Supporting Information for:

Facile synthesis of propargylamines by metal-free doubly decarboxylative coupling

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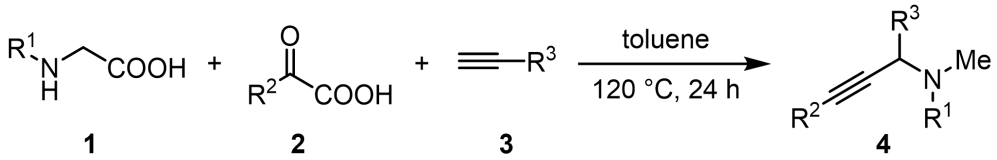
General Information

Unless otherwise noted, all commercial reagents (include part starting compounds **1** and **2**) were used directly as purchased. All workup and purification procedures were carried out with reagent-grade solvents that had not been predried under an ambient atmosphere. Thin-layer chromatography (TLC) was performed, and visualization of the compounds was accomplished with UV light (254 nm) or iodine. Products were purified by flash chromatography on silica gel (100-200 mesh). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel and eluted with petroleum/ethyl acetate to afford the desired product . ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ operating at 400 MHz and 100 MHz, respectively. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent $CDCl_3$ (7.29 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (77.10 ppm). Chemical shifts are reported in δ (parts per million) values. Coupling constants J are reported in Hz. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), and multiple (m). High-resolution mass spectra were recorded on a liquid chromatograph mass spectrometer (LCMS-IT-TOF).

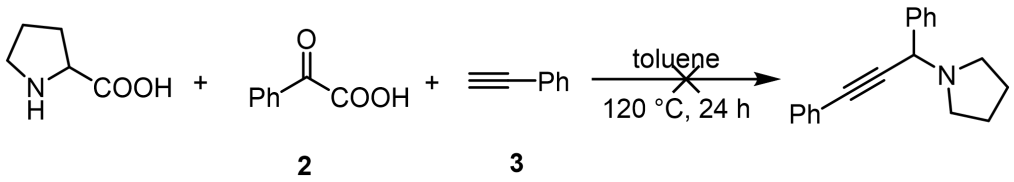
General Procedure for the Preparation of Propargylamines 4



1 **2** **3** **4**

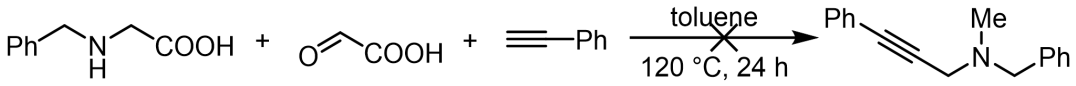
To a dried tube with a stirring bar were added amino acids **1** (0.60 mmol), α-keto acids **2** (0.75 mmol), and terminal alkynes **3** (0.50mmol), and toluene (2 mL). Then place the reaction tube in a preheated oil bath and stir at 120 ℃ for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography. The required products **4a**-**4x** were obtained using petroleum ether/ethyl acetate (30/1). The analysis data of propargylamines **4a**-**4x** are shown below.

Restriction Substrate Studies



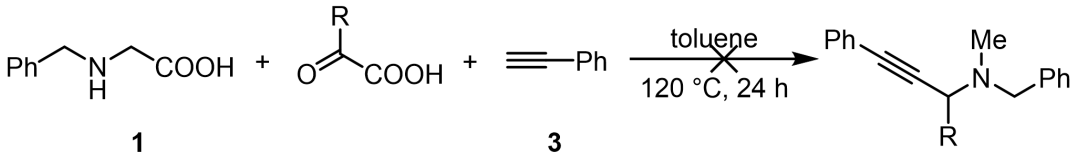
2 **3**

To a dried tube with a stirring bar were added proline (0.60 mmol), phenylglyoxylic acid **2** (0.75 mmol), and phenacetylene **3** (0.50mmol), and toluene (2 mL). Then place the reaction tube in a preheated oil bath and stir at 120 ℃ for 24 h. After cooling to room temperature, the corresponding target product was not observed using thin layer chromatography.



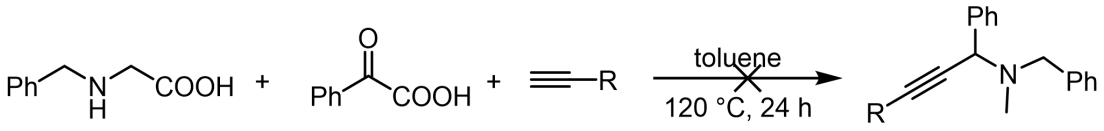
1 **3**

To a dried tube with a stirring bar were added *N*-benzylglycine **1** (0.60 mmol), glyoxylic acid **2** (0.75 mmol), and phenacetylene **3** (0.50mmol), and toluene (2 mL). Then place the reaction tube in a preheated oil bath and stir at 120 ℃ for 24 h. After cooling to room temperature, the corresponding target product was not observed using thin layer chromatography.



1 **3**

To a dried tube with a stirring bar were added *N*-benzylglycine **1** (0.60 mmol), alkyl α-keto acid **2** (0.75 mmol), and phenacetylene **3** (0.50mmol), and toluene (2 mL). Then place the reaction tube in a preheated oil bath and stir at 120 ℃ for 24 h. After cooling to room temperature, the corresponding target product was not observed using thin layer chromatography.

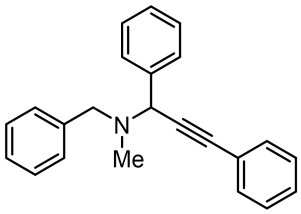


1 **2**

To a dried tube with a stirring bar were added *N*-benzylglycine **1** (0.60 mmol), phenylglyoxylic acid **2** (0.75 mmol), and alkyl alkyne **3** (0.50mmol), and toluene (2 mL). Then place the reaction tube in a preheated oil bath and stir at 120 ℃ for 24 h. After cooling to room temperature, the corresponding target product was not observed using thin layer chromatography.

^{1}H NMR and ^{13}C NMR Data of the Propargylamines 4

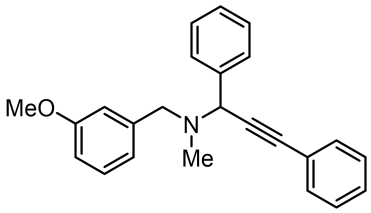
***N*-benzyl-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.69–7.61 (m, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.47–7.31 (m, 9H), 5.01 (s, 1H), 3.82 (d, *J* = 13.1 Hz, 1H), 3.73 (d, *J* = 13.1 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 139.1, 132.0, 129.1, 128.4, 128.4, 128.3, 128.2, 127.6, 127.2, 123.3, 88.8, 84.8, 59.65, 59.0, 38.1. Known compound.[1]

N-(3-methoxybenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4b)

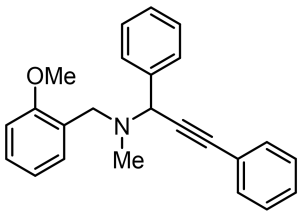


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.62 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.41 (dd, *J* = 8.4, 4.6 Hz, 5H), 7.36 – 7.27 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 9.2 Hz, 1H), 4.98 (s, 1H), 3.86 (s, 3H), 3.71 (dd, *J* = 38.0, 13.2 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 141.0, 139.0, 131.9, 129.3, 128.4, 128.4, 128.3, 128.2, 127.6, 123.3, 121.4, 114.4, 112.6, 88.7, 84.6, 59.5, 58.9, 55.2, 38.1.

HRMS m/z (ESI^+): Calculated for $C_{24}H_{23}NO$ ($[M+H]^+$): 342.1852, found: 342.1854.

N-(2-methoxybenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4c)

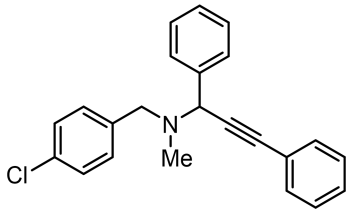


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.66 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.43 (dd, *J* = 10.8, 4.6 Hz, 5H), 7.39 – 7.28 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 5.08 (s, 1H), 3.91 – 3.84 (m, 4H), 3.75 (d, *J* = 13.7 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 139.3, 132.0, 130.4, 128.6, 128.4, 128.2, 128.2, 128.1, 127.5, 127.3, 123.5, 120.4, 110.5, 88.5, 85.3, 60.3, 55.5, 52.7, 38.3.

HRMS m/z (ESI^+): Calculated for $C_{24}H_{23}NO$ ($[M+H]^+$): 342.1852, found: 342.1852.

N-(4-chlorobenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4d)

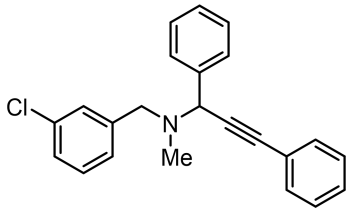


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.63 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.45 – 7.39 (m, 7H), 7.38 – 7.34 (m, 3H), 4.96 (s, 1H), 3.73 (d, *J* = 13.3 Hz, 1H), 3.66 (d, *J* = 13.3 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.9, 132.8, 131.9, 130.3, 128.5, 128.4, 128.4, 128.3, 128.3, 127.7, 123.2, 88.8, 84.5, 59.7, 58.1, 38.1.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}ClN$ ($[M+H]^+$): 346.1357, found: 346.1362.

N-(3-chlorobenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4e)

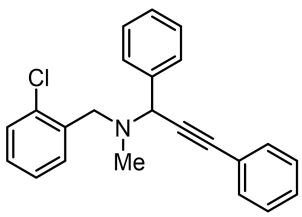


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.63 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.48 – 7.28 (m, 10H), 4.98 (s, 1H), 3.73 (d, *J* = 13.5 Hz, 1H), 3.66 (d, *J* = 13.4 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 138.8, 134.2, 131.9, 129.6, 129.0, 128.4, 128.4, 128.3, 128.3, 127.7, 127.3, 127.1, 123.2, 88.8, 84.5, 60.0, 58.2, 38.2.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}ClN$ ($[M+H]^+$): 346.1357, found: 346.1360.

N-(2-chlorobenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4f)

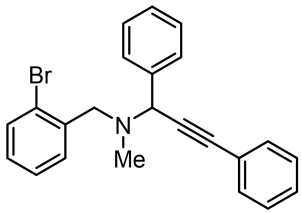


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.65 – 7.56 (m, 3H), 7.40 (dt, *J* = 6.3, 4.0 Hz, 6H), 7.27 (ddd, *J* = 31.5, 14.8, 8.2 Hz, 3H), 5.02 (s, 1H), 3.97 (d, *J* = 13.8 Hz, 1H), 3.77 (d, *J* = 13.8 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.7, 134.7, 131.9, 131.0, 129.6, 128.4, 128.3, 128.2, 127.6, 126.6, 123.3, 88.8, 84.7, 60.2, 56.2, 37.7.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}ClN$ ($[M+H]^+$): 346.1357, found: 346.1360.

N-(2-bromobenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4g)

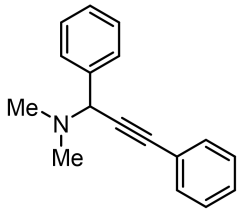


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.66 – 7.55 (m, 4H), 7.40 (dt, *J* = 7.0, 4.0 Hz, 5H), 7.36 – 7.30 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.03 (s, 1H), 3.97 (d, *J* = 13.8 Hz, 1H), 3.76 (d, *J* = 13.8 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 138.3, 132.9, 131.9, 131.1, 128.6, 128.4, 128.2, 128.2, 127.6, 127.2, 125.0, 123.3, 88.8, 84.7, 60.1, 58.8, 37.5.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}BrN$ ($[M+H]^+$): 390.0852, found: 390.0856.

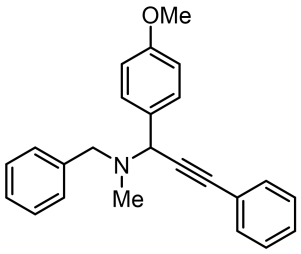
N,*N*-dimethyl-1,3-diphenylprop-2-yn-1-amine (4h)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 2H), 7.59 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.46 – 7.36 (m, 6H), 4.90 (s, 1H), 2.39 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 131.9, 128.6, 128.4, 128.3, 128.3, 127.8, 123.2, 88.5, 84.8, 62.3, 41.7. Known compound.[2]

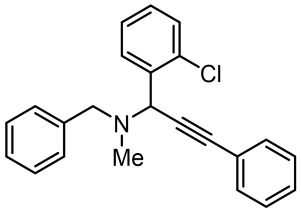
N-benzyl-1-(4-methoxyphenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4i)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 14.1, 5.2 Hz, 3H), 7.62 – 7.36 (m, 10H), 7.05 (d, *J* = 8.7 Hz, 1H), 5.04 (s, 1H), 3.92 (s, 3H), 3.80 (dd, *J* = 27.3, 15.7 Hz, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 139.5, 132.1, 131.3, 129.6, 129.2, 128.5, 128.5, 128.4, 127.2, 123.4, 113.6, 88.7, 85.2, 59.2, 58.9, 55.4, 38.1. Known compound.[1]

N-benzyl-1-(2-chlorophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4j)

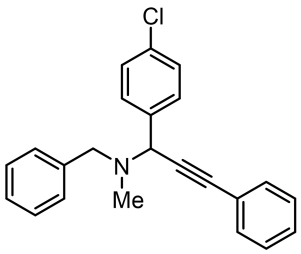


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.61 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.45 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.41 (dd, *J* = 6.1, 2.8 Hz, 4H), 7.32 (ddd, *J* = 13.0, 10.8, 4.3 Hz, 5H), 5.33 (s, 1H), 3.75 (t, *J* = 8.3 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 136.4, 134.8, 131.9, 130.8, 130.1, 129.3, 129.1, 128.4, 128.4, 128.2, 127.1, 126.2, 123.1, 88.8, 84.3, 59.4, 58.2, 37.2.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}ClN$ ($[M+H]^+$): 346.1357, found: 346.1360.

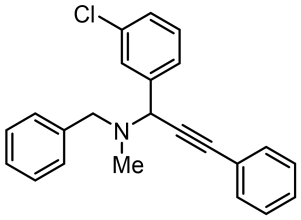
N-benzyl-1-(4-chlorophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4k)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.44 (dt, *J* = 12.9, 6.7 Hz, 7H), 7.35 (t, *J* = 7.2 Hz, 1H), 4.95 (s, 1H), 3.80 (d, *J* = 13.1 Hz, 1H), 3.71 (d, *J* = 13.1 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 137.8, 133.3, 132.0, 129.8, 129.1, 128.5, 128.5, 128.4, 127.3, 123.1, 89.1, 84.1, 59.0, 38.1. Known compound.[1]

N-benzyl-1-(3-chlorophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4l)

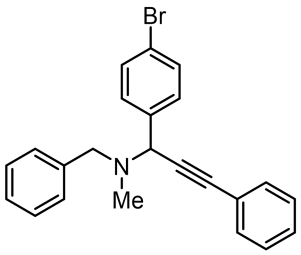


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.68 – 7.60 (m, 3H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.38 (m, 5H), 7.34 (q, *J* = 8.0 Hz, 3H), 4.94 (s, 1H), 3.79 (d, *J* = 13.1 Hz, 1H), 3.70 (d, *J* = 13.1 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.0, 134.2, 132.0, 129.5, 129.1, 128.5, 127.8, 127.3, 126.6, 123.0, 89.2, 83.8, 59.1, 59.1, 38.0.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}ClN$ ($[M+H]^+$): 346.1357, found: 346.1358.

N-benzyl-1-(4-bromophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4m)

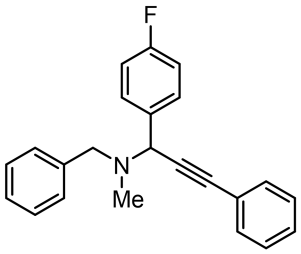


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 4H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.36 (m, 7H), 7.32 (d, *J* = 7.2 Hz, 1H), 4.90 (s, 1H), 3.76 (d, *J* = 13.1 Hz, 1H), 3.67 (d, *J* = 13.1 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.3, 131.9, 131.3, 130.1, 129.0, 128.4, 127.2, 123.0, 121.5, 89.1, 84.0, 59.0, 58.9, 38.0.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}BrN$ ($[M+H]^+$): 390.0852, found: 390.0855.

N-benzyl-1-(4-fluorophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4n)

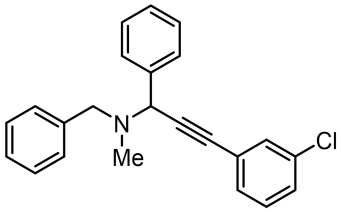


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.63 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.37 (m, 5H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 8.7 Hz, 2H), 4.94 (s, 1H), 3.78 (d, *J* = 13.1 Hz, 1H), 3.69 (d, *J* = 13.1 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 242.4 Hz), 139.2, 134.9 (d, *J* = 3.0 Hz), 132.0, 130.0, 129.9, 129.0, 128.4 (d, *J* = 8.1 Hz), 127.2, 123.1, 115.1, 115.0 (d, *J* = 22.2 Hz), 88.9, 84.4, 58.9, 58.9, 38.0.

