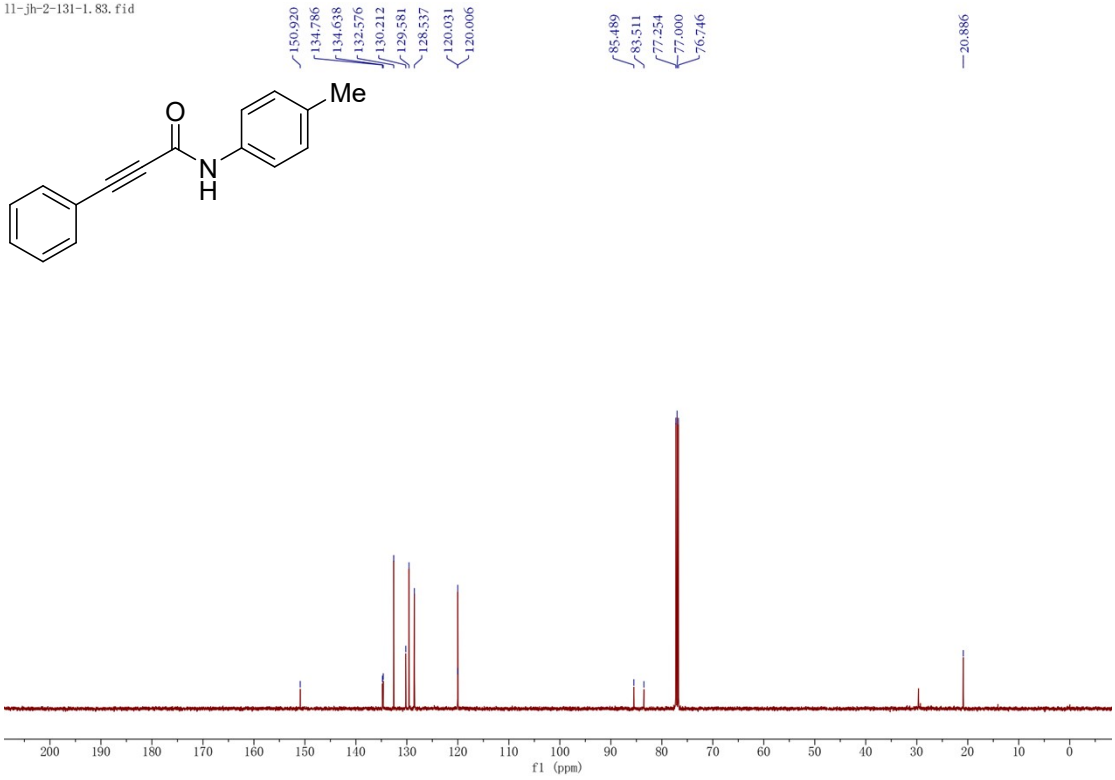
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ma**



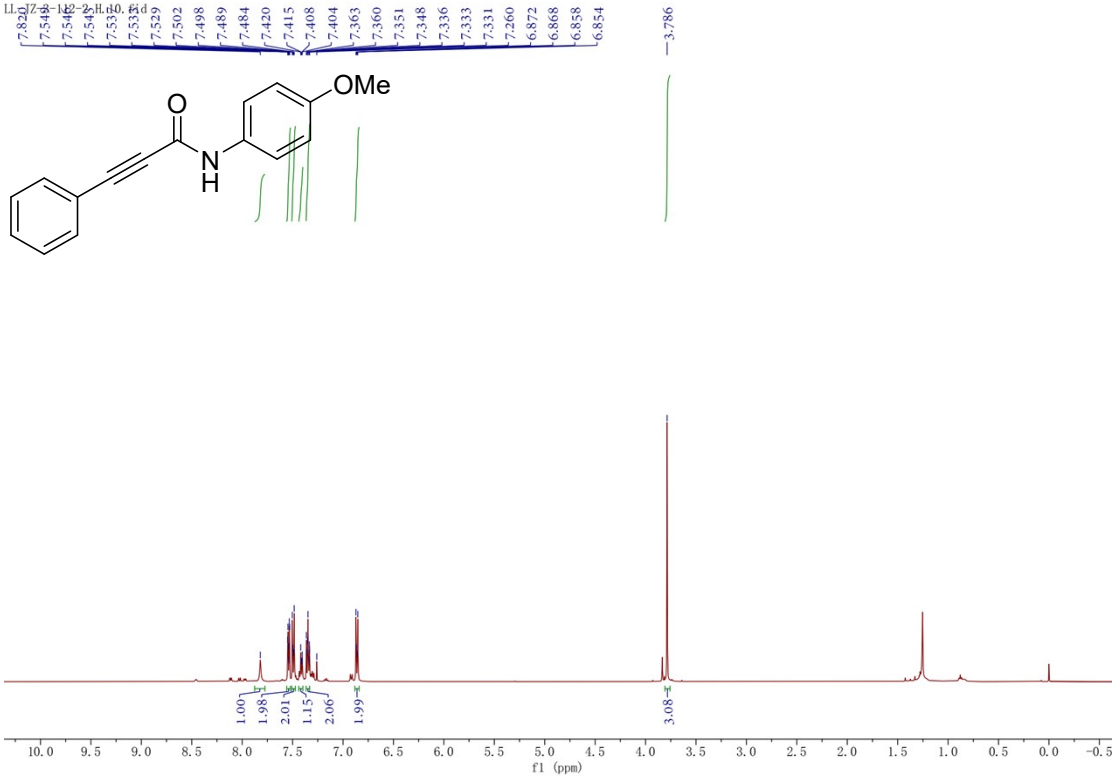
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3na**



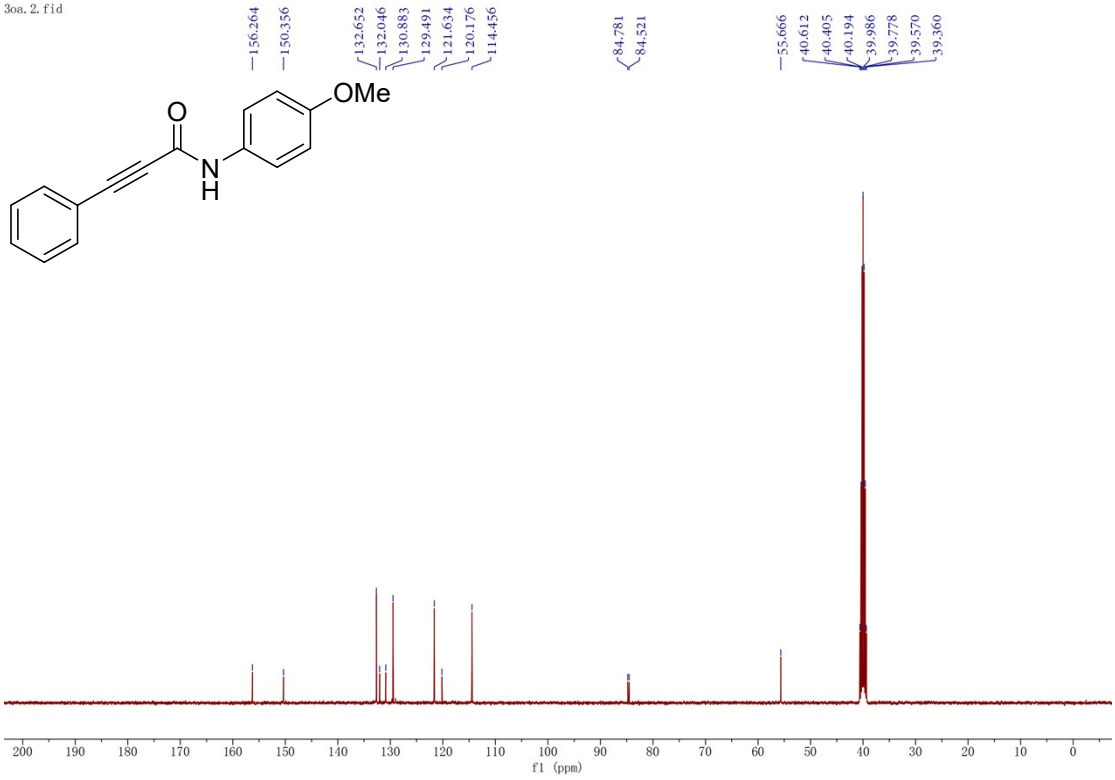
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3na**



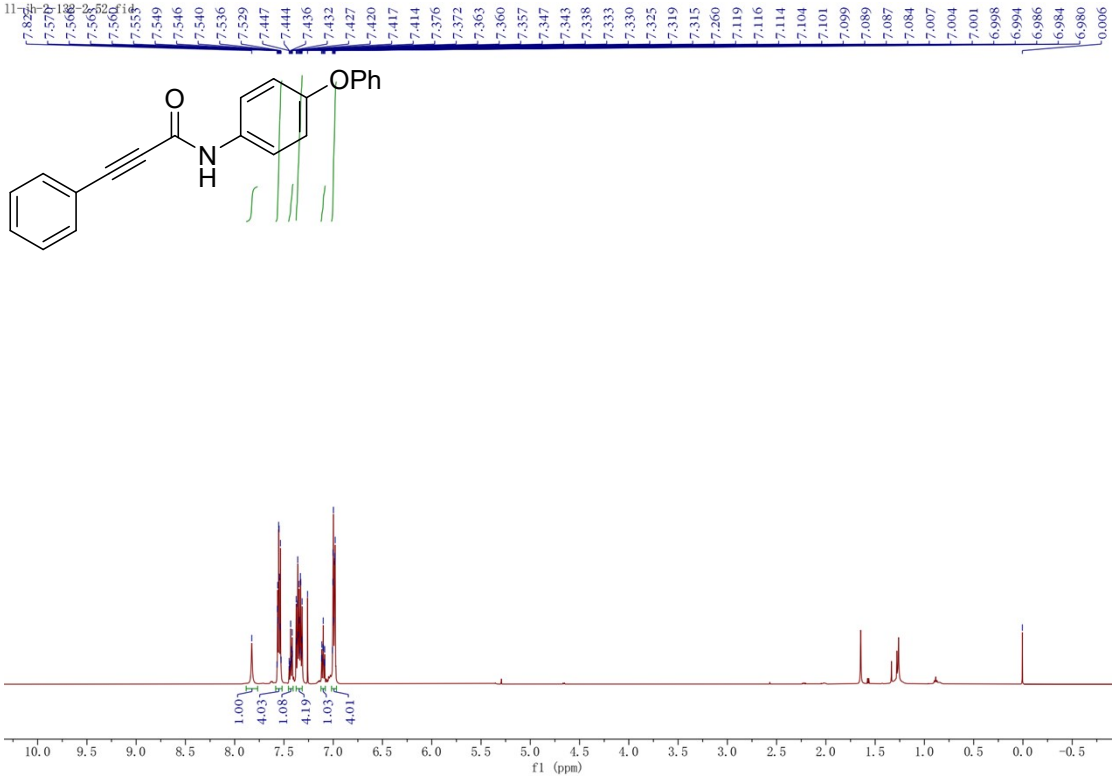
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3oa**



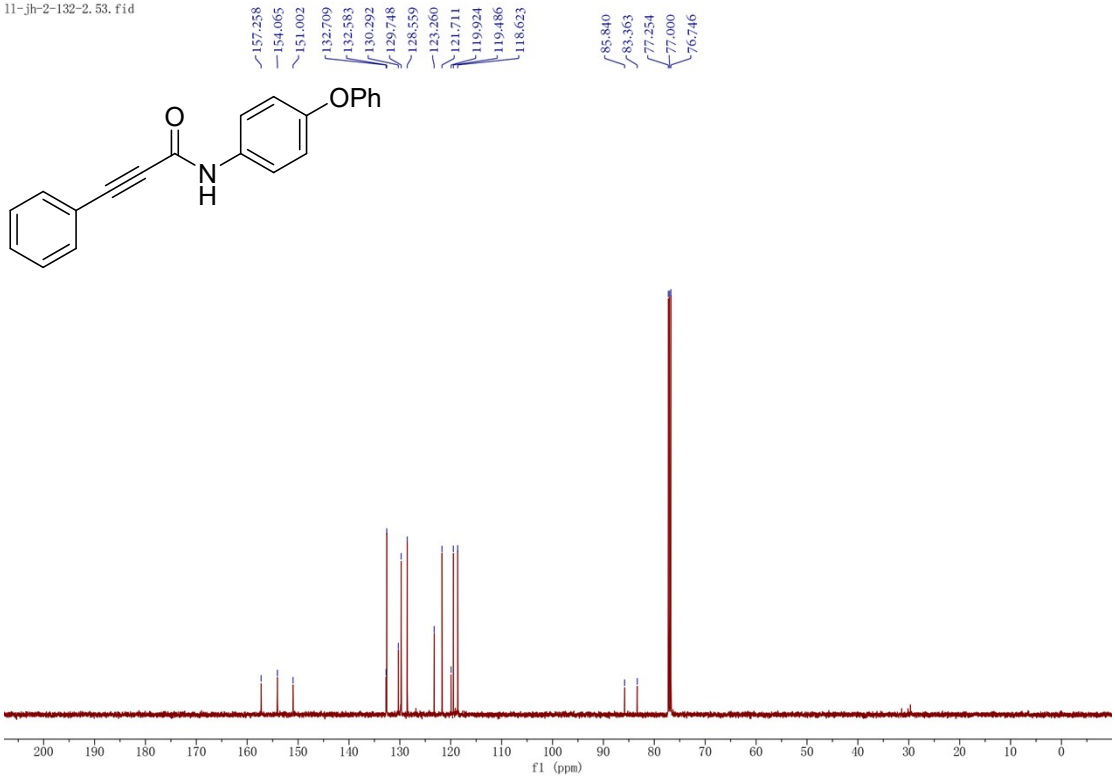
^{13}C NMR-spectrum (100 MHz, DMSO-d_6) of **3oa**



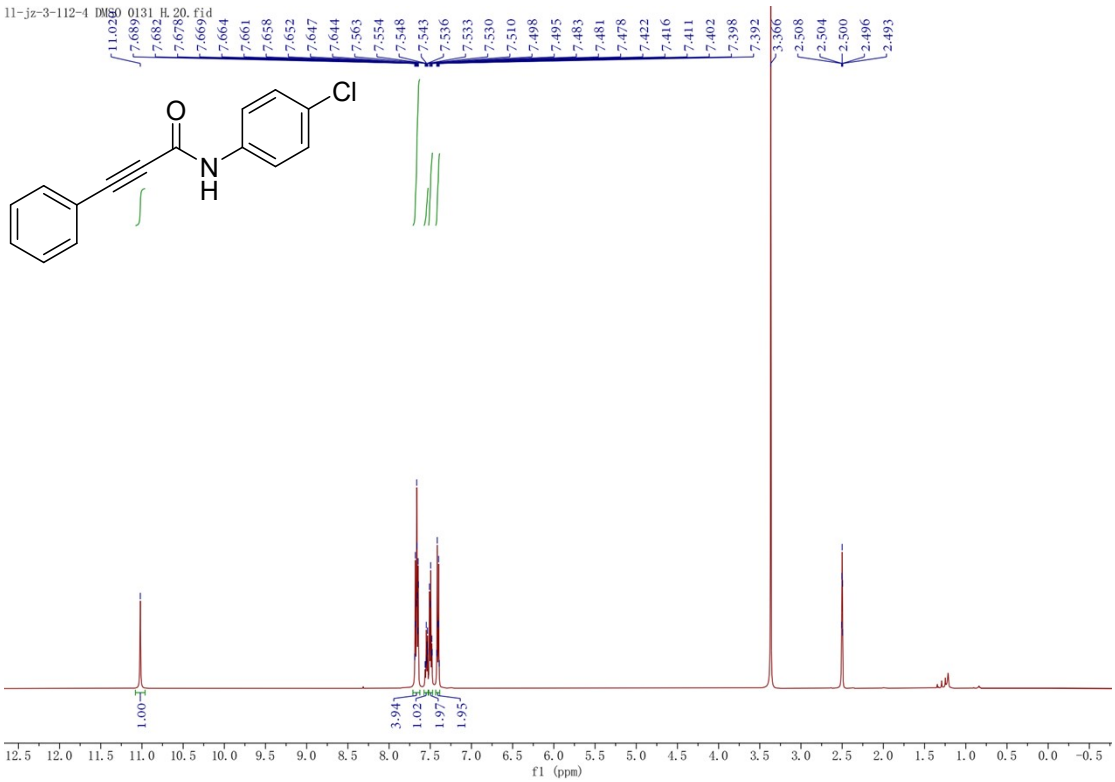
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3pa**



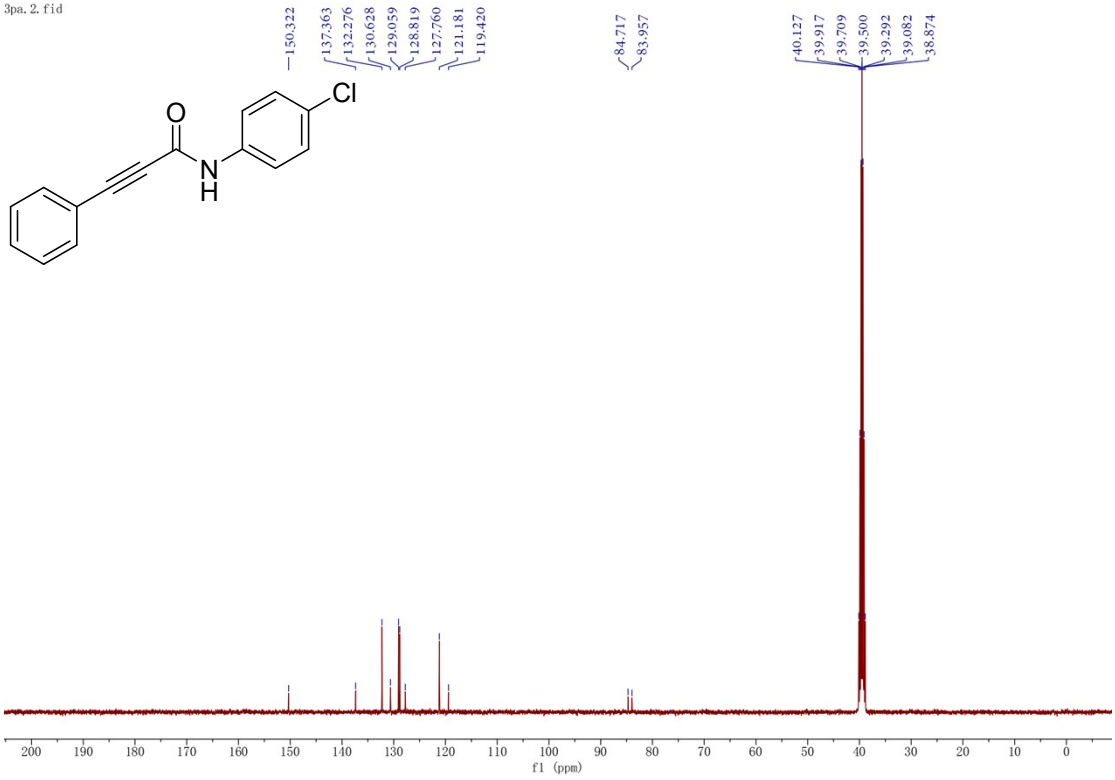
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3pa**



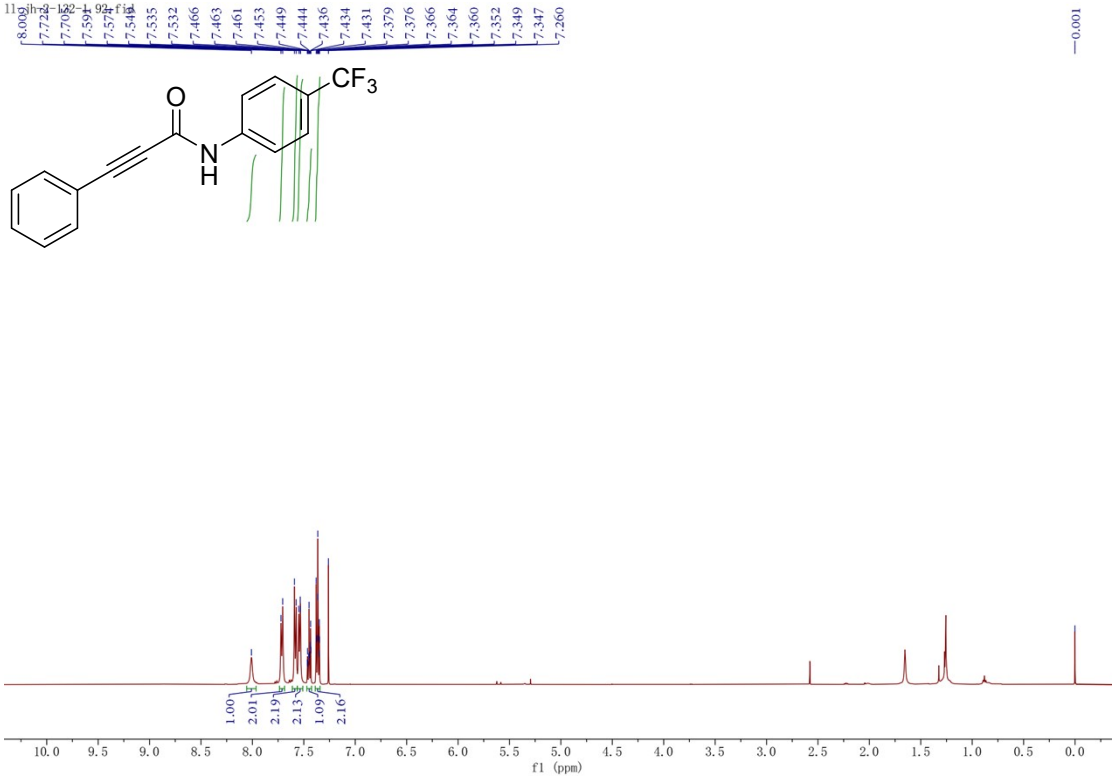
^{1}H NMR-spectrum (500 MHz, DMSO-d_6) of **3qa**



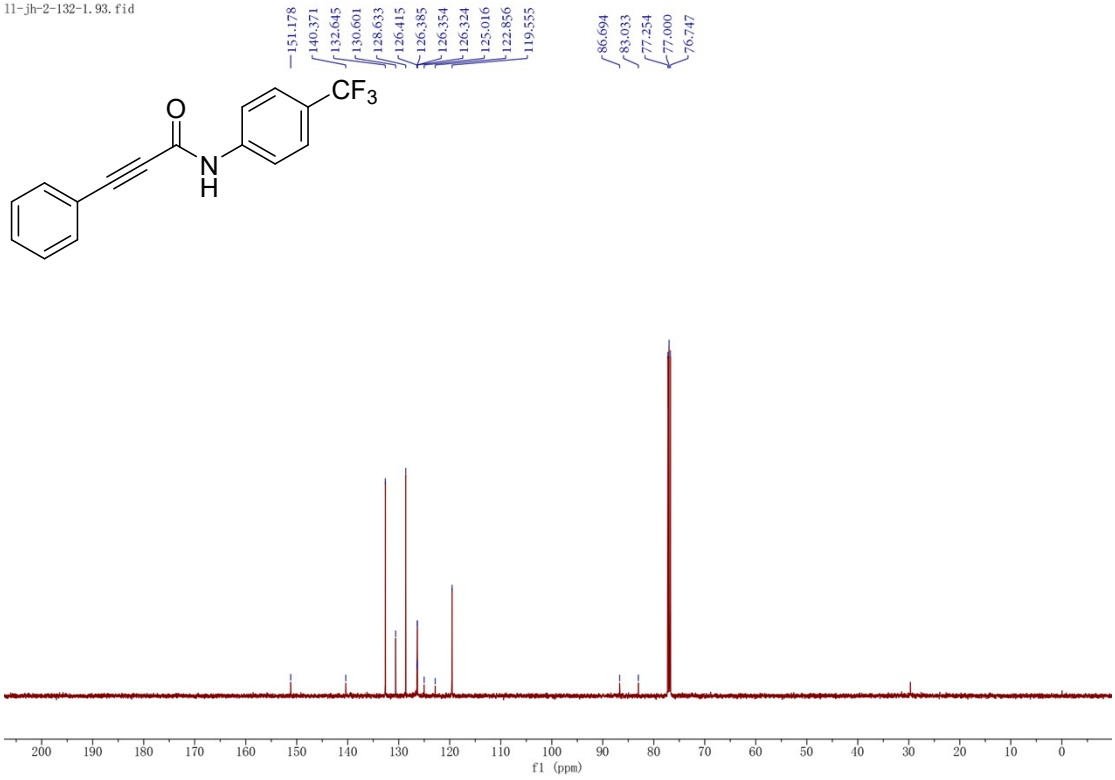
^{13}C NMR-spectrum (100 MHz, DMSO-d_6) of **3qa**



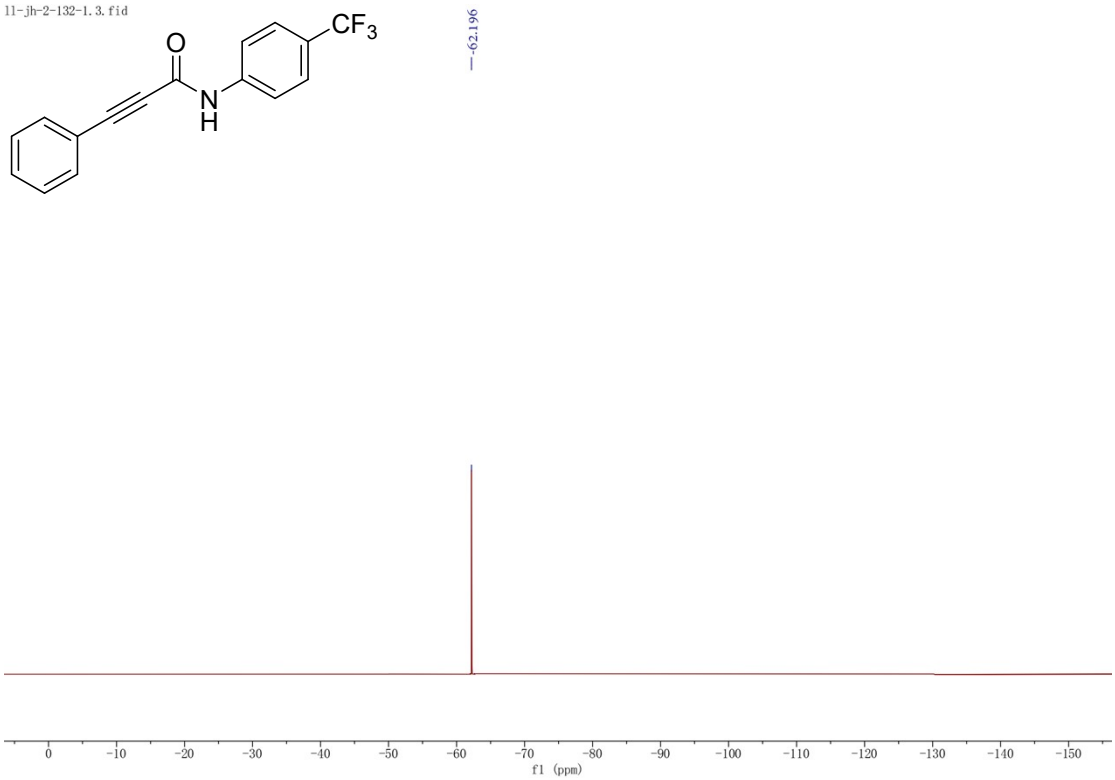
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ra**