^{19}F NMR (400 MHz, $CDCl_3$)δ -115.20 (s). Known compound.[1]

N-benzyl-3-(3-chlorophenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4p)

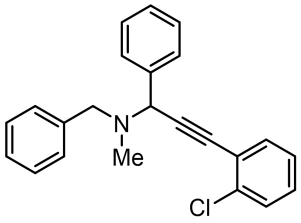


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.60 (s, 1H), 7.49 – 7.44 (m, 3H), 7.42 – 7.35 (m, 6H), 7.32 (dd, *J* = 7.7, 3.4 Hz, 2H), 4.96 (s, 1H), 3.77 (d, *J* = 13.0 Hz, 1H), 3.66 (d, *J* = 13.1 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.7, 134.2, 131.8, 130.1, 129.6, 129.1, 129.0, 128.5, 128.4, 128.3, 128.2, 127.8, 127.2, 124.9, 87.3, 86.2, 59.5, 59.0, 38.1.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}ClN$ ($[M+H]^+$): 346.1357, found: 346.1360.

N-benzyl-3-(2-chlorophenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4q)

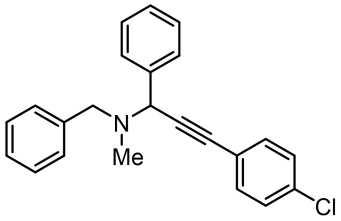


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.68 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 3H), 7.48 – 7.31 (m, 8H), 5.06 (s, 1H), 3.82 (dd, *J* = 28.6, 13.1 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 138.8, 136.1, 133.7, 129.4, 129.3, 129.2, 128.5, 128.4, 128.3, 127.7, 127.2, 126.6, 123.2, 90.4, 85.4, 59.6, 59.0, 38.1.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}ClN$ ($[M+H]^+$): 346.1357, found: 346.1362.

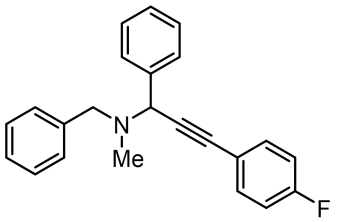
N-benzyl-3-(4-chlorophenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4r)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.28 (m, 8H), 4.96 (s, 1H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.66 (d, *J* = 13.1 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.8, 134.2, 133.2, 129.0, 128.7, 128.4, 128.3, 128.2, 127.7, 127.2, 121.7, 87.6, 85.9, 59.6, 59.0, 38.1. Known compound.[1]

N-benzyl-3-(4-fluorophenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4s)

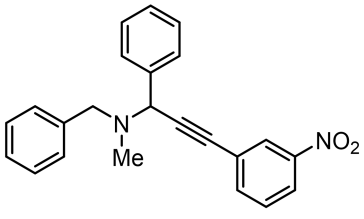


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.62 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.54 – 7.31 (m, 8H), 7.13 (t, *J* = 8.7 Hz, 2H), 4.98 (s, 1H), 3.75 (dd, *J* = 41.5, 13.1 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 242.4 Hz), 139.3, 139.0, 133.8 (d, *J* = 8.1 Hz), 129.1, 128.4 (d, *J* = 5.1 Hz), 128.3, 127.7, 127.2, 119.3, 115.7 (d, *J* = 22.2 Hz), 87.6, 84.4, 59.5, 59.0, 38.1.

^{19}F NMR (400 MHz, $CDCl_3$)δ -110.97 (s). Known compound.[1]

N-benzyl-*N*-methyl-3-(3-nitrophenyl)-1-phenylprop-2-yn-1-amine (4t)

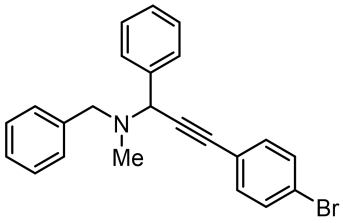


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.25 (d, *J* = 9.6 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.51 – 7.28 (m, 8H), 5.00 (s, 1H), 3.74 (dd, *J* = 50.1, 13.1 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 139.0, 138.4, 137.8, 129.5, 129.0, 128.5, 128.4, 128.3, 127.8, 127.3, 126.7, 125.0, 123.1, 87.9, 86.4, 59.5, 59.0, 38.1.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}N_2O_2$ ($[M+H]^+$): 357.1598, found: 357.1602.

N-benzyl-3-(4-bromophenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4u)

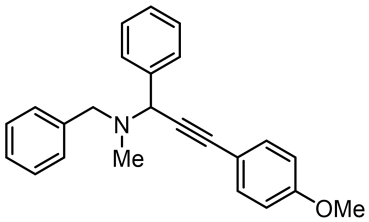


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.46 (m, 4H), 7.46 – 7.32 (m, 6H), 4.97 (s, 1H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.69 (d, *J* = 13.1 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.8, 133.4, 131.7, 129.1, 128.4, 128.4, 128.3, 127.7, 127.2, 122.4, 122.2, 87.7, 86.1, 59.6, 59.0, 38.1.

HRMS m/z (ESI^+): Calculated for $C_{23}H_{20}BrN$ ($[M+H]^+$): 390.0852, found: 390.0856.

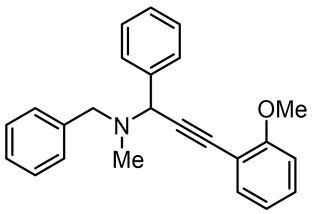
N-benzyl-3-(4-methoxyphenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4v)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.44 – 7.29 (m, 6H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.95 (s, 1H), 3.88 (s, 3H), 3.77 (d, *J* = 13.1 Hz, 1H), 3.68 (d, *J* = 13.1 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 139.4, 139.3, 133.3, 129.1, 128.4, 128.3, 128.2, 127.5, 127.1, 115.4, 114.0, 88.5, 83.1, 59.6, 58.9, 55.4, 38.1. Known compound.[1]

N-benzyl-3-(2-methoxyphenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4w)

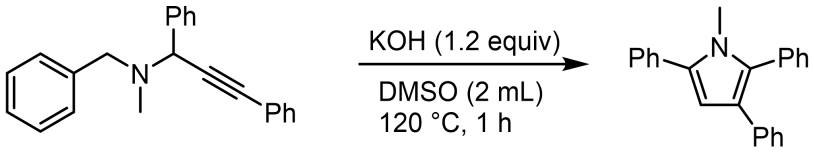


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 2H), 7.62 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.46 – 7.32 (m, 7H), 7.01 (dd, *J* = 17.4, 7.6 Hz, 2H), 5.04 (s, 1H), 3.99 (s, 3H), 3.82 (d, *J* = 13.1 Hz, 1H), 3.77 (d, *J* = 13.1 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 139.5, 139.3, 133.6, 129.6, 129.2, 128.6, 128.4, 128.1, 127.5, 127.1, 120.5, 112.6, 110.8, 89.0, 84.9, 59.9, 58.9, 55.9, 38.1.

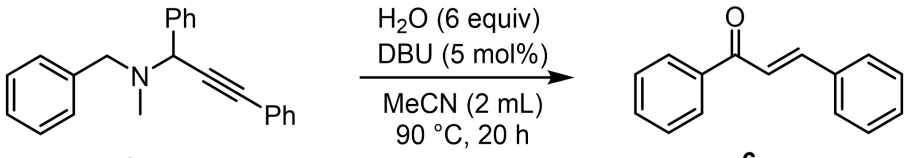
HRMS m/z (ESI$^+$): Calculated for $C_{24}H_{23}NO$ ([M+H]$^+$): 342.1852, found: 342.1857.

Further Application and Transformation of 4a



4a **5**

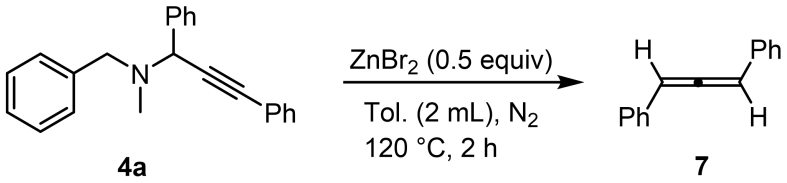
Synthesis of Compounds 5: The propargylamines **4a** (0.5 mmol), KOH (1.2equiv), and DMSO (2 mL) were charged into a 25 mL tube along with a magnetic stir bar. The mixture was stirred in an oil bath at 120 °C for 1 h. The resulting reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL) for three times. The layers were separated, and the organic layer was washed with saturated brine solution and dried over $NaSO_4$. After that, the mixture was purified by running column chromatography on silica gel using petroleum ether/ethyl acetate =60:1. Flash column chromatography was performed on silica gel (100−200 mesh). The product **5** was obtained (148.5 mg, 96%) as colorless oil.



4a **6**

Synthesis of Compounds 6: The propargylamines **4a** (0.5 mmol), water (3.0 mmol), and DBU (5 mol%) in toluene (2 mL) were heated to 90 °C in an oil bath for 20 h under air. After the reaction completed (as determined by TLC), the reaction mixture was cooled to room temperature,

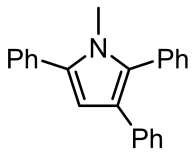
extracted with CH_2Cl_2, and washed with brine. Then filtered, and the solvent was removed in a rotary evaporator. The residue was purified by flash chromatography (ethyl acetate and petroleum ether, 1:30, v/v) to provide the desired product **6** (56.2 mg, 90%).



4a **7**

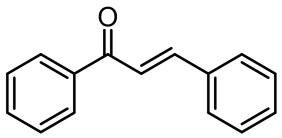
Synthesis of Compounds 7: The propargylamine 4a (0.5 mmol) was added to a stirred suspension of $ZnBr_2$ (0.25 mmol) in dry toluene (2 mL) and the contents were refluxed for 2 h at 120 °C under nitrogen atmosphere. Toluene was removed under reduced pressure and the crude product was purified on silica gel (100-200) using hexane as eluent to isolate the allenes **7** (53.6 mg, 93%).

1-methyl-2,3,5-triphenyl-1H-pyrrole (5)



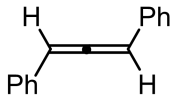
1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.48 (dd, J = 10.4, 4.8 Hz, 2H), 7.44 – 7.35 (m, 6H), 7.28 – 7.20 (m, 4H), 7.16 – 7.11 (m, 1H), 6.54 (s, 1H), 3.52 (s, 3H). Known compound.[3]

(E)-chalcone (6)



1H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.84 (d, J = 15.7 Hz, 1H), 7.68 (dd, J = 6.7, 2.8 Hz, 2H), 7.59 (dt, J = 14.9, 4.2 Hz, 4H), 7.49 – 7.41 (m, 3H).

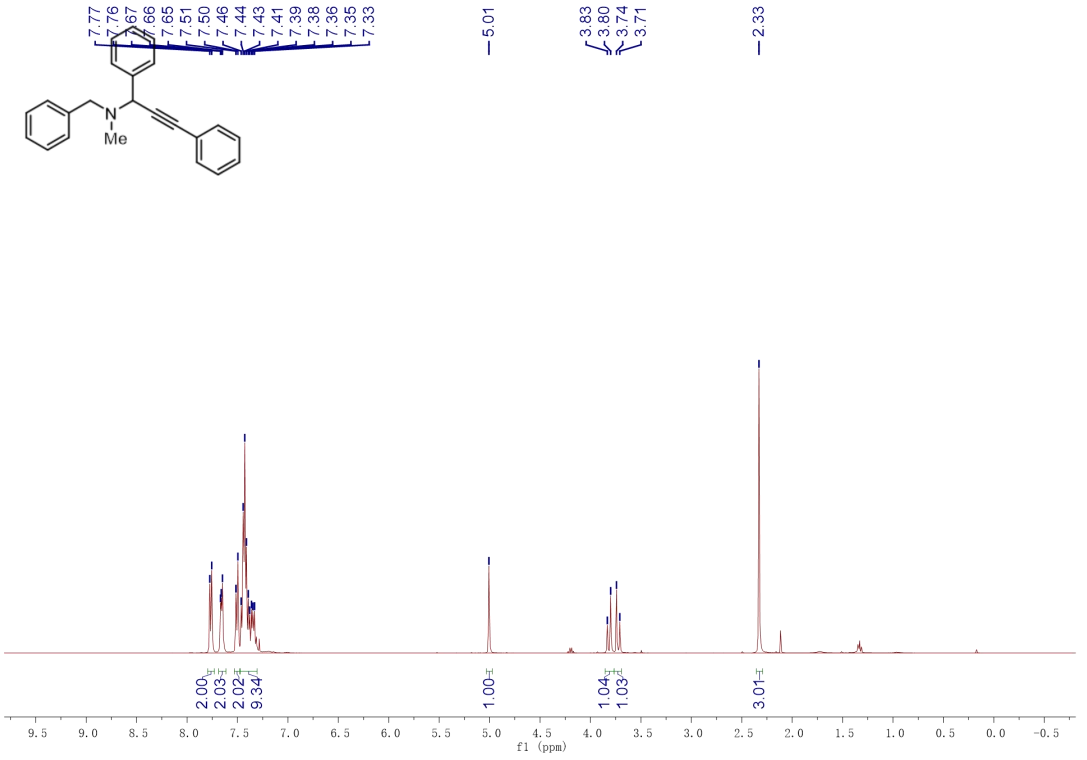
1,3-diphenylpropa-1,2-diene (7)

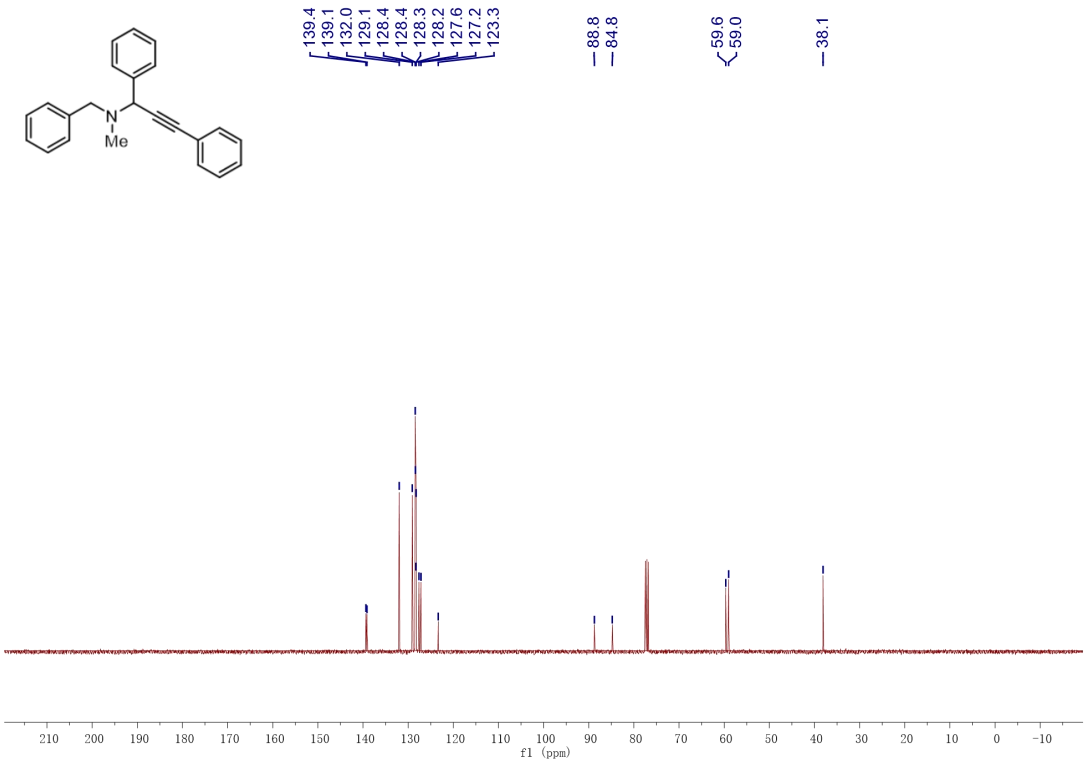


1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.25 (m, 10H), 3.88 (s, 2H).