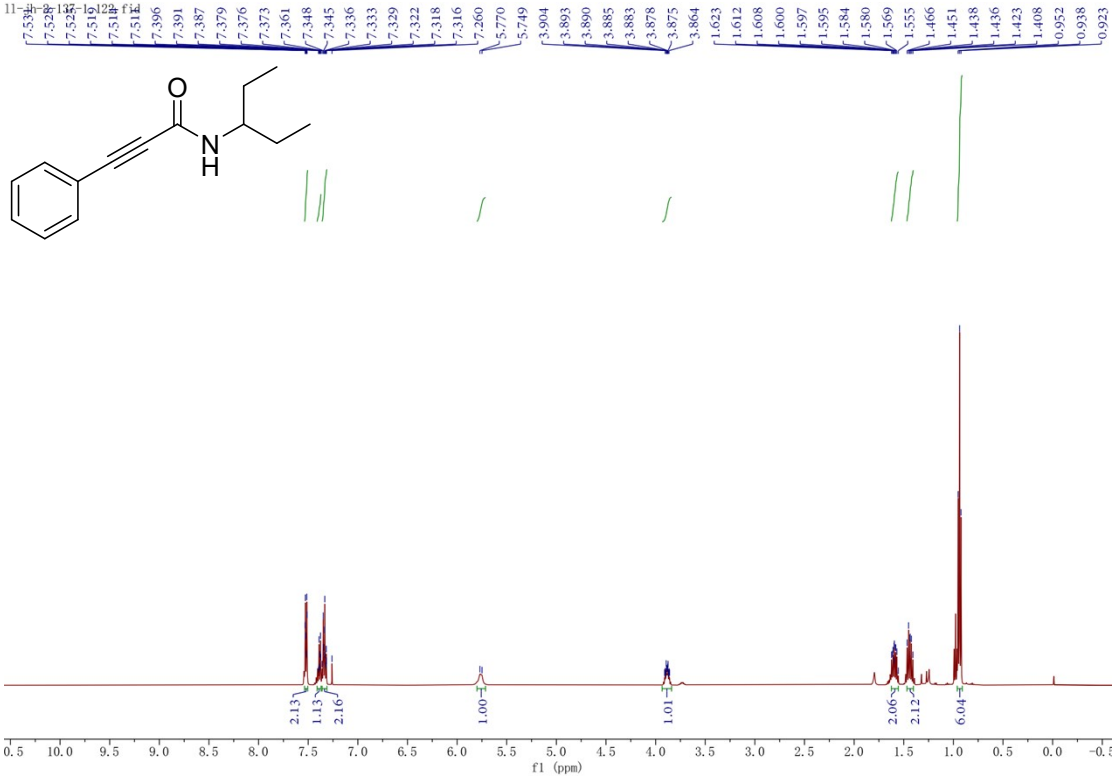
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ra**



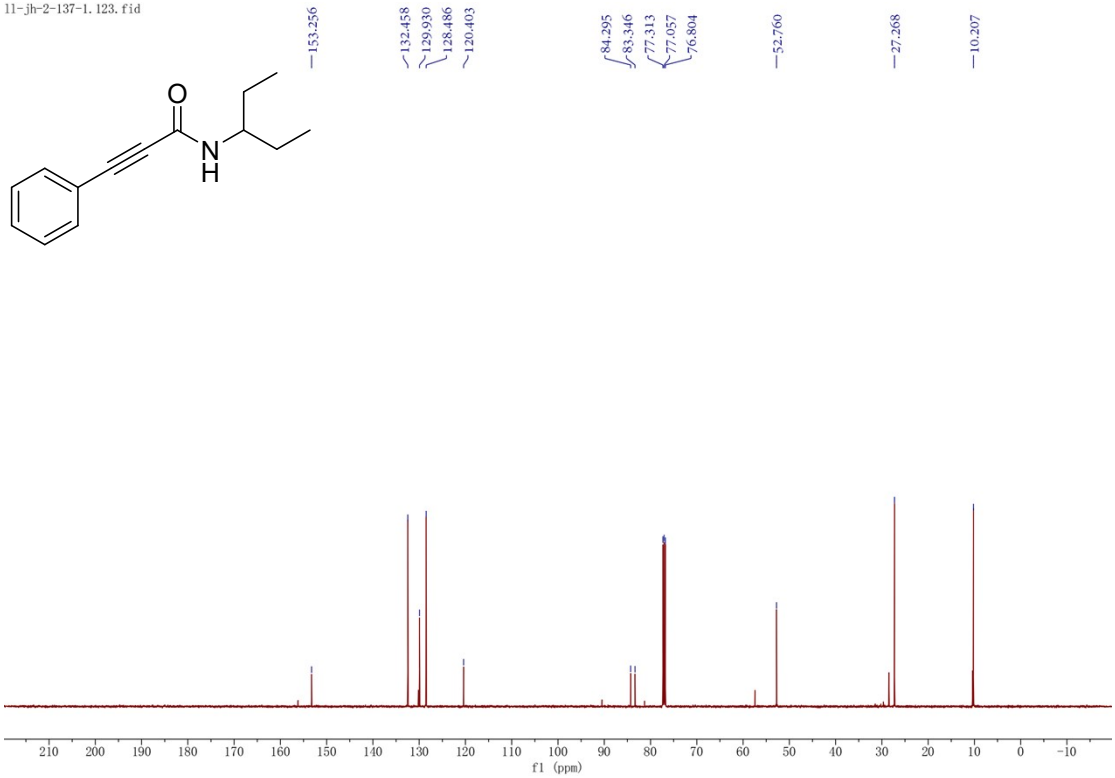
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3ra**



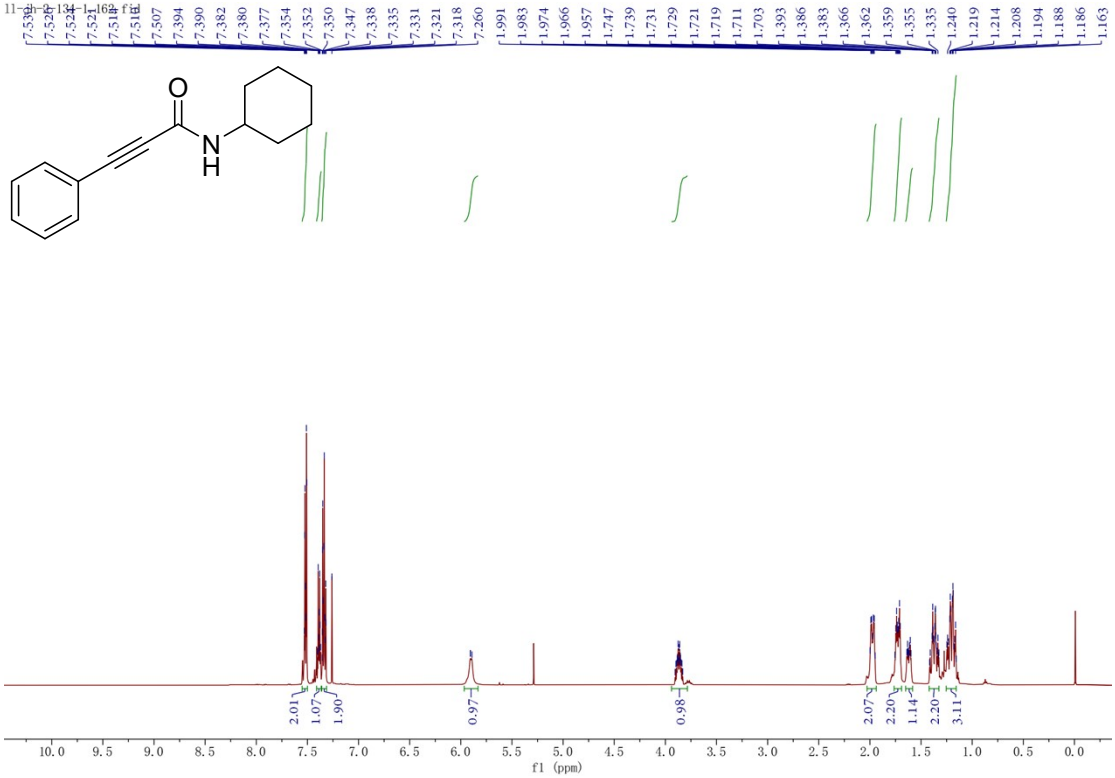
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3sa**



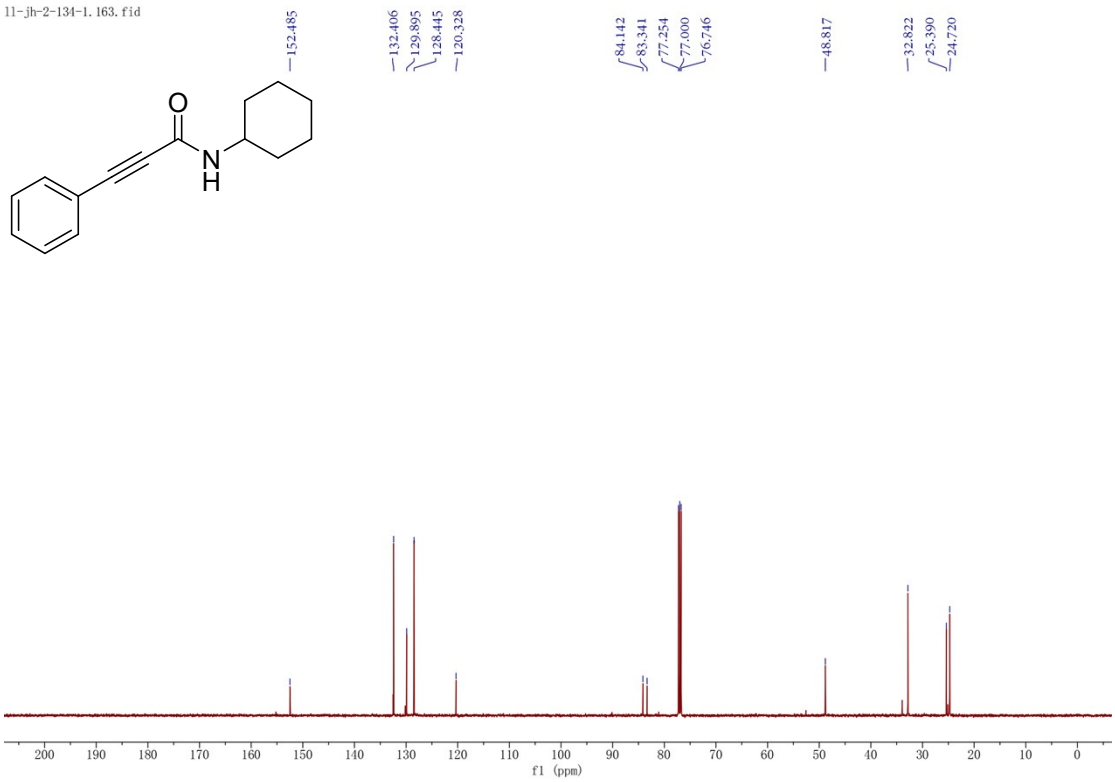
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3sa**



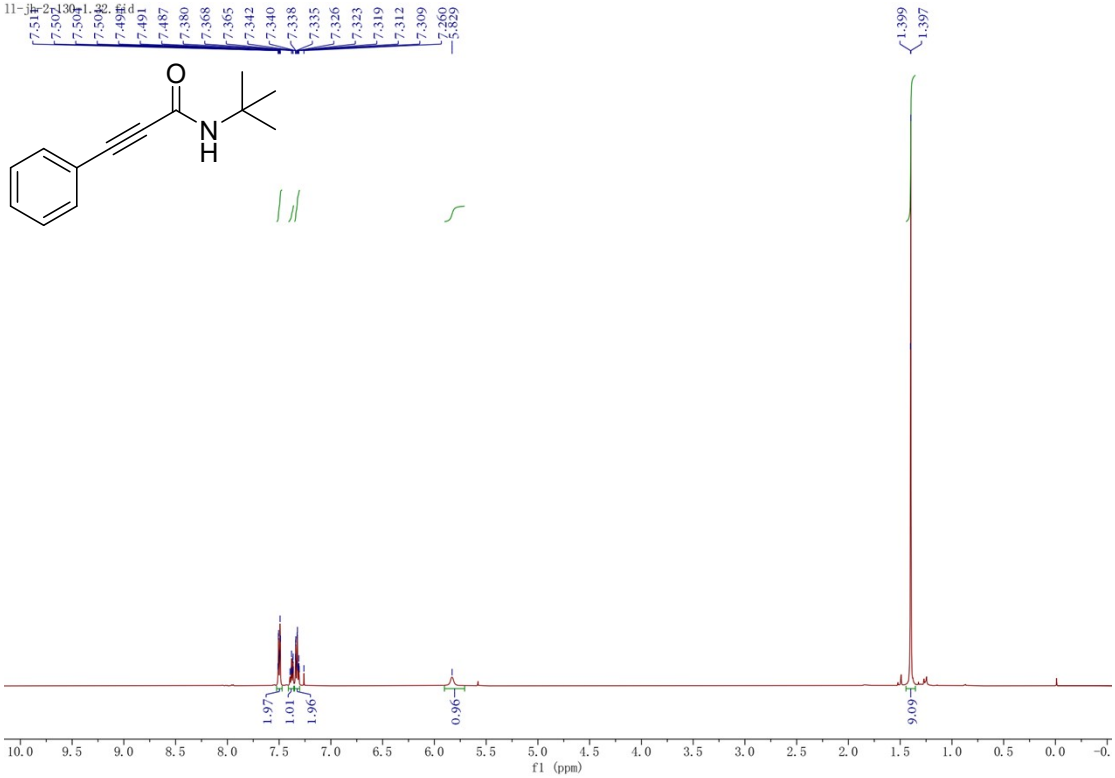
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ta**



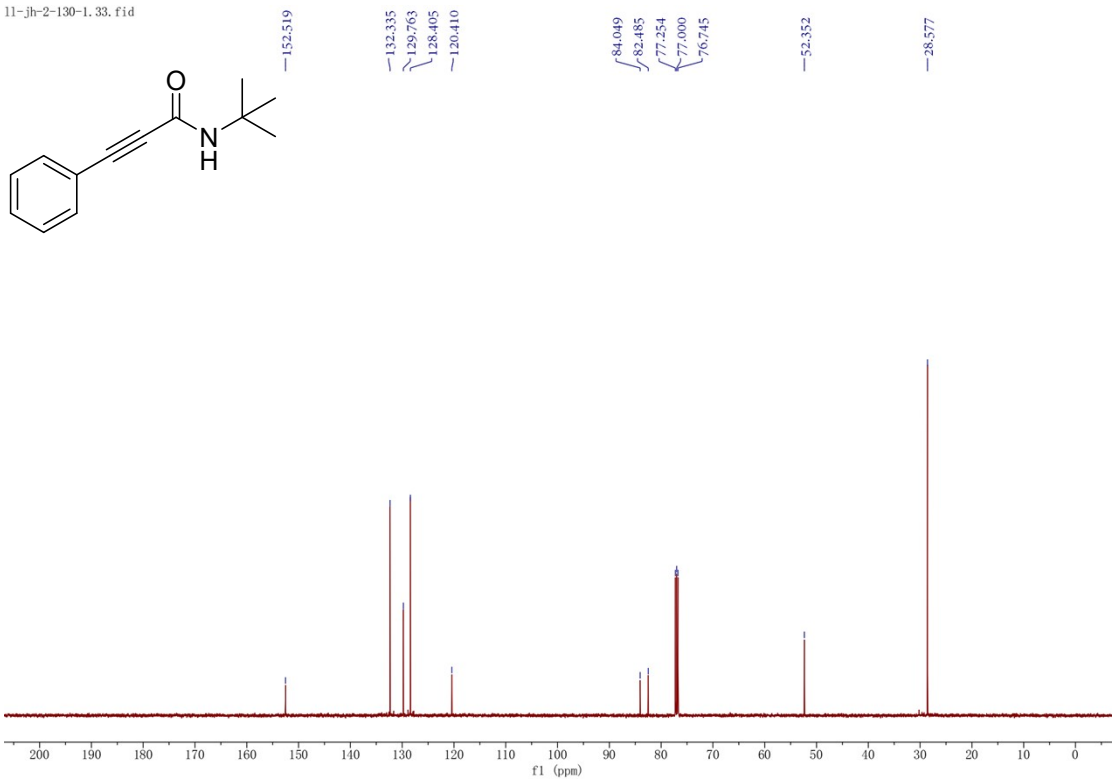
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ta**



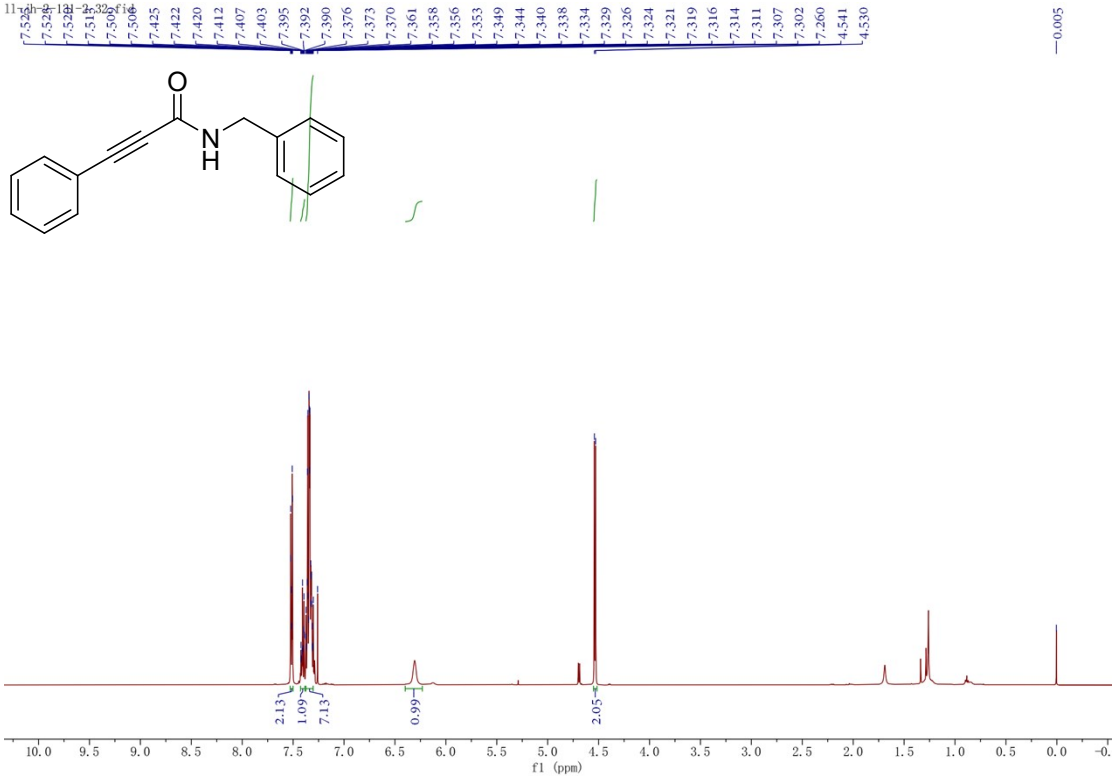
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ua**



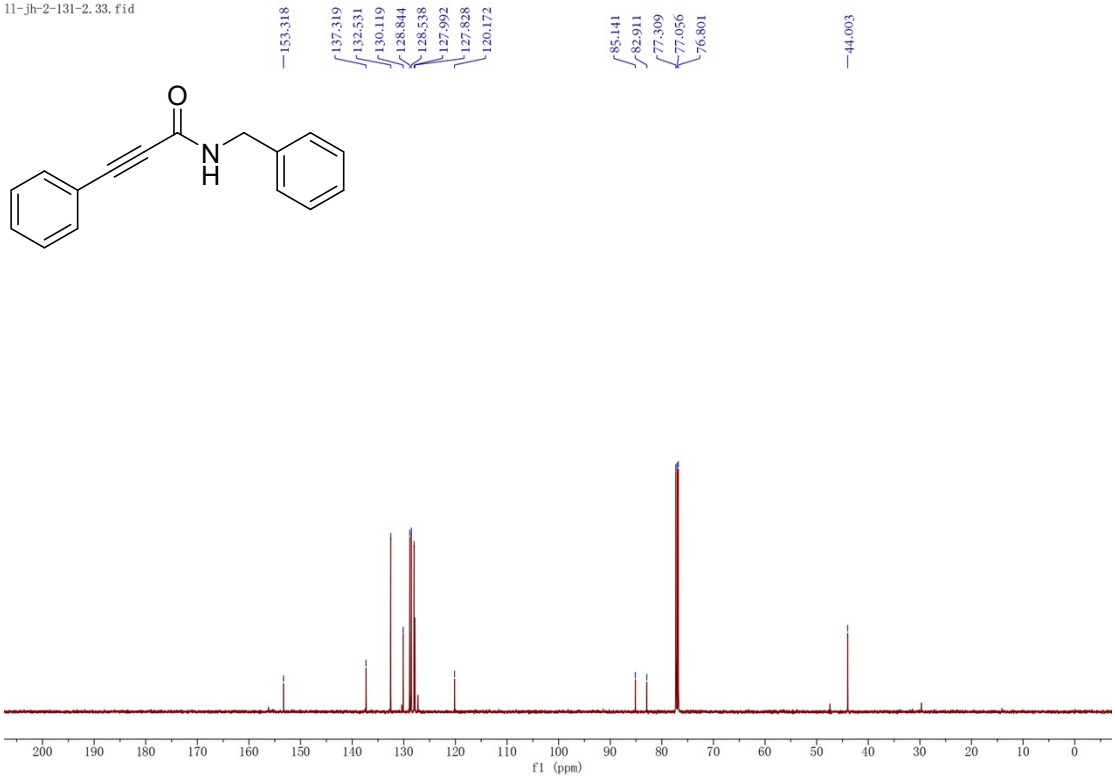
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ua**



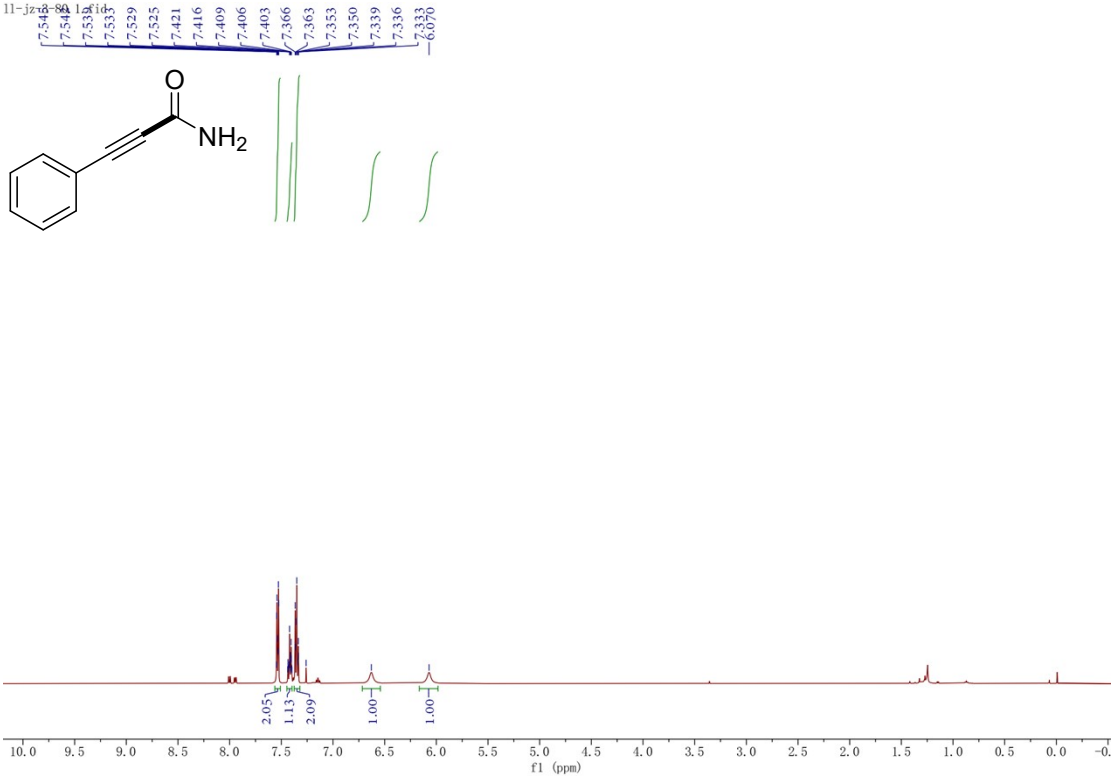
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3va**



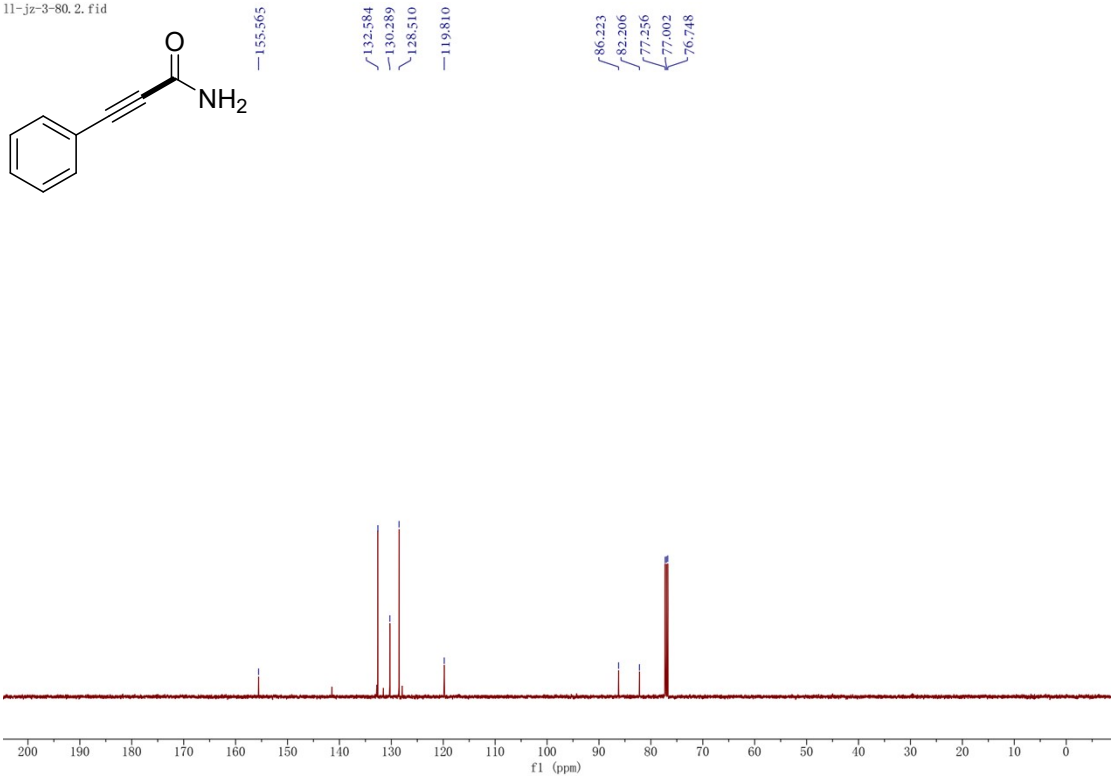
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3va**