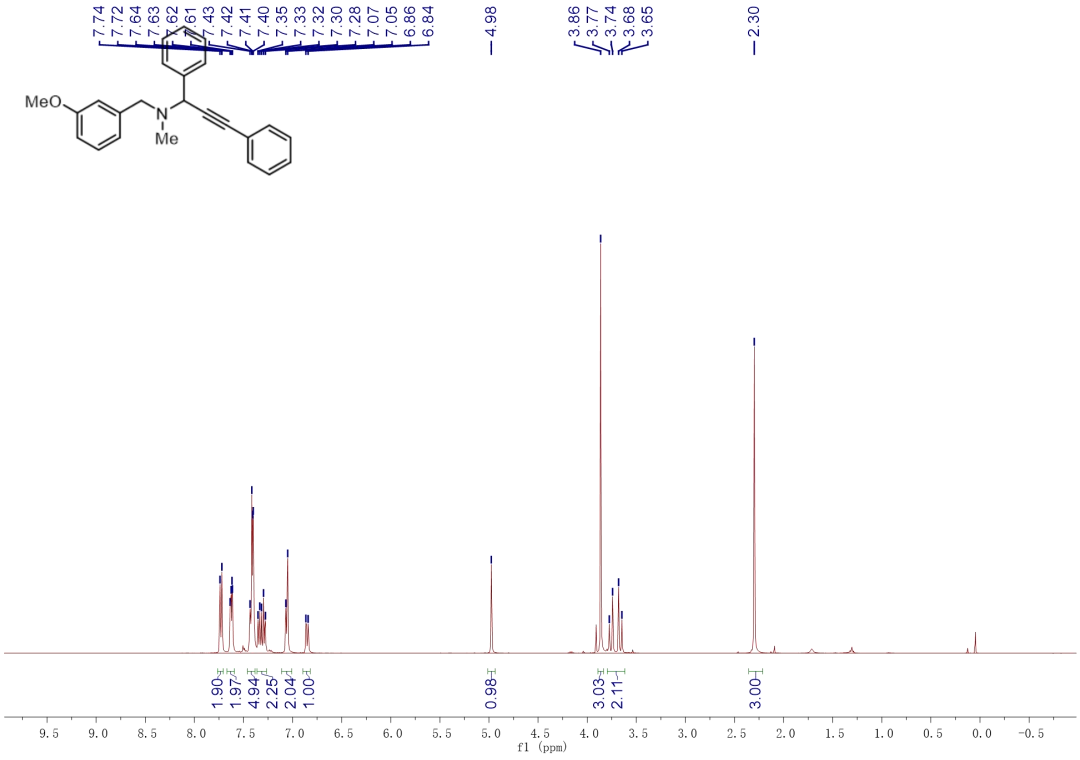
^{1}H NMR、^{13}C NMR and ^{19}F NMR spectra

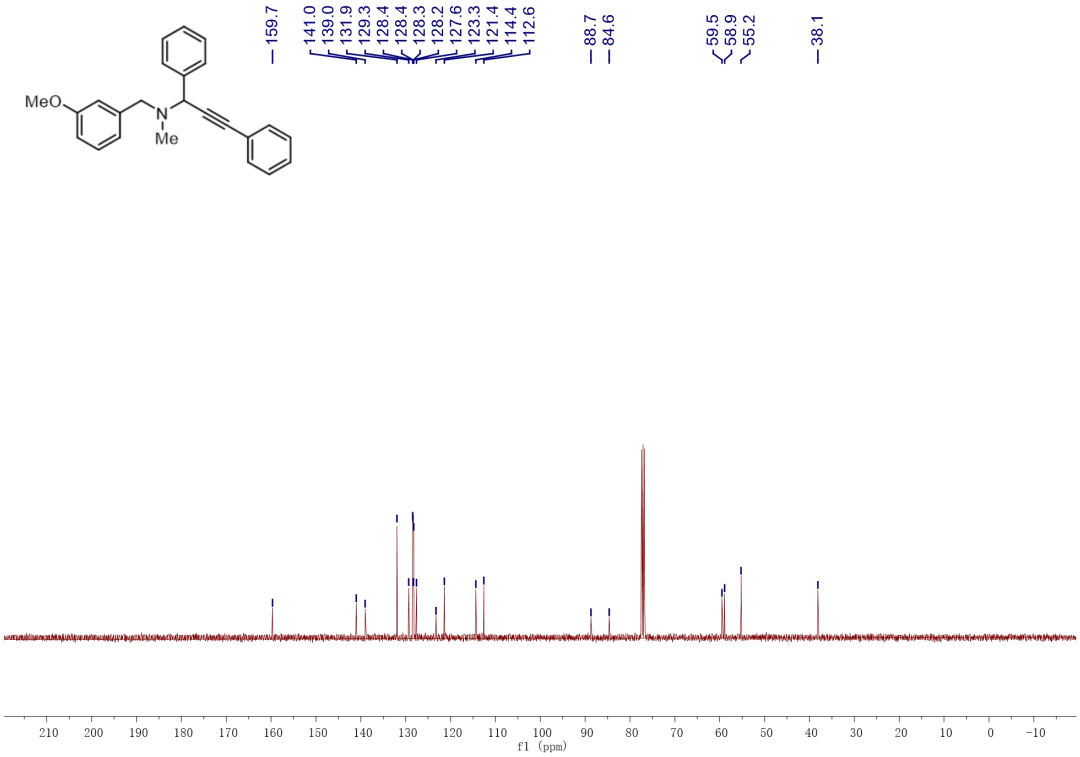
N-benzyl-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4a)



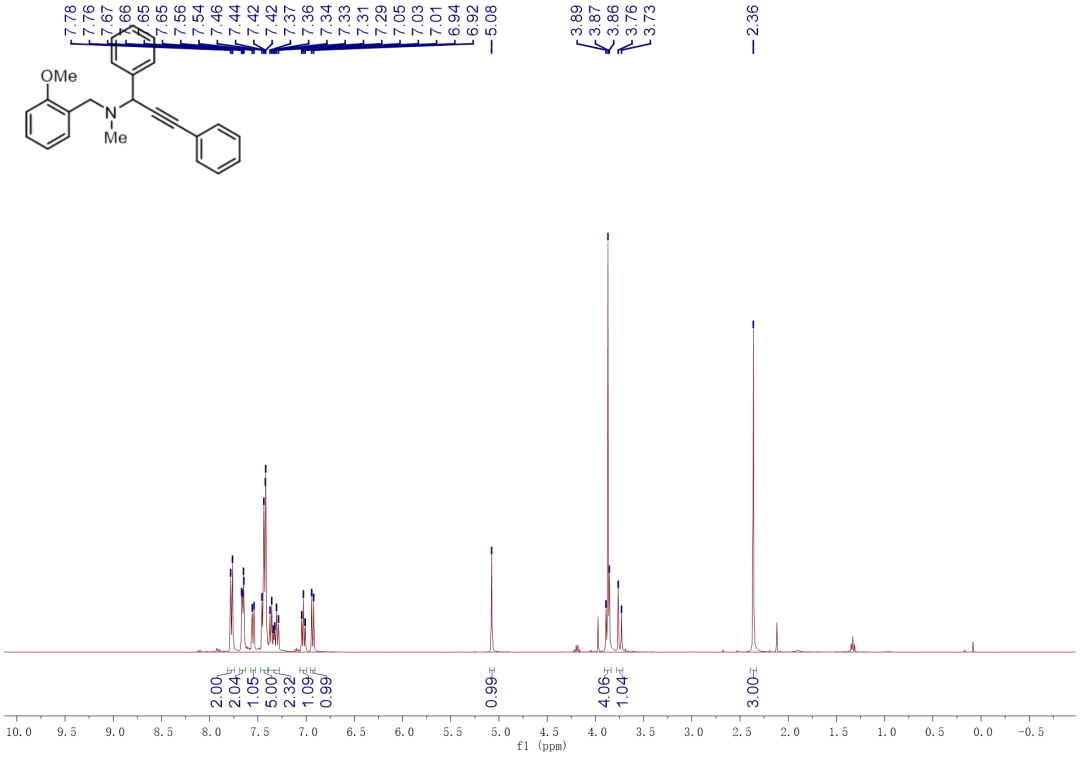


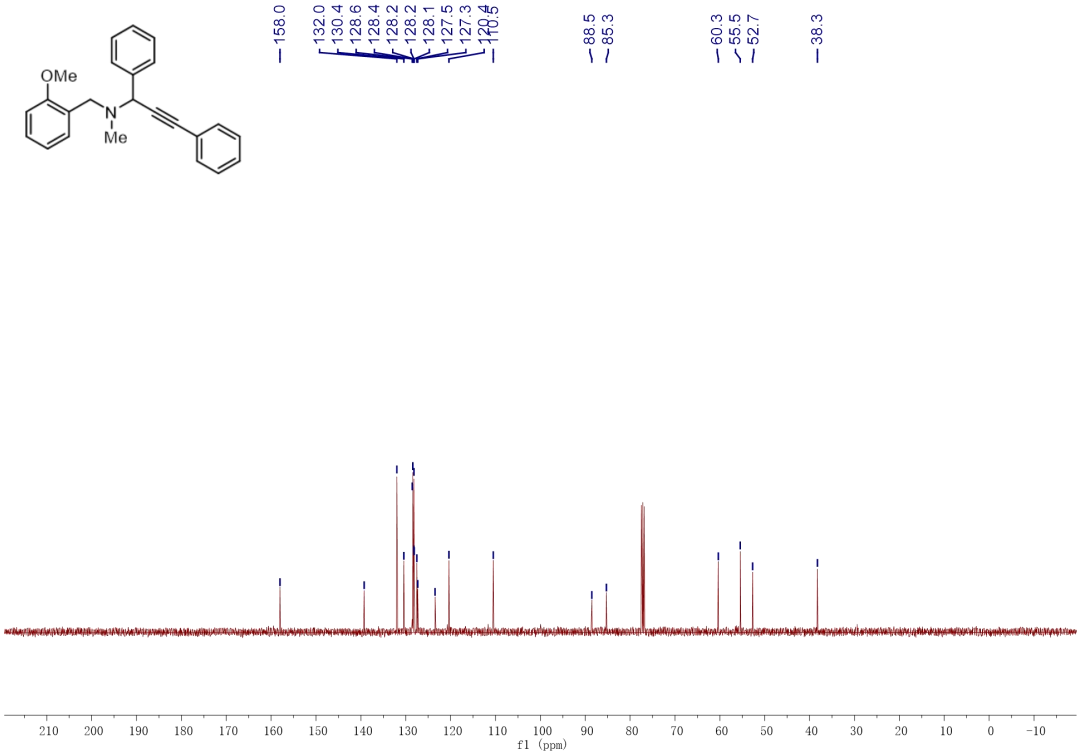
N-(3-methoxybenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4b)



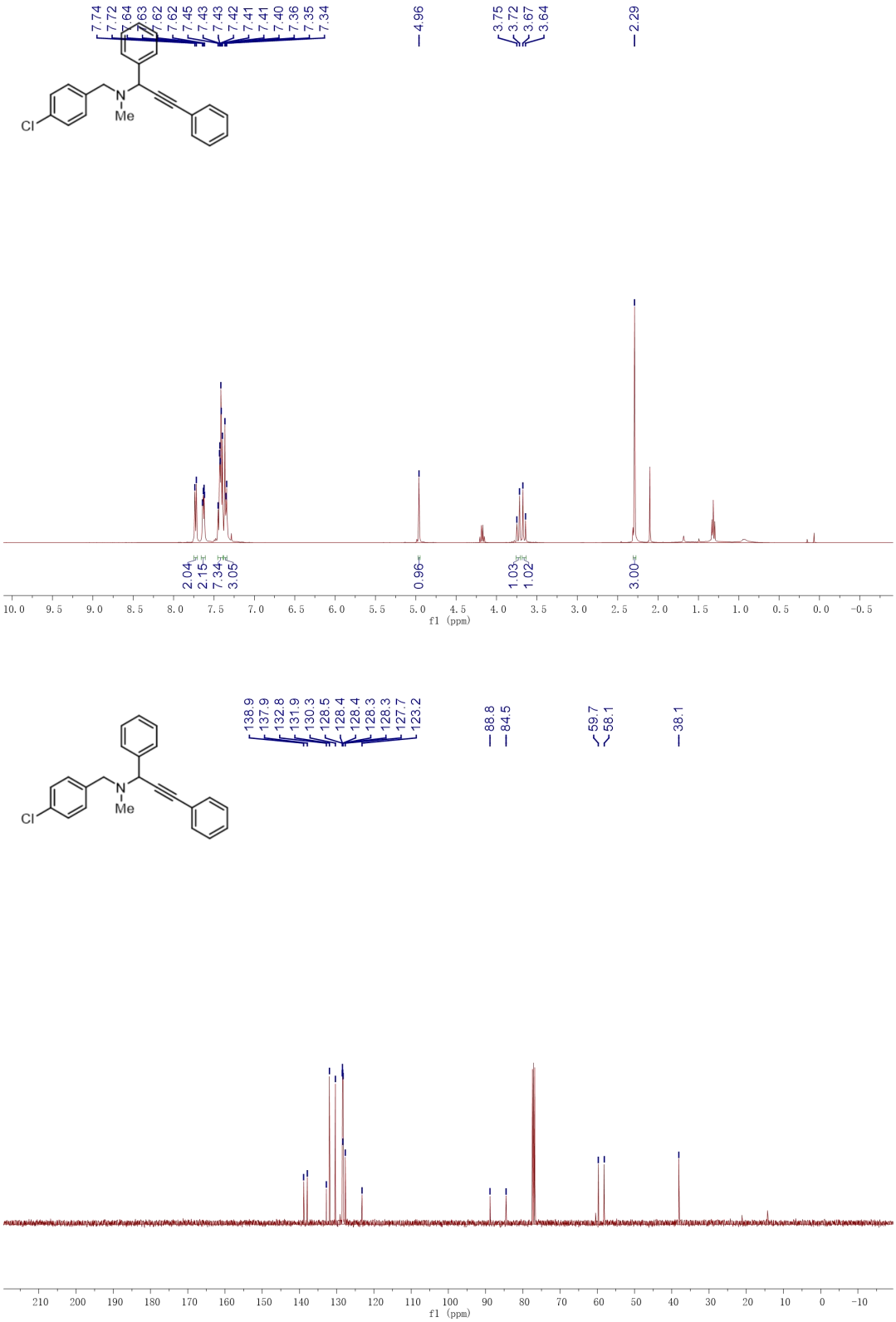


N-(2-methoxybenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4c)