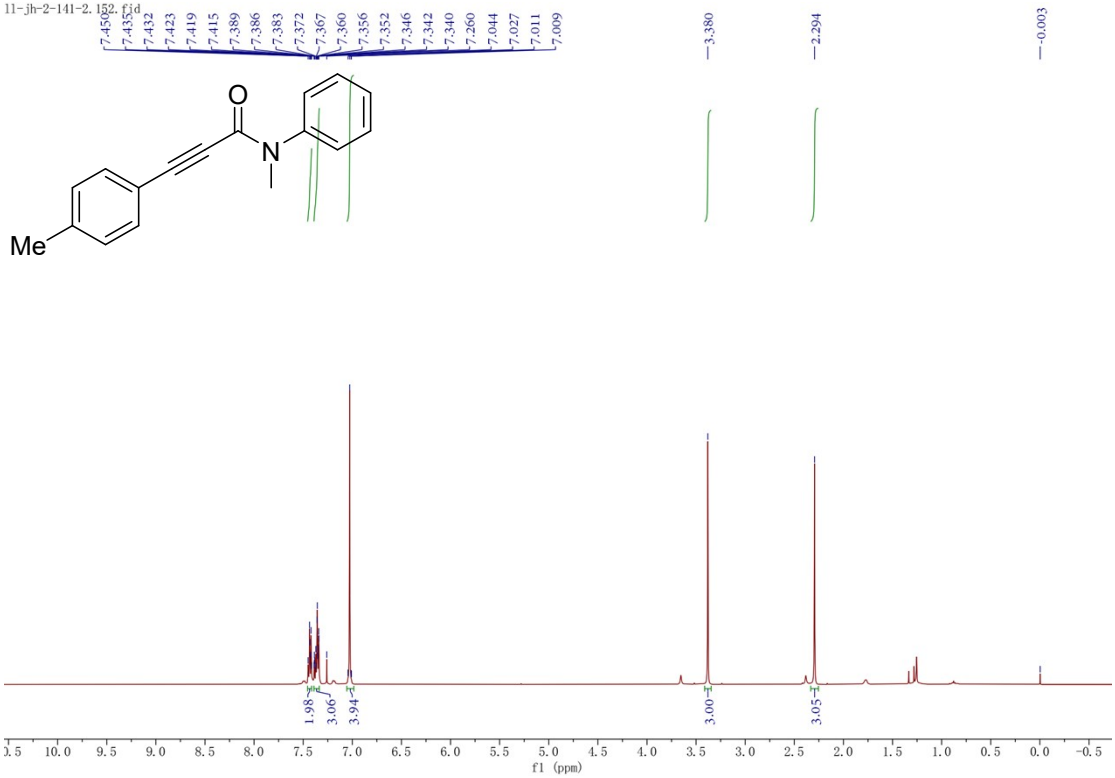
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3wa**



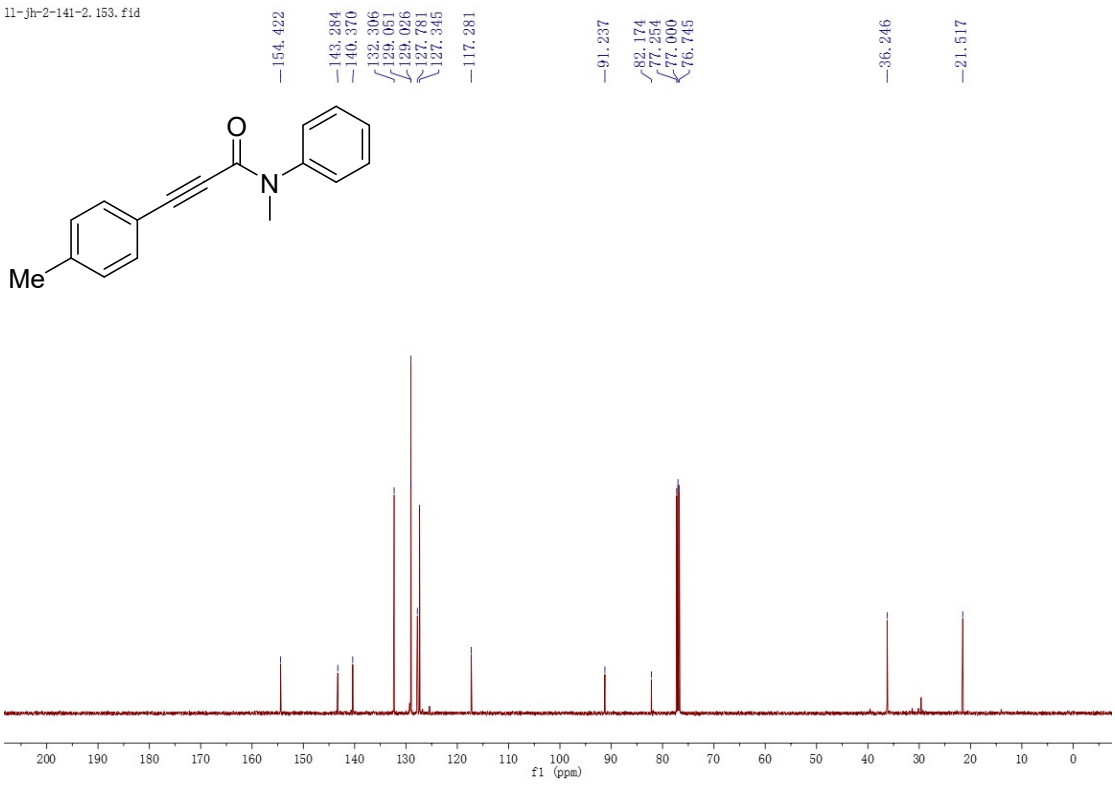
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3wa**



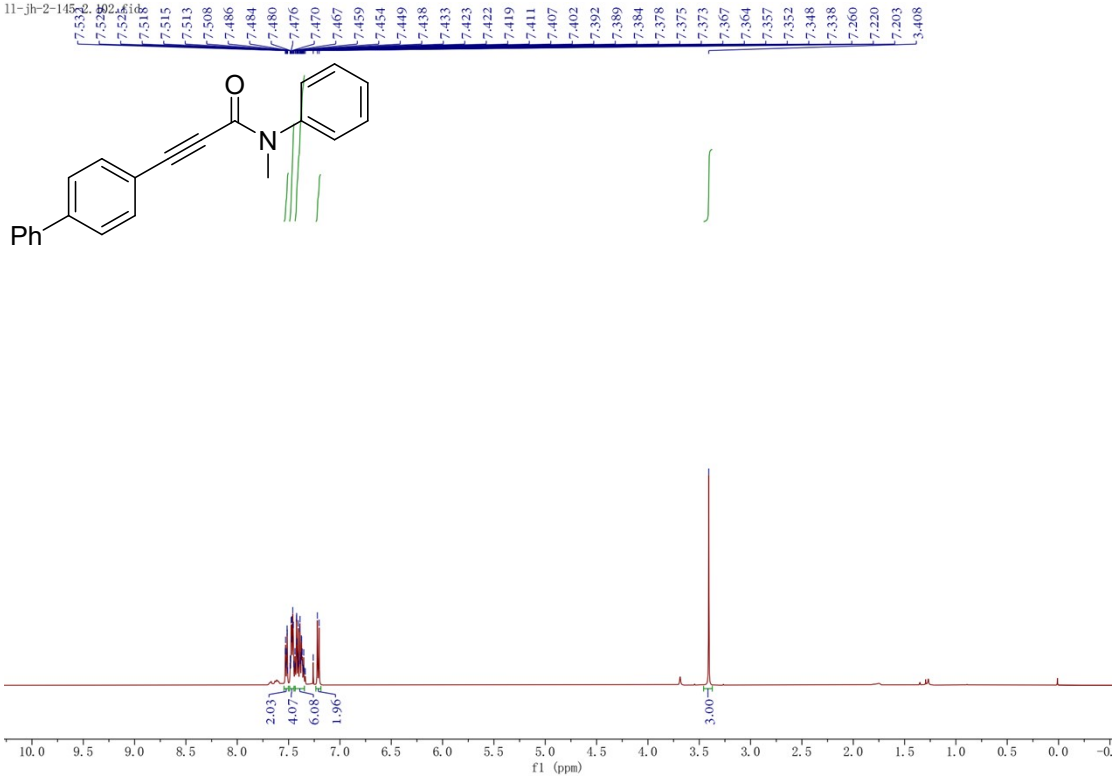
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ab**



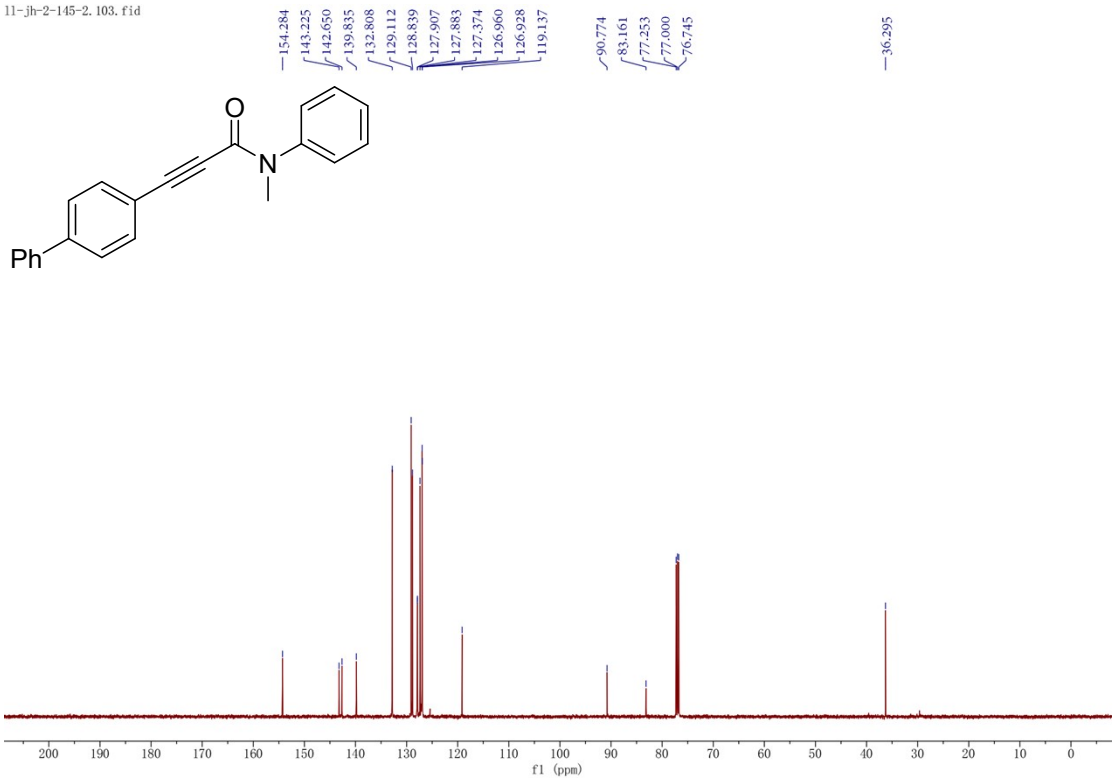
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ab**



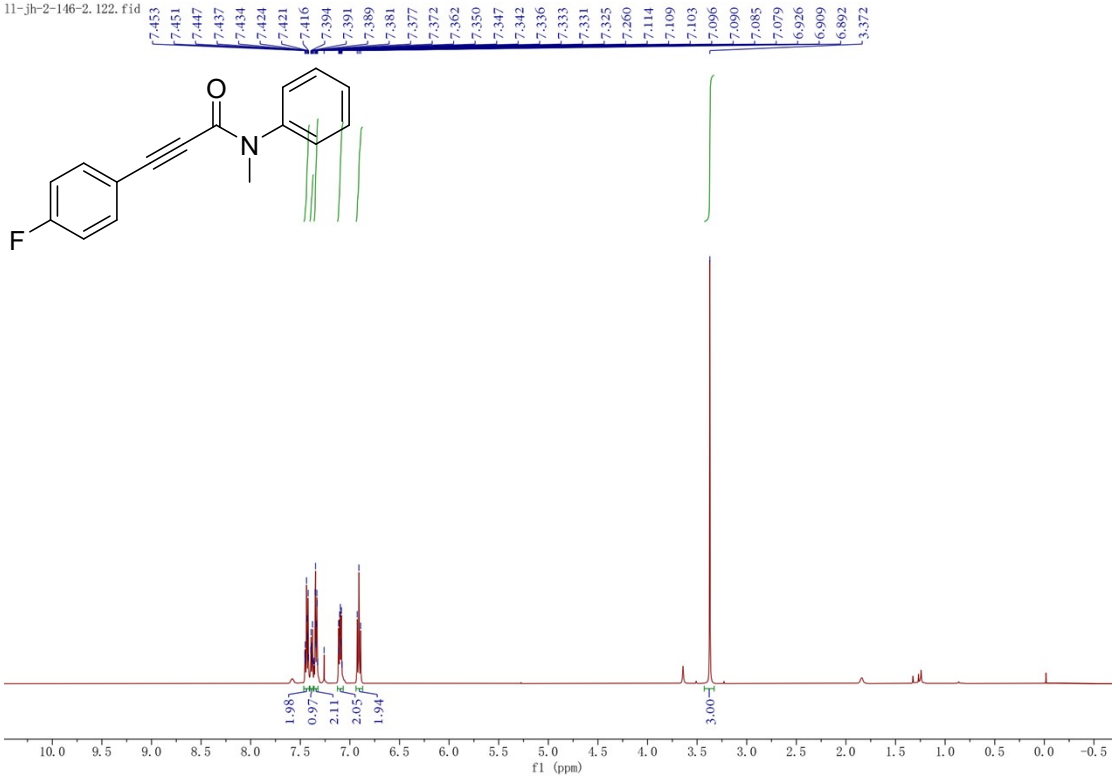
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ac**



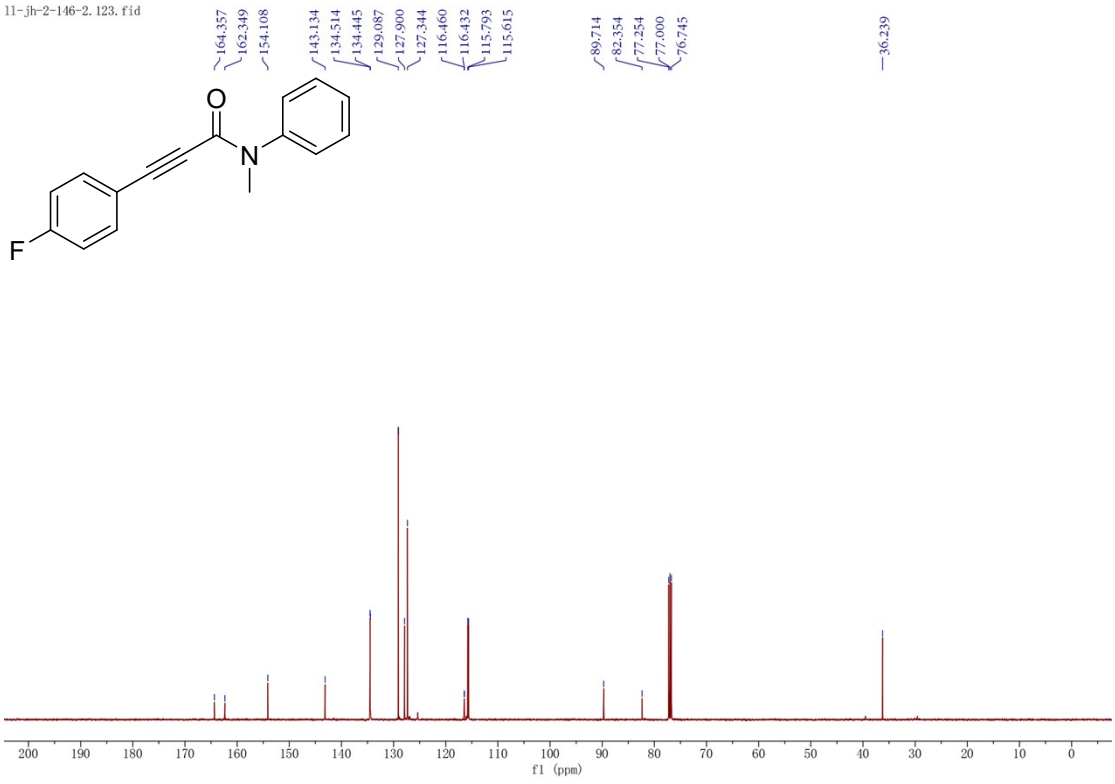
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ac**



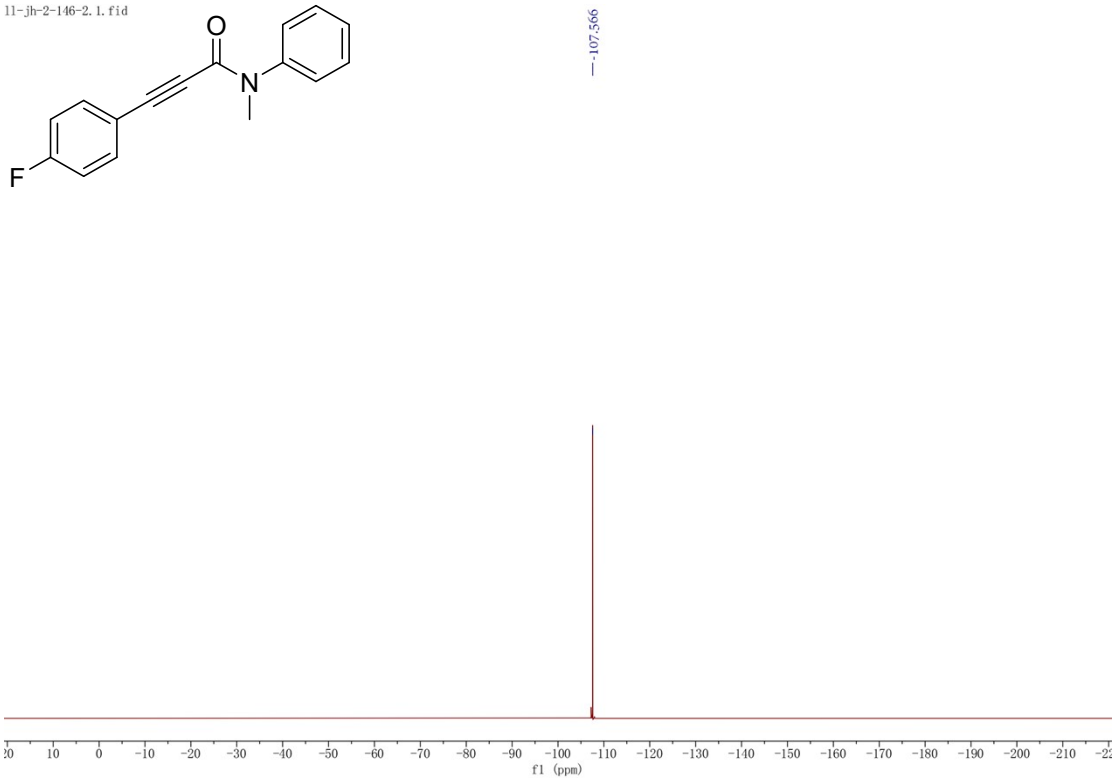
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ad**



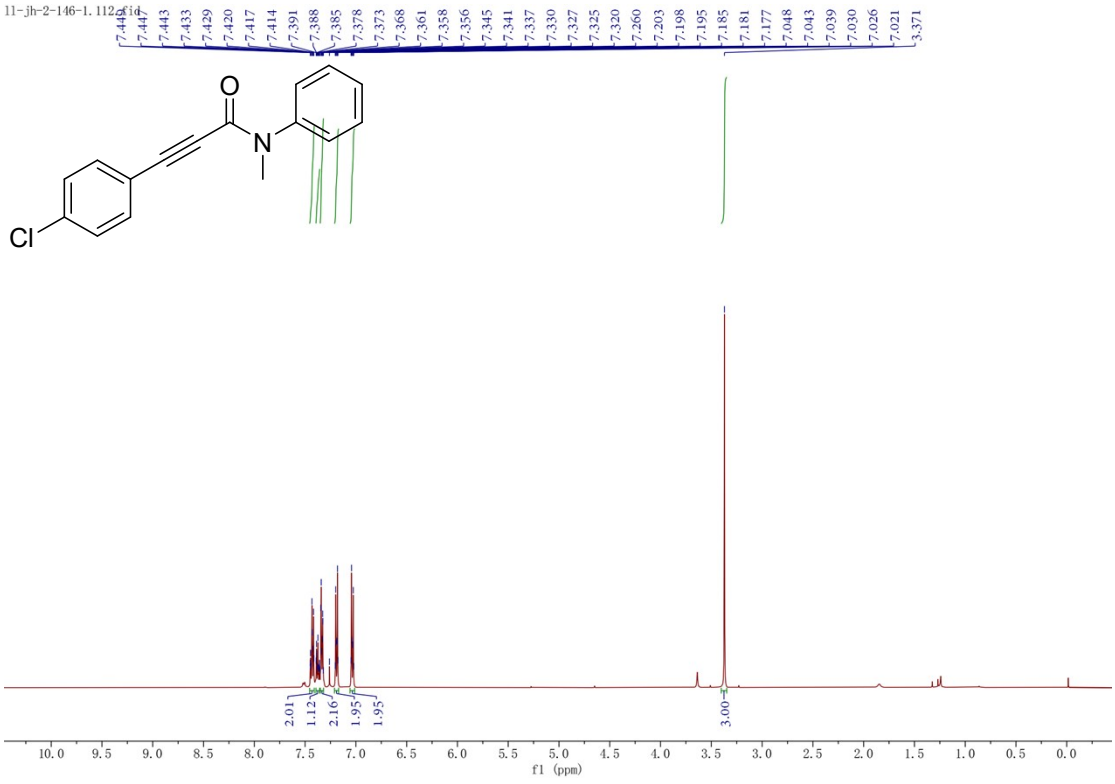
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ac**



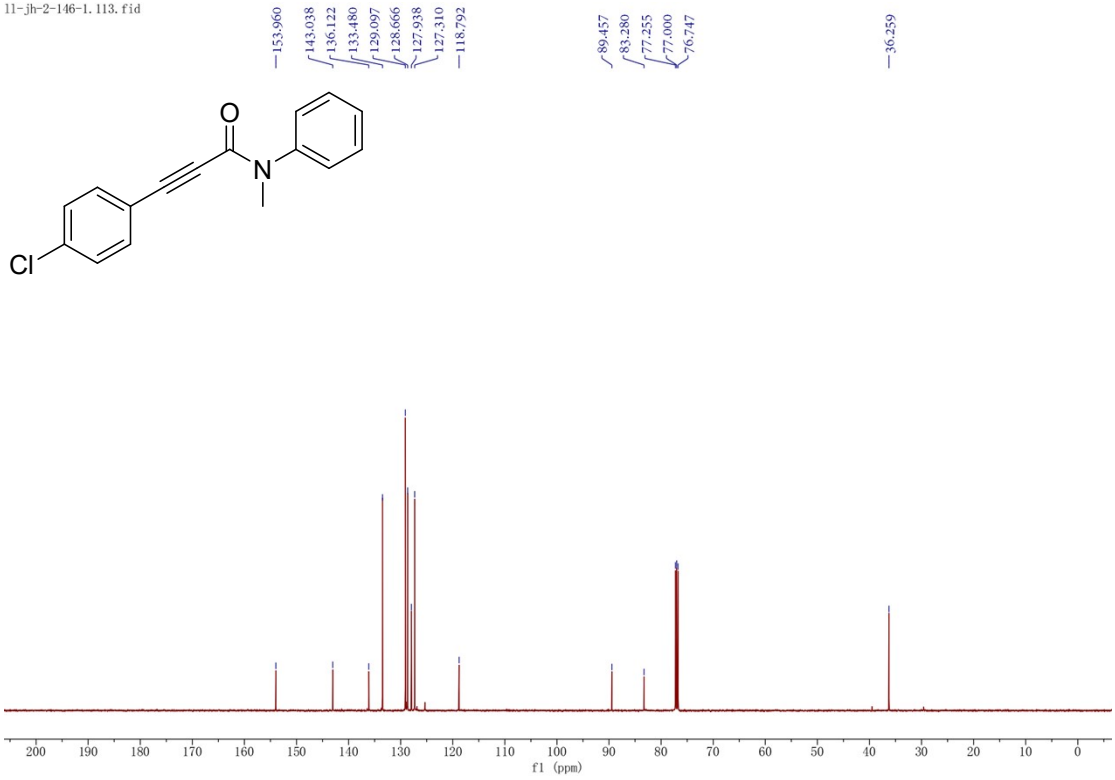
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3ad**



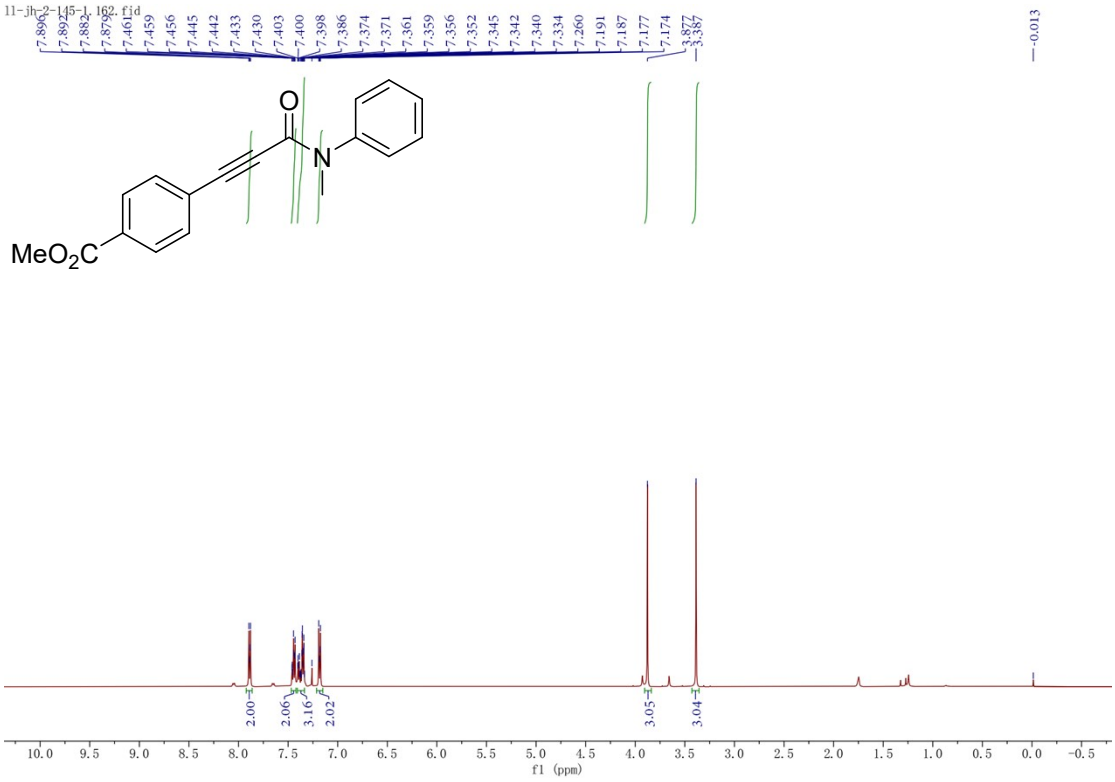
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ae**



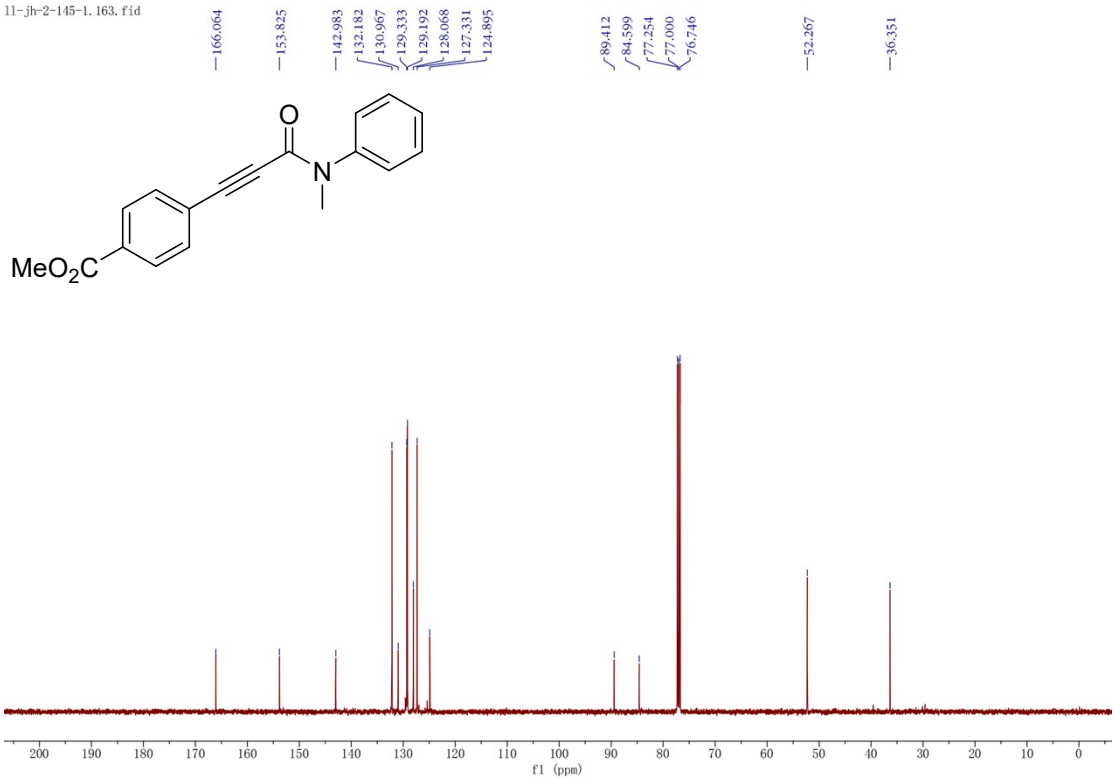
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3ae**



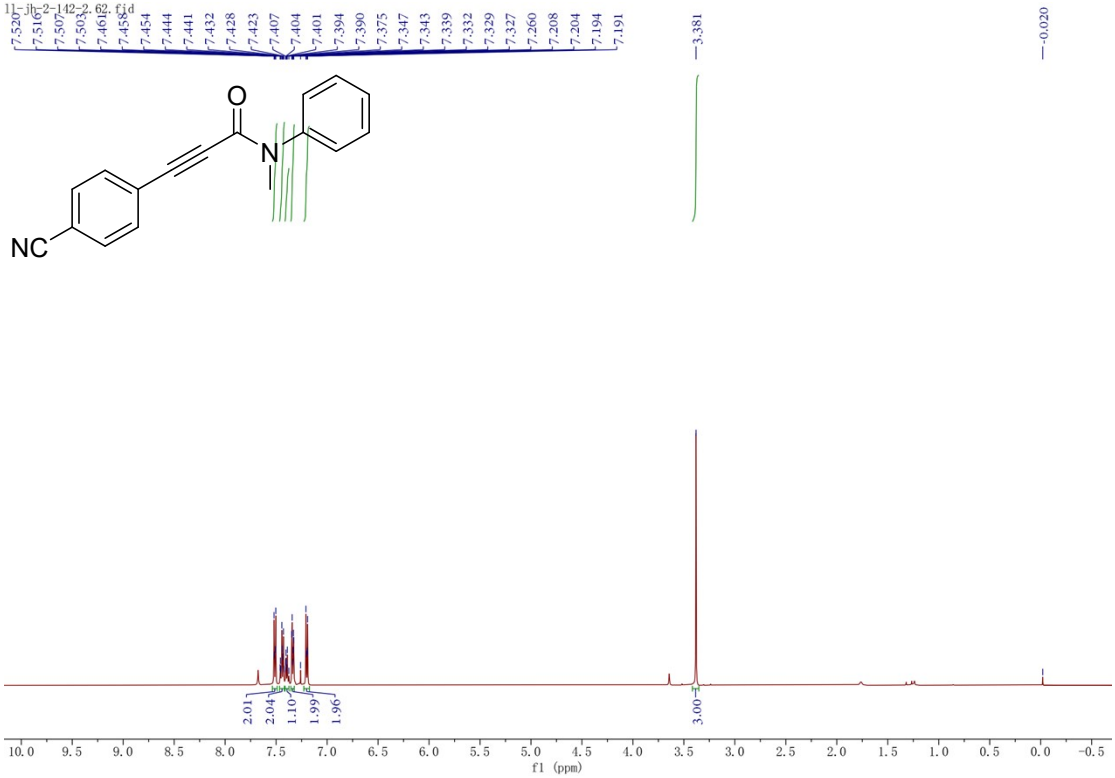
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3af**



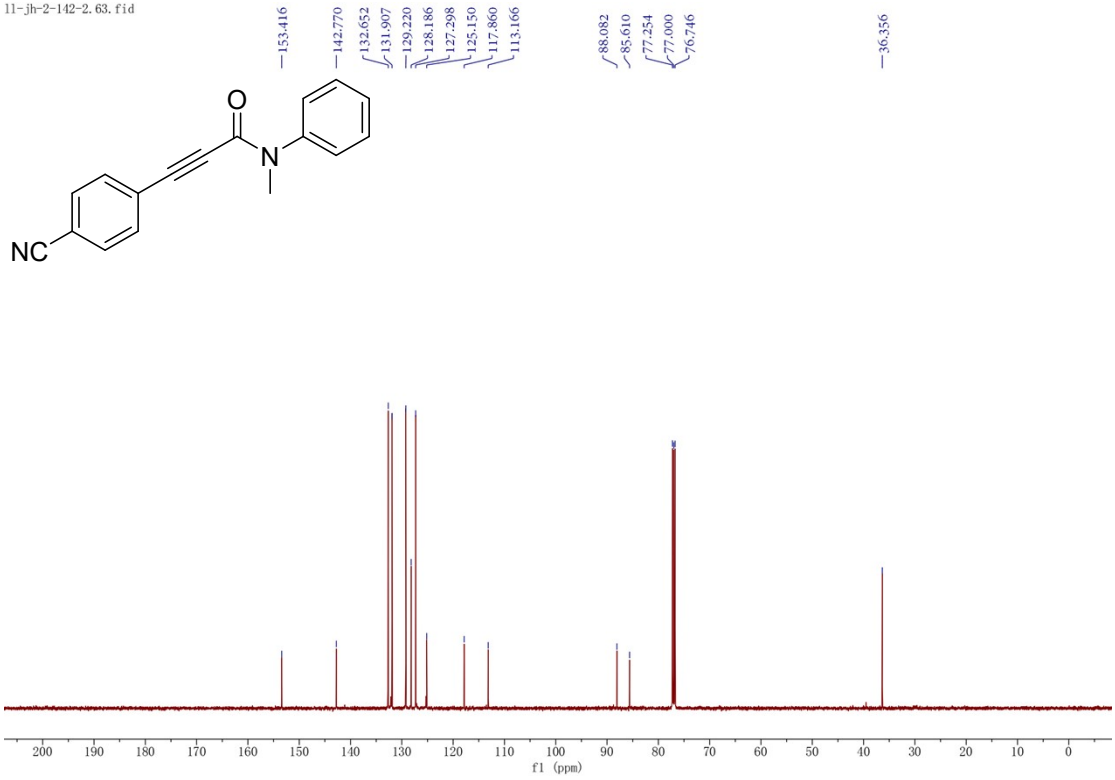
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3af**



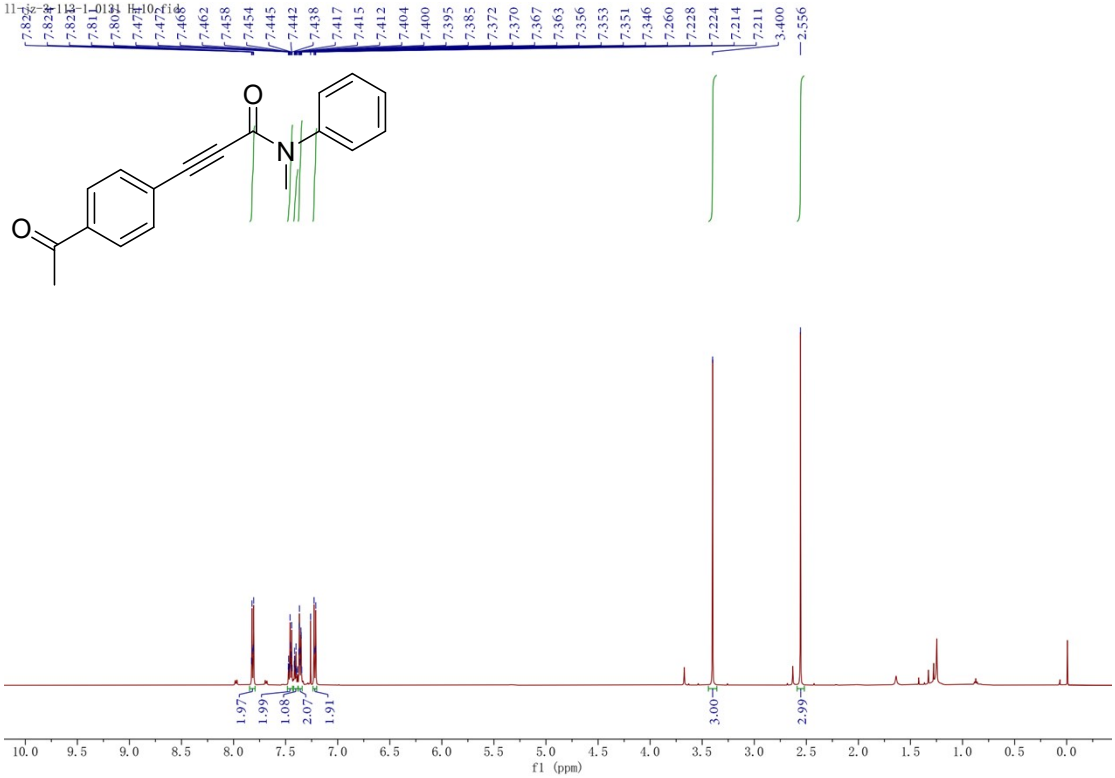
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ag**



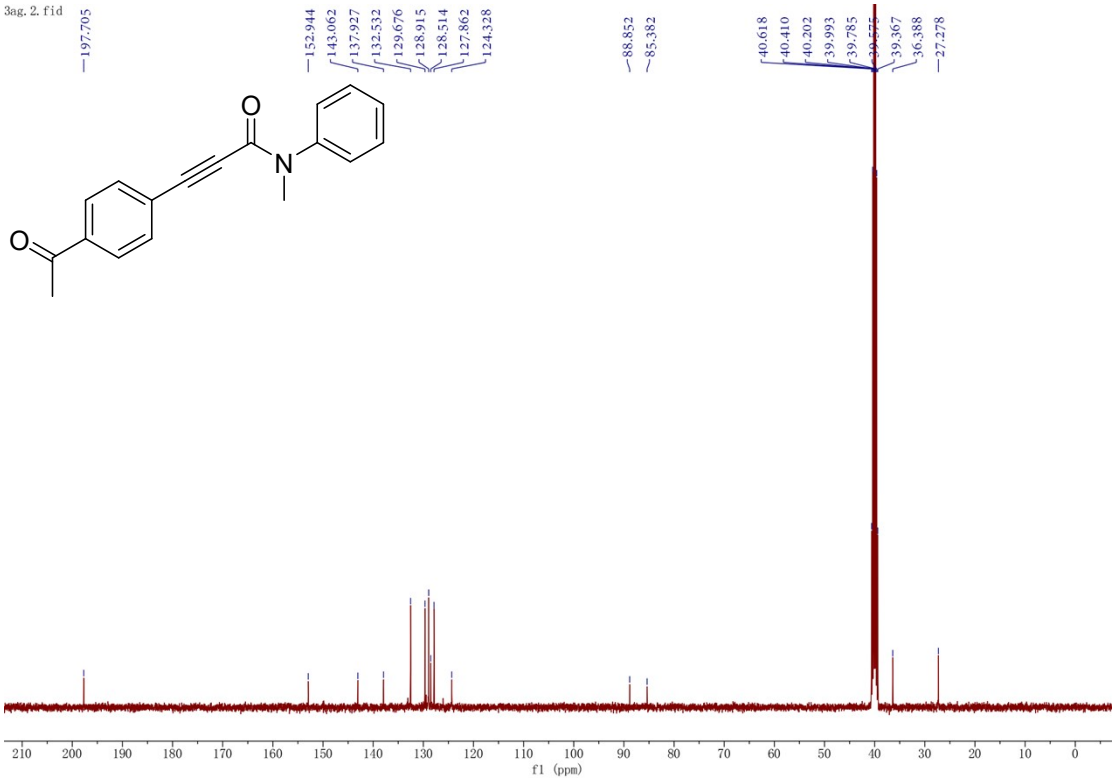
^{13}C NMR-spectrum (125 MHz, DMSO-d_6) of **3ag**



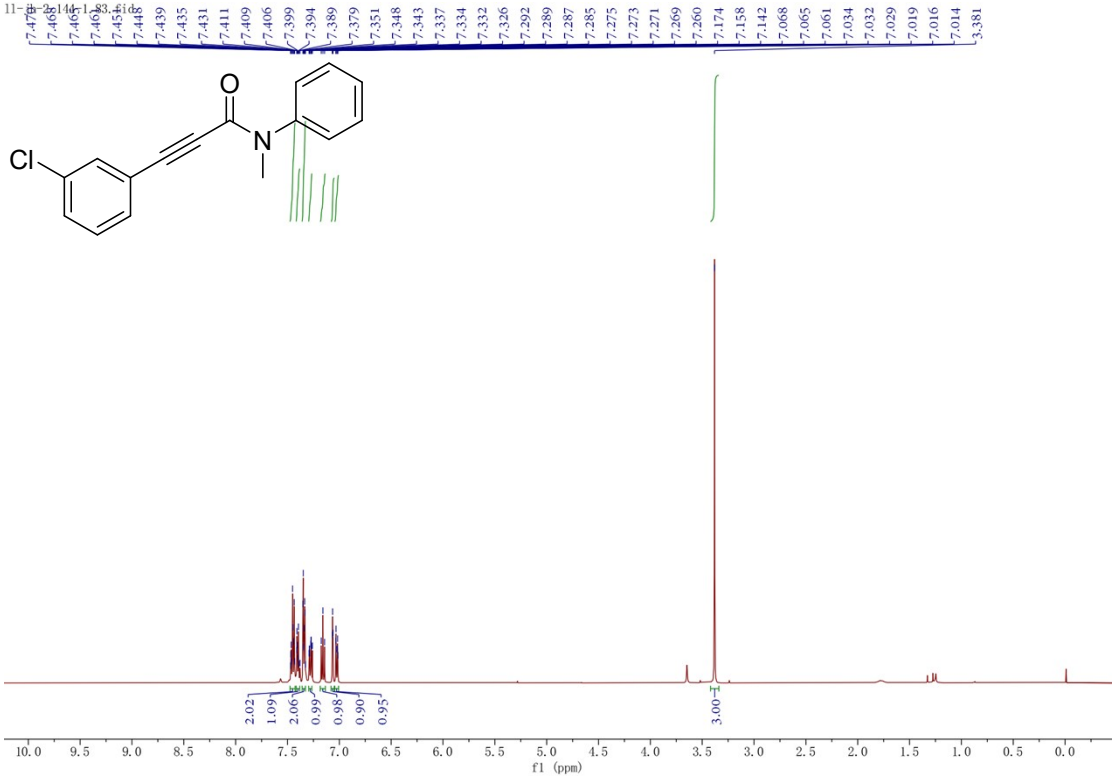
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ah**



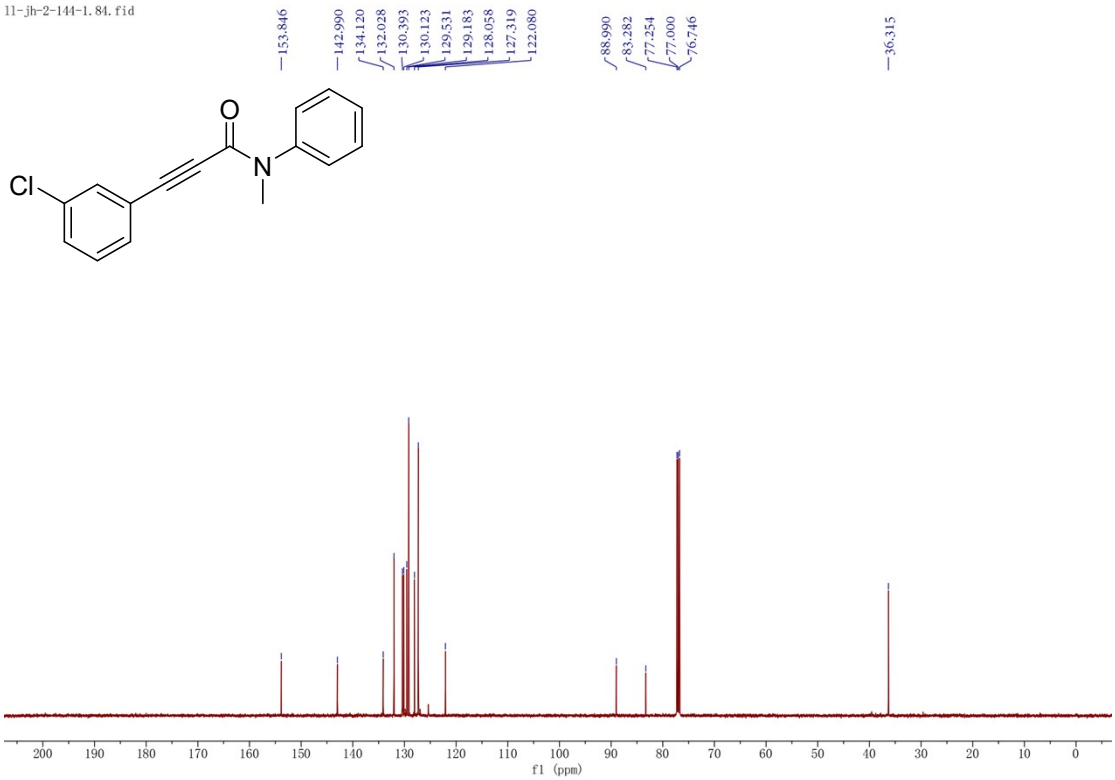
^{13}C NMR-spectrum (100 MHz, $CDCl_3$) of **3ah**



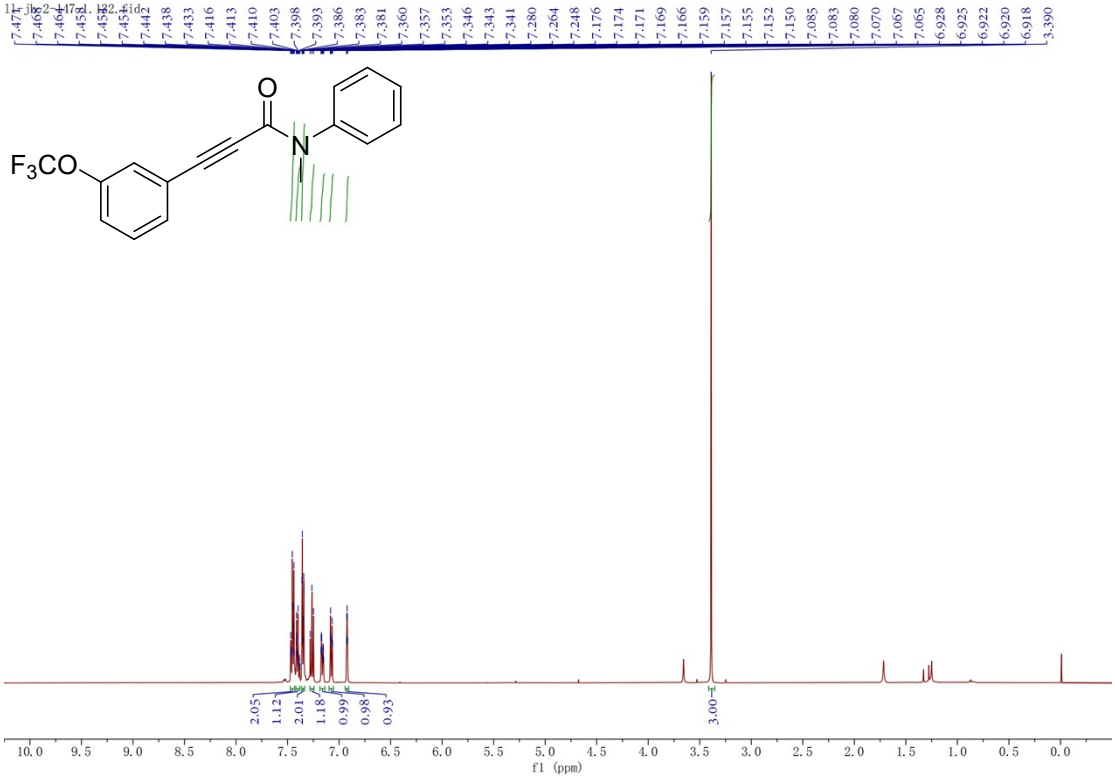
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ai**



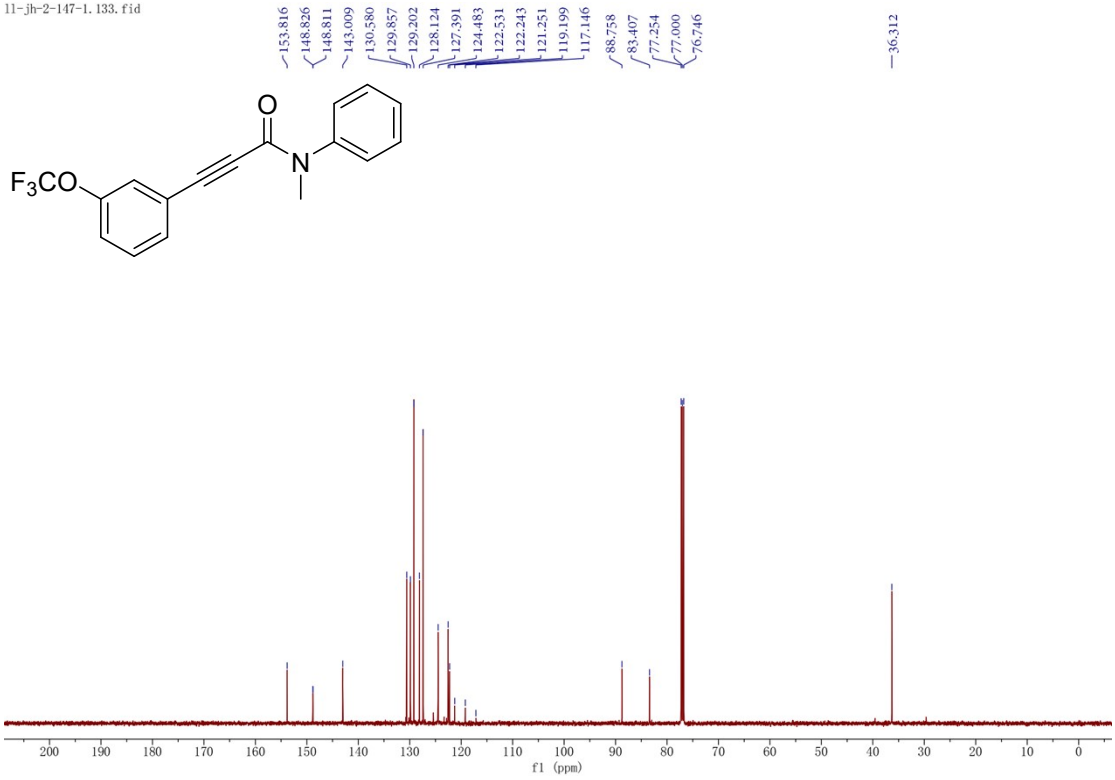
^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **3ai**



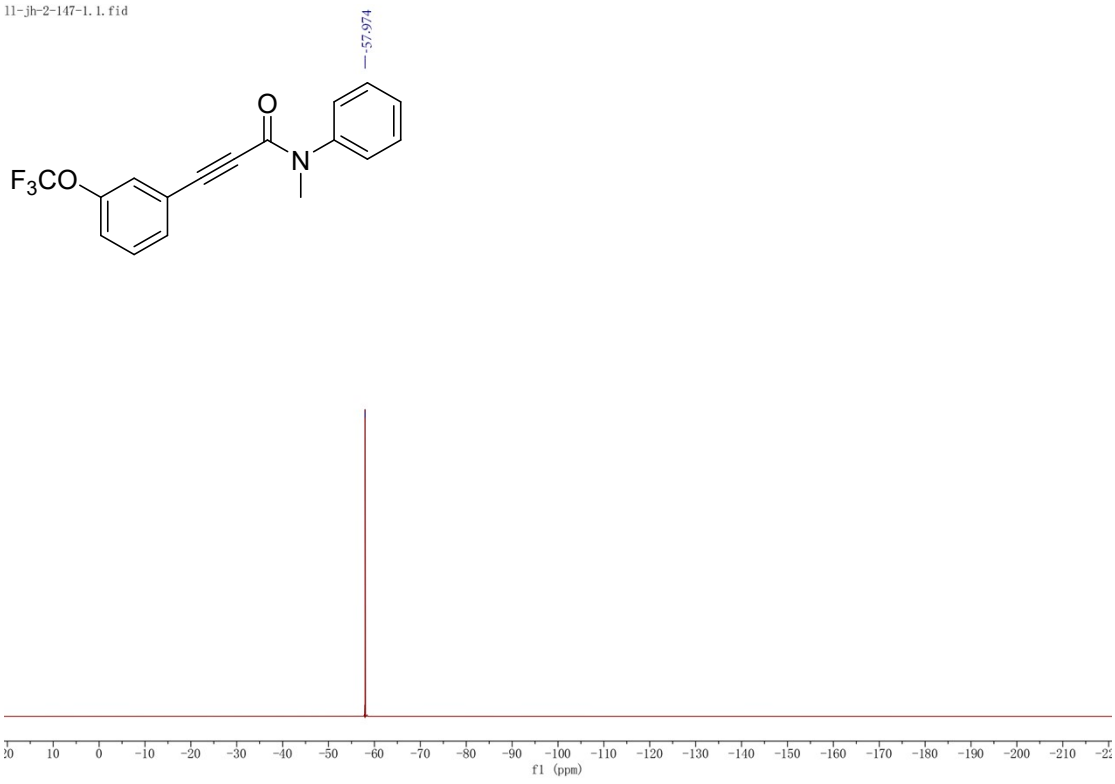
^{1}H **NMR**-spectrum (500 MHz, $CDCl_3$) of **3aj**