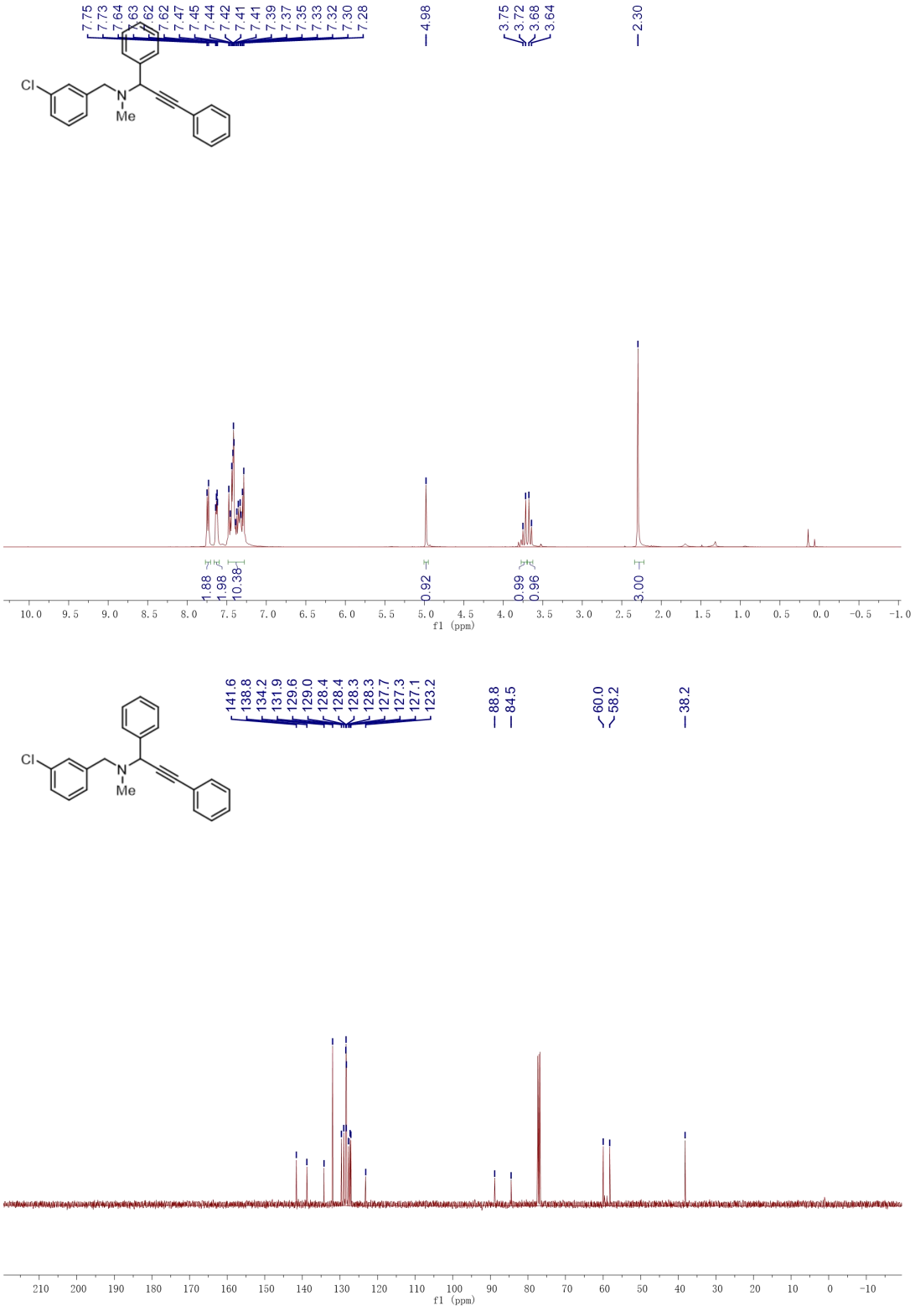




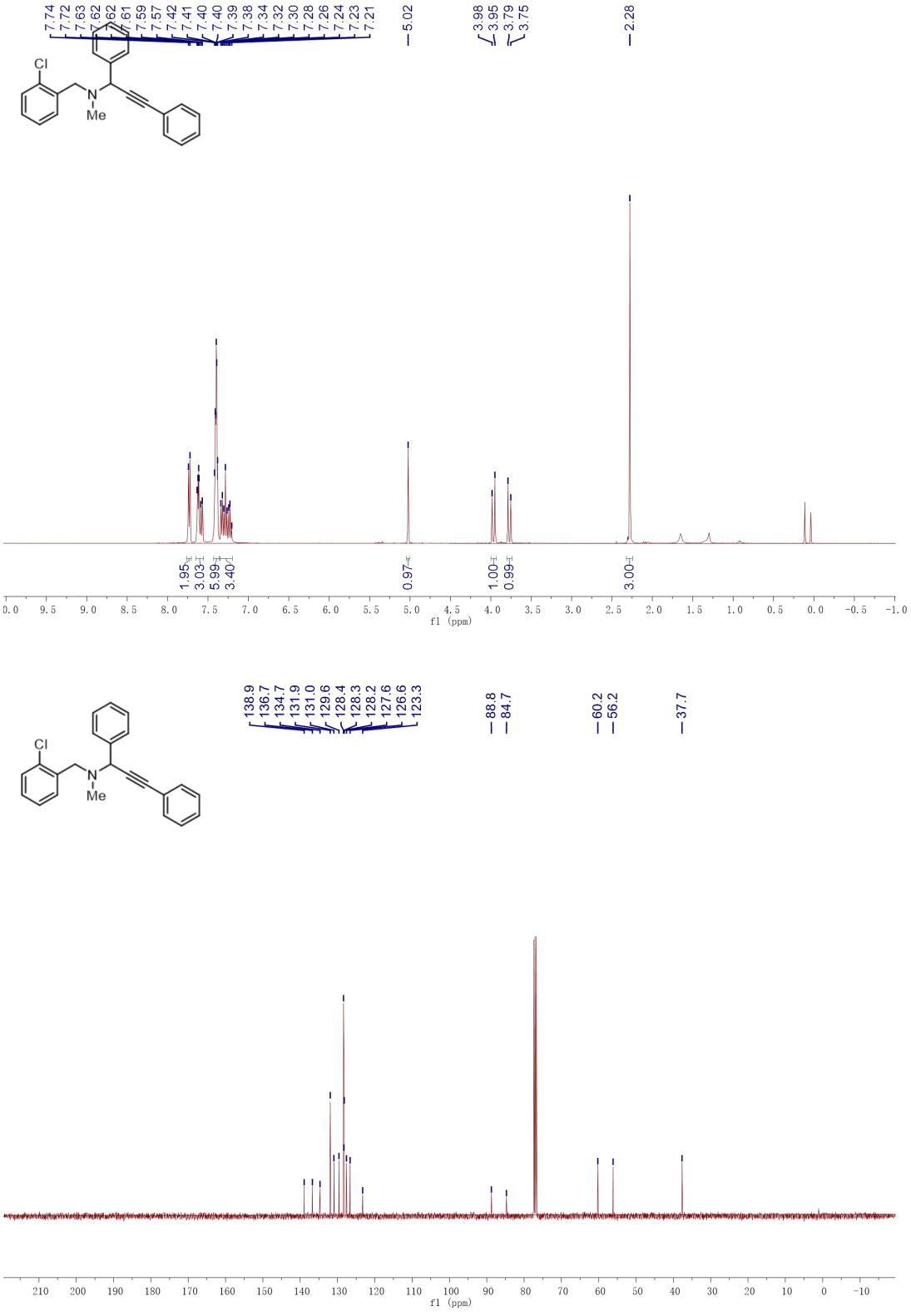
N-(4-chlorobenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4d)



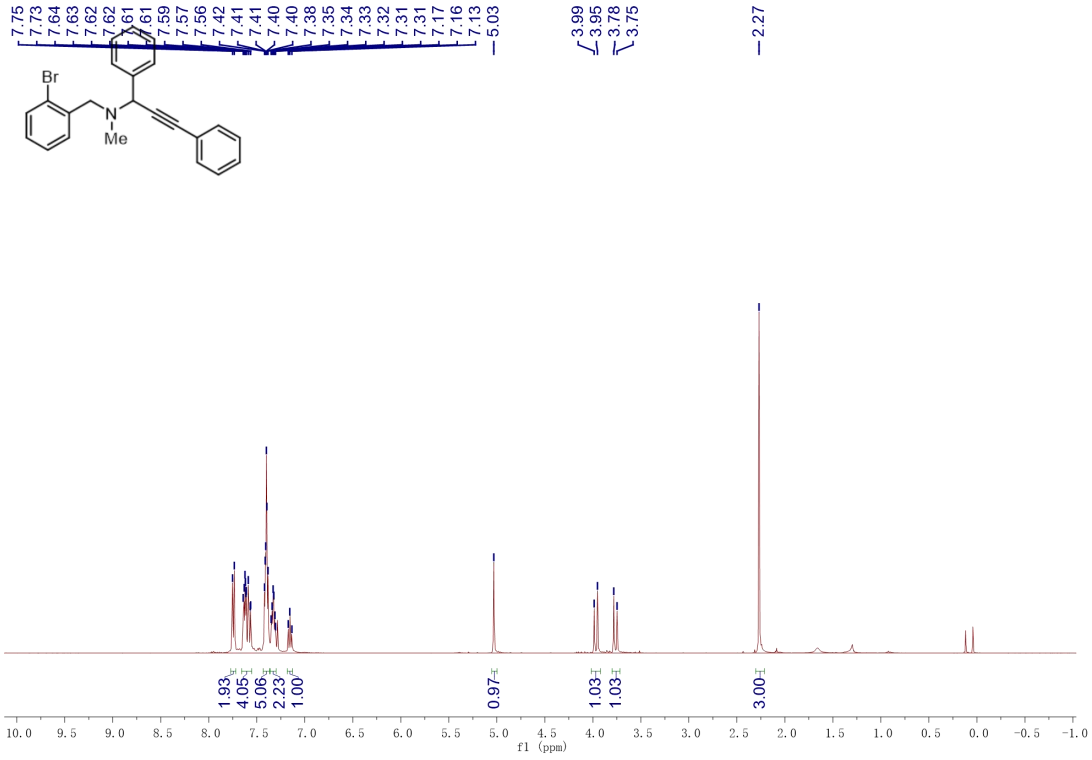
N-(3-chlorobenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4e)

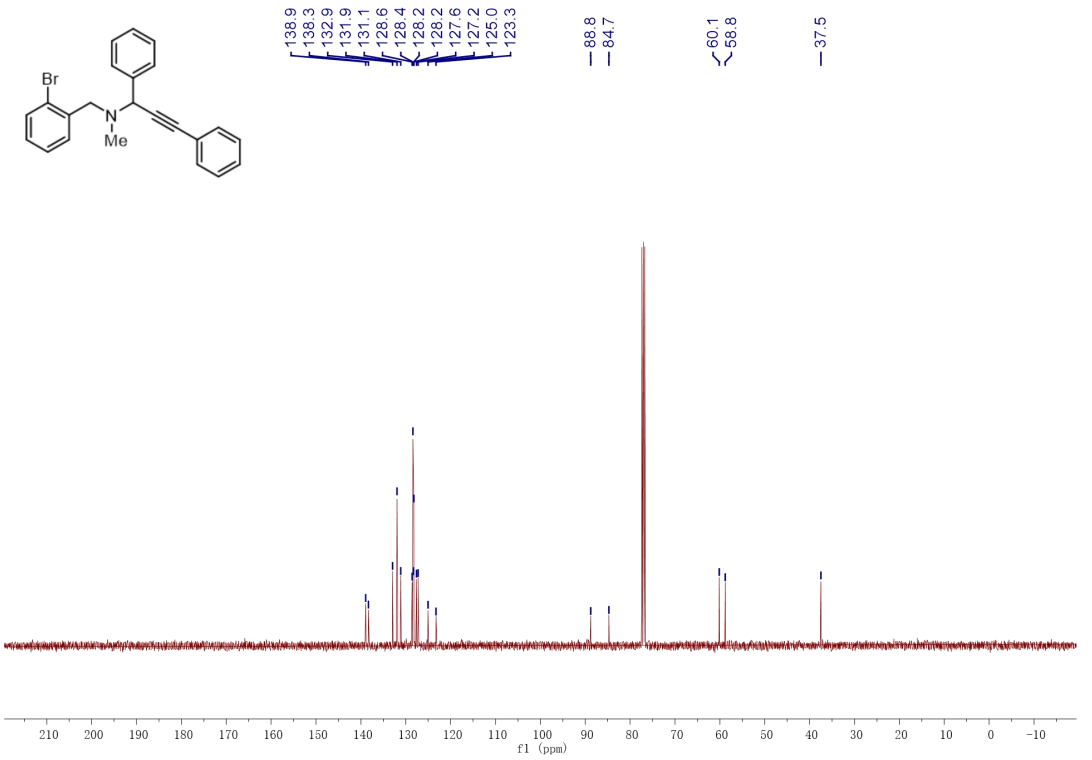


N-(2-chlorobenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4f)

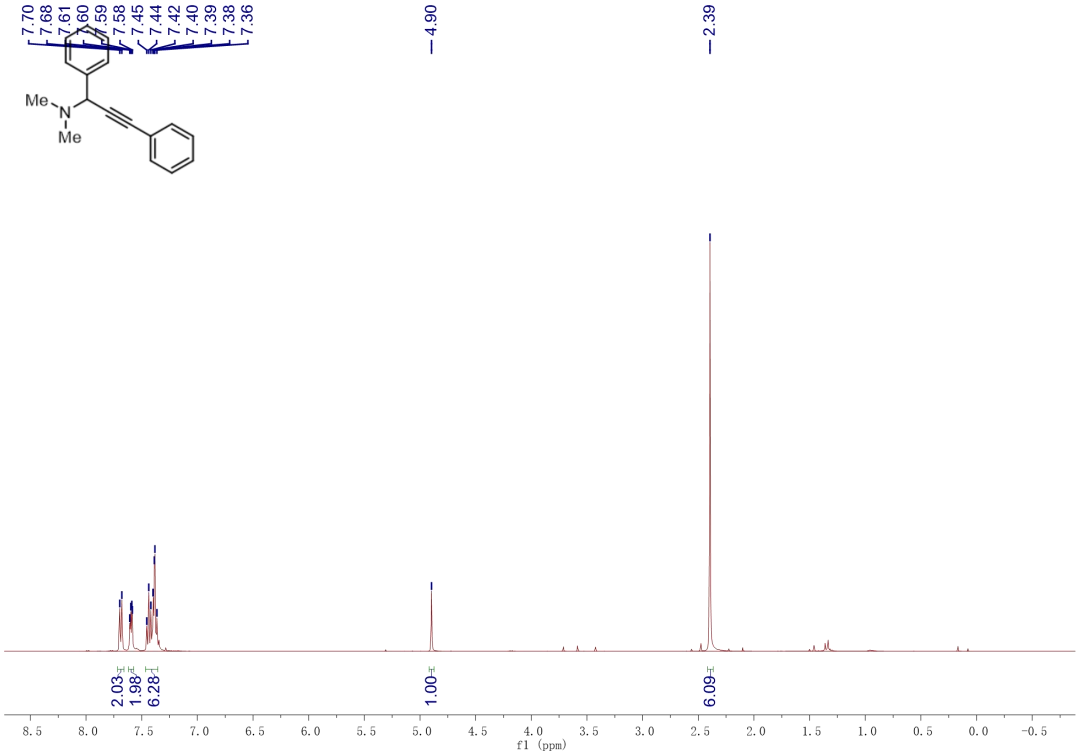


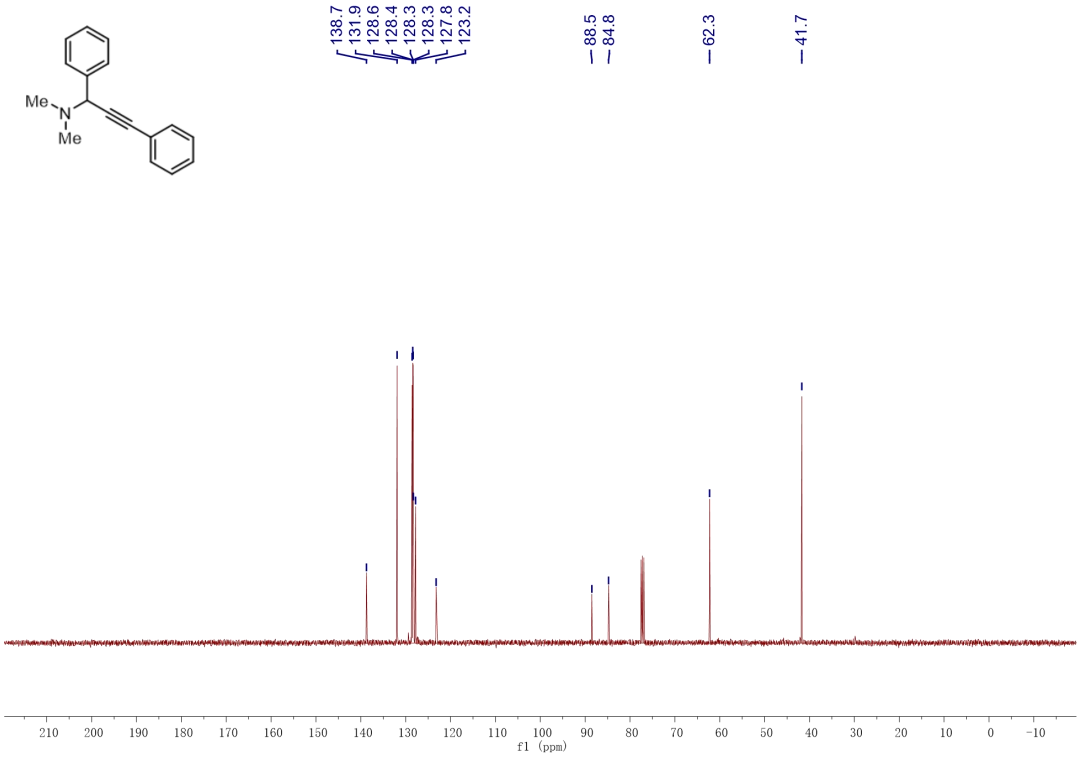
N-(2-bromobenzyl)-*N*-methyl-1,3-diphenylprop-2-yn-1-amine (4g)



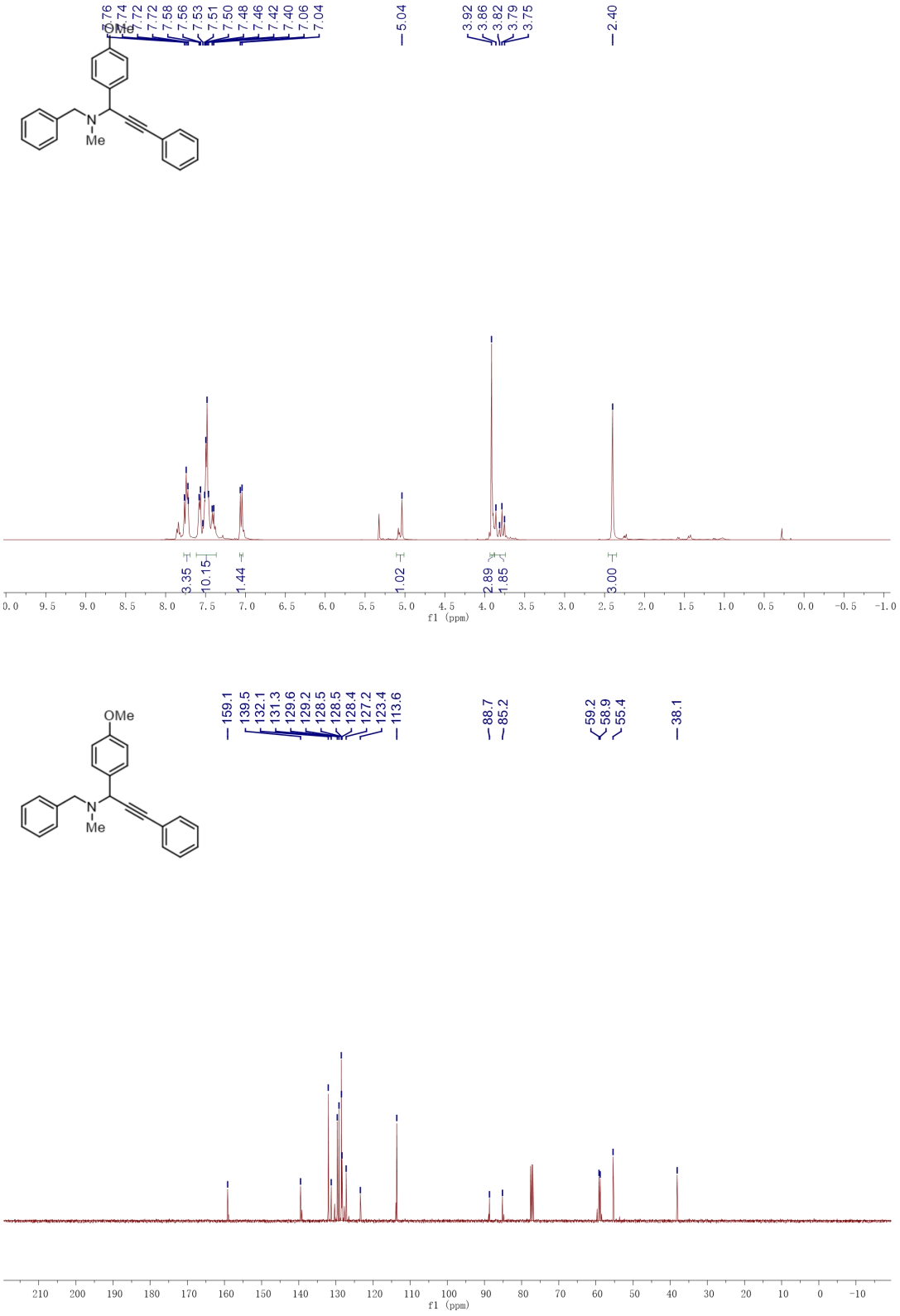


N,*N*-dimethyl-1,3-diphenylprop-2-yn-1-amine (4h)

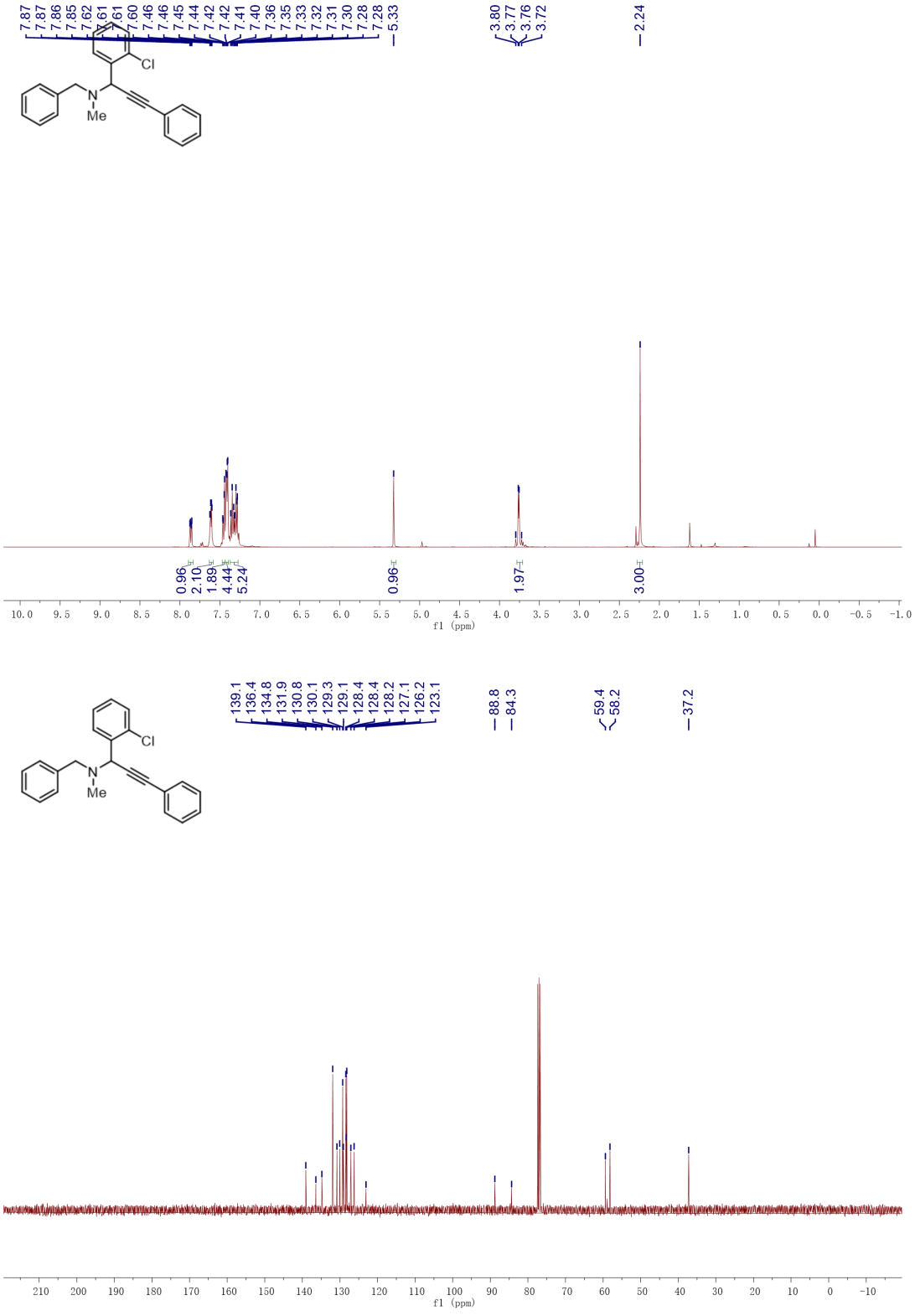




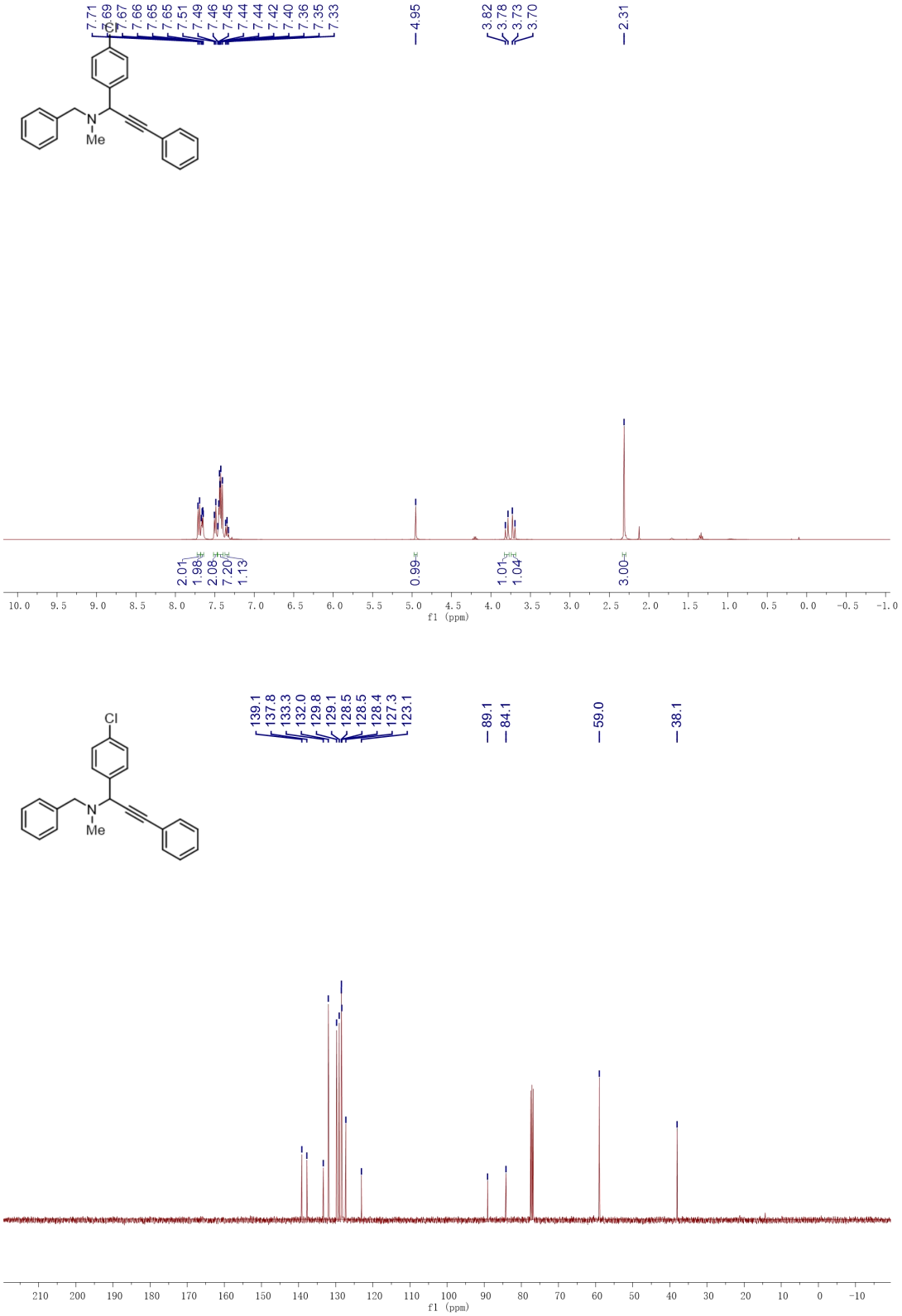
N-benzyl-1-(4-methoxyphenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4i)



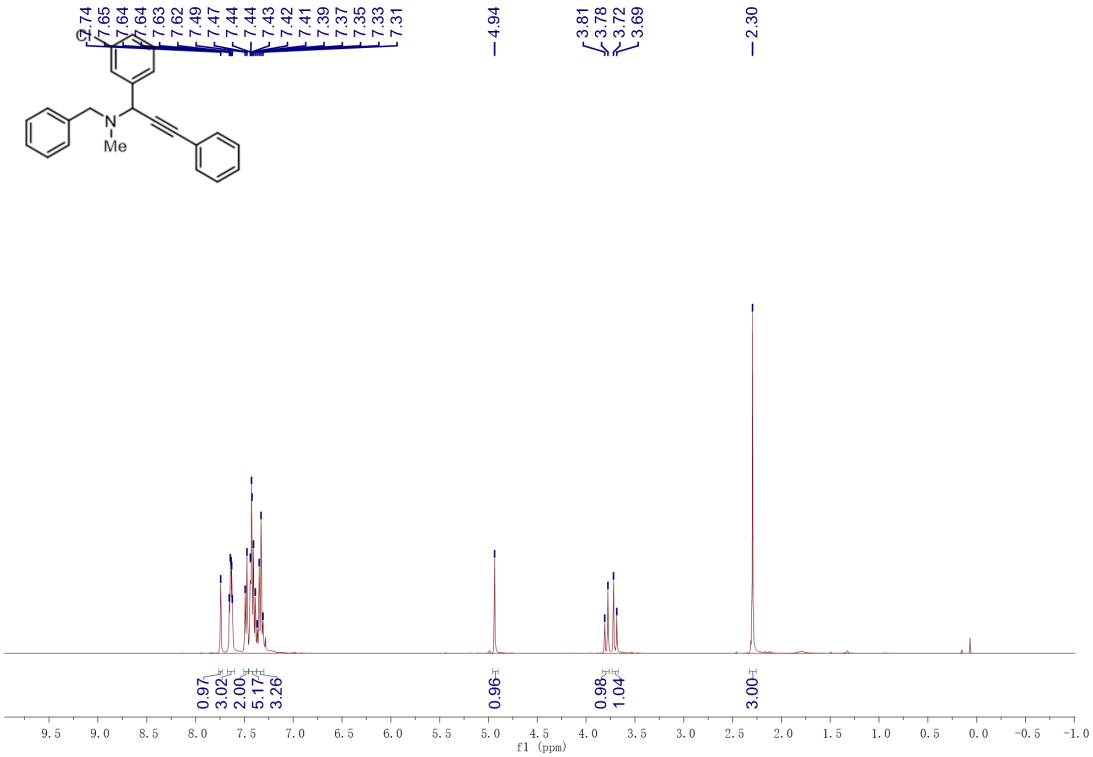
_N_-benzyl-1-(2-chlorophenyl)-_N_-methyl-3-phenylprop-2-yn-1-amine (4j)

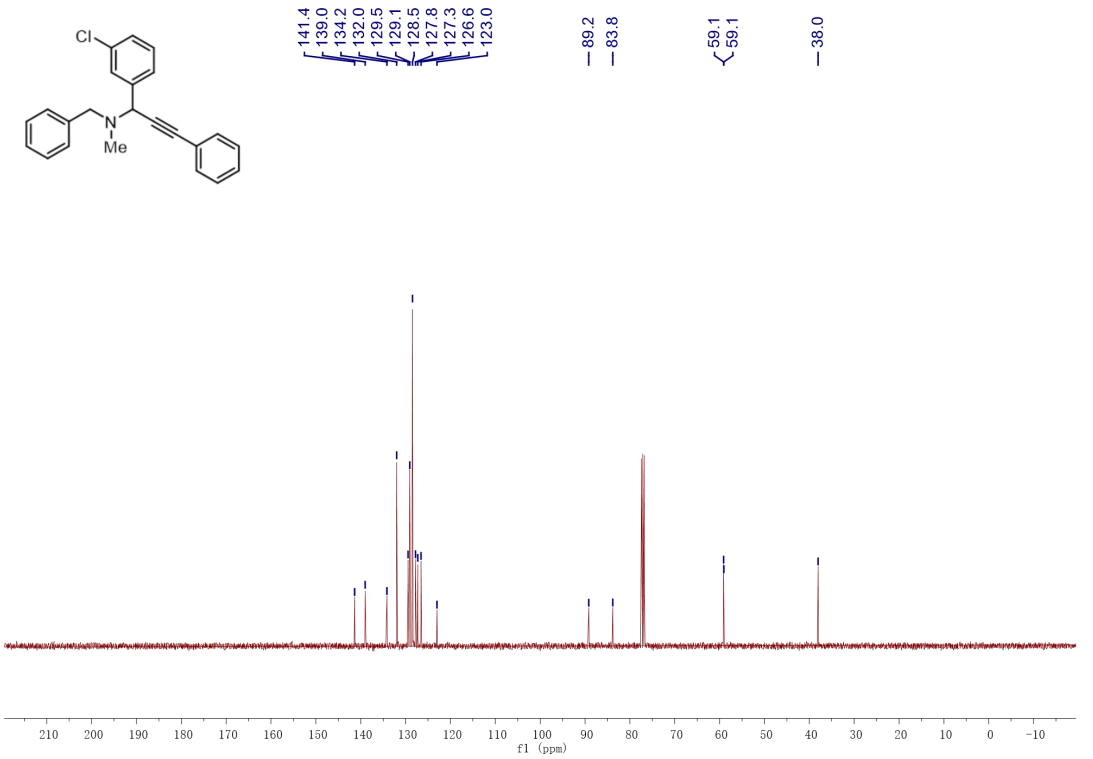


N-benzyl-1-(4-chlorophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4k)