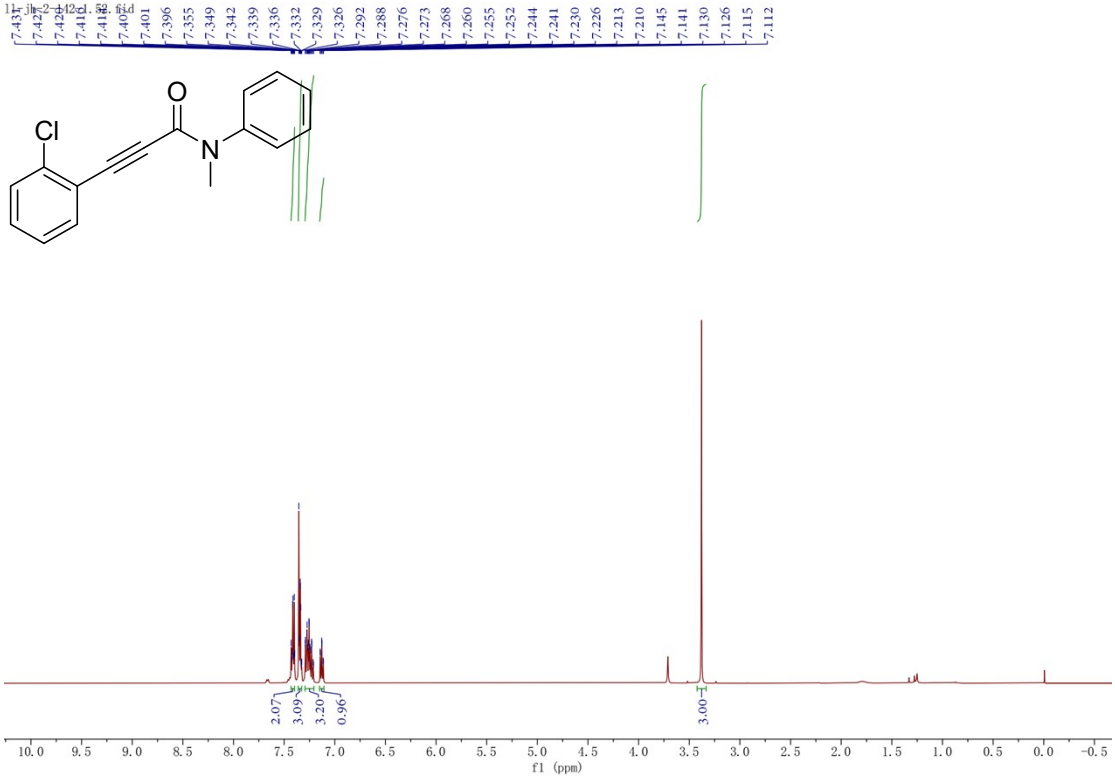
^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **3aj**



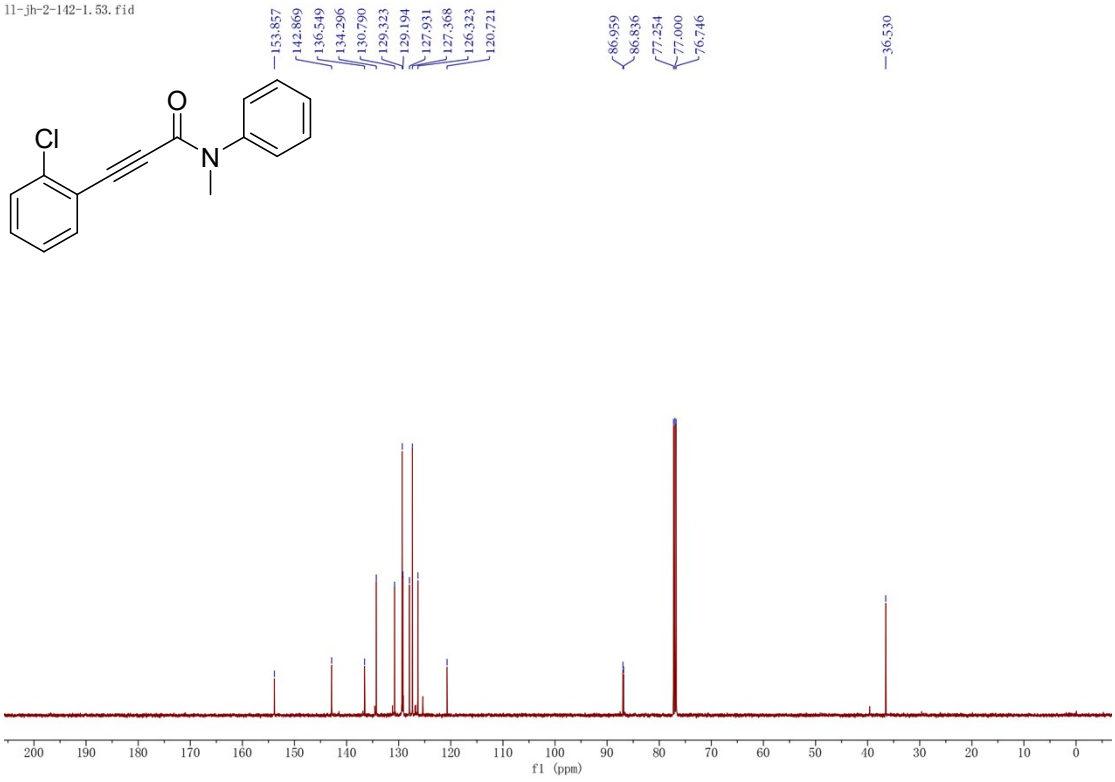
^{19}F **NMR**-spectrum (471 MHz, $CDCl_3$) of **3aj**



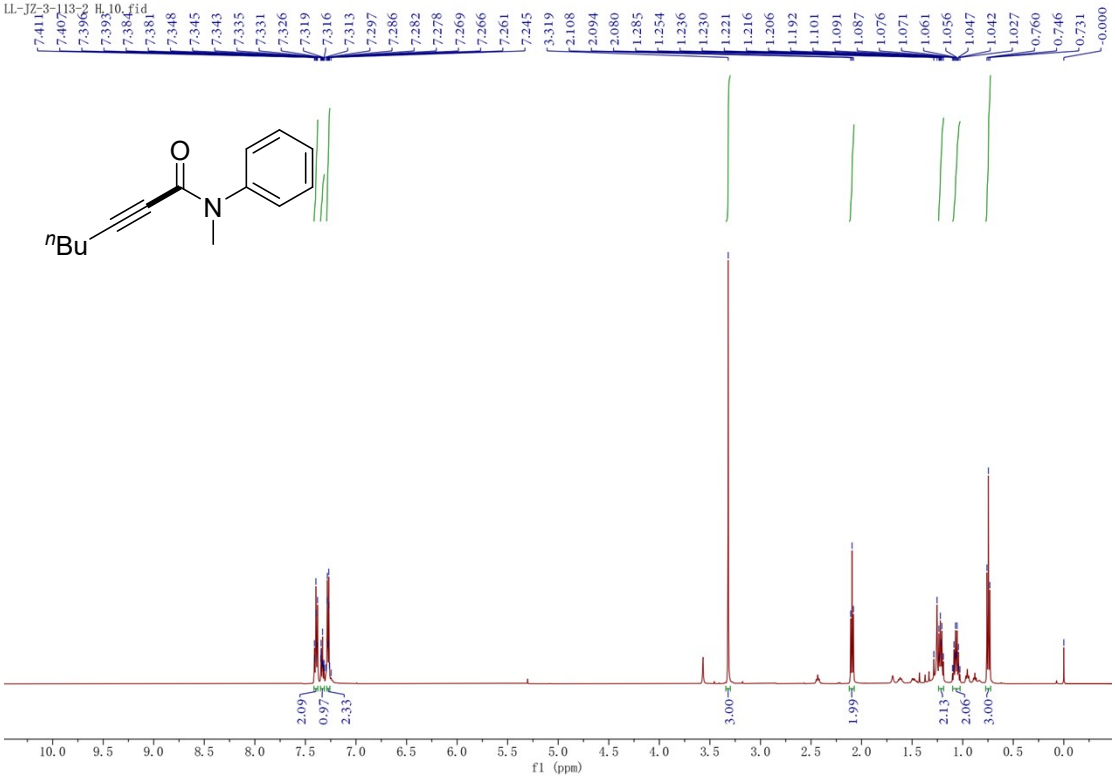
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3ak**



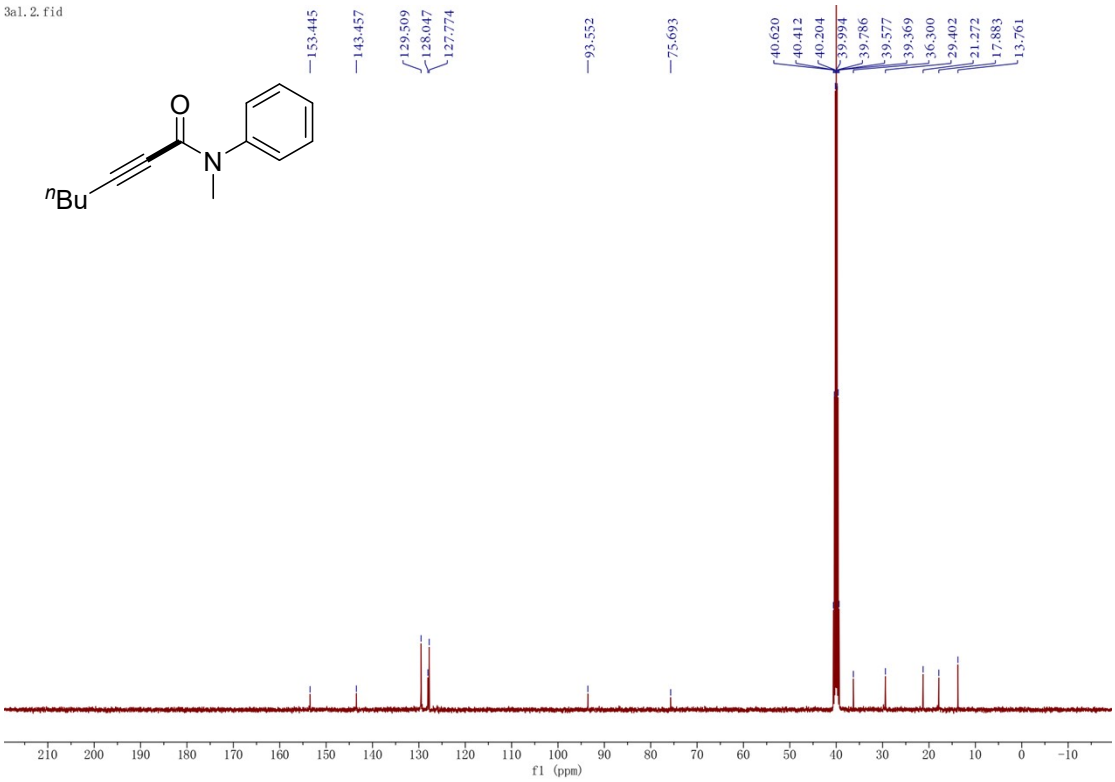
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3aj**



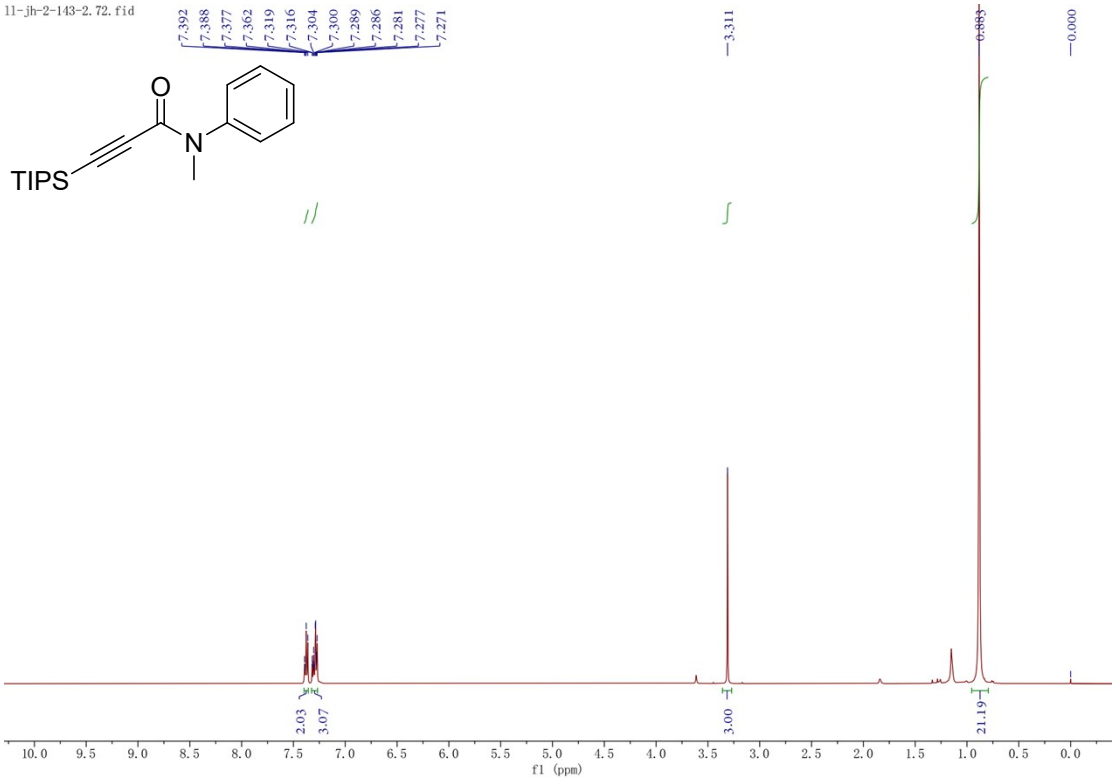
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3al**



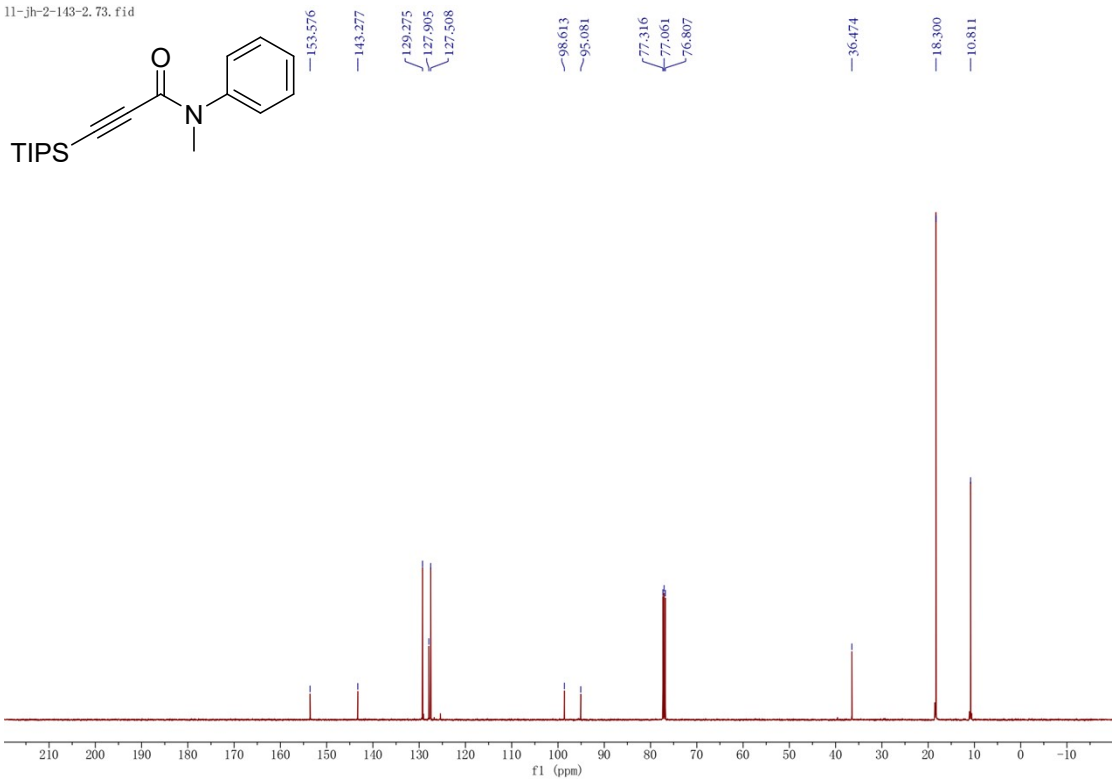
^{13}C NMR-spectrum (100 MHz, DMSO-d_6) of **3al**



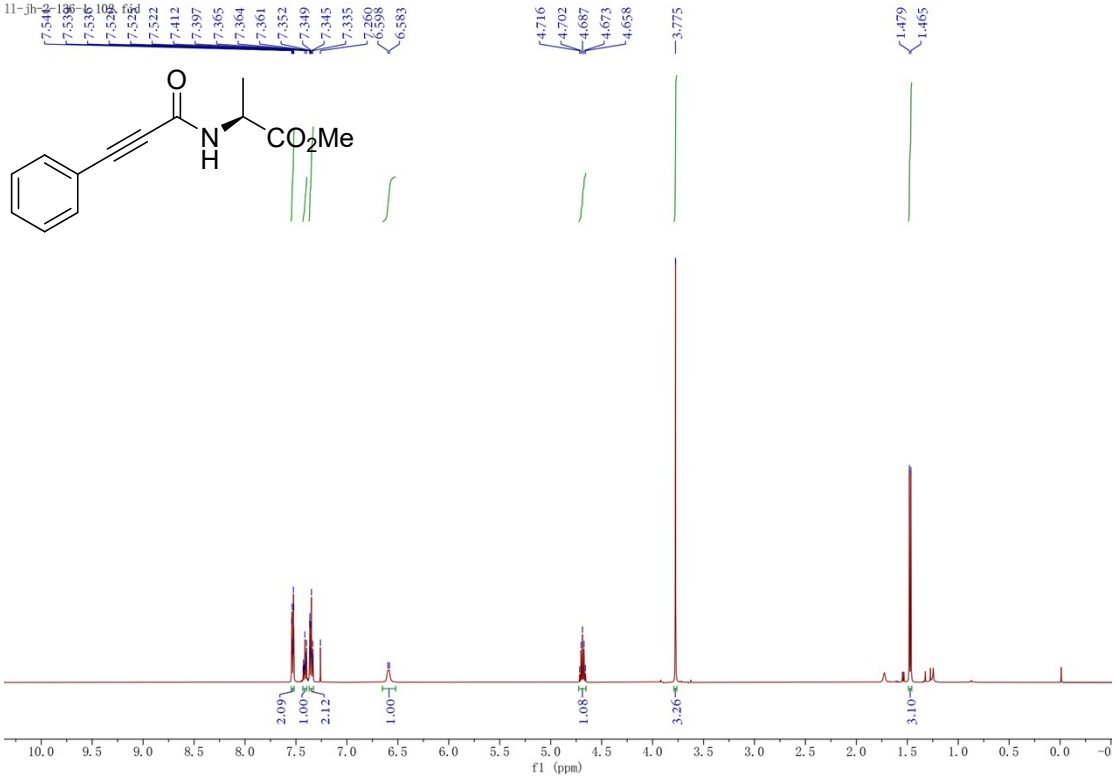
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3am**



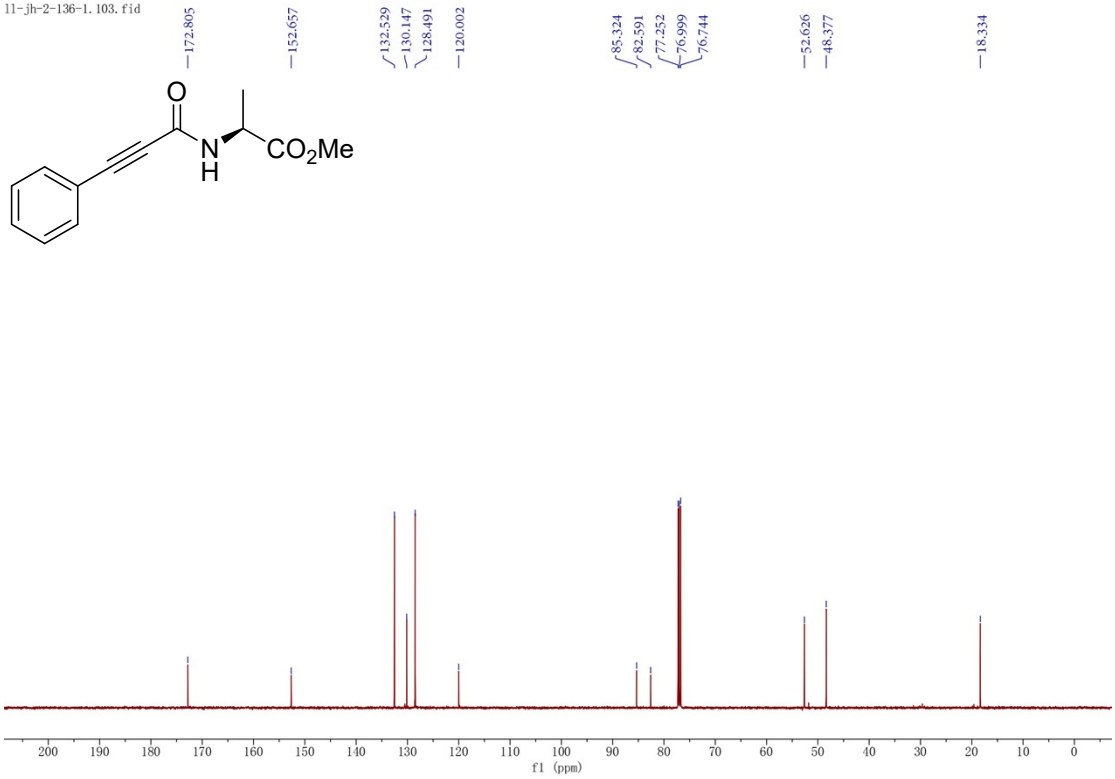
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3am**



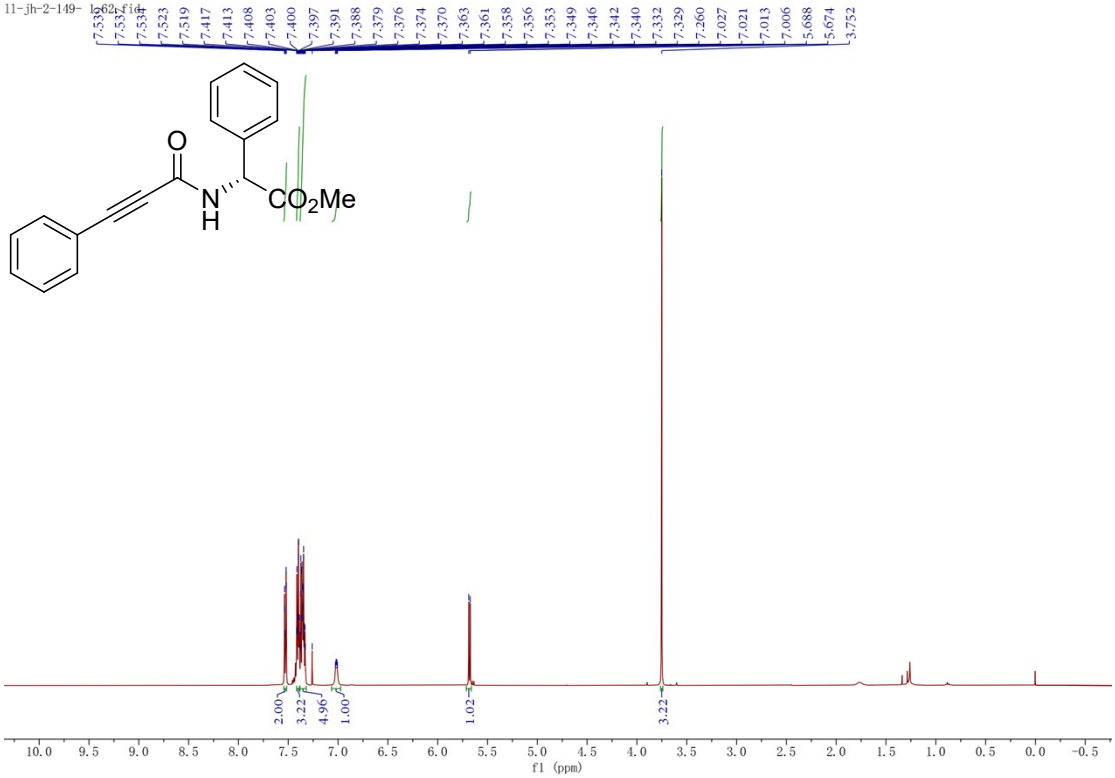
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5aa**



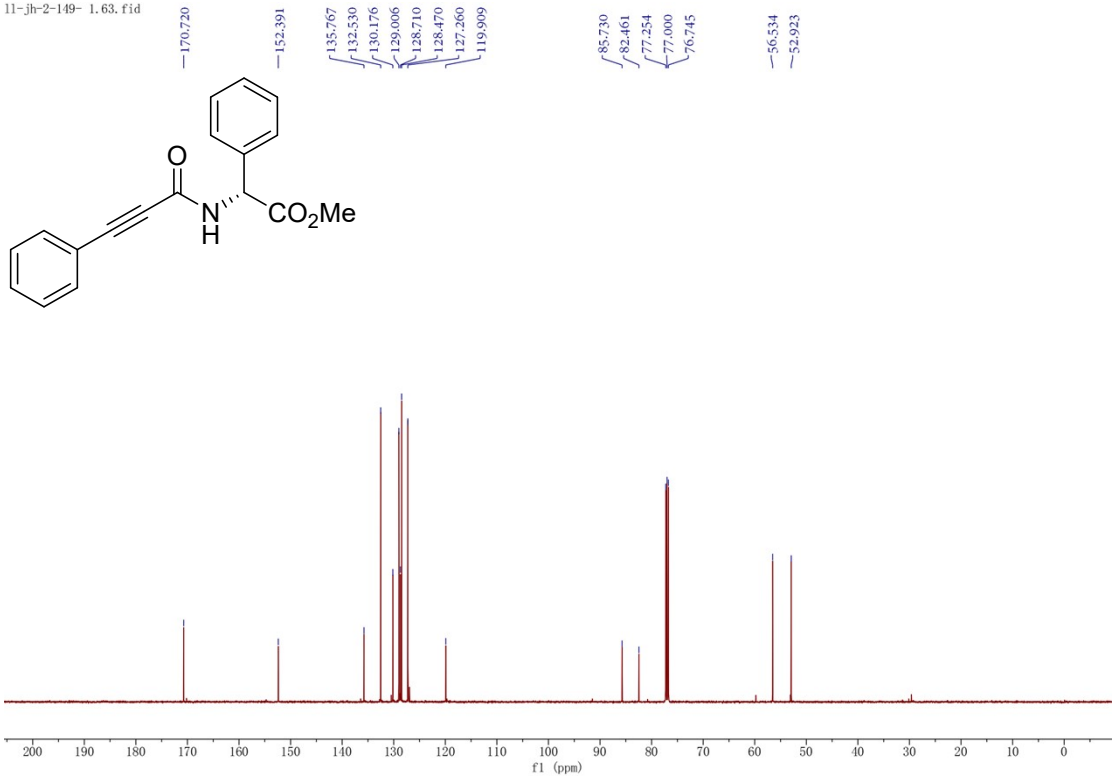
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5aa**