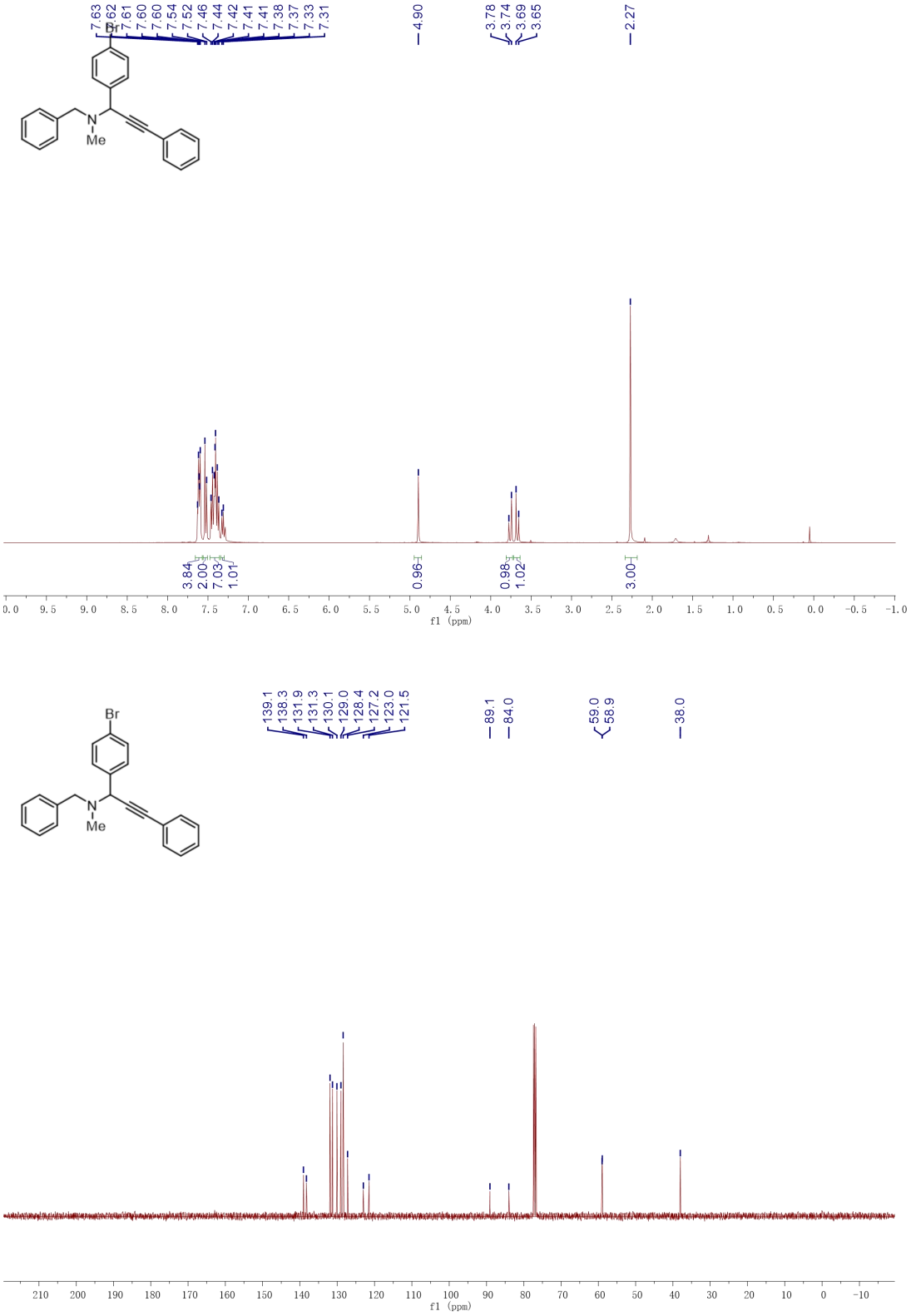


N-benzyl-1-(3-chlorophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4l)

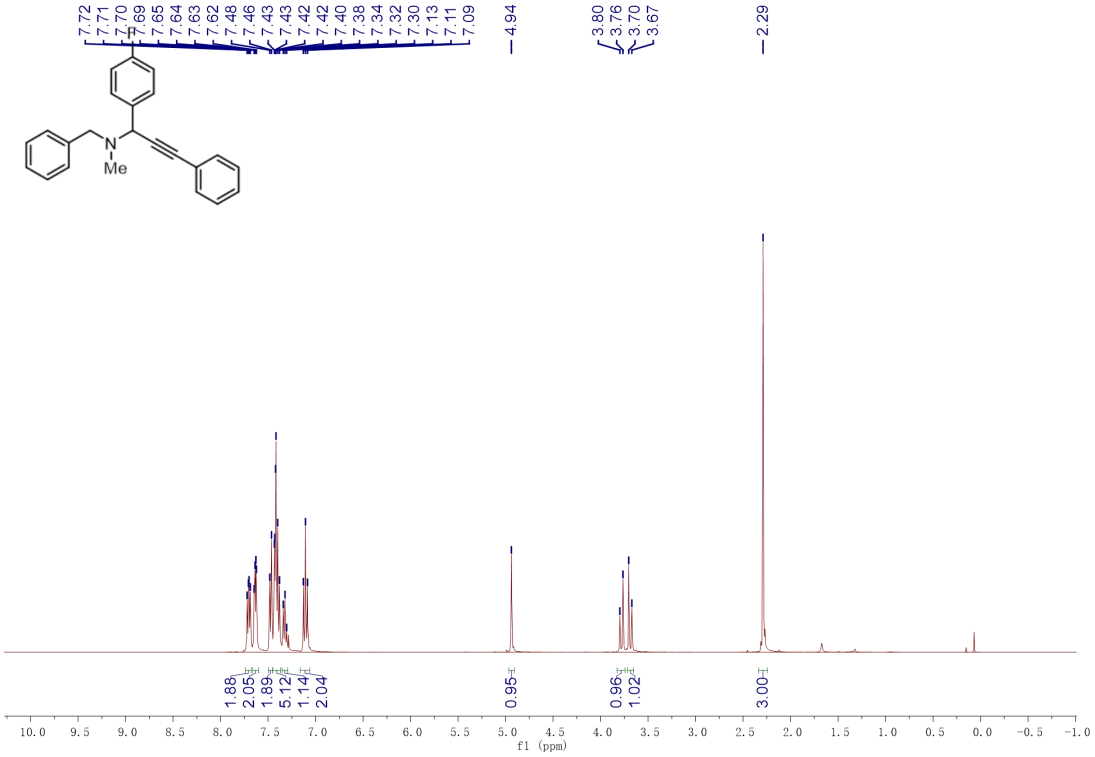


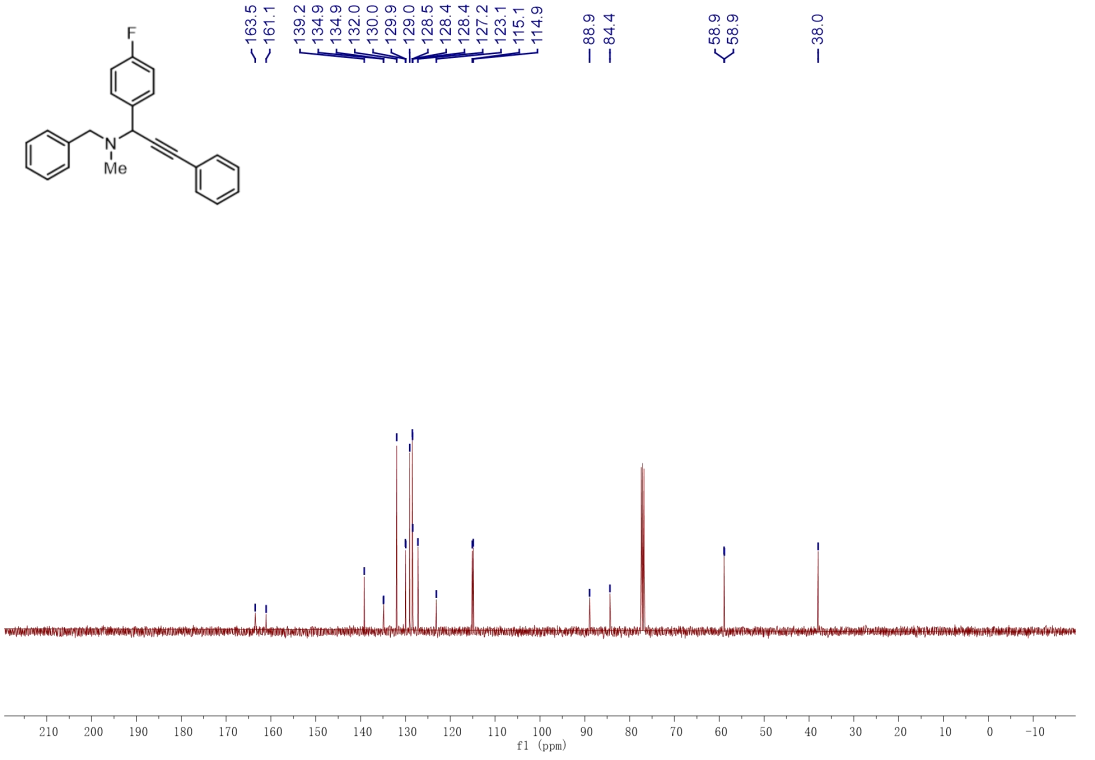


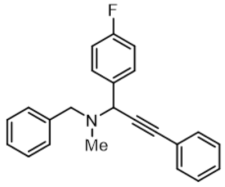
N-benzyl-1-(4-bromophenyl)-*N*-methyl-3-phenylprop-2-yn-1-amine (4m)



_N_-benzyl-1-(4-fluorophenyl)-_N_-methyl-3-phenylprop-2-yn-1-amine (4n)

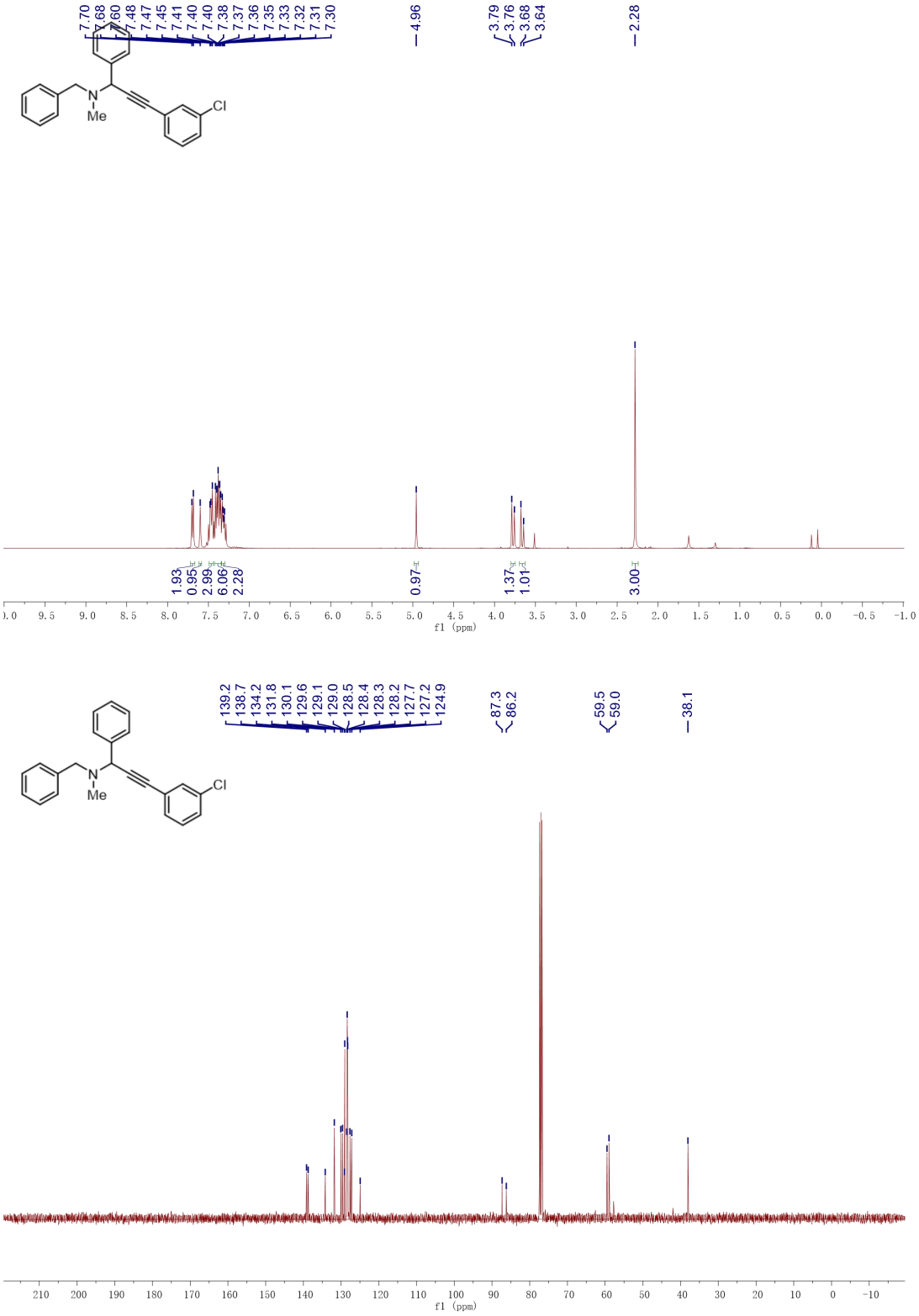





F
N
Me

-115.20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

_N_-benzyl-3-(3-chlorophenyl)-_N_-methyl-1-phenylprop-2-yn-1-amine (4p)