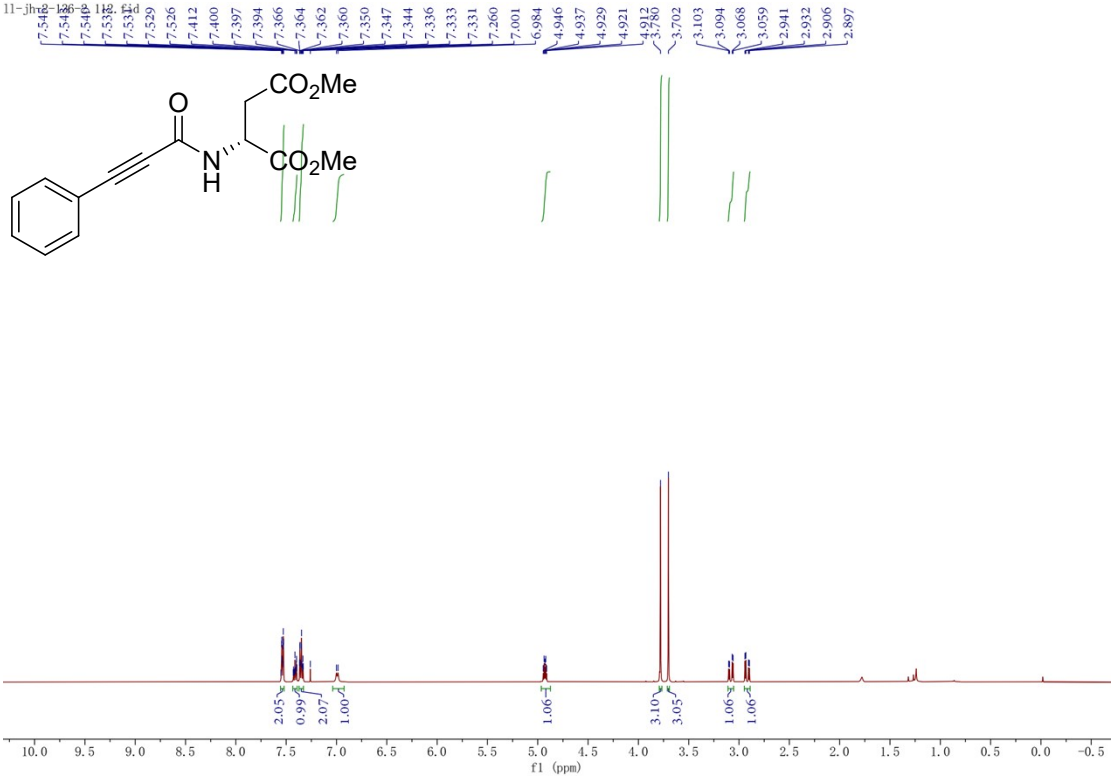
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ba**



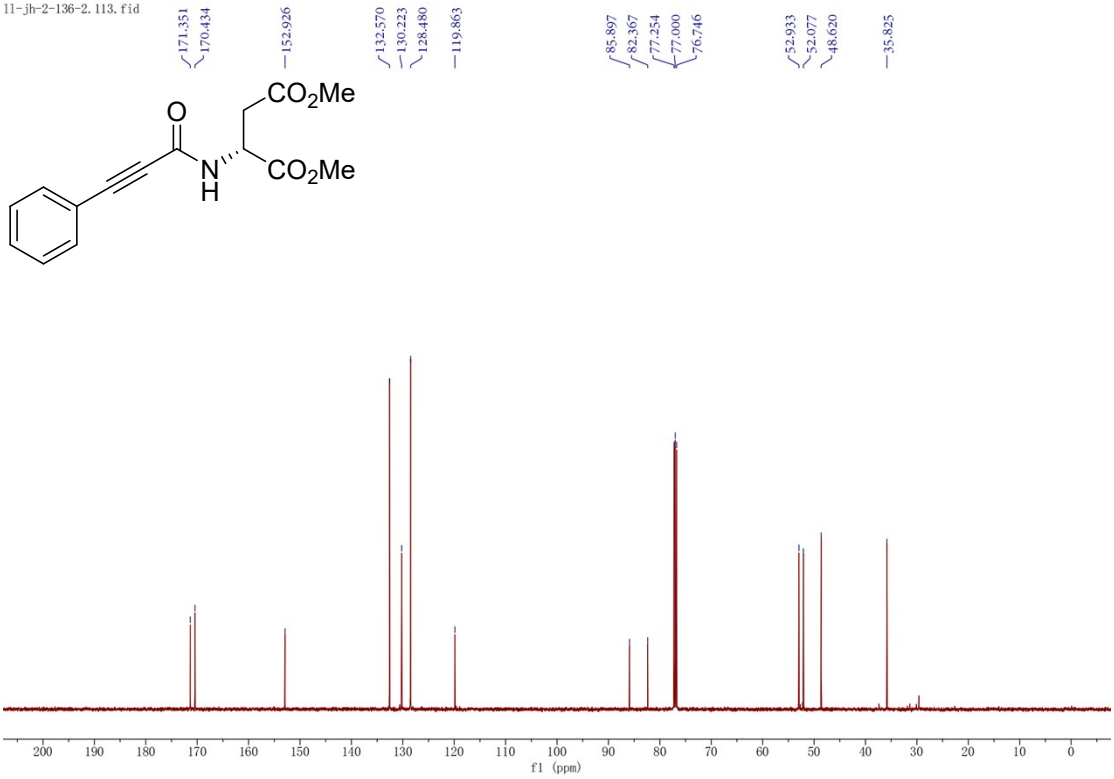
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ba**



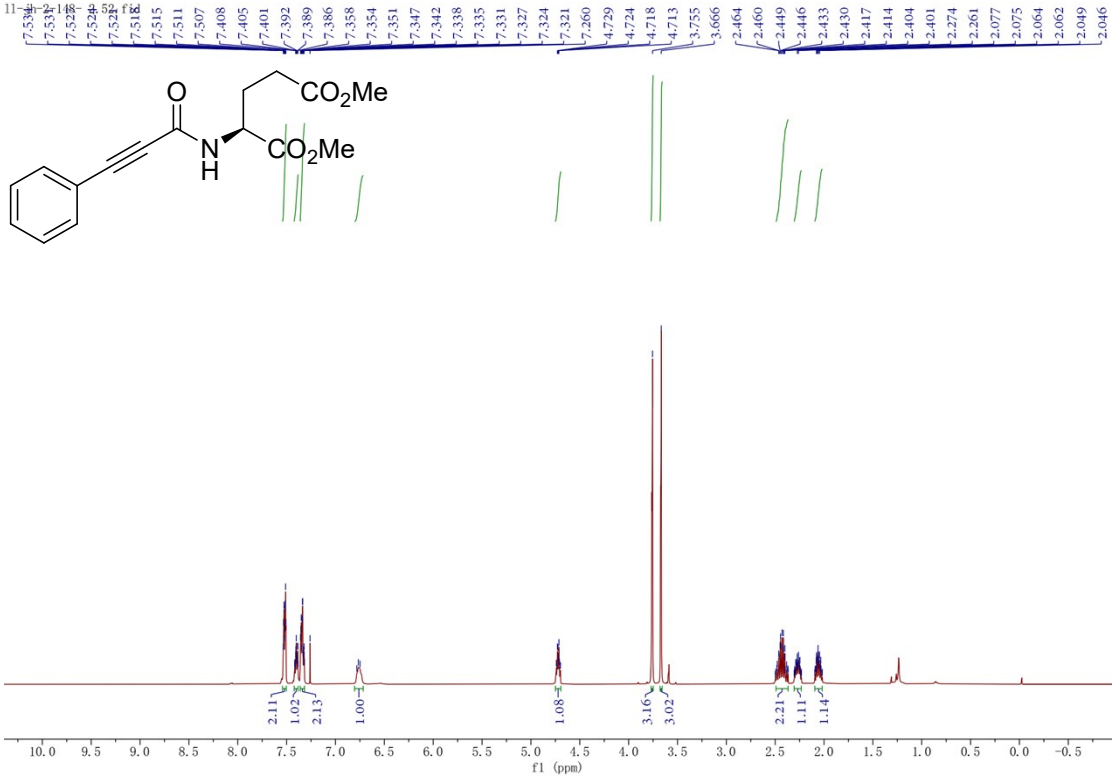
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ca**



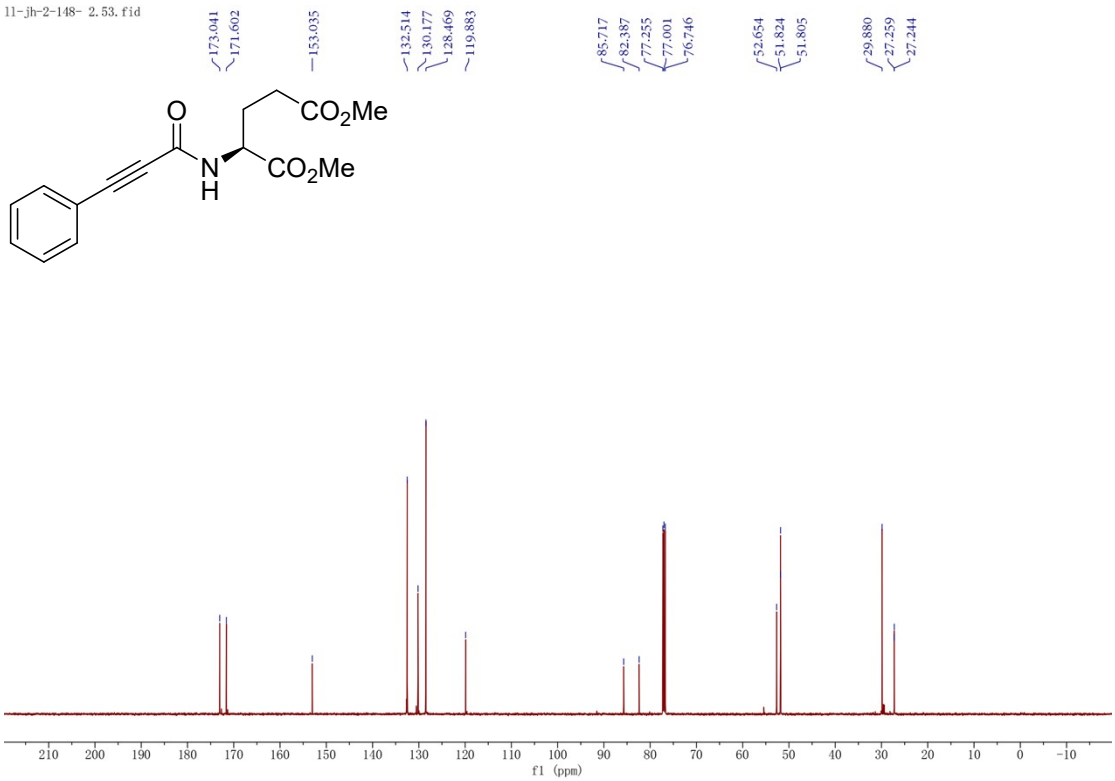
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ca**



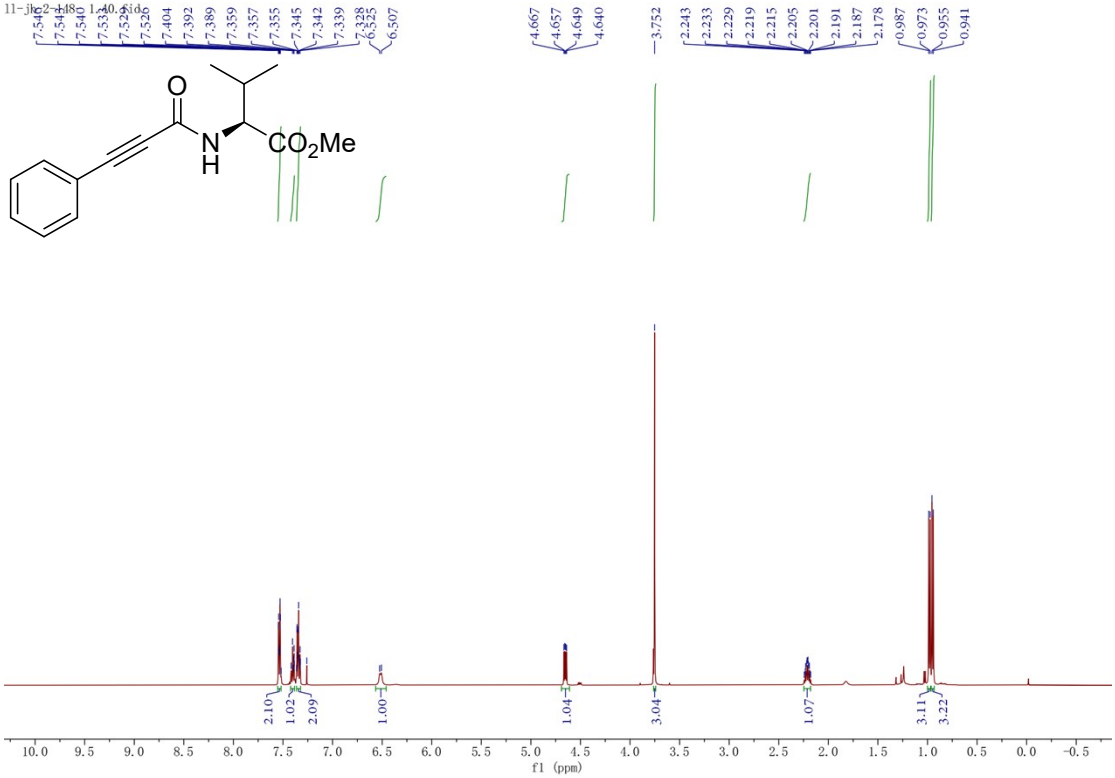
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5da**



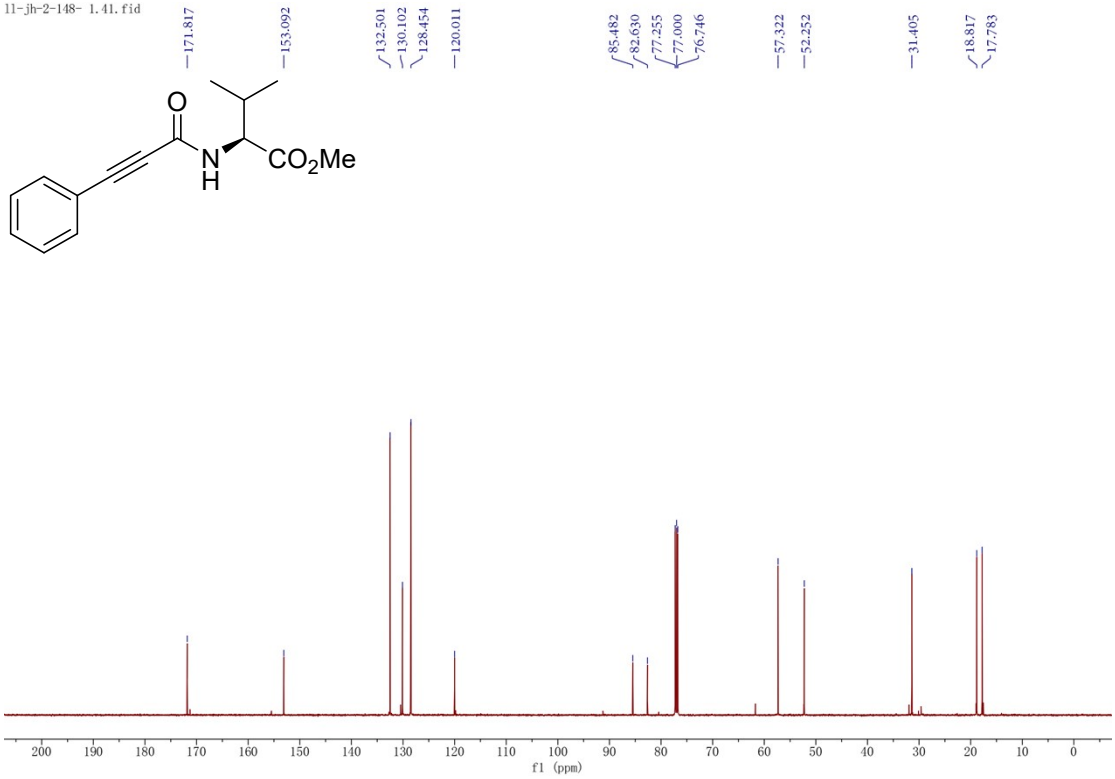
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5da**



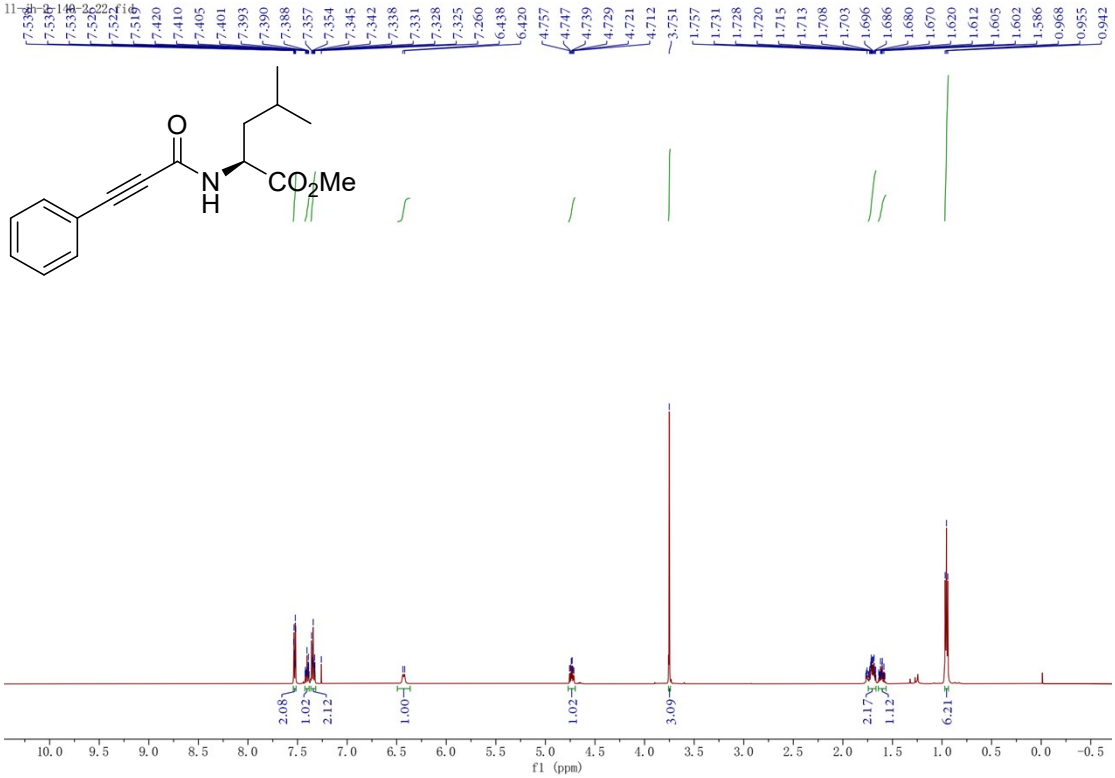
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ea**



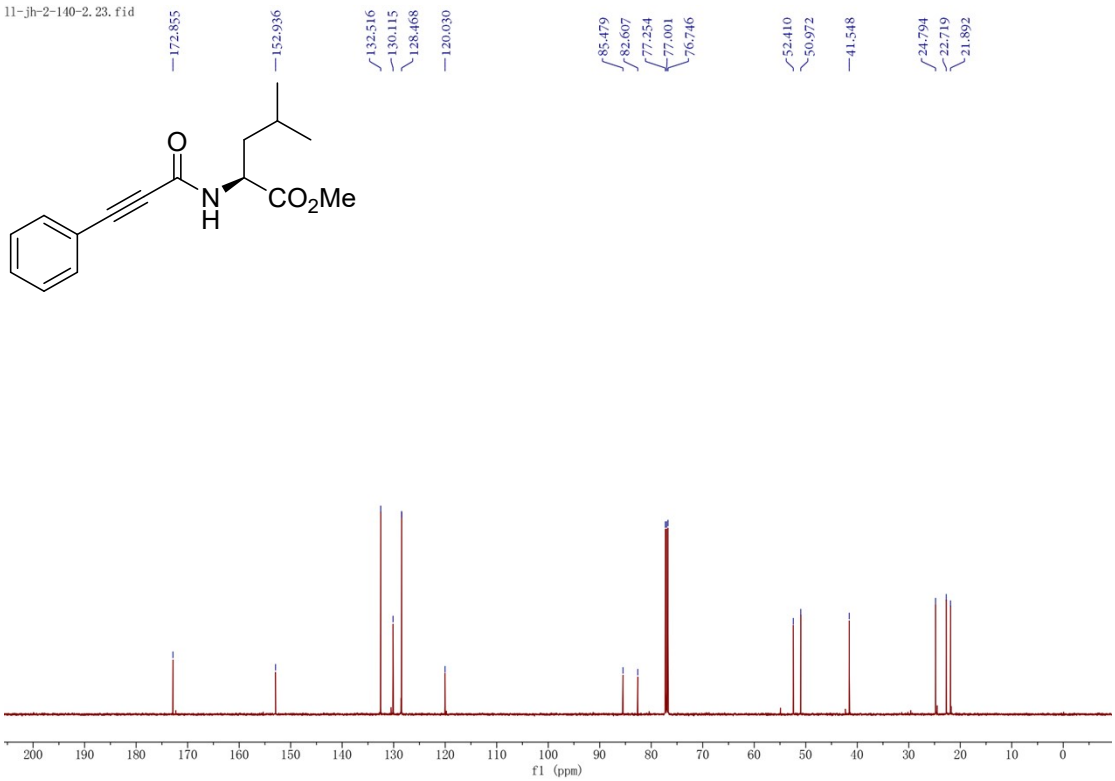
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ea**



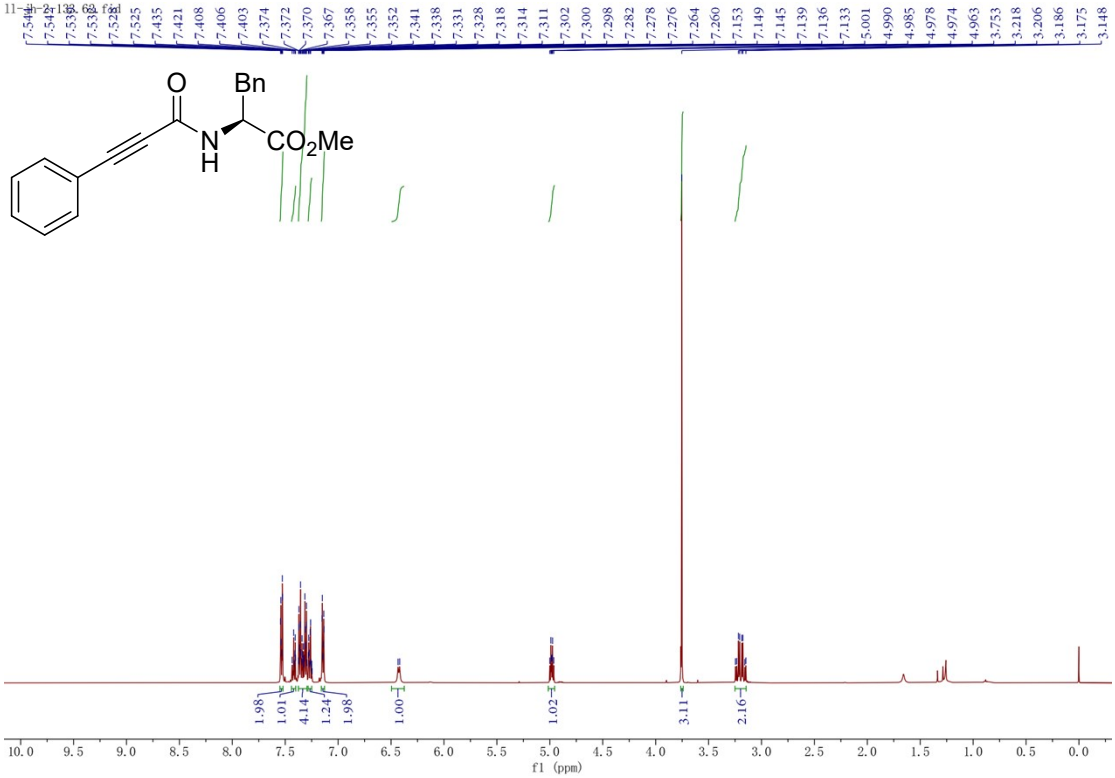
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5fa**



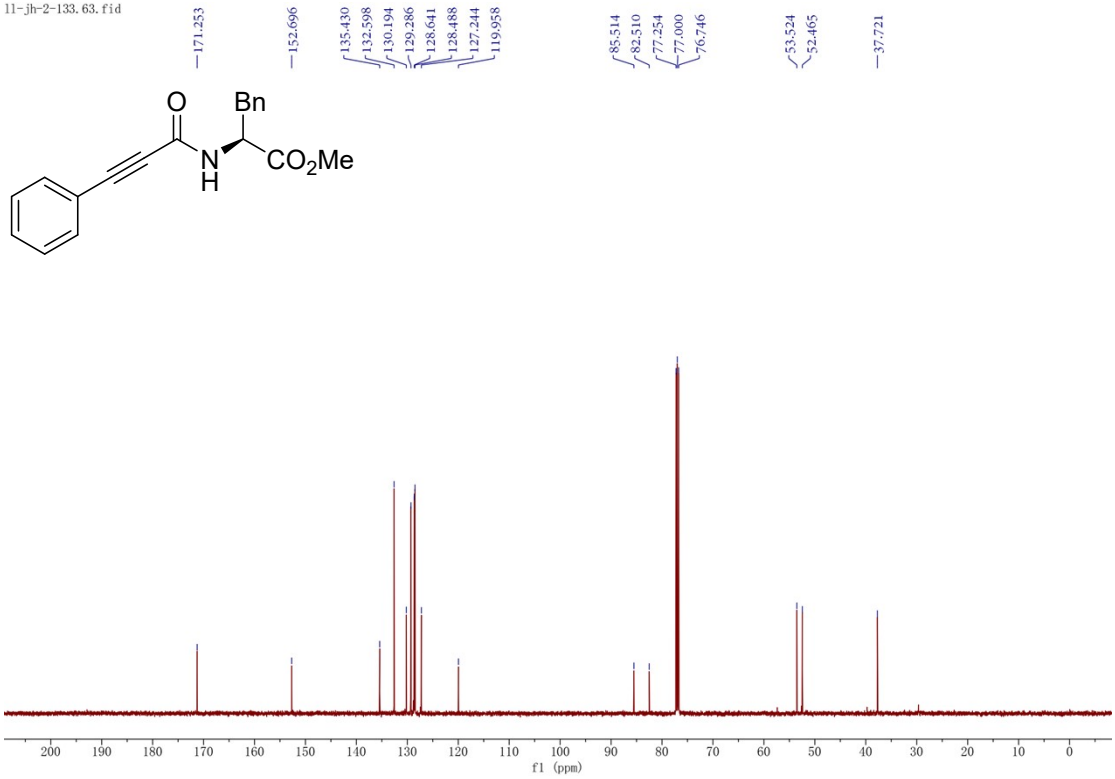
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ea**