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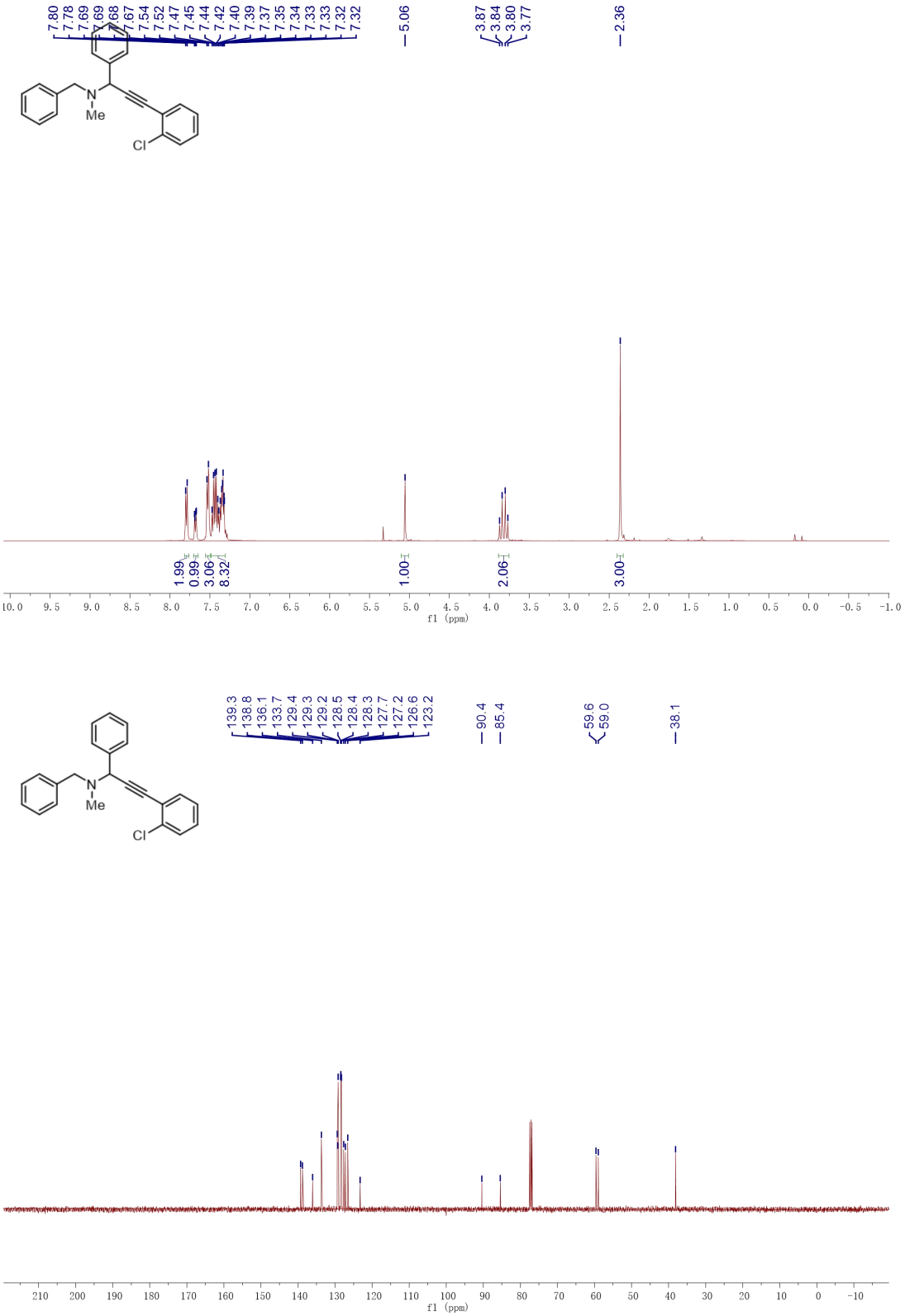
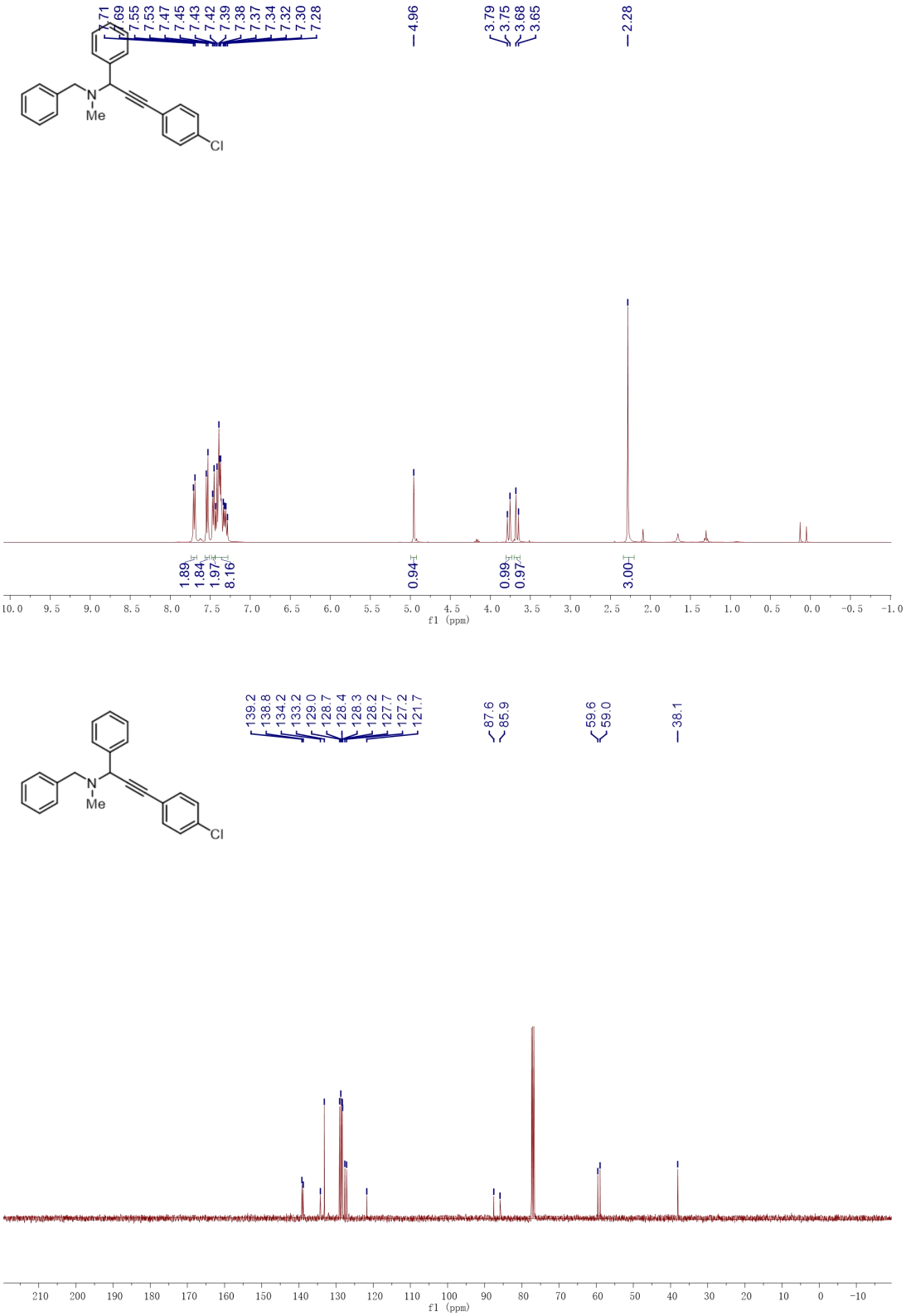
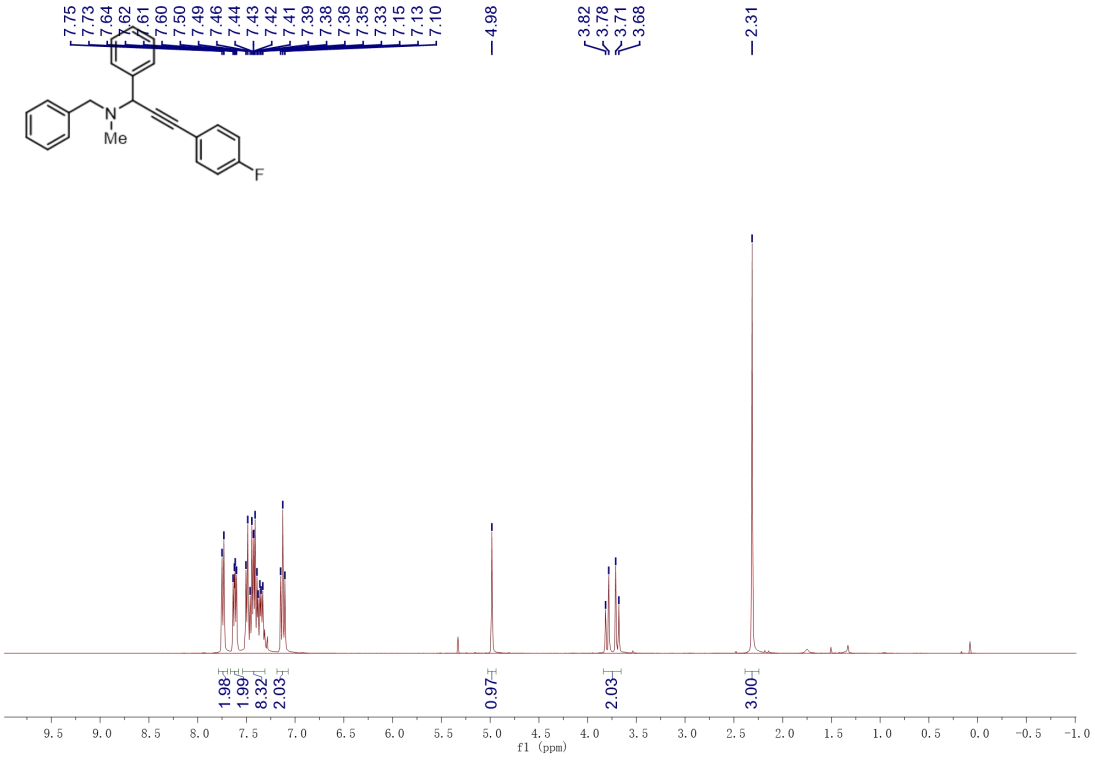
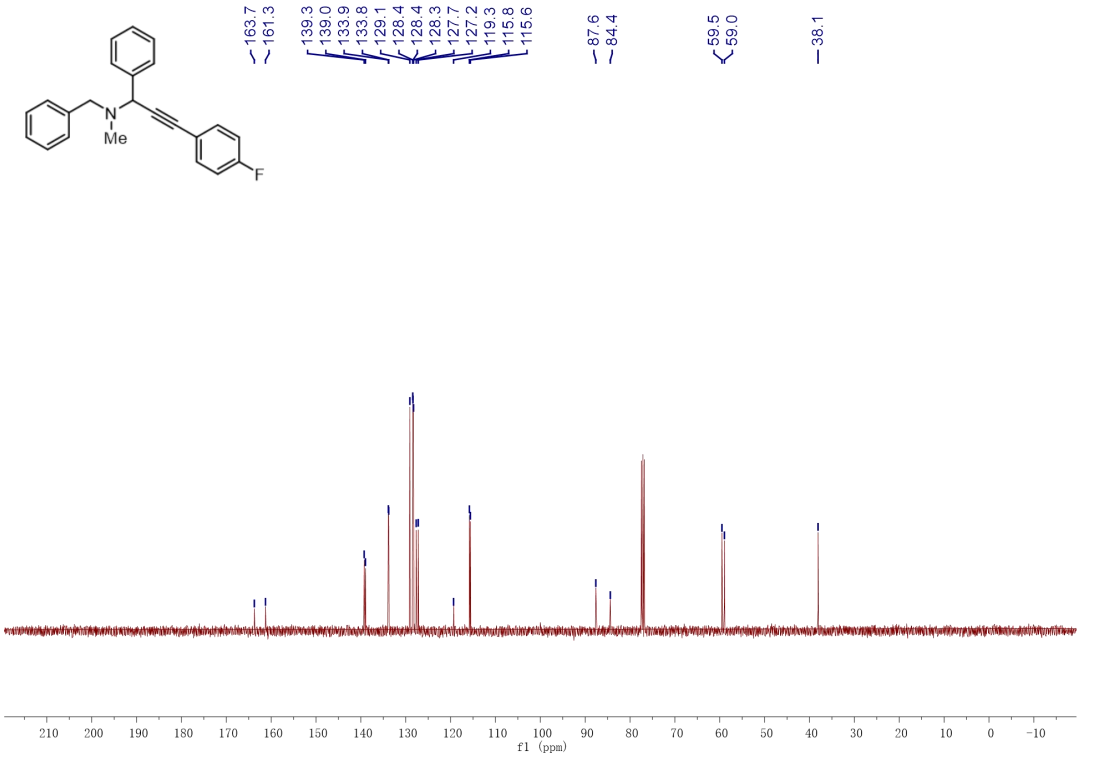


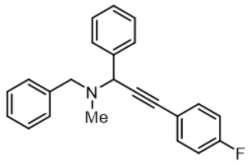
N-benzyl-3-(4-chlorophenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4r)



_N_-benzyl-3-(4-fluorophenyl)-_N_-methyl-1-phenylprop-2-yn-1-amine (4s)