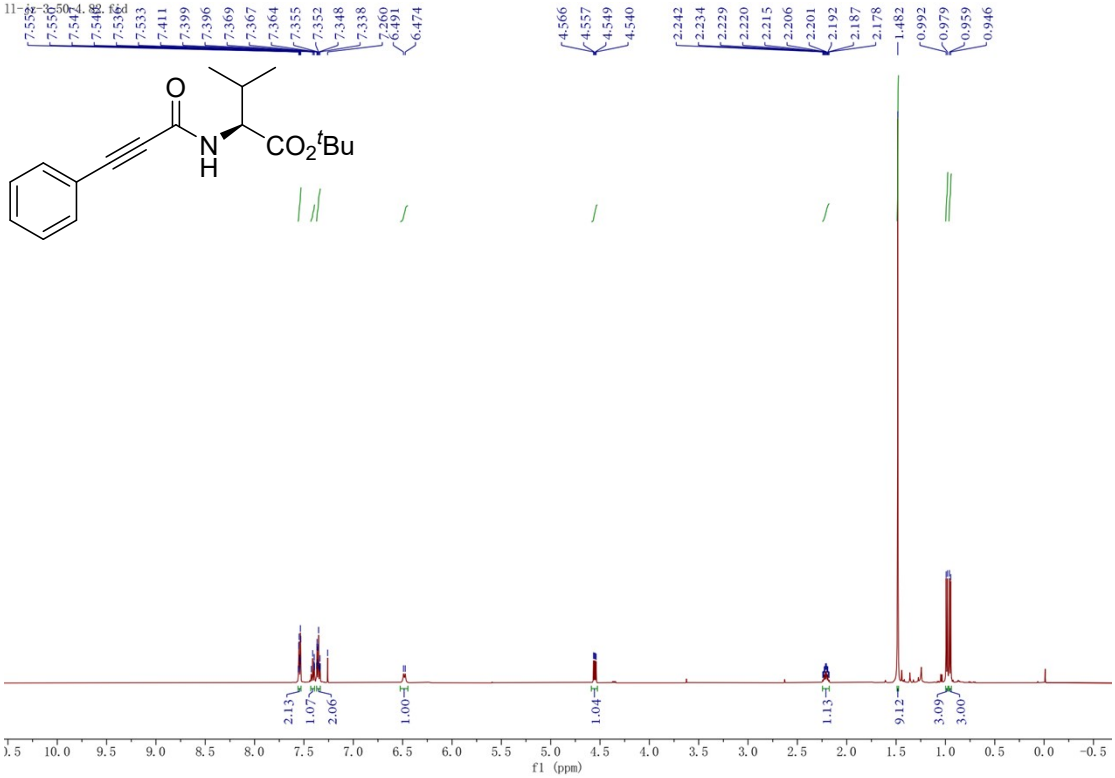
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ga**



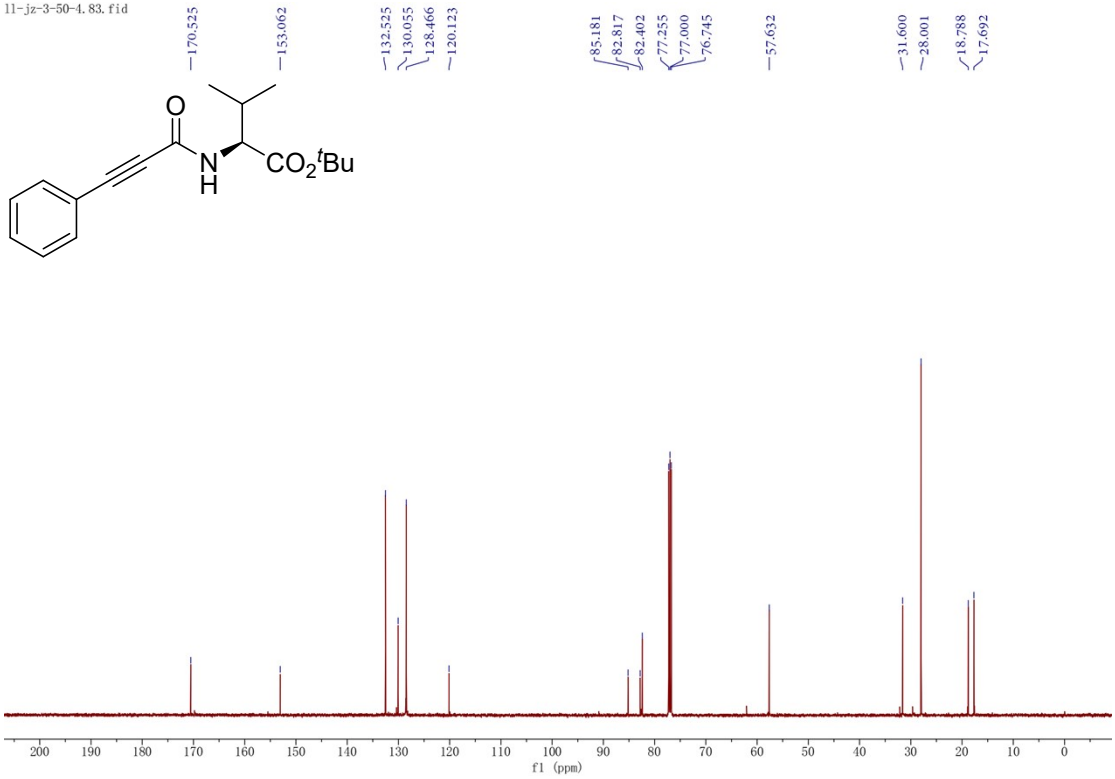
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ga**



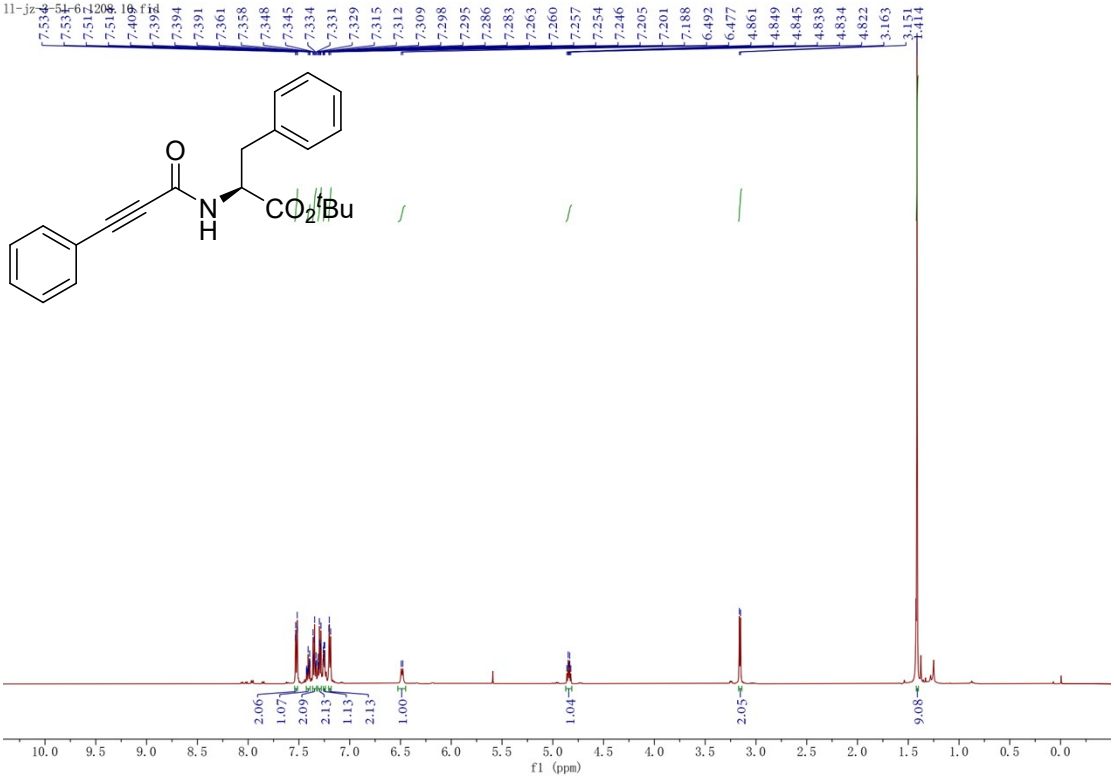
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ha**



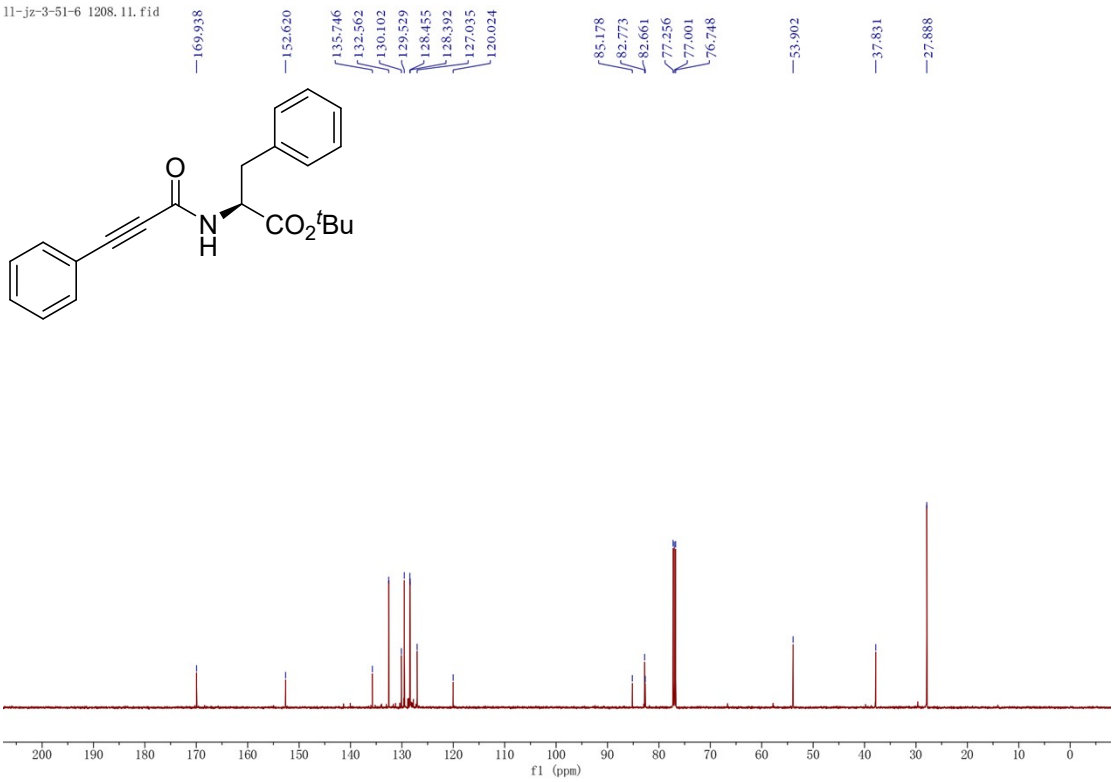
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ha**



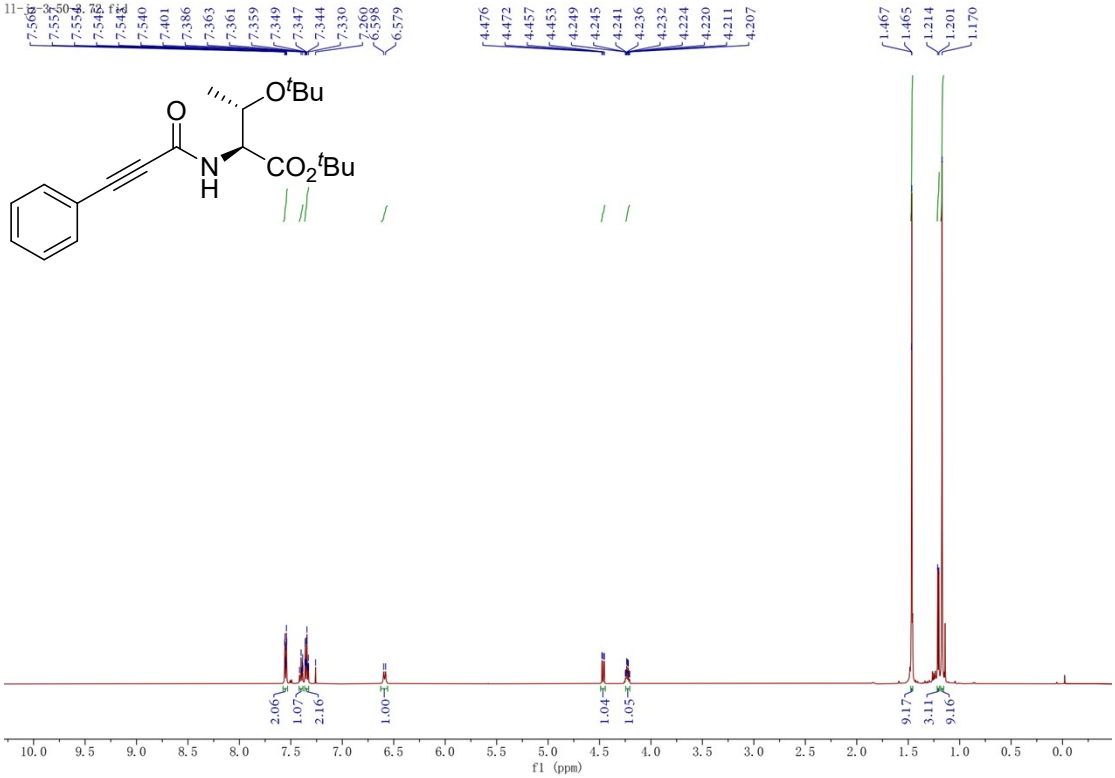
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ia**



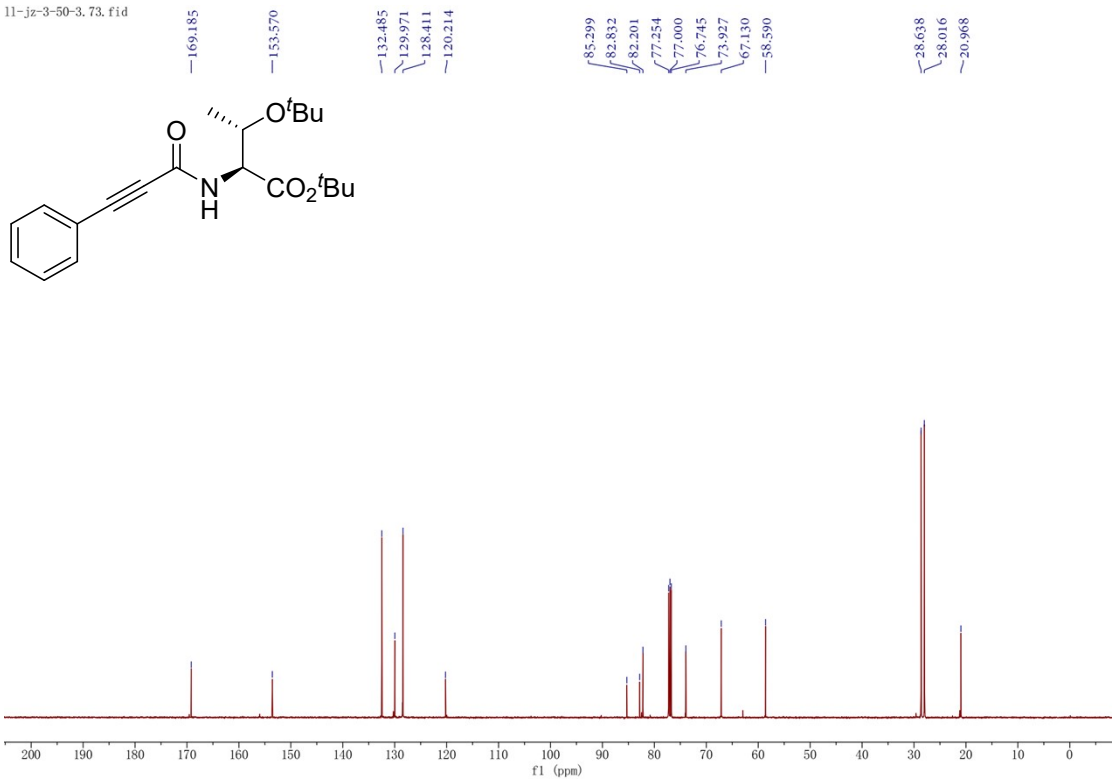
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ia**



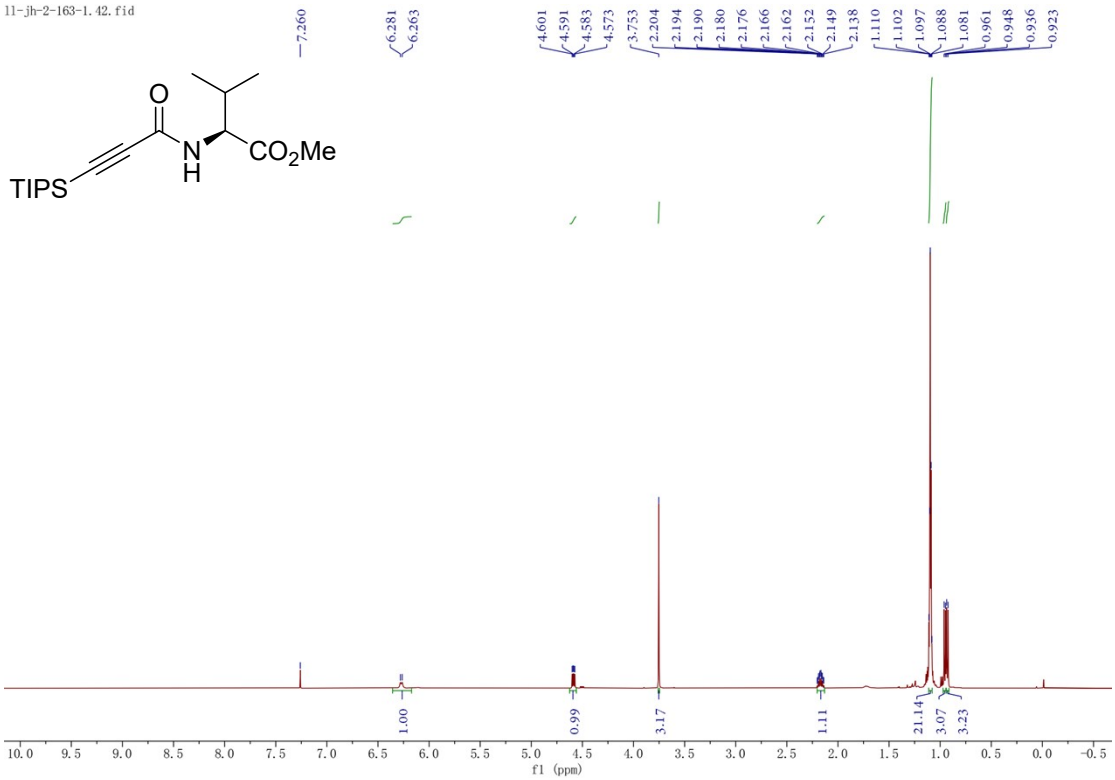
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ja**



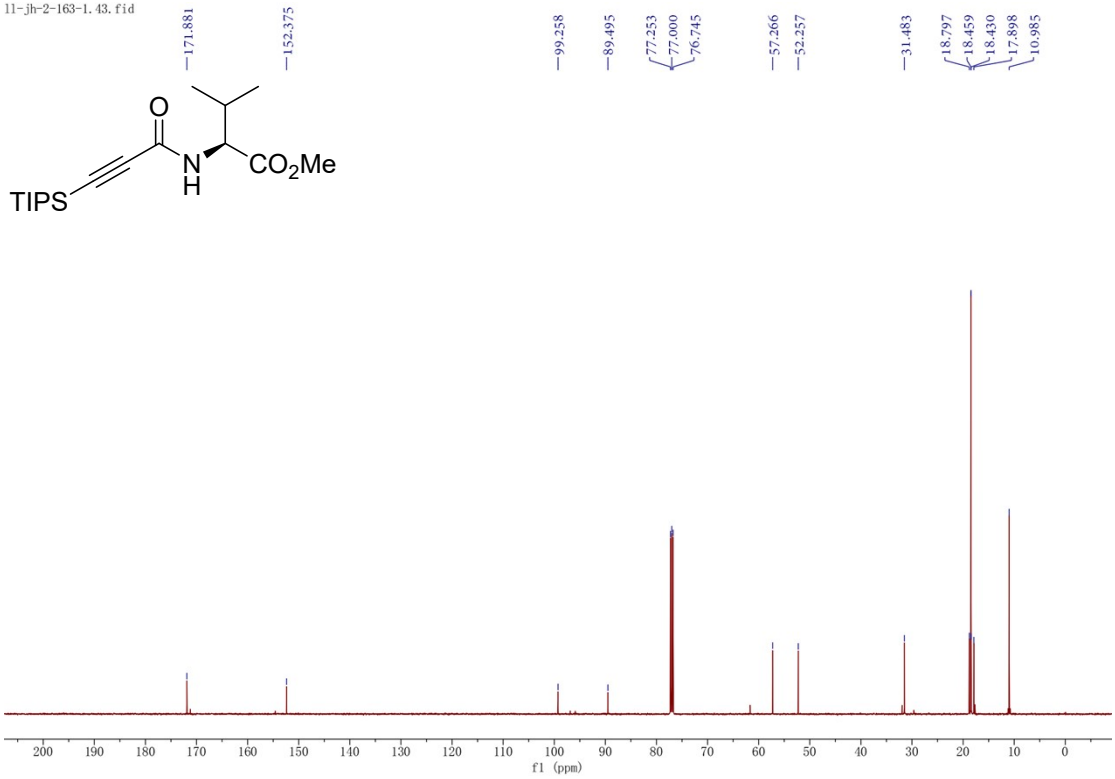
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ja**



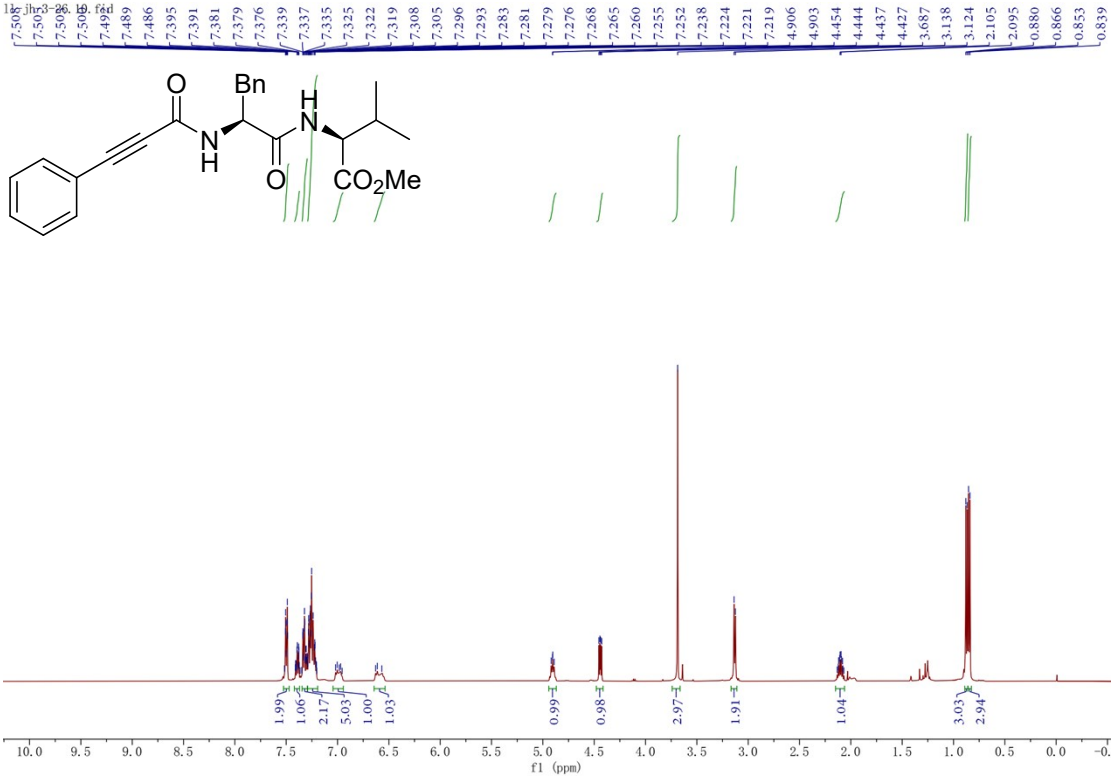
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5bm**



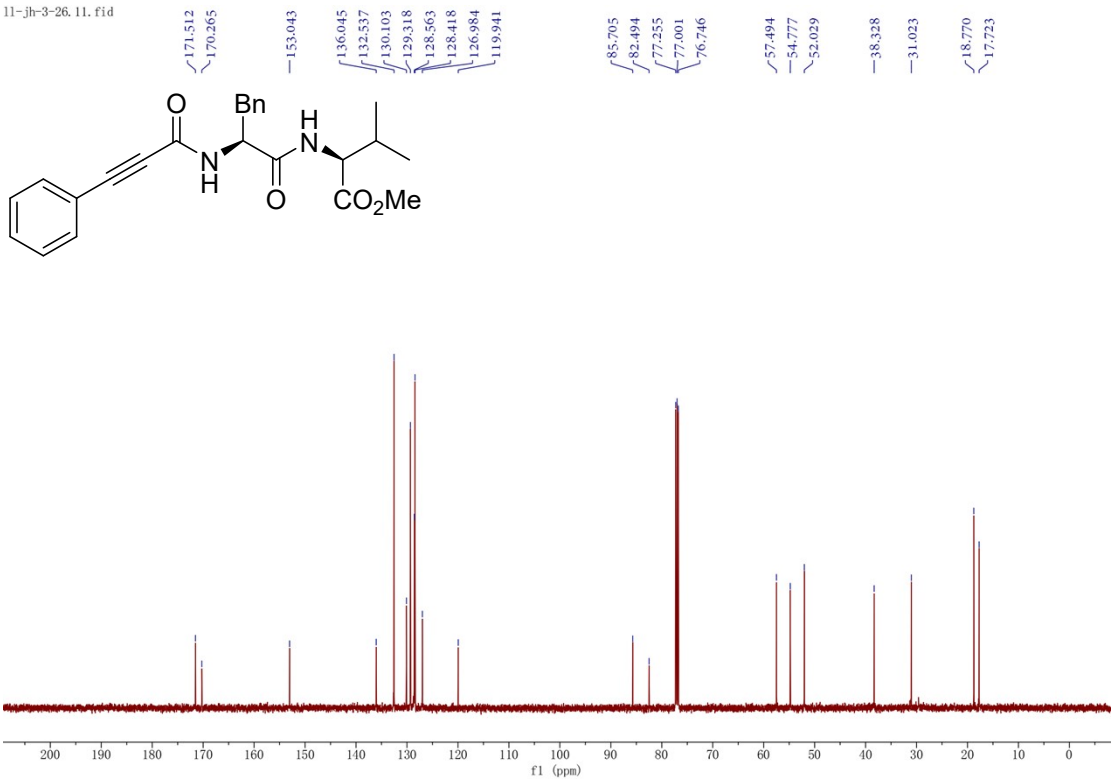
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5bm**



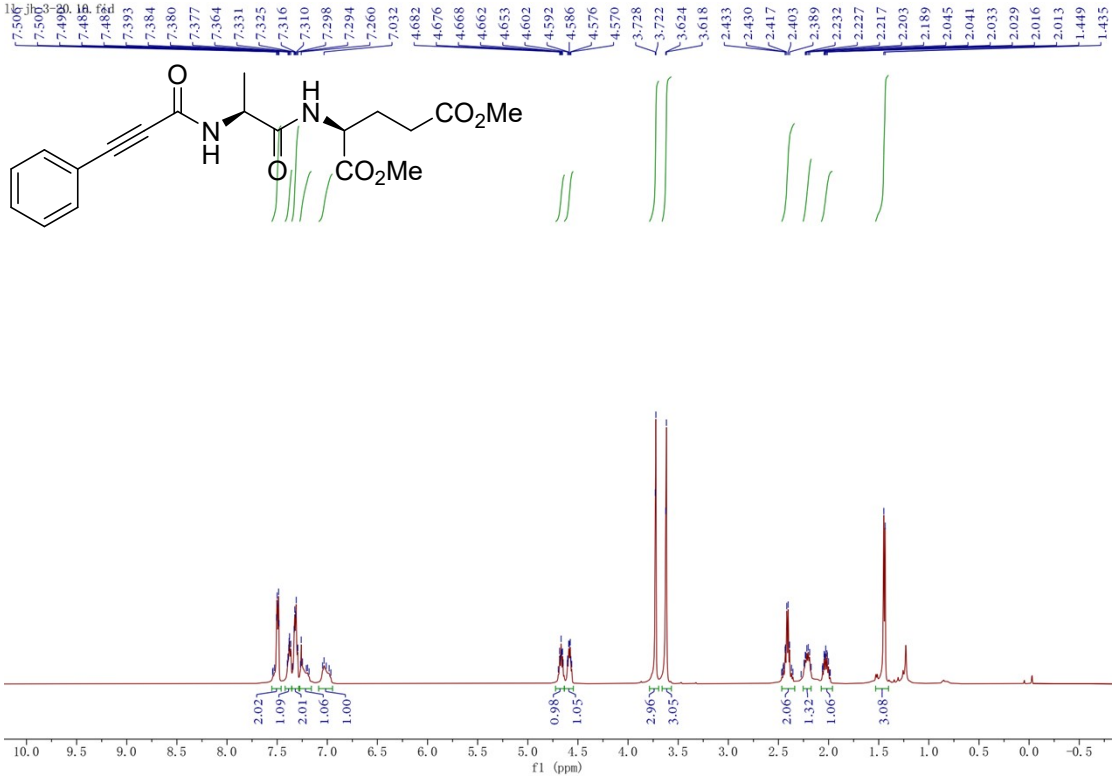
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ka**



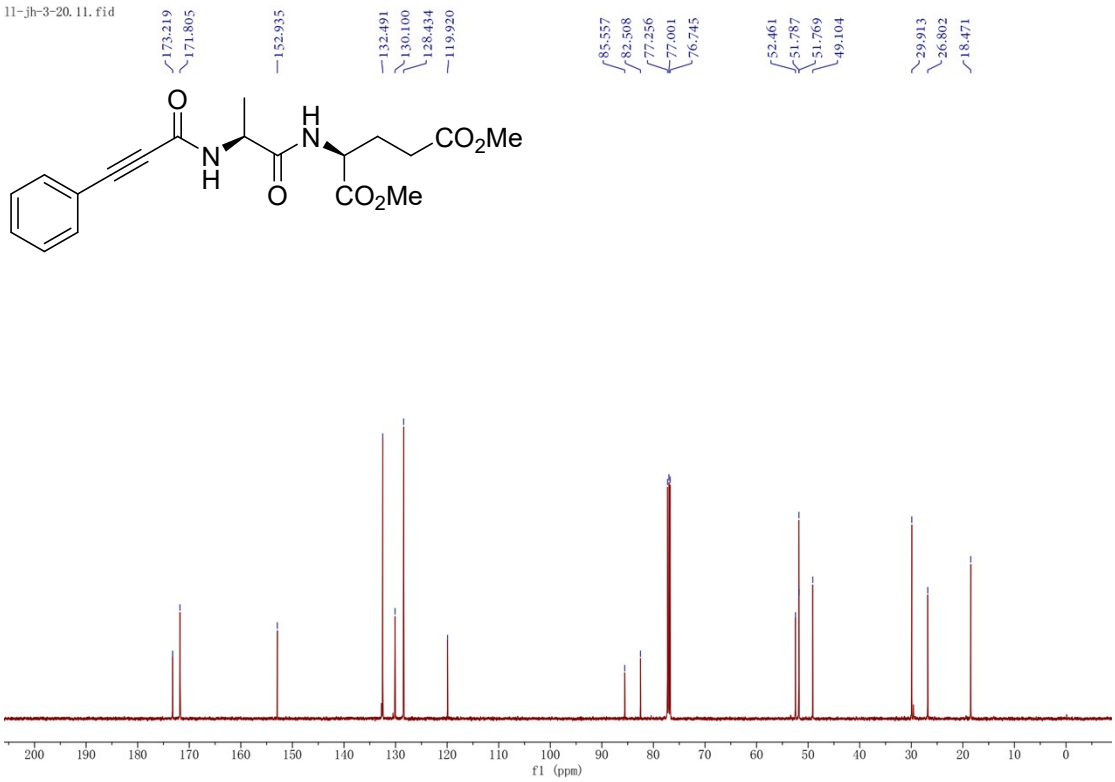
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ka**



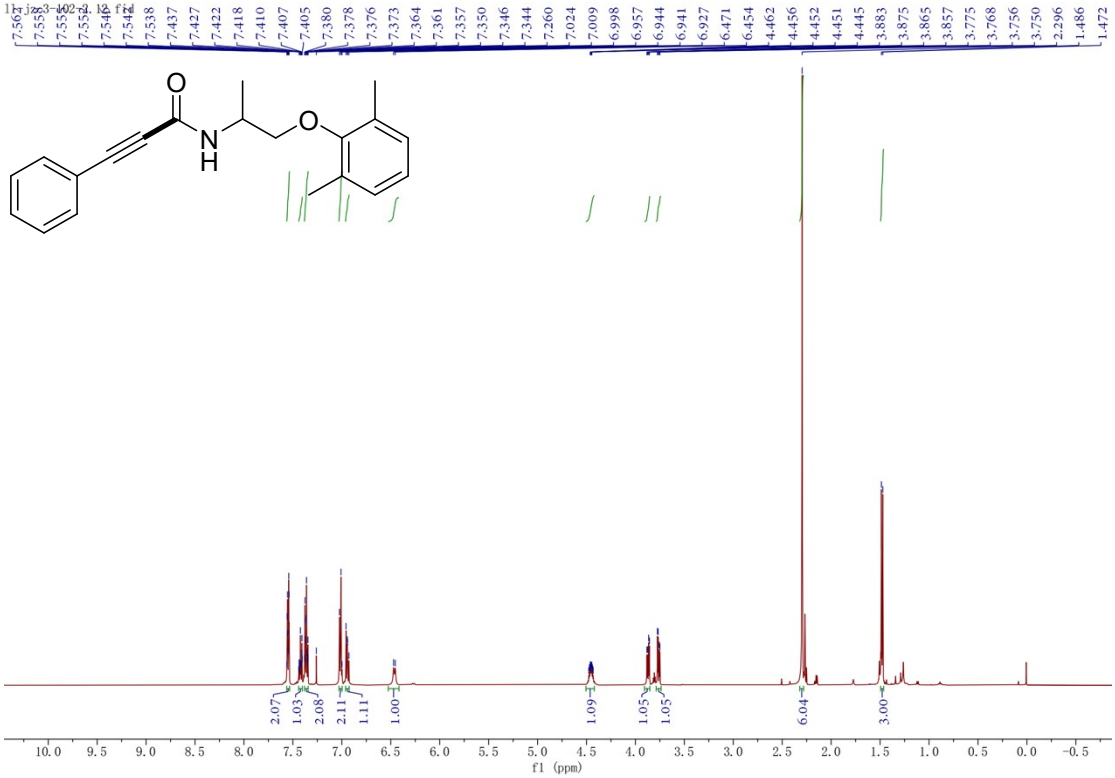
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5la**



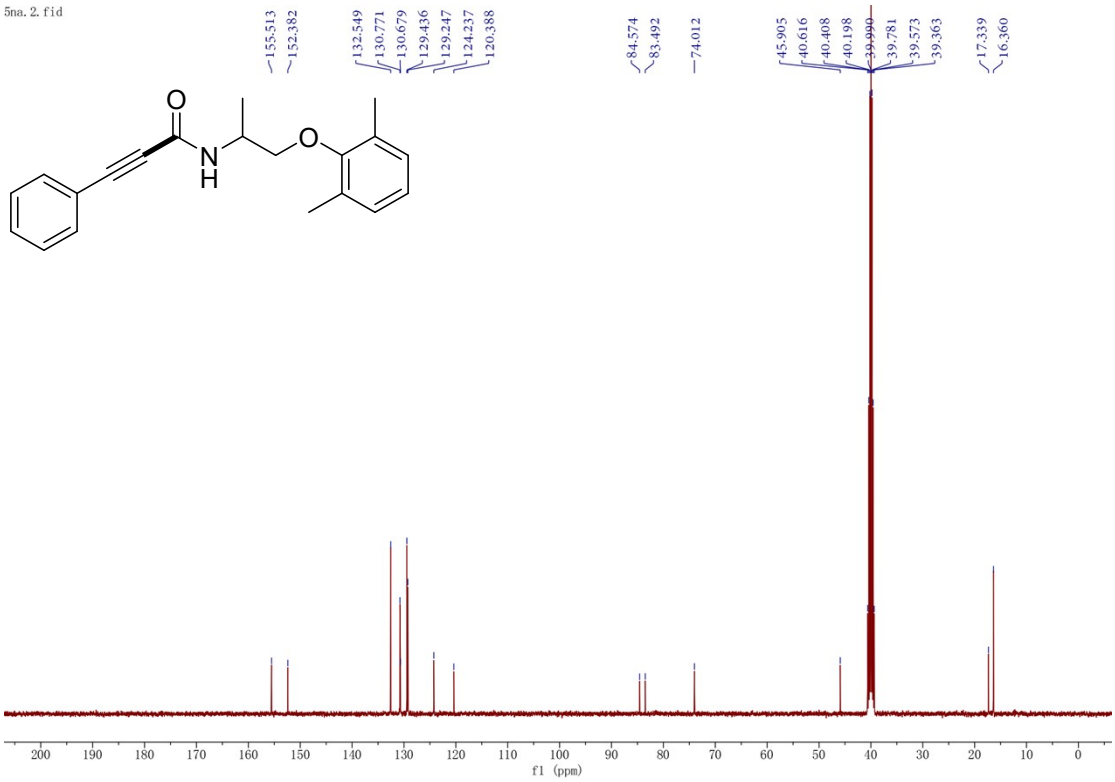
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5la**



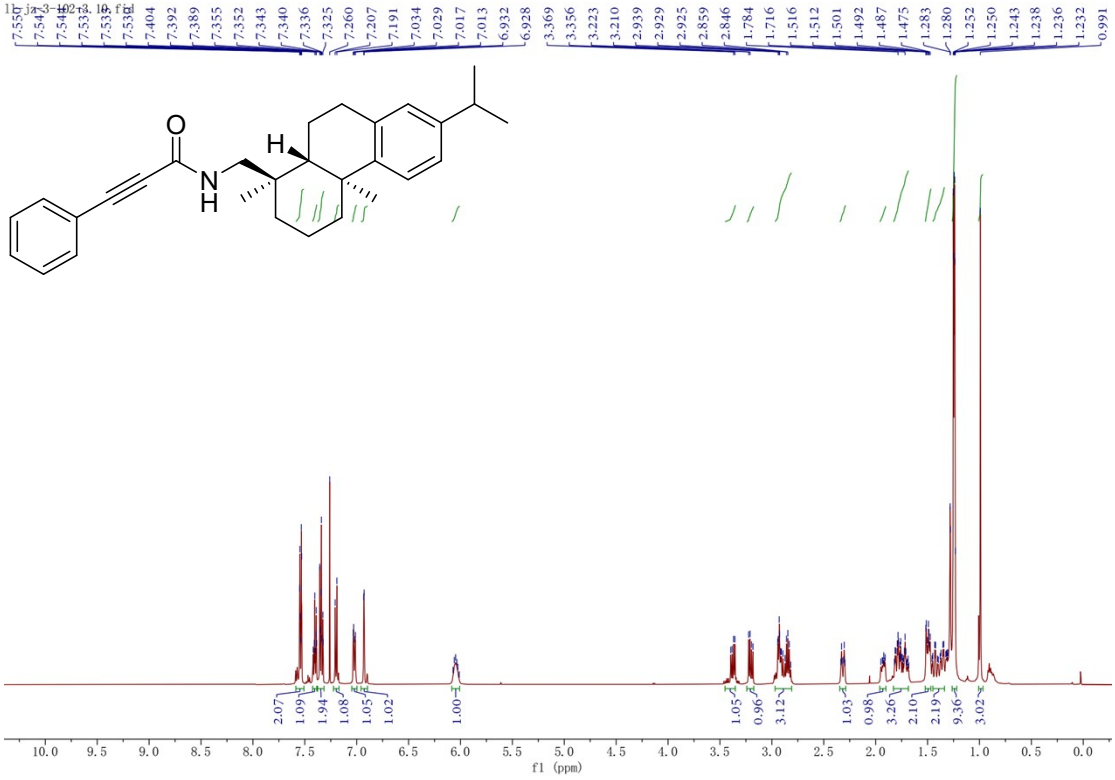
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ma**



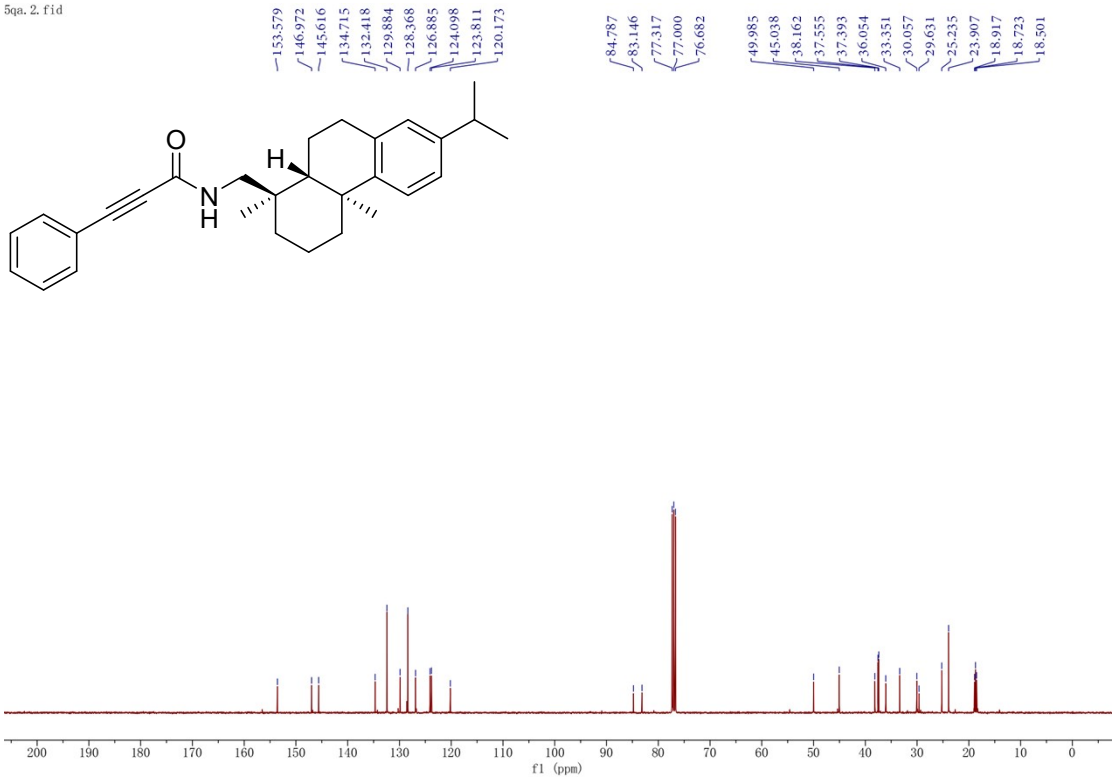
^{13}C NMR-spectrum (125 MHz, DMSO-d_6) of **5ma**



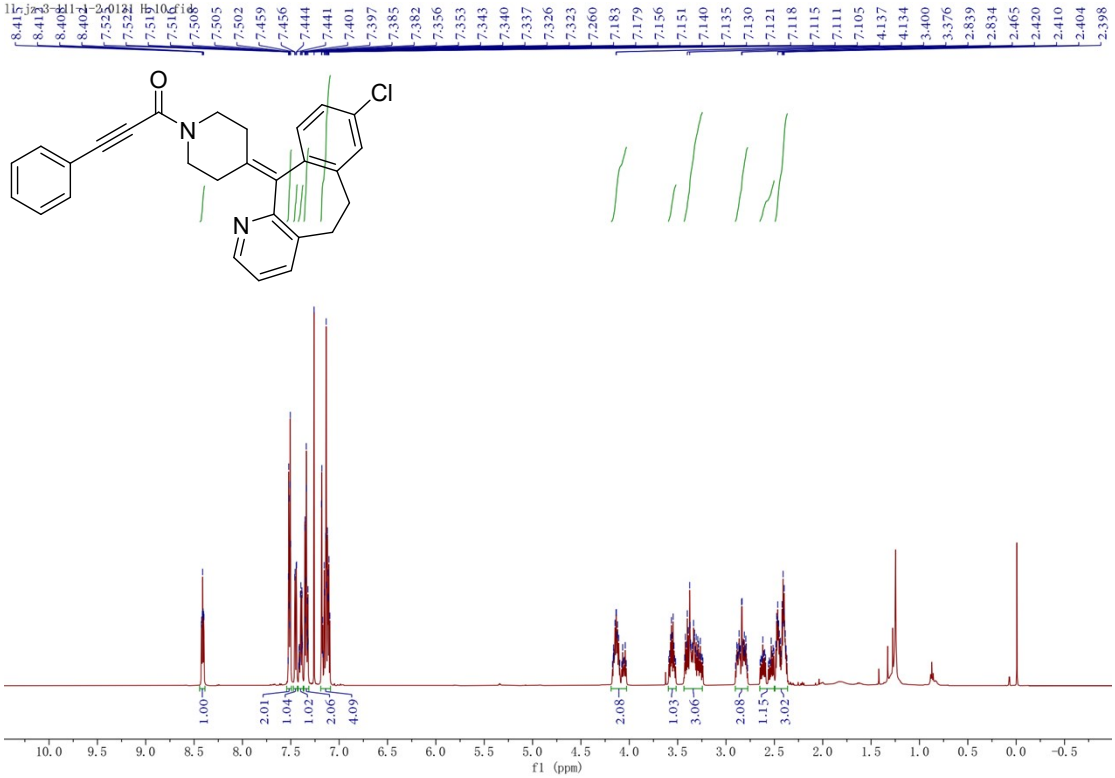
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5na**



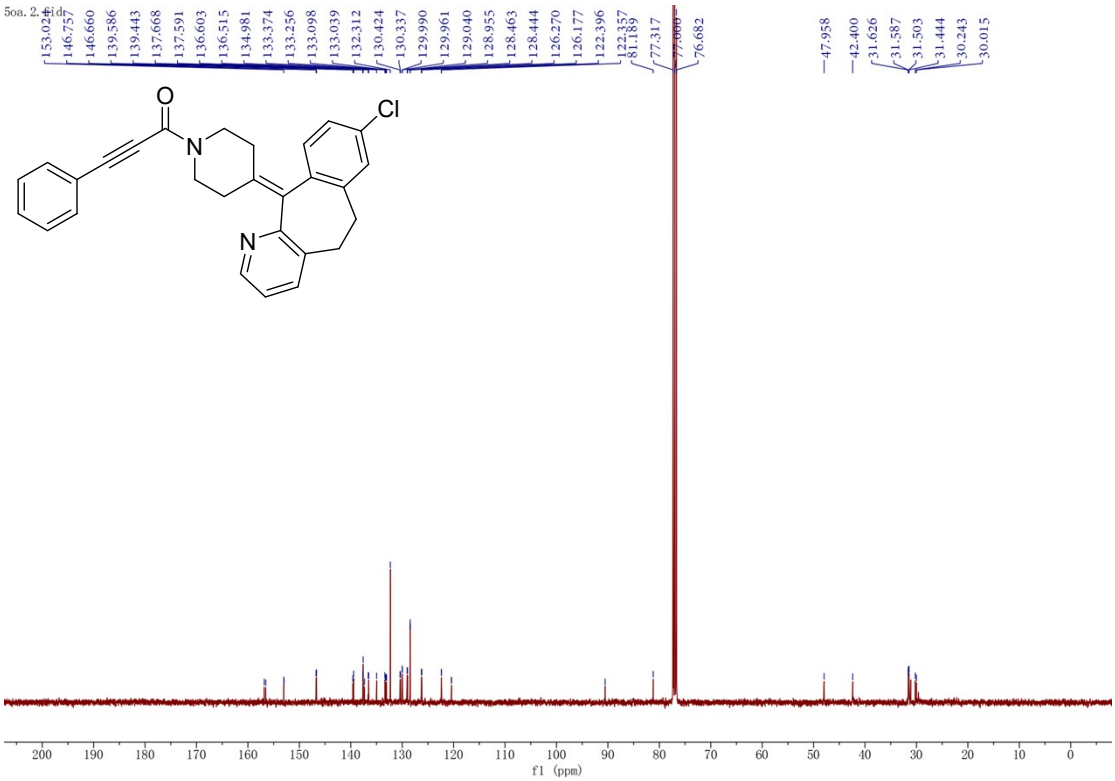
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5na**



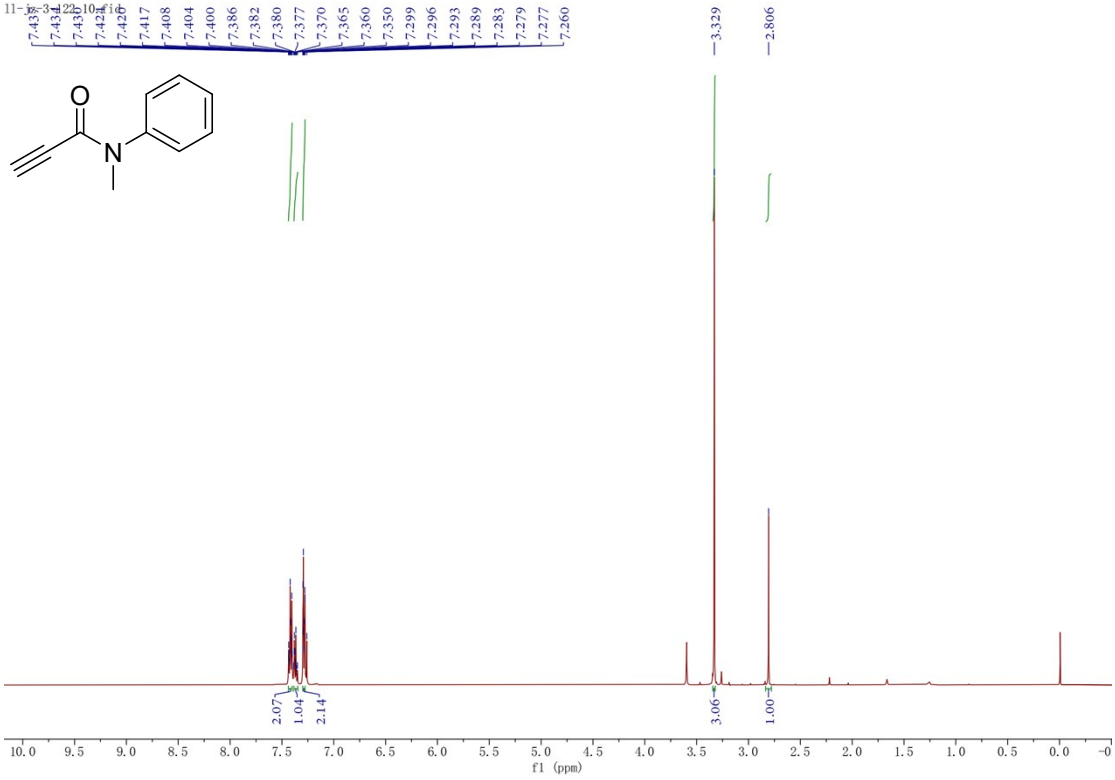
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5oa**



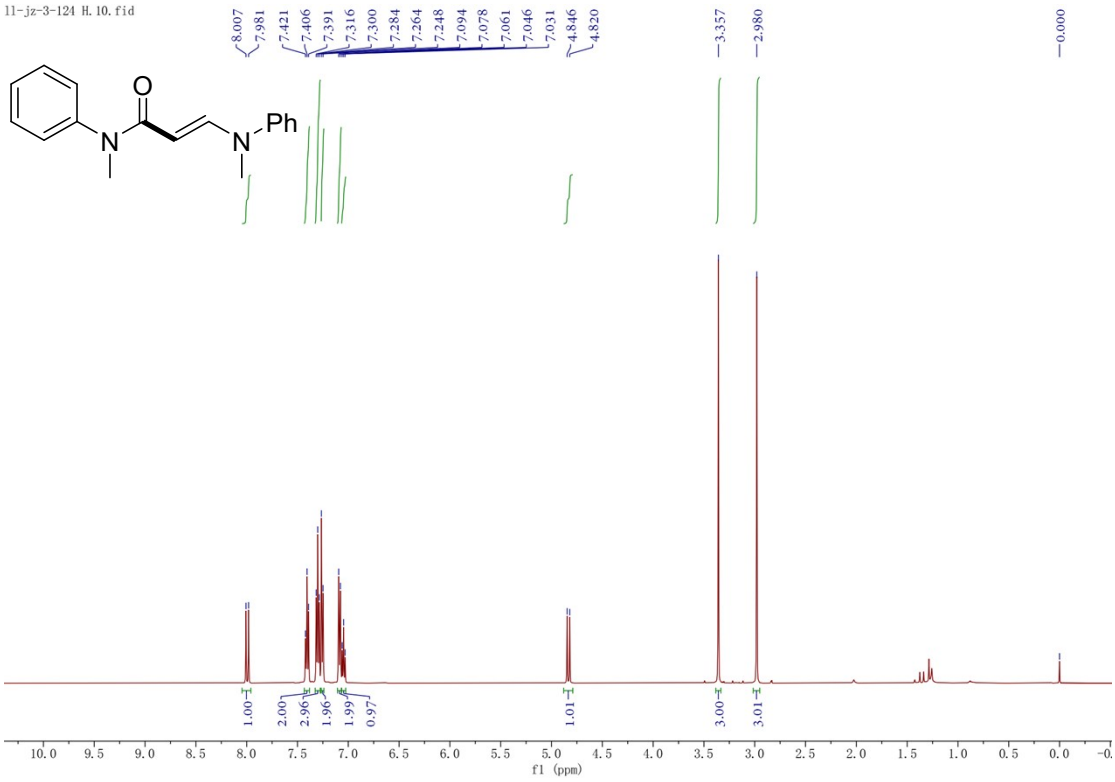
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5oa**



^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **6**



^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7**



^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **8**