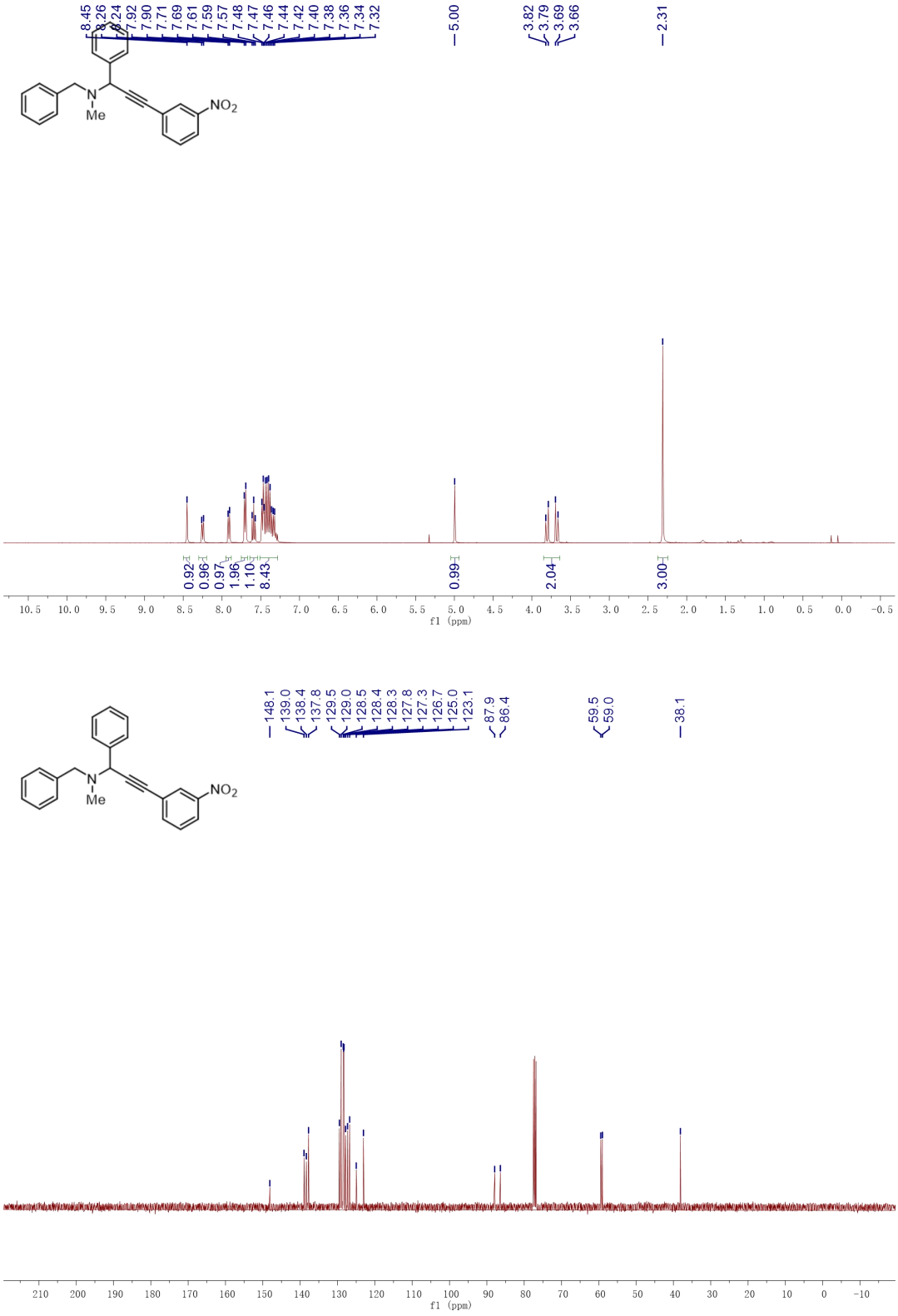




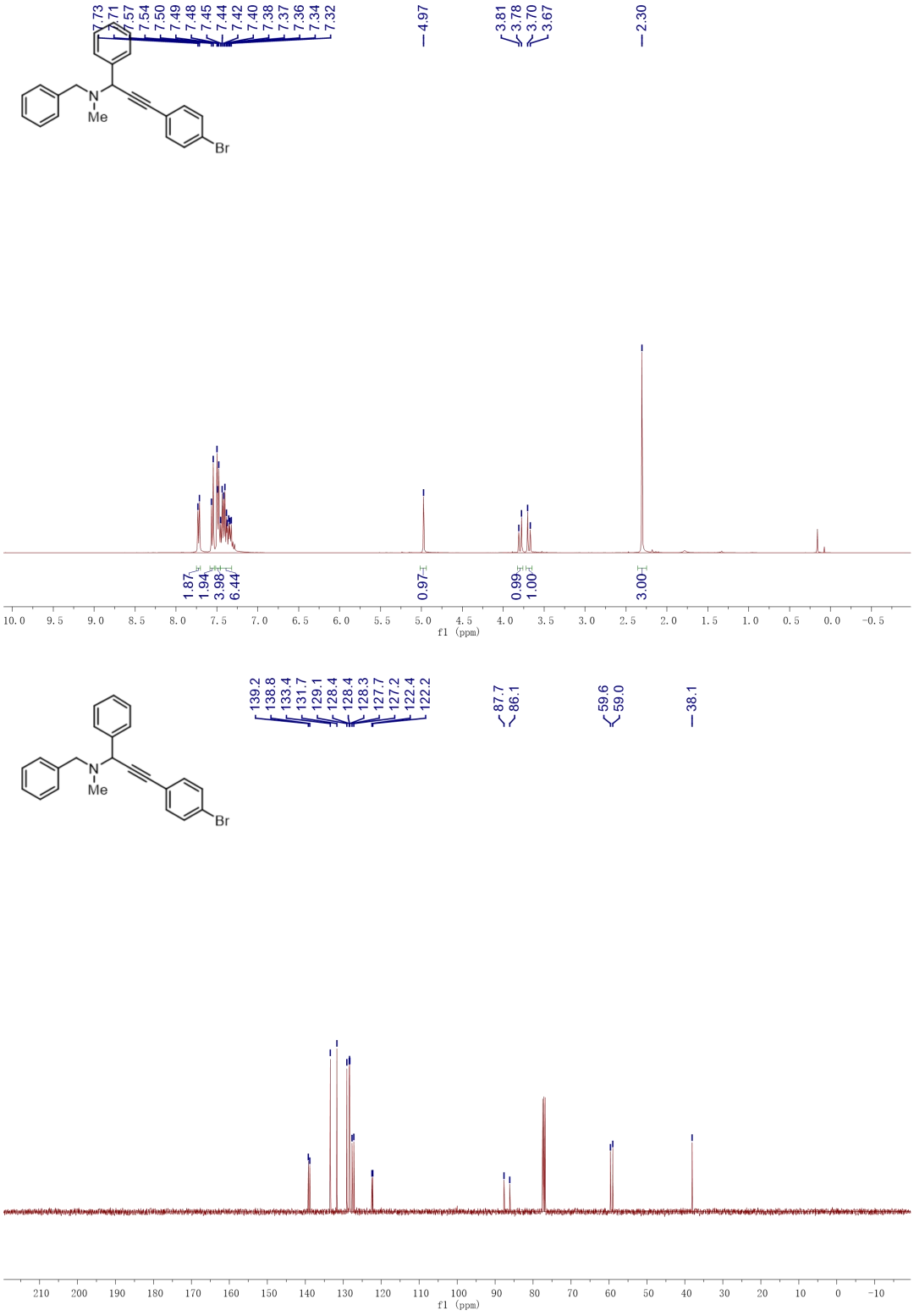

N
Me
F

-110.97
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

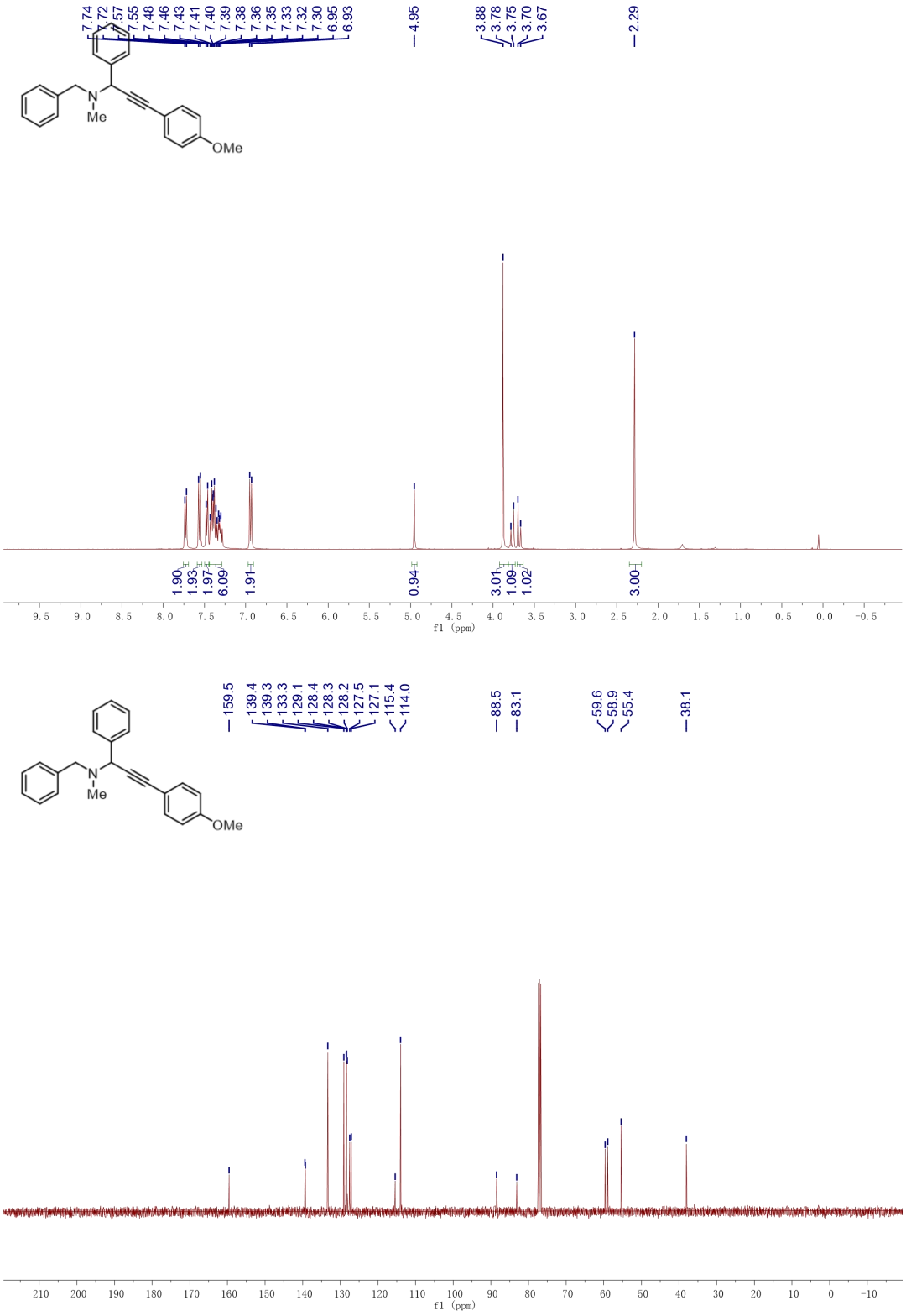
N-benzyl-*N*-methyl-3-(3-nitrophenyl)-1-phenylprop-2-yn-1-amine (4t)



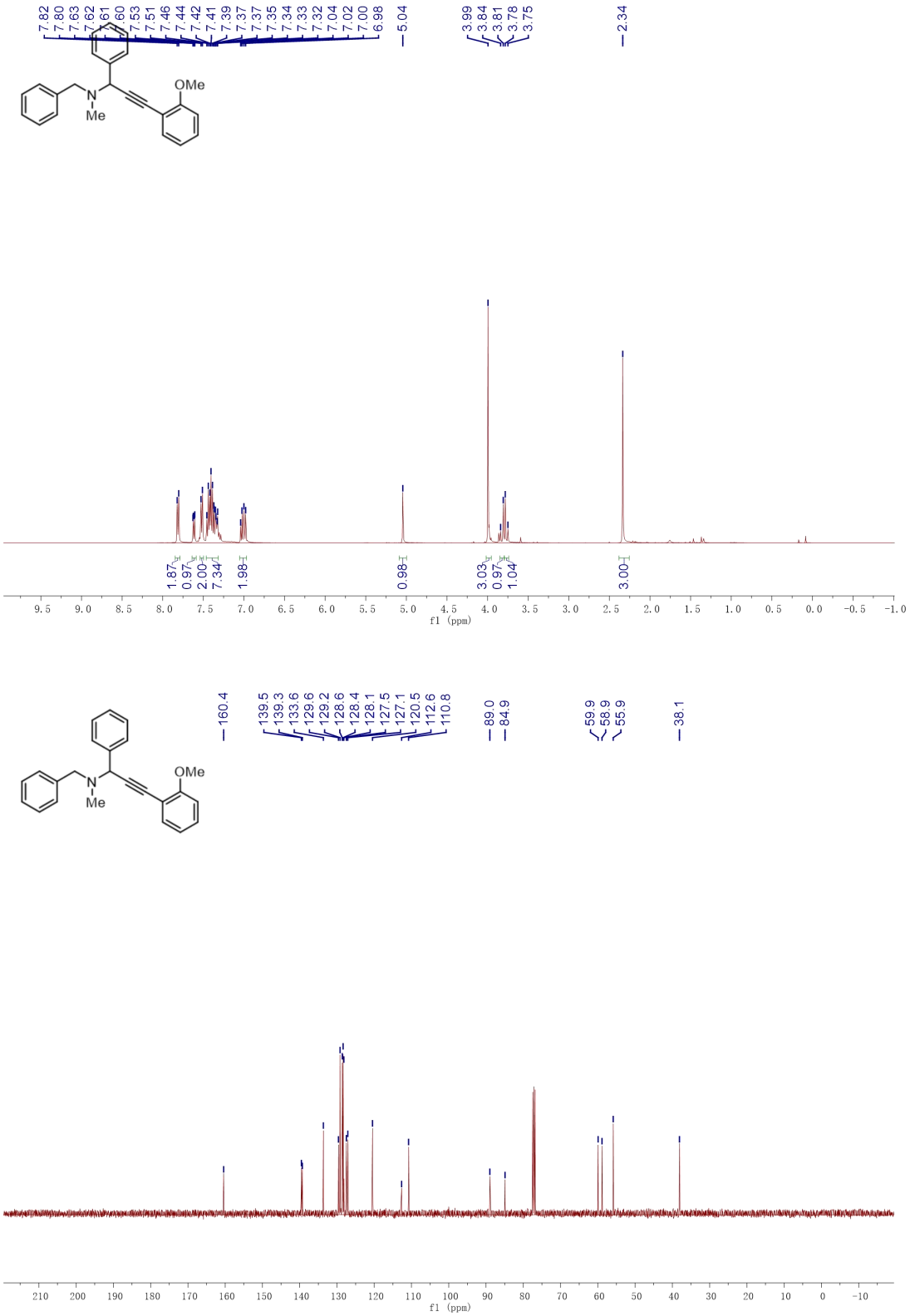
_N_-benzyl-3-(4-bromophenyl)-_N_-methyl-1-phenylprop-2-yn-1-amine (4u)



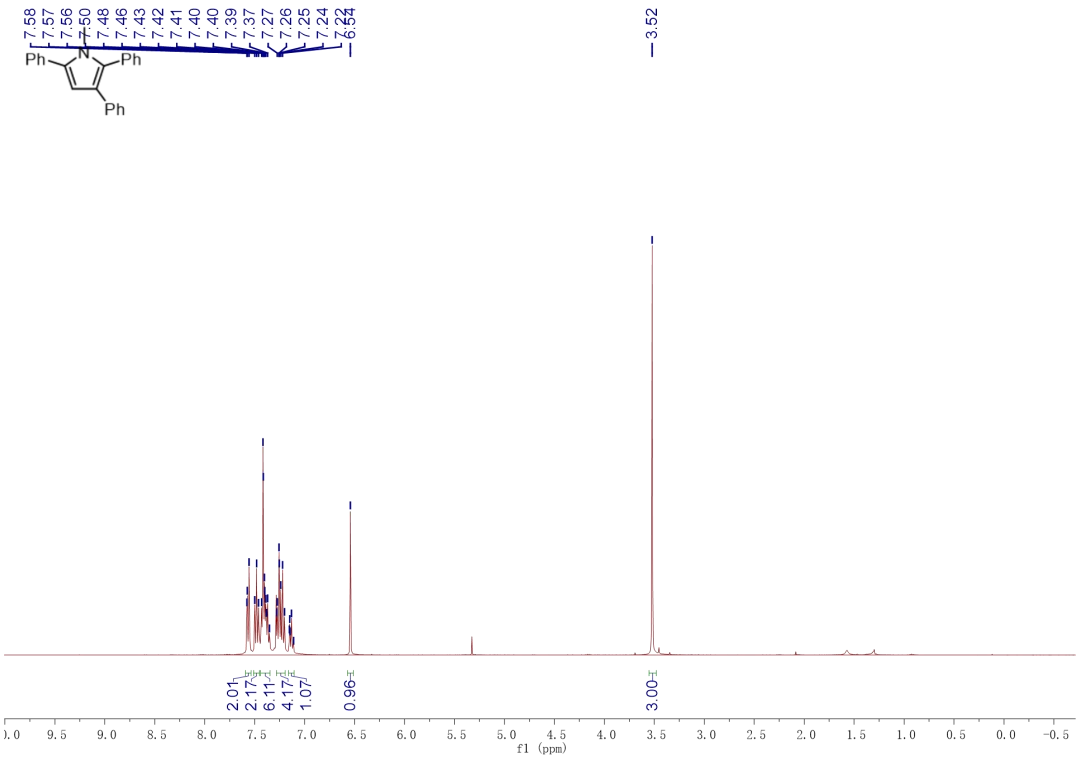
_N_-benzyl-3-(4-methoxyphenyl)-_N_-methyl-1-phenylprop-2-yn-1-amine (4v)



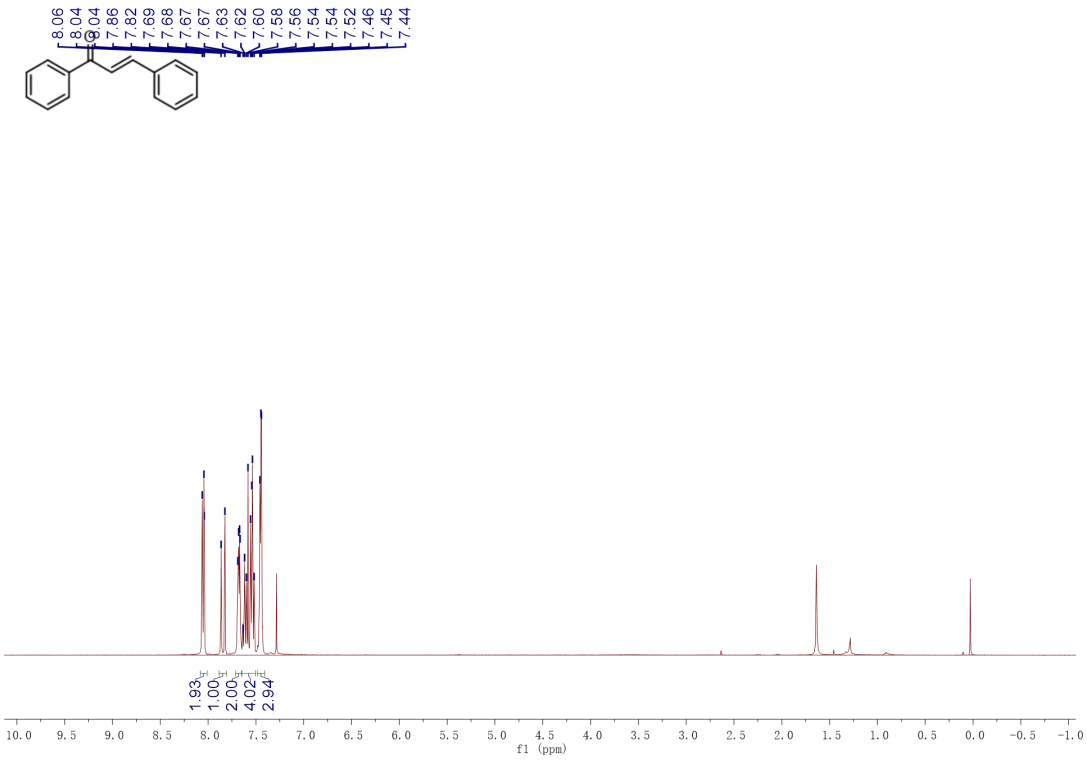
N-benzyl-3-(2-methoxyphenyl)-*N*-methyl-1-phenylprop-2-yn-1-amine (4w)



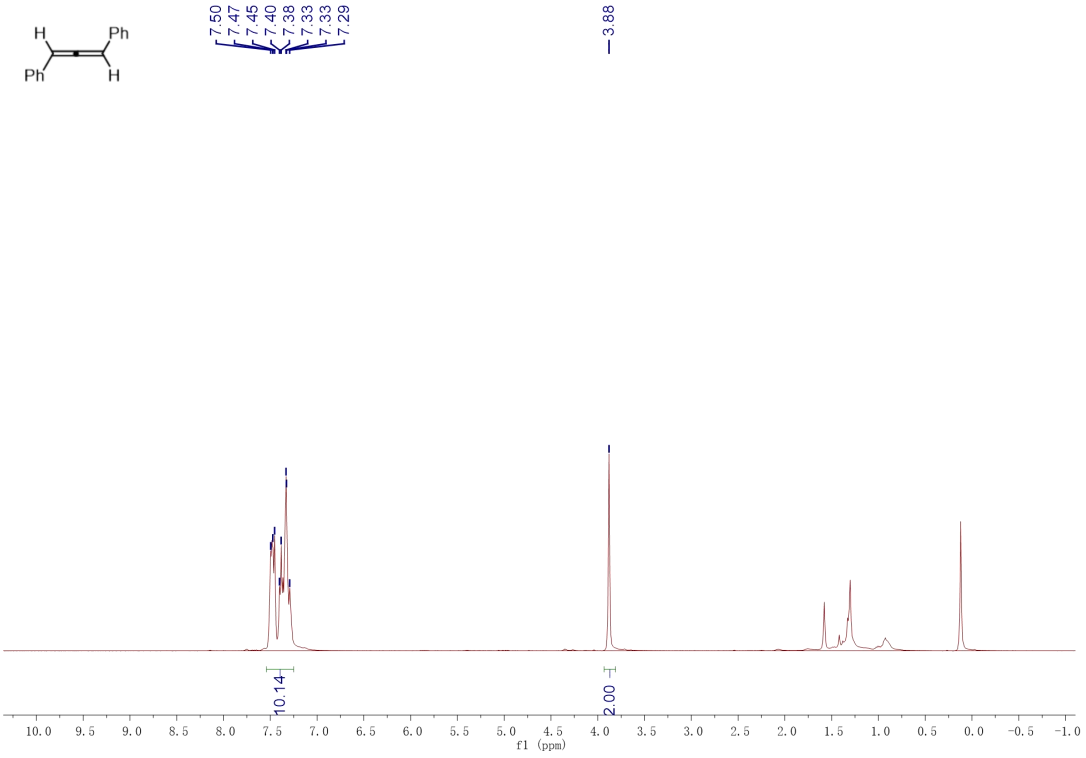
1-methyl-2,3,5-triphenyl-1H-pyrrole (5)



(E)-chalcone (6)



1,3-diphenylpropa-1,2-diene (7)



